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Electrochemical incorporation of sulfur dioxide towards value-added products

Dissertation

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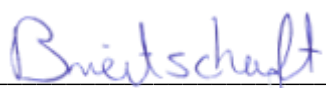
The experimental work of this thesis was carried out from September 2021 to January 2024 at the Johannes Gutenberg University Mainz in the Department of Chemistry, and continued at the Max-Planck-Institute for Chemical Energy Conversion (MPI CEC, Mülheim an der Ruhr) from February 2024 to April 2025, both under the supervision of Prof. Dr. Siegfried R. Waldvogel.

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Für Mama

"Sometimes science is more art than science,
a lot of people don't get that."

Richard Daniel "Rick" Sanchez

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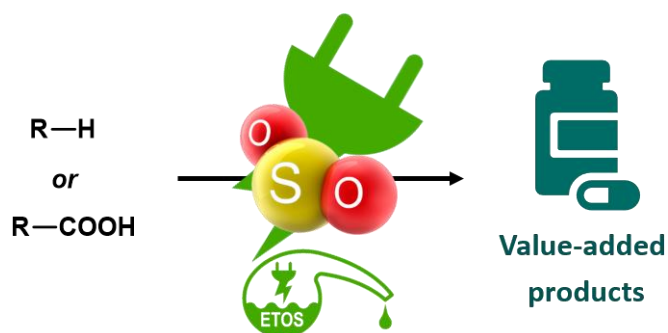
Ganz herzlich bedanke ich mich bei Anne Storm. Nicht nur für all die wunderbaren Momente, die vielen schönen Erlebnisse und unseren unvergesslichen Kanada-Urlaub – sondern vor allem für deine unglaubliche Unterstützung. Du schaffst es immer wieder, meinen Kopf frei zu bekommen und mir neue Kraft zu geben. Mit deiner Stärke bist du mir eine Quelle der Inspiration und Motivation, aber vor allem auch ein echtes Vorbild. Ich bin unendlich dankbar, dich an meiner Seite zu haben!

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Abstract

As part of the BMBF future cluster ETOS (Electrifying Technical Organic Syntheses), this dissertation explored the development, optimization, and application of novel electrochemical multi-component sulfonylation reactions utilizing abundant and broadly applicable starting materials. Stock solutions of sulfur dioxide were used as an efficient and convenient way to incorporate the toxic pollutant SO_2 into value-added products. The electrophilic nature of SO_2 enables its formal insertion into O–H bonds of alcohols, forming monoalkylsulfites in-situ with the assistance of an organic base. The nucleophilic properties of these intermediates were then harnessed to engage with anodically oxidized substrates, facilitating the formation of new C–S bonds.

The methodology was first applied to styrene derivatives, enabling direct electrosulfonylation to afford β -styrenesulfonates. A similar transformation was achieved using cinnamic acids as a biogenic feedstock through a decarboxylative sulfonylation pathway. Furthermore, the scope of the reaction was extended to non-aromatic substrates by employing readily oxidizable tertiary amines as precursors for enamines, resulting in the formation of enaminylsulfonates.

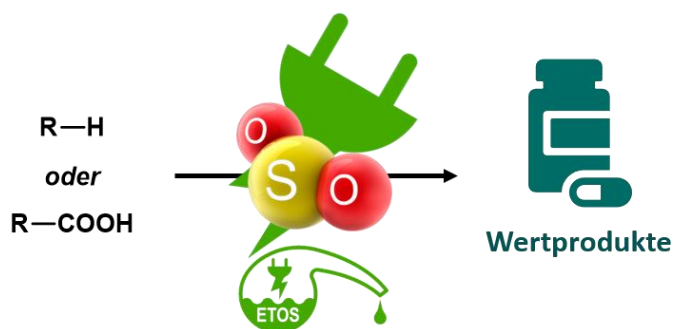


These advancements significantly expanded the applicability of electrochemical sulfonylation reactions, overcoming previous limitations such as the necessity for prefunctionalization, the use of surrogate reagents, toxic solvents, or complex electrochemical setups, while at the same time broadening the substrate scope of electrochemical sulfonylation reactions.

Kurzzusammenfassung

Im Rahmen des BMBF-Zukunftsclusters ETOS (Elektrifizierung Technischer Organischer Synthese) wurde in dieser Dissertation die Entwicklung, Optimierung und Anwendung neuartiger elektrochemischer Mehrkomponenten-Sulfonylierungsreaktionen unter Verwendung leicht zugänglicher und breit einsetzbarer Ausgangsmaterialien untersucht. Stammlösungen von Schwefeldioxid wurden als effiziente und praktische Möglichkeit genutzt, den giftigen Schadstoff SO_2 in höherwertige Produkte einzubauen. Die elektrophile Natur von SO_2 ermöglicht seine formale Inkorporation in O–H-Bindungen von Alkoholen, wobei mit Hilfe einer organischen Base Monoalkylsulfite *in situ* gebildet werden. Die nucleophilen Eigenschaften dieser Zwischenprodukte wurden anschließend genutzt, um zuvor anodisch oxidierte Substrate anzugreifen und die Bildung neuer C–S-Bindungen zu ermöglichen.

Die Methodik wurde zunächst auf Styrolerivate angewendet, wodurch eine direkte elektrochemische Sulfonylierung zur Herstellung von β -Styrolsulfonsäureestern ermöglicht wurde. Eine ähnliche Transformation wurde mit Zimtsäuren als biogenen Ausgangsmaterialien mittels decarboxylierender Sulfonylierung erreicht. Darüber hinaus wurde der Anwendungsbereich der Reaktion auf nicht-aromatische Substrate erweitert, indem leicht oxidierbare, tertiäre Amine als Vorläufer für Enamine verwendet wurden, was zur Bildung von Enaminylsulfonaten führte.



Diese Fortschritte haben die Anwendungsbreite von elektrochemischen Sulfonylierungsreaktionen erweitert und den Substratscope erheblich vergrößert. Darüber hinaus konnten frühere Einschränkungen wie die Notwendigkeit von Vorfunktionalisierungen, die Verwendung von Surrogaten, toxischen Lösungsmitteln oder komplexen elektrochemischen Aufbauten überwunden werden.

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1 Motivation

The criteria for assessing, evaluating, and benchmarking new chemical transformations have undergone significant evolution in recent decades. Traditionally, metrics such as yield, selectivity, and the number of steps have been used to characterize the efficiency of a reaction (sequence).^[1] In 1975, Hendrickson defined the *ideal synthesis* as a reaction that "creates a complex skeleton from simpler starting materials, [...] linking them together directly, in a sequence only of successive construction reactions involving no intermediary refunctionalizations".^[2] Additional considerations include the cost of starting materials, the safety and timescale of the process, and its environmental impact.^[3] Trying to quantify the sustainability of a given reaction, measures like the atom efficiency,^[4] the environmental factor,^[5] or the effective mass efficiency^[6] have been proposed. This broader perspective, emphasizing on both the chemical transformation itself and its environmental and societal effects, was ultimately summed up in the *12 Principles of Green Chemistry* (Figure 1) formulated by Anastas and Warner in 1998.^[7] These key values have since served as a guideline for sustainable chemical synthesis, not only on lab scale, but also in industry, where they help to streamline processes as well as reducing costs and emissions.



Figure 1: The 12 Principles of Green Chemistry.^[7]

Since a few years, the environmental impact of a chemical production process can be systematically evaluated and quantized using life-cycle assessment (LCA).^[8] This ISO-certified methodology^[9] allows for a direct comparison of different feedstocks, reaction conditions, downstream procedures, and other factors, ideally encompassing the entire value chain from raw material extraction to end-of-life disposal ("from cradle to grave"). LCA serves as a tool to identify potentials for reducing emissions, especially, but not limited to, those of the greenhouse gas (GHG) carbon dioxide.

Although CO₂ is not the most potent GHG – sulfur hexafluoride, for instance, has a global warming potential of approximately 25.200 CO₂eq – it is responsible for about two-thirds of the

anthropogenic warming effect.^[10] This renders CO₂ the single most significant driver of human-induced climate change. Over the past centuries, the substantial quantities of CO₂ released into the atmosphere have increased its concentration by ca. 50%, reaching levels of 420 ppm. This has contributed to an increase in global temperatures by roughly 1.0 °C over the last 170 years (Figure 2).^[11]

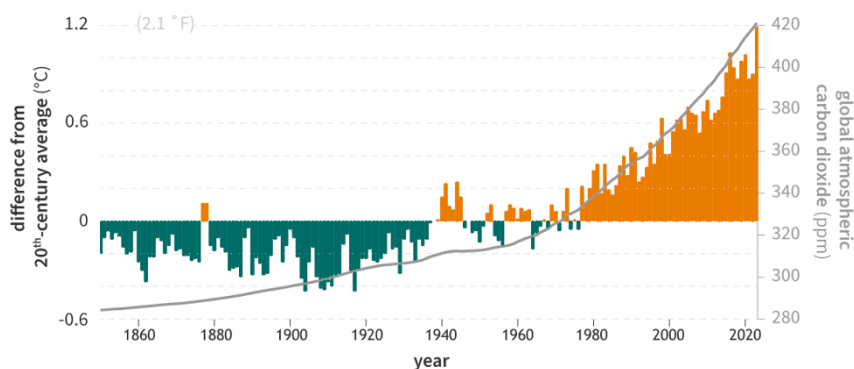


Figure 2: Earth's surface temperature (left axis) and atmospheric CO₂ content (right axis, grey line) from 1850 to 2023. Graphic adapted from reference ^[11] with general permission.

Emitting more than 3 billion metric tons of CO₂eq every year either directly or indirectly, the chemical industry accounts for about 5% of global and 19% of industrial GHG emissions,^[12] placing it among the top 3 industrial sources, along with steel and cement. The efforts to transition the chemical industry towards net-zero emissions are broadly categorized into *defossilization* and *decarbonization*. Defossilization centers around replacing fossil-based raw materials such as crude oil, natural gas, and coal with renewable feedstocks like biomass or existing plastic waste,^[13] thereby contributing to circular economy. In contrast, decarbonization, understood narrowly as the complete elimination of carbon from any processes, is neither feasible nor desirable, as carbon is fundamental to organic materials. Within the context of chemistry, decarbonization instead refers to the electrification of chemical processes.^[14] Upgrading reactor heating from steam to electrical systems may represent an intermediate step towards more sustainable chemical production. However, achieving long-term objectives will necessitate the direct use of electricity as the primary energy source, facilitated by novel synthetic transformations and next-generation chemical reactors and production facilities.^[15] In this context, electrosynthesis plays a disruptive role by driving chemical reactions through an electric potential difference instead of thermal energy, making it a green methodology.^[16]

Multi-component reactions, on the other hand, allow for the efficient one-step synthesis of complex molecules from simple precursors, meeting many criteria of the ideal synthesis.^[1] Combining electrosynthesis and multi-component reactions presents a promising strategy for the development of innovative pathways to produce value-added chemicals.^[17] This approach, ideally utilizing renewable starting materials, aligns closely with the principles of green chemistry and promotes a more sustainable chemical synthesis.

1.1 Electrosynthesis

When an electric potential is applied across a solution containing charged species, the particles reorganize to form the electrochemical double layer. This phenomenon was first described by Helmholtz^[18] in 1853 and refined in the early 20th century by Gouy and Chapman,^[19] as well as Stern^[20]. Initially, Marcus^[21] developed a theoretical foundation to describe the homogeneous electron transfer between two species in solution. This framework, which became later known as Marcus theory, was subsequently extended to include electron transfer (ET) processes at electrode-solution interfaces, which are classified as inner-sphere or outer-sphere mechanisms.^[22] An inner-sphere ET involves a direct interaction between the electrode and the substrate, often through a chemical bond or coordination. The formation of this inner-sphere complex is accompanied by removal of the solvent shell. Inner-sphere ET is typically observed with electrode materials exhibiting an active layer which promotes interaction with the substrate, such as a NiO(OH) layer on a nickel electrode, for example (Figure 3 left). In contrast, outer-sphere ET does not require such close interactions and is often observed with inert electrodes, such as platinum. In this case, the electron overcomes the distance in space between the two species via quantum tunnelling (Figure 3 right).

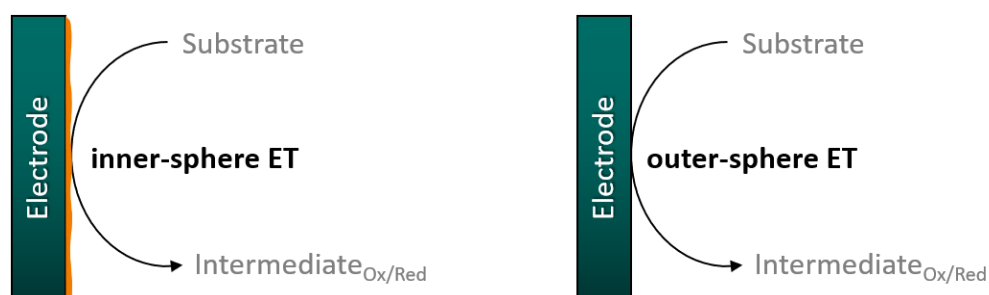


Figure 3: Examples of an inner-sphere electron transfer at an electrode with an active layer (orange) and outer-sphere electron transfer at an inert electrode.

A fundamental requirement for such heterogeneous electron transfer is that the (adjustable) Fermi level of the electrode has to align appropriately: it must be lower than the highest occupied molecular orbital (HOMO) of the substrate for oxidation reactions, and higher than the lowest unoccupied molecular orbital (LUMO) for reduction reactions (Figure 4).^[23] In practical application, kinetic barriers associated with the electron transfer – such as the work function of the electrode, substrate desolvation, or diffusion limitations – necessitate that the Fermi level of the electrode is lower (for oxidations) or higher (for reductions) than the HOMO or LUMO of the substrate, respectively. The additional energy required to overcome these barriers is referred to as the overpotential η .^[24]

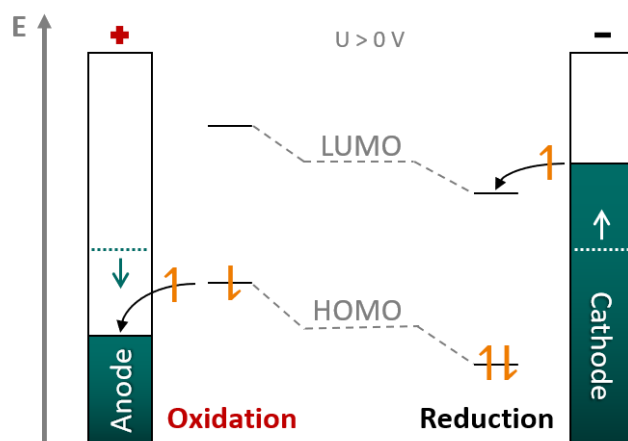


Figure 4: Basic principle of electrochemical reactions. The fermi-levels of the anode and cathode can be varied with the applied difference in potential, until a redox reaction occurs.

The addition or removal of an electron often results in an unstable intermediate, especially for organic substrates. When the HOMO or LUMO is sufficiently localized, this can directly activate a specific region of the molecule or even a particular bond due to a decrease in bond order. The electroactive region of a molecule can be referred to as the electrophore, analogous to the concept of chromophores in photochemistry.^[25] In more sophisticated substrates, the electrophore with the lowest oxidation or reduction potential generally undergoes electron transfer first.^[26]

Advantages

Activating a bond using electric potential instead of thermal energy or precious transition metal catalysis offers several advantages.^[16, 26b, 27] Notably, since electricity can be generated from renewable energy sources, such as solar, wind, hydro, or geothermal power, the driving force of the reaction can be considered environmentally benign. This also eliminates the need for conventional stoichiometric oxidants or reductants, thereby reducing waste. Additionally, electrosynthesis enables milder reaction conditions, can reduce process steps, and offers alternative synthetic reactivities and pathways, thereby expanding intellectual property (IP) space.^[28] As an electrochemical reaction halts immediately when the power is turned off, safety is enhanced. This especially mitigates the risk of (thermal) runaway reactions, a common challenge in conventional chemical processes across both laboratory and industrial scales.^[29] The ability to stop and restart an electrochemical reaction on demand also facilitates the alignment of chemical production with fluctuations in electricity supply and demand, enabling the utilization of excess energy that would otherwise go unused.^[30] However, achieving such highly flexible production necessitates the development of robust chemical processes, electrolyzers, and auxiliary equipment, including pumps, stirrers, and thermostats.

Disadvantages and challenges

While electro(organic)chemistry offers significant potential for greener chemical synthesis, its implementation still faces several challenges.^[31] Although standardized equipment for laboratory-scale reactions has become commercially available in recent years^[32] (e.g. IKA Screening System,^[33] IKA ElectraSyn 2.0,^[34] or Sigma-Aldrich SynLectro™ series^[35]), self-made cells and electrodes remain prevalent in contemporary research, hindering reproducibility and comparability among electrochemists.^[25a] In chemical industry, electrolyzers are generally custom-designed for specific processes, although an increasing number of cell components and auxiliary parts can be bought "off-the-shelf".^[36] Examples of electroorganic reactions already performed on an industrial scale include the production of adiponitrile (ca. 3×10^5 t/a, Ascend Performance Materials) or 1-(*tert*-butyl)-4-(dimethoxymethyl)benzene (ca. 2×10^4 t/a, BASF), a precursor for the fragrance lysmeral.^[37]

Electrochemical transformations in organic reaction media frequently require additives to ensure sufficient conductivity. These supporting electrolytes (SE) must remain inert to both chemical and electrochemical reactions. A modular approach is commonly used, where lithium, sodium, or tetraalkylammonium cations are paired with unreactive anions such as tetrafluoroborate, hexafluorophosphate, perchlorate, sulfate, or triflate.^[38] As one can imagine, the choice of supporting electrolyte heavily influences electrode-substrate interactions and in some cases, the SE even serves a dual role as reagent or mediator.^[39] While supporting electrolytes are essential for electrochemical reactions, they not only pose additional costs but they must be removed and ideally recycled, complicating work-up and downstream processing, which are major cost drivers in chemical production.^[27b] When compatible with the target reaction, acids such as H₂SO₄, HCOOH or AcOH can serve as alternatives, providing conductivity while also supplying protons for hydrogen evolution – an often-employed counter reaction for oxidative processes.^[40] Additional challenges for the widespread adoption of electrochemical methods include the need to optimize a larger number of parameters (*vide infra*) and the potentially high cost of electrode and separator materials.

Important electrochemical parameters

Optimizing an electrochemical reaction involves a broader parameter space compared to conventional synthesis, encompassing not only factors such as solvent, temperature, concentration, and stoichiometries but also electrochemical-specific parameters (Figure 5).^[41] Generally speaking, variables can be categorized as continuous or discontinuous. Discontinuous parameters, also called discrete or categorical variables, can only be changed in defined steps. Examples include the type of electrochemical cell, electrode material, or the supporting electrolyte. Continuous parameters, on the other hand, can in theory be varied in indefinitely small increments. In practice, this is hindered by technical limitations of the control devices, e.g. the temperature controller or the galvanostat.

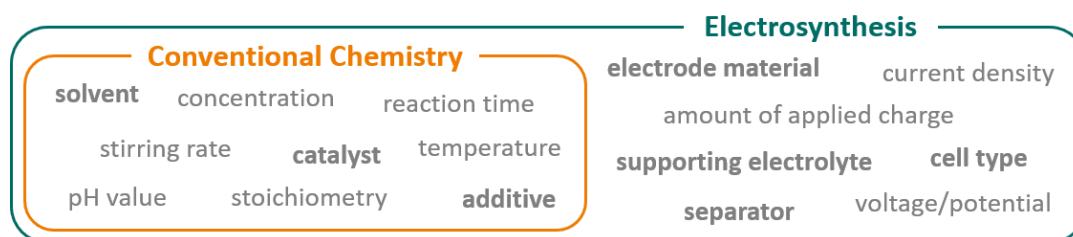


Figure 5: The parameter space of electrochemical reactions includes the one of conventional synthesis and multiple discrete (printed in bold) and continuous factors.

Two important continuous parameters in electrosynthesis are the current density ($[j] = \text{mA}/\text{cm}^2$) and the charge ($[Q] = C = \text{A}\cdot\text{s}$). Normalizing the applied current to the geometric area of the electrode allows for better comparison between different reactions, reactors, electrodes, and batch sizes. While expressing Q in coulombs is common in physics and battery research, in electrosynthesis it is more practical to use the *unit faraday*, which is equal to the amount of Coulombs carried per mole of electrons ($[Q] = F \approx 96\,485 \text{ C/mol e}^-$). This allows for the amount of applied charge Q (expressed in F) to be interpreted as redox equivalents. The current density j then corresponds to the rate at which these redox equivalents are supplied, analogous to an addition rate in conventional chemistry.^[42] Importantly, the *unit faraday* should not be confused with the Faraday *constant* ($F \approx 9.6485 \times 10^4 \text{ C/mol}$).

With expansion of the parameter space, traditional optimization methods such as the one-variable-at-a-time (OVAT) approach are being increasingly accompanied or replaced entirely by statistical techniques like design-of-experiments (DoE).^[41a, 43] DoE enhances the likelihood of identifying the global maximum rather than settling on a local optimum, as it accounts for interactions between parameters. Additionally, DoE seeks to minimize the number of experiments required, enabling a more time- and cost-efficient optimization of reaction conditions.

Modes of operation

In electrochemical experiments, two modes of operation are distinguished.^[26b, 38, 44] Under galvanostatic conditions (Figure 6 left), the clamp voltage U is dynamically adjusted to maintain a constant applied current I . Given a moderate current density j , the species with the lowest oxidation potential undergoes oxidation at the anode, while the species with the lowest reduction potential undergoes reduction at the cathode. This forms a redox pair characterized by the smallest absolute difference in redox potentials. As the reaction progresses and the substrate of interest is depleted, the clamp voltage gradually increases in accordance with the Nernst equation. This leads to reduced selectivity and increased solvent degradation, particularly during the later stages of the experiment.^[25a] Nevertheless, the galvanostatic approach offers the advantages of a simplified setup and a precisely defined electrolysis duration, which can be determined using the following equation:

$$t = \frac{n * z * F}{j * A}$$

where n = limiting reagent [mol]
 z = equivalents of electrons
 F = Faraday constant [A·s/mol]
 j = current density [A/m²]
 A = submerged area of the electrode [m²]

If a reference electrode (RE) is positioned near the electrode where the reaction of interest occurs (called working electrode, WE), electrolysis can be performed under potentiostatic conditions (Figure 6 right). In this mode, the potential difference U between the working and the reference electrode is maintained constant, while the electric current I varies during the reaction. Although this setup is more complex, it generally provides enhanced selectivity, as the oxidation or reduction potential of the target substrate can be precisely addressed.^[44] However, at the endpoint of an potentiostatic experiment (> 98% of starting material consumed), the current has typically dropped to less than 5% of its starting value.^[45] This leads to prolonged and challenging-to-predict reaction durations, which are often five times longer than a comparable galvanostatic electrolysis. Therefore, with regard to scalability and technical application, the latter is often preferred.^[46]

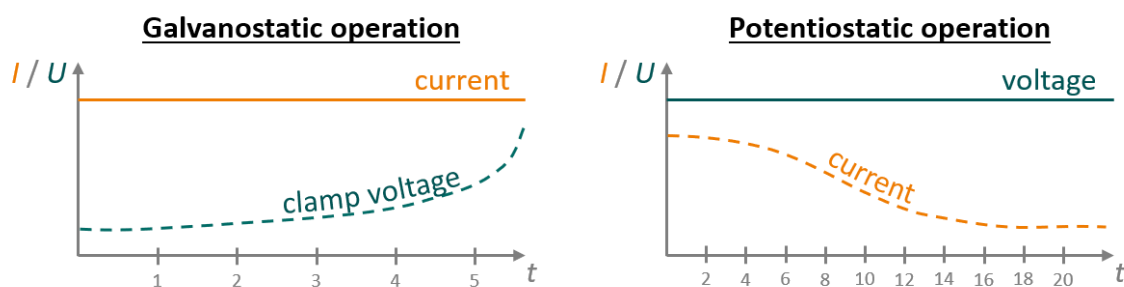


Figure 6: Galvanostatic and potentiostatic mode of operation.

1.1.1 Electrosynthetic cell design

In addition to its mode of operation, the design of the electrolytic cell plays a critical role in determining the reaction outcome. Batch electrolyzers can be classified into three types: undivided cells, divided cells (due to their shape commonly referred to as H-type cells), and quasi-divided cells (Figure 7).^[45, 47]

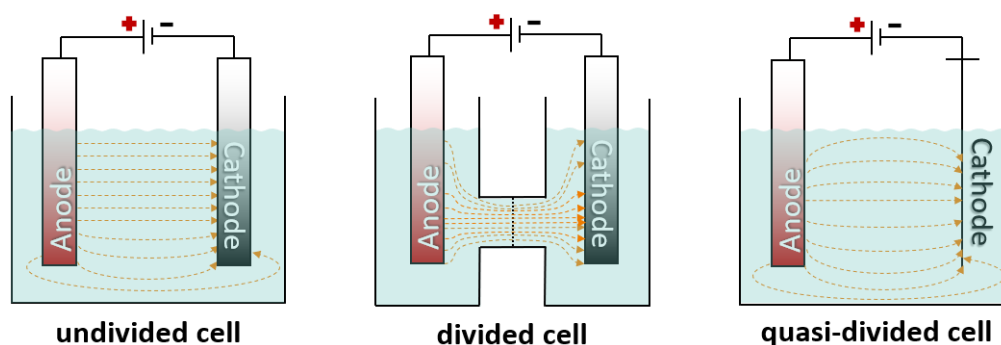


Figure 7: Different types of electrochemical batch cells.

Undivided cell

The undivided cell represents the simplest configuration, in which both electrodes share the same electrolyte.^[38] Consequently, the substrate, intermediates and target product must remain stable against redox reaction at the counter electrode (CE). Furthermore, any products formed at the CE should not interfere with the desired reaction at the WE. Since the electrolyte is common to both electrodes, there is a possibility for certain stable species to "shuttle" electrons between the electrodes, creating a chemical short circuit, thus reducing efficiency. In a parallel electrode arrangement, the electric field lines remain relatively uniform, ensuring an even distribution of current density. The rear side of the electrode only contributes minimally to the electrochemically active electrode area due to reduced density of the electric field lines, and is therefore typically excluded from calculations of current density.^[26a, 48]

Divided cell

If interactions between different species hinder an efficient electrolysis, a porous material that still allows for conductivity, but prohibits extensive mixing, can be placed between the electrodes, dividing the electrolyte into an anolyte and a catholyte. This is typically associated with a significant voltage drop due to the increased resistance within the cell. In batch cells, the separator is often positioned within a constricted region and does not extend across the entire area between the electrodes. The eponymous H-shape of these cells causes an inhomogeneous distribution of electric field lines,^[26a] leading to an average rather than uniform current density. This issue can be addressed by utilizing a flow-based setup, where the interelectrode gap is reduced and the separator covers the entire electrode surface.^[46]

As separators, simple and inexpensive frits made from glass or ceramic are commonly used, but suffer from scalability issues.^[48] More advanced materials, derived from inert polymers, not only prevent mixing but also allow for a selective discrimination between differently charged species. This is achieved through functionalization with ionic groups. Nafion® (Chemours, Figure 8), a perfluorinated copolymer similar to polytetrafluoroethylene (PTFE, also known as Teflon® by DuPont), bears negatively charged sulfonate groups. This allows it to selectively conduct small positively charged species, such as protons, lithium, or sodium cations. The polymeric anions and the absorbed electrolyte phase-separate from the hydrophobic fluorocarbon backbone, forming approximately spherical clusters interconnected by narrow channels.^[49] Anions, including hydroxide, are electrostatically repelled, preventing their passage through the membrane even in the presence of steep concentration gradients. Nafion® was specifically developed as a membrane for the chloralkali process, tolerating high temperatures, electrical currents and a very corrosive environment, but lifetime in organic media is limited.^[50] Similarly, membranes functionalized with quaternary

ammonium groups facilitate selective anion conductivity and are commonly used in fuel cells and water electrolyzers,^[51] but found application in organic electrosynthesis as well.^[52]

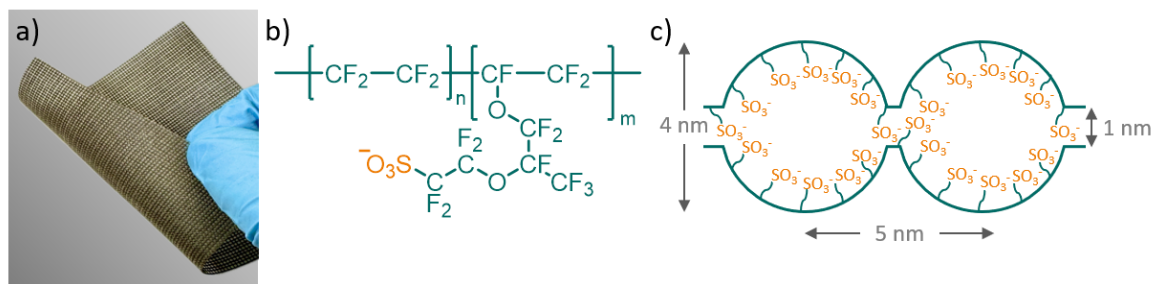


Figure 8: A sheet of Nafion® membrane (a), its chemical structure (b) and morphology according to the cluster-network-model (c).^[49]

Quasi-divided cell

A quasi-divided cell, also referred to as a pseudo-divided cell, represents a specialized configuration of an undivided electrolysis cell. In this setup, the counter electrode is designed with a significantly smaller surface area compared to the working electrode, resulting in vastly different current densities.^[45] Practically, this is achieved by combining a standard-sized plate as the WE with a thin wire or rod made from stainless steel, platinum, graphite, or glassy carbon serving as the CE.

Since diffusion to the smaller electrode is hindered, a large portion of the current is used to electrolyze the solvent instead of the substrate with the lowest redox potential. This mass transfer limitation combines the benefits of an undivided cell – such as a simplified setup and low to medium resistance – with the advantages of divided cells, including improved selectivity, reduced side reactions and the prevention of chemical short circuits.^[53] A quasi-divided cell can be used for both anodic^[54] and cathodic^[55] transformations and has been demonstrated to be scalable as well.^[56] The distribution of electric field lines varies based on the specific cell geometry, being relatively uniform when a cylindrical WE surrounds the CE or slightly distorted/bent in configurations with a flat WE.

1.1.2 Carbon-based electrode materials

The choice of electrode material is foremost decided by the envisioned chemical reaction, its yield and selectivity. While there are theoretical considerations for identifying an appropriate material, such as the electrochemical window, overpotential for (undesired) hydrogen evolution or oxygen reduction, or the formation of a catalytically active layer, the ideal electrode is often found empirically through simple screening experiments.^[41a, 57] Secondary considerations, including cost, ease of manufacturing, long-term stability, and toxicity have driven the development of a wide range of materials. Among these, platinum and carbon-based substances, such as graphite (in various forms), glassy carbon (gC), and boron-doped diamond (BDD), constitute the majority (Figure 9).

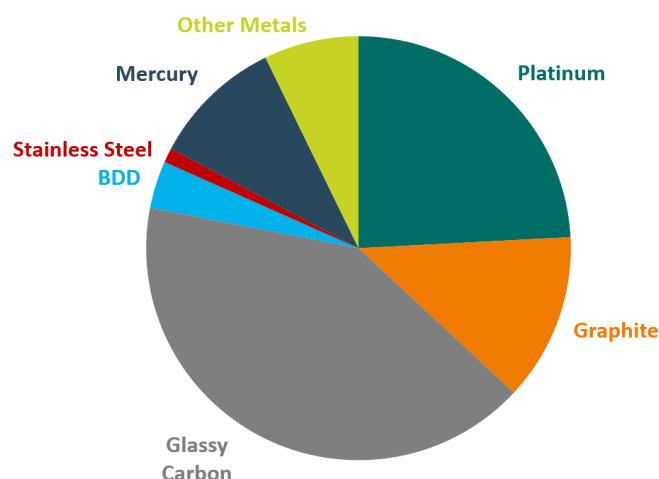


Figure 9: Occurrence of electrode materials (anode and cathode) used in contemporary electrosynthesis research from 2000–2017. Graphic adapted from reference ^[57] via a Creative Commons CC BY license.

Graphite and its fabrics

Graphite is one of the most cost-effective materials, characterized by its relatively soft structure and moderate to high porosity. Although graphite occurs naturally in the form of amorphous coal or crystalline flake graphite, electrodes are produced synthetically *via* the pyrolysis of petroleum coke and pitch under an inert atmosphere at approximately 2500–3000 °C.^[58] This process yields a material composed of laminar layers of hexagonally arranged carbon atoms (Figure 10a). Within each graphene layer, the sp²-hybridized carbon atoms are chemically bonded, while the layers themselves are held together solely by Van der Waals forces, leading to a significant anisotropy.

If small graphite flakes are subjected to cold isostatic pressure molding, a material known as *iso-graphite* is obtained.^[59] It exhibits greater isotropy, resulting in enhanced electrical and thermal conductivity, high chemical resistance, and very high purity, although trace metal contamination is still not entirely excluded.^[25a, 60] The presence of paramagnetic defects in iso-graphite was hypothesized to be the reason for the tendency of radicals to adsorb onto it, facilitating a subsequent electron transfer.^[61] This is exploited in the Hofer-Moest variant^[62] of the Kolbe electrolysis,^[63] where carboxylates are oxidized to carbocations instead of generating radicals at a platinum anode.

Treating graphite flakes with concentrated acids, such as H₂SO₄, in combination with strong oxidizing agents (e.g., H₂O₂) induces intercalation of the anions between the graphene layers. Following washing and rapid heating, the material undergoes a significant volumetric expansion, resulting in what is known as *expanded graphite* (EG, Figure 10b).^[64] Due to its very low density, EG has found applications in energy storage^[65], as halogen-free flame retardant,^[66] and for the sorption of oil and heavy metals.^[67]

Mechanical compression of EG produces a soft and flexible material called *graphite foil* (commercially available as Sigraflex™ by SGL Carbon^[68], Figure 10c). The anisotropic material is

characterized by high resilience and thermal stability, as well as low gas permeability, making it ideal for applications such as gaskets and seals.^[69] Due to the absence of additives or binders, graphite foil exhibits excellent chemical stability. Notably, its porosity can be tailored by adjusting the compression pressure, an important feature for its use as an electrode material.

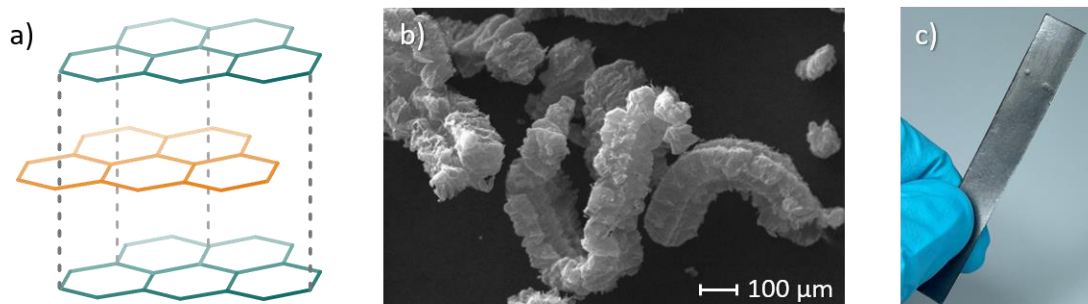


Figure 10: a) Alternating graphene layers in graphite. b) Worm-like structure of expanded graphite. c) Sigralflex™ graphite foil electrode. SEM image reprinted from reference ^[69b] via a Creative Commons CC BY license.

Glassy Carbon

When phenol-formaldehyde resins are gradually heated above 1200 °C in an inert atmosphere, nitrogen, oxygen, and eventually hydrogen are progressively eliminated, leading to the carbonization of the polymer. Subsequent high-temperature treatment reduces structural defects and anneals the amorphous material, yielding glassy carbon (gC).^[70] Due to this annealing process, gC is predominantly composed of sp^2 -hybridized carbon, distinguishing it from amorphous graphite. The microscopic structure of gC has been extensively debated, with proposed models ranging from disordered graphite-like units to interwoven fibrous structures (Figure 11a) that retain features of the polymer precursor.^[71] More recent studies^[72] indicate the presence of curved carbon sheet fragments with variable connectivity, along with minor quantities of fully closed particles resembling fullerene-like structures.

Glassy carbon is a shiny material characterized by its impermeability to liquids and gases, as well as its exceptional chemical inertness and resistance to thermal stress, making it a widely utilized material for electrodes.^[73] Although its hardness renders it quite brittle, gC can be processed into various forms, including large monolithic structures, fine particles, thin films, sheets, and fibers.^[74] A special form of glassy carbon, called reticulated vitreous carbon (RVC), is obtained by rapidly heating the precursor polymer. The fast carbonization prevents the diffusion of formed gases to the surface, resulting in a highly interconnected porous network with a macroscopic foam-like structure (Figure 11b).^[71] As a three-dimensional electrode material, RVC provides enhanced mass transport properties and a high surface area, enabling operation at elevated current densities (with regard to geometric surface area).^[75]

Boron-doped diamond

Doping the tetrahedral crystal structure of the insulating carbon allotrope diamond with boron atoms introduces an unoccupied acceptor level just above the valence band. This significantly reduces the band gap to 0.37 eV, transforming the material into a conductor. Boron-doped diamond (BDD) is manufactured through chemical vapor deposition (CVD), a process that deposits thin polycrystalline films onto a substrate, typically silicon, using a mixture of methane, diborane, and small amounts of hydrogen at elevated temperatures and reduced pressures.^[76] Variations in substrate material, doping level, film thickness, grain size, surface termination, as well as amount and spatial distribution of sp^2 -carbon centers enable the customization and fine-tuning of electrodes.^[77]

Boron-doped diamond is characterized by exceptional chemical and electrochemical stability, attributed to strong σ -bonds of the sp^3 -hybridized carbon atoms. BDD exhibits the widest electrochemical window among all electrode materials, exceeding 5 V in organic media.^[78] In aqueous systems, it demonstrates remarkably high overpotentials for both hydrogen and oxygen evolution. This property is particularly advantageous in wastewater treatment, where, under very high current densities (up to 1900 mA/cm²), anodically generated hydroxyl radicals facilitate the degradation of organic pollutants.^[79]

BDD is also extensively employed in electroanalysis, chemical sensing, and electrosynthesis.^[80] It has demonstrated outstanding performance in anodic coupling reactions, as well as in fluorinations, methoxylations, and cyanations, particularly when used in combination with the solvent 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).^[78, 80b, 81] While BDD is a versatile high-performance material, its high cost – varying greatly with electrode size and exact specifications, but at least two orders of magnitude higher than the cost of a similar sized graphite electrode^[82] – requires careful consideration for its intended application.

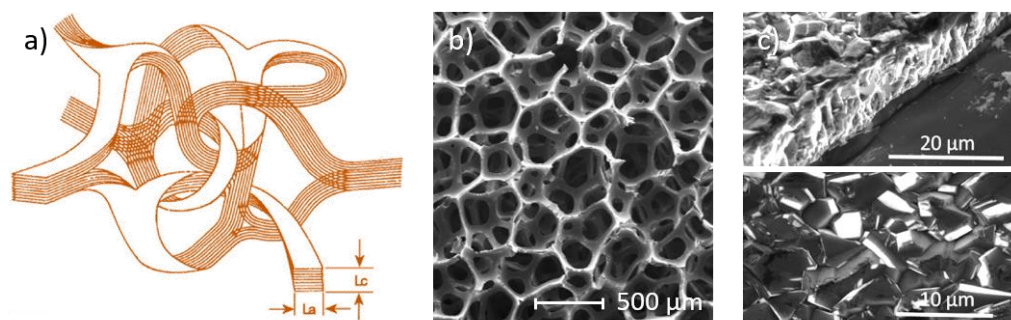


Figure 11: a) Structure of glassy carbon according to the band-model. b) Porous structure of RVC. c) Cross section (top) and surface (bottom) of a polycrystalline BDD film. Graphic and SEM images adapted from references ^[71, 75, 80a] via Creative Commons CC BY licenses or general permission for dissertations.

1.2 Multi-component reactions

A multi-component reaction (MCR) is a chemical process that involves three or more reactants, in which the majority of the atoms from the starting materials are incorporated into the final product through the formation of at least two new bonds.^[83] This differentiates MCRs from catalytic reactions, where the catalyst facilitates the transformation through the formation of an intermediate, but is ultimately not incorporated into the final product. MCRs can be considered a subset of one-pot syntheses, characterized by the fact that, once initiated, no additional reactants, reagents, or catalysts are added, and no significant alterations to the reaction conditions are made.^[84] Multi-component reactions are categorized based on the number of reactants involved as 3-CR, 4-CR, 5-CR and so forth.

Importantly, MCRs are rarely trimolecular in the context of chemical kinetics (Figure 12a), as the simultaneous collision of three molecules, as required by collision theory, is statistically improbable.^[85] Consequently, the reaction rate of true trimolecular processes is typically very slow. Instead, MCRs proceed *via* a sequence of consecutive bimolecular reactions (Figure 12b), gradually forming the desired product.

A key feature of MCRs is their modularity, since typically only very specific functional groups selectively react with one another.^[86] This allows for the flexible substitution of individual components, easily and quickly generating a large variety of similar compounds. This strategy is particularly valuable in medicinal chemistry, where MCRs are frequently employed in combinatorial approaches to synthesize extensive libraries of related molecules for high-throughput screening in the field of drug discovery.^[87]

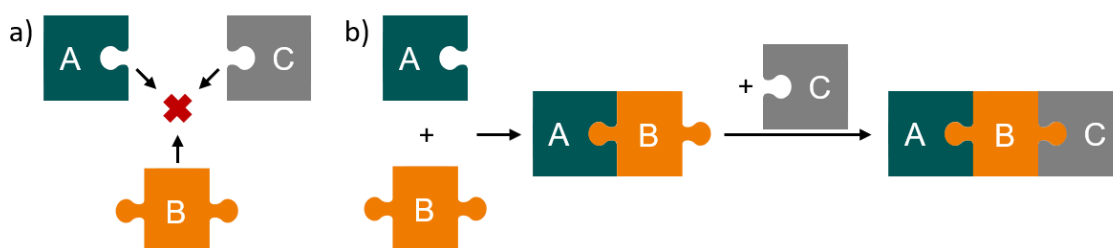


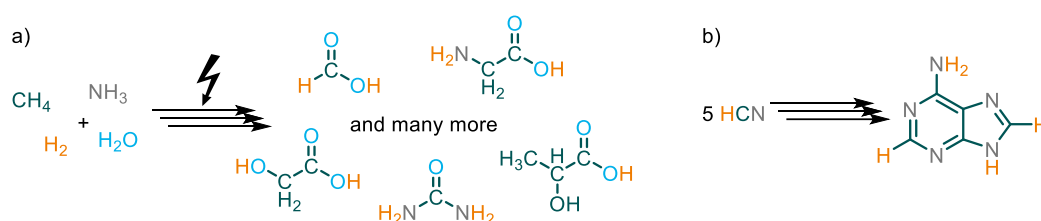
Figure 12: MCRs do not proceed *via* one trimolecular step (a), but by a sequence of bimolecular reactions (b). Each component can be replaced flexibly, resulting in high modularity.

Multi-component reactions are characterized by several notable features, including high atom economy, convergent synthesis, and the possibility to generate structural complexity from simple starting materials in a single step.^[88] Conducted in a single reaction vessel without the need for isolation or purification of intermediate products, MCRs minimize solvent consumption and waste generation, thereby reducing both environmental impact and overall costs. Ideally, these reactions exhibit high yields, broad functional group tolerance, and operate under mild reaction conditions.

Such attributes align closely with the principles of Green Chemistry and make MCRs a classic example of the *ideal synthesis*, exemplifying an efficient and sustainable approach to chemical reaction design.^[1]

1.2.1 Historically important multi-component reactions

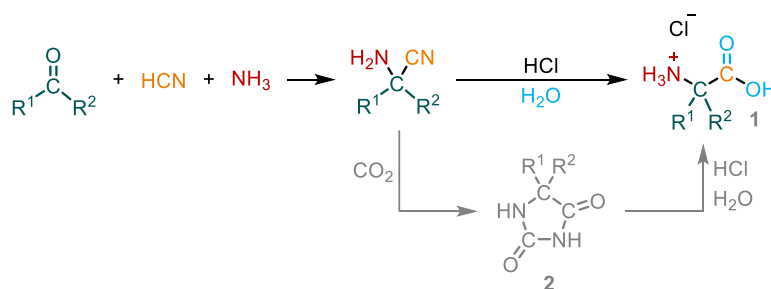
In nature, multi-component reactions are primarily used to rapidly generate complexity and structural diversity, making MCRs a common tool in natural product synthesis.^[89] The famous Miller-Urey experiment^[90], in which simple organic molecules were formed from methane, ammonia, hydrogen, and water through activation by an electric arc (Scheme 1a), can be classified as a multi-component reaction. Another example is the nucleotide base adenosine, which can not only be seen as a pentamer of hydrogen cyanide (Scheme 1b), but may have also formed this exact way under prebiotic conditions.^[91]



Scheme 1: a) Experiment by Miller and Urey producing the basic building blocks for life. b) Nucleotide base adenine as pentamer of hydrogen cyanide.

The origin of synthetic MCRs: Strecker amino acid synthesis

From a synthetic standpoint, the first multi-component reaction was discovered by Strecker in 1850,^[92] involving the use of a ketone, hydrogen cyanide, and ammonia to synthesize α -amino acids (**1**). This reaction was later refined by Bucherer and Bergs through the addition of carbon dioxide prior to acidic hydrolysis.^[93] The modified process affords a hydantoin derivative (**2**) with very high yield, which can subsequently be hydrolyzed to produce the desired amino acid. Today, this approach remains one of the primary industrial methods for producing racemic amino acids, particularly *DL*-methionine and glycine – the latter being achiral and, therefore, straightforward to synthesize chemically.^[94]



Scheme 2: Strecker synthesis for racemic amino acids and variant by Bucherer and Bergs (grey).

Isocyanide based MCRs

Multi-component reactions are largely associated with isocyanide chemistry, which offers an expansive chemical space. This is due to their exceptional amphiphilic character, exhibiting nucleophilicity and electrophilicity *at the same atom*, which is why isocyanides are occasionally described as "stable carbenes".^[95] They quickly react with a variety of substrates to form so-called α -adducts,^[96] while at the same time demonstrating remarkable functional group tolerance and high levels of chemo-, regio-, and stereoselectivity.

Isocyanide-based multi-component reactions were first introduced by Passerini in 1921, who developed a reaction yielding α -acyloxy amides (**3**) from isocyanides, ketones (or aldehydes), and carboxylic acids (Scheme 3a).^[97] Nearly 40 years later, Ugi recognized the broader potential of MCRs, particularly in the fields of diversity-oriented synthesis and combinatorial chemistry.^[95a, 98] By adding a primary amine into the Passerini reaction, the ketone undergoes initial conversion to an imine, ultimately producing a bis-amide (**4**) as the final product (Scheme 3b).^[99]

a) Passerini reaction



a) Ugi reaction



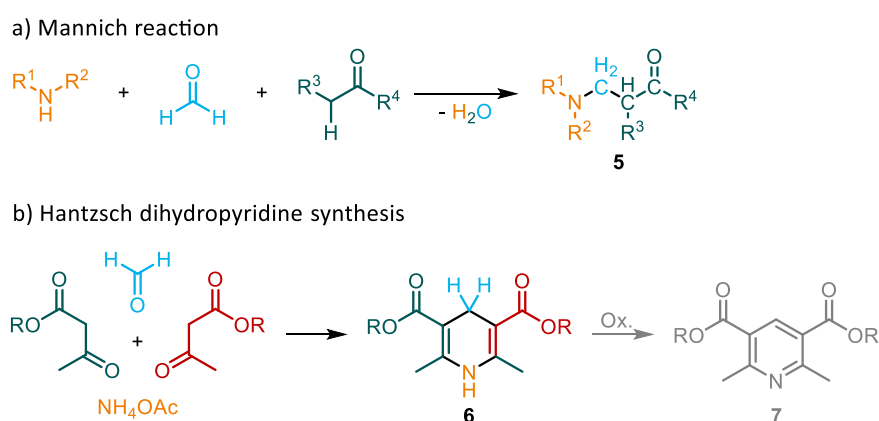
Scheme 3: Historically important multi-component reactions involving isocyanides (blue).

Since their discovery, both reactions have been extensively studied,^[100] and are frequently employed in heterocycle- and natural product synthesis,^[101] polymer chemistry,^[102] and drug discovery.^[103] Through modification with a chiral phosphoric acid catalyst, a stereoselective construction of the bis-amide was achieved.^[104] The Ugi reaction, in particular, serves as a versatile platform for combination with follow-up reactions, such as the Diels-Alder reaction, Smiles rearrangement, or Heck reaction, further enhancing structural complexity.^[105]

Aldehyde based MCRs

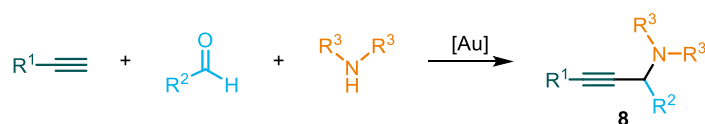
Aldehydes are versatile and reactive substrates, which undergo a plethora of different reactions, due to their highly polarized carbonyl bond, sterical accessibility and α -C,H-acidity.^[106] Formaldehyde, the simplest representative of this substance class, is frequently utilized as a C₁ building block in both lab-scale (commonly in the forms of formalin or paraformaldehyde) as well as in technical synthesis.^[107]

The textbook example of an MCR involving formaldehyde is the Mannich reaction, synthesizing β -amino carbonyl compounds (**5**) from amines and α -C,H-acidic carbonyls (Scheme 4a).^[108] Utilizing boronic acids instead of carbonyls, Petasis adapted the reaction,^[109] gaining access to allylic amines. This modification is therefore sometimes referred to as the *boronic acid mannich reaction*. An notable example of a 4-CR using formaldehyde is the Hantzsch dihydropyridine synthesis (Scheme 4b).^[110] The 1,4-dihydropyridine (**6**) can be oxidized in a one-pot-synthesis to give the pyridine (**7**). Compound **6**, also known as Hantzsch ester, has gathered significant attention as a synthetic hydride donor analogous to nicotinamide adenine dinucleotide (NADH), and for its diverse bioactivities.^[111]



Scheme 4: Examples of MCRs using the C₁ building block formaldehyde (blue).

In the 21st century, the so called A³-coupling reaction (aldehyde-alkyne-amine, Scheme 5)^[112] has emerged as one of the most direct, efficient, and atom-economical synthetic approaches to generate propargylamine derivatives (**8**).^[107, 113] These compounds serve as valuable precursors for constructing nitrogen-containing heterocycles and have demonstrated potential applications in treating neurodegenerative diseases.^[114] Typically catalyzed by Au(I) or Au(III), the A³ reaction proceeds *via* a gold acetylide intermediate facilitating the addition of the alkyne to an iminium ion, formed in-situ from the aldehyde and the amine. Recently, a catalyst-free access to propargylamines featuring a 4-CR with a primary amine, formaldehyde, boronic acid, and propargylic acid has been developed.^[115]



Scheme 5: The gold-catalyzed A³-coupling reaction.

1.2.2 Multi-component reactions involving inorganic gases

Today, the large-scale synthesis of commodities frequently employs MCRs involving inorganic gases such as CO, H₂, NH₃, Cl₂, H₂O (as steam), or SO₂, in combination with organic building blocks like alkenes or alkynes. This approach is rooted in early research on the Fischer-Tropsch process in the

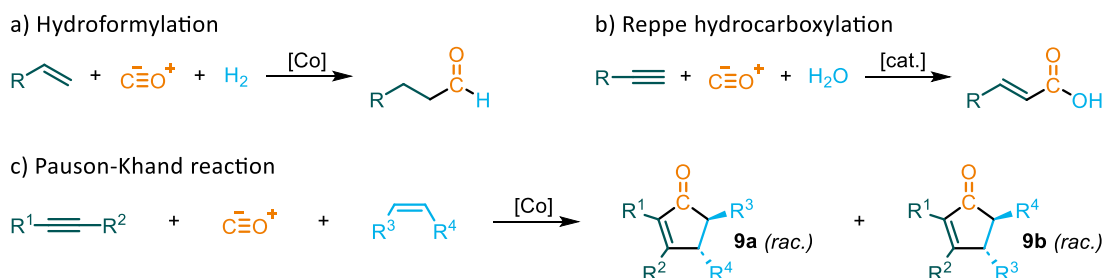
1920s, which utilized syngas – a mixture of CO and H₂ in varying proportions. While several researchers observed the formation of oxygenated byproducts, optimization failed at that time.^[116]

Carbon monoxide insertion

In 1938, Roelen identified deposits of propane-1-imine during his studies and correctly interpreted the formation of propionaldehyde as a distinct reaction (instead of a Fischer-Tropsch byproduct), driven by the addition of ethylene within the reactor.^[117] Subsequent improvements, including the use of cobalt tetracarbonyl hydride as a homogeneous catalyst, resulted in the patenting of the oxo synthesis,^[118] which is now known as hydroformylation of olefins (Scheme 6a).^[119] By 2009, the global production capacity for aldehydes and alcohols with this method reached 12×10⁶ t/a, establishing it as one of the most significant organic synthesis processes worldwide.^[120]

Formally replacing H₂ with water enables the synthesis of carboxylic acids through a process known as Reppe hydrocarboxylation (Scheme 6b).^[121] This method is highly versatile, as a variety of olefins and numerous substances containing protic groups can be utilized. For instance, alcohols can be transformed into esters, amines into carboxamides, and carboxylic acids into anhydrides.^[122]

Frequently, transition-metal catalysis allows for the incorporation of the CO building block into the product *via* the insertion into an activated bond.^[123] For example, the Pauson-Khand reaction (Scheme 6c)^[124] enables the synthesis of cyclopentenone derivatives (**9a** and **9b**) from alkynes, alkenes, and carbon monoxide using a cobalt catalyst. The classification of CO-insertion variants of traditional cross-coupling reactions, such as the Suzuki coupling, Heck reaction, or Stille reaction as MCRs remains a subject of debate. This is due to the fact that with carbonylative cross-coupling reactions, an increasing portion of atoms or mass is not incorporated into the final product. Consequently, the distinction between multi-component reactions, insertion-condensation mechanisms, and leaving-group chemistry becomes ambiguous.^[125]

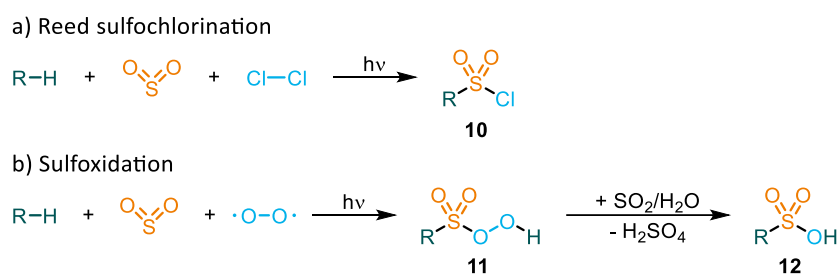


Scheme 6: Prominent examples of MCRs utilizing the gas carbon monoxide as a key building block.

In industrial applications, the incorporation of sulfur dioxide into organic molecules is predominantly achieved by the means of photochemistry. A prominent example is the Reed sulfochlorination,^[126] established in 1936, which enables the direct synthesis of sulfonyl chlorides (**10**) from alkanes, sulfur dioxide, and chlorine (Scheme 7a). Mechanistically, the reaction begins with the photolysis of Cl₂,

generating chlorine radicals that abstract a hydrogen atom from the alkane. The resulting alkyl radical adds to SO_2 , followed by a reaction with molecular chlorine, forming the desired product and propagating the chain reaction.^[127] Due to the harsh reaction conditions, this method is generally restricted to simple, linear alkanes. Even then, the process suffers from competing side reactions, such as chlorination and oxygen interference, as well as poor selectivity, leading to products with almost random substitution patterns.^[128]

Although molecular oxygen typically acts as an inhibitor in photochemical reactions, the sulfoxidation process utilizes alkanes, sulfur dioxide, and triplet oxygen to produce peroxysulfonic acids (**11**), which can be hydrolyzed in the presence of SO_2 , yielding alkane sulfonic acids (**12**, Scheme 7b).^[129] In this case, it is hypothesized that the chain reaction starts by photoexcitation of sulfur dioxide dissolved in the alkane.^[130] In the absence of water, **11** undergoes homolytic cleavage to form $\text{RSO}_2\text{O}^\bullet$ and $\text{HO}^\bullet$, both of which can propagate the reaction sequence. This mechanism suggests the potential for the sulfoxidation process to become autocatalytic, requiring irradiation only to initiate the reaction. However, in practical applications, continuous extraction with water is preferred, as it prevents the formation of polysubstituted alkanes.^[128]



Scheme 7: Sulfochlorination and sulfoxidation, two industrially important MCRs with SO_2 .

In laboratory settings, there are only a few reported instances of true multi-component reactions involving the use of sulfur dioxide gas; the majority of SO_2 transformations are sequential one-pot processes.^[131]

1.3 Sulfur dioxide

Sulfur dioxide (IUPAC recommended spelling; sometimes also referred to as sulphur dioxide) is a colorless, toxic gas with the molecular formula SO_2 . It possesses a pungent smell, reminiscent of burnt matches. At concentrations above 10 ppm, irritation of the mucus membranes of the eyes and the respiratory system starts, leading to tearing and coughing spasms.^[132] Prolonged exposure and/or higher concentrations result in chemical burns, followed by inflammation or pulmonary edema. This is due to the formation of sulfurous acid (H_2SO_3) upon contact of SO_2 with water. Sulfur dioxide is stored and transported as a liquified gas in pressurized tanks or cylinders marked with a yellow stripe, indicating its toxicity and corrosiveness. The high-purity gas ($\geq 99.98\%$, < 50 ppm H_2O) is commercially available for ca. 5 €/kg, making it comparable inexpensive.^[133] The most important physical properties of sulfur dioxide are summarized in Figure 13.

Key facts sulfur dioxide (CAS 7446-09-05):

- Molecular weight: 64.06 g/mol
- Melting point: -76°C
- Boiling point: -10°C
- Vapor pressure: 3.3 bar at 20°C
- Water solubility: 113 g/l at 20°C
- Electrochemical window: -0.4 to 5 V vs. FcH/FcH^+

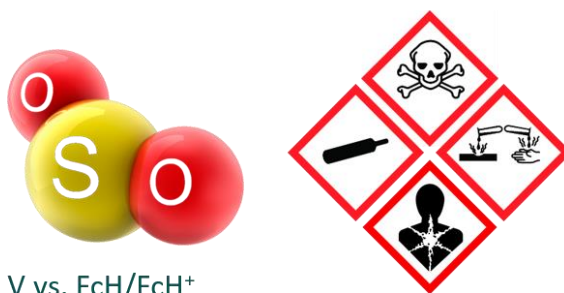


Figure 13: Important physical properties and GHS pictograms for SO_2 .^[132, 134]

1.3.1 Chemical structure

Being isoelectronic to ozone, sulfur dioxide exhibits an angular geometry with C_{2v} symmetry. This can be explained by valence shell electron pair repulsion (VSEPR) theory, as the free electron pair at the sulfur atom also occupies spatial volume. Combined with the highly different electronegativities ($\Delta\text{EN} = 3.50 - 2.44 = 1.06$), SO_2 exhibits a very high dipole moment of 1.61 D,^[135] rendering it an excellent solvent (at lowered temperatures) for both organic and inorganic salts.^[136]

The exact bonding situation of the molecule has long been a topic of extensive debate.^[137] Historically, the sulfur atom's 3d orbitals were considered too high in energy to significantly contribute to bonding. Consequently, a model analogous to ozone was proposed, featuring charge-separated resonance structures with one S–O single bond and one S=O double bond, stabilized by mesomeric resonance (Figure 14, **13a** and **13b**), resulting in an effective bond order of 1.5. However, this model does not fully align with experimentally observed bond lengths and angles. Newer research suggests a minor contribution from 3d orbitals or the involvement of the S atom lone pair *via* a recoupled pair bond dyad, leading to a description of sulfur dioxide containing two S=O double bonds (structure **14**), which is now the generally accepted representation.^[137, 138]

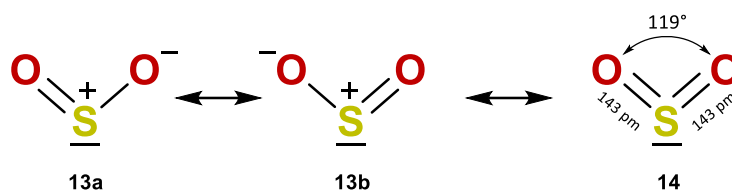


Figure 14: Geometry and bonding nature of the sulfur dioxide molecule.

Responsible for the diverse reactivity of SO_2 are its frontier orbitals (Figure 15). Sulfur dioxide possesses a high-in-energy $4n$ -HOMO, showing significant participation from all three atoms, although the S atom being the primary contributor. This configuration explains the observed nucleophilicity and its capability to act as a donor ligand for soft transition metals, forming linear $\text{M}-\text{SO}_2$ complexes.^[139] The $1\pi^*$ -LUMO, on the other hand, is more strictly localized on the S atom and mainly formed by its p_x -orbital arranged perpendicular to the SO_2 plane. It only includes minor antibonding contributions from the p_x -orbitals of the oxygen atoms. Due to the relatively low energy of the LUMO, SO_2 also exhibits electrophilic properties at the same atom (!), enabling various nucleophiles to form $\text{S}-\text{X}$ bonds.

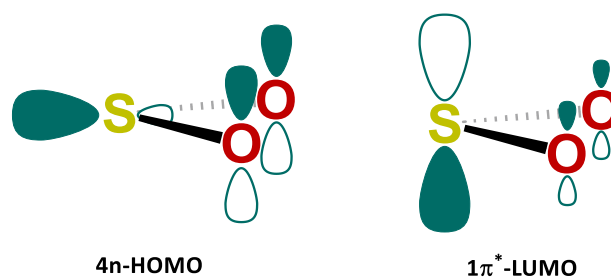


Figure 15: Frontier orbitals of sulfur dioxide.^[58b, 139a]

Importantly, sulfur dioxide may also form a sufficiently stable singly occupied molecular orbital (SOMO).^[140] This renders SO_2 a popular radical trap in organic synthesis, enabling its incorporation and consequently the formation of numerous structural motifs, e.g. sulfones, sulfonates, sulfonamides, sulfonylhalogenides or sulfinate salts.^[141]

1.3.2 Production, natural appearance and applications

The majority of industrially produced sulfur dioxide ultimately originates from waste streams, either through roasting and smelting of nonferrous metals, or generated as a byproduct during the refinement of crude oil and natural gas (Figure 16).^[142] To produce high-octane gasoline from naphtha, the crude feedstock must first undergo desulfurization, as even trace amounts of sulfur or sulfur-containing compounds can deactivate the noble metal catalysts used in catalytic reforming. This is achieved through hydrodesulfurization, a reductive treatment that generates hydrogen sulfide (H_2S). In the subsequent Claus process, a portion of the H_2S is oxidized to sulfur dioxide, which

then reacts with the remaining H_2S in a comproportionation reaction, yielding elemental sulfur. Sulfur dioxide is finally obtained through combustion in an oxygen-rich environment.^[143]

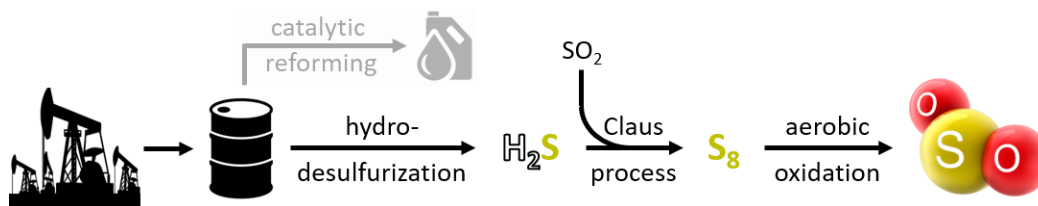


Figure 16: Industrial production of SO_2 .

Atmospheric sulfur dioxide is naturally emitted during volcanic eruptions. However, its current concentration of approximately 15 ppb is predominantly anthropogenic. Significant quantities of SO_2 are released through the combustion of coal and low-grade marine diesel and bunker fuel. In developing and emerging countries, regulations governing flue-gas desulfurization are less stringent compared to industrialized nations, leading to increasing SO_2 emissions.^[144] This is a matter of concern, as sulfur dioxide is a well-known pollutant. It's directly responsible for the formation of acid rain and can influence global climate in multiple ways.^[145] Despite this, some countries, notably China, have experimented with the deliberate injection of SO_2 into the atmosphere. This practice, known as cloud seeding, intends to induce rainfall through nucleation, scatter shortwave solar radiation and enhance longwave absorption.^[146] However, geoengineering remains highly controversial due to the unpredictable and potentially adverse long-term effects of intervening in earth's sensitive climate systems.^[147]

Due to its unique properties as a mild oxidant and reductant, sulfur dioxide possesses many important applications, not only in industry but in daily life as well (Figure 17). The majority of intentionally produced SO_2 is directly utilized in the synthesis of sulfuric acid (H_2SO_4), one of the most widely used of all industrial chemicals.^[148] This conversion is carried out *via* the contact process, where sulfur dioxide is oxidized to sulfur trioxide (SO_3) using molecular oxygen and a vanadium pentoxide (V_2O_5) catalyst. SO_3 is subsequently absorbed into sulfuric acid to produce oleum, which is then diluted with water to obtain sulfuric acid of very high concentration.

In the food industry, sulfur dioxide is widely applied as an antioxidant and preservative.^[149] Its aqueous derivative, sulfite (HSO_3^- , additive E220), is commonly employed in wine making and storage of dried fruits in order to extend shelf life and for the antimicrobial treatment of containers and wooden barrels. The pulp and paper industry utilizes the reducing properties of SO_2 by bleaching paper and cloths with sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$).^[150] In wastewater treatment plants, sulfur dioxide serves dual purposes, as it removes excess chlorine from disinfected wastewater prior to environmental discharge, and acts as an antimicrobial agent.^[151] Similarly, its moderate but acute toxicity has been exploited in the United States for post-harvest pest control through crop

fumigation.^[152] Due to its ease of condensation and high heat of evaporation, sulfur dioxide was historically used as a refrigerant in home appliances.^[153] However, it was later replaced by less toxic, though more environmentally harmful, hydrochlorofluorocarbons (HCFCs). In response to the ban on sulfur hexafluoride (SF₆) due to its extremely high global warming potential (*vide supra*), SO₂ is currently being investigated as an inexpensive alternative cover gas for handling and processing molten magnesium.^[154]



Figure 17: Applications and uses of sulfur dioxide.

1.3.3 Handling sulfur dioxide in the lab

The safe handling of a toxic gas such as SO₂, while manageable in chemical production environments, frequently presents challenges in academic laboratory settings. Due to its corrosive nature, specialized equipment, including inert valves and tubing, is required. This equipment must be leak-free and undergo regular inspections to ensure safety. Furthermore, experimental setups for gas introduction are typically more intricate, controlling the stoichiometry of gaseous compounds is inherently challenging, and any excess gas must be appropriately quenched prior to disposal to ensure safety and regulatory compliance. This effectively hindered the widespread application of sulfur dioxide in research laboratories.^[155]

Instead, six-valent sulfur moiety's like sulfonates, sulfones or sulfonamides have predominantly been synthesized through prefunctionalization strategies, utilizing thiols, sulfides, sulfoxides, sulfinates or sulfonyl halides as precursors.^[156] Similarly, sulfur(VI) fluoride exchange (SuFEx) click chemistry, which was introduced by Sharpless in 2014^[157], can be used to display sulfonyl-derived compounds, but the number of suitable precursors remains limited and fluorination is often non-trivial.^[158]

Surrogates

An alternative approach for the construction of SO₂ moieties involves the use of surrogates, which are bench-stable, non-gaseous compounds that act as substitutes by releasing the desired gas in-situ. This allows for a safer, more controlled and convenient introduction into the desired reaction.^[159] Surrogates for the highly toxic gas carbon monoxide (CO), such as molybdenum hexacarbonyl (Mo(CO)₆), COgen or dimethylformamide, have been widely utilized in carbonylation reactions for some time.^[160] But similar reagents, releasing SO₂ for sulfonylation reactions, have only seen very limited use. This changed in 2011 with the introduction of the 1,4-diazabicyclo[2.2.2]octane-SO₂ adduct DABSO by Willis,^[161] which revitalized interest in sulfur dioxide chemistry.^[162] Since then, a number of SO₂-releasing reagents have been found/rediscovered (Figure 18 top).^[155, 163] For instance, alkali metabisulfites (e.g. K₂S₂O₅) release sulfur dioxide upon acidification, while thiourea dioxide is capable of producing the sulfur dioxide dianion under alkaline conditions, which in turn can be oxidized to the radical monoanion for further synthetic use. Thermal decomposition of sulfolene *via* cheletropic cycloreversion generates SO₂ along with 1,3-butadiene. Perbromothiophene-1,1-dioxide, termed SOgen, can be used for the on-demand ex-situ generation of SO₂ gas *via* a Diels-Alder reaction with 4-methylstyrene and subsequent retro-cycloaddition. With the introduction of DABSO, additional surrogates have been developed that exploit the formation of complexes between SO₂ and basic nitrogen atoms through dative bonding (Figure 18 bottom). Notable examples include the *N*-methylpyrrolidine-SO₂ adduct TIMSO^[164] or the *N,N*-dimethylaminopyridine-SO₂ complex DMAP-SO₂.

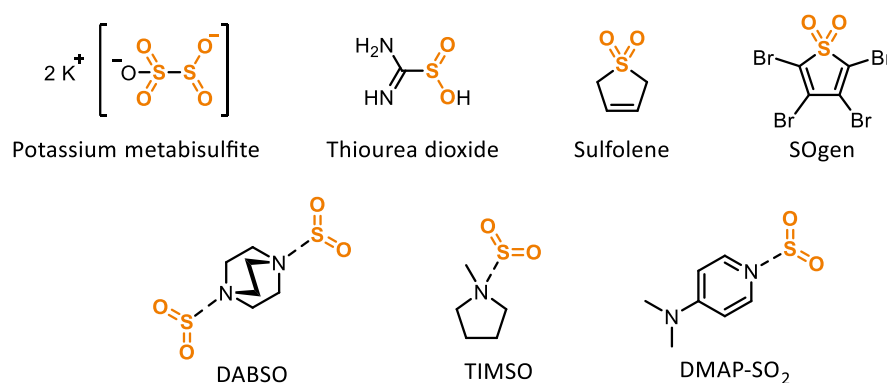


Figure 18: Commercially available and frequently used SO₂ surrogates.

While unarguably being safer and more convenient than sulfur dioxide gas itself, the use of surrogates is also associated with several drawbacks.^[140a] Firstly, they often exhibit low atom efficiency, with the sulfur dioxide content typically comprising less than 50% of their mass. Some surrogates only generate reduced sulfur dioxide species, such as the radical anion (SO₂^{•-}) or the dianion (SO₂²⁻), and the ex-situ generation of SO₂ using SOgen still requires specialized equipment. Amine-SO₂ complexes, such as DABSO, are not only expensive but also exhibit limited solubility in

many commonly used organic solvents. In photochemical reactions, suspensions can drastically interfere with the irradiation through scattering and/or absorption of light. As a result, elevated reaction temperatures are required, in some cases even exceeding the solvent's boiling point, necessitating the use of pressurized reaction vessels. Poor solubility is also the most significant limitation of alkali metabisulfites, although they are relatively inexpensive and offer comparatively high atom efficiency. Finally, the residual skeleton of the surrogates can complicate reaction workup and, in some cases, interfere with the desired reactivity. For example, in electrochemical reactions the easy-to-oxidize 1,4-diazabicyclo[2.2.2]octane-skeleton of DABSO can lead to competing reactions at the anode, reducing efficiency or prohibiting the desired reaction entirely.^[165]

Stock solutions

These limitations can be addressed by utilizing simple stock solutions of sulfur dioxide. One well-known example is the Karl-Fischer reagent,^[166] a methanolic solution containing 15–20 wt.% SO_2 along with small amounts of pyridine. Sulfur dioxide demonstrates moderate to high solubility (up to 6 mol/L at room temperature)^[167] in various polar solvents,^[167] such as MeCN, DMF, DMSO, DMA, propylene carbonate, HFIP, THF, or DCM. Stock solutions can be readily prepared by introducing SO_2 gas into the solvent at 0 °C (Figure 19), a simple technique commonly taught to undergraduate chemistry students. Alternatively, they can be bought through a commercial vendor like Sigma Aldrich.^[168]

Stock solutions offer several advantages over surrogates, including high atom efficiency and an easy, straightforward handling. Moreover, the concentration of SO_2 can be precisely determined *via* iodometric titration,^[169] photometry, or simple gravimetric weighing, enabling accurate control of the stoichiometry in reaction mixtures. Importantly, these stock solutions proved to be storable in a fridge (around +4 °C) for over months, without losing much of their sulfur dioxide content, particularly when kept below the solvent's saturation limit.^[170] Not saturating the solution is advised anyway, as it simplifies handling and enhances safety. SO_2 stock solutions have been sparsely applied for electroanalytical measurements and put to limited synthetic use since the 1970s, but have seen a revival in recent years together with the general interest in sulfur dioxide chemistry.^[140a]

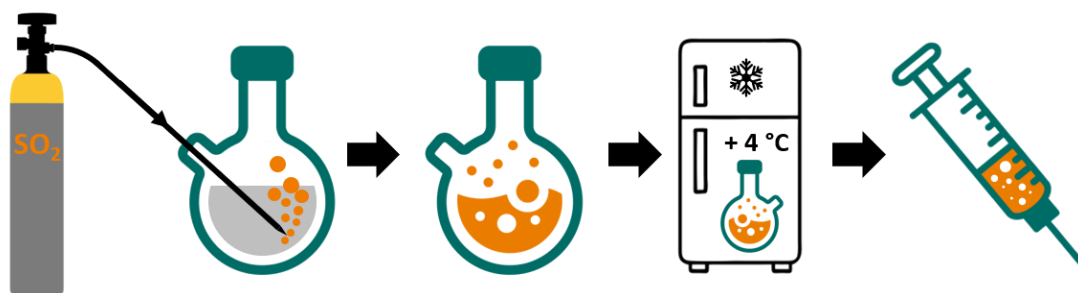
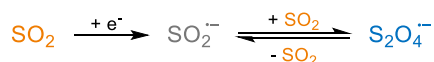


Figure 19: Preparation, storage and usage of SO_2 stock solutions.

1.4 Preceding work

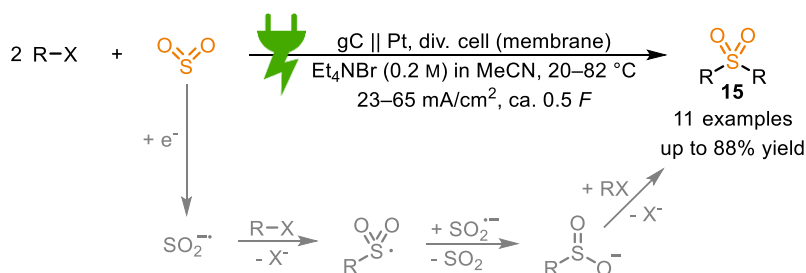
Electrochemical sulfonylation reactions utilizing sulfur dioxide stock solutions can be broadly classified into cathodic (reductive) and anodic (oxidative) transformations. Sulfur dioxide is virtually non-oxidizable electrochemically, but it is readily reduced at approximately -0.4 V vs. FcH/FcH⁺.^[134] Depending on the electrode and the exact conditions present, SO₂ reduction often occurs prior to hydrogen evolution. Cathodic reduction of SO₂ generates the radical anion SO₂^{•-}, which is considered quite stable and has been extensively documented in the electroanalytical literature.^[171] It has been proposed^[172] that this radical anion exists in equilibrium with the S₂O₄^{•-} radical anion, formed *via* the addition of a closed-shell, unreacted SO₂ molecule, resulting in a deep blue solution (Scheme 8). Kinetic measurements indicate equilibrium constants between 230 l/mol and 8400 l/mol.^[173] Additionally, the SO₂^{•-} radical anion can dimerize to form dithionite S₂O₄²⁻.^[171b] If an anodic transformation is envisioned, attention must be given to potential interference from these species or the possibility of chemical shortcuts, leading to losses in efficiency.



Scheme 8: Electroreduction of SO₂ and the equilibrium of SO₂^{•-} with the deep blue S₂O₄^{•-} radical anion.

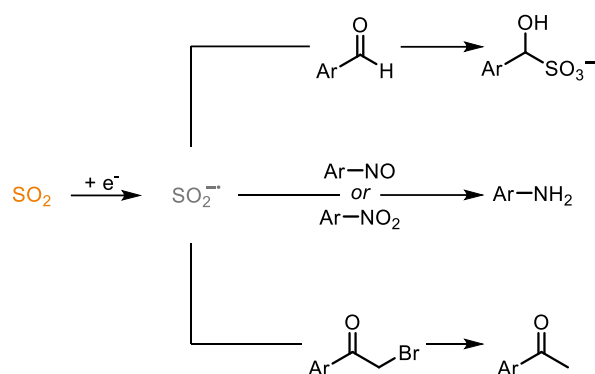
1.4.1 Cathodic transformation

In the 1970s, KNITTEL pioneered the synthetic application of the sulfur dioxide radical anion, enabling the synthesis of symmetrical sulfones (**15**) from alkyl, allyl, acyl, or benzyl halides (Scheme 9).^[174] The reaction proceeds *via* a nucleophilic attack on the halide by SO₂^{•-}, cleaving the R–X bond and generating an S-centered R–SO₂[•] radical. This intermediate is subsequently reduced by another SO₂^{•-}, followed by a nucleophilic attack of the resulting sulfinate on an unreacted halide, ultimately yielding the symmetrical sulfone **15** in good to excellent yields. When 1,X-dihalides are used, cyclic sulfones can be synthesized, though 1,2-dihalides undergo reductive elimination, producing terminal alkenes instead.^[175] Later on, a paired electrolysis approach, utilizing anodically generated Br₂ and reacting it with alcohols forming the alkyl halides in-situ, was developed as well.^[176]



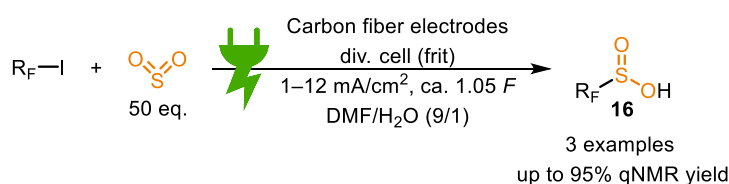
Scheme 9: Cathodic synthesis of symmetrical sulfones *via* reduction of SO₂ with the amount of applied charge as limiting component.^[174] R = alkyl, allyl, acyl, benzyl. X = Cl, Br, I.

Knittel also explored the sulfur dioxide radical anion $\text{SO}_2^{\bullet-}$ as a reducing agent in a two-step "ex-cell" process. After electrolysis of SO_2 -containing solutions leading to the formation of a deep blue mixture, various substrates bearing reducible functionalities were added. It was found that aromatic nitro or nitroso compounds were readily reduced to the corresponding anilines, aldehydes converted to alcohols and that α -bromoketones could be dehalogenated in the presence of water.^[172] The reactive species in this case is believed to be the radical anion $\text{SO}_2^{\bullet-}$, and not its colorful SO_2 -adduct.



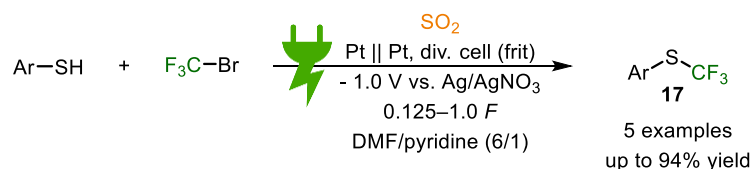
Scheme 10: Using the electrochemically generated $\text{SO}_2^{\bullet-}$ radical anion as a reducing agent.^[172] Ar = aryl.

In 1988, the group of Commeyras reported the sulfonylation of perfluorated iodoalkanes in a DMF/ H_2O mixture, yielding perfluoroalkylsulfonic acids (**16**) after an acidic workup (Scheme 11).^[177] Since cyclic voltammetry studies revealed similar reduction potentials for perfluoroiodohexane and SO_2 , it was hypothesized that the reaction mechanism involves the simultaneous reduction of the two species and subsequent radical recombination. Using 1,4-diiodoperfluorobutane, the corresponding disulfonylated product could be obtained. Notably, a lowered water content lead to the formation of the corresponding carboxylic acids.



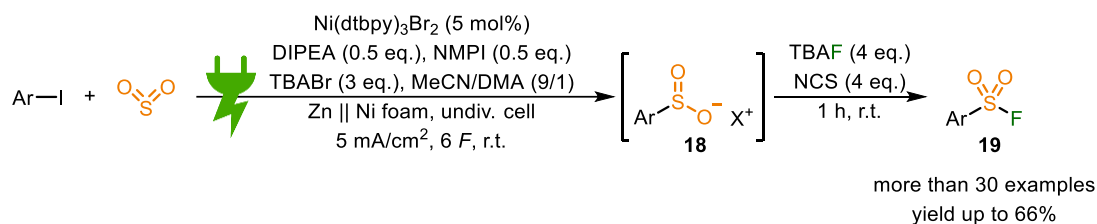
Scheme 11: Synthesis of perfluoroalkylsulfonic acids with a SO_2 stock solution.^[177] R_F = perfluoroalkyl.

Koshechko and coworkers leveraged the exceptional stability of the $\text{SO}_2^{\bullet-}$ radical anion to mediate the trifluoromethylation of aromatic thiols under potentiostatic conditions (Scheme 12).^[178] In this process, electrochemically generated $\text{SO}_2^{\bullet-}$ reduces bromotrifluoromethane, generating a trifluoromethyl radical. Sulfur dioxide mediation lowers the activation barrier for CF_3Br reduction and subsequent C-Br bond cleavage, as evidenced by literature reports.^[179] The $\text{CF}_3^{\bullet}$ radical then adds to the thiophenol substrate, followed by deprotonation and electron back transfer to SO_2 , completing the catalytic cycle and yielding the desired trifluoromethyl sulfides (**17**) in very high yields of up to 94%.



Scheme 12: Using the $\text{SO}_2/\text{SO}_2^{\bullet-}$ pair as a mediator for the trifluoromethylation of thiophenols.^[178] Ar = aryl.

In 2022, the Baran group used stock solutions of sulfur dioxide in a Ni-catalyzed cathodic approach to access aryl sulfinate salts (**18**).^[170] These can be converted to the corresponding sulfonyl fluorides (**19**) in a one-pot protocol using excess of tetrabutylammonium fluoride (TBAF) and *N*-chlorosuccinimide (NCS) as external oxidizer. Although yields are limited, the reaction proceeds with both electron-rich and electron-poor arenes, tolerating various functional groups including (Boc-protected) amides, sulfides, halo-substituents, ketones or carboxylic acids. Using aryl bromides instead of iodides is possible as well. Trying to explain the numerous additives necessary for the reaction, the mechanistic proposal features multiple interlocking catalytic cycles, with the key step being the activation of the Ni(II) catalyst at a Nickel foam cathode.



Scheme 13: One-pot electrochemical multi-component reaction to access aryl sulfonyl fluorides (**19**) via intermediate sulfinate salts (**18**).^[170] Ar = Aryl.

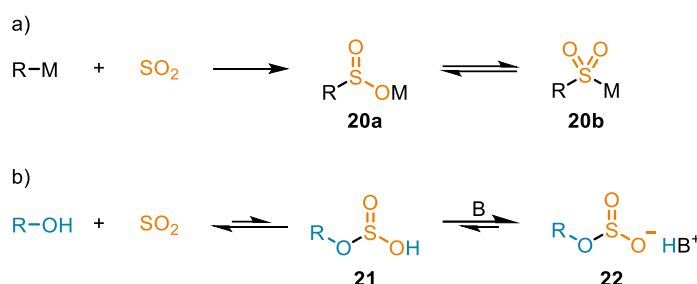
1.4.2 Anodic transformations

The use of sulfur dioxide stock solutions in anodic reactions was pioneered in the group of Waldvogel.^[180] Given the inherent difficulty of oxidizing SO_2 directly, it was hypothesized that other substrates could more readily undergo anodic oxidation to generate sufficiently stable radical cations. These intermediates could subsequently add to species derived from SO_2 , forming sulfur(VI) compounds like sulfonates, sulfonamides or sulfamides.

In-situ generation of monoalkylsulfites

The electrophilic nature of sulfur dioxide has long been recognized and utilized in conjunction with carbon nucleophiles, such as organometallic reagents, to produce highly reactive metal sulfinate salts (**20a** and **20b**, Scheme 14a). These nucleophilic intermediates demonstrate broad reactivity and are involved in a wide array of transformations.^[162] When heteroatom nucleophiles (e.g. alcohols) are employed instead, sulfur dioxide is known to formally insert into the O–H bond, forming monoalkylsulfurous acids (**21**, Scheme 14b) – a behavior analogous to that of CO_2 , CS_2 , and SeO_2 .^[181]

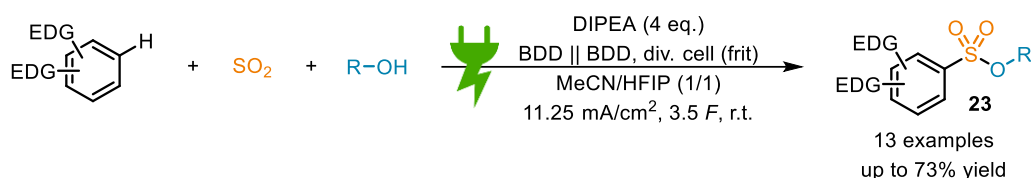
In the presence of an organic base, the equilibrium shifts toward the deprotonated monoalkylsulfite (**22**), which is stabilized by mesomeric effects. The stoichiometric mixture of an alcohol, SO_2 , and an organic base produces a so-called switchable ionic liquid (SIL).^[182] SILs exhibit the ability to reversibly alter their physical properties upon gas uptake or release and have been used as matrices for NMR studies^[183] and as solvents for the delignification of lignocellulosic materials.^[184] However, the synthetic application of sulfite-based SILs as reactants remained largely unexplored.



Scheme 14: Comparison between the synthesis of metal sulfinates (a) and the formation of monoalkylsulfites (b) from alcohols, SO_2 and an organic base (B). M = MgX, Li, ZnX.

Multi-component electrosynthesis using monoalkylsulfites

Utilizing these species, the constant current electrosynthesis of alkyl arylsulfonates (**23**, Scheme 15) was explored.^[185] Various arenes containing multiple electron-donating methoxy groups were successfully sulfonated, achieving yields of up to 73%. The alcohol component was varied within a limited range, demonstrating that simple alkyl alcohols could be used. Key requirements of the process are the use of a divided cell setup (frit), inert but expensive BDD electrodes and a solvent mixture of equal volumes of MeCN and HFIP. The separator effectively minimized interference from the $\text{SO}_2^{\bullet-}$ radical anion (generated at the cathode as a counter reaction), while the fluorinated cosolvent HFIP is thought to stabilize both the anodically generated aryl radicals through cluster formation and the monoalkylsulfite *via* hydrogen bonding.^[186]



Scheme 15: Multi-component electrosynthesis of alkyl aryl sulfonates developed in the Waldvogel group.
EDG = electron-donating group, OMe; R = alkyl.^[185]

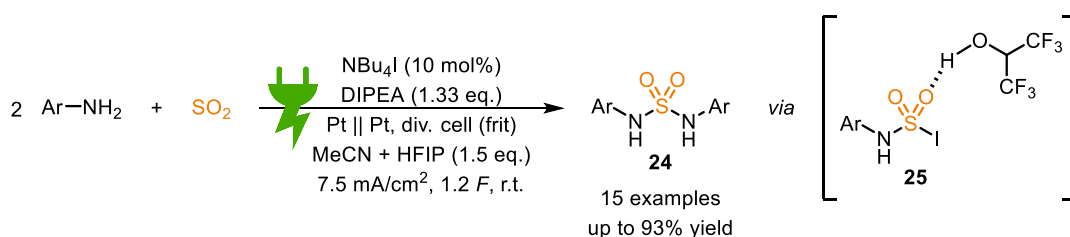
Cyclic voltammetry experiments revealed that the very electron-rich arene undergoes oxidation first, while the in-situ generated monoalkylsulfite **22** remains unexpectedly stable under the reaction conditions. The mechanistic proposal therefore features a nucleophilic sulfur-centered attack of **22** to the anodically oxidized arene, followed by second oxidation and proton abstraction, rearomatizing the arene and forming the sulfonate product **23**. Notably, *O*-attack by the monoalkylsulfite **22** was

not observed, presumably due to suppression of the *O*-nucleophilicity *via* hydrogen bonding from HFIP. Due to the ionic nature of **22**, the system inherently provides excellent conductivity, eliminating the need for additional supporting electrolytes.

This transformation was successfully adapted to flow chemistry and served as a model reaction for the automated optimization of reaction conditions using a combined OVAT and DoE approach.^[187] Replacing alcohols with primary or secondary amines produces amidosulfonates, enabling the methodology to be adapted for the synthesis of highly valuable alkyl aryl sulfonamides, with otherwise only minor modifications to the reaction conditions.^[188] The sulfonamide synthesis was later on adapted to flow chemistry as well, employing an undivided cell in a single-pass configuration and utilizing a more cost-effective stainless-steel cathode, enhancing overall productivity, simplicity and economic feasibility.^[189]

Iodine-mediated synthesis of symmetrical sulfamides

The anodic chemistry of sulfur dioxide stock solutions was ultimately paired with anilines as substrates, forming symmetrical arylsulfamides (**24**) *via* an I^-/I_2 mediated process (Scheme 16).^[190] A critical advancement was the effective suppression of the polymerization of anilines into aniline black,^[191] achieved by introducing catalytic amounts of iodide. Iodide, being more readily oxidized than anilines, generates molecular iodine, which is hypothesized to activate the aniline- SO_2 adduct by forming a sulfamoyl iodide intermediate (**25**). This intermediate, stabilized through hydrogen bonding interactions with the additive HFIP, subsequently undergoes a nucleophilic substitution reaction with another aniline molecule, forming the desired sulfamide product. The byproduct HI is intercepted by the organic base (DIPEA) already present in the system.



Scheme 16: I^-/I_2 -mediated electrosynthesis of symmetrical arylsulfamides.^[190] Ar = aryl.

2 Objectives

By employing efficient and easy-to-use stock solutions of sulfur dioxide for the in-situ generation of sulfonyl-based nucleophilic reactants, the present work aimed to expand the methodology developed within the research group to more widely utilized substance classes (Figure 20). The versatility of this approach for synthetically and industrially relevant compounds should be demonstrated on both aromatic and non-aromatic substrates as well as more complex alcohols and/or amines. Ideally, starting materials derived from biobased, renewable feedstocks should be used, promoting a more sustainable approach towards chemical synthesis.

For further optimization of the process, the use of SO_2 reduction as the counter reaction should be avoided, as it generates excessive waste and leads to the formation of comparably stable radicals that can interfere with the desired transformations. Accompanying, the electrochemical setup should be simplified by eliminating the need for a divided cell and utilizing more cost-effective electrode materials. Furthermore, the previously used fluorinated (co)solvent HFIP is classified as reprotoxic and environmentally persistent,^[192] necessitating its replacement. Additionally, the simultaneous use of the alcohol reactant as solvent drastically limits the possibility of applicable substrates and is therefore to be avoided as well.

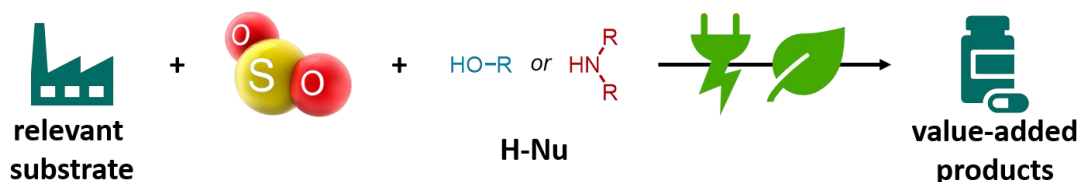


Figure 20: Conceptual design for the electrochemical multi-component synthesis of sulfonyl-based products.

Implementing these improvements would help to establish electrochemical multi-component sulfonylations as a sustainable, straight forward and efficient strategy for synthesizing value-added products from simple and abundant starting materials by incorporation of the pollutant SO_2 .

3 Results and discussion

As part of the BMBF future cluster *Electrifying Technical Organic Syntheses* (ETOS)^[193] and its subproject *Electrochemical incorporation of SO₂ and late-stage functionalization of complex molecules* (E-SONATA, FKZ 03ZU12051A), this work explored the efficient synthesis of highly functionalized sulfonyl-containing motifs through "reagent-free" SO₂ incorporation utilizing stock solutions. The findings are categorized into three sections based on the starting materials central to the conducted transformations (Figure 21). A unifying theme across all segments is the electrochemical multi-component sulfonylation of substrates bearing a conjugated double bond.

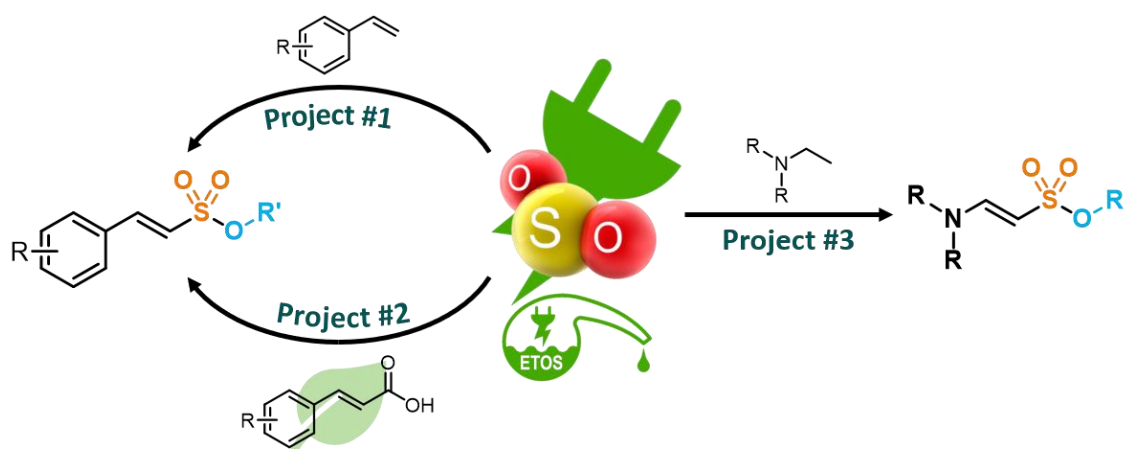


Figure 21: Project overview of the work conducted within this thesis.

In the first project, the electrochemical reaction of styrenes, sulfur dioxide, and alcohols was investigated, leading to the sulfonylation of the double bond in the β -position. A divided cell setup employing cost-effective graphite foil and stainless-steel electrodes was used, with the counter reaction efficiently substituted by hydrogen evolution from stoichiometric amounts of acetic acid. Furthermore, the need for HFIP as a stabilizing cosolvent was successfully avoided.

This straightforward approach prompted collaboration with the research group of Manolikakes from the University of Kaiserslautern-Landau (RPTU) to explore alternative, "greener" starting materials for the synthesis of β -styrenesulfonates. This effort led to the second project, which focused on the decarboxylative electrosulfonylation of cinnamic acids. Unlike styrenes, which are derived from fossil resources, cinnamic acids can be obtained from biomass. Therefore, they can be classified as a renewable feedstock, enhancing the sustainability of the given transformation and aligning it further with the principles of Green Chemistry.

In the third project, the adaption of the developed techniques to non-aromatic substrates was explored. Building on the previous findings and literature reports, enamines, widely known in organic chemistry for their synthetic versatility, were identified as suitable starting materials for the

sulfonylation reaction. Given that enamines can be generated electrochemically through the anodic oxidation of trialkylamines, a one-pot synthesis of enaminyll sulfonates was developed, starting from abundant alkylamines, SO_2 , and alcohols and (to limited extend) amines. Notably, the divided electrochemical cell was successfully replaced with a quasi-divided one, greatly simplifying the reaction setup while simultaneously improving overall sustainability.

3.1 Electrochemical sulfonylation of styrenes

A manuscript was published on this chapter

Aloisio de A. Bartolomeu, [‡] [Florian A. Breitschaft](#), [‡] Dieter Schollmeyer, Ronaldo A. Pilli, Siegfried R. Waldvogel, *Electrochemical Multicomponent Synthesis of Alkyl Alkenesulfonates using Styrenes, SO₂ and Alcohols*, *Chem. Eur. J.* **2024**, *30*, e202400557.

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[‡]These authors contributed equally to this work and are listed in alphabetical order.

Contributions:

The project was conceived by A. de A. Bartolomeu, S. R. Waldvogel, and me. The laboratory work including optimization of reaction conditions, synthesis, purification and isolation of compounds as well as mechanistic investigations and analytical measurements were conducted in equal amounts by A. de A. Bartolomeu and me. D. Schollmeyer measured and interpreted X-ray crystallographic data. The original draft of the manuscript and its Supporting Information was written by A. de A. Bartolomeu and me. S. R. Waldvogel and R. A. Pilli proof-read as well as corrected the manuscript prior to submission.

3.1.1 Introduction

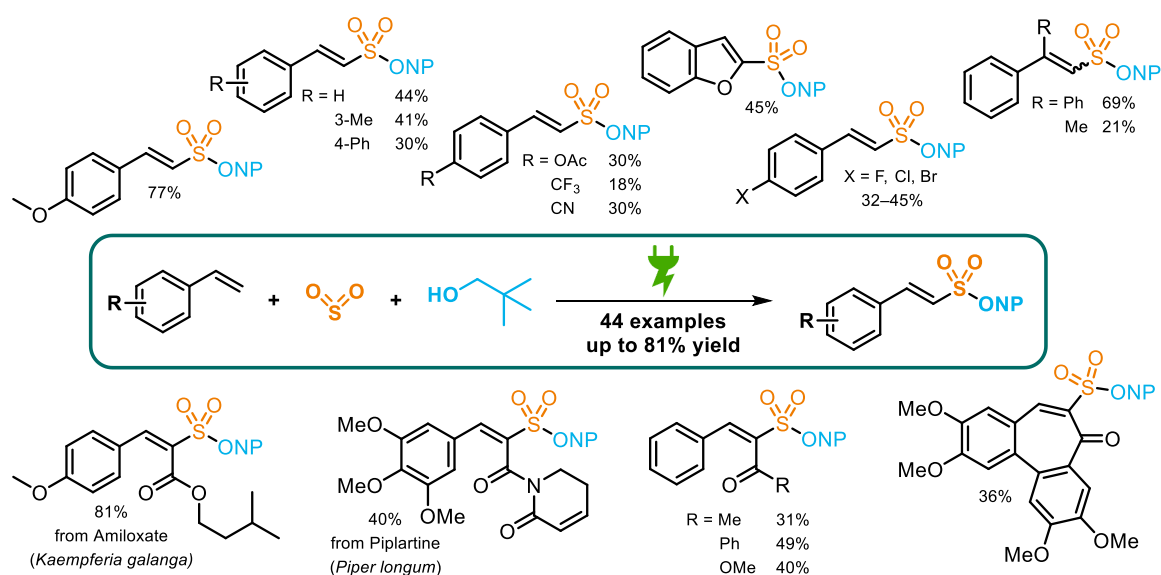
Due to their unique properties, alkenesulfonates have gathered significant attention in both medicinal and polymer chemistry. Linking the sulfonate moiety directly to the polymer chain, these monomers serve as essential building blocks for materials such as hydrogels, proton exchange membranes or for the modification of dyes.^[194] In medicinal research, styrene-derived sulfonate esters have demonstrated significant bioactivity, particularly in targeting pathways relevant to the treatment of diabetes, obesity, and cancer.^[195] Furthermore, these compounds are promising candidates for anti-inflammatory and antioxidant therapies associated with Parkinson's disease.^[196]

The conventional synthesis of β -styrenesulfonates typically necessitates harsh reaction conditions, including treatment with sulfur trioxide (SO₃), phosphorus pentachloride (PCl₅), or sulfuryl chloride (SO₂Cl₂).^[197] Contemporary approaches rely on prefunctionalization, high temperatures and precious transition metal catalysis *via* a Heck-type coupling reaction.^[198] By utilizing sulfur dioxide stock solutions in an electrochemical approach, a more sustainable and direct synthetic route to β -styrenesulfonates has been established.

3.1.2 Summary of the results

Optimization began using 4-methoxystyrene, SO₂ stock solution and neopentyl alcohol as substrates with 8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as auxiliary base and MeCN as solvent in a divided cell with a glassy carbon anode, yielding the desired product in 48% (qNMR). By using a Sigraflex™ (graphite foil) anode and increasing the stoichiometry of alcohol and base as well as the current density, the yield could be improved to 69%. Further changes to the separator material (Nafion® membrane), the catholyte (adding acetic acid to promote hydrogen evolution) and optimizing the amount of applied charge enhanced the yield to 81%. Finally, increasing the SO₂ stoichiometry to 10 equivalents resulted in 85% qNMR yield, of which 77% could be isolated.

The scope of the reaction (Scheme 17) demonstrated broad functional group compatibility. Electron-rich styrenes, such as those bearing methoxy or *tert*-butoxy substituents, exhibited high reactivity, yielding the corresponding β -styrenesulfonates in up to 77%. Non- and electron-neutral substituted styrenes provided moderate yields, whereas electron-deficient substrates, including those with trifluoromethyl, nitrile, or acetoxy groups, afforded lower yields (18–30%) and required increased charge. Halogenated styrenes displayed moderate reactivity. Notably, α -phenyl substitution significantly improved yield due to enhanced conjugation, whereas α -methyl substitution resulted in a low yield and an isomeric mixture. The reaction scope was further expanded to include heteroaromatic and multicyclic systems, as well as cinnamic esters and chalcones. Additionally, two structurally complex natural products underwent successful sulfonylation in yields up to 81%, demonstrating the method's applicability for late-stage functionalization. Overall, the reaction proceeds with high regio- and stereoselectivity, predominantly yielding (*E*)-configured β -styrenesulfonates.

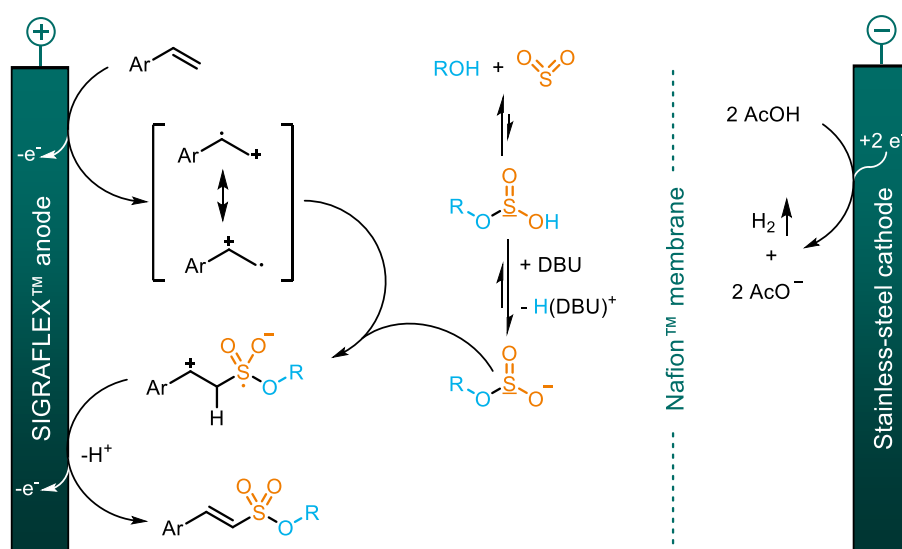


Scheme 17: Selected examples from the scope of styrenes. NP = neopentyl.

Evaluating the scope of alcohols, it was found that the simple primary alcohols methanol, ethanol, and neopentanol yielded good results (50–77%), while more sterically demanding compounds such as cyclohexanol, menthol, and borneol showed moderate yields (32–48%). Tertiary alcohols including *tert*-butanol were not applicable. Functionalized, chiral or very electron-deficit alcohols like HFIP were tolerated, forming the desired sulfonate ester in yields between 21–53%. Easy-to-oxidize phenols or *N*-alkylated amino alcohols failed to give the desired results.

The utility and robustness of the protocol was demonstrated in a scale-up experiment as well as reusability tests for the Sigraflex™ electrode. In the gram-scale reaction the qNMR yield did not change and the isolated yield dropped only insignificantly (73% vs. 77% on the micromolar scale). Reusing the graphite foil anode multiple times lead to a small, but steady decrease in yield (85% to 75% in four runs), which can be explained by electrode fouling.

Control experiments revealed that both electric charge and base are essential for product formation. The addition of radical scavengers TEMPO and BHT not only reduced the yield, but lead to the trapping of a monoalkylsulfite intermediate. Cyclic voltammetry studies revealed the early oxidation of the styrene substrate, while the monoalkylsulfite, formed from the alcohol, SO₂ and base in-situ, remained stable, as expected. Consequently, a mechanism was proposed (Scheme 18), featuring the terminal radical addition of the monoalkylsulfite to anodically oxidized styrene. Subsequent second oxidation and deprotonation through excess of base finally affords the desired β -styrenesulfonate product.



Scheme 18: Mechanistic proposal for the multi-component electro-synthesis of β -styrenesulfonates. Ar = aryl.

Electrochemical Multicomponent Synthesis of Alkyl Alkenesulfonates using Styrenes, SO₂ and Alcohols

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A novel electrochemical approach to access alkyl alkenesulfonates via a multicomponent reaction was developed. The metal-free method features easy-to-use SO₂ stock solution forming monoalkylsulfites from alcohols with an auxiliary base in-situ. These intermediates serve a dual role as starting materials and as supporting electrolyte enabling conductivity. Anodic oxidation of the substrate styrene, radical addition of these monoalkylsulfites and consecutive second oxidation and

deprotonation preserve the double bond and form alkyl β-styrenesulfonates in a highly regio- and stereoselective fashion. The feasibility of this electrosynthetic method is demonstrated in 44 examples with yields up to 81%, employing various styrenes and related substrates as well as a diverse set of alcohols. A gram-scale experiment underlines the applicability of this process, which uses inexpensive and readily available electrode materials.

Introduction

Alkenesulfonates have recently been found to exhibit unique biological activity. Cruzain, a cysteine protease found in *Trypanosoma cruzi*, the parasite responsible for Chagas disease with large occurrence in Africa and Latin America, is reversibly inhibited by these compounds (1, Figure 1).^[1] Human tyrosine phosphatase 1B (PTP1B), which is involved in insulin signaling, has been identified as a promising target for the treatment of diabetes, obesity and cancer.^[2] Numerous reports have shown that PTP1B is inhibited by molecules containing the alkene-sulfonate motif (2, Figure 1)^[3] with the key step being the Michael addition of an active cysteine residue to the electrophilic double bond. Furthermore, styrene-derived sulfonate

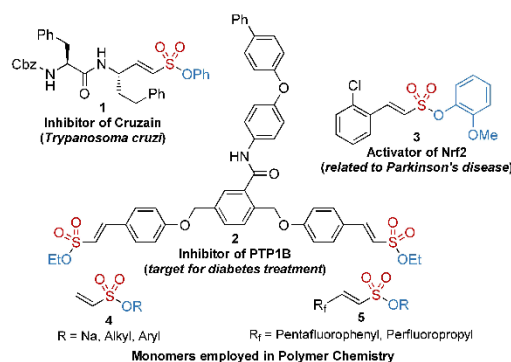


Figure 1. Relevant examples of alkenesulfonates.

esters (3, Figure 1) have been found to induce expression of nuclear factor E2-related factor-2 (Nrf2)^[4] and to inhibit the expression of inducible nitric oxide synthase.^[5] This renders them as potential candidates for the development of anti-inflammatory or antioxidant therapy related to Parkinson's disease.^[4] Additionally, alkenesulfonates represent a common motif in polymer chemistry, linking the sulfonate moiety directly to the polymer chain (4, Figure 1).^[6] Such polymers have a number of interesting properties and applications, ranging from thermoresponsivity,^[7] as hydrogels,^[8] modification of dyes,^[9] as blood-compatible materials,^[10] as polychelator,^[11] or for proton exchange membranes (PEMs) similar to Nafion™ (5, Figure 1).^[12]

The synthesis of β-styrenesulfonates is traditionally achieved by addition of sulfur trioxide to styrene, subsequent chlorination followed by substitution with an alcohol (Scheme 1a).^[13] Other approaches feature the use of sulfonyl chloride^[14] or Horner-Wadsworth-Emmons reactions.^[15] Contemporary methods rely on Pd-catalyzed Heck-type coupling starting either from aryl bromides^[16] or aryl diazonium salts (Scheme 1b).^[17] Additionally, sulfur fluoride exchange chemistry has been used

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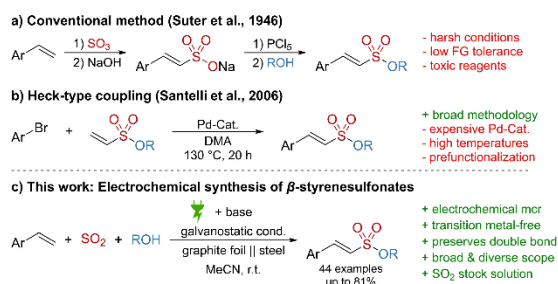
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Scheme 1. Selected methods for the synthesis of β -styrenesulfonates.

to construct alkenesulfonates.^[18] Whilst these strategies often lead to key intermediates allowing the synthesis of many different sulfonyl moieties,^[19] prefunctionalization and expensive transition metal- or photocatalysts are needed. Most vinyl sulfonyl building blocks have limited commercial availability and must therefore be synthesized when required.^[20] The use of electric current as green oxidant^[21,22] allows for the design of complex molecules in an inherently safe manner,^[23] while omitting toxic and/or expensive catalysts.^[24] Sulfur dioxide, despite being a powerful greenhouse gas with severe impacts on health and environment,^[25] is also a chemical feedstock produced annually on a million ton scale.^[26] Direct conversion of such a pollutant into value-added products like sulfonates,^[27] sulfonamides^[28,29] or sulfamides^[30] has been demonstrated using electrochemistry.^[31] Recently, electrochemical methods using SO₂ surrogates were published by the Han and the Ye groups.^[32] But they end up with β -alkoxyl sulfonates, losing the valuable double bond needed for further reactivity. Preserving this functionality and accessing highly desired β -styrenesulfonates, we now report an electrochemical multicomponent reaction

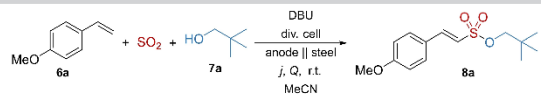
(mcr, Scheme 1c). It features the use of SO₂ stock solution and avoids prefunctionalization while also allowing the formation of complex sulfonates.

Results and Discussion

Optimization of Reaction Conditions

The investigation was started by employing 4-methoxystyrene (**6a**), SO₂ stock solution (0.75 M in acetonitrile) and neopentyl alcohol (**7a**) together with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) as auxiliary base in a divided setup using a glassy carbon electrode, the most common anode material.^[33] The catholyte simply consisted of supporting electrolyte (0.1 M Bu₄NBF₄ in acetonitrile) with small amounts of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) for promoting hydrogen evolution on a stainless-steel cathode, a well known additive in electroorganic transformations.^[22,34] Under these conditions the desired alkenesulfonate ester **8a** was formed in 48% yield (Table 1, Entry 1, see Supporting Information for detailed optimization studies). Higher amounts of alcohol and base proved to be beneficial (Entry 2), while screening of current density *j* improved the yield slightly to 64% with a glassy carbon anode (Entries 3–5). By using a SIGRAFLEX™ (graphite foil) anode, the yield could be enhanced up to 69% (Entry 6). SIGRAFLEX™ is an inexpensive material widely used for sealing or heat transfer purposes.^[35] The glass frit was then replaced by a Nafion™ membrane for easier handling (Entry 7) and optimizing the amount of applied charge (Entry 8) improved the yield to 74%. Replacement of the proton source in the catholyte to acetic acid instead of HFIP not only helped to avoid a toxic additive, but also increased the formation of **8a** to 81% (Entry 9). The impact of the counter reaction is often overlooked.^[36] Finally, additional SO₂ stock

Table 1. Optimization of reaction conditions.^[a]

				
Entry	<i>j</i> [mA×cm ⁻²]	Anode material	Q [F]	Yield [%] ^[b]
1	7.5	glassy carbon	2.5	48 ^[c]
2	7.5	glassy carbon	2.5	61
3	4.0	glassy carbon	2.5	55
4	10	glassy carbon	2.5	60
5	15	glassy carbon	2.5	64
6	10	SIGRAFLEX™	2.5	69
7	10	SIGRAFLEX™	2.5	72 ^[d]
8	10	SIGRAFLEX™	2.8	74 ^[d]
9	10	SIGRAFLEX™	2.8	81 ^[d,e]
10	10	SIGRAFLEX™	2.8	85 (77) ^[d,e,f]

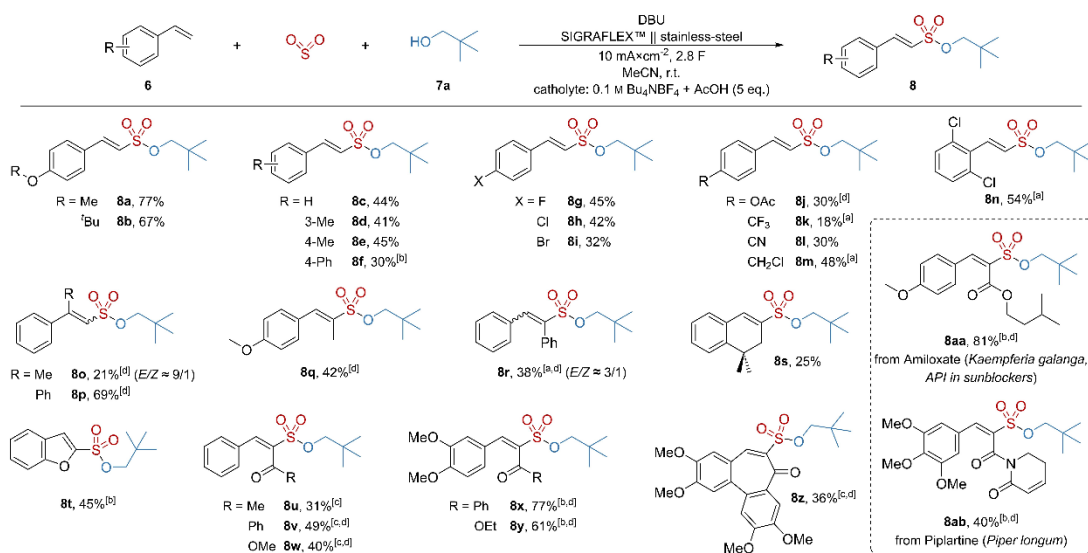
^[a] 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (7.5 eq.), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (glass frit), anode | stainless-steel, *j*, *Q*, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + HFIP (5 eq.). ^[b] Yield determined by ¹H NMR (ISTD). ^[c] 3 eq. alcohol and 5 eq. DBU. ^[d] Nafion™ membrane (N324). ^[e] Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[f] 10 eq. SO₂. Isolated yield in parentheses. ISTD = internal standard.

solution (10 eq.) afforded the desired alkenesulfonate in a yield of 85% (^1H NMR, Entry 10), of which 77% could be isolated. The structure of **8a** and its configuration were then fully proven by X-ray analysis of a suitable single crystal (CCDC 2300959).^[47]

Scope of the Reaction

With the optimized conditions in hand, the feasibility of the newly developed protocol was explored by employing various styrenes and related starting materials (Scheme 2). Electron-rich substrates with a methoxy (**8a**) or *tert*-butoxy group (**8b**) could be converted into the corresponding β -styrenesulfonates in yields of 77% and 67%, respectively. While the non-substituted styrene **8c** yielded 44%, substitution with a methyl group (**8d–e**) only had minor influence. A yield of only 30% was obtained when employing 4-vinylbiphenyl (**8f**), which is due to extensive electrode fouling, as evident by a sluggish layer formed on the anode during this experiment. 4-Halosubstituted arenes (**8g–i**) gave yields of 45%, 42% and 32% in decreasing order. Electron-withdrawing groups like acetoxy (**8j**), trifluoromethyl (**8k**) or nitrile (**8l**) not only lowered yields to 18–30%, but also needed more applied charge to reach full conversion. Bearing a valuable benzyl chloride functionality, **8m** gave a satisfying yield of 48%. A yield of 54% was achieved for the 2,6-dichlorostyryl derivative **8n**. Considering substitutions at the position α , we found that a methyl group only yielded 21% (**8o**) with the product being an isomeric mixture strongly in favor of the (*E*)-isomer (*E/Z* $\approx$ 9/1). Replacing the methyl by a phenyl group increased the yield drastically to 69% (**8p**). This is probably due to the planarity of the system, which enables good conjugation to the Ph-group and explains the increase in yield compared to the unsubstituted congener **8c**. In agree-

ment with the results above, methylation in position β seems unfavorable (**8q**, 42% yield, from *trans*-anethole) compared to the product obtained from 4-methoxystyrene (**8a**, 77% yield). In this case, 29% of doubly-sulfonylated by-product was isolated (see mechanistic discussion), explaining the declined yield. Starting with *trans*-stilbene, the corresponding alkenesulfonate **8r** was obtained as an isomeric mixture (*E/Z* $\approx$ 3/1) in 38% yield, which is due to the symmetrical nature of the substrate, always forcing an α -sulfonylation relative to one of the phenyl substituents. Bicyclic compound **8s** was isolated in 25% yield. Substrates with electron-withdrawing groups at position β , like nitro or cyano moieties, did not yield the desired products at all (see Supporting Information). But heteroaromatic benzofuran could also be sulfonylated in position 2, affording the corresponding sulfonate **8t** in 45% yield. Upon using indene, we observed decomposition of the starting material (see Supporting Information). Focusing on carbonyl groups, we found that methyl styryl ketone could be converted successfully into **8u** (31% yield) under these conditions. Bearing a phenyl substituent, chalcone and its related compounds are of great importance in medicinal chemistry.^[37] Sulfonylation of three of these structures yielded 49% (**8v**), 77% (**8x**) and 36% (**8z**), respectively. Another widespread class of substances are cinnamic esters, which were also converted into alkenesulfonates using the developed protocol. Cinnamic esters **8w** and **8y** yielded 40% and 61%, respectively, while the functionalization of amiloxate, a natural product found in *Kaempferia galanga* that's also approved as UV-absorbent in sun blockers,^[38] gave a very good yield of 81% (**8aa**). Piplartine, also named piperlongumine (isolated from *Piper longum*), an alkaloid recently discussed as a lead compound for anticancer agents,^[39] was also successfully sulfonylated (**8ab**, 40% yield). Unfortunately, dibenzofulvene was insoluble in the reaction mixture



Scheme 2. Scope of styrenes and related substrates for the synthesis of alkenesulfonates **8**. Conditions: substrate **6** (600 μmol , 1 eq., 0.1 M), SO_2 (10 eq.), neopentyl alcohol **7a** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA x cm $^{-2}$, 2.8 F, r.t., catholyte: 0.1 M Bu_4NBF_4 in MeCN + AcOH (5 eq.).^[a]3.5 F,^[b] 4 F,^[c] 5 F,^[d] 7.5 eq. SO_2 . Isolated yields are displayed.

(see Supporting Information). In general, it should be noted that the reaction exhibits excellent regio- and stereoselectivity, since the sulfonated products were obtained as pure (*E*)-isomers (except for **8o** and **8r**), although all starting materials were *trans*-configured. This intermediate rotation during the reaction is likely attributed to the steric demand of the sulfonate moiety and electronic conjugation.

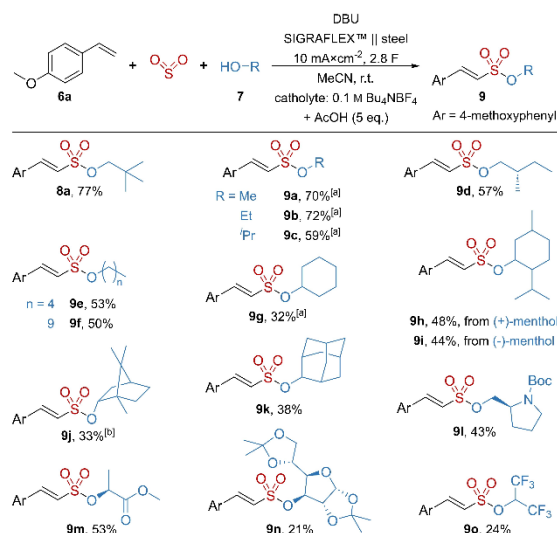
Following these promising results, different alcohols were also evaluated (Scheme 3). Besides neopentanol (**8a**, 77% yield), simple primary alcohols like methanol (**9a**) or ethanol (**9b**) were converted into the corresponding alkyl styrenesulfonate in good yields of 70% and 72%, respectively. Isopropyl sulfonate **9c** was obtained in an acceptable yield of 59%. Similar yields were obtained when using (2*S*)-methyl butanol (**9d**), 1-pentanol (**9e**) and even apolar 1-decanol (**9f**). While cyclohexyl sulfonate **9g** was obtained in 32% yield, employing (+)- and (−)-menthol yielded 48% and 44%, respectively (**9h–i**), indicating that chirality on the carbon of the OH-group does not influence the reaction. Sterically demanding (−)-borneol (**9j**, 33% yield) and even 2-adamantol derivative **9k** (38% yield) still afforded acceptable yields. Showcasing the range of applicable alcohols, better yields were obtained for Boc-protected amino alcohol (**9l**, 43% yield) as well as for methyl lactate (**9m**, 53% yield). An α -D-glucufuranose (**9n**) and even non-nucleophilic hexafluoro-isopropanol (**9o**) were also converted to the desired products, albeit with lowered yields of 21% and 24%, respectively. *N*-alkylated amino alcohols did not yield any alkyl alkenesulfonates (see Supporting Information), which is probably due to the lower oxidation potential of aliphatic amines and their follow-up reactions.^[40] Unfortunately, sterically highly demanding tertiary alcohols such as *tert*-

butanol or 1-adamantol were not applicable with this protocol. Easy to oxidize phenol indicated no desired product and upon using 2,4-dichlorophenol we observed the formation of dimers (see Supporting Information).

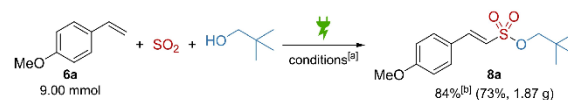
Scale-Up and Reusability Tests

To showcase the utility of our protocol, we conducted a 15-fold scale-up experiment (Scheme 4), wherein no significant change in ¹H NMR yield was observed. Isolation of alkyl styrenesulfonate **8a** yielded 73% in the gram-scale reaction, compared to 77% with the micromolar-scale experiment.

Additionally, the electrolysis setup was tested for repeated use. The reaction was carried out at identical conditions four consecutive times, exchanging only the anolyte after each batch while reusing everything else (see Supporting Information). These experiments revealed only a minor, gradual drop in yield (Figure 2). This can be explained by electrofouling. In electroanalytical measurements of styrenes, the formation of a polymer layer reaching a steady state of porosity is reported.^[41,42] Furthermore, we recently proved that electrolyte mixtures consisting of alcohol, amine and SO₂ can be easily recycled.^[29] The simple evaporation of the anolyte components facilitates down-stream processing for larger electrolysis and is a key step for translation in technical application.^[43] Together with the scale-up experiment, these results showcases the applicability of the method developed.



Scheme 3. Scope of alcohols for the synthesis of alkyl β -styrenesulfonates **9**. Conditions: substrate **6a** (600 μ mol, 1 eq., 0.1 M), SO₂ (10 eq.), alcohol **7** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA $\times$ cm^{−2}, 2.8 F, r.t., Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[a]7.5 eq. SO₂, ^[b]3.5 F. Ar = 4-methoxyphenyl. Isolated yields are displayed.



Scheme 4. Gram-scale experiment. ^[a]**6a** (9.00 mmol, 1 eq., 0.1 M), SO₂ (10 eq.), **7a** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA $\times$ cm^{−2}, 2.8 F, r.t., Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[b]Yield determined by ¹H NMR (ISTD). Isolated yield in parentheses.

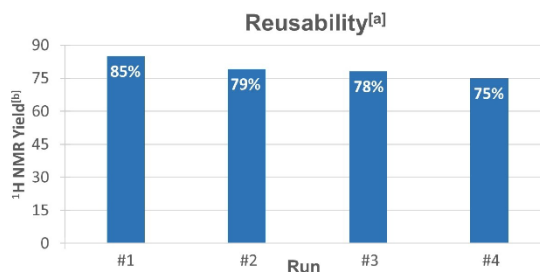


Figure 2. Tests for reusing the cell, only exchanging the anolyte. ^[a]**6a** (600 μ mol, 1 eq., 0.1 M), SO₂ (10 eq.), **7a** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA $\times$ cm^{−2}, 2.8 F, r.t., Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[b]Yield determined by ¹H NMR (ISTD).

Control Experiments and Mechanistic Studies

To elucidate the mechanism, control experiments were conducted (Table 2). No formation of the alkenesulfonate **8a** was observed when omitting electric current or the auxiliary base DBU (Entry 1 and 2). Upon addition of the radical scavengers 2,6-di-*tert*-butyl-4-methylphenol (BHT, Entry 3) or 2,2,6,6-tetramethylpiperidinyl-oxyl (TEMPO, Entry 4) yield dropped signifi-

Table 2. Control Experiments.		
Entry	Deviation from the standard conditions ^a	Yield of 8a [%] ^b
1	No current	0 ^c
2	No DBU (+ 0.1 M Bu ₄ NBF ₄ for conductivity)	0
3	+ BHT (3 eq.)	23
4	+ TEMPO (3 eq.)	10

^a **6a** (600 μmol, 1 eq., 0.1 M), SO₂ (10 eq.), **7a** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA x cm⁻², 2.8 F, r.t., Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^b Yield determined by ¹H NMR (ISTD). ^c Traces of the product detected via GC/MS.

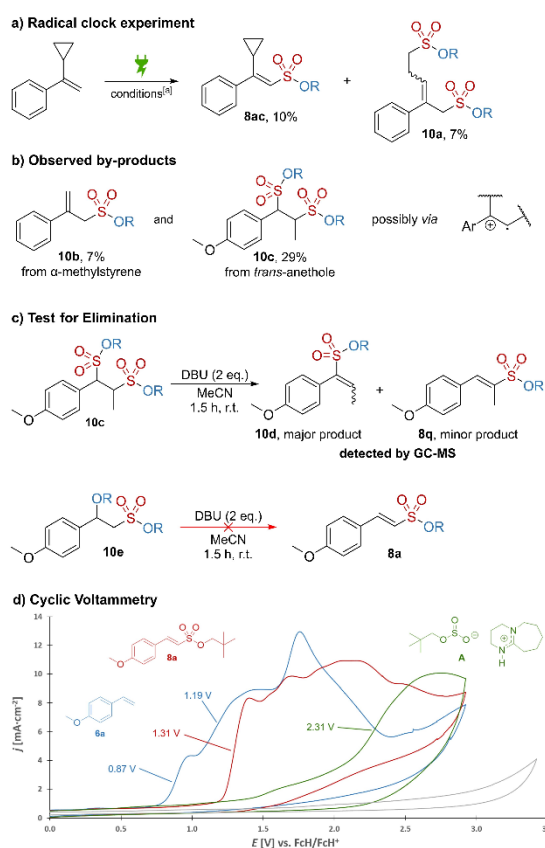


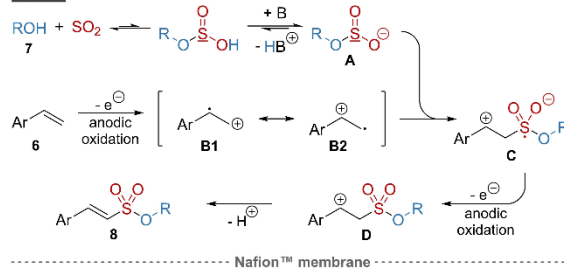
Figure 3. Mechanistic investigations. ^a α -cyclopropylstyrene (600 μmol, 1 eq., 0.1 M), SO₂ (10 eq.), **7a** (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324), SIGRAFLEX™ || stainless-steel, 10 mA x cm⁻², 2.0 F, r.t., Catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). R = neopentyl. Cyclic Voltammetry: styrene **6a** (blue), β -styrenesulfonate **8a** (red), monoalkylsulfite intermediate **A** (green), blank measurement (0.1 M Bu₄NBF₄ in MeCN; grey).

cantly. With BHT we detected a trapped intermediate (see Supporting Information), indicating the radical addition of an alkoxy sulfonyl species.

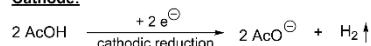
These findings were supported by a radical clock experiment involving α -cyclopropylstyrene (Figure 3a), where, besides the expected β -styrenesulfonate **8ac**, we were able to isolate a doubly-sulfonylated ring-opening product **10a**. During our investigation regarding the scope of styrene derivatives, we encountered by-products **10b** and **10c** (Figure 3b). They are most probably formed from an intermediate bearing a positive charge at position α of the styrene, leading to either subsequent deprotonation (**10b**) or nucleophilic trapping by a monoalkylsulfite as intermediate (**10c**). Further investigation of **10c** revealed the possibility to convert it into the desired product **8q** using DBU in acetonitrile. But the regioselectivity of this elimination is strongly in favor of the α -sulfonate **10d**, suggesting only a minor pathway for the electrochemical transformation reported herein. More importantly, β -alkoxylated compound **10e** (see Supporting Information for synthesis details) could not be converted to the product **8a** using conditions like the one employed in the electrolysis (Figure 3c), excluding such a route for the formation of β -styrenesulfonates. Finally, cyclic voltammetry (Figure 3d, see Supporting Information for details) revealed the early oxidation of the styrene, while the sulfonated product and the monoalkylsulfite intermediate **A** (vide infra) are stable towards (over-)oxidation.

Based on these experimental results we propose the following mechanism (Scheme 5): First, *O*-monoalkylsulfite **A** is formed in-situ from the alcohol **7** and SO₂, with DBU shifting the equilibrium towards the deprotonated species. These intermediates are described in the literature^[44] and have already been used as nucleophiles in electrosynthesis.^[27–29] Electrochemically, styrene substrate **6** undergoes one-electron oxidation at the anode,^[41,42,45] affording radical cation **B**. Monoalkylsulfite **A** adds to resonance structure **B2**, minimizing steric interference with the aryl group and yielding the stabilized zwitterion **C** bearing a S-centered radical. Second anodic oxidation leads to **D** and subsequent deprotonation by excess of DBU finally affords alkyl β -styrenesulfonate **8**. On the cathode, acetic acid is consumed for hydrogen evolution

Anode:



Cathode:



Scheme 5. Proposed mechanism for the synthesis of alkyl alkenesulfonates **8**.

reaction (HER), allowing for a simple and inexpensive counter reaction.

Conclusions

In summary, we developed a new and first of its kind electrochemical multicomponent reaction for the synthesis of alkyl β -styrenesulfonates via the radical addition of intermediate monoalkylsulfites to an oxidized double bond. This approach features the use of widely available styrene substrates, SO_2 stock solution and alcohols as well as inexpensive electrode and separator materials. The applicability was demonstrated in a substrate scope with 44 examples of up to 81% yield, where we observed excellent regio- and stereoselectivity. The scalability and easy downstream processing of the anolyte has been demonstrated with this method making these valuable products accessible. Our method opens a new and straightforward pathway for the construction of the highly desired styrenesulfonate scaffold.

Supporting Information

The Supporting Information (PDF) including detailed optimization studies, experimental procedures, mechanistic studies, crystallographic data and copies of NMR spectra is available in the supplementary materials of this article. The authors have cited additional references within the Supporting Information.^[46]

Acknowledgements

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Conflict of Interests

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: electrochemistry • multicomponent reactions • alkenesulfonates • styrenes • sulfur dioxide

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3.2 Decarboxylative electrochemical sulfonylation of cinnamic acids

A manuscript was published on this chapter

Po-Chung Chien, [Florian A. Breitschaft](#), Harald Kelm, Siegfried R. Waldvogel, Georg Manolikakes, *Electrochemical 3-Component Synthesis of Alkenesulfonates from Cinnamic Acids, SO₂ and Alcohols*, *ChemSusChem* **2025**, e202500186.



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Contributions:

The project was conceived by P.-C. Chien, S.R. Waldvogel, G. Manolikakes and me. The majority of laboratory work, including optimization studies, synthesis, purification, isolation and analytics of compounds, as well as mechanistic investigations was conducted by P.-C. Chien of the University of Kaiserslautern-Landau (RPTU). I was responsible for the scale-up experiment, including selection of the electrochemical cell, synthesis, purification and analysis of the obtained compounds. H. Kelm measured and interpreted X-ray crystallographic data. The original draft of the manuscript was written by G. Manolikakes, the Supporting Information was written by P.-C. Chien and me. Proof-reading prior to submission was done by P.-C. Chien, S.R. Waldvogel, G. Manolikakes, and me.

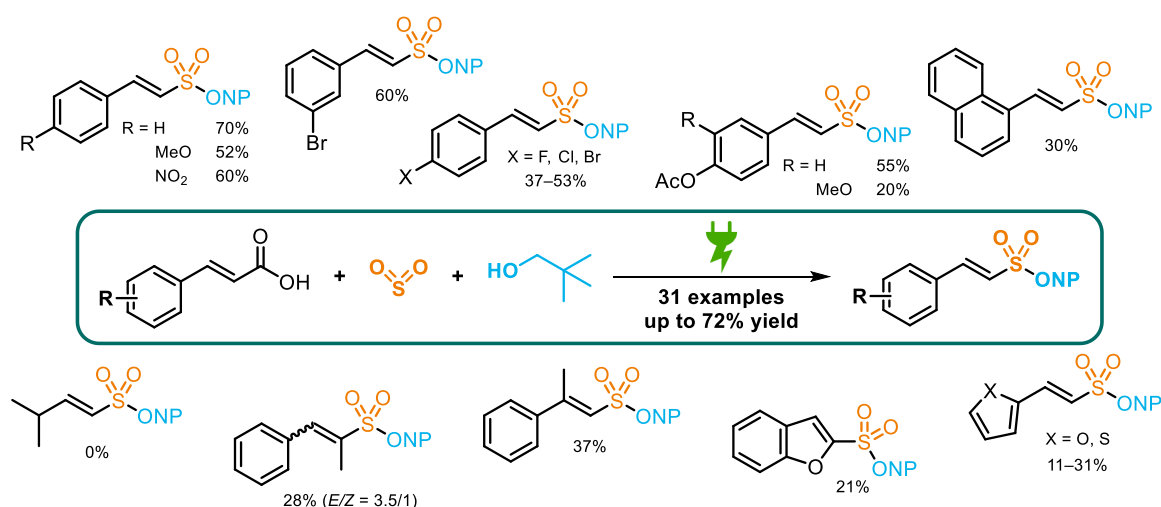
3.2.1 Introduction

Owing to the significant utility and high potential of β -styrenesulfonates in polymer and medicinal chemistry (see section 3.1.1), more sustainable precursors for their electrochemical synthesis were explored. Here, cinnamic acids are particularly attractive because they can be readily sourced either from biomass extraction or through engineered microbial production.^[199] Decarboxylative transformations of cinnamic acids have already proven effective for synthesizing various functionalized styrene derivatives *via* both conventional synthetic and photochemical methods.^[200] At the same time, integrating SO₂ chemistry with radical processes provides an efficient approach to access a wide range of organic sulfonyl compounds.^[140a, 201] While the research groups of Huang and Wang have previously reported electrochemical strategies for synthesizing β -styrenesulfones from cinnamic acids using sulfinate or sulfonylhydrazide precursors,^[202] a decarboxylative sulfonylation of cinnamic acids leading to sulfonate esters remained unexplored. In this context, the electrochemical sulfonylation developed within the Waldvogel group (section 3.1), which enables the direct incorporation of SO₂, effectively bridges this gap, while the use of cinnamic acids as starting materials instead of fossil-based styrenes promotes a more sustainable approach towards β -styrene-sulfonates.

3.2.2 Summary of the results

Building on the findings from the electrochemical sulfonylation of styrenes (Section 3.1), screening commenced using cinnamic acid, SO₂ stock solution, and neopentyl alcohol in the presence of an auxiliary base and tetrabutylammonium salts as supporting electrolytes in a divided setup using a glass frit. Among various anode materials tested, graphite electrodes exhibited the highest efficiency. Simple trialkylamines bases like DIPEA resulted in only trace product formation, heterocyclic bases such as pyridine or DBU provided moderate yields (54–62%), with 2,6-lutidine proving optimal. Evaluation of supporting electrolytes identified 0.1 m ⁿBu₄NPF₆ as the most effective. Systematic optimization of current density, charge, and reactant stoichiometry established optimal conditions, which yielded the β -styrenesulfonate in 71% (qNMR), of which 70% were isolated.

Regarding the scope of the reaction, electron-donating (methoxy- or methyl-) and electron-withdrawing groups (acetyl- and even nitro substituents) on the aromatic ring were well tolerated, yielding the corresponding alkenesulfonates in moderate to good yields (47–70%). Halogenated substrates provided the desired products in similar yields, regardless of the halogen or substitution pattern. Hydroxy-substituted cinnamic acids unfortunately failed to yield the desired products, likely due to oxidative degradation.^[203] Protecting these free phenolic OH-groups restored the reactivity, albeit with variable yields (20–55%). Naphthyl derivatives or heterocyclic acids afforded sulfonates in lowered yields (11–31%) due to competing aromatic sulfonylation, resulting in difunctionalized products instead. The reaction consistently delivered the (*E*)-isomer, except for α -methylcinnamic acid, which formed a diastereomeric mixture (*E*/*Z* = 3.5/1). Here, the absence of double-bond translocation, unlike the previous study, suggests a distinct mechanistic pathway. Attempts using simple acrylic acids were unsuccessful, underscoring a substrate-specific reactivity involving the aromatic core.

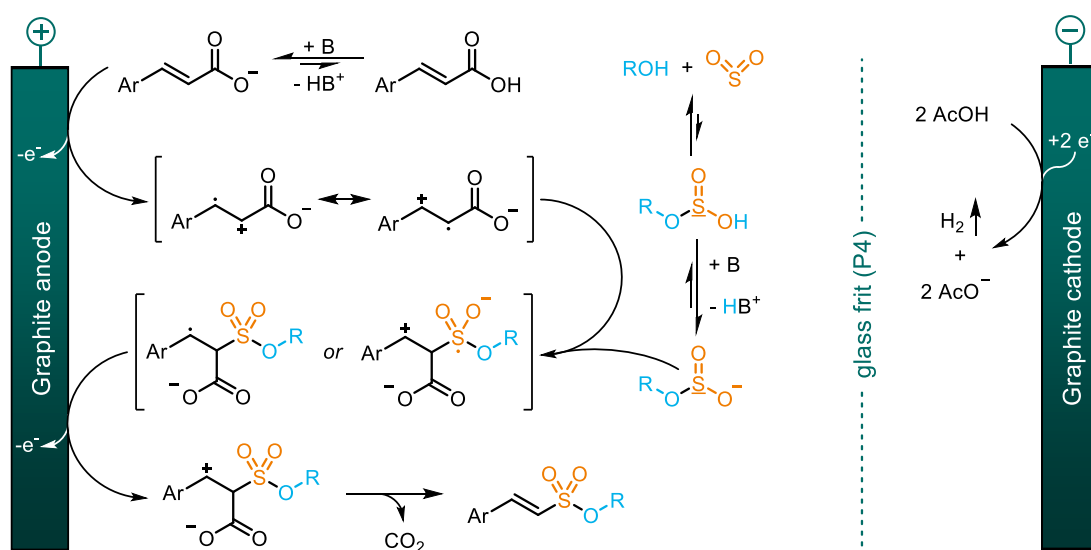


Scheme 19: Selected examples from the scope of cinnamic acids. NP = neopentyl.

The reaction scope was expanded to various alcohols. Simple primary and secondary alcohols resulted in yields of 51–60%. Even benzylic alcohol, usually more sensitive to anodic oxidation, was well tolerated, affording the expected β -styrenesulfonate in 51% yield. As previously reported, cyclohexanol derivatives gave slightly lower yields (39–44%), and tertiary alcohols or phenols failed to give the desired sulfonate esters. Structurally more complex alcohols, like protected furanoses or Roche ester, reacted inefficiently (15–17%), though incorporation remained feasible. Fluorinated alcohols (trifluoroethanol or HFIP) yielded fluoroalkylsulfonates in yields up to 56%, demonstrating broader substrate applicability than in the study before.

A 33-fold scale-up of the electrochemical transformation demonstrated its robustness, yielding the desired product in 72%, comparable to the micromolar-scale reaction (70%). Repeated use of the electrolysis setup over four runs led to a gradual yield decline (70% to 57%) and incomplete conversion due to minor electro-fouling on the anode. Mechanistic studies and control experiments confirmed the necessity of both base and electric current. Addition of radical scavengers (BHT or TEMPO) completely inhibited product formation, suggesting a radical process. GC/MS analysis of the reaction mixtures confirmed the in-situ formation of monoalkylsulfite species. Cyclic voltammetry indicated that cinnamate oxidation occurs prior to oxidation of these intermediates.

Therefore, a pseudo-Kolbe reaction mechanism^[204] was proposed (Scheme 20), where the initial oxidation of the cinnamate does not occur at the carboxyl functionality, but in the aromatic system in conjugation with the double bond. The resulting radical is subsequently attacked by monoalkylsulfite. Second oxidation to a benzylic cation and follow-up decarboxylation yields the final sulfonylated alkenes, with hydrogen evolution as the cathodic counter-reaction. This mechanistic framework expands the known reactivity of pseudo-Kolbe processes beyond benzylic substrates.



Scheme 20: Pseudo-Kolbe mechanistic proposal for the decarboxylative sulfonylation. Ar = aryl.

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RESEARCH ARTICLE

Electrochemical 3-Component Synthesis of Alkenesulfonates from Cinnamic Acids, SO₂ and Alcohols

Po-Chung Chien,^[a] Florian A. Breitschaft,^[b] Harald Kelm,^[a] Siegfried R. Waldvogel,^[b] and Georg Manolikakes^{*[a]}

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A novel, electrochemical 3-component reaction for the synthesis of alkyl alkenesulfonates from cinnamic acids, SO₂, and alkyl alcohols is reported. This metal-free process employs inexpensive and readily available graphite electrodes in combination with easy-to-use stock solutions of SO₂ and enables a straightforward construction of the styrene sulfonate scaffold *via* a decarboxylative transformation. Mechanistic studies indicate a pseudo-Kolbe type reaction. This novel reaction pathway enables a regioselective synthesis of alkenesulfonates from substituted cinnamic acids without double bond translocation. Gram-scale and anolyte reusability experiments demonstrate the applicability of this process for the construction of alkenesulfonates from cinnamic acids as potential biogenic feedstock.

Introduction

The toxic and corrosive gas sulfur dioxide (SO₂) is both, an important feedstock for the chemical industry, produced annually on a million-ton scale,^[1] and a major air pollutant with severe impacts on environment and health.^[2] The direct incorporation of SO₂ into organic molecules enables an efficient and modular synthesis of various interesting scaffolds bearing different sulfonyl (-SO₂-) based functional groups, such as sulfones or sulfonamides.^[3–5] The introduction of easy-to-handle SO₂ surrogates, in particular the solid DABCO-bis(sulfur dioxide) adduct, DABSO (1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct),^[6,7] has paved the way for the development of novel approaches for the synthesis of sulfur-containing molecules for potential applications in agrochemistry, drug development or materials sciences.^[8–11] Among the various methods established in recent years, approaches based on radical transformations are particularly well suited for the incorporation of SO₂ in organic molecules.^[12,13] In this regard, both photo- and electrochemistry are enabling tools for the development of novel, sustainable processes for the direct fixation of SO₂ into value-added products.^[14,15] In particular, electrochemical reactions have

greatly expanded the toolbox of synthetic chemists. In many cases, the otherwise necessary pre-functionalization of the substrates and redox reagents can be omitted, which leads to a minimized amount of reagent waste, thus simplifies the work-up and costs.^[16–20] Recently, the groups of Waldvogel, Han and Ye have described the electrochemical dehydrogenative synthesis of sulfonates,^[21–23] sulfonamides,^[24–26] and sulfamides.^[27] Among the different sulfonyl-based molecular entities, alkenesulfonates play an important role. The alkenesulfonate motif can be found in molecules with interesting biological features. Three representative examples, the styrene sulfonate **1**,^[28,29] an inhibitor of the human tyrosine phosphatase 1B (target for diabetes treatment), the cysteine protease inhibitor **2** (potential therapeutic for Chagas disease)^[30], and the nuclear factor E2-related factor-2 (Nrf2) activator **3** (anti-inflammatory and antioxidant properties)^[31] are depicted in Figure 1. Furthermore, alkenesulfonates, such as **4** or **5**, are common monomers employed in the synthesis of polymers containing sulfonate groups attached directly to the polymer backbone.^[32] These polymers display interesting properties and have found application in blood-compatible materials,^[33] or proton exchange membranes.^[34]

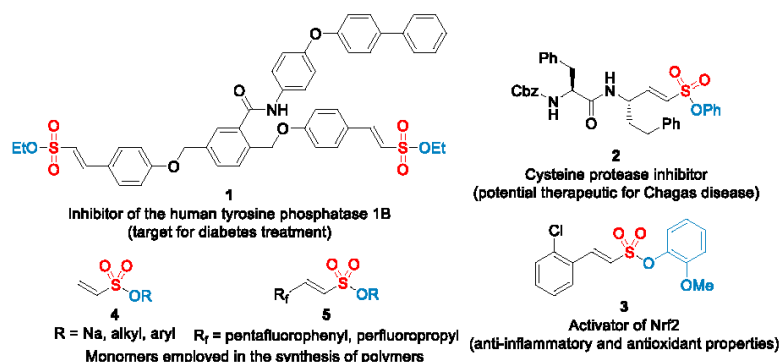


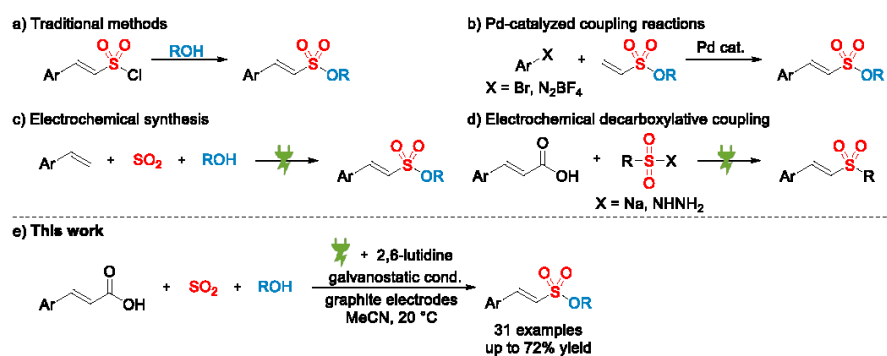
Figure 1. Representative examples of relevant alkenesulfonates.

RESEARCH ARTICLE

Traditional methods for the synthesis of alkenesulfonates utilize the corresponding vinyl sulfonyl chlorides (Scheme 1a).^[35,36] These key intermediates can be prepared by addition of sulfur trioxide^[37] or sulfonyl chloride to an olefin.^[38] More contemporary processes are based on palladium-catalyzed coupling reactions of vinyl sulfonates with aryl bromides,^[39] aryldiazonium salts,^[40] or sulfur-fluoride-exchange (SuFEx) chemistry employing the corresponding vinyl sulfonyl fluorides (Scheme 1b).^[41] Although the latter two methods do not require harsh conditions or reagents associated with the traditional approaches, they rely exclusively on vinyl building blocks already containing a sulfonyl functionality, which necessitates additional synthetic efforts. In 2024, the Waldvogel group reported an electrochemical multi-component synthesis of alkenesulfonates from styrenes, alcohols, and SO₂, which enables a direct construction of the sulfonate functionality from two simple organic starting materials (Scheme 1c).^[42–44] However, this dehydrogenative anodic transformation exhibits a limited scope. In the last years, decarboxylative coupling reactions of carboxylic acids have emerged as a powerful tool for the construction of C-C and C-heteroatom bonds.^[45–49]

Decarboxylative transformations of cinnamic acids enable the efficient synthesis of various functionalized styrene derivatives.^[50,51] Numerous groups have disclosed methods for the decarboxylative coupling of cinnamic acids with sodium sulfonates or sulfonyl hydrazides for the synthesis of vinyl sulfones,^[52–54] including an electrochemical process from the Huang and Wang groups (Scheme 1d).^[55,56] To the best of our knowledge, decarboxylative sulfonylations of cinnamic acids with direct SO₂ incorporation have not yet been reported. However, such processes would offer an attractive approach for the direct transformations of cinnamic acids as biobased, renewable feedstock^[57,58] into value-added sulfonyl-compounds.

Herein, we describe a so far unprecedented electrochemical three-component reaction for the synthesis of alkenesulfonates based on the decarboxylation of cinnamic acids with simultaneous incorporation of SO₂ (Scheme 1e). This novel approach features the use of easy-to-handle SO₂ stock solutions and inexpensive graphite electrodes and affords β -styryl sulfonates with CO₂ and H₂ as the only formed byproducts.



Scheme 1. Selected approaches towards β -styryl sulfonates and β -styryl sulfonates.

Results and Discussion

Optimization of the Reaction Conditions

We started our investigations with the electrolysis of cinnamic acid (**6a**), a SO₂ stock solution (5.0 M in MeCN, see SI for further details), and neopentyl alcohol (**7a**) together with an auxiliary base and tetrabutylammonium salts as supporting electrolyte using different anode materials in a divided setup (Table 1). For the cathodic reaction a catholyte consisting of the tetrabutylammonium salt as supporting electrolyte together with 5 equiv. of AcOH as proton source for hydrogen evolution^[59–61] in combination with the same electrode materials as for the anodic reaction was used. Best yields were obtained with inexpensive graphite electrodes, *n*Bu₄NPF₆ (0.1 M) as supporting electrolyte, a current density of 10 mA/cm², and an amount of applied charge of 3.5 F, leading to the alkenesulfonate **8a** in 70% isolated yield (entry 1). Whereas the use of pyridine, 2,4,6-collidine, or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), as auxiliary base afforded the sulfonate product in slightly decreased yields of 54–62% (entries 2–4), simple amine bases, such as *N,N*-

diisopropylethylamine (DIPEA), led to the desired product only in trace amounts, presumably due to competing anodic oxidation of the amine itself (entry 5). *n*Bu₄NPF₆ with a concentration of 0.1 M proved to be the optimal supporting electrolyte. Increased or decreased concentrations of *n*Bu₄NPF₆ as well as other supporting electrolytes, such as *n*Bu₄NBF₄, resulted in lower yields (entries 6–8). The use of other electrode materials commonly used in electrochemical SO₂ fixation,^[24–27,42] e.g. glassy carbon, platinum, or boron-doped diamond (BDD), furnished the styrene sulfonate **8a** in lower yields of 25–46% (entries 9–11). Modulation of the current density (5 or 15 mA/cm²) or the applied amount of charge (3.0 or 3.8 F) led to decreased yields of 54–65% (entries 12–15). Best yields were obtained with 3.0 equiv. of neopentyl alcohol (**7a**), 6.0 equiv. of the 2,6-lutidine and 10.0 equiv. of SO₂ (entry 1). Lowering or increasing the amount of alcohol, base, or SO₂ furnished product **8a** in diminished yields (entries 16–21). As already reported before, DABSO is unfortunately unsuitable for electrosynthesis due to the quite low oxidation potential of DABCO (1,4-diazabicyclo[2.2.2]octan), leading to competitive anodic oxidation processes.^[15] Finally, no product formation was observed in the absence of a base or without the application of electric current (entries 22 and 23). Noteworthy, selective formation of the *E*-alkenesulfonate was observed in all cases.^[62]

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Table 1. Influence of different parameters on the reaction outcome.

$\text{6a (0.3 mmol)} + \text{SO}_2 (10.0 \text{ equiv.}) + \text{7a (3.0 equiv.)} \xrightarrow[\text{graphite electrodes, divided cell}]{\text{2,6-lutidine (6.0 equiv.)}, \text{nBu}_4\text{NPF}_6 (0.1 \text{ M}), \text{CH}_3\text{CN, 3.5 F, 10 mA/cm}^2, 20 \text{ }^\circ\text{C}}$
 8a

Entry	Deviation from the standard conditions	Yield [%] ^[a]	Entry	Deviation from the standard conditions	Yield [%] ^[a]
1	None	71 (70) ^[b]	12	5 mA/cm ²	55
2	Pyridine	54	13	15 mA/cm ²	65
3	2,4,6-Collidine	55	14	3.0 F	63
4	DBU	62	15	3.8 F	54
5	DIPEA	Traces	16	Neopentyl alcohol (2.0 equiv.)	50
6	nBu ₄ NPF ₆ (0.2 M)	43	17	Neopentyl alcohol (4.0 equiv.)	47
7	nBu ₄ NPF ₆ (0.05 M)	58	18	2,6-Lutidine (4.0 equiv.)	43
8	nBu ₄ NBF ₄	50	19	2,6-Lutidine (8.0 equiv.)	49
9	Glassy carbon electrodes	46	20	SO ₂ (7.5 equiv.)	63
10	Pt foil electrodes	40	21	SO ₂ (12.5 equiv.)	68
11	BDD electrodes	25	22	No base	0
			23	No electric current	0

^[a]¹H NMR yield with the use of CHPh₃ as the internal standard. ^[b]Isolated yield

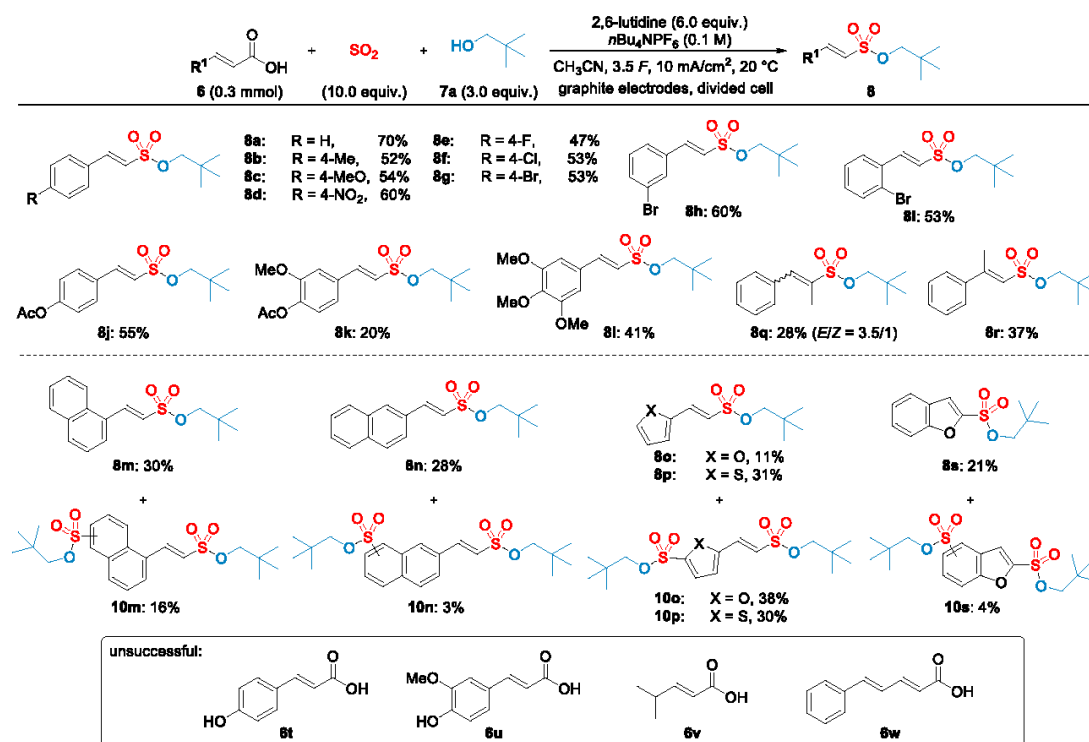
Scope of the Reaction

With the optimized conditions, the scope of the reaction was explored with different cinnamic acids was investigated (Scheme 2). In general, both electron-donating and electron-withdrawing substituents on the aromatic core were well tolerated, affording the alkenesulfonates **8a** – **8i** in 47–70% yield. Reactions with halogenated cinnamic acids **6e** – **6i** furnished the desired products **8e** – **8i** in 47–60% yield, without a significant influence of the substitution pattern. Both electron-rich (**6b** or **6c**) and electron-poor substrates (**6d**) underwent a smooth decarboxylative sulfonylation to the desired alkenesulfonates in comparable yields of 52–60%. Even a sensitive nitro functionality (**6d**) was well tolerated. Unfortunately, reactions with hydroxy cinnamic acids, such as **6t** and **6u**, did not yield the desired product, presumable due to oxidative degradation of the phenolic core.^[59–61] On the other hand, transformations of different hydroxycinnamic acid derivatives without free OH-functionalities, such as **6j** (from p-hydroxycinnamic acid), **6k** (from ferulic acid), or **6l** (from sinapinic acid), afforded the corresponding alkenesulfonates **8j** – **8l** in 20–55% yield. Since hydroxycinnamic acids can be easily obtained from lignocellulosic biomass,^[57,58]

our novel process provides an attractive opportunity to access interesting alkenesulfonates from renewable feedstocks.

Reactions of the two naphthyl derivatives **6m** and **6n** furnished the corresponding sulfonates **8m** and **8n** in 30% and 28% yield. In both cases, side products **10m** and **10n** arising from an additional sulfonylation of the aromatic core were obtained in 16% and 3% yield. Furthermore, the two heterocyclic acid derivatives **6o** and **6p** underwent decarboxylative SO₂ insertion delivering the sulfonate products **8o** and **8p** in lowered yields of 11% and 31%, together with substantial amounts of the disulfonylated products **10o** and **10p**. In all cases, a selective formation of the *E*-configured product was observed. Reactions of the α- or β-methylcinnamic acids **6q** and **6r** afforded the trisubstituted alkenesulfonates **8q** and **8r** in 28% and 37% yield, respectively. Whereas the sulfonate **8r** was again obtained exclusively as *E*-isomer, the sulfonylated product **8q** was formed as diastereomeric mixture (*E/Z* = 3.5:1). Contrary to the previous work from Waldvogel^[42] no translocation of the double bond was observed, indicating an alternative reaction pathway. Interestingly, also 2-benzofuranoic acid **6s** could be converted into the sulfonate **8s**, albeit in only 21% yield together with 4% of the disulfonylated product **10s**. Unfortunately, all attempts to convert simple acrylic acid derivatives, such as **6v**, or conjugated dienoic acids, such as **6w**, failed under our standard reaction conditions.

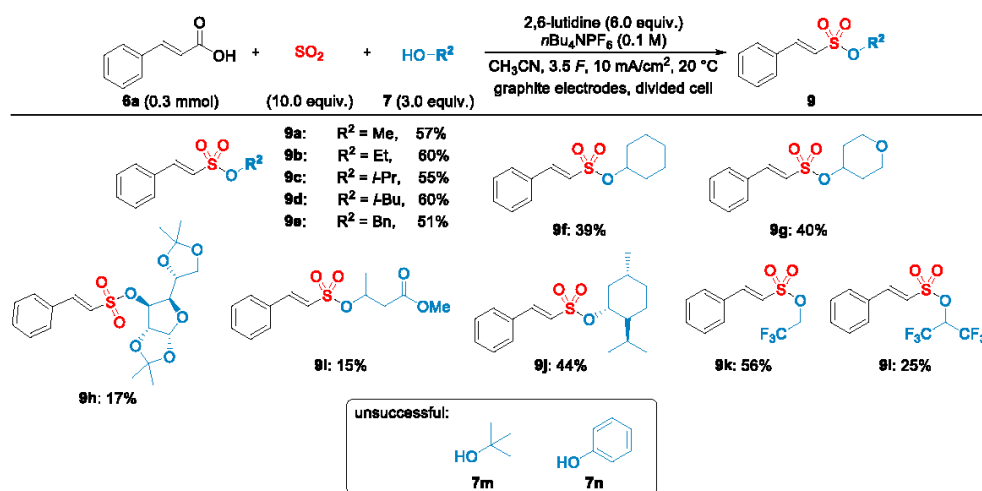
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Scheme 2. Scope of cinnamic acids and related substrates for the synthesis of alkenesulfonates **8** and **10**. Isolated yields are shown.

Next, reactions of cinnamic acid **6a** with different alcohols **7** were investigated using the optimized conditions (Scheme 3). Yields of 51–60% were obtained with different simple primary or secondary alcohols, such as MeOH, EtOH, or *i*PrOH. Even benzylic alcohol **7e**, usually more sensitive to anodic oxidation, was well tolerated, affording the expected alkenesulfonate **9e** in 51% yield. In the case of cyclohexanol **7f** and the tetrahydropyran-derived alcohol **7g** the desired products, **9f** and **9g** were isolated in slightly reduced yields of 39% and 40%. Reactions with tertiary alcohols, such as the α -D-glucofuranose derivative **7h**

and methyl 3-hydroxybutyrate **7i**, did proceed less efficiently and yielded the sulfonates **9h** and **9i** in only 17% and 15% yield. Still, these examples show, that the incorporation of structurally more complex alcohols is feasible. On the other hand, the reaction of menthol **7j** afforded the desired product **9j** in 44% yield. Reactions with tertiary alcohols, such as *t*BuOH, or with phenols did not afford the desired products. On the other hand, fluorinated alcohols, such as 2,2,2-trifluoroethanol (TFE) or 1,1,1,3,3,3-hexafluoroisopropan-2-ol (HFIP) delivered the fluoroalkyl sulfonates **9k** and **9l** in 56% and 25% yield.



Scheme 3. Scope of alcohols for the synthesis of alkenesulfonates **9**. Isolated yields are shown.

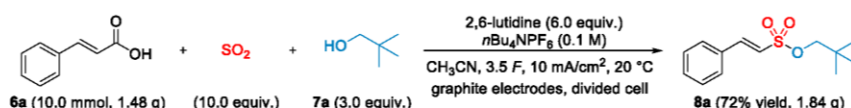
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Scale-up and Reusability Tests

In order to demonstrate the applicability of this new protocol, a 33-fold scale-up experiment was performed (Scheme 4). To our delight, this electro-transformation turns out to be scalable in a robust manner. Alkenesulfonate **8a** could be isolated in 72% yield (equals to 41% current efficiency (CE); max. CE (for 3.5 F) = 57%) in the gram-scale reaction compared to 70% in the micromolar setup.

Furthermore, we evaluated the electrolysis setup for repeated use. Therefore, the reaction was carried out at identical conditions four consecutive times. Only the anolyte was exchanged after each

run, while the catholyte and electrodes were reused directly (see Supporting Information). These experiments showed a gradual drop in yield from 70% to 57% together with an incomplete conversion of the cinnamic acid after the third and fourth run (Figure 2). This can be rationalized by minor electro-fouling, due to the formation of a polymer layer on the anode (see supporting information for further details) as observed in similar transformations.^[42,63,64] As shown by the Waldvogel group, recycling of electrolyte mixtures containing an alcohol, an amine, and SO₂ is straightforward.^[25] Therefore, evaporation of the anolyte components can facilitate down-stream processing for larger electrolysis applications, a key step towards the translation in technical processes.^[65] In combination, these studies showcase the utility of the developed method for larger technical applications.



Scheme 4. Scale-up experiment.

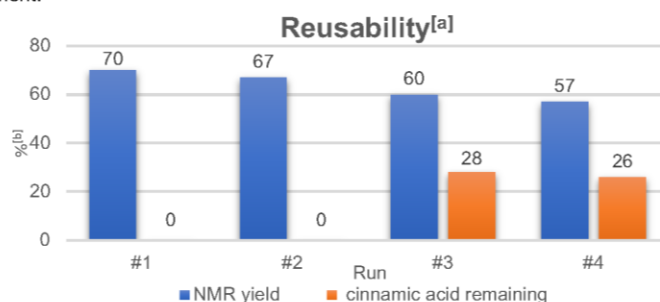


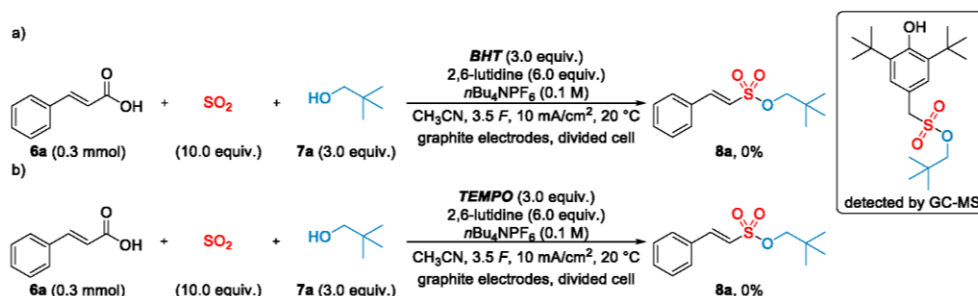
Figure 2. Reusability tests. ^[a]Anolyte: **6a** (0.3 mmol, 0.1 M), SO₂ (10.0 equiv.), **7a** (3.0 equiv.), 2,6-lutidine (6.0 equiv.), nBu₄NPF₆ (0.1 M), MeCN, divided cell (glass frit), graphite electrodes, 10 mA/cm², 3.5 F, 20 °C. Catholyte: nBu₄NPF₆ (0.1 M), AcOH (5.0 equiv.), MeCN. ^[b]¹H NMR yield with the use of CHPh₃ as the internal standard.

Mechanistic Studies

Finally, further studies and control experiments were performed, in order to elucidate the reaction mechanism. As shown in Table 1, no product formation was observed in the absence of a base or when the electric current was omitted (entries 22 and 23). Addition of radical scavengers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) no product was detected in the crude reaction mixture (Scheme 5). In both

cases, only partial decomposition of cinnamic acid **6a** was observed. In the presence of BHT an adduct, potentially arising either from trapping of an alkoxy sulfonyl radical species or Michael-type addition of a monoalkylsulfite to an in situ formed quinoid methide, could be detected by GC-MS (see supporting information for further details).

Finally, cyclic voltammetry revealed, that under the standard reaction conditions (excess of base), an early oxidation of the cinnamate salt should take place before oxidation of the monoalkyl sulfite or overoxidation of the alkenesulfonate (Figure 3, see supporting information for further details).



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Scheme 5. Control experiments

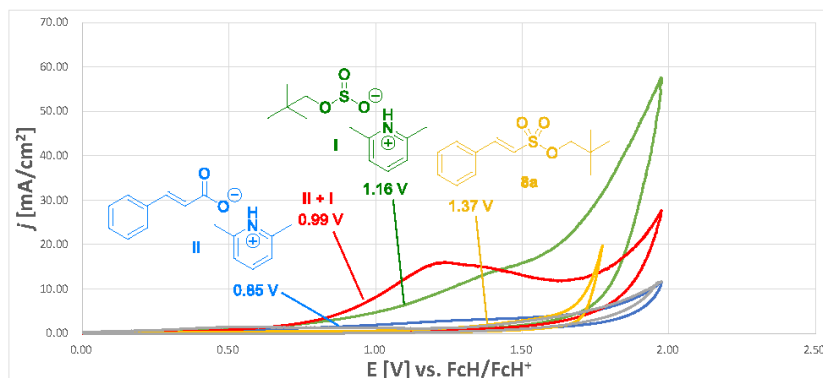
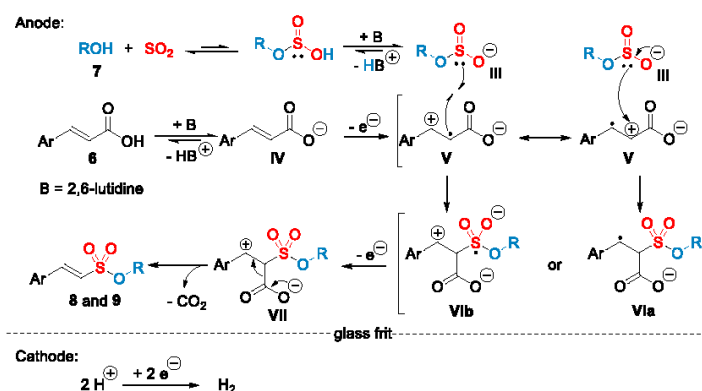


Figure 3. Cyclic voltammograms: Cinnamate II (blue), monoalkylsulfite intermediate I (green), alkenesulfonate 8a (yellow), mixture of cinnamate II and monoalkylsulfite intermediate I (red), and blank measurement (0.1 M $n\text{Bu}_4\text{NPF}_6$ in MeCN; grey). The numbers given refer to the half-wave oxidation potential of the respective compounds or mixtures.

These results, together with the absence of any disulfonated products in the reaction of β -methylcinnamic acid, indicate an alternative reaction pathway compared to the previously described sulfonation of styrenes.^[42] Based on the results from our mechanistic investigations and precedents from the literature,^[52–56] we propose pseudo-Kolbe type reaction pathway, viz oxidation of the carbon scaffold instead of the carboxylic acid functionality (Scheme 6).^[65,67] At first, *O*-monoalkylsulfite III is generated in-situ from the alcohol 7 and SO_2 . The base, 2,6-lutidine, assists in shifting the equilibrium towards the deprotonated species.^[21–26,68–71] Furthermore, cinnamic acid will be deprotonated to the corresponding carboxylate IV. One-electron oxidation of cinnamate IV affords radical cation V. Regioselective addition of *O*-monoalkylsulfite I to V can furnish the stabilized zwitterion VIIb containing an S-centered radical.

Alternatively, addition of *O*-monoalkylsulfite III to V can also lead to the stabilized benzylic radical VIIa. A second anodic oxidation of VIIa or VIIb yields the benzylic cationic VIII, which undergoes a decarboxylation to generate the final products 8 and 9. The stereoselective formation of the *E*-isomer presumably occurs through the most stable staggered conformation in kinetically controlled fashion. On the cathodic side, hydrogen is generated from acetic acid in a hydrogen evolution process (HER) as simple and efficient counter reaction.

Noteworthy, pseudo-Kolbe systems are usually limited to benzylic-type substrates. To the best of our knowledge, we herein describe a so far unprecedented pseudo-Kolbe type decarboxylation of cinnamic acids. We envision that the extension of the pseudo-Kolbe reaction to a new scaffold can be utilized for other decarboxylative functionalizations as well.^[72,73]



Scheme 6. Proposed reaction pathway.

Conclusion

In summary, a novel electrochemical three-component reaction for the synthesis of alkyl β -styrenesulfonates is described. This metal-free process utilizes widely available cinnamic acids, alcohols, and SO_2 stock solution in combination with inexpensive

graphite electrodes. The utility of this transformation was demonstrated in a substrate scope of 31 examples with up to 72% yield as well as in scale-up into multi-gram range and anolyte reusability studies. Mechanistic investigations indicate a so far unprecedented pseudo-Kolbe type decarboxylation of cinnamic acids. Contrary to previous methods, this new approach enables the regioselective synthesis of substituted styrene sulfonates

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without double bond translocation or double addition products. The direct decarboxylative conversion of bio-based cinnamic acid derivatives opens an attractive access to the intriguing styrenesulfonate scaffold from renewable building blocks. Studies to exploit the synthetic utility of electrochemically the pseudo-Kolbe decarboxylation of conjugated alkenoic acid as well as investigations to extend the electrochemical, decarboxylative SO₂ insertion to other scaffolds are currently ongoing in our laboratories.

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Data Availability Statement

The data underlying this study are available in the published article, in its Supporting Information, and openly available in Chemotion Repository (<https://www.chemotion-repository.net/>) at https://dx.doi.org/10.14272/collection/PCC_2024-07-25.^[74] All DOIs minted for the data are linked in Supporting Information file 1.

Notes

An initial version of the manuscript was deposited to the chemRxiv repository prior to submission.^[75] The authors declare no competing financial interest.

Supporting Information

Supporting Information File 1: Experimental details, spectral and crystal data, DOIs, and copies of NMR spectra for all compounds prepared in this study. X-Ray Data: cif and checkcif files for compound **10o** (CCDC 2381294). The authors have cited additional references within the Supporting Information.^[76–81]

Keywords: Sulfur dioxide • Alkenesulfonates • Electrochemistry • Multicomponent reactions • Decarboxylative functionalization

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3.3 Dehydrogenative electrochemical sulfonylation of amines

A manuscript was published on this chapter

Florian A. Breitschaft, Alicia L. Saak, Christian Krumbiegel, Aloisio de A. Bartolomeu, Thomas Weyhermüller, Siegfried R. Waldvogel, *Multicomponent Electrosynthesis of Enaminyl Sulfonates Starting from Alkylamines, SO₂, and Alcohols*, *Org. Lett.* **2025**, 27, 1210–1215.

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Contributions:

The project was conceived by A. de A. Bartolomeu, S. R. Waldvogel, and me. I conducted the majority of the laboratory work, including parts of the optimization and the full synthesis, purification and isolation of compounds as well as some control experiments. A. L. Saak supported me during the optimization studies as part of her Bachelor thesis at the Johannes Gutenberg University Mainz under my supervision. C. Krumbiegel conducted and interpreted cyclic voltammetry experiments, and T. Weyhermüller measured and interpreted X-ray crystallographic data. The original draft of the manuscript and its Supporting Information was written me. A. de A. Bartolomeu and S. R. Waldvogel proof-read/corrected the manuscript prior to submission.

3.3.1 Introduction

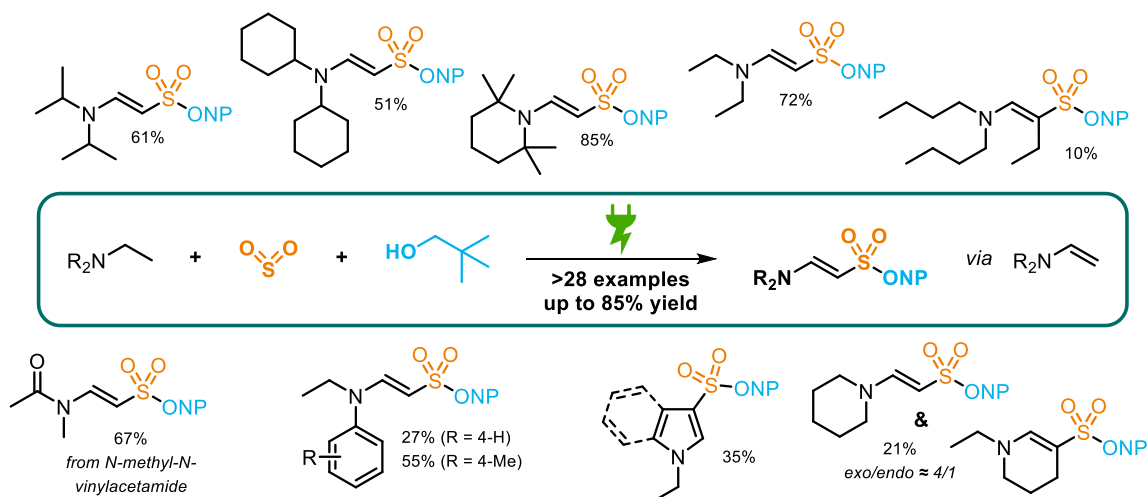
The β -amino sulfonyl functionality is a prevalent motif in pharmaceuticals and natural products. Taurine, representing the core structure, is biosynthesized from cysteine and exhibits diverse physiological roles and also possesses therapeutic potential.^[205] The β -amino sulfone Apremilast (Otezla®, Amgen), a phosphodiesterase 4 (PDE4) inhibitor used in dermatology, achieved sales over \$2 billion in 2021.^[206] TSAO-T, a spirocyclic enaminyl sulfone, acts as a selective HIV-1 reverse transcriptase inhibitor, making it a promising lead structure for anti-AIDS drug development.^[207]

Traditional approaches for constructing these moieties, including aza-Michael addition, Knoevenagel reaction, Horner-Wadsworth-Emmons reaction, and the condensation of functionalized sp³ carbons with formamides,^[208] typically require prefunctionalization and/or stoichiometric amounts of external oxidants.^[209] While electrosynthetic strategies have facilitated the synthesis of enaminyl sulfones from aryl sulfonyl precursors,^[210] the formation of enaminyl sulfonates remains unexplored. By integrating electrochemistry with SO₂ stock solutions, a novel dehydrogenative electrochemical multi-component reaction was developed, enabling the efficient synthesis of these structures.

3.3.2 Summary of the results

The electrochemical synthesis of enaminyll sulfonates was optimized using *N,N*-diisopropylethylamine (DIPEA), SO₂ stock solution, and neopentyl alcohol under galvanostatic conditions. A graphite anode and stainless-steel cathode in an undivided cell initially yielded 24% (qNMR). Yield improved to 50% by switching to a quasi-divided cell and adjustment of reactant stoichiometry. Graphite foil (Sigraflex™) was identified as the optimal anode, while base screening showed no further improvement to the previously used DBU. Utilizing DoE optimization for stoichiometry and electrochemical parameters increased yield to 65%. Pretreatment of the graphite foil electrode in MeCN finally increased the yield to 70% (qNMR), of which 61% could be isolated.

The scope of the electrochemical sulfonylation was investigated across diverse alkyl- and aromatic amines as well as amides (Scheme 21). Ethylamines bearing isopropyl or cyclohexyl groups exhibited moderate to good yields (51–61%), while yield increased up to 85% with steric demand and protection of the α -carbons next to the N atom. A significant decline in yield was observed with increasing alkyl chain length, from triethyl- (72%) to tributylamine (10%), presumably due to a mix of kinetic effects and excessive dealkylation. Sulfonylation of saturated nitrogen heterocycles exhibited *exo/endo* competition, resulting in low yields and product mixtures for *N*-ethylpiperidine (21%) and *N*-ethylazepane (14%). For *N*-functionalized heteroaromatics, sulfonylation selectively occurred at the 3-position of the aromatic ring (35%), likely due to the stabilization of the aromatic system upon oxidation. This reactivity is similar to the previously conducted studies by Waldvogel and coworkers utilizing very electron-rich arenes.^[185, 188] Despite the propensity of aniline derivatives to undergo polymerization, two examples were successfully sulfonylated in moderate yields up to 55%. *N*-acetylated substrates were surprisingly unreactive, not even Shono-type reactivity was observed. However, starting from the *N*-vinyl compounds, and therefore skipping the initial oxidation from amide to enamide, reestablished the desired reactivity, yielding 27–67%.



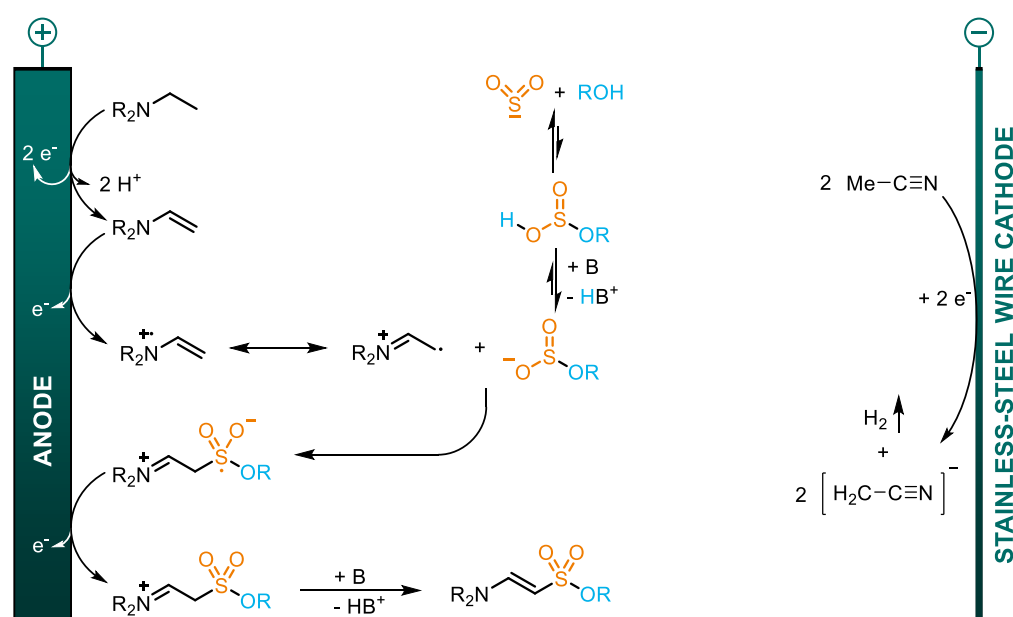
Scheme 21: Selected examples from the scope of trialkylamines. NP = neopentyl.

Investigating the scope of applicable alcohols, it was found that primary alcohols exhibited excellent reactivity (up to 85%) and good yields could be obtained with secondary alcohols (58–67%). Tertiary alcohols were again unreactive due to steric hindrance. Multiple functionalized alcohols could be employed, resulting in yields ranging from 21% to 62%. Notably, *N*-protected alkanolamines showed selective reactivity at the OH-functionality. Attempts using secondary amines instead of alcohols led to low sulfonamide yields, likely due to product degradation during workup and purification.

The dehydrogenative sulfonylation was successfully scaled up by 20 times, with *N*-ethyl-2,2,6,6-tetramethylpiperidine yielding 84% by ^1H NMR and 76% isolated in the gram-scale reaction (slightly lower than the small-scale yield of 85%). A similar scale-up with *N*-methyl-*N*-vinylacetamide yielded 84%, a significant improvement over the micromolar-scale yield of 67%.

Expectably, cyclic voltammetry showed early oxidation of the amine substrate, while the enaminy sulfonate product and monoalkylsulfite remained stable. Control experiments and the deliberate addition of radical scavengers (BHT and TEMPO) with subsequent trapping indicated that electrochemically generated enamines serve as key intermediates for the sulfonylation reaction.

Based on the results, a plausible reaction mechanism was proposed: The tertiary alkylamine substrate undergoes oxidation at the anode, forming the corresponding enamine, which is further oxidized to a stabilized radical cation. In-situ formed *O*-monoalkylsulfite then adds to the α -imino radical, producing an *S*-centered radical. This species undergoes additional oxidation and deprotonation through excess of base to yield the desired enaminy sulfonate. Due to the nature of the quasi-divided cell, the high current density at the cathode wire leads to mostly solvent degradation and hydrogen evolution.



Scheme 22: Mechanistic proposal for the dehydrogenative electrosynthesis of enaminy sulfonates.

Multicomponent Electrosynthesis of Enaminyll Sulfonates Starting from Alkylamines, SO₂, and Alcohols

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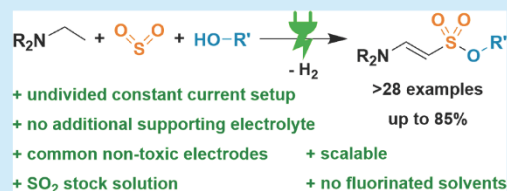
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ABSTRACT: An electrochemical one-pot synthesis of enaminyll sulfonate esters was established, featuring a quasidivided cell under constant current conditions. The multicomponent reaction utilizes simple and readily available alkylamines and an easy-to-use stock solution of SO₂ and alcohols. Omission of additional supporting electrolyte through in-situ-generated monoalkylsulfite facilitates the downstream processing. A diverse scope with more than 28 examples and yields up to 85% as well as a 20-fold scale-up reaction prove the feasibility of this novel protocol.



The β -amino sulfonyl functionality is a prevalent motif in many pharmaceuticals or natural products. The simplest representative of this class is the nonproteinogenic ammonium sulfonate taurine (Figure 1). Biosynthesized from cysteine,

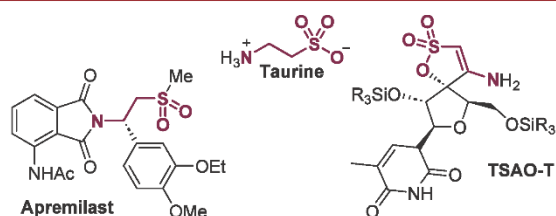


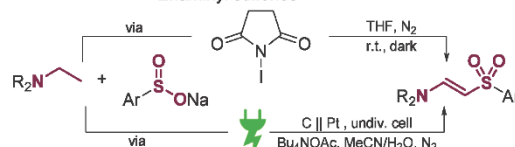
Figure 1. Prominent compounds containing the β -amino sulfonyl motif.

taurine provides numerous physiological activities, ranging from cytoprotection¹ and neurotransmitter² to its highly discussed role as a (semi)essential nutrient³ and its application as a therapeutic.⁴ Taurine-derived taurocholic acid is naturally occurring in the bile of mammals and has found application as a choleretic.⁵ Structurally related, the β -amino sulfone apremilast (Otezla, Amgen, Figure 1) is one of the most-sold pharmaceuticals worldwide, accounting for more than 2 billion USD in sales in 2021.⁶ As a phosphodiesterase 4 (PDE 4) inhibitor, apremilast is administered in cases of severe psoriasis and psoriatic arthritis. The penicillin-derived drug sulbactam, also exhibiting a β -amino sulfone motif, is applied together with β -lactam antibiotics to inhibit the effects of β -lactamase, increasing the efficiency of the antibiotic drastically.⁷ TSAO-T (Figure 1), a spirocyclic enaminyl sulfonate, is able to inhibit HIV-1 reverse transcriptase in a highly selective and non-competitive way,⁸ rendering it a potential lead structure for the development of anti-AIDS medications.⁹ Installation of these

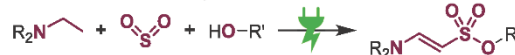
moieties can be achieved by conventional chemistry including aza-Michael addition,¹⁰ cycloaddition,¹¹ Knoevenagel reaction,¹² Horner-Wadsworth-Emmons reaction,¹³ or the condensation of functionalized sp³ carbons with formamides.¹⁴ Recently, sodium sulfonates¹⁵ (Scheme 1) or sulfonyl

Scheme 1. Selected Methods for the Construction of the β -Enaminyll Sulfonate Moiety

Well established: Enaminyll sulfones



Underexplored: Enaminyll sulfonates (this work)



hydrazides¹⁶ have emerged for the generation of vinyl sulfones, requiring an additional oxidant in stoichiometric amounts. Electrochemistry on the other hand uses electric current as a green oxidant,¹⁷ therefore omitting toxic and/or expensive catalysts while being inherently safe.¹⁸ Electrosynthetic methods for the construction of enaminyll sulfones have been developed by several groups (Scheme 1), utilizing different aryl

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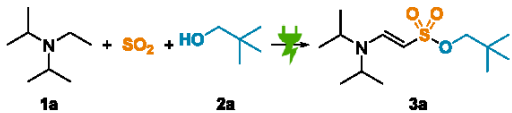
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sulfonyl precursors.¹⁹ However, this restricts the resulting products to sulfones, while enamynyl sulfonates are hardly accessed and seem to be underexplored. Sulfur fluoride exchange chemistry may be used²⁰ but is crucially limited by the commercial availability of suitable sulfonyl fluorides. Utilizing the inexpensive chemical feedstock sulfur dioxide as a central building block,²¹ we report a novel dehydrogenative electrochemical multicomponent reaction for the construction of enamynyl sulfonates starting from simple amines, SO₂, and alcohols (Scheme 1). This approach circumvents the need for prefunctionalization and allows for the direct incorporation of the pollutant sulfur dioxide into value-added products like sulfonates,²² sulfonamides,²³ or sulfamides.²⁴ As a source of SO₂, we employ readily available and easy-to-use stock solutions, minimizing waste and facilitating downstream processing, a key step for the translation into technical application.^{23b,25}

The initial reactivity was discovered using *N,N*-diisopropylamine (1a), SO₂ stock solution, and neopentyl alcohol (2a) employing a graphite anode and stainless-steel cathode in an undivided cell under galvanostatic conditions (Table 1).

Table 1. Optimization of Reaction Conditions^a



Entry	2a [eq.]	Base	Anode material	Yield ^b
1	2.0	DBU ^c	Graphite	24% ^d
2	4.0	DBU	Graphite	41% ^d
3	4.0	DBU	Graphite	50%
4	4.0	DBU	Glassy Carbon	16%
5	4.0	DBU	BDD	18%
6	4.0	DBU	Sigraflex	55%
7	4.0	DBN	Sigraflex	51%
8	4.0	TMG	Sigraflex	49%
9	4.0	2,6-Lutidine	Sigraflex	0%
10	5.2	DBU ^e	Sigraflex	65% ^f
11	5.2	DBU ^e	Sigraflex	70% ^{fg} (61%)

^aConditions: 1a (500 μmol, 1 equiv, 0.1 M), SO₂ (1.5 × [equiv 2a]), 2a, base (8.0 equiv), MeCN, anode/stainless-steel wire, 40 mA/cm², 10 F, r.t. ^bYield determined by ¹H NMR with 1,3,5-trimethoxybenzene as internal standard. Isolated yield in parentheses. ^c5.0 equiv.

^dPlanar stainless-steel cathode. ^e9.0 equiv. ^f67.5 mA/cm², 11.5 F.

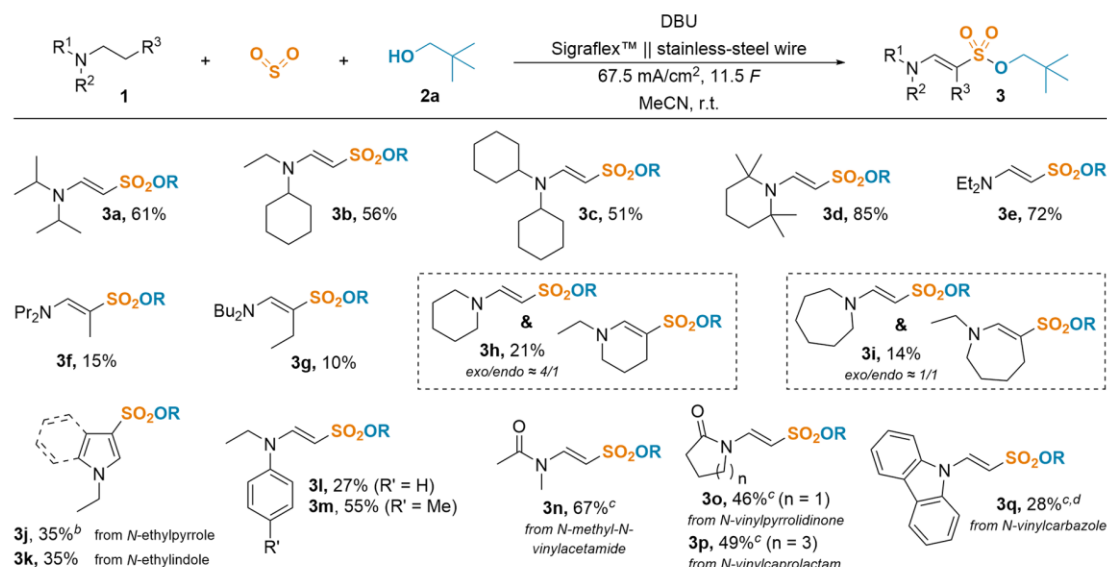
^gPretreating of Sigraflex electrode in acetonitrile 2 h before usage.

Neopentanol was chosen due to the enhanced stability as sulfonate.²⁶ With the help of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 3a was obtained in an ¹H NMR yield of 24% (Entry 1). Increasing the stoichiometry of the reactants (Entry 2) as well as altering the geometry of the cathode from a plate to a thin wire improved the yield to 50% (Entry 3). This setup, commonly known as a quasidivided cell,²⁷ can help to prevent undesired counter reactions,²⁸ since the electron transfer becomes diffusion-limited, leading to mostly solvent degradation. Screening of anode materials (Entries 4–6 and Supporting Information) showed the best results with an inexpensive and readily available graphite foil (Sigraflex). Testing of different bases (Entries 7–9 and Supporting Information) showed no improvement. Using a design-of-experiments study²⁹ (2^{4–1}-design plan with star points, see Supporting Information), the stoichiometry of alcohol and

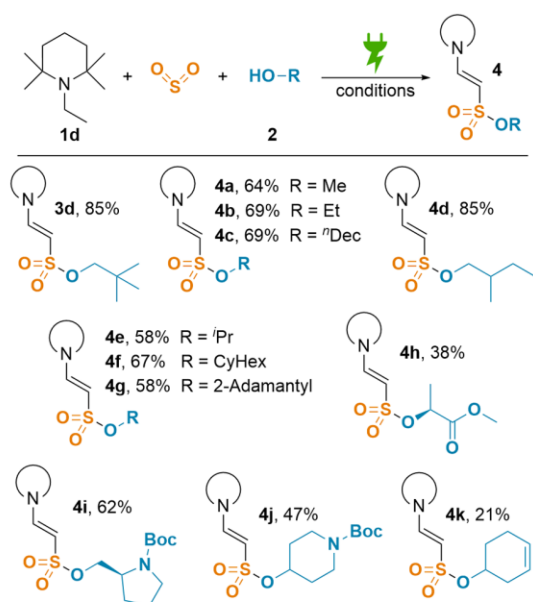
base, the current density, and amount of applied charge were optimized, which resulted in an enhanced yield of 65% (Entry 10). Pretreating the Sigraflex electrode in MeCN prior to use resulted in minor swelling, and the qNMR yield of 3a was increased to 70%, of which 61% could be isolated (Entry 11). The pretreating is believed to improve the diffusion of the substrates into the porous electrode.

With these optimized conditions in hand, we explored the scope of our newly discovered reactivity using various alkyl and aromatic amines as well as amides (Scheme 2). Ethylamines bearing isopropyl (3a) or cyclohexyl moieties (3b and 3c) gave good yields ranging from 51% to 61%. Highly hindered and rigid *N*-ethyl-2,2,6,6-tetramethylpiperidine was sulfonylated in an excellent yield of 85% (3d). Its structure was verified by single-crystal X-ray analysis (CCDC 2407541). Investigating different alkyl chain lengths, we found a sharp decline in yield when switching from ethyl (3e, 72%) to propyl (3f, 15%) or butyl groups (3g, 10%). This agrees with previous reports suggesting a kinetic preference of *n*-alkylamines to dehydrogenate in the terminal position.³⁰ Additionally, numerous dealkylated byproducts were observed for 3f and 3g (see Supporting Information for details). NMR experiments confirmed the displayed (*E*)-configuration. While *N*-ethylpyrrolidine lead to overoxidation (see Supporting Information), nitrogen heterocycles could be applied with our methodology. In these cases, a competing reaction between the *exo*- and *endo*-product was observed. Product mixtures were obtained for the sulfonylation of *N*-ethylpiperidine (3h, 21%) and *N*-ethylazepane (3i, 14%) with *exo/endo* ratios of 4/1 and 1/1, respectively. Sulfonylation of unsaturated *N*-functionalized heteroaromatics occurred not at the ethyl group but solely on the 3-position of the aromatic ring (3j, from *N*-ethylpyrrole, and 3k, from *N*-ethylindole, both 35%). Since the lone pair of the N atom is part of the aromatic system, removal of an electron leads to a more stable intermediate rather than the exocyclic cation. While the electrolysis of aniline derivatives often results in polymerization and the formation of aniline black,³¹ we were pleased to see that *N,N*-diethylaniline was sulfonylated in an acceptable yield of 27% (3l). By substitution of the *para*-position by a methyl group, yield could be increased to 55% (3m). Surprisingly, *N*-acetylation lead to no conversion of the starting material (see Supporting Information for examples); not even Shono-type reactivity³² was observed. However, starting from *N*-vinyl compounds and therefore skipping the oxidation from amide to enamide reestablished the desired reactivity. *N*-Vinylamides are common motifs frequently employed in polymer chemistry.³³ We achieved a good yield of 67% for the sulfonylation of *N*-methyl-*N*-vinylacetamide (3n) and moderate yields of 46% (3o) and 49% (3p) for the two cyclic analogues. Lastly, after the solvent was changed to benzonitrile due to limited solubility, *N*-vinylcarbazole could be sulfonylated in an acceptable yield of 28% (3q).

Following these promising results, we explored the scope of the alcohols (Scheme 3). Besides neopentanol (3d, 85%), simple primary alkyl alcohols like methanol or ethanol yielded 64% (4a) and 69% (4b), respectively. Even very apolar 1-decanol could be converted into the respective sulfonate ester in a satisfying yield of 69% (4c). With racemic 2-methylbutanol, an excellent yield of 85% was achieved (4d). Using secondary alcohols resulted in yields of 58% (4e, with isopropanol), 67% (4f, with cyclohexanol), and 58% (4g) for the sterically demanding 2-adamantol. Tertiary alcohols such

Scheme 2. Scope of Amines, Anilines, and Vinyl Amides^a

^aIsolated yields displayed. R = neopentyl. Conditions: amine **1** (500 μmol, 1 equiv, 0.1 M), SO_2 (7.8 equiv), **2a** (5.2 equiv), DBU (9.0 equiv), Sigraflex/stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t. ^b17.25 F. ^c5.75 F. ^dPhCN as solvent.

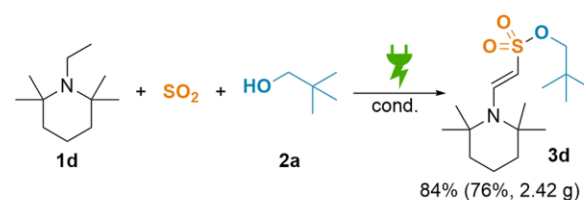
Scheme 3. Scope of Alcohols^a

^aConditions: **1d** (500 μmol, 1 equiv, 0.1 M), SO_2 (7.8 equiv), alcohol **2** (5.2 equiv), DBU (9.0 equiv), Sigraflex/stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t. Isolated yields displayed.

as *tert*-butanol however could not be converted with our methodology (see [Supporting Information](#) for limitations), most probably due to their bulkiness. Similar observations were made in previous projects.²² Demonstrating the range of applicable alcohols, an acceptable yield of 38% was achieved for methyl lactate (**4h**). Since amides do not interfere with the desired reactivity, two *N*-Boc-protected aminoalcohols were tested, which resulted in yields of 62% (**4i**) and 47% (**4j**), respectively. Even labile 3-cyclohexenol was converted into the

corresponding sulfonate, albeit with a lowered yield of 21% (**4k**). Unfortunately, the use of phenols such as 2,4-dichlorophenol did not yield the desired product but resulted in the formation of dimers instead (see [Supporting Information](#)). Using secondary amines instead of alcohols, we could isolate only minor amounts of the desired sulfonamides (see [Supporting Information](#) for examples). Since an ¹H NMR sample of the crude reaction mixture indicated a moderate yield of 44%, we suspect degradation of the enaminyl sulfonamide during column chromatography.

To showcase robustness and scalability of our dehydrogenative sulfonylation, enaminyl sulfonate **3d** was synthesized in a gram scale reaction ([Scheme 4](#), 20-fold scale-up, see

Scheme 4. Gram Scale Synthesis of **3d**^a

^aConditions: **1d** (10.0 mmol, 1 equiv, 0.1 M), SO_2 (7.8 equiv), **2a** (5.2 equiv), DBU (9.0 equiv), Sigraflex/stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t. Yield determined via ¹H NMR. Isolated yield in parentheses.

[Supporting Information](#)). Herein, we observed a similar ¹H NMR yield (84% vs 90% in the small scale) and only a minor decline in isolated yield (76% vs 85%). A similar scale-up experiment with *N*-methyl-*N*-vinylacetamide yielded 84% of **3n** (compared to 67% in the small-scale, see [Supporting Information](#) for details).

To gain insight toward a possible reaction mechanism, several control experiments were conducted ([Table 2](#)). As expected, no signs of the desired product were detected when

Table 2. Control Experiments

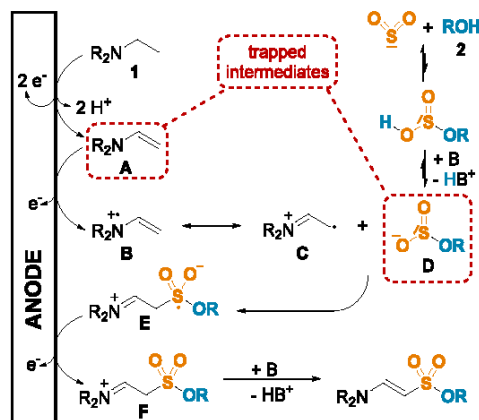
Entry	Deviation from the standard conditions ^a	Yield ^b
1	No charge passed	0%
2	No base (+ 0.1 M Bu ₄ NBF ₄ for conductivity)	0%
3	+ TEMPO (3 equiv)	38%
4	+ BHT (3 equiv)	20%

^a1a (500 μmol, 1 equiv, 0.1 M), SO₂ (7.8 equiv), 2a (5.2 equiv), DBU (9.0 equiv), Sigraflex stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t. ^bYield determined via ¹H NMR.

omitting electric charge or base (Entries 1 and 2). By addition of radical scavengers 2,2,6,6-tetramethylpiperidinyloxy (TEMPO, Entry 3) or butylated hydroxytoluene (BHT, Entry 4), the yield dropped significantly but did not diminish completely. This may be attributed to the fact that TEMPO as well as BHT are readily oxidized, which competes with oxidation of the amine substrate.³⁴ With BHT, *N,N*-diisopropylvinylamine (which, according to literature reports,^{30b,35} is only stable below −20 °C for prolonged time) and a neopentyl sulfonyl species could be trapped and detected via GC/MS, respectively (see Supporting Information). Unsurprisingly, cyclic voltammetry experiments (see Supporting Information) showed the early oxidation of the amine substrate, while the products and alkoxy sulfonyl intermediate were stable toward oxidation.

Based on these results and previous literature reports, we propose the following mechanism (Scheme 5): First, the

Scheme 5. Proposed Reaction Mechanism



tertiary alkylamine substrate 1 gets oxidized at the anode to the enamine A, releasing two protons in the process, which are intercepted by an excess of base. Electrochemical oxidation of amines to enamines is well-established in the literature³⁶ and has been used in similar transformations for the construction of enaminyl sulfones.¹⁹ Subsequently, A is oxidized again in a one-electron fashion,³⁷ yielding radical cation B, which is stabilized by allylic resonance structure C. Multiple literature reports³⁸ have identified C as the predominant form of the enamine radical cation, which is better described as an α -imino radical.³⁹ O-Monoalkylsulfite D can be formed in situ by insertion of SO₂ into the O–H bond of the alcohol 2, with DBU shifting the equilibrium toward the deprotonated species. Such intermediates have been known for a long time⁴⁰ and put to synthetic use on multiple occasions already.^{22,23} They also provide the conductivity necessary for electrolysis, which is

why the need for an additional supporting electrolyte is circumvented. D adds to resonance structure C, forming the S-centered radical E. Noteworthy, we did not find any evidence for a nucleophilic O- or S-attack of D to the iminium carbon of ion C. On the other hand, the ability of SO₂-derived species to trap free radicals and the extraordinary stability of the resulting S-centered radicals is well-known.^{21,41} Subsequently, E undergoes another anodic oxidation to F, and deprotonation through an excess of base finally affords the desired enaminyl sulfonate. As a counter reaction, the high current density on the stainless-steel wire leads mostly to solvent degradation and hydrogen evolution, as evidenced by the formation of bubbles observed during the scale-up experiment.

In summary, we developed a new electrochemical dehydrogenative multicomponent reaction affording enaminyl sulfonates from abundant alkylamines, SO₂, and alcohols. The process features inexpensive electrode materials and utilizes a simple quasidivided setup under galvanostatic conditions. An extensive scope of more than 28 examples with yields up to 85% as well as a gram-scale reaction demonstrates the feasibility of this first-of-its-kind transformation. Our one-pot method opens a new and straightforward pathway for the construction of up-to-date underexplored enaminyl sulfonate esters.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.4c04746>.

Experimental details, spectra of isolated compounds, and crystallographic data. Additional references are cited herein. (PDF)

Accession Codes

Deposition Number 2407541 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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4 Conclusions

This doctoral dissertation explored the expansion of multi-component sulfonylation reactions for the synthesis of value-added products. Electrosynthesis as a potentially green methodology was used to drive the activation of aromatic and non-aromatic substrates bearing an electron-rich double bond. Utilizing efficient and easy-to-use stock solutions of sulfur dioxide and leveraging its tendency to form monoalkylsulfites in-situ, the direct incorporation of this abundant pollutant was successfully demonstrated in three studies (Figure 22 and Figure 23).

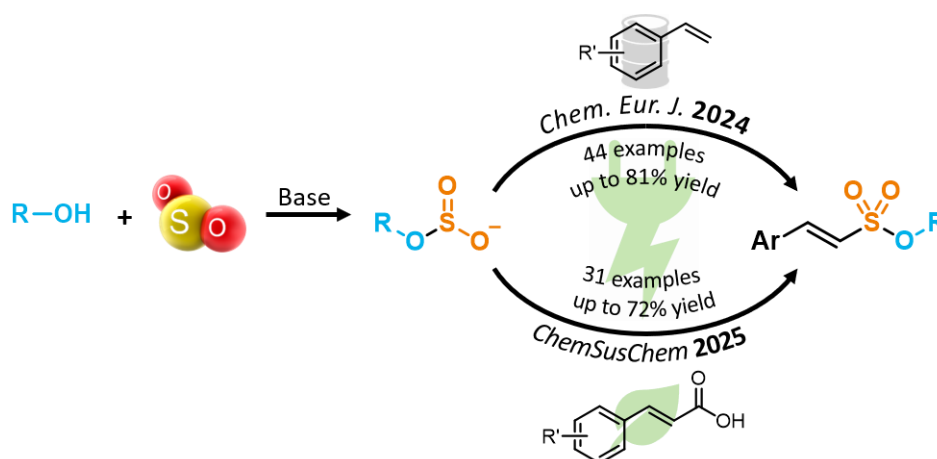


Figure 22: Electrochemical access to β -styrenesulfonates using either fossil-derived styrenes or bio-based cinnamic acids.

Initially, styrenes were selected as cost-effective and widely available feedstock to afford β -styrenesulfonates. Following extensive optimization studies, the developed protocol demonstrated broad applicability, as evidenced by a substrate scope of 44 examples. The methodology was shown to be compatible with electron-rich and electron-deficient styrenes, halogenated derivatives, functionalized substrates such as chalcones and cinnamates, and natural products. Furthermore, a diverse range of alcohols, including primary and secondary alkyl alcohols, as well as substrates containing ester, amide, ether, and highly electron-withdrawing functionalities, were tolerated. The scalability and robustness of the reaction were validated through a 15-fold scale-up and a reusability study of the electrochemical setup.

Expanding the methodology by replacing fossil-derived styrenes with biogenic cinnamic acids further broadened the reaction scope and enhanced its sustainability. Employing cost-efficient graphite electrodes enabled the synthesis of 31 (hetero)aromatic alkenesulfonates. Notably, substrates bearing redox-sensitive functionalities, such as bromo and nitro groups, were well tolerated, achieving high yields of up to 72%. The robustness of the reaction was again corroborated by a 33-fold scale-up experiment and reusability studies, which maintained consistent yields. Mechanistic

investigations suggested a decarboxylative pseudo-Kolbe-type pathway, expanding the scope of such mechanisms beyond the known benzylic substrates and distinguishing this transformation from the previous styrene-based protocol.

Finally, the electrochemical multi-component sulfonylation was extended to non-aromatic substrates, utilizing simple trialkylamines for the construction of β -enaminylsulfonates. The electrochemical setup was significantly improved through the implementation of a quasi-divided cell and an inexpensive graphite foil anode. The oxidation of trialkylamines to enamines, followed by subsequent oxidative sulfonylation, facilitated a broad substrate scope encompassing over 28 examples while achieving yields of up to 85%. The practical applicability of this method was further demonstrated through two independent 20-fold scale-up reactions, confirming its suitability to easily and efficiently obtain multi-gram amounts of the desired products.

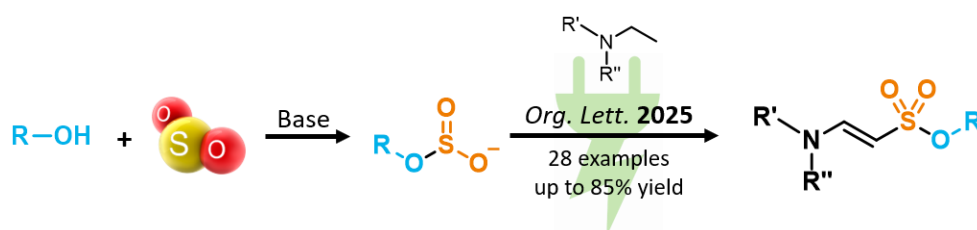
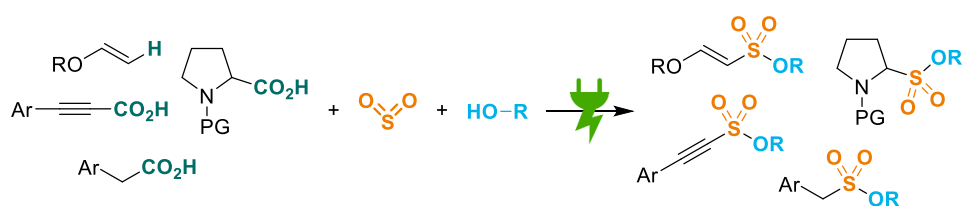


Figure 23: Accessing enaminyl sulfonates *via* an electrochemical sulfonylation.

5 Outlook

The established electrochemical multi-component methodology facilitates a modular substitution of components, thereby creating extensive opportunities for further investigation. Following previous studies, the adaptation of the developed reactions into flow chemistry could improve space-time-yields and efficiency. Furthermore, the electrochemical multi-component sulfonylation poses an ideal model reaction for extension of the *Laboratory Automation and Batch Scheduling* (LABS) system developed within the working group,^[187, 211] as it requires the handling of multiple reactants and an excessive number of parameters need to be optimized.

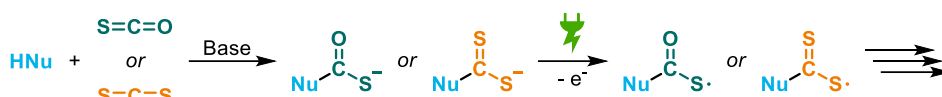
Given their structural similarity and comparable reactivity to the enamines employed in this work, the methodology could be adapted to enol ethers.^[212] Moreover, the decarboxylative sulfonylation could be extended to triple bonds through the use of phenylpropionic acid, affording alkynesulfonates or the corresponding sulfonamides. Generally speaking, the pseudo-Kolbe reactivity remains an underexplored aspect of electrochemical synthesis,^[204b] which might enable decarboxylative sulfonylations *via* an easily oxidizable redox tag near to the carboxylate.^[213] Suitable candidates for such transformations would include phenylacetic acids or α -carboxylamides.



Scheme 23: Readily oxidizable substrates for the expansion of electrochemical multi-component sulfonylation. Ar = Aryl. PG = protecting group.

Employing mediated electrolysis in conjunction with hydrogen atom transfer (HAT) reagents such as TEMPO, *N*-hydroxyphthalimide (NHPI), or quinuclidine enables the mild generation of free radicals from redox-inactive substrates.^[214] These radicals could be efficiently trapped by sulfur dioxide, thereby offering broad potential for expanding the substrate scope towards redox-inactive substrates.

Besides SO₂, small molecules such as carbonyl sulfide and carbon disulfide can generate intermediates analogous to those used in the present work (Scheme 24).^[182b] As the resulting anions are more readily oxidized than monoalkylsulfites,^[215] the proposed approach would proceed *via* a distinct mechanistic pathway. Decoupling the electrochemical oxidation from the organic substrate would expand the scope electrochemical multi-component reactions to include unsubstituted arenes or even electron-deficient heterocycles.



Scheme 24: In-situ formation of conductive intermediates analogue the monoalkylsulfites.

Furthermore, the exploration of nucleophiles beyond alcohols and amines should be pursued. Thiols, for instance, might undergo conversion to the corresponding thiosulfonates, while diols, diamines, or aminoalcohols would facilitate the formation of difunctionalized molecules or cyclic structures such as sultones. In the long term, a small and readily exchangeable molecule could serve as a versatile platform for the synthesis of a broad array of sulfur(VI) compounds, either *via* ex-cell nucleophilic substitution or through a stepwise approach. In this context, fluoride is of particular interest, as it enables access to the rapidly expanding field of SuFEx chemistry (Scheme 25). Other suitable building blocks for the envisioned transformation may include cyanide, azide, (thio)cyanate, or imidazole.



Scheme 25: Formation of a sulfonyl fluoride intermediate as a versatile and widely applicable sulfonyl building block.

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7 Abbreviations

°C	degrees Celsius	DMA	dimethylacetamide
μL	microliter	DMF	dimethylformamide
μmol	micromole	DMSO	dimethyl sulfoxide
a	year (lat.: <i>annum</i>)	DoE	design of experiments
A	surface	DOI	digital object identifier
Å	Ångstrom	dtbpy	4,4'-di- <i>tert</i> -butyl-2,2'-dipyridyl
A ³	aldehyde-alkyne-amine	EA	ethyl acetate
AcOH	acetic acid	EDG	electron-donating group
AI	artificial intelligence	EG	expanded graphite
AIDS	acquired immunodeficiency syndrome	EI	electron ionization
aq.	aqueous	E _{ox}	oxidation potential
Ar	aryl	EPDM	ethylene propylene diene monomer
B	base	ESI	electrospray ionization
b.p.	boiling point	ET	electron transfer
BDD	boron-doped diamond	Et	ethyl
BHT	butylated hydroxytoluene	EtOH	ethanol
BMBF	Bundesministerium für Bildung und Forschung	ETOS	Electrifying Technical Organic Syntheses
Bn	benzyl	EWG	electron-withdrawing group
Boc	<i>tert</i> -butoxycarbonyl	<i>F</i>	Faraday
c	concentration	Fc	ferrocene
C	Coulomb	FID	flame ionization detector
CC	Creative Commons	g	gram
CCE	constant current electrolysis	gC	glassy carbon
CE	counter electrode	GC/MS	gas chromatography - mass spectrometry
CH	cyclohexane	GDCh	Gesellschaft Deutscher Chemiker
cm	centimeter	GHG	greenhouse gas
CO ₂ eq	CO ₂ equivalents	GHS	Globally Harmonized System of Classification and Labelling of Chemicals
cond.	conditions	h	hour(s)
COSY	correlation spectroscopy	HAT	Hydrogen atom transfer
CV	cyclic voltammetry	HER	hydrogen evolution reaction
CVD	chemical vapor deposition	HFIP	1,1,1,3,3,3-hexafluoroisopropanol
D	Debye	HMBC	heteronuclear multiple bond correlation
<i>d</i>	distance	HOMO	highest occupied molecular orbital
DABSO	1,4-diazabicyclo[2.2.2]octane-SO ₂ adduct	HPLC/MS	high-performance liquid chromatography - mass spectrometry
DBN	1,5-Diazabicyclo(4.3.0)non-5-ene		
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene		
DCM	dichloromethane		
DIPEA	<i>N,N</i> -diisopropylethylamine		
div. cell	divided cell		

HSQC	heteronuclear single quantum coherence	OVAT	one-variable-at-a-time
Hz	Hertz	<i>p</i>	<i>para</i>
<i>I</i>	current	PG	protecting group
IP	intellectual property	Ph	phenyl
<i>i</i> Pr	<i>iso</i> -propyl	ppm	parts per million
ISO	International Organization for Standardization	PTFE	polytetrafluorethylene
IUPAC	International Union of Pure and Applied Chemistry	<i>Q</i>	amount of charge
<i>J</i>	coupling constant	qNMR	quantitative nuclear magnetic resonance
<i>j</i>	current density	R	general (organic) residue
JGU	Johannes-Gutenberg University	r.t.	room temperature
LABS	Laboratory Automation and Batch Scheduling	RE	reference electrode
LCA	life-cycle assessment	R _F	perfluoroalkyl
Lit	literature	rpm	revolutions per minute
LUMO	lowest unoccupied molecular orbital	RPTU	University of Kaiserslautern-Landau
<i>m</i>	mass	RVC	reticulated vitreous carbon
M	molarity (in mol/l)	SE	supporting electrolyte
<i>m</i>	<i>meta</i>	SEM	scanning electron microscope
m.p.	melting point	SET	single electron transfer
mA	milliampere	SI	Supporting Information
MCR	multi-component reaction	SIL	switchable ionic liquid
Me	methyl	SOgen	perbromothiophene-1,1-dioxide
MeCN	acetonitrile	SOMO	singly occupied molecular orbital
MeOH	methanol	SuFEx	sulfur(VI) fluoride exchange click chemistry
mg	milligram	<i>t</i>	time
min	minute(s)	<i>T</i>	temperature
mL	milliliter	TBAF	tetrabutylammonium fluoride
mm	millimeter	^t Bu	<i>tert</i> -butyl
mmol	millimole	TEA	triethylamine
MPI KoFo	Max-Planck-Institute for Coal Research	TEMPO	(2,2,6,6-tetramethylpiperidin-1-yl)oxyl
MPI CEC	Max-Planck-Institute for Chemical Energy Conversion	THF	tetrahydrofuran
MS	molecular sieves	TIMSO	N-methylpyrrolidine-SO ₂ adduct
<i>n</i>	amount of substance	TMG	1,1,3,3-tetramethylguanidine
NADH	nicotinamide adenine dinucleotide	undiv. cell	undivided cell
NCS	<i>N</i> -chlorosuccinimide	UV	ultra violett
nm	nanometer	V	Volt
NOESY	nuclear Overhauser effect spectroscopy	<i>V</i>	volume
NP	neopentyl	<i>v</i>	scan rate
Nu	nucleophile	VESPR	valence shell electron pair repulsion
<i>o</i>	<i>ortho</i>	vs.	versus
		WE	working electrode
		X	halogen substituent
		<i>z</i>	charge number

Appendix A

A1 Use of AI tools

The following artificial intelligence (AI) tools have been used during the process of researching, writing and proofreading this doctoral thesis:

AI tool	Used for	Why	When
DeepL translate	Translation of papers in other languages than English or German	Finding relevant papers	During literature review for the introduction
DeepL write	Proofreading and reformulation of my text drafts	Better clarity and readability	Throughout the entire work (except from publications)
ChatGPT	Proofreading and reformulation of my text drafts; explanation of concepts; summarizing papers	Better clarity and readability; overview over basic concepts	Throughout the entire work (except from publications)

A2 Publications

A. de A. Bartolomeu,[†] **F. A. Breitschaft**,[†] D. Schollmeyer, R. A. Pilli, S. R. Waldvogel, *Electrochemical Multicomponent Synthesis of Alkyl Alkenesulfonates using Styrenes, SO₂ and Alcohols*, *Chem. Eur. J.* **2024**, *30*, e202400557.

P-C. Chien, **F. A. Breitschaft**, H. Kelm, S. R. Waldvogel, G. Manolikakes, *Electrochemical 3-Component Synthesis of Alkenesulfonates from Cinnamic Acids, SO₂ and Alcohols*, *ChemSusChem* **2025**, e202500186.

F. A. Breitschaft, A. L. Saak, C. Krumbiegel, A. de A. Bartolomeu, T. Weyhermüller, S. R. Waldvogel, *Multicomponent Electrosynthesis of Enaminy Sulfonates starting from Alkylamines, SO₂ and Alcohols*, *Org. Lett.* **2025**, *27*, 1210–1215.

[†]These authors contributed equally to this work and are listed in alphabetical order.

A3 Selected conference contributions

27th Annual Spring Symposium of the GDCh, Münster **2025** (poster presentation): *Multicomponent Electrosynthesis of Enaminy Sulfonates starting from Alkylamines, SO₂, and Alcohols*.

75th Annual Meeting of the ISE, Montréal **2024** (oral presentation): *Electrochemical Upcycling of SO₂ into Alkyl Alkenyl Sulfonates using a Multicomponent Approach*.

Annual Meeting of the Division “Sustainable Chemistry” of the GDCh, *Mülheim an der Ruhr* **2024** (poster presentation): *Electrochemical Multicomponent Synthesis of Alkyl Alkenylsulfonates using Styrenes, SO₂ and Alcohols*.

Electrochemistry, *Berlin* **2022** (poster presentation): *Electrochemical Upcycling of SO₂ Using Multicomponent Reactions*.

A4 Supervision of undergraduates

- | | |
|-------------------|---|
| since 04/2025 | Alicia L. Saak: <i>Elektrochemische Studien mit Schwefeldioxid</i> (Master's Thesis) |
| since 02/2024 | Marit "Ari" Schrötter: General assistance with laboratory activities (2 nd year apprentice for Physics Lab Technician) |
| 07/2024 – 08/2024 | Rihards Lācis: <i>Electrochemical Sulfonylations using a Multicomponent Approach</i> (ERASMUS Research Internship) |
| 04/2023 – 07/2023 | Alicia L. Saak: <i>Elektrochemische Multikomponentenreaktion zur Darstellung von Enaminylsulfonsäureestern ausgehend von aliphatischen Aminen</i> (Bachelor's Thesis) |

A5 Licensing disclaimer

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Appendix B

B1 Supporting Information S1: Electrosulfonylation of styrenes

Supporting Information
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Electrochemical Multicomponent Synthesis of Alkyl Alkenesulfonates using Styrenes, SO₂ and Alcohols

Aloisio de A. Bartolomeu,[‡] Florian A. Breitschaft,[‡] Dieter Schollmeyer, Ronaldo A. Pilli and Siegfried R. Waldvogel*

Abstract: A novel electrochemical approach to access alkyl alkenesulfonates *via* a multicomponent reaction was developed. The metal-free method features easy-to-use SO₂ stock solution forming monoalkylsulfites from alcohols with an auxiliary base in-situ. These intermediates serve a dual role as starting materials and as supporting electrolyte enabling conductivity. Anodic oxidation of the substrate styrene, radical addition of these monoalkylsulfites and consecutive second oxidation and deprotonation preserve the double bond and form alkyl β-styrenesulfonates in a highly regio- and stereoselective fashion. The feasibility of this electrosynthetic method is demonstrated in 44 examples with yields up to 81%, employing various styrenes and related substrates as well as a diverse set of alcohols. A gram-scale experiment underlines the applicability of this process, which uses inexpensive and readily available electrode materials.

[‡]These authors contributed equally to this work and are listed in alphabetical order.

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1 General Aspects

General Information

If not stated otherwise, all reactions were performed under ambient conditions and chemicals in analytical grade were used as purchased without further purification. Cyclohexane and ethyl acetate were purchased in technical grade and purified by distillation under reduced pressure prior to use. Anhydrous acetonitrile was commercially obtained and stored over molecular sieves (3 Å) prior use.

1.1 Instruments and Analytical Methods

Chromatography

Thin layer chromatography was performed using DC Kieselgel 60 F₂₅₄ on aluminium plates (Merck KGaA, Darmstadt, Germany). An UV lamp ($\lambda = 254$ nm, UV-4 S/L, Herolab GmbH Laborgeräte, Wiesloch, Germany) and potassium permanganate solution (3 g KMnO₄, 20 g K₂CO₃, 5 mL NaOH (5%), 300 mL H₂O) were used for substance detection. Preparative column chromatography was performed on prepacked puriFlash™ silica columns (15 μ m or 30 μ m, PF-15SIHP-F0012, PF-15SIHP-F0025, PF-30SIHP-F0025, Interchim, Montlucon Cedex, France) or on self-packed silica 60 M (0.040–0.063 mm, Macherey-Nagel GmbH & Co, Düren, Germany) using a puriFlash™-System (puriFlash™ XS520Plus, Interchim, Montlucon Cedex, France) with an integrated UV detector.

High Resolution Mass Spectrometry

Mass spectra via electrospray-ionization (ESI+) mass spectrometry was recorded using an Agilent 6545 QTOF-MS (Agilent, Santa Clara (CA), USA). Mass-charge ratios (m/z) were obtained for the characterized compounds.

X-ray Crystallography

The measurement of the crystal structure was carried out on a STOE IPDS-2T (STOE & Cie GmbH, Darmstadt, Germany) using a Mo source with graphite tube monochromator.

Gas Chromatography (GC)

Analysis of crude reaction mixtures and purified products were performed using a GC-2030 (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 μ m thickness. Hydrogen was used as carrier gas with a constant velocity of 40 cm $\times$ s⁻¹. Measurements were performed at an injector temperature of 270 °C and a detector temperature of 320 °C, starting 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/min (method: 2_medium, total program time: 20.0 min).

Gas Chromatography coupled with Mass Spectrometry (GC/MS)

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 analyzer. 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 μ m thickness. Helium was used as carrier gas with a constant velocity of 30 cm $\times$ 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/min (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.

High Performance Liquid Chromatography (HPLC)

Analysis of crude reaction mixtures and purified products were performed using a modular system LC-20A Prominence (Shimadzu Deutschland GmbH, Duisburg, Germany), UV/VIS-detector SPD-20A/AV (Shimadzu Deutschland GmbH, Duisburg, Germany), and LCMS-2020 Single Quadrupole (Shimadzu Deutschland GmbH, Duisburg, Germany). Analytical separation was performed using an Eurospher II 100-5 C-18-Trennsäule (Knauer Wissenschaftliche Geräte GmbH, Berlin, Germany) column (length of 150 mm, diameter of 4 mm, pore size of 100 Å, particle size 5 μ m). As eluents, acetonitrile and water with 5% (v/v) acetonitrile and formic acid (1 mL $\times$ L⁻¹) were used.

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), ¹³C NMR (101 MHz), and ¹⁹F NMR (376 MHz) analysis. The spectra were recorded 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] CDCl₃ (¹H NMR: $\delta = 7.26$ ppm, ¹³C NMR: $\delta = 77.16$ ppm), dichloromethane-*d*₂ (¹H NMR: $\delta = 5.32$ ppm, ¹³C NMR: $\delta = 53.84$ ppm), acetonitrile-*d*₃ (¹H NMR: $\delta = 1.94$ ppm, ¹³C NMR: $\delta = 1.32$ ppm). ¹⁹F spectra were referenced using the internal calibration of the NMR device. Besides ¹H, ¹³C and ¹⁹F NMR experiments, the 2D techniques ¹H,¹H-COSY, ¹H,¹³C-HSQC, ¹H,¹³C-HMBC and ¹H,¹H-NOESY were used assisting to assign the signals. Determination of stereochemistry (*E/Z*-isomerism) was done using ¹H,¹H-³J vicinal coupling, ¹H,¹H-NOESY and ³J(C,H)-HMBC-Coupling. 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).

Cyclic Voltammetry (CV) Measurements

Cyclic voltammetry was performed using a Metrohm 663 VA Stand equipped with a Autolab type III potentiostat (Metrohm AG, Herisau, Switzerland). WE: glassy carbon electrode ($d = 2$ mm); CE: glassy carbon rod; RE: Ag/AgCl; Scan rate $v = 100$ mV $\times$ s $^{-1}$. Electrolyte: 0.1 m Bu₄NBF₄ in acetonitrile; $c(\text{substrate}) = 10$ mmol $\times$ L $^{-1}$; $c(\text{SO}_2) = 40$ mmol $\times$ L $^{-1}$; $V = 5$ mL. All solutions except for the ones containing SO₂ have been deoxygenated by bubbling with argon for 10 min prior to measurement. Electrodes have been thoroughly rinsed before and after each measurement. The glassy carbon WE was polished with alumina paste (1 μ m followed by 0.1 μ m) and sonicated for 5 min in between measurements. All data is displayed against the half-wave potential of ferrocene/ferrocenium redox couple (FcH/FcH⁺; 0.58 V vs. Ag/AgCl) as internal reference. Oxidation potentials are marked and displayed as the half-wave potential of the respective peak.

1.2 Electrochemical Setup

Galvanostat

Electrochemical reactions were carried out using a multichannel galvanostat HMP4040 (Rohde & Schwarz, München, Germany). The cells used for screening or batch reactions are described below (Figure S1 and S2).

Screening and small-scale batch reactions

Divided Teflon™ cells with a volume of 6 mL per half-cell equipped with a Nafion™ membrane (Nafion™ N324, Ion Power GmbH, Munich, Germany, $d = 10$ mm) or a glass frit (P4, $d = 10$ mm). Glass frits and Nafion™ N324 membrane used as separator materials were pretreated in the corresponding solvent prior to use. Stirring bars were used during electrolysis in each cell. The described screening system is commercially available as IKA Screening System Package (IKA™ Werke GmbH & Co. KG, Staufen, Germany).

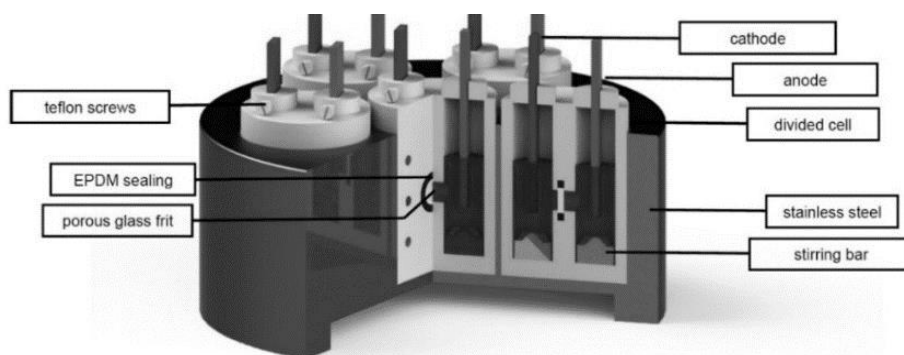


Figure S1: Divided screening setup.^[2]

The screening was carried out using various electrode materials (7 cm $\times$ 1 cm $\times$ 0.3 cm). Graphite electrodes were sanded using 600 grit followed by 1000 grit sandpaper and cleaned with acetonitrile prior to use. Platinum foil electrodes were flame treated before use and fixed to Teflon™ supports for electrolysis. BDD electrodes were electrochemically treated ($j = 50$ mA $\times$ cm $^{-2}$) in 20% (v/v) sulfuric acid for 10 min before use. SIGRAFLEX™ electrodes (7 cm $\times$ 1 cm $\times$ 0.02 cm) were pretreated in the corresponding solvent for at least 1 h prior to use. The electrodes were immersed 3.1 cm into the electrolyte. This resulted in a geometric active electrode area of 3.1 cm 2 used for electrolysis.

Electrode Materials

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

Entry	Electrode Material	Specification	Supplier
1	Boron-doped diamond (DIACHEM™)	15 μ m boron-doped diamond layer on silicon	CONDIAS GmbH, Itzehoe, Germany
2	Glassy carbon	Sigradur G	HTW, Thierhaupten, Germany
3	Graphite	highly isostatic, V2100	SGL Carbon, Bonn, Germany
4	Graphite foil (SIGRAFLEX™)	F02012Z	SGL Carbon, Meitingen, Germany
5	Platinum	>99% Pt	ÖGUSSA, Vienna, Austria
6	Stainless-steel	1.4571	various suppliers

Scale-up Cell

The scale-up experiment was performed in a jacketed divided glass cell with a volume of 90 mL per half-cell equipped with a PTFE stopper and sleeve, electrodes, and electrode holders, a Nafion™ membrane (Nafion™ N324, *Ion Power GmbH*, Munich, Germany, $d = 30$ mm) and stirring bars. The electrolysis was conducted using a TDK-Lambda Z+ series (*TDK-Lambda UK Limited*, Devon, United Kingdom) as power source. The SIGRAFLEX™ electrode (*SGL Carbon*, Meitingen, Germany) was held in place using a PTFE support frame. The SIGRAFLEX™ anode dimensions (excluding the area covered by the frame) were 7 cm × 1.8 cm × 0.02 cm, with 6 cm submerged into the reaction mixture, resulting in an active anode area of 10.8 cm². The stainless-steel cathode had dimensions of 8 cm × 2.5 cm × 0.3 cm, from which 6 cm were submerged into the solution. The stoppers and electrode holders are available Sigma-Aldrich within the SynLectro™ series.



Figure S2: Comparison of the different cells used. Left: Teflon™ screening cell with 6 mL per half-cell equipped with SIGRAFLEX™ and stainless-steel electrodes, Nafion™ N324 membrane and EPDM-O-Ring. Right: jacketed glass cell with 90 mL per half-cell equipped with a Nafion™ N324 membrane, SIGRAFLEX™ and stainless-steel electrodes, Teflon™ plug and electrode holders.

2 Experimental Procedures

2.1 Preparation of the SO₂ stock solution

In a gas-inlet apparatus connected to a washing bottle filled with aq. NaOH (20 wt-%) with Woulff bottles placed before and after the washing bottle, acetonitrile (350 mL, anhydrous) was enriched with SO₂ at 0 °C under constant stirring for 15 minutes. After usage, the gas-inlet apparatus was flushed with Argon and molecular sieve (3 Å) was added to the obtained solution. The stock solution was sealed by a PTFE stopper and stored in a fridge at 7 °C.

2.2 Determination of the SO₂ concentration of the stock solution

The SO₂ molarity was determined according to the principles of the “Excess Iodine Method” described by Ferguson.^[3] To a solution of I₂ (1.27 g, 5.00 mmol) and KI (2.20 g, 13.3 mmol) in H₂O (100 mL) was slowly added the freshly prepared SO₂ stock solution (1 mL). The solution was then back titrated with a freshly prepared solution of Na₂S₂O₃ (aq., 0.2 m) as titrant. After full reduction of the iodine, the concentration of SO₂ (mostly 3–5 m) was calculated according to the previously reduced iodine by aq. SO₂. The titration was conducted three successive times, and the molarity of the stock solution was determined by averaging the three measurements.

2.3 General Protocol for the Synthesis of Alkyl Alkenesulfonates (GP1)

The reactions were carried out using the divided Teflon™ cells with a Nafion™ N324 membrane as described in the section before.

Anolyte: In a 10 mL pear shaped flask an alcohol (3.00 mmol, 5 eq.) was combined with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 639 mg, 626 µL, 4.20 mmol, 7 eq.). The mixture was cooled to 0 °C in an ice bath and SO₂ stock solution (10 eq., 1–2 mL depending on the concentration of SO₂) was added. The solution was diluted with acetonitrile (anhydrous) so that a total volume of 6 mL was achieved.

Catholyte: A solution of tetrabutylammonium tetrafluoroborate (198 mg, 600 µmol, 1 eq.) and acetic acid (180 mg, 172 µL, 3.00 mmol, 5 eq.) in acetonitrile (anhydrous) was prepared, so that a total volume of 6 mL was reached.

The reaction mixtures were transferred with syringes to their respective compartment simultaneously and the anolyte was additionally loaded with a styrene substrate (600 µmol, 1 eq.). The amperage was set accordingly so that a current density of 10 mA×cm⁻² was reached (31 mA with the setup described herein) and the amount of applied charge was set to 2.8 F. The electrolysis was conducted at room temperature under constant stirring (400 rpm) for ca. 1.5 h. After completion of the electrolysis the anolyte was transferred to a beaker and the compartment was rinsed with acetonitrile (3 x 2 mL). The combined solutions were filtered over a short layer of silica (ca. 1 cm) and the solvent was removed under reduced pressure. The crude product (ca. 300 mg) was purified by flash column chromatography (cyclohexane/ethyl acetate and/or dichloromethane/methanol) with an appropriate gradient.

2.4 General Protocol for the Optimization of Reaction Conditions (GP2)

The reactions were carried out using the divided Teflon™ cells with a glass frit or Nafion™ N324 membrane as described in the section above.

Anolyte: In a 10 mL pear shaped flask neopentyl alcohol was combined with a base. SO₂ stock solution (ca. 1–2 mL depending on the concentration and equivalents of SO₂) was added. The solution was diluted with acetonitrile (anhydrous) so that a total volume of 6 mL was achieved.

Catholyte: A solution of tetrabutylammonium tetrafluoroborate (198 mg, 600 µmol, 1 eq.) and HFIP (504 mg, 316 µL, 3.00 mmol, 5 eq.) or acetic acid (180 mg, 172 µL, 3.00 mmol, 5 eq.) in acetonitrile (anhydrous) was prepared, so that a total volume of 6 mL was achieved.

The reaction mixtures were transferred with syringes to their respective compartment simultaneously and the anolyte was additionally loaded with 4-methoxystyrene (80.5 mg, 81.0 µL, 600 µmol, 1 eq.). The amperage and amount of applied charge was set to the desired values and the electrolysis was conducted at room temperature under constant stirring (400 rpm). After completion, the anolyte was transferred to a beaker, the anode compartment was rinsed with acetonitrile (3 x 2 mL) and the washing solutions were combined with the anolyte. ¹H NMR yields were calculated by addition of 1,3,5-trimethoxybenzene (50.5 mg, 300 µmol, 0.5 eq.) as internal standard to this mixture. After 5 min of stirring, an aliquot (ca. 0.5 mL) was taken, and the solvent was removed under reduced pressure.

2.5 Protocol for the Scale-up Reaction

The reaction was carried out using the divided glass cell with a Nafion™ N324 membrane as described in the section above.

Anolyte: In a 100 mL pear shaped flask a mixture of neopentyl alcohol (3.97 g, 45.0 mmol, 5 eq.) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 9.59 g, 9.4 mL, 63.0 mmol, 7 eq.) was prepared. The mixture was cooled to 0 °C and SO₂ stock solution (3.52 m, 25.6 mL, 10 eq.) was added. The resulting solution was diluted with acetonitrile (51.1 mL, anhydrous) so that a total volume of 90 mL was achieved.

Catholyte: A solution of tetrabutylammonium tetrafluoroborate (2.96 g, 9.00 mmol, 1 eq.) and acetic acid (2.70 g, 2.57 mL, 45.0 mmol, 5 eq.) in acetonitrile (anhydrous) was prepared, so that a total volume of 90 mL was reached as well.

The reaction mixtures were transferred to their respective compartment and the anolyte was additionally loaded with 4-methoxystyrene (1.21 g, 1.21 mL, 9.00 mmol, 1 eq.). The amperage was set accordingly so that a current density of $10 \text{ mA} \times \text{cm}^{-2}$ was reached (108 mA with the setup described herein) and the amount of applied charge was set to 2.8 F. The electrolysis was conducted at 20°C with active temperature control through the help of a cryostat and under constant stirring for ca. 6 h. After completion of the electrolysis the anolyte was transferred into a beaker and the compartment was rinsed with acetonitrile ($3 \times 20 \text{ mL}$). The solvent of the combined solutions was removed under reduced pressure. The residue was mixed with water (100 mL) and extracted with ethyl acetate ($3 \times 75 \text{ mL}$). The combined organic phases were washed with water ($3 \times 50 \text{ mL}$), dried over magnesium sulfate and the solvent was evaporated under reduced pressure. The crude (ca. 3.50 g) was purified by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 89/11) and the desired product neopentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (**8a**, 1.87 g, 6.58 mmol, 73%) was obtained as a colorless solid.

Spectroscopic data of the isolated compound matched the one obtained from the screening reactions.

Note: An ^1H NMR yield of 84% was calculated by addition of 1,3,5-trimethoxybenzene (229.9 mg, 1.36 mmol) as internal standard to the anolyte upon removal from the cell.

2.6 Protocol for the Reusability Tests

The reactions were carried out using the divided Teflon™ cells with a Nafion™ N324 membrane as described in the section before.

Anolyte: In a 10 mL pear shaped flask neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) was combined with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 639 mg, 626 μL , 4.20 mmol, 7 eq.). The mixture was cooled to 0°C and SO_2 stock solution (4.57 mL, 1.31 mL, 10 eq.) was added. The resulting solution was diluted with acetonitrile (3.8 mL, anhydrous) so that a total volume of 6 mL was achieved.

Catholyte: A solution of tetrabutylammonium tetrafluoroborate (198 mg, 600 μmol , 1 eq.) and acetic acid (180 mg, 172 μL , 3.00 mmol, 5 eq.) in acetonitrile (anhydrous) was prepared, so that a total volume of 6 mL was reached as well.

The reaction mixtures were transferred with syringes to their respective compartments and the anolyte was additionally loaded with 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.). The amperage was set accordingly so that a current density of $10 \text{ mA} \times \text{cm}^{-2}$ was reached (31 mA with the setup described herein) and the amount of applied charge was set to 2.8 F. The electrolysis was conducted at r.t. under constant stirring (400 rpm) for ca. 1.5 h. After completion of the electrolysis the anolyte was transferred to a flask, the compartment was rinsed with acetonitrile ($3 \times 2 \text{ mL}$) and 1,3,5-trimethoxybenzene (50.5 mg, 300 μmol , 0.5 eq.) was added to the combined solutions as internal standard for determining ^1H NMR yield. After 5 min of stirring, an aliquot (ca. 0.5 mL) was taken from this mixture and the solvent was removed under reduced pressure.

For the subsequent runs, the anolyte was prepared as described, transferred to the respective compartment and 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.) was added. The SIGRAFLEX™ electrode, Nafion™ N324 membrane and catholyte (an additional amount of acetic acid (108 mg, 103 μL , 1.80 mmol, 3 eq.) was added to compensate for the loss from H_2 evolution from the previous experiment) were reused for the following experiments. The electrolysis and subsequent workup for determining ^1H NMR yield was conducted as described above. The complete procedure was conducted four times in total (Figure S3).

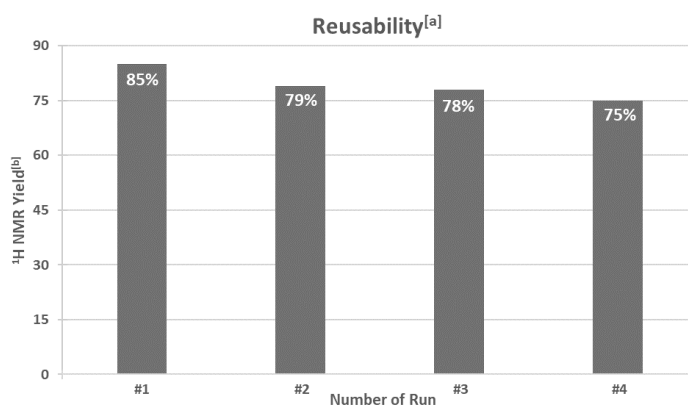
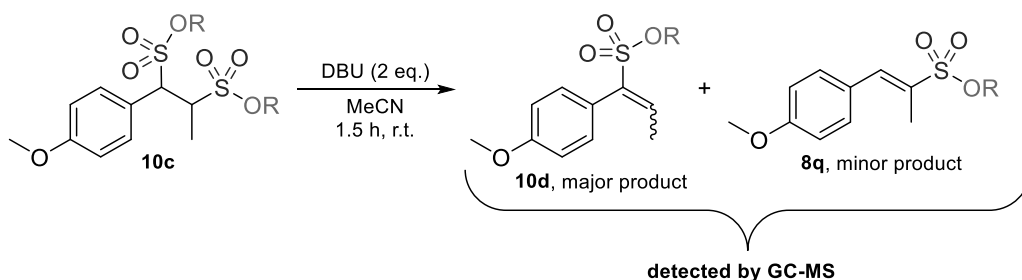


Figure S3: Tests for reusing the electrodes, Nafion™ N324 membrane and catholyte. ^[a]conditions described above. ^[b]Yield determined by ^1H NMR (internal standard).

2.7 Test for Elimination of Byproduct 10c



In a 5 mL vial with a stirring bar, doubly-sulfonylated compound **10c** (45.0 mg, 100 μ mol, 1 eq.) was dissolved in acetonitrile (1 mL). DBU (30.4 mg, 30.0 μ L, 200 μ mol, 2 eq.) was added and the mixture stirred at r.t. for 1.5 h. Thereafter, a sample from the reaction mixture was taken for GC/MS analysis (Figure S4).

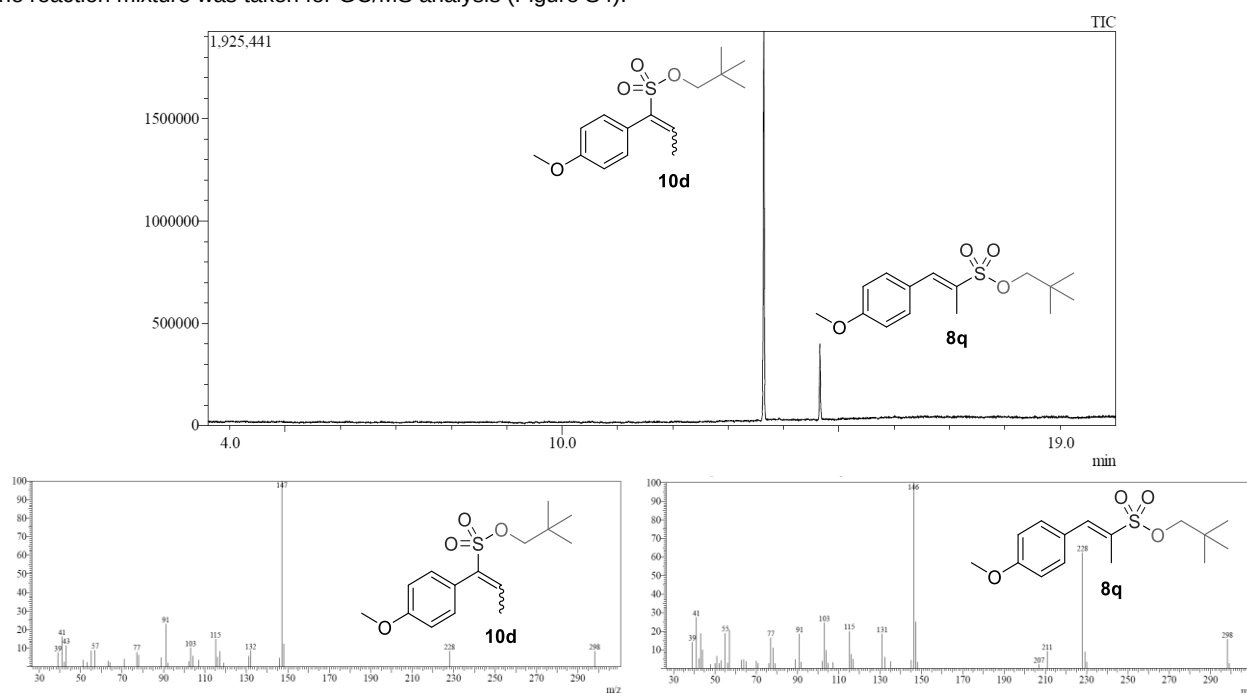
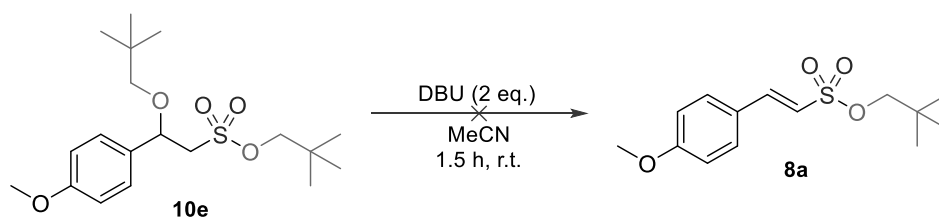


Figure S4: GC/MS measurement of the reaction from **10c** with DBU, showing the complete consumption of starting material and the formation of two products exhibiting very similar mass spectra.

2.8 Test for Elimination of Byproduct 10e



In a 5 mL vial with a stirring bar, alkoxyated compound **10e** (37.2 mg, 100 μ mol, 1 eq.) was dissolved in acetonitrile (1 mL). DBU (30.4 mg, 30.0 μ L, 200 μ mol, 2 eq.) was added and the mixture stirred at r.t. for 1.5 h. Thereafter, a sample from the reaction mixture was taken for GC/MS analysis. Only the starting material **10e** could be detected, with no signal of alkyl alkenesulfonate **8a**.

3 Optimization of the Reaction Conditions

Optimization of the conditions was carried out by using linear screening with 4-methoxystyrene and neopentyl alcohol as substrates according to the procedure described in GP2. Neopentyl alcohol was chosen due to the enhanced stability of the respective sulfonate ester.^[4] Yields were determined by ¹H NMR spectroscopy by addition of 1,3,5-trimethoxybenzene as an internal standard after the end of electrolysis.

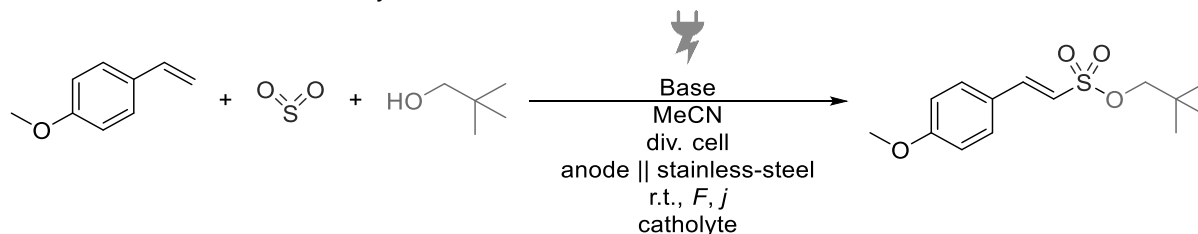


Table S2: Screening of anode materials.

Entry	Anode material	Yield (¹ H NMR) ^[a]
1	Platinum	25%
2	BDD	8%
3	Graphite	49%
4	SIGRAFLEX™	50%
5	Glassy carbon	48%

Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (7.5 eq.), neopentyl alcohol (3 eq.), DBU (5 eq.), MeCN, div. cell (frit), anode || stainless-steel, 7.5 mA×cm⁻², 2.5 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + HFIP (5 eq.). ^[a]Yield determined by ¹H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

For ease of use, it was decided to continue the optimization with a glassy carbon electrode. SIGRAFLEX™ (graphite foil) anode improved yield later during further optimization (vide infra). In the next step, the stoichiometry of alcohol and base (so in essence the amount of monoalkylsulfite nucleophile formed) was investigated.

Table S3: Screening of the stoichiometry of alcohol and base.

Entry	Amount of alcohol	Amount of base	Yield (¹ H NMR) ^[a]
1	2 eq.	4 eq.	41%
2	3 eq.	5 eq.	48%
3	4 eq.	6 eq.	57%
4	5 eq.	7 eq.	61%

Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (7.5 eq.), neopentyl alcohol (2–5 eq.), DBU (4–7 eq.), MeCN, div. cell (frit), glassy carbon || stainless-steel, 7.5 mA×cm⁻², 2.5 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + HFIP (5 eq.). ^[a]Yield determined by ¹H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

Table S4: Screening of current density *j*.

Entry	Current density <i>j</i> [mA×cm ⁻²]	Anode	Yield (¹ H NMR) ^[a]
1	2	Glassy carbon	35%
2	4	Glassy carbon	55%
3	6	Glassy carbon	60%
4	7.5	Glassy carbon	61%

5	10	Glassy carbon	60%
6	12	Glassy carbon	65%
7	15	Glassy carbon	64%
8	10	SIGRAFLEX™	69%
9	12	SIGRAFLEX™	65%
10	20	SIGRAFLEX™	59%

Conditions (GP2): 4-Methoxystyrene (600 μmol , 1 eq., 0.1 m), SO_2 (7.5 eq.), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (frit), anode || stainless-steel, j, 2.5 F, r.t., catholyte: 0.1 M Bu_4NBF_4 in MeCN + HFIP (5 eq.). ^[a]Yield determined by ^1H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

Table S5: Variation of base.

Entry	Base	Yield (^1H NMR) ^[a]
1	Triethylamine	9%
2	Diisopropylamine	2%
3	1,1,3,3-Tetramethylguanidine	0%
4	<i>N''-tert-Butyl-N,N,N',N'</i> -tetramethylguanidine (tBuTMG)	51%
5	1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU)	69%
6	Pyrrolidine	22%
7	2,4,6-Collidine	0%

Conditions (GP2): 4-Methoxystyrene (600 μmol , 1 eq., 0.1 m), SO_2 (7.5 eq.), neopentyl alcohol (5 eq.), base (7 eq.), MeCN, div. cell (frit), SIGRAFLEX™ || stainless-steel, 10 $\text{mA}\times\text{cm}^{-2}$, 2.5 F, r.t., catholyte: 0.1 M Bu_4NBF_4 in MeCN + HFIP (5 eq.). ^[a]Yield determined by ^1H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

Table S6: Testing of applied charge and separator material.

Entry	Applied charge [F]	Separator material	Yield (^1H NMR) ^[a]
1	2.0	Glass frit	62%
2	2.3	Glass frit	65%
3	2.5	Glass frit	69%
4	2.8	Glass frit	66%
5	3.0	Glass frit	65%
6	2.5	Nafion™ N324 membrane	72%
7	2.8	Nafion™ N324 membrane	74%

Conditions (GP2): 4-Methoxystyrene (600 μmol , 1 eq., 0.1 m), SO_2 (7.5 eq.), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (separator material), SIGRAFLEX™ || stainless-steel, 10 $\text{mA}\times\text{cm}^{-2}$, F, r.t., catholyte: 0.1 M Bu_4NBF_4 in MeCN + HFIP (5 eq.). ^[a]Yield determined by ^1H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

By pretreating the SIGRAFLEX™ anode in acetonitrile for 2 h prior to usage, the yield improved slightly to 78% (^1H NMR). We then exchanged the proton source in the catholyte and found that acetic acid instead of HFIP increased the yield to 81%. Finally, changing the amount of SO_2 to 10 eq. and adding the stock solution under active cooling in an ice bath (0 °C) afforded the desired β -styrenesulfonate product **8a** in a yield of 85% (^1H NMR).

Table S7: Other parameters.

Entry	Parameter	^[d] Yield (¹ H NMR)
1 ^[a]	Pretreating of SIGRAFLEX™ electrode in acetonitrile 2 h before usage	78%
2 ^[b]	Catholyte: 0.1 M Bu ₄ NBF ₄ + AcOH (5 eq.)	81%
3 ^[c]	10 eq. SO ₂ with cooling while adding the stock solution	85%

^[a]Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (7.5 eq.), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324 membrane), SIGRAFLEX™ || stainless-steel, 10 mA×cm⁻², 2.8 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + HFIP (5 eq.). ^[b]Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (7.5 eq.), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324 membrane), SIGRAFLEX™ (pretreated) || stainless-steel, 10 mA×cm⁻², 2.8 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[c]Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (10 eq.) under active cooling (0 °C), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324 membrane), SIGRAFLEX™ (pretreated) || stainless-steel, 10 mA×cm⁻², 2.8 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[d]Yield determined by ¹H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis.

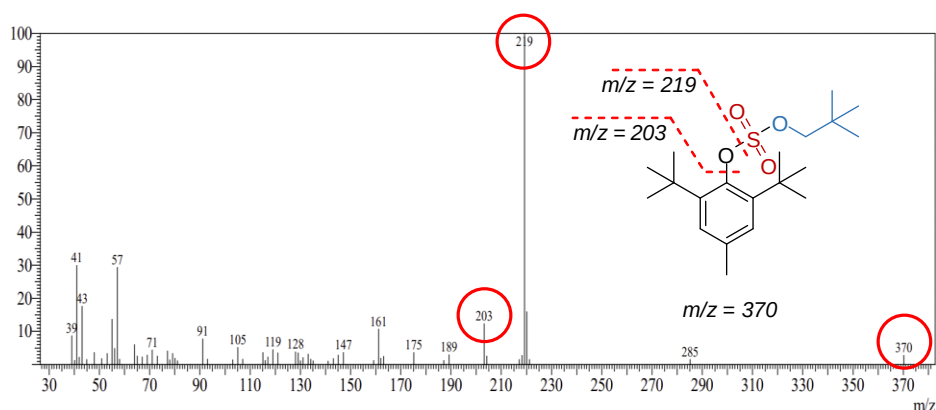
To gain insight into the reaction, some control experiments were performed using the optimized conditions from Table S7, Entry 3:

Table S8: Control experiments.

Entry	Deviation from the optimized conditions ^[a]	^[b] Yield (¹ H NMR)
1	No charge applied	0% ^[c]
2	No DBU (0.1 M Bu ₄ NBF ₄ instead to ensure conductivity)	0%
3	+ 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, 3 eq.)	10%
4	+ 2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT, 3 eq.)	23%

^[a]Conditions (GP2): 4-Methoxystyrene (600 μmol, 1 eq., 0.1 M), SO₂ (10 eq.) under active cooling (0 °C), neopentyl alcohol (5 eq.), DBU (7 eq.), MeCN, div. cell (Nafion™ N324 membrane), SIGRAFLEX™ (pretreated) || stainless-steel, 10 mA×cm⁻², 2.8 F, r.t., catholyte: 0.1 M Bu₄NBF₄ in MeCN + AcOH (5 eq.). ^[b]Yield determined by ¹H NMR via the addition of 1,3,5-trimethoxybenzene (0.5 eq.) after the end of electrolysis. ^[c]Traces of the product could be detected using GC/MS.

In the case of BHT (Table S8, Entry 4), we were able to detect a trapped product resulting from the radical addition of an alkoxy sulfonate species by GC/MS (Figure S5):

**Figure S5:** Mass spectrum obtained by GC/MS of a BHT-trapped intermediate.

4 Cyclic Voltammetry Results

The following measurements were used for the postulation of the reaction mechanism: The initial oxidation of the styrene substrate is confirmed by cyclic voltammetry (Figure S6). This oxidation step occurs before the oxidation of the monoalkylsulfite, even in the case of electron-deficient substrates like 4-chlorostyrene.

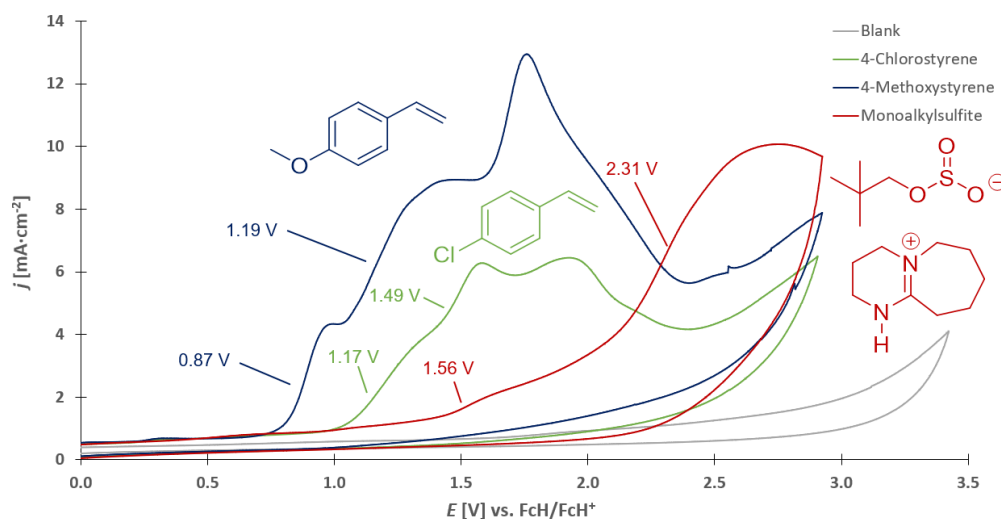


Figure S6: Cyclic voltammograms of 4-chlorostyrene (green), 4-methoxystyrene (dark blue), the intermediate monoalkylsulfite (red) and a blank measurement (grey). Measurement conditions: 0.1 m Bu_4NBF_4 in MeCN; $c(\text{substrate}) = 10 \text{ mmol} \cdot L^{-1}$; $c(SO_2) = 40 \text{ mmol} \cdot L^{-1}$; $\nu = 100 \text{ mV} \cdot s^{-1}$.

In the case of the styrene substrates, the measured current decreases significantly with the number of CV-cycles (Figure S7). This indicates an adsorption on the surface of the glassy carbon WE and possibly the formation of a polymeric layer. Adsorption of styrenes to carbon-based electrodes and the subsequent formation of a polymer layer during electroanalytic measurements has been described in the literature^[5,6] and is suspected to be the reason for some electrocatalytic behavior observed with styrenes. It is supposed^[6] that the polymeric layer reaches a steady state of porosity, which would explain the only slightly reduced yields observed in our reusability studies. The formation of a polymeric layer might also be the reason for reduced yields observed in some of the substrates.

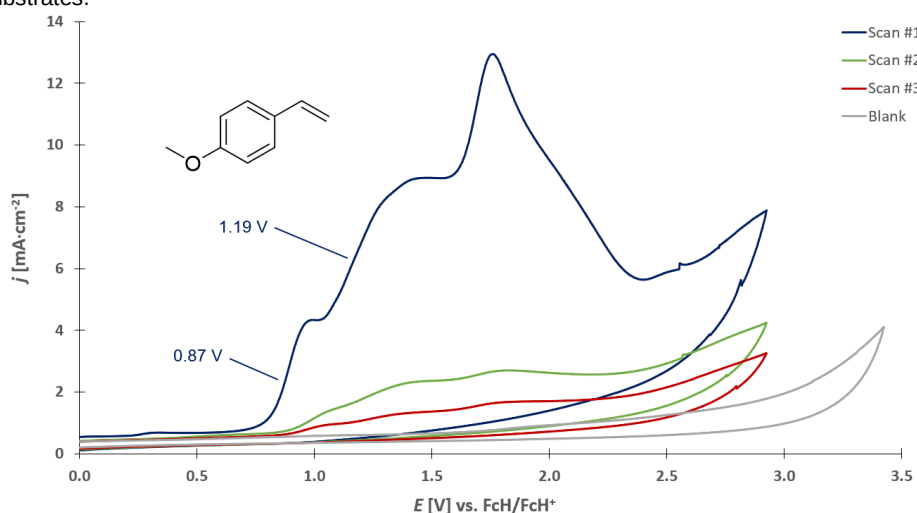


Figure S7: Cyclic voltammogram of 4-methoxystyrene shows a decrease in current with increasing number of scans (Scan #1: dark blue; Scan #2: green; Scan #3: red). Measurement conditions: 0.1 m Bu_4NBF_4 in MeCN; $c(4\text{-methoxystyrene}) = 10 \text{ mmol} \cdot L^{-1}$; $\nu = 100 \text{ mV} \cdot s^{-1}$.

Although not relevant as long enough substrate is present, a similar decrease in current is observed when measuring the corresponding styrenesulfonate product (Figure S8). However, the effect is by far not as pronounced. Therefore, adsorption and/or polymerization of the products may happen at least partially. In general, the oxidation peak of the alkenesulfonate product is shifted towards more positive potentials (ca. + 400 mV), indicating that overoxidation will not occur in significant amounts.

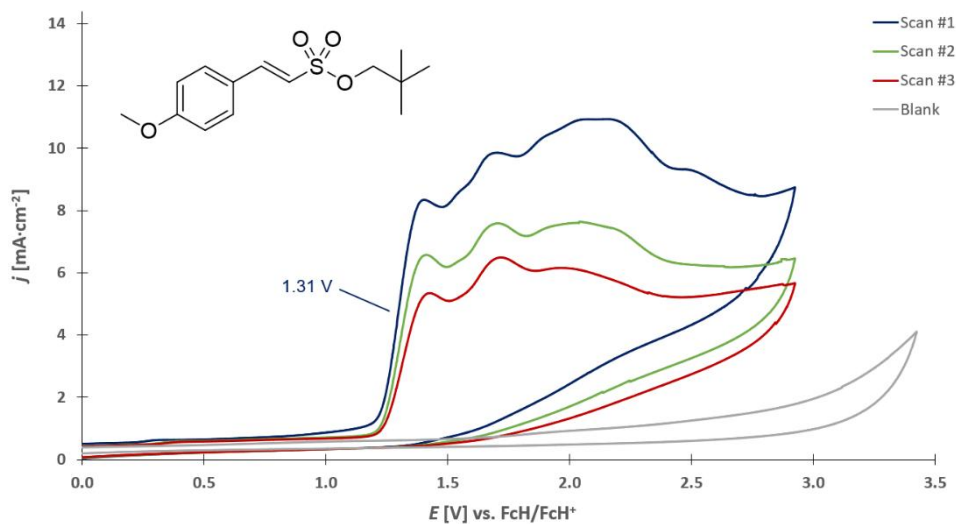
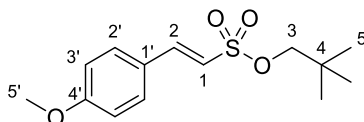


Figure S8: Cyclic voltammogram of neopentyl (E)-2-(4-methoxyphenyl)ethene-1-sulfonate (**8a**) also shows a slight decrease in current with increasing number of scans (Scan #1: dark blue; Scan #2: green; Scan #3: red). Measurement conditions: 0.1 m Bu_4NBF_4 in MeCN; $c(\mathbf{8a}) = 10 \text{ mmol}\cdot\text{L}^{-1}$; $\nu = 100 \text{ mV}\cdot\text{s}^{-1}$.

5 Compound Characterization

5.1 Neopentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (8a)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 89/11), the desired product (132 mg, 464 μmol , 77%) was obtained as a colorless solid.



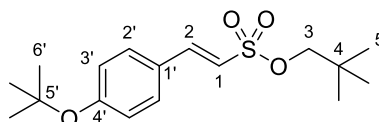
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.54 (d, J = 15.5 Hz, 1H, 2-*H*), 7.49 – 7.44 (m, 2H, 2'-*H*), 6.97 – 6.92 (m, 2H, 3'-*H*), 6.58 (d, J = 15.5 Hz, 1H, 1-*H*), 3.86 (s, 3H, 5'-*H*), 3.78 (s, 2H, 3-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.4, 144.6, 130.4, 124.8, 118.3, 114.8, 79.5, 55.6, 31.9, 26.3.

HRMS (ESI+): m/z for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 307.0975, found: 307.0977.

5.2 Neopentyl (*E*)-2-(4-*tert*-butoxyphenyl)ethene-1-sulfonate (8b)

According to GP1, 4-*tert*-butoxystyrene (106 mg, 112 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 93/7), the desired product (131 mg, 402 μmol , 67%) was obtained as a colorless solid.



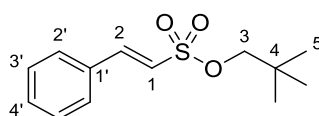
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.55 (d, J = 15.5 Hz, 1H, 2-*H*), 7.46 – 7.41 (m, 2H, 2'-*H*), 7.05 – 7.00 (m, 2H, 3'-*H*), 6.61 (d, J = 15.5 Hz, 1H, 1-*H*), 3.78 (s, 2H, 3-*H*), 1.40 (s, 9H, 6'-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 159.0, 144.5, 129.7, 126.6, 123.8, 119.2, 79.8, 79.5, 31.9, 29.0, 26.3.

HRMS (ESI+): m/z for $\text{C}_{17}\text{H}_{26}\text{O}_4\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 344.1890, found: 344.1893.

5.3 Neopentyl (*E*)-2-phenylethene-1-sulfonate (8c)

According to GP1, styrene (63.1 mg, 70.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification via flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 90/10), the desired product (67.0 mg, 263 μmol , 44%) was obtained as a colorless solid.



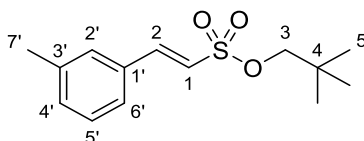
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.60 (d, J = 15.6 Hz, 1H, 2-*H*), 7.54 – 7.49 (m, 2H, 2'-*H*), 7.48 – 7.39 (m, 3H, 3'-*H*, 4'-*H*), 6.75 (d, J = 15.6 Hz, 1H, 1-*H*), 3.80 (s, 2H, 3-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 144.8, 132.1, 131.5, 129.3, 128.6, 121.1, 79.7, 31.8, 26.2.

HRMS (ESI+): m/z for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 272.1315, found: 272.1307.

5.4 Neopentyl (*E*)-2-(3-methylphenyl)ethene-1-sulfonate (8d)

According to GP1, 3-methylstyrene (70.9 mg, 78.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 95/5), the desired product (66.0 mg, 246 μmol , 41%) was obtained as a colorless oil.



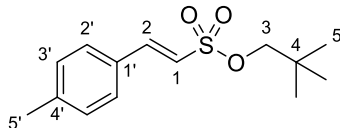
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.57 (d, J = 15.5 Hz, 1H, 2-*H*), 7.35 – 7.26 (m, 4H, Ar-*H*), 6.72 (d, J = 15.5 Hz, 1H, 1-*H*), 3.79 (s, 2H, 3-*H*), 2.39 (s, 3H, 7'-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 145.0, 139.1, 132.4, 132.1, 129.2, 129.2, 125.8, 120.9, 79.7, 31.9, 26.2, 21.4.

HRMS (ESI⁺): m/z for $C_{14}H_{20}O_3S(NH_4)^+$ $[M+NH_4]^+$: calc.: 286.1471, found: 286.1470.

5.5 Neopentyl (E)-2-(4-methylphenyl)ethene-1-sulfonate (8e)

According to GP1, 4-methylstyrene (70.9 mg, 78.0 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 95/5), the desired product (73.0 mg, 272 μ mol, 45%) was obtained as a colorless solid.



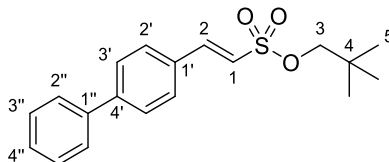
1H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.57 (d, J = 15.5 Hz, 1H, 2-*H*), 7.44 – 7.39 (m, 2H, 2'-*H*), 7.26 – 7.21 (m, 2H, 3'-*H*), 6.68 (d, J = 15.5 Hz, 1H, 1-*H*), 3.79 (s, 2H, 3-*H*), 2.40 (s, 3H, 5'-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 144.9, 142.3, 130.1, 129.4, 128.6, 119.9, 79.6, 31.9, 26.2, 21.7.

HRMS (ESI⁺): m/z for $C_{14}H_{20}O_3S(NH_4)^+$ $[M+NH_4]^+$: calc.: 286.1471, found: 286.1472.

5.6 Neopentyl (E)-2-([1,1'-biphenyl]-4-yl)ethene-1-sulfonate (8f)

According to GP1, 4-phenylstyrene (108 mg, 600 μ mol, 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 90/10), the desired product (59.8 mg, 181 μ mol, 30%) was obtained as a colorless oil.



1H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.69 – 7.58 (m, 7H, 2-*H*, Ar-*H*), 7.50 – 7.45 (m, 2H, Ar-*H*), 7.43 – 7.38 (m, 1H, Ar-*H*), 6.77 (d, J = 15.5 Hz, 1H, 1-*H*), 3.82 (s, 2H, 3-*H*), 0.99 (s, 9H, 5-*H*).

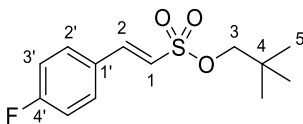
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 144.43, 144.37, 139.9, 131.0, 129.1, 128.3, 128.0, 127.2, 120.9, 79.7, 77.5, 77.2, 76.8, 31.9, 26.3.

HRMS (ESI⁺): m/z for $C_{19}H_{22}O_3S(Na)^+$ $[M+Na]^+$: calc.: 353.1182, found: 353.1178.

Note: After the electrolysis, a white, insoluble residue covered the SIGRAFLEX™ anode, which is believed to be a layer of polymers.

5.7 Neopentyl (E)-2-(4-fluorophenyl)ethene-1-sulfonate (8g)

According to GP1, 4-fluorostyrene (74.8 mg, 76.0 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 86/14), the desired product (74.2 mg, 272 μ mol, 45%) was obtained as a colorless solid.



1H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.55 (d, J = 15.6 Hz, 1H, 2-*H*), 7.53 – 7.48 (m, 2H, 2'-*H*), 7.16 – 7.08 (m, 2H, 3'-*H*), 6.68 (d, J = 15.6 Hz, 1H, 1-*H*), 3.79 (s, 2H, 3-*H*), 0.97 (s, 9H, 5-*H*).

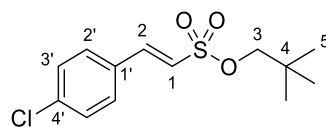
^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 164.6 (d, J_{C-F} = 253.3 Hz), 143.4, 130.7 (d, J_{C-F} = 8.8 Hz), 128.4 (d, J_{C-F} = 3.4 Hz), 120.9, 116.6 (d, J_{C-F} = 22.0 Hz), 79.7, 31.8, 26.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ [ppm] = -108.50 – 108.64 (m, 1F).

HRMS (ESI⁺): m/z for $C_{13}H_{17}FO_3S(NH_4)^+$ $[M+NH_4]^+$: calc.: 290.1221, found: 290.1218.

5.8 Neopentyl (E)-2-(4-chlorophenyl)ethene-1-sulfonate (8h)

According to GP1, 4-chlorostyrene (84.0 mg, 77.0 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 89/11), the desired product (72.1 mg, 250 μ mol, 42%) was obtained as a colorless solid.



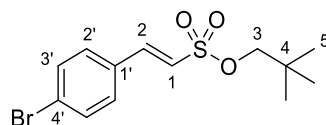
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.54 (d, J = 15.6 Hz, 1H, 2-*H*), 7.47 – 7.43 (m, 2H, 2'-*H*), 7.42 – 7.37 (m, 2H, 3'-*H*), 6.73 (d, J = 15.6 Hz, 1H, 1-*H*), 3.80 (s, 2H, 3-*H*), 0.97 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 143.3, 137.6, 130.6, 129.8, 129.6, 121.8, 79.8, 31.8, 26.2.

HRMS (ESI⁺): m/z for $\text{C}_{13}\text{H}_{17}\text{ClO}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$]⁺: calc.: 306.0925 (^{35}Cl), found: 306.0920.

5.9 Neopentyl (E)-2-(4-bromophenyl)ethene-1-sulfonate (8i)

According to GP1, 4-bromostyrene (114 mg, 82.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 90/10), the desired product (63.6 mg, 191 μmol , 32%) was obtained as a colorless solid.



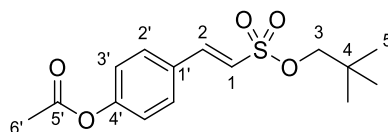
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.59 – 7.55 (m, 2H, 3'-*H*), 7.53 (d, J = 15.6 Hz, 1H, 2-*H*), 7.40 – 7.35 (m, 2H, 2'-*H*), 6.74 (d, J = 15.5 Hz, 1H, 1-*H*), 3.80 (s, 2H, 3-*H*), 0.97 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 143.3, 132.6, 131.0, 129.9, 126.0, 121.9, 79.8, 31.8, 26.2.

HRMS (ESI⁺): m/z for $\text{C}_{13}\text{H}_{17}\text{BrO}_3\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$]⁺: calc.: 354.9974 (^{79}Br), found: 354.9964.

5.10 Neopentyl (E)-2-(4-acetoxyphenyl)ethene-1-sulfonate (8j)

According to GP1, 4-acetoxystyrene (97.3 mg, 91.8 μL , 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 65/35), the desired product (56.3 mg, 180 μmol , 30%) was obtained as a colorless solid.



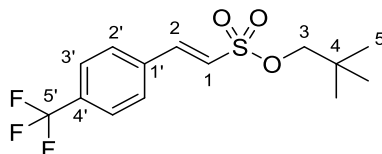
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.57 (d, J = 15.6 Hz, 1H, 2-*H*), 7.55 – 7.51 (m, 2H, 2'-*H*), 7.20 – 7.15 (m, 2H, 3'-*H*), 6.69 (d, J = 15.6 Hz, 1H, 1-*H*), 3.79 (s, 2H, 3-*H*), 2.32 (s, 3H, 6'-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 169.1, 153.1, 143.7, 129.8, 129.8, 122.7, 121.3, 79.8, 31.9, 26.2, 21.3.

HRMS (ESI⁺): m/z for $\text{C}_{15}\text{H}_{20}\text{O}_5\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$]⁺: calc.: 330.1370, found: 330.1369.

5.11 Neopentyl (E)-2-(4-(trifluoromethyl)phenyl)ethene-1-sulfonate (8k)

According to GP1, 4-(trifluoromethyl)styrene (105 mg, 91.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 3.5 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 87/13 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 99/1), the desired product (35.0 mg, 109 μmol , 18%) was obtained as a colorless solid.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.72 – 7.67 (m, 2H, 3'-*H*), 7.66 – 7.59 (m, 3H, 2'-*H*, 2-*H*), 6.85 (d, J = 15.6 Hz, 1H, 1-*H*), 3.83 (s, 2H, 3-*H*), 0.98 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 142.8, 135.5 (q, $J_{\text{C-F}}$ = 1.8 Hz), 133.0 (q, $J_{\text{C-F}}$ = 32.9 Hz), 128.8, 126.3 (q, $J_{\text{C-F}}$ = 3.7 Hz), 124.0, 123.7 (q, $J_{\text{C-F}}$ = 272.4 Hz), 80.0, 31.9, 26.2.

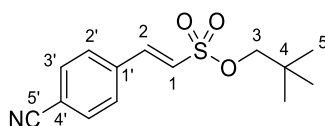
^{19}F NMR (377 MHz, CDCl_3) δ [ppm] = -63.03 (s, 3F).

HRMS (ESI⁺): m/z for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{H}$]⁺: calc.: 340.1189, found: 340.1183.

5.12 Neopentyl (E)-2-(4-cyanophenyl)ethene-1-sulfonate (8l)

According to GP1, 4-cyanostyrene (79.9 mg, 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column

chromatography (cyclohexane/ethyl acetate = 98/2 → 71/29), the desired product (49.9 mg, 179 μ mol, 30%) was obtained as a colorless solid.



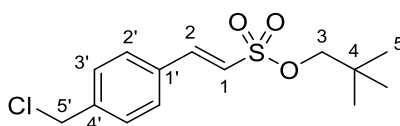
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.75 – 7.69 (m, 2H, 3'-H), 7.65 – 7.61 (m, 2H, 2'-H), 7.59 (d, J = 15.6 Hz, 1H, 2-H), 6.87 (d, J = 15.6 Hz, 1H, 1-H), 3.82 (s, 2H, 3-H), 0.97 (s, 9H, 5-H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 142.1, 136.3, 133.0, 129.0, 125.0, 118.1, 114.6, 80.1, 31.8, 26.1.

HRMS (ESI+): m/z for $\text{C}_{14}\text{H}_{17}\text{NO}_3\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 302.0821, found: 302.0815.

5.13 Neopentyl (E)-2-(4-(chloromethyl)phenyl)ethene-1-sulfonate (8m)

According to GP1, 4-(chloromethyl)styrene (102 mg, 94.0 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 3.5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 → 82/18), the desired product (88.1 mg, 291 μ mol, 48%) was obtained as a colorless solid.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.58 (d, J = 15.6 Hz, 1H, 2-H), 7.54 – 7.49 (m, 2H, 2'-H), 7.47 – 7.43 (m, 2H, 3'-H), 6.75 (d, J = 15.6 Hz, 1H, 1-H), 4.59 (s, 2H, 5'-H), 3.80 (s, 2H, 3-H), 0.97 (s, 9H, 5-H).

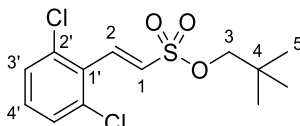
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 143.9, 140.9, 132.1, 129.4, 128.9, 121.8, 79.8, 45.5, 31.8, 26.2.

HRMS (ESI+): m/z for $\text{C}_{14}\text{H}_{19}\text{ClO}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 320.1082 (^{35}Cl), found: 320.1086.

Note: The purity of the starting material used was 90% according to the supplier.

5.14 Neopentyl (E)-2-(2,6-dichlorophenyl)ethene-1-sulfonate (8n)

According to GP1, 2,6-dichlorostyrene (106 mg, 84.0 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 3.5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 → 93/7), the desired product (105 mg, 326 μ mol, 54%) was obtained as a colorless solid.



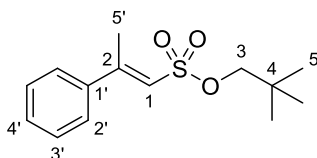
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.70 (d, J = 15.9 Hz, 1H, 2-H), 7.42 – 7.36 (m, 2H, 3'-H), 7.30 – 7.23 (m, 1H, 4'-H), 6.97 (d, J = 15.9 Hz, 1H, 1-H), 3.84 (s, 2H, 3-H), 0.98 (s, 9H, 5-H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 137.9, 135.2, 131.1, 129.7, 129.6, 129.1, 80.2, 31.8, 26.2.

HRMS (ESI+): m/z for $\text{C}_{13}\text{H}_{16}\text{Cl}_2\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 340.0536 (^{35}Cl , ^{35}Cl), found: 340.0527.

5.15 Neopentyl (E)-2-phenylpropene-1-sulfonate (8o-E)

According to GP1, α -methylstyrene (70.9 mg, 77.9 μ L, 600 μ mol, 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 → 95/5), the desired product (30.8 mg, 115 μ mol, 19%) was obtained as a colorless oil.



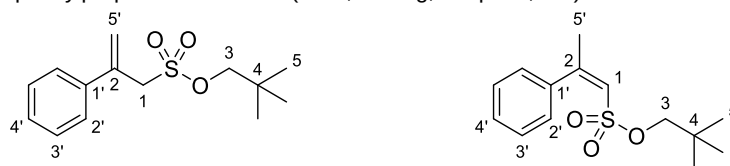
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.48 – 7.39 (m, 5H, Ar-H), 6.49 (q, J = 1.3 Hz, 1H, 1-H), 3.83 (s, 2H, 3-H), 2.55 (d, J = 1.3 Hz, 3H, 5'-H), 1.00 (s, 9H, 5-H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 155.3, 139.8, 130.2, 129.0, 126.5, 121.7, 79.3, 31.8, 26.3, 18.1.

HRMS (ESI+): m/z for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 286.1471, found: 286.1471.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 3-*H* and 5'-*H*, which is only possible in the (*E*)-configured molecule.

As a byproduct, neopentyl 2-phenylprop-2-ene-1-sulfonate (**10b**, 11.6 mg, 43.2 μmol , 7%) was obtained together with small amounts of neopentyl (*Z*)-2-phenylpropene-1-sulfonate (**8o-Z**, 2.5 mg, 9.3 μmol , 2%) in the same fraction:



10b (Left): ^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.50 – 7.47 (m, 1H, Ar-*H*), 7.44 – 7.28 (m, 4H, Ar-*H*), 5.76 (brs, 1H, 5'-*H*), 5.58 (d, J = 0.7 Hz, 1H, 5'-*H*), 4.28 (d, J = 0.7 Hz, 2H, 1-*H*), 3.74 (s, 2H, 3-*H*), 0.85 (s, 9H, 5-*H*).

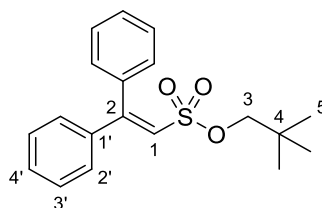
8o-Z (Right): ^1H NMR (400 MHz, CDCl_3) δ [ppm] = δ 7.47 – 7.45 (m, 5H, Ar-*H*), 6.34 (q, J = 1.5 Hz, 1H, 1-*H*), 3.63 (s, 2H, 3-*H*), 2.26 (d, J = 1.5 Hz, 3H, 5'-*H*), 0.87 (s, 9H, 5-*H*).

Mixture of **10b** and **8o-Z**: ^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 139.0, 137.7, 136.3, 129.2, 128.8, 128.5, 128.3, 127.3, 126.4, 122.1, 122.0, 79.4, 79.0, 56.0, 31.8, 27.3, 26.1, 26.0.

Note: ^{13}C NMR signals not completely resolved.

5.16 Neopentyl 2,2-diphenylethene-1-sulfonate (**8p**)

According to GP1, 1,1-diphenylethylene (108 mg, 106 μL , 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 92/8), the desired product (138 mg, 417 μmol , 69%) was obtained as a colorless solid.



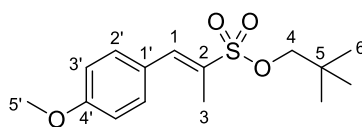
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.45 – 7.34 (m, 8H, Ar-*H*), 7.29 – 7.25 (m, 2H, Ar-*H*), 6.73 (s, 1H, 1-*H*), 3.73 (s, 2H, 3-*H*), 0.91 (s, 9H, 5-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 156.5, 139.5, 136.1, 130.5, 129.8, 129.6, 128.8, 128.6, 128.2, 121.7, 79.3, 31.8, 26.2.

HRMS (ESI+): m/z for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 348.1628, found: 348.1629.

5.17 Neopentyl (*E*)-1-(4-methoxyphenyl)prop-1-ene-2-sulfonate (**8q**)

According to GP1, *trans*-anethole (89.8 mg, 91.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 82/18), the desired product (75.1 mg, 252 μmol , 42%) was obtained as a colorless solid.



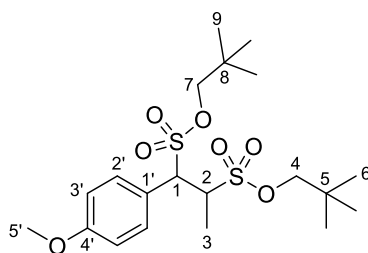
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.55 (d, J = 1.5 Hz, 1H, 1-*H*), 7.43 – 7.37 (m, 2H, 2'-*H*), 6.99 – 6.92 (m, 2H, 3'-*H*), 3.85 (s, 3H, 5'-*H*), 3.71 (s, 2H, 4-*H*), 2.28 (d, J = 1.5 Hz, 3H, 3-*H*), 0.98 (s, 9H, 6-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 160.7, 138.8, 131.7, 129.7, 126.0, 114.4, 79.3, 55.5, 31.8, 26.3, 13.8.

HRMS (ESI+): m/z for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 316.1577, found: 316.1580.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 4-*H* and 1-*H*, which is only possible in the (*E*)-configured molecule.

As a byproduct, dineopentyl 1-(4-methoxyphenyl)propane-1,2-disulfonate (**10c**, 77.3 mg, 172 μmol , 29%) was obtained as a colorless solid (eluent: cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 79/21).



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.42 – 7.36 (m, 2H, 2'-H), 6.94 – 6.88 (m, 2H, 3'-H), 4.62 (d, J = 9.7 Hz, 1H, 1-H), 3.93 (dq, J = 9.7, 7.2 Hz, 1H, 2-H), 3.79 (s, 3H, 5'-H), 3.70 (d, J = 9.1 Hz, 1H, OCH_2), 3.58 (d, J = 9.2 Hz, 1H, OCH_2), 3.50 (d, J = 9.2 Hz, 1H, OCH_2), 3.38 (d, J = 9.1 Hz, 1H, OCH_2), 1.92 (d, J = 7.2 Hz, 3H, 3-H), 0.79 (brs, 18H, 6-H, 9-H).

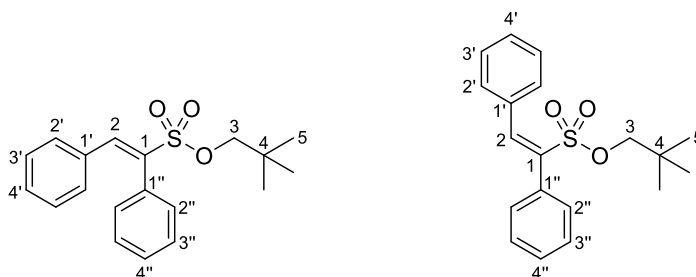
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 160.5, 130.8, 124.6, 114.4, 80.7, 79.5, 67.5, 59.8, 55.5, 31.8, 31.7, 26.0, 25.9, 14.8.

HRMS (ESI+): m/z for $\text{C}_{20}\text{H}_{34}\text{O}_7\text{S}_2(\text{K})^+$ [$\text{M}+\text{K}$] $^+$: calc.: 489.1378, found: 489.1381.

Note: Coupling constant $^3J(1\text{-H}, 2\text{-H})$ = 9.7 Hz suggests a *trans*-configuration for **10c**, but *cis*-configuration cannot be ruled out entirely.

5.18 Neopentyl (*E*-Z)-1,2-diphenylethene-1-sulfonate (**8r**)

According to GP1, *trans*-stilbene (113 mg, 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 3.5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 95/5), the desired product (75.6 mg, 229 μmol , 38%) was obtained as a colorless solid.



8r-E (Left): ^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.84 (s, 1H, 2-H), 7.50 – 7.47 (m, 5H, Ar-H), 7.35 – 7.31 (m, 1H, Ar-H), 7.27 – 7.22 (m, 2H, Ar-H), 7.16 – 7.12 (m, 2H, Ar-H), 3.78 (s, 2H, 3-H), 0.93 (s, 9H, 5-H).

8r-Z (Right): ^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.70 – 7.63 (m, 4H, Ar-H), 7.52 – 7.42 (m, 6H, Ar-H), 7.31 – 7.30 (m, 1H, 2-H), 3.59 (s, 2H, 3-H), 0.74 (s, 9H, 5-H).

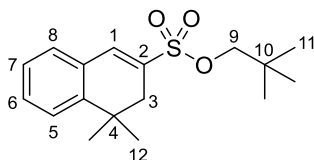
E/Z-mixture: ^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 141.7, 139.7, 138.7, 136.6, 136.0, 133.5, 132.6, 131.3, 130.7, 130.5, 130.3, 129.8, 129.6, 129.4, 129.2, 129.1, 129.0, 128.6, 128.6, 128.2, 79.8, 79.7, 31.8, 31.5, 26.2, 25.8.

HRMS (ESI+): m/z for $\text{C}_{19}\text{H}_{22}\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 348.1628, found: 348.1624.

The stereoisomeric ratio was determined to be 3/1 (*E*/*Z*) by NMR integration of the corresponding methylene signals (3-H). ^1H , ^1H -NOESY-contact between 3-H and 2-H is observed in the (*E*)-configured molecule.

5.19 Neopentyl 4,4-dimethyl-3,4-dihydronaphthalene-2-sulfonate (**8s**)

According to GP1, 1,1-dimethyl-1,2-dihydronaphthalene (94.9 mg, 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 95/5), the desired product (45.4 mg, 147 μmol , 25%) was obtained as a colorless oil.



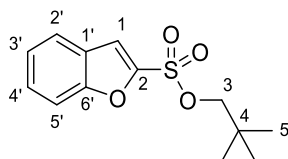
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.43 (t, J = 1.5 Hz, 1H, 1-H), 7.42 – 7.35 (m, 2H, Ar-H), 7.29 – 7.23 (m, 2H, Ar-H), 3.75 (s, 2H, 9-H), 2.56 (d, J = 1.5 Hz, 2H, 3-H), 1.33 (s, 6H, 12-H), 0.98 (s, 9H, 11-H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 145.0, 136.3, 131.8, 131.5, 129.8, 129.5, 127.0, 124.4, 79.3, 37.0, 34.9, 31.8, 28.5, 26.3.

HRMS (ESI+): m/z for $\text{C}_{17}\text{H}_{24}\text{O}_3\text{S}(\text{NH}_4)^+$ [$\text{M}+\text{NH}_4$] $^+$: calc.: 326.1784, found: 326.1784.

5.20 Neopentyl benzofuran-2-sulfonate (8t)

According to GP1, benzofuran (70.9 mg, 64.4 μ l, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 95/5), the desired product (73.0 mg, 272 μ mol, 45%) was obtained as a colorless solid.



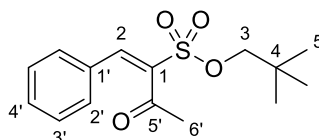
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.72 (ddd, *J* = 8.0, 1.0, 1.0 Hz, 1H, 2'-*H*), 7.60 (ddd, *J* = 8.3, 1.0, 1.0 Hz, 1H, 5'-*H*), 7.54 – 7.49 (m, 2H, 1-*H*, 4'-*H*), 7.38 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H, 3'-*H*), 3.92 (s, 2H, 3-*H*), 0.94 (s, 9H, 5-*H*).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 156.2, 146.6, 128.5, 125.7, 124.6, 123.3, 114.7, 112.6, 81.7, 31.9, 26.1.

HRMS (ESI⁺): *m/z* for C₁₃H₁₆O₄S(Na)⁺ [*M*+Na]⁺: calc.: 291.0662, found: 291.0660.

5.21 Neopentyl (*E*)-3-oxo-1-phenylbut-1-ene-2-sulfonate (8u)

According to GP1, (*E*)-4-phenylbut-3-en-2-one (87.7 mg, 86.8 μ l, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 75/25), the desired product (55.6 mg, 188 μ mol, 31%) was obtained as a colorless oil.



¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.68 (s, 1H, 2-*H*), 7.50 – 7.36 (m, 5H, Ar-*H*), 3.87 (s, 2H, 3-*H*), 2.41 (s, 3H, 6'-*H*), 0.99 (s, 9H, 5-*H*).

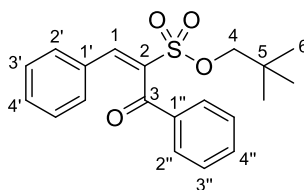
¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 198.2, 141.7, 137.0, 131.6, 131.3, 129.9, 129.4, 80.9, 32.0, 31.6, 26.2.

HRMS (ESI⁺): *m/z* for C₁₅H₂₀O₄S(NH₄)⁺ [*M*+NH₄]⁺: calc.: 314.1421, found: 314.2125.

E/Z-isomerism was determined via a ¹H,¹H-NOESY-contact between 3-*H* and 2-*H*, which is only possible in the (*E*)-configured molecule.

5.22 Neopentyl (*E*)-3-oxo-1,3-diphenylprop-1-ene-2-sulfonate (8v)

According to GP1, *trans*-chalcone (129 mg, 600 μ mol, 1 eq.), SO₂ stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 91/9), the desired product (106 mg, 296 μ mol, 49%) was obtained as a colorless solid.



¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.99 – 7.92 (m, 2H, 2''-*H*), 7.88 (s, 1H, 1-*H*), 7.55 – 7.49 (m, 1H, 4''-*H*), 7.41 – 7.35 (m, 2H, 3''-*H*), 7.32 – 7.19 (m, 5H, 2'-*H*, 3'-*H*, 4'-*H*), 3.94 (s, 2H, 4-*H*), 0.96 (s, 9H, 6-*H*).

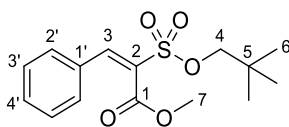
¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 191.1, 142.6, 135.1, 134.8, 134.5, 131.4, 131.2, 130.3, 130.1, 129.1, 129.0, 80.9, 32.0, 26.2.

HRMS (ESI⁺): *m/z* for C₂₀H₂₂O₄S(Na)⁺ [*M*+Na]⁺: calc.: 381.1131, found: 381.1135.

E/Z-isomerism was determined via a ¹H,¹H-NOESY-contact between 4-*H* and 1-*H*, which is only possible in the (*E*)-configured molecule.

5.23 Methyl (*E*)-2-((neopentyloxy)sulfonyl)-3-phenylacrylate (8w)

According to GP1, methyl *trans*-cinnamate (98.3 mg, 600 μ mol, 1 eq.), SO₂ stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 84/16), the desired product (74.6 mg, 239 μ mol, 40%) was obtained as a colorless oil.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.78 (s, 1H, 3-*H*), 7.50 – 7.39 (m, 5H, 2'-*H*, 3'-*H*, 4'-*H*), 3.89 (s, 2H, 4-*H*), 3.86 (s, 3H, 7-*H*), 1.00 (s, 9H, 6-*H*).

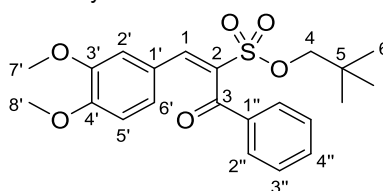
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 163.2, 144.9, 131.8, 131.2, 129.9, 129.4, 129.1, 81.0, 53.4, 31.9, 26.2.

HRMS (ESI⁺): m/z for $\text{C}_{15}\text{H}_{20}\text{O}_5\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$]⁺: calc.: 335.0924, found: 335.0922.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 4-*H* and 3-*H*, which is only possible in the (*E*)-configured molecule.

5.24 Neopentyl (*E*)-1-(3,4-dimethoxyphenyl)-3-oxo-3-phenylprop-1-ene-2-sulfonate (8x)

According to GP1, 3,4-dimethoxychalcone (161 mg, 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 63/37 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 99/1), the desired product (194 mg, 465 μmol , 77%) was obtained as a yellow oil.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 8.04 – 7.99 (m, 2H, 2''-*H*), 7.80 (s, 1H, 1-*H*), 7.59 – 7.53 (m, 1H, 4''-*H*), 7.45 – 7.39 (m, 2H, 3''-*H*), 6.99 (dd, J = 8.4, 2.2 Hz, 1H, 6'-*H*), 6.75 (d, J = 8.4 Hz, 1H, 5'-*H*), 6.71 (d, J = 2.2 Hz, 1H, 2'-*H*), 3.94 (s, 2H, 4-*H*), 3.82 (s, 3H, 7'-*H*), 3.53 (s, 3H, 8'-*H*), 0.98 (s, 9H, 6-*H*).

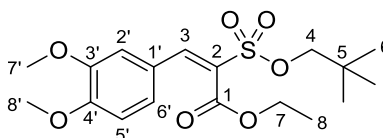
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 191.5, 151.9, 149.0, 142.6, 135.3, 134.9, 131.3, 130.0, 129.2, 125.8, 123.7, 112.1, 111.0, 80.6, 56.0, 55.6, 31.9, 26.2.

HRMS (ESI⁺): m/z for $\text{C}_{22}\text{H}_{26}\text{O}_6\text{S}(\text{H})^+$ [$\text{M}+\text{H}$]⁺: calc.: 419.1523, found: 419.1524.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 4-*H* and 1-*H*, which is only possible in the (*E*)-configured molecule.

5.25 Ethyl (*E*)-3-(3,4-dimethoxyphenyl)-2-((neopentyloxy)sulfonyl)acrylate (8y)

According to GP1, ethyl 3-(3,4-dimethoxyphenyl)acrylate (142 mg, 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 62/38 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 98/2), the desired product (142 mg, 366 μmol , 61%) was obtained as a colorless oil, which solidified after storage in the refrigerator.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.66 (s, 1H, 3-*H*), 7.12 (dd, J = 8.5, 2.1 Hz, 1H, 6'-*H*), 7.05 (d, J = 2.1 Hz, 1H, 2'-*H*), 6.88 (d, J = 8.5 Hz, 1H, 5'-*H*), 4.36 (q, J = 7.2 Hz, 2H, 7-*H*), 3.92 (s, 3H, 7'-*H*), 3.86 (s, 3H, 8'-*H*), 3.86 (s, 2H, 4-*H*), 1.32 (t, J = 7.2 Hz, 3H, 8-*H*), 0.99 (s, 9H, 6-*H*).

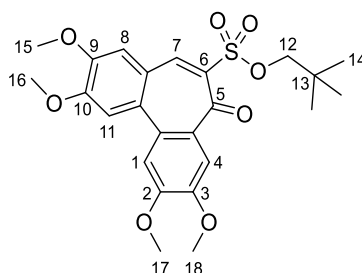
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 163.2, 152.4, 149.1, 144.6, 126.7, 125.4, 123.8, 112.3, 111.1, 80.6, 62.8, 56.2, 56.0, 31.9, 26.2, 14.0.

HRMS (ESI⁺): m/z for $\text{C}_{18}\text{H}_{26}\text{O}_7\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$]⁺: calc.: 409.1291, found: 409.1297.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 4-*H* and 3-*H*, which is only possible in the (*E*)-configured molecule.

5.26 Neopentyl 2,3,9,10-tetramethoxy-5-oxo-5H-dibenzo[a,c]cycloheptene-6-sulfonate (8z)

According to GP1, 2,3,9,10-tetramethoxy-5H-dibenzo[a,c]cycloheptene-5-one (196 mg, 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 5 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 94/6 $\rightarrow$ 88/12 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 92/8), the desired product (102 mg, 214 μmol , 36%) was obtained as a yellow solid.



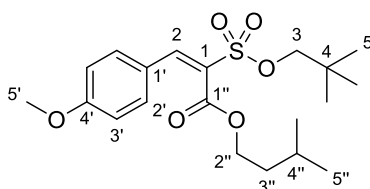
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 8.32 (s, 1H, 7-*H*), 7.49 (s, 1H, 4-*H*), 7.30 (s, 1H, 11-*H*), 7.22 (s, 1H, 1-*H*), 7.12 (s, 1H, 8-*H*), 4.05 (s, 5H, 12-*H*, 16-*H*), 4.04 (s, 3H, 17-*H*), 4.00 (s, 3H, 15-*H*), 3.99 (s, 3H, 18-*H*), 1.00 (s, 9H, 14-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 184.7, 152.4, 150.0, 148.9, 144.6, 135.5, 134.9, 134.2, 130.7, 123.2, 115.2, 112.8, 111.5, 111.0, 81.3, 56.4, 56.4, 56.3, 32.0, 26.3.

HRMS (ESI⁺): m/z for $\text{C}_{24}\text{H}_{28}\text{O}_8\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$]⁺: calc.: 499.1397, found: 499.1398.

5.27 Isopentyl (*E*)-3-(4-methoxyphenyl)-2-((neopentoxysulfonyl)acrylate (8aa)

According to GP1, isoamyl 4-methoxycinnamate (149 mg, 144 μL , 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 75/25), the desired product (194 mg, 486 μmol , 81%) was obtained as a colorless solid.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.69 (s, 1H, 2-*H*), 7.47 – 7.42 (m, 2H, 2'-*H*), 6.94 – 6.89 (m, 2H, 3'-*H*), 4.33 (t, J = 6.8 Hz, 2H, 2''-*H*), 3.86 (s, 2H, 3-*H*), 3.86 (s, 3H, 5'-*H*), 1.71 – 1.60 (m, 1H, 4''-*H*), 1.60 – 1.53 (m, 2H, 3''-*H*), 0.99 (s, 9H, 5-*H*), 0.89 (d, J = 6.5 Hz, 6H, 5''-*H*).

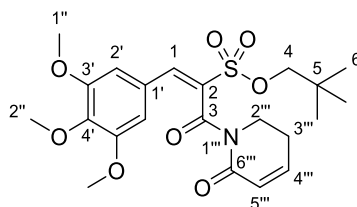
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 163.3, 162.6, 144.5, 132.5, 126.7, 123.8, 114.6, 80.7, 65.4, 55.6, 37.0, 31.9, 26.2, 24.9, 22.5.

HRMS (ESI⁺): m/z for $\text{C}_{20}\text{H}_{30}\text{O}_6\text{S}(\text{H})^+$ [$\text{M}+\text{H}$]⁺: calc.: 399.1836, found: 399.1834.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 3-*H* and 2-*H*, which is only possible in the (*E*)-configured molecule.

5.28 Neopentyl (*E*)-3-oxo-3-(6-oxo-3,6-dihydropyridin-1(2*H*)-yl)-1-(3,4,5-trimethoxyphenyl)prop-1-ene-2-sulfonate (8ab)

According to GP1, piperlongumine (190 mg, 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 4 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 65/35), the desired product (112 mg, 239 μmol , 40%) was obtained as a colorless solid.



^1H NMR (400 MHz, CD_3CN) δ [ppm] = 7.45 (s, 1H, 1-*H*), 6.99 (dt, J = 9.8, 4.2 Hz, 1H, 4'''-*H*), 6.71 (s, 2H, 2'-*H*), 5.86 (dt, J = 9.8, 1.9 Hz, 1H, 5'''-*H*), 4.14 – 3.85 (m, 4H, 4-*H*, 2'''-*H*), 3.76 (s, 6H, 1''-*H*), 3.74 (s, 3H, 2''-*H*), 2.54 – 2.27 (m, 2H, 3'''-*H*), 0.96 (s, 9H, 6-*H*).

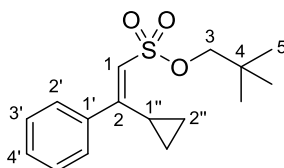
^{13}C NMR (101 MHz, CD_3CN) δ [ppm] = 165.1, 165.0, 154.5, 148.9, 141.3, 140.5, 133.8, 128.2, 124.7, 107.8, 81.3, 61.0, 56.8, 42.6, 32.3, 26.3, 25.0.

HRMS (ESI⁺): m/z for $\text{C}_{22}\text{H}_{29}\text{NO}_8\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$]⁺: calc.: 490.1506, found: 490.1504.

E/Z-isomerism was determined via a ^1H , ^1H -NOESY-contact between 4-*H* and 1-*H*, which is only possible in the (*E*)-configured molecule.

5.29 Neopentyl (*E*)-2-cyclopropyl-2-phenylethene-1-sulfonate (8ac)

According to GP1, α -cyclopropylstyrene^[7] (86.5 mg, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 86/14 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 99/1), the desired product (17.9 mg, 60.8 μ mol, 10%) was obtained as a colorless solid.

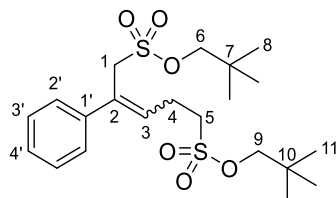


¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.40 – 7.34 (m, 3H, Ar-*H*), 7.23 – 7.18 (m, 2H, Ar-*H*), 6.27 (s, 1H, 1-*H*), 3.61 (s, 2H, 3-*H*), 1.79 – 1.71 (m, 1H, 1''-*H*), 0.94 – 0.90 (m, 2H, 2''-*H*), 0.90 (s, 9H, 5-*H*), 0.65 – 0.60 (m, 2H, 2''-*H*).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 161.7, 134.7, 128.8, 128.1, 127.9, 119.5, 78.8, 31.7, 26.2, 19.9, 7.6.

HRMS (ESI⁺): m/z for C₁₆H₂₂O₃S(NH₄)⁺ [M+NH₄]⁺: calc.: 312.1628, found: 312.1633.

As a byproduct, dineopentyl 2-phenylpent-2-ene-1,5-disulfonate (**10a**, 18.0 mg, 40.3 μ mol, 7%) was obtained as a colorless oil (eluent: cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 78/22).



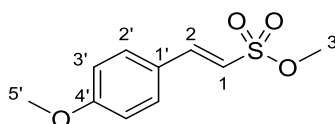
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.42 – 7.25 (m, 5H, 2'-*H*, 3'-*H*, 4'-*H*), 6.13 (t, J = 7.4 Hz, 1H, 3-*H*), 4.34 (s, 2H, 1-*H*), 4.25 – 4.18 (m, 1H, 5-*H*), 4.13 – 4.04 (m, 1H, 5-*H*), 3.71 (d, J = 9.5 Hz, 1H, OCH₂), 3.64 (s, 2H, OCH₂), 3.54 (d, J = 9.5 Hz, 1H, OCH₂), 2.76 (q, J = 6.6 Hz, 2H, 4-*H*), 0.94 (s, 9H, C(CH₃)₃), 0.77 (s, 9H, C(CH₃)₃).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 140.8, 133.2, 130.5, 128.8, 128.0, 126.7, 79.2, 71.7, 60.9, 51.8, 31.8, 31.6, 30.1, 26.4, 25.9.

HRMS (ESI⁺): m/z for C₂₁H₃₄O₆S₂(NH₄)⁺ [M+NH₄]⁺: calc.: 464.2135, found: 464.2138.

5.30 Methyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9a)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (7.5 eq.) and methanol (91.6 mg, 122 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 60/40), the desired product (96.1 mg, 421 μ mol, 70%) was obtained as a colorless solid.



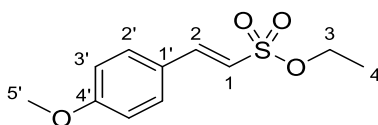
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.56 (d, J = 15.5 Hz, 1H, 2-*H*), 7.49 – 7.45 (m, 2H, 2'-*H*), 6.96 – 6.92 (m, 2H, 3'-*H*), 6.56 (d, J = 15.5 Hz, 1H, 1-*H*), 3.86 (s, 3H, 5'-*H*), 3.84 (s, 3H, 3-*H*).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 162.5, 145.3, 130.5, 124.6, 117.3, 114.8, 56.1, 55.6.

HRMS (ESI⁺): m/z for C₁₀H₁₂O₄SN⁺ [M+Na]⁺: calc.: 251.0349, found: 251.0346.

5.31 Ethyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9b)^[8]

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (7.5 eq.) and ethanol (138 mg, 175 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 65/35), the desired product^[8] (105 mg, 434 μ mol, 72%) was obtained as a colorless oil.



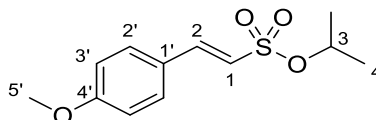
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.55 (d, J = 15.5 Hz, 1H, 2-*H*), 7.48 – 7.44 (m, 2H, 2'-*H*), 6.96 – 6.91 (m, 2H, 3'-*H*), 6.59 (d, J = 15.5 Hz, 1H, 1-*H*), 4.21 (q, J = 7.1 Hz, 2H, 3-*H*), 3.86 (s, 3H, 5'-*H*), 1.39 (t, J = 7.1 Hz, 3H, 4-*H*).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 162.4, 144.6, 130.4, 124.7, 118.4, 114.8, 66.7, 55.6, 15.0.

HRMS (ESI⁺): m/z for $C_{11}H_{14}O_4SH^+$ [$M+H$]⁺: calc.: 243.0686, found: 243.0687.

5.32 Isopropyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9c)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (7.5 eq.) and isopropyl alcohol (180 mg, 231 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 70/30), the desired product (90.1 mg, 352 μ mol, 59%) was obtained as a colorless oil.



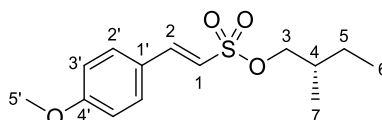
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.54 (d, J = 15.5 Hz, 1H, 2'-H), 7.48 – 7.43 (m, 2H, 2'-H), 6.96 – 6.91 (m, 2H, 3'-H), 6.60 (d, J = 15.5 Hz, 1H, 1'-H), 4.81 (sept, J = 6.3 Hz, 1H, 3-H), 3.85 (s, 3H, 5'-H), 1.40 (d, J = 6.3 Hz, 6H, 4-H).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 162.3, 143.6, 130.3, 124.9, 119.7, 114.7, 77.0, 55.6, 23.2.

HRMS (ESI⁺): m/z for $C_{12}H_{16}O_4SNa^+$ [$M+Na$]⁺: calc.: 279.0662, found: 279.0660.

5.33 (S)-2-Methylbutyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9d)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and (S)-(-)-2-methylbutanol (264 mg, 323 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 80/20), the desired product (97.3 mg, 342 μ mol, 57%) was obtained as a colorless oil.



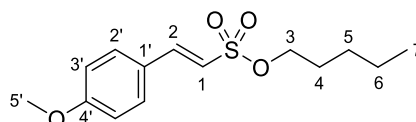
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 2'-H), 7.49 – 7.43 (m, 2H, 2'-H), 6.96 – 6.90 (m, 2H, 3'-H), 6.58 (d, J = 15.5 Hz, 1H, 1'-H), 3.98 (dd, J = 9.5, 5.9 Hz, 1H, 3-H), 3.92 (dd, J = 9.4, 6.5 Hz, 1H, 3-H), 3.85 (s, 3H, 5'-H), 1.85 – 1.72 (m, 1H, 4-H), 1.53 – 1.41 (m, 1H, 5-H), 1.27 – 1.15 (m, 1H, 5-H), 0.95 (d, J = 6.8 Hz, 3H, 7-H), 0.89 (t, J = 7.5 Hz, 3H, 6-H).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 162.3, 144.5, 130.4, 124.7, 118.2, 114.7, 74.8, 55.6, 34.5, 25.6, 16.1, 11.1.

HRMS (ESI⁺): m/z for $C_{14}H_{20}O_4S(NH_4)^+$ [$M+Na$]⁺: calc.: 302.1421, found: 302.1421.

5.34 Pentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9e)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and 1-pentanol (264 mg, 326 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 78/22), the desired product (89.9 mg, 316 μ mol, 53%) was obtained as a colorless oil.



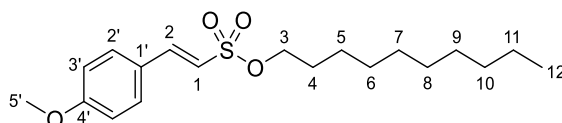
¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 2'-H), 7.48 – 7.42 (m, 2H, 2'-H), 6.96 – 6.90 (m, 2H, 3'-H), 6.58 (d, J = 15.5 Hz, 1H, 1'-H), 4.12 (t, J = 6.6 Hz, 2H, 3-H), 3.84 (s, 3H, 5'-H), 1.72 (p, J = 6.6 Hz, 2H, 4-H), 1.41 – 1.26 (m, 4H, 5-H, 6-H), 0.88 (t, J = 7.0 Hz, 3H, 7-H).

¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 162.3, 144.5, 130.4, 124.7, 118.3, 114.7, 70.6, 55.6, 28.8, 27.6, 22.2, 14.0.

HRMS (ESI⁺): m/z for $C_{14}H_{20}O_4S(Na)^+$ [$M+Na$]⁺: calc.: 307.0975, found: 307.0975.

5.35 Decyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9f)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and 1-decanol (475 mg, 594 μ L, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 85/15), the desired product (106 mg, 298 μ mol, 50%) was obtained as a colorless solid.



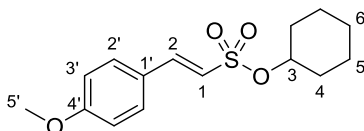
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 2-*H*), 7.48 – 7.43 (m, 2H, 2'-*H*), 6.96 – 6.90 (m, 2H, 3'-*H*), 6.58 (d, J = 15.5 Hz, 1H, 1-*H*), 4.12 (t, J = 6.7 Hz, 2H, 3-*H*), 3.84 (s, 3H, 5'-*H*), 1.71 (p, J = 6.7 Hz, 2H, 4-*H*), 1.37 (p, J = 7.3 Hz, 2H, 5-*H*), 1.32 – 1.19 (m, 12H, 6-*H*, 7-*H*, 8-*H*, 9-*H*, 10-*H*, 11-*H*), 0.86 (t, J = 6.9 Hz, 3H, 12-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.3, 144.5, 130.4, 124.7, 118.3, 114.7, 70.6, 55.6, 31.9, 29.6, 29.5, 29.4, 29.1, 29.0, 25.5, 22.7, 14.2.

HRMS (ESI+): m/z for $\text{C}_{19}\text{H}_{30}\text{O}_4\text{S}(\text{NH}_4)^+$ $[\text{M}+\text{NH}_4]^+$: calc.: 372.2203, found: 372.2199.

5.36 Cyclohexyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9g)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (7.5 eq.) and cyclohexanol (300 mg, 316 μL , 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 80/20), the desired product (56.8 mg, 192 μmol , 32%) was obtained as a colorless solid.



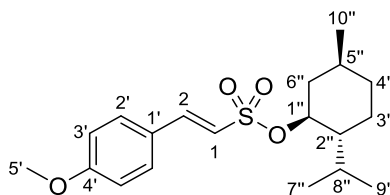
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 2-*H*), 7.48 – 7.42 (m, 2H, 2'-*H*), 6.96 – 6.90 (m, 2H, 3'-*H*), 6.61 (d, J = 15.5 Hz, 1H, 1-*H*), 4.60 – 4.53 (m, 1H, 3-*H*), 3.85 (s, 3H, 5'-*H*), 2.00 – 1.72 (m, 4H, Cy-*H*), 1.69 – 1.59 (m, 2H, Cy-*H*), 1.54 – 1.46 (m, 1H, Cy-*H*), 1.41 – 1.24 (m, 3H, Cy-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.3, 143.4, 130.3, 124.9, 119.9, 114.7, 81.6, 55.6, 32.8, 25.0, 23.6.

HRMS (ESI+): m/z for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: calc.: 319.0975, found: 319.0970.

5.37 (1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9h)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and (+)-menthol (469 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 83/17), the desired product (101 mg, 285 μmol , 48%) was obtained as a colorless oil.



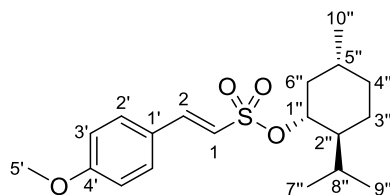
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.52 (d, J = 15.5 Hz, 1H, 2-*H*), 7.47 – 7.40 (m, 2H, 2'-*H*), 6.96 – 6.89 (m, 2H, 3'-*H*), 6.60 (d, J = 15.5 Hz, 1H, 1-*H*), 4.40 (td, J = 10.8, 4.6 Hz, 1H, 1''-*H*), 3.84 (s, 3H, 5'-*H*), 2.29 (dddd, J = 12.2, 5.2, 3.4, 2.0 Hz, 1H, 6''-*H*), 2.10 (septd, J = 7.0, 2.5 Hz, 1H, 8''-*H*), 1.72 – 1.62 (m, 2H, 3''-*H*, 4''-*H*), 1.49 – 1.36 (m, 2H, 2''-*H*, 5''-*H*), 1.31 – 1.20 (m, 1H, 6''-*H*), 1.07 – 0.95 (m, 1H, 3''-*H*), 0.91 (d, J = 6.5 Hz, 3H, CH_3), 0.90 (d, J = 7.0 Hz, 3H, CH_3), 0.88 – 0.80 (m, 1H, 4''-*H*), 0.74 (d, J = 6.9 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.2, 143.2, 130.3, 124.9, 120.1, 114.7, 83.6, 55.5, 47.7, 42.4, 33.9, 31.8, 25.6, 23.1, 22.0, 21.0, 15.8.

HRMS (ESI+): m/z for $\text{C}_{19}\text{H}_{28}\text{O}_4\text{S}(\text{Na})^+$ $[\text{M}+\text{Na}]^+$: calc.: 375.1601, found: 375.1599.

5.38 (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9i)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and (–)-menthol (469 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 83/17), the desired product (92.4 mg, 262 μmol , 44%) was obtained as a colorless oil.



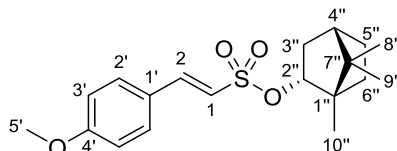
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.52 (d, J = 15.5 Hz, 1H, 2-*H*), 7.47 – 7.41 (m, 2H, 2'-*H*), 6.95 – 6.89 (m, 2H, 3'-*H*), 6.60 (d, J = 15.5 Hz, 1H, 1-*H*), 4.40 (td, J = 10.8, 4.6 Hz, 1H, 1''-*H*), 3.84 (s, 3H, 5'-*H*), 2.29 (dddd, J = 12.1, 5.2, 3.4, 1.9 Hz, 1H, 6''-*H*), 2.10 (septd, J = 7.0, 2.4 Hz, 1H, 8''-*H*), 1.73 – 1.62 (m, 2H, 3''-*H*, 4''-*H*), 1.50 – 1.37 (m, 2H, 2''-*H*, 5''-*H*), 1.31 – 1.20 (m, 1H, 6''-*H*), 1.07 – 0.95 (m, 1H, 3''-*H*), 0.91 (d, J = 6.5 Hz, 3H, CH_3), 0.90 (d, J = 7.0 Hz, 3H, CH_3), 0.88 – 0.80 (m, 1H, 4''-*H*), 0.75 (d, J = 6.9 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.2, 143.2, 130.3, 124.9, 120.1, 114.7, 83.6, 55.5, 47.7, 42.4, 33.9, 31.8, 25.6, 23.1, 22.0, 21.0, 15.8.

HRMS (ESI⁺): m/z for $\text{C}_{19}\text{H}_{28}\text{O}_4\text{S}(\text{Na})^+$ $[\text{M}+\text{Na}]^+$: calc.: 375.1601, found: 375.1603.

5.39 (1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9j)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and (–)-borneol (463 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 3.5 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 81/19), the desired product (69.3 mg, 198 μmol , 33%) was obtained as a colorless solid.



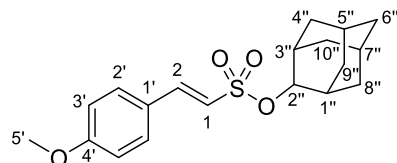
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.51 (d, J = 15.5 Hz, 1H, 2'-H), 7.47 – 7.41 (m, 2H, 2'-H), 6.96 – 6.89 (m, 2H, 3'-H), 6.59 (d, J = 15.5 Hz, 1H, 1'-H), 4.67 (ddd, J = 9.9, 3.4, 1.9 Hz, 1H, 2''-H), 3.84 (s, 3H, 5'-H), 2.36 – 2.26 (m, 1H, 3''-H), 1.98 – 1.89 (m, 1H, 6''-H), 1.80 – 1.67 (m, 2H, 4''-H, 5''-H), 1.38 – 1.25 (m, 3H, 3''-H, 5''-H, 6''-H), 0.89 (s, 3H, 10''-H), 0.86 (s, 3H, CH_3), 0.85 (s, 3H, CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.3, 143.6, 130.3, 124.9, 119.5, 114.7, 87.9, 55.6, 49.6, 47.8, 44.9, 36.7, 27.9, 26.7, 19.8, 18.9, 13.3.

HRMS (ESI⁺): m/z for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{S}(\text{NH}_4)^+$ $[\text{M}+\text{NH}_4]^+$: calc.: 368.1890, found: 368.1894.

5.40 (1*r*,3*r*,5*r*,7*r*)-Adamantan-2-yl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (9k)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and 2-adamantanol (466 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 81/19 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 98/2), the desired product (79.5 mg, 228 μmol , 38%) was obtained as a colorless solid.



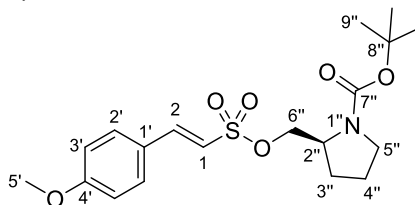
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 2'-H), 7.48 – 7.42 (m, 2H, 2'-H), 6.96 – 6.90 (m, 2H, 3'-H), 6.63 (d, J = 15.5 Hz, 1H, 1'-H), 4.73 (t, J = 3.5 Hz, 1H, 2''-H), 3.85 (s, 3H, 5'-H), 2.19 – 2.08 (m, 4H, Ad-H), 1.90 – 1.80 (m, 4H, Ad-H), 1.76 – 1.68 (m, 4H, Ad-H), 1.60 – 1.54 (m, 2H, Ad-H).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.2, 143.2, 130.3, 124.9, 120.0, 114.7, 86.3, 55.6, 37.2, 36.6, 33.1, 31.3, 27.0, 26.7.

HRMS (ESI⁺): m/z for $\text{C}_{19}\text{H}_{24}\text{O}_4\text{S}(\text{NH}_4)^+$ $[\text{M}+\text{NH}_4]^+$: calc.: 366.1734, found: 366.1739.

5.41 *tert*-Butyl (*S,E*)-2-(((4-methoxystyryl)sulfonyl)oxy)methylpyrrolidine-1-carboxylate (9l)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and *N*-Boc-L-prolinol (604 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 48/52 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 93/7), the desired product (103 mg, 259 μmol , 43%) was obtained as a colorless solid.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.54 (d, J = 15.5 Hz, 1H, 2'-H), 7.49 – 7.42 (m, 2H, 2'-H), 6.97 – 6.88 (m, 2H, 3'-H), 6.57 (brd, J = 15.5 Hz, 1H, 1'-H), 4.26 – 3.95 (m, 3H, 2''-H, 6''-H), 3.85 (s, 3H, 5'-H), 3.42 – 3.26 (m, 2H, 5''-H), 2.07 – 1.78 (m, 4H, 3''-H, 4''-H), 1.40 (s, 9H, 9''-H).

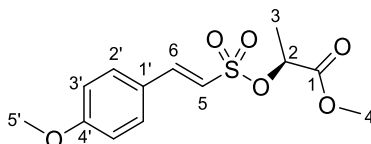
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.4, 154.3, 144.9, 130.5, 124.6, 118.0, 114.7, 79.8, 69.9, 55.8, 55.6, 46.7, 28.5, 27.9, 23.0.

HRMS (ESI⁺): m/z for $\text{C}_{19}\text{H}_{27}\text{NO}_6\text{S}(\text{Na})^+$ $[\text{M}+\text{Na}]^+$: calc.: 420.1451, found: 420.1446.

In ^1H and ^{13}C NMR experiments, a splitting of the signals is observed due to the presence of *N*-Boc rotamers (~1:1 ratio).^[9] Since ^{13}C NMR chemical shifts of both rotamers appeared side by side, the high-field-peak of each set was reported, which is expected to belong to one of the rotamers. The target compound was found to undergo partial degradation both in CDCl_3 and CD_2Cl_2 .

5.42 Methyl (S,E)-2-(((4-methoxystyryl)sulfonyl)oxy)propanoate (9m)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and methyl (S)-(-)-lactate (322 mg, 295 μL , 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 95/5 $\rightarrow$ 55/45), the desired product (94.8 mg, 316 μmol , 53%) was obtained as a colorless oil.



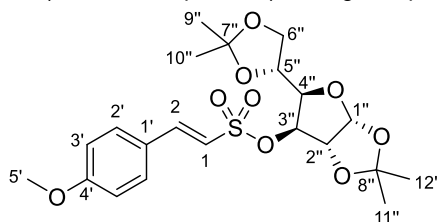
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.53 (d, J = 15.5 Hz, 1H, 6-*H*), 7.48 – 7.43 (m, 2H, 2'-*H*), 6.95 – 6.89 (m, 2H, 3'-*H*), 6.67 (d, J = 15.5 Hz, 1H, 5-*H*), 4.98 (q, J = 7.0 Hz, 1H, 2-*H*), 3.84 (s, 3H, 5'-*H*), 3.73 (s, 3H, 4-*H*), 1.59 (d, J = 7.0 Hz, 3H, 3-*H*).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 170.1, 162.5, 144.7, 130.5, 124.5, 118.7, 114.7, 74.1, 55.6, 52.8, 18.5.

HRMS (ESI+): m/z for $\text{C}_{13}\text{H}_{16}\text{O}_6\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 323.0560, found: 323.0565.

5.43 (3aR,5R,6S,6aR)-5-(((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (E)-2-(4-methoxyphenyl)ethene-1-sulfonate (9n)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and 1,2:5,6-di-*O*-isopropylidene- α -D-glucufuranose (781 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 60/40 then dichloromethane/ethyl acetate = 100/0 $\rightarrow$ 95/5), the desired product (58.3 mg, 128 μmol , 21%) was obtained as a colorless solid.



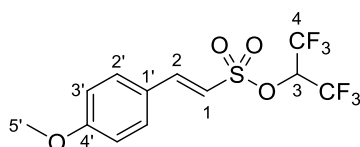
^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.55 (d, J = 15.5 Hz, 1H, 2-*H*), 7.48 – 7.43 (m, 2H, 2'-*H*), 6.95 – 6.90 (m, 2H, 3'-*H*), 6.64 (d, J = 15.5 Hz, 1H, 1-*H*), 5.94 (d, J = 3.6 Hz, 1H, 1''-*H*), 4.85 (d, J = 3.7 Hz, 1H, 2''-*H*), 4.77 (d, J = 3.0 Hz, 1H, 3''-*H*), 4.25 (ddd, J = 8.8, 5.9, 4.0 Hz, 1H, 5''-*H*), 4.11 – 4.05 (m, 2H, 4''-*H*, 6''-*H*), 4.00 (dd, J = 8.9, 4.0 Hz, 1H, 6''-*H*), 3.85 (s, 3H, 5'-*H*), 1.48 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.18 (s, 3H, CH_3).

^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 162.5, 145.1, 130.5, 124.7, 118.1, 114.7, 112.7, 109.5, 105.3, 83.8, 82.1, 79.8, 72.2, 67.4, 55.6, 27.0, 26.7, 26.3, 25.3.

HRMS (ESI+): m/z for $\text{C}_{21}\text{H}_{28}\text{O}_9\text{S}(\text{Na})^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 479.1346, found: 479.1340.

5.44 1,1,1,3,3,3-Hexafluoropropan-2-yl (E)-2-(4-methoxyphenyl)ethene-1-sulfonate (9o)

According to GP1, 4-methoxystyrene (80.5 mg, 81.0 μL , 600 μmol , 1 eq.), SO_2 stock solution (10 eq.) and HFIP (504 mg, 316 μL , 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 81/19), the desired product (52.8 mg, 145 μmol , 24%) was obtained as a colorless solid.



^1H NMR (400 MHz, CDCl_3) δ [ppm] = 7.67 (d, J = 15.4 Hz, 1H, 2-*H*), 7.52 – 7.46 (m, 2H, 2'-*H*), 6.99 – 6.92 (m, 2H, 3'-*H*), 6.63 (d, J = 15.4 Hz, 1H, 1-*H*), 5.22 (sept, J = 5.7 Hz, 1H, 3-*H*), 3.87 (s, 3H, 5'-*H*).

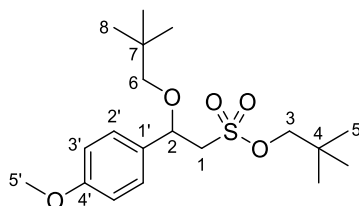
^{13}C NMR (101 MHz, CDCl_3) δ [ppm] = 163.2, 147.5, 131.1, 123.9, 120.1 (q, $J_{\text{C-F}}$ = 283.5 Hz), 116.6, 115.0, 72.1 (sept, $J_{\text{C-F}}$ = 35.3 Hz), 55.7.

^{19}F NMR (376 MHz, CDCl_3) δ [ppm] = -74.28 (d, J = 5.5 Hz, 6F)

HRMS (ESI+): m/z for $\text{C}_{12}\text{H}_{10}\text{F}_6\text{O}_4\text{S}(\text{H})^+$ [$\text{M}+\text{H}$] $^+$: calc.: 365.0277, found: 365.0272.

5.45 Neopentyl 2-(4-methoxyphenyl)-2-(neopentyloxy)ethane-1-sulfonate (10e)

According to GP1 with 3 eq. of DBU (274 mg, 270 μ L, 1.80 mmol), 4-methoxystyrene (80.5 mg, 81.0 μ L, 600 μ mol, 1 eq.), SO₂ stock solution (10 eq.) and neopentyl alcohol (264 mg, 3.00 mmol, 5 eq.) were used as substrates and the electrolysis was carried out using 2.8 F. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 86/14), the desired product (86.1 mg, 231 μ mol, 39%) was obtained as a colorless oil.



¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.31 – 7.25 (m, 2H, 2'-H), 6.96 – 6.87 (m, 2H, 3'-H), 4.78 (dd, J = 8.6, 3.9 Hz, 1H, 2-H), 3.88 – 3.80 (m, 2H, 6-H), 3.83 (s, 3H, 5'-H), 3.61 (dd, J = 14.5, 8.6 Hz, 1H, 1-H), 3.29 (dd, J = 14.5, 3.9 Hz, 1H, 1-H), 3.03 – 2.95 (m, 2H, 3-H), 0.97 (s, 9H, 5-H), 0.92 (s, 9H, 8-H).

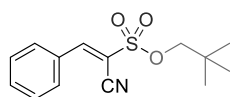
¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 159.8, 131.7, 128.0, 114.3, 79.5, 78.9, 76.8, 57.7, 55.4, 32.1, 31.8, 26.8, 26.2.

HRMS (ESI⁺): m/z for C₁₉H₃₂O₅S(K)⁺ [M+K]⁺: calc.: 411.1602, found: 411.1604.

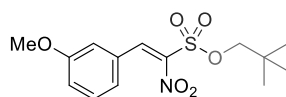
5.46 Limitations of the Scope

The following substrates were also tried, but for the reasons given below, the desired alkenesulfonate could not be isolated.

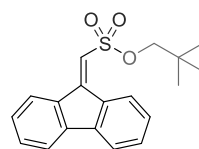
Styrenes and Related Substrates:



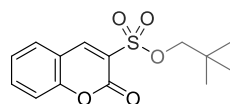
only traces detected
from (E)-β-cyanostyrene



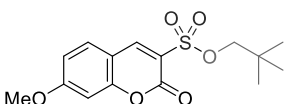
only traces detected
from (E)-β-nitro-3-methoxystyrene



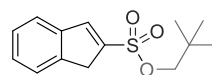
starting material insoluble
from dibenzofulvene



no conversion
from coumarin

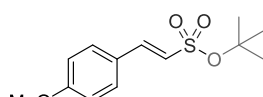


no conversion
from 7-methoxycoumarin

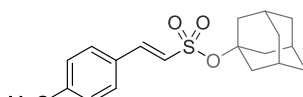


decomposition
from indene

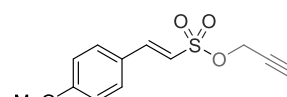
Alcohols and Phenols:



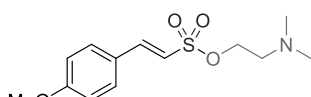
too sterically demanding
from tert-butanol



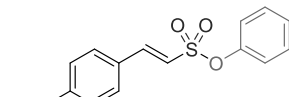
too sterically demanding
from 1-adamantol



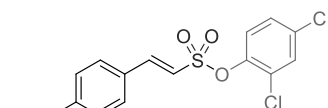
no alkenesulfonate product detected
from prop-2-yn-1-ol



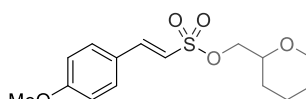
degradation of the amino alcohol
from 2-(dimethylamino)ethanol



no alkenesulfonate product detected
from phenol



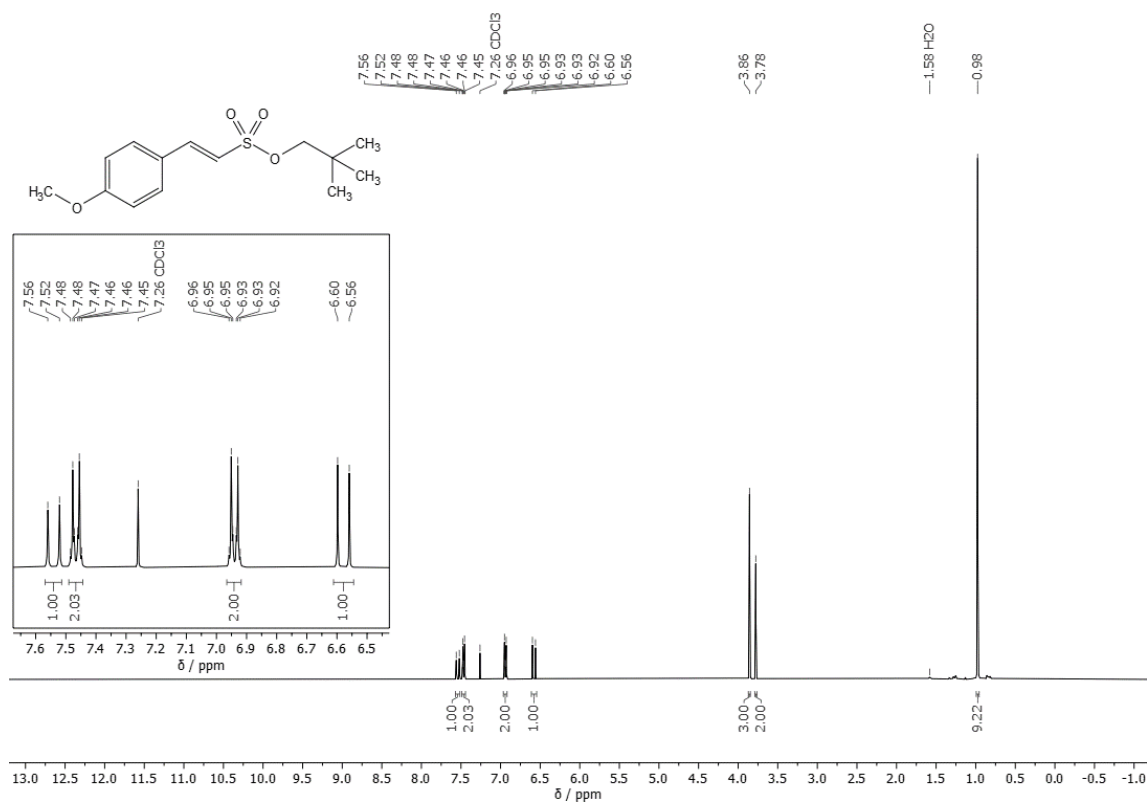
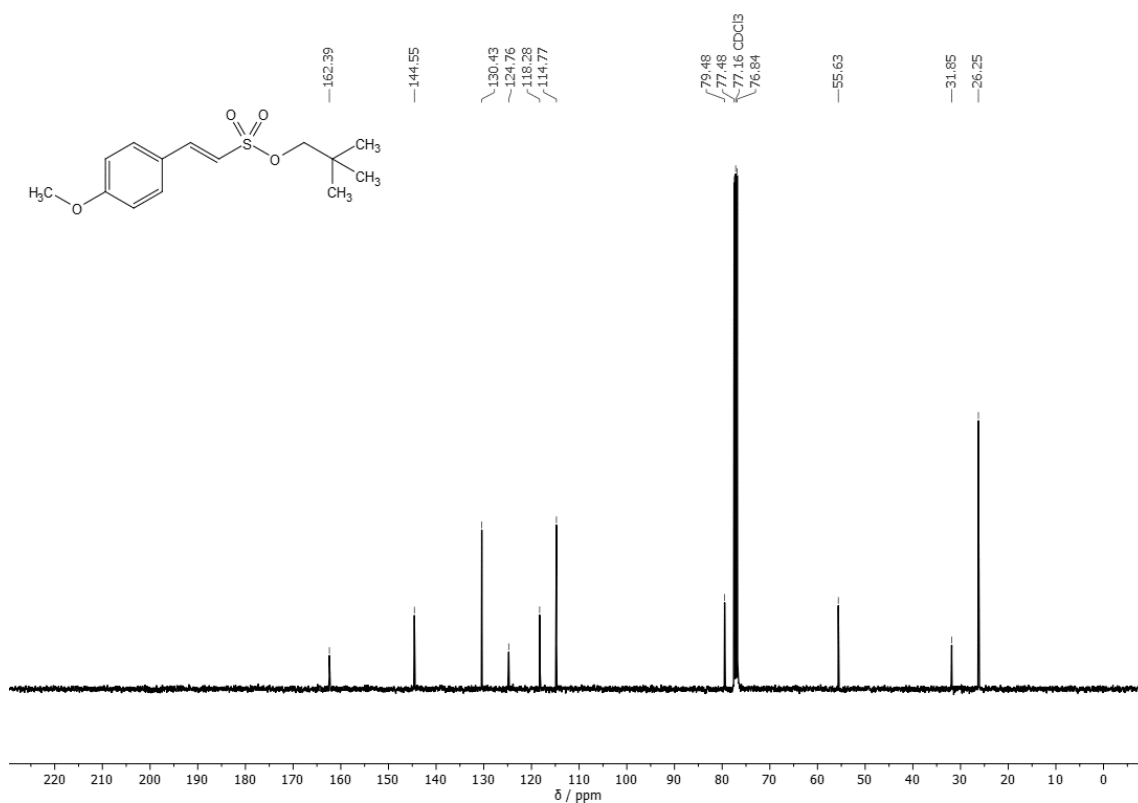
formation of biphenols detected via GC/MS
from 2,4-dichlorophenol



only traces detected
from tetrahydropyran-2-methanol

Figure S9: Unsuccessful derivatives under the standard conditions (GP1).

6 NMR Spectra

Figure S10: ¹H NMR spectrum (400 MHz, CDCl₃) of 8a.Figure S11: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8a.

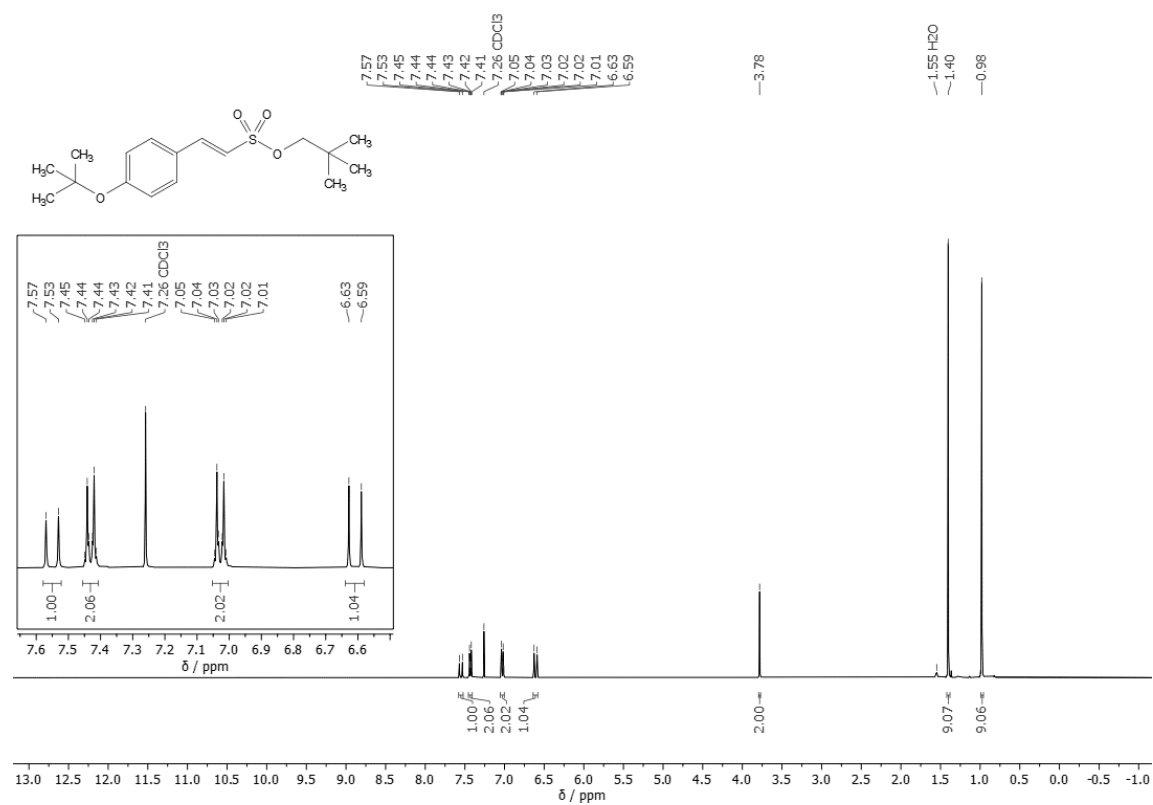


Figure S12: ¹H NMR spectrum (400 MHz, CDCl₃) of **8b**.

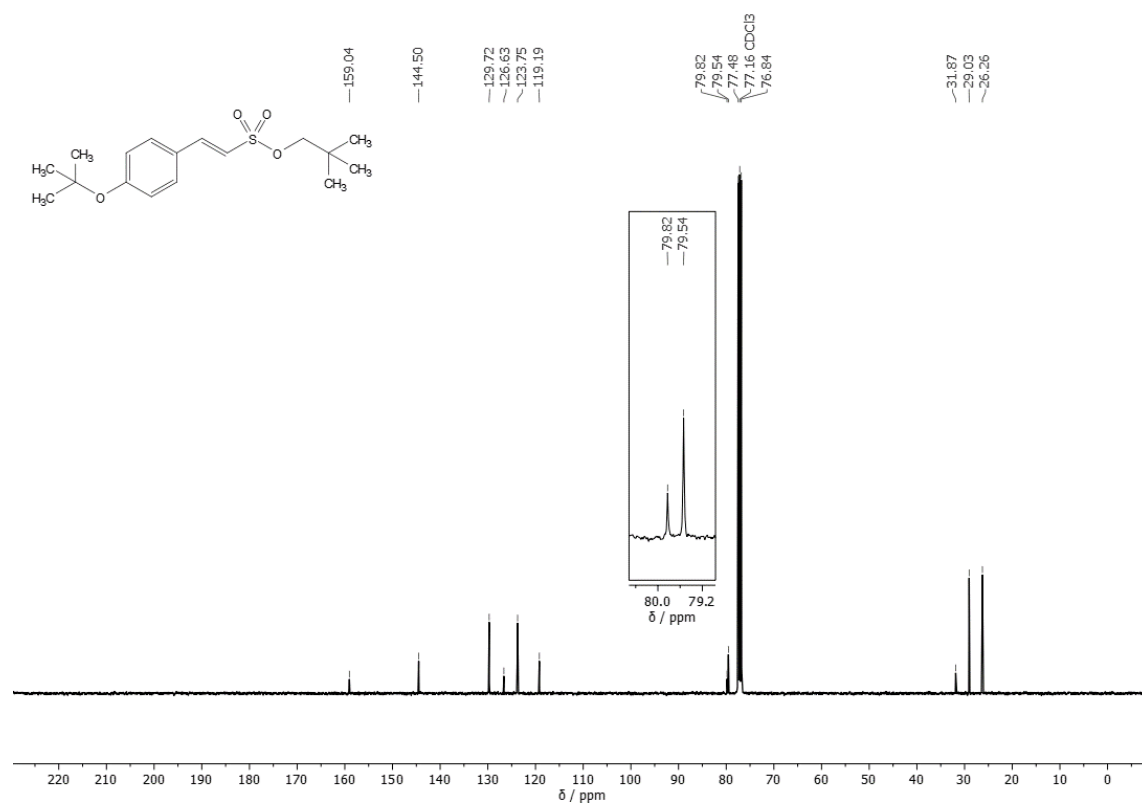


Figure S13: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8b**.

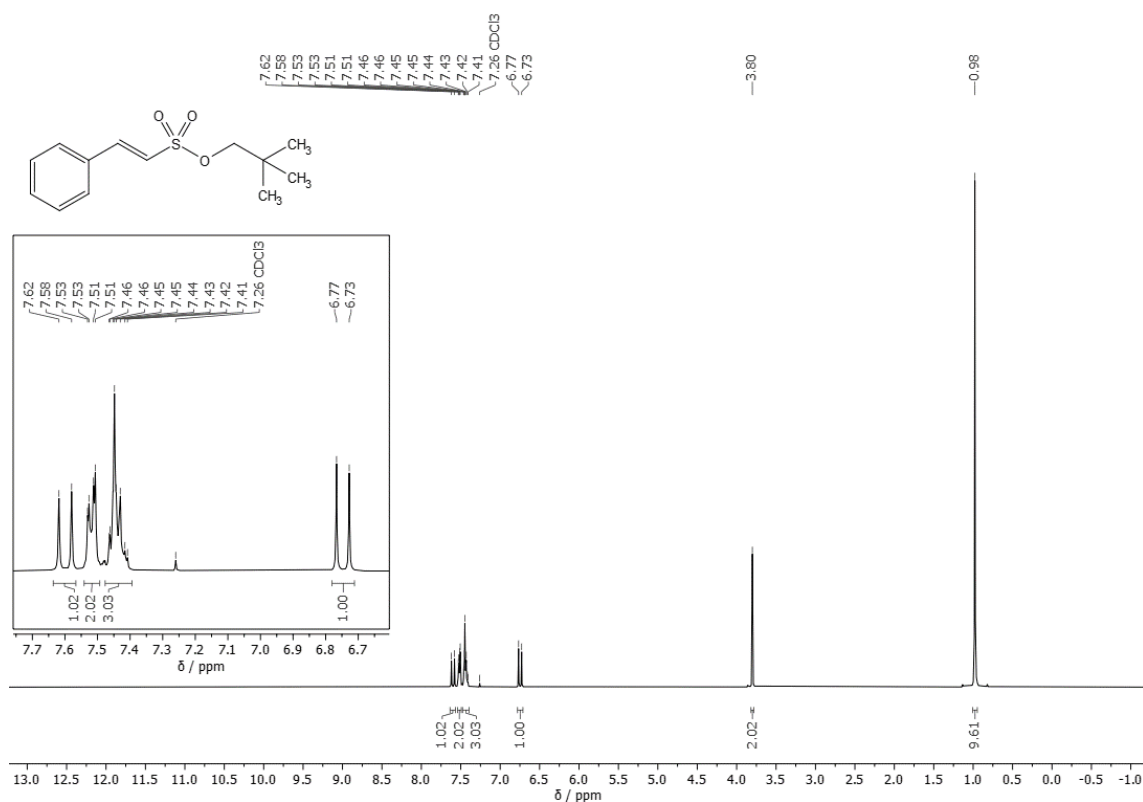


Figure S14: ¹H NMR spectrum (400 MHz, CDCl₃) of **8c**.

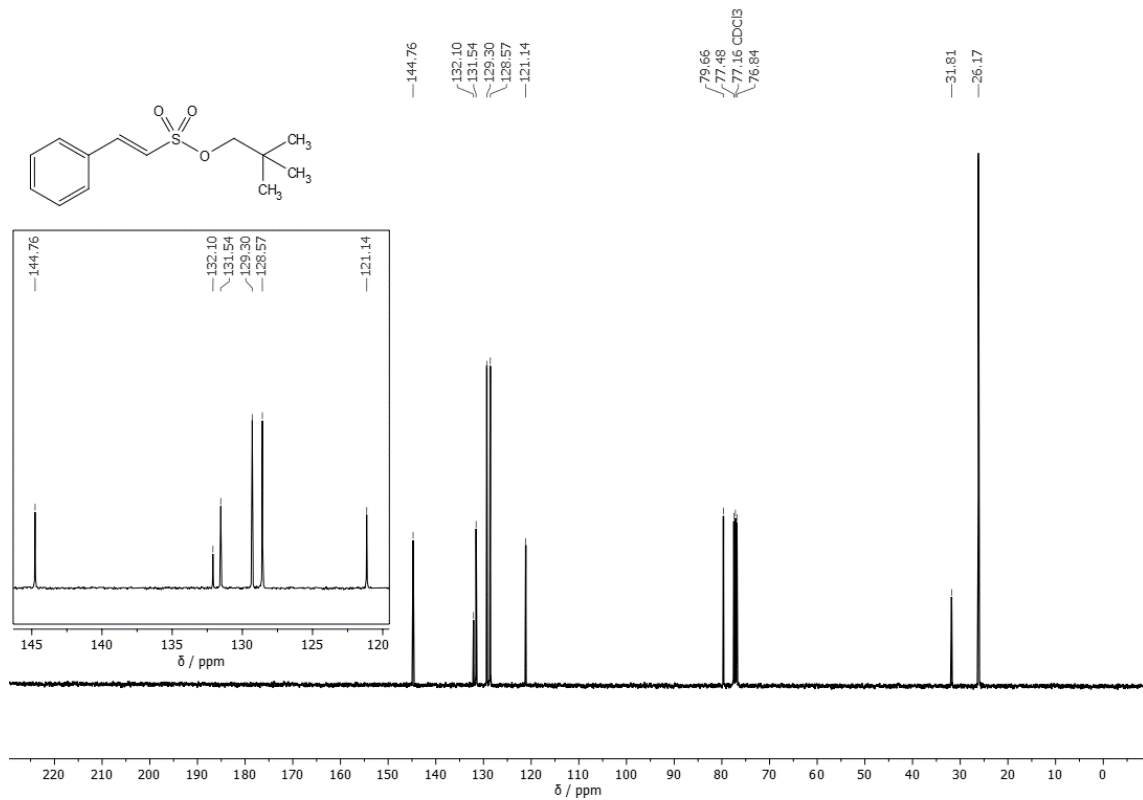


Figure S15: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8c**.

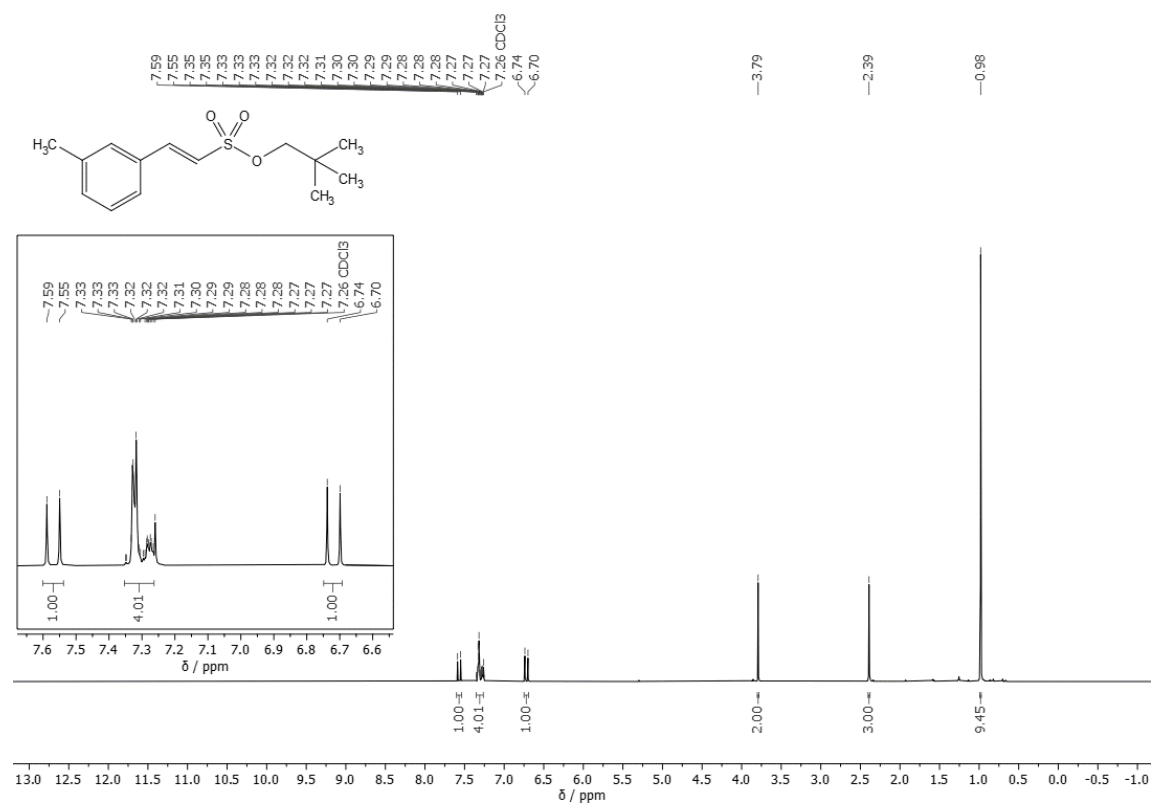


Figure S16: ¹H NMR spectrum (400 MHz, CDCl₃) of **8d**.

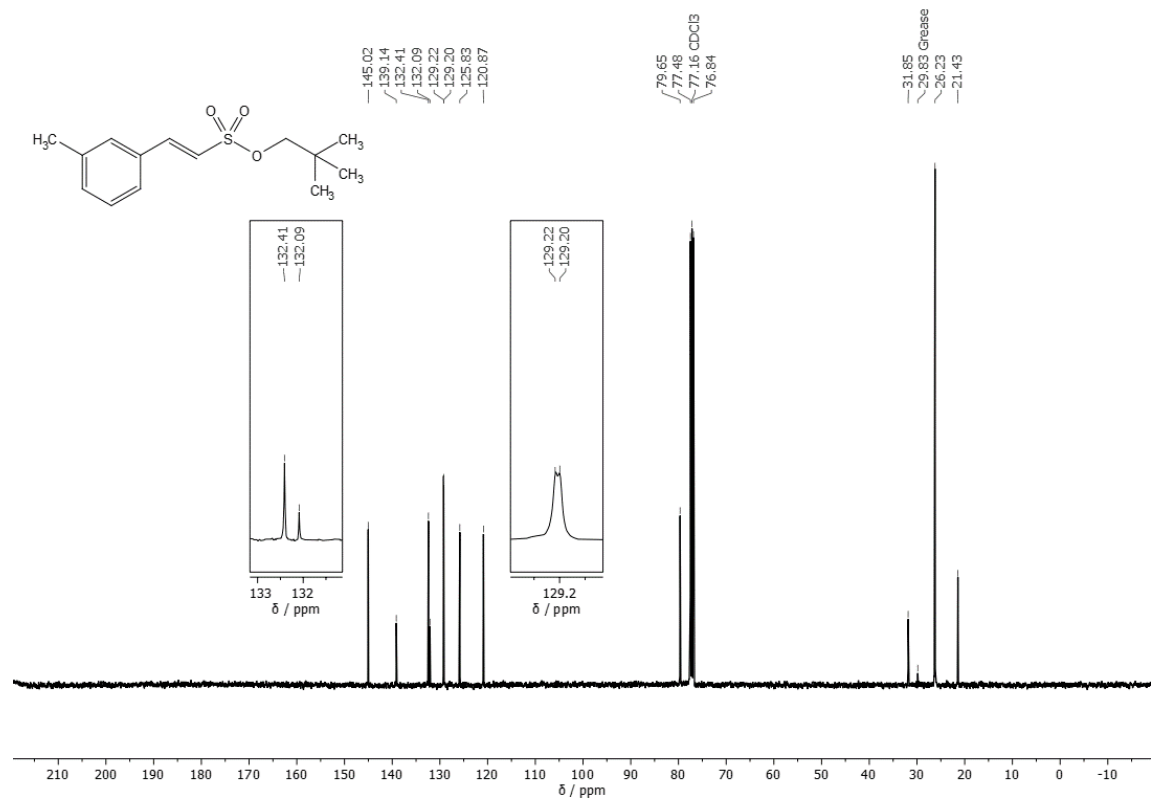


Figure S17: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8d**.

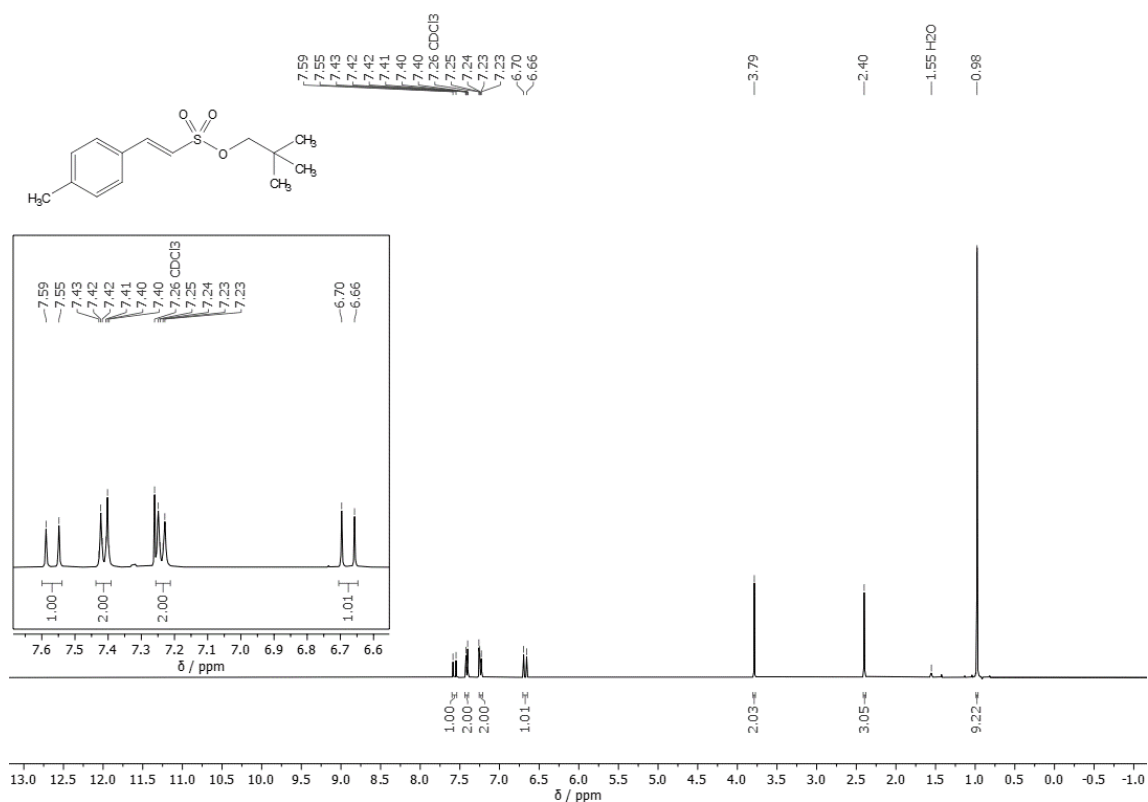


Figure S18: ¹H NMR spectrum (400 MHz, CDCl₃) of 8e.

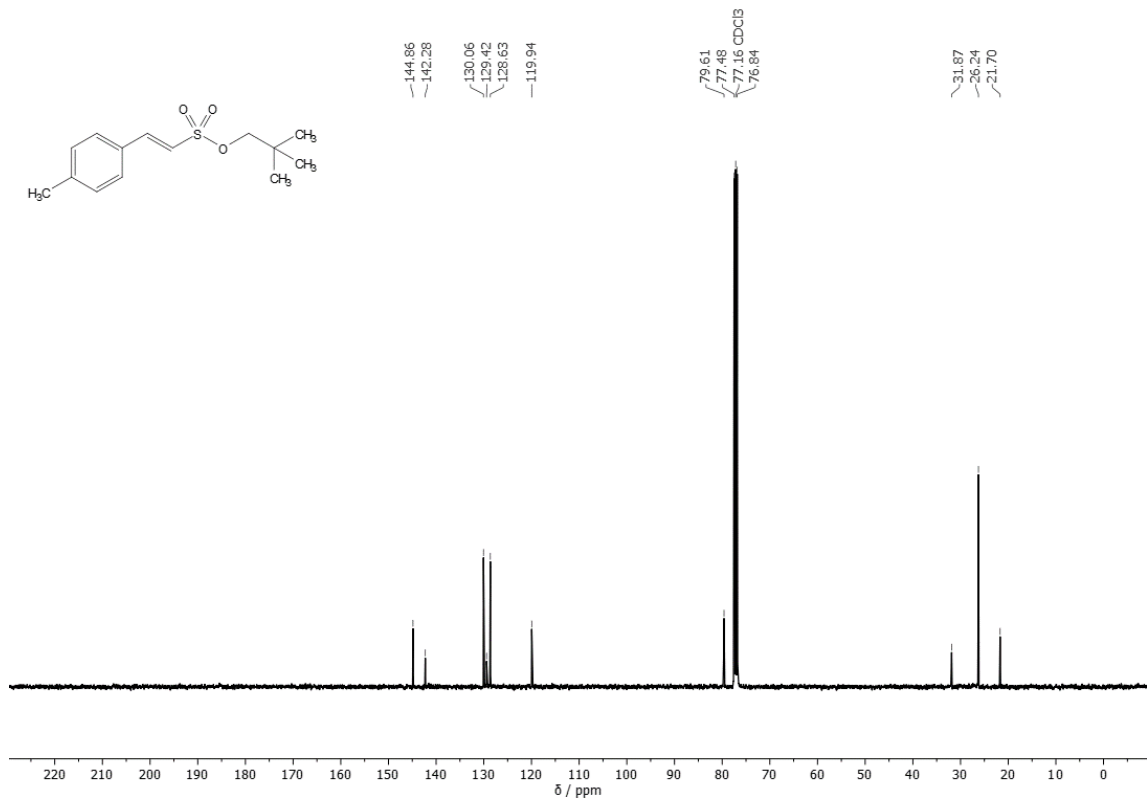
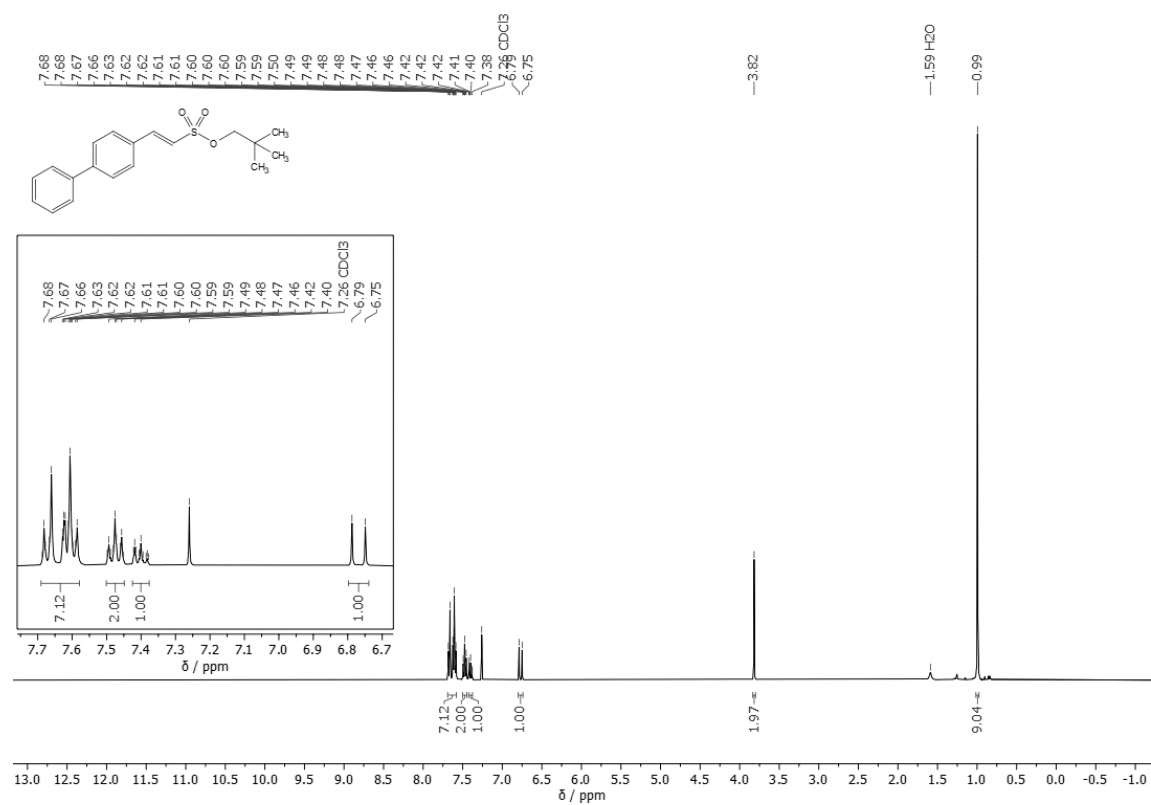
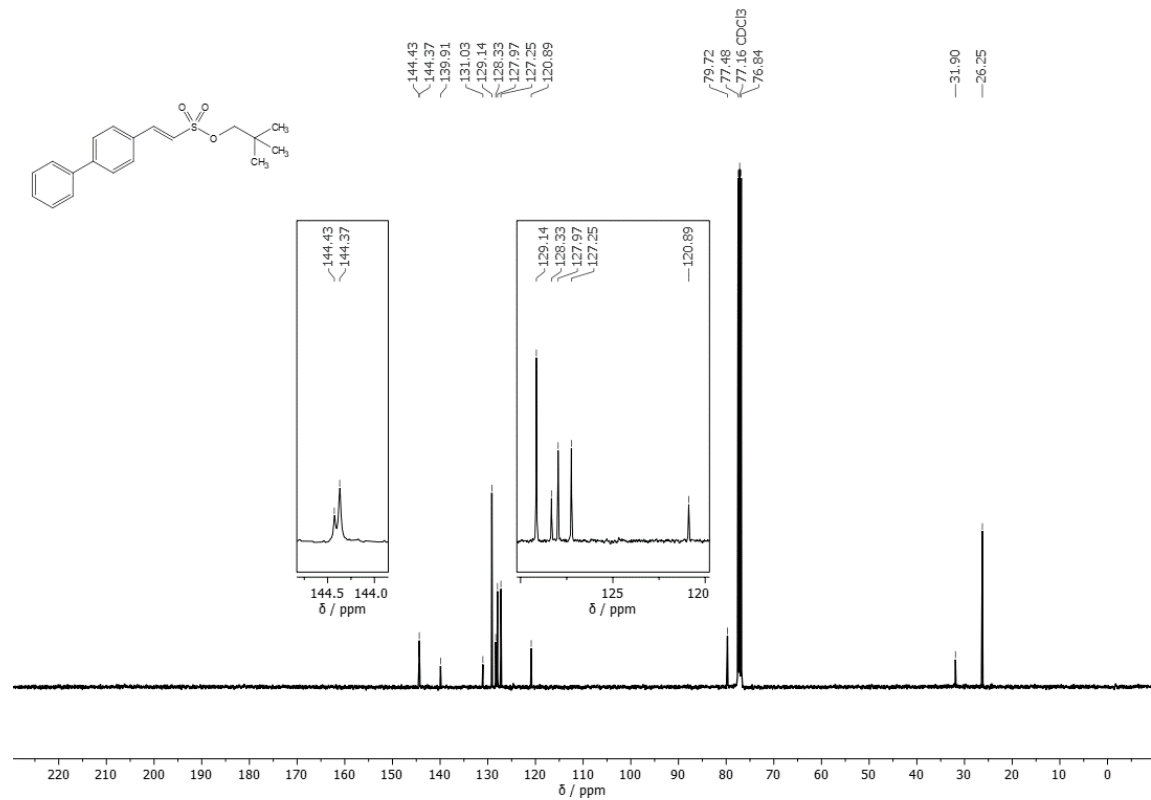
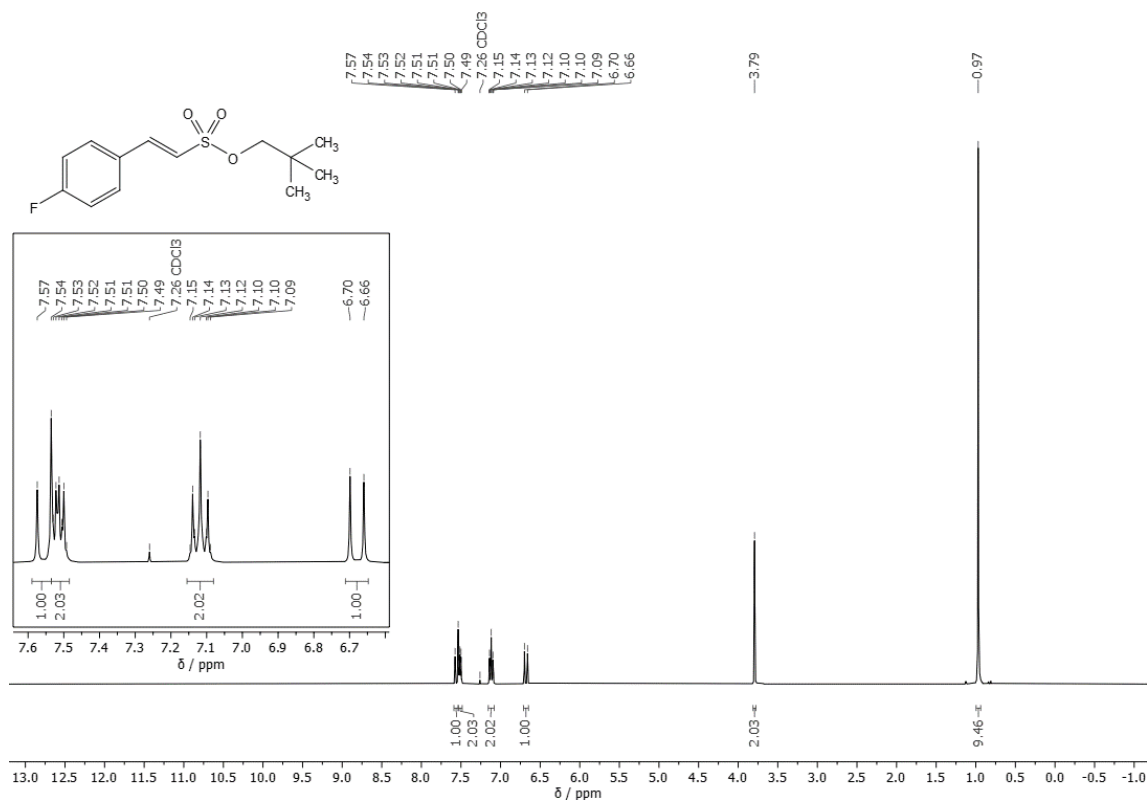
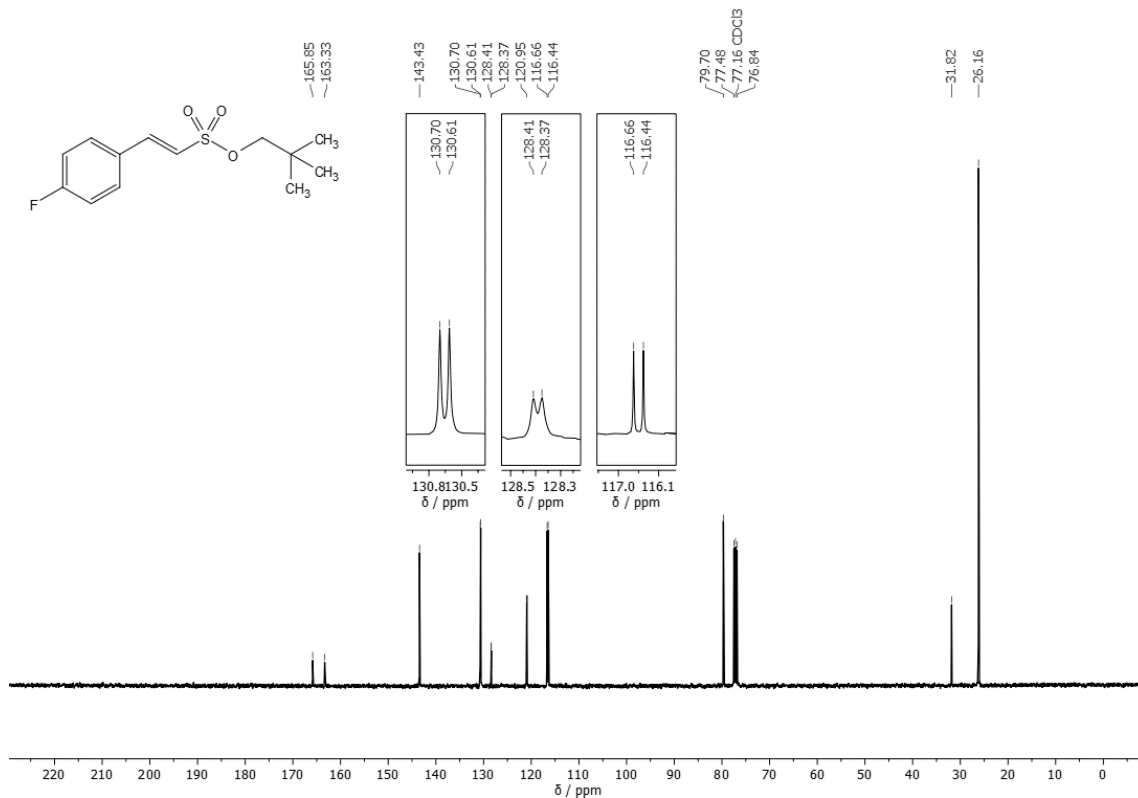


Figure S19: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8e.

Figure S20: ¹H NMR spectrum (400 MHz, CDCl₃) of **8f**.Figure S21: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8f**.

Figure S22: ¹H NMR spectrum (400 MHz, CDCl₃) of 8g.Figure S23: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8g.

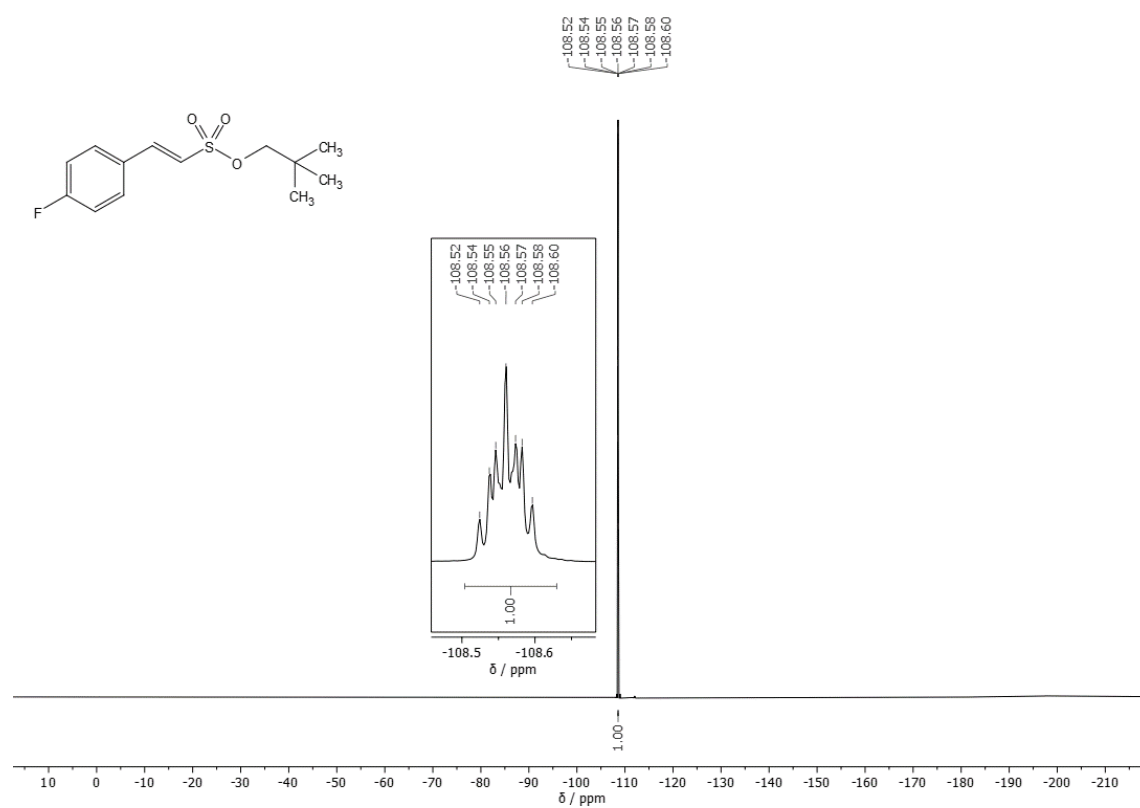
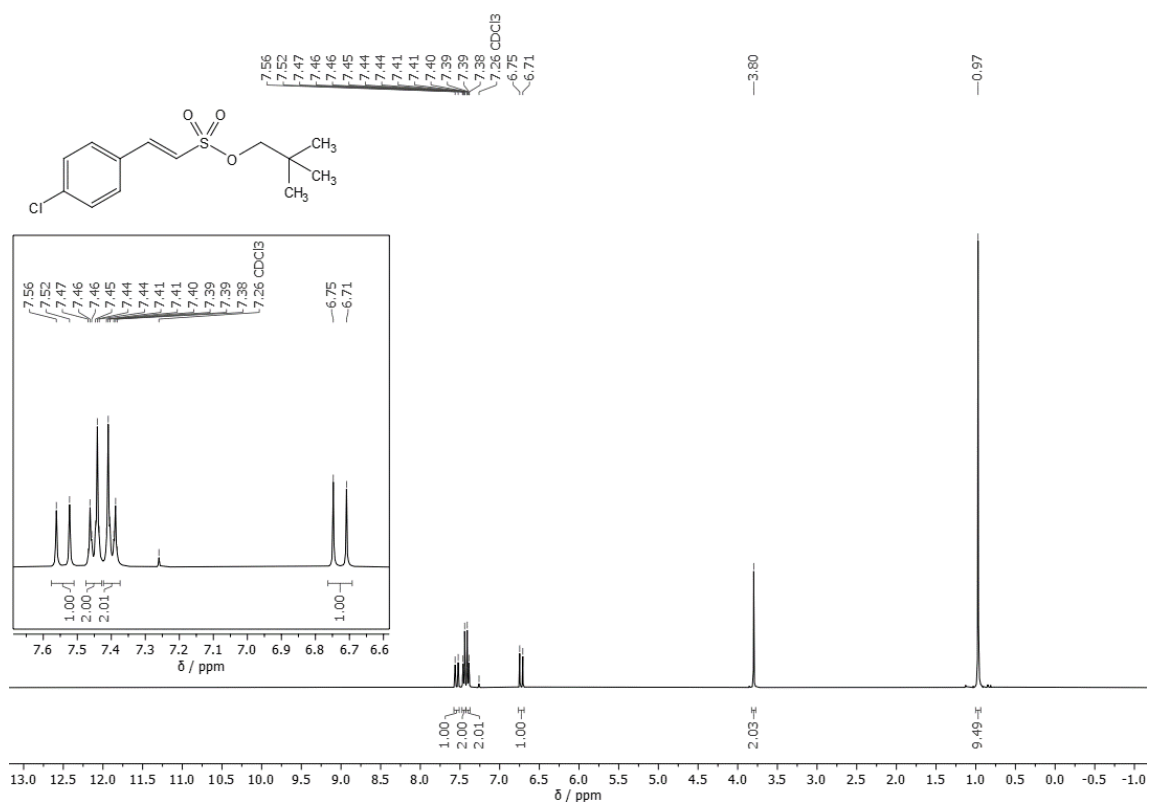
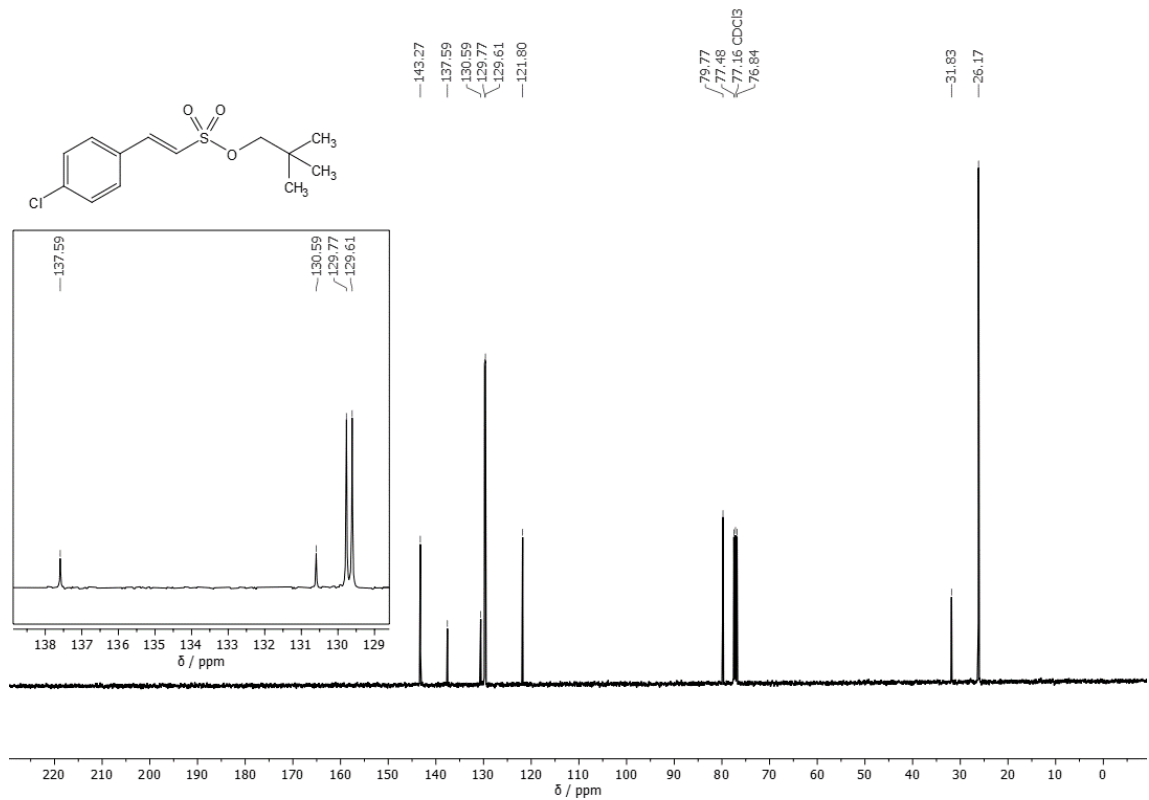
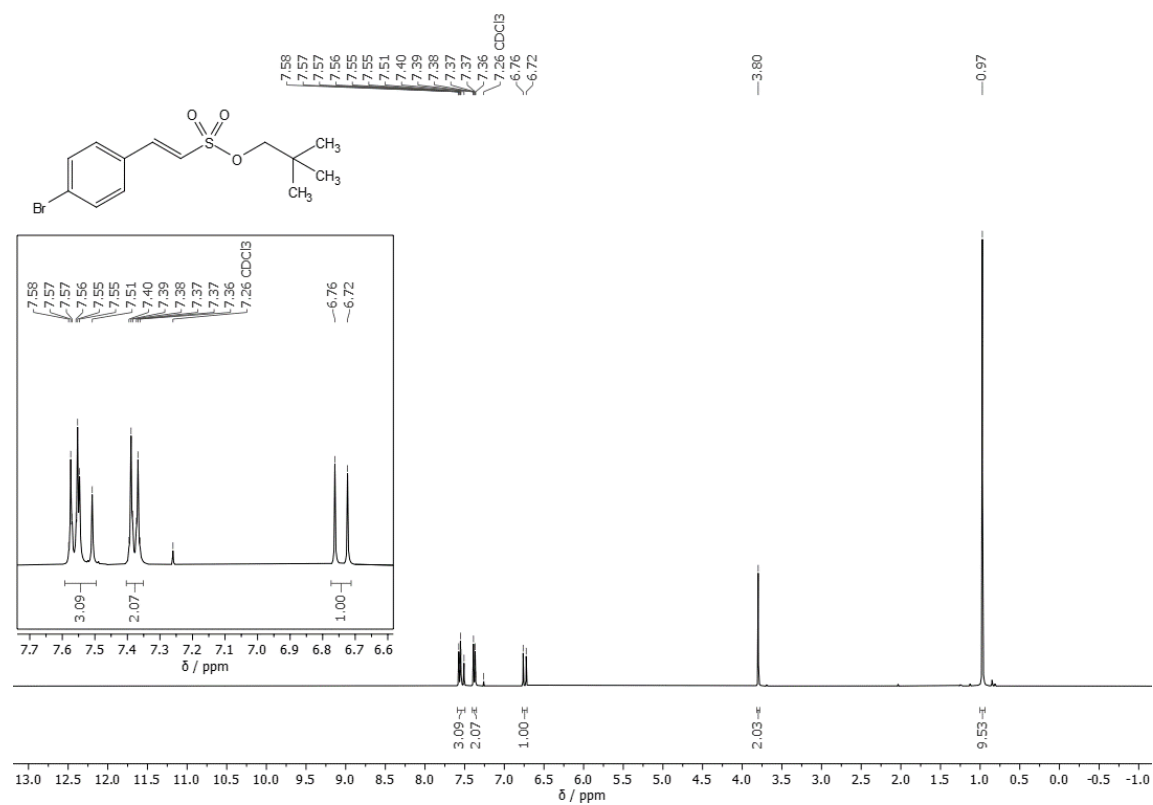
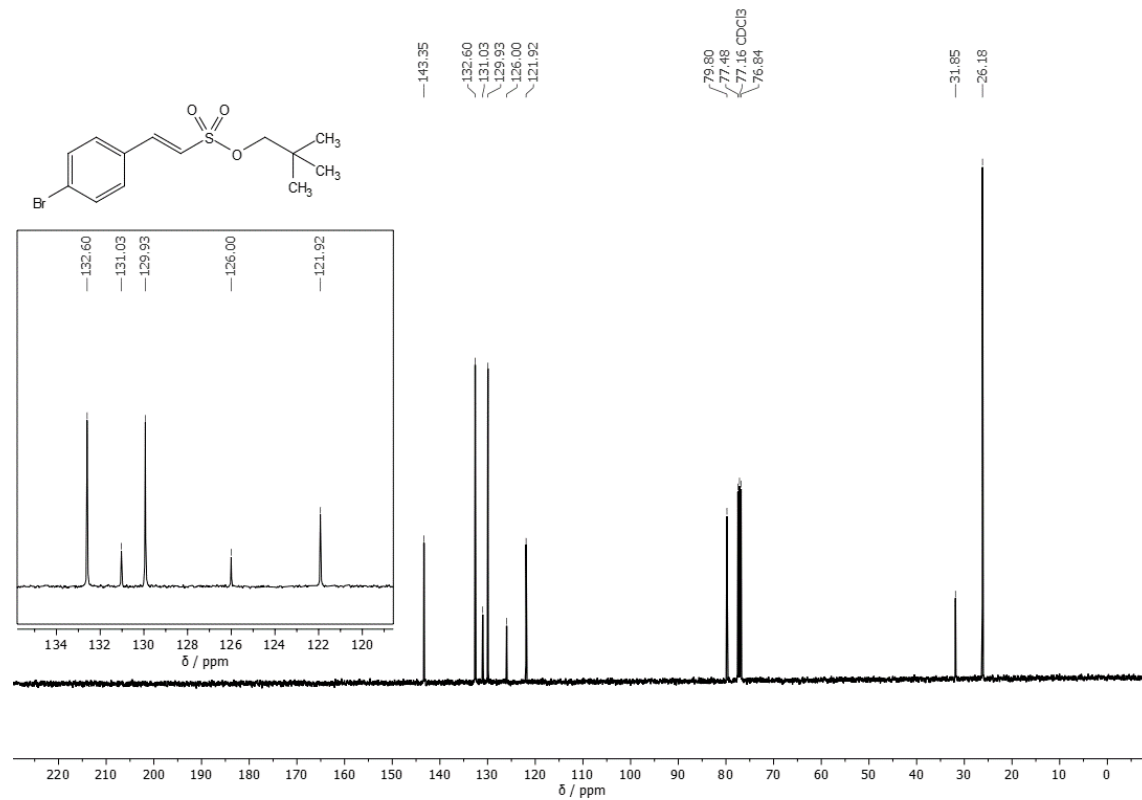


Figure S24: ^{19}F NMR spectrum (376 MHz, CDCl_3) of **8g**.

Figure S25: ¹H NMR spectrum (400 MHz, CDCl₃) of 8h.Figure S26: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8h.

Figure S27: ^1H NMR spectrum (400 MHz, CDCl_3) of **8i**.Figure S28: ^{13}C NMR spectrum (101 MHz, CDCl_3) of **8i**.

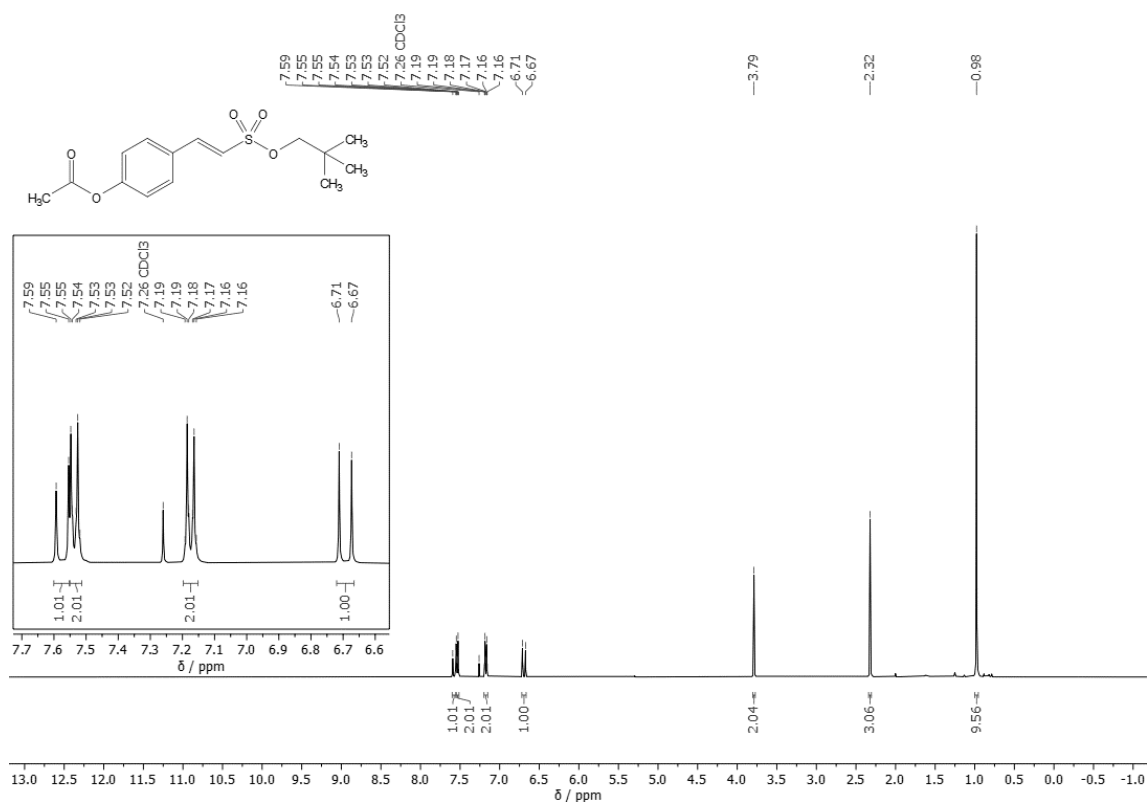


Figure S29: ¹H NMR spectrum (400 MHz, CDCl₃) of **8j**.

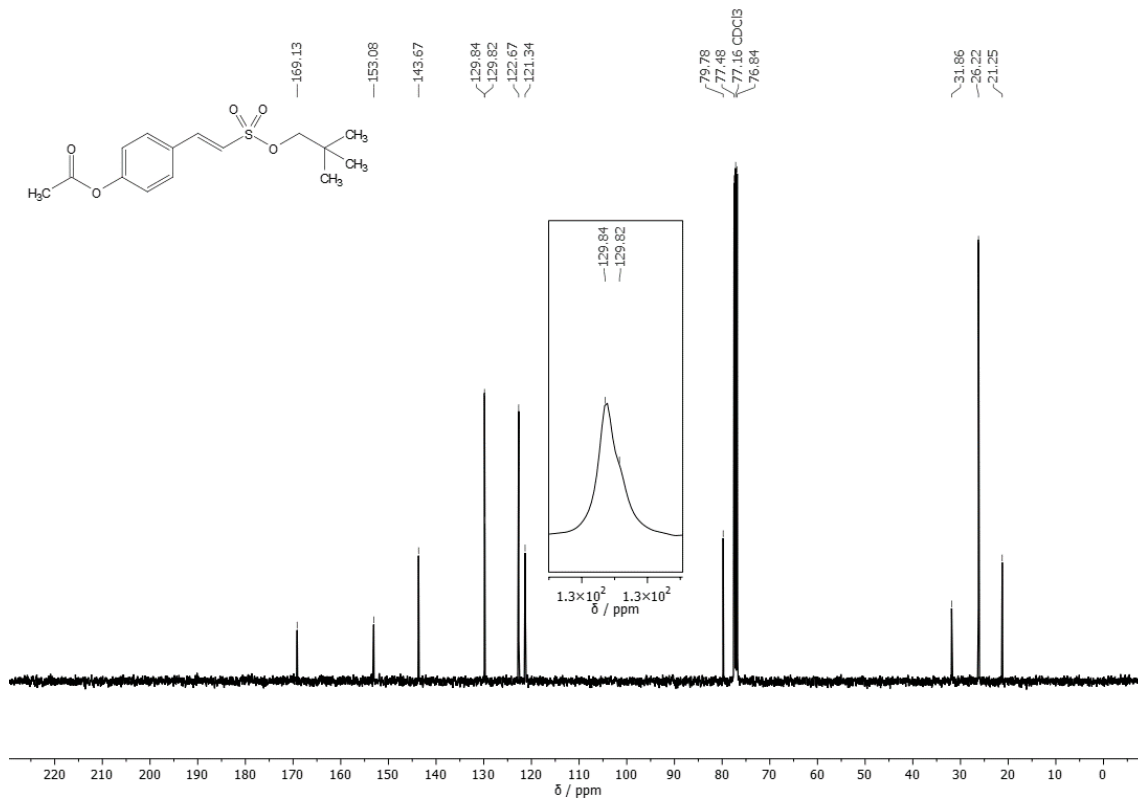
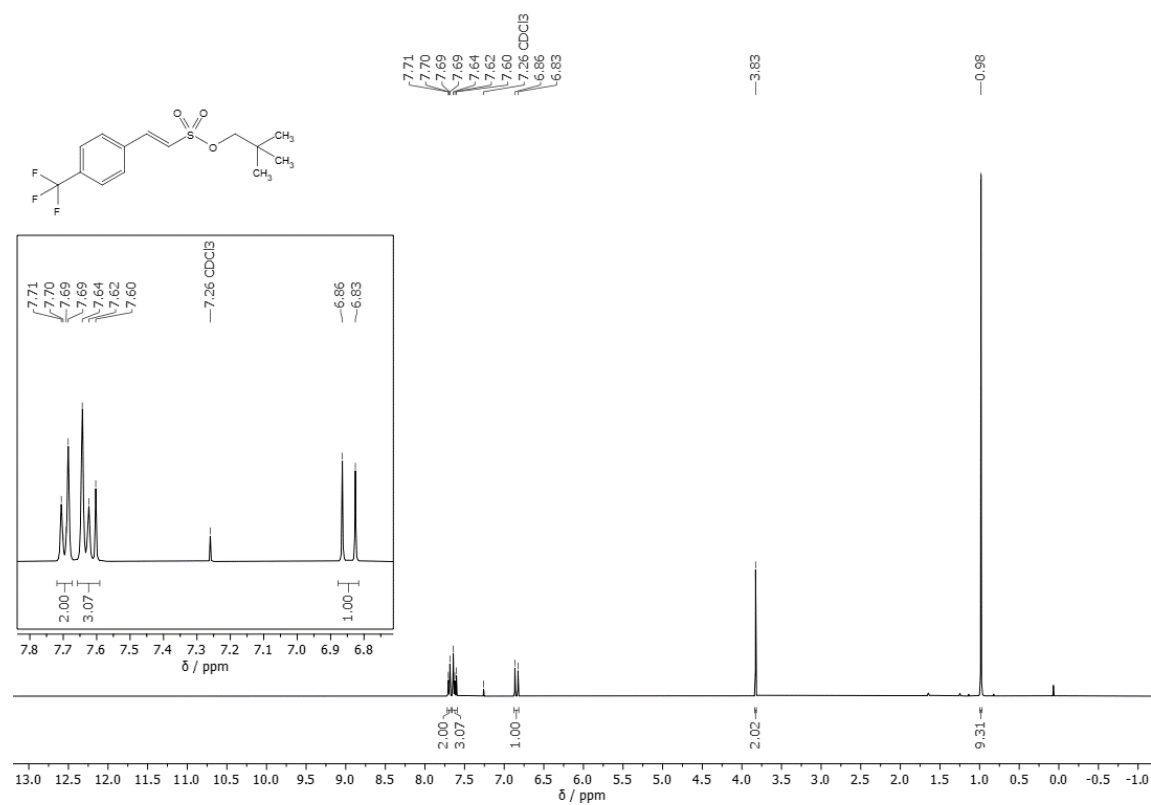
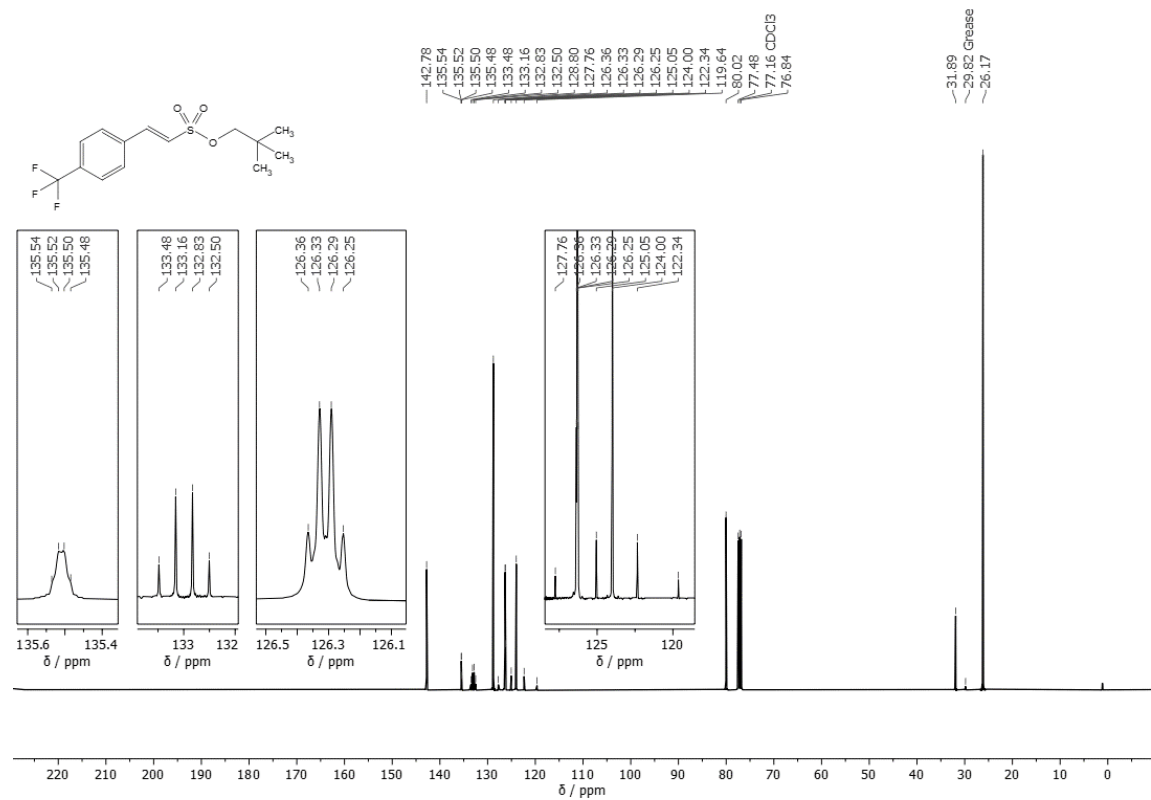


Figure S30: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8j**.

Figure S31: ¹H NMR spectrum (400 MHz, CDCl₃) of 8k.Figure S32: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8k.

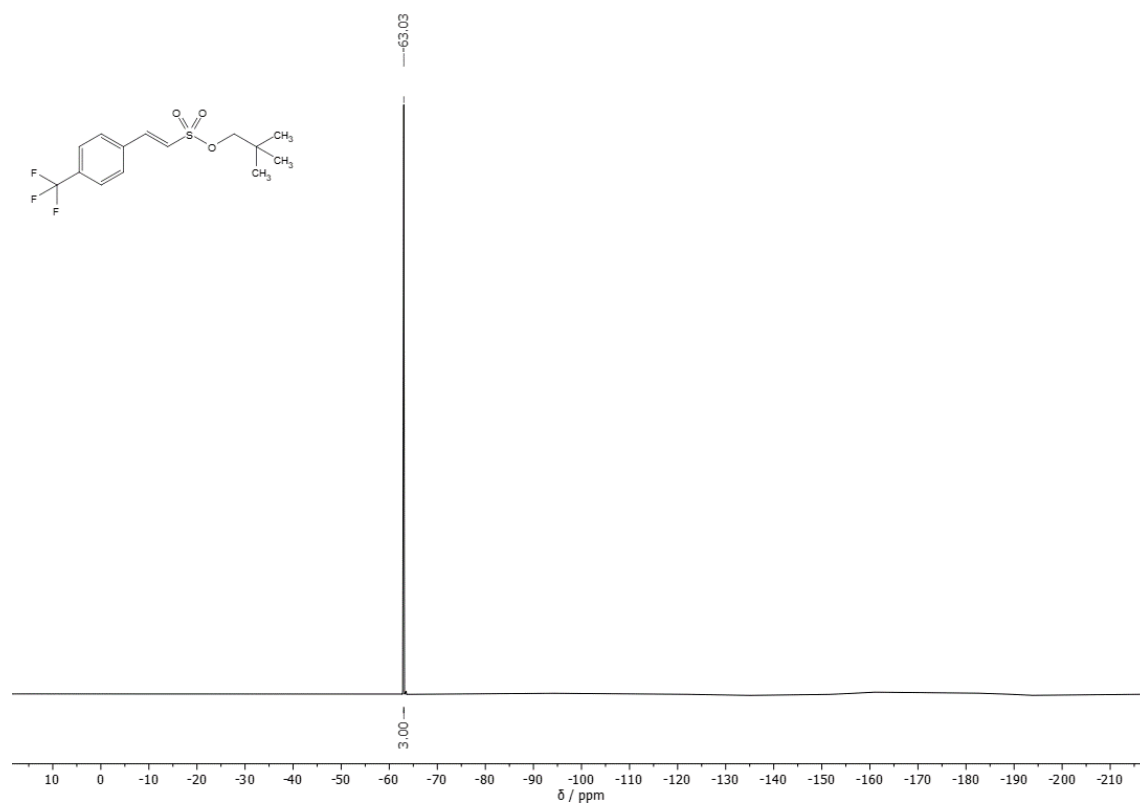


Figure S33: ^{19}F NMR spectrum (377 MHz, CDCl_3) of **8k**.

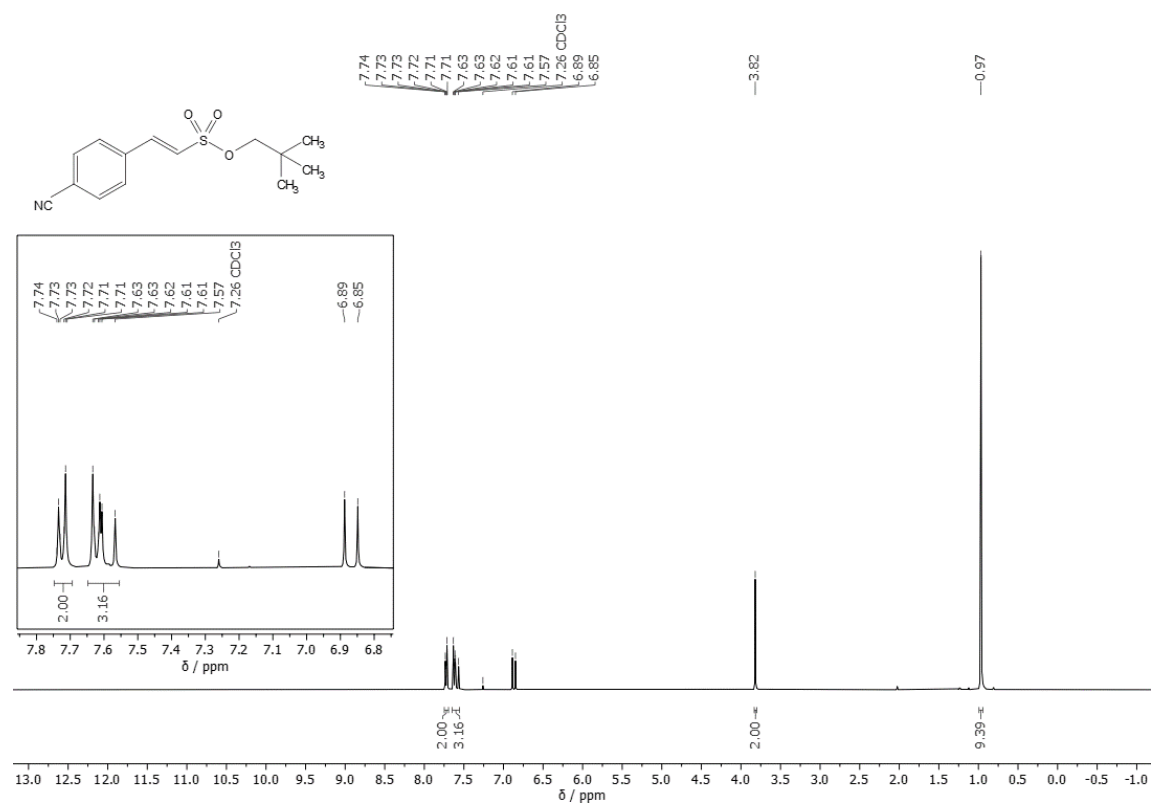


Figure S34: ¹H NMR spectrum (400 MHz, CDCl₃) of **8I**.

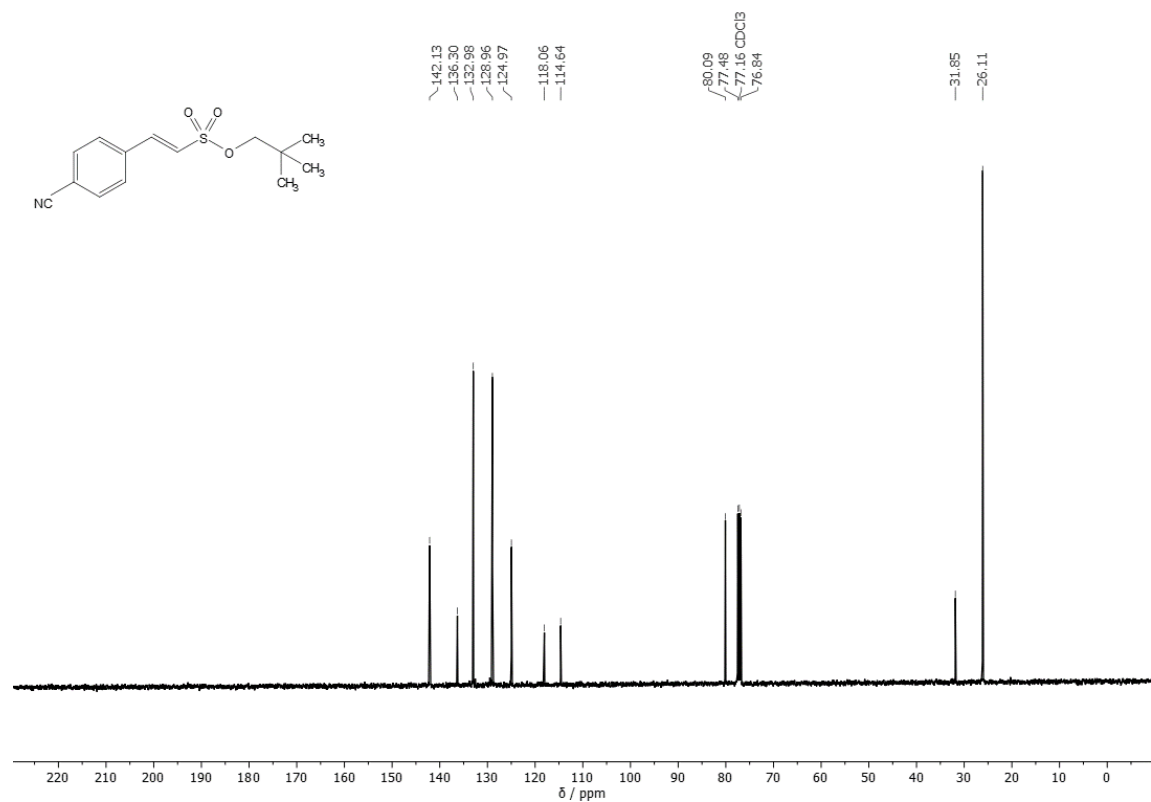


Figure S35: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8I**.

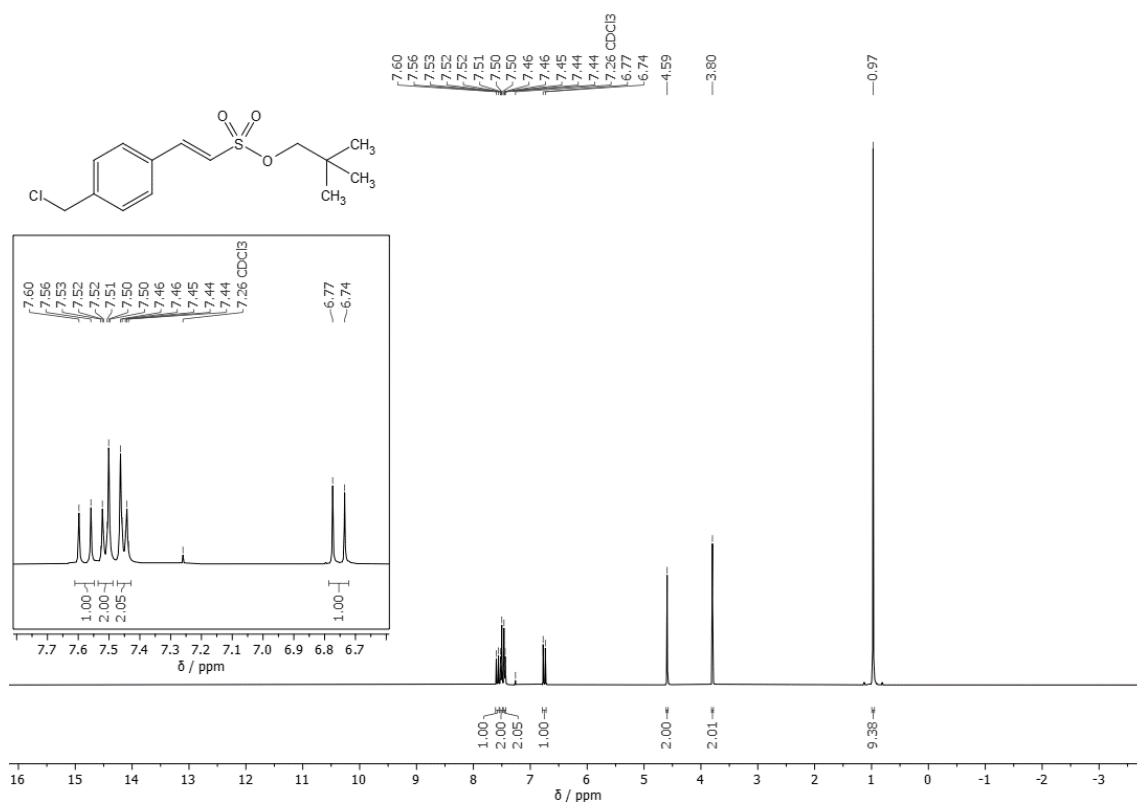


Figure S36: ¹H NMR spectrum (400 MHz, CDCl₃) of **8m**.

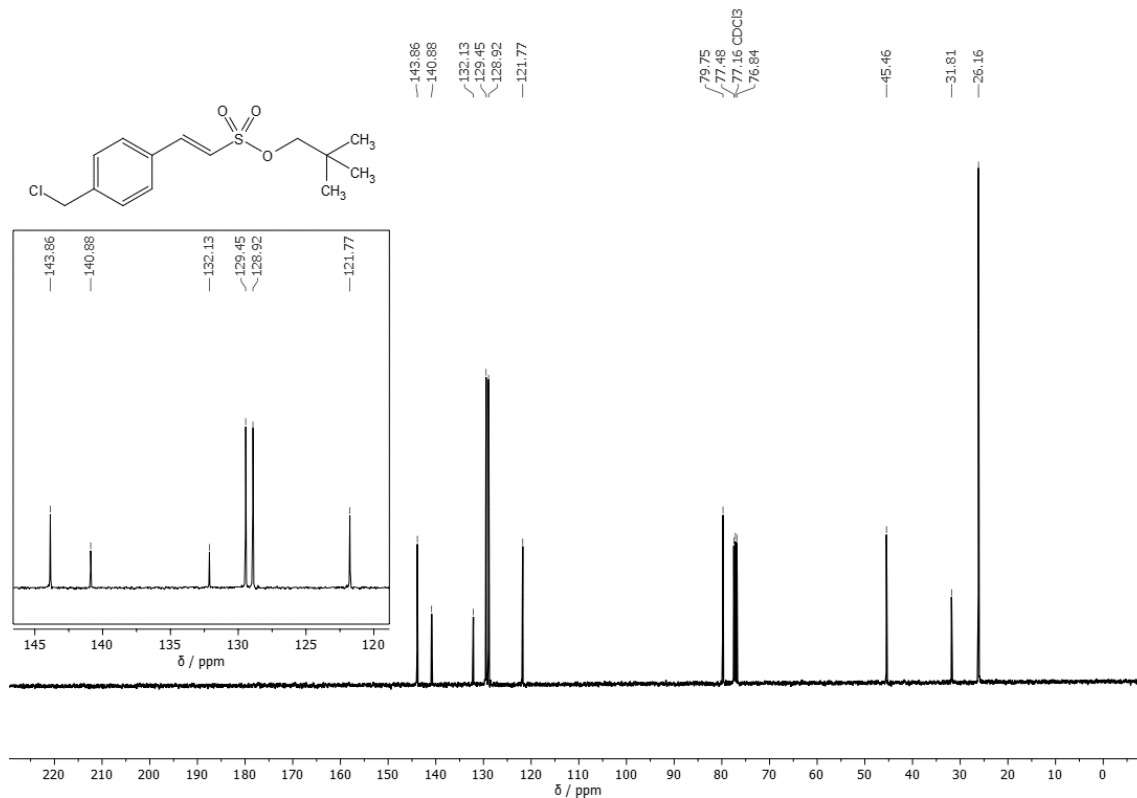
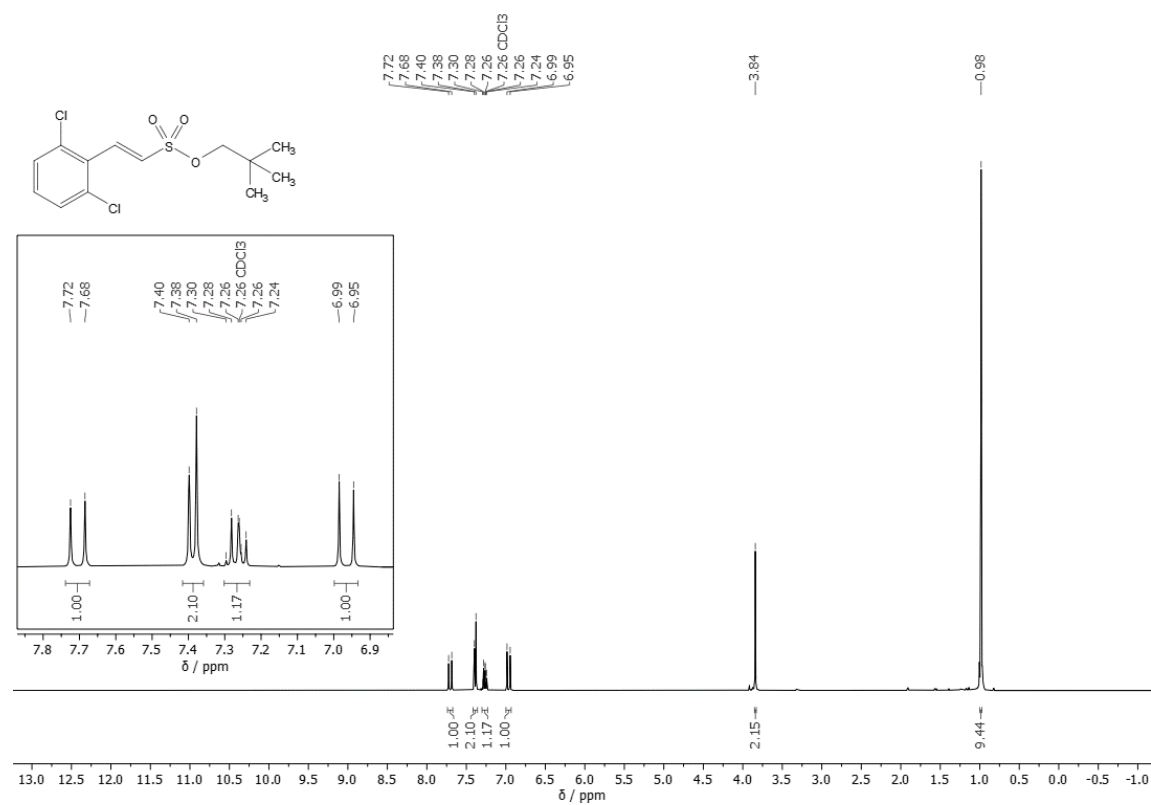
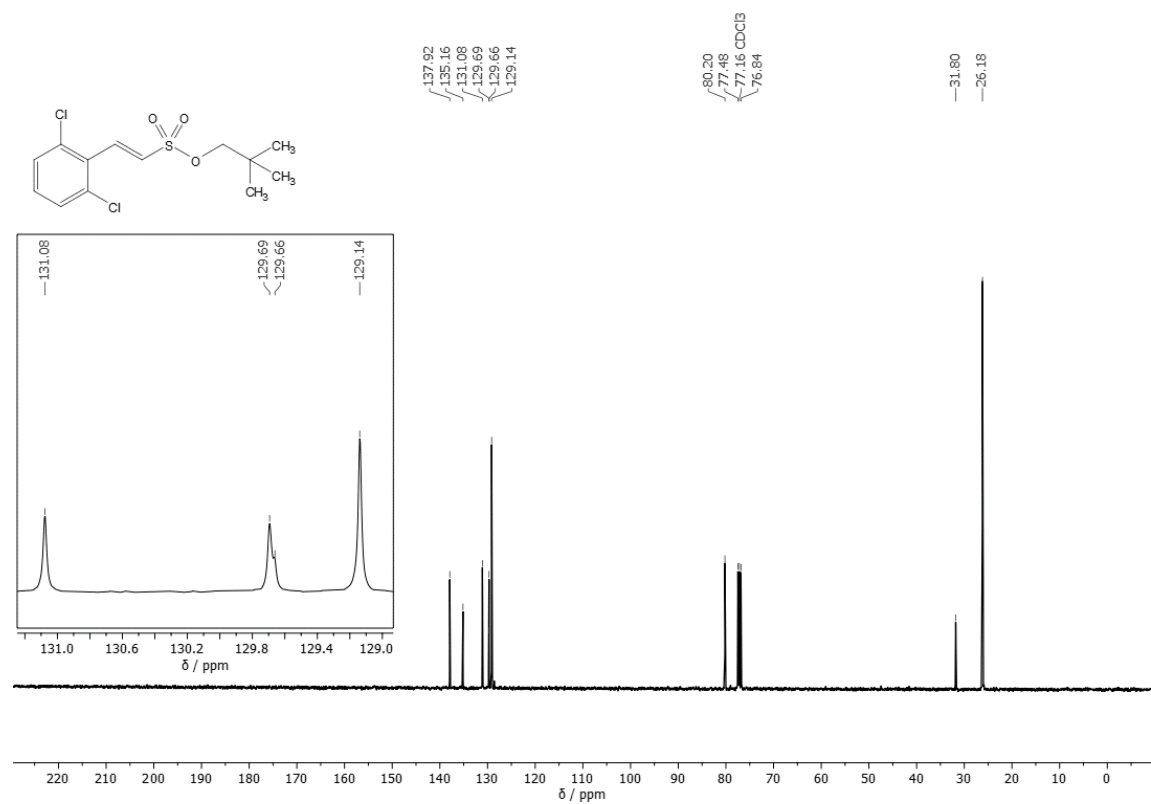
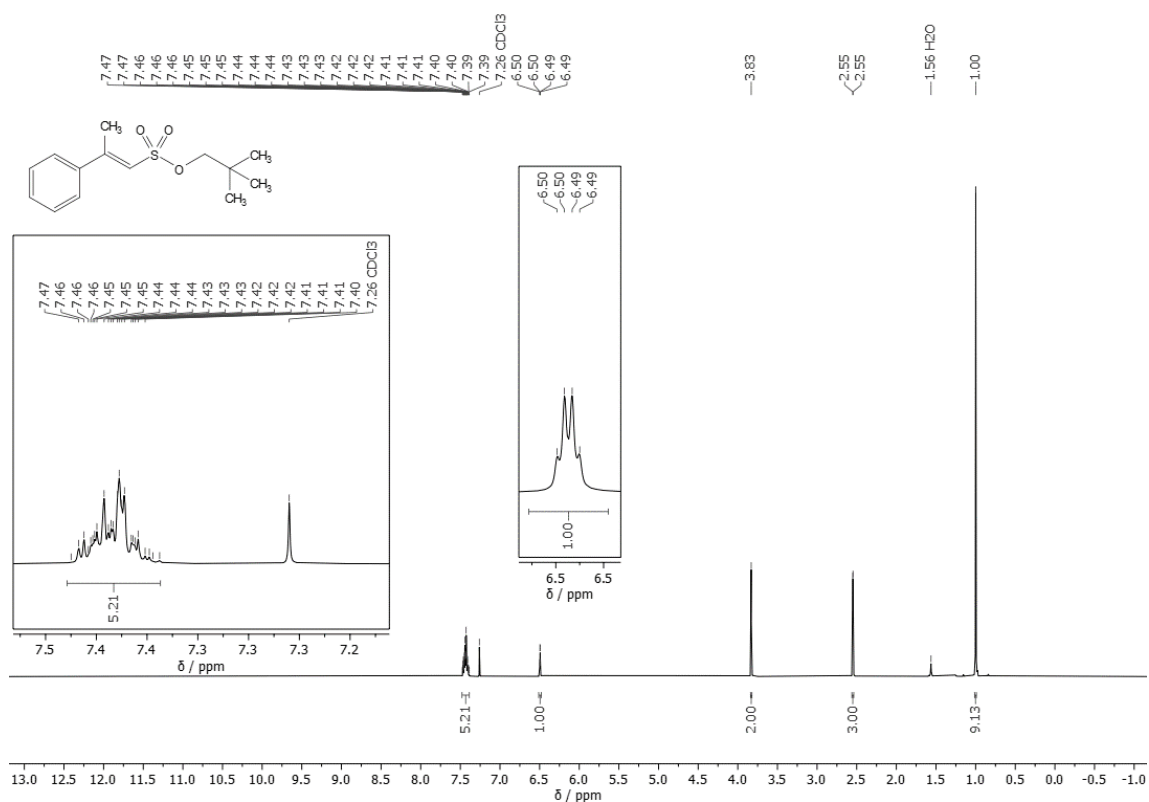
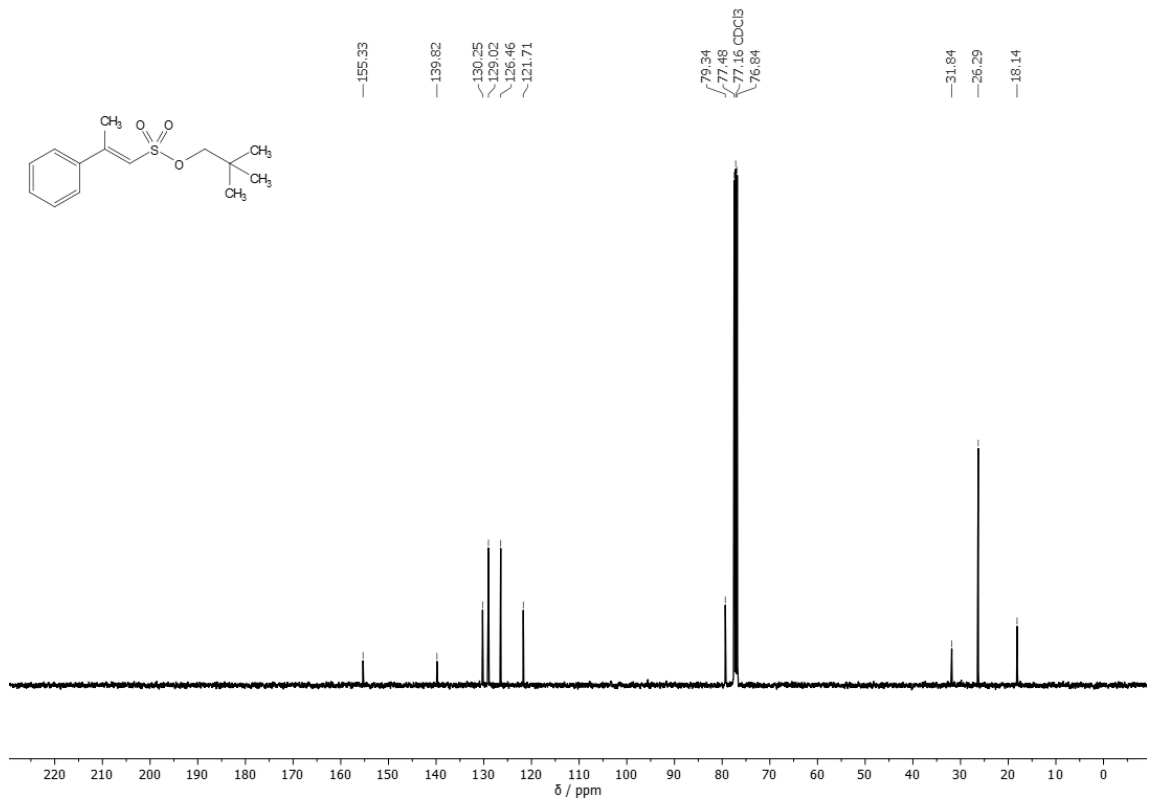
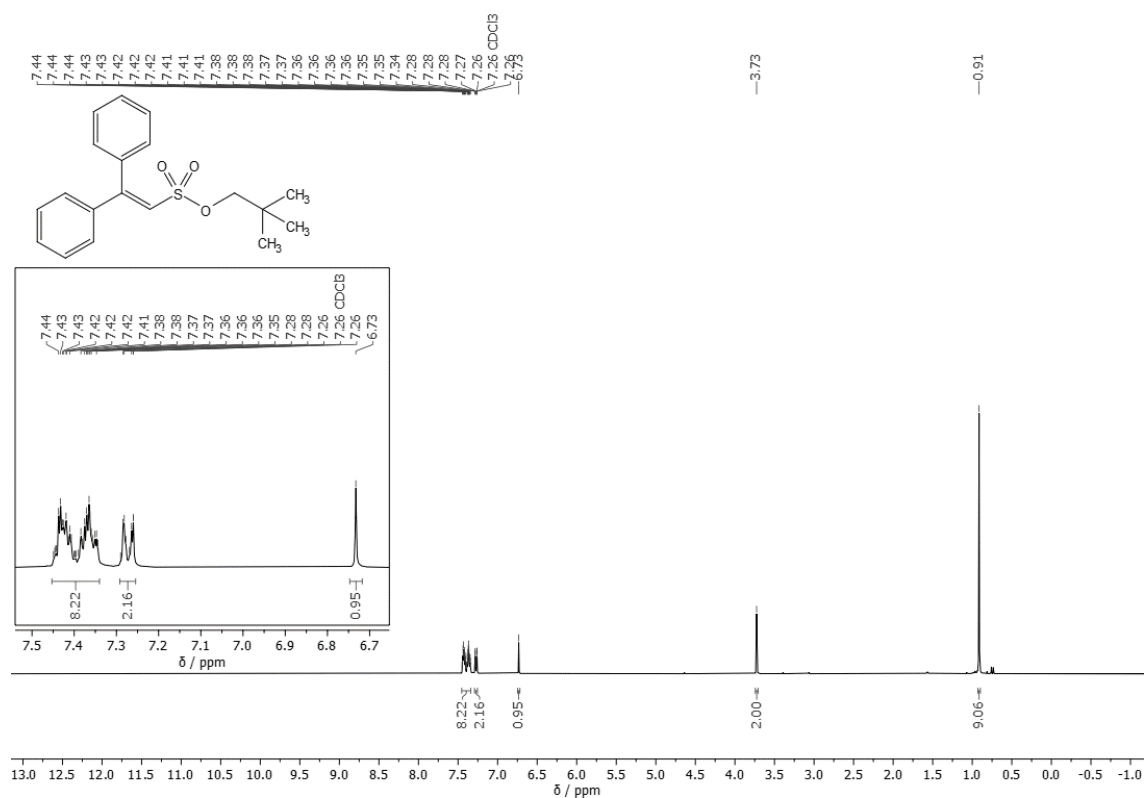
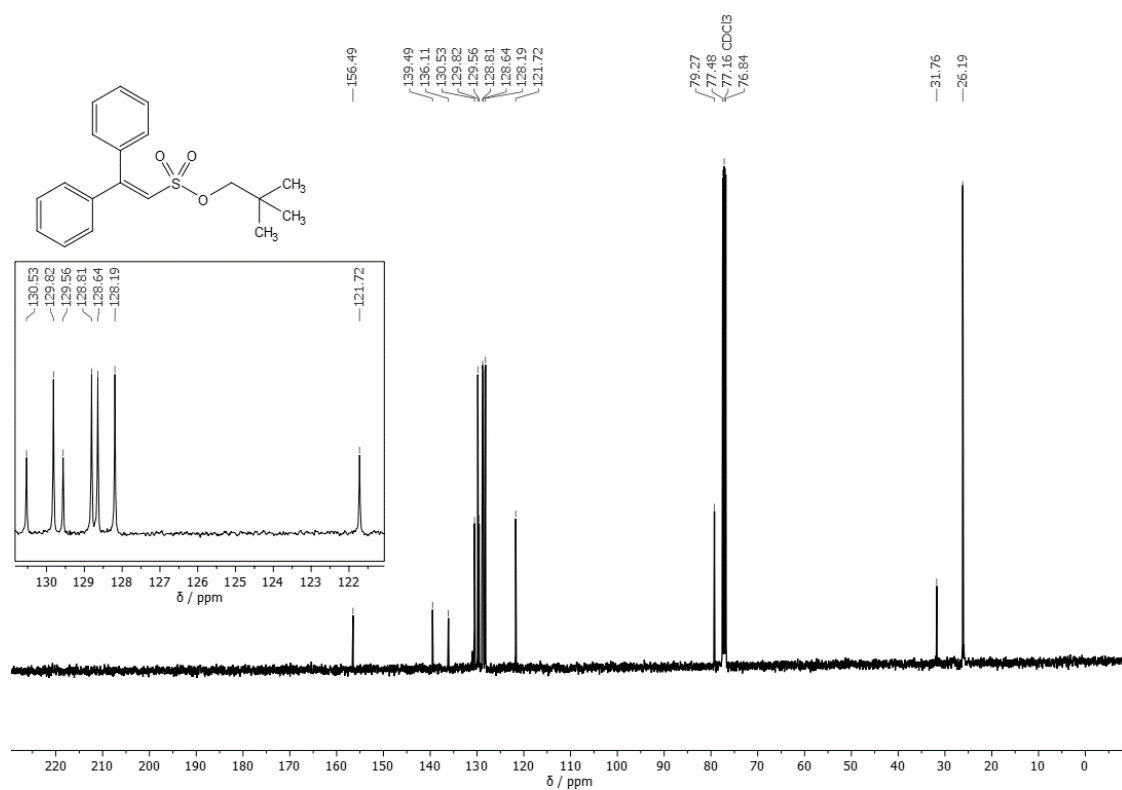


Figure S37: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8m**.

Figure S38: ¹H NMR spectrum (400 MHz, CDCl₃) of **8n**.Figure S39: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8n**.

Figure S40: ¹H NMR spectrum (400 MHz, CDCl₃) of 8o-E.Figure S41: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8o-E.

Figure S42: ¹H NMR spectrum (400 MHz, CDCl₃) of 8p.Figure S43: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8p.

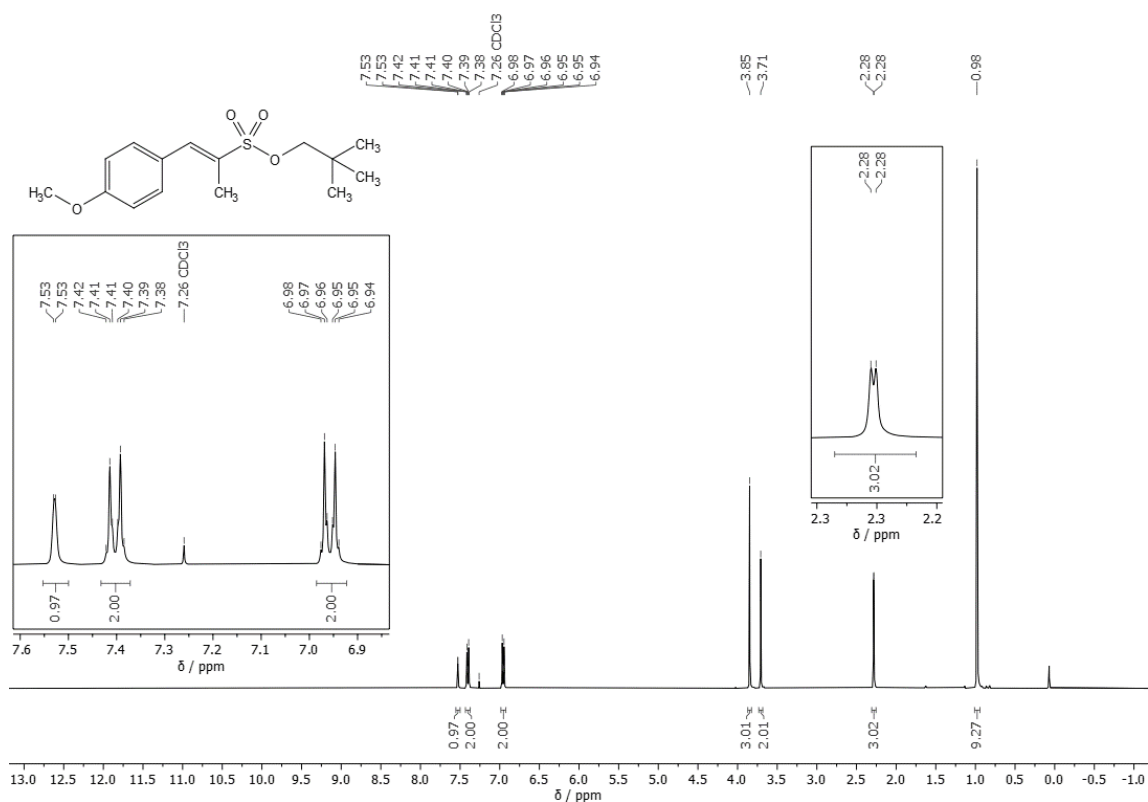


Figure S44: ¹H NMR spectrum (400 MHz, CDCl₃) of 8q.

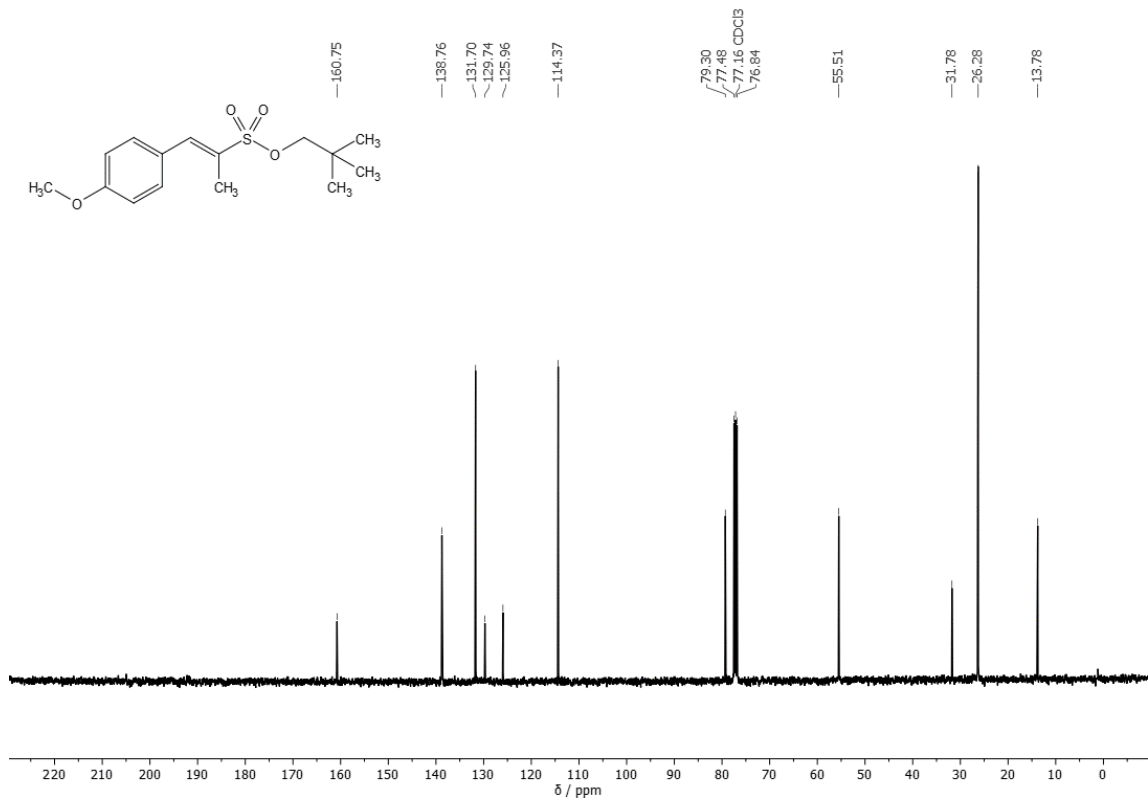


Figure S45: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8q.

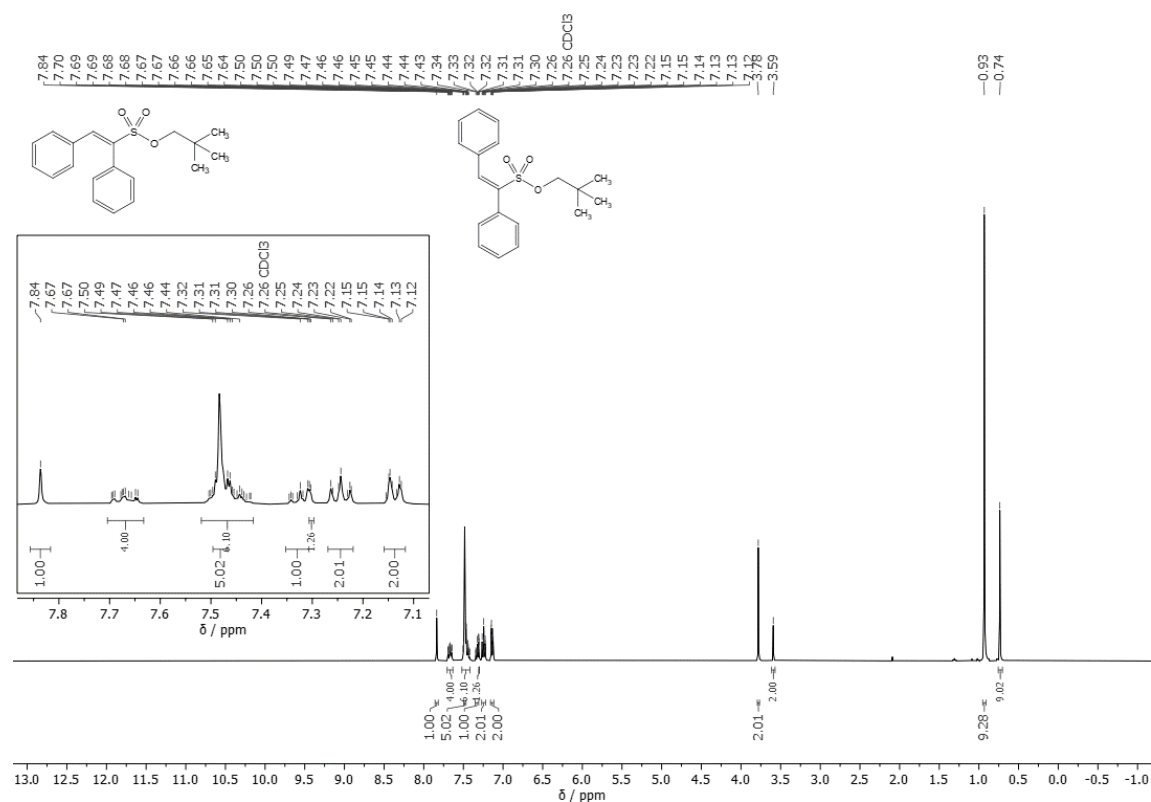


Figure S46: ^1H NMR spectrum (400 MHz, CDCl_3) of **8r**.

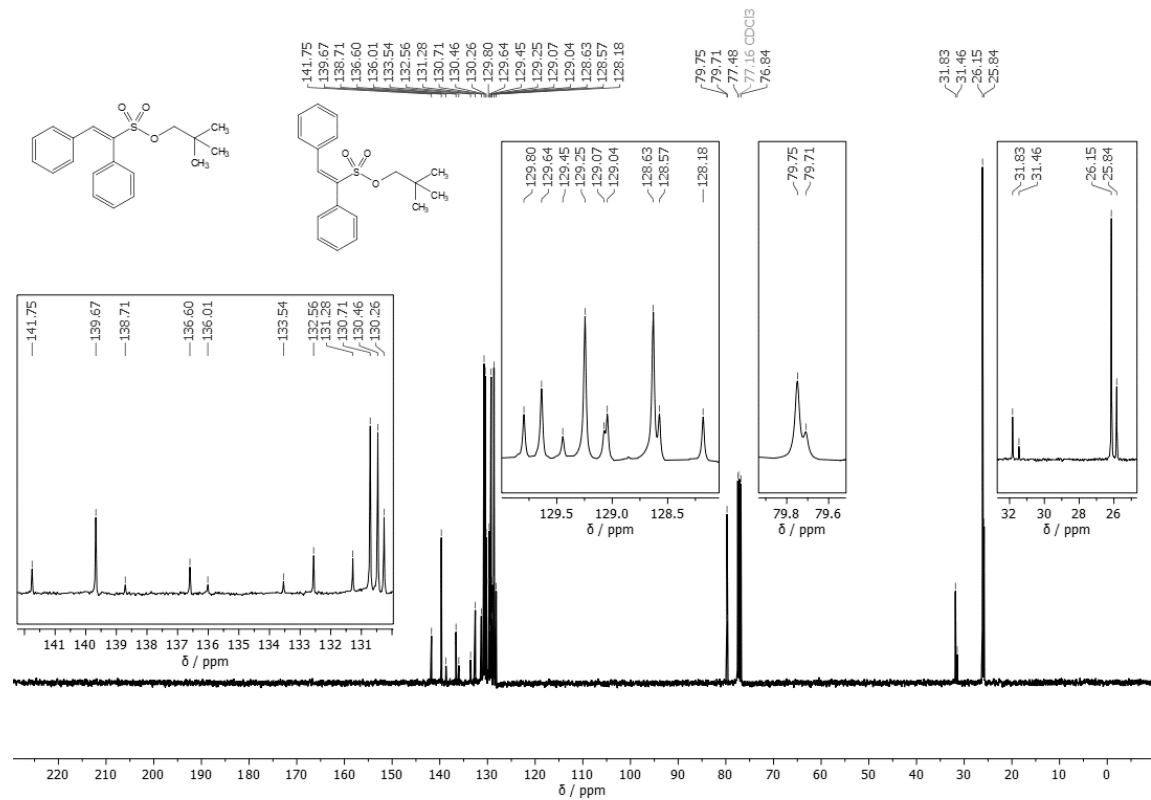
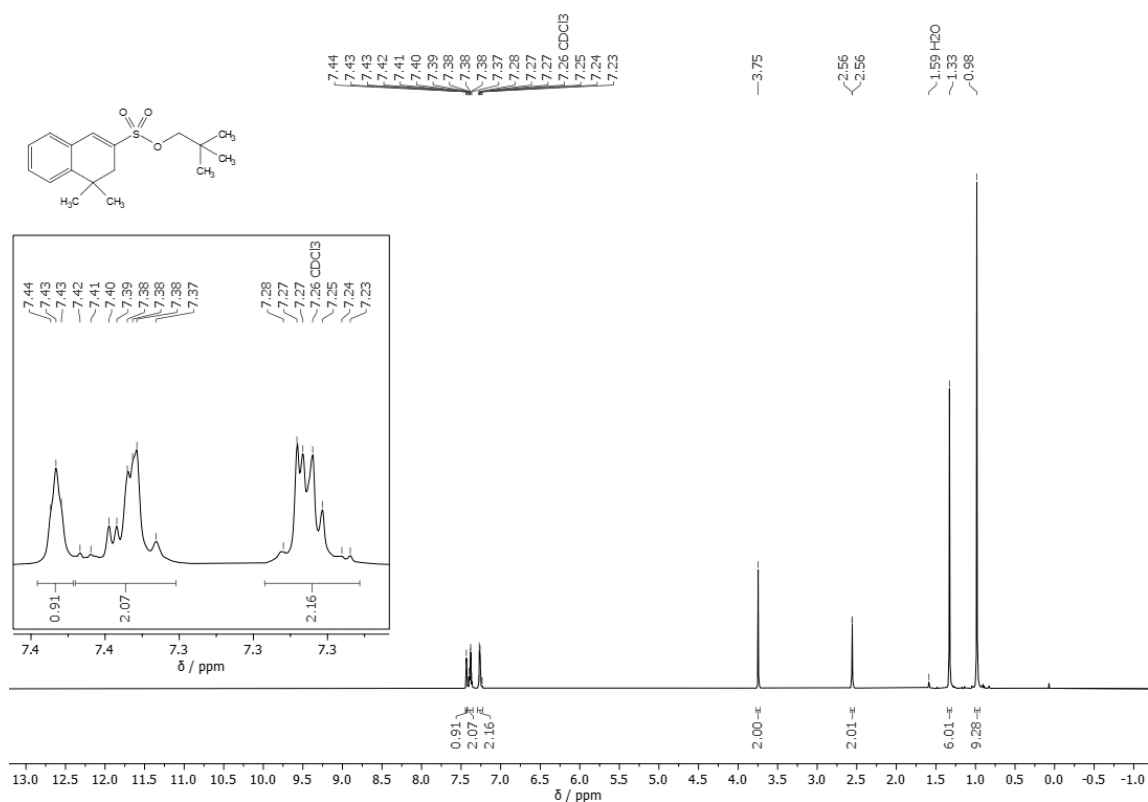
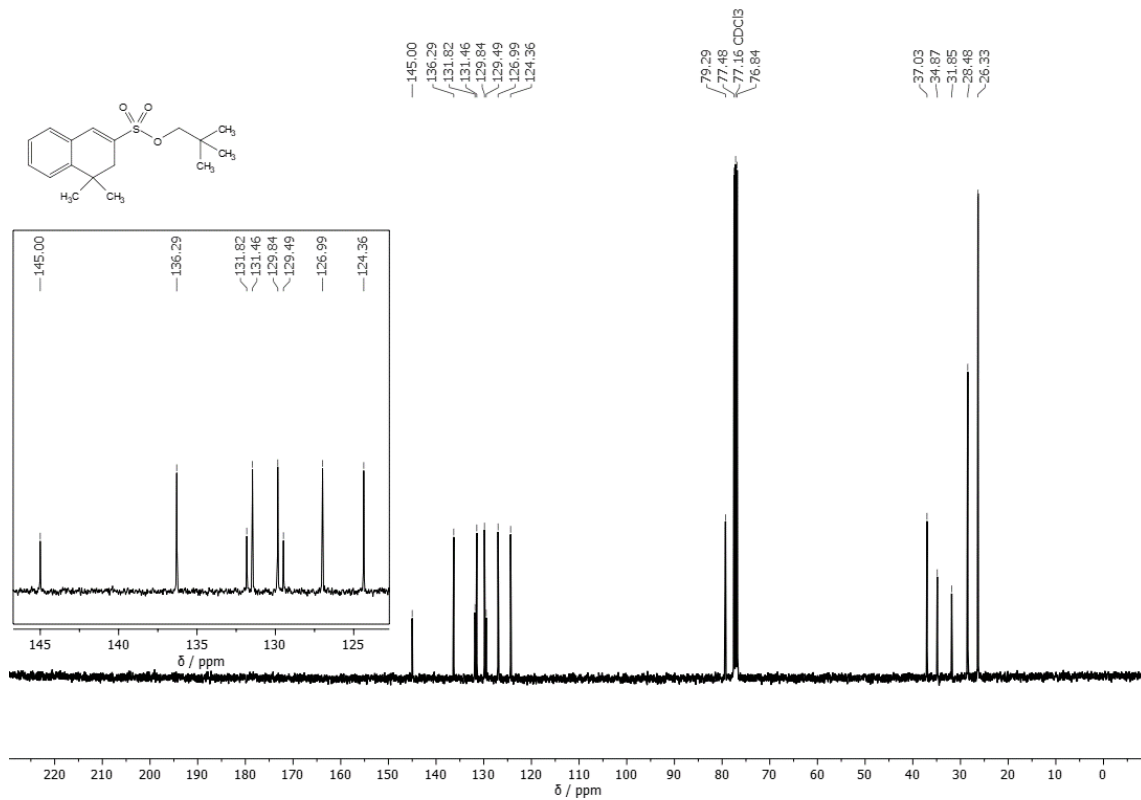
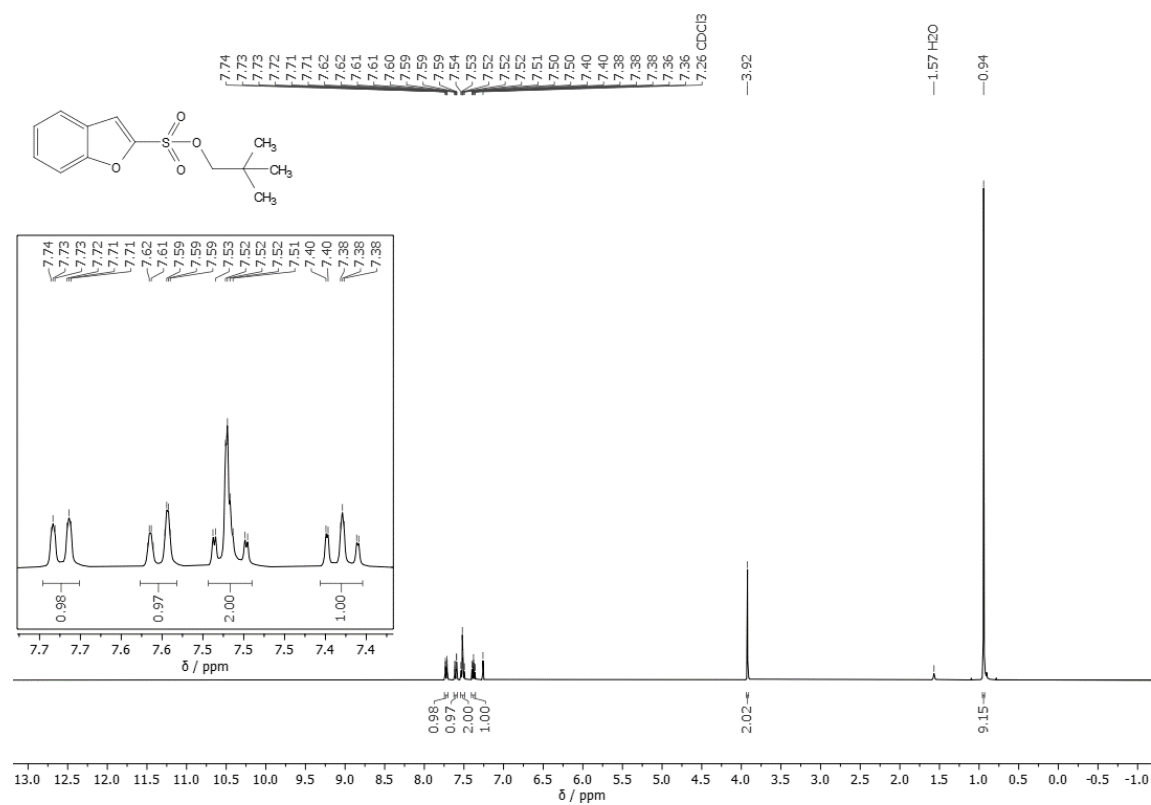
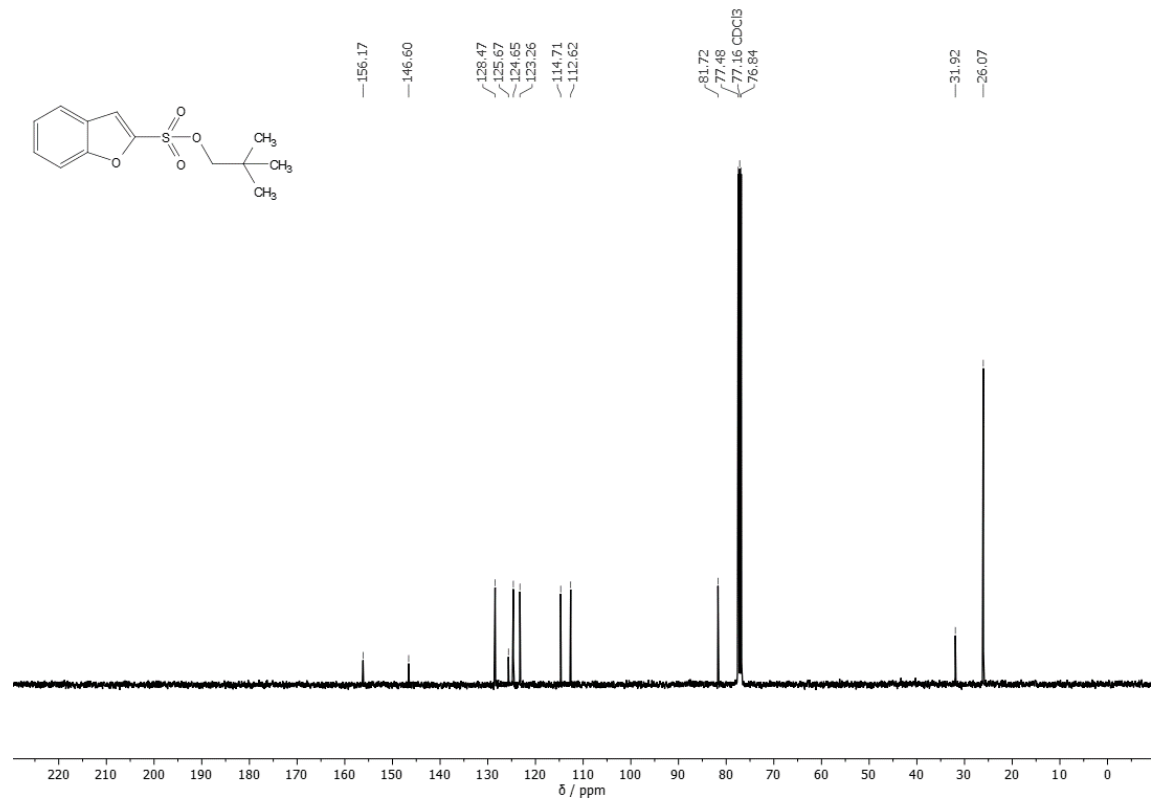
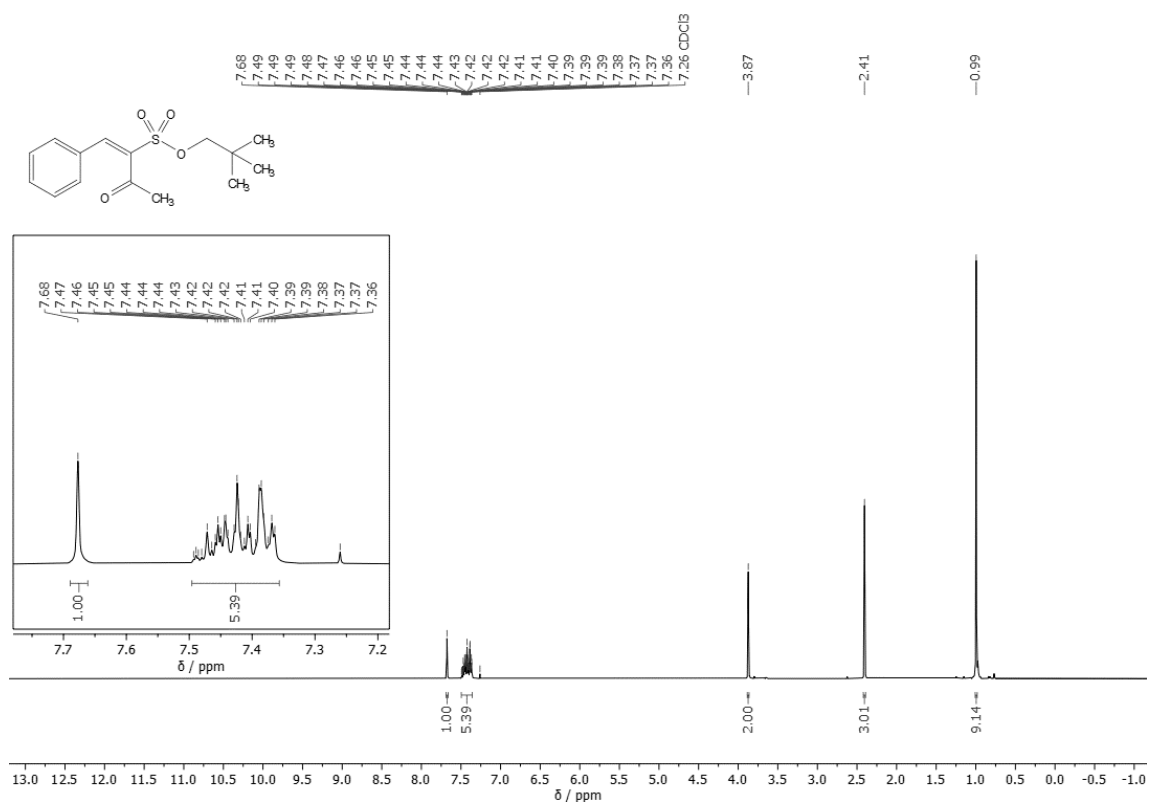
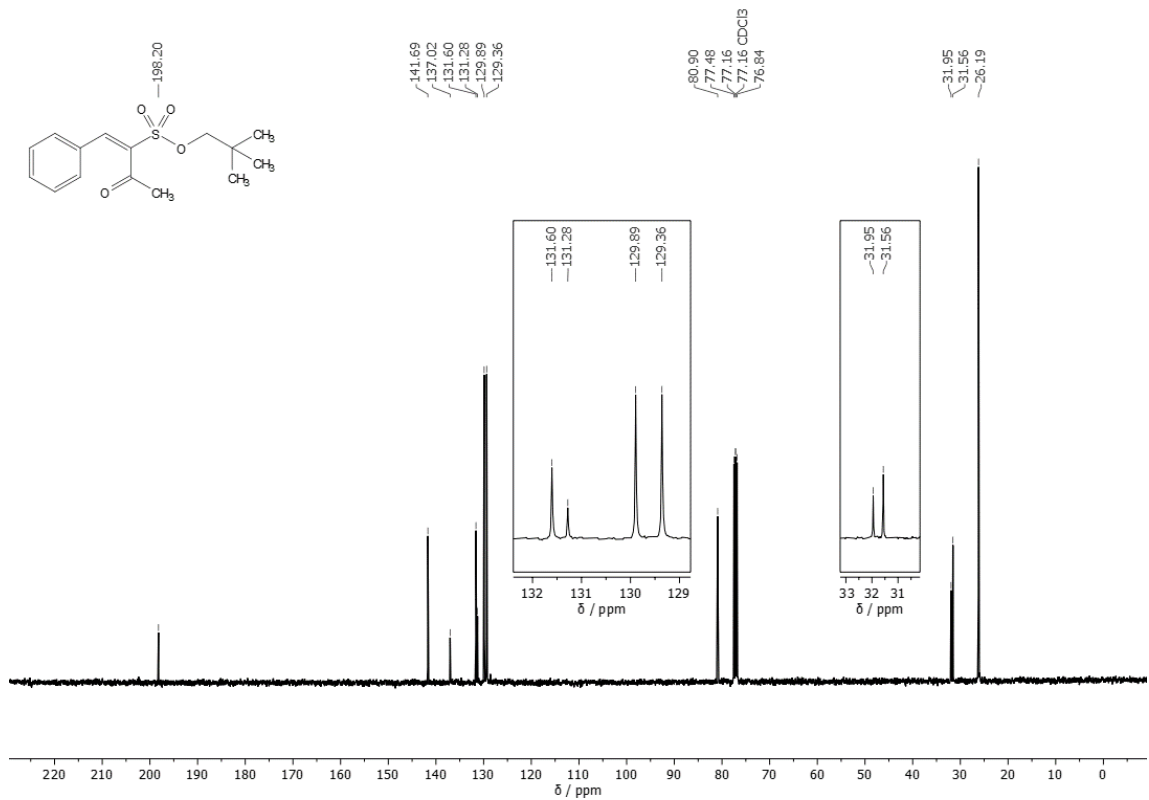
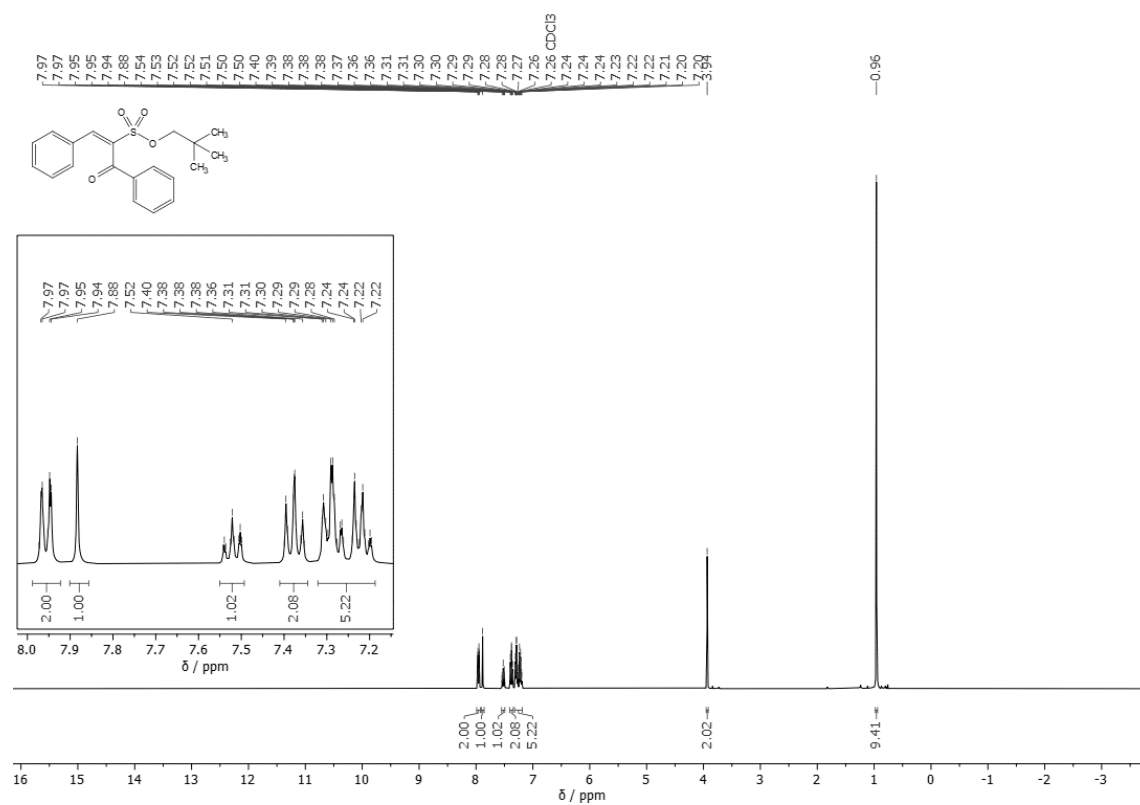
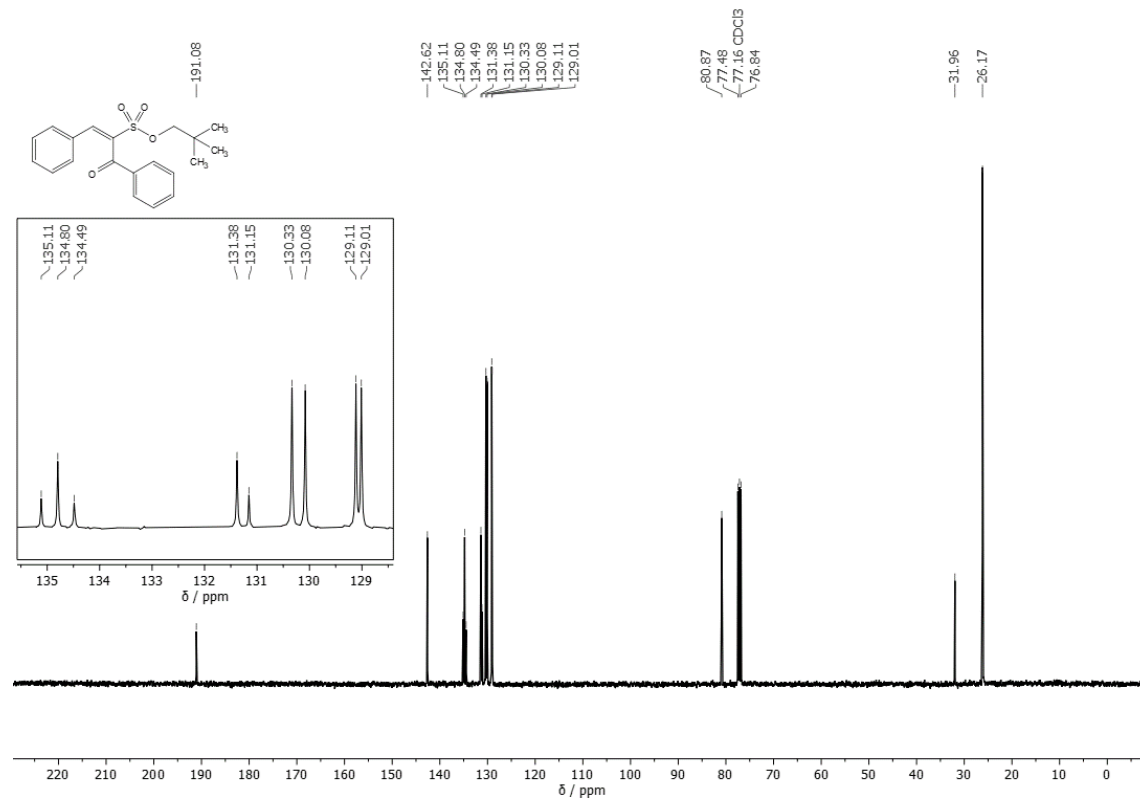


Figure S47: ^{13}C NMR spectrum (101 MHz, CDCl_3) of **8r**.

Figure S48: ¹H NMR spectrum (400 MHz, CDCl₃) of 8s.Figure S49: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8s.

Figure S50: ¹H NMR spectrum (400 MHz, CDCl₃) of **8t**.Figure S51: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8t**.

Figure S52: ¹H NMR spectrum (400 MHz, CDCl₃) of **8u**.Figure S53: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8u**.

Figure S54: ¹H NMR spectrum (400 MHz, CDCl₃) of **8v**.Figure S55: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8v**.

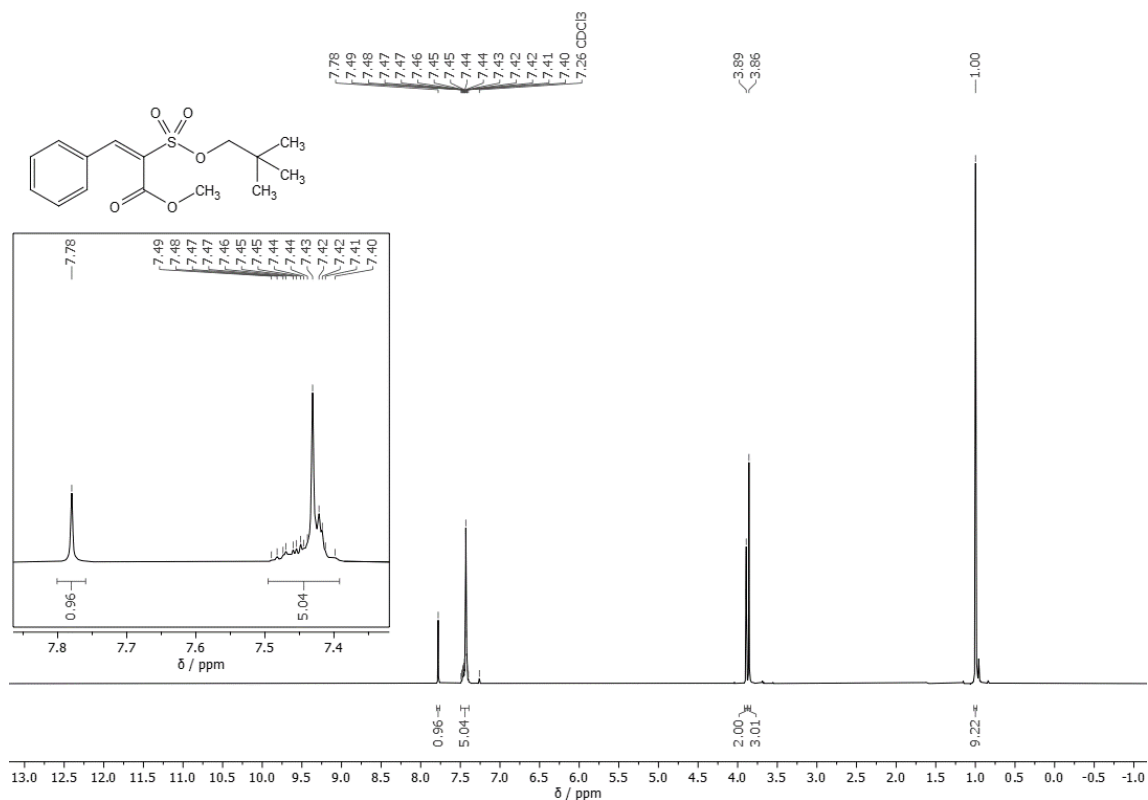


Figure S56: ¹H NMR spectrum (400 MHz, CDCl₃) of **8w**.

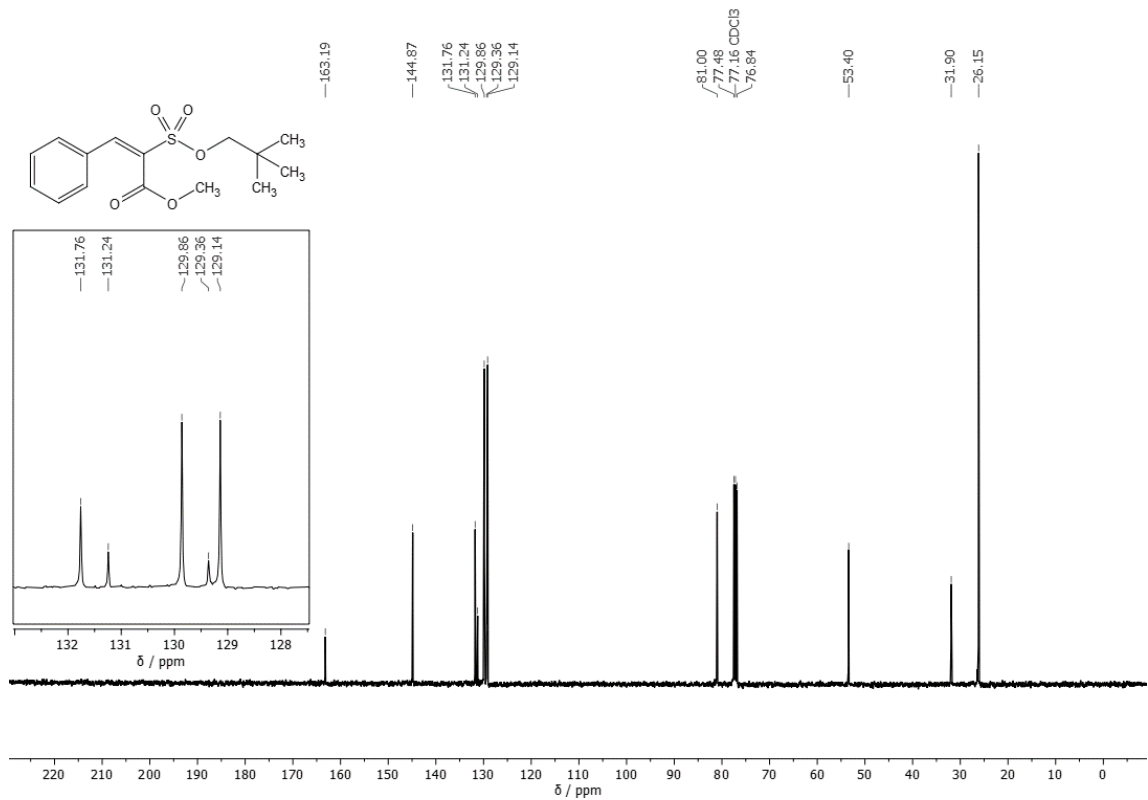


Figure S57: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8w**.

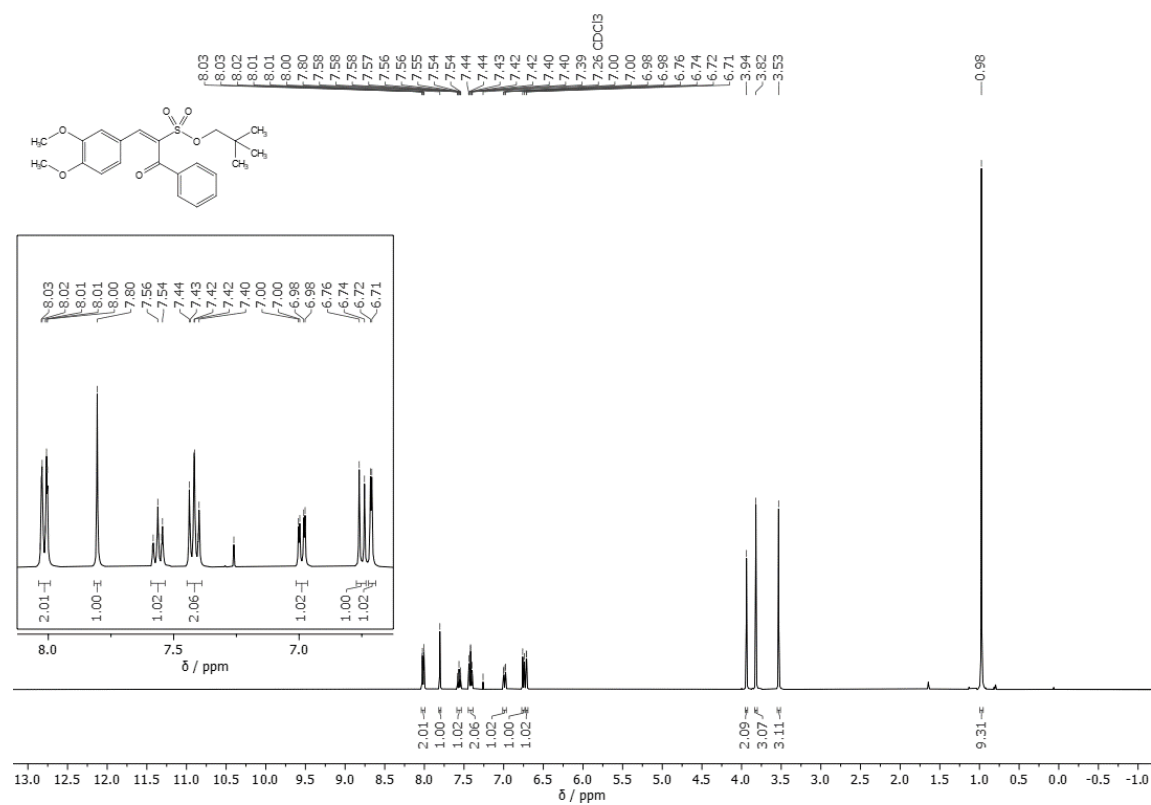


Figure S58: ^1H NMR spectrum (400 MHz, CDCl_3) of **8x**.

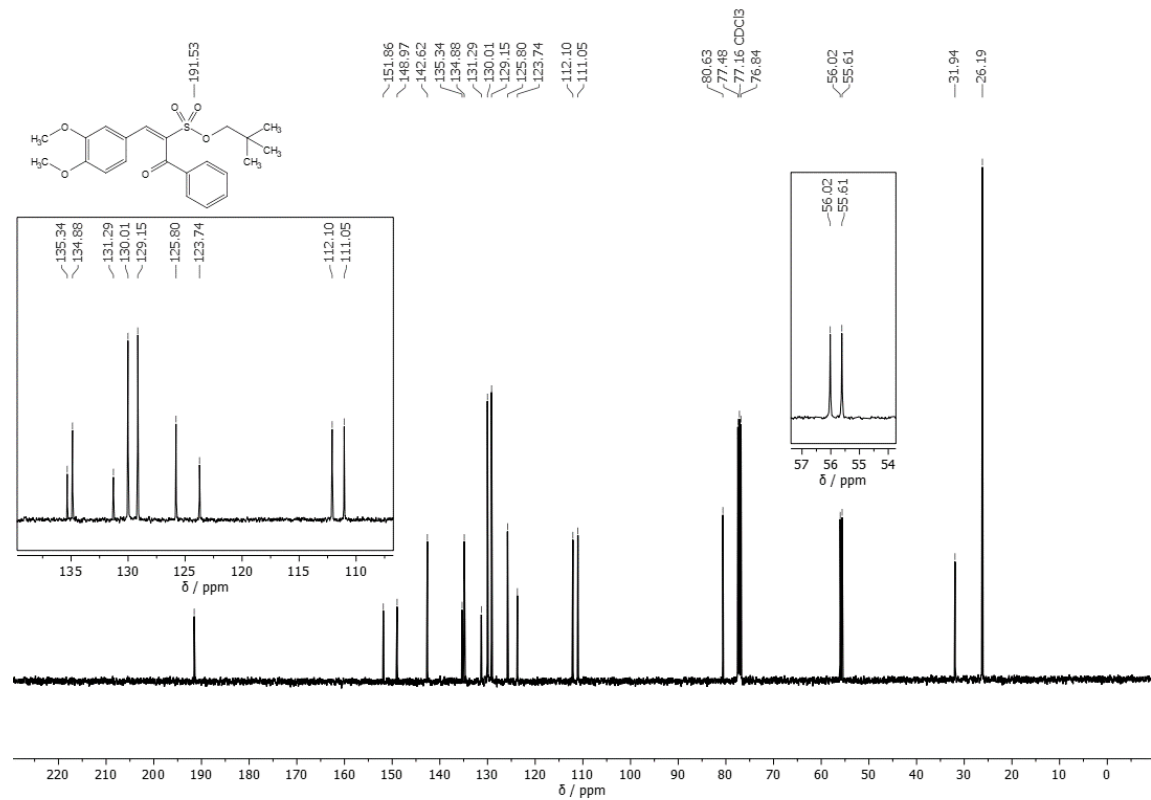
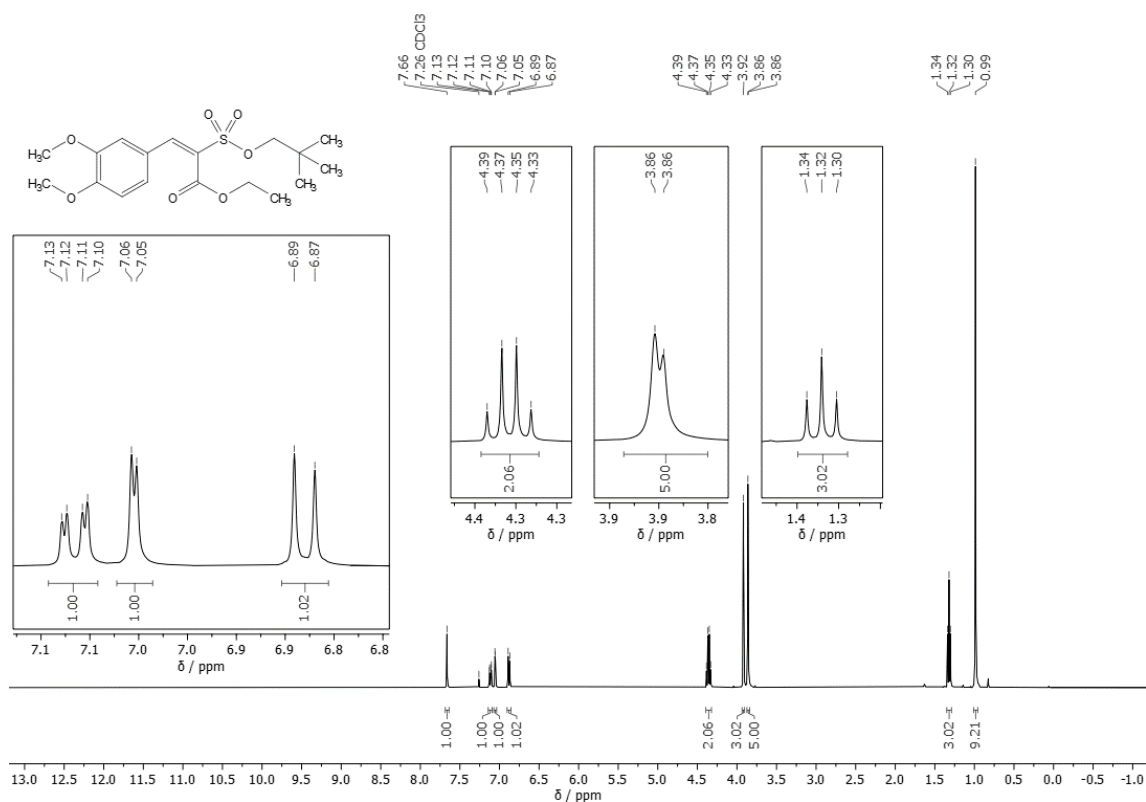
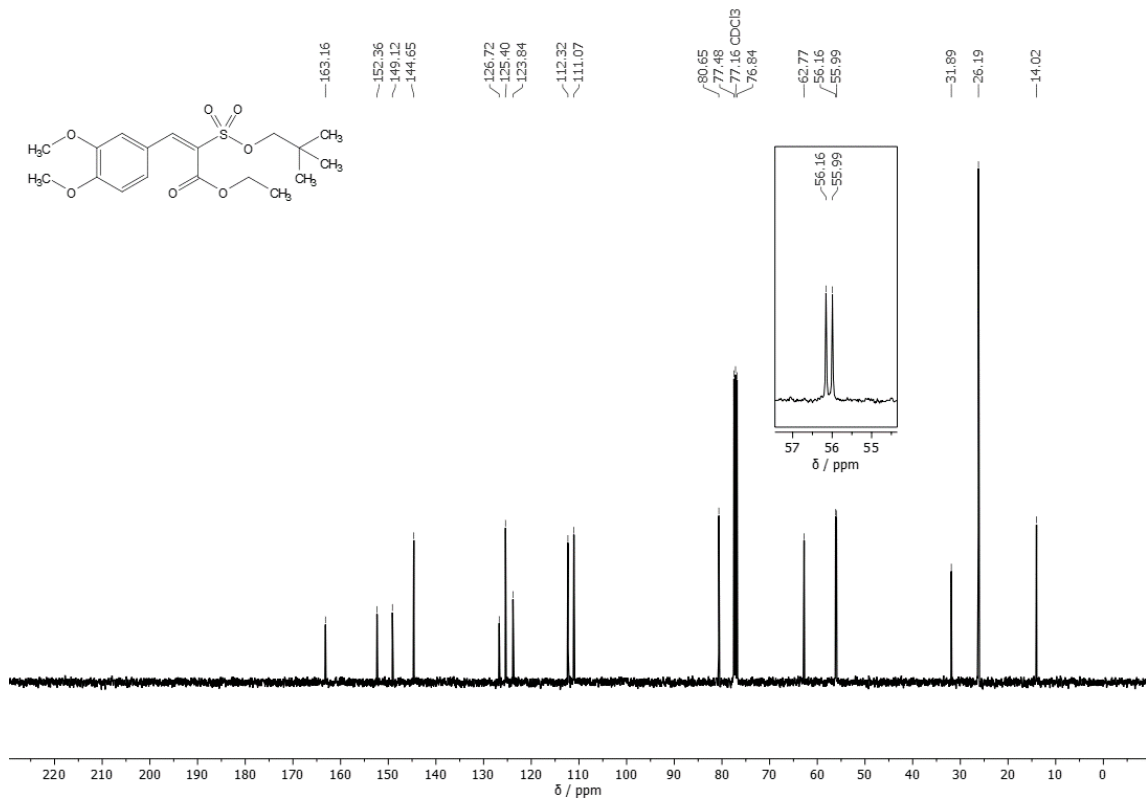
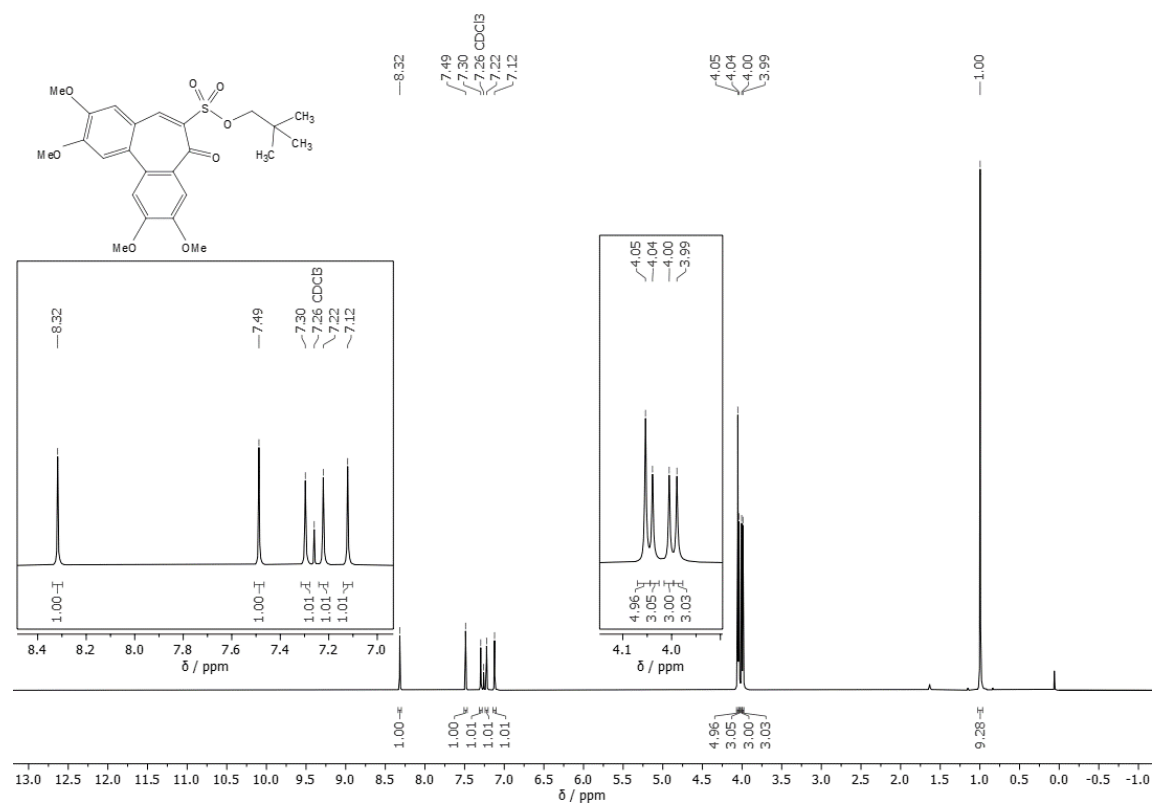
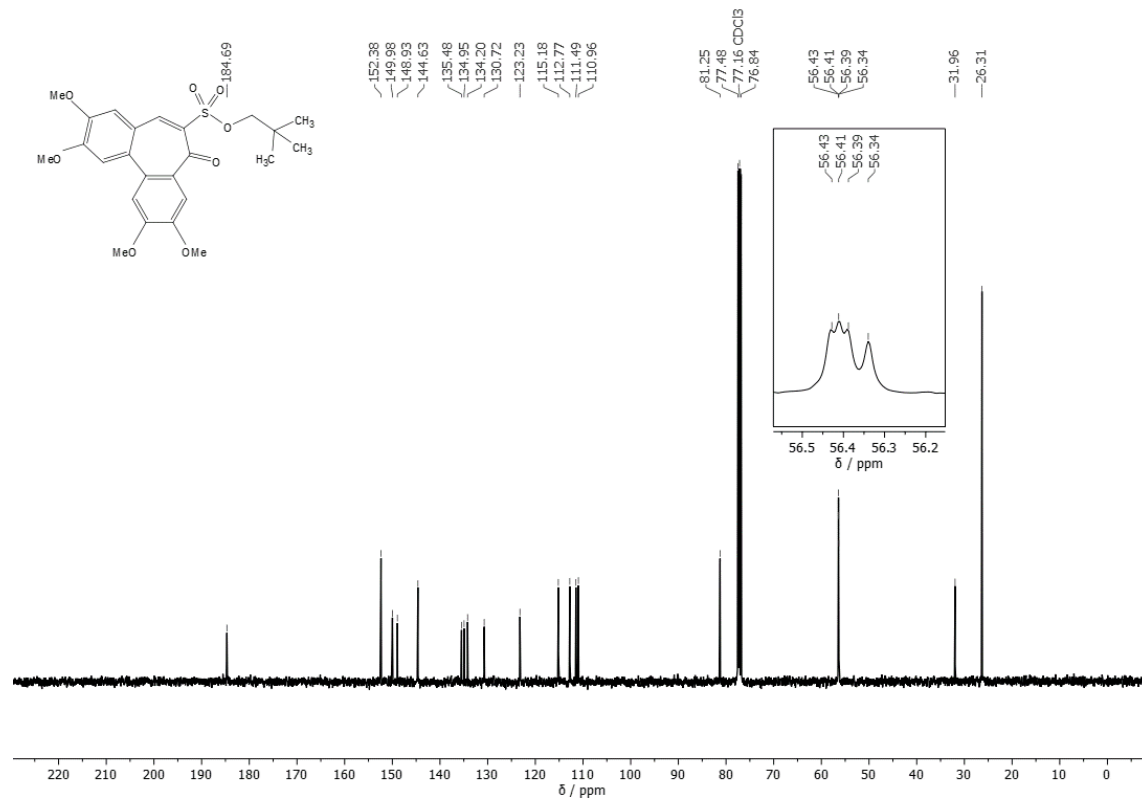
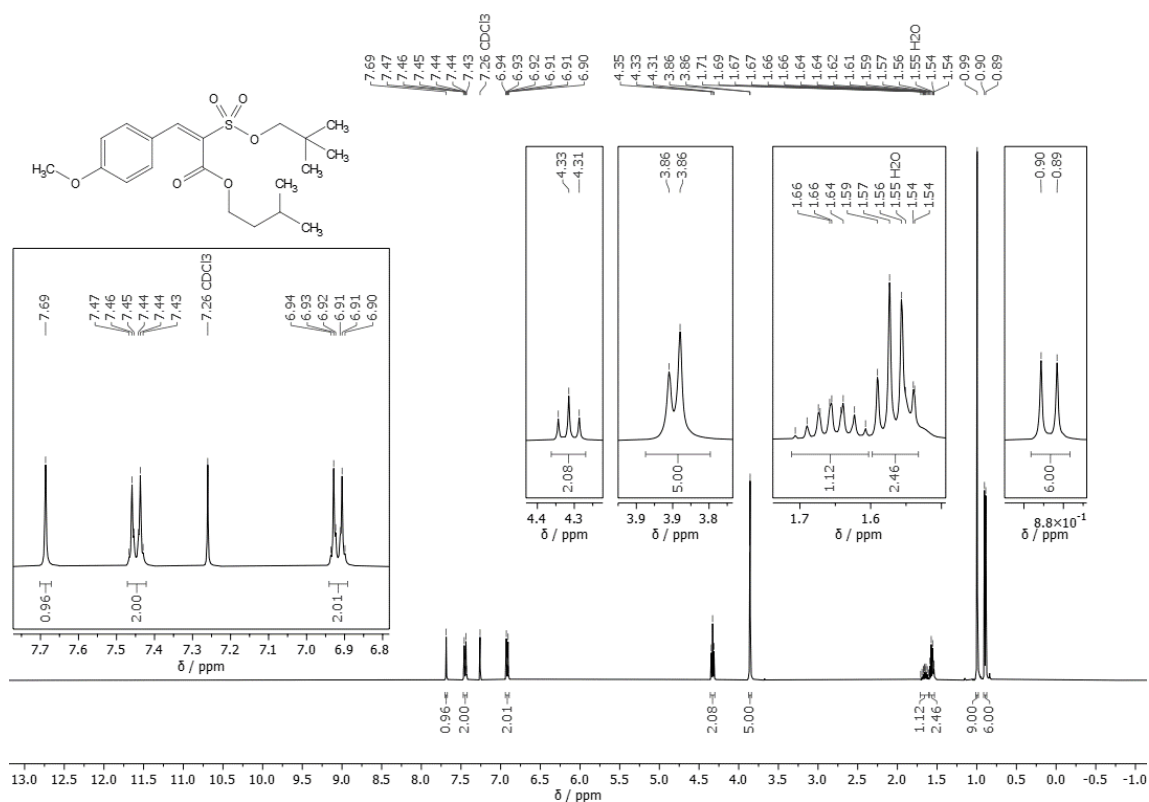
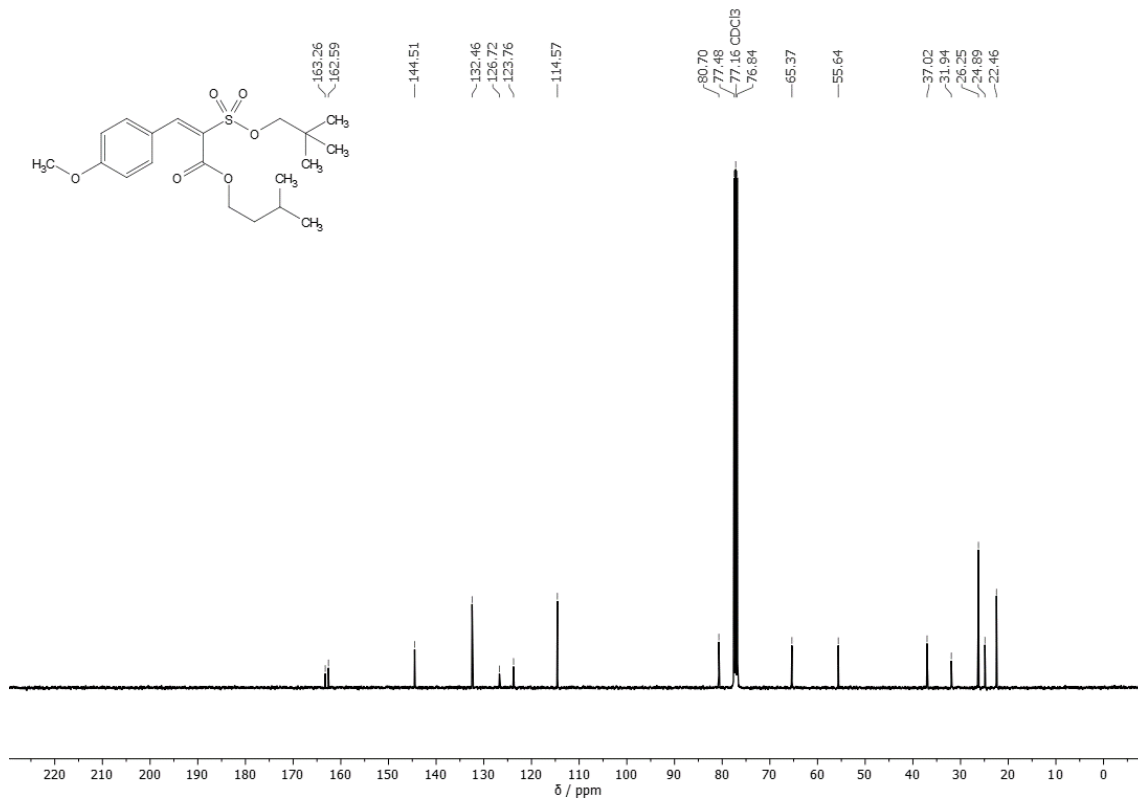
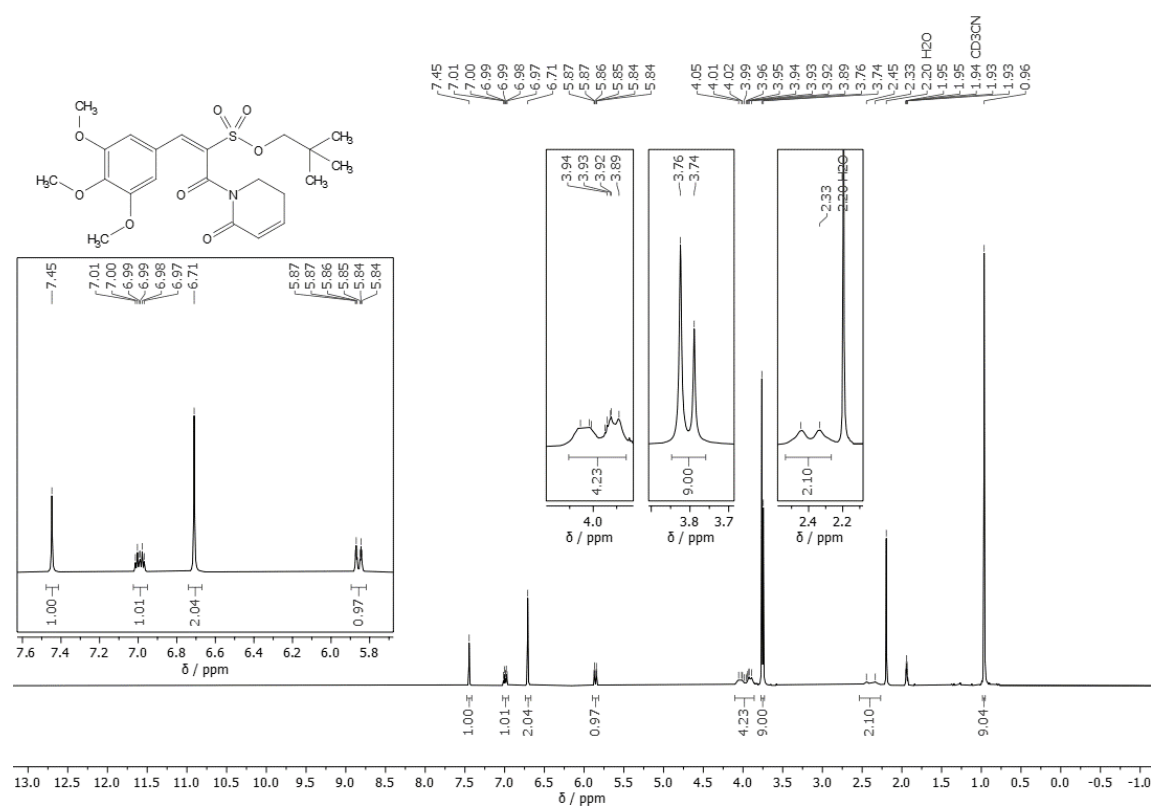
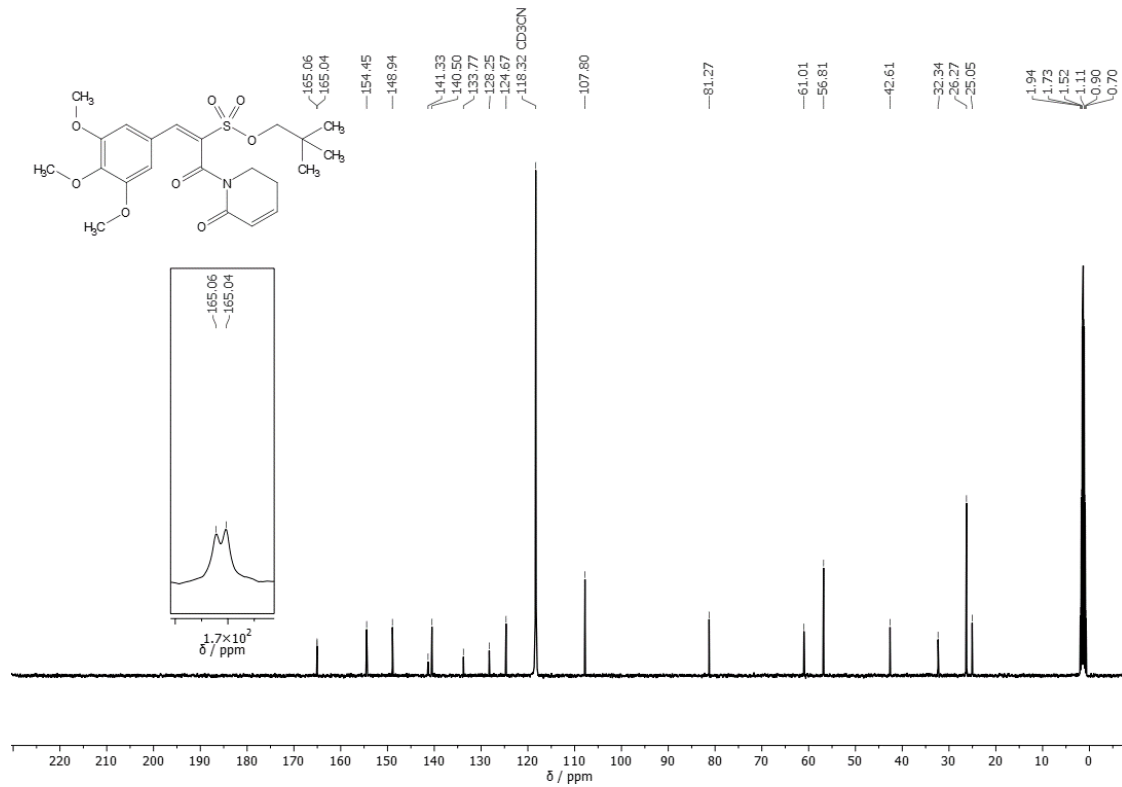


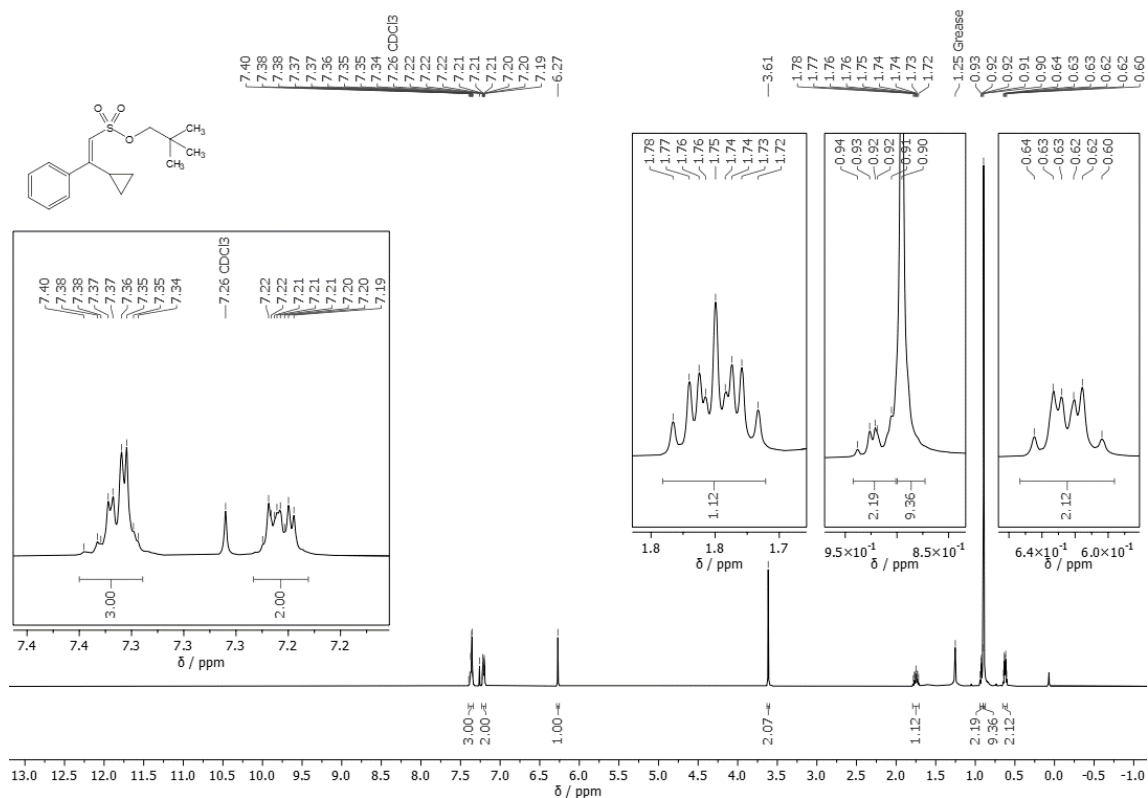
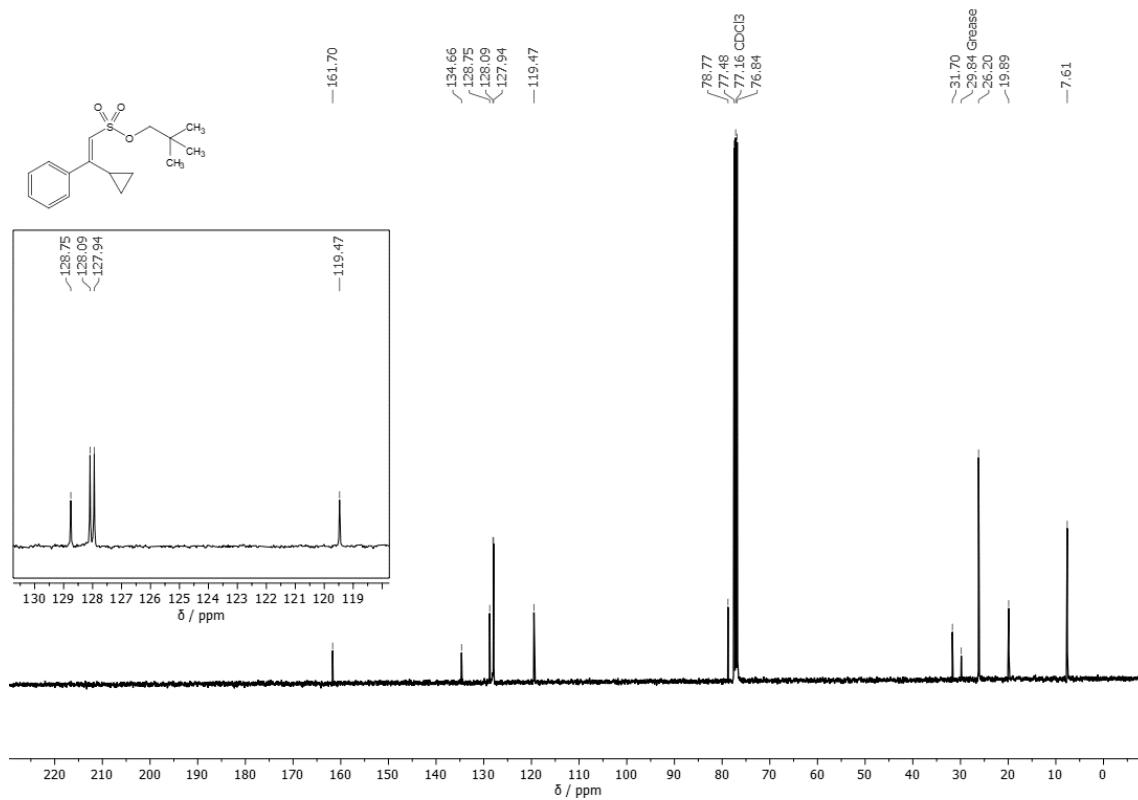
Figure S59: ^{13}C NMR spectrum (101 MHz, CDCl_3) of **8x**.

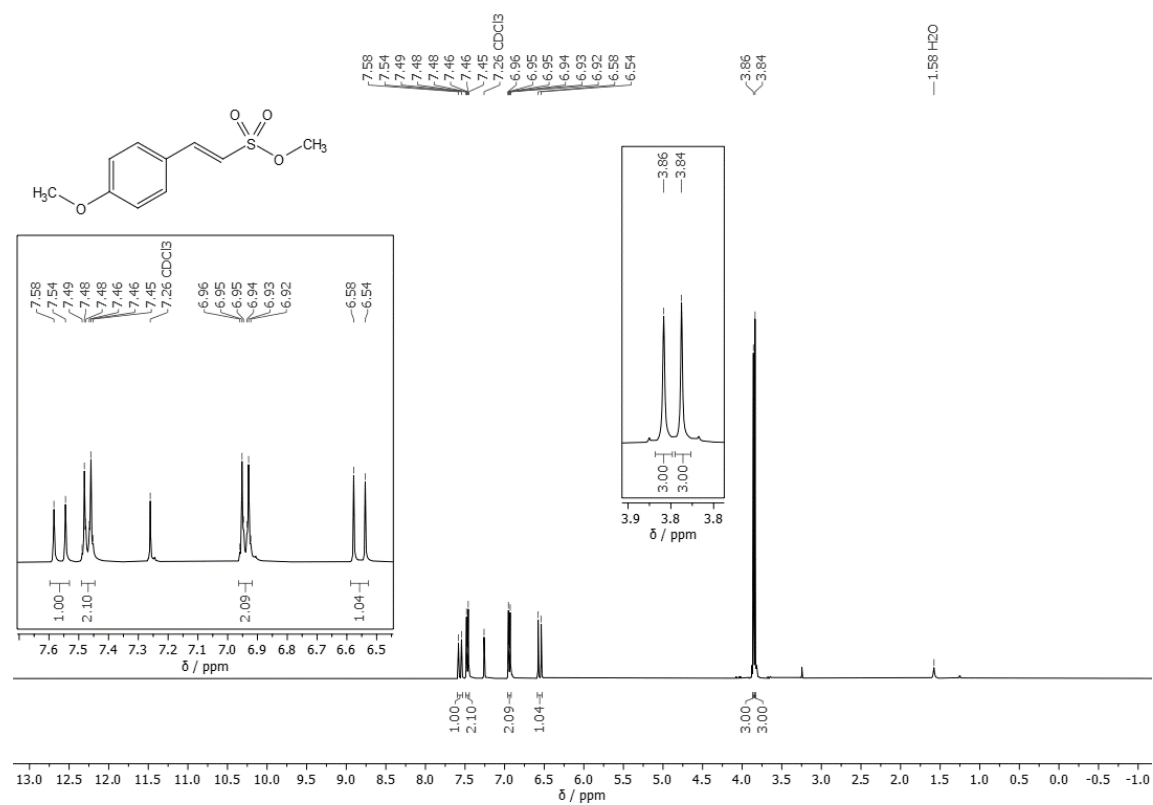
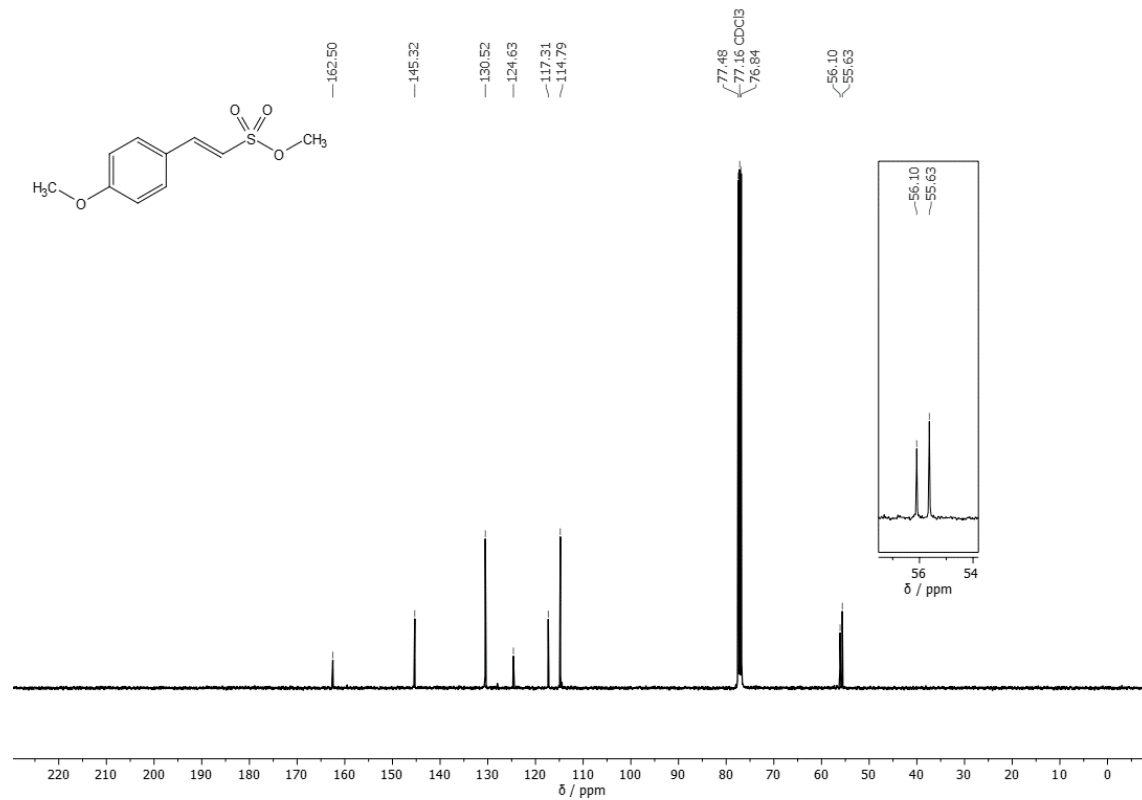
Figure S60: ¹H NMR spectrum (400 MHz, CDCl₃) of **8y**.Figure S61: ¹³C NMR spectrum (101 MHz, CDCl₃) of **8y**.

Figure S62: ^1H NMR spectrum (400 MHz, CDCl_3) of **8z**.Figure S63: ^{13}C NMR spectrum (101 MHz, CDCl_3) of **8z**.

Figure S64: ¹H NMR spectrum (400 MHz, CDCl₃) of 8aa.Figure S65: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8aa.

Figure S66: ¹H NMR spectrum (400 MHz, CD₃CN) of **8ab**.Figure S67: ¹³C NMR spectrum (101 MHz, CD₃CN) of **8ab**.

Figure S68: ¹H NMR spectrum (400 MHz, CDCl₃) of 8ac.Figure S69: ¹³C NMR spectrum (101 MHz, CDCl₃) of 8ac.

Figure S70: ¹H NMR spectrum (400 MHz, CDCl₃) of 9a.Figure S71: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9a.

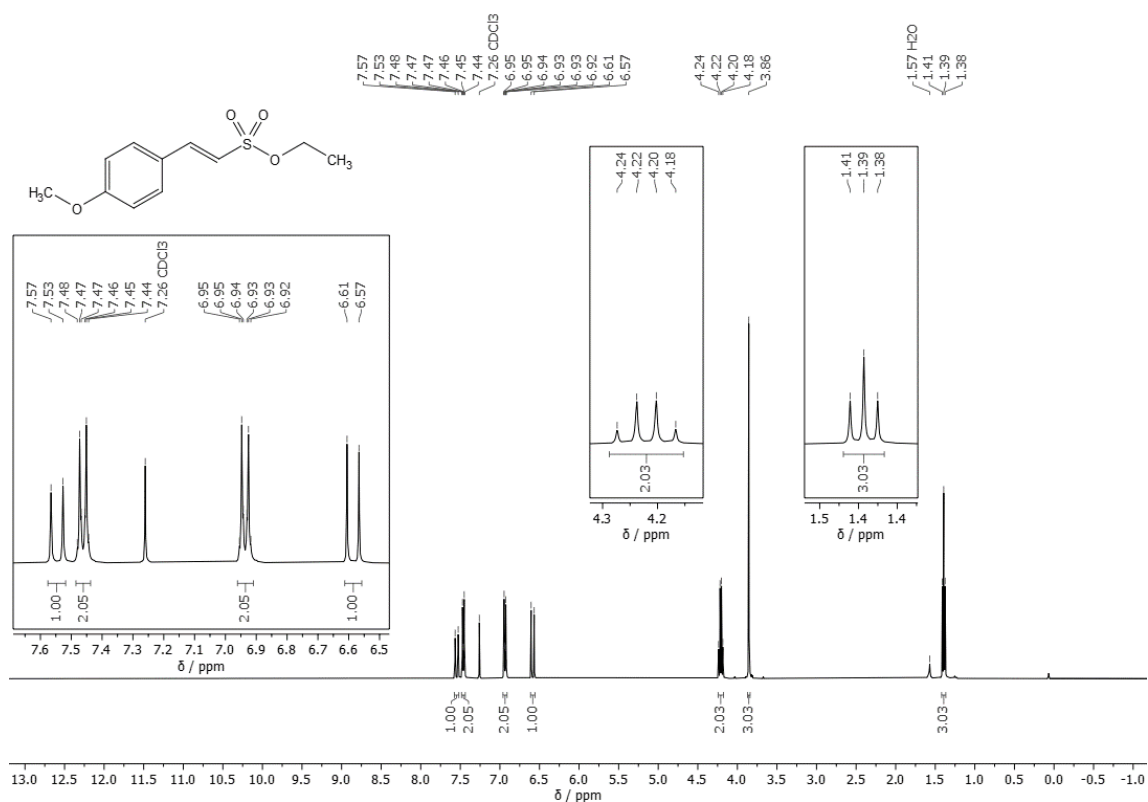


Figure S72: ¹H NMR spectrum (400 MHz, CDCl₃) of **9b**.

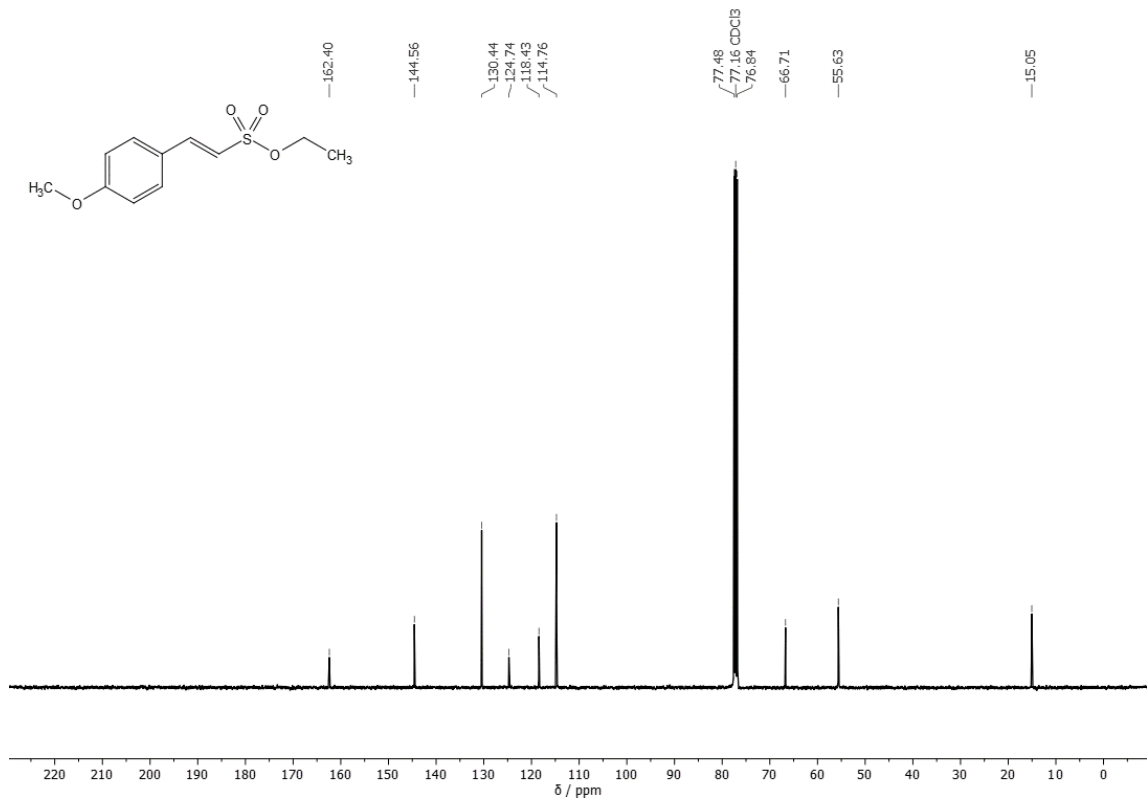
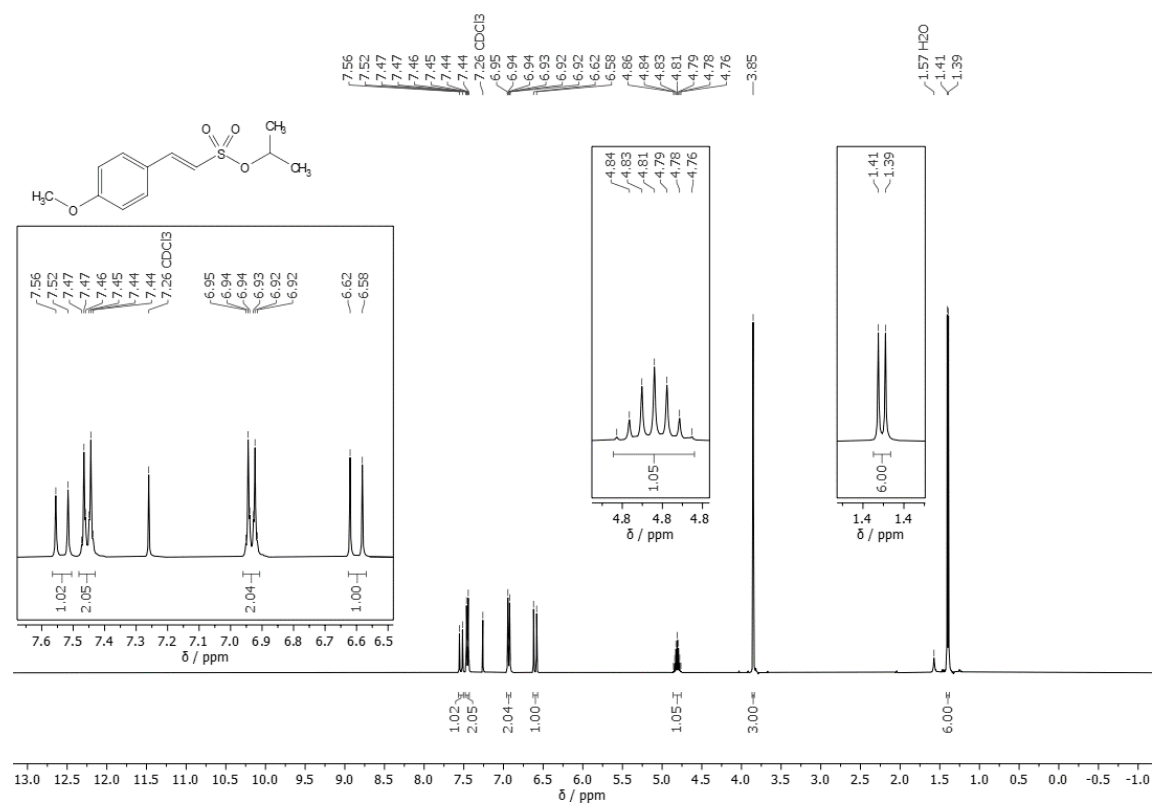
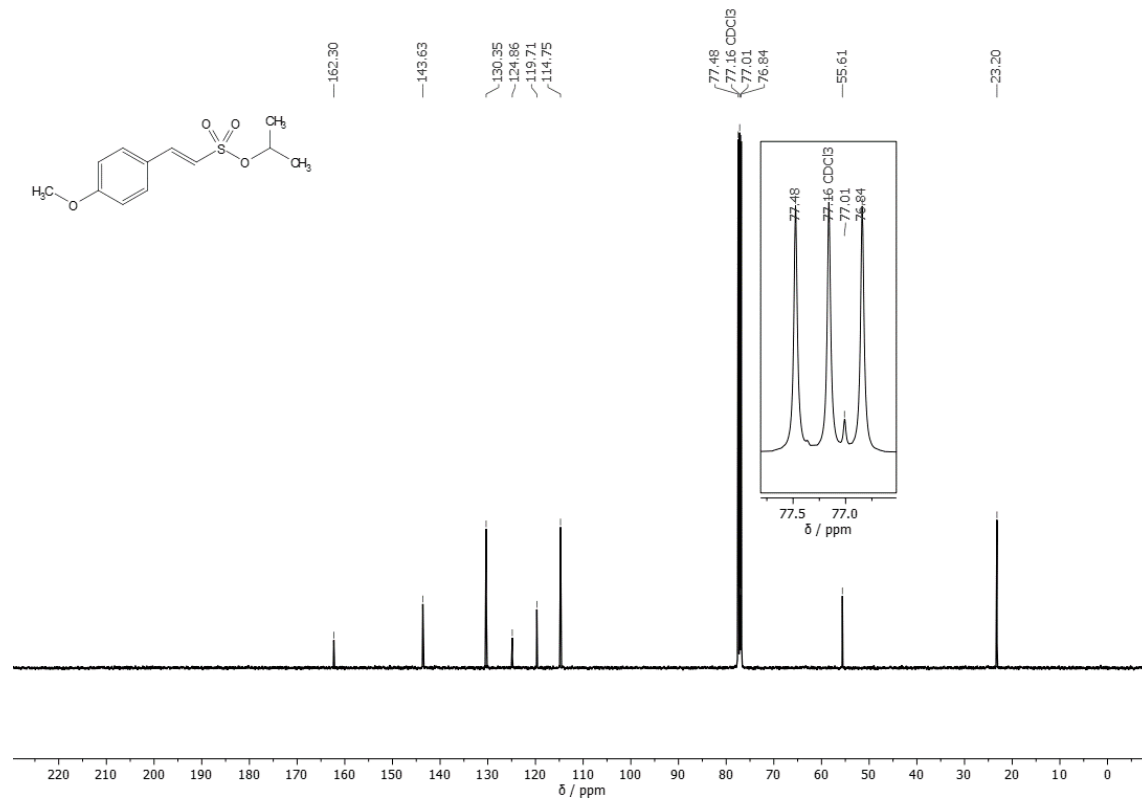
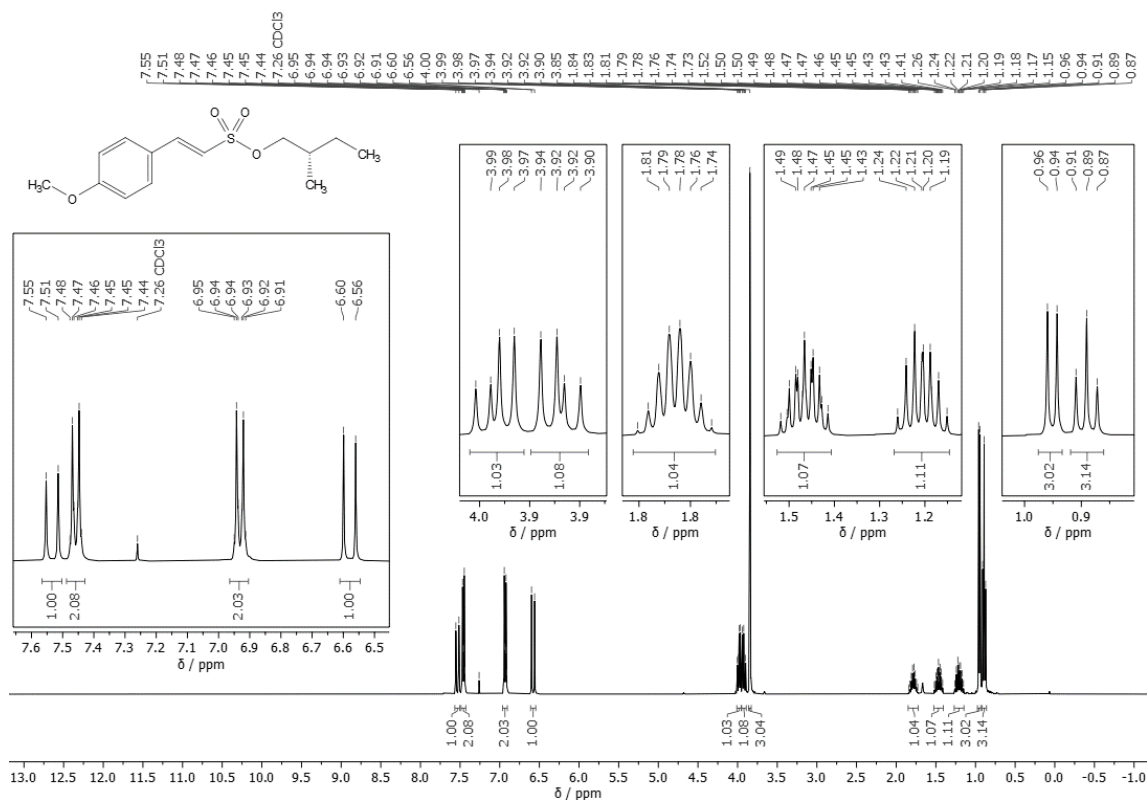
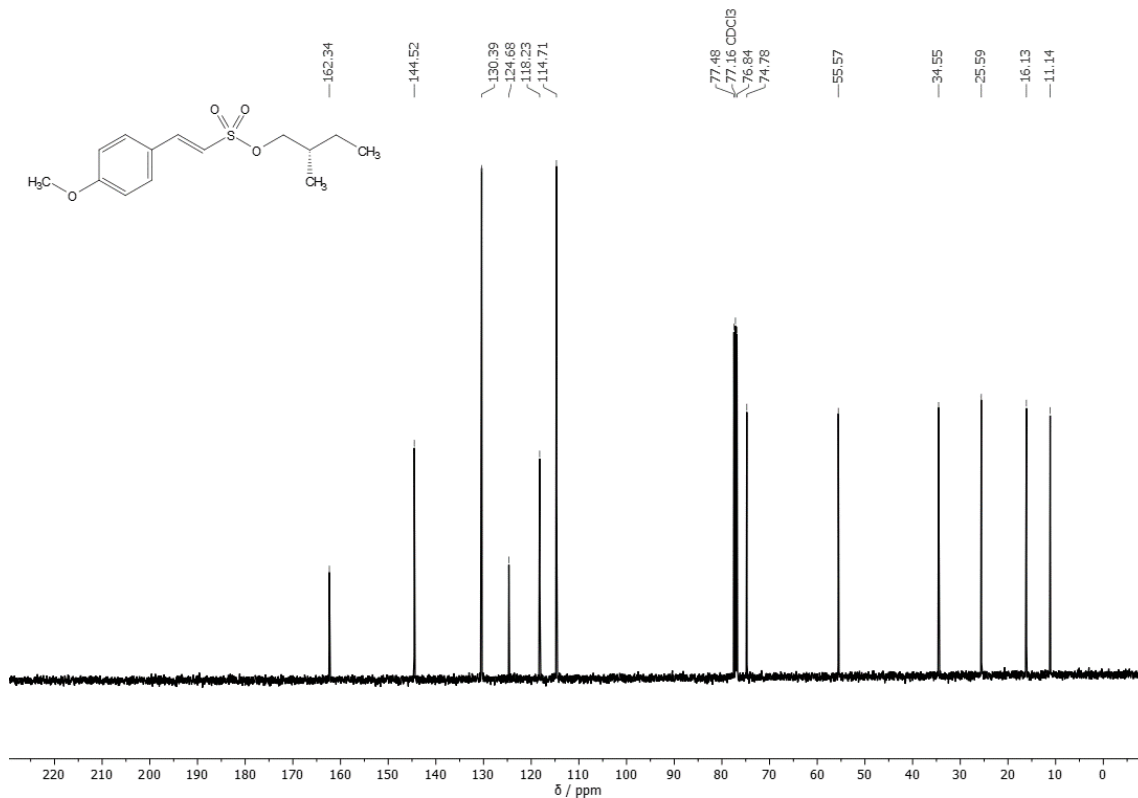
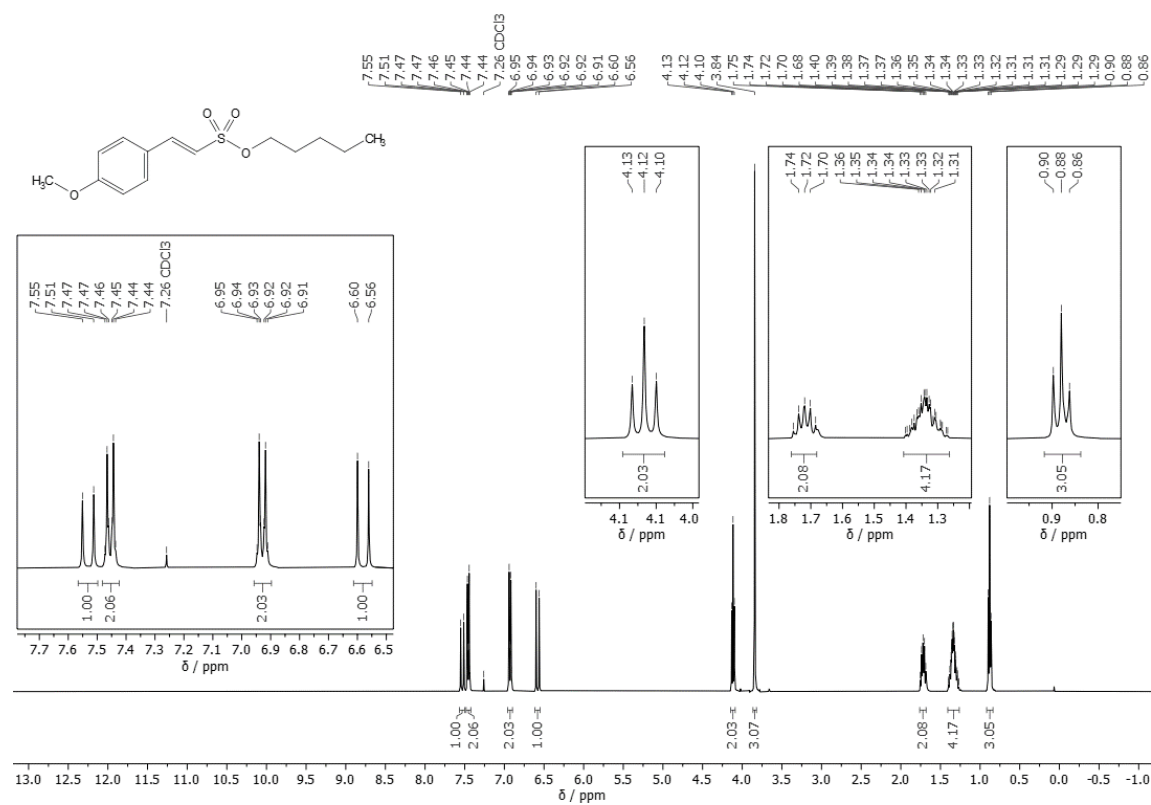
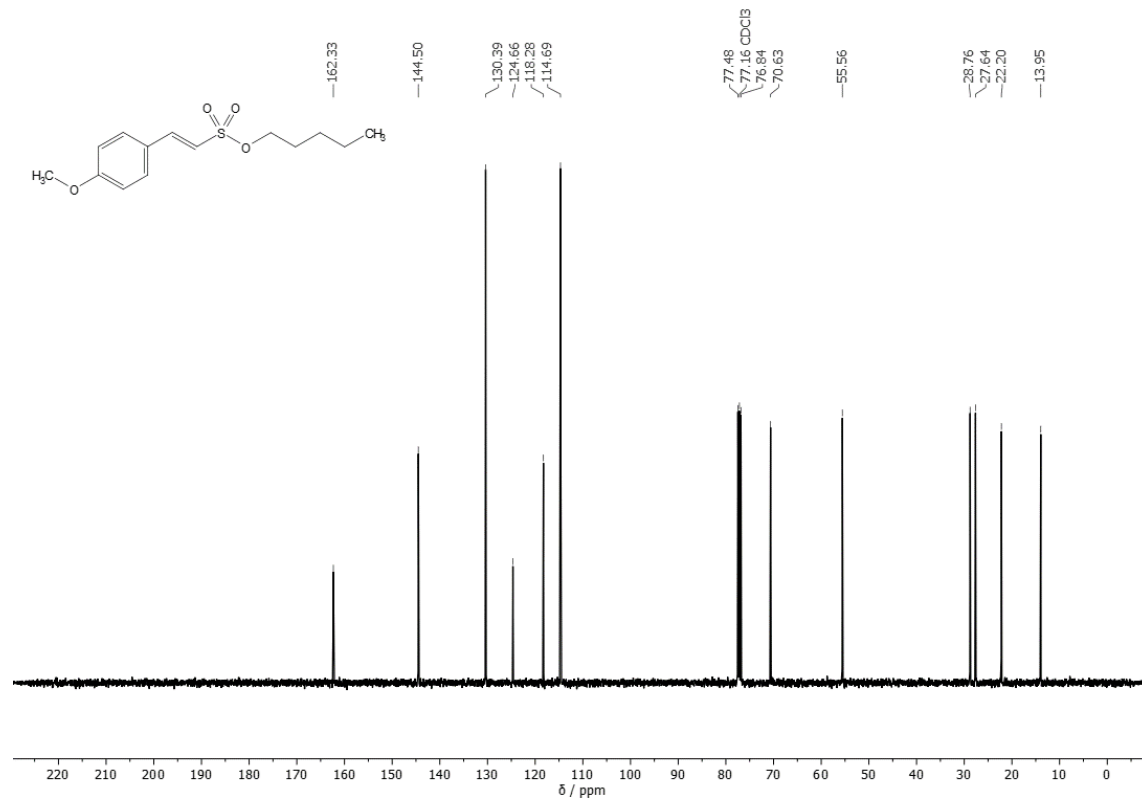
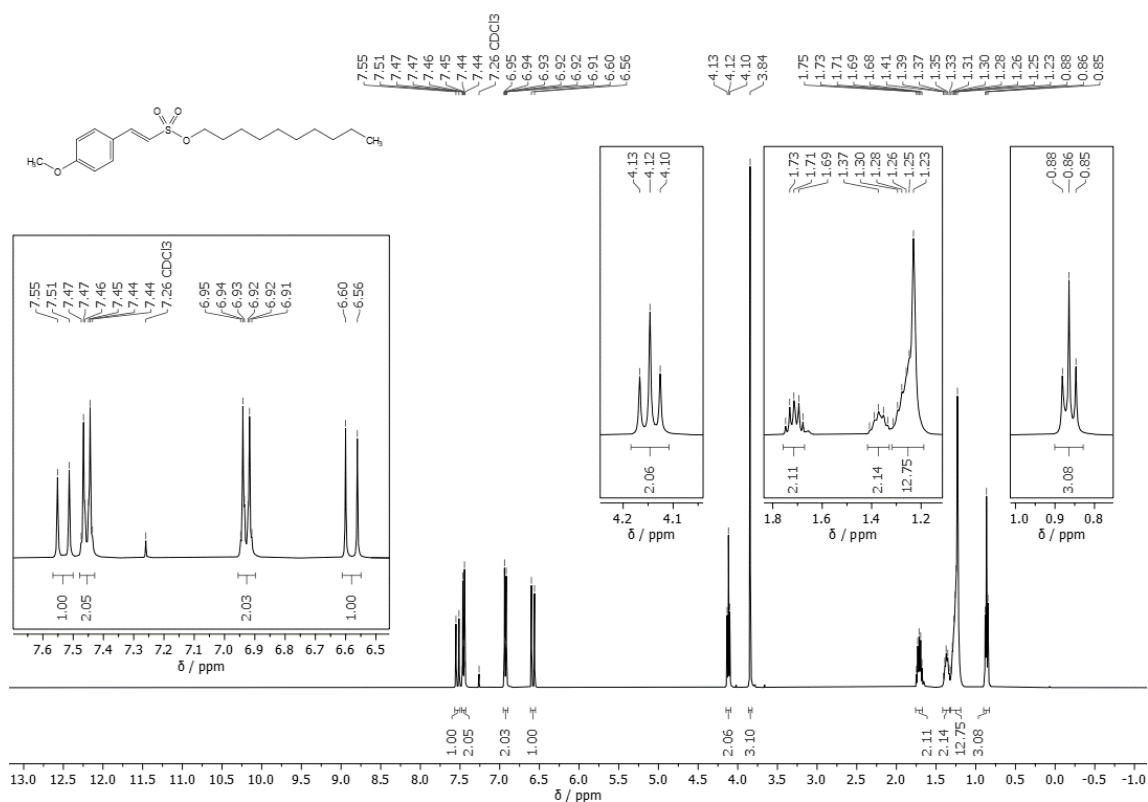
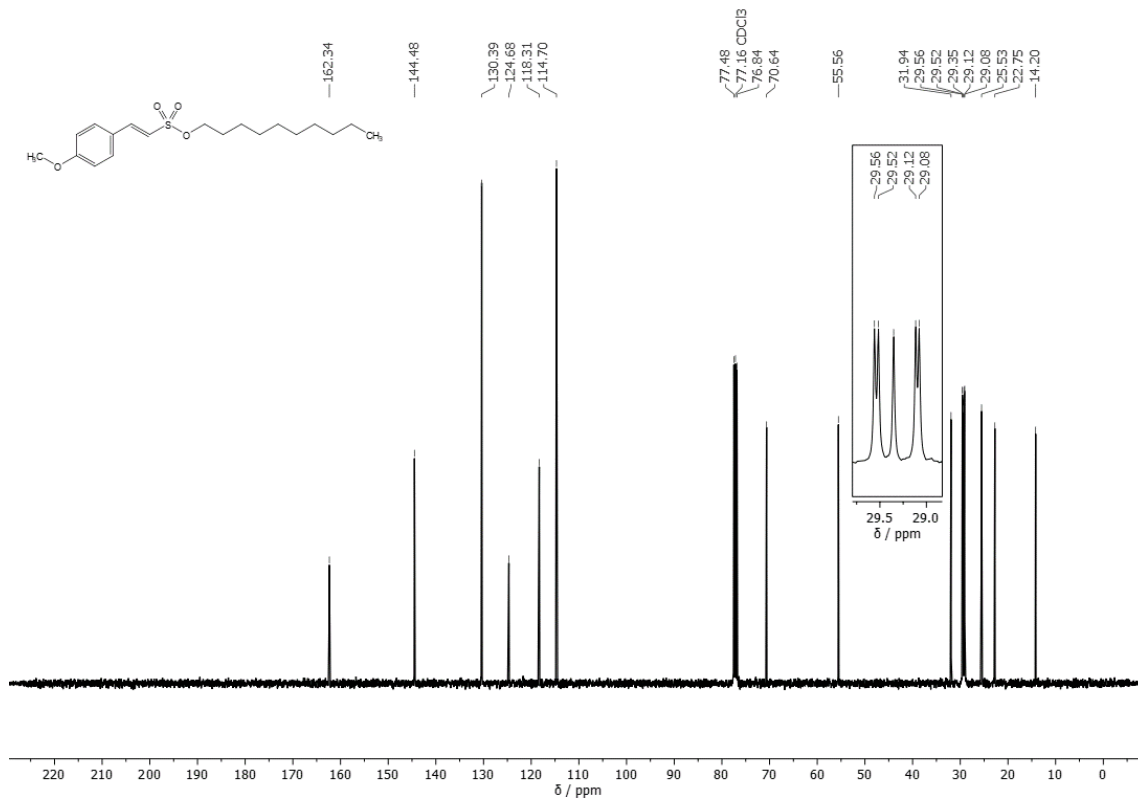


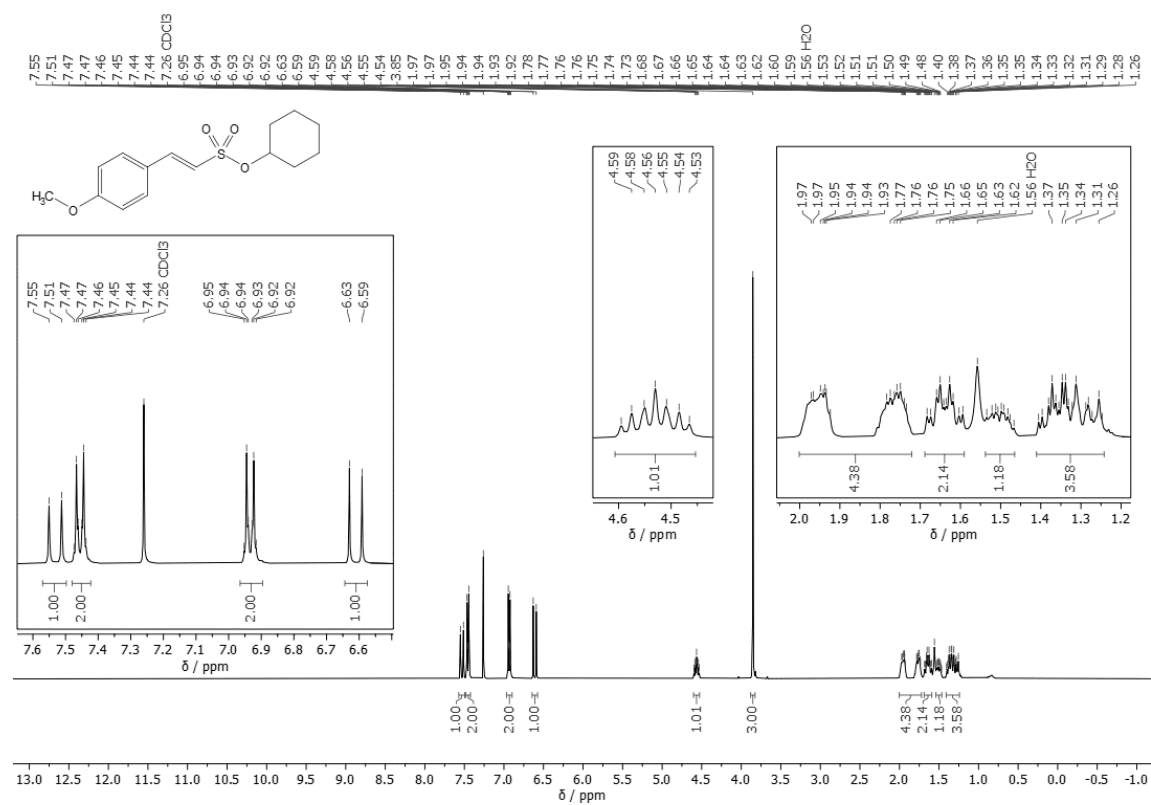
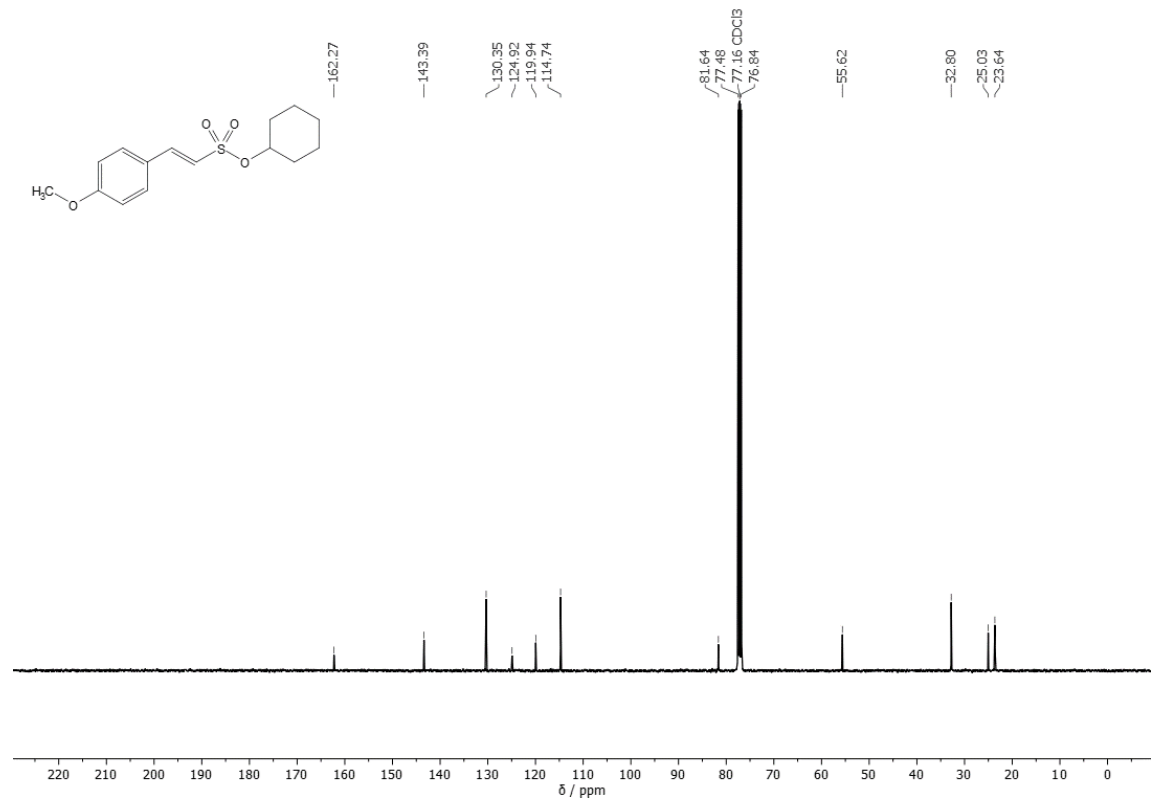
Figure S73: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9b**.

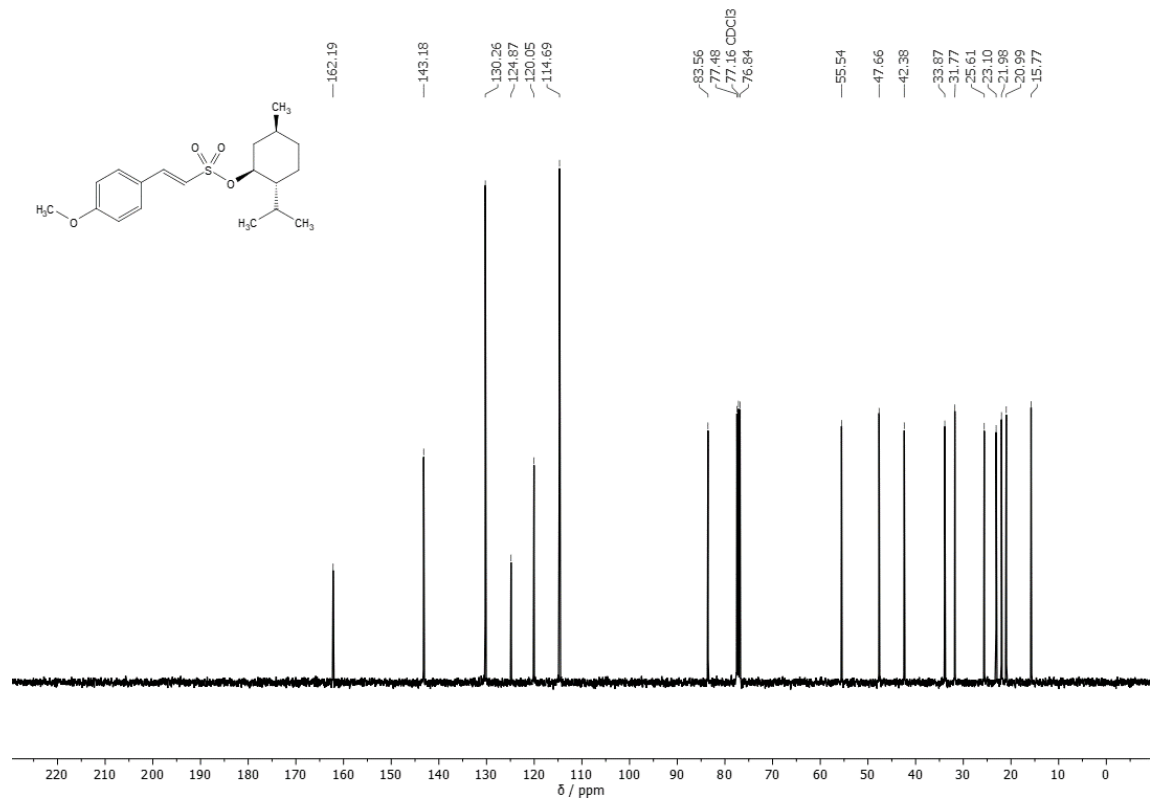
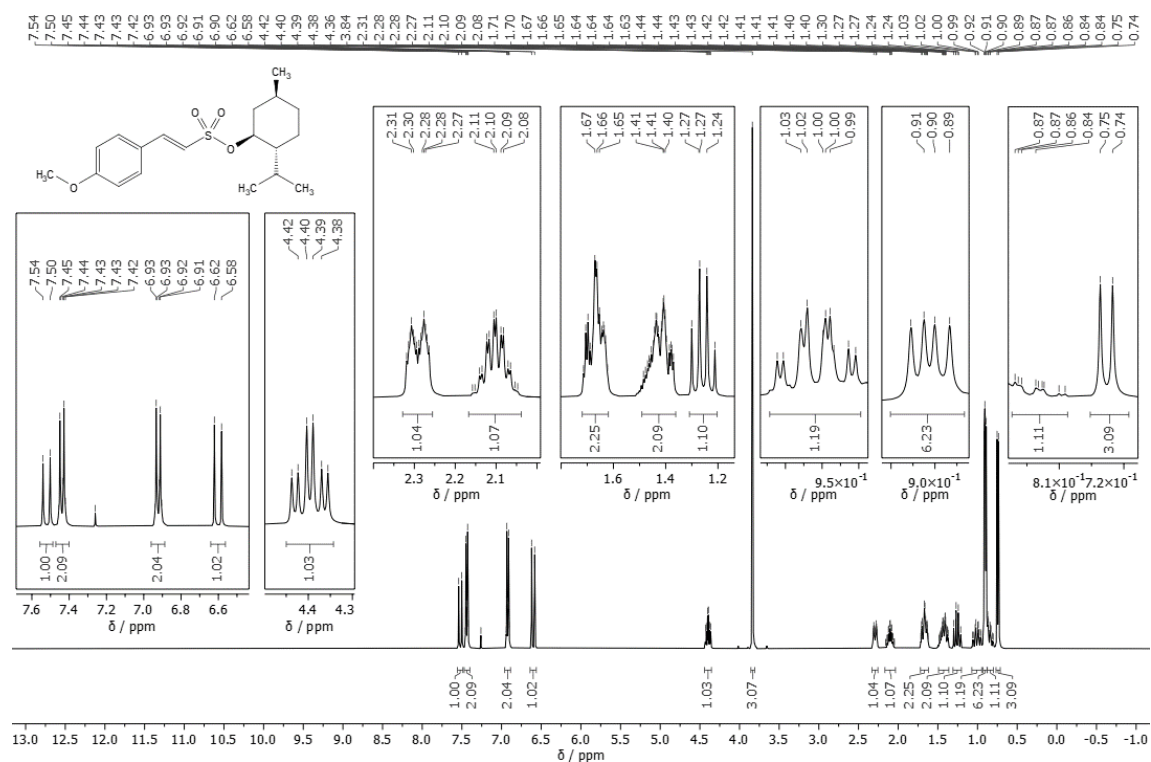
Figure S74: ¹H NMR spectrum (400 MHz, CDCl₃) of 9c.Figure S75: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9c.

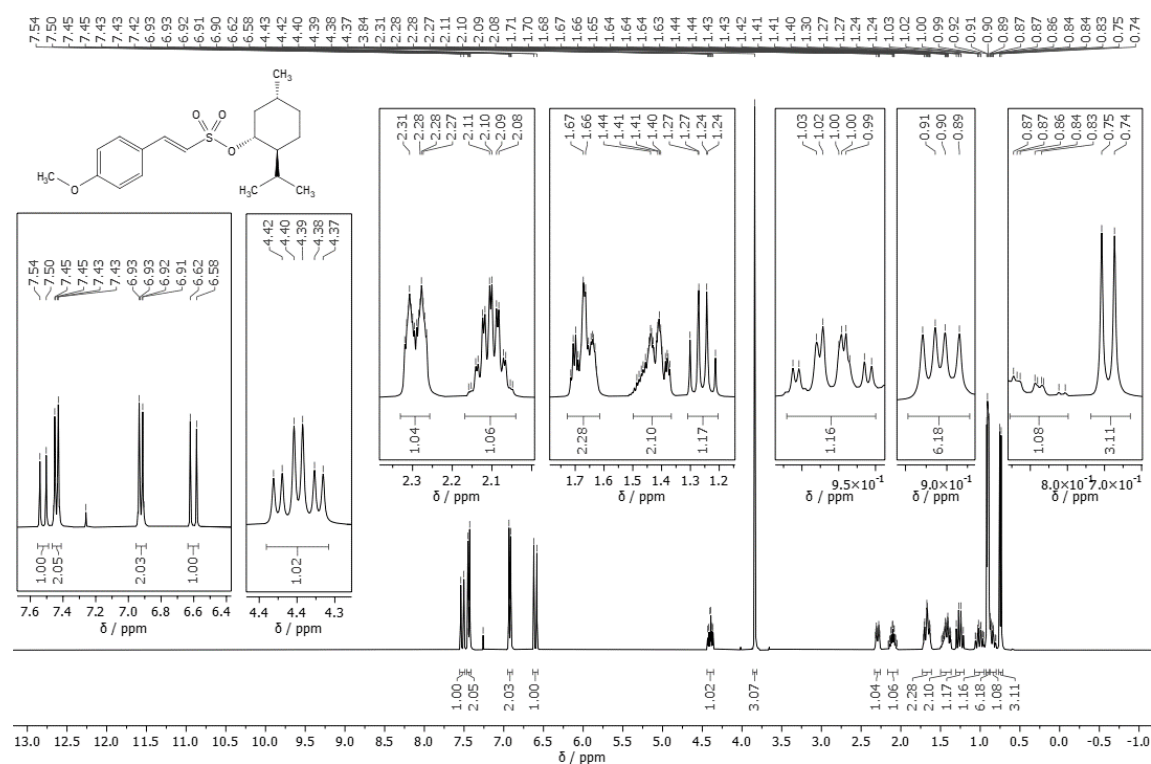
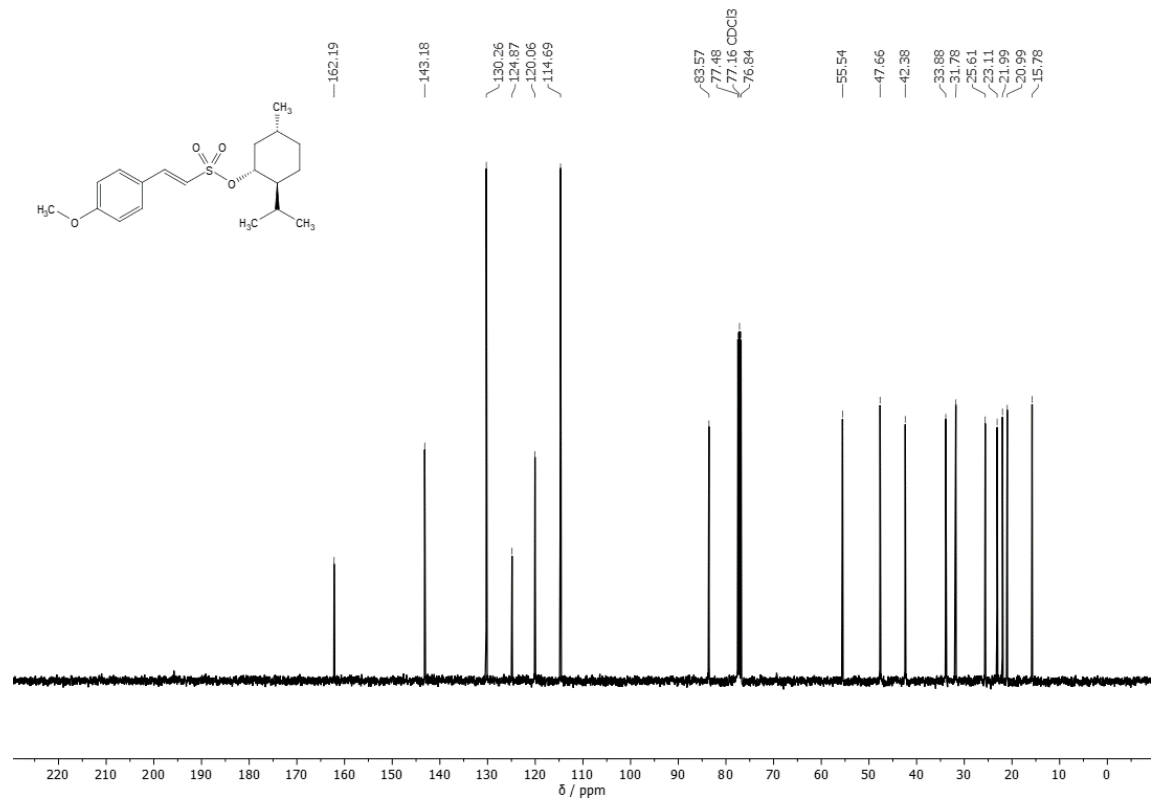
Figure S76: ¹H NMR spectrum (400 MHz, CDCl₃) of 9d.Figure S77: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9d.

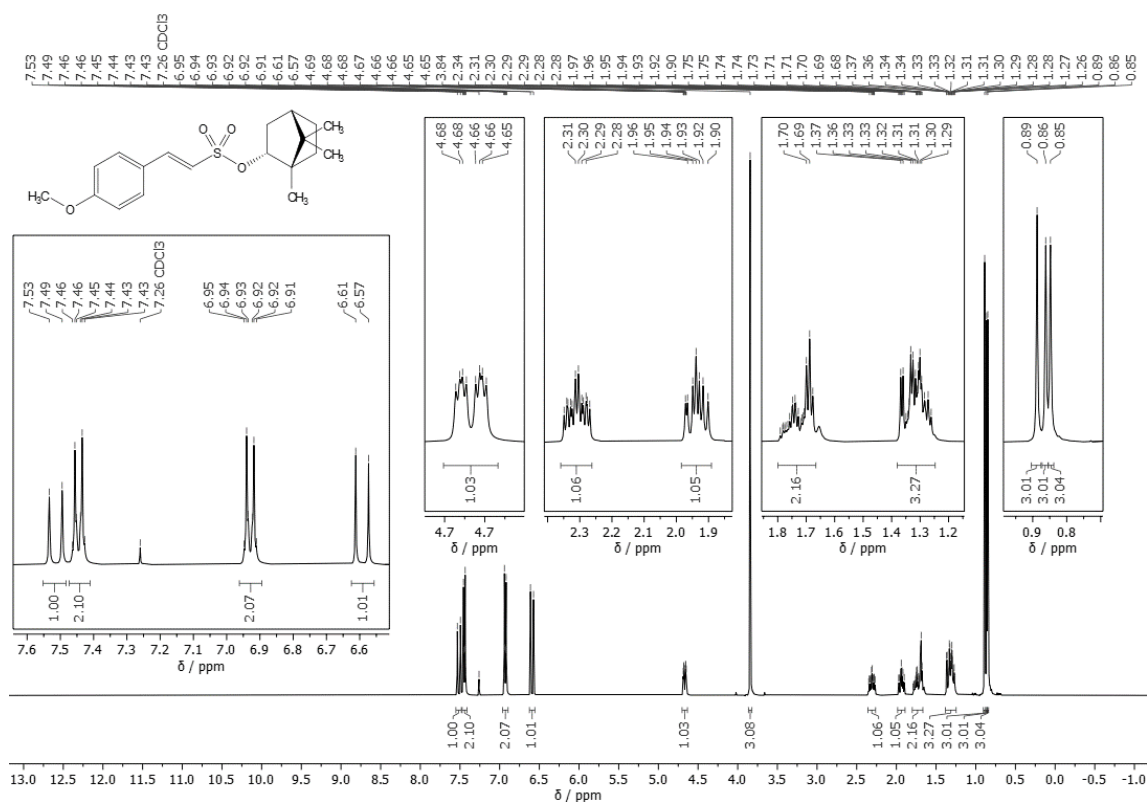
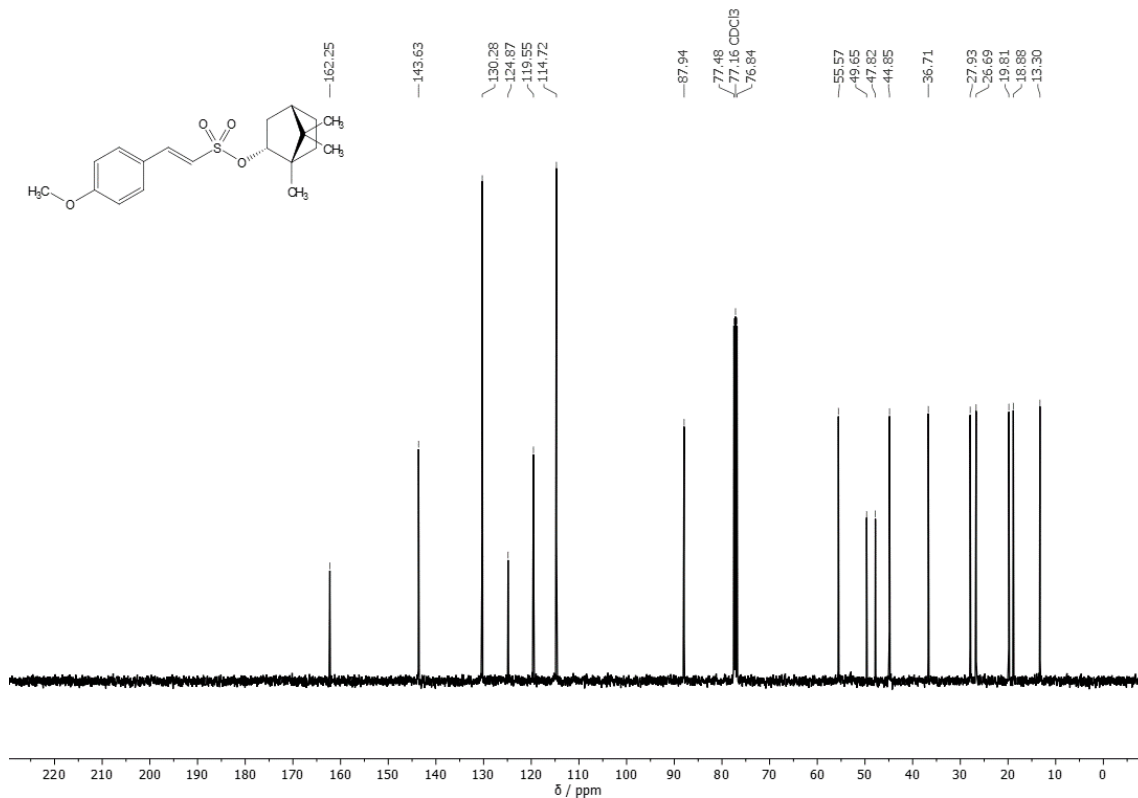
Figure S78: ¹H NMR spectrum (400 MHz, CDCl₃) of 9e.Figure S79: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9e.

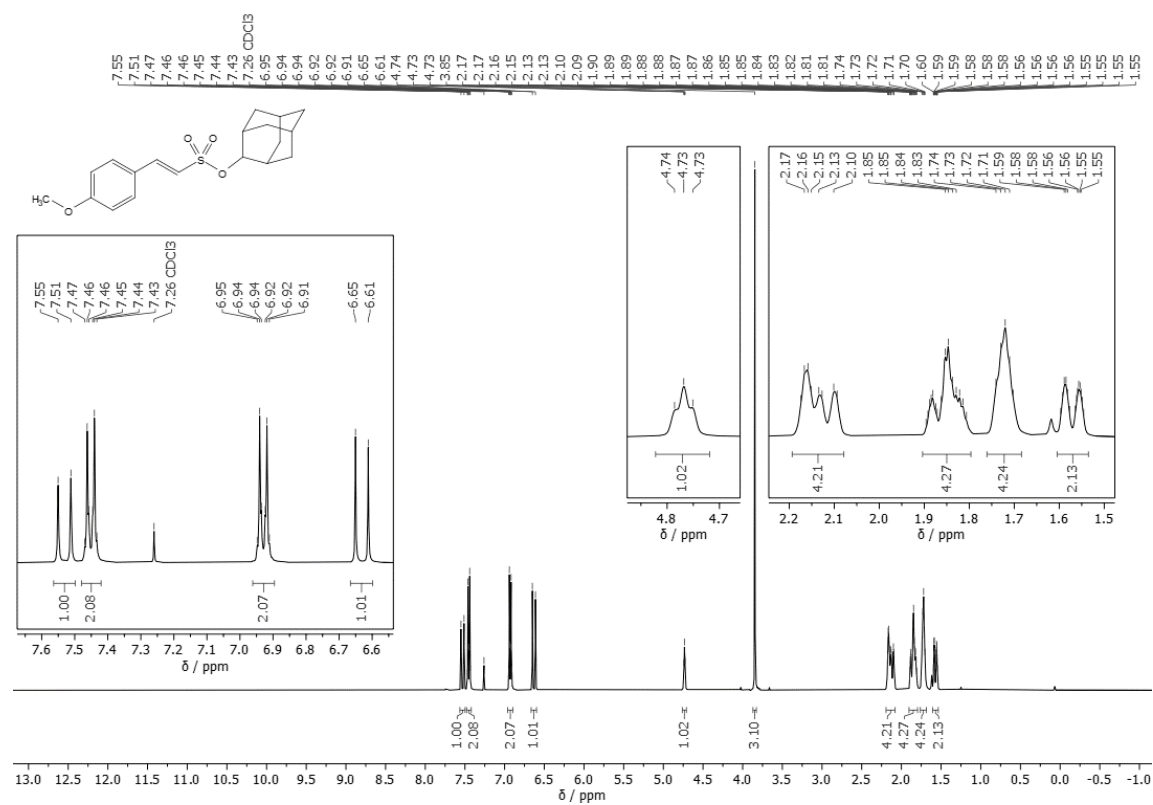
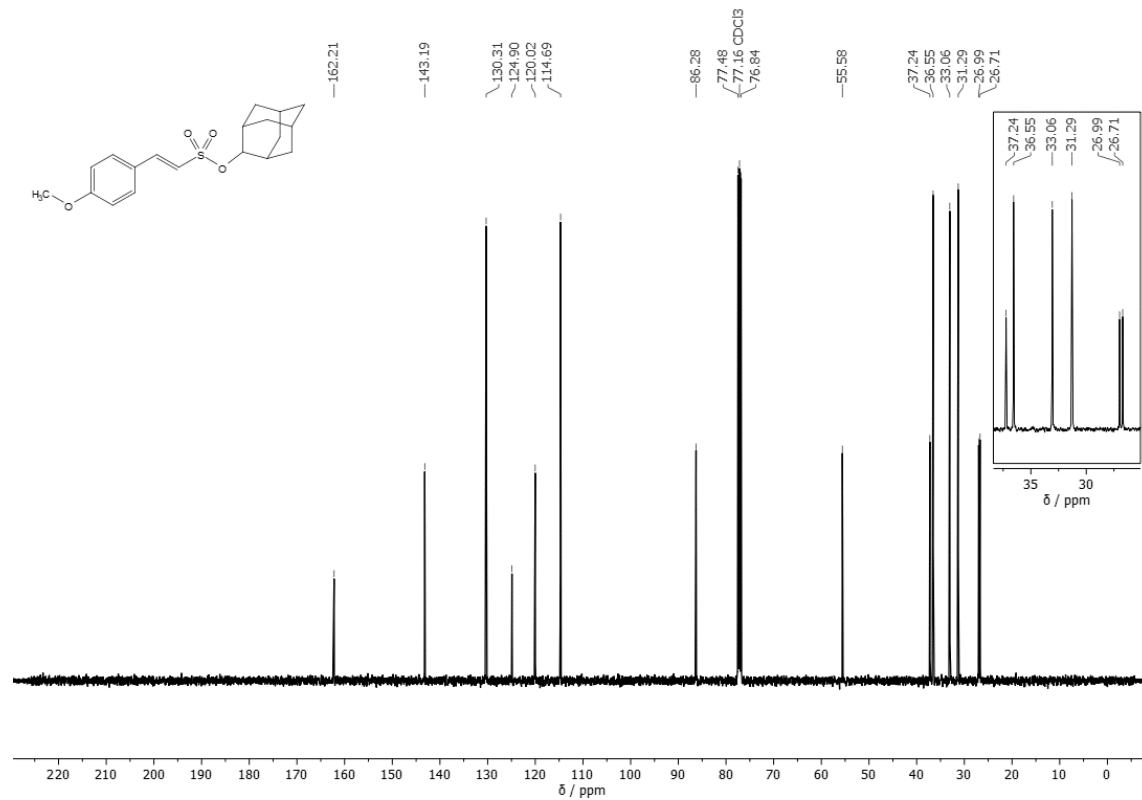
Figure S80: ¹H NMR spectrum (400 MHz, CDCl₃) of **9f**.Figure S81: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9f**.

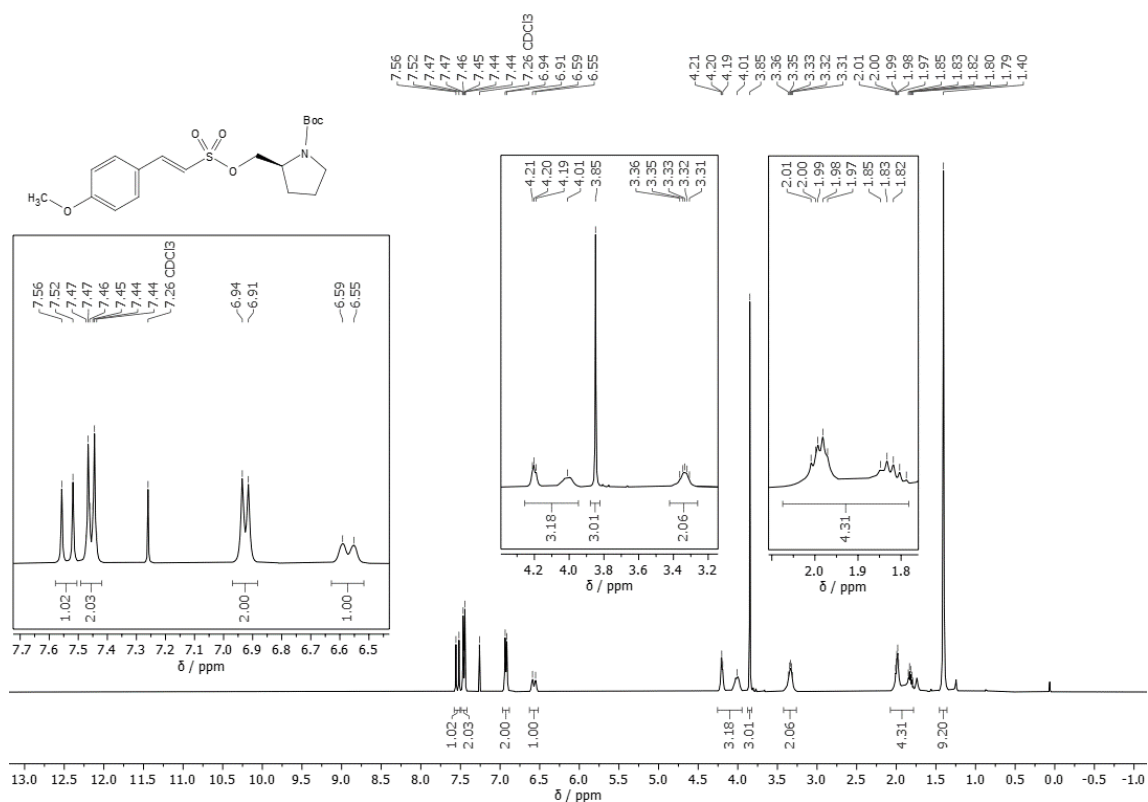
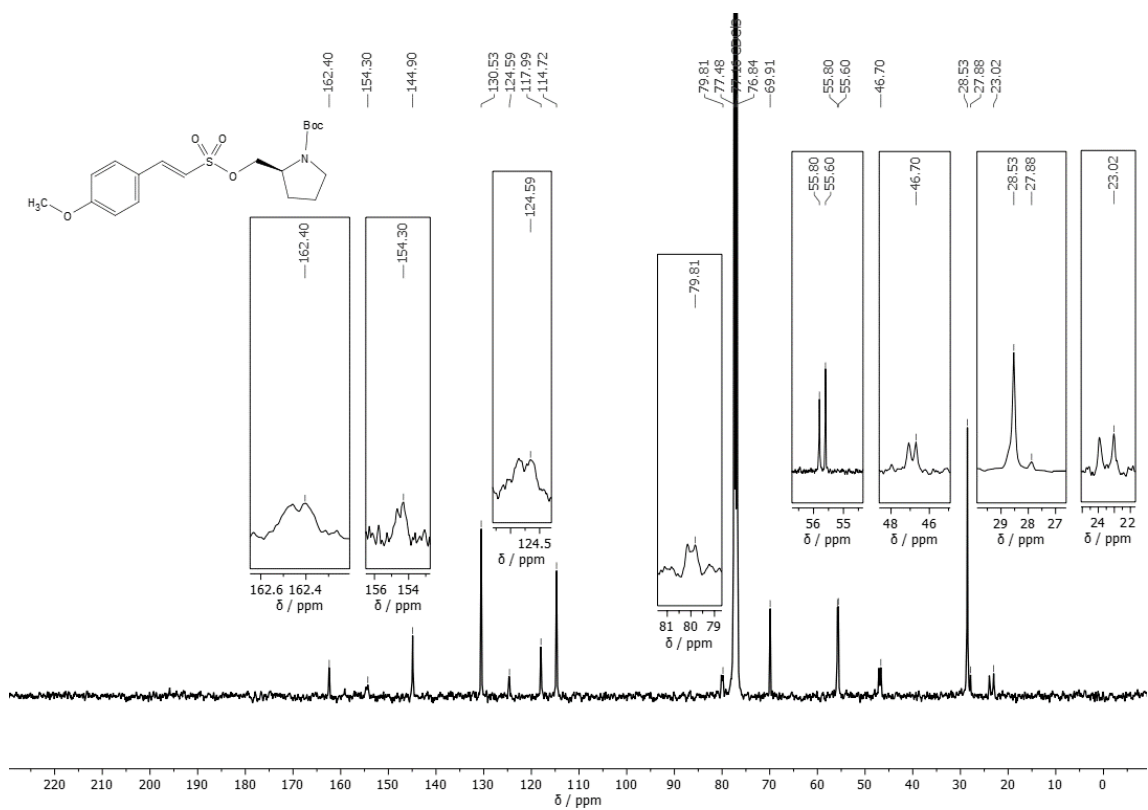
Figure S82: ¹H NMR spectrum (400 MHz, CDCl₃) of **9g**.Figure S83: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9g**.

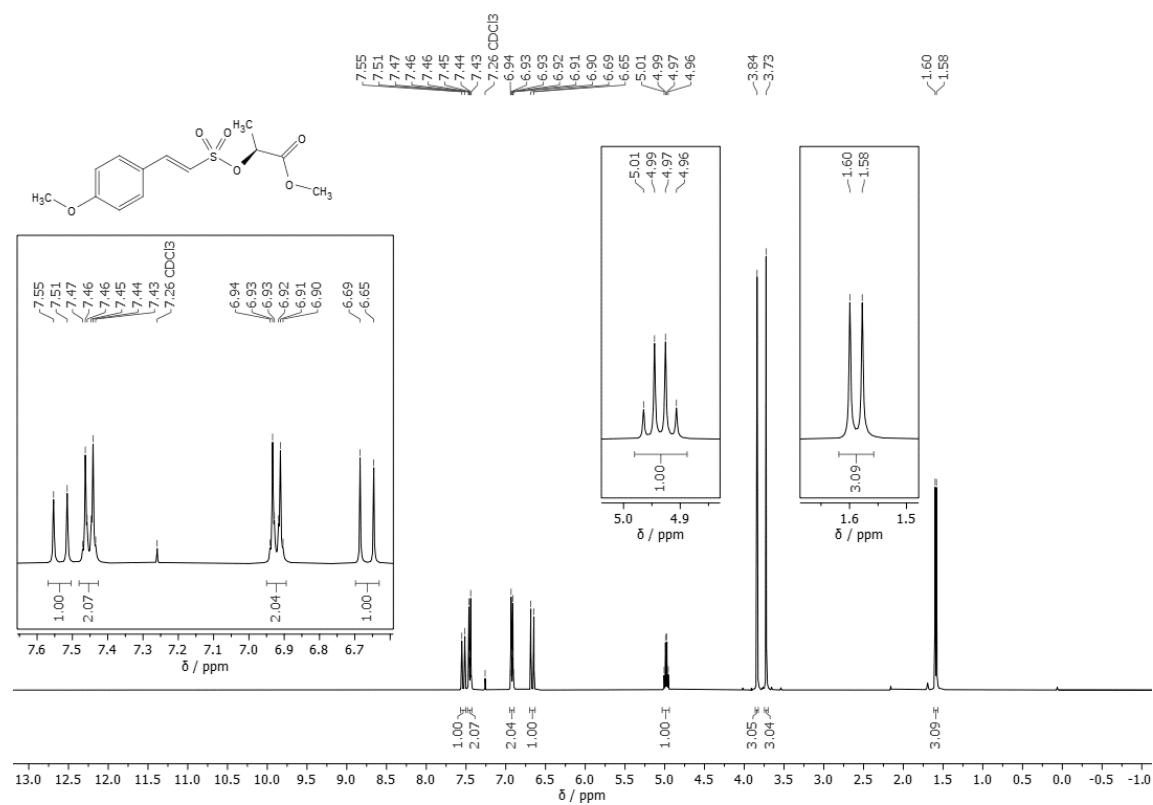
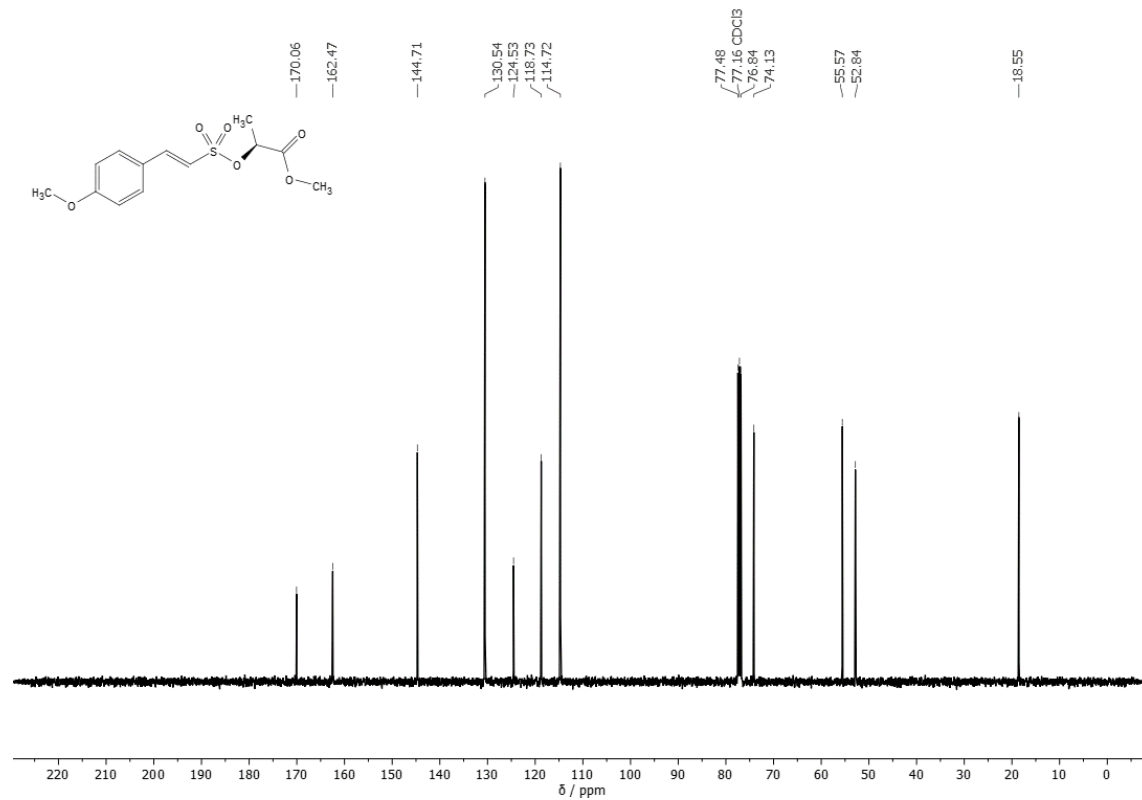


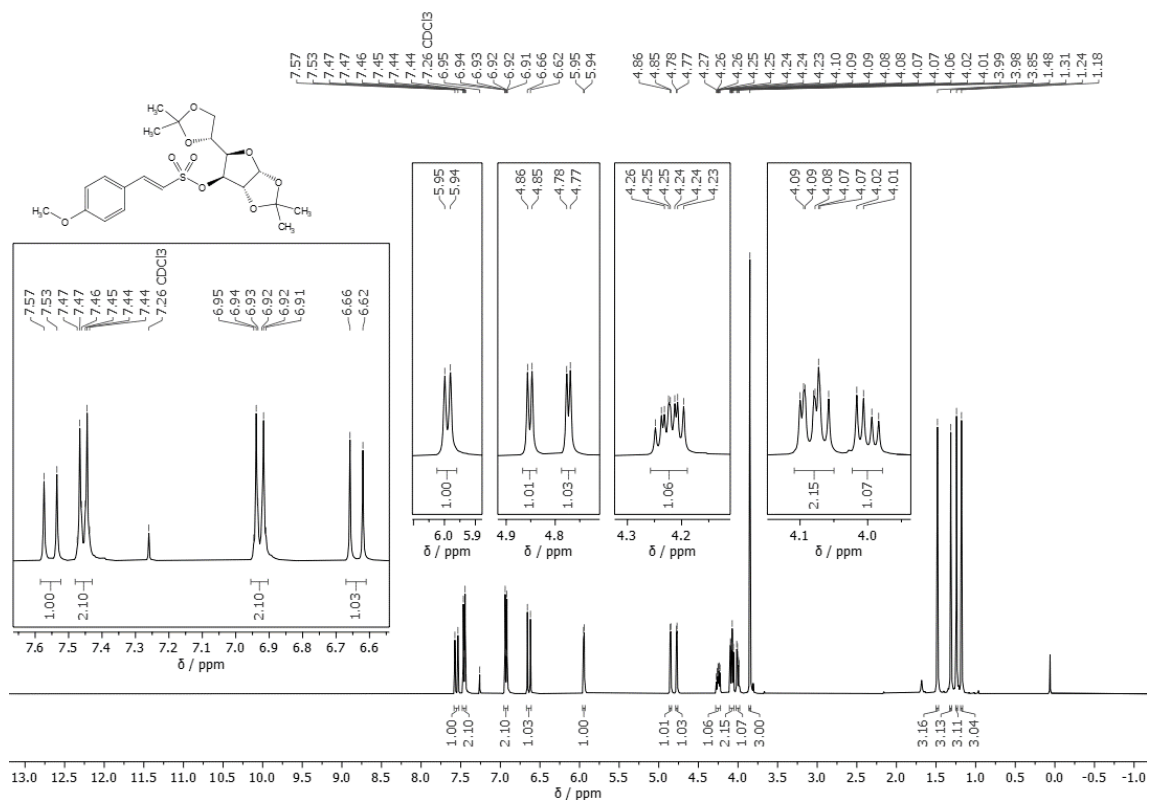
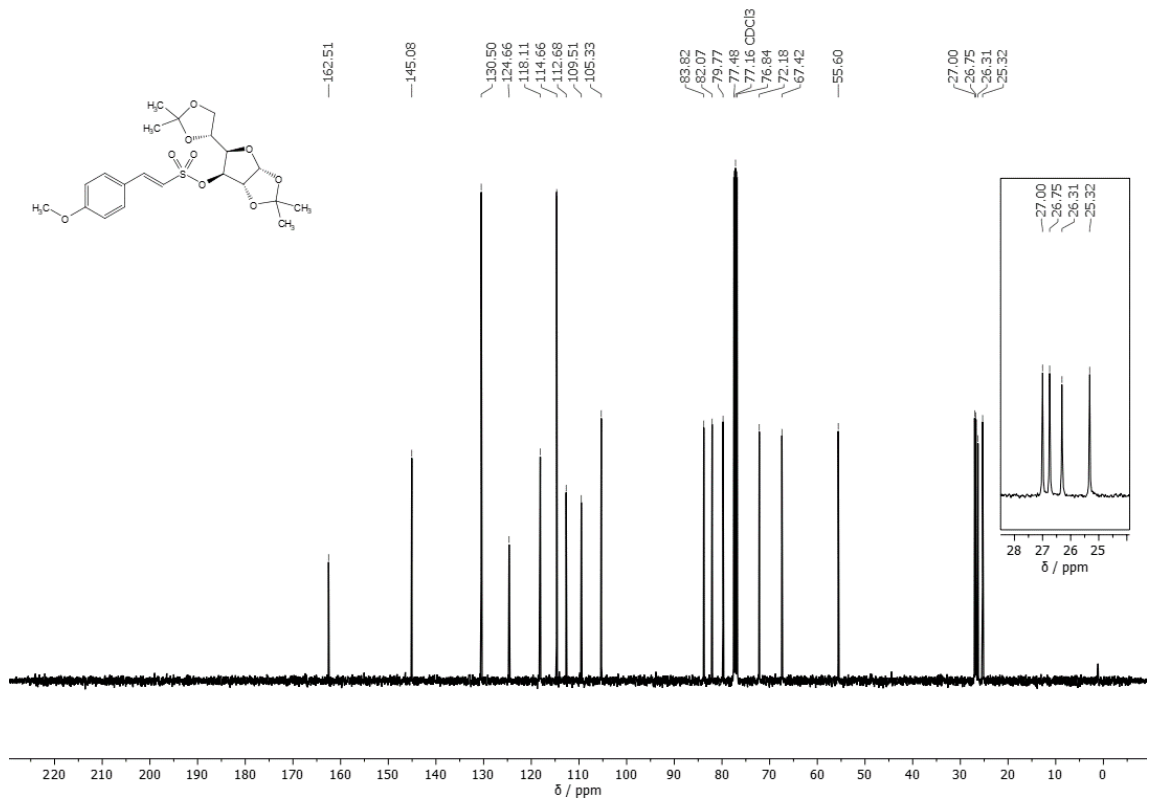
Figure S86: ¹H NMR spectrum (400 MHz, CDCl₃) of **9i**.Figure S87: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9i**.

Figure S88: ¹H NMR spectrum (400 MHz, CDCl₃) of **9j**.Figure S89: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9j**.

Figure S90: ¹H NMR spectrum (400 MHz, CDCl₃) of 9k.Figure S91: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9k.

Figure S92: ¹H NMR spectrum (400 MHz, CDCl₃) of **9l**.Figure S93: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9l**.

Figure S94: ¹H NMR spectrum (400 MHz, CDCl₃) of **9m**.Figure S95: ¹³C NMR spectrum (101 MHz, CDCl₃) of **9m**.

Figure S96: ¹H NMR spectrum (400 MHz, CDCl₃) of 9n.Figure S97: ¹³C NMR spectrum (101 MHz, CDCl₃) of 9n.

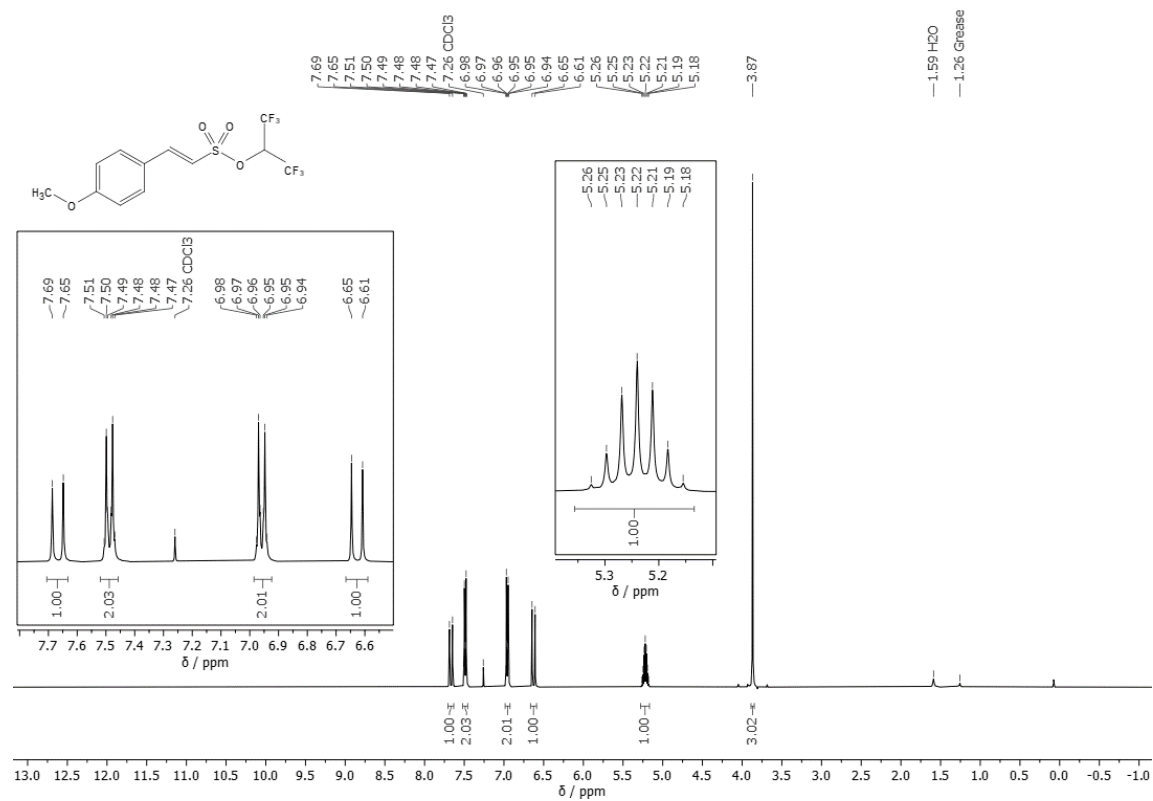


Figure S98: ^1H NMR spectrum (400 MHz, CDCl_3) of **9o**.

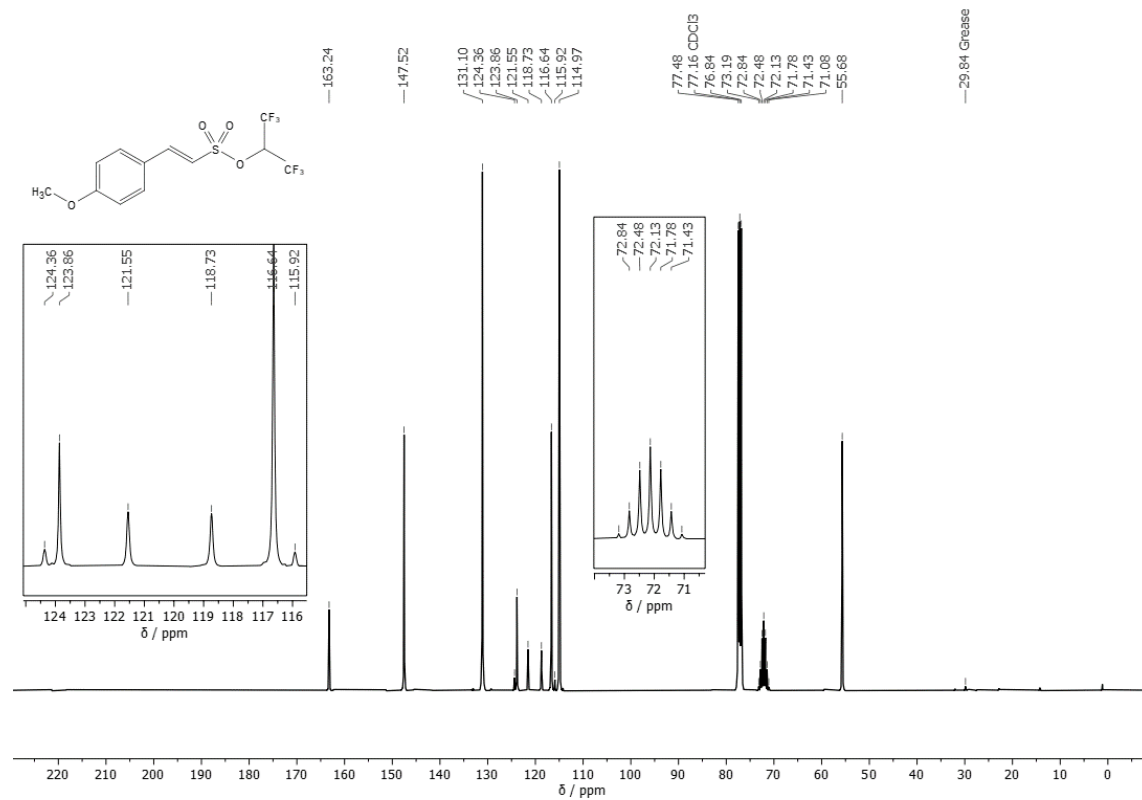


Figure S99: ^{13}C NMR spectrum (101 MHz, CDCl_3) of **9o**.

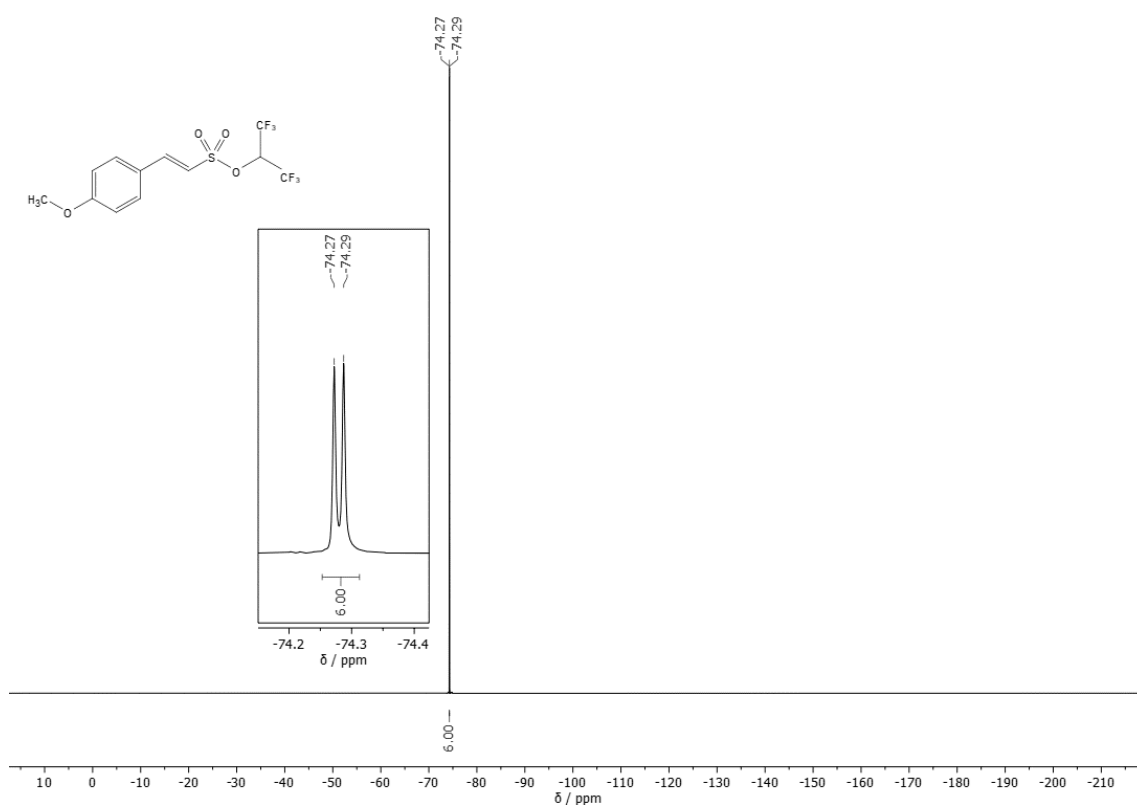
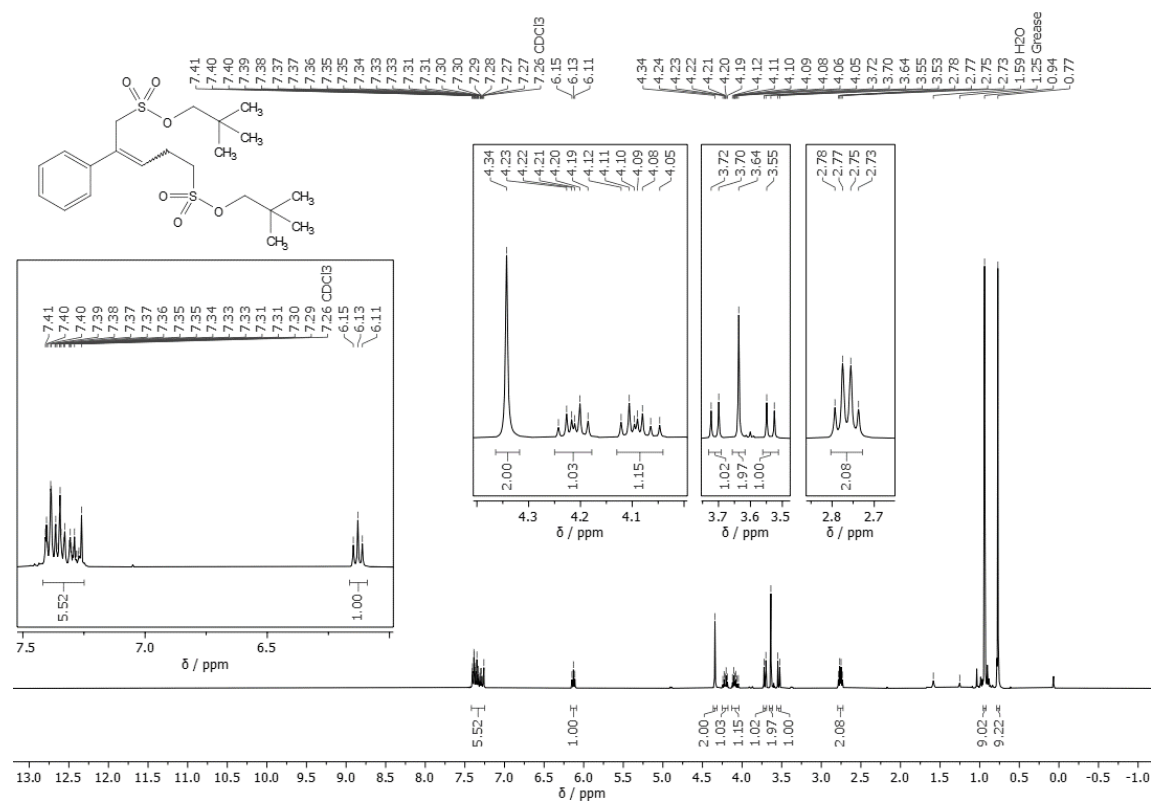
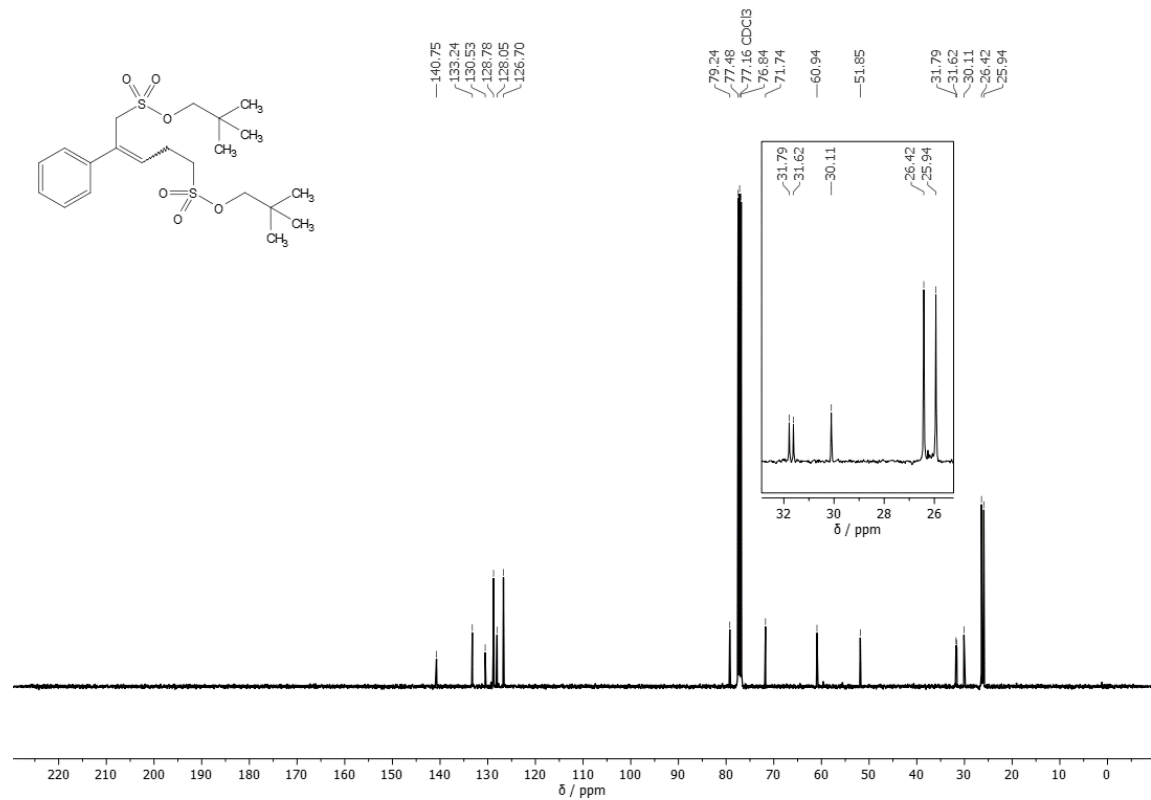
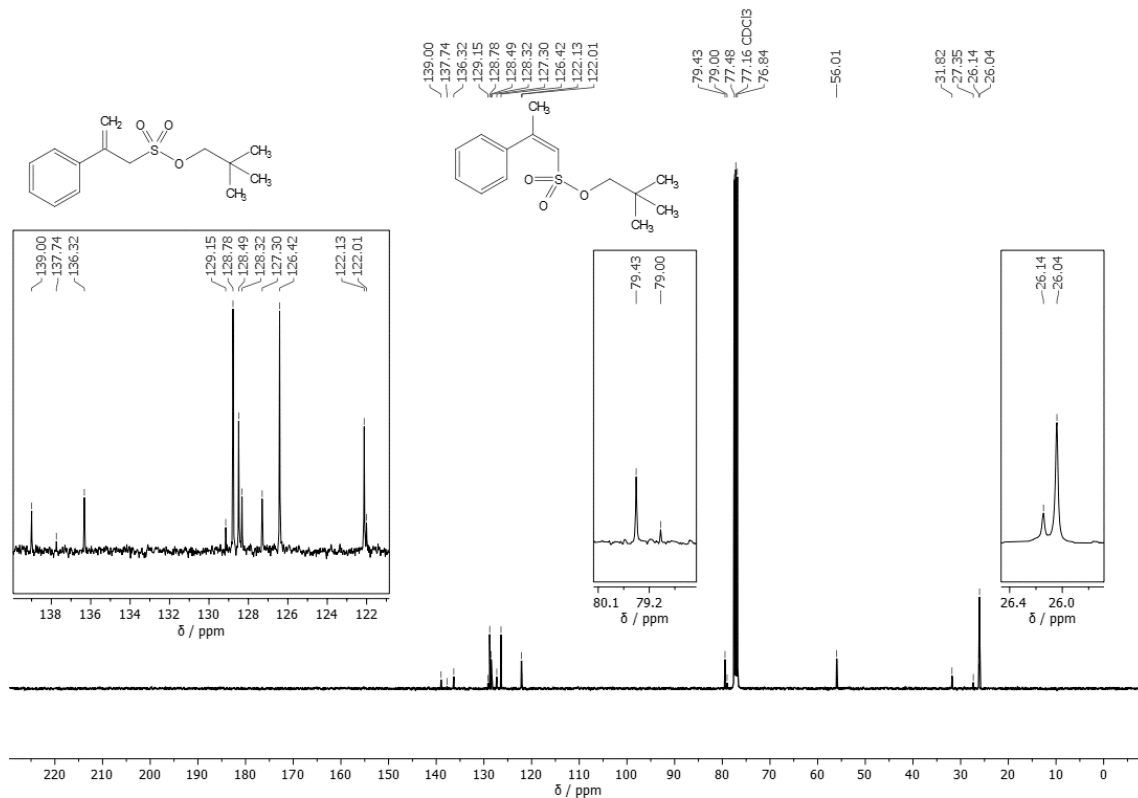
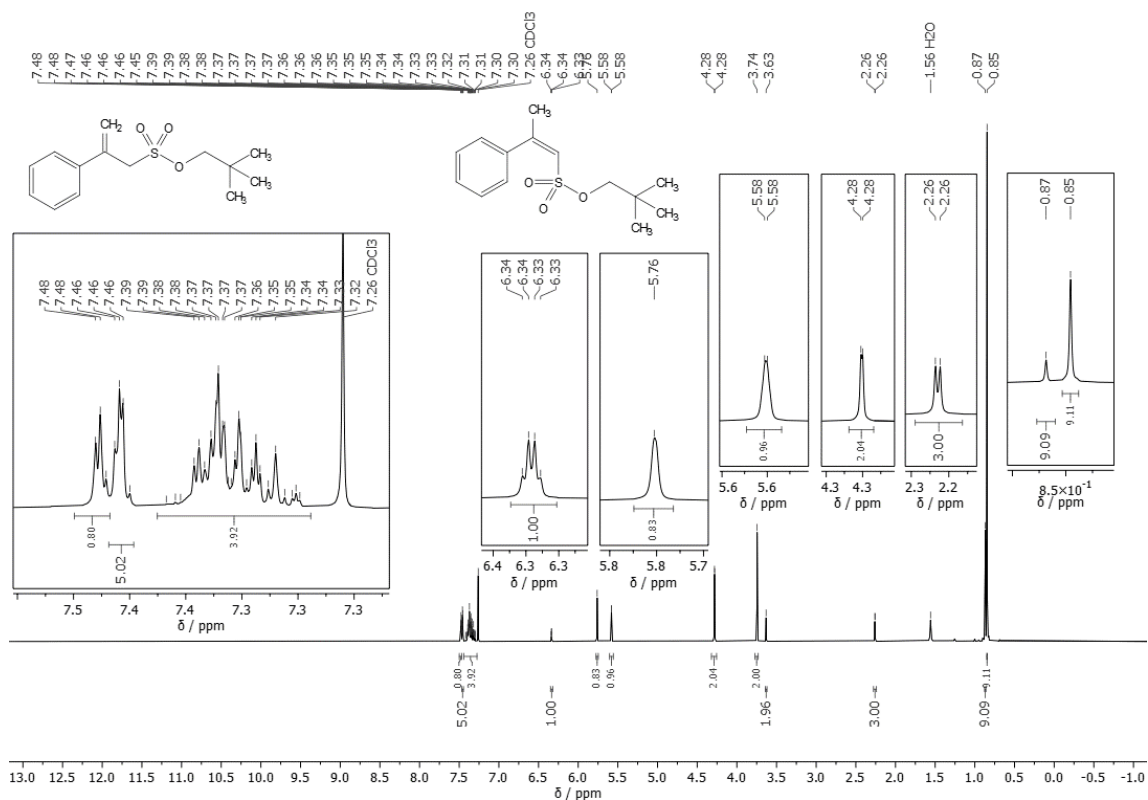
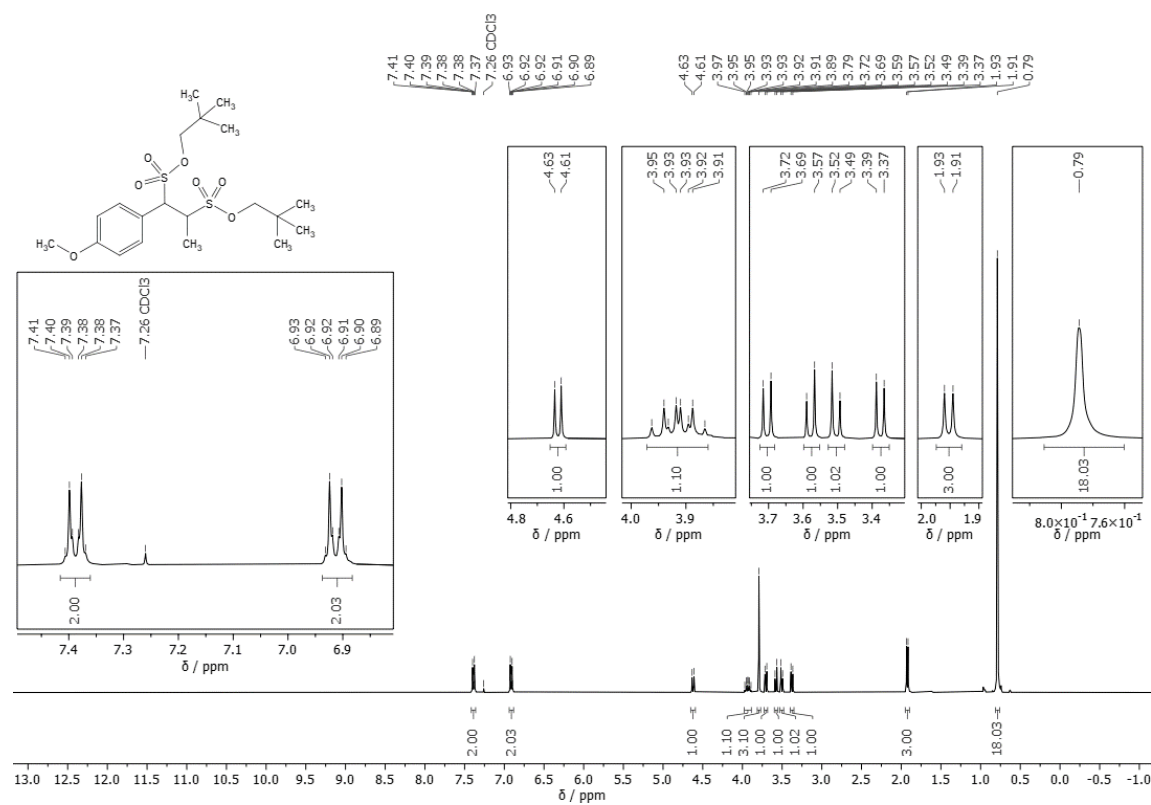
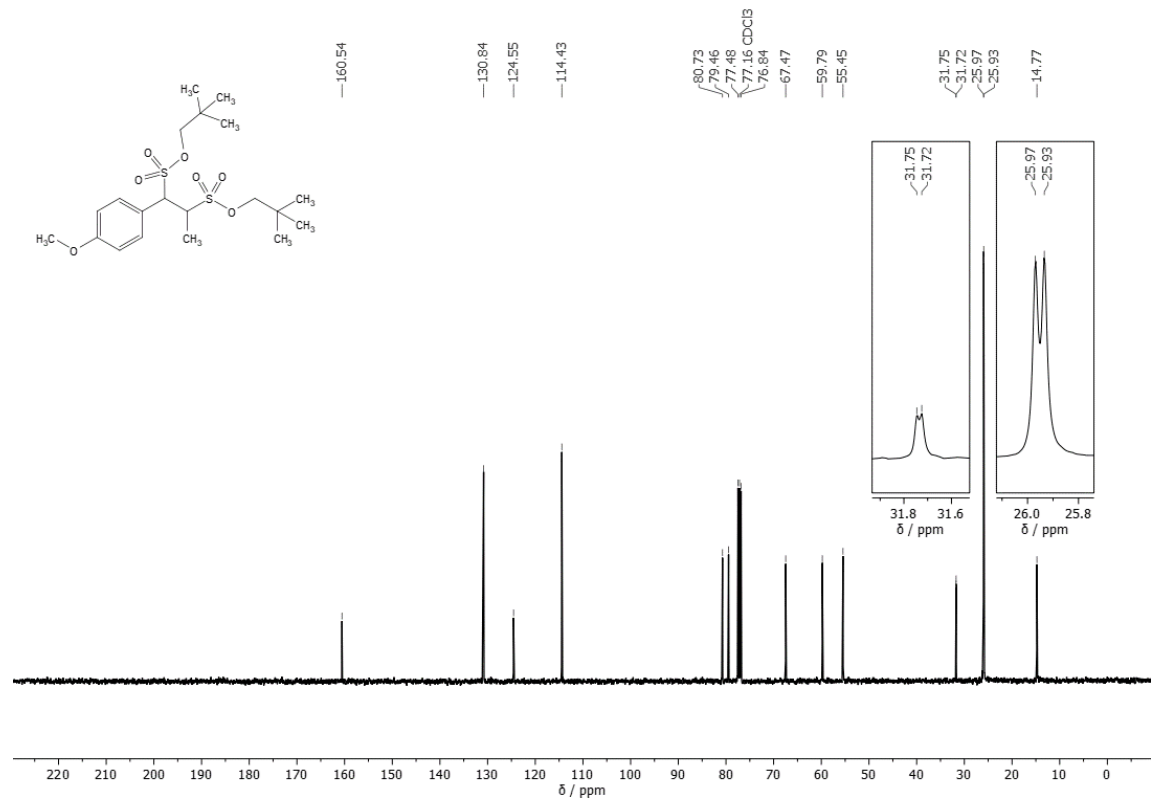
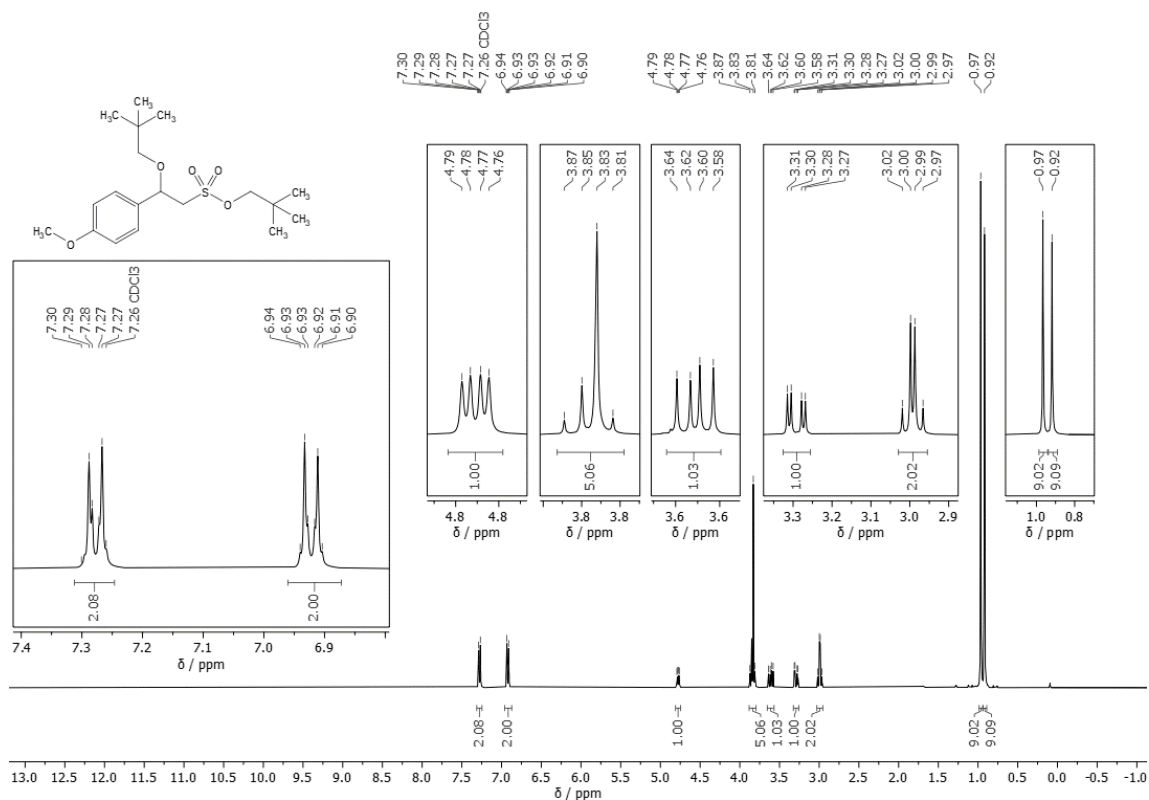
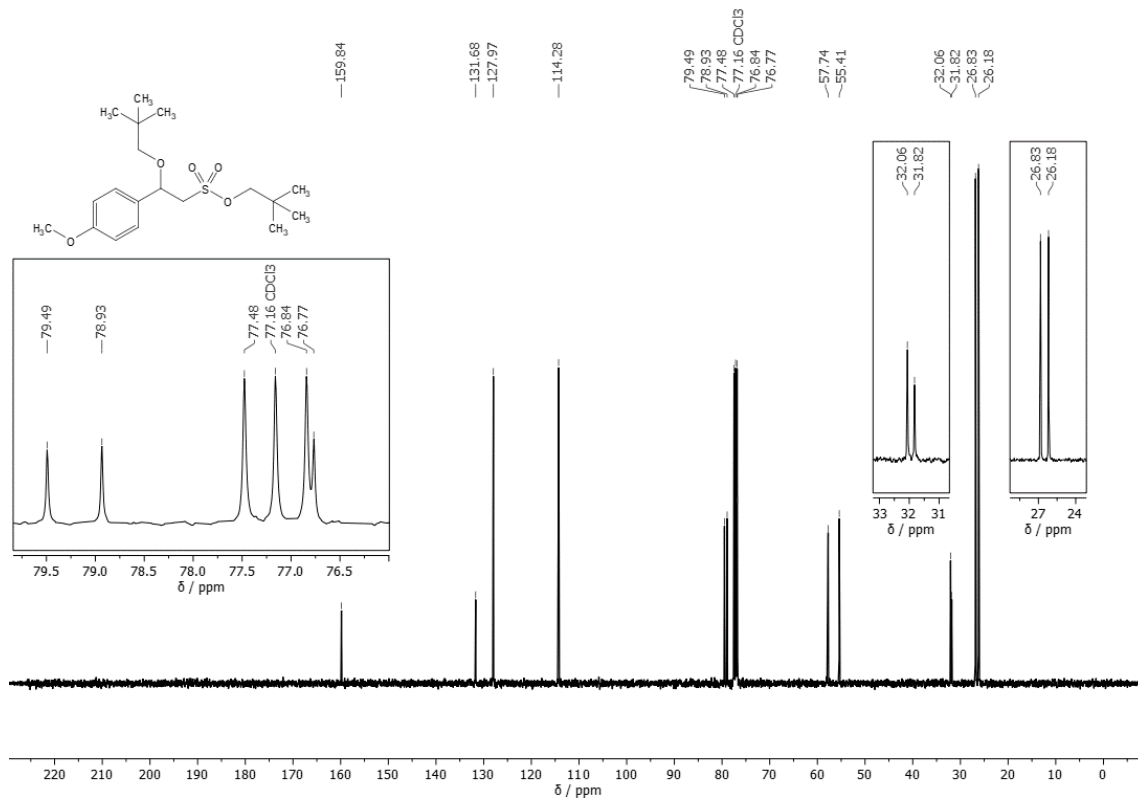


Figure S100: ^{19}F NMR spectrum (376 MHz, CDCl_3) of **9o**.

Figure S101: ¹H NMR spectrum (400 MHz, CDCl₃) of 10a.Figure S102: ¹³C NMR spectrum (101 MHz, CDCl₃) of 10a.



Figure S105: ¹H NMR spectrum (400 MHz, CDCl₃) of 10c.Figure S106: ¹³C NMR spectrum (101 MHz, CDCl₃) of 10c.

Figure S107: ¹H NMR spectrum (400 MHz, CDCl₃) of 10e.Figure S108: ¹³C NMR spectrum (101 MHz, CDCl₃) of 10e.

7 Crystallographic Data

The crystallization was carried out by dissolving compound **8a** in dichloromethane and carefully covering it with cyclohexane. Diffusion of the cyclohexane into the dichloromethane phase resulted in crystal formation.

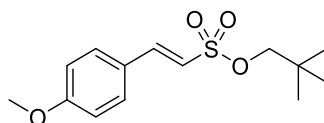


Table S1: Crystallographic data for neopentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (**8a**)

Parameter	Value
CCDC Number	2300959
Empirical formular	C ₁₄ H ₂₀ O ₄ S
Moiety formular	C ₁₄ H ₂₀ O ₄ S
Formular weight	284.36 g×mol ⁻¹
Temperature	120(2) K
Wavelength, radiation type	0.71073Å, MoKα
Diffractometer	STOE IPDS 2T
Crystal system	Monoclinic
Space group name, number	P 2 ₁ /c, (14)
Unit cell dimensions	a = 10.6562(4) Å α = 90° b = 12.7136(7) Å β = 90.039(3)° c = 10.9091(5) Å γ = 90°
Volume	1477.95(12) Å ³
Number of reflections	15016
And range used for lattice parameters	2.67° ≤ Θ ≤ 28.26°
Z	4
Density (calculated)	1.278 g×cm ⁻³
Absorption coefficient	0.226 mm ⁻¹
Method of absorption correction	Integration
Transmission (min. and max.)	0.8791 and 0.9638
F(000)	608
Crystal size, colour and form	0.120-0.390-0.600 mm ³ , colorless block
Theta range for data collection	3.115 – 27.947°
Index ranges	-13 ≤ h ≤ 14, -16 ≤ k ≤ 16, -14 ≤ l ≤ 12
Number of reflections:	
collected	8332
independent	3504 [R _{int} = 0.0219]
observed [I>2σ(I)]	3056
Completeness to theta = 25.2°	99.9%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3504 / 0 / 176
Goodness-of-fit on F ²	1.077
Final R indices [I>2σ(I)]	R1 = 0.0442, wR2 = 0.1116
R indices (all data)	R1 = 0.0530, wR2 = 0.1192
Largest diff. peak and hole	0.558 and -0.291 eÅ ⁻³

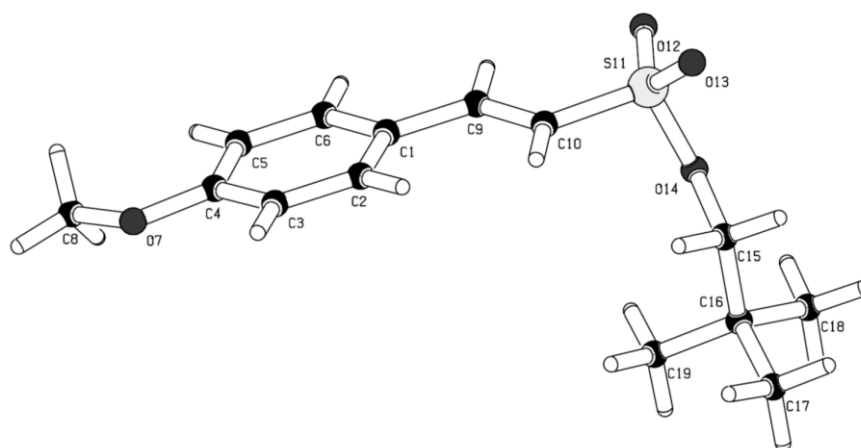


Figure S109: Molecular structure of neopentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (**8a**) as determined by single crystal X-ray analysis.

8 References

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9 Author Contributions

A.A.B.: Conceptualization: Equal, Investigation: Equal, Methodology: Equal, Data curation: Equal, Formal analysis: Equal, Writing the original draft: Equal.

F.A.B.: Conceptualization: Equal, Investigation: Equal, Methodology: Equal, Data curation: Equal, Formal analysis: Equal, Writing the original draft: Equal.

D. S.: Investigation: X-ray analysis, Supporting.

R.A.P.: Supervision: Supporting.

S. R. W.: Conceptualization: Equal, Funding acquisition, Project administration, Resources, Supervision, Writing the original draft: Equal.

B2 Supporting Information S2: Decarboxylative electrosulfonylation of cinnamic acids

Supporting Information

Electrochemical 3-Component Synthesis of Alkenesulfonates from Cinnamic Acids, SO₂ and Alcohols

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1 General Information

Unless otherwise mentioned, all reactions were performed under ambient conditions and chemicals in analytical grade were used as purchased without further purification. Trifluoroethanol and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) were freshly distilled from 3 Å molecular sieves and stored over 3 Å molecular sieves. All yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^1H -NMR.

1.1 Instruments and Analytical Methods

Chromatography: Thin-layer chromatography was performed on precoated aluminum-backed silica gel plate (Merck 60 F254, 0.2 mm thickness) which was visualized by fluorescence quenching. Flash-chromatography was performed on silica gel (Macherey-Nagel Kieselgel 60 0.063–0.2 mm).

Automated flash column chromatography: Preparative flash column chromatography was performed on a prepacked puriFlash™ silica column (80 g, 25 μm , PF-25SiHC-F0080, *Interchim*, Montlucon Cedex, France) using a puriFlash™-System (puriFlash™ XS520Plus, *Interchim*, Montlucon Cedex, France) with an integrated UV detector and fraction collector. Detection of the product was achieved using the absorption at 254 nm.

Solvents: Anhydrous acetonitrile (CH_3CN), purchased from Thermo Fisher Scientific was used without any further purification. The solvents for column chromatography were technical standard.

Materials: Starting materials which were not commercially available were synthesized according to the previously reported methods.^[76,77]

NMR spectroscopy: Spectra of proton (^1H), carbon (^{13}C) and fluorine (^{19}F) nuclear magnetic resonance were recorded at 400 MHz, 101 MHz and 376 MHz respectively. Chemical shifts are reported in δ ppm referenced to an internal standard, such as TMS for ^1H -NMR ($\delta = 0.0$ ppm), CDCl_3 for ^{13}C -NMR ($\delta = 77.16$ ppm), $\text{DMSO}-d_6$ for ^1H -NMR ($\delta = 2.50$ ppm), $\text{DMSO}-d_6$ for ^{13}C -NMR ($\delta = 39.52$ ppm). The coupling constants (J) are reported in Hz and the following abbreviations were used to explain the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), td (triplet of doublet), tt (triplet of triplet), qq (quartet of quartet), and septetd (septet of doublet).

Melting points: Melting points were measured on a hot stage melting point apparatus and are uncorrected.

Mass spectrometry: Mass spectra (MS) were measured using electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) techniques with a quadrupole mass analyzer. High resolution mass spectra (HRMS) were measured using electron ionization mass spectroscopy with a time-of-flight mass analyzer (EI-MS-TOF), electrospray ionization mass spectroscopy (ESI-MS) with quadrupole-orbitrap mass analyzer, and gas chromatography coupled with electron ionization mass spectroscopy (GC-EI-MS) and quadrupole-orbitrap mass analyzer.

Gas Chromatography coupled with Mass Spectrometry (GC/MS): Analysis of crude reaction mixtures was performed using Thermo Scientific ISQ 7000 equipped with an electron ionization (EI) source and a quadrupole mass analyzer.

Infrared spectroscopy: Infrared spectra (IR) of neat substances were recorded on an FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm^{-1}) and only selected peaks are shown.

X-ray Crystallography: The measurement of the crystal structure was carried out on a Rigaku/Oxford diffraction Xcalibur/Gemini dual wavelength diffractometer with a $\text{Cu-K}\alpha$ ($\lambda = 1.54178$ Å) radiation X-ray source.

Cyclic Voltammetry (CV) Measurements: Cyclic voltammetry was performed using Interface 1010T (Gamry Instruments, Pennsylvania, United States of America). WE: Pt electrode; CE: Pt electrode; RE: Ag/AgCl ; Scan rate $v = 100$ mV/s. All data is displayed against the half-wave potential of ferrocene/ferrocenium redox couple (FcH/FcH^+ ; 0.02 V vs. Ag/AgCl) as the internal reference. Oxidation potentials are marked and displayed as the half-wave potential of the respective peak.

1.1. Electrochemical Setup

Screening and small-scale reactions: Electrochemical reactions were carried out using an IKA ElectraSyn 2.0. Parallel reactions were performed with the IKA Carousel. The divided cell used for screening or small-scale reactions was an IKA Pro-Divide equipped with a glass frit (pore size 10-16 microns). All used electrodes were purchased from IKA.



Figure S1: IKA ElectraSyn 2.0 and IKA Carousell.



Figure S2: IKA Pro-Divide divided cell.

Scale-up cell: The scale-up experiment was performed in a divided glass cell with a volume of 100 mL per half-cell equipped with a PTFE stopper and sleeve, electrodes, and electrode holders, a glass frit (P4, $d = 24$ mm) and cross-shaped stirring bars. The electrolysis was conducted using a TDK-Lambda Z+ series (*TDK-Lambda UK Limited*, Devon, United Kingdom) as power source. The electrode dimensions were 60 mm $\times$ 20 mm $\times$ 2 mm, with 45 mm submerged into the reaction mixture, resulting in an active electrode area of 9.0 cm². The graphite employed was Sigrasine™ V2100 by SGL Carbon/Bad Godesberg, Germany. The stoppers, sleeves, electrodes and their holders are available at Sigma-Aldrich within the SynLectro™ series.

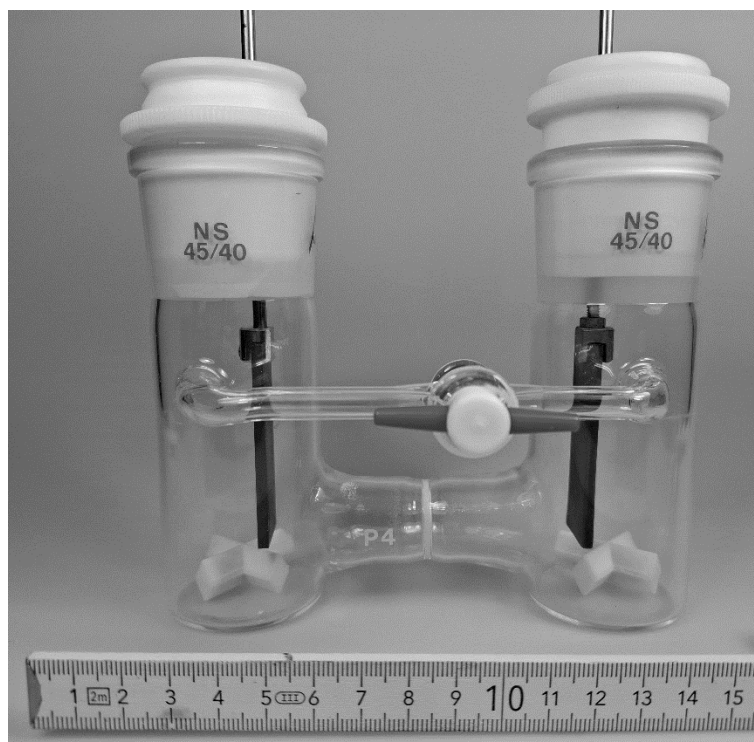


Figure S3: Electrochemical glass cell with 100 mL per half-cell used for the scale-up experiment equipped with a P4 frit, graphite electrodes, Teflon™ plug, and electrode holders. Scale is given in cm.

2 Preparation of the SO₂ Stock Solutions

2.1 The Procedure for Preparation of the SO₂ Stock Solutions

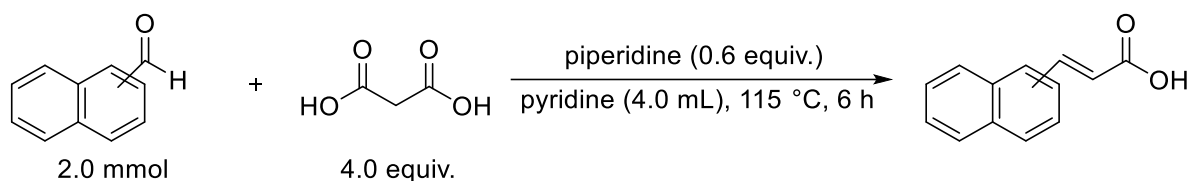
300 mL of anhydrous acetonitrile and molecular sieves (3 Å, 50.0 g) were transferred into a dry two-neck round bottom flask. Sulfur dioxide was bubbled into the solution at a slow flow rate for 15 minutes at 0 °C. Excess gaseous sulfur dioxide leaving the apparatus was purged with aq. NaOH solution.

2.2 Determination of the SO₂ Concentration of the Stock Solution

The exact concentration of the prepared SO₂ solution was determined according to iodometric titration.^[78] To a solution of I₂ (1.27g, 5.00 mmol) and KI (2.20 g, 13.3 mmol) in H₂O (100 mL) was slowly added the freshly prepared SO₂ stock solution (1.0 mL). The resulting solution was then titrated with a freshly prepared aq. Na₂S₂O₃ solution (0.2 M) as titrant to determine the amount of excess I₂ (end point marked a color change from brown to colorless; optionally starch can be added for better visualization). Titrations of individual batches of stock solutions were repeated three times for a more accurate determination of the concentration.

3 Synthesis of Starting Materials

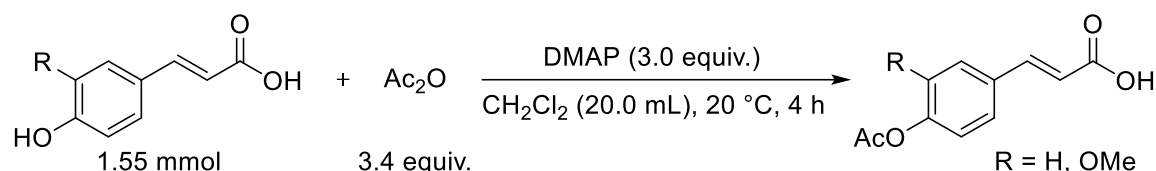
3.1 Typical Procedure for the Preparation of Naphthylacrylic Acid (TP-1)



The naphthylacrylic acid was synthesized according to the reported literature.^[76]

A 25.0 mL single neck round-bottomed flask equipped with a magnetic stir bar was charged with the corresponding naphthaldehyde (312.4 mg, 2.0 mmol), malonic acid (832.5 mg, 4.0 equiv.), piperidine (0.13 mL, 0.6 equiv.), and pyridine (4.0 mL) and heated to 115 °C for 6 h. Afterwards, the reaction mixture was cooled to room temperature, poured into an Erlenmeyer flask, and acidified with 2.0 M HCl to a final pH = 1. The resulting precipitate was filtered and washed with distilled water (30.0 mL) to afford the naphthylacrylic acid.

3.2 Typical Procedure for the Preparation of Acetoxycinnamic Acid (TP-2)

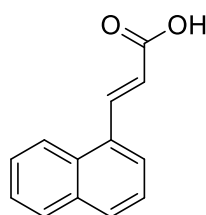


The acetoxycinnamic acid was synthesized according to the reported literature.^[77]

A 50.0 mL single neck round-bottomed flask equipped with a magnetic stir bar was charged with hydroxycinnamic acid (1.55 mmol), CH_2Cl_2 (20.0 mL), acetic anhydride (0.5 mL, 3.4 equiv.), and DMAP (568.1 mg, 3.0 equiv.). The resulting solution was stirred at 20 °C for 4 h. After completion of the reaction, the reaction mixture was acidified (pH = 1) with 2.0 M HCl and extracted with CH_2Cl_2 (3 x 20.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude residue was subjected to flash column chromatography on silica gel to obtain acetoxycinnamic acid.

3.3 Analytical Data for Starting Materials of Type 6

(E)-3-(Naphthalen-1-yl)acrylic acid (6m)



Following the **TP-1**, 1-naphthaldehyde (312.4 mg, 2.0 mmol), malonic acid (832.5 mg, 4.0 equiv.), and piperidine (0.13 mL, 0.6 equiv.) were used as substrates. After 6 h, the reaction mixture was acidified. The resulting precipitate was filtered and washed with distilled water to obtain **6m** as a colorless solid (337.5 mg, 85%). Analytical data for **6m** match those previously described in the literature.^[79]

mp: 178.9–179.8 °C. **R_f** = 0.38 (*n*-hexane/EtOAc = 1:1).

¹H NMR (400 MHz, DMSO-*d*₆): δ 12.62 (s, 1H), 8.41 (d, *J* = 15.6 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.64–7.50 (m, 3H), 6.61 (d, *J* = 15.6 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, DMSO-*d*₆): δ 167.5, 140.2, 133.3, 131.0, 130.8, 130.4, 128.7, 127.1, 126.3, 125.7, 125.2, 123.0, 122.0.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3046, 1677, 1614, 975, 763.

MS (APCI): m/z calcd. for $C_{13}H_9O_2$ ($[M-H]^-$) 197.1, found 197.3.

HRMS (El^+): m/z calcd. for $C_{13}H_{10}O_2$ ($[M]^+$) 198.0675, found 198.0686.

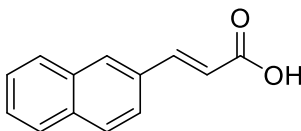
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WPXMLUUYWN-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/WPXMLUUYWNHQOR-CMDGGOBGSA-N.1>

3.4 (E)-3-(Naphthalen-2-yl)acrylic acid (6n)



Following the **TP-1**, 2-naphthaldehyde (312.4 mg, 2.0 mmol), malonic acid (832.5 mg, 4.0 equiv.), and piperidine (0.13 mL, 0.6 equiv.) were used as substrates. After 6 h, the reaction mixture was acidified. The resulting precipitate was filtered and washed with distilled water to obtain **6n** as a colorless solid (315.3 mg, 80%). Analytical data for **6n** match those previously described in the literature.^[80]

mp: 176.7–177.3 °C. **R_f** = 0.30 (*n*-hexane/EtOAc = 1:1).

¹H NMR (400 MHz, DMSO-*d*₆): δ 12.47 (s, 1H), 8.18 (s, 1H), 7.99–7.90 (m, 3H), 7.87 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.61–7.50 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, DMSO-*d*₆): δ 167.7, 143.9, 133.7, 132.9, 131.9, 129.7, 128.53, 128.47, 127.7, 127.3, 126.8, 124.0, 119.6.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3045, 1680, 1624, 983, 739.

MS (APCI): m/z calcd. for $C_{13}H_{11}O_2$ ($[M+H]^+$) 199.1, found 199.3.

HRMS (El^+): m/z calcd. for $C_{13}H_{10}O_2$ ($[M]^+$) 198.0675, found 198.0687.

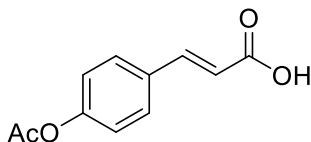
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-KWGPBDBAAX-UHFFFADPSC-NUHFF-NCGTV-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/KWGPBDBAAXYWOJ-SOFGYWHQSA-N.1>

3.5 (E)-3-(4-Acetoxyphenyl)acrylic acid (6j)



Following the **TP-2**, *p*-hydroxycinnamic acid (254.4 mg, 1.55 mmol), acetic anhydride (0.5 mL, 3.4 equiv.), and DMAP (568.1 mg, 3.0 equiv.) were used as substrates. After 4 h, the reaction mixture was acidified. The crude residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 2:1) to obtain **6j** as a colorless solid (287.0 mg, 90% yield). Analytical data for **6j** match those previously described in the literature.^[81]

mp: 207.5–208.2 °C. **R_f** = 0.30 (*n*-hexane/EtOAc = 1:1).

¹H NMR (400 MHz, DMSO-*d*₆): δ 12.44 (s, 1H), 7.89–7.68 (m, 2H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.33–7.06 (m, 2H), 6.52 (d, *J* = 15.6 Hz, 1H), 2.27 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, $\text{DMSO}-d_6$): δ 169.1, 167.6, 151.9, 143.0, 132.0, 129.5, 122.4, 119.4, 20.9.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 2816, 1741, 1672, 1192, 992, 793.

MS (APCI): m/z calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_4$ ($[\text{M}+\text{H}]^+$) 207.1, found 207.3.

HRMS (EI^+): m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_4$ ($[\text{M}]^+$) 206.0574, found 206.0574.

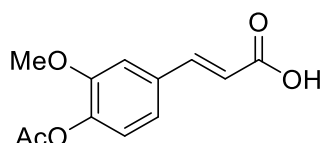
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-BYHBHNKBIS-UHFFFADPSC-NUHFF-NUHD-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/BYHBHNKBISXCEP-QPJXVBHSA-N.1>

3.6 (*E*)-3-(4-Acetoxy-3-methoxyphenyl)acrylic acid (**6k**)



Following the **TP-2**, (*E*)-3-(4-hydroxy-3-methoxyphenyl)acrylic acid (301.0 mg, 1.55 mmol), acetic anhydride (0.5 mL, 3.4 equiv.), and DMAP (568.1 mg, 3.0 equiv.) were used as substrates. After 4 h, the reaction mixture was acidified. The crude residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 2:1) to obtain **6k** as a colorless solid (306.1 mg, 84% yield). Analytical data for **6k** match those previously described in the literature.^[81]

mp: 199.5–200.3 °C. R_f = 0.20 (*n*-hexane/EtOAc = 1:1).

^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 12.43 (s, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.26 (dd, J = 8.2, 1.6 Hz, 1H), 7.12 (d, J = 8.2 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 3.82 (s, 3H), 2.26 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, $\text{DMSO}-d_6$): δ 168.5, 167.7, 151.2, 143.4, 140.8, 133.3, 123.2, 121.4, 119.6, 111.9, 56.0, 20.4.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3012, 1760, 1630, 1221, 1198, 983.

MS (APCI): m/z calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_5$ ($[\text{M}+\text{H}]^+$) 237.1, found 237.1.

HRMS (ESI^-): m/z calcd. for $\text{C}_{12}\text{H}_{11}\text{O}_5$ ($[\text{M}-\text{H}]^-$) 235.061200, found 235.061300.

Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-IHKNVZISLL-UHFFFADPSC-NUHFF-NDUUA-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/IHKNVZISLLDMOR-GQCTYLIASA-N.1>

4 Optimization of Reaction Conditions

4.1 Typical Procedure for the Optimization of Reaction Conditions (TP-3)

The reactions were carried out using IKA Pro-Divide cells with a glass frit membrane.

Anolyte: An oven-dried 10.0 mL pear-shaped flask was charged with cinnamic acid (44.5 mg, 0.3 mmol), neopentyl alcohol, ammonium salt, and anhydrous acetonitrile. The mixture was cooled to 0 °C in an ice bath, followed by the addition of SO₂ stock solution and base so that a total volume of 3.0 mL was achieved.

Catholyte: An oven-dried 10.0 mL pear-shaped flask was charged with ammonium salt, acetic acid (5.0 equiv.), and anhydrous acetonitrile so that a total volume of 3.0 mL was achieved as well.

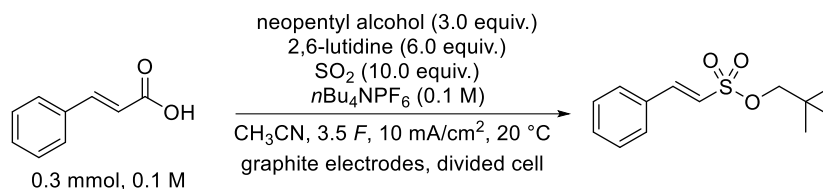
The reaction mixtures were transferred with syringes to their respective compartment simultaneously. The amperage and amount of applied charge was set to the desired values and the electrolysis was conducted at room temperature under constant stirring (400 rpm).

After completion of the electrolysis, the anolyte was transferred to a round bottom flask, and the anode compartment was rinsed with additional EtOAc (2 x 3.0 mL). ¹H NMR yields were calculated by addition of triphenylmethane (73.2 mg, 1.0 equiv.) as the internal standard to this mixture. After 5 min of stirring, 1.0 mL of the mixture was taken, and the solvent was removed under reduced pressure. The crude residue was dissolved in CDCl₃ for ¹H NMR experiments.

4.2 Optimization of Reaction Conditions

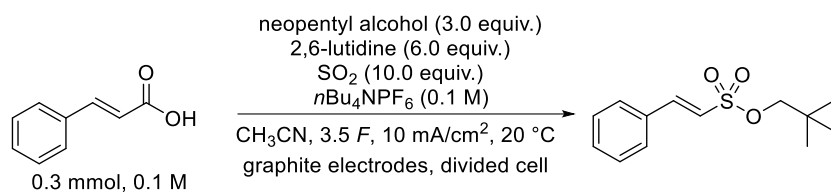
Optimization of the conditions was carried out by using linear screening with cinnamic acid and neopentyl alcohol as substrates according to the procedure described in **TP-3**. Neopentyl alcohol was chosen due to the enhanced stability of sulfonate neopentyl esters.

Table S1: Screening of electrodes, applied charge, current density, base, and electrolyte.



entry	deviation from the standard conditions	yield (%) ^[a]	cinnamic acid (%) ^[a]
1	none	71 (70)^[b]	0
2	BDD electrodes	25	25
3	glassy carbon electrodes	46	traces
4	Pt foil electrodes	40	15
5	3.0 <i>F</i>	63	0
6	3.8 <i>F</i>	54	0
7	15 mA/cm ²	65	0
8	5 mA/cm ²	55	0
9	2,4,6-collidine	55	traces
10	pyridine	54	traces
11	DBU	62	0
12	DIPEA	traces	53
13	<i>n</i> Bu ₄ NBF ₄	50	0

^[a]¹H-NMR yield with the use of CHPh₃ as the internal standard. ^[b]Isolated yield.

Table S2: Screening of the stoichiometry of alcohol, base, SO₂, and other parameters.

entry	deviation from the standard conditions	yield (%) ^[a]	cinnamic acid (%) ^[a]
1	none	71 (70)^[b]	0
2	nBu ₄ NPF ₆ (0.05 M)	58	0
3	nBu ₄ NPF ₆ (0.2 M)	43	0
4	neopentyl alcohol (2.0 equiv.)	50	0
5	neopentyl alcohol (4.0 equiv.)	47	0
6	2,6-lutidine (4.0 equiv.)	43	0
7	2,6-lutidine (8.0 equiv.)	49	0
8	SO ₂ (7.5 equiv.)	63	0
9	SO ₂ (12.5 equiv.)	68	0
10	CH ₃ CN:HFIP = 1:1	56	0

^[a]¹H-NMR yield with the use of CHPh₃ as the internal standard. ^[b]Isolated yield.

5 Synthesis of Alkyl Alkenesulfonates [Scope of Cinnamic Acids and Related Substrates]

5.1 Typical Procedure for the Preparation of Alkyl Alkenesulfonates [Scope of Cinnamic Acids and Related Substrates] (TP-4)

The reactions were carried out using IKA Pro-Divide cells with a glass frit membrane.

Anolyte: An oven-dried 10.0 mL pear-shaped flask was charged with neopentyl alcohol (79.3 mg, 3.0 equiv.), $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), and anhydrous acetonitrile (2.1 mL). The mixture was cooled to 0 °C in an ice bath, followed by the addition of SO_2 stock solution (0.6 mL, 5.0 M in acetonitrile, 10.0 equiv.) and 2,6-lutidine (0.21 mL, 6.0 equiv.) so that a total volume of 3.0 mL was achieved.

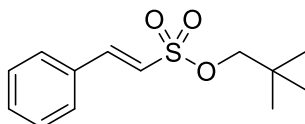
Catholyte: An oven-dried 10.0 mL pear-shaped flask was charged with $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), acetic acid (0.09 mL, 5.0 equiv.), and anhydrous acetonitrile (2.9 mL) so that a total volume of 3.0 mL was achieved as well.

The reaction mixtures were transferred with syringes to their respective compartment simultaneously and the anolyte was additionally loaded with the respective acid (0.3 mmol). The amperage was set accordingly so that a current density of $10 \text{ mA} \times \text{cm}^{-2}$ was reached (8.8 mA with the setup described herein) and the amount of applied charge was set to 3.5 F . The electrolysis was conducted at room temperature under constant stirring (400 rpm) for ca. 3 h 11 min.

After completion of the electrolysis, the anolyte was transferred to a separatory funnel and the anode compartment was rinsed with additional EtOAc (2 x 3.0 mL). Distilled water (10.0 mL) was added and the obtained mixture extracted with EtOAc (2 x 10.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was subjected to flash column chromatography on silica gel to obtain the product.

5.2 Analytical Data for Compounds of Type 8 and 10

Neopentyl (*E*)-2-phenylethene-1-sulfonate (**8a**)



Following the **TP-4**, cinnamic acid (44.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (n -hexane/EtOAc = 97:3) to obtain **8a** as a colorless solid (53.5 mg, 70% yield). Analytical data for **8a** match those previously described in the literature.^[42]

mp: 71.3–72.1 °C. **R_f** = 0.55 (n -hexane/EtOAc = 4:1).

^1H NMR (400 MHz, CDCl_3): δ 7.60 (d, J = 15.6 Hz, 1H), 7.55–7.50 (m, 2H), 7.50–7.41 (m, 3H), 6.75 (d, J = 15.6 Hz, 1H), 3.80 (s, 2H), 0.98 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 144.8, 132.1, 131.6, 129.3, 128.6, 121.1, 79.7, 31.8, 26.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3067, 2966, 1625, 1348, 1159, 953, 746.

MS (APCI): m/z calcd. for $\text{C}_{13}\text{H}_{19}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 255.1, found 255.4.

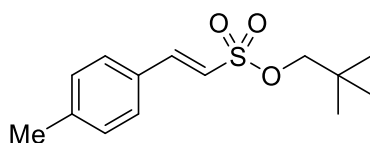
HRMS (EI^+): m/z calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{S}$ ($[\text{M}]^+$) 254.0971, found 254.0989.

Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-JSPSUKCDZR-UHFFFADPSC-NUHFF-NAIXQ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/JSPSUKCDZRFMIT-MDZDMLPSA-N.1>

Neopentyl (*E*)-2-(*p*-tolyl)ethene-1-sulfonate (8b**)**

Following the **TP-4**, (*E*)-3-(*p*-tolyl)acrylic acid (48.7 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8b** as a colorless solid (41.8 mg, 52% yield). Analytical data for **8b** match those previously described in the literature.^[42]

mp: 82.3–82.5 °C. **R_f** = 0.32 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 15.6 Hz, 1H), 7.44–7.39 (m, 2H), 7.26–7.21 (m, 2H), 6.68 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 2H), 2.40 (s, 3H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 144.9, 142.3, 130.1, 129.4, 128.6, 119.9, 79.6, 31.9, 26.2, 21.7.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3059, 2959, 1620, 1338, 1161, 955, 795.

MS (APCI): *m/z* calcd. for C₁₄H₂₁O₃S ([M+H]⁺) 269.1, found 269.4.

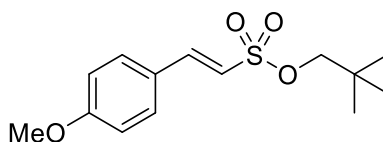
HRMS (EI⁺): *m/z* calcd. for C₁₄H₂₀O₃S ([M]⁺) 268.1128, found 268.1142.

Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-NRHDKVMGUT-UHFFFADPSC-NUHFF-NAIXQ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/NRHDKVMGUTWHAC-MDZDMLPSA-N.1>

Neopentyl (*E*)-2-(4-methoxyphenyl)ethene-1-sulfonate (8c**)**

Following the **TP-4**, (*E*)-3-(4-methoxyphenyl)acrylic acid (53.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8c** as a colorless solid (46.3 mg, 54% yield). Analytical data for **8c** match those previously described in the literature.^[42]

mp: 125.0–126.0 °C. **R_f** = 0.20 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.54 (d, *J* = 15.6 Hz, 1H), 7.49–7.45 (m, 2H), 6.97–6.92 (m, 2H), 6.58 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 3H), 3.78 (s, 2H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 162.4, 144.6, 130.4, 124.7, 118.2, 114.7, 79.5, 55.6, 31.8, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3065, 2956, 1604, 1349, 1158, 962, 792.

MS (APCI): *m/z* calcd. for C₁₄H₂₁O₄S ([M+H]⁺) 285.1, found 285.4.

HRMS (EI⁺): *m/z* calcd. for C₁₄H₂₀O₄S ([M]⁺) 284.1077, found 284.1100.

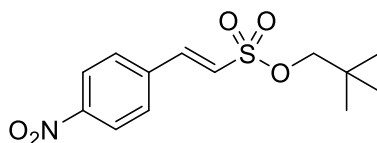
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-CXLLNBAHTN-UHFFFADPSC-NUHFF-NAIXQ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/CXLLNBAHTNGKGY-MDZDMXLPSA-N.1>

Neopentyl (*E*)-2-(4-nitrophenyl)ethene-1-sulfonate (8d**)**



Following the **TP-4**, (*E*)-3-(4-nitrophenyl)acrylic acid (58.0 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 95:5) to obtain **8d** as a colorless solid (53.7 mg, 60% yield).

mp: 88.8–89.7 °C. **R_f** = 0.15 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 8.33–8.28 (m, 2H), 7.73–7.69 (m, 2H), 7.66 (d, *J* = 15.6 Hz, 1H), 6.92 (d, *J* = 15.6 Hz, 1H), 3.86 (s, 2H), 1.00 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 149.3, 141.6, 138.1, 129.3, 125.7, 124.5, 80.2, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3126, 2960, 1625, 1529, 1344, 1165, 959, 803.

MS (APCI): *m/z* calcd. for C₁₃H₁₈NO₅S ([M+H]⁺) 300.1, found 300.5.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₇NO₅S ([M]⁺) 299.0822, found 299.0838.

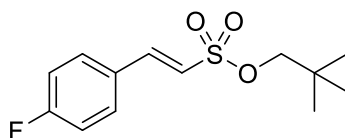
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-MFGOXJJGCZ-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/MFGOXJJGCZRRRX-CMDGGOBGSA-N.1>

Neopentyl (*E*)-2-(4-fluorophenyl)ethene-1-sulfonate (8e**)**



Following the **TP-4**, (*E*)-3-(4-fluorophenyl)acrylic acid (49.8 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8e** as a colorless liquid (38.5 mg, 47% yield). Analytical data for **8e** match those previously described in the literature.^[42]

R_f = 0.25 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 15.6 Hz, 1H), 7.55–7.50 (m, 2H), 7.10–7.02 (m, 2H), 6.68 (d, *J* = 15.6 Hz, 1H), 3.80 (s, 2H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 164.6 (d, ¹*J*_{C-F} = 253.4 Hz, 1C), 143.4, 130.7 (d, ³*J*_{C-F} = 8.8 Hz, 2C), 128.4 (d, ⁴*J*_{C-F} = 3.4 Hz, 1C), 121.0 (d, ⁵*J*_{C-F} = 2.0 Hz, 1C), 116.6 (d, ²*J*_{C-F} = 22.0 Hz, 2C), 79.7, 31.9, 26.2.

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ -107.4.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3003, 2963, 1710, 1358, 1221, 1166, 966, 852.

MS (APCI): *m/z* calcd. for C₁₃H₁₈O₃FS ([M+H]⁺) 273.1, found 273.2.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₇O₃FS ([M]⁺) 272.0877, found 272.0886.

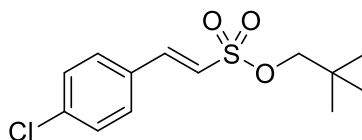
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-RAAPJZFEUQ-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/RAAPJZFEUQUCRF-CMDGGOBGSA-N.1>

Neopentyl (*E*)-2-(4-chlorophenyl)ethene-1-sulfonate (8f**)**



Following the **TP-4**, (*E*)-3-(4-chlorophenyl)acrylic acid (54.8 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8f** as a colorless solid (45.5 mg, 53% yield). Analytical data for **8f** match those previously described in the literature.^[42]

mp: 97.3–97.9 °C. **R_f** = 0.25 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 15.6 Hz, 1H), 7.48–7.44 (m, 2H), 7.44–7.39 (m, 2H), 6.72 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 2H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.3, 137.7, 130.6, 129.8, 129.7, 121.8, 79.8, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3056, 2957, 1620, 1359, 1165, 971, 836, 796.

MS (APCI): *m/z* calcd. for C₁₃H₁₈O₃SCl ([M+H]⁺) 289.1, found 289.4.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₇O₂SCl ([M]⁺) 288.0581, found 288.0594.

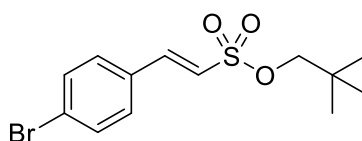
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-VXGBLHDVVU-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/VXGBLHDVVUZHMT-CMDGGOBGSA-N.1>

Neopentyl (*E*)-2-(4-bromophenyl)ethene-1-sulfonate (8g**)**



Following the **TP-4**, (*E*)-3-(4-bromophenyl)acrylic acid (68.1 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8g** as a colorless solid (52.5 mg, 53% yield). Analytical data for **8g** match those previously described in the literature.^[42]

mp: 133.3–134.1 °C. **R_f** = 0.25 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.60–7.56 (m, 2H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.41–7.36 (m, 2H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 2H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.4, 132.6, 131.0, 129.9, 126.0, 121.9, 79.8, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 2955, 1620, 1358, 1162, 975, 795, 566.

MS (APCI): *m/z* calcd. for C₁₃H₁₈O₃SBr ([M+H]⁺) 333.0, found 333.5.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₇O₃SBr ([M]⁺) 332.0076, found 332.0086.

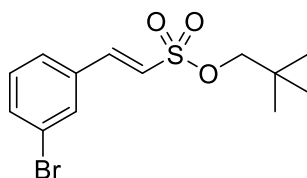
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-UBHWQYVHFI-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/UBHWQYVHFIXUHK-CMDGGGOBGS-A-N.1>

Neopentyl (*E*)-2-(3-bromophenyl)ethene-1-sulfonate (8h)



Following the **TP-4**, (*E*)-3-(3-bromophenyl)acrylic acid (68.1 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8h** as a colorless solid (60.0 mg, 60% yield).

mp: 65.2–66.1 °C. **R_f** = 0.30 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.66 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 15.6 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 2H), 0.99 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.0, 134.3, 134.2, 131.2, 130.8, 127.2, 123.4, 122.8, 79.9, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3063, 2959, 1621, 1348, 1161, 955, 773, 540.

MS (APCI): *m/z* calcd. for C₁₃H₁₈O₃SBr ([M+H]⁺) 333.0, found 333.1.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₇O₃SBr ([M]⁺) 332.0076, found 332.0090.

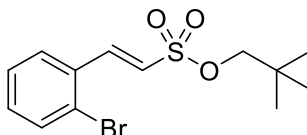
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-IWWPEDCMKL-UHFFFADPSC-NUHFF-NSXYH-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/IWWPEDCMKLEIS-BQYQJAHWSA-N.1>

Neopentyl (*E*)-2-(2-bromophenyl)ethene-1-sulfonate (8i)



Following the **TP-4**, (*E*)-3-(2-bromophenyl)acrylic acid (68.1 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8i** as a colorless solid (53.0 mg, 53% yield).

mp: 74.6–75.4 °C. **R_f** = 0.20 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 15.6 Hz, 1H), 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.31 (td, *J* = 7.8, 1.4 Hz, 1H), 6.72 (d, *J* = 15.6 Hz, 1H), 3.84 (s, 2H), 1.00 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.2, 133.9, 132.5, 132.4, 128.3, 128.1, 125.5, 124.2, 80.0, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3063, 2966, 1624, 1341, 1159, 956, 750, 546.

MS (APCI): m/z calcd. for C₁₃H₁₈O₃SBr ([M+H]⁺) 333.0, found 333.5.

HRMS (EI⁺): m/z calcd. for C₁₃H₁₇O₃SBr ([M]⁺) 332.0076, found 332.0093.

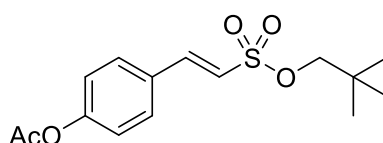
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-CAPWWSFATX-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/CAPWWSFATXLFOT-CMDGGOBGSA-N.1>

(E)-4-(2-((Neopentyloxy)sulfonyl)vinyl)phenyl acetate (8j)



Following the **TP-4**, (*E*)-3-(4-acetoxyphenyl)acrylic acid (61.9 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8j** as a colorless solid (51.5 mg, 55% yield). Analytical data for **8j** match those previously described in the literature.^[42]

mp: 118.5–119.0 °C. **R_f** = 0.20 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.58 (d, *J* = 15.6 Hz, 1H), 7.55–7.52 (m, 2H), 7.20–7.15 (m, 2H), 6.70 (d, *J* = 15.6 Hz, 1H), 3.79 (s, 2H), 2.32 (s, 3H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 169.1, 153.0, 143.6, 129.81, 129.76, 122.6, 121.2, 79.7, 31.8, 26.2, 21.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3063, 2960, 1761, 1621, 1345, 1159, 955, 802.

MS (APCI): m/z calcd. for C₁₅H₂₁O₅S ([M+H]⁺) 313.4, found 313.5.

HRMS (EI⁺): m/z calcd. for C₁₅H₂₀O₅S ([M]⁺) 312.1026, found 312.1041.

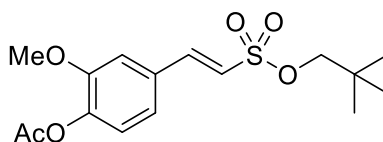
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XSFAWQKH XV-UHFFFADPSC-NUHFF-NAIXQ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/XSFAWQKH XVRJFW-MDZDMXLPSA-N.1>

(E)-2-Methoxy-4-(2-((neopentyloxy)sulfonyl)vinyl)phenyl acetate (8k)



Following the **TP-4**, (*E*)-3-(4-acetoxy-3-methoxyphenyl)acrylic acid (70.9 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 90:10) to obtain **8k** as a colorless solid (20.9 mg, 20% yield).

mp: 136.3–136.8 °C. **R_f** = 0.30 (*n*-hexane/EtOAc = 4:1).

¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 15.6 Hz, 1H), 7.15–7.05 (m, 3H), 6.69 (d, *J* = 15.6 Hz, 1H), 3.88 (s, 3H), 3.79 (s, 2H), 2.33 (s, 3H), 0.98 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 168.8, 151.8, 144.1, 142.4, 131.0, 123.7, 121.7, 121.3, 111.8, 79.8, 56.1, 31.9, 26.2, 20.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3063, 2966, 1760, 1618, 1354, 1161, 951.

MS (APCI): m/z calcd. for $\text{C}_{16}\text{H}_{23}\text{O}_6\text{S}$ ($[\text{M}+\text{H}]^+$) 343.1, found 343.2.

HRMS (ESI $^+$): m/z calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_6\text{SNa}$ ($[\text{M}+\text{Na}]^+$) 365.102931, found 365.102900.

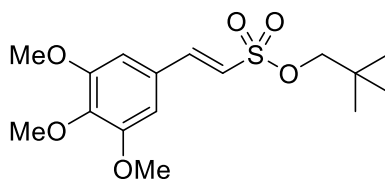
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-VWCNVJOEAV-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/VWCNVJOEAVXQIX-CMDGGOBGSA-N.1>

Neopentyl (*E*)-2-(3,4,5-trimethoxyphenyl)ethene-1-sulfonate (8l**)**



Following the **TP-4**, (*E*)-3-(3,4,5-trimethoxyphenyl)acrylic acid (71.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 93:7) to obtain **8l** as a colorless solid (42.3 mg, 41% yield).

mp: 110.9–111.2 °C. **R_f** = 0.25 (*n*-hexane/EtOAc = 4:1).

^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, J = 15.6 Hz, 1H), 6.74 (s, 2H), 6.67 (d, J = 15.6 Hz, 1H), 3.89 (s, 9H), 3.79 (s, 2H), 0.97 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 153.7, 144.8, 141.1, 127.4, 120.1, 105.8, 79.6, 61.1, 56.3, 31.8, 26.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3059, 2947, 1614, 1336, 1158, 958, 789.

MS (APCI): m/z calcd. for $\text{C}_{16}\text{H}_{25}\text{O}_6\text{S}$ ($[\text{M}+\text{H}]^+$) 345.1, found 345.6.

HRMS (EI $^+$): m/z calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_6\text{S}$ ($[\text{M}]^+$) 344.1288, found 344.1308.

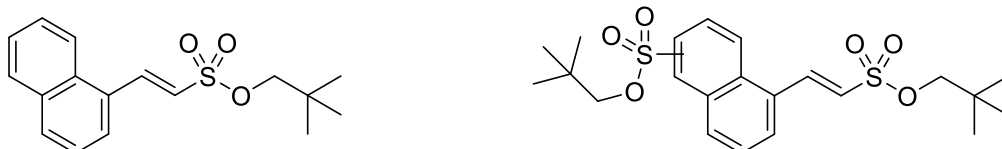
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-YQRZVSXQCQ-UHFFFADPSC-NUHFF-NSXYH-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/YQRZVSXQCQZRPB-BQYQJAHWSA-N.1>

Neopentyl (*E*)-2-(naphthalen-1-yl)ethene-1-sulfonate (8m**)**



Following the **TP-4**, (*E*)-3-(naphthalen-1-yl)acrylic acid (59.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8m** as a colorless solid (26.9 mg, 30% yield) together with the side product **10m** (21.8 mg, 16% yield, colorless solid).

Analytical data for **8m**:

mp: 76.1–77.1 °C. **R_f** = 0.31 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 8.43 (d, *J* = 15.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.65–7.60 (m, 1H), 7.60–7.55 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.87 (s, 2H), 1.01 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 141.9, 133.8, 131.8, 131.3, 129.4, 129.1, 127.6, 126.8, 125.8, 125.5, 123.6, 123.1, 79.8, 31.9, 26.3.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3066, 2965, 1612, 1344, 1162, 953, 863, 793.

MS (APCI): *m/z* calcd. for C₁₇H₂₁O₃S ([M+H]⁺) 305.1, found 305.5.

HRMS (EI⁺): *m/z* calcd. for C₁₇H₂₀O₃S ([M]⁺) 304.1128, found 304.1134.

Analytical data for **10m**:

10m was formed as single regioisomer. However, the regiochemistry of **10m** could not be assigned unambiguously within this study.

mp: 133.1–134.1 °C. **R_f** = 0.20 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 8.72 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 15.4 Hz, 1H), 8.30 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.82–7.77 (m, 1H), 7.77–7.72 (m, 2H), 6.94 (d, *J* = 15.4 Hz, 1H), 3.92 (s, 2H), 3.66 (s, 2H), 1.02 (s, 9H), 0.85 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 140.5, 136.4, 134.0, 131.9, 129.7, 129.2, 128.8, 128.6, 127.5, 126.1, 124.2, 123.8, 80.4, 80.2, 32.0, 31.7, 26.24, 26.16.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3060, 2960, 1609, 1345, 1166, 952, 818.

MS (APCI): *m/z* calcd. for C₄₄H₆₁O₁₂S₄ ([2M+H]⁺) 909.3, found 908.9.

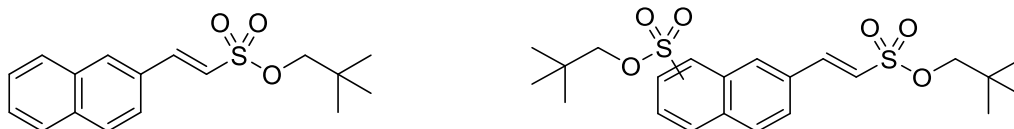
HRMS (EI⁺): *m/z* calcd. for C₂₂H₃₀O₆S₂ ([M]⁺) 454.1474, found 454.1497.

Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-NNWNPNOQF-UHFFFADPSC-NUHFF-NZJBK-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/NNWNPNOQFFLLH-VAWYXSNFSA-N.1>

Neopentyl (*E*)-2-(naphthalen-2-yl)ethene-1-sulfonate (8n**)**

Following the **TP-4**, (*E*)-3-(naphthalen-2-yl)acrylic acid (59.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8n** as a colorless solid (26.0 mg, 28% yield) together with the side product **10n** (3.7 mg, 3% yield, colorless liquid).

Analytical data for **8n**:

mp: 117.1–117.8 °C. **R_f** = 0.31 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.96 (s, 1H), 7.91–7.84 (m, 3H), 7.76 (d, *J* = 15.4 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.59–7.52 (m, 2H), 6.84 (d, *J* = 15.4 Hz, 1H), 3.83 (s, 2H), 0.99 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 144.9, 134.7, 133.2, 131.1, 129.6, 129.3, 128.9, 128.1, 128.0, 127.3, 123.3, 121.2, 79.7, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3060, 2966, 1612, 1349, 1162, 951, 860, 806.

MS (APCI): m/z calcd. for $\text{C}_{17}\text{H}_{21}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 305.1, found 305.5.

HRMS (EI^+): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{S}$ ($[\text{M}]^+$) 304.1128, found 304.1131.

Analytical data for **10n**:

10n was formed as single regioisomer. However, the regiochemistry of **10n** could not be assigned unambiguously within this study.

R_f = 0.20 (n -hexane/EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 8.83 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 15.4 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.74 (td, J = 8.4, 1.4 Hz, 1H), 7.66 (td, J = 8.4, 1.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 6.56 (d, J = 15.4 Hz, 1H), 3.98 (s, 2H), 3.66 (s, 2H), 1.00 (s, 9H), 0.86 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 145.5, 135.4, 134.7, 134.6, 130.7, 129.5, 129.4, 128.9, 128.2, 126.2, 126.0, 125.9, 80.5, 80.2, 31.9, 31.8, 26.22, 26.21.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3005, 2970, 1712, 1359, 1219, 962, 848.

MS (APCI): m/z calcd. for $\text{C}_{22}\text{H}_{31}\text{O}_6\text{S}_2$ ($[\text{M}+\text{H}]^+$) 455.2, found 455.6.

HRMS (EI^+): m/z calcd. for $\text{C}_{22}\text{H}_{30}\text{O}_6\text{S}_2$ ($[\text{M}]^+$) 454.1478, found 454.1481.

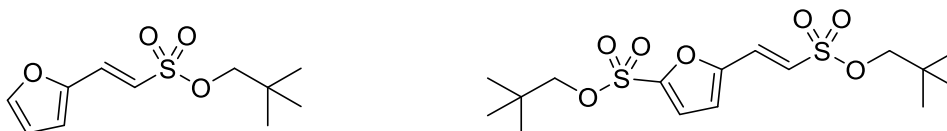
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-RBMWJOBAYR-UHFFFADPSC-NUHFF-NZAE-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/RBMWJOBAYRKEOU-ZHACJKMWSA-N.1>

Neopentyl (*E*)-2-(furan-2-yl)ethene-1-sulfonate (8o**)**



Following the **TP-4**, (*E*)-3-(furan-2-yl)acrylic acid (41.4 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (n -hexane/EtOAc = 98:2) to obtain **8o** as a colorless liquid (7.9 mg, 11%) together with the side product **10o** (45.3 mg, 38% yield, colorless solid).

Analytical data for **8o**:

R_f = 0.25 (n -hexane/EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.55–7.52 (m, 1H), 7.35 (d, J = 15.2 Hz, 1H), 6.72 (d, J = 3.4 Hz, 1H), 6.61 (d, J = 15.2 Hz, 1H), 6.52 (dd, J = 3.4, 1.6 Hz, 1H), 3.78 (s, 2H), 0.98 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 148.4, 145.9, 131.1, 118.5, 117.2, 112.8, 79.7, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3005, 2965, 1711, 1358, 1219, 1091.

MS (APCI): m/z calcd. for $\text{C}_{11}\text{H}_{17}\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 245.1, found 245.3.

HRMS (EI^+): m/z calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_4\text{S}$ ($[\text{M}]^+$) 244.0764, found 244.0785.

Analytical data for **10o**:

mp: 112.6–113.0 °C. R_f = 0.13 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 15.4 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 6.87 (d, *J* = 15.4 Hz, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 3.88 (s, 2H), 3.83 (s, 2H), 0.99 (s, 9H), 0.95 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 151.9, 147.0, 129.2, 124.0, 119.9, 116.3, 81.8, 80.3, 31.94, 31.90, 26.2, 26.0.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3003, 2969, 1711, 1358, 1219, 1092.

MS (APCI): *m/z* calcd. for C₁₆H₂₇O₇S₂ ([M+H]⁺) 395.1, found 395.1.

HRMS (EI⁺): *m/z* calcd. for C₁₆H₂₆O₇S₂ ([M]⁺) 394.1114, found 394.1134.

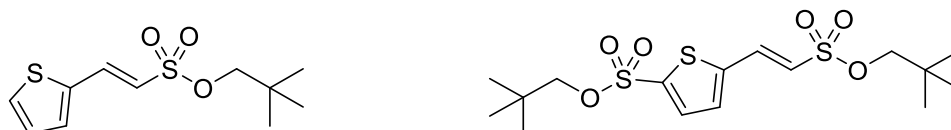
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-MJDINSPTRU-UHFFFADPSC-NUHFF-NXL0P-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/GOJGFMQYZBAXMX-SOFGYWHQSA-N.1>

<https://doi.org/10.14272/JXPGRUREMBXEGE-MDZDMXLPSA-N.1>

Neopentyl (*E*)-2-(thiophen-2-yl)ethene-1-sulfonate (8p**)**

Following the **TP-4**, (*E*)-3-(thiophen-2-yl)acrylic acid (46.3 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **8p** as a colorless solid (24.2 mg, 31% yield) together with the side product **10p** (36.6 mg, 30% yield, colorless solid).

Analytical data for **8p**:

mp: 60.2–60.8 °C. R_f = 0.25 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 15.2 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 3.6 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.52 (d, *J* = 15.2 Hz, 1H), 3.79 (s, 2H), 0.98 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 137.3, 136.6, 132.7, 130.2, 128.6, 119.2, 79.7, 31.9, 26.2.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3067, 2962, 1602, 1348, 1159, 955.

MS (APCI): *m/z* calcd. for C₁₁H₁₇O₃S₂ ([M+H]⁺) 261.1, found 261.3.

HRMS (EI⁺): *m/z* calcd. for C₁₁H₁₆O₃S₂ ([M]⁺) 260.0535, found 260.0554.

Analytical data for **10p**:

mp: 125.1–125.9 °C. R_f = 0.15 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 15.4 Hz, 1H), 7.65 (d, *J* = 4.0 Hz, 1H), 7.33 (d, *J* = 4.0 Hz, 1H), 6.70 (d, *J* = 15.4 Hz, 1H), 3.84 (s, 2H), 3.82 (s, 2H), 0.99 (s, 9H), 0.95 (s, 9H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.3, 139.0, 135.1, 134.4, 131.2, 123.9, 81.2, 80.3, 31.92, 31.86, 26.2, 26.1.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3059, 2959, 1614, 1356, 1164, 952.

MS (APCI): *m/z* calcd. for C₁₆H₂₇O₆S₃ ([M+H]⁺) 411.1, found 411.5.

HRMS (EI^+): m/z calcd. for $C_{16}H_{26}O_6S_3$ ($[M]^+$) 410.0886, found 410.0913.

Additional information on the chemical synthesis is available via Chemotion repository:

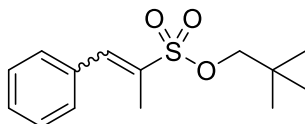
<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZREWVIAMZP-UHFFFADPSC-NUHFF-NXLOP-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/JHKIXXQIDLWUAN-SOFGYWHQSA-N.1>

<https://doi.org/10.14272/MPYVFYCPJCYBAC-MDZDMLPSA-N.1>

Neopentyl (*E*-Z)-1-phenylprop-1-ene-2-sulfonate (8q)



Following the **TP-4**, (*E*)-2-methyl-3-phenylacrylic acid (48.7 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 99:1) to obtain **8q** as a colorless liquid as inseparable mixture of the *E*- and the *Z*-isomer (22.4 mg, 28% yield, *E*:*Z* = 3.5:1).

R_f = 0.48 (*n*-hexane/EtOAc = 9:1).

8q-(*E*): 1H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.48–7.41 (m, 5H), 3.75 (s, 2H), 2.29 (d, J = 1.4 Hz, 3H), 0.99 (s, 9H).

8q-(*Z*): 1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.31 (m, 5H), 7.06 (s, 1H), 3.60 (s, 2H), 2.29 (d, J = 1.4 Hz, 3H), 0.81 (s, 9H).

8q-(*E*): $^{13}C\{^1H\}$ -NMR (101 MHz, $CDCl_3$): δ 139.0, 129.8, 129.7, 129.4, 128.9, 128.1, 79.5, 31.8, 26.3, 13.7.

8q-(*Z*): $^{13}C\{^1H\}$ -NMR (101 MHz, $CDCl_3$): δ 138.7, 133.9, 133.5, 133.3, 132.6, 129.2, 128.9, 125.6, 79.3, 31.6, 26.0, 21.5.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3059, 2960, 1345, 1176, 963, 836.

MS (APCI): m/z calcd. for $C_{14}H_{21}O_3S$ ($[M+H]^+$) 269.1, found 269.1.

HRMS (EI^+): m/z calcd. for $C_{14}H_{20}O_3S$ ($[M]^+$) 268.112768, found 268.112960.

The stereoisomeric ratio was determined to be 3.5/1 (*E*/*Z*) by NMR integration of the corresponding methylene signals.

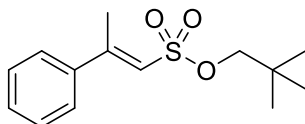
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-YBXNPAWLMZ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/YBXNPAWLMZRFQT-UHFFFAOYSA-N.1>

Neopentyl (*E*)-2-phenylprop-1-ene-1-sulfonate (8r)



Following the **TP-4**, (*E*)-3-phenylbut-2-enoic acid (48.7 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 99:1) to obtain **8r** as a colorless liquid (29.5 mg, 37% yield). Analytical data for **8r** match those previously described in the literature.^[42]

R_f = 0.43 (*n*-hexane/EtOAc = 9:1).

1H NMR (400 MHz, $CDCl_3$): δ 7.50–7.38 (m, 5H), 6.50 (d, J = 1.2 Hz, 1H), 3.83 (s, 2H), 2.55 (d, J = 1.2 Hz, 3H), 1.00 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 155.3, 139.8, 130.2, 129.0, 126.4, 121.7, 79.3, 31.8, 26.3, 18.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3063, 2960, 1352, 1164, 965, 850.

MS (APCI): m/z calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 269.1, found 269.1.

HRMS (EI^+): m/z calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{S}$ ($[\text{M}]^+$) 268.112768, found 268.112750.

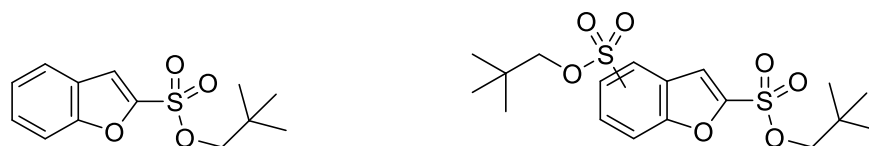
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-GYVBCVAVQX-UHFFFADPSC-NUHFF-NLXOU-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/GYVBCVAVQXRFIW-ZRDIBKRKSA-N.1>

Neopentyl benzofuran-2-sulfonate (**8s**)



Following the **TP-4**, benzofuran-2-carboxylic acid (49.3 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/ EtOAc = 98:2) to obtain **8s** as a colorless liquid (16.9 mg, 21% yield) together with the side product **10s** (4.5 mg, 4% yield, colorless solid). Analytical data for **8s** match those previously described in the literature.^[42]

Analytical data for **8s**:

R_f = 0.38 (*n*-hexane/ EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, J = 8.2 Hz, 1H), 7.61 (dd, J = 8.2, 0.8 Hz, 1H), 7.55–7.49 (m, 2H), 7.41–7.35 (m, 1H), 3.92 (s, 2H), 0.94 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 156.2, 146.6, 128.5, 125.7, 124.6, 123.3, 114.7, 112.6, 81.7, 31.9, 26.1.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3129, 2965, 1382, 1172, 932, 756.

MS (APCI): m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 269.1, found 269.3.

HRMS (EI^+): m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$ ($[\text{M}]^+$) 268.0764, found 268.0781.

Analytical data for **10s**:

10s was formed as single regioisomer. However, the regiochemistry of **10s** could not be assigned unambiguously within this study.

mp: 108.2–109.0 °C. R_f = 0.13 (*n*-hexane/ EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.97 (dd, J = 8.2, 0.8 Hz, 1H), 7.94 (d, J = 0.8 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.71–7.66 (m, 1H), 3.95 (s, 2H), 3.71 (s, 2H), 0.95 (s, 9H), 0.88 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 156.0, 149.2, 130.3, 127.9, 125.8, 123.9, 118.2, 113.5, 82.3, 80.5, 32.0, 31.8, 26.1, 26.0.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3142, 2962, 1364, 1176, 932, 799.

MS (APCI): m/z calcd. for $\text{C}_{18}\text{H}_{27}\text{O}_7\text{S}_2$ ($[\text{M}+\text{H}]^+$) 419.1, found 419.5.

HRMS (EI^+): m/z calcd. for $\text{C}_{18}\text{H}_{26}\text{O}_7\text{S}_2$ ($[\text{M}]^+$) 418.1114, found 418.1137.

Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-DOFKASQWDJ-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/DOFKASQWDJPMSY-UHFFFAOYSA-N.1>

5.3 Scale-up Reaction

The reaction was carried out using the divided glass cell with a P4 frit as described in section 1.2.

Anolyte: In a 100 mL pear-shaped flask a mixture of neopentyl alcohol (2.64 g, 30.0 mmol, 3.0 equiv.) and 2,6-lutidine (6.43 g, 6.97 mL, 60.0 mmol, 6.0 equiv.) was prepared. The mixture was chilled to 0 °C in an ice bath and SO₂ stock solution (3.30 M, 30.3 mL, 10.0 equiv.) was added, resulting in a pale yellowish color. The mixture was diluted with acetonitrile (58.6 mL) so that a total volume of 100.0 mL was achieved.

Catholyte: A solution of *n*Bu₄NPF₆ (3.87 g, 10.0 mmol, 1.0 equiv.) and acetic acid (3.00 g, 2.86 mL, 50.0 mmol, 5.0 equiv.) in acetonitrile was prepared so that a total volume of 100.0 mL was reached as well.

The anodic compartment was charged with cinnamic acid (1.48 g, 10.0 mmol, 1.0 equiv.) and the prepared electrolyte mixtures above were transferred to their respective compartments. The cell was equipped with a graphite anode and a graphite cathode. The current was set accordingly so that a current density of 10 mA×cm⁻² was reached (90 mA with the setup described herein) and the amount of applied charge was set to 3377 C (corresponding to 3.5 *F*). The electrolysis was conducted at room temperature under constant stirring for 10 h 25 min.

After completion of the electrolysis, both the anolyte and catholyte were combined into a beaker and the compartments were rinsed with acetonitrile (3 x 15 mL each). Water (200 mL) was added. Then the mixture was extracted with EtOAc (4 x 200 mL). The combined organic fractions were washed with water (3 x 100 mL), dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product (ca. 12.7 g) was loaded onto silica, purified *via* automated flash column chromatography (cyclohexane/ethyl acetate = 98/2 → 75/25, column: PF-25SiHC-F0080, detection @ 254 nm) and the desired product neopentyl (*E*)-2-phenylethene-1-sulfonate (**8a**, 1.84 g, 7.22 mmol, 72%) was obtained as a colorless solid.

Spectroscopic data of the isolated compound matched the one obtained from the small-scale reaction described in section 5.2.

Note: An ¹H NMR yield of 70% was calculated by addition of triphenylmethane (684.4 mg, 2.80 mmol) as internal standard to the crude product before column chromatography.

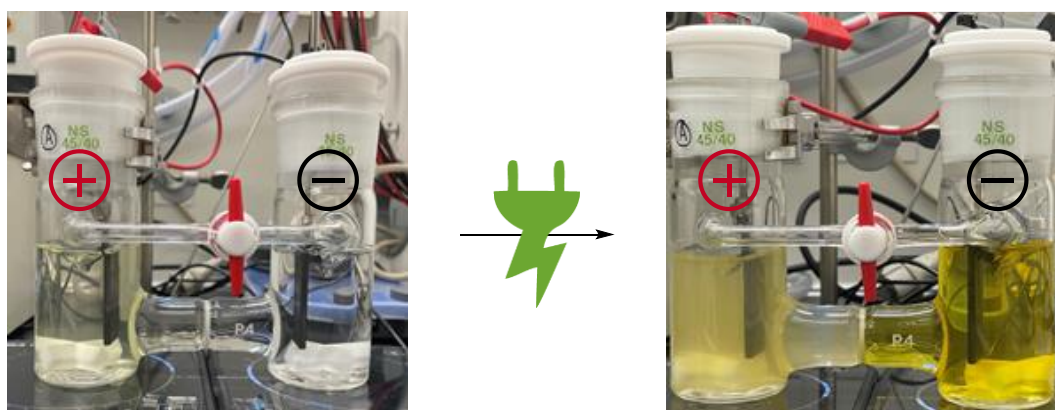


Figure S4: Scale-up experiment in a 2 x 100 mL glass cell before (left) and after (right) the electrolysis.

5.4 Reusability Tests

The reactions were carried out using IKA Pro-Divide cells with a glass frit membrane as described in the section before.

Anolyte: An oven-dried 10.0 mL pear-shaped flask was charged with cinnamic acid (44.5 mg, 0.3 mmol), neopentyl alcohol (79.3 mg, 3.0 equiv.), $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), and anhydrous acetonitrile (2.1 mL). The mixture was cooled to 0 °C in an ice bath, followed by the addition of SO_2 stock solution (4.60 M, 0.65 mL, 10.0 equiv.) and 2,6-lutidine (0.21 mL, 6.0 equiv.) so that a total volume of 3.0 mL was achieved.

Catholyte: An oven-dried 10.0 mL pear-shaped flask was charged with $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), acetic acid (0.09 mL, 5.0 equiv.), and anhydrous acetonitrile (2.9 mL) so that a total volume of 3.0 mL was achieved as well.

The reaction mixtures were transferred with syringes to their respective compartment simultaneously. The amperage was set accordingly so that a current density of $10 \text{ mA} \times \text{cm}^{-2}$ was reached (8.8 mA with the setup described herein) and the amount of applied charge was set to 3.5 F . The electrolysis was conducted at room temperature under constant stirring (400 rpm) for ca. 3 h 11 min. After completion of the electrolysis, the anolyte was transferred to a round bottom flask, the anode compartment was rinsed with acetonitrile (2 x 3.0 mL). ^1H NMR yields were calculated by addition of triphenylmethane (73.2 mg, 1.0 equiv.) as the internal standard to this mixture. After 5 min of stirring, 1.0 mL of the mixture was taken, and the solvent was removed under reduced pressure.

For the subsequent runs, the anolyte was prepared as described and transferred to the respective compartment. The graphite electrode, glass frit membrane and catholyte (an additional amount of 0.07 mL acetic acid (4.0 equiv.) was added for each subsequent run to compensate for the loss from H_2 evolution from the previous experiment) were reused in the following experiments. The electrolysis and subsequent workup for determining ^1H NMR yield was conducted as described above. The complete procedure was conducted four times in total (**Figure S5**).

During the reusability test, gradual formation of a polymer layer was observed at the anode (**Figure S6**). Attempts to analyze the nature of the polymer layer were unsuccessful.

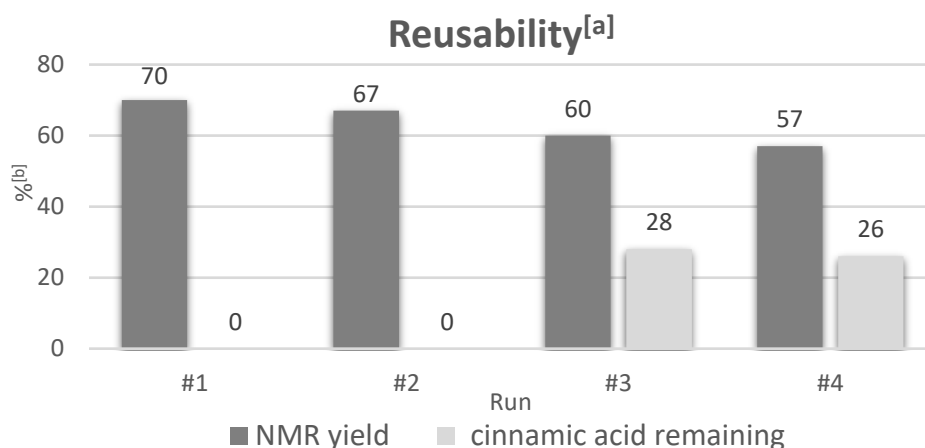


Figure S5: Tests for reusing the electrodes, glass frit membrane and catholyte. ^[a]Conditions described above. ^[b] ^1H -NMR yield with the use of CHPh_3 as the internal standard.

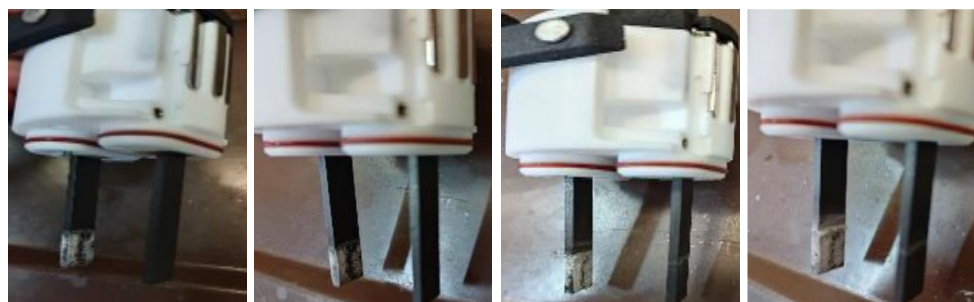


Figure S6: Pictures of the electrodes after run 1 to 4 (from left to right) show the consecutive formation of a polymer layer after.

6 Synthesis of Alkyl Alkenesulfonates [Scope of Alcohols]

6.1 Typical Procedure for the Preparation of Alkyl Alkenesulfonates [Scope of Alcohols] (TP-5)

The reactions were carried out using IKA Pro-Divide cells with a glass frit membrane.

Anolyte: An oven-dried 10.0 mL pear-shaped flask was charged with cinnamic acid (44.5 mg, 0.3 mmol), alcohol (3.0 equiv.), $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), and anhydrous acetonitrile. The mixture was cooled to 0 °C in an ice bath, followed by the addition of SO_2 stock solution (0.6 mL, 5.0 M in acetonitrile, 10.0 equiv.) and 2,6-lutidine (0.21 mL, 6.0 equiv.) so that a total volume of 3.0 mL was achieved.

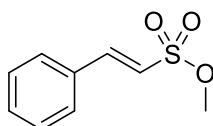
Catholyte: An oven-dried 10.0 mL pear-shaped flask was charged with $n\text{Bu}_4\text{NPF}_6$ (116.3 mg, 1.0 equiv.), acetic acid (0.09 mL, 5.0 equiv.), and anhydrous acetonitrile (2.9 mL) so that a total volume of 3.0 mL was achieved as well.

The reaction mixtures were transferred with syringes to their respective compartment simultaneously. The amperage was set accordingly so that a current density of $10 \text{ mA} \times \text{cm}^{-2}$ was reached (8.8 mA with the setup described herein) and the amount of applied charge was set to 3.5 F . The electrolysis was conducted at room temperature under constant stirring (400 rpm) for ca. 3 h 11 min.

After completion of the electrolysis, the anolyte was transferred to a separatory funnel and the anode compartment was rinsed with additional EtOAc (2 x 3.0 mL). Distilled water (10.0 mL) was added and the obtained mixture extracted with EtOAc (2 x 10.0 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude residue was subjected to flash column chromatography on silica gel to obtain the product.

6.2 Analytical Data for Compounds of Type 9

Methyl (*E*)-2-phenylethene-1-sulfonate (9a)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), methanol (36.4 μL , 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (n -hexane/EtOAc = 90:10) to obtain **9a** as a colorless solid (34.0 mg, 57% yield).

mp: 65.3–65.8 °C. **R_f** = 0.21 (n -hexane/EtOAc = 4:1).

^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, J = 15.6 Hz, 1H), 7.55–7.50 (m, 2H), 7.50–7.41 (m, 3H), 6.73 (d, J = 15.6 Hz, 1H), 3.86 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 145.5, 132.0, 131.7, 129.3, 128.7, 120.3, 56.3.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3072, 2959, 1618, 1344, 1154, 963, 739.

MS (APCI): m/z calcd. for $\text{C}_9\text{H}_{11}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 199.0, found 199.3.

HRMS (EI^+): m/z calcd. for $\text{C}_9\text{H}_{10}\text{O}_3\text{S}$ ($[\text{M}]^+$) 198.0345, found 198.0360.

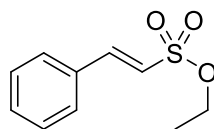
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-FSMDHYUPDK-UHFFFADPSC-NUHFF-NSXYH-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/FSMDHYUPDKNFEI-BQYQJAHWSA-N.1>

Ethyl (*E*)-2-phenylethene-1-sulfonate (**9b**)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), ethanol (52.5 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 95:5) to obtain **9b** as a colorless liquid (38.3 mg, 60% yield).

R_f = 0.25 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.61 (d, *J* = 15.6 Hz, 1H), 7.54–7.49 (m, 2H), 7.49–7.40 (m, 3H), 6.75 (d, *J* = 15.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 144.8, 132.1, 131.6, 129.3, 128.6, 121.3, 67.0, 15.0.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3003, 1620, 1358, 1221, 1005, 752.

MS (APCI): *m/z* calcd. for C₁₀H₁₃O₃S ([M+H]⁺) 213.1, found 213.4.

HRMS (EI⁺): *m/z* calcd. for C₁₀H₁₂O₃S ([M]⁺) 212.0502, found 212.0519.

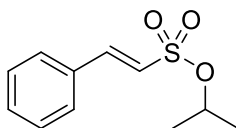
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LEDCJBCTEY-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/LEDCJBCTEYLBJO-CMDGGGOBGSA-N.1>

Isopropyl (*E*)-2-phenylethene-1-sulfonate (**9c**)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), 2-propanol (68.8 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 95:5) to obtain **9c** as a colorless liquid (37.0 mg, 55% yield).

R_f = 0.35 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.54–7.48 (m, 2H), 7.48–7.40 (m, 3H), 6.77 (d, *J* = 15.6 Hz, 1H), 4.84 (septet, *J* = 6.2 Hz, 1H), 1.41 (d, *J* = 6.2 Hz, 6H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.8, 132.2, 131.4, 129.3, 128.5, 122.5, 77.4, 23.1.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3056, 2986, 1618, 1356, 1168, 978, 750.

MS (APCI): *m/z* calcd. for C₁₁H₁₅O₃S ([M+H]⁺) 227.1, found 227.3.

HRMS (EI⁺): *m/z* calcd. for C₁₁H₁₄O₃S ([M]⁺) 226.0658, found 226.0675.

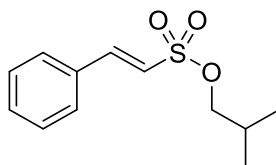
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-OPTQKNRBAM-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/OPTQKNRBAMBSSR-CMDGGGOBGSA-N.1>

Isobutyl (*E*)-2-phenylethene-1-sulfonate (9d)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), isobutanol (83.2 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 95:5) to obtain **9d** as a colorless liquid (43.6 mg, 60% yield).

R_f = 0.40 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.54–7.49 (m, 2H), 7.49–7.41 (m, 3H), 6.75 (d, *J* = 15.6 Hz, 1H), 3.92 (d, *J* = 6.6 Hz, 2H), 2.04 (nonet, *J* = 6.6 Hz, 1H), 0.98 (d, *J* = 6.6 Hz, 6H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 144.7, 132.1, 131.5, 129.3, 128.6, 121.2, 76.5, 28.2, 18.8.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3005, 2965, 1621, 1358, 1168, 976, 749.

MS (APCI): *m/z* calcd. for C₁₂H₁₇O₃S ([M+H]⁺) 241.1, found 241.4.

HRMS (EI⁺): *m/z* calcd. for C₁₂H₁₆O₃S ([M]⁺) 240.0815, found 240.0826.

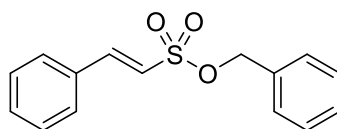
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-KIKXBEOFOK-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/KIKXBEOFOKXQCA-CMDGGGOBGSA-N.1>

Benzyl (*E*)-2-phenylethene-1-sulfonate (9e)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), benzyl alcohol (93.6 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 95:5) to obtain **9e** as a colorless liquid (42.3 mg, 51% yield).

R_f = 0.20 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 15.6 Hz, 1H), 7.50–7.31 (m, 10H), 6.64 (d, *J* = 15.6 Hz, 1H), 5.19 (s, 2H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 144.8, 133.5, 132.1, 131.6, 129.4, 129.3, 128.94, 128.92, 128.6, 121.7, 72.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3026, 1624, 1169, 968, 745.

MS (APCI): m/z calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 275.1, found 275.4.

HRMS (EI^+): m/z calcd. for $\text{C}_{15}\text{H}_{14}\text{O}_3\text{S}$ ($[\text{M}]^+$) 274.0658, found 274.0658.

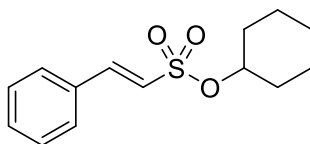
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-NAJYROHLEL-UHFFFADPSC-NUHFF-NZJBK-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/NAJYROHLELDYQG-VAWYXSNFSA-N.1>

Cyclohexyl (*E*)-2-phenylethene-1-sulfonate (9f)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), cyclohexanol (90.1 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (n -hexane/ EtOAc = 95:5) to obtain **9f** as a colorless liquid (31.4 mg, 39% yield).

R_f = 0.35 (n -hexane/ EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.59 (d, J = 15.6 Hz, 1H), 7.54–7.48 (m, 2H), 7.48–7.40 (m, 3H), 6.77 (d, J = 15.6 Hz, 1H), 4.65–4.55 (m, 1H), 2.04–1.91 (m, 2H), 1.83–1.72 (m, 2H), 1.72–1.59 (m, 2H), 1.57–1.46 (m, 1H), 1.42–1.22 (m, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 143.6, 132.3, 131.4, 129.3, 128.5, 122.8, 81.9, 32.7, 25.0, 23.6.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3050, 2936, 1618, 1351, 1162, 926, 746.

MS (APCI): m/z calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_3\text{S}$ ($[\text{M}+\text{H}]^+$) 267.1, found 267.4.

HRMS (EI^+): m/z calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{S}$ ($[\text{M}]^+$) 266.0971, found 266.0992.

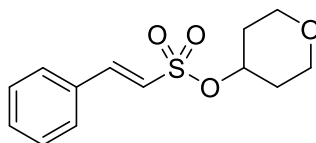
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-NABCLFIQWW-UHFFFADPSC-NUHFF-NZJBK-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/NABCLFIQWWOVSR-VAWYXSNFSA-N.1>

Tetrahydro-2H-pyran-4-yl (*E*)-2-phenylethene-1-sulfonate (9g)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), tetrahydro-2H-pyran-4-ol (85.8 μL , 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (n -hexane/ EtOAc = 93:7) to obtain **9g** as a colorless liquid (31.9 mg, 40% yield).

R_f = 0.10 (n -hexane/ EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.62 (d, J = 15.6 Hz, 1H), 7.54–7.49 (m, 2H), 7.49–7.41 (m, 3H), 6.79 (d, J = 15.6 Hz, 1H), 4.83–4.75 (m, 1H), 4.01–3.89 (m, 2H), 3.58–3.50 (m, 2H), 2.08–1.99 (m, 2H), 1.94–1.83 (m, 2H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 144.3, 132.0, 131.6, 129.3, 128.6, 122.3, 77.5, 64.9, 32.8.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3003, 2963, 1622, 1358, 1221, 949, 750.

MS (APCI): m/z calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 269.1, found 269.4.

HRMS (EI^+): m/z calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$ ($[\text{M}]^+$) 268.0764, found 268.0763.

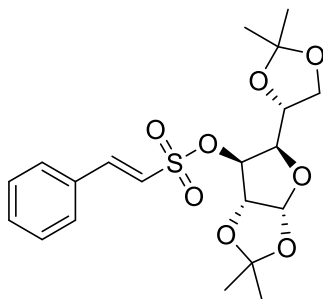
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-XMTQMZHLYL-UHFFFADPSC-NUHFF-NFMKG-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/XMTQMZHLYLURMF-DHZHZOJOSA-N.1>

(3aR,5R,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl (E)-2-phenylethene-1-sulfonate (9h)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), 1,2:5,6-di-*O*-isopropylidene- α -D-glucufuranose (234.3 mg, 3.0 equiv.), and SO_2 stock solution (10.0 equiv.) were used as substrates. The residue was twofold purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 93:7 then $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ = 95:5) to obtain **9h** as a colorless liquid (21.6 mg, 17% yield).

R_f = 0.20 (*n*-hexane/EtOAc = 9:1).

^1H NMR (400 MHz, CDCl_3): δ 7.63 (d, J = 15.6 Hz, 1H), 7.55–7.50 (m, 2H), 7.50–7.41 (m, 3H), 6.82 (d, J = 15.6 Hz, 1H), 5.96 (d, J = 3.6 Hz, 1H), 4.87 (d, J = 3.6 Hz, 1H), 4.80 (d, J = 3.0 Hz, 1H), 4.31–4.22 (m, 1H), 4.13–4.06 (m, 2H), 4.01 (dd, J = 9.0, 4.0 Hz, 1H), 1.50 (s, 3H), 1.33 (s, 3H), 1.23 (s, 3H), 1.17 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3): δ 145.2, 132.1, 131.8, 129.3, 128.6, 121.2, 112.7, 109.6, 105.3, 83.8, 82.3, 79.8, 72.2, 67.5, 27.0, 26.7, 26.3, 25.2.

IR (ATR) $\tilde{\nu}$ (cm^{-1}): 3003, 2922, 1358, 1219, 1171, 981, 750.

MS (APCI): m/z calcd. for $\text{C}_{20}\text{H}_{27}\text{O}_8\text{S}$ ($[\text{M}+\text{H}]^+$) 427.1, found 427.6.

HRMS (EI^+): m/z calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_8\text{S}$ ($[\text{M}]^+$) 426.1343, found 426.1371.

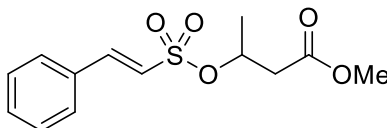
Additional information on the chemical synthesis is available via Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-FOZZOCLQRR-UHFFFADPSC-NUHFF-NBFOL-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available via Chemotion repository:

<https://doi.org/10.14272/FOZZOCLQRRJRQC-PPRZOJQRSA-N.1>

Methyl (E)-3-((styrylsulfonyl)oxy)butanoate (9i)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), methyl 3-hydroxybutanoate (101.0 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 94:6) to obtain **9i** as a colorless liquid (13.2 mg, 15% yield).

R_f = 0.13 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.56–7.51 (m, 2H), 7.49–7.40 (m, 3H), 6.80 (d, *J* = 15.6 Hz, 1H), 5.06 (sextet, *J* = 6.4 Hz, 1H), 3.65 (s, 3H), 2.88–2.79 (m, 1H), 2.63–2.55 (m, 1H), 1.50 (d, *J* = 6.4 Hz, 3H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 170.1, 144.3, 132.3, 131.5, 129.3, 128.6, 122.1, 76.0, 52.1, 41.4, 21.5.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3003, 2962, 1710, 1620, 1358, 1221, 1168, 979, 750.

MS (APCI): *m/z* calcd. for C₁₃H₁₇O₅S ([M+H]⁺) 285.1, found 285.4.

HRMS (EI⁺): *m/z* calcd. for C₁₃H₁₆O₅S ([M]⁺) 284.0713, found 284.0727.

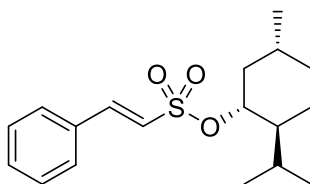
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-PFQIXBDZPI-UHFFFADPSC-NUHFF-NSEGZ-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/PFQIXBDZPIDCQY-CMDGGGOBGSA-N.1>

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*E*)-2-phenylethene-1-sulfonate (9j**)**



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), (-)-menthol (140.6 mg, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **9j** as a colorless solid (42.9 mg, 44% yield).

mp: 74.5–75.3 °C. **R_f** = 0.38 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, *J* = 15.6 Hz, 1H), 7.53–7.47 (m, 2H), 7.47–7.40 (m, 3H), 6.77 (d, *J* = 15.6 Hz, 1H), 4.45 (td, *J* = 10.8, 4.6 Hz, 1H), 2.34–2.26 (m, 1H), 2.11 (septet, *J* = 7.0, 2.2 Hz, 1H), 1.75–1.63 (m, 2H), 1.53–1.38 (m, 2H), 1.33–1.23 (m, 1H), 1.09–0.96 (m, 1H), 0.93 (d, *J* = 3.4 Hz, 3H), 0.91 (d, *J* = 4.0 Hz, 3H), 0.90–0.81 (m, 1H), 0.76 (d, *J* = 6.8 Hz, 3H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 143.4, 132.3, 131.4, 129.3, 128.5, 123.0, 84.0, 47.6, 42.4, 33.9, 31.8, 25.7, 23.1, 22.0, 21.0, 15.8.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3029, 2956, 1620, 1345, 1161, 981, 749.

MS (APCI): *m/z* calcd. for C₁₈H₂₇O₃S ([M+H]⁺) 323.2, found 323.5.

HRMS (EI⁺): *m/z* calcd. for C₁₈H₂₆O₃S ([M]⁺) 322.1597, found 322.1618.

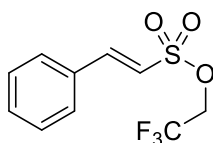
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-FKWGKMBPKN-UHFFFADPSC-NUHFF-NSOOW-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/FKWGKMBPKNXHII-XVOPWDCPSA-N.1>

2,2,2-Trifluoroethyl (*E*)-2-phenylethene-1-sulfonate (9k**)**



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), 2,2,2-trifluoroethanol (64.8 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **9k** as a colorless solid (44.4 mg, 56% yield).

mp: 93.8–94.0 °C. **R_f** = 0.35 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 15.6 Hz, 1H), 7.56–7.51 (m, 2H), 7.51–7.42 (m, 3H), 6.78 (d, *J* = 15.6 Hz, 1H), 4.46 (q, *J* = 8.0 Hz, 2H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 146.8, 132.2, 131.5, 129.5, 128.9, 122.1 (q, ¹*J*_{C-F} = 277.8 Hz, 1C), 120.0, 64.7 (q, ²*J*_{C-F} = 38.0 Hz, 1C).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ -73.8.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3073, 2973, 1615, 1358, 1288, 1159, 961, 745.

MS (APCI): *m/z* calcd. for C₁₀H₁₀O₃F₃S ([M+H]⁺) 267.0, found 267.3.

HRMS (EI⁺): *m/z* calcd. for C₁₀H₉O₃F₃S ([M]⁺) 266.0219, found 266.0244.

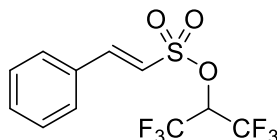
Additional information on the chemical synthesis is available *via* Chemotion repository:

<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-WTISUMKEBZ-UHFFFADPSC-NUHFF-NZMGP-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

<https://doi.org/10.14272/WTISUMKEBZKMEP-VOTSOKGWSA-N.1>

1,1,1,3,3,3-Hexafluoropropan-2-yl (*E*)-2-phenylethene-1-sulfonate (**9l**)



Following the **TP-5**, cinnamic acid (44.5 mg, 0.3 mmol), 1,1,1,3,3,3-hexafluoroisopropanol (94.5 μ L, 3.0 equiv.), and SO₂ stock solution (10.0 equiv.) were used as substrates. The residue was purified by flash chromatography over silica gel (*n*-hexane/EtOAc = 98:2) to obtain **9l** as a colorless solid (24.8 mg, 25% yield).

mp: 49.6–49.8 °C. **R_f** = 0.45 (*n*-hexane/EtOAc = 9:1).

¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, *J* = 15.4 Hz, 1H), 7.57–7.50 (m, 3H), 7.50–7.44 (m, 2H), 6.80 (d, *J* = 15.4 Hz, 1H), 5.24 (septet, *J* = 5.6 Hz, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ 147.7, 132.6, 131.3, 129.5, 129.1, 120.1 (qq, ¹*J*_{C-F} = 282.8 Hz, ³*J*_{C-F} = 2.6 Hz, 2C), 119.9, 72.3 (septet, ²*J*_{C-F} = 35.4 Hz, 1C).

¹⁹F{¹H}-NMR (376 MHz, CDCl₃): δ -73.1.

IR (ATR) $\tilde{\nu}$ (cm⁻¹): 3073, 2973, 1614, 1361, 1292, 1171, 962, 746.

MS (APCI): *m/z* calcd. for C₁₁H₇O₃F₆S ([M+H]⁺) 335.0, found 335.5.

HRMS (EI⁺): *m/z* calcd. for C₁₁H₆O₃F₆S ([M]⁺) 334.0093, found 334.0103.

Additional information on the chemical synthesis is available *via* Chemotion repository:

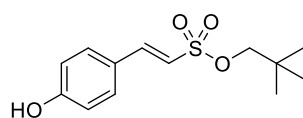
<https://doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-ZNKPMXBNDG-UHFFFADPSC-NUHFF-NZMGP-NUHFF-ZZZ>

Additional information on the analysis of the target compound is available *via* Chemotion repository:

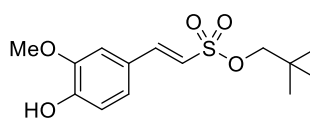
<https://doi.org/10.14272/ZNKPMXBNDGNEFX-VOTSOKGWSA-N.1>

7 Unsuccessful Substrates

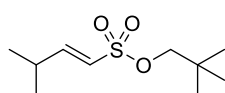
Cinnamic acids and related substrates:



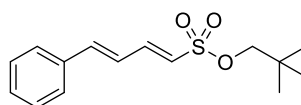
oxidation of phenol



oxidation of phenol

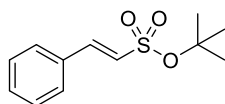


no alkenesulfonate product detected

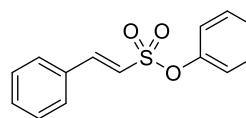


no alkenesulfonate product detected

Alcohols and phenol:



too sterically demanding



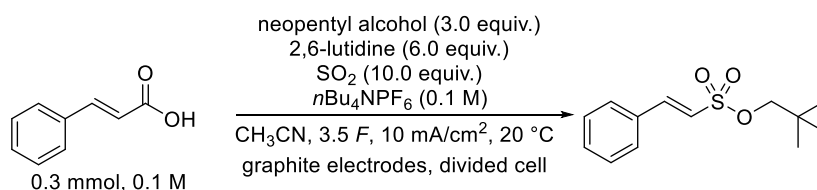
oxidation of phenol

Figure S7: Unsuccessful derivatives under the standard conditions.

8 Control Experiments

The control experiments were performed to elucidate the reaction mechanism. As shown in **Table S3**, no product formation was observed in the absence of a base or when the electric current was omitted (entries 2 and 3). No product was detected in the crude reaction mixture when the radical scavengers, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) were added. In both cases, only partial decomposition of cinnamic acid **6a** was observed. In the presence of BHT, the addition of an alkoxy sulfonyl radical species, could be detected by GC-MS (**Figure S8**).

Table S3: Control experiments.



entry	deviation from the standard conditions	yield (%) ^[a]	cinnamic acid (%) ^[a]
1	none	71 (70)^[b]	0
2	no electric current	0	65
3	no 2,6-lutidine	0	trace
4	+BHT (3.0 equiv.)	0	64
5	+TEMPO (3.0 equiv.)	0	trace

^[a]¹H-NMR yield with the use of CHPh₃ as the internal standard. ^[b]Isolated yield.

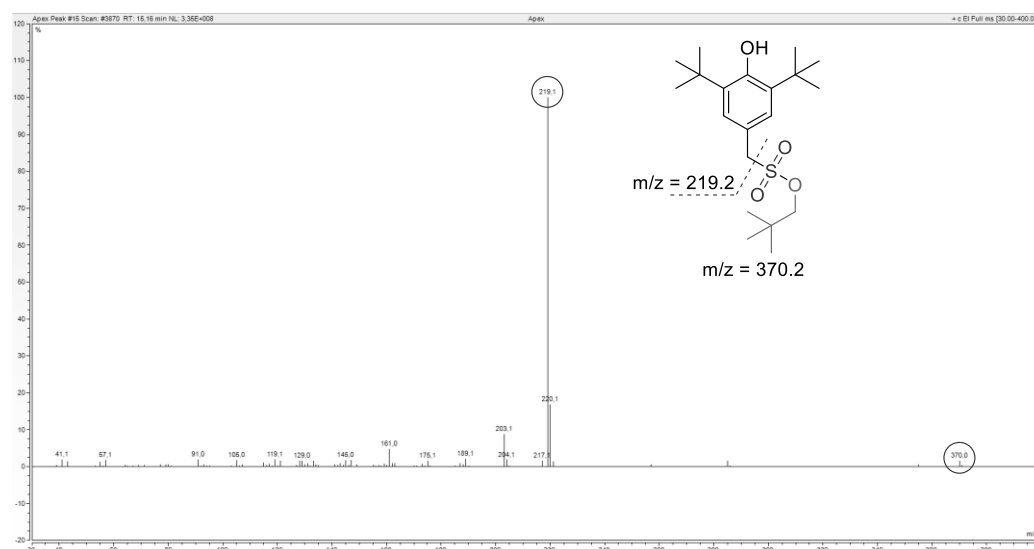


Figure S8: Mass spectrum obtained by GC/MS of a BHT-trapped intermediate.

9 Cyclic Voltammetry Results

The following measurements were used for the postulation of the reaction mechanism: the oxidation of the cinnamate **II** should take place before the oxidation of the monoalkylsulfite **I** (Figure S9, Measurement conditions: 0.1 M $n\text{Bu}_4\text{NPF}_6$ in MeCN; $c(\text{cinnamic acid or neopentyl alcohol}) = 0.01 \text{ M}$; $c(\text{SO}_2) = 0.05 \text{ M}$; $c(2,6\text{-lutidine}) = 0.011 \text{ M}$; $v = 100 \text{ mV/s.}$).

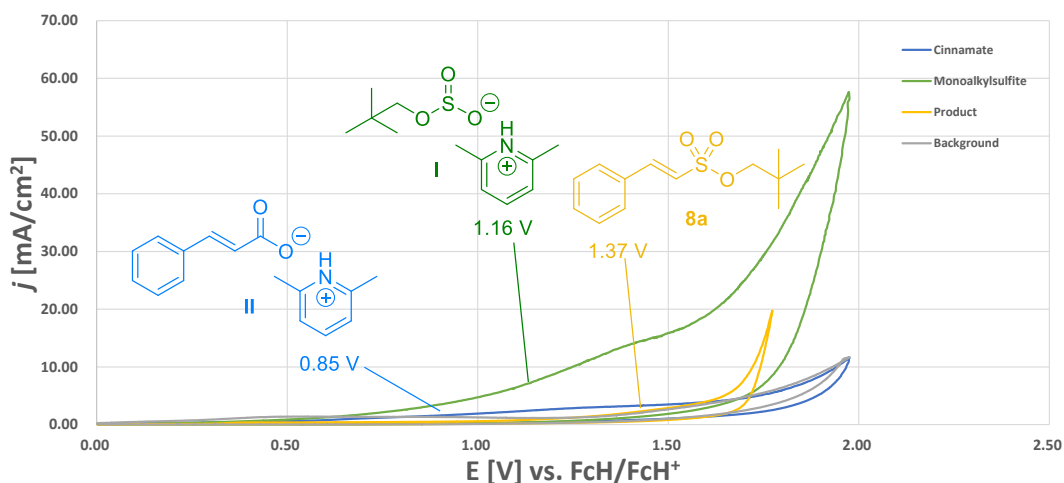


Figure S9: Cyclic voltammograms of cinnamate **II** (blue), monoalkylsulfite **I** (green), alkenesulfonate **8a** (yellow), and blank measurement (0.1 M $n\text{Bu}_4\text{NPF}_6$ in MeCN; grey).

In the case of the cinnamate **II**, the measured current decreases slightly with the number of scans (Figure S10, Measurement conditions: 0.1 M $n\text{Bu}_4\text{NPF}_6$ in MeCN; $c(\text{cinnamic acid}) = 0.01 \text{ M}$; $c(2,6\text{-lutidine}) = 0.011 \text{ M}$; $v = 100 \text{ mV/s.}$).

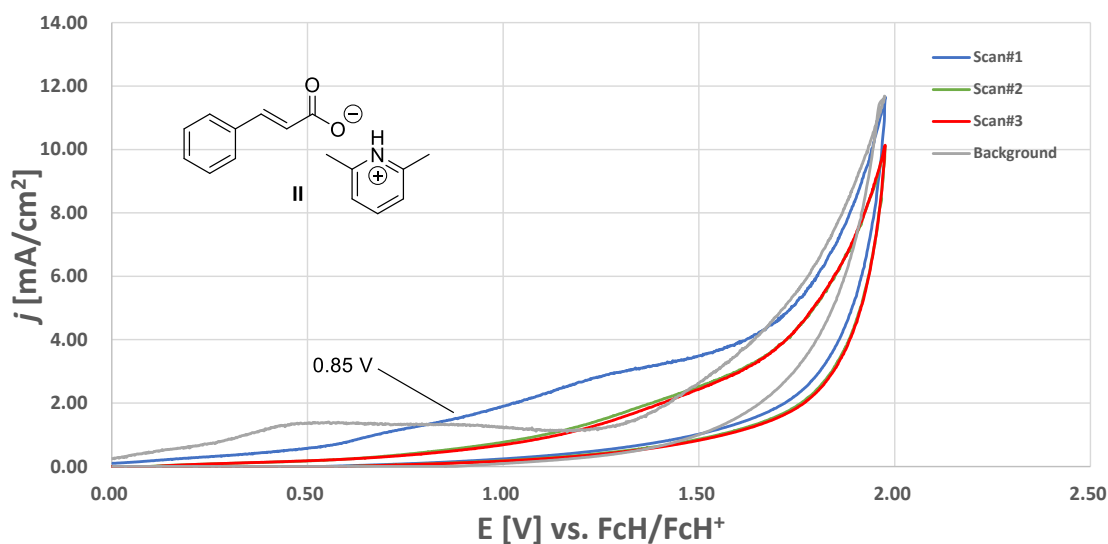


Figure S10: Cyclic voltammograms of cinnamate **II**.

There is no obvious current change with the number of scans when measuring the product **8a**. Thus, overoxidation of the product should be negligible. (Figure S11, Measurement conditions: 0.1 M *n*Bu₄NPF₆ in MeCN; *c*(**8a**) = 0.01 M; *v* = 100 mV/s.).

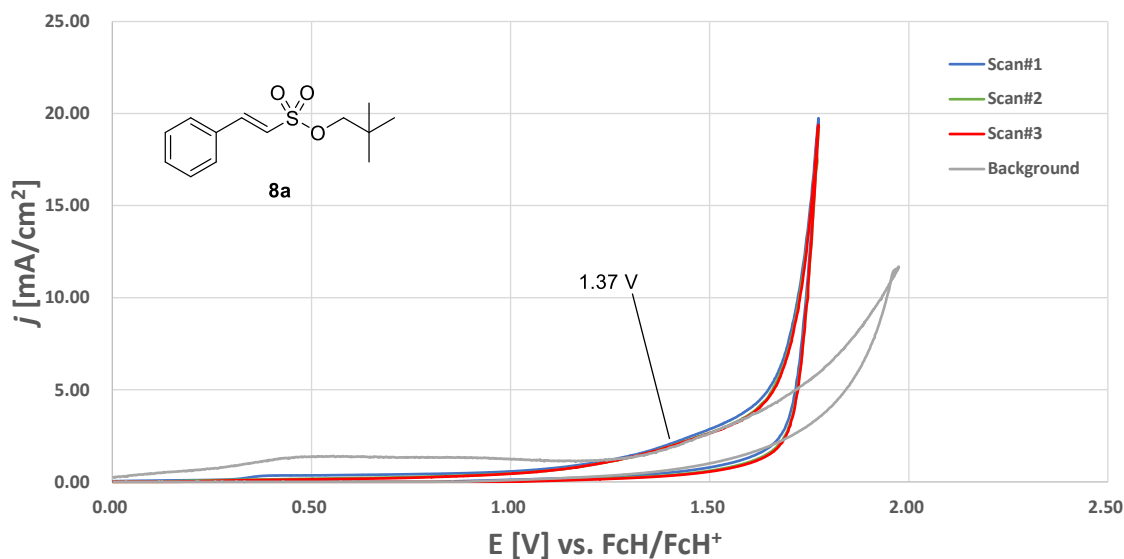


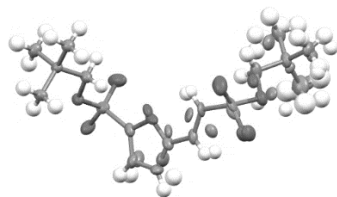
Figure S11: Cyclic voltammograms of neopentyl (E)-2-phenylethene-1-sulfonate **8a**.

10 References

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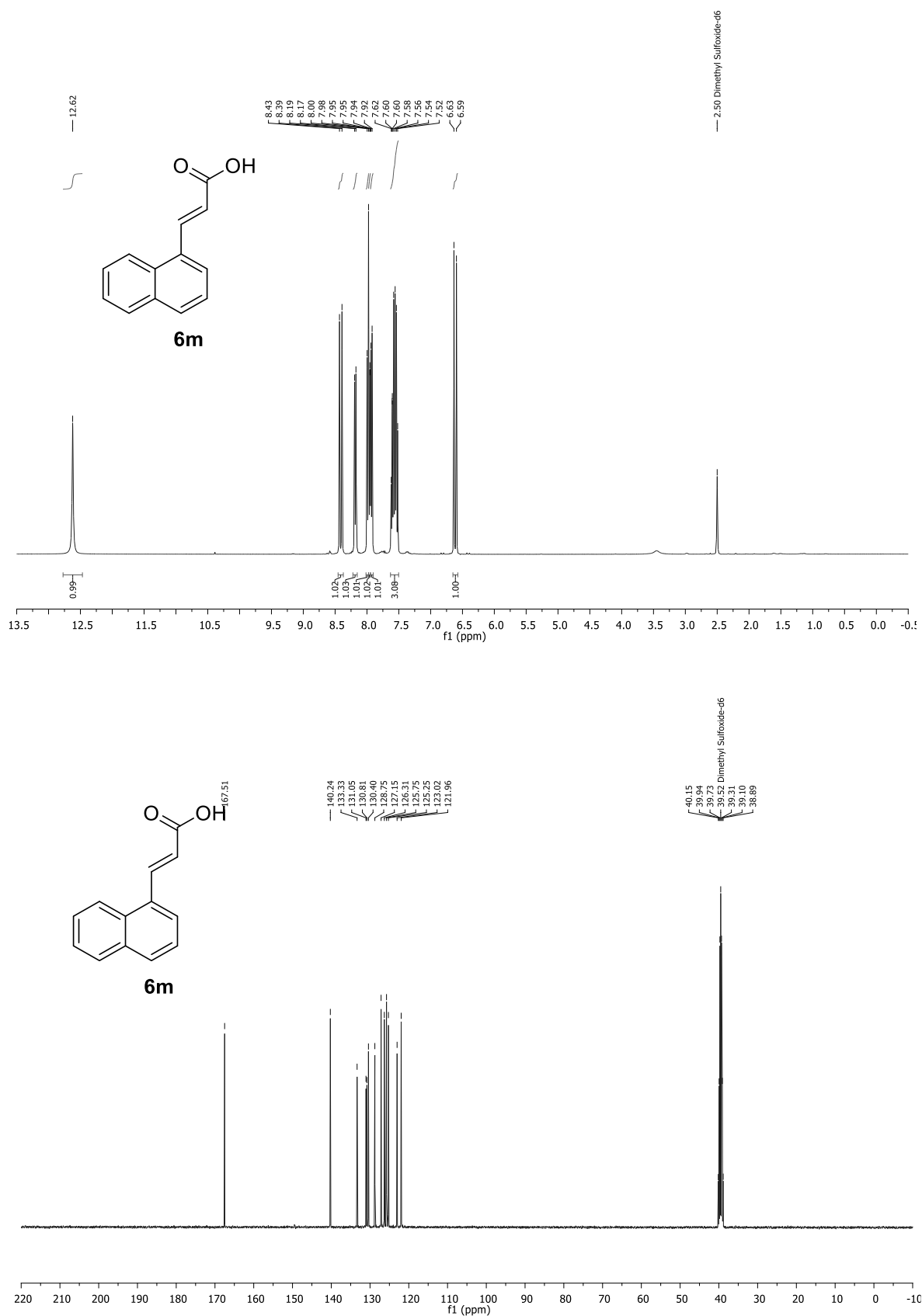
11 X-ray crystallographic data for selected compounds

Table S4: Crystal data for **10o** (CCDC no. 2381294, the thermal ellipsoid drawn at 50% probability level.).



The purified compound **10o** was dissolved in a minimal amount of EtOAc in a glass vial. Hexanes were then added until the solution became turbid. The solution was allowed to slowly evaporate. After a few days, colorless crystals were obtained.

Empirical formula	C ₁₆ H ₂₆ O ₇ S ₂	
Formula weight	394.49	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pna2 ₁	
Unit cell dimensions	a = 11.8362(6) Å	α = 90°.
	b = 5.6743(3) Å	β = 90°.
	c = 29.0528(14) Å	γ = 90°.
Volume	1951.25(17) Å ³	
Z	4	
Density (calculated)	1.343 Mg/m ³	
Absorption coefficient	2.772 mm ⁻¹	
F(000)	840	
Crystal size	0.195 x 0.118 x 0.049 mm ³	
Theta range for data collection	6.093 to 70.060°.	
Index ranges	-12 ≤ h ≤ 14, -6 ≤ k ≤ 6, -35 ≤ l ≤ 35	
Reflections collected	25464	
Independent reflections	3640 [R(int) = 0.0683]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.769	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3640 / 205 / 369	
Goodness-of-fit on F ²	1.098	
Final R indices [I > 2σ(I)]	R1 = 0.0288, wR2 = 0.0727	
R indices (all data)	R1 = 0.0334, wR2 = 0.0734	
Absolute structure parameter	0.18(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.303 and -0.246 e.Å ⁻³	

12 ^1H , ^{13}C NMR, and ^{19}F NMR spectra for compounds 6, 8, 9, and 10Figure S12: ^1H ($\text{DMSO}-d_6$, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ ($\text{DMSO}-d_6$, 101 MHz) NMR Spectrum of **6m**.

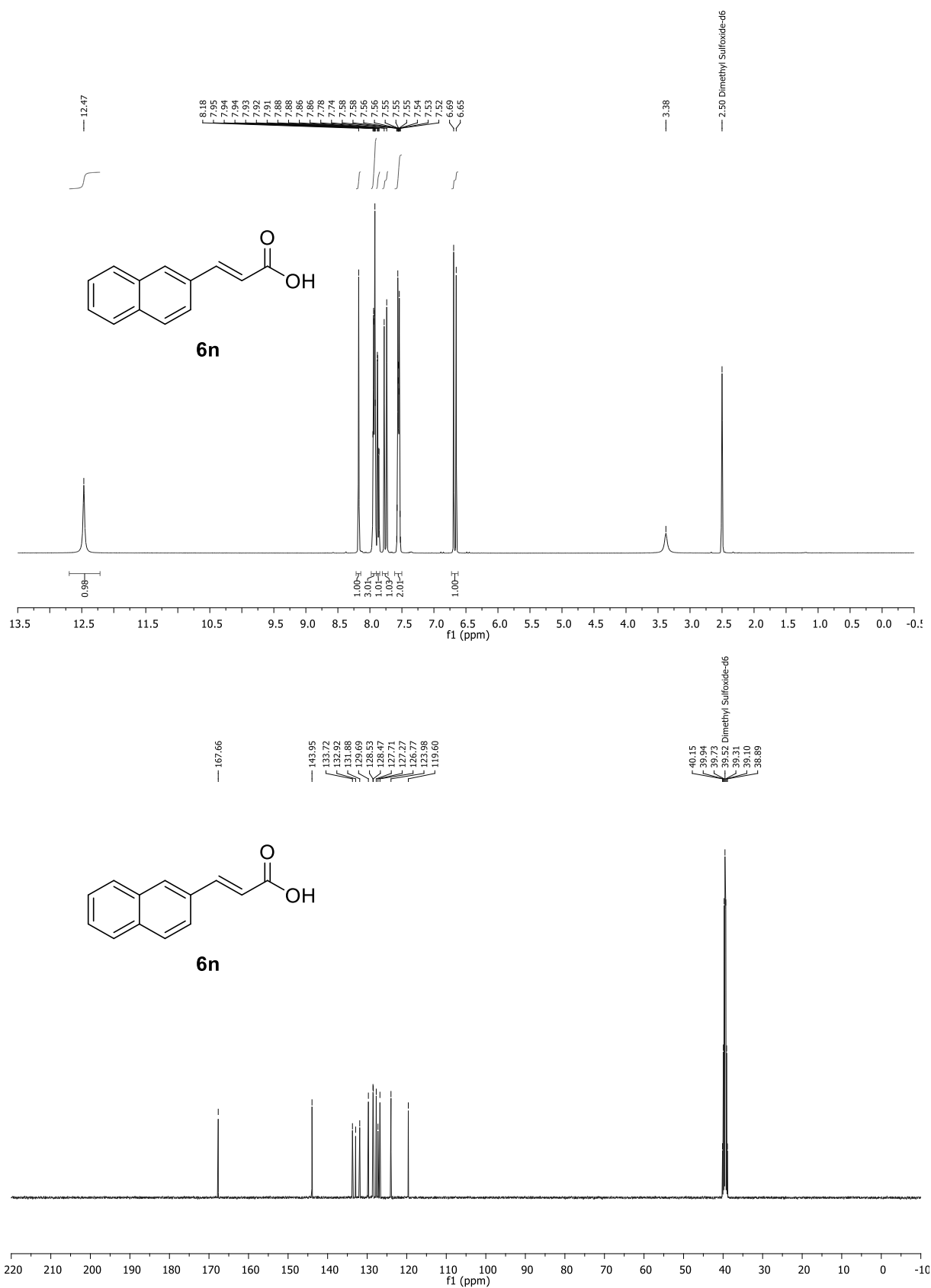


Figure S13: ^1H ($\text{DMSO}-d_6$, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ ($\text{DMSO}-d_6$, 101 MHz) NMR Spectrum of **6n**.

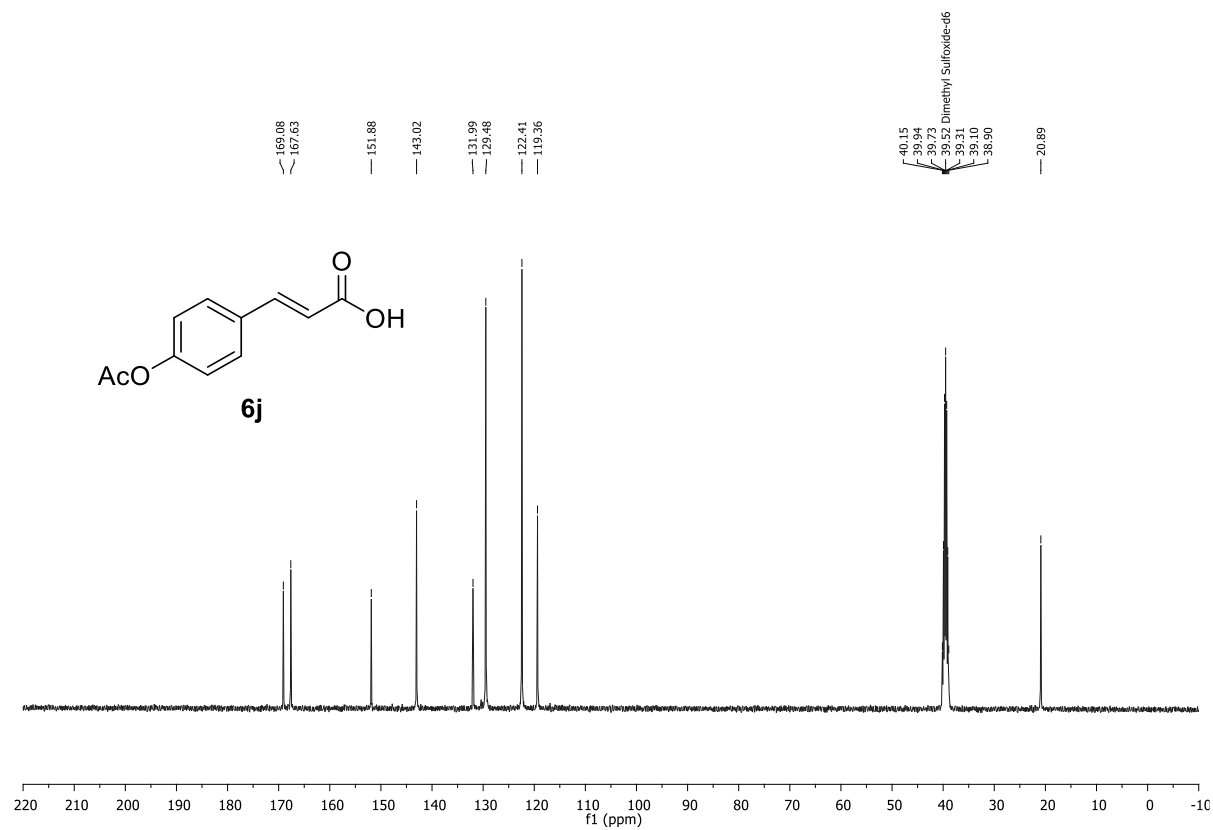
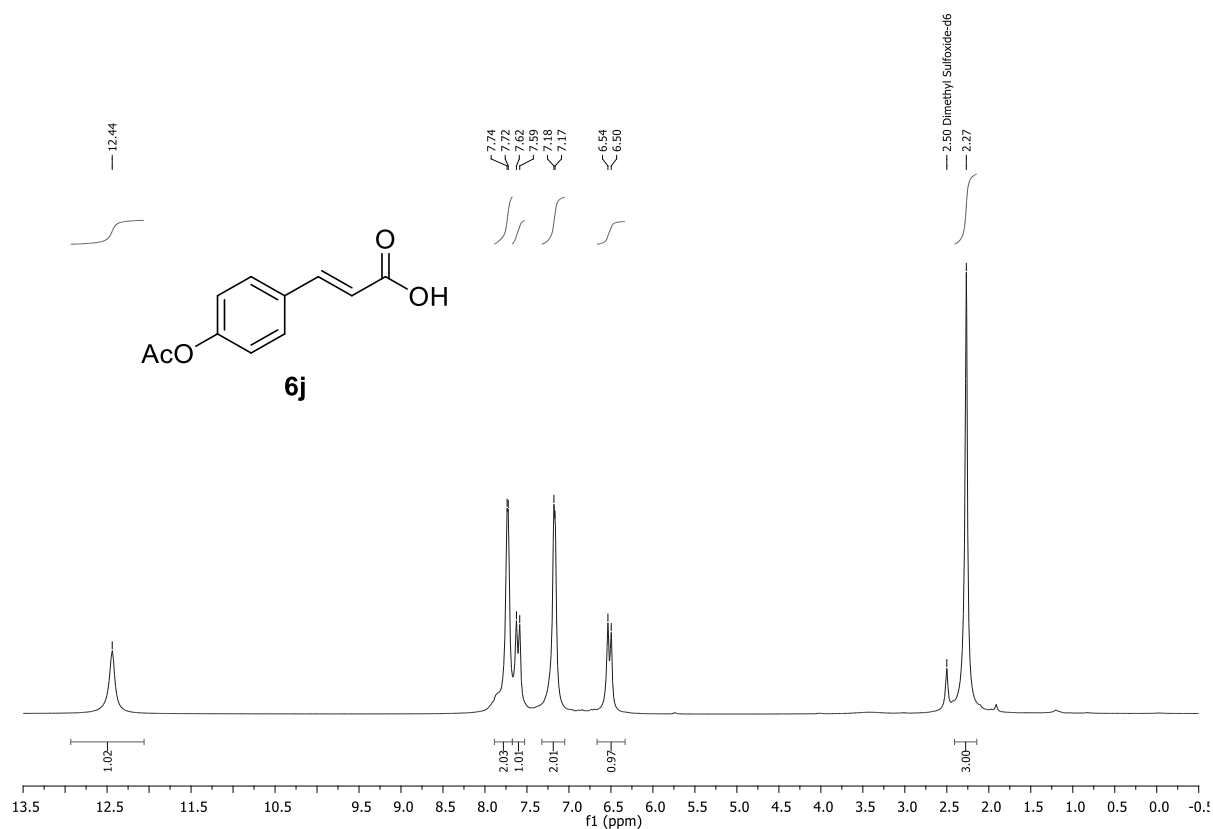


Figure S14: ¹H (DMSO-*d*₆, 400 MHz) and ¹³C{¹H} (DMSO-*d*₆, 101 MHz) NMR Spectrum of **6j**.

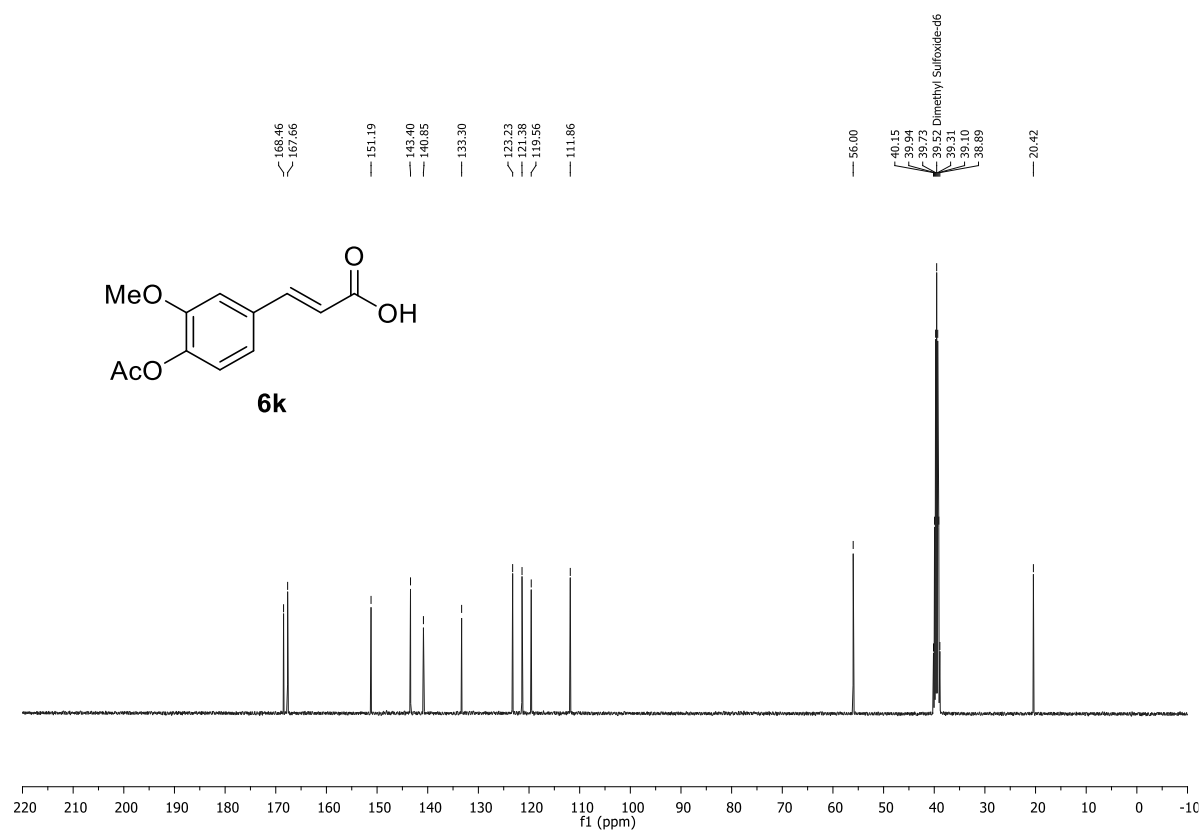
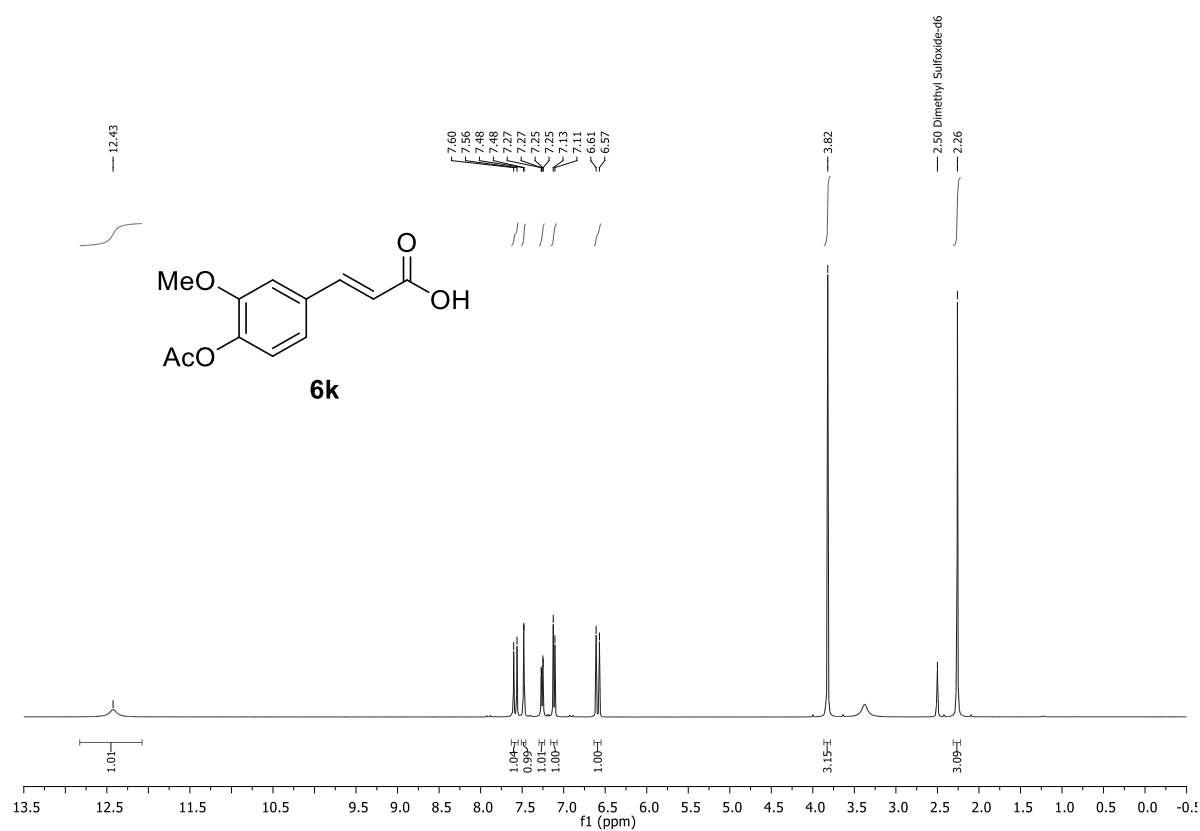


Figure S15: ^1H (DMSO- d_6 , 400 MHz) and ^{13}C (DMSO- d_6 , 101 MHz) NMR Spectrum of **6k**.



Figure S16: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8a**.

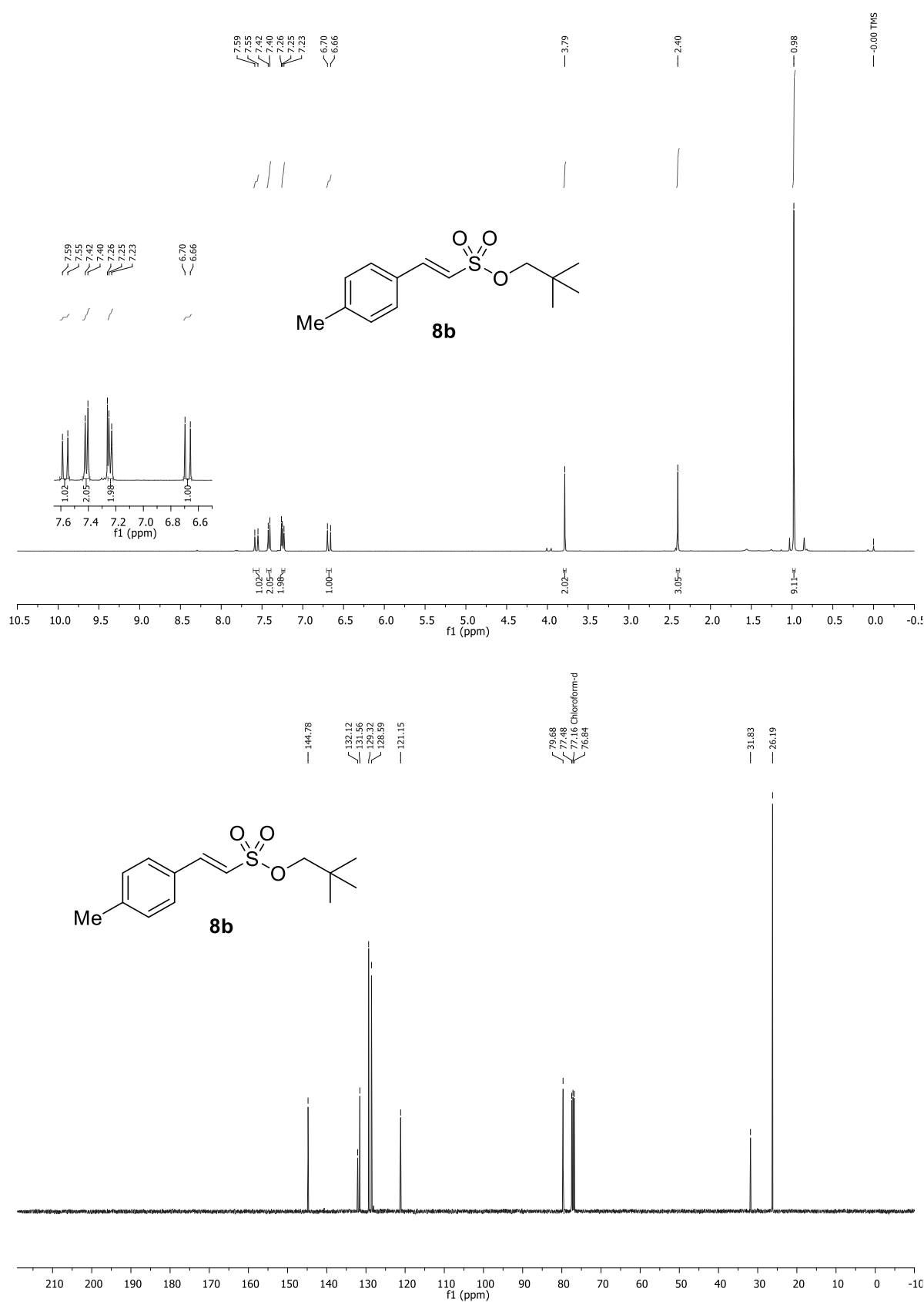


Figure S17: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8b**.

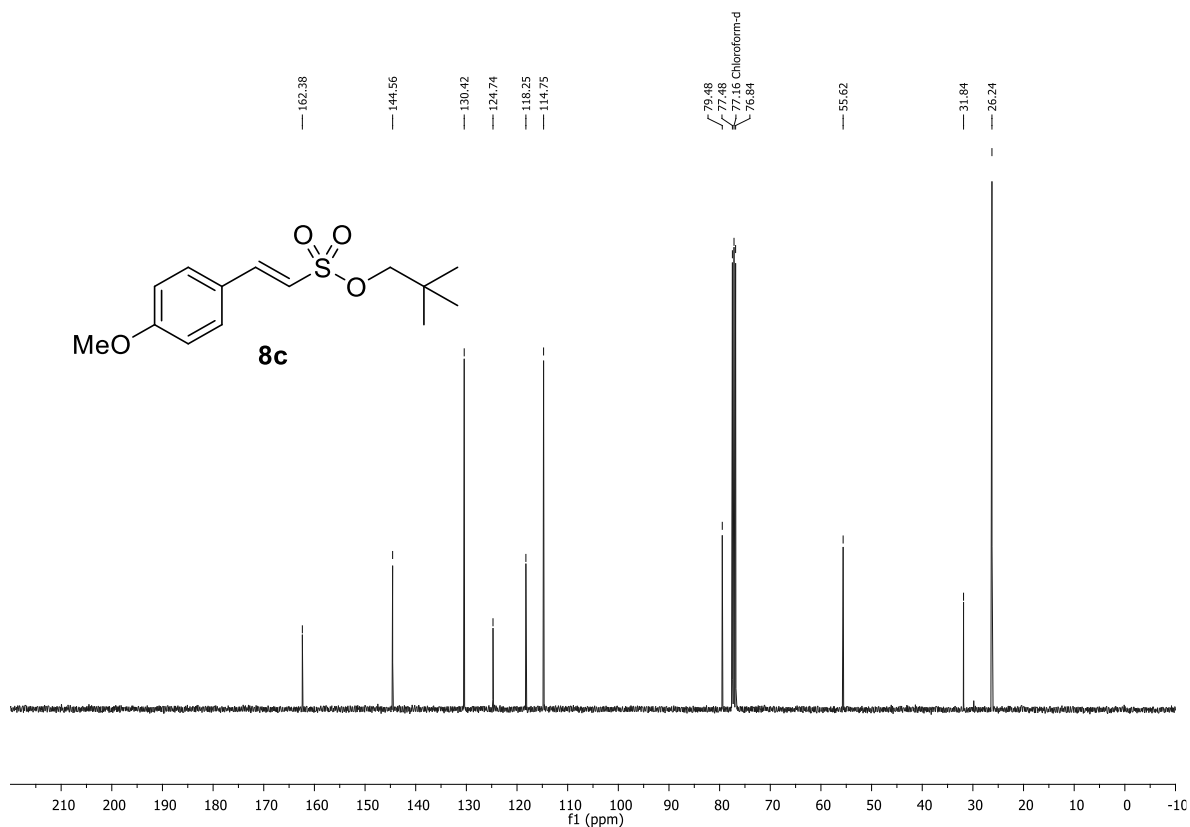
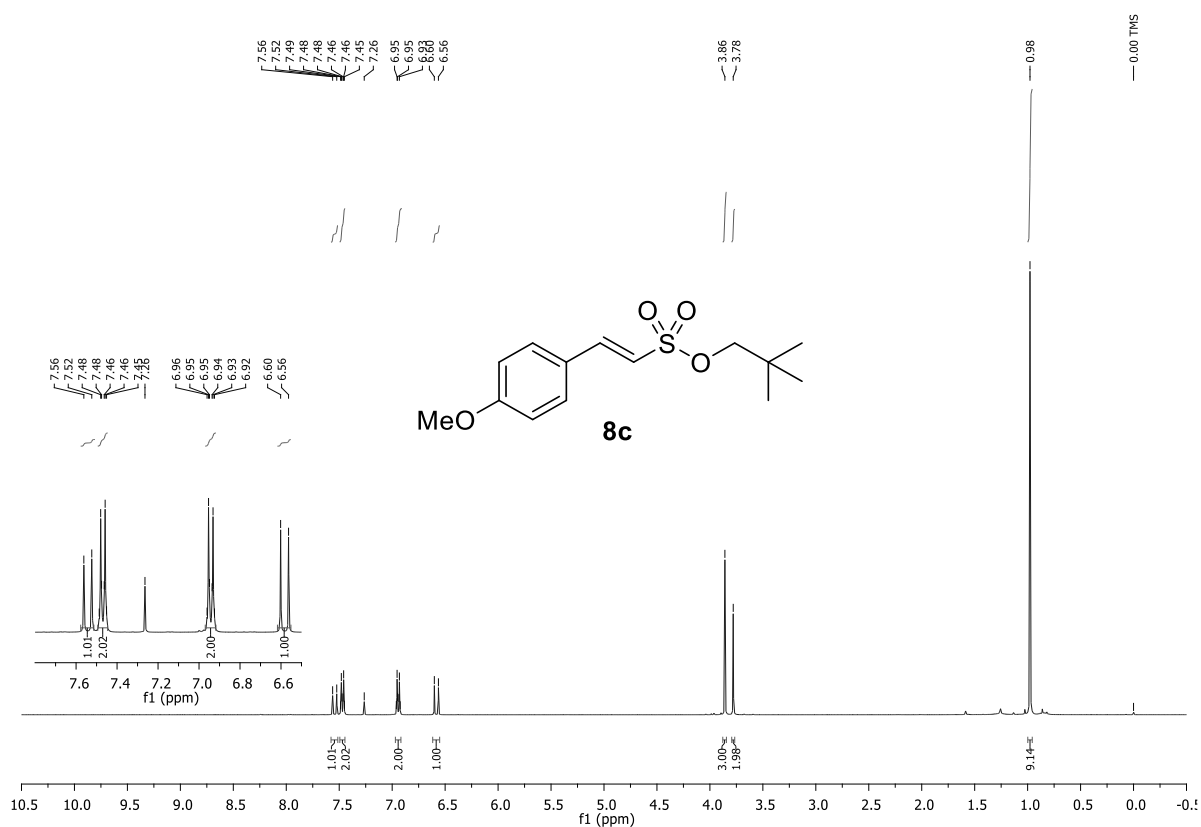
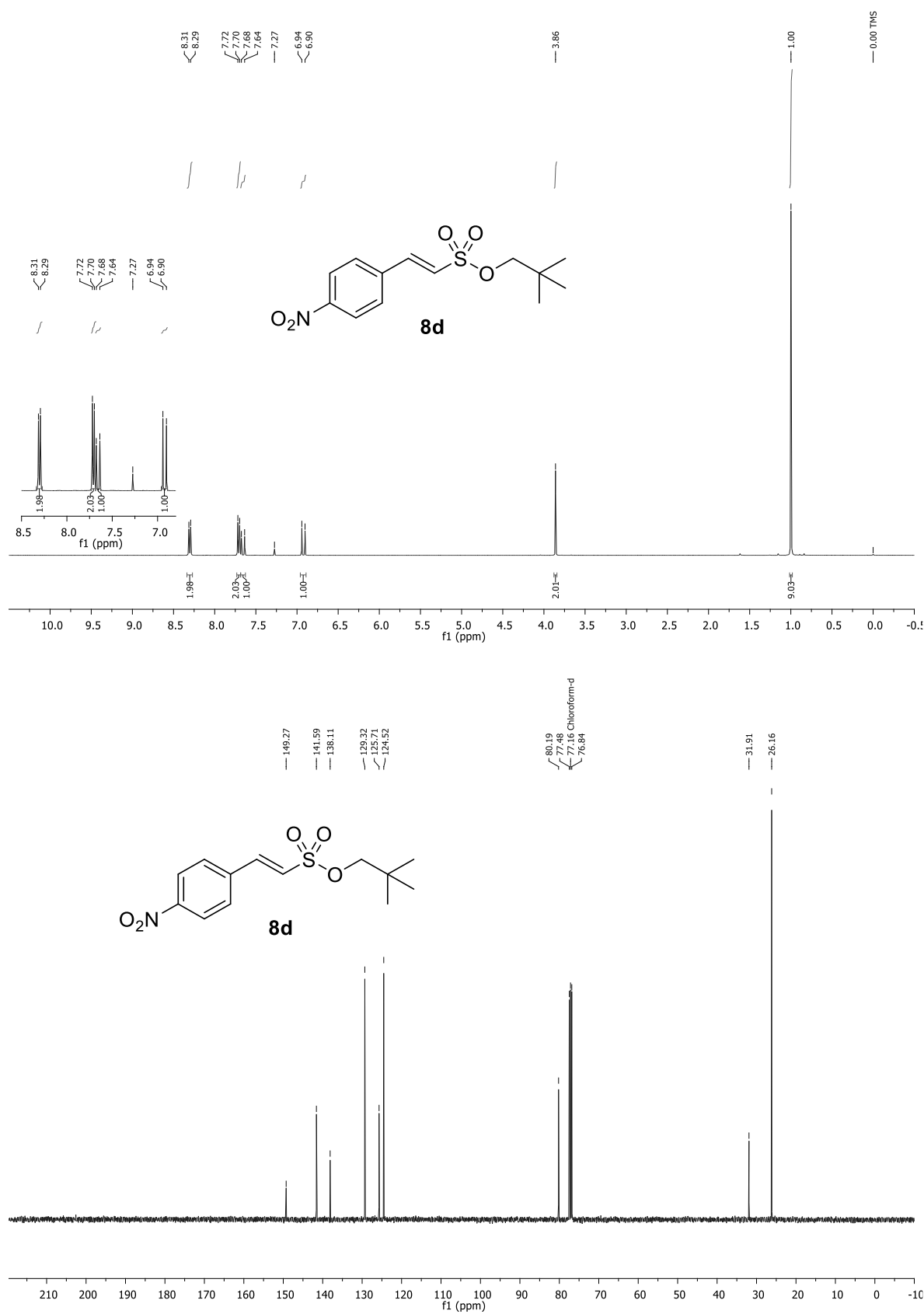
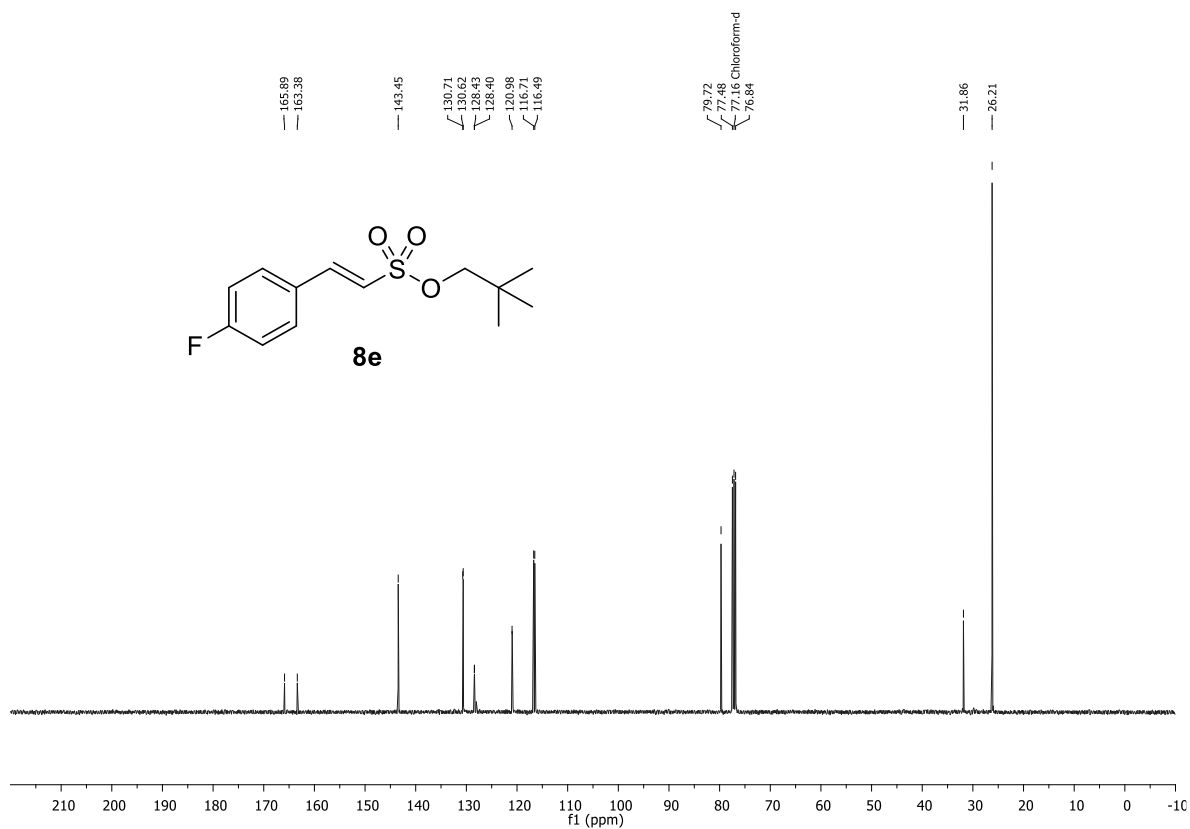
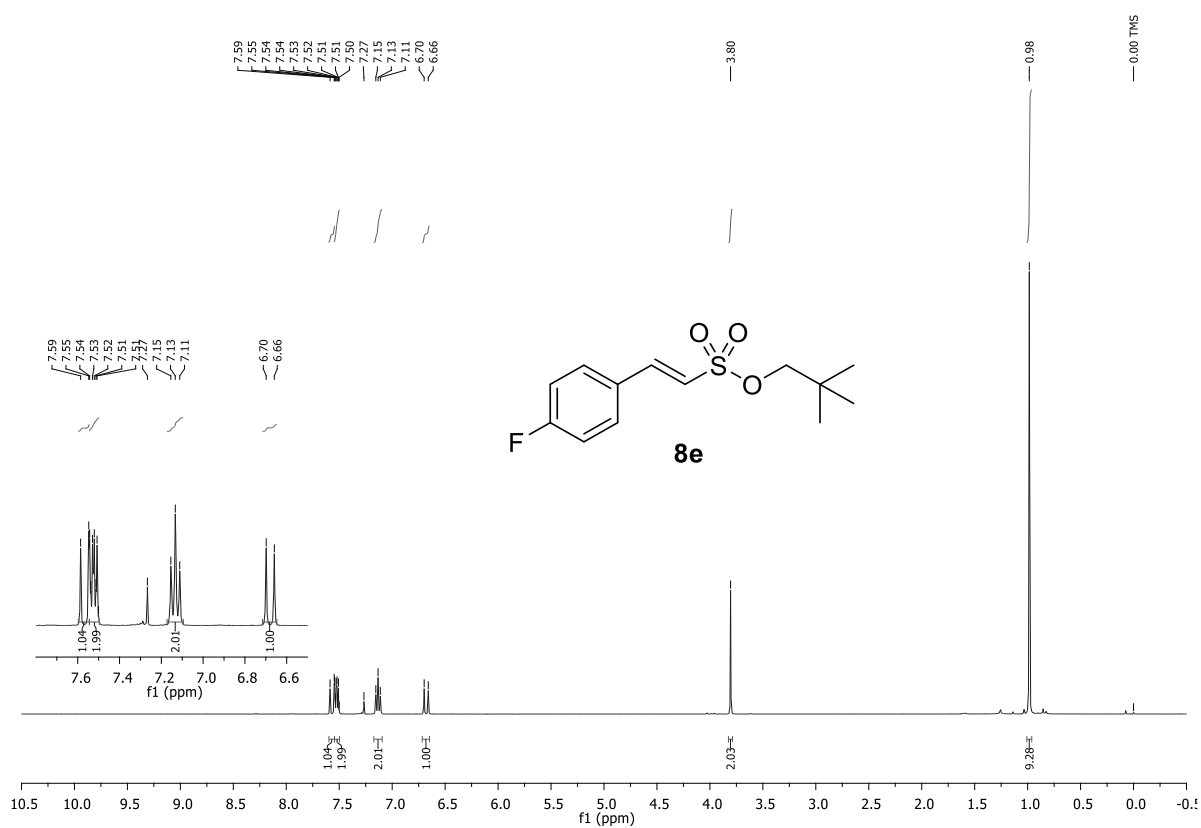


Figure S18: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **8c**.





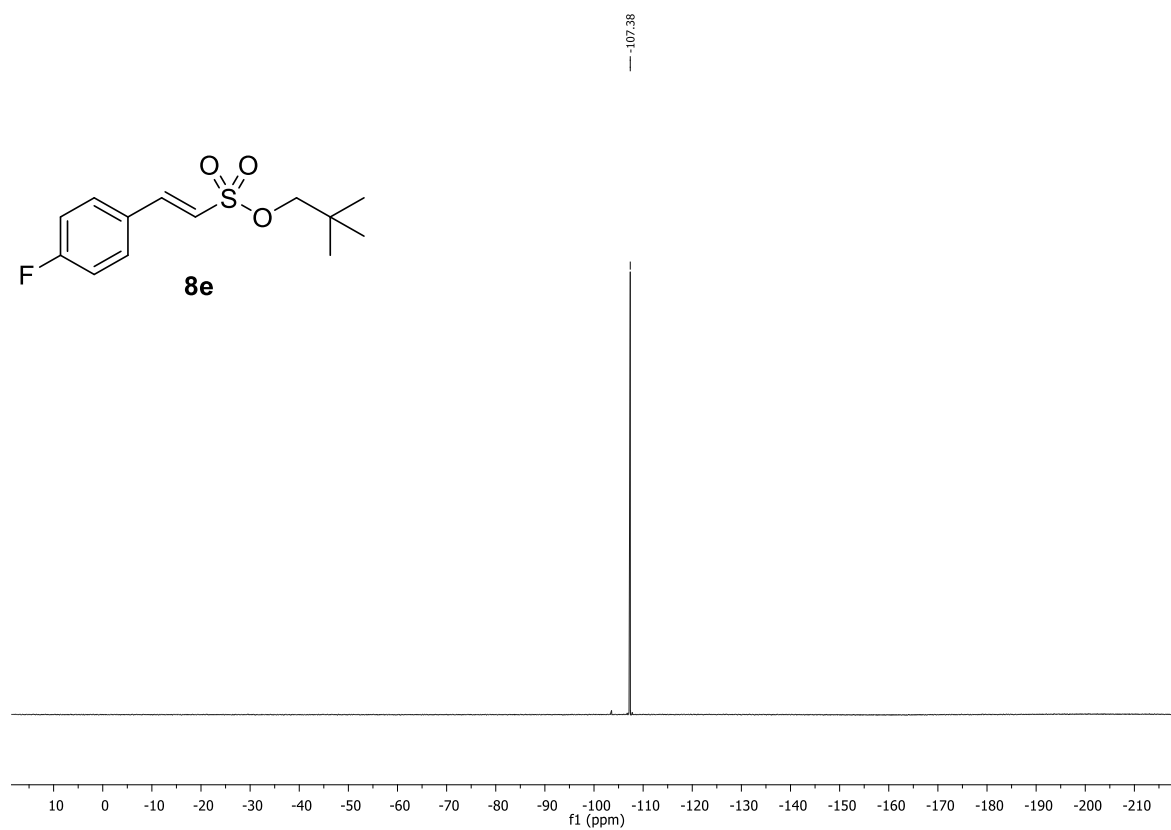


Figure S20: ^1H (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 101 MHz), and $^{19}\text{F}\{^1\text{H}\}$ (CDCl_3 , 376 MHz) NMR Spectrum of **8e**.

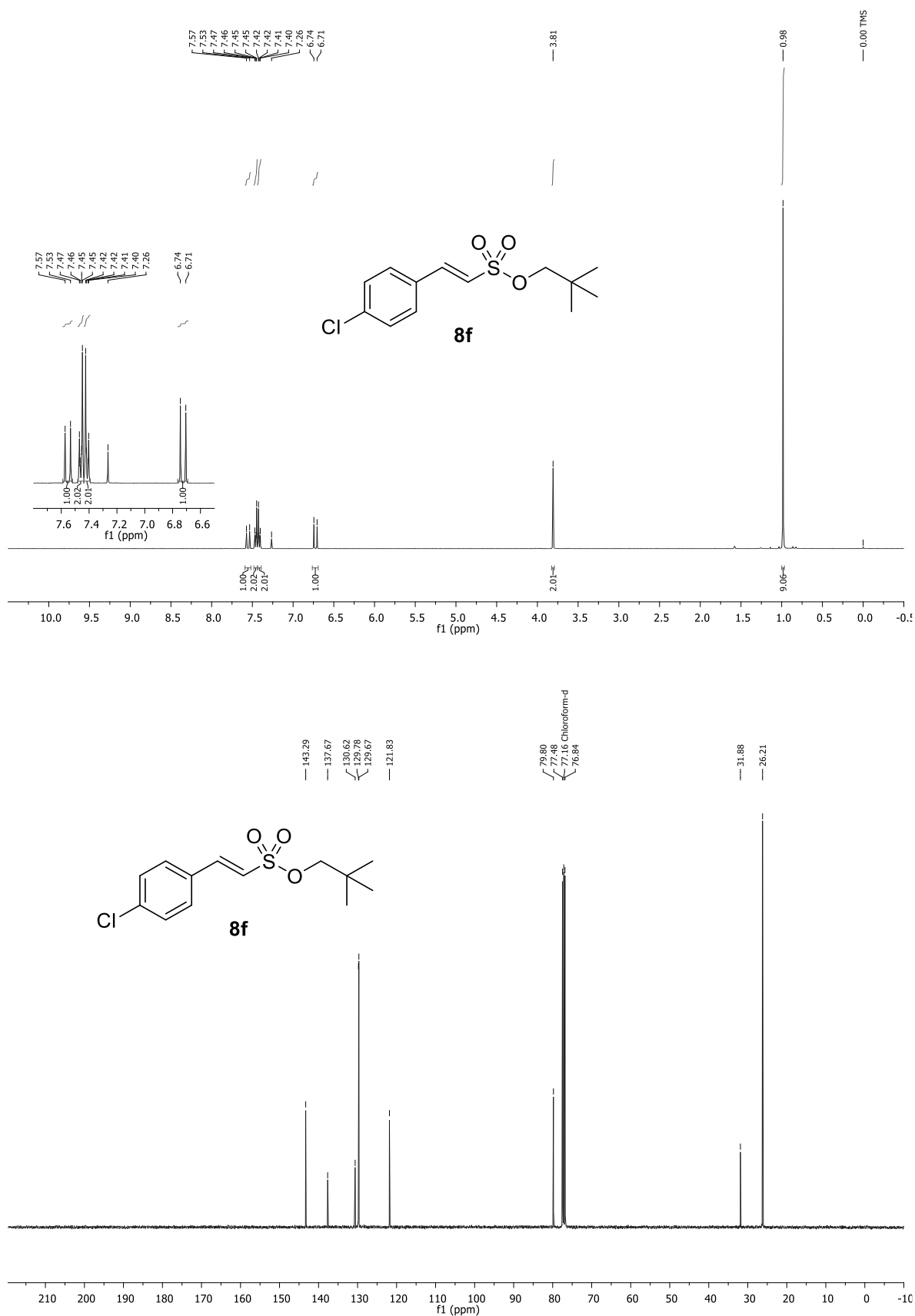


Figure S21: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8f**.

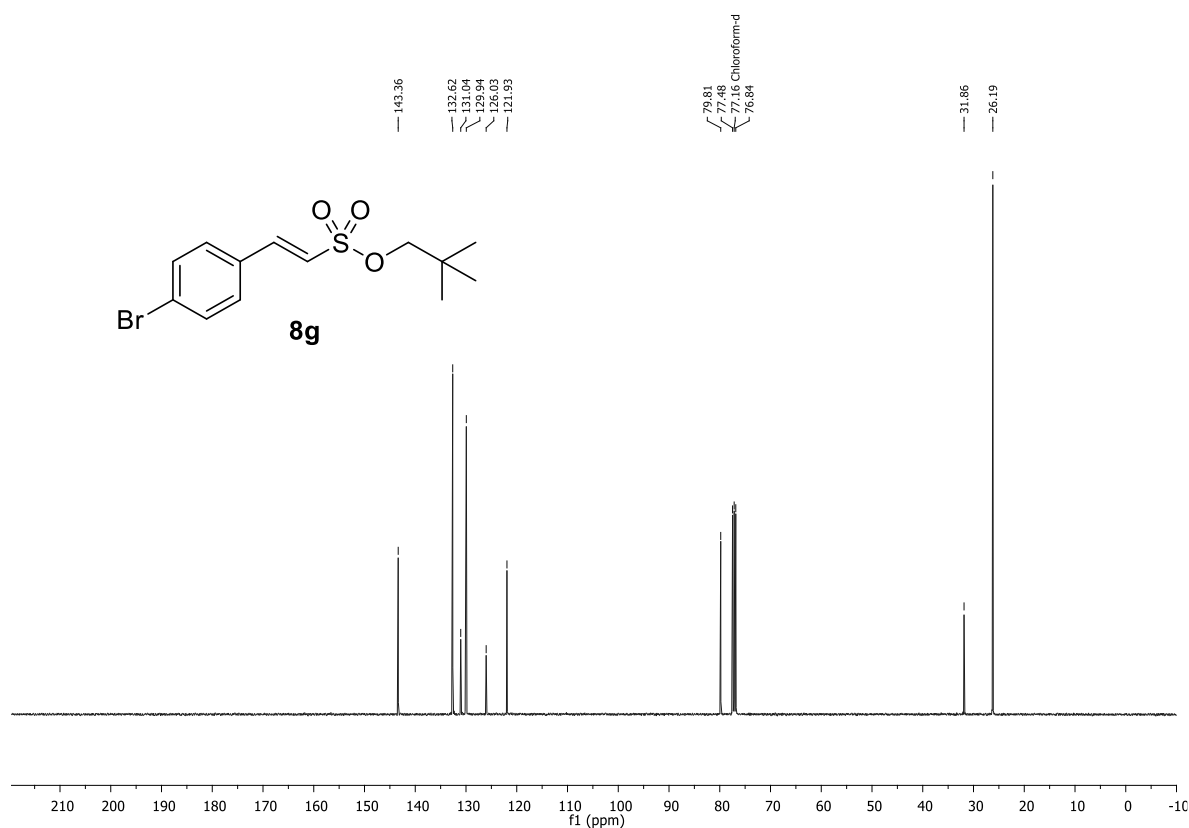
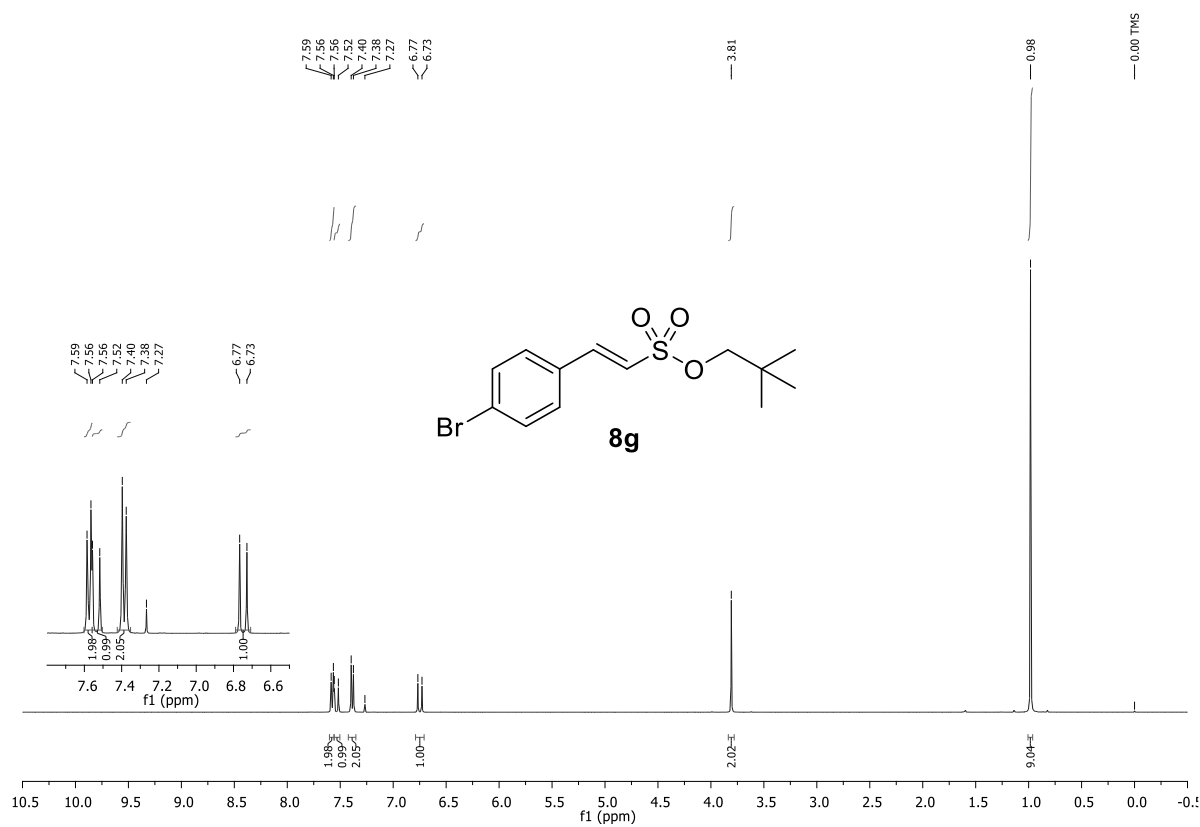


Figure S22: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of 8g.

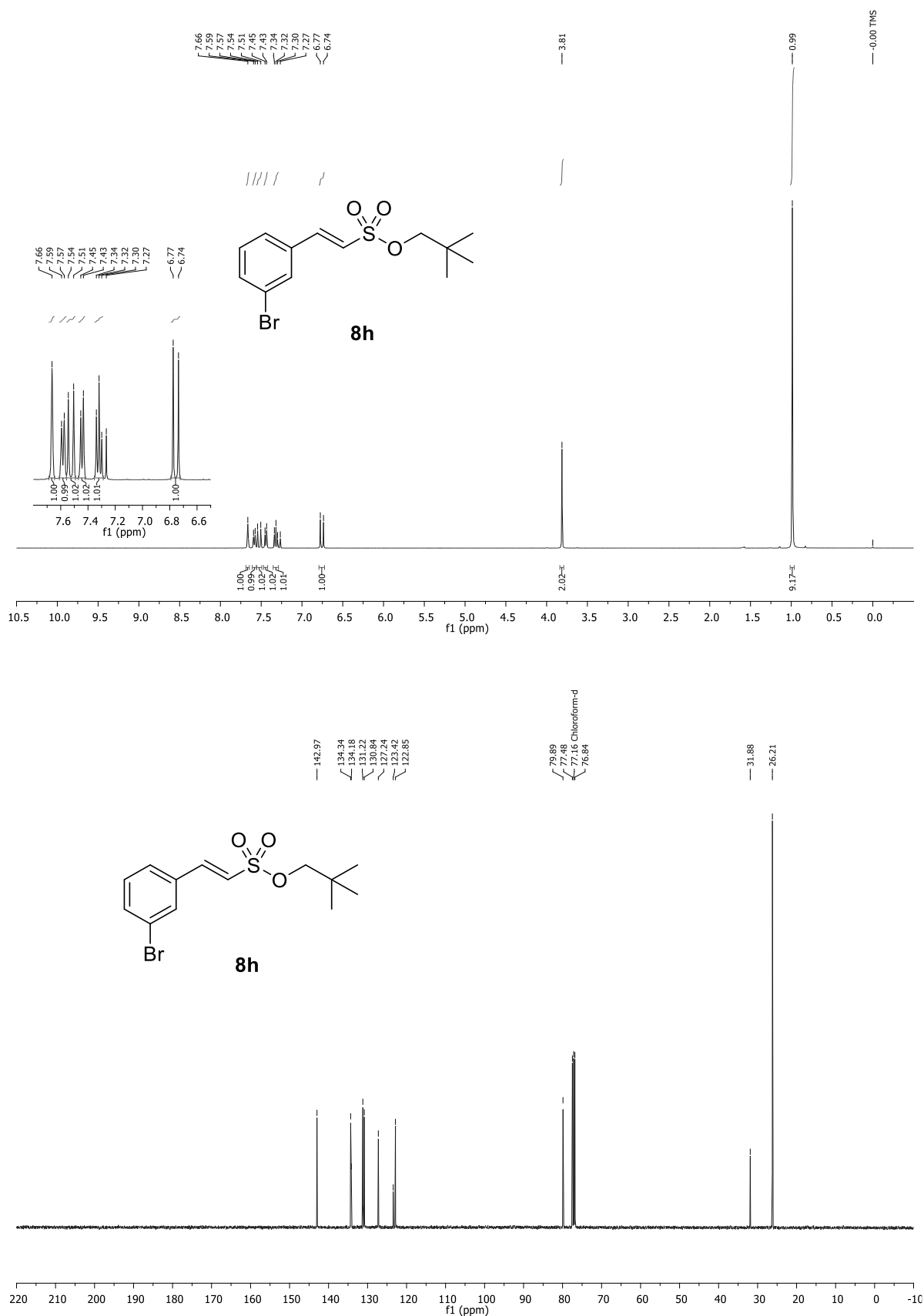


Figure S23: ^1H (CDCl_3 , 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 101 MHz) NMR Spectrum of **8h**.

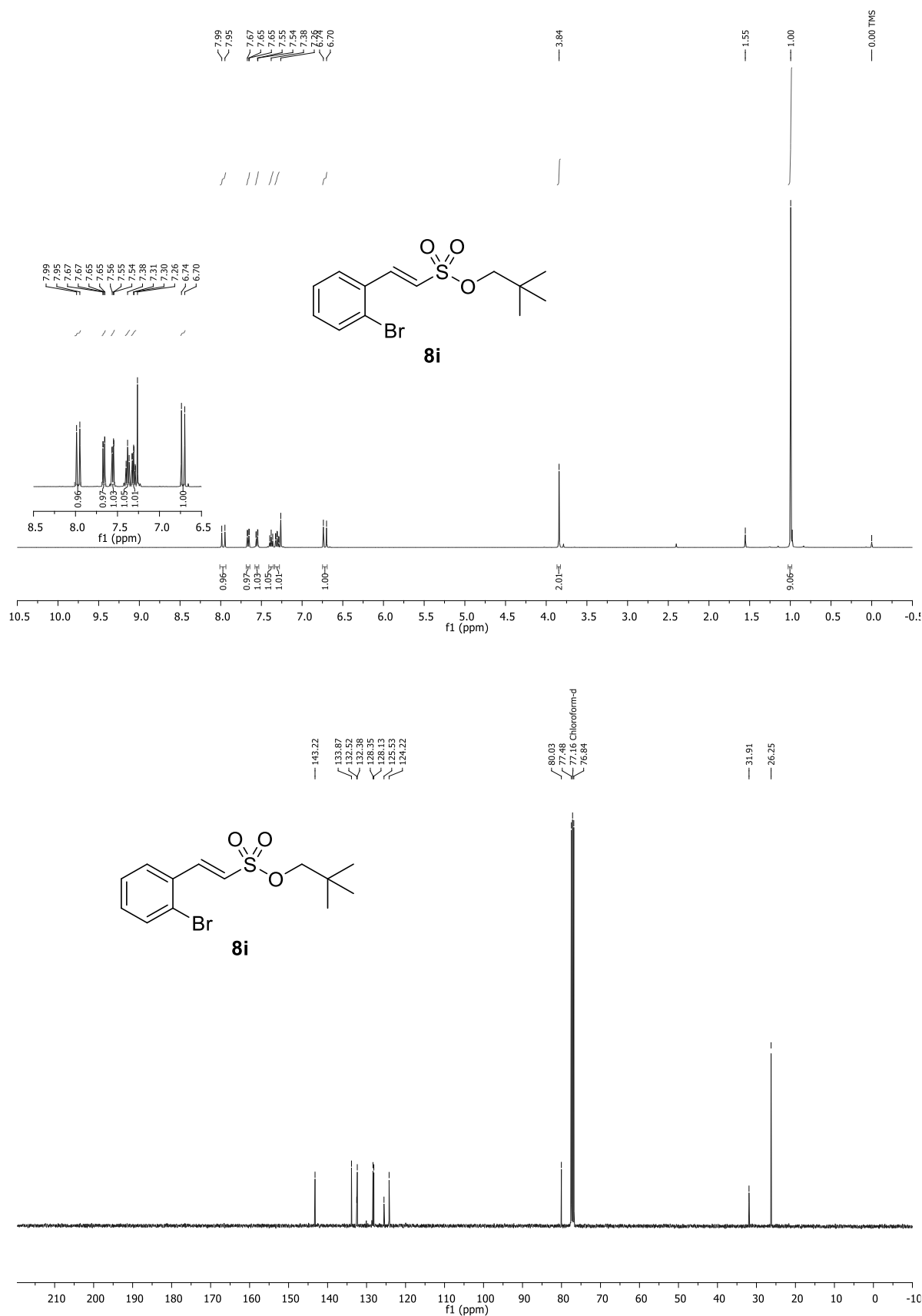


Figure S24: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8i**.

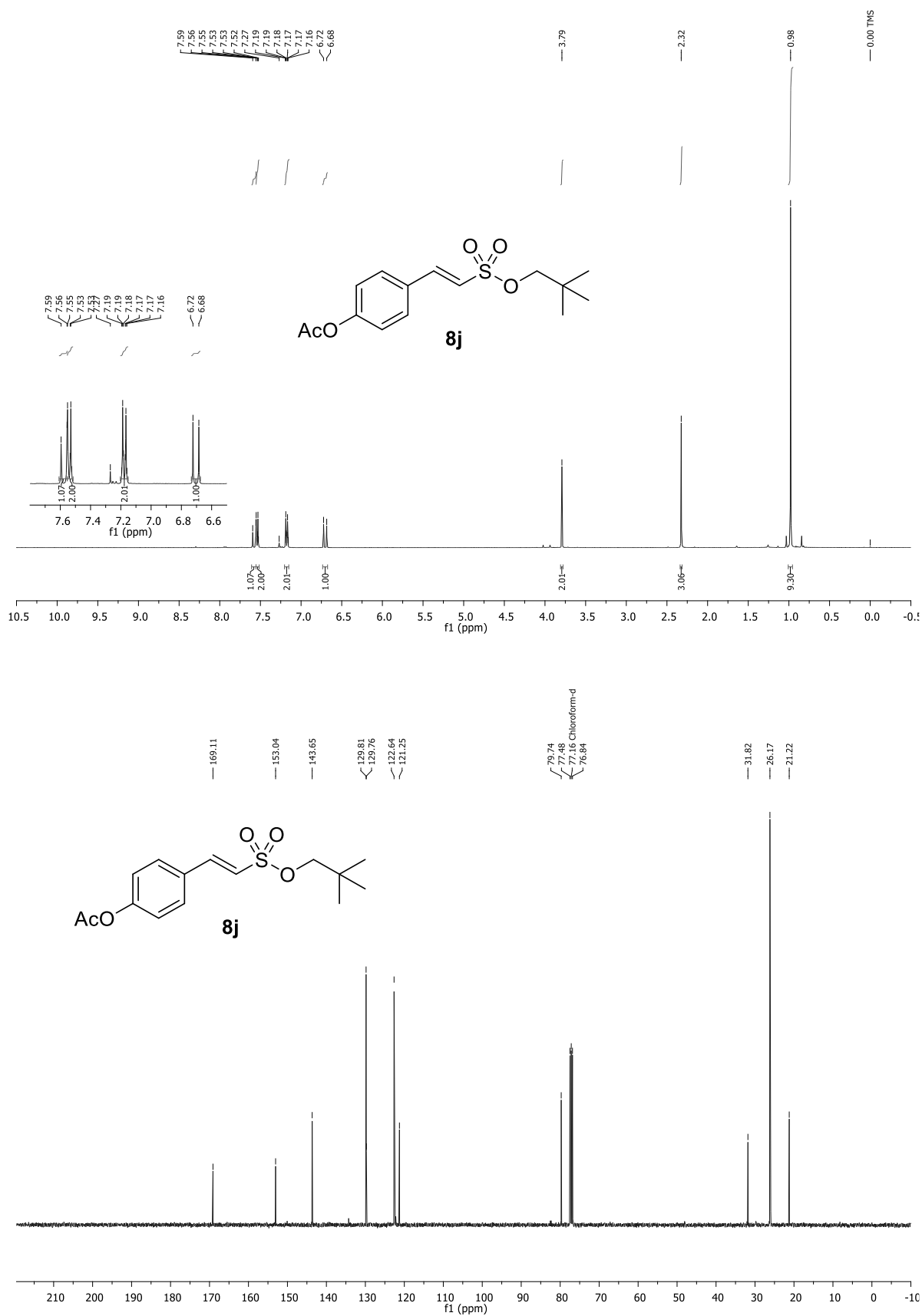


Figure S25: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8j**.

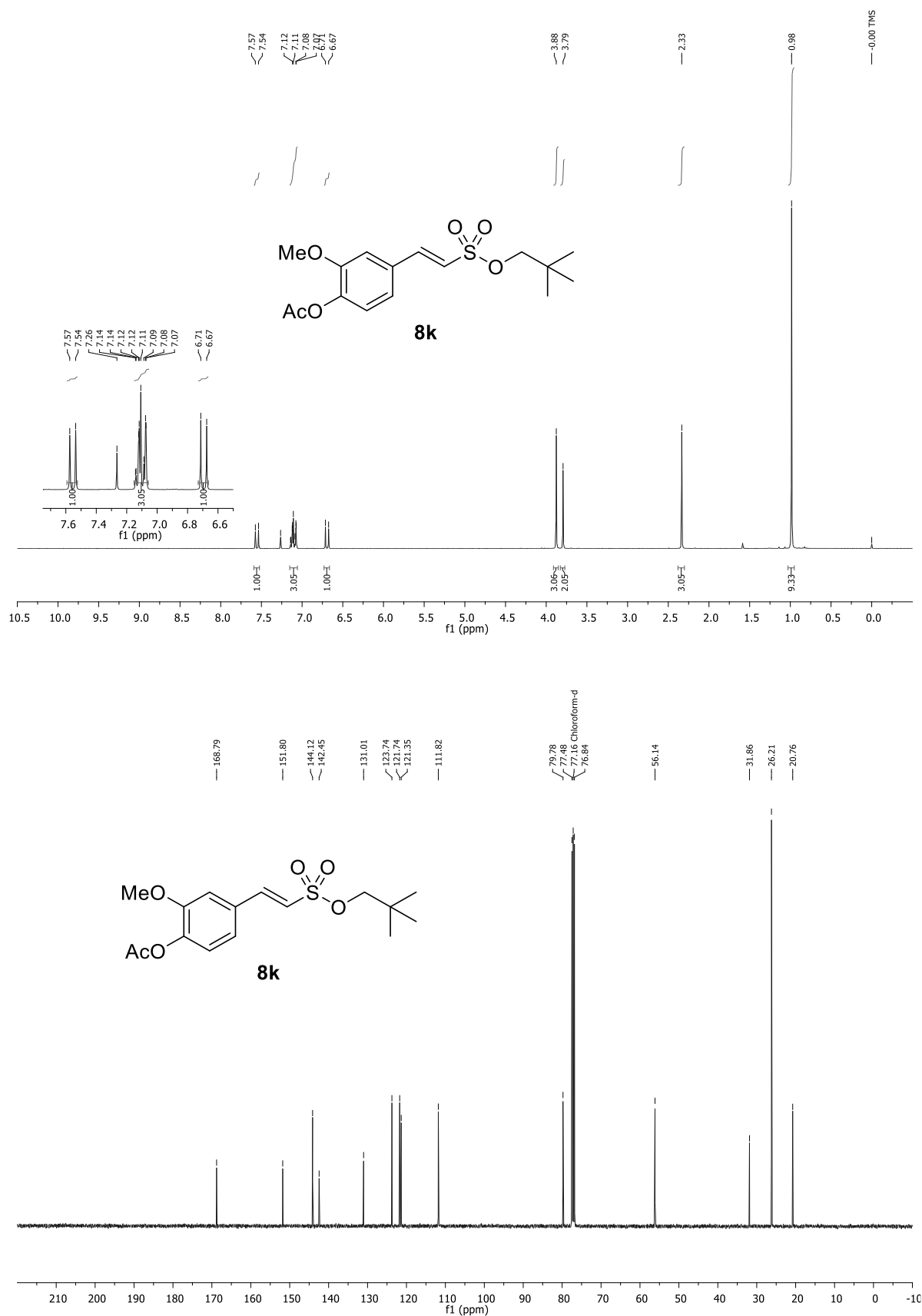


Figure S26: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **8k**.

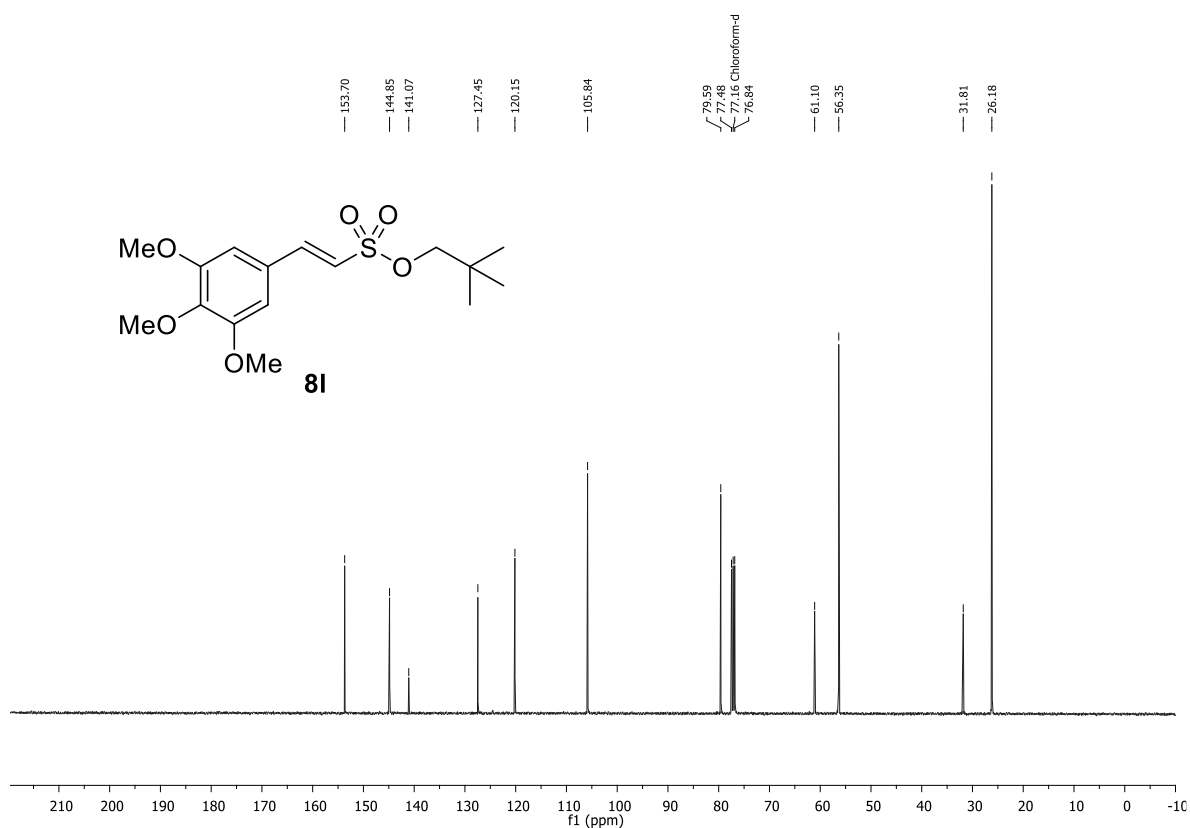


Figure S27: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8I**.

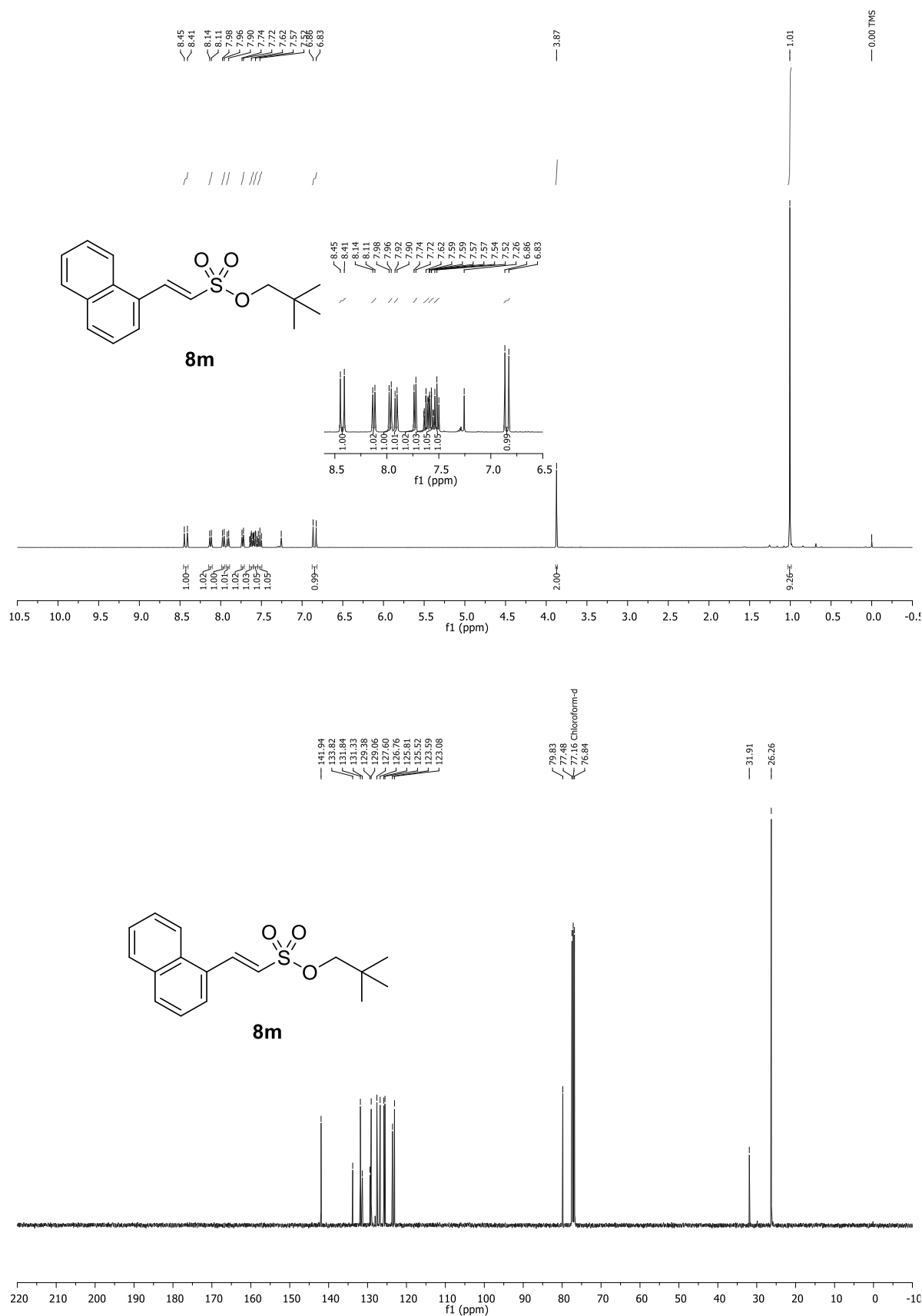


Figure S28: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **8m**.

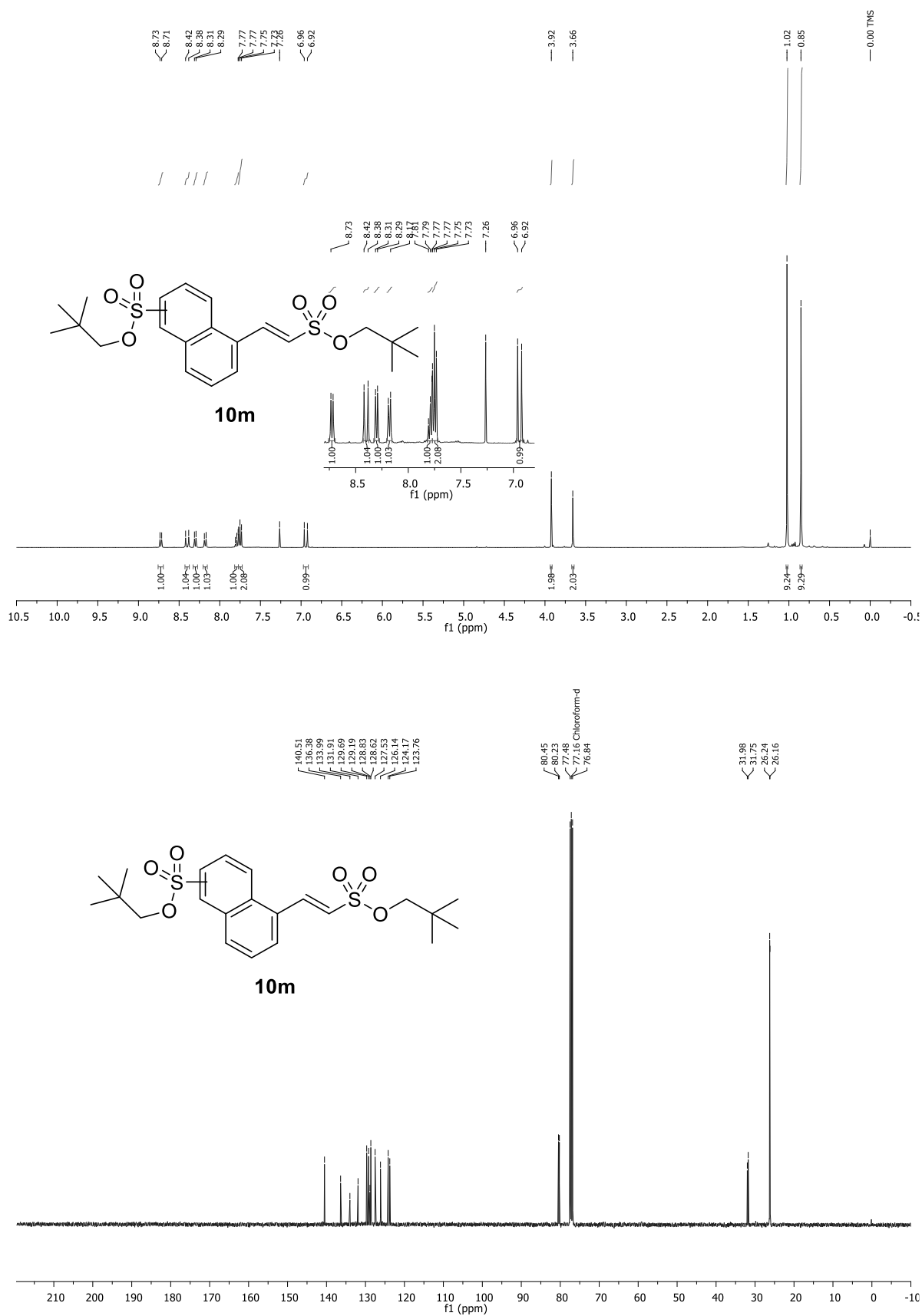


Figure S29: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of 10m.

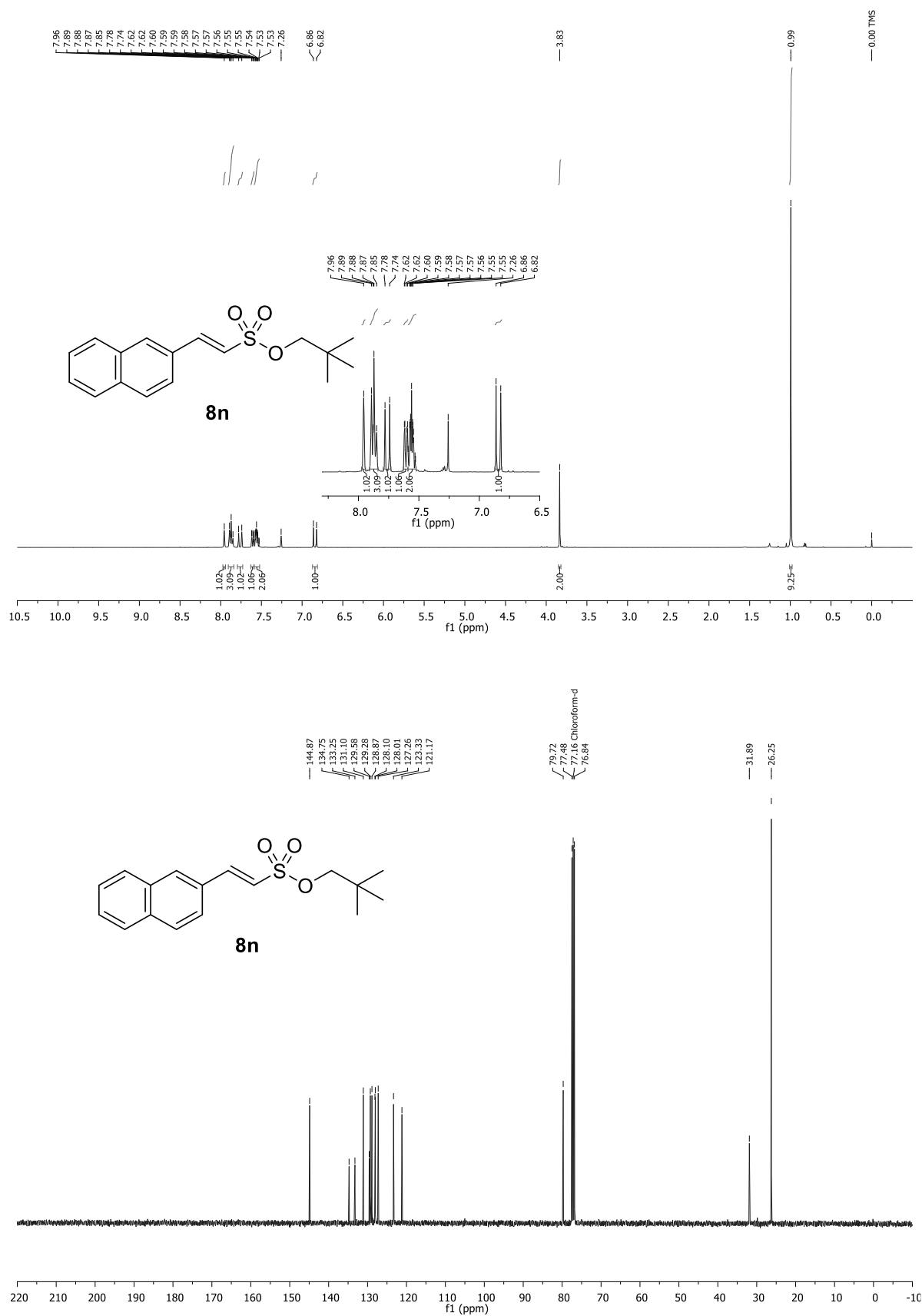


Figure S30: ^1H (CDCl_3 , 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 101 MHz) NMR Spectrum of **8n**.



Figure S31: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **10n**.

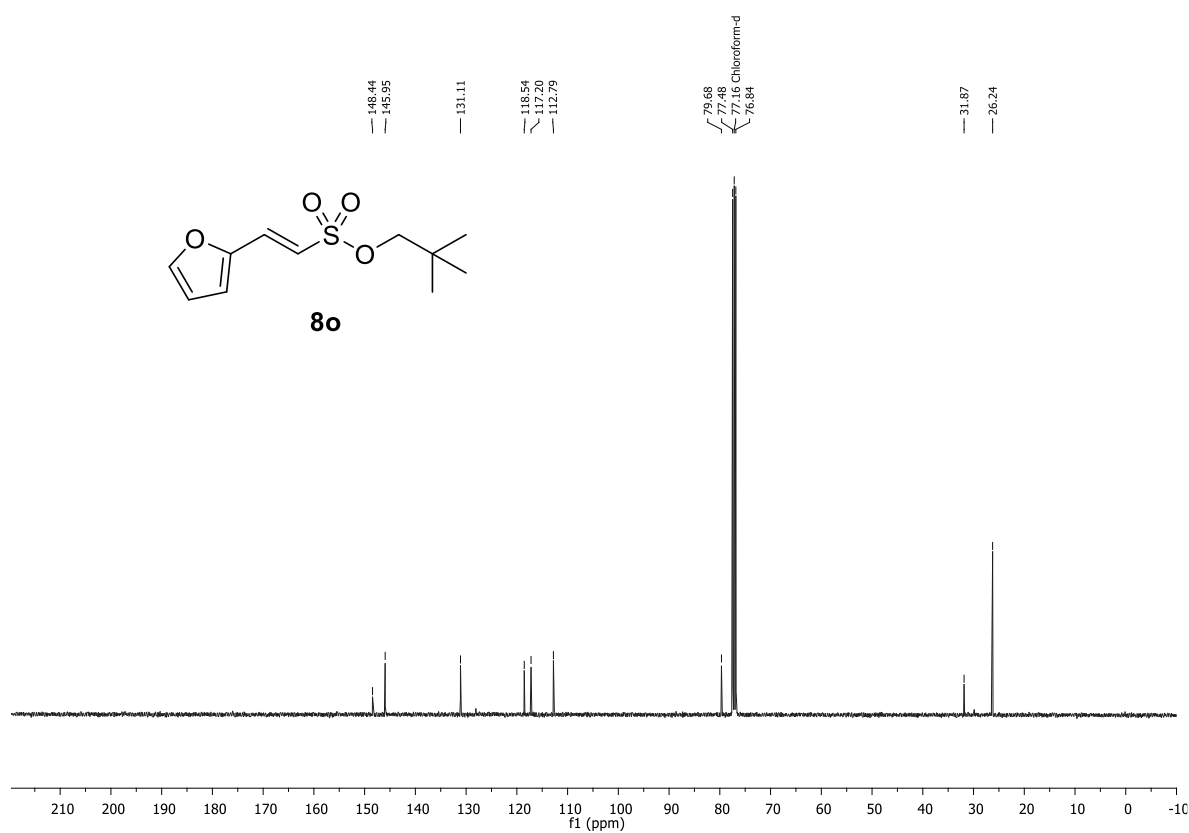
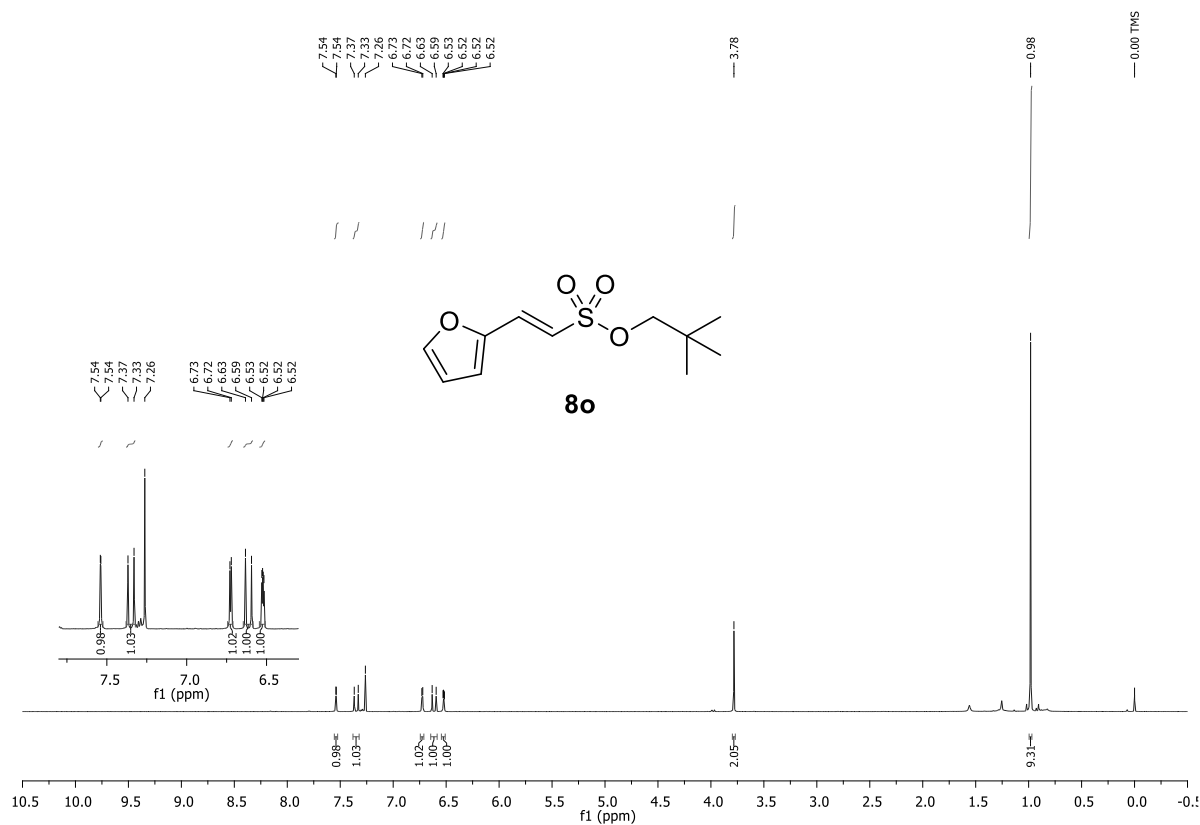


Figure S32: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **8o**.

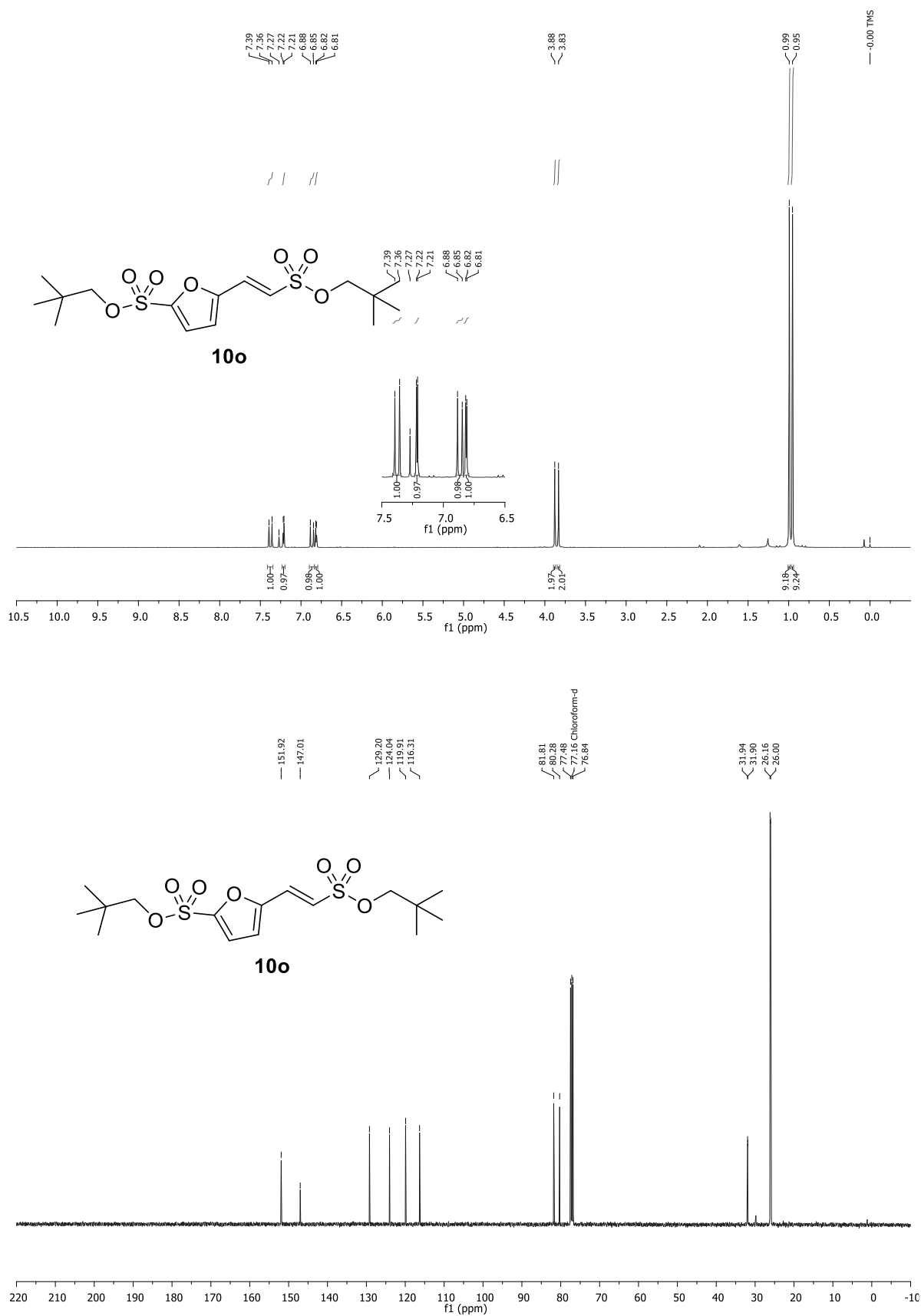


Figure S33: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **10o**.

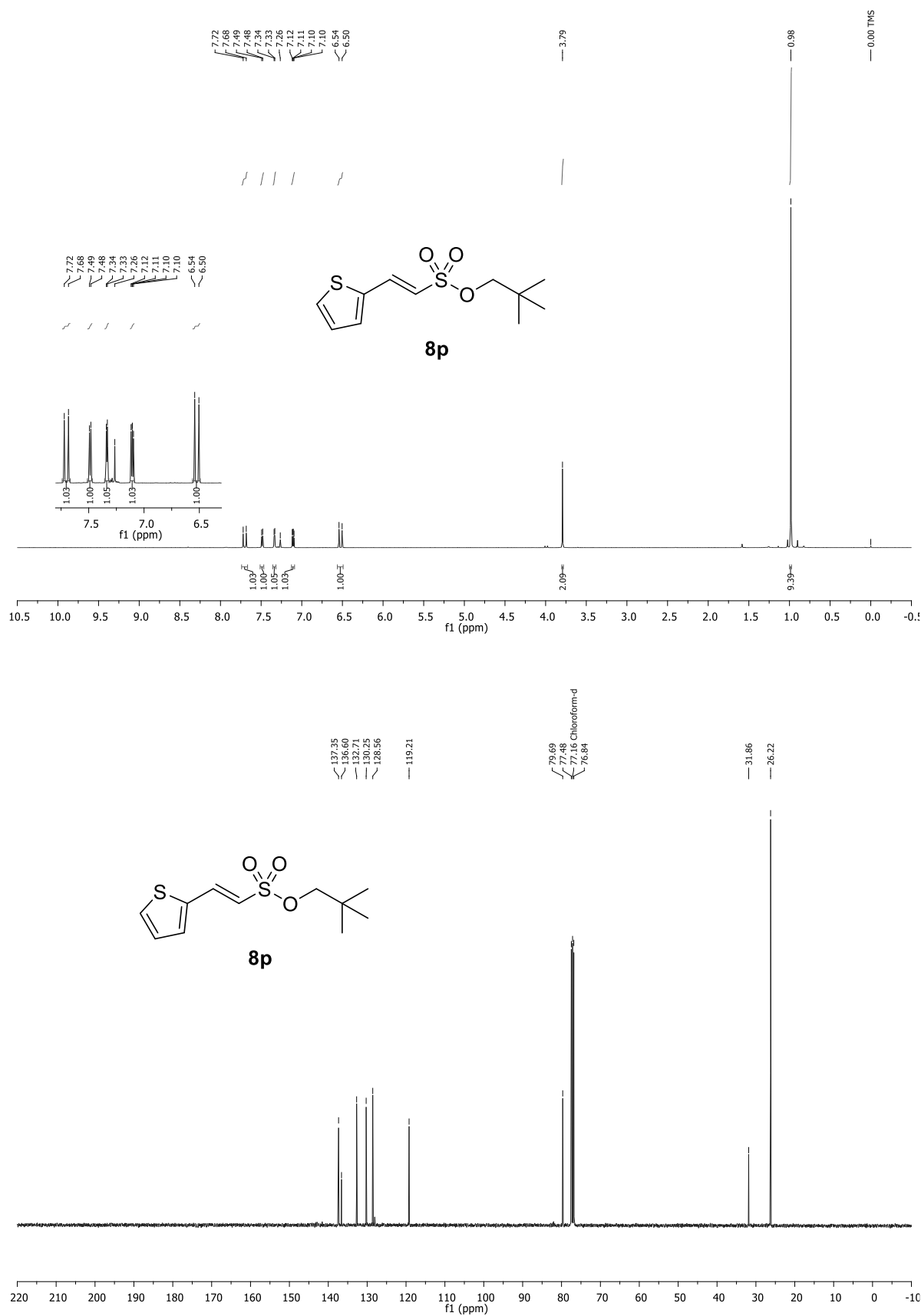


Figure S34: ^1H (CDCl_3 , 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 101 MHz) NMR Spectrum of **8p**.

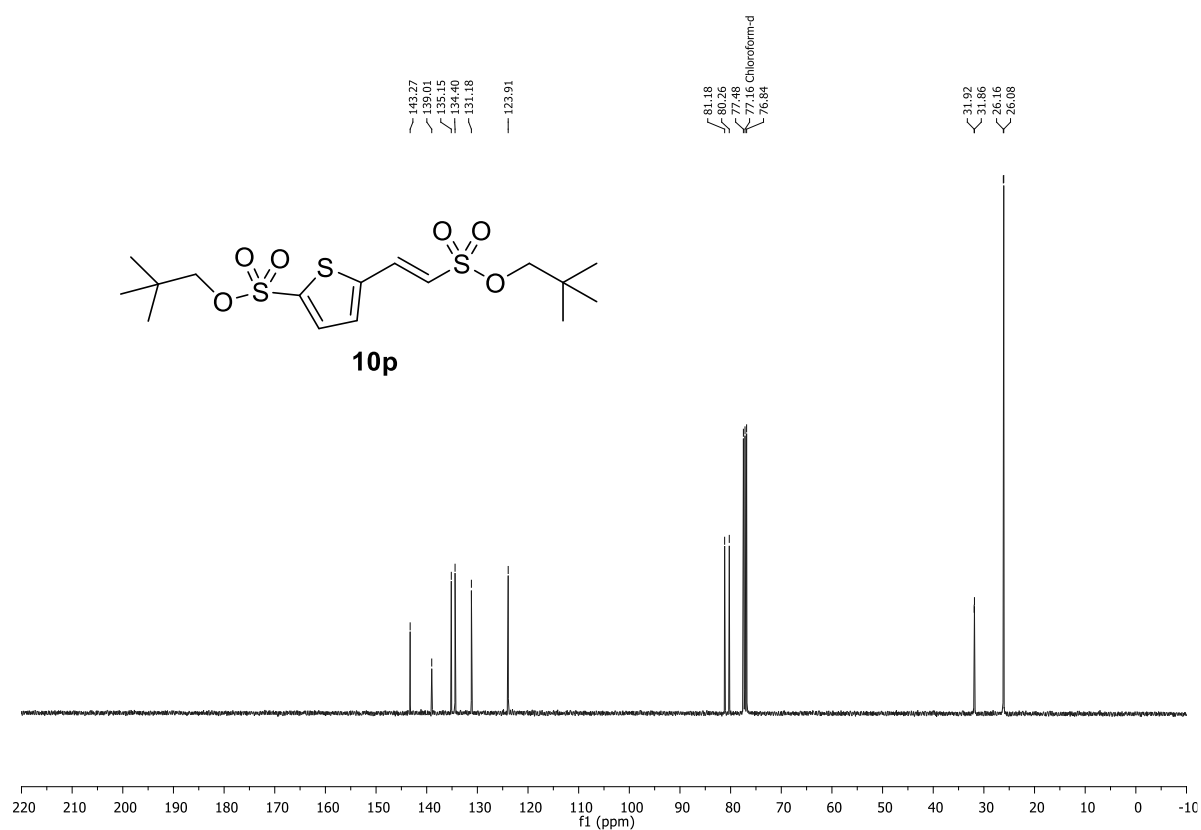
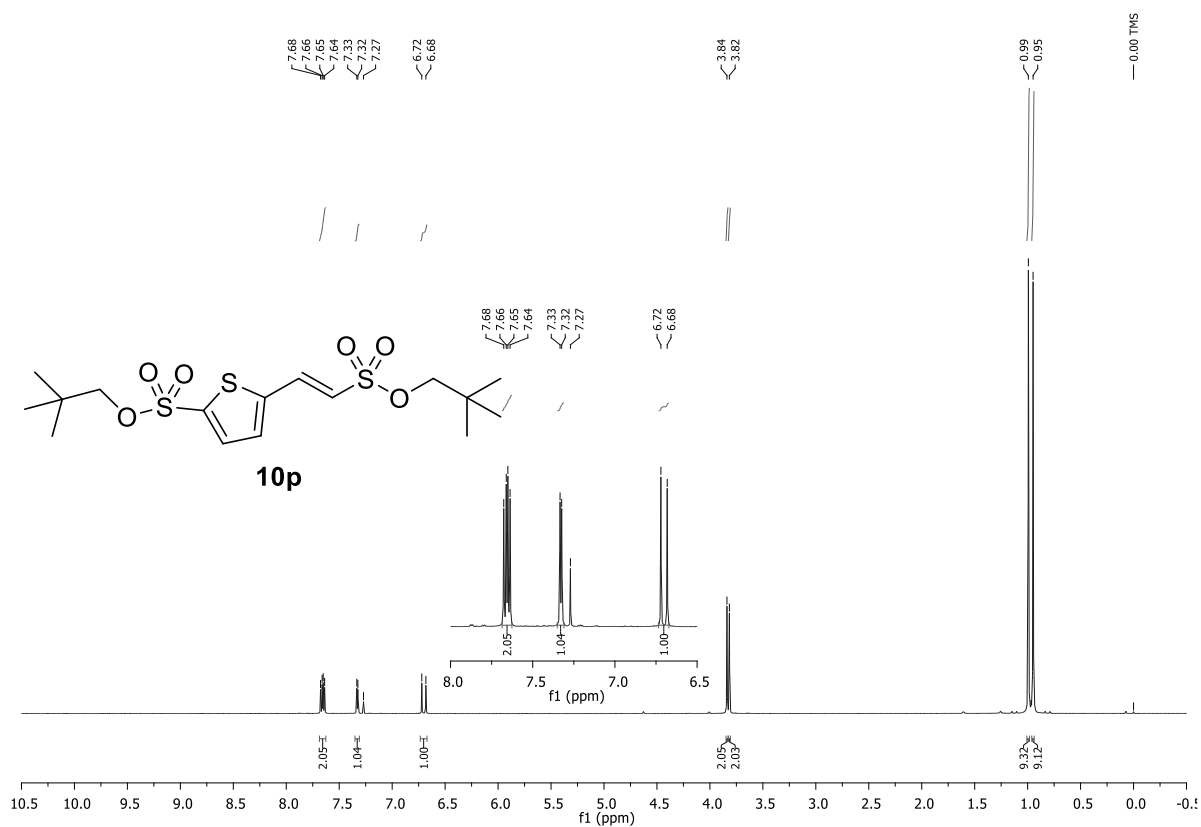


Figure S35: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **10p**.

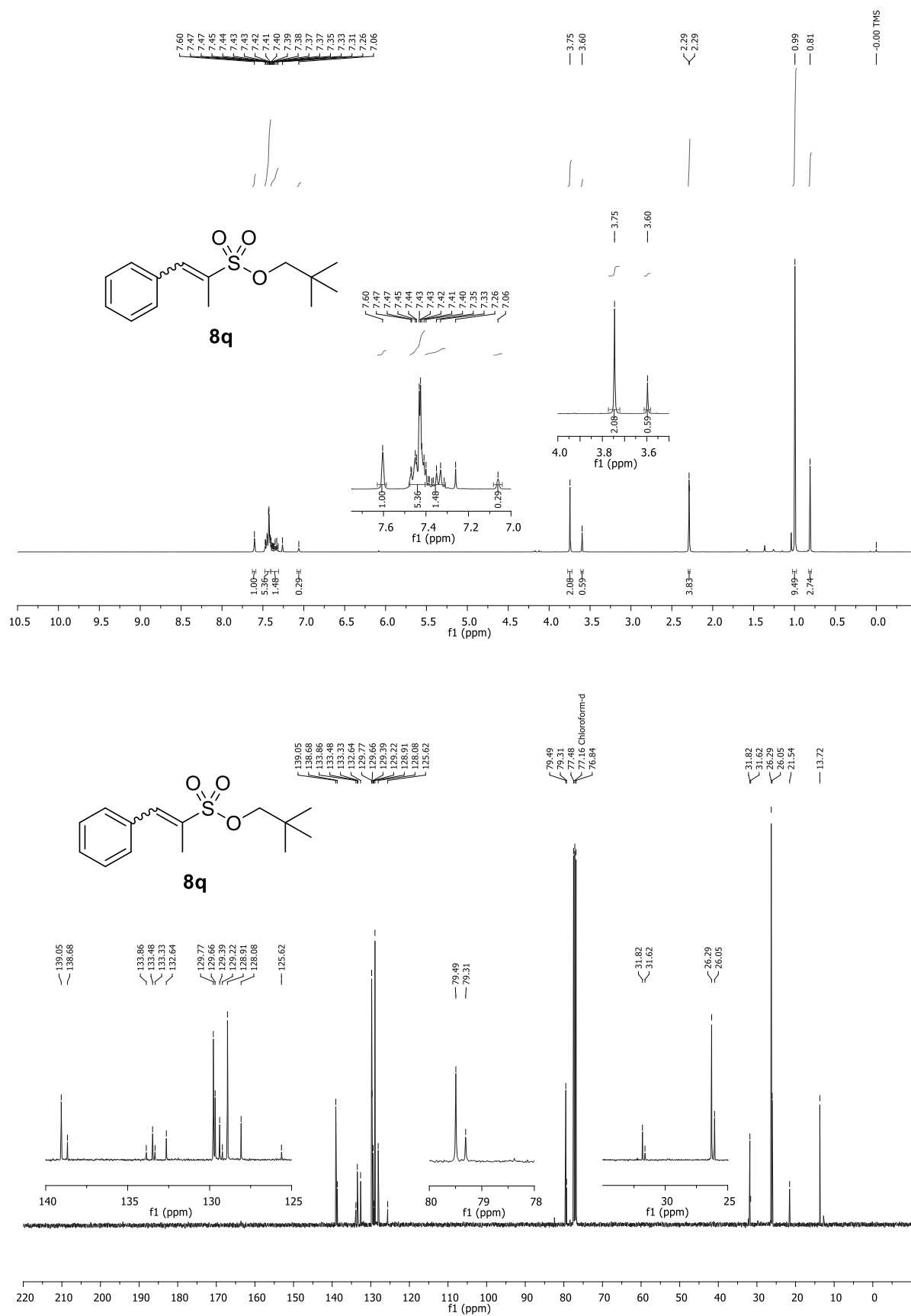


Figure S36: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of 8q.

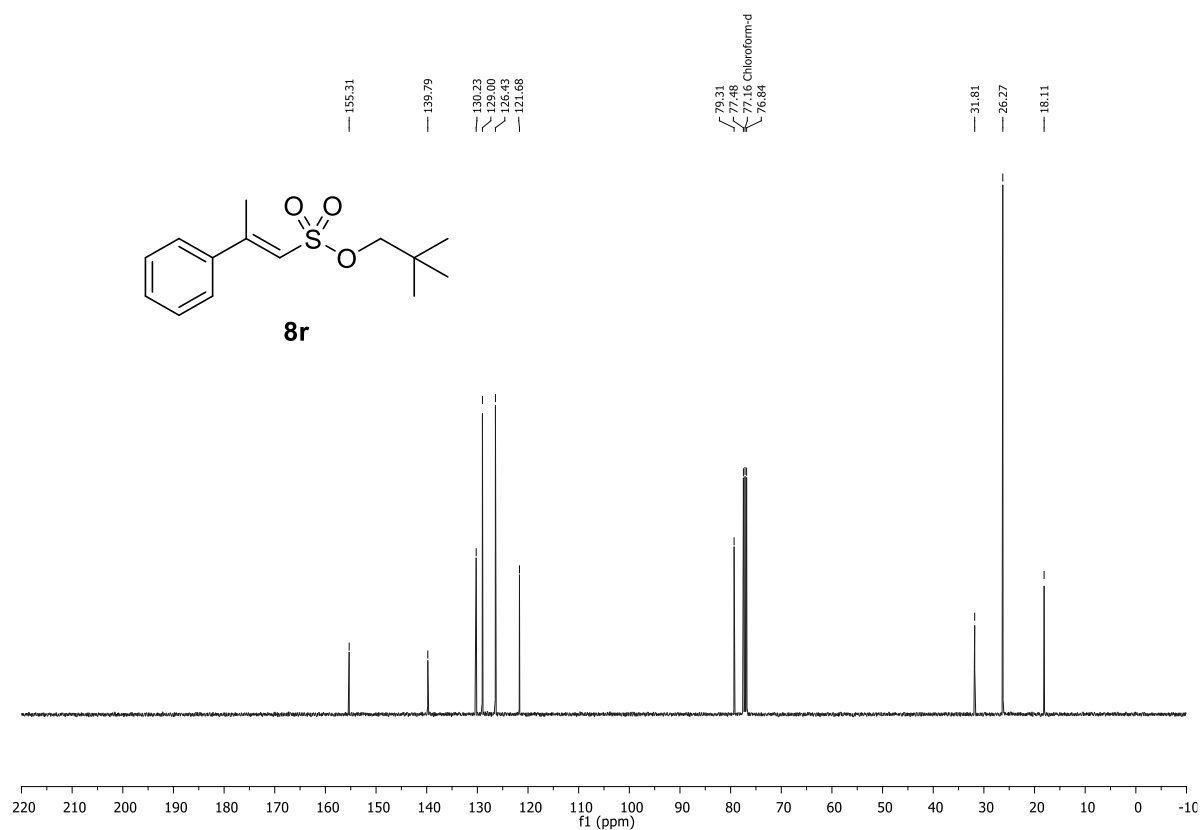
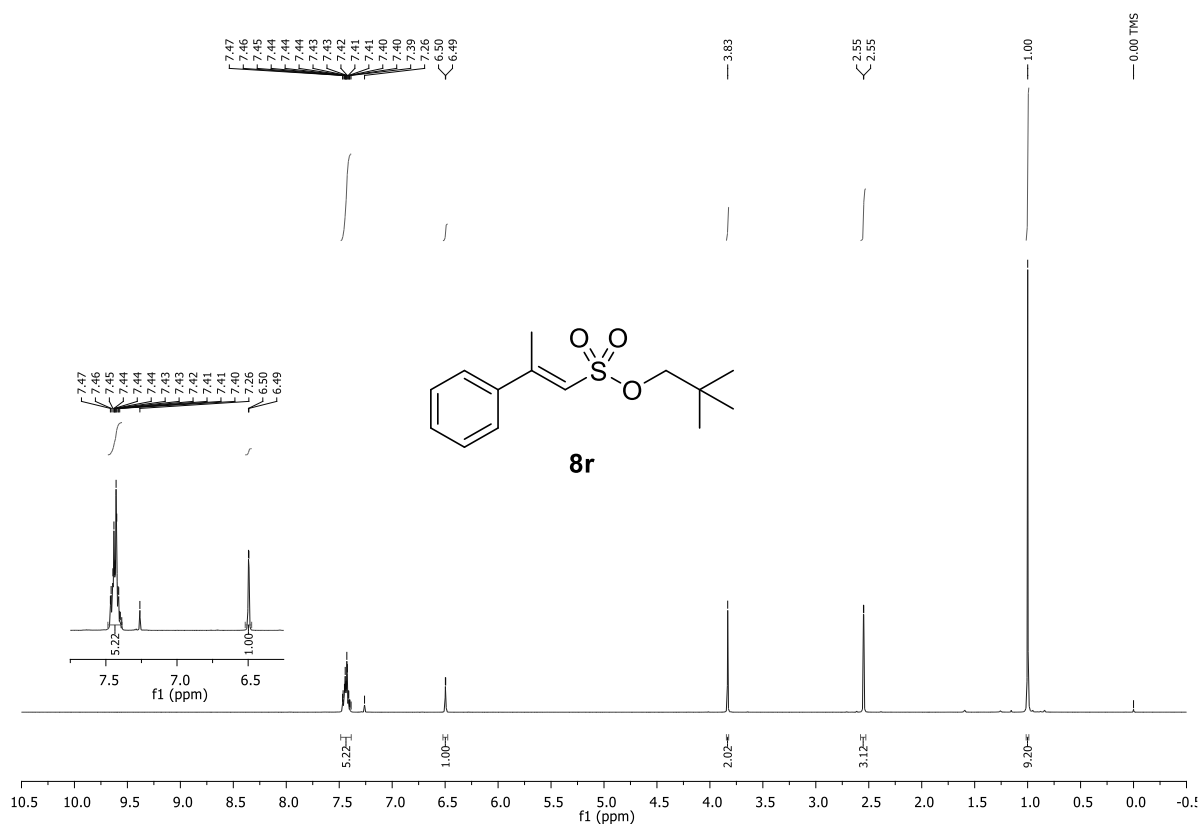


Figure S37: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **8r**.

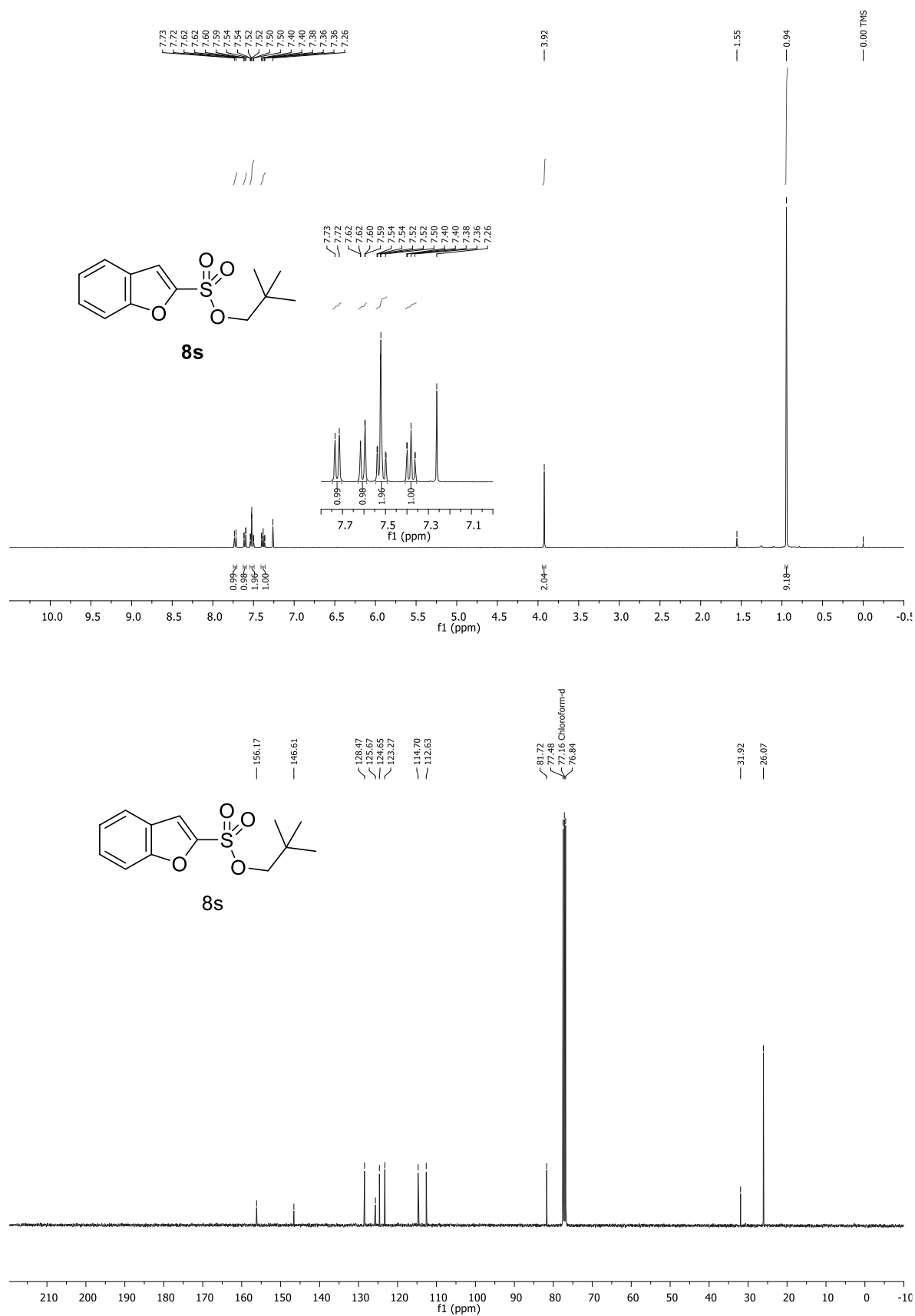


Figure S38: ^1H (CDCl₃, 400 MHz) and ^{13}C (CDCl₃, 101 MHz) NMR Spectrum of **8s**.

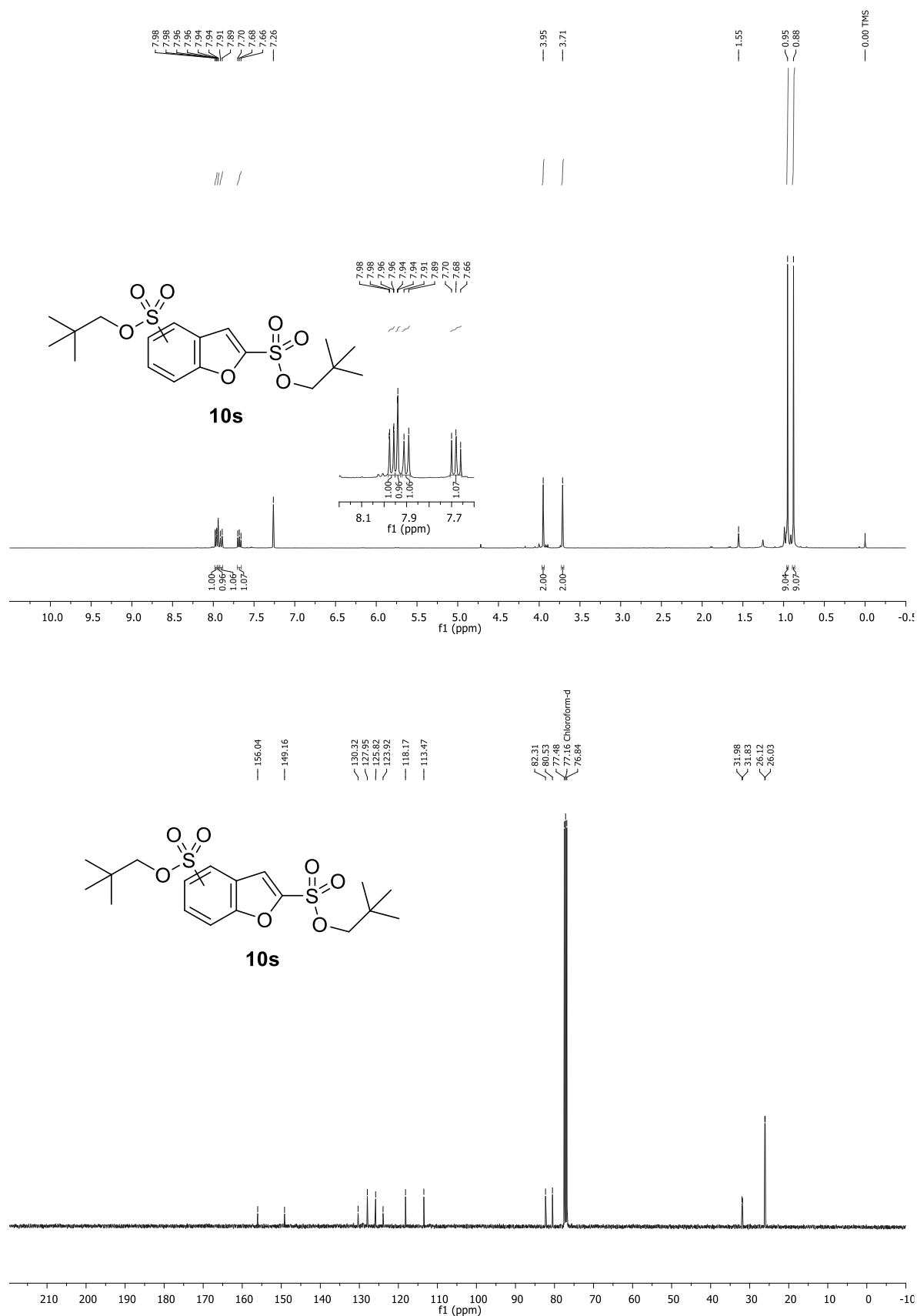


Figure S39: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **10s**.

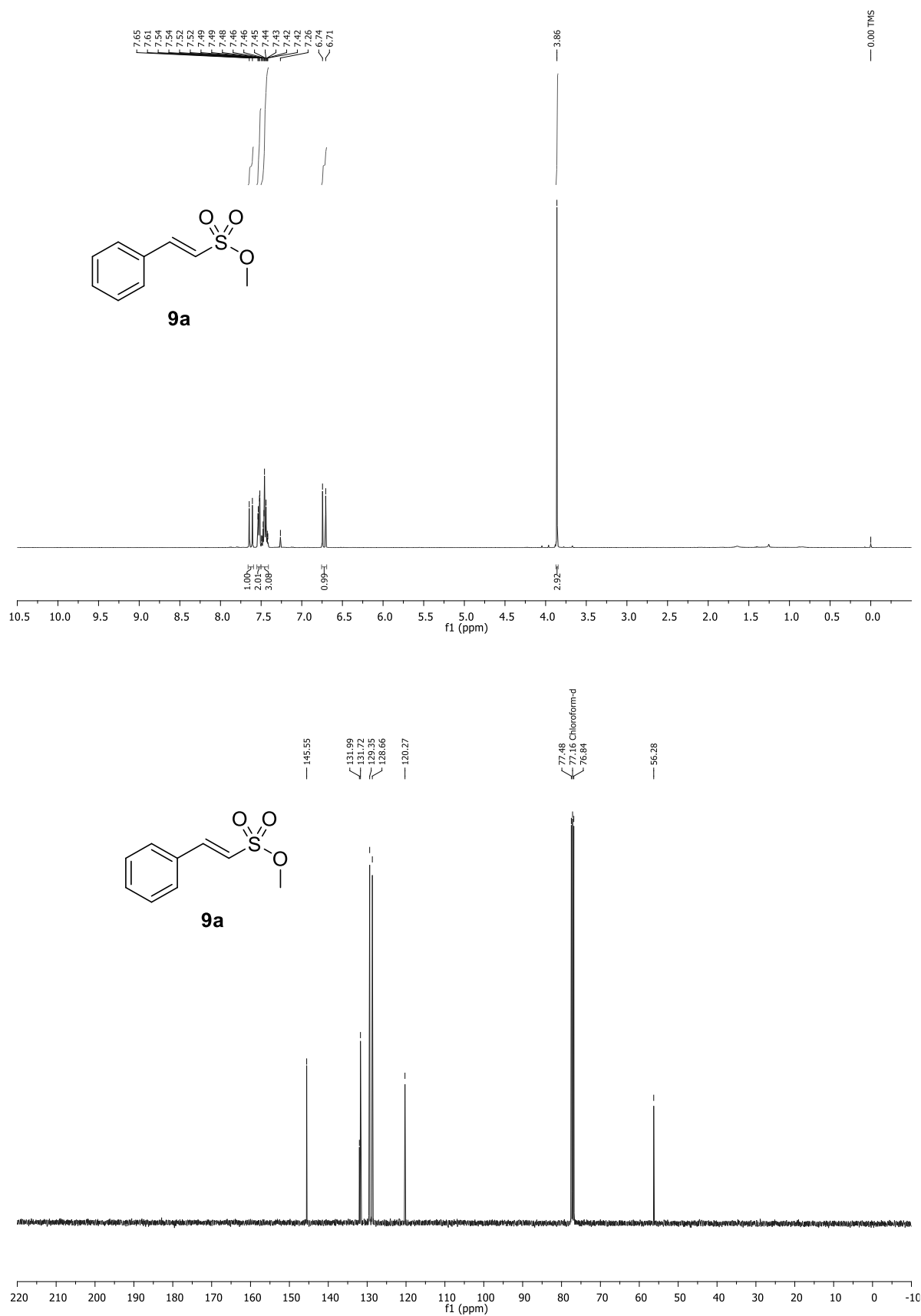


Figure S40: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **9a**.

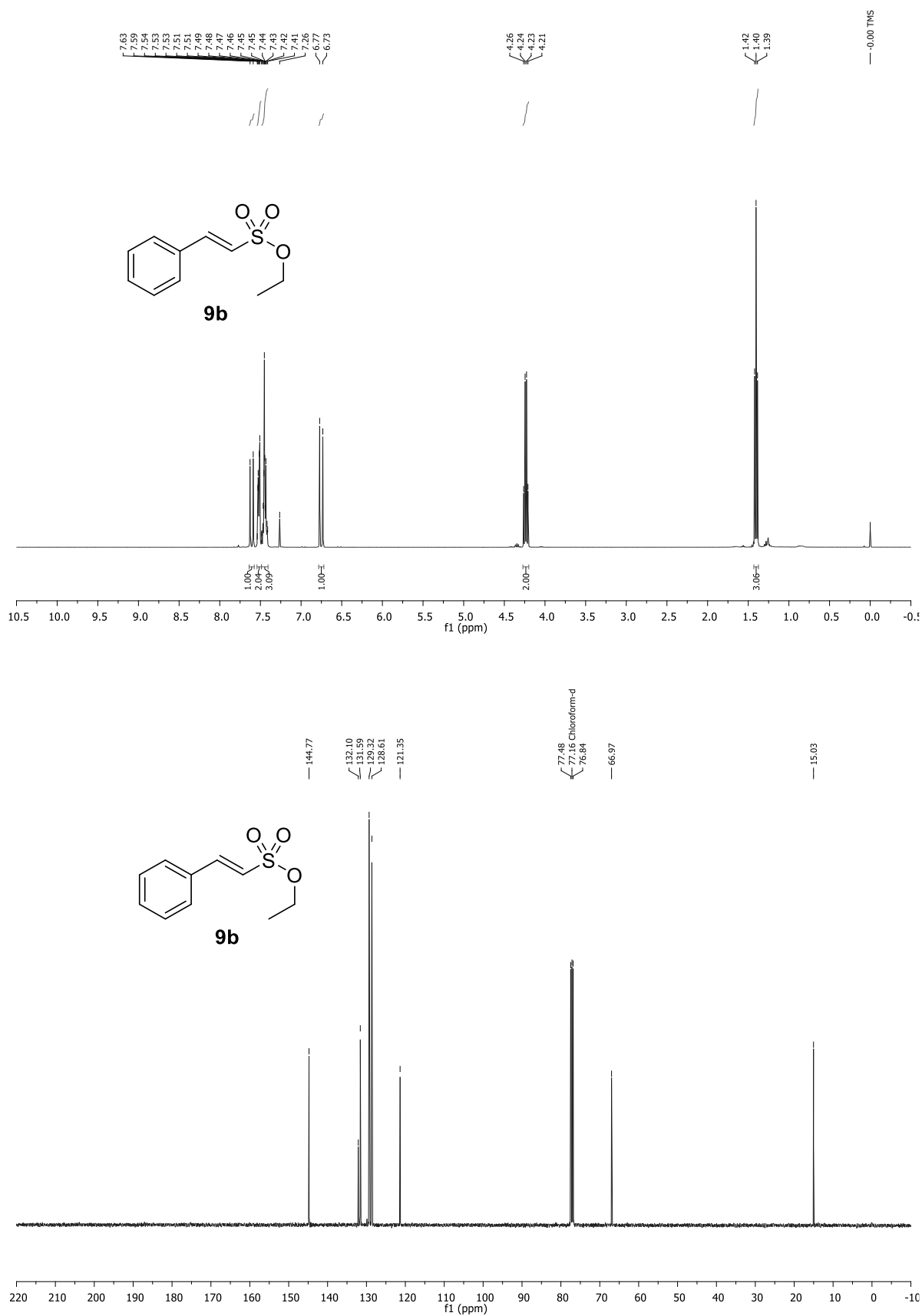


Figure S41: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **9b**.

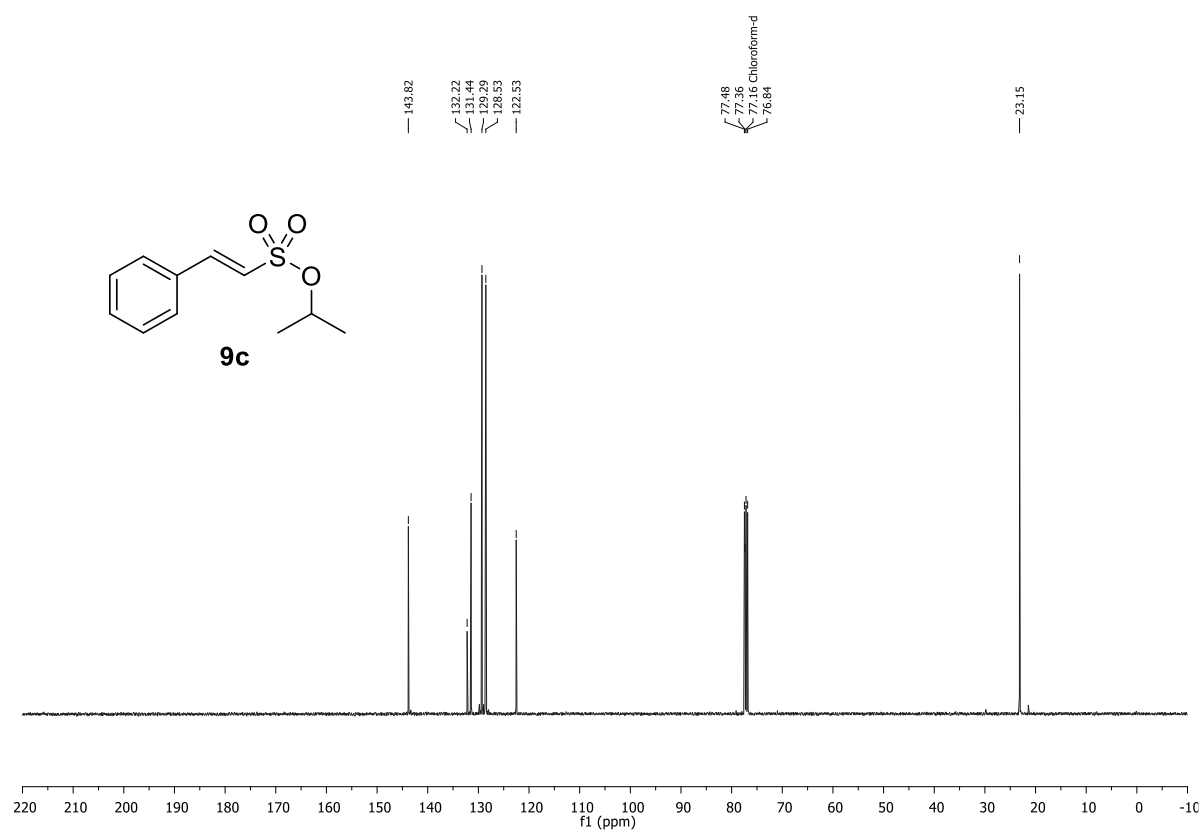
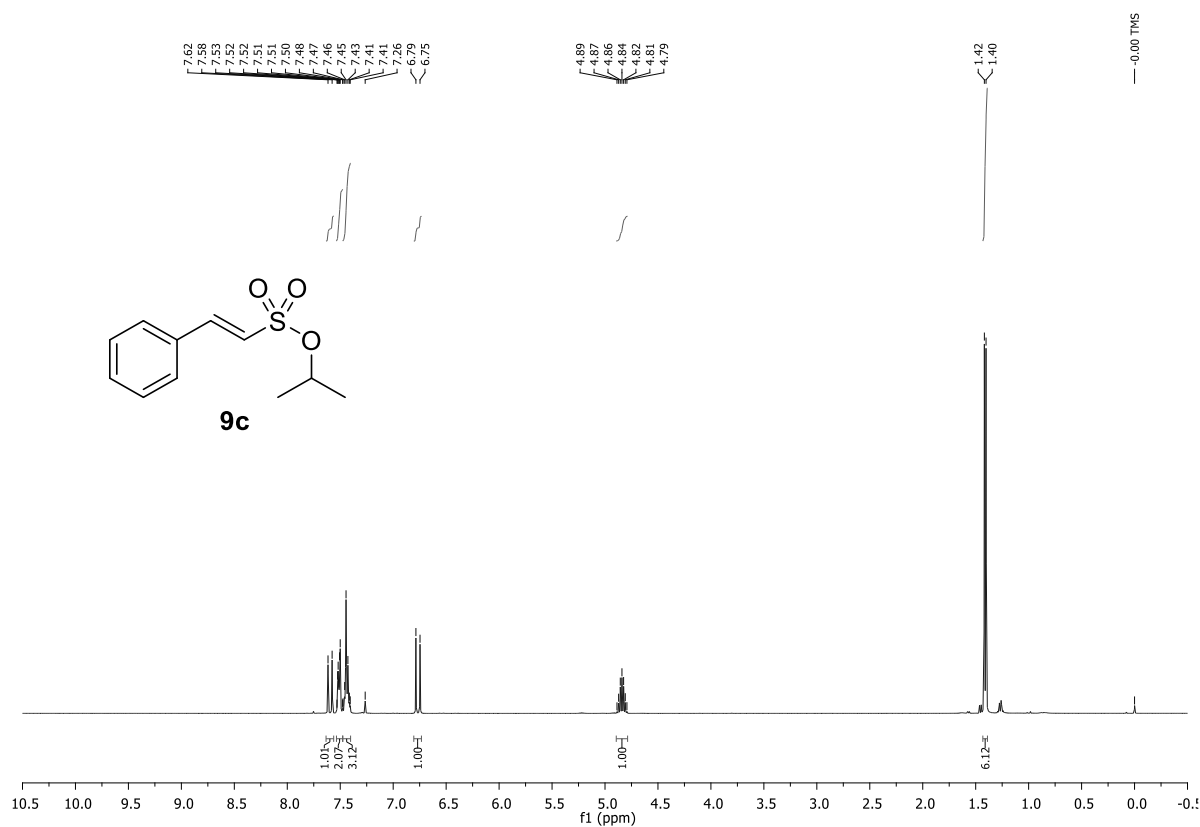


Figure S42: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9c**.

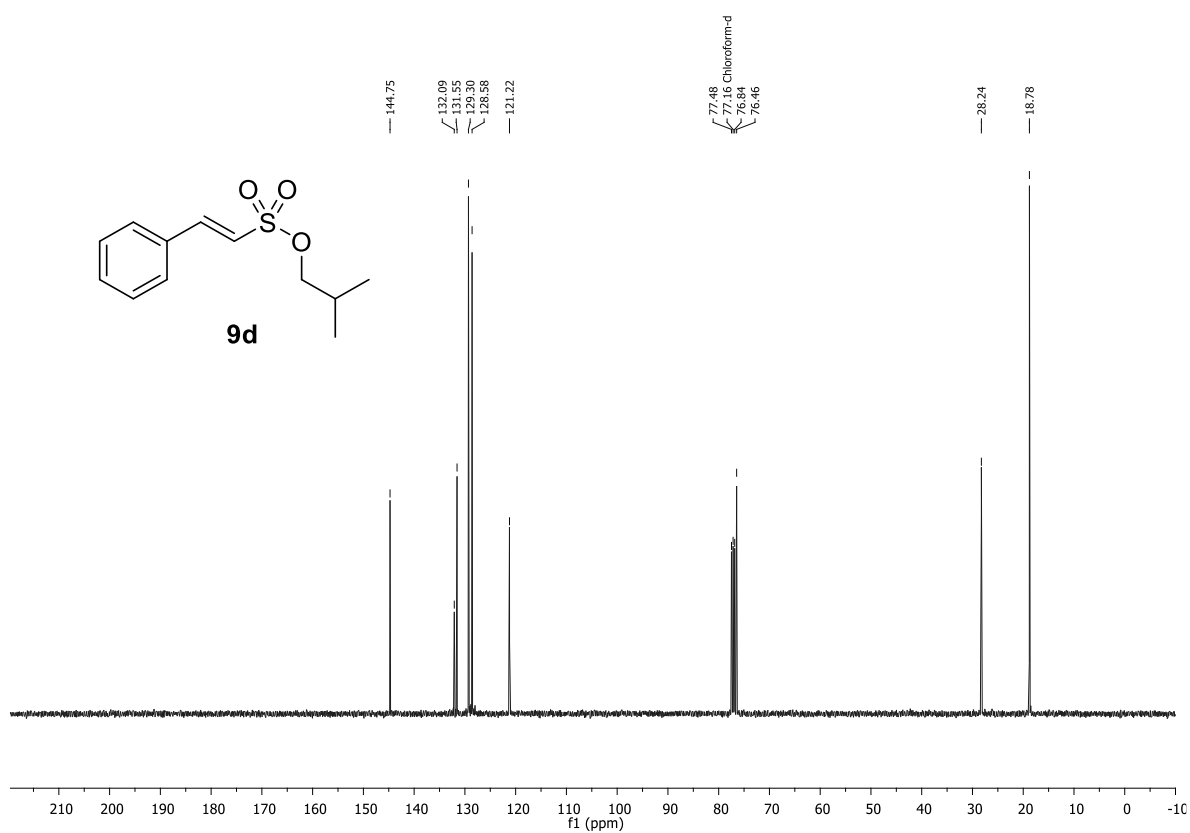
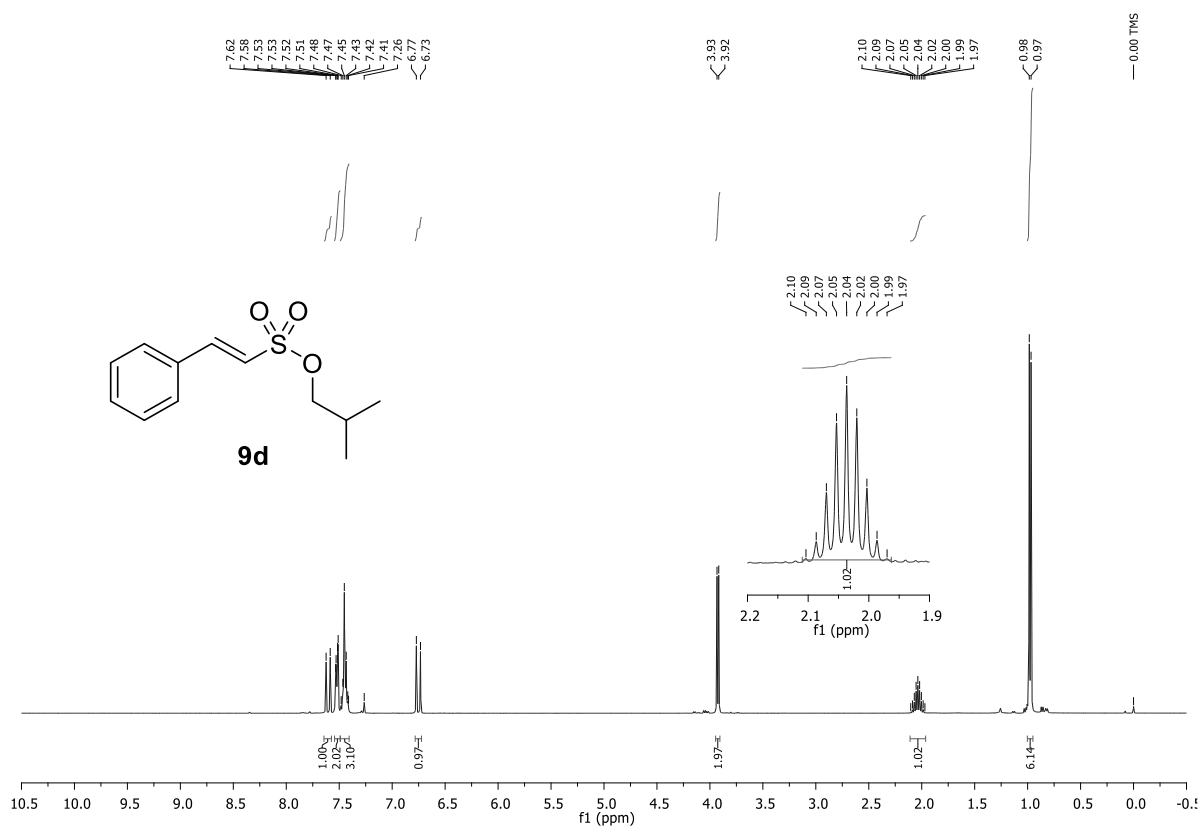


Figure S43: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9d**.

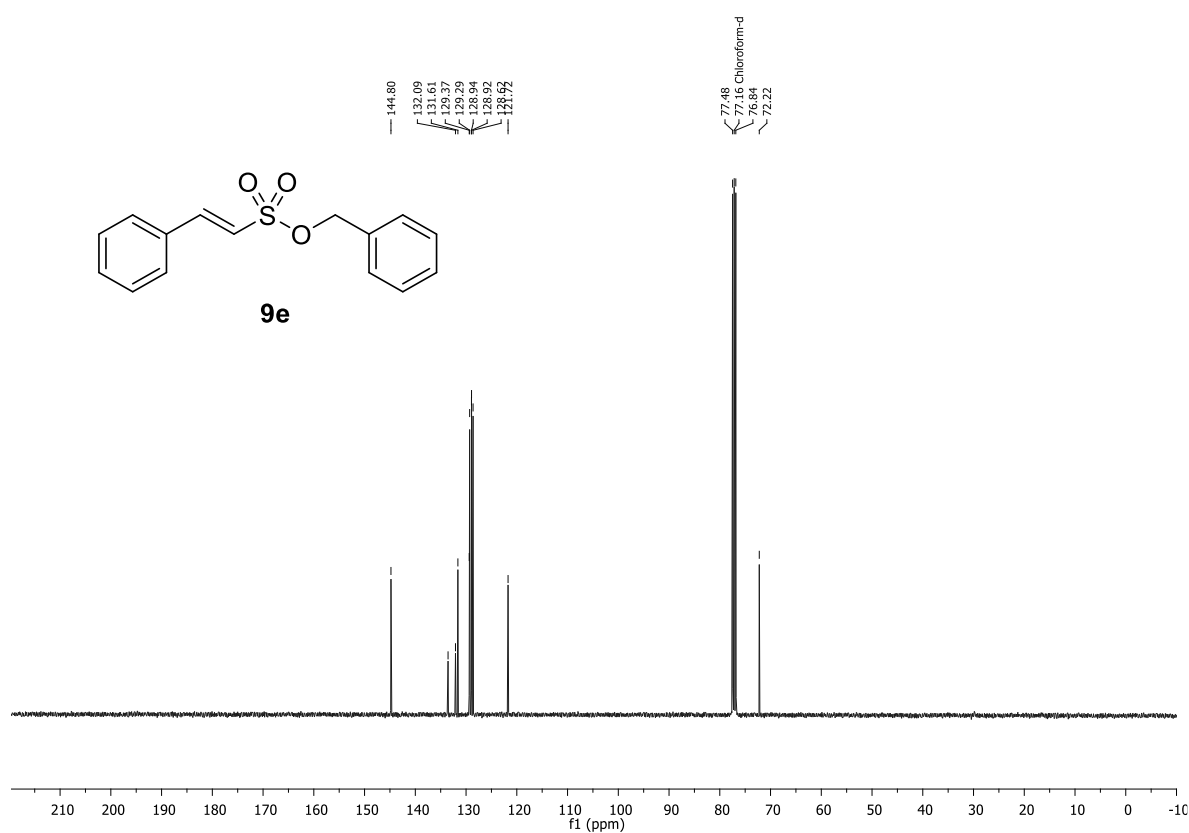
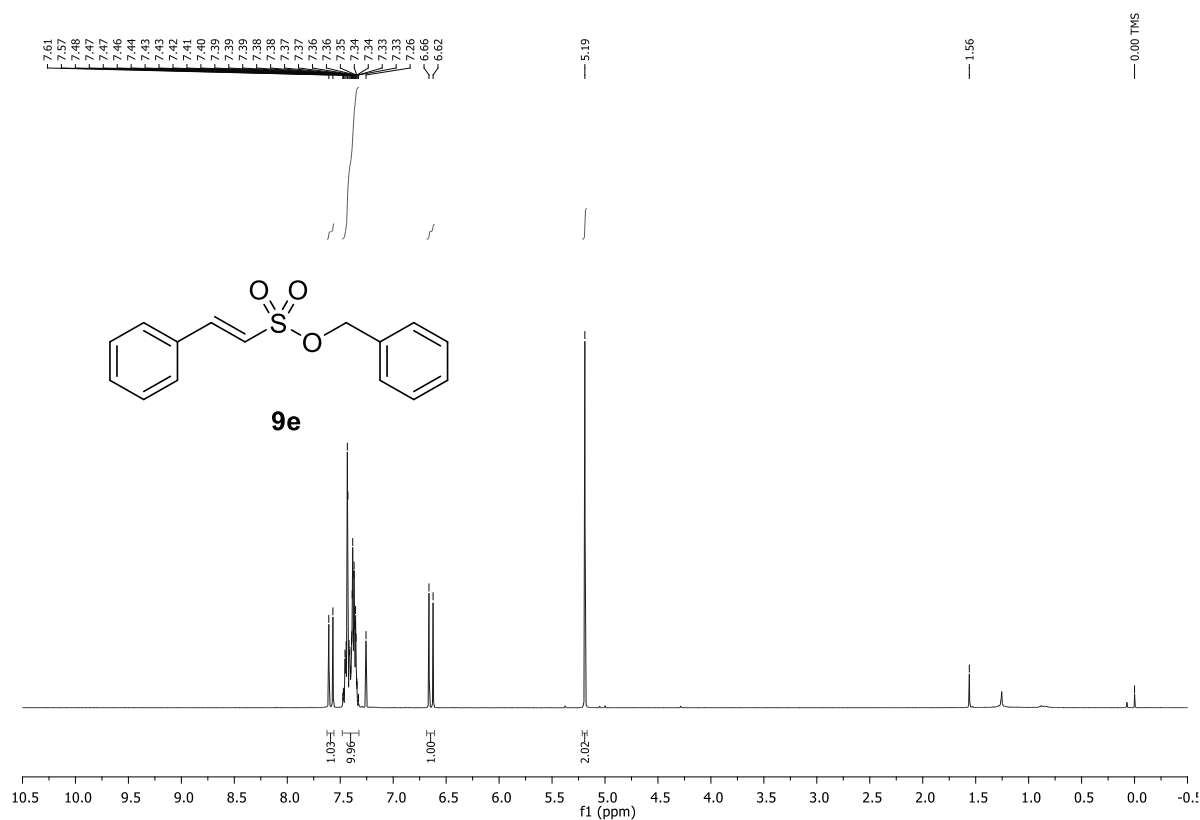


Figure S44: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9e**.

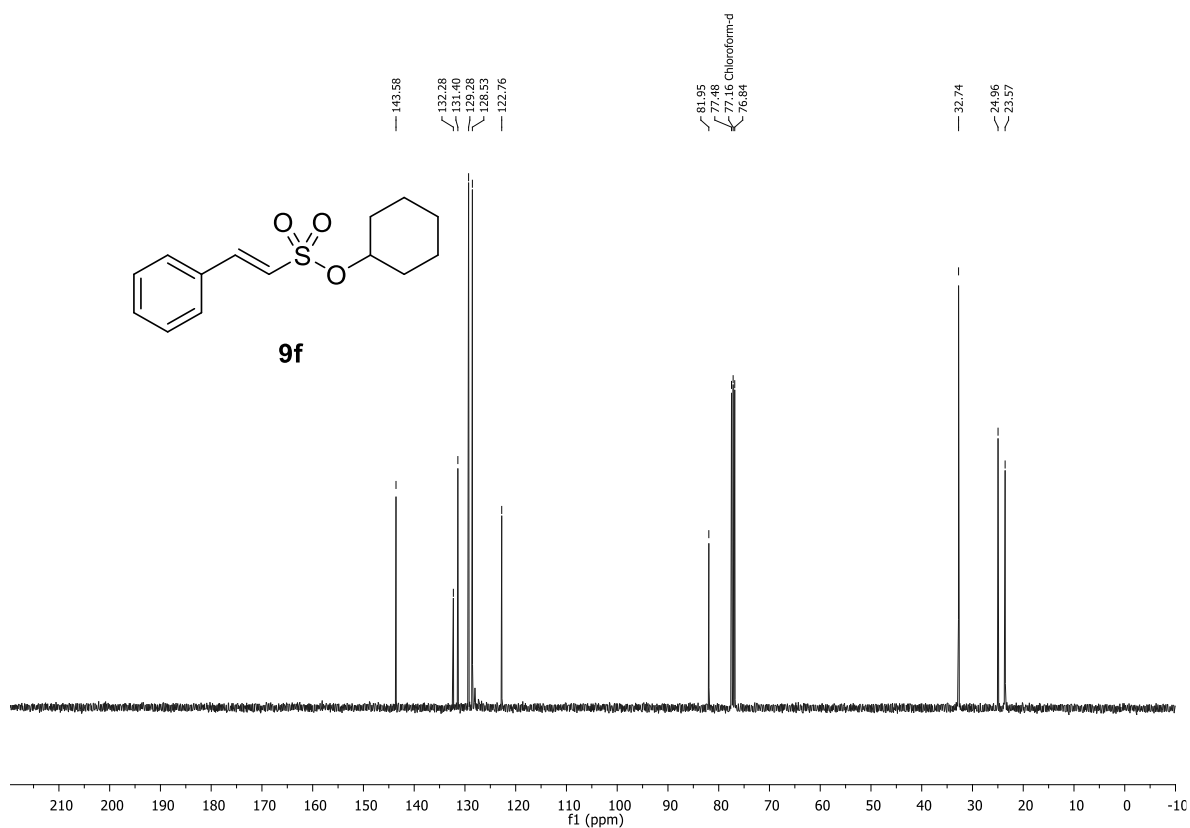
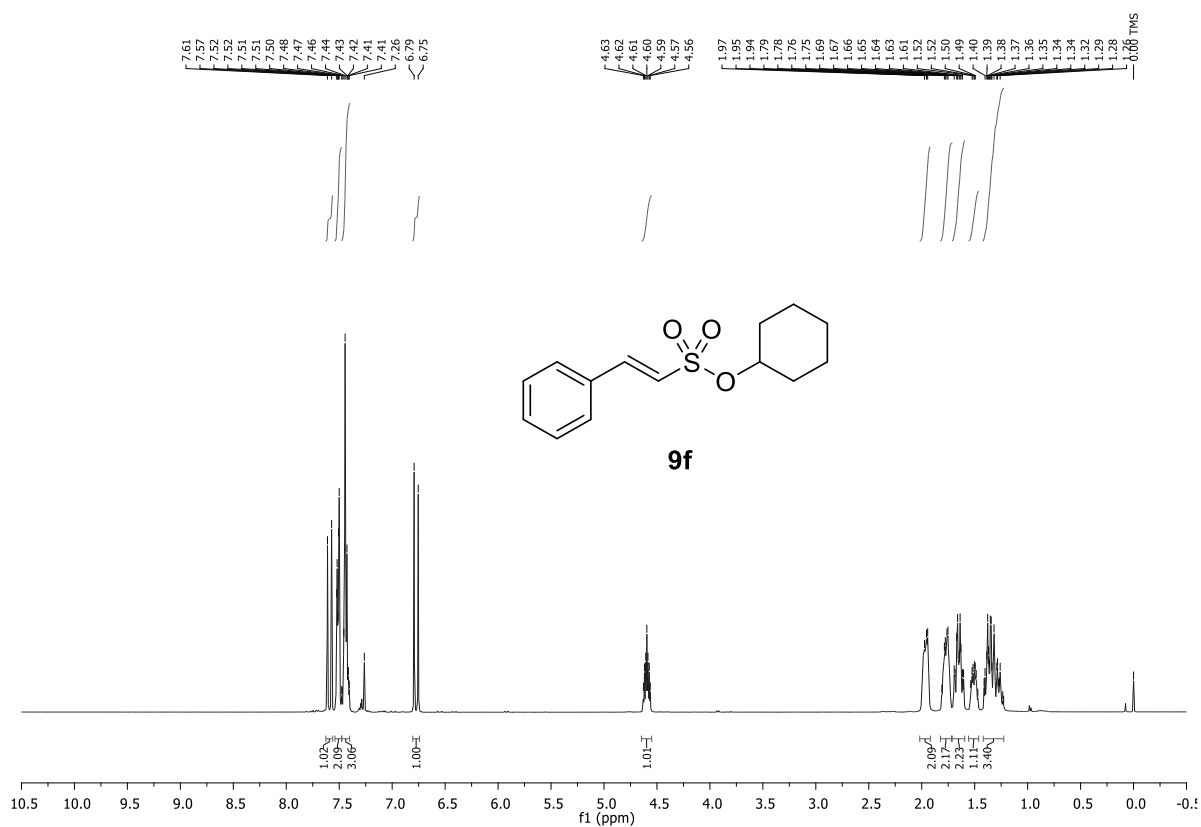


Figure S45: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9f**.

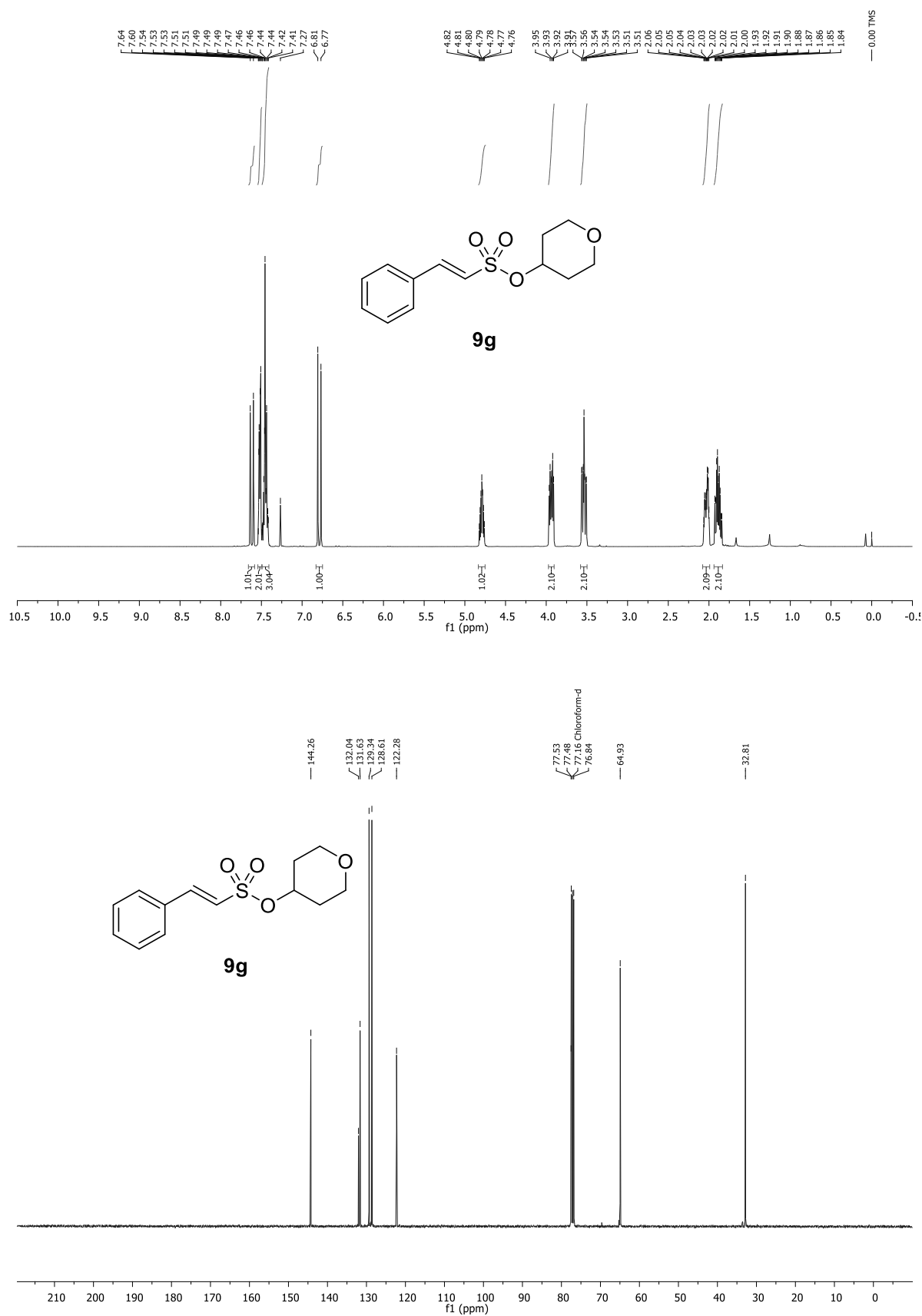


Figure S46: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9g**.

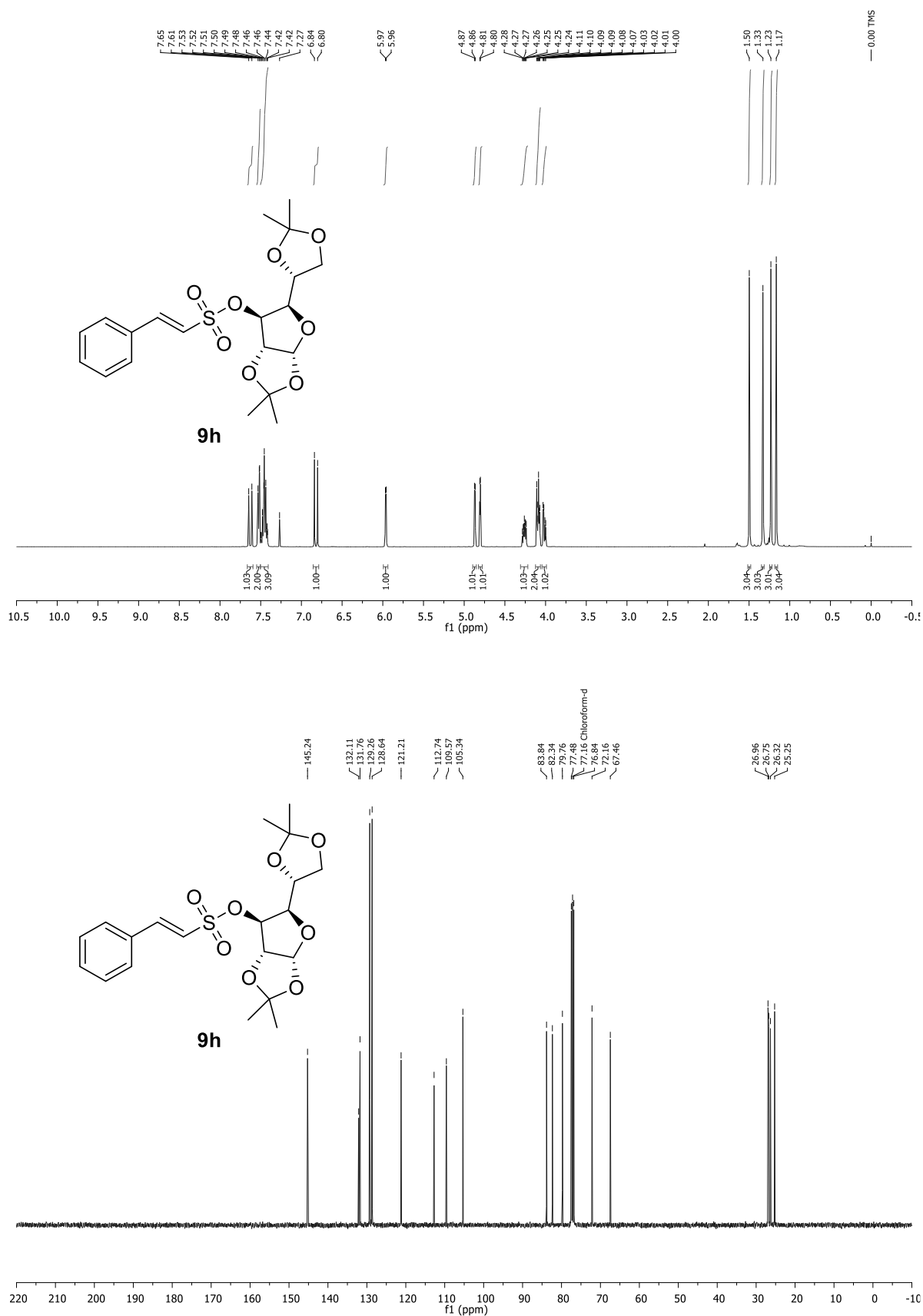


Figure S47: ^1H (CDCl₃, 400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (CDCl₃, 101 MHz) NMR Spectrum of **9h**.

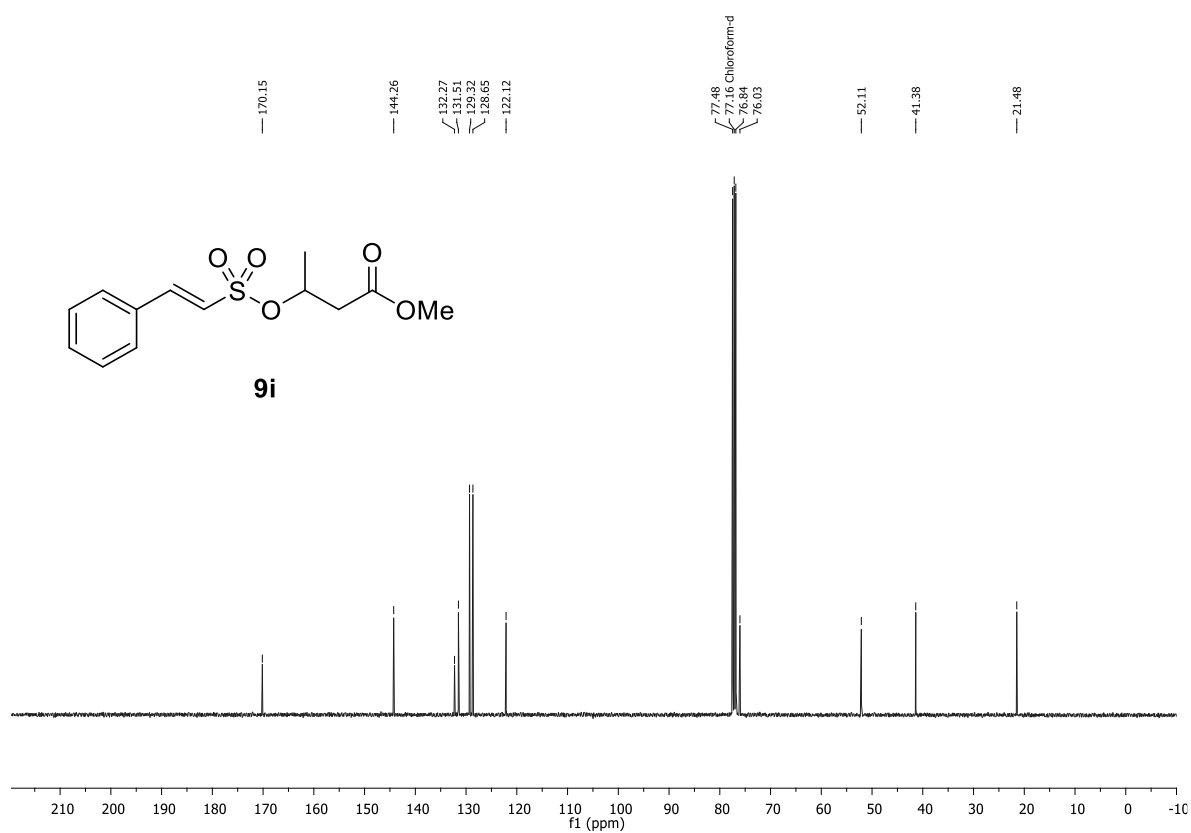
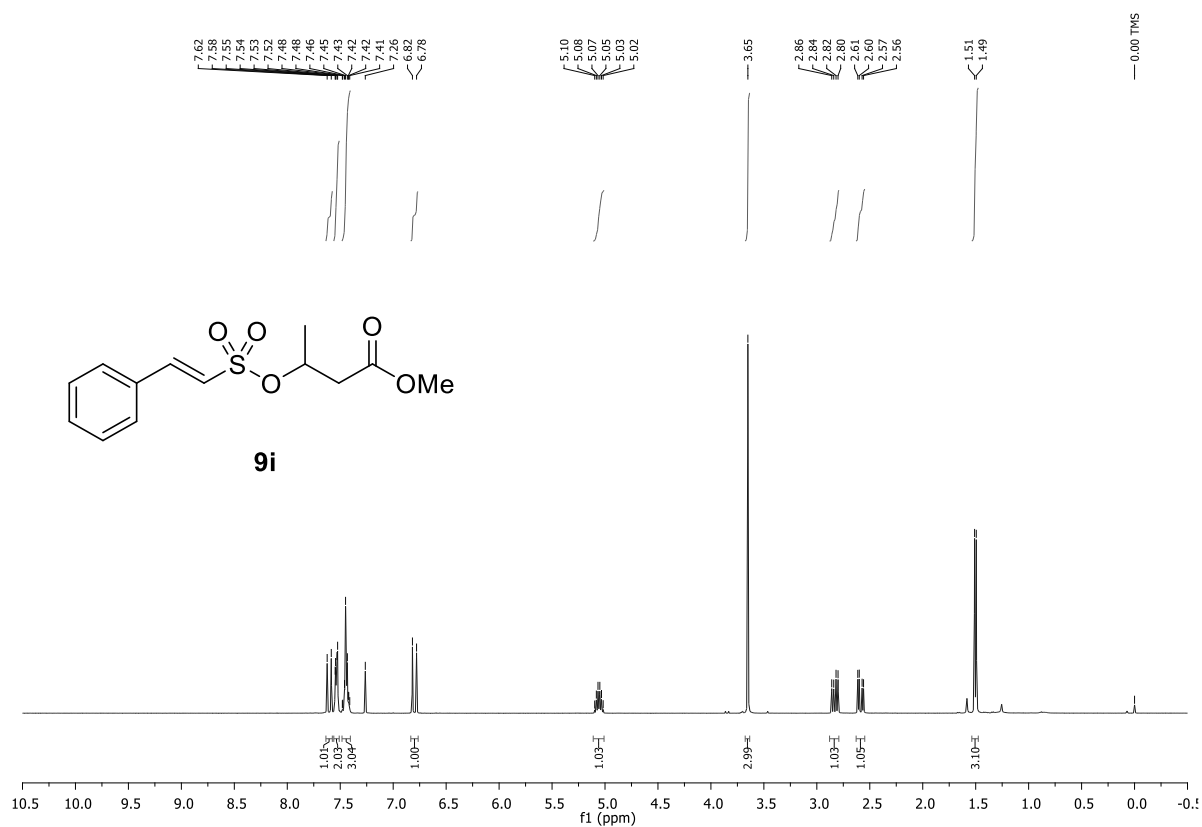


Figure S48: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9i**.

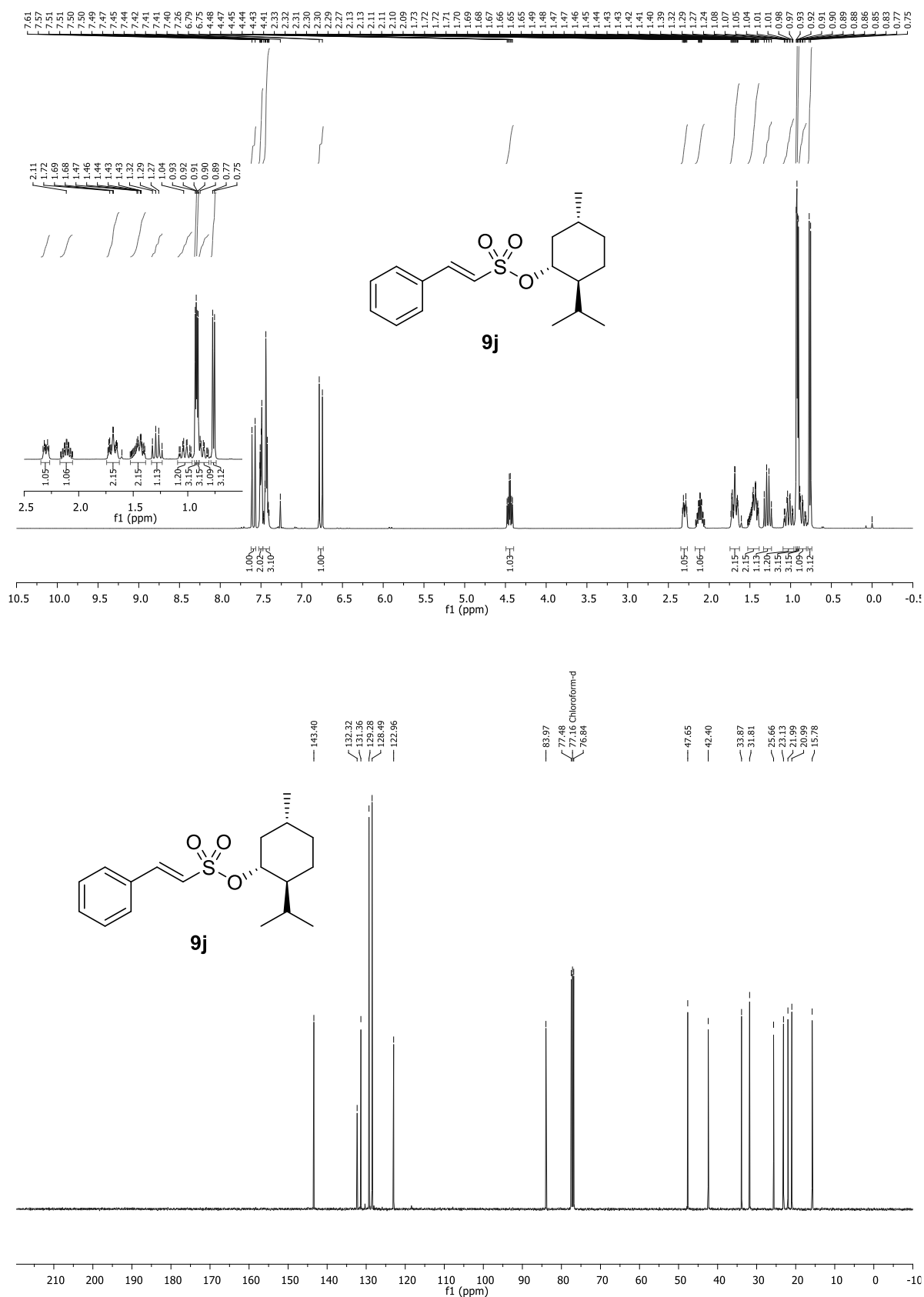
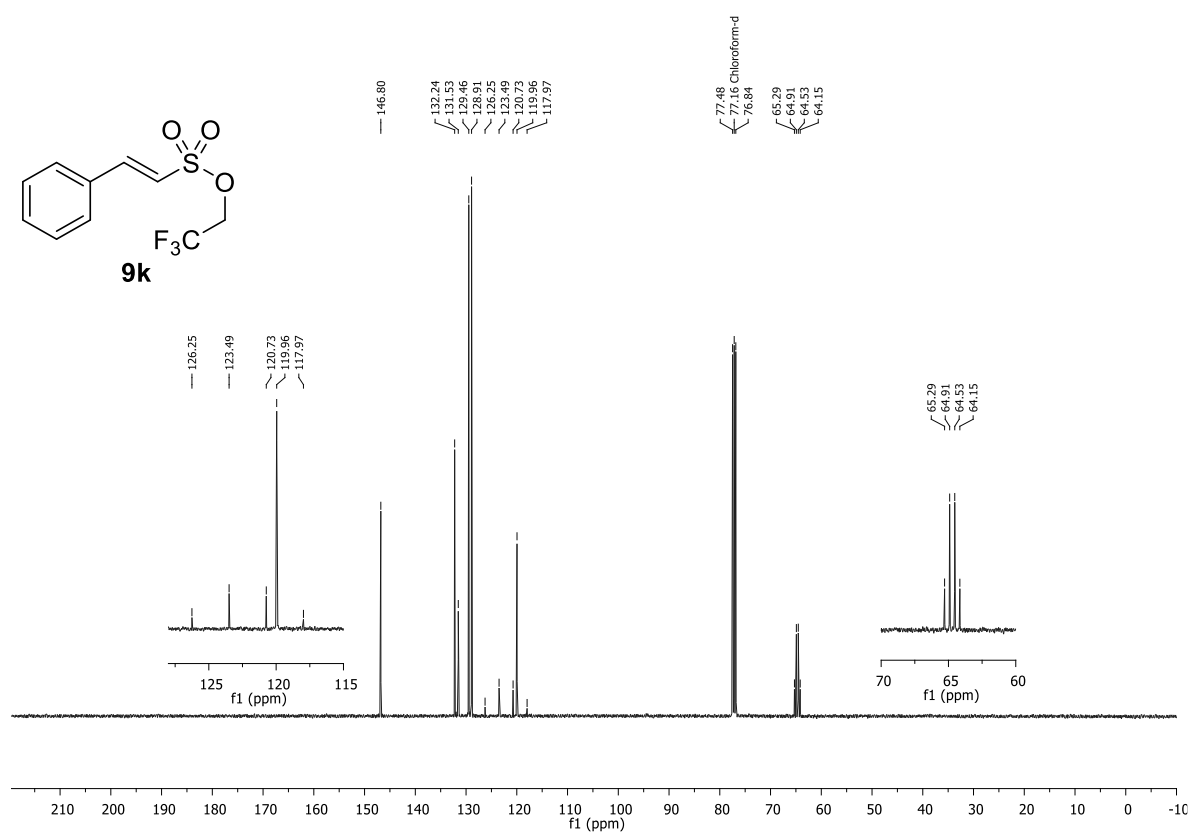
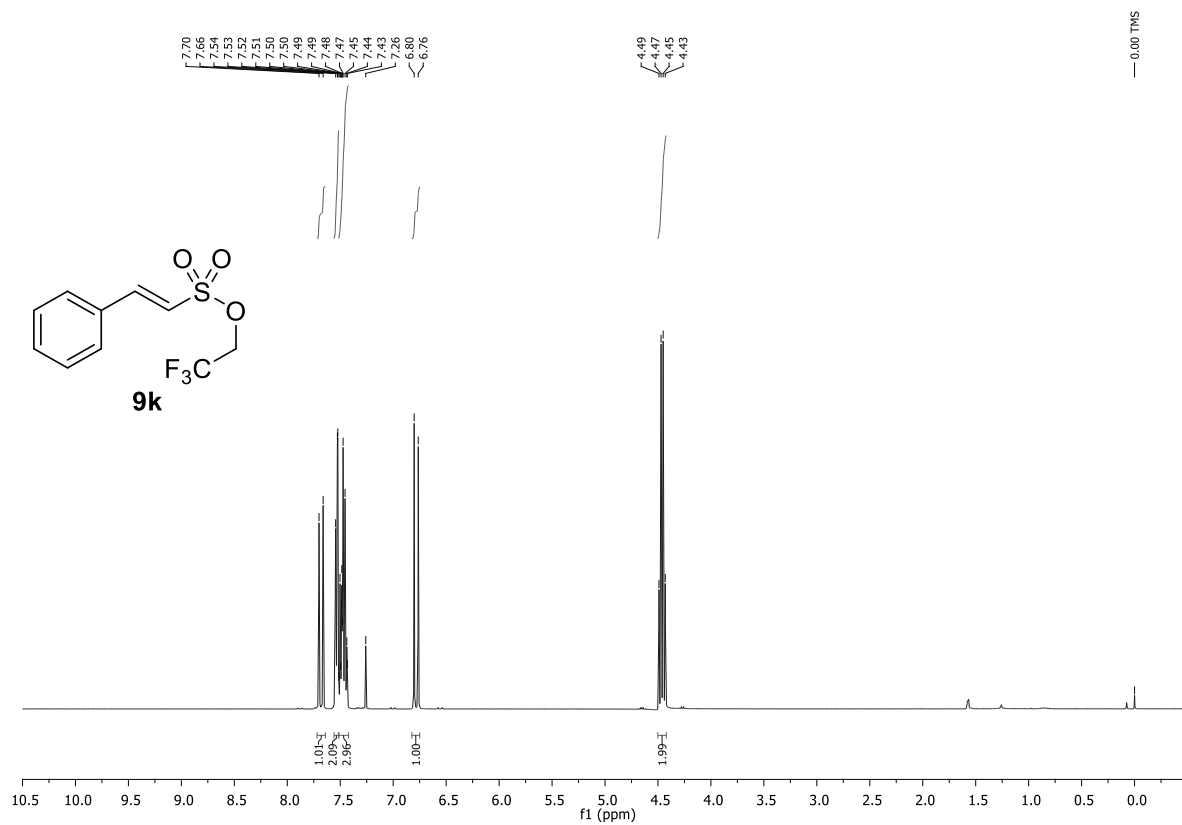


Figure S49: ¹H (CDCl₃, 400 MHz) and ¹³C{¹H} (CDCl₃, 101 MHz) NMR Spectrum of **9j**.



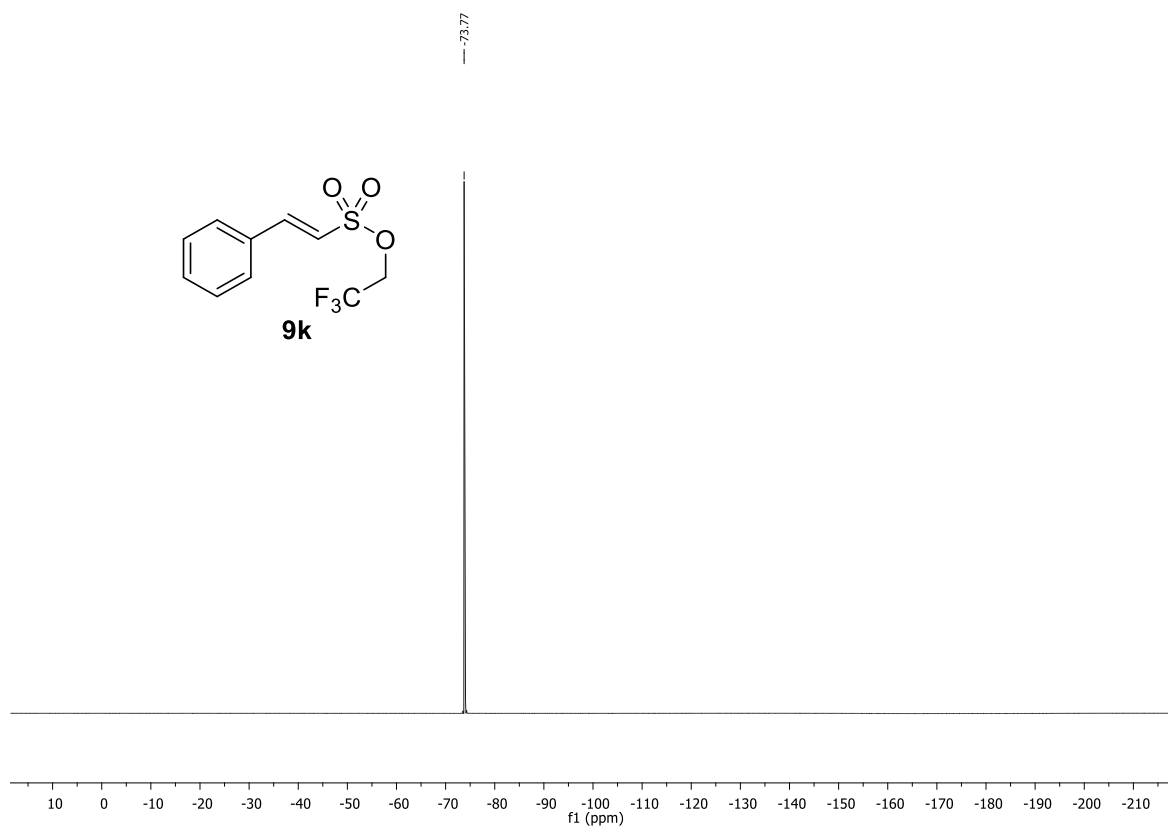
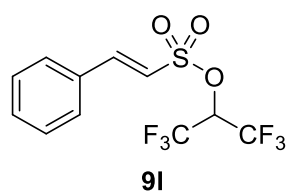
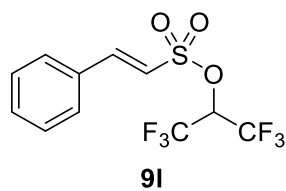


Figure S50: ¹H (CDCl₃, 400 MHz), ¹³C{¹H} (CDCl₃, 101 MHz), and ¹⁹F{¹H} (CDCl₃, 376 MHz) NMR Spectrum of **9k**.



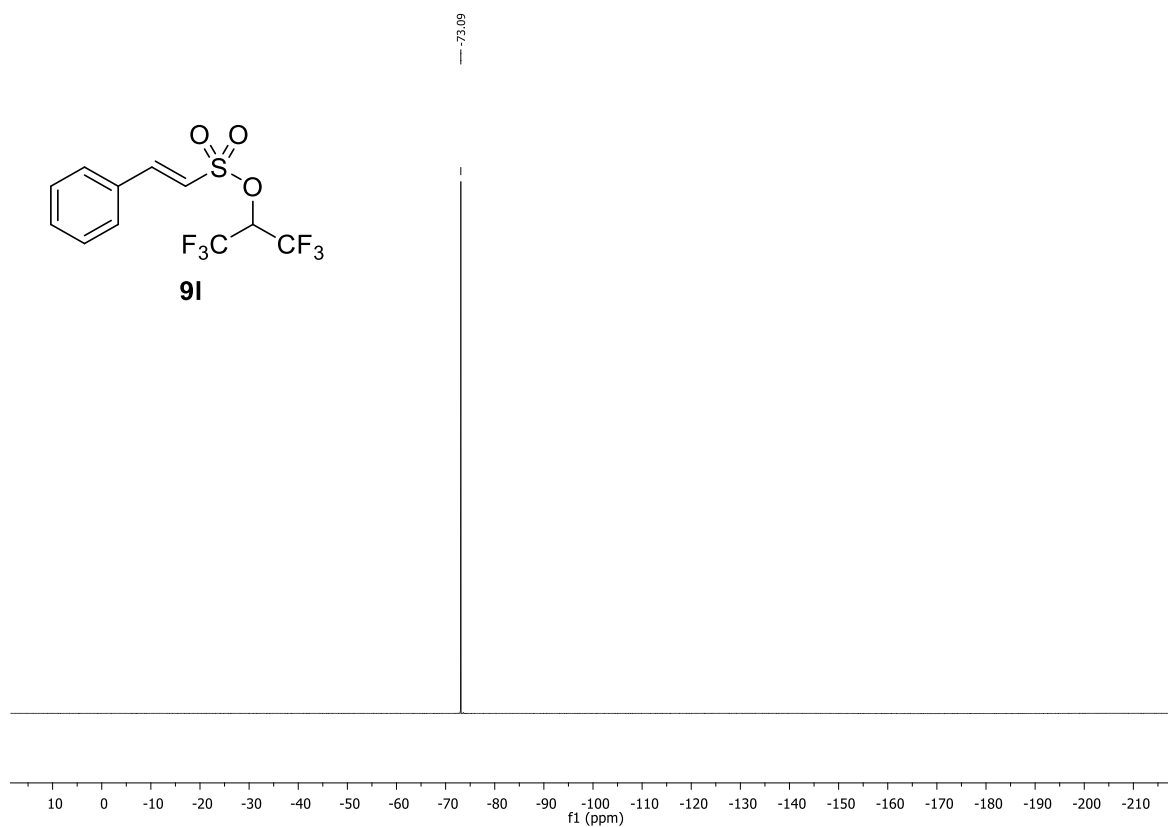


Figure S51: ^1H (CDCl_3 , 400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (CDCl_3 , 101 MHz), and $^{19}\text{F}\{^1\text{H}\}$ (CDCl_3 , 376 MHz) NMR Spectrum of **9l**.

B3 Supporting Information S3: Dehydrative electrosulfonylation of amines

Supporting Information

**Multicomponent Electrosynthesis of Enaminyll Sulfonates
starting from Alkylamines, SO₂ and Alcohols**

Florian A. Breitschaft, Alicia L. Saak, Christian Krumbiegel, Aloisio de A. Bartolomeu, Thomas Weyhermüller and Siegfried R. Waldvogel

Abstract: A electrochemical one-pot synthesis of enaminyll sulfonate esters was established, featuring a quasi-divided cell under constant current conditions. The multicomponent reaction utilizes simple and readily available alkylamines, easy-to-use stock solution of SO₂ and alcohols. Omission of additional supporting electrolyte through in-situ generated monoalkylsulfite facilitates the down-stream processing. A diverse scope with more than 28 examples and yields up to 85% as well as a 20-fold scale-up reaction prove the feasibility of this novel protocol.

DOI: 10.1021/acs.orglett.4c04746

1 General aspects

1.1 General Information

If not stated otherwise, all reactions were performed under ambient conditions and chemicals in analytical grade were used as purchased without further purification. Cyclohexane and ethyl acetate used for column chromatography were purchased in HPLC-grade. Acetonitrile was commercially obtained in LCMS-grade and stored over molecular sieves (3 Å) prior use.

1.2 Instruments and Analytical Methods

Chromatography

Thin layer chromatography for reaction monitoring was performed using DC Kieselgel 60 F₂₅₄ on aluminium plates (*Merck KGaA*, Darmstadt, Germany). An UV lamp ($\lambda = 254$ nm, UV-4 S/L, *Herolab GmbH Laborgeräte*, Wiesloch, Germany) and potassium permanganate solution (3 g KMnO₄, 20 g K₂CO₃, 5 mL NaOH (5%), 300 mL H₂O) were used for substance detection. Preparative column chromatography was performed on prepacked puriFlash™ silica columns (15 μ m or 30 μ m, PF-15SIHP-F0012, PF-15SIHP-F0025, PF-25SIHC-F0025, PF-15SIHP-F0040, PF-25SIHC-F0120 *Interchim*, Montlucon Cedex, France) using a puriFlash™-System (puriFlash™ XS520Plus, *Interchim*, Montlucon Cedex, France) with an integrated UV detector.

High Resolution Mass Spectrometry

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).

X-Ray Crystallography

Measurement of the single-crystal structure was carried out on a Bruker D8 Venture Kappa Diffractometer equipped with I μ S3 diamond Mo-source (50 kV, 1.4 mA; Mo-K-alpha radiation, $\lambda = 0.71073$ Å), Oxford cryostream 800 cooler, Incoatec Helios mirror optics and a Photon III detector.

Gas Chromatography (GC)

Analysis of crude reaction mixtures and purified products were performed using a GC-2030 (*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 μ m thickness. Hydrogen was used as carrier gas with a constant velocity of 40 cm/s. Measurements were performed at an injector temperature of 270 °C and a detector temperature of 320 °C, starting 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/min (method: 2_medium, total program time: 20.0 min).

Gas Chromatography coupled with Mass Spectrometry (GC/MS)

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 analyzer. 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 μ m thickness. Helium was used as carrier gas with a constant velocity of 30 cm/s. 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/min (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

¹H NMR and ¹³C{¹H} NMR spectra were recorded at 25 °C on a Bruker AVANCE III HD 500 MHz NMR spectrometer with a Bruker Prodigy probe (*Bruker BioSpin GmbH*, Rheinstetten, Germany) using CDCl₃ or CD₃CN as deuterated solvent. All chemical shifts are reported in δ -scale as parts per million [ppm] (multiplicity, coupling constant J, number of protons), relative to the solvent residual peaks as the internal standard. Coupling constants J are given in Hertz [Hz]. Besides ¹H and ¹³C experiments, the 2D techniques ¹H,¹H-COSY, ¹H,¹³C-HSQC, ¹H,¹³C-HMBC and ¹H,¹H-NOESY were used assisting to assign the signals. Determination of stereochemistry (*E/Z*-isomerism) was done using ¹H,¹H-³J vicinal coupling, ¹H,¹H-NOESY or ³J_{C,H}-HMBC-Coupling. The following abbreviations were used to describe the signals: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), sext (sextet), hept (heptet), m (multiplet), br (broad signal). The spectra obtained were evaluated with MestReNova 14 (*Mestrelab Research S.L.*, Spain).

Cyclic Voltammetry (CV) Measurements

Cyclic voltammetry was performed using a Metrohm 663 VA Stand equipped with an Autolab type III potentiostat (*Metrohm AG*, Herisau, Switzerland). WE: glassy carbon electrode ($d = 2$ mm); CE: glassy carbon rod; RE: Ag/AgNO₃; Scan

rate $v = 100$ mV/s. Electrolyte: 0.1 m Bu₄NBF₄ in acetonitrile; $c(\text{substrate}) = 10$ mmol/L; $c(\text{SO}_2) = 40$ mmol/L; $V = 5$ mL. All solutions except for the ones containing SO₂ have been deoxygenated by bubbling with argon for 10 min prior to measurement. Electrodes have been thoroughly rinsed before and after each measurement with acetone and acetonitrile. The glassy carbon working electrode was polished with alumina paste (1 μm followed by 0.1 μm) and sonicated for 5 min each in between measurements. All data is displayed against the half-wave potential of ferrocene/ferrocenium redox couple (FcH/FcH⁺; -0.10 V vs. Ag/AgNO₃) as internal reference. Oxidation potentials are marked and displayed as the half-wave potential of the respective peak.

1.3 Electrochemical Setup

Galvanostat

Electrochemical reactions were carried out using a multichannel galvanostat HMP4040 (Rohde & Schwarz, München, Germany). The cells used for screening or large-scale batch reactions are described below (Figure S1).

Screening and small-scale batch reactions

Screening reactions were carried out in undivided/quasi-divided Teflon™ cells with a volume of 5 mL equipped with two electrodes (interelectrode gap: 6 mm) and a round, cross-shaped stirring bar. The described system is commercially available as IKA Screening System Package (IKA™ Werke GmbH & Co. KG, Staufen, Germany).

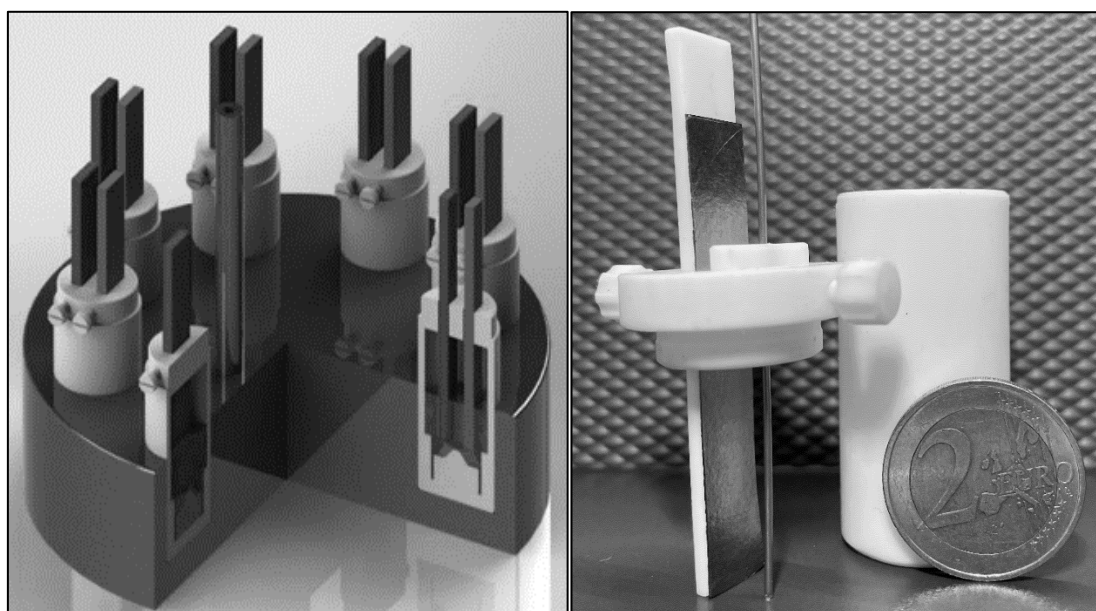


Figure S1: Undivided screening setup as available through IKA¹ (left) and quasi-divided (right) cell with Sigraflex™ anode and stainless-steel wire cathode. Diameter of the coin 25.75 mm.

The screening was carried out using various electrode materials (7 cm × 1 cm × 0.3 cm). Graphite electrodes were sanded using 600 grit followed by 1000 grit sandpaper and cleaned with acetonitrile prior to use. BDD electrodes were electrochemically treated ($j = 50$ mA/cm²) in 20% (v/v) sulfuric acid for 10 min before use. Sigraflex™, an inexpensive graphite foil that is frequently used for sealing or heat transfer purposes,² was cut into electrodes (7 cm × 1 cm × 0.02 cm) and pretreated in the corresponding solvent for at least 2 h prior to use and fixed to PTFE supports. The anodes were immersed 1.8 cm (planar cathode) or 1.6 cm (wire cathode) into the electrolyte. This resulted in a geometric active electrode area of 1.8 cm² or 1.6 cm² used for electrolysis. The stainless-steel wire ($d = 0.1$ cm; $l = 7$ cm) was fixated using an inhouse-made PTFE adapter.

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

Entry	Electrode Material	Specification	Supplier
1	Boron-doped diamond	15 μm boron-doped diamond on silicon support	CONDIAS GmbH, Itzehoe, Germany
2	Glassy Carbon	Sigradur G	HTW, Thierhaupten, Germany
3	Graphite	highly isostatic, V2100	SGL Carbon, Bonn, Germany
4	Graphite foil (Sigraflex™)	F02012Z	SGL Carbon, Meitingen, Germany
5	Stainless-steel	1.4571	various suppliers (metal traders)

Scale-up Cell

The scale-up experiment was performed in a jacketed undivided glass cell with a volume of 100 mL equipped with a PTFE stopper and sleeve, electrodes (interelectrode gap: 13 mm), electrode holders and a cross-shaped stirring bar. The cell is commercially available via *HWS Labortechnik* (Mainz, Germany). The electrolysis was conducted using a TDK-Lambda Z+ series (*TDK-Lambda UK Limited*, Devon, United Kingdom) as power source. The Sigraflex™ anode was held in place using a PTFE support frame. Its dimensions (excluding the area covered by the frame) were 6 cm × 2 cm × 0.02 cm and was fully submerged into the solution. This resulted in an active electrode area of 12 cm². As cathode, a stainless-steel wire (l = 7 cm, d = 0.1 cm) was used and fixated in front of the middle of the anode by a PTFE support frame. The stoppers and electrode holders are available through Sigma-Aldrich within the SynLectro™ series.



Figure S2: 100-mL quasi-divided glass cell with Sigraflex™ anode and stainless-steel wire cathode, electrode holders and stirring bar used for the scale-up experiment. Diameter of the coin 25.75 mm.

2 Experimental Procedures

2.1 Preparation of the SO₂ stock solution

In a gas-inlet apparatus connected to a washing bottle filled with aq. NaOH (20% v/v) with Woulff bottles placed before and after the washing bottle, acetonitrile (350 mL, anhydrous) was enriched with SO₂ at 0 °C under constant stirring for 15 minutes. After usage, the gas-inlet apparatus was flushed with Argon and molecular sieve (3 Å) was added to the obtained solution. The stock solution was sealed by a PTFE septum and stored in a fridge at 7 °C.

2.2 Determination of the SO₂ concentration of the stock solution

The SO₂ molarity was determined according to the principles of the “Excess Iodine Method” described by Ferguson.³ To a solution of I₂ (1.27 g, 5.00 mmol) and KI (2.20 g, 13.3 mmol) in H₂O (100 mL) was slowly added the freshly prepared SO₂ stock solution (1 mL). The solution was then back titrated with a freshly prepared solution of Na₂S₂O₃ × 5 H₂O (aq., 0.2 mol/L) as titrant. After full reduction of the iodine, the concentration of SO₂ (mostly 3–5 mol/L) was calculated according to the previously reduced iodine by aq. SO₂. The titration was conducted three successive times, and the molarity of the stock solution was determined by averaging the three measurements.

2.3 General protocol for the synthesis of alkyl enaminylsulfonates (GP1)

The reactions were carried out using the undivided Teflon™ cells with a pretreated Sigraflex™ anode and a stainless-steel wire as a cathode as described in the section before.

Electrolyte: An undivided Teflon™ cell was charged with an alcohol **2** (2.60 mmol, 5.2 eq.), 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU, 685 mg, 672 μ L, 4.50 mmol, 9 eq.), SO₂ stock solution (7.8 eq., 1–2 mL, depending on the concentration of SO₂ in the stock solution used) and diluted with acetonitrile (anhydrous) so that a total volume of 5 mL was achieved. The cell was additionally loaded with a tertiary alkyl amine substrate **1** (500 μ mol, 1 eq., 0.1 M).

The lid including a prefixed Sigraflex™ anode and a stainless-steel wire cathode was attached to the cell, the amperage was set accordingly so that a current density of 67.5 mA/cm² was reached (108 mA with the setup described herein) and the amount of applied charge was set to 11.5 *F* (555 C using 500 μ mol of starting material). The electrolysis was conducted at room temperature under constant stirring (400 rpm) for ca. 1 h 25 min. After completion of the electrolysis the reaction mixture was transferred to a beaker and the cell as well as the electrodes were rinsed with acetonitrile (3 x 2 mL). The combined solutions were filtered over a short layer of silica (ca. 2 cm) using acetonitrile and the solvent was removed under reduced pressure. The crude product (approx. 250 mg) was loaded onto Celite™ (diatomaceous earth) using dichloromethane and purified by automated flash column chromatography (cyclohexane/ethyl acetate) with an appropriate gradient. Detection of the product was achieved by monitoring the UV-trace at 254 nm.

2.4 General protocol for the optimization of reaction conditions (GP2)

The reactions were carried out using the undivided Teflon™ cells with a PTFE lid including the anode and a stainless-steel cathode as described in the section before.

Electrolyte: An undivided Teflon™ cell was charged with neopentyl alcohol (**2a**), an organic base, SO₂ stock solution (in acetonitrile, anhydrous) and diluted with acetonitrile (anhydrous) so that a total volume of 5 mL was achieved. The cell was additionally loaded with *N,N*-diisopropylamine (DIPEA, **1a**, 64.6 mg, 87 μ L, 500 μ mol, 1 eq., 0.1 M) as a substrate.

The lid including the electrodes was attached to the cell, the amperage and amount of applied charge were set to the desired values and the electrolysis was conducted at room temperature under constant stirring (400 rpm). After completion, 1,3,5-trimethoxybenzene (1,3,5-TMB, 50 mg) was added to the reaction mixture as an internal standard. The solution was stirred for 5 min at room temperature and an aliquot (ca. 0.5 mL) was taken for qNMR measurement (¹H NMR, 400 MHz). The yield was calculated using the two alkenyl-protons of product **3a** (Figure S3).

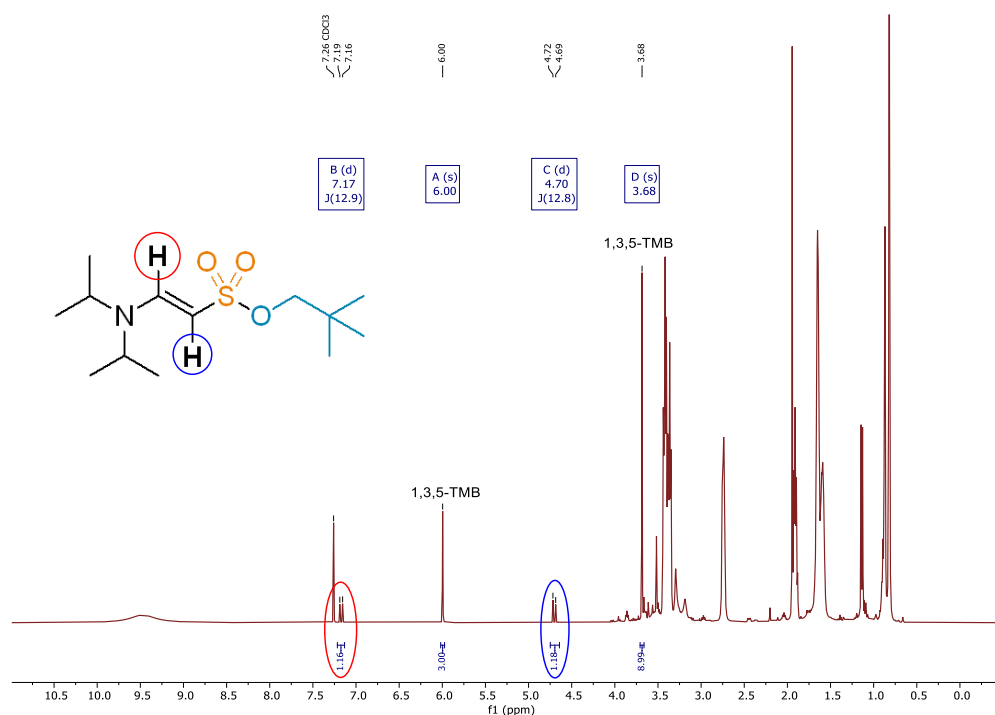


Figure S3: Typical ¹H NMR spectrum of a reaction mixture used for quantification of product **3a**.

2.5 Protocol for the large-scale synthesis

The reactions were carried out using the undivided glass cell with a Sigraflex™ anode and a stainless-steel wire as a cathode as described in the section above.

Neopentyl (E)-2-(2,2,6,6-tetramethyl-piperidinyl)ethene sulfonate (3a)

Electrolyte: The glass cell was charged with *N*-ethyl-2,2,6,6-tetramethylpiperidine (**4a**, 1.69 g, 10.0 mmol, 1 eq.), neopentanol (**2a**, 4.58 g, 52.0 mmol, 5.2 eq.), 1,8-diaza-bicyclo[5.4.0]undec-7-ene (13.7 g, 13.4 mL, 90.0 mmol, 9 eq.), SO₂ stock solution (2.95 mol/L, 26.4 mL, 78.0 mmol of SO₂, 7.8 eq.) and diluted with acetonitrile (67.3 mL, anhydrous) so that a total volume of 100 mL was achieved.

The stopper including the electrodes and electrode holders was attached to the cell and connected to the power source. The amperage was set accordingly so that a current density of 67.5 mA/cm² was reached (810 mA with the setup described herein) and the amount of applied charge was set to 11.5 *F* (corresponds to 11096 C when using 10.0 mmol of starting material). The electrolysis was conducted at 23° C with active temperature control through the help of a cryostat and under constant stirring (700 rpm) for ca. 3 h 48 min. After completion of the electrolysis, the reaction mixture was transferred to a flask, the cell was thoroughly rinsed with acetonitrile and the solvent was removed under reduced pressure. The remaining mixture was filtered over a layer of silica (ca. 5 cm) using ethyl acetate (ca. 400 mL). The crude (ca. 10 g) was loaded onto Celite™ (diatomaceous earth) using dichloromethane and purified by automated flash column chromatography (cyclohexane/ethyl acetate = 98/2 → 70/30). The desired product neopentyl (E)-2-(2,2,6,6-tetramethyl-piperidinyl)ethene sulfonate (**3a**, 2.42 g, 7.62 mmol, 76%) was obtained as a colorless solid.

Spectroscopic data of the isolated compound matched the one obtained from the small-scale reaction.

Note: During the reaction, extensive bubble formation was observed on the cathode. The gas is believed to be H₂ originating from the degradation of solvent or the reduction of protonated base. An ¹H NMR yield of 84% was calculated by addition of 1,3,5-trimethoxybenzene (508.6 mg) as internal standard to the reaction mixture upon removal from the cell. After filtration over silica, a second ¹H NMR sample was taken and a yield of 83% was calculated.

Neopentyl (E)-2-(*N*-methylacetamido)ethene sulfonate (3n)

Electrolyte: The glass cell was charged with *N*-methyl-*N*-vinylacetamide (991 mg, 1.03 mL, 10.0 mmol, 1 eq.), neopentanol (**2a**, 4.58 g, 52.0 mmol, 5.2 eq.), 1,8-diaza-bicyclo[5.4.0]undec-7-ene (13.7 g, 13.4 mL, 90.0 mmol, 9 eq.), SO₂ stock solution (4.15 mol/L, 18.8 mL, 78.0 mmol of SO₂, 7.8 eq.) and diluted with acetonitrile (75.6 mL, anhydrous) so that a total volume of 100 mL was achieved.

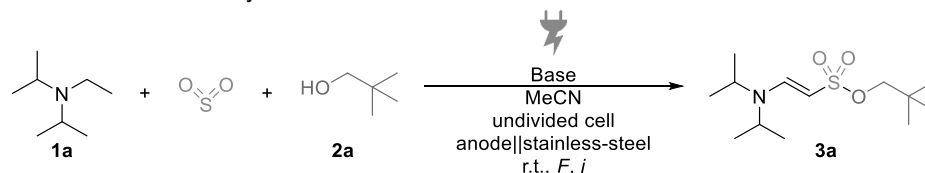
The stopper including the electrodes and electrode holders was attached to the cell and connected to the power source. The amperage was set accordingly so that a current density of 67.5 mA/cm² was reached (810 mA with the setup described herein) and the amount of applied charge was set to 5.75 *F* (corresponds to 5548 C when using 10.0 mmol of starting material). The electrolysis was conducted at 23° C with active temperature control through the help of a cryostat and under constant stirring (700 rpm) for ca. 1 h 54 min. After completion of the electrolysis, the reaction mixture was transferred to a flask, the cell was thoroughly rinsed with acetonitrile and the solvent was removed under reduced pressure. The remaining mixture was filtered over a layer of silica (ca. 5 cm) using ethyl acetate (ca. 400 mL). The crude (ca. 10 g) was loaded onto Celite™ (diatomaceous earth) using dichloromethane and purified by automated flash column chromatography (cyclohexane/ethyl acetate = 96/4 → 60/40). The desired product neopentyl (E)-2-(*N*-methylacetamido)ethene sulfonate (**3n**, 2.08 g, 8.35 mmol, 84 %) was obtained as a colorless solid.

Spectroscopic data of the isolated compound matched the one obtained from the small-scale reaction.

Note: During the reaction, extensive bubble formation was observed on the cathode. The gas is believed to be H₂ originating from the degradation of solvent or the reduction of protonated base. An ¹H NMR yield of 51% was calculated by addition of 1,3,5-trimethoxybenzene (456.5 mg) as internal standard to the reaction mixture upon removal from the cell. After filtration over silica, a second ¹H NMR sample was taken and a yield of 59% was calculated. The difference in NMR- to isolated yield is probably due to insufficient relaxation time during ¹H NMR measurement.

3 Optimization

Optimization of the conditions was carried out by using linear screening for the discrete and design-of-experiment-studies (DoE) for continuous parameters. *N,N*-diisopropylamine (**1a**, DIPEA) and neopentyl alcohol (**2a**) were used as substrates according to the procedure described in GP2. Neopentyl alcohol was chosen due to the enhanced stability of the respective sulfonate ester.⁴ Yields were determined by ¹H NMR spectroscopy via the addition of 1,3,5-trimethoxybenzene (50 mg) as an internal standard after the end of electrolysis.



Initial experiments were carried out in an undivided Teflon™ cell with a planar graphite anode and a planar stainless-steel cathode (Table S2, Entry 1 & 2), with 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU) as a supporting base. When the geometry of the cathode was changed to a thin wire (d = 0.1 cm), yield improved significantly (Entry 3).

Table S2: First experiments.

Entry	Neopentanol [eq.]	SO ₂ [eq.]	DBU [eq.]	Cathode	Yield (¹ H NMR)
1	2.0	3.0	5.0	Stainless-steel plate	24%
2	4.0	6.0	8.0	Stainless-steel plate	41%
3	4.0	6.0	8.0	Stainless-steel wire	50%

Conditions (GP2): *N,N*-diisopropylamine (500 μmol, 1 eq., 0.1 M), SO₂ stock solution (3–6 eq.), neopentyl alcohol (2–4 eq.), DBU (5–8 eq.), MeCN, graphite||stainless-steel, 40 mA/cm², 10 F, r.t., 400 rpm.

Next, several carbon-based anode materials were tested (Table S3). Sigraflex™ (Entry 4), an inexpensive graphite foil, gave the best results. Supposedly, this is due to the materials improved porosity, compared to a standard isostatic graphite electrode. Screening was continued with this material.

Table S3: Screening of anode materials.

Entry	Anode material	Yield (¹ H NMR)
1	Graphite	50%
2	Glassy Carbon	16%
3	Boron-doped diamond	18%
4	Sigraflex™	55%

Conditions (GP2): *N,N*-diisopropylamine (500 μmol, 1 eq., 0.1 M), SO₂ stock solution (6 eq.), neopentyl alcohol (4 eq.), DBU (8 eq.), MeCN, anode||stainless-steel wire, 40 mA/cm², 10 F, r.t., 400 rpm.

Screening of different bases (Table S4) showed no improvement to the previously used conditions, so the optimization was continued with 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU, Entry 1).

Table S4: Screening of bases.

Entry	Base	Yield (¹ H NMR)
1	1,8-Diaza-bicyclo[5.4.0]undec-7-ene (DBU)	55%
2	1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)	51%
3	1,1,3,3-Tetramethylguanidine (TMG)	49%
4	2- <i>tert</i> -Butyl-1,1,3,3-tetramethylguanidine (^t BuTMG, Bartons Base)	55%
5	2,4,6-Collidine	0%
6	2,6-Lutidine	0%
7	7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-en (MeTBD)	49%

Conditions (GP2): *N,N*-diisopropylamine (500 μmol, 1 eq., 0.1 M), SO₂ stock solution (6 eq.), neopentyl alcohol (4 eq.),

base (8 eq.), MeCN, Sigraflex™||stainless-steel wire, 40 mA/cm², 10 F, r.t., 400 rpm.

To improve the yield further, a design-of-experiment study was conducted (2⁴⁻¹-design plan, duplicates for each experiment, triplicate for the center point (CP), randomized order of experiments). The following parameters were investigated in their respective ranges:

- Amount of neopentyl alcohol: 2–5 eq.
- Amount of base: 5–10 eq.
- Current density *j*: 25–75 mA/cm².
- Amount of applied charge *Q*: 5–10 F.

To maintain an excess of SO₂, its amount was adjusted according to the stoichiometric equivalents of neopentyl alcohol, with the molar ratio of SO₂ to neopentyl alcohol set at 1.5:1 (eq. [SO₂] = 1.5 × eq. [ROH]). Since initial data evaluation revealed curvature of the model, additional star point (SP) experiments were added. The experimental results are summarized in Table S5.

Table S5: Design-of-experiment study.

Entry	Type	Neopentyl alcohol [eq.]	DBU [eq.]	Q [F]	<i>j</i> [mA/cm ²]	Yield (¹ H NMR)
1	-	5.0	10	10	75	69%
2	CP	3.5	7.5	7.5	50	56%
3	-	5	5	5	75	38%
4	-	2	10	5	75	28%
5	-	2	5	5	25	38%
6	-	2	5	5	25	36%
7	-	2	10	5	75	29%
8	-	2	10	5	25	37%
9	-	2	5	10	75	53%
10	-	2	10	10	25	23%
11	CP	3.5	7.5	7.5	50	59%
12	-	5	5	10	25	44%
13	-	2	5	10	25	44%
14	-	5	5	10	25	51%
15	-	2	10	10	25	22%
16	CP	3.5	7.5	7.5	50	58%
17	-	5	5	5	75	39%
18	-	5	10	5	25	37%
19	-	5	10	10	75	60%
20	SP	1.1	7.5	7.5	50	23%
21	SP	5.9	7.5	7.5	50	46%
22	SP	3.5	3.5	7.5	50	51%
23	SP	3.5	11.5	7.5	50	37%
24	SP	3.5	7.5	3.5	50	35%
25	SP	3.5	7.5	11.5	50	56%
26	SP	3.5	7.5	7.5	10	34%
27	SP	3.5	7.5	7.5	90	53%

Conditions (GP2): *N,N*-diisopropylamine (500 μmol, 1 eq., 0.1 M), SO₂ stock solution (1.5 × eq. [neopentyl alcohol]), neopentyl alcohol (1.1–5.9 eq.), DBU (3.5–11.5 eq.), MeCN, Sigraflex™||stainless-steel wire, 10–90 mA/cm², 3.5–11.5 F, r.t., 400 rpm.

The following analyses were conducted, demonstrating adequate statistical significance to support the validity of the DoE:

Table S6: Statistical evaluation of the DoE study.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	12	4005.63	333.803	31.91	0.000
Blocks	1	119.13	119.133	11.39	0.005
Linear	4	2236.23	559.057	53.45	0.000
ROH [eq.]	1	912.19	912.189	87.21	0.000
DBU [eq.]	1	172.73	172.735	16.51	0.001
Q [F]	1	654.82	654.818	62.60	0.000
j [mA/cm ²]	1	496.48	496.485	47.47	0.000
Square	4	893.87	223.467	21.36	0.000
ROH [eq.] * ROH [eq.]	1	627.69	627.685	60.01	0.000
DBU [eq.] * DBU [eq.]	1	146.20	146.200	13.98	0.002
Q [F] * Q [F]	1	100.90	100.895	9.65	0.008
j [mA/cm ²] * j [mA/cm ²]	1	163.16	163.164	15.60	0.001
2-Way Interactions	3	865.50	288.500	27.58	0.000
ROH [eq.] * DBU [eq.]	1	625.00	625.000	59.75	0.000
ROH [eq.] * Q [F]	1	240.25	240.250	22.97	0.000
ROH [eq.] * j [mA/cm ²]	1	0.25	0.250	0.02	0.879
Error	14	146.44	10.460		
Lack-of-Fit	4	32.77	8.193	0.72	0.597
Pure Error	10	113.67	11.367		

Table S7: Model summary.

S	R ²	R ² (adj)	R ² (pred)
3.23419	96.47%	93.45%	86.62%

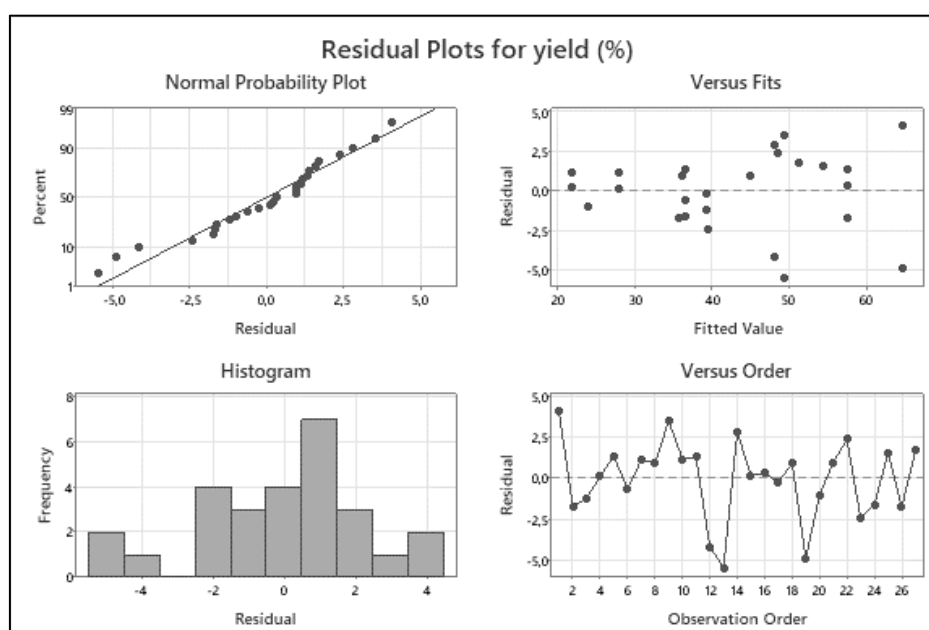


Figure S4: Residual plots.

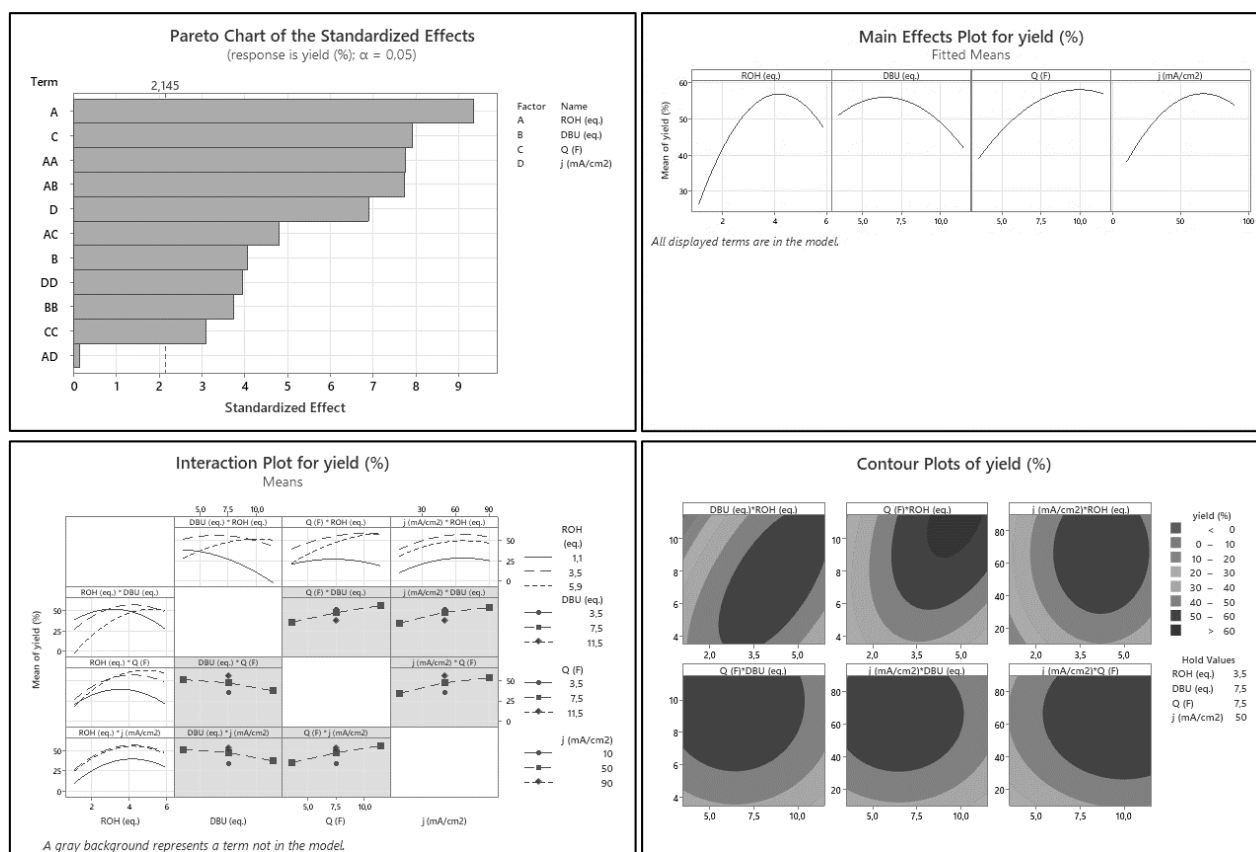


Figure S5: Analysis of main effects and interactions.

Response optimization analysis (Figure S6) determined the following optimal parameter values, with a predicted yield of 65%:

- Amount of neopentyl alcohol: 5.2 eq.
- Amount of base: 9.0 eq.
- Current density j : 67.5 mA/cm²
- Amount of applied charge Q : 11.5 F

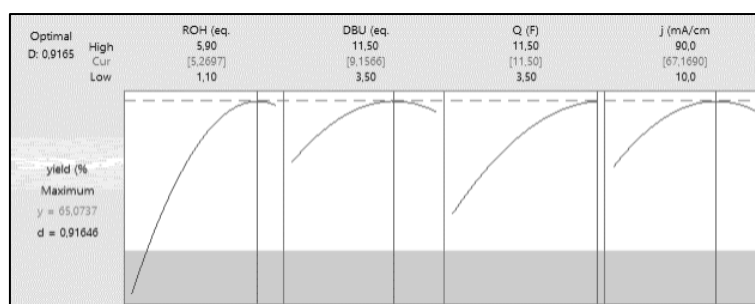


Figure S6: Results of the response optimization.

This prediction was verified in an experiment using the calculated parameter settings (Table S8, Entry 1). Yield was further improved to 70% by pretreating the SigraflexTM anode in acetonitrile for two hours prior to use (Entry 2). This caused some minor swelling, which is believed to improve diffusion of reactants into the porous electrode. The conditions of Table S8, Entry 2 were regarded as optimal and, if not stated otherwise, used in all following experiments.

Table S8: Final reaction conditions.

Entry	Neopentyl alcohol [eq.]	SO ₂ [eq.]	DBU [eq.]	j [mA/cm²]	Q [F]	Yield (1H NMR)
1	5.2	7.8	9.0	67.5	11.5	65%
2	5.2	7.8	9.0	67.5	11.5	70% ^[a]

Conditions (GP2): *N,N*-diisopropylamine (500 μ mol, 1 eq., 0.1 M), SO₂ stock solution (7.8 eq.), neopentyl alcohol (5.2 eq.), DBU (9.0 eq.), MeCN, SigraflexTM||stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t., 400 rpm. ^[a]Pretreating of SigraflexTM electrode in acetonitrile 2 h before usage.

4 Control Experiments

To gain insight into the reaction, some control experiments (Table S9) were performed using the optimized conditions from Table S8, Entry 2:

Table S9: Control experiments.

Entry	Deviation from the standard conditions ^[a]	Yield (¹ H NMR)
1	No electricity; stirred for 1.5 h at room temperature	0%
2	No DBU (0.1 M Bu ₄ NBF ₄ added for conductivity)	0%
3	+ (2,2,6,6-Tetramethylpiperidinyl)oxyl (TEMPO, 3 eq.)	38%
4	+ 2,6-Di-tert-butyl-4-methylphenol (BHT, 3 eq.)	20%

^[a]Conditions (GP2): *N,N*-diisopropylamine (500 μmol, 1 eq., 0.1 M), SO₂ stock solution (7.8 eq.), neopentyl alcohol (5.2 eq.), DBU (9.0 eq.), MeCN, Sigraflex™||stainless-steel wire, 67.5 mA/cm², 11.5 F, r.t., 400 rpm.

In the case of BHT (Table S9, Entry 4), we were able to detect two trapped products *via* GC/MS (EI). They result from the addition of a DIPEA-derived enamine (Figure S7 top) or neopentyl-alcohol-derived sulfinate (Figure S7 bottom) to oxidized BHT, respectively:

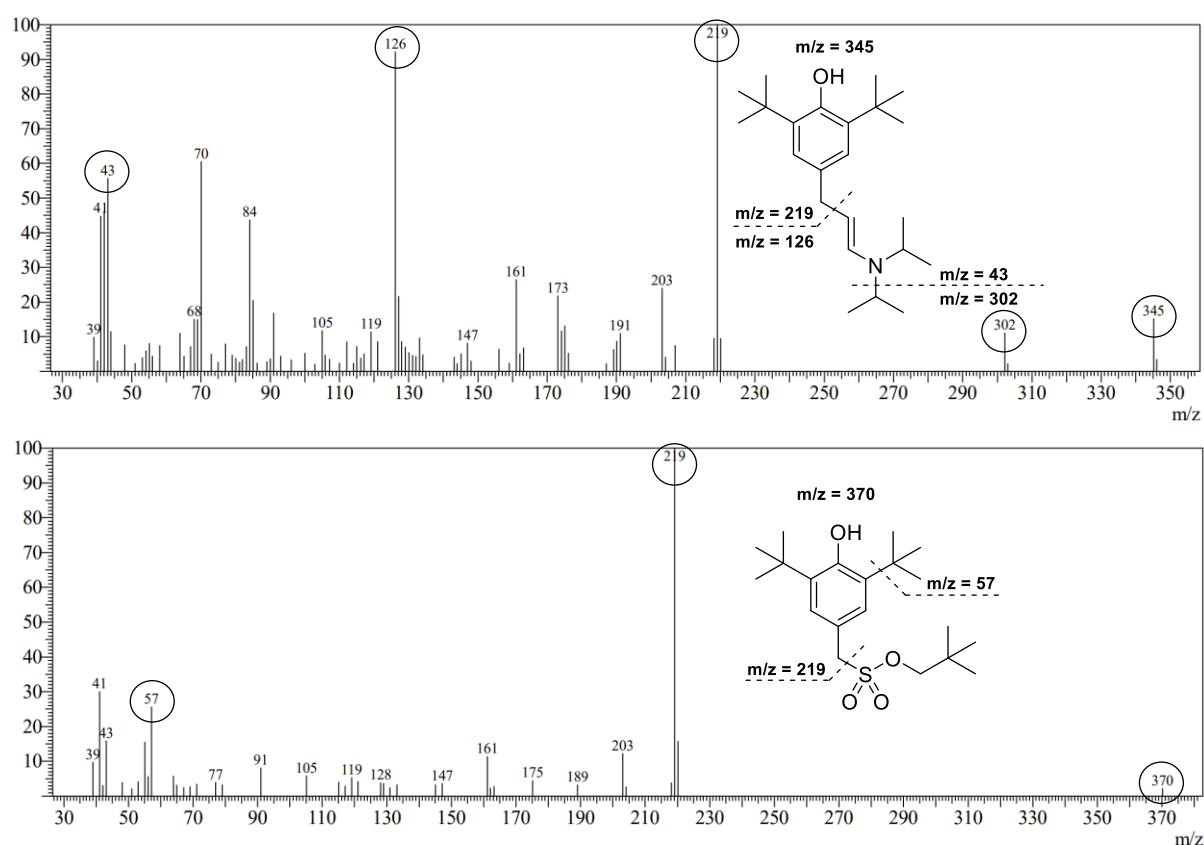


Figure S7: Trapped intermediates using BHT detected in GC/MS (EI).

5 Cyclovoltammetry Studies

For the elucidation of the mechanism cyclic voltammetry was performed (Figure S8). The redox behavior of the starting material DIPEA (**1a**) shows an oxidation wave at 0.66 V vs. FcH/FcH⁺ (red trace). Oxidation of the enaminy sulfonate **3a** is shifted towards a more positive potential (1.25 V vs. FcH/FcH⁺, green trace), therefore overoxidation is prevented. The in-situ generated monoalkylsulfite intermediate **D** (blue trace) shows an oxidation peak at 2.09 V and a second oxidation/ degradation wave at 2.94 V. This clearly shows that during electrolysis, the amine substrate **1a** is initially oxidized, as evidenced by literature reports as well.⁵

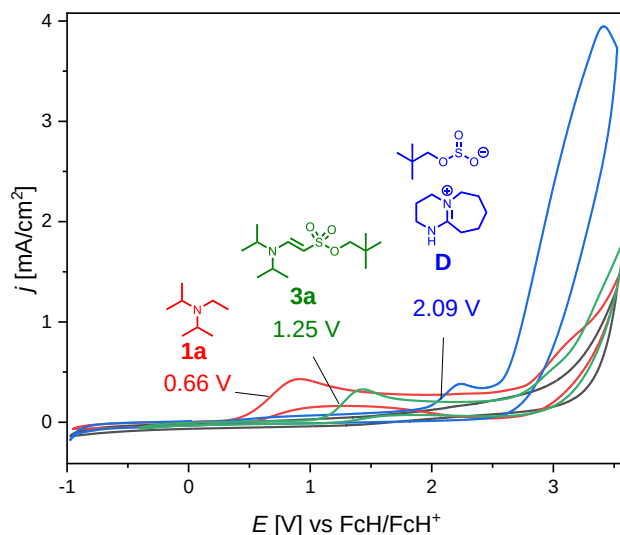


Figure S8: Cyclic voltammogram of *N,N*-diisopropylethylamine (**1a**, red), the corresponding enaminy sulfonate product **3a** (green), the intermediate monoalkylsulfite **D** (blue) and a blank measurement (grey). Measurement conditions: 0.1 M Bu₄NBF₄ in MeCN; c(substrate) = 10 mmol/L; c(SO₂) = 40 mmol/L; v = 100 mV/s. WE: Glassy Carbon, RE: Ag/AgNO₃, CE: Glassy Carbon rod. All measurements were performed at room temperature. Graphic displayed according to IUPAC convention.

The redox potentials regarding the substrate 1-ethyl-2,2,6,6-tetramethylpiperidine (**1d**, Figure S9) shows a similar behavior, where the starting material oxidizes at 0.66 V vs. FcH/FcH⁺ (red trace) and at a lower potential than the corresponding enaminy sulfonate (**3d**, green) at 1.29 V and the in-situ generated monoalkylsulfite intermediate **D** (blue trace) at 2.09 V and 2.94 V, respectively.

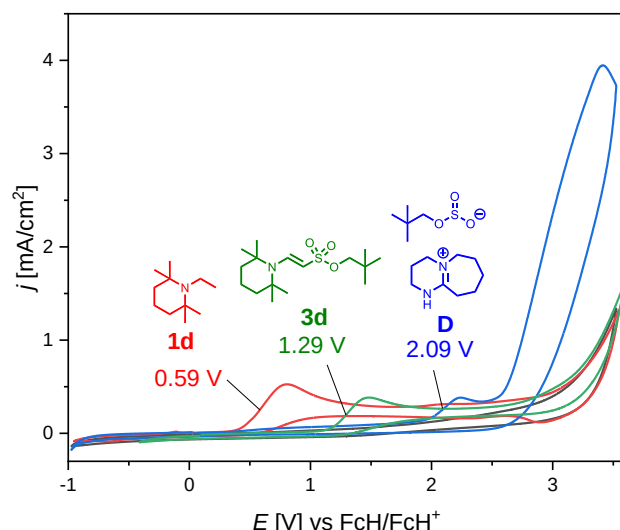


Figure S9: Cyclic voltammogram of 1-ethyl-2,2,6,6-tetramethylpiperidine (**1d**, red), the corresponding enaminy sulfonate product **3d** (green), the intermediate monoalkylsulfite **D** (blue) and a blank measurement (grey). Measurement conditions: 0.1 M Bu₄NBF₄ in MeCN; c(substrate) = 10 mmol/L; c(SO₂) = 40 mmol/L; v = 100 mV/s. WE: Glassy Carbon, RE: Ag/AgNO₃, CE: Glassy Carbon rod. All measurements were performed at room temperature. Graphic displayed according to IUPAC convention.

When a similar intermediate was formed with morpholine instead of neopentyl alcohol,⁶ a gradual oxidation wave starting at ca. 0.93 V was observed (Figure S10). This peak is within the oxidation range of the aforementioned DIPEA. This possible competing oxidation reaction offers an additional explanation for the lower yields observed for the formation of the sulfonamides **5a** and **5b**.

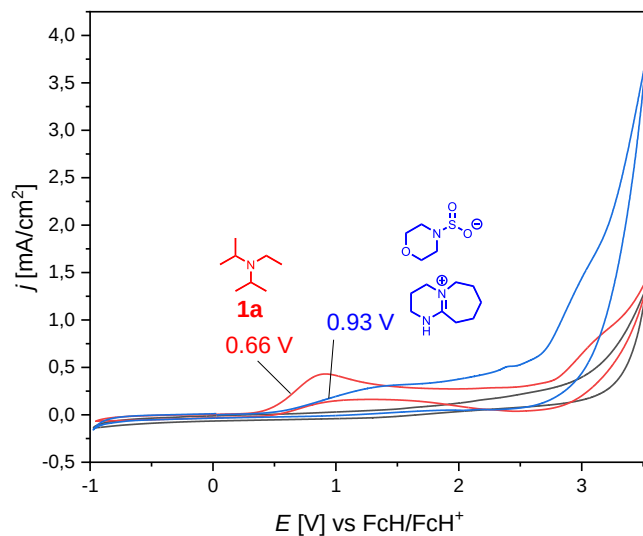
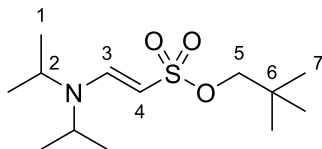


Figure S10: Cyclic voltammogram of *N,N*-diisopropylethylamine (**1a**, red) and a possible intermediate amidosulfinate (blue). Measurement conditions: 0.1 M Bu_4NBF_4 in MeCN; $c(\text{substrate}) = 10 \text{ mmol/L}$; $c(\text{SO}_2) = 40 \text{ mmol/L}$; $v = 100 \text{ mV/s}$. WE: Glassy Carbon, RE: Ag/AgNO_3 , CE: Glassy Carbon rod. All measurements were performed at room temperature. Graphic displayed according to IUPAC convention.

6 Compound Characterization

6.1 Neopentyl (*E*)-2-(diisopropylamino)ethene sulfonate (3a)

According to GP1, *N,N*-diisopropylethylamine (64.4 mg, 87 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 82/18), the desired product (84.3 mg, 304 μ mol, 61%) was obtained as a colorless solid.



¹H NMR (500 MHz, CD₃CN, 25 °C) δ = 7.22 (d, *J* = 12.8 Hz, 1H, 3-*H*), 4.86 (d, *J* = 12.8 Hz, 1H, 4-*H*), 3.69 (brs, 2H, 2-*H*), 3.57 (s, 2H, 5-*H*), 1.18 (d, *J* = 6.7 Hz, 12H, 1-*H*), 0.93 (s, 9H, 7-*H*) ppm.

¹H NMR (500 MHz, CD₃CN, -30 °C) δ = 7.18 (d, *J* = 12.8 Hz, 1H, 3-*H*), 4.84 (d, *J* = 12.8 Hz, 1H, 4-*H*), 3.72 (hept, *J* = 6.7 Hz, 1H, 2-*H*), 3.62 (hept, *J* = 6.7 Hz, 1H, 2'-*H*), 1.15 (dd, *J* = 8.5, 6.7 Hz, 12H, 1-*H*), 0.89 (s, 9H, 7-*H*) ppm.

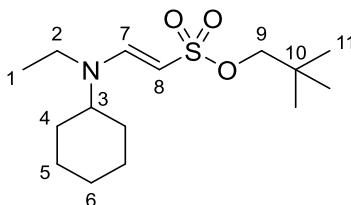
¹³C NMR (126 MHz, CD₃CN) δ = 147.6, 84.8, 78.2, 50.1, 48.8, 32.1, 26.4, 23.4, 19.4 ppm.

HRMS (EI): *m/z* for C₁₃H₂₇NO₃S⁺ [M]⁺: calc.: 277.1706, found: 277.1711.

Note: Hindered rotation around the N-3-bond caused broadened peaks in the ¹H NMR spectrum (3.69 ppm) and doublet peaks in the ¹³C NMR spectrum (50.1 & 48.8 ppm, 26.4 & 23.4 ppm) measured at 25 °C. This could be resolved by lowering the measurement temperature to -30 °C.

6.2 Neopentyl (*E*)-2-(cyclohexyl(ethyl)amino)ethene sulfonate (3b)

According to GP1, *N,N*-diethylcyclohexylamine (77.6 mg, 92 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 82/18), the desired product (84.4 mg, 278 μ mol, 56%) was obtained as a colorless solid.



¹H NMR (500 MHz, CDCl₃) δ = 7.26 (d, *J* = 12.8 Hz, 1H, 7-*H*), 4.71 (d, *J* = 12.7 Hz, 1H, 8-*H*), 3.62 (s, 2H, 9-*H*), 3.14 (q, *J* = 7.4 Hz, 2H, 2-*H*), 3.03 (brd, *J* = 14.5 Hz, 1H, 3-*H*), 1.87 – 1.81 (m, 4H, CyHex-*H*), 1.70 – 1.64 (m, 1H, CyHex-*H*), 1.41 (qd, *J* = 12.7, 3.7 Hz, 2H, CyHex-*H*), 1.33 – 1.24 (m, 3H, CyHex-*H*), 1.16 – 1.11 (m, 3H, 1-*H*), 0.96 (s, 9H, 11-*H*) ppm.

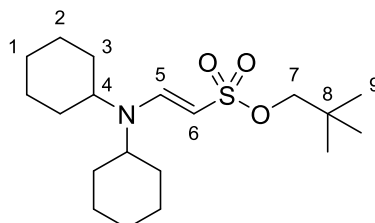
¹³C NMR (126 MHz, CDCl₃) δ = 148.7, 84.1, 77.7, 65.2, 60.7, 56.9, 41.9, 39.7, 32.6, 31.7, 29.9, 29.3, 26.4, 26.2, 26.1, 25.9, 25.3, 24.9, 24.7, 12.2, 11.5 ppm.

HRMS (EI): *m/z* for C₁₅H₂₉NO₃S⁺ [M]⁺: calc.: 303.1863, found: 303.1861.

Note: Hindered rotation around the N-7 bond caused doublet peaks for some of the carbon atoms in the ¹³C NMR spectrum.

6.3 Neopentyl (*E*)-2-(dicyclohexylamino)ethene sulfonate (3c)

According to GP1, *N,N*-dicyclohexylethylamine (105 mg, 115 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 84/16), the desired product (90.6 mg, 253 μ mol, 51%) was obtained as a colorless solid.



^1H NMR (500 MHz, CDCl_3) δ = 7.27 (d, J = 12.7 Hz, 1H, 5-*H*), 4.78 (d, J = 12.7 Hz, 1H, 6-*H*), 3.61 (s, 2H, 7-*H*), 3.23 – 3.01 (brm, 2H, 4-*H*), 1.83 (d, J = 12.0 Hz, 5H, *CyHex-H*), 1.77 – 1.55 (m, 3H, *CyHex-H*), 1.44 (qd, J = 12.4, 3.4 Hz, 4H, *CyHex-H*), 1.37 – 1.19 (m, 6H, *CyHex-H*), 1.12 (qt, J = 11.6, 2.9 Hz, 2H, *CyHex-H*), 0.96 (s, 9H, 9-*H*) ppm.

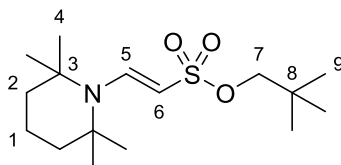
^{13}C NMR (126 MHz, CDCl_3) δ = 147.2, 84.0, 77.6, 58.5, 56.6, 54.1, 34.8, 34.3, 31.7, 30.5, 30.0, 29.4, 26.4, 26.0, 25.4, 24.9, 24.9 ppm.

HRMS (EI): m/z for $\text{C}_{19}\text{H}_{35}\text{NO}_3\text{S}^+$ [M] $^+$: calc.: 357.2332, found: 357.2334.

Note: Due to hindered rotation around the N-5 bond a full set of peaks was observed for the two cyclohexyl groups in the ^{13}C NMR spectrum.

6.4 Neopentyl (*E*)-2-(2,2,6,6-tetramethylpiperidiny)ethene sulfonate (3d)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 80/20), the desired product (135 mg, 423 μmol , 85%) was obtained as a colorless solid.



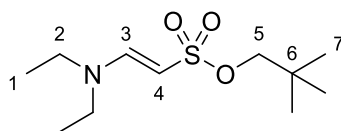
^1H NMR (500 MHz, CDCl_3) δ = 7.45 (d, J = 13.8 Hz, 1H, 5-*H*), 5.03 (d, J = 13.8 Hz, 1H, 6-*H*), 3.60 (s, 2H, 7-*H*), 1.67 – 1.61 (m, 6H, 1-*H*, 2-*H*), 1.36 (s, 12H, 4-*H*), 0.95 (s, 9H, 9-*H*) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ = 146.7, 91.2, 77.8, 57.8, 41.1, 31.6, 28.8, 26.4, 16.4 ppm.

HRMS (EI): m/z for $\text{C}_{16}\text{H}_{31}\text{NO}_3\text{S}^+$ [M] $^+$: calc.: 317.2019, found: 317.2019.

6.5 Neopentyl (*E*)-2-(diethylamino)ethene sulfonate (3e)

According to GP1, triethylamine (50.6 mg, 69 μL , 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 71/29), the desired product (89.2 mg, 358 μmol , 72%) was obtained as a colorless oil.



^1H NMR (500 MHz, CDCl_3) δ = 7.18 (d, J = 12.8 Hz, 1H, 3-*H*), 4.69 (d, J = 12.7 Hz, 1H, 4-*H*), 3.60 (s, 2H, 5-*H*), 3.29 – 3.05 (brm, 4H, 2-*H*), 1.22 – 1.10 (brm, 6H, 1-*H*), 0.94 (s, 9H, 7-*H*) ppm.

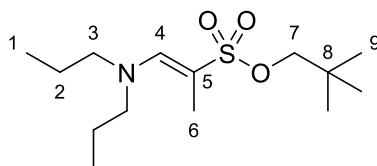
^{13}C NMR (126 MHz, CDCl_3) δ = 150.2, 84.4, 77.8, 50.2, 42.7, 42.3, 31.6, 26.3, 14.8, 11.2, 11.1 ppm.

HRMS (EI): m/z for $\text{C}_{11}\text{H}_{23}\text{NO}_3\text{S}^+$ [M] $^+$: calc.: 249.1393, found: 249.1395.

Note: Hindered rotation around the N-3 bond caused broadened signals in the ^1H NMR and a full set of peaks in the ^{13}C NMR spectrum.

6.6 Neopentyl (*E*)-1-(dipropylamino)prop-1-ene-2-sulfonate (3f)

According to GP1, tripropylamine (71.6 mg, 96 μL , 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 83/17), the desired product (21.4 mg, 73.4 μmol , 15%) was obtained as a colorless oil.



^1H NMR (500 MHz, CDCl_3) δ = 7.07 (s, 1H, 4-*H*), 3.52 (s, 2H, 7-*H*), 3.23 – 3.05 (m, 4H, 3-*H*), 2.01 (d, J = 0.8 Hz, 3H, 6-*H*), 1.59 (tq, J = 7.4, 7.4 Hz, 4H, 2-*H*), 0.96 (s, 9H, 9-*H*), 0.90 (t, J = 7.4 Hz, 6H, 1-*H*) ppm.

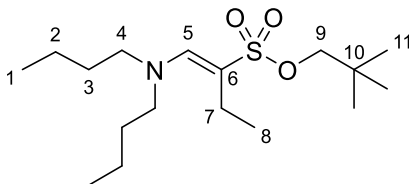
^{13}C NMR (126 MHz, CDCl_3) δ = 146.7, 91.9, 77.8, 54.8, 31.6, 26.5, 22.7, 11.3, 11.0 ppm.

HRMS (EI): m/z for $C_{14}H_{29}NO_3S^+$ $[M]^+$: calc.: 291.1863, found: 291.1864.

Note: $^4J_{H,H}$ coupling constant between 4-*H* and 6-*H* was determined to be 0.8 Hz. No $^1H,^1H$ -NOESY-contact was found between these two protons. $^1H,^{13}C$ -HMBC showed a $^3J_{C,H}$ coupling constant of 8.0 Hz between 4-*H* and carbon #6. Therefore, the product was determined to be (*E*)-configured. Numerous byproducts originating from the dealkylation and/or oxidation of the amine substrate were detected via GC/MS (e.g. dipropylamine or *N,N*-dipropylformamide), offering an explanation for the reduced yield.

6.7 Neopentyl (*E*)-1-(dibutylamino)but-1-ene-2-sulfonate (3g)

According to GP1, tributylamine (92.7 mg, 119 μ L, 500 μ mol, 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 87/13), the desired product (17.0 mg, 51.0 μ mol, 10%) was obtained as a yellowish oil.



1H NMR (500 MHz, $CDCl_3$) δ = 7.05 (s, 1H, 5-*H*), 3.54 (s, 2H, 9-*H*), 3.19 – 3.12 (m, 4H, 4-*H*), 2.38 (q, J = 7.4 Hz, 2H, 7-*H*), 1.58 – 1.50 (m, 4H, 3-*H*), 1.35 – 1.26 (m, 4H, 2-*H*), 1.16 (t, J = 7.4 Hz, 3H, 8-*H*), 0.95 (s, 9H, 11-*H*), 0.94 (t, J = 7.4 Hz, 6H, 1-*H*) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ = 146.2, 99.0, 77.5, 52.8, 31.6, 31.3, 26.5, 19.9, 19.0, 16.0, 14.0 ppm.

HRMS (ESI+): m/z for $C_{17}H_{35}NO_3SNa^+$ $[M+Na]^+$: calc.: 356.2330, found: 356.2233.

Note: No $^1H,^1H$ -NOESY-contact was found between 5-*H* and 7-*H* or 8-*H*. 7-*H* showed a NOESY-contact to 4-*H*. Therefore, the product was determined to be *E*-configured. Numerous byproducts originating from the dealkylation and/or oxidation of the amine substrate were detected via GC/MS (e.g. dibutylamine or *N,N*-dibutylformamide), offering an explanation for the reduced yield.

6.8 Neopentyl (*E*)-2-(piperidinyl)ethene sulfonate (3h)

According to GP1, *N*-Ethylpiperidine (56.6 mg, 69 μ L, 500 μ mol, 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 75/25), a product mixture of the *exo*- and the *endo*-product was obtained in the same fraction (27.0 mg, 103 μ mol, 21%) as a colorless solid.



1H NMR (500 MHz, $CDCl_3$, *exo*-product) δ = 7.15 (d, J = 12.8 Hz, 1H, 4'-*H*), 4.77 (d, J = 12.8 Hz, 1H, 5'-*H*), 3.63 (s 2H, 6'-*H*), 3.22 – 3.12 (m, 4H, 3'-*H*), 1.68 – 1.56 (m, 6H, 1'-*H*, 2'-*H*), 0.95 (s, 9H, 8'-*H*) ppm.

1H NMR (500 MHz, $CDCl_3$, *endo*-product) δ = 7.14 (s, 1H, 6-*H*), 3.54 (s, 2H, 8-*H*), 3.11 – 3.09 (m, 2H, 3-*H*), 2.29 (t, J = 6.1 Hz, 2H, 2-*H*), 1.93 – 1.80 (m, 4H, 4-*H*, 5-*H*), 1.16 (t, J = 7.2 Hz, 3H, 1-*H*), 0.95 (s, 9H, 10-*H*) ppm.

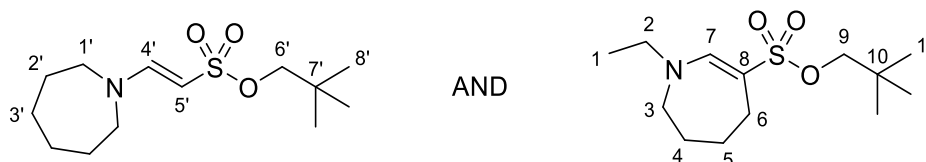
^{13}C NMR (126 MHz, $CDCl_3$, *exo/endo*-mixture) δ = 151.1, 145.0, 93.8, 85.1, 77.8, 77.8, 50.5, 44.9, 44.8, 31.7, 31.6, 26.4, 26.4, 26.1, 23.9, 22.7, 22.6, 21.1, 20.0, 13.9 ppm.

HRMS (EI): m/z for $C_{12}H_{23}NO_3S^+$ $[M]^+$: calc.: 261.1393, found: 261.1395 (*exo*-product) and 261.1294 (*endo*-product).

Note: An *exo/endo*-ratio of ca. 4/1 was calculated via 1H NMR and confirmed by GC measurements.

6.9 Neopentyl (*E*)-2-(azepanyl)ethene sulfonate (3i)

According to GP1, *N*-Ethylazepane (63.6 mg, 64 μ L, 500 μ mol, 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 77/23), two products (*exo*-product: 9.9 mg, 35.9 μ mol, 7%; *endo*-product: 35.2 μ mol, 7%) could be isolated as yellowish solids.

*Exo-product:*

¹H NMR (500 MHz, CDCl₃) δ = 7.29 (d, *J* = 12.6 Hz, 1H, 4'-*H*), 4.68 (d, *J* = 12.6 Hz, 1H, 5-*H*), 3.63 (s, 2H, 6'-*H*), 3.42 – 3.33 (m, 2H, 1'-*H*), 3.19 – 3.11 (m, 2H, 1'-*H*), 1.79 – 1.68 (m, 4H, 2'-*H*), 1.64 – 1.53 (m, 4H, 3'-*H*), 0.96 (s, 9H, 8'-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 151.7, 84.2, 77.8, 55.8, 48.9, 46.3, 31.7, 30.6, 28.3, 27.2, 26.8, 26.5, 26.4, 26.4, 26.3, 25.5, 25.3 ppm.

HRMS (EI): *m/z* for C₁₂H₂₃NO₃S⁺ [*M*]⁺: calc.: 261.1393, found: 261.1394.

Note: Hindered rotation around the N-4' bond caused doublet peaks for some of the carbon atoms in the ¹³C NMR spectrum.

Endo-product:

¹H NMR (500 MHz, CDCl₃) δ = 7.17 (s, 1H, 7-*H*), 3.56 (s, 2H, 9-*H*), 3.26 – 3.23 (m, 2H, 3-*H*), 3.20 (q, *J* = 7.1 Hz, 2H, 2-*H*), 2.48 (dd, *J* = 7.3, 4.2 Hz, 2H, 6-*H*), 1.81 – 1.76 (m, 4H, 4-*H*, 5-*H*), 1.19 (t, *J* = 7.1 Hz, 3H, 1-*H*), 0.96 (s, 9H, 11-*H*) ppm.

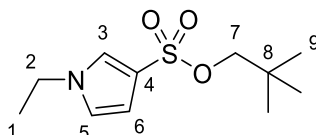
¹³C NMR (126 MHz, CDCl₃) δ = 148.6, 99.6, 77.8, 54.0, 51.9, 31.7, 28.7, 26.9, 26.5, 26.5, 14.5 ppm.

HRMS (EI): *m/z* for C₁₂H₂₃NO₃S⁺ [*M*]⁺: calc.: 261.1393, found: 261.1395.

Note: An *exo/endo*-ratio of ca. 1/1 was calculated via the isolated yields.

6.10 Neopentyl N-ethyl-1H-pyrrole-3-sulfonate (3j)

According to GP1, *N*-ethylpyrrole (47.6 mg, 53 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 17.25 *F*. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 91/9, followed by cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 93/7), the desired product (42.7 mg, 174 μ mol, 35%) was obtained as a colorless liquid.



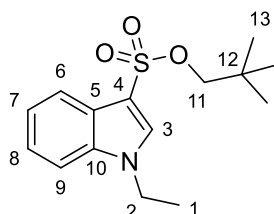
¹H NMR (500 MHz, CDCl₃) δ = 6.93 (dd, *J* = 2.7, 1.9 Hz, 1H, 3-*H*), 6.90 (dd, *J* = 4.0, 1.9 Hz, 1H, 5-*H*), 6.19 (dd, *J* = 4.0, 2.7 Hz, 1H, 6-*H*), 4.22 (q, *J* = 7.3 Hz, 2H, 2-*H*), 3.63 (s, 2H, 7-*H*), 1.46 (t, *J* = 7.3 Hz, 3H, 1-*H*), 0.91 (s, 9H, 9-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 127.6, 122.0, 119.7, 108.3, 79.8, 43.5, 31.6, 26.2, 16.7 ppm.

HRMS (EI): *m/z* for C₁₁H₁₉NO₃S⁺ [*M*]⁺: calc.: 245.1080, found: 245.1077.

6.11 Neopentyl N-ethyl-1H-indole-2-sulfonate (3k)

According to GP1, *N*-ethylindole (72.6 mg, 73 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 65/35), the desired product (51.7 mg, 175 μ mol, 35%) was obtained as a colorless liquid.



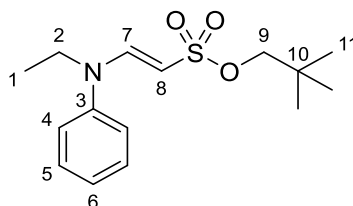
¹H NMR (500 MHz, CDCl₃) δ = 7.95 – 7.87 (m, 1H, 6-*H*), 7.77 (s, 1H, 3-*H*), 7.42 (dt, *J* = 8.2, 1.3 Hz, 1H, 9-*H*), 7.35 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H, 7-*H*), 7.30 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H, 8-*H*), 4.23 (q, *J* = 7.3 Hz, 2H, 2-*H*), 3.67 (s, 2H, 11-*H*), 1.54 (t, *J* = 7.3 Hz, 3H, 1-*H*), 0.88 (s, 9H, 13-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 136.3, 132.6, 124.5, 123.8, 122.6, 120.3, 110.5, 109.2, 79.2, 42.0, 31.6, 26.2, 15.2 ppm.

HRMS (EI): *m/z* for C₁₅H₂₁NO₃S⁺ [*M*]⁺: calc.: 295.1237, found: 295.1237.

6.12 Neopentyl (*E*)-2-(ethyl(phenyl)amino)ethene sulfonate (3l)

According to GP1, *N,N*-diethylaniline (74.6 mg, 80 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 81/19), the desired product (40.2 mg, 135 μ mol, 27%) was obtained as a colorless solid.



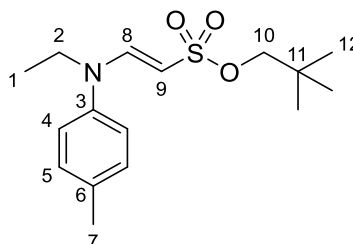
¹H NMR (500 MHz, CDCl₃) δ = 7.60 (d, *J* = 12.8 Hz, 1H, 7-*H*), 7.42 – 7.35 (m, 2H, 4-*H*), 7.22 (t, *J* = 7.5 Hz, 1H, 6-*H*), 7.17 – 7.11 (m, 2H, 5-*H*), 5.08 (d, *J* = 12.8 Hz, 1H, 8-*H*), 3.68 (q, *J* = 7.1 Hz, 2H, 2-*H*), 3.67 (s, 2H, 9-*H*), 1.26 (t, *J* = 7.1 Hz, 3H, 1-*H*), 0.97 (s, 9H, 11-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 147.8, 129.9, 129.6, 125.9, 121.9, 90.8, 78.2, 31.7, 29.8, 26.4, 12.0 ppm.

HRMS (EI): *m/z* for C₁₅H₂₃NO₃S⁺ [*M*]⁺: calc.: 297.1393, found: 297.1392.

6.13 Neopentyl (*E*)-2-(ethyl(*p*-tolyl)amino)ethene sulfonate (3m)

According to GP1, *N,N*-diethyl-4-methylaniline (81.6 mg, 89 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 80/10), the desired product (86.0 mg, 276 μ mol, 55%) was obtained as a colorless oil.



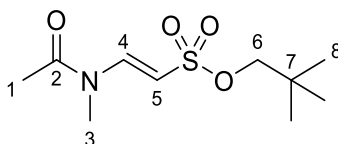
¹H NMR (500 MHz, CDCl₃) δ = 7.54 (d, *J* = 13.0 Hz, 1H, 8-*H*), 7.20 – 7.15 (m, 2H, 4-*H*), 7.07 – 6.98 (m, 2H, 5-*H*), 5.01 (brs, 1H, 9-*H*), 3.69 – 3.58 (m, 4H, 2-*H*, 10-*H*), 2.34 (s, 3H, 7-*H*), 1.22 (t, *J* = 7.2 Hz, 3H, 1-*H*), 0.96 (s, 9H, 12-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 148.1, 142.1, 135.9, 130.4, 129.9, 121.7, 89.9, 78.1, 31.6, 29.8, 26.3, 20.9 ppm.

HRMS (EI): *m/z* for C₁₆H₂₅NO₃S⁺ [*M*]⁺: calc.: 311.1550, found: 311.1549.

6.14 Neopentyl (*E*)-2-(*N*-methylacetamido)ethene sulfonate (3n)

According to GP1, *N*-methyl-*N*-vinyl acetamide (49.6 mg, 52 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 5.75 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 95/5 $\rightarrow$ 55/45), the desired product (83.7 mg, 336 μ mol, 67%) was obtained as a colorless solid.



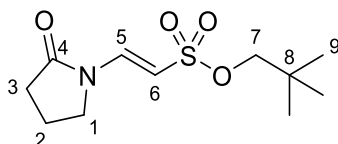
¹H NMR (500 MHz, CDCl₃) δ = 7.90 (brs, 1H, 4-*H*), 5.60 (d, *J* = 13.4 Hz, 1H, 5-*H*), 3.75 (s, 2H, 6-*H*), 3.13 (s, 3H, 3-*H*), 2.37 (s, 3H, 1-*H*), 0.98 (s, 9H, 8-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 169.9, 143.3, 102.0, 79.3, 31.8, 29.9, 26.3, 21.8 ppm.

HRMS (ESI⁺): *m/z* for C₁₀H₁₉NO₄Na⁺ [*M*+Na]⁺: calc.: 272.0927, found 272.0926.

6.15 Neopentyl (*E*)-2-(2-oxopyrrolidinyl)ethene sulfonate (3o)

According to GP1, *N*-vinylpyrrolidinone (55.6 mg, 53 μ L, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 5.75 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 93/7 $\rightarrow$ 70/30), the desired product (60.5 mg, 231 μ mol, 46%) was obtained as a colorless solid.



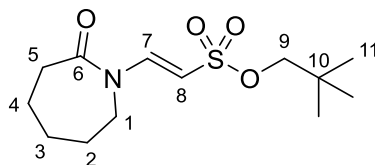
^1H NMR (500 MHz, CDCl_3) δ = 8.01 (d, J = 13.8 Hz, 1H, 5-*H*), 5.58 (d, J = 13.8 Hz, 1H, 6-*H*), 3.73 (s, 2H, 7-*H*), 3.60 – 3.53 (m, 2H, 1-*H*), 2.59 (dd, J = 8.6, 7.7 Hz, 2H, 3-*H*), 2.26 – 2.18 (m, 2H, 2-*H*), 0.97 (s, 9H, 9-*H*) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ = 174.3, 137.6, 103.8, 79.3, 45.2, 31.8, 30.8, 26.3, 17.6 ppm.

HRMS (ESI $^+$): m/z for $\text{C}_{11}\text{H}_{19}\text{NO}_4\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 284.0927, found 284.0926.

6.16 Neopentyl (*E*)-2-(2-oxopyrrolidinyl)ethene sulfonate (3p)

According to GP1, *N*-vinylcaprolactam (69.6 mg, 68 μL , 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 5.75 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 54/56), the desired product (71.3 mg, 246 μmol , 49%) was obtained as a colorless solid.



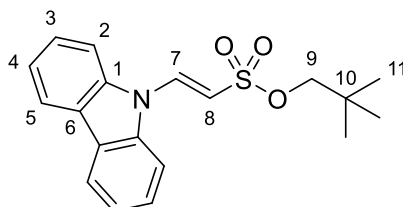
^1H NMR (500 MHz, CDCl_3) δ = 8.26 (d, J = 14.1 Hz, 1H, 7-*H*), 5.72 (d, J = 14.1 Hz, 1H, 8-*H*), 3.72 (s, 2H, 9-*H*), 3.66 – 3.52 (m, 2H, 1-*H*), 2.81 – 2.62 (m, 2H, 5-*H*), 1.95 – 1.71 (m, 6H, 2-*H*, 3-*H*, 4-*H*), 0.96 (s, 9H, 11-*H*) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ = 174.9, 141.1, 102.6, 79.2, 46.8, 37.1, 31.8, 29.3, 27.5, 26.3, 23.4 ppm.

HRMS (ESI $^+$): m/z for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{SNa}^+$ [$\text{M}+\text{Na}$] $^+$: calc.: 312.1240, found 312.1239.

6.17 Neopentyl (*E*)-2-(9H-carbazol-9-yl)ethene sulfonate (3q)

Similar to GP1, *N*-vinylcarbazole (96.6 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq., in MeCN) and neopentyl alcohol (229 mg, 2.60 mmol, 5.2 eq.) were used as substrates with benzonitrile as solvent and the electrolysis was carried out using 5.75 *F*. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 90/10 followed by cyclohexane/ethyl acetate = 100/0 $\rightarrow$ 88/12), the desired product (47.5 mg, 138 μmol , 28%) was obtained as a colorless solid.



^1H NMR (500 MHz, CDCl_3) δ = 8.40 (d, J = 14.0 Hz, 1H, 7-*H*), 8.06 (ddd, J = 7.7, 1.2, 0.7 Hz, 2H, 5-*H*), 7.68 (dt, J = 8.4, 0.8 Hz, 2H, 3-*H*), 7.55 (ddd, J = 8.4, 7.3, 1.3 Hz, 2H, 4-*H*), 7.43 (td, J = 7.5, 0.9 Hz, 2H, 2-*H*), 6.60 (d, J = 13.9 Hz, 1H, 8-*H*), 3.85 (s, 2H, 9-*H*), 1.01 (s, 9H, 11-*H*) ppm.

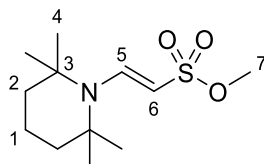
^{13}C NMR (126 MHz, CDCl_3) δ = 138.9, 136.9, 127.5, 126.0, 123.7, 120.8, 111.8, 103.9, 79.5, 31.9, 26.3 ppm.

HRMS (EI): m/z for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}^+$ [M] $^+$: calc.: 343.1237, found: 343.1240.

Note: Despite extensive purification efforts, the compound could not be isolated in a fully pure state, as indicated by the presence of carbazole as a minor impurity in the NMR spectra. This may also be attributed to potential degradation of the compound during the column chromatography process.

6.18 Methyl (*E*)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4a)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and methanol (83.0 mg, 105 μL , 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 60/40), the desired product (83.3 mg, 319 μmol , 64%) was obtained as a colorless solid.



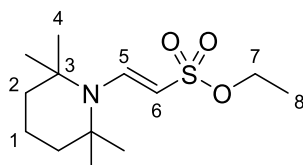
¹H NMR (500 MHz, CDCl₃) δ = 7.48 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.00 (d, *J* = 13.8 Hz, 1H, 6-*H*), 3.69 (s, 3H, 7-*H*), 1.68 – 1.61 (m, 6H, 1-*H*, 2-*H*), 1.37 (s, 12H, 4-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 147.3, 89.7, 58.0, 54.6, 41.0, 28.8, 16.3 ppm.

HRMS (EI): *m/z* for C₁₂H₂₃NO₃S⁺ [*M*]⁺: calc.: 261.1393, found: 261.1396.

6.19 Ethyl (E)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4b)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and ethanol (120 mg, 152 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 72/28), the desired product (94.7 mg, 344 μ mol, 69%) was obtained as a colorless solid.



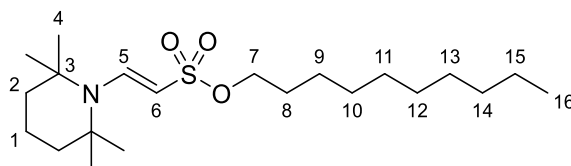
¹H NMR (500 MHz, CDCl₃) δ = 7.47 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.04 (d, *J* = 13.8 Hz, 1H, 6-*H*), 4.04 (q, *J* = 7.2 Hz, 2H, 7-*H*), 1.66 – 1.60 (m, 6H, 1-*H*, 2-*H*), 1.37 – 1.32 (m, 15H, 4-*H*, 8-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 146.8, 91.2, 64.6, 57.9, 41.0, 28.8, 16.3, 15.0 ppm.

HRMS (EI): *m/z* for C₁₃H₂₅NO₃S⁺ [*M*]⁺: calc.: 275.1550, found: 275.1549.

6.20 nDecyl (E)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4c)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and n-decanol (412 mg, 496 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 89/11), the desired product (133 mg, 343 μ mol, 69%) was obtained as a colorless liquid.



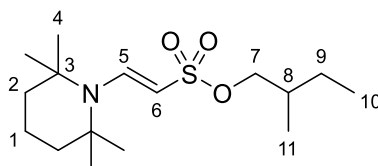
¹H NMR (500 MHz, CDCl₃) δ = 7.46 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.02 (d, *J* = 13.9 Hz, 1H, 6-*H*), 3.95 (t, *J* = 6.6 Hz, 2H, 7-*H*), 1.73 – 1.58 (m, 9H, 1-*H*, 2-*H*, 8-*H*, 9-*H*), 1.35 (s, 12H, 4-*H*), 1.33 – 1.18 (m, 13H, 9-15-*H*), 0.87 (t, *J* = 6.9 Hz, 3H, 16-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 146.7, 91.2, 68.8, 57.8, 41.0, 32.0, 29.6, 29.6, 29.4, 29.2, 29.1, 28.8, 25.8, 22.8, 16.3, 14.2 ppm.

HRMS (ESI⁺): *m/z* for C₂₁H₄₁NO₃SN⁺ [*M*+Na]⁺: calc.: 410.2699, found: 410.2702.

6.21 2-Methylbutyl (E)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4d)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and racemic 2-methylbutanol (229 mg, 281 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 84/16), the desired product (135 mg, 426 μ mol, 85%) was obtained as a colorless liquid.



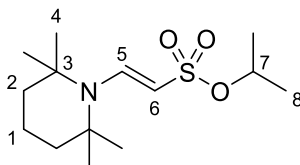
¹H NMR (500 MHz, CDCl₃) δ = 7.46 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.03 (d, *J* = 13.8 Hz, 1H, 6-*H*), 3.83 (dd, *J* = 9.4, 5.9 Hz, 1H, 7-*H*), 3.75 (dd, *J* = 9.4, 6.5 Hz, 1H, 7-*H*), 1.79 – 1.73 (m, 1H, 8-*H*), 1.69 – 1.58 (m, 6H, 1-*H*, 2-*H*), 1.51 – 1.41 (m, 1H, 9-*H*), 1.36 (s, 12H, 4-*H*), 1.28 – 1.14 (m, 1H 9-*H*), 0.94 (d, *J* = 6.8 Hz, 3H, 11-*H*), 0.89 (t, *J* = 7.5 Hz, 3H, 10-*H*).

¹³C NMR (126 MHz, CDCl₃) δ = 146.7, 91.2, 73.1, 57.9, 41.1, 34.5, 28.8, 25.8, 16.4, 16.3, 11.3 ppm.

HRMS (ESI⁺): *m/z* for C₁₆H₃₁NO₃Na⁺ [*M*+Na]⁺: calc.: 340.1917, found: 340.1918.

6.22 Isopropyl (*E*)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4e)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and isopropanol (156 mg, 200 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 85/15), the desired product (83.3 mg, 288 μ mol, 58%) was obtained as a colorless solid.



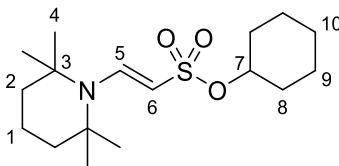
¹H NMR (500 MHz, CDCl₃) δ = 7.47 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.08 (d, *J* = 13.8 Hz, 1H, 6-*H*), 4.57 (hept, *J* = 6.3 Hz, 1H, 7-*H*), 1.68 – 1.60 (m, 6H, 1-*H*, 2-*H*), 1.36 (s, 12H, 4-*H*), 1.34 (d, *J* = 6.3 Hz, 6H, 8-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 146.2, 92.9, 74.3, 57.8, 41.1, 28.8, 23.2, 16.4 ppm.

HRMS (EI): *m/z* for C₁₄H₂₇NO₃S⁺ [*M*]⁺: calc.: 289.1706, found: 289.1704

6.23 Cyclohexyl (*E*)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4f)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and cyclohexanol (260 mg, 274 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 79/21), the desired product (110.6 mg, 336 μ mol, 67%) was obtained as a colorless oil.



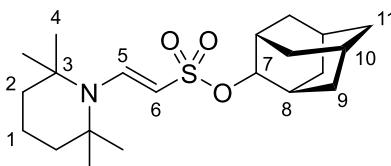
¹H NMR (500 MHz, CDCl₃) δ = 7.46 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.08 (d, *J* = 13.8 Hz, 1H, 6-*H*), 4.30 (tt, *J* = 8.8, 3.9 Hz, 1H, 7-*H*), 1.92 (dt, *J* = 13.7, 4.3 Hz, 2H, 8-*H*), 1.79 – 1.73 (m, 2H, 8-*H*), 1.65 – 1.56 (m, 8H, 1-*H*, 2-*H*, 10-*H*), 1.35 (s, 12H, 4-*H*), 1.35 – 1.19 (m, 4H, 9-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 146.1, 93.2, 79.2, 57.8, 41.1, 32.8, 28.8, 25.2, 23.9, 16.4 ppm.

HRMS (ESI⁺): *m/z* for C₁₇H₃₁NO₃Na⁺ [*M*+Na]⁺: calc.: 352.1917, found: 352.1916.

6.24 Adamantan-2-yl (*E*)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4g)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and 2-adamantol (396 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 82/18 followed by cyclohexane/ethyl acetate = 99/1 $\rightarrow$ 84/16), the desired product (110 mg, 289 μ mol, 58%) was obtained as a colorless solid.



¹H NMR (500 MHz, CDCl₃) δ = 7.46 (d, *J* = 13.8 Hz, 1H, 5-*H*), 5.09 (d, *J* = 13.8 Hz, 1H, 6-*H*), 4.47 (d, *J* = 3.5 Hz, 1H, 7-*H*), 2.16 – 2.10 (m, 4H, Ad-*H*), 1.92 – 1.79 (m, 4H, Ad-*H*), 1.76 – 1.67 (m, 6H, Ad-*H*), 1.66 – 1.59 (m, 6H, 1-*H*, 2-*H*), 1.35 (s, 12H, 4-*H*) ppm.

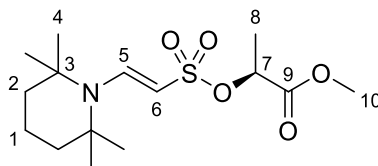
¹³C NMR (126 MHz, CDCl₃) δ = 146.0, 93.4, 83.8, 57.7, 57.1, 41.1, 37.4, 36.8, 36.7, 36.5, 35.5, 34.7, 33.2, 33.0, 31.4, 31.2, 28.8, 27.9, 27.1, 26.9, 16.4.

HRMS (ESI⁺): *m/z* for C₂₁H₃₅NO₃Na⁺ [*M*+Na]⁺: calc.: 404.2230, found: 404.2230.

Note: Despite extensive purification efforts, the compound could not be isolated in a fully pure state, as indicated by the presence of minor impurities in the NMR spectra. This may also be attributed to potential degradation of the compound during the column chromatography process.

6.25 S-Methylactyl (E)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4h)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and S-methyl lactate (271 mg, 246 μ L, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 66/34 followed by cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 58/42), the desired product (63.0 mg, 189 μ mol, 38%) was obtained as a colorless liquid.



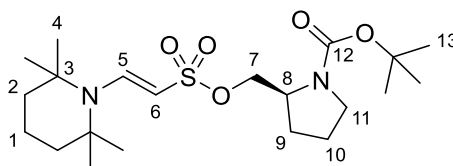
¹H NMR (500 MHz, CDCl₃) δ = 7.49 (d, J = 13.8 Hz, 1H, 5-*H*), 5.07 (d, J = 13.8 Hz, 1H, 6-*H*), 4.79 (q, J = 7.0 Hz, 1H, 7-*H*), 3.75 (s, 3H, 10-*H*), 1.66 – 1.61 (m, 6H, 1-*H*, 2-*H*), 1.55 (d, J = 7.0 Hz, 3H, 8-*H*), 1.35 (d, J = 2.8 Hz, 12H, 4-*H*) ppm.

¹³C NMR (126 MHz, CDCl₃) δ = 171.0, 147.3, 91.0, 72.6, 58.1, 52.6, 40.9, 28.9, 18.8, 16.3 ppm.

HRMS (EI): *m/z* for C₁₅H₂₇NO₅S⁺ [M]⁺: calc.: 333.1604, found: 333.1605.

6.26 N-Butyloxycarbonylprolinyl (E)-2-(2,2,6,6-tetramethylpiperidinyl)ethene sulfonate (4i)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and *N*-Boc prolinol (523 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 79/21 followed by cyclohexane/acetone = 97/3 $\rightarrow$ 85/15), the desired product (133 mg, 308 μ mol, 62%) was obtained as a colorless solid.



¹H NMR (500 MHz, CD₃CN) δ = 7.43 (d, J = 13.8 Hz, 1H, 5-*H*), 5.07 (dd, J = 14.2, 8.2 Hz, 1H, 6-*H*), 4.03 – 3.88 (m, 2H, 7-*H*), 3.82 (t, J = 9.0 Hz, 1H, 8-*H*), 3.32 – 3.20 (m, 2H, 11-*H*), 2.00 – 1.75 (m, 4H, 9-*H*, 10-*H*), 1.70 – 1.58 (m, 6H, 1-*H*, 2-*H*), 1.42 (s, 9H, 13-*H*), 1.34 (s, 12H, 4-*H*) ppm.

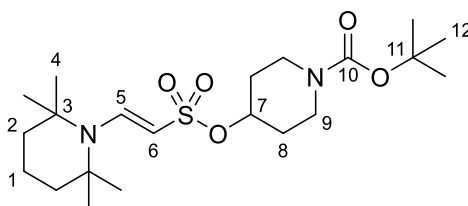
¹³C NMR (126 MHz, CD₃CN) δ = 155.2, 154.9, 147.9, 147.8, 118.3, 91.0, 90.7, 79.9, 79.8, 69.4, 68.7, 58.7, 56.6, 47.7, 47.3, 41.2, 29.2, 28.9, 28.9, 28.6, 28.4, 24.4, 23.5, 16.7 ppm.

HRMS (ESI⁺): *m/z* for C₂₁H₃₈N₂O₅SN⁺ [M+Na]⁺: calc.: 453.2394, found: 453.2393.

Note: Due to hindered rotation around the amide bond N-12, doublets were observed in the ¹³C NMR spectra for some of the signals.

6.27 Tert-butyl (E)-4-(((2-(2,2,6,6-tetramethylpiperidinyl)vinyl)sulfonyl)oxy)piperidine carboxylate (4j)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μ mol, 1 eq.), SO₂ stock solution (3.90 mmol, 7.8 eq.) and *N*-Boc piperidinol (523 mg, 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 F. After twofold purification by flash column chromatography (cyclohexane/ethyl acetate = 97/3 $\rightarrow$ 72/28 followed by cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 72/28), the desired product (101 mg, 235 μ mol, 47%) was obtained as a colorless oil.



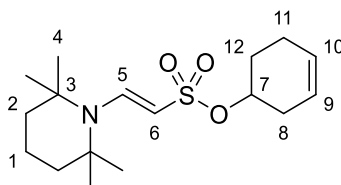
^1H NMR (500 MHz, CDCl_3) δ = 7.49 (d, J = 13.8 Hz, 1H, 5-*H*), 5.08 (d, J = 13.8 Hz, 1H, 6-*H*), 4.51 (tt, J = 7.5, 3.7 Hz, 1H, 7-*H*), 3.65 (ddd, J = 12.0, 6.8, 3.7 Hz, 2H, 9-*H*), 3.29 (ddd, J = 13.5, 7.6, 3.8 Hz, 2H, 9-*H*), 1.92 – 1.83 (m, 2H, 8-*H*), 1.82 – 1.72 (m, 2H, 8-*H*), 1.69 – 1.59 (m, 6H, 1-*H*, 2-*H*), 1.45 (s, 9H, 12-*H*), 1.36 (s, 12H, 4-*H*) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ = 154.9, 146.5, 92.5, 79.9, 75.5, 58.0, 41.0, 31.7, 28.9, 28.5, 16.3 ppm.

HRMS (ESI+): m/z for $\text{C}_{21}\text{H}_{38}\text{N}_2\text{O}_5\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: calc.: 453.2394, found: 453.2394.

6.28 Cyclohex-3-enyl (*E*)-2-(2,2,6,6-tetramethylpiperidin-1-yl)ethene sulfonate (4k)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and 3-cyclohexenol (255 mg, 258 μL , 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 76/24), the desired product (33.8 mg, 103 μmol , 21%) was obtained as a colorless liquid.



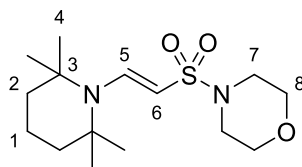
^1H NMR (500 MHz, CDCl_3) δ = 7.47 (d, J = 13.8 Hz, 1H, 5-*H*), 5.69 – 5.61 (m, 1H, 9-*H*), 5.58 – 5.50 (m, 1H, 10-*H*), 5.09 (d, J = 13.8 Hz, 1H, 6-*H*), 4.55 (dddd, J = 9.8, 7.4, 5.4, 3.2 Hz, 1H, 7-*H*), 2.48 – 2.33 (m, 1H, 8-*H*), 2.32 – 2.17 (m, 2H, 8-*H*, 11-*H*), 2.16 – 2.03 (m, 1H, 11-*H*), 2.03 – 1.93 (m, 1H, 12-*H*), 1.90 – 1.78 (m, 1H, 12-*H*), 1.69 – 1.56 (m, 6H, 1-*H*, 2-*H*), 1.35 (s, 12H, 4-*H*) ppm.

^{13}C NMR (126 MHz, CDCl_3) δ = 146.2, 126.9, 123.5, 92.8, 76.0, 57.8, 41.0, 31.9, 28.8 (d), 28.5, 23.6, 16.3 ppm.

HRMS (ESI+): m/z for $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: calc.: 350.1760, found: 350.1759.

6.29 (*E*)-4-((2-(2,2,6,6-tetramethylpiperidinyl)vinyl)sulfonyl)morpholine (5a)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and morpholine (227 mg, 227 μL , 2.60 mmol, 5.2 eq.) were used as substrates and the electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 96/4 $\rightarrow$ 50/50), the desired product (17.7 mg, 55.9 μmol , 11%) was obtained as a colorless oil.



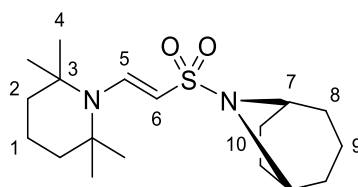
^1H NMR (400 MHz, CDCl_3) δ = 7.32 (d, J = 13.8 Hz, 1H, 5-*H*), 4.93 (d, J = 13.8 Hz, 1H, 6-*H*), 3.78 (t, J = 4.3 Hz, 4H, 8-*H*), 3.00 (t, J = 4.6 Hz, 4H, 7-*H*), 1.69 – 1.59 (m, 6H, 1-*H*, 2-*H*), 1.36 (s, 12H, 4-*H*) ppm.

HRMS (ESI+): m/z for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}_3\text{SNa}^+$ $[\text{M}+\text{Na}]^+$: calc.: 339.1713, found: 339.1716.

Note: An ^1H NMR yield of 44% was calculated by addition of 1,3,5-trimethoxybenzene as internal standard to the reaction mixture after the electrolysis. We therefore suspect a rapid degradation of the enaminy sulfonamide product during workup and column chromatography. The synthetic application of an amidosulfinate-intermediate formed from an amine and SO_2 with the help of a base, similar to the monoalkylsulfite, has been demonstrated before, forming stable alkyl aryl sulfonamides.⁶ Enaminy sulfonamides on the other hand seem to be unstable, probably due to rapid hydrolysis. Due to degradation and the small quantity of the isolated product, a ^{13}C NMR could not be measured in sufficient quality.

6.30 (1*R*,5*S*)-8-(((*E*)-2-(2,2,6,6-tetramethylpiperidinyl)vinyl)sulfonyl)-8-azabicyclo[3.2.1]octane (5b)

According to GP1, 1-ethyl-2,2,6,6-tetramethylpiperidine (84.7 mg, 500 μmol , 1 eq.), SO_2 stock solution (3.90 mmol, 7.8 eq.) and 8-azabicyclo[3.2.1]octane hydrochloride (384 mg, 2.60 mmol, 5.2 eq.) were used as substrates. Differently to GP1, 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU, 1.08 g, 1.06 mL, 7.10 mmol, 14.2 eq.) was used in excess to account for the additional hydrochloride from 8-azabicyclo[3.2.1]octane salt. The electrolysis was carried out using 11.5 *F*. After purification by flash column chromatography (cyclohexane/ethyl acetate = 98/2 $\rightarrow$ 71/29), the desired product (11.2 mg, 32.9 μmol , 7%) was obtained as a colorless oil.



¹H NMR (400 MHz, CDCl₃) δ = 7.38 (d, J = 13.9 Hz, 1H, 5-*H*), 4.99 (d, J = 13.9 Hz, 1H, 6-*H*), 4.08 (dq, J = 5.4, 2.9 Hz, 2H, 7-*H*), 2.05 – 1.95 (m, 2H, 10-*H*), 1.88 – 1.77 (m, 2H, 8-*H*), 1.75 – 1.43 (m, 12H, 1-*H*, 2-*H*, 8-*H*, 9-*H*, 10-*H*), 1.33 (s, 12H, 4-*H*) ppm.

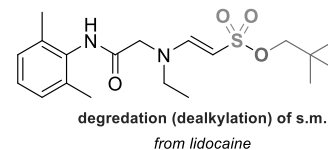
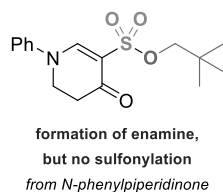
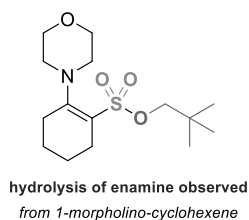
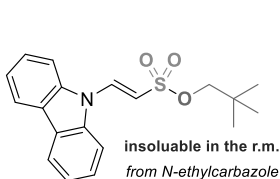
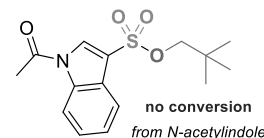
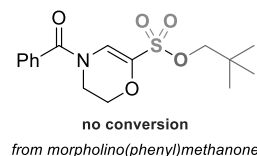
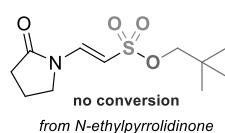
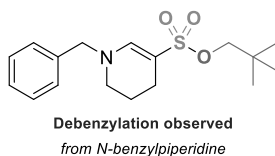
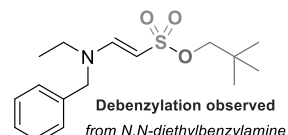
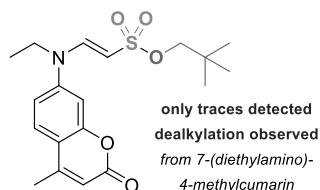
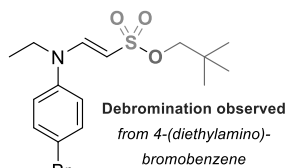
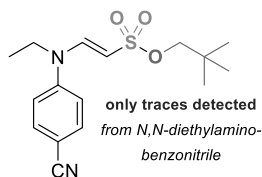
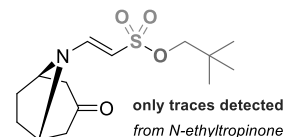
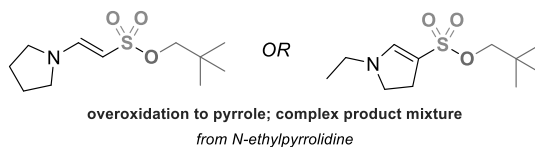
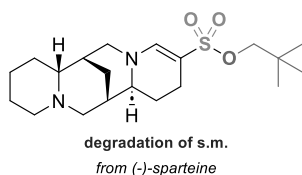
HRMS (ESI+): m/z for C₁₈H₃₂N₂O₂SNa⁺ [M+Na]⁺: calc.: 363.2077, found: 363.2080z.

Note: We suspect similar degradation of the enaminy sulfonamide, due to which only a small quantity of the desired product was isolated. A ¹³C NMR could not be measured in sufficient quality.

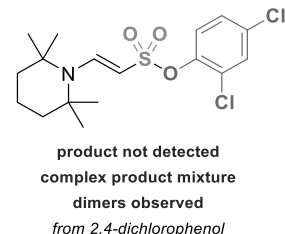
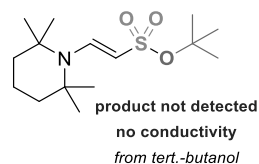
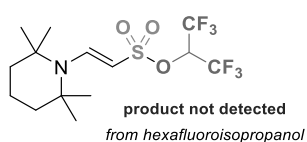
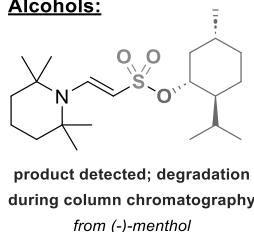
6.31 Limitations of the Scope/Unsuccessful substrates

The following substrates were also tried, but for the reason stated below, the desired product could not be isolated in sufficient quantities.

(En)amines:



Alcohols:



Other nucleophiles:

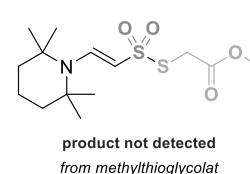
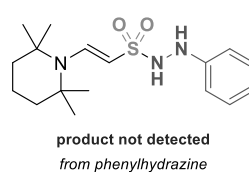
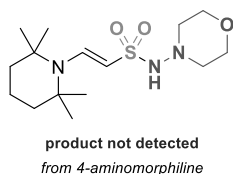
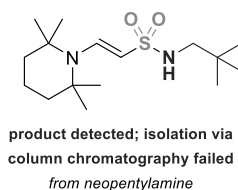
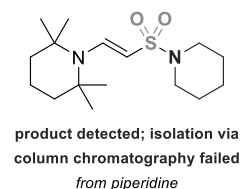
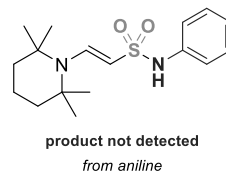
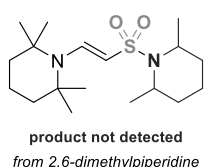
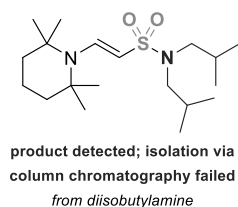


Figure S11: Unsuccessful substrates.

7 Crystallographic Data

Crystallization was carried out by dissolving compound **3d** in ⁿhexane using heat and a vortexer. Slow but incomplete (!) evaporation of the solvent resulted in crystal formation.

Table S10: Crystallographic data for neopentyl (*E*)-2-(2,2,6,6-tetramethylpiperidiny)ethene sulfonate (**3d**).

Parameter	Value
CCDC Number	2407541
Empirical formular	C ₁₆ H ₃₁ NO ₃ S
Formular weight	317.48 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Crystal size and habit	0.061 x 0.099 x 0.384 mm clear colourless needle
Space group name	P 1 21/c 1 (Nr. 14)
Unit cell dimensions	$a = 6.3217(2) \text{ Å}$ $\alpha = 90^\circ$ $b = 14.4116(4) \text{ Å}$ $\beta = 97.7009(9)^\circ$ $c = 19.7403(5) \text{ Å}$ $\gamma = 90^\circ$
Volume	1782.24(9) Å ³
Number of reflections	114870
Z	4
Density (calculated)	1.183 g×cm ⁻³
Absorption coefficient	0.191/mm
Method of absorption correction	Numerical Mu From Formula
Transmission (min. and max.)	0.9300 and 0.9880
F(000)	696
Theta range for data collection	$2.08^\circ \leq \Theta \leq 36.36^\circ$
Index ranges	$-10 \leq h \leq 10$, $-24 \leq k \leq 24$, $-32 \leq l \leq 32$
Number of reflections collected (independend)	114870 (8673); R(int) = 0.0367
observed [$I > 2\sigma(I)$]	7732
Refinement method	Full-matrix least-squares on F ² (SHELXL-2019/1)
Data / restraints / parameters	8673 / 26 / 234
Goodness-of-fit on F ²	1.028
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0343, wR2 = 0.0949
R indices (all data)	R1 = 0.0390, wR2 = 0.0997
Largest diff. peak and hole	0.537 and -0.385 eÅ ⁻³

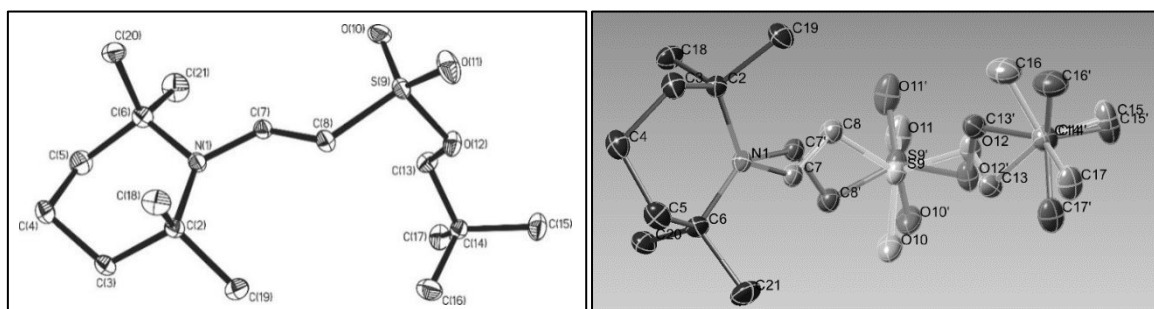
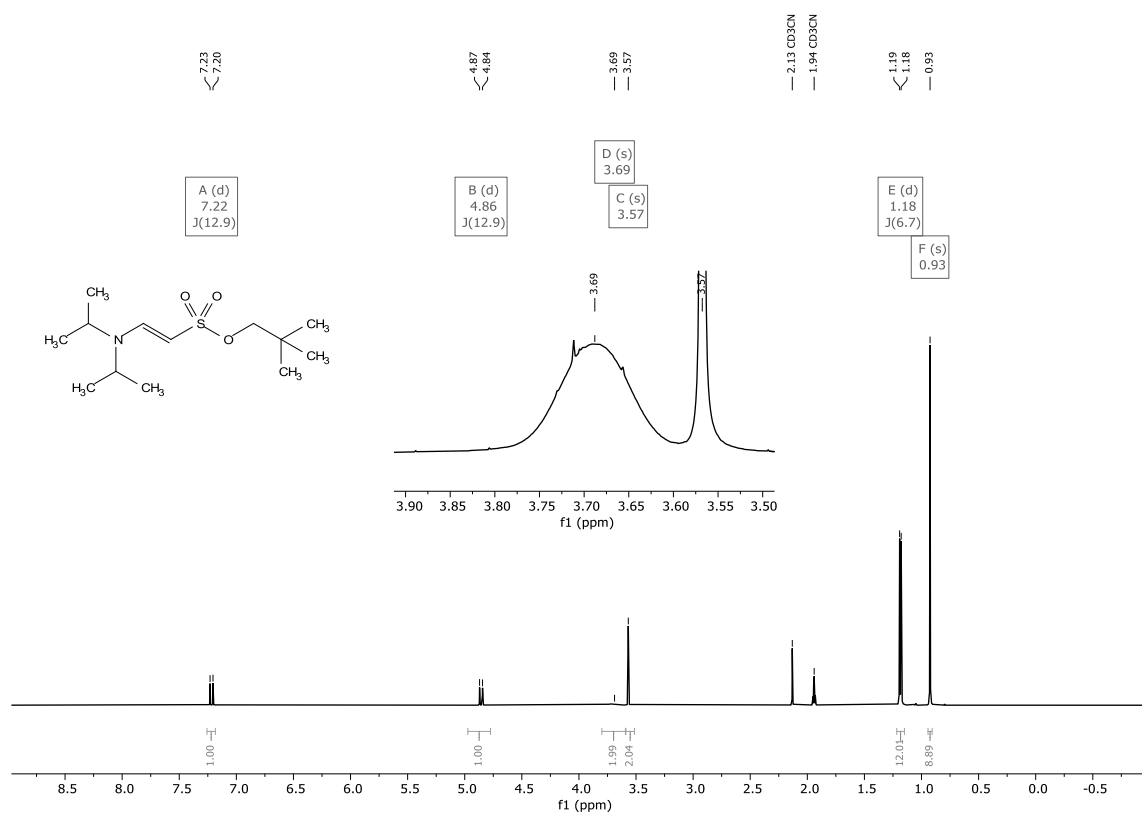
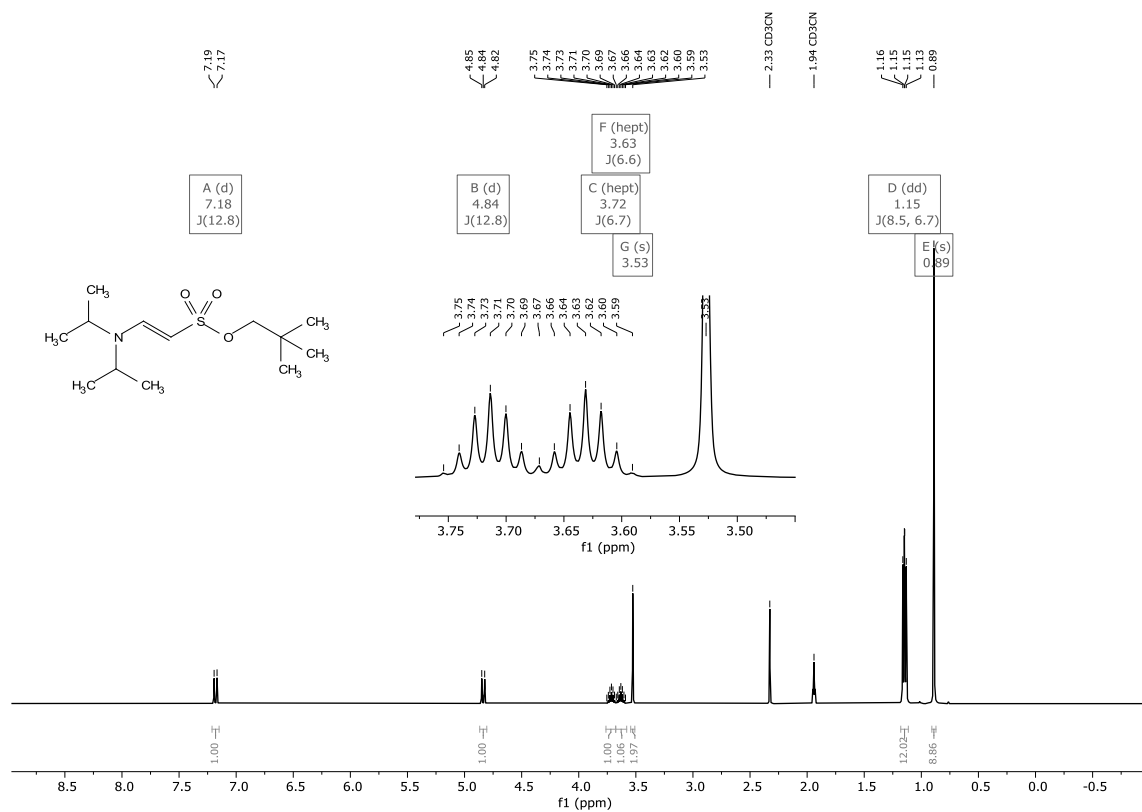


Figure S12: Molecular structure of neopentyl (*E*)-2-(2,2,6,6-tetramethylpiperidiny)ethene sulfonate (**3d**) as determined by single crystal X-ray analysis. The side chain of the Me₄-Piperidine unit is disordered on two positions. Refinement results in an occupation ratio of approx. 0.85/0.15. The ORTEP diagram is drawn at the 40% probability level.

8 NMR Spectra

Figure S13: ^1H NMR spectrum (500 MHz, 25°C, CD_3CN) of **3a**.Figure S14: ^1H NMR spectrum (500 MHz, -30°C, CD_3CN) of **3a**.

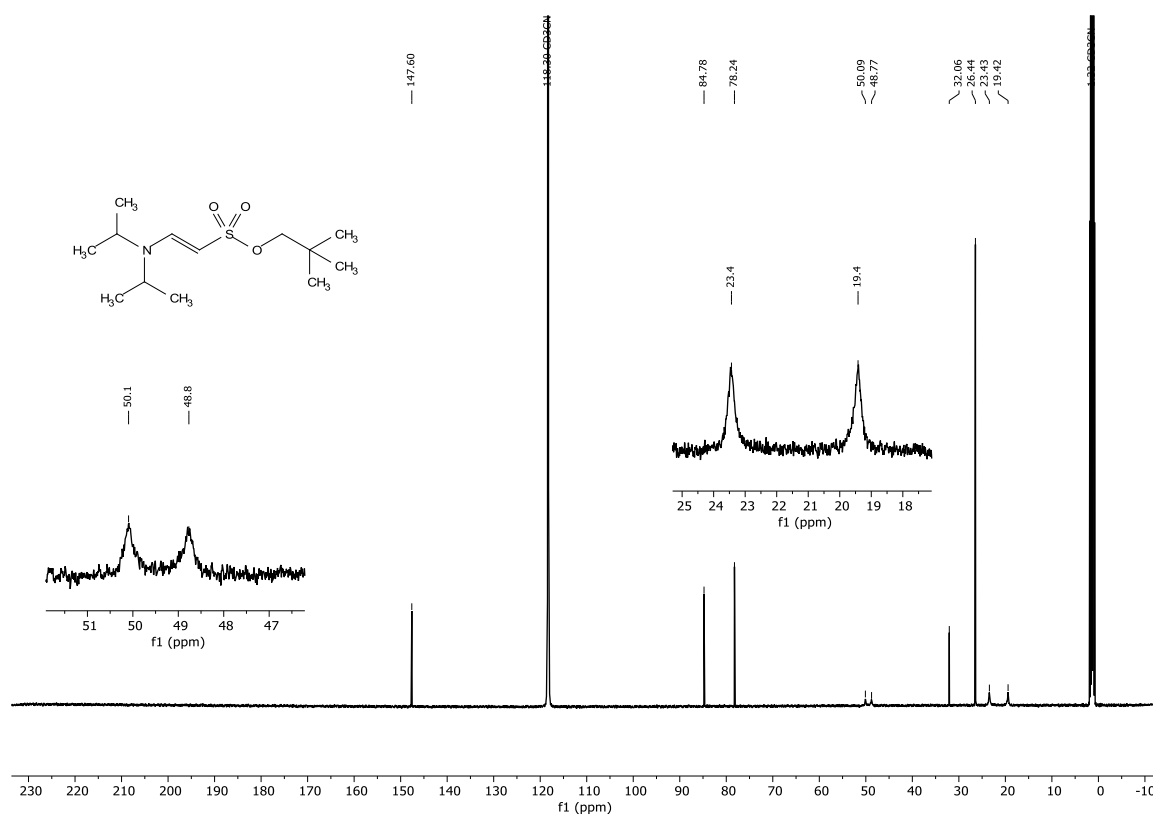
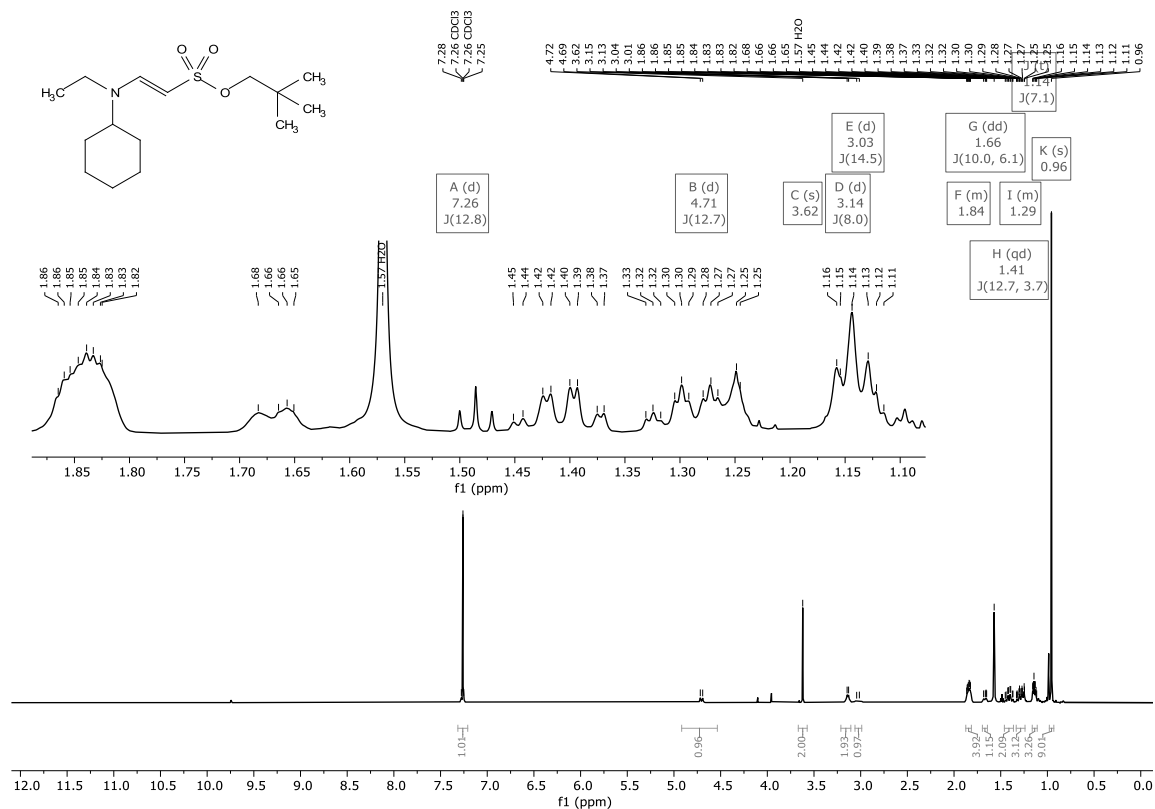
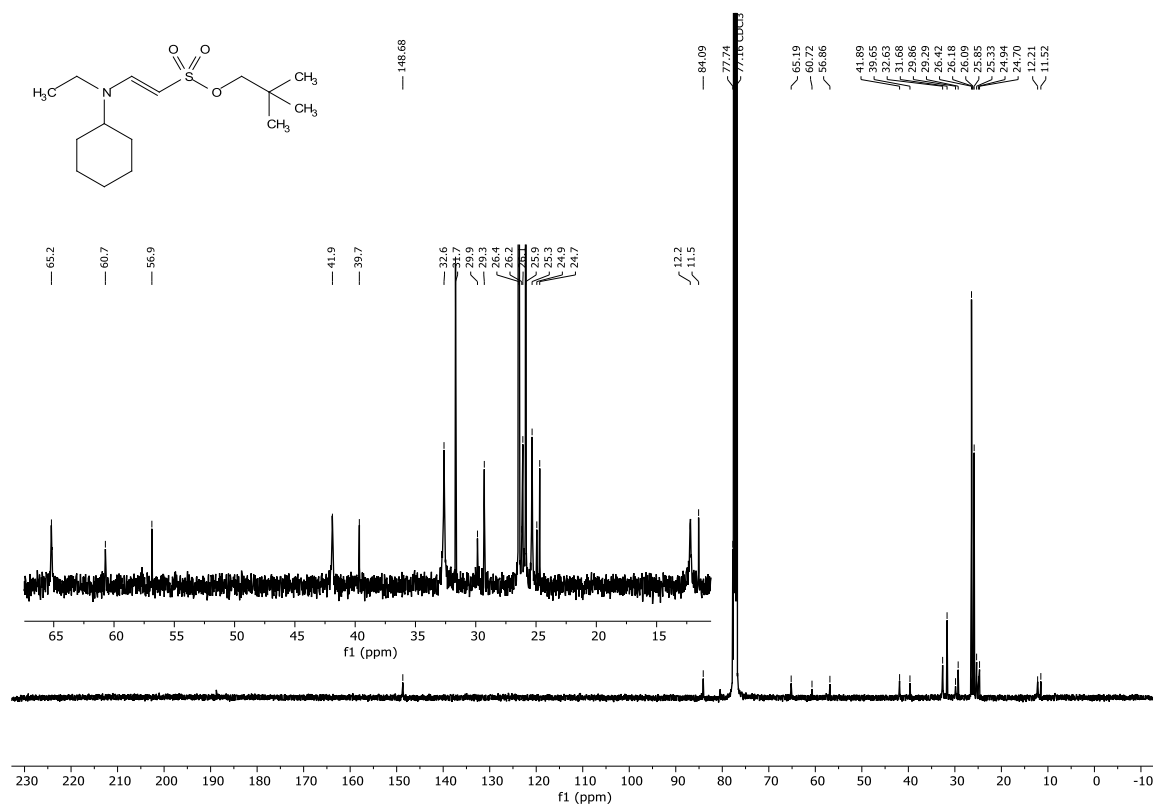
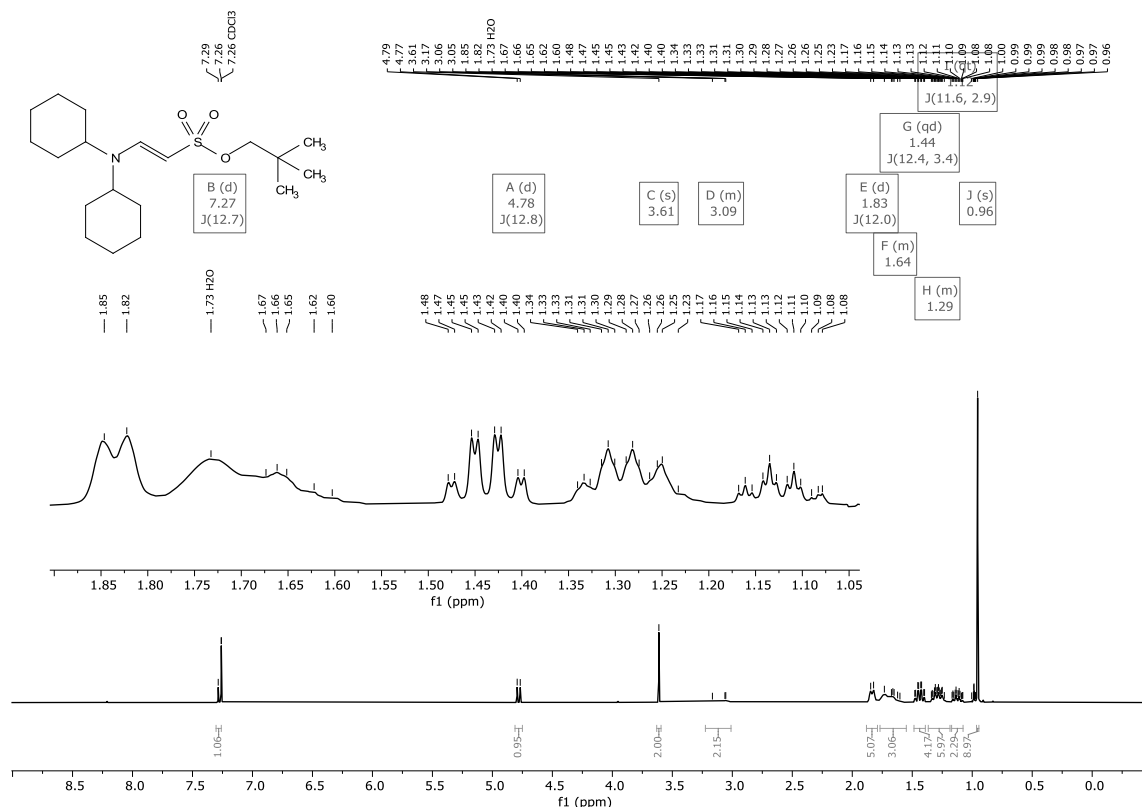
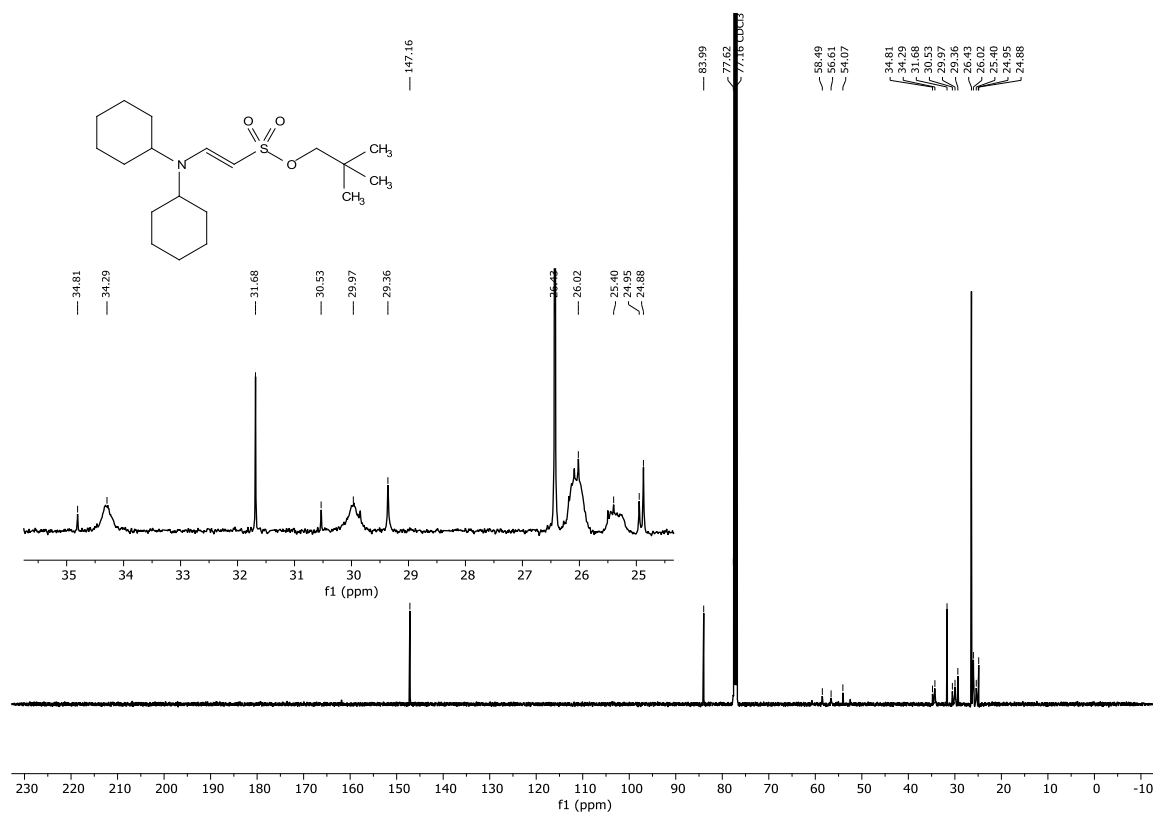
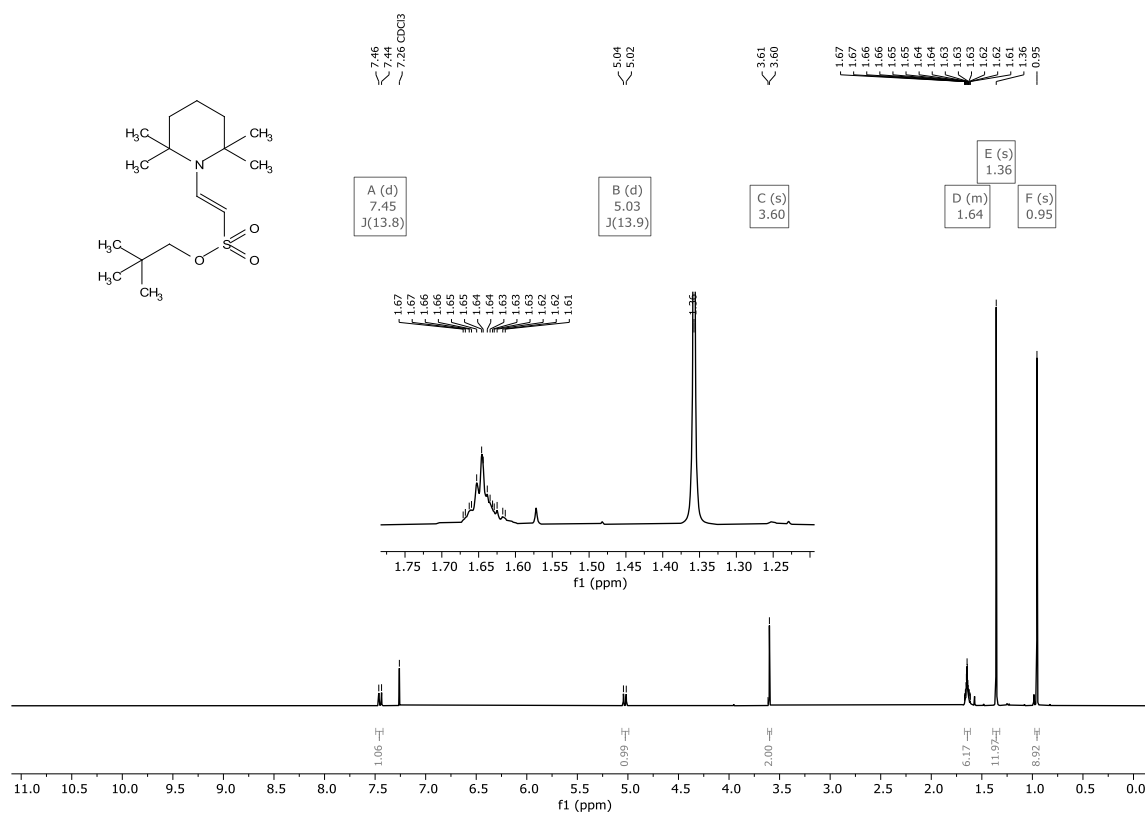
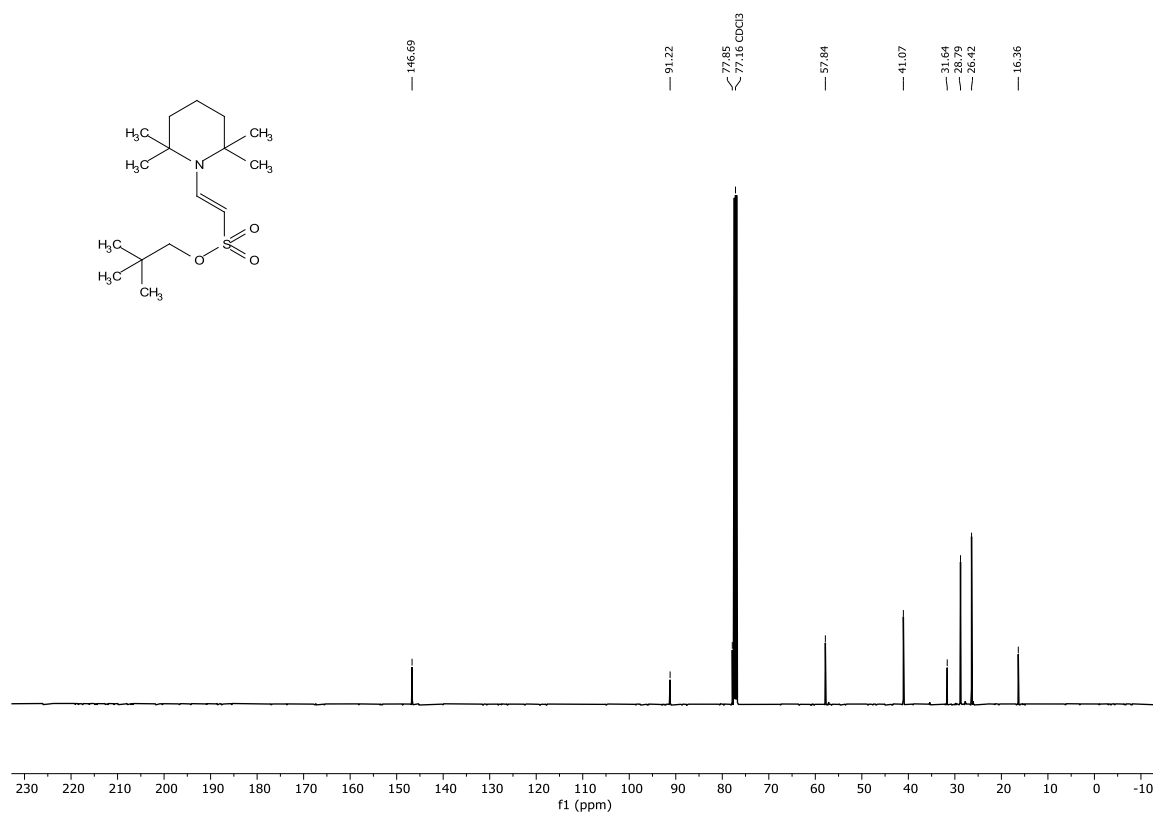
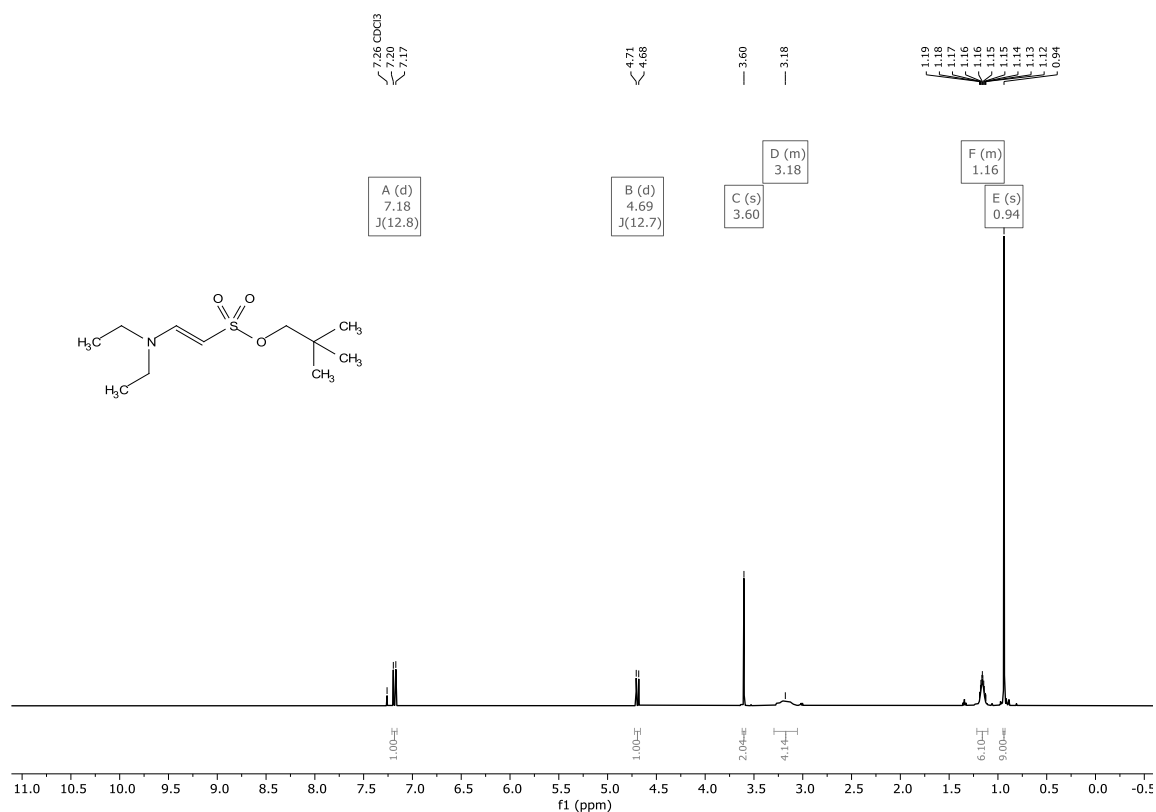
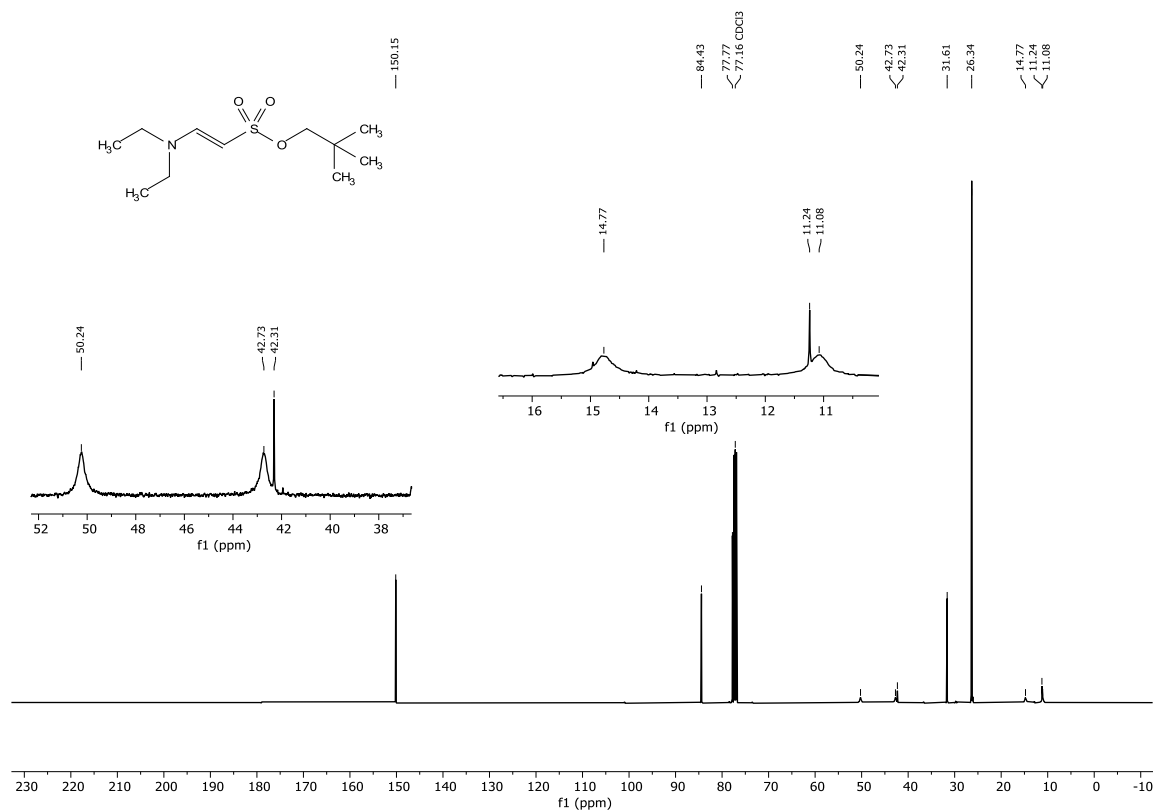


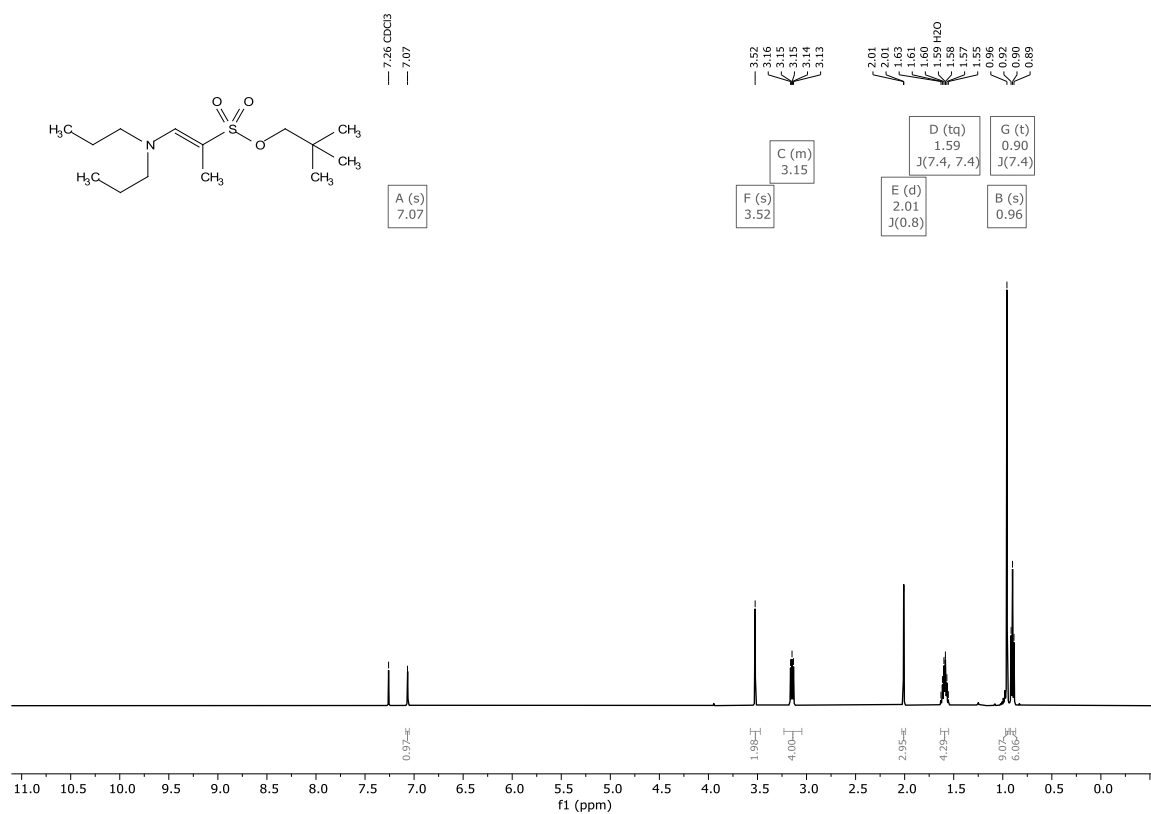
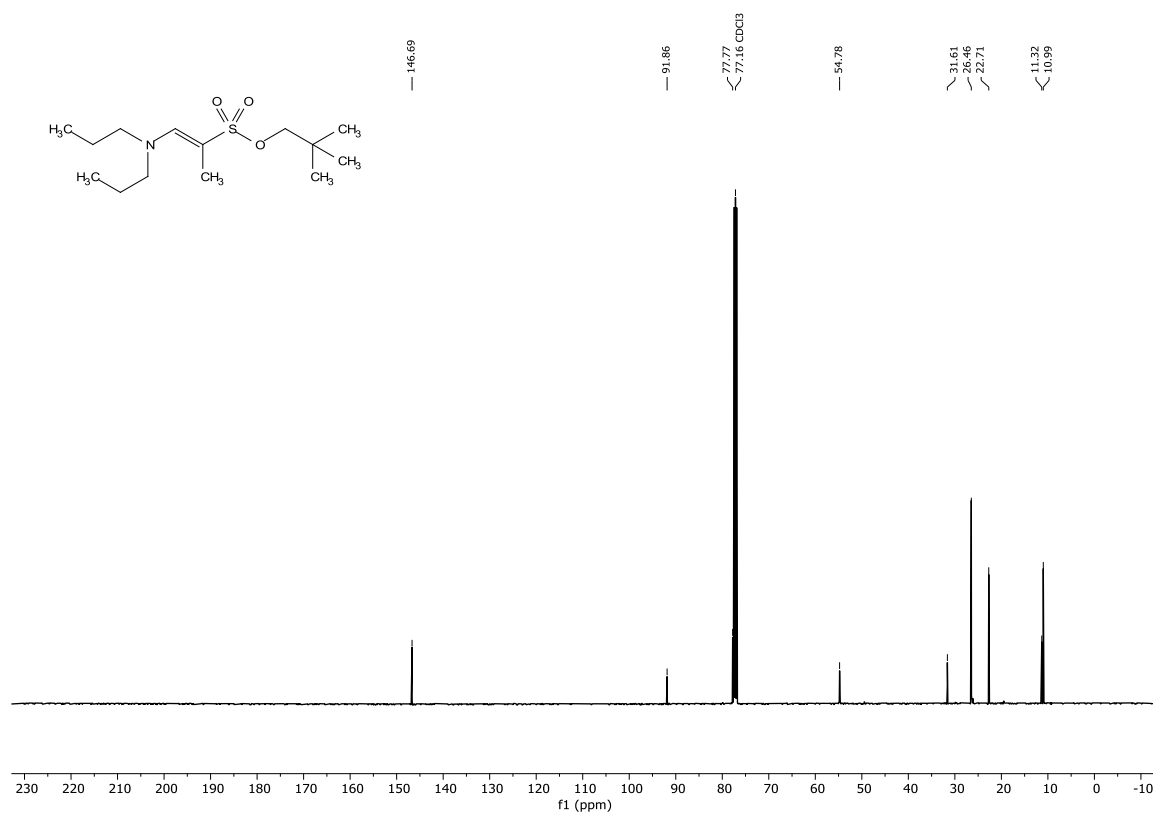
Figure S15: ¹³C NMR spectrum (126 MHz, 25°C, CD₃CN) of **3a**.

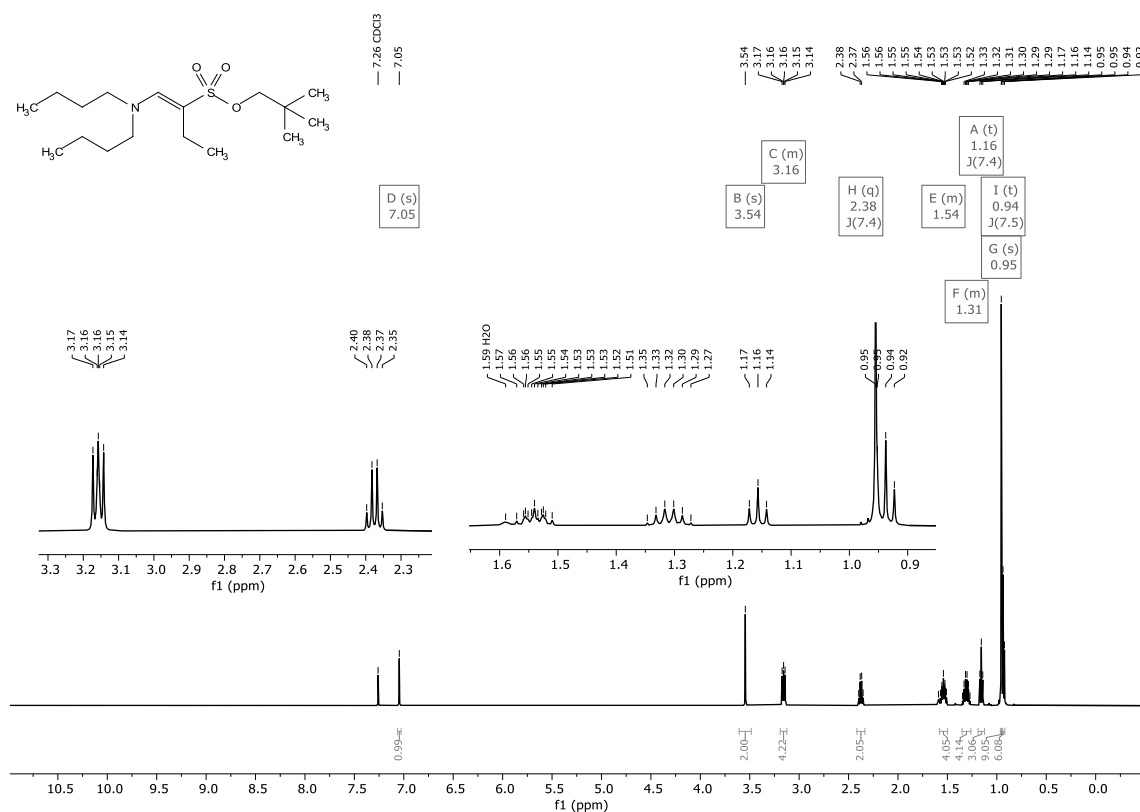
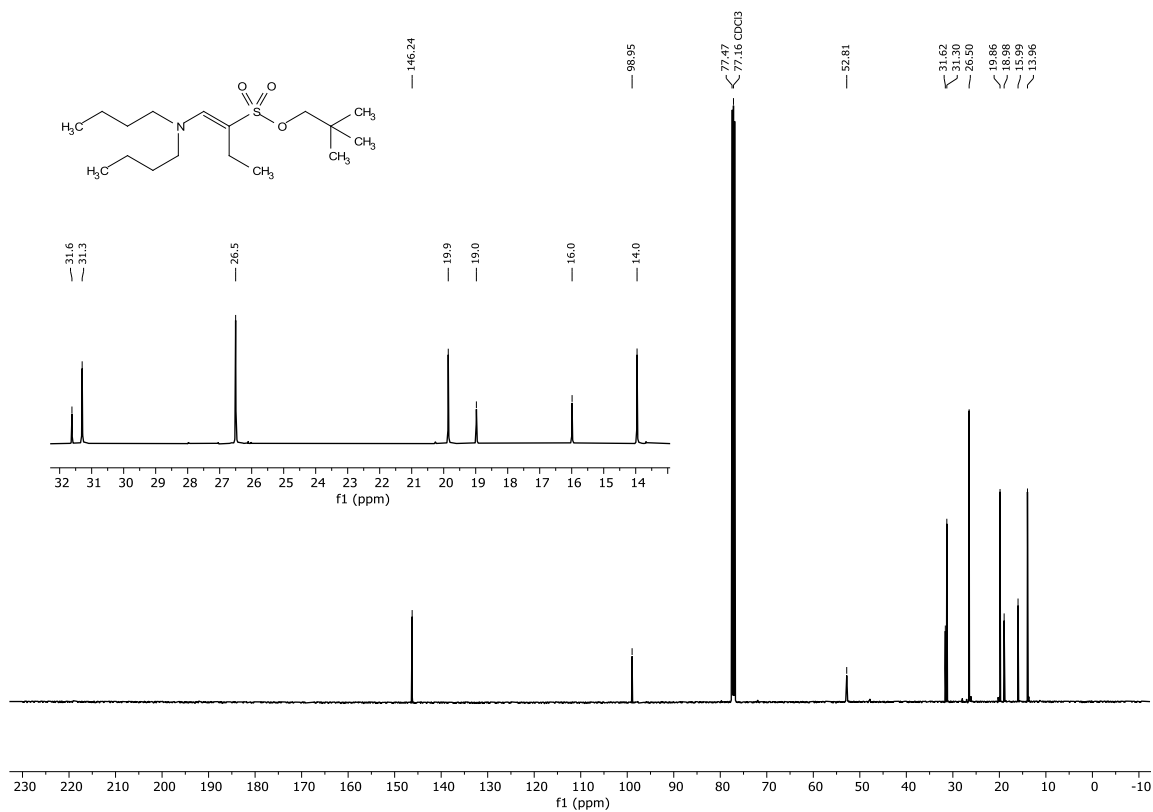
Figure S16: ¹H NMR spectrum (500 MHz, CDCl₃) of 3b.Figure S17: ¹³C NMR spectrum (126 MHz, CDCl₃) of 3b.

Figure S18: ^1H NMR spectrum (500 MHz, CDCl_3) of **3c**.Figure S19: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3c**.

Figure S20: ¹H NMR spectrum (500 MHz, CDCl₃) of **3d**.Figure S21: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3d**.

Figure S22: ¹H NMR spectrum (500 MHz, CDCl₃) of **3e**.Figure S23: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3e**.

Figure S24: ¹H NMR spectrum (500 MHz, CDCl₃) of **3f**.Figure S25: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3f**.

Figure S26: ¹H NMR spectrum (500 MHz, CDCl₃) of **3g**.Figure S27: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3g**.

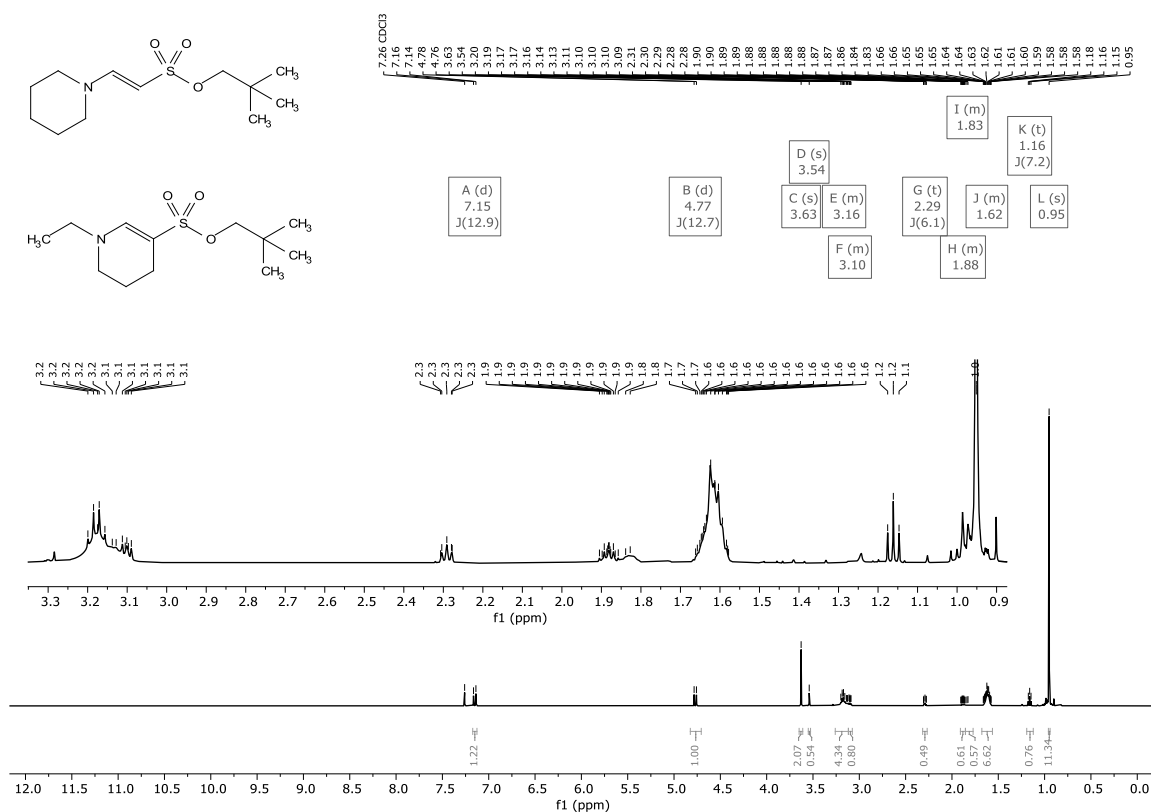


Figure S28: ¹H NMR spectrum (500 MHz, CDCl₃) of the product mixture of **3h-exo** and **3h-endo**.

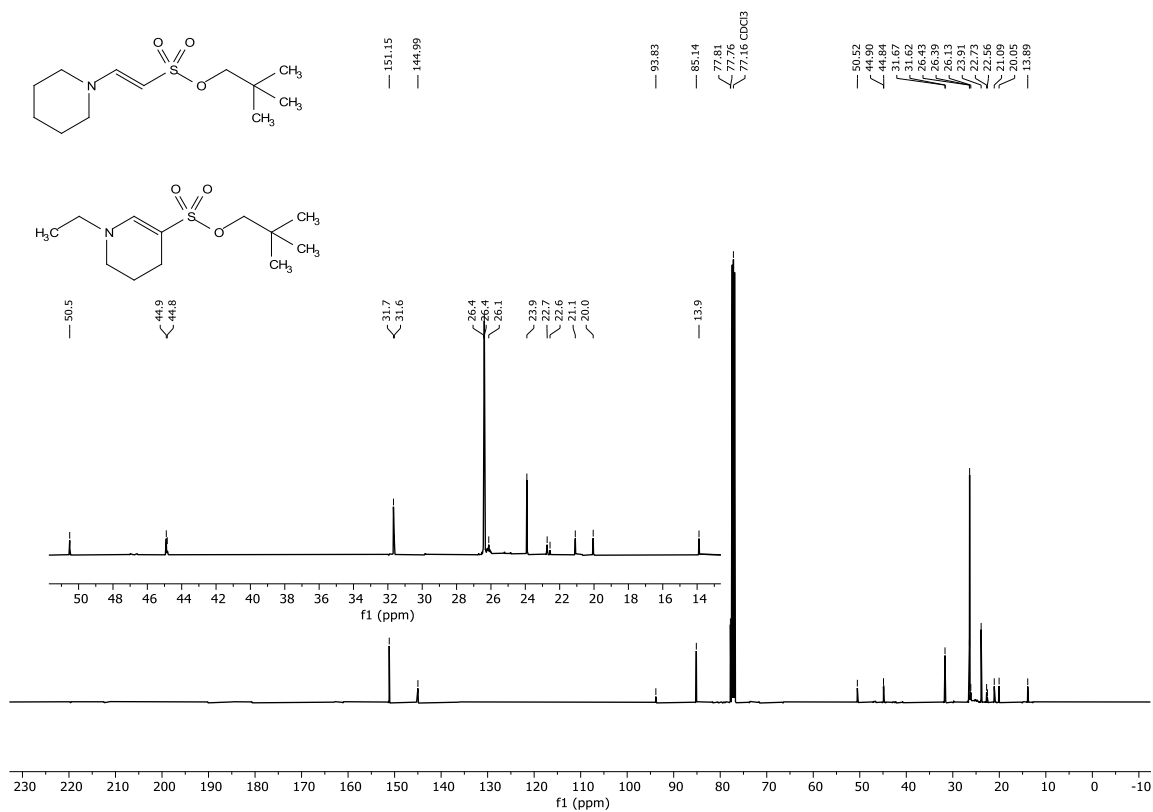
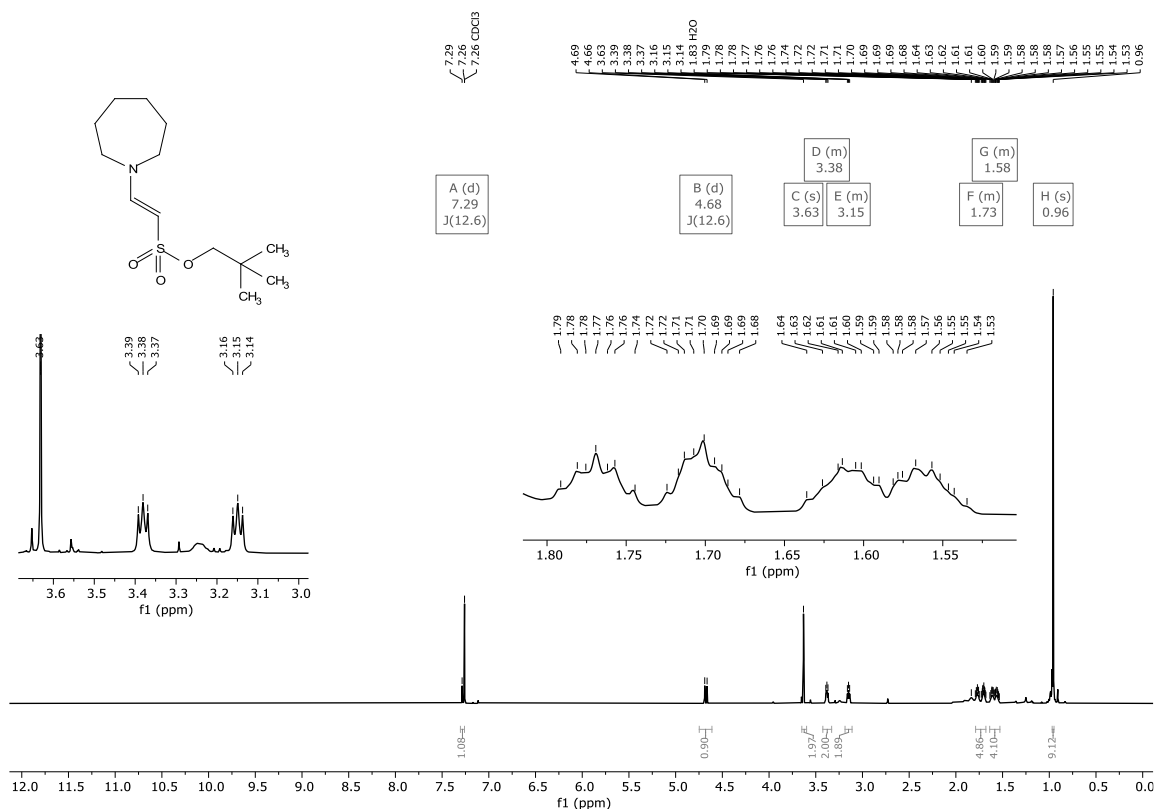
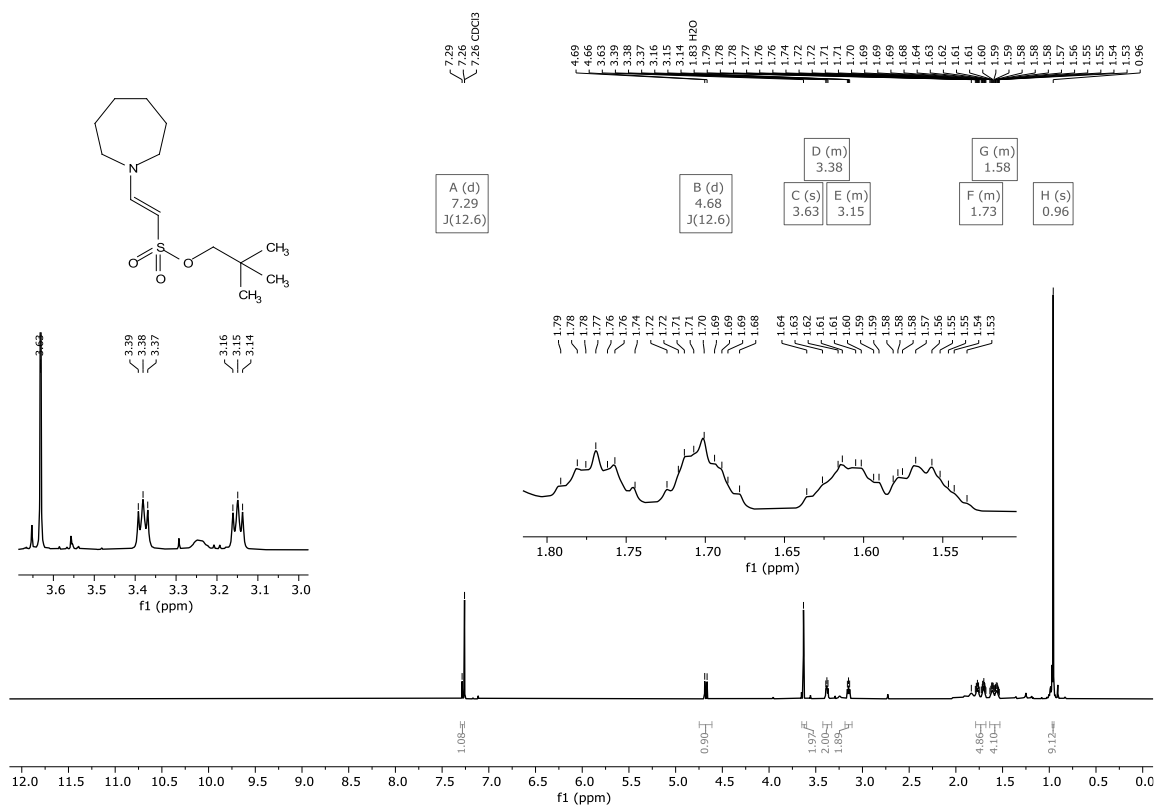
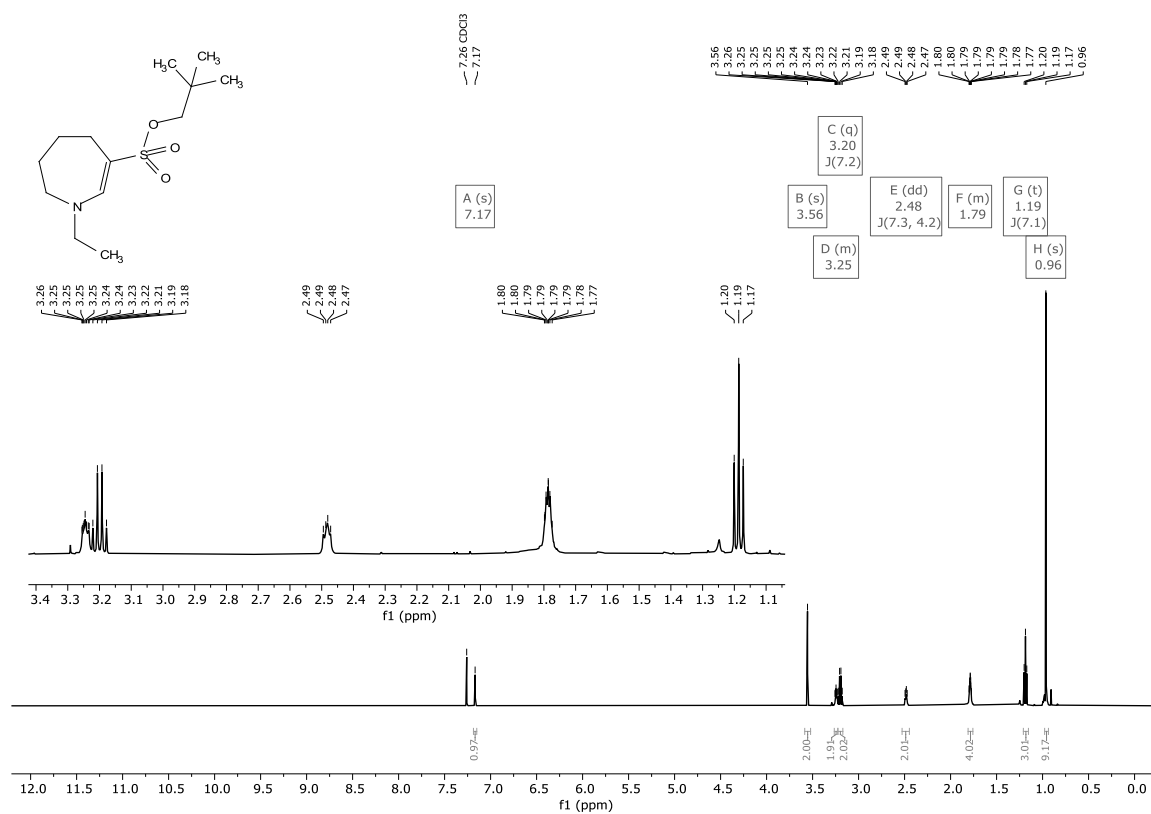
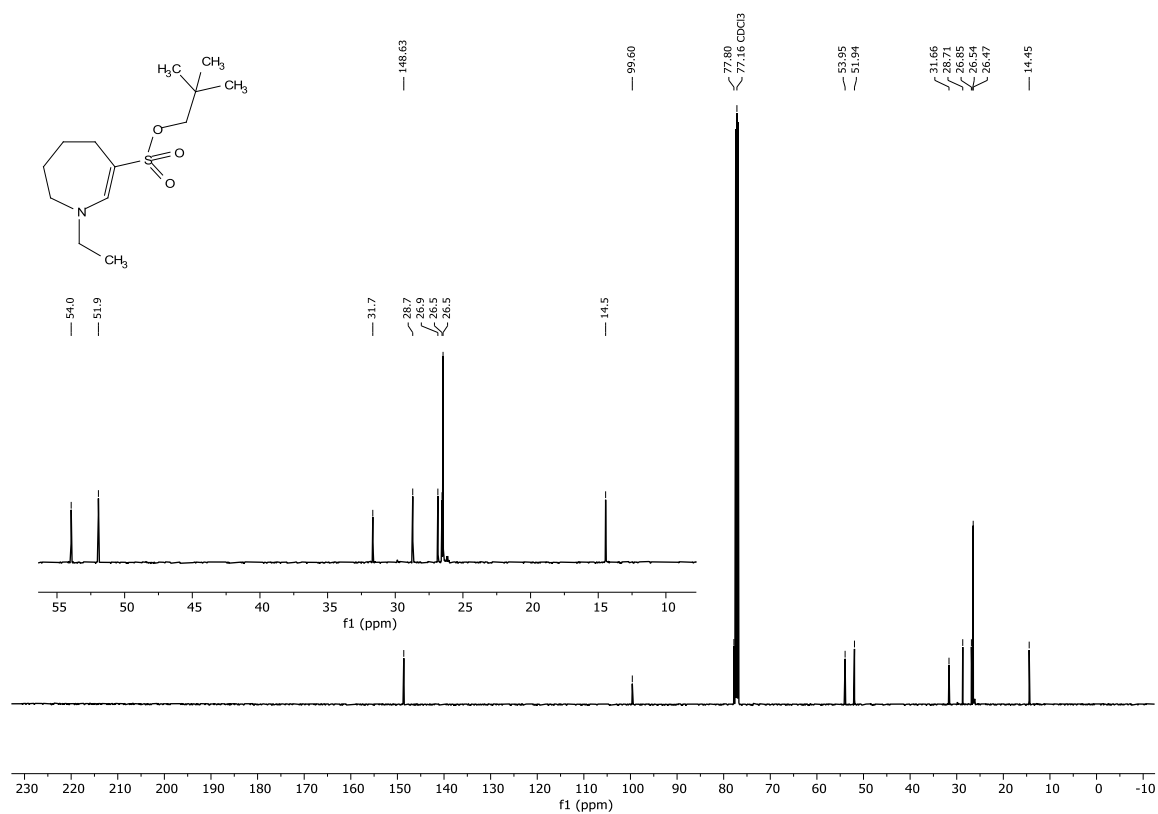
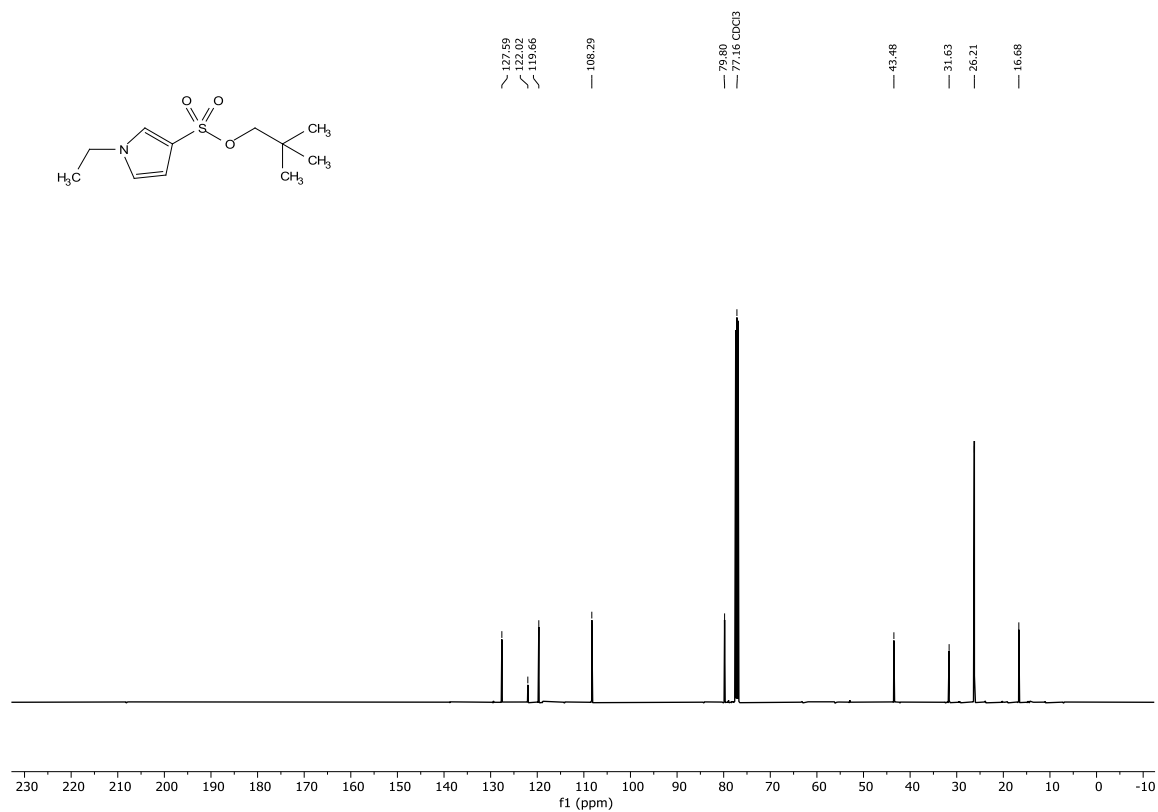
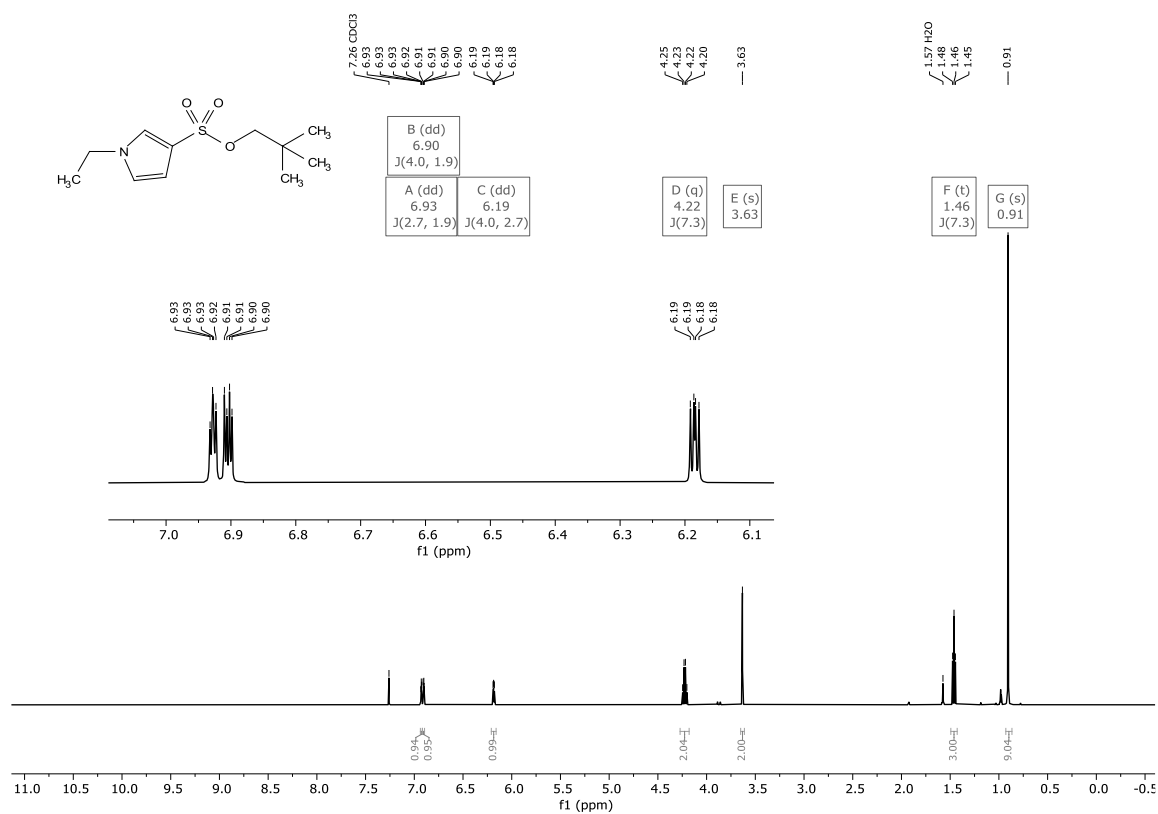


Figure S29: ¹³C NMR spectrum (126 MHz, CDCl₃) of the product mixture of **3h-exo** and **3h-endo**.

Figure S30: ¹H NMR spectrum (500 MHz, CDCl₃) of **3i-exo**.Figure S31: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3i-exo**.

Figure S32: ^1H NMR spectrum (500 MHz, CDCl_3) of **3i-endo**.Figure S33: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3i-endo**.



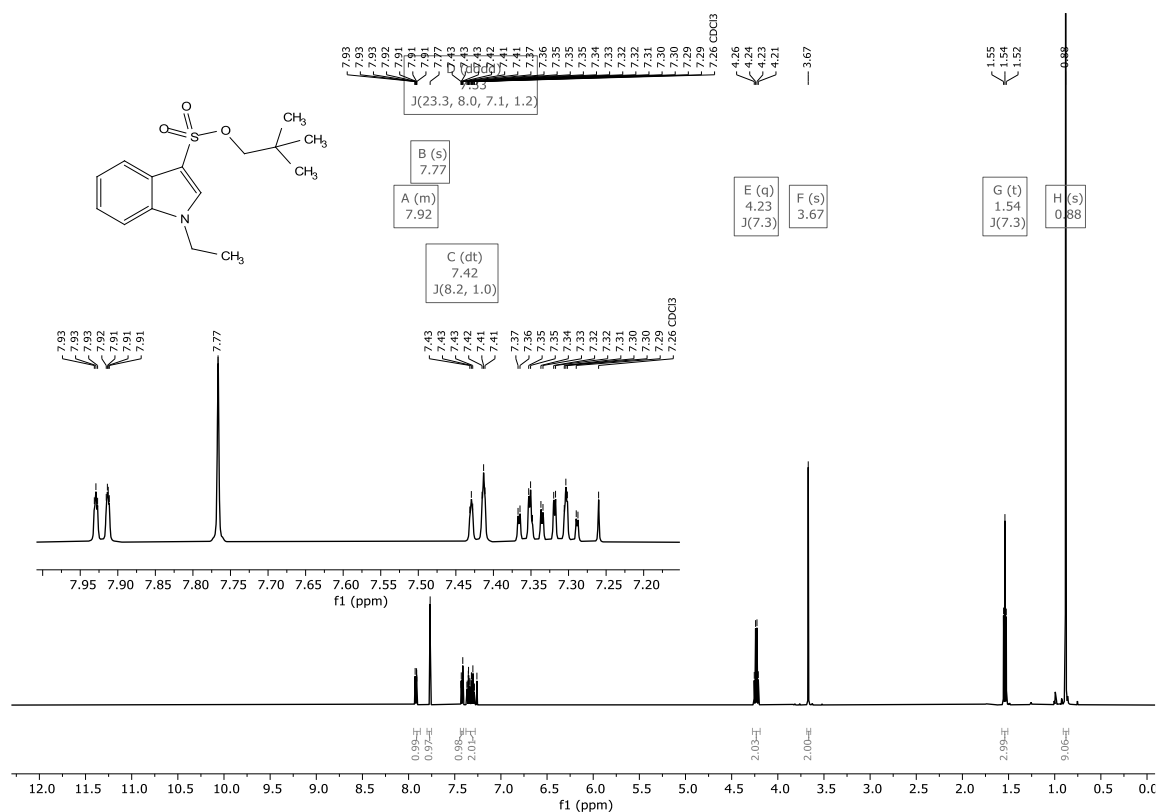


Figure S36: ^1H NMR spectrum (500 MHz, CDCl_3) of **3k**.

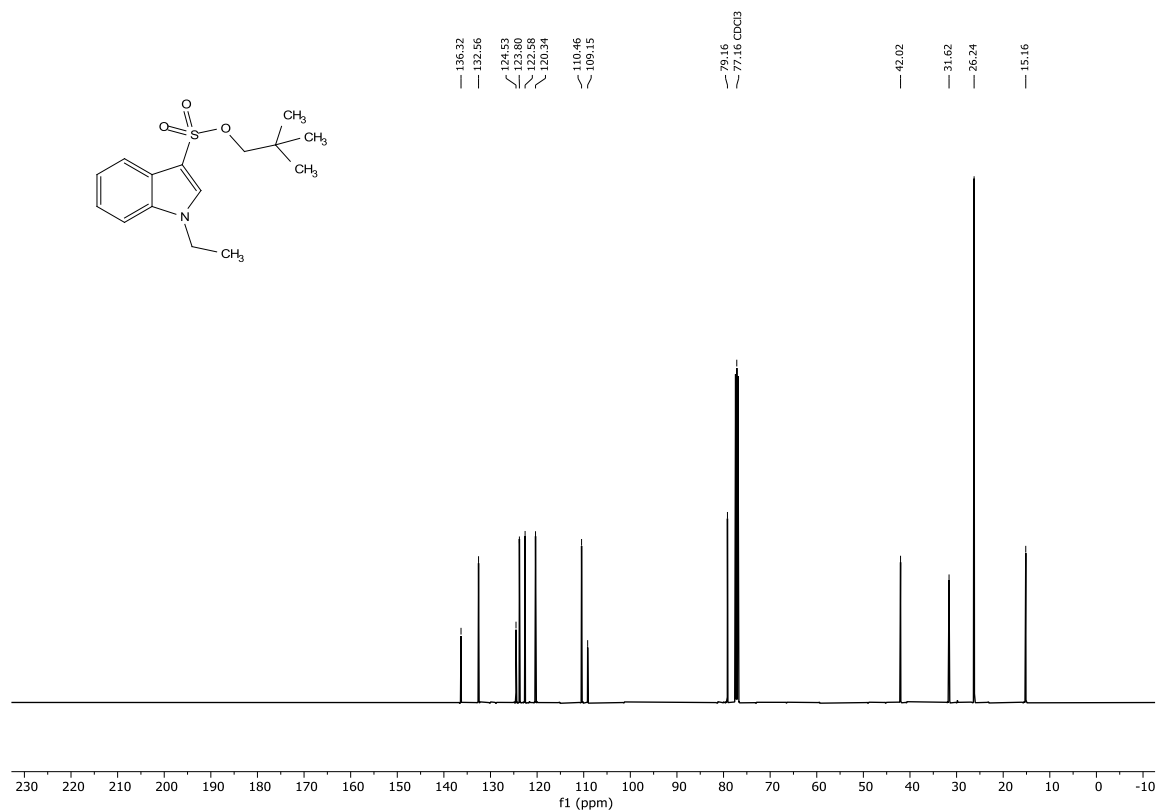
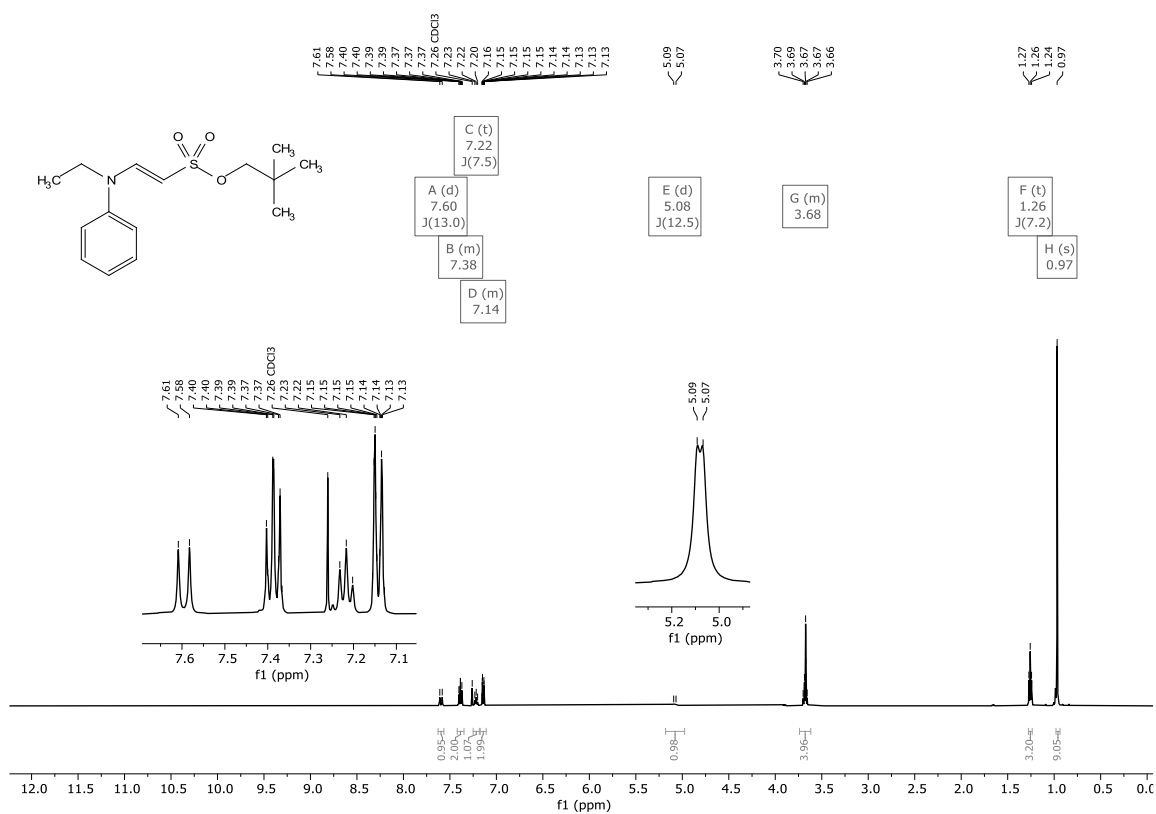
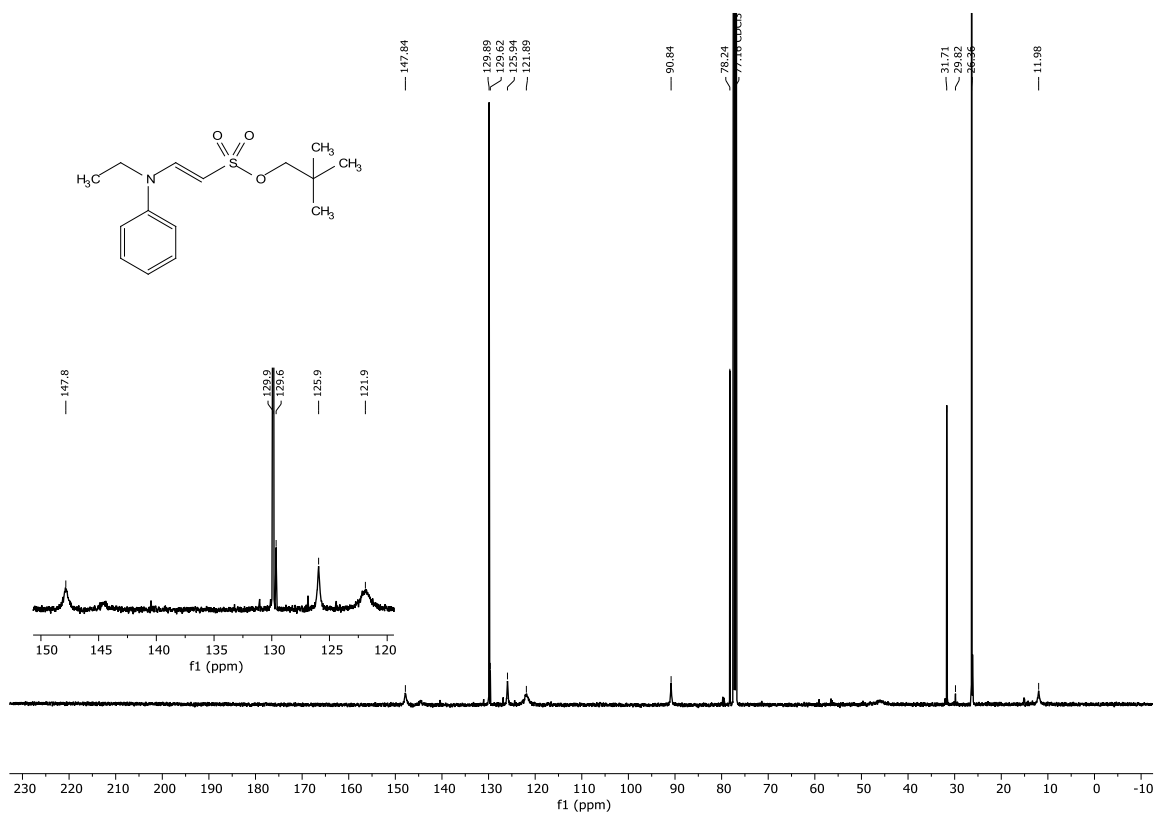


Figure S37: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3k**.

Figure S38: ¹H NMR spectrum (500 MHz, CDCl₃) of **3I**.Figure S39: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3I**.

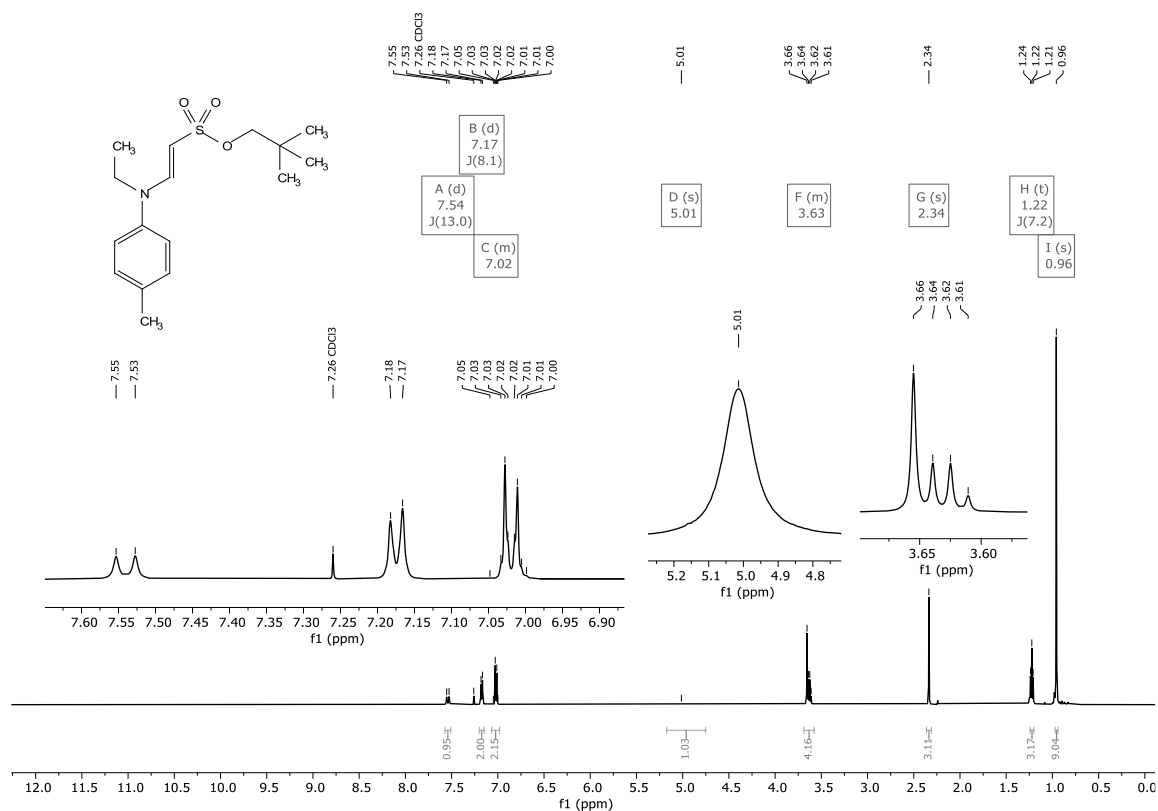
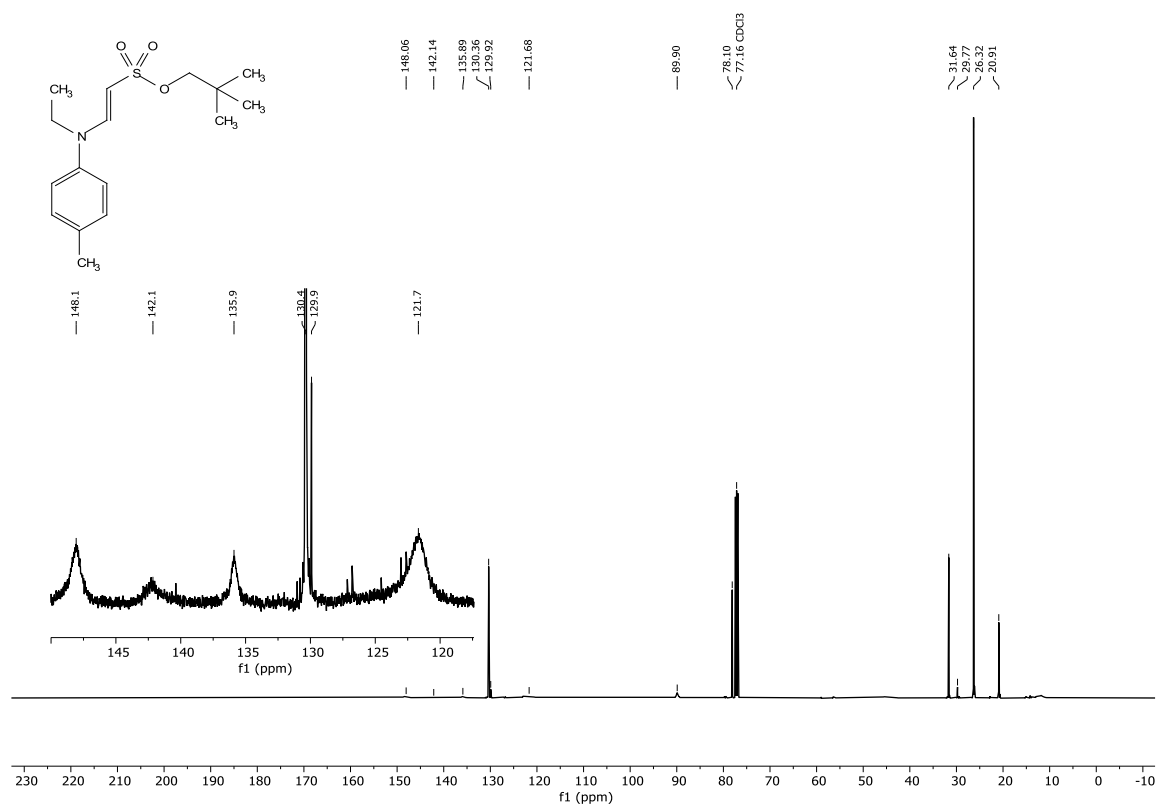
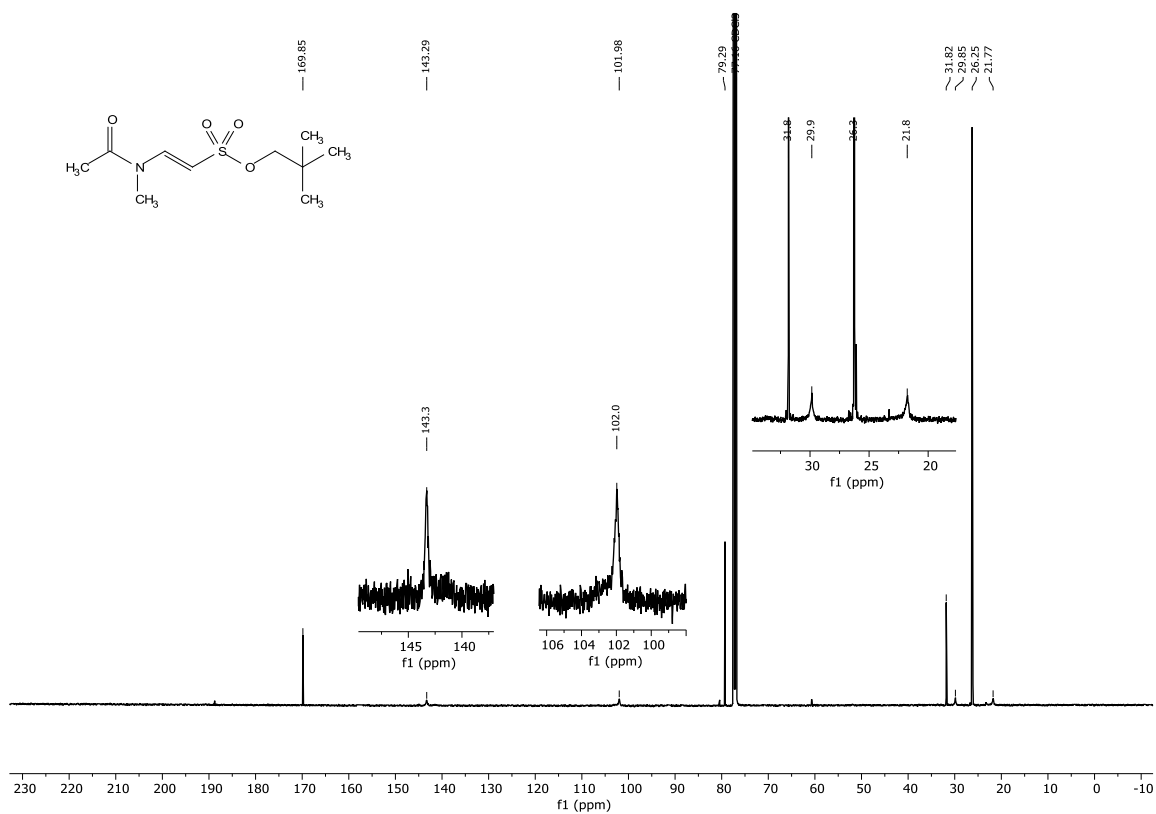
Figure S40: ¹H NMR spectrum (500 MHz, CDCl₃) of 3m.Figure S41: ¹³C NMR spectrum (126 MHz, CDCl₃) of 3m.

Figure S42: ¹H NMR spectrum (500 MHz, CDCl₃) of **3n**.Figure S43: ¹³C NMR spectrum (126 MHz, CDCl₃) of **3n**.

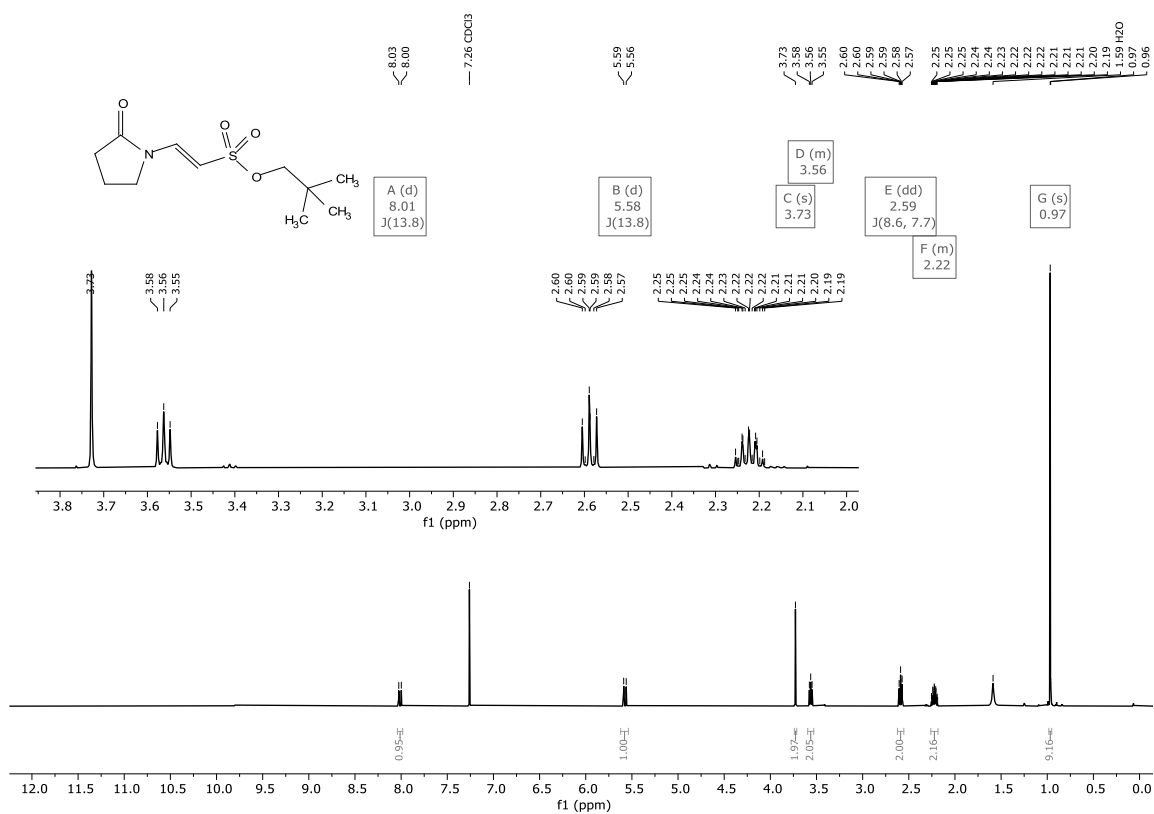


Figure S44: ^1H NMR spectrum (500 MHz, CDCl_3) of **3o**.

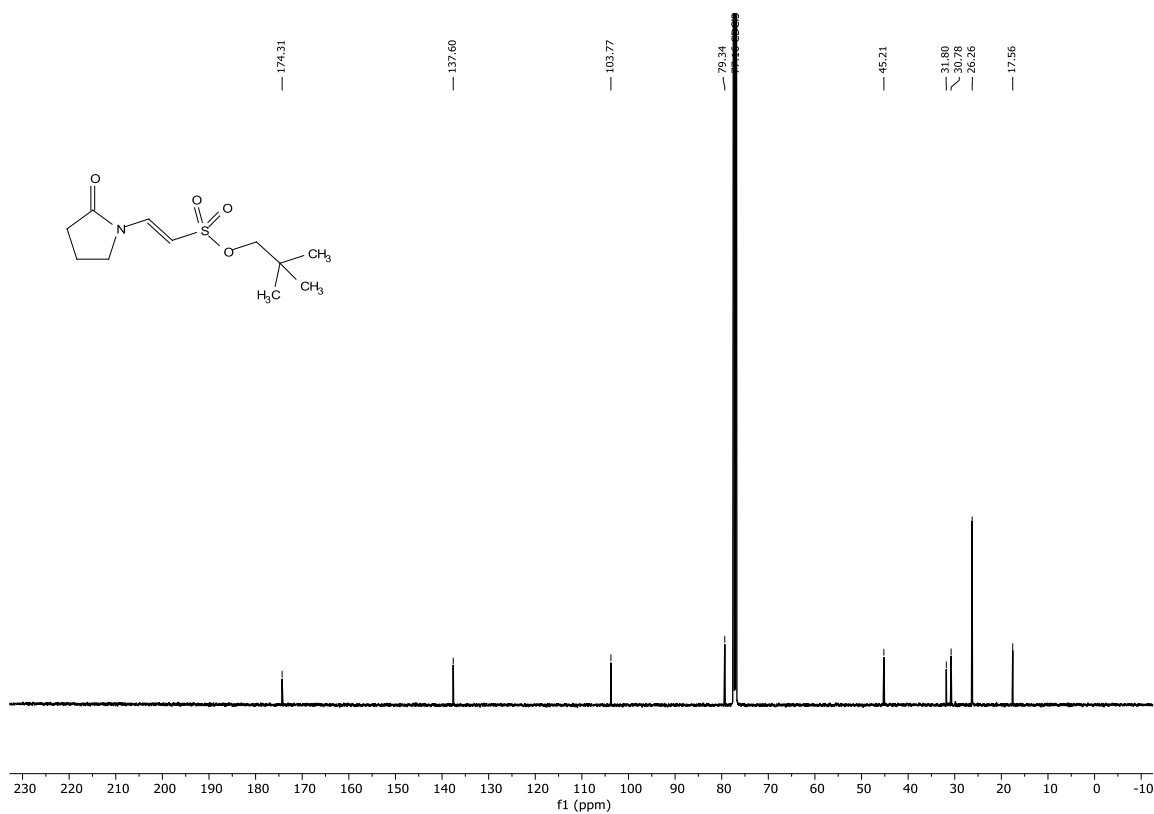


Figure S45: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3o**.

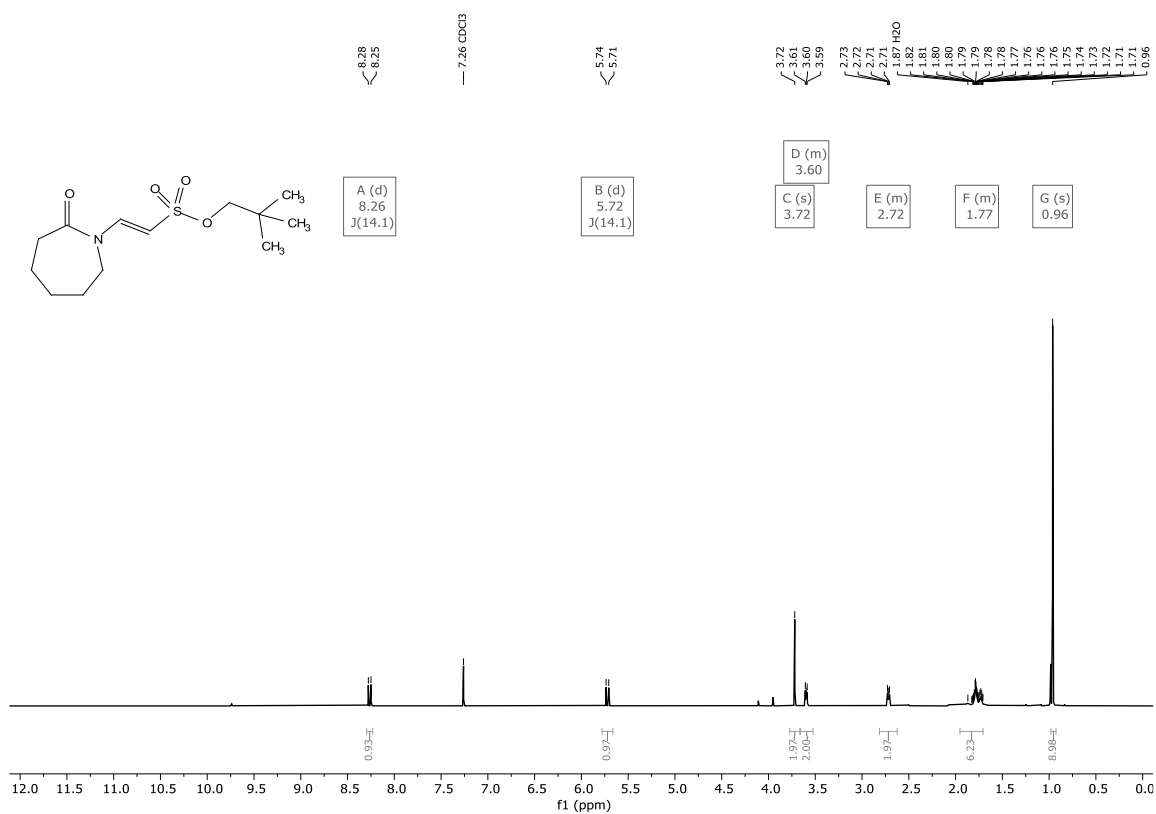


Figure S46: ^1H NMR spectrum (500 MHz, CDCl_3) of **3p**.

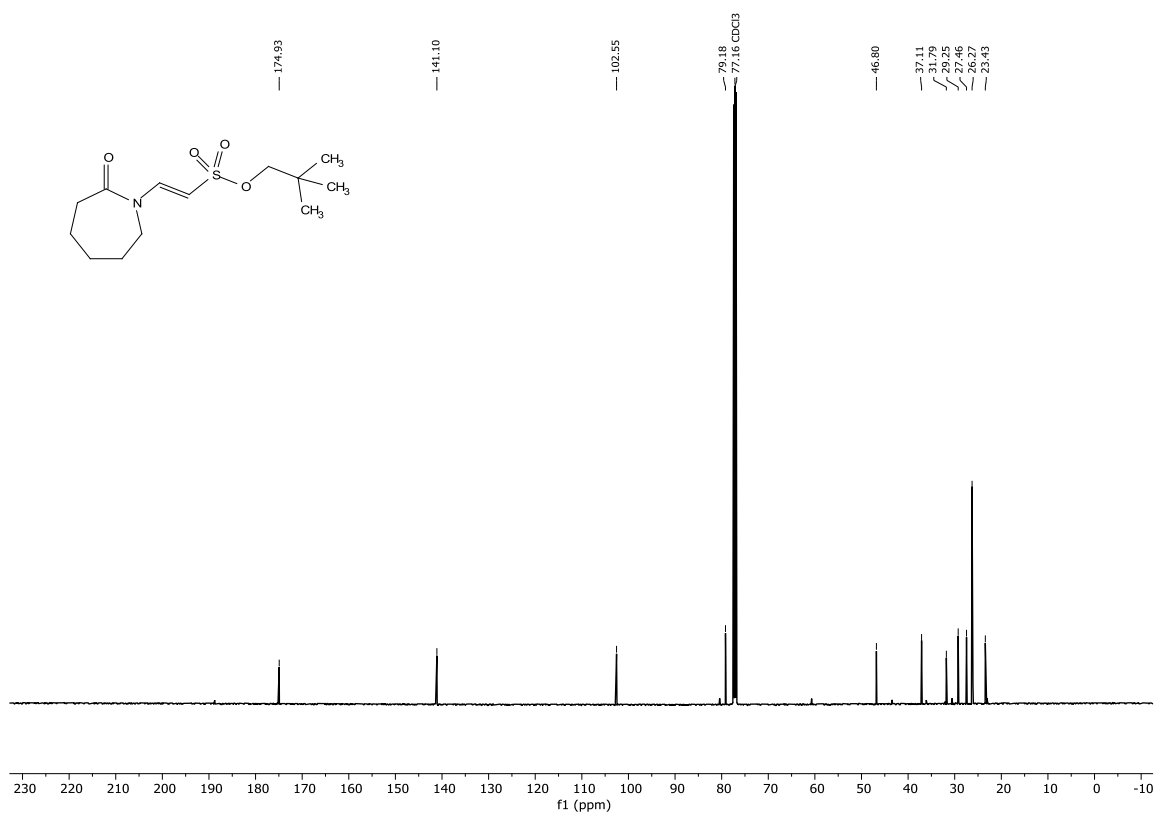
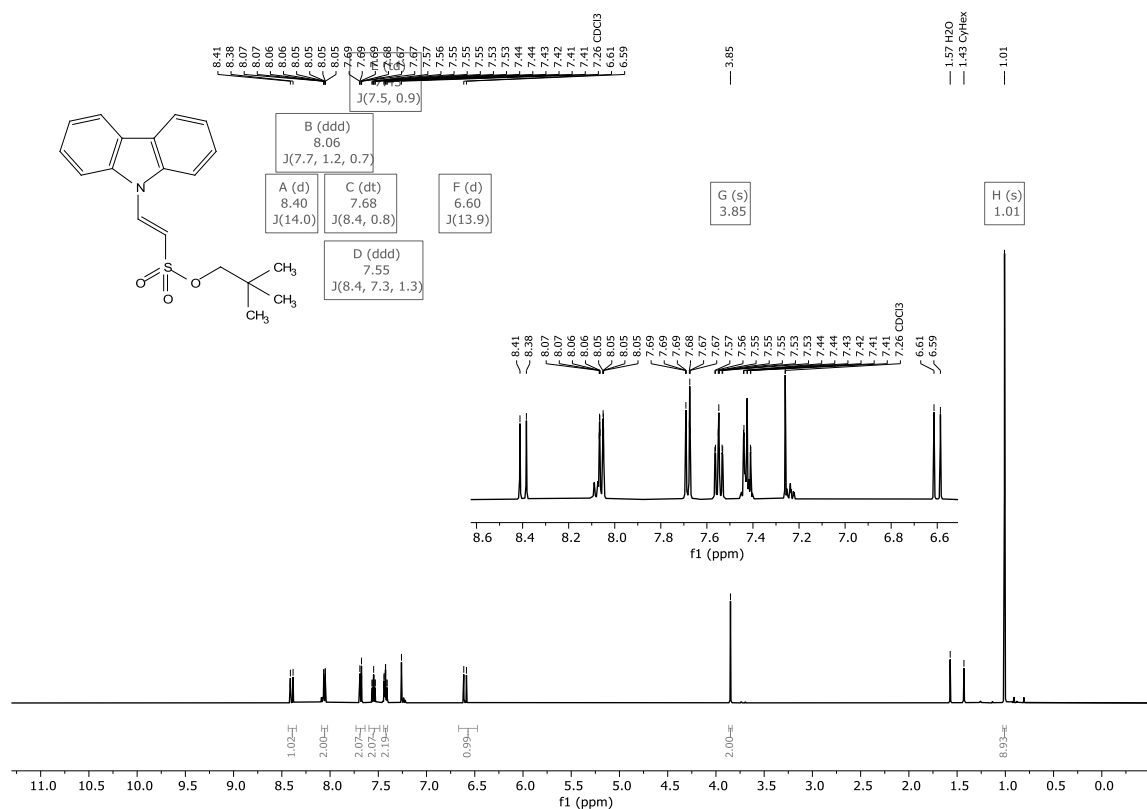
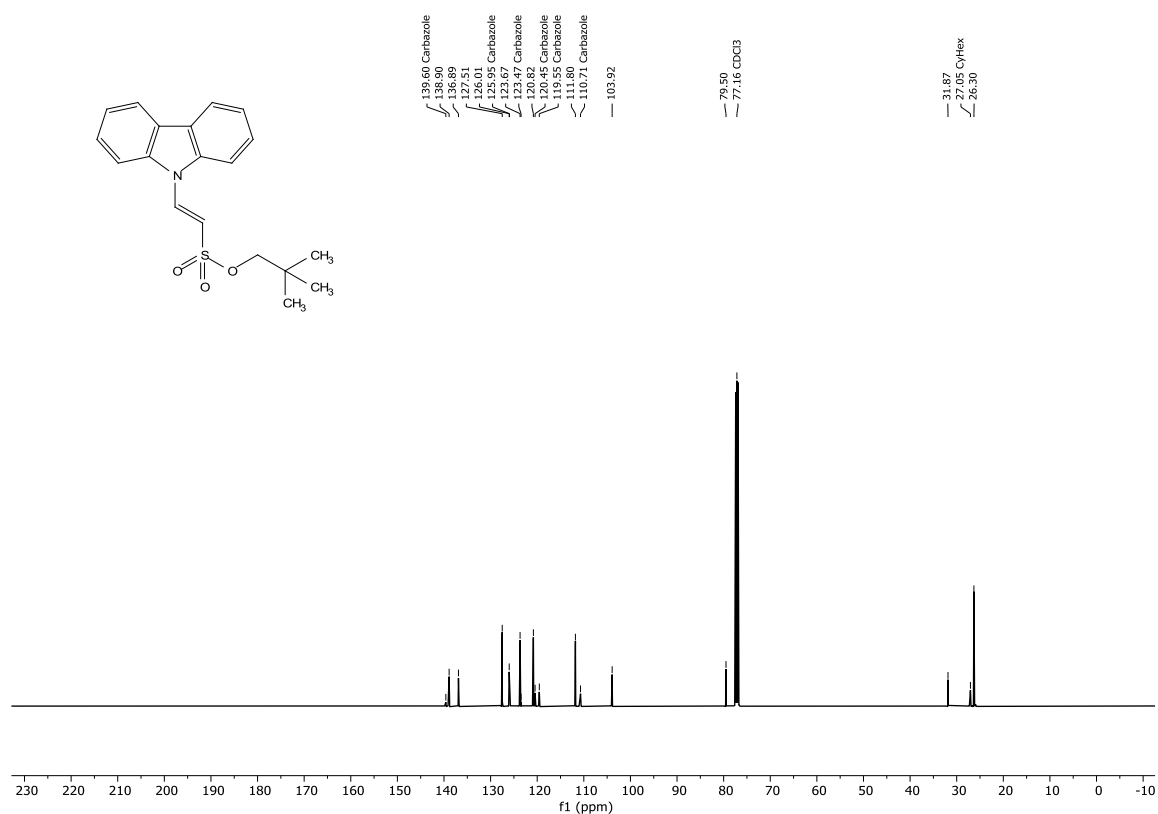
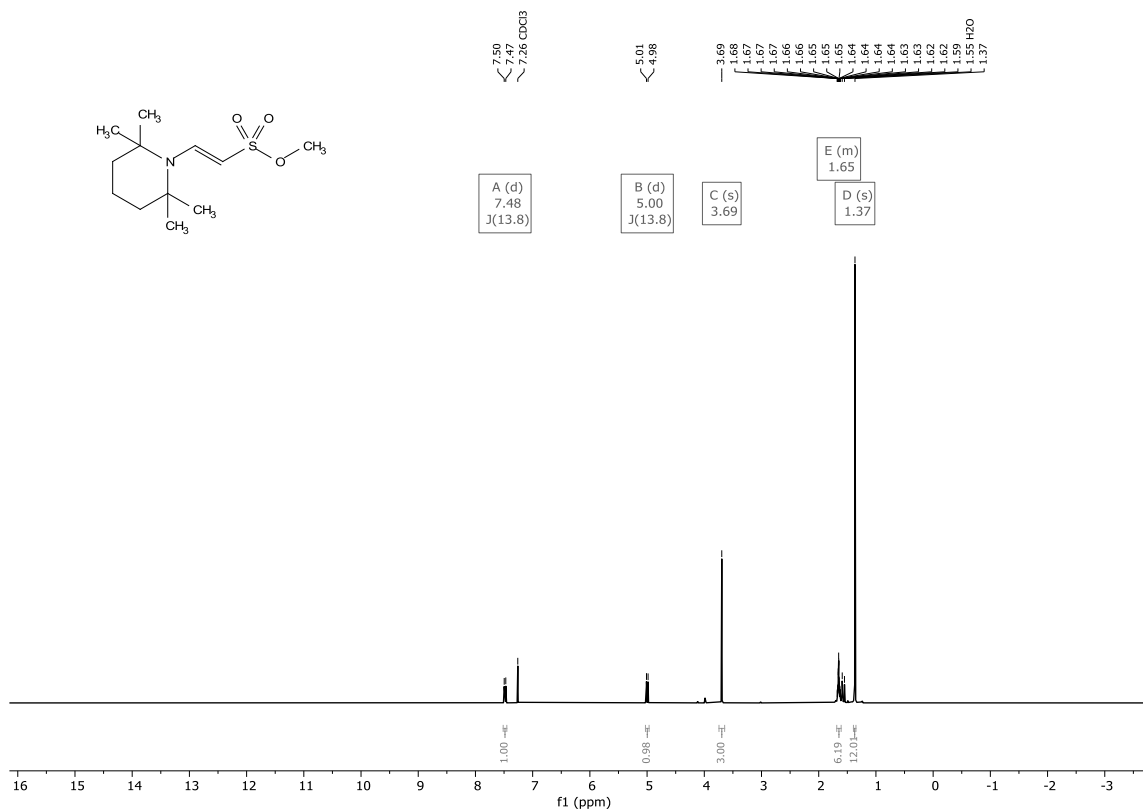
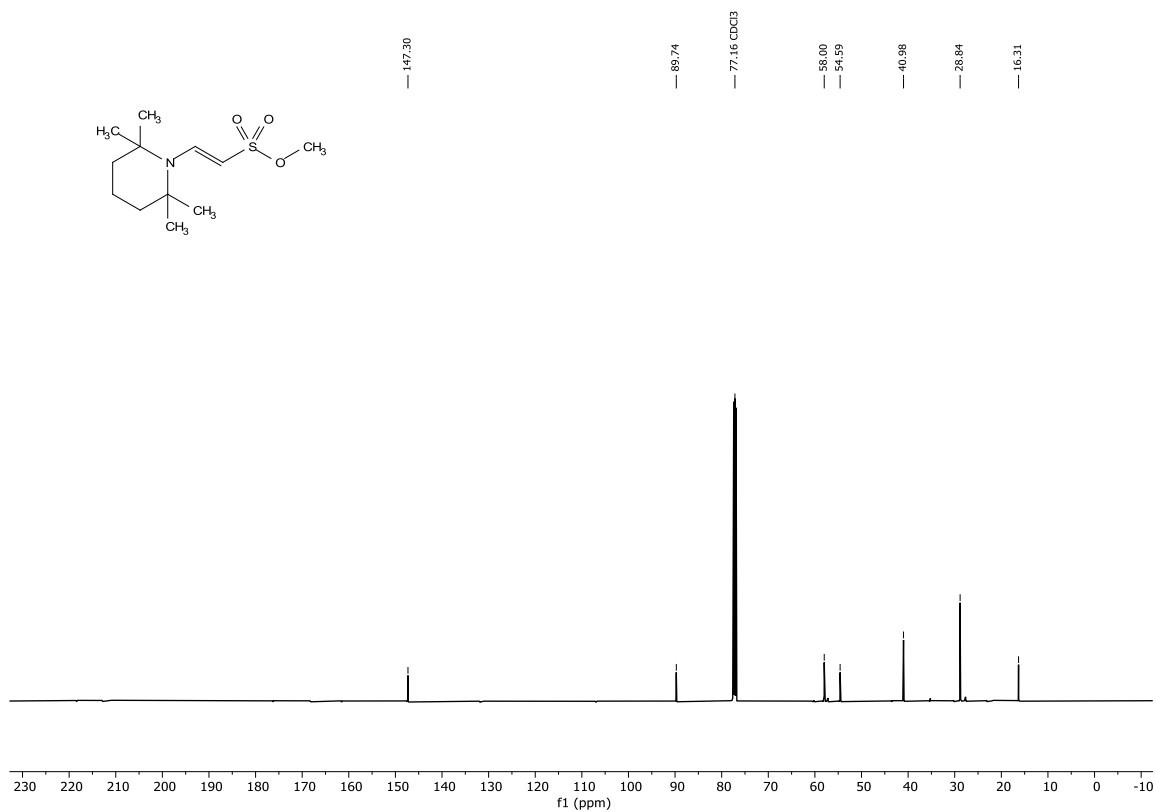
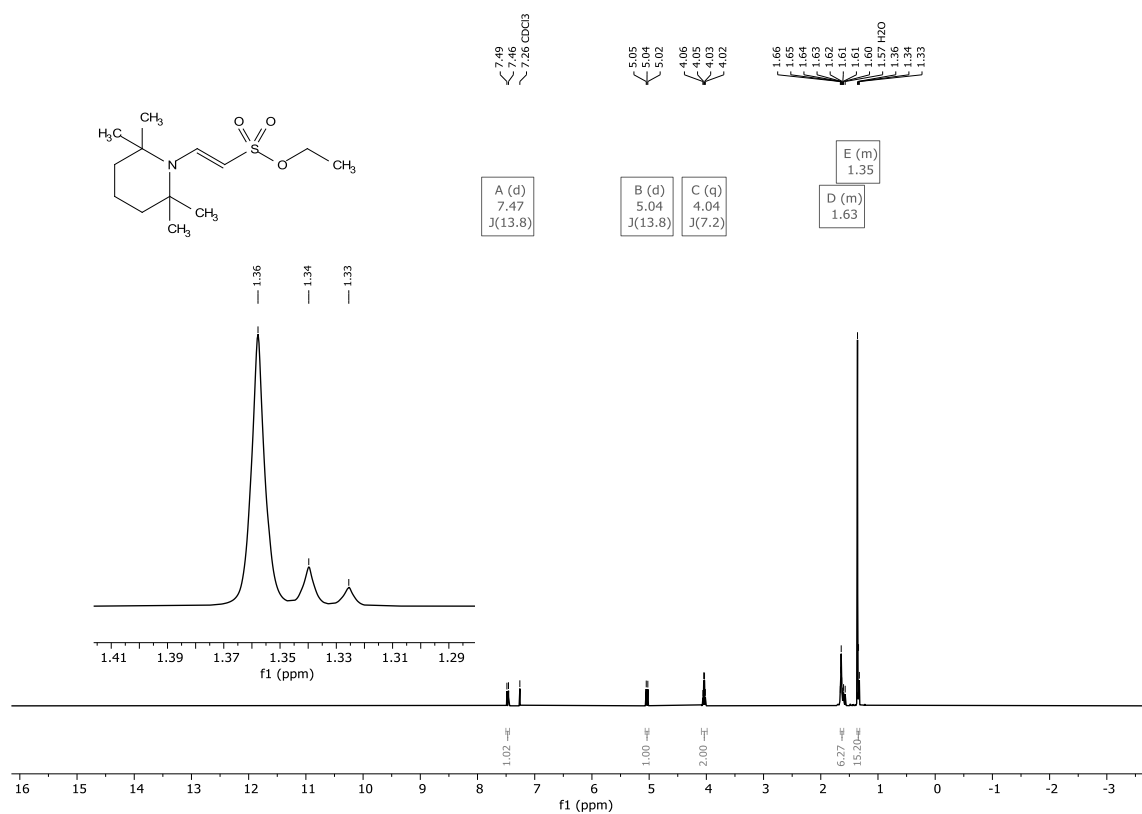
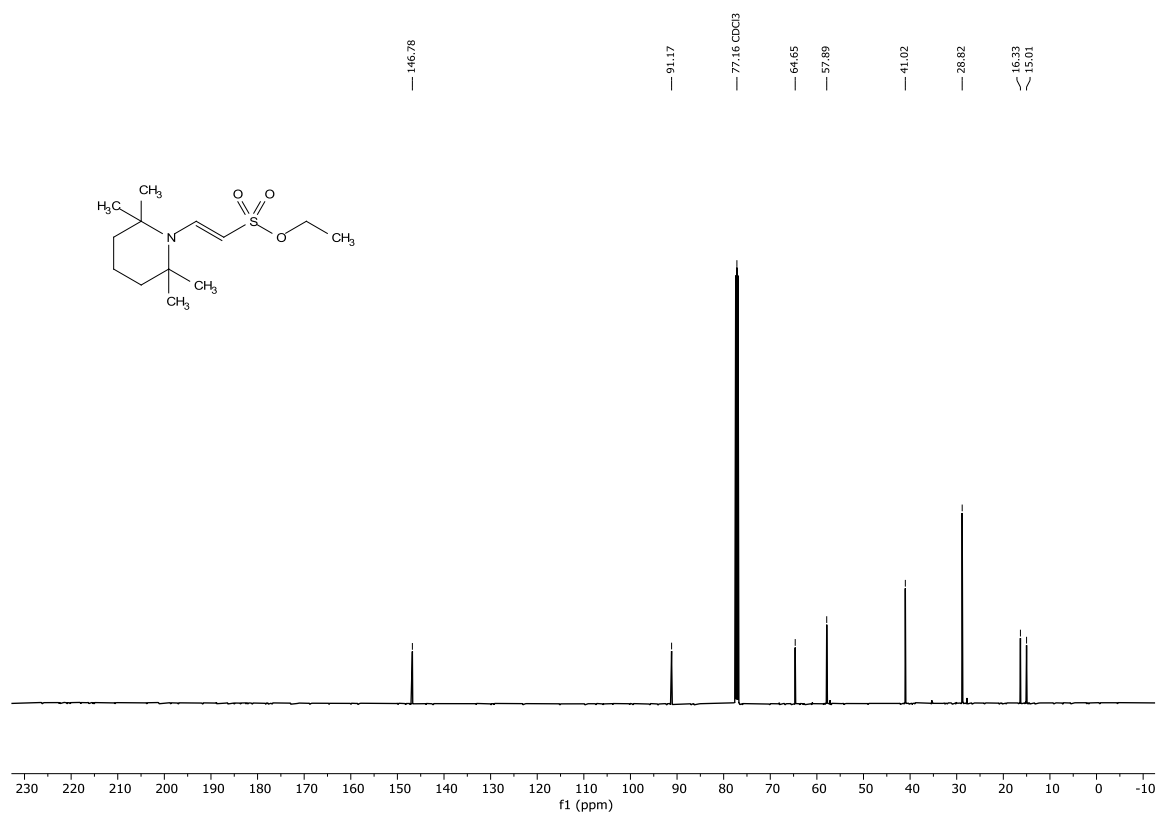
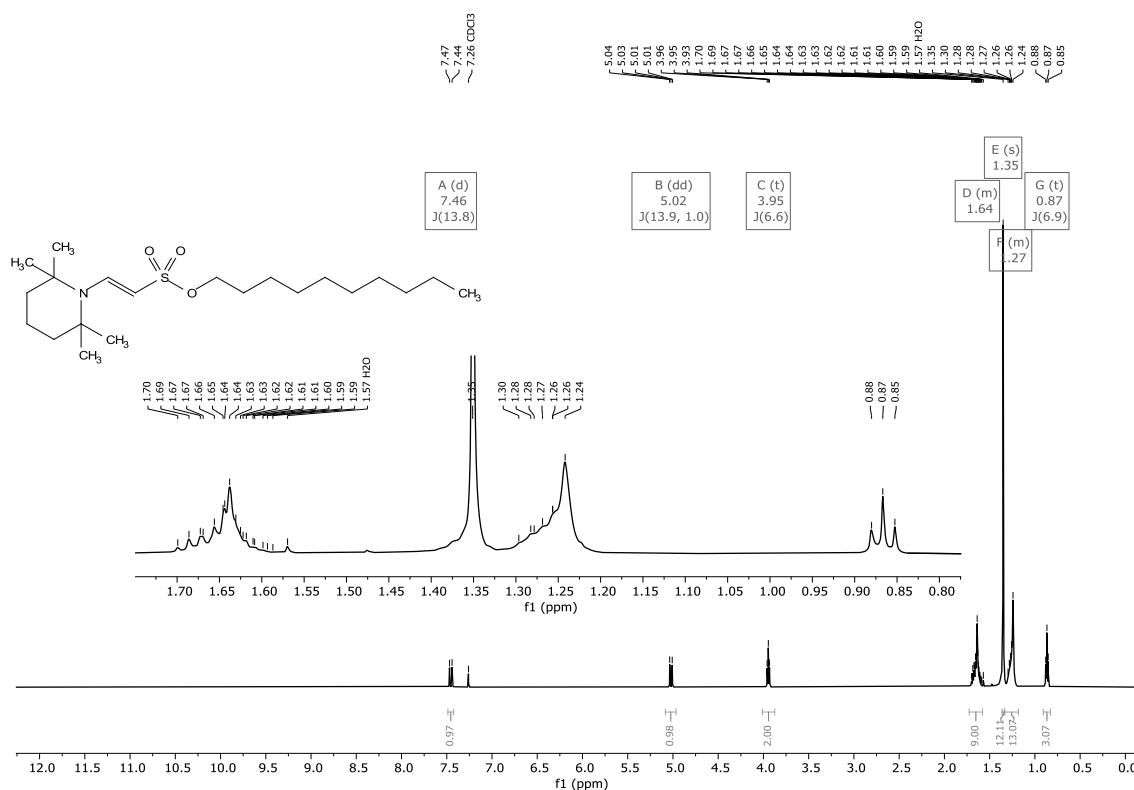
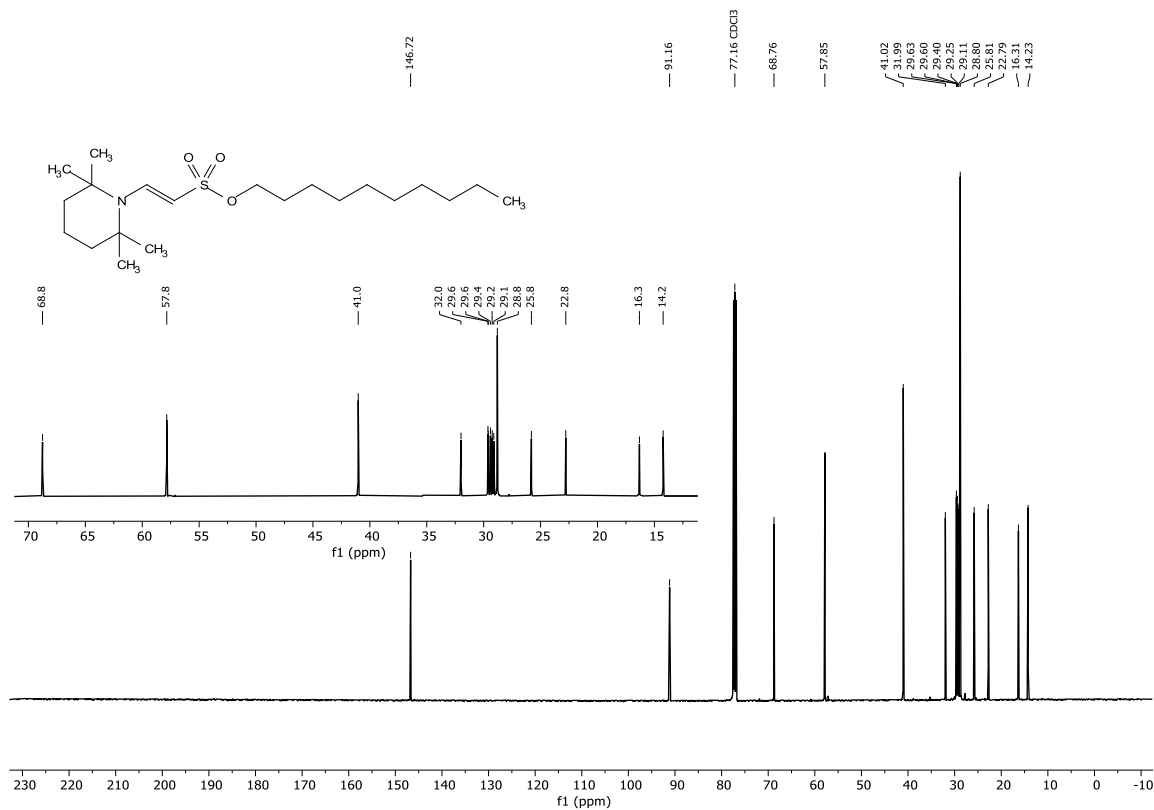


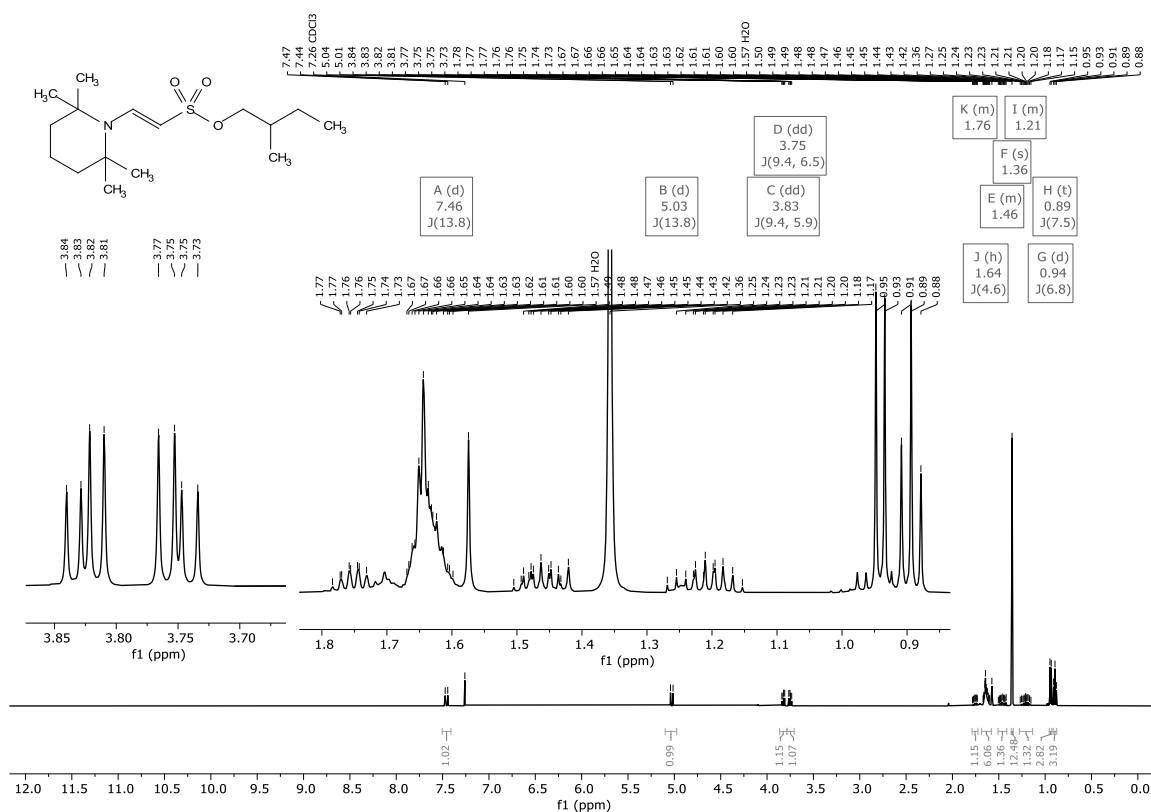
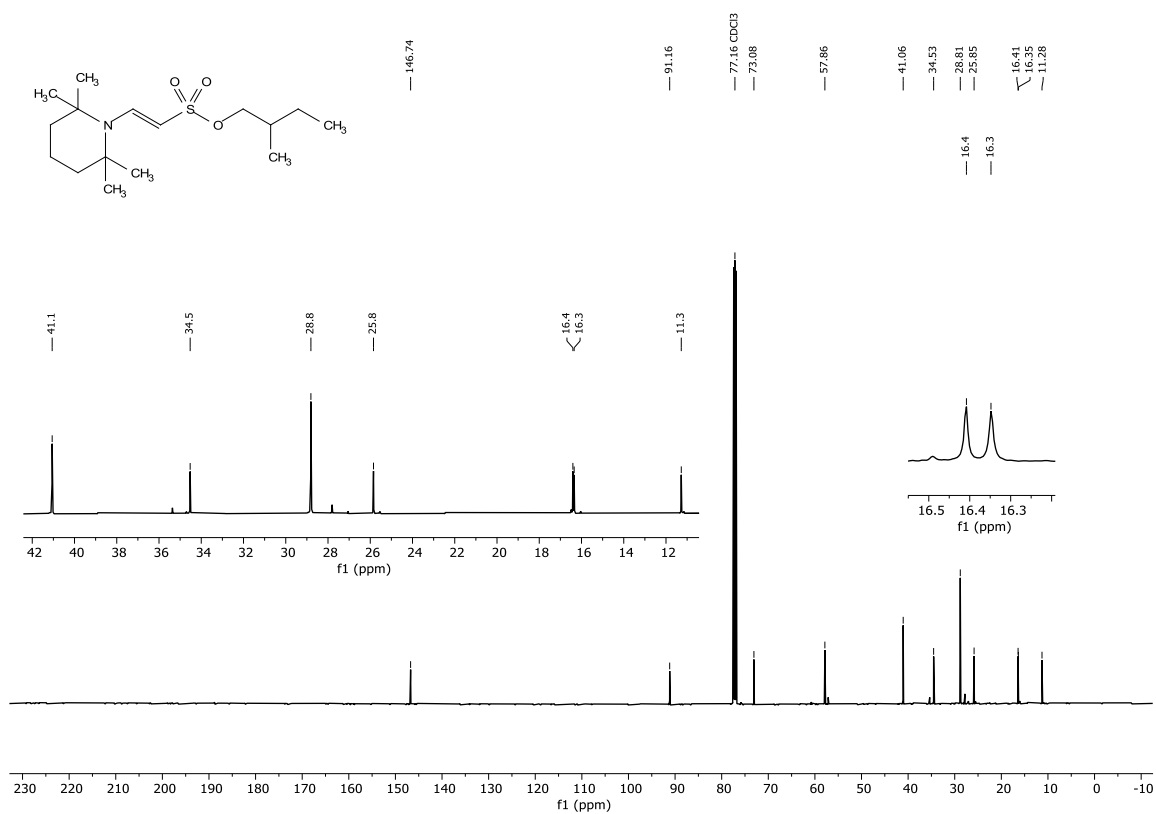
Figure S47: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3p**.

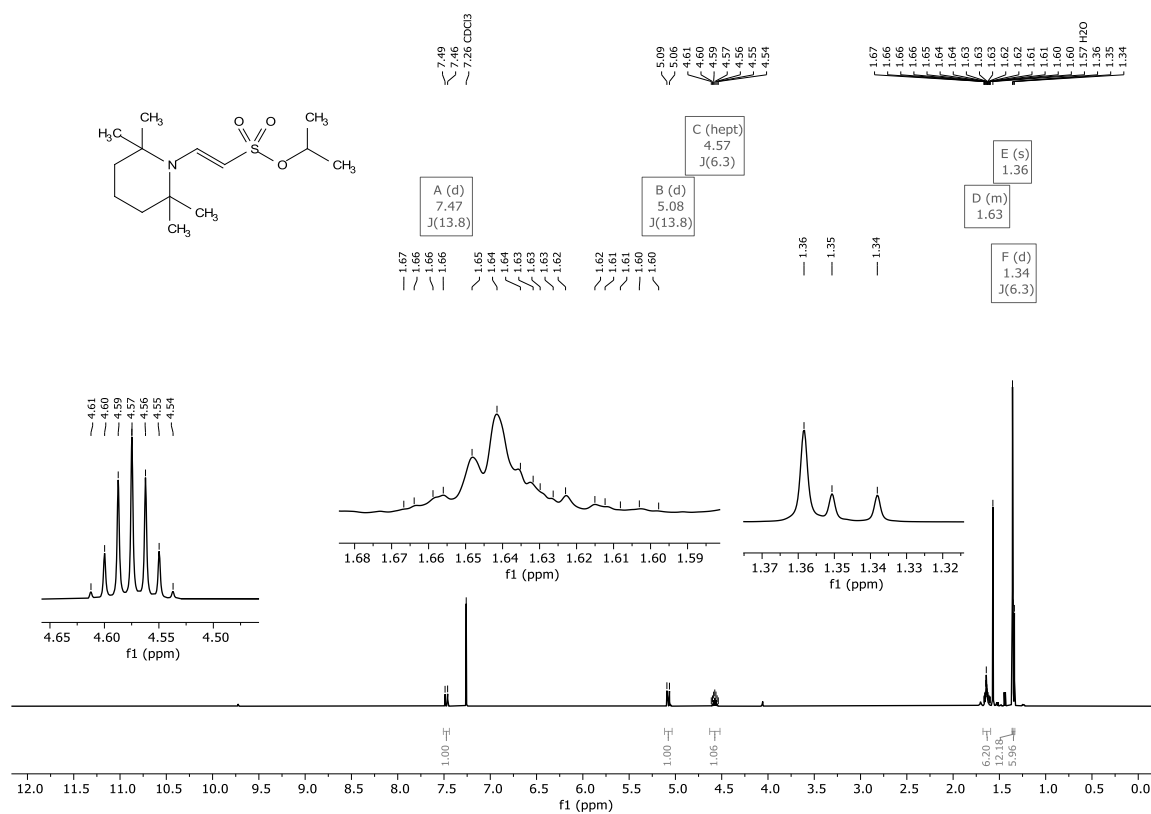
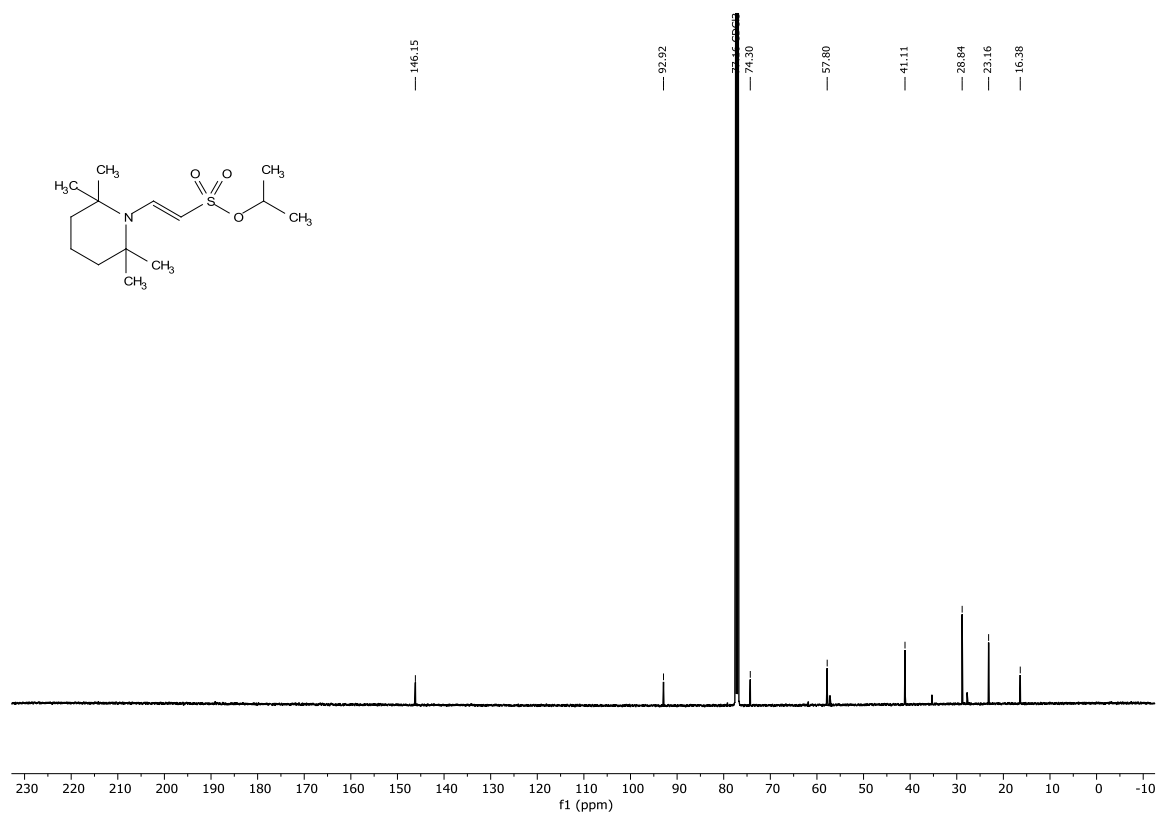
Figure S48: ^1H NMR spectrum (500 MHz, CDCl_3) of **3q**.Figure S49: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **3q**.

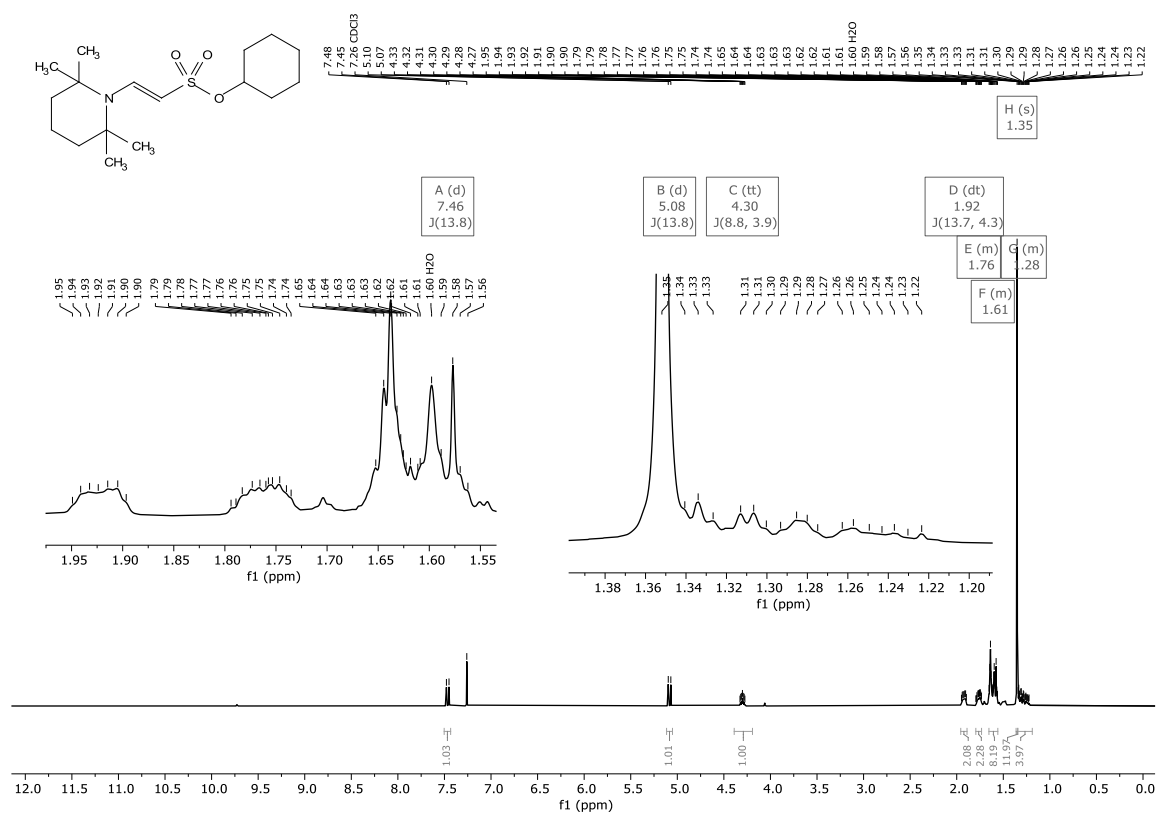
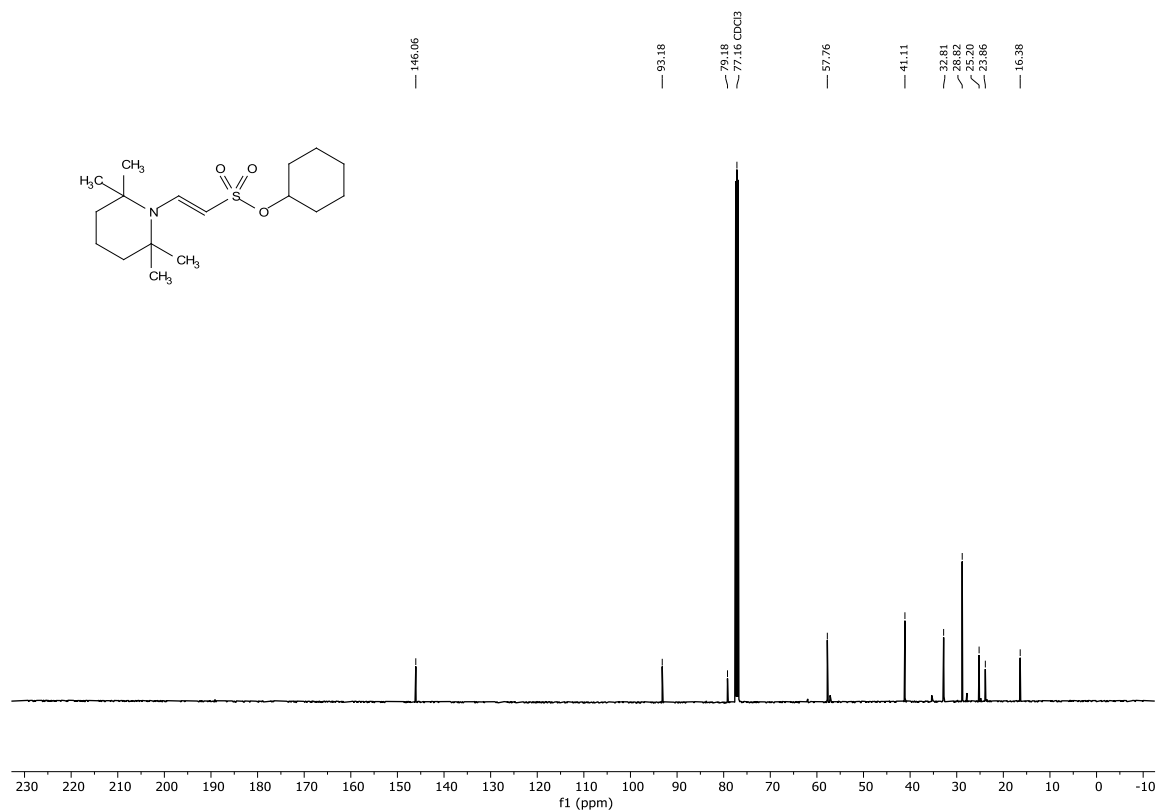
Figure S50: ¹H NMR spectrum (500 MHz, CDCl₃) of **4a**.Figure S51: ¹³C NMR spectrum (126 MHz, CDCl₃) of **4a**.

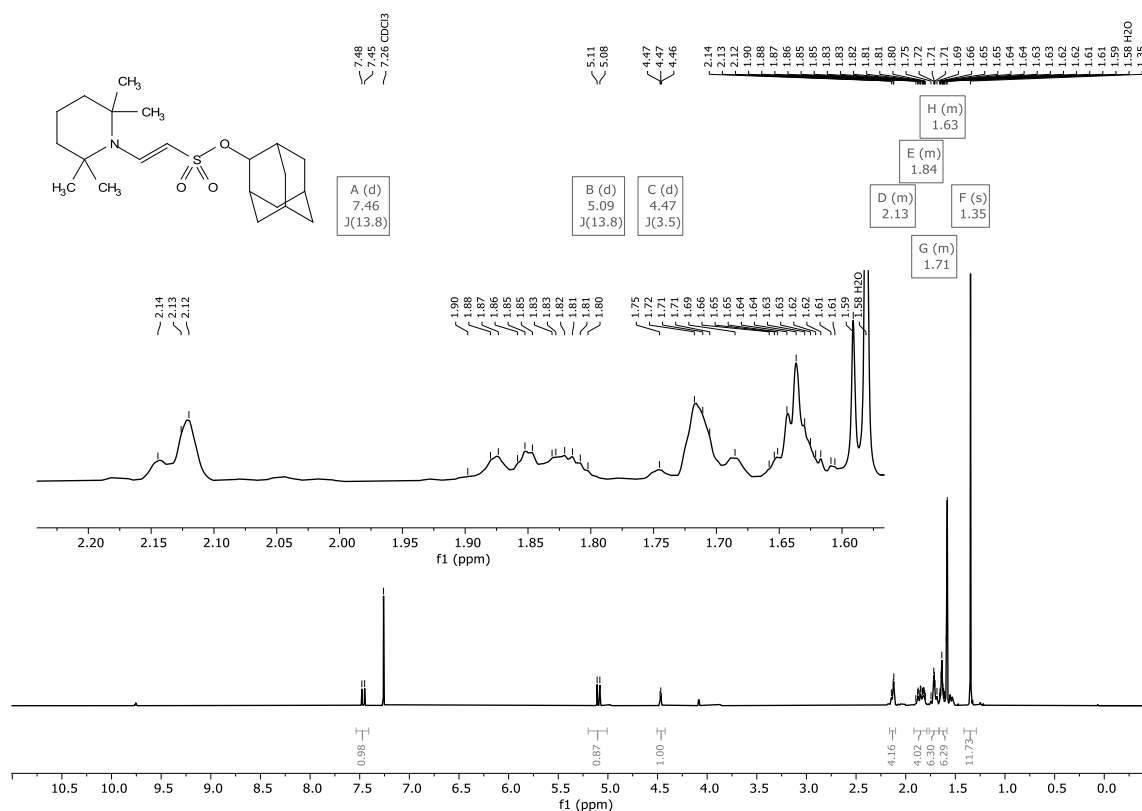
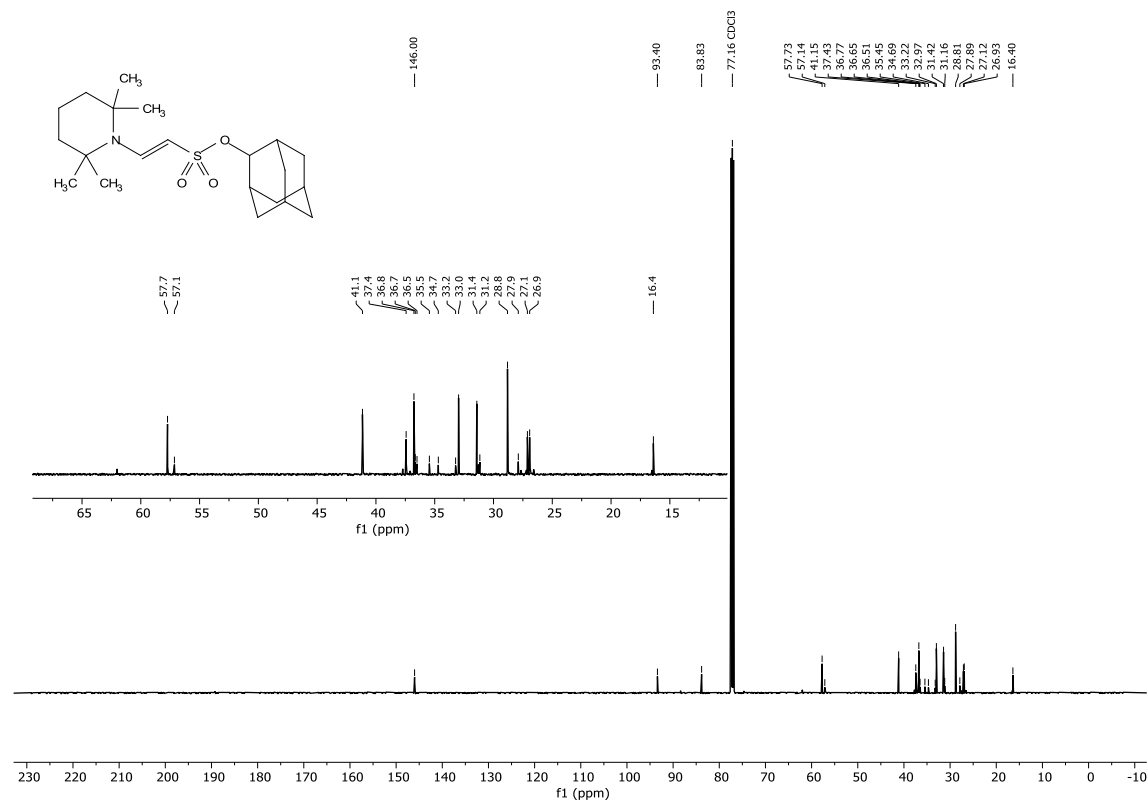
Figure S52: ¹H NMR spectrum (500 MHz, CDCl₃) of **4b**.Figure S53: ¹³C NMR spectrum (126 MHz, CDCl₃) of **4b**.

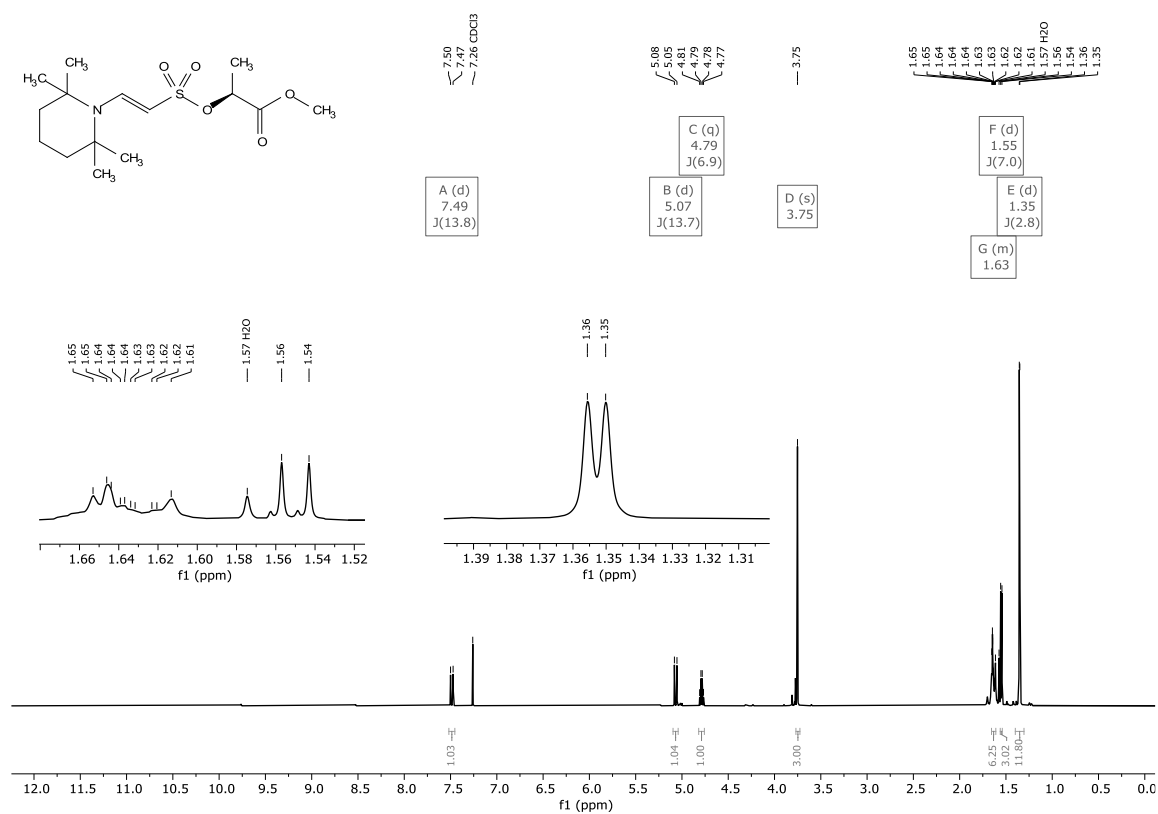
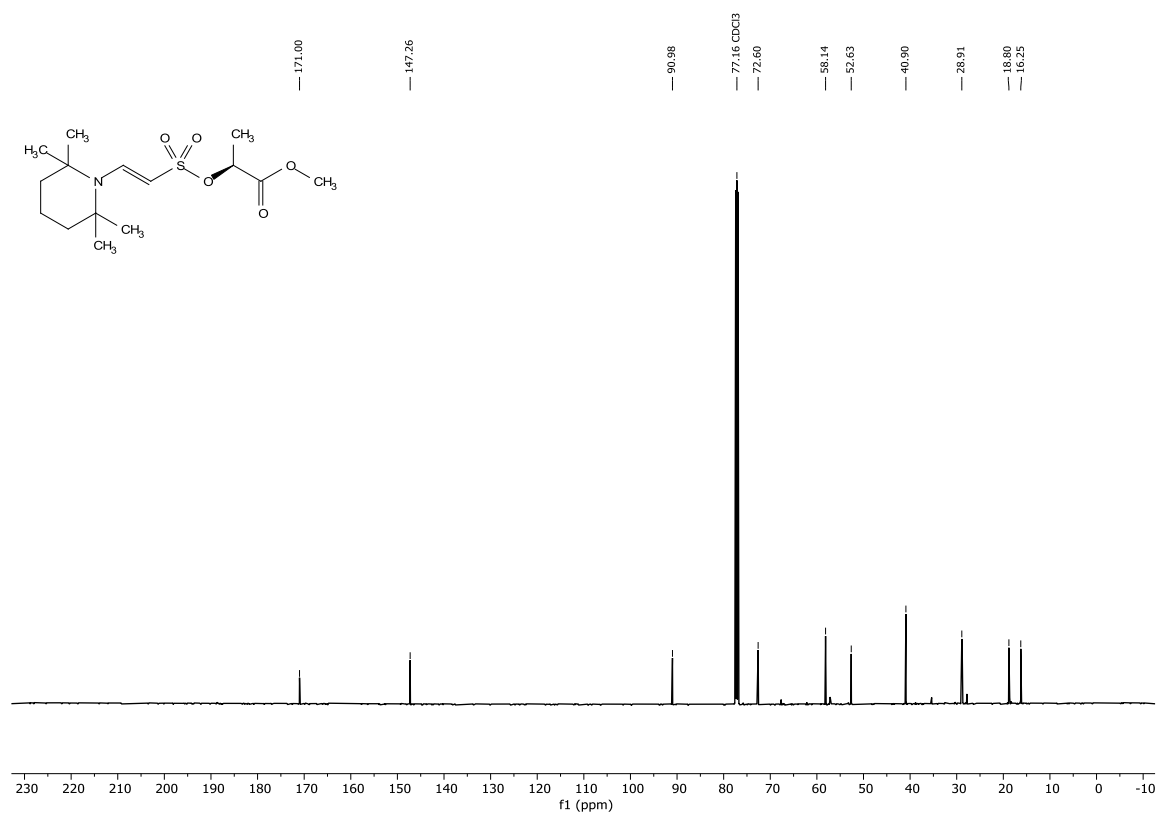
Figure S54: ¹H NMR spectrum (500 MHz, CDCl₃) of 4c.Figure S55: ¹³C NMR spectrum (126 MHz, CDCl₃) of 4c.

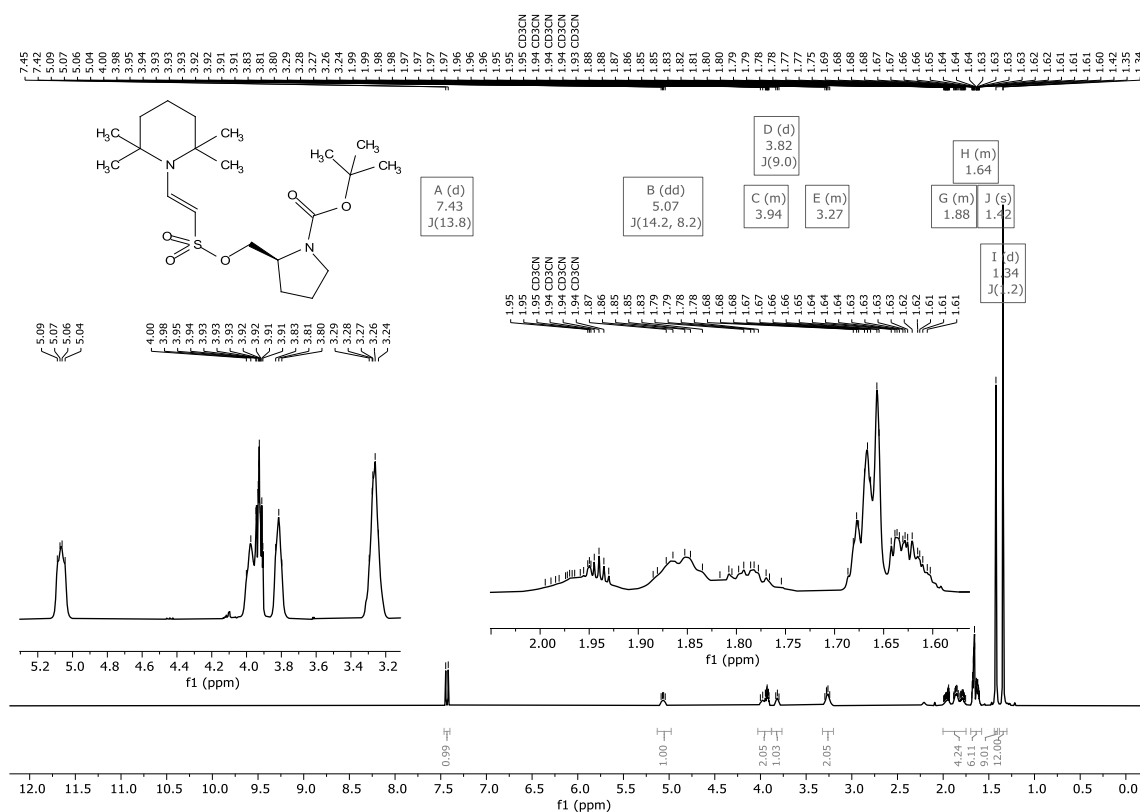
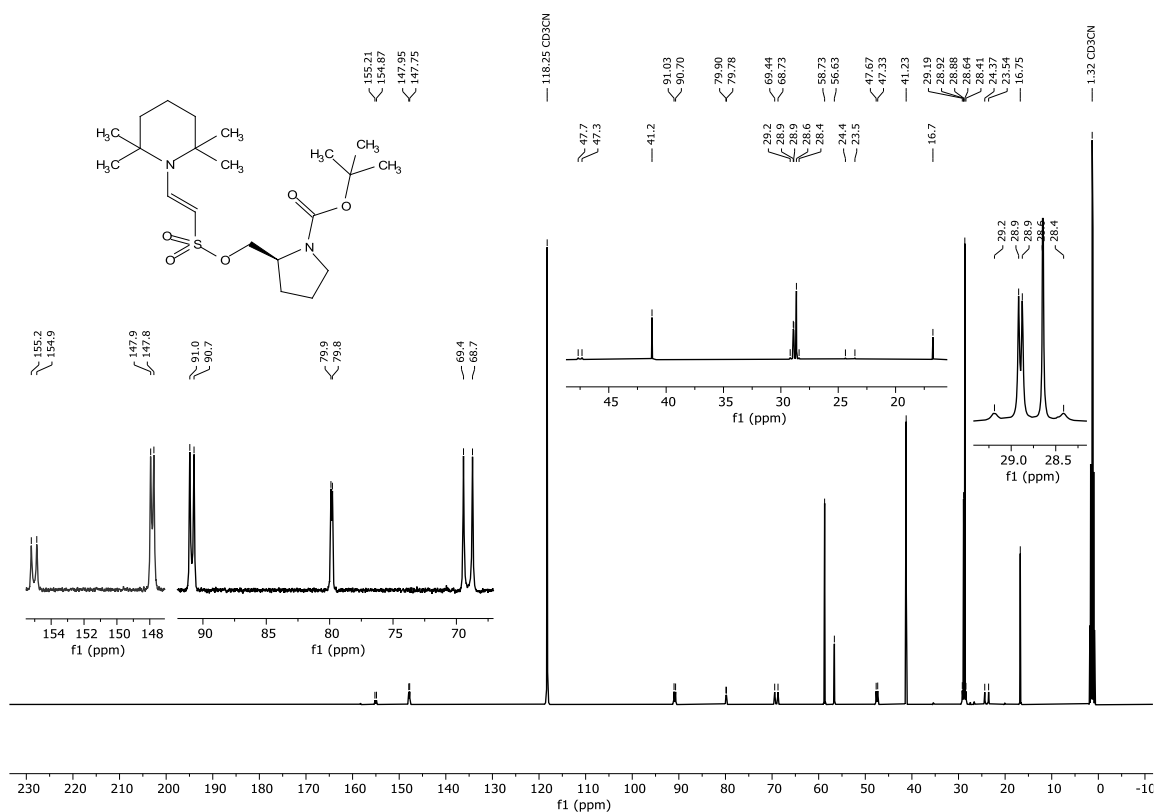
Figure S56: ¹H NMR spectrum (500 MHz, CDCl₃) of 4d.Figure S57: ¹³C NMR spectrum (126 MHz, CDCl₃) of 4d.

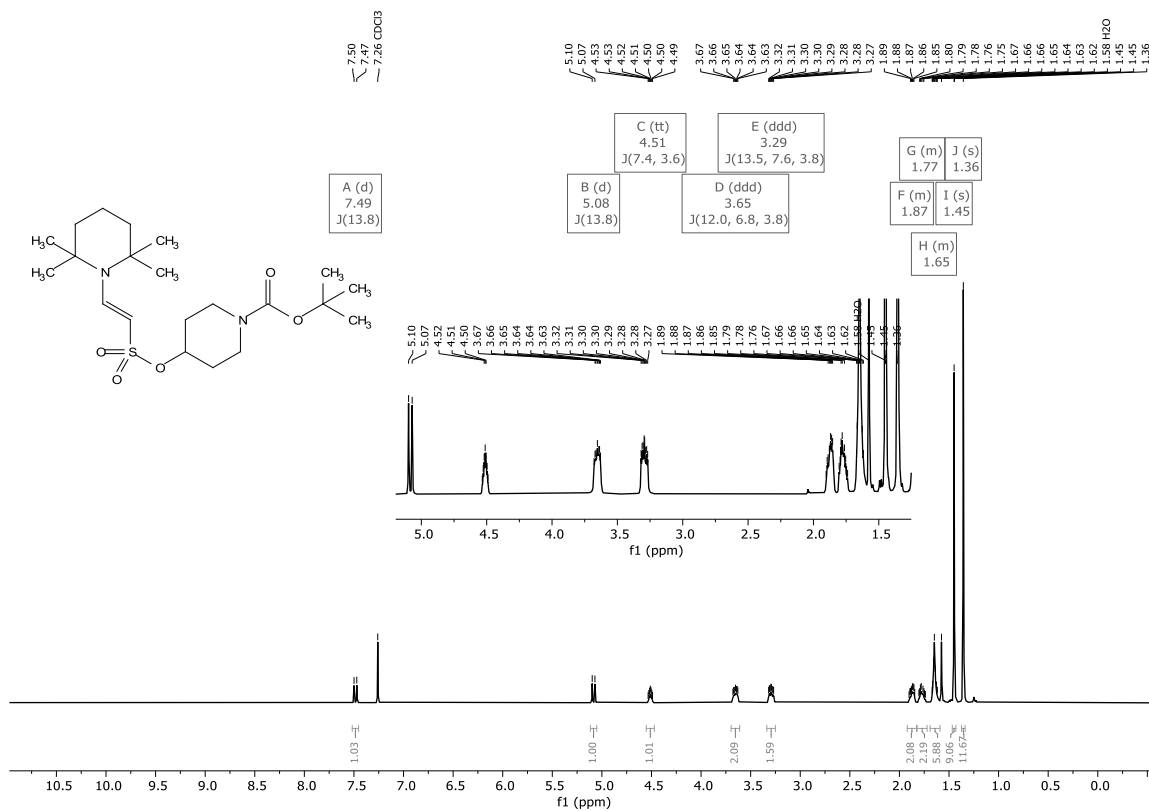
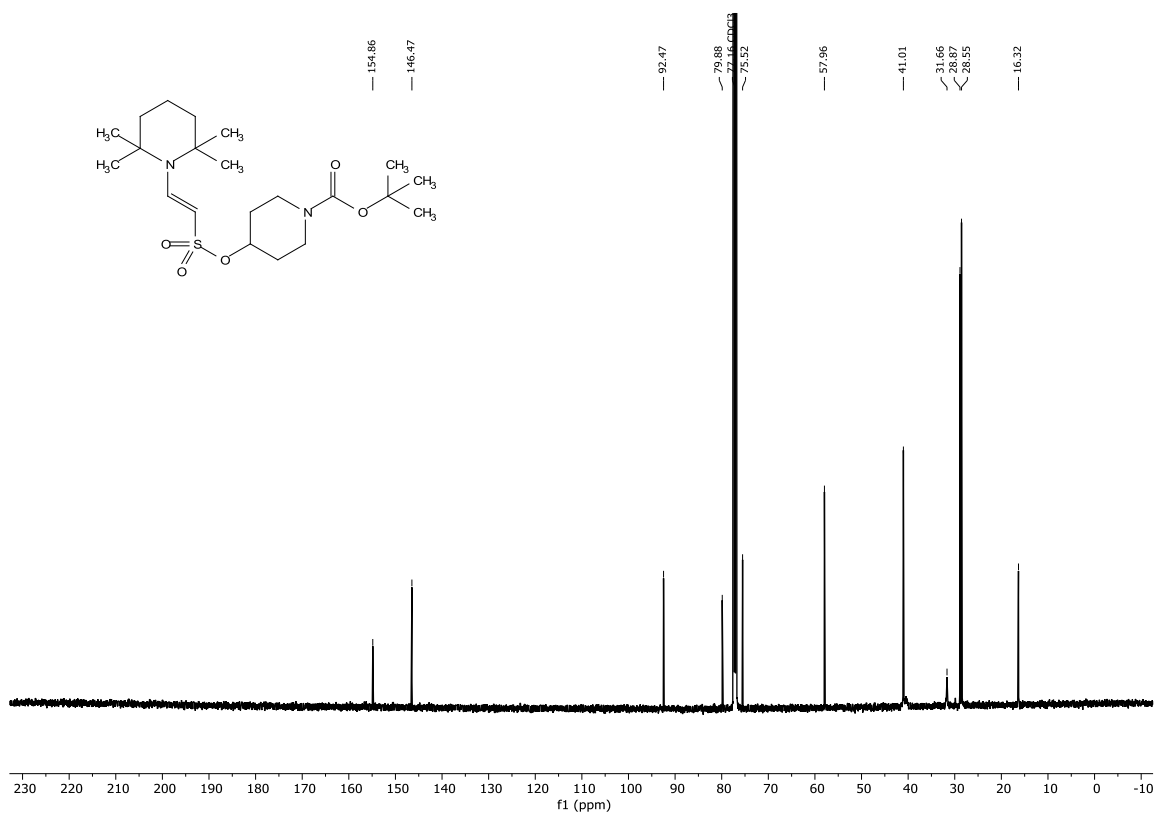
Figure S58: ¹H NMR spectrum (500 MHz, CDCl₃) of **4e**.Figure S59: ¹³C NMR spectrum (126 MHz, CDCl₃) of **4e**.

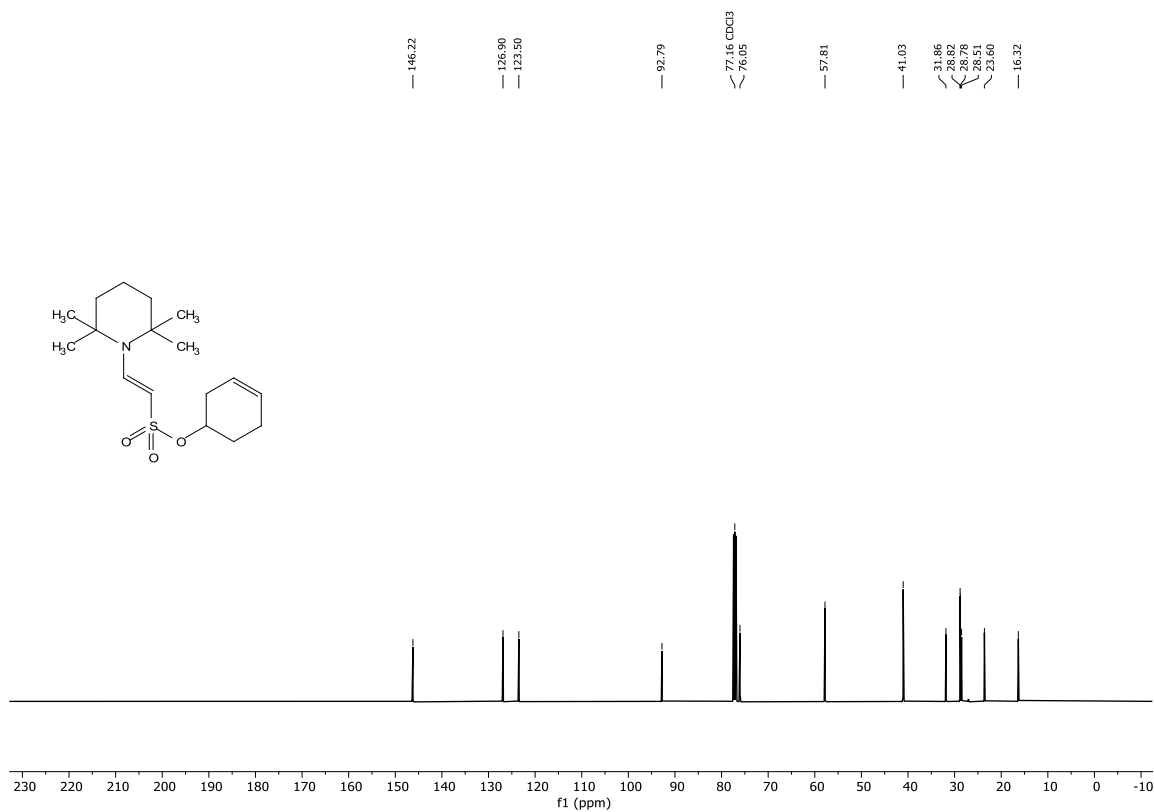
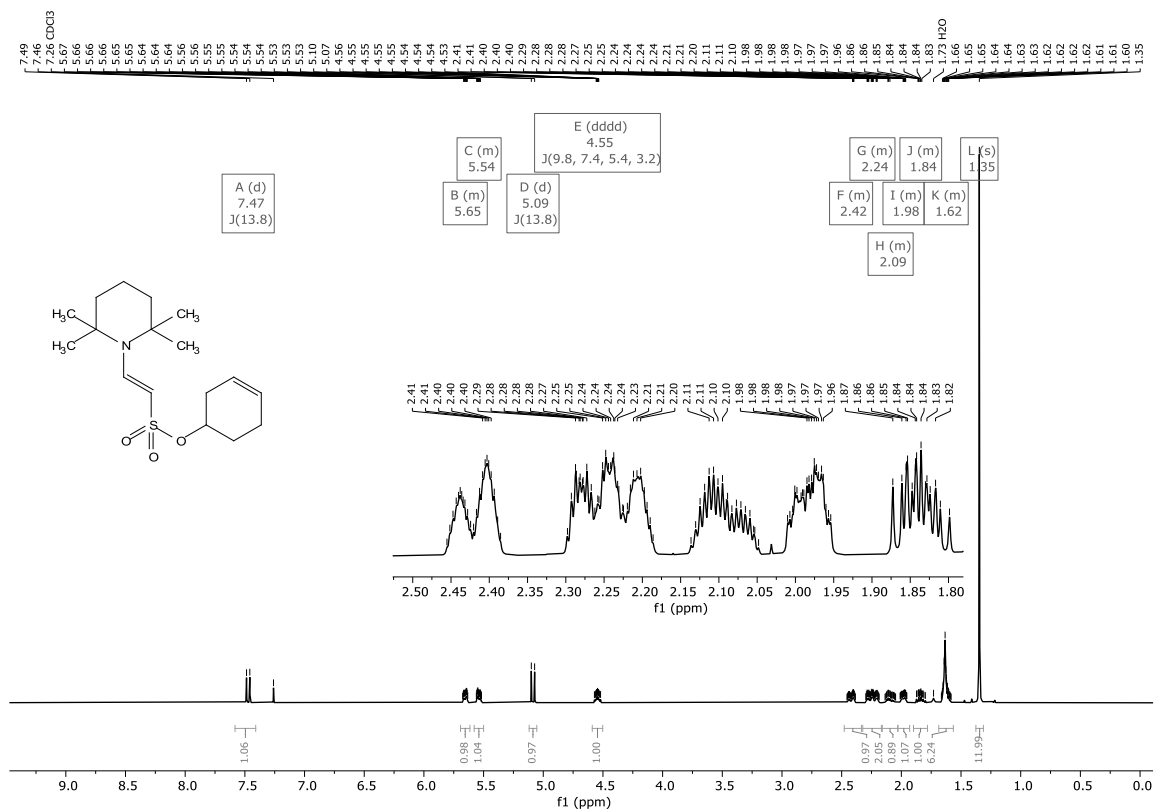
Figure S60: ¹H NMR spectrum (500 MHz, CDCl₃) of **4f**.Figure S61: ¹³C NMR spectrum (126 MHz, CDCl₃) of **4f**.

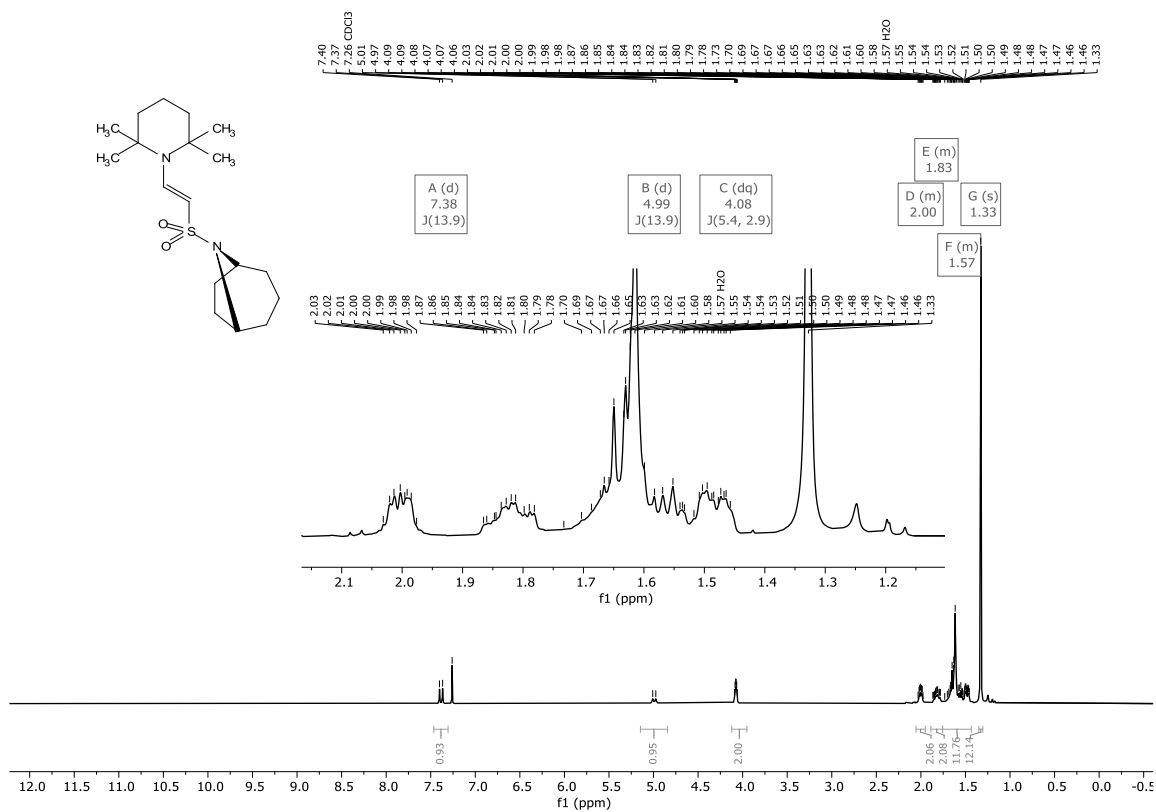
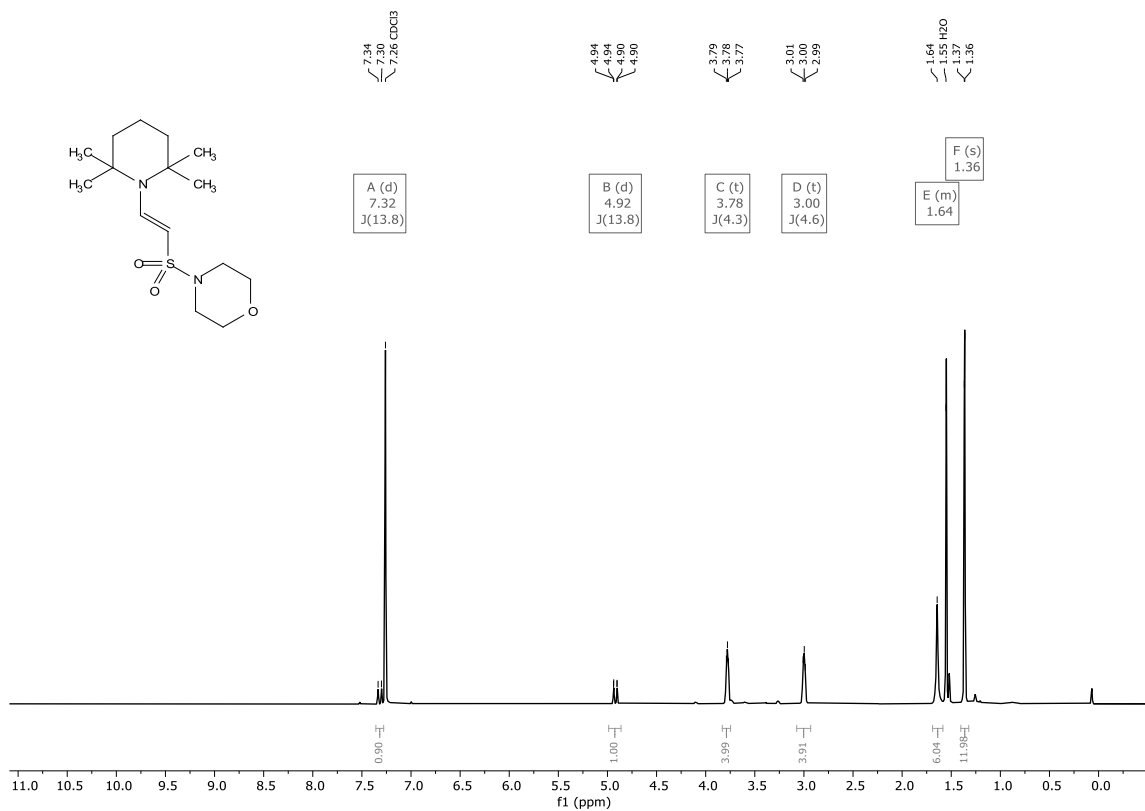
Figure S62: ¹H NMR spectrum (500 MHz, CDCl₃) of 4g.Figure S63: ¹³C NMR spectrum (126 MHz, CDCl₃) of 4g.

Figure S64: ¹H NMR spectrum (500 MHz, CDCl₃) of **4h**.Figure S65: ¹³C NMR spectrum (126 MHz, CDCl₃) of **4h**.

Figure S66: ^1H NMR spectrum (500 MHz, CD_3CN) of 4i.Figure S67: ^{13}C NMR spectrum (126 MHz, CD_3CN) of 4i.

Figure S68: ^1H NMR spectrum (500 MHz, CDCl_3) of **4j**.Figure S69: ^{13}C NMR spectrum (126 MHz, CDCl_3) of **4j**.





9 Author contributions

F.A.B.:	Conceptualization, Investigation, Methodology, Data curation and analysis, Writing the original draft.
A.L.S.:	Investigation: Supporting (optimization of reaction conditions)
C. K.:	Investigation: Supporting (cyclic voltammetry measurements)
A. A. B.:	Preliminary investigations
T. W.:	Investigation: Supporting (crystallographic measurements and interpretation of X-ray data)
S.R.W.:	Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing the original draft.

10 References

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- (2) Komoda, M.; Nishina, Y. Electrochemical Production of Graphene Analogs from Various Graphite Materials. *Chemistry Letters* **2020**, *50*, 503-509.
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- (5) (a) Mann, C. K. Cyclic Stationary Electrode Voltammetry of Some Aliphatic Amines. *Analytical Chemistry* **1964**, *36*, 2424-2426. (b) Mruthunjaya, A. K. V.; Torriero, A. A. J. Mechanistic Aspects of the Electrochemical Oxidation of Aliphatic Amines and Aniline Derivatives. *Molecules* **2023**, *28*, 471-502.
- (6) (a) Blum, S. P.; Karakaya, T.; Schollmeyer, D.; Klapars, A.; Waldvogel, S. R. Metal-Free Electrochemical Synthesis of Sulfonamides Directly from (Hetero)arenes, SO₂, and Amines. *Angewandte Chemie International Edition* **2021**, *60*, 5056-5062. (b) Schneider, J.; Blum, S. P.; Waldvogel, S. R. Electrochemical Synthesis of Sulfonamides in Single-Pass Flow. *ChemElectroChem* **2023**, *10*, e202300456.