

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Visible-light-induced photocatalytic azotrifluoromethylation of alkenes with aryldiazonium salts and sodium triflinate

Received 00th April 20xx,
Accepted 00th May 20xx

Xing-Long Yu,^a Jia-Rong Chen,^{*a} Dong-Zhen Chen,^a and Wen-Jing Xiao^{*a,b}

DOI: 10.1039/x0xx00000x

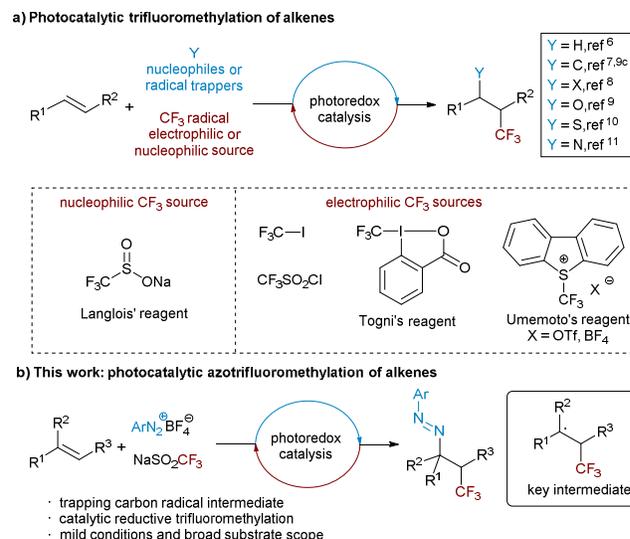
www.rsc.org/

An efficient visible light photocatalytic azotrifluoromethylation of alkenes with aryldiazonium salts and sodium triflinate is described, which gave the corresponding trifluoromethylated azo compounds in generally good yields. The trifluoromethylated azo products can be easily transformed into useful heterocycles and nitrogen-containing building blocks.

Alkenes are a class of easily accessible feedstock and privileged chemicals because of the diverse range of functionalizations that can occur at the carbon-carbon double bonds. Over the several past decades, the vicinal difunctionalization of alkenes has been established as one of the most versatile approaches to functional diversification of hydrocarbons by simultaneous formation of two C-C or C-X (X = heteroatom or halogen) bonds.¹ In this context, a plethora of efficient methods have been developed for addition of the CF₃ group to an alkene moiety with concomitant incorporation of additional functional groups due to the unique advantageous biological effects of the CF₃ moiety on the parent molecules.^{2,3} Despite the predominance of transition metal catalysis in this area, the development of more efficient and general catalytic variants for trifluoromethylation of alkenes under mild conditions is still a research topic of great interest.

In recent years, with the development of visible light photocatalysis,⁴ extensive research efforts have been directed to the field of visible light photocatalytic olefin difunctionalization reactions.⁵ In particular, employing this strategy, a wide variety of three-component olefin trifluoromethylation reactions with concomitant formation of C-H,⁶ C-C,^{7,9c} C-X,⁸ C-O,⁹ C-S,¹⁰ and C-N^{9c,11} bonds have also been successfully realized using various CF₃ reagents, providing a facile access to various synthetically useful

and biologically important CF₃-containing frameworks (Scheme 1a). In most of these reactions, the photocatalytic single-electron transfer (SET)-mediated conversion of various electrophilic CF₃ reagents into highly reactive CF₃ radical and trap of the resultant β-CF₃-substituted carbocations by diverse nucleophiles have been postulated to be involved as the key steps.



Scheme 1 Photocatalytic trifluoromethylation of alkenes and reaction design.

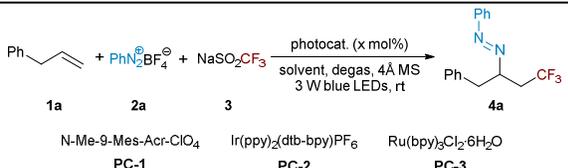
In contrast, the commercially available, inexpensive, and shelf-stable sodium trifluoromethanesulfinate salt (CF₃SO₂Na, Langlois' reagent)¹² has rarely been used in catalytic reductive trifluoromethylation of olefins, especially by visible light photocatalysis.^{6b-d} In connection with our ongoing project on visible light induced photocatalytic heterocycle synthesis,¹³ we recently started a program aimed at CF₃ radical-mediated functionalization of carbon-carbon multiple bonds.¹⁴ Surprisingly, we found that the aryldiazonium salts could trap the C-centered radical intermediate instead of serving as the source of aryl radicals.¹⁵ Herein, we describe a new and general visible light induced photocatalytic

^aCCNU-uOttawa Joint Research Centre, Key Laboratory of Pesticide & Chemical Biology, Ministry of Education; College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China. E-mail: chenjiarong@mail.ccnu.edu.cn.; wxiao@mail.ccnu.edu.cn Fax: +86 27 67862041; Tel: +86 27 67862041.

^bState Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

† Electronic Supplementary Information (ESI) available: Experimental procedures and compound characterization data. For ESI and other electronic format, see DOI: 10.1039/x0xx00000x

three-component azotrifluoromethylation of alkenes with aryldiazonium salts and sodium triflate (Scheme 1b). Notably, the resulting azo products are also useful building blocks in the context of heterocyclic synthesis, such as tetrahydropyridazines, cinnolines, 1,2,4-triazoles, and pyridazinones.¹⁶ Recently, the group of Antonchick reported an elegant Ag(I)-catalyzed cascade multicomponent reaction of alkenes, diazonium salts, and sodium triflate using stoichiometric H₂O₂, providing an efficient entry to various indoles and other nitrogen heterocycles.^{17c} Thus, our mild method constitutes the first example of visible light photocatalytic azotrifluoromethylation of olefins without stoichiometric oxidants.¹⁷

Table 1 Condition Optimization^a


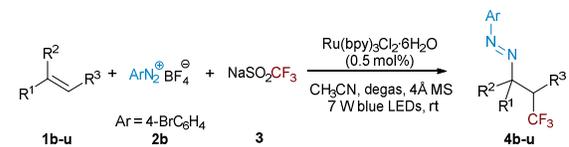
Entry	Solvent (conc.)	1a/3	PC (x)	Yield ^b (%)
1	MeOH (0.1 M)	1/2	PC-1 (2)	20
2	DMF (0.1 M)	1/2	PC-1 (2)	11
3	DCM (0.1 M)	1/2	PC-1 (2)	20
4	MeCN (0.1 M)	1/2	PC-1 (2)	29
5	MeCN (0.04 M)	1/2	PC-1 (2)	38
6	MeCN (0.04 M)	1/2	PC-2 (2)	46
7	MeCN (0.04 M)	1/2	PC-3 (2)	57
8	MeCN (0.04 M)	1/2	PC-3 (0.5)	56
9	MeCN (0.04 M)	1/1	PC-3 (0.5)	55
10 ^c	MeCN (0.1 M)	1/1	PC-3 (0.5)	56
11 ^c	MeCN (0.1 M)	1.5/1	PC-3 (0.5)	66
12 ^c	MeCN (0.1 M)	1.5/1	-	11
13 ^d	MeCN (0.1 M)	1.5/1	PC-3 (0.5)	12

^aUnless otherwise noted, reactions were performed on 0.3 mmol scale of **1a** or **3**, and **2a** (0.6 mmol), photocatalyst (x mol %), 4 Å MS (30 mg/mL) in 3.0 mL or 7.5 mL of solvent at rt under irradiation by 3 W blue LEDs for 4 h.

^bIsolated yield. ^cUnder irradiation by 7 W blue LEDs for 0.5 h. ^dWithout visible light irradiation.

Initially, we chose allylbenzene **1a**, phenyldiazonium tetrafluoroborate **2a**, and CF₃SO₂Na (Langlois' reagent) as the model substrates for the visible light photoredox-catalyzed three-component azotrifluoromethylation and representative results are summarized in Table 1.¹⁸ Employing 2 mol% of the organic dye photosensitizer, N-Me-9-Mes-Acr-ClO₄, as the photocatalyst under irradiation by 3 W blue LEDs, the reaction did indeed proceed to give the expected product **4a** in 20 % yield (entry 1). Encouraged by this result, we then continued to optimize conditions to improve the yield. A simple screen of reaction media showed that MeCN gave rise to superior result than other commonly used solvents (entries 2-4). A slightly diluted reaction mixture resulted in a slight increase of the yield (entry 5). Then, we examined several other photocatalysts with different redox potentials, and identified

Ru(bpy)₃Cl₂·6H₂O (**PC-3**) as the best candidate with **4a** being obtained in a yield of 57% (entry 7). With only 0.5 mol% catalyst loading, product **4a** was still obtained in similar yields with the ratio of **1a** to **3** being 1/2 or 1/1 (entries 8 and 9). Remarkably, under irradiation of 7 W blue LEDs, the reaction proceeded to complete conversion in only 30 min and furnished a 66% yield of **4a** with 1.5/1 molar ratio of **1a** to **3** (entry 11). Control experiments clearly confirmed that both photocatalyst and visible light irradiation are critical for this process (entries 12 and 13).

Table 2 Scope of Unactivated Alkenes^{a,b}


4b , n = 1, 78%	4d , R = OAc, 81%	4f , 69%	4g , R = OAc, 54%
4c , n = 2, 74%	4e , R = OMe, 86%		4h , R = TMS, 34%
4i , n = 3, 79%	4j , n = 4, 72%	4k , n = 4, 91%	4l , n = 3, 90%
4m , n = 8, 92%	4n , n = 2, 78%	4p , 71%	4q , 76%
4o , n = 4, 82%			4v , 62%
4r , 70%, 1.8:1 d.r. ^c	4s , n = 1, 74%, 4:1 d.r. ^c		
	4t , n = 2, 67%, 18:1 d.r. ^c		
	4u , n = 3, 72%, >19:1 d.r. ^c		

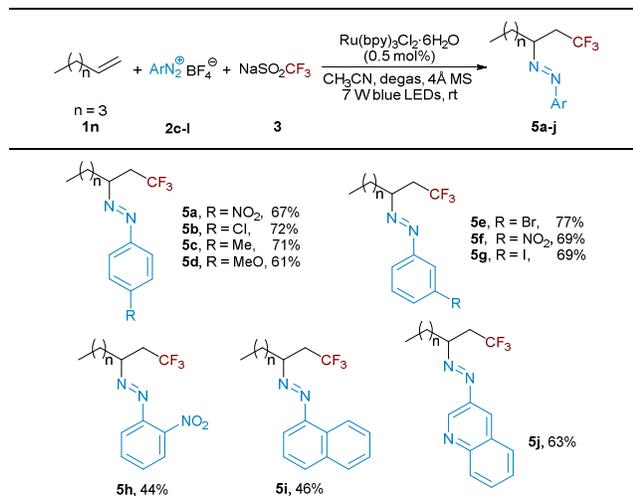
x-ray crystal structure of **4v**

^aReactions were performed with **1** (0.45 mmol), **2b** (0.60 mmol), **3** (0.30 mmol), Ru(bpy)₃Cl₂·6H₂O (0.50 mol%), 4 Å MS (30 mg/mL) in MeCN (3.0 mL) at rt under irradiation by 7 W blue LEDs for 40 min. ^bIsolated yield. ^cDiastereomeric ratio was determined by ¹⁹F NMR analysis of the crude mixture.

Under the optimized reaction conditions, the reaction with 4-bromophenyldiazonium salt **2b** also proceeded smoothly to give the corresponding product **4b** in 78% yield (Table 2). Thus, a range of other substituted unactivated terminal alkenes were then evaluated to explore the substrate scope. As for the aryl group at the alkyl terminus, a series of electron-withdrawing or -donating groups could be well tolerated at the phenyl ring to give the products **4c-f** in 69-84% yields. Alkenes **1g-m** bearing various functional groups, such as ester, TMS, phenyl ether and hydroxy, could be readily tolerated in this reaction, yielding the products **4g-m** in moderate to excellent yields. Alkenes **1n-p** with a linear

aliphatic or carbocyclic moiety also proved to be suitable for this reaction, with the products **4n-p** being formed in 71-82% yields. The reaction with 1,1-disubstituted alkene **1q** also worked well to regioselectively give the desired product **4q** in 76% yield. Linear (**1r**) and cyclic (**1s-u**) internal alkenes also participated in the reaction very well to produce the corresponding azo compounds **4r-u** in good yields, albeit with variable diastereoselectivities which might be resulted by the different stability of the related C-centred radicals.¹⁹ In addition to **2b**, the reaction with alkene **1a**, CF₃SO₂Na and 4-nitrophenyldiazonium salt **2c** also gave product **4v** in 62% yield, which was confirmed by X-ray crystallography analysis.²⁰

Table 3 Scope of Aryldiazonium Salts^{a,b}

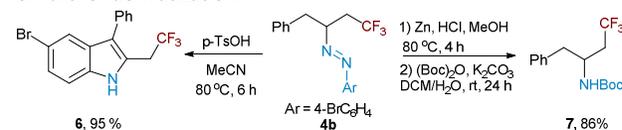


^aReactions were carried out with **1n** (0.45 mmol), **2** (0.60 mmol), **3** (0.30 mmol), Ru(bpy)₃Cl₂·6H₂O (0.50 mol %), 4 Å MS (30 mg/mL) in MeCN (3.0 mL) at rt under irradiation by 7 W blue LEDs for 40 min.
^bIsolated yield.

Encouraged by these results, we further explored the scope of this method by evaluating a range of diazonium salts **2c-l** together with **1n** and CF₃SO₂Na under the standard conditions (Table 3). It was found that aryldiazonium salts **2c-l** bearing electron-withdrawing or -donating groups at the para-, meta-, or ortho-positions were all well tolerated, affording the corresponding products **5a-h** in moderate to good yields. Moreover, the reactions with 1-phthyldiazonium salt **2j** and heteroaryldiazonium salt **2k** also proceeded smoothly to give the expected products **5i** and **5j** in 46% and 63% yields, respectively. Noted that prolonging the reaction time led to an obvious decrease of yield due to the conversion of the (*E*)-products into their (*Z*)-isomers and decomposition in part.¹⁸

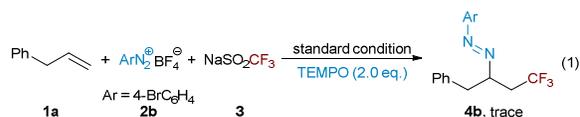
The broad scope and high functional group tolerance of the current protocol allows further transformation of our products into other useful building blocks. For example, by employing the strategy of Fischer indole synthesis, azo compound **4b** could be conveniently transformed into the corresponding trifluoromethylated indole **6** in 95% yield through a sequential isomerization and cyclization cascade under acidic conditions (Scheme 2). Moreover, a two-step sequence involving reductive cleavage of the N=N bond of azo compound **4b** by Zn/HCl and subsequent amine-protection provided useful CF₃-containing amine **7** in 86% yield. These transformations highlight the versatility of the

azo compounds and provide an approach to molecules with handles for further derivatization.

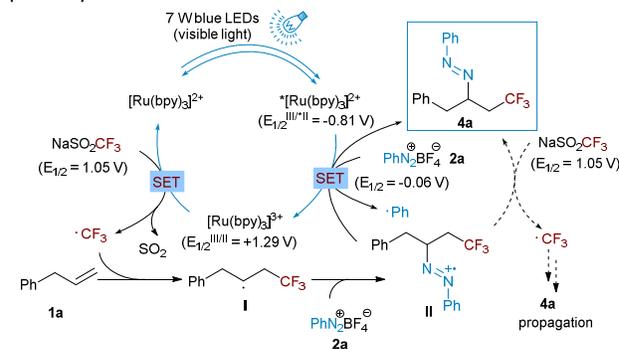


Scheme 2 Derivatization of the azo compound **4b**.

Preliminary mechanistic studies with alkene **1a**, 4-bromophenyldiazonium salt **2b** and CF₃SO₂Na were also carried out to gain insight into the reaction pathway (Eq. 1). In the presence of stoichiometric radical trap reagent, TEMPO, the reaction was completely suppressed under the standard conditions; this observation suggests that the reaction may involve a radical process.¹⁸



Although further studies are still required to clarify the precise mechanism of the reaction, we proposed a possible photocatalytic cycle based on known literature^{5,17} and our previous works¹⁴ (Scheme 3). First, photoexcitation of photocatalyst [Ru(bpy)₃]²⁺ by visible light irradiation generates the excited state *[Ru(bpy)₃]²⁺ species. This species can be converted into the oxidizing photocatalyst [Ru(bpy)₃]³⁺ upon SET oxidation by the phenyldiazonium salt **2a**.¹⁵ This species serves as a strong oxidant (E_{1/2}^{III/II} = +1.29 V) to oxidize Langlois' reagent (E_{1/2} = 1.05 V vs. SCE),²¹ giving the electrophilic CF₃ radical upon expulsion of SO₂ and returning the photocatalyst to the ground state. Subsequently, the CF₃ radical undergoes a radical addition to the alkene **1a** to generate the radical intermediate **I**, which could be easily trapped by the aryldiazonium salt **2a** to give the radical cation **II**.¹⁷ Another SET reduction of the intermediate **II** by the reducing *[Ru(bpy)₃]²⁺ species gives rise to the final product **4a**. At the current stage, we cannot rule out an alternative pathway involving SET reduction of cation radical **II** by NaSO₂CF₃ to give **4a** and CF₃ radical, which might initiate radical chain propagation. A light on-off experiment confirmed that the present process requires continuous irradiation of visible light, indicating the photoredox cycle as the main pathway.¹⁸



Scheme 3 Proposed catalytic cycle.

In summary, we have developed a new and efficient photoredox-catalyzed azotrifluoromethylation of alkenes with aryldiazonium salts and sodium triflinate. The mild catalytic system shows broad substrate scope and high functional group tolerance with respect to both unactivated alkenes and aryldiazonium salts, enabling facile synthesis of various useful azo compounds with generally good yields. Further application of this method to the late-stage difunctionalization of bioactive compounds containing an alkene moiety is currently underway in our laboratory.

We are grateful to the NSFC (No. 21472058, 21272087, and 21472057), the Youth Chen-Guang Project of Wuhan (No. 2015070404010180) and the self-determined research funds of CCNU (No. CCNU15A02009) for support of this research.

Notes and references

- For selected reviews on olefin difunctionalization, see: (a) R. I. McDonald, G. S. Liu and S. S. Stahl, *Chem. Rev.*, 2011, **111**, 2981; (b) S. R. Chemler and M. T. Bovino, *ACS Catal.*, 2013, **3**, 1076; (c) Y. Shimizu and M. Kanai, *Tetrahedron Lett.*, 2014, **55**, 3727; (d) R. M. Romero, T. H. Woste and K. Muniz, *Chem. Asian J.*, 2014, **9**, 972; (e) E. Bernoud, C. Lepori, M. Mellah, E. Schulz and J. Hannedouche, *Catal. Sci. Technol.*, 2015, **5**, 2017; (f) J.-R. Chen, X.-Y. Yu and W.-J. Xiao, *Synthesis*, 2015, **47**, 604; (g) L. Huang, M. Arndt, K. Gooßen, H. Heydt and L. J. Gooßen, *Chem. Rev.*, 2015, **115**, 2596; (h) S. Tang, K. Liu, C. Liu and A. Lei, *Chem. Soc. Rev.*, 2015, **44**, 1070.
- (a) P. Kirsch, *Modern Fluoroorganic Chemistry*; Wiley-VCH: Weinheim, 2004; (b) Fluorine in Medicinal Chemistry and Chemical Biology; I. Ojima, Ed.; J. Wiley & Sons: Chichester, U.K., 2009; (c) K. Müller, C. Faeh and F. Diederich, *Science*, 2007, **317**, 1881; (d) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320; (e) J. Wang, M. Sanchez-Rosello, J. L. Acena, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2014, **114**, 2432.
- For selected reviews on trifluoromethylation, see: (a) J. A. Ma and D. Cahard, *Chem. Rev.*, 2004, **104**, 6119; (b) A. Studer, *Angew. Chem. Int. Ed.*, 2012, **51**, 8950; (c) T. Liang, C. N. Neumann and T. Ritter, *Angew. Chem. Int. Ed.*, 2013, **52**, 8214; (d) H. Egami and M. Sodeoka, *Angew. Chem. Int. Ed.*, 2014, **53**, 8294; (e) E. Merino and C. Nevado, *Chem. Soc. Rev.*, 2014, **43**, 6598; (f) X. Liu, C. Xu, M. Wang and Q. Liu, *Chem. Rev.*, 2015, **115**, 683; (g) X. Yang, T. Wu, R. J. Phipps and F. D. Toste, *Chem. Rev.*, 2015, **115**, 826; (h) J. Charpentier, N. Früh and A. Togni, *Chem. Rev.*, 2015, **115**, 650; (i) C. Ni, M. Hu and J. Hu, *Chem. Rev.*, 2015, **115**, 765; (j) C. Alonso, E. Martínez de Marigorta, G. Rubiales and F. Palacios, *Chem. Rev.*, 2015, **115**, 1847.
- For selected recent reviews on visible light photocatalysis, see: (a) J. Xuan and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2012, **51**, 6828. (b) C. K. Prier, D. A. Rankic and D. W. Macmillan, *Chem. Rev.*, 2013, **113**, 5322; (c) D. M. Schultz and T. P. Yoon, *Science* 2014, **343**, 985; (d) R. Brimiouille, D. Lenhart, M. M. Maturi and T. Bach, *Angew. Chem. Int. Ed.*, 2015, **54**, 3872; (e) J. Xuan, Z.-G. Zhang and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2015, **54**, 15632; (f) F. Tan and W.-J. Xiao, *Acta Chim. Sinica*, 2015, **73**, 85; (g) J.-R. Chen, X.-Q. Hu, L.-Q. Lu and W.-J. Xiao, *Chem. Soc. Rev.*, 2016, **45**, 2044.
- (a) T.-T. Zeng, J. Xuan, J.-R. Chen, L.-Q. Lu and W.-J. Xiao, *Imag. Sci. Photochem.*, 2014, **32**, 415. (b) T. Koike and M. Akita, *Top. Catal.*, 2014, **57**, 967; (c) M.-Y. Cao, X. Ren and Z. Lu, *Tetrahedron Lett.*, 2015, **56**, 3732.
- (a) S. Mizuta, S. Verhoog, K. M. Engle, T. Khotavivattana, M. O'Duill, K. Wheelhouse, G. Rassias, M. Médebielle and V. Gouverneur, *J. Am. Chem. Soc.*, 2013, **135**, 2505; (b) D. J. Wilger, N. J. Gesmundo and D. A. Nicewicz, *Chem. Sci.*, 2013, **4**, 3160; (c) S. P. Pitre, C. D. McTiernan, H. Ismaili and J. C. Scaiano, *ACS Catal.*, 2014, **4**, 2530; (d) Q. Lefebvre, N. Hoffmann and M. Rueping, *Chem. Commun.*, 2016, **52**, 2493. (e) L. Zhu, L.-S. Wang, B. Li, B. Fu, C. P. Zhang and W. Li, *Chem. Commun.*, 2016, doi: 10.1039/c6cc01944g.
- A. Carboni, G. Dagousset, E. Magnier and G. Masson, *Chem. Commun.*, 2014, **50**, 14197.
- (a) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2011, **133**, 4160; (b) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875; (c) S. H. Oh, Y. R. Malpani, N. Ha, Y.-S. Jung and S. B. Han, *Org. Lett.*, 2014, **16**, 1310.
- (a) Y. Yasu, T. Koike and M. Akita, *Angew. Chem. Int. Ed.*, 2012, **51**, 9567; (b) R. Tomita, Y. Yasu, T. Koike and M. Akita, *Angew. Chem. Int. Ed.*, 2014, **53**, 7144; (c) A. Carboni, G. Dagousset, E. Magnier and G. Masson, *Org. Lett.*, 2014, **16**, 1240.
- D. B. Bagal, G. Kachkovskiy, M. Knorn, T. Rawner, B. M. Bhanage and O. Reiser, *Angew. Chem. Int. Ed.*, 2015, **54**, 6999.
- (a) Y. Yasu, T. Koike and M. Akita, *Org. Lett.*, 2013, **15**, 2136; (b) G. Dagousset, A. Carboni, E. Magnier and G. Masson, *Org. Lett.*, 2014, **16**, 4340.
- C. Zhang, *Adv. Synth. Catal.*, 2014, **356**, 2895.
- For selected examples, see: (a) J. Xuan, X.-D. Xia, T.-T. Zeng, Z.-J. Feng, J.-R. Chen, L.-Q. Lu and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2014, **53**, 5653; (b) X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2014, **53**, 12163; (c) X.-Q. Hu, X. Qi, J.-R. Chen, Q.-Q. Zhao, Q. Wei, Y. Lan and W.-J. Xiao, *Nat. Commun.*, 2016, 7:11188, doi: 10.1038/ncomms11188.
- (a) Q.-H. Deng, J.-R. Chen, Q. Wei, Q.-Q. Zhao, L.-Q. Lu and W.-J. Xiao, *Chem. Commun.*, 2015, **51**, 3537; (b) Q. Wei, J.-R. Chen, X.-Q. Hu, X.-C. Yang, B. Lu and W.-J. Xiao, *Org. Lett.*, 2015, **17**, 4464.
- For selected reviews on the chemistry of aryldiazonium salts, see: (a) M. R. Heinrich, *Chem. Eur. J.*, 2009, **15**, 820; (b) D. P. Hari and B. König, *Angew. Chem. Int. Ed.*, 2013, **52**, 4734; (c) F. Y. Mo, G. B. Dong, Y. Zhang and J. B. Wang, *Org. Biomol. Chem.*, 2013, **11**, 1582.
- (a) M. Kawasaki and H. Yamamoto, *J. Am. Chem. Soc.*, 2006, **128**, 16482; (b) D. Zhao, Q. Wu, X. Huang, F. Song, T. Lv and J. You, *Chem. Eur. J.*, 2013, **19**, 6239; (c) S. K. Fehler, G. Pratsch and M. R. Heinrich, *Angew. Chem. Int. Ed.*, 2014, **53**, 11361; (d) R. Lasch and M. R. Heinrich, *Tetrahedron*, 2015, **71**, 4282.
- (a) A. Citterio, F. Minisci, A. Albinati and S. Bruckner, *Tetrahedron Lett.*, 1980, **21**, 2909; (b) M. R. Heinrich, O. Blank and S. Wölfel, *Org. Lett.*, 2006, **8**, 3323; (c) K. Matcha and A. P. Antonchick, *Angew. Chem. Int. Ed.*, 2014, **53**, 11960; (d) S. Kindt, K. Wicht and M. R. Heinrich, *Org. Lett.*, 2015, **17**, 6122.
- Please see the ESI for more details.
- Radical clock experiments with vinylcyclopropane derivatives only gave complex mixtures. Attempts for the separation met failure. See the ESI for details.
- CCDC 1470637 (**4v**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/daa_request/cif.
- P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson and J.-M. Savéant, *J. Am. Chem. Soc.*, 1997, **119**, 201.