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Very Important Publication

In situ Generated Copper(II)-Quinoline Complexes as Robust and Versatile Photocatalysts for the Chlorosulfonylation of Olefins

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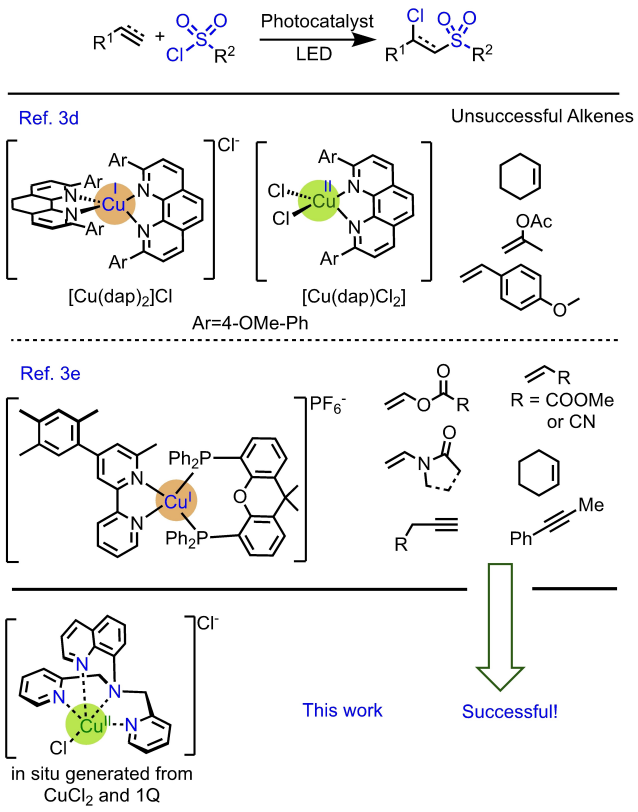
Abstract: A series of copper complexes was synthesized and studied as photocatalysts for the chlorosulfonylation of olefins. Featuring a tetradentate ligand consisting of one amino quinoline and two methyl pyridine moieties, the resulting Cu(II)-complex is effective under visible light irradiation to add sulfonyl chlorides to alkenes and alkynes, including unactivated aliphatic olefins. A weak base additive such as Na_2CO_3 prevents catalyst poisoning, resulting in an improvement of reaction yields and catalyst lifetime. A broad scope of sulfonyl chlorides and alkenes/alkynes as coupling partners are amenable for the title process, including examples previously reported unsuccessful with established copper-based photocatalysts.

Keywords: Chlorosulfonylation; Copper-quinoline complex; Photocatalyst

Photomediated atom transfer radical additions (ATRA) have proven to be powerful tools for the functionalization of alkenes.[1] In this context, homo- and heteroleptic copper(I) complexes have been reported as highly active photocatalysts due to their sufficient fluorescent lifetime and photoelectron transfer capacity, but also due to the ability of Cu(II) that is formed after an initial SET to capture and thus stabilize transient radicals for a subsequent coupling.[2,3] Air-stable Cu(II) complexes have also been proven as robust and effective photocatalyst precursors for various ATRA processes based on the facile visible light-induced homolysis (VLIH) that Cu(II)-halide complexes undergo upon irradiation to form the active Cu(I) species (Scheme 1).[3a–d] Bidentate ligands, especially those with phenanthroline ligands such as 2,9-bis(*p*-anisyl)-1,10-phenanthroline (dap) and 2,9-dimethyl-1,10-phenanthroline (dmp) have been most commonly applied in copper photocatalysis. In contrast, tri- and tetradentate ligands have found less attention, although a multidentate coordination should rigidify the complex and this way extend excited-state lifetimes, being essential for efficient intramolecular SET processes.[4]

Recently, we demonstrated that Cu(II) complexes with tetradentate quinoline ligands are capable photocatalysts in the haloalkylation of alkenes, giving comparable results to other established photocatalysts.[3a] In extension, we evaluate here the application of such a catalyst for the chlorosulfonylation of olefins. This transformation is attractive for the synthesis of sulfone derivatives,[5] which represent an important class of bioactive molecules and pharmaceuticals.[6] The Cu(II)-quinoline complex $CuCl_2$/**1Q** (Figure 1) is identified to catalyze the title transformation in a broad way and especially allows the conversion of substrates that have been unsuccess-

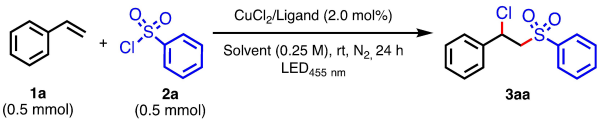


Scheme 1. Comparison of copper photocatalyst used in chlorosulfonylation of olefins.

ful with previously reported homo and heteroleptic copper(I) photocatalysts.[3b–e]

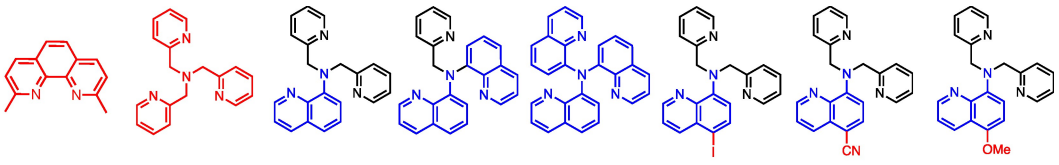
We began our study by evaluating Cu(II)-complexes formed in situ from $CuCl_2$ with quinoline ligands **1Q-3Q** (Figure 1) for the chlorosulfonylation of styrene (**1a**) with benzenesulfonyl chloride (**2a**) under irradiation at 455 nm (LED). As benchmark served $Cu(dmp)_2Cl_2$ (Table 1, Entry 1), which has been shown to be one of the most efficient ligands in this process,[3b] and $Cu(TMPA)Cl_2$ (TMPA = tris(2-pyridylmethyl)amine), representing the lower homolog to the quinoline ligands being effective in the thermal or UV-mediated coupling of perhaloalkanes and alkenes.[7] However, the latter provided only a trace amount (< 10%) of the addition product **3aa** (Entry 2)

Table 1. Catalytic activity screening of Cu(II) complexes with various ligands.



Entry	Ligand	Solvent	Condition variation	Yield (%)[a]
1	dmp	CH_3CN	30 h	97[b]
2	TPMA	CH_3CN	–	7
3	**1Q**	CH_3CN	–	53
4	**2Q**	CH_3CN	–	57
5	**3Q**	CH_3CN	–	16
6	**1Q-I**	CH_3CN	–	35
7	**1Q-CN**	CH_3CN	–	45
8	**1Q-OMe**	CH_3CN	–	44
9	**1Q**	CH_3CN	LED 530 nm	ND[c]
10	**1Q**	CH_3CN	LED 367 nm	56
11	**1Q**	CH_2Cl_2	–	60
12	**1Q**	CH_2Cl_2	4.0 mol% $CuCl_2$/**1Q**	73
13	**1Q**	CH_2Cl_2	With Na_2CO_3 (1.0 equiv.)	66
14	**1Q**	CH_2Cl_2	White CFL, with Na_2CO_3 (1.0 equiv.)	94
15	**1Q**	CH_2Cl_2	No $CuCl_2$	ND
16	**1Q**	CH_2Cl_2	No **1Q**	ND
17	**1Q**	CH_2Cl_2	dark	ND
18	**1Q**	CH_2Cl_2	CuCl/**1Q**, dark	ND

[a] Yield determined by ^1H NMR using 1,3,5-trimethoxybenzene as the standard added after product purification.
[b] Taken from reference 3b.
[c] ND = not detected.



Ligand	dmp[3b]	TPMA	**1Q**	**2Q**	**3Q**	**1Q-I**	**1Q-CN**	**1Q-OMe**
$E_{1/2}(Cu^{2+}/Cu^{+})$	0.63	0.36[b]	0.29	0.17	0.03	0.24	0.14	0.32
$E_{1/2}(Cu^{*,2+}/Cu^{+})$[a]	2.17	2.07	2.10	2.10	2.04	1.99	2.24	2.07
$E_{1/2}(Cu^{2+}/Cu^{*,+})$[a]	-1.54	-1.79	-1.77	-1.77	-1.61	-1.63	-1.75	-1.79
λ CuL(nm)	454	303	470	473	487	483	461	413

Figure 1. Structures of dmp, TPMA, and quinoline based ligands used in this study. [a] $E_{1/2}(Cu^{*,2+}/Cu^{+}) = E_{1/2} + E_{gap}$ and $E_{1/2}(Cu^{2+}/Cu^{*,+}) = E_{1/2} - E_{gap}$, whereas E_{gap} is energy gap determined from the onset of the absorption wavelength (λ_{onset}) (Figure S3-S4 and Table S1-S2) [b] Obtained $E_{1/2}$ value is similar to previous reported.[6]

upon irradiation at 455 nm, while copper(II) complexes with quinoline ligands **1Q** or **2Q** gave significantly higher yields (Entry 3–4, 6–8) owing to their improved absorption characteristics in the region around 450 nm (Figure 1 and S2). The copper(II) complex containing the ligand with three units of quinoline (**3Q**), however, gave a distinctively lower yield (Entry 5) despite the very similar photophysical properties compared to **2Q**. The core structure of **1Q** was preferred due to its lower molecular weight and ease of synthesis and was, therefore, further evaluated. In line with its UV/Vis spectra (Figure S2), no product was observed upon irradiation with green LED (530 nm, Entry 9), but a comparable yield (56%) was obtained upon irradiation with a UV LED (367 nm, Entry 10). A substituent on C5 of the quinoline ring, including a heavy atom, electron withdrawing group and electron donating group, (**1Q-I**, **1Q-CN** and **1Q-OMe**) showed little effect on the reaction yield (Entry 6–8).

Our previous study showed that the formation of the active Cu(I)-catalyst from it corresponding Cu(II)•1**Q** is more effective in CH_3OH compared to CH_3CN.[3a] Nevertheless, the use of alcohols as solvents for the title reaction is prohibitive due to their rapid reaction with sulfonyl chlorides to form sulfonates.

However, switching to the non-coordinating solvent CH_2Cl_2 improved the yield (Entry 11). While doubling the catalyst amount (Entry 12) resulted in a further improvement, the comparably small increase in yield (60 to 73%) suggested a deactivation of the catalyst over time. Suspecting that HCl, which could build-up through hydrolysis of the sulfonyl chloride, constitutes a catalyst poison,[3d] we were pleased to find that the reaction greatly benefitted from inorganic base additives, culminating in a virtually quantitative yield upon switching the light source to white CFL light (Entries 13, 14). The role of the base in preventing acid poisoning of the catalyst was confirmed by UV-Vis spectroscopy studies showing the destruction of $CuCl_2$/**1Q** upon the addition of HCl and its reformation upon subsequent addition of NaOAc (Figure S5). Control experiments confirmed that no reaction occurs in the absence of copper or the ligand (Entry 15–16) or in the dark (Entry 17–18).

Having identified $CuCl_2$/**1Q** as an operationally convenient and effective in situ photocatalyst, we investigated the reactions between sulfonyl chlorides **2a** or **2b** and various alkenes (Scheme 2) under conditions A–C, which differ in the light source and using Na_2CO_3 as an HCl scavenger. Less reactive alkenes (i.e., electron deficient, sterically hindered or alkyl rather than aryl substitution) benefit from the addition of the inorganic base and irradiation by a CFL light source.

Styrenes performed well in general, but a pleasant surprise was the virtually quantitative product formation (**3ca**, **3cb**, **3da**/**4da**)[8] with electron-rich and, in particular, 4-methoxy styrene, which has been reported to be unsuccessful with various copper-phenanthroline photocatalysts.[3b–e] α-Methyl substitution (**3ea**) is tolerated well, while α-phenyl substitution led directly to the vinyl sulfones **4fa** and **4fb**.

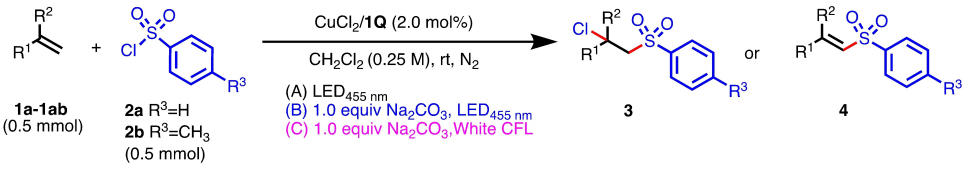
Not unexpectedly, vinyl pyridines proved to be challenging substrates due to competitive reactions between the pyridine moiety and the sulfonyl chloride as observed by intense color spots on the TLC trace. Moreover, the basic pyridine moiety triggers the subsequent elimination of the initially formed ATRA product. Nevertheless, by adding an external base to drive the reaction towards the vinyl sulfones, we were pleased to obtain (*E*)–**4gb** and (*E*)–**4ha**, albeit only with moderate yields. Cyclic styrene derivatives were excellent substrates, giving rise to *anti*-**3ib** and *anti*-**3jb** with perfect diastereoselectivity in almost quantitative yields.

α,β-Unsaturated alkenes have proven to be challenging substrates for the chlorosulfonylation in the past requiring α-methyl substitution to stabilize the incipient radical.[3e] Such substrates also worked well with $CuCl_2$/**1Q** (**3ka** and **3la**), and even reacted chemoselectively in the presence of an allylic ester group (**3ma**). For the latter, scale-up was demonstrated using only a slight excess (1.2 equiv.) of alkene. We were especially pleased that either (*E*)–**4oa** or **3oa** could be selectively obtained in high yield from simple acrylate depending on the strength of the inorganic base additive (for screening details, see Table S3), which was previously reported not possible for this transformation.[3d] Also, acrylonitrile or internal alkenes that proved to be unsuitable alkenes in previous reports,[3d–e] gave good results with $CuCl_2$/**1Q** (**4pa**, **3qa**, *anti*-**3za**, *anti*-**3zb**).

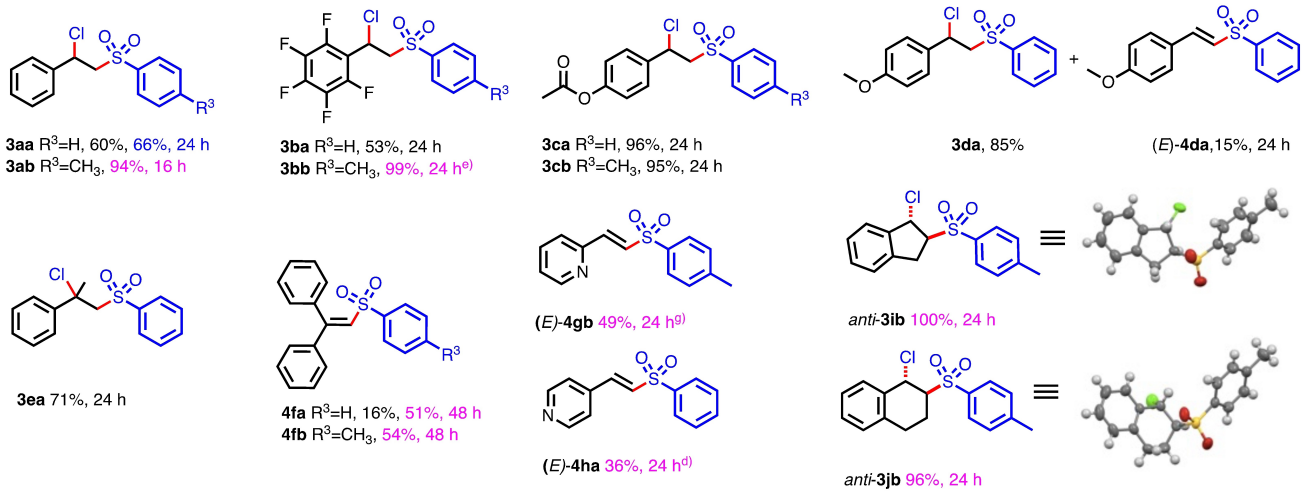
On the other end of the electronic spectrum, electron-rich alkenes also performed well with $CuCl_2$/**1Q**. Simple enol acetate, which again failed as substrate in a previous study,[3e] smoothly gave rise to **3ra**, and related donor-substituted alkenes could also be converted to the chlorosulfonylated adducts (**3sa**) or the corresponding vinylsulfones ((*E*)–**4ta**, **4aaa**, and **4aab**).

Using acrylates and acrylamides as representative alkenes, substituted aryl-, heteroaryl-, and alkylsulfonylchlorides performed all well in the title reaction (Scheme 3) (**3kd** characterized by X-ray, see SI). As an example with relevance for pharmaceutical chemistry, the addition of 4-fluorobenzenesulfonyl chloride gave an excellent yield of a precursor of bicalutamide (Casodex™) **3abh**, which is used to treat prostate cancer.

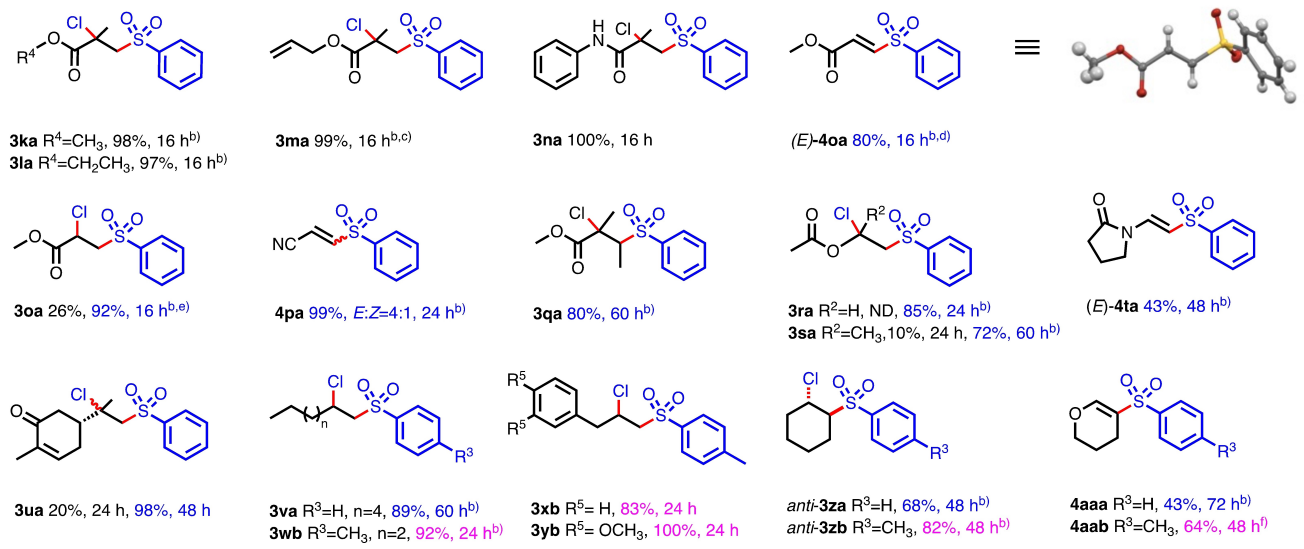
$CuCl_2$/**1Q** also proved to be a capable catalyst for the chlorosulfonylation of various alkynes (Scheme 4). High yield and (*E*)-selectivity for aryl alkynes was observed, comparing favorably to previous reports,[3d–e]



Activated alkenes;



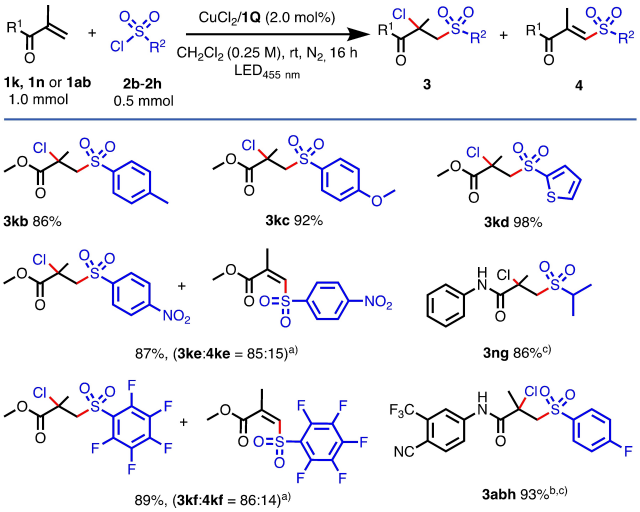
Unactivated alkenes;



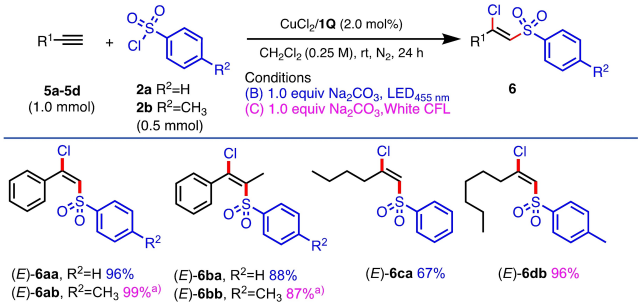
Scheme 2. Chlorosulfonylation of various alkenes with arylsulfonyl chlorides. [a] Determined by ^{1}H NMR yield using toluene as an internal standard. [b] 2.0 equiv of alkene were used. [c] Benzenesulfonyl chloride (5.0 mmol) and alkene (6.0 mmol), 1.3 g of isolated **3 ma** was obtained. [d] 2.0 equiv. NaOAc instead of Na_2CO_3. [e] 0.2 equivalent $NaHCO_3$. [f] 5.0 equiv. of olefin. [g] The crude reaction mixture was treated with triethylamine (2 equiv) for 2 hours.

but also terminal alkyl-substituted alkynes, contrasting the lack of reactivity observed previously,[3e] gave the correspondding adducts (*E*)–**6 ca** or (*E*)–**6 db**. Noteworthy, this is the first time the (*E*)-product was obtained selectively using a homoleptic copper complex.

The combination of Cu(II)/**1Q** proved to result in one of the most active as well as selective copper photocatalysts for the chlorosulfonylation of alkenes and alkynes. In line with previous reports[3] showing that $LCu(II)Cl_2$ complexes upon irradiation rapidly form LCu(I)Cl by homolysis of the Cu–Cl bond, being also demonstrated for Cu(II)•**1Q**,[3a] it is plausible that the catalytically active species also, in this case, is Cu(I)•**1Q**. The initial step of the catalytic cycle, i. e. the formation of the sulfonyl radicals by SET (e. g.



Scheme 3. Chlorosulfonylation of acrylates and acrylamides using various sulfonyl chlorides. [a]Determined by ^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [b]White CFL for 44 hours. [c] 1.0 equivalent of alkene.



Scheme 4. Chlorosulfonylation of various alkynes with arylsulfonyl chlorides. [a] 1.0 equivalent of alkyne.

TsCl ($E_{1/2}(Cu^{2+}/Cu^{*,+}$ −1.37 V)[9]) should be more facile with Cu(I)•**1Q** ($E_{1/2}(Cu^{2+}/Cu^{*,+}$ −1.77 V) compared to established copper photocatalyst such as $Cu(dap)_2Cl$ ($E_{1/2}(Cu^{2+}/Cu^{*,+}$ −1.43 V) for the title reaction. We furthermore attribute the superior performance of Cu(I)•**1Q** to the greater accessibility of the copper center of the resulting Cu(II)•**1Q** after SET compared to homo- or heteroleptic Cu(II)-complexes with bulky phenanthroline or phosphine ligands.

This would allow a more facile interaction with transient radicals, either by a Cu(III)-intermediate or by direct chloride abstraction from the copper(II) center (Figure 2). Representative Xray-structures of Cu(II)•**1Q**[3a] and $Cu(II)(dmp)_2Cl$[3b] appear to be in line with this reasoning (Figure 3).

In summary, the quinoline based ligand **1Q** was proven to be a suitable ligand for Cu(II). The Cu(II)-**1Q** complex can catalyze the chlorosulfonylation of activated and unactivated alkenes and alkynes, the latter with excellent (>99:1) (*E*)-selectivity, and

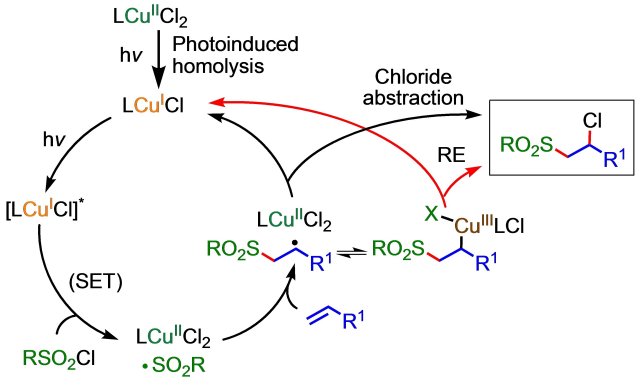


Figure 2. Simplified mechanism for Cu(II) catalyzed chlorosulfonylation via initial visible light induced homolysis (VLIH) of the Cu–Cl bond in $LCu^{II}Cl_2$.

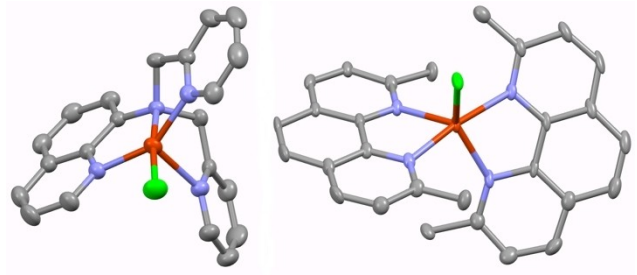


Figure 3. X-ray structures of copper(II) complexes $[CuCl•1Q]^+$ (left) and $[Cu(dmp)_2Cl]^+$ (right) adopted from references 3a and 3b.

especially of substrates that have been previously reported not to be amenable for the title transformation.

Experimental Section

All commercially available chemicals were used without further purification. The reactions were monitored by TLC and visualized by a dual short (254 nm) / long (366 nm) wavelength UV lamp. Column chromatography was run on silica 60 (70–230 mesh) or aluminium oxide 90 active neutrals. Solvents used for extraction and chromatography such as dichloromethane, hexane and ethyl acetate were commercial grade and distilled before use. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were obtained using a Bruker Advance 300 MHz, 400 MHz and 600 MHz spectrometers with chemical shifts given in ppm relative to residual solvent peak of $CHCl_3$ at 7.26 ppm for ^{1}H NMR and 77.2 ppm for ^{13}C NMR. MestReNova and topspin software were used to process NMR spectra. Coupling constants (J) are given in Hertz (Hz). Mass spectra were recorded at the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS. UV-visible spectra were obtained using HP 8453 UV-Visible spectrometer in 1.00 cm path-length quartz cuvettes and recorded at a range from 290–900 nm at room temperature. X-ray crystallographic analysis

was performed by the Central Analytic Department of the University of Regensburg. Suitable crystals were mounted on a Lindemann tube oil and kept at a steady temperature of T = 293 K during data collection. The structures were solved with the SheIXT (Scheldrick 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.[10] The model was refined with SheIXL using Least Squares minimization. The irradiation was done using blue light emitting diodes CREE XP or Oslon SSL (2.5 W electric power @700 mA, λ_{max} = 455 nm) and white light (32 W, 2080 lumen).

Synthesis of Quinoline Derivative Ligands

Quinoline derivative ligands **1Q-3Q** were synthesized according to reported procedures.[3a]

5-Iodo-*N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine, 1Q-I: To a solution of *N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine in pyridine (5.0 mL) and dichloromethane (5.0 mL) was added at 0 °C with **1Q** (230 mg, 0.7 mmol) and iodine (630 mg, 2.5 mmol). After stirring for 1 h, the solution was brought to room temp, upon which iodine (270 mg, 1.0 mmol) was added once more. Stirring at room temperature continued for 1 hour. A saturated solution of sodium thiosulfate was gradually added to the solution until the brown color disappeared. The crude was extracted with dichloromethane and water 3 times. The organic layer was concentrated, and the product was purified by column chromatography on alumina (hexanes/EtOAc 8:2, R_f 0.29). The product was recrystallized from dichloromethane and hexane, receiving **1Q-I** as a light-yellow solid (260 mg, 82% yield). ^{1}H-NMR (400 MHz, DMSO): δ 8.80 (dd, J = 4.1, 1.2 Hz, 1H), 8.47 (d, J = 4.5 Hz, 2H), 8.27 (dd, J = 8.5, 1.2 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.67 (td, J = 7.7, 1.4 Hz, 2H), 7.61 (dd, J = 8.5, 4.1 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.26–7.14 (m, 2H), 6.84 (d, J = 8.3 Hz, 1H), 4.91 (s, 4H) ppm. ^{13}C NMR (101 MHz, DMSO, 298 K): δ 158.86, 148.80, 148.01, 147.30, 142.59, 140.03, 137.19, 136.47, 130.23, 123.04, 122.01, 121.88, 118.51, 87.00, 58.73. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calc. for $C_{21}H_{18}IN_4$ 453.0571; Found 453.0578.

5-Methoxy-*N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine, 1Q-OMe: A mixture of 5-methoxy-8-aminoquinoline (430 mg, 2.5 mmol), 2-(chloromethyl)pyridine hydrochloride (1.5 g, 9.5 mmol), KI (41 mg, 2.0 mmol) and K_2CO_3 (490 mg, 3.6 mmol) in 50 mL acetonitrile was refluxed for 48 hours. Extraction with ethyl acetate and brine (3 times) and concentration of the organic layer yielded the crude product, which was purified on alumina (hexanes/ EtOAc 8:2, R_f 0.26) to yield **1Q-OMe** as a yellow solid (350 mg, 39% yield). ^{1}H-NMR (400 MHz, DMSO) δ 8.94 (dd, J = 4.0, 1.6 Hz, 1H), 8.49 (dd, J = 8.4, 1.6 Hz, 1H), 8.45 (d, J = 4.7 Hz, 2H), 7.65 (td, J = 7.7, 1.5 Hz, 2H), 7.57–7.51 (m, 3H), 7.20–7.16 (m, 2H), 7.01 (d, J = 8.5 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 4.71 (s, 4H), 3.86 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO, 298 K): δ ^{13}C NMR (101 MHz, DMSO) δ 159.42, 149.37, 148.63, 148.59, 143.10, 139.27, 136.32, 130.54, 122.10, 121.91, 121.09, 120.47, 118.85, 104.42, 59.04, 55.65. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calc. for $C_{22}H_{21}N_4O$ 357.1710; Found 357.1717.

5-Carbonitrile-*N,N*-8-bis(pyridin-2-ylmethyl)quinoline-8-amine, 1Q-CN: A solution of 5-iodo-N,N-bis(pyridin-2-ylmethyl)quinolin-8-amine, **1Q-I** (680 mg, 1.5 mmol), CuCN (12 mg, 0.1 mmol), and NaCN (170 mg, 2.8 mmol) in anhydrous dimethylformamide was refluxed under nitrogen atmosphere for 72 hours. Extraction with ethyl acetate and brine (3 times) and concentration of the organic layer yielded the crude product, which was purified on alumina (hexane/EtOAc 8:2, R_f 0.31). A product was obtained as a yellow solid (410 mg, 77% yield). ^{1}H NMR (400 MHz, DMSO) δ 8.76 (d, J = 1.4 Hz, 1H), 8.50 (d, J = 4.7 Hz, 2H),8.38 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.78–7.63 (m, 3H),7.45 (d, J = 7.8 Hz, 2H),7.24 (t, J = 4.7 Hz, 2H), 6.98 (d, J = 8.5 Hz, 1H), 5.20 (s, 4H) ppm. ^{13}C NMR (101 MHz, DMSO, 298 K): δ ^{13}C NMR (101 MHz, DMSO) δ 158.74, 151.22, 149.52, 147.90, 140.11, 137.14, 134.59, 133.56, 129.71, 123.87, 122.63, 122.16, 118.44, 113.68, 96.93, 59.36. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calc. for $C_{22}H_{18}N_5$ 352.1567; Found 352.1557.

General Procedures for Chlorosulfonylation Under Blue Light

To a flame-dried Schlenk tube (10 mL) equipped with a magnetic stirring bar was added $CuCl_2$ (1.3 mg, 10 µmol) and **1Q** (3.3 mg, 10 µmol) in anhydrous dichloromethane (2.0 mL). For activated alkenes, the sulfonyl chloride (0.5 mmol, 1.0 equiv.) was added to the reaction. For unactivated alkenes, the sulfonyl chloride (0.5 mmol, 1.0 equiv.) and Na_2CO_3 (0.5 mmol, 1.0 equiv.) were added. The reaction was sealed with a screwcap and degassed by three consecutive freeze-pump- thaw cycles. The alkene (0.5–1.0 mmol, 1.0–2.0 equiv.) was added to the reaction mixture under a nitrogen atmosphere, and the vessel was sealed with a Teflon inlet to which a quartz glass rod was attached (see Figure S1). The reaction mixture, cooled in a water bath, was irradiated at 455 nm for the indicated time (monitoring by TLC). Upon completion, the reaction mixture was concentrated in vacuo, and the residue was purified by flash column chromatography on silica (hexanes/EtOAc).

Large-Scale Synthesis of Compound 3 ma

To a flame-dried Schlenk tube (40 mL) equipped with a magnetic stirring bar was added $CuCl_2$ (13 mg, 0.1 mmol) and **1Q** (33 mg, 0.1 mmol) dissolved in anhydrous dichloromethane (20 mL). Benzenesulfonyl chloride (880 mg, 5.0 mmol, 1.0 equiv.) was added, and the reaction vessel was sealed with a screwcap and degassed by three consecutive freeze-pump-thaw cycles. Allyl methacrylate (760 mg, 6.0 mmol, 1.2 equiv.) was added to the reaction mixture under nitrogen atmosphere, and the vessel was sealed with a Teflon inlet to which a glass rod was attached which acts as a light transmitter upon irradiation from the top. The reaction mixture, cooled by a water bath, was irradiated (4 × 2.5 W, Figure S1b) at 455 nm for 16 hours and subsequently concentrated in vacuo. The residue was purified by column chromatography on silica (hexanes/EtOAc 9:1, R_f 0.34) to afford **3 ma** as a clear oil (1.3 g, 86% yield).

General Procedures for Chlorosulfonylation Under White Light

To a test tube with a screwcap (10 mL) equipped with a magnetic stirring bar was added $CuCl_2$ (1.3 mg, 10 µmol) and **1Q** (3.3 mg, 10 µmol) dissolved in anhydrous dichloromethane (2.0 mL). Then, the sulfonyl chloride (0.5 mmol, 1.0 equiv.), Na_2CO_3 (0.5 mmol, 1.0 equiv.) and alkene (0.5 mmol, 1.0 equiv.) was added to the reaction mixture. The reactin mixture was degassed by passing through nitrogen gas for a minute. The vessel was sealed with a screwcap and wrapped with Teflon tape to ensure a tight seal. The reaction tube was placed under a white light source for the indicated time (monitoring by TLC) with an electric cooling fan to maintain a reaction temperature of around 35 °C (Figure S1c). The reaction mixture was concentrated in vacuo, and the crude was purified on silica (hexanes/EtOAc).

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[10] CCDC 2235798 (*anti*-**3ib**), 2235799 (*anti*-**3jb**), 2243941 (**3kd**), and 2249340 ((*E*)–**4oa**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/).

UPDATES

In situ Generated Copper(II)-Quinoline Complexes as Robust and Versatile Photocatalysts for the Chlorosulfonylation of Olefins

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