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FULL PAPER

Making Copper Photocatalysis even more robust and economic: Photoredox Catalysis with $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$

Sebastian Enql^[a] and Oliver Reiser^{*[a]}

Abstract: The Cu(II)-complex [Cu^{II}(dmp)₂]Cl (dmp = 2,9-dimethyl-1,10-phenanthroline) is evaluated as an oxidation stable precursor for visible-light-mediated Cu(I)-photoredox catalysis, being efficient and considerable more cost-effective compared to previously established copper(I) photocatalysts. Its performance and efficiency are demonstrated within a broad scope of atom transfer radical addition (ATRA) reactions, allowing the 1,2-difunctionalization of alkenes, as well as for decarboxylative coupling and an Appel reaction. Moreover, the utility of the complex is shown by various gram-scale functionalizations of styrene, thus suggesting [Cu^{II}(dmp)₂]Cl to be a low-priced alternative precatalyst for processes run on scale. Furthermore, this study provides UV-vis evidence on the mechanism for the visible light activation of Cu(II) complexes.

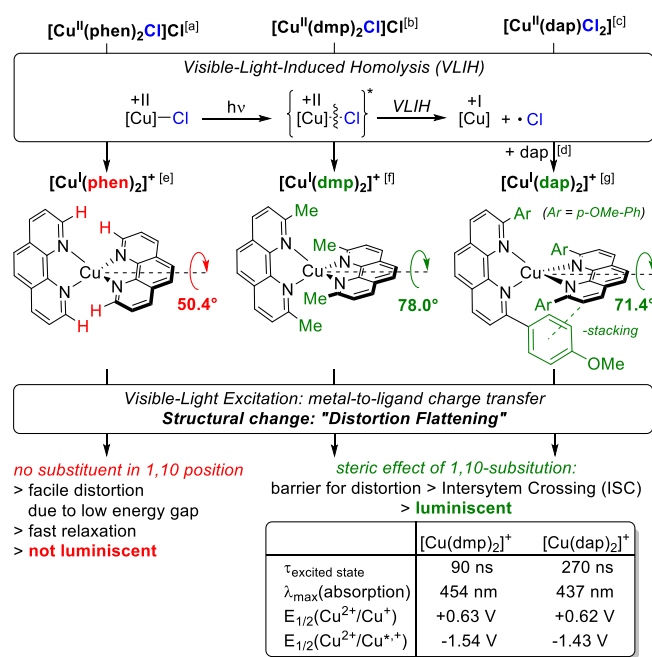
Introduction

In recent years, visible light photocatalysis has emerged as a powerful tool for carbon-carbon and carbon-heteroatom bond forming reactions, increasing molecular complexity under mild and ecologically benign reaction conditions.^[1,2] By now, the most commonly employed photocatalysts are represented by transition metal complexes based on ruthenium(II) and iridium(III), having the desired features for photocatalysts such as photostability, long excited state lifetimes, strong absorption in the visible region and high redox potentials.^[3] However, rather high cost, potential toxicity and the scarcity of the corresponding metal salts are major drawbacks of this class of catalysts.^[4] Organic dye photocatalysts provide a low-cost and metal-free alternative, but suffer in general from lower photostability.^[2,5] In this context, copper complexes are gaining importance for visible-light-mediated transformations. Besides the economic benefits, copper complexes, especially copper-phenanthrolines provide strong photo-excited reducing power, sufficient excited state lifetimes and are prone to undergo structural redistribution and ligand exchange which open up unique reaction pathways.^[6] However, although the copper salts are low-priced and highly economic, most copper complexes suffer from time- and price-consuming ligand synthesis.^[6-8] For instance, [Cu^I(dap)₂]Cl (dap = 2,9-(*p*-anisyl)-1,10-phenanthroline) being the leading representative among copper photocatalysts.

calls for a four-step ligand synthesis including a Pd-catalyzed cross-coupling reaction.^[9–11]

Results and Discussion

Recently, we have established a visible-light-mediated vicinal chlorosulfonylation of olefins utilizing the Cu(I) complex $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ and the corresponding Cu(II) complex $[\text{Cu}^{\text{II}}(\text{dap})\text{Cl}_2]$.^[12] The latter proved to be highly efficient in the title reaction, being at the same time beneficial from an economic point of view since only half the amount of dap ligand is required compared to $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$. Based on this study, we were searching for Cu(II) complexes for photoredox catalysis utilizing alternative ligands that would be commercially available or could be easily accessed.



Scheme 1. Comparison of Cu(II)- and the corresponding Cu(I)-complexes in photocatalysis. [a] Ref.^[13] [b] Ref.^[14] [c] Ref.^[15] [d] For details, see SI. [e] Ref.^[16] [f] Ref.^[17] [g] Ref.^[18].

Arguably the most readily available copper(II)phenanthroline complex would be $[\text{Cu}^{\text{II}}(\text{phen})_2\text{Cl}]\text{Cl}$, which can be prepared according to the literature from CuCl_2 and 1,10-phenanthroline (phen).^[13] Following the previously reported concept of visible-

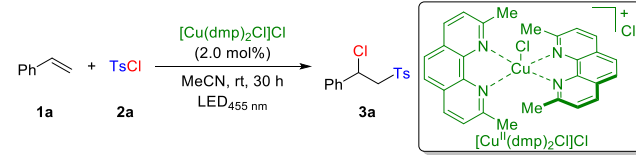
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FULL PAPER

light-induced homolysis (VLIH) of Cu(II) complexes in photoreactions^[12], [Cu^{II}(phen)₂Cl]Cl should be reduced *in situ* to the corresponding Cu(I) complex (*vide infra*), representing the catalytically active species in the ATRA reactions studied (Scheme 1). Upon visible-light irradiation and metal-to-ligand charge transfer (MLCT), photoinduced “flattening” of the geometry in the excited state occurs. However, due to the lack of substitution in the 1,10-position of the ligand, [Cu^I(phen)]⁺ is conformationally mobile and thus prone to rapidly return to its electronic ground state. As a consequence, this complex shows no luminescence.^[19,20] In line with this property, no ATRA reaction between styrene (**1a**) and tosyl chloride (**2a**) is observed when [Cu^{II}(phen)₂Cl]Cl was used as a potential precatalyst (Table 1, entry 1), contrasting [Cu^{II}(dap)Cl₂] which catalyzes the formation of **3a** in 95%^[12] (entry 2). In the latter, the steric effect of the *para*-aryl substitution prevents a rapid geometrical relaxation and thus quenching of the excited state, allowing intersystem crossing (ISC) to attain a stable triplet excited state, which then can act as the reductant in the photoreaction.

Table 1. Optimization and Control experiments^[a]

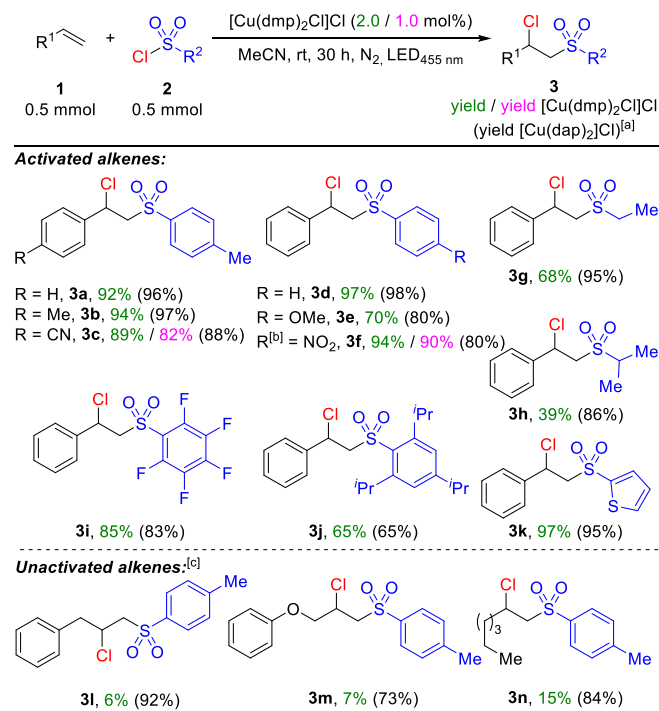


Entry	Conditions	NMR-yield ^[b]
1	[Cu ^{II} (phen) ₂ Cl]Cl (1.0 mol%)	nr
2 ^[c]	[Cu ^{II} (dap)Cl ₂] (1.0 mol%)	95%
3	1.0 mol% catalyst; green LED	75%
4	1.0 mol% catalyst; blue LED	86%
5 ^[d]	2.0 mol% catalyst; blue LED	92% (92%)
6	no catalyst	nr
7	no light	nr
8	CuCl ₂ (10.0 mol%)	nr
9	dmp (10.0 mol%)	4%
10 ^[e]	AIBN (10.0 mol%); T = 80 °C	nr

[a] Reaction conditions: styrene (**1a**) (0.5 mmol, 1.0 equiv), tosyl chloride (**2a**) (0.5 mmol, 1.0 equiv), catalyst (2.0 mol%) in MeCN (dry, degassed, 2.0 mL); Irradiation at 455 nm (blue LED) under N₂ atmosphere for 30 h at room temperature. [b] ¹H NMR yield using diphenoxymethane as an internal standard. [c] Ref.^[12] [d] Isolated yield in parenthesis. [e] Polymerization adducts of styrene observed. nr = no reaction.

Maintaining the steric effect of the 1,10-substitution but still simplifying the ligand, we next switched to [Cu^{II}(dmp)₂Cl]Cl, readily prepared from CuCl₂ and two equivalents of dmp, following

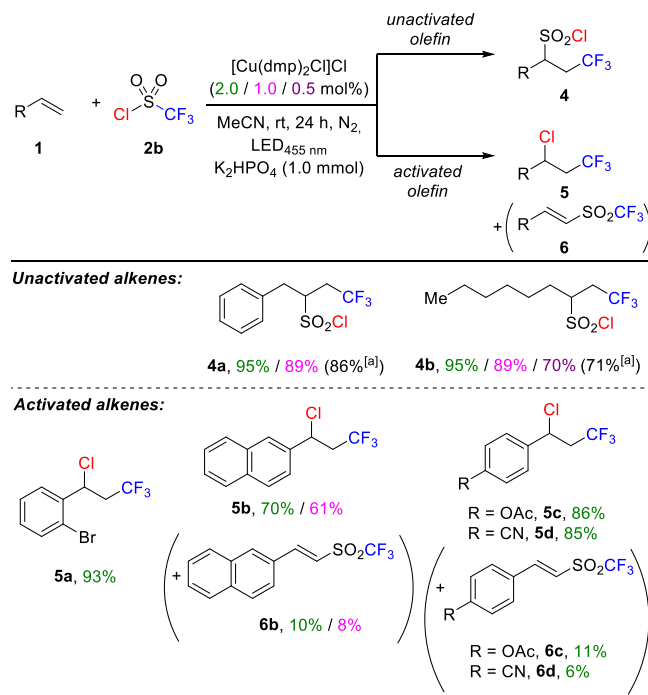
the procedure recently reported by Kloo and co-workers^[14]. The corresponding Cu(I) complex [Cu^I(dmp)₂]⁺ indeed shows luminescence, an even higher excited state reduction potential compared to that of [Cu^I(dap)₂]Cl, but an excited state lifetime of 90 ns^[17], being significantly shorter than that of [Cu(dap)₂]Cl (270 ns^[18a]). Although these photochemical parameters of [Cu^I(dmp)₂]⁺ were reported^[19,21], there have been only few applications in photoredox catalysis reflected by a small number of reports using [Cu^I(dmp)₂]⁺ as part of screening efforts for reaction optimization.^[8,16,22] Therefore, we wondered, if [Cu^{II}(dmp)₂Cl]Cl can serve as an oxidation- and bench-stable precursor for VLIH to [Cu^I(dmp)₂]⁺ and then the excited state lifetime of the latter is still sufficient for diffusion-controlled photoredox catalysis. Gratifyingly, [Cu^{II}(dmp)₂Cl]Cl proved indeed to be a capable precatalyst for the aforementioned ATRA process between styrene (**1a**) and tosyl chloride (**2a**), giving rise to **3a** in up to 92% yield (entries 3-5). Control experiments, omitting either catalyst or light, did not lead any conversion (entries 6,7). Employing CuCl₂ or the dmp ligand as potential stand-alone catalysts resulted in no product formation (entries 8,9). Notably, using 2.0 mol% of [Cu^{II}(dmp)₂Cl]Cl precatalyst afforded a slightly higher yield of 92% (entry 5) of the desired product compared to 1.0 mol% (entry 2), contrasting previous conditions with [Cu^I(dap)₂]Cl or [Cu^{II}(dap)Cl₂] for which 1.0 mol% catalyst loading was sufficient to generally give yields >90%. Given the low cost of [Cu^{II}(dmp)₂Cl]Cl prompted us to explore the substrate scope with best-optimized conditions (entry 5), but selected examples were also tested with lower catalyst loading to probe the limit of the catalytic activity and to make a better comparison with [Cu(dap)₂]Cl possible (Scheme 2).



FULL PAPER

Scheme 2. Scope of chlorosulfonylation reaction. *Reaction conditions:* olefin **1** (0.5 mmol, 1.0 equiv), sulfonyl chloride **2** (0.5 mmol, 1.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (2.0 mol%) in MeCN (dry, degassed, 2.0 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 30 h at room temperature. Isolated yields are given. [a] Catalyst loading 1.0 mol%, 24 h irradiation at 530 nm (green LED); results taken from previous report^[12]. [b] Reaction time 48 h. [c] Olefin **1** (1.0 mmol, 2.0 equiv), Na_2CO_3 (0.5 mmol, 1.0 equiv), reaction time 48 h.

We were pleased to find that both electron-rich and electron-poor styrenes with sterically or electronically differentiated aromatic sulfonyl chlorides gave rise to the corresponding photoproducts **3a-3f** in high yields comparable to $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$, in the case of **3f** even outperforming $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$. Further increase of electron deficiency or sterically bulk was also well tolerated giving rise to the ATRA products **3i** and **3j** in good yields. However, subjecting alkyl substituted sulfonyl chlorides to the reaction conditions resulted in a significant decrease of yield (**3g**, **3h**) compared to $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$. In our previous study^[12], switching to unactivated alkenes required the use of one equivalent of Na_2CO_3 preventing the $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ catalyst from being poisoned. Applying this protocol, $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ gave nevertheless only low yields of 6–15% for the desired products **3l-3n**. Catalyst stability tests (see SI) concluded a significant poisoning of the catalytically active species within one hour of irradiation presumably due to formation of acidic traces originating from sulfonyl chloride. Contrasting the case of $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$, the protective effect of Na_2CO_3 cannot prevent the poisoning of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$.

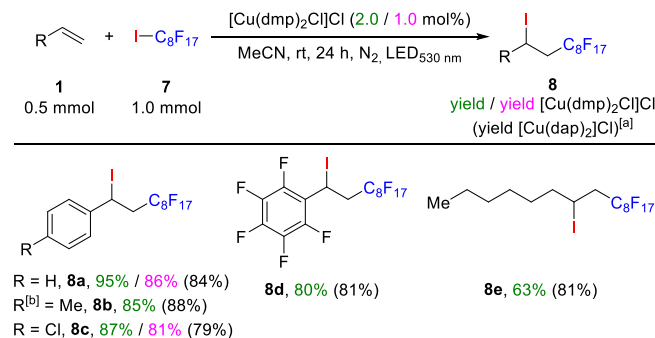


Scheme 3. Trifluoromethylchlorosulfonylation and Chlorotrifluoromethylation reaction. *Reaction conditions:* olefin **1** (0.5 mmol, 1.0 equiv), TiCl_4 **2b** (1.0 mmol, 2.0 equiv), K_2HPO_4 (1.0 mmol, 2.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (2.0 mol%) in MeCN (dry, degassed, 1.5 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 24 h at room temperature. Isolated yields are given. [a] Yield for $[\text{Cu}(\text{dap})_2]\text{Cl}$

(1.0 mol%) under 530 nm (green LED) irradiation; results taken from previous report^[23].

We next investigated trifluoromethylchlorosulfonylation of unactivated alkenes, being unique for copper(I)-photocatalysts such as $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$.^[23,24] We were pleased to see that also $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ is able to convert unactivated alkenes to the desired products **4a** and **4b** in almost quantitative yields even outperforming the established $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ catalyst (Scheme 3, top). In the case of **4b**, lowering of the catalyst loading to 0.5 mol% still yielded the desired product in an appreciable yield of 70%. Recently, Bissember and co-workers investigated several homoleptic 2,9-diaryl-1,10-phen Cu(I) complexes towards the influence of the ligand in the described trifluoromethylchlorosulfonylation.^[16] Surprisingly, they only observed 24% of **4b** under similar reaction conditions using the corresponding Cu(I) complex $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$, presumably due to the use of an elevated temperature (45 °C).

Furthermore, while $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ did not tolerate the use of activated alkenes instead leading to mixtures of various products (exception of *para*-nitrostyrene), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ also enables the conversion of styrene derivatives, however, the corresponding products with extrusion of SO_2 are observed (Scheme 3, bottom). These findings are in accordance with two recent literature reports, who also observed copper catalyzed chlorotrifluoromethylation when using different styrenes.^[25,26]



Scheme 4. Scope of Iodoperfluorination. *Reaction conditions:* olefin **1** (0.5 mmol, 1.0 equiv), $\text{C}_8\text{F}_{17}\text{I}$ (**7**) (1.0 mmol, 2.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (2.0 mol%) in MeCN (dry, degassed, 1.0 mL); Irradiation at 530 nm (green LED) under N_2 atmosphere for 30 h at room temperature. Isolated yields are given. [a] Catalyst loading 1.0 mol%, 16–20 h irradiation; results taken from previous report^[10]. [b] DCM (dry, degassed, 1.0 mL) was used as a solvent.

Recently, our group successfully showed the iodoperfluorination of styrene derivatives with the $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ catalyst, a reaction that fails with organic dyes, iridium- or ruthenium-based photocatalysts, emphasizing the unique character of copper photocatalysis.^[10] Gratifyingly, also $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ performed well in this reaction both with activated (**8a-8d**) as well as with unactivated (**8e**) alkenes (Scheme 4).

FULL PAPER

ATRA reactions with various bromine containing radical precursors that proved to be successful with $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$, were also evaluated with $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ (Table 2).^[9,27]

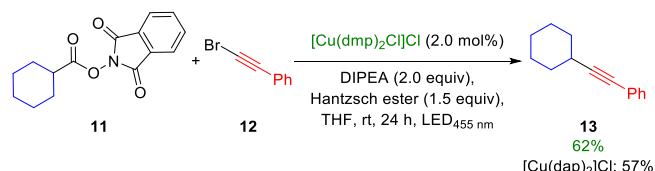
Table 2. Scope of other ATRA reagents^[a]

$\text{R}^1\text{CH=CH}_2 + \text{Br}-\text{R}^2 \xrightarrow[\text{MeCN, rt, 30 h, N}_2, \text{LED}_{455 \text{ nm}}]{[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl} (2.0 / 1.0 \text{ mol}\%)} \text{R}^1\text{CH(Br)CH}_2\text{R}^2$				
Entry	Alkene 1	Halide 9	Product 10	Yield
1				97% / 91% (88% ^[d])
2				92% / 88% (78% ^[d])
3 ^[b]				62% (75% ^[d])
4 ^[b]				12% (98% ^[d])
5 ^[c]				15% (87% ^[d])

[a] Reaction conditions: olefin **1** (0.5 mmol, 1.0 equiv), halide **9** (0.5 mmol, 1.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ (2.0 mol%) in MeCN (dry, degassed, 1.0 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 30 h at room temperature. Isolated yields are given. [b] Halide **9** (1.0 mmol, 2.0 equiv), LiBr (1.0 mmol, 2.0 equiv) was added, solvent DMF/water (1:4, 1.0 mL). [c] 5.0 equiv (2.5 mmol) of styrene (**1a**). [d] Catalyst loading 1.0 mol%, 24 h irradiation at 530 nm (green LED); results taken from previous reports^[9,27].

Tetrabromomethane (**9a**) addition to styrene (**1a**) is a widely used test reaction for photocatalytic activity.^[28] Two previous reports screened the corresponding Cu(I) complex $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ in the aforementioned reaction, yielding product **10a** in 12%^[22b] (0.3 mol% catalyst, 525 nm irradiation) and 60%^[22a] (1.0 equiv 2,6-lutidine in DCM for one hour at 400 nm irradiation), respectively. Starting from the Cu(II) complex $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ and given reaction conditions, both activated alkene **1a** and unactivated alkene **1b** were cleanly transformed into the desired products **10a** and **10b** in almost quantitative yields (Table 4, entries 1-2). Next, we switched to bromomalonate **9b** as ATRA reagent affording the desired photoproduct **10c** in a synthetically useful yield of 62%, being still comparable to using $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ (entry 3). A limitation of the $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ seems to be reached for α-bromoacetophenone (**9c**) and benzyl bromide **9d**, giving the corresponding products **10d** and **10e** in much lower yields (12-15%) compared to $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ (87-98%). In light of the stronger reducing power of excited $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$, this result was surprising and might point towards an insufficient excited state lifetime of the former which makes single electron transfer (SET) to **9c** or **9d** inefficient.

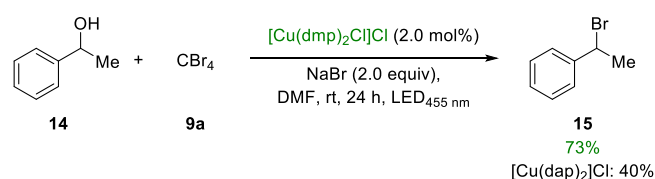
Having addressed a broad scope of different activated halides for copper-catalyzed visible-light-mediated ATRA reaction, we wanted next to examine mechanistically different photocatalytic transformations. First, we targeted the visible light decarboxylative fragmentation of *N*-(acyloxy)phthalimide **11** with subsequent $\text{C}_{\text{sp}^3}\text{-C}_{\text{sp}}$ coupling to bromoalkyne **12** (Scheme 5).



Scheme 5. Decarboxylative coupling reaction. Reaction conditions: **11** (0.5 mmol, 1.0 equiv), **12** (0.75 mmol, 1.5 equiv), DIPEA (1.0 mmol, 2.0 equiv), Hantzsch ester (0.75 mmol, 1.5 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ (2.0 mol%) in THF (dry, degassed, 1.5 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 24 h at room temperature. Isolated yield is given.

Indeed, subjecting the mentioned starting materials to the reaction conditions indicated, the desired product **13** was formed in good yields of 62% employing 2.0 mol% of $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ as precatalyst. The previously reported ruthenium catalyst only yielded **13** in 28%^[29], whereas heteroleptic Cu(I) $[\text{Cu}^{\text{I}}(\text{dq})(\text{BINAP})]\text{BF}_4$ complex evaluated by Collins and co-workers afforded 87% of coupling product^[8].

Additionally, Collins^[30] and co-workers showed that the heteroleptic complex $[\text{Cu}^{\text{I}}(\text{tmp})(\text{BINAP})]\text{BF}_4$ is an effective alternative in the photocatalytic Appel-type conversion of alcohols to the corresponding bromides developed by Stephenson^[31] and co-workers in 2011. Gratifyingly, also $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ was effective in this reaction yielding (1-bromoethyl)benzene (**15**) in synthetical useful yield of 73% (Scheme 6), contrasting results previously reported for the homoleptic $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ complex, which failed to achieve these transformations.^[30]

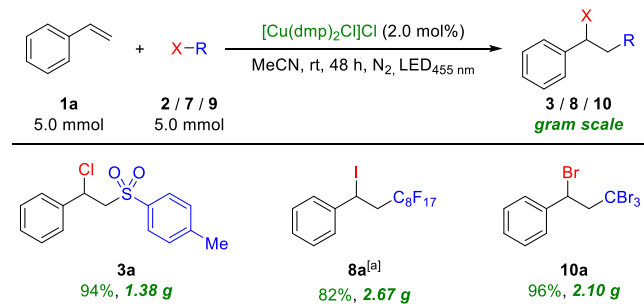


Scheme 6. Photocatalytic Appel reaction. Reaction conditions: **14** (0.5 mmol, 1.0 equiv), **9a** (1.0 mmol, 2.0 equiv), NaBr (1.0 mmol, 2.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$ (2.0 mol%) in DMF (dry, degassed, 3.0 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 24 h at room temperature. Isolated yield is given.

With quite a variety of different copper-catalyzed photoreactions successfully established for $[\text{Cu}^{\text{II}}(\text{dmp})_2]\text{Cl}$, we set out to demonstrate the viability of the complex on larger scale. Therefore, scale-up of three different difunctionalization reactions for styrene (**1a**) were tested (Scheme 7). Chlorosulfonylation, iodoperfluorination as well as CBr_4 -addition were performed on a 5.0 mmol

FULL PAPER

scale giving rise to the desired photoproducts **3a**, **8a** and **10a** in excellent yields (82–96%) in gram quantities of 1.38–2.67 g highlighting the possible application of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ to produce synthetically useful quantities of product in ATRA reactions.



Scheme 7. Gram-scale functionalization of styrene. *Reaction conditions:* styrene (**1a**) (5.0 mmol, 1.0 equiv), halide **2 / 7 / 9** (5.0 mmol, 1.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (2.0 mol%) in MeCN (dry, degassed, 15.0 mL); Irradiation at 455 nm (blue LED) under N_2 atmosphere for 48 h at room temperature. Isolated yields are given. [a] $\text{C}_8\text{F}_{17}\text{I}$ (**7**) (10.0 mmol, 2.0 equiv); Irradiation at 530 nm (green LED).

So far, there are only few examples that consider ligand to metal charge transfer (LMCT) for Cu(II)-complexes resulting in visible-light-induced homolysis (VLIH) to Cu(I) as a conceivable mechanistic proposal for photochemistry starting from Cu(II) complexes,^[12,15,32] based on the pioneering study by Kochi investigating the photolysis of the Cu(II)-Cl bond in CuCl_2 upon UV irradiation.^[33] However, by now there is only scarce experimental evidence present supporting this hypothesis. In the case of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$, the resulting Cu(I) species would be a Cu(I) complex like $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$, which would then be the active photocatalyst being able to promote transformations as shown above. Contrasting $[\text{Cu}^{\text{II}}(\text{dap})\text{Cl}_2]$ and $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$, for which both catalysts show similar UV-vis spectra,^[15] the corresponding UV-vis spectra of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (green line) and $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ (red line) significantly differ from each other (Figure 1, A). While the absorption measurement of $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ in anhydrous MeCN shows a distinct maximum in the blue region, the corresponding Cu(II) complex is much less luminescent, thus enabling the monitoring of the different species by UV-vis spectroscopy. Therefore, we subjected the model reaction between styrene (**1a**) and tosyl chloride (**2a**) catalyzed with both complexes to UV-vis analysis (Figure 1). Besides the similar results in reaction yield, it was already noticed upon visual inspection that both catalysts showed a strong color change during irradiation (for more details see SI).

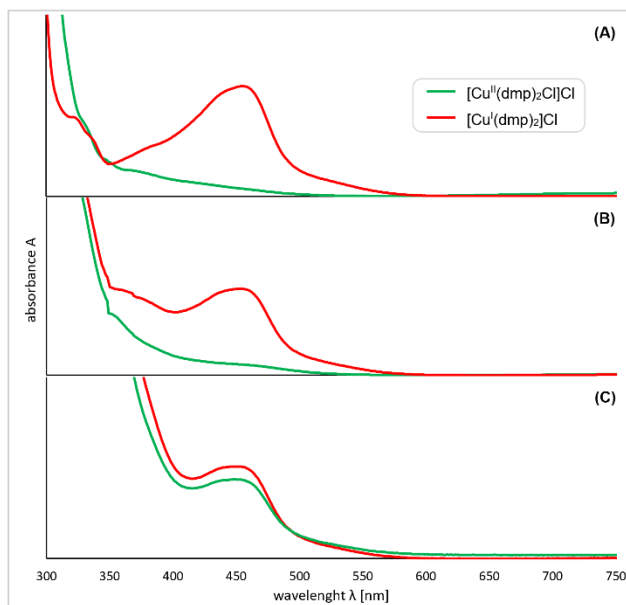


Figure 1. UV-vis monitoring of chlorosulfonylation reaction using $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (green) and $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ (red). (A) Copper catalysts alone; (B) Reaction mixture for chlorosulfonylation: styrene **1a**, tosyl chloride **2a** and $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (green) / $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ (red); (C) Crude reaction mixture **B** after irradiation at 455 nm (blue LED) under N_2 atmosphere for 30 h at room temperature. All UV-vis spectra are measured in MeCN (dry, 0.02 mM).

In the first step, we added the starting materials styrene (**1a**) and tosyl chloride (**2a**) to the respective catalyst solutions (Figure 1, B). No change of the UV-vis spectra in the case of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ was observed, whereas the UV-vis spectrum showed some differences for $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$, indicating an interaction of the latter with the substrates. Further UV-vis measurements suggest that in particular tosyl chloride (**2a**) is responsible for the aforementioned change in the spectra (see SI). Subsequently, both reaction mixtures were irradiated for 30 h at 455 nm (blue LED) and UV-vis spectra were recorded again (Figure 1, C). Remarkably, both spectra converged and, henceforth, show a high similarity regarding the absorption pattern, being characteristic for the Cu(I) species. These results indicate that both catalysts go through the same catalytic cycle, most likely having a Cu(I) complex as the photocatalytically active species, which then can undergo photoinduced SET to the substrate, following our previous reported mechanistic proposal for $[\text{Cu}^{\text{II}}(\text{dap})\text{Cl}_2]$ and $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$.^[12] Control UV-vis experiment with catalyst combined with product molecule ruled out potential interaction influencing the spectra (see SI). Thus, this study provides experimental evidence for the initiation of photocatalyzed reactions with Cu(II) complexes via VLIH.^[12,15,32] However, this experimental setup relies on long-term irradiation and steady-state UV-vis spectroscopy, hence further detailed mechanistic investigations concentrating on the exact wavelength and corresponding energy for the VLIH of the Cu(II)-chloride bond are required and ongoing in our laboratories.

FULL PAPER

Conclusions

In conclusion, we have evaluated the Cu(II)-complex $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ as a visible-light-mediated photoredox precatalyst. The complex is robust and economic compared to other copper photocatalysts, especially to the well-established $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$. The present complex does not suffer from time- and price-consuming ligand synthesis, thus providing an abundant alternative in copper photochemistry. The catalytic activity was demonstrated for various ATRA reactions enabling the economic difunctionalization of alkenes. In some cases, $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ even outperformed the established $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ system. Furthermore, the successful decarboxylative coupling and an Appel reaction further broadened the scope. By various gram-scale functionalizations of styrenes, the viability of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ for synthetic use was demonstrated, underlining the role of a low-priced and economic alternative. Notably, both complex $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ and $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ show good solubility in the examined solvents. Moreover, we provide mechanistic evidence for visible-light-induced activation of Cu(II) complexes for photocatalysis by UV-vis reaction monitoring.

Experimental Section

More detailed information, as well as characterization data, copies of NMR spectra, detailed UV-vis studies, catalyst stability test, VLIH details for $[\text{Cu}^{\text{I}}(\text{dap})_2]\text{Cl}$ and product yield comparison of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ and $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ can be found in the Supporting Information. This material is available free of charge via the Internet. CCDC 1922265 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033).

Commercially available chemical materials were purchased in high quality and were used without further purification. All reactions were carried out in oven-dried glassware under atmospheric conditions unless otherwise stated. Reactions with moisture or oxygen sensitive reagents were performed in anhydrous solvent in flame-dried glassware under an atmosphere of predried nitrogen. Photochemical reactions were carried out in anhydrous solvents in flame-dried glassware applying three consecutive freeze-pump-thaw cycles. Thereby, irradiation was performed using a LED-stick as irradiation source (for detail setup and light sources see SI). Reactions were monitored by thin layer chromatography (TLC) with TLC precoated aluminum sheets (Merck) Silica gel 60 F254, 0.2 mm layer thickness and visualized by a dual short ($\lambda = 254 \text{ nm}$) / long ($\lambda = 366 \text{ nm}$) wavelength UV lamp. Anhydrous solvents were prepared by established laboratory procedures.^[34] EtOAc and hexanes (40–60 °C) for chromatography were distilled prior to use. The reported yields are referred to isolated compounds unless otherwise stated. Column chromatography was performed with flash silica gel (Merck, 0.040–0.063 mm particle size). ^1H -NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz) or Bruker Avance III 400 "Nanobay" (400 MHz) Spectrometer. Spectra were evaluated in first order and coupling constants J are reported in Hertz (Hz). Splitting patterns for the spin multiplicity of the signals in the spectra are given as the following: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, hept = heptet, m = multiplet and combinations thereof. Chemical shifts for ^1H -NMR were reported as δ , parts per million (ppm),

relative to the signal of CHCl_3 at 7.26 ppm. ^{13}C -NMR spectra were recorded on Bruker Avance 300 (75 MHz), Bruker Avance 400 (101 MHz) or Bruker Avance III 400 "Nanobay" (101 MHz) Spectrometer. Chemical shifts for ^{13}C -NMR were reported as δ , parts per million (ppm), relative to the center line signal of the CDCl_3 triplet at 77.2 ppm. ^{19}F -NMR spectra were recorded on Bruker Avance 300 (282 MHz), Bruker Avance 400 (376 MHz) or Bruker Avance III 400 "Nanobay" (376 MHz) Spectrometer. FTIR spectroscopy was carried out on a Cary 630 FTIR Spectrometer. Solid and liquid compounds were measured neatly and the wave numbers are reported as cm^{-1} . UV-vis absorption measurements were performed on an Agilent Technologies Cary Series 100 UV-vis Spectrometer. Mass spectra were recorded using Jeol AccuTOF GCX and Agilent Q-TOF 6540 UHD Spectrometer. X-ray crystallographic analysis was performed using an Agilent Technologies SuperNova, an Agilent Technologies Gemini R Ultra, an Agilent GV 50 or a Rigaku GV 50 diffractometer. The measurement of melting point (mp) was carried out on a SRS MPA 100 – Automated melting point system by OptiMelt using a ramp rate of 1 K/min.

Synthesis of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ ^[14]: A round-bottom flask equipped with a magnetic stirring bar was charged with CuCl_2 (268.9 mg, 2.0 mmol) and dissolved in ethanol (120 mL). After complete dissolution, 2,9-dimethyl-1,10-phenanthroline (916.4 mg, 4.4 mmol, 2.2 equiv) was added to the stirred reaction mixture resulting in a green precipitate after a few minutes. The suspension was left to fully react by stirring at room temperature for another 2 h. Afterwards, the green precipitate was collected by vacuum filtration using a fritted funnel. The solid was washed with cold ethanol and cold diethyl ether and dried under vacuum to yield 840.7 mg (1.5 mmol, 76%) $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ as a bright green solid. Suitable crystals for X-ray analysis were obtained by slow evaporation of a MeCN solution containing $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$. The crystals obtained were green and needle-shaped (see SI).

Synthesis of $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$: A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with 2,9-dimethyl-1,10-phenanthroline (833.1 mg, 4.0 mmol, 2.0 equiv), dissolved in chloroform (40 mL) and stirred at room temperature for 30 min. CuCl (198.0 mg, 2.0 mmol, 1.0 equiv) was added slowly and the resulting mixture was stirred for 2 h at room temperature followed by precipitation in diethyl ether. Afterwards, the red precipitate was collected by vacuum filtration using a fritted funnel. The solid was washed with cold diethyl ether and dried under vacuum to yield 734.6 mg (1.4 mmol, 71%) $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$ as a red solid. ^1H -NMR (300 MHz, CDCl_3): $\delta = 8.53$ (d, $J = 8.2 \text{ Hz}$, 4H), 8.04 (s, 4H), 7.78 (d, $J = 8.2 \text{ Hz}$, 4H), 2.41 (s, 12H); ^{13}C -NMR (75 MHz, CDCl_3): $\delta = 157.6$, 143.1, 137.5, 127.7, 126.2, 125.7, 26.0. Suitable crystals for X-ray analysis were obtained by slow evaporation of a MeCN solution containing $[\text{Cu}^{\text{I}}(\text{dmp})_2]\text{Cl}$. The crystals obtained were red and plate-shaped.

General procedure for "standard ATRA reactions" (GP-A): A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with halide **2** / **7** / **9**, $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (10.0 μmol , 2.0 mol%) and dissolved in anhydrous solvent, sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **1** was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with LED took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 30 – 48 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

General procedure for chlorosulfonylation of unactivated alkenes (GP-B): A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with sulfonyl chloride **2** (0.5 mmol,

FULL PAPER

1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (5.5 mg, 10.0 μmol , 2.0 mol%) and dissolved in anhydrous MeCN (2.0 mL, 0.25 M) sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **1** (1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED (blue LED) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 48 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was saturated by addition of brine solution (20 mL) and the aqueous phase was washed with EtOAc (3 x 20 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 , concentrated in vacuo and the crude residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

General procedure for Trifluoromethylchlorosulfonylation of unactivated alkenes and Chlorotrifluoromethylation of activated alkenes (GP-C): A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (5.5 mg, 10.0 μmol , 2.0 mol%) and dissolved in anhydrous MeCN (1.5 mL, 0.33 M) sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **1** (0.5 mmol, 1.0 equiv) and triflyl chloride **2b** (168.5 mg, 1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED (blue LED) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water (5 mL) and the crude mixture was extracted with DCM (3 x 5 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 , concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

General procedure for ATRA reaction with *N*-Boc allylamine (GP-D): A Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with *N*-Boc allylamine (**1c**) (78.6 mg, 0.5 mmol, 1.0 equiv), halide **9** (1.0 mmol, 2.0 equiv), LiBr (86.6 mg, 1.0 mmol, 2.0 equiv), $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ (5.5 mg, 10.0 μmol , 2.0 mol%) and dissolved in a DMF (0.2 mL)/water (0.8 mL) mixture (1:4, 1.0 mL, 0.5 M) sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. The screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with a 455 nm high power LED (blue LED) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 30 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was saturated by addition of brine solution (20 mL) and the aqueous phase was washed with EtOAc (3 x 20 mL). The combined organic fractions were dried over anhydrous Na_2SO_4 , concentrated in vacuo and the crude residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

Compound 3a^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 135.6 mg (460 μmol , 92%) of **3a** as a white solid after flash column purification (hexanes / EtOAc 10:1 to 6:1). R_f (hexanes / EtOAc 5:1) = 0.30, Staining: UV, Vanillin; $^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 7.63$ (d, $J = 8.4 \text{ Hz}$, 2H), 7.30 – 7.19 (m, 7H), 5.33 (t, $J = 6.9 \text{ Hz}$, 1H), 3.95 (dd, $J = 14.7$, 6.9 Hz, 1H), 3.84 (dd, $J = 14.7$, 6.9 Hz, 1H), 2.41 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 145.0$, 138.7, 136.3, 129.9, 129.2, 129.0, 128.3, 127.2, 64.2, 55.2, 21.8. Spectral data are in accordance to literature.

Compound 3b^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 145.3 mg (471 μmol , 94%)

of **3b** as a white solid after flash column purification (hexanes / EtOAc 10:1 to 6:1). R_f (hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.62$ (d, $J = 8.3 \text{ Hz}$, 2H), 7.23 (d, $J = 8.0 \text{ Hz}$, 2H), 7.15 (d, $J = 8.2 \text{ Hz}$, 2H), 7.06 (d, $J = 8.0 \text{ Hz}$, 2H), 5.29 (t, $J = 6.9 \text{ Hz}$, 1H), 3.93 (dd, $J = 14.7$, 6.8 Hz, 1H), 3.83 (dd, $J = 14.7$, 7.1 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 144.9$, 139.3, 136.4, 135.8, 129.8, 129.6, 128.3, 127.2, 64.3, 55.2, 21.8, 21.3. Spectral data are in accordance to literature.

Compound 3c^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 143.0 mg (447 μmol , 89%) of **3c** as a white solid after flash column purification (hexanes / EtOAc 1:1). R_f (hexanes / EtOAc 5:1) = 0.18, Staining: UV, Vanillin; $^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 7.58$ (d, $J = 8.3 \text{ Hz}$, 2H), 7.52 (d, $J = 8.4 \text{ Hz}$, 2H), 7.39 (d, $J = 8.4 \text{ Hz}$, 2H), 7.22 (d, $J = 7.7 \text{ Hz}$, 2H), 5.32 (dd, $J = 7.7$, 6.4 Hz, 1H), 3.91 (dd, $J = 14.7$, 6.4 Hz, 1H), 3.83 (dd, $J = 14.7$, 7.7 Hz, 1H), 2.38 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 145.3$, 143.2, 135.8, 132.5, 129.9, 128.1, 128.0, 118.0, 112.7, 63.3, 53.9, 21.6. Spectral data are in accordance to literature.

Compound 3d^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 136.3 mg (485 μmol , 97%) of **3d** as a white solid after flash column purification (hexanes / EtOAc 5:1). R_f (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.79$ – 7.69 (m, 2H), 7.62 – 7.54 (m, 1H), 7.47 – 7.40 (m, 2H), 7.30 – 7.22 (m, 5H), 5.35 (t, $J = 6.9 \text{ Hz}$, 1H), 3.97 (dd, $J = 14.8$, 6.9 Hz, 1H), 3.87 (dd, $J = 14.8$, 7.0 Hz, 1H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 139.3$, 138.5, 133.9, 129.3, 129.2, 129.0, 128.2, 127.2, 64.1, 55.2. Spectral data are in accordance to literature.

Compound 3e^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 108.9 mg (350 μmol , 70%) of **3d** as a white solid after flash column purification (hexanes / EtOAc 5:1). R_f (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.67$ (d, $J = 8.9 \text{ Hz}$, 2H), 7.28 (s, 5H), 6.89 (d, $J = 8.9 \text{ Hz}$, 2H), 5.32 (t, $J = 6.9 \text{ Hz}$, 1H), 3.93 (dd, $J = 14.8$, 6.9 Hz, 1H), 3.87 – 3.79 (m, 4H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 164.0$, 138.8, 130.8, 130.5, 129.2, 129.1, 127.3, 114.5, 64.4, 55.8, 55.4. Spectral data are in accordance to literature.

Compound 3f^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 48 h yielded 152.8 mg (469 μmol , 94%) of **3f** as a white solid after flash column purification (hexanes / EtOAc 5:1). R_f (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin; $^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 8.23$ (d, $J = 8.9 \text{ Hz}$, 2H), 7.88 (d, $J = 8.8 \text{ Hz}$, 2H), 7.33 – 7.21 (m, 5H), 5.37 (t, $J = 7.1 \text{ Hz}$, 1H), 4.05 (dd, $J = 15.1$, 6.9 Hz, 1H), 3.94 (dd, $J = 15.1$, 7.2 Hz, 1H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 150.7$, 144.8, 137.9, 129.8, 129.6, 129.2, 127.4, 124.2, 64.2, 55.0. Spectral data are in accordance to literature.

Compound 3g^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 79.2 mg (340 μmol , 68%) of **3g** as a yellowish solid after flash column purification (hexanes / EtOAc 5:1). R_f (hexanes / EtOAc 5:1) = 0.18, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.46$ – 7.36 (m, 5H), 5.40 (dd, $J = 7.7$, 5.9 Hz, 1H), 3.81 (dd, $J = 15.2$, 7.7 Hz, 1H), 3.59 (dd, $J = 15.2$, 5.9 Hz, 1H), 2.94 – 2.74 (m, 2H), 1.32 (t, $J = 7.5 \text{ Hz}$, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): $\delta = 138.9$, 129.6, 129.3, 127.2, 60.7, 55.6, 49.0, 6.6. Spectral data are in accordance to literature.

Compound 3h^[12]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 48.3 mg (196 μmol , 39%) of **3h** as colorless oil after flash column purification (hexanes / EtOAc 5:1).

FULL PAPER

R_f (hexanes / EtOAc 5:1) = 0.25, Staining: UV, Vanillin; ¹H-NMR (400 MHz, CDCl₃): δ = 7.49 – 7.36 (m, 5H), 5.42 (dd, *J* = 7.6, 5.9 Hz, 1H), 3.84 (dd, *J* = 15.0, 7.6 Hz, 1H), 3.57 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.98 (hept, *J* = 6.9 Hz, 1H), 1.34 (dd, *J* = 13.4, 6.8 Hz, 6H); ¹³C-NMR (101 MHz, CDCl₃): δ = 139.1, 129.5, 129.2, 127.2, 58.3, 55.5, 54.1, 15.4, 14.8. Spectral data are in accordance to literature.

Compound 3i^[12]: Following general procedure (GP-A) irradiation using with blue LED (λ_{max} = 455 nm) for 30 h yielded 157.7 mg (425 μmol, 85%) of **3i** as white solid after flash column purification (hexanes / EtOAc 5:1). **R_f** (hexanes / EtOAc 5:1) = 0.65, Staining: UV, Vanillin; ¹H-NMR (300 MHz, CDCl₃): δ = 7.36 – 7.25 (m, 5H), 5.41 (t, *J* = 7.2 Hz, 1H), 4.11 (s, 1H), 4.09 (d, *J* = 1.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 146.9 – 146.4 (m), 143.4 – 143.0 (m), 139.6 – 139.0 (m), 137.4, 136.3 – 135.8 (m), 129.8, 129.1, 127.3, 64.9, 55.0; ¹⁹F-NMR (282 MHz, CDCl₃): δ = 135.35 – -135.57 (m, 2F), -143.38 (tt, *J* = 21.0, 8.0 Hz, 1F), -158.46 – -158.78 (m, 2F). Spectral data are in accordance to literature.

Compound 3j^[12]: Following general procedure (GP-A) using irradiation with blue LED (λ_{max} = 455 nm) for 30 h yielded 132.3 mg (325 μmol, 65%) of **3j** as white solid after flash column purification (hexanes / EtOAc 5:1). **R_f** (hexanes / EtOAc 5:1) = 0.73, Staining: UV, Vanillin; ¹H-NMR (400 MHz, CDCl₃): δ = 7.38 – 7.27 (m, 5H), 7.15 (s, 2H), 5.50 (dd, *J* = 7.5, 5.7 Hz, 1H), 4.11 (hept, *J* = 6.7 Hz, 2H), 4.01 (dd, *J* = 14.6, 7.5 Hz, 1H), 3.86 (dd, *J* = 14.6, 5.7 Hz, 1H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.31 – 1.23 (m, 18H); ¹³C-NMR (101 MHz, CDCl₃): δ = 154.2, 151.1, 139.4, 132.9, 129.2, 129.1, 127.1, 124.2, 66.2, 55.3, 34.4, 29.8, 25.2, 25.0, 23.7, 23.7. Spectral data are in accordance to literature.

Compound 3k^[12]: Following general procedure (GP-A) using irradiation with blue LED (λ_{max} = 455 nm) for 30 h yielded 139.4 mg (486 μmol, 97%) of **3k** as yellowish solid after flash column purification (hexanes / EtOAc 5:1). **R_f** (hexanes / EtOAc 5:1) = 0.33, Staining: UV, Vanillin; ¹H-NMR (300 MHz, CDCl₃): δ = 7.65 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.47 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.01 (dd, *J* = 5.0, 3.8 Hz, 1H), 5.37 (t, *J* = 6.9 Hz, 1H), 4.06 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.97 (dd, *J* = 14.8, 7.0 Hz, 1H); ¹³C-NMR (75 MHz, CDCl₃): δ = 140.0, 138.5, 135.0, 134.7, 129.3, 129.1, 128.0, 127.2, 65.3, 55.2. Spectral data are in accordance to literature.

Compound 3l^[12]: Following general procedure (GP-B) using irradiation with blue LED (λ_{max} = 455 nm) for 48 h yielded 9.9 mg (32 μmol, 6%) of **3l** as a white solid after flash column purification (hexanes / EtOAc 9:1 to 4:1). **R_f** (hexanes / EtOAc 4:1) = 0.22, Staining: UV, KMnO₄; ¹H-NMR (300 MHz, CDCl₃): δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.19 (m, 7H), 4.50 (dq, *J* = 7.7, 6.3 Hz, 1H), 3.53 (d, *J* = 6.3 Hz, 2H), 3.29 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.10 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.45 (s, 3H); ¹³C-NMR (75 MHz, CDCl₃): δ = 145.3, 136.4, 135.9, 130.1, 129.7, 128.6, 128.2, 127.4, 62.4, 54.5, 43.9, 21.8. Spectral data are in accordance to literature.

Compound 3m^[12]: Following general procedure (GP-B) using irradiation with blue LED (λ_{max} = 455 nm) for 48 h yielded 11.5 mg (35 μmol, 7%) of **3m** as colorless oil after flash column purification (hexanes / EtOAc 9:1 to 4:1). **R_f** (hexanes / EtOAc 4:1) = 0.41, Staining: UV, KMnO₄; ¹H-NMR (400 MHz, CDCl₃): δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.08 – 6.92 (m, 1H), 6.85 (dd, *J* = 8.8, 1.1 Hz, 2H), 4.60 (ddd, *J* = 11.3, 6.6, 5.5 Hz, 1H), 4.25 (dd, *J* = 10.3, 4.8 Hz, 1H), 4.19 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.88 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.58 (dd, *J* = 14.8, 6.7 Hz, 1H), 2.43 (s, 3H); ¹³C-NMR (101 MHz, CDCl₃): δ = 157.8, 145.5, 136.4, 130.2, 129.7, 128.3, 121.9, 114.9, 70.2, 60.1, 51.3, 21.8. Spectral data are in accordance to literature.

Compound 3n^[12]: Following general procedure (GP-B) using irradiation with blue LED (λ_{max} = 455 nm) for 48 h yielded 22.9 mg (76 μmol, 15%) of **3n** as colorless oil after flash column purification (hexanes / EtOAc 9:1 to 4:1). **R_f** (hexanes / EtOAc 4:1) = 0.68, Staining: UV, KMnO₄; ¹H-NMR (400 MHz, CDCl₃): δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.30 (dtd, *J* = 8.9, 6.3, 3.8 Hz, 1H), 3.56 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.45 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.46 (s, 3H), 1.97 (dddd, *J* = 14.1, 9.9, 5.8, 3.9 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.54 – 1.36 (m, 2H), 1.34 – 1.22 (m, 6H), 0.92 – 0.84 (m, 3H); ¹³C-NMR (101 MHz, CDCl₃): δ = 145.3, 136.7, 130.1, 128.3, 63.7, 54.8, 38.1, 31.7, 28.6, 25.9, 22.7, 21.8, 14.2. Spectral data are in accordance to literature.

Compound 4a^[23]: Following general procedure (GP-C) using irradiation with blue LED (λ_{max} = 455 nm) for 24 h yielded 136.8 mg (477 μmol, 95%) of **4a** as colorless oil after flash column purification (hexanes / EtOAc 9:1). **R_f** (hexanes / EtOAc 9:1) = 0.73, Staining: UV, KMnO₄; ¹H-NMR (400 MHz, CDCl₃): δ = 7.44 – 7.32 (m, 3H), 7.30 – 7.22 (m, 2H), 4.07 (qt, *J* = 9.6, 4.7 Hz, 1H), 3.58 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.27 (dd, *J* = 14.9, 6.9 Hz, 1H), 3.14 – 2.96 (m, 1H), 2.76 – 2.58 (m, 1H); ¹³C-NMR (101 MHz, CDCl₃): δ = 133.9, 129.5, 129.2, 128.1, 124.8 (q, *J* = 278.0 Hz), 71.0 (q, *J* = 2.4 Hz), 36.2, 34.0 (q, *J* = 31.1 Hz); ¹⁹F-NMR (376 MHz, CDCl₃): δ = -63.95 (s, 3F). Spectral data are in accordance to literature.

Compound 4b^[23]: Following general procedure (GP-C) using irradiation with blue LED (λ_{max} = 455 nm) for 24 h yielded 133.4 mg (475 μmol, 95%) of **4b** as colorless oil after flash column purification (hexanes / EtOAc 9:1). **R_f** (hexanes / EtOAc 9:1) = 0.34, Staining: UV, KMnO₄; ¹H-NMR (400 MHz, CDCl₃): δ = 3.76 (dtd, *J* = 8.6, 5.7, 2.8 Hz, 1H), 3.07 (dq, *J* = 15.6, 10.6, 2.8 Hz, 1H), 2.59 (ddt, *J* = 18.3, 15.6, 9.7 Hz, 1H), 2.20 (ddt, *J* = 15.8, 10.2, 6.1 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.57 (dddd, *J* = 12.1, 10.2, 6.8, 5.0 Hz, 2H), 1.41 – 1.27 (m, 6H), 0.93 – 0.86 (m, 3H); ¹³C-NMR (101 MHz, CDCl₃): δ = 24.92 (d, *J* = 277.9 Hz), 69.98 (q, *J* = 2.6 Hz), 34.66 (q, *J* = 30.8 Hz), 31.24, 30.42, 28.78, 25.92, 22.44, 13.95; ¹⁹F-NMR (376 MHz, CDCl₃): δ = -64.26 (s, 3F). Spectral data are in accordance to literature.

Compound 5a^[25,34,35]: Following general procedure using irradiation with blue LED (λ_{max} = 455 nm) for 24 h yielded 134.4 mg (467 μmol, 93%) of **5a** as colorless oil after flash column purification (hexanes / EtOAc 9:1). **R_f** (hexanes / EtOAc 9:1) = 0.33, Staining: UV, KMnO₄; ¹H-NMR (400 MHz, CDCl₃): δ = 7.60 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 2H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 5.68 (dd, *J* = 7.8, 5.9 Hz, 1H), 2.98 – 2.81 (m, 2H); ¹³C-NMR (101 MHz, CDCl₃): δ = 152.2, 138.8, 133.4, 130.5, 128.6 (d, *J* = 32.9 Hz), 124.8 (q, *J* = 278.1 Hz), 122.6, 53.4 (q, *J* = 3.6 Hz), 43.0 (q, *J* = 28.9 Hz); ¹⁹F-NMR (376 MHz, CDCl₃): δ = -64.54 (s, 3F). Spectral data are in accordance to literature.

Compound 5b^[25,34] and **6b**^[25]: Following general procedure (GP-C) using irradiation with blue LED (λ_{max} = 455 nm) for 24 h yielded 90.7 mg (351 μmol, 70%) of **5b** as colorless oil and 14.1 mg (49 μmol, 10%) of **6b** as white solid after flash column purification (hexanes / EtOAc 12:1 to 9:1). **R_f** (**5b**, hexanes / EtOAc 9:1) = 0.60, Staining: UV, KMnO₄; ¹H-NMR (**5b**, 300 MHz, CDCl₃): δ = 8.08 – 7.77 (m, 4H), 7.75 – 7.44 (m, 3H), 5.32 (t, *J* = 7.1 Hz, 1H), 3.24 – 2.89 (m, 2H); ¹³C-NMR (**5b**, 75 MHz, CDCl₃): δ = 136.9, 133.5, 133.1, 129.3, 128.3, 127.9, 127.0, 126.9, 126.8 (q, *J* = 277.9, 277.5 Hz), 126.3, 124.0, 55.3 (q, *J* = 3.4 Hz), 43.8 (q, *J* = 28.3 Hz); ¹⁹F-NMR (**5b**, 282 MHz, CDCl₃): δ = -64.40 (s, 3F). Spectral data are in accordance to literature. **R_f** (**6b**, hexanes / EtOAc 9:1) = 0.35, Staining: UV, KMnO₄; ¹H-NMR (**6b**, 300 MHz, CDCl₃): δ = 8.09 – 8.01 (m, 2H), 7.96 – 7.86 (m, 3H), 7.70 – 7.54 (m, 3H), 6.92 (dd, *J* = 15.5, 0.9 Hz, 1H); ¹³C-NMR (**6b**, 75 MHz, CDCl₃): δ = 154.0, 135.5, 133.4, 133.0, 129.6, 129.3, 129.1, 128.7, 128.1, 127.6, 123.3, 122.0 (q, *J* = 324.9 Hz), 116.4; ¹⁹F-NMR (**6b**, 282 MHz, CDCl₃): δ = -79.20 (s, 3F). Spectral data are in accordance to literature.

FULL PAPER

Compound 5c^[25,34,35] and **6c**: Following general procedure (GP-C) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 24 h yielded 114.7 mg (430 μmol , 86%) of **5c** as white solid and 16.8 mg (57 μmol , 11%) of **6c** as white solid after flash column purification (hexanes / EtOAc 12:1 to 9:1). R_f (hexanes / EtOAc 9:1) = 0.53, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (**5c**, 400 MHz, CDCl_3): $\delta = 7.41$ (d, $J = 8.6 \text{ Hz}$, 2H), 7.12 (d, $J = 8.6 \text{ Hz}$, 2H), 5.11 (t, $J = 6.4 \text{ Hz}$, 1H), $3.06 - 2.78$ (m, 2H), 2.30 (s, 3H); $^{13}\text{C-NMR}$ (**5c**, 101 MHz, CDCl_3): $\delta = 169.3$, 151.1 , 137.4 , 128.1 , 126.2 (q, $J = 277.9 \text{ Hz}$), 122.3 , 54.2 (q, $J = 3.4 \text{ Hz}$), 44.0 (q, $J = 28.5 \text{ Hz}$), 21.2 ; $^{19}\text{F-NMR}$ (**5c**, 376 MHz, CDCl_3): $\delta = -64.55$ (s, 3F). Spectral data are in accordance to literature. R_f (**6c**, hexanes / EtOAc 9:1) = 0.33, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (**6c**, 400 MHz, CDCl_3): $\delta = 7.86$ (d, $J = 15.5 \text{ Hz}$, 1H), 7.63 (d, $J = 8.6 \text{ Hz}$, 2H), 7.24 (d, $J = 8.6 \text{ Hz}$, 2H), 6.78 (d, $J = 15.4 \text{ Hz}$, 1H), 2.33 (s, 3H); $^{13}\text{C-NMR}$ (**6c**, 75 MHz, CDCl_3): $\delta = 168.9$, 154.5 , 152.7 , 131.0 , 128.9 , 123.0 , 121.4 (q, $J = 321.3 \text{ Hz}$), 116.8 , 21.3 ; $^{19}\text{F-NMR}$ (**6c**, 376 MHz, CDCl_3): $\delta = -79.23$ (s, 3F). HRMS (**6c**, ESI) m/z calculated for $\text{C}_{11}\text{H}_9\text{F}_3\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$) 295.0246, found 295.0247. IR (**6c**, neat): 3064, 1744, 1603, 1591, 1510, 1425, 1361, 1328, 1185, 1115, 1047, 1021, 988, 970, 921, 869, 823, 801, 793, 712. mp (**6c**): 105 °C.

Compound 5d^[25,34,35] and **6d**: Following general procedure (GP-C) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 24 h yielded 99.8 mg (427 μmol , 85%) of **5d** as colorless oil and 7.7 mg (29 μmol , 6%) of **6d** as white solid after flash column purification (hexanes / EtOAc 12:1 to 9:1). R_f (**5d**, hexanes / EtOAc 9:1) = 0.43, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (**5d**, 400 MHz, CDCl_3): $\delta = 7.69$ (d, $J = 8.4 \text{ Hz}$, 2H), 7.52 (d, $J = 8.4 \text{ Hz}$, 2H), 5.12 (t, $J = 7.1 \text{ Hz}$, 1H), $3.08 - 2.79$ (m, 2H); $^{13}\text{C-NMR}$ (**5d**, 101 MHz, CDCl_3): $\delta = 144.5$, 132.9 , 127.9 , 125.9 (q, $J = 278.5 \text{ Hz}$), 118.2 , 113.2 , 53.7 (q, $J = 3.4 \text{ Hz}$), 43.6 (q, $J = 28.7 \text{ Hz}$); $^{19}\text{F-NMR}$ (**5d**, 376 MHz, CDCl_3): $\delta = -64.37$ (s, 3F). Spectral data are in accordance to literature. R_f (**6d**, hexanes / EtOAc 9:1) = 0.20, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (**6d**, 400 MHz, CDCl_3): $\delta = 7.90$ (d, $J = 15.5 \text{ Hz}$, 1H), 7.79 (d, $J = 8.4 \text{ Hz}$, 2H), 7.71 (d, $J = 8.3 \text{ Hz}$, 2H), 6.96 (d, $J = 15.6 \text{ Hz}$, 1H); $^{13}\text{C-NMR}$ (**6d**, 101 MHz, CDCl_3): $\delta = 151.0$, 135.1 , 133.2 , 129.9 , 121.3 (q, $J = 324.4 \text{ Hz}$), 120.9 , 117.7 , 116.4 ; $^{19}\text{F-NMR}$ (**6d**, 376 MHz, CDCl_3): $\delta = -78.79$ (s, 3F). HRMS (**6d**, ESI) m/z calculated for $\text{C}_{10}\text{H}_6\text{F}_3\text{N}_2\text{O}_2\text{S}$ ($[\text{M}+\text{H}]^+$) 262.0144, found 262.0143. IR (**6d**, neat): 3101, 3090, 2233, 1610, 1588, 1510, 1416, 1357, 1319, 1301, 1189, 1107, 984, 865, 820, 798, 716. mp (**6d**): 169 °C.

Compound 8a^[10]: Following general procedure (GP-A) using irradiation with green LED ($\lambda_{\text{max}} = 530 \text{ nm}$) for 30 h yielded 308.3 mg (474 μmol , 95%) of **8a** as a white solid after flash column purification (hexanes). R_f (hexanes) = 0.51, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.46 - 7.41$ (m, 2H), $7.35 - 7.27$ (m, 3H), 5.45 (dd, $J = 9.7$, 5.2 Hz , 1H), $3.39 - 3.08$ (m, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 142.9$, 129.1 , 128.7 , 126.9 , $122.9 - 107.0$ (m), 42.7 (t, $J = 20.8 \text{ Hz}$), 16.7 . $^{19}\text{F-NMR}$ (282 MHz, CDCl_3): $\delta = -81.23$ (t, $J = 9.9 \text{ Hz}$, 3F), $-111.68 - -113.69$ (m, 1F), $-111.33 - -115.83$ (m, 1F), $-121.68 - -122.65$ (m, 6F), -123.21 (s, 2F), $-123.77 - -124.31$ (m, 2F), $-126.24 - -126.99$ (m, 2F). Spectral data are in accordance to literature.

Compound 8b^[10]: Following general procedure (GP-A) using irradiation with green LED ($\lambda_{\text{max}} = 530 \text{ nm}$) for 30 h yielded 282.4 mg (425 μmol , 85%) of **8b** as a white solid after flash column purification (hexanes). R_f (hexanes) = 0.59, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.32$ (d, $J = 8.1 \text{ Hz}$, 2H), 7.13 (d, $J = 7.9 \text{ Hz}$, 2H), 5.46 (dd, $J = 9.8$, 5.1 Hz , 1H), $3.38 - 3.08$ (m, 2H), 2.32 (s, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 140.0$, 138.8 , 129.7 , $129.6 - 127.3$ (m), 126.7 , 42.7 (t, $J = 20.6 \text{ Hz}$), 21.4 , 17.2 . $^{19}\text{F-NMR}$ (376 MHz, CDCl_3): $\delta = -81.30$ (t, $J = 10.0 \text{ Hz}$, 3F), $-112.18 - -113.42$ (m, 1F), $-112.05 - -115.96$ (m, 1F), $-114.58 - -115.78$ (m, 6F), $-121.93 - -122.88$ (m, 2F), $-123.24 - -124.03$ (s, 2F), -126.63 (s, 2F). Spectral data are in accordance to literature.

Compound 8c^[10]: Following general procedure (GP-A) using irradiation with green LED ($\lambda_{\text{max}} = 530 \text{ nm}$) for 30 h yielded 298.4 mg (436 μmol , 87%) of **8c** as a white solid after flash column purification (hexanes). R_f (hexanes) = 0.54, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.37$ (d, $J = 8.6 \text{ Hz}$, 2H), 7.30 (d, $J = 8.6 \text{ Hz}$, 2H), 5.41 (dd, $J = 10.0$, 5.0 Hz , 1H), $3.34 - 3.07$ (m, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 141.4$, 134.4 , 129.3 , 128.2 , $121.0 - 107.4$ (m), 42.7 (t, $J = 20.4 \text{ Hz}$), 15.3 . $^{19}\text{F-NMR}$ (376 MHz, CDCl_3): $\delta = -81.23$ (t, $J = 9.9 \text{ Hz}$, 3F), $-111.62 - -113.20$ (m, 1F), $-114.25 - -116.01$ (m, 1F), $-121.83 - -122.64$ (m, 6F), -123.22 (s, 2F), $-123.76 - -124.13$ (m, 2F), $-126.47 - -126.90$ (m, 2F). Spectral data are in accordance to literature.

Compound 8d^[10]: Following general procedure (GP-A) using irradiation with green LED ($\lambda_{\text{max}} = 530 \text{ nm}$) for 30 h yielded 297.7 mg (402 μmol , 80%) of **8d** as a colorless oil after flash column purification (hexanes). R_f (hexanes) = 0.90, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 5.66$ (dd, $J = 11.3$, 4.6 Hz , 1H), $3.56 - 3.36$ (m, 1H), $3.19 - 2.99$ (m, 1H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 144.1 - 136.1$ (m), $118.8 - 108.2$ (m), 40.4 (t, $J = 20.7 \text{ Hz}$), -3.9 ; $^{19}\text{F-NMR}$ (376 MHz, CDCl_3): $\delta = -81.32$ (t, $J = 9.8 \text{ Hz}$, 3F), $-113.67 - -114.19$ (m, 1F), $-115.79 - -116.61$ (m, 1F), $-122.00 - -122.53$ (m, 6F), -123.25 (s, 2F), -123.98 (s, 2F), -126.65 (s, 2F), -139.69 (bs, 1F), -143.52 (bs, 1F), -153.26 (t, $J = 9.8 \text{ Hz}$, 1F), -161.21 (td, $J = 21.5$, 7.9 Hz , 2F). Spectral data are in accordance to literature.

Compound 8e^[10]: Following general procedure (GP-A) using irradiation with green LED ($\lambda_{\text{max}} = 530 \text{ nm}$) for 30 h yielded 297.7 mg (402 μmol , 80%) of **8e** as a colorless oil after flash column purification (hexanes). R_f (hexanes) = 0.80, Staining: UV, KMnO_4 ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 4.34$ (tdd, $J = 8.3$, 5.6 , 4.3 Hz , 1H), $3.01 - 2.68$ (m, 2H), 1.80 (dddd, $J = 21.6$, 14.7 , 9.7 , 4.6 Hz , 2H), 1.53 (q, $J = 5.9$, 5.2 Hz , 1H), $1.46 - 1.26$ (m, 7H), 0.90 (t, $J = 6.3 \text{ Hz}$, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 118.8 - 113.5$ (m), 41.9 (t, $J = 20.8 \text{ Hz}$), 40.5 (d, $J = 2.1 \text{ Hz}$), 31.7 , 29.7 , 28.3 , 22.7 , 21.0 , 14.2 ; $^{19}\text{F-NMR}$ (282 MHz, CDCl_3): $\delta = -81.25$ (t, $J = 10.0 \text{ Hz}$, 3F), $-111.47 - -112.92$ (m, 1F), $-114.40 - -115.89$ (m, 1F), $-121.80 - -122.61$ (m, 6F), -123.22 (s, 2F), $-123.91 - -124.32$ (m, 2F), $-126.46 - -126.81$ (m, 2F). Spectral data are in accordance to literature.

Compound 10a^[9]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 211.4 mg (485 μmol , 97%) of **10a** as a yellowish oil after flash column purification (hexanes). R_f (hexanes) = 0.48, Staining: UV, Vanillin; $^1\text{H-NMR}$ (300 MHz, CDCl_3): $\delta = 7.54 - 7.46$ (m, 2H), $7.42 - 7.28$ (m, 3H), 5.34 (dd, $J = 7.5$, 4.3 Hz , 1H), $4.19 - 4.01$ (m, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 140.9$, 129.1 , 129.0 , 128.3 , 66.6 , 50.2 , 35.2 . Spectral data are in accordance to literature.

Compound 10b^[9]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 203.1 mg (458 μmol , 92%) of **10b** as a colorless oil after flash column purification (hexanes). R_f (hexanes) = 0.72, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 4.20$ (dq, $J = 9.0$, 4.5 Hz , 1H), 3.83 (dd, $J = 16.2$, 4.5 Hz , 1H), 3.54 (dd, $J = 16.2$, 4.9 Hz , 1H), 2.08 (dddd, $J = 14.2$, 10.1 , 6.1 , 4.2 Hz , 1H), 1.97 (dtd, $J = 14.3$, 9.3 , 4.8 Hz , 1H), $1.66 - 1.46$ (m, 2H), $1.42 - 1.26$ (m, 6H), $0.93 - 0.84$ (m, 2H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 67.1$, 52.2 , 39.9 , 36.5 , 31.8 , 28.6 , 27.5 , 22.7 , 14.2 . Spectral data are in accordance to literature.

Compound 10c^[9,36]: Following general procedure (GP-D) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 122.0 mg (308 μmol , 62%) of **10c** as a colorless oil after flash column purification (hexanes / EtOAc 10:1 to 5:1). R_f (hexanes) = 0.30, Staining: Ninhydrin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 4.98$ (bs, 1H), $4.26 - 4.15$ (m, 4H), $4.14 - 4.08$ (m, 1H), 3.73 (dd, $J = 9.5$, 5.0 Hz , 1H), 3.50 (p, $J = 7.9$, 6.6 Hz , 2H), 2.46 (ddd, $J = 14.9$, 9.5 , 3.7 Hz , 1H), 2.25 (ddd, $J = 15.0$, 10.1 , 5.0 Hz , 1H), 1.43 (s, 9H), 1.26 (td, $J = 7.1$, 2.2 Hz , 6H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 169.0$, 168.6 ,

FULL PAPER

155.7, 80.0, 61.9, 53.3, 50.3, 47.2, 34.8, 28.4, 14.2, 14.1. Spectral data are in accordance to literature.

Compound 10d^[9]: Following general procedure (GP-D) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 21.7 mg (61 μmol , 12%) of **10d** as a white solid after flash column purification (hexanes / EtOAc 9:1 to 4:1). R_f (hexanes) = 0.43, Staining: UV, vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 8.00 - 7.94$ (m, 2H), 7.60 – 7.53 (m, 1H), 7.46 (dd, $J = 8.4$, 7.0 Hz, 2H), 5.05 (bfs, 1H), 4.23 (dq, $J = 12.4$, 4.2 Hz, 1H), 3.61 (dt, $J = 14.9$, 5.7 Hz, 1H), 3.48 (ddd, $J = 14.5$, 7.2, 5.9 Hz, 1H), 3.23 (qdd, $J = 17.9$, 8.2, 6.0 Hz, 2H), 2.36 (dddd, $J = 14.9$, 8.2, 6.6, 3.9 Hz, 1H), 2.17 (ddd, $J = 14.6$, 10.0, 5.7 Hz, 1H), 1.45 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 198.8$, 155.8, 136.8, 133.4, 128.8, 128.2, 79.9, 56.3, 47.5, 36.4, 30.2, 28.5. Spectral data are in accordance to literature.

Compound 10e^[27]: Following general procedure (GP-A) using irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) for 30 h yielded 24.3 mg (76 μmol , 15%) of **10e** as a colorless oil after flash column purification (hexanes / EtOAc 12:1 to 9:1). R_f (hexanes / EtOAc 9:1) = 0.45, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 8.16$ (d, $J = 8.7$ Hz, 2H), 7.41 – 7.28 (m, 7H), 4.88 (dd, $J = 8.7$, 6.1 Hz, 1H), 2.95 (ddd, $J = 14.4$, 9.1, 5.6 Hz, 1H), 2.82 (ddd, $J = 13.9$, 8.9, 6.6 Hz, 1H), 2.63 (dtd, $J = 14.4$, 8.8, 5.7 Hz, 1H), 2.45 (ddt, $J = 14.3$, 9.1, 6.4 Hz, 1H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 148.4$, 146.8, 141.5, 129.5, 129.0, 128.8, 127.3, 123.9, 54.1, 40.9, 34.3. Spectral data are in accordance to literature.

Decarboxylative coupling reaction^[8,29]: A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with 1,3-dioxoisindolin-2-yl cyclohexanecarboxylate (**11**) (136.6 mg, 0.5 mmol, 1.0 equiv), (bromoethynyl)benzene (**12**) (135.8 mg, 0.75 mmol, 1.5 equiv), Hantzsch ester (190.0 mg, 0.75 mmol, 1.5 equiv), $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl}$ (10.0 μmol , 2.0 mol%) and dissolved in anhydrous THF (1.5 mL, 0.33 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, diisopropylethylamine (129.3 mg, 1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes) to yield 57.1 mg (310 μmol , 62%) of (cyclohexylethynyl)benzene (**13**) as a slightly yellow oil. R_f (hexanes) = 0.50, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.44 - 7.38$ (m, 2H), 7.32 – 7.24 (m, 3H), 2.60 (tt, $J = 9.2$, 3.8 Hz, 1H), 1.89 (ddt, $J = 12.6$, 5.8, 3.4 Hz, 2H), 1.77 (qq, $J = 6.5$, 2.1 Hz, 2H), 1.55 (ddt, $J = 13.7$, 9.7, 4.9 Hz, 3H), 1.44 – 1.30 (m, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 131.7$, 128.3, 127.5, 124.3, 94.6, 80.7, 32.9, 29.8, 26.1, 25.1. Spectral data are in accordance to literature.

Photocatalytic Appel reaction^[30,31]: A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with perbromomethane (**9a**) (331.6 mg, 1.0 mmol, 2.0 equiv), sodium bromide (102.9 mg, 1.0 mmol, 2.0 equiv), $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl}$ (5.5 mg, 10.0 μmol , 2.0 mol%) and dissolved in anhydrous DMF (3.0 mL, 0.17 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, 1-phenylethan-1-ol (**14**) (61.1 mg, 0.5 mmol, 1.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with blue LED ($\lambda_{\text{max}} = 455 \text{ nm}$) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched by addition of water (10 mL) and diethyl ether (10 mL). The layers were separated, and the aqueous phase was extracted with diethyl ether (2x 10 mL). The combined

organic layers were washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes) to yield 67.6 mg (365 μmol , 73%) of (1-bromoethyl)benzene (**15**) as a colorless oil. R_f (hexanes) = 0.58, Staining: UV, Vanillin; $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.49 - 7.41$ (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 5.23 (q, $J = 6.9$ Hz, 1H), 2.06 (d, $J = 6.9$ Hz, 3H); $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): $\delta = 143.4$, 128.8, 128.5, 126.9, 49.7, 27.0. Spectral data are in accordance to literature.

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Keywords: ATRA reaction • copper(II) • difunctionalization • homogenous catalysis • photocatalysis

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FULL PAPER

- [14] The synthesis of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ and X-ray structure of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{PF}_6$ (CCDC 1819088) (V. Leandri, Q. Daniel, H. Chen, L. Sun, J. M. Gardner, L. Kloo, *Inorg. Chem.* **2018**, 57, 4556) as well as the X-ray structure of $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}\cdot\text{MeOH}$ (CCDC 1861809) have been reported. Since we evaluated $[\text{Cu}^{\text{II}}(\text{dmp})_2\text{Cl}]\text{Cl}$ and its catalytic performance in MeCN, a X-ray structure of this complex crystallized from MeCN was obtained by us (CCDC 1922265 contain the supplementary crystallographic data for this complex. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033). (For details see SI)
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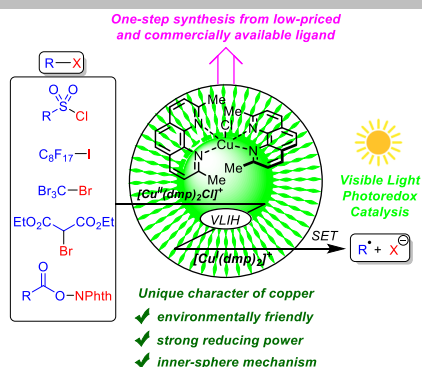
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Layout 1:

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The Cu(II)-complex $[\text{Cu}(\text{dmp})_2\text{Cl}]\text{Cl}$ is introduced to visible-light photocatalysis, being efficient but considerable more cost-effective compared to previously established Cu(I) photocatalysts within a broad scope of different reactions. Furthermore, this study provides UV-vis evidence for the visible light activation of Cu(II) complexes, suggesting an LMCT process resulting in the visible light homolysis of Cu(II)-Cl to give rise to catalytically active Cu(I) species.



Copper(II) Photoredox Catalysis*

Sebastian Engl, Oliver Reiser*

Page No. – Page No.

Making Copper Photocatalysis even more robust and economic: Photoredox Catalysis with $[\text{Cu}^\text{II}(\text{dmp})_2\text{Cl}]\text{Cl}$

*one or two words that highlight the emphasis of the paper or the field of the study