



Prozessentwicklung zur Aufbereitung von HCH-Rückständen

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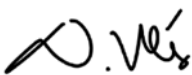
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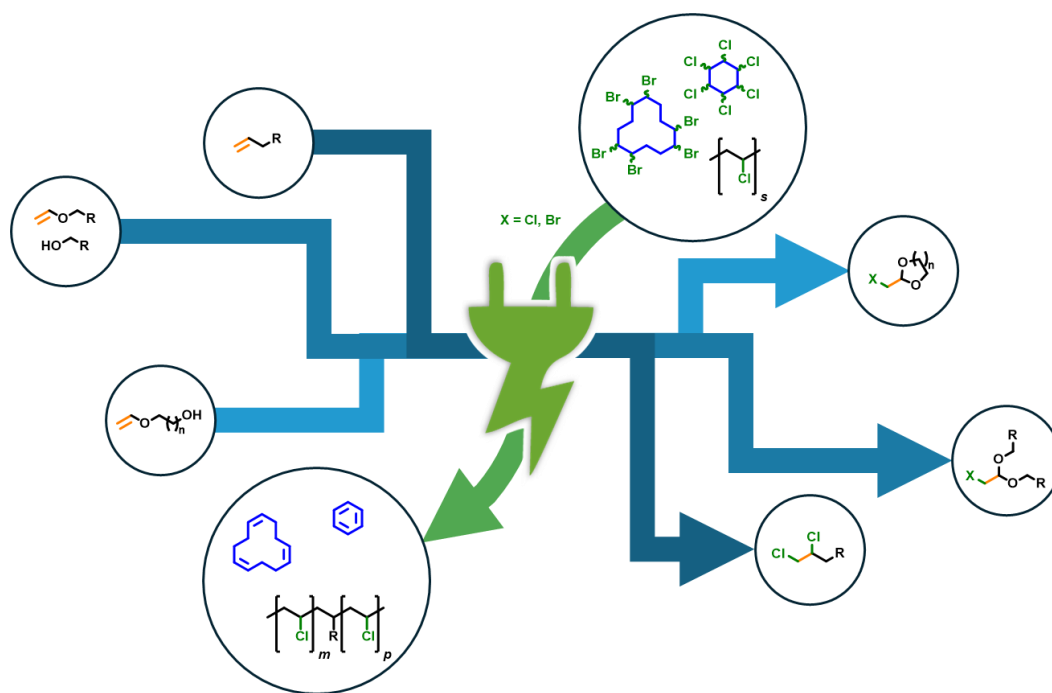
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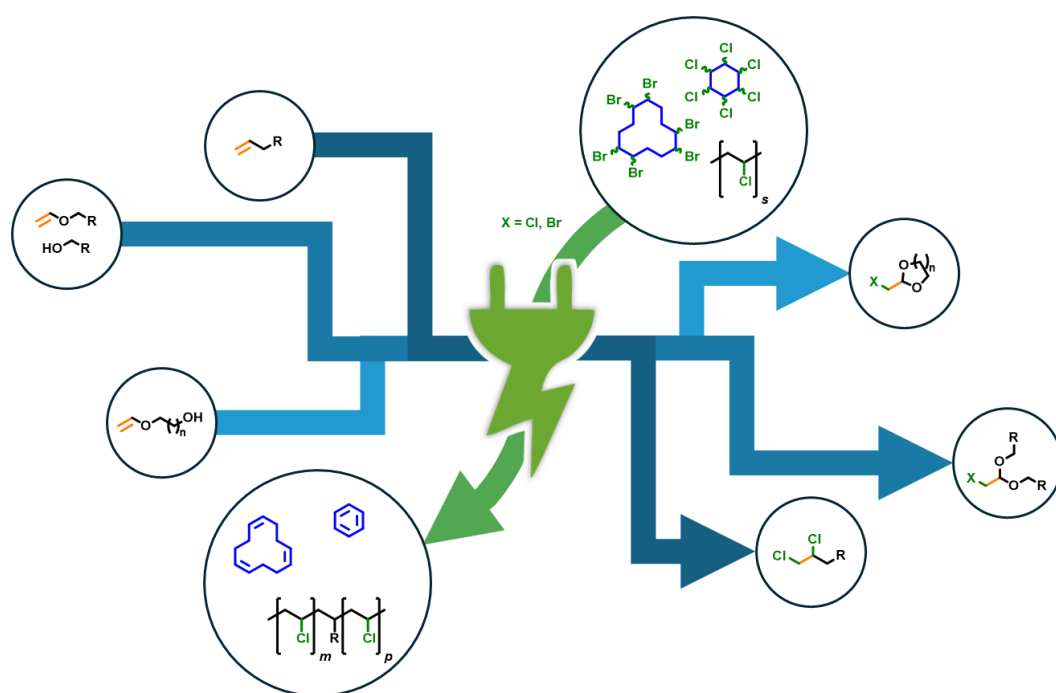
Abstract

In the context of this doctoral thesis, the e-shuttle principle was investigated as an electrochemical strategy for the upcycling of persistent halogenated compounds. It was demonstrated that the electrochemical conversion of HCH, HBCD, and PVC can be utilized for the targeted synthesis of industrially relevant platform chemicals. Through systematic screening and statistically supported experimental design using Design of Experiments, the electrolysis parameters were optimized and significant main and interaction effects were identified. The selective dechlorination of HCH isomers to benzene and the simultaneous synthesis of vicinal dichlorides as well as open and cyclic acetals of chloroacetaldehyde were achieved with yields of up to 79% (2,3-dichloro-1-propanol) and 86% (2-chloromethyl-1,3-dioxepane), respectively. The transfer of this approach to PVC enabled dichlorination reaction rates of up to 94% while retaining the polymer backbone. An economic assessment furthermore confirmed the large-scale viability of the process.



Zusammenfassung

Im Rahmen dieser Doktorarbeit wurde das *e-shuttle*-Prinzip als elektrochemische Strategie zum Upcycling persistenter Halogenverbindungen untersucht. Dabei konnte gezeigt werden, dass die elektrochemische Umwandlung von HCH, HBCD und PVC zur gezielten Synthese industrierelevanter Plattformchemikalien genutzt werden kann. Durch systematisches Screening und statistisch gestützte Versuchsplanung mittels Design of Experiments wurden die Elektrolyseparameter optimiert sowie signifikante Haupt- und Wechselwirkungseffekte identifiziert. Die selektive Dechlorierung der HCH-Isomere zu Benzol und die gleichzeitige Darstellung vicinaler Dichloride sowie offener und zyklischer Acetale des Chloracetaldehyds konnten mit Ausbeuten von bis zu 79% (2,3-Dichlor-1-propanol) und 86% (2-Chlormethyl-1,3-dioxepan) realisiert werden. Die Übertragung des Ansatzes auf PVC ermöglichte Entchlorungsraten von bis zu 94% unter Erhalt der Polymerrückgraten. Eine wirtschaftliche Bewertung belegte zudem die großtechnische Tragfähigkeit des Verfahrens.



„It is well-known fact that those people who most want to rule people are, ipso facto, those least suited to do it.“

– Douglas Adams, THE RESTAURANT AT THE END OF THE UNIVERSE

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1 Einleitung

1.1 Relevanz der Elektrochemie für heutige Synthesen

Die chemische Industrie steht vor der doppelten Herausforderung,^[1–3] einerseits die Synthese industrierelevanter Verbindungen nachhaltig zu gestalten und andererseits das Erbe vergangener Jahrzehnte in Form persistenter organischer Schadstoffe zu bewältigen.^[4] Halogenierte Verbindungen wie 1,2,3,4,5,6-Hexachlorcyclohexan (HCH),^[5–8] 1,2,5,6,9,10-Hexabromcyclododecan (HBCD)^[9,10] und Polyvinylchlorid (PVC)^[11–14] stehen dabei exemplarisch für eine Stoffklasse, deren industrielle Nutzung mit erheblichen ökologischen Langzeitfolgen verbunden ist und deren umweltgerechte Entsorgung bis heute eine ungelöste technische und wirtschaftliche Herausforderung darstellt.^[15–17]

Klassische Entsorgungsstrategien wie die Hochtemperaturverbrennung sind energieintensiv, kostspielig und erzeugen ihrerseits saure und zu behandelnde Abgase, ein Widerspruch zu den Zielen des Pariser Abkommens von 2015,^[18,19] das 195 Staaten auf eine deutliche Reduktion globaler Treibhausgasemissionen verpflichtet.^[20–22] Vor diesem Hintergrund gewinnen innovative Strategien an Bedeutung, die Abfallströme nicht lediglich entsorgen, sondern gezielt in wertvolle Ressourcen überführen.^[4,18]

Die elektroorganische Synthese bietet hierfür einen vielversprechenden Ansatz. Sie ermöglicht Redoxprozesse unter milden Bedingungen ohne den Einsatz gefährlicher oder toxischer Reagenzien und erfüllt, insbesondere unter Nutzung erneuerbarer Energien, zentrale Kriterien nachhaltiger Chemie.^[23–33] Die präzise Steuerung der Stromzufuhr, die *in situ*-Generierung reaktiver Spezies sowie die inhärente Prozesssicherheit bieten dabei wesentliche Vorteile gegenüber klassischen chemischen Methoden.^[32,34–36] Unter konsequenter Berücksichtigung der Prinzipien der grüneren Chemie besitzt die Elektrosynthese das Potenzial, zu einer Schlüsseltechnologie für die nachhaltige Herstellung von Feinchemikalien, pharmazeutischen Wirkstoffen, Duftstoffen und Agrochemikalien zu werden.^[23,35,37–41] In den vergangenen Jahren haben zahlreiche Studien belegt, dass die Elektrosynthese ihre einstige Nischenrolle zunehmend überwindet und breite Akzeptanz in der präparativen organischen Chemie gewinnt.^[23,38,42–46]

1.1.1 Entwicklung und Meilensteine der elektroorganischen

Synthese

Grundlagen der elektrochemischen Synthese: Die wissenschaftlichen Grundlagen der Elektrochemie wurden im 19. Jahrhundert gelegt, insbesondere durch FARADAY, dessen Gesetze der Elektrolyse bis heute grundlegende Prinzipien elektrochemischer Reaktionen definieren.^[47] Einen zentralen Meilenstein der organischen Elektrochemie setzte KOLBE mit der anodischen decarboxylativen C,C-Bindungsknüpfung von Carbonsäuren.^[48,49] Diese Arbeiten bildeten die konzeptionelle Basis des modernen Verständnisses elektroorganischer Synthesen.

Entwicklung elektroanalytischer Methoden: Gegen Ende des 19. und zu Beginn des 20. Jahrhunderts folgte eine Phase intensiver Forschung zu elektrochemischen Oxidationen und Reduktionen, darunter bedeutende Studien von HABER zur kathodischen Reduktion von Nitroaromaten.^[50–53] Einen grundlegenden Fortschritt markierte die Entwicklung der Polarografie durch HEYROVSKÝ in den 1920er-Jahren,^[54,55] die den Grundstein für heutige elektroanalytische Techniken legte und eine systematische Untersuchung elektrochemischer Prozesse ermöglichte.

Industrielle Anwendungen: Im späten 19. Jahrhundert gewann in der anorganischen Chemie die elektrochemische Gewinnung von Metallen^[56–58] und Halogenen^[59–61] sowie die Chlor-Alkali-Elektrolyse zunehmend an Bedeutung.^[62–64] Vom Amalgamverfahren (Castner-Kellner-Verfahren)^[65] über das Diaphragma-^[66,67] und Membranverfahren^[68] bis hin zur Sauerstoffverzehrkatode (Covestro AG)^[69,70] wurde die Chlor-Alkali-Elektrolyse kontinuierlich umweltschonender und energieeffizienter weiterentwickelt.^[71]

Ab der Mitte des 20. Jahrhunderts gewann die organische Elektrochemie industriechemische Relevanz. Prägende Anwendungen waren die Simons-Fluorierung,^[72] der Baizer-Prozess^[73–75] (Monsanto) sowie die Lysmeral-Synthese (BASF SE),^[76,77] die elektrochemischen Verfahren erstmals in großtechnischem Maßstab etablierten.

Moderne elektroorganische Methodik: Bereits im 19. Jahrhundert wurde der Einsatz von Redox-Mediatoren beschrieben, beispielsweise in der anodischen Oxidation von Chinolinen mit Cer(III).^[78] Die theoretische Grundlage der indirekten Elektrolyse wurde jedoch erst in den 1970er-Jahren durch STECKHAN systematisch entwickelt.^[79,80] In den folgenden Jahrzehnten etablierten sich weitere

Schlüsselmethoden, darunter die SHONO-Oxidation^[81,82] zur α -Funktionalisierung von Aminen und Amiden sowie die von YOSHIDA^[46,83–86] geprägten Konzepte der Elektro-Auxiliare, der Kationen-Pool-Methode und elektrochemischer C,H-Aminierungen.

In den letzten Jahren hat die organische Elektrochemie eine deutliche Renaissance erfahren, wobei Arbeitsgruppen um BARAN,^[87–89] LIN,^[90–92] ACKERMANN,^[93] WALDVOGEL^[30,94,95] eine Vielzahl innovativer elektrochemischer Transformationen entwickelt und das Spektrum synthetischer Anwendungen erheblich erweitert haben.^[96,97]

1.2 Parameter und Einflussgrößen der elektroorganischen Synthese

Die elektroorganische Synthese basiert auf elektrochemischen Redoxprozessen, bei denen an der Anode Oxidationen und an der Kathode Reduktionen erfolgen.^[23,30,32,43,98] Die Umsetzung erfolgt überwiegend über Einzelelektronentransfers und wird durch eine Vielzahl elektrochemischer und physikochemischer Parameter bestimmt, die sich den Komponenten Elektrode, Elektrolyt sowie den Betriebsbedingungen des Gesamtsystems zuordnen lassen (Abbildung 1).^[30,32]

Der Elektronentransfer erfolgt heterogen an der Grenzfläche zwischen Elektrode und Substrat beziehungsweise einem Redoxmediator. Material, Oberfläche und Stabilität der Elektrode haben daher einen entscheidenden Einfluss auf Reaktionskinetik, Selektivität und Langzeitverhalten.^[32,43,99,100]

Der Elektrolyt, bestehend aus Lösungsmittel und Leitsalz, bestimmt maßgeblich die Stabilität und Reaktivität der gebildeten Intermediate. Neben der Solvatisierung beeinflussen insbesondere Stofftransportprozesse wie Diffusion und Konvektion sowie die Ionenstärke das Reaktionsgeschehen. Darüber hinaus legt der Elektrolyt in Kombination mit dem Elektrodenmaterial das elektrochemische Potentialfenster fest und begrenzt damit den zugänglichen Reaktionsbereich.^[30,32,100–102]

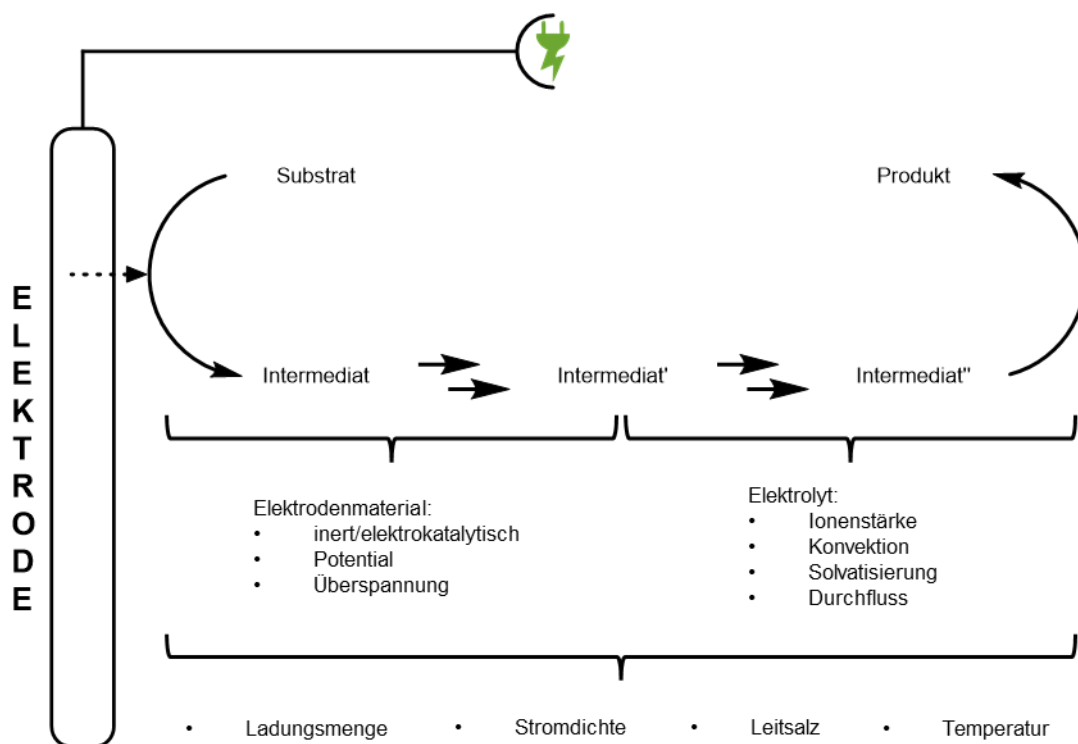


Abbildung 1: Prozesse und Parameter elektroorganischer Synthese. Adaptiert von WALDVOGEL *et al.* unter CC-BY-NC-ND 4.0. © 2018 Wiley-VCH GmbH.^[32]

Das Leitsalz übernimmt mehrere Funktionen innerhalb des elektrochemischen Systems. Es gewährleistet die erforderliche Leitfähigkeit und beeinflusst zugleich die Struktur der elektrochemischen Doppelschicht an der Elektrodenoberfläche, wodurch es sowohl den heterogenen Elektronentransfer als auch den Transport von Intermediaten aus der Doppelschicht in die Lösung beeinflusst. Darüber hinaus kann die gezielte Wahl des Leitsalzes zur Inhibierung von Elektrodenkorrosion beitragen und in bestimmten Fällen fungiert es zusätzlich als Redoxmediator.^[98,99,103–108]

Die applizierte Ladungsmenge Q entspricht der eingesetzten Stoffmenge an Redoxäquivalenten und ersetzt damit stöchiometrische Oxidations- oder Reduktionsmittel. Gleichzeitig ist die an der Gegenelektrode ablaufende Reaktion zu berücksichtigen, da sie das Gesamtsystem wesentlich beeinflusst. Neben der häufig auftretenden Zersetzung von Elektrolytkomponenten sind auch die gezielte Generierung von Basenäquivalenten, der Einsatz von Opferelektroden sowie gepaarte Elektrolysen als Reaktionsführungen möglich.^[23,30,98,99,109–113]

Ein zentraler Betriebsparameter ist die Stromdichte j , definiert als Stromstärke bezogen auf die aktive Elektrodenoberfläche. Sie steht in direktem Zusammenhang mit dem Elektrodenpotential und beeinflusst maßgeblich die Bildungsrate reaktiver Spezies sowie die Selektivität der Reaktion. Für die Umsetzung elektroorganischer

Prozesse im technischen Maßstab sind hohe Stromdichten von besonderem Interesse, da sie hohe Umsätze und eine verbesserte Raum-Zeit-Ausbeute ermöglichen.^[23,30,32,44,98,113,114]

1.2.1 Elektrolyseverfahren, Zellaufbauten und Elektrodenmaterialien

Der Elektronenübertrag zwischen Elektrode und Substrat erfolgt durch heterogene Elektronentransferprozesse, die je nach System über unterschiedliche Mechanismen ablaufen und maßgeblich Reaktivität sowie Selektivität bestimmen.^[43,100,115]

Beim direkten Elektronentransfer erfolgt die Ladungsübertragung unmittelbar zwischen Substrat und einer inerten Elektrode an der Elektrodenoberfläche, wobei Reaktionsverlauf und Selektivität insbesondere durch das Elektrodenmaterial sowie das angelegte Potential bestimmt werden. Eine weitere Möglichkeit stellt die indirekte Elektrolyse dar, bei der ein elektrochemisch regenerierter Redoxmediator als homogener Elektronentransferkatalysator fungiert und dadurch alternative Selektivitäten zugänglich macht (Abbildung 2).^[38,43,80,100,103,116–119]

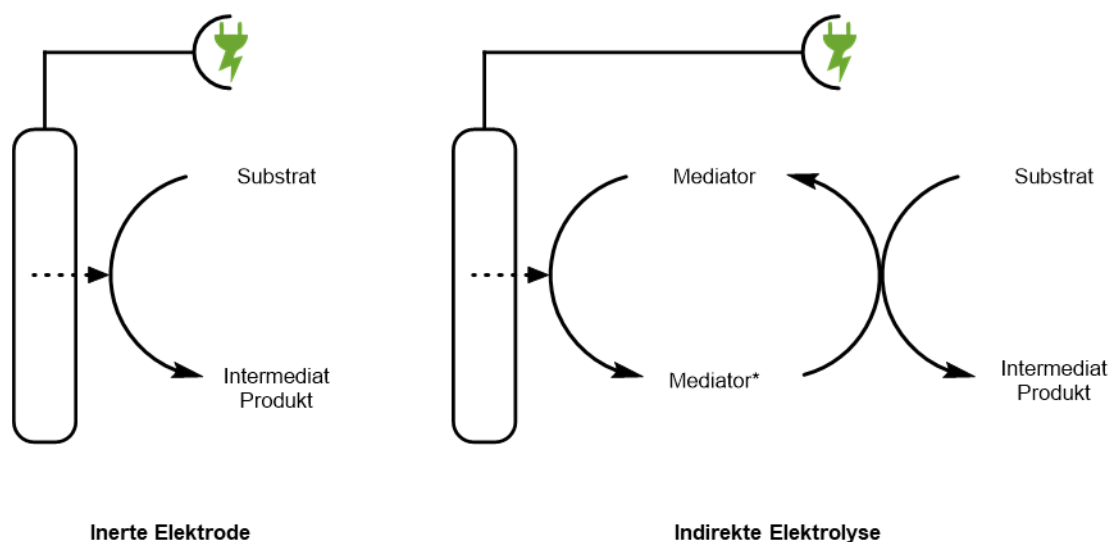


Abbildung 2: Funktionsweisen von Elektroden: Inerte Elektrode (links) und indirekte Elektrolyse (rechts). Adaptiert von WALDVOGEL *et al.* unter CC-BY-NC-ND 3.0. © 2020 Royal Society of Chemistry.^[23]

Ein weiterer relevanter Aspekt im Elektrolysesystem ist die Zersetzung des Lösungsmittels an der Gegenelektrode, die häufig zur unerwünschten

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Wasserstoffentwicklung führt. Durch die gezielte Nutzung beider Elektrodenreaktionen, sowohl der Anoden- als auch der Kathodenreaktion, lässt sich diese Zersetzung vermeiden und das Verfahren hinsichtlich Effizienz und Nachhaltigkeit erheblich verbessern. Diesen Ansatz bezeichnet man als gepaarte Elektrolyse. Aufgrund der effizienten Nutzung des eingesetzten Stroms sowie der Minimierung des Energie- und Chemikalienbedarfs und der Abfallbildung ermöglicht sie eine äußerst ressourcenschonende Synthese.^[32,120] Dieser Ansatz wird bereits im industriellen Maßstab genutzt, etwa bei der elektrochemischen Gewinnung von Metallen sowie bei der Erzeugung von Chlor und Natriumhydroxid im Chlor-Alkali-Prozess.^[57,60,69–71] Die gepaarte Elektrolyse kann in verschiedenen Konfigurationen, auch in ungeteilten Zellaufbauten, realisiert werden (Abbildung 3).^[121–123]

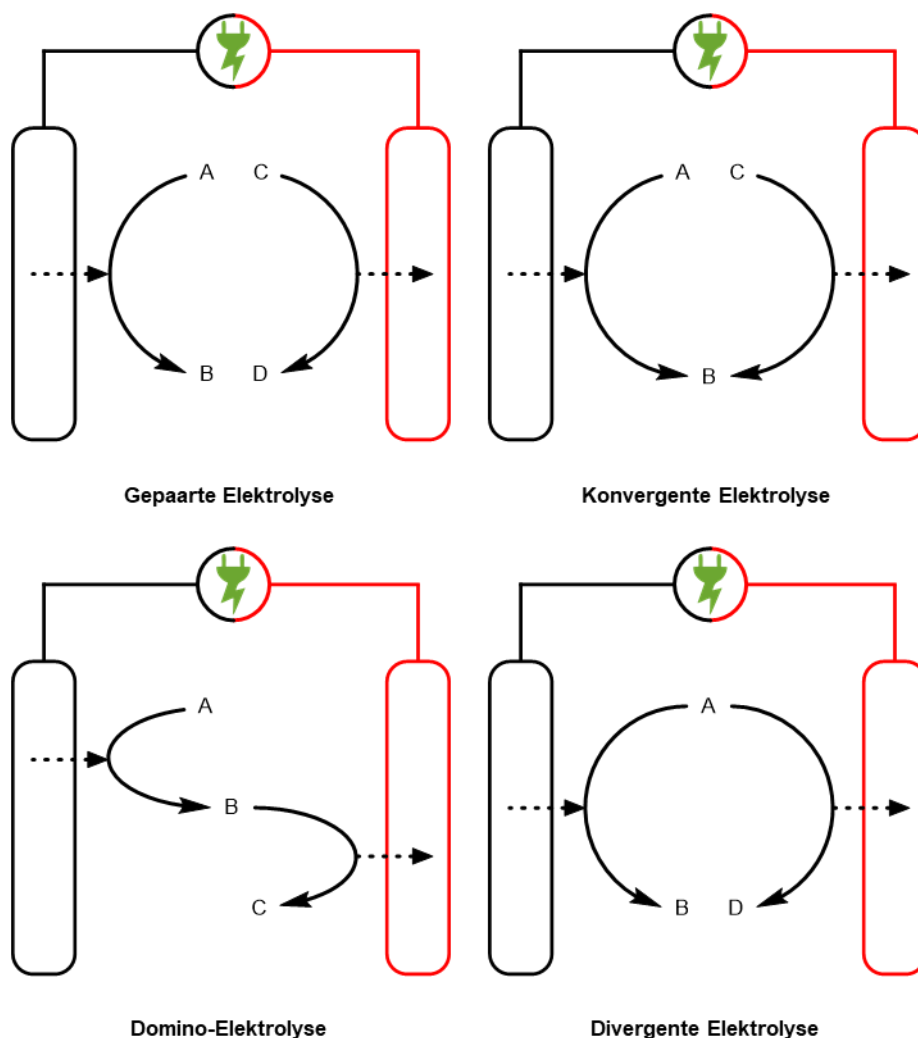


Abbildung 3: Verschiedene Arten der gepaarten Elektrolyse. Adaptiert von WALDVOGEL *et al.* unter CC-BY-NC-ND 3.0. © 2020 Royal Society of Chemistry.^[23]

Als Beispiel einer gepaarten Elektrolyse kann die Lysmeral-Synthese (BASF SE)^[76,124–126] oder im Labormaßstab die Nitratreduktion zu Ammoniak gepaart mit der Oxidation von Glycerol zur Ameisensäure angeführt werden.^[127] Bei der konvergenten Elektrolyse wird aus zwei Substraten ein Produkt erzeugt, wobei eine genaue Abstimmung der Redoxpotentiale erforderlich ist, beispielsweise bei der Synthese von Glyoxylsäure aus Oxalsäure und Glyoxal.^[128] Eine weitere Variante stellt die Dominosynthese dar, bei der ein Substrat in einer ungeteilten Zelle zunächst an der Arbeitselektrode umgewandelt und das resultierende Intermediat anschließend durch Diffusion an der Gegenelektrode weiterreagiert. Ein Beispiel hierfür ist die von WALDVOGEL *et al.* beschriebene Umwandlung von Mesitylaldoxim über das Nitriloxid-Zwischenprodukt zum entsprechenden Mesitylnitril.^[129] Bei der divergenten Elektrolyse hingegen werden aus einem Substrat zwei verschiedene Produkte dargestellt, wie etwa bei der Umwandlung von Glucose in Gluconat durch Oxidation und Sorbit durch Reduktion.^[130] Eine erfolgreiche gepaarte Elektrolyse hängt dabei stets vom Zusammenwirken mehrerer kinetischer Prozesse sowie einer sorgfältigen Reaktionsoptimierung ab.^[23]

Unabhängig vom Mechanismus stellt das Elektrodenmaterial einen zentralen Parameter für Reaktivität und Selektivität dar. Von besonderer Bedeutung ist dabei die Überspannung für die Wasserstoffentwicklung an Kathoden beziehungsweise für die Sauerstoffentwicklung an Anoden. Diese beschreibt die Differenz zwischen dem thermodynamischen Redoxpotential und dem tatsächlich angelegten Potential und stellt eine kinetische Größe dar, die sowohl vom Elektrodenmaterial als auch vom jeweiligen Substrat abhängt. Neben den elektrochemischen Eigenschaften sind bei der Materialwahl auch mechanische und chemische Stabilität, Verfügbarkeit, Kosten sowie toxikologische und ökologische Aspekte zu berücksichtigen.^[23,24,98–100]

Metalle werden aufgrund ihrer hohen elektrischen Leitfähigkeit häufig eingesetzt, erfordern jedoch insbesondere bei anodischer Verwendung eine ausreichende Stabilität unter oxidativen Bedingungen. Neben aktiven Materialien und Opferanoden kommen auch Edelmetalle sowie dimensionsstabile Anoden auf Basis von Metalloxiden zum Einsatz. Unter Nachhaltigkeits- und Kostengesichtspunkten gewinnen kohlenstoffbasierte Elektroden zunehmend an Bedeutung. Diese zeichnen sich durch hohe chemische Beständigkeit, geringe Materialkosten sowie ein breites elektrochemisches Potentialfenster aus und sind sowohl für anodische als auch für kathodische Prozesse geeignet.^[99,100,110,131–137]

Kohlenstoffelektroden unterscheiden sich insbesondere hinsichtlich ihrer makroskopischen Struktur sowie ihrer elektronischen Eigenschaften, die durch das Verhältnis von sp^2 - zu sp^3 -hybridisierten Kohlenstoffzentren und mögliche Dotierungen bestimmt werden. Graphit stellt aufgrund seiner nahezu vollständigen sp^2 -Hybridisierung, hohen chemischen Beständigkeit, guten elektrischen Leitfähigkeit sowie breiten und kostengünstigen Verfügbarkeit ein besonders attraktives Elektrodenmaterial dar. Neben Graphit finden auch Glaskohlenstoff sowie dotierte Diamantmaterialien Anwendung, die sich durch hohe chemische und mechanische Stabilität sowie erweiterte Potentialfenster auszeichnen.^[34,37,100,109,131,134,138–145]

Neben der Materialzusammensetzung beeinflusst auch die makroskopische Struktur der Elektrode die elektrochemischen Eigenschaften maßgeblich. Poröse Materialien wie Filze, Fasern, Gewebe oder Schäume ermöglichen eine Vergrößerung der aktiven Elektrodenoberfläche und damit die Realisierung höherer Stromdichten bei verkürzten Reaktionszeiten, was insbesondere für die Übertragung elektroorganischer Prozesse in den technischen Maßstab von Bedeutung ist.^[33,34,99,100,146–150]

Vor dem Hintergrund der genannten Anforderungen und Vorteile bilden kohlenstoffbasierte Elektroden den Schwerpunkt der vorliegenden Arbeit. Insbesondere isostatischer Graphit wird aufgrund seiner chemischen Stabilität, wirtschaftlichen Verfügbarkeit und vielseitigen Einsetzbarkeit sowohl als Anoden- als auch als Kathodenmaterial eingesetzt.

1.3 Statistische Versuchsplanung

Elektroorganische Reaktionen sind durch das Zusammenspiel heterogener Elektronentransferprozesse an der Elektrodenoberfläche und nachfolgender chemischer Reaktionsschritte gekennzeichnet.^[32] Im Vergleich zu klassischen synthetischen Verfahren resultiert daraus eine signifikant erhöhte Anzahl an Einflussparametern, die Reaktionsverlauf, Ausbeute und Selektivität bestimmen.^[151] Diese Parameter lassen sich systematisch in kontinuierliche und kategoriale Größen einteilen. Kontinuierliche Parameter sind auf einer stetigen Skala variierbar und quantitativ erfassbar, während kategoriale Parameter diskrete Ausprägungen aufweisen und sich einer kontinuierlichen Beschreibung entziehen.

Zu den zentralen kategorialen Parametern elektroorganischer Reaktionen zählen die Wahl des Lösungsmittels, des Leitsalzes, des Elektrodenmaterials für Anode und Kathode, des Katalysators sowie das Design der elektrochemischen Zelle. Neben klassischen kontinuierlichen Reaktionsparametern wie Temperatur T , den Konzentrationen c von Edukten, Leitsalz und Katalysatoren sowie dem Volumenstrom $\dot{V}$ beziehungsweise der Zugabegeschwindigkeit sind in der elektroorganischen Synthese zusätzlich elektrochemisch spezifische Größen von entscheidender Bedeutung, insbesondere die Stromdichte j und die insgesamt übertragene Ladungsmenge Q . Die hohe Dimensionalität und die unterschiedliche Natur dieser Parameter erschweren eine zielgerichtete Optimierung der Reaktionsbedingungen erheblich und machen den Einsatz systematischer Optimierungsmethoden erforderlich.^[151–153]

Eine verbreitete Variante der Versuchsplanung stellt das OVAT-Screening (*one variable at a time*) dar, bei dem jeweils nur ein Faktor variiert wird, während alle übrigen Parameter konstant gehalten werden. Auf diese Weise lässt sich die optimale Einstellung einer Einflussgröße in Abhängigkeit der festgehaltenen Parameterwerte ermitteln.^[151,154] Diese Strategie berücksichtigt jedoch keine Parameterwechselwirkungen, was zu einer eingeschränkten Aussagekraft hinsichtlich der tatsächlich optimalen Parameterkombination führen kann und den Einsatz effizienterer Methoden der statistischen Versuchsplanung, wie dem *Design of Experiments* (DoE), nahelegt.^[155,156]

1.3.1 Voll- und teilfaktorielle Versuchspläne

Eine effizientere Vorgehensweise in der Versuchsplanung stellt das DoE dar. Ziel ist es, Ursache-Wirkungs-Beziehungen systematisch zu identifizieren und Zielgrößen, beispielsweise die Ausbeute, gezielt zu optimieren. Hierzu werden die relevanten Einflussgrößen x_p nicht isoliert, sondern simultan und strukturiert variiert (Abbildung 4). Die konkrete Ausgestaltung des Versuchsplans hängt von Anzahl und Art der untersuchten Faktoren ab. Typischerweise erfolgt die Planung als vollfaktorieller 2^n -Versuchsplan oder als teilfaktorieller 2^{n-k} -Plan, häufig im Rahmen einer sequenziellen Vorgehensweise mit schrittweiser Auswertung und Anpassung. Ein vollfaktorieller Versuchsplan berücksichtigt sämtliche möglichen Kombinationen der definierten Faktorstufen. Ein teilfaktorieller Plan hingegen umfasst lediglich eine gezielt ausgewählte Teilmenge („Fraktion“) dieser Kombinationen. Dadurch lässt sich der experimentelle Aufwand insbesondere bei einer hohen Faktoranzahl oder begrenzten Ressourcen deutlich reduzieren, ohne auf zentrale Informationen zu Haupteffekten und, bei geeigneter Planung, ausgewählten Wechselwirkungen verzichten zu müssen.^[155,157]

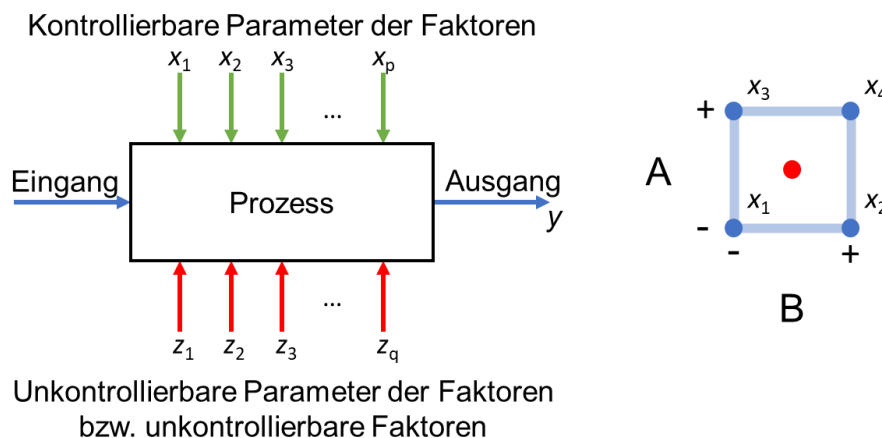


Abbildung 4: Abstraktes Modell eines Prozesses, dessen Ursache-Wirkungs-Beziehung durch die statistische Versuchsplanung untersucht werden soll (links). Die kontrollierbaren Faktoren x_p fließen als Ober- und Untergrenze (- und +) der Gesamtfaktoren A und B ein, die zu einem Ergebnis y führen (rechts).^[155]

Für die einzelnen Faktoren werden Wertstufen festgelegt, die mit denen der übrigen Faktoren kombiniert werden, um Wechselwirkungen und Richtungstendenzen aufzuzeigen. Je mehr Parameter parallel untersucht werden sollen, desto größer wird der experimentelle Aufwand. Tabelle 1 gibt einen Überblick über die Anzahl erforderlicher Versuche in Abhängigkeit von der Faktorenanzahl für verschiedene

Auflösungsstufen teilfaktorieller Versuchspläne. Die Auflösung eines teilfaktoriellen Versuchsplans gibt an, inwieweit Haupt- und Wechselwirkungseffekte voneinander unterscheidbar sind. Bei einer Auflösung V sind sowohl Haupteffekte als auch Zweifachwechselwirkungen vollständig trennbar. Darüber hinaus existieren Versuchspläne mit noch höherer Auflösung, die eine weiter gesteigerte Trennschärfe bieten: Bei Auflösung VI sind Haupteffekte und Zweifachwechselwirkungen frei von gegenseitiger Konfundierung, während lediglich Wechselwirkungen höherer Ordnung miteinander vermischt sein können. Die Auflösungen VII und VIII erweitern diese Trennschärfe weiter, sodass zunehmend auch Wechselwirkungen dritter und höherer Ordnung voneinander unterscheidbar werden. Mit steigender Auflösung nimmt jedoch der erforderliche Versuchsumfang zu, sodass stets ein Kompromiss zwischen statistischer Aussagekraft und experimentellem Aufwand abgewogen werden muss.^[155,157]

Tabelle 1: Verfügbare Versuchspläne nach der Statistiksoftware Minitab. Die Auflösung der teilfaktoriellen Versuchspläne ist in römischen Ziffern wiedergegeben.^[158]

Anzahl Versuche	Anzahl Faktoren									
	2	3	4	5	6	7	8	9	10	...
4	Voll	III								
8		Voll	IV	III	III	III				
16			Voll	V	IV	IV	IV	III	III	...
32				Voll	VI	IV	IV	IV	IV	...
64					Voll	VII	V	IV	IV	...
128						Voll	VIII	VI	V	...
...							...	...	...	...

Als Beispiel ergibt sich für einen vollständigen 2^2 -Plan die in Tabelle 2. dargestellte Versuchsmatrix, wobei „-“ die Untergrenze, „+“ die Obergrenze und „0“ den Zentralpunkt der jeweiligen Faktoren kennzeichnet.^[155]

Tabelle 2: Beispielhafte Darstellung eines 2^2 -Versuchsplans.

Faktoren	
A	B
-	-
+	-
-	+
+	+
0	0

Mithilfe einer linearen Regression lassen sich Tendenzen zur Optimierung von Zielgrößen, wie beispielsweise Ausbeuten, ableiten, die vereinfacht in einem Einfluss-Zielgrößen-Diagramm visualisiert werden können.

Die Regression basiert auf der Designmatrix X (Tabelle 3) des Versuchsplans (Tabelle 2) sowie den experimentell ermittelten Zielgrößen $\hat{y}_i$. Ziel ist die Schätzung der Koeffizienten $\hat{\beta}$ der einzelnen Faktoren und Terme gemäß Gleichung 1. Die Konstante entspricht dabei dem Gesamtmittelwert aller Versuchsergebnisse des Plans.^[155]

Tabelle 3: Beispielhafte Darstellung einer Designmatrix X eines 2²-Versuchsplans.

	Konstante	A	B	AB	Zentralpunkt
Konstante	+1	-1	-1	+1	0
A	+1	+1	-1	-1	0
B	+1	-1	+1	-1	0
AB	+1	+1	+1	+1	0
Zentralpunkt	0	0	0	0	+1

$$\hat{\beta} = (X^T X)^{-1} X^T \cdot \hat{y}_i \quad \text{Gleichung 1}$$

Das resultierende lineare Modell des Versuchsplans ist in Gleichung 2 dargestellt. Es beschreibt die Zielgröße y als Funktion der geschätzten Koeffizienten $\hat{\beta}$, wobei neben den Haupteffekten der einzelnen Faktoren, sowie x_A und x_B , auch deren Wechselwirkungsterme $x_A x_B$ berücksichtigt werden. Quadratische Terme bleiben an dieser Stelle unberücksichtigt und werden im Rahmen des erweiterten Versuchsplans nach dem Wirkungsflächenversuchsplan eingeführt.

$$y = \hat{\beta}_{\text{Konstante}} + \hat{\beta}_A x_A + \hat{\beta}_B x_B + \hat{\beta}_{AB} x_A x_B + \dots + \hat{\beta}_{\text{Zentralpunkt}} \quad \text{Gleichung 2}$$

Das Haupteffektdiagramm stellt die Mittelwerte der Zielgröße für die jeweiligen Stufen eines Faktors dar und verbindet diese durch eine Linie. Die Steigung dieser Linie ist ein direktes Maß für die Stärke des Haupteffekts: Je größer die Steigung, desto ausgeprägter ist der Einfluss des betreffenden Faktors auf die Zielgröße (Abbildung 5).^[155,158]

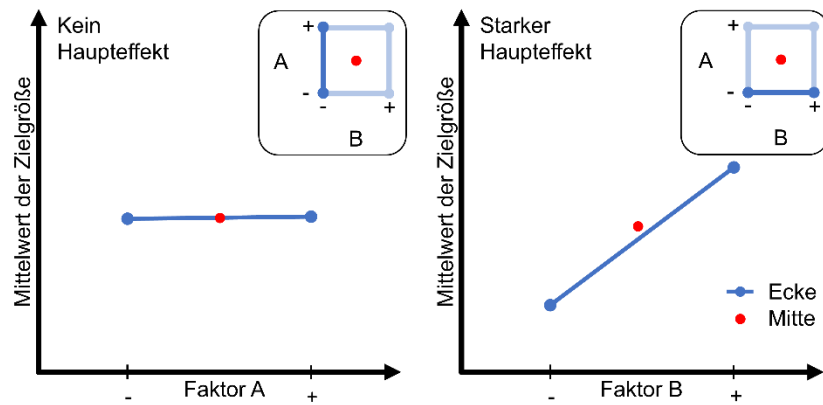


Abbildung 5: Beispiele eines Haupteffektdiagramms mit keinem Haupteffekt (links), wie auch eines mit starkem Haupteffekt (rechts).^[155,158]

Die Stärke des Haupteffekts sowie der Wechselwirkungen ergibt sich aus dem zweifachen Koeffizienten $2 \times \hat{\beta}$ oder die Stärke des Haupteffekts kann vereinfacht gemäß Gleichung 3 als Differenz der mittleren Zielgrößenwerte an der Obergrenze $\bar{y}_+$ und der Untergrenze $\bar{y}_-$ berechnet werden.

$$\text{Haupteffekt} = \bar{y}_+ - \bar{y}_-$$

Gleichung 3

Um die Abhängigkeit einer Zielgröße von zwei Faktoren, und damit das Vorliegen einer Wechselwirkung, zu veranschaulichen, werden Wechselwirkungsdiagramme herangezogen. Dabei werden die Mittelwerte der Zielgröße für die Stufen eines Faktors auf der x-Achse aufgetragen, während jeweils eine separate Linie die Stufen des zweiten Faktors repräsentiert. Verlaufen die Linien parallel, liegt keine Wechselwirkung zwischen den Faktoren vor. Je stärker die Linien von der Parallelität abweichen, desto ausgeprägter ist die Wechselwirkung (Abbildung 6).^[155,158]

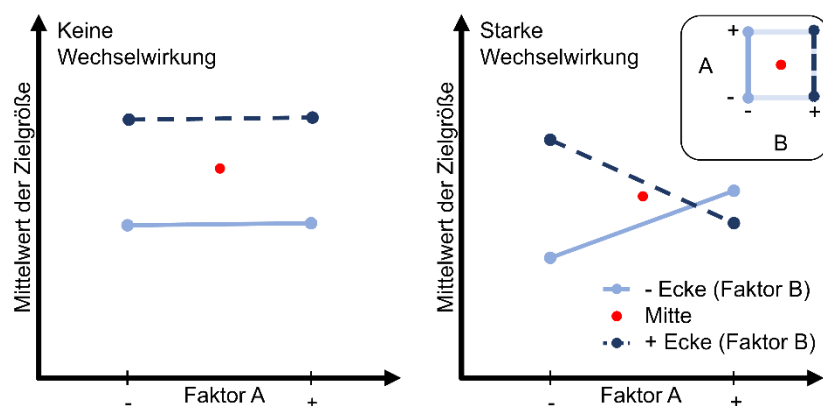


Abbildung 6: Beispiele der Wechselwirkungsdiagramme der Faktoren A und B. Keine Wechselwirkung (links), wie auch eine starke Wechselwirkung (rechts), sind dargestellt.^[155,158]

14 | Einleitung

Die Stärke des Wechselwirkungseffekts ergibt sich vereinfacht aus den mittleren Zielgrößen an den Eckpunkten des Versuchsplans gemäß Gleichung 4. Die Indizes bezeichnen dabei die jeweilige Stufenkombination der beiden Faktoren: $\bar{y}_{++}$ und $\bar{y}_{--}$ entsprechen den Eckpunkten, an denen beide Faktoren auf der gleichen Stufe liegen, während $\bar{y}_{+-}$ und $\bar{y}_{-+}$ die Eckpunkte mit entgegengesetzten Stufenkombinationen beschreiben.

$$\text{Wechselwirkung} = \frac{((\bar{y}_{++} - \bar{y}_{-+}) - (\bar{y}_{+-} - \bar{y}_{--}))}{2} \quad \text{Gleichung 4}$$

Zur Beurteilung der statistischen Signifikanz der Effekte und Wechselwirkungen werden die Absolutwerte der standardisierten Effekte in einem Pareto-Diagramm dargestellt. Dieses visualisiert die Größe und den relativen Einfluss der einzelnen Effekte und kennzeichnet über eine Referenzlinie jene Effekte, die statistische Signifikanz erreichen (Abbildung 7). Die Referenzlinie basiert auf der Quantilen der t -Verteilung nach Student, $t_{1-\alpha/2,df}$, und wird durch das gewählte Signifikanzniveau α sowie den Freiheitsgrad df des Versuchsplans bestimmt.^[155,158]

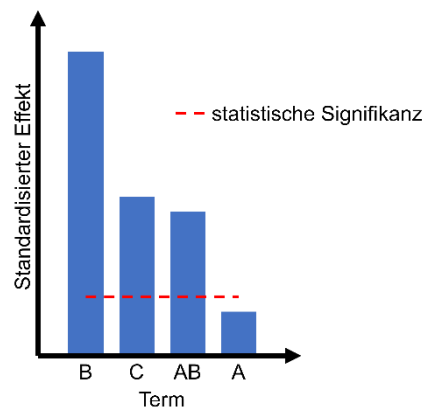


Abbildung 7: Beispiel eines Pareto-Diagramms der Haupteffekte B, C und A wie auch der Wechselwirkung AB.^[155,158]

Um die standardisierten Effekte der einzelnen Faktoren zu berechnen, wird zunächst die Kovarianzmatrix $\text{Cov}(\hat{\beta})$ gemäß Gleichung 6 aus der Designmatrix X und der geschätzten Varianz $\hat{\sigma}^2$ der Zielgrößen (Gleichung 5) bestimmt werden.

$$\hat{\sigma}^2 = \frac{1}{n-p} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad \text{Gleichung 5}$$

$$\text{Cov}(\hat{\beta}) = \hat{\sigma}^2 \cdot (X^T X)^{-1} \quad \text{Gleichung 6}$$

Aus den Diagonalelementen der Kovarianzmatrix $\text{Cov}(\hat{\beta})$ wird der Standardfehler $\text{SE}(\hat{\beta}_j)$ der jeweiligen Koeffizienten gemäß $\sqrt{|\text{Cov}(\hat{\beta})|_{jj}}$ bestimmt. Der Quotient aus dem geschätzten Koeffizienten $\hat{\beta}_j$ und seinem Standardfehler $\text{SE}(\hat{\beta}_j)$ ergibt den sogenannten t -Wert, welcher den standardisierten Effekt des jeweiligen Faktors widerspiegelt und als Grundlage für die Signifikanzbeurteilung im Pareto-Diagramm dient (Gleichung 7).

$$t\text{-Wert (standardisierter Effekt)} = \frac{\hat{\beta}_j}{\text{SE}(\hat{\beta}_j)} \quad \text{Gleichung 7}$$

1.3.2 Wirkungsflächenversuchsplan

Liegt eine Krümmung im System vor, beispielsweise in der Nähe eines Maximums oder Minimums, ist eine lineare Regression nicht mehr ausreichend. Im Haupteffektdiagramm äußert sich diese Krümmung durch eine Abweichung des Zentralpunkts von der Verbindungslinie der Stufenmittelwerte. Die Signifikanz der Krümmung wird mittels eines t -Tests überprüft, wobei sich der t -Wert gemäß Gleichung 8 aus der mittleren Zielgröße der Zentralpunkte $\bar{y}_0$, der mittleren Zielgröße der Eckpunkte $\bar{y}_{\text{Eckpunkte}}$ sowie der Varianz und der Anzahl der Zentralpunkte r_0 ergibt. Überschreitet der berechnete t -Wert des Zentralpunkts den kritischen Wert der t -Verteilung nach Student $t_{1-\alpha/2,df}$, liegt eine statistisch signifikante Krümmung vor.^[155,158]

$$t = \frac{\bar{y}_0 - \bar{y}_{\text{Eckpunkte}}}{\sqrt{\frac{\frac{1}{n} \sum_{i=1}^n (y_0 - \bar{y}_0)^2}{r_0}}} \quad \text{Gleichung 8}$$

In diesem Fall kann der Versuchsplan zu einem Wirkungsflächenversuchsplan (*response surface design*) erweitert werden. Durch die Ergänzung von Zentral- und Sternpunkten wird die Krümmung mithilfe einer polynomialen Regression modelliert (Abbildung 8).

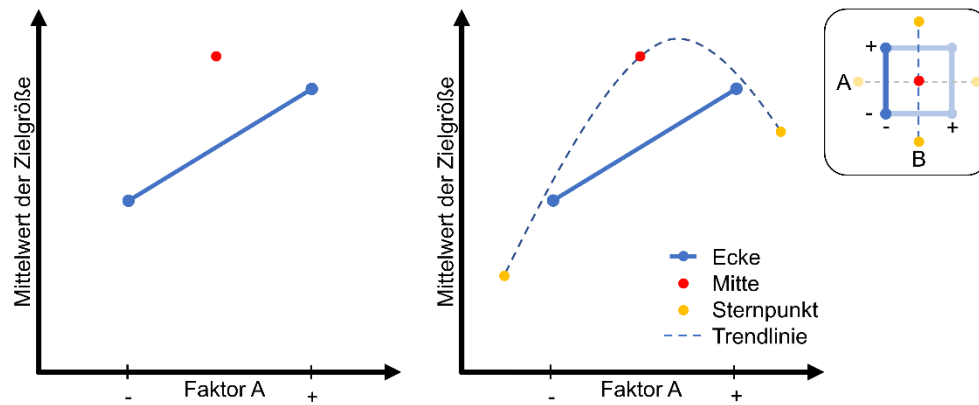


Abbildung 8: Beispiel einer aus einem Wirkungsflächenversuchsplan ermittelten Krümmung. Zum Vergleich wurde eine lineare Darstellung mit abgebildet.^[155,158]

Für die polynomiale Regression werden die quadratischen Terme, wie x_A^2 , x_B^2 usw., in die Designmatrix aufgenommen und die zugehörigen Koeffizienten bestimmt. Durch partielle Ableitung von Gleichung 9 bzw. durch Bestimmung der stationären Punkte lassen sich die lokalen Maxima der Zielgröße in Abhängigkeit von den jeweiligen Faktoren ermitteln.

$$y = \hat{\beta}_{\text{Konstante}} + \hat{\beta}_A x_A + \hat{\beta}_B x_B + \hat{\beta}_{AB} x_A x_B + \hat{\beta}_{AA} x_A^2 + \hat{\beta}_{BB} x_B^2 + \dots$$

Gleichung 9

Eine weiterführende Betrachtung der Methodik des DoE ist nicht Gegenstand dieser Arbeit; sie wurde im Rahmen der vorliegenden Untersuchungen als Werkzeug zur systematischen Optimierung eingesetzt.^[155]

1.4 Hexachloryclohexan (HCH), Hexabromcyclododecan (HBCD) und Polyvinylchlorid (PVC)

1.4.1 Historie

1,2,3,4,5,6-Hexachlorcyclohexan (HCH) ist eine Verbindung aus der Gruppe der Halogenkohlenwasserstoffe und liegt als Gemisch verschiedener Stereoisomere vor. Das als Insektizid genutzte und technisch genutzte Isomer ist das γ -HCH (**1**), welches unter dem Namen Lindan bekannt wurde. Es wurde erstmals 1825 von FARADAY synthetisiert.^[159,160] Die großtechnische Herstellung erfolgte durch photochemische Chlorierung von Benzol (**2**) mit Chlorgas.^[161,162] Ab 1947 wurden Technologien zur Anreicherung von Lindan entwickelt, die je nach Synthesebedingungen verschiedene Isomerengemische lieferten. Diese setzten sich typischerweise aus 60–70% α -HCH (**3**), 5–12% β -HCH (**4**), 10–15% γ -HCH (**1**), 6–10% δ -HCH (**5**) und 3–4% ϵ -HCH (**6**) zusammen (Abbildung 9).^[5,6] Mehr als 85 % der anfallenden Isomere waren somit als Insektizid nicht verwertbar und fielen als Abfall an, was einem Depositenanfall von 9–12 Tonnen je produzierter Tonne Lindan entsprach.^[5]

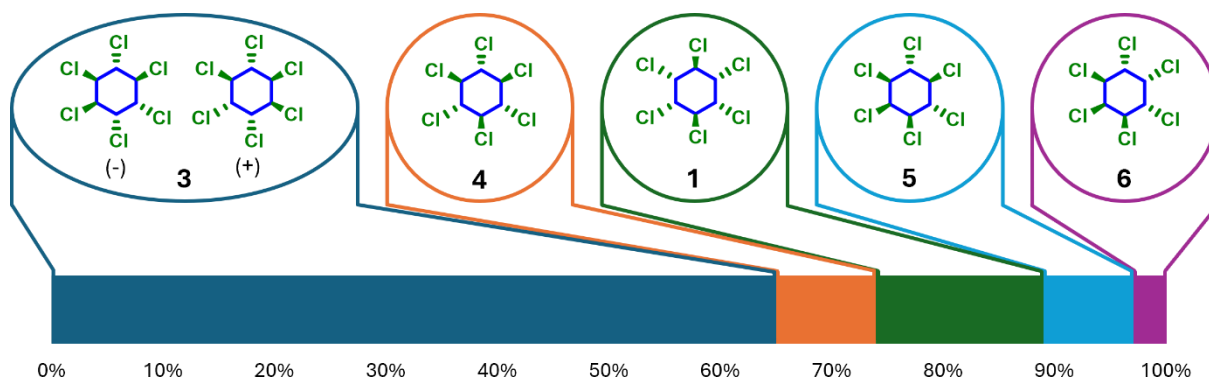


Abbildung 9: Isomere des HCH: α -HCH (**3**), β -HCH (**4**), γ -HCH (**1**), δ -HCH (**5**) und ϵ -HCH (**6**) mit mittlere prozentualer Darstellung des Isomer-Gemisches.^[5]

Von 1942 bis 2009 wurde Lindan in Europa als Insektizid eingesetzt, bis alle HCH-Isomere in das Stockholmer Übereinkommen aufgenommen wurden, welches den Einsatz und die Herstellung persistenter organischer Schadstoffe (POP) international untersagt.^[7,163–165] Die ökotoxikologischen Folgen des weltweiten HCH-Einsatzes sind weitreichend: Im menschlichen Blut, in der Muttermilch sowie im Fettgewebe wurden weltweit Anreicherungen nachgewiesen.^[166] Darüber hinaus verursacht Lindan Immuntoxizität und beeinträchtigt das Wachstum sowie die Fortpflanzung von Tieren

und Wasserorganismen.^[163,167] Die durch den HCH-Einsatz verursachte Umweltkontamination ist global verbreitet und aufgrund der Persistenz der Verbindungen bis heute allgegenwärtig.^[168] Weltweit lagern zudem große Mengen toxischer Altbestände an technischem HCH auf Deponien.^[7,163–165]

Ein weiteres POP, das 2013 ebenfalls in das Stockholmer Übereinkommen aufgenommen wurde, ist 1,2,5,6,9,10-Hexabromcyclododecan (HBCD, **7**).^[17] Es wird seit den 1960er Jahren durch Bromierung von Cyclododecatrien (**8**) hergestellt und fand vor allem als kostengünstiges halogenhaltiges Flammenschutzmittel breite Anwendung.^[169–171] Im Jahr 2011 betrug die weltweite Produktionsmenge etwa 28 Kilotonnen.^[9] Ähnlich wie bei der HCH-Synthese entsteht bei der Herstellung ein Isomerengemisch aus α - (10–13%), β - (1–12%) und γ -HBCD (75–89%) sowie Spuren von δ - und ε -HBCD.^[10] Obwohl Neurotoxizität,^[172] endokrine Wirkungen,^[173] Stoffwechselstörungen^[174] sowie Reproduktions- und Entwicklungstoxizität umfassend dokumentiert sind,^[175,176] wird HBCD in den Vereinigten Staaten bis heute produziert.^[177] Inzwischen wurde die Verbindung weltweit in verschiedenen Umweltmatrizen, darunter Luft,^[178] Boden^[179] und Wasser, nachgewiesen.^[180,181] Dies führt zu einer Bioakkumulation entlang der Nahrungskette und einem Eintrag in das menschliche Blut führt.^[182,183]

Polyvinylchlorid (PVC) ist das weltweit drittmeistproduzierte Polymermaterial nach Polyethylen und Polypropylen.^[184] 39% der industriellen Chlorproduktion entfallen auf die PVC-Herstellung, was einen Großteil der Cl₂-Produktion in einen einseitigen Stoffstrom hin zu chlororganischen Abfallprodukten lenkt.^[11,12] Der gesamte Herstellungsprozess ist endotherm, da die Chlorproduktion mittels Chlor-Alkali-Elektrolyse äußerst energieintensiv ist und allein in Deutschland etwa 2% des gesamten Stromverbrauchs ausmacht.^[13,185] Aufgrund des hohen Chlorgehalts, seiner Funktion als Flammenschutzmittel sowie des umfangreichen Einsatzes von Additiven, deren Gewichtsanteil in der Endformulierung bis zu 60% betragen kann, ist eine energetische Verwertung durch Verbrennung mit erheblichen Schwierigkeiten verbunden.^[14,186] Die Recyclingquoten sind weltweit äußerst gering, in den USA beispielsweise beträgt die PVC-Recyclingrate lediglich 3%.^[187] Ausgedienter PVC-Abfall gilt als gefährlicher und wirtschaftlich unattraktiver Abfallstoff, der sich auf Deponien ansammelt und durch das Auslaugen toxischer Additive nach wie vor ein Umweltrisiko darstellt.^[188–190] Dennoch bleibt Chlorchemie im industriellen Maßstab unverzichtbar: Sie bildet die Grundlage für die Synthese von Lösungsmitteln,

Katalysatoren und zentralen chemischen Bausteinen in nahezu allen Industriezweigen.^[191]

1.4.2 Bisher bekannte Abbaustrategien

Die umweltgerechte Entsorgung von HCH stellt eine erhebliche technische und wirtschaftliche Herausforderung dar. Die thermische Verbrennung erfordert Temperaturen von über 1000 °C, um die Bildung toxischer Nebenprodukte wie Dioxine oder Phosgen zu vermeiden, und macht zudem den Einsatz kalorienreicher Zuschlagstoffe sowie eine aufwendige Rauchgasbehandlung erforderlich.^[192,193] Dies führt zu Entsorgungskosten von bis zu 2000 € pro Tonne, die sich durch die zunehmende CO₂-Bepreisung weiter erhöhen.^[8]

Zur Entwicklung alternativer Abbaustrategien wurden verschiedene thermische^[194–196] und nicht-thermische Verfahren untersucht,^[197] darunter mechanochemische Prozesse,^[198–200] photochemischer Abbau,^[201–205] mikrobieller Abbau^[206–208] sowie der Einsatz ionisierender Strahlung.^[209–212] Diese Verfahren stoßen jedoch an verfahrenstechnische Grenzen: Entweder ist die Produktselektivität aufgrund der unkontrollierten Bildung toxischer Chlorbenzole und polychlorierter Biphenyle unzureichend, oder die erzielbaren Abbauraten sind für einen großtechnischen Einsatz zu gering.^[213]

1.4.3 Elektrochemische Abbaustrategien

Die Elektrochemie hat sich insbesondere für die Wasseraufbereitung als vielversprechende Methode erwiesen und ermöglicht den Abbau von HCH unter milden Bedingungen ohne den Einsatz externer Reagenzien.^[214–220] Die geringe Löslichkeit von HCH in Wasser stellt jedoch einen limitierenden Faktor für die Prozessintensität dar.^[221]

Gegenüber den zuvor genannten Verfahren bietet die elektrochemische Synthese sowohl ökologische als auch ökonomische Vorteile. Der Einsatz von Elektrizität als Reaktionsantrieb macht zusätzliche Oxidations- und Reduktionsmittel überflüssig^[43,222] und vermeidet so die Entstehung von Sekundärabfällen.^[32] Darüber hinaus lässt sich der Prozess im Bedarfsfall, etwa bei einem Stromausfall, unmittelbar unterbrechen, was die Betriebssicherheit erhöht.^[23] Die wirtschaftliche Tragfähigkeit

des Verfahrens setzt jedoch eine hohe Umsatzeffizienz sowie eine geeignete Aufarbeitung der Produkte voraus.^[31] Der Einsatz umweltfreundlicher Lösungsmittel wie zyklischer Carbonate verbessert die Löslichkeit von HCH und erhöht aufgrund ihrer geringen Entflammbarkeit zugleich die Prozesssicherheit.^[223]

1.4.4 Elektrochemische Transferhalogenierung

LIN *et al.* untersuchten die elektrokatalytische radikalische vicinale Dichlorierung von Alkenen mit nukleophilen Chlorquellen.^[224,225] Durch die Kombination von Elektrochemie und Mangan(II)-chlorid-Katalyse gelang eine Dichlorierung von Alkenen unter Verwendung von Magnesiumchlorid (MgCl_2) als Chlorquelle unter milden Bedingungen, wobei eine Chlorgasentwicklung durch den Radikalweg gezielt unterbunden wurde.^[226]

Eine innovative Weiterentwicklung dieses Ansatzes stellt die von MORANDI, WALDVOGEL *et al.* entwickelte Kombination aus Shuttle-Reaktion und gepaarter Elektrolyse (*e-shuttle*) dar, die erstmals eine skalierbare und umweltfreundliche Methode für das Upcycling von Lindan und HBCD ermöglicht.^[94] Bei diesem Verfahren wurde Lindan elektrochemisch zu Benzol und HBCD zu Cyclododecatrien reduziert, wobei die Methode gleichzeitig den Transfer von Halogenen wie Brom und Chlor erlaubt. Mechanistisch wird angenommen, dass in zwei aufeinanderfolgenden Ein-Elektronen-Reduktionsschritten des Dichlorids an der Kathode jeweils ein Halogenidanion freigesetzt wird (Abbildung 10, I). Die anschließende Halogenierungsreaktion erfolgt über den katalytischen Zyklus (II) des Mangan-Katalysators, wobei die katalytische Aktivität von Mn(III)X_3 den $\text{Cl}^\bullet$ -Transfer zur vicinalen Dichlorierung vermittelt. Dies ermöglicht eine kontrollierbare radikalische Umwandlung unter milden Reaktionsbedingungen.^[227–230]

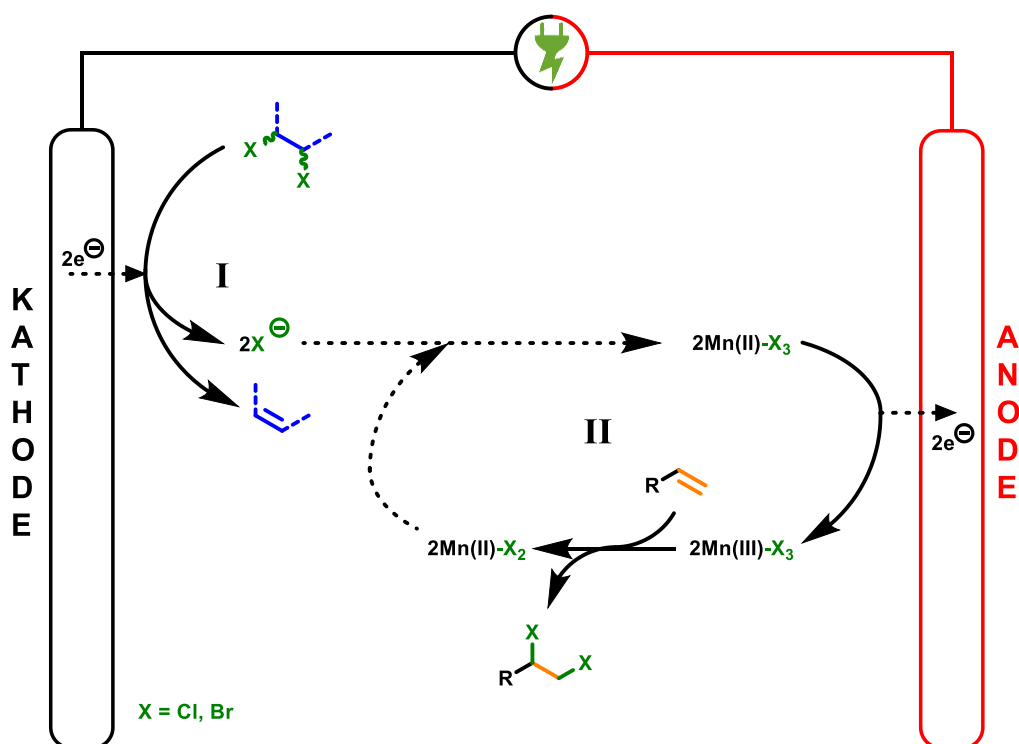


Abbildung 10: Vorgeschlagener Mechanismus zur vicinalen Dichlorierung im *e-shuttle*.^[94]

2 Aufgabenstellung

Der elektrochemische *e-shuttle*-Prozess bietet eine vielversprechende Möglichkeit, HCH, PVC und HBCD großtechnisch umzusetzen, indem Chlor und Brom auf ein Akzeptorsubstrat übertragen werden und so auf beiden Seiten eine Wertsteigerung erzielt wird. Zur Untersuchung dieser Reaktion wurden im Rahmen der vorliegenden Arbeiten zunächst grundlegende Parameter, darunter Elektrodenmaterialien, Lösungsmittel, Leitsalze und Katalysatoren, in einem OVAT-Screening variiert und deren Einflüsse analysiert.

In einer anschließenden statistischen und kinetischen Versuchsplanung wurden die elektrochemischen Parameter Ladungsmenge Q , Stromdichte j , Temperatur T , Eduktäquivalente Eq sowie die Stoffmenge des Katalysators n gezielt untersucht. Darüber hinaus war die Ermittlung signifikanter Haupt- und Wechselwirkungseffekte sowie die Beurteilung der Langzeitstabilität der Elektroden und des Elektrolyten von zentraler Bedeutung (Abbildung 11).

Als relevante Substrate wurden sowohl Verbindungen des monochlorierten Acetaldehyds als auch vicinal dichlorierte funktionalisierte Alkane untersucht, mit dem Ziel, prozessrelevante Substrate zu identifizieren, die in einen mehrstufigen Syntheseprozess eingebunden werden können. Ein zentraler Synthesebaustein war dabei das Acetal des Chloracetaldehyds, für dessen Darstellung mehrere Synthesestrategien abgewogen wurden.

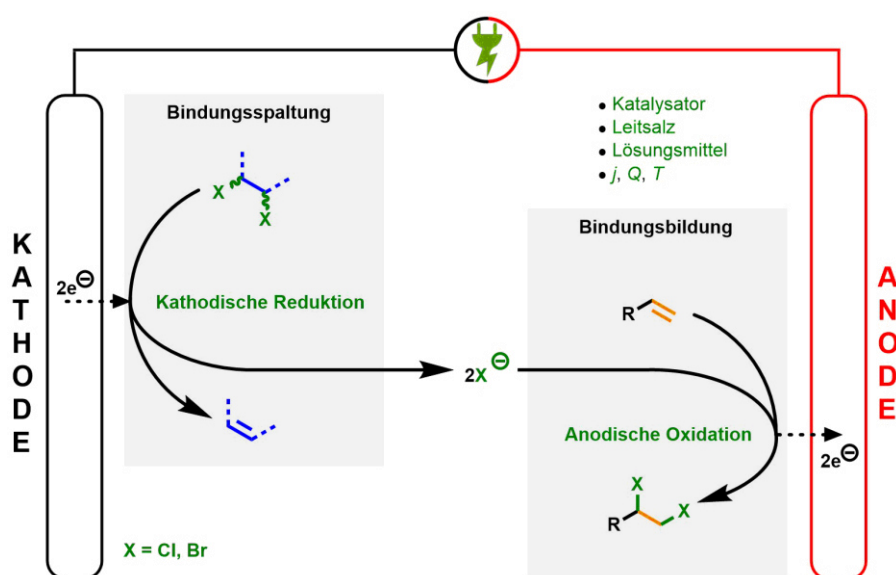


Abbildung 11: Darstellung des *e-shuttle*-Konzeptes in einer aufeinanderfolgenden gepaarten Elektrolyse mit den zugrundeliegenden Parametern. Adaptiert von MORANDI und WALDVOGEL *et al.* unter CC-BY 4.0. © 2021 American Association for the Advancement of Science.^[94]

3 Hintergrund und Ergebnisse

Gemäß bekannter industrieller Synthesepfade kann Chloracetaldehyd (**12**) entweder über die Chlorierung von Vinylacetat (**9**) unter Bildung von 1,2-Dichlorethylacetat (**10**)^[231–234] oder durch direkte Chlorierung von Acetaldehyd (**11**)^[234,235] mit Chlorgas dargestellt werden.^[236] Ausgehend von 1,2-Dichlorethylacetat (**10**) lässt sich Chloracetaldehyd (**12**) durch saure Hydrolyse gewinnen oder direkt durch Zugabe geeigneter Alkohole in das entsprechende Acetal (**13**) überführen.^[234,237–239] Beide Verbindungen stehen über eine Gleichgewichtsreaktion miteinander in Beziehung und lassen sich ineinander umwandeln. Hinsichtlich der Lagerung bestehen jedoch wesentliche Unterschiede: Während **12** vorwiegend als 45%ige wässrige Lösung gehandhabt wird, kann **13** überwiegend in Reinform aufbewahrt werden (Abbildung 12).^[236,240]

Sowohl **12** als auch **13** sind weitverbreitete C₂-Baustein in der Pharmazie,^[239,241–244] der Duftstoff-,^[236] Polymer-^[245–248] und Agrarchemie.^[249–251]

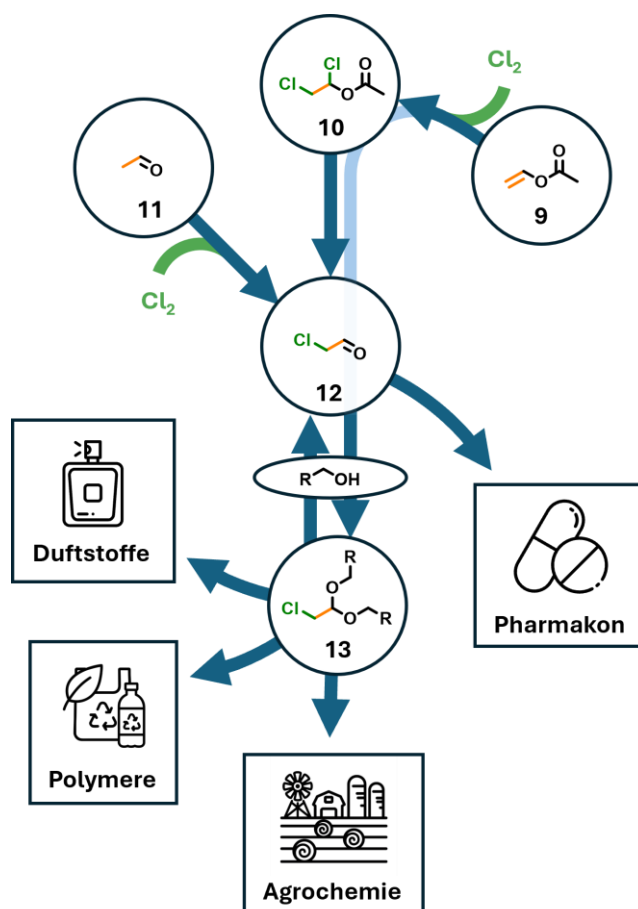


Abbildung 12: Schematische Darstellung und Anwendung von Chloracetaldehyd (**12**). Adaptiert von WALDVOGEL *et al.* unter CC-BY 4.0. © 2026 American Chemical Society.^[236]

Untergliedert in drei Arbeiten wurde die Darstellung von 1,2-Dichlorethylacetat (**10**) sowie die des Acetals des Chlor- (**13**) und Bromacetaldehyds durch elektrochemische Umsetzung von HCH (**3** und **4**) bzw. HBCD (**7**) und PVC näher untersucht. Aufbauend auf der Veröffentlichung von MORANDI, WALDVOGEL *et al.* in Science^[94] wurde das Prinzip des *e-shuttles* vertieft untersucht (Kapitel 4.1), wobei Elektrodenmaterialien, Lösungsmittel, Leitsalze und Katalysatoren im Hinblick auf einen skalierbaren industriellen Prozess erneut evaluiert wurden.

Die Untersuchung der grundlegenden Parameter erfolgte anhand der vicinalen Chlorierung von 10-Undecensäuremethylester (**14**). Weiterführende Experimente im Rahmen der statistischen Versuchsplanung wurden zudem an den Substraten 1-Dodecen (**15**), Vinylacetat (**9**) und Allylalkohol (**21**) durchgeführt. Die resultierenden Produkte 10,11-Dichlorundecansäuremethylester (**16**) und 1,2-Dichlordodecan (**17**) besitzen eine nachgeordnete Relevanz als Zusätze in Schmierstoffen (Abbildung 13).^[252] Hierbei konnten Ausbeuten von 81% für **16** und 56% für **17** erzielt werden (Tabelle 4).

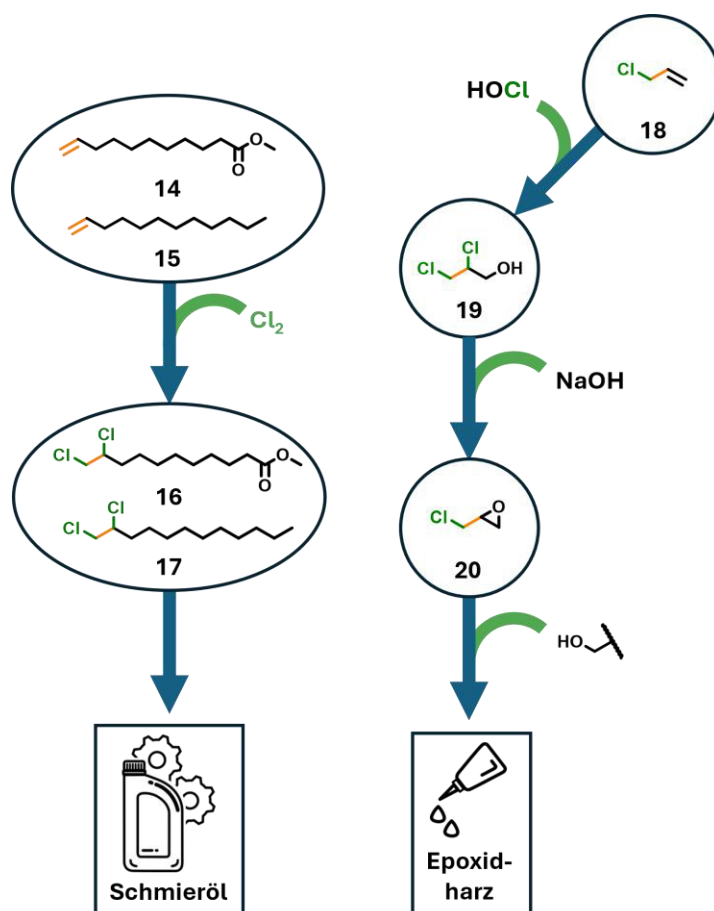


Abbildung 13: Schematische Darstellung und Anwendung von vicinal chlorierten Substanzen.^[252–255]

Als Zwischensubstrate für industrielle Syntheserouten wurden neben dem bereits beschriebenen 1,2-Dichlorethylacetat (**10**) auch 2,3-Dichlor-1-propanol (**19**) untersucht.^[256,257] Letzteres ist von Bedeutung in der Polymerchemie, da es als Ausgangsstoff **19** für die Darstellung von Epichlorhydrin (**20**) dient, welches durch basische Hydrolyse zugänglich ist.^[253–255] In der konventionellen Synthese wird Verbindung **19** ausgehend von Allylchlorid (**18**) dargestellt (Abbildung 13).^[254] Durch Erhöhung der Katalysatorkonzentration und Halbierung der Konzentration des Leitsalzes auf $0.05 \text{ mol} \cdot \text{L}^{-1}$ wurden schließlich Ausbeuten von 89% für **10** und 79% für **19** erreicht (Tabelle 4).

Tabelle 4: Schematische Darstellung (oben) des Halogenübertrags von **3**, **4** (α - und β -HCH) auf terminale ungesättigte Verbindungen sowie der Substratumfang (unten) des Cl-Halogenübertrags auf terminale ungesättigte Verbindungen unter individuell optimierten Bedingungen.^[256,258]

$ \begin{array}{c} \text{Graphit} \parallel \text{Graphit} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \\ \text{Lösungsmittel,} \\ 500 \text{ rpm} \end{array} $				
	10 , 89%	16 , 81%	17 , 56%	19 , 79%
Stromdichte / $\text{mA} \cdot \text{cm}^{-2}$	5.0	30.0	30.8	11.7
Ladungsmenge (Ref. zu 3 , 4) / F	7.2	10.1	8.5	6.5
Temperatur / $^{\circ}\text{C}$	25	75	50	25
Konzentration von 3 , 4 / $\text{mol} \cdot \text{L}^{-1}$	0.2	0.1	0.1	0.25
Äquivalente n	3.0	2.7	3.7	3.0
Konzentration von $(\text{C}_2\text{H}_5)_4\text{NCl}$ / $\text{mol} \cdot \text{L}^{-1}$	0.05	0.1	0.1	0.05
Stoffmengenanteil von $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ / mol%	14.8	5.0	5.0	20.0
Lösungsmittel	Propylen-carbonat	Propylen-carbonat	Acetonitril	Propylen-carbonat

GC-Ausbeute: Mesitylen als interner Standard.

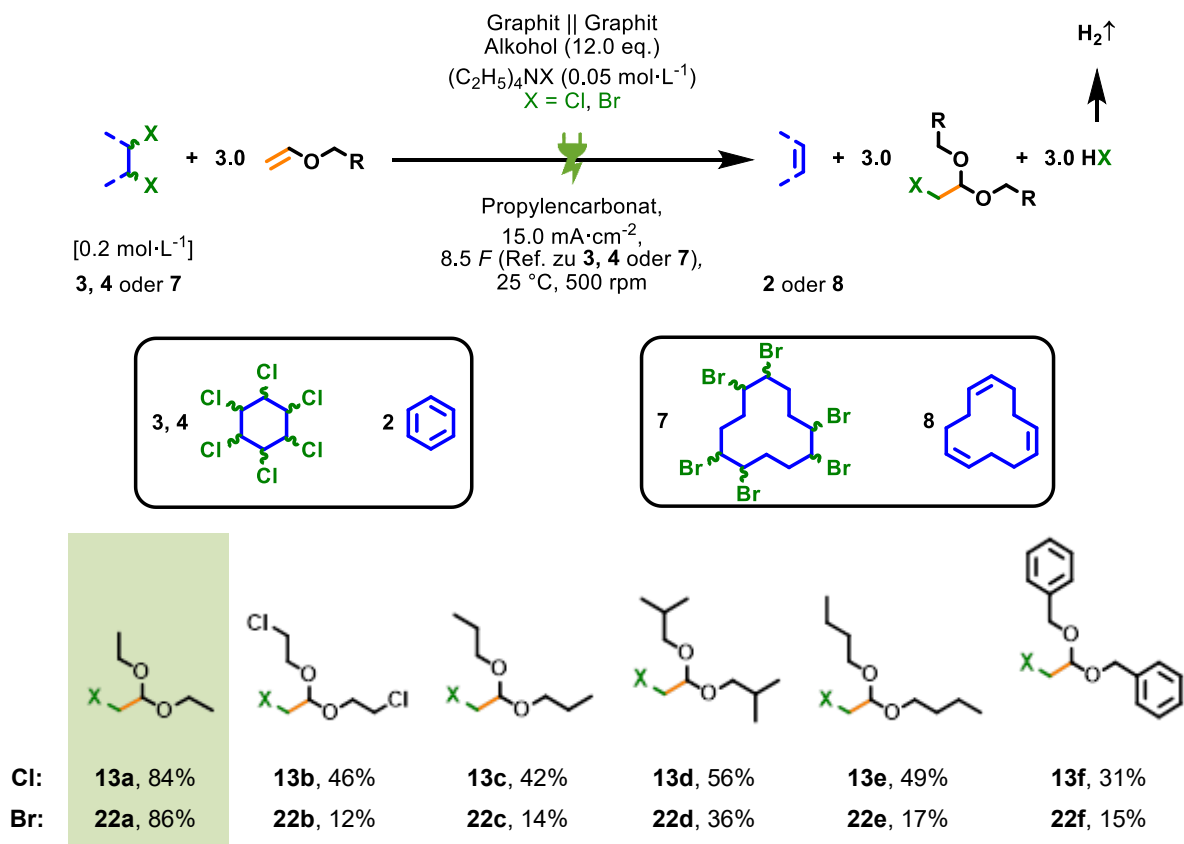
Zudem wurde eine wirtschaftliche Bewertung eines auf einen Jahresdurchsatz von 5000 Tonnen HCH skalierten Prozesses auf **19** durchgeführt, um die großtechnische Machbarkeit des *e-shuttle*-Ansatzes zu evaluieren (Kapitel 4.1).

Eine weitere mögliche Darstellung von Chloracetaldehyd (**12**) wurde durch vicinale Chlorierung von Ethylvinylether in Analogie zu Vinylacetat (**9**) untersucht. Dabei wurde jedoch vorwiegend die Bildung des Diethylacetals des Chloracetaldehyds (**13a**) beobachtet, was durch vergleichbare Literatur gestützt wird.^[259–261] Dies eröffnete eine weitere Syntheseroute zur Darstellung von Chloracetaldehyd über die direkte Synthese der entsprechenden Acetale, die in einer weiterführenden Arbeit eingehender behandelt wird (Kapitel 4.2).

Im Fall von **13a** wirkte sich die Ethanoloxidation tendenziell positiv aus, da das entstehende Chloracetaldehyd ebenfalls in das Acetal zurückgeführt werden kann, wodurch Ausbeuten von bis zu 84% erzielt wurden. Im Gegensatz dazu verläuft die Oxidation von 1-Propanol im Fall von Chloracetaldehyd-Dipropylacetal (**13c**) über die Zwischenprodukte Propionaldehyd und 2-Chlorpropionaldehyd, was zu einer Vielzahl konkurrierender Acetalisierungsprodukte und damit zu einem erheblichen Selektivitätsverlust führt.^[262] Verzweigte Alkohole wie 2-Methyl-1-propanol (**13d**) zeigten hingegen deutlich geringere Oxidationstendenzen (Tabelle 5).

Die Anwendung der für **13a** optimierten Reaktionsbedingungen auf die Bromierung von Vinylethern unter Verwendung von HBCD (**7**) als Bromquelle lieferte das Diethylacetal des Bromacetaldehyds (**22a**) in einer vergleichbaren Ausbeute von 86%. Bei anderen Vinyletherderivaten waren die relativen Ausbeuten jedoch deutlich geringer, was auf die verstärkte Bildung von Alkylhypobromiten aus den eingesetzten Alkoholen zurückzuführen ist.^[263–265] Unter den gewählten Bedingungen ergaben das 2-Chlorethyl- (**22b**), Propyl- (**22c**) und Butylacetal (**22e**) lediglich Ausbeuten zwischen 12% und 17%. Außer im Fall des 2-Methyl-1-propylacetals von Bromacetaldehyd (**22d**) wurde eine vergleichbare Beziehung zu den Alkylacetalen des Chloracetaldehyds (**13b–13f**) beobachtet, mit Ausbeuten von bis zu 36% (Tabelle 5).

Tabelle 5: Schematische Darstellung (oben) des Halogenübertrags von **3**, **4** (α - und β -HCH) und **7** auf offene Acetale sowie der Substratumfang (unten) des Cl- und Br-Halogenübertrags auf offene Acetale unter den für **13a** optimierten Bedingungen.^[257,266]



GC-Ausbeute: 1,10-Dichlordecan als interner Standard.

Ergänzend zu offenkettigen Acetalen wurden auch zyklische Acetale untersucht, darunter 2-Chlormethyl-1,3-dioxepan (**24**). Am Beispiel dieses zyklischen Acetals, dargestellt unter Verwendung von 4-Hydroxybutylvinylether (**23**) als Vinylethermonoalkohol, wurde der Reaktionsmechanismus eingehend untersucht, der Unterschiede zum bislang postulierten Mechanismus des *e-shuttles* aufzeigte. Als plausible Schlussfolgerung ergibt sich aus dem beobachteten Anstieg freier Chloridionen im Elektrolyten, dass Chloridionen zu aktivem Chlor (Abbildung 14, „Cl₂“, **III**) oxidiert werden, welches anschließend additiv an die Vinylgruppe addiert wird (**IV**).^[267] Der nachfolgende Zyklisierungsschritt setzt dabei äquimolare Mengen HCl als Kupplungsprodukt frei (**V**). Nach den Baldwin-Regeln stellen 7-exo-trig-Zyklisierungen bevorzugte Sequenzen dar,^[268] was sowohl mit den experimentellen Beobachtungen als auch mit der mechanistischen Begründung übereinstimmt, dass selbst eine erhöhte Zugabe von **23** nur bis zu drei Äquivalenten umgesetzt werden konnten. Darüber hinaus wurde die Wasserstoffentwicklung während der Elektrolyse mittels GC-Analyse quantifiziert, was plausibel auf die kathodische Reduktion von HCl

Beispiel von HCH zu betrachten. Das resultierende Polymer bewahrte seine strukturelle Integrität und zeigte eine interne Plastifizierung infolge kovalenter Rekombination mit Fragmenten der Phthalat-Weichmacher.

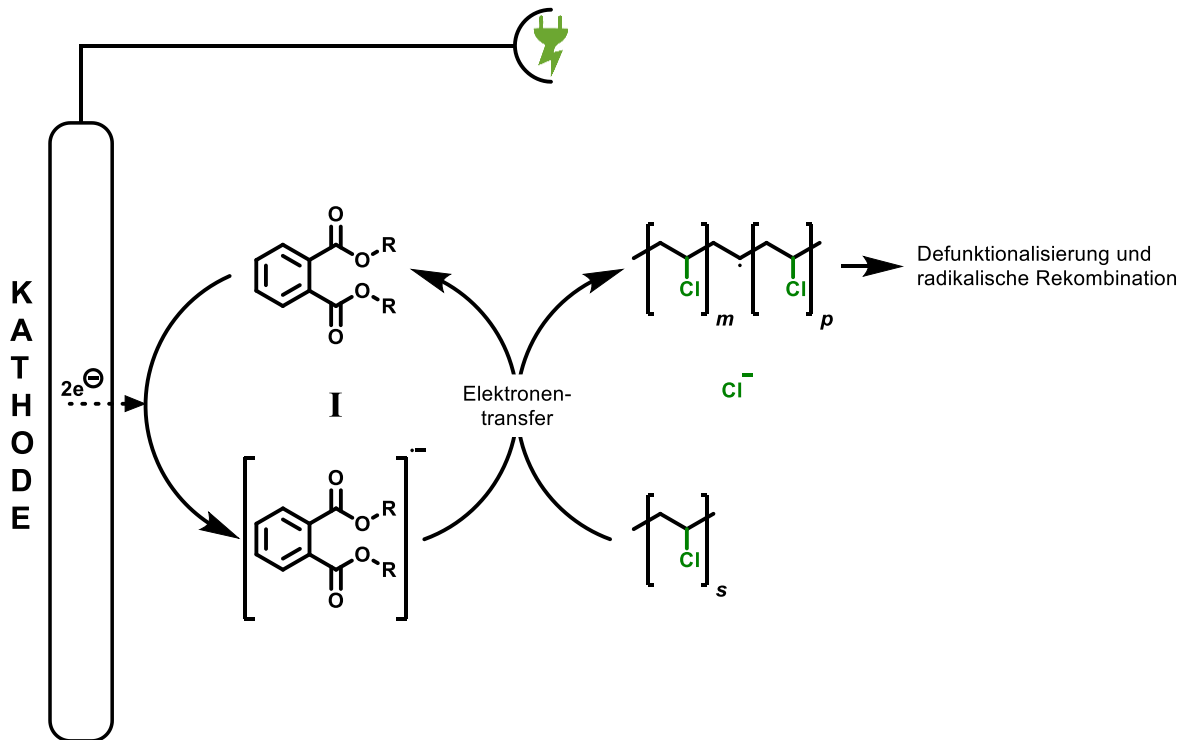


Abbildung 15: Postulierter Mechanismus mit mediierten Elektrolyseweg durch reduktive Spaltung der Kohlenstoff-Chlor-Bindung an der Kathode durch Alkylphthalate. Adaptiert von WALDVOGEL und BESENIUS *et al.* unter CC-BY 4.0. © 2025 Wiley-VCH GmbH.^[270,271]

Diese Ergebnisse belegen, dass sich das auf dem *e-shuttle*-Prinzip basierende Verfahren zur Chlorrückgewinnung erfolgreich auf PVC, und insbesondere auf PVC-basierte Konsumgüter, übertragen lässt und das Anwendungsspektrum des Prozesses damit gezielt erweitert wird.^[270]

4 Überblick der publizierten Werke

4.1 Von technischen HCH-Rückständen zu industriell relevanten vicinalen dichlorierten Verbindungen: Elektrochemischer Chlortransfer als Strategie zur Abfallverwertung?

Zu diesem Kapitel wurde ein Manuskript veröffentlicht:

S. Horsinka, **D. Weis**, T. Langner, P. Beeskow, J. Sauer, S. R. Waldvogel, „From technical HCH residues to industrial relevant vicinal dichlorinated compounds: Electrochemical chlorine transfer as a strategy for waste valorisation“ *J. Hazard. Mat.* **2026**, 508, 141851

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Erklärung meines Beitrags:

Das Projekt wurde im Rahmen des BMBF Cluster4Future ETOS (FKZ: 03ZU1205IA and FKZ: 03ZU1205GC) von S. Horsinka und **D. Weis** bearbeitet. S. Horsinka und **D. Weis** führten die Reaktionsoptimierung mittels statistischen Verfahrens (DoE) durch. Die Elektrolysen der Derivate und Skalierungen der Reaktionen wurden durch S. Horsinka und **D. Weis** durchgeführt. S. Horsinka und **D. Weis** führten die Vorläufersynthesen und die Strukturaufklärung via ^1H -, ^{13}C -NMR und HRMS durch. Prozesssimulationen wurden von P. Beeskow und S. Horsinka durchgeführt. S. Horsinka verfasste das Manuskript und stellte es in Zusammenarbeit mit **D. Weis**, J. Sauer und S. R. Waldvogel fertig.



From technical HCH residues to industrial relevant vicinal dichlorinated compounds: Electrochemical chlorine transfer as a strategy for waste valorisation

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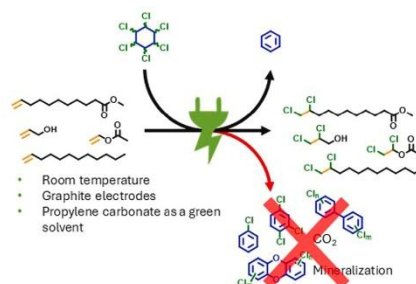
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HIGHLIGHTS

- The *e-shuttle* approach enables upcycling for all isomers of HCH to benzene, using graphite electrodes.
- Electron-rich polar unsaturated bonds are well suited for halogenation in propylene carbonate.
- Kinetic measurements of technical HCH degradation on dichloro product formation were obtained.
- Various process development experiments demonstrated the feasibility of scale up and down streaming.
- Monte Carlo modelling quantifies the economic and ecological viability of the process.

GRAPHICAL ABSTRACT



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ABSTRACT

For over 70 years, the remains of Lindane production have contributed to tremendous global environmental problems. The manufacturing process of 1,2,3,4,5,6-hexachlorocyclohexane (HCH) yields approximately 15% of the insecticidal γ -isomer, which is called Lindane. This has led to the accumulation of estimated 7.4 million tons of waste worldwide that have in most cases not been properly disposed. In addition, the HCH has carcinogenic, genotoxic, mutagenic, and teratogenic effects. The large quantities of this persistent residue, which continue to spread into the environment, highlight the urgent need for remediation. Although numerous processes for water treatment have been extensively described, all the established methods currently rely on incineration. In this context, electrosynthesis represents a promising and sustainable approach to transform HCH into benzene, while

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simultaneously enabling the released chlorine to upcycle terminal alkenes into vicinal dichloro products. Since this process must be economically competitive with conventional incineration, the present study investigates the key characteristics of the proposed *e-shuttle* reaction. Several industrially relevant chloro compounds are optimized in terms of their molar yields related to HCH input. Additionally, the kinetics of the reaction are studied using a representative substrate, and the potential for chlorine upcycling is assessed. Finally, an economic feasibility analysis is conducted for a plant designed to upcycle annually 5 000 metric tons of HCH.

1. Introduction

Pesticides are crucial to agricultural sector, as they increase food productivity on less land by preventing crop losses caused by fungi and insects. [1] After the World War II, 1,2,3,4,5,6-hexachlorocyclohexane (HCH) became the most widely produced and used insecticide on industrial scale. [2,3] HCH was initially synthesized by MICHAEL FARADAY in 1825 by photochlorination of benzene. [4] Industrially, HCH was also obtained in a set of five different diastereomers with varying isomer ratios depending on the process employed (Fig. 1). [2] Although HCH is a very effective insecticide, applying it on crops often resulted in very unpleasant musty smell and taste, rendering the harvest inedible. [5] Therefore, in the early 1950s, the γ -isomer, known as Lindane, was separated by methanol extraction [6] due to its tastelessness at low concentrations [7] and its effectiveness as an insecticide. [5] As consequence of the low yield of approx. 15% the production of Lindane over almost six decades has led to one of the biggest global hazardous waste problems. For every ton of Lindane produced, 8–12 tons of waste consisting of non-insecticidal isomers were generated, which are collectively known as technical HCH (1). [6]

Instead of being properly incinerated, [8] this waste was often ruthlessly disposed into the environment at production sites worldwide. [8,9] In most cases, the remains were buried, but only rarely sealed, which is why HCH is still leaking from these seams into the environment. In other cases, such as in Spain or India, the material was simply left above ground and spread to surrounding areas. [10]

Due to its carcinogenic, persistent, and bio-accumulative features, Lindane production was largely discontinued in the early 2000s. [7,11] In 2009, all of the isomers of HCH were added to the Stockholm Convention on Persistent Organic Pollutants (POPs), [12] which bans their production and use as well as restricts their transportation to prevent further environmental exposure. [13] It is estimated that up to 7.4 megatons of HCH have been produced globally. [11] As a result of prolonged environmental contamination, HCH isomers can now be found in groundwater, [14] surface water, human fatty tissue, [15] blood, [16] and even breast milk. [17]

Over time, various methods have been developed to utilize the vast quantities of HCH as a Lindane source [18,19] or to decompose it safely. [20] Isomerization processes were developed to increase the yield of Lindane. [21–25] However, these methods were not economically viable. Additionally, attempts were made to convert HCH isomers into trichlorobenzenes by alkaline or thermal treatment, [26–33] but these methods are no longer technically useful. [11] The trichlorobenzenes produced are not used today and are now themselves becoming a waste problem. [11,34] Currently, aside from thermal treatment, no

large-scale industrial process exists for processing HCH deposits on a bulk scale. An example of such processing is the conversion into additives for road construction, as implemented in Macedonia between 2017 and 2022. This project, which disposed of around 1.8 kilotons of HCH, cost approx. 15.5 million €. [35] The challenge with incinerating HCH is that complete destruction means the loss of all carbon components and large amounts of chlorine added to the economic cycle. Like many polychlorinated compounds, HCH represent as superb flame retardant, requiring large amounts of energy for incineration. Additionally, achieving the necessary temperatures above 1000 °C to prevent formation of polychlorinated dioxins and phosgene requires substantial amounts of fuels like oil or high caloric waste. In addition, the resulting acidic flue gases must be neutralized. [11,36] This results in treatment and in modern incineration plants of around 5 000 €•t⁻¹. [37] These costs will continue to rise in the near future due to increased CO₂ taxation and cost for fuels as well as post-treatment chemicals. [38] Various non thermal strategies have been developed for the degradation of HCH, [20] such as mechanochemical [39–41] or photochemical degradation, [42–45] the use of microorganisms, [46–48] and further, [49–51] to convert HCH into less harmful materials. Even the use of X-rays has been investigated. [52] However, photodegradation, as well as pyrolysis, [53,54] often results in the formation of various chlorobenzene derivatives, along with chlorophenols and polychlorinated biphenyls (PCB). [45] Like HCH, PCB are also toxic, carcinogenic, and persistent chlorinated compounds. PCB and eleven other substances formed the basis of the Stockholm Convention of 2001, and are commonly referred to as the "Dirty Dozen". [55] Bacterial reactions selectively produce benzene and chlorobenzene, though these processes require low concentrations of HCH to be successful and can take up to several days. [46,56,57] Biological degradation of HCH has advantage that it can also be used directly to purify contaminated soil. In addition, the natural degradation products of HCH, such as polychlorinated benzenes, are also degraded. This can even increase the fertility of the treated soil again. [58,59] Electrosynthesis has so far proven to be the most practical alternative to remove HCH, particularly for water purification (Fig. 2). [60] This offers the possibility of removing not only HCH but also other polychlorinated pollutants. Leading in this field is the work of HERRAIZ-CARBONÉ *et al.*, who uses mixed metal oxide (MMO) [61] and boron-doped diamond (BDD) [62] anodes to break down polychlorinated pollutants. In this process, the chlorine of the pollutants is oxidized to less harmful chlorates and perchlorates through the generation of potent oxidants, such as percarbonates and persulfates, and the remaining hydrocarbons are mineralized to CO₂ and H₂O. [61,62] However, due to the low solubility of HCH in water, only very limited space-time yields are achieved, making bulk degradation of the deposits

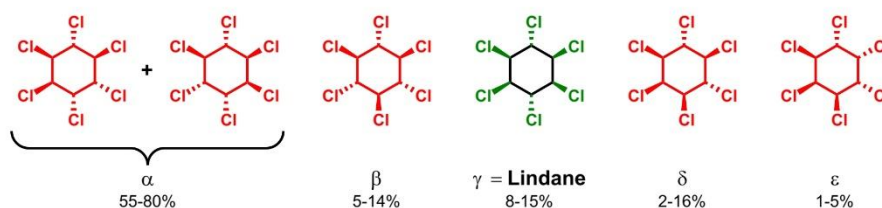


Fig. 1. Isomers of HCH. Those marked in red are described as technical HCH.

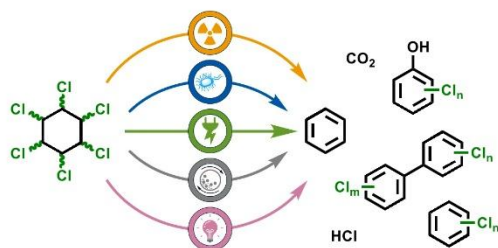


Fig. 2. Different non-thermal degradation approaches for HCH.

unattractive. Systems, such as surfactant-enhanced aquifer remediation (SEAR), can greatly improve degradation from water by solvolyzing polychlorinated pollutants in non-aqueous media. [63] The electrolyses can be conducted by constant potential [64–66] or galvanostatically. [67–69] The large-scale application of a potentiostatic reaction has not yet been realized. The use of complex and cost-intensive mediators [70–72] also proves unsuitable for scaling up. However, the process by OTURAN *et al.* achieves complete decomposition to CO_2 , water, and chloride by electrochemically generated Fe^{2+} . [68] Despite this, all the processes result in the formation of chloride, which must be reprocessed into chlorine to be usable again for synthesis. [73]

For this purpose, electrosynthesis offers the first scalable, environmentally friendly method of upcycling Lindane using the *e-shuttle* developed by DONG and ROECKL *et al.* [69] HCH (1) is initially cathodically reduced to benzene (2). The generated chloride (I) can then be transferred to terminal alkenes using oxidizable transition metal salts as catalyst. This process valorises alkenes as acceptor substrates by chlorination, making them usable as technical starting materials or intermediates in value chains. [69] The mechanism of chlorination reaction was described by LIN *et al.* (Fig. 3). The oxidation of Mn^{II} at the anode leads to the uptake of the chloride (II), which is then transferred to the acceptor substrate (AS) in the first step, resulting in a radical species (III). In the second step, the radical species reacts with another oxidized Mn^{II} to form vicinal dichloro compound (IV). [74] Additionally, this method can be used in electrosynthesis to transfer bromine. [75,76]

Electrosynthesis offers numerous ecological and economic advantages for the development of a cost-efficient and scalable process. Firstly, the use of electricity eliminates the need for additional oxidizing and reducing agents, [77,78] thereby preventing the generation of additional waste. [79,80] Furthermore, the reaction process is inherently safe, as it can be immediately stopped by switching off the electricity. [81] In addition, green, organic solvents such as cyclic carbonates can be used, [82] which not only have a high solubility for HCH, but also

provide additional process safety due to their low flammability. [83]

The choice of acceptor substrate is crucial for ensuring the economic viability of an HCH upcycling process. A high level of valorisation must be achieved by chlorination, and simple, cost-effective downstream processing must be guaranteed to maintain economic feasibility. [84] This describes the avoidance of chromatographic separation methods and only permits easily scalable methods such as distillation, extraction or crystallisation. Furthermore, the selective dechlorination of all HCH isomers to benzene must be ensured. On the one hand, the non-fossil benzene is generated by this way could be easily integrated into existing value chains. On the other hand, the formation of dioxin, PCBs, or chlorinated benzenes must be prevented, as this would only result in additional hazardous waste.

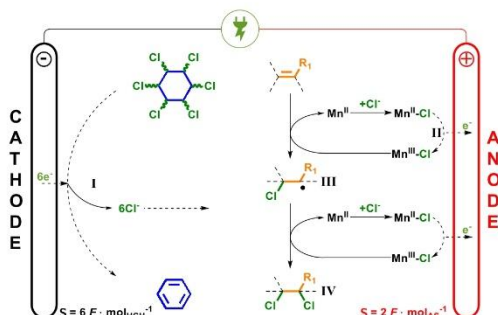
2. Materials and methods

2.1. Chemicals, electrode materials and electrochemical setup

If not stated otherwise, all reactions were performed at ambient conditions. Chemicals were of analytical quality and were purchased from common chemical suppliers without further purification. (Table S1.1). The technical HCH was provided by FLUXUM, Merck KGaA in Gernsheim, Germany. The technical HCH was stored underground in seam 1 (Flöz 1). The isostatic graphite (SIGRAFINE™, highly isostatic, V2100) was purchased from SGL Carbon, Bonn, Germany, the boron-doped diamond (BDD) (DIACHEM™, 15 μm boron-doped diamond layer on silicon) from CONDIAS GmbH, Itzehoe, Germany, the glassy carbon (SIGRADUR® G) from HTW Hochtemperatur Werkstoffe GmbH, Tierhaupten, Germany, the graphite foil (SIGRAFLEX™; F02012Z) from SGL Carbon, Melting, Germany and the various metal electrodes were from various metal suppliers (Table S1.2). For electrochemical reactions a HMP4040 Programmable Power Supply 384 W from Rohde & Schwarz GmbH & Co. KG, München, Germany and a MR Hei-Tec magnetic stirrer from Heidolph Instruments GmbH & Co. KG, Kelkheim, Germany were used. For the screening, optimization and kinetics a 5 mL vial with stirring bars in each cell during electrolysis were used (SI Figure S1.1). The electrolysis set-up is commercially available as IKA Screening System Package (IKA® Werke GmbH & Co. KG, Staufen, Germany). The lids were manufactured by the in-house workshop, as the materials of the original lids (stainless steel) cannot tolerate the corrosive conditions. For the recyclability tests the electrolysis set-up was also made by the in-house workshop, based on the dimensions of the 5 mL IKA glass cell. A geometric factor of 2.3 was used to scale up the glass cell to 50 mL, whereby the distance between the electrodes remains constant at 5 mm. For the last scale up to 500 mL a geometric factor of 2.3 was also used and the glass and lids made by the in-house workshop (Chapter S 1.2).

2.2. Pretreatment of HCH

After excavation from the seam, the technical HCH must be separated from soil residues, stones, and other impurities before use. For this purpose, a Soxhlet extractor is used (Figure S2.1). The HCH is then dissolved in refluxing ethyl acetate and filtered. Subsequently, the HCH is concentrated under reduced pressure and the precipitate then filtrated off. The solids are then washed with cold ethyl acetate and pre-dried by air suction. The pre-dried HCH is powdered and dried again in a high vacuum. Afterwards, the technical HCH obtained composed of 85% α -HCH, 15% β -HCH and < 1% δ -HCH, which corresponds to the composition prior to purification. Finally, the technical HCH was stored at room temperature (21–24 °C). Small amounts of β -penta-chlorocyclohexene (β -PCX), a byproduct of the Lindane production, [85] was washed out during the pretreatment of the technical HCH and not detected by GC or GC-MS after drying (Chapter S 2.1).

Fig. 3. Mechanism of the *e-shuttle* for vicinal chlorination reaction. [69,74].

3. Results and Discussion

3.1. Screening and Optimization

Identifying a suitable product for transfer chlorination is the essential task for the development of an economically viable process. This requires not only sufficient valorisation of the acceptor compound, but also selective degradation of the various HCH isomers to benzene. [86] As has already been proven for Lindane, the *e-shuttle* is suitable for a selective reaction to benzene. [69] We initially envisioned ethylene as the acceptor, which can be further processed after dichlorination to vinyl chloride and thus to polyvinyl chloride (PVC). This has the advantage that the sales market is large enough to absorb the processing of 7.4 megatons of HCH over the years of its degradation. Furthermore, even more requirements are placed on the system: Since the downstream processing is the essential cost factor, the solvent should have a higher boiling point to isolate the product from it, to replenish the electrolyte system with new starting material, and to use it again. Finally, the materials used should be sustainable and cost-effective. The cell type used was a further development of the electrochemical screening system by IKA® (Figure S1.1–9). Based on the publication by DONG and ROECKL *et al.*, [69] instead of pure Lindane, deposits of real technical HCH were used. Methyl 10-undecenoate (3) was selected as test substrate due to its good solubility in various solvents and the potential use of the product methyl-10,11-dichloro undecanoate (4) as a lubricant additive. [87] In addition to the conditions of DONG and ROECKL *et al.*, [69] isotactic graphite electrodes, manganese chloride tetrahydrate as a catalyst, and acetonitrile as a solvent were adopted. The expensive tetraethylammonium tetrafluoroborate was replaced with the cost efficient tetraethylammonium chloride (page S24). A GC yield of 45% of 4 was determined with a Faraday efficiency *FE* of 30% (Fig. 4). The chemical yield and Faraday efficiency were determined using gas chromatography with mesitylene as internal standard. In addition to benzene, chlorobenzene was found. This is due to the dechlorination of the α -HCH, whereby, as already reported, various chlorinated benzenes can be formed. [70] This was previously not observed when Lindane was used as a chlorine source. Due to the alignment of the chlorine atoms in Lindane, [50,64] as well as in β -HCH, [88] dechlorination favours the formation of benzene. [89] The aim of the following screening and optimization was to suppress the formation of chlorobenzenes. For this, various carbon-based and metal electrodes were screened (Table S3.1 and S3.2). Metal electrodes showed a high selectivity for the formation of various multiply chlorinated benzenes. This is a result of the higher selectivity

for β -H elimination. Higher yields of benzene could result from using zirconium as the cathode. Only the graphite electrodes as well as the graphite foil and felt showed good selectivity towards benzene. However, the felt also led to the formation of some chlorobenzenes. The foil on the other hand showed comparable selectivity towards benzene as the isotactic graphite but could not surpass the conversion of 1 and the yields of the target product, which is why further reactions were carried out with isotactic graphite. When screening the solvents, propylene carbonate proved to be the best (Table S3.3). Not only does it lead to the formation of more of 4 with 56% and a better yield of 2, but as a green high-boiling solvent it also has very important properties for establishing an industrially applicable process. The screening of the supporting electrolytes (Table S3.4) and catalysts (Table S3.5) showed that the optimum process participants from DONG and ROECKL *et al.* are already being used. [69] Although tetrabutylammonium tetrafluoroborate has superior yields, it is not being pursued further because we want to avoid the use of other persistent substances such as fluoride-containing salts. In addition, only one type of anion is available, which prevents unwanted side reactions, as the anion can decompose, which would release corrosive hydrogen fluoride. Notably, opposing yield trends for 4 are observed between chlorides and tetrafluoroborates. The use of $(C_2H_5)_4NCl$ results in a yield of 87%, which decreases to 41% with increasing alkyl chain length, as observed for $(C_4H_9)_4NCl$. In contrast, the tetrafluoroborate salts show an increasing yield with longer alkyl chains, rising from 3% with tetramethylammonium to 94% with tetrabutylammonium tetrafluoroborate. The subsequent statistical optimization aimed to improve the yield of the chlorinated product and to optimize the conversion of 1 with high selectivity for 2. Therefore, Design-of-Experiments (DoE) was utilized for this purpose. For this the amount of applied charge, current density, temperature, ratio of 3 to 1, and the amount of catalyst were varied. In addition, high production rates shall be achieved. Consequently, an attempt was made to increase the current density to minimize the electrolysis time.

This first fractional factorial experimental design improved the yield of 4 to 76%, with high conversions of 1 of 88%. The higher conversion of 1 compared to the amount of 4 formed can be explained by the fact that the supporting electrolyte and the catalyst can act as a chlorine reservoir. Experiments without acceptor showed that 1 is also reduced without acceptor, but only up to about 17%, even at more than 9 F of applied charge. The oxidation of the chloride and its stabilization in the form of polychloride chains without forming chlorine can occur at the anode. [90] We assume that these polychlorides are reduced preferably compared to 1 above a certain concentration, which is why the

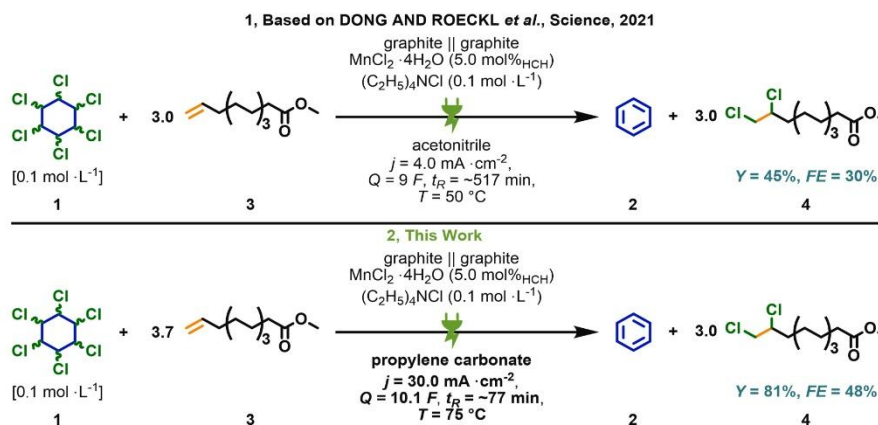


Fig. 4. Optimization of the GC yield *Y* and Faraday efficiency *FE* of 4 via linear screening and DoE.

Table 1
Optimization reactions of 4.

Entry	Deviation from standard conditions	Conversion X(1) / %	Yield Y(2) / %	Conversion X(3) / %	Yield Y(4) / %
1	Anode: Graphite, Cathode: Graphite	72	21	> 99	45
2	Anode: Graphite, Cathode: BDD	86	0	92	37
3	Anode: GC, Cathode: GC	61	0	66	27
4	Anode: Graphite, Cathode: Nb	86	0	99	46
5	Acetonitrile	72	21	> 99	45
6	Propylene carbonate	94	96	99	56
7	Tetramethylammonium chloride	> 99	71	98	87
8	Tetraethylammonium chloride	94	96	99	56
9	Tetrabutylammonium chloride	> 99	94	> 99	41
10	Tetramethylammonium tetrafluoroborate	13	13	89	3
11	Tetraethylammonium tetrafluoroborate	79	64	90	69
12	Tetrabutylammonium tetrafluoroborate	90	95	97	94
13	Without catalyst	89	73	> 99	23
14	Manganese(II) chloride tetrahydrate	> 99	75	> 99	67
15	Without 1	-	-	> 99	5
16	Without 3	17	17	-	-

GC Yield/Conversion: Mesitylene as internal standard.

conversion stagnates despite the higher amount of applied charge. This is consistent with the observations we have already made in a similar reaction, which leads to the formation of acetals. Ion-exchange chromatography (IC) revealed an increase in the concentration of chloride in the solution. [91] In the example of entry 16, the reaction solution absorbs 0.51 mmol of chloride. These polychloride chains are then oxidized or reduced as a side reaction on the anode and cathode, thereby partially reducing the *FE* of the reaction.

The amount of applied charge and temperature are also relevant for the degradation of 1. Interactions between the factors have no significant influence on the conversion of 1. For the formation of the acceptor product 4, interactions between the factors are more significant. High current density at 25 °C increased the yield by seven percentage points, while at 75 °C low current density was advantageous. A full factorial experimental design of these parameters was carried out to further investigate the effects of the amount of charge, the equivalents of acceptor 3 to 1 and the influence of the catalyst. A temperature of 75 °C and a current density of 30 mA•cm² were kept constant. After a Central Composite Design (CCD), this optimization enables a maximum yield of 81% with a Faraday efficiency of 48% under the conditions (Fig. 4). By increasing of the yield and the current density from 4 to 30 mA•cm², the production rate could be increased twelvefold. In addition, kinetic studies were carried out to investigate the various influencing factors, which will be discussed later.

Furthermore, 1-dodecene (5) was investigated as a possible acceptor to investigate the effects when using apolar acceptors. However, since 5 and propylene carbonate are not completely miscible, the use of acetonitrile (MeCN) as a solvent was necessary. Therefore, based on the screening of the 3, only the supporting electrolyte was screened. The chlorination of 5 shows a different trend regarding the chain length of the ammonium salt compared to the chlorination of 3. The highest yields of compound 6 were achieved using tetraethylammonium salts, with the chloride affording 58% and the tetrafluoroborate 74%. In this case as well, tetrafluoroborates generally lead to higher yields than the chlorides. To optimize the yield of 6, a full factorial experimental design was carried out. For this purpose, the significant parameters identified in the DoE of 4 were initially focused on. Thus, the amount of charge, current density, and the ratio of 5 to 1 were evaluated. The temperature was limited to 50 °C and not increased to 75 °C to prevent the extensive evaporation of MeCN. The design of the cell didn't allow an additional cooler to be attached on top.

Overall, for the conversion of 1 and 5 as well as the yield of 2 and 4, the ratio of 5 to 1, the amount of charge, and their interaction were significant. The conversion of 1 and the yield of 2 increase with the applied amount of charge. In contrast, a maximum in the conversion of 5

and the yield of 6 is observed within the investigated range, which can be attributed to the dimerization of 5. As with 4, the central point of 30 mA•cm⁻² proves to be the optimal value. Subsequently, a CCD was carried out again, resulting in a yield of 56% under the conditions displayed (Fig. 5). Thus, although the final yield could not be significantly improved, the production rate was increased sevenfold with less use of the starting material and amount of applied charge. Although the reaction conditions were optimized, chlorobenzene remained detectable via GC as a co-product in the reaction mixtures of both 6 and 4.

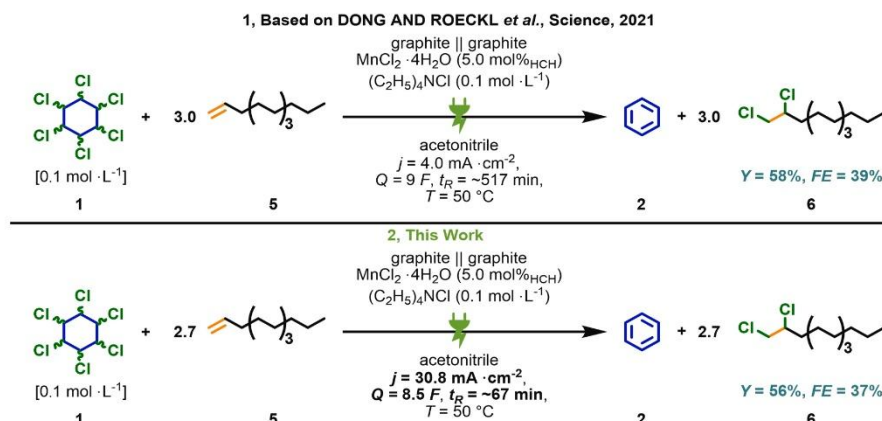
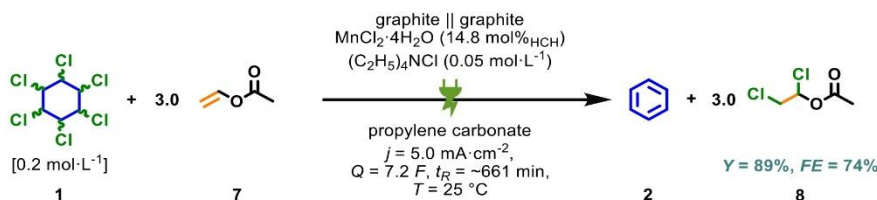
Not only end products can be suitable for industrial applications but also intermediates. These can have higher production volumes, as they serve as platform chemicals supplying multiple value chains. One of these intermediates is produced by the chlorination of vinyl acetate (7). [92] The 1,2-dichloroethyl acetate (8) obtained this way is converted in the respective acid to chloroacetaldehyde, which is required to produce various heterocycles, [93] or is converted directly to dimethyl or diethyl acetal. [94]

We started with a 2⁵⁻¹ partial factorial design to optimize the yield of 8. For this again the amount of applied charge, current density, temperature, ratio of the acceptor 7 to 1, and the amount of catalyst were varied.

This shows again that anode and cathode reactions occur independently. For conversion of 1, high amounts of charge are particularly beneficial, whereas higher yields of 8 can be achieved with a lower amount of charge. After the first CCD, a product yield of 49% was already achieved at room temperature with an applied charge of 7.2 F. Due to the small amount above the amount of current to be applied quantitatively, a Faraday efficiency close to the material yield of 41% could even be achieved.

By subsequently linearly measuring the concentration of 1, a yield of 76% of 8 was obtained by doubling the concentration. This was followed by a second full factorial DoE in which the ratio of 7 to 1 and the supporting electrolyte and catalyst concentration were investigated in detail. By increasing the catalyst concentration to 14.8 mol%_{HCH} and cutting the supporting electrolyte concentration in half to 0.05 mol•L⁻¹, this finally led to a yield of 89% with *FE* = 74%. The optimized conditions are shown in Fig. 6. Moreover, GC analysis confirmed that chlorobenzene was no longer present in the reaction mixture under the optimized conditions.

Another interesting substrate for chlorination is allyl alcohol (9). The 2,3-dichloro-1-propanol (10) formed from it can be converted to epichlorohydrin in Solvay's Epicerol® process, which is added to various adhesives or resins on a million-ton scale every year. [95] This gives the volume of the HCH deposits a suitable sales market to recoup the 73% chlorine from the 7.4 million tons of HCH. Based on the previously


 Fig. 5. Optimization of the GC yield Y and Faraday efficiency FE of 6 via linear screening and DoE.

 Fig. 6. Optimization of the GC yield Y and Faraday efficiency FE of 8 via linear screening and DoE.

gained knowledge, the yield of **10** was again optimized via DoE.

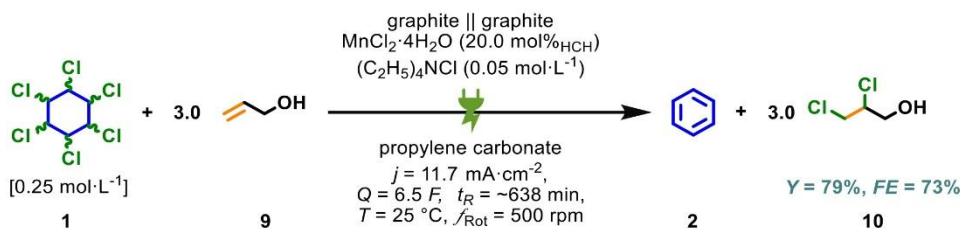
The initial fractional factorial design demonstrated that the concentration of **1**, and consequently the proportional concentration of **9** when using three equivalents, had a significant effect on the yield of **10**. An increase in concentration led to an improvement in yield of approximately 13%. Furthermore, an increased concentration of catalyst also led to a notable improvement in the yield of **10**, with gains of around 8%. A significant dependence of the space-time yield on the interaction between the amount of applied charge and the concentration of **1** was observed. At a concentration of 0.2 mol·L⁻¹ of **1**, a slight decrease in the yield of compound **10** was noted within an applied charge range of 6–8 F . In contrast, lower concentrations of 0.1 mol·L⁻¹ of **1** resulted in a more pronounced increase in yield under the same conditions. Nevertheless, overall higher yields of **10** were achieved with concentrations of **1** of 0.2 mol·L⁻¹, particularly at lower charge levels (Table S3.42). Optimization of the central composite design based on the initial fractional factorial experiments led to yields of **10** up to 79%

(Fig. 7). This was achieved by increasing the concentration of **1** to 0.25 mol·L⁻¹ and, accordingly, the concentration of **9** to 0.75 mol·L⁻¹, while applying a charge of 6.5 F .

In a further small full factorial design, the effects of temperature and supporting electrolyte concentration were also investigated. Only minor influences on the yield of **10** were observed. Temperatures around 50 °C and supporting electrolyte concentrations of approximately 0.03 mol·L⁻¹ led to a modest yield improvement of about 5%. However, considering energy efficiency, these conditions should be regarded as optional rather than essential.

3.2. Kinetic Studies

The kinetic investigation was carried out using the optimized conditions for **4**. Different reaction temperatures, the comparison to acetonitrile as a solvent, different catalyst concentrations, and the dependence of the dechlorination of **1** on the chlorination of **3** by


 Fig. 7. Optimization of the GC yield Y and Faraday efficiency FE of **10** via linear screening and DoE.

changing the concentration of **1** were investigated. Assuming first order kinetics, the linearization of the change in concentration was plotted against the amount of applied charge amount. The reaction process of the optimized reaction conditions serves as a comparison (Fig. 8 A).

The conversion of **1** and the yield of **2** proceeds evenly over the electrolysis. The fact that the two do not completely overlap is due to the

parallel formation of the chlorobenzene and the evaporation of benzene. From over 8 F, the conversion of **1** and formation of **2** slows down. The conversion of **3** and yield of **4** show a similar curve up to about 10 F, where the maximum yield was also found in the DoE. Thereafter, the yield of **4** decreases, which can be attributed to dimerization reactions taking place. [74] These could be observed via GC-MS. Since the

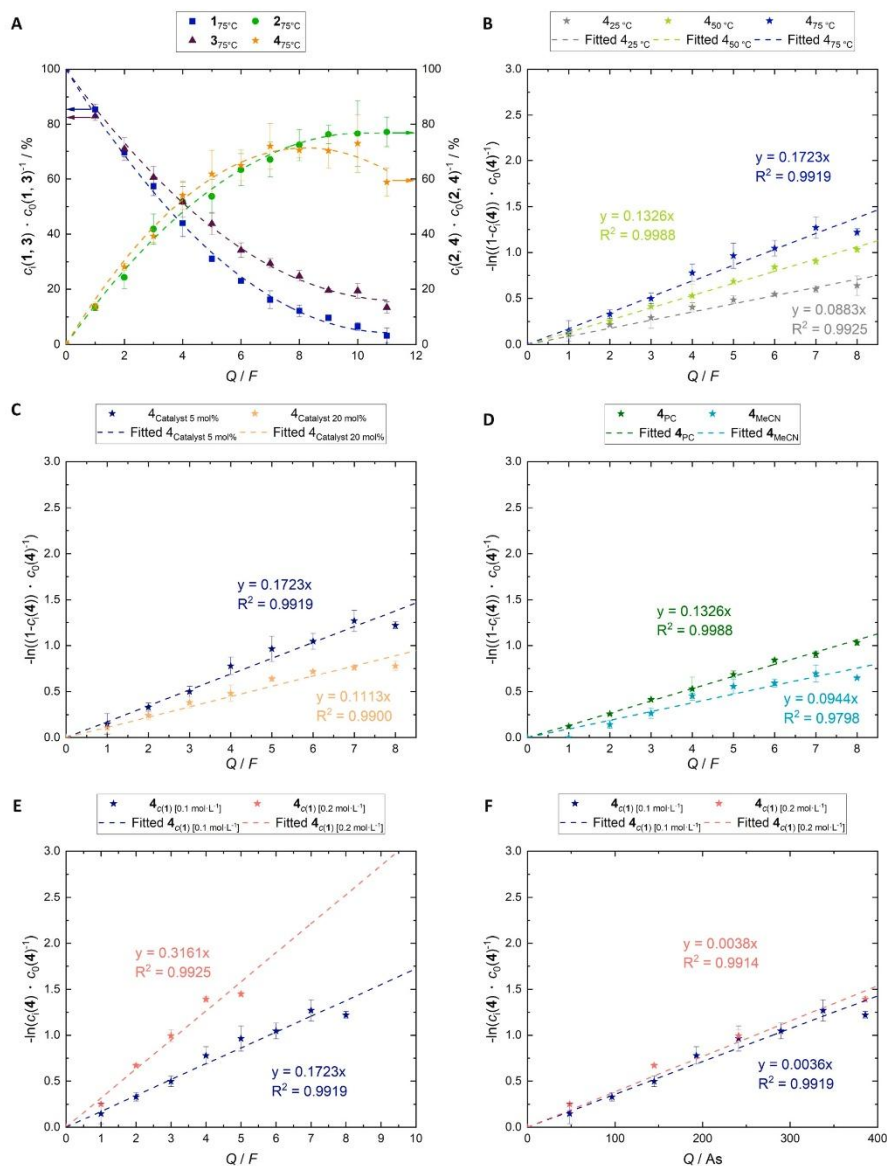


Fig. 8. A: Measured change of concentration based on the amount of starting material of **1**, **2**, **3** and **4** over the amount of applied charge using the optimized reaction conditions. Measured formation rate coefficient of **4** (**4**) as a function of temperature (B), of solvent (C), of catalyst concentration (D) and of concentration of HCH (c(1)) over the amount of applied charge in F (E) and As (F).

concentration of **1** decreases significantly towards the end of the electrolysis, more of the formed product **4** degrades. Like **1**, this is a vicinal dichloride, which can also be cathodically dechlorinated. Initially, the conversion of **1** proceeds faster, as the formation of the aromatic state of benzene is thermodynamically favoured. There is therefore an equilibrium reaction between **3** and **4**, which is shifted towards **4** at the start of electrolysis by the chloride of **1** formed. Since the decreasing in the chloride concentration at the end of the electrolysis, due to the lack of **1**, shifts the equilibrium between **3** and **4** slightly back to **3**. As the dimerization reaction always takes place in parallel, there is a decrease in **4** over 10 F. This is an essential finding when considering the synthesis of a scope with this reaction, as high amounts of charge applied at low chloride concentrations can also lead to a drop in the amount of product during electrolysis. A plot of the Faraday efficiency of **2** and **4** (Figure S3.28, 29) shows that up to about 4 F there was a constant Faraday efficiency of around 80%, which then drops constantly to around 40% up to 11 F.

For the comparison of the kinetic measurements, the conversion of **1** and the yield of **2** were only considered up to 6 F for better linearization. In analogy to **3** and **4** however, up to 8 F is required, as a relatively linear course can be observed up to this point.

The main effect diagrams of the DoE are often reflected in the reaction kinetics. When looking at the conversion of **1** at different temperatures, the highest conversion per amount of applied charge was measured at 50 °C, whereas the formation of **2** is favoured at 75 °C (Figure S3.22). This is since the formation of 1,2,4-trichlorobenzene was observed at 50 °C. It was not possible to determine why there is selectivity for β -H elimination here. One assumption would be that the temperature dependent resistance and viscosity of the solvent changes in such a way that β -H elimination also occurs at the cathode. The conversion of **3** and the yield of **4** also increase with rising temperature (Fig. 8 B).

A comparison of the solvents at 50 °C shows that the conversion of **1** and yield of **2** are favoured in acetonitrile (MeCN). It is interesting to note that the formation of **4** is delayed by 1 F in MeCN (Fig. 8 C). In general, MeCN shows a stronger deviation of 36% of **3** and **4**. In propylene carbonate (PC), on the other hand, these deviate from each other by only 2%. This is due to the increased amount of side reactions of **3** in MeCN.

The investigation of the concentration of the catalyst shows that it only influences the formation of **4** and not **2**. Although an increased amount slightly improves the degradation of **1**, it is not significant, as shown by the DoE. In contrast, lower concentrations of the catalyst have a positive effect on the reaction kinetics for the formation of **4** (Fig. 8 D). The DoE, on the other hand, shows that its increased concentration of the catalyst in combination with high amounts of applied charge produces better yields (Table S3.10). Since the kinetics are only determined up to 8 F, the rate of formation at 5 mol% predominates.

The cathode reaction was further investigated by changing the concentration of **1**. This shows that the conversion of **1** is slightly faster. The kinetics of **2** basically show no changes due to the doubled concentration of **1**. Since the concentration of **3** was kept constant and thus the equiv. between **3** and **1** was halved, the kinetics for **3** and **4** are plotted against the amount of applied charge in As (Fig. 8 F). A plot against the amount of charge in F would distort the results, as for the same yield, doubling the initial concentration of **1** also leads to a twofold faster conversion (Fig. 8 E). Due to the high amount of chloride, **3** is already completely converted after 4 F. After 5 F, the peak of the yield of **4** is reached, which is why the points are not included in the kinetics. Here, the curve is quite similar to the already optimized conditions. Since increasing concentration of **1** does not appear to have a negative effect on the reaction, it is included for further optimization.

3.3. Process Development

After electrolysis, the cathodes have a roughened surface, which

makes them look much darker (Figure S3.58). To investigate the effects of this change in topology and to ensure the long-term use of the electrodes, recyclability tests were carried out. For this purpose, the electrodes were no longer polished between runs but simply rinsed with acetonitrile and acetone. For this purpose, the reaction solution is prepared fresh after each run, and the conversions or yields are plotted against the runs (Fig. 9 A). Although this shows that the conversions and yields fluctuate slightly, no significant drop was measured even after ten runs. Maintaining electrode performance over extended periods without necessitating changes in reaction conditions represents a key aspect of process economic efficiency. Other materials, such as MMO and BDD, would be more advantageous for the mechanical stability of the electrodes, but graphite has not shown a decline in performance even over multiple runs in other similar application. [91]

Another important step was the upscaling of the electrolyser. For this purpose, the dimensions of the 5 mL IKA cells were transferred to a 50 mL and 500 mL cell (Figure S1.10–13). For each tenfold increase in the reaction volume, a geometric scale-up of 2.3 for the cell is required. However, the electrode spacing remained constant. As shown in Table S3.65 the geometric scale-up allows the electrolysis condition to be transferred well and a constant yield and conversion is achieved in each 10-fold step. Only in the 500 mL cell did the stirring speed has to be increased to ensure sufficient mass transport over the entire height of the cell. [96] In each cell a measurement of the voltammetry over the electrolysis was carried out to determine the amount of charge that is consumed (Figure S3.63–71). This demonstrates that employing larger electrolyzers can decrease the electrical energy demand per unit of HCH converted or per unit of product generated. The conversions and yields can be easily transferred when scaling up, but depend on the starting materials used. In particular, the increased conversion and production rates demonstrate the advantages of larger cells. (Table S3.65). The isolation and recyclability of the optimized reaction conditions for **4**, **8** and **10** are compared with each other to examine the economic viability of a possible HCH upcycling process. This provides an important insight into whether electrolysis solutions can be reused after removal of the product, which will be a very important cost factor. The reactions were carried out in 50 mL cells, as the purification can be carried out directly on the cell. After the product was isolated from the electrolyte solution, it was re-fed until the starting conditions were reached.

Extraction with heptane was used to isolate **4** shown in Figure S3.61. The conversion of **1** and **3** and the yield of **2** were stable over the runs. Only the yield of **4** slightly increases over the runs. This may be due to residual **4** from the previous run, which was not extracted and accumulates over the following runs (Fig. 9 B). The high amount of **4** isolated of 92% also shows that this method can be used very well for down streaming the reaction solution after electrolysis. How often this can be used until the electrolysis is depleted was not determined here.

Distillation had to be carried out to isolate **8** and **10**. The isolation of larger quantities of **8** revealed partial decomposition. After just a few minutes, colorless **8** turned yellow until it turned on a dark brown color and increased viscosity. This observation suggests that **8** is highly sensitive to hydrolysis and undergoes further transformation under acidic conditions, likely forming chloroacetaldehyde, which then forms the hemihydrate as in water. [93] This decomposition was particularly evident during recycling experiments. The yield of **8** progressively decreased with each cycle, until no detectable amount remained after three runs (Table S3.61). Even the use of anhydrous catalyst in the form of manganese(II) acetate could not prevent the degradation of the product, resulting in no detectable amount after four runs. (Table S3.62). In contrast, the addition of CaCO₃ as a desiccant and trapping agent for HCl successfully stabilized the electrolyte solution, enabling repeated recyclability (Table S3.63). However, the use of the CaCO₃ also leads to lower yields of **8**. The course of recyclability also shows the inaccuracy of the distillation. Under reduced pressure of the pump, the boiling points of the components become too similar, leading

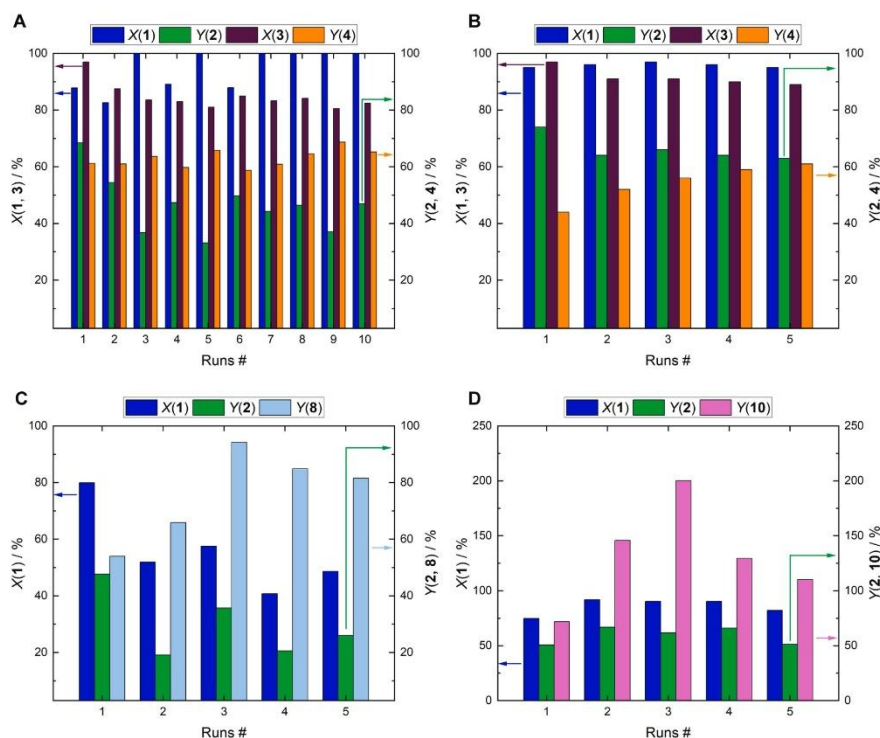


Fig. 9. A: Change of conversions of HCH (1) and 3 and yield of benzene (2) and 4 after each run without polishing the electrodes. B: Change of conversions of HCH (1) and 3 and yield of benzene (2) and 4 after extracting 3 and 4 after each electrolysis with heptane. C: Change of conversions of HCH (1) and yield of benzene (2) and 8 after distillation of 2 and 8 after each electrolysis. The electrolysis was performed by adding CaCO_3 . D: Change of conversions of HCH (1) and yield of benzene (2) and 10 after distillation of 2 and 10 after each electrolysis.

to co-condensation of the solvent and product. As a result, **8** was not fully removed during distillation and accumulated over successive runs. Although this method does not achieve complete separation of **8**, the overall recyclability of the reaction mixture could still be demonstrated (Fig. 9 C).

Similar issues with distillation were observed during the recyclability experiments of **10**. The HCH conversion and benzene yield remained stable over multiple runs. Compared to the first run, an increase in HCH conversion by 15 %age points was observed, closely matching the results obtained in the 5 mL cell. However, the isolation efficiency was significantly lower, resulting in substantial amounts of propylene carbonate in the product fraction. Consequently, the concentration of **10** in the electrolyte solution increased. Interestingly, the amount of **10** nearly doubled after the second electrolysis, suggesting that the product is electrochemically stable. Although **10** could potentially be dechlorinated back to **9** at the cathode, the dechlorination of HCH remains thermodynamically more favorable (Fig. 9 D).

3.4. Economical Process Evaluation

Evaluating newly developed processes at an early development stage allows for the technological development to take shape while focussing on the goal of an economically viable process. The goal is therefore, to allow for a rapid and simplified evaluation that can quickly adapt to further generated knowledge whilst guiding the process development with economic performance indicators. Starting point for the evaluation

is the process design and scale up, which is based on the prior presented results and a consecutive theoretical extrapolation. The gained reaction and process knowledge for the conversion of HCH to **2** and **9** to **10** is chosen as suitable base case for an initial process evaluation and is combined into the proposed process design (Fig. 10), for which the evaluated scale up goal is a throughput of 5000 metric tons of HCH a year. The process is divided into two stages: the electrochemical reaction unit, which is run in a batch process, and the continuous downstream treatment, supplying the products **2** and **10** in approximate amounts of 1300 t a^{-1} and 6400 t a^{-1} respectively.

The electrochemical reactor will be operated in loop reactor mode; therefore, stirred tank reactors with a volume of 1 m^3 and graphite electrodes of $200 \text{ m}^2 \text{ reactor}^{-1}$ are used as reactor model in the process simulation. To supply the sufficient production capacity, 17 reactors are employed. The reaction conditions, resulting yield and efficiency are assumed to be constant and are directly taken from the laboratory experiments (Fig. 7). For the downstream process, a cascade of three rectification columns is considered for which the separation was modelled with Aspen Plus. The dimensions of the packed distillation columns were calculated with the methodology reported by TOWLER AND SINNOTT[97], with further details given in the SI 3.6.2. Based on an extrapolation from the five-run stability and reproducibility results presented in Fig. 9 D, a 20-fold batch reaction is considered before replacing the recycled allyl alcohol, HCH and reaction additives propylene carbonate, dry tetraethylammonium chloride and manganese chloride, resulting in a 5% purge stream. It is to be noted that, due to the

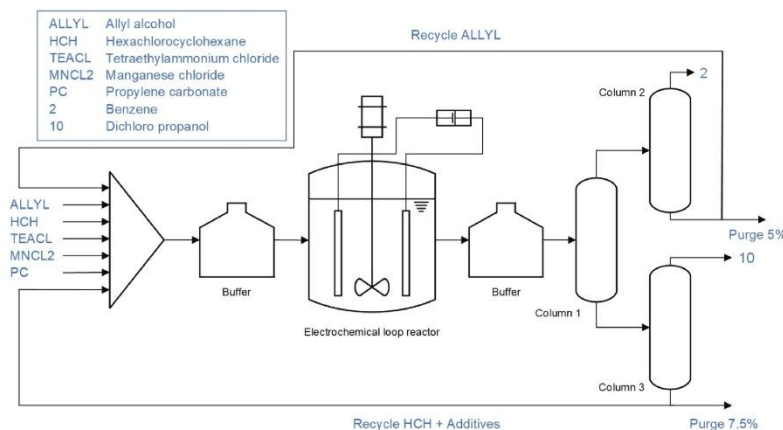


Fig. 10. Process flow diagram of the HCH conversion process design.

scarcity of experimental knowledge on the side products that are possibly dimers and polymers, no further separation from the reaction additives is considered. An additional purge stream of 2.5% is therefore added, accounting for reduction of side products recycled into the reaction, but therefore requiring an additional supply of reaction additives. Power requirements by the reaction (P_R) are calculated as:

$$P_R = \dot{n}_{Benzol} \cdot Q \cdot F \cdot V_{cell} \quad (1)$$

where $\dot{n}_{Benzol}$ is the molar flow of 2 produced, Q is the amount of charge passed, F is the Faraday constant and V_{cell} is the applied cell voltage. Power losses, which can result from heat in the electrolyser array, the power supply and stirring, which currently cannot be considered in further detail, are accounted for with the addition of a 25% loss. Temperature changes are regarded in the adjacent cooling capacity following the downstream process, as all products leave the system at 25 °C. The downstream power requirements are directly taken from the Aspen model (SI 3.6.1) and electrical heating and cooling with cooling water and a temperature gradient of 5 K is assumed. No further heat integration is considered at this early stage of process development resulting in a conservative approach to process evaluation.

The economic process evaluation is based on the general methodology for chemical plants reported by TOWLER and SINNOTT [97] utilising the main equipment cost and the plants power requirements and the feedstock as basis for the total capital to be employed and operational expenses. The calculation follows the prior proposed methodology by CAMPOS *et al.* [98] in a simplified manner, who reported the evaluation of an innovative process for the methanol synthesis and is adapted to the unique requirements of electrochemical processes, in accordance with BOOR *et al.* [99]. It can, therefore, be considered as a baseline calculation for the cost estimation of electrochemical and electro organic processes, while profiting from the considerable experience of years of chemical plant design knowledge in the literature. [97,100,101]

The cost of the major equipment items (CE) is estimated based on the reference cost (C_{ref}) reported in literature, and scaled up with specific equipment scaling factors (S), via the characteristic dimension of the reference (D_{ref}) and the scale up goal (DE). To account for the cost of inflation a correction with the Chemical Engineering Plant Cost Indexes ($CEPCI$) is performed. [102] In case of required currency conversion from US dollars (USD) to euros (EUR) a factor of 1.10 USD-EUR⁻¹ is employed (Nov 2025). [103] The CE are therefore calculated by Eq. 2, and are given in Table 2:

Table 2
Cost of the major equipment items (CE).

Item	Cost [k€]	Ref.
Electrochemical loop reactor (17x)	44.6	[100]
Electrodes (Graphite)	45.7	[104]
Rectification column 1 Diameter = 0.25 m, Height = 2.25 m	85.4	[100,105, 106]
Rectification column 2 Diameter = 0.25 m, Height = 7.00 m	194.1	[100,105, 106]
Rectification column 3 Diameter = 0.25 m, Height = 2.25 m	101.1	[100,105, 106]
Buffer storage (20 m ³ , 2x)	90.5	[100]
Heat exchanger	14.4	[100]
Total costs of major equipment	2100.0	

$$CE_i = C_{i,ref} \cdot \left(\frac{DE_i}{D_{i,ref}} \right)^{S_i} \cdot \left(\frac{CEPCI_{2024}}{CEPCI_{ref}} \right) \quad (2)$$

Subsequent estimation of the capital expenses (CEX) (Eq. 3) is performed by multiplication with the Lang Factor (LF), which is employed to account for cost related to the plant construction in absence of detailed equipment information. [97] The employed LF of 4.675 is further detailed in the SI 3.6.3. Under the assumption of an annual interest rate (IR) of 10% and a conservative operating lifetime of the plant (OTP) of 10 years, the equivalent annual capital costs (ACC) is estimated by the annuity method (Eq. 4): [107]

$$CEX = LF \cdot \sum_i CE_i \quad (3)$$

$$ACC = \frac{CEX \cdot IR \cdot (1 + IR)^{OTP}}{(1 + IR)^{OTP} - 1} \quad (4)$$

In this work the direct operational expenses (OE_{dir}) and the disposal expenses (OE_{disp}) are considered. They account for the time dependent costs and are directly calculated from the mass and energy balance calculated for the process outlined above. The estimated cost of purchase and disposal of the raw materials, reaction additives, electricity, cooling water and separation additives is presented in Table 2. It is to be noted for future comparison that the assumed costs are based on currently available market pricing. In combination with the ACC , the net conversion cost (NCC) is calculated (Eq. 5). With the introduction of the products 2 and 10 to the market revenue can be generated. In addition, a

valorisation of the uptake of HCH can be set at $2500 \text{ €} \cdot \text{t}^{-1}$, which is directly linked to the disposal cost of the supplier. [108] The estimated values are combined as revenue (*REV*) and are given in Table 3. The pretax cash flow (*CF*) is calculated as follows in Eq. 6:

$$NCC \left[\frac{\text{€}}{\text{a}} \right] = ACC + OE_{\text{dir}} + OE_{\text{disp}} \quad (5)$$

$$CF \left[\frac{\text{€}}{\text{a}} \right] = REV - NCC \quad (6)$$

As a result of the economic calculations, the *CF* is estimated to be $4.5 \text{ M€} \cdot \text{a}^{-1}$, clearly showcasing the economic feasibility of the electrochemical HCH valorisation and proving it to be a suitable conversion method. When considering the *NCC* of $17.3 \text{ M€} \cdot \text{a}^{-1}$ in detail, the contributions of *ACC*, *OE_{dir}* and *OE_{disp}* are 9.4%, 78.2% and 12.4%, respectively, presenting the overarching influence of the direct operational expenses. The further partition of the contributors is presented as *CE* in Fig. 11 A, and as a combination of *OE_{dir}* and *OE_{disp}* in Fig. 11 B.

The main cost drivers to the major equipment items are the electrochemical loop reactors and the graphite electrodes, accounting for approx. 75% of the proposed *CEX* of 10 M€. Both exhibit similar costs, showing a possible investment disadvantage of electrolytic processes requiring high-cost electrode materials. Nevertheless, also the possibility of future electrode material price reduction by scale of production and production advances is given. With the *ACC* making up approx. 10% of the *NCC*, the focus is shifted to the operational expenses. From Fig. 11 B, the purchase and the purge disposal cost of 9 present the main expense with a share of approx. 43%. As 9 is the reactant, the purchase is inevitable; the *OE* and therefore *NCC* and *CF* are directly linked to the market price, having a main influence on profitability. With a share of 31%, the power requirements of the reaction directly showcase the possibility of profitability increases as a result of process development advances and improvements. Also, the cost of electricity carries a significant effect, increasing the market influence on the HCH conversion process. Both *CE* and *OE* show the electrolyser unit having an outstanding effect when compared to the downstream process, therefore presenting the main driver to process optimisation. It is to be noted that the effect of the downstream process might be underestimated due to the scarcity of experimental insight. The introduction of the process into the existing process landscape can be assumed much favorable from an economic, a solvent and waste management as well as a regulatory point of view. The presented process has the possibility to showcase a scaled electro organic synthesis profiting and supporting the transition period to a circular economy with the use of existing process chains

Table 3
Cost assumptions for the purchase and disposal of process media and additives.

Item	Purchase [€·t ⁻¹]	Disposal [€·t ⁻¹]	Ref.
Allyl alcohol (9)	2200	1200 (Solvent disposal)	[109–111]
Tetraethylammonium chloride	3000	7200 (Hazardous waste)	[111–113]
Manganese chloride	3400*	7200 (Hazardous waste)	[111,113, 114]
Propylene carbonate	940	7200 (Hazardous waste)	[111,113, 115]
Cooling water	0.1	-	[100]
Electricity [€·kWh ⁻¹]	0.16	-	[116]
Revenue [€·t ⁻¹]			
Benzene (2)	630	1200 (Solvent disposal)	[117]
2,3-dichloro-1-propanol (10)	1300	-	[118]
HCH (1)	2000	7200 (Hazardous waste)	[108,111, 113]

* Estimated by laboratory purchase price minimized by a factor of 10

incorporating benzene as valuable intermediate whilst repurposing now available chlorine. [119,120]

4. Conclusion

Building on the previously demonstrated success of the *e-shuttle* approach in the upcycling of lindane, we have extended this methodology to the upcycling of technical hexachlorocyclohexane. A key factor was the use of propylene carbonate as a solvent in combination with polar, energy-rich double bonds, which enabled the selective dechlorination of the different HCH isomers into benzene. Electrolysis parameters were optimized by Design of Experiment using methyl 10-undecenoate as a model substrate, and reaction kinetics were monitored throughout the process. High current density of $30 \text{ mA} \cdot \text{cm}^{-2}$ and temperatures of 75°C proved to be optimal for 4. Only polar molecules such as vinyl acetate and allyl alcohol enabled optimal yields at room temperature without the formation of chlorinated benzenes. Further investigations explored the application potential of the substrates 4, 8 and 10 and the reusability of the graphite electrodes was proven. Furthermore, the isolation of 4 by extraction and of 8 and 10 by distillation was realized. Both methods enable the electrolyte solution to be recycled by feeding it with new starting material. Finally, an economic assessment was conducted for a process scaled to an annual throughput of 5000 metric tons of HCH, demonstrating the feasibility of the *e-shuttle* approach. Operational expenses have shown to be the cost driver, accounting for approx. 90% of the net conversion cost. From both the operational and the capital expenditure, the electrochemical reaction unit is identified as key to further economic advances. With a positive cash flow of $4.5 \text{ M€} \cdot \text{a}^{-1}$, the economic viability is given. The presented work therefore not only demonstrates experimental feasibility, but also the economic potential.

Environmental implication

The *e-shuttle* method enables the selective conversion of actual HCH deposits waste into benzene at high concentrations using propylene carbonate as green solvent. This establishes, after more than seven decades, a foundation for the upcycling of HCH into industrially relevant products. Although benzene, a carcinogenic product, is still produced in this process, it can be fed directly into existing value chains to produce e. g. cyclohexane or cumol. Other polychlorinated benzenes would only generate additional waste. This would make it possible to generate almost 2.0 million tons of benzene from known contaminate sites, which would otherwise be obtained from fossil sources. Furthermore, the *e-shuttle* enables the direct reuse of the separated chlorine. In other processes or incineration, the separated chlorine is mineralized and must then be reprocessed into chlorine in order to be used. Since this additional intermediate step is not necessary here, up to 5.4 million tons of chlorine could be transferred directly into industrial relevant products. In addition, this method, which uses electricity as a reagent, not only emits significantly less CO₂ compared to incineration of HCH but also enables a cost-effective process. This sustainable and scalable technology could be a key factor in upcycling huge quantities of HCH residues, thereby significantly curbing their spread in the environment.

CRedit authorship contribution statement

Siegfried R. Waldvogel: Writing – review & editing, Writing – original draft, Supervision, Resources, Funding acquisition, Conceptualization. **Jörg Sauer:** Writing – review & editing, Supervision, Funding acquisition. **Simon Horsinka:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Till Langner:** Writing – review & editing, Funding acquisition. **Philipp Beeskow:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Dominik Weis:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation.

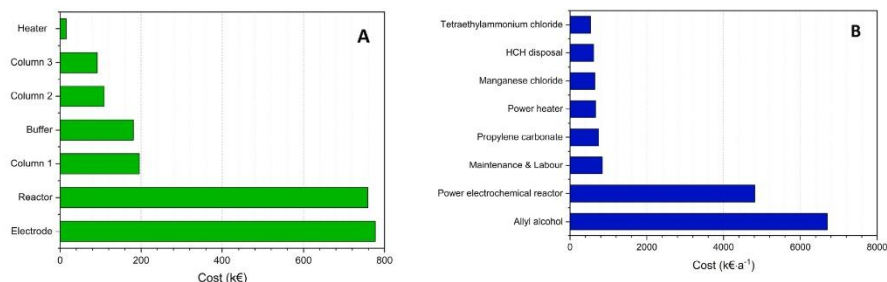


Fig. 11. A: Cost contributors in CEX. B: Cost contributors in OE_{dir} and OE_{disp} .

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Siegfried R. Waldvogel reports financial support was provided by Federal Ministry of Education and Research Berlin Office. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supporting Information

Supporting Information File 1: Experimental detail, spectral data, and copies of NMR spectra for all compounds prepared in this study. The authors have cited additional references within the Supporting Information.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jhazmat.2026.141851](https://doi.org/10.1016/j.jhazmat.2026.141851).

Data Availability

All data are available in supplementary information provided.

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4.2 Von polyhalogenorganischen und persistenten Abfällen zu Acetalen: Ein elektrochemischer Transferansatz

Zu diesem Kapitel wurde ein Manuskript veröffentlicht:

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Article

From Polyhalo-organic and Persistent Waste to Acetals: An Electrochemical Transfer Approach

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ABSTRACT: Persistent legacy contaminants such as 1,2,3,4,5,6-hexachlorocyclohexane (HCH) and 1,2,5,6,9,10-hexabromocyclododecane (HBCD) remain a major environmental burden for the chemical industry. Their electrochemical valorization offers a promising strategy for remediation. In this work, the e-shuttle concept was successfully applied to the selective transformation of HCH and HBCD into acetals of chloroacetaldehyde and bromoacetaldehyde. Due to high selectivity and increasing industrial relevance, 2-chloromethyl-1,3-dioxepane was synthesized as a test substrate. Systematic optimization using fractional factorial designs and response surface methodology identified current density and the amount of applied charge as key influencing parameters. While ring sizes ≥ 7 afforded moderate to good yields, five-membered acetals were dominated by ring-opening reactions competing with the formation of esters. Complementary mechanism studies employing CV, IC, titration, and GC revealed that 50% of the released chloride is transferred to chloro acetals. Scaling up the reaction from a 0.218 g HCH to a 21.8 g HCH scale system with a stacked electrode arrangement increased the electrode surface area by a factor of 167, allowing a significant shortening of electrolysis time while maintaining product yields. For 2-chloromethyl-1,3-dioxepane, product accumulation was further investigated: repeated substrate addition enabled concentrations of up to $0.9 \text{ mol} \cdot \text{L}^{-1}$ within the electrolysis mixture. Direct electrolyte reusability was confirmed after more than 15 cycles. These results highlight the potential of electrosynthesis as a scalable and sustainable method for converting HCH to valuable platform chemicals. The integration of mechanistic insight, process optimization, and scale-up paves the way for future technical implementation.

KEYWORDS: Electrolysis, Hexachlorocyclohexane, Lindane, POPs, Halogen Transfer, Electrochemical Upcycling, Greener Chemistry, Process Development



INTRODUCTION

After World War II, 1,2,3,4,5,6-hexachlorocyclohexane (HCH) became the world's most widely produced insecticide.¹ Together with other pesticides, it played a central role in securing global food production by effectively limiting crop losses caused by pests and fungal infestations.² Industrially, it is produced as a mixture of isomers, with its distribution highly dependent on the manufacturing process.³ A major issue is the intense, musty odor of most HCH isomers, which renders treated crops inedible. Therefore, starting in the 1950s, preference was given to the γ -isomer (Lindane), which is odorless and an effective insecticide at low concentrations.⁴ However, the industrial production of Lindane is extremely inefficient; with a yield of only about 15%, up to 12 tons of difficult-to-dispose waste (wrong isomers) are generated per ton of product.⁵ Across the world, these noninsecticidal isomers, also referred to as technical HCH, were frequently disposed of improperly, often buried, or openly dumped. To this day, they continue to be released into nature, causing severe environmental damage.^{6–8} Due to its persistent, bioaccumulative,⁹ and potentially carcinogenic properties,^{10,11}

Lindane was globally banned in the early 2000s.¹² Since 2009, all HCH isomers have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), which restricts their production, use, and transport. In total, an estimated 7.4 megatons of HCH have been produced worldwide.^{11,13–15}

Another POP that was added to the Stockholm Convention in 2013 is 1,2,5,6,9,10-hexabromocyclododecane (HBCD).¹⁶ It has been produced since the 1960s¹⁷ via the bromination reaction of cyclododecatene¹⁸ and is primarily used as a cost-effective halo-based flame retardant.¹⁹ In the year 2011, approximately 28 kilotons were produced worldwide.²⁰ Similar to HCH, its production results in an isomeric mixture consisting of α - (10–13%), β - (1–12%), γ -HBCD (75–

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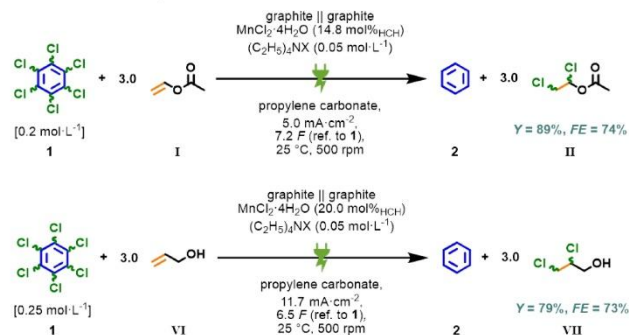
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Scheme 1. Reaction Conditions for the Electrochemical Chlorination of Electron-Rich Double Bonds Such as Vinyl Acetate (I) (Top) and Allyl Alcohol (VI) (Bottom) by HCH (1)⁸⁶



89%) and traces of δ - and ϵ -HBCD.²¹ Although its potential neurotoxicity,²² endocrine-disrupting effects,²³ metabolic disorders,²⁴ and reproductive and developmental toxicity have been extensively studied,^{25,26} it is still produced in the United States today.²⁷ In the meantime, HBCD has been detected worldwide in various environmental matrices such as air,²⁸ soil,²⁹ and water.^{30,31} This also results in bioaccumulation within the food chain,³² and it can therefore be detected in human blood.³³

Environmentally appropriate disposal presents a significant technical and economic challenge. Incineration requires temperatures above 1000 °C to avoid toxic products such as dioxins or phosgene.^{34,35} Additionally, high-caloric additives and complex flue gas treatment are necessary, resulting in costs of up to €2000 per ton with rising costs, among other reasons, due to CO₂ pricing for greenhouse gases.^{36,37} Various thermal^{38–40} and nonthermal methods⁴¹ have been investigated for the development of alternative degradation strategies, including mechanochemical processes,^{42–44} photochemistry,^{45–49} microbial degradation,^{50–52} and the use of ionizing radiation.^{53–56} However, these methods face limitations: either product selectivity is uncontrolled due to the formation of toxic chlorobenzenes and polychloro biphenyls or degradation rates are too low for large-scale applications.⁵⁷

Electrochemistry has proven to be a promising method, particularly for water treatment.⁵⁸ This technique enables the degradation of HCH and other POPs under mild conditions without the use of external reagents.^{59–64} However, the low solubility of HCH in water remains a limiting factor for the process intensity. Electrosynthesis offers numerous ecological and economic advantages for the development of a cost-efficient and scalable process. First, the use of electricity eliminates the need for additional oxidizing and reducing agents,^{65,66} thereby preventing the generation of additional waste.⁶⁷ Moreover, the process can be immediately stopped in the event of a power switch-off, providing additional safety.⁶⁸ Electrosynthesis pays off when the conversion is efficient and a suitable downstream processing can be established.⁶⁹ Environmentally friendly solvents such as cyclic carbonates improve HCH solubility and enhance process safety due to their low flammability.⁷⁰ An innovative approach is the merging of shuttle reaction and paired electrolysis (e-shuttle), developed by Morandi, Waldvogel et al.,⁷¹ which for the first time offers a

scalable and environmentally friendly method for the upcycling of Lindane. In this process, HCH is electrochemically reduced to benzene. Additionally, this method that allows for the transfer of halogens such as bromine and chlorine has already been successfully applied to the vicinal chlorination of vinyl acetate, a precursor to chloroacetaldehyde derivatives,⁷² which are essential for the synthesis of pharmaceutical ingredients,^{73–77} as well as fragrances,⁷⁸ polymers,^{79–81} and agrochemicals.^{82–85}

This work presents an alternative synthetic route for the production of acyclic and cyclic acetals from chloroacetaldehyde and bromoacetaldehyde. We thereby present a path toward the environmentally friendly utilization of halo-organic hazardous waste such as HCH and HBCD through electrochemical strategies while simultaneously synthesizing technically relevant platform chemicals.

RESULTS AND DISCUSSION

Classification, Screening, and Optimization

In earlier work, we focused on identifying suitable products for transfer chlorination and developing an economically viable electrochemical process. Key requirements included not only the valorization of the respective acceptor compound but also the selective degradation of the various HCH isomers (1) to benzene (2). As demonstrated for Lindane, the e-shuttle concept is ideally suited for targeted and selective dechlorination reactions to benzene (2).⁷¹ Systematic investigations of electrode materials, solvents, supporting electrolytes, and catalysts revealed that isostatic graphite as the electrode material provided the highest selectivity and suppressed the formation of undesirable byproducts such as chlorobenzenes. The optimal electrolyte composition consisted of propylene carbonate as the solvent, tetraethylammonium chloride as the supporting electrolyte, and manganese(II) chloride (tetrahydrate or anhydrous) as the catalyst. For electron-rich double bonds, this system delivered high yields for the desired product and current efficiencies, for example, 89% yield (Y) and 74% Faradaic efficiency (FE) for 1,2-dichloroethyl acetate (I), and 79% yield with 73% current efficiency for 2,3-dichloro-1-propanol (VII) (Scheme 1).^{86,87}

1,2-Dichloroethyl acetate (II) is an important precursor for the synthesis of chloroacetaldehyde (IV), a key intermediate in the production of active pharmaceutical ingredients,^{73–77}

agrochemicals,^{82–84} fragrances,⁷⁸ and biodegradable polymers.^{79–81,85} Due to its high reactivity and instability, pure chloroacetaldehyde (IV) can only be stored as a 45% aqueous solution.⁷⁸ Stable derivatives such as dialkyl acetals (V) are also highly important as market-relevant platform chemicals (Figure 1). These acetals can be selectively converted back

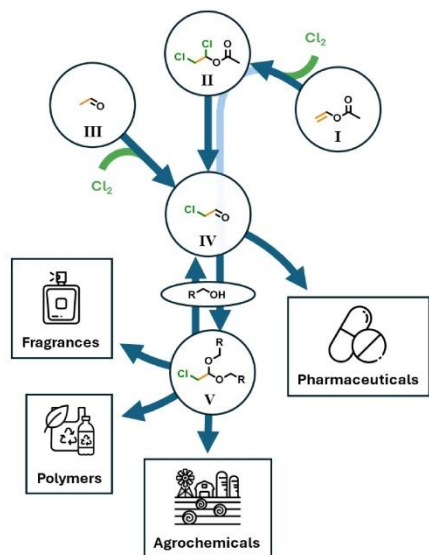


Figure 1. Schematic representation and application of chloroacetaldehyde.⁷⁸

into chloroacetaldehyde (IV) under mild conditions in the presence of catalytic amounts of acids, making them attractive for both transport and controlled downstream processing.⁷⁸

However, the compound 1,2-dichloroethyl acetate (II) proved significantly more susceptible to decomposition reactions under protic conditions.^{86,87} Nevertheless, the formation of chloroacetaldehyde diethyl acetal (4) was detected in appreciable amounts, with yields of up to 39% under the same reaction conditions as those used for 1,2-

dichloroethyl acetate (Supporting Information S55). Purified HCH (1) with an isomer ratio of α - and β -HCH of 85:15 and a purity of 99% was used for electrolysis (Figure S10). Bromination was carried out using commercial HBCD (8) with a purity of 95% (Table S1). The formation of the corresponding diethyl acetal suggests a reaction with ethanol released during the process, originating from the hydrolysis or transformation of ethyl vinyl (3) ether. This effect could be circumvented by addition of ethanol: A simple additive screening revealed that the yield of chloroacetaldehyde diethyl acetal (4) could be doubled to 80% at a molar ratio of ethyl vinyl ether (3) to ethanol (n/n) of 1:4. To further optimize the reaction conditions, a statistical design of experiments (DoE) was performed. In a 2^{5-1} fractional factorial design, key parameters were systematically varied: applied charge amount Q , current density j , HCH concentration $c(\text{HCH})$, amount of catalyst $n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$, and ethanol $\text{eq}(\text{C}_2\text{H}_5\text{OH})$ (Table S10). The conversion of HCH, as well as the yield of benzene and 4, was quantified using an internal standard (1,10-dichlorodecane) by GC. The objective was to maximize the yield of the chloro product while minimizing side reactions.

The 2^{5-1} fractional factorial design revealed significant effects, particularly for current density j , the amount of electric charge Q , and the concentration of 1 (Table S11). An increase in current density from 5 to 15 $\text{mA} \cdot \text{cm}^{-2}$ led to an increase in both HCH conversion and benzene yield by +17% and +18%, respectively. Similarly, increasing the amount of applied charge to 8 F resulted in a general improvement in conversion rates of +12% for 1 and yields for the product, with increases ranging between +12% and +17% for 2 and 4. When the HCH concentration was varied, a concentration of $0.2 \text{ mol} \cdot \text{L}^{-1}$ was found to be optimal for simultaneously maximizing HCH conversion and the yield of the target acetal 4. No significant positive influence of the catalyst could be detected under the selected conditions. This observation can be classified within the context of a predominantly ionic reaction mechanism, which is discussed in more detail in the section on Mechanism Study. This suggests that the catalyst can be omitted entirely, which not only simplifies process control but also improves economic feasibility. Under optimized conditions, a yield of up to 84% of 4 was achieved at a current density of $15 \text{ mA} \cdot \text{cm}^{-2}$ without the addition of a catalyst. These parameters thus provide a solid foundation for the scalable implementation of the process.

Scheme 2. Schematic Representation of the Halo Transfer of 1 and 8 to Acyclic Acetals

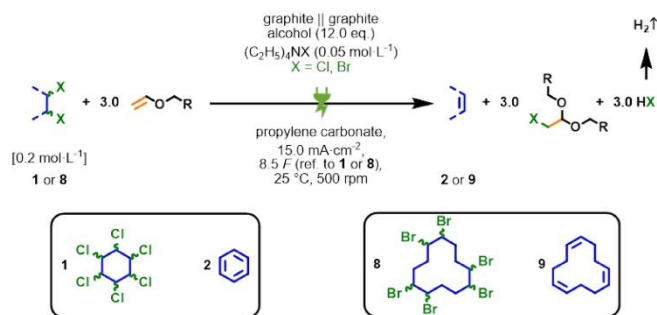
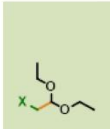
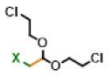
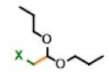
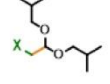
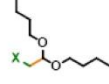
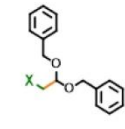


Table 1. Scope of Cl and Br Halo Transfer of 1 and 8 to Acyclic Acetals under the Optimized Conditions for 4^a

						
Cl:	4, 84%	4a, 46%	4b, 42%	4c, 56%	4d, 49%	4e, 31%
Br:	10, 86%	10a, 12%	10b, 14%	10c, 36%	10d, 17%	10e, 15%

^aGC yield; 1,10-dichlorodecane as an internal standard.

Based on the optimal reaction parameters identified in the DoE approach,⁸⁸ the substrate scope of the protocol was examined using a selection of commercially available vinyl ethers. Under these conditions, the corresponding dialkyl acetals of chloroacetaldehyde (4a–4e) could be quantified in moderate yields. The oxidation susceptibility of alcohol proved to be a limiting factor for both the yield and selectivity. In the case of 4, ethanol oxidation tends to have a positive effect, since the resulting chloroacetaldehyde can be reconverted into the acetal.⁸⁹ In contrast, the oxidation of 1-propanol in the case of chloroacetaldehyde dipropyl acetal (4c) proceeds *via* the intermediates propionaldehyde and 2-chloropropionaldehyde, leading to a variety of competing acetalization products and thus to a significant loss in selectivity.⁹⁰ Branched alcohols, such as 2-methyl-1-propanol, on the other hand, exhibited significantly lower oxidation tendencies. Given the lower industrial relevance of ethoxy derivatives, further optimization of this substrate class was not pursued (Scheme 2, Table 1).

Applying the reaction conditions optimized for 4 to the bromination reaction of vinyl ethers using HBCD (8) as a bromine source afforded bromoacetaldehyde diethyl acetal (10) in a comparable yield of 86%. For other vinyl ether derivatives, however, the relative yields were significantly lower. This decrease can be attributed to the increased formation of alkyl hypobromites from the alcohols used. Compared to hypochlorites, these intermediates are more persistent and, through oxidation of the alcohols with bromine, lead to the formation of a wide variety of competing acetalization products.^{91–93} This directly limits the formation of the target product (10a–10e). Under the conditions selected here, the 2-chloroethyl (10a), propyl (10b), and butyl acetals (10d) afforded only yields between 12% and 17%. Only in the case of the 2-methyl-1-propyl acetal of bromoacetaldehyde (4c) was a comparable relationship to the alkyl acetals of chloroacetaldehyde (4a–4e) observed, with yields of up to 36% (Scheme 2, Table 1).

Following the substrate studies on dialkyl acetals, the focus shifted to the synthesis of cyclic acetals of chloroacetaldehyde. In this context, 2-chloromethyl-1,3-dioxolane (6) and 2-chloromethyl-1,3-dioxepane (6b) proved to be of application-oriented interest, as they are widely used in the targeted functionalization of herbicides.⁹⁴ In addition, these compounds offer an efficient route to the corresponding ketene acetals.^{80,95} These monomers are of steadily increasing relevance in the synthesis of polyesters and copolyesters, particularly for applications where biodegradable or functionalized polymer structures are required.^{96–99} The electrochemical process therefore represents not only an environmentally friendly approach to the valorization of halogenated waste materials but

also a means of accessing high-value products with strong industrial demand.

Building on the findings from the synthesis of acyclic and cyclic acetals, we investigated the electrochemical chlorination of 4-hydroxybutyl vinyl ether (5b). Notably, due to the intramolecular arrangement of the hydroxyl group and the double bond, no addition of an external alcohol is required to form the desired cyclic acetal. This also allows an intermediate step, which under conventional conditions would involve an open acetal of chloroacetaldehyde.^{79,94,100,101} An initial electrolysis under the same starting conditions (7.2 F, 5 mA·cm^{−2}, 15 mol % MnCl₂·4H₂O, 0.2 mol·L^{−1} HCH) as for 4 afforded a yield of 61% of the target product 6b. For systematic optimization of this reaction, a 2^{4−1} fractional factorial design was employed, in which the amount of applied charge *Q*, the current density *j*, the concentration of HCH *c*(HCH), and the catalyst loading *n*(MnCl₂·4H₂O) were varied analogously to the study of 4.

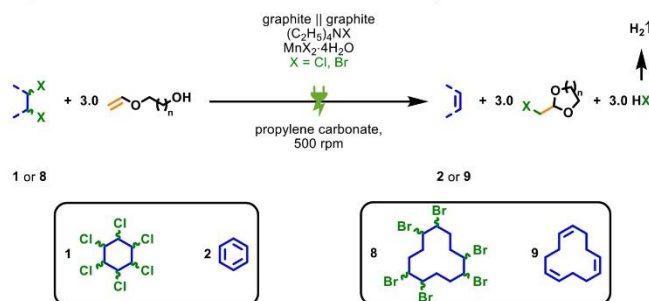
Statistical evaluation of the 2^{4−1} fractional factorial design revealed that, in particular, the current density *j* and the amount of applied charge *Q* had a pronounced influence on the conversion of 1 to 2 (Table S24). Current densities in the range of 5–15 mA·cm^{−2} and applied charges between 6 and 8 F led to increases in conversion and benzene yield of 11–13% and 6–11%, respectively. For the yield of 6b, increasing the amount of applied charge from 6 to 8 F was especially effective, resulting in an improvement of +9%. A higher HCH concentration also had a positive effect on the product yield (+18%). In contrast to the investigations with 4, a small but statistically significant positive effect (+5%) was observed for 6b when the catalyst concentration was increased. Analysis of the center point indicated an optimum within the studied parameter ranges. Consequently, a response surface methodology was applied to determine the maximum more precisely for conversion and product yield (Figure S44).

The data obtained from the response surface methodology confirmed the previously identified key influencing factors and enabled the precise localization of the optimal reaction conditions. For 6b, the model indicated a pronounced interaction between current density and the amount of applied charge, with moderate current densities in combination with elevated applied charges maximizing product yield. The calculated response surfaces display a well-defined maximum within the investigated parameter space, allowing for targeted process control (Figure S44). Under the optimal conditions of 10 mA·cm^{−2} current density, 7 F as the amount of applied charge, 0.15 mol·L^{−1} HCH, and 10 mol % MnCl₂·4H₂O, an HCH conversion of 79% and a product yield of 79% were achieved. If a catalyst is not used, a yield of 73% of 6b is

Table 2. Scope of Cl and Br Halo Transfer of **1** and **8** to Cyclic Acetals under Individual Optimized Conditions^a

Cl:	6 , 35%	6b , 79%	6c , 38%	6d , traces
Br:	10 , 49%	10b , 29%	10c , traces	10d , traces
current density / mA·cm ⁻²	10.0	10	6.5	6.5
amount of applied charge (ref. to 1 or 8) / <i>F</i>	7.4	7.0	9.0	9.0
temperature / °C	57	25	8	8
concentration of 1 or 8 / mol·L ⁻¹	0.15	0.15	0.15	0.15
concentration of (C ₂ H ₅) ₄ NX / mol·L ⁻¹	0.05	0.05	0.1	0.1
mole fraction of MnX ₂ ·4H ₂ O / mol%	10.0	10.0	-	-

^aGC yield; 1,10-dichlorodecane as an internal standard.

Scheme 3. Schematic Representation of the Halo Transfer of **1** and **8** to Cyclic Acetals


obtained, corresponding to the determined effect. Interestingly, direct comparison of the main effect plots for both target variables using an equalization approach made it possible to determine the intersection points of the reaction profiles. For current density, two characteristic intersection points were identified, representing potential compromises between maximum HCH conversion and high yield of **6b**. These results demonstrate that the combination of statistical experimental design and electrochemical process optimization constitutes a powerful tool for targeted control of selectivity and maximization of yield.

Additional investigations using a 2² full factorial design with the factors temperature *T* (16–30 °C) and supporting electrolyte concentration *c*((C₂H₅)₄NCl) (0.025–0.075 mol·L⁻¹) revealed no significant effects on conversion or product yield within the selected parameter ranges (Table S31). Although these results did not indicate any potential for further optimization, they nevertheless provide important practical insight: cooling under industrial process conditions is likely feasible without any significant impairment of reaction performance.

In a further series of experiments, 2-chloromethyl-1,3-dioxolane (**6**) was synthesized electrochemically under the conditions optimized for **6b** (Table S14). Already in the initial trials, a pronounced limitation in yields of the products was observed. The main cause was the predominant formation of

the side product 2-chloroethyl acetate (**7**). Comparable behavior had already been described in 1960 by Meerwein et al.: in the conversion of cyclic orthoesters to 1,3-dioxolenium salts, subsequent reaction with lithium chloride, hydrogen bromide, or sodium iodide led to ring opening and the formation of carboxylic acid esters of *ω*-substituted alcohols.¹⁰² Control experiments confirmed that chlorination of 2-methyl-1,3-dioxane under identical conditions afforded similar yields of the corresponding carboxylic acid esters (SI S62). The results suggest the presence of an equilibrium between cyclization and ring opening of *ω*-hydroxyalkyl vinyl ethers,^{103,104} which under the reaction conditions employed here is shifted in favor of the formation of the esters.

Clear ring-size-dependent differences were observed among the cyclic acetals studied. For **6b**, formation of the corresponding ring-opening product, 4-chlorobutyl acetate could be completely excluded, whereas in the case of **6**, side-product formation predominated.

This is consistent with the results of Romano et al., which show that the seven-membered ring is preferentially formed due to its conformational flexibility.¹⁰⁵ Nevertheless, the yield of **6** could be increased to a moderate 35% using a 2⁴⁻¹ fractional factorial design and a 2² full factorial design (optimized conditions: 7.4 *F* as the amount of applied charge, 5 mA·cm⁻² current density, 0.15 mol·L⁻¹ HCH, 10 mol % MnCl₂·4H₂O, 57 °C) (Table 2).

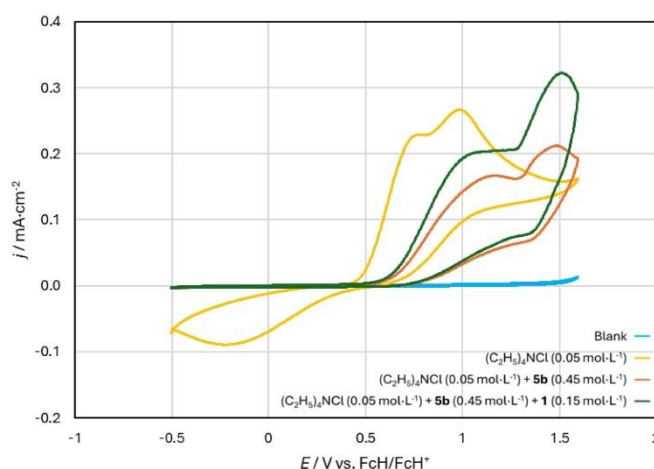


Figure 2. CV study of the electrolyte system with supporting electrolyte ((C₂H₅)₄NCl), 4-hydroxybutyl vinyl ether (**5b**), and HCH (**1**) (scan rate: 0.1 V·s⁻¹). The blank was measured in propylene carbonate with (C₂H₅)₄NBF₄.

Eight-membered cyclic acetals were also investigated. While 5-hydroxypentyl vinyl ether (**5d**) could be converted only in trace amounts under the selected conditions, di(ethylene glycol) vinyl ether (**5c**), after analogous optimization, afforded moderately significant yields of 38% of 2-chloromethyl-1,3,6-trioxane (Scheme 3, Table 2).

For the bromination of vinyl alkyl alcohols with **8** as a bromine source, the reaction conditions investigated here yielded limited applicability with respect to cyclic acetals. Conversion to eight-membered rings (**10c** and **10d**) could only be detected in trace amounts, which is consistent with the fact that even the classical synthesis of such ring sizes presents a particular challenge.¹⁰⁶ In contrast, ring sizes below seven members resulted in moderate yet improved yields of 49%, respectively, compared with **6** and **6b** (Scheme 3, Table 2).

An analysis of the chlorine mass balance revealed that only about half of the chlorine released from **1** is transferred to the alkyl vinyl ethers. Studies with an excess of chlorine acceptor molecules further indicated a limitation at approximately three equivalents of acceptor. The increase in the chlorine acceptor showed a constant conversion rate of around 75 ± 3% for **1**. Plausibly, the yield decreased from **6b** to 38% with an equivalent of 4.5 for **5b** (Table S3). This observation points to a fundamental, reaction-specific limiting mechanism.

Mechanism Study

To gain insight into the underlying reaction pathways in the electrochemical conversion of HCH (**1**) with ω -hydroxyalkyl vinyl ethers, mechanistic investigations were carried out exemplarily on 2-chloromethyl-1,3-dioxepane (**6b**). This substrate was chosen due to its high selectivity in target product formation and its industrial relevance. For the experiments, a 50 mL cell was employed on a 2.18 g HCH scale.

Complementary methods were applied for the analysis: cyclic voltammetry (CV) to identify electrochemically active intermediates, ion chromatography (IC) to determine the anion composition before and after electrolysis, quantitative hydrogen determination to capture cathodic reactions, and

collection and analysis of gaseous products by absorption in caustic soda, followed by evaluation *via* IC and titration.

In the CV study, measurement of tetraethylammonium chloride ((C₂H₅)₄NCl) revealed two anodic current peaks at +0.22 V and +0.89 V, as well as a corresponding cathodic peak at -0.2 V in the reverse scan, which can be attributed to the reduction of electrochemically generated chlorine. Upon addition of the target molecule 4-hydroxybutyl vinyl ether (**5b**), this cathodic peak disappeared completely. This observation is consistent with chloride oxidation at +0.89 V and its subsequent transfer to the vinyl ether, leading to the formation of electrochemically inert compound **6b** (Figure S37). The addition of **1** resulted in a pronounced increase in the intensity of the anodic peaks due to the release of additional chlorine, thereby confirming the role of HCH as an additional chlorine source (Figure 2).

IC measurements before and after electrolysis showed an increase in chloride concentration in the electrolyte of approximately 6098 mg·L⁻¹. In contrast, no chloride above the detection limit could be detected in the caustic soda solution used for gas absorption (Table S5). Only after condensation of the evolved gases under reduced pressure (using liquid nitrogen) was a chloride content of 4.75 mmol determined using Mohr titration. Since the gases were introduced *via* a constant nitrogen stream, it can be assumed that part of the HCl formed was retained in the propylene carbonate solvent due to its solubility (for comparison: HCl solubilities in THF and 1,4-dioxane are 584 and 433 g·kg⁻¹, respectively).¹⁰⁷ Nevertheless, the increase in the number of chlorides in the electrolyte clearly points to the reduction (**I**) of **1** (Figure 3). Notably, only about half of the released chloride is transferred to three equivalents of **5b**. As a result, the overall proportion of free chloride ions in the electrolyte continues to increase (Table S5). A plausible conclusion is the oxidation of free chloride ions to active chlorine (**III**, "Cl₂"),¹⁰⁸ which subsequently adds to the vinyl group (**IV**).¹⁰⁹ The following cyclization process then releases equimolar amounts of HCl as a coupling product (**V**). According to Baldwin's

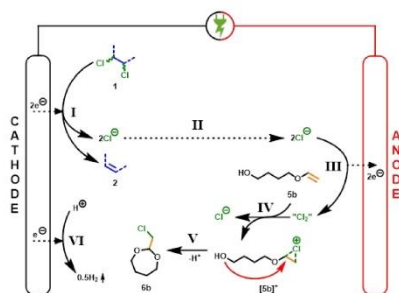


Figure 3. Postulated mechanism of cyclic acetal formation using the example of 2-chloromethyl-1,3-dioxepane (**6b**). A similar mechanism can be assumed for bromine.¹⁰⁹

rules, 7-exo-trig cyclizations are all preferred sequences.¹¹⁰ This is consistent with both the experimental observations and the mechanistic rationale that even increased addition of **5b** could only be converted up to three equivalents (Figure 3).

In addition, the hydrogen formation during electrolysis was quantified by GC analysis. A concentration of 60 vol% H_2 was detected (Table S7), which can plausibly be attributed to the cathodic reduction of HCl (VI). This competing cathodic reaction explains, on one hand, the observed losses in current efficiency during the conversion of **1**. On the other hand, it simultaneously provides the possibility of regenerating the coupling product HCl into an active chlorine species, which can in turn be reintegrated into the reaction cycle (Figure 3). This also has the mitigating effect on HCl.

Process Development

To assess the relevance of the favored compounds, chloroacetaldehyde diethyl acetal (**4**) and 2-chloromethyl-1,3-dioxepane (**6b**) for potential process development, studies on scalability, product accumulation, and electrolyte reusability were conducted. Due to experimental effort, studies on accumulation and reusability were carried out exclusively for compound **6b**.

The scale-up experiments were realized by transferring the reaction mixture from a 5 mL cell to a 500 mL cell with a staggered electrode arrangement. This not only increased the reaction volume by a factor of 100 but also enlarged the

electrode surface area by a factor of 167 (from 3.5 cm² to 585 cm²). As a result of the increased electrode area, the electrolysis time could be significantly shortened and the production rate was enhanced. Owing to the altered cell geometry, adjustment of the stirring rate was required to ensure sufficient mass transport. Under optimized conditions, yields of 69% for **4** at 500 rpm and 82% for **6b** at 970 rpm were obtained (with 29.08 and 21.81 g of HCH, respectively). For the derivatives shown in the scope, comparable and transferable yields were achieved (Table S49).

The accumulation of product **6b** was investigated both in the 5 and 500 mL cells. After each electrolysis run, fresh **1** and **5b** were added again. Due to the limited cell volume, this cycle could be carried out three times in total. In this way, concentrations of up to 0.84 mol·L⁻¹ and 0.90 mol·L⁻¹ were achieved.

In addition, the continuous addition of **5b** during electrolysis was examined. When dosed over a period of 0 to 6 F with an addition rate of 1.46 eq·h⁻¹, the yield of **6b** could be increased by 10%. This effect proved particularly advantageous in electrolyte reuse studies. After each electrolysis run, the coproduct benzene (**2**) was first removed at room temperature under reduced pressure, followed by separation of **6b** at 70 °C and 10⁻³ mbar. To monitor the electrolyte composition, a GC analysis with an internal standard was performed before and after each workup, allowing the consumed amount of **1** to be replenished precisely. Under these conditions, average yields of more than 86% for **6b** were achieved in at least 16 repeated cycles in laboratory applications (Figure 4).

CONCLUSION

This work demonstrates that the electrochemical conversion of HCH (**1**) and HBCD (**8**) in combination with vinyl ethers represents an efficient strategy for the targeted synthesis of acetals of chloroacetaldehyde and bromoacetaldehyde. Using the e-shuttle concept, not only open-chain dialkyl acetals such as chloroacetaldehyde diethyl acetal (**4**) could be obtained in good yields of up to 86% but also cyclic acetals such as 2-chloromethyl-1,3-dioxepane (**6b**). In particular, **6b** proved to be a key substrate with high selectivity and process relevance.

Mechanistic investigations (IC, Mohr titration, and GC analyses) showed that during the reduction of **1**, half of the released chloride ions are transferred to the reaction with vinyl ethers. The remainder contributes to the formation of active

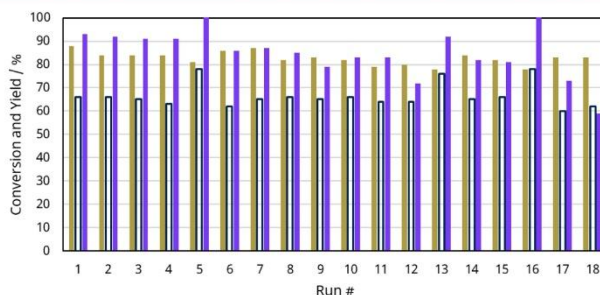


Figure 4. Conversion of HCH (**1**, muddy green filled box). Yields for benzene (**2**, dark blue open box) and 2-chloromethyl-1,3-dioxepane (**6b**, purple filled box) were obtained over 18 repetitions in laboratory applications, with reuse of the electrolyte after each reprocessing. Due to the open system, the values for benzene are not representative.

chlorine species, which in turn activate the vinyl group. In addition, marginal hydrogen evolution was detected, plausibly attributable to a competing cathodic side reaction.

At the process scale, the reaction was successfully scaled up from a 0.218 g HCH to a 21.8 g HCH scale system, with a 167-fold increase in electrode surface area, leading to a significant reduction in electrolysis time and an increase in production rate. Furthermore, accumulation and electrolyte reuse were demonstrated for **6b**. Through continuous substrate addition and targeted recycling, yields above 86% were maintained for at least 16 consecutive cycles.

Overall, this work establishes a scalable and sustainable method to convert HCH and HBCD to valuable platform chemicals. By transforming persistent waste into useful resources, it offers a pathway to mitigate the environmental impact of once-dumped chemical waste.

■ EXPERIMENTAL METHODS

Purification of Hexachlorocyclohexane (HCH, 1)

The HCH samples excavated at the Merck site (Gernsheim, Germany) must be separated from soil residues, stones, and other impurities before use. For this purpose, a Soxhlet extractor is used (Figure S9). HCH is then dissolved in refluxing ethyl acetate and then filtered. Subsequently, HCH is concentrated under reduced pressure, and the precipitate is then filtered off. The solids are then washed with cold ethyl acetate and predried by air suction. The predried HCH is powdered and dried again in a high vacuum.

Determination of Hydrogen

The determination of hydrogen was realized by Merck KGaA (Darmstadt, Germany). Analysis of hydrogen evolution was performed using an Agilent 7890A (Agilent, Santa Clara, United States) equipped with a thermal conductivity detector and a molecular sieve column Rt-MSieve 5A (Restek, Bellefonte, United States) with the following specifications: a length of 30 m, an inner diameter of 0.32 mm, and a stationary phase of 30 μm thickness. Nitrogen was used as the carrier gas with makeup flow: 5 $\text{mL}\cdot\text{min}^{-1}$, column flow: 5.00 $\text{mL}\cdot\text{min}^{-1}$, reference flow: 23 $\text{mL}\cdot\text{min}^{-1}$, and split ratio: 1:10. Measurements were performed at an injector temperature of 150 $^{\circ}\text{C}$ and a detector temperature of 220 $^{\circ}\text{C}$.

A solution of HCH (**1**) (2182.7 mg, 7.5 mmol, 1.0 equiv), tetraethylammonium chloride (413.7 mg, 2.5 mmol), 4-hydroxybutyl vinyl ether (**5b**) (2.7 mL, 21.8 mmol; 2.9 equiv), and 50 mL of propylene carbonate was prepared and added to the electrolysis cell (with stirrer). The volume of the solution was previously determined to be 51 mL, and the volume of the cell was determined in order to calculate the resulting gas volume from the difference to the volume of the solution used (total volume of cell: 106 mL; volume of gas phase: 55 mL). The electrodes with stoppers were inserted into the cell and adjusted to a height of 8.3 cm from the meniscus. The cell was gassed with nitrogen via the side nozzle using a hose. The plug with the electrodes was opened slightly. After a few minutes, the gas supply was stopped, the side nozzle was closed with a stopper, and the stopper with the electrodes was closed tightly. As a starting value, 250 μL of gas was sampled via the stopper using a gas-tight syringe and analyzed immediately (between sampling and manual dosing into the GC, the syringe needle was sealed with a septum). The stirrer was set at 500 rpm. The power supply for the electrodes was switched on and started with a current of $I =$

194 mA. At 1 h intervals, 250 μL of gas was sampled using a gas-tight syringe and analyzed immediately. After 437 min, the power supply was switched off, and two more gas samples were taken at 15 min intervals (Table S7).

Determination of HCl

The determination of halogens was realized by Merck KGaA (Darmstadt, Germany). Analysis of halogens was performed using an IC Metrohm system (Metrohm AG, Herisau, Switzerland) equipped with a conductivity detector and an anion exchange column (poly(vinyl alcohol) with quaternary ammonium groups), Metrosep A Supp 5 250/4.0 (Metrohm AG, Herisau, Switzerland) with the following specifications: a length of 250 mm, an inner diameter of 4.0 mm, and a particle size of 5 μm . As eluent, 3.2 mM Na_2CO_3 /1.0 mM NaHCO_3 were used. Measurements were performed at a temperature of 30 $^{\circ}\text{C}$ and a flow rate of 0.700 $\text{mL}\cdot\text{min}^{-1}$.

A solution of HCH (**1**) (2184.0 mg, 7.5 mmol, 1.0 equiv), tetraethylammonium chloride (415.8 mg, 2.5 mmol), 4-hydroxybutyl vinyl ether (**5b**) (2.7 mL, 21.8 mmol; 2.9 equiv), and 50 mL of propylene carbonate was prepared and added to the electrolysis cell (with stirrer). A sample (approximately 1 mL) of this solution was taken as an initial value. The electrodes with plugs were inserted into the cell and adjusted to a height of 8.3 cm from the meniscus (Figure S38). Nitrogen was fed through two cannulas via a stopper on the side nozzle with tubing. The outlet was connected to a gas washing bottle filled with 200 mL of 1 $\text{mol}\cdot\text{L}^{-1}$ NaOH, and the gas was passed through during the entire electrolysis (Figure S39). This method was used to collect and quantify HCl from the gas phase. The stirrer was set to 500 rpm. The power supply for the electrodes was switched on and started with a current of $I = 194$ mA. After 437 min, the power supply was switched off and samples were taken from the electrolysis cell and the content of the gas washing bottle.

Cyclovoltammetry

Cyclic voltammetry measurement was performed using a Metrohm 663 VA Stand equipped with an Autolab Type III potentiostat (Metrohm AG, Herisau, Switzerland). Cyclic voltammetry was conducted with isostatic graphite as the working electrode, a glassy carbon rod as the counter electrode, and Ag/AgCl as the reference electrode. The potential window was set to -0.5 ± 1.5 V, and the scan rate to 0.1 $\text{V}\cdot\text{s}^{-1}$. The start and stop potentials were set to 0.5 V. The blank was measured in propylene carbonate with $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ ($c((\text{C}_2\text{H}_5)_4\text{NBF}_4) = 0.05 \text{ mol}\cdot\text{L}^{-1}$). All data are displayed against the half-wave potential of the ferrocene/ferrocenium redox couple (FcH/FcH^+ ; -0.01 V vs Ag/AgCl) as the reference.

Cyclic voltammetry experiments were conducted in a 10 mL glass vial fitted with a graphite working electrode (3 mm in diameter, BASi), a Ag/AgNO₃ reference electrode, and a glassy carbon counter electrode (3 mm in diameter, BASi). The solution of interest was sparged with argon for 3–5 min before data collection.

Recyclability of the Electrolyte

The recyclability of the electrolyte was repeated up to 18 times. After each electrolysis and workup, approximately 1 mL of the electrolyte was removed and measured with the internal standard. An amount of 21.81 g of HCH (**1**) was used for electrolysis at the start. After each electrolysis, the determined converted amount of HCH was added again. The recyclability

was carried out using the example of 2-chloromethyl-1,3-dioxepane (**6b**) in a 500 mL stacked batch-type electrolysis cell (Figure S7). 4-Hydroxybutyl vinyl ether was added via a pump (SF-10 (Vapourtec Ltd, Bury St Edmunds, UK)) over a period of 0–6 F (226 $\mu\text{L}\cdot\text{min}^{-1}$) in every electrolysis run (Table S52).

■ ASSOCIATED CONTENT

Data Availability Statement

The data supporting this article have been included as part of the Supplementary Information (SI).

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acselecchem.Sc00498>.

Additional experimental information; additional details of the design of experiments; CVs of various substrates and electrolysis; kinetic studies; ^1H NMR and ^{13}C NMR spectra of the corresponding starting materials and products (PDF)

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4.3 Elektrochemischer Chlor-Shuttle von PVC-Abfällen zu Vinylether-Akzeptoren für die Synthese biologisch abbaubarer Polyester-Vorläufer

Zu diesem Kapitel wurde ein Manuskript veröffentlicht:

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Das Projekt wurde im Rahmen des Halocycles Projekt (FKZ: P2021-10-007) von S. Becker bearbeitet. S. Becker, **D. Weis** und S. Horsinka führten initiale Experimente durch. Die grundlegende Reaktionsoptimierung im Screening-Maßstab sowie mittels statistischer Versuchsplanung (DoE) wurde von S. Becker durchgeführt, wobei die entsprechenden Methoden von **D. Weis** und S. Horsinka vermittelt wurden. Weiterführende Optimierungen, Substratbreite und Skalierungen wurden von S. Becker und D. Wördehoff durchgeführt. S. Becker verfasste das Manuskript und stellte es in Zusammenarbeit mit S. R. Waldvogel und P. Besenius fertig.

RESEARCH ARTICLE

Electrochemical Chlorine Shuttle from PVC Waste to Vinyl Ether Acceptors for the Synthesis of Biodegradable Polyester Precursors

Sebastian Becker, Dominik Wördehoff, Dominik Weis, Simon Horsinka, Siegfried R. Waldvogel,* and Pol Besenius*

Poly(vinyl chloride) (PVC) remains one of the most widely produced polymers globally but poses significant environmental and energetic challenges due to its high chlorine content, low recyclability, and the energy-intensive nature of both production and disposal. Here, a sustainable electrochemical approach is reported for the dechlorination of PVC and simultaneous synthetic generation of cyclic acetals, precursors for biodegradable polyesters, employing a Cl_2 -shuttle reaction onto vinyl ethers. By systematic electrochemical screening and a Design of Experiments (DoE) optimization strategy, high yields of cyclic acetal formation and elevated dechlorination rates of up to 94% for PVC are achieved. The resulting polymer retains its structural integrity and exhibits internal plasticization via covalent recombination with phthalate plasticizer fragments. This shows that beyond chlorine recovery, the process opens up attractive upcycling pathways through tunable thermal properties of partially dechlorinated PVC. Additionally, our method is tolerant to common plastic additives and applicable to real PVC waste streams, highlighting its robustness and industrial potential. The broad scope of accessible cyclic acetals expands the utility of the reported process using PVC as a chlorine source, providing a platform to produce valuable monomer precursors and enabling facilitated access to versatile, biodegradable polyester materials.

1. Introduction

The recycling of poly(vinyl chloride), the third most produced polymer material worldwide after polyethylene and polypropylene, remains a major challenge.^[1] Due to the extensive use of additives, reaching weight percentages of up to 60% in the final material formulation, and the high intrinsic chlorine content and its action as flame retardant, make energy recovery through combustion very difficult.^[2,3] PVC recycling rates are extremely low, such as 3% in the US.^[4] End-of-life PVC is widely regarded as hazardous and an economically unattractive waste material that accumulates in landfills and still poses risks, such as leaching toxic additives.^[5–7] Non-recycled PVC waste streams contribute to the material's extremely poor energy profile. The overall manufacturing process of PVC is endothermic, since the industrial production of chlorine via chlor-alkali electrolysis is highly energy intensive and accounts for $\approx 2\%$ of the total electricity consumption in

Germany.^[8,9] Nevertheless, on an industrial scale, chlorine chemistry is ubiquitous. It is essential in all sectors for the synthesis of solvents, catalysts, and key chemical building blocks. Notably, 90% of pharmaceuticals and 86% of crop protection chemicals contain chlorine, or chlorine chemistry is involved in their intermediates.^[10] The high energy content of chlorine enables the synthesis of acid chlorides (e.g., PCl_3 , SiCl_4 , COCl_2), which provide an enormous thermodynamic driving force for downstream synthetic routes.^[11] Importantly, 39% of industrial chlorine production is used for PVC manufacturing, representing a major Cl_2 -One-Way-Road towards chloro-organic waste products.^[12,13] Hence, there is a high demand for innovative chemical recycling strategies for PVC to establish a circular economy of chlorine on industrial scales.

The central concept in chemical PVC recycling involves the cleavage of the carbon-chlorine (C–Cl) bond to recover both carbon scaffold and chlorine content separately. The high bond dissociation energy of the C–Cl bond combined with the macromolecular nature of the substrate, exhibits a significant challenge for the desired quantitative dechlorination of

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the polymer material.^[14,15] Various strategies have been developed for the dechlorination of PVC using thermal/basic eliminations, catalytic pathways, or electrochemical reduction, many include sequential techniques to avoid polymer degradation or crosslinking.^[14,16–31] However, most of these approaches put large emphasis on polymer re- and/or upcycling only, and strategies to efficiently recover both the polymer scaffold and the chlorine content remain rare. Focusing on the dechlorination of PVC, catalytic approaches stand out compared to thermal eliminations, with high dechlorination rates enabling precise reaction control over the C–Cl bond cleavage and leading to quantitative dechlorination.^[17,19–21] The applicability for industrial scales remains limited, however, since the used catalysts typically require inert conditions, are sensitive to plasticizers and stabilizers, operate at elevated temperatures or pose a severe cost factor.

Here, we propose that the electrochemical dechlorination of PVC via a paired electrolysis strategy represents a promising route to recover both chlorine and the polymer backbone efficiently, while retaining industrial scalability.^[32] Electrochemistry, particularly electro-organic synthesis, combines the use of renewable energy and selective chemical reactivity.^[33–36] Key benefits include the replacement of chemical reagents by electrical current, and the separation of halides or halogens, which are often gaseous and corrosive, is avoided. An ideal scenario would be the in situ transfer of halides from a stable feedstock like waste PVC, circumventing the use of chlorine.^[37] Numerous examples of halogen transfer in electro-organic synthesis have been reported so far.^[32,38–48] The electrochemical dihalogenation has a technical impact, wherein for sophisticated building blocks the dibromination is often preferred over the dichlorination.^[49,50] The WALDVOGEL and MORANDI labs reported conditions to use dibromo- or dichloroethane, the latter in combination with manganese catalysis, as halide sources which were transferred electrochemically to olefins, thus yielding new vicinal dichlorides or dibromides. Importantly, this chemistry is amenable to the use of γ -hexachlorocyclohexane (Lindane) as a potent chlorine donor. For example, 1-dodecene could be chlorinated, obtaining high yields (91%) on a multigram scale (16 g) using Lindane as chlorine source while liberating benzene. Even soil samples artificially contaminated with Lindane could serve as a substrate, highlighting the robustness of this electrochemical upcycling strategy.^[48] A few examples on electrochemical re- and upcycling of PVC exist.^[22,31,51–53] Remarkably, McNEIL and coworkers successfully harnessed the liberated chlorine from PVC in a direct oxidative chlorination of arenes. Additionally, they investigated the mediative properties of phthalate esters, plasticizers used in PVC, for electrochemical cleavage of the C–Cl bond.^[31] Despite the innovative paired electrolysis approach, the dechlorination rate of PVC remains low, and the practical relevance of chlorinated arenes reported at an industrial scale remains uncertain.

Given the vast amount of PVC waste, the danger of shifting the waste issue from PVC to the chlorine acceptor molecule is a significant concern. Consequently, finding innovative and industrially relevant chlorine acceptors is crucial for establishing truly circular material streams. One promising approach involves the electrochemical chlorination of vinyl ethers with a terminal hydroxy group, such as 4-hydroxybutyl vinyl ether, yielding 2-chloromethyl-1,3-dioxepane. This compound can be used for the manufacturing of poly(caprolactone) (PCL), a biodegrad-

able polyester, via one step elimination and polymerization.^[54–56] Additionally, this monomer can also enhance the degradation profile of otherwise persistent commodity polymer materials. Due to the radical polymerization mechanism, ketene acetal monomers can be incorporated via drop-in copolymerization into materials such as polystyrene (PS) and polymethyl methacrylate (PMMA).^[54,57–59] This copolymerization introduces hydrolysable ester bonds in the polymer backbone that facilitate polymer degradation: this highlights the usefulness of the synthesized chlorine acceptor for multiple materials sectors on an industrial scale.^[56]

2. Results and Discussion

2.1. Electrochemical Screening

The electrochemical chlorination of vinyl ethers using Lindane as a chlorine source has previously been reported by WALDVOGEL and coworkers.^[48] The electrochemical chlorination of vinyl ethers bearing an electron-rich double bond, like ethyl vinyl ether, yields the corresponding dichloro product only in trace amounts. The main product observed is the acetal 2-chloro-1,1-di(ethoxy)ethane. The presence of a terminal hydroxyl group enables intramolecular ring formation, yielding cyclic acetals. Combining this oxidative chlorination reaction at the anode with the electrochemical reductive dechlorination of PVC at the cathode represents an innovative paired electrolysis for PVC recycling.^[60] McNEIL and coworkers have reported the selective chlorination of arenes while the electron deficient aromatic plasticizer di(2-ethylhexyl) phthalate is not chlorinated.^[31] Here, we hypothesize that the electron-rich double bond of vinyl ethers enables similar selectivity during electrolysis and subsequently enables efficient acetal formation via intramolecular cyclisation. **Figure 1** depicts the proposed mechanism of the paired electrolysis pathway. The phthalate plasticizer enables electron transfer from the cathode onto PVC, initiating the cleavage of the C–Cl bond.^[31] Since the second reduction of the polymer radical is emphasized to proceed faster than the reductive C–Cl cleavage, a subsequent immediate second reduction and protonation lead to defunctionalized PVC (dPVC).^[61,62] Another possible pathway is the radical recombination of polymer backbone radicals. Besides the recombination with other polymer radicals, phthalate esters are known to be electrochemically unstable and degrade into fragments.^[63] These species can also recombine with the polymer backbone.

Electrochemical screening was started with low molecular weight PVC ($M_n = 22,000 \text{ g mol}^{-1}$), and dimethyl phthalate (DMP) was chosen to simplify analysis of the polymers via nuclear magnetic resonance (NMR) spectroscopy. Starting with the initial conditions, we performed systematic screening, which led to the optimized conditions yielding 77% of the cyclic acetal **3** according to gas chromatography (GC) analysis (**Figure 2**; Tables S2–S12, Supporting Information). Key parameters investigated were the solvent and supporting electrolyte, using *N,N*-dimethylacetamide (DMA) in combination with alkylammonium chloride salts to significantly increase the GC yield of the cyclic acetal. Due to the use of chloride salts as supporting electrolytes, control experiments were performed to confirm that PVC dechlorination is essential for cyclic acetal formation. Electrolysis in the absence of PVC resulted in a substantially lower product yield

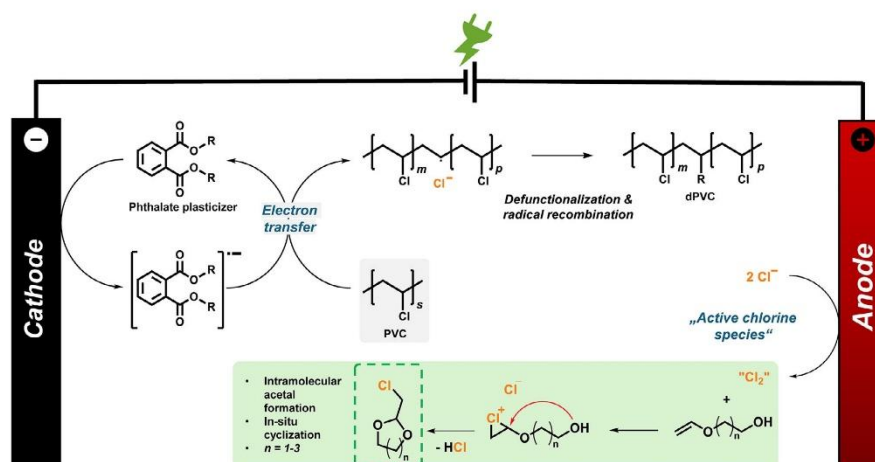


Figure 1. Chlorine shuttle (proposed mechanism) with paired electrolysis pathway: Reductive cleavage of the carbon-chlorine bond (cathode) mediated by alkyl phthalates. Generation of active chlorine species (anode) leading to double bond chlorination and in situ cyclization of the vinyl ether to the cyclic acetal.

of **3** (8%). Besides optimizing the yield of the cyclic acetal, our main focus was to avoid polymer network formation via radical recombination. To this end, slow alternating polarity was applied to prevent cathode corrosion or passivation caused by crosslinked polymer material. Screening results of the alternating polarity frequency (Table S12, Supporting Information), together with the trend that longer alkyl chain lengths of the ammonium cations led to higher GC yields of (**3**) suggested that an

intact electrochemical double layer with an apolar microenvironment is crucial for the generation of active chlorine species and subsequent cyclic acetal formation.^[64,65] Consequently, a compromise between maximizing cyclic acetal formation and minimizing network formation was necessary. Such trade-offs are characteristic of paired electrolysis methods.^[60] Applying the optimized conditions resulted in high cyclic acetal yields of 77%, and GC-MS analysis confirmed the absence of side reactions

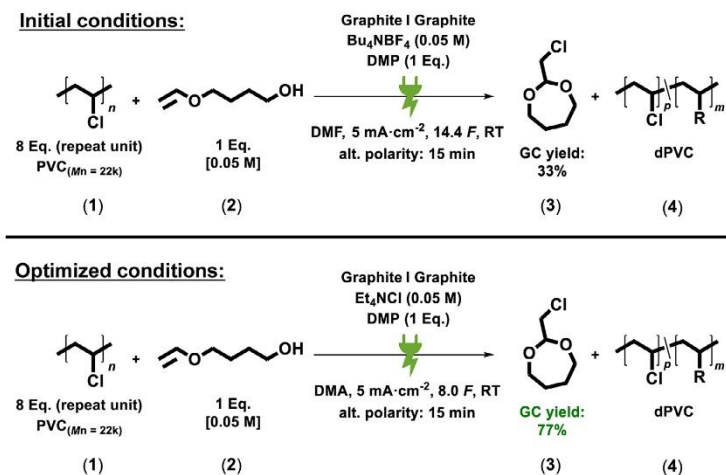


Figure 2. Initial conditions: Electrochemical reaction conditions used for optimization. Optimized conditions were obtained after electrochemical parameter screening was performed.

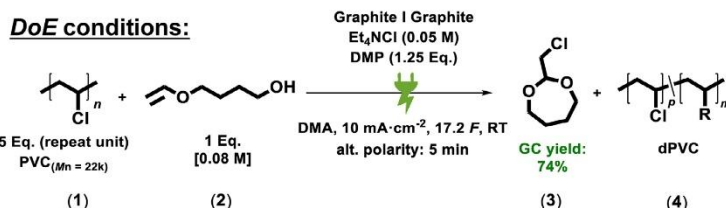


Figure 3. DoE conditions with decreased excess PVC (1) to enhance the dechlorination rate of the polymer material.

such as recombination of (2) to dimers (Figure S2, Supporting Information).

2.2. Increasing the Dechlorination Rate of PVC by Design of Experiments Approach

Having the optimized conditions in hand, further effort was invested toward increasing the dechlorination rate of PVC via electrochemical reduction. An eight-fold excess of the PVC repeating units relative to the chlorine acceptor, 4-hydroxybutyl vinyl ether (2), was applied in the optimization screening. In order to increase polymer dechlorination and subsequent Cl-shuttle to the vinyl ether, the PVC excess was reduced to a 5:1 ratio, which led to a decreased GC yield of 63% regarding the cyclic acetal formation. This experiment served as a starting point for the optimization via Design of Experiment (DoE) approach.^[66–68]

For the DoE screening plan, parameters such as current density, amount of applied charge, and phthalate concentration were selected (Table S13, Supporting Information). Having polymers involved, previous DoE screenings taught that the choice of screening parameters with reasonable framework conditions is crucial for successful optimization. For example, the screening of the polymer concentrations or polymer/chlorine acceptor ratio results in significant viscosity changes of the electrolyte, influencing mass transport and convection. This effect introduces considerable amounts of noise into the statistical model and reduces reproducibility, leading to a low R^2_{corr} value.^[67] The subsequent addition of star points and target value optimization led to adjusted values for the screened parameters that increased the obtained GC yield of the cyclic acetal from an initial 63% to 74% (control experiment without PVC: 9%). Figure 3 illustrates the conditions that were obtained via DoE screening. Compared to the optimized conditions, the DoE-derived adjustment of the selected parameters is suggested to result in a significantly increased dechlorination rate due to the lower excess of PVC.

DoE screening provided access to interaction plots of the selected parameters (current density, amount of applied charge, and phthalate concentration).^[66] These interaction plots (Table S14, Supporting Information) reveal that the phthalate concentration influences the optimal current density and optimal amount of applied charge for efficient cyclic acetal formation. Notably, this result could be particularly valuable for the recycling of real PVC products, which intrinsically contain certain phthalate loadings in their material formulation. Considering the electrochemical recycling of various PVC waste stream batches, the phthalate concentration could be determined, and subsequently,

the electrochemical parameters (e.g., current density and applied charge) could easily and rapidly be adjusted to ensure optimal electrolysis performance for cyclic acetal formation.

In order to maximize the dechlorination of PVC using electrochemical reductive pathways, the DoE conditions were applied repeatedly for the same PVC material (Figure 4). After each electrolysis, the material was precipitated, dried, and subsequently redissolved in DMA for reuse in the next electrolysis cycle. The GC yield of the cyclic acetal decreased stepwise from 74% in the first electrolysis to 54% in the second, 32% in the third, and 17% in the fourth, gradually approaching the value of the negative control (without PVC, 9%). Due to the coiled nature of the PVC material in solution, the inhomogeneous accessibility of C–Cl sites and the decreasing excess of PVC repeat units over the multiple electrolysis cycles influence and limit the cyclic acetal formation. Nevertheless, the experiment strongly suggests that high dechlorination rates are obtained.

2.3. Polymer Characterization

The dechlorinated PVC was analyzed upon electrolysis by NMR spectroscopy and size exclusion chromatography (SEC). Additionally, thermogravimetric analysis (TGA) and elemental analysis were performed to gain deeper insight into the extent of PVC dechlorination. First, ^1H NMR analysis (Figure 5) of PVC samples obtained after electrolysis under optimized and DoE conditions revealed a stepwise decrease in the relative intensity of the broad ^1H NMR signals for the R_2CHCl group in the range of 4.2–4.7 ppm, confirming dechlorination of PVC. In addition, the broadening of the ^1H NMR signals in the aliphatic region and the emerging signals between 3.6–3.9 ppm indicate defunctionalization and incorporation of methoxy groups, due to phthalate methyl ester fragmentation with subsequent radical recombination.^[63] McNEIL and coworkers not only observed recombination with methoxy groups for higher dechlorination rates, but also additional ^1H NMR signals in the aromatic region and a significant amount of double bond formation during electrochemical dechlorination with dimethyl phthalate. In contrast, our optimized and DoE electrolysis conditions in this work exclusively led to recombination with methoxy groups.^[31] Interestingly, the incorporation of the fragmented aromatic phthalate moiety and double bond formation appear to be suppressed under these conditions.

The observed dechlorination of PVC was confirmed by TGA analysis (Figure S3, Supporting Information). Elemental analysis (Table S16, Supporting Information) further revealed a

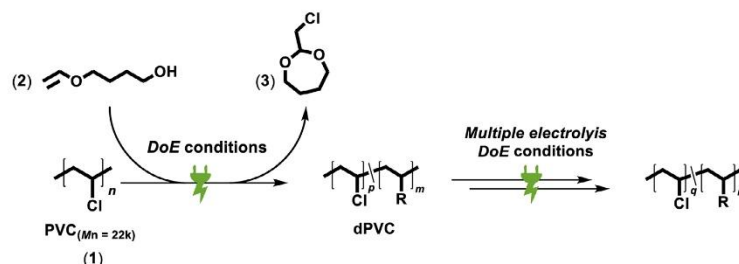


Figure 4. Multiple electrolysis reactions are applied to the same PVC (1) material to enhance the rate of dechlorination induced by electrochemical reduction.

dechlorination rate of 25% under optimized conditions and 36% under DoE conditions, corresponding to a reduction of the chlorine content of the starting material from 56 to 42 and 36 wt.%, respectively. After four electrolytic cycles under DoE conditions, the previously discussed trend is furthermore confirmed: The characteristic PVC signal in the 4.2–4.7 ppm area is not detectable anymore, indicating that the original polymer backbone has been almost completely dechlorinated. Methoxy recombination accumulates over the four electrolysis cycles and, in contrast to the other polymer samples, additional ^1H NMR signals indicative of recombination with aromatic phthalate groups become apparent. Notably, elemental analysis revealed chlorine content as low as 3.6 wt.% and corresponds to a 94% dechlorination rate. Although radical recombination involving aromatic and methoxy groups distorts the elemental composition, the results suggest close to quantitative dechlorination reactions.

The potential and efficiency of the electrochemical modification of the PVC polymer backbone is remarkable, especially given the harsh conditions typically required to cleave high-energy bonds such as the carbon–chlorine (C–Cl) bond. Size exclusion chromatography was furthermore employed and reveals a shift toward lower apparent molecular weights for all samples (Figure 6a). We attribute this observation to the mass loss during dechlorination and altered hydrodynamic properties of the defunctionalized PVC in *N,N*-dimethylformamide (DMF). Importantly, the absence of high molecular weight species confirms that no recombination reactions of polymer backbone radicals occurred.

The established electrochemical reaction under optimized or DoE conditions can be readily performed and reproduced using a variety of phthalate esters, such as di(2-ethylhexyl) phthalate (DEHP). Functionalization of the polymer material with alkoxy

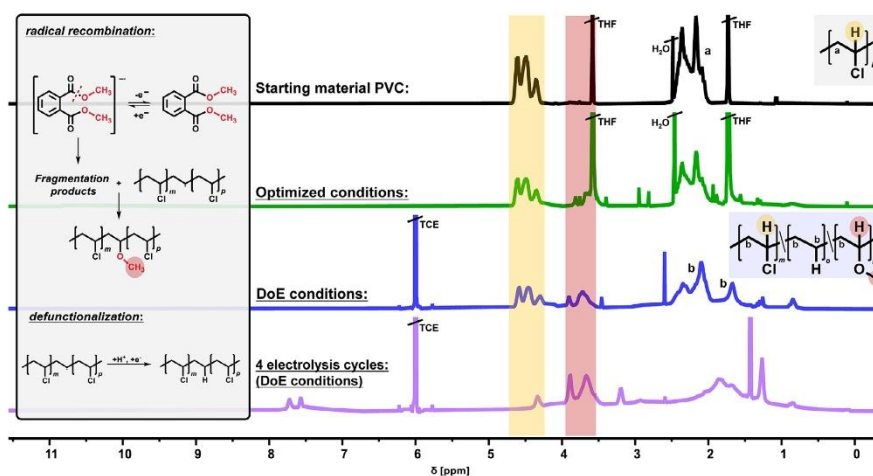


Figure 5. ^1H NMR analysis of the starting material (black, 400 MHz, THF-d_3 , 298 K) and the dechlorinated PVC obtained from the optimized conditions (green, 400 MHz, THF-d_3 , 298 K), DoE conditions (blue, 400 MHz, TCE-d_2 , 298 K) and multiple electrolytic cycles (violet, 400 MHz, TCE-d_2 , 298 K) using the DoE conditions. The decreasing intensity in the area between $\delta = 4.2$ –4.7 ppm (yellow area) indicates a gradual increase of the dechlorination rate. Recombination reactions with phthalate ester fragments are observable in between $\delta = 3.6$ –3.9 ppm (red area) with proposed mechanisms for the defunctionalization and radical recombination reaction.

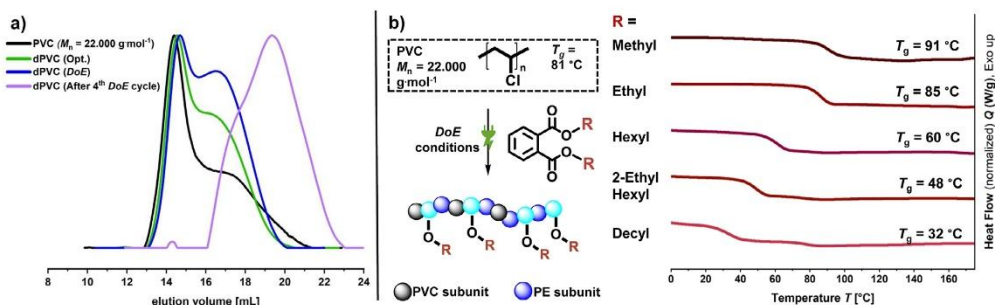


Figure 6. a) SEC elution traces of the starting material (black) and the dechlorinated PVC after electrolysis obtained from the optimized conditions (green), DoE conditions (blue) and multiple electrolytic cycles (violet). RI signal; eluent: DMF, 40 °C; standard: PMMA. b) Five different phthalate esters employed during electrolysis and their impact on the thermal properties of the produced dechlorinated PVC polymer materials.

side chains derived from fragmented phthalate esters, in combination with partial defunctionalization and conservation of the macromolecular architecture, results in an internally plasticized, partially dechlorinated PVC species. This material could be of interest for advanced upcycling strategies.^[69–72] Differential scanning calorimetry (DSC) experiments and measurements of the glass transition temperatures (T_g) were therefore performed of the dechlorinated PVC after employing phthalate esters with increasing aliphatic chain lengths in the electrochemical reaction (Figure 6b). While the recombination of dimethyl and diethyl phthalate fragments leads to an increase in T_g compared to PVC (anti-plasticization), using industrially relevant phthalate esters such as DEHP in electrolysis cause a stepwise reduction in T_g with increasing alkyl chain length, reaching 32 °C for the didecyl phthalate. Analysis by ^1H NMR spectroscopy revealed a further lowering in chlorine content in the dechlorinated PVC when using DEHP or didecyl phthalate during electrolysis, yielding chlorine weight percentages of 29 and 30 wt.%, respectively. This decrease is attributed to the incorporation of longer alkoxy side chains from these plasticizers, which alters the elemental composition of the resulting material. In comparison, using dimethyl phthalate in electrolysis resulted in a chlorine content of 36 wt.% as already discussed, since the shorter alkyl chains have a smaller impact on the overall elemental balance.

Internal PVC plasticization prevents embrittlement and avoids migration of toxic plasticizers, as no diffusion-based leaching can occur. This is usually realized via polymer modification by nucleophilic substitution (S_N) reactions using amines, azides, or thiols, graft polymerizations, or copolymerization.^[69–71,73–76] However, most approaches are not realizable on industrial scales due to high costs and the requirement of at least one, often several, additional synthetic steps.^[73] In our case, the internal plasticized material through this electrochemical process, yielding T_g values between 32–60 °C, could already find application of semi-rigid PVC products, such as in flooring, trays, and blister packaging.^[76] This highlights the utility of the established paired electrolysis process not only for cyclic acetal synthesis as a precursor for polyesters, but also for generating partially dechlorinated, flexible materials with tunable mechanical properties and lower health risks. The process may be further optimized by adjusting electrochemical parameters and the amount of phthalate esters used dur-

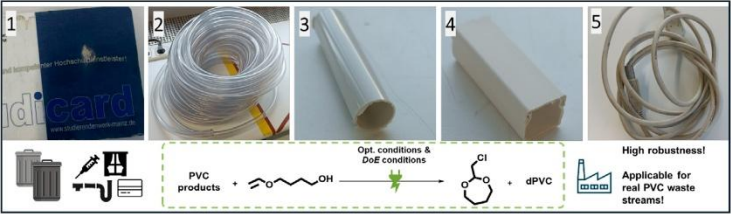
ing electrolysis, enabling the design of upcycled PVC materials with targeted thermal properties, which is a central aim of future investigations.

2.4. Process Stability

To evaluate the robustness, scalability, and applicability to real PVC waste streams, several additional experiments were conducted. Upscaling the electrochemical reaction to a 10 mL cell using DoE conditions showed no decrease in GC yield obtained for the cyclic acetal (3). A 50-fold scale-up using a 500 mL cell (250 mL reaction volume, 6.25 g PVC, 2.33 g (2)) resulted in a reduced yield of 35%, likely due to different cell architecture and stirring efficiency, indicating that while upscaling is feasible, further optimization for the corresponding cell size and reactor geometry is necessary. As expected, using high-molecular-weight PVC ($M_n = 99,000 \text{ g mol}^{-1}$) led to slightly reduced yields: 64% under optimized conditions and 58% under DoE conditions. This can be attributed to two factors. First, a lower average accessibility of the carbon–chlorine sites, making dechlorination more challenging, and, second, increased viscosity which decreases mass transport during electrolysis. Rheological measurements showed how the different molecular weight PVC species (22,000 and 99,000 g mol^{-1}) influence the viscosity of the electrolyte solution (Figure S5, Supporting Information). Control experiments without stirring, carried out under optimized conditions in a 5 mL screening cell, showed a lower GC yield of 32% (down from 77%), highlighting the critical importance of mass transport and consistent stirring during electrolysis and offering a rationale for the decreased yields observed in scale-up and high molecular weight PVC experiments.

To further assess the robustness of the electrochemical reaction, a range of hard and soft PVC products were collected, cut into small pieces, and dissolved in DMA for electrolysis. NMR analysis confirmed the presence of PVC along with typical additives such as plasticizers, stabilizers, and minor impurities (Figure S6, Supporting Information). Some samples, such as polymer blends containing PE films (e.g., credit card coatings), resulted in suspensions that were subjected to electrolysis without filtration. The resulting GC yields of cyclic acetal (3) are

Table 1. Use of PVC waste and consumer goods for the synthesis of 2-chloromethyl-1,3-dioxepane (**3**). Optimized (Figure 2) and DoE conditions (Figure 3) were applied.



PVC material	GC yield (2-chloromethyl-1,3-dioxepane (3))/%	
	Optimized Cond.	DoE-Conditions
PVC ($M_n = 99.000 \text{ g mol}^{-1}$)	64	58
1-credit card	71	43
2-water hose	72	63
3-tube	68	56
4-cable casing	59	70
5-cable sheathing	65	51

summarized in **Table 1**, and the results demonstrate the applicability of this electrochemical method to real PVC waste streams, including commercial additives, polymer blends, and non-PVC formulation impurities.

Additionally, the PVC materials that exhibited the lowest GC yields under the DoE conditions, material-1 (credit card, 43%) and material-5 (cable sheathing, 51%), as listed in **Table 1**, were selected for additional experiments, in order to verify the conclusions obtained from the DoE screening described in section 2.2. NMR and GC-MS analysis of material-5 (cable sheathing) revealed high additive loadings and characteristic phthalate signals in the ^1H NMR spectrum and mass spectra (di-isononyl phthalate). Consequently, the PVC to chlorine acceptor ratio shifted from 5:1 to a much lower, unknown value. As the DoE prescreening had shown that a further decrease in this ratio leads to a significant loss in yield, an additional estimated amount of 20 wt.% PVC was used in the electrochemical reaction. This adjustment increased the obtained GC yield of (**3**) from 51% to 65%. For the credit card sample, analytical data showed no presence of phthalate esters; however, mass spectrometry indicated the abundance of UV absorbers (benzotriazole UV-326). As the phthalate concentration is lower compared to other PVC products, the interaction plots suggested a lower optimal current density for the electrolysis of this unplasticized, hard PVC. Reducing the current density from 10 to 6 mA cm^{-2} increased the GC yield from 43% to 64%, thereby underlining and confirming the key conclusions from the parameter interaction study by the DoE approach of the electrochemical reaction.

2.5. Scope of Cyclic Acetals

The reported electrochemical conditions for the formation of the seven-membered acetal moiety (**3**) were applied to other vinyl

ethers, altering the alkyl chain between the ether and the terminal hydroxy group. As a result, cyclic acetals with different ring sizes from five-membered (**5**) to eight-membered rings (**7**) were obtained (**Figure 7**). The electrochemical reaction with intramolecular in situ cyclisation proceeded successfully, and the corresponding product formation was observed for all ring sizes, yielding the cyclic acetals (**5**)–(**7**) in moderate GC yields. The following basic elimination that provides the ketene acetal monomer is well documented in literature and proceeds in high yields.^[77] In this body of work, the established electrochemical reaction has been optimized for the seven-membered cyclic acetal (**3**), since the corresponding ketene acetal shows superior polymerization features compared to the five- and six-membered cyclic ketene acetals, which are prone to side reactions during radical polymerization.^[55] The reactivity during polymerization is highly dependent on ring size (ring strain) and steric hindrance.^[56] To optimize the yield of the cyclic acetal 2-chloromethyl-1,3-dioxolane (**5**), we adjusted the electrolysis conditions by using lower current densities and a lower supporting electrolyte concentration. Note that besides the seven-membered cyclic ketene acetal, the eight-membered ketene acetal also undergoes radical ring-opening under a broad range of experimental conditions for homopolymer and copolymer synthesis.^[56] In particular, the eight-membered ring (**7**) incorporates an additional oxygen atom, forming a diethylene glycol subunit within the resulting polyester repeat unit, which enhances water solubility. Hence, this substrate scope of cyclic acetals highlights the potential of our approach for providing easy access to a versatile platform of ketene acetal monomers that enable the design of novel, biodegradable materials.^[54,56,57,59,78]

3. Conclusion

We have established a robust electrochemical paired electrolysis strategy for the dechlorination of PVC, enabling shuttle of

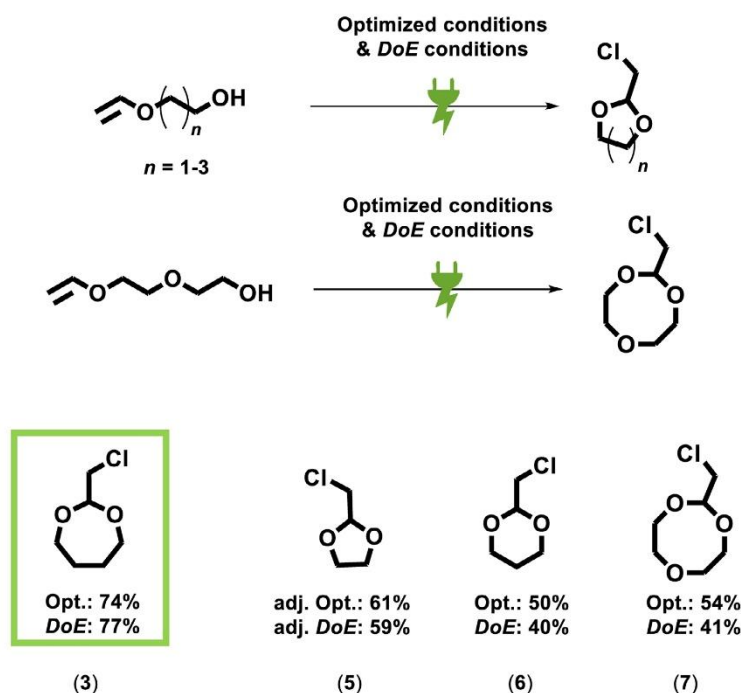


Figure 7. Scope of cyclic acetals, the electrochemical reaction conditions developed for efficient acetal formation of the seven-membered ring applied to different sizes. Obtained GC yields using 1,10-dichlorodecane as internal standard.

chlorine equivalents from PVC to organic acceptors (vinyl ethers) and the concurrent formation of cyclic acetals. This process avoids the use and generation of hazardous molecular chlorine, proceeds under mild conditions and electric energy from renewable resources can be utilized. It yields useful monomer precursors, thereby avoiding the shift of waste problems to other chlorinated organic compounds on an industrial scale. Guided by a Design of Experiments (DoE) screening, this approach achieves high acetal yields and dechlorination efficiencies of up to 94% over multiple electrolysis cycles—significantly surpassing all previously reported electrochemical PVC dechlorination methods. Notably, the process maintains excellent functional robustness across different PVC types and waste products, in contrast to most literature-known catalytic methods, which suffer from poor tolerance to additives and impurities, or challenges regarding scalability. The resulting PVC material exhibits internal plasticization, giving an optimal starting point for further upcycling strategies that will be addressed in the future. These findings highlight the potential of electrochemical chlorine shuttle chemistry as an innovative route for PVC recycling and set the stage for a platform of cyclic acetals monomer precursors enabling advanced and versatile material design of biodegradable polyesters on industrial scales.

4. Experimental Section

Electrolysis Equipment & Setup: Electrochemical reactions were performed in undivided cells (5 mL, IKA, ElectraSyn®) with constant current provided by a galvanostat power supply (Rohde & Schwarz R&S® HMP4040). For upscale experiments, undivided 10 mL (10 mL, IKA, ElectraSyn®) and 250 mL (Institute workshop) undivided cells were used. The isotactic graphite was cut by the Institute workshop into the needed dimensions (50 x 10 x 2 mm, for 5- and 10 mL cells). The caps for the electrochemical cells made of Teflon were milled by the institute's workshop to fit the cell thread and were equipped with suitable openings for the electrode holders. Polarization changers have been installed between the power supply and electrochemical cell to change polarity (direct current to alternating current) during electrolysis and were manufactured by the institute's electricity workshop. For the electrochemical screenings, the starting materials were weighed directly into the electrochemical cell (5 mL). After complete homogenization, the Teflon cap with the electrode holders and electrodes was screwed onto the electrochemical cell. After the determination of the immersion depth, the contact clips were attached to the electrode holders. The electrochemical cell was put into a screening block (made of stainless steel by the institute's workshop) located on top of a stirring plate. For the upscale experiments, Teflon caps, electrodes, and electrode holders were used also manufactured by the institute's workshop. The 10 mL cell has been purchased commercially; the 500 mL cell was customized by the university's glass workshop.

Nuclear Magnetic Resonance Spectroscopy: All NMR measurements (^1H , ^{13}C , HSQC, HMBC, and COSY) were carried out using an AVANCE II

400 MHz spectrometer from Bruker (^1H : 400 MHz, ^{13}C : 101 MHz) (Rheinstetten, Germany). All measurements were carried out at room temperature in a deuterated solvent. The chemical shifts were reported in relation to the solvent peak as an internal standard in parts per million (ppm), and the coupling constants J were measured in Hertz (Hz). The splitting patterns were labeled as s, singlet; d, doublet; t, triplet; dd, doublet of doublet; q, quartet; m, multiplet. The spectra were analyzed using *Mestrenova* software from *Mestrelab Research*. The deuterated solvents used were tetrahydrofuran- d_8 , tetrachloroethane- d_2 , dichloromethane- d_2 , and chloroform- d_3 , which were purchased from *Deutero*, (Germany).

Gas chromatography: For the yield determination of electrochemical reactions were measured using the gas chromatograph GC 2010 from *Shimadzu* with a quartz capillary column ZB-5 from the company *Phenomenex*. The column has a length of 30 m with an inner diameter of 0.025 mm. The covalently bonded stationary phase had a film thickness of 0.25 μm . The standard method included the following system settings: Hydrogen with a flow rate of 40.0 mL min^{-1} was used as carrier gas. The injection temperature was 250 $^\circ\text{C}$ and the detection temperature 320 $^\circ\text{C}$. The method with a total run time of 19.94 min was used with a starting temperature of 40 $^\circ\text{C}$. The starting temperature was maintained for 1 min. and then heated to 110 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C min}^{-1}$. The temperature was then increased by 32 $^\circ\text{C min}^{-1}$ to 300 $^\circ\text{C}$ and held for 6 min. For yield determinations, product signal calibrations were performed using 1,10-dichlorodecane (t_R = 11.21 min) as an internal standard.

Size exclusion chromatography (SEC) measurements were performed in DMF on an Agilent 1100 Series chromatograph from Agilent Technologies, Inc. The HEMA column set has a 300/100/40 Å porosity, and the samples were detected by RI and UV detectors (254 nm). *N,N*-Dimethylformamide with 1 g mL^{-1} lithium bromide at 50 $^\circ\text{C}$ served as the mobile phase with a flow rate of 1 mL min^{-1} . Toluene (1 $\mu\text{L mL}^{-1}$) was used as an internal reference. For calibration, PMMA standards from Polymer Standard Service GmbH were used.

Differential scanning calorimetry (DSC) measurements were carried out using a DSC 250 instrument (TA Instruments) equipped with an RCS 90 cooling unit. The system was calibrated with indium and *n*-octane as standard reference materials. $\approx 4\text{--}7$ mg of each polymer sample was weighed into an aluminum pan, which was then sealed. All measurements were performed under a constant nitrogen stream to prevent oxidative degradation. To eliminate any prior thermal history, samples were initially heated to 190 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C min}^{-1}$. Subsequently, DSC scans were conducted over a temperature range of -20 to 190 $^\circ\text{C}$ with a constant heating rate of 20 $^\circ\text{C min}^{-1}$. Each experiment included two heating cycles and one intermediate cooling cycle. The glass transition temperature (T_g) was determined from the second heating run, based on the inflection point of the corresponding heat capacity change.

Elemental analysis was performed by micro analytical laboratory Kolbe in Oberhausen, Germany.

Design of Experiments Software: Evaluation of the experiments and response optimization of the DoE experimental plan were performed using *Minitab* Statistical Software 22 (Minitab LLC).

General Electrolysis Procedure: (5 mL cell size, Optimized conditions) The polymer material PVC (100 mg, 1.6 mmol, 8 eq. (repeat unit)), the supporting electrolyte tetraethylammonium chloride (33.1 mg, 0.2 mmol, 1 eq, 0.05 M), dimethyl phthalate (38.8 mg, 0.2 mmol, 1 eq.) and 1,4-butanediol mono vinyl ether (23.2 mg, 25 μL , 0.2 mmol, 1 eq.) were transferred into the electrochemical cell (ElectraSyn® 5mL) and dissolved in *N,N*-dimethylacetamide (4 mL). The reaction mixture was stirred (500 RPM) for 15 min at room temperature using a Teflon-coated magnetic stir bar. The electrodes and the teflon cap were attached to the reaction vessel, and the electrolysis was started. ($Q = 8\text{ F}$, $j = 5\text{ mA cm}^{-2}$, alt. Polarity = 15 min (4 h^{-1}), electrode surface area $\approx 3.0\text{ cm}^2$). After the reaction was finished, the internal standard 1,10-dichlorodecane (50 μL) was added and stirred for 5 min. For yield/conversion determination, samples for gas chromatography were prepared. For polymer analysis, the solution was added dropwise into methanol (50 mL) to induce polymer precipitation. After centrifugation, the obtained polymer was redissolved in THF (3 mL) and precipitated again in methanol. After centrifugation, the polymer was dried *in vacuo* and obtained as an amorphous, colorless solid.

Isolation of 2-Chloromethyl-1,3-Dioxepane (3): After the electrolysis was finished, the reaction solution was added dropwise into methanol. The precipitated polymer was centrifuged, and the solution was transferred into a round bottom flask. Methanol was removed under reduced pressure. Lithium chloride solution (5%) was added to the residual mixture, and the aqueous solution was extracted with diethyl ether. The organic phase was extracted with 5% lithium chloride solution and dried with MgSO_4 . After filtration, the solvent was removed *in vacuo*, and obtained the product via distillation at 82 $^\circ\text{C}/22\text{ mbar}$. (Colorless liquid, isolated yield of 53%) $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298K): δ/ppm = 4.85 (td, $J = 5.2, 1.2\text{ Hz}$, 1H, O-CH-O), 3.95 (m, 2H, O-CH $_2$), 3.77 (m, 2H, O-CH $_2$), 3.47 (dd, $J = 5.3, 1.1\text{ Hz}$, 2H, Cl-CH $_2$), 1.71 (m, 4H, CH $_2$ -CH $_2$). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 298K): δ/ppm = 100.96 (O-CH-O), 66.76 (O-CH $_2$), 44.40 (CH-Cl), 29.32 (O-CH $_2$ -CH $_2$). GC-MS (Std. method, column: Rxi-5Sil MS): t_R = 5.67 min. GC (Std. method, column: ZB-5): t_R = 7.90 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

chlorine transfer, dechlorination reaction, DoE, electrolysis, PVC, recycling

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5 Zusammenfassung

In den vorliegenden Arbeiten konnte gezeigt werden, dass die elektrochemische Umwandlung von HCH (**3** und **4**), HBCD (**7**) sowie PVC zur Herstellung industrierelevanter Intermediate und Produkte genutzt werden kann. Die Ergebnisse belegen, dass das *e-shuttle*-Prinzip nicht auf das Lindan (**1**) beschränkt ist, sondern als generelle elektrochemische Strategie zum Upcycling persistenter Halogenverbindungen, von HCH und HBCD bis hin zu PVC, eingesetzt werden kann. Aufbauend auf dem zuvor nachgewiesenen Erfolg des *e-shuttle*-Ansatzes beim Upcycling von Lindan wurde die Methodik erfolgreich auf weitere Isomerengemische des HCH ausgeweitet. Ein entscheidender Faktor war dabei die Verwendung von Propylencarbonat als Lösungsmittel in Kombination mit polaren, elektronenreichen Doppelbindungen, wodurch die selektive Dechlorierung der verschiedenen HCH-Isomere zu Benzol (**2**) ermöglicht wurde. Die Elektrolyseparameter wurden mittels Design of Experiments (DoE) unter Verwendung von 10-Undecensäuremethylester (**14**) als Modellsubstrat optimiert. Polare Substrate wie Vinylacetat (**9**) und Allylalkohol (**21**) ermöglichten optimale Ausbeuten von 89% und 79% bei Raumtemperatur ohne Bildung chlorierter Benzole. In weiterführenden Untersuchungen wurde das Anwendungspotenzial dieser Substrate genutzt, um die Wiederverwendbarkeit der Graphitelektroden nachzuweisen. Die Aufarbeitung erfolgte durch Extraktion im Fall von 10-Undecensäuremethylester (**14**) sowie durch Destillation für Vinylacetat (**9**) und Allylalkohol (**21**), wobei beide Verfahren das Recycling der Elektrolytlösung durch Zugabe frischen Ausgangsmaterials ermöglichen. Im Rahmen dieser Arbeit wurde zudem eine wirtschaftliche Bewertung eines auf einen Jahresdurchsatz von 5000 Tonnen HCH skalierten Prozesses durchgeführt, um die großtechnische Machbarkeit des *e-shuttle*-Ansatzes zu evaluieren. Die Betriebskosten erwiesen sich dabei als wesentlicher Kostentreiber und machen etwa 90% der Netto-Umwandlungskosten aus. Sowohl bei den Betriebs- als auch bei den Investitionskosten wurde die elektrochemische Reaktionseinheit als Schlüsselement für weitere wirtschaftliche Optimierungen identifiziert. Dabei konnte das wirtschaftliche Potenzial für eine großtechnische Umsetzung nachgewiesen werden.

Unter Verwendung des *e-shuttle*-Konzepts konnten nicht nur offenkettige Dialkylacetale wie das Diethylacetal des Chloracetaldehyds (**13a**) in guten Ausbeuten

von bis zu 86% erhalten werden, sondern auch zyklische Acetale wie 2-Chlormethyl-1,3-dioxepan (**24**) mit einer Ausbeute von 79%. Mechanistische Untersuchungen zeigten, abweichend vom gängigen *e-shuttle*-Mechanismus, dass während der Reduktion von HCH lediglich die Hälfte der freigesetzten Chloridionen in die Reaktion mit Vinylethern übergeht, während der verbleibende Anteil zur Bildung aktiver Chlorspezies beiträgt, die ihrerseits die Vinylgruppe aktivieren. Darüber hinaus wurde eine geringfügige Wasserstoffentwicklung beobachtet, die plausibel auf eine konkurrierende kathodische Nebenreaktion zurückgeführt werden kann. Die Reaktion wurde erfolgreich von einem 0.218 g-HCH-Maßstab auf 21.8 g HCH hochskaliert, wobei die Elektrodenoberfläche um das 167-fache vergrößert wurde, was zu einer erheblichen Verkürzung der Elektrolysezeit sowie einer Steigerung der Produktionsrate führte. Für 2-Chlormethyl-1,3-dioxepan (**24**) wurden zudem Produktakkumulation von 3 Zyklen und Elektrolytwiederverwendung über mindestens 16 Zyklen nachgewiesen.

In einer weiteren Arbeit konnte die Darstellung zyklischer Acetale des Chloracetaldehyds erfolgreich auf die elektrochemische Dechlorierung von PVC übertragen werden. Dabei wurden hohe Acetalausbeuten sowie Entchlorungseffizienzen von bis zu 94% über mehrere Elektrolysezyklen erzielt. Der Prozess zeigte zudem eine ausgeprägte funktionelle Robustheit gegenüber verschiedenen PVC-Typen und realen Abfallströmen. Das resultierende Polymermaterial wies eine interne Plastifizierung infolge kovalenter Rekombination mit Phthalat-Weichmacherfragmenten auf, was einen vielversprechenden Ausgangspunkt für weiterführende Upcycling-Strategien darstellt.

Insgesamt etablieren die vorliegenden Arbeiten eine skalierbare und nachhaltige Methode zur Umwandlung von HCH, HBCD und PVC in wertvolle Plattformchemikalien. Durch die gezielte Überführung persistenter Abfallstoffe in nutzbare Ressourcen eröffnen sie einen vielversprechenden Weg zur Minderung der Umweltauswirkungen einst unkontrolliert entsorgter Halogenverbindungen.

6 Ausblick

Im Rahmen dieser Arbeit wurden ausgewählte Substanzklassen hinsichtlich ihrer Eignung für das elektrochemische Upcycling von HCH, HBCD und PVC auf Basis des *e-shuttle*-Prinzips untersucht. Weitere Substanzklassen und Anwendungsgebiete chlorierter sowie bromierter Verbindungen bleiben dabei noch unerschlossen. So sind beispielsweise analog zu den α -Halogenaldehyden auch α -Halogenketone (**26**) über den elektrochemischen Weg zugänglich (Abbildung 16, I).^[272,273] Darüber hinaus könnte der elektrochemische Reaktionspfad alternativ genutzt werden, um aus allylischen Verbindungen monohalogenierte Vinylverbindungen (**27**) darzustellen, die auf konventionellem Weg vorwiegend über die MOFFATT-SWERN-Oxidation zugänglich sind (II).^[274]

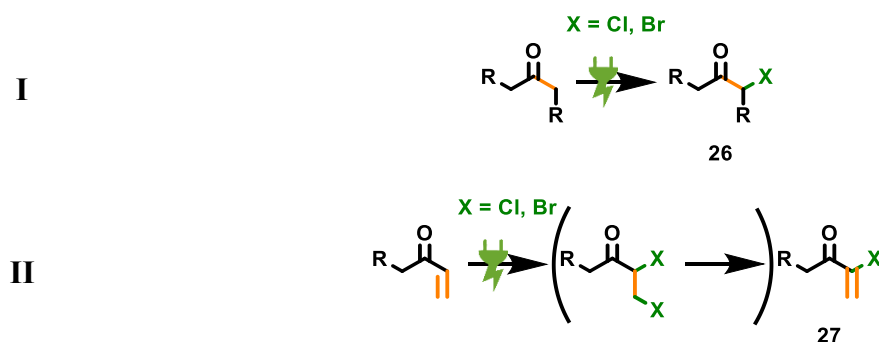


Abbildung 16: Elektrochemische Darstellung von α -Chlorketonen (I) und monohalogenierte Vinylverbindungen (II).

Im Rahmen der Untersuchungen zur Darstellung zyklischer Acetale des Chloracetaldehyds wurde als Nebenreaktion die Bildung von 2-Halogenethylacetat (**29**) aus 2-Methyl-1,3-dioxan (**28**) beobachtet,^[266] welches je nach Reaktionsbedingungen sogar quantitativ erhalten werden konnte. Obwohl diese Reaktion im ursprünglichen Prozesskontext unerwünscht war, eröffnet sie eine interessante Perspektive: Durch gezielte Anpassung der Reaktionsbedingungen könnte die selektive Darstellung monochlorierter Ester als eigenständiger Synthesepfad etabliert werden, der unter anderem in der Polymerchemie als Etherbaustein zur Synthese von Monomeren Anwendung finden könnte (Abbildung 17, III).^[275]

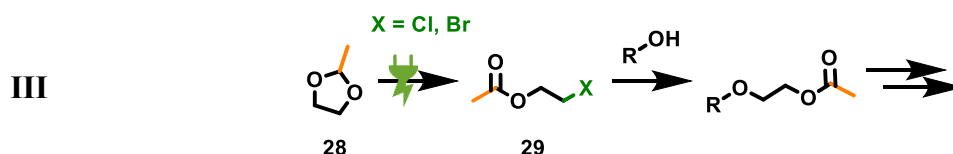


Abbildung 17: Elektrochemische Darstellung und Anwendung von 2-Chlorethylacetat (III).^[275]

Neben diesen substratbezogenen Erweiterungen bleibt auch die Untersuchung weiterer polyhalogener Abfallverbindungen als potenzielle Halogendonoren ein vielversprechendes Forschungsfeld. Die Übertragbarkeit des *e-shuttle*-Konzepts auf weitere persistente halogenorganische Verbindungen könnte den Anwendungsbereich des Verfahrens erheblich erweitern und zur Entwicklung einer generellen Plattformstrategie für das elektrochemische Recycling halogener Altlasten beitragen.

Ein weiterer offener Aspekt betrifft die mechanistische Rolle des Mangan-Katalysators. Die Beobachtung, dass unter bestimmten Bedingungen auf den Katalysator verzichtet werden kann, deutet auf einen überwiegend ionischen Reaktionspfad hin. Eine systematische Untersuchung des Wechselspiels zwischen ionischem und radikalischem Mechanismus in Abhängigkeit vom jeweiligen Substrat und den Reaktionsbedingungen könnte nicht nur das mechanistische Verständnis vertiefen, sondern auch gezielte Prozessoptimierungen hinsichtlich Selektivität und Katalysatoreinsatz ermöglichen.

Neben der Erschließung weiterer Substanzklassen gilt es, die Weiterentwicklung des Zelldesigns für den *e-shuttle*-Ansatz voranzutreiben, insbesondere im Hinblick auf Topfzellen- und Flusszellenkonfigurationen. Bei der Skalierung der gestaffelten Topfzelle zeigte sich mit zunehmender Elektrodenfläche und entsprechend steigender Stromstärke eine erhöhte Wärmeentwicklung. Die Grenzen der weiteren Skalierung sollten daher systematisch ermittelt werden, um geeignete Kompensationsstrategien wie *numbering up* oder weitere Anpassungen des Zelldesigns gezielt in Betracht ziehen zu können. Mit den bisher eingesetzten Flusszellen konnten keine mit der gestaffelten Topfzelle vergleichbaren Ergebnisse erzielt werden. Reaktionen wie die Darstellung der Acetale des Chloracetaldehyds erwiesen sich als abhängig von turbulenten Strömungsprofilen, vergleichbar mit hohen Rührgeschwindigkeiten in der Topfzelle, die mit dem bisherigen Flusszellendesign und den eingesetzten Pumpen nicht realisiert werden konnten. Die Entwicklung geeigneter Flusszellenkonfigurationen

stellt daher eine wesentliche Voraussetzung für die großtechnische Umsetzung des *e-shuttle*-Prozesses dar.

Schließlich sollte der Einfluss realer HCH-Deponieproben mit variablen Isomerenverhältnissen auf die Prozessstabilität eingehender untersucht werden. Während in den vorliegenden Arbeiten überwiegend aufgereinigtes HCH eingesetzt wurde, weisen reale Deponieproben schwankende Zusammensetzungen sowie potenzielle Verunreinigungen auf. Die Bewertung der Robustheit des *e-shuttle*-Prozesses gegenüber solchen Variationen stellt eine wesentliche Voraussetzung für die großtechnische Anwendung unter realen Bedingungen dar und schließt damit den Bogen von der grundlegenden Prozessentwicklung hin zur praktischen Implementierung.

7 Publikationen

- S. Horsinka,[‡] **D. Weis**,[‡] T. Langner, P. Beeskow, J. Sauer, S. R. Waldvogel, „From technical HCH residues to industrial relevant vicinal dichlorinated compounds: Electrochemical chlorine transfer as a strategy for waste valorisation“ *J. Hazard. Mat.* **2026**, 508, 141851. DOI: 10.1016/j.jhazmat.2026.141851.
- **D. Weis**,[‡] S. Horsinka,[‡] R. Bhattacharya,[‡] T. Langner, S. R. Waldvogel, “From Polyhalo-organic and Persistent Waste to Acetals: An Electrochemical Transfer Approach” *ACS Electrochem.* **2026**, 2, 529–540. DOI: 10.1021/acselectrochem.5c00498.
- S. Becker, D. Wördehoff, **D. Weis**, S. Horsinka, S. R. Waldvogel, P. Besenius, “Electrochemical Chlorine Shuttle from PVC Waste to Vinyl Ether Acceptors for the Synthesis of Biodegradable Polyester Precursors” *Adv. Mater.* **2025**, e17489. DOI: 10.1002/adma.202517489.

[‡]Diese Autoren haben gleichermaßen zu dem Manuskript beigetragen.

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9 Anhang

9.1 Abkürzungsverzeichnis

A	Ampere
ACC	jährliche Kapitalkosten (<i>annual capital costs</i>)
AS	Akzeptorsubstrat
BDD	Bor-dotierter Diamant
c	Konzentration
CCD	Wirkungsflächenversuchsplan (<i>central composite design</i>)
CE	Ausrüstungskosten (cost of equipment)
CEPCI	Kostenindex für chemische Anlagen (<i>chemical engineering plant cost index</i>)
CEX	Investitionsausgaben (capital expenses)
CF	Geldfluss (<i>cashflow</i>)
Coef	Koeffizient
COSY	Korrelationsspektroskopie (<i>correlation spectroscopy</i>)
CR	Umsatzrate (<i>conversion rate</i>)
Cref	Referenzkosten (<i>reference cost</i>)
CV	Cyclovoltammetrie
DE	Skalierungsziel
DEHP	Diethylhexylphthalat
DoE	statistische Versuchsplanung (<i>design of experiments</i>)
DMA	N,N-Dimethylacetamid
DMP	Dimethylphthalat
dPVC	defunktionalisiertes PVC
Dref	Dimension der Referenz (<i>dimension of the reference</i>)
DSA	formstabile Anode (<i>dimensionally stable anode</i>)
DSC	dynamische Differenzkalorimetrie (<i>differential scanning calorimetry</i>)
Et	Ethyl
Eq.	Äquivalent (<i>equivalent</i>)
ESI	Elektrosprayionisation
F	Faraday
FE	Faraday-Effizienz

FcH	Ferrocen
FID	Flammenionisationsdetektor (<i>flame ionization detector</i>)
GC	Glaskohlenstoff (<i>glassy carbon</i>)
GC (SI)	Gaschromatographie
HBCD	Hexabromcyclododecan
HCH	Hexachlorcyclohexan
HMBC	heteronukleare Mehrfachbindungskorrelation (<i>heteronuclear multiple bond correlation</i>)
HRMS	Hochauflösende Massenspektrometrie (<i>high resolution mass spectrometry</i>)
HSQC	heteronukleare Einzelquanten-Kohärenz (<i>heteronuclear single quantum coherence</i>)
IC	Ionenaustauschchromatographie
IR	Zinssatz (<i>interest rate</i>)
j	Stromdichte
k	Geschwindigkeitskonstante
LF	Lang-Faktor (<i>lang factor</i>)
M	Stoffmengenkonzentration/Molarität
L	Liter
Mol	Mol
MS	Massenspektrometrie
NCC	Netto-Konversionskosten (<i>net conversion cost</i>)
NMR	Kernspinresonanz (<i>nuclear magnetic resonance</i>)
OE _{dir}	direkte Betriebskosten (<i>direct operational expenses</i>)
OE _{disp}	Entsorgungskosten (<i>disposal expenses</i>)
OTP	Betriebsdauer der Anlage (<i>operating lifetime of the plant</i>)
PC	Propylencarbonat
PCL	Polycaprolactone
PE	Polyethylen
PCB	Polychlorierte Biphenyle
PMMA	Polymethylmethacrylat
POP	Persistente organische Schadstoffe (<i>persistent organic pollutants</i>)
ppm	Anteile pro Million (<i>parts per million</i>)
PR	Produktionsrate (<i>production rate</i>)

PS	Polystyrol
P_{tu}	Elektrische Leistung (<i>electrical power</i>)
PVC	Polyvinylchlorid
Q	Ladungsmenge
REV	Einnahmen (<i>revenue</i>)
rpm	Umdrehungen pro Minute (<i>revolutions per minute</i>)
RT	Zimmertemperatur
S	Skalierungsfaktor (<i>scaling factor</i>)
SE	Standardfehler (<i>standard error</i>)
SEC	Größenausschluss-Chromatographie (<i>size exclusion chromatography</i>)
SM	Ausgangsstoff (<i>starting material</i>)
T	Temperatur
TCE	Trichlorethen
TEACL	Tetratehylammoniumchlorid
T_g	Glasübergangstemperatur
TGA	thermogravimetrische Analyse (<i>thermogravimetric analysis</i>)
THF	Tetrahydrofuran
U	Spannung
V	Volt
wt. %	Gewichtsprozent (<i>weight percent</i>)
X	Umsatz
Y	Ausbeute (<i>yield</i>)

9.2 Supporting Informationen der Publikationen

Supplementary Information

From technical HCH residues to industrial relevant vicinal dichlorinated compounds: Electrochemical chlorine transfer as a strategy for waste valorisation

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1. General Information

General Information

If not stated otherwise, all reactions were performed at ambient conditions. **Chemicals** were of analytical quality and were purchased from common chemical suppliers without further purification, which are listed in supplementary (Table S1.1).

Table S1.1: Commercially available chemicals used with CAS registry number and their supplier.

Substance	CAS registry number	Supplier
α -Hexachlorocyclohexane, 98%	319-84-6	Sigma-Aldrich
β -Hexachlorocyclohexane, 98%	319-85-7	Sigma-Aldrich
γ -Hexachlorocyclohexane, 97%	58-89-9	Sigma-Aldrich
δ -Hexachlorocyclohexane, 98%	319-86-8	Sigma-Aldrich
Benzene, 99.5%	71-43-2	VWR
Chlorobenzene, $\geq 99.5\%$	108-90-7	Sigma-Aldrich
1,2-Dichlorobenzene, 98%	95-50-1	Sigma-Aldrich
1,3-Dichlorobenzene, 98%	541-73-1	Sigma-Aldrich
1,4-Dichlorobenzene, $>99\%$	106-46-7	Sigma-Aldrich
1,2,3-Trichlorobenzene, 99%	87-61-6	TCI
1,2,4-Trichlorobenzene, 99%	120-82-1	Acros Organics
1,3,5-Trichlorobenzene, 99%	108-70-3	Sigma-Aldrich
Acetonitrile, $\geq 99.9\%$	75-05-8	VWR Chemicals
Dimethyl sulfoxide, $\geq 99.7\%$	67-68-5	Sigma-Aldrich
Dimethyl acetamide, $\geq 99\%$	127-19-5	Carl Roth
Dimethyl formamide, $\geq 99.8\%$	68-12-2	VWR Chemicals
Ethylene carbonate, 99%	96-49-1	Sigma-Aldrich
Isobutyl acetate, $>99\%$	110-19-0	Merck Millipore
Isobutyronitrile, $>98\%$	78-82-0	TCI
Propylene carbonate, $\geq 99.7\%$	108-32-7	Carl Roth
<i>n</i> -Pentane, $\geq 99\%$	109-66-0	Fisher Scientific
<i>N</i> -Methyl-2-pyrrolidone, 99.5%	872-50-4	Acros Organics
1,3-Dichloro-2-propanol, 98%	96-23-1	TCI
1-Dodecene, 93–95%	112-41-4	Acros Organics
2,3-Dichloro-1-propanol, 98%	616-23-9	TCI
Allyl alcohol, 99%	107-18-6	Thermo Scientific
Methyl 10-undecenoate, $>96\%$	111-81-9	TCI
Vinyl acetate, 99%	108-05-4	Sigma Aldrich
Mesitylene, 98%	108-67-8	Sigma Aldrich
1-Ethyl-3-methylimidazolium chloride	65039-09-0	Sigma-Aldrich
Benzyltriethylammonium chloride, 98%	56-37-1	Acros Organics
Benzyltrimethylammonium chloride	56-93-9	TCI
Tetrabutylammonium acetate	10534-59-5	Sigma-Aldrich
Tetrabutylammonium chloride hydrate, 96%	37451-68-6	Thermo Scientific
Tetrabutylammonium chloride, $>98\%$	1112-67-0	TCI
Tetrabutylammonium tetrafluoroborate, 98%	429-42-5	abcr GmbH
Tetraethylammonium chloride	56-34-8	Alfa Aesar
Tetraethylammonium tetrafluoroborate, 99%	429-06-1	Acros Organics
Tetraethylammonium trifluoromethanesulfonate, 98%	35895-69-3	Merck Millipore
Tetramethylammonium chloride	75-57-0	Sigma-Aldrich
Tetramethylammonium hexafluorophosphate	558-32-7	Strem Chemicals
Tetramethylammonium tetrafluoroborate	661-36-9	Sigma-Aldrich
Triethylmethylammonium chloride, 98%	10052-47-8	abcr
Chromium(II) chloride, 99.9%	10049-05-5	Sigma-Aldrich
Chromium(III) chloride	10025-73-7	Merck Millipore
Cobalt(II) acetate tetrahydrate, $\geq 98\%$	6147-53-1	Sigma-Aldrich
Cobalt(II) chloride	7646-79-9	Sigma-Aldrich
Copper(II) acetate hydrate	6046-93-1	Riedel-de-Haën
Copper(II) chloride	7447-39-4	Sigma-Aldrich
Iron(II) chloride tetrahydrate, 98%	13478-10-9	Thermo Scientific
Manganese(II) acetate tetrahydrate, 99+%	6156-78-1	Sigma-Aldrich
Manganese(II) chloride tetrahydrate, $\geq 99\%$	13446-34-9	Sigma-Aldrich
Manganese(II) trifluoromethanesulfonate	55120-76-8	Sigma-Aldrich
Nickel(II) acetate tetrahydrate	6018-89-9	Merck Millipore
Nickel(II) chloride hexahydrate	7791-20-0	Merck

1.1 Instruments and Analytical Methods

Gas chromatography (GC):

Analysis of crude reaction mixtures and purified products was performed using a GC-2025 (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) and a quartz capillary column HI-5MS (Avantor VWR, Radnor, USA) with following specification: length of 30 m, inner diameter of 0.25 mm and a stationary phase ((5%-phenyl)-dimethylsiloxane) of 0.25 μm thickness. Hydrogen was used as carrier gas with constant velocity: 42.0 $\text{cm}\cdot\text{s}^{-1}$, total flow: 43.3 $\text{mL}\cdot\text{min}^{-1}$, column flow: 1.55 $\text{mL}\cdot\text{min}^{-1}$, purge flow: 3.0 $\text{mL}\cdot\text{min}^{-1}$, split ratio: 25.0. Measurements were performed at an injector temperature of 280 °C and a detector temperature of 280 °C.

GC-Methods:

Method „super-soft“: Starting temperature: 30 °C for 2 min, 1st heating rate: 2.5 °C $\cdot\text{min}^{-1}$ up to 60 °C, 2nd heating rate: 15 °C $\cdot\text{min}^{-1}$ up to 290°C holding for 5 min.

Method “Performance DWE-SHS”: Starting temperature: 40 °C for 6 min, 1st heating rate: 30.0 °C $\cdot\text{min}^{-1}$ up to 90 °C, 2nd heating rate: 10 °C $\cdot\text{min}^{-1}$ up to 205°C, 3rd heating rate: 50 °C $\cdot\text{min}^{-1}$ up to 285 °C.

Gas Chromatography coupled with Mass Spectrometry (GC/MS):

For GC sample preparation a column filtration was performed over silica gel 60 M (0.040–0.063 mm, Macherey-Nagel GmbH & Co. KG, Düren, Germany). Analysis of crude reaction mixtures and purified products were performed using a GCMS QP2010SE (Shimadzu, Kyoto, Japan) equipped with an electron ionization (EI) source and a quadrupole mass analyser. A quartz capillary column HI-5MS (Avantor VWR, Radnor, USA) with the following specification was used: length of 30 m, inner diameter of 0.25 mm and a stationary phase ((5%-phenyl)- dimethylsiloxane) of 0.25 μm thickness. Helium was used as carrier gas with a constant velocity of 30 $\text{cm}\cdot\text{s}^{-1}$. The GC temperature ramp started at 50 °C (holding for 1 min) and heating to 300 °C (holding for 4.71 min) with a temperature ramp of 17.5 °C $\cdot\text{min}^{-1}$ (method: 2_medium, total program time: 20.0 min). Measurements were performed at an injector temperature of 270 °C and a temperature of the EI source of 250 °C.

Nuclear Magnetic Resonance (NMR) Spectroscopy:

Nuclear magnetic resonance experiments were performed using a nuclear magnetic resonance spectrometer Avance II 400 (Bruker, Karlsruhe, Germany) for ^1H NMR (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) analysis. The spectra were recorded at 25 °C using deuterated solvents. To normalize the spectra obtained, reference was made to the existing solvent signal of non-deuterated fractions according to the data provided by Gottlieb et al.: [11] CDCl_3 (^1H NMR: δ = 7.26 ppm, ^{13}C NMR: δ = 77.16 ppm). Besides ^1H and ^{13}C NMR experiments, the 2D techniques ^1H , ^1H -COSY, ^1H , ^{13}C -HSQC and ^1H , ^{13}C -HMBC were used to assist the assignment of the signals. The following abbreviations were used to describe the signals: s (singlet), brs (broad singlet), d (doublet), brd (broad doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dddd (doublet of doublets of doublets of doublets), dt (doublet of triplets), t (triplet), td (triplet of doublets), q

(quartet), sept (septet), septd (septet of doublets), m (multiplet). The spectra obtained were evaluated with MestReNova 14 (*Mestrelab Research S.L.*, Spain).

1.2 Electrochemical Setup

Power source & stirrer

For electrochemical reactions a HMP4040 Programmable Power Supply 384 W (*Rohde & Schwarz GmbH & Co. KG*, München, Germany) and a MR Hei-Tec magnetic stirrer (*Heidolph Instruments GmbH & Co. KG*, Kelkheim, Germany) were used.

Screening and small-scale batch reactions

For the screening and optimizations reactions a 5 mL vial with stirring bars in each cell during electrolysis were used, as shown in supplementary figure 1.1 (Figure S1.1). The electrolysis set-up is commercially available as IKA Screening System Package (*IKA®-Werke GmbH & Co. KG*, Staufen, Germany). The lids were manufactured by the in-house workshop, as the materials of the original lids (stainless steel) cannot tolerate the corrosive conditions.



Figure S1.1: 5 mL glass vial from IKA.^[2]



Figure S1.2: 5 mL glass vial with a stirring bar, various lids for different electrode types and isostatic graphite electrodes attached to titanium contacts.

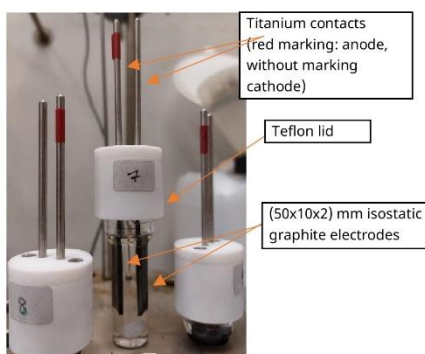


Figure S1.3: Filled 5 mL glass vial with Teflon lid, two (50 x 10 x 2) mm isostatic graphite electrodes and titanium contacts.

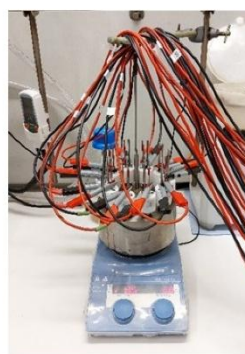


Figure S1.4: Screening Setup with 5 mL glass vials.



Figure S1.5: Cross-section of a Teflon lid for (50x 10 x 2) mm electrodes.

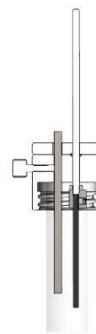


Figure S1.6: Cross-section of a Teflon lid for (70 x 10 x 2) mm (left) and for (50 x 10 x 2) mm (right) electrodes.



Figure S1.7: Cross-section of a Teflon lid for two (70 x 10 x 2) mm electrodes.

The screening was carried out using various electrode materials (70 × 10 × 3) mm. Graphite electrodes (50 × 10 × 2) mm were sanded using 1000 grit sandpaper and cleaned with acetonitrile prior to use^[3] BDD electrodes were electrochemically treated ($j = 50 \text{ mA} \cdot \text{cm}^{-2}$) in 20% (v/v) sulfuric acid for 10 min before use. SIGRAFLEX™ electrodes (70 mm × 10 mm × 0.2) mm were pre-treated in the corresponding solvent for at least 1 h prior to use. The electrodes were immersed 3.5 cm into the electrolyte. This resulted in a geometric active anode respectively cathode area of 3.5 cm^2 used for electrolysis.

Electrode materials

Table S1.2: Electrode materials, purity, and their supplier.

Anode or cathode	Specification	Supplier
Isostatic graphite	SIGRAFINE™, highly isostatic, V2100	SGL Carbon, Bonn, Germany
Boron-doped diamond (BDD)	DIACHEM™, 15 µm boron-doped diamond layer on silicon	CONDIAS GmbH, Itzehoe, Germany
Glassy carbon	SIGRADUR® G	HTW Hochtemperatur Werkstoffe GmbH, Thierhaupten, Germany
Graphite foil	SIGRAFLEX™, F02012Z	SGL Carbon, Meitingen, Germany
Ti, V, Ni, Zr, Nb, Mo, Ag, Ta, W, Pb and CuSn7Pb15	>99% of the metal	various suppliers

Recyclability tests

The electrolysis set-up was also made by the in-house workshop, based on the dimensions of the 5 mL IKA glass cell. A geometric factor of 2.3 was used to scale up the glass cell to 50 mL, whereby the distance between the electrodes remains constant at 5 mm.



Figure S1.8: Cross-section of a NS34 Teflon lid for two (120 x 23 x 3) mm electrodes.



Figure S1.11: 50 mL glass vial with (120 x 23 x 3) mm isostatic graphite electrodes.

Process Development

The electrolysis set-up was also made by the in-house workshop, based on the dimensions of the 5 mL IKA glass cell. A geometric factor of 2.3 for the already scaled up 50 mL cell was used to scale up the glass cell to 500 mL, whereby the distance between the electrodes remains constant at 5 mm.



Figure S1.12: Cross-section of a NS71 Teflon lid for two (225 x 58 x 3) mm electrodes.



Figure S1.13: 500 mL glass vial with (225 x 58 x 3) mm isostatic graphite electrodes.

Used Equations

The amount of charge applied Q in coulombs for example $n = 0.5$ mmol substrate and number of electrons used $z = 10.1$ and the Faraday constant ($F = 96485.332 \text{ C} \cdot \text{mol}^{-1}$) is calculated as follows:

$$Q = n \times z \times F = 0.5 \text{ mmol} \times 10.1 \times 96485.332 \text{ C} \cdot \text{mol}^{-1} = 487.3 \text{ C} = 487.3 \text{ As}$$

The current I applied for electrolysis is calculated from the product of the current density j and the area of the anode respectively cathode A_E , which depends on the width W_E and immersion depth of the electrode $L_{\text{I.D.E.}}$:

$$I = j \times A_E = j \times W_E \times L_{\text{I.D.E.}}$$

Thus, for example, with an immersion depth of 3.5 cm and an electrode width of 1 cm, and a current density of $30 \text{ mA} \cdot \text{cm}^{-2}$, the amount of applied charge is as follows:

$$I = 30 \text{ mA} \cdot \text{cm}^{-2} \times 1 \text{ cm} \times 3.5 \text{ cm} = 105 \text{ mA}$$

If the electrolysis takes place under galvanostatic conditions, the reaction time t of the electrolysis can be determined from the quotient of the amount of applied charge Q and the applied current I :

$$t = \frac{Q}{I} = \frac{487.3 \text{ As}}{0.105 \text{ A}} = 4\,640.95 \text{ s} = 77.35 \text{ min}$$

To determine yields Y_i and conversions X_i via gas chromatography GC, calibration curves were determined for all substances. The ratio of the measured areas of the internal standard A_{IS} to use the substance A_i was plotted against the ratio of the known amount of substance of the internal standard n_{IS} to the used substance n_i . The slope for each substance m_i was determined by linear regression.

$$m_i = \frac{A_i/A_{IS}}{n_i/n_{IS}}$$

Yield and conversion are calculated from the ratio of the measured substance n_i to the quantity of the starting material at the beginning of electrolysis $n_{SM,0}$.

$$Y_i = \frac{n_i}{n_{SM,0}} \times 100\% = \left(\frac{A_i}{A_{IS}} \times \frac{n_{IS}}{m_i} \right) \times \frac{1}{n_{SM,0}} \times 100\%$$

$$X_i = \left(1 - \frac{n_i}{n_{SM,0}} \right) \times 100\% = \left(1 - \left(\frac{A_i}{A_{IS}} \times \frac{n_{IS}}{m_i} \right) \times \frac{1}{n_{SM,0}} \right) \times 100\%$$

Furthermore, the Faraday efficiency FE is determined, as more amount of charge is applied Q_{used} than is theoretically necessary Q_{theo} .

$$FE_i = Y_i \times X_i \times \frac{Q_{theo}}{Q_{used}} \times 100\%$$

To determine the rate constants k of the respective substances, a linearization of the 1st order kinetics is carried out according to unimolecular reactions.

$$1^{\text{st}} \text{ order kinetics: } c_i = c_{i,0} \times e^{-kQ}$$

The resulting slope m of the linear regression of the measured values through zero is plotted against the amount of applied charge Q . However, a distinction must be made between conversion X_i and yield Y_i :

$$y = m \times x = k \times Q$$

$$\text{For conversion } X_i: x_i = -\ln\left(\frac{c_i}{c_{i,0}}\right) = kQ$$

$$\text{For yield } Y_i: y_i = -\ln\left(1 - \frac{c_i}{c_{i,0}}\right) = kQ$$

2. Experimental Protocols

2.1 Extraction of technical Hexachlorocyclohexane (HCH, 1)

The HCH samples excavated from the ground at the Merck site (Gernsheim/Germany) must be separated from soil residues, stones, and other impurities before use. For this purpose, a Soxhlet extractor is used (Figure S2.1). The HCH is then dissolved in refluxing ethyl acetate and then filtered.

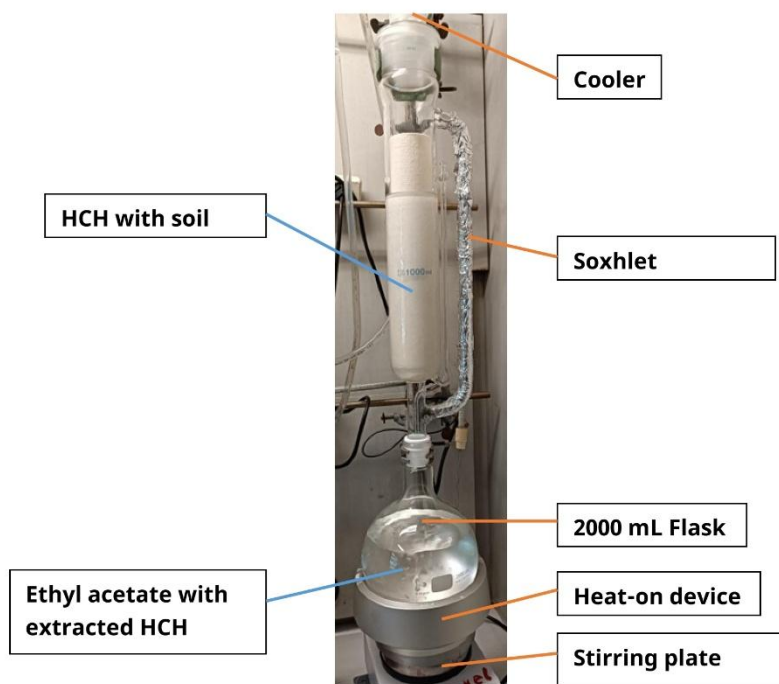


Figure S2.1: Soxhlet extractor for purification of the soil contaminated HCH.

Subsequently, the HCH is concentrated under reduced pressure and the precipitate then filtrated off. The solids are then washed with cold ethyl acetate and pre-dried by air suction. The pre-dried HCH is powdered and dried again in a high vacuum.

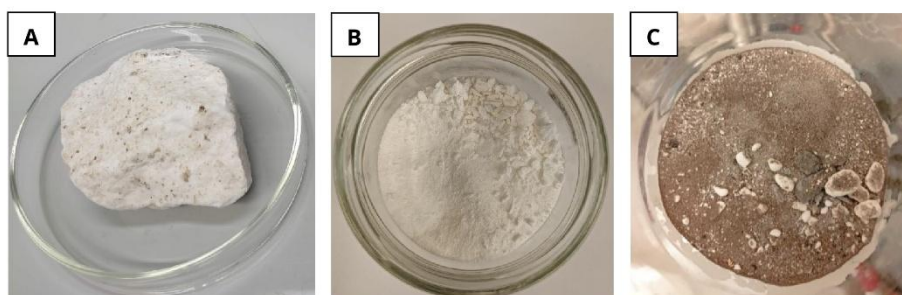
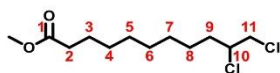


Figure S2.2: A: HCH contaminated with soil residues from seam 1 at Fluxum, Merck KGaA, Gernsheim, Germany. B: Pure recrystallized HCH. C: Soxhlet remains of the HCH upon extraction.

2.2 Synthesis of Methyl 10,11-dichloroundecanoate (**4**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) and methyl 10-undecenoate (**3**) (411.5 μ l, 362.9 mg, 1.83 mmol, 1.8 eq.) are dissolved in propylene carbonate (5 mL), tetraethylammonium chloride (82.8 mg, 0.5 mmol, 0.5 equiv.) and manganese(II) chloride tetrahydrate (4.9 mg, 0.025 mmol, 0.025 eq.) are added and the electrolyte is transferred into the 5 mL IKA glass cell (Figure S1.1). The electrolysis is started using isostatic graphite anode and cathode at a temperature $T = 75\text{ }^{\circ}\text{C}$, a current density $j = 30\text{ mA}\cdot\text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 105 mA is applied) and an amount of charge $Q = 4.7\text{ F}$ ($\cong 449.7\text{ C}$). After cooling the electrolyte solution, it is extracted with *n*-pentane (3 x 5 mL). The fractions are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product was purified in a distillation under reduced pressure ($1\cdot 10^{-3}$ mbar). In the first fraction, the starting material (**3**) is recovered at 90–100 $^{\circ}\text{C}$. The product (**4**) is obtained as a colorless viscous liquid in the second fraction at 130–135 $^{\circ}\text{C}$.



Yield: 50% (271 mg, 0.92 mmol)

Characterization:

GC (methode super-soft, column: HP-5): $t_{R,GC} = 24.9\text{ min}$

^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.08–3.97 (m, 1H, H-11), 3.76 (dd, $J = 11.3, 5.2\text{ Hz}$, 1H, H-10), 3.68–3.62 (m, 4H, H-11, OMe), 2.30 (t, $J = 7.5\text{ Hz}$, 2H, H-2), 2.03–1.92 (m, 1H, H-3), 1.76–1.65 (m, 1H, H-9), 1.63–1.58 (m, 2H, H-9), 1.46–1.33 (m, 2H, H-4), 1.34–1.26 (m, 8H, H-5, H-6, H-7, H-8).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 174.4 (C-1), 61.4 (C-10), 51.6 (OMe), 48.4 (C-11), 35.2 (C-9), 34.2 (C-2), 29.3 (C-6), 29.2 (C-5), 29.2 (C-7), 29.0 (C-4), 25.9 (C-8), 25.0 (C-3).

HRMS (ESI+): m/z for $\text{C}_{12}\text{H}_{22}^{35}\text{Cl}_2\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc: 291.0889; found: 291.0888.

2.3 Synthesis of 1,2-Dichlorododecane (6)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (145.4 mg, 0.5 mmol, 1.0 eq.) and 1-dodecene (**5**) (477.5 μL , 324.9 mg, 1.93 mmol, 3.9 eq.) are dissolved in acetonitrile (5 mL), tetraethylammonium chloride (82.8 mg, 0.5 mmol, 0.5 eq.) and manganese(II) chloride tetrahydrate (4.9 mg, 0.025 mmol, 0.025 eq.) are added and the electrolyte is transferred into the 5 mL IKA glass cell (Figure S1.1). The electrolysis is applied using isostatic graphite anode and cathode at a temperature $T = 50\text{ }^{\circ}\text{C}$, a current density $j = 10\text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 35 mA was applied) and a charge $Q = 10.1\text{ F}$ ($\triangleq 487.3\text{ C}$). After cooling the electrolyte solution, it is extracted with *n*-pentane (3 x 5 mL). The extracts are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product is purified in a distillation under reduced pressure ($1 \cdot 10^{-3}\text{ mbar}$). In the first fraction, the starting material (**5**) is recovered at 50–60 $^{\circ}\text{C}$. The product (**6**) is obtained as a colorless viscous liquid in the second fraction at 90–100 $^{\circ}\text{C}$.



Yield: 41% (189 mg, 0.79 mmol)

Characterization:

GC (methode super-soft, column: HP-5): $t_{R,GC} = 23.2\text{ min}$.

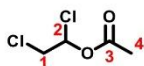
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.07–4.00 (m, 1H, H-1), 3.76 (dd, $J = 11.3, 5.2\text{ Hz}$, 1H, H-2), 3.65 (dd, $J = 11.3, 7.4\text{ Hz}$, 1H, H-1), 2.03–1.94 (m, 1H, H-3), 1.77–1.65 (m, 1H, H-3), 1.60 (m, 1H, H-4), 1.46–1.36 (m, 1H, H-4), 1.30–1.27 (m, 14H, H-5, H-6, H-7, H-8, H-9, H-10, H-11), 0.88 (t, $J = 6.6\text{ Hz}$, 3H, H-12).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 61.4 (C-1), 48.4 (C-2), 35.2 (C-3), 32.0 (C-10), 29.7 (C-6, C-7, C-8), 29.5 (C-9), 29.1 (C-5), 26.0 (C-4), 22.8 (C-11), 14.3 (C-12).

HRMS (ESI+): m/z for $\text{C}_{12}\text{H}_{24}^{35}\text{Cl}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc: 262.2132; found: 262.1595

2.4 Synthesis of 1,2-Dichloroethyl acetate (**8**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) and vinyl acetate (**7**) (276.5 μ l, 258.3 mg, 3.00 mmol, 3.0 eq.) are dissolved in propylene carbonate (5 mL), tetraethylammonium chloride (41.4 mg, 0.25 mmol, 0.25 eq.) and manganese(II) chloride tetrahydrate (30 mg, 0.15 mmol, 0.15 eq.) are added and the electrolyte is transferred into the 5 mL IKA glass cell (Figure S1.1). The electrolysis is applied using isostatic graphite anode and cathode at a temperature $T = 25\text{ }^{\circ}\text{C}$, a current density $j = 5\text{ mA}\cdot\text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 17.5 mA is applied) and a charge $Q = 7.2\text{ F}$ ($\approx 694.7\text{ C}$). The product is purified in a distillation under reduced pressure ($1\cdot 10^{-3}\text{ mbar}$). The product (**8**) is obtained as a colorless viscous liquid in the first fraction at $40\text{--}50\text{ }^{\circ}\text{C}$.



Yield: 87% (409.8 mg, 2.61 mmol)

Characterization:

GC (methode DWE-SHS Performance, column: HP-5): $t_{R,GC} = 7.5\text{ min}$.

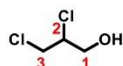
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 6.49 (dd, $J = 7.3, 4.5\text{ Hz}$, 1H, H-2), 3.85 (dd, $J = 4.2, 1.3\text{ Hz}$, 2H, H-1), 2.18 (s, 3H, H-4).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 168.4 (C-3), 80.8 (C-1), 45.9 (C-2), 20.8 (C-4).

HRMS (ESI+): m/z for $\text{C}_5\text{H}_9^{35}\text{Cl}_2\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc: 178.9643; found: 178.8825

2.5 Synthesis of 2,3-Dichloro-1-propanol (**10**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (3.635 g, 12.5 mmol, 1.0 equiv.) and allyl alcohol (**9**) (2.56 mL, 2.178 g, 37.5 mmol, 3.0 eq.) are dissolved in propylene carbonate (50 mL), tetraethylammonium chloride (414 g, 2.5 mmol, 2.5 eq.) and manganese(II) chloride tetrahydrate (49.5 mg, 0.25 mmol, 0.2 eq.) are added and the electrolyte is transferred into the 50 mL glass cell (Figure S1.8). The electrolysis is applied using isostatic graphite anode and cathode at a temperature $T = 25\text{ }^{\circ}\text{C}$, a current density $j = 11.7\text{ mA}\cdot\text{cm}^{-2}$ (since the electrodes have an immersion depth of 8.0 cm, 225.8 mA is applied) and a charge $Q = 6.5\text{ F}$ ($\triangleq 7839.4\text{ C}$). The product is purified in a distillation under reduced pressure ($1\cdot 10^{-3}\text{ mbar}$). The product (**10**) is obtained as a colorless viscous liquid in the first fraction at 50–70 $^{\circ}\text{C}$.



Yield: 79% (3.82 g, 29.6 mmol)

Characterization:

GC (methode DWE-SHS Performance, column: HP-5): $t_{R,GC} = 7.9\text{ min}$.

^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.21–4.12 (m, 1H, H-2), 3.96–3.92 (m, 2H, H-1, H-3), 3.85–3.75 (m, 2H, H-1, H-3), 2.17 (s, 1H, OH).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 63.5 (C-1), 61.4 (C-2), 44.1 (C-3).

HRMS (ESI+): m/z for $\text{C}_3\text{H}_5^{35}\text{Cl}_2\text{O}$ [M-]: calc: 126.9723; found: 126.9723.

3. Supplementary Results

3.1 External GC-Calibration with an Internal Standard for Yield Determination

For the yield determination via gas chromatography, an external calibration was carried out. Mesitylene (70 μ L, 60.5 mg for each measurement) was used for hexachlorocyclohexane HCH (**1**), benzene and dichlorinated products. For the linear regression, the molar ratio of the substance (S) to mesitylene (Std) was plotted against the resulting area ratio of the GC integration values. From the obtained linear regression equation, the molar amount of the substrate after the reaction can be determined. The statistical software Origin 2023 (OriginLab Corporation, Northampton, Massachusetts) was used for linear regression analysis. Mathematical calculations and linear regression analysis were performed using Excel® from Microsoft® 365 for Enterprise.

Preparation of the calibration solutions and the qualitative analysis:

The analyte is dissolved together with the internal standard in acetonitrile in different concentrations. Three drops from the solution are filtered over silica gel 60 M (approx. 500 mg) into a GC vial using acetonitrile as eluent.

The allyl alcohol as starting material for the synthesis of for 2,3-dichloro-1-propanol (**10**) could not be detected by the GC even at different concentrations, which is why it could not be calibrated.

For the qualitative determination of chlorinated benzenes (the side products of the dechlorination of HCH), commercially available substrates were first measured to determine the retention time (methode used: super-soft).

Compound	$t_{R,GC}$ Retention time / min
Benzene	2.908
Chlorobenzene	8.260
1,3-Dichlorobenzene	15.684
1,4-Dichlorobenzene	15.902
1,2-Dichlorobenzene	16.452
1,3,5-Trichlorobenzene	18.294
1,2,4-Trichlorobenzene	18.961
1,2,3-Trichlorobenzene	19.418

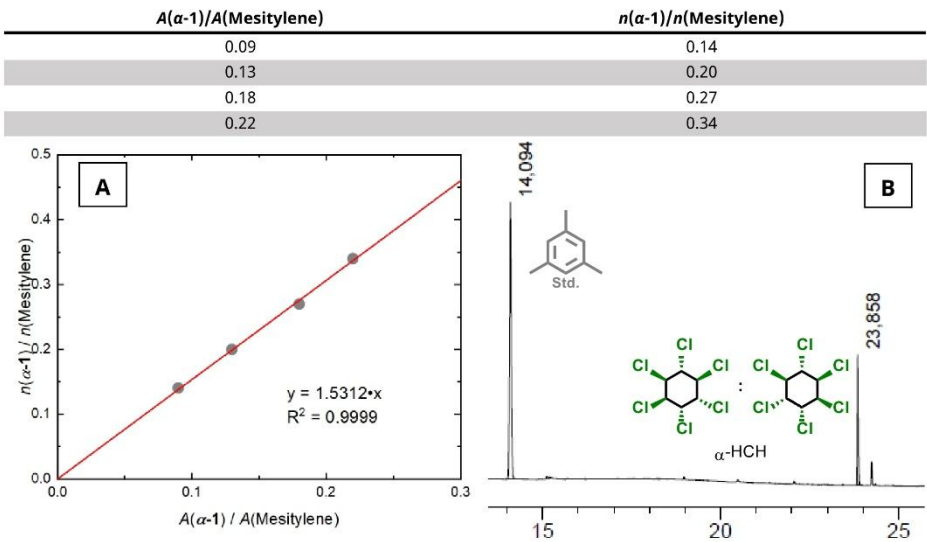


Figure S3.1: Data of the calibration measurements for α -hexachlorocyclohexane ($\alpha\text{-1}$). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of $\alpha\text{-HCH}$ ($\alpha\text{-1}$) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

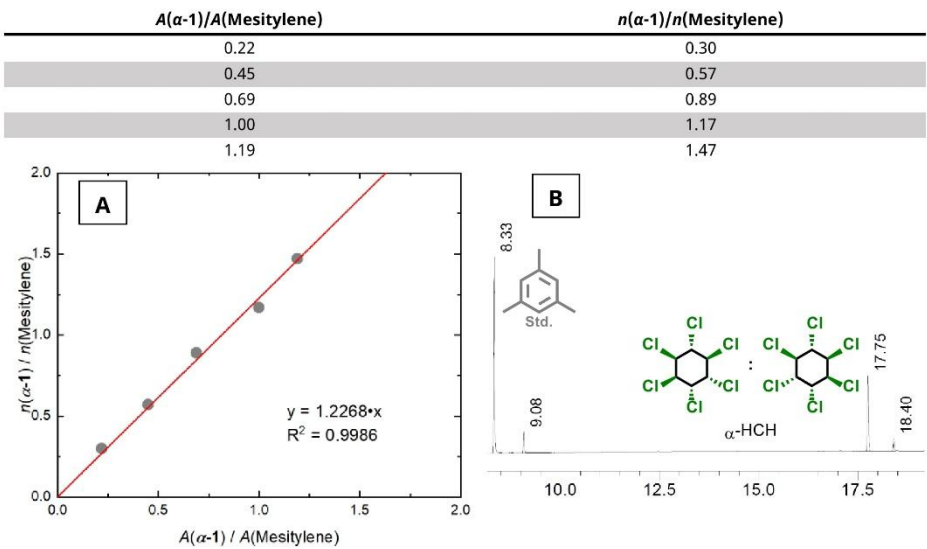


Figure S3.2: Data of the calibration measurements for α -hexachlorocyclohexane ($\alpha\text{-1}$). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of $\alpha\text{-HCH}$ ($\alpha\text{-1}$) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

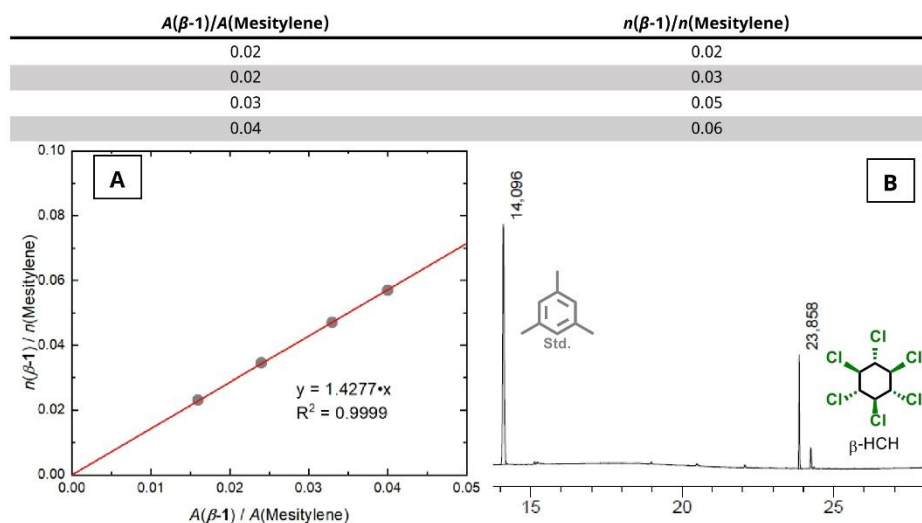


Figure S3.3: Data of the calibration measurements for β -hexachlorocyclohexane ($\beta\text{-1}$). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of $\beta\text{-HCH}$ ($\beta\text{-1}$) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

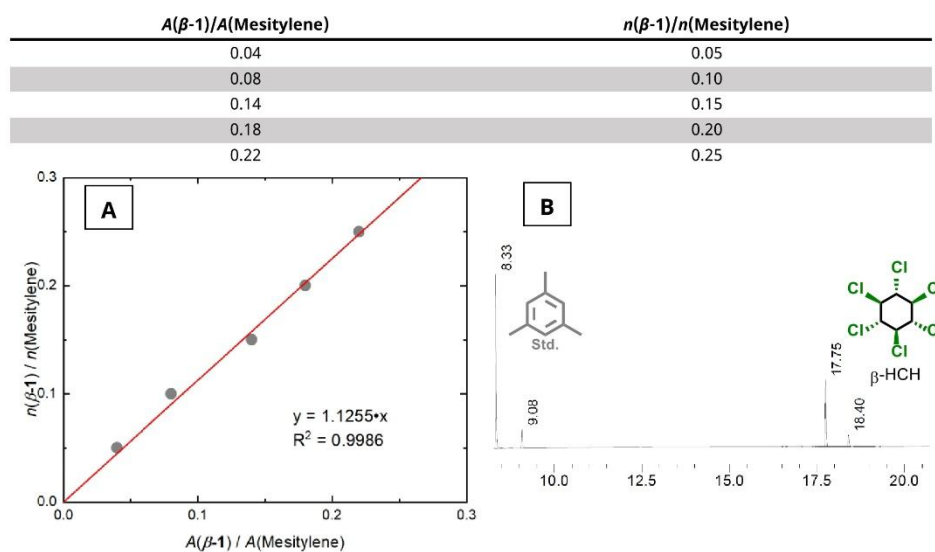


Figure S3.4: Data of the calibration measurements for β -hexachlorocyclohexane ($\beta\text{-1}$). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of $\beta\text{-HCH}$ ($\beta\text{-1}$) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

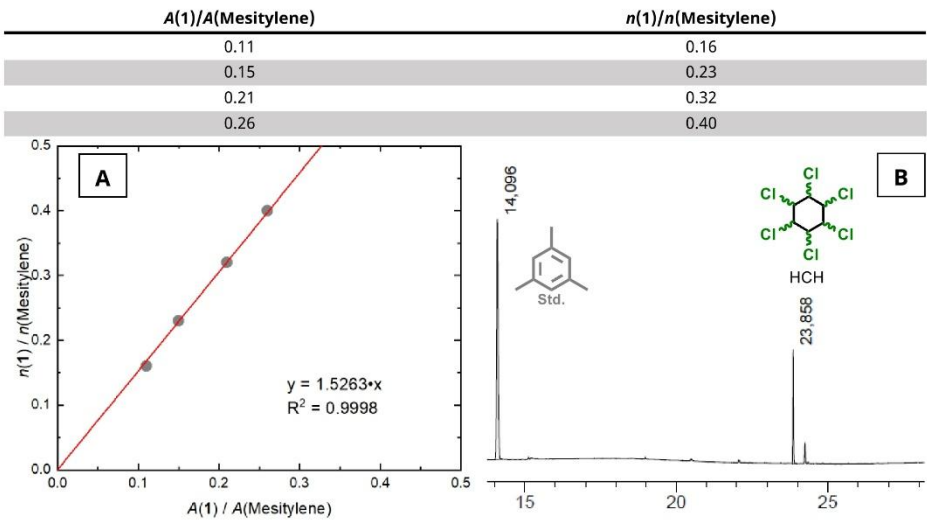


Figure S3.5: Data of the calibration measurements for *T*-hexachlorocyclohexane HCH (**1**) (α -HCH+ β -HCH). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of HCH (**1**) using 70 μ L of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

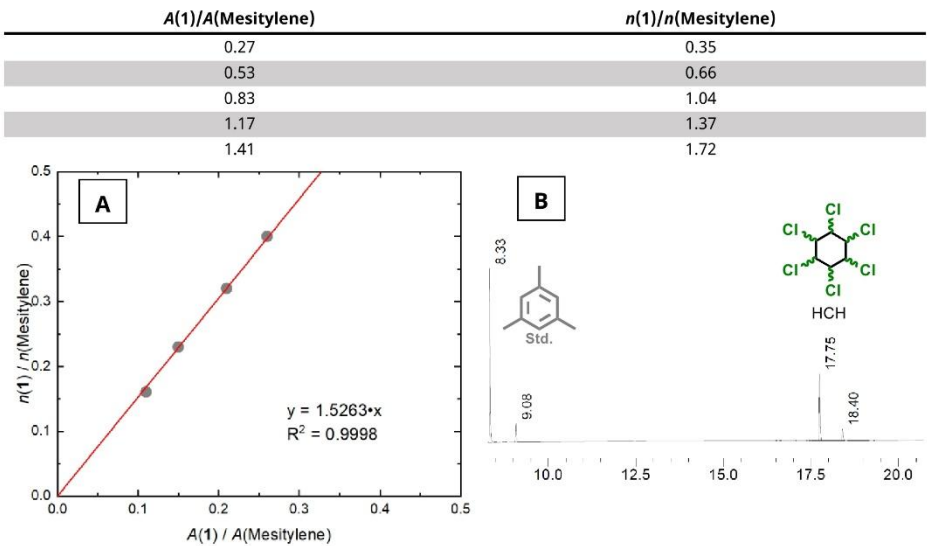


Figure S3.6: Data of the calibration measurements for *T*-hexachlorocyclohexane HCH (**1**) (α -HCH+ β -HCH). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of HCH (**1**) using 70 μ L of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

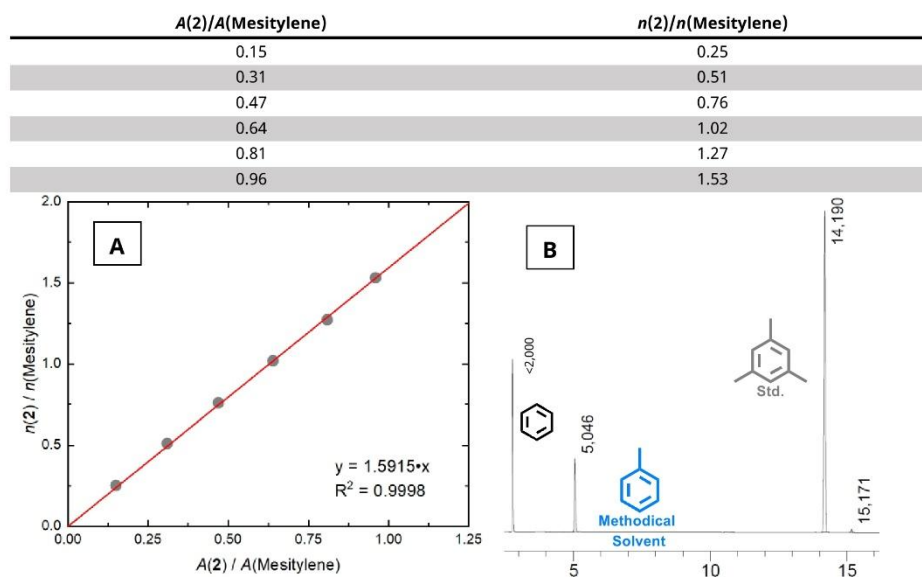


Figure S3.7: Data of the calibration measurements for benzene (**2**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of benzene (**2**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation. Methodical solvent is part of the rinsing process (method used: super-soft).

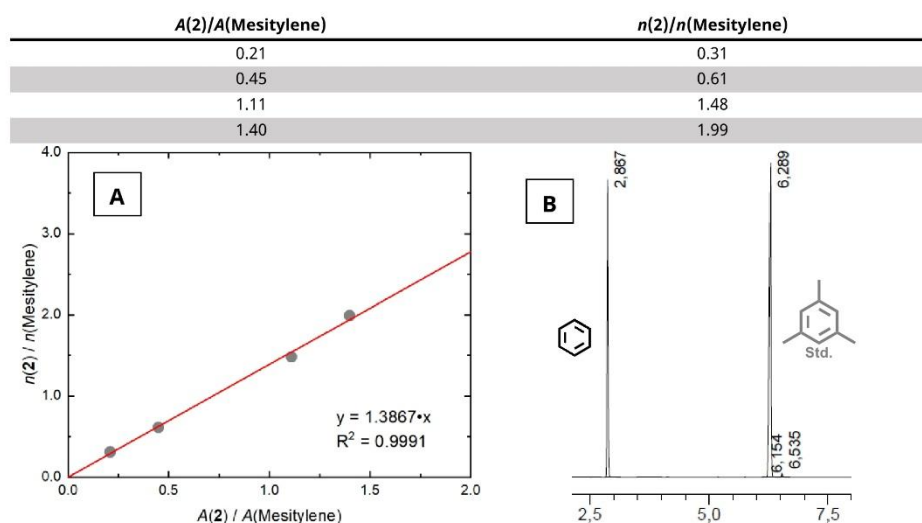


Figure S3.8: Data of the calibration measurements for benzene (**2**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of benzene (**2**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

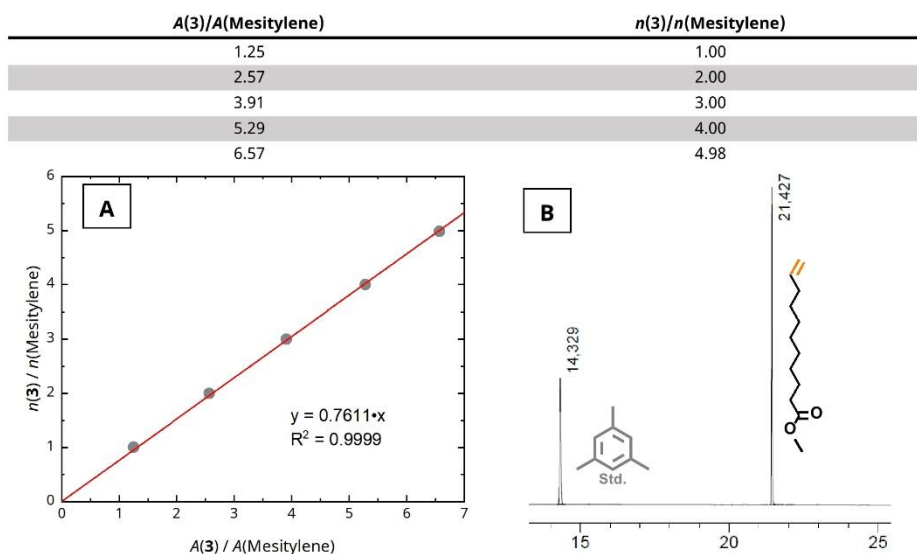


Figure S3.9: Data of the calibration measurements for methyl undecenoate (**3**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of methyl 10-undecenoate (**3**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

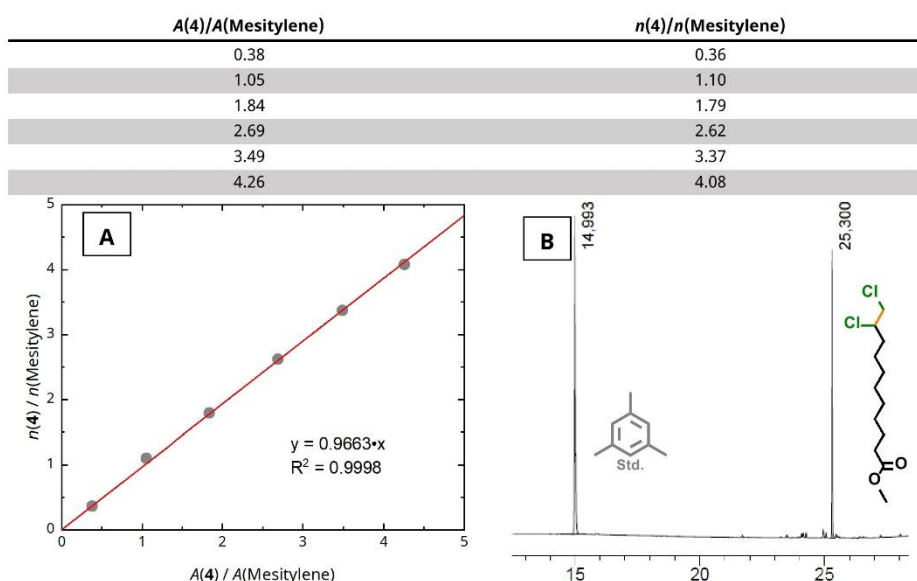


Figure S3.10: Data of the calibration measurements for 10,11-dichloromethyl undecanoate (**4**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of methyl 10,11-dichloroundecanoate (**4**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

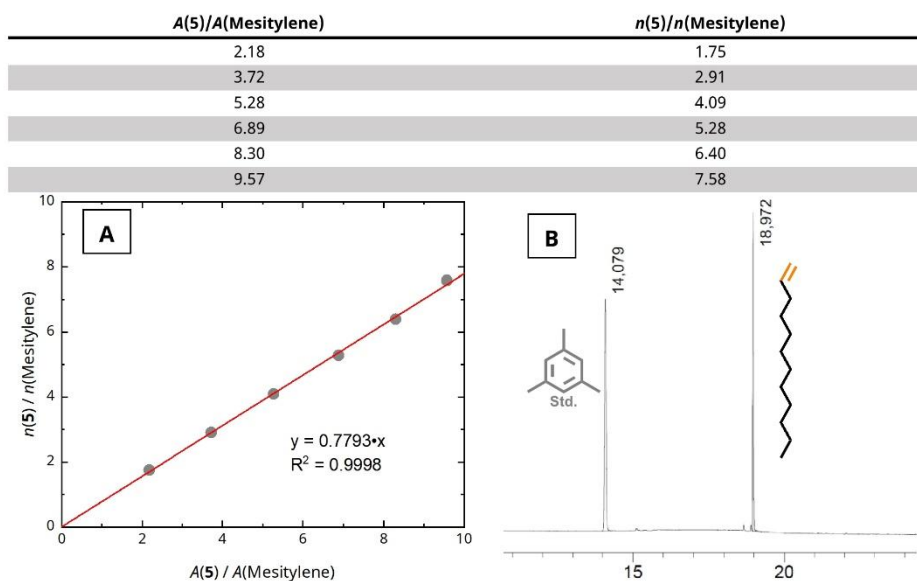


Figure S3.11: Data of the calibration measurements for 1-dodecene (**5**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 1-dodecene (**5**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

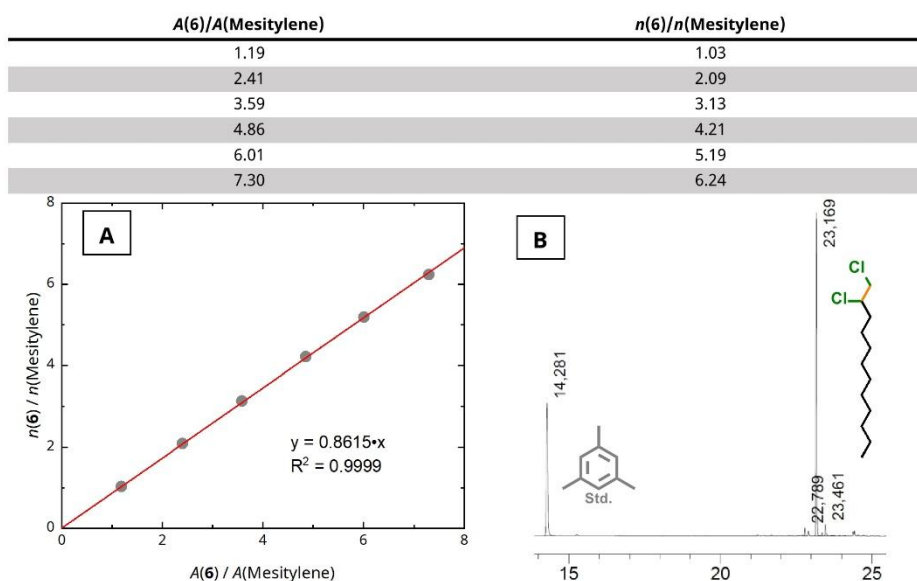


Figure S3.12: Data of the calibration measurements for 1,2-dichlorododecane (**6**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 1,2-dichlorododecane (**6**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: super-soft).

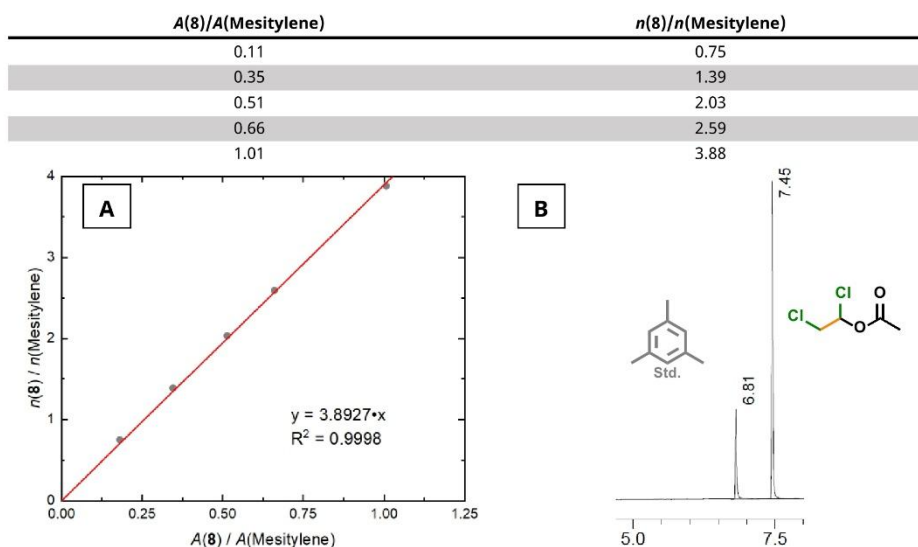


Figure S3.13: Data of the calibration measurements for 1,2-dichloroethyl acetate (**8**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 1,2-dichloroethyl acetate (**8**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

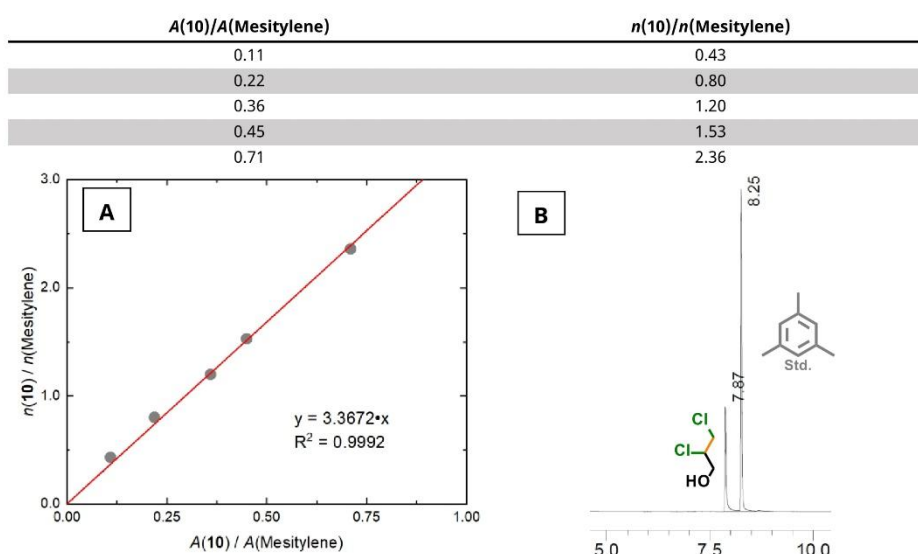
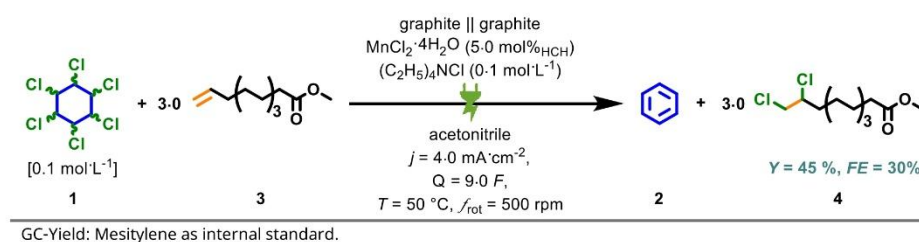


Figure S3.14: Data of the calibration measurements for 2,3-dichloro-1-propanol (**10**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2,3-dichloro-1-propanol (**10**) using 70 μL of mesitylene as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

3.2 Optimization of Reaction Conditions of Methyl 10,11-dichloro undecanoate (4)

Initially, the method developed by DONG AND ROECKL et al.^[4] was used for the chlorination of the methyl 10-undecenoate (3). It was modified so that HCH (1) is used instead of Lindane. For this purpose, HCH (145.5 mg, 0.5 mmol, 1.0 eq.) is added to methyl 10-undecenoate (337.2 μ L, 1.5 mmol, 3.0 eq.) in a 5 mL IKA-cell (as shown in Figure S1.2). Subsequently, tetraethylammonium chloride (41.4 mg, 0.5 mmol, 1.0 eq.), manganese(II) chloride tetrahydrate (4.9 mg, 0.025 mmol, 0.05 eq.) and acetonitrile (5 mL) are added. The solution is electrolyzed undivided at different electrodes galvanostatically at a temperature of 50 °C. A current density of $j = 4 \text{ mA} \cdot \text{cm}^{-2}$ (immersion depth of the electrodes is 3.5 cm, resulting in a current of 14 mA) and a current of 9 F (434.2 C, reaction time $t \approx 516.9 \text{ min}$) are used. This results in the following general reaction equation:



For the subsequent screening, the electrodes, solvent, supporting electrolyte and catalyst were varied and the optimum parameter was retained for further screening.

Table S3.1: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecenoate (**3**) of the electrode screening.

anode || cathode
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹)
 acetonitrile
 $j = 4.0 \text{ mA} \cdot \text{cm}^{-2}$
 $Q = 9.0 F$
 $T = 50 \text{ }^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$

Anode	Cathode	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Conversion $X(3) / \%$	Yield $Y(4) / \%$
Graphite	Graphite	72	21	>99	45
Graphite	BDD	86	0	92	37
BDD	Graphite	55	4	68	13
BDD	BDD	65	0	79	22
GC	GC	61	0	66	27
GC	Graphite	92	0	>99	25
Graphite	Graphite felt	92	33	95	32
Graphite	Graphite foil	68	41	94	38
Graphite	Ti	90	0	99	37
Graphite	V	94	0	>99	27
Graphite	Ni	74	8	>99	39
Graphite	Zr	82	32	99	42
Graphite	Nb	86	0	99	46
DSA (RuO ₂)	Graphite	90	0	>99	40
Graphite	Mo	>99	0	>99	27
Graphite	Ag	72	6	96	39
Graphite	Ta	90	0	>99	31
Graphite	W	88	0	98	36
Graphite	Pb	76	8	99	42
Graphite	CuSn7Pb15	86	0	97	34

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.2: Qualitative determined side products of HCH (1) during the electrode screening
(x = found in the GC).

$\text{anode} \parallel \text{cathode}$
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O} \text{ (5.0 mol\%}_{\text{HCH}}\text{)}$
 $(\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.1 mol}\cdot\text{L}^{-1}\text{)}$
 acetonitrile
 $j = 4.0 \text{ mA}\cdot\text{cm}^{-2}$
 $Q = 9.0 F$
 $T = 50 \text{ }^\circ\text{C}, f_{\text{rot}} = 500 \text{ rpm}$

Anode	Cathode	Chloro- benzene	1,2- Dichloro- benzene	1,3- Dichloro- benzene	1,4- Dichloro- benzene	1,3,5- Trichloro- benzene	1,2,3- Trichloro- benzene	1,2,4- Trichloro- benzene
Graphite	Graphite	x						
Graphite	BDD		x	x	x		x	x
BDD	Graphite		x					x
BDD	BDD	x	x	x	x			x
GC	GC	x	x		x		x	x
GC	Graphite		x	x	x		x	x
Graphite	Graphite felt	x	x	x	x		x	x
Graphite	Graphite foil	x						
Graphite	Ti		x	x	x		x	x
Graphite	V	x	x	x	x		x	x
Graphite	Ni	x	x		x			x
Graphite	Zr	x	x					x
Graphite	Nb		x	x				x
DSA (RuO ₂)	Graphite		x	x	x		x	x
Graphite	Mo		x	x	x		x	x
Graphite	Ag	x	x	x	x		x	x
Graphite	Ta		x					
Graphite	W	x	x	x	x		x	x
Graphite	Pb	x	x	x	x			x
Graphite	CuSn7Pb15	x	x	x	x		x	x

Qualitative analysis by GC.

Table S3.3: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecanoate (**3**) in the solvent screening.

Solvent	Conversion $X(1)$ / %	Yield $Y(2)$ / %	Conversion $X(3)$ / %	Yield $Y(4)$ / %
Acetonitrile	72	21	>99	45
Isobutyronitrile	92	63	98	52
Ethylene carbonate	>99	91	>99	31
Propylene carbonate	94	96	99	56
<i>N,N</i> -Dimethylformamide	96	76	97	24
<i>N,N</i> -Dimethylacetamide	78	29	46	12
Dimethyl sulfoxide	71	15	35	16
<i>N</i> -Methyl-2-pyrrolidone	95	48	90	36

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.4: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecanoate (**3**) in the supporting electrolyte screening.

Supporting electrolyte	Conversion $X(1)$ / %	Yield $Y(2)$ / %	Conversion $X(3)$ / %	Yield $Y(4)$ / %
Tetramethylammonium chloride	>99	71	98	87
Tetraethylammonium chloride	94	96	99	56
Tetrabutylammonium chloride	>99	94	>99	41
Tetramethylammonium tetrafluoroborate	13	13	89	3
Tetraethylammonium tetrafluoroborate	79	64	90	69
Tetrabutylammonium tetrafluoroborate	90	95	97	94
Tetrabutylammonium acetate	>99	63	>99	78
Tetrabutylammonium trifluoromethanesulfonate	93	86	95	79
1-Ethyl-3-methylimidazolium chloride	51	51	99	28

GC-Yield/Conversion: Mesitylene as internal standard.

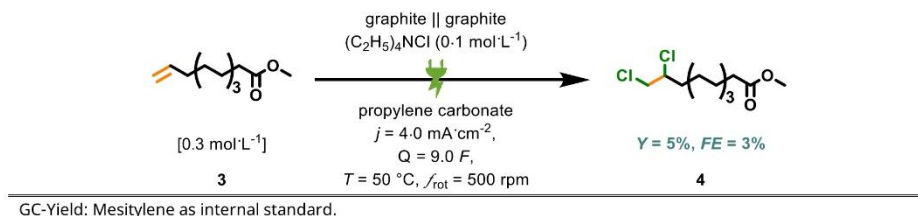
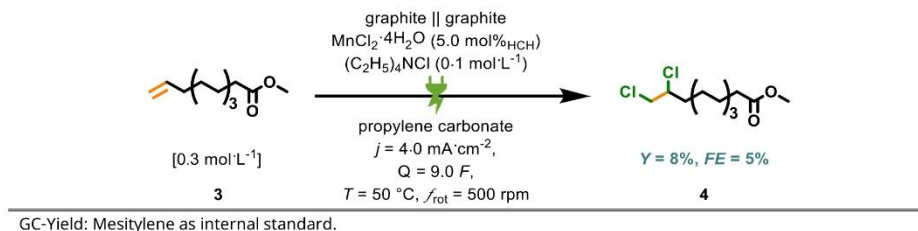
Table S3.5: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecenoate (**3**) in the catalyst screening.

 1 $[0.1 \text{ mol} \cdot \text{L}^{-1}]$ + 3 → 2 + 4 graphite graphite catalyst (5.0 mol%_{HCH}) $(\text{C}_2\text{H}_5)_4\text{NCl}$ ($0.1 \text{ mol} \cdot \text{L}^{-1}$) propylene carbonate $j = 4.0 \text{ mA} \cdot \text{cm}^{-2}$, $Q = 9.0 \text{ F}$, $T = 50 \text{ }^\circ\text{C}$, $n_{\text{rot}} = 500 \text{ rpm}$				
Catalyst	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Conversion $X(3) / \%$	Yield $Y(4) / \%$
-	89	73	>99	23
Manganese(II) chloride tetrahydrate	>99	75	>99	67
Manganese(II) triflate	>99	70	>99	64
Copper(II) chloride	92	70	>99	66
Cobalt(II) chloride	>99	83	>99	65
Nickel(II) chloride hexahydrate	83	69	>99	57
Chromium(II) chloride	88	70	>99	59
Chromium(III) chloride	91	77	>99	61
Vanadium(III) chloride	84	72	>99	58
Iron(II) chloride tetrahydrate	81	66	>99	23

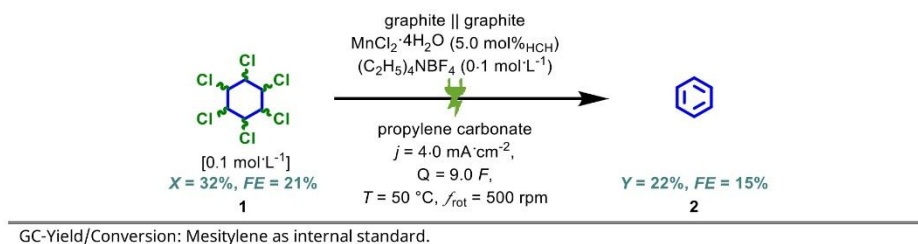
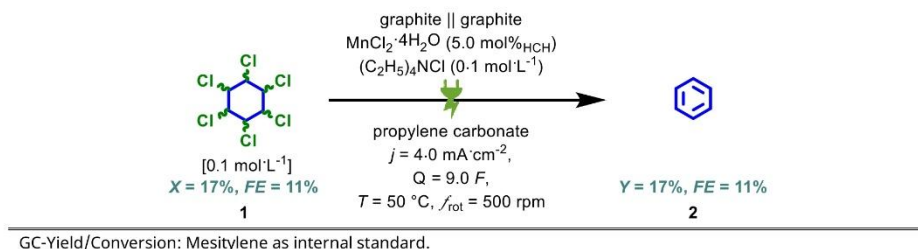
GC-Yield/Conversion: Mesitylene as internal standard.

Control experiments:

The effects of the supporting electrolyte and the catalyst on the conversion and yield of methyl 10,11-dichloroundecanoate (**4**) and HCH (**1**) to benzene (**2**) were determined in controlled experiments. Significant yields of methyl 10,11-dichloroundecanoate (**4**) due to avoidable chlorine sources such as manganese(II) chloride or tetraethylammonium chloride could be excluded here.



In addition, no significant conversions and yields of HCH (**1**) to benzene (**2**) could be determined in the absence of methyl undecenoate (**3**).



Optimization by design of experiment (DOE):

Further optimizations were carried out with the help of design of experiments (DOE). The design and evaluation of the plans was carried out by Minitab® 21.1. The decisive electrochemical parameters (amount of charge Q , current density j), concentration of HCH ($c(1)$), equivalents of the acceptor molecules $eq(3)$ and percentage catalyst substance quantities in relation to HCH $n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$ and temperature T were defined as terms. Conversions X_i and yields Y_i of the respective compounds were defined as target values (Table S3.6).

Table S3.6: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecenoate (**3**) in the 2^{5-1} fractional factorial experimental design (Resolution V).

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0–20.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹)
 propylene carbonate
 $j = 10.0\text{--}50.0 \text{ mA}\cdot\text{cm}^{-2}$,
 $Q = 5.0\text{--}8.0 \text{ F}$,
 $T = 25\text{--}75 \text{ }^\circ\text{C}$, $n_{\text{rot}} = 500 \text{ rpm}$

Term					Target value			
A	B	C	D	E	Conversion	Yield	Conversion	Yield
Q / F	$j / \text{mA}\cdot\text{cm}^{-2}$	$eq(3)$	$T / ^\circ\text{C}$	$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol}\%_{\text{HCH}}$	$X(1) / \%$	$Y(2) / \%$	$X(3) / \%$	$Y(4) / \%$
5	10	2	25	20	46±9	61±1	94±2	33±6
8	10	2	25	5	74±6	78±7	99±0	35±3
5	50	2	25	5	58±3	24±3	74±1	61±1
8	50	2	25	20	54±12	37±10	86±2	72±4
5	10	4	25	5	56±1	65±5	44±2	59±5
8	10	4	25	20	87±3	79±5	75±1	76±2
5	50	4	25	20	42±6	24±1	32±0	44±2
8	50	4	25	5	67±8	36±11	47±8	56±5
5	10	2	75	5	68±1	66±7	99±0	47±5
8	10	2	75	20	88±3	81±7	99±0	91±1
5	50	2	75	20	62±1	47±2	89±2	44±3
8	50	2	75	5	78±0	50±3	99±1	48±5
5	10	4	75	20	69±1	67±4	55±4	60±4
8	10	4	75	5	93±3	99±1	84±1	75±6
5	50	4	75	5	68±1	37±3	50±3	57±4
8	50	4	75	20	93±1	51±5	65±0	72±1
6.5	30	3	50	12.5	76±5	51±6	77±0	66±5

GC-Yield/Conversion: Mesitylene as internal standard.

The following tables show the results of the evaluation of the individual target variables in graphical and tabular form. The first four main effects and interactions were depicted graphically. Further information on the remaining main effects and interactions can be found in the table of coded coefficients.

Table S3.7: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

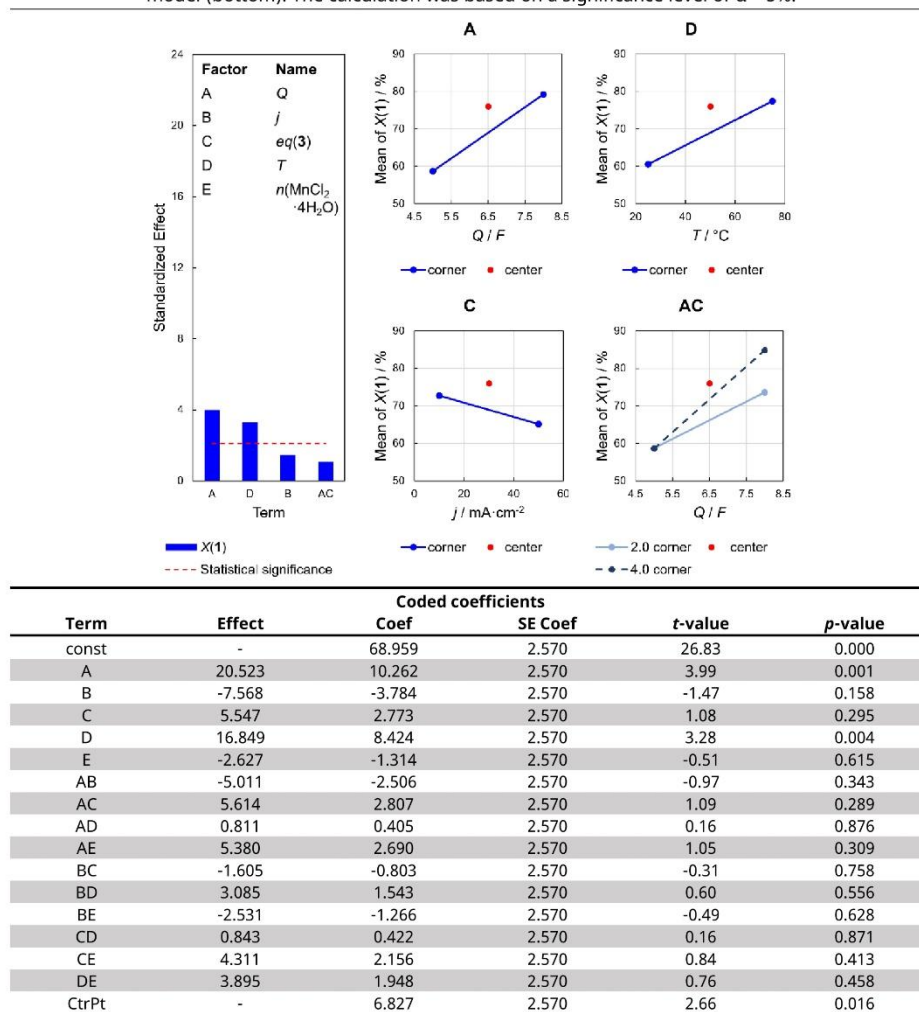


Table S3.8: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

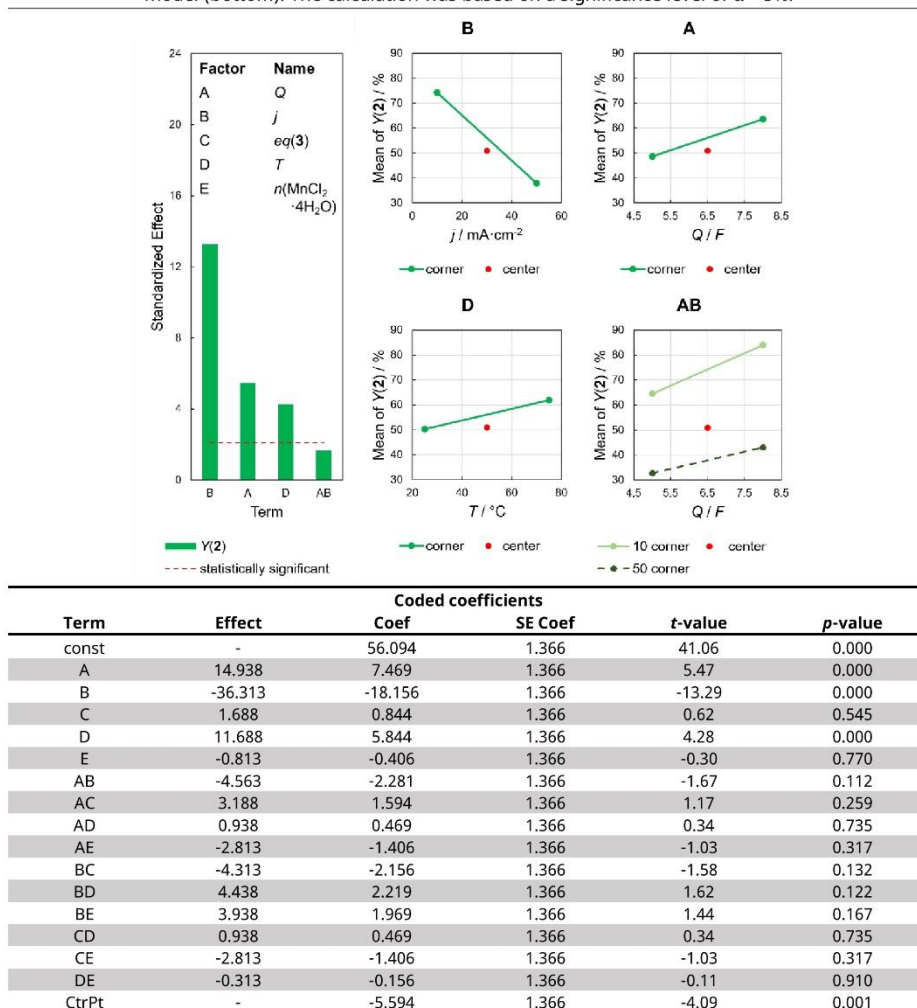


Table S3.9: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the conversion of methyl 10-undecenoate ($X(3)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

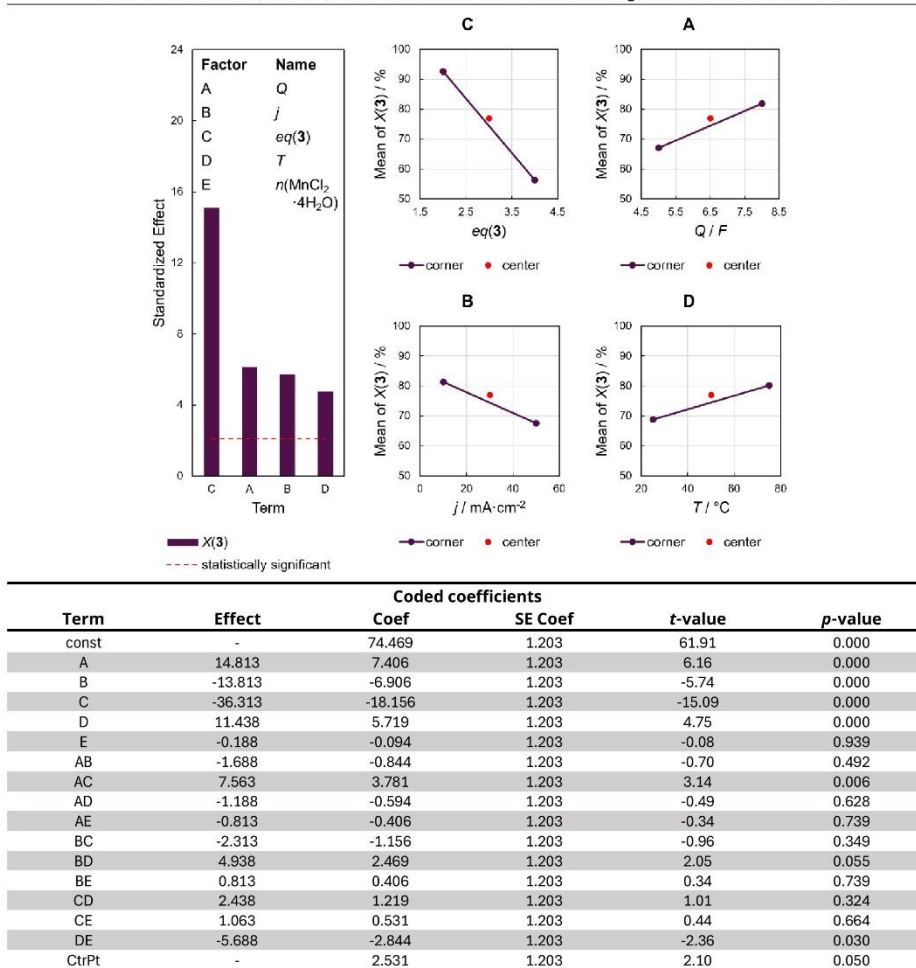
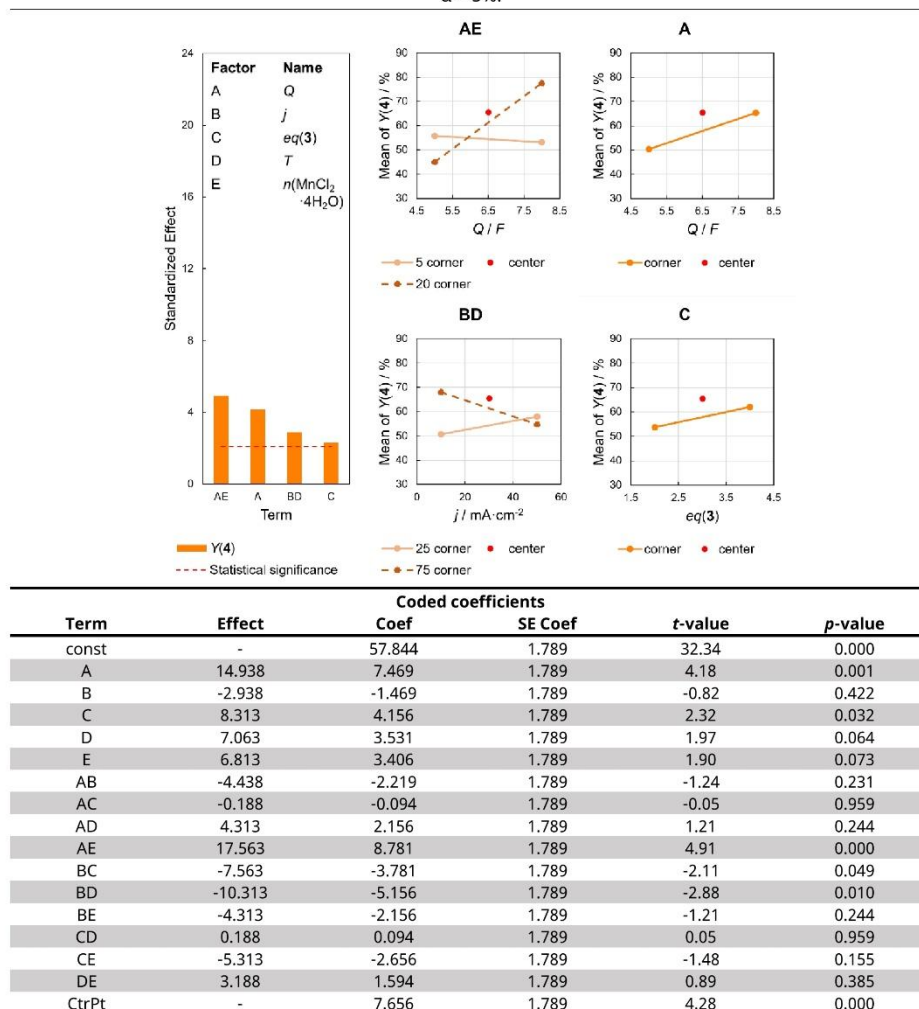


Table S3.10: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of methyl 10,11-dichloroundecanoate ($Y(4)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



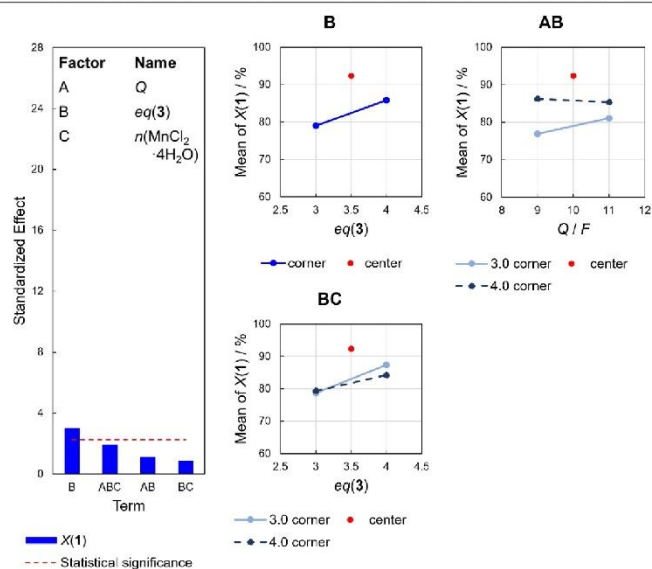
In a second DOE, individual terms were expanded, or new terms were added depending on the first DOE. If a significant curvature (deviation of the central point from the mean corner points) was observed in the model, the design was extended with additional central points in a central composite design (CCD) (Table S3.11).

Table S3.11: Determined yields Y_i of benzene (**2**), methyl 10,11-dichloroundecanoate (**4**) and conversion X_i of technical HCH (**1**) and methyl 10-undecenoate (**3**) in the 2^3 full factorial experimental with central composite design (CCD).

graphite | graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0–30.0 mol%)
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹)
 propylene carbonate
 $j = 30.0 \text{ mA} \cdot \text{cm}^{-2}$,
 $Q = 8.0\text{--}12.0 \text{ F}$,
 $T = 75 \text{ }^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$

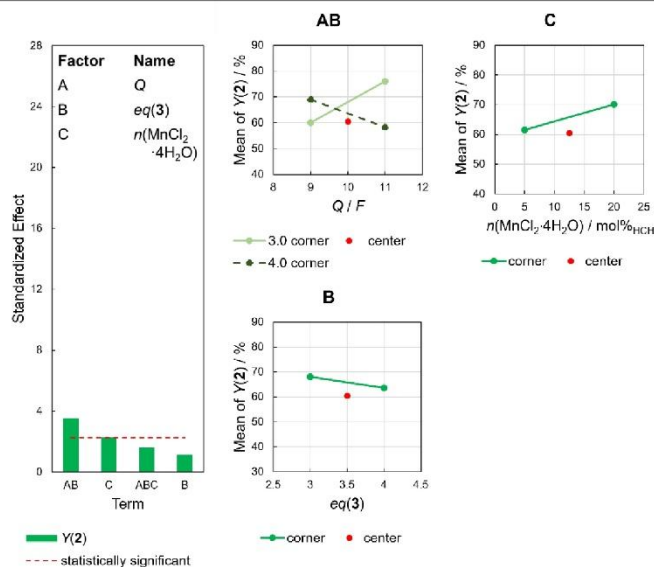
Term			Target value			
A	B	C	Conversion $X(1)$ / %	Yield $Y(2)$ / %	Conversion $X(3)$ / %	Yield $Y(4)$ / %
Q / F	$eq(3)$ (3:1)	$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol}\%_{\text{HCH}}$				
9	3.0	5.0	75±7	52±1	80±2	77±5
11	3.0	5.0	82±1	73±5	92±2	80±2
9	4.0	5.0	91±3	70±7	70±1	77±5
11	4.0	5.0	84±5	52±7	77±2	66±2
9	3.0	20.0	79±1	69±5	90±0	80±3
11	3.0	20.0	80±1	79±3	91±1	76±4
9	4.0	20.0	82±1	69±2	64±1	72±5
11	4.0	20.0	87±2	65±10	66±2	84±1
10	3.5	12.5	92±1	61±5	78±0	85±2
8	3.5	12.5	94	74	68	85
12	3.5	12.5	>99	66	82	69
10	2.5	12.5	79	84	>99	72
10	4.5	12.5	94	57	67	60
10	3.5	0.0	87	62	92	18
10	3.5	27.5	89	78	82	73

Table S3.12: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the conversion of HCH (X(1)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

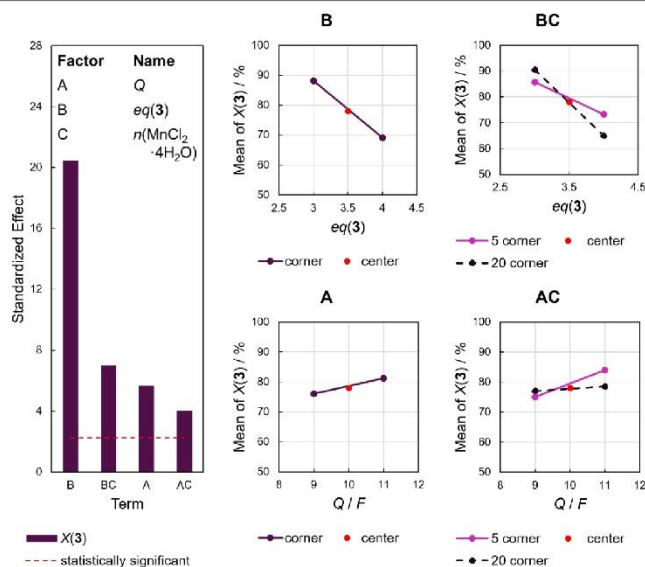


Term	Effect	Coded coefficients			
		Coef	SE Coef	t-value	p-value
const	-	82.411	1.127	73.12	0.000
A	1.653	0.827	1.127	0.73	0.482
B	6.785	3.392	1.127	3.01	0.015
C	-1.235	-0.617	1.127	-0.55	0.597
AB	-2.538	-1.269	1.127	-1.13	0.289
AC	1.572	0.786	1.127	0.70	0.503
BC	-1.968	-0.984	1.127	-0.87	0.405
ABC	4.365	2.183	1.127	1.94	0.085
CtrPt	-	9.99	3.381	2.95	0.016

Table S3.13: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



Coded coefficients					
Term	Effect	Coef	SE Coef	t-value	p-value
const	-	65.813	1.895	34.73	0.000
A	2.625	1.313	1.895	0.69	0.506
B	-4.375	-2.188	1.895	-1.15	0.278
C	8.625	4.313	1.895	2.28	0.049
AB	-13.375	-6.688	1.895	-3.53	0.006
AC	0.625	0.313	1.895	0.16	0.873
BC	-2.875	-1.438	1.895	-0.76	0.467
ABC	6.125	3.063	1.895	1.62	0.140
CtrlPt	-	-5.31	5.684	-0.93	0.374



Coded coefficients					
Term	Effect	Coef	SE Coef	t-value	p-value
const	-	78.625	0.464	169.46	0.000
A	5.250	2.625	0.464	5.66	0.000
B	-19.000	-9.500	0.464	-20.48	0.000
C	-1.750	-0.875	0.464	-1.89	0.092
AB	-1.000	-0.500	0.464	-1.08	0.309
AC	-3.750	-1.875	0.464	-4.04	0.003
BC	-6.500	-3.250	0.464	-7.00	0.000
ABC	1.500	0.750	0.464	1.62	0.140
CtrPt	-	-0.63	1.392	-0.45	0.664

Table S3.15: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the yield of methyl 10,11-dichloroundecanoate ($Y(4)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

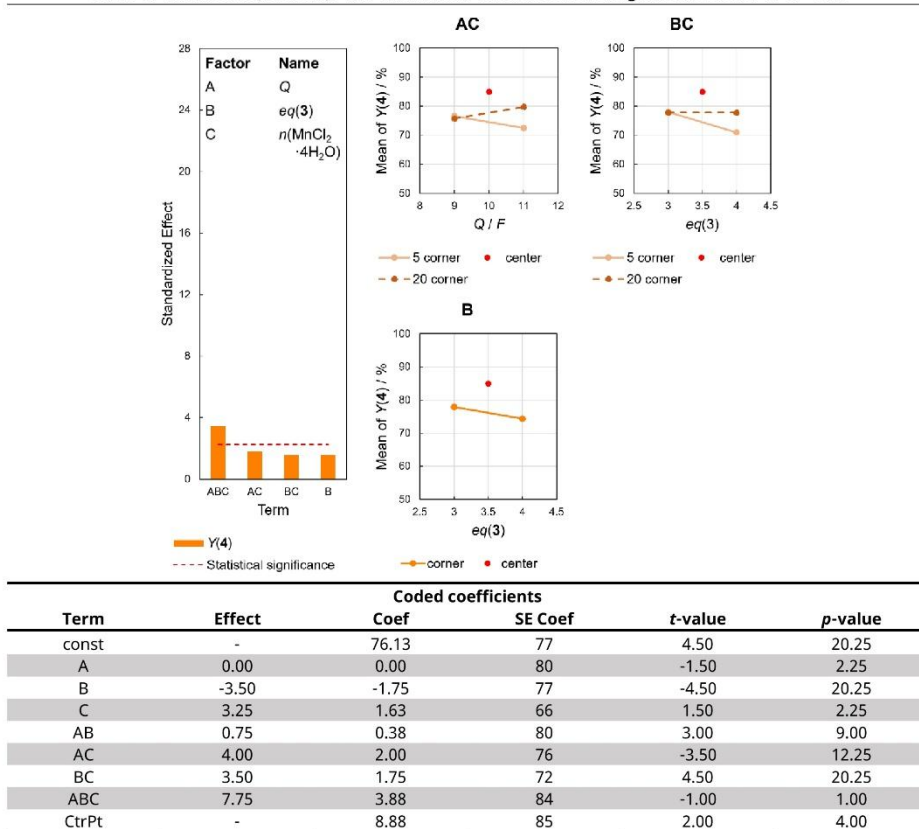


Figure S3.15 shows the main effect diagram of the target variables as a function of the parameters. By deriving the quadratic function from the polynomial regression, the mathematical maxima of the HCH (1) conversion and the methyl 10,11-dichloroundecanoate (4) yield could be determined. It should be noted that the main effect diagram is only a simplified mathematical approximation of the model (Figure S3.15).

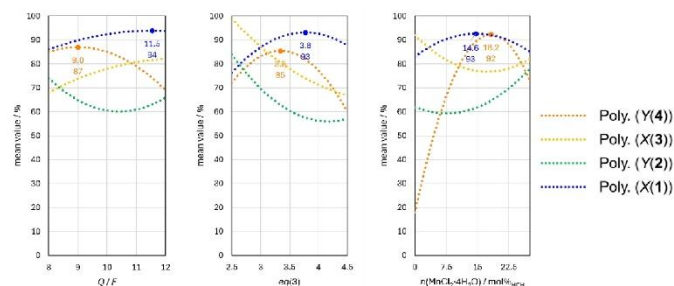
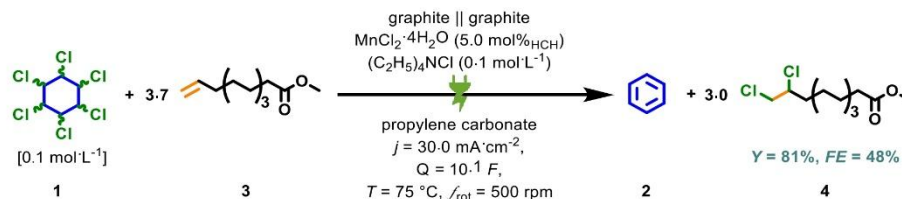


Figure S3.15: Main effect diagrams of the conversion and yield of methyl 10-undecenoate (3) to methyl 10,11-dichloroundecanoate (4) and HCH (1) to benzene (2) according to the 2^3 full factorial experimental with central composite design (CCD).

Optimized parameters for the yield of methyl 10,11-dichloroundecanoate (4) with a limited concentration of manganese(II) chloride tetrahydrate:

The following parameters and yields of methyl 10,11-dichloroundecanoate (4) were determined according to a proposal from Minitab© with a limited concentration of manganese(II) chloride.



GC-Yield/Conversion: Mesitylene as internal standard.

3.3 Optimization of Reaction Conditions for 1,2-Dichlorododecane (6)

In accordance with the synthesis protocol from section 3.1, we start with the conditions from the paper by DONG AND ROECKL et al.^[4] HCH (**1**) (145.5 mg, 0.5 mmol, 1.0 eq.) is added to 1-dodecene (**5**) (332.2 μ L, 1.5 mmol, 3.0 eq.) in a 5 mL IKA-cell (as shown in Figure S1.2). Subsequently, tetraethylammonium chloride (41.4 mg, 0.5 mmol, 1.0 eq.), manganese(II) chloride tetrahydrate (4.9 mg, 0.025 mmol, 0.05 eq.) and acetonitrile (5 mL) is added. The solution is electrolyzed in an undivided cell using different electrodes galvanostatically at a temperature of 50 °C. A current density of $j = 4 \text{ mA} \cdot \text{cm}^{-2}$ (immersion depth of the electrodes is 3.5 cm, resulting in a current of 14 mA) and a current of 9 F (434.2 C, reaction time $t \approx 516.9 \text{ min}$) are used (Table S3.16).

Table S3.16: Determined yields Y_i of benzene (**2**), 1,2-dichlorododecane (**6**) and conversion X_i of the starting materials technical hexachlorocyclohexane HCH (**1**) and 1-dodecene (**5**) in the supporting electrolyte screening.

Supporting electrolyte	Conversion $X(1)$ / %	Yield $Y(2)$ / %	Conversion $X(5)$ / %	Yield $Y(6)$ / %
Tetramethylammonium chloride	>99	67	99	46
Tetraethylammonium chloride	82	71	>99	58
Tetrabutylammonium chloride	88	70	>99	54
Tetramethylammonium tetrafluoroborate	86	72	99	60
Tetraethylammonium tetrafluoroborate	87	75	>99	74
Tetrabutylammonium tetrafluoroborate	87	72	>99	64
Tetrabutylammonium trifluoromethanesulfonate	91	76	>99	81

GC-Yield/Conversion: Mesitylene as internal standard.

In a simplified DOE, the electrochemical terms a concentration of 1-dodecene (**5**), as a non-polar compound, were determined (Table S3.17).

Table S3.17: Determined yields Y_i of benzene (**2**), 1,2-dichlorododecane (**6**) and conversion X_i of the starting materials technical HCH (**1**) and 1-dodecene (**5**) of the 2^{3-} full factorial experimental with central composite design (CCD).

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹)
 acetonitrile
 $j = 1.0\text{--}43.0 \text{ mA}\cdot\text{cm}^{-2}$,
 $Q = 4.5\text{--}10.5 \text{ F}$,
 $T = 50 \text{ }^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$

Term			Target value			
A	B	C	Conversion	Yield	Conversion	Yield
Q / F	$j / \text{mA}\cdot\text{cm}^{-2}$	$eq(5)$	$X(1) / \%$	$Y(2) / \%$	$X(5) / \%$	$Y(6) / \%$
6.0	4.0	2.0	62±3	46±2	99±0	49±1
6.0	30.0	2.0	72±1	57±2	99±0	50±1
9.0	4.0	2.0	68±1	53±0	99±0	47±1
9.0	30.0	2.0	75±1	59±0	99±0	48±1
6.0	4.0	4.0	79±1	62±0	73±0	38±0
6.0	30.0	4.0	82±0	66±2	75±1	41±1
9.0	4.0	4.0	97±4	82±2	98±1	54±1
9.0	30.0	4.0	99±0	77±1	92±3	45±1
7.5	17.0	3.0	85±0	78±2	98±1	54±3
4.5	17.0	3.0	64	37	76	37
10.5	17.0	3.0	92	64	99	50
7.5	1.0	3.0	78	57	>99	45
7.5	43.0	3.0	89	66	97	54
7.5	17.0	1.0	38	26	>99	44
7.5	17.0	5.0	88	53	75	36

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.18: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

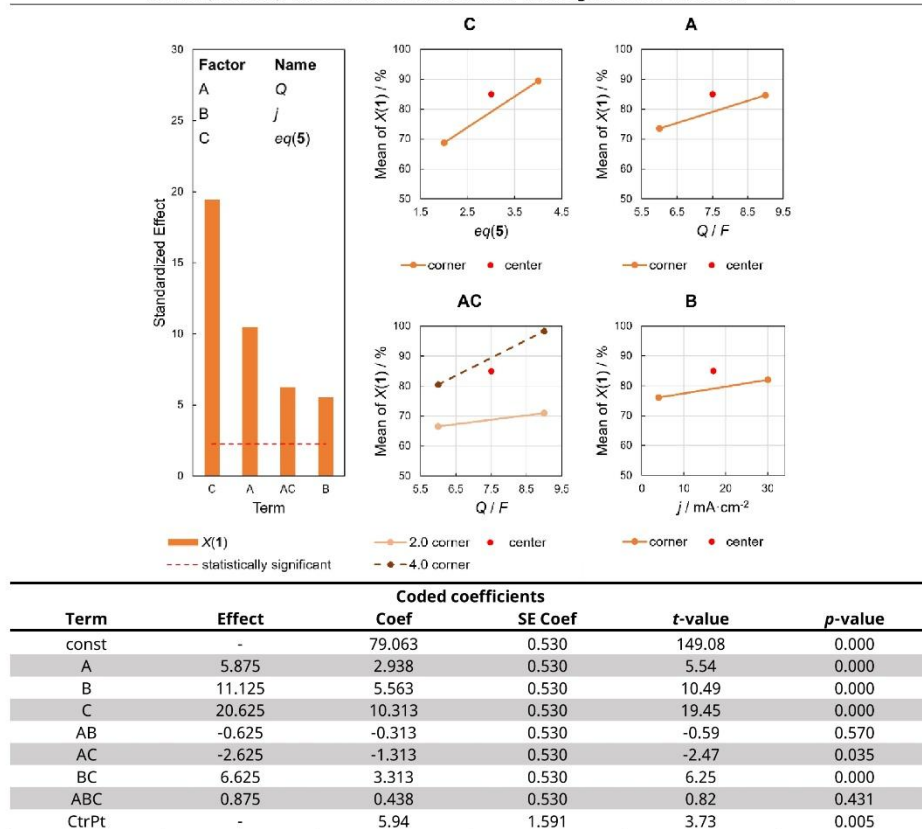


Table S3.19: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

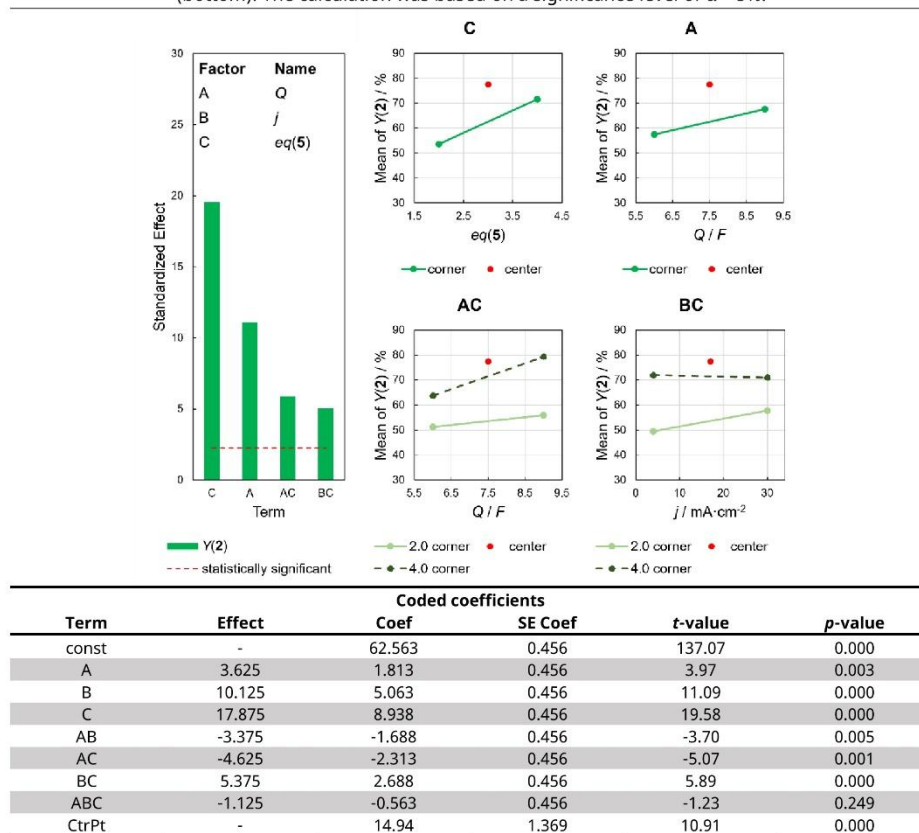


Table S3.20: Pareto, Main and Interaction plots of the 2^3 fractional factorial experimental design for the conversion of 1-dodecene ($X(5)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

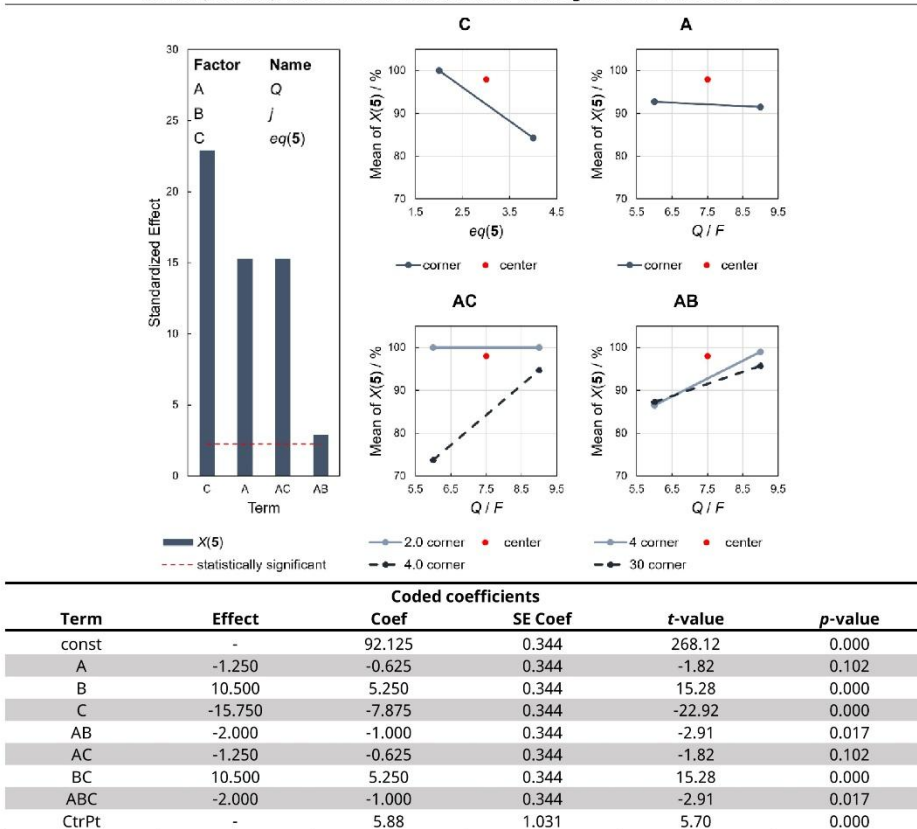
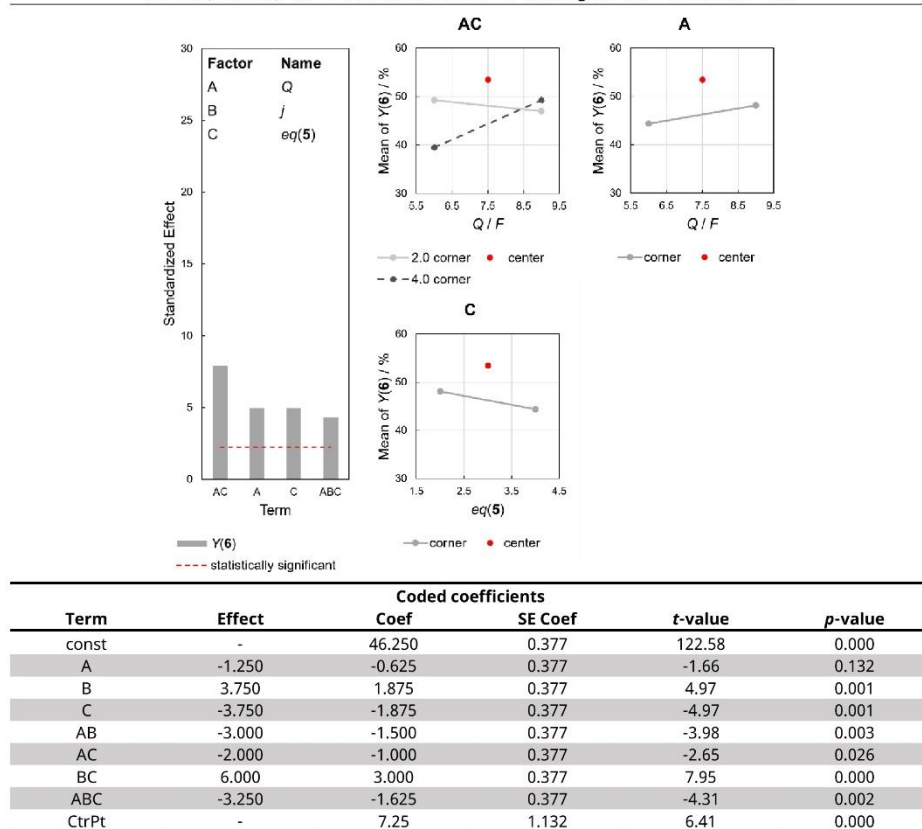


Table S3.21: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the yield of 1,2-dichlorododecane ($Y(6)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



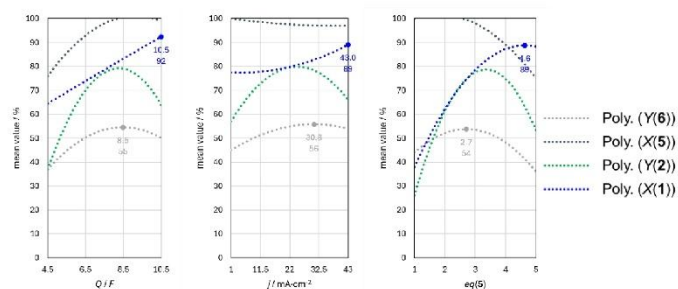
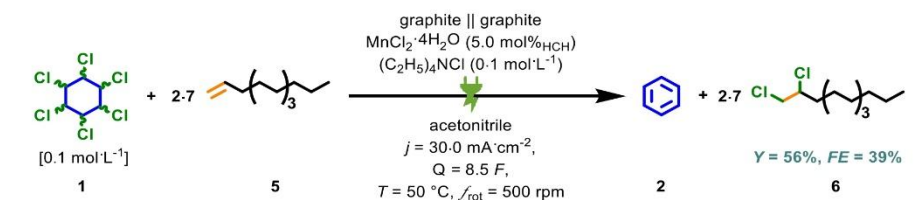


Figure S3.16: Main effect diagrams of the conversion and yield of 1-dodecene (**5**) to 1,2-dichlorododecane (**6**) and HCH (**1**) to benzene (**2**) according to the 2^3 full factorial experimental with central composite design (CCD).

Optimized parameters for the yield of 1,2-dichlorododecane (**6**):

Under the limited conditions, only moderate yields could be achieved here.



GC-Yield/Conversion: Mesitylene as internal standard.

3.3 Optimization of Reaction Conditions for 1,2-Dichloroethyl acetate (8)

In a further analogy, DOEs were performed for compounds with electron-rich double bonds. Table S3.22 below shows the results of the first DoE.

Table S3.22: Determined yields Y_i of benzene (2), 1,2-dichloroethyl acetate (8) and conversion X_i of technical hexachlorocyclohexane (1) and vinyl acetate (7) in the 2^{5-1} fractional factorial experimental (Resolution V) with central composite design (CCD).

Term					Target value			
A	B	C	D	E	Conversion	Yield	Yield	
Q / F	$j / \text{mA}\cdot\text{cm}^{-2}$	$eq(7)$	$T / ^\circ\text{C}$	$n(\text{MnCl}_2\cdot 4\text{H}_2\text{O}) / \text{mol}\%_{\text{HCH}}$	$X(1) / \%$	$Y(2) / \%$	$Y(8) / \%$	
6.0	5.0	3.0	25.0	15.0	47±1	47±2	56±2	
6.0	5.0	3.0	65.0	5.0	14±2	23±0	26±0	
6.0	40.0	3.0	25.0	5.0	45±1	26±0	27±2	
6.0	40.0	3.0	65.0	15.0	47±0	32±1	31±4	
12.0	5.0	3.0	25.0	5.0	54±1	48±0	36±0	
12.0	5.0	3.0	65.0	15.0	44±11	36±5	37±6	
12.0	40.0	3.0	25.0	15.0	65±4	32±1	12±1	
12.0	40.0	3.0	65.0	5.0	76±0	46±1	19±0	
6.0	5.0	4.0	25.0	5.0	34±4	38±1	36±3	
6.0	5.0	4.0	65.0	15.0	30±1	30±0	32±3	
6.0	40.0	4.0	25.0	15.0	41±2	26±3	34±4	
6.0	40.0	4.0	65.0	5.0	52±2	27±6	33±6	
12.0	5.0	4.0	25.0	15.0	71±3	52±0	27±8	
12.0	5.0	4.0	65.0	5.0	45±2	35±4	29±1	
12.0	40.0	4.0	25.0	5.0	66±5	23±3	14±0	
12.0	40.0	4.0	65.0	15.0	78±2	37±4	17±0	
9.0	22.5	3.5	45.0	10.0	71±1	57±2	57±3	
1.9	22.5	3.5	45.0	9.0	5	14	19	
16.1	22.5	3.5	45.0	9.0	86	61	24	
9.0	1.0	3.5	45.0	9.0	53	30	31	
9.0	64.1	3.5	45.0	9.0	59	21	18	
9.0	22.5	2.3	45.0	9.0	64	44	22	
9.0	22.5	4.7	45.0	9.0	75	57	43	
9.0	22.5	3.5	-2.6	9.0	67	37	27	
9.0	22.5	3.5	92.6	9.0	73	45	36	
9.0	22.5	3.5	45.0	0.0	38	22	5	
9.0	22.5	3.5	45.0	21.9	71	61	44	

GC-Yield/Conversion: Mesitylene as internal standard. The conversion of vinyl acetate (7) was not detected by the GC.

Table S3.23: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

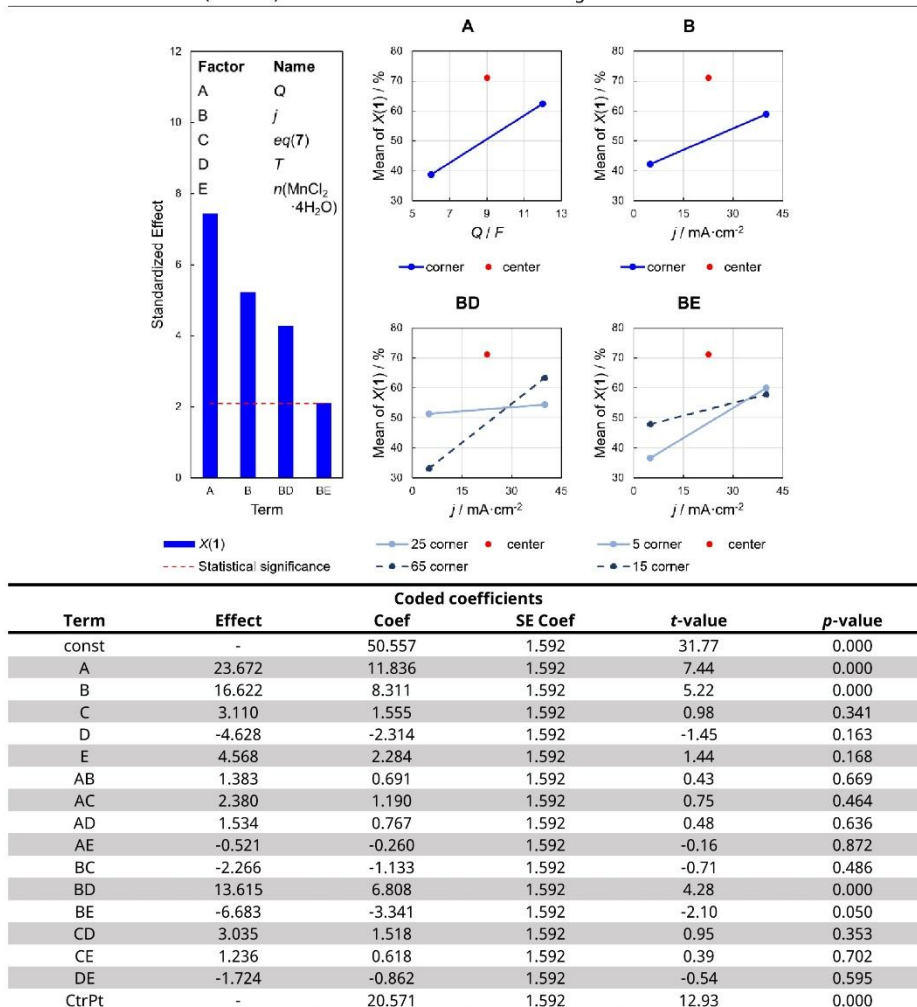


Table S3.24: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

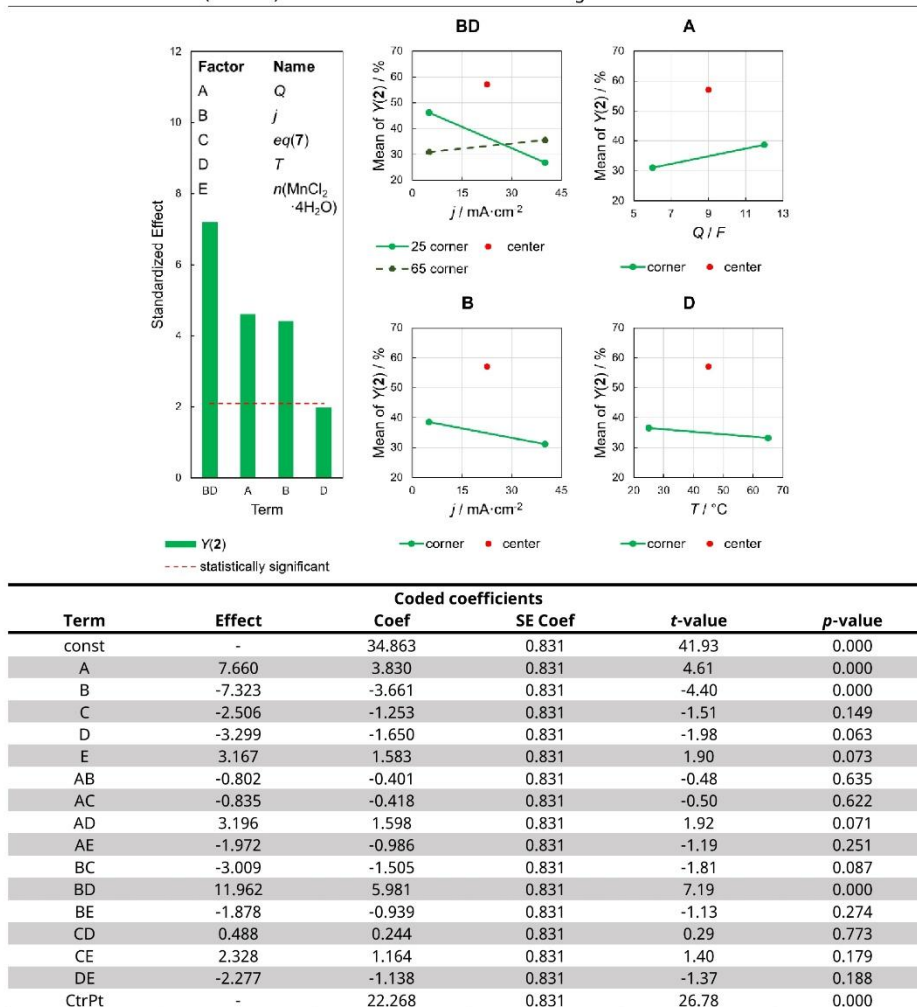
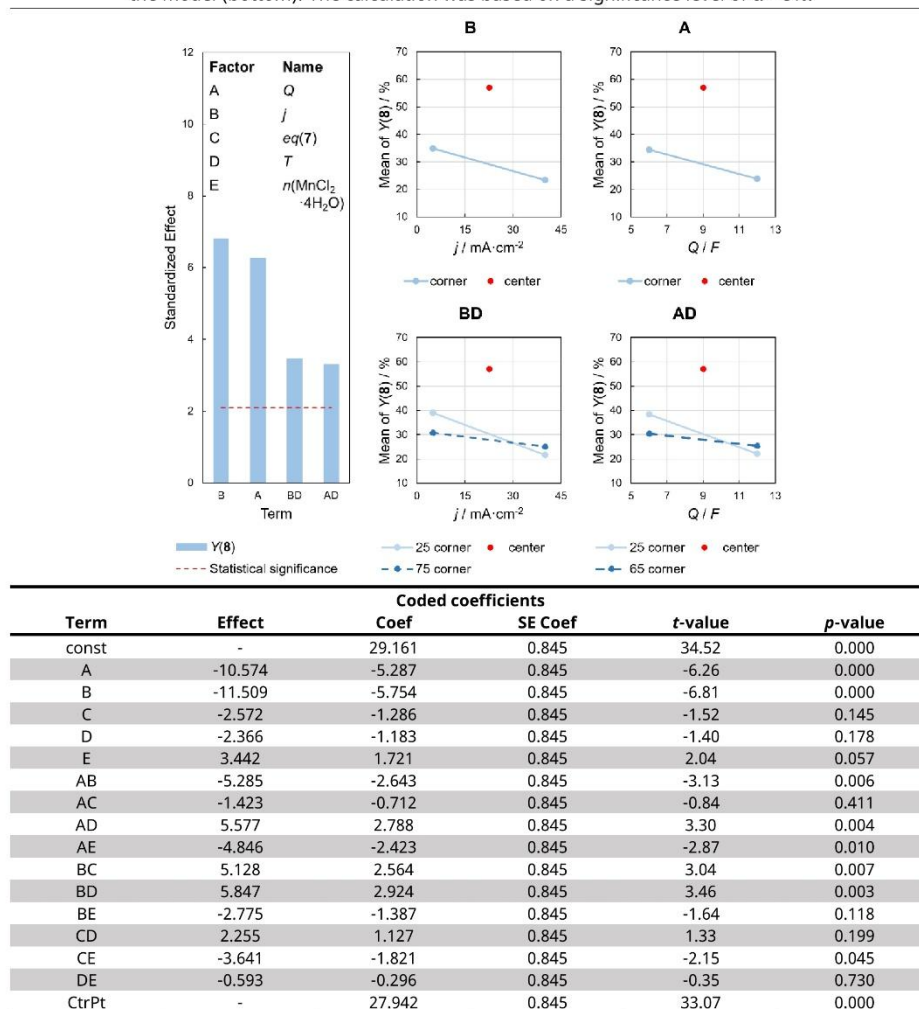


Table S3.25: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of 1,2-dichloroethyl acetate ($Y(8)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



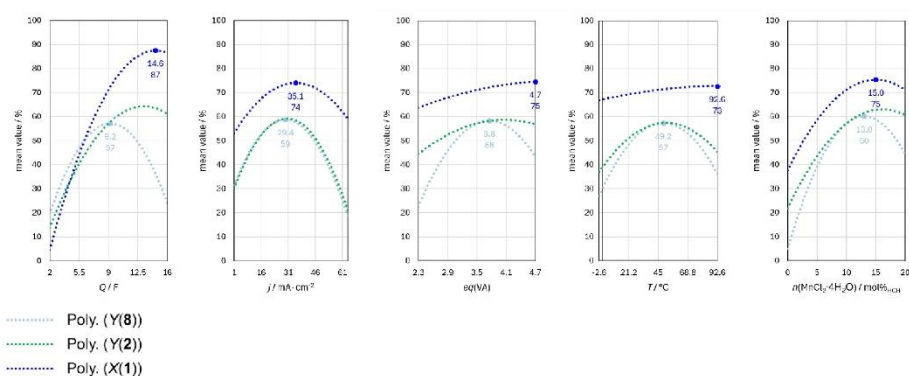
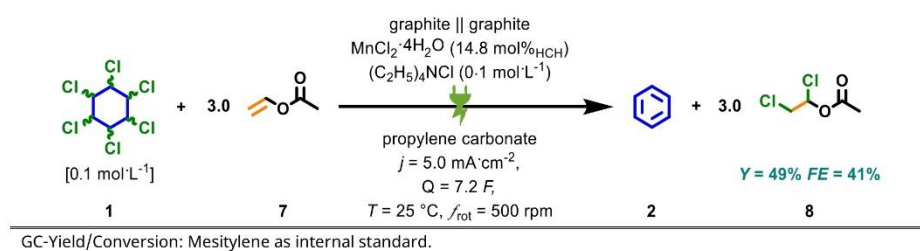


Figure S3.17: Main effect diagrams of the conversion and yield of 1,2-dichloroethyl acetate (8) and HCH (1) to benzene (2) according to the 2^{5-1} fractional factorial experimental (V) with central composite design (CCD).

Optimized parameters for the yield of 1,2-dichloroethyl acetate (8) after the first DoE:



Linear Screening of the HCH (1) concentration

Table S3.26: Determined yields Y_i of benzene (2), 1,2-dichloroethyl acetate (8) and conversion X_i of technical hexachlorocyclohexane (1) of the linear HCH ($c(1)$) concentration screening.

$ \begin{array}{c} \text{graphite graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} (14.8 \text{ mol}\%_{\text{HCH}}) \\ (\text{C}_2\text{H}_5)_4\text{NCl} (0.1 \text{ mol}\cdot\text{L}^{-1}) \\ \text{propylene carbonate} \\ j = 5.0 \text{ mA}\cdot\text{cm}^{-2}, \\ Q = 7.2 F, \\ T = 25^\circ\text{C}, j_{\text{rot}} = 500 \text{ rpm} \end{array} $			
$ \begin{array}{c} \text{1} \\ [0.05\text{--}0.30 \text{ mol}\cdot\text{L}^{-1}] \end{array} $	$ \begin{array}{c} \text{7} \\ 3.0 \end{array} $	$ \begin{array}{c} \text{2} \\ \text{8} \end{array} $	
$c(1) / \text{mol}\cdot\text{L}^{-1}$	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Yield $Y(8) / \%$
0.100	69	50	48
0.150	70	52	68
0.175	74	57	73
0.200	75	55	76
0.225	73	55	73
0.250	63	45	61
0.300	71	48	46

GC-Yield/Conversion: Mesitylene as internal standard.

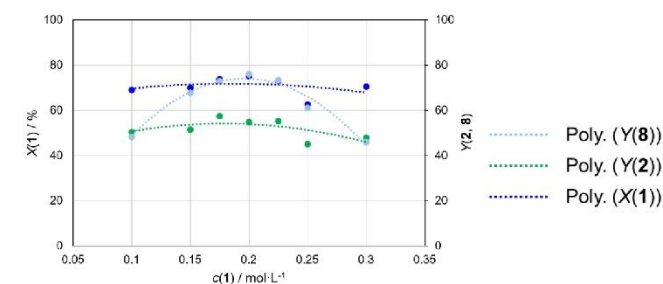


Figure S3.18: Yields Y_i of benzene (2), 1,2-dichloroethyl acetate (8) and conversion X_i of technical HCH (1) against the HCH ($c(1)$) concentration.

Optimized parameters for the yield of 1,2-dichloroethyl acetate (8) after linear screening of HCH:

$ \begin{array}{c} \text{graphite graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} (14.8 \text{ mol}\%_{\text{HCH}}) \\ (\text{C}_2\text{H}_5)_4\text{NCl} (0.1 \text{ mol}\cdot\text{L}^{-1}) \\ \text{propylene carbonate} \\ j = 5.0 \text{ mA}\cdot\text{cm}^{-2}, \\ Q = 7.2 F, \\ T = 25^\circ\text{C}, j_{\text{rot}} = 500 \text{ rpm} \end{array} $			
$ \begin{array}{c} \text{1} \\ [0.2 \text{ mol}\cdot\text{L}^{-1}] \end{array} $	$ \begin{array}{c} \text{7} \\ 3.0 \end{array} $	$ \begin{array}{c} \text{2} \\ \text{8} \end{array} $	$ \begin{array}{c} Y = 76\% \text{ FE} = 63\% \end{array} $

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.27: Determined yields Y_i of benzene (2), 1,2-Dichloroethyl acetate (8) and conversion X_i of the starting material technical HCH (1) and in a 2^3 full factorial experimental design.

1

[0.2 mol·L⁻¹]

+

7

3.0–3.5

→

2

+

8

3.0

graphite || graphite

MnCl₂·4H₂O (5.0–15.0 mol%_{HCH})

(C₂H₅)₄NCl (0.05–0.15 mol·L⁻¹)

propylene carbonate

j = 5.0 mA·cm⁻²,

Q = 7.2 F,

T = 25 °C, f_{rot} = 500 rpm

Term		Target value			
A	B	C	Conversion	Yield	Yield
eq(7)	n(MnCl ₂ 4H ₂ O) / mol% _{HCH}	c((C ₂ H ₅) ₄ NCl) / mol·L ⁻¹	X(1) / %	Y(2) / %	Y(8) / %
3.00	5.0	0.05	80±1	59±2	81±1
3.00	15.0	0.05	84±1	60±2	89±1
3.00	5.0	0.15	54±3	37±3	41±3
3.00	15.0	0.15	61±1	42±1	52±6
3.25	5.0	0.05	78±5	58±4	69±8
3.25	15.0	0.05	89±0	67±1	90±1
3.25	5.0	0.15	52±1	36±2	37±1
3.25	15.0	0.15	69±4	49±3	60±5
3.125	10.0	0.10	71±2	52±1	66±2

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.28: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

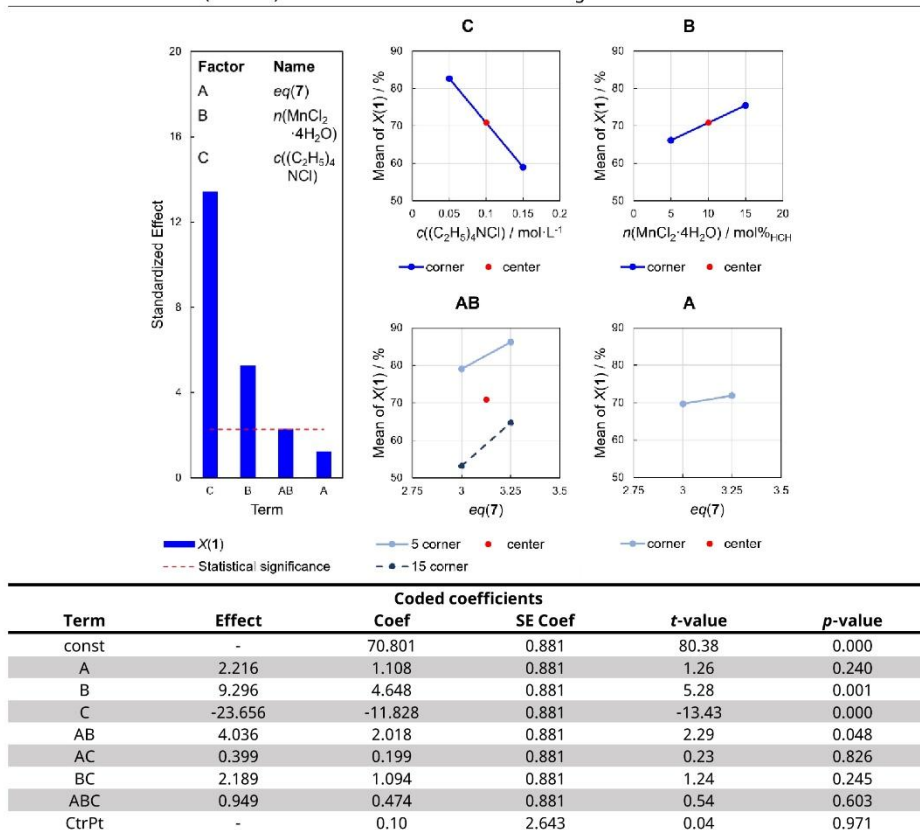
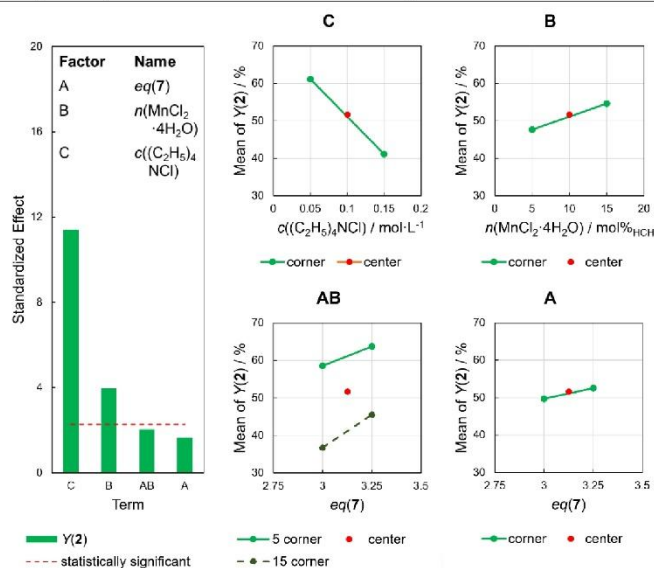
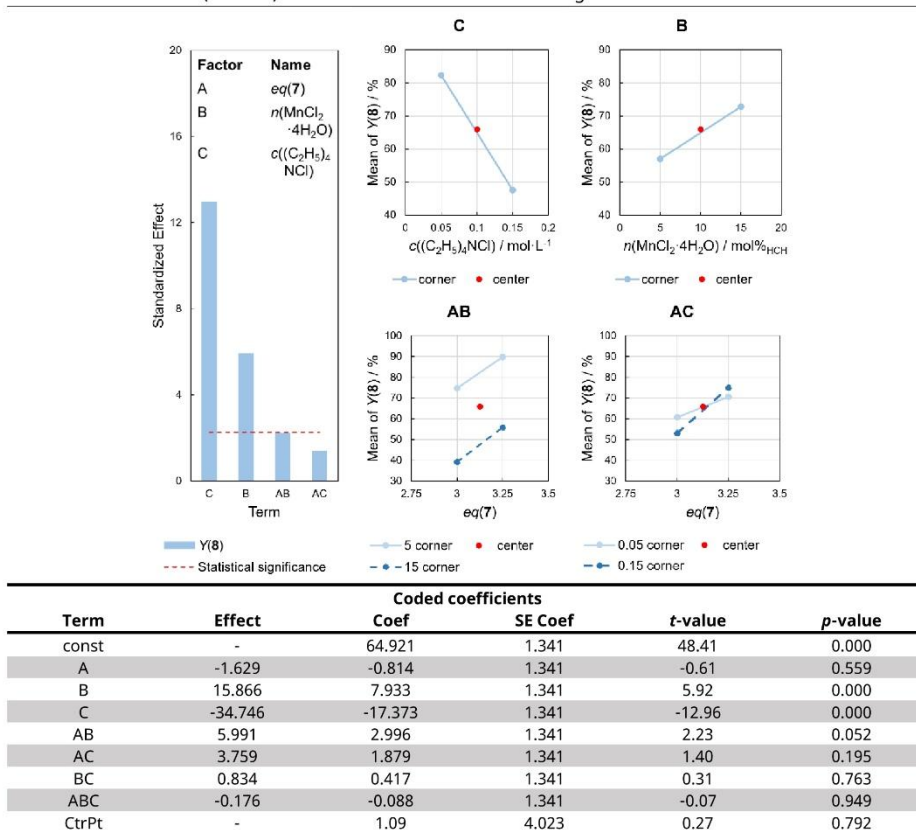


Table S3.29: Pareto, Main and Interaction plots of the 2³ full factorial experimental design for the yield of benzene (Y(2)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

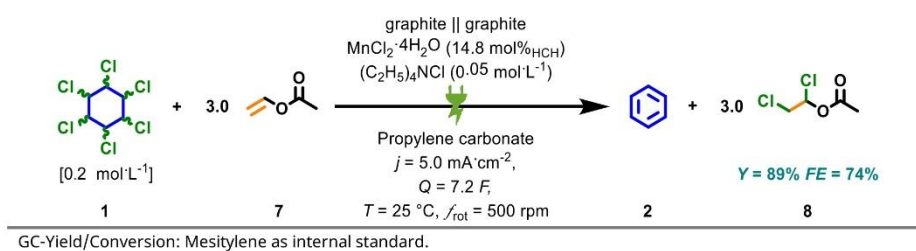


Term	Effect	Coded coefficients		t-value	p-value
		Coef	SE Coef		
const	-	51.124	0.876	58.38	0.000
A	2.890	1.445	0.876	1.65	0.133
B	6.963	3.481	0.876	3.98	0.003
C	-19.970	-9.985	0.876	-11.40	0.000
AB	3.585	1.793	0.876	2.05	0.071
AC	-0.393	-0.196	0.876	-0.22	0.828
BC	1.865	0.933	0.876	1.06	0.315
ABC	0.062	0.031	0.876	0.04	0.972
CtrPt	-	0.57	2.627	0.22	0.833

Table S3.30: Pareto, Main and Interaction plots of the 2^3 full factorial experimental design for the yield of 1,2-dichloroethyl acetate ($Y(8)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

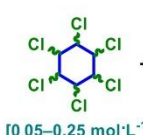
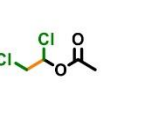


Optimized parameters for the yield of 1,2-dichloroethyl acetate (8) after second DoE:



Since small amounts of water can impair the work-up of 1,2-dichloroethyl acetate (**8**), the conditions were re-examined with anhydrous manganese(II) chloride (Table S3.31). Significant amounts of water can lead to the decomposition of 1,2-dichloroethyl acetate (**8**).^[5]

Table S3.31: Determined yields Y_i of benzene (**2**), 1,2-dichloroethyl acetate (**8**) and conversion X_i of technical HCH (**1**) in the 2^{4-1} fractional factorial experimental design (Resolution V).

 1 [0.05–0.25 mol·L⁻¹] +  7 →  2 +  8 graphite graphite $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0–20.0 mol%_{HCH}) $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹) propylene carbonate $j = 1.0\text{--}20.0 \text{ mA}\cdot\text{cm}^{-2}$, $Q = 5.0\text{--}9.0 \text{ F}$, $T = 25^\circ\text{C}$, $n_{\text{rot}} = 500 \text{ rpm}$						
A	B	Term C	E	Target value		
Q / F	$j / \text{mA}\cdot\text{cm}^{-2}$	$c(1) / \text{mol}\cdot\text{L}^{-1}$	$n(\text{MnCl}_2) / \text{mol}\%_{\text{HCH}}$	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Yield $Y(8) / \%$
6	5	0.10	5	77±10	48±0	46±1
8	5	0.10	15	83±0	68±0	60±1
6	15	0.10	15	68±1	56±1	41±1
8	15	0.10	5	74±1	61±2	42±2
6	5	0.20	15	72±2	54±1	57±1
8	5	0.20	5	75±6	58±3	54±3
6	15	0.20	5	68±1	49±2	43±2
8	15	0.20	15	75±0	58±0	49±1
7	10	0.15	10	72±2	56±3	51±2

GC-Yield/Conversion: Mesitylene as internal standard. The conversion of vinyl acetate (**7**) was not detected by the GC.

Table S3.32: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

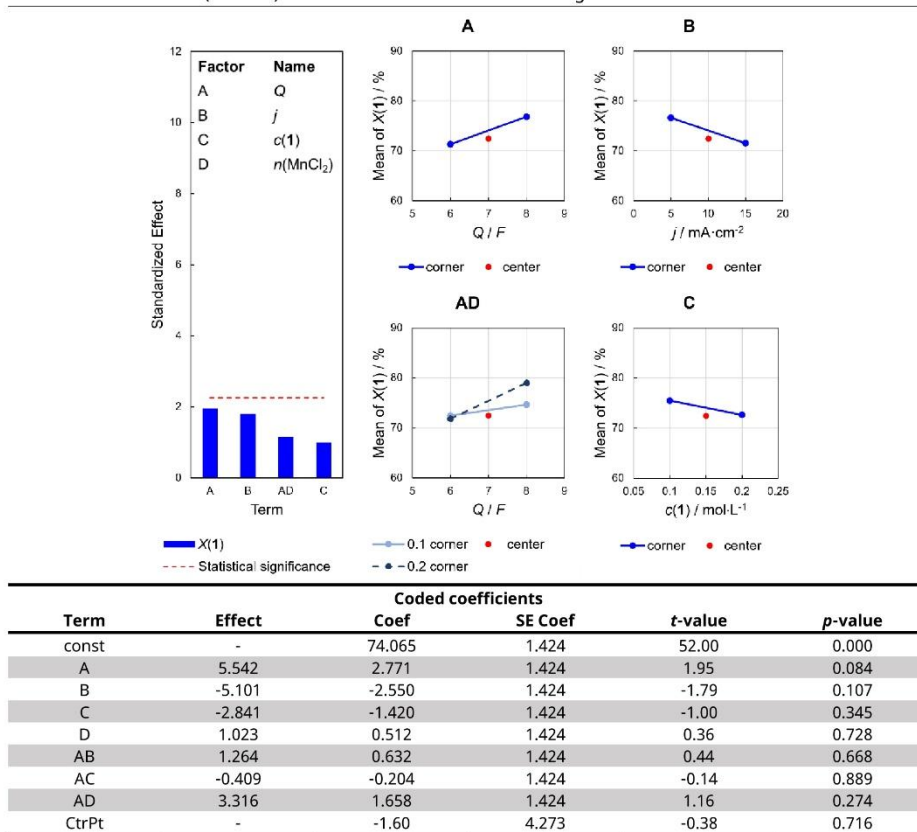


Table S3.33: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

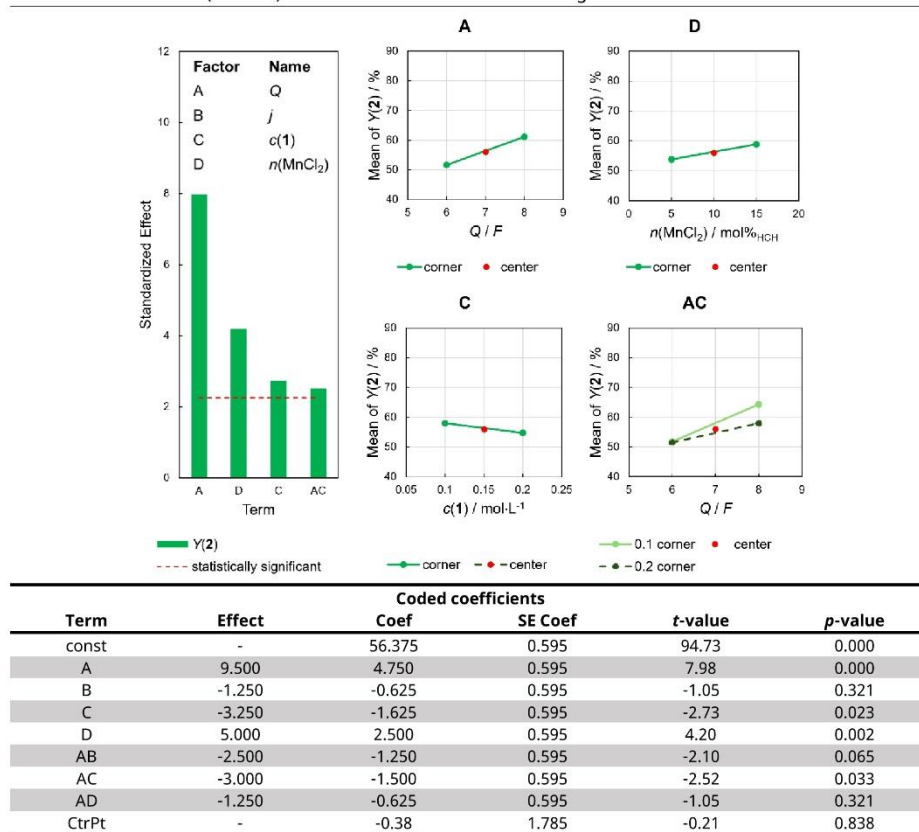


Table S3.34: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 1,2-dichloroethyl acetate ($Y(8)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

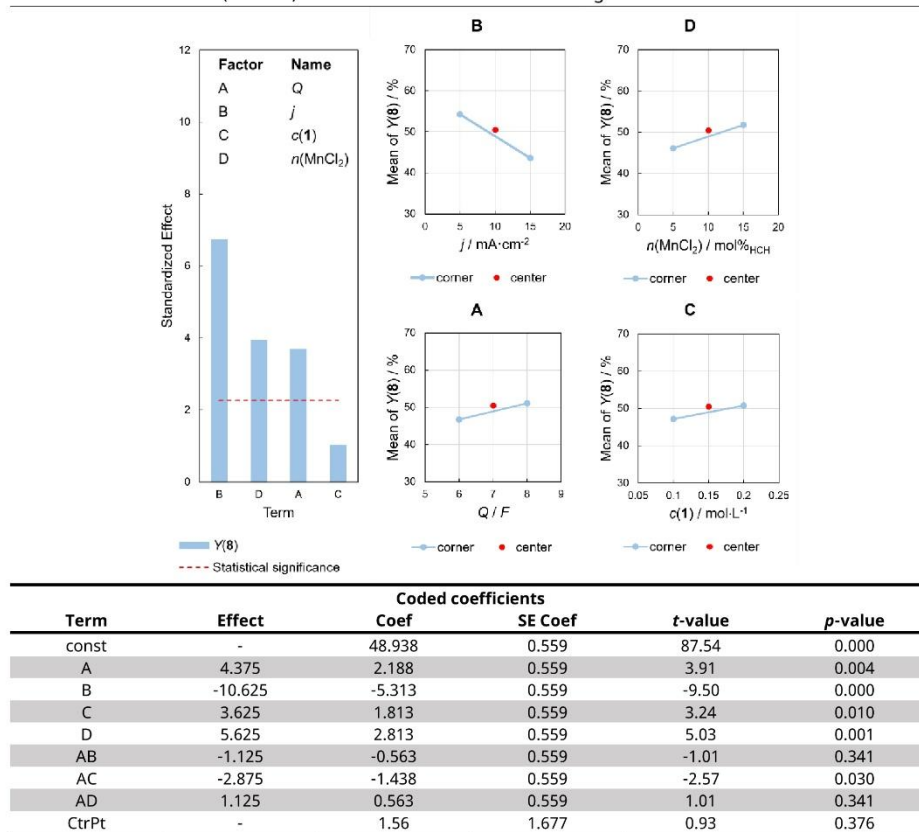
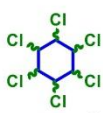


Table S3.35: Determined yields Y_i of benzene (**2**), 1,2-dichloroethyl acetate (**8**) and conversion X_i of the starting material technical HCH (**1**) and in a 2^2 full factorial experimental with central composite design (CCD).

 1 [0.2 mol·L⁻¹] +  7 →  2 +  8 graphite graphite MnCl₂·4H₂O (15 mol%_{HCH}) (C₂H₅)₄NCl (0.01–0.09 mol·L⁻¹) propylene carbonate <i>j</i> = 5 mA·cm⁻², <i>Q</i> = 7.2 F, <i>T</i> = 11–35 °C, <i>f</i>_{rot} = 500 rpm				
Term		Target value		
A	B	Conversion <i>X</i> (1) / %	Yield <i>Y</i> (2) / %	Yield <i>Y</i> (8) / %
<i>T</i> / °C	<i>c</i> ((C ₂ H ₅) ₄ NCl) / mol·L ⁻¹			
16	0.025	62±2	42±0	37±1
30	0.025	62±1	44±4	45±4
16	0.075	77±0	66±1	67±2
30	0.075	78±1	64±1	65±3
23	0.050	81±3	61±4	67±3
11	0.05	49	29	26
35	0.05	68	54	55
23	0.01	55	40	42
23	0.09	78	64	66

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.36: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

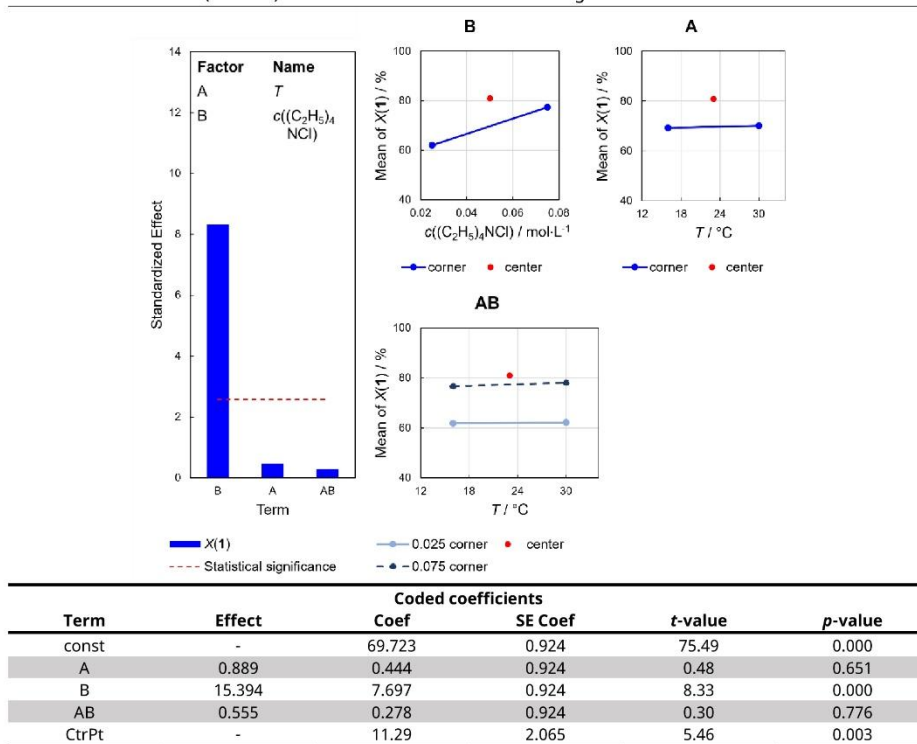


Table S3.37: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

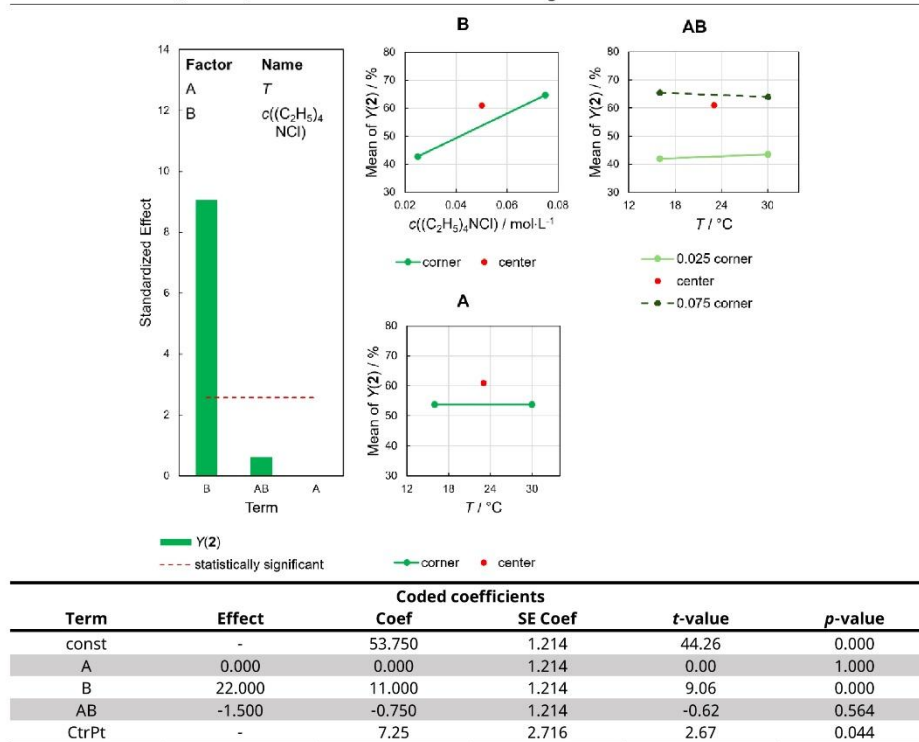


Table S3.38: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of 1,2-dichloroethyl acetate ($Y(8)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

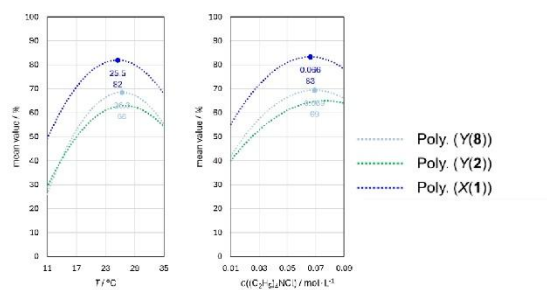
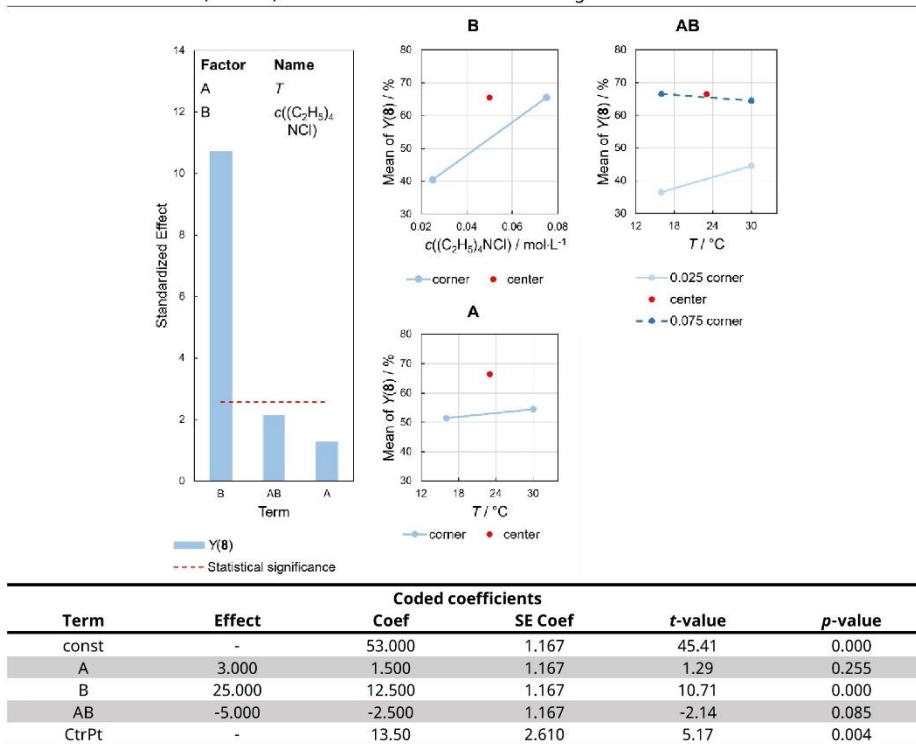


Figure S3.19: Main effect diagrams of the conversion and yield of 1,2-dichloroethyl acetate (8) and HCH (1) to benzene (2) according to the 2^2 full factorial experimental with central composite design (CCD).

3.4 Optimization of Reaction Conditions for 2,3-Dichloro-1-propanol (10)

For the start of the optimization, further parameters were changed compared to the previous optimizations. Firstly, a solvent should be used for an industrial process application which is above the boiling point of the product 2,3-dichloro-1-propanol (10) (184 °C).^[6] For this reason, acetonitrile is avoided, and propylene carbonate is used instead. This does not show the conversion of the allyl alcohol (9), as this was not detected by the GC (Table S3.39).

Table S3.39: Determined yields Y_i of benzene (2), 2,3-dichloro-1-propanol (10) and conversion X_i of technical HCH (1) in the 2^{4-1} fractional factorial experimental (Resolution V) with central composite design (CCD).

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0–20.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.05 mol·L⁻¹)
 propylene carbonate
 $j = 0.1\text{--}20.0 \text{ mA}\cdot\text{cm}^{-2}$,
 $Q = 5.0\text{--}9.0 F$,
 $T = 25^\circ\text{C}$, $f_{\text{Tot}} = 500 \text{ rpm}$

A	B	Term C	E	Target value		
Q / F	$j / \text{mA}\cdot\text{cm}^{-2}$	$c(1) / \text{mol}\cdot\text{L}^{-1}$	$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol}\%_{\text{HCH}}$	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Yield $Y(10) / \%$
6	5	0.1	5	78±2	60±3	49±4
8	5	0.1	15	94±1	73±4	64±1
6	15	0.1	15	62±4	44±6	57±6
8	15	0.1	5	88±1	72±1	60±2
6	5	0.2	15	86±0	59±2	77±2
8	5	0.2	5	96±0	64±1	62±3
6	15	0.2	5	86±5	67±6	70±1
8	15	0.2	15	88±9	73±6	74±4
7	10	0.15	10	93±1	76±1	76±1
5	10	0.15	10	48	25	37
9	10	0.15	10	96	72	65
7	0.1	0.15	10	35	8	13
7	20	0.15	10	70	50	63
7	10	0.05	10	80	61	44
7	10	0.25	10	95	73	83
7	10	0.15	0	91	69	52
7	10	0.15	20	80	63	73
5	10	0.15	10	48	25	37

GC-Yield/Conversion: Mesitylene as internal standard. The conversion of vinyl acetate (9) was not detected by the GC.

Table S3.40: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

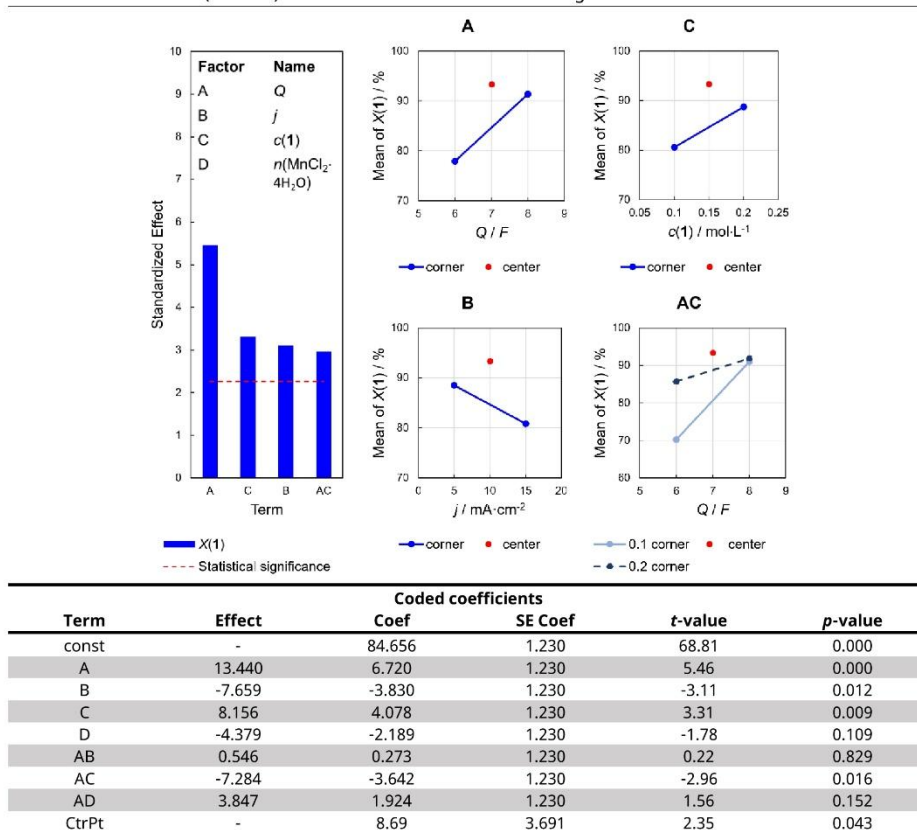


Table S3.41: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

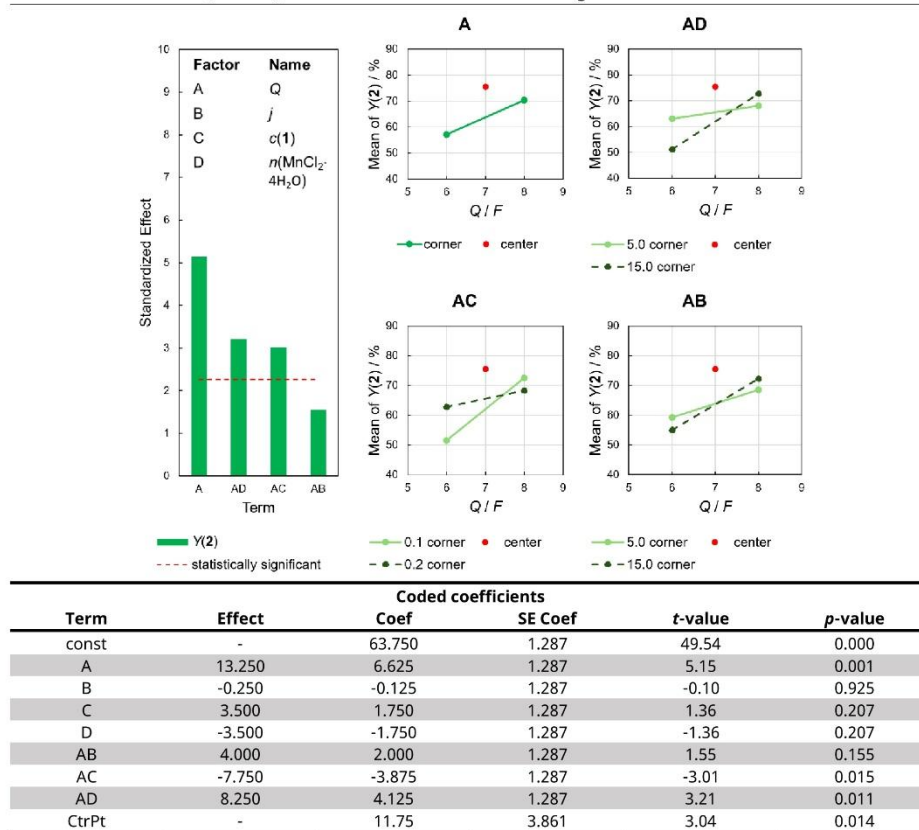


Table S3.42: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 2,3-dichloro-1-propanol ($Y(10)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

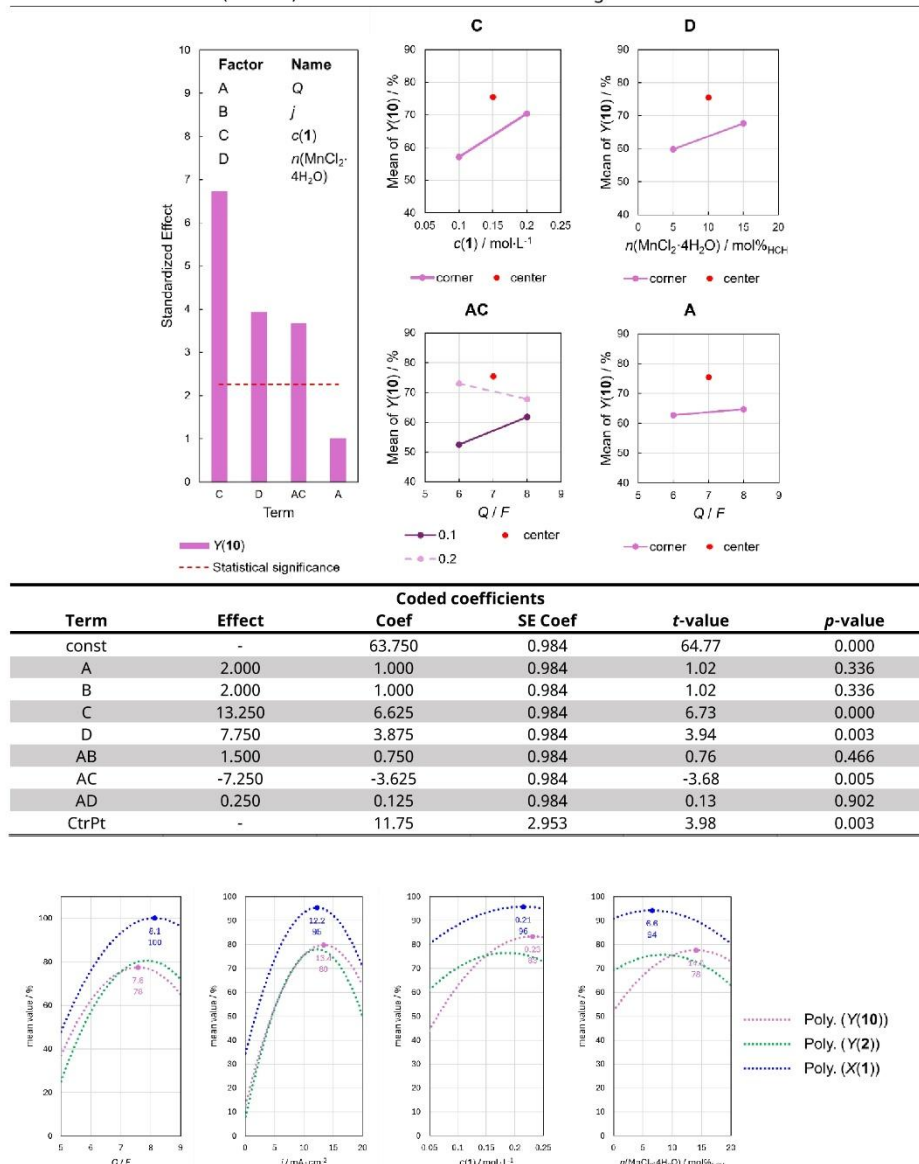


Figure S3.20: Main effect diagrams of the conversion and yield of 2,3-dichloro-1-propanol (10) and HCH (1) to benzene (2) according to the 2^{4-1} fractional factorial experimental design with central composite design (CCD).

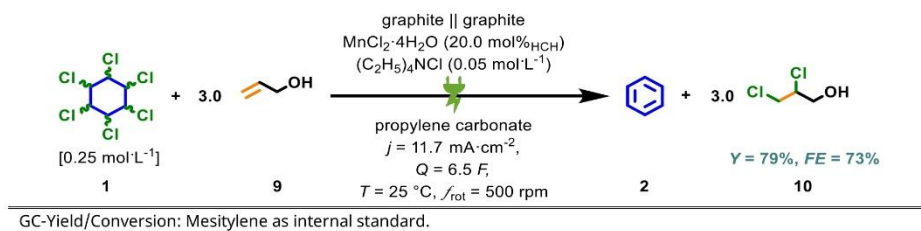
1st Optimized parameters for the yield of 2,3-dichloro-1-propanol (10):

Table S3.43: Determined yields Y_i of benzene (**2**), 2,3-dichloro-1-propanol (**10**) and conversion X_i of the starting material technical HCH (**1**) and in a 2² full factorial experimental with central composite design (CCD).

Term		Target value		
A	B	Conversion $X(1)$ / %	Yield $Y(2)$ / %	Yield $Y(10)$ / %
$T / ^\circ\text{C}$	$c((\text{C}_2\text{H}_5)_4\text{NCl}) / \text{mol}\cdot\text{L}^{-1}$			
17.0	0.025	89±0	73±1	76±1
50.0	0.025	92±0	78±1	80±2
17.0	0.075	81±5	68±6	75±4
50.0	0.075	70±4	54±2	63±4
33.5	0.050	89±0	74±1	81±3
5.8	0.05	44	24	39
61.2	0.05	90	73	76
33.5	0.01	90	81	80
33.5	0.09	69	57	65

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.44: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

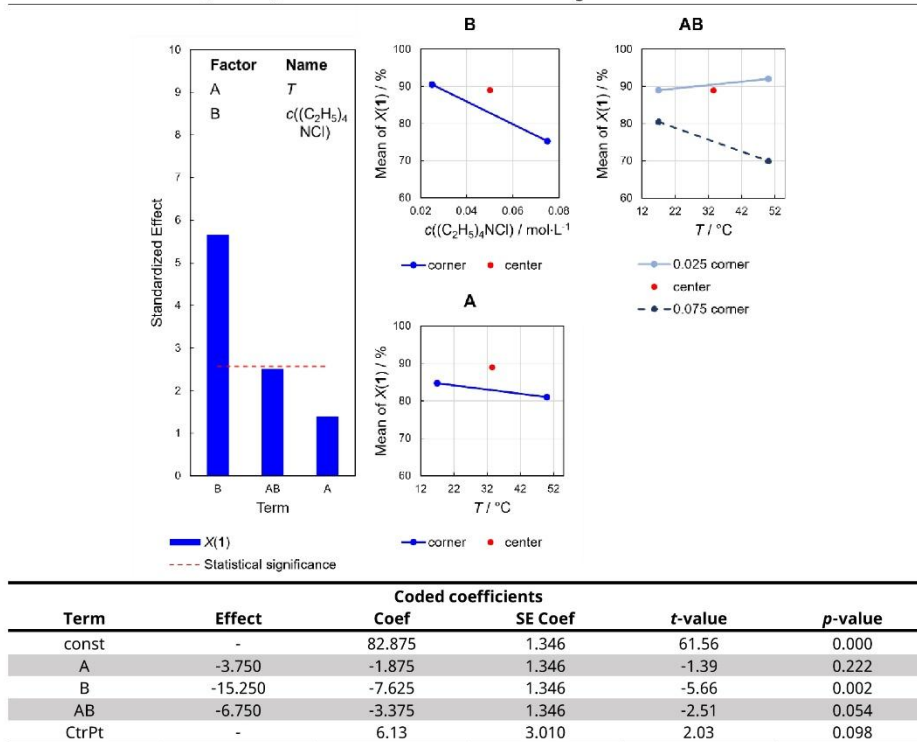


Table S3.45: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

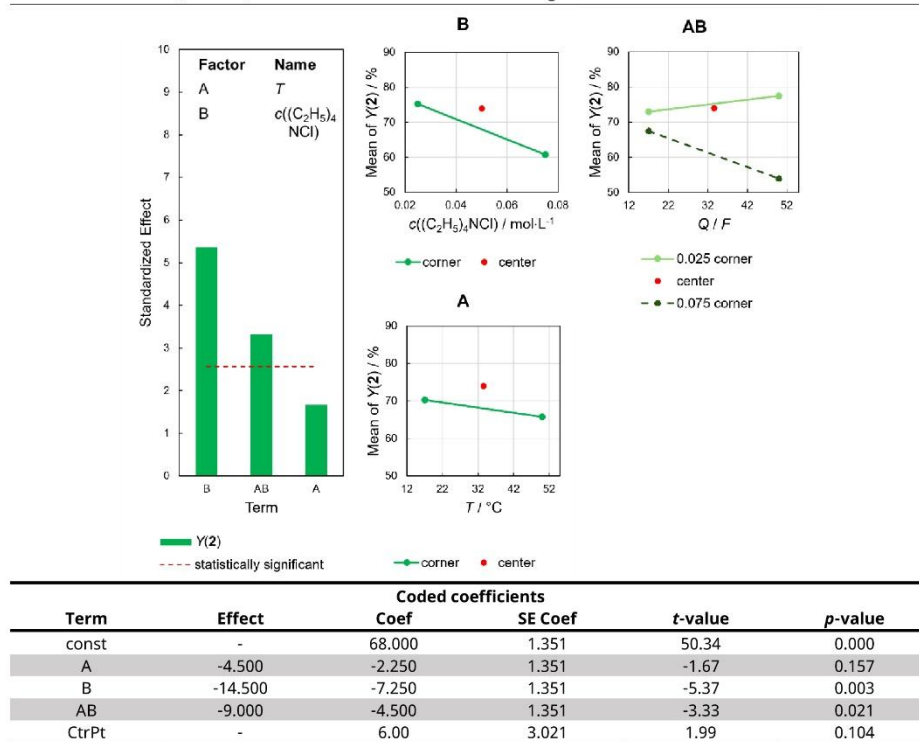


Table S3.46: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of 2,3-dichloro-1-propanol (Y(10)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

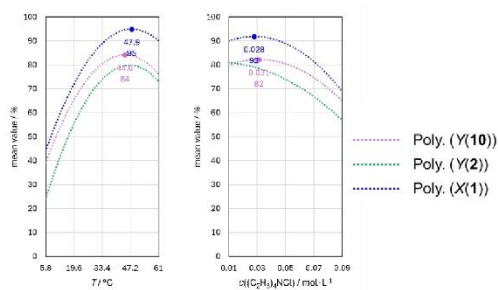
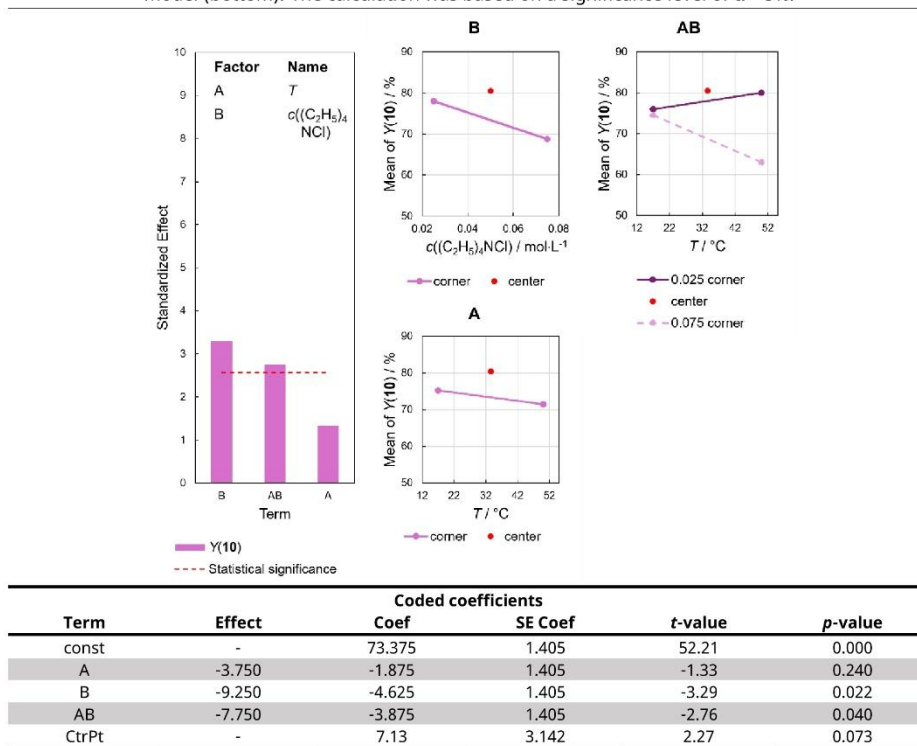
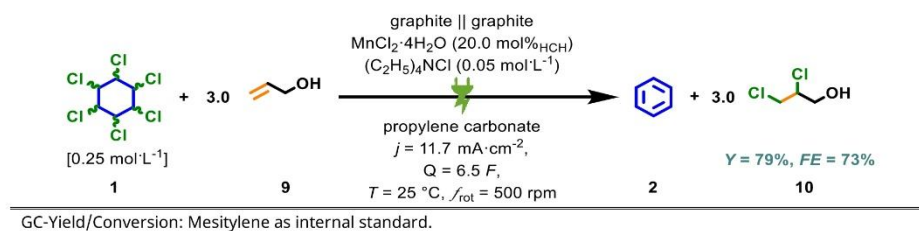


Figure S3.21: Main effect diagrams of the conversion and yield of 2,3-dichloro-1-propanol (10) and HCH (1) to benzene (2) according to the 2^2 fractional factorial experimental with central composite design (CCD).

Optimized parameters for the yield of 2,3-dichloro-1-propanol (10)

Since increasing the temperature and the associated heating costs or reducing the supporting electrolyte concentration and the associated increase in resistance only have a minor influence on the yield, the parameters were not changed. Therefore, optimization remains with the following parameters:



3.5 Kinetic Measurements

To investigate the reaction processes, various kinetic measurements were carried out and the reaction rate coefficients k were determined. The rate coefficients k of different temperatures (25 °C, 50 °C and 75 °C), solvents (acetonitrile and propylene carbonate), amounts of the catalyst manganese(II) chloride tetrahydrate (5 mol% and 20 mol%) and the HCH (**1**) concentration (0.1 mol·L⁻¹ and 0.2 mol·L⁻¹) at unchanged methyl 10-undecenoate (**3**) concentration were determined. Measurements per 1 F up to 8 F were carried out (Table S3.47).

Table S3.47: Determined amounts n_i of HCH (**1**), benzene (**2**), methyl 10-undecenoate (**3**) and methyl 10,11-dichloroundecanoate (**4**) of the kinetic investigation in propylene carbonate by changing the amount of applied charge Q at 25 °C.

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol·L⁻¹)
 propylene carbonate
 $j = 30.0 \text{ mA} \cdot \text{cm}^{-2}$,
 $Q = 0-8 F$,
 $T = 25 \text{ }^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$

Q / F	$n(1) / \text{mmol}$			$n(2) / \text{mmol}$			$n(3) / \text{mmol}$			$n(4) / \text{mmol}$		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	0.500	0.500	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
1	0.431			0.032			1.405			0.191		
	0.427	0.425	0.007	0.035	0.033	0.002	1.496	1.460	0.048	0.176	0.186	0.009
	0.418			0.032			1.478			0.192		
2	0.363			0.070			1.287			0.354		
	0.363	0.364	0.001	0.080	0.074	0.005	1.298	1.290	0.008	0.356	0.352	0.005
	0.365			0.071			1.283			0.347		
3	0.325			0.070			1.197			0.422		
	0.322	0.325	0.003	0.122	0.096	0.026	1.132	1.166	0.033	0.523	0.462	0.054
	0.327			0.094			1.168			0.441		
4	0.268			0.126			0.989			0.582		
	0.271	0.273	0.006	0.118	0.130	0.015	1.032	1.013	0.022	0.597	0.606	0.030
	0.280			0.147			1.018			0.640		
5	0.270			0.130			0.970			0.669		
	0.240	0.257	0.016	0.167	0.146	0.019	0.898	0.947	0.042	0.729	0.701	0.030
	0.261			0.141			0.973			0.703		
6	0.178			0.180			0.789			0.755		
	0.184	0.186	0.009	0.178	0.181	0.004	0.798	0.775	0.032	0.770	0.766	0.010
	0.196			0.185			0.738			0.774		
7	0.177			0.163			0.711			0.811		
	0.191	0.187	0.009	0.174	0.164	0.010	0.768	0.759	0.045	0.801	0.823	0.029
	0.194			0.154			0.799			0.856		
8	0.147			0.205			0.613			0.966		
	0.170	0.164	0.015	0.180	0.183	0.020	0.649	0.659	0.052	0.802	0.861	0.091
	0.175			0.165			0.716			0.816		

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.48: Determined amounts n_i of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) of the kinetic investigation in propylene carbonate by changing the amount of applied charge Q at 50 °C.

Q / F	$n(1) / \text{mmol}$			$n(2) / \text{mmol}$			$n(3) / \text{mmol}$			$n(4) / \text{mmol}$		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	0.500	0.500	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
1	0.432			0.054			1.496			0.214		
	0.414	0.423	0.009	0.053	0.054	0.000	1.433	1.475	0.036	0.209	0.209	0.005
	0.424			0.054			1.496			0.209		
2	0.362			0.103			1.310			0.409		
	0.344	0.346	0.015	0.104	0.101	0.005	1.285	1.298	0.012	0.419	0.414	0.005
	0.333			0.95			1.299			0.414		
3	0.284			0.149			1.104			0.616		
	0.264	0.272	0.010	0.139	0.148	0.009	1.103	1.092	0.020	0.617	0.617	0.001
	0.267			0.157			1.069			0.617		
4	0.201			0.115			0.930			0.642		
	0.216	0.211	0.008	0.182	0.165	0.045	0.966	0.949	0.018	0.781	0.749	0.095
	0.215			0.200			0.952			0.823		
5	0.164			0.206			0.850			0.899		
	0.161	0.164	0.002	0.203	0.216	0.020	0.830	0.832	0.017	0.873	0.905	0.036
	0.166			0.238			0.817			0.944		
6	0.121			0.237			0.684			1.046		
	0.117	0.119	0.002	0.224	0.239	0.015	0.727	0.692	0.032	1.019	1.038	0.017
	0.120			0.255			0.665			1.049		
7	0.070			0.337			0.489			1.135		
	0.082	0.076	0.006	0.249	0.250	0.087	0.592	0.562	0.063	1.120	1.087	0.039
	0.075			0.162			0.604			1.044		
8	0.000			0.216			0.558			1.189		
	0.000	0.000	0.000	0.300	0.257	0.042	0.427	0.502	0.067	1.190	1.175	0.036
	0.000			0.254			0.520			1.201		
9	0.000			0.251			0.436			1.186		
	0.000	0.000	0.000	0.237	0.253	0.017	0.460	0.432	0.030	1.245	1.216	0.030
	0.000			0.271			0.400			1.216		
10	0.000			0.212			0.425			1.209		
	0.000	0.000	0.000	0.195	0.216	0.023	0.466	0.443	0.021	1.181	1.200	0.017
	0.000			0.240			0.438			1.212		

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.49: Determined amounts n_i of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) of the kinetic investigation in propylene carbonate by changing the amount of applied charge Q at 75 °C.

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0 mol% $_{\text{HCH}}$)
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.1 mol L $^{-1}$)
 propylene carbonate
 $j = 30.0 \text{ mA cm}^{-2}$,
 $Q = 0\text{--}11 F$,
 $T = 75 \text{ }^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$

1 **3** **2** **4**

Q / F	$n(1) / \text{mmol}$	$n(2) / \text{mmol}$	$n(3) / \text{mmol}$	$n(4) / \text{mmol}$								
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	0.500	0.500	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
	0.435			0.073			1.495			0.246		
1	0.430	0.427	0.009	0.068	0.068	0.006	1.499	1.514	0.030	0.281	0.251	0.028
	0.417			0.061			1.548			0.225		
2	0.339			0.145			1.283			0.540		
	0.350	0.348	0.008	0.106	0.122	0.021	1.222	1.293	0.076	0.494	0.514	0.024
3	0.355			0.114			1.373			0.508		
	0.306			0.240			1.145			0.759		
4	0.283	0.287	0.017	0.201	0.209	0.027	1.023	1.105	0.071	0.711	0.716	0.041
	0.272			0.187			1.148			0.678		
5	0.248			0.299			1.041			1.097		
	0.211	0.220	0.025	0.246	0.259	0.035	0.839	0.944	0.101	0.926	0.988	0.095
6	0.202			0.233			0.951			0.940		
	0.159			0.302			0.887			1.297		
7	0.158	0.155	0.005	0.262	0.269	0.031	0.764	0.800	0.076	1.097	1.129	0.155
	0.149			0.241			0.749			0.993		
8	0.119			0.333			0.608			1.293		
	0.113	0.115	0.003	0.335	0.317	0.029	0.584	0.623	0.048	1.092	1.184	0.101
9	0.113			0.284			0.677			1.168		
	0.090			0.360			0.570			1.468		
10	0.091	0.081	0.016	0.345	0.335	0.031	0.508	0.536	0.032	1.304	1.312	0.152
	0.063			0.300			0.531			1.164		
11	0.055			0.383			0.430			1.335		
	0.073	0.061	0.010	0.373	0.362	0.029	0.433	0.452	0.036	1.286	1.286	0.050
12	0.054			0.329			0.494			1.236		
	0.050			0.398			0.350			1.364		
13	0.051	0.048	0.004	0.381	0.381	0.017	0.353	0.357	0.010	1.332	1.281	0.116
	0.044			0.364			0.386			1.148		
14	0.041			0.451			0.403			1.531		
	0.029	0.033	0.007	0.359	0.383	0.060	0.307	0.354	0.048	1.309	1.330	0.191
15	0.028			0.338			0.351			1.151		
	0.023			0.389			0.285			1.183		
16	0.000	0.016	0.014	0.411	0.385	0.027	0.212	0.245	0.037	1.013	1.074	0.095
	0.026			0.357			0.238			1.027		

GC-Yield/Conversion: Mesitylene as internal standard.

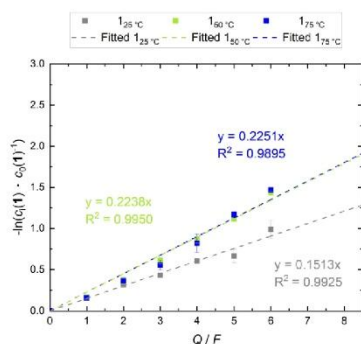


Figure S3.22: Measured degradation rate coefficient of HCH $k(1)$ as a function of temperature.

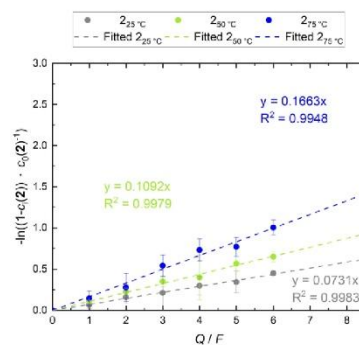


Figure S3.23: Measured formation rate coefficient of benzene $k(2)$ as a function of temperature.

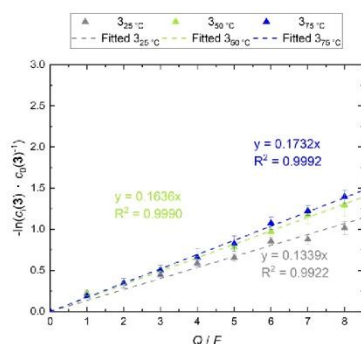


Figure S3.24: Measured degradation rate coefficient of methyl 10-undecenoate $k(3)$ as a function of temperature.

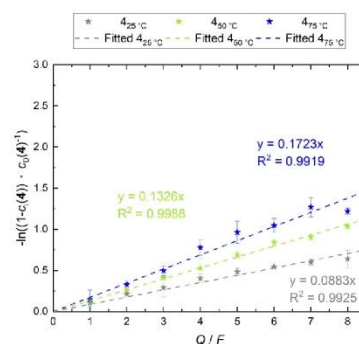


Figure S3.25: Measured formation rate coefficient of methyl 10,11-dichloroundecanoate $k(4)$ as a function of temperature.

Table S3.50: Measured reaction rate coefficients k of degradation and evolution as a function of temperature.

$T / ^\circ\text{C}$	$k(1) / 1 \cdot \text{F}^{-1}$	$k(2) / 1 \cdot \text{F}^{-1}$	$k(3) / 1 \cdot \text{F}^{-1}$	$k(4) / 1 \cdot \text{F}^{-1}$
25	0.1513	0.0731	0.1339	0.0883
50	0.2238	0.1092	0.1636	0.1326
75	0.2251	0.1663	0.1732	0.1723

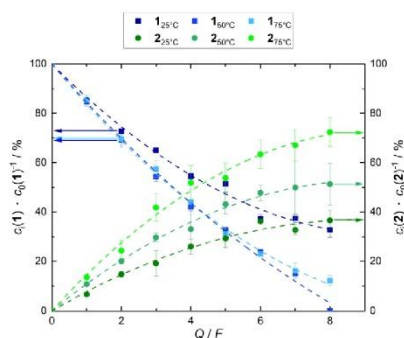


Figure S3.26: Measured relative concentration based on their starting concentration of HCH (1) and benzene (2) as function of temperature.

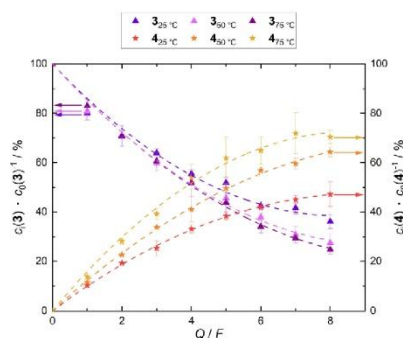


Figure S3.27: Measured relative concentration based on their starting concentration of methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) as function of temperature.

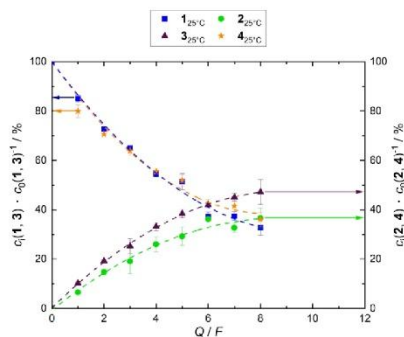


Figure S3.28: Measured relative concentration based on their starting concentration of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) at 25 °C.

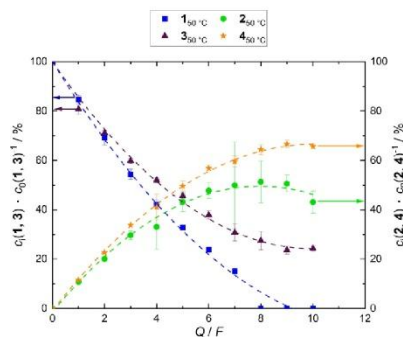


Figure S3.29: Measured relative concentration based on their starting concentration of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) at 50 °C.

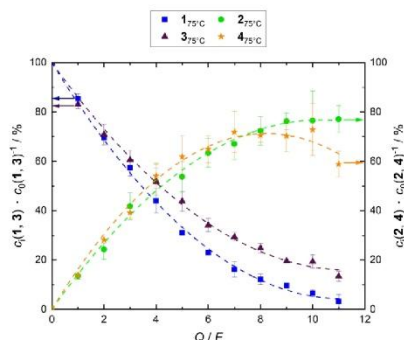


Figure S3.30: Measured relative concentration based on their starting concentration of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) at 75 °C.

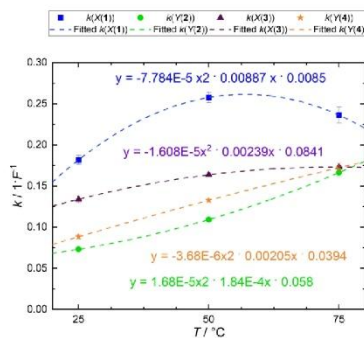


Figure S3.31: Measured reaction rate coefficients k of degradation and formation as a function of temperature.

Table S3.51: Conversion of HCH X(1) and methyl 10-undecenoate X(3) and yield of benzene Y(2), methyl 10,11-dichloroundecanoate Y(4) and their current yields *FE* in propylene carbonate over the amount of applied charge *Q* at 75 °C.

<i>Q</i> / <i>F</i>	X(1) / %	FE(1) / %	Y(2) / %	FE(2) / %	X(3) / %	FE(3) / %	Y(4) / %	FE(4) / %
0	100.0	100.0	0.0	100.0	100.0	100.0	0.0	100.0
1	85.4	87.4	13.5	81.2	83.0	102.1	13.7	82.5
2	69.6	91.3	24.3	73.0	70.8	87.5	28.2	84.5
3	57.4	85.2	41.8	83.6	60.6	78.9	39.2	78.5
4	44.0	84.0	51.8	77.7	51.7	72.4	54.1	81.2
5	31.1	82.7	53.7	64.5	43.8	67.4	61.9	74.2
6	23.0	77.0	63.4	63.4	34.1	65.9	64.9	64.9
7	16.2	71.8	67.0	57.5	29.4	60.5	71.9	61.6
8	12.2	65.9	78.3	54.3	24.8	56.4	70.4	52.8
9	9.7	60.2	76.2	50.8	19.6	53.6	70.2	46.8
10	6.5	56.1	76.5	45.9	19.4	48.4	72.9	43.7
11	3.2	52.8	77.1	42.1	13.4	47.2	58.9	32.1

GC-Yield/Conversion: Mesitylene as internal standard.

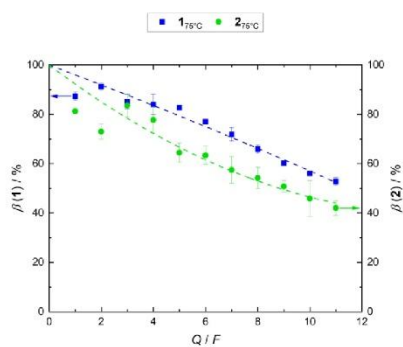


Figure S3.32: Measured current yield of HCH FE(1) and Benzene FE(2).

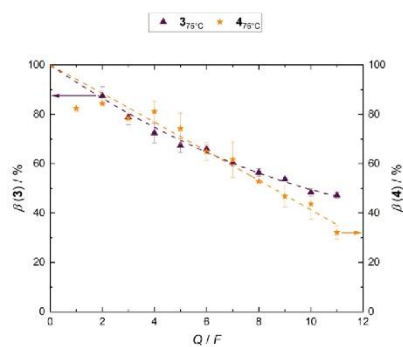
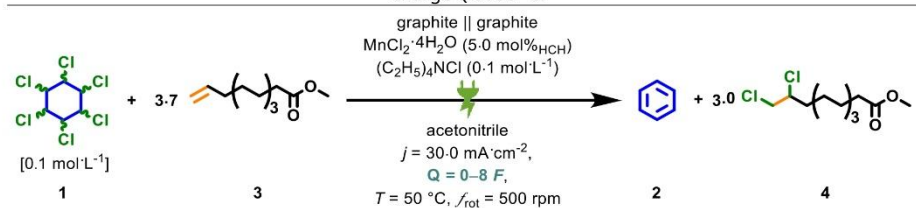


Figure S3.33: Measured current yield of methyl 10-undecenoate FE(3) and 10,11-dichloroundecanoate FE(4).

Table S3.52: Determined amounts n_i of HCH (1), benzene (2), methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) of the kinetic investigation in acetonitrile by changing the amount of applied charge Q at 50 °C.



Q / F	n(1) / mmol			n(2) / mmol			n(3) / mmol			n(4) / mmol		
	Values	$\varnothing$	Δ	Values	$\varnothing$	Δ	Values	$\varnothing$	Δ	Values	$\varnothing$	Δ
0	0.500	0.500	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
	0.381			0.060			1.374			0.000		
1	0.390	0.394	0.016	0.065	0.061	0.003	1.378	1.402	0.044	0.000	0.000	0.000
	0.411			0.059			1.452			0.000		
2	0.309	0.305	0.023	0.125	0.128	0.003	1.164			0.233		
	0.280			0.132			1.121	1.206	0.037	0.252	0.244	0.010
3	0.326			0.128			1.233			0.247		
	0.246			0.193			0.988			0.399		
4	0.214	0.228	0.017	0.202	0.197	0.005	0.990	0.998	0.015	0.429	0.425	0.024
	0.223			0.194			1.015			0.446		
5	0.174	0.156	0.016	0.251	0.267	0.014	0.820			0.686		
	0.145			0.278			0.755	0.783	0.034	0.649	0.665	0.019
6	0.150			0.272			0.772			0.661		
	0.104	0.101	0.004	0.325	0.334	0.009	0.565			0.805		
7	0.104			0.343			0.555	0.568	0.014	0.709	0.778	0.060
	0.097			0.335			0.583			0.819		
8	0.058	0.057	0.001	0.391	0.388	0.003	0.409			0.831		
	0.057			0.386			0.373	0.392	0.018	0.772	0.814	0.036
9	0.056			0.388			0.394			0.838		
	0.000	0.000	0.000	0.431	0.434	0.002	0.273			0.968		
10	0.000			0.435			0.218	0.250	0.028	0.817	0.914	0.085
	0.000			0.435			0.259			0.958		
11	0.000	0.000	0.000	0.423	0.435	0.013	0.150			0.871		
	0.000			0.449			0.141	0.145	0.005	0.868	0.869	0.002
12	0.000			0.434			0.144			0.869		

GC-Yield/Conversion: Mesitylene as internal standard.

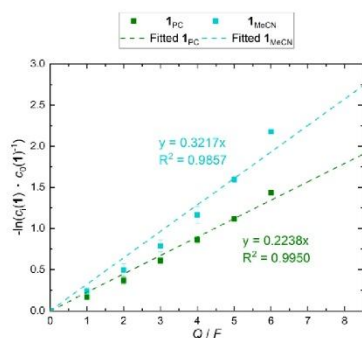


Figure S3.34: Measured degradation rate coefficient of HCH $k(1)$ as a function of solvent.

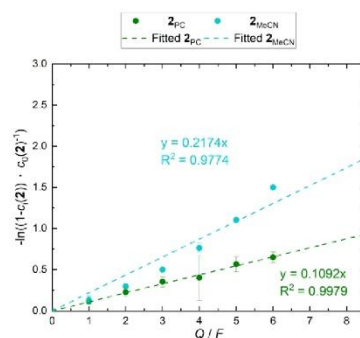


Figure S3.35: Measured formation rate coefficient of benzene $k(2)$ as a function of solvent.

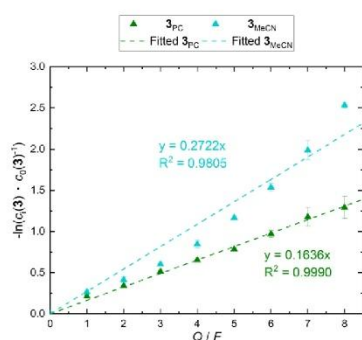


Figure S3.36: Measured degradation rate coefficient of methyl 10-undecenoate $k(3)$ as a function of solvent.

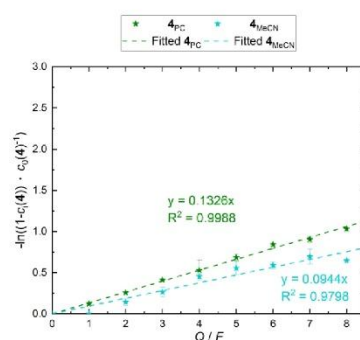


Figure S3.37: Measured formation rate coefficient of methyl 10,11-dichloroundecanoate $k(4)$ as a function of solvent.

Table S 3.53: Measured reaction rate coefficients k of degradation and evolution as a function of solvent at 50 °C.

Solvent	$k(1) / 1 \cdot F^{-1}$	$k(2) / 1 \cdot F^{-1}$	$k(3) / 1 \cdot F^{-1}$	$k(4) / 1 \cdot F^{-1}$
PC	0.2238	0.1092	0.1636	0.1326
ACN	0.3217	0.2174	0.2722	0.0944

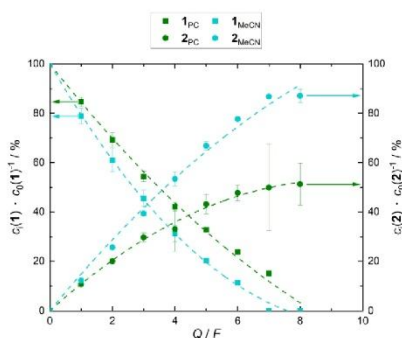


Figure S3.38: Measured relative concentration based on their starting concentration of HCH (1) and benzene (2) as function of the solvent at 50 °C.

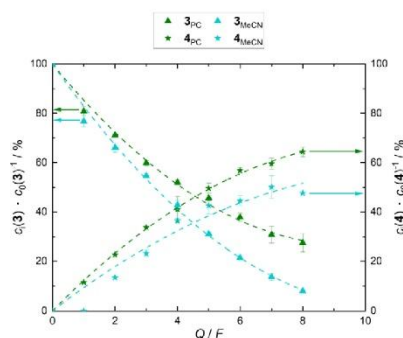


Figure S3.39: Measured relative concentration based on their starting concentration of methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) as function of the solvent at 50 °C.

Table S3.54: Determined amounts n_i of HCH (3), benzene (2), methyl 10-undecanoate (3) and methyl 10,11-dichloroundecanoate (4) of the kinetic investigation in propylene carbonate by changing the amount of applied charge Q at 75 °C with 20 mol% catalyst.

ClC1(Cl)C(Cl)C(Cl)C(Cl)C1Cl + 3.7 CCCCCCCCC(=O)OC $\xrightarrow[\text{propylene carbonate}]{\text{graphite || graphite, MnCl}_2 \cdot 4\text{H}_2\text{O (20.0 mol\% HCH), (C}_2\text{H}_5)_4\text{NCl (0.1 mol L}^{-1}\text{), } j = 30.0 \text{ mA cm}^{-2}, Q = 0-8 F, T = 75 \text{ }^\circ\text{C, } f_{\text{rot}} = 500 \text{ rpm}}$ c1ccccc1 + 3.0 ClC1(Cl)C(Cl)C(Cl)C(Cl)C1Cl

1 3 2 4
 [0.1 mol L⁻¹]

Q / F	n(1) / mmol			n(2) / mmol			n(3) / mmol			n(4) / mmol		
	Values	$\bar{\theta}$	Δ	Values	$\bar{\theta}$	Δ	Values	$\bar{\theta}$	Δ	Values	$\bar{\theta}$	Δ
0	0.500	0.500	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
1	0.390	0.401	0.011	0.055	0.060	0.004	1.467	1.444	0.004	0.175	0.187	0.012
	0.411			0.060			1.438			0.198		
	0.401			0.063			1.428			0.189		
2	0.311	0.319	0.007	0.115	0.119	0.004	1.254	1.233	0.004	0.371	0.392	0.019
	0.322			0.120			1.217			0.397		
	0.325			0.123			1.230			0.408		
3	0.230	0.250	0.018	0.184	0.171	0.011	1.017	1.043	0.011	0.547	0.578	0.035
	0.252			0.164			1.039			0.571		
	0.267			0.166			1.073			0.616		
4	0.175	0.192	0.015	0.233	0.196	0.062	0.887	0.895	0.062	0.685	0.695	0.062
	0.202			0.125			0.925			0.639		
	0.200			0.231			0.873			0.762		
5	0.117	0.118	0.014	0.270	0.288	0.016	0.696	0.678	0.016	0.836	0.860	0.021
	0.105			0.292			0.654			0.876		
	0.133			0.301			0.684			0.867		
6	0.057	0.074	0.015	0.297	0.302	0.013	0.547	0.574	0.013	0.924	0.934	0.014
	0.081			0.292			0.582			0.929		
	0.084			0.316			0.592			0.950		
7	0.043	0.051	0.008	0.340	0.344	0.003	0.462	0.478	0.003	0.951	0.973	0.025
	0.049			0.345			0.460			0.968		
	0.059			0.347			0.511			1.000		
8	0.033	0.044	0.015	0.365	0.345	0.047	0.418	0.428	0.047	0.978	0.987	0.050
	0.061			0.291			0.446			0.943		
	0.037			0.379			0.419			1.042		

GC-Yield/Conversion: Mesitylene as internal standard.

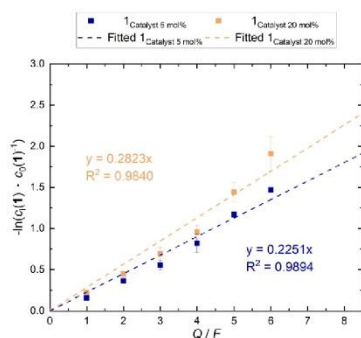


Figure S3.40: Measured degradation rate coefficient of HCH $k(1)$ as a function of catalyst concentration.

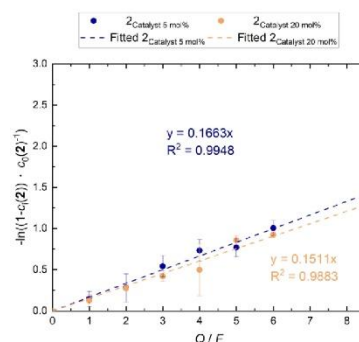


Figure S3.41: Measured formation rate coefficient of benzene $k(2)$ as a function of catalyst concentration.

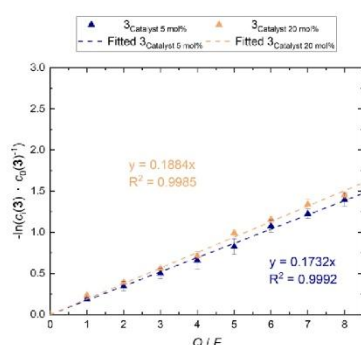


Figure S3.42: Measured degradation rate coefficient of methyl 10-undecenoate $k(3)$ as a function of catalyst concentration.

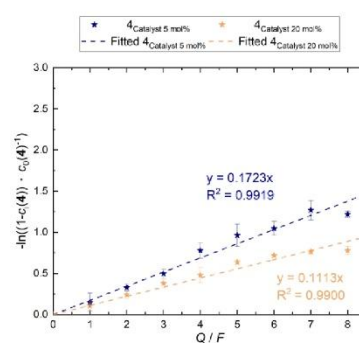


Figure S3.43: Measured formation rate coefficient of methyl 10,11-dichloroundecanoate $k(4)$ as a function of catalyst concentration.

Table S3.55: Measured reaction rate coefficients k of degradation and formation as a function of the concentration of the catalyst (manganese(II) chloride tetrahydrate) at a temperature of 75 °C.

$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) /$ $\text{mol}\%_{\text{HCH}}$	$k(1) /$ $1 \cdot \text{F}^{-1}$	$k(2) /$ $1 \cdot \text{F}^{-1}$	$k(3) /$ $1 \cdot \text{F}^{-1}$	$k(4) /$ $1 \cdot \text{F}^{-1}$
5	0.2251	0.1663	0.1732	0.1723
20	0.2823	0.1511	0.1884	0.1113

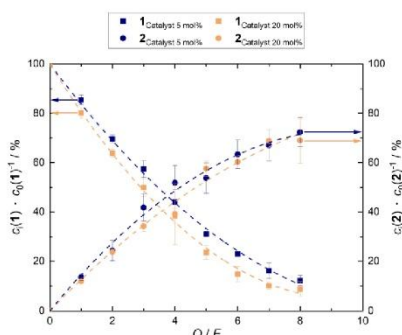


Figure S3.44: Measured relative concentration based on their starting concentration of HCH (1) and benzene (2) as function of catalyst concentration at 75 °C.

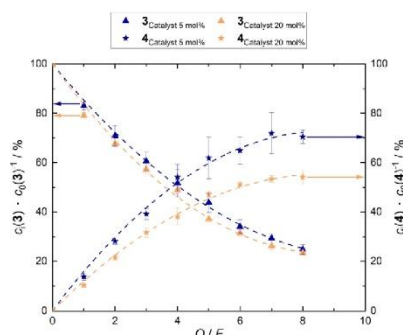
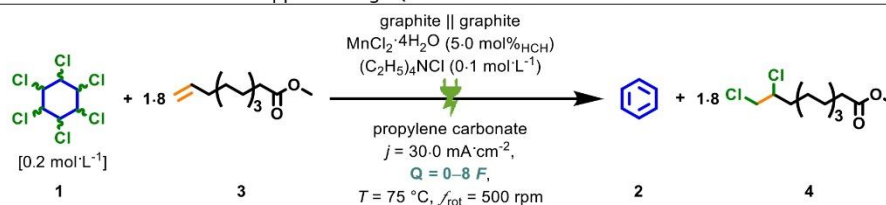


Figure S3.45: Measured relative concentration based on their starting concentration of methyl 10-undecenoate (**3**) and methyl 10,11-dichloroundecanoate (**4**) as function of catalyst concentration at 75 °C.

Table S3.56: Determined amounts n_i of HCH (**1**), benzene (**2**), methyl 10-undecanoate (**3**) and methyl 10,11-dichloroundecanoate (**4**) of the kinetic investigation in propylene carbonate by changing the amount of applied charge Q at 75 °C with 0.2 mol·L⁻¹ of **1**.



Q / F	n(1) / mmol			n(2) / mmol			n(3) / mmol			n(4) / mmol		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	1.000	1.000	0.000	0.000	0.000	0.000	1.825	0.000	0.000	0.000	0.000	0.000
	0.770			0.117			1.165			0.400		
1	0.786	0.797	0.035	0.127	0.123	0.005	1.195	1.186	0.019	0.410	0.405	0.005
	0.837			0.125			1.199			0.406		
2	0.628	0.626	0.013	0.269	0.264	0.008	0.766	0.768	0.004	0.886	0.890	0.016
	0.638			0.255			0.766			0.907		
3	0.612			0.269			0.773			0.877		
	0.473	0.473	0.003	0.388	0.342	0.053	0.437	0.458	0.036	1.237	1.149	0.076
	0.476			0.284			0.499			1.102		
4	0.470			0.352			0.437			1.110		
	0.357	0.343	0.014	0.523	0.521	0.004	0.112	0.092	0.018	1.334	1.372	0.044
	0.343			0.516			0.077			1.420		
5	0.329			0.523			0.087			1.361		
	0.229	0.232	0.006	0.602	0.587	0.013	0.000	0.000	0.000	1.369	1.396	0.032
	0.239			0.582			0.000			1.432		
6	0.229			0.578			0.000			1.388		
	0.175	0.169	0.011	0.694	0.671	0.020	0.000	0.000	0.000	0.978	0.960	0.045
	0.175			0.655			0.000			0.992		
7	0.156			0.665			0.000			0.908		
	0.106	0.101	0.005	0.742	0.713	0.033	0.000	0.000	0.000	1.203	1.140	0.121
	0.101			0.678			0.000			1.216		
8	0.095			0.718			0.000			1.000		
	0.063	0.060	0.003	0.730	0.756	0.024	0.000	0.000	0.000	0.934	0.999	0.183
	0.059			0.778			0.000			1.206		
	0.057			0.758			0.000			0.857		

GC-Yield/Conversion: Mesitylene as internal standard.

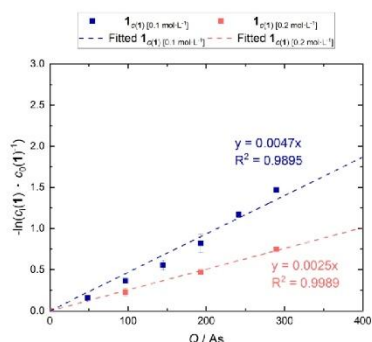


Figure S3.46: Measured degradation rate coefficient of HCH $k(1)$ as a function of concentration of HCH ($c(1)$).

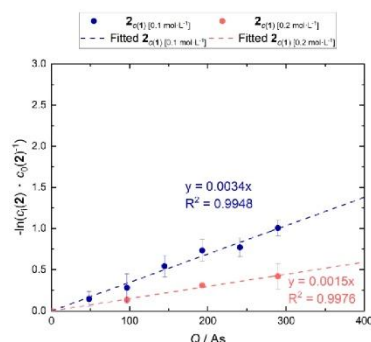


Figure S3.47: Measured formation rate coefficient of benzene $k(2)$ as a function of concentration of HCH ($c(1)$).

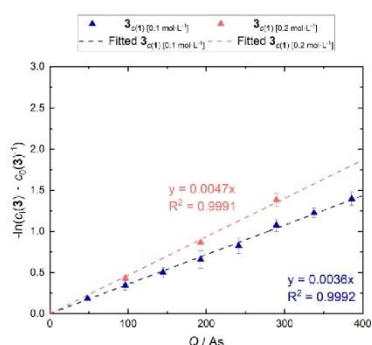


Figure S3.48: Measured degradation rate coefficient of methyl 10-undecenoate $k(3)$ as a function of concentration of HCH ($c(1)$).

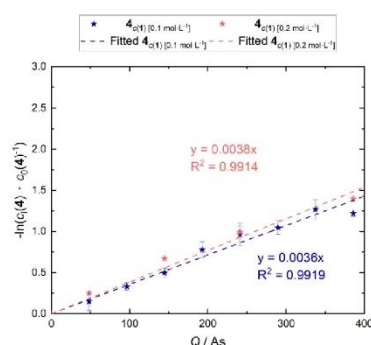


Figure S3.49: Measured formation rate coefficient of methyl 10,11-dichloroundecanoate $k(4)$ as a function of concentration of HCH ($c(1)$).

Table S3.57: Measured reaction rate coefficients k of degradation and formation as a function of the HCH concentration at a temperature of 75 °C.

$c(1) / \text{mol} \cdot \text{L}^{-1}$	$k(1) / 1 \cdot \text{F}^{-1}$	$k(2) / 1 \cdot \text{F}^{-1}$	$k(3) / 1 \cdot \text{F}^{-1}$	$k(4) / 1 \cdot \text{F}^{-1}$
0.1	0.0047	0.0034	0.0036	0.0036
0.2	0.0025	0.0015	0.0047	0.0038

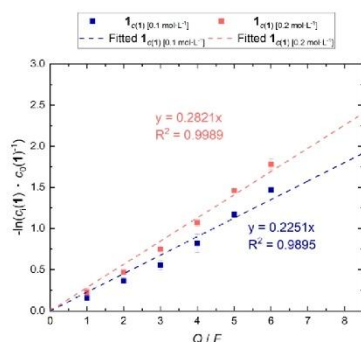


Figure S3.50: Measured degradation rate coefficient of HCH $k(1)$ as a function of concentration of HCH ($c(1)$).

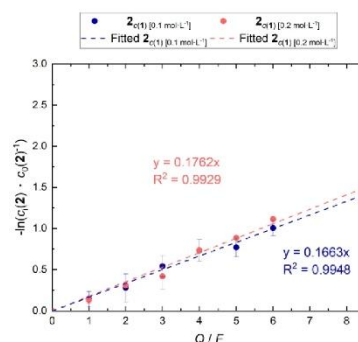


Figure S3.51: Measured formation rate coefficient of benzene $k(2)$ as a function of concentration of HCH ($c(1)$).

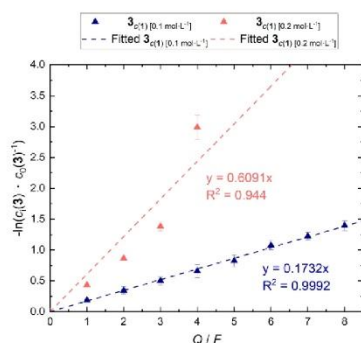


Figure S3.52: Measured degradation rate coefficient of methyl 10-undecenoate $k(3)$ as a function of concentration of HCH ($c(1)$).

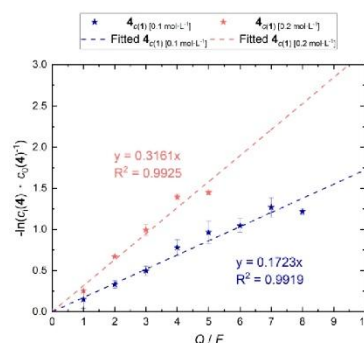


Figure S3.53: Measured formation rate coefficient of methyl 10,11-dichloroundecanoate $k(4)$ as a function of concentration of HCH ($c(1)$).

Table S3.58: Measured reaction rate coefficients k of degradation and formation as a function of the HCH concentration at a temperature of 75 °C.

$c(1) /$ $\text{mol} \cdot \text{L}^{-1}$	$k(1) /$ $1 \cdot \text{F}^{-1}$	$k(2) /$ $1 \cdot \text{F}^{-1}$	$k(3) /$ $1 \cdot \text{F}^{-1}$	$k(4) /$ $1 \cdot \text{F}^{-1}$
0.1	0.2251	0.1663	0.1732	0.1723
0.2	0.2821	0.1762	0.6091	0.3161

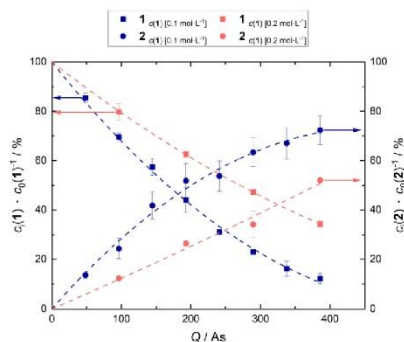


Figure S3.54: Measured relative concentration based on their starting concentration of HCH (1) and benzene (2) as function of HCH concentration ($c(1)$).

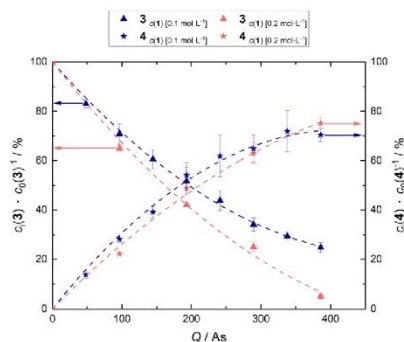


Figure S3.55: Measured relative concentration based on their starting concentration of methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) as function of HCH concentration ($c(1)$).

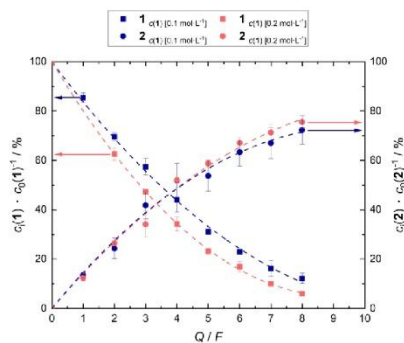


Figure S3.56: Measured relative concentration based on their starting concentration of HCH (1) and benzene (2) as function of HCH concentration ($c(1)$).

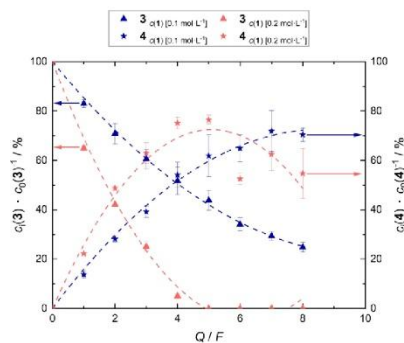


Figure S3.57: Measured relative concentration based on their starting concentration of methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) as function of HCH concentration ($c(1)$).

3.5 Process Development

Recyclability of the electrodes

After electrolysis, the graphite electrodes show surface changes due to cathodic fouling. This is caused by the diffusion of ions between the graphite layers during electrolysis. Such intercalation leads, over time, to slight diffraction of the graphite and the flaking of small amounts of superficial graphite material (right).

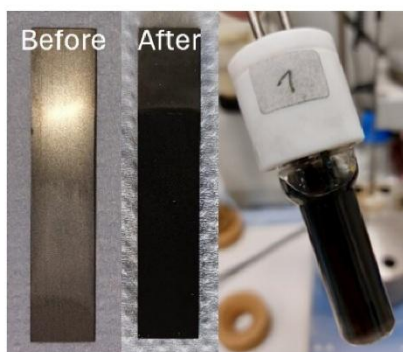


Figure S3.58: Electrodes before and after electrolysis (left) and solution after methyl 10-undecenoate (3) electrolysis with graphite particles.

The recyclability was carried out during the optimization of the substrate with only 3.0 equivalents of methyl 10-undecenoate (3). For this reason, the yields of benzene (2) and methyl 10,11-dichloroundecanoate (4) deviate from the final optimized yield. Nevertheless, the results can be transferred to other electrolysis processes.

Table S3.59: Effects of the electrodes over 10 repetitions on the example reaction of methyl 10,11-dichloroundecanoate (4).

$ \begin{array}{c} \text{graphite} \parallel \text{graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \text{ (5.0 mol\%}_{\text{HCH}}\text{)} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.1 mol L}^{-1}\text{)} \\ \text{propylene carbonate} \\ j = 30.0 \text{ mA cm}^{-2}, \\ Q = 10.1 F, \\ T = 75^\circ\text{C}, \text{ } \omega_{\text{rot}} = 500 \text{ rpm} \end{array} $				
<chem>ClC1(Cl)C(Cl)C(Cl)C(Cl)C1</chem> + 3.0 <chem>CCCCCCCCC=CC(=O)OC</chem> [0.1 mol L ⁻¹]			<chem>c1ccccc1</chem> + 3.0 <chem>ClCCCCCCCCC(=O)OC</chem>	
1	3		2	4
Run	X(1) / %	Y(2) / %	X(3) / %	Y(4) / %
1	88	68	97	61
2	83	54	87	61
3	>99	37	84	64
4	89	47	83	60
5	>99	33	81	66
6	88	50	85	59
7	>99	44	83	61
8	>99	46	84	65
9	>99	37	81	69
10	>99	47	82	65

GC-Yield/Conversion: Mesitylene as internal standard.

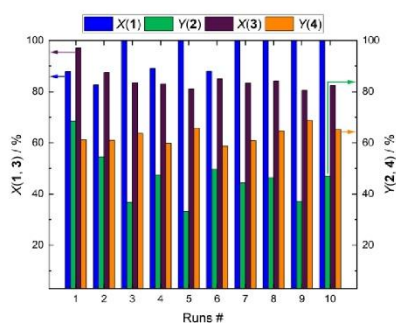


Figure S3.59: Measured conversion of HCH X(1) and methyl 10-undecenoate X(3) yield of benzene Y(2) and methyl 10,11-dichloroundecanoate Y(4) per run.

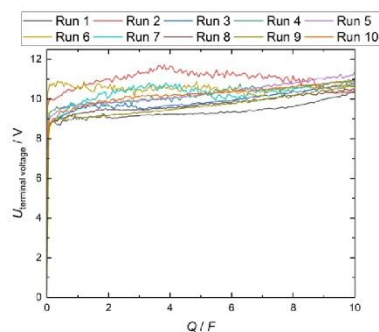


Figure S3.60: Terminal voltage during the recyclability of electrodes without polishing.

Recyclability of the reaction solution - Extraction of methyl 10,11-dichloroundecanoate (4)

To investigate the industrial down-streaming of the substrates, the synthesis of 6 is carried out in a 50 mL cell, as the import of tubes can be carried out directly on the cell. After completion of the electrolysis, 1 mL of the reaction solution was collected and 70 μ L of mesitylene was added and measured via GC. After removing the sample, the solution was sparged multiple times with 5 mL of heptane each time, stirred for 5 minutes and the extract was removed after settling using a pump (SF-10 (Vapourtec Ltd, Bury St Edmunds, UK)).



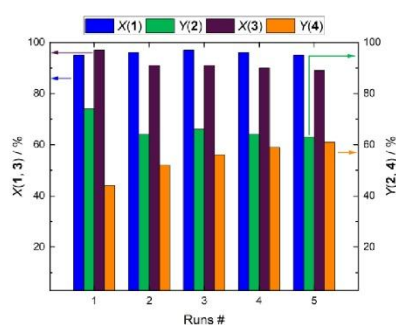
Figure S3.61: Extraction of methyl 10-undecenoate (3) and methyl 10,11-dichloroundecanoate (4) with heptane after electrolysis.

After the extraction, 1 mL of propylene carbonate was added back to the sample with the equivalent amount of supporting electrolyte and catalyst. The converted amount of HCH (1) and fresh methyl 10-undecenoate (3) was then added again, as it was completely removed during the extraction. The electrolysis was then started again (Table S3.60 and Figure S3.64).

Table S3.60: Effects of the extraction of the product over 5 repetitions on the example reaction of methyl 10,11-dichloroundecanoate (**4**).

$ \begin{array}{c} \text{graphite} \parallel \text{graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \text{ (5.0 mol\%}_{\text{HCH}}\text{)} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.1 mol\%)} \\ \text{propylene carbonate} \\ j = 30.0 \text{ mA}\cdot\text{cm}^{-2}, \\ Q = 10.1 \text{ F}, \\ T = 75^\circ\text{C}, \omega_{\text{rot}} = 500 \text{ rpm} \end{array} $				
<chem>ClC1C(Cl)C(Cl)C(Cl)C(Cl)C1</chem> + 3-7 <chem>CCCCCCCCC(=O)OCC</chem> [0.1 mol·L ⁻¹]			<chem>c1ccccc1</chem> + 3-0 <chem>ClC1C(Cl)C(Cl)C(Cl)C(Cl)C1</chem> 2 4	
1	3		2	4
Run	X(1) / %	Y(2) / %	X(3) / %	Y(4) / %
1	95	74	97	44
2	96	64	91	52
3	97	66	91	56
4	96	64	90	59
5	95	63	89	61

GC-Yield/Conversion: Mesitylene as internal standard.

**Figure S3.62:** Measured conversion of HCH X(1) and methyl 10-undecenoate X(3) yield of benzene Y(2) and methyl 10,11-dichloroundecanoate Y(4) per run with extraction of **3** and **4**.

The extracts were combined; the heptane removed under reduced pressure and the residue distilled off. In the process, 7.379 g of the product was isolated. This corresponds to an average extraction efficiency of 92%. This also explains the increase in product in the reaction solution over the number of runs.

Recyclability of the reaction solution – Distillation of 1,2-dichloroethyl acetate (**8**)

Since 1,2-dichloroethyl acetate (**8**) cannot be extracted out of propylene carbonate, a distillation was carried out after the reaction. After the reaction, another 1 mL sample was taken, 70 μL mesitylene was added and measured by GC. The remaining vinyl acetate and benzene are then condensed into liquid nitrogen under reduced pressure (Figure S3.65). A distillation bridge is then set up and the expected amount of product is distilled off.



Figure S3.63: Distillation system for the distillation of 1,2-dichloroethyl acetate (**8**).

After the distillation, 1 mL of propylene carbonate was added back to the sample with the equivalent amount of supporting electrolyte and catalyst. The converted amount of HCH and fresh allyl alcohol was then added, as it was completely removed during distillation. The electrolysis was then restarted (Table S3.63-63).

Table S3.61: Effects of the distillation of the product over 5 repetitions on the example reaction of 1,2-dichloroethyl acetate (**8**). Without drying agent.

$ \begin{array}{c} \text{graphite} \parallel \text{graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \text{ (15 mol\%}_{\text{HCH}}\text{)} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.05 mol\%L}^{-1}\text{)} \\ \text{propylene carbonate} \\ j = 5 \text{ mA}\cdot\text{cm}^{-2}, \\ Q = 7.2 \text{ F,} \\ T = 25 \text{ }^\circ\text{C, } f_{\text{rot}} = 500 \text{ rpm} \end{array} $			
 [0.2 mol·L ⁻¹]	 3.0	 2	 3.0
Run	X(1) / %	Y(2) / %	Y(8) / %
1	82	54	83
2	67	52	102
3	89	21	33
4	76	37	42
5	51	16	24

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.62: Effects of the distillation of the product over 5 repetitions on the example reaction of 1,2-dichloroethyl acetate (**8**). Without drying agent.

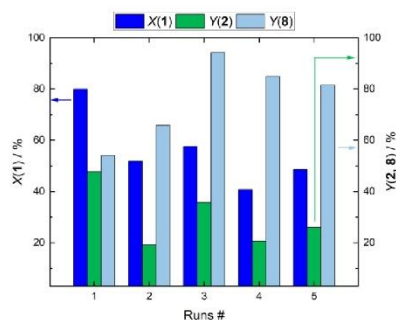
$ \begin{array}{c} \text{graphite} \parallel \text{graphite} \\ \text{Mn(OAc)}_2 \text{ (15 mol\%}_{\text{HCH}}\text{)} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.05 mol\%L}^{-1}\text{)} \\ \text{propylene carbonate} \\ j = 5 \text{ mA}\cdot\text{cm}^{-2}, \\ Q = 7.2 \text{ F,} \\ T = 25 \text{ }^\circ\text{C, } f_{\text{rot}} = 500 \text{ rpm} \end{array} $			
 [0.2 mol·L ⁻¹]	 3.0	 2	 3.0
Run	X(1) / %	Y(2) / %	Y(8) / %
1	82	49	57
2	74	47	63
3	61	36	52
4	52	27	37
Further attempts abandoned			

GC-Yield/Conversion: Mesitylene as internal standard.

Table S3.63: Effects of the distillation of the product over 5 repetitions on the example reaction of 1,2-dichloroethyl acetate (**8**). 20 mmol of CaCO_3 was added for each run before starting the electrolysis.

graphite graphite $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (15 mol%$_{\text{HCH}}$) $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.05 molL^{-1}) 20 mmol CaCO_3 propylene carbonate $j = 5 \text{ mA}\cdot\text{cm}^{-2}$, $Q = 7.2 F$, $T = 25^\circ\text{C}$, $f_{\text{rot}} = 500 \text{ rpm}$			
<chem>ClC1=CC=C(Cl)C(Cl)=C1</chem> 1 [0.2 mol L^{-1}]	+ 3.0 <chem>CC(=O)OCCl</chem> 7	<chem>c1ccccc1</chem> 2 + 3.0 <chem>CC(=O)OCCl</chem> 8	
Run	$X(1) / \%$	$Y(2) / \%$	$Y(8) / \%$
1	80	48	54
2	52	19	66
3	58	36	94
4	41	21	85
5	49	26	82

GC-Yield/Conversion: Mesitylene as internal standard.

**Figure S3.64:** Measured conversion of HCH $X(1)$ yield of benzene $Y(2)$ and 1,2-dichloroethyl acetate $Y(8)$ per run with Distillation of **2** and **8**. 20 mmol of CaCO_3 was added for each run before starting the electrolysis.

The fractions were combined and distilled again under reduced pressure 8.19 g of the product was isolated. This corresponds to an average distillation efficiency of 71%.

Recyclability of the reaction solution – Distillation of 2,3-dichloro-1-propanol (**10**)

As 2,3-dichloro-1-propanol (**10**) cannot be extracted, a distillation was carried out after the reaction. After the reaction, another 1 mL sample was taken, 70 μL mesitylene was added and measured by GC. The remaining allyl alcohol and benzene are then condensed into liquid nitrogen under reduced pressure (Figure S3.65). A distillation bridge is then set up and the expected amount of product is distilled off.



Figure S3.65: Distillation system for the distillation of 2,3-dichloro-1-propanol (**10**).

After the distillation, 1 mL of propylene carbonate was added back to the sample with the equivalent amount of supporting electrolyte and catalyst. The converted amount of HCH and fresh allyl alcohol was then added. The electrolysis was then restarted (Table S3.64).

Table S3.64: Effects of the distillation of the product over 5 repetitions on the example reaction of 2,3 dichloro-1-propanol (**10**).

$ \begin{array}{c} \text{graphite} \parallel \text{graphite} \\ \text{MnCl}_2 \cdot 4\text{H}_2\text{O} \text{ (20.0 mol\% HCH)} \\ (\text{C}_2\text{H}_5)_4\text{NCl} \text{ (0.05 mol\% L}^{-1}\text{)} \\ \text{Propylene carbonate} \\ j = 11.7 \text{ mA cm}^{-2}, \\ Q = 6.5 \text{ F}, \\ T = 25^\circ\text{C}, \omega_{\text{rot}} = 500 \text{ rpm} \end{array} $			
<chem>ClC1(Cl)C(Cl)C(Cl)C(Cl)C1Cl</chem> 1 [0.25 mol·L ⁻¹]	+ 3.0 <chem>C=CCO</chem> 9	$\xrightarrow{\hspace{1cm}}$	<chem>c1ccccc1</chem> + 3.0 <chem>ClC(Cl)CO</chem> 2 10
Run	X(1) / %	Y(2) / %	Y(10) / %
1	75	51	72
2	91	67	146
3	90	62	200
4	90	66	130
5	82	51	110

GC-Yield/Conversion: Mesitylene as internal standard.

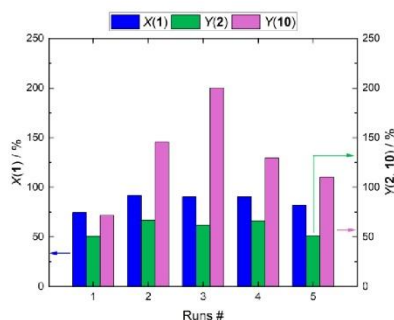
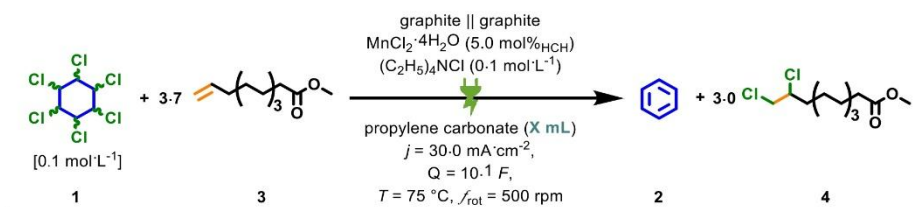


Figure S3.66: Measured conversion of HCH X(1) yield of benzene Y(2) and 2,3-dichloro-1-propanol Y(10) per run with Distillation of **2** and **10**.

The fractions were combined and distilled again under reduced pressure. 8.92 g of the product was isolated. This corresponds to an average distillation efficiency of 45%.

Electrical power of electrolysis

To determine the electrical power of the reactions of methyl 10,11-dichloroundecanoate (**4**), 1,2-dichloroethyl acetate (**8**) and 2,3-dichloro-1-propanol (**10**), the power was integrated against time (Figure S3.68 and Figure S3.74).



GC-Yield: Mesitylene as internal standard.

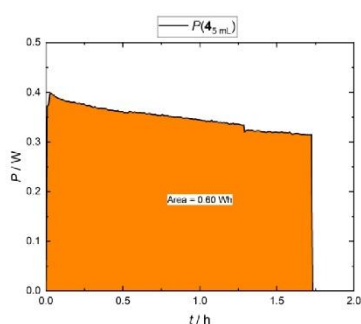


Figure S3.67: Chrono voltammetry of the optimized methyl 10,11-dichloroundecanoate (**4**) reaction in 5 mL propylene carbonate.

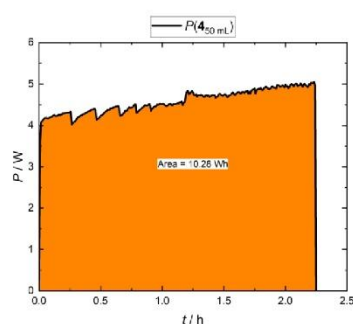


Figure S3.68: Chrono voltammetry of the optimized methyl 10,11-dichloroundecanoate (**4**) reaction in 50 mL propylene carbonate.

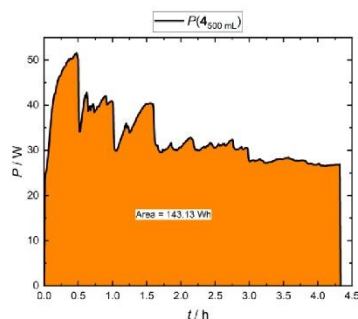


Figure S3.69: Chrono voltammetry of the optimized methyl 10,11-dichloroundecanoate (**4**) reaction in 500 mL propylene carbonate.

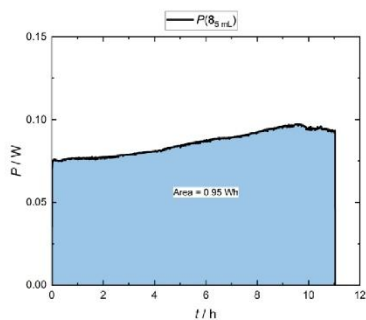
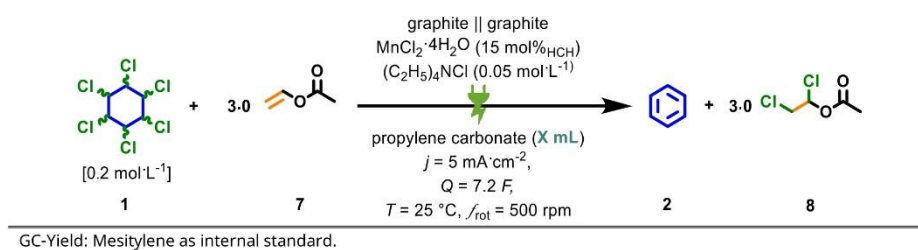


Figure S3.70: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**8**) reaction in 5 mL propylene carbonate.

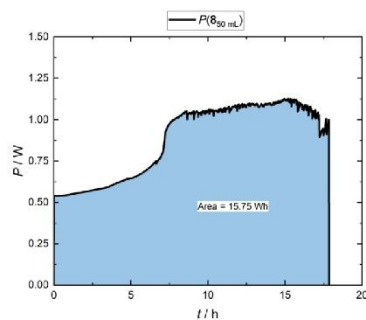


Figure S3.71: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**8**) reaction in 50 mL propylene carbonate.

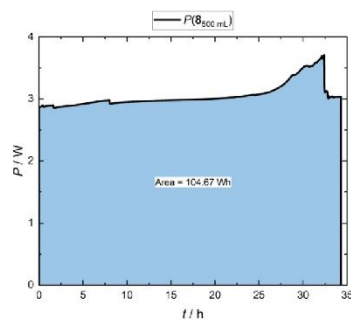


Figure S3.72: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**8**) reaction in 500 mL propylene carbonate.

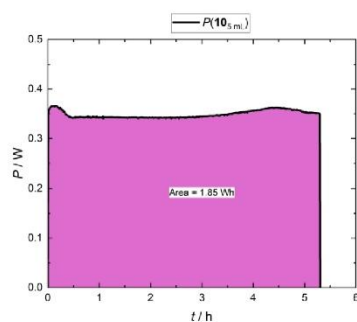
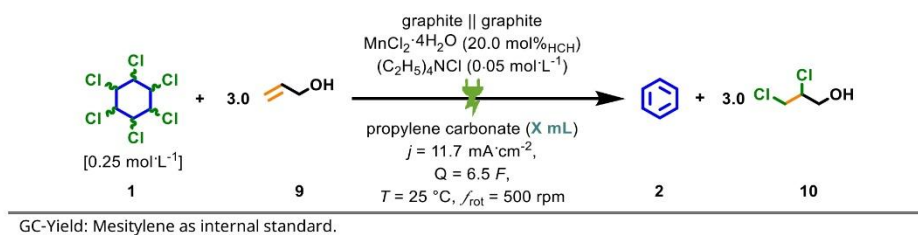


Figure S3.73: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**10**) reaction in 5 mL propylene carbonate.

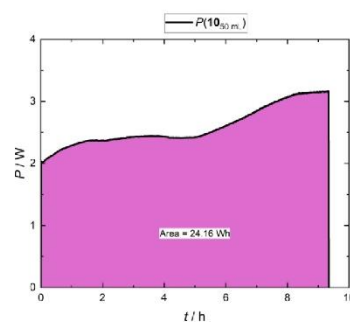


Figure S3.74: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**10**) reaction in 50 mL propylene carbonate.

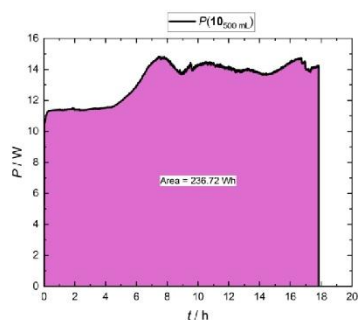


Figure S3.75: Chrono voltammetry of the optimized 2,3-dichloro-1-propanol (**10**) reaction in 500 mL propylene carbonate.

Table S3.65: Electrical power (P_{el}), conversion rate (CR) and production rate (PR) of the optimized electrolysis for **4**, **8**, and **10** in different batch volumes of the geometrically upscaled electrolysis cells.

Substance	$V_{\text{Propylene carbonate}} / \text{mL}$	$m(1) / \text{g}$	$X(1) / \%$	$Y(i) / \%$	$P_{\text{el}} / \text{Wh}$	$P_{\text{el}} \cdot m(X(1))^{-1} / \text{Wh} \cdot \text{g}^{-1}$	$P_{\text{el}} \cdot m(Y(i))^{-1} / \text{Wh} \cdot \text{g}^{-1}$	$\text{CR} (1) / \text{g} \cdot \text{h}^{-1}$	$\text{PR} (1) / \text{g} \cdot \text{h}^{-1}$
4	5	0.145	80	82	0.60	5.2	1.8	0.067	0.190
	50	1.454	95	61	10.28	7.5	4.2	0.614	1.095
	500	14.542	93	64	143.13	10.6	6.1	3.131	5.983
8	5	0.291	94	87	0.95	3.5	2.2	0.025	0.037
	50	2.908	90	84	15.75	6.0	4.0	0.146	0.221
	500	29.083	83	84	104.67	4.3	2.6	0.710	1.164
10	5	0.364	91	79	1.85	5.6	4.8	0.063	0.072
	50	3.653	89	79	24.16	7.5	6.3	0.350	0.413
	500	36.354	85	68	236.72	7.7	7.2	1.736	1.848

3.6 Economical Process Evaluation

Downstream Aspen Modell

The downstream processing is assessed via the Aspen Plus simulation software employing the Peng Robinson equation of state, with the assessed structure given in Figure S3.72 cascading structure of three distillation columns is employed separating the compounds for sale and recycle. Given the limited experimental data and the separate assessment of the electro organic reaction the cascade is calculated without recycle stream, which is later added in the economic assumptions. It is assumed that HCH is fully converted and is therefore not present in the separation. As for the reaction additives propylene carbonate (PRPC), tetraethylammonium chloride and manganese chloride, PRPC is employed in the calculation as model substance. Furthermore, it is assumed that tetraethylammonium chloride and manganese chloride are following the PRPC as recycle stream. The considered compounds are therefore **2**, **9**, **10** and propylene carbonate. As an initial approach the system pressure was chosen the be kept in alignment with the reaction conditions which is atmospheric. The molar and mass flow as well as the temperature of each regarded stream is given in Table S3.66, and the corresponding molar composition is given in Table S3.67.

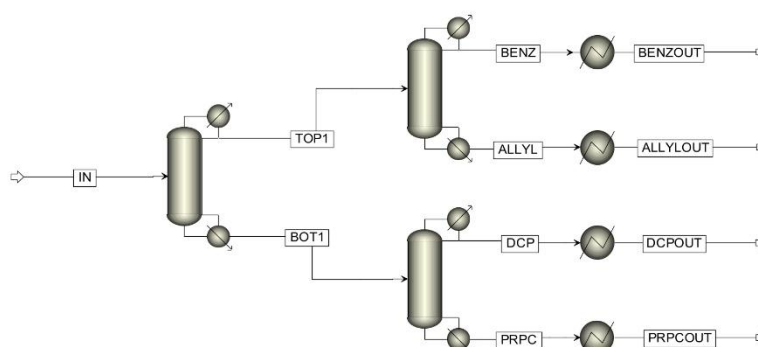


Figure S 3.76: Downstream process streams.

Table S3.66: Properties of the downstream process streams.

Stream	Mole flow [kmol h ⁻¹]	Mass flow [t h ⁻¹]	Temperature [°C]
IN	11.837	1.353	25.0
Top1	3.600	0.252	85.4
BOT1	8.237	1.102	189.1
BENZ	2.070	0.162	79.7
ALLYL	1.530	0.090	95.1
DCP	6.228	0.803	181.9
PRPC	2.009	0.298	236.5
BENZOUT	2.070	0.162	25.0
ALLYLOUT	1.530	0.090	25.0
DCPOUT	6.228	0.803	25.0
PRPCOUT	2.009	0.298	25.0

Table S 3.67: Molar composition (% mol·mol⁻¹) of the downstream process streams.

Stream	9 [% mol·mol ⁻¹]	2 [% mol·mol ⁻¹]	10 [% mol·mol ⁻¹]	Propylene carbonate [% mol·mol ⁻¹]
IN	0.041	0.125	0.179	0.529
Top1	0.000	0.410	0.590	0.000
BOT1	0.059	0.000	0.000	0.760
BENZ	0.000	0.001	0.999	0.000
ALLYL	0.000	0.964	0.036	0.000
DCP	0.000	0.000	0.000	0.999
PRPC	0.243	0.000	0.000	0.020
BENZOUT	0.000	0.001	0.999	0.000
ALLYLOUT	0.000	0.964	0.036	0.000
DCPOUT	0.000	0.000	0.000	0.999
PRPCOUT	0.243	0.000	0.000	0.020

Power requirements resulting from the downstream processing are consequently taken from the performed separation calculations and are presented in Table S3.68. Column 1 is the initial separation column that supplies the following two, Column 2 is the column separating **2** and **9**, Column 3 is the column separating **10** and propylene carbonate. The heaters employed in cooling the products are named accordingly. Heating duty is assumed to be supplied electrically and is therefore included in the plant's power requirements. Cooling is performed via cooling water at 15 °C, with a heat capacity of 4.19 kJ·(mol·K⁻¹), and a temperature increase of 5 K, to allow for a temperature gradient of 5 K to the product temperature goal of 25 °C.

Table S 3.68: Heat duty of the downstream process.

Item	Condenser [kW]	Heater [kW]
Column 1	-59.76	147.18
Column 2	-140.14	139.98
Column 3	-216.33	219.49
Sum	-416.23	506.64
Heater BENZ	-4.04	-
Heater ALLYL	-4.51	-
Heater DCP	-57.36	-
Heater PRPC	-26.01	-
Sum	-87.89	-

Column Dimensioning

The dimensions of the three packed distillation columns are estimated via the methodology reported by TOWLER AND SINNOTT,^[7] and PETERS et al.^[8] With the flooding and pressure drop correlations for packed columns, the cross-sectional area (A_C) and, therefore, the diameter of the column is estimated. For the packing, 25 mm metal Pall rings are assumed, resulting in an approximate theoretical plate height of 0.25 m and a packing factor F_P of 160 m⁻¹. From the recommended information for atmospheric columns, a pressure drop of 400 Pa·m⁻¹ is assumed. From the resulting constant Y ($Y_{C1} = 1.3$, $Y_{C2} = 1.5$, $Y_{C3} = 1.5$), the cross-sectional area is estimated as:

$$A_C = \dot{m}_V \cdot \sqrt{\frac{13.1 \cdot F_P}{\rho_V(\rho_L - \rho_V) \cdot Y} \cdot \left(\frac{\mu_L}{\rho_L}\right)^{0.1}} \quad [1]$$

where $\dot{m}_V$ is the gas flow rate, μ_L is the liquid viscosity and ρ_V and ρ_L are the gaseous and liquid densities, respectively, taken from the theoretical stage with the highest flow rate. The employed factors, the resulting A_c and the height (H) for each column are presented in Table S3.69.

Table S 3.69: Column dimensioning data.

Item	$\dot{m}_V$ [kg·s ⁻¹]	$\dot{m}_L$ [kg·s ⁻¹]	μ_L [mPa·s]	ρ_V [kg·m ⁻³]	ρ_L [kg·m ⁻³]	A_c [m ²]	D [m]	H [m]
Column 1	0.38	0.68	0.34	3.49	1117.13	0.11	0.38	2.5
Column 2	0.36	0.31	0.32	2.74	814.87	0.14	0.42	7.00
Column 3	0.55	0.62	0.34	3.46	1107.90	0.16	0.45	2.5

Equipment reference pricing is taken from PETERS et al.,^[8] apart from the electrical heating unit of columns 1-3^[9] and the graphite electrodes.^[10] The electrical heating unit pricing is represented by current market pricing based on available web-based data; a representative median value was chosen.^[9] Furthermore, all equipment except the heating units is constructed in nickel alloy steel, with an adaptation factor of 7.4 when compared to carbon steel. Dimensions of the heaters for the distillation columns and the final cooling step are estimated with a heat transfer coefficient of 700 W·(m²·K)⁻¹.^[8,11] The cost of the heaters implemented for the final cooling is assumed as one with the required capacity. Column costing is presented in Table S 3.70.

Table S 3.70: Detailed costs of the downstream process column.

Item	Cost Column 1 [k€]	Cost Column 2 [k€]	Cost Column 3 [k€]	Ref.
Column shell	53.6	140.6	53.6	[8]
Packing	10.7	14.7	10.7	[8]
Condenser	10.0	22.6	27.1	[8]
Reboiler	4.5	4.5	4.5	[9]
Reboiler shell	13.0	13.0	13.0	[8]

Economics

Factors for the capital expense estimation are used in accordance with available literature.^[7,8,12] It is to be noted that the electrical systems correction is assumed to be increased, accounting for the additional power supply requirements by an electrochemical plant.

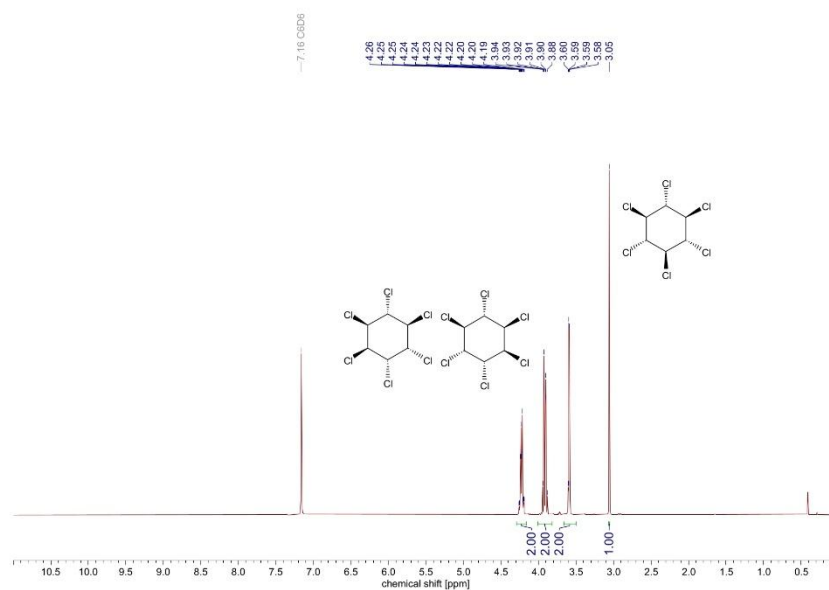
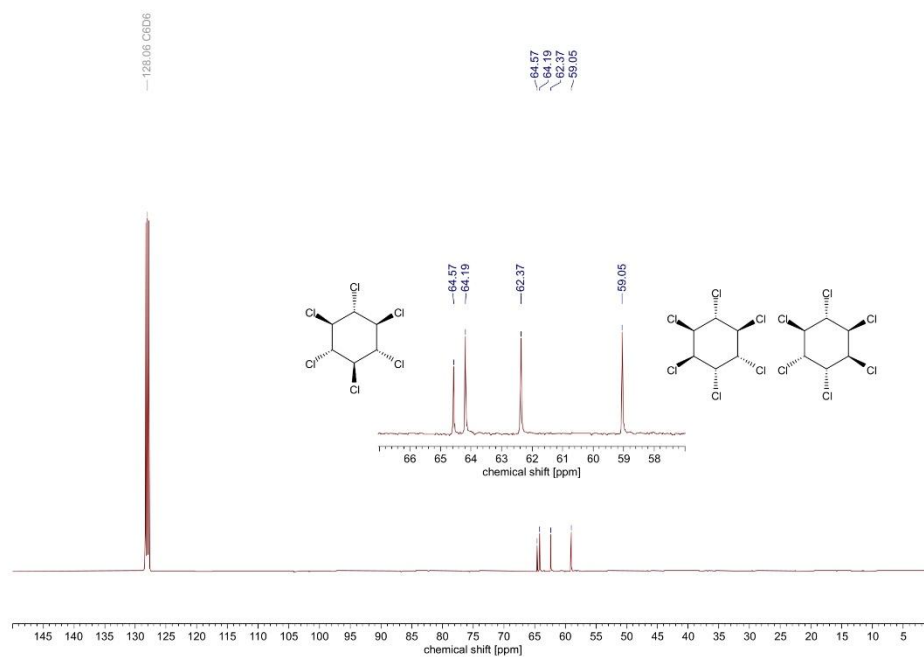
Table S 3.71: Capital Expenses (CEX) estimation from the cost equipment (CE).

Item	Cost
Major equipment items cost	$ME = \sum_i CE_i$
Pipes and Fittings	$0.5 \cdot ME$
Instrumentation controls	$0.8 \cdot ME$
Electrical	$1 \cdot ME$
Installation	$0.15 \cdot ME$
Building	$0.3 \cdot ME$
Engineering	$0.5 \cdot ME$
Contingency (10 %)	$0.425 \cdot ME$

Maintenance and labour costs are considered as an addition to direct operational expenses (OEdir) and are valued at 5 % and 3.5 % of the CEX, respectively.^[7] Labour cost is estimated at a rate of 1 shift position, valued at 60 k€ and an overhead of 50 %, with 4 operational shifts, under the assumption of duty sharing with other operators due to the plant size. As plant size and CEX are directly linked, the labour cost is assumed to correlate according. Maintenance includes a proposed electrode reoptimisation by

rework as an addition to general performed operations.^[13] The cost of cooling water is estimated at 63 k€·a⁻¹, which is a share of <1 % and is therefore not further presented.

4. NMR Spectra

Figure S4.1: ^1H NMR spectrum of technical HCH (1) (400 MHz, C_6D_6 , 298 K).Figure S4.2: ^{13}C NMR spectrum of technical HCH (1) (101 MHz, C_6D_6 , 298 K).

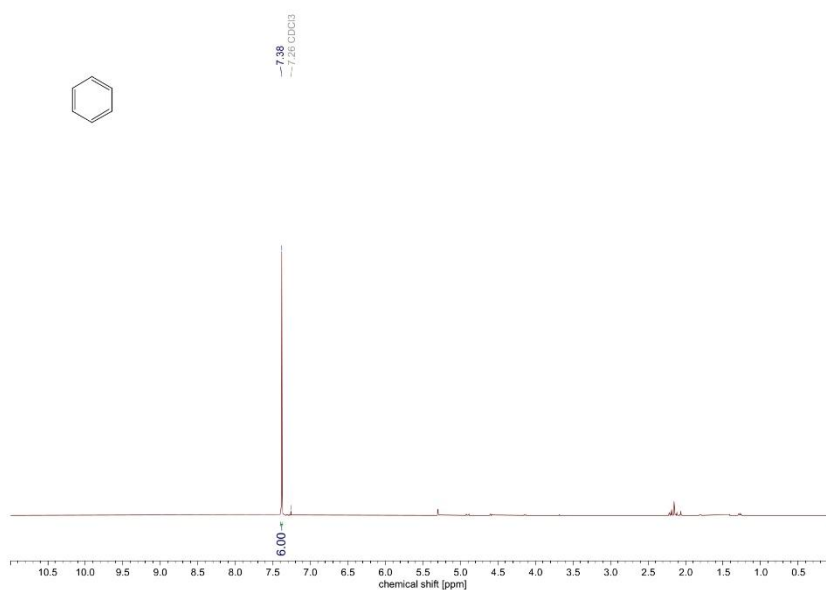


Figure S4.3: ^1H NMR spectrum of benzene (**2**) (400 MHz, CDCl_3 , 298 K).

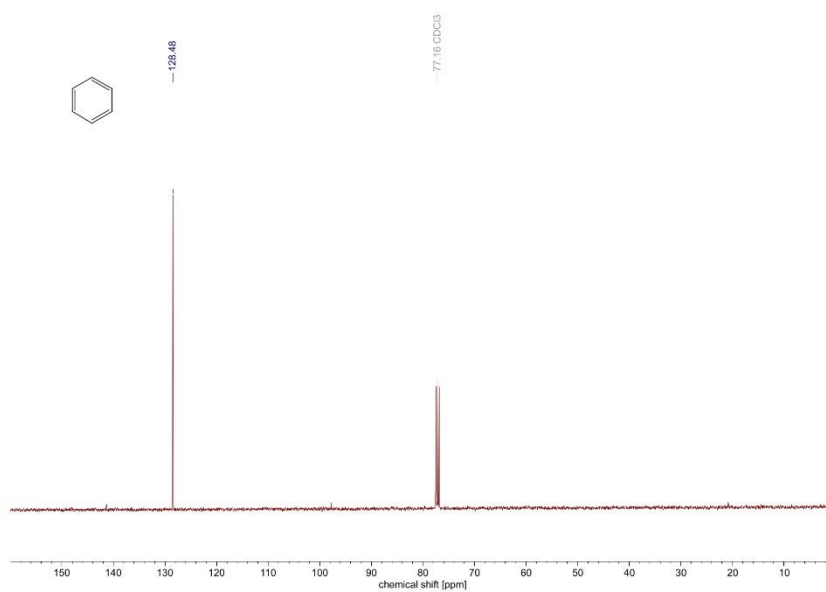


Figure S4.4: ^{13}C NMR spectrum of benzene (**2**) (101 MHz, CDCl_3 , 298 K).

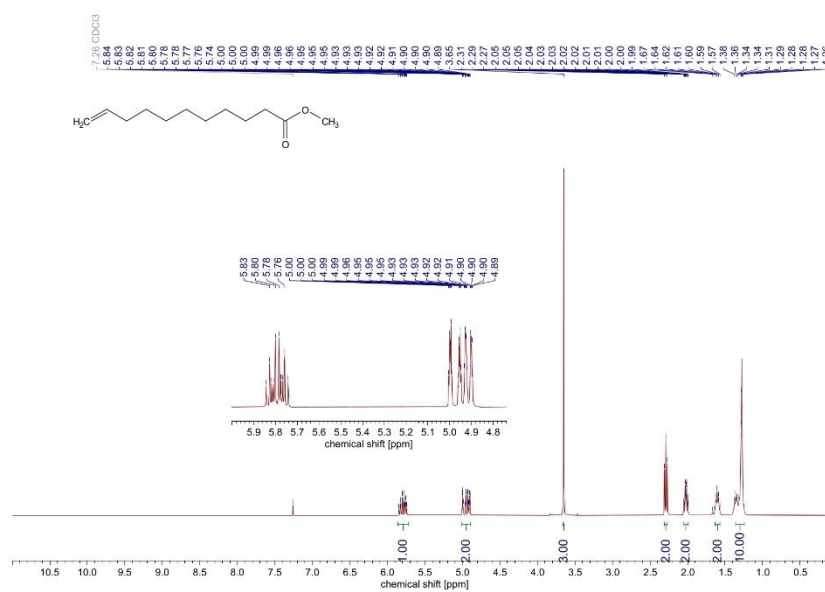


Figure S4.5: ^1H NMR spectrum of methyl 10-undecenoate (**3**) (400 MHz, CDCl_3 , 298 K).

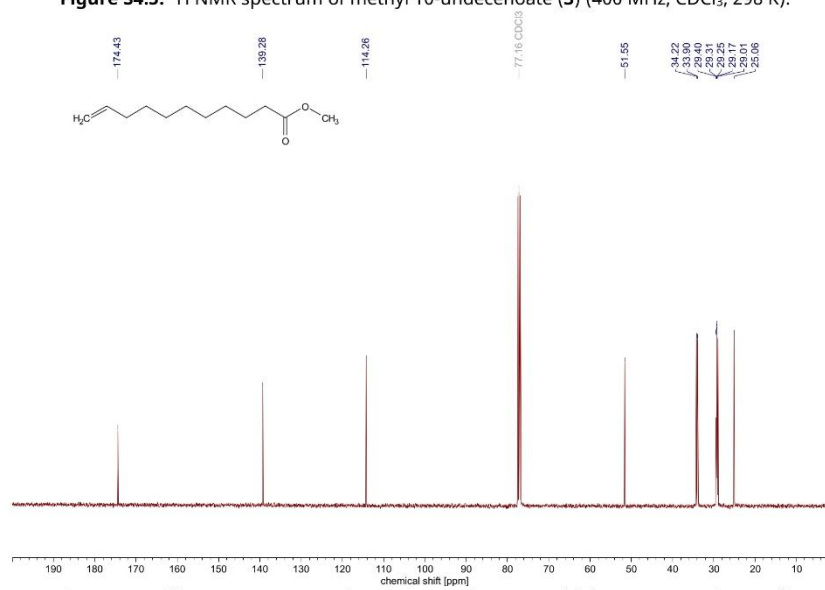


Figure S4.6: ^{13}C NMR spectrum of methyl 10-undecenoate (**3**) (101 MHz, CDCl_3 , 298 K).

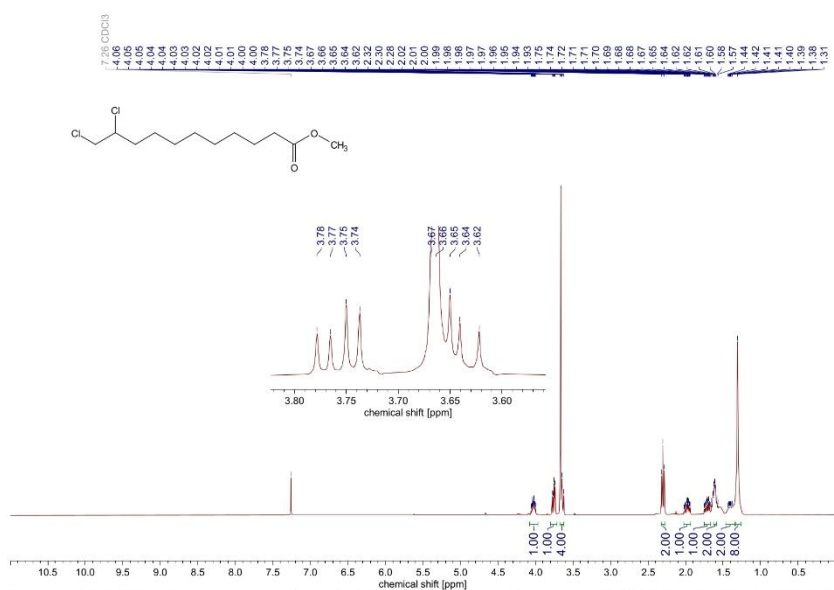


Figure S4.7: ^1H NMR spectrum of methyl 10,11-dichloroundecanoate (**4**) (400 MHz, CDCl_3 , 298 K).

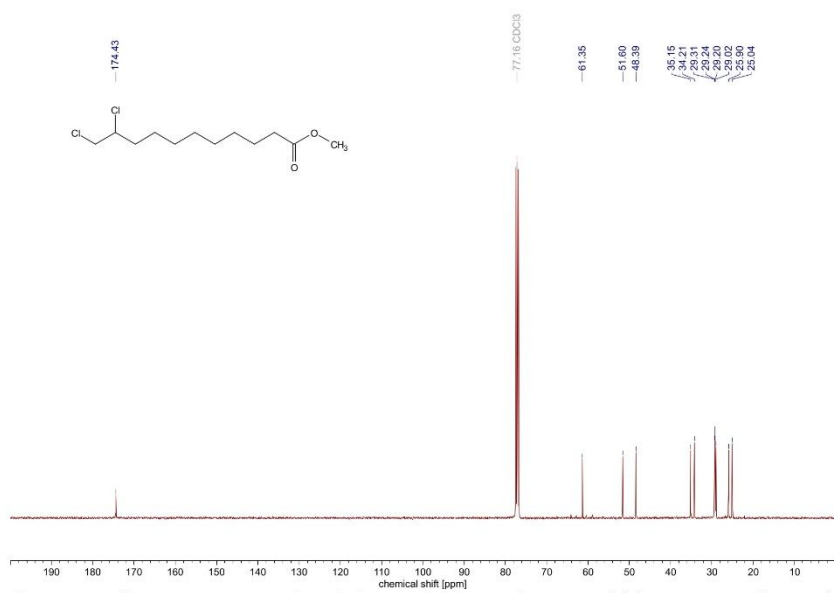


Figure S4.8: ^{13}C NMR spectrum of methyl 10,11-dichloroundecanoate (**4**) (101 MHz, CDCl_3 , 298 K).

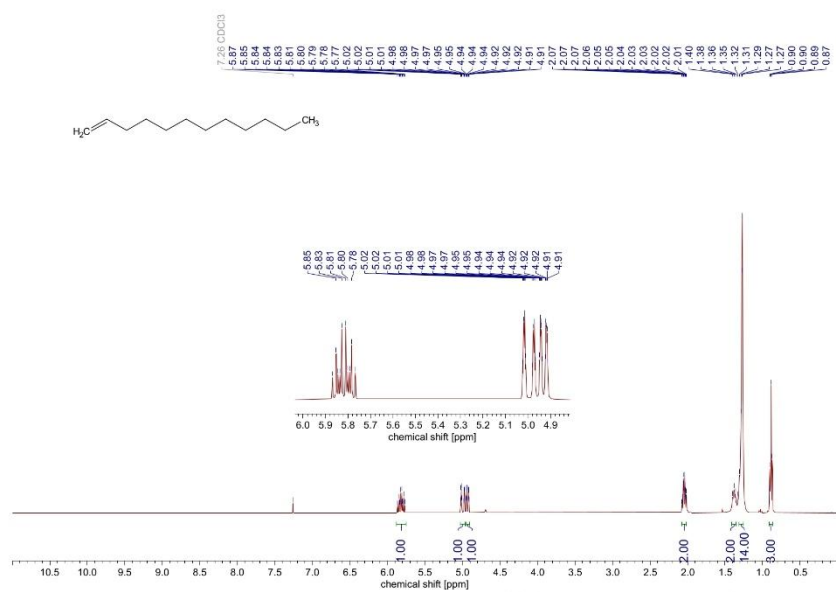


Figure S4.9: ¹H NMR spectrum of 1-dodecene (**5**) (400 MHz, CDCl₃, 298 K).

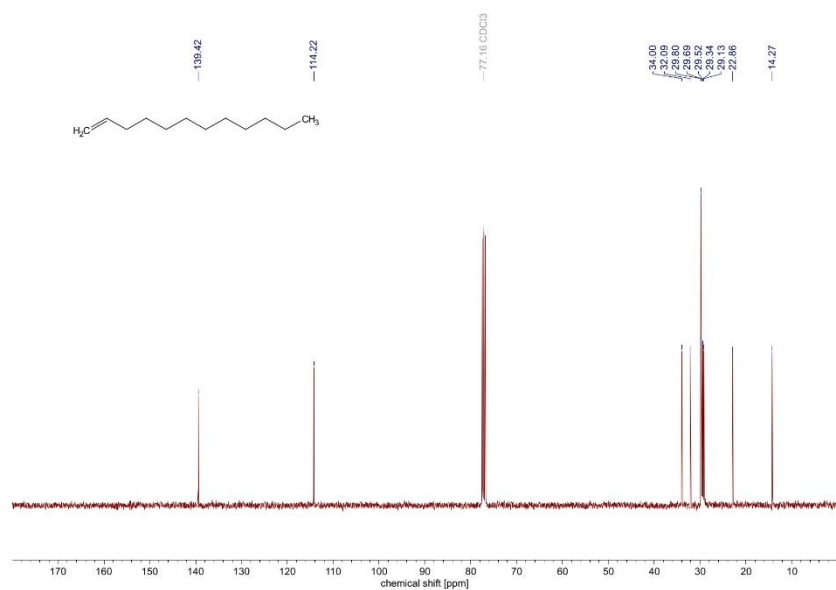


Figure S4.10: ¹³C NMR spectrum of 1-dodecene (**5**) (101 MHz, CDCl₃, 298 K).



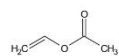


Figure S4.13: ^1H NMR spectrum of vinyl acetate (**7**) (400 MHz, CDCl_3 , 298 K).

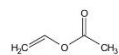
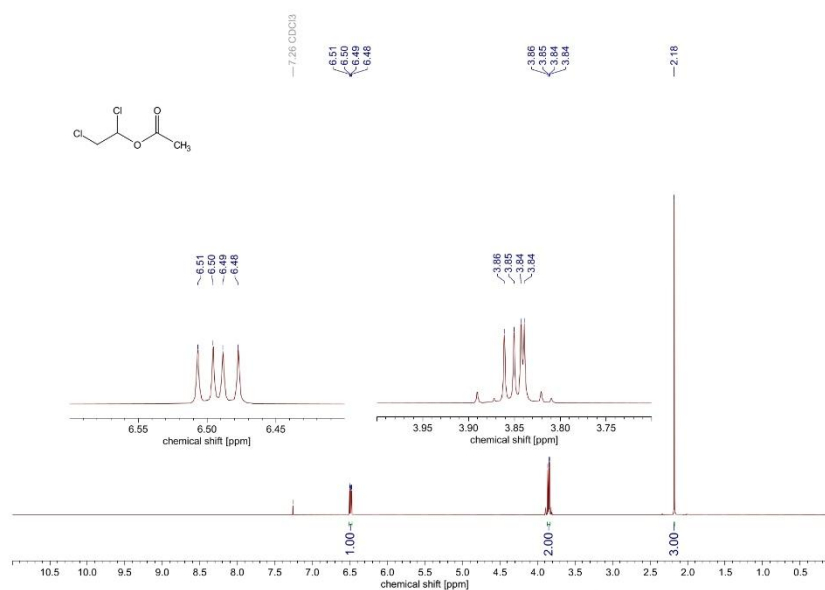
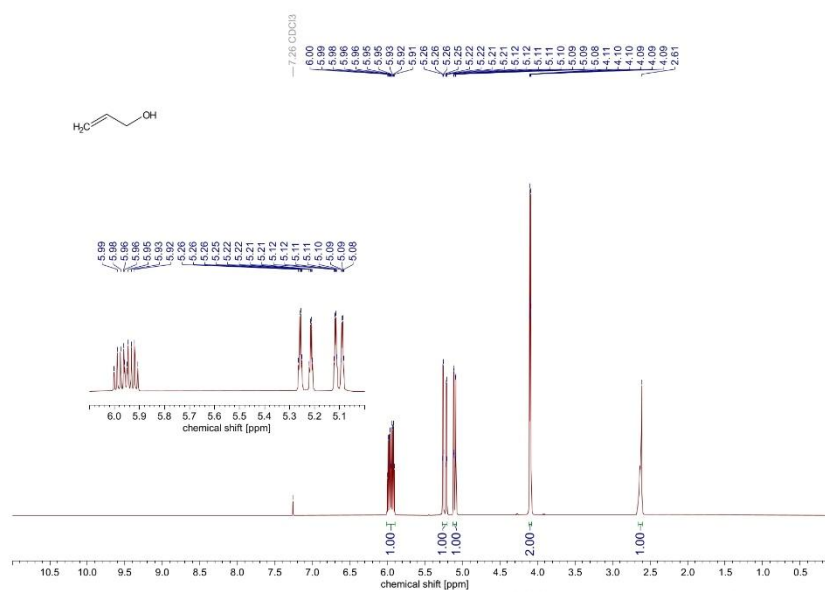
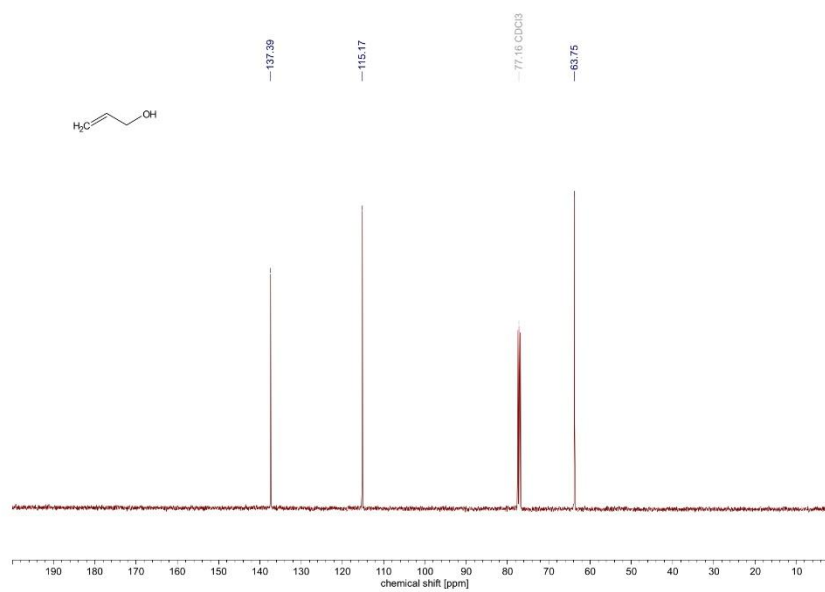


Figure S4.14: ^{13}C NMR spectrum of vinyl acetate (**7**) (101 MHz, CDCl_3 , 298 K).



Figure S4.17: ¹H NMR spectrum of allyl alcohol (**9**) (400 MHz, CDCl₃, 298 K).Figure S4.18: ¹³C NMR spectrum of allyl alcohol (**9**) (101 MHz, CDCl₃, 298 K).

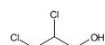


Figure S4.19: ^1H NMR spectrum of 2,3-dichloro-1-propanol (**10**) (400 MHz, CDCl_3 , 298 K).

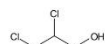


Figure S4.20: ^{13}C NMR spectrum of 2,3-dichloro-1-propanol (**10**) (101 MHz, CDCl_3 , 298 K).

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Supplementary Information

From Polyhalo-organic and Persistent Waste to Acetals: An Electrochemical Transfer Approach

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1. General Information

General Information

If not stated otherwise, all reactions were performed at ambient conditions. Chemicals were of analytical quality and were purchased from common chemical suppliers without further purification, which are listed in supplementary (Table S1).

Table S1: Commercially available chemicals used with CAS registry number and their supplier.

Substance	CAS registry number	Supplier
α -Hexachlorocyclohexane, 98%	319-84-6	Sigma-Aldrich
β -Hexachlorocyclohexane, 98%	319-85-7	Sigma-Aldrich
1,2,5,6,9,10-Hexabromocyclododecan, 95%	3194-55-6	Sigma-Aldrich
Benzene, 99.5%	71-43-2	VWR
Chlorobenzene, $\geq 99.5\%$	108-90-7	Sigma-Aldrich
Propylene carbonate, $\geq 99.7\%$	108-32-7	Carl Roth
Acetaldehyde dimethyl acetal	534-15-6	Sigma-Aldrich
Methanol, 99.8%	67-56-1	Thermo Fisher Scientific
Ethyl vinyl ether, 99%	109-92-2	TCI
Ethanol absolute, $\geq 99.2\%$	64-17-5	VWR
2-Chloroethyl vinyl ether, 97%	110-75-8	TCI
2-Chloroethanol, 99%	107-07-3	Sigma-Aldrich
Propyl vinyl ether, 97%	764-47-6	TCI
1-Propanol, 99.5%	71-23-8	Carl Roth
Isobutyl vinyl ether, 99%	109-53-5	TCI
2-Methyl-1-propanol, 99.5%	78-83-1	Sigma-Aldrich
Butyl vinyl ether, 98%	111-34-2	TCI
1-Butanol, 99.5%	71-36-3	Carl Roth
((Vinylloxy)methyl)benzene, 98.7%	935-04-6	BLD Pharm
Benzyl alcohol, 99%	100-51-6	Acros Organics
2-Hydroxyethyl vinyl ether, 98%	764-48-7	TCI
2-Methyl-1,3-dioxolane, $>98.0\%$	497-26-7	TCI
2-Chloroethyl acetate, 97%	542-58-5	TCI
2-Bromoethyl acetate, 97%	927-68-4	TCI
3-Chloropropyl acetate, 97%	628-09-1	Thermo Fisher Scientific
3-Bromopropyl acetate, 99.78%	592-33-6	BLD Pharm
4-Hydroxybutyl vinyl ether, $>97.0\%$	17832-28-9	TCI
1,4-Butanediol, 99%	110-63-4	Carl Roth
Acetaldehyde, 99%	75-07-0	Sigma-Aldrich
<i>p</i> -Toluenesulfonic hydrate	6192-52-5	Honeywell
Triethylamine, 99%	121-44-8	Thermo Fisher Scientific
Dichloromethane, 99.8%	75-09-2	Thermo Fisher Scientific
Sodium sulfate, 99%	7757-82-6	Acros Organics
Di(ethylene glycol) vinyl ether, 96%	929-37-3	TCI
4-Chlorobutyl acetate, 98%	6962-92-1	Thermo Fisher Scientific
4-Bromobutyl acetate, 98%	4753-59-7	BLD Pharm
1,5-Pentanediol, 97%	111-29-5	TCI
Potassium hydroxide	1310-58-3	Honeywell
Calcium carbide, 80%	75-20-7	Sigma-Aldrich
Dimethylsulfoxide, 99%	67-68-5	Fisher Scientific
Diethyl ether, $>99.8\%$	60-29-7	Carl Roth
1,10-Dichlorodecane, 97%	2162-98-3	TCI
Tetraethylammonium chloride	56-34-8	Alfa Aesar
Manganese(II) chloride tetrahydrate, $\geq 99\%$	13446-34-9	Sigma-Aldrich
Manganese(II) chloride	7773-01-5	Sigma-Aldrich

1.1 Instruments and Analytical Methods

Gas chromatography (GC-I):

Analysis of crude reaction mixtures and purified products was performed using a GC-2025 (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector (FID) and a quartz capillary column HI-5MS (Avantor VWR, Radnor, United States) with following specification: length of 30 m, inner diameter of 0.25 mm and a stationary phase ((5%-phenyl)-dimethylsiloxane) of 0.25 μm thickness. Hydrogen was used as carrier gas with constant velocity: 42.0 $\text{cm}\cdot\text{s}^{-1}$, total flow: 43.3 $\text{mL}\cdot\text{min}^{-1}$, column flow: 1.55 $\text{mL}\cdot\text{min}^{-1}$, purge flow: 3.0 $\text{mL}\cdot\text{min}^{-1}$, split ratio: 25.0. Measurements were performed at an injector temperature of 280 °C and a detector temperature of 280 °C.

GC-Methods:

Method "Performance DWE-SHS": Starting temperature: 40 °C for 6 min, 1st heating rate: 30.0 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 90 °C, 2nd heating rate: 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 205°C, 3rd heating rate: 50 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 285 °C.

Method "2_medium": Starting temperature: 50 °C for 1 min, heating rate: 17.50 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 300 °C for 4.71 min.

Gas chromatography (GC-II):

The determination of hydrogen was realized by Merck kGaA (Darmstadt, Germany). Analysis of Hydrogen evolution was performed using an Agilent 7890A (Agilent, Santa Clara, United States) equipped with a thermal conductivity detector (TCD) and a molecular sieve column Rt-Msieve 5A (Restek, Bellefonte, United States) with following specification: length of 30 m, inner diameter of 0.32 mm and a stationary phase of 30 μm thickness. Nitrogen was used as carrier gas with makeup flow: 5 $\text{mL}\cdot\text{min}^{-1}$, column flow: 5.00 $\text{mL}\cdot\text{min}^{-1}$, reference flow: 23 $\text{mL}\cdot\text{min}^{-1}$, split ratio: 1:10. Measurements were performed at an injector temperature of 150 °C and a detector temperature of 220 °C.

Hydrogen gas standard:

A Tedlar bag was filled with a gas standard from the gas pressure can with 1% hydrogen in nitrogen. Using a gas-tight syringe, 250 μL was removed from the Tedlar bag via the removal nozzle and manually injected into the GC.

GC-Method:

Method: Starting temperature: 40 °C for 5 min, heating rate: 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ up to 280 °C for 1.5 min.

Gas Chromatography coupled with Mass Spectrometry (GC/MS):

For GC sample preparation a column filtration was performed over silica gel 60 M (0.040–0.063 mm, Macherey-Nagel GmbH & Co. KG, Düren, Germany). Analysis of crude reaction mixtures and purified products were performed using a GCMS QP2010SE (Shimadzu, Kyoto, Japan) equipped with an electron ionization (EI) source and a quadrupole mass analyser. A quartz capillary column HI-5MS (Avantor VWR, Radnor, USA) with the following specification was used: length of 30 m, inner diameter of 0.25 mm and a stationary phase ((5%-phenyl)- dimethylsiloxane) of 0.25 μm thickness. Helium was used as carrier gas with a constant velocity of 30 $\text{cm}\cdot\text{s}^{-1}$. The GC temperature ramp started at 50 °C (holding for 1 min) and heating to 300 °C (holding for 4.71 min) with a temperature ramp of 17.5 $^{\circ}\text{C}\cdot\text{min}^{-1}$ (method: 2_medium, total program time: 20.0 min). Measurements were performed at an injector temperature of 270 °C and a temperature of the EI source of 250 °C.

Ion Chromatography:

The determination of halogens was realized by Merck kGaA (Darmstadt, Germany). Analysis of Halogens was performed using a IC Metrohm system (Metrohm AG, Herisau, Switzerland) equipped with a conductivity detector (CD) and an anion exchange column (Polyvinyl alcohol with quaternary ammonium groups) Metrosep A Supp 5 250/4.0 (Metrohm AG, Herisau, Switzerland) with following specification: length of 250 mm, inner diameter of 4.0 mm and a particle size of 5 μm . As eluent, 3.2 mM Na_2CO_3 / 1.0 mM NaHCO_3 were used. Measurements were performed at a temperature of 30 °C and a flow of 0.700 $\text{mL}\cdot\text{min}^{-1}$.

Nuclear Magnetic Resonance (NMR) Spectroscopy:

Nuclear magnetic resonance experiments were performed using a nuclear magnetic resonance spectrometer Avance II 400 (Bruker, Karlsruhe, Germany) for ^1H NMR (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz) analysis. The spectra were recorded at 25 °C using deuterated solvents. To normalize the spectra obtained, reference was made to the existing solvent signal of non-deuterated fractions according to the data provided by Gottlieb et al.:^[1] CDCl_3 (^1H NMR: δ = 7.26 ppm, ^{13}C NMR: δ = 77.16 ppm). Besides ^1H and ^{13}C NMR experiments, the 2D techniques $^1\text{H}, ^1\text{H}$ -COSY, $^1\text{H}, ^{13}\text{C}$ -HSQC and $^1\text{H}, ^{13}\text{C}$ -HMBC were used to assist the assignment of the signals. The following abbreviations were used to describe the signals: s (singlet), brs (broad singlet), d (doublet), brd (broad doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), dddd (doublet of doublets of doublets of doublets), dt (doublet of triplets), t (triplet), td (triplet of doublets), q (quartet), sept (septet), septd (septet of doublets), m (multiplet). The spectra obtained were evaluated with MestReNova 14 (Mestrelab Research S.L., Spain).

High Resolution Mass Spectrometry (HRMS)

Mass spectra via electrospray-ionization (ESI+) were recorded using a Q Exactive™ mass spectrometer (Thermo Fischer Scientific™, Waltham, USA). Mass spectra *via* electron-ionization (EI) were recorded using a Q Exactive™ GC Orbitrap™ GC-MS/MS (Thermo Fischer Scientific™, Waltham, USA) equipped with an XTI-5 column (Restek GmbH, Bad Homburg v.d. Höhe, Deutschland).

Cyclovoltammetry:

Measurements Cyclic voltammetry was performed using a Metrohm 663 VA Stand equipped with an Autolab type III potentiostat (Metrohm AG, Herisau, Switzerland). Cyclic voltammetry was conducted with isostatic graphite as working electrode, a glassy carbon rod as counter electrode, and Ag/AgCl as reference electrode. The potential window was set to -0.5–+1.5 V, the scan rate to 0.1 V·s⁻¹. The start and stop potentials were set to 0.5 V. The blank was measured in propylene carbonate with (C₂H₅)₄NBF₄ (*c*((C₂H₅)₄NBF₄) = 0.05 mol·L⁻¹). All data is displayed against the half-wave potential of ferrocene/ferrocenium redox couple (FcH/FcH⁺; -0.01 V vs. Ag/AgCl) as reference.

1.2 Electrochemical Setup

Power source & Stirrer

For electrochemical reactions a HMP4040 Programmable Power Supply 384 W (*Rohde & Schwarz GmbH & Co. KG*, München, Germany) and a MR Hei-Tec magnetic stirrer (*Heidolph Instruments GmbH & Co. KG*, Kelkheim, Germany) were used.

Electrode materials

Table S2: Electrode materials, purity, and their supplier.

Electrode material	Specification	Supplier
Isostatic graphite	SIGRAFINE™, highly isostatic, V2100	SGL Carbon, Bonn, Germany

Screening and small-scale batch-type reactions

For the screening and optimizations reactions a 5 mL vial with stirring bars in each cell during electrolysis were used, as shown in supplementary figure 1 (**Figure S1**). The electrolysis set-up is commercially available as IKA Screening System Package (*IKA™-Werke GmbH & Co. KG*, Staufen, Germany). The lids were manufactured by the in-house workshop, as the materials of the original lids (stainless steel) cannot tolerate the corrosive conditions.



Figure S1: Cross-section of a Teflon lid for (50x10x2) mm electrodes for 5 mL glass vial from IKA.^[2]



Figure S2: 5 mL glass vial with a stirring bar, Teflon lid and isostatic graphite electrodes attached to titanium holders.

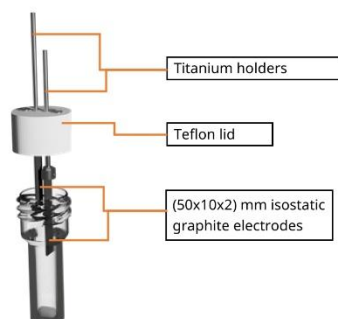


Figure S3: 3D model of the 5 mL glass vial with Teflon lid, two (50x10x2) mm isostatic graphite electrodes and titanium holders.

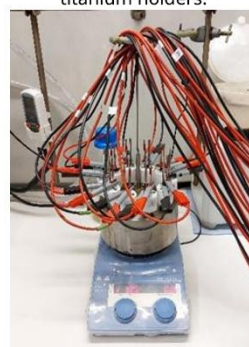


Figure S4: Screening Setup with 5 mL glass vials.

The screening was carried out using various electrode materials ($70 \times 10 \times 3$) mm. Graphite electrodes ($50 \times 10 \times 2$) mm were sanded using 1000 grit sandpaper and cleaned with acetonitrile prior to use.^[3] This resulted in a geometric surface of anode respectively cathode area of 3.5 cm^2 used for electrolysis.

Scale-up, recyclability and gas evolution tests

The electrolysis set-up was also made by the in-house workshop.



Figure S5: Cross-section of an NS34 Teflon lid for two (120x 23 x 3) mm electrodes.



Figure S6: 50 mL glass vial with (120 x 23 x 5) mm isostatic graphite electrodes attached to titanium holders.

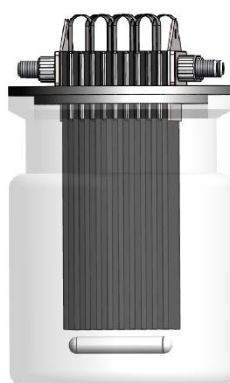


Figure S7: Cross-section of 500 mL stacked glass batch-type cell with (160x 65 x 3) mm electrodes.



Figure S8: 500 mL stacked glass batch-type cell with (160x 65 x 3) mm isostatic graphite electrodes.

Used Equations

The amount of charge applied Q in coulombs for example $n = 1.0 \text{ mmol}$ ($\pm 0.001 \text{ mol}$) substrate and number of electrons used $z = 7.0$ and the Faraday constant $F = 96485.332 \text{ C} \cdot \text{mol}^{-1}$ is calculated as follows:

$$Q = n \times z \times F = 0.001 \text{ mol} \times 7.0 \times 96485.332 \text{ C} \cdot \text{mol}^{-1} = 675.0 \text{ C} \pm 675.0 \text{ As}$$

The current I applied for electrolysis is calculated from the product of the current density j and the area of the anode respectively cathode A_E , which depends on the width W_E and immersion depth of the electrode $L_{\text{I.D.E.}}$:

$$I = j \times A_E = j \times W_E \times L_{\text{I.D.E.}}$$

Thus, for example, with an immersion depth of 3.5 cm and an electrode width of 1.0 cm, and a current density of $10 \text{ mA} \cdot \text{cm}^{-2}$, the amount of applied charge is as follows:

$$I = 10 \text{ mA} \cdot \text{cm}^{-2} \times (1.0 \times 3.5) \text{ cm}^2 = 35 \text{ mA} (\pm 0.035 \text{ A})$$

If the electrolysis takes place under galvanostatic conditions, the reaction time t of the electrolysis can be determined from the quotient of the amount of applied charge Q and the applied current I :

$$t = \frac{Q}{I} = \frac{675.0 \text{ As}}{0.035 \text{ A}} = 19300 \text{ s} = 5 \text{ h } 21 \text{ min } 40 \text{ s}$$

To determine yields Y_i and conversions X_i via gas chromatography GC, calibration curves were determined for all substances. The ratio of the measured areas of the internal standard A_{IS} to use the substance A_i was plotted against the ratio of the known amount of substance of the internal standard n_{IS} to the used substance n_i . The slope for each substance m_i was determined by linear regression.

$$m_i = \frac{A_i/A_{\text{IS}}}{n_i/n_{\text{IS}}}$$

Yield and conversion are calculated from the ratio of the measured substance n_i to the quantity of the starting material at the beginning of electrolysis $n_{\text{SM},0}$.

$$Y_i = \frac{n_i}{n_{\text{SM},0}} \times 100\% = \left(\frac{A_i}{A_{\text{IS}}} \times \frac{n_{\text{IS}}}{m_i} \right) \times \frac{1}{n_{\text{SM},0}} \times 100\%$$

$$X_i = \left(1 - \frac{n_i}{n_{\text{SM},0}} \right) \times 100\% = \left(1 - \left(\frac{A_i}{A_{\text{IS}}} \times \frac{n_{\text{IS}}}{m_i} \right) \times \frac{1}{n_{\text{SM},0}} \right) \times 100\%$$

Furthermore, the faraday efficiency FE is determined, as more amount of charge is applied Q_{used} than is theoretically necessary Q_{theo} .

$$FE_i = Y_i \times X_i \times \frac{Q_{\text{theo}}}{Q_{\text{used}}} \times 100\%$$

To determine the rate constants k of the respective substances, a linearization of the 1st order kinetics is carried out according to unimolecular reactions.

$$1^{\text{st}} \text{ order kinetics: } c_i = c_{i,0} \times e^{-kQ}$$

The resulting slope m of the linear regression of the measured values through zero is plotted against the amount of applied charge Q . However, a distinction must be made between conversion X_i and yield Y_i :

$$y = m \times x = k \times Q$$

$$\text{For conversion } X_i: x_i = -\ln\left(\frac{c_i}{c_{i,0}}\right) = kQ$$

$$\text{For yield } Y_i: y_i = -\ln\left(1 - \frac{c_i}{c_{i,0}}\right) = kQ$$

2. Experimental Protocols

2.1 Extraction of technical Hexachlorocyclohexane (HCH, 1)

The HCH samples excavated at the Merck site (Gernsheim/Germany) must be separated from soil residues, stones, and other impurities before use. For this purpose, a Soxhlet extractor is used (**Figure S9**). The HCH is then dissolved in refluxing ethyl acetate and then filtered.

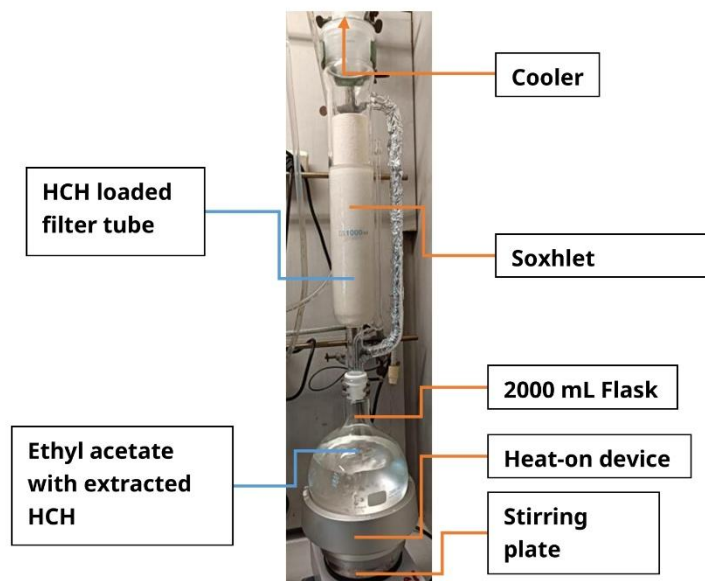


Figure S9: Soxhlet extractor for purification of the soil contaminated HCH.

Subsequently, the HCH is concentrated under reduced pressure and the precipitate then filtrated off. The solids are then washed with cold ethyl acetate and pre-dried by air suction. The pre-dried HCH is powdered and dried again in a high vacuum.

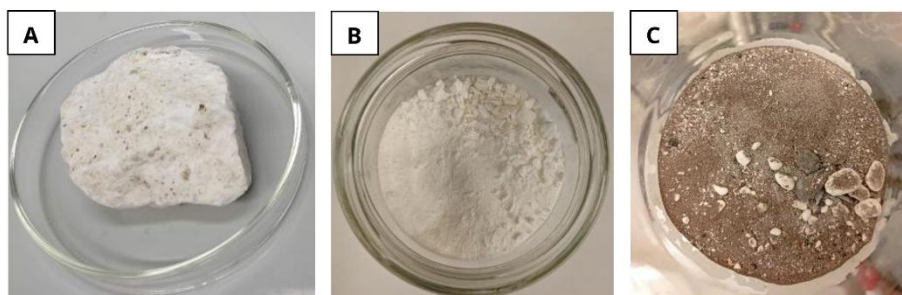
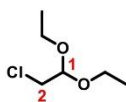


Figure S10: A: HCH contaminated with soil residues from seam 1 at Fluxum, Merck KGaA, Gernsheim, Germany. B: Pure recrystallized HCH. C: Soxhlet remains of the HCH upon extraction.

2.2 Synthesis of 2-Chloro-1,1-di(ethoxy)-ethane (4)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with ethyl vinyl ether (**3**) (219 mg, 290 μ L, 3.0 mmol, 3.0 eq.) and ethanol (552 mg, 700 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F$ (± 820.1 C) with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloro-1,1-di(ethoxy)-ethane (**4**) is obtained as a colorless viscous liquid in the first fraction at 40–50 °C.



Yield: 88% (403 mg, 2.64 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 7.78$ min

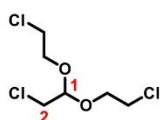
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.62 (t, $J = 5.5$ Hz, 1H, H-1), 3.73–3.67 (m, 2H, OCH_2^-), 3.61–3.54 (m, 2H, OCH_2^-), 3.50 (d, $J = 5.5$ Hz, 2H, H-2), 1.22 (t, $J = 7.0$ Hz, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.8 (C-1), 62.7 (OCH_2^-), 44.1 (C-2), 15.3 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{13}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 175.04963, found: 175.04971.

2.3 Synthesis of 2-Chloro-1,1-di(2-chloroethoxy)-ethane (4a)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-chloroethyl vinyl ether (**3a**) (320 mg, 304 μ L, 3.0 mmol, 3.0 eq.) and 2-chloroethanol (966 mg, 800 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\triangleq 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The solvent is removed under reduced pressure and the product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**) is obtained as a yellow viscous liquid in the first fraction at 90–100 °C.



Yield: 46% (306 mg, 1.38 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 14.17 \text{ min}$

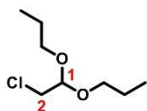
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.80 (t, $J = 5.6 \text{ Hz}$, 1H, H-1), 3.93 (dt, $J = 11.2, 5.6 \text{ Hz}$, 2H, OCH_2^-), 3.84 (dt, $J = 11.2, 5.6 \text{ Hz}$, 2H, OCH_2^-), 3.66 (t, $J = 5.6 \text{ Hz}$, 4H, $-\text{CH}_2\text{Cl}$), 3.57 (d, $J = 5.6 \text{ Hz}$, 2H, H-2).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.9 (C-1), 66.8 (OCH_2^-), 43.2 ($-\text{CH}_2\text{Cl}$), 43.0 (C-2).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{11}^{35}\text{Cl}_3\text{O}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 242.9667, found: 242.9716.

2.4 Synthesis of 2-Chloro-1,1-di(propoxy)-ethane (**4b**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with propyl vinyl ether (**3b**) (258 mg, 340 μ L, 3.0 mmol, 3.0 eq.) and propanol (721 mg, 900 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F$ (± 820.1 C) with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloro-1,1-di(propoxy)-ethane (**4b**) is obtained as a colorless viscous liquid in the first fraction at 50–60 °C.



Yield: 42% (233 mg, 1.29 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 10.09$ min

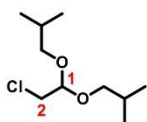
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.62 (t, $J = 5.5$ Hz, 1H, H-1), 3.60 (dt, $J = 9.3, 6.7$ Hz, 2H, OCH_2 -), 3.51 (d, $J = 5.5$ Hz, 2H, H-2), 3.46 (dt, $J = 9.3, 6.7$ Hz, 2H, OCH_2 -), 1.65–1.58 (h, $J = 7.4$ Hz, 4H, $-\text{CH}_2$ -), 0.94 (t, $J = 7.4$ Hz, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.0 (C-1), 68.8 (OCH_2 -), 44.0 (C-2), 23.1 ($-\text{CH}_2$ -), 10.7 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_8\text{H}_{17}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 203.0809, found: 203.0809.

2.5 Synthesis of 2-Chloro-1,1-di(2-methylpropoxy)-ethane (**4c**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-methylpropyl vinyl ether (**3c**) (301 mg, 390 μ L, 3.0 mmol, 3.0 eq.) and 2-methylpropan-1-ol (889 mg, 1110 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F$ ($\pm 820.1 C$) with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The electrolyte solution is extracted with *n*-pentane (3 x 5 mL). The fractions are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product was purified in a distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**) is obtained as a colorless viscous liquid in the first fraction at 60–70 °C.



Yield: 56% (351 mg, 1.68 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 11.29 \text{ min}$

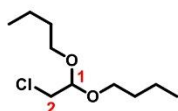
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.60 (t, $J = 5.5 \text{ Hz}$, 1H, H-1), 3.51 (d, $J = 5.5 \text{ Hz}$, 2H, H-2), 3.40 (dd, $J = 9.0, 6.7 \text{ Hz}$, 2H, OCH_2 -), 3.26 (dd, $J = 9.0, 6.7 \text{ Hz}$, 2H, OCH_2 -), 1.86 (hept, $J = 6.7 \text{ Hz}$, 2H, -CH-), 0.92 (d, $J = 6.7 \text{ Hz}$, 12H, - CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.2 (C-1), 73.8 (OCH_2 -), 43.9 (C-2), 28.8 (-CH-), 19.5 (- CH_3).

HRMS (ESI+): m/z for $\text{C}_{10}\text{H}_{12}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 231.1122, found: 231.1122.

2.6 Synthesis of 2-Chloro-1,1-di(butoxy)-ethane (**4d**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-methylpropyl vinyl ether (**3d**) (301 mg, 390 μ L, 3.0 mmol, 3.0 eq.) and butanol (889 mg, 1110 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\triangleq 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The electrolyte solution is extracted with *n*-pentane (3 x 5 mL). The fractions are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product was purified in a distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloro-1,1-di(butoxy)-ethane (**4d**) is obtained as a colorless viscous liquid in the first fraction at 60–70 °C.



Yield: 49% (307 mg, 1.47 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 12.57 \text{ min}$

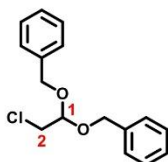
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.60 (t, $J = 5.4 \text{ Hz}$, 1H, H-1), 3.63 (dt, $J = 9.2, 6.5 \text{ Hz}$, 2H, OCH_2 -), 3.53–3.47 (m, 4H, OCH_2 -, H-2), 1.61–1.54 (m, 4H, $-\text{CH}_2-\text{CH}_2$ -), 1.43–1.34 (m, 4H, $-\text{CH}_2-\text{CH}_2$ -), 0.92 (t, $J = 7.3 \text{ Hz}$, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.0 (C-1), 66.9 (OCH_2 -), 44.0 (C-2), 31.9 ($-\text{CH}_2$ -), 19.4 ($-\text{CH}_2$ -), 14.0 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_{10}\text{H}_{12}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 231.1122, found: 231.1124.

2.7 Synthesis of 2-Chloro-1,1-di(benzyloxy)-ethane (4e)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (290.8 mg, 1.0 mmol, 1.0 eq.) was dissolved with benzyl vinyl ether (**3e**) (403 mg, 415 μ L, 3.0 mmol, 3.0 eq.) and benzyl alcohol (1298 mg, 1250 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\pm 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The solvent is removed under reduced pressure and the product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3} \text{ mbar}$). 2-chloro-1,1-di(benzyloxy)-ethane (**4e**) is obtained as a yellow viscous liquid in the first fraction at 180–200 °C.



Yield: 31% (260 mg, 0.93 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 12.57 \text{ min}$

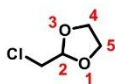
^1H NMR (400 MHz, CD_2Cl_2) δ [ppm] = 7.41–7.29 (m, 10H, $-\text{C}_6\text{H}_5$), 4.88 (t, $J = 5.4 \text{ Hz}$, 1H, H-1), 4.72 (d, $J = 11.6 \text{ Hz}$, 2H, OCH_2^-), 4.63 (d, $J = 11.6 \text{ Hz}$, 2H, OCH_2^-), 3.64 (d, $J = 5.4 \text{ Hz}$, 2H, H-2).

^{13}C NMR (101 MHz, CD_2Cl_2) δ [ppm] = 138.2 ($-\text{C}_6\text{H}_5$), 129.0 ($m\text{-C}_6\text{H}_5$, $o\text{-C}_6\text{H}_5$), 128.4 ($p\text{-C}_6\text{H}_5$), 101.5 (C-1), 69.3 (OCH_2^-), 44.5 (C-2).

HRMS (ESI+): m/z for $\text{C}_{16}\text{H}_{17}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 299.0809, found: 299.0811.

2.8 Synthesis of 2-Chloromethyl-1,3-dioxolane (6)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (218 mg, 0.75 mmol, 1.0 eq.) was dissolved with ethylene glycol vinyl ether (**5**) (198 mg, 202 μ L, 2.25 mmol, 3.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) and manganese(II) chloride tetrahydrate (14.8 mg, 0.075 mmol) was added to the solution and electrolyzed at 57 °C under room atmosphere and an amount of applies charge $Q = 7.4 F$ ($\triangleq 535$ C) with a current density of $j = 10.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 35.0 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloromethyl-1,3-dioxolane (**6**) is obtained as a colorless viscous liquid in the first fraction at 50–60 °C.



Yield: 35% (96 mg, 0.79 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 7.33$ min

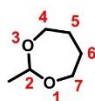
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 5.14 (t, $J = 4.0$ Hz, 1H, H-2), 4.06–4.01 (m, 2H, H-4, H-5), 3.95–3.89 (m, 2H, H-4, H-5), 3.52 (d, $J = 4.0$ Hz, 2H, $-\text{CH}_2\text{Cl}$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.5 (C-2), 65.7 (C-4, C-5), 44.6 ($-\text{CH}_2\text{Cl}$).

HRMS (ESI+): m/z for $\text{C}_4\text{H}_8^{35}\text{ClO}_2$ [M+H]: calc. 123.0207, found: 123.0207.

2.9 Synthesis of 2-Methyl-1,3-dioxepane (5b.1)

1,4-Butanediol (76.6 g, 0.85 mol, 1.0 eq.) and acetaldehyde (217.2 g, 4.93 mol, 5.8 eq.) were placed together with 1 L dichloromethane in an oven-dried 2 L three-necked round-bottom flask, *p*-toluenesulfonic acid (1.3 g, 6.4 mmol, 0.007 eq.) and activated mole sieves (3 Å, 80 g) and stirred overnight under argon atmosphere. A few drops of triethylamine were then added to the reaction mixture, filtered through Celite and neutralized with saturated sodium bicarbonate solution. The filtrate was dried over sodium sulfate and the solvent was removed under reduced pressure. The product was obtained as a colorless liquid by distillation.^[4]



Yield: 59% (58.7 g, 0.51 mol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 5.88$ min

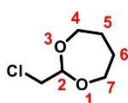
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.90 (q, $J = 5.1$ Hz, 1H, H-2), 3.92–3.86 (m, 2H, H-4, H-7), 3.66–3.60 (m, 2H, H-4, H-7), 1.74–1.67 (m, 4H, H-5, H-6), 1.29 (d, $J = 5.1$ Hz, 3H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 99.53 (C-2), 65.49 (C-4, C-7), 29.36 (C-5, C-6), 20.84 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{13}\text{O}_2$ $[\text{M}+\text{H}]$: calc. 117.0910, found: 117.0909.

2.10 Synthesis of 2-Chloromethyl-1,3-dioxepane (6b)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (218 mg, 0.75 mmol, 1.0 eq.) was dissolved with 4-hydroxybutyl vinyl ether (**5b**) (261 mg, 275 μ L, 2.25 mmol, 3.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (41.4 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applied charge $Q = 7.0 F$ ($\approx 507 C$) with a current density of $j = 10.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 35.0 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloromethyl-1,3-dioxepane (**6b**) is obtained as a colorless viscous liquid in the first fraction at 70–80 °C.



Yield: 74% (251 mg, 1.67 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 9.97 \text{ min}$

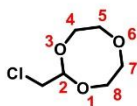
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.85 (t, $J = 5.3 \text{ Hz}$, 1H, H-2), 3.96–3.91 (m, 2H, H-4, H-7), 3.71–3.63 (m, 2H, H-4, H-7), 3.46 (d, $J = 5.3 \text{ Hz}$, 2H, $-\text{CH}_2\text{Cl}$), 1.77–1.67 (m, 4H, H-5, H-6).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.0 (C-2), 66.8 (C-4, C-7), 44.4 ($-\text{CH}_2\text{Cl}$), 29.3 (C-5, C-6).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{11}^{35}\text{ClO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 173.0340, found: 173.0338.

2.11 Synthesis of 2-Chloromethyl-1,3,6-trioxocane (**6c**)

Technical and pretreated 1,2,3,4,5,6-hexachlorocyclohexane (**1**) (218 mg, 0.75 mmol, 1.0 eq.) was dissolved with diethylene glycol monovinyl ether (**5c**) (297 mg, 289 μ L, 2.25 mmol, 3.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium chloride (82.8 mg, 0.5 mmol) was added to the solution and electrolyzed at 8 °C under room atmosphere and an amount of applies charge $Q = 12.0 F (\approx 869 C)$ with a current density of $j = 6.5 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 22.8 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The solvent is removed under reduced pressure and the product is isolated from the crude electrolyte by sublimation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-chloromethyl-1,3,6-trioxocane (**6c**) is obtained as a colorless solid in the first fraction at 100–110 °C.



Yield: 38% (143 mg, 0.86 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 10.86 \text{ min}$

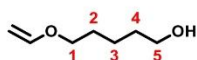
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.77 (t, $J = 5.4 \text{ Hz}$, 1H, H-2), 4.01–3.92 (m, 4H, H-4, H-5, H-7, H-8), 3.79–3.64 (m, 4H, H-4, H-5, H-7, H-8), 3.45 (d, $J = 5.4 \text{ Hz}$, 2H, $-\text{CH}_2\text{Cl}$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 106.4 (C-2), 73.9 (C-5, C-7), 71.9 (C-4, C-8), 45.4 ($-\text{CH}_2\text{Cl}$).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{11}^{35}\text{ClO}_3\text{Na}$ [$\text{M}+\text{Na}$]: calc. 189.0289, found: 189.0288.

2.12 Synthesis of 5-Hydroxypentyl vinyl ether (**5d**)

In a 25ml pressure tube a mixture of the 1,3-Pentanediol (5.0 g, 48 mmol, 1.0 eq.), powdered KOH (2.7 g, 48 mmol, 1.0 eq.) and water (4 vol%) in DMSO was prepared. This mixture was stirred at room temperature for 30 minutes while observing a change in color, calcium carbide (4.6 g, 72 mmol, 1.5 eq.) was added, the flask was sealed closed. The reaction was stirred at 120 °C for 5 h then cooled to room temperature. The product was extracted by working up the mixture with diethyl ether (3 x 50 mL) and Ice-cold water (3 x 10 mL). The organic layer was collected and was evaporated under vacuum to remove diethyl Ether and obtain the desired product as a faint yellow oil with trace amounts of DMSO. The removal of DMSO was done using fractional distillation and simultaneous washing with ice cold water and diethyl ether to remove traces of DMSO and obtain the corresponding vinyl ether (**5d**) as a yellow viscous liquid.^[5]



Yield: 24% (1.5 g, 12 mmol)

Characterization:

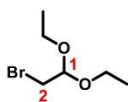
¹H NMR (400 MHz, CD₂Cl₂) δ [ppm] = 6.45 (q, *J* = 6.9 Hz, 1H, CH), 4.15 (dd, *J* = 14.3, 1.8 Hz, 1H, =CH₂), 3.95 (dd, *J* = 6.9, 1.8 Hz, 1H, =CH₂), 3.67 (t, *J* = 6.5 Hz, 2H, H-1), 3.58 (t, *J* = 6.5 Hz, 2H, H-5), 2.14 (s, 1H, OH), 1.70–1.63 (m, 2H, H-2), 1.59–1.52 (m, 2H, H-4), 1.46–1.40 (m, 2H, H-3).

¹³C NMR (101 MHz, CD₂Cl₂) δ [ppm] = 152.34 (CH), 86.36 (=CH₂), 68.41 (C-1), 62.78 (C-5), 32.82 (C-4), 29.23 (C-2), 22.67 (C-3).

HRMS (ESI⁺): *m/z* for C₇H₁₅O₂ [M+H]⁺: calc. 131.1067, found: 131.1077.

2.13 Synthesis of 2-Bromo-1,1-di(ethoxy)-ethane (**10**)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with ethyl vinyl ether (**3**) (219 mg, 290 μ L, 3.0 mmol, 3.0 eq.) and ethanol (552 mg, 700 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\triangleq 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3} \text{ mbar}$). 2-bromo-1,1-di(ethoxy)-ethane (**10**) is obtained as a colorless viscous liquid in the first fraction at 40–50 °C.



Yield: 86% (510 mg, 2.59 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 8.74 \text{ min}$

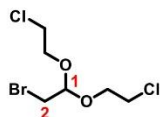
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.66 (t, $J = 5.5 \text{ Hz}$, 1H, H-1), 3.72–3.55 (m, 4H, OCH_2 -), 3.36 (d, $J = 5.5 \text{ Hz}$, 2H, H-2), 1.23 (t, $J = 7.1 \text{ Hz}$, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.6 (C-1), 62.6 (OCH_2 -), 32.0 (C-2), 15.3 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{13}^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 218.9991, found: 218.9992.

2.14 Synthesis of 2-Bromo-1,1-di(2-chloroethoxy)-ethane (10a)

Technical 1,2,5,6,9,10-Hexabromcyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-chloroethyl vinyl ether (**3a**) (320 mg, 304 μ L, 3.0 mmol, 3.0 eq.) and 2-chloroethanol (966 mg, 800 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F$ (± 820.1 C) with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The solvent is removed under reduced pressure and the product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**) is obtained as a yellow viscous liquid in the first fraction at 90–100 °C.



Yield: 12% (93 mg, 0.35 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 15.15$ min

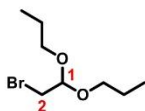
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.82 (t, $J = 5.5$ Hz, 1H, H-1), 3.92 (dt, $J = 11.0, 5.5$ Hz, 2H, OCH_2 -), 3.83 (dt, $J = 11.0, 5.5$ Hz, 2H, OCH_2 -), 3.67 (t, $J = 5.5$ Hz, 4H, $-\text{CH}_2\text{Cl}$), 3.43 (d, $J = 5.5$ Hz, 2H, H-2).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.2 (C-1), 67.2 (OCH_2 -), 43.7 ($-\text{CH}_2\text{Cl}$), 31.4 (C-2).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{11}^{79}\text{Br}^{35}\text{Cl}_2\text{ONa}$ [$\text{M}+\text{Na}$]: calc. 286.9212, found: 286.9212.

2.15 Synthesis of 2-Bromo-1,1-di(propoxy)-ethane (**10b**)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with propyl vinyl ether (**3b**) (258 mg, 340 μ L, 3.0 mmol, 3.0 eq.) and propanol (721 mg, 900 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\triangleq 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3} \text{ mbar}$). 2-bromo-1,1-di(propoxy)-ethane (**10b**) is obtained as a colorless viscous liquid in the first fraction at 50–60 °C.



Yield: 14% (94 mg, 0.42 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 11.05 \text{ min}$

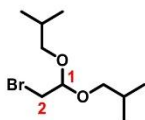
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.66 (t, $J = 5.5 \text{ Hz}$, 1H, H-1), 3.60 (dt, $J = 9.2, 6.7 \text{ Hz}$, 2H, OCH_2 -), 3.46 (dt, $J = 9.2, 6.7 \text{ Hz}$, 2H, OCH_2 -), 3.37 (d, $J = 5.5 \text{ Hz}$, 2H, H-2), 1.62 (h, $J = 7.4 \text{ Hz}$, 4H, $-\text{CH}_2$ -), 0.94 (t, $J = 7.4 \text{ Hz}$, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.8 (C-1), 68.7 (OCH_2 -), 31.9 (C-2), 23.1 ($-\text{CH}_2$ -), 10.8 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_8\text{H}_{17}^{79}\text{BrO}_2\text{Na}$ [M+Na]: calc. 247.0304, found: 247.0305.

2.16 Synthesis of 2-Bromo-1,1-di(2-methylpropoxy)-ethane (**10c**)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-methylpropyl vinyl ether (**3c**) (301 mg, 390 μ L, 3.0 mmol, 3.0 eq.) and 2-methylpropan-1-ol (889 mg, 1110 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\triangleq 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The electrolyte solution is extracted with *n*-pentane (3 x 5 mL). The fractions are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product was purified in a distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**) is obtained as a colorless viscous liquid in the first fraction at 60–70 °C.



Yield: 36% (272 mg, 1.07 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 12.25 \text{ min}$

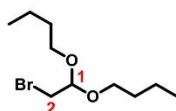
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.65 (t, $J = 5.6 \text{ Hz}$, 1H, H-1), 3.42–3.37 (m, 4H, OCH_2 -, H-2), 3.25 (dd, $J = 9.0, 6.6 \text{ Hz}$, 2H, OCH_2 -), 1.87 (hept, $J = 6.7 \text{ Hz}$, 2H, -CH-), 0.93 (d, $J = 6.7 \text{ Hz}$, 12H, - CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.00 (C-1), 73.66 (OCH_2 -), 31.86 (C-2), 28.73 (-CH-), 19.52 (- CH_3).

HRMS (ESI+): m/z for $\text{C}_{10}\text{H}_{21}^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 275.0617, found: 275.0617.

2.17 Synthesis of 2-Bromo-1,1-di(butoxy)-ethane (**10d**)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with 2-methylpropyl vinyl ether (**3d**) (301 mg, 390 μ L, 3.0 mmol, 3.0 eq.) and butanol (889 mg, 1110 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\pm 820.1 C)$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The electrolyte solution is extracted with *n*-pentane (3 x 5 mL). The fractions are combined, dried over magnesium sulfate and the solvent is removed under reduced pressure. The crude product was purified in a distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-bromo-1,1-di(butoxy)-ethane (**10d**) is obtained as a colorless viscous liquid in the first fraction at 60–70 °C.



Yield: 17% (126 mg, 0.50 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 13.47 \text{ min}$

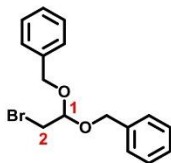
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.65 (t, $J = 5.5 \text{ Hz}$, 1H, H-1), 3.63 (dt, $J = 9.2, 6.6 \text{ Hz}$, 2H, OCH_2 -), 3.49 (dt, $J = 9.2, 6.6 \text{ Hz}$, 2H, OCH_2 -), 3.36 (d, $J = 5.5 \text{ Hz}$, 2H, H-2), 1.61–1.55 (m, 4H, $-\text{CH}_2-\text{CH}_2-$), 1.43–1.37 (m, 4H, $-\text{CH}_2-\text{CH}_2-$), 0.92 (t, $J = 7.4 \text{ Hz}$, 6H, $-\text{CH}_3$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 101.81 (C-1), 66.77 (OCH_2 -), 31.92 (C-2, $-\text{CH}_2-$), 19.43 ($-\text{CH}_2-$), 13.99 ($-\text{CH}_3$).

HRMS (ESI+): m/z for $\text{C}_{10}\text{H}_{21}^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 275.0617, found: 275.0618.

2.18 Synthesis of 2-Bromo-1,1-di(benzyloxy)-ethane (10e)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (642 mg, 1.0 mmol, 1.0 eq.) was dissolved with benzyl vinyl ether (**3e**) (403 mg, 415 μ L, 3.0 mmol, 3.0 eq.) and benzyl alcohol (1298 mg, 1250 μ L, 12.0 mmol, 12.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 8.5 F (\pm 820.1 \text{ C})$ with a current density of $j = 15.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 52.5 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The solvent is removed under reduced pressure and the product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3} \text{ mbar}$). 2-bromo-1,1-di(benzyloxy)-ethane (**10e**) is obtained as a yellow viscous liquid in the first fraction at 180–200 °C.



Yield: 15% (149 mg, 0.47 mmol)

Characterization:

GC (method: 2_medium, column: HI-5MS): $t_{R,GC} = 12.80 \text{ min}$

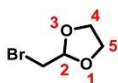
^1H NMR (400 MHz, CD_2Cl_2) δ [ppm] = 7.41–7.31 (m, 10H, $-\text{C}_6\text{H}_5$), 4.92 (t, $J = 5.4 \text{ Hz}$, 1H, H-1), 4.72 (d, $J = 11.5 \text{ Hz}$, 2H, OCH_2^-), 4.62 (d, $J = 11.5 \text{ Hz}$, 2H, OCH_2^-), 3.50 (d, $J = 5.4 \text{ Hz}$, 2H, H-2).

^{13}C NMR (101 MHz, CD_2Cl_2) δ [ppm] = 138.2 ($-\text{C}_6\text{H}_5$), 129.0 ($o\text{-C}_6\text{H}_5$), 128.4 ($m\text{-C}_6\text{H}_5$), 128.4 ($p\text{-C}_6\text{H}_5$), 101.2 (C-1), 69.2 (OCH_2^-), 32.3 (C-2).

HRMS (ESI+): m/z for $\text{C}_{16}\text{H}_{17}^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 343.0304, found: 343.0306.

2.19 Synthesis of 2-Bromomethyl-1,3-dioxolane (11)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (481 mg, 0.75 mmol, 1.0 eq.) was dissolved with ethylene glycol vinyl ether (**5**) (198 mg, 202 μ L, 2.25 mmol, 3.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 57 °C under room atmosphere and an amount of applies charge $Q = 7.4 F$ ($\triangleq 535 C$) with a current density of $j = 10.0 \text{ mA} \cdot \text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 35.0 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1 \cdot 10^{-3}$ mbar). 2-bromomethyl-1,3-dioxolane (**11**) is obtained as a colorless viscous liquid in the first fraction at 50–60 °C.



Yield: 49% (184 mg, 1.10 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 7.33 \text{ min}$

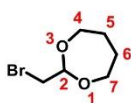
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 5.14 (t, $J = 4.0 \text{ Hz}$, 1H, H-2), 4.06–4.01 (m, 2H, H-4, H-5), 3.95–3.89 (m, 2H, H-4, H-5), 3.52 (d, $J = 4.0 \text{ Hz}$, 2H, $-\text{CH}_2\text{Br}$).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 102.52 (C-2), 65.69 (C-4, C-5), 44.59 ($-\text{CH}_2\text{Br}$).

HRMS (ESI+): m/z for $\text{C}_4\text{H}_7^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 166.9702, found: 166.9703.

2.20 Synthesis of 2-Bromomethyl-1,3-dioxepane (**11b**)

Technical 1,2,5,6,9,10-Hexabromocyclododecan (**8**) (481 mg, 0.75 mmol, 1.0 eq.) was dissolved with 4-hydroxybutyl vinyl ether (**5b**) (261 mg, 275 μ L, 2.25 mmol, 3.0 eq.) in 5 mL propylene carbonate into the 5 mL IKA glass cell (**Figure S1**). In addition, tetraethylammonium bromide (52.5 mg, 0.25 mmol) was added to the solution and electrolyzed at 25 °C under room atmosphere and an amount of applies charge $Q = 7.0 F$ ($\triangleq 507 C$) with a current density of $j = 10.0 \text{ mA}\cdot\text{cm}^{-2}$ (since the electrodes have an immersion depth of 3.5 cm, 35.0 mA is applied). Isostatic graphite electrodes were preferably used as anode and cathode. The product is isolated from the electrolyte by distillation under reduced pressure ($1\cdot 10^{-3}$ mbar). 2-bromomethyl-1,3-dioxepane (**11b**) is obtained as a colorless viscous liquid in the first fraction at 70–80 °C.



Yield: 29% (127 mg, 0.65 mmol)

Characterization:

GC (method: Performance DWE-SHS, column: HI-5MS): $t_{R,GC} = 10.91 \text{ min}$

^1H NMR (400 MHz, CDCl_3) δ [ppm] = 4.89 (t, $J = 5.3 \text{ Hz}$, 1H, H-2), 3.96–3.90 (m, 2H, H-4, H-7), 3.69–3.64 (m, 2H, H-4, H-7), 3.32 (d, $J = 5.3 \text{ Hz}$, 2H, $-\text{CH}_2\text{Br}$), 1.76–1.68 (m, 4H, H-5, H-6).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 100.76 (C-2), 66.68 (C-4, C-7), 32.40 ($-\text{CH}_2\text{Br}$), 29.29 (C-5, C-6).

HRMS (ESI+): m/z for $\text{C}_6\text{H}_{11}^{79}\text{BrO}_2\text{Na}$ [$\text{M}+\text{Na}$]: calc. 216.9835, found: 216.9835.

3. Supplementary Results

3.1 External GC Calibration with an Internal Standard for Yield Determination

For the yield determination via gas chromatography, an external calibration was carried out. 1,10-Dichlorodecane (70 μ L, 69.6 mg for each measurement) was used for hexachlorocyclohexane (HCH), benzene and monochlorinated products. For the linear regression, the molar ratio of the substance to 1,10-Dichlorodecane was plotted against the resulting area ratio of the GC integration values. From the obtained linear regression equation, the molar amount of the substrate after the reaction can be determined. Mathematical calculations and linear regression analysis were performed using Excel® from Microsoft® 365 for Enterprise.

Preparation of the calibration solutions and the qualitative analysis:

The analyte is dissolved together with the internal standard in acetonitrile in different concentrations. Three drops from the solution are filtered over silica gel 60 M (approx. 500 mg) into a GC vial using acetonitrile as eluent.

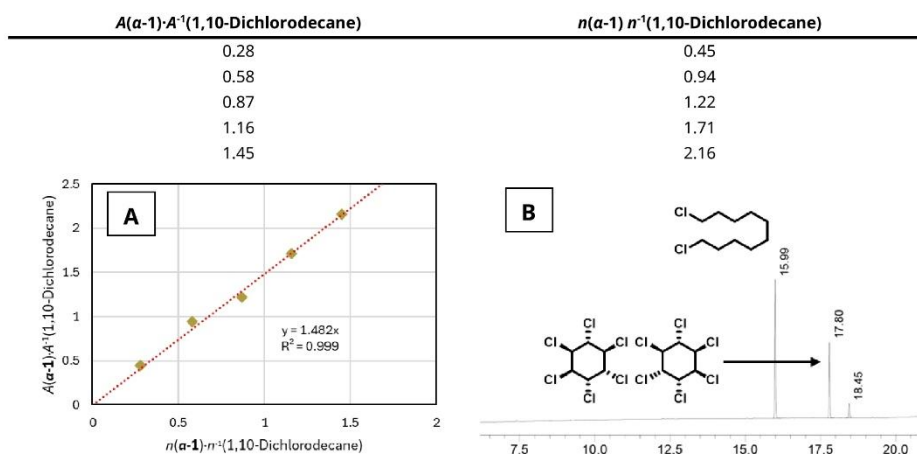


Figure S11: Data of the calibration measurements for α -hexachlorocyclohexane $\alpha\text{-HCH}$ ($\alpha\text{-1}$). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of $\alpha\text{-HCH}$ ($\alpha\text{-1}$) using 70 μ L of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

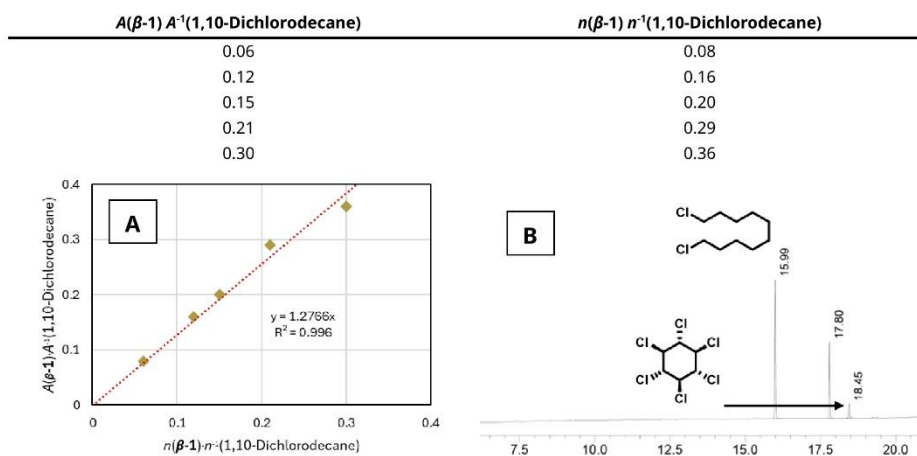


Figure S12: Data of the calibration measurements for β -hexachlorocyclohexane β -HCH (β -1). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of β -HCH (β -1) using 70 μ L of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

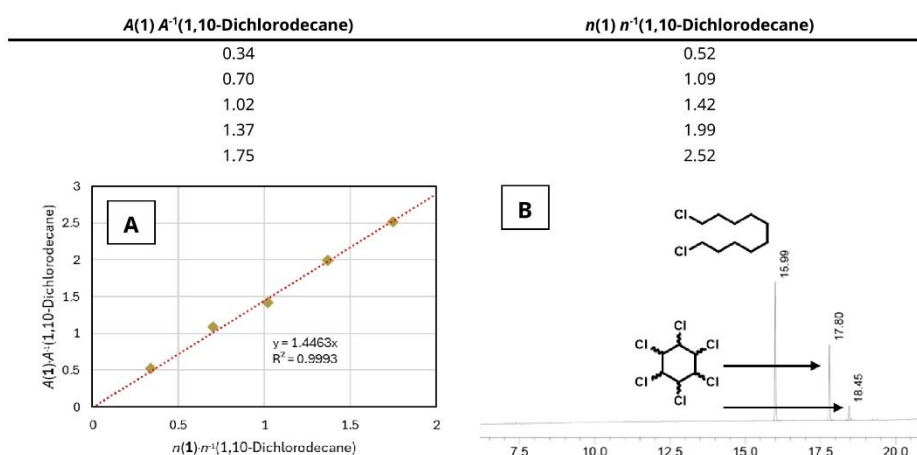


Figure S13: Data of the calibration measurements for hexachlorocyclohexane HCH (**1**) (α -HCH + β -HCH). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of HCH (**1**) using 70 μ L of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

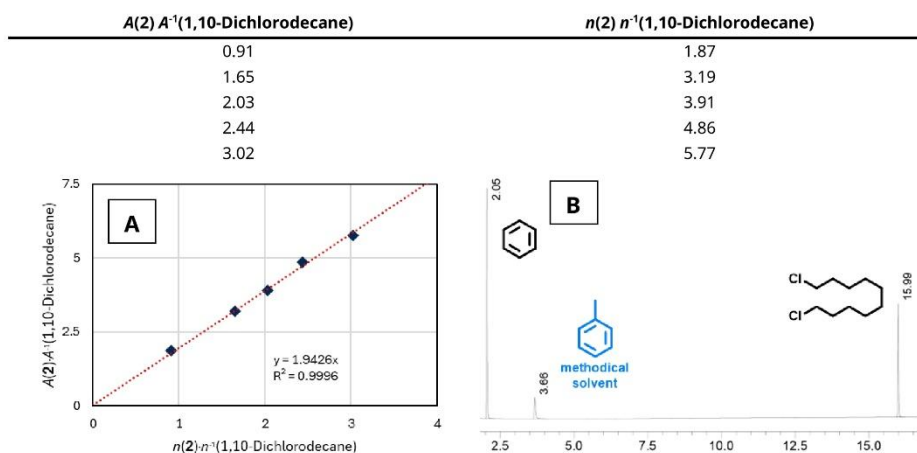


Figure S14: Data of the calibration measurements for benzene (2). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of benzene (2) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS). Methodical solvent is part of the rinsing process.

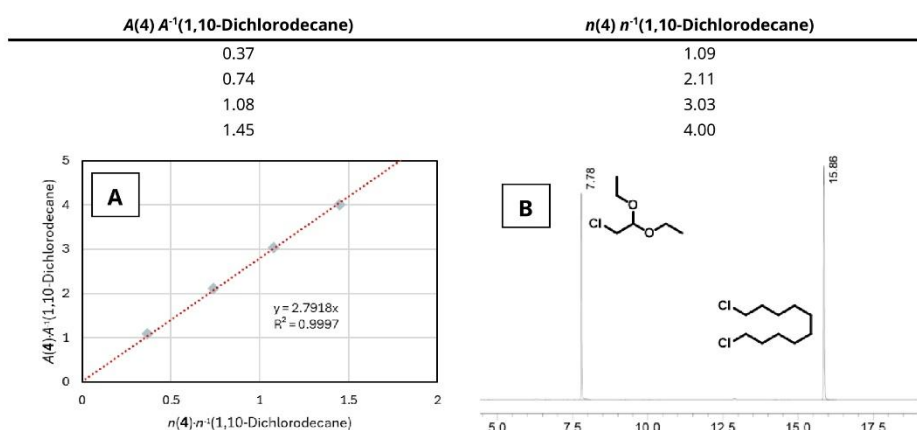


Figure S15: Data of the calibration measurements for 2-chloro-1,1-di(ethoxy)-ethane (4). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(ethoxy)-ethane (4) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

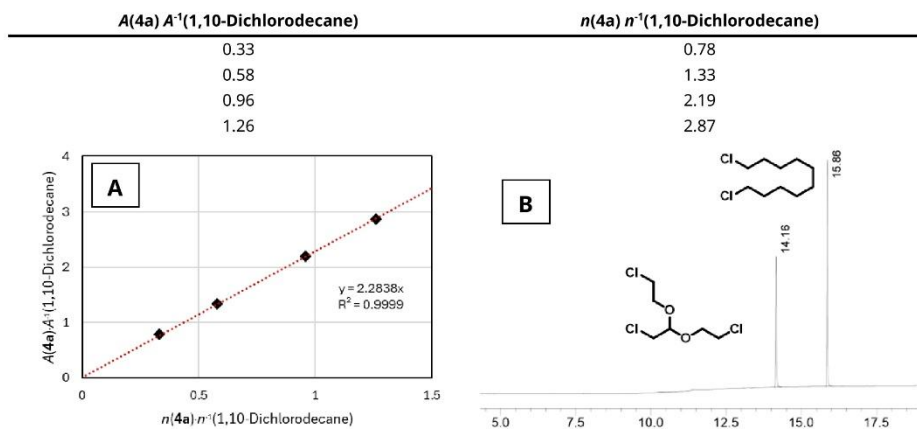


Figure S16: Data of the calibration measurements for 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

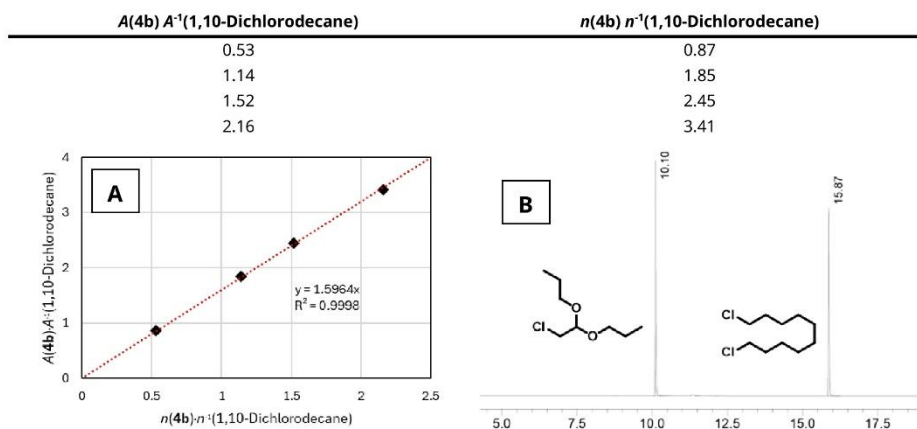


Figure S17: Data of the calibration measurements for 2-chloro-1,1-di(propoxy)-ethane (**4b**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(propoxy)-ethane (**4b**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

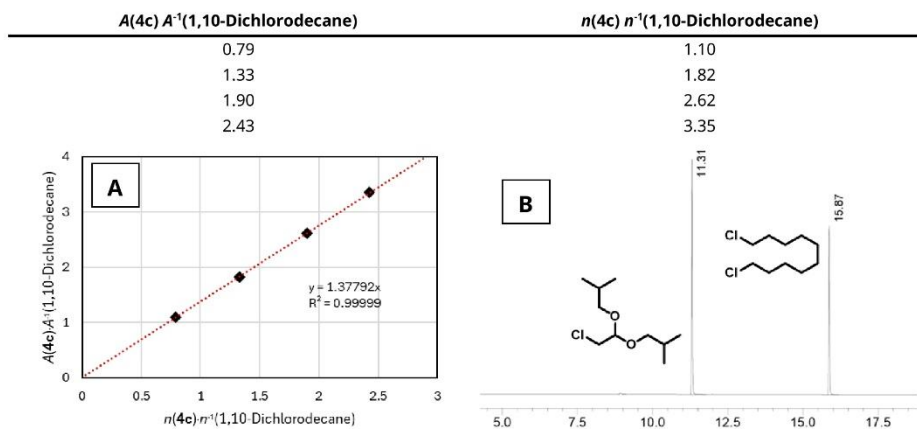


Figure S18: Data of the calibration measurements for 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

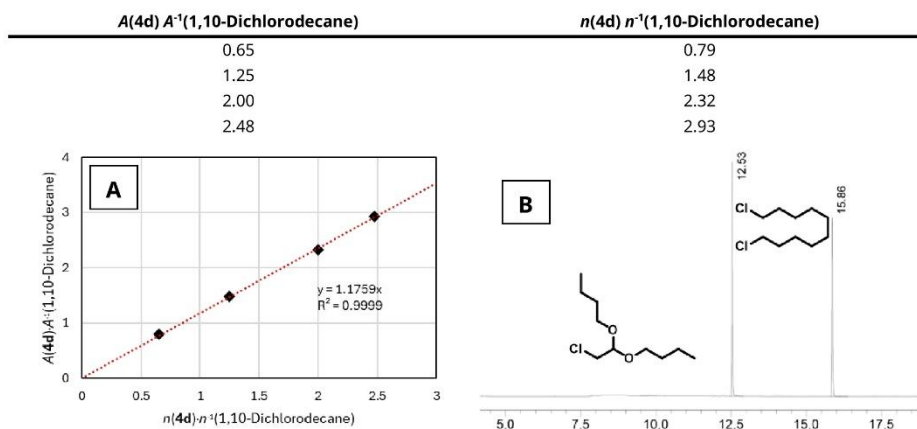


Figure S19: Data of the calibration measurements for 2-chloro-1,1-di(butoxy)-ethane (**4d**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(butoxy)-ethane (**4d**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

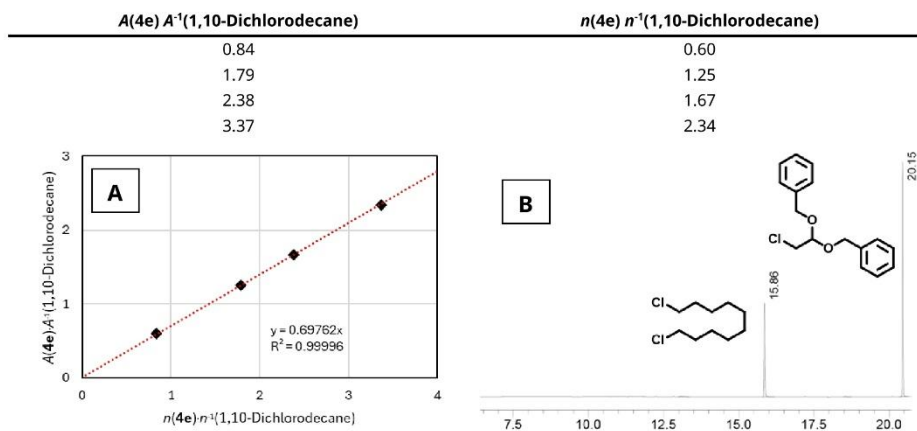


Figure S20: Data of the calibration measurements for 2-chloro-1,1-di(benzyloxy)-ethane (**4e**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

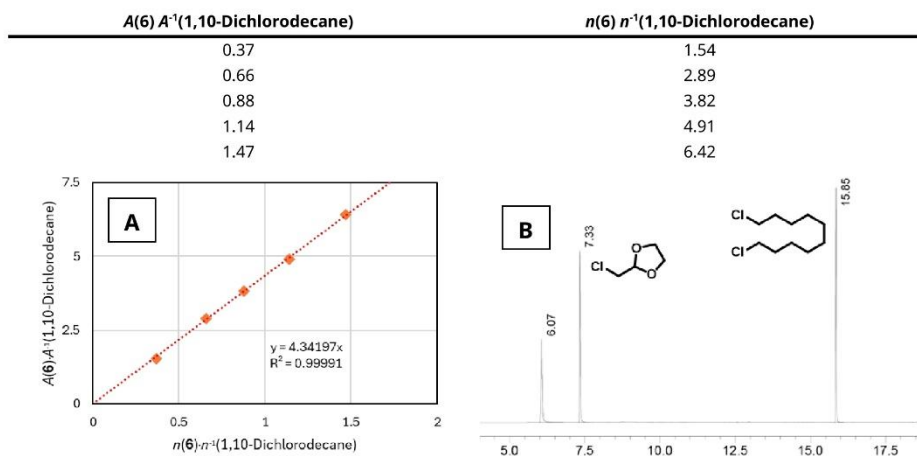


Figure S21: Data of the calibration measurements for 2-chloromethyl-1,3-dioxolane (**6**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloromethyl-1,3-dioxolane (**6**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

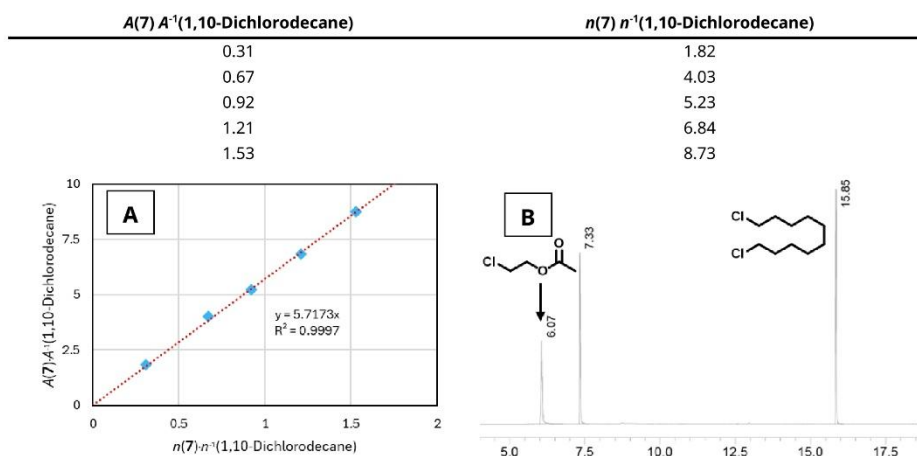


Figure S22: Data of the calibration measurements for 2-chloroethyl acetate (**7**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of for 2-chloroethyl acetate (**7**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

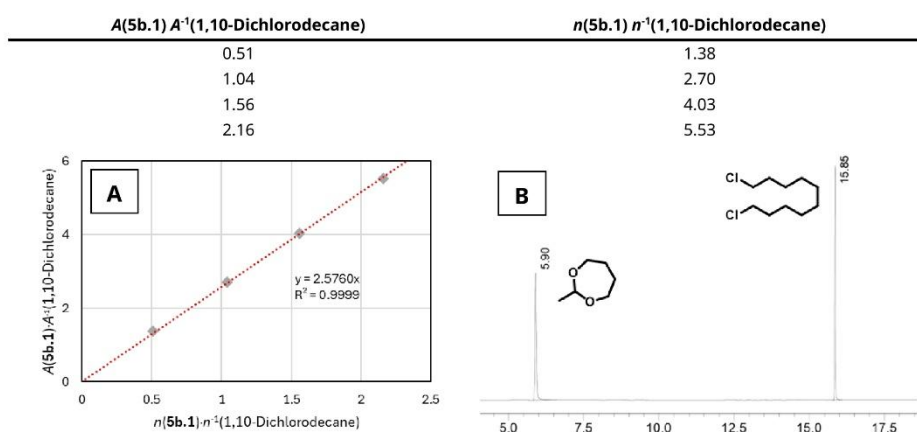


Figure S23: Data of the calibration measurements for 2-methyl-1,3-dioxepane (**5b.1**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-methyl-1,3-dioxepane (**5b.1**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

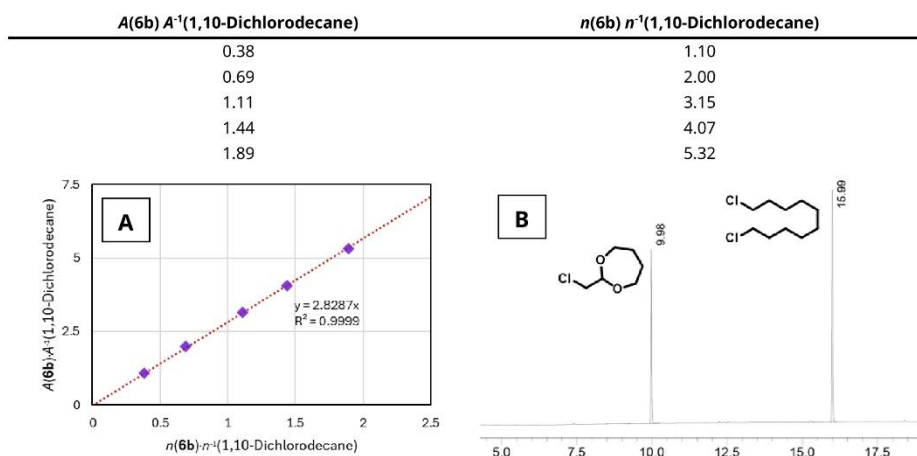


Figure S24: Data of the calibration measurements for 2-chloromethyl-1,3-dioxepane (**6b**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloromethyl-1,3-dioxepane (**6b**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

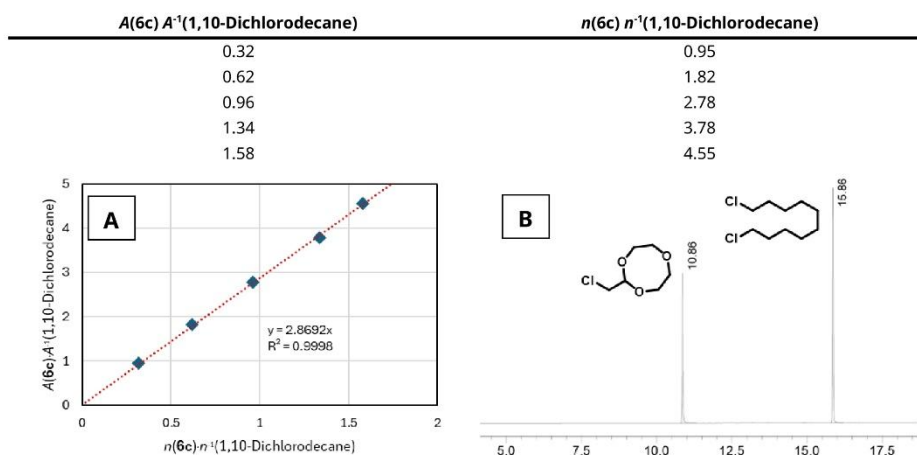


Figure S25: Data of the calibration measurements for 2-chloromethyl-1,3,6-trioxocane (**6c**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-chloromethyl-1,3,6-trioxocane (**6c**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

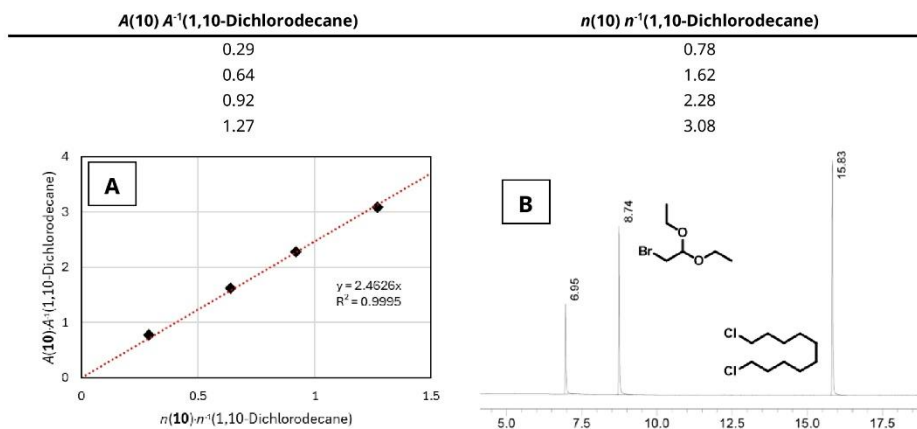


Figure S26: Data of the calibration measurements for 2-bromo-1,1-diethoxyethane (**10**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-diethoxyethane (**10**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

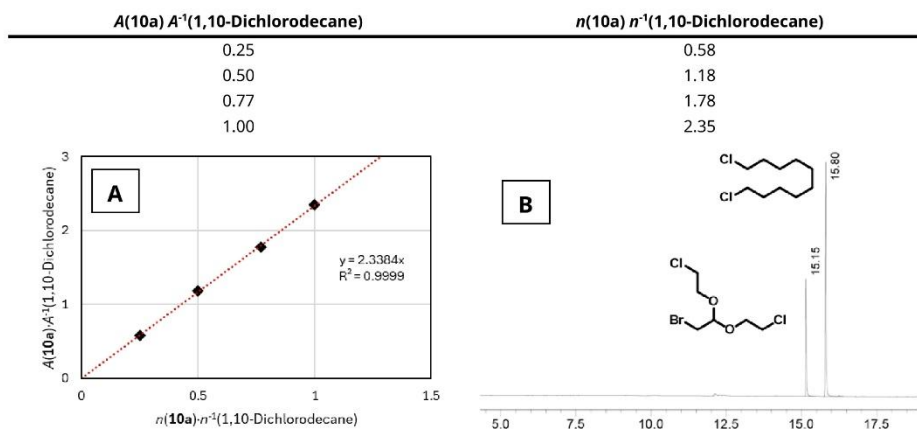


Figure S27: Data of the calibration measurements for 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

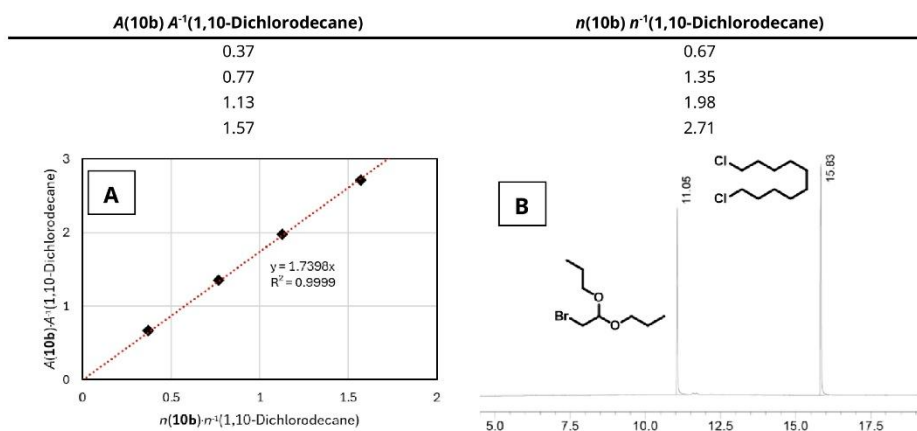


Figure S28: Data of the calibration measurements for 2-bromo-1,1-di(propoxy)-ethane (**10b**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-di(propoxy)-ethane (**10b**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

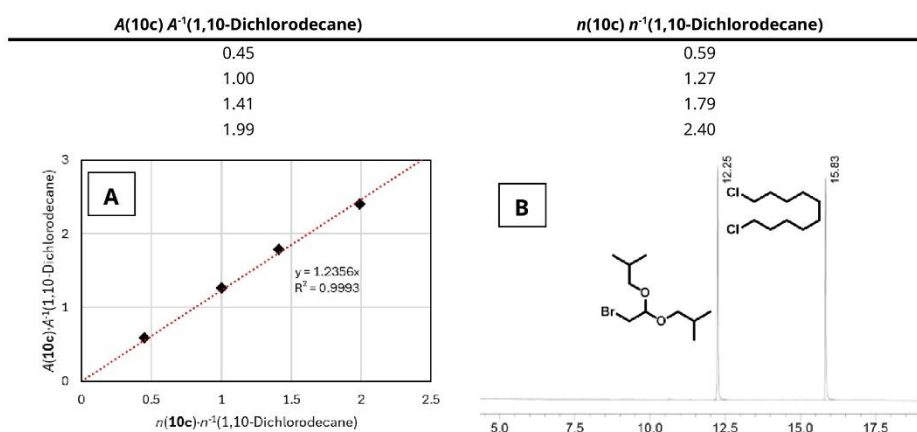


Figure S29: Data of the calibration measurements for 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

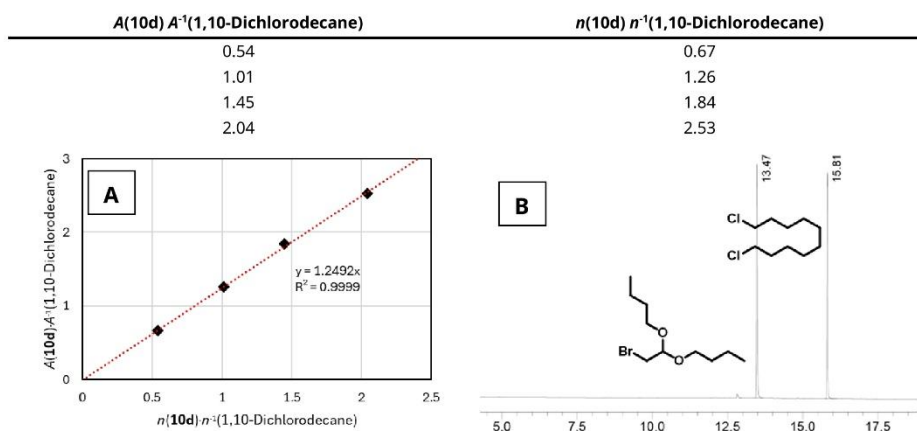


Figure S30: Data of the calibration measurements for 2-bromo-1,1-di(butoxy)-ethane (**10d**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-di(butoxy)-ethane (**10d**) using 70 μ L of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

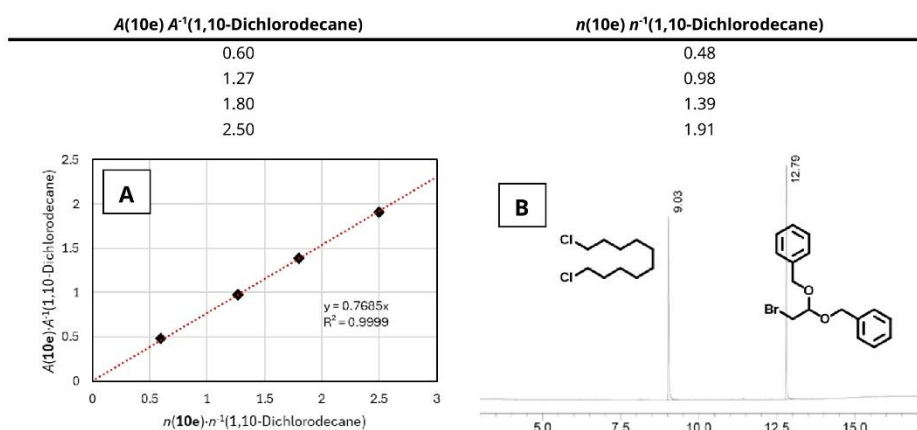


Figure S31: Data of the calibration measurements for 2-bromo-1,1-di(benzyloxy)-ethane (**10e**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromo-1,1-di(benzyloxy)-ethane (**10e**) using 70 μ L of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: 2_medium).

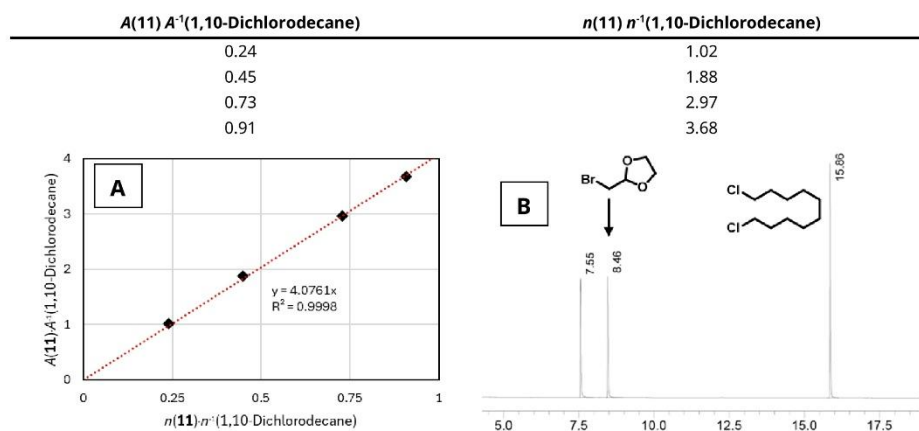


Figure S32: Data of the calibration measurements for 2-bromomethyl-1,3-dioxolane (**11**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromomethyl-1,3-dioxolane (**11**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

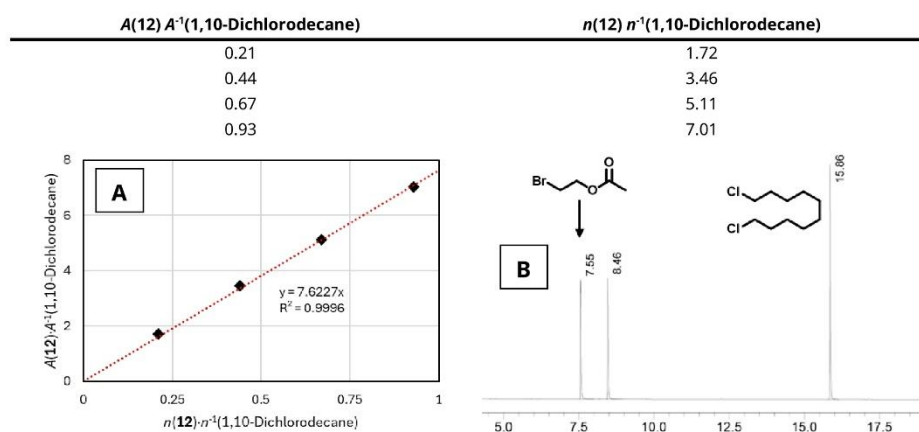


Figure S33: Data of the calibration measurements for 2-bromoethyl acetate (**12**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromoethyl acetate (**12**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

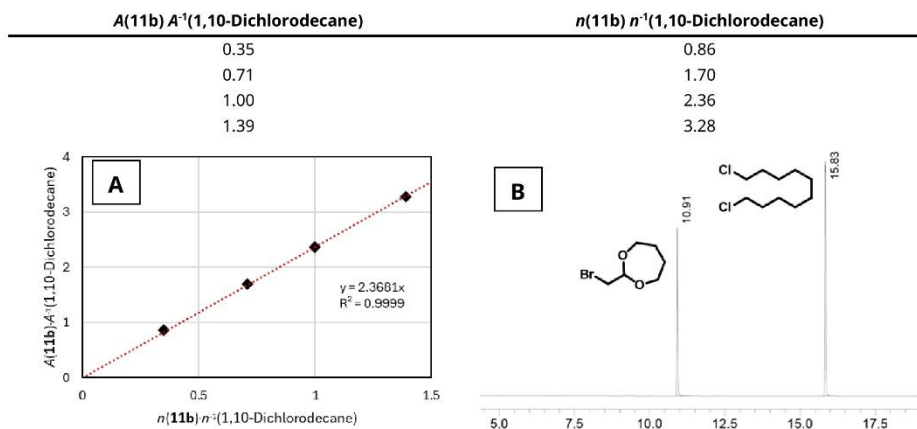


Figure S34: Data of the calibration measurements for 2-bromomethyl-1,3-dioxepane (**11b**). Of each concentration, three samples were prepared and analyzed. **A:** External GC calibration of 2-bromomethyl-1,3-dioxepane (**11b**) using 70 μL of 1,10-dichlorodecane as internal standard for each measurement. **B:** Example GC chromatogram of the calibration to visualize the evaluation (method used: Performance DWE-SHS).

3.2 Mechanism studies

Discussion of the main mechanism

The mechanism is discussed using the example of cyclic acetals. The HCH (1) is reduced cathodically to benzene (2) with the release of 2 chlorides per double bond (**Figure S35, I**). The released chloride is anodically oxidized into an active chlorine species "Cl₂" (**III**).^[6] The formation of the cyclic product suggested an addition of the "active chlorine" to the chloronium ion at the unsaturated bond (**IV**). The subsequent cyclic addition of the hydroxyl group to the activated double bond leads **[5-5b]*** to the formation of the cyclic chlorinated acetal (**6-6b**) with equimolar amounts of HCl (**V**).^[7] The formation of open acetals can be understood in the same way.

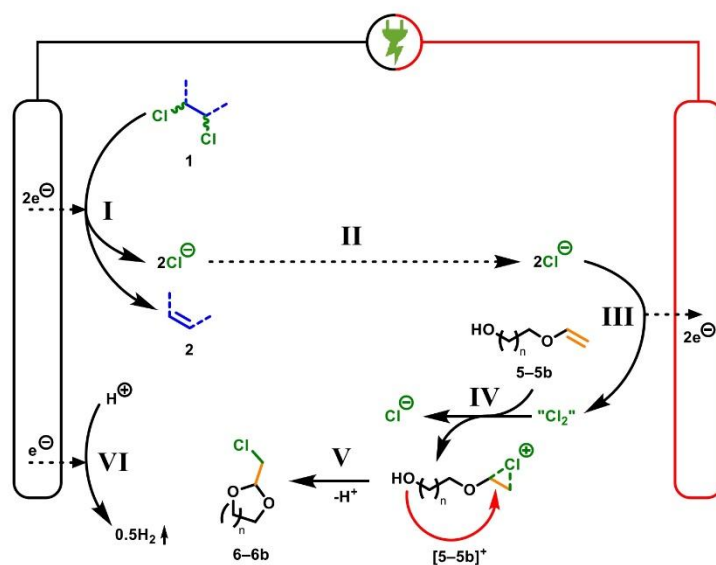


Figure S35: Postulated mechanism of the formation of cyclic acetals (**6-6b**).^[7]

Cathodically, the formation of hydrogen cannot be ruled out either (**VI**).

A screening of the equivalents of 4-hydroxybutyl vinyl ether (**5b**) revealed its limitations (Table S3).

Table S3: Determined yields Y_i of benzene (**2**), 2-chloro-1,3-dioxepan (**6b**) and conversion X_i of technical HCH (**1**) increased addition of 4-hydroxybutyl vinyl (**5b**) ether.

graphite || graphite
(C₂H₅)₄NCl (0.05 mol·L⁻¹)

propylene carbonate,
10.0 mA·cm⁻²,
7.0 F (ref. to 1),
25 °C, 500 rpm

1 + n 5b → 2 + n 6b

eq(5b)

eq(5b)	Conversion X(1) / %	Yield Y(2) / %	Yield Y(6b) / %
3.0	78	57	79
3.5	73	51	46
4.0	76	56	49
4.5	74	54	38
6.0 (14 F)	99	81	46

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard.

The theoretical balance of the reaction is summarized in **Table S4**.

Table S4: Theoretical balancing of the postulated mechanism of the cathodic and anodic reaction using the example of cyclic acetals.

Example of cyclic acetals

Cathode	Anode
 1 2	
Follow-up reaction with by-product HCl	
IV+V 	
Electrolysis of HCl	
Cathode	Anode
VI 	II 

Cyclovoltammetry study

Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a graphite working electrode (3 mm in diameter, BASi), a Ag/AgNO₃ reference electrode, and a glassy carbon counter electrode (3 mm in diameter, BASi). The solution of interest was sparged with argon for 3–5 minutes before data collection.

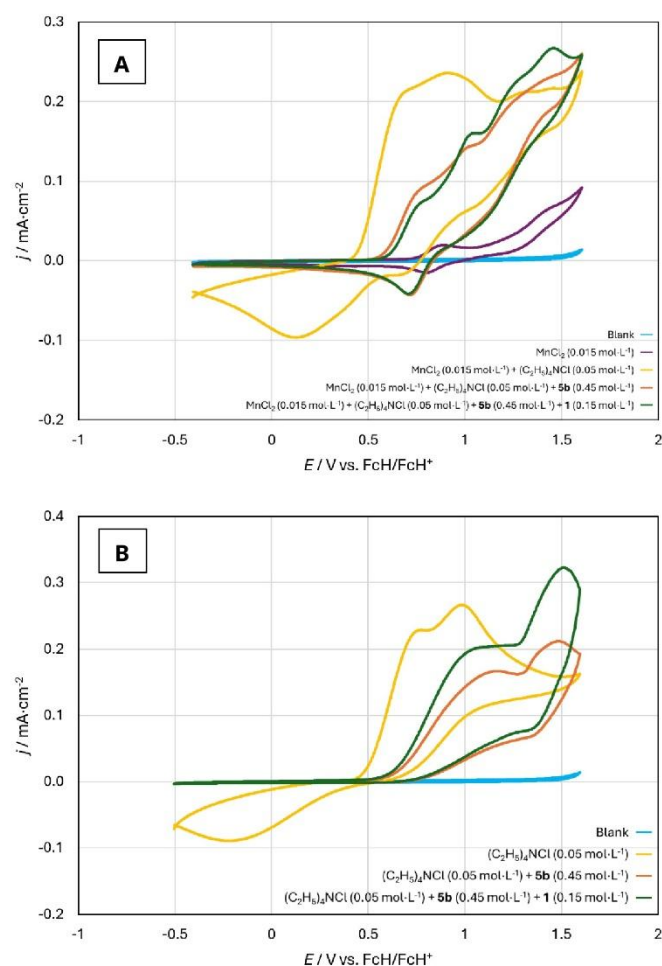


Figure S36: CV study of the electrolyte system with supporting electrolyte ((C₂H₅)₄NCl), 4-hydroxybutyl vinyl ether (**5b**) and HCH (**1**). **A:** With manganese(II) chloride. **B:** Without manganese(II) chloride.

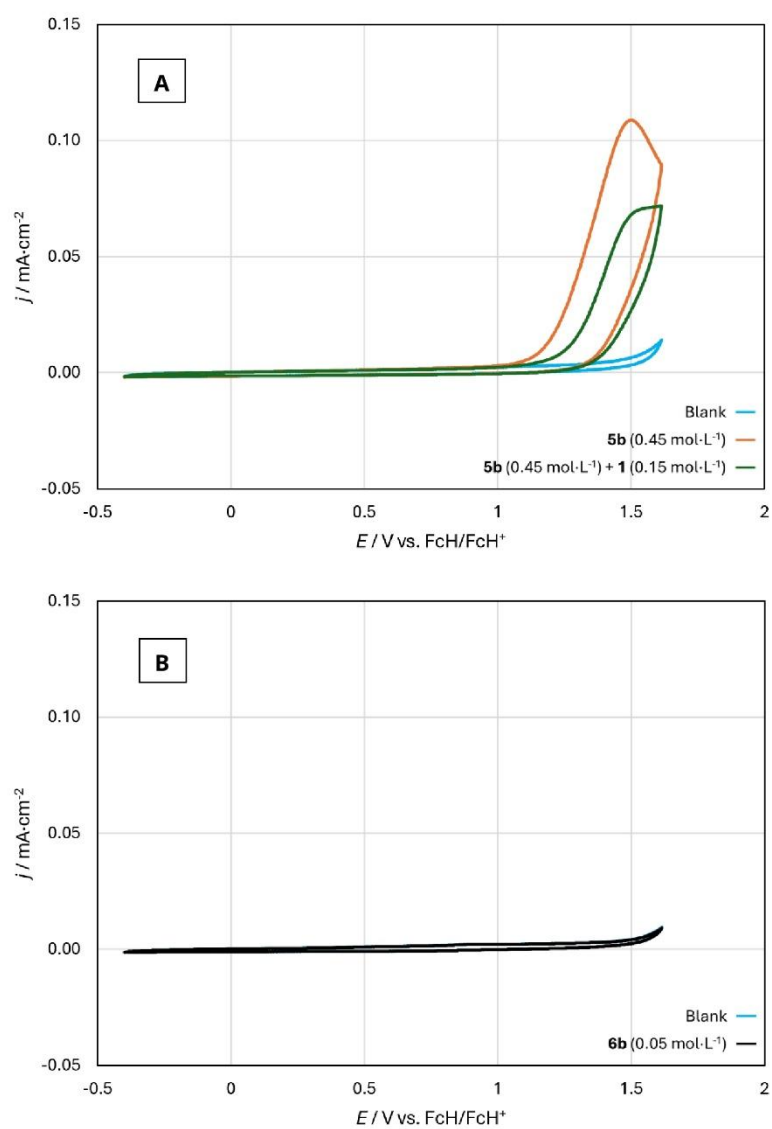


Figure S37: CV study of the electrolyte system with 4-hydroxybutyl vinyl ether (**5b**), HCH (**1**) and 2-chloromethyl-1,3-dioxepan (**6b**). **A:** Only with **5b** and **1**. **B:** Electrochemical stability test of the product (**6b**).

Determination of HCl in the electrolyte of the 2-chloromethyl-1,3-dioxepane (**6b**) synthesis (IV+V)

A solution of HCH (**1**) (2184.0 mg, 7.5 mmol, 1.0 eq.), tetraethylammonium chloride (415.8 mg, 2.5 mmol), 4-hydroxybutyl vinyl ether (**5b**) (2.7 mL, 21.8 mmol; 2.9 eq.) and 50 mL propylene carbonate was prepared and added to the electrolysis cell (with stirrer). A sample (approx. 1 mL) of this solution was taken as an initial value. The electrodes with plugs were inserted into the cell and adjusted to a height of 8.3 cm from the meniscus (**Figure S38**). Nitrogen was fed through two cannulas via the stopper on the side nozzle with tubing. The outlet was connected to a gas washing bottle filled with 200 mL 1 mol·L⁻¹ NaOH and the gas was passed through during the entire electrolysis (**Figure S39**). This was used to collect and quantify HCl from the gas phase.



Figure S38: Electrolysis cell with connected electrodes and nitrogen gassing.



Figure S39: Washing bottle with 200 mL of 1 mol·L⁻¹ NaOH.

The stirrer was set to 500 rpm. The power supply for the electrodes was switched on and started with a current of $I = 194$ mA. After 437 min, the power supply was switched off and samples were taken from the electrolysis cell and the content of the gas washing bottle. The determination of chlorides is summarized in **Table S5**.

Table S5: Determination of Chloride Cl in the electrolyte of the 2-chloromethyl-1,3-dioxepane (**6b**) synthesis via IC.

Sample	mass concentration $\rho(\text{Cl}) / \text{mg} \cdot \text{L}^{-1} \text{ ppm}$
LOD	259
LOQ	777
Electrolyte before electrolysis a	1135
Electrolyte before electrolysis b	1449
1 mol·L ⁻¹ NaOH after electrolysis a	<LOD
1 mol·L ⁻¹ NaOH after electrolysis b	<LOD
Recovery	111
Electrolyte after electrolysis a	7171
Electrolyte after electrolysis b	7608
Recovery	126

LOD: Limit of detection; LOQ: Limit of quantitation

Chloride determination according to Mohr^[8]

To determine the chlorides via titration according to Mohr, all gases were condensed into liquid nitrogen under reduced pressure (10 mbar) during and after electrolysis. A solution of HCH (**1**) (2181.0 mg, 7.5 mmol, 1.0 eq.), tetraethylammonium chloride (414.5 mg, 2.5 mmol), 4-hydroxybutyl vinyl ether (**5b**) (2.8 mL, 22.5 mmol; 3.0 eq.) and 50 mL propylene carbonate was prepared and added to the 50 mL electrolysis cell (**Figure S40**) (with stirrer). The electrodes with plugs were inserted into the cell and adjusted to a height of 8.3 cm from the meniscus. The cold trap was connected with a hose on the side nozzle of the cell and sealed with Parafilm®.



Figure S40: Electrolysis cell with connected cooling trap.

The stirrer was set to 750 rpm. The power supply for the electrodes was switched on and started with a current of $I = 194$ mA. After 437 min, the power supply was switched off and samples were taken from the cooling trap.

The condensate from the cold trap was rinsed with Milli-Q® water and transferred to a volumetric flask. The pH value of the solution was adjusted to pH 7 with the addition of sodium acetate. The volumetric flask was filled up to the 250 mL mark with Milli-Q® water. 25 mL of the prepared solution was taken with a volumetric pipette and transferred to an Erlenmeyer flask for measurement. The titration was carried out with a $1.0 \text{ mol} \cdot \text{L}^{-1}$ AgNO_3 solution. A 5% $\text{K}_2\text{Cr}_2\text{O}_7$ solution was used as an indicator (**Table S6**).

Table S6: Determination of HCl in the electrolyte of the 2-chloromethyl-1,3-dioxepane (**6b**) synthesis.

$ \begin{array}{c} \text{Cl} \\ \\ \text{Cl} - \text{C}_6\text{H}_4 - \text{Cl} \\ \\ \text{Cl} \end{array} + 3.0 \text{ } \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \end{array} \text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[\text{propylene carbonate, } 10.0 \text{ mA}\cdot\text{cm}^{-2}, 7.0 \text{ F (ref. to 1)}, 25^\circ\text{C, 750 rpm}]{\text{graphite graphite, } (\text{C}_2\text{H}_5)_4\text{NCl (0.05 mol}\cdot\text{L}^{-1})} \begin{array}{c} \text{C}_6\text{H}_6 \\ \text{2} \end{array} + 3.0 \text{ } \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \end{array} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} $				
1	5b		2	6b
[0.15 mol·L ⁻¹]				
Conversion <i>X</i> (1) / %	<i>n</i> _{Cl} (1) / mmol	Yield <i>Y</i> (6b) / %	<i>n</i> _{Cl} (6b) / mmol	<i>n</i> _{Cl} (HCl) / mmol (V(AgNO ₃) / mL)
81	36.4	81	18.4	4.75±0.05 (4.75±0.05)

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard.

A blind test showed that HCl can also be used to chlorinate 4-hydroxybutyl vinyl ether (**5b**). However, excessive amounts of water can lead to a weakening of the reaction.

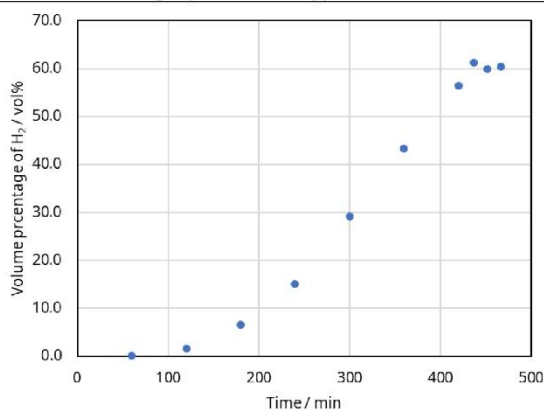
$ \text{HCl} + \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \end{array} \text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[\text{propylene carbonate, } 10.0 \text{ mA}\cdot\text{cm}^{-2}, 2.3 \text{ F (ref. to 5b)}, 25^\circ\text{C, 500 rpm}]{\text{graphite graphite, } (\text{C}_2\text{H}_5)_4\text{NCl (0.05 mol}\cdot\text{L}^{-1})} \text{H}_2\uparrow + \begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{O} \end{array} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} $				
[100 μL of 35% HCl]	5b			6b
	[0.45 mol·L ⁻¹]			
				<i>Y</i> = 26%, <i>FE</i> = 22%

GC Yield: 1,10-Dichlorodecane as internal standard.

Determination of hydrogen evolution in the electrolyte of the 2-chloromethyl-1,3-dioxepane (6b) synthesis (VI)

A solution of HCH (**1**) (2182.7 mg, 7.5 mmol, 1.0 eq.), tetraethylammonium chloride (413.7 mg, 2.5 mmol), 4-hydroxybutyl vinyl ether (**5b**) (2.7 mL, 21.8 mmol; 2.9 eq.) and 50 mL propylene carbonate was prepared and added to the electrolysis cell (with stirrer). The volume of the solution was previously determined to be 51 mL, and the volume of the cell was determined in order to calculate the resulting gas volume from the difference to the volume of the solution used (total volume of cell: 106 mL, volume of gas phase: 55 mL). The electrodes with stoppers were inserted into the cell and adjusted to a height of 8.3 cm from the meniscus. The cell was gassed with nitrogen via the side nozzle using a hose. The plug with the electrodes was opened slightly. After a few minutes, the gas supply was stopped, the side nozzle was closed with a stopper and the stopper with the electrodes was closed tightly. As a starting value, 250 μ L of gas was sampled via the stopper using a gas-tight syringe and analyzed immediately (between sampling and manual dosing into the GC, the syringe needle was sealed with a septum). The stirrer was set to 500 rpm. The power supply for the electrodes was switched on and started with a current of $I = 194$ mA. At 1 h intervals, 250 μ L of gas was sampled using a gas-tight syringe and analyzed immediately. After 437 min, the power supply was switched off and two more gas samples were taken at 15 min intervals (**Table S7**).

Table S7: Quantification of hydrogen with a final concentration of approx. 61% hydrogen by volume in the gas phase of the apparatus.



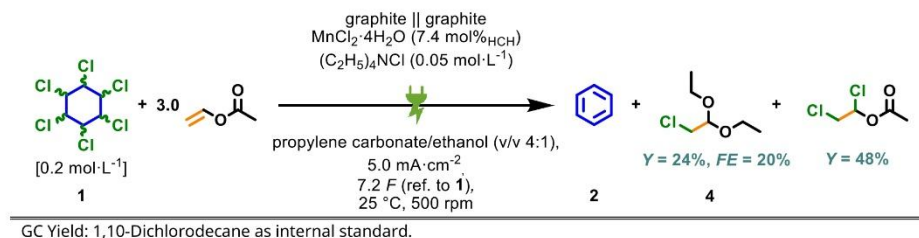
Time / min	Peak area	Volume percent / vol%
60	19.285	0.2
120	185.2	1.5
180	782.5	6.5
240	1805.2	15.0
300	3511.2	29.3
360	5199.7	43.3
420	6769.6	56.4
437	7360.3	61.3
452	7200.6	60.0
467	7254.8	60.4

Table S8: Determination of the area of the H₂ standard (1% H₂ in air).

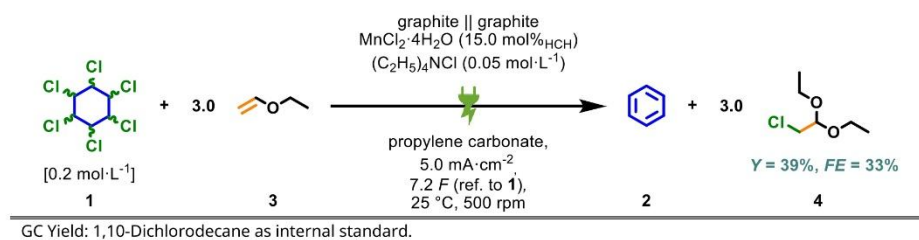
#	Peak area
1	116.928
2	121.993
3	121.165
Mean value	120.0

3.3 Optimization of Reaction Conditions of 2-chloro-1,1-di(ethoxy)-ethane (4)

Based on the industrial synthesis of acetates with 1,2-dichloroethyl acetate, the chlorination of ethyl vinyl ether (3) was also determined.^[9]

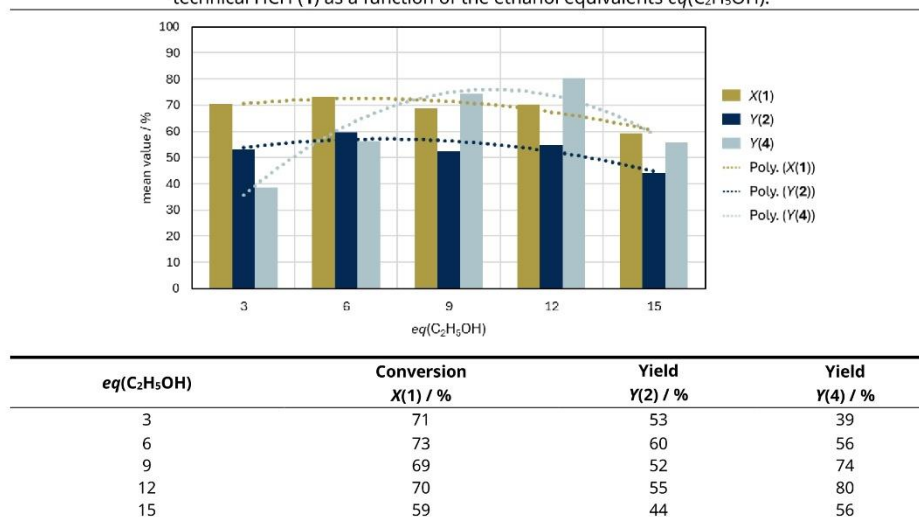


With the intention of obtaining 1,2-dichloroethyl vinyl ether, it was found that the ethyl vinyl ether is cleaved and the 2-chloro-1,1-di(ethoxy)-ethane (4) is formed. This results in the consumption of ethyl vinyl ether with the formation of diethyl acetal.



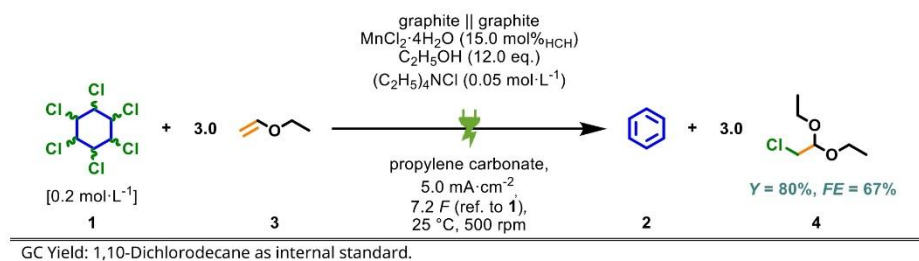
To prevent the decomposition of ethyl vinyl ether (**3**), ethanol ($\text{C}_2\text{H}_5\text{OH}$) was also added. The addition of ethanol was investigated in OVAT (one-variable-at-a-time) screening (**Table S9**). Up to 15 equivalents of ethanol were added in relation to HCH (**1**).

Table S9: Determined yields Y_i of benzene (**2**), 2-chloro-1,1-di(ethoxy)-ethane (**4**) and conversion X_i of technical HCH (**1**) as a function of the ethanol equivalents $eq(\text{C}_2\text{H}_5\text{OH})$.



GC Yield/Conversion: 1,10-Dichlorodecane as internal standard.

1st Optimized parameters for the yield of 2-chloro-1,1-di(ethoxy)-ethane (**4**):



GC Yield: 1,10-Dichlorodecane as internal standard.

Optimization by design of experiment (DoE) in a 2^{5-1} fractional factorial design of experiments:

Further optimizations were carried out with the help of design of experiments (DoE). The design and evaluation of the plans was carried out by Minitab® 21.1. The decisive electrotechnical parameters (amount of charge Q , current density j), concentration of HCH ($c(\text{HCH})$), percentage catalyst substance quantities in relation to HCH ($n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$) and the ethanol equivalents $eq(\text{C}_2\text{H}_5\text{OH})$ were defined as terms. Conversions X_i and yields Y_i of the respective compounds were defined as target values (Table S10).

Table S10: Determined yields Y_i of benzene (2), 2-chloro-1,1-di(ethoxy)-ethane (4) and conversion X_i of technical HCH (1) in the 2^{5-1} fractional factorial experimental design (Resolution VI).

Term					target value		
A Q / F	B $j / \text{mA} \cdot \text{cm}^{-2}$	C $c(\text{HCH}) / \text{mol} \cdot \text{L}^{-1}$	D $n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol} \%_{\text{HCH}}$	E $eq(\text{C}_2\text{H}_5\text{OH})$	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Yield $Y(4) / \%$
6	5	0.10	5	12.0	55±4	37±7	52±2
8	5	0.10	5	9.0	63±2	46±5	61±5
6	15	0.10	5	9.0	74±2	56±7	40±1
8	15	0.10	5	12.0	87±1	73±3	70±1
6	5	0.20	5	9.0	49±2	30±1	54±3
8	5	0.20	5	12.0	57±0	41±0	74±2
6	15	0.20	5	12.0	58±2	40±2	58±1
8	15	0.20	5	9.0	83±6	65±8	76±4
6	5	0.10	15	9.0	54±2	35±3	51±1
8	5	0.10	15	12.0	61±1	45±1	53±1
6	15	0.10	15	12.0	71±7	53±7	46±1
8	15	0.10	15	9.0	75±0	62±3	64±2
6	5	0.20	15	12.0	44±0	25±0	49±2
8	5	0.20	15	9.0	57±2	41±1	73±4
6	15	0.20	15	9.0	58±1	40±3	55±2
8	15	0.20	15	12.0	75±2	59±1	75±4
7	10	0.15	10	10.5	57±0	42±0	53±1

GC-Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of ethyl vinyl ether (3) was not detected by the GC.

Table S11: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

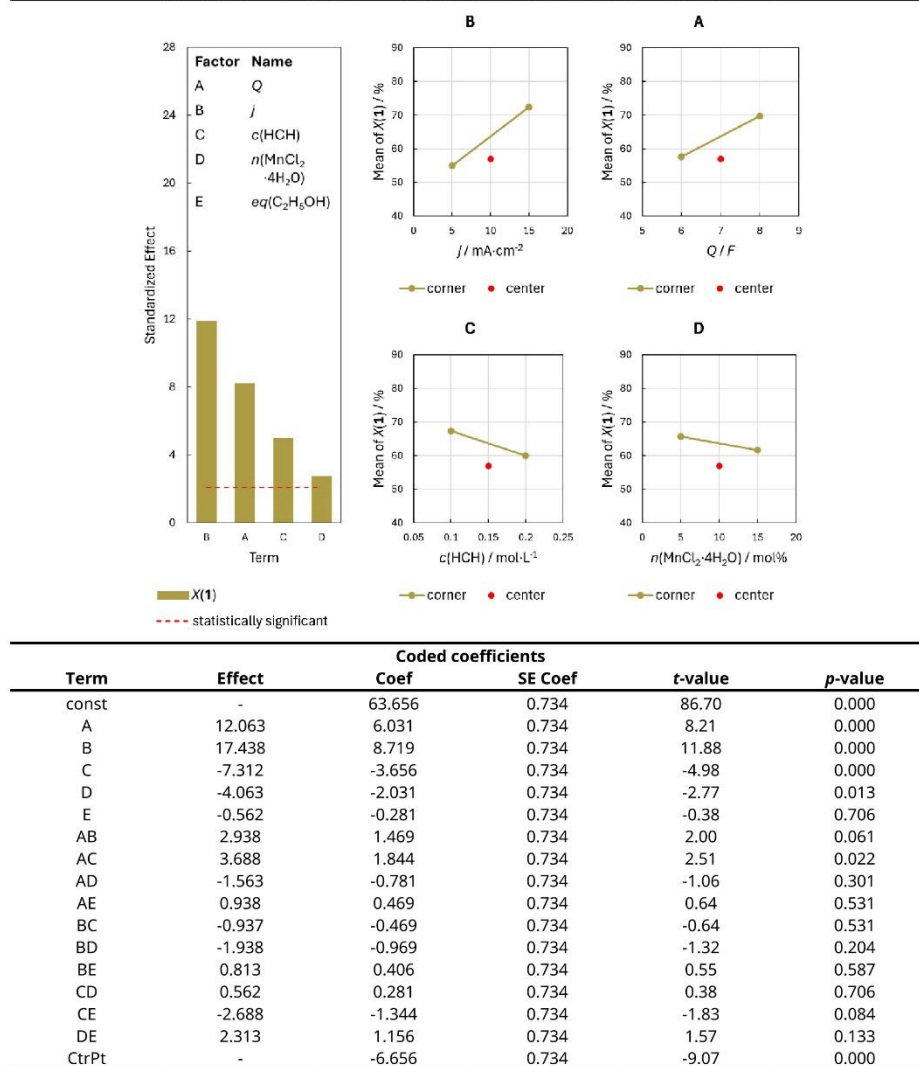


Table S12: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

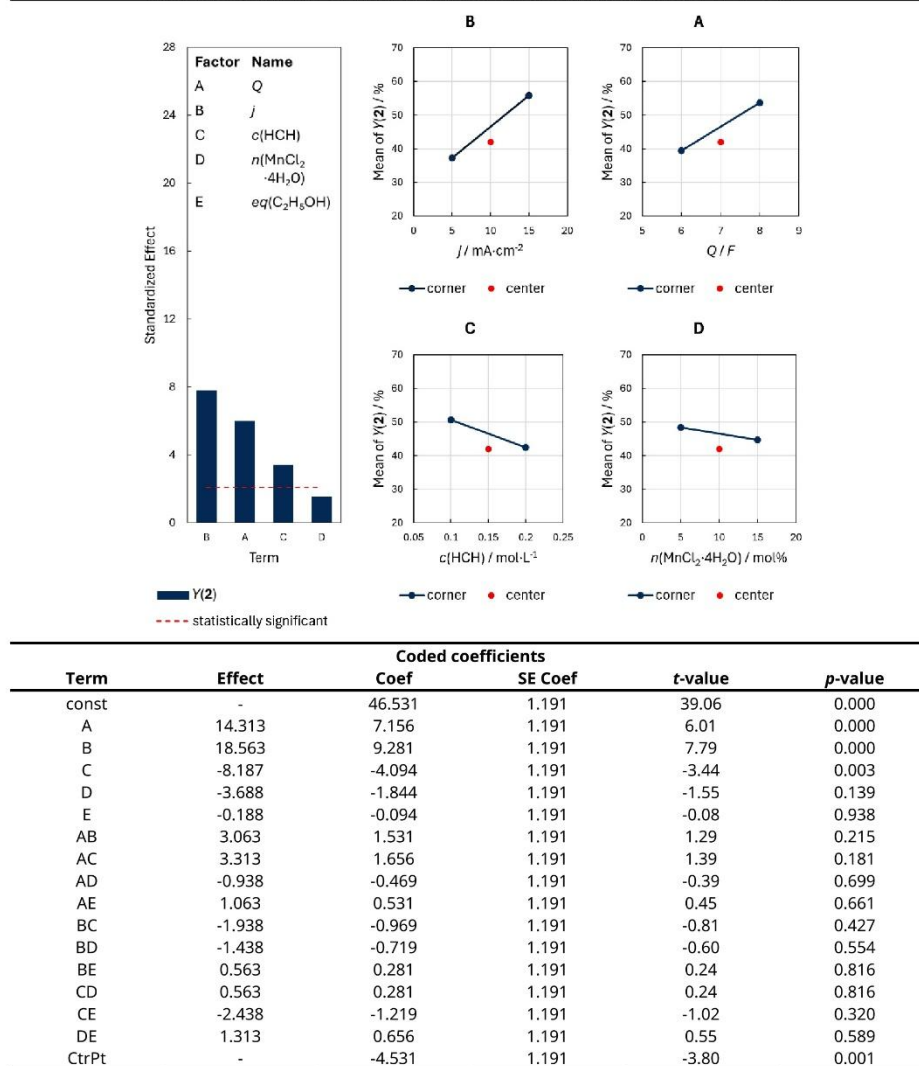
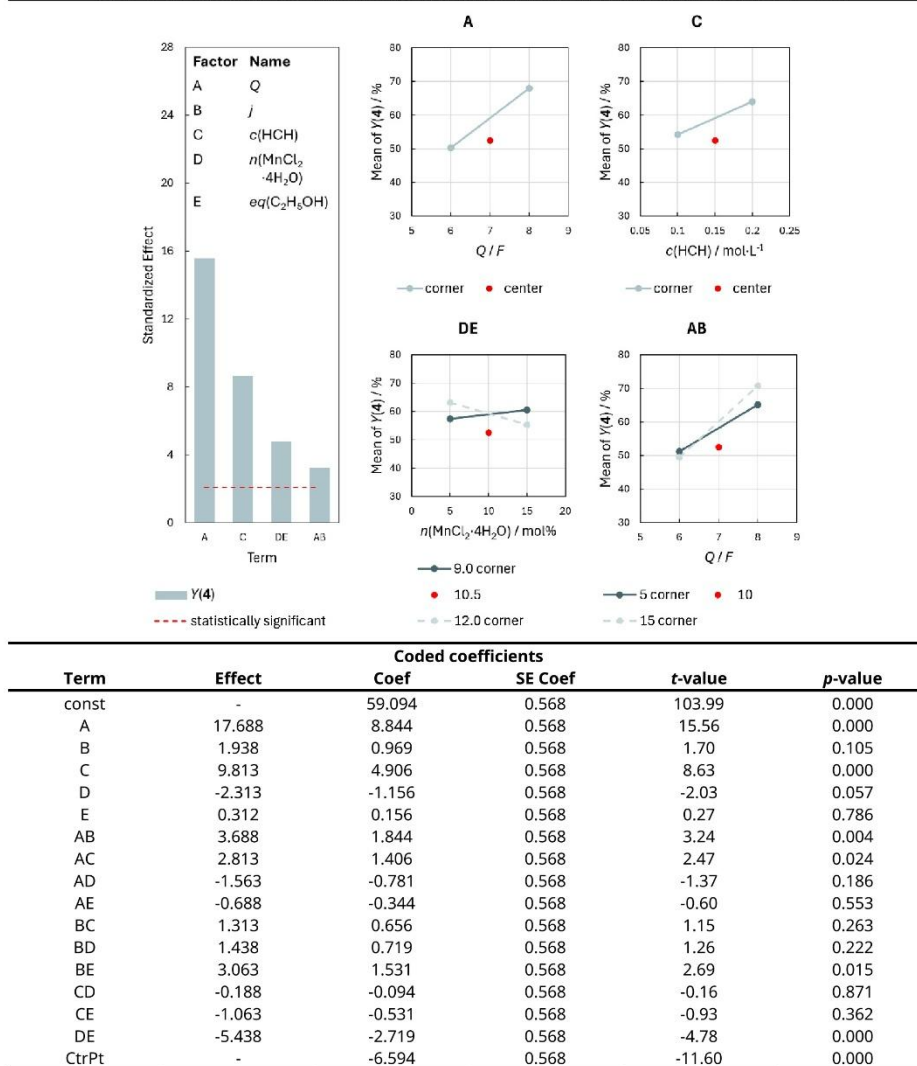
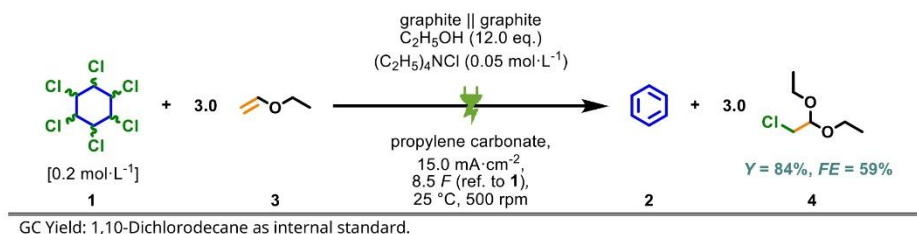
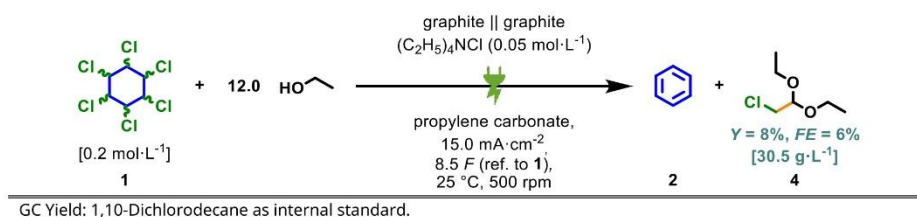


Table S13: Pareto, Main and Interaction plots of the 2^{5-1} fractional factorial experimental design for the yield of 2-chloro-1,1-di(ethoxy)-ethane ($Y(4)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

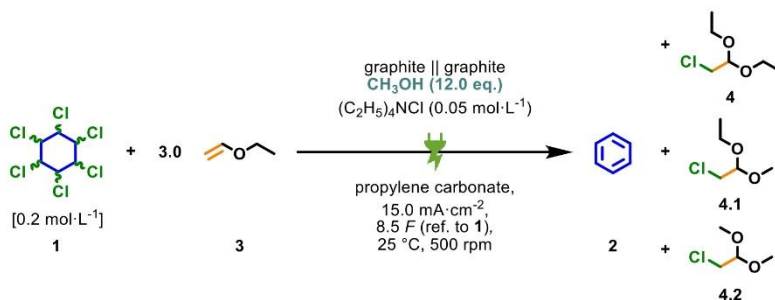


Optimized parameters for the yield of 2-chloro-1,1-di(ethoxy)-ethane (4):**Control experiments:**

According to the literature,^[10] it is also possible to synthesize the 2-chloro-1,1-di(ethoxy)-ethane (4) from ethanol. This possibility was also determined under the optimized conditions. However, the use of ethanol alone made only a small contribution to conversion.



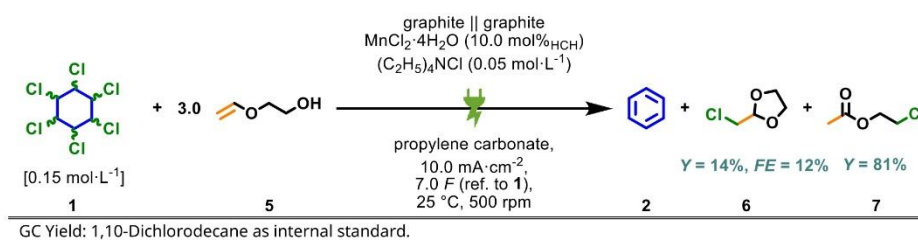
The addition of other alcohols, such as methanol, also enables access to other acetals. "Symmetric" (4 and 4.2) as well as "mixed acetals" (4.1). With a relative ratio of 2:19:47 for 4/4.1/4.2, the 2-chloro-1,1-di(methoxy)-ethane (4.2) can be formed in significant quantities.



3.4 Optimization of Reaction Conditions of 2-chloromethyl-1,3-dioxolane (6)

In addition to open acetals, the synthesis of cyclic acetals was also researched. Analogous to the vinyl ethers, the monovinyl ethers of the diols were used. The addition of alcohol was not necessary.

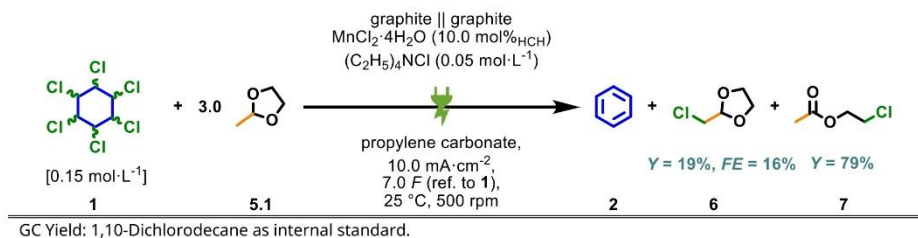
The formation of 2-chloromethyl-1,3-dioxolane (**6**) from the 2-hydroxyethyl vinyl ether (**5**) was determined using the optimized conditions of 2-chloromethyl-1,3-dioxepane (**6b**). The formation of 2-chloroethyl acetate (**7**) was also detected.



In further optimizations by design of experiment (DOE) the yield of **6** should be improved.

Discussion of the side reaction

During the synthesis of 2-chloromethyl-1,3-dioxolane (**6**) the formation of 2-chloroethyl acetate (**7**) was observed. A blank test suggests that the formation of 2-methyl-1,3-dioxolane (**5.1**) can precede the formation of the chloronium species.



The anodic oxidation of the 2-methyl-1,3-dioxolane (**5.1**) (**Figure S41, II**) enables a nucleophilic attack of the chloride in the 4th or 5th position of the ring (**III**).^[11]

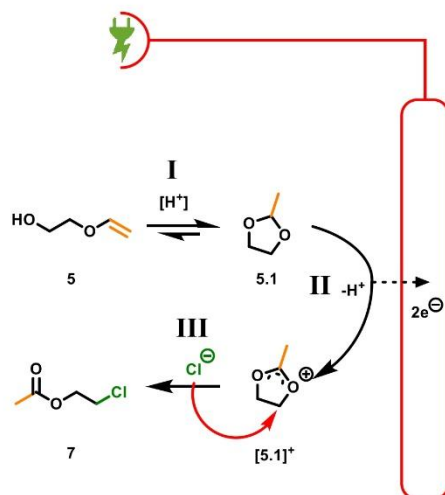


Figure S41: Postulated mechanism of the side path reaction of 2-chloromethyl-1,3-dioxolane (**6**) to 2-chloroethyl acetate (**7**).

Furthermore, the formation of 2-chloromethyl-1,3-dioxolane (**6**) was also observed. The acidic conditions could lead to ring opening and enolization of the 2-methyl-1,3-dioxolane (**I**) and follow the postulated mechanism of the chloronium species (**Figure S35**).^[12]

1st Optimization by design of experiment (DoE) in a 2⁴⁻¹ fractional factorial design of experiments:

The design and evaluation of the plans was carried out by Minitab© 21.1. The decisive electrotechnical parameters (amount of charge Q , current density j), concentration of HCH ($c(\text{HCH})$) and the percentage catalyst substance quantities in relation to HCH ($n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$) were defined as terms. Conversions X_i and yields Y_i of the respective compounds were defined as target values (**Table S14**).

Table S14: Determined yields Y_i of benzene (**2**), 2-chloromethyl-1,3-dioxolane (**6**), 2-chloroethyl acetate (**7**) and conversion X_i of technical HCH (**1**) in the 2⁴⁻¹ fractional factorial experimental (Resolution V) with central composite design (CCD).

1	5				2	6	7
Term				target value			
A	B	C	E	Conversion	Yield	Yield	Yield
Q / F	$j / \text{mA} \cdot \text{cm}^{-2}$	$c(\text{HCH}) / \text{mol} \cdot \text{L}^{-1}$	$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol} \%_{\text{HCH}}$	$X(1) / \%$	$Y(2) / \%$	$Y(6) / \%$	$Y(7) / \%$
6	5	0.10	5	75±1	49±5	16±1	63±4
8	5	0.10	15	71±2	50±1	18±1	65±3
6	15	0.10	15	68±3	52±2	10±1	46±2
8	15	0.10	5	85±0	65±1	7±0	68±0
6	5	0.20	15	45±6	24±1	14±1	43±1
8	5	0.20	5	78±3	60±3	20±0	74±2
6	15	0.20	5	79±0	64±0	14±1	85±3
8	15	0.20	15	75±5	65±3	11±0	90±4
7	10	0.15	10	75±1	58±2	15±0	75±1
5	10	0.15	10	69	49	8	60
9	10	0.15	10	86	64	8	77
7	1	0.15	10	28	43	5	11
7	20	0.15	10	69	41	6	52
7	10	0.05	10	69	48	6	36
7	10	0.25	10	61	49	10	79
7	10	0.15	0	78	72	12	94
7	10	0.15	20	59	53	14	58

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of 2-hydroxyethyl vinyl ether (**5**) was not detected by the GC.

Table S15: Pareto, Main and Interaction plots of the 2^{4+1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

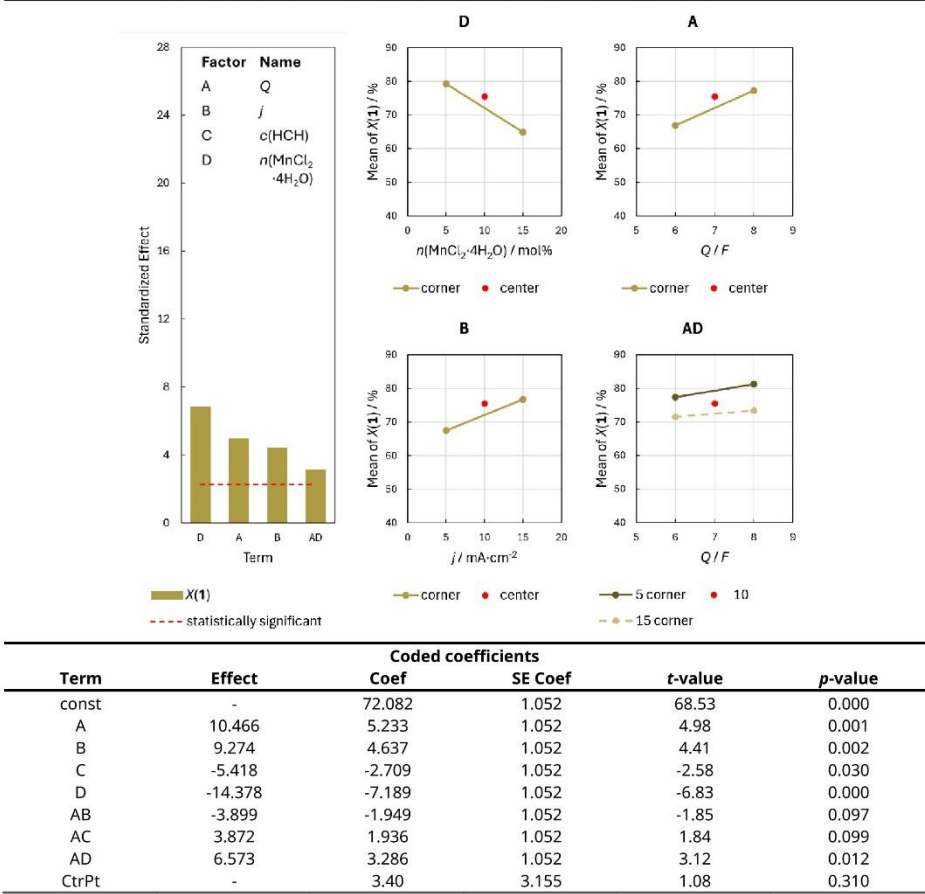


Table S16: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

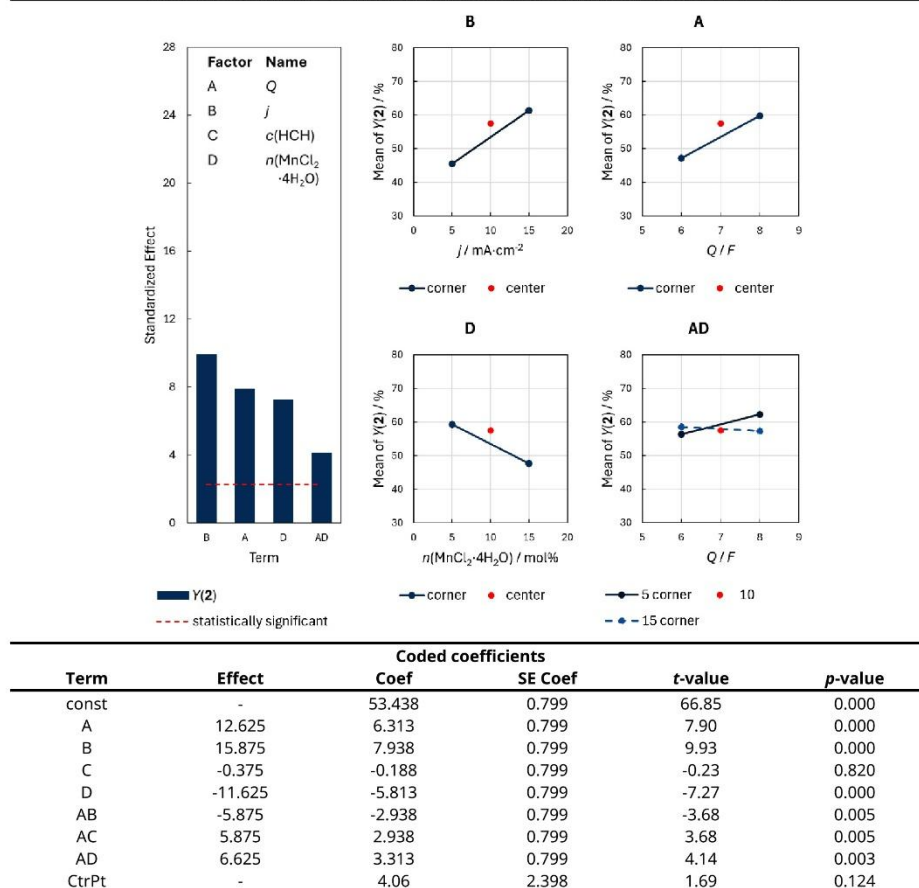


Table S17: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 2-chloromethyl-1,3-dioxolane ($Y(6)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

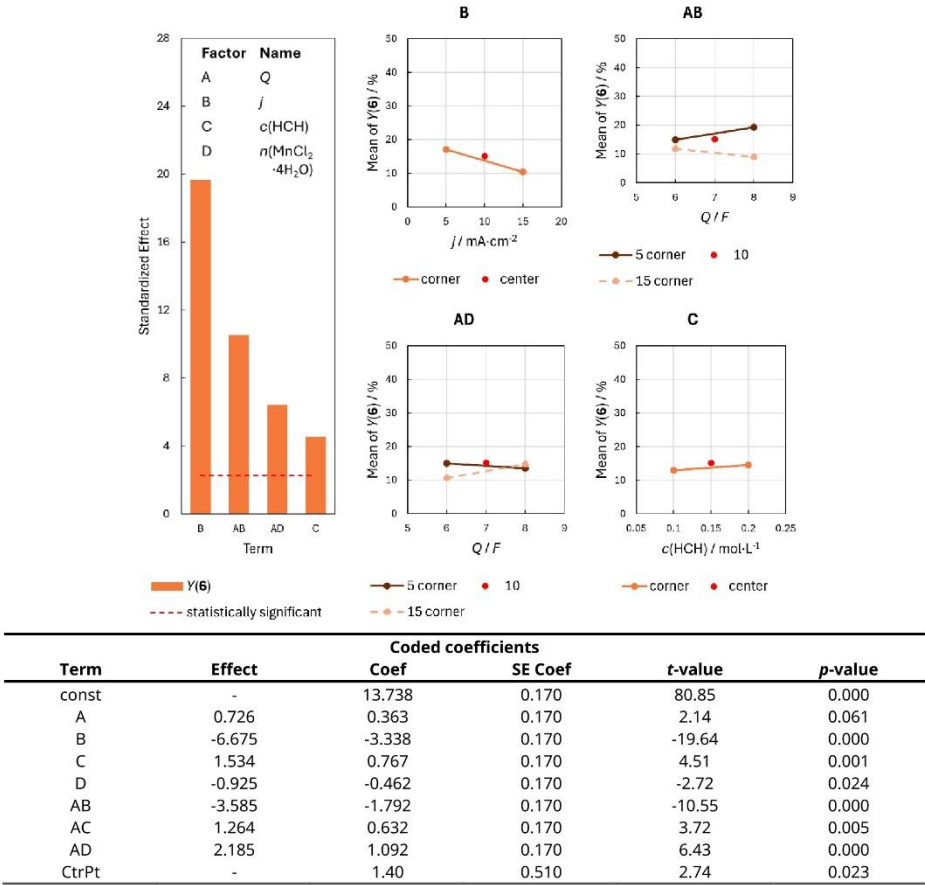
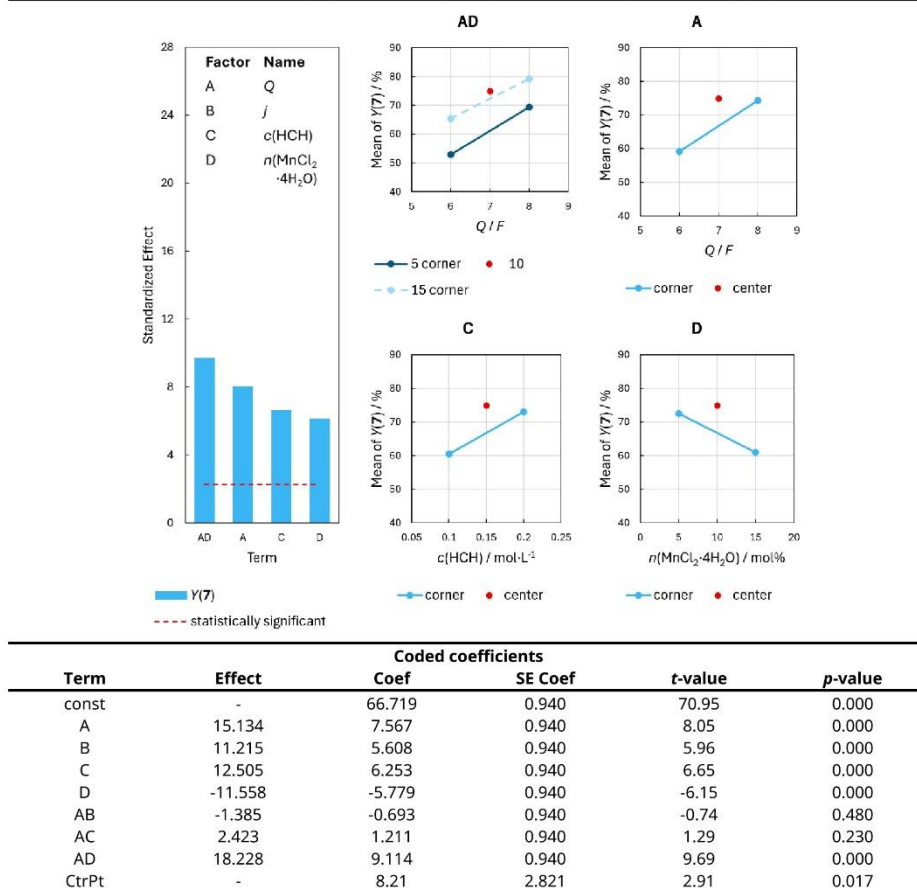


Table S18: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 2-chloroethyl acetate (Y(7)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



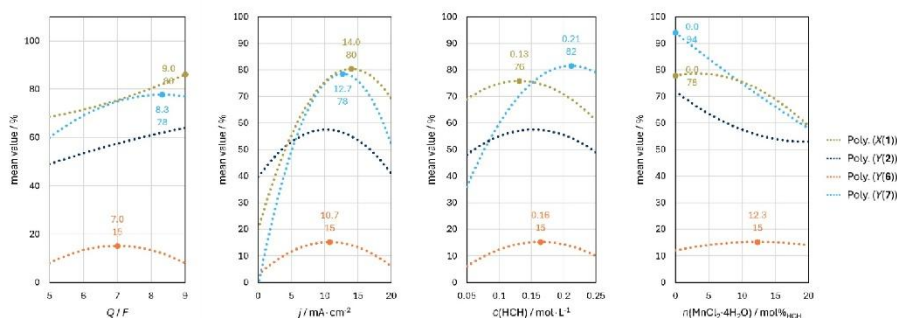
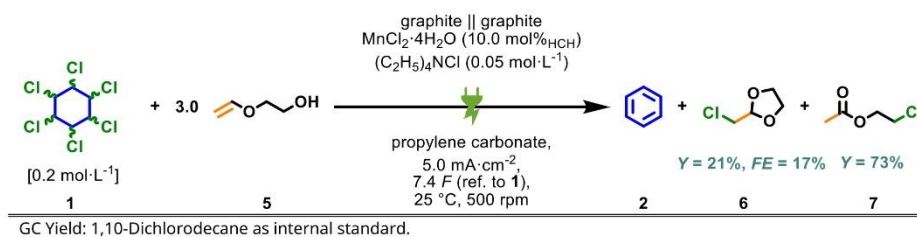


Figure S42: Main effect diagrams of the conversion and yield of 2-chloromethyl-1,3-dioxolane (6), 2-chloroethyl acetate (7) and HCH (1) to benzene (2) according to the 2^{4-1} fractional factorial experimental design with central composite design (CCD).

1st Optimized parameters for the yield of 2-chloromethyl-1,3-dioxolane (6):



2nd Optimization by design of experiment (DoE) in a 2² full factorial design of experiments:

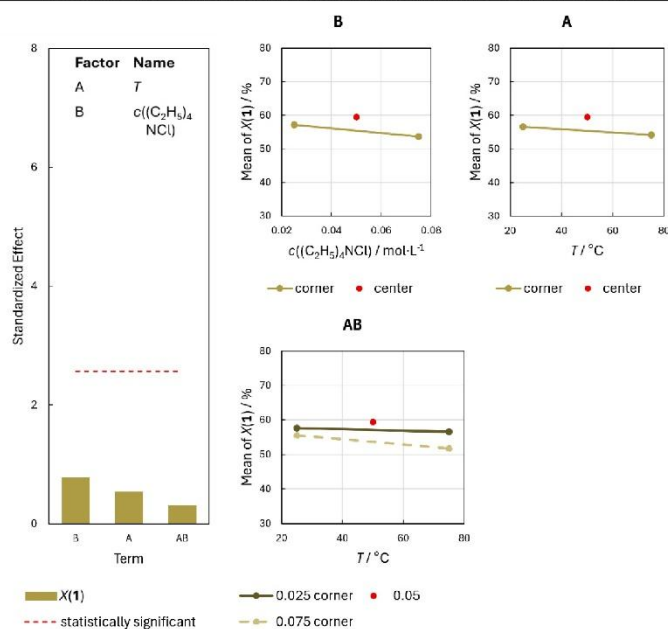
The design and evaluation of the plans was carried out by Minitab© 21.1. The temperature T and the concentration of the supporting electrolyte $c((C_2H_5)_4NCl)$ were defined as. Conversions X_i and yields Y_i of the respective compounds were defined as target values (**Table S19**).

Table S19: Determined yields Y_i of benzene (**2**), 2-chloromethyl-1,3-dioxolane (**6**), 2-chloroethyl acetate (**7**) and conversion X_i of the starting material technical HCH (**1**) and in a 2² full factorial experimental with central composite design (CCD).

TERM		target value			
A	B	Conversion	Yield	Yield	Yield
$T / ^\circ C$	$c((C_2H_5)_4NCl) / \text{mol} \cdot L^{-1}$	$X(1) / \%$	$Y(2) / \%$	$Y(6) / \%$	$Y(7) / \%$
25	0.025	58±3	43±4	16±1	63±3
75	0.025	57±3	32±0	17±1	67±3
25	0.075	56±5	40±4	21±2	52±3
75	0.075	52±7	34±2	16±6	59±3
50	0.05	59±1	41±0	30±0	58±2
8	0.05	58	45	10	85
92	0.05	51	32	20	47
50	0.01	64	47	5	82
50	0.09	65	51	13	80

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of 2-hydroxyethyl vinyl ether (**5**) was not detected by the GC.

Table S20: Pareto, Main and Interaction plots of the 2² full factorial experimental design for the conversion of HCH (X(1)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



Coded coefficients					
Term	Effect	Coef	SE Coef	t-value	p-value
const	-	55.374	2.223	24.91	0.000
A	-2.417	-1.209	2.223	-0.54	0.610
B	-3.445	-1.723	2.223	-0.77	0.473
AB	-1.379	-0.689	2.223	-0.31	0.769
CtrPt	-	4.09	4.972	0.82	0.448

Table S21: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

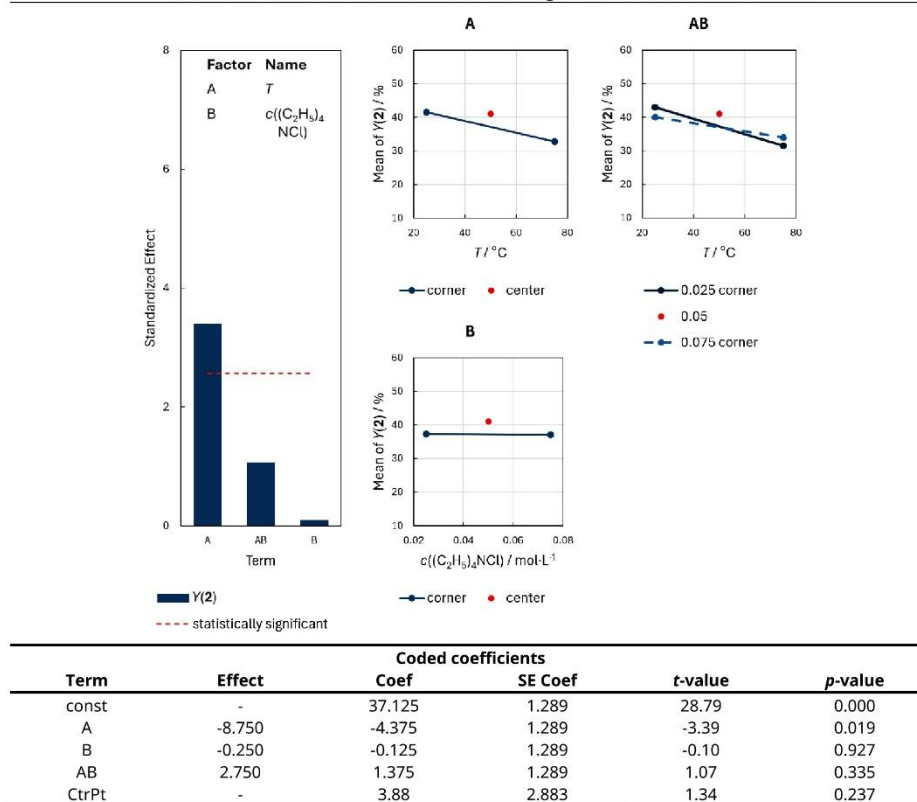


Table S22: Pareto, Main and Interaction plots of the 2² full factorial experimental design for the yield of 2-chloromethyl-1,3-dioxolane (Y(6)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of α = 5%.

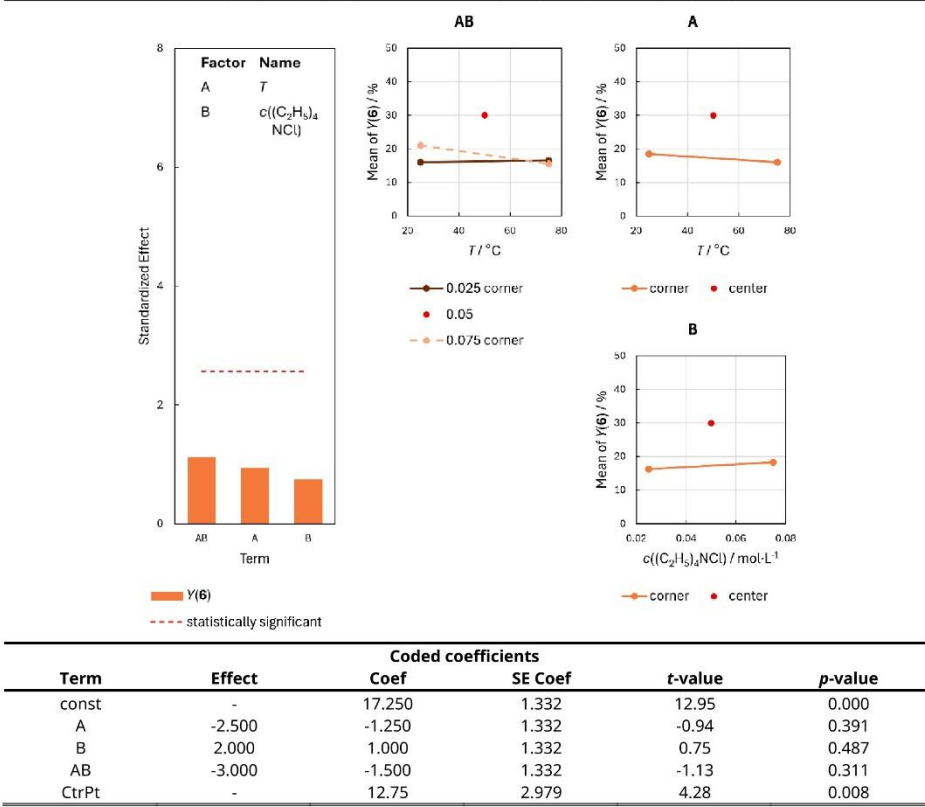
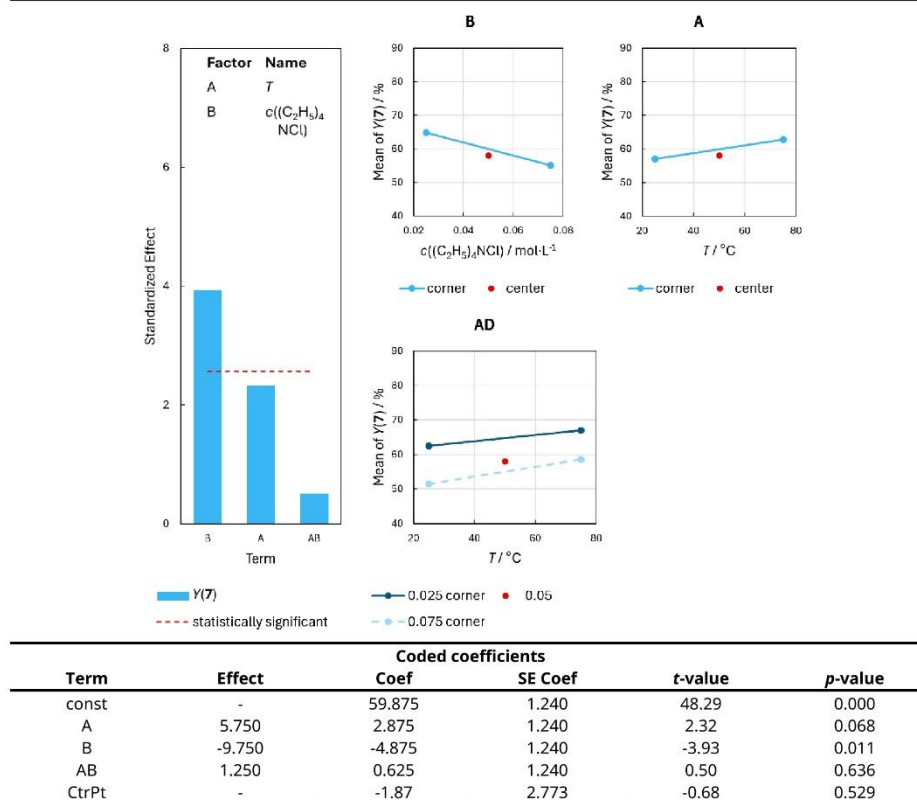


Table S23: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of 2-chloroethyl acetate ($Y(7)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



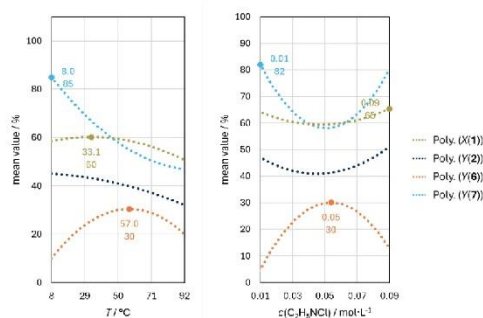
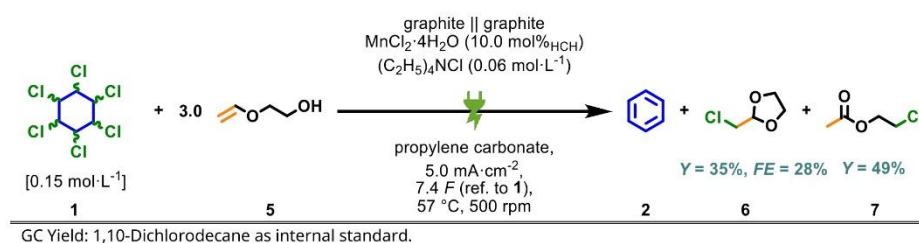


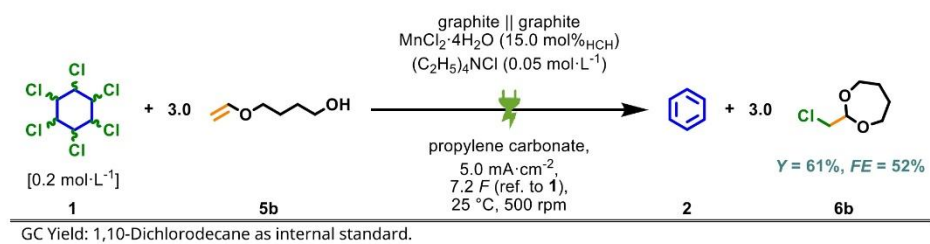
Figure S43: Main effect diagrams of the conversion and yield of 2-chloromethyl-1,3-dioxolane (**6**), 2-chloroethyl acetate (**7**) and HCH (**1**) to benzene (**2**) according to the 2² fractional factorial experimental with central composite design (CCD).

Optimized parameters for the yield of 2-chloromethyl-1,3-dioxolane (**6**):



3.5 Optimization of Reaction Conditions of 2-chloromethyl-1,3-dioxepane (**6b**)

Analogous to the 2-chloromethyl-1,3-dioxolane (**6**), the 2-chloromethyl-1,3-dioxepane (**6b**) was optimized for a 7-membered ring. Significantly higher yields compared to the **6** were found right from the start. In addition, the formation of a monochlorinated ester of the acetate could be excluded.



1st Optimization by design of experiment (DoE) in a 2⁴⁻¹ fractional factorial design of experiments:

The design and evaluation of the plans was carried out by Minitab© 21.1. The decisive electrotechnical parameters (amount of charge Q , current density j), concentration of HCH ($c(\text{HCH})$) and the percentage catalyst substance quantities in relation to HCH ($n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$) were defined as terms. Conversions X_i and yields Y_i of the respective compounds were defined as target values (**Table S24**).

Table S24: Determined yields Y_i of benzene (**2**), 2-chloromethyl-1,3-dioxepane (**6b**) and conversion X_i of technical HCH (**1**) in the 2⁴⁻¹ fractional factorial experimental (Resolution V) with central composite design (CCD).

A	B	Term		target value		
Q / F	$j / \text{mA} \cdot \text{cm}^{-2}$	C	E	Conversion $X(1) / \%$	Yield $Y(2) / \%$	Yield $Y(6b) / \%$
6	5	0.10	5	64±1	40±3	46±6
8	5	0.10	15	78±6	48±0	80±3
6	15	0.10	15	82±1	52±2	62±1
8	15	0.10	5	96±4	62±1	66±2
6	5	0.20	15	75±4	31±0	61±1
8	5	0.20	5	73±0	53±1	82±2
6	15	0.20	5	78±2	52±0	68±1
8	15	0.20	15	80±1	56±1	79±0
7	10	0.15	10	78±1	57±2	79±1
5	10	0.15	10	79	37	48
9	10	0.15	10	75	56	80
7	1	0.15	10	61	9	23
7	20	0.15	10	70	46	54
7	10	0.05	10	75	57	59
7	10	0.25	10	58	39	68
7	10	0.15	0	73	54	74
7	10	0.15	20	67	48	72

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of 4-hydroxybutyl vinyl ether (**5b**) was not detected by the GC.

Table S25: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

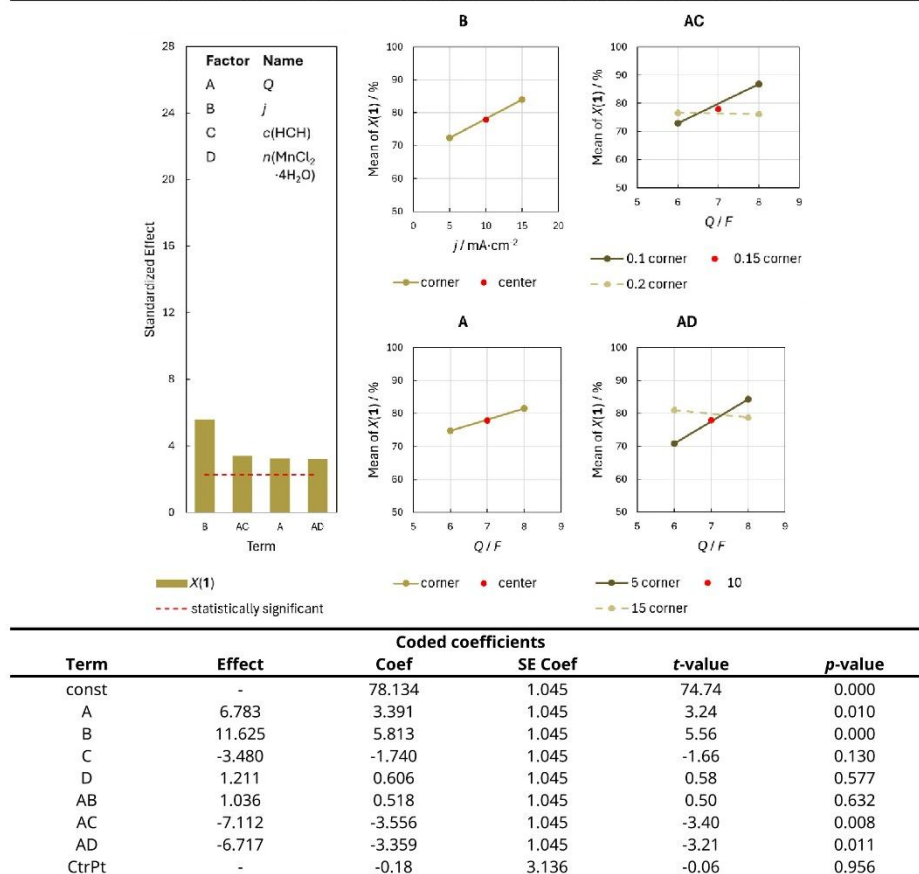


Table S26: Pareto, Main and Interaction plots of the 2⁴⁻¹ fractional factorial experimental design for the yield of benzene (Y(2)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of α = 5%.

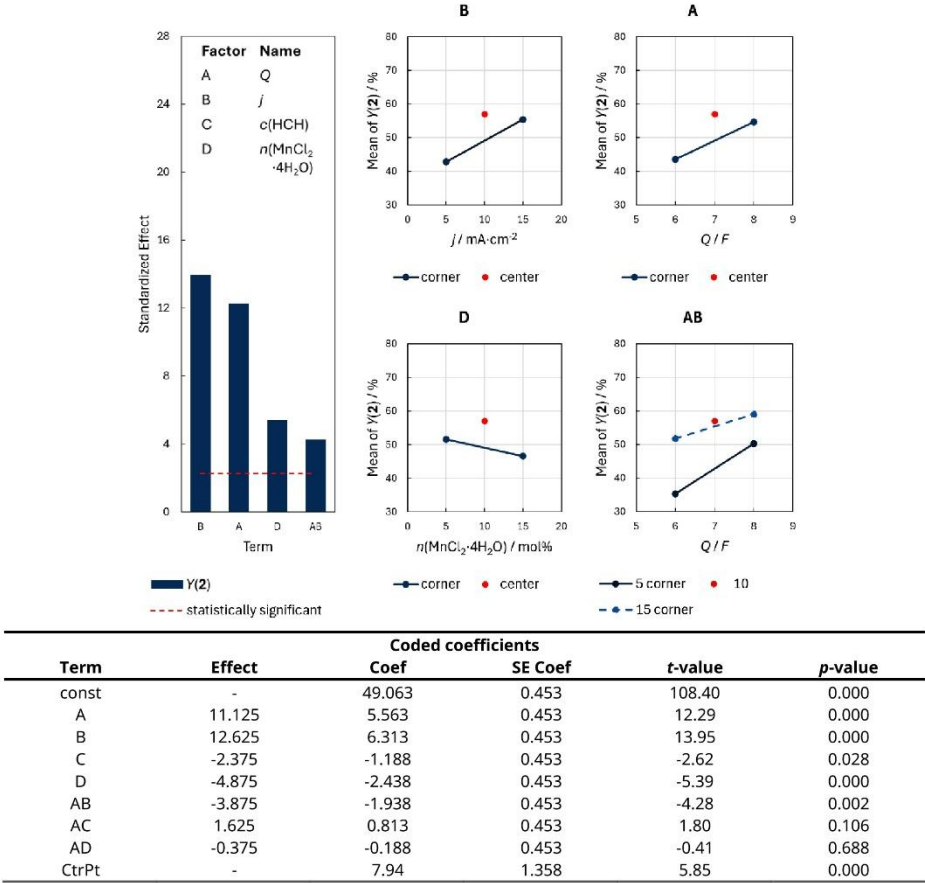
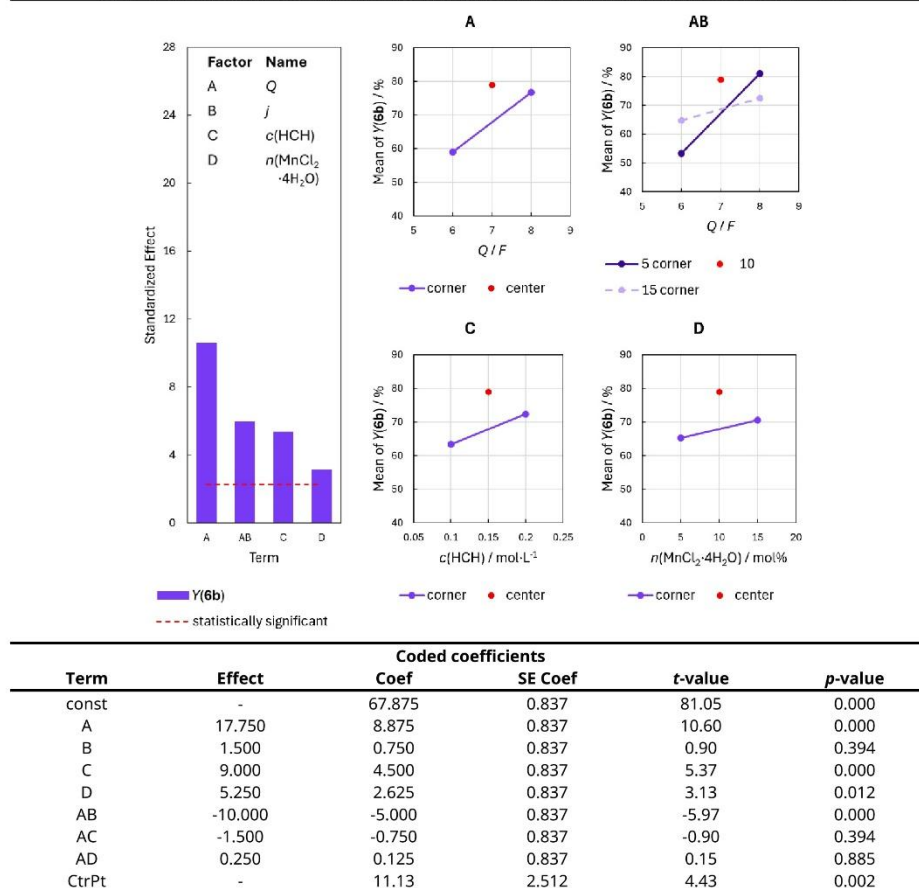


Table S27: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 2-chloromethyl-1,3-dioxepane (**Y(6b)**) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



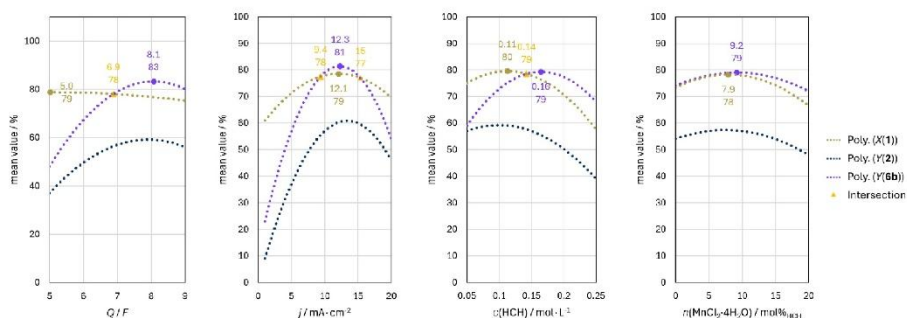
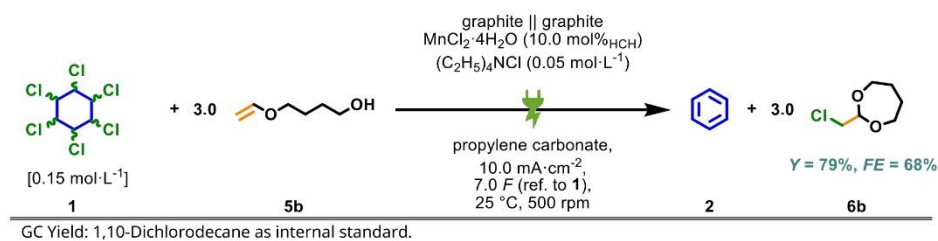


Figure S44: Main effect diagrams of the conversion and yield of 2-chloromethyl-1,3-dioxepane (**6b**) and HCH (**1**) to benzene (**2**) according to the 2^{4-1} fractional factorial experimental with central composite design (CCD).

1st Optimized parameters for the yield of 2-chloromethyl-1,3-dioxepane (**6b**):



2nd Optimization by design of experiment (DoE) in a 2² full factorial design of experiments:

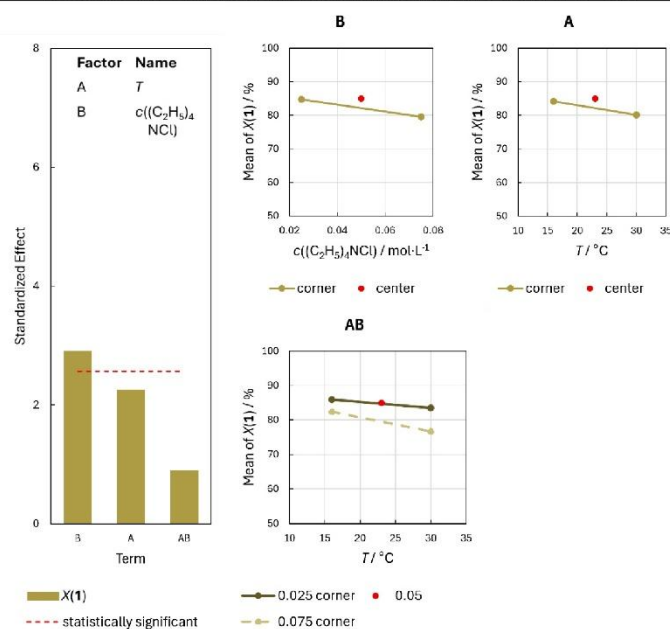
The design and evaluation of the plans was carried out by Minitab© 21.1. The temperature T and the concentration of the supporting electrolyte $c((C_2H_5)_4NCl)$ were defined as. Conversions X_i and yields Y_i of the respective compounds were defined as target values (**Table S28**).

Table S28: Determined yields Y_i of benzene (**2**), 2-chloromethyl-1,3-dioxepane (**6b**) and conversion X_i of the starting material technical HCH (**1**) and in a 2² full factorial experimental with central composite design (CCD).

 1 $[0.15 \text{ mol} \cdot \text{L}^{-1}]$ + 3.0 $\xrightarrow[\text{propylene carbonate, } 10 \text{ mA} \cdot \text{cm}^{-2}, 7.0 \text{ F (ref. to 1), } 16-30 \text{ }^\circ\text{C}, 500 \text{ rpm}]{\text{graphite graphite, MnCl}_2 \cdot 4\text{H}_2\text{O (10.0 mol\%}_{\text{HCH}}), (C_2H_5)_4NCl (0.025-0.075 \text{ mol} \cdot \text{L}^{-1})}$ 2 + 3.0 6b				
TERM		target value		
A	B	Conversion	Yield	Yield
$T / ^\circ\text{C}$	$c((C_2H_5)_4NCl) / \text{mol} \cdot \text{L}^{-1}$	$X(1) / \%$	$Y(2) / \%$	$Y(6b) / \%$
16	0.025	86±2	70±2	69±2
30	0.025	84±3	65±0	77±3
16	0.075	82±0	68±1	79±2
30	0.075	77±0	61±1	77±1
23	0.05	85±2	68±5	77±3

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of 4-hydroxybutyl vinyl ether (**5b**) was not detected by the GC.

Table S29: Pareto, Main and Interaction plots of the 2² full factorial experimental design for the conversion of HCH (X(1)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



Coded coefficients					
Term	Effect	Coef	SE Coef	t-value	p-value
const	-	82.111	0.894	91.81	0.000
A	-4.027	-2.013	0.894	-2.25	0.074
B	-5.202	-2.601	0.894	-2.91	0.033
AB	-1.607	-0.803	0.894	-0.90	0.410
CtrPt	-	2.85	2.000	1.43	0.213

Table S30: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

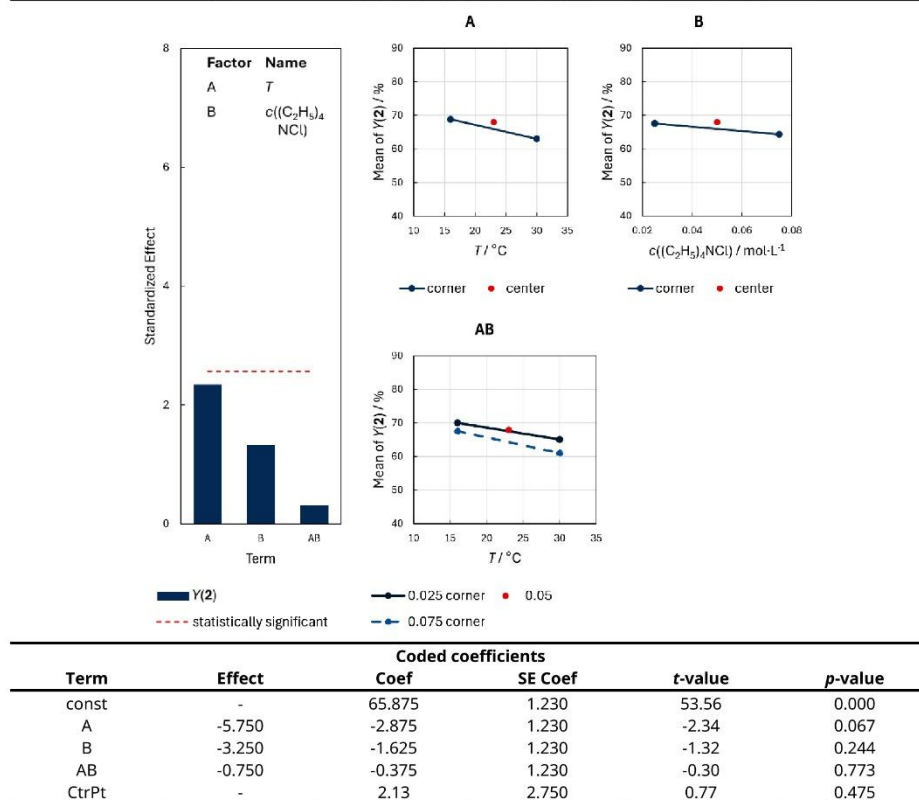
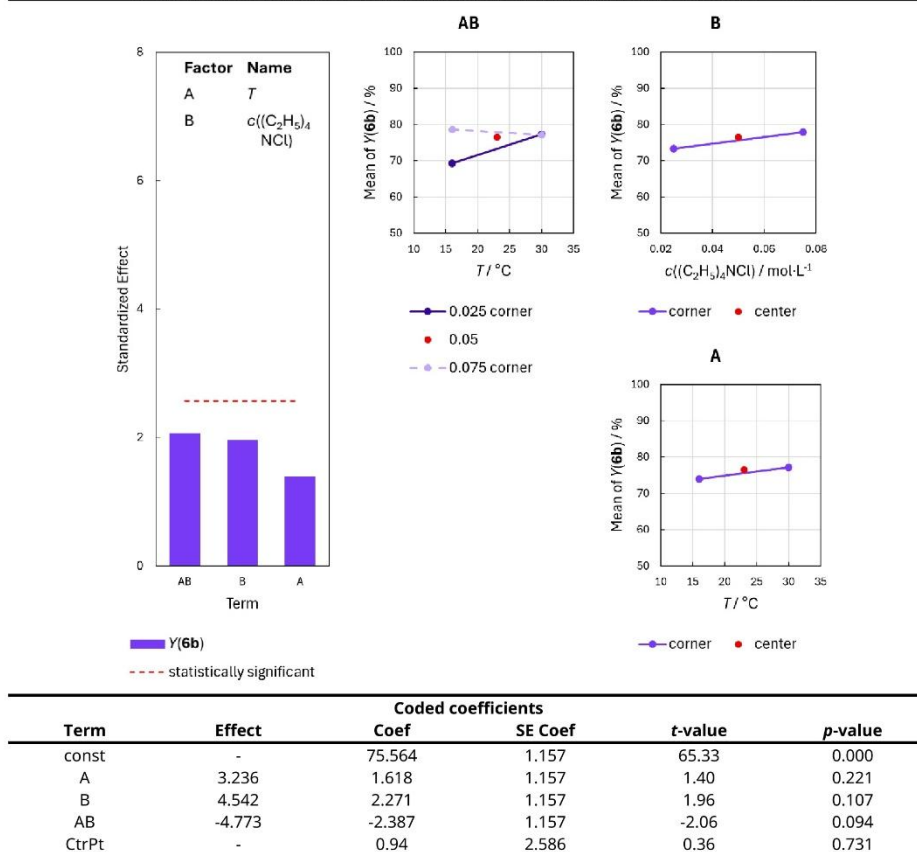
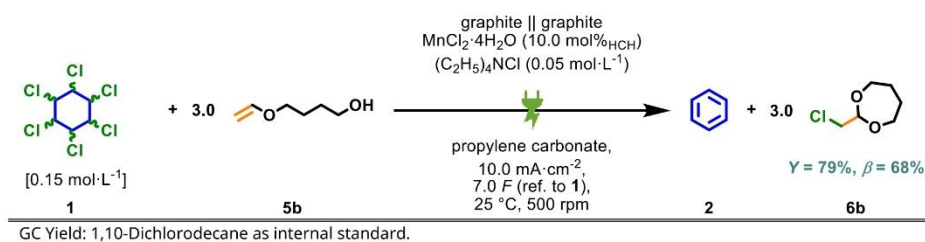


Table S31: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of 2-chloromethyl-1,3-dioxepane (**Y(6b)**) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

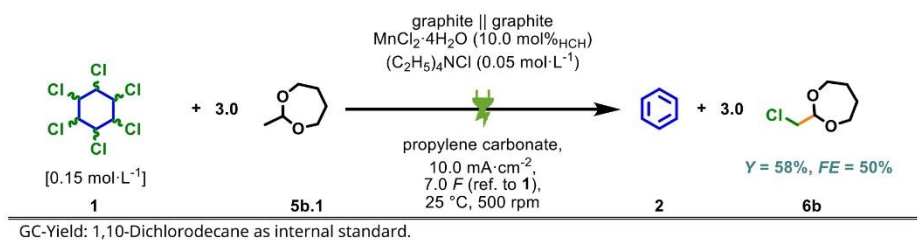


Optimized parameters for the yield of 2-chloromethyl-1,3-dioxolane (**6b**):

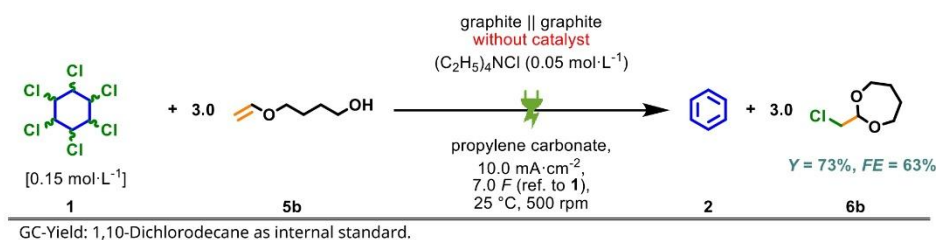


Control experiments:

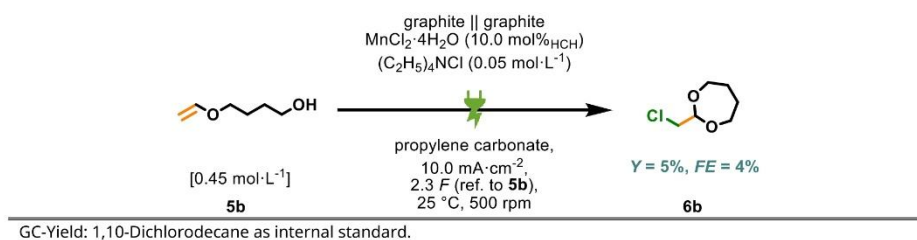
Furthermore, the chlorination of 2-methyl-1,3-dioxepane (**5b.1**) also showed no formation of monochlorinated esters of acetate. It could be shown that the equilibrium between 4-hydroxybutyl vinyl ether (**5b**) and 2-methyl-1,3-dioxepane (**5b.1**) also leads to significant yields of **6b**.



As with the 2-chloro-1,1-di(ethoxy)-ethane (**4**), the catalyst can also be dispensed here, but with a loss in yield of around 6% for **6b**.



In a further blank test, it was demonstrated that the formation of 2-chloromethyl-1,3-dioxolane (**6b**) does not occur in significant quantities by the catalyst ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) and the supporting electrolyte ($(\text{C}_2\text{H}_5)_4\text{NCl}$). In addition, a steady decrease in conductivity was observed during electrolysis.



Furthermore, a by-product was detected in the gas chromatogram. The by-product could be identified as 2-dichloromethyl-1,3-dioxepane (**6b.1**) (Figure S45).

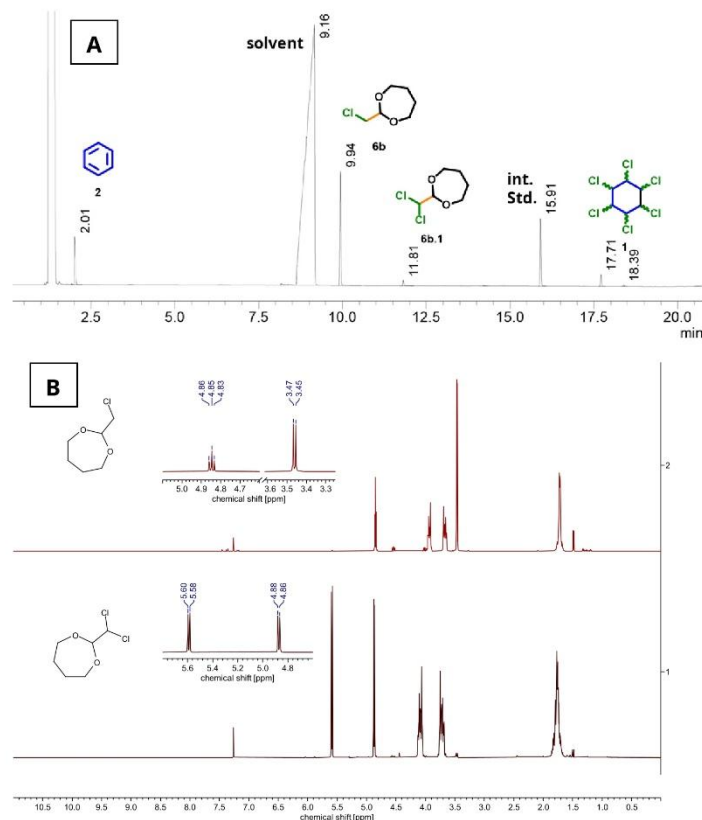
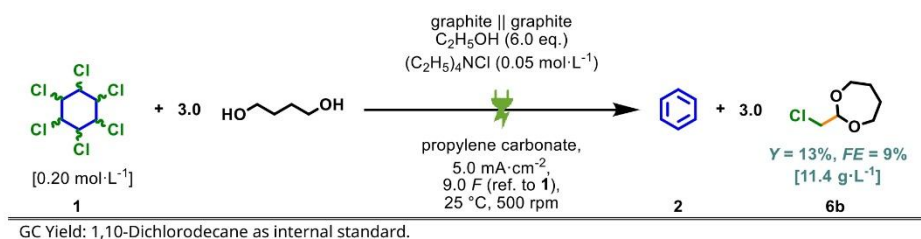


Figure S45: A: GC chromatogram of the electrolyte of the 2-chloromethyl-1,3-dioxepane (**6b**) synthesis with the by-product 2-dichloromethyl-1,3-dioxepane (**6b.1**) (retention time = 11.81 min) (method used: Performance DWE-SHS). B: ¹H NMR (400 MHz, CDCl₃, 298 K) of the isolated by-product (**6b.1**) compared to the main product (**6b**).

The oxidation of ethanol with subsequent acetal formation with 1,4-butanediol allows only very low yields of 2-chloromethyl-1,3-dioxolane (**6b**) under the given conditions (independent optimization).



3.6 Optimization of Reaction Conditions of 2-Chloromethyl-1,3,6-trioxocane (6c)

To determine the reaction conditions of an 8-membered ring, the commercially available di(ethylene glycol) vinyl ether (**5c**) was used for the synthesis of 2-chloromethyl-1,3,6-trioxocane (**6c**).

1st Optimization by design of experiment (DoE) in a 2⁴⁻¹ fractional factorial design of experiments:

The design and evaluation of the plans was carried out by Minitab® 21.1. The decisive electrotechnical parameters (amount of charge Q , current density j), concentration of HCH ($c(\text{HCH})$) and the percentage catalyst substance quantities in relation to HCH ($n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O})$) were defined as terms. Conversions X_i and yields Y_i of the respective compounds were defined as target values (Table S32).

Table S32: Determined yields Y_i of benzene (2), 2-Chloromethyl-1,3,6-trioxocane (6c) and conversion X_i of technical HCH (1) in the 2⁴⁻¹ fractional factorial experimental (Resolution V) with central composite design (CCD).

graphite || graphite
 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.0–20.0 mol%_{HCH})
 $(\text{C}_2\text{H}_5)_4\text{NCl}$ (0.05 mol·L⁻¹)
 propylene carbonate,
 0.3–20.0 mA·cm⁻²,
 5.0–9.0 F (ref. to 1),
 25 °C, 500 rpm

A		B		Term C		E		target value		
Q / F		$j / \text{mA} \cdot \text{cm}^{-2}$		$c(\text{HCH}) / \text{mol} \cdot \text{L}^{-1}$		$n(\text{MnCl}_2 \cdot 4\text{H}_2\text{O}) / \text{mol} \%_{\text{HCH}}$		Conversion	Yield	Yield
								$X(1) / \%$	$Y(2) / \%$	$Y(6c) / \%$
6	5.0	0.10	5	69±1	50±1	21±1				
8	5.0	0.10	15	79±0	57±0	26±1				
6	15.0	0.10	15	71±1	48±3	20±1				
8	15.0	0.10	5	76±0	46±3	16±2				
6	5.0	0.20	15	69±3	44±3	16±1				
8	5.0	0.20	5	84±0	61±1	21±0				
6	15.0	0.20	5	80±0	59±0	18±0				
8	15.0	0.20	15	76±4	51±7	17±3				
7	10.0	0.15	10	81±0	60±1	22±0				
5	10.0	0.15	10	70	50	20				
9	10.0	0.15	10	89	67	24				
7	0.3	0.15	10	28	3	3				
7	20.0	0.15	10	74	42	19				
7	10.0	0.05	10	73	54	18				
7	10.0	0.25	10	80	61	20				
7	10.0	0.15	0	84	63	24				
7	10.0	0.15	20	78	59	20				

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of di(ethylene glycol) vinyl ether (**5c**) was not detected by the GC.

Table S33: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

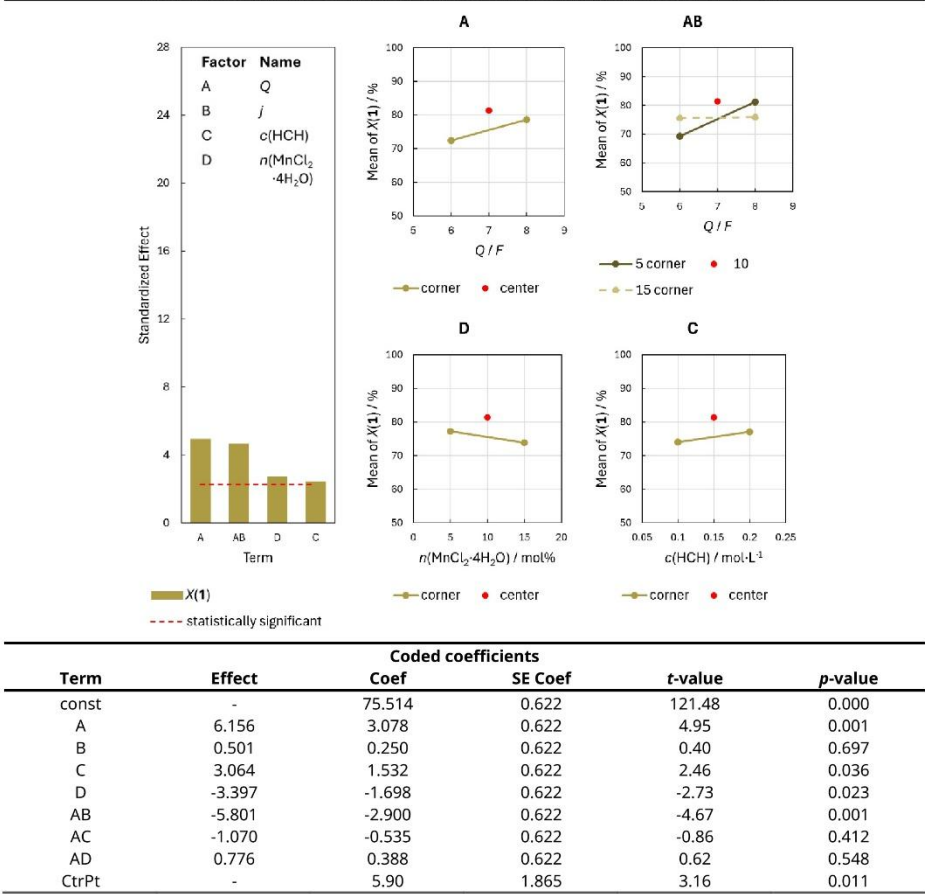


Table S34: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of benzene ($Y(2)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

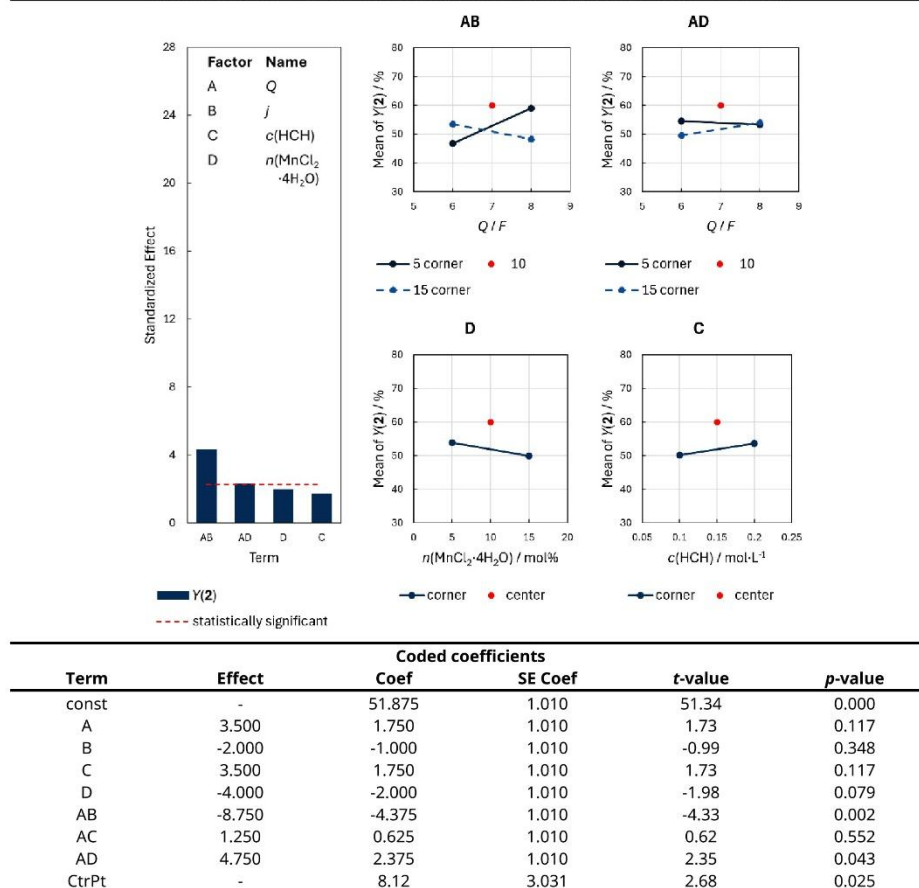
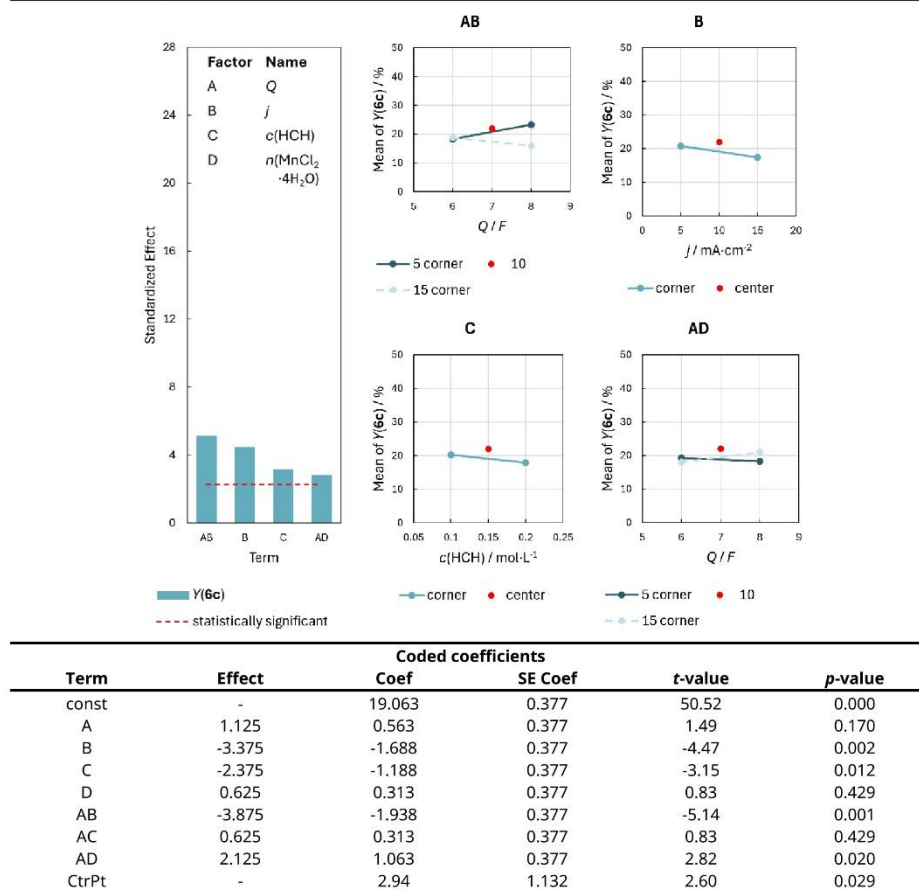


Table S35: Pareto, Main and Interaction plots of the 2^{4-1} fractional factorial experimental design for the yield of 2-Chloromethyl-1,3,6-trioxocane (**Y(6c)**) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



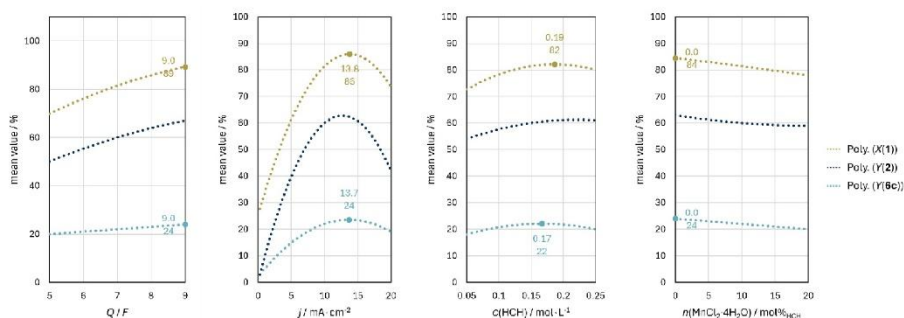
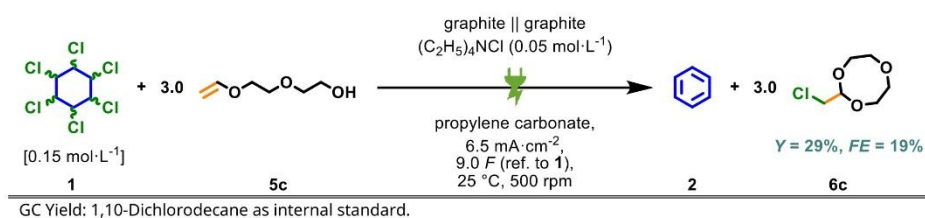


Figure S46: Main effect diagrams of the conversion and yield of 2-chloromethyl-1,3,6-trioxocane (**6c**) and HCH (**1**) to benzene (**2**) according to the 2⁴⁻¹ fractional factorial experimental with central composite design (CCD).

1st Optimized parameters for the yield of 2-chloromethyl-1,3,6-trioxocane (6c):



2nd Optimization by design of experiment (DoE) in a 2² full factorial design of experiments:

The design and evaluation of the plans was carried out by Minitab© 21.1. The temperature T and the concentration of the supporting electrolyte $c((\text{C}_2\text{H}_5)_4\text{NCl})$ were defined as. Conversions X_i and yields Y_i of the respective compounds were defined as target values.

Table S36: Determined yields Y_i of benzene (**2**), 2-chloromethyl-1,3,6-trioxocane (**6c**) and conversion X_i of the starting material technical HCH (**1**) and in a 2² full factorial experimental with central composite design (CCD).

1 [0.15 mol·L ⁻¹]		5c	2 6c	
TERM		target value		
A	B	Conversion	Yield	Yield
<i>T</i> / °C	<i>c</i> ((C ₂ H ₅) ₄ NCl) / mol·L ⁻¹	<i>X</i> (1) / %	<i>Y</i> (2) / %	<i>Y</i> (6c) / %
17.0	0.025	94±0	68±1	27±1
50.0	0.025	84±2	50±2	15±0
17.0	0.075	95±0	72±1	30±0
50.0	0.075	82±6	53±9	23±2
33.5	0.050	93±0	51±2	21±1

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard. The conversion of di(ethylene glycol) vinyl ether (**5c**) was not detected by the GC.

Table S37: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the conversion of HCH ($X(1)$) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

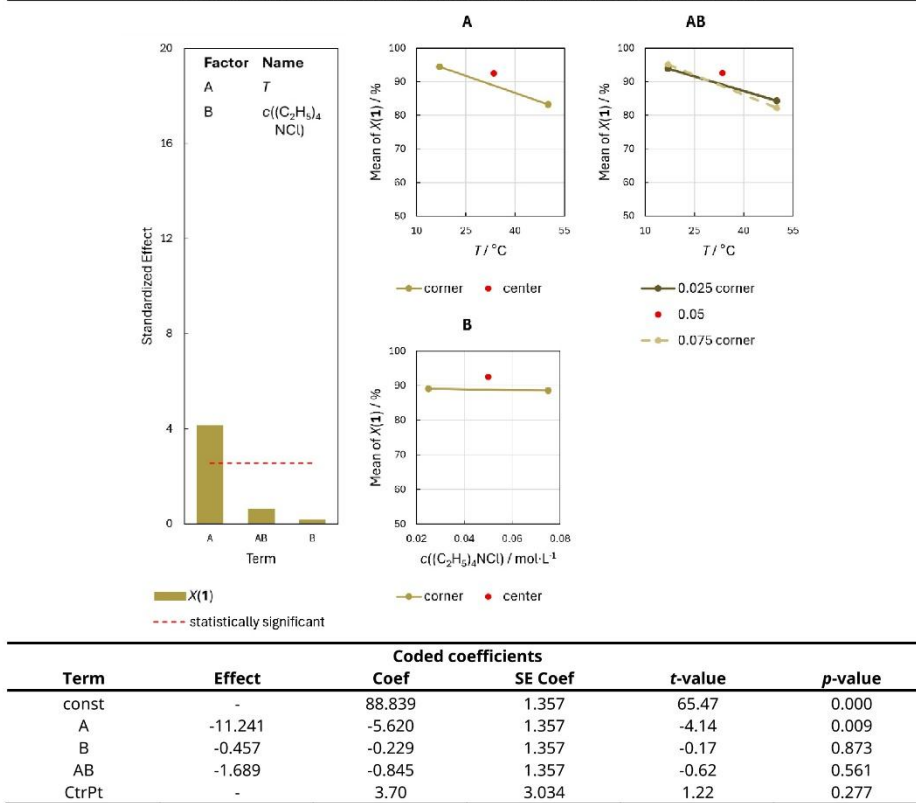


Table S38: Pareto, Main and Interaction plots of the 2² full factorial experimental design for the yield of benzene (Y(2)) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of α = 5%.

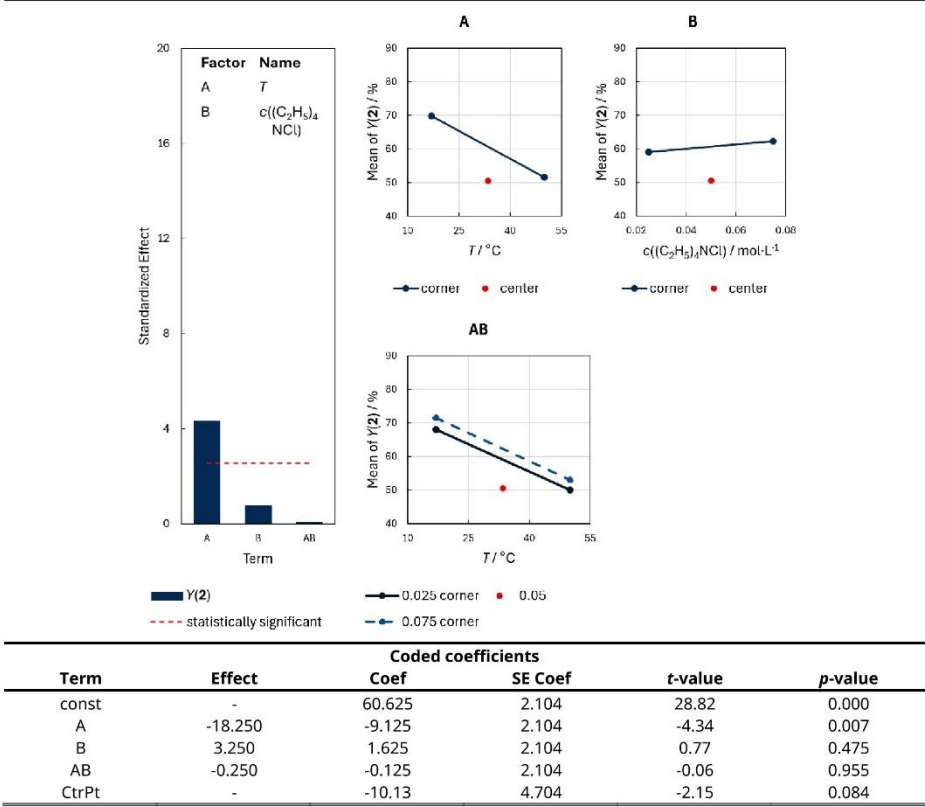
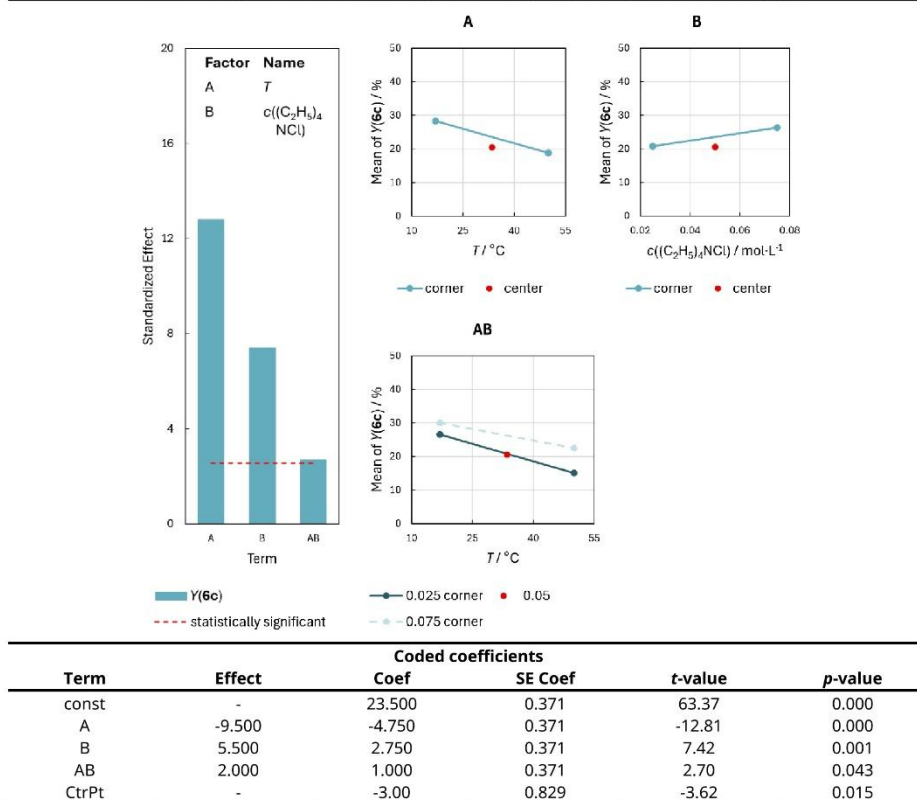
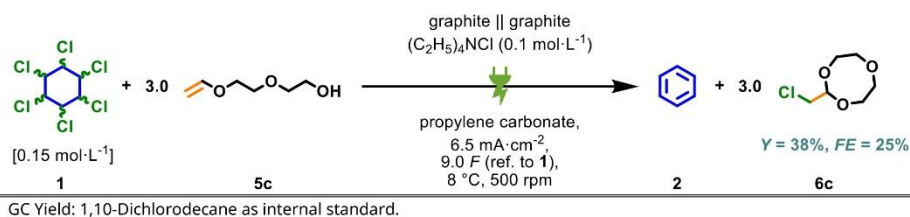


Table S39: Pareto, Main and Interaction plots of the 2^2 full factorial experimental design for the yield of 2-chloromethyl-1,3-dioxepane (**Y(6c)**) (top). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, *t*- and *p*-value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.



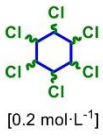
Optimized parameters for the yield of 2-chloromethyl-1,3,6-trioxocane (**6c**):



3.7 Kinetic Measurements

To investigate the reaction processes, various kinetic measurements were carried out and the rate coefficients k were determined.

Table S40: Determined amounts n_i of technical HCH (1), benzene (2), 2-chloro-1,1-di(ethoxy)-ethane (4) of the kinetic investigation in propylene carbonate by changing the amount of charge Q at the optimized conditions.

 1 [0.2 mol·L⁻¹] +  3.0 →  2 +  3.0 4 graphite graphite C₂H₅OH (12.0 eq.) (C₂H₅)₄NCl (0.05 mol·L⁻¹) propylene carbonate, 15.0 mA·cm⁻², 0–8 F (ref. to 1), 25 °C, 500 rpm									
Q / F	$n(1) / \text{mmol}$			$n(2) / \text{mmol}$			$n(4) / \text{mmol}$		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	1.000	1.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.555 0.551	0.553	0.002	0.089 0.092	0.090	0.002	0.207 0.216	0.212	0.006
2	0.442 0.420	0.431	0.016	0.232 0.235	0.234	0.002	0.497 0.512	0.505	0.010
3	0.378 0.377	0.378	0.000	0.248 0.255	0.252	0.005	0.744 0.888	0.816	0.102
4	0.240 0.263	0.252	0.016	0.429 0.427	0.428	0.002	1.041 1.210	1.126	0.119
5	0.171 0.160	0.166	0.008	0.472 0.475	0.473	0.002	1.500 1.443	1.471	0.040
6	0.238 0.182	0.210	0.039	0.474 0.552	0.513	0.055	1.716 1.776	1.746	0.043
7	0.125 0.084	0.105	0.029	0.573 0.610	0.591	0.026	2.031 2.069	2.050	0.027
8	0.052 0.020	0.036	0.023	0.741 0.788	0.764	0.033	2.356 2.169	2.263	0.132

GC amount of substance: 1,10-Dichlorodecane as internal standard.

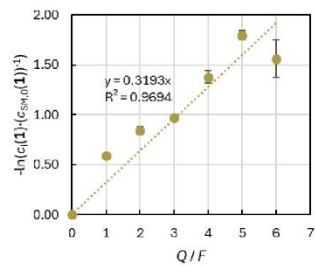


Figure S47: Measured consumption rate coefficient of HCH $k(1)$ at the optimized conditions.

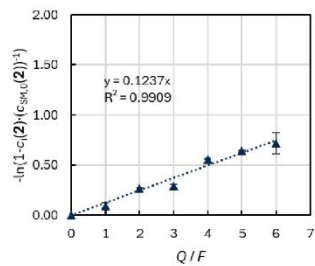


Figure S48: Measured formation rate coefficient of benzene $k(2)$ at the optimized conditions.

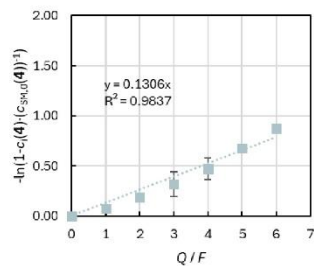


Figure S49: Measured formation rate coefficient of 2-chloro-1,1-di(ethoxy)-ethane $k(4)$ at the optimized conditions.

Table S41: Measured reaction rate coefficients k of consumption and formation.

$k(1) / 1 \cdot F^{-1}$	$k(2) / 1 \cdot F^{-1}$	$k(4) / 1 \cdot F^{-1}$
0.3193	0.1237	0.1306

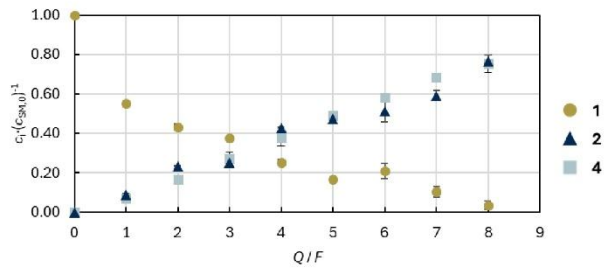
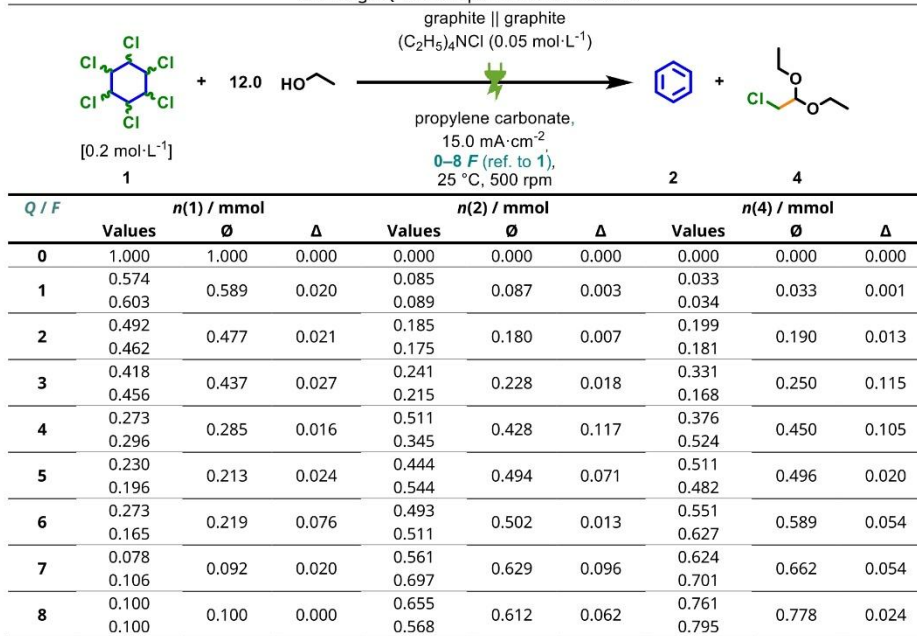


Figure S50: Measured consumption of HCH (1) and formation of benzene (2) and 2-chloro-1,1-di(ethoxy)-ethane (4) from ethyl vinyl ether and ethanol.

Table S42: Determined amounts n_i of technical HCH (**1**), benzene (**2**), 2-chloro-1,1-di(ethoxy)-ethane (**4**) of the kinetic investigation in propylene carbonate with ethanol as starting material by changing the amount of charge Q at the optimized conditions.



GC amount of substance: 1,10-Dichlorodecane as internal standard.

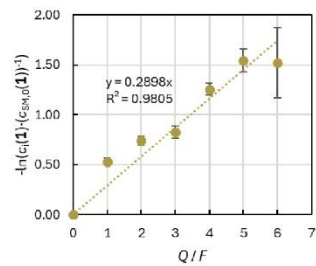


Figure S51: Measured consumption rate coefficient of HCH $k(1)$ at the optimized conditions.

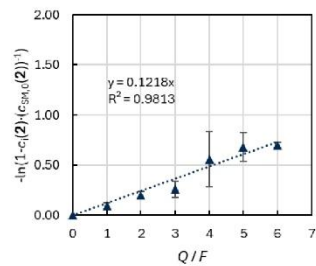


Figure S52: Measured formation rate coefficient of benzene $k(2)$ at the optimized conditions.

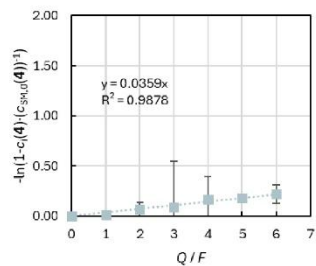


Figure S53: Measured formation rate coefficient of 2-chloro-1,1-di(ethoxy)-ethane $k(4)$ at the optimized conditions.

Table S43: Measured reaction rate coefficients k of consumption and formation at the optimized conditions.

$k(1) / 1 \cdot F^{-1}$	$k(2) / 1 \cdot F^{-1}$	$k(4) / 1 \cdot F^{-1}$
0.2898	0.1218	0.0359

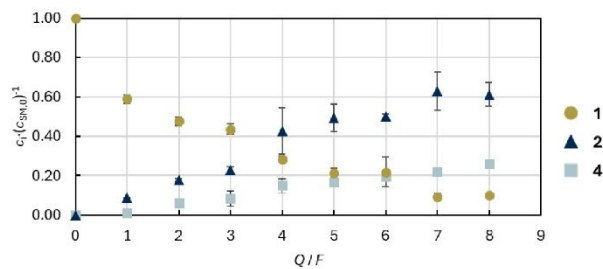
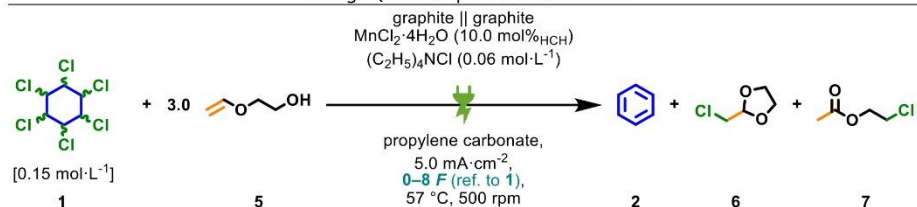


Figure S54: Measured consumption of HCH (1) and formation of benzene (2) and 2-chloro-1,1-di(ethoxy)-ethane (4) from ethanol.

Table S44: Determined amounts n_i of technical HCH (**1**), benzene (**2**), 2-chloromethyl-1,3-dioxolane (**6**) and 2-chloroethyl acetate (**7**) of the kinetic investigation in propylene carbonate by changing the amount of charge Q at the optimized conditions.



Q / F	n(1) / mmol			n(2) / mmol			n(6) / mmol			n(7) / mmol		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	0.750	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	0.595	0.596	0.001	0.066	0.077	0.014	0.127	0.127	0.001	0.194	0.223	0.041
	0.596			0.087			0.126			0.252		
2	0.568	0.552	0.023	0.083	0.110	0.039	0.201	0.242	0.058	0.342	0.398	0.080
	0.536			0.138			0.283			0.455		
3	0.461	0.492	0.044	0.164	0.167	0.005	0.424	0.407	0.024	0.638	0.610	0.040
	0.523			0.171			0.389			0.582		
4	0.425	0.408	0.024	0.175	0.211	0.051	0.512	0.564	0.074	0.809	0.829	0.028
	0.391			0.247			0.617			0.849		
5	0.413	0.420	0.010	0.190	0.215	0.035	0.539	0.528	0.015	1.018	1.046	0.039
	0.427			0.239			0.517			1.074		
6	0.359	0.374	0.022	0.263	0.261	0.002	0.663	0.634	0.041	1.296	1.256	0.057
	0.390			0.259			0.604			1.216		
7	0.316	0.307	0.012	0.285	0.332	0.068	0.838	0.857	0.026	1.288	1.379	0.128
	0.298			0.380			0.875			1.469		
8	0.302	0.310	0.011	0.330	0.333	0.004	0.690	0.667	0.032	1.571	1.559	0.018
	0.318			0.336			0.645			1.546		

GC amount of substance: 1,10-Dichlorodecane as internal standard.

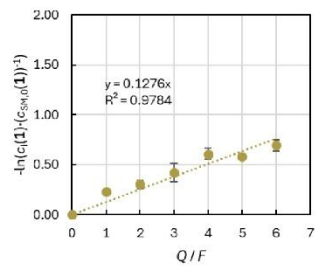


Figure S55: Measured consumption rate coefficient of HCH $k(1)$ at the optimized conditions.

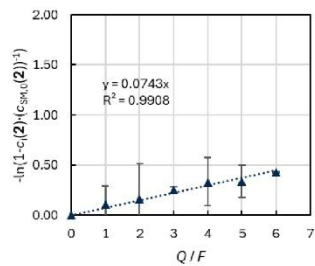


Figure S56: Measured formation rate coefficient of benzene $k(2)$ at the optimized conditions.

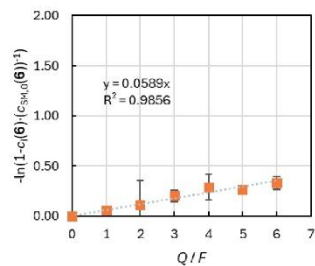


Figure S57: Measured formation rate coefficient of 2-chloromethyl-1,3-dioxolane $k(6)$ as the optimized conditions.

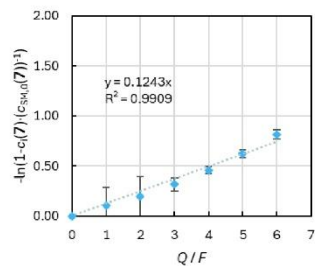


Figure S58: Measured formation rate coefficient of 2-chloroethyl acetate $k(7)$ at the optimized conditions.

Table S45: Measured reaction rate coefficients k of consumption and formation at the optimized conditions.

$k(1) / 1 \cdot F^{-1}$	$k(2) / 1 \cdot F^{-1}$	$k(6) / 1 \cdot F^{-1}$	$k(7) / 1 \cdot F^{-1}$
0.1257	0.0743	0.0589	0.1243

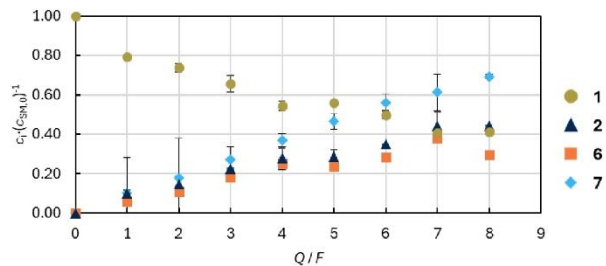
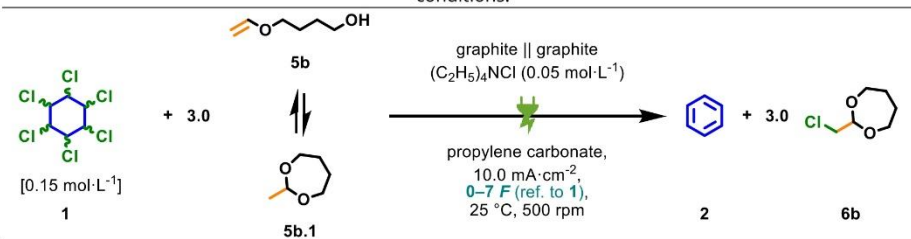


Figure S59: Measured consumption of HCH (1) and formation of benzene (2), 2-chloromethyl-1,3-dioxolane (6) and 2-chloroethyl acetate (7).

Table S46: Determined amounts n_i of technical HCH (**1**), benzene (**2**), 2 chloromethyl-1,3-dioxepane (**6b**) of the kinetic investigation in propylene carbonate by changing the amount of charge Q at the optimized conditions.



Q / F	n(1) / mmol			n(2) / mmol			n(5b.1) / mmol			n(6b) / mmol		
	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ	Values	$\emptyset$	Δ
0	0.750	0.000	0.000	0.000	0.000	0.000	-	-	-	0.000	0.000	0.000
1	0.522	0.529	0.007	0.093	0.091	0.002	0.852	0.662	0.191	0.159	0.159	0.000
	0.536			0.089			0.471			0.159		
2	0.452	0.453	0.001	0.159	0.161	0.002	0.269	0.341	0.072	0.376	0.364	0.012
	0.454			0.162			0.413			0.352		
3	0.365	0.370	0.005	0.237	0.236	0.001	0.186	0.264	0.078	0.566	0.597	0.031
	0.374			0.234			0.341			0.627		
4	0.296	0.314	0.018	0.292	0.284	0.008	0.115	0.161	0.046	0.824	0.771	0.054
	0.331			0.275			0.207			0.717		
5	0.238	0.244	0.006	0.362	0.361	0.001	0.029	0.034	0.005	1.058	1.038	0.020
	0.250			0.360			0.038			1.018		
6	0.181	0.184	0.003	0.413	0.421	0.008	0.021	0.033	0.012	1.300	1.267	0.033
	0.186			0.428			0.045			1.234		
7	0.226	0.233	0.006	0.410	0.400	0.010	0.010	0.005	0.005	1.602	1.525	0.077
	0.239			0.390			0.000			1.448		

GC amount of substance: 1,10-Dichlorodecane as internal standard.

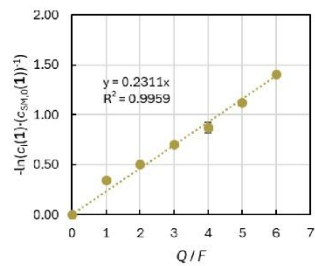


Figure S60: Measured consumption rate coefficient of HCH $k(1)$ at the optimized conditions.

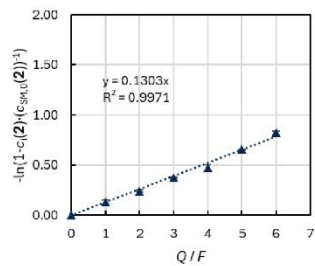


Figure S61: Measured formation rate coefficient of benzene $k(2)$ at the optimized conditions.

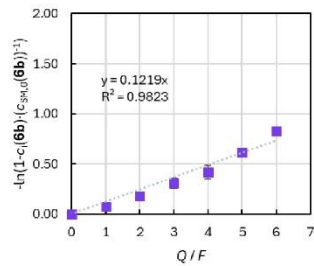


Figure S62: Measured formation rate coefficient of 2-chloromethyl-1,3-dioxolane $k(6b)$ at the optimized conditions.

Table S47: Measured reaction rate coefficients k of consumption and formation at the optimized conditions.

$k(1) / 1 \cdot F^{-1}$	$k(2) / 1 \cdot F^{-1}$	$k(6b) / 1 \cdot F^{-1}$
0.2311	0.1303	0.1219

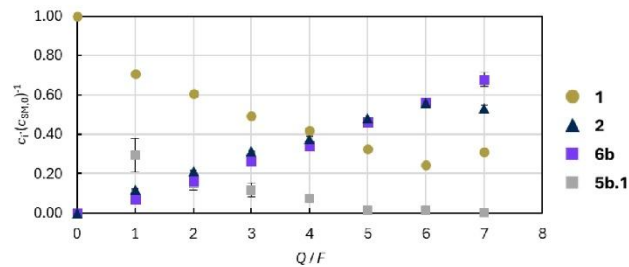


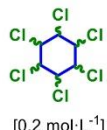
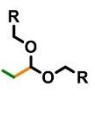
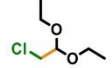
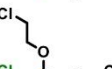
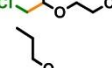
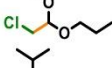
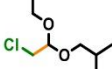
Figure S63: Measured consumption of HCH (1) and formation of benzene (2), 2-methyl-1,3-dioxepan (5b.1) and 2-chloromethyl-1,3-dioxepane (6b).

3.8 Process Development

Scale-up Reactions of the acetals

Scaling reactions were carried out in a 500 mL stacked batch-type cell (**Figure S7**). The electrolysis of the 500 mL stacked batch-type cell was carried out with an immersion surface of about 585 cm².

Table S48: Scale-up Reactions of acyclic acetals in a 500 mL stacked batch-type cell.

 1 +  3.0 graphite graphite alcohol (12.0 eq.) (C₂H₅)₄NCl (0.05 mol·L⁻¹) propylene carbonate, 15 mA·cm⁻², 8.5 F (ref. to 1), 25 °C, 970 rpm  2 +  3.0			
Compound	#	Yield / %	
	4	52 69 (500 rpm)	
	4a	44	
	4b	43	
	4c	54	
	4d	47	
	4e	38	

GC Yield: 1,10-Dichlorodecane as internal standard.

Scaling reactions of cyclic Acetals were also carried out in a 500 mL stacked batch-type cell (**Figure S7**). The electrolysis of the 500 mL stacked batch-type cell was carried out with an immersion surface of about 585 cm².

Table S49: Scale-up Reactions of cyclic acetals in a 500 mL stacked batch-type cell.

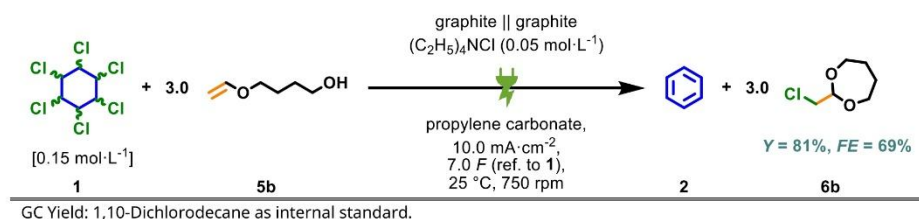
Compound	#	Conditions	Yield / %
	6	(C ₂ H ₅) ₄ NCl (0.05 mol·L ⁻¹) <i>n</i> (MnCl ₂ ·4H ₂ O) (10 mol%) <i>j</i> = 10 mA·cm ⁻² <i>Q</i> = 7.4 <i>F</i> (ref. to 1) <i>T</i> = 57 °C	33
	6b	(C ₂ H ₅) ₄ NCl (0.05 mol·L ⁻¹) <i>j</i> = 10 mA·cm ⁻² <i>Q</i> = 7.0 <i>F</i> (ref. to 1) <i>T</i> = 25 °C	82
	6c	(C ₂ H ₅) ₄ NCl (0.1 mol·L ⁻¹) <i>j</i> = 6.5 mA·cm ⁻² <i>Q</i> = 9.0 <i>F</i> (ref. to 1) <i>T</i> = 8 °C	23

GC Yield: 1,10-Dichlorodecane as internal standard.

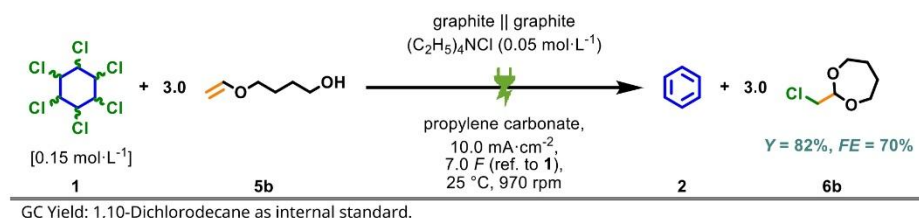
Scale-up Reaction of 2-chloromethyl-1,3-dioxepane (6b)

Scaling reactions were carried out in a 50 mL (**Figure S5**) batch-type cell and a 500 mL stacked batch-type cell (**Figure S7**) using 2-chloromethyl-1,3-dioxepane (**6b**).

The electrolysis of the 50 mL batch-type cell was carried out with an immersion surface of about 19.3 cm². An amount of 2.181 g of HCH (**1**) was used for electrolysis.



The electrolysis of the 500 mL stacked batch-type cell was carried out with an immersion surface of about 585 cm². An amount of 21.812 g of HCH (**1**) was used for electrolysis.



Accumulation of the product in the electrolyte over several electrolysis

To accumulate the product, starting material was added again after each electrolysis. The experiments were carried out over three electrolysis in a 5 mL batch-type cell (**Figure S1**) and in a 500 mL stacked batch-type cell (**Figure S7**).

The electrolysis in the 5 mL cell was measured directly with an internal standard for each test series repeat (**Table S50**).

Table S50: Accumulation of 2-chloromethyl-1,3-dioxepane (**6b**) via 3 electrolysis in a 5 mL batch-type cell.

1	5b	2	6b
Run #		c(6b) / mol·L ⁻¹	
1		0.32	
2		0.62	
3		0.84	

GC Concentration: 1,10-Dichlorodecane as internal standard.

For the electrolysis in the 500 mL batch-type cell, approximately 1 mL was removed after each electrolysis and measured with the internal standard (**Table S51**).

Table S51: Accumulation of 2-chloromethyl-1,3-dioxepane (**6b**) via 3 electrolysis in a 500 mL stacked batch-type cell.

1	5b	2	6b
Run #		c(6b) / mol·L ⁻¹	
1		0.37	
2		0.69	
3		0.90	

GC Concentration: 1,10-Dichlorodecane as internal standard.

Recyclability of the electrolyte

The recyclability of the electrolyte was repeated up to 18 times. After each electrolysis and work-up, approximately 1 mL of the electrolyte was removed and measured with the internal standard. The amount of 21.81 g HCH (**1**) was used for electrolysis at the start. After each electrolysis, the determined converted amount of HCH was added again. The recyclability was carried out using the example of 2-chloromethyl-1,3-dioxepane (**6b**) in a 500 mL stacked batch-type electrolysis cell (**Figure S7**). The 4-hydroxybutyl vinyl ether was added via a pump (SF-10 (Vapourtec Ltd, Bury St Edmunds, UK)) over a period of 0–6 F (226 $\mu\text{L}\cdot\text{min}^{-1}$) in every electrolysis run (**Table S52**).

Table S52: Recyclability of the electrolyte over 18 repetitions on the example reaction of 2-chloromethyl-1,3-dioxepane (**6b**).

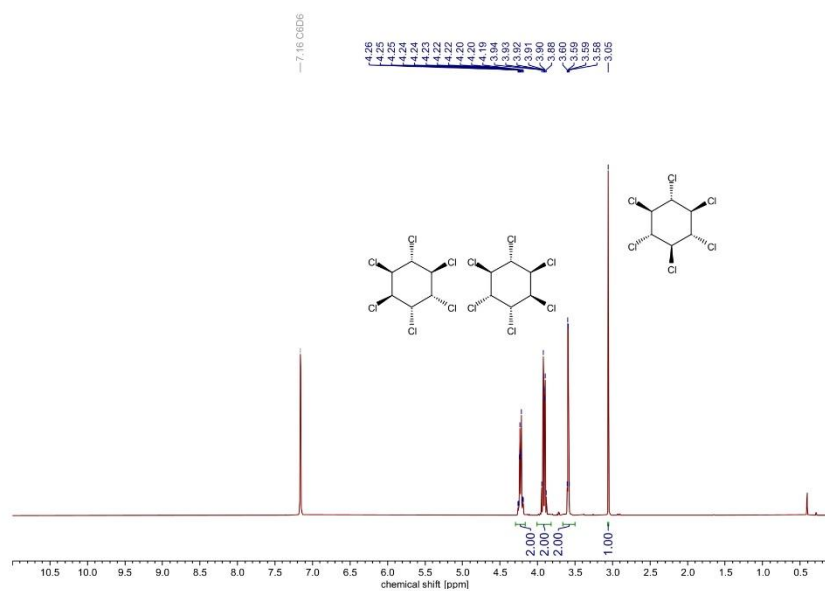
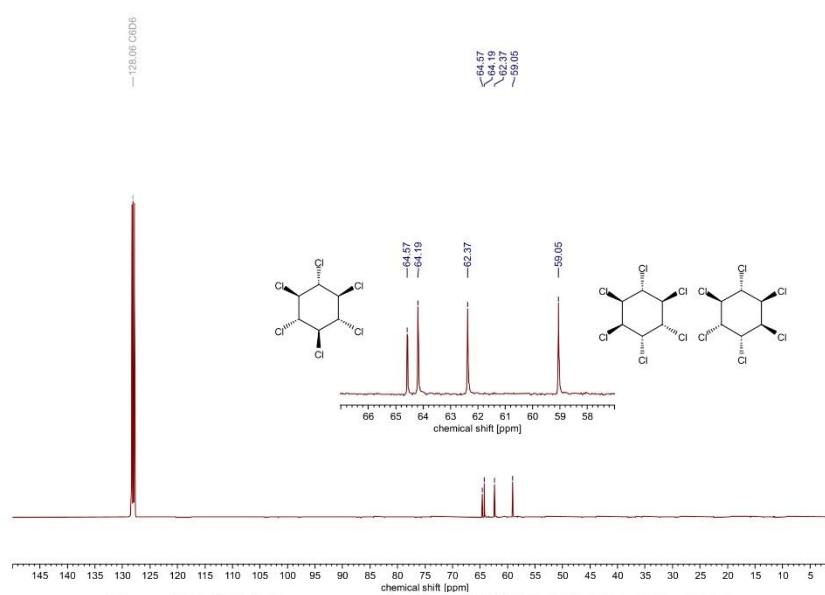
ClC1=CC=CC=C1 (1) + 3.0 CCOC(=O)CCO (5b) $\xrightarrow[\text{graphite || graphite}]{\text{Z-chloromethyl-1,3-dioxepane (6b), (C}_2\text{H}_5)_4\text{NCl (0.05 mol}\cdot\text{L}^{-1}\text{)}}$ c1ccccc1 (2) + 3.0 ClC1CCOCCO1 (6b)

[0.15 mol·L⁻¹] 10.0 mA·cm⁻², 7.0 F (ref. to 1), 25 °C, 970 rpm

Run #	Conversion X(1) / %	Yield Y(2) / %	Yield Y(6b) / %
1	88	66	93
2	84	66	92
3	84	65	91
4	84	63	91
5	81	78	108
6	86	62	86
7	87	65	87
8	82	66	85
9	83	65	79
10	82	66	83
11	79	64	83
12	80	64	72
13	78	76	92
14	84	65	82
15	82	66	81
16	78	78	114
17	83	60	73
18	83	62	59

GC Yield/Conversion: 1,10-Dichlorodecane as internal standard.

4. NMR Spectra

Figure S50: ^1H NMR spectrum of technical HCH (1) (400 MHz, C_6D_6 , 298 K).Figure S51: ^{13}C NMR spectrum of technical HCH (1) (101 MHz, C_6D_6 , 298 K).

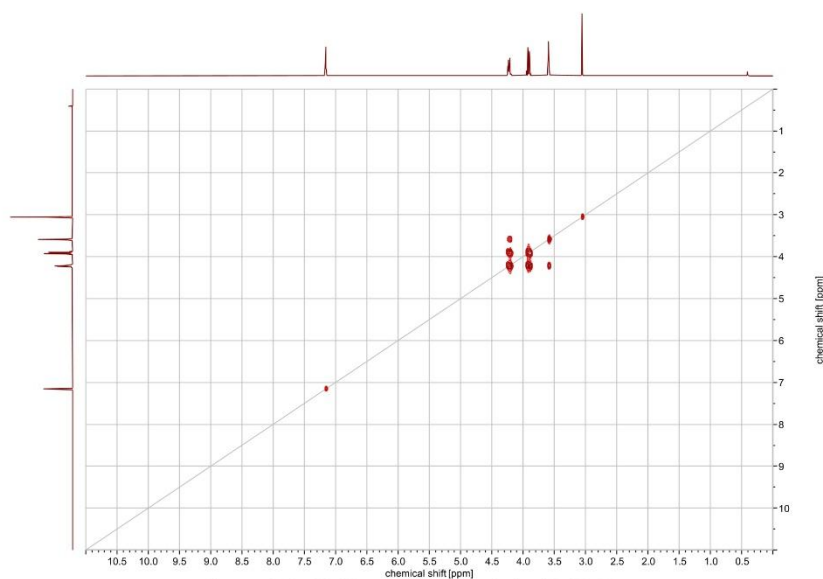


Figure S52: COSY spectrum of technical HCH (1).

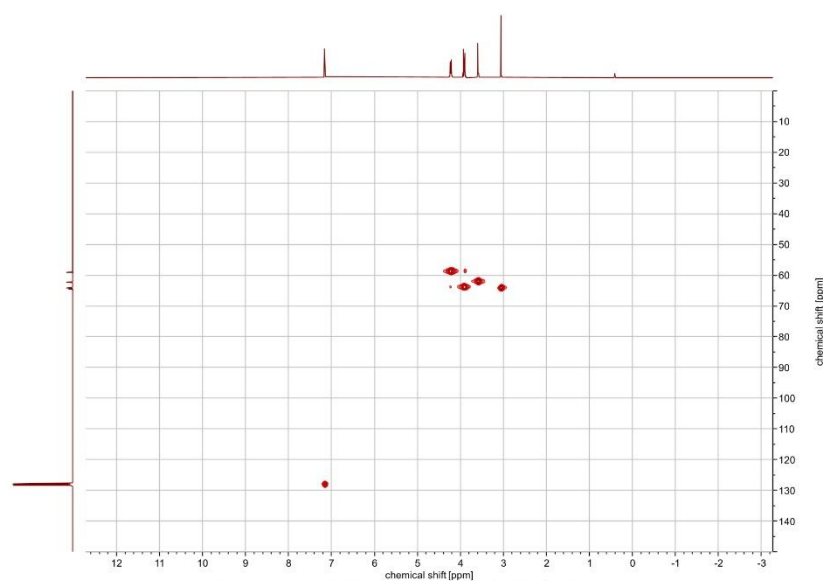


Figure S53: HSQC spectrum of technical HCH (1).

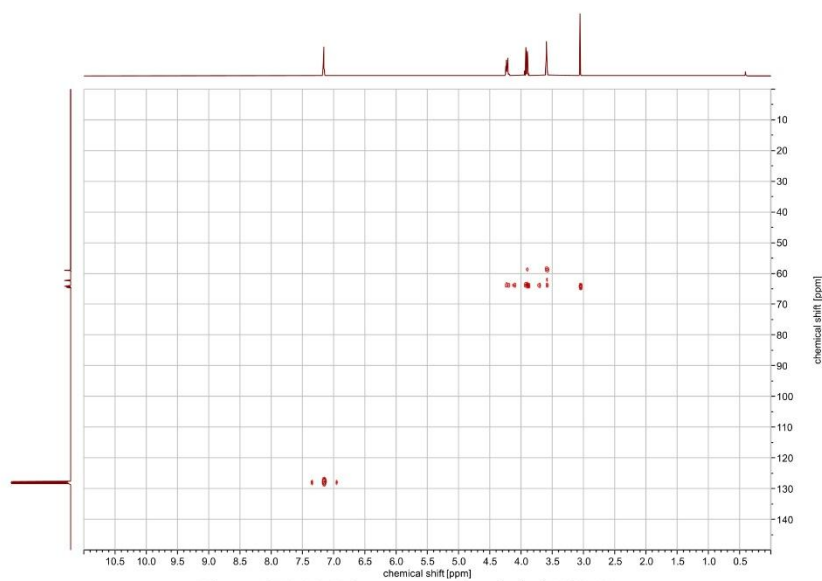


Figure S54: HMBC spectrum of technical HCH (1).

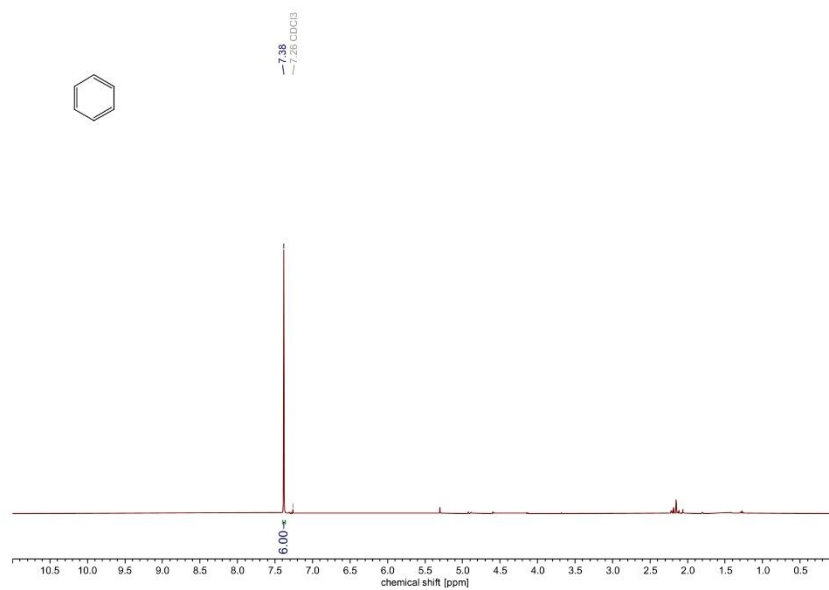


Figure S55: ^1H NMR spectrum of benzene (2) (400 MHz, CDCl_3 , 298 K).

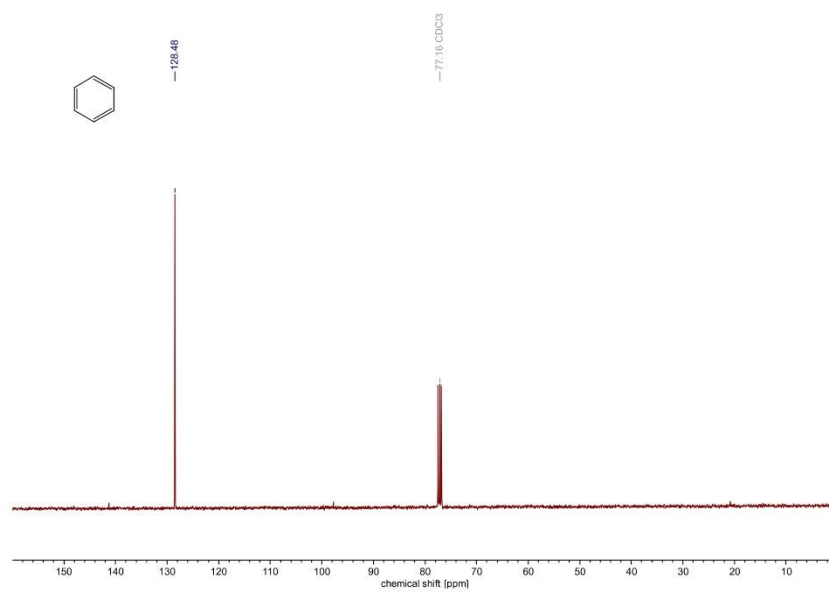


Figure S56: ^{13}C NMR spectrum of benzene (2) (101 MHz, CDCl_3 , 298 K).

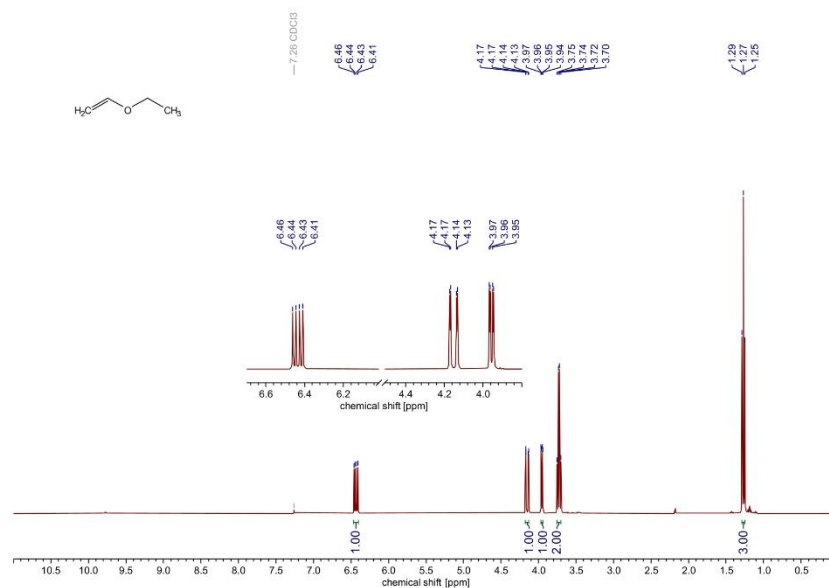


Figure S57: ¹H NMR spectrum of ethyl vinyl ether (3) (400 MHz, CDCl₃, 298 K).

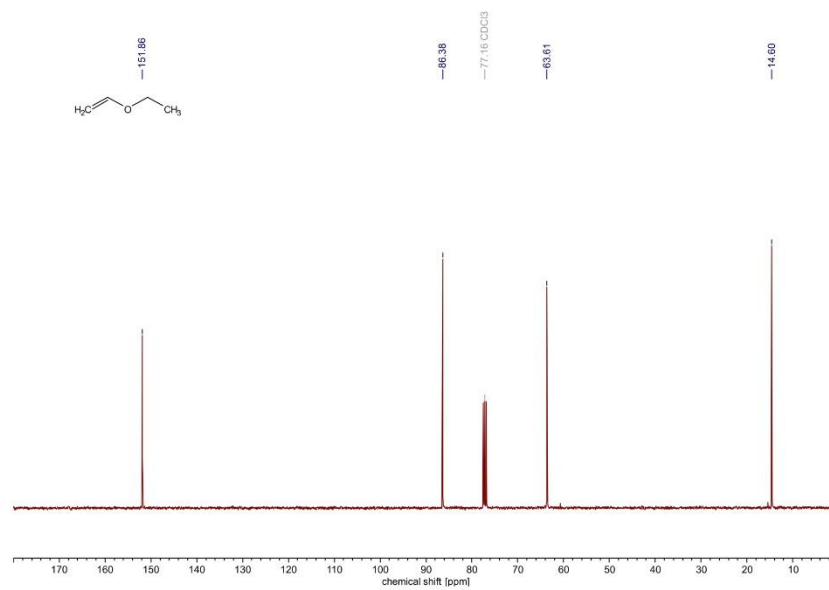


Figure S58: ¹³C NMR spectrum of ethyl vinyl ether (3) (101 MHz, CDCl₃, 298 K).

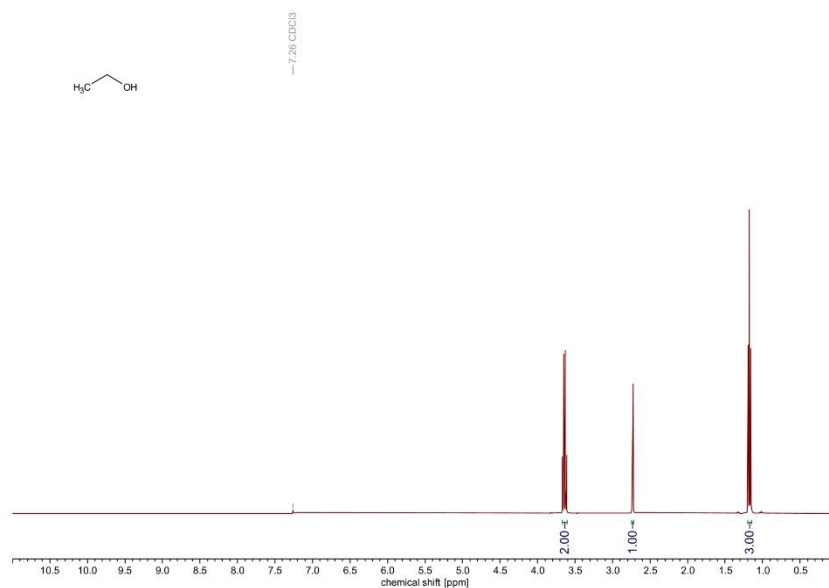


Figure S59: ^1H NMR spectrum of ethanol (400 MHz, CDCl_3 , 298 K).

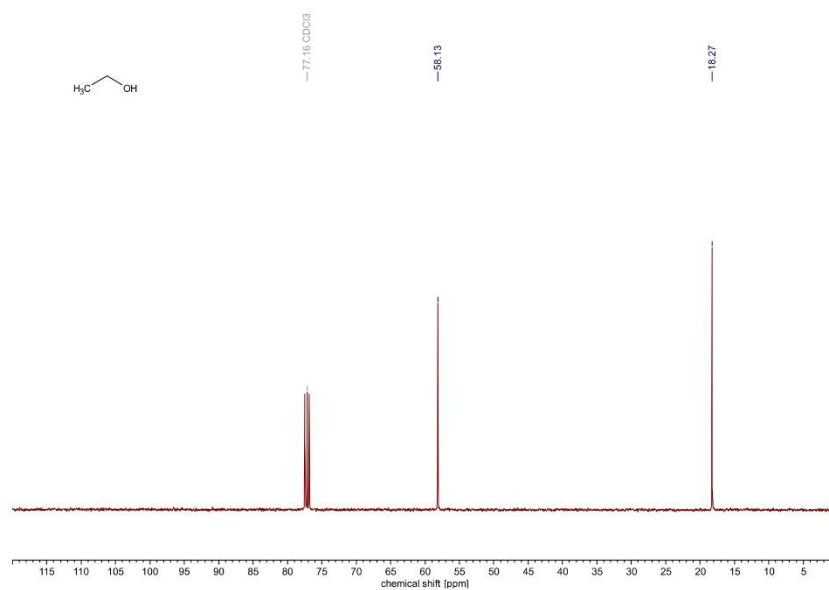


Figure S60: ^{13}C NMR spectrum of ethanol (101 MHz, CDCl_3 , 298 K).

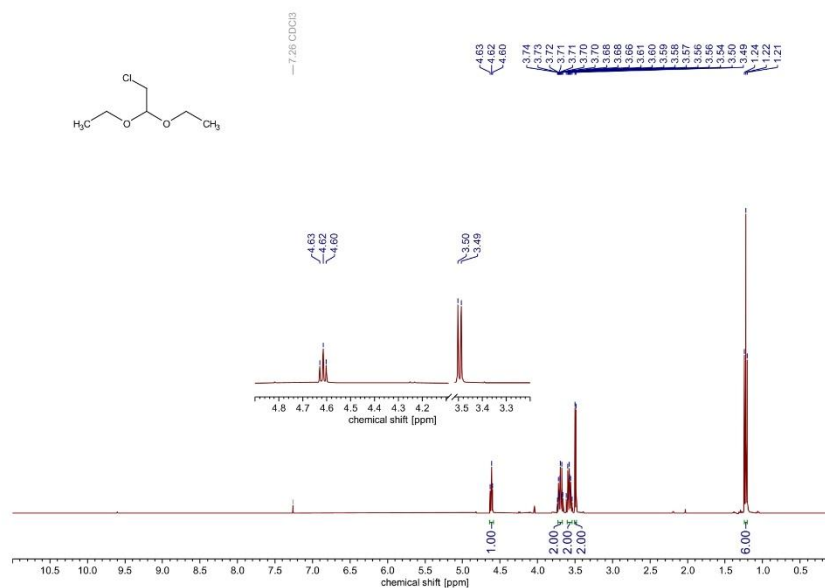


Figure S61: ¹H NMR spectrum of 2-chloro-1,1-di(ethoxy)-ethane (4) (400 MHz, CDCl₃, 298 K).

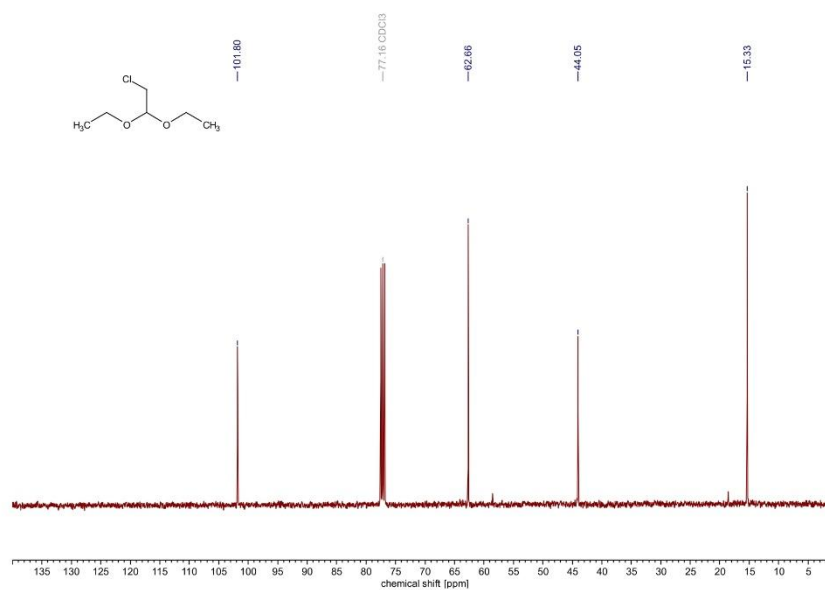


Figure S62: ¹³C NMR spectrum of 2-chloro-1,1-di(ethoxy)-ethane (4) (101 MHz, CDCl₃, 298 K).

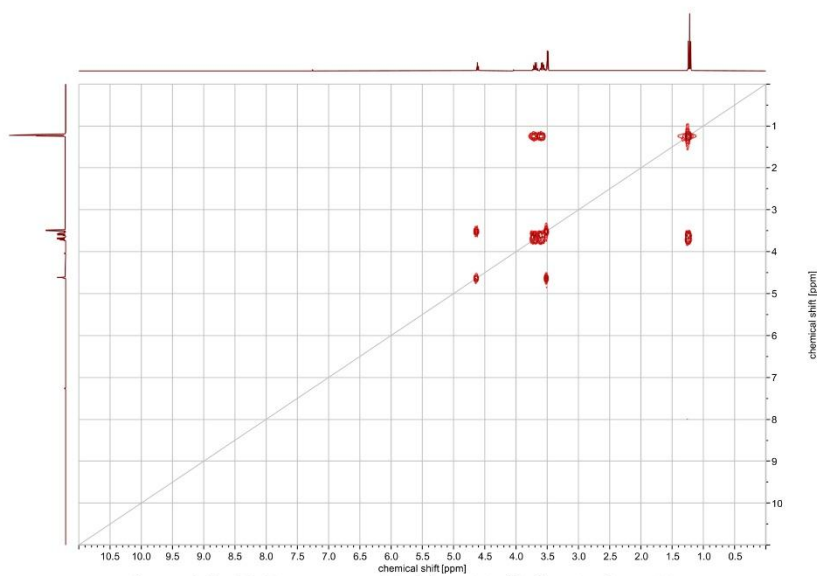


Figure S63: COSY spectrum of 2-chloro-1,1-di(ethoxy)-ethane (**4**).

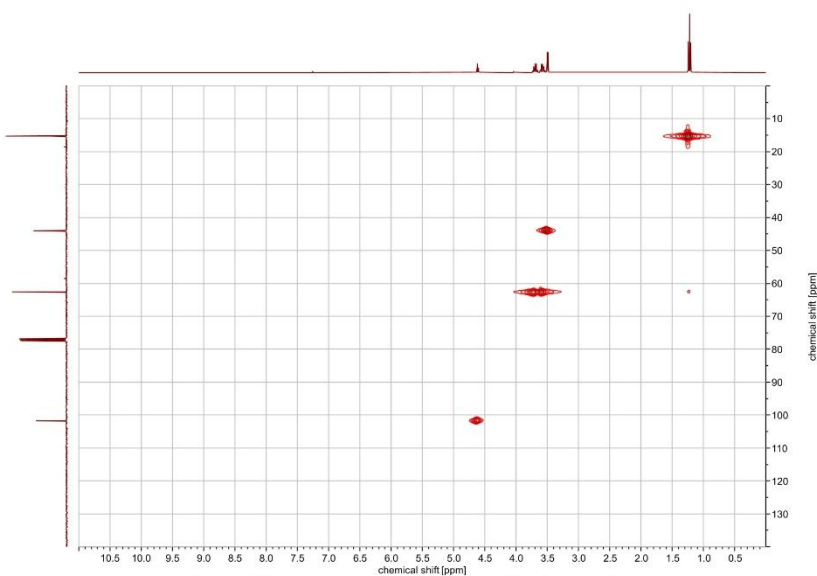


Figure S64: HSQC spectrum of 2-chloro-1,1-di(ethoxy)-ethane (**4**).

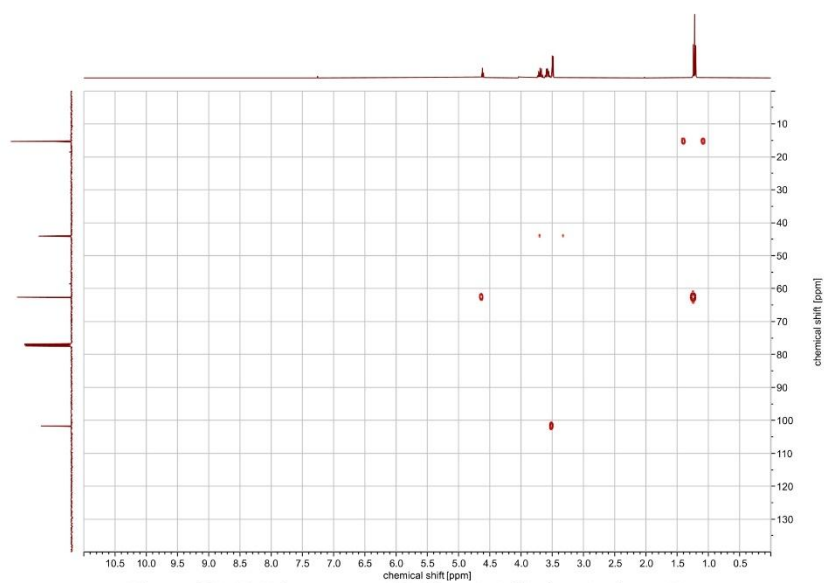


Figure S65: HMBC spectrum of 2-chloro-1,1-di(ethoxy)-ethane (**4**).

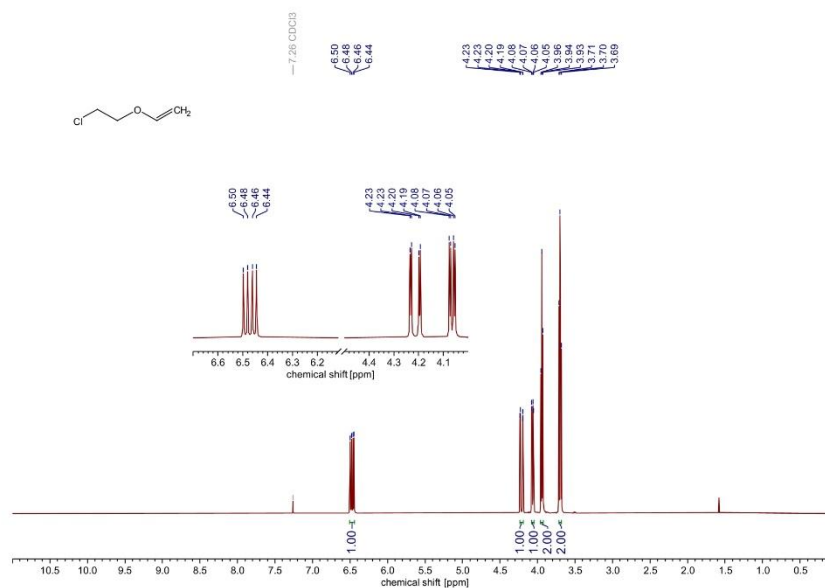


Figure S66: ¹H NMR spectrum of 2-chloroethyl vinyl ether (3a) (400 MHz, CDCl₃, 298 K).

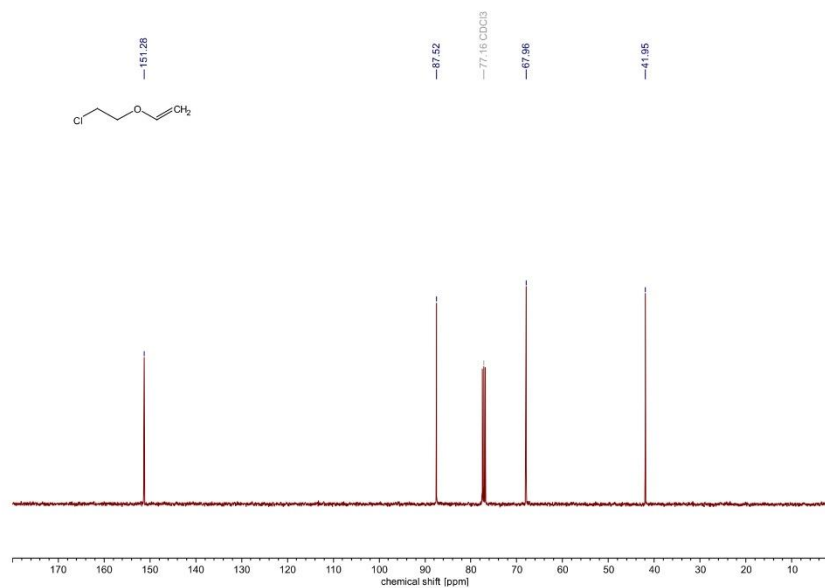


Figure S67: ¹³C NMR spectrum of 2-chloroethyl vinyl ether (3a) (101 MHz, CDCl₃, 298 K).

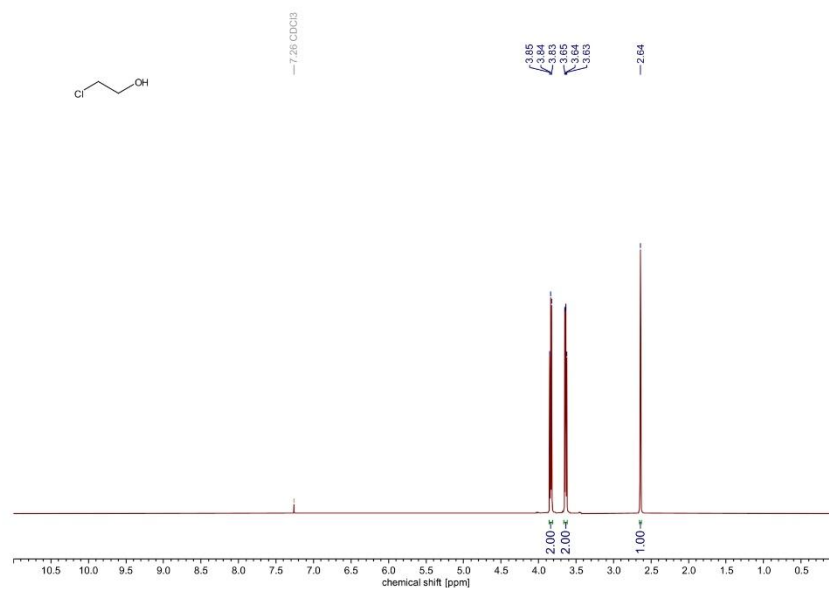


Figure S68: ¹H NMR spectrum of 2-chloroethanol (400 MHz, CDCl₃, 298 K).

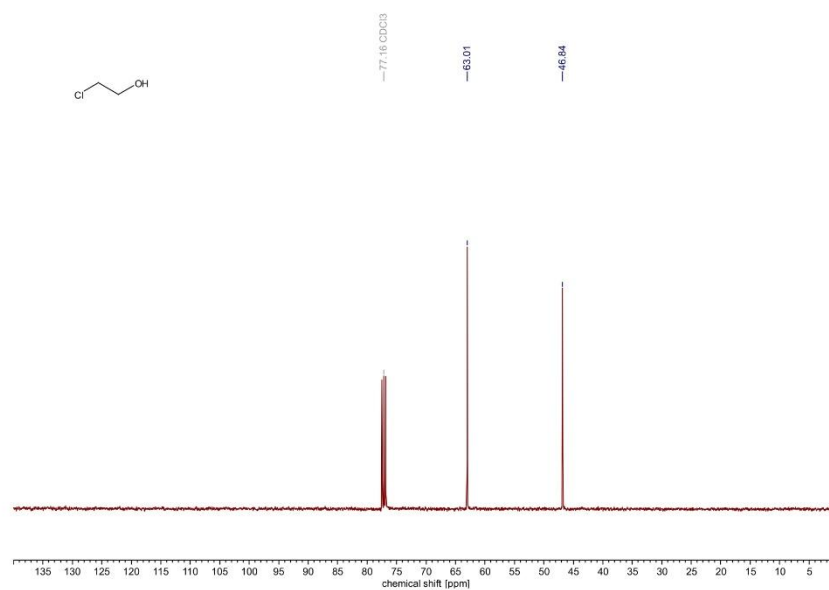


Figure S69: ¹³C NMR spectrum of 2-chloroethanol (101 MHz, CDCl₃, 298 K).

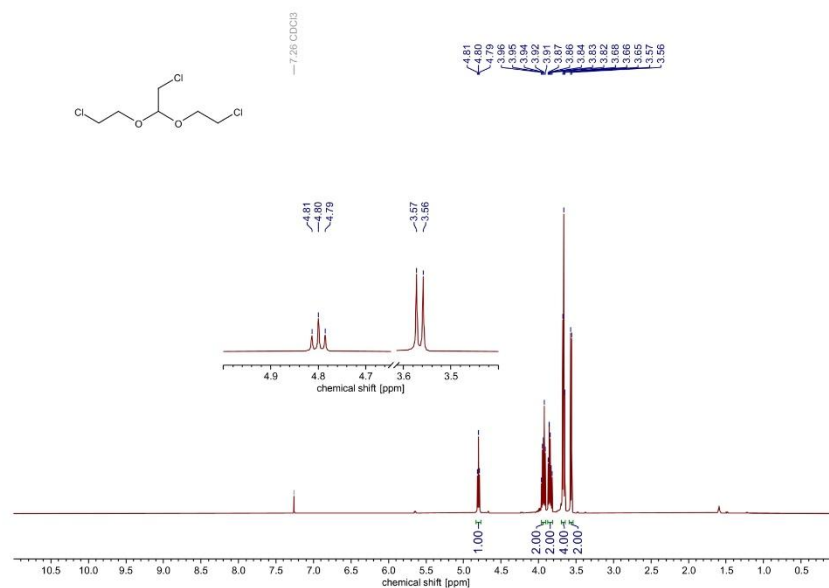


Figure S70: ¹H NMR spectrum of 2-chloro-1,1-di(2-chloroethoxy)-ethane (4a) (400 MHz, CDCl₃, 298 K).

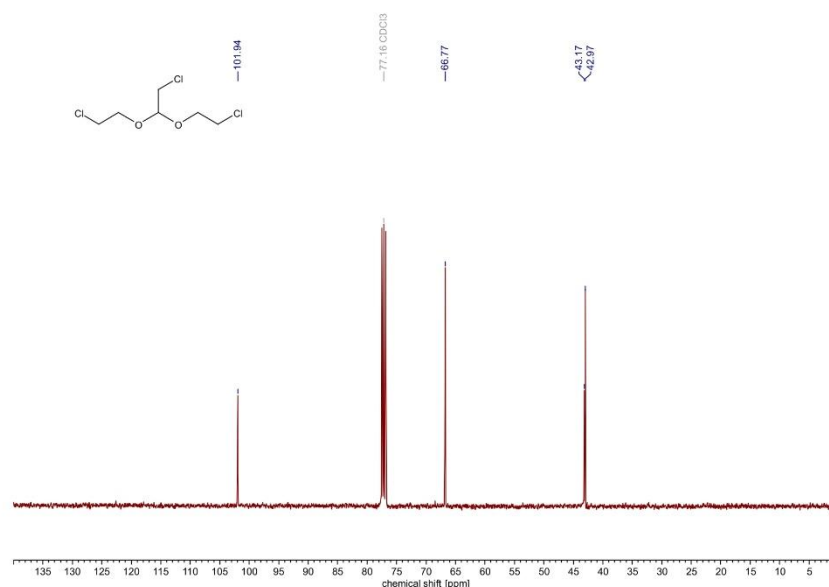


Figure S71: ¹³C NMR spectrum of 2-chloro-1,1-di(2-chloroethoxy)-ethane (4a) (101 MHz, CDCl₃, 298 K).

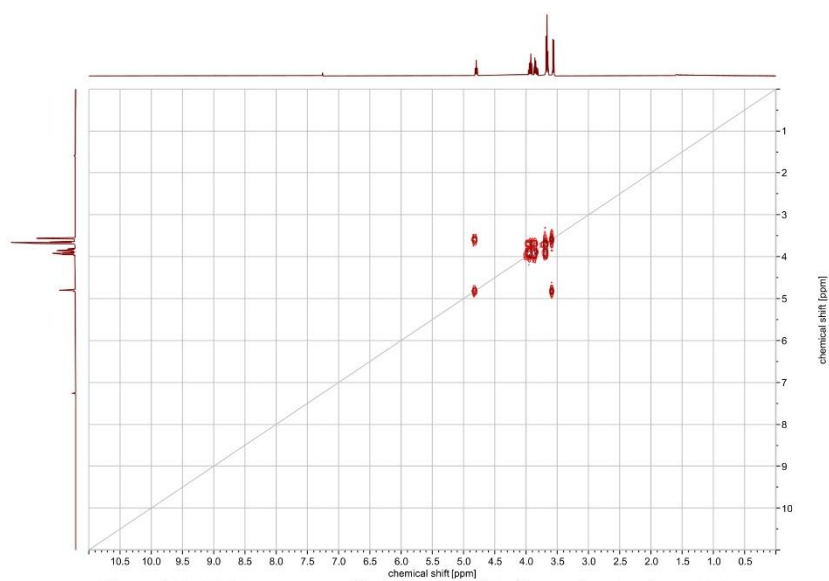


Figure S72: COSY spectrum of 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**).

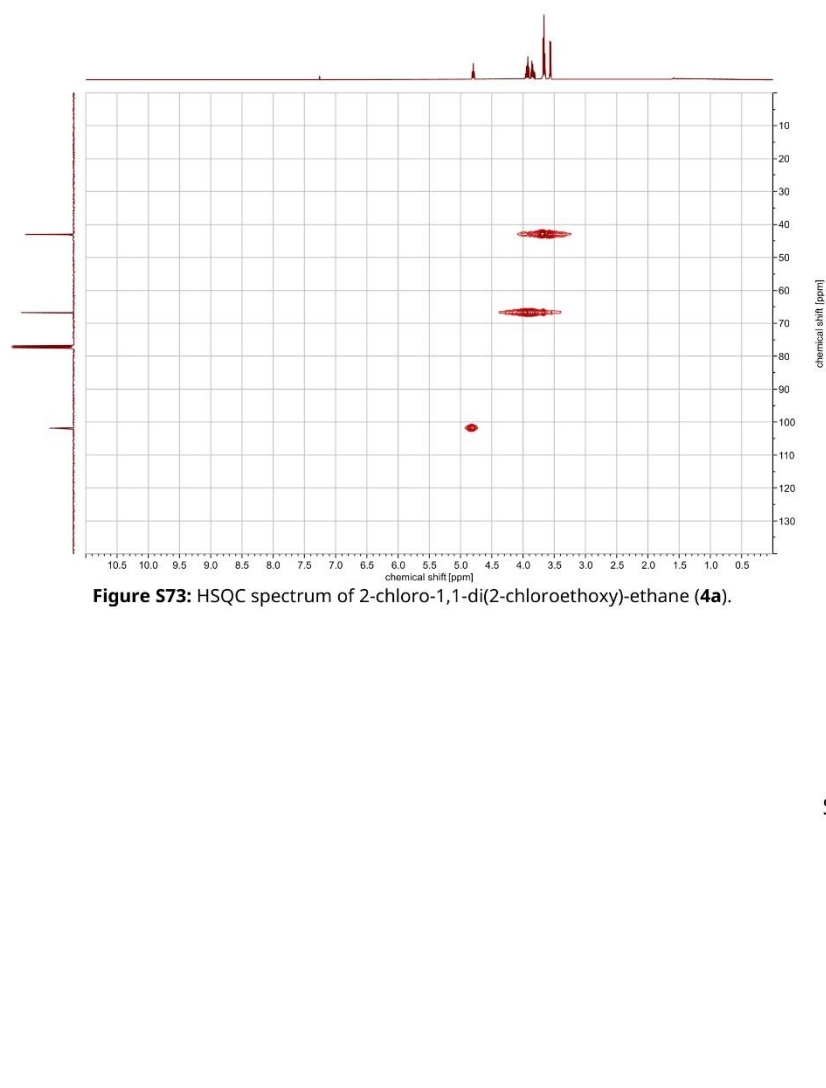


Figure S73: HSQC spectrum of 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**).

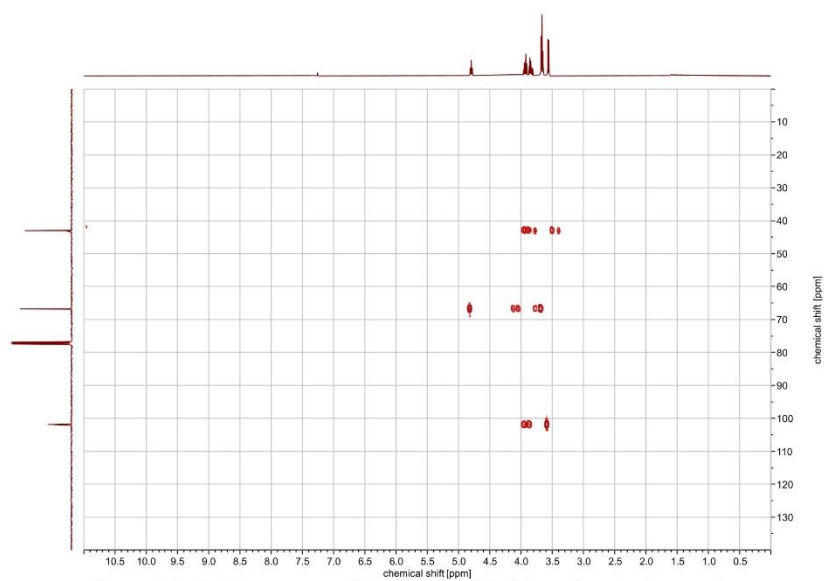


Figure S74: HMBC spectrum of 2-chloro-1,1-di(2-chloroethoxy)-ethane (**4a**).

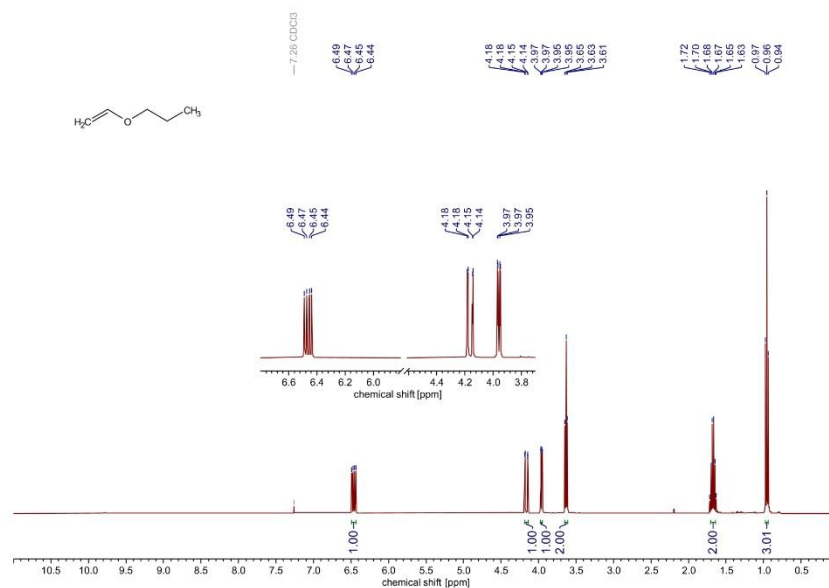


Figure S75: ¹H NMR spectrum of propyl vinyl ether (3b) (400 MHz, CDCl₃, 298 K).

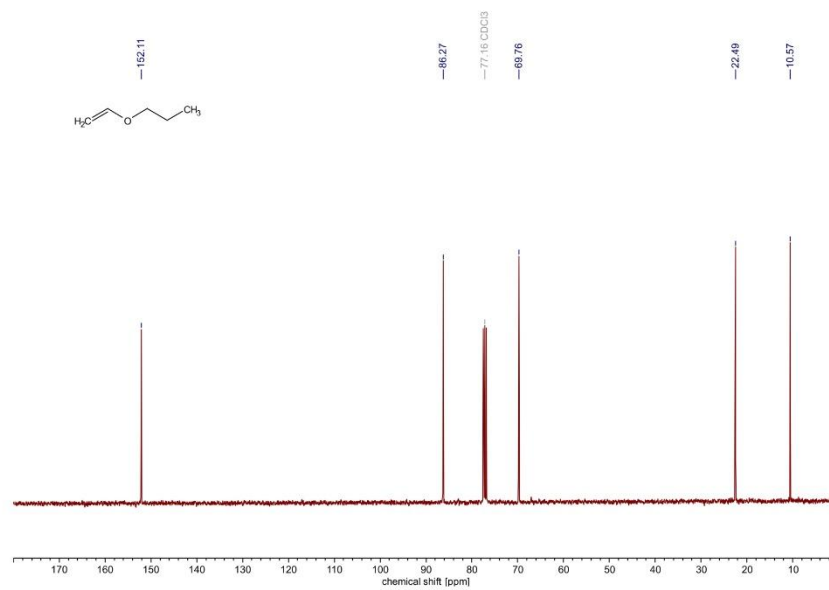


Figure S76: ¹³C NMR spectrum of propyl vinyl ether (3b) (101 MHz, CDCl₃, 298 K).

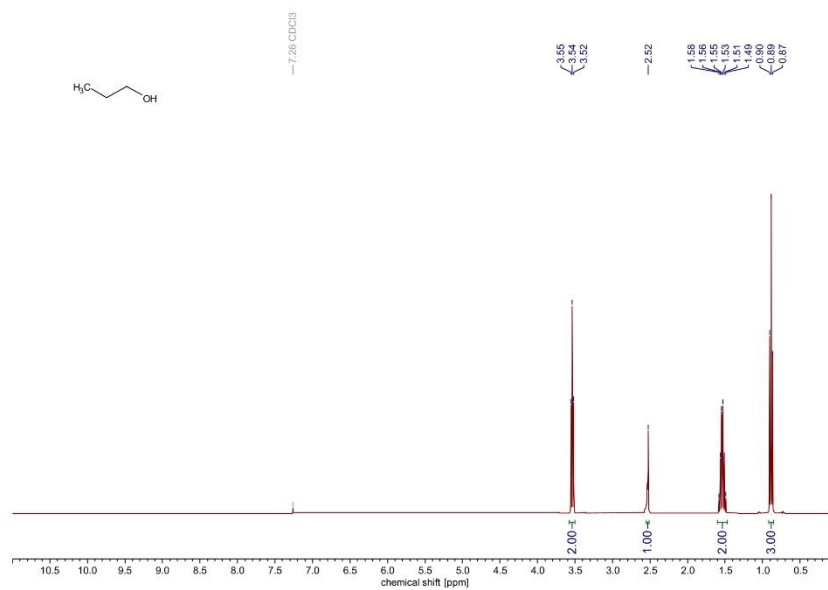


Figure S77: ¹H NMR spectrum of 1-propanol (400 MHz, CDCl₃, 298 K).

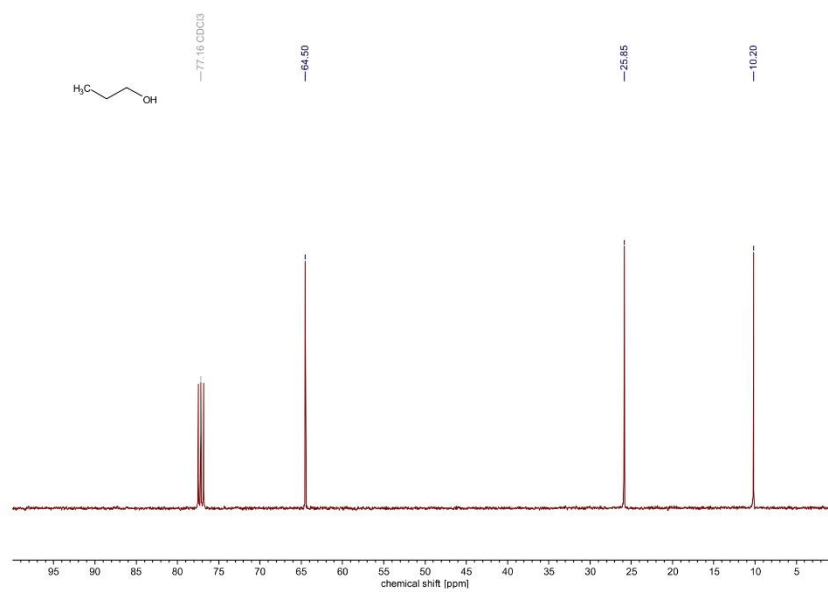


Figure S78: ¹³C NMR spectrum of 1-propanol (101 MHz, CDCl₃, 298 K).

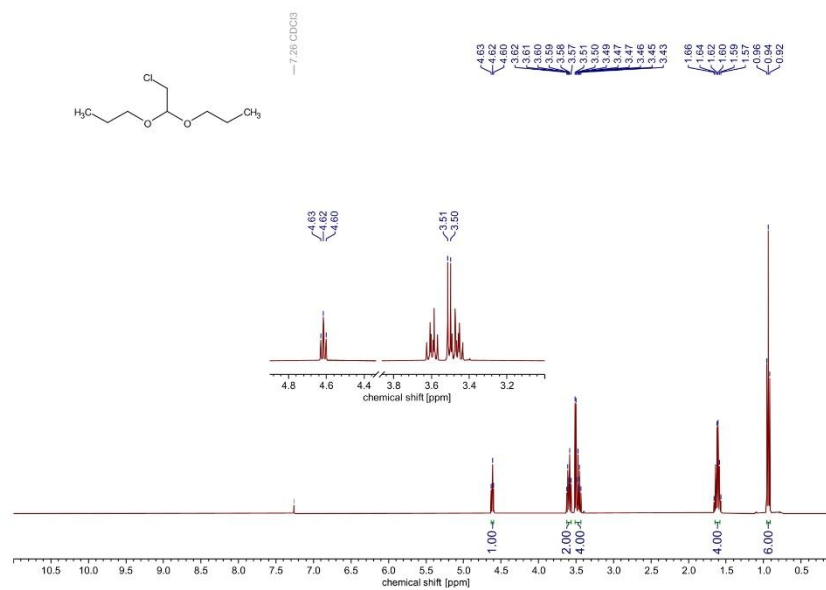


Figure S79: ¹H NMR spectrum of 2-chloro-1,1-di(propoxy)-ethane (**4b**) (400 MHz, CDCl₃, 298 K).

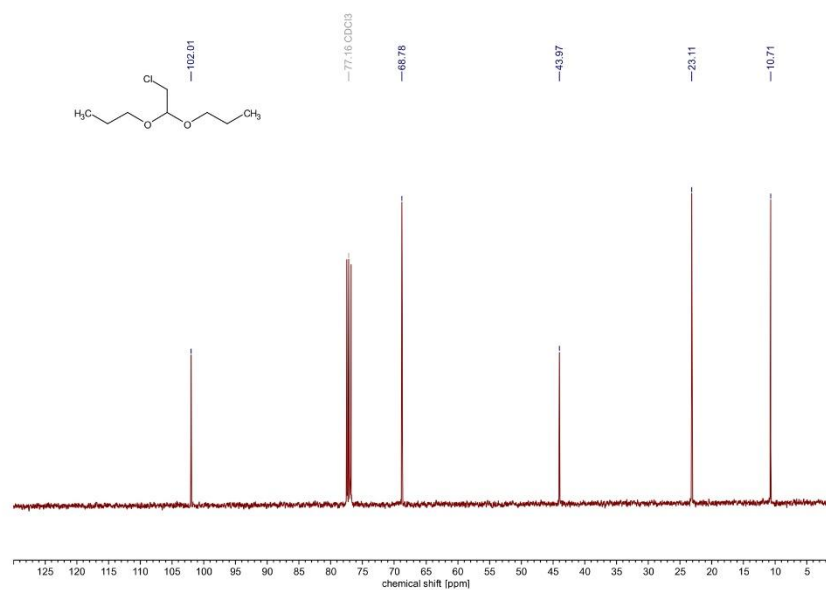


Figure S80: ¹³C NMR spectrum of 2-chloro-1,1-di(propoxy)-ethane (**4b**) (101 MHz, CDCl₃, 298 K).

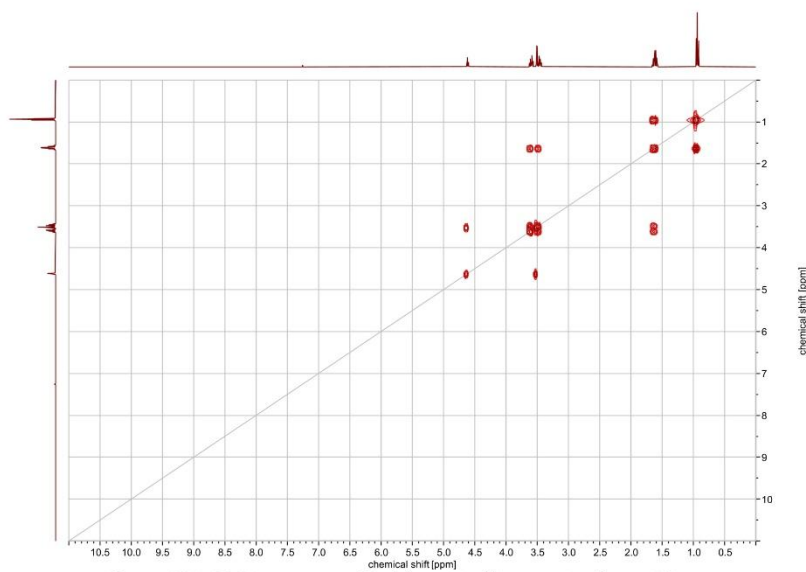


Figure S81: COSY spectrum of 2-chloro-1,1-di(propoxy)-ethane (**4b**).

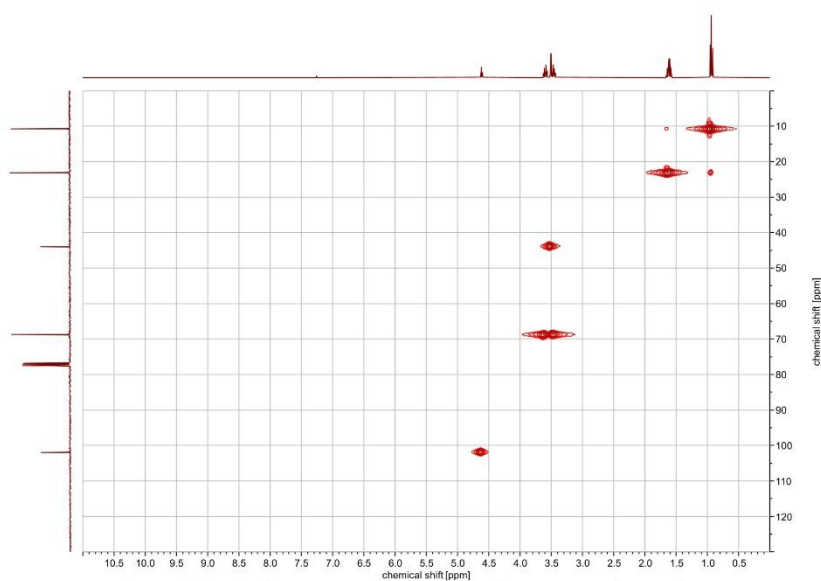


Figure S82: HSQC spectrum of 2-chloro-1,1-di(propoxy)-ethane (**4b**).

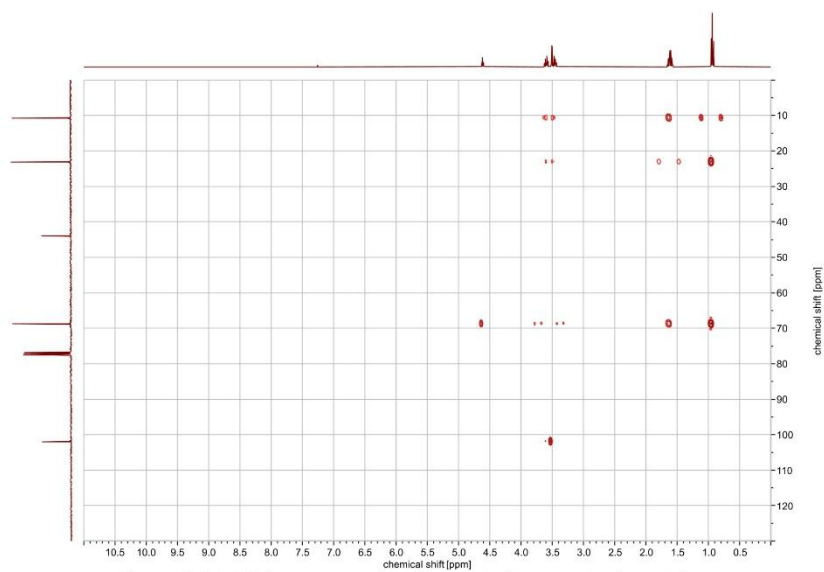
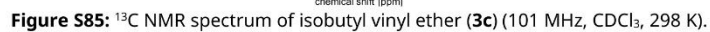
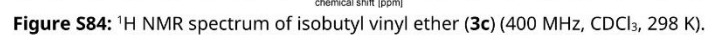


Figure S83: HMBC spectrum of 2-chloro-1,1-di(propoxy)-ethane (**4b**).



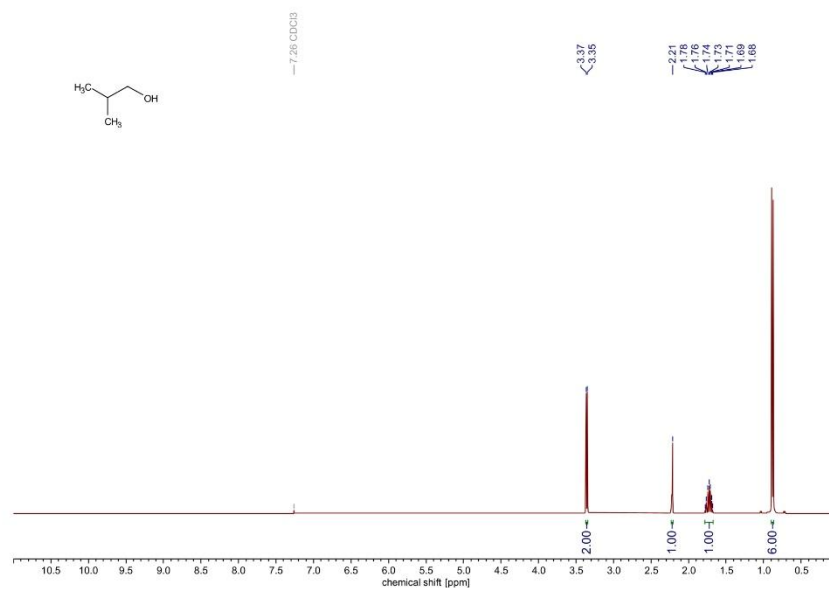


Figure S86: ¹H NMR spectrum of 2-methyl-1-propanol (400 MHz, CDCl₃, 298 K).

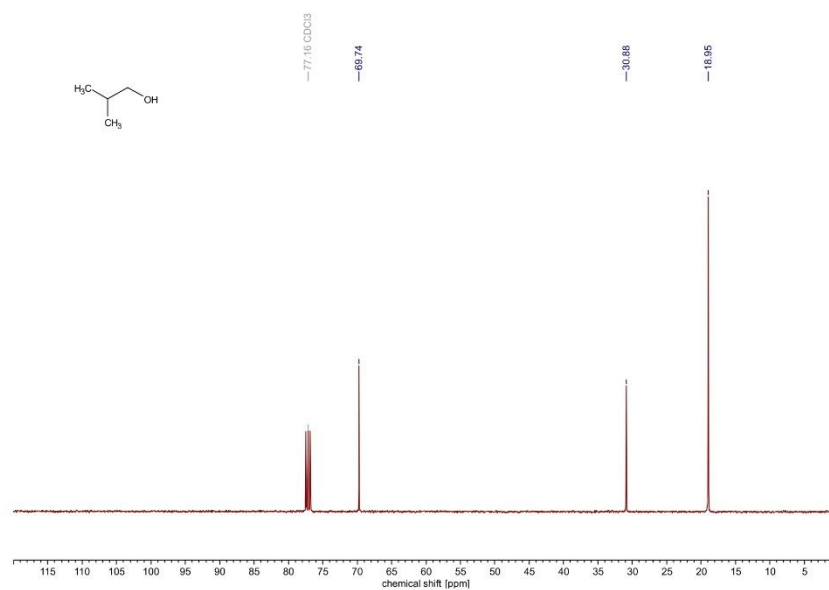


Figure S87: ¹³C NMR spectrum of 2-methyl-1-propanol (101 MHz, CDCl₃, 298 K).

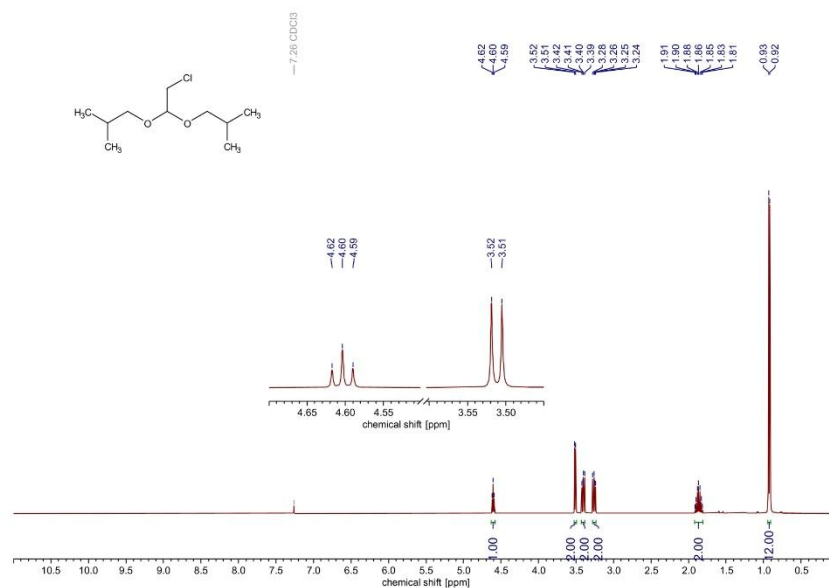


Figure S88: ¹H NMR spectrum of 2-chloro-1,1-di(2-methylpropoxy)-ethane (4c) (400 MHz, CDCl₃, 298 K).

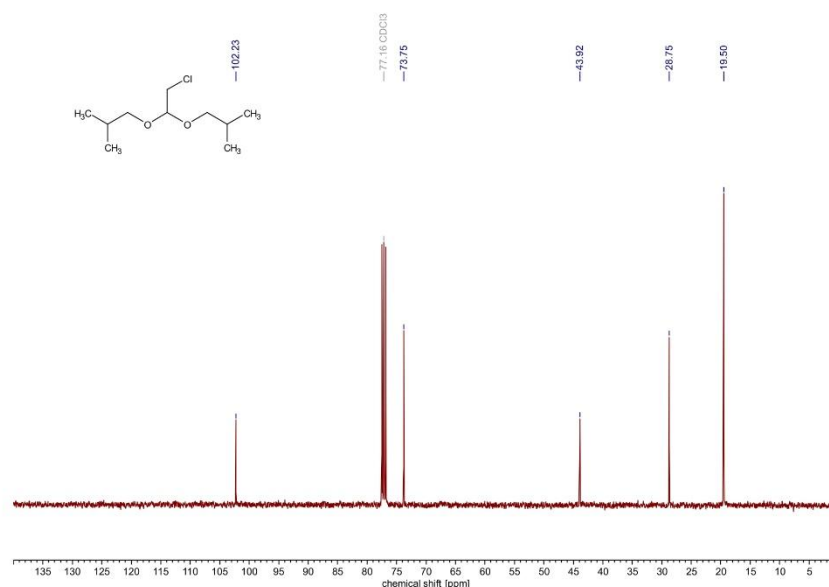


Figure S89: ¹³C NMR spectrum of 2-chloro-1,1-di(2-methylpropoxy)-ethane (4c) (101 MHz, CDCl₃, 298 K).

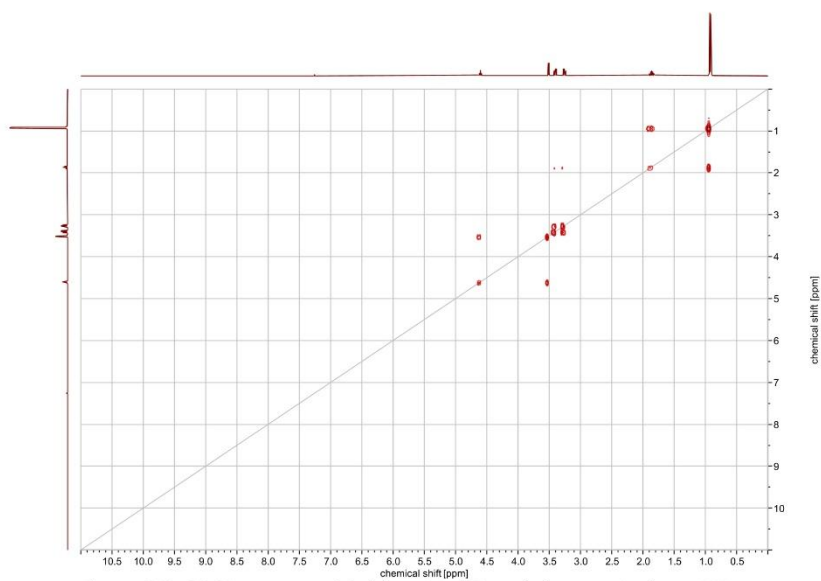


Figure S90: COSY spectrum of 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**).

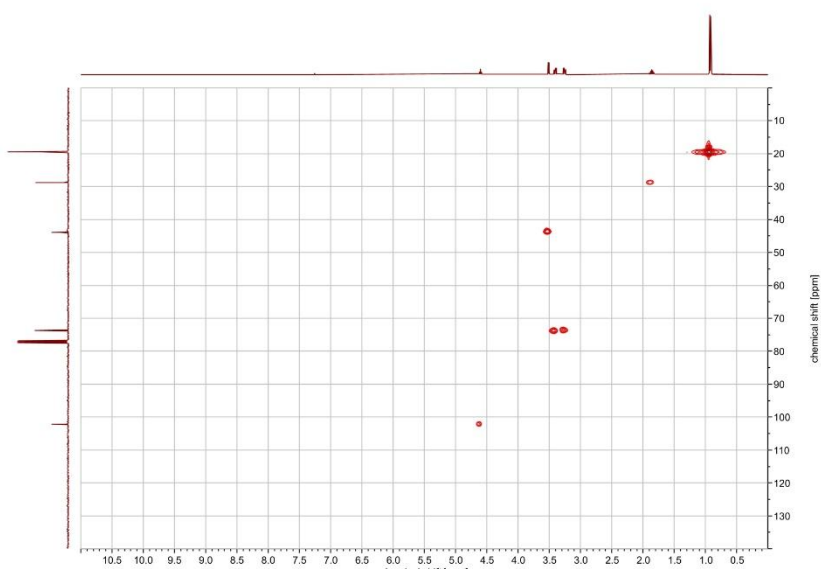


Figure S91: HSQC spectrum of 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**).

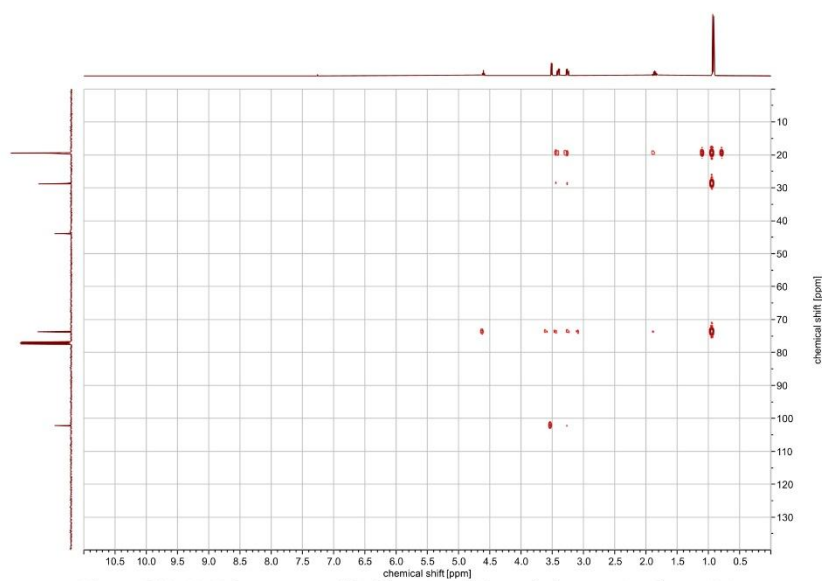


Figure S92: HMBC spectrum of 2-chloro-1,1-di(2-methylpropoxy)-ethane (**4c**).

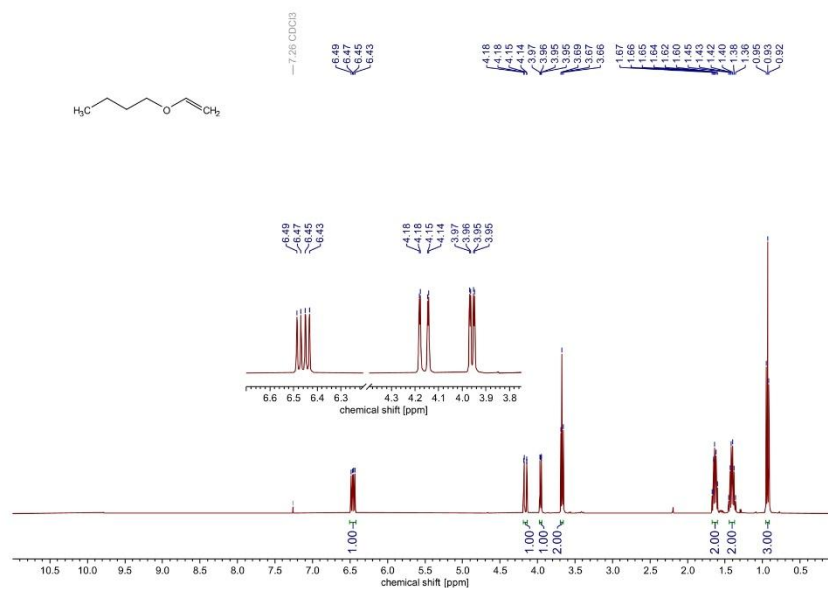


Figure S93: ¹H NMR spectrum of butyl vinyl ether (3d) (400 MHz, CDCl₃, 298 K).

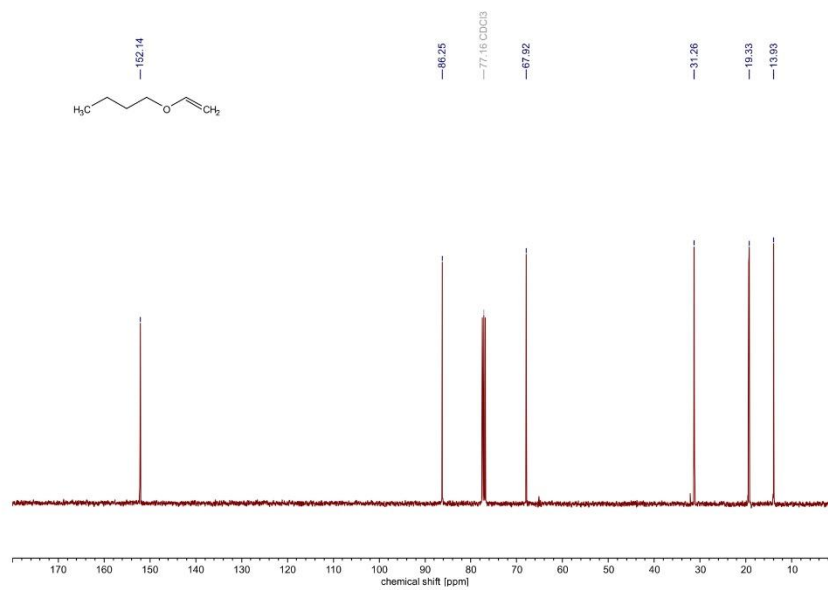
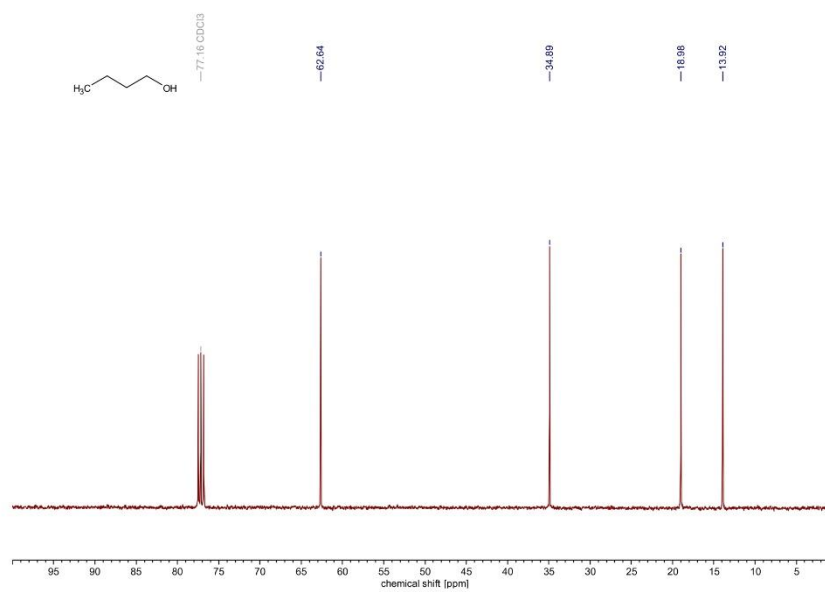
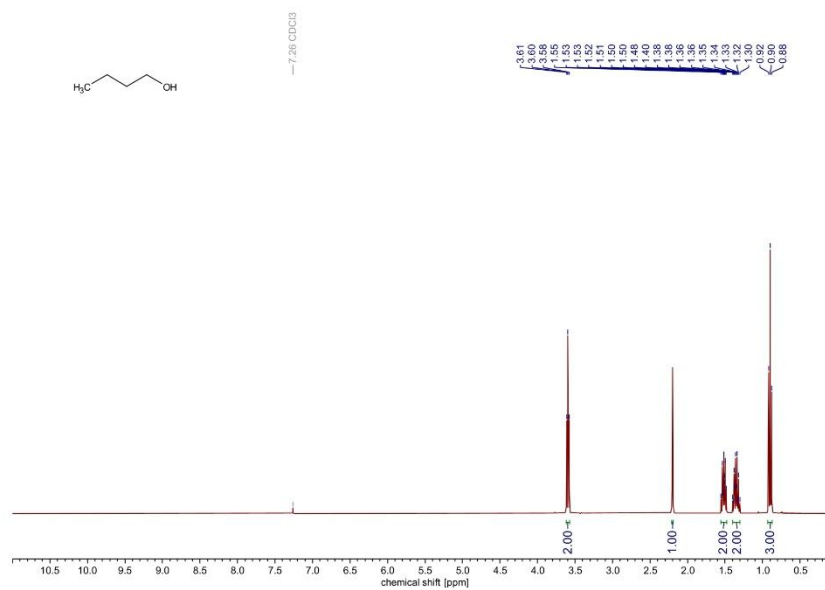


Figure S94: ¹³C NMR spectrum of butyl vinyl ether (3d) (101 MHz, CDCl₃, 298 K).



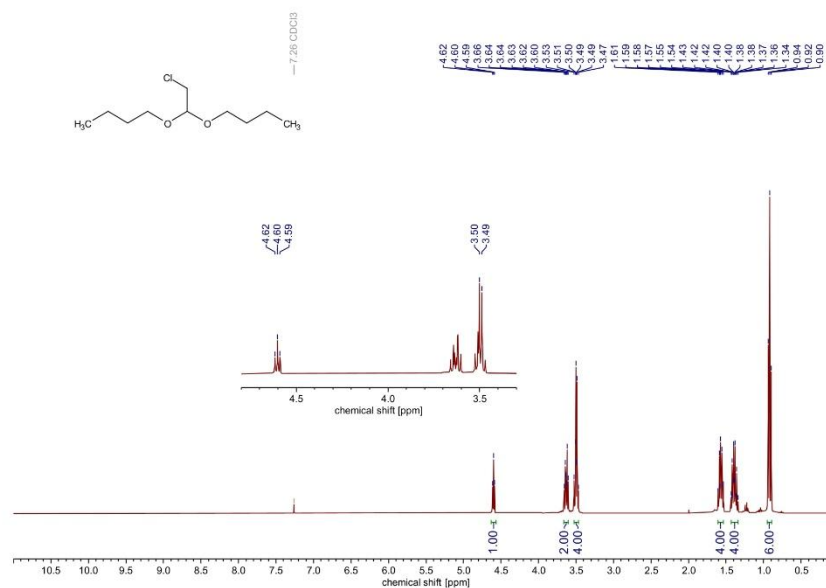


Figure S97: ¹H NMR spectrum of 2-chloro-1,1-di(butoxy)-ethane (4d) (400 MHz, CDCl₃, 298 K).

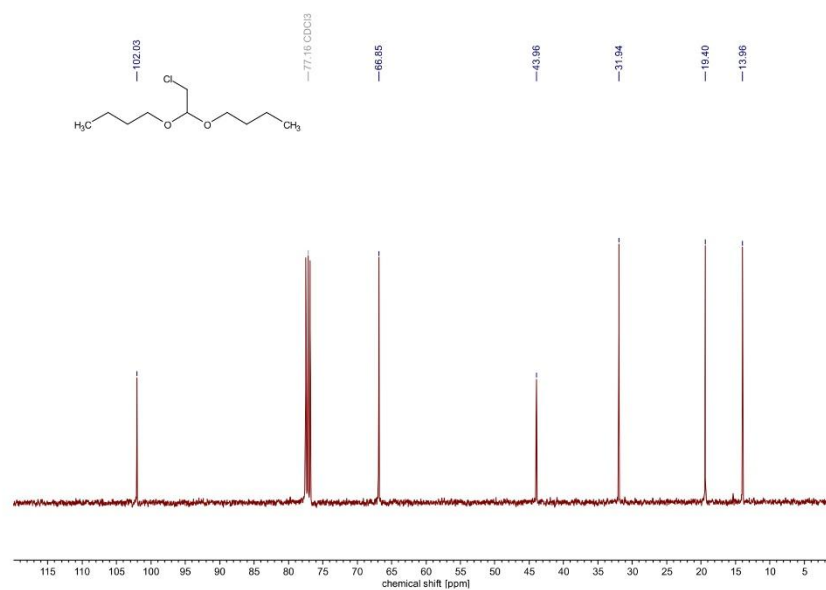


Figure S98: ¹³C NMR spectrum of 2-chloro-1,1-di(butoxy)-ethane (4d) (101 MHz, CDCl₃, 298 K).

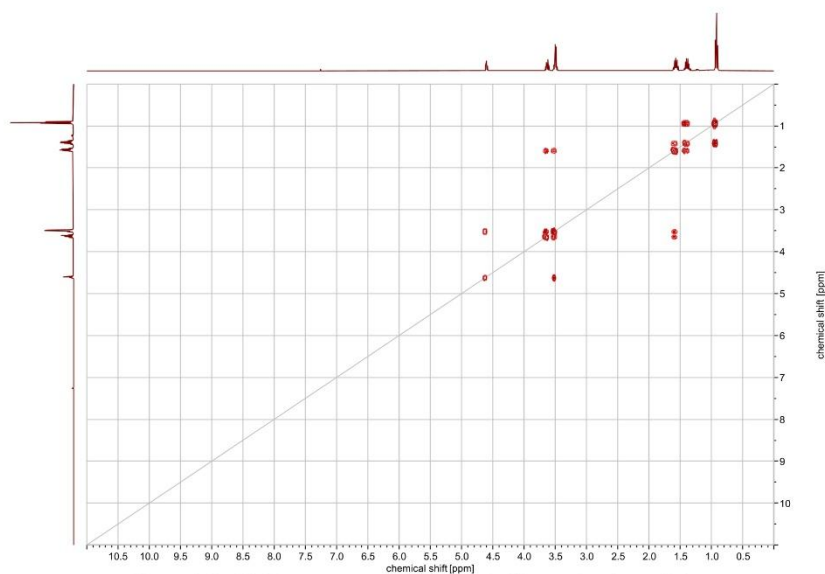


Figure S99: COSY spectrum of 2-chloro-1,1-di(butoxy)-ethane (**4d**).

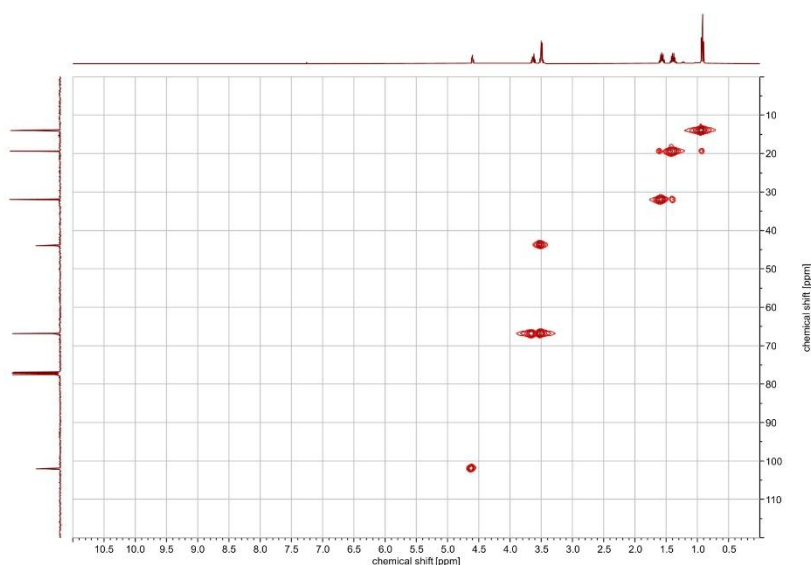


Figure S100: HSQC spectrum of 2-chloro-1,1-di(butoxy)-ethane (**4d**).

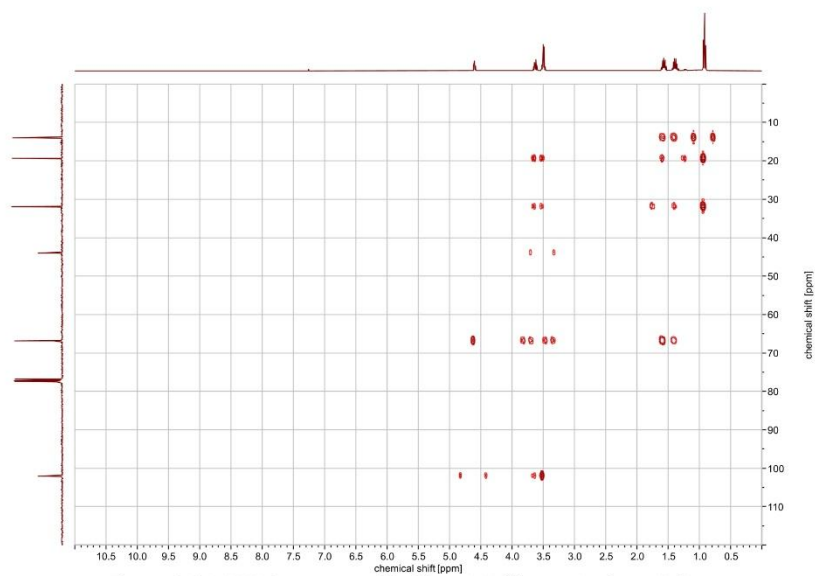


Figure S101: HMBC spectrum of 2-chloro-1,1-di(butoxy)-ethane (**4d**).

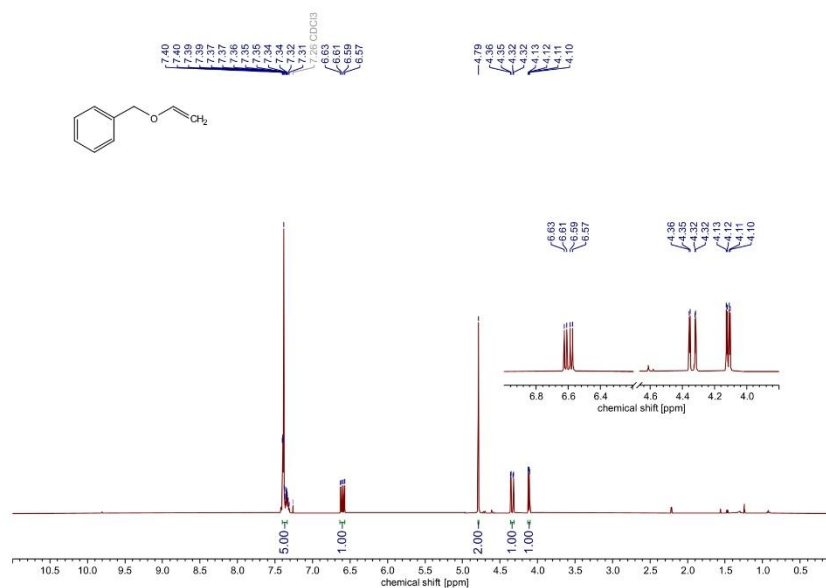


Figure S102: ¹H NMR spectrum of ((vinylloxy)methyl)benzene (3e) (400 MHz, CDCl₃, 298 K).

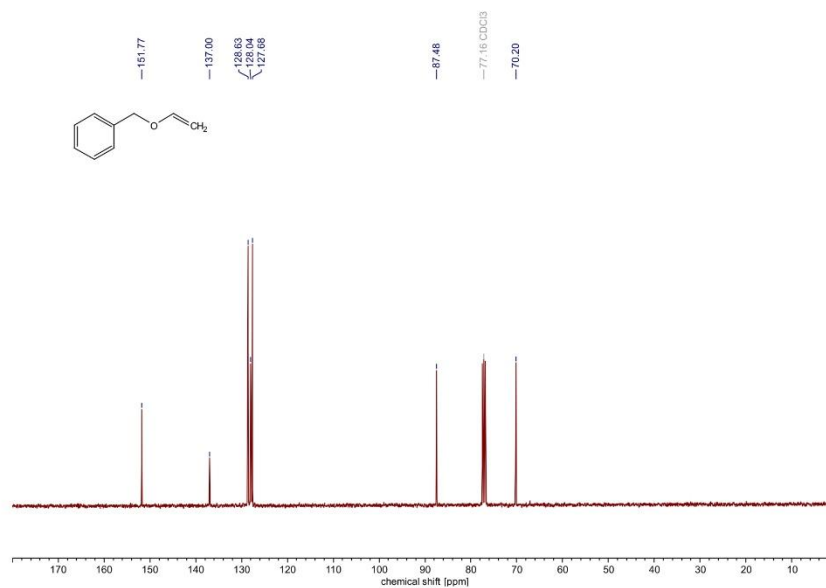


Figure S103: ¹³C NMR spectrum of ((vinylloxy)methyl)benzene (3e) (101 MHz, CDCl₃, 298 K).

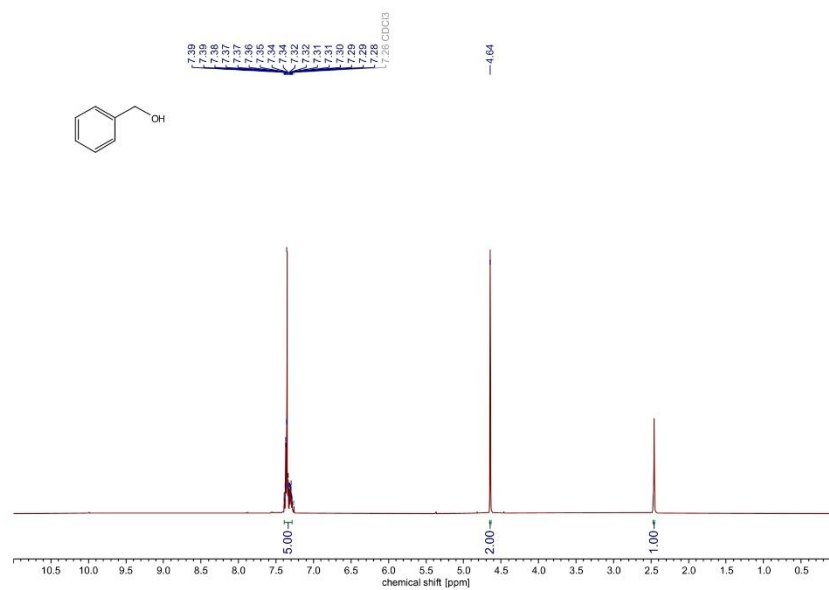


Figure S104: ^1H NMR spectrum of benzyl alcohol (400 MHz, CDCl_3 , 298 K).

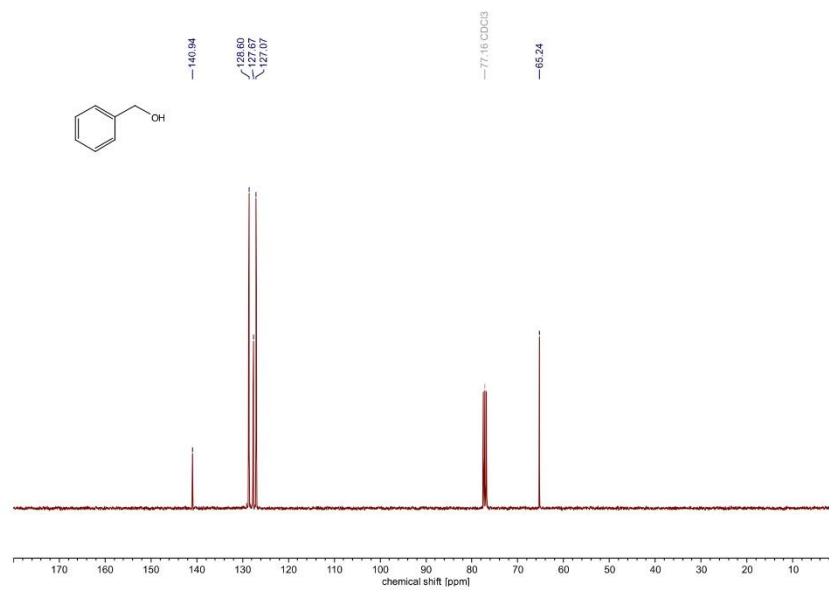


Figure S105: ^{13}C NMR spectrum of benzyl alcohol (101 MHz, CDCl_3 , 298 K).

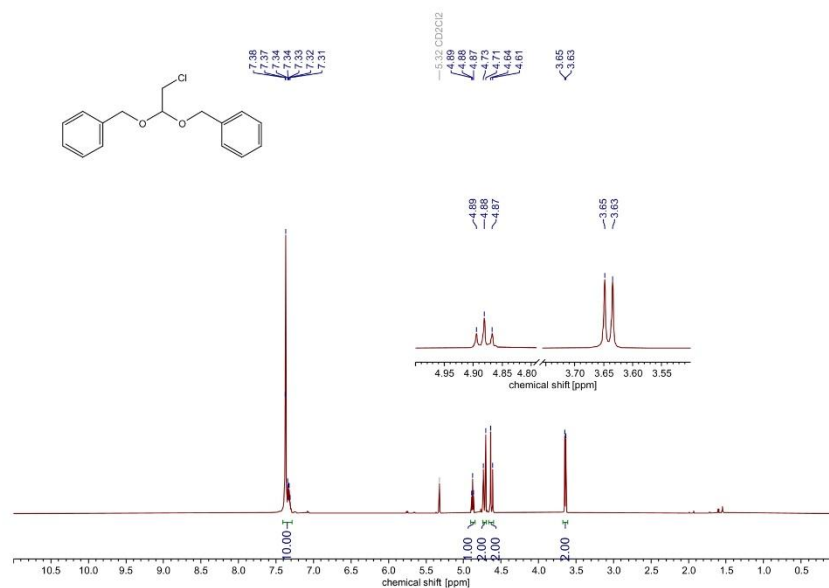


Figure S106: ¹H NMR spectrum of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**) (400 MHz, CD₂Cl₂, 298 K).

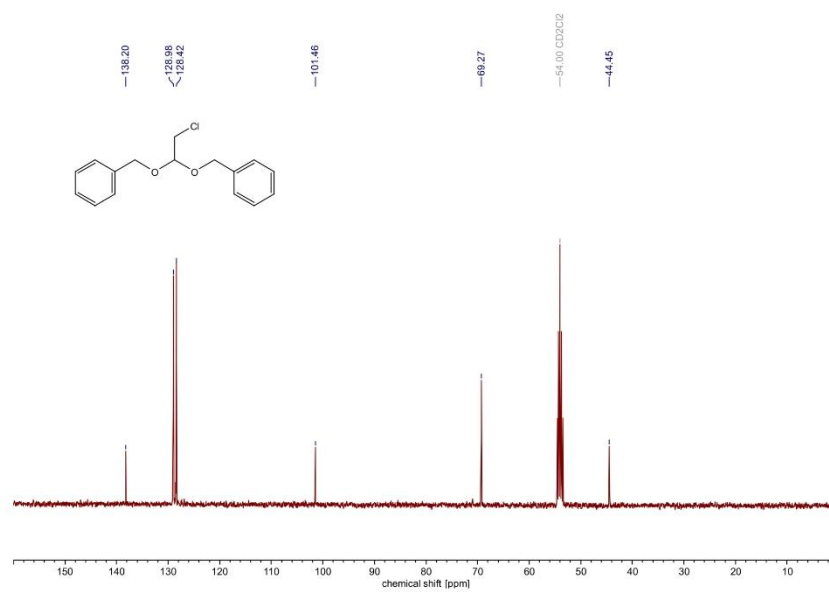


Figure S107: ¹³C NMR spectrum of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**) (101 MHz, CD₂Cl₂, 298 K).

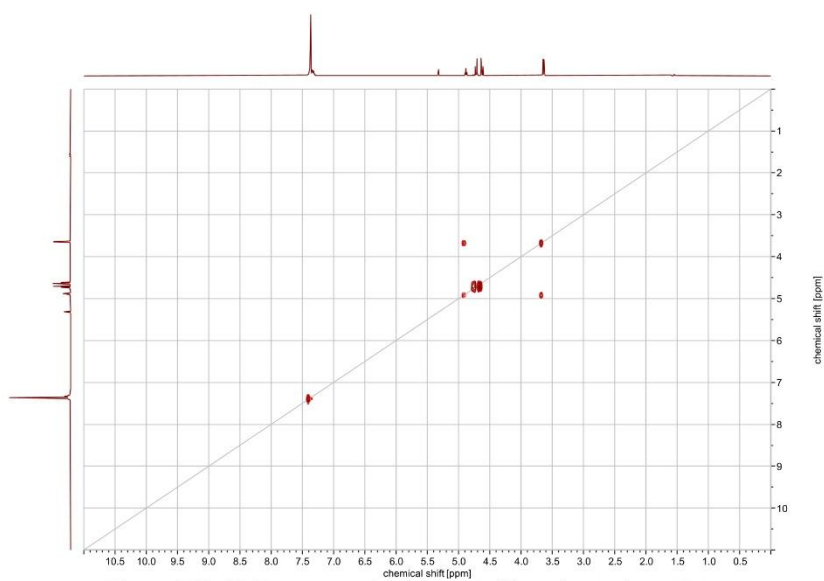


Figure S108: COSY spectrum of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**).

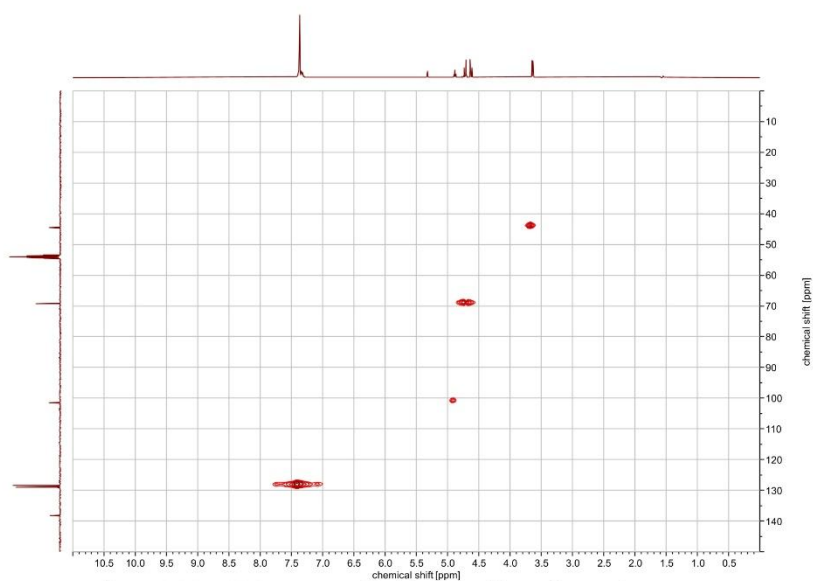


Figure S109: HSQC spectrum of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**).

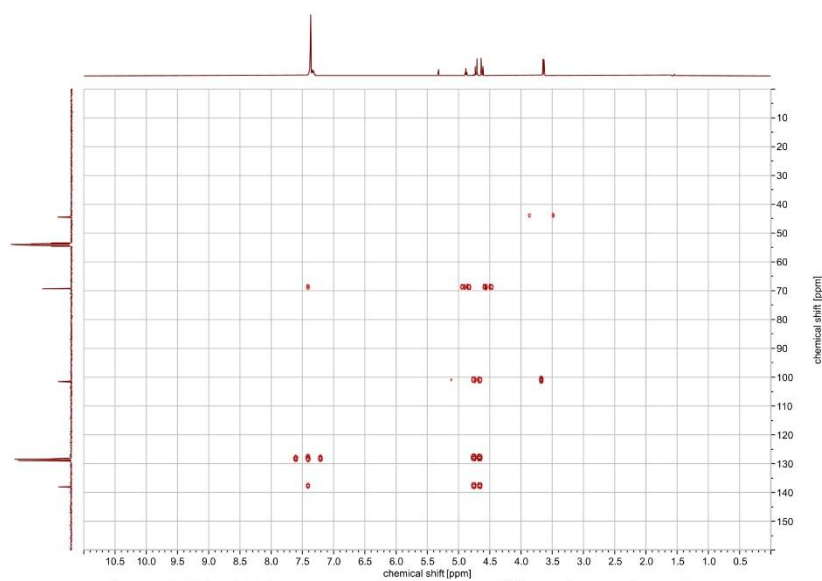


Figure S110: HMBC spectrum of 2-chloro-1,1-di(benzyloxy)-ethane (**4e**).

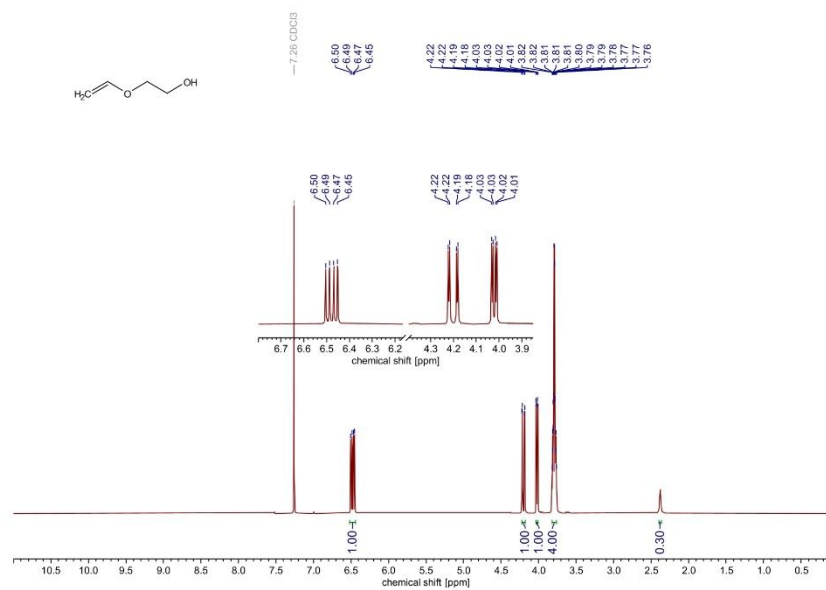


Figure S111: ¹H NMR spectrum of 2-hydroxyethyl vinyl ether (**5**) (400 MHz, CDCl₃, 298 K).

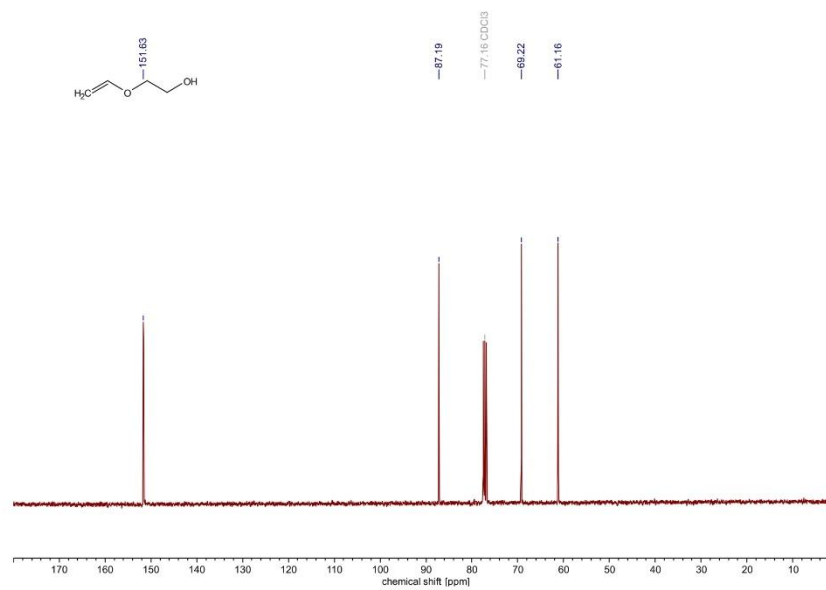


Figure S112: ¹³C NMR spectrum of 2-hydroxyethyl vinyl ether (**5**) (101 MHz, CDCl₃, 298 K).

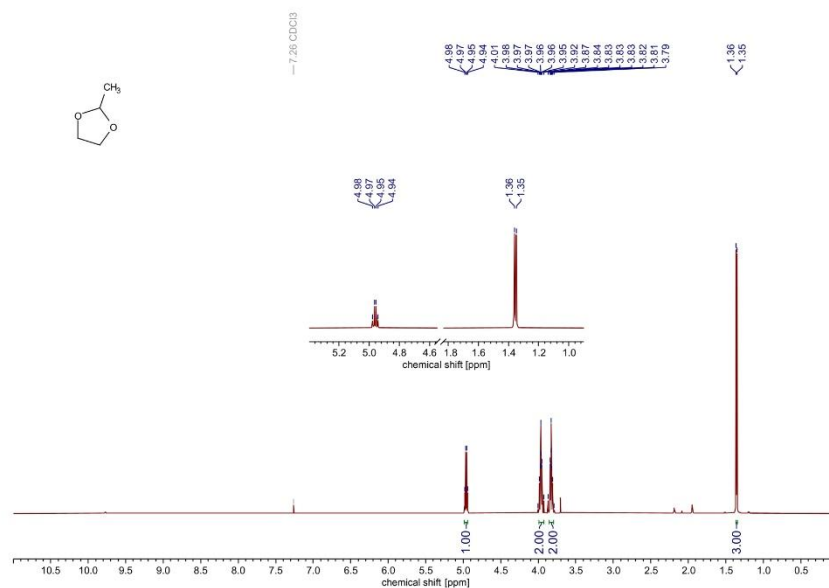


Figure S113: ¹H NMR spectrum of 2-methyl-1,3-dioxolane (5.1) (400 MHz, CDCl₃, 298 K).

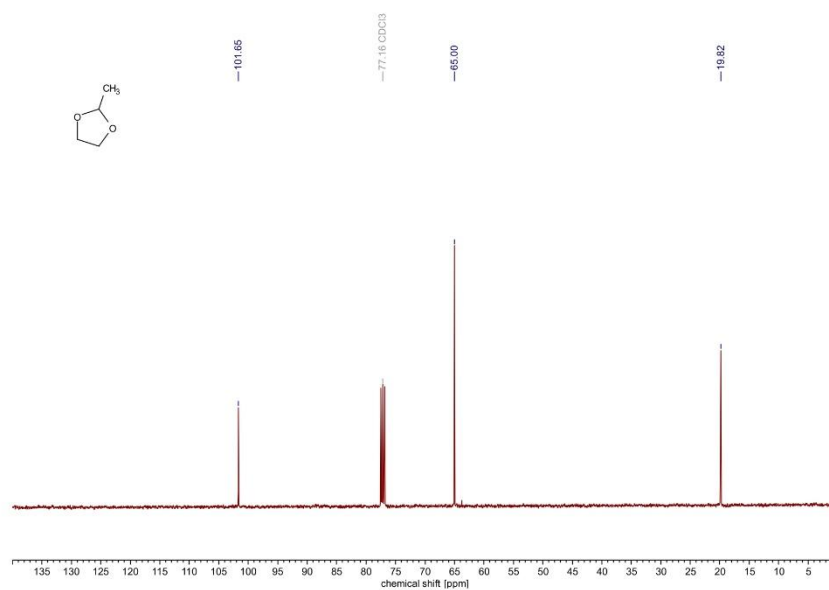


Figure S114: ¹³C NMR spectrum of 2-methyl-1,3-dioxolane (5.1) (101 MHz, CDCl₃, 298 K).

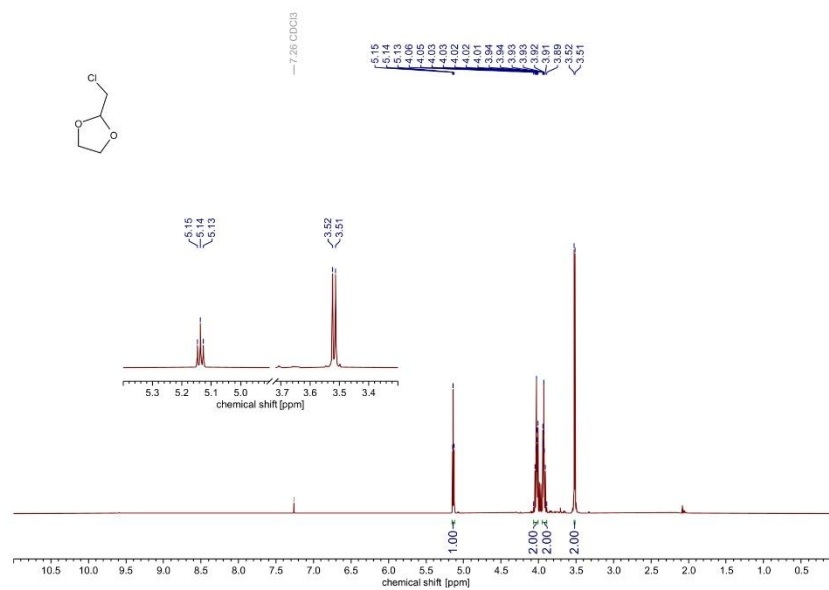


Figure S115: ^1H NMR spectrum of 2-chloromethyl-1,3-dioxolane (6) (400 MHz, CDCl_3 , 298 K).

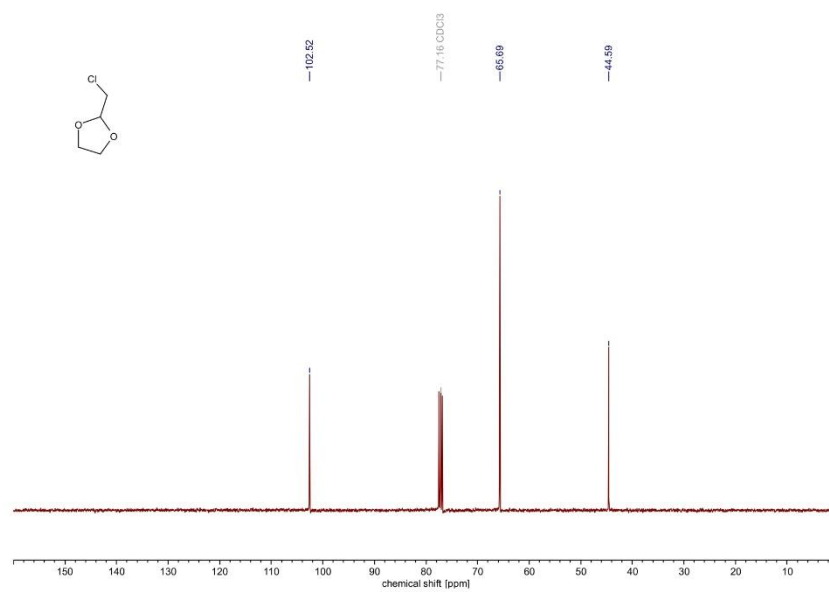


Figure S116: ^{13}C NMR spectrum of 2-chloromethyl-1,3-dioxolane (6) (101 MHz, CDCl_3 , 298 K).

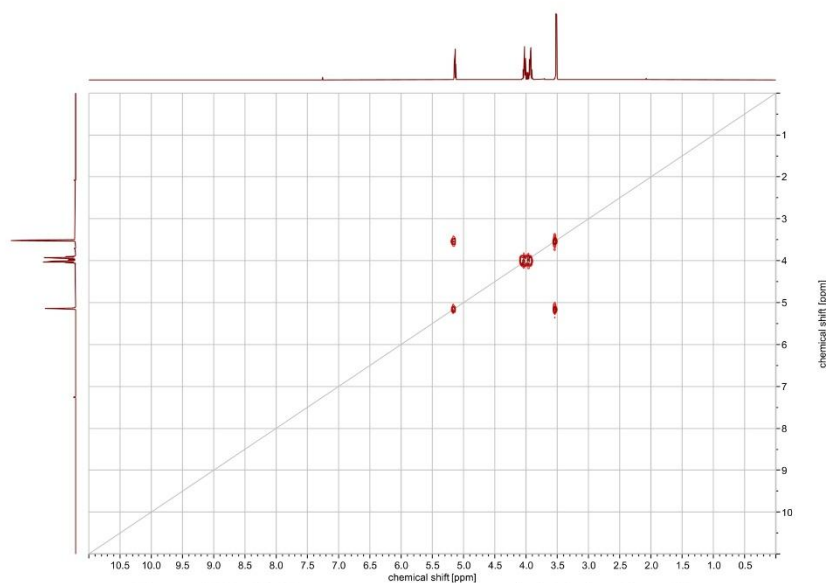


Figure S117: COSY spectrum of 2-chloromethyl-1,3-dioxolane (**6**).

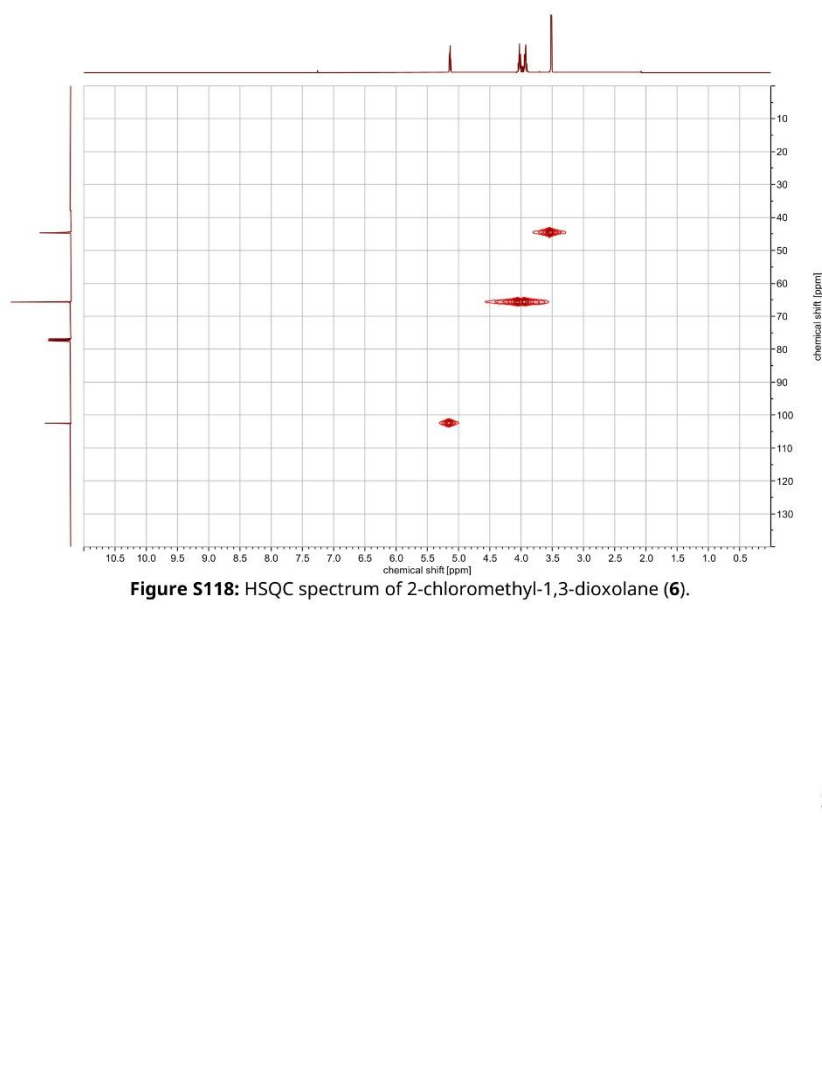


Figure S118: HSQC spectrum of 2-chloromethyl-1,3-dioxolane (**6**).

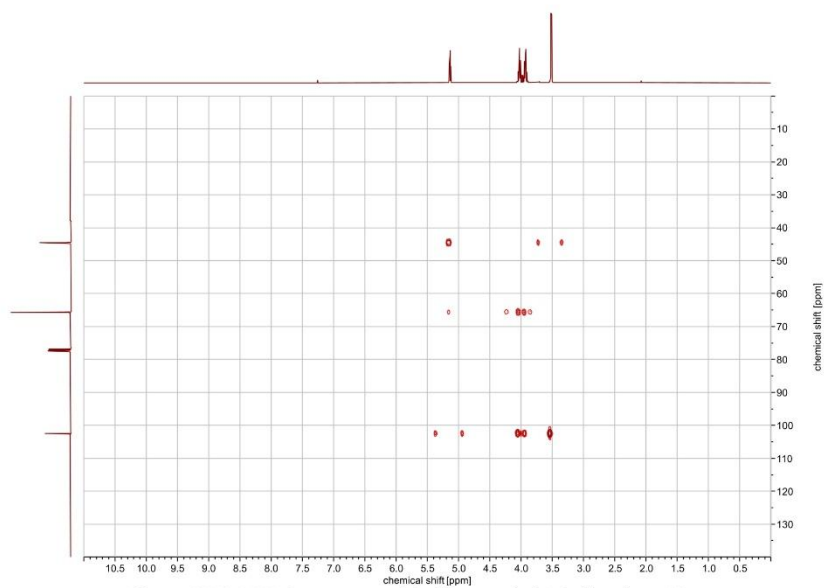


Figure S119: HMBC spectrum of 2-chloromethyl-1,3-dioxolane (**6**).

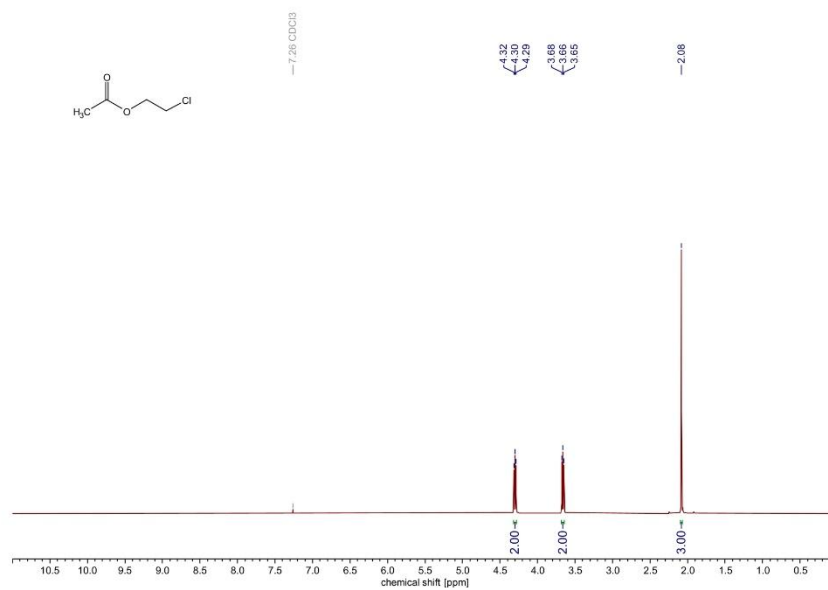


Figure S120: ^1H NMR spectrum of 2-chloroethyl acetate (**7**) (400 MHz, CDCl_3 , 298 K).

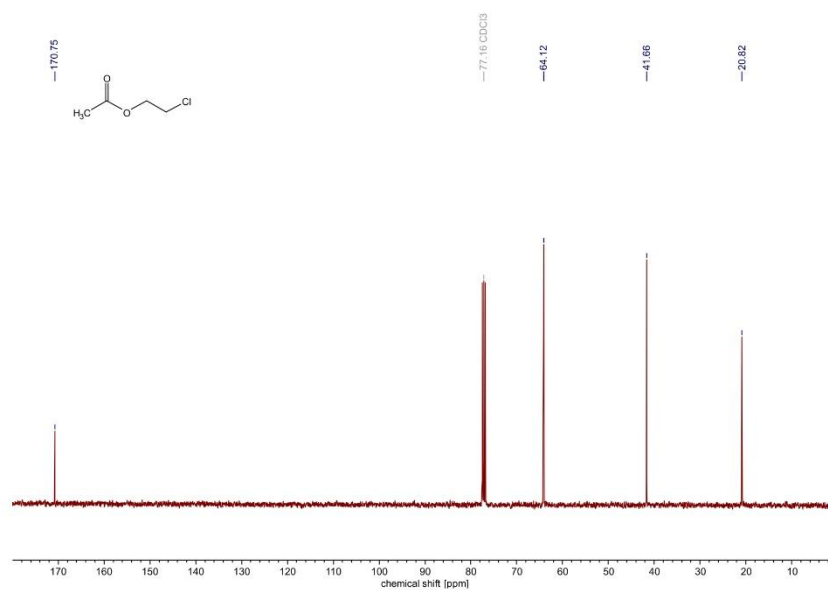


Figure S121: ^{13}C NMR spectrum of 2-chloroethyl acetate (**7**) (101 MHz, CDCl_3 , 298 K).

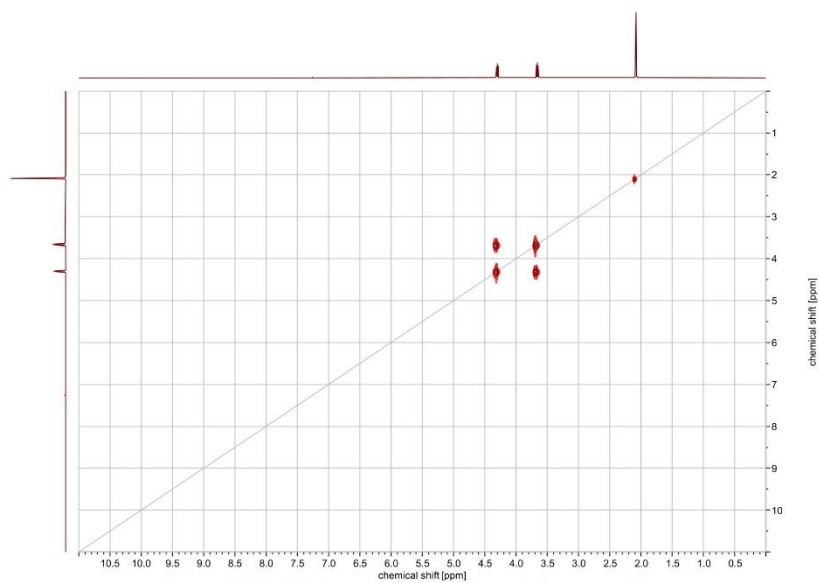


Figure S122: COSY spectrum of 2-chloroethyl acetate (7).

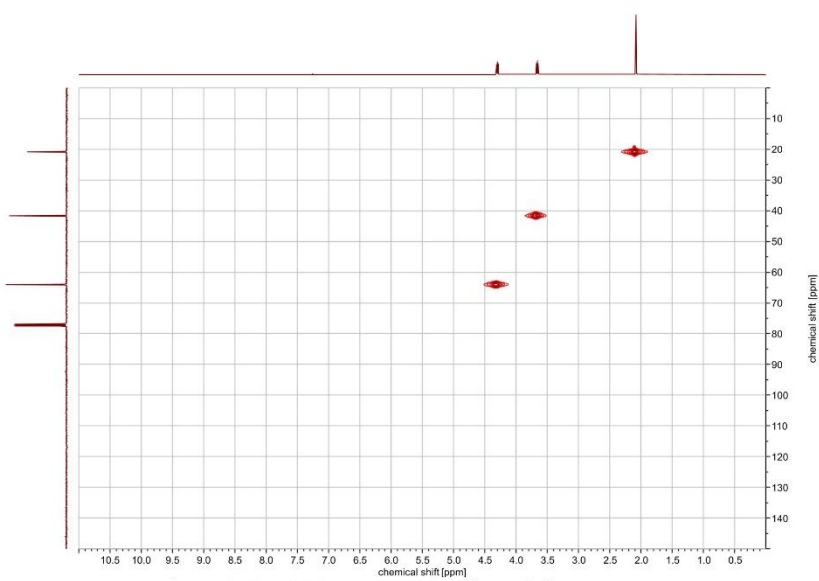


Figure S123: HSQC spectrum of 2-chloroethyl acetate (7).

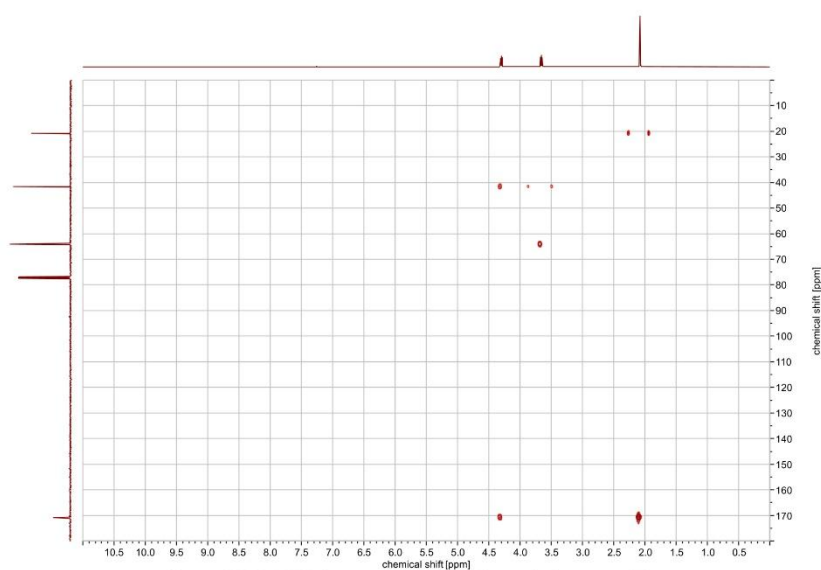


Figure S124: HMBC spectrum of 2-chloroethyl acetate (7).

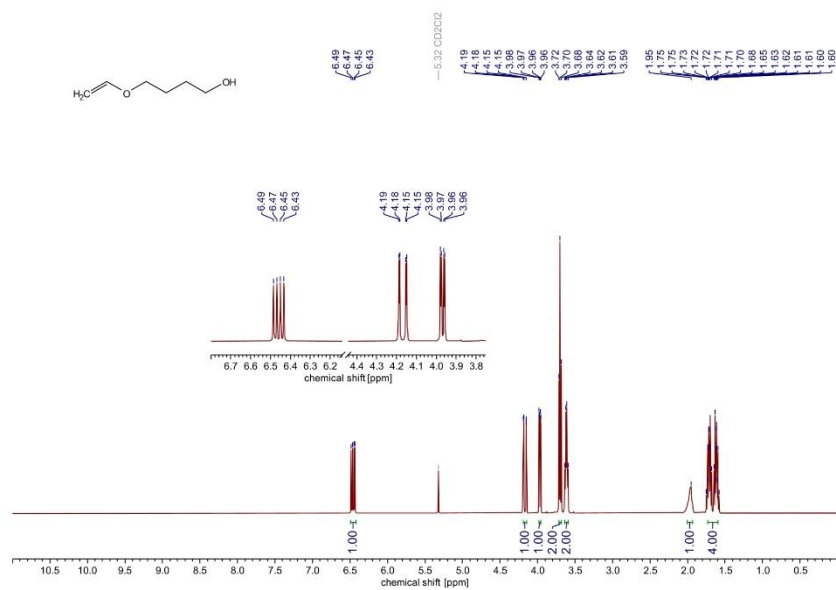


Figure S125: ¹H NMR spectrum of 4-hydroxybutyl vinyl ether (**5b**) (400 MHz, CD₂Cl₂, 298 K).

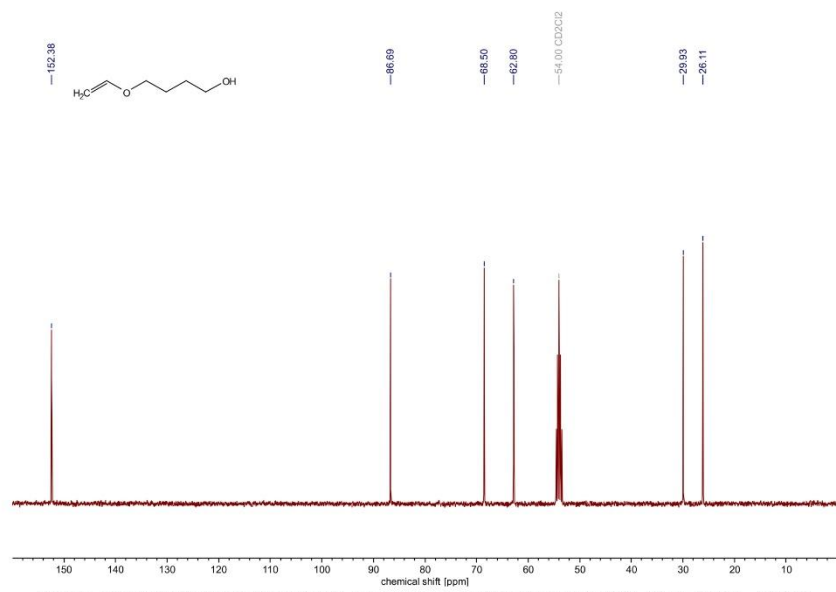


Figure S126: ¹³C NMR spectrum of 4-hydroxybutyl vinyl ether (**5b**) (101 MHz, CD₂Cl₂, 298 K).

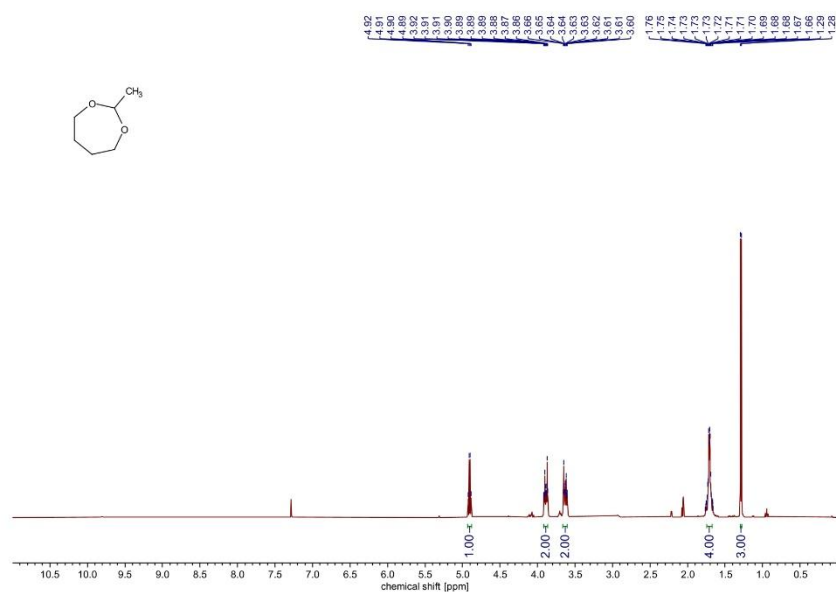


Figure S127: ¹H NMR spectrum of 2-methyl-1,3-dioxepane (5b.1) (400 MHz, CDCl₃, 298 K).

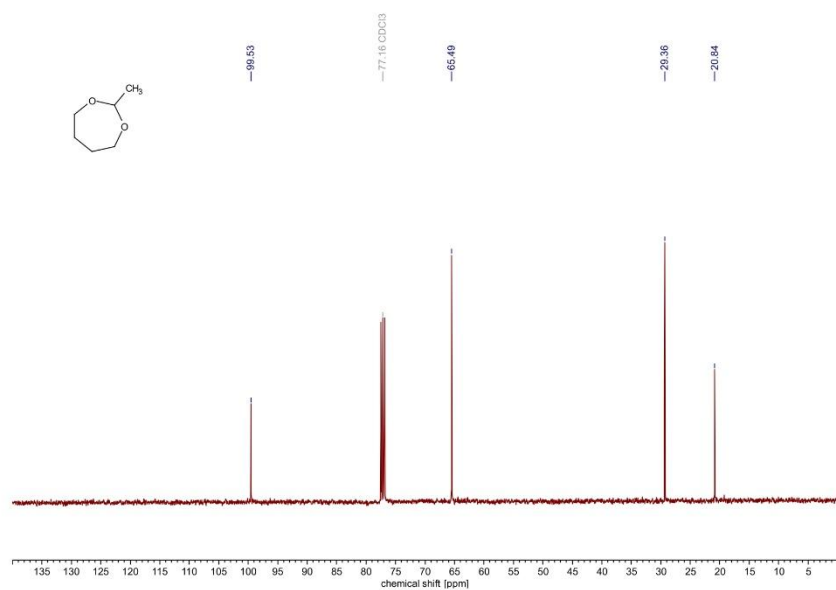


Figure S128: ¹³C NMR spectrum of 2-methyl-1,3-dioxepane (5b.1) (101 MHz, CDCl₃, 298 K).

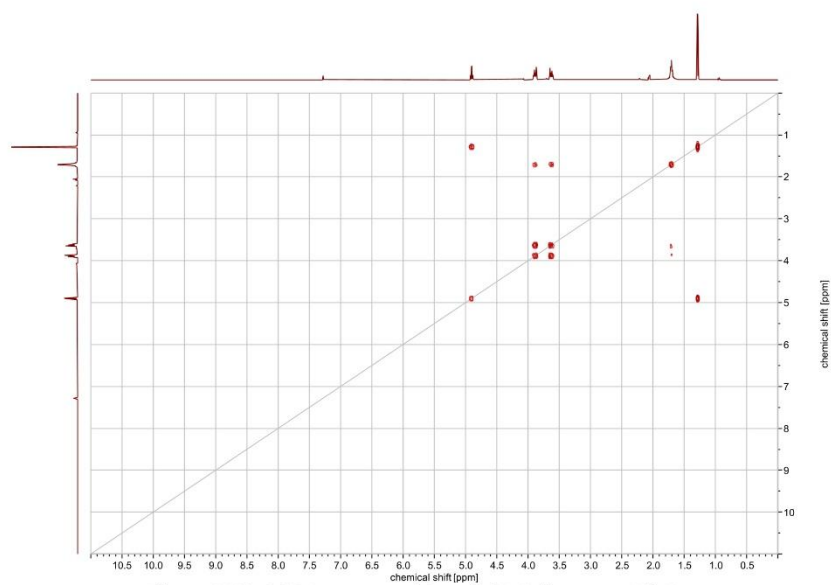


Figure S129: COSY spectrum of 2-methyl-1,3-dioxepane (5b.1).

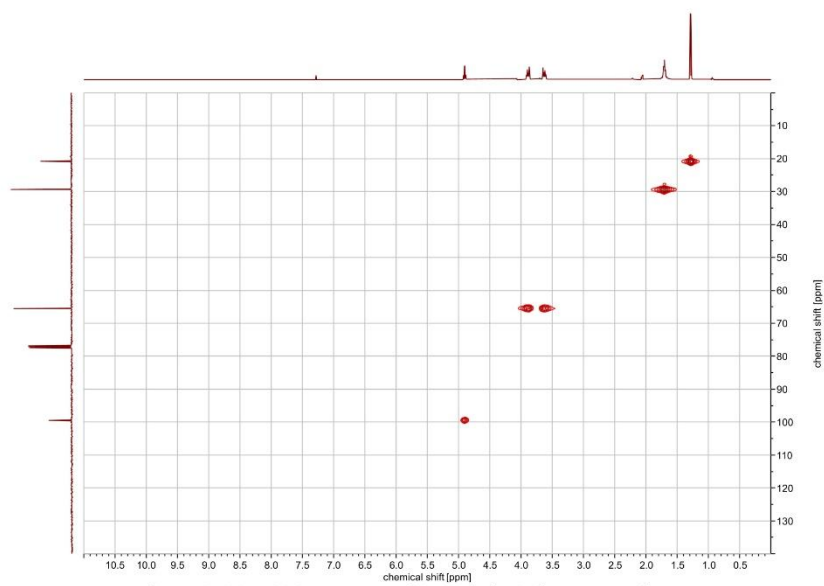


Figure S130: HSQC spectrum of 2-methyl-1,3-dioxepane (5b.1).

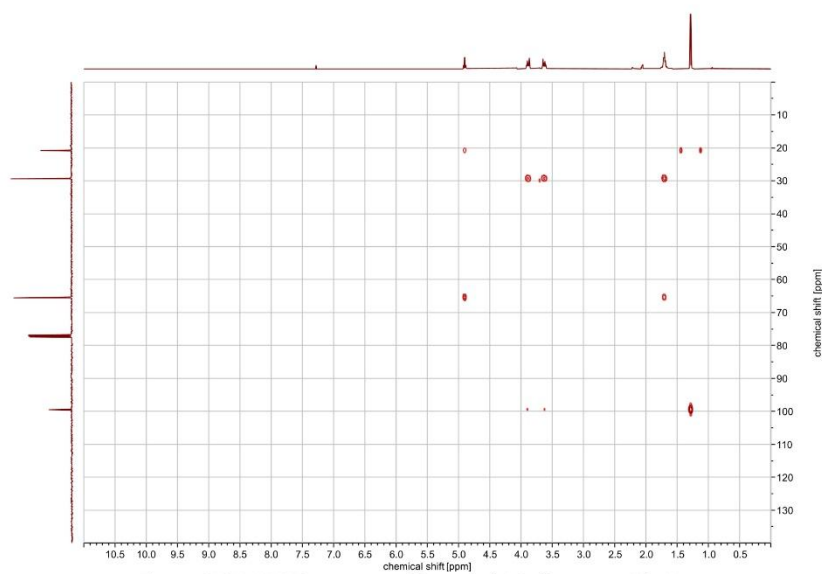


Figure S131: HMBC spectrum of 2-methyl-1,3-dioxepane (5b.1).

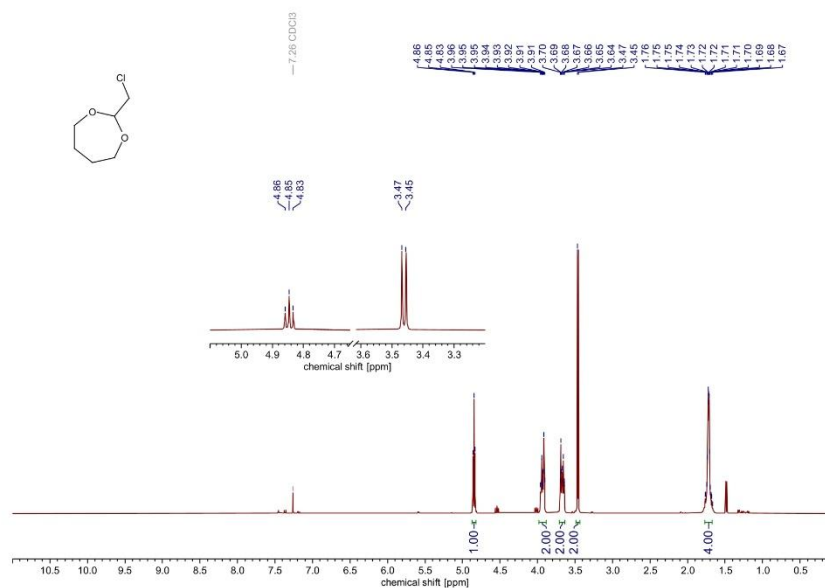


Figure S132: ^1H NMR spectrum of 2-chloromethyl-1,3-dioxepane (**6b**) (400 MHz, CDCl_3 , 298 K).

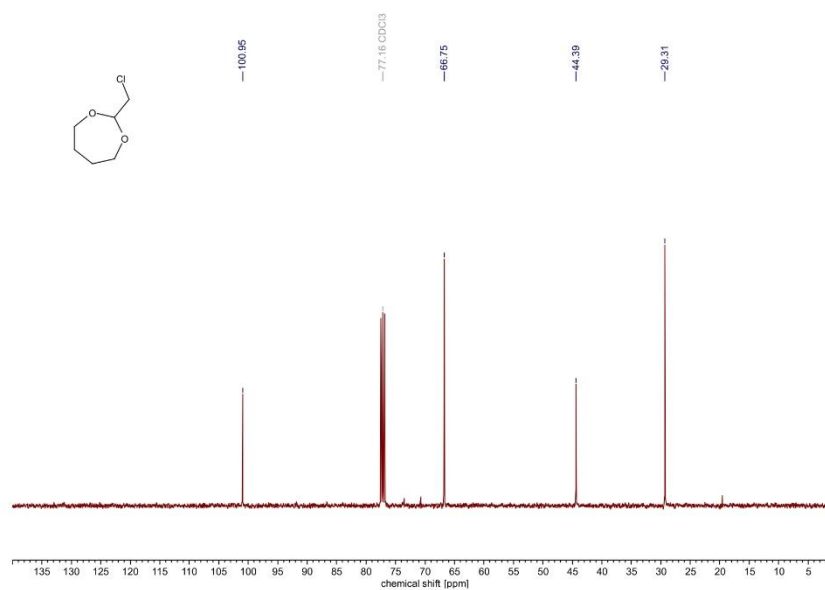


Figure S133: ^{13}C NMR spectrum of 2-chloromethyl-1,3-dioxepane (**6b**) (101 MHz, CDCl_3 , 298 K).

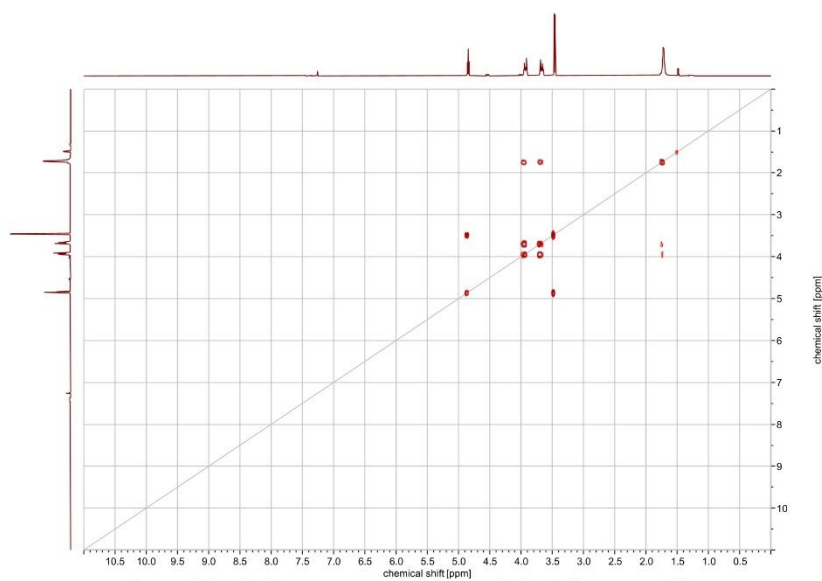


Figure S134: COSY spectrum of 2-chloromethyl-1,3-dioxepane (**6b**).

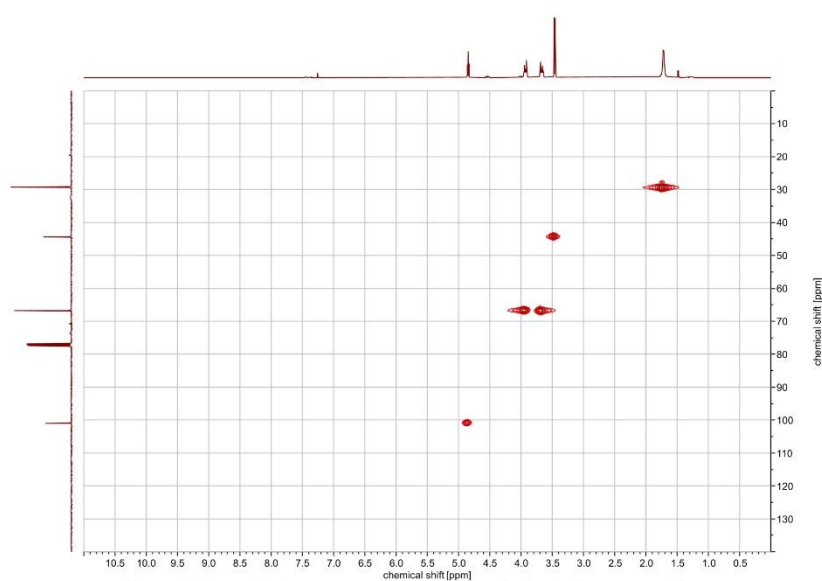


Figure S135: HSQC spectrum of 2-chloromethyl-1,3-dioxepane (**6b**).

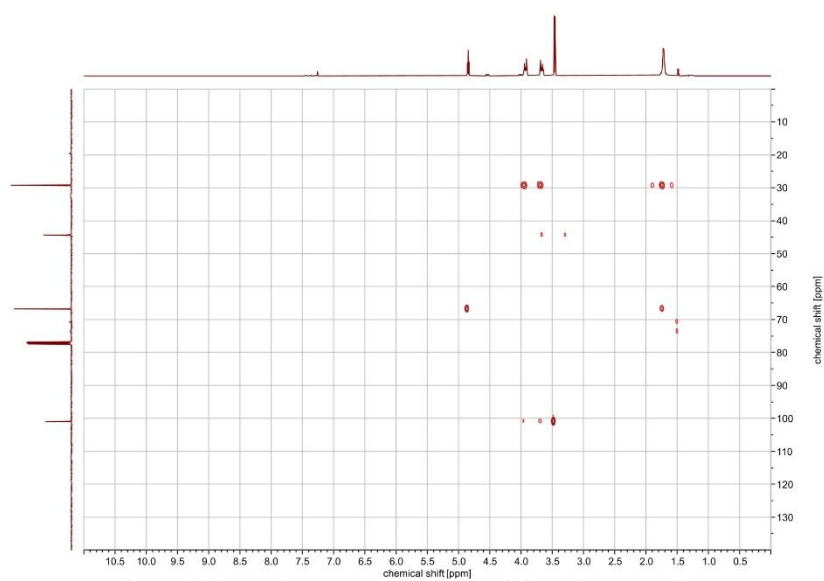


Figure S136: HMBC spectrum of 2-chloromethyl-1,3-dioxepane (**6b**).

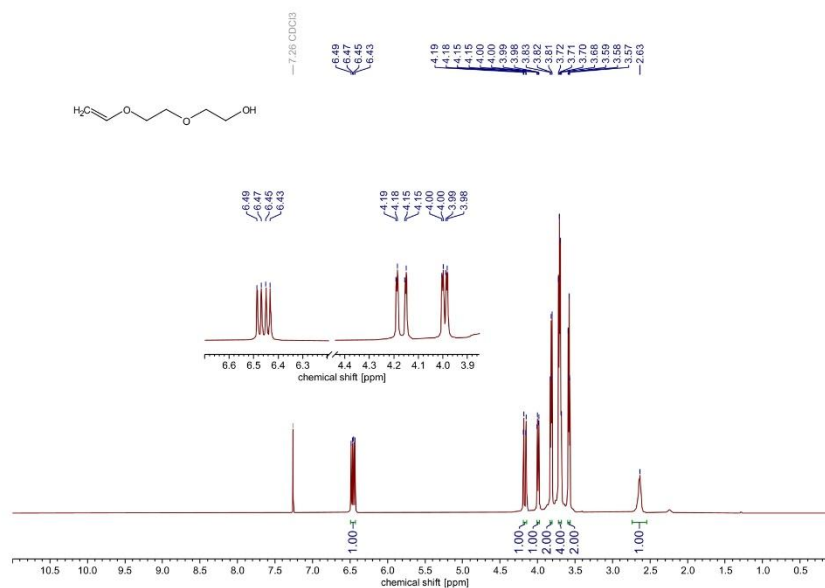


Figure S137: ¹H NMR spectrum of di(ethylene glycol) vinyl ether (**5c**) (400 MHz, CDCl₃, 298 K).

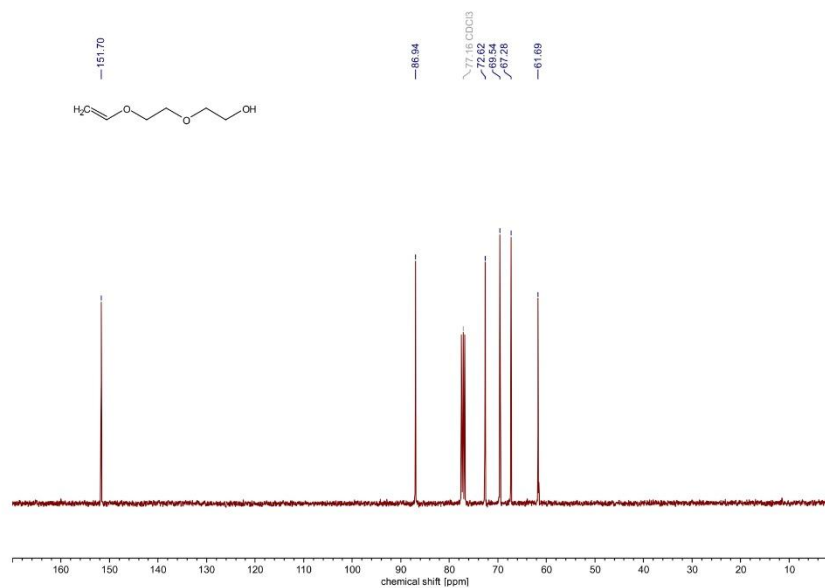


Figure S138: ¹³C NMR spectrum of di(ethylene glycol) vinyl ether (**5c**) (101 MHz, CDCl₃, 298 K).

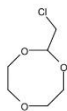


Figure S139: ^1H NMR spectrum of 2-chloromethyl-1,3,6-trioxocane (**6c**) (400 MHz, CDCl_3 , 298 K).

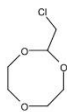


Figure S140: ^{13}C NMR spectrum of 2-chloromethyl-1,3,6-trioxocane (**6c**) (101 MHz, CDCl_3 , 298 K).

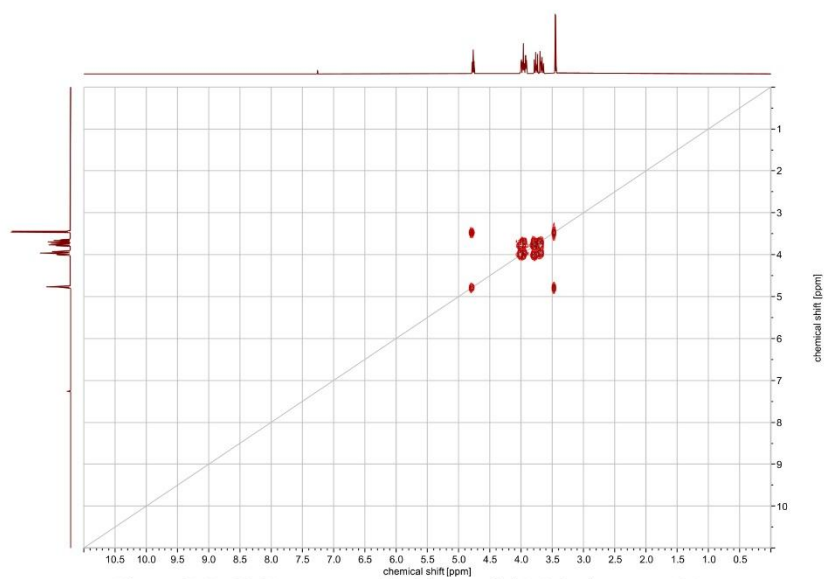


Figure S141: COSY spectrum of 2-chloromethyl-1,3,6-trioxocane (**6c**).

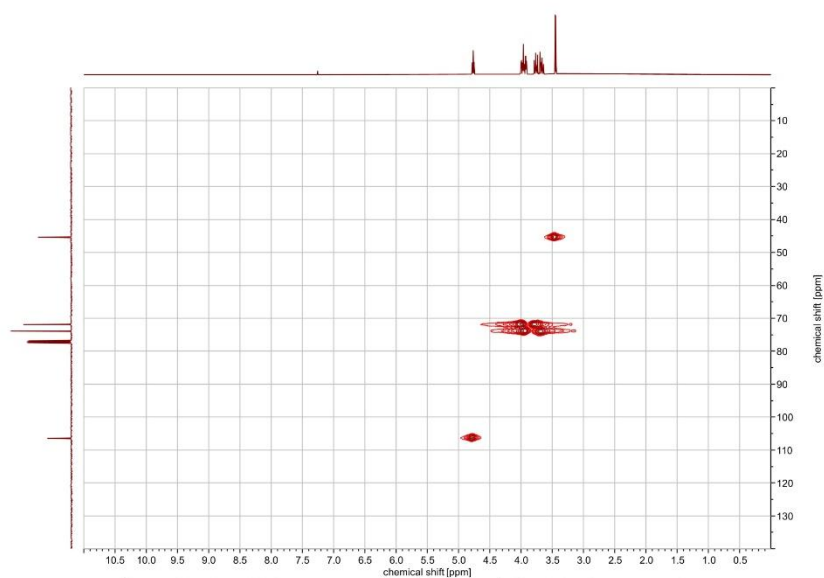


Figure S142: HSQC spectrum of 2-chloromethyl-1,3,6-trioxocane (**6c**).

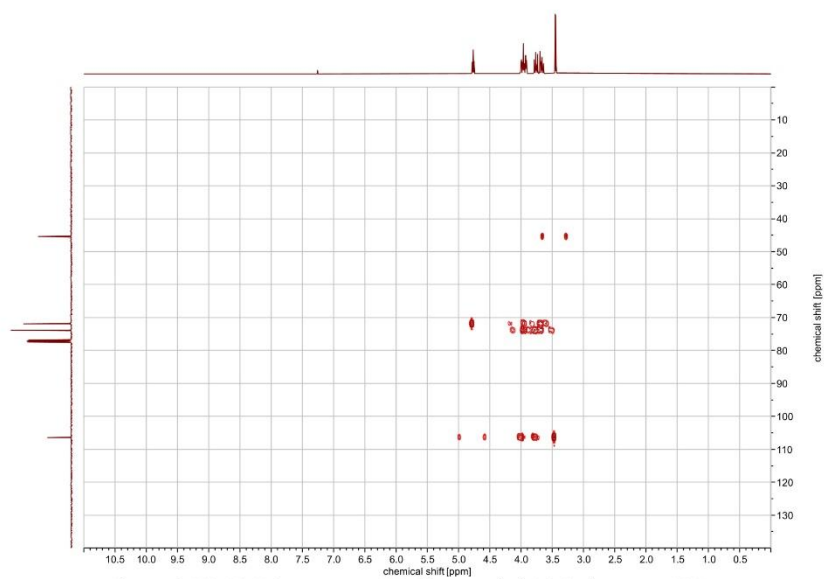


Figure S143: HMBC spectrum of 2-chloromethyl-1,3,6-trioxocane (**6c**).

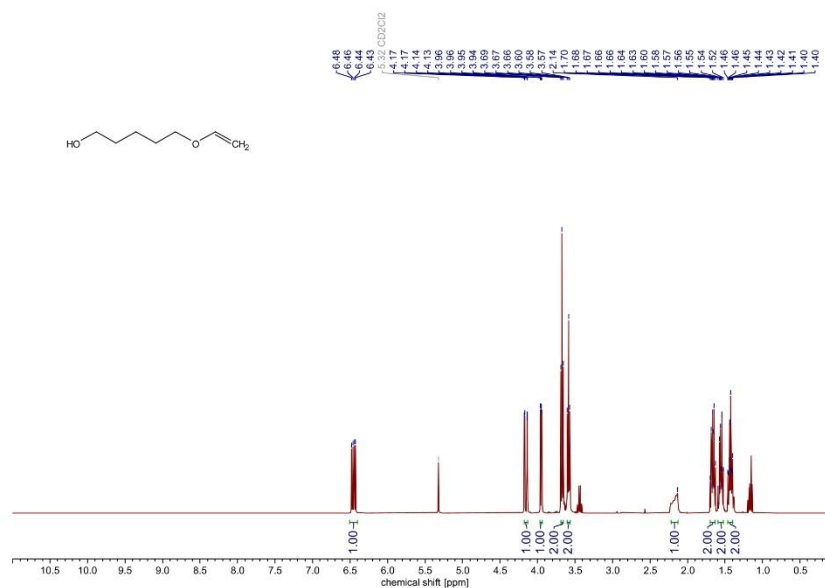


Figure S144: ¹H NMR spectrum of 5-hydroxypentyl vinyl ether (**5d**) (400 MHz, CDCl₃, 298 K).

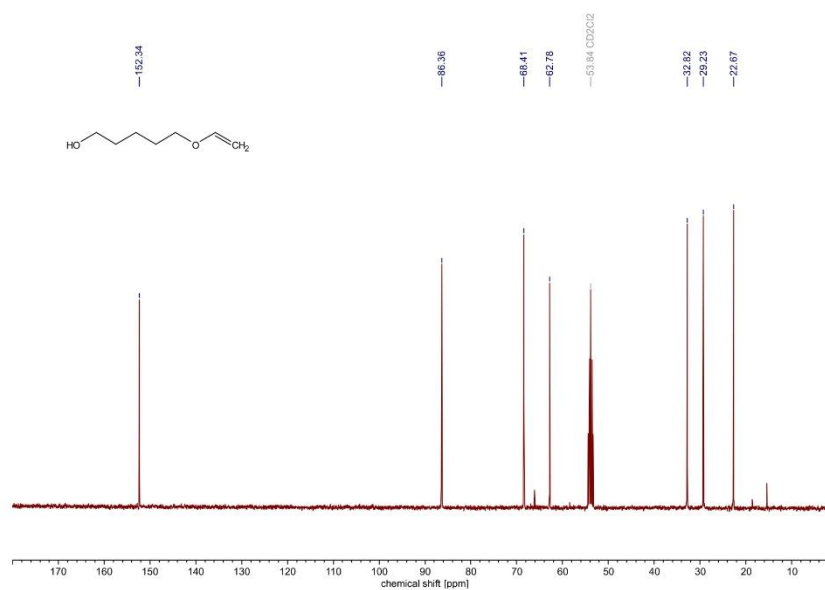


Figure S145: ¹³C NMR spectrum of 5-hydroxypentyl vinyl ether (**5d**) (101 MHz, CDCl₃, 298 K).

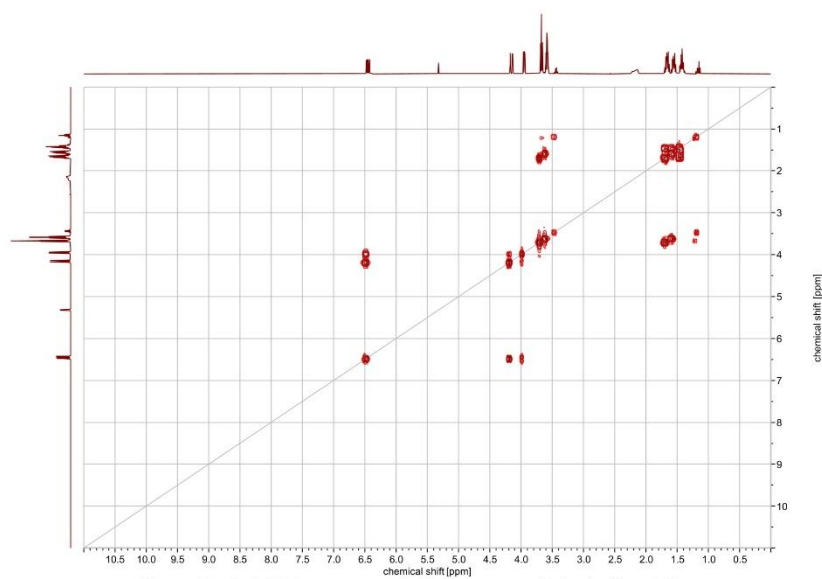


Figure S146: COSY spectrum of 5-hydroxypentyl vinyl ether (**5d**).

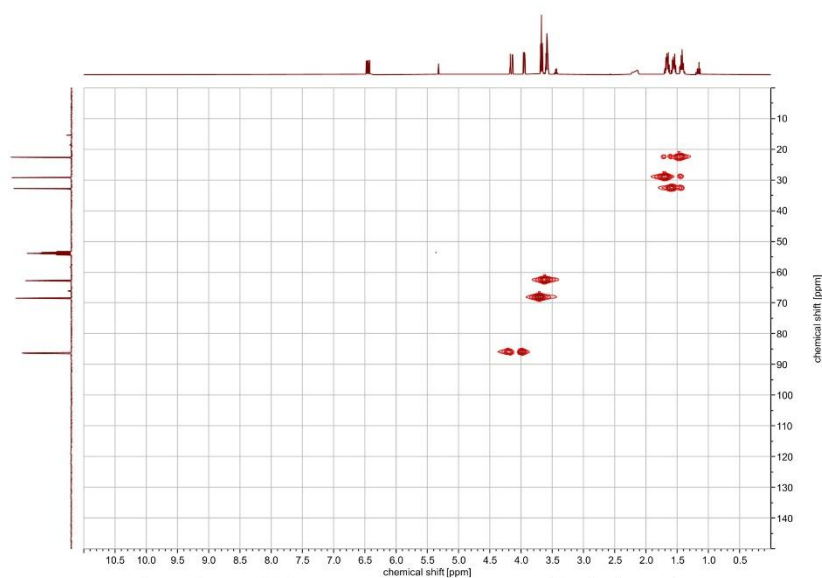


Figure S147: HSQC spectrum of 5-hydroxypentyl vinyl ether (**5d**).

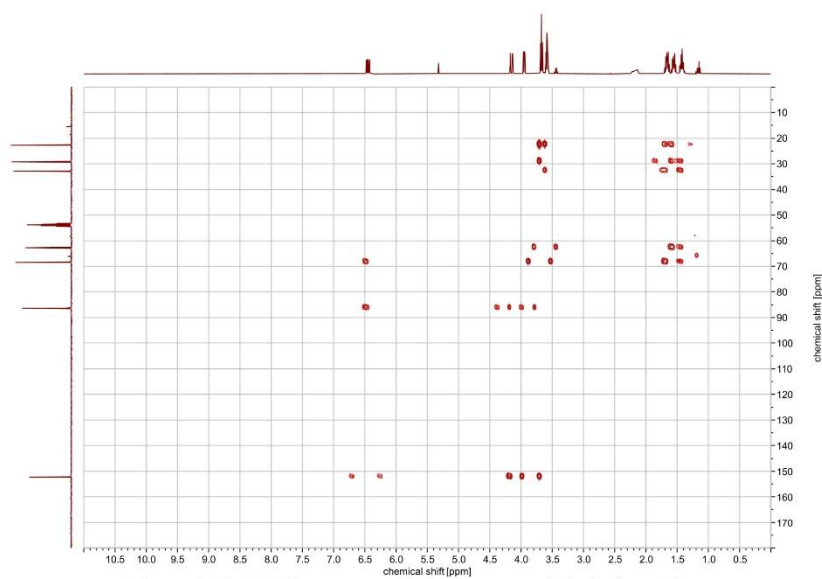


Figure S148: HMBC spectrum of 5-hydroxypentyl vinyl ether (**5d**).

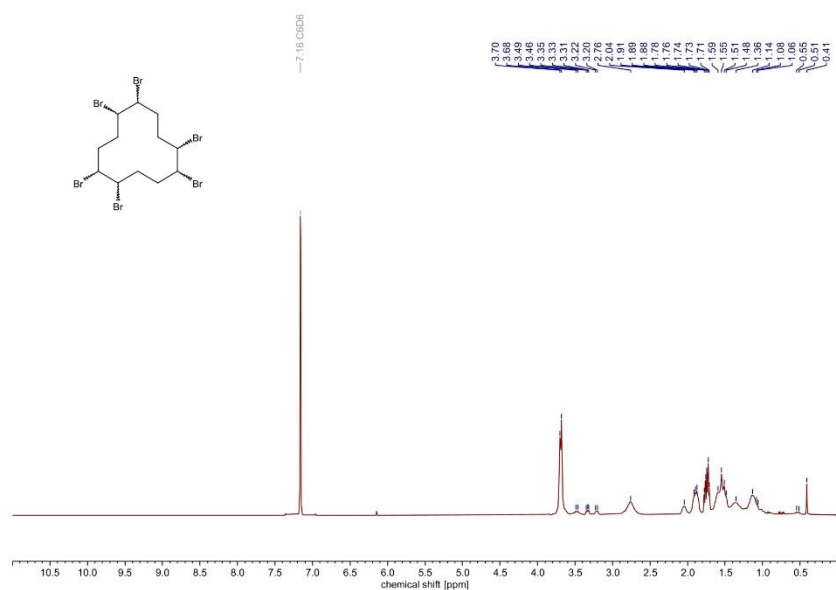


Figure S149: ^1H NMR spectrum of technical HBCD (**8**) (400 MHz, C_6D_6 , 298 K).

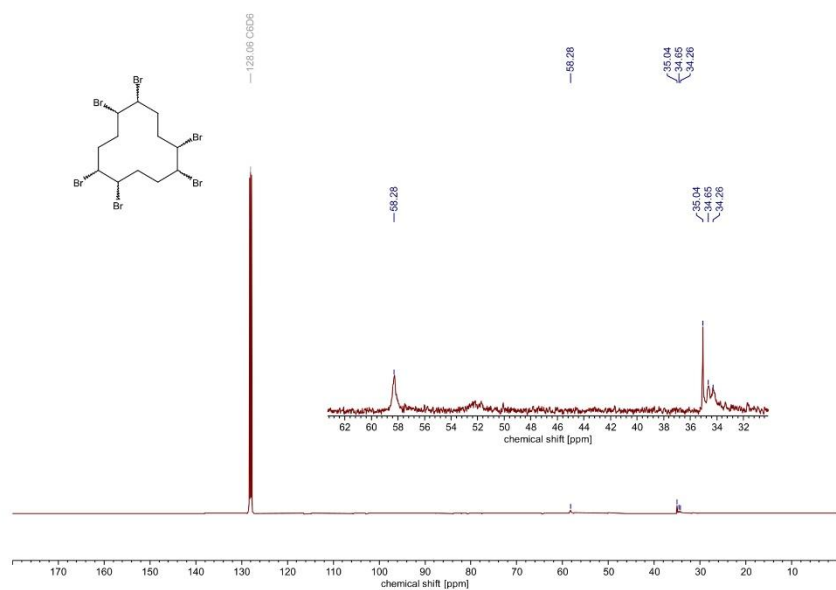


Figure S150: ^{13}C NMR spectrum of technical HBCD (**8**) (101 MHz, C_6D_6 , 298 K).

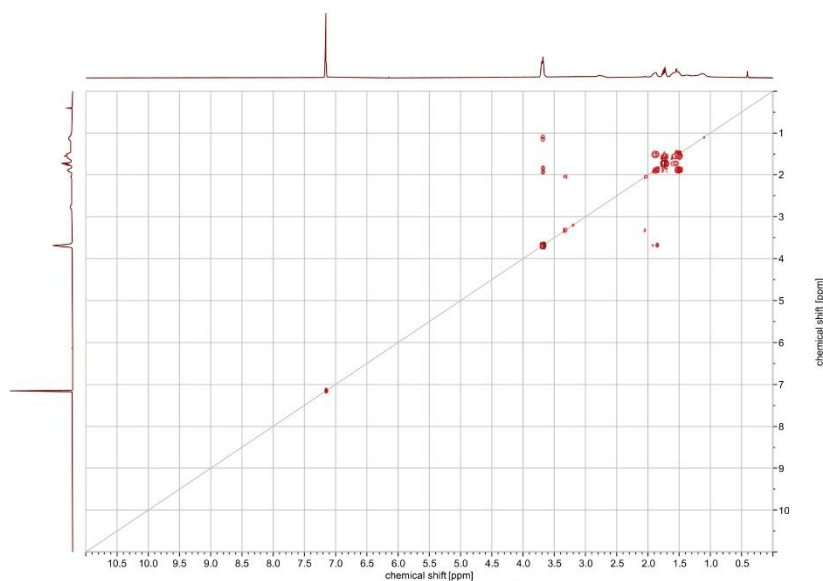


Figure S151: COSY spectrum of technical HBCD (8).

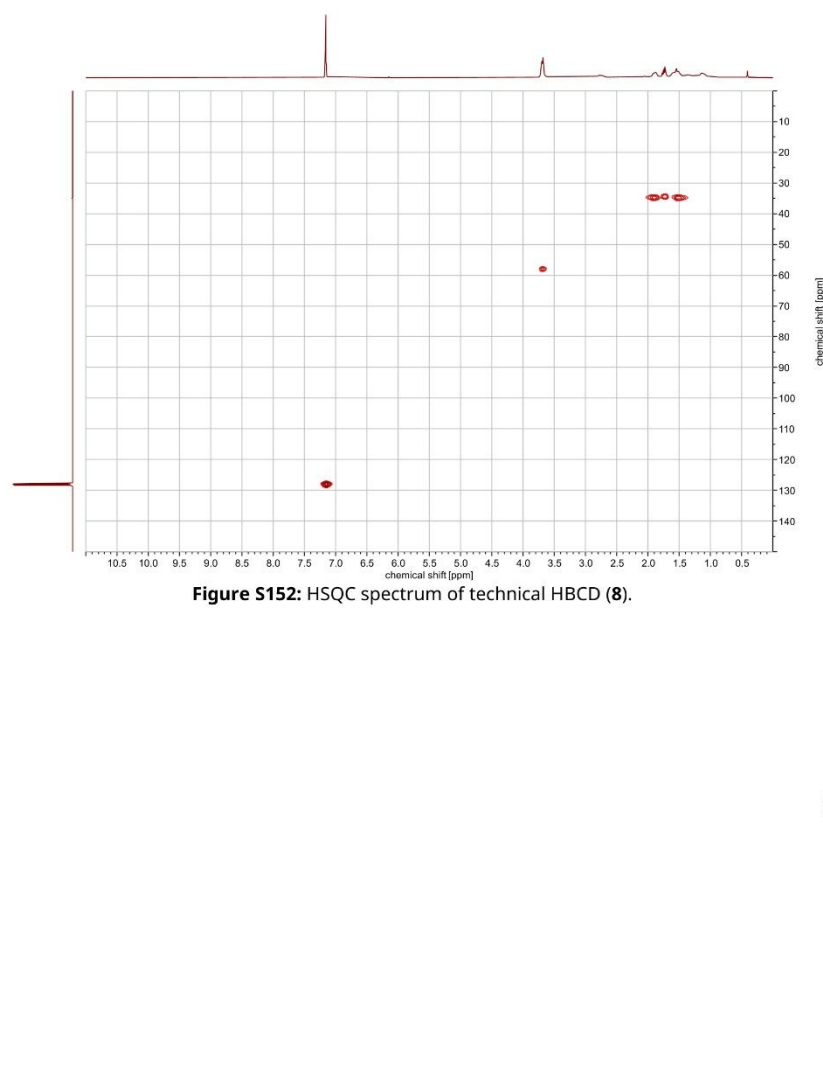


Figure S152: HSQC spectrum of technical HBCD (8).

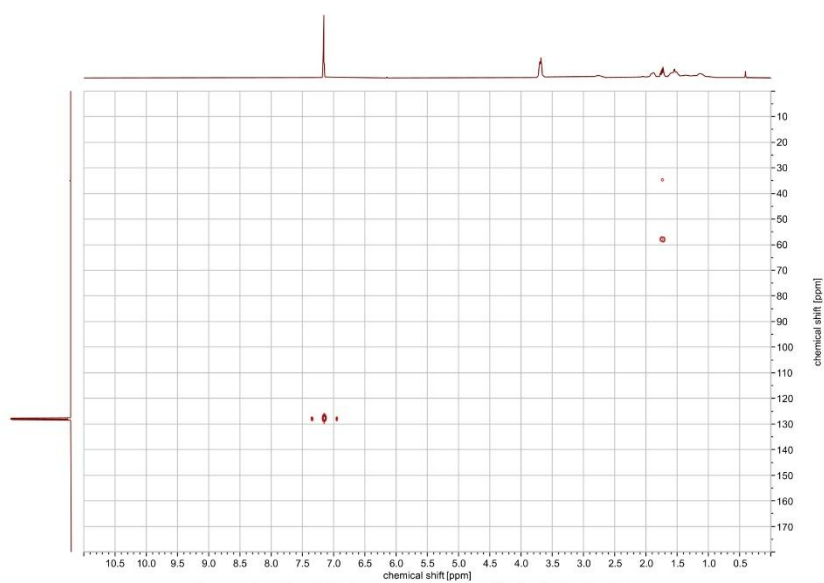


Figure S153: HMBC spectrum of technical HBCD (**8**).

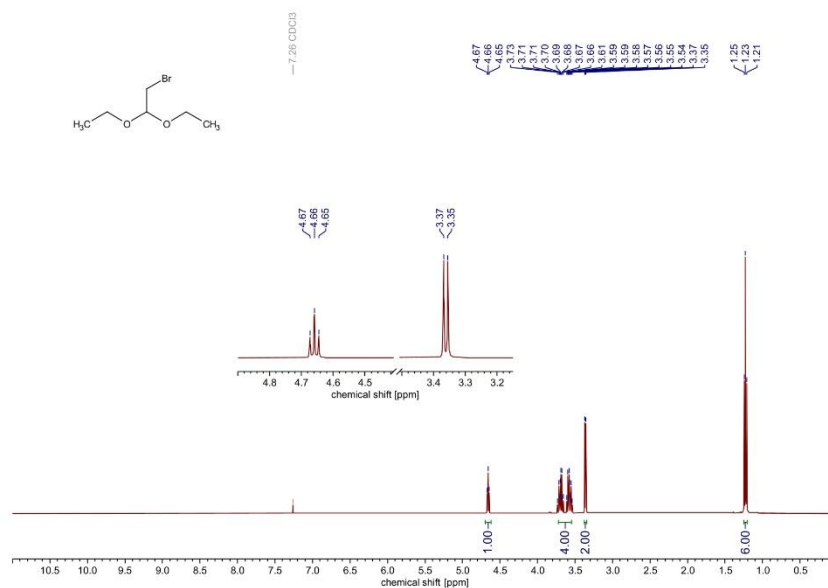


Figure S154: ^1H NMR spectrum of 2-bromo-1,1-di(ethoxy)-ethane (**10**) (400 MHz, CDCl_3 , 298 K).

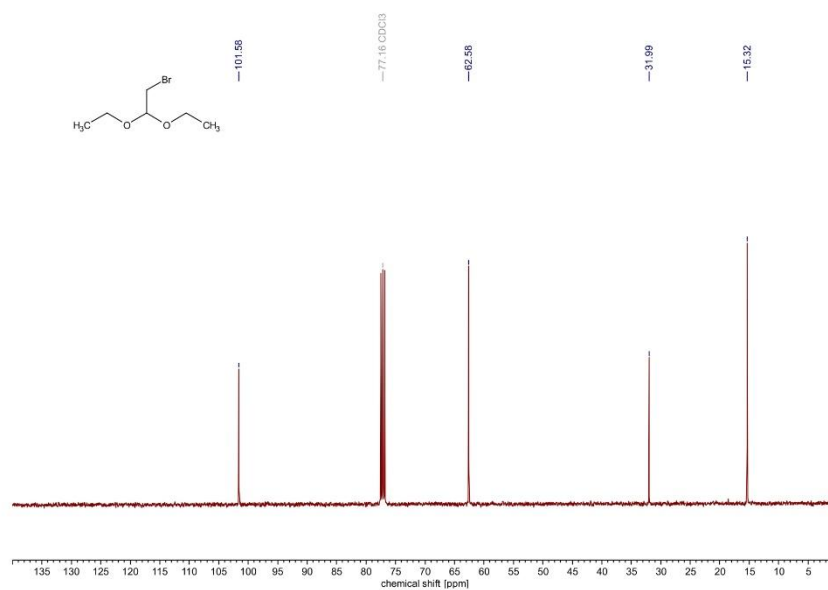


Figure S155: ^{13}C NMR spectrum of 2-bromo-1,1-di(ethoxy)-ethane (**10**) (101 MHz, CDCl_3 , 298 K).

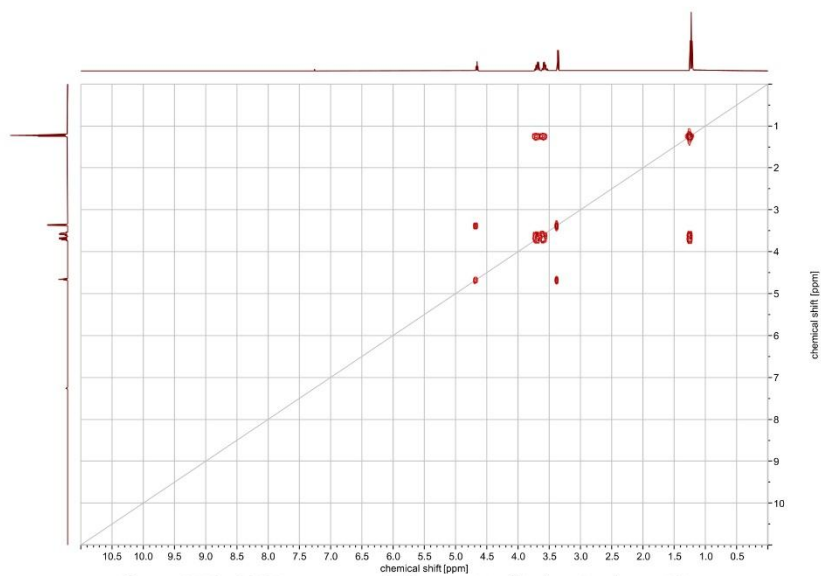


Figure S156: COSY spectrum of 2-bromo-1,1-di(ethoxy)-ethane (10).

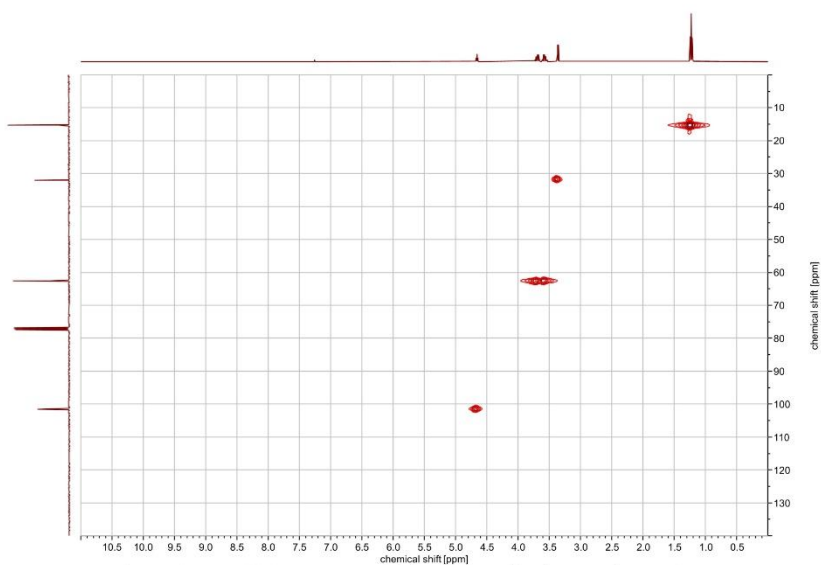


Figure S157: HSQC spectrum of 2-bromo-1,1-di(ethoxy)-ethane (10).

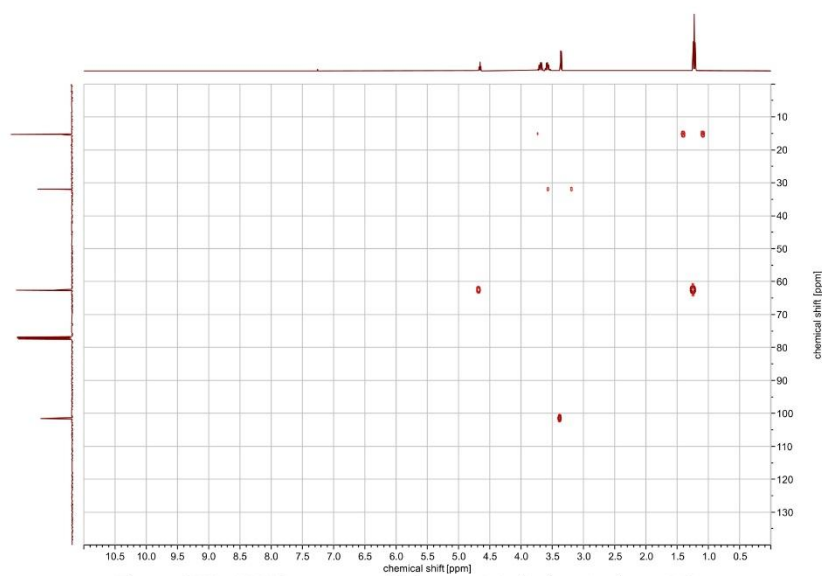


Figure S158: HMBC spectrum of 2-bromo-1,1-di(ethoxy)-ethane (**10**).

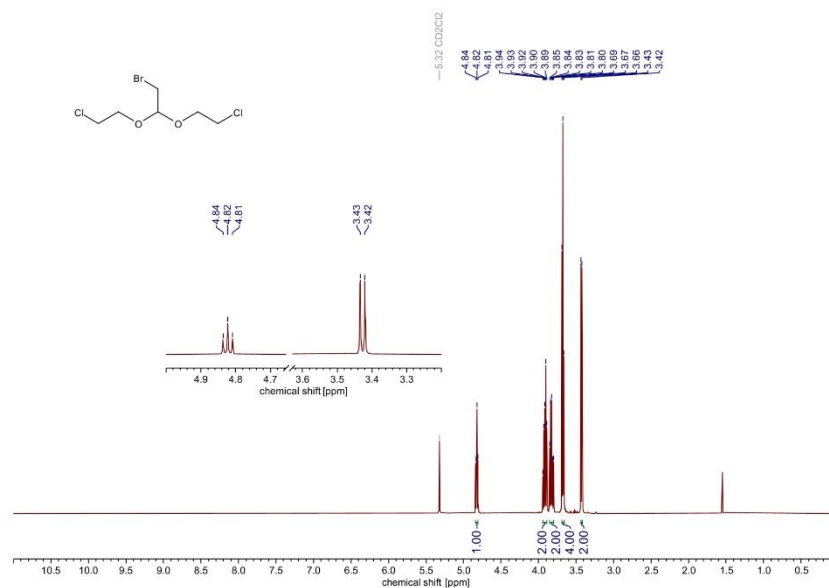


Figure S159: ^1H NMR spectrum of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**) (400 MHz, CD_2Cl_2 , 298 K).

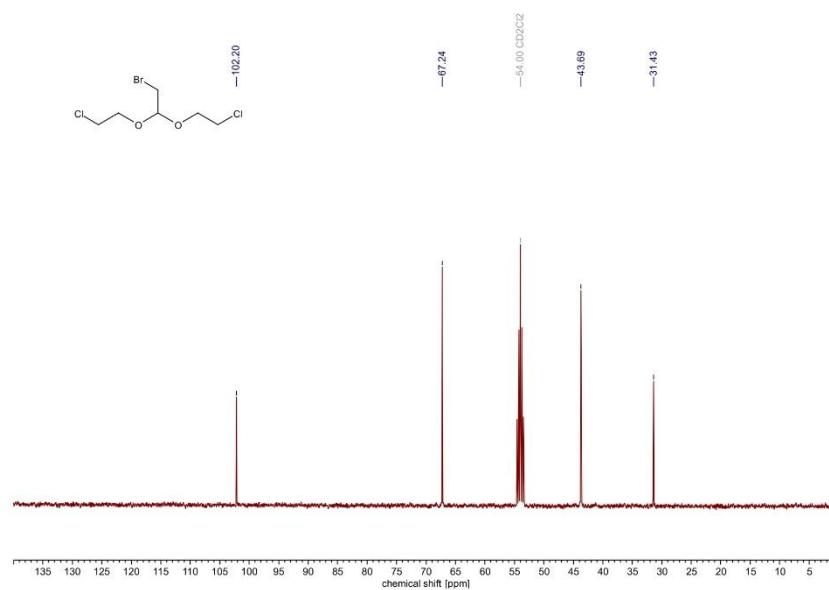


Figure S160: ^{13}C NMR spectrum of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**) (101 MHz, CD_2Cl_2 , 298 K).

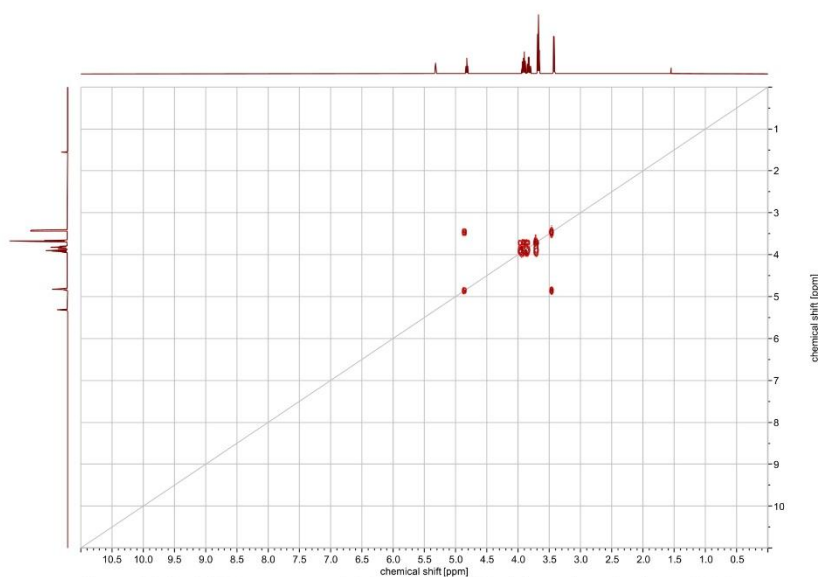


Figure S161: COSY spectrum of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**).

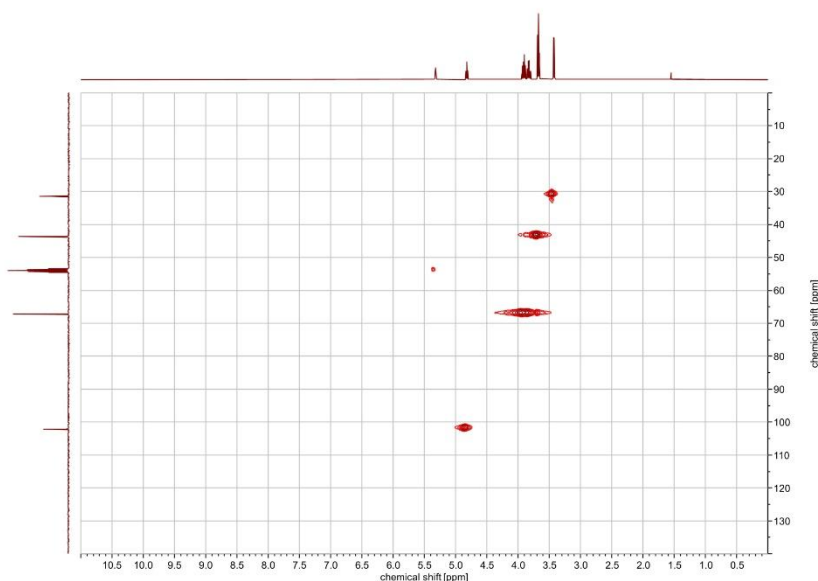


Figure S162: HSQC spectrum of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**).

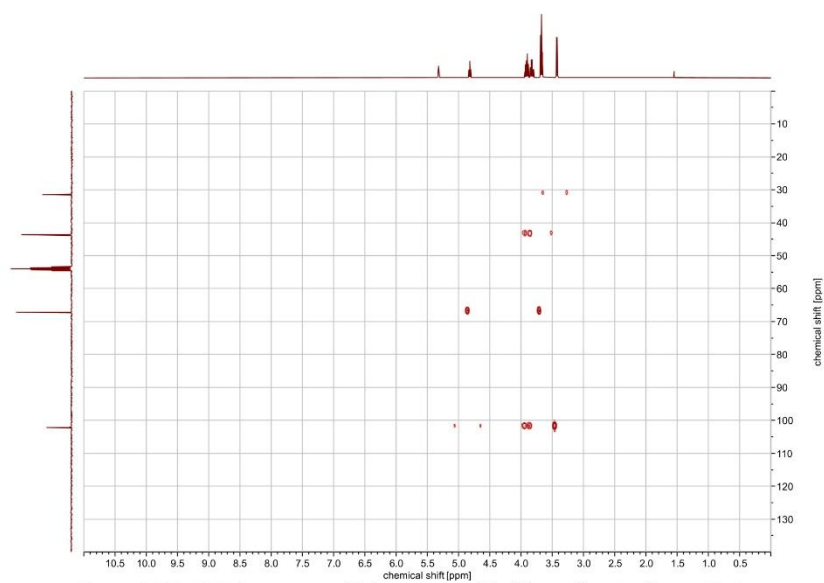


Figure S163: HMBC spectrum of 2-bromo-1,1-di(2-chloroethoxy)-ethane (**10a**).

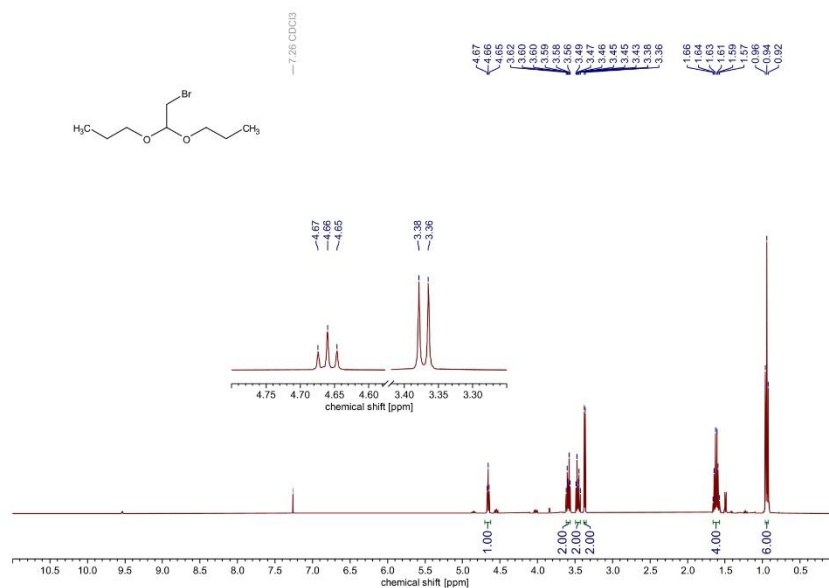


Figure S164: ¹H NMR spectrum of 2-bromo-1,1-di(propoxy)-ethane (**10b**) (400 MHz, CDCl₃, 298 K).

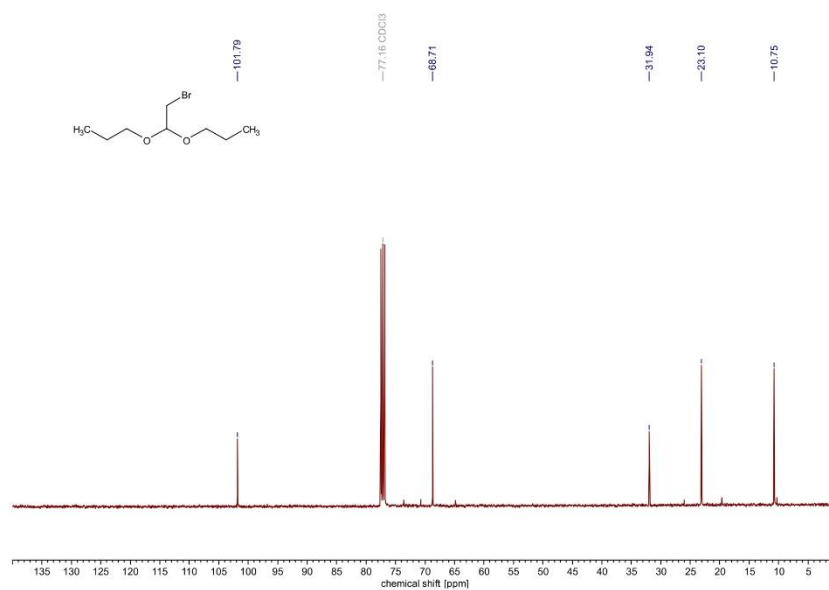


Figure S165: ¹³C NMR spectrum of 2-bromo-1,1-di(propoxy)-ethane (**10b**) (101 MHz, CDCl₃, 298 K).

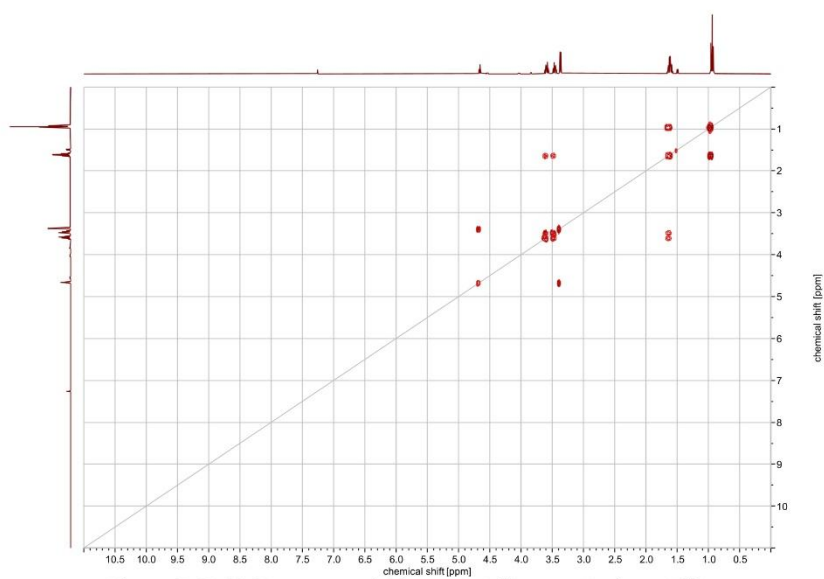


Figure S166: COSY spectrum of 2-bromo-1,1-di(propoxy)-ethane (**10b**).

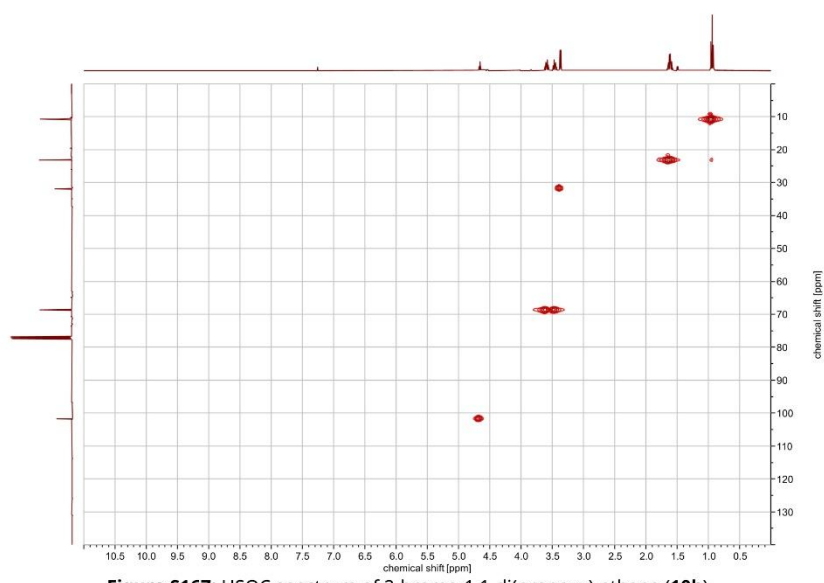


Figure S167: HSQC spectrum of 2-bromo-1,1-di(propoxy)-ethane (**10b**).

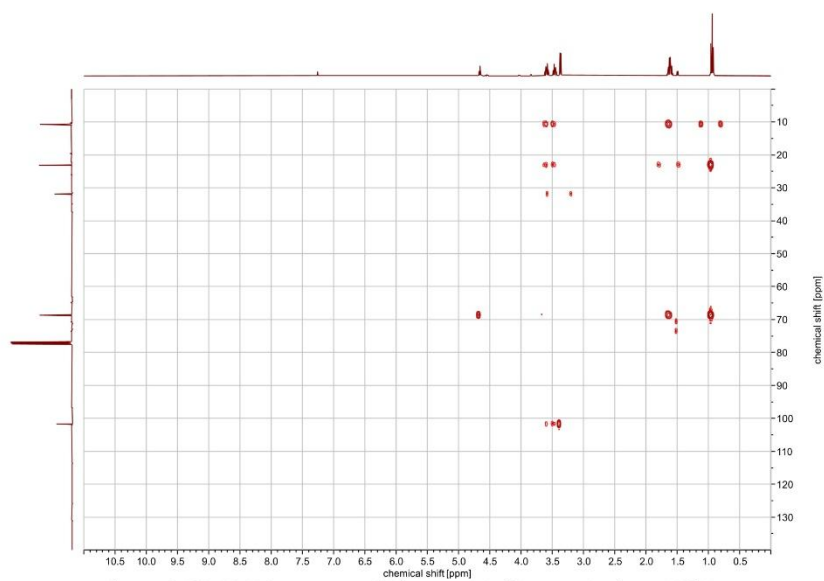


Figure S168: HMBC spectrum of 2-bromo-1,1-di(propoxy)-ethane (**10b**).

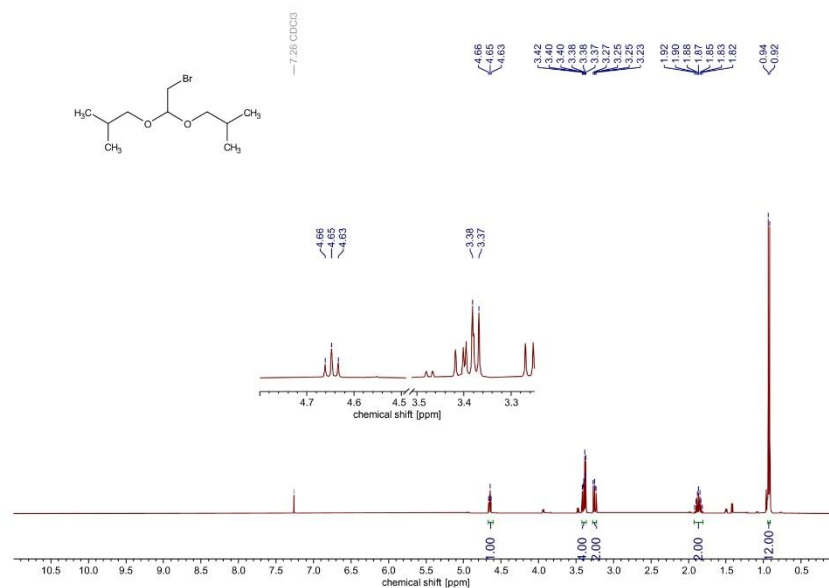


Figure S169: ¹H NMR spectrum of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**) (400 MHz, CDCl₃, 298 K).

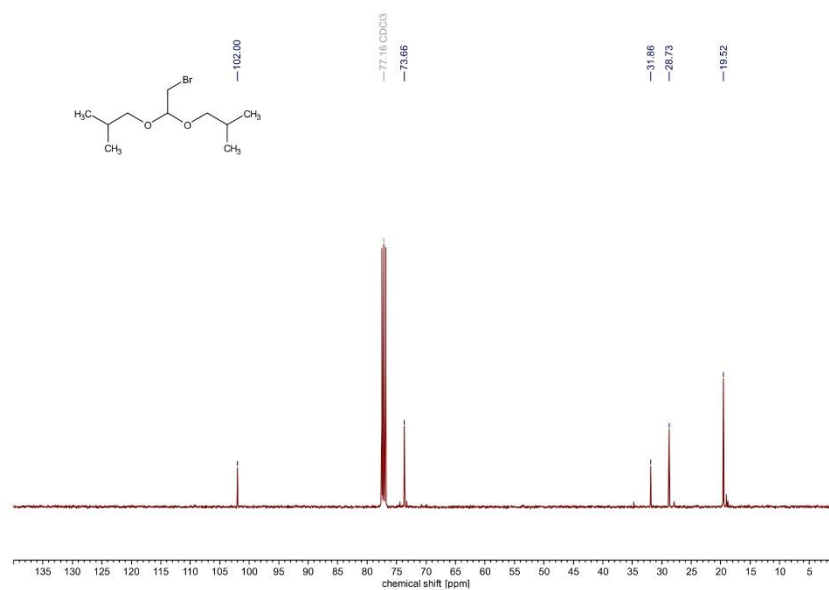


Figure S170: ¹³C NMR spectrum of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**) (101 MHz, CDCl₃, 298 K).

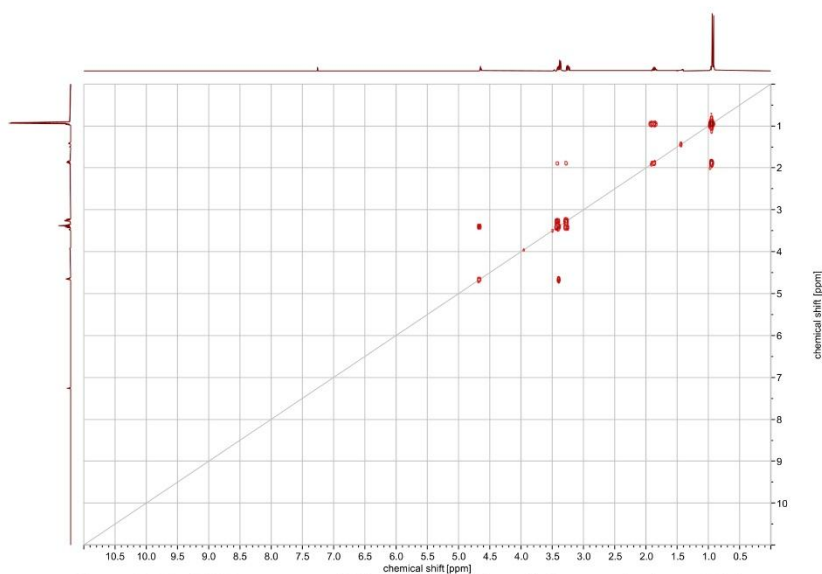


Figure S171: COSY spectrum of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**).

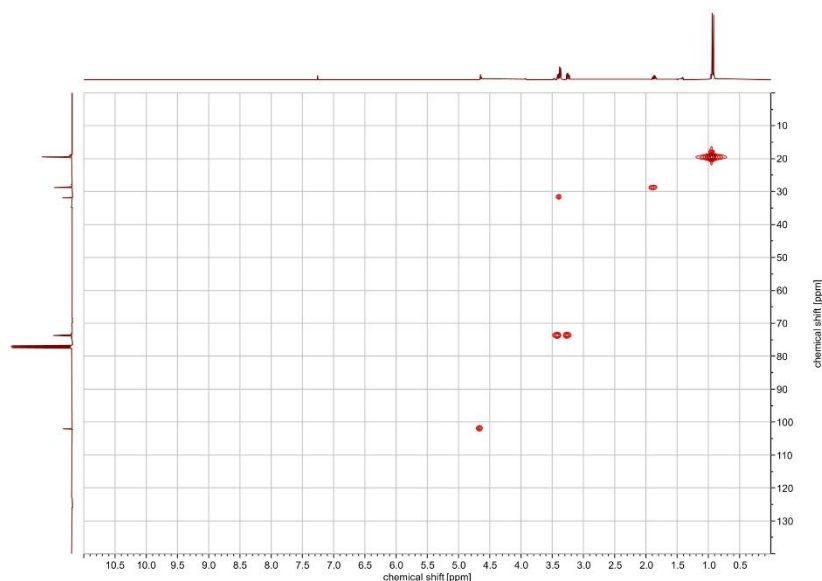


Figure S172: HSQC spectrum of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**).

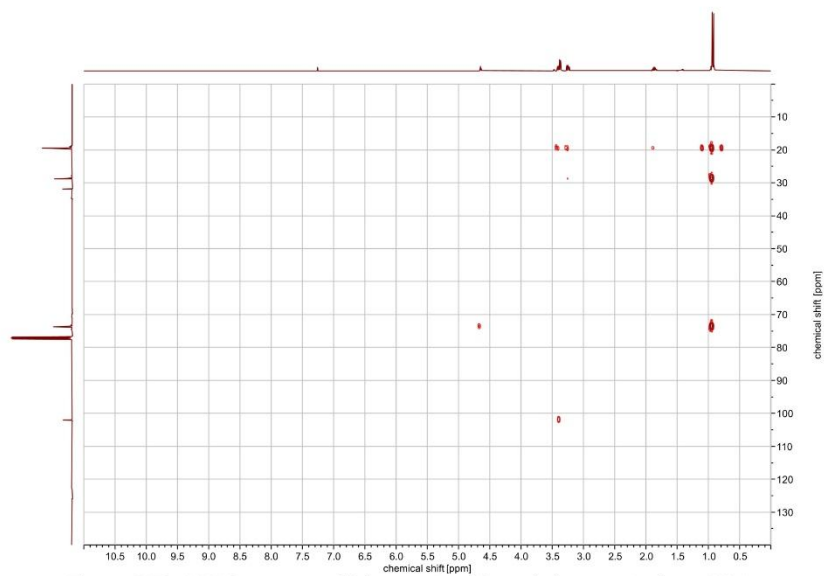


Figure S173: HMBC spectrum of 2-bromo-1,1-di(2-methylpropoxy)-ethane (**10c**).

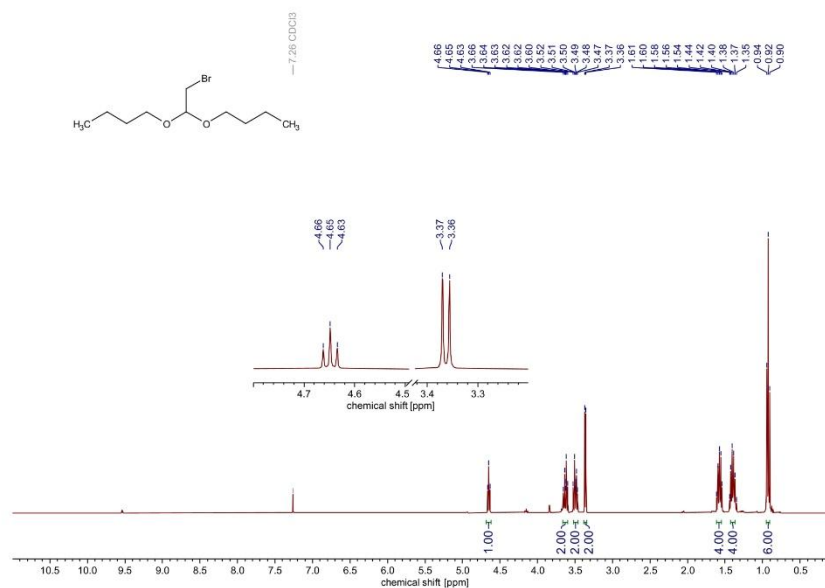


Figure S174: ¹H NMR spectrum of 2-bromo-1,1-di(butoxy)-ethane (**10d**) (400 MHz, CDCl₃, 298 K).

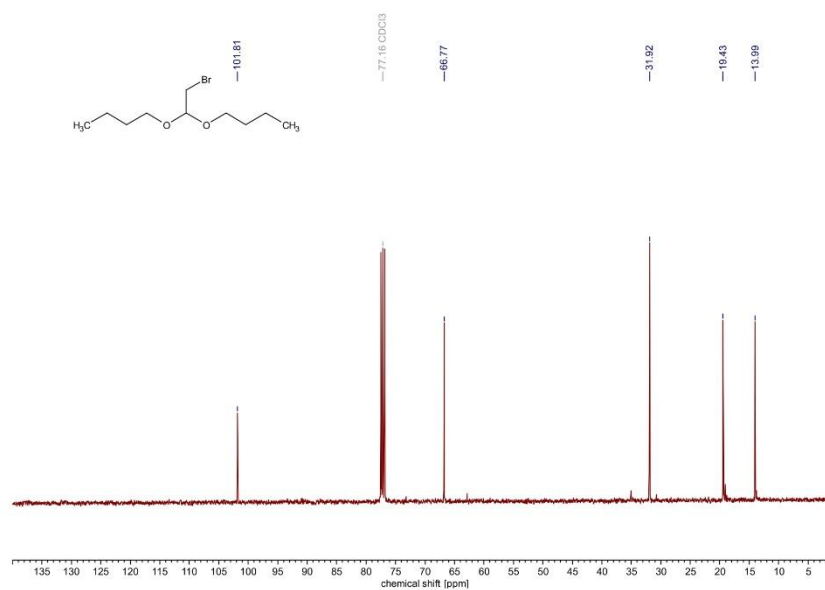


Figure S175: ¹³C NMR spectrum of 2-bromo-1,1-di(butoxy)-ethane (**10d**) (101 MHz, CDCl₃, 298 K).

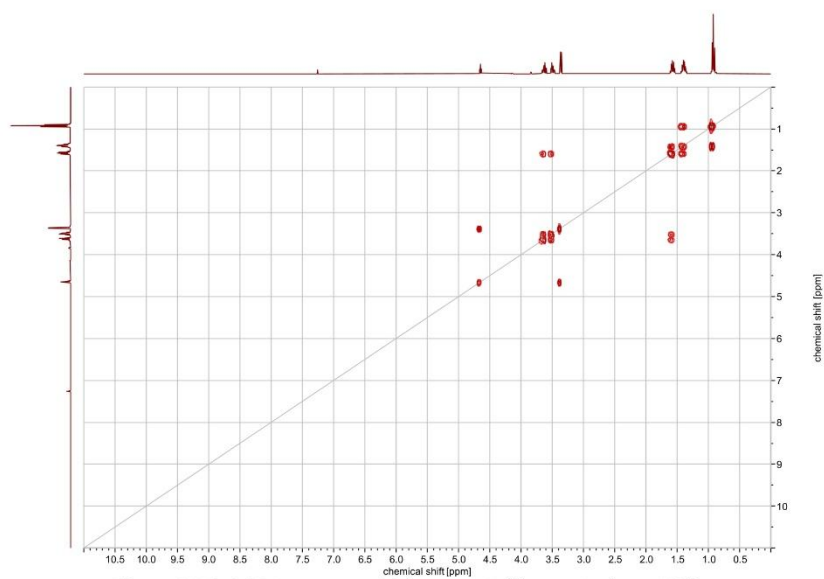


Figure S176: COSY spectrum of 2-bromo-1,1-di(butoxy)-ethane (**10d**).

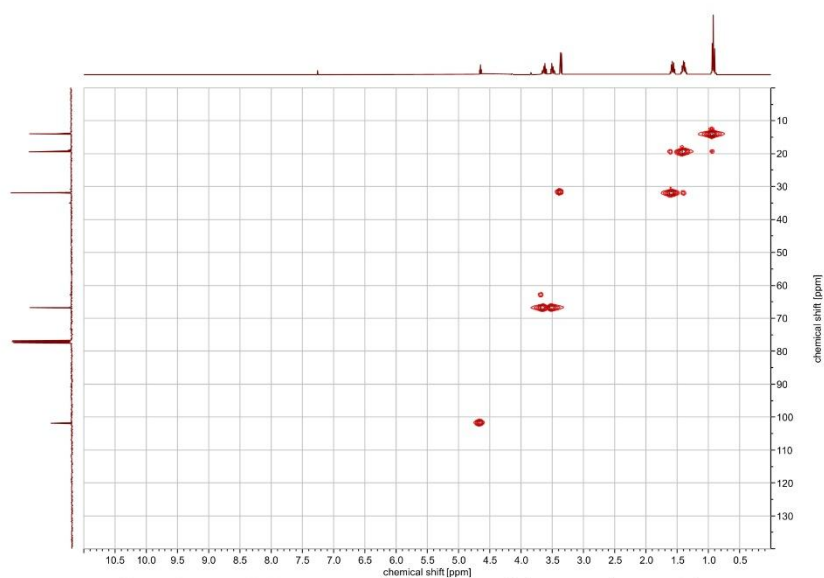


Figure S177: HSQC spectrum of 2-bromo-1,1-di(butoxy)-ethane (**10d**).

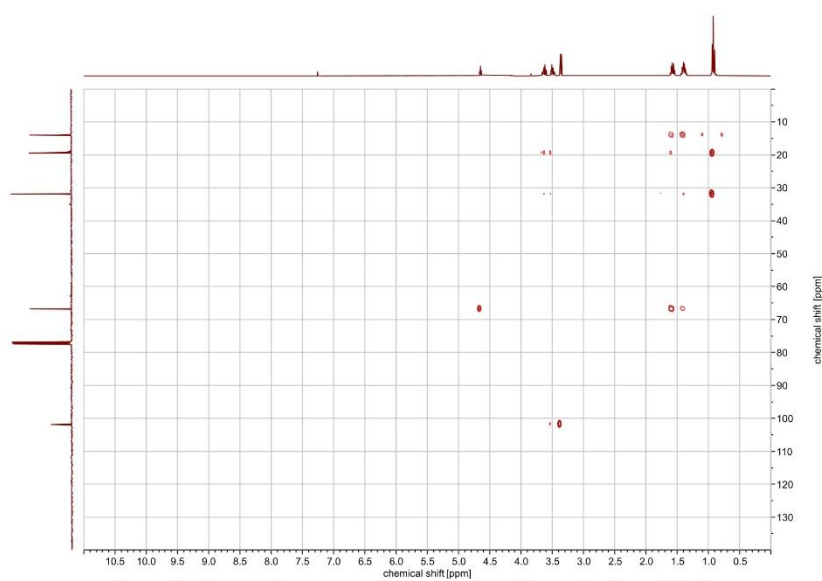


Figure S178: HMBC spectrum of 2-bromo-1,1-di(butoxy)-ethane (**10d**).

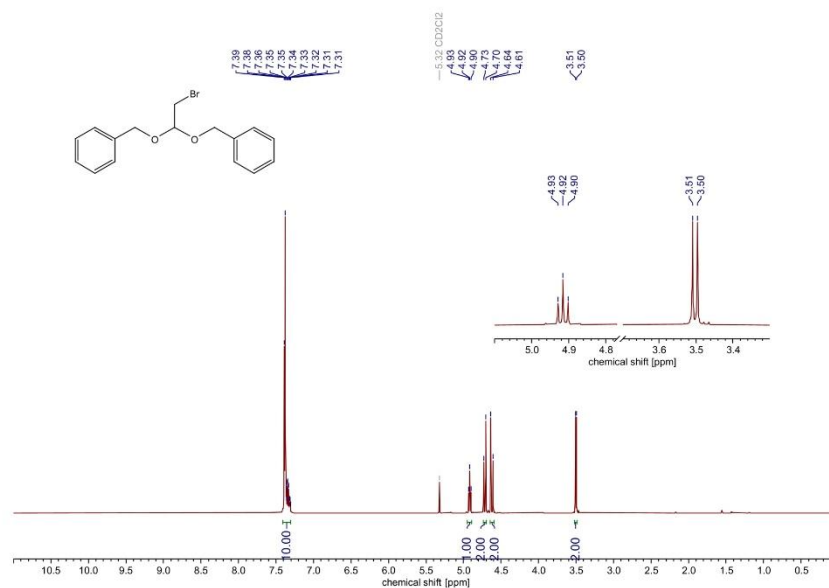


Figure S179: ^1H NMR spectrum of 2-bromo-1,1-di(benzyloxy)-ethane (**10e**) (400 MHz, CDCl_3 , 298 K).

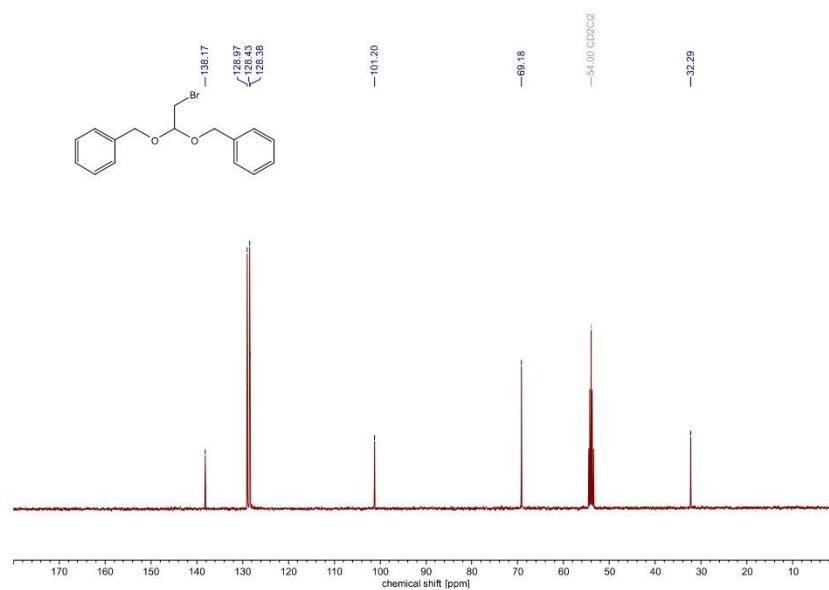
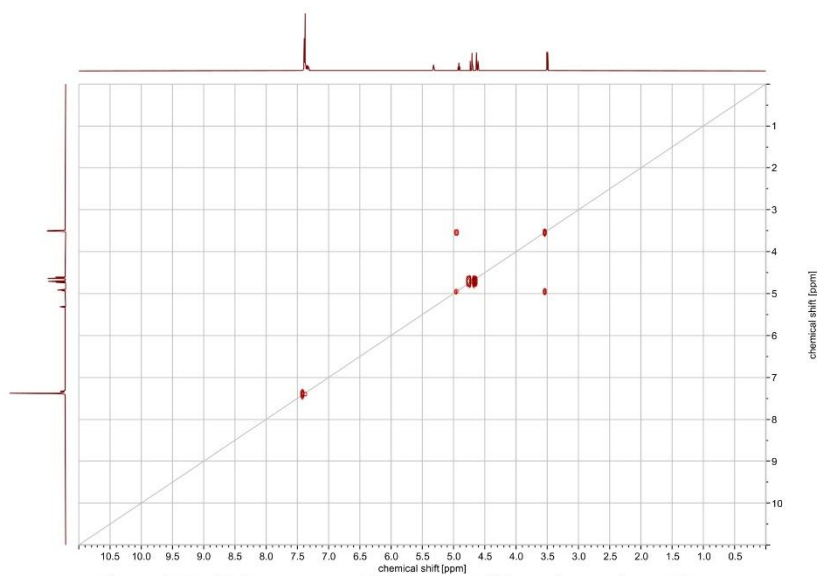


Figure S180: ^{13}C NMR spectrum of 2-bromo-1,1-di(benzyloxy)-ethane (**10e**) (101 MHz, CDCl_3 , 298 K).



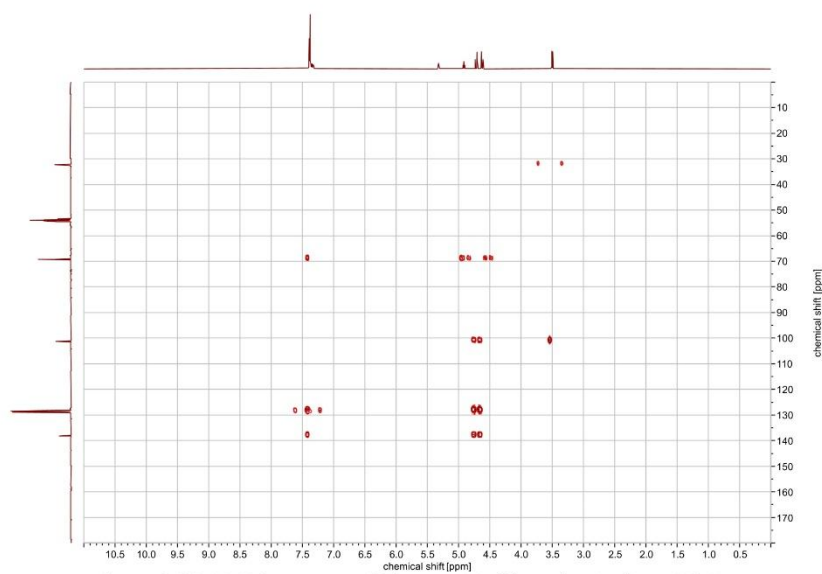


Figure S183: HMBC spectrum of 2-bromo-1,1-di(benzyloxy)-ethane (**10e**).

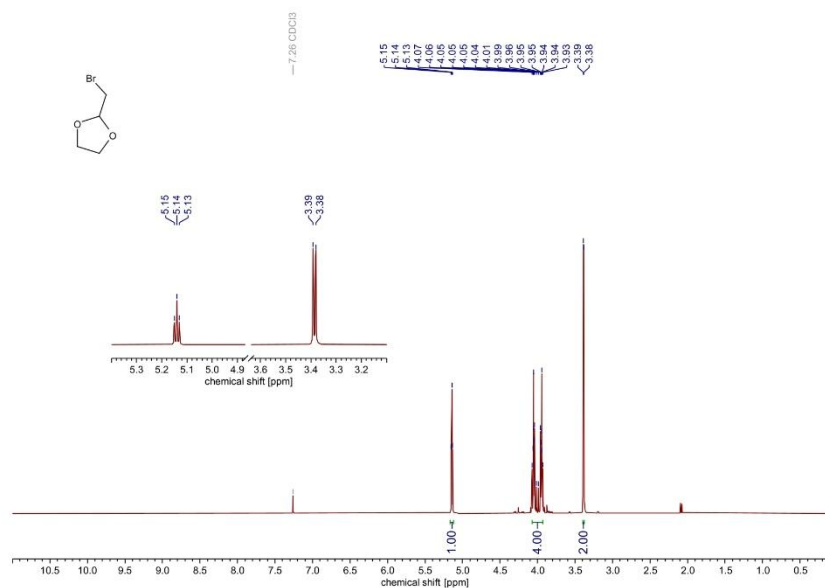


Figure S184: ¹H NMR spectrum of 2-bromomethyl-1,3-dioxolane (**11**) (400 MHz, CDCl₃, 298 K).

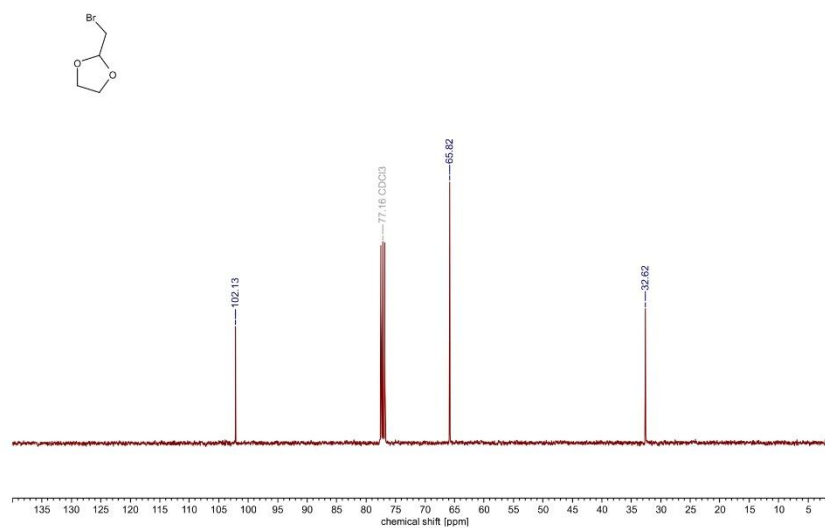


Figure S185: ¹³C NMR spectrum of 2-bromomethyl-1,3-dioxolane (**11**) (101 MHz, CDCl₃, 298 K).

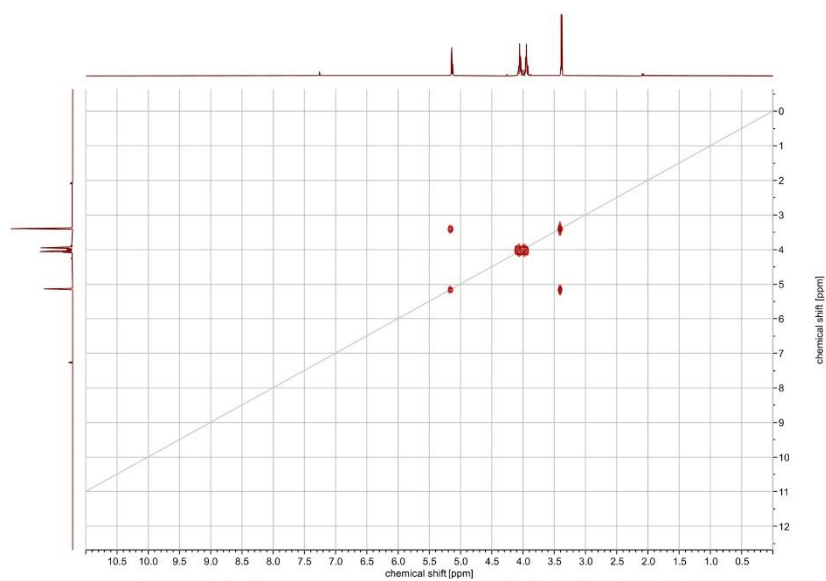


Figure S186: COSY spectrum of 2-bromomethyl-1,3-dioxolane (**11**).

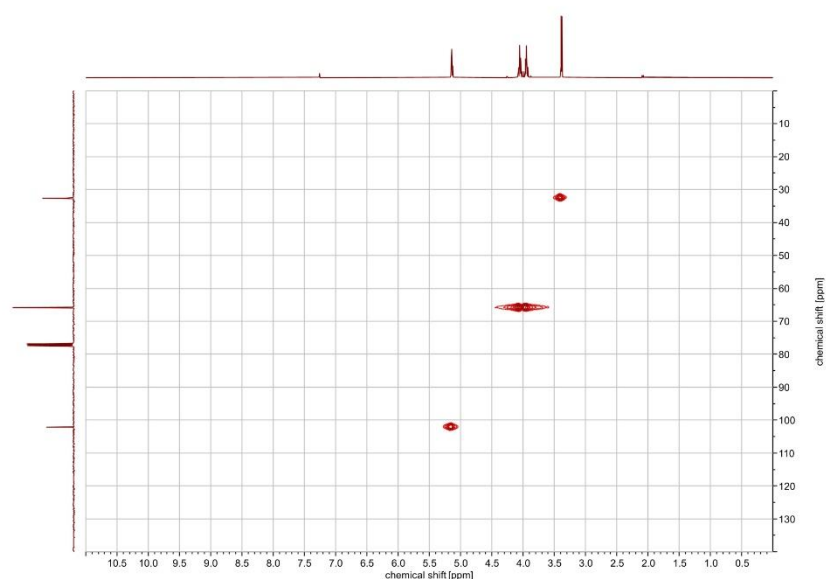


Figure S187: HSQC spectrum of 2-bromomethyl-1,3-dioxolane (**11**).

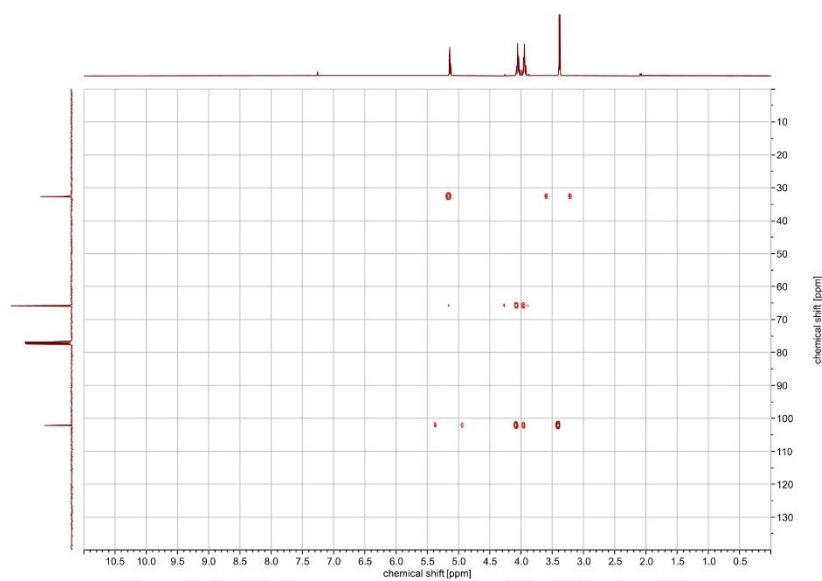


Figure S188: HMBC spectrum of 2-bromomethyl-1,3-dioxolane (**11**).

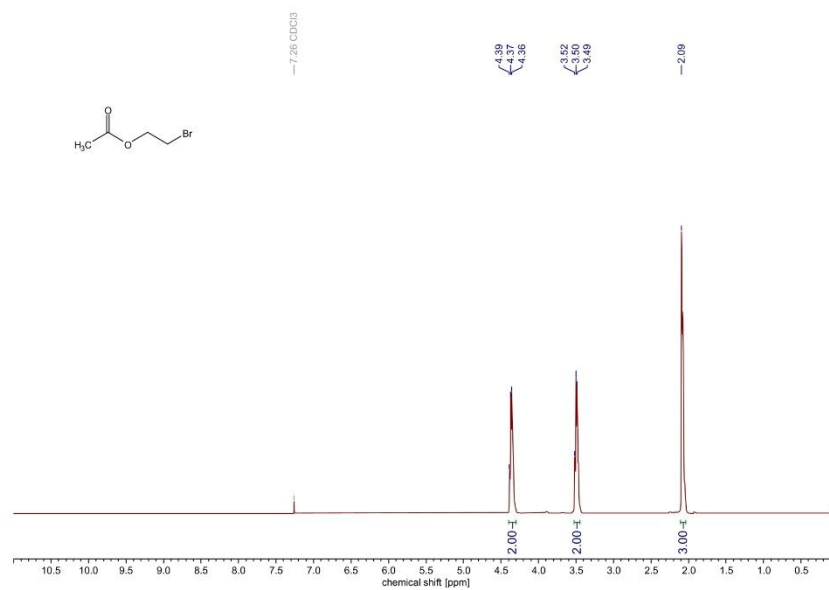


Figure S189: ¹H NMR spectrum of 2-bromoethyl acetate (12) (400 MHz, CDCl₃, 298 K).

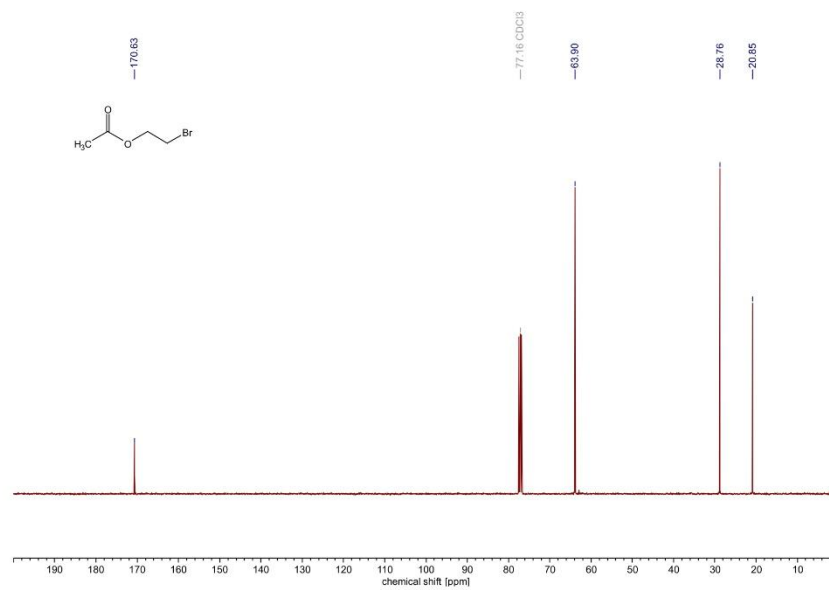
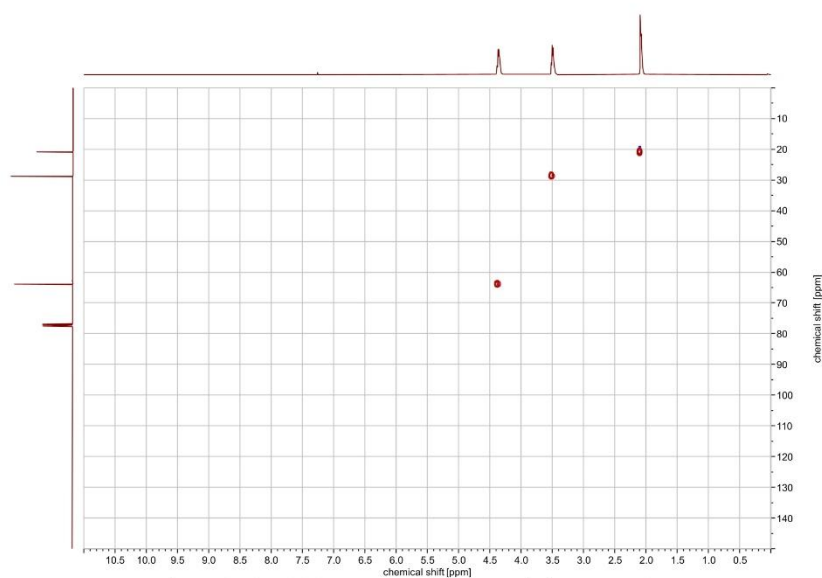
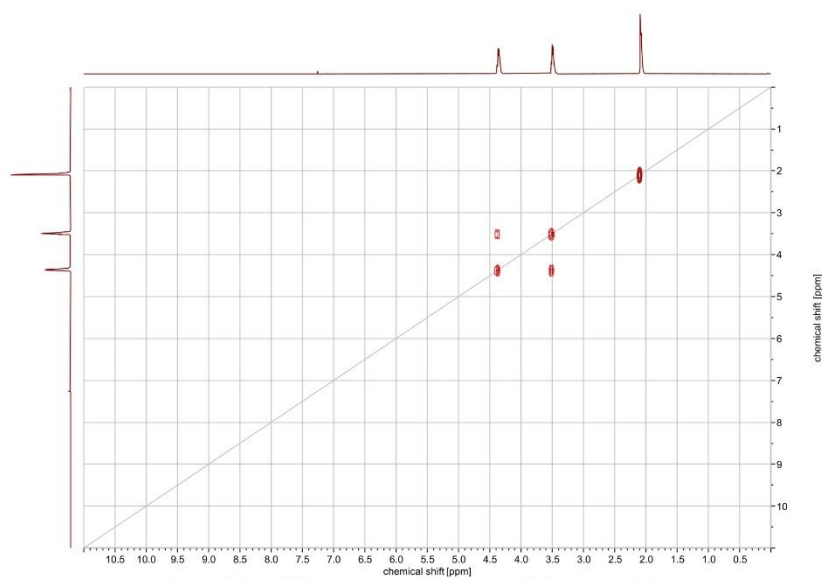


Figure S190: ¹³C NMR spectrum of 2-bromoethyl acetate (12) (101 MHz, CDCl₃, 298 K).



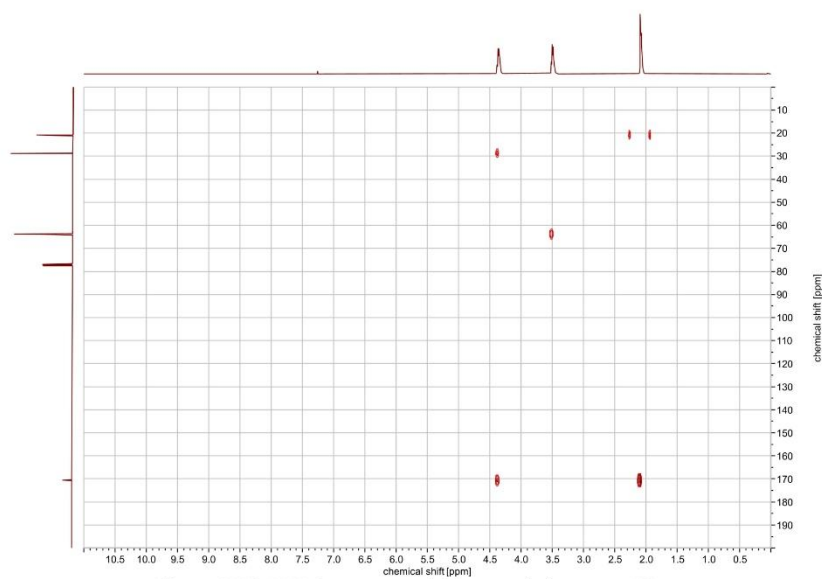


Figure S193: HMBC spectrum of 2-bromoethyl acetate (12).

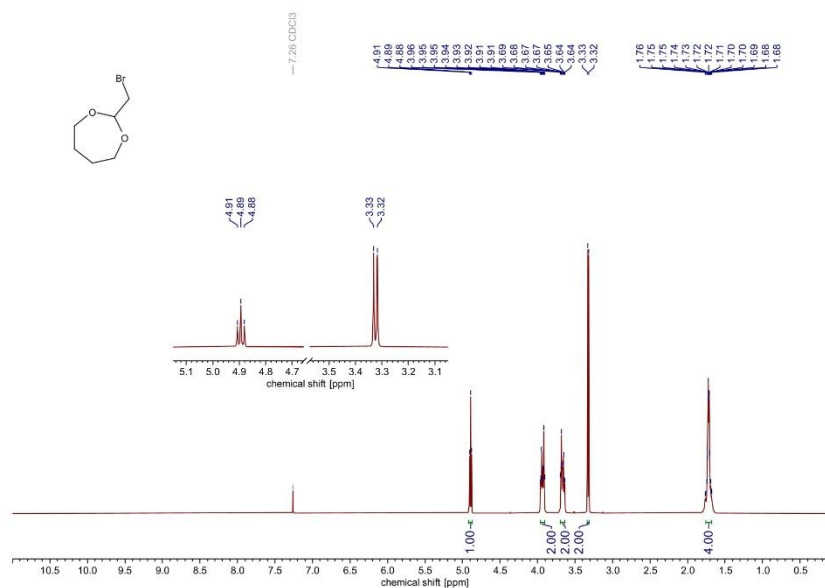


Figure S194: ¹H NMR spectrum of 2-bromomethyl-1,3-dioxepane (11b) (400 MHz, CDCl₃, 298 K).

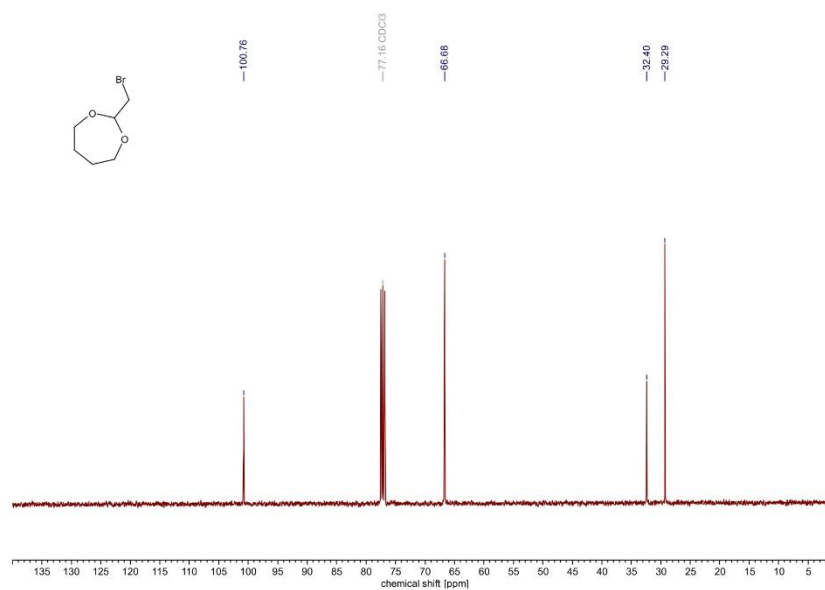


Figure S195: ¹³C NMR spectrum of 2-bromomethyl-1,3-dioxepane (11b) (101 MHz, CDCl₃, 298 K).

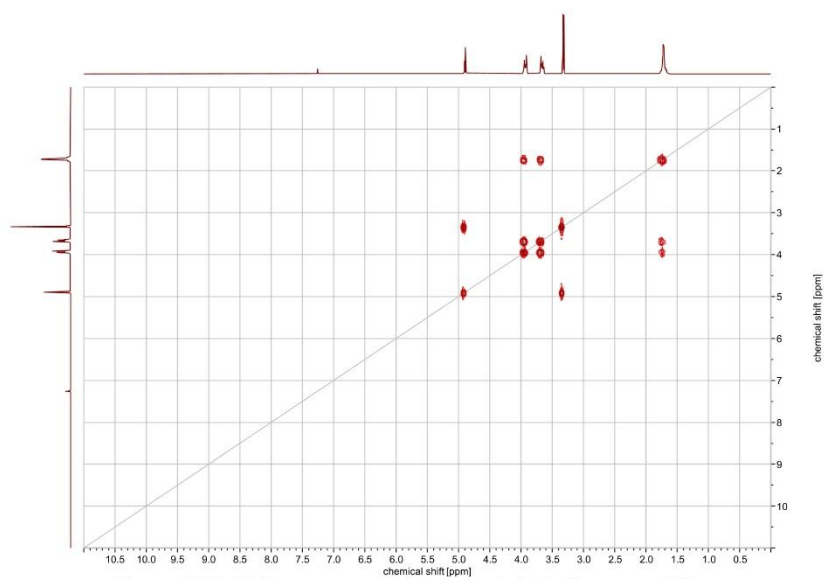


Figure S196: COSY spectrum of 2-bromomethyl-1,3-dioxepane (**11b**).

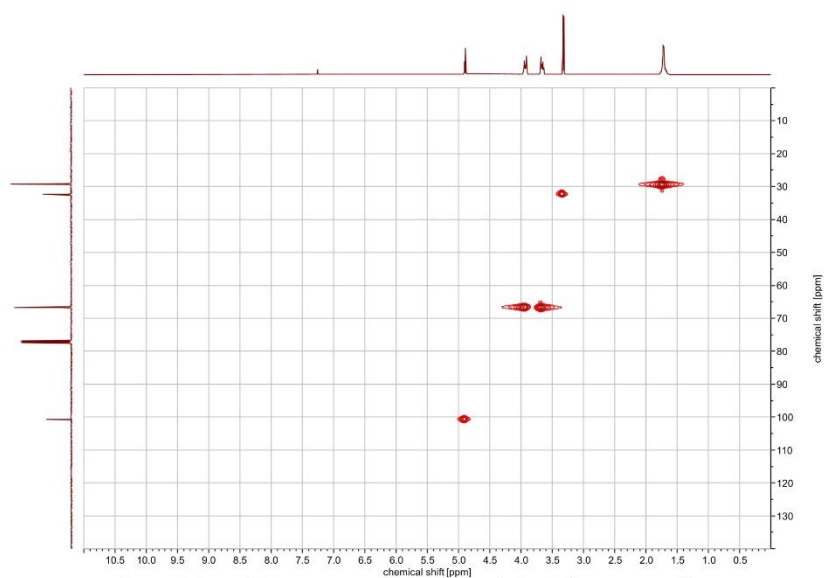


Figure S197: HSQC spectrum of 2-bromomethyl-1,3-dioxepane (**11b**).

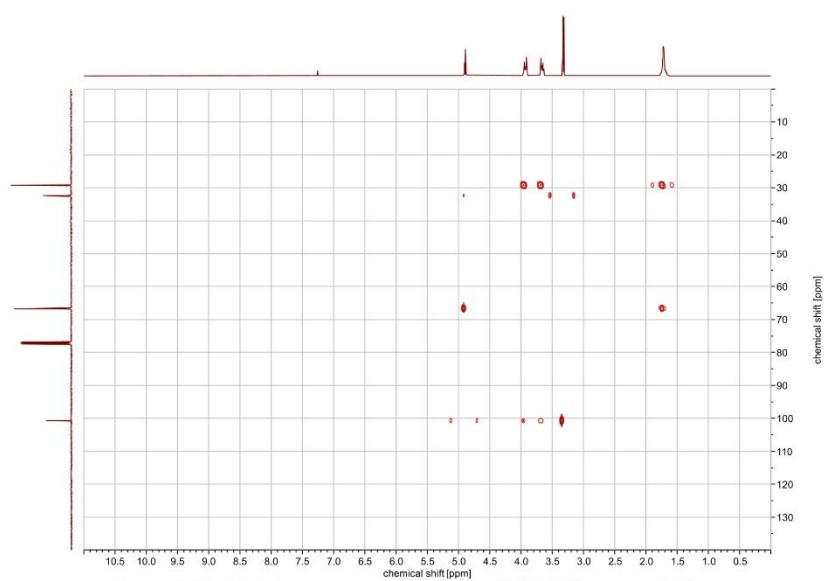


Figure S198: HMBC spectrum of 2-bromomethyl-1,3-dioxepane (**11b**).

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ADVANCED MATERIALS

Supporting Information

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Supplementary Information for

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General Information

NMR Spectroscopy

All NMR measurements (^1H , ^{13}C , HSQC, HMBC and COSY) were carried out using an AVANCE II 400 MHz spectrometer from Bruker (^1H : 400 MHz, ^{13}C : 101 MHz) (Rheinstätten, Germany). All measurements were carried out at room temperature in deuterated solvent. The chemical shifts are reported in relation to the solvent peak as internal standard in parts per million (ppm) and the coupling constants J are measured in Hertz (Hz). The splitting patterns are labeled as s, singlet; d, doublet; t, triplet; dd, doublet of doublet; q, quartet; m, multiplet.

The spectra were analyzed using *Mestrenova* software from *Mestrelab Research*. The deuterated solvents used were Tetrahydrofuran- d_8 , Tetrachloroethane- d_2 , Dichloromethane- d_2 and Chloroform- d_1 that have been purchased from *Deutero*. (Germany)

Gas Chromatography (GC/GC-MS)

GC

GC-samples for yield determination of electrochemical reactions were measured using the gas chromatograph GC 2010 from *Shimadzu* with a quartz capillary column ZB-5 from the company *Phenomenex*. The column has a length of 30 m with an inner diameter of 0.025 mm. The covalently bonded stationary phase had a film thickness of 0.25 μm . The standard method included the following system settings: Hydrogen with a flow rate of 40.0 mL/min was used as carrier gas. The injection temperature was 250 °C and the detection temperature 320 °C. The method with a total run time of 19.94 min was used with a starting temperature of 40 °C. The starting temperature was maintained for one minute and then heated to 110 °C at a rate of 10 °C/min. The temperature was then increased by 32 °C/min to 300 °C and held for six minutes. For yield determinations product signal calibrations were performed using 1,10-dichlorodecan ($t_{\text{R}} = 11.21$ min) as internal standard.

GC/MS

Gas chromatographic measurements combined with mass spectroscopy were carried out on a *Clarus 600* gas chromatograph with an electron ionization detector from *Perkin-Elmer*. A quartz capillary column Rxi-5Sil MS from *RESTEK* (20 m long with an inner diameter of 0.18 mm) with a film thickness of 18 μm was used. Helium served as carrier gas and the sample injection volume was 1 μL . The standard method included the following temperature program with a total run time of 15 minutes: The starting temperature of 40 °C was maintained for 0.97 min. Then it was heated with a gradient of 13 °C/min to 85 °C and afterwards with a rate of 30 °C/min to 210 °C. This temperature was maintained for 6.40 min.

The chromatograms and the mass spectra were analyzed using *Mestrenova* software from *Mestrelab Research*.

Size exclusion chromatography (SEC/GPC)

GPC measurements were performed in DMF on an Agilent 1100 Series chromatograph from Agilent Technologies, Inc. The HEMA column set has a 300/100/40 Å porosity and the samples were detected by RI and UV detectors (254 nm). *N,N*-Dimethylformamide with 1 g/mL lithium bromide at 50 °C served as the mobile phase with a flow rate of 1 mL/min. Toluene (1 $\mu\text{L/mL}$) was used as internal

reference. For calibration Poly(methyl methacrylate) (PMMA) standards from Polymer Standard Service GmbH were used.

Thermo gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on a TGA 2 STAR[®] system by *Mettler Toledo*. The samples (ca. 8 mg) were placed in crucibles made of polycrystalline aluminum oxide (PCA/Saphir). The samples were heated to 550 °C (10 °C/min) and the final temperature was kept for 60 minutes.

Elemental analysis

Elemental analysis was performed by micro analytical laboratory *Kolbe* in Oberhausen, Germany.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were carried out using a DSC 250 instrument (TA Instruments) equipped with an RCS 90 cooling unit. The system was calibrated with indium and *n*-octane as standard reference materials. Approximately 8-10 mg of each polymer sample was weighed into an aluminum pan, which was then sealed. All measurements were performed under a constant nitrogen stream to prevent oxidative degradation.

To eliminate any prior thermal history, samples were initially heated to 120 °C at a rate of 10 °C min⁻¹. Subsequently, DSC scans were conducted over a temperature range of -90 °C to 120 °C with a constant heating rate of 10 °C·min⁻¹. Each experiment included two heating cycles and one intermediate cooling cycle. The glass transition temperature (T_g) was determined from the second heating run, based on the inflection point of the corresponding heat capacity change.

Design of Experiments Software

Evaluation of the experiments and response optimization of the DoE experimental plan were performed using *Minitab* Statistical Software 22 (Minitab LLC).

Electrolysis Equipment

All electrochemical reactions were performed in undivided cells (5 mL, *IKA*, ElectraSyn[®]) with constant current provided by a galvanostat (*Rohde & Schwarz R&S[®]* HMP4040). For upscale experiments undivided 10 mL (10 mL, *IKA*, ElectraSyn[®]) and 250 mL (Institute workshop) undivided cells were used. The isostatic graphite was cut by the Institute workshop into needed dimensions (50 x 10 x 2 mm, for 5- and 10 mL cell). The caps for the electrochemical cells made of Teflon were milled by the institute's workshop to fit the cell thread and were equipped with suitable openings for the electrode holders, which were made out of titanium to prevent corrosion. Polarization changers have been installed between power supply and electrochemical cell to change polarity (direct current to alternating current) during electrolysis and were manufactured by the institute's electricity workshop.

Electrolysis Setup

For all electrochemical screenings the starting materials were weighed directly into the electrochemical cell (5 mL, *IKA*, ElectraSyn[®]). After complete homogenization the Teflon cap with the electrode holders and electrodes was screwed onto the electrochemical cell. After the determination of the immersion depth, the contact clips were attached to the electrode holders. The

electrochemical cell was put into a screening block (made of stainless steel by the institute's workshop) located on top of a stirring plate.

For the upscale experiments Teflon caps, electrodes and electrode holders were used also manufactured by the institute's workshop. The 10 mL cell has been purchased commercially; the 500 mL cell was customized by the universities glass workshop.

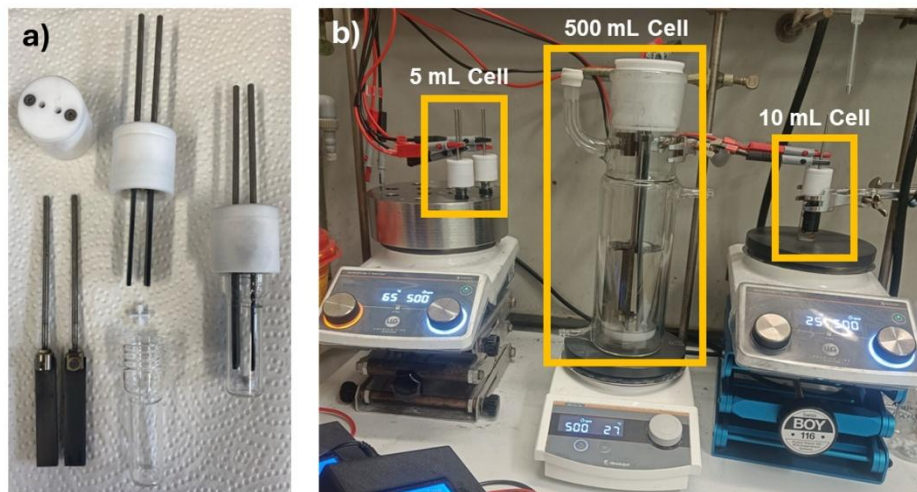
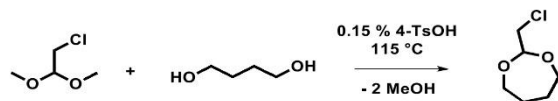


Figure S1: a) Components of the 5 mL cell for electrochemical screenings. b) reaction setup for electrochemical screening (left) and upscale experiments (500 mL cell (middle), 10 mL cell (right)).

Synthesis of 2-Chloromethyl-1,3-dioxepane (3)

Classical synthesis was performed according to a protocol published from TARDY *et al.* After characterization, the obtained product was used for GC calibration and GC-MS identification.^[1]



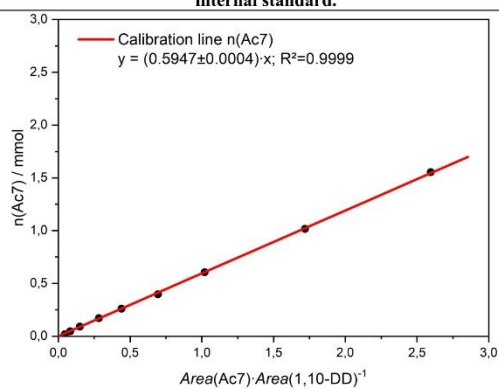
The synthesis was carried out in a distillation apparatus equipped with a stirring bar, a vigreux-column and cooling condenser. The following starting materials were introduced into the 250 mL round bottom flask: butane-1,4-diol (15.0 g, 166 mmol, 15.2 mL, 1 eq.), chloroacetaldehyde dimethylacetal (20.7 g, 166 mmol, 22.7 mL, 1 eq.) and 4-toluene sulfonic acid (0.04 g, 0.25 mmol, 0.002 eq.). Under constant stirring the solution was heated at 115 °C at a pressure of 700 mbar. After the produced methanol has been distilled (9.2 g obtained MeOH, theoretically 10.6 g of MeOH) the product was obtained as a colorless liquid at 95 °C/ 52 mbar applying a bath temperature of 139 °C. (22.6 g, 150 mmol, 90 % yield)

¹H-NMR (400 MHz, CDCl₃, 298K): δ /ppm = 4.85 (td, J = 5.2, 1.2 Hz, 1H, O-CH-O), 3.95 (m, 2H, O-CH₂), 3.77 (m, 2H, O-CH₂), 3.47 (dd, J = 5.3, 1.1 Hz, 2H, Cl-CH₂), 1.71 (m, 4H, CH₂-CH₂).

¹³C-NMR (101 MHz, CDCl₃, 298K): δ /ppm = 100.96 (O-CH-O), 66.76 (O-CH₂), 44.40 (CH-Cl), 29.32 (O-CH₂-CH₂).

GC-MS (Std. method, column: Rxi-5Sil MS): t_R = 5.67 min.

GC (Std. method, column: ZB-5): t_R = 7.90 min.

GC-calibration plot for yield determination of 2-Chloromethyl-1,3-dioxepane (**3**)Table S1: GC calibration for yield determination of 2-chloromethyl-1,3-dioxepane (**3**) using 1,10-dichlorodecane (1,10-DD) as internal standard.

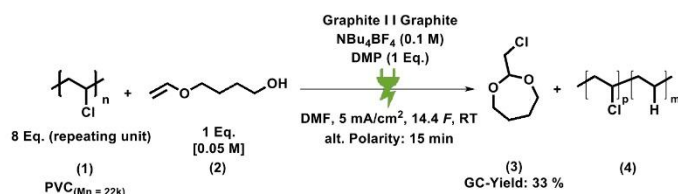
$A(3) \cdot A^{-1}(1,10\text{-dichlorodecane})$	$n(3) / \text{mmol}$
0.046	0.018
0.083	0.046
0.150	0.090
0.283	0.170
0.440	0.261
0.695	0.397
1.020	0.606
1.720	1.016
2.596	1.553

GC yield, 1,10-dichlorodecane as internal standard.

Electrochemical Screening

The starting conditions of the electrochemical screening are inspired by the electrochemical chlorination of arenes using PVC from McNEILL *et al.*^[2]

Initial conditions:



Starting from these electrochemical conditions the parameter screening was started by using the *OVAT* (*One variable at one time*)-screening approach. Major goal was increasing the obtained GC yield of the 2-chloromethyl-1,3-dioxepane (3), while avoiding crosslinking of PVC leading to precipitation and cathode passivation. The highlighted conditions in the tables (green line) have been chosen for following experiments.

Screening of solvents

Table S2: Solvent screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

Reaction scheme showing the electrochemical synthesis of 2-chloromethyl-1,3-dioxepane (3) from PVC (1) and allyl alcohol (2). The reaction conditions are: Graphite | Graphite, NBu_4BF_4 (0.05 M), DMP (1 Eq.), Solvents, 5 mA/cm², 8.0 F, RT, alt. Polarity: 15 min.

Solvent	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
DMF	33
NMP	16
Pyridine	0
Benzonitrile	0
TMU	13
DMA	47
Dioxane	0
DMF/Propylene carbonate 1:1 (v:v)	20
DMA/Propylene carbonate 1:1 (v:v)	30

GC yield, 1,10-dichlorodecane as internal standard.

Screening of supporting electrolytes

Table S3: Supporting electrolyte screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

Graphite | | Graphite
supporting electrolyte (0.05 M)
DMP (1 Eq.)
DMA, 5 mA·cm⁻², 8.0 F, RT
alt. Polarity: 15 min

(1) (2) (3) (4)

PVC (Mn = 22k)

Supporting Electrolyte	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
Bu ₄ NI	12
Bu ₄ NBr	4
Et ₄ NPF ₆	37
Bu ₄ NPF ₆	44
Et ₄ NBF ₄	44
Bu ₄ NBF ₄	47
Bu ₄ NOTf	51
Et ₄ NHCO ₃	34
Bu ₄ NOH (in H ₂ O)	26
Bu ₄ NOH (in MeOH)	32
Bu ₄ NOAc	39
MeEt ₃ NCl	76
Et ₄ NCl	77
Bu ₄ NCl	79
Oct ₃ MeNCl	81

GC yield, 1,10-dichlorodecane as internal standard.

All ammonium chloride supporting electrolytes led to highly increased GC-yields of (3). The use of chloride containing supporting electrolytes required the execution of control experiments. (See next section) It was continued with the ammonium chloride salts, specifically due to its low costs with Et₄NCl to develop an economically attractive electrochemical reaction.

Screening of electrochemical mediators

Table S4: Screening of mediators for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

Graphite | | Graphite
Bu₄NOTf (0.05 M)
Mediators (1 Eq.)
DMA, 5 mA·cm⁻², 8.0 F, RT
alt. Polarity: 15 min

(1) (2) (3) (4)

PVC (Mn = 22k)

Mediator	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
Dimethylphthalate (DMP)	51
None	37
Benzonitrile	30
Phthalonitrile	51
4-Cyanopyridine	29
9-Phenylcarbazole	2
Dimethylterephthalate	36
Mn(OTf) ₂	4
Mn(OAc) ₂	35
Ni(acac) ₂	35

GC yield, 1,10-dichlorodecane as internal standard.

Concentration screening

Screening of supporting electrolyte concentration

Table S5: Supporting electrolyte concentration screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

$c(\text{Et}_4\text{NCl}) / \text{mol L}^{-1}$	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
0.01	71
0.02	75
0.03	75
0.04	77
0.05	77

GC yield, 1,10-dichlorodecane as internal standard.

Screening of the mediator concentration

Table S6: Mediator concentration screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

$c(\text{DMP}) / \text{Eq.}$	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
None	34
0.5	40
1	66
1.5	66

GC yield, 1,10-dichlorodecane as internal standard.

Screening of the polymer concentrations

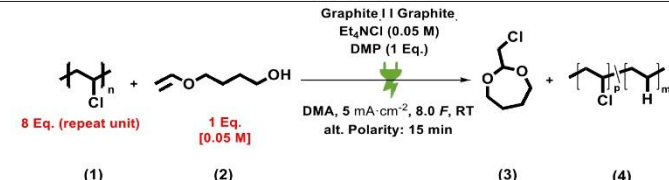
Table S7: Polymer concentration screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

Polymer concentration / mg mL^{-1}	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
25 ($c(\text{repeat unit}) = 0.4 \text{ M}$)	77
37.5 ($c(\text{repeat unit}) = 0.6 \text{ M}$)	62
50 ($c(\text{repeat unit}) = 0.8 \text{ M}$)	52
62.5 ($c(\text{repeat unit}) = 1.0 \text{ M}$)	46

GC yield, 1,10-dichlorodecane as internal standard.

Screening of PVC and chlorine acceptor ratio (excess of PVC)

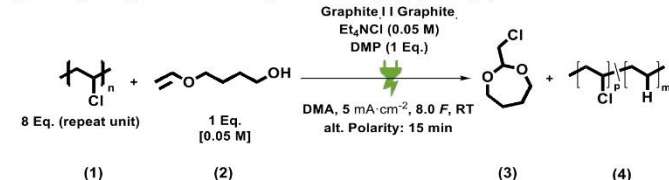
Table S8: PVC (repeat unit) and chlorine acceptor (2) ratio screening for the optimization of the electrochemical reaction. Yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

		
(1) PVC (Mn = 22k) (2) 1 Eq. [0.05 M]		(3) (4)
Eq. (PVC: chlorine acceptor (2))		GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
(8:1)		77
(6.7:1)		63
(5.7:1)		64
(5:1)		63
(4.4:1)		47

GC yield, 1,10-dichlorodecane as internal standard.

Screening the influence of water

Table S9: Determining the influence of water for the optimization of the electrochemical reaction. GC yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

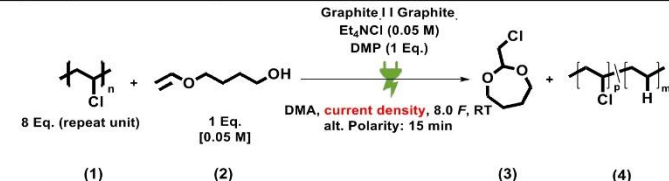
		
(1) PVC (Mn = 22k) (2) 1 Eq. [0.05 M]		(3) (4)
Added H ₂ O / Eq.		GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
0 (Dry DMA, stored under Ar)		75
0		77
0.5		71
1		68
10		37
50		19

GC yield, 1,10-dichlorodecane as internal standard.

Screening of electrochemical, technical parameters

Screening the current density

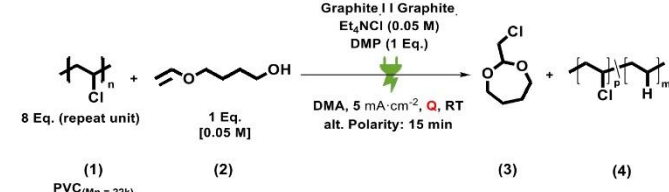
Table S10: Screening of the current density for the optimization of the electrochemical reaction. GC yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

		
(1) PVC (Mn = 22k) (2) 1 Eq. [0.05 M]		(3) (4)
Current density / mA·cm ⁻²		GC yield (2-chloromethyl-1,3-dioxepane (3)) / %
2.5		50
5.0		77
7.5		73
10.0		55
12.5		34
15.0		42

GC yield, 1,10-dichlorodecane as internal standard.

Screening of the applied charge

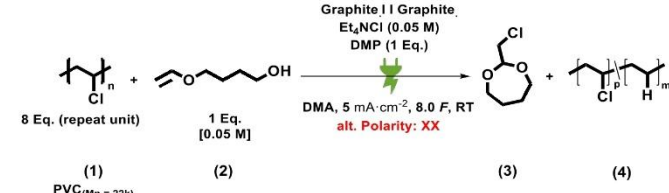
Table S11: Screening of the applied charge for the optimization of the electrochemical reaction. GC yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

		
Applied charge Q / F .	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %	
0 (no current)	0	
0.1	29	
0.2	50	
0.3	70	
0.4	73	
0.5	74	
1.0	77	
1.5	76	
2.0	73	
2.5	74	

GC yield, 1,10-Dichlorodecane as internal standard.

Screening the alternating polarity frequency

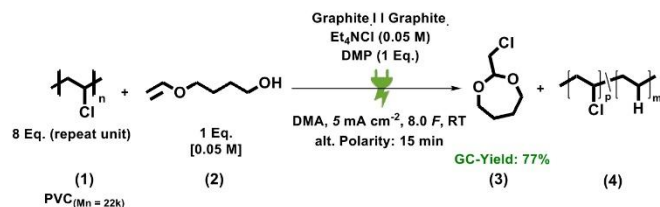
Table S12: Screening of the alternating polarity frequency for the optimization of the electrochemical reaction. GC yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

		
Alt. Polarity	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %	
3 s	7	
15 s	65	
30 s	71	
3 min	74	
30 min	75	
Direct current	76	

GC yield, 1,10-dichlorodecane as internal standard.

Optimized Conditions and Negative Controle

Optimized conditions: The electrochemical screening led to the following optimized conditions:



Besides the GC measurements for yield determination, GC-MS was performed. GC-MS showed full conversion of the starting material (2) and only the peaks of product (3), mediator (DMP) and the added internal standard. No side reactions have been observed.

GC-MS:

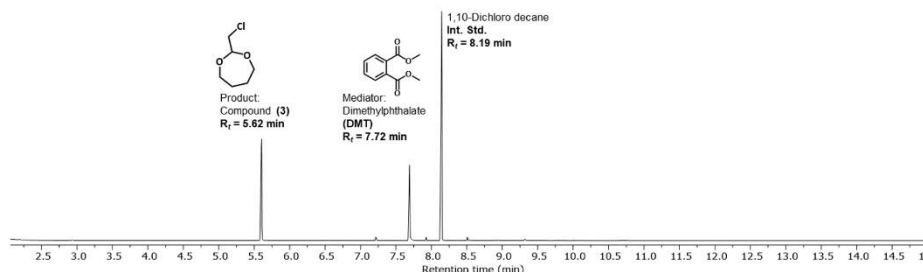
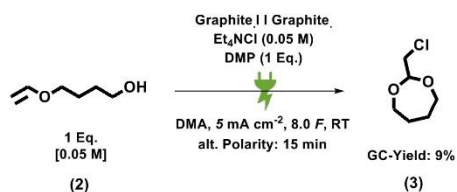


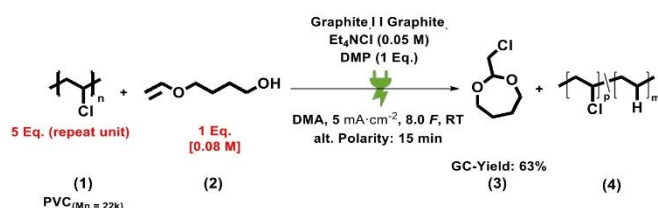
Figure S2: GC-MS chromatogram of the reaction solution after electrolysis.

Negative control: Due to the use of Et_4NCl as supporting electrolyte many control experiments have been performed (electrolysis reactions without PVC) during the electrochemical screening. The control experiments showed that PVC is essential for efficient product formation and only small amounts of chloride from the supporting electrolyte are involved in product formation. Also, the screening of supporting electrolytes concentration (Table S6) reveals that very low concentrations of Et_4NCl still lead to high GC yields of (3), proving that chlorine is cleaved electrochemically from PVC and used for product formation. Using the optimized conditions without PVC led to an obtained GC yield of 9%.



Increasing the Chlorine cleavage using *Design of Experiments* approach

To increase the dechlorination of the polymer material further the PVC (repeat unit): Chlorine acceptor ratio was changed to 5:1 (lower excess of PVC) leading to a decreased GC-yield of 63% for product (3). (Table 9)



In the following, a *Design of Experiments* approach was chosen to study the influence of three parameters (current density, applied charge and mediator concentration) and their interactions in detail. A 2³ full factorial experiment design was created, and certain parameter limits (current density j , amount of applied charge Q , and phthalate concentration $c(\text{DMT})$) were chosen. (Table S14) The evaluation of the experiments was performed using *Minitab* Statistical Software 22 (Minitab LLC).

Table S13: Determined yields of 2-chloromethyl-1,3-dioxepane (3) in a 2³ full factorial experimental with central composite design (CCD).

TERM		target value	
A	B	C	yield
Current density j / mA cm ²	Applied charge Q / F	DMP (Eq.)	(2-Chloromethyl-1,3-dioxepane (3)) / %
2.5	3.2	0.5	55 ± 0
2.5	12.8	0.5	57 ± 3
7.5	3.2	0.5	48 ± 2
7.5	12.8	0.5	38 ± 1
2.5	3.2	1.5	54 ± 2
2.5	12.8	1.5	61 ± 1
7.5	3.2	1.5	58 ± 1
7.5	12.8	1.5	64 ± 0
5.0	8.0	1.0	65 ± 1
5.0	0.8	1.0	16
5.0	17.6	1.0	65
0.5	8.0	1.0	41
10.0	8.0	1.0	62
5.0	8.0	0.1	39
5.0	8.0	2.0	63

GC yield: 1,10-dichlorodecane as internal standard.

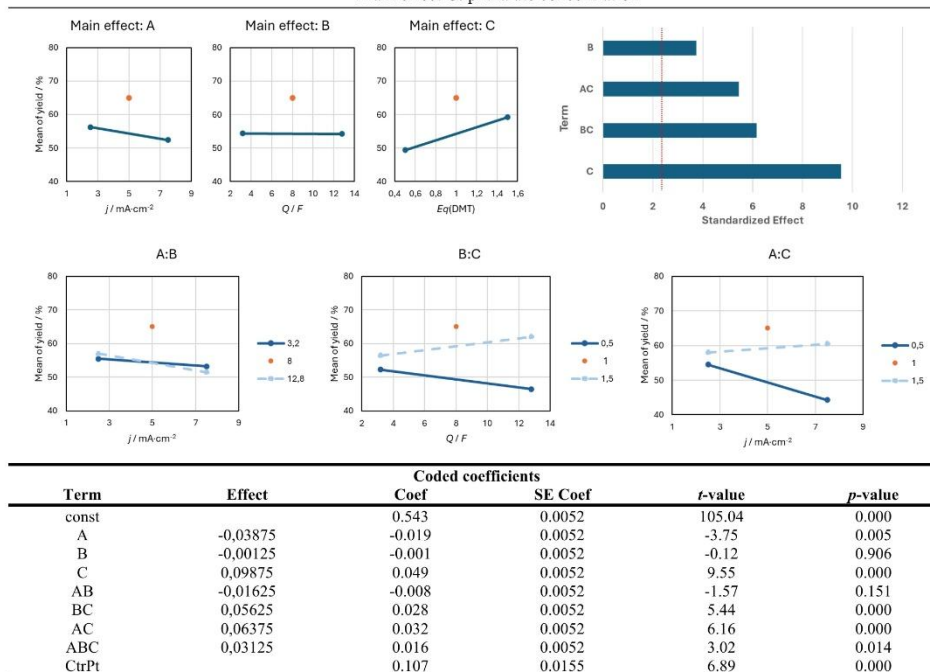
The corner and central points of the 2³ full factorial experiment design have been executed in duplicates. The standard deviation of these duplicates was chosen as error margin. The performed duplicates were well-reproducible. The statistical model exhibited an R^2_{corr} value of 92.9%.

Table S14: Main, Pareto and Interaction plots of the 2^2 full factorial experimental design for the product formation of 2-Chloromethyl-1,3-dioxepane (**3**). In addition, the coded coefficients of the experimental design with the respective effects, coefficients (Coef), standard errors (SE Coef) of the coefficients, t - and p -value of the model (bottom). The calculation was based on a significance level of $\alpha = 5\%$.

Main effect A: current density

Main effect B: applied charge

Main effect C: phthalate concentration

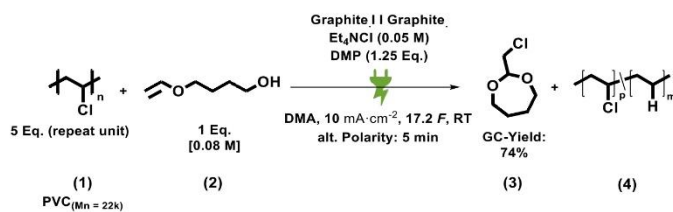


After the evaluation of the 2^3 full factorial experiment design a surface response experimental design was added and a target value optimization for obtained GC yield of (**3**) was performed that predicted parameter values for further experiment optimization.

The target value optimization suggested the following adjustments of applied charge, current density and mediator concentration to increase the GC yield of (**3**) further. ($j = 10 \text{ mA} \cdot \text{cm}^{-2}$, $Q = 17.2 F$, $c(\text{DMT}) = 0.1 \text{ M}$ (1.25 Eq.)). Applying these conditions led to an increase in GC yield of (**3**) from an initial 63% to 74%. These new conditions with a hypothesized higher chlorine transfer rate were named DoE-Conditions.

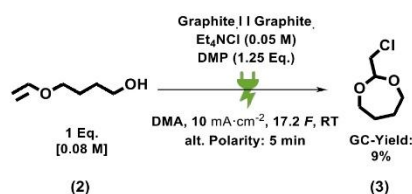
Design of Experiments Conditions and Control Experiment

DoE-conditions: The second optimization by DoE-approach.



The GC yield of 2-chloromethyl-1,3-dioxepane (3) was increased from 63% to 74% using a stoichiometry of PVC (1) (repeat unit) to chlorine acceptor (2) of 5:1.

Control experiment: The electrolysis without PVC led to a GC yield of 9%. Confirming that only small amounts of chlorine atoms from the supporting electrolyte are used for product formation of (3).



General procedures

General procedure A for the electrolysis in 5 mL IKA electrochemical cell (Optimized Conditions)

The polymer material PVC (100 mg, 1.6 mmol, 8 eq.(repeat unit)), the supporting electrolyte tetraethylammonium chloride (33.1 mg, 0.2 mmol, 1 eq, 0.05 M), dimethyl phthalate (38.8 mg, 0.2 mmol, 1 eq.) and 4-hydroxybutyl vinyl ether (23.2 mg, 25 μ L, 0.2 mmol, 1 eq.) were transferred into the electrochemical cell (ElectraSyn® 5mL) and dissolved in *N,N*-dimethylacetamide (4 mL). The reaction mixture was stirred (500 rpm) for 15 minutes at room temperature using a Teflon-coated magnetic stir bar. The electrodes and the teflon cap were attached to the reaction vessel and the electrolysis was started. ($Q = 8 F, j = 5 \text{ mA}\cdot\text{cm}^{-2}$, alt. Polarity = 15 min (4 h⁻¹), electrode surface area ca. 3.0 cm²). After the reaction was finished, the internal standard 1,10-dichlorodecane (50 μ L) was added and stirred for 5 minutes. For yield/conversion determination, samples for gas chromatography were prepared. For polymer analysis, the solution was added dropwise into methanol (50 mL) to induce polymer precipitation. After centrifugation the obtained polymer was redissolved in Tetrahydrofuran (3 mL) and precipitated again in methanol. After centrifugation the polymer was dried *in vacuo* and obtained as amorphous, colorless solid.

General procedure B for the electrolysis in 5 mL IKA electrochemical cell (DoE Conditions)

The polymer material PVC (100 mg, 1.6 mmol, 5 eq.(repeat unit)), the supporting electrolyte tetraethylammonium chloride (33.1 mg, 0.2 mmol, 0.625 Eq, 0.05 M), dimethyl phthalate (77.7 mg, 0.4 mmol, 1.25 eq.) and 4-hydroxybutyl vinyl ether (37.2 mg, 38 μ L, 0.32 mmol, 1 eq.) were transferred into the electrochemical cell (ElectraSyn® 5mL) and dissolved in *N,N*-dimethylacetamide (4 mL). The reaction mixture was stirred (500 rpm) for 15 minutes at room temperature. The electrodes and the teflon cap were attached to the reaction vessel and the electrolysis was started. ($Q = 17.2 F, j = 10 \text{ mA}\cdot\text{cm}^{-2}$, alt. Polarity = 5 min (4 h⁻¹), electrode surface area ca. 3.0 cm²) After the reaction was finished, the internal standard 1,10-dichlorodecane (50 μ L) was added and the solution was stirred for 5 minutes. For yield/conversion determination, samples for gas chromatography were prepared. For polymer analysis, the solution was added dropwise into methanol (50 mL) to induce polymer precipitation. After centrifugation the obtained polymer was redissolved in Tetrahydrofuran (3 mL) and precipitated again in methanol. After centrifugation the polymer was dried *in vacuo* and obtained as amorphous, colorless solid.

Isolation of 2-Chloromethyl-1,3-dioxepane (3): After the electrolysis was finished the reaction solution was added dropwise into methanol. The precipitated polymer was centrifuged, and the solution was transferred into a round bottom flask. Methanol was removed under reduced pressure. Lithium chloride solution (5%) was added to the residual mixture and the aqueous solution was extracted with diethyl ether. The organic phase was extracted with 5% lithium chloride solution and dried with MgSO₄. After filtration, the solvent was removed *in vacuo* and obtained the product via distillation at 82 °C/22 mbar. (Colorless liquid, isolated yield of 53%)

Polymer Analysis

After the development of the Optimized and DoE Conditions the obtained dechlorinated PVC was analyzed using size exclusion chromatography, NMR Spectroscopy, thermogravimetric analysis, differential scanning calorimetry and elemental analysis.

Size exclusion chromatography

The SEC elugram of the starting material shows a shoulder towards lower molecular weights. After the electrolysis using the optimized conditions the peak of the main species shifts to lower molecular weights, and the shoulder intensifies.

The defunctionalization leads to a poly(ethylene) subunit with different swelling behavior in DMF. The electrochemical backbone chain scission at random positions is less likely as no low molecular weight fragments or oligomers are visible in the elugram. Additionally, there are no species of higher molecular weights observed, hence recombination of polymer backbone radicals does not occur during electrolysis.

NMR Spectroscopy

Deuterated *d*8-Tetrahydrofuran was used to record the ¹H-NMR spectra of the starting material PVC. The polymer material became soluble in *d*₂-Tetrachlorethane after electrolysis, which was preferred for spectra evaluation due to less signal overlap.

It was shown that the phthalate esters are not electrochemically stable during the electrolysis with PVC. McNEILL *et al.* showed that bulk electrolysis of di(2-ethylhexyl) phthalate (DEHP) showed the cleavage of the molecule's ester bonds leading to the detection of the alcohol (2-ethylhexanol). Due to the use of Dimethyl phthalate (DMP) in the electrolysis the generated methoxy species react with the polymer backbone leading to methoxy functionalization of the polymer.^[2]

Multiple Electrolysis cycles

After the first electrolysis the polymer material was precipitated in MeOH as described in general procedure B, dried *in vacuo* and was redissolved in DMA for the next electrolysis reaction, applying again DoE conditions. This has been repeated four times. After each cycle the GC yield of 2-chloromethyl-1,3-dioxepane (**3**) has been determined.

Table S15: GC yields of 2-chloromethyl-1,3-dioxepane (3) of multiple electrolysis cycles using the PVC material as chlorine source four times. GC yields determined via gas chromatography using 1,10-dichlorodecane as internal standard.

(1) PVC (Mn = 22k)	(2)
Multiple electrolysis cycles	
GC yield (2-chloromethyl-1,3-dioxepane (3)) / %	
1 st cycle	74
2 nd cycle	57
3 rd cycle	32
4 th cycle	17

GC yield, 1,10-dichlorodecane as internal standard.

The obtained polymer after the fourth electrolysis cycle was soluble in MeOH and had to be precipitated in a mixture of cold hexane:diethyl ether (1:1).

In SEC chromatography no higher molecular weight species are observed that result out of uncontrolled radical backbone formation and network formation. ¹H NMR spectroscopy shows that the chemical nature of the starting material has been modified extensively, while the original PVC peak at a chemical shift of $\delta = 4.2\text{--}4.6$ ppm is not observable. This observation suggests a particularly high dechlorination rate of the polymer material using the method of multiple electrolysis cycles.

Thermogravimetric analysis (TGA)

To learn more about the dechlorination rates of the electrochemically treated PVC material TGA measurements were executed. In general, PVC is thermally unstable, releasing HCl at around 280 °C. The second mass loss occurs around 450 °C indicates hydrocarbon backbone degradation. The theoretical mass loss of pure PVC due to HCl release is expected to be 58wt% leaving 42wt% of hydrocarbon material behind. The starting material PVC (1) (Sample 1, **a**) reveals a mass loss of 61% at 280 °C. This mass loss is particularly sharp due to the zipper mechanism of thermal PVC elimination.^[3] If we compare this sample with the electrochemically dechlorinated samples the mass loss at 280 °C decreases and broadens, likely due to polymer inhomogeneity and dechlorination.

The trend of decreased mass loss at 280 °C from optimized (b) via DoE conditions (c) to multiple electrolysis cycles (d) agrees with the findings from ¹H NMR spectroscopy and elemental analysis going down to a 11% mass loss for sample 4 (multiple electrolysis cycles).

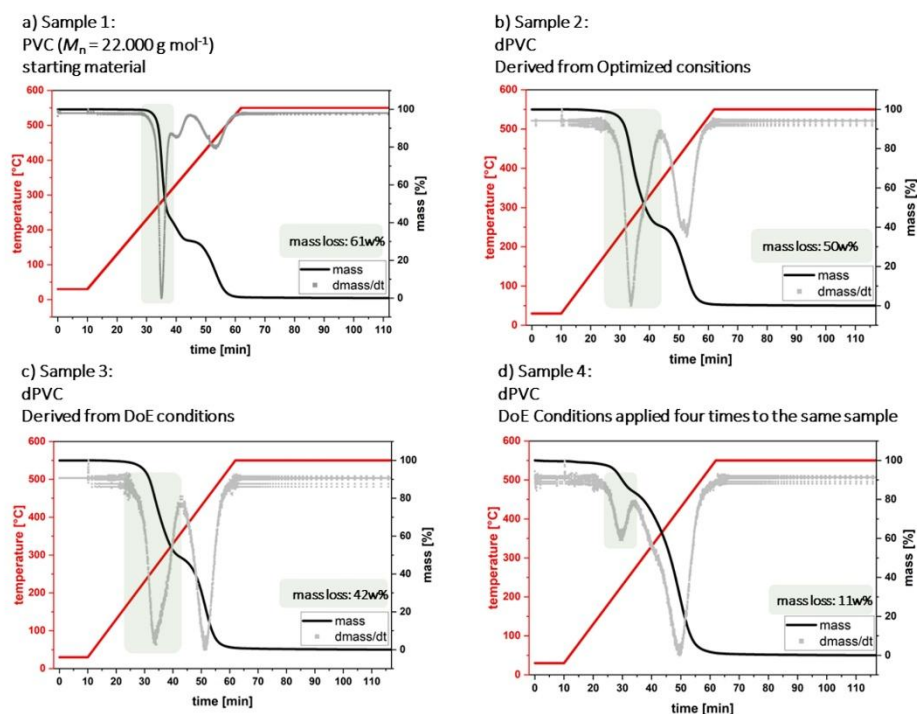


Figure S3: TGA data for the starting material (a) and the dechlorinated polymer samples. (b)- d))

NMR-spectroscopy showed significant amount of methoxy recombination of the polymer during the electrolysis. The elimination of the methoxy groups that could occur below 300°C introduces distortions to the interpretation of the TGA data, which may result in erroneous conclusions regarding the degree of dechlorination. Consequently, supplementary elementary analyses were conducted.

Elemental analysis

Elemental analysis shows that the chlorine content decreases in all electrochemically treated samples. The optimized conditions lead to a dechlorination rate of 25% of PVC while the DoE conditions show more efficient dechlorination of 35%. The multiple treatment of PVC material applying the DoE conditions leads to a residual chlorine content of 3.58% after four electrolysis, yielding a PVC dechlorination rate of 94%.

Table S16: Elemental Analysis of the starting material, theoretical values and dechlorinated PVC samples.

Sample	%C	%H	%N	%O	%Cl	Sum / %
Starting Material – PVC ($M_n = 22k$)	37.96	4.88	0.00	0.82	55.98	99.64
PVC (theoretical)	38.46	4.83	0.00	0.00	56.71	100.00
Sample 2 - Optimized Conditions – dechlorinated PVC	44.84	5.27	0.43	6.38	42.35	99.27
DoE Conditions – dechlorinated PVC	48.19	5.39	0.15	9.28	36.36	99.37
DoE Conditions (Applied four times) – dechlorinated PVC	64.25	6.84	0.76	23.93	3.58	99.36

Elemental analysis of the starting material was executed and served as control experiment; the obtained result agrees well with the theoretical elemental composition.

Upscale and PVC (waste) products

Table S17: Screening of the current density for the optimization of the electrochemical reaction. GC yields of 2-chloromethyl-1,3-dioxepane (3) determined via gas chromatography using 1,10-dichlorodecane as internal standard.

Polymer material	GC yield (2-chloromethyl-1,3-dioxepane (3)) / %	
	Optimized Cond.	DoE-Conditions
5 mL vessel, PVC ($M_n = 22k$)	77	74
10 mL vessel, PVC ($M_n = 22k$)	66	65
250 mL vessel, PVC ($M_n = 22k$)	-	34
5 mL vessel, PVC ($M_n = 99k$)	64	58
1-credit card	71	43
2-water hose	72	63
3-tube	68	56
4-cable channel	59	70
5-cable coating	65	51

GC yield, 1,10-dichlorodecane as internal standard.

Upscale experiments

For the upscale experiments general procedure B was executed while the weights and volumes of used chemicals were multiplied by the upscale factor (2x for the 10 mL vessel and 50x for the 250 mL vessel).

High molecular weight PVC

Since industrially produced PVC for everyday products has usually a higher molecular weight (approx. 100.000 g/mol), the influence of the molecular weight on the electrochemical reaction was investigated.

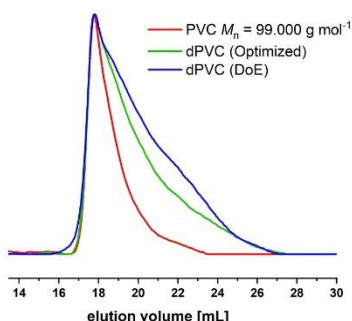


Figure S4: SEC elution traces of the starting material (red) and the dechlorinated PVC after electrolysis obtained from the optimized conditions (green), DoE conditions (blue). RI signal; eluent: DMF, 40 °C; standard: PMMA.

As discussed in section 2.4, the GC yield of the cyclic acetal decreases using high-molecular-weight PVC due to reasons such as lower average accessibility of carbon-chloride sites and increased viscosity of the reaction solution that decreases efficient mass transport during electrolysis. Therefore, we determined the viscosities of polymer solutions using PVC species with different molecular

weights. (Figure S5) In the left graph the viscosities of just the PVC polymer solutions in DMA were determined with the concentration how it's used in electrolysis ($c = 0.4$ M, PVC (repeat unit)). The polymer solution of low-molecular-weight PVC exhibits a viscosity of $\eta = 4.5$ Pa s, whereas the higher-molecular weight PVC solution gives an expected higher viscosity of $\eta = 12.7$ Pa s. In the right graph the viscosities of the electrolyte solutions (DoE conditions, $c = 0.4$ M, PVC (repeat unit)) additionally containing supporting electrolyte, the chlorine acceptor and the phthalate ester were determined. The obtained viscosities of the electrolyte solutions (PVC ($22.000 \text{ g mol}^{-1}$) $\eta = 4.4$ Pa s, PVC ($99.000 \text{ g mol}^{-1}$) $\eta = 12.8$ Pa s) are comparable with the viscosities obtained for solutions of PVC in DMA. These findings indicate that the molecular weight of the polymer PVC highly influences the viscosity of the reaction solution, while other components such as supporting electrolyte, phthalate ester and chlorine acceptor do not have a major impact on the solution viscosity.

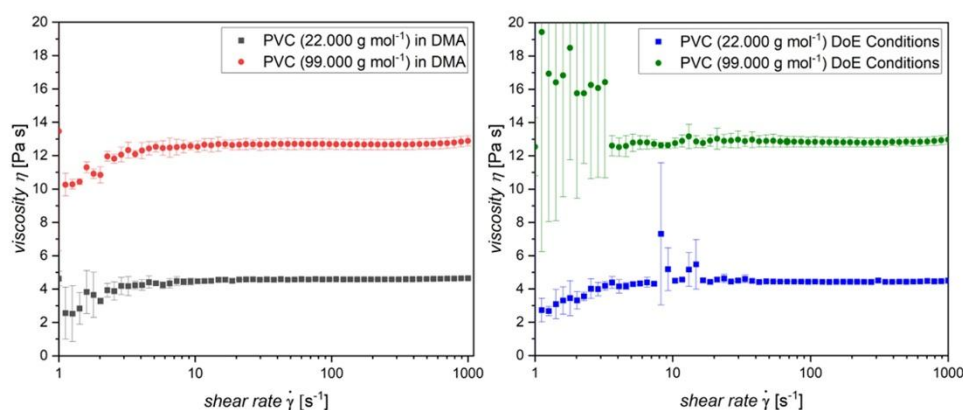
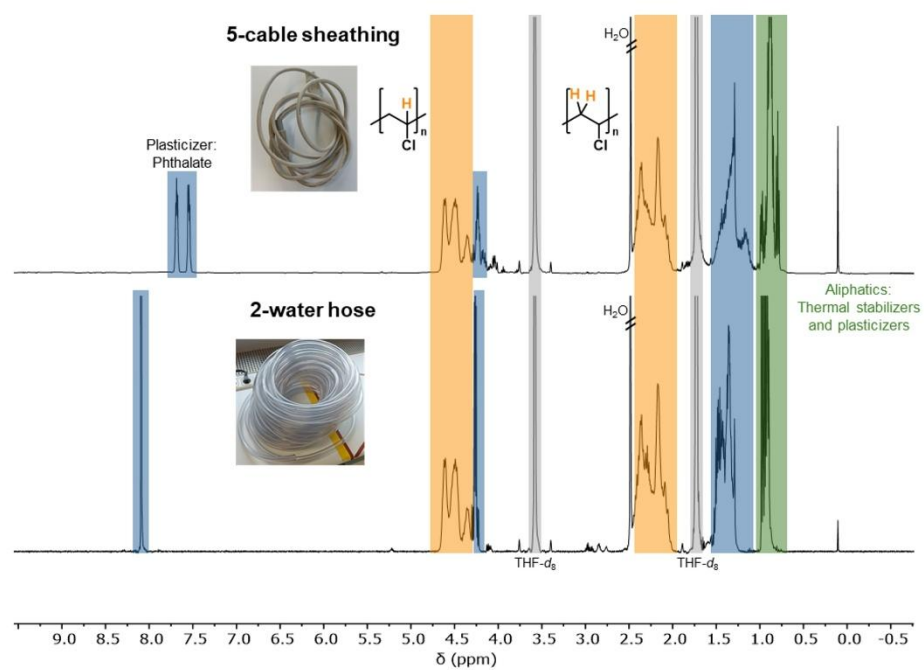


Figure S5: Determination of the viscosity of the polymer solutions containing different molecular weight PVC species. Left: PVC ($c = 0.4$ M, PVC (repeat unit)) in DMA using low-molecular-weight PVC ($M_n = 22.000 \text{ g mol}^{-1}$, *black graph*) and high molecular weight PVC ($M_n = 99.000 \text{ g mol}^{-1}$, *red graph*). Right: Solutions used for electrolysis (DoE conditions) with Et_4NCl (33.1 mg, 0.2 mmol, 0.625 Eq, 0.05 M), dimethyl phthalate (77.7 mg, 0.4 mmol, 1.25 eq.) and 4-hydroxybutyl vinyl ether (37.2 mg, 38 μL , 0.32 mmol, 1 eq.) using low-molecular-weight PVC ($M_n = 22.000 \text{ g mol}^{-1}$, *blue graph*) and high molecular weight PVC ($M_n = 99.000 \text{ g mol}^{-1}$, *black graph*).

Table S18: Overview of the viscosity measurements.

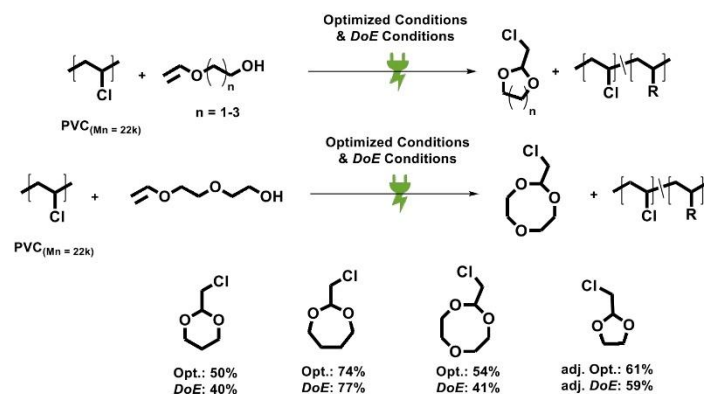
	η (PVC ($M_n = 22.000 \text{ g mol}^{-1}$)) / Pa s	η (PVC ($M_n = 99.000 \text{ g mol}^{-1}$)) / Pa s
In DMA ($c = 0.4$ M, PVC (repeat unit))	4.5	12.7
DoE Conditions ($c = 0.4$ M, PVC (repeat unit))	4.4	12.8

Analysis of PVC waste products

Figure S6: ^1H NMR of PVC products. (400 MHz, $\text{THF}-d_8$, 298 K)

Cyclic acetal scope

Overview



Synthesis of 2-chloromethyl-1,3-dioxolane (5-membered Ring)

The starting material ethyleneglycol monovinylether and the product 2-chloromethyl-1,3-dioxolane for GC-calibration were purchased commercially.

Ethyleneglycol monovinylether

$^1\text{H-NMR}$ (400 MHz, CD_2Cl_2 , 298 K): $\delta/\text{ppm} = 6.50$ (dd, $J = 14.3, 6.8$ Hz, 1H, **CH**-O), 4.27 – 3.98 (m, 2H, **CH**₂), 3.78 (d, $J = 4.0$ Hz, 4H, O-**CH**₂), 2.16 – 2.08 (m, 1H, **OH**).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 152.06$ (**HC**=**CH**₂), 87.10 (**HC**=**CH**₂), 69.83 (O-**CH**₂), 61.51 (**CH**₂-OH).

2-Chloromethyl-1,3-dioxolane

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 5.16$ (t, $J = 4.0$ Hz, 1H, O-**CH**-O), 4.07 – 3.92 (m, 4H, O-**CH**₂), 3.54 (d, $J = 4.0$ Hz, 2H, **CH**₂-Cl).

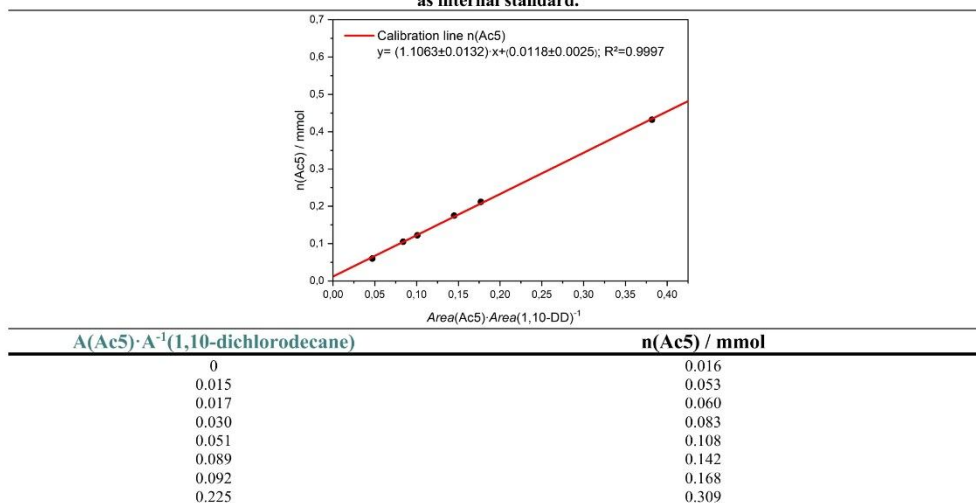
$^{13}\text{C-NMR}$ (101 MHz, CDCl_3 , 298 K): $\delta/\text{ppm} = 102.78$ (O-**CH**-O), 65.96 (O-**CH**₂), 45.04 (**CH**₂-Cl).

GC-MS (Std. method, column: Rxi-5Sil MS): $t_R = 3.70$ min.

GC (Std. method, column: ZB-5): $t_R = 4.84$ min.

GC calibration for yield determination of 2-chloromethyl-1,3-dioxolane

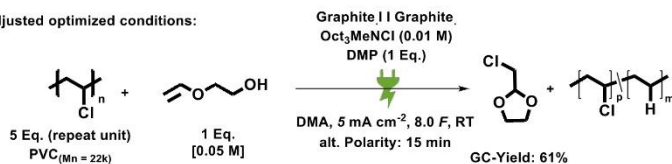
Table S19: GC calibration for yield determination of 2-chloromethyl-1,3-dioxolane (5) using 1,10-dichlorodecane (1,10-DD) as internal standard.



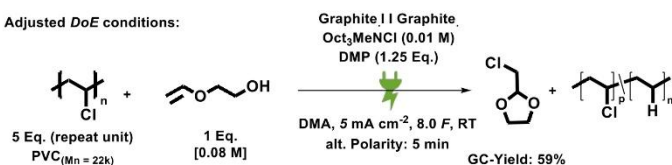
GC yield, 1,10-dichlorodecane as internal standard.

The general procedures A & B using the starting material instead of (2) were applied to test the transferability towards different ring sizes. Due to the very low GC-yields the optimized and DoE conditions were adjusted: The supporting electrolyte Oct₃MeNCl (0.01 M) was used with a smaller applied charge. These changes led yields of 61% and 59% for the optimized conditions and the DoE conditions.

Adjusted optimized conditions:



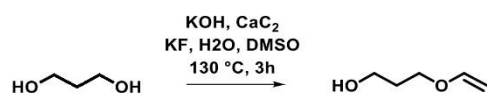
Adjusted DoE conditions:



Synthesis of 2-chloromethyl-1,3-dioxane (6-membered ring)

The starting material 1-vinyl-propandi-1,3-ol^[4] and the product 2-chloromethyl-1,3-dioxane^[1] for the electrochemical cyclic acetal formation have been synthesized according to the following procedures:

Classical synthesis of 1-vinyl-propandi-1,3-ol



A pressure pipe flask (25 mL) was charged with potassium hydroxide (29 mmol, 1.63 g, 1 eq.), 1,3-propanediol (29 mmol, 2.21 g, 2.1 mL, 1 eq.), potassium fluoride (116 mmol, 6.70 g), and calcium carbide (58 mmol, 3.70 g). Dry DMSO (10 mL) was then added, and the flask was sealed with a septum. After stirring at room temperature for 5 minutes, water (120 mmol, 2.2 mL) was introduced through the valve. The mixture was subsequently heated to 130 °C with vigorous stirring for 3 h. Upon cooling to 25 °C, the reaction mixture was extracted with diethyl ether (3 × 50 mL). The combined organic layers were concentrated under reduced pressure to give 1-vinyl propanedi-1,3-ol as a colorless oil. (21%)

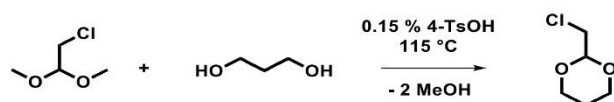
¹H-NMR (400 MHz, CDCl₃, 298 K): δ/ppm = 6.43 (dd, *J* = 14.3, 6.8 Hz, 1H, CH=CH₂), 4.18 (dd, *J* = 14.3, 2.1 Hz, 1H, CH=CH₂), 3.98 (dd, *J* = 6.8, 2.1 Hz, 1H, CH=CH₂), 3.80 (t, *J* = 6.0 Hz, 2H, =CH₂-O-CH₂), 3.73 (q, *J* = 5.7 Hz, 2H, CH₂-OH), 2.42 (t, *J* = 5.2 Hz, 1H, CH₂-OH), 1.88 (p, *J* = 6.0 Hz, 2H, CH₂-CH₂-CH₂).

¹³C-NMR (101 MHz, CDCl₃, 298 K): δ/ppm =

GC-MS (Std. method, column: Rxi-5Sil MS): t_R = 3.13 min.

GC (Std. method, column: ZB-5): t_R = 4.32 min.

Classical synthesis of the 2-chloromethyl-1,3-dioxane



2-Chloromethyl-1,3-dioxane was synthesized by fractional vacuum distillation. 1,3-propanediol (10.02 g, 0.13 mol, 1 eq.), chloroacetaldehyde dimethylacetal (16.41 g, 0.13 mol, 1 eq.) and 4-toluenesulfonic acid (38 mg, 0.203 mmol, 0.002 eq.) were added to in a round bottom flask. The reaction mixture was heated under normal pressure and MeOH was distilled off at 58 °C. Fractional distillation was then carried out at 58 mbar. The colorless product was obtained in the collecting flask at a temperature of 30 °C. (77%)

¹H-NMR (400 MHz, CDCl₃, 298 K): δ/ppm = 4.69 (t, *J* = 4.5 Hz, 1H, O-CH-O), 4.11 (ddd, *J* = 12.0, 5.0, 1.4 Hz, 2H, O-CH₂), 3.85 – 3.73 (m, 2H, O-CH₂), 3.45 (d, *J* = 4.5 Hz, 2H, Cl-CH₂), 2.05 (dt, *J* = 13.5, 12.5, 5.0 Hz, 1H, CH₂), 1.35 (dt, *J* = 13.5, 2.6, 1.4 Hz, 1H, CH₂).

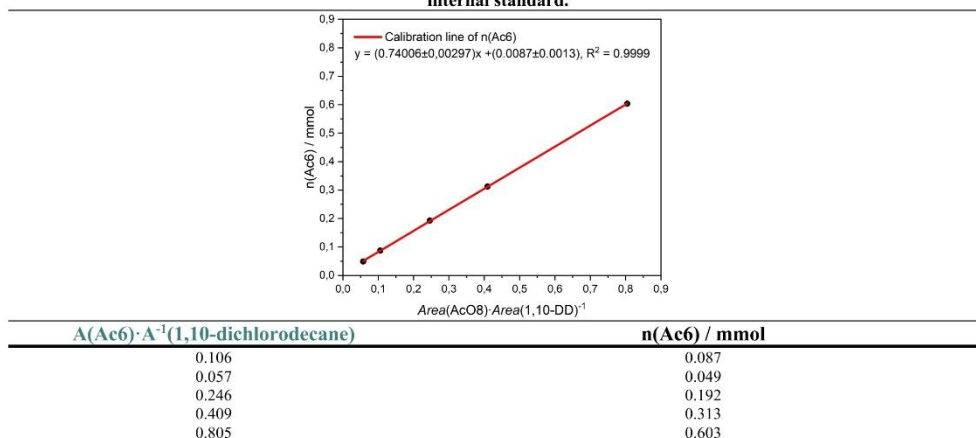
¹³C-NMR (101 MHz, CDCl₃, 298 K): δ/ppm = 100.03 (O-CH-O), 66.95 (O-CH₂), 44.69 (Cl-CH₂), 25.50 (CH₂).

GC-MS (Std. method, column: Rxi-5Sil MS): t_R = 4.70 min.

GC (Std. method, column: ZB-5): t_R = 6.44 min.

GC calibration for yield determination of 2-chloromethyl-1,3-dioxane

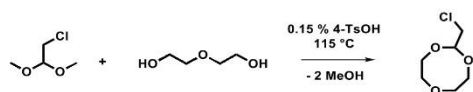
Table S20: GC calibration for yield determination of 2-chloromethyl-1,3-dioxane (6) using 1,10-dichlorodecane (1,10-DD) as internal standard.



GC yield, 1,10-dichlorodecane as internal standard.

Synthesis of 2-chloromethyl-[1,3,6] trioxocane (8-membered ring)

The starting material di ethylene glycol mono vinyl ether was purchased commercially. The product was synthesized according to a synthesis protocol published from TARDY *et al.* The product was used for GC calibration and GC-MS identification.^[1]

Classical synthesis of of 2-chloromethyl-[1,3,6] trioxocane

2-chloromethyl-1,3,6-trioxocane was synthesized by fractional vacuum distillation. Diethylene glycol (10.02 g, 0.094 mol, 8.95 mL, 1 eq.), chloroacetaldehyde dimethylacetal (11.74 g, 0.094 mol, 10.73 mL, 1 eq.) and 4-toluenesulfonic acid (28 mg, 0.147 mmol, 0.002 eq.) were added to in a round bottom flask. The reaction mixture was heated under normal pressure and MeOH was distilled off at 58 °C. Fractional distillation was then carried out at 57 mbar. The colorless product crystallized out in the condenser and in the collecting flask at a temperature of 30 °C.

¹H-NMR (400 MHz, CDCl₃, 298 K): δ /ppm = 4.78 (t, J = 5.4 Hz, 1H, O-CH-O), 4.05 – 3.91 (m, 4H, CH-O-CH₂), 3.83 – 3.61 (m, 4H, CH₂-O), 3.47 (d, J = 5.4 Hz, 2H, CH₂-Cl).

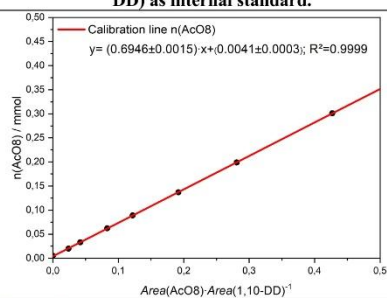
¹³C-NMR (101 MHz, CDCl₃, 298 K): δ /ppm = 106.47 (O-CH-O), 73.97 (CH-O-CH₂), 71.96 (O-CH₂), 45.49 (CH₂-Cl).

GC-MS (Std. method, column: Rxi-5Sil MS): t_R = 6.14 min.

GC (Std. method, column: ZB-5): t_R = 8.75 min.

GC calibration for yield determination of 2-chloromethyl-[1,3,6] trioxocane

Table S21: GC calibration for yield determination of 2-chloromethyl-[1,3,6] trioxocane (7) using 1,10-dichlorodecane (1,10-DD) as internal standard.



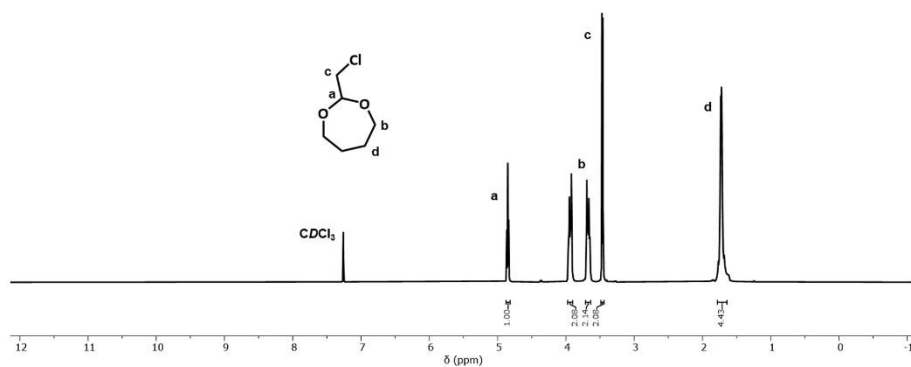
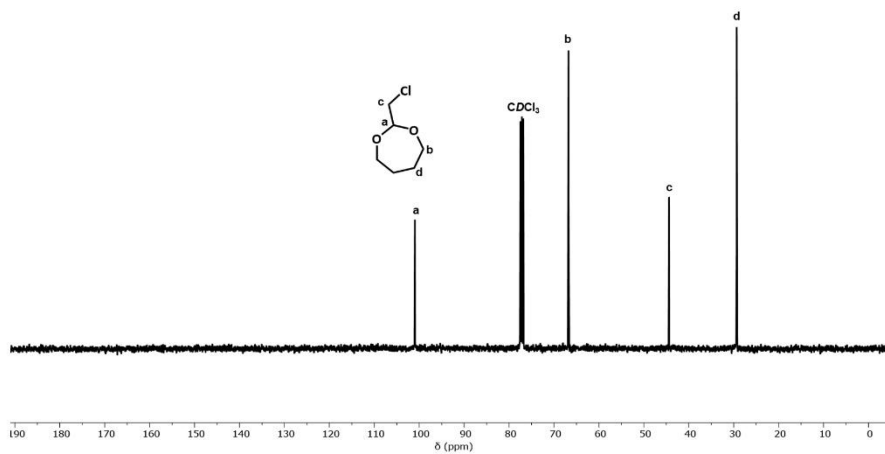
$A((7)) \cdot A^{-1}(1,10\text{-dichlorodecane})$	$n((7)) / \text{mmol}$
0	0.005
0.024	0.020
0.042	0.033
0.083	0.062
0.122	0.089
0.192	0.137
0.281	0.199
0.427	0.301

GC yield, 1,10-dichlorodecane as internal standard.

References

- [1] A. Tardy, N. Gil, C. M. Plummer, D. Siri, D. Gigmes, C. Lefay, Y. Guillaneuf, *Angew. Chem. Int. Ed.* **2020**, *59*, 14517.
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- [3] J. Yu, L. Sun, C. Ma, Y. Qiao, H. Yao, *Waste Manag.* **2016**, *48*, 300.
- [4] G. Werner, K. S. Rodygin, A. A. Kostin, E. G. Gordeev, A. S. Kashin, V. P. Ananikov, *Green Chem.* **2017**, *19*, 3032.

Spectra

Figure S7: ^1H NMR spectrum of compound 3. (400 MHz, CDCl_3 , 298 K)Figure S8: ^{13}C NMR spectrum of compound 3. (101 MHz, CDCl_3 , 298 K)

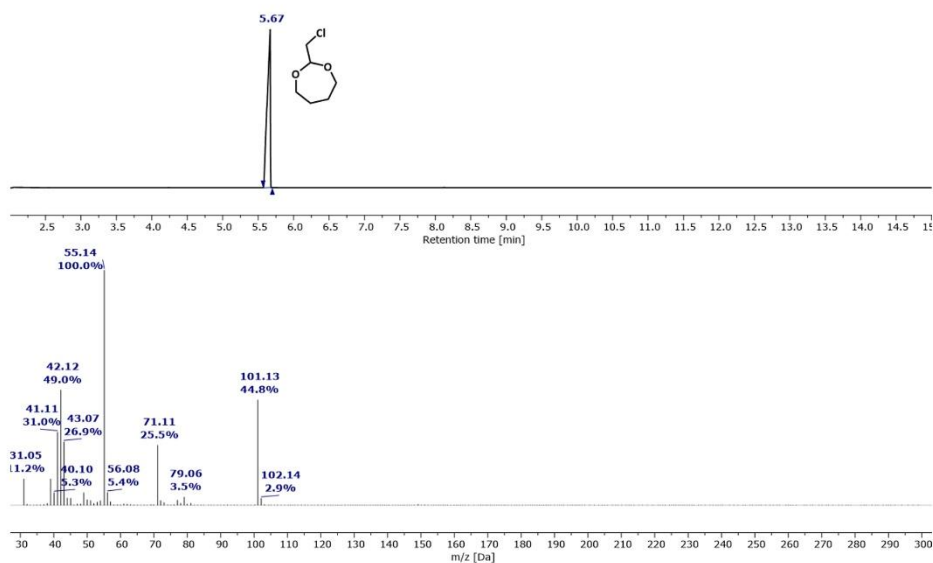


Figure S9: GC-MS trace and mass fragmentation pattern of compound 3.

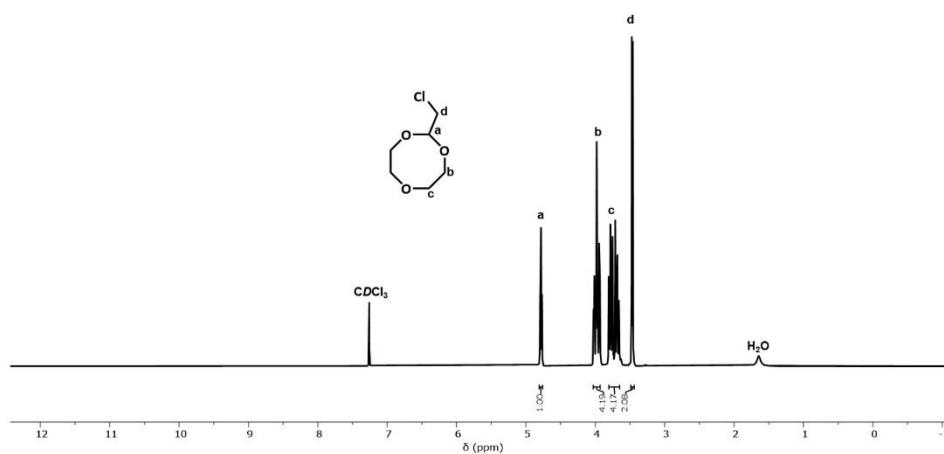


Figure S10: ¹H NMR spectrum of compound 7. (400 MHz, CDCl₃, 298 K)

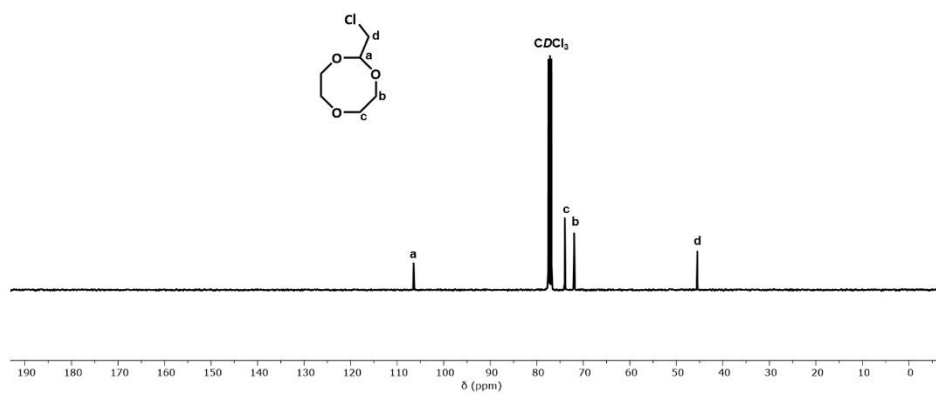
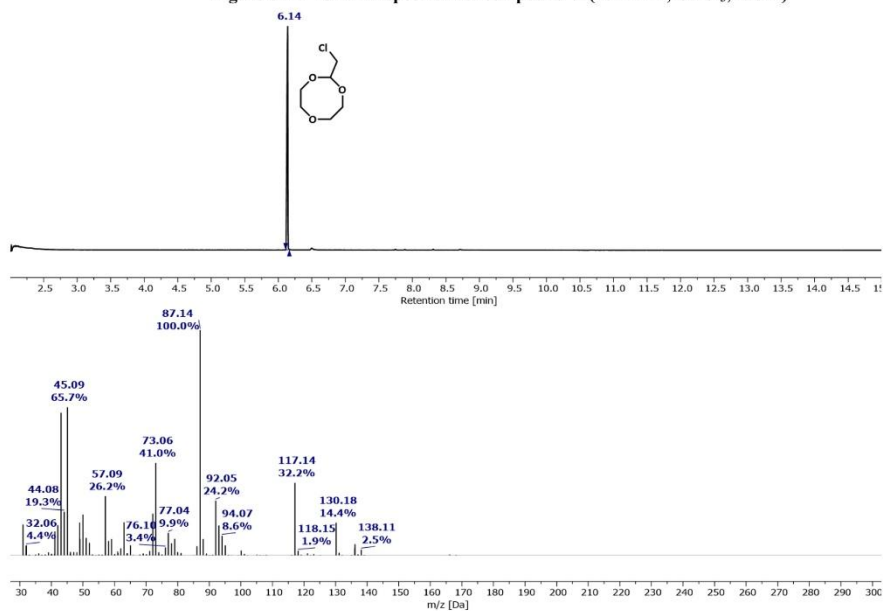
Figure S11: ¹³C NMR spectrum of compound 7. (101 MHz, CDCl₃, 298 K)

Figure S12: GC-MS trace and mass fragmentation pattern of compound 7.

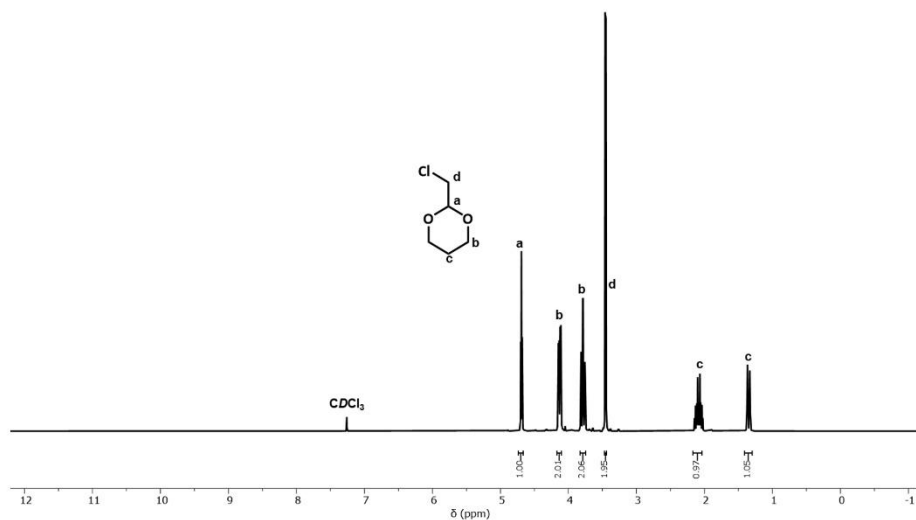


Figure S13: ¹H NMR spectrum of compound 6. (400 MHz, CDCl₃, 298 K)

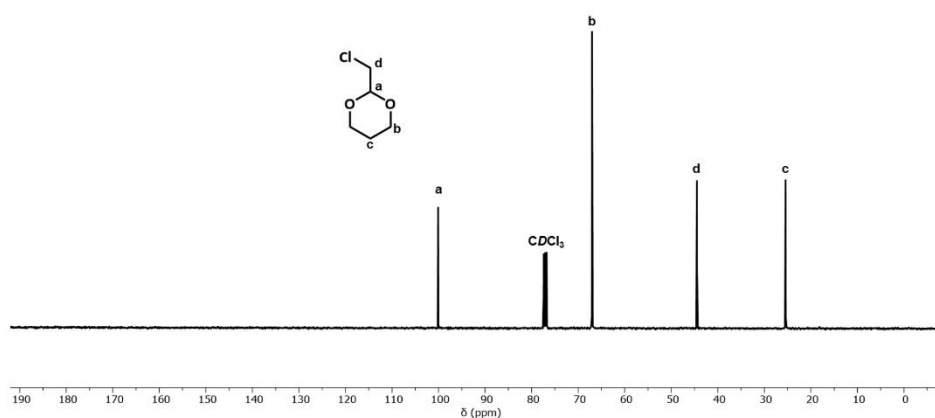


Figure S14: ¹³C NMR spectrum of compound 7. (101 MHz, CDCl₃, 298 K)

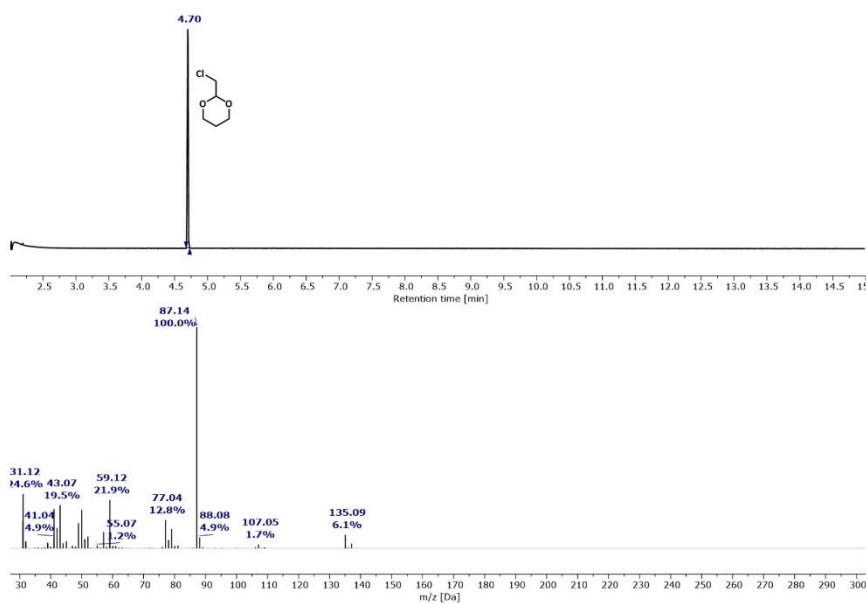


Figure S15: GC-MS trace and mass fragmentation pattern of compound 7.

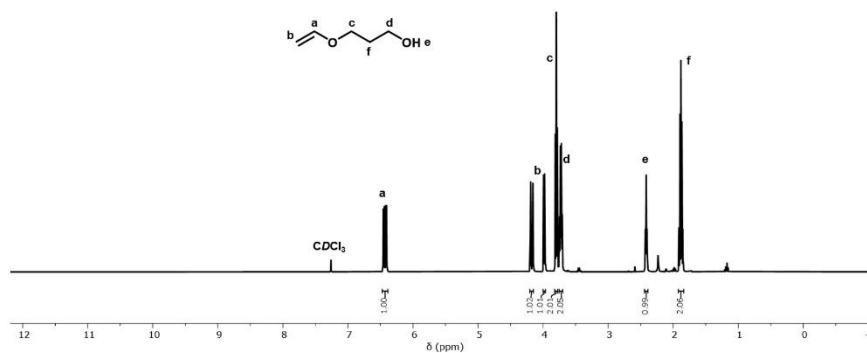


Figure S16: ¹H NMR spectrum of 3-hydroxypropyl vinyl ether. (400 MHz, CDCl₃, 298 K)

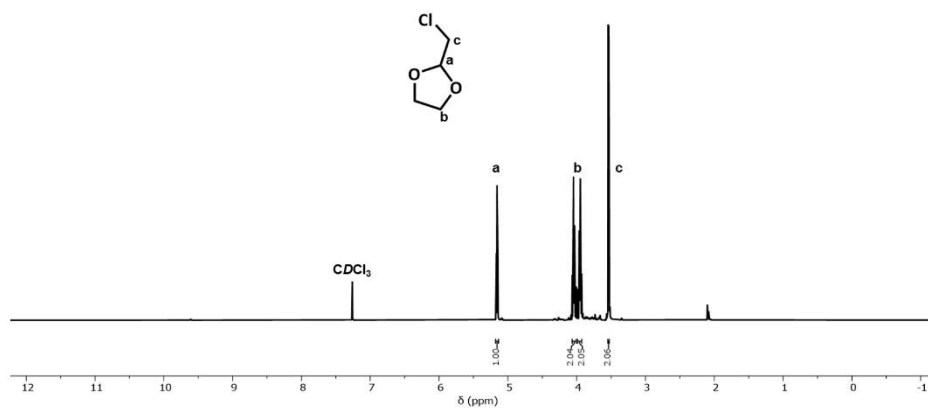


Figure S17: ¹H NMR spectrum of compound 5. (400 MHz, CDCl₃, 298 K)

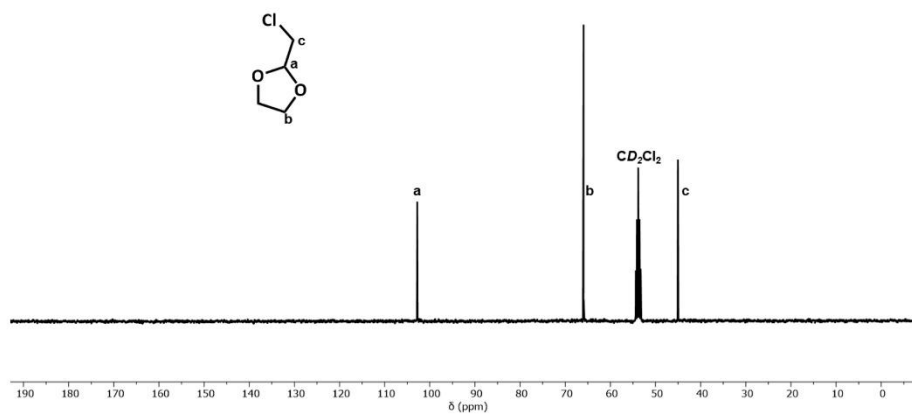


Figure S18: ¹³C NMR spectrum of compound 5. (101 MHz, CD₂Cl₂, 298 K)

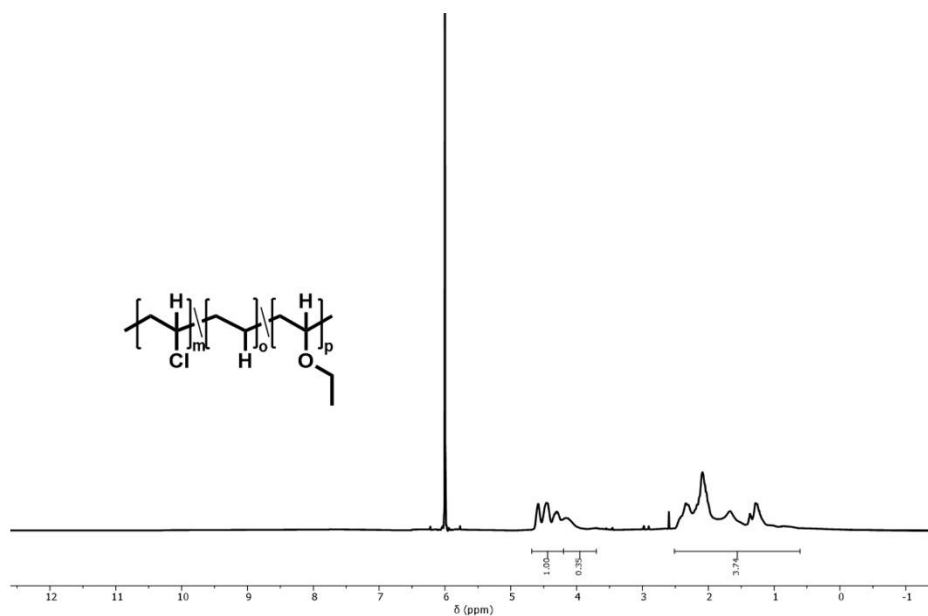


Figure S19: ^1H NMR spectrum of dPVC using diethyl phthalate in electrolysis applying DoE conditions. (400 MHz, $\text{TCE-}d_2$, 298 K)

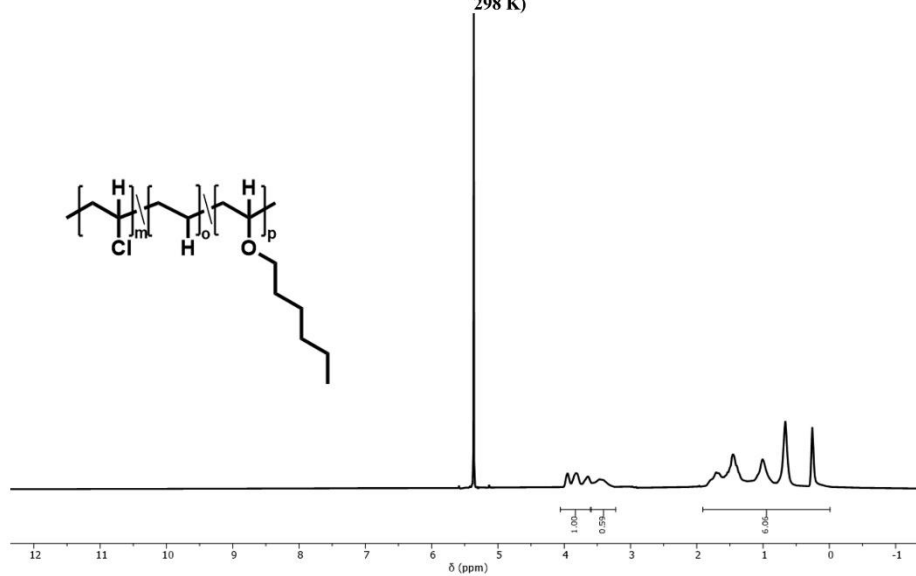


Figure S20: ^1H NMR spectrum of dPVC using dihexyl phthalate in electrolysis applying DoE conditions. (400 MHz, $\text{TCE-}d_2$, 298 K)

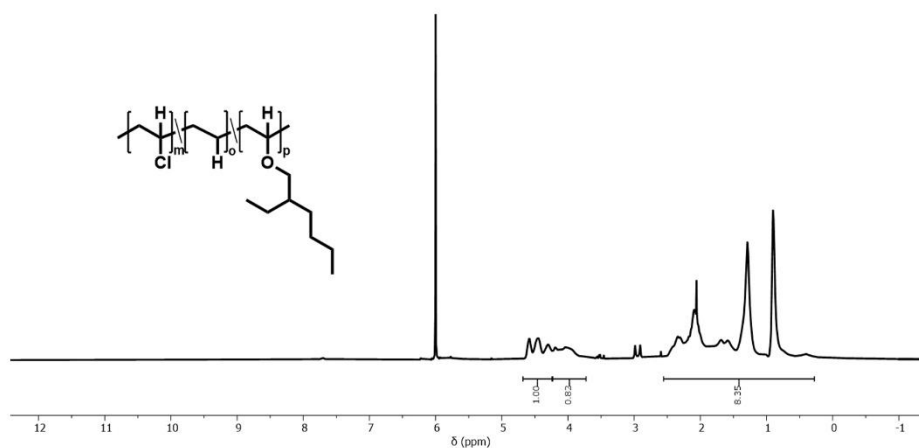


Figure S21: ^1H NMR spectrum of dPVC using bis(2-ethylhexyl) phthalate in electrolysis applying DoE conditions. (400 MHz, $\text{TCE-}d_2$, 298 K)

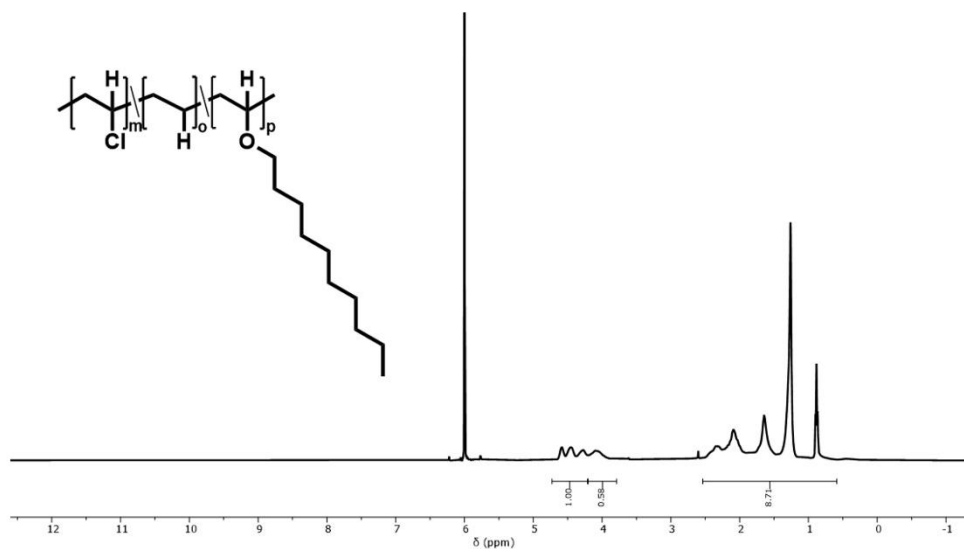


Figure S22: ^1H NMR spectrum of dPVC using didecyl phthalate in electrolysis applying DoE conditions. (400 MHz, $\text{TCE-}d_2$, 298 K)

9.3 Lehrtätigkeit

Sommersemester 2023 an der Johannes Gutenberg-Universität, Mainz

Praktikum Elektrochemie (Prof. Dr. Siegfried R. Waldvogel)

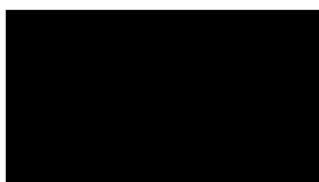
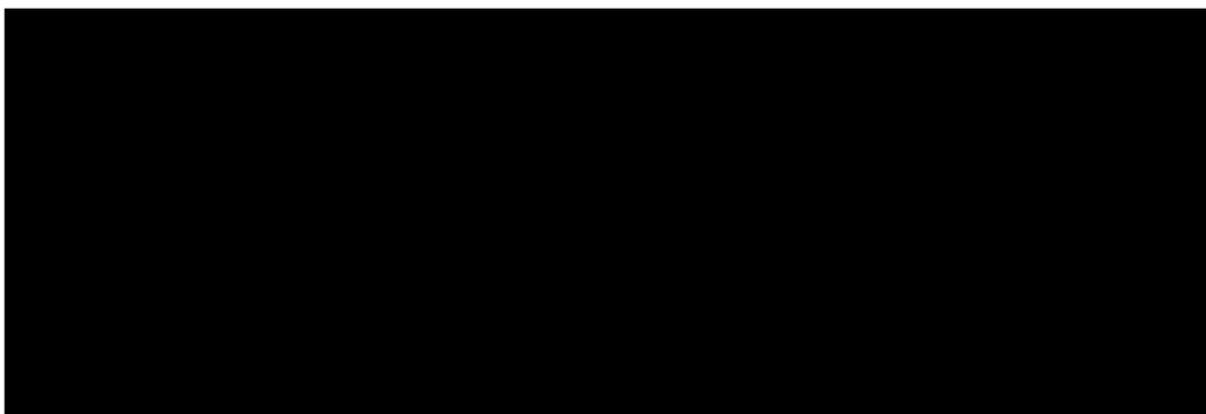
Wintersemester 2023/24 an der Johannes Gutenberg-Universität, Mainz

Praktikum Organische Chemie / Synthesepraktikum für Fortgeschrittene
(Prof. Dr. Heiner Detert)

Sommersemester 2024 an der Johannes Gutenberg-Universität, Mainz

Praktikum Organische Chemie / Synthesepraktikum für Fortgeschrittene
(Prof. Dr. Heiner Detert)

9.4 Curriculum Vitae



9.5 „Nutzung KI-Tools“:

KI-Tool	Genutzt für	Warum	Wann
DeepL Translator (DeepL SE)	Übersetzung englischsprachiger Artikel	Hilfe für grammatikalische Korrektur	Bei der Literatursichtung und -auswahl
ChatGPT (OpenAI)	Konzept der statistischen Versuchsplanung erklären lassen	Klärung von Verständnisfragen zu Auswertung von statistischen Versuchsplänen via Excel	Bei der Auswertung anhand von beispielhaften Daten
ChatGPT (OpenAI) & Claude (Anthropic)	Neuformulierung meiner Textentwürfe	Bessere Lesbarkeit	Über die gesamte Arbeit hinweg