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Visible-Light-Mediated Regioselective Chlorosulfonylation of Alkenes and Alkynes: Introducing the Cu(II) complex [Cu(dap)Cl_2] to photochemical ATRA reactions

Asik Hossain‡, Sebastian Engl‡, Eugen Lutsker‡, and Oliver Reiser*

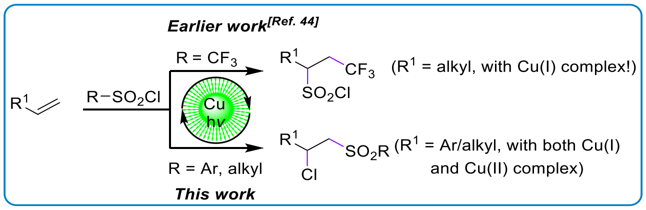
Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93053 Regensburg, Germany.

ABSTRACT: A visible light mediated photocatalyzed protocol utilizing copper-phenanthroline based catalysts has been developed, which can convert a large number of olefins into their chlorosulfonylated products. Besides the Cu(I)-complex $[Cu(dap)_2]Cl$, being by now well-established in photo-ATRA processes, the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ proved to be often even more efficient in the title reaction, being advantageous from an economic point of view, but also opening up new avenues for photoredox catalysis. Moreover, the copper complexes outperformed commonly used ruthenium, iridium or organic dye based photocatalysts, owing to their ability to stabilize or interact with transient radicals by inner sphere mechanisms. The use of stoichiometric Na_2CO_3 in combination with the copper photocatalysts was found to be essential to convert unactivated olefins to the desired products contrasting activated olefins for which no additive was required. As suggested by appropriate control experiments, the role of Na_2CO_3 is attributed to prevent poisoning of the catalyst.

KEYWORDS: photocatalysis, copper, ATRA reaction, hetero-difunctionalization, sulfone.

In synthetic organic chemistry, carbon-carbon and carbon-heteroatom bond-forming reactions are fundamental to achieve the synthesis of a desired product through consecutive increase in molecular complexity. As a result, the development of new catalytic methodologies by employing inexpensive catalysts at low loading are highly desirable in terms of sustainable chemistry. In this regard, visible light photocatalysis[1–9] mediated by metal complexes has become useful to achieve unique transformations under mild reaction conditions.[10] Recently, this strategy has been utilized for the difunctionalization of carbon-carbon multiple bonds[11] by various scientific groups[12–19] including our own,[20–23] which offers unique opportunities to diversify alkenes or alkynes for further transformations.

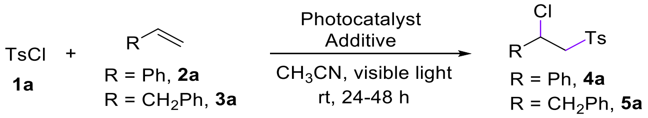
Sulfones are important motifs which can be found in many drugs and natural products[24–27]. Many efforts[28–31] have been made by various scientific groups[32–43] for the direct incorporation of a sulfone functionality into organic molecules. Recently[44,45] our group has discovered that CF_3SO_2Cl can be used as an Atom Transfer Radical Addition (ATRA) reagent[46,47] under photochemical condition using $[Cu(dap)_2]Cl$ as a photocatalyst without extrusion of SO_2. In this case, copper(I)-complexes served as singular catalysts because of their ability to interact with substrates either via direct ligand transfer, or via a rebound mechanism involving organocopper(III)-species.[48] Intrigued by this unique transformation, we questioned about the reactivity of other sulfonyl chlorides as ATRA reagents. A single electron transfer (SET) from the excited state of a photocatalyst to an aryl or alkyl sulfonyl chloride may form a *S*-centered radical[49–50] which can add to olefins and ultimately give rise to hetero-difunctionalized products (Scheme 1). In fact, seminal work by Stephenson and co-workers[53] describes this idea with two examples, *i.e.* with the $[Ru(bpy)_3]Cl_2$ photocatalyzed addition of *para*-toluenesulfonylchloride (**1a**) to styrene (**2a**) or norbornene, while pioneering studies using CuCl or $CuCl_2$ for the title reaction under thermal conditions (≥ 100 °C) were reported as well.[51,52]



Scheme 1: Switchable bond formation using different sulfonyl chlorides as ATRA reagent using copper photocatalysts.

Thus, we also started our investigation with *para*-toluenesulfonylchloride (**1a**) (E_{red} = −0.94 V vs SCE) and styrene (**2a**) (1 equiv) in the presence of 1 mol % $[Cu(dap)_2]Cl$[54,55] ($E_{Cu(II)/Cu(I)^*}$ = −1.43 V vs. SCE; dap = 2,9-bis(*p*-anisyl)-1,10-phenanthroline) as a photocatalyst under visible light irradiation (λ_{max} = 530 nm). We were pleased to observe formation of the desired product **4a** in an excellent yield (Table 1, Entry 1) after 24 h. Unexpectedly, the analogous copper(II) complex $[Cu(dap)Cl_2]$[20] also produced the desired product **4a** in 95% yield (Table 1, Entry 2). Instead, with $[Ru(bpy)_3]Cl_2$ ($E_{Ru(III)/Ru(II)^*}$ = −0.81 V vs. SCE; bpy = 2,2'-bipyridine), highly reducing *fac*-$[Ir(ppy)_3]$ ($E_{Ir(IV)/Ir(III)^*}$ = −1.73 V vs. SCE; ppy = 2-phenylpyridine) or $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ ($E_{Ir(IV)/Ir(III)^*}$ = −0.89 V vs. SCE; $dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-trifluoromethylpyridine, dtbbpy = 4,4' - di-*tert*-butyl-2,2'

Table 1. Reaction Optimization[a]



entry	photocatalyst (1 mol %)	additive (equiv)	olefin (equiv)	yield[b]
1[c]	$[Cu(dap)_2]Cl$	No	**2a** (1)	96(96)
2	$[Cu(dap)Cl_2]$	No	**2a** (1)	95
3	$[Ru(bpy)_3]Cl_2$	No	**2a** (1)	80
4	*fac*-$[Ir(ppy)_3]$	No	**2a** (1)	45
5	[**Ir-F**]	No	**2a** (1)	07
6	Na_2-Eosin Y	No	**2a** (1)	NR
7	$[Cu(dap)_2]Cl$	No	**3a** (1 or 2)	05 or 09
8	$[Cu(dap)_2]Cl$	K_2HPO_4 (1)	**3a** (2)	60
9	$[Cu(dap)_2]Cl$	K_2CO_3 (1)	**3a** (2)	18
10[c]	$[Cu(dap)_2]Cl$	Na_2CO_3 (1)	**3a** (2)	97(92)
11	$[Cu(dap)_2]Cl$	NaCl (1)	**3a** (2)	08
12	$[Cu(dap)_2]Cl$	Na_2CO_3 (0.3)	**3a** (2)	55
13	$[Ru(bpy)_3]Cl_2$	Na_2CO_3 (1)	**3a** (2)	20
14	$[Ru(bpy)_3]Cl_2$	No	**3a** (2)	55
15	*fac*-$[Ir(ppy)_3]$	Na_2CO_3 (1)	**3a** (2)	26
16	*fac*-$[Ir(ppy)_3]$	No	**3a** (2)	30
17	Na_2-Eosin Y	Na_2CO_3 (1)	**3a** (2)	03
18	No	Na_2CO_3 (1)	**3a** (2)	NR
19[d]	$[Cu(dap)_2]Cl$	Na_2CO_3 (1)	**3a** (2)	NR
20[c,e]	$[Cu(dap)Cl_2]$	Na_2CO_3 (1)	**3a** (2)	77(72)
21[f,g]	CuCl or $CuCl_2$	No	**2a** (1)	NR
22[f,g]	dap	No	**2a** (1)	NR
23[g,h]	CuCl/phen	No	**2a** (1)	NR
24[g,h]	$CuCl_2$/phen	No	**2a** (1)	NR

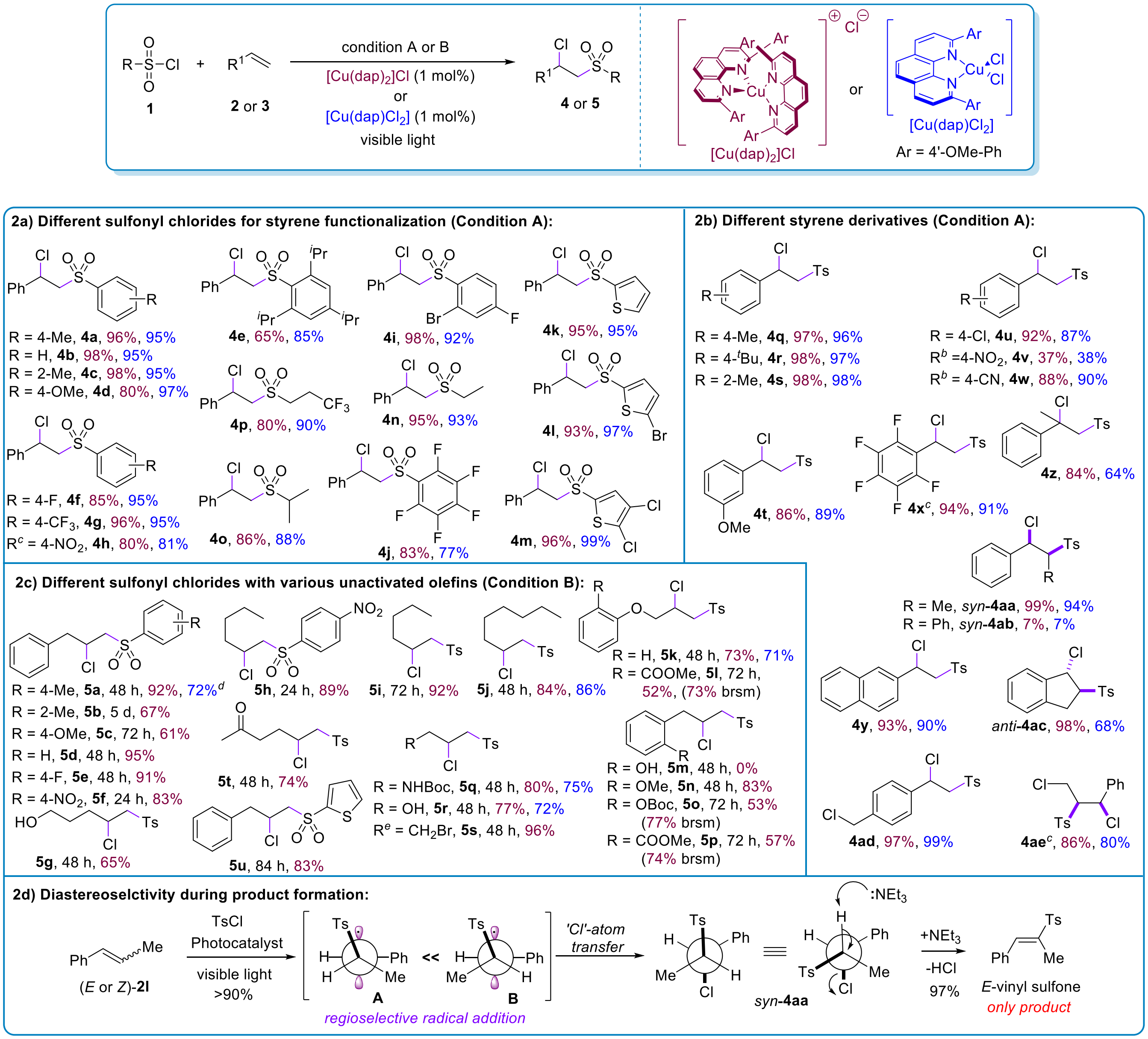
Reaction conditions: [a]**1a** (0.50 mmol, 1 equiv), photocatalyst (1 mol %), in CH_3CN (0.25 M) under N_2 at room temperature (25–30 °C). Reaction times were 24 h for **2a** and 48 h for **3a**. LEDs have been used for irradiation (see SI). For [Cu] and Na_2-Eosin Y, Green LED (λ_{max} = 530 nm) and for other photocatalysts Blue LED (λ_{max} = 455 nm). [b]^{1}H NMR yields. [c]Isolated yields are in parenthesis. [d]Reaction was performed in the dark. [e]72 h reaction time. [f]5 mol% catalyst was employed. [g]traces (<6%) of product formation was observed when **3a** was used in combination with Na_2CO_3 (see SI). [h]5 mol% copper salt with 10 mol% phen was used. NR = No Reaction. phen = 1,10-phenanthroline.

-dipyridyl, [**Ir-F**]) or Na_2-Eosin Y ($E_{EY^{\cdot+}/EY^*}$ = −1.11 V vs SCE) under irradiation the yield of the desired product **4a** was found to be significantly lower (Table 1, entries 3 - 6) which is consistent with the report by Stephenson and co-workers[53] but surprisingly not consistent with a more recent report,[56] according to which **1a** does not result in any product formation in the title reaction. It should be noted that the reduction potential of all catalysts is sufficient to generate the toluylsulfonyl radical upon PET to TsCl (**1a**).

Under the best conditions established for styrene (**2a**, Table 1, Entry 1), employing the unactivated olefin **3a** gave only low amounts of the desired ATRA product **5a** (Table 1, Entry 7). However, when this reaction was performed in the presence of 1 equivalent of K_2HPO_4, a drastic increase in product yield (60%) was observed (Table 1, Entry 8). The use of stoichiometric amounts of K_2CO_3 lowers the product yield to 18% (Table 1, Entry 9), while the use of 1 equivalent Na_2CO_3 instead of K_2CO_3 increases the isolated product yield to 92% (Table 1, Entry 10). Using 1 equivalent NaCl as an additive instead again drastically decreases the yield of **5a** to 8% (Table 1, Entry 11), making it unlikely that the process is dependent on Na^+-cocatalysis. Given that the overall reaction is a net addition, substoichiometric amounts of base should be sufficient, *i.e.* to scavenge traces of HCl that could form in the process. Nevertheless, reducing the amount of Na_2CO_3 to 30 mol % is accompanied by a decrease in product formation (55%, Table 1, Entry 12). Moreover, when other photocatalysts were employed such as $[Ru(bpy)_3]Cl_2$, *fac*-$[Ir(ppy)_3]$ or Na_2-Eosin Y, poor yields were observed and notably, irrespective if Na_2CO_3 is used as an additive or not (Table 1, Entries 13–17). Again, the use of the copper(II)-catalyst $[Cu(dap)Cl_2]$ was also possible, producing **5a** in 72% isolated yield (Table 1, Entry 20) after 72 h irradiation. Control experiments proved the necessity of both catalyst and light (Table 1, Entries 18-19) as well as the importance of dap ligand in combination with copper salts for this transformation (Entries 21-24, also see SI). Thus, the conditions established in entry 1 and 2 (for activated olefins **2**) and entry 10 and 20 (for unactivated olefins **3**) were found to be best and were subsequently applied to explore the scope for this reaction. It should be noted that the possibility of using $[Cu(dap)Cl_2]$ offers a considerable cost advantage, given that only half the amount of dap ligand has to be employed.

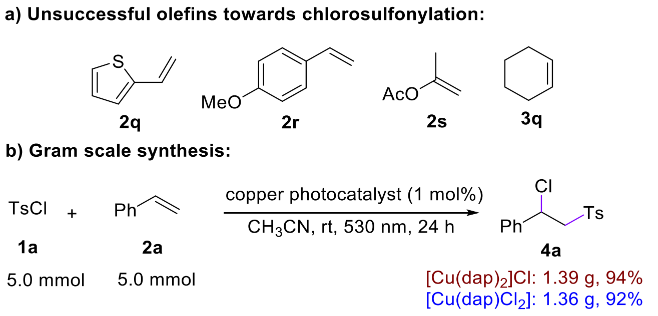
For a wide variety of vinyl arene substrates **2**, both Cu(I)- and Cu(II)-dap catalysts could be successfully employed in the title reaction (Schemes 2a and 2b). We were pleased to observe that both electron rich and electron poor sulfonyl chlorides **4a**–**4j** underwent the coupling with styrene **2a** in high yields (80-98%, Scheme 2a). Considering thiophene derived substrates a potential poison for the copper(I)-photocatalyst, they nevertheless also provided the ATRA products **4k**–**4m** in excellent yields (>90%). Likewise, alkyl sulfonyl chlorides and gave the desired ATRA products **4n**–**4p** in high yields (>80%). Noteworthy, halogenated sulfonyl chlorides as well as alkylsulfonyl chlorides have been reported to be incompatible for such ATRA reactions using $[Ru(bpy)_3]Cl_2$.[54] Different styrene derivatives in the coupling with tosyl chloride **1a** as an ATRA reagent (Scheme 2b) were broadly applicable (**4q**–**4u**, **4w**–**4y**, 84 – 97% yield) with few limitations (**4v**). *Alpha* or *beta* alkyl substitution on the styrene was also found to be suitable for this reaction (**4z**, **4aa**, **4ac**), while stilbene showed poor reactivity giving only 7% yield of **4ab**. Remarkably, when two new stereocenters are formed (**4aa, 4ab, 4ac, 4ae, 5w**), only one diastereomer was formed. Interestingly, both *trans* and *cis-beta* methyl styrene provided a single diastereomer[57] of **4aa** which upon treatment with triethylamine gave the corresponding *E*-vinyl sulfone exclusively (Scheme 2d). Benzylic or allylic chlorides showed no cross reactivity, allowing the isolation of **4ad** in 97% and of **4ae** in 86%, yield, respectively. Notably, the Cu(II) catalyst $[Cu(dap)Cl_2]$ performed in general at least as well but in a number of cases significantly better (**4d**, **4e**, **4f**, **4p**) compared to the Cu(I) catalyst $[Cu(dap)_2]Cl$.

Scheme 2: Scope of the reaction[a].



[a] General reaction conditions: Sulfonyl chloride **1** (0.50 mmol, 1 equiv), [Cu(dap)$_2$]Cl (1 mol %) or [Cu(dap)Cl$_2$] (1 mol %) in CH$_3$CN. Condition A: Activated olefin **2** (0.50 mmol, 1 equiv), reaction time was 24 h unless otherwise noted. Condition B: Unactivated olefin **3** (1.00 mmol, 2 equiv), Na$_2$CO$_3$ (0.50 mmol, 1 equiv). [b] 48 h reaction time. [c] single diastereomer, tentatively assigned analogously to *syn*-**4aa**. [d] 72 h reaction time. [e] 4 equiv olefin was used. All reactions were performed under N$_2$ atmosphere at room temperature (25–30 °C) with green LED (λ_{max} = 530 nm). Isolated yields are given.

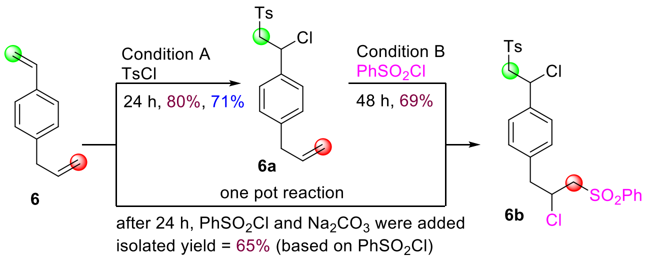
Scheme 3: Unsuccessful olefins and reaction scale up.



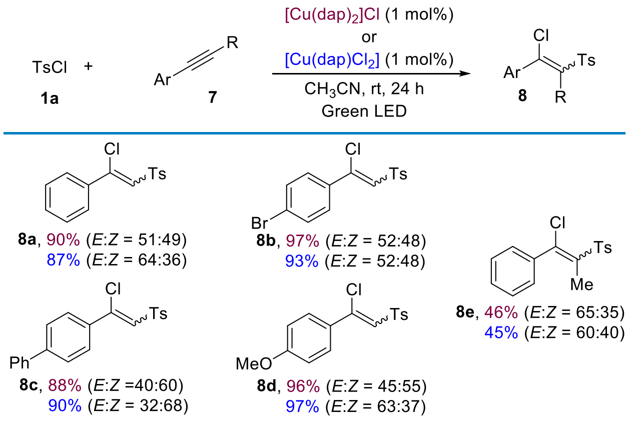
Further screening of a number of substrates (see SI, Scheme S2) confirmed the results detailed in Table 1, in which the copper photocatalysts outperform ruthenium and iridium-based ones as well as organic dyes.

Moving to unactivated olefins **3a** (Scheme 2c), the coupling with a variety of arylsufonyl chlorides proceeded well, provided that the reaction now is performed in the presence of 1 equiv of Na$_2$CO$_3$ (**5a**-**g**). Various potentially sensitive functionalities like hydroxyl, carbonyl, N-Boc-amine, primary bromine etc. were tolerated well giving rise to **5g**–**5j**, **5q**–**5t** in 65%–96% isolated yields. A phenolic OH

Scheme 4: Sequential functionalization of two different olefins.



Scheme 5: Scope for alkynes[a].



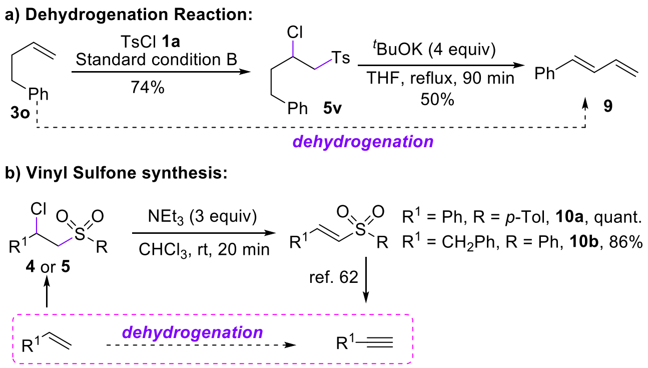
[a]Reaction condition: **1a** (0.50 mmol, 1 equiv), alkyne **7** (0.50 mmol, 1 equiv) and copper photocatalyst (1 mol %) in CH_3CN under N_2 atmosphere at room temperature with green LED (λ_{max} = 530 nm). Isolated yields are given. *E* and *Z* ratios are based on the isolated products.

group under the basic conditions is deprotonated and as a result we could not obtain **5m**, but the corresponding methyl or Boc-protected substrates cleanly gave rise to **5n** and **5o**. In general, *ortho*-substitution decreases the reaction rates, as it was also observed in the synthesis of **5p**. Thiophene derived sulfonyl chlorides were again found to be compatible with the reaction condition but required a longer reaction time, allowing the isolation of **5u** in 83% yield after 84 h irradiation. The limitation for unactivated olefins **3** is found for the coupling with alkyl sulfonyl chlorides, which did not yield any product. Strongly activated olefins (**2q**-**2s**) and cyclohexene **3q** yielded mostly polymerized products[58] (Scheme 3a). Scale up with either catalyst was demonstrated with the synthesis of **4a** on gram scale in excellent yields (>90%) without the need to prolong the reaction time or the catalyst loading (Scheme 3b).

Given the necessity for employing Na_2CO_3 as an additive for alkenes **3** for the chlorosulfonylation, we seized the opportunity to perform the sequential functionalization of **6** (Scheme 4). Indeed, **6a** could be obtained in the first step in 80% yield using TsCl (Condition A) followed by a second ATRA reaction with $PhSO_2Cl$ (Condition B) to give rise to **6b** in 69% isolated yield. An even better overall yield (65%) was obtained when a single flask reaction was performed in which 1 mol% $[Cu(dap)_2]Cl$ was found to be sufficient for the sequential functionalization of the two different double bonds.

Next, we evaluated alkynes[59,60,61] for the ATRA reaction with sulfonylchlorides (Scheme 5). Gratifyingly, phenylacetylene derived substrates **7** were suitable substrates and the ATRA products were isolated in good to excellent yields as a single regioisomer (**8a**-**8d**, up to 97% isolated yields as a separable mixture of *E* and *Z* isomers). In case of disubstituted alkyne **7e**, the ATRA product was still formed, however, the yield was moderate in this case (45-46%). However, unactivated alkynes such as 1-hexyne were found to be inactive towards this reaction, which is consistent with a recent report.[61]

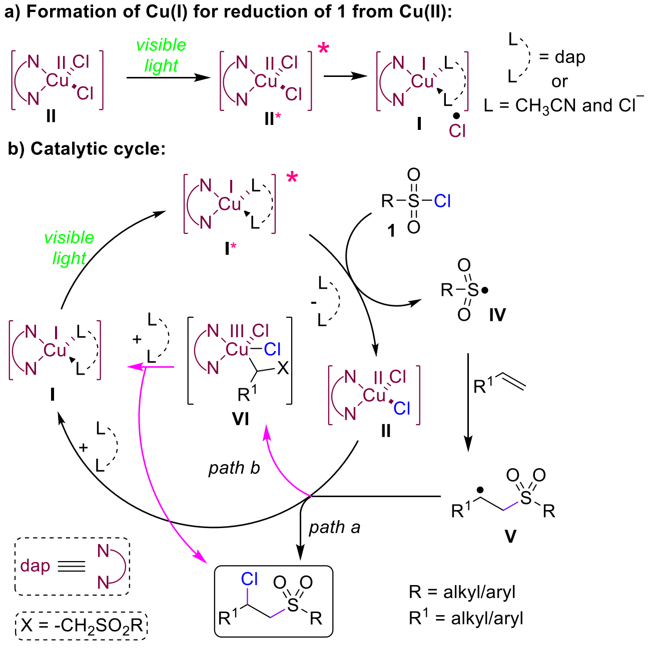
Scheme 6: Further Transformations of ATRA products.



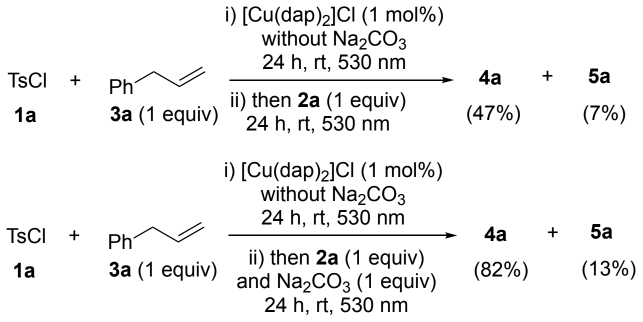
To show the synthetic utility of this transformation, we tested some of the ATRA products in their reactivity with bases. Upon treatment of **5v** with potassium *tert*-butoxide[62] a twofold elimination occurred giving rise to **9** (Scheme 6a), while weak bases (NEt_3) resulted in the formation of vinylsulfones[24] **10** in high yield (Scheme 6b). Vinyl sulfones have been proven to be valuable synthons in asymmetric reactions[63,64], cycloadditions[65,66], and metalations,[67] but can also be transformed to alkynes,[62] thus offering overall a route for the dehydrogenation of alkenes.

A plausible mechanism considering the unique role of the copper catalysts in the title transformation is outlined in Scheme 7. When the reaction was performed with $[Cu(dap)Cl_2]$ as a catalyst, we assume that nevertheless a reduction to Cu(I) occurs being the catalytically active species, for example via a visible-light-induced

Scheme 7: Proposed reaction mechanism



Scheme 8: Catalyst stability test[a]



[a] ^{1}H NMR yields with diphenylmethane as internal standard.

homolytic cleavage of the Cu(II)-Cl bond[68,20] (Scheme 7a) forming a Cu(I) intermediate **I**. **I** might get coordinated either by another dap ligand with chloride as a counter anion (which results in the formation of [Cu(dap)$_2$]Cl) or by the solvent[69]. **I** in its excited state **I*** can form sulfonyl radicals **IV** upon one electron reduction of sulfonyl chloride **1** (Scheme 7b). In turn, a Cu(II) species of type **II** such as [Cu(dap)Cl$_2$] is formed, which has been independently synthesized from CuCl$_2$ and dap[20] being found to be a capable photocatalyst for the title reaction in this study as well. The radical **IV** can add to the olefin forming a C-centered radical **V** which takes back chlorine from **II** concurrent with the regeneration of catalyst **I** (path a, black arrow). Intermediate **V** could also bind to the Cu(II) species **II** (path b, pink arrow), being a persistent radical, to give rise to a Cu(III) intermediate[70,71] **VI**. Reductive elimination from **VI** leads to the formation of the desired product and the active catalyst **I** is regenerated by trapping the free ligand.

We surmised that the distinct requirement for employing heterogeneous inorganic bases, in particular Na$_2$CO$_3$, which has also been shown to be beneficial in other photoredox reactions,[44,46,47] might also prevent the poisoning of the copper catalysts. When a mixture of **1a** and **3a** was irradiated in absence of Na$_2$CO$_3$ for 24 h (Scheme 8c) followed by addition of styrene (**2a**) with continuing irradiation for another 24 h, the formation of only 47% (^{1}H NMR yield) of **4a** was observed along with 7% **5a**. When the experiment was repeated but Na$_2$CO$_3$ was added together with styrene, the respective yields were 82% and 13%, clearly suggesting the protective nature of the heterogeneous base for the copper catalyst. The more reactive vinylarenes, being more efficient acceptors for radicals formed in the process, apparently prevent catalyst deactivation as well, since these alkenes do not require any base. The quantum yield for this reaction was found to be 9% which also makes the possibility of a free radical chain mechanism less likely[72,73] and supports the rebound mechanism.

In conclusion, we have developed a highly efficient, first row transition metal based photocatalytic protocol to convert a large variety of olefins to their corresponding vicinal chlorosulfonylated adducts. Moreover, the obtained adducts can be subjected to mono elimination reaction which produced vinyl sulfones in high yields. On the other hand, double elimination can produce alkynes, thus, the sulfonylchloride mimics Br$_2$ traditionally used for the conversion of alkenes to corresponding alkynes. Evidence that the role of inorganic bases, especially Na$_2$CO$_3$, that are often employed as additives in photoredox catalyzed processes prevent catalyst poisoning is provided. Last but not least, the bench stable Cu(II)-complex [Cu(dap)Cl$_2$] is shown for the first time to promote efficiently ATRA reactions, being beneficial from an economic point of view by requiring only half the amount of dap ligand compared to [Cu(dap)$_2$]Cl.

ASSOCIATED CONTENT

Supporting Information. Experimental details, further optimization, product yield comparisons with different photocatalysts, characterization data, mechanistic experiments and copies of NMR spectra of new compounds and X-Ray of compound **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: oliver.reiser@chemie.uni-regensburg.de

Author Contributions

‡These authors contributed equally.

Notes

The authors declare no competing financial interest.

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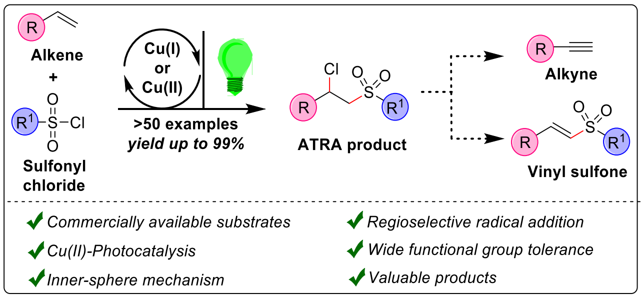
Alkene
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Sulfonyl chloride
Cu(I) or Cu(II)
>50 examples
yield up to 99%
ATRA product
Alkyne
Vinyl sulfone
✓ Commercially available substrates
✓ Cu(II)-Photocatalysis
✓ Inner-sphere mechanism
✓ Regioselective radical addition
✓ Wide functional group tolerance
✓ Valuable products