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# Efficient direct 2,2,2-trifluoroethylation of indoles via C–H functionalization†‡

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**A novel highly C3 selective metal free trifluoroethylation of indoles using 2,2,2-trifluoroethyl(mesityl)-iodonium triflate was developed. The methodology enables the introduction of a trifluoroethyl group in a fast and efficient reaction under mild conditions with high functional group tolerance. Beyond the synthetic developments, quantum chemical calculations provide a deeper understanding of the transformation.**

The presence of fluorine in organic molecules often provides advantageous properties to the molecules, as fluorinated functional groups can beneficially modify the electronic properties of the compounds, improve their metabolic stability, and enhance their lipophilicity. Therefore the development of new synthetic methods for the installation of fluorine and fluorine functional groups is an emerging field in synthetic organic chemistry.<sup>1</sup>

Modification of lead compounds with fluorine functional groups to fine-tune their biological activity is one of the most frequently used strategies in medicinal chemistry. Aside from the simple fluorine atom and CF<sub>3</sub> group, the presence of other related small fluorine functional groups such as trifluoromethoxy,<sup>2</sup> trifluoromethylthio<sup>3</sup> or structurally similar trifluoroethyl<sup>4</sup> groups on an aromatic core structure has also gained exceptional attention from the fields of synthetic organic and medicinal chemistry.

Due to the importance of the indole framework in the structure of drug candidates much attention has been focused

on the synthesis of fluoroalkylated indole derivatives. In general, trifluoroethylated indoles are accessible through indole core functionalization *via* multistep syntheses (3–6 synthetic steps)<sup>5</sup> or ring constructions such as a novel radical Fisher indole type synthesis developed by Antonchick.<sup>6</sup> Compared to trifluoromethylation, the synthetic transformations to access trifluoroethylated compounds *via* C–C bond formation are underdeveloped. The main, but still uncommon methods for the construction of trifluoroethyl groups involve the trifluoromethylation of a benzylic position,<sup>7</sup> the addition of a trifluoromethyl group to alkenes,<sup>8</sup> and the utilization of gaseous trifluoromethyl diazomethane.<sup>9</sup> Although the unique electronic properties of the CF<sub>3</sub>CH<sub>2</sub>X (X = Br, I, OTf) compounds limit their use as simple electrophiles,<sup>10</sup> recently several cross-coupling approaches were developed for the introduction of trifluoroethyl groups into aromatic systems.<sup>11</sup> The direct C–H functionalization with a trifluoroethyl group is seldom explored. Very recently Ackermann described the first nickel catalyzed trifluoroethylation process utilizing an 8-aminoquinoline directing group and trifluoroethyl iodide as alkyl sources.<sup>12</sup> A Catellani type palladium catalyzed cascade trifluoroethylation was developed by Liu for the synthesis of olefinated trifluoroethyl arenes.<sup>13</sup> A unique example for transition metal catalyst free direct trifluoroethylation of heterocycles is Baran's radical alkylation strategy using zinc sulfinate salts.<sup>14</sup>

In our work, we aimed to develop a new alkylation methodology for the direct trifluoroethylation of indoles with the aid of an electrophilic trifluoroethyl synthon originated from hypervalent iodonium salts. Introduction of hypervalent iodonium salts as useful reagents in organic chemistry<sup>15</sup> opens new possibilities for the formation of carbon–heteroatom and carbon–carbon bonds *via* C–H activation.<sup>16</sup> Besides numerous synthetic applications,<sup>15a,17</sup> the use of λ<sup>3</sup> iodo compounds provides an emerging transition metal catalyzed strategy for the direct functionalization of indoles.<sup>18</sup> The pioneering work of Umemoto in the field of fluoroalkyl-iodonium salts<sup>19</sup> inspired us to use hypervalent iodine reagents for the trifluoroethylation of indoles. These reagents were mostly used for the fluoroalkylation of heteroatom<sup>20</sup> and soft

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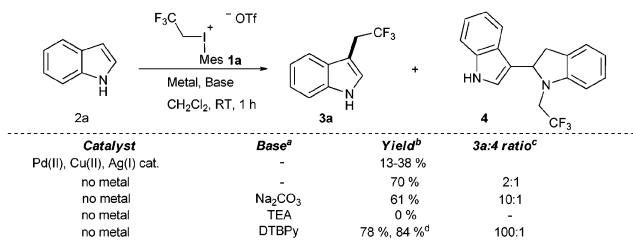
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‡ Electronic supplementary information (ESI) available: Detailed experimental procedures, characterization of products and the details of DFT calculations. See DOI: 10.1039/c5cc00519a

§ Both authors contributed equally to this work.





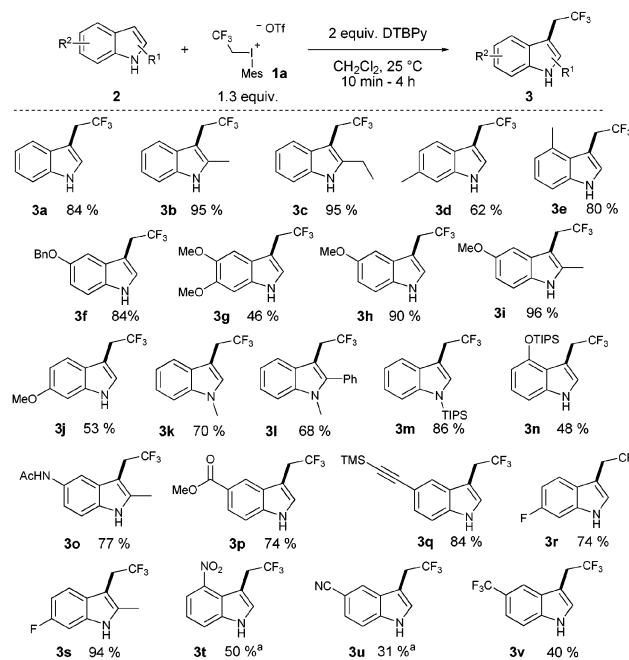
**Scheme 1** Adjustment of reactivity by different bases. <sup>a</sup> 2 equivalents of the base, 1 equivalent of the **1a** reagent. <sup>b</sup> Isolated yield of the mixture. <sup>c</sup> Determined by <sup>19</sup>F NMR measurements. <sup>d</sup> 1.3 equivalent of the iodonium salt (**1a**) was used.

carbon<sup>21</sup> nucleophiles to build C–N, C–O, C–S and C(sp<sup>3</sup>)–C(sp<sup>3</sup>) bonds.

For the realization of the desired transformation we synthesized the 2,2,2-trifluoroethyl(mesityl)-iodonium triflate salt (**1a**) as a new reagent from bis(trifluoroacetatoxy)(2,2,2-trifluoroethyl)iodide and mesitylene in 94% isolated yield on a multigram scale. We strategically chose the mesityl group (Mes) as a frequently used aromatic system for the synthesis of aryl-iodonium salts with high stability and activity. However, two additional trifluoroethyl-aryliodonium salts were prepared, but the phenyl (**1b**) and 4-tolyl (**1c**) derivatives were obtained with lower efficiency (68% and 83% respectively).

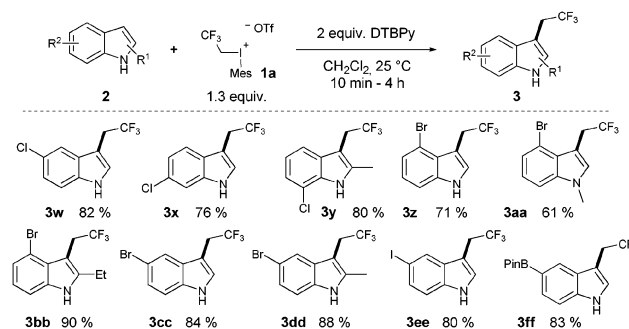
After having the designed reagents in hand, we turned our attention to the possible C–H functionalization of unprotected indoles to develop a powerful synthetic methodology to enable C–C bond formation without the necessity for protecting groups. First, we studied the trifluoroethylation reaction of indole (**2a**) with **1a** in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) at 25 °C with or without transition metal catalysts (Cu(II), Pd(II), and Ag(I) salts). To our delight the reaction of unsubstituted indole provided the desired C3 trifluoroethylated product **3a** (Scheme 1). In contrast to the known iodonium salt based transition metal catalyzed indole functionalization methodologies, we found that the presence of transition metal catalysts had deleterious effects on the trifluoroethylation reaction.<sup>22</sup>

Despite the high reactivity of the polyfluoroalkyl λ<sup>3</sup> iodonium compounds toward heteroatom nucleophiles<sup>20a,b</sup> trifluoroethylation did not occur on the indole nitrogen due to its lower nucleophilicity. Besides these beneficial features, we observed the formation of a significant amount of *N*-trifluoroethylated indolino-indole derivative (**4**). The presence of trifluoromethanesulfonic acid, generated in the reaction, accelerates the dimerization of indole, and the formed indoline moiety undergoes straightforward *N*-trifluoroethylation.<sup>22</sup> It was anticipated that the amount of this side product could be decreased by adding an appropriate base such as 2,6-di-*tert*-butylpyridine (DTBPy) and target compound **3a** was isolated in 84% yield.<sup>22</sup> Next, we explored the synthetic utility of this reaction by examining the substrate scope in CH<sub>2</sub>Cl<sub>2</sub> at 25 °C.<sup>22</sup> Indole and alkyl indoles reacted smoothly with **1a** under our conditions to provide trifluoroethyl indoles **3a–3e** in 10 minute reaction time (Scheme 2). In the case of 3-methylindole, formation of any trifluoroethylated product were not observed (not shown).



**Scheme 2** Substrate scope of the transformation: <sup>a</sup> without base, 2 equiv. of the iodonium salt.

More electron rich alkoxyindoles were also successfully functionalized in a rapid reaction (10–60 minutes) and the desired compounds (**3f–j**) could also be isolated in good to excellent yields (46–96%). Although, the indole nitrogen does not require protection, the tested *N*-methyl and *N*-TIPS derivatives were also successfully trifluoroethylated (**3k–m**). Nucleophilic functional groups connected to the indole frame such as free hydroxyl, amino and carboxyl functions could be masked with different protecting groups for the efficient trifluoroethylation (**3n–p**) of indole at position 3 to obtain valuable heterocyclic building blocks. Indole containing TMS protected alkyne was also converted to its corresponding trifluoroethylated compound (**3q**) in 84% yield, opening the way for further synthetic transformations through the acetylene part. To further explore the real synthetic power of the method, we examined the scope with electron withdrawing groups on the indole skeleton. To our delight the presence of fluorine, nitro, cyano and trifluoromethyl groups on the indole core was well tolerated, and the desired products (**3r–v**) were isolated in 31–94% yield after



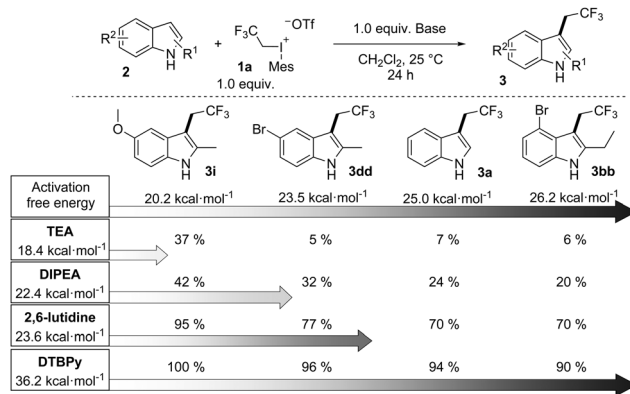
**Scheme 3** Trifluoroethylated indoles for cross-coupling chemistry.



1.5–4 hours of reaction time. Demonstrating the power of the methodology we examined the trifluoroethylation of indoles bearing functional groups suitable for cross coupling chemistry (Cl, Br, I, and boronic ester; Scheme 3). Each halogen substituted indole gave the desired products (**3w–3ee**) in good to excellent yields (61–90%), as well as the boronic ester derivative (**3ff**, 83%).

We employed DFT calculations to understand the mechanism and the selectivity of the present reaction. First we considered the reaction between indole (**2a**) and 2,2,2-trifluoroethyl(mesityl)-iodonium triflate (**1a**) (Scheme 4). The dissociation of the triflate anion proved to be slightly exergonic ( $-0.9$  kcal mol $^{-1}$ ) suggesting a dissociated resting state. The rate-determining step is the trifluoroethylation of the indole-ring. The next step is the deprotonation of the  $\sigma$ -complex by the basis with a 18.3 kcal mol $^{-1}$  barrier. Both steps are highly exergonic indicating irreversible transformations. Formation of 1- and 2-substituted indoles is much less favourable, which explains that they could not be observed in experiment.<sup>22</sup> We have also calculated the free energy barrier heights for the all the substrates indicated in Schemes 2 and 3.<sup>22</sup> Within the expected accuracy the calculations nicely correlate with experiment providing confidence in the conclusion. The formation of 3-indolyl-trifluoroethyl-mesityl-iodonium salt from **1a** and **2a** as another possible intermediate of the reaction and subsequent product formation through reductive elimination have also been taken into consideration. This reaction pathway has been safely excluded on the basis of the prohibitively high barrier (52 kcal mol $^{-1}$ ) for the formation of the key intermediate from **1a** and **2**.

To explain the special efficiency of DTBPy as a base in the reaction we have also calculated the activation barriers of the alkylations of different amine bases such as TEA, DIPEA, 2,6-lutidine and DTBPy. It was found that the activation energies of the *N*-trifluoroethylation of these bases with **1a** were 18.4 kcal mol $^{-1}$ , 22.4 kcal mol $^{-1}$  and 23.6 kcal mol $^{-1}$ , respectively, which are in the same range as the barriers of the C alkylations of the studied indoles. However, computation



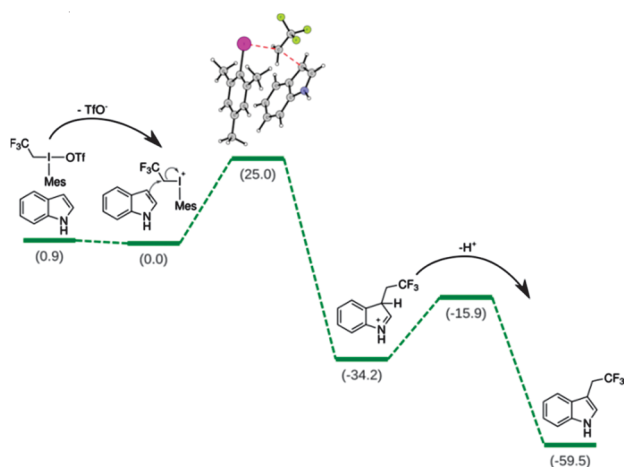
**Scheme 5** GC Conversion of trifluoroethyl indole derivatives obtained from reactions carried out in the presence of different amines. Activation energies of trifluoroethylation of indole derivatives and bases are indicated.

results showed that the *N*-trifluoroethylation of DTBPy required an extremely high activation energy (36.2 kcal mol $^{-1}$ ) due to the significant steric repulsion.<sup>22</sup> These results indicate that variations in the barrier heights of trifluoroethylations can strongly influence the outcome of the reaction, which is important from a synthetic standpoint. Additional experiments have convincingly confirmed this prediction as shown in Scheme 5. In this scheme we collected the conversions of four indole derivatives in the presence of different bases. From left to right the reactivity (TS barriers of trifluoroethylation) of the indole derivatives are tuned by varying their substituents. Going down in the columns, the barriers of *N*-alkylation increase. The trends obtained for the all possible combinations of indole-base pairs demonstrate that the efficiency of a substrate-base combination is determined by the activation barrier differences of the competing *N*- and *C*-alkylations. Clearly, alkylations of the bases and substrates are competitive reactions, and the yields support the postulated kinetic control.

In conclusion, we have developed a transition metal free direct C–H trifluoroethylation reaction, which enables the selective trifluoroethylation of a heterocyclic system for the first time resulting in C(sp $^2$ )–C(sp $^3$ ) bond formation.

The readily accessible new 2,2,2-trifluoroethyl(mesityl)-iodonium triflate reagent ensures the straightforward trifluoroethylation of indoles at position 3 under very mild conditions in a rapid reaction (10–240 minutes of reaction time). The excellent functional group tolerance of the developed transformation enables the access of chemically diverse compound classes with potential medicinal interest. Additionally, with the aid of DFT studies we revealed the mechanistic steps of the reaction, and explained the important role of basic additives in the transformation process. Beyond these mechanistic studies and the synthesis of 3-trifluoroethyl indoles with high versatility the developed methodology opens new doors to the synthesis of other trifluoroethylated aromatic and heterocyclic compounds *via* C–H functionalization or transition metal catalyzed C–H activation. The study of these synthetic possibilities is currently undergoing in our laboratory.

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**Scheme 4** Free energy profile in kcal mol $^{-1}$  of the transformation based on DFT calculations.



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## Notes and references

- (a) C. N. Neumann and T. Ritter, *Angew. Chem., Int. Ed.*, 2015, DOI: 10.1002/anie.201410288; (b) C. Ni, M. Hu and J. Hu, *Chem. Rev.*, 2015, **115**, 765; (c) J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok and H. Liu, *Chem. Rev.*, 2013, **114**, 2432; (d) J. Charpentier, N. Früh and A. Togni, *Chem. Rev.*, 2015, **115**, 650; (e) A. Harsanyi and G. Sandford, *Green Chem.*, 2015, DOI: 10.1039/C4GC02166E; (f) Z. Gonda, S. Kovács, C. Weber, T. Gáti, A. Mészáros, A. Kotschy and Z. Novák, *Org. Lett.*, 2014, **16**, 4268.
- (a) C. Huang, T. Liang, S. Harada, E. Lee and T. Ritter, *J. Am. Chem. Soc.*, 2011, **133**, 13308; (b) O. Marrec, T. Billard, J.-P. Vors, S. Pazenok and B. R. Langlois, *Adv. Synth. Catal.*, 2010, **352**, 2831; (c) F. Venturini, W. Navarrini, A. Famulari, M. Sansotera, P. Dardani and V. Tortelli, *J. Fluorine Chem.*, 2012, **140**, 43.
- (a) R. Pluta, P. Nikolaienko and M. Rueping, *Angew. Chem., Int. Ed.*, 2014, **53**, 1650; (b) A. Tlili and T. Billard, *Angew. Chem., Int. Ed.*, 2013, **52**, 6818; (c) Y.-D. Yang, A. Azuma, E. Tokunaga, M. Yamasaki, M. Shiro and N. Shibata, *J. Am. Chem. Soc.*, 2013, **135**, 8782; (d) E. V. Vinogradova, P. Müller and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 2014, **53**, 3125; (e) G. Danoun, B. Bayarmagnai, M. F. Gruenberg and L. J. Goossen, *Chem. Sci.*, 2014, **5**, 1312; (f) J. Xu, X. Mu, P. Chen, J. Ye and G. Liu, *Org. Lett.*, 2014, **16**, 3942; (g) X.-L. Zhu, J.-H. Xu, D.-J. Cheng, L.-J. Zhao, X.-Y. Liu and B. Tan, *Org. Lett.*, 2014, **16**, 2192; (h) A. Harsányi, É. Dorkó, Á. Csapó, T. Bakó, C. Peltz and J. Rábai, *J. Fluorine Chem.*, 2010, **132**, 1241; (i) S. Alazet, L. Zimmer and T. Billard, *Chem. – Eur. J.*, 2014, **20**, 8589; (j) C. Xu, B. Ma and Q. Shen, *Angew. Chem., Int. Ed.*, 2014, **53**, 9316.
- (a) M. D. Krasowski, *Neuropharmacology*, 2000, **39**, 1168; (b) N. Kumar, L. A. Solt, J. J. Conkright, Y. Wang, M. A. Istrate, S. A. Busby, R. D. Garcia-Ordóñez, T. P. Burris and P. R. Griffin, *Mol. Pharmacol.*, 2010, **77**, 228; (c) T. W. Ho, L. K. Mannix, X. Fan, C. Assaid, C. Furtek, C. J. Jones, C. R. Lines and A. M. Rapoport, *Neurology*, 2008, **70**, 1304.
- (a) T. Konno, J. Chae, T. Ishihara and H. Yamanaka, *J. Org. Chem.*, 2004, **69**, 8258; (b) P. Stjernlöf, T. Elebring, J. Nilsson, B. Andersson, S. Lagerkvist, K. Svensson, A. Ekman, A. Carlsson and H. Wikström, *J. Med. Chem.*, 1994, **37**, 3263; (c) Y. Qiao, T. Si, M. H. Yang and R. A. Altman, *J. Org. Chem.*, 2014, **79**, 7122; (d) A. Hall, A. Billinton, S. H. Brown, A. Chowdhury, G. M. Giblin, P. Goldsmith, D. N. Hurst, A. Naylor, S. Patel, T. Scoccitti and P. J. Theobald, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 2684.
- K. Matcha and A. P. Antonchick, *Angew. Chem., Int. Ed.*, 2014, **53**, 11960–11964.
- (a) H. Kawai, T. Furukawa, Y. Nomura, E. Tokunaga and N. Shibata, *Org. Lett.*, 2011, **13**, 3596; (b) Y. Miyake, S. Ota, M. Shibata, K. Nakajima and Y. Nishibayashi, *Org. Biomol. Chem.*, 2014, **12**, 5594; (c) N. V. Kondratenko, E. P. Vechirko and L. M. Yagupolskii, *Synthesis*, 1980, 932; (d) L. Zhu, S. Liu, J. T. Douglas and R. A. Altman, *Chem. – Eur. J.*, 2013, **19**, 12800–12805; (e) G. K. S. Prakash, P. V. Jog, P. T. D. Batamack and G. A. Olah, *Science*, 2012, **338**, 1324; (f) G. G. Dubinina, H. Furutachi and D. A. Vici, *J. Am. Chem. Soc.*, 2008, **130**, 8600.
- (a) P. G. Janson, I. Ghoneim, N. O. Ilchenko and K. J. Szabó, *Org. Lett.*, 2012, **14**, 2882; (b) J. Xu, Y. Fu, D.-F. Luo, Y.-Y. Jiang, B. Xiao, Z.-J. Liu, T.-J. Gong and L. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 15300; (c) Y. Li and A. Studer, *Angew. Chem., Int. Ed.*, 2012, **51**, 8221; (d) R. Zhu and S. L. Buchwald, *J. Am. Chem. Soc.*, 2012, **134**, 12462.
- (a) B. Morandi and E. M. Carreira, *Angew. Chem., Int. Ed.*, 2011, **50**, 9085; (b) C.-B. Liu, W. Meng, F. Li, S. Wang, J. Nie and J.-A. Ma, *Angew. Chem., Int. Ed.*, 2012, **51**, 6227.
- (a) N. Bodor, M.-J. Huang, C. Szántay Jr. and C. Szántay, *Tetrahedron*, 1992, **48**, 5823; (b) K. Tanaka, T. Nakai and N. Ishikawa, *Chem. Lett.*, 1979, 175.
- (a) Y. Zhao and J. Hu, *Angew. Chem., Int. Ed.*, 2012, **51**, 1033; (b) A. Liang, X. Li, D. Liu, J. Li, D. Zou, Y. Wu and Y. Wu, *Chem. Commun.*, 2012, **48**, 8273; (c) F. Leng, Y. Wang, H. Li, J. Li, D. Zou, Y. Wu and Y. Wu, *Chem. Commun.*, 2013, **49**, 10697; (d) L. M. Kreiss, S. Krautwald, N. Pfeiffer, R. E. Martin and E. M. Carreira, *Org. Lett.*, 2013, **15**, 1634; (e) Y.-S. Feng, C.-Q. Xie, W.-L. Qiao and H.-J. Xu, *Org. Lett.*, 2013, **15**, 936; (f) J. Hwang, K. Park, J. Choe, H. Min, K. H. Song and S. Lee, *J. Org. Chem.*, 2014, **79**, 3267.
- W. Song, S. Lackner and L. Ackermann, *Angew. Chem., Int. Ed.*, 2014, **53**, 2477–2480.
- H. Zhang, P. Chen and G. Liu, *Angew. Chem., Int. Ed.*, 2014, **53**, 10174–10178.
- Y. Fujiwara, J. A. Dixon, F. O'Hara, E. D. Funder, D. D. Dixon, R. A. Rodriguez, R. D. Baxter, B. Herle, N. Sach, M. R. Collins, Y. Ishihara and P. S. Baran, *Nature*, 2012, **492**, 95.
- (a) P. J. Stang and V. V. Zhdankin, *Chem. Rev.*, 1996, **96**, 1123; (b) V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2002, **102**, 2523; (c) V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299; (d) E. A. Merritt and B. Olofsson, *Angew. Chem., Int. Ed.*, 2009, **48**, 9052; (e) V. V. Zhdankin, *Hypervalent Iodine Chemistry*, Wiley, Chichester, 2014.
- (a) J. J. Topczewski and M. S. Sanford, *Chem. Sci.*, 2015, **6**, 70; (b) T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147.
- (a) A. Székely, Á. Sinai, E. B. Tóth and Z. Novák, *Synthesis*, 2014, 1871; (b) Á. Sinai, Á. Mészáros, T. Gáti, V. Kudar, A. Palló and Z. Novák, *Org. Lett.*, 2013, **15**, 5654; (c) F. Zhang, S. Das, A. J. Walkinshaw, A. Casitas, M. Taylor, M. G. Suero and M. J. Gaunt, *J. Am. Chem. Soc.*, 2014, **136**, 8851; (d) B. S. L. Collins, M. G. Suero and M. J. Gaunt, *Angew. Chem., Int. Ed.*, 2013, **52**, 5799; (e) Q. Y. Toh, A. McNally, S. Vera, N. Erdmann and M. J. Gaunt, *J. Am. Chem. Soc.*, 2013, **135**, 3772; (f) A. J. Walkinshaw, W. Xu, M. G. Suero and M. J. Gaunt, *J. Am. Chem. Soc.*, 2013, **135**, 12532.
- (a) J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem., Int. Ed.*, 2009, **48**, 9346; (b) J. P. Brand, C. Chevalley and J. Waser, *Beilstein J. Org. Chem.*, 2011, **7**, 565–569; (c) G. L. Tolnai, S. Ganss, J. P. Brand and J. Waser, *Org. Lett.*, 2013, **15**, 112; (d) R. J. Phipps, N. P. Grimster and M. J. Gaunt, *J. Am. Chem. Soc.*, 2008, **130**, 8172; (e) N. R. Deprez, D. Kalyani, A. Krause and M. S. Sanford, *J. Am. Chem. Soc.*, 2006, **128**, 4972.
- T. Umemoto and Y. Gotoh, *J. Fluorine Chem.*, 1985, **28**, 235.
- (a) T. Umemoto and Y. Gotoh, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2008; (b) V. Montanari and K. Kumar, *J. Am. Chem. Soc.*, 2004, **126**, 9528; (c) V. Montanari and G. Resnati, *Tetrahedron Lett.*, 1994, **35**, 8015.
- (a) T. Umemoto and Y. Gotoh, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3823; (b) T. Umemoto and Y. Gotoh, *J. Fluorine Chem.*, 1986, **31**, 231.
- For further data and detailed optimization results see ESI†.

