



Cite this: *Chem. Commun.*, 2016, 52, 5997

Received 15th March 2016,  
Accepted 31st March 2016

DOI: 10.1039/c6cc02284g

www.rsc.org/chemcomm

# Radical perfluoroalkylation – easy access to 2-perfluoroalkylindol-3-imines via electron catalysis†

Dirk Leifert, Denis G. Artiukhin, Johannes Neugebauer, Anzhela Galstyan, Cristian Alejandro Strassert and Armido Studer\*

**Arylisonitriles (2 equivalents) react with alkyl and perfluoroalkyl radicals to form 2-alkylated indole-3-imines via two sequential additions to the isonitrile moiety followed by homolytic aromatic substitution. The three component reaction comprises three C–C bond formations. The endocyclic imine functionality in the products is more reactive in follow up chemistry and hydrolysis of the exocyclic imine leads to 3-oxindoles that show fluorescence properties.**

Indoles generally show high biological activity<sup>1</sup> and accordingly they are observed to be prominent substructures in many natural products and drug candidates.<sup>2</sup> Therefore, the development of novel methods allowing easy access to indoles and their derivatives is of importance.<sup>3</sup> The introduction of a CF<sub>3</sub> group into a lead compound has become a general strategy to further improve lipophilicity, bioactivity and metabolic stability<sup>4</sup> of the given lead candidate in agrochemical and medicinal chemistry.<sup>5</sup> Along these lines, the synthesis of 2-trifluoromethylindoles has gained great attention recently.<sup>6</sup>

Radical chemistry has become valuable for simple and efficient incorporation of CF<sub>3</sub> groups into various compounds via direct trifluoromethylation.<sup>7</sup> Recently, we<sup>8</sup> and Yu *et al.*<sup>9</sup> introduced the radical trifluoromethylation of 2-isocyanobiphenyls as a practical method for the modular synthesis of 6-trifluoromethylated phenanthridines.<sup>10,11</sup> Isonitriles have also been successfully applied to the preparation of 2-trifluoromethylated indoles **3** via radical trifluoromethylation of 2-isocyanostyrene derivatives **1** with the Togni reagent **2a** (Fig. 1a).<sup>12,13</sup>

The advantages of these radical trifluoromethylation methods over existing processes<sup>6,14</sup> are that transition metals are not required and the introduction of the CF<sub>3</sub> group occurs regioselectively. Moreover, radical chemistry is ideally suited to run cascades allowing for multiple C–C bond formations. Herein we

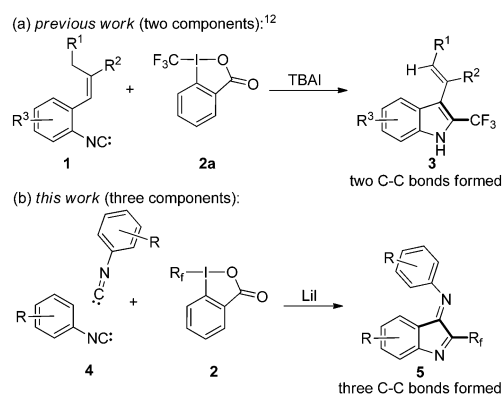


Fig. 1 Strategies towards 2-perfluoroalkyl indoles.

report the preparation of 2-perfluoroalkylindol-3-imines **5** via a three component cascade comprising two subsequent radical additions to isonitriles **4** using reagents of type **2** (Fig. 1b).<sup>15</sup>

4-Methoxyphenylisonitrile (**4a**) was used as a test substrate for optimization (Table 1). Pleasingly, the reaction of **4a** (4.8 equiv.), **2a** (1.0 equiv.) as a CF<sub>3</sub> source and tetrabutylammonium iodide (TBAI, 4.8 mol%) as an initiator at 80 °C in 1,4-dioxane for 22 hours provided 40% of the targeted 2-trifluoromethylindol-3-imine **5a** (Table 1, entry 1). Solvent screening revealed that ethyl acetate among the tested solvents provides the highest yield (Table 1, entries 2–4). We also varied the amount of isonitrile **4a** and found that with 3.8 equiv. the best result is obtained. 90 °C was identified as the ideal reaction temperature (Table 1, entries 6, 8 and 9) and 4.8 mol% of TBAI-initiator was sufficient (54%). Reactions at higher (0.52 molar) or at lower (0.09 molar) concentration provided lower yields (see the ESI,† Table S1). Among the iodide sources tested (LiI, NaI, KI, CsI, MgI<sub>2</sub>, CaI<sub>2</sub>), LiI provided the highest yield (60%) (Table 1, entries 8 and 12 and ESI,† Table S1). Addition of an external base (Li<sub>2</sub>CO<sub>3</sub> or LiOH) did not lead to any further improvement of the yield (Table 1, entries 13 and 14).

Under optimized conditions (Table 1, entry 13) we next investigated the scope and limitations (Fig. 2). Electronic effects strongly influence the reaction outcome and generally better

Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany. E-mail: studer@uni-muenster.de

† Electronic supplementary information (ESI) available: Experimental procedures, and spectroscopic and crystallographic data as well as computational details are included. See DOI: 10.1039/c6cc02284g



Table 1 Optimization studies

Entry	Equiv. (4a)	Init. (mol%)	Solvent	Temp. (°C)	Yield <sup>a</sup> (%)
1	4.8	TBAI (4.8)	Dioxane	80	40
2	4.8	TBAI (4.8)	CHCl <sub>3</sub>	80	40
3	4.8	TBAI (4.8)	MeCN	80	35
4	4.8	TBAI (4.8)	EtOAc	80	41
5	2.9	TBAI (4.8)	EtOAc	80	36
6	3.8	TBAI (4.8)	EtOAc	80	41
7	9.6	TBAI (4.8)	EtOAc	80	19
8	3.8	TBAI (4.8)	EtOAc	90	54
9	3.8	TBAI (4.8)	EtOAc	100	47
10	3.8	TBAI (2.9)	EtOAc	90	54
11	3.8	TBAI (9.6)	EtOAc	90	42
12	3.8	LiI (4.9)	EtOAc	90	60
13	3.8	LiI (4.9)	EtOAc	90	57 <sup>b</sup>
14	3.8	LiI (4.9)	EtOAc	90	58 <sup>c</sup>

<sup>a</sup> Isolated yield (reactions run at 0.26 molar). <sup>b</sup> Addition of Li<sub>2</sub>CO<sub>3</sub> (0.25 mmol). <sup>c</sup> Addition of LiOH (0.25 mmol).

results are obtained for isonitriles bearing electron-donating groups at the *para*-position. The silyloxy-isonitrile **4b** in the reaction with **2a** provided **5b** in 41% and the dimethylamino-derivative **4d** gave **5d** in 39% yield. Alkyl-substituted phenyl isonitriles **4e** and **4f** provided the methyl and the *tert*-butyl derivatives **5e** and **5f** in 32% and 22% yields. The yield further dropped for the methylthyl-isonitrile and the parent phenylisonitrile (see **5c**, **5g**). The lower yields for the electron deficient systems are likely caused by the low stability of the corresponding isonitriles.<sup>16</sup> Reaction with the *m*-MeOC<sub>6</sub>H<sub>4</sub>CN **4h** provided a mixture of the two regioisomers **5h** and **5h'** with a 2.3:1 selectivity. The selectivity was far higher (8:1) for 5-isocyanobenzo[d][1,3]dioxole **4i** to give **5i** as the major isomer.

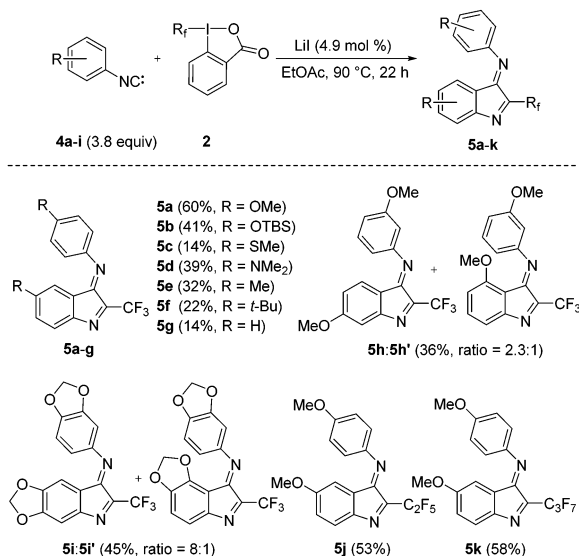


Fig. 2 Various prepared 2-trifluoromethyl or perfluoroalkylindol-3-imines **5a–k** (isolated yields).

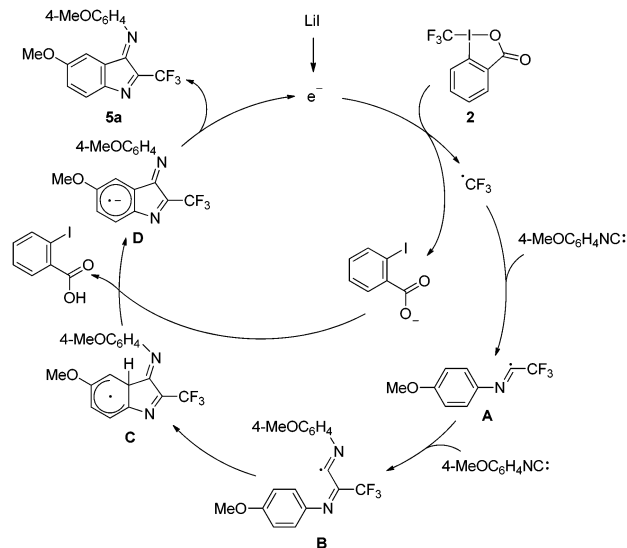


Fig. 3 Suggested mechanism exemplified by the synthesis of **5a**.

Homologues of Togni reagent **2a** bearing longer perfluoroalkyl chains (C<sub>2</sub>F<sub>5</sub> and C<sub>3</sub>F<sub>7</sub>) in the reaction with **4a** gave the indoles **5j** and **5k** in 53% and 58% yields, respectively.

The suggested mechanism comprising a base-promoted homolytic aromatic substitution<sup>17</sup> *via* electron-catalysis<sup>18</sup> is depicted in Fig. 3. The initiation of the cascade likely occurs by reduction of the I(III)-reagent **2** with LiI as a formal electron donor<sup>8,19</sup> to generate a CF<sub>3</sub> radical. It is likely that there is an initial substitution of the carboxylate functionality of **2** by the iodide to give an aryl-I(III)ICF<sub>3</sub>-compound. The I–I bond is weak and upon homolysis the generated iodanyl radical fragments to give a CF<sub>3</sub> radical and 2-iodobenzoate. This CF<sub>3</sub>-radical adds to **4a** to give the imidoyl radical **A**, which further adds to a second isonitrile to generate the imidoyl radical **B**. Cyclization onto the arene of the first aryl isonitrile leads the cyclohexadienyl radical **C**, that gets deprotonated by 2-iodobenzoate<sup>8</sup> to form the radical anion **D**. 2-Iodobenzoate is generated in the chain by reduction of **2**. **D** is an efficient SET reducing reagent which formally liberates an electron giving product **5a** thereby closing the catalytic cycle.<sup>17</sup>

Due to the high values of these indole imines (see below) we decided to develop an alternative non-chain process to the target compounds that uses readily accessible azo compounds as radical precursors (Fig. 4).<sup>11b</sup> After some experimentation we found that heating of isonitrile **4a** (3.8 equiv.) in the presence of AIBN (azobis(isobutyronitrile)) **6a** in benzene at 100 °C provided the 2-cyanoprop-2-yl indole imine **7a** in 81% yield. The yield is calculated on the basis that one equivalent of AIBN is necessary for product formation (AIBN acts as a radical precursor and an oxidant)<sup>20</sup> and that only about 60% of the AIBN-derived radicals escape the solvent cage.<sup>21</sup> In analogy, by using 1,1'-azobis(cyclohexanecarbonitrile) **6b** the indole **7b** was obtained in 78% yield. The yield further improved upon switching to the ester derivative **6c** as a radical precursor to give the indole **7c** in a high yield (92%).

Notably, all of the indole imines **5** and **7** show a very intense colour. For example, the indol-3-imine **5a** with methoxy-substituents



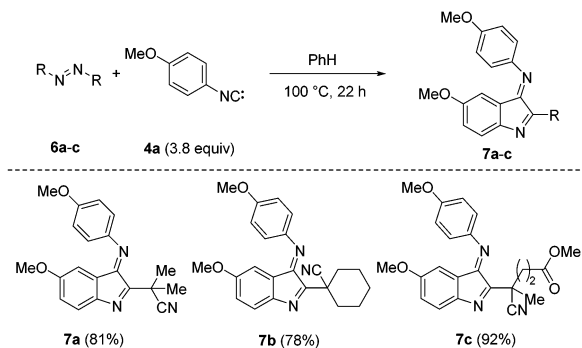


Fig. 4 Synthesis of indole imines using azo compounds.

at the aromatic moiety has a deep red colour ( $\lambda_{\text{max}} = 478 \text{ nm}$ ) and the dimethylamino congener **5d** shows an intense violet colour ( $\lambda_{\text{max}} = 564 \text{ nm}$ ). The UV/vis spectra of these compounds are included in the ESI†. Quantum chemical calculations for these compounds reproduce this difference in absorption very well ( $\lambda_{\text{max}}$  (**5a**) = 479 nm,  $\lambda_{\text{max}}$  (**5d**) = 549 nm with ADC(2)). According to our calculations, these absorption bands are caused by the two lowest-energy singlet-singlet excitations, which are dominated by HOMO  $\rightarrow$  LUMO and (HOMO-1)  $\rightarrow$  LUMO orbital transitions. Their energetic positions are strongly dependent on the electronic nature of the substituents (see the ESI† for details of the calculations).

We next investigated the reactivity of the product indoles using **5a** and **7a** as substrates. Hydrogenation in ethyl acetate at room temperature ( $\text{H}_2$ , Pd(C)) provided the corresponding 3-arylamino-2-(trifluoromethyl)-1H-indole **8a** and 2-methyl-2-(3-(phenylamino)-1H-indol-2-yl)propanenitrile **8b** in 80% and 83% yield, respectively (Fig. 5).

Reaction of **5a** with *para*-toluenesulfonic acid monohydrate (1.0 equiv.) in diethyl ether at an elevated temperature (sealed tube) provided quantitatively half amination **9a**, showing that the endocyclic imine functionality is more reactive (Fig. 6). Hydrolysis of the exocyclic imine can be achieved upon treatment with aqueous HCl (see **10a**, 99%). Butyllithium undergoes addition with complete regioselectivity to the endocyclic imine and subsequent hydrolysis of the remaining imine with aq. HCl leads to 3-oxindoles, as documented by the successful preparation of **11a**, **11d**, and **11e**.<sup>22</sup>

Whereas the parent indole imines **5** and **7** show intense colour but no fluorescence, all 3-oxindoles prepared are photoluminescent.<sup>23</sup> Notably, imine **9a** is not fluorescent indicating that the keto functionality in these compounds is important to attain photoluminescence. For hemiaminal **10a** we observed

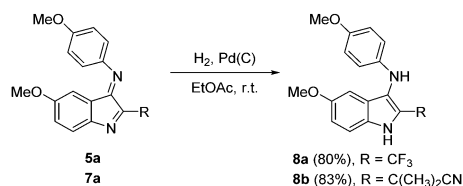


Fig. 5 Hydrogenation of **5a** and **7a**.

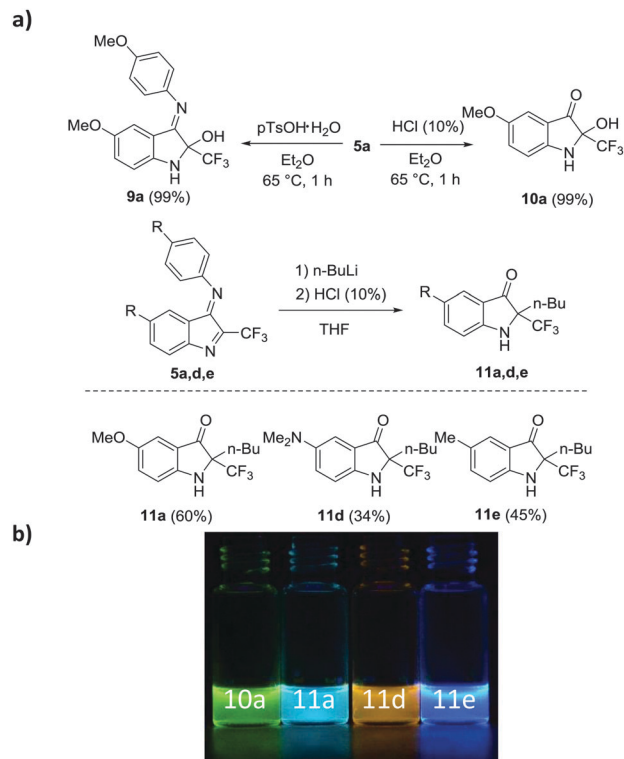


Fig. 6 (a) Follow-up chemistry (b) observed fluorescence under UV excitation (365 nm).

strong green emission and a light blue emission was measured for compound **11a**. As expected, substituents at the indole moiety influence the emission properties: the amino derivative **11d** shows an orange and the methyl derivative **11e** a deep blue emission.

The fluorescent species have been further characterized in terms of absorption spectroscopy and photoluminescence quantum yields, as well as fluorescence excitation, emission, and excited state lifetimes in the solid state, in solution at room temperature and in frozen glassy matrices at 77 K (the results can be found in the ESI†). A summary of the photophysical data is listed in Table 2. The broad, unstructured emission bands reveal a significant charge-transfer character for the excited states, as opposed to vibrationally resolved  $\pi-\pi$  states. Consequently, strong  $\pi$ -donors generate significant red-shifts. Interestingly, no significant blue-shifts can be traced in frozen matrices at 77 K, even though the solvent molecules cannot rearrange their dipole moments to stabilize the excited states. It should be noted that a higher push-pull character has a detrimental effect on the fluorescence quantum yield, which can be related to a stronger solvent coupling both in the excited as well as in the ground state. In the solid state, the quantum yields drop significantly, which can be ascribed to intermolecular interactions (see Table 2).

In summary, we have presented a straightforward access to 2-alkylated indol-3-imines *via* reaction of (perfluoro)alkyl radicals with two equivalents of an aryl isocyanide. The radical cascade comprises three C-C bond formations. As radical precursors perfluoroalkyl-iodine(III) reagents can be used and

Table 2 Summary of photophysical data

		10a	11a	11d	11e
$\lambda_{\text{abs}}$ [nm]		420	408	447	392
$\epsilon$ [ $\text{M}^{-1} \text{cm}^{-1}$ ]		(3309)	(3742)	(361)	(3182)
$\lambda_{\text{em}}$ [nm]		520	488	557	447
	Solution	574	486	579	511
	77 K	501	475	540	450
$\tau$ ( $\pm 0.05$ ) [ns]		14.65	15.08	14.96	8.31
	Solution	1.71	1.74	4.79	2.72
	Solid	0.67	0.90	0.14	9.76
	77 K	21.62	17.58	24.20	12.81
				33.95	6.91
$\Phi_{\text{em}}$ ( $\pm 0.02$ )	Solution	0.36	0.49	0.29	0.58
	Solid	0.02	0.04	0.01	0.03

LiI is applied as the initiator for these electron-catalyzed processes. Alternatively, AIBN or its derivatives can be applied as C-radical precursors. The product imines show intense colour. The value of the method has been documented by some follow-up reactions. Importantly, hydrolysis of the exocyclic imine leads to 3-oxindoles that show fluorescence properties.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

## Notes and references

- 1 J.-H. Lee and J. Lee, *FEMS Microbiol. Rev.*, 2010, **34**, 426.
- 2 (a) J. E. Saxton, *Nat. Prod. Rep.*, 1993, **10**, 349; (b) *The Chemistry of Heterocyclic Compounds*, ed. E. C. Taylor and J. E. Saxton, Wiley-Interscience, New York, 1983/1994, vol. 25; (c) R. Sundberg, *Indoles*, Academic Press, New York, 1996; (d) T. Kawasaki and K. Higuchi, *Nat. Prod. Rep.*, 2005, **22**, 761; (e) N. Saracoglu, *Top. Heterocycl. Chem.*, 2007, **11**, 145; (f) J. J. Li and G. W. Gribble, in *Palladium in Heterocyclic Chemistry*, ed. J. E. Baldwin and F. R. S. M. R. Williams, Pergamon Press, New York, 2000, vol. 20.
- 3 Recent reviews regarding the synthesis and modification of indoles, see: (a) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2005, **105**, 2873; (b) G. R. Humphrey and J. T. Kuethe, *Chem. Rev.*, 2006, **106**, 2875; (c) S. Cacchi and G. Fabrizi, *Chem. Rev.*, 2011, **111**, PR215; (d) N. Yoshikai and Y. Wei, *Asian J. Org. Chem.*, 2013, **2**, 466; (e) X.-F. Xiao, H. Neumann and M. Beller, *Chem. Rev.*, 2013, **113**, 1; (f) A. V. Karchava, F. S. Melkonyan and M. A. Yurovskaya, *Chem. Heterocycl. Compd.*, 2012, **48**, 391; (g) M. Bandini and A. Eichholzer, *Angew. Chem., Int. Ed.*, 2009, **48**, 9608; (h) G. Bartoli, G. Bencivenni and R. Daipozzo, *Chem. Soc. Rev.*, 2010, **39**, 4449. For selected examples, see: (i) S. Kirchberg, R. Fröhlich and A. Studer, *Angew. Chem., Int. Ed.*, 2010, **49**, 4235; (j) V. Ramella, Z. He, C. G. Daniliuc and A. Studer, *Org. Lett.*, 2015, **17**, 664; (k) H. Tokuyama, T. Yamashita, M. T. Reding, Y. Kaburagi and T. Fukuyama, *J. Am. Chem. Soc.*, 1999, **121**, 3791; (l) S. Beaumont, V. Pons, P. Retailleau and R. H. Dauban, *Angew. Chem., Int. Ed.*, 2010, **49**, 1634; (m) T. W. Greulich, C. G. Daniliuc and A. Studer, *Org. Lett.*, 2015, **17**, 254.
- 4 (a) K. Müller, C. Feah and F. Diederich, *Science*, 2007, **317**, 1881; (b) S. Purser, P. R. Moore, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320.
- 5 (a) G. C. B. Harriman, K. G. Carson, D. L. Flynn, M. E. Solomon, Y. Song, B. K. Trivedi, B. D. Roth, C. N. Kolz, L. Pham and K.-L. Sun, *Pat.*, WO2002072549, 2002; (b) M. T. Baker and M. N. Attala, *Pat.*, WO2003070177, 2003; (c) M. A. Akanmu, C. Songkram, H. Kagechika and K. Honda, *Neurosci. Lett.*, 2004, **364**, 199; (d) W. H. Romines, R. S. Kania, J. Lou, M. R. Collins, S. R. Cripps, M. He, R. Zhou, C. L. Palmer and J. G. Deal, *Pat.*, WO2003106462, 2003; (e) Y. Zhou, J. Wang, Z. Gu, S. Wang, W. Zhu, J. L. Aceña, V. A. Soloshonok, K. Izawa and H. Liu, *Chem. Rev.*, 2016, **116**, 422.
- 6 Recent examples: (a) V. M. Muzalevskiy, V. G. Nenajdenko, A. V. Shastin, E. S. Balenkova and G. Haufe, *Tetrahedron*, 2009, **65**, 7553; (b) H. Jiang, Y. Wang, W. Wan and J. Hao, *Tetrahedron*, 2010, **66**, 2746; (c) B. I. Usachev, D. L. Obydenov and V. Y. J. Sosnovskikh, *J. Fluorine Chem.*, 2012, **135**, 278; (d) Z. Chen, J. Zhu, H. Xie, S. Li, Y. Wu and Y. Gong, *Adv. Synth. Catal.*, 2011, **353**, 325.
- 7 (a) W. R. Dolbier Jr., *Chem. Rev.*, 1996, **96**, 1557; (b) W. R. Dolbier Jr., in *Top. Curr. Chem.*, ed. R. D. Chambers, Springer, Berlin, 1997, vol. 192; (c) A. Studer, *Angew. Chem., Int. Ed.*, 2012, **51**, 8950.
- 8 B. Zhang, C. Mück-Lichtenfeld, C. G. Daniliuc and A. Studer, *Angew. Chem., Int. Ed.*, 2013, **52**, 10792.
- 9 Y. Cheng, H. Jiang, Y. Zhang and S. Yu, *Org. Lett.*, 2013, **15**, 5520.
- 10 (a) B. Zhang and A. Studer, *Chem. Soc. Rev.*, 2015, **44**, 3505; (b) I. Ryu, N. Sonoda and D. P. Curran, *Chem. Rev.*, 1996, **96**, 177; (c) M. Tobisu and K. Koh, *Angew. Chem., Int. Ed.*, 2012, **51**, 11363; (d) D. Leifert, C. G. Daniliuc and A. Studer, *Org. Lett.*, 2013, **15**, 6286; (e) H. Jiang, Y. Cheng, R. Wang, M. Zheng, Y. Zhang and S. Yu, *Angew. Chem., Int. Ed.*, 2013, **50**, 13289.
- 11 Isonitriles as radical acceptors: (a) T. Saegusa, Y. Ito, S. Kobayashi and K. Hirota, *J. Am. Chem. Soc.*, 1967, **89**, 2240; (b) D. Nanni, P. Pareschi, C. Rizzaoli, P. Sgarabotto and A. Tundo, *Tetrahedron*, 1995, **51**, 9045; (c) D. P. Curran, S.-B. Ko and H. Josien, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2683; (d) B. Janza and A. Studer, *Org. Lett.*, 2006, **8**, 1875.
- 12 B. Zhang and A. Studer, *Org. Lett.*, 2014, **16**, 1216.
- 13 J. Charpentier, N. Früh and A. Togni, *Chem. Rev.*, 2015, **115**, 650.
- 14 (a) M. S. Wiehn, E. V. Vinogradova and A. Togni, *J. Fluorine Chem.*, 2010, **131**, 951; (b) R. Shimizu, H. Egami, T. Nagi, J. Chae and Y. Hamashima, *Tetrahedron Lett.*, 2010, **51**, 5947; (c) N. Iqbal, S. Choi, E. Ko and E. J. Cho, *Tetrahedron Lett.*, 2012, **53**, 2005; (d) E. Mejía and A. Togni, *ACS Catal.*, 2012, **2**, 521; (e) Y. Girard, J. G. Atkinson, P. C. Belanger, J. J. Fuentes, J. Rokach and C. S. Rooney, *J. Org. Chem.*, 1983, **48**, 3220; (f) D. A. Nagib and D. W. C. MacMillan, *Nature*, 2011, **480**, 224; (g) M. Yoshida, T. Yoshida, M. Kobayashi and N. Kamigata, *J. Chem. Soc., Perkin Trans. 1*, 1989, 909; (h) Q.-Y. Chen and Z.-T. Li, *J. Chem. Soc., Perkin Trans. 1*, 1993, 645; (i) T. Kino, Y. Nagase, Y. Ohtsuka, K. Yamamoto, D. Uruguchi, K. Tokuhisa and T. Yamakawa, *J. Fluorine Chem.*, 2010, **131**, 98.
- 15 There is only a single example on the radical double isonitrile addition. A *t*Bu-radical, derived from *t*BuHgCl, reacts with PhNC in a low yield to 2-*t*-butylindole-3-imine, see: (a) G. A. Russell, R. Rajaratnam and P. Chen, *Acta Chem. Scand.*, 1998, **52**, 528. Non radical process: (b) Y. Tian, L. Tian, C. Li, X. Jia and J. Li, *Org. Lett.*, 2016, **18**, 840.
- 16 C. Grundmann, *Chem. Ber.*, 1958, **91**, 1380.
- 17 (a) A. Studer and D. P. Curran, *Angew. Chem., Int. Ed.*, 2011, **50**, 5018; (b) S. Wertz, D. Leifert and A. Studer, *Org. Lett.*, 2013, **15**, 928.
- 18 (a) A. Studer and D. P. Curran, *Nat. Chem.*, 2014, **6**, 765; (b) A. Studer and D. P. Curran, *Angew. Chem., Int. Ed.*, 2016, **55**, 58.
- 19 D. Leifert and A. Studer, *Org. Lett.*, 2015, **17**, 386.
- 20 Yield is calculated by assuming that one molecule of AIBN leads theoretically to one product molecule, see: A. L. J. Beckwith, V. W. Bowry, W. R. Russell, E. Mann, J. Parr and J. M. D. Storey, *Angew. Chem., Int. Ed.*, 2004, **43**, 95.
- 21 (a) J. Lalevée and J. P. Fouassier, in *Encyclopedia of Radicals in Chemistry, Biology and Materials*, ed. C. Chatgililoglu and A. Studer, Wiley, Chichester, UK, 2012, p. 42; *The Chemistry of Radical Polymerization*, ed. G. Moad and D. H. Solomon, Elsevier, New York, 2006, pp. 60–77; (b) In the corrected yields we are taking into account that in the thermal decomposition of the azo compounds 8 the yield of a free radical is just 60% due to the dimerization in the solvent cage.
- 22 (a) C. Berti and L. Greci, *J. Org. Chem.*, 1981, **46**, 3060; (b) Y. Liu and W. W. McWhorter Jr., *J. Org. Chem.*, 2003, **68**, 2618; (c) W. Ding, Q.-Q. Zhou, J. Xuan, T.-R. Li, L.-Q. Lu and W.-J. Xiao, *Tetrahedron Lett.*, 2014, **55**, 4648.
- 23 (a) Y. Goriya and C. V. Ramana, *Chem. Commun.*, 2013, **49**, 6376; (b) S. Lerch, L.-N. Unkel and M. Brasholz, *Angew. Chem., Int. Ed.*, 2014, **53**, 6558.

