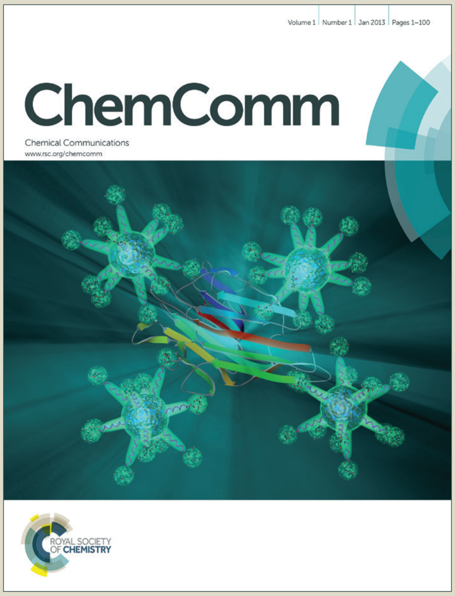
View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. K. Patel, M. Ganesh, S. Guin, S. K. Rout and A. Behera, *Chem. Commun.*, 2014, DOI: 10.1039/C4CC05050A.



www.rsc.org/chemcomm

View Article Online
DOI: 10.1039/C4CC05050A

Journal Name

RSCPublishing

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Cyclic ethers to esters and monoesters to *bis*-esters with unconventional coupling partners under metal free conditions via sp^3 C–H functionalisation

Received 00th January 2012,
Accepted 00th January 2012

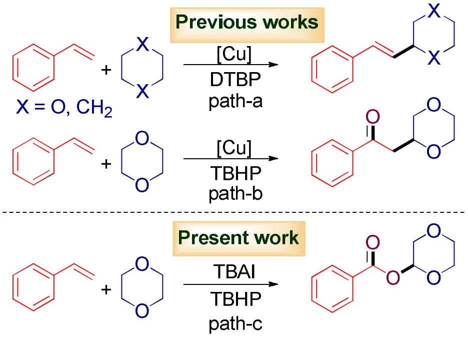
DOI: 10.1039/x0xx00000x

www.rsc.org/

Ganesh Majji, Srimanta Guin, Saroj K. Rout, Ahalya Behera and Bhisma K. Patel*

An efficient metal free oxidative esterification of sp^3 C–H bonds (adjacent to an oxygen atom) in simple solvents like 1,4-dioxane, tetarhydropyran, tetrahydrofuran and ethyl acetate has been achieved using terminal aryl alkenes and alkynes as ArCOO– sources.

Organic chemists continue to strive towards the development of atom and step economic process for the synthesis of complex molecular structures from simple precursors. What a better way than to manipulate the ubiquitous C–H bonds to achieve this?[1] In this regard, the cross dehydrogenative coupling (CDC) has played a pivotal role in bringing about transformation of C–H bonds of all types to C–C and C–heteroatom bonds.[2] In fact, the CDC has mostly been directed towards C–C bond formation as it provides the requisite connectivity to build larger and complex structures.[2a,2b,2g] One of the extensively studied approaches in this forum is the substrate directed alkenylations using Rh, Ru and Pd catalysts.[1h,3] However, scrutiny entails that most of these transformations are for sp^2 C–H bonds facilitated by a multitude of directing groups.[4] In contrast, due to their intrinsic low reactivity (high p*K*a and bond energy) similar alkenylation at sp^3 C–H bonds remain virtually unexplored. The recently developed radically induced vinylation of sp^3 C–H bonds of cyclic ethers and cycloalkanes using copper catalyst are the only two reports till date (Scheme 1, path-a).[5] The current trend in organic synthesis is to use and encourage metal-free catalysts such as iodine, iodide salts and organoammonium iodides, which are often appropriate substitutes to transition metals.[2e,2f,6] These metal free catalysts (in combination with oxidant) either complement or show similar reactivity to that of transition metals in bringing about requisite transformations. In addition, their use is highly advantageous from the enviroeconomic point of view for sustainable future. In order to achieve the same, we attempted similar alkenylation of cyclic ethers under metal free conditions.



Scheme 1 Differential reactivity of alkenylbenzene with cyclic ethers.

The query that arose was whether the radically induced vinylation at inert α sp^3 C–H bonds of cyclic ethers using copper salts/oxidant[5] can similarly be accomplished with tetrabutylammonium iodide (TBAI) and TBHP combinations. This intent encouraged a trial reaction between cyclic ether 1,4-dioxane (**a**) and styrene (**1**) in the presence of TBAI (10 mol%) and aqueous TBHP (4 equiv.) at 80 °C. The surprising outcome of this reaction was the unexpected α-esterification of dioxane to give product (**1a**) in 20% yield (entry 1, Table S1, see ESI‡). This observation clearly indicates that the reactivity of TBAI/TBHP combination is in sharp contrast to Cu salts/oxidant combination which gives ester (**1a**) (Scheme 1, path-c) as the sole product rather than the expected vinylation (Scheme 1, path-a). Notably, the coupling of styrene with cyclic ether in presence of CuBr/TBHP is reported to undergo oxyalkylation i.e. ketone formation (Scheme 1, path-b).[7] Thus the divergence in selectivities achieved with various catalyst/oxidant combinations further highlights the significance of the present finding. The *in situ* generation of other coupling partner, *viz.* the benzoxy group (PhCOO$^-$) derived from styrene is not surprising, since recently under a similar condition (Cu/TBHP) is reported to generate the same.[8] Thus the TBAI/TBHP combination is also expected to give

---

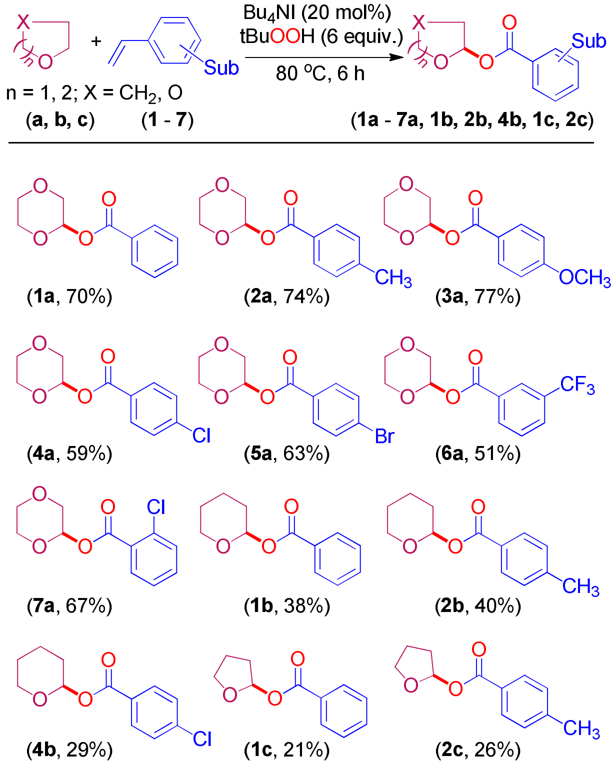
Department of Chemistry, Indian Institute of Technology Guwahati, 781 039, Assam, India. Fax no. +91-3612690762; E-mail: patel@iitg.ernet.in

†Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra For ESI or other electronic format see DOI: 10.1039/xxxxxx.

View Article Online
DOI: 10.1039/C4CC05050A

$PhCOO^-$ group from styrene under identical conditions. Prior to this report, synthesis of α-acyloxy ethers has been achieved by other strategies that can be classified into five main categories: (i) esterification of hemiacetals with acids or its derivatives,[9] (ii) addition of carboxylic acids to alkenyl ethers,[10] (iii) complex routes comprising of two-step synthesis,[11] (iv) α-halo substitution of ethers with carboxylic acids,[12] and (v) CDC transformations involving carboxylic acids and ethers in the presence of either transition metal or metal free catalysts in combination with various oxidants.[13] Following the CDC strategy, our group has recently developed a protocol for the synthesis of α-acyloxy ethers via a Cu mediated solvent-solvent coupling between alkylbenzenes and cyclic ethers.[14] Apart from these results there are other oxidative C–O bond forming reactions most of which are for acetoxylation and hydroxylation.

Scheme 2 Substrate scope for α-acyloxyether.[a,b]

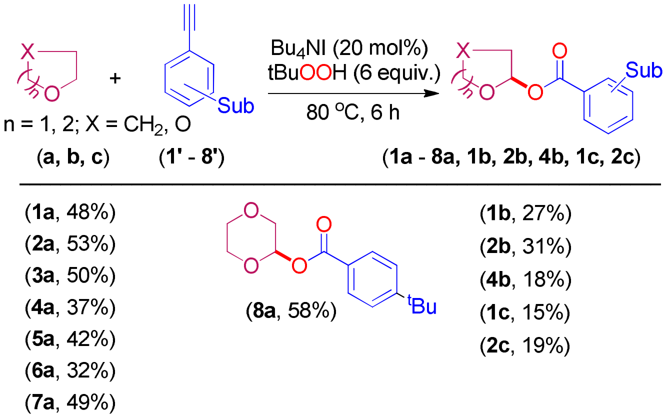


[a]Reaction conditions: styrene (1 mmol), cyclic ethers (1 mL), TBAI (0.2 mmol), TBHP (6 mmol) at 80 °C. [b]Isolated yields.

After the preliminary success on unusual esterification further attempts were made to improve the yield of (**1a**) by varying reaction parameters. When the above coupling reaction was performed with a decane solution of TBHP (5-6 M) (4 equiv.) instead of an aqueous TBHP (70% in water) the yield improved up to 45% (entry 2, Table S1, see ESI‡). By increasing the TBHP quantity from 4 to 6 equiv. and Bu_4NI from 10 to 20 mol% the yield improved from 45% to 70% (entries 3–5, Table S1, see ESI‡). Further, no enhancement in the yield was observed with increase in the catalyst Bu_4NI (30 mol%), oxidant TBHP (7 equiv.) and reaction temperature (100 °C) (entries 6–8, Table S1, see ESI‡). Other oxidants such as di-*tert* butyl peroxide (DTBP), aq. H_2O_2, oxone, $K_2S_2O_8$ and benzoylperoxide were completely ineffective for this transformation (entries 9–13, Table S1, see ESI‡). Instead of Bu_4NI other halogen species such as Bu_4NBr, KI and I_2 (entries 14–16, Table S1, see ESI‡) were completely unproductive. The control experiments carried out with either TBHP or catalyst (Bu_4NI) alone were ineffective towards this CDC coupling (entries 17–18, Table S1, see ESI‡). Thus the ideal condition arrived is the use of styrene (1 mmol), 1,4-dioxane (1 mL), Bu_4NI (20 mol%), decane solution of TBHP (5–6 M) (6 equiv.) and a reaction temperature of 80 °C.

Having established the optimised parameters, the oxidative esterifications of 1,4-dioxane (**a**) with various substituted styrenes were tested and the results are summarised in Scheme 2. Under the optimised conditions, electron neutral styrene –H (**1**) and styrenes possessing either electron-donating substituents such as *p*-Me (**2**), *p*-OMe (**3**) or electron-withdrawing substituents such as *p*-Cl (**4**), *p*-Br (**5**), *m*-CF_3 (**6**) and *o*-Cl (**7**) were found to serve as ArCOO– surrogates providing the desired α-acyloxyethers (**1a–7a**) in good yields (Scheme 2). It was observed that, substituted styrenes containing electron-donating groups provided the corresponding products in higher yields than those bearing electron-withdrawing groups. These results imply that the electronic factor of substituents on the phenyl ring of styrenes affects the reaction rates as well as the product yields. This reactivity trend is consistent with our recent *o*-benzoxylation of 2-phenylpyridine using styrenes as aryl carboxy source.[8] This approach was further examined with other cyclic ethers possessing single oxygen i.e. tetrahydropyran (**b**) and tetrahydrofuran (**c**). The oxidative esterification of tetrahydropyran (**b**) with styrenes (**1**, **2** and **4**) were not so effective in terms of yields as compared to 1,4-dioxane and it afforded α-acyloxy ethers (**1b**, **2b** and **4b**) in lower yields (Scheme 2). Tetrahydrofuran (**c**) with styrenes (**1** and **2**) provided much lower yields of α-acyloxyethers (**1c** and **2c**) (Scheme 2). In the case of 1,4-dioxane (**a**) there are eight equivalent sp^3 C–H's where as in tetrahydropyran (**b**) and tetrahydrofuran (**c**) there are only four such sp^3 C–H's, thus the yield obtained in the later two are lower compared to the former due to statistical factor.

Scheme 3 Substrate scope for α-acyloxyether.[a,b]



[a]Reaction conditions: phenylacetylene (1 mmol), cyclic ethers (1 mL), TBAI (0.2 mmol), TBHP (6 mmol) at 80 °C. [b]Isolated yields.

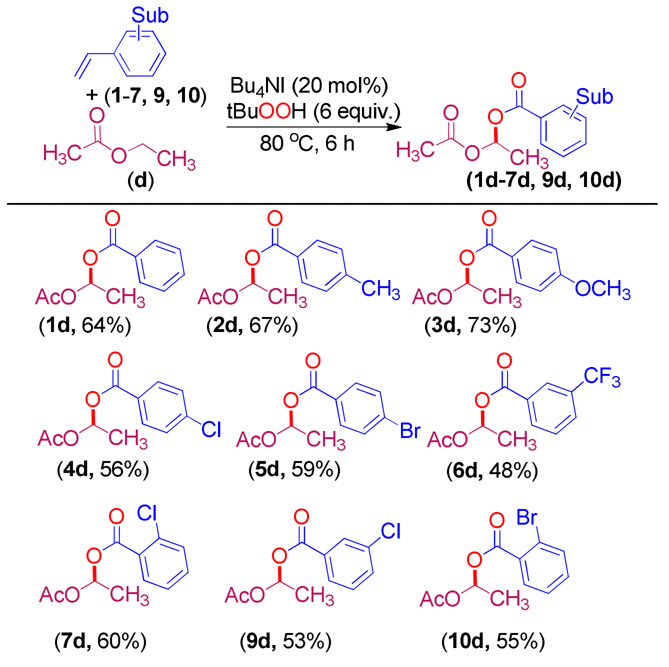
Beside styrenes, phenylacetylenes are efficient arylcarboxy source under Cu(II)/TBHP conditions.[8] Thus we were curious to see whether under the present metal free conditions phenylacetylenes alike styrene can similarly generate arylcarboxy group and couple with cyclic ethers. With this objective phenylacetylene (**1′**) was treated with 1,4-dioxane (**a**) under the previous optimised conditions. It was heartening to observe that the product α-acyloxyethers (**1a**) was obtained in 48% yield. Thus alike styrene the benzoxy group ($PhCOO^-$) can be generated from phenylacetylene under a metal free condition which is unprecedented. In order to generalise this methodology, 1,4-dioxane (**a**) was treated with various phenylacetylenes (**2′–8′**) and the results are summarised in Scheme 3. Phenylacetylenes having either electron-donating groups such as *p*-Me (**2′**), *p*-OMe (**3′**), *p*-tBu (**8′**) or electron-withdrawing groups such as *p*-Cl (**4′**), *p*-Br (**5′**), *m*-CF_3 (**6′**) and *o*-Cl (**7′**) served as

View Article Online
DOI: 10.1039/C4CC05050A

ArCOO– surrogates under the present conditions providing their desired esters (**2a–8a**) in moderate yields (Scheme 3). Additionally, the oxidative esterification of tetrahydropyran (**b**) with various phenylacetylenes (**1′**, **2′** and **4′**) gave α-acyloxy THP ethers (**1b**, **2b** and **4b**) in lower yields (Scheme 3). Tetrahydrofuran (**c**) with phenylacetylenes (**1′** and **2′**) provided much lower yields of α-acyloxy THF ethers (**1c** and **2c**) (Scheme 3). The lesser yields of products obtained with phenylacetylenes compared to styrenes is due to competitive homocoupling of terminal alkynes to diynes under the reaction conditions.

Cyclic ethers such as 1,4-dioxane, tetrahydrofuran and tetrahydropyran are the only common solvents utilised for α C–H functionalisations.[13,14] Ethyl acetate (bearing sp^3 C–H α to oxygen) is predominantly used as a solvent and a diluent. The oxidative α C–H functionalisation of ethyl acetate (**d**) is a very exigent task because it is prone to hydrolysis and *trans*-esterification. Thus selective functionalisations of ethyl acetate would not only be a challenging task but also exciting if achieved. To explore this, the above optimised conditions were implemented on ethyl acetate (**d**) by treating it with styrene (**1**). Interestingly, the product obtained was found to be a double ester (**1d**) formed via functionalisation at the α sp^3 C–H of ethyl acetate without affecting the existing ester functionality. The double ester is nothing but an unsymmetrical *gem*-diacylates.[16] This double esterification of ethyl acetate was then tested with other styrenes having electron-donating groups such as *p*-Me (**2**), *p*-OMe (**3**) and electron-withdrawing groups such as *p*-Cl (**4**), *p*-Br (**5**), *m*-CF_3 (**6**), *o*-Cl (**7**), *m*-Cl (**9**) and *o*-Br (**10**) all provided unsymmetrical *gem*-diacylates (**2d–7d**, **9d** and **10d**) in moderate yields as shown in Scheme 4. In these cases also the benzoxy groups originated from respective styrenes.[8] It may be noted here that active methylene compounds possessing sp^3 C–H α to oxygen upon reaction with carboxylic acids under similar conditions give double esters via oxidative esterification at the active methylene C–H.[17]

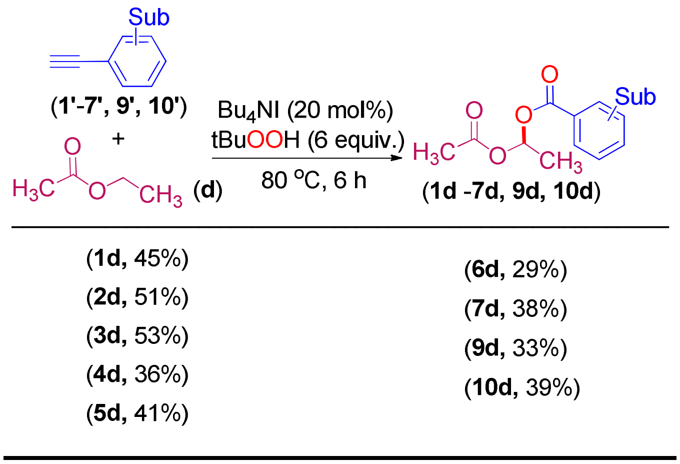
Scheme 4 Substrate scope for esterification of ethyl acetate.[a,b]



[a]Reaction conditions: styrene (1 mmol), ethylacetate (2 mL), TBAI (0.2 mmol), TBHP (6 mmol) at 80 °C. [b]Isolated yields.

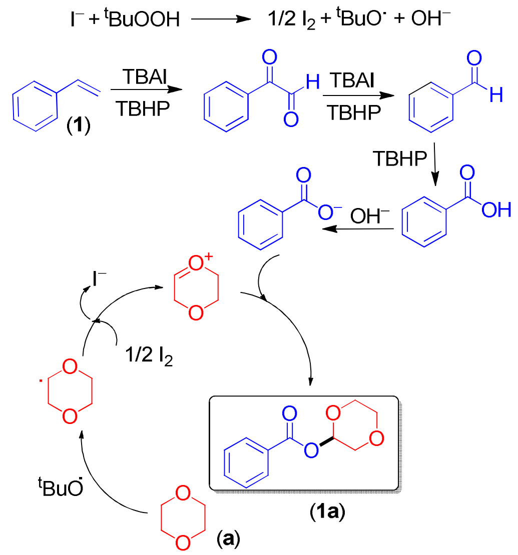
Since phenylacetylenes too are potential benzoxy surrogates as observed during esterification of cyclic ethers, the same was utilised towards double esterification of ethyl acetate. Various substituted phenylacetylenes with electron neutral –H (**1′**), electron-donating groups such as *p*-Me (**2′**), *p*-OMe (**3′**) and electron-withdrawing groups such as *p*-Cl (**4′**), *p*-Br (**5′**), *m*-CF_3 (**6′**), *o*-Cl (**7′**), *m*-Cl (**9′**) and *o*-Br (**10′**) enacted as corresponding arylcarboxy surrogates for the formation of unsymmetrical *gem*-diacylates (**1d–7d**, **9d** and **10d**) but in relatively lower yields (Scheme 5).

Scheme 5 Substrate scope for esterification of ethyl acetate.[a,b]



[a]Reaction conditions: phenylacetylene (1 mmol), ethylacetate (2 mL), TBAI (0.2 mmol), TBHP (6 mmol) at 80 °C. [b]Isolated yields.

Several control experiments were carried out to depict a plausible mechanism for these coupling reactions. Analysis of the reaction mixture obtained by reacting 1,4-dioxane (**a**) with styrene (**1**) revealed the presence of intermediate benzaldehyde and benzoic acid in the medium (Scheme 6). Formation of benzaldehyde from styrene is expected to go via decarbonylation of in situ generated phenylglyoxal intermediate (see ESI).[8] Under oxidative reaction conditions, benzaldehyde gets converted to benzoic acid which could be the possible source of carboxy group in these reactions.[6a] When benzoic acid was treated with 1,4-dioxane (**a**) under the present reaction condition exclusive formation of (**1a**) was observed (90%) implying the coupling partners are carboxylic acid and dioxane.[13a] Apart from benzoic acid when phenylglyoxal and benzaldehyde were reacted independently with 1,4-dioxane (**a**), the desired ester (**1a**) was obtained in 84 and 87% yields respectively; thus confirming their intermediacy in this transformation.



Scheme 6 Proposed mechanism for oxidative esterification

A standard reaction performed between (**a**) and (**1**) in the presence of radical quencher 2,2,6,6-tetramethylpyridine *N*-oxide (TEMPO) led to drastic quenching of the product (**1a**) yield; suggesting a radical pathway for this transformation. The results of the above experiments and related literature reports[8,13a] convey the operation of following paths for the oxidative esterification. Styrene (**1**) in the presence of TBAI/TBHP is converted to benzoic acid via the intermediacy of phenylglyoxal and benzaldehyde (Scheme S1, see ESI‡). To rule out the source of oxygen from molecular oxygen, esterifications of 1,4-dioxane (**a**) with styrene (**1**) was carried out in an argon atmosphere under anhydrous conditions. The reaction proceeded smoothly giving product (**1a**) in identical yield suggesting that the oxygen atom in ester/carboxylic acid is indeed originating from TBHP only.[18] The benzoic acid so generated is deprotonated to give an anionic benzoate. In another path, radical abstraction of sp^3 C–H α to ethereal oxygen in dioxane gives the radical intermediate (Scheme 6). This species then undergoes a further one electron oxidation (SET) with iodine forming the oxonium species. In the ultimate step, nucleophilic attack of benzoate ion on the α carbon of oxonium species gives α acyloxy ether (**1a**) (Scheme 6). A similar mechanism can be proposed involving ethyl acetate instead of cyclic ether.

In conclusion, we have developed a method for cyclic ethers to esters and monoesters to diesters (*gem*-diacylates) under metal free conditions cleaving sp^3 C–H bonds in simple solvents like 1,4-dioxane, tetrahydropyran, tetrahydrofuran and ethyl acetate with terminal aryl alkenes and alkynes. The coupling partners are the *in situ* generated ArCOO$^-$ from styrenes and phenylacetylenes and the solvents (cyclic ethers and ethyl acetate). Conceptually C=C bond cleavage of styrene to generate benzaldehyde can be considered as substitute of ozonolysis

B. K. P acknowledges the support of this research by the Department of Science and Technology (DST) (SB/S1/OC-53/2013), New Delhi, and the Council of Scientific and Industrial Research (CSIR) (02(0096)/12/EMR-II).

Notes and References

1 For reviews of C–H bond activation see the following: (a) X.-S. Zhang, K. Chen and Z.-J. Shi, *Chem. Sci.*, 2014, **5**, 2146; (b) I. D. G. Watson and F. D. Toste, *Chem. Sci.*, 2012, **3**, 2899; (c) S. I. Kozhushkov and L. Ackermann, *Chem. Sci.*, 2013, **4**, 886; (d) A. E. Nako, A. J. P. White and M. R. Crimmin, *Chem. Sci.*, 2013, **4**, 691; (e) Y. Zhang, Q. Wu and S. Cui, *Chem. Sci.*, 2014, **5**, 297; (f) T. Satoh and M. Miura, *Chem. Eur. J.*, 2010, **16**, 11212; (g) X. Chen, K. M. Engle, D.-H. Wang and J.-Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **48**, 5094; (h) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; (i) L.-M. Xu, B.-J. Li, Z. Yang and Z.-J. Shi, *Chem. Soc. Rev.*, 2010, **39**, 712; (j) D. A. Colby, R. G. Bergman and J. A Ellman, *Chem. Rev.*, 2010, **110**, 624; (k) J. Wencel-Delord, T. Droge, F. Liu and F. Glorius, *Chem. Soc. Rev.*, 2011, **40**, 4740; (l) S. H. Cho, J. Y. Kim, J. Kwak and S. Chang, *Chem. Soc. Rev.*, 2011, **40**, 5068; (m) C.-L. Sun, B.-J. Li and Z.-J. Shi, *Chem. Rev.*, 2011, **111**, 1293; (n) L. Ackermann, *Chem. Rev.*, 2011, **111**, 1315; (o) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936; (p) K. M. Engle, T.-S. Mei, M. Wasa and J.-Q. Yu, *Acc. Chem. Res.*, 2012, **45**, 788.

2 (a) C.-J. Li, *Acc. Chem. Res.*, 2009, **42**, 335; (b) S. A. Girard, T. Knauber and C.-J. Li, *Angew. Chem., Int. Ed.,* 2014, **53**, 74; (c) J. A. Ashenhurst, *Chem. Soc. Rev.,* 2010, **39**, 540; (d) C. J. Scheuermann, *Chem. Asian J.,* 2010, **5**, 436; (e) R. Samanta, K. Matcha and A. P. Antonchick, *Eur. J. Org. Chem.,* 2013, 5769; (f) X.-F. Wu, J.-L. Gong and X. Qi, *Org. Biomol. Chem.*, 2014, doi: 10.1039/C4OB00276H; (g) Y. Wu, J. Wang, F. Mao and F. Y. Kwong, *Chem. Asian J.,* 2014, **9**, 26.

3 (a) H. M. L. Davies, J. D. Bois and J.-Q. Yu, *Chem. Soc. Rev.*, 2011, **40**, 1855; (b) D. H. Wang, K. M. Engle, B. F. Shi and J.-Q. Yu, *Science*, 2010, **327**, 315; (c) F. W. Patureau, T. Besset and F. Glorius, *Angew. Chem., Int. Ed.*, 2011, **50**, 1064; (d) M. Brasse, J. Campora, J. A. Ellman and R. G. Bergman, *J. Am. Chem. Soc.*, 2013, **135**, 6427; (e) K. J. Stowers, K. C. Fortner and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 6541.

4 (a) C. S. Yeung and V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; (b) E. M. Beccalli, G. Broggini, M. Martinelli and S. Sottocornola, *Chem. Rev.*, 2007, **107**, 5318.

5 (a) D. Liu, C. Liu, H. Li and A. Lei, *Chem. Commun.*, 2014, **50**, 3623; (b) Y. Zhu and Y. Wei, *Chem. Sci.*, 2014, **5**, 2379.

6 (a) G. Majji, S. Guin, A. Gogoi, S. K. Rout and B. K. Patel, *Chem. Commun.*, 2013, **49**, 3031; (b) S.-r. Guo, Y.-q. Yuan and J.-n. Xiang, *Org. Lett.*, 2013, **15**, 4654; (c) B. Tan, N. Toda and C. F. Barbas III, *Angew. Chem., Int. Ed.*, 2012, **51**, 12538; (d) W. Wei, C. Zhang, Y. Xu and X. Wan, *Chem. Commun*., 2011, **47**, 10827; (e) L. Ma, X. Wang, W. Yu and B. Han, *Chem. Commun*., 2011, **47**, 11333; (f) M. Uyanik and K. Ishihara, *ChemCatChem,* 2012, **4**, 177.

7 K. Cheng, L. Huang and Y. Zhang, *Org. Lett.*, 2009, **11**, 2908.

8 S. K. Rout, S. Guin, A. Gogoi, M. Ganesh and B. K. Patel, *Org. Lett.*, 2014, **16**, 1614.

9 (a) C. Singh, S. Chaudhary and S. K. Puri, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 1436; (b) M. A. Huffman, J. H. Smitrovich, J. D. Rosen, G. N. Boice, C. Qu, T. D. Nelson and J. M. McNamara, *J. Org. Chem.*, 2005, **70**, 4409.

10 W. J. Croxall, F. J. Glavis and H. T. Neher, *J. Am. Chem. Soc*., 1948, **70**, 2805.

11 (a) D. J. Kopecky and S. D. Rychnovsky, *J. Org. Chem*., 2000, **65**, 191; (b) Y. Zhang and T. Rovis, *Org. Lett*., 2004, **6**, 1877.

12 R. K. Summerbell and H. E. Lunk, *J. Am. Chem. Soc*., 1958, **80**, 604.

13 (a) L. Chen, E. Shi, Z. Liu, S. Chen, W. Wei, H. Lei, K. Xu and X. Wan, *Chem. Eur. J*., 2011, **17**, 4085; (b) S. Priyadarshini, P. Amal, J. Joseph and M. L. Kantam, *RSC Adv*., 2013, **3**, 18283; (c) S. Zhang, Li.-Na. Guo, H. Wang and X.-H. Duan, *Org. Biomol. Chem.*, 2013, **11**, 4308; (d) Z.-Q. Liu, L. Zhao, X. Shang and Z. Cui, *Org. Lett*., 2012, **14**, 3218; (e) J. Zhao, H. Fang, W. Zhou, J. Han and Y. Pan, *J. Org. Chem.*, 2014, **79**, 3847.

14 S. K. Rout, S. Guin, W. Ali, A. Gogoi and B. K. Patel, *Org. Lett.*, 2014, **16**, 3086.

15\. (a) D. Kalyani and M. S. Sanford, *Org. Lett*., 2005, **7**, 4149; (b) F.-R. Gou, X.-C. Wang, P.-F. Huo, H.-P. Bi, Z.-H. Guan and Y.-M. Liang, *Org. Lett*.,2009, **11**, 5726; (c) X. Zheng, B. Song and B. Xu, *Eur. J. Org. Chem*., 2010, 4376; (d) L. Wang, X.-D. Xia, W. Guo, J.-R. Chen and W.-J. Xiao, *Org. Biomol. Chem*., 2011, **9**, 6895; (e) R. K. Rit, R. Yadav and A. K. Sahoo, *Org. Lett*., 2012, **14**, 3724; (f) R. Yadav, R. K. Rit and A. K. Sahoo, *Chem. Eur. J*., 2012, **18**, 5541. (g) X. Chen, X.-S. Hao, C. E. Goodhue and J.-Q. Yu, *J. Am. Chem. Soc*., 2006, **128**, 6790; (h) S. H. Kim, H. S. Lee, S. H. Kim and J. N. Kim, *Tetrahedron Lett*., 2008, **49**, 5863; (i) A. Company and S. Enthaler, *Chem. Soc. Rev*., 2011, **40**, 4912; (j) D. A. Alonso, C. Najera, I. M. Pastor and M. Yus, *Chem. Eur. J*., 2010, **16**, 5274; (k) V. S. Thirunavukkarasu, S. I. Kozhushkov and L. Ackermann, *Chem. Commun*., 2014, **50**, 29.

16 V. Kavala and B. K. Patel, *Eur. J. Org. Chem.*, 2005, 441.

17 M. Uyanik, D. Suzuki, T. Yasui and K. Ishihara, *Angew. Chem., Int. Ed.*, 2011, **50**, 5331.

18\. (a) H. Jiang, H. Huang, H. Cao and C. Qi, *Org. Lett.*, 2010, **12**, 5561; (b) W.-T. Wei, R.-J. Song, X.-H. Ouyang, Y. Li, H.-B. Li and J.-H. Li, *Org. Chem. Front.*, 2014, **1**, 484; (c) X.-H. Ouyang, R.-J. Song, Y. Li, B. Liu and J.-H. Li, *J. Org. Chem.,* 2014, **79**, 4582.