Visible-light photocatalyzed synthesis of 2-aryl N-methylpyrroles, furans and thiophenes utilizing arylsulfonyl chlorides as a coupling partner

Palani Natarajan, Anu Bala, S.K. Mehta, K.K. Bhasin

PII: S0040-4020(16)30229-0
DOI: 10.1016/j.tet.2016.03.087
Reference: TET 27627

To appear in: *Tetrahedron*

Received Date: 4 January 2016
Revised Date: 23 March 2016
Accepted Date: 25 March 2016

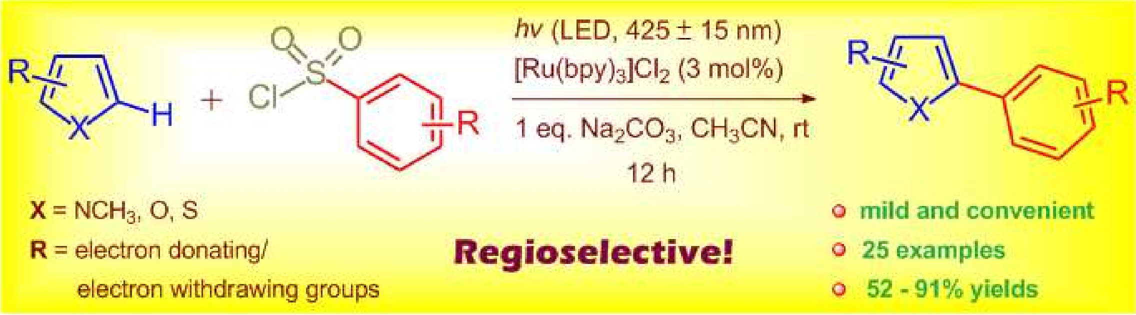
Please cite this article as: Natarajan P, Bala A, Mehta SK, Bhasin KK, Visible-light photocatalyzed synthesis of 2-aryl N-methylpyrroles, furans and thiophenes utilizing arylsulfonyl chlorides as a coupling partner, *Tetrahedron* (2016), doi: 10.1016/j.tet.2016.03.087.

Visible-light photocatalyzed synthesis of 2-aryl N-methylpyrroles, furans and thiophenes utilizing arylsulfonyl chlorides as a coupling partner

Palani Natarajan*, Anu Bala, S. K. Mehta and K. K. Bhasin

Department of Chemistry & Centre for Advanced Studies in Chemistry, Panjab University, Chandigarh - 160 014, India
pnataraj@pu.ac.in

Only for table of contents



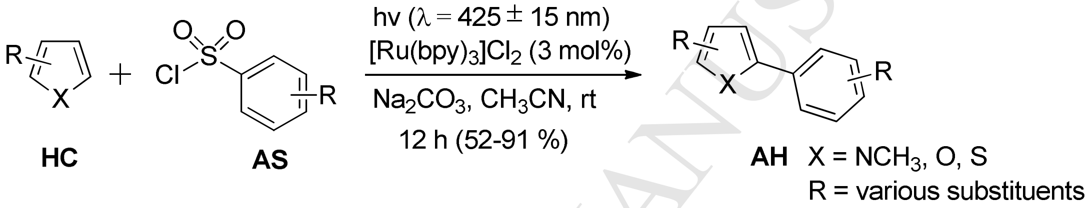
Visible-light (Blue LED lamp: hν = 425±15 nm) photocatalyzed cross-coupling reactions of arylsulfonyl chloride with N-methylpyrrole, furan, thiophene and their derivatives have been achieved in moderate to good yields at room temperature. A plausible mechanism has been proposed for the reaction. The arylation takes place at the C–H bond (C_2–H or C_5–H) next to the heteroatom with a high regioselective manner! Moreover, arylsulfonyl chlorides utilized in this study are inexpensive, environmentally benign and relatively more stable towards temperature, moisture and air as compared to diazonium salts normally used as coupling partners in the previously reported methods for the synthesis of heterobiaryls through visible-light photocatalyzed conditions.

Introduction

The visible-light-induced organic transformations developed by groups of MacMillan,[1] Stephenson,[2] Yoon[3] and many others[4] have been demonstrated as one of the most powerful tools for the construction of carbon-carbon and carbon-heteroatom bonds in syntheses. Significant energy efficiency, simple setup and mild reaction conditions are important features of this class of reactions.[1-4] Moreover, photoredox catalyzed reactions have been found numerous applications in both industries and academics for the preparations of natural products,[5] drugs[6] and functional materials.[7] All of the visible-light-induced formations of aryl-aryl and aryl-heteroaryl bonds, known in time, have normally been realized utilizing aryl-/heteroaryl diazonium salts as a coupling partner.[1-8] For example, Konig and co-workers[9] recently described a visible-light-promoted eosin Y catalyzed direct C–H arylation of furans, thiophenes and *N*-Boc-pyrroles with different aryl diazonium salts as a aryl radical source. Although diazonium salts have been found very useful coupling partners to afford bi- and polyaryls, they suffer from several disadvantages including unstable at ambient conditions, explosive in nature, cannot be stored for longer periods of time even at low temperatures, expensive and being functionalized are not commercially available.[10] As a consequence, the extension of visible-light-induced cross-coupling reactions utilizing readily available and environmentally benign aryl germ is highly desirable.

Arylsulfonyl halides,[11] in particular arylsulfonyl chlorides, are biocompatible, relatively cheap, can be stored for longer periods of time under ambient conditions, wide variety of derivatives are commercially available, provide only gaseous by-products (SO_2 and HCl) and widely applicable as electrophilic aryl partners in conventional transition metal-catalyzed cross-coupling reactions[12] to synthesize unsaturated carbonyl compounds, carboxylic acids, polyarenes, biaryls and heterobiaryls.[12f] However, only few instances have hitherto been reported on the visible-light photocatalyzed synthesis of biaryls or polyaryls using arylsulfonyl chlorides as a coupling partner.[13] For examples, Li and co-workers[14] reported the sequential arylation of alkynes and carbocyclization with benzylic C-H bonds using arylsulfonyl chlorides as aryl radical precursors. The same group[15] also described a synthesis of functionalized 10a,11-dihydro-10H-benzo[b]fluorenes through tandem cyclization of 1,6-enynes with arylsulfonyl chlorides under visible-light-promoted conditions.[15] In these cases,[14,15] authors proposed that single electron transfer (SET) from the excited-state photo-catalyst to arylsulfonyl chlorides provides an aryl radical (vide infra) that subsequently reacts with unsaturated compounds to yield the products.

Herein, we demonstrate a novel protocol for the preparations of 2-aryl N-methylpyrrole, furan, thiophene and their derivatives from arylsulfonyl chlorides and corresponding heteroarenes in the presence of 3 mol% of $[Ru(bpy)_3]Cl_2$ under visible-light (Blue LED lamp: hν = 425±15 nm) irradiation conditions, cf. Scheme 1. Moreover, a plausible mechanism has been proposed for the coupling reaction (vide infra). Although synthesis of heterobiaryls using aryl diazonium salts as aryl radical source has been reported,[8,9] the arylsulfonyl chlorides employed synthesis of 2-aryl N-methylpyrrole, furan, thiophene and their derivatives is not realized yet.



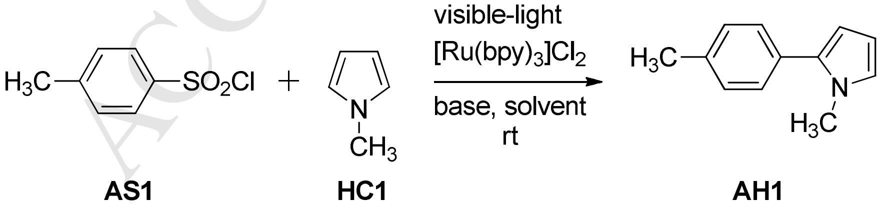
Scheme 1. Visible-light-induced desulfonylative coupling of arylsulfonyl chlorides with five-membered heteroarenes reported in this work.

Results and Discussion

At the outset of this investigation, the reaction conditions were optimized for the C-H arylation of N-methylpyrrole (**HC1**, 1.0 equiv.) with *p*-toluenesulfonyl chloride (**AS1**, 1.0 equiv.) in the presence of K_2CO_3 (1.0 equiv.), fluorescent light irradiation and 3 mol% of $[Ru(bpy)_3]Cl_2$ as a photoredox catalyst in CH_2Cl_2 at room temperature. After about 24 h, the desired 2-aryl-N-methylpyrrole (**AH1**) was obtained in 23% yield (Table 1 and Entry 1). Encouraged by this initial result, a series of trial experiments were performed to optimize the influences of radiation source, solvents, base and catalyst quantity for the proposed reaction (Scheme 1). Interestingly, the yield of **AH1** enhanced to 39% when the reaction was performed with 5W blue LED lights (hν = 425±15 nm, Table 1 and Entry 2). In contrast, the yield of **AH1** was lowered to 10-20% when reaction was irradiated with either 5W green LED lights or ambient lights (Table 1, Entries 3 and 4). However, no product was detected in the absence of the light source (Table 1 and Entry 5). Afterwards, the influence of solvents on the formation of **AH1** was explored. The investigation revealed that CH_3CN was the most effective medium to promote the reaction with

78% yield (Table 1 and Entry 6). While the use of other solvents such as hexane, heptane, diethyl ether, glyme and $CHCl_3$ resulted in lower yields (Table 1 and Entries 7-11) even after 24 h of irradiation. A maximum yield of **AH1** in CH_3CN may be due to the greater solubility of both the catalyst and substrates in that medium. We then went on to study the effect of base on the reaction (Scheme 1). Indeed, a better yield of **AH1** was obtained when Na_2CO_3 was used (Table 1 and Entry 12). Nevertheless, other inorganic/organic bases including Li_2CO_3, $NaHCO_3$, NaOAc, NaOH, K_2CO_3, *t*-BuOK, Cs_2CO_3 and Et_3N afforded moderate to low yields of the desired product (Table 1 and Entries 13-19). Hence, Na_2CO_3 was selected as a base for the transformation outlined in Scheme 1. Moreover, optimization of amount of Na_2CO_3 revealed that the excess base decreased the product yield (Table 1 and Entries 20-21), which perhaps attributed to the direct reaction of a base with **AS1**.[11] The influence of quantity of catalyst on the product yield was also investigated. An increase in the catalyst amount from 3 mol% to 5 mol%, the reaction time was obviously shortened with 94% yield of **AH1** (Table 1 and Entry 22). Further increase in the catalyst amount showed profound effect on neither in reaction time nor in yield of the desired product (Table 1 and Entry 23). However, no product was observed in the absence of catalyst $[Ru(bpy)_3]Cl_2$ (Table 1 and Entry 24). Subsequently, we investigated the influence of atmosphere on the reaction. Under O_2, the yield of **AH1** decreased to 28%, whereas under N_2/Ar atmosphere the product yield increased up to 91-94% (Table 1, Entries 12 and 22). Thus, the combinations of 3 mol% of $[Ru(bpy)_3]Cl_2$, 1 equiv. of Na_2CO_3 and 5W blue LED light in CH_3CN at room temperature for 12 h are the optimal conditions for this transformation, cf. Scheme 1.[16]

Table 1. Selected results of screening the optimal conditions for the photocatalytic cross-coupling of *p*-toluenesulfonyl chloride (**AS1**) with *N*-methylpyrrole (**HC1**)[a]



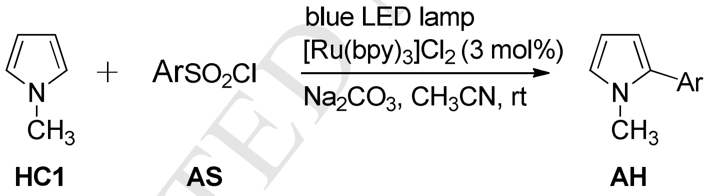
Entry	Solvent [b]	Base [b]	Time (h)	Yield (%) [c]
1	CH_2Cl_2	K_2CO_3	24	23
2	CH_2Cl_2	K_2CO_3	24	39[d]

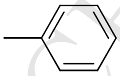
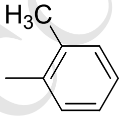
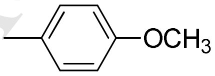
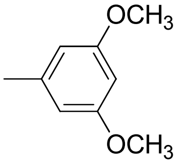
3	CH_2Cl_2	K_2CO_3	24	20[e]
4	CH_2Cl_2	K_2CO_3	24	<5[f]
5	CH_2Cl_2	K_2CO_3	24	0[g]
6	CH_3CN	K_2CO_3	12	78
7	hexane	K_2CO_3	24	<5
8	heptane	K_2CO_3	24	<5
9	diethyl ether	K_2CO_3	24	<10
10	glyme	K_2CO_3	24	≈20
11	$CHCl_3$	K_2CO_3	24	≈20
12	CH_3CN	Na_2CO_3	12	92
13	CH_3CN	Li_2CO_3	24	44
14	CH_3CN	$NaHCO_3$	24	53
15	CH_3CN	NaOAc	24	13
16	CH_3CN	NaOH	24	<5
17	CH_3CN	*t*-BuOK	24	<10
18	CH_3CN	Cs_2CO_3	24	<5
19	CH_3CN	$(CH_3CH_2)_3N$	24	<10
20	CH_3CN	Na_2CO_3	12	83[h]
21	CH_3CN	Na_2CO_3	12	61[i]
22	CH_3CN	Na_2CO_3	7	94[j]
23	CH_3CN	Na_2CO_3	7	93[k]
24	CH_3CN	Na_2CO_3	48	0[l]
25	CH_3CN	Na_2CO_3	24	28[m]

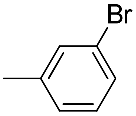
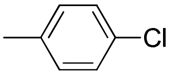
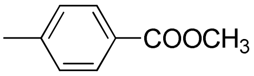
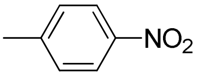
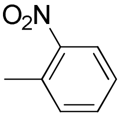
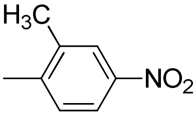
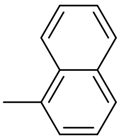
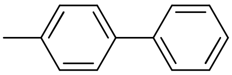
[a] Unless stated otherwise all reactions were performed in a Schlenk tube with 1.0 equiv. of **HC1**, 1.0 equiv. of **AS1**, 1.0 equiv. of base and 3 mol% of $[Ru(bpy)_3]Cl_2$ in dry solvent under inert atmosphere with the irradiation of a visible-light source.
[b] Solvents and bases were rigorously purified following the methods described in reference 17.
[c] Isolated yields.
[d] 5W blue LED lamp, hν = 425±15 nm, used.
[e] 5W green LED lamp, hν = 535±5 nm, used.
[f] 15W ambient lamp used.
[g] no irradiation source used.
[h] 1.5 mmol of Na_2CO_3 used
[i] 2.0 mmol of Na_2CO_3 used
[j] 5.0 mol% of $[Ru(bpy)_3]Cl_2$ used
[k] 10 mol% of $[Ru(bpy)_3]Cl_2$ used
[l] no catalyst, $[Ru(bpy)_3]Cl_2$, used
[m] Reaction performed under O_2 atmosphere

Under the optimized conditions (Table 1), the substrate scope of the transformation (Scheme 1) was investigated. The reaction between N-methylpyrrole (**HC1**) and various arylsulfonyl chlorides (**AS2-AS13**) was looked at first and the results are summarized in Table 2. Notice that the reaction was significantly affected by the electronic effects of substituents in the arylsulfonyl chlorides. The arylsulfonyl chlorides (**AS1**, **AS3**, **AS4**, **AS5** and **AS13**) bearing electron-donating groups showed slightly lower yields than those bearing electron-deficient groups (Cl, Br, NO_2, and $COOCH_3$): probably due to the higher reduction potentials of latter precursors.[11] In addition, a strong dependence on the position of the substituents was observed, cf. Table 2 and Entries 2, 4, 5, 9, 10 and 11. For example, the reaction with *para*-methyl substituted arylsulfonyl chloride afforded higher yields than those of *ortho*-methyl substituted arylsulfonyl chloride (Tables 1 and 2). This is likely attributed to the steric hindrance of the *ortho*-functionalized arylsulfonyl chlorides (**AS3**, **AS10**, **AS11** and **AS12**) as similar findings have been well documented in the literatures.[11, 12] Thus, a wide range of electronically and structurally diverse arylsulfonyl chlorides and N-methylpyrrole can be cross-coupled efficiently with moderate to good yields of desired products, cf. Tables 1 and 2. In addition, this transformation has been found compatible to various functional groups including chloro, bromo, nitro and carboxylate groups that generally advantageous for further functionalization.

Table 2. Direct C-H arylation of N-methylpyrrole (**HC1**) with different arylsulfonyl chlorides (**AS**) [a]



Entry	Ar [b]	Substrate [b]	Product [c]	Yield [d] (%)
1		**AS2**	**AH2**	83
2		**AS3**	**AH3**	64
3		**AS4**	**AH4**	72
4		**AS5**	**AH5**	67

5		**AS6**	**AH6**	82
6		**AS7**	**AH7**	86
7		**AS8**	**AH8**	89
8		**AS9**	**AH9**	78
9		**AS10**	**AH10**	69
10		**AS11**	**AH11**	67
11		**AS12**	**AH12**	70
12		**AS13**	**AH13**	73

---

[a] Unless stated otherwise all reactions were performed in a Schlenk tube with 1.0 equiv. of **HC1**, 1.0 equiv. of **AS**, 1.0 equiv. of Na_2CO_3 and 3 mol% of $[Ru(bpy)_3]Cl_2$ in dry CH_3CN under the irradiation of 5W blue LED lamp, hν = 425±15 nm at room temperature for 12 h.

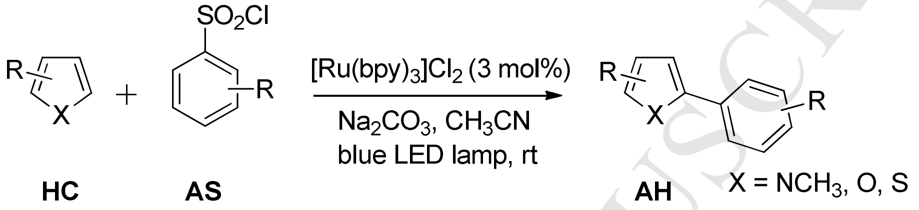
[b] Arylsulfonyl chlorides were distilled prior to use.[16]

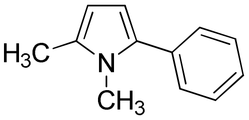
[c] All products were characterized by ^1H and ^{13}C NMR spectroscopy (Supporting Information) in comparison with known compounds from literature data.

[d] Isolated yield was calculated based on N-methylpyrrole.

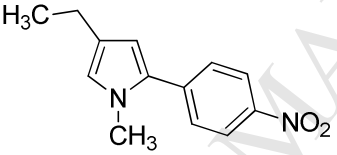
Next, we varied the substituents on the N-methylpyrrole. Moreover, the direct arylation of other readily available five membered heteroarenes such as furan, thiophene and their derivatives were also examined (Table 3). Unsurprisingly, the desired C-H arylated products were obtained in moderate to good yields (Table 3) regardless of the heterocyclic groups under the optimized reaction conditions (Table 1). In fact, this is not a common feature with aryl diazonium salts[8,9] a well-known coupling partner used in the synthesis of heterobiaryls under photocatalyzed and palladium mediated reactions.[12f] In general, the conventional transition metal-catalyzed direct desulfitative arylation reactions happen at elevated temperatures (110-150 °C) and afford diarylated products most often.[12] We also observed an unprecedented selectivity for the arylation, i.e., the C−H bond (C_2–H or C_5–H) next to the heteroatom was arylated with a high selectivity for all of the heteroarenes examined (Table 3). This regioselective arylation is a result of resonance stabilization of intermediate radical generated by coupling of the aryl radical with an electron-rich heterocycle, vide infra. Thus, the arylsulfonyl chlorides may be used as arylating reagents for the synthesis of 2-aryl N-methylpyrrole, furan, thiophene and their derivatives under visible-light photocatalyzed conditions.

Table 3. Direct C–H arylation of various five-membered heteroarenes with arylsulfonyl chlorides [a]

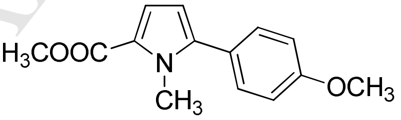




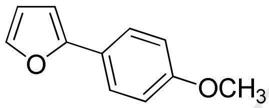
AH14 (76%)



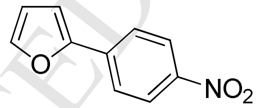
AH15 (79%)



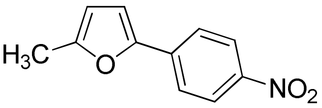
AH16 (56%)



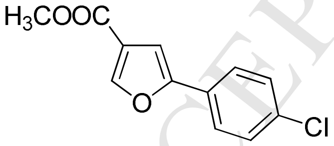
AH17 (69%)



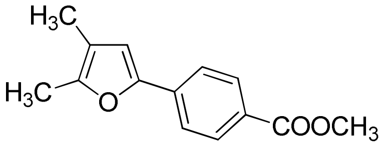
AH18 (74%)



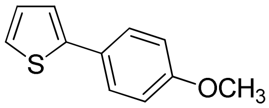
AH19 (69%)



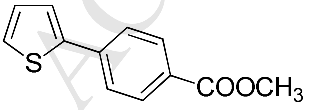
AH20 (52%)



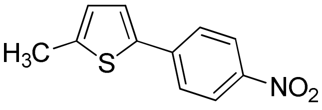
AH21 (72%)



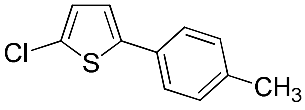
AH22 (78%)



AH23 (88%)



AH24 (73%)

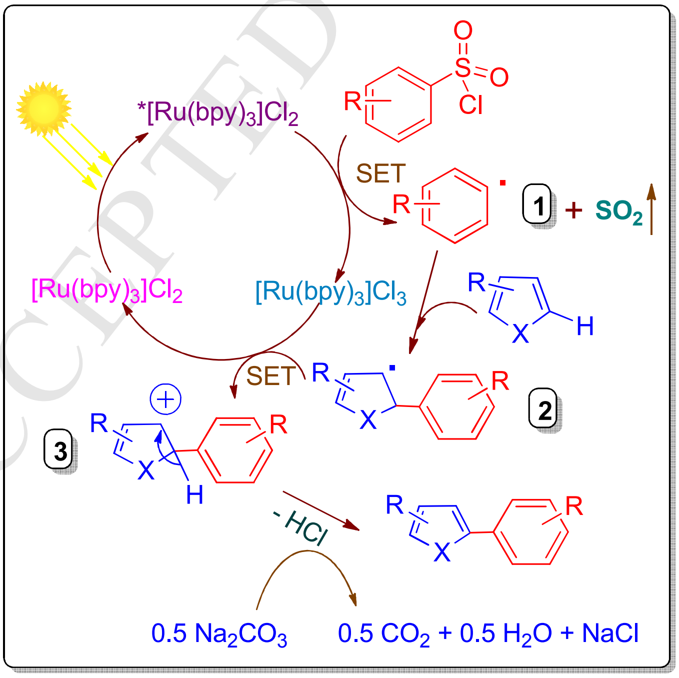


AH25 (61%)

---

[a] Unless stated otherwise all reactions were performed in a Schlenk tube with 1.0 equiv. of **HC**, 1.0 equiv. of **AS**, 1.0 equiv. of Na_2CO_3 and 3 mol% of $[Ru(bpy)_3]Cl_2$ in dry CH_3CN under the irradiation of 5W blue LED lamp, hν = 425±15 nm at room temperature for 12 h.

The C–H arylation reported here seems to proceed through a radical pathway.[11] Because the irradiation of *p*-tolylsulfonyl chloride in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, a radical trap) leads to **aryl-TEMPO** adduct in 26% yield (Supporting Information). Likewise, addition of TEMPO to the photocatalytic reaction of **AS1** with **HC1** suppressed the arylation process significantly (**AH1** was obtained only about 17% yield). On the basis of these results and literature reports,[1-7,9,14,15] a plausible mechanism for the arylation of five-membered heteroarenes has been proposed in Scheme 2. The irradiation of $[Ru(bpy)_3]Cl_2$ with a visible light promotes metal-to-ligand charge transfer generating a photoexcited $*[Ru(bpy)_3]Cl_2$. A single electron transfer from the excited $*[Ru(bpy)_3]Cl_2$ species to the arylsulfonyl chloride affords $[Ru(bpy)_3]Cl_3$ and the phenyl radical (**1**, Scheme 2) by extrusion of SO_2Cl.[14,15,18] The coupling of the phenyl radical with an electron-rich heterocycle to give a new radical intermediate (**2**) that subsequently transformed into a carbocation intermediate (**3**, Scheme 2) by oxidation by the $[Ru(bpy)_3]Cl_3$ (parent $[Ru(bpy)_3]Cl_2$ catalyst is regenerated). The unstable carbocation intermediate (**3**) then undergoes deprotonation to give the desired heterobiaryl and hydrogen chloride, cf. Scheme 2. The base (Na_2CO_3) employed in the reaction neutralizes the hydrogen chloride generated as a byproduct in the reaction.



Scheme 2. A plausible mechanism for the visible-light-induced desulfonylative coupling of arylsulfonyl chlorides with five-membered heteroarenes. SET, single electron transfer.

As mentioned at the outset, arylsulfonyl halides have several advantages over aryldiazonium salts in view of both economic and environmental standpoints. Moreover, heterobiaryls are highly important structural motifs frequently found in natural products, pharmaceuticals (Figure 1) and functional materials.[19] Thus, we believe that results reported here will find a bright future in industrial applications for the direct C–H arylation of heteroarenes to synthesize heterobiaryls and heteropolyaryls.

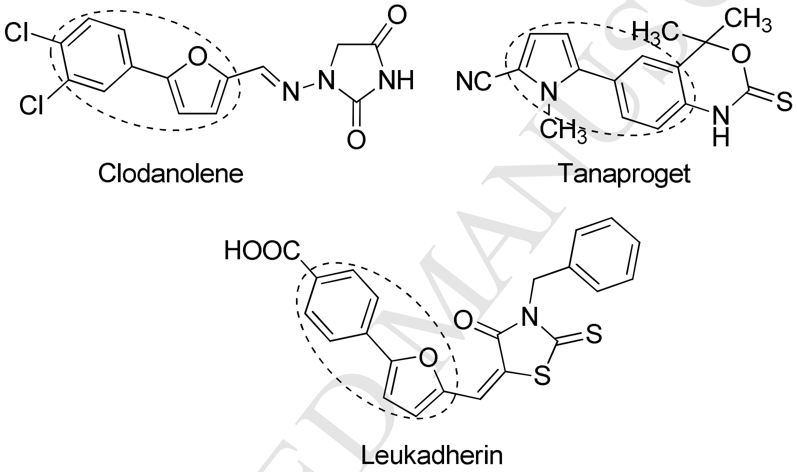


Figure 1. Few selected drug molecules containing heterobiaryl scaffold that is shown with a circle.

Conclusion

In summary, a visible-light photocatalyzed direct desulfitative arylation of electron-rich heteroarenes with arylsulfonyl chlorides is described. The method tolerates a variety of functional groups on the phenyl ring of sulfonyl chlorides as well as heteroarenes and gives the desired heterobiaryls in moderate to good yields at room temperature. Further work is in progress to broaden the scope of this transformation to synthesize natural products and pharmaceuticals.

Acknowledgments

Financial support from the Department of Science & Technology (DST), India through INSPIRE Faculty Fellowship [IFA12-CH-62] is gratefully acknowledged. Also, we thank anonymous reviewers for their insightful comments and suggestions.

Supplementary data

Supplementary data (general aspects, experimental characterization data for products and copies of ^{1}H and ^{13}C NMR spectra for selected products) associated with this article can be found, in the online version, at doi:00.0000/j.tet.00.

References and notes

(1) (a) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, 322, 77; (b) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2011**, 50, 6119.

(2) (a) Dai, C.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2011**, 3, 140; (b) Furst, L.; Narayanam, J. M. R.; Stephenson, C. R. J. *Angew. Chem., Int. Ed.* **2011**, 50, 9655.

(3) (a) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, 130, 12886; (b) Yoon, T. P.; Ischay, M. A.; Du, J. N. *Nat. Chem.* **2010**, 2, 527; (c) Du, J.; Espelt, L. R.; Guzei, I. A.; Yoon, T. P. *Chem. Sci.* **2011**, 2, 2115; (d) Hurtley, A. E.; Cismesia, M. A.; Ischay, M. A.; Yoon, T. P. *Tetrahedron* **2011**, 67, 4442; (e) Schultz, D. M.; Yoon, T. P. *Science* **2014**, 343, 6174.

(4) (a) Maji, T.; Karmakar, A.; Reiser, O. *J. Org. Chem.* **2011**, 76, 736; (b) Rueping, M.; Leonori, D.; Poisson, T. *Chem. Commun.* **2011**, 47, 9615; (c) Rueping, M.; Vila, C.; Koenigs, R. M.; Poscharny, K.; Fabry, D. C. *Chem. Commun.* **2011**, 47, 2360; (d) Rueping, M.; Zhu, S.; Koenigs, R. M. *Chem. Commun.* **2011**, 47, 8679; (e) Su, Y. J.; Zhang, L. R.; Jiao, N. *Org. Lett.* **2011**, 13, 2168; (f) Xie, Z.; Wang, C.; deKrafft, K. E.; Lin, W. *J. Am. Chem. Soc.* **2011**, 133, 2056; (g) Xuan, J.; Cheng, Y.; An, J.; Lu, L.-Q.; Zhang, X.-X.; Xiao, W.-J. *Chem. Commun.* **2011**, 47, 8337; (h) Zhu, M.; Zheng, N. *Synthesis* **2011**, 2223; (i) Zou, Y.-Q.; Lu, L.-Q.; Fu, L.; Chang, N.-J.; Rong, J.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2011**, 50, 7171.

(5) (a) Zeitler, K. *Angew. Chem., Int. Ed.* **2009**, 48, 9785; (b) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* **2011**, 40, 102.

(6) Shi, L.; Xia, W. *Chem. Soc. Rev.* **2012**, 41, 7687.

(7) (a) Xuan, J.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2012**, 51, 6828; (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013,** 113, 5322; (c) Zou, Y. Q.; Chen, J. R.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2013**, 52, 11701.

(8) (a) Maity, P.; Kundu, D.; Ranu, B. C. *Eur. J. Org.* **2015**, 1727; (b) Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, 322, 77; (c) Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, 131, 10875; (d) Shih, H.-W.; Wal, M. N. V.; Grange, R. L.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010,** 132, 13600; (e) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2011,** 50, 6119; (f) Du, J.; Espelt, L. R.; Guzei, I. A.; Yoon, T. P. *Chem. Sci.* **2011**, 2, 2115; (g)

Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc*. **2008**, 130, 12886; (h) Ischay, M. A.; Lu, Z.; Yoon, T. P. *J. Am. Chem. Soc*. **2010,** 132, 8572; (i) Lu, Z.; Shen, M.; Yoon, T. P. *J. Am. Chem. Soc.* **2011**, 133, 1162; (j) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem*. **2010**, 2, 527; (k) Furst, L.; Matsuura, B. S.; Narayanam, J. M. R.; Tucker, J. W.; Stephenson, C. R. J. *Org. Lett*. **2010**, 12, 3104; (l) Narayanam, J. M. R.; Stephenson, C. R. *J. Chem. Soc. Rev*. **2011**, 40, 102; (m) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc*. **2011**, 133, 4160; (n) Hari, D. P.; Koenig, B. *Org. Lett***. 2011**, 13, 3852; (o) Neumann, M.; Fueldner, S.; Koenig, B.; Zeitler, K. *Angew. Chem., Int. Ed.* **2011,** 50, 951; (p) Larraufie, M.-H.; Pellet, R.; Fensterbank, L.; Goddard, J.-P.; Lacôte, E.; Malacria, M.; Ollivier, C. *Angew. Chem., Int. Ed*. **2011**, 50, 4463; (q) McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* **2011**, 334, 1114; (r) Rueping, M.; Leonori, D.; Poisson, T. *Chem. Commun*. **2011**, 47, 9615; (s) Zou, Y.-Q.; Lu, L.-Q.; Fu, L.; Chang, N.-J.; Rong, J.; Chen, J.-R.; Xiao, W.-J. *Angew. Chem., Int. Ed*. 2011, 50, 7171; (t) Mo, F.; Dong, G.; Zhang, Y.; Wang, *J. Org. Biomol. Chem*. **2013**, *11*, 1582; (u) Majek, M.; Filace, F.; Jacobi von Wangelin, A. *Beilstein J. Org. Chem.* **2014**, *10*, 981; (v) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18566.

(9) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, 134, 2958.

(10) (a) Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds*, 3rd ed.; Edward Arnold: London, 1985; (b) Murphy, A. R.; Frechet, J. M. *J.΄ Chem. Rev*. **2007**, 107, 1066; (c) Anthony, J. E. *Chem. Rev*. **2006**, 106, 5028.

(11) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 5th ed.; A. Bacon, Boston, MA, 1987.

(12) (a) Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *Tetrahedron Lett*. **1989**, *30*, 975; (b) Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 8, 2207; (c) Miura, M.; Itoh, K.; Nomura, M. *Chem. Lett*. **1989**, 77; (d) Miura, M.; Hashimoto, H.; Itoh, K.; Nomura, M. *Chem. Lett.* **1990**, 459; (e) Dubbaka, S. R.; Vogel, P. *Org. Lett.* **2004**, 6, 95; (f) Jin, R.; Yuan, K.; Chatelain, E.; Soule, J.-F.; Doucet, H. *Adv. Synth. Catal*. **2014**, *356*, 3831.

(13) (a) Gu, L.; Jin, C.; Liu, J.; Ding, H.; Fan, B. *Chem. Commun.* **2014**, 50, 4643; (b) Cao, M.-Y.; Ren, X.; Lu, Z. *Tetrahedron Lett.* **2015**, *56*, 3732.

(14) Xia, J.-D.; Deng, G.-B.; Zhou, M.-B.; Liu, W.; Xie, P.; Li, J.-H. *Synlett* **2012**, *23*, 2707.

(15) Deng, G.-B.; Wang, Z.-Q.; Xia, J.-D.; Qian, P.-C.; Song, R.-J.; Hu, M.; Gong, L.-B.; Li, J.-H. *Angew. Chem., Int. Ed.* **2013**, *52*, 1535.

(16) **General procedure for the synthesis of heterobiaryls**: To an oven-dried Schlenk tube equipped with a magnetic stir bar was charged with tris(2,2′-bipyridyl)ruthenium(II) chloride (3 mol%), arenesulfonyl chloride (1.0 equiv.), heteroarene (1.0 equiv.), Na_2CO_3 (1.0 equiv.) and dry acetonitrile. The mixture was degassed by the freezepump-thaw procedure, and then the Schlenk tube was irradiated under a 3W Blue LED bulb at a distance of 5 cm. After stirring at 25 °C for 12 h, the solvent was removed under reduced pressure and the residue was then diluted with water. The aqueous solution was extracted (3 times) with ethyl acetate. The combined organic phases were dried over Na_2SO_4 and filtered. The filtrate was evaporated under reduced pressure to get the crude product, which was purified by column chromatography using hexane-ethyl acetate mixtures. The identity and purity of the product was confirmed by ^{1}H and ^{13}C NMR spectroscopy, cf. Supporting Information.

(17) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth-Heinemann, Oxford, 2009.

(18) (a) Nagib, D. A.; Macmillan, D. W. C. *Nature* **2011**, 480, 224. (b) Houmam, A.; Hamed, E. M. *Phys. Chem. Chem. Pyhs.* **2012**, 14, 113.

(19) (a) Murphy, A. R.; Frechet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066; (b) Anthony, J. E. *Chem. Rev.* **2006**, 106, 5028; (c) Hassan, J.; Sevignon, M.; Gozzi, C.; Schulz, E.;′ Lemaire, M. *Chem. Rev.* **2002**, 102, 1359; (d) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. *Chem. Rev.* **2012**, 112, 2208.