ChemPubSoc Europe

DOI: 10.1002/ejoc.201901176

EurJOC European Journal of Organic Chemistry

Full Paper

Photochemistry

A Copper-Catalyzed Synthesis of Pyrroles through Photochemically Generated Acylazirines

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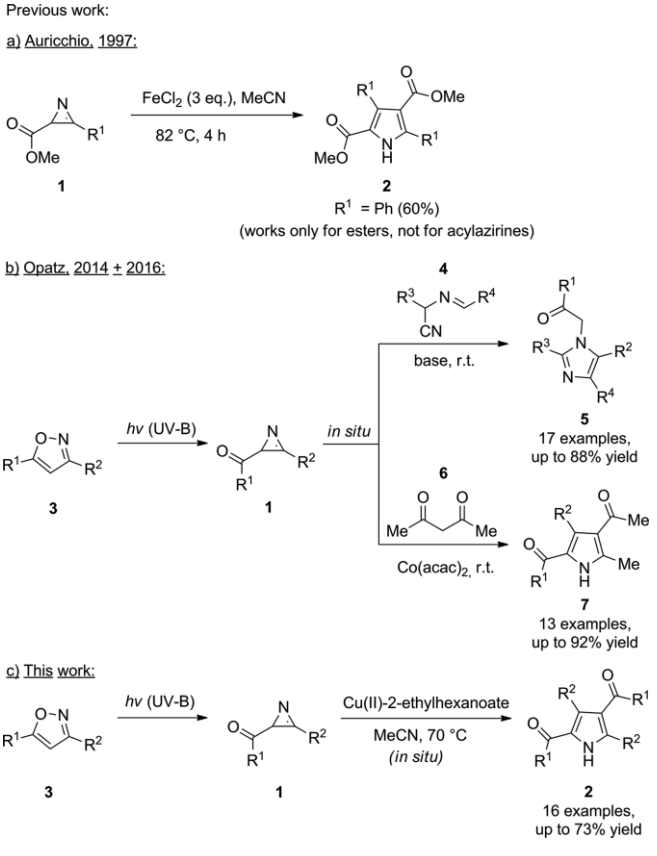
Abstract: A synthesis of highly substituted 2,4-diacylpyrroles through a Cu-catalyzed dimerization of acylazirines generated in situ by a photochemical valence isomerization is described. The shown methodology allows the use of simple precursors and a readily available copper(II)-catalyst. Since the reaction is best performed at elevated temperatures, a method to adjust the temperature of the reaction mixture during this dual light and metal-induced process was established. Additionally, mechanistic studies of the reaction were performed in order to provide a deeper understanding of the chemistry of 2-acylazirines.

Introduction

The utilization of light-induced ring strain as a driving force in the synthesis of heterocycles can serve as an attractive and eco-friendly alternative to schemes associated with the formation of low-energy co-products such as borate salts or metal halides as frequently seen in traditional C–C or C–heteroatom bond formations. Small-ring systems often exhibit a high reactivity but also a certain sensitivity.[1] The ideal strained intermediate therefore can be generated in situ from stable precursors and is directly transformed into the desired heterocyclic product under the conditions of its formation. If the subsequent step is faster than competing side reactions, highly reactive short-lived intermediates can also be employed. Small-ring systems can be prepared via UV photochemistry, as the energy injected into the molecule by absorption of a photon of short wavelength can lead to valence isomerizations or other processes providing products of high energy content.[2] The chemistry of the *2H*-azirines is attractive in this context, as these intermediates can be used as substrates in cycloadditions as well as for other syntheses of various heterocyclic compounds.[3] They are most commonly synthesized using the Neber rearrangement[4] or by a thermal or photochemical conversion starting from vinyl azides.[5] Another type of precursors for *2H*-azirines are isoxazoles bearing at least one aromatic substituent, that can be converted into the corresponding 2-acylazirines under irradiation with UV-light.[6] Unfortunately, the formation of the 2-acylazirines competes with further isomerization to the thermodynamically stable oxazoles, limiting the maximum isolated yield of the strained intermediate.[6] Besides, isoxazoles bearing electron donating substituents such as alkoxy or amino groups were found by Auricchio and co-workers to be converted into the corresponding 2-alkoxycarbonyl-*2H*-azirines under iron dichloride catalysis. In the same publication, the authors reported



Scheme 1. a) Iron dichloride catalyzed dimerization of isoxazoles forming 2,4-alkoxycarbonylpyrroles b) photochemically in situ-generated 2-acylazirines in the synthesis of imidazoles and 2,4-diacylpyrroles c) copper(II)-2-ethylhexanoate-catalyzed dimerization of in situ-generated 2-acylazirines.[7–9]

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Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201901176.

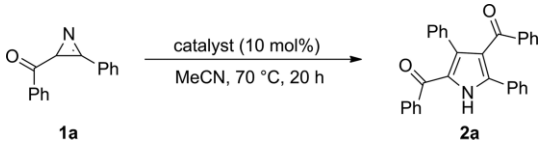
a dimerization reaction of the formed *2H*-azirines at elevated temperatures yielding in tetrasubstituted pyrroles **2**.[7] A similar observation was made by Komendantov and Bekmukhametov, who had presumably found the same kind of dimerization on 2-alkoxycarbonylazirines under copper(II)-stearate catalysis, but reported a different regioselectivity (2,3-dialkoxycarbonylpyrroles instead of 2,4-dialkoxycarbonylpyrroles).[8]

Recently, our group has reported methodologies for the synthesis of imidazoles and 2,4-diacylpyrroles starting from 2-acylazirines generated in situ employing the photoisomerization of the corresponding isoxazoles (Scheme 1).[9] In these cases, the subsequent step could conveniently be carried out at room temperature and did not interfere with any photochemically or thermally induced competing reactions such as oxazole formation. To ensure a sufficiently fast rate of the metal-catalyzed step which matches the mostly temperature independent UV-driven isomerization, it might be necessary to control the temperature of the reaction vessel during the irradiation. To avoid the use of expensive and sensitive immersion lamps, we opted for immersion temperature control in combination with external irradiation in a rayonet-type circular lamp array (vide infra). This should allow to match the kinetics of the two subsequent steps in order to minimize undesired side reactions. As a test case, the well-known UV isomerization of isoxazoles was combined with a subsequent step, which we found to require elevated temperatures. As the reported dimerization reaction of Auricchio and co-workers (see Scheme 1) is limited to azirines containing alkoxycarbonyl substituents, a Lewis acid able to perform the same transformation on the photochemically generated azirines bearing an arylmethanone moiety had to be found.

Results and Discussion

The initial task was the identification of a suitable catalyst for the dimerization of the model azirine **1a**.

Therefore, several inexpensive and earth-abundant Lewis acids were screened (see Scheme 2 and Table 1). In the absence of a catalyst, no product formation was observed (see entry 1). When frequently used Lewis acids such as aluminium chloride and zinc chloride were tested, no turnover of the azirine was observed. Iron chloride catalysts (as used by Auricchio and co-workers) only afforded smaller amounts of the desired product (see entries 4 + 5).[7] Significant catalytic activity was only found for copper catalysts containing carboxylate, alkoxide or iodide counterions. Surprisingly, the outcome of the reaction was not affected by the initial oxidation state of the copper salt: Both cuprous acetate and cupric acetate furnished pyrrole **2a** in ca. 45 % yield (see entries 11 + 12). When the lipophilicity of the carboxylate counterion was increased by adding branching or increasing the chain length, the isolated yield of the pyrrole could be improved to 65 % with Cu(II)-2-ethylhexanoate (entries 12 - 15). As assumed, no product formation was observed when the reaction was carried out at room temperature (see entry 16).



Scheme 2. Catalyst screening with model azirine **1a**.

Table 1. Catalyst screening for the dimerization reaction.[a]

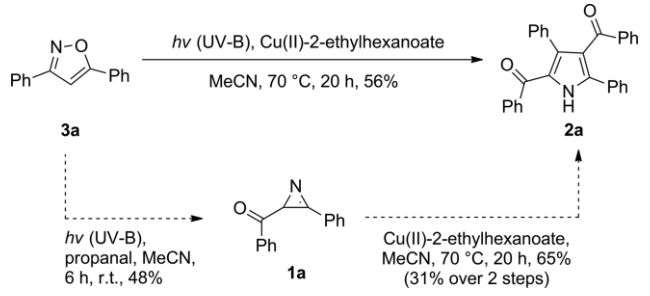
Entry	Catalyst	Yield[b]
1	None	–[c]
2	$AlCl_3$	–[c]
3	$ZnCl_2$	–[c]
4	$FeCl_2$	7
5	$FeCl_3$	8
6	CuI	59
7	CuCl	–[c]
8	CuO	–[c]
9	$Cu[N(SO_2CF_3)_2]$	–[c]
10	Cu(O*t*Bu)	27
11	Cu(OAc)	47
12	$Cu(OAc)_2$	46
13	Cu(II)-benzoate	57
14	Cu(II)-laurate	55
15	**Cu(II)-2-ethylhexanoate**	65
16	Cu(II)-2-ethylhexanoate	–[c][d]

[a] Reaction conditions: **1a** (0.45 mmol), catalyst (10 mol-%), MeCN (4.5 mL, 0.1 M substrate concentration), 70 °C, 20 h. [b] Isolated yields after chromatography. [c] Not determined; no product formation observed by LC/MS. [d] Reaction was carried out at room temperature.

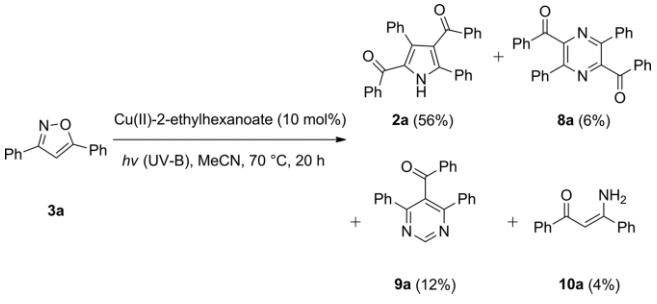
With the optimum catalyst in hand, it was attempted to combine the photoisomerization of isoxazoles with the subsequent dimerization reaction in a one-pot procedure. Since the photoisomerization (with wavelengths of 300 nm) is beyond the spectral window of the frequently used thermofluids, no classic external heating bath could be employed for tempering the reaction mixture. Instead, the temperature was adjusted with an external circulator connected to a ''cold finger'' placed inside the reaction vessel during irradiation (see the SI for a more detailed description).

Applying this setup to isoxazole **3a**, the corresponding pyrrole **2a** was obtained in 56 % yield (see Scheme 3). As the photoisomerization of isoxazole **3a** to the corresponding 2-acylazirine **1a** had been found to provide a maximum isolated yield of around 50 % in our laboratory, the theoretical maximum overall yield of the separate reactions would amount to 31 %. Thus, it is advantageous to perform the two steps in a one-pot photoreaction furnishing the dimerization product in an almost doubled yield. Several control experiments were carried out and the reaction parameters were varied (see the SI): In the absence of the catalyst, only the formation of the *2H*-azirine and the oxazole was detected by LC/MS. Furthermore, the pure isoxazole remained unchanged when it was stirred with the copper catalyst at 70 °C in the dark. Thus, a direct condensation of two molecules of isoxazole can be ruled out. Next, the influence of temperature, solvent and concentration was investigated. Methanol, cyclohexane or THF turned out to be inferior to 1,2-dichloroethane and acetonitrile. Among those two, acetonitrile is the preferred solvent regarding toxicity and eco-friendliness. Lowering the initial catalyst loading of 10 mol-% to 5 mol-% resulted in a reduced yield, while using 20 mol-% did not increase the amount of pyrrole **2a**. A variation of the concentra-

tion was also not effective, increasing or decreasing the solvent volume led to a reduction in yield. Finally, the scalability was investigated using the threefold amount of isoxazole **3a**. Besides pyrrole **2a**, which was again obtained in 56 % yield, the primary by-products could be isolated and characterized. Chromatography afforded pyrazine **8a** in 6 %, pyrimidine **9a** (unambiguously determined by NMR spectroscopy and X-ray crystallography) in 12 % and enaminone **10a** in 4 % yield (Scheme 4).

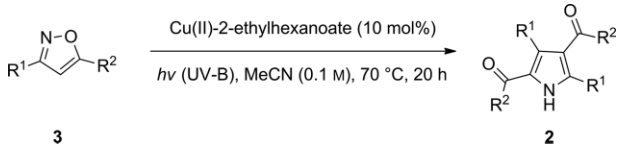


Scheme 3. Comparison of the one-pot synthesis of tetrasubstituted pyrroles from isoxazoles with a divided reaction setup.



Scheme 4. Isolated compounds of the upscaled one-pot reaction.

Under the improved reaction conditions, the substrate scope was investigated by applying them to several isoxazoles bearing mostly aromatic substituents on both the 3- and the 5-position, which were previously synthesized using standard methods (see Scheme 5 and Table 2).[6b,10]



Scheme 5. Substrate scope of the copper catalyzed dimerisation of in situ generated 2-acylazirines.

The obtained pyrroles are shown in Table 2. The R^1 group in the isoxazole starting material was varied first by changing the substitution pattern of the phenyl group. Replacement of the unsubstituted phenyl group (**1a**) with both the *p*-tolyl (**1b**) and the *m*-tolyl (**1c**) substituent furnished the corresponding dimerization product in comparable yields, whereas the reaction failed with the *o*-tolyl substituent (entries 2 – 4). The introduction of 4′-halogen substituents led to a reduction in yield most pronounced in the case of bromine (entries 5 – 7), possibly due to a heavy atom effect reducing the lifetime of the S_1-state from

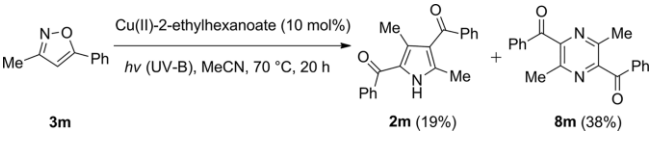
Table 2. Substrate scope of the copper catalyzed dimerisation of in situ generated 2-acylazirines.[a]

Entry	isoxazole	R^1	R^2	Yield[b] [%]
1	**3a**	Ph	Ph	56
2	**3b**	4-Tol	Ph	51
3	**3c**	3-Tol	Ph	46
4	**3d**	2-Tol	Ph	–[c]
5	**3e**	4-F-C_6H_4	Ph	47
6	**3f**	4-Cl-C_6H_4	Ph	45
7	**3g**	4-Br-C_6H_4	Ph	35
8	**3h**	4-CF_3-C_6H_4	Ph	39
9	**3i**	4-MeO_2C-C_6H_4	Ph	33
10	**3j**	2-naphthyl	Ph	48[d]
11	**3k**	4–MeO-C_6H_4	Ph	41[d]
12	**3l**	2-furanyl	Ph	43[d]
13	**3m**	Me	Ph	19
14	**3n**	Ph	4-*t*Bu-C_6H_4	57
15	**3o**	Ph	4-F-C_6H_4	54
16	**3p**	Ph	4-MeO-C_6H_4	73
17	**3q**	Ph	4-MeO_2C-C_6H_4	46
18	**3r**	Ph	pentyl	28[e]

[a] Standard conditions: **3** (1.0 mmol), Cu(II)-2-ethylhexanoate (0.1 mmol), MeCN (10 mL, 0.1 M substrate concentration), UV–B irradiation, 70 °C. [b] Isolated yields after chromatography. [c] Not determined; low product formation observed by LC/MS. [d] Reaction was performed at c = 0.05 M. [e] Reaction incomplete after 96 h, 43 % yield b.r.s.m.

which the acylazirine is formed.[11] The incorporation of electron-withdrawing groups resulted in a decreased yield of the dimerization products (see entries 8 – 9). Replacement of the phenyl with a naphthyl group led to very long reaction times and poor yields. The same observations were made when an electron-donating substituent was attached to the phenyl group (entry 11). The photoisomerization turned out to be very sluggish, possibly due to extensive light absorption by the product formed. We were able to overcome this problem by decreasing the concentration to 0.05 M, which allows more photons to penetrate the reaction mixture resulting in a faster isomerization rate.

This modification increased the yield of the naphthyl derivative **2j** from 21 % to 48 %. The regioselectivity of the dimerization could be unambiguously determined using X-ray crystallography of *p*-methoxyphenyl-substituted pyrrole **2k** (see the SI). When a methyl group was employed as the R^1 substituent, the chemoselectivity was changed and pyrazine **8m** was obtained as the main product in 38 % yield (Scheme 6). Thus, an aromatic substituent as R^1 is presumably crucial in order to stabilize the formed intermediate **12** (vide infra) and to suppress the direct dimerization yielding in the corresponding pyrazines **8**.



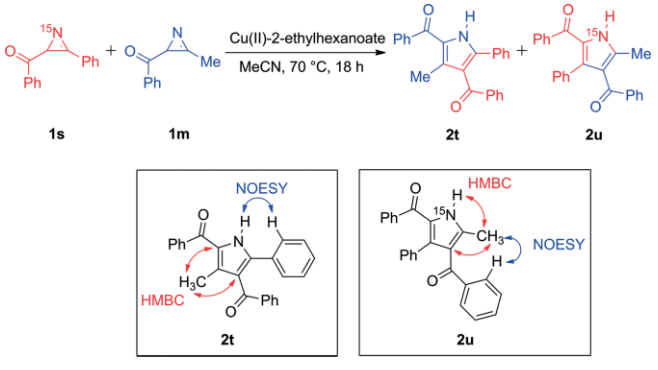
Scheme 6. Isolated products of the dimerization reaction applying standard conditions on isoxazole **3m**.

Secondly, the R^2-substituent of the isoxazole was varied. Both alkyl and halogens on the phenyl ring were well tolerated (entries 14 + 15). By introducing an electron-withdrawing sub-

stituent, the pyrrole was obtained in a slightly decreased yield (entry 17). Aromatic substituents bearing an electron-donating moiety produced an increased yield (entry 16). The replacement of the aryl moiety in R^2 position with an alkyl group resulted in very long reaction times. Even after 96 h, only partial consumption of the starting material was detected using LC/MS and pyrrole **2r** was obtained in 28 % yield. The UV/Vis spectrum of isoxazole **3r** exhibits a noticeable hypsochromic shift of the absorption maximum (λ_{max} = 240 nm for **3r** in comparison to 270 nm for **3a**) explaining the slow isomerization rate under UV–B irradiation. A possible selective cross coupling between two azirines was tested by applying the standard conditions on a 1:1 mixture of isoxazoles **3i** and **3p.** As the reaction provided an almost equimolar mixture of the homocoupled pyrroles **2i** and **2p** and the two-cross coupled regioisomers **2w** and **2x** (see the SI), a selective cross coupling of two isoxazoles under the applied conditions appears not to be feasible.

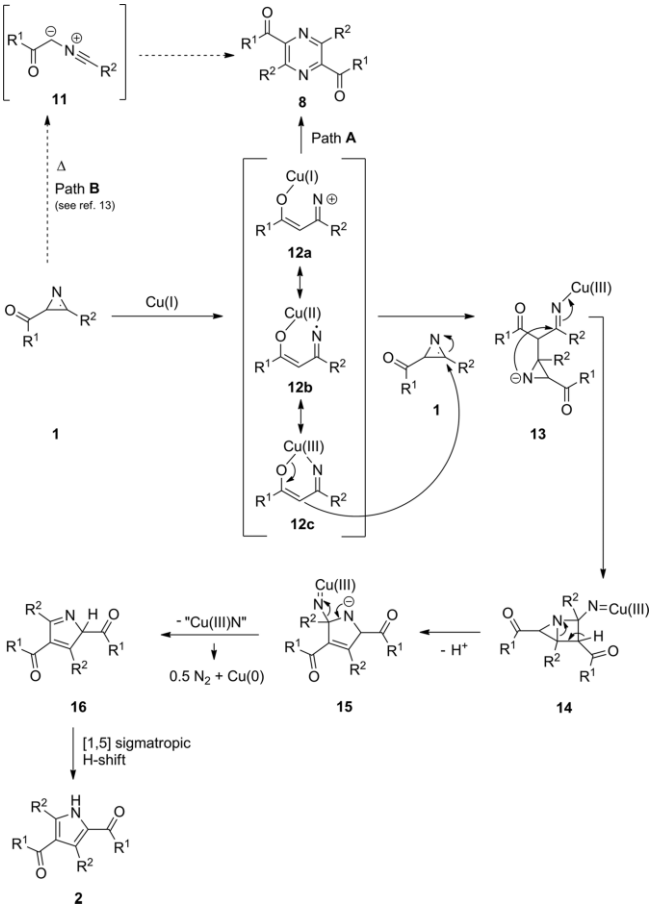
Finally, we carried out several control experiments regarding the mechanism of the dimerization. As stated before, Auricchio and co-workers found iron dichloride to promote the dimerization reaction of *2H*-azirines bearing an alkoxycarbonyl group.[7] In their manuscript, the formation of the pyrrole was proposed to proceed via the cyclization of the reduced enaminone **10** with remaining azirine **1**. Enaminone **10** was suggested to be formed via reduction of the azirine with water and the iron salt. Nevertheless, no detailed mechanistic studies were carried out regarding this type of dimerization to the best of our knowledge. Based on this mechanistic hypothesis, the influence of water on the dimerization reaction was investigated first. Therefore, the dimerization of model azirine **1a** was reperformed under glove box conditions in the presence of molecular sieves (MS 3 Å). The dimerization product was obtained in comparable yield as under standard conditions, so water as an external proton donor can be ruled out.

Secondly, ^{15}N labeled azirine **1s** was prepared in two steps starting from ^{15}N-hydroxylamine and reacted with unlabeled methyl derivative **1m** to determine which of the two available nitrogen atoms is integrated into the cross coupled pyrroles **2t** and **2u**. The structure of the formed isomers (shown in Scheme 7 and determined using ^1H-^1H-NOESY and ^1H-^{13}C-HMBC experiments) are indicating two fundamental findings. First, the reaction features the cleavage of the C–N single bond,



Scheme 7. Isolated cross coupling products and determination of their structure via NMR experiments.

as an intermediate similar to complex **14** has to be passed to explain the found structures. Furthermore, the ^{15}N labeling of the products indicates the elimination of the nitrogen of the azirine, which is ring opened to the complex **14**. Additionally, a glovebox experiment with only the labeled azirine **1r** in dry deuterated acetonitrile revealed the formation of enaminone **10** even under rigorous exclusion of water (vide infra). Based on these findings, the following reaction mechanism (shown in Scheme 8) appears plausible: As stated before, the reaction yields the same product distribution, both when cuprous acetate and cupric acetate are used and an oxidative addition of the copper(I)-species seems more reasonable. Therefore, we assume a copper(I)-species is initially generated. This catalyst should be able to reductively cleave the C–N σ bond of the *2H*-azirine **1** resulting in the copper complex **12a–c**.



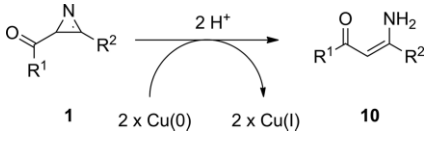
Scheme 8. Plausible mechanism for the formation of the tetrasubstituted pyrroles **2.** (For the simplicity, the ligands/conterions of the copper catalyst are not shown).

Since the energy differences between the oxidation states of copper are narrow and other ring opening reactions of *2H*-azirines are known to furnish both radical and ionic intermediates,[12] the addition complex **12c** can also be described by resonance structures of a stabilized dipole **12a** and imine radical **12b**. The formation of pyrazine by-product **8** can be understood from the dipole character of structure **12a**, which allows a direct dimerization yielding in pyrazine **8** (Path A, Scheme 8). Another pathway for the formation of **8** might be the known

dimerization of nitrile ylide **11**, which could arise from a thermal C–C bond scission of azirine **1** (Path B, Scheme 8)**.**[13] However, we never observed formation of pyrazine 8 in the absence of copper.

As we found the 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) radical to not to interfere with the pyrrole formation (vide infra), we assume the reaction to involve an ionic mechanism. Therefore, intermediate **12** presumably adds to the C=N-bond of another molecule of azirine resulting in the aziridine anion **13**, which undergoes a 4–exo–trig-cyclization onto the copper-activated C=N bond. By-products arising from the potentially competing addition to the carbonyl of the former β-imino ketone were not found in our experiments. The [2.1.0]-bicyclic system **14** was already proposed as key intermediate in the synthesis of 2,4-diacylpyrroles by Khlebnikov and co-workers[14] and in our former study.[9b] Via elimination of a proton and a copper nitrene complex, we assume *(2H)*-pyrrole **16** to be formed which should directly undergo a [1,5] sigmatropic H-shift yielding in the *(1H)*-pyrrole **2.** The regeneration of the active catalyst most likely involves the decomposition of the copper nitrene complex generating a copper(0)-species and molecular nitrogen.

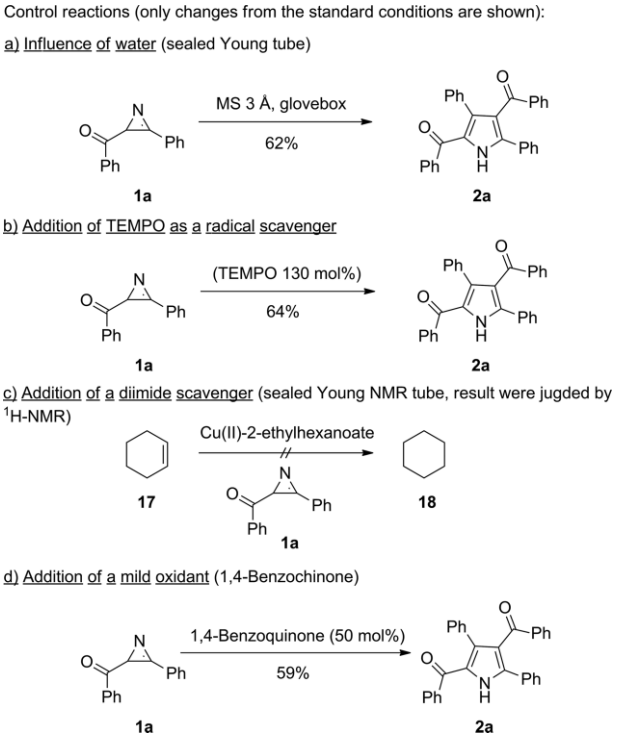
We assume the copper(0) to be reoxidized in situ: The observed enaminone by-product **10** could arise from a reduction of the remaining azirine **1**, which regenerates the active copper(I)-species (see Scheme 9). The formed enaminone can also contribute to the formation of the dimerized pyrrole **2** (see Scheme 11).



Scheme 9. Plausible reoxidation pathway for the active copper species.

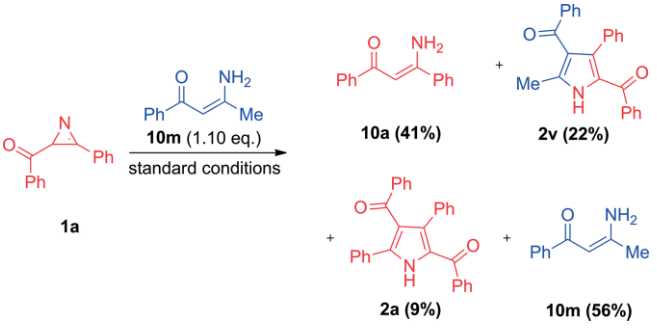
An attempt to use 1,4-benzoquinone for the reoxidation of the assumed copper(0) complex resulted in a slightly decreased yield (see Scheme 10). Possible other mechanisms for the reoxidation would for example involve the generation of diimide starting from a formed copper–imido complex, which could decompose to furnish molecular nitrogen and hydrogen or ammonia and nitrogen via a disproportionation reaction or itself reduce the azirine **1** to the corresponding enaminone **10**. In a control reaction with cyclohexene (which is known to be reduced by diimide quantitatively)[15] no cyclohexane formation was observed by ^{1}H-NMR (see Scheme 10 and the SI). Additionally no molecular hydrogen or ammonia could be detected in this experiment (yet the detection level has not been determined). Thus, we have found no contradiction to the proposed mechanism so far.

While a selective cross-coupling would be synthetically more appealing than a dimerization, our attempts in the latter direction have met with limited success so far. When applying the standard conditions to a mixture of model azirine **1a** and enaminone **10u**, the copper-catalyst induced a formal intermolecular redox reaction and formed the reduced enaminone **10a** as



Scheme 10. Control experiments regarding the mechanism of the pyrrole formation.

the main product along with only 22 % (NMR) of the desired mixed pyrrole **2v** (see Scheme 11).



Scheme 11. Product distribution using the standard conditions with an external enaminone; yields were calculated using phenanthrene as an internal standard (^{1}H-NMR).

Further attempts to effect a cross-coupling in acceptable yields are currently ongoing but will most probably require a different metal catalyst.

Conclusions

In summary, a consecutive photochemical and metal-catalyzed ring-contraction/dimerization sequence in a rayonet-type photoreactor under internal temperature control was established. Adjustment of the temperature allowed to match the rates of the thermal and the photoinduced step. Aryl-substituted isoxazoles could be converted through the corresponding 2-acylazirine intermediates to highly substituted 2,4-diacylpyrroles. A

variety of previously unknown pyrroles could be obtained from simple precursors and using an inexpensive and readily available copper catalyst.

Experimental Section

Acetonitrile (MeCN), dichloromethane (DCM), 1,2-dichloroethane (DCE) and cyclohexane were distilled from calcium hydride under an nitrogen atmosphere. Solvents were degassed using freeze-pump-thaw cycles or by bubbling argon through the liquid in an ultrasonic bath. Deuteriochloroform was stored over basic alumina (Brockmann activity I). All reagents were purchased from commercial suppliers and used without further purification. Water or oxygen sensitive reactions were performed under an atmosphere of nitrogen in oven-dried glassware using standard Schlenk technique. Photochemical reactions were performed in quartz tubes using a photochemical reactor equipped with a circular array of 16 UV lamps (λ = 300 nm, power: 8 W per lamp), a magnetic stirrer and a cooling fan. The temperature in the photochemical reactions were adjusted using an external circulator connected to a cold finger, which was then placed into the quartz tube. Thin layer chromatography was carried out on silica gel 60 F_{254} plates and visualized using UV light. Preparative normal phase chromatography was carried out on silica gel (35 – 70 µm) using manual flash chromatography or an automatic flash purification system. Preparative reversed-phase chromatography was performed on a HPLC system with a C_{18}PFP column (pore size: 5 µm, length: 15 cm, diameter: 30 mm) or on an automatic flash purification system with C_{18} modified silica gel columns and by using mixtures of acetonitrile and water as eluent. Melting points were determined in open capillary tubes and are not corrected. NMR spectra were recorded on a 300, 400 or 600 MHz instrument at 23 °C using standard pulse sequences. The ^{1}H and the ^{13}C chemical shifts (δ) were referenced to the residual solvent signal as internal standard ($CDCl_3$: δ = 7.26 ppm and 77.16 ppm, [D_3]MeCN: δ = 1.94 ppm and 118.26 ppm for ^{1}H and ^{13}C NMR).[16] The ^{15}N NMR and ^{19}F NMR were referenced to an external standard (^{15}N: nitromethane in $CDCl_3$ = 0.0 ppm; ^{19}F: α,α,α-trifluorotoluene in $CDCl_3$, δ = –63.9 ppm). FT-IR spectra (given in cm^{-1}) were recorded using a diamond ATR unit. ESI-MS spectra were recorded using an HPLC system with a UV diode array detector coupled with a LC/MSD ion trap. Mixtures of water (with 0.1 % formic acid) and acetonitrile were used as eluent at a total flow rate of 1.0 mL/min. High resolution masses (APCI-MS and ESI-MS) were recorded using a Q–ToF instrument with dual source and suitable external calibrant.

Isoxazole Synthesis. Isoxazoles **3a** and **3i–m** were previously synthesized using standard conditions.[9] The isoxazoles **1c-l** and **1n–r** were synthesized applying an optimized method of Fokin and co-workers:[10] To a solution of the corresponding aldehyde (1.00 equiv.) and hydroxylamine hydrochloride (1.05 equiv.) in *tert*-butanol/water (1:1, c = 0.25 mmol/mL) was added sodium hydroxide (1.05 equiv.) and the solution was stirred at room temperature for 1 h. Chloramine–T trihydrate (1.05 equiv.) was added in small portions over 5–10 minutes. The corresponding terminal alkyne (1.05 equiv.), copper sulfate pentahydrate (0.03 equiv.) and copper wire (0.04 equiv.) were added and the pH was adjusted to approximately 6 by addition of aqueous NaOH (1 N). The mixture was stirred overnight and poured into water (150 mL). Aqueous NaOH (1 N, 10 mL) was added and the mixture extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried with Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by automatic flash column chromatography (eluent: cyclohexane/ethyl acetate) to afford the crude isoxazoles **3c–q**. Some of the isoxazoles were further purified by recrystallization using mixtures of acetonitrile and water.

3-(4-Methylphenyl)-5-phenylisoxazole (**3b**). Following the general procedure using 4-tolualdehyde (8.32 mmol, 0.98 mL, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.91 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 85:15) afforded the title compound (921 mg, 3.90 mmol, 47 %) as a colorless solid. R_f = 0.44 (4:1 cyclohexane/ethyl acetate). Mp: 123–124 °C. IR (ATR): $\tilde{\nu}$ = 2916, 1612, 1569, 1494, 1448, 949, 829, 763, 686. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.82 (m, 2H), 7.79–7.73 (m, 2H), 7.54–7.42 (m, 3H), 7.32–7.27 (m, 2H), 6.81 (s, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.2, 162.9, 140.2, 130.2, 129.6, 129.0, 127.5, 126.7, 126.3, 125.8, 97.4, 21.5. MS (ESI): *m/z* = 236.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[17]

3-(3-Methylphenyl)-5-phenylisoxazole (**3c**). Following the general procedure using 3-tolualdehyde (8.32 mmol, 0.98 mL, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 85:15) afforded the title compound (882 mg, 3.80 mmol, 45 %) as a colorless solid. R_f = 0.42 (4:1 cyclohexane/ethyl acetate). Mp: 131–132 °C. IR (ATR): $\tilde{\nu}$ = 2920, 1573, 1469, 1450, 1416, 835, 787, 763, 690. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.82 (m, 2H), 7.73–7.70 (m, 1H), 7.68–7.64 (m, 1H), 7.54–7.44 (m, 3H), 7.38 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.30 – 7.25 (m, 1H), 6.83 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.3, 163.1, 138.7, 130.8, 130.2, 129.0, 128.8, 127.5, 127.4, 125.8, 124.0, 97.5, 21.4. MS (ESI): *m/z* = 236.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[18]

3-(2-Methylphenyl)-5-phenylisoxazole (**3d**). Following the general procedure using 2-tolualdehyde (8.32 mmol, 0.97 mL, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 85:15) afforded the title compound (1.02 g, 4.34 mmol, 52 %) as a colorless oil. R_f = 0.50 (4:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 2920, 1573, 1469, 1450, 1416, 835, 787, 763, 690. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.82 (m, 2H), 7.60 – 7.54 (m, 1H), 7.54–7.42 (m, 3H), 7.41–7.27 (m, 3H), 6.71 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.5, 163.7, 136.9, 131.1, 130.2, 129.5, 129.0, 128.9, 127.5, 126.0, 125.9, 100.2, 21.1. MS (ESI): *m/z* = 236.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[19]

3-(4-Fluorophenyl)-5-phenylisoxazole (3e). Following the general procedure using 4-fluorobenzaldehyde (8.32 mmol, 0.89 mL, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 80:20) afforded the title compound (893 mg, 3.74 mmol, 45 %) as a colorless solid. R_f = 0.42 (4:1 cyclohexane/ethyl acetate). Mp: 165–166 °C. IR (ATR): $\tilde{\nu}$ = 3054, 1605, 1526, 1448, 916, 845, 816, 766, 693, 534. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.78 (m, 4H), 7.56–7.40 (m, 3H), 7.24–7.10 (m, 2H), 6.80 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.6, 163.8 (d, $^1J_{CF}$ = 249.8 Hz), 162.1, 130.3, 129.0, 128.7 (d, $^3J_{CF}$ = 8.5 Hz), 127.3, 125.8, 125.4 (d, $^4J_{CF}$ = 3.3 Hz), 116.1 (d, $^2J_{CF}$ = 22.0 Hz), 97.3. ^{19}F-NMR (282 MHz, $CDCl_3$) δ–(111.51 – 111.90). MS (ESI): *m/z* = 240.0 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[9b]

3-(4-Chlorophenyl)-5-phenylisoxazole (3f). Following the general procedure using 4′-chlorobenzaldehyde (8.32 mmol, 1.17 g, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 80:20) afforded the title compound (869 mg, 3.41 mmol, 41 %) as a colorless solid. R_f = 0.42 (4:1 cyclohexane/ethyl acetate).

Mp: 169–170 °C. IR (ATR): $\tilde{\nu}$ = 3112, 1489, 1447, 1095, 950, 840, 815, 767, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.77 (m, 4H), 7.55–7.43 (m, 5H), 6.80 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.8, 162.0, 136.0, 130.4, 129.2, 129.1, 128.1, 127.6, 127.3, 125.9, 97.3. MS (ESI): m/z = 256.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[20]

3-(4-Bromophenyl)-5-phenylisoxazole (3g). Following the general procedure using 4-bromobenzaldehyde (8.32 mmol, 1.54 g, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 80:20) afforded the title compound (949 mg, 3.18 mmol, 38 %) as a colorless solid. R_f = 0.41 (4:1 cyclohexane/ethyl acetate). Mp: 182–183 °C. IR (ATR): $\tilde{\nu}$ = 3113, 1597, 1488, 1426, 918, 815, 767, 692, 507. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.88–7.80 (m, 2H), 7.79–7.71 (m, 2H), 7.66 – 7.59 (m, 2H), 7.54–7.43 (m, 3H), 6.81 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.8, 162.1, 132.2, 130.4, 129.1, 128.3, 128.1, 127.3, 125.9, 124.3, 97.3. MS (ESI): m/z = 300.1 $[M(^{79}Br) + H]^+$, 302.0 $[M(^{81}Br) + H]^+$. The spectroscopic data are in accordance to the literature.[21]

3-(4-(Trifluoromethyl)phenyl)-5-phenylisoxazole (3h). Following the general procedure using 4-(trifluoromethyl)benzaldehyde (8.32 mmol, 1.14 mL, 1.00 equiv.) and phenylacetylene (8.74 mmol, 0.96 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:5 → 80:20) afforded the title compound (644 mg, 2.22 mmol, 27 %) as a colorless solid. R_f = 0.41 (4:1 cyclohexane/ethyl acetate). Mp: 186–187 °C. IR (ATR): $\tilde{\nu}$ = 2924, 1450, 1390, 1158, 950, 818, 768, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03–7.97 (m, 2H), 7.89 – 7.81 (m, 2H), 7.80 – 7.70 (m, 2H), 7.50 (m, 3H), 6.87 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.2, 162.0, 132.7, 132.0 (middle signals of q, $^2J_{CF}$ = 32.7 Hz), 130.7, 129.3, 127.3, 126.2, 126.1 ($^3J_{CF}$ = 3.8 Hz), 124.0 (middle signals of q, $^1J_{CF}$ = 272 Hz), 122.2, 97.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ = 63.99. MS (ESI): m/z = 290.2 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[9b]

3-Phenyl-5-(4-(*tert*-butyl)phenyl)isoxazole (3n). Following the general procedure using benzaldehyde (8.32 mmol, 0.78 mL, 1.00 equiv.) and 4-(*tert*-butyl)phenylacetylene (8.74 mmol, 1.58 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 60:40) afforded the title compound (837 mg, 3.02 mmol, 36 %) as a colorless solid. R_f = 0.52 (4:1 cyclohexane/ethyl acetate). Mp: 95–96 °C. IR (ATR): $\tilde{\nu}$ = 2963, 1618, 2499, 1464, 1399, 950, 840, 765, 691. ^{1}H NMR, COSY (300 MHz, $CDCl_3$): δ = 7.92–7.88 (m, 2H, H-2′ + H-6′), 7.85–7.76 (m, 2H, H-2″ + H-6″), 7.60–7.46 (m, 5H, H-3′-5′ + H-3″ + H-5″), 6.82 (s, 1H, H-4), 1.39 (s, 9H, $C(CH_3)_3$). ^{13}C NMR, HSQC, HMBC (75 MHz, $CDCl_3$) δ = 170.7 (C-5), 163.1 (C-3), 153.8 (C-4″), 130.1 (C-4′), 129.4 (C-1′), 129.0 (C-3′ + C-5′), 127.0 (C-2′ + C-6′), 126.1 (C-3″ + C-5″), 125.8 (C-2″ + C-6″), 124.9 (C-1″), 97.1 (C-4), 35.1 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$). MS (ESI): m/z = 278.2 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{19}H_{20}NO]^+$ 278.1539, found 278.1539.

3-Phenyl-5-(4-fluorophenyl)isoxazole (3o). Following the general procedure using benzaldehyde (7.00 mmol, 0.66 mL, 1.00 equiv.) and 4-fluorophenylacetylene (7.35 mmol, 0.98 g, 1.05 equiv.) a after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 60:40) afforded the title compound (670 mg, 2.80 mmol, 40 %) as a colorless solid. R_f = 0.43 (4:1 cyclohexane/ethyl acetate). Mp: 126 – 128 °C. IR (ATR): $\tilde{\nu}$ = 3115, 1616, 1518, 1500, 1235, 844, 814, 768, 697. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92–7.77 (m, 4H), 7.53–7.44 (m, 3H), 7.24–7.14 (m, 2H), 6.78 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.4, 163.8 (d, $^1J_{CF}$ = 251.2 Hz), 163.1, 130.1, 129.0, 127.9 (d, $^3J_{CF}$ = 8.7 Hz), 126.8, 123.8 (d, $^4J_{CF}$ = 3.3 Hz), 116.3 (d, $^2J_{CF}$ = 22.2 Hz), 97.3. ^{19}F NMR (282 MHz, $CDCl_3$) δ–(111.51–111.90) (m). MS (ESI): m/z = 240.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[22]

3-Phenyl-5-(4-methoxyphenyl)isoxazole (3p). Following the general procedure using benzaldehyde (8.32 mmol, 0.78 mL, 1.00 equiv.) and 4-methoxyphenylacetylene (8.74 mmol, 1.13 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 60:40) afforded the title compound (860 mg, 3.42 mmol, 41 %) as a colorless solid. R_f = 0.50 (2:1 cyclohexane/ethyl acetate). Mp: 128–129 °C. IR (ATR): $\tilde{\nu}$ = 1616, 1519, 1467, 1402, 1262, 1179, 1034, 769, 691. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.83 (m, 2H), 7.82–7.75 (m, 2H), 7.54 – 7.42 (m, 3H), 7.05 – 6.97 (m, 2H), 6.71 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.5, 163.1, 161.3, 130.1, 129.4, 129.0, 127.6, 127.0, 120.5, 114.6, 96.3, 55.6. MS (ESI): m/z = 252.2 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[6b]

3-Phenyl-5-(4-methoxycarbonylphenyl)isoxazole (3q). Following the general procedure using benzaldehyde (5.50 mmol, 0.52 mL, 1.00 equiv.) and 4-(methoxycarbonyl)phenylacetylene (5.78 mmol, 1.03 g, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 60:40) afforded the title compound (472 mg, 1.69 mmol, 31 %) as a colorless solid. R_f = 0.23 (4:1 cyclohexane/ethyl acetate). Mp: 200 – 202 °C. IR (ATR): $\tilde{\nu}$ = 1712, 1441, 1415, 1279, 1112, 825, 771, 706, 697. ^{1}H NMR, COSY (300 MHz, $CDCl_3$): δ = 8.20–8.11 (m, 2H, H-3″ + H-5″), 7.94–7.90 (m, 2H, H-2″ + H-6″), 7.90 – 7.85 (m, 2H, H-2′ + H-6′), 7.55 – 7.45 (m, 3H, H-3′-5′), 6.94 (s, 1H, H-4), 3.96 (s, 3H, C-4″-$COCH_3$). ^{13}C NMR, HSQC, HMBC (75 MHz, $CDCl_3$) δ = 169.2 (C-5), 166.3 (C-4″-$COCH_3$), 163.2 (C-3), 131.4 (C-4″), 131.2 (C-1″), 130.3 (C-3″ + C-5″), 130.2 (C-4′), 129.0 (C-3′ + C-5′), 128.8 (C-1′), 126.8 (C-2′ + C-6′), 125.7 (C-2″ + C-6″), 99.0 (C-4), 52.4 (C-4″-$COCH_3$). MS (ESI): m/z = 280.2 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{17}H_{14}NO_3]^+$ 280.0968, found 280.0968.

3-Phenyl-5-pentylisoxazole (3r). Following the general procedure using benzaldehyde (8.32 mmol, 0.84 mL, 1.00 equiv.) and 1-heptyne (8.74 mmol, 1.15 mL, 1.05 equiv.) after column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 98:2 → 85:15) afforded the title compound (472 mg, 1.69 mmol, 31 %) as a colorless oil. R_f = 0.54 (4:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 2956, 1602, 1580, 1471, 1443, 1408, 950, 767, 693. ^{1}H NMR, COSY (300 MHz, $CDCl_3$): δ = 7.92–7.72 (m, 2H, H-2′ + H-6′), 7.53–7.41 (m, 3H, H-3′-5′), 6.29 (s, 1H, H-4), 2.91–2.70 (m, 2H, H-1″), 1.89–1.67 (m, 2H, H-2″), 1.38 (m, 4H, H-3″-4″), 1.02–0.83 (m, 3H, H-5″). ^{13}C NMR, HSQC, HMBC (75 MHz, $CDCl_3$) δ = 174.3 (C-5), 162.3 (C-3), 129.8 (C-4′), 129.4 (C-1′), 128.8 (C-3′ + C-5′), 126.7 (C-2′ + C-6′), 98.8 (C-4), 31.2 (C-4″), 27.2 (C-2″), 26.8 (C-1″), 22.3 (C-3″), 13.9 (C-5″). MS (ESI): m/z = 236.1 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{14}H_{18}NO]^+$ 216.1383, found 216.1388.

Azirine and ^{15}N labeled azirine. ^{15}N-3,5-Diphenylisoxazole (3s). The labeled isoxazole was synthesized using the method of Griesbeck and co-workers:[6b] A mixture of dibenzoylmethane (6.81 mmol, 1.53 g, 1.00 equiv.), ^{15}N-hydroxylamine hydrochloride (7.15 mmol, 0.50 g, 1.05 equiv.), water (12 mL) and ethanol (6 mL) was stirred at 90 °C for 18 h. The mixture was poured into water (50 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried with sodium sulfate and the solvent removed in vacuo to afford the ^{15}N labeled isoxazole (1.24 g, 5.58 mmol, 82 %) as a colourless solid. R_f = 0.44 (4:1 cyclohexane/ethyl acetate). Mp: 141–142 °C. IR (ATR): $\tilde{\nu}$ = 3114, 1593, 1459, 1398, 820, 762, 691. ^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 7.98–7.83 (m, 4H, H-2′ + H-6′ + H-2″ + H-6″), 7.61 – 7.44 (m, 6H, H-3′-5′ + H-3‴-5‴), 6.87 (d, $^3J_{NH}$ = 1.3 Hz, 1H, H-4). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 170.4 (d, $^2J_{CN}$ = 1.1 Hz), 163.0 (d, $^1J_{CN}$ = 2.1 Hz), 130.3 (C-4″), 130.1 (C-4′), 129.2 (d, $^2J_{CN}$ = 7.3 Hz, C-1′), 129.0 (C-3′ +

C-5′ + C-3″ + C-5″), 127.5 (C-1″) 126.8 (d, $^3J_{CN}$ = 2.3 Hz, C-2′ + C-6′), 125.9 (C-2″ + C-6″), 97.5 (C-4). ^{15}N NMR (41 MHz, $CDCl_3$) δ = 366.93. MS (ESI): *m/z* = 223.1 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{15}H_{12}[^{15}N]O]^+$ 223.0886, found 223.0884.

The azirines **1a**, **1l** and **1m** were prepared according to the procedure of Singh et al.[6a] and using the modification of Griesbeck and co-workers:[6b] In an oven-dried quartz tube, the isoxazole **3** (1.00 equiv.) and freshly distilled propionaldehyde (10 equiv.) were dissolved in dry acetonitrile (c = 0.1 M). The solution was degassed and irradiated for 6 h (λ_{max} = 300 nm). The solvent was removed in vacuo and the crude mixture purified by flash column chromatography (eluent: cyclohexane/ethyl acetate) to afford azirine **1**.

Phenyl(3-phenyl-*2H*-aziren-2-yl)methanone (1a). Following the general procedure using 3,5-diphenylisoxazole **3a** (4.0 mmol, 885 mg, 1.00 equiv.) after flash column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 65:35) afforded the title compound (430 mg, 1.94 mmol, 48 %) as a yellow oil. R_f = 0.37 (4:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 1775, 1672, 1449, 1352, 1230, 1024, 762, 721, 688, 653. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33–8.06 (m, 2H), 8.00–7.78 (m, 2H), 7.67 – 7.60 (m, 2H), 7,58–7.52 (m, 4H), 3.86 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.8, 157.4, 137.6, 134.3, 133.9, 131.0, 129.8, 129.2, 128.8, 122.8, 34.0. MS (ESI): *m/z* = 222.0 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[9b]

Phenyl(3-methyl-*2H*-aziren-2-yl)methanone (1m). Following the general procedure using 3-methyl-5-phenylisoxazole **3l** (5.0 mmol, 796 mg, 1.00 equiv.) after flash column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 70:30) afforded the title compound (241 mg, 1.51 mmol, 30 %) as yellow oil. R_f = 0.23 (2:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 3064, 1699, 1449, 1355, 1231, 1211, 720, 689. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14–7.94 (m, 2H), 7.64–7.56 (m, 1H), 7.53 – 7.46 (m, 2H), 3.47 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.1, 157.2, 137.3, 133.4, 128.8, 128.3, 32.6, 12.7. MS (ESI): *m/z* = 160.1 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[23]

^{15}N-Phenyl(3-phenyl-*2H*-aziren-2-yl)methanone (1s). Following the general procedure using ^{15}N-3,5-diphenylisoxazole **3s** (2.5 mmol, 555 mg, 1.00 equiv.) after flash column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 65:35) afforded the title compound (178 mg, 0.80 mmol, 33 %) as yellow oil. R_f = 0.37 (4:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 3062, 1671, 1597, 1449, 1230, 971, 761, 721, 688, 649. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18–8.10 (m, 2H, H-2′ + H-6′), 7.92 – 7.85 (m, 2H, H-2‴ + H-6‴), 7.68 – 7.60 (m, 2H, H-4′ + H-4‴), 7.60–7.51 (m, 4H, H-3′ + H-5′ + H-3‴ + H-5‴), 3.86 (d, $^2J_{NH}$ = 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 197.5 (CO), 157.0 (d, $^1J_{CN}$ = 6.6 Hz, C-3″), 137.3 (C-1′), 134.0 (C-4‴), 133.5 (C-4′), 130.7 C-2′ + C-6′), 129.5 (C-3‴ + C-5‴), 128.9 (C-3′ + C-5′), 128.5 (C-2′ + C-6′), 122.5 (C-1‴), 33.6 (d, $^1J_{CN}$ = 10.4 Hz, C-2″). ^{15}N NMR (41 MHz, $CDCl_3$) δ = 261.58. MS (ESI): *m/z* = 223.1 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{15}H_{12}[^{15}N]O]^+$ 223.0886, found 223.0889.

General protocol for the synthesis of pyrroles 2a–r: In an oven-dried quartz tube under nitrogen atmosphere, isoxazoles **3** (1.0 mmol, 1.00 equiv.) and Cu(II)-2-ethylhexanoate (0.1 mmol, 35 mg, 0.10 equiv.) were dissolved or suspended in dry acetonitrile (10 mL, c = 0.1 M (method **A**) or 20 mL, c = 0.05 M (method **B**). The reaction tube was degassed and placed into the photoreactor. A cold finger connected to a circulator was placed into the solution and the reaction mixture was preheated to 70 °C. The vessel was irradiated (λ_{max} = 300 nm, 16 × 8 W) at that temperature until TLC or LC/MS indicated full consumption of the starting material (20 – 48 h). The solvent was removed in vacuo and the residue purified by flash chromatography. Some of the pyrroles were further purified using preparative HPLC with mixtures of water and acetonitrile as eluent.

(3,5-Diphenyl-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2a). Following general procedure **A**, 3,5-diphenylisoxazole (1.0 mmol, 221 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 94:6 → 70:30) the title compound (119 mg, 0.28 mmol, 56 %) was obtained as yellow solid. R_f = 0.16 (4:1 cyclohexane/ethyl acetate). Mp: 220 – 222 °C. IR (ATR): $\tilde{\nu}$ = 3265, 1653, 1599, 1575, 1493, 1463, 1417, 1260, 914, 736, 695. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ = 10.53 (s, 1H, NH), 7.68–7.62 (m, 2H, H-2‴ + H-6‴), 7.56 (m, 2H, H-2⁗ + H-6⁗), 7.44–7.37 (m, 2H, H-2′ + H-6′), 7.33–7.24 (m, 4H, H-3⁗ + H-5⁗), 7.20 (m, 1H, H-4′), 7.12 (m, 2H, H-3‴ + H-5‴), 7.00 (m, 2H, H-3′ + H-5′), 6.95–6.91 (m, 2H, H-2″ + H-6″), 6.84 (m, 3H, H-3″-5″). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 194.2 (C-4-*C*O), 187.8 (C-2-*C*O), 138.1 (C-5), 138.0 (C-1‴), 137.3 (C-1′), 133.9 (C-3), 133.2 (C-1″), 132.7 (C-4‴), 131.4 (C-4′), 130.7 (C-2″ + C-6″), 130.3 (C-1⁗), 129.8 (C-2‴ + C-6‴), 129.3 (C-2′ + C-6′), 128.9 (C-4⁗), 128.8 (C-3⁗ + C-5⁗), 128.0 (C-2 + C-2⁗ + C-6⁗), 127.9 (C-3‴ + C-5‴), 127.4 (C-3′ + C-5′ + C-3″ + C-5″), 126.9 (C-4″), 123.2 (C-4). MS (ESI): *m/z* = 427.2 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[9b]

In an upscaled reaction following general procedure **A**, 3,5-diphenylisoxazole (3.16 mmol, 700 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. Beside pyrrole **2a** (373 mg, 0.87 mmol, 56 %), column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 94:6 → 70:30) and reverse phase column chromatography (SiO_2–C_{18}, eluent: acetonitrile/water, 50:50 → 90:10) afforded the following primary by-products.

(3,6-Diphenyl-pyrazine-2,5-diyl)bis(phenylmethanone) (8a). The title compound (42 mg, 0.10 mmol, 6 %) was obtained as a colorless solid. R_f = 0.20 (4:1 cyclohexane/ethyl acetate). Mp: 160 – 162 °C. IR (ATR): $\tilde{\nu}$ = 3060, 1669, 1526, 1492, 1218, 924, 768, 732, 694, 647. ^{1}H NMR, COSY (300 MHz, $CDCl_3$): δ = 8.20 – 8.13 (m, 2H, H-2′ + H-6′), 7.68–7.60 (m, 7H, H-4′ + H-2″ + H-6″ + H-2‴ + H-6‴ + H-2⁗ + H-6⁗), 7.56 – 7.49 (m, 2H, H-3′ + H-5′), 7.48–7.41 (m, 1H, H-4‴), 7.37 – 7.22 (m, 8H, H-3″ + H-5″ + H-3‴ + H-5‴ + H-3⁗ + H-5⁗). ^{13}C NMR, HSQC, HMBC (75 MHz, $CDCl_3$) δ = 196.1 (C-2-CO), 191.2 (C-5-CO), 165.1 (C-3 + C-6), 162.5 (C-2 + C-5), 136.7 (2C, C_{Ar}), 134.9 (C-1′), 134.0 (C_{Ar}), 133.9 (C-4′), 131.0 (C-2′ + C-6′), 130.8 (C_{Ar}), 130.3 (C_{Ar}), 129.3 (C_{Ar}), 128.8 (C_{Ar}), 128.6 (C_{Ar}), 128.5 (C-3′ + C-5′). MS (ESI): *m/z* = 441.2 $[M + H]^+$. The spectroscopic data are in accordance to the literature.[7]

(4,6-Diphenyl-5-benzoylpyrimidine) (9a). The title compound (65 mg, 0.19 mmol, 12 %) was obtained as a colorless solid. R_f = 0.13 (2:1 cyclohexane/ethyl acetate). Mp: 149 – 150 °C. IR (ATR): $\tilde{\nu}$ = 3059, 1667, 1536, 1518, 1430, 1226, 926, 755, 696. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ = 9.44 (s, 1H, H-2), 7.61 – 7.57 (m, 2H, H-2″ + H-6″), 7.57–7.54 (m, 4H, H-2′ + H-6′ + H-2‴ + H-6‴), 7.43–7.38 (m, 1H, H-4″), 7.36–7.23 (m, 9H, H-3′-5′ + H-3″ + H-5″ + H-3‴-5‴). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 196.1 (C-5-*C*O), 164.6 (C-4 + C-6), 158.4 (C-2), 137.2 (C-1′ + C-1‴), 137.0 (C-1″), 133.8 (C-4″), 130.5 (C-5), 130.0 (C-4′ + C-4‴), 129.3 (C-2″ + C-6″), 129.0 (C-2′ + C-6′ + C-2‴ + C-6‴), 128.6 (C-3″ + C-5″), 128.5 (C-3′ + C-5′ + C-3‴ + C-5‴). MS (ESI): *m/z* = 337.1 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{23}H_{17}N_2O]^+$ 337.1335, found 337.1335. Crystals suitable for X-ray crystallography could be obtained by recrystallization of **9a** from cyclohexane/ethyl acetate (2:1).

(3-Amino-1,3-diphenylprop-2-en-1-one) (10a). The title compound (29 mg, 0.13 mmol, 4 %) was obtained as a colorless

solid. R_f = 0.47 (1:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 3352, 3167, 1599, 1565, 1525, 1484, 1307, 1226, 740, 694. ^{1}H NMR, COSY (300 MHz, $CDCl_3$): δ = 10.43 (s, 1H, NH), 8.00–7.92 (m, 2H, C-2′ + C-6′), 7.68–7.61 (m, 2H, C-2″, C-6″), 7.53–7.40 (m, 6H, C-3′–5′, C-3″–5″), 6.16 (s, 1H, C-2), 5.45 (s, 1H, NH). ^{13}C NMR, HSQC, HMBC (75 MHz, $CDCl_3$) δ = 190.3 (C-1), 163.0 (C-3), 140.5 (C-1′), 137.8 (C-1″), 131.2 (C-4′), 130.9 (C-4″), 129.2 (C-3′ + C-5′), 128.4 (C-3″ + C-5″), 127.4 (C-2′+ C-6′), 126.5 (C-2″ + C-6″), 92.1 (C-2). MS (ESI): m/z = 224.1 [M + H]$^+$. The spectroscopic data are in accordance to the literature.[24]

(3,5-Di–(4-methylphenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2b). Following general procedure **A**, 3-(4-methylphenyl)-5-phenylisoxazole (1.0 mmol, 235 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 94:6 → 70:30) the title compound (116 mg, 0.26 mmol, 52 %) was afforded as a yellow solid. R_f = 0.13 (4:1 cyclohexane/ethyl acetate). Mp: 230 – 232 °C. IR (ATR): $\tilde{\nu}$ = 3263, 1597, 1535, 1448, 1296, 904, 819, 727, 693. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ = 10.32 (s, 1H, NH), 7.68 – 7.63 (m, 2H, H-2‴ + H-6‴), 7.44–7.37 (m, 4H, H-2′ + H-6′ + H-2⁗ + H-6⁗), 7.32–7.24 (m, 1H, H-4‴), 7.23–7.17 (m, 1H, H-4′), 7.16–7.11 (m, 2H, H-3‴ + H-5‴), 7.11–7.07 (m, 2H, H-3⁗ + H-5⁗), 7.03–6.97 (m, 2H, H-3′ + H-5′), 6.84–6.78 (m, 2H, H-2″ + H-6″), 6.63 (m, 2H, H-3″ + H-5″), 2.30 (s, 3H, C-4⁗-CH_3), 2.07 (s, 3H, C-4″-CH_3). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 194.5 (C-2-*C*O), 187.7 (C-4-*C*O), 138.9 (C-4‴), 138.1 (C-5), 138.0 (C-1‴), 137.5 (C-1′), 136.5 (C-4″), 134.1 (C-3), 132.6 (C-4‴), 131.1 (C-4′), 130.6 (C-2″ + C-6″), 130.2 (C-1″), 129.9 (C-2‴ + C-6‴), 129.5 (C-3⁗ + C-5⁗), 129.3 (C-2′ + C-6′), 128.1 (C-3″ + C-5″), 127.9 (C-3‴ + C-5‴), 127.8 (C-2 + C-2⁗ + C-6⁗), 127.5 (C-1⁗), 127.4 (C-3′ + C-5′), 122.9 (C-4), 21.3 (C-4⁗-CH_3), 21.0 (C-4″-CH_3). MS (ESI): m/z = 456.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{32}H_{25}NO_2Na]^+$ 478.1778, found 478.1773.

(3,5-Di–(3-methylphenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2c). Following general procedure **A**, 3-(3-methylphenyl)-5-phenylisoxazole (1.0 mmol, 235 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 80:20) the title compound (105 mg, 0.23 mmol, 46 %) was afforded as a yellow solid. R_f = 0.25 (4:1 cyclohexane/ethyl acetate). Mp: 195–197 °C. IR (ATR): $\tilde{\nu}$ = 3261, 1599, 1449, 1402, 1210, 944, 914, 751, 695. ^{1}H NMR, COSY (600 MHz, $CDCl_3$): δ = 10.16 (s, 1H, NH), 7.66–7.62 (m, 2H, H-2′ + H-6′), 7.41 – 7.37 (m, 2H, H-2‴ + H-6‴), 7.34–7.29 (m, 2H, H-4″ + H-6″), 7.30–7.25 (m, 1H, H-4′), 7.22 – 7.16 (m, 2H, H-5″ + H-4‴), 7.16–7.08 (m, 3H, H-2′ + H-3′ + H-5′), 7.00 (m, 2H, H-3‴ + H-5‴), 6.80 – 6.73 (m, 2H, H-5⁗ + H-6⁗), 6.68–6.64 (m, 2H, H-2⁗ + H-4⁗), 2.29 (s, 3H, C-3″-CH_3), 1.92 (s, 3H, C-3⁗-CH_3). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 194.3 (C-4-*C*O), 187.8 (C-2-*C*O), 138.5 (C-3⁗), 138.3 (C-4), 138.2 (C-1‴), 137.5 (C-1′), 136.8 (C-3″), 134.2 (C-3), 132.9 (C-1″), 132.6 (C-4‴), 131.8 (C-4″), 131.3 (C-4′), 130.2 (C-1⁗), 129.7 (C-2‴ C-6‴ + C-2⁗), 129.0 (C-2′ + C-6′), 128.7 (C-5⁗), 128.6 (C-4⁗), 127.9 (C-2 + C-3‴ +C-5‴), 127.6 (C-2″), 127.4 (C-5″ + C-6″), 127.3 (C-3′ + C-5′), 125.2 (C-6⁗), 123.0 (C-4), 21.4 (C-3⁗-CH_3), 20.9 (C-3″-CH_3). MS (ESI): m/z = 456.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{32}H_{25}NO_2Na]^+$ 478.1778, found 478.1775.

(3,5-Di–(4-fluorophenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2e). Following general procedure **A**, 3-(4-fluorophenyl)-5-phenylisoxazole (1.0 mmol, 239 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 96:4 → 80:20) and preparative HPLC (eluent: acetonitrile/water, 60:40, t_r = 11.5–13.5 min) the title compound (110 mg, 0.24 mmol, 48 %) was obtained as a colorless solid. R_f = 0.17 (4:1 cyclohexane/ethyl acetate). Mp: 223 – 225 °C. IR (ATR): $\tilde{\nu}$ = 3259, 1597, 1595, 1504, 1420, 1258, 1234, 912, 838, 734. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.63 (s, 1H, NH), 7.63–7.59 (m, 2H, H-2‴ + H-6‴), 7.57 – 7.51 (m, 2H, H-2⁗ + H-6⁗), 7.36–7.33 (m, 2H, H-2′ + H-6′), 7.33–7.29 (m, 1H, H-4′), 7.29 – 7.23 (m, 1H, H-4‴), 7.15 (m, 2H, H-3‴ + H-5‴), 7.04 (m, 2H, H-3′ + H-5′), 6.96 (m, 2H, H-3⁗ + H-5⁗), 6.92–6.86 (m, 2H, H-2″ + H-6″), 6.53 (m, 2H, H-3″ + H-5″). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 194.0 (C-4-*C*O), 187.8 (C-2-*C*O), 163.00 (d, $^1J_{CF}$ = 248.6 Hz, C-4⁗), 161.8 (d, $^1J_{CF}$ = 248.6 Hz, C-4″), 137.8 (C-1‴), 137.5 (C-1′), 137.2 (C-5), 133.0 (C-4′), 132.9 (C-3), 132.3 (d, $^3J_{CF}$ = 8.4 Hz, C-2″ + C-6″), 131.7 (C-4‴), 130.1 (d, $^3J_{CF}$ = 8.4 Hz, C-2⁗ + C-6⁗), 129.7 (C-2‴ + C-6‴), 129.2 (C-1″ + C-2′ + C-6′), 128.1 (C-2), 128.0 (C-3‴ + C-5‴), 127.6 (C-3′ + C-5′), 126.4 (d, $^4J_{CF}$ = 3.4 Hz, C-1⁗), 123.2 (C-4), 115.9 (d, $^2J_{CF}$ = 21.8 Hz, C-3⁗ + C-5⁗), 114.4 (d, $^2J_{CF}$ = 21.8 Hz, C-3″ + C-5″). ^{19}F NMR (282 MHz, $CDCl_3$) δ = 112.65 (*m*), - 116.04 (m). MS (ESI): m/z = 464.2 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{30}H_{20}F_2NO_2]^+$ 464.1457, found 464.1455.

(3,5-Di–(4-chlorophenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2f). Following general procedure **A**, 3-(4-chlorophenyl)-5-phenylisoxazole (1.0 mmol, 255 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 80:20) the title compound (110 mg, 0.22 mmol, 45 %) was afforded as a colorless solid. R_f = 0.50 (2:1 cyclohexane/ethyl acetate). Mp: 233 – 235 °C. IR (ATR): $\tilde{\nu}$ = 3259, 1599, 1490, 1419, 1277, 1255, 1094, 911, 833, 731. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.72 (s, 1H, NH), 7.64–7.58 (m, 2H, C-2‴ + C-6‴), 7.50 – 7.45 (m, 2H, C-2⁗ + C-6⁗), 7.36–7.32 (m, 3H, C-2′ + C-6′ + C-4‴), 7.29 (m, 1H, C-4′), 7.23 (m, 2H, C-3⁗ + C-5⁗), 7.19–7.14 (m, 2H, C-3‴ + C-5‴), 7.05 (m, 2H, C-3′ + C-5′), 6.82 (m, 4H, C-2″-3″ + C-5″-6″). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.9 (C-4-*C*O), 187.8 (C-2-*C*O), 137.6 (C-1‴), 137.1 (C-5), 137.0 (C-1′), 135.1 (C-4⁗), 133.1 (C-4″ + C-4‴), 132.6 (C-3), 131.8 (C-2″ + C-6″ + C-4′), 131.6 (C-1″), 129.7 (C-2‴ + C-6‴), 129.4 (C-2⁗ + C-6⁗), 129.2 (C-2′ + C-6′), 129.0 (C-3⁗ + C-5⁗), 128.5 (C-1⁗), 128.3 (C-2), 128.2 (C-3‴ + C-5‴), 127.6 (C-3′ + C-5′ + C-3″ + C-5″), 123.3 (C-4). MS (ESI): m/z = 496.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{30}H_{20}Cl_2NO_2]^+$ 496.0863, found 496.0863.

(3,5-Di–(4-bromophenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2g). Following general procedure **A**, 3-(4-bromophenyl)-5-phenylisoxazole (1.0 mmol, 298 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 96:4 → 80:20) the title compound (102 mg, 0.18 mmol, 35 %) was obtained as a yellow solid. R_f = 0.25 (4:1 cyclohexane/ethyl acetate). Mp: 244 – 245 °C. IR (ATR): $\tilde{\nu}$ = 3257, 1598, 1450, 1253, 1042, 1009, 907, 828, 730, 696. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.80 (s, 1H, NH), 7.65–7.59 (m, 2H, H-2‴ + H-6‴), 7.44 – 7.36 (m, 4H, H-2⁗ + H-3⁗ + H-5⁗ + H-6⁗), 7.36–7.28 (m, 4H, H-2′ + H-4′ + H-6′ + H-4‴), 7.16 (m, 2H, H-3‴ + H-5‴), 7.06 (m, 2H, H-3′ + H-5′), 6.96 (m, 2H, H-2″ + H-6″), 6.77 (m, 2H, H-3″ + H-5″). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.8 (C-4-*C*O), 187.8 (C-2-*C*O), 137.6 (C-1‴), 137.1 (C-5), 137.0 (C-1′), 133.2 (C-4‴), 132.7 (C-1″), 132.1 (C-3″ + C-5″), 132.0 (C-3 + C-3⁗ + C-5⁗), 131.8 (C-4′), 130.6 (C-2″ + C-6″), 129.7 (C-2‴ + C-6‴), 129.6 (C-2⁗ + C-6⁗), 129.2 (C-2′ + C-6′), 129.0 (C-1⁗), 128.3 (C-2), 128.2 (C-3‴ + C-5‴), 127.7 (C-3′ + C-5′), 123.4 (C-4⁗), 123.2 (C-4), 121.4 (C-4″). MS (ESI): m/z = 584.3 [M(2 × ^{79}Br) + H]$^+$, 586.1 [M(^{79}Br + ^{81}Br) + H]$^+$, 588.0 [M(2 × ^{81}Br) + H]$^+$. HRMS (ESI) calcd. for $[C_{30}H_{20}[^{79}Br]_2NO_2]^+$ 583.9855, found 583.9850.

(3,5-Di–(4-(trifluoromethyl)phenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2h). Following general procedure **A**, 3-(4-(trifluoromethyl)phenyl)-5-phenylisoxazole (1.0 mmol, 289 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chroma-

tography (SiO_2, eluent: cyclohexane/ethyl acetate, 96:4 → 80:20) and preparative HPLC (eluent: acetonitrile/water, 70:30, t_r = 11–13 min) the title compound (109 mg, 0.19 mmol, 40 %) was obtained as a colorless solid. R_f = 0.22 (4:1 cyclohexane/ethyl acetate). Mp: 213–215 °C. IR (ATR): $\tilde{\nu}$ = 3256, 1652, 1607, 1321, 1166, 1123, 1067, 905, 731, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 11.10 (s, 1H, NH), 7.68 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-2‴ + H-6‴), 7.63–7.60 (m, 2H, H-2‴ + H-6‴), 7.50 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-3‴ + H-5‴), 7.32 (m, 1H, H-4‴), 7.29 – 7.27 (m, 2H, H-2′ + H-6′), 7.24 (m, 1H, H-4′), 7.18–7.13 (m, 2H, H-3‴ + H-5‴), 7.09 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-3″ + H-6″), 7.03 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-2″ + H-6″), 7.00 (m, 2H, H-3′ + H-5′). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.5 (C-4-*C*O), 187.9 (C-2-*C*O), 137.5 (C-1‴), 136.9 (C-5 + C-1′), 136.8 (C-1″), 133.4 (C-1‴), 133.3 (C-4‴), 132.5 (C-3), 132.0 (C-4′), 130.9 (C-2″ + C-6″), 130.7 (q, $^2J_{CF}$ = 32.7 Hz, C-4‴), 129.7 (C-2‴ + C-6‴), 129.0 (C-2′ + C-6′), 129.0 (q, $^2J_{CF}$ = 32.7 Hz, C-4″), 128.0 (C-2) 128.6 (C-2‴ + C-6‴), 128.2 (C-3‴ + C-5‴), 127.6 (C-3′ + C-5′), 125.7 (q, $^3J_{CF}$ = 3.7 Hz, C-3‴ + C-5‴), 124.3 (q, $^3J_{CF}$ = 3.7 Hz, C-3″ + C-5″), 123.8 (2 × q, $^1J_{CF}$ = 272.1 Hz, C-4″-CF_3 + C-4‴-CF_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ = 64.01 (s), – 64.19 (s). MS (ESI): *m/z* = 564.2 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{32}H_{20}F_6NO_2]^+$ 564.1393, found 564.1394.

(3,5-Di–(4-(methoxylcarbonyl)phenyl)-*1H*-pyrrole-2,4-diyl)bis-(phenylmethanone) (2i). Following general procedure **A**, 3-(4-(methoxycarbonyl)phenyl)-5-phenylisoxazole (1.0 mmol, 279 mg, 1.00 equiv.) was irradiated for 30 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 85:15 → 60:40) and preparative HPLC (eluent: acetonitrile/water, 55:45, t_r = 12–14 min) the title compound (90 mg, 0.17 mmol, 34 %) was obtained as a colorless solid. R_f = 0.17 (4:1 cyclohexane/ethyl acetate). Mp: 250–253 °C. IR (ATR): $\tilde{\nu}$ = 3327, 3000, 1718, 1609, 1400, 1275, 1190, 1106, 732, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.80 (s, 1H, NH), 7.96–7.92 (m, 2H, H-3‴ + H-5‴), 7.62 (m, 4H, H-2‴ + H-6‴), 7.53–7.49 (m, 2H, H-3″ + H-5″), 7.39–7.35 (m, 2H, H-2′ + H-6′), 7.29 (m, 1H, H-4‴), 7.21 (m, 1H, H-4′), 7.14 (m, 2H, H-3‴ + H-5‴), 7.03–6.96 (m, 4H, H-2″ + H-6″ + H-3′ + H-5′), 3.90 (s, 3H, C-4‴-$COOCH_3$), 3.80 (s, 3H, C-4″-$COOCH_3$). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.7 (C-4-*C*O), 187.8 (C-2-*C*O), 166.7 (C-4″-*C*$OOCH_3$), 166.4 (C-2″-*C*$OOCH_3$), 137.9 (C-1‴), 137.5 (C-1‴), 136.9 (C-1′), 136.7 (C-5), 134.2 (C-1‴), 133.3 (C-4‴), 132.5 (C-3), 132.1 (C-4′), 130.6 (C-2″ + C-6″), 130.2 (C-4‴), 130.0 (C-3‴ + C-5‴), 129.7 (C-2‴ + C-5‴), 129.2 (C-2′ + C-6′), 128.7 (C-2, C-3″ + C-5″), 128.3 (C-4″), 128.2 (C-3‴ + C-5‴), 127.9 (C-2‴ + C-6‴), 127.7 (C-3′ + C-5′), 123.9 (C-4), 52.3 (C-4‴-CO_2CH_3), 52.1 (C-4″-CO_2CH_3). MS (ESI): *m/z* = 544.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{34}H_{25}NO_6]^+$ 544.1755, found 544.1764.

(3,5-Di–(2-naphthyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2j). Following general procedure **B**, 3-(2-naphthyl)-5-phenylisoxazole (1.0 mmol, 271 mg, 1.00 equiv.) was irradiated for 48 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 80:20) and preparative HPLC (eluent: acetonitrile/water, 65:35, t_r = 14–16 min) the title compound (128 mg, 0.24 mmol, 48 %) was obtained as a colorless solid. R_f = 0.22 (4:1 cyclohexane/ethyl acetate). Mp: 203–206 °C. IR (ATR): $\tilde{\nu}$ = 3255, 3056, 1598, 1450, 1262, 907, 819, 728, 695, 645. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.41 (s, 1H, NH), 8.09 (d, $^4J_{HH}$ = 1.8 Hz, 1H, H-1‴), 7.83 – 7.78 (m, 2H, H-5‴ + H-8‴), 7.77 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H-4‴), 7.72–7.68 (m, 2H, H-2‴ + H-6‴), 7.61 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.8 Hz, 1H, H-3‴), 7.57–7.54 (m, 1H, H $_{Naph(C-3)}$), 7.52–7.46 (m, 2H, H-6‴ + H-7‴), 7.45 – 7.42 (m, 2H, H-1″ + $H_{Naph(C-3)}$), 7.41–7.37 (m, 2H, H-2′ + H-6′), 7.34–7.27 (m, 4H, H-4″ + $H_{Naph(C-3)}$), 7.18–7.12 (m, 1H, H-4‴), 7.05 (m, 3H, H-3‴ + H-5‴ + H-3‴), 6.95–6.90 (m, 1H, H-4′), 6.78 (m, 2H, H-3′ + H-5′). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 194.4 (C-4-*C*O), 187.8 (C-2-*C*O), 138.0 (C-1‴), 137.9 (C-5), 137.3 (C-1′), 133.8 (C-3), 133.1 (C-4a‴ + C-8a‴), 132.8 (C-4‴), 132.5 ($C_{Naph(C-3)}$), 131.9 (C-4a″), 131.3 (C-4′), 130.6 (C-2″), 130.3 (C-1″), 129.7 (C-2‴ + C-6‴), 129.0 (C-2′ + C-6′), 128.7 (C-4‴), 128.4 (C-2, C-8‴), 128.3 (C-3‴), 128.0 (C-3‴ + C-5‴), 127.7 (C-5‴ + $C_{Naph(C-3)}$), 127.6 (C-2‴), 127.4 (C-1‴), 127.3 (C-3′ + C-5′), 127.2 ($C_{Naph(C-3)}$), 127.0 + 126.7 (C-6‴ + C-7‴), 126.9 ($C_{Naph(C-3)}$), 125.8 ($C_{Naph(C-3)}$), 125.6 ($C_{Naph(C-3)}$), 125.6 ($C_{Naph(C-3)}$), 123.7 (C-4). MS (ESI): *m/z* = 528.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{38}H_{26}NO_2]^+$ 528.1958, found 528.1952.

(3,5-Di-(4-methoxyphenyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2k). Following general procedure **B**, 3-(2-naphthyl)-5-phenylisoxazole (1.0 mmol, 251 mg, 1.00 equiv.) was irradiated for 40 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 94:6 → 70:30) the title compound (29 mg, 0.10 mmol, 19 %) was obtained as a colorless solid. R_f = 0.08 (4:1 cyclohexane/ethyl acetate). Mp: 207–209 °C. IR (ATR): $\tilde{\nu}$ = 3263, 1608, 1574, 1505, 1420, 1248, 1177, 913, 834, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.15 (s, 1H, NH), 7.67–7.61 (m, 2H, H-2‴ + H-6‴), 7.48 – 7.45 (m, 2H, H-2‴ + H-6‴), 7.41–7.39 (m, 2H, H-2′ + H-6′), 7.30–7.26 (m, 1H, H-4‴), 7.21 (m, 1H, H-4′), 7.16–7.11 (m, 2H, H-3‴ + H-5‴), 7.05–6.99 (m, 2H, H-3′ + H-5′), 6.86–6.83 (m, 2H, H-2″ + H-4″), 6.82 – 6.79 (m, 2H, H-2‴ + H-6‴), 6.39–6.35 (m, 2H, H-3″ + H-5″), 3.77 (s, 3H, C-4‴-OCH_3), 3.59 (s, 3H, C-4″-OCH_3). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 194.5 (C-4-*C*O), 187.6 (C-2-*C*O), 160.1 (C-4‴), 158.5 (C-4″), 138.1 (C-5), 138.0 (C-1‴), 137.5 (C-1′), 133.9 (C-3), 132.7 (C-4‴), 131.9 (C-2″ + C-6″), 131.2 (C-4′), 129.8 (C-2‴ + C-6‴), 129.3 (C-2‴ + C-6‴), 129.2 (C-2′ + C-6′), 127.9 (C-3‴ + C-5‴), 127.6 (C-2), 127.4 (C-3′ + C-5′), 125.6 (C-1″), 122.8 (C-1‴), 122.6 (C-4), 114.2 (C-3‴ + C-5‴), 112.9 (C-3″ + C-5″), 55.3 (C-4‴-OCH_3), 55.1 (C-4″-OCH_3). MS (ESI): *m/z* = 488.3 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{32}H_{26}NO_4]^+$ 488.1856, found 488.1855. Crystals suitable for X-ray crystallography could be obtained by recrystallization of **2k** from dichloromethane/diethyl ether (1:4).

(3,5-Di-(2-furanyl)-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2l). Following general procedure **B**, 3-(2-furanyl)-5-phenylisoxazole (1.0 mmol, 211 mg, 1.00 equiv.) was irradiated for 30 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 94:6 → 70:30) and preparative HPLC (eluent: acetonitrile/water, 55:45, t_r = 11–13 min) the title compound (88 mg, 0.22 mmol, 43 %) was obtained as a colorless solid. R_f = 0.22 (4:1 cyclohexane/ethyl acetate). Mp: 188–191 °C. IR (ATR): $\tilde{\nu}$ = 3247, 3061, 1611, 1598, 1494, 1431, 1267, 943, 920, 729, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.15 (s, 1H, NH), 7.69 (m, 2H, H-2‴ + H-6‴), 7.58 (m, 2H, H-2′ + H-6′), 7.44 (m, 1H, H-5‴), 7.37 (m, 2H, H-4′ + H-4‴), 7.23 (m, 4H, H-3′ + H-5′ + H-3‴ + H-5‴), 6.84 (m, 1H, H-3‴), 6.73 (m, 1H, H-5″), 6.41 (m, 1H, H-4‴), 6.00 (m, 1H, H-3″), 5.90 (m, 1H, H-4″). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.0 (C-4-*C*O), 186.8 (C-2-*C*O), 145.3 (C-2″), 144.3 (C-2‴), 143.1 (C-5‴), 142.2 (C-5″), 137.9 + 137.8 (C-1′ + C-1‴), 132.7 (C-4‴), 131.7 (C-4′), 129.3 (C-2‴ + C-6‴), 128.6 (C-5), 128.5 (C-2′ + C-5 ′), 128.1 + 128.0 (C-3′ +C-5′ + C-3‴ + C-5‴), 127.2 (C-2), 121.9 (C-3), 120.3 (C-4), 112.3 (C-4‴), 111.9 (C-3″), 111.1 (C-3‴), 111.0 (C-4″). MS (ESI): *m/z* = 408.2 [M + H]$^+$. HRMS (ESI) calcd. for $[C_{26}H_{18}NO_4]^+$ 408.1230, found 408.1238.

(3,5-Dimethyl-*1H*-pyrrole-2,4-diyl)bis(phenylmethanone) (2m). Following general procedure **A**, 3-methyl-5-phenylisoxazole (1.0 mmol, 159 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 90:10 → 75:25) the title compound (100 mg, 0.20 mmol, 41 %) was obtained as a colorless solid. R_f = 0.13 (4:1 cyclohexane/ethyl acetate). Mp: 193 – 195 °C. IR (ATR): $\tilde{\nu}$ = 3269, 1597, 1550, 1500, 1420, 1284, 952, 911, 734, 700. ^{1}H NMR, COSY (400 MHz,

$CDCl_3$): δ = 9.69 (s, 1H, NH), 7.79–7.72 (m, 2H, H-2‴ + H-6‴), 7.72–7.65 (m, 2H, H-2′ + H-6′), 7.58 – 7.51 (m, 2H, H-4′ + H-4‴), 7.50–7.42 (m, 4H, H-3′ + H-5′ H-3‴ + H-5‴), 2.25 (s, 3H, C-5-CH_3), 1.90 (s, 3H, C-3-CH_3). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 194.1 (C-4-*C*O), 187.2 (C-2-*C*O), 140.3 (C-1′), 139.5 (C-1‴), 139.0 (C-5), 132.5 (C-4‴), 131.9 (C-4′), 130.3 (C-2), 129.3 (C-2‴ + C-6‴), 128.6 (C-2′ + C-3′ + C-5′ + C-6′ + C-3‴ + C-5‴), 128.1 (C-3), 124.2 (C-4), 13.9 (C-5-CH_3), 13.7 (C-3-CH_3). MS (ESI): *m/z* = 304.2 [M + H]$^+$. The spectroscopic data is in accordance to the literature.[25]

Additionally **(3,6-Dimethylpyrazine-2,5-diyl)bis(phenylmethanone) (8m)** (57 mg, 0.18 mmol, 36 %) was obtained as yellow solid. R_f = 0.22 (4:1 cyclohexane/ethyl acetate). Mp: 170–172 °C. IR (ATR): $\tilde{\nu}$ = 2978, 1670, 1596, 1548, 1449, 1220, 921, 697. ^{1}H NMR, COSY (400 MHz, $CDCl_3$): δ = 9.69 (s, 1H, NH), 7.79 – 7.72 (m, 2H, H-2‴ + H-6‴), 7.72–7.65 (m, 2H, H-2′ + H-6′), 7.58–7.51 (m, 2H, H-4′ + H-4‴), 7.50 – 7.42 (m, 4H, H-3′ + H-5′ H-3‴ + H-5‴), 2.25 (s, 3H, C-5-CH_3), 1.90 (s, 3H, C-3-CH_3). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 196.1 (C-5-*C*O), 191.5 (C-2-*C*O), 164.0 (C-2 + C-5), 162.1 (C-3 + C-6), 135.8 (C-1‴), 135.1 (C-4‴), 135.0 (C-1′), 133.9 (C-4′), 131.1 (C-2′ + C-6′), 129.5 (C-3‴ + C-5‴), 129.4 (C-2‴ + C-6‴), 128.5 (C-3′ + C-5′), 22.8 (C-2-CH_3 + C-5-CH_3). MS (ESI): *m/z* = 317.2 [M + H]$^+$. The spectroscopic data are in accordance to the literature.[26]

(3,5-Diphenyl-*1H*-pyrrole-2,4-diyl)bis((4-(*tert*-butyl)phenyl)methanone) (2n). Following general procedure **A**, 3-phenyl-5-((4-*tert*-butyl)phenyl)isoxazole (1.0 mmol, 277 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 97:3 → 85:15) the title compound (146 mg, 0.28 mmol, 57 %) was obtained as a yellow solid. R_f = 0.34 (4:1 cyclohexane/ethyl acetate). Mp: 224–227 °C. IR (ATR): $\tilde{\nu}$ = 3258, 2963, 1601, 1445, 1419, 1262, 1108, 907, 732, 696. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.33 (s, 1H, NH),, 7.56–7.55 (m, 2H, H-2‴ + H-6‴), 7.55 – 7.53 (m, 2H, H-2′′′′ + H-6′′′′), 7.31 (m, 2H, H-2′ + H-6′), 7.30–7.27 (m, 3H, H-3′′′′-5′′′′), 7.14 – 7.11 (m, 2H, H-3‴ + H-5‴), 7.00–6.96 (m, 2H, H-3′ + H-5′), 6.90–6.87 (m, 2H, H-2′′ + H-6′′), 6.83–6.77 (m, 3H, H-3′′-5′′), 1.18 (s, 9H, C-4′-C(CH_3)$_3$), 1.17 (s, 9H, C-4‴-C(CH_3)$_3$). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 194.1 (C-4-*C*O), 187.7 (C-2-*C*O), 156.3 (C-4‴), 154.7 (C-4′), 137.5 (C-5), 135.4 (C-1‴), 134.5 (C-1′), 133.9 (C-3), 133.8 (C-1′′), 130.7 (C-2′′ + C-6′′), 130.4 (C-1′′′′), 129.8 (C-2‴ + C-6‴), 129.0 (C-2′ + C-6′), 128.8 (C-3′′′′ + C-5′′′′), 128.7 (C-4′′′′), 128.2 (C-2), 127.9 (C-2′′′′ + C-6′′′′), 127.2 (C-3′′ + C-5′′), 126.5 (C-4′′), 124.8 (C-3‴ + C-5‴), 124.3 (C-3′ + C-5′), 123.4 (C-4), 34.9 (C-4‴-*C*(CH$_3$)$_3$), 34.8 (C-4′-*C*(CH$_3$)$_3$), 30.9 ((C-4′-C(CH_3)$_3$ + C-4‴-C(CH_3)$_3$). MS (ESI): *m/z* = 540.4 [M + H]$^+$. HRMS (ESI) calcd. for [$C_{38}H_{38}NO_2$]$^+$ 540.2897, found 540.2896.

(3,5-Diphenyl-*1H*-pyrrole-2,4-diyl)bis((4-fluorophenyl)methanone) (2o). Following general procedure **A**, 3-phenyl-5-(4-fluorophenyl)isoxazole (1.0 mmol, 239 mg, 1.00 equiv.) was irradiated for 25 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 95:5 → 80:20) and preparative HPLC (eluent: acetonitrile/water, 60:40, t_r = 10.5–13.5 min) the title compound (126 mg, 0.27 mmol, 54 %) was afforded as colorless solid. R_f = 0.22 (4:1 cyclohexane/ethyl acetate). Mp: 204 – 208 °C. IR (ATR): $\tilde{\nu}$ = 3262, 3066, 1597, 1420, 1260, 1230, 1186, 905, 731, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.38 (s, 1H, NH), 7.68–7.63 (m, 2H, H-2‴ + H-6‴), 7.56 – 7.50 (m, 2H, H-2′′′′ + H-6′′′′), 7.42–7.38 (m, 2H, H-2′ + H-6′), 7.35–7.31 (m, 3H, H-3′′′′-5′′′′), 6.97–6.93 (m, 1H, H-4′′), 6.93 – 6.87 (m, 4H, H-2′′-3′′ + H-5′′-6′′), 6.79 (m, 2H, H-3‴ + H-5‴), 6.70 – 6.64 (m, 2H, H-3′ + H-5′). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 192.6 (C-4-*C*O), 186.3 (C-2-*C*O), 165.47 (d, $^1J_{CF}$ = 254.0 Hz, C-4‴), 164.7 (d, $^1J_{CF}$ = 254.0 Hz, C-4′), 138.2 (C-5), 134.3 (d, $^4J_{CF}$ = 2.9 Hz, C-1‴), 133.6 (C-3), 133.4 (d, $^4J_{CF}$ = 2.9 Hz, C-1′), 132.9 (C-1′′), 132.4 (d, $^3J_{CF}$ = 9.3 Hz, C-2‴ + C-6‴), 131.7 (d, $^3J_{CF}$ = 9.3 Hz, C-2′ + C-6′), 130.7 (C-2′′ + C-6′′), 130.1 (C-1′′′′), 129.1 (C-4′′′′), 128.9 (C-3′′′′ + C-5′′′′), 128.0 (C-2′′′′ + C-6′′′′), 127.8 (C-2), 127.6 (C-3′′ + C-5′′), 127.3 (C-4′′), 122.9 (C-4), 115.1 (d, $^2J_{CF}$ = 22.0 Hz, C-3‴ + C-5‴), 114.6 (d, $^2J_{CF}$ = 22.0 Hz, C-3′ + C-5′). ^{19}F NMR (282 MHz, $CDCl_3$) δ = –106.49 (tt, *J* = 8.4, 5.5 Hz), – 108.14 (tt, *J* = 8.4, 5.5 Hz). MS (ESI): *m/z* = 464.2 [M + H]$^+$. HRMS (ESI) calcd. for [$C_{30}H_{20}F_2NO_2$]$^+$ 464.1457, found 464.1455.

3,5-Diphenyl-*1H*-pyrrole-2,4-diyl)bis((4-methoxyphenyl)methanone) (2p). Following general procedure **A**, 3-phenyl-5-(4-methoxyphenyl)isoxazole (1.0 mmol, 251 mg, 1.00 equiv.) was irradiated for 30 h at 70 °C. After automatic column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 85:15 → 70:30) and reverse phase column chromatography (SiO_2-C_{18}, eluent: acetonitrile/water, 50:50 → 90:10) the title compound (179 mg, 0.37 mmol, 73 %) was obtained as a colorless solid. R_f = 0.16 (4:1 cyclohexane/ethyl acetate). Mp: 223–225 °C. IR (ATR): $\tilde{\nu}$ = 3251, 1592, 1572, 1422, 1249, 1112, 1024, 842, 726, 697. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.71 (s, 1H, NH), 7.64 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-2‴ + H-6‴), 7.57–7.52 (m, 2H, H-2′′′′ + H-6′′′′), 7.43 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-2′ + H-6′), 7.32–7.27 (m, 3H, H-3′′′′-5′′′′), 6.96–6.91 (m, 2H, H-2′′ + H-6′′), 6.91–6.85 (m, 3H, H-3′′-5′′), 6.59 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-3‴ + H-5‴), 6.49 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-3′ + H-5′), 3.68 + 3.69 (2 × s, 6H, C-4′-OCH_3 + C-4‴-OCH_3). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.3 (C-4-*C*O), 186.7 (C-2-*C*O), 163.2 (C-4‴), 162.4 (C-4′), 136.7 (C-5), 133.5 (C-1′′′′), 132.7 (C-3), 132.2 (C-2‴ + C-6‴), 131.9 (C-2′ + C-6′), 131.1 (C-1‴), 130.7 (C-2′′ + C-6′′), 130.5 (C-1′′), 129.8 (C-1′), 128.8 (C-3′′′′ + C-5′′′′), 128.6 (C-4′′′′), 128.1 (C-2), 127.7 (C-2′′′′ + C-6′′′′), 127.5 (C-3′′ + C-5′′), 126.7 (C-4′′), 123.1 (C-4), 113.2 (C-3‴ + C-5‴), 112.8 (C-3′ + C-5′), 55.3 (C-4′-OCH_3 + C-4‴-OCH_3). MS (ESI): *m/z* = 488.3 [M + H]$^+$. HRMS (ESI) calcd. for [$C_{32}H_{26}NO_4$]$^+$ 488.1856, found 488.1860.

(3,5-Diphenyl-*1H*-pyrrole-2,4-diyl)bis((4-methoxycarbonylphenyl) methanone) (2q). Following general procedure **A**, 3-phenyl-5-(4-methoxycarbonylphenyl)isoxazole (1.0 mmol, 279 mg, 1.00 equiv.) was irradiated for 20 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 90:10 → 70:30) and preparative HPLC (eluent: acetonitrile/water, 55:45, t_r = 14–17 min) the title compound (126 mg, 0.23 mmol, 46 %) was obtained as a colorless solid. R_f = 0.23 (4:1 cyclohexane/ethyl acetate). Mp: 253–256 °C. IR (ATR): $\tilde{\nu}$ = 3273, 2952, 1723, 1604, 1421, 1278, 1107, 917, 743, 650. ^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 10.31 (s, 1H, NH), 7.79 – 7.74 (m, 2H, H-3‴ + H-5‴), 7.68 – 7.63 (m, 4H, H-3′ + H-5′ + H-2‴ + H-6‴), 7.55–7.50 (m, 2H, H-2′′′′ + H-6′′′′), 7.43–7.37 (m, 2H, H-2′ + H-6′), 7.32 (m, 3H, H-3′′′′-5′′′′), 6.91–6.88 (m, 2H, H-2′′ + H-6′′), 6.87–6.85 (m, 1H, H-4′′), 6.81 (m, 2H, H-3′′ + H-5′′), 3.87 (s, 3H, C-4′-COOCH_3), 3.84 (s, 3H, C-4‴-COOCH_3). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 193.1 (C-4-*C*O), 186.8 (C-2-*C*O), 166.2 (C-4′-*C*OOCH$_3$), 166.2 (C-4‴-*C*OOCH$_3$), 141.3 (C-1‴), 141.1 (C-1′), 139.2 (C-5), 134.5 (C-3), 133.2 (C-4‴), 132.5 (C-1′′), 132.1 (C-4′), 130.6 (C-2′′ + C-6′′), 129.9 (C-1′′′′), 129.5 (C-2‴ + C-6‴), 129.4 (C-4′′′′), 129.1 (C-3‴ + C-5‴), 128.9 (C-3′ + C-5′), 128.6 (C-2′ + C-6′ + C-3′′′′ + C-5′′′′), 128.2 (C-2′′′′ + C-6′′′′), 127.9 (C-2), 127.6 (C-3′′ + C-5′′), 127.5 (C-4′′), 122.9 (C-4), 52.4 + 52.3 (C-4′-COOCH$_3$, C-4‴-COOCH$_3$). MS (ESI): *m/z* = 544.3 [M + H]$^+$. HRMS (ESI) calcd. for [$C_3H_{25}NO_6Na$]$^+$ 566.1574, found 566.1561.

(1,1′-(3,5-diphenyl-*1H*-pyrrole-2,4-diyl)dihexan-1-one) (2t). Following general procedure **A**, 3-phenyl-5-pentylisoxazole (1.0 mmol, 215 mg, 1.00 equiv.) was irradiated for 96 h at 70 °C. After column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 96:4 → 75:25) and the title compound (57 mg, 0.14 mmol, 46 %) was obtained as a yellow oil. R_f = 0.54 (4:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 3270, 1597, 1576, 1550, 1420, 1284, 952, 911, 734, 700.

^{1}H NMR, COSY, NOESY (600 MHz, $CDCl_3$): δ = 9.60 (s, 1H, NH), 7.55–7.51 (m, 2H, H-2′′′′ + H-6′′′′), 7.48 – 7.40 (m, 6H, H-3′′-5′′ + H-3′′′′-5′′′′), 7.39 (m, 2H, H-2′′ + H-6′′), 2.16–2.07 (m, 4H, H-2′ + H-2′′′), 1.46–1.31 (m, 4H, H-3′ + H-5′), 1.15–1.03 (m, 4H, H-4′ + H-4′′′), 1.01–0.90 (m, 4H, H-3′ + H-3′′′), 0.81 – 0.72 (m, 6H, H-5′ + H-5′′′). ^{13}C NMR, HSQC, HMBC (151 MHz, $CDCl_3$) δ = 200.4 (C-4-*C*O), 192.5 (C-2-*C*O), 137.8 (C-5), 134.9 + 131.1 (C-1′′ + C-1′′′′), 131.2 (C-3), 130.1 (C-2′′ + C-6′′), 129.2 (C-4′′′′), 128.9 (C-2), 128.7 (C-2′′′′ + C-6′′′′), 128.6 + 128.3 (C-3′′ + C-5′′ + C-3′′′′ + C-5′′′′), 128.2 (C-4′′), 125.2 (C-4), 43.3 (C-1′′′), 39.4 (C-1′), 31.3 (C-3′), 31.1 (C-3′′′), 24.4 (C-2′), 24.0 (C-2′′′), 22.2 (C-4′ + C-4′′′), 13.9 (C-5′ + C-5′′′). MS (ESI): *m*/*z* = 416.4 $[M + H]^+$. HRMS (ESI) calcd. for $[C_{34}H_{25}NO_6Na]^+$ 416.2584, found 416.2594. Additionally 3-phenyl-5-pentylisoxazole (75 mg, 0.35 mmol, 35 %) was recovered.

(3-Methyl-5-phenyl-*1H*-pyrrol-2,4-diyl)bis(phenylmethanone) (2t). A mixture of ^{15}N-labeled azirine **1s** (0.3 mmol, 67 mg, 1.0 equiv.), unlabeled azirine **1m** (0.6 mmol, 96 mg, 2.0 equiv.) and copper(2-ethylhexanoate)$_2$ (0.1 mmol, 31 mmol, 0.1 equiv.) in anhydrous acetonitrile (9 mL, c = 0.1 M) was stirred at 70 °C for 18 h. The solvent was removed in vacuo and the residue purified using automatic flash column chromatography (SiO_2, eluent: cyclohexane/ethyl acetate, 86:4 → 75:25) and preparative HPLC (eluent: acetonitrile/water, 45:55, t_r = 27–28 min) to afford the title compound (8.9 mg, 0.02 mmol, 3 %) as colorless lyophilizate. R_f = 0.33 (2:1 cyclohexane/ethyl acetate). IR (ATR): $\tilde{\nu}$ = 3258, 3061, 1597, 1471, 1420, 1293, 1259, 909, 732, 695. ^{1}H NMR, COSY, NOESY (400 MHz, $CDCl_3$): δ = 9.47 (s, 1H, NH), 7.77–7.73 (m, 2H, H-2′ + H-6′), 7.73–7.69 (m, 2H, H-2′′′ + H-6′′′), 7.60–7.54 (m, 1H, H-4′), 7.53–7.47 (m, 2H, H-3′ + H-5′), 7.40–7.34 (m, 1H, H-4′′′), 7.33–7.28 (m, 2H, H-2′′′′ + H-6′′′′), 7.26 – 7.22 (m, 2H, H-3′′′ + H-5′′′), 7.22–7.19 (m, 3H, H-3′′′′-5′′′′), 2.04 (s, 3H, C-4-*C*H$_3$). ^{13}C NMR, HSQC, HMBC (101 MHz, $CDCl_3$) δ = 200.4 (C-4-*C*O), 192.5 (C-2-*C*O), 137.8 (C-5), 134.9 + 131.1 (C-1′′ + C-1′′′′), 131.2 (C-3), 130.1 (C-2′′ + C-6′′), 129.2 (C-4′′′′), 128.9 (C-2), 128.7 (C-2′′′′ + C-6′′′′), 128.6 + 128.3 (C-3′′ + C-5′′ + C-3′′′′ + C-5′′′′), 128.2 (C-4′′), 125.2 (C-4), 43.3 (C-1′′′), 39.4 (C-1′), 31.3 (C-3′), 31.1 (C-3′′′), 24.4 (C-2′), 24.0 (C-2′′′), 22.2 (C-4′ + C-4′′′), 13.9 (C-5′ + C-5′′′). MS (ESI): *m*/*z* = 366.2 $[M + H]^+$. HRMS (APCI) calcd. for $[C_{25}H_{20}NO_2]^+$ 366.1489, found 366.1491.

Additionally, preparative HPLC (eluent: acetonitrile/water, 45:55, t_r = 20 – 22 min) afforded an impure sample of **^{15}N-(3-phenyl-5-methyl-*1H*-pyrrol-2,4-diyl)bis(phenylmethanone)** (**2u**) as a colorless lyophilizate (8.9 mg, 0.02 mmol, 3 %), which could be characterized by NMR to distinguish the structure of pyrrole **2u**. (See the SI for spectra).

CCDC 1946259 (for **2k**), and 1946260 (for **9a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

Financial support of the DFG (Grant Op90/12-1) is gratefully acknowledged. The authors would like to thank Dr. Johannes C. Liermann (Mainz) for NMR spectroscopy, Dr. Christopher Kampf (Mainz) for mass spectrometry and Dr. Dieter Schollmeyer for X-ray crystallography.

Keywords: Photochemistry · Small ring systems · Nitrogen heterocycles · Copper · Reaction mechanisms

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Received: August 8, 2019