

Note

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Synthesis of 3-Fluoroindoles via Photoredox Catalysis

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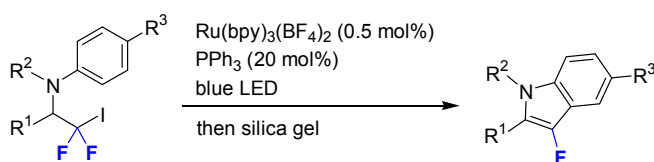
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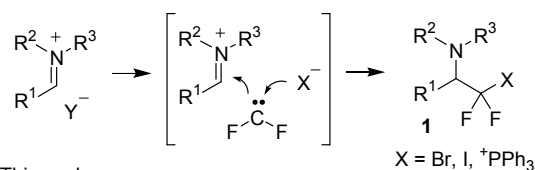
Abstract A method for the synthesis of 3-fluoroindoles from *N*-arylamines substituted with the CF_2I group is described. The reaction is mediated by a ruthenium photocatalyst in the presence of substoichiometric amount of triphenylphosphine upon irradiation with blue light. The starting *N*-arylamines are readily obtained by nucleophilic iododifluoromethylation of iminium ions.

Importance of organofluorine compounds for medicinal chemistry¹ has stimulated the development of methods for their synthesis.² Of particular interest are reactions allowing for assembling of molecules bearing single fluorine atom or a fluorinated group in a specified position from simple building blocks.^{1a,3} Despite significant progress in this field, synthesis of heterocycles substituted with the fluorine in a specific position still may be problematic.⁴ For example, there are no general methods for the synthesis of 3-fluoroindoles. Thus, all reported approaches to 3-fluoroindoles rely on electrophilic fluorination reactions which either are accompanied by overfluorination,⁵ or require biased substrates such 3-stannylindoles⁶ or *ortho*-alkynylanilines.⁷ In this work, we describe a straightforward access to 3-fluoroindoles starting from *N*-aryliminium salts with the fluorine substituent originating from difluorocarbene⁸ (Scheme 1).

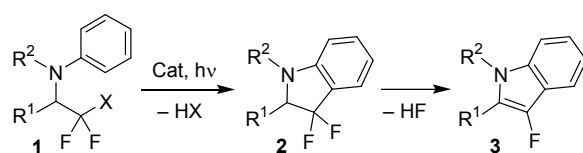
Recently, we reported facile methods of nucleophilic fluoroalkylation of carbonyl compounds and iminium ions affording products containing CF_2X groups,^{9,10} where X is either halogen (Br, I) or a triphenylphosphonium fragment (Scheme 1). It is also known that fluorinated iodides¹¹ and phosphonium salts¹² can serve as sources of fluorinated radicals under photoredox conditions.¹³ Herein, we demonstrate the application of photoredox catalysis to effect cyclization of *N*-aryl-substituted amines **1** ($\text{R}^3 = \text{Ar}$). Difluorinated indolines **2** are the primary products of photoredox processes, whereas subsequent elimination of hydrogen fluoride would lead to the indole system.¹⁴

Scheme 1. Approach to the synthesis of 3-fluoroindoles.

Previous work:



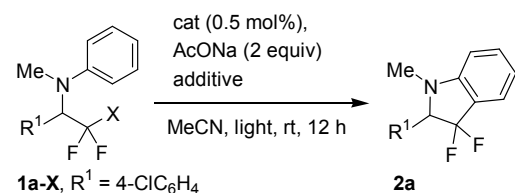
This work:



A series of substrates **1a-X** were evaluated in the presence of photocatalyst (0.5 mol%) irradiating either with blue LED for ruthenium or with UV LED for iridium complexes (Table 1). Reactions were performed in acetonitrile using sodium acetate as basic scavenger, and the mixtures were analyzed by ^{19}F NMR. In reaction of phosphonium salt no product was formed with ruthenium catalyst, whereas *fac*-Ir(ppy)₃ was markedly more efficient (entries 1 and 2). When iodosubstituted substrate **1a-I** was used, traces of product **2a** were observed, with the starting iodide being virtually unconsumed (entries 4 and 5). Surprisingly, addition of 20 mol % of triphenylphosphine to both ruthenium and iridium catalysts had profound effect, and product **2a** was formed in high yields (entries 6 and 10). Ruthenium system was particularly effective affording the product in a virtually quantitative yield. Bromo-substituted starting compound **1a-Br** was less efficient compared to an iodo-counterpart (entries 12 and 13). When Hünig's base, a typical reductive additive in photoredox processes,¹⁵ was used instead of phosphine, the product was formed in low yield (entry 7).

However, with 2 equiv of Hünig's base, complete conversion of starting substrate was noted along with high yield of the product (entry 8). It is likely that acetic acid formed during the reaction scavenges the amine base ($pK_a = 11.51$), whereas less basic phosphine ($pK_a = 2.73$) remains unprotonated and can be employed in substoichiometric amounts.

Table 1. Optimization studies.



no	X	cat. ^a	Additive	yield of 2a , % ^b
1	⁺ PPh ₃	Ru(bpy) ₃ (BF ₄) ₂	–	–
2	⁺ PPh ₃	Ir(ppy) ₃	–	27
3	⁺ PPh ₃	Ru(bpy) ₃ (BF ₄) ₂	PPh ₃ (0.2 equiv)	–
4	I	Ru(bpy) ₃ (BF ₄) ₂	–	–
5	I	Ir(ppy) ₃	–	< 5
6	I	Ru(bpy) ₃ (BF ₄) ₂	PPh ₃ (0.2 equiv)	98
7	I	Ru(bpy) ₃ (BF ₄) ₂	<i>i</i> -Pr ₂ NEt (0.2 equiv)	23
8	I	Ru(bpy) ₃ (BF ₄) ₂	<i>i</i> -Pr ₂ NEt (2.0 equiv)	89
9	I	Ru(bpy) ₃ (BF ₄) ₂	PPh ₃ (0.05 equiv)	16
10	I	Ir(ppy) ₃	PPh ₃ (0.2 equiv)	79
11	I	Ir(ppy) ₃	PPh ₃ (1 equiv)	79
12	Br	Ru(bpy) ₃ (BF ₄) ₂	PPh ₃ (0.2 equiv)	–
13	Br	Ir(ppy) ₃	PPh ₃ (0.2 equiv)	65

^a For Ru-catalyst, blue LED; for Ir-catalyst, 400-nm LED.

^b Determined by ¹⁹F NMR of reaction mixtures with 4-fluorotoluene as an internal standard.

The isolation of difluoroindoline **2a** by chromatography on silica gel was unsuccessful, since a significant portion of the product underwent elimination of hydrogen fluoride leading to corresponding 3-fluoroindole. Surprisingly, numerous attempts to intentionally cause dehydrofluorination by treatment of **2a** with mild bases or acids did not furnish complete conversion. Finally, for the isolation of indole, dehydrofluorination was performed by simple stirring of a solution of the crude indoline with silica gel for 4–16 hours at room temperature.

Accordingly, under the optimized conditions, a series of iododifluoromethylated amines **1** were converted into 3-fluoroindoles **3** (Table 2). Starting substrates **1** were obtained by iododifluoromethylation of *in situ* generated iminium ions using a combination of Me₃SiCF₂Br and NaI as a source of CF₂I carbanion.^{9c,16} Various substrates bearing aromatic, heteroaromatic, as well as aliphatic substituents, worked well in this reaction. Substrates having methoxy or halogen groups provided indoles **3** in high yields. Tetrahydroquinoline derivative furnished tricyclic product **3n**.

Table 2. Synthesis of 3-fluoroindoles 3.

<div><div>$\begin{array}{c} \text{R}^2-\text{N}-\text{R}^3 \\ \\ \text{H} \end{array}$</div><div>or</div><div>$\text{R}^2-\text{OTf}$</div><div>$\text{R}^1-\text{C}(=\text{O})$</div><div>or</div><div>$\text{R}^1-\text{C}(\text{N}=\text{R}^3)=\text{C}$</div></div> <td><div>$\text{Me}_3\text{SiCF}_2\text{Br (2 equiv)}$</div><div>$\text{NaI (3-5 equiv)}$</div><div>$\text{HMPA (1.5-2 equiv)}$</div></td> <td><div>$\text{R}^2-\text{N}-\text{C}_6\text{H}_4-\text{Y}$</div><div>$\text{R}^1-\text{C}(\text{N}=\text{R}^3)-\text{C}(\text{F})_2-\text{I}$</div><div>1</div></td> <td><div>(a) $\text{Ru}(\text{bpy})_3(\text{BF}_4)_2$ (0.5 mol%)</div><div>PPh_3 (0.2 equiv)</div><div>AcONa (2 equiv)</div><div>blue LED, rt, 12–16 h</div><div>(b) work-up</div><div>then silica gel, rt, 4–16 h</div></td> <td><div>$\text{Me}-\text{N}-\text{C}_6\text{H}_3(\text{F})-\text{Y}$</div><div>$\text{R}^1-\text{C}(\text{F})=\text{C}$</div><div>3</div></td>		<div>$\text{Me}_3\text{SiCF}_2\text{Br (2 equiv)}$</div> <div>$\text{NaI (3-5 equiv)}$</div> <div>$\text{HMPA (1.5-2 equiv)}$</div>	<div>$\text{R}^2-\text{N}-\text{C}_6\text{H}_4-\text{Y}$</div> <div>$\text{R}^1-\text{C}(\text{N}=\text{R}^3)-\text{C}(\text{F})_2-\text{I}$</div> <div>1</div>	<div>(a) $\text{Ru}(\text{bpy})_3(\text{BF}_4)_2$ (0.5 mol%)</div> <div>PPh_3 (0.2 equiv)</div> <div>AcONa (2 equiv)</div> <div>blue LED, rt, 12–16 h</div> <div>(b) work-up</div> <div>then silica gel, rt, 4–16 h</div>	<div>$\text{Me}-\text{N}-\text{C}_6\text{H}_3(\text{F})-\text{Y}$</div> <div>$\text{R}^1-\text{C}(\text{F})=\text{C}$</div> <div>3</div>
starting	product	yield, % ^a	starting	product	yield, % ^a
<div></div>	<div></div>	3a 98	<div></div>	<div></div>	3h 98
<div></div>	<div></div>	3b 98	<div></div>	<div></div>	3i 92
<div></div>	<div></div>	3c 89	<div></div>	<div></div>	3j 81
<div></div>	<div></div>	3d 90	<div></div>	<div></div>	3k 90
<div></div>	<div></div>	3e 97	<div></div>	<div></div>	3l 87
<div></div>	<div></div>	3f 80	<div></div>	<div></div>	3m 86
<div></div>	<div></div>	3g 85	<div></div>	<div></div>	3n 88

^a Isolated yield for the conversion of **1** to **3**.

To probe the reaction mechanism, the light/dark experiment for the reaction of **1a-I** under standard conditions was performed (Figure 1). The reaction stops during periods when the light is turned off, and restores when irradiation is resumed. This result excludes a light-initiated chain process and suggests the involvement of the photocatalyst in the reaction.

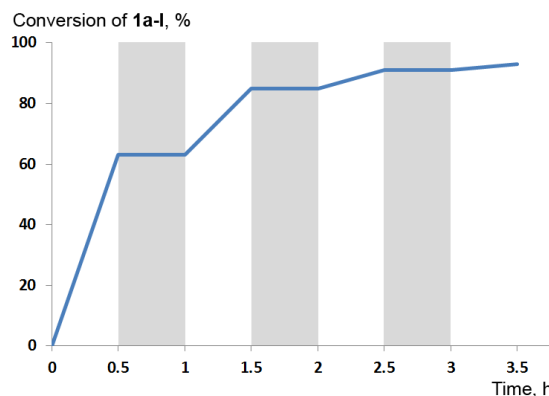
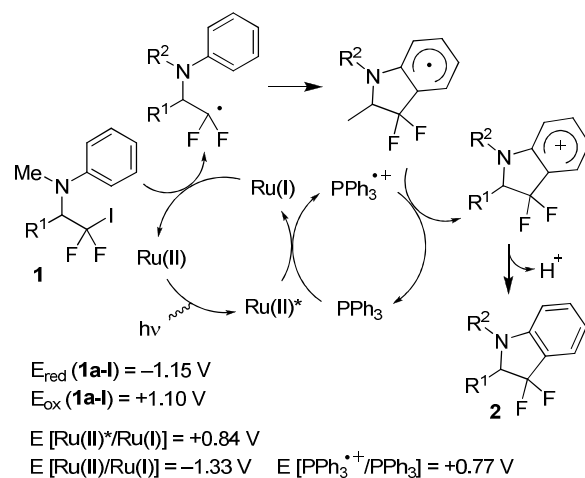


Figure 1. Conversion of **1a-I** in the light/dark sequence. Dark periods are shown in grey.

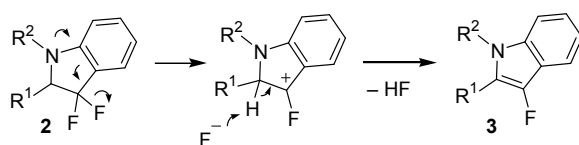
To evaluate the feasibility of electron transfer steps, the redox potentials of compound **1a-I** were measured by cyclic voltammetry (CV). Thus, the reduction potential of -1.15 V corresponding to the CF_2I -fragment and oxidation potential of $+1.10$ V corresponding to the aniline fragment were obtained (all values are given vs. S.C.E., see Supporting Information for CV curves). The oxidation potential of triphenylphosphine was measured to be $+0.77$ V. Taken together, these data allow to propose the mechanism shown in Scheme 2. The reductive quenching of excited photocatalyst by triphenylphosphine provides Ru(I) , which reduces the substrate generating difluorinated radical. Subsequent intramolecular attack of the radical onto aromatic ring followed by oxidation by phosphine radical cation and elimination of the proton affords product **2**.

Scheme 2. Proposed mechanism.



Concerning the mechanism of hydrogen fluoride elimination from indolines **2**, we may propose that it starts from cleavage of the carbon-fluorine bond, which is facilitated by mesomeric donation from *ortho*-nitrogen. Finally, elimination of a proton assisted by the fluoride anion leads to a stable indole system (Scheme 3).

Scheme 3. Proposed mechanism for indole formation.



In summary, a method for the synthesis of 3-fluoroindoles from difluoroiodomethyl-substituted amines under photoredox conditions is described. The use of ruthenium (II) photocatalyst in combination with triphenylphosphine to generate difluorinated radical is the key feature responsible for the reaction efficiency.

Experimental section

General Methods. All reactions were performed under an argon atmosphere. Acetonitrile was distilled from CaH_2 . High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For blue light irradiation, a strip of light emitting diodes (2835-120LED-1M-BLUE 12V) was used. Column chromatography was carried out employing silica gel (230-400

mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or aq. KMnO_4 solution. (Bromodifluoromethyl)trimethylsilane^{16a} was obtained according to a literature procedure.

Measurement of redox potentials by cyclic voltammetry (CV). Voltammetric studies were carried out in a temperature-controlled (25 °C) cell ($V = 10 \text{ mL}$) with the scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$. A platinum wire (diameter 1 mm) in a Teflon casing was used as the working electrode. A saturated calomel electrode (S.C.E.) separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.1 M Et_4NClO_4 in MeCN) was used as the reference electrode. A platinum plate ($S = 3 \text{ cm}^2$) was used as the counter electrode.

Tris(2,2'-bipyridine)ruthenium(II) tetrafluoroborate was obtained by modified literature procedure.¹⁷ A mixture of ruthenium chloride hydroxide (2 g, 9 mmol), hydrochloric acid (5 mL of aqueous 30% solution) and ethanol (10 mL) was refluxed for 3 hours. Then, volatiles were evaporated under vacuum. Chloroform (5 mL) was added to the residue, and volatiles were evaporated under vacuum. The residue was treated with ethylene glycol (30 mL) and 2,2'-bipyridine (4.2 g, 27 mmol), and the mixture was refluxed for 3 hours. The heating was discontinued, and a solution of NaBF_4 (4.9 g, 45 mmol) in water (2 mL) was added. The mixture was cooled and kept overnight in a refrigerator at 0 °C to effect crystallization. The precipitate was filtered off, washed with ethanol ($3 \times 10 \text{ mL}$), and dried affording 5.5 g of red powder (82%). Mp >200 °C. ^1H NMR (300 MHz, $(\text{CD}_3)_2\text{SO}$) δ : 8.82 (d, $J = 8.3 \text{ Hz}$, 6H), 8.22–8.10 (m, 6H), 7.73 (d, $J = 5.0 \text{ Hz}$, 6H), 7.57–7.48 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, $(\text{CD}_3)_2\text{SO}$) δ : 156.6, 151.2, 138.0, 127.9, 124.5, 96.8.

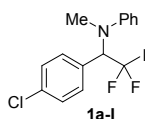
***N*-[2-Bromo-1-(4-chlorophenyl)-2,2-difluoroethyl]-*N*-methyl-*N*-phenylamine (1a-Br).** Prepared according to a literature procedure^{9b} from *p*-chlorobenzaldehyde (2.0 mmol) and *N*-methylaniline (2.2 mmol); yield 526 mg (73 %). Colorless oil. Chromatography: hexane. R_f 0.24 (hexane). ^1H NMR (300 MHz, CDCl_3) δ : 7.37 (s, 4H), 7.34 (dd, $J = 8.7 \text{ Hz}$, 7.3 Hz, 2H), 6.98 (d, $J = 8.2 \text{ Hz}$, 2H), 6.92 (t, $J = 7.3 \text{ Hz}$, 1H), 5.60 (dd, $J = 14.0, 12.6 \text{ Hz}$, 1H), 2.77 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.9, 134.7, 132.0 (t, $J = 1.4 \text{ Hz}$), 130.2 (t, $J = 2.3 \text{ Hz}$), 129.6, 129.0,

123.9 (dd, $J = 316.1, 314.4$ Hz), 119.5, 114.5, 71.4 (dd, $J = 22.7$ Hz, 20.1 Hz), 33.8 (t, $J = 2.3$ Hz).
 ^{19}F NMR (282 MHz, CDCl_3), δ : -49.1 (dd, $J = 165.3, 12.6$ Hz, 1F), -50.1 (dd, $J = 165.3, 14.0$ Hz, 1F). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{BrClF}_2\text{N}$ (M+H) 361.9940; found 361.9954.

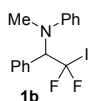
Synthesis of iododifluoromethyl-susbtituted amines.

General procedure 1. Methyl triflate (274 μL , 2.5 mmol) was added to a solution of imine (2 mmol) in acetonitrile (3 mL), and the mixture was stirred at room temperature for 2 h. The mixture was cooled with ice/water bath, and NaI (900 mg, 6 mmol), $\text{Me}_3\text{SiCF}_2\text{Br}$ (650 μL , 4 mmol) and HMPA (696 μL , 4 mmol) were successively added. The cooling bath was removed, and the mixture was stirred at room temperature for 8 h. For the work-up, saturated aq. Na_2CO_3 (2 mL) was added, and the mixture was washed with EtOAc/hexane (1/1, 3 \times 5 mL). The combined organic layers were filtered through Na_2SO_4 , concentrated under vacuum, and the residue was purified by column chromatography.

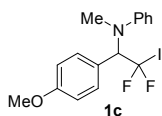
General procedure 2. Me_3SiCl (0.51 mL, 4.0 mmol) was added dropwise to a vigorously stirred mixture of NaI (1.50 g, 10.0 mmol), 1,8-bis(dimethylamino)naphthalene (428 mg, 2.0 mmol), *N*-alkyl-*N*-arylamine (2.0 mmol), aldehyde (2.0 mmol), and acetonitrile (4 mL) at 0 $^\circ\text{C}$. Then, the cooling bath was removed, and the reaction mixture was stirred at room temperature for one hour. The reaction flask was immersed into ice/water cooling bath, $\text{Me}_3\text{SiCF}_2\text{Br}$ (610 mg, 3.0 mmol) and HMPA (523 μL , 3.0 mmol) were added successively. The cooling bath was removed, and the mixture was stirred at room temperature for one hour. The reaction mixture was worked-up by successive addition of hexane/ CH_2Cl_2 mixture (4/1, 8 mL), saturated aqueous Na_2CO_3 (4 mL) and water (4 mL). Organic layer was separated, aqueous layer was washed with hexane/ CH_2Cl_2 mixture (4/1, 2 \times 8 mL). The combined organic layers were washed with 1.0 M aqueous NaHSO_4 (4 mL), while acidic aqueous layer was washed with hexane/ CH_2Cl_2 mixture (4/1, 2 \times 8 mL). All organic layers were combined, filtered through Na_2SO_4 , concentrated under vacuum, and the residue was purified by column chromatography.



N-(1-(4-Chlorophenyl)-2,2-difluoro-2-iodoethyl)-*N*-methylaniline (**1a-I**). According to General procedure 1, from *N*-[(4-chlorophenyl)methylene]-*N*-phenylamine, yield 415 mg (51%). Yellow oil. Chromatography: hexanes/EtOAc, 20/1. R_f 0.60 (hexanes/EtOAc, 20/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.50–7.31 (m, 6H), 7.10–6.90 (m, 3H), 5.63 (t, J = 14.5 Hz, 1H), 2.84 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.7, 134.6, 131.7, 130.4 (t, J = 2.3 Hz), 129.5, 129.0, 119.4, 114.5, 105.1 (dd, J = 323.6, 322.8 Hz), 73.7 (dd, J = 20.7, 19.5 Hz), 34.0 (t, J = 2.3 Hz). ^{19}F NMR (282 MHz, CDCl_3) δ : –42.7 (dd, J = 180.1, 14.5 Hz, 1F), –43.6 (dd, J = 182.3, 14.5 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{14}\text{ClF}_2\text{IN}$ ($\text{M}+\text{H}$) 407.9822; found 407.9812.

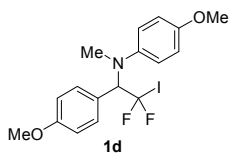


N-(2,2-Difluoro-2-iodo-1-phenylethyl)-*N*-methylaniline (**1b**). According to General procedure 1, from *N*-(phenylmethylene)-*N*-phenylamine, yield 522 mg (70%). Yellow oil. Chromatography: hexanes/EtOAc, 20/1. R_f 0.26 (hexanes/EtOAc, 20/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.53–7.29 (m, 7H), 7.01 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 6.8 Hz, 1H), 5.63 (t, J = 14.8 Hz, 1H), 2.81 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.9, 133.3, 129.5, 129.1 (t, J = 2.3 Hz), 128.8, 128.6, 119.1, 114.4, 105.6 (dd, J = 323.6 Hz, 319.0 Hz), 74.1 (dd, J = 21.8, 19.5 Hz), 34.1 (t, J = 2.3 Hz). ^{19}F NMR (282 MHz, CDCl_3) δ : –42.2 (dd, J = 180.2, 14.8 Hz, 1F), –43.3 (dd, J = 180.2, 14.8 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{15}\text{F}_2\text{IN}$ ($\text{M}+\text{H}$) 374.0212; found 374.0207.

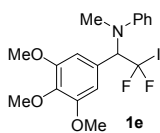


N-(2,2-Difluoro-2-iodo-1-(4-methoxyphenyl)ethyl)-*N*-methylaniline (**1c**). According to General procedure 1, from *N*-[(4-methoxyphenyl)methylene]-*N*-phenylamine, yield 500 mg (62%). Yellow oil. Chromatography: from hexanes/EtOAc, 20/1. R_f 0.46 (hexanes/EtOAc, 20/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.53–7.33 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H), 7.02–6.88 (m, 3H), 5.66 (dd, J =

14.1, 14.1 Hz, 1H), 3.88 (s, 3H), 2.87 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 159.6, 149.9, 130.4 (t, $J = 2.2$ Hz), 129.4, 125.2 (t, $J = 1.9$ Hz), 119.0, 114.4, 114.0, 106.1 (dd, $J = 324.0$, 323.2 Hz), 73.7 (dd, $J = 20.7$, 18.4 Hz), 55.6, 34.0. ^{19}F NMF (282 MHz, CDCl_3) δ : -42.0 (dd, $J = 180.1$, 14.1 Hz, 1F), -43.8 (dd, $J = 178.0$, 14.1 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{17}\text{F}_2\text{INO}$ (M+H) 404.0317; found 404.0310.

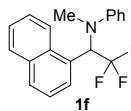


N-(2,2-Difluoro-2-iodo-1-(4-methoxyphenyl)ethyl)-4-methoxy-*N*-methylaniline (**1d**). According to General procedure 1, from *N*-(4-methoxyphenyl)-*N*-[(4-methoxyphenyl)methylene]amine, yield 450 mg (52%). Yellow oil. Chromatography: hexanes/EtOAc, 15/1. R_f 0.26 (hexanes/EtOAc, 15/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.32 (d, $J = 8.5$ Hz, 2H), 7.05–6.81 (m, 6H), 5.34 (t, $J = 15.1$ Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.76 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 159.7, 153.5, 144.7, 130.6 (t, $J = 2.3$ Hz), 125.0, 117.4, 114.7, 114.0, 107.2 (dd, $J = 323.6$, 323.0 Hz), 76.1 (dd, $J = 21.8$, 18.4 Hz), 55.7, 55.4, 34.8. ^{19}F NMF (282 MHz, CDCl_3) δ : -42.8 (dd, $J = 178.0$, 15.1 Hz, 1F), -44.0 (dd, $J = 178.0$, 15.1 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{19}\text{F}_2\text{INO}_2$ (M+H) 434.0423; found 434.0410.



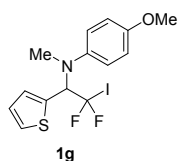
N-[2,2-difluoro-2-iodo-1-(3,4,5-trimethoxyphenyl)ethyl]-*N*-methyl-*N*-phenylamine (**1e**). According to General procedure 2 from 3,4,5-trimethoxybenzaldehyde and *N*-methylaniline, yield 485 mg (52%). Colorless oil. Chromatography: hexane/EtOAc, 7/1. R_f 0.31 (hexane/EtOAc, 5/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.32 (t, $J = 7.8$ Hz, 2H), 6.98 (d, $J = 8.2$ Hz, 2H), 6.89 (t, $J = 7.3$ Hz, 1H), 6.60 (s, 2H), 5.50 (t, $J = 14.4$ Hz, 1H), 3.88 (s, 3H), 3.82 (s, 6H), 2.82 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 153.3, 150.0, 138.5, 129.5, 128.6, 119.3, 114.7, 106.7, 105.5 (t, $J = 323.2$ Hz), 74.2 (dd, $J = 20.7$, 18.9 Hz), 61.0, 56.4, 34.2. ^{19}F NMR (282 MHz, CDCl_3) δ : -41.9 (dd, $J = 180.1$,

14.4 Hz, 1F), -43.4 (dd, $J = 180.1$, 14.4 Hz, 1F). HRMS (ESI): calcd for $C_{18}H_{20}F_2INO_3Na$ ($M+Na$) 486.0348; found 486.0324.



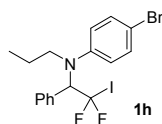
N-[2,2-Difluoro-2-iodo-1-(1-naphthyl)ethyl]-*N*-methyl-*N*-phenylamine (**1f**).

According to General procedure 2 from 1-naphthaldehyde and *N*-methylaniline, yield 637 mg, (75 %). White crystals. Mp 125–126 °C. Chromatography: CH_2Cl_2 /hexane, from 1/7 to 1/3. R_f 0.31 (CH_2Cl_2 /hexane, 1/7). 1H NMR (300 MHz, $CDCl_3$) δ : 8.05 (d, $J = 7.3$ Hz, 1H), 7.92 (t, $J = 7.6$ Hz, 2H), 7.62–7.32 (m, 6H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 7.3$ Hz, 1H), 6.27 (dd, $J_{H-F} = 23.3$ Hz, $J = 5.5$ Hz, 1H), 2.72 (d, $J = 0.9$ Hz, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ : 148.9, 134.1, 132.4 (t, $J = 1.7$ Hz), 129.9 (dd, $J = 5.2$ Hz, 2.3 Hz), 129.6, 129.2, 128.0, 127.9, 127.2, 126.1, 124.8, 123.3, 118.8, 113.39, 113.37, 105.3 (dd, $J = 327.6$ Hz, 316.7 Hz), 69.3 (t, $J = 18.4$ Hz), 34.2 (d, $J = 2.9$ Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ : -39.0 (dd, $J = 180.6$, 5.5 Hz, 1F), -50.0 (dd, $J = 180.6$, 23.3 Hz, 1F). HRMS (ESI): calcd for $C_{19}H_{17}F_2IN$ ($M+H$) 424.0368; found 424.0346.

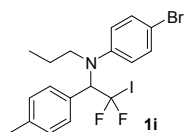


N-(2,2-Difluoro-2-iodo-1-(thiophen-2-yl)ethyl)-4-methoxy-*N*-methylaniline (**1g**).

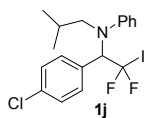
According to General procedure 1 from *N*-(4-methoxyphenyl)-*N*-[thien-2-ylmethylene]amine, yield 417 mg (51%). Yellow crystals. Mp 29–30 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.33 (hexanes/EtOAc, 20/1). 1H NMR (300 MHz, $CDCl_3$) δ : 7.34 (d, $J = 5.6$ Hz, 1H), 7.22–7.17 (m, 1H), 7.06 (t, $J = 4.7$ Hz, 1H), 6.98 (d, $J = 9.2$ Hz, 2H), 6.92 (d, $J = 9.0$ Hz, 2H), 5.57 (dd, $J = 14.7$, 13.3 Hz, 1H), 3.82 (s, 3H), 2.86 (s, 3H). $^{13}C\{H\}$ NMR (75 MHz, $CDCl_3$) δ : 153.8, 144.1, 134.1, 128.3 (t, $J = 2.3$ Hz), 127.0, 126.1, 117.8, 114.7, 105.5 (dd, $J = 323.6$, 323.6 Hz), 72.8 (dd, $J = 21.8$, 19.5 Hz), 55.7, 34.6 (t, $J = 2.3$ Hz). ^{19}F NMF (282 MHz, $CDCl_3$) δ : -43.0 (dd, $J = 180.2$, 13.3 Hz, 1F), -44.7 (dd, $J = 180.1$, 14.7 Hz, 1F). HRMS (ESI): calcd for $C_{14}H_{14}F_2INOS$ (M^+) 408.9803; found 408.9821.



N-(4-Bromophenyl)-*N*-(2,2-difluoro-2-iodo-1-phenylethyl)-*N*-propylamine (**1h**). According to General procedure 2 from benzaldehyde and *N*-(4-bromophenyl)-*N*-propylamine, yield 551 mg (57%). Pale yellow crystals. Mp 90–91 °C. Chromatography: hexane. R_f 0.32 (hexane). ^1H NMR (300 MHz, CDCl_3) δ : 7.39 (d, J = 9.1 Hz, 2H), 7.38 (s, 4H), 6.87 (d, J = 9.1 Hz, 2H), 5.45 (dd, J = 16.9, 12.8 Hz, 1H), 3.15 (ddd, J = 14.9, 9.4, 5.5 Hz, 1H), 2.98 (ddd, J = 14.7, 9.5, 5.2 Hz, 1H), 1.54–1.37 (m, 1H), 1.34–1.13 (m, 1H), 0.72 (t, J = 7.3 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3), δ : 147.4, 133.8 (t, J = 2.3 Hz), 132.2, 129.3 (dd, J = 2.9, 1.7 Hz), 128.8, 128.7, 118.5, 112.0, 105.4 (dd, J = 324.7, 320.7 Hz), 75.6 (dd, J = 20.7, 17.8 Hz), 48.2, 20.1, 11.3. ^{19}F NMR (282 MHz, CDCl_3), δ : –42.1 (dd, J = 179.5, 12.8 Hz, 1F), –45.5 (dd, J = 179.5, 16.9 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{18}\text{BrF}_2\text{IN}$ ($\text{M}+\text{H}$) 481.9610; found 481.9622.

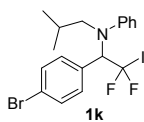


N-(4-Bromophenyl)-*N*-[2,2-difluoro-2-iodo-1-(4-methylphenyl)ethyl]-*N*-propylamine (**1i**). According to General procedure 2 from 4-methylbenzaldehyde and *N*-(4-bromophenyl)-*N*-propylamine, yield 672 mg (68%). Colorless oil. Chromatography: hexane. R_f 0.29 (hexane). ^1H NMR (300 MHz, CDCl_3) δ : 7.39 (d, J = 9.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 9.2 Hz, 2H), 5.41 (dd, J = 17.4, 12.4 Hz, 1H), 3.15 (ddd, J = 15.1, 9.5, 5.6 Hz, 1H), 2.99 (ddd, J = 14.6, 9.5, 5.1 Hz, 1H), 2.38 (s, 3H), 1.54–1.37 (m, 1H), 1.34–1.15 (m, 1H), 0.73 (t, J = 7.6 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3), δ : 147.5, 138.6, 132.1, 130.7 (t, J = 2.3 Hz), 129.4, 129.2 (dd, J = 2.3, 1.7 Hz), 118.5, 111.9, 105.7 (dd, J = 324.4, 320.9 Hz), 75.5 (dd, J = 20.7, 18.4 Hz), 48.2, 21.3, 20.1, 11.4. ^{19}F NMR (282 MHz, CDCl_3), δ : –41.8 (dd, J = 180.1, 12.4 Hz, 1F), –45.7 (dd, J = 180.1, 17.4 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{BrF}_2\text{IN}$ ($\text{M}+\text{H}$) 495.9767; found 495.9792.

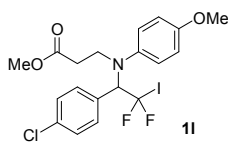


N-[1-(4-Chlorophenyl)-2,2-difluoro-2-iodoethyl]-*N*-isobutyl-*N*-phenylamine (**1j**).

According to General procedure 2 from 4-chlorobenzaldehyde and *N*-isobutylaniline, yield 555 mg (62 %). Colorless oil. Chromatography: hexane. R_f 0.29 (hexane). ^1H NMR (300 MHz, CDCl_3) δ : 7.40–7.34 (m, 6H), 7.08 (d, $J = 7.8$ Hz, 2H), 7.00 (t, $J = 7.3$ Hz, 1H), 5.31 (dd, $J_{\text{H-F}} = 18.5$ Hz, $J = 11.7$ Hz, 1H), 2.90 (dd, $J = 13.5$, 8.0 Hz, 1H), 2.73 (dd, $J = 13.5$, 6.2 Hz, 1H), 1.66–1.85 (m, 1H), 0.89 (d, $J = 6.4$ Hz, 3H), 0.60 (d, $J = 6.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.1, 134.5, 132.3, 131.0, 129.2, 128.8, 121.8, 120.5, 105.6 (dd, $J = 323.5$, 320.7 Hz), 78.8 (t, $J = 19.2$ Hz), 54.3, 25.5, 20.6, 20.3. ^{19}F NMR (282 MHz, CDCl_3) δ : –41.3 (dd, $J = 178.0$, 11.7 Hz, 1F), –46.0 (dd, $J = 178.0$, 18.5 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{ClF}_2\text{IN}$ ($\text{M}+\text{H}$) 450.0292; found 450.0273.

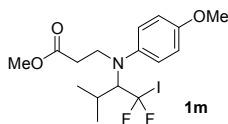


N-[1-(4-Bromophenyl)-2,2-difluoro-2-iodoethyl]-*N*-isobutyl-*N*-phenylamine (**1k**). According to General procedure 2 from 4-bromobenzaldehyde and *N*-isobutylaniline, yield 635 mg (64 %). Colorless oil. Chromatography: hexane. R_f 0.30 (hexane). ^1H NMR (300 MHz, CDCl_3) δ : 7.50 (d, $J = 8.2$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 7.07 (d, $J = 8.2$ Hz, 2H), 7.00 (t, $J = 7.1$ Hz, 1H), 5.27 (dd, $J_{\text{H-F}} = 18.3$, $J = 11.9$ Hz, 1H), 2.88 (dd, $J = 13.5$, 8.0 Hz, 1H), 2.72 (dd, $J = 13.7$, 6.0 Hz, 1H), 1.66–1.83 (m, 1H), 0.88 (d, $J = 6.4$ Hz, 3H), 0.60 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 149.1, 132.8 (t, $J = 2.6$ Hz), 131.8, 131.3 (t, $J = 2.0$ Hz), 129.3, 122.8, 121.9, 120.7, 105.6 (dd, $J = 324.1$, 320.7 Hz), 78.9 (dd, $J = 20.1$, 17.8 Hz), 54.4 (t, $J = 1.7$ Hz), 25.5, 20.6, 20.3. ^{19}F NMR (282 MHz, CDCl_3) δ : –41.3 (dd, $J = 178.0$, 11.9 Hz, 1F), –46.0 (dd, $J = 178.0$, 18.3 Hz, 1F). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{20}\text{BrF}_2\text{IN}$ ($\text{M}+\text{H}$) 495.9767; found 495.9740.



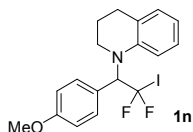
Methyl N-[1-(4-chlorophenyl)-2,2-difluoro-2-iodoethyl]-N-(4-methoxyphenyl)-β-alaninate (1l).

According to General procedure 2 from 4-chlorobenzaldehyde and methyl *N*-(4-methoxyphenyl)-β-alaninate, yield 701 mg (69%). Pale yellow oil. Chromatography: from CH₂Cl₂/hexane (1/2) to CH₂Cl₂. R_f 0.54 (CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ: 7.32 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 9.2 Hz, 2H), 6.83 (d, *J* = 9.2 Hz, 2H), 4.98 (dd, *J* = 15.6 Hz, 14.2 Hz, 2H), 3.79 (s, 3H), 3.61 (s, 3H), 3.60–3.47 (m, 1H), 3.28 (dd, *J* = 13.7, 8.2, 5.5 Hz, 1H), 2.48–2.24 (m, 2H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 172.4, 155.8, 140.6, 134.7, 131.8, 131.0 (t, *J* = 2.0 Hz), 128.8, 123.6, 114.6, 106.6 (dd, *J* = 322.7 Hz, 321.0 Hz), 78.2 (dd, *J* = 20.9 Hz, 18.1 Hz), 55.6, 51.7, 45.0, 33.2. ¹⁹F NMR (282 MHz, CDCl₃) δ: –42.5 (dd, *J* = 179.1, 14.2 Hz, 1F), –45.9 (dd, *J* = 179.1, 15.6 Hz, 1F). HRMS (ESI): calcd for C₁₉H₁₉ClF₂INO₃Na (M+Na) 531.9958; found 531.9940.



Methyl N-{1-[difluoro(iodo)methyl]-2-methylpropyl}-N-(4-methoxyphenyl)-β-alaninate (1m).

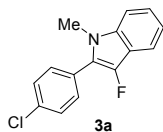
According to General procedure 2 from isobutyraldehyde and methyl *N*-(4-methoxyphenyl)-β-alaninate, yield 287 mg (33 %). Colorless oil. Chromatography: CH₂Cl₂/hexane, from 1/2 to CH₂Cl₂. R_f 0.53 (CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ: 6.92–6.82 (m, 4H), 3.78 (s, 3H), 3.71 (t, *J* = 7.8 Hz, 2H), 3.69 (s, 3H), 3.58 (dd, *J*_{H-F} = 18.8 Hz, *J* = 9.4, 6.6 Hz, 1H), 2.74–2.55 (m, 2H), 2.44–2.26 (m, 1H), 1.17–1.10 (m, 3H), 0.98 (d, *J* = 6.4 Hz, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 172.7, 153.4, 141.9, 117.9, 114.8, 109.8 (dd, *J* = 327.3, 325.0 Hz), 78.0 (t, *J* = 19.8 Hz), 55.7, 51.8, 40.8 (d, *J* = 2.9 Hz), 32.7, 29.6, 21.7, 20.6 (dd, *J* = 6.0, 2.0 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ: –30.7 (d, *J* = 178.0 Hz, 1F), –40.7 (dd, *J* = 178.0, 18.8 Hz, 1F). HRMS (ESI): calcd for C₁₆H₂₃F₂INO₃ (M+H) 442.0685; found 442.0669.



1-[2,2-Difluoro-2-iodo-1-(4-methoxyphenyl)ethyl]-1,2,3,4-tetrahydroquinoline (1n). According to General procedure 2 from 4-methoxybenzaldehyde and 1,2,3,4-tetrahydroquinoline, yield 439 mg

(51%). Pale yellow oil. Chromatography: CH₂Cl₂/hexane, 1/2. R_f 0.42 (CH₂Cl₂/hexane, 1/2). ¹H NMR (300 MHz, CDCl₃) δ: 7.39 (d, *J* = 8.7 Hz, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 5.65 (dd, *J* = 17.4, 12.4 Hz, 1H), 3.84 (s, 3H), 3.32 (ddd, *J* = 11.2, 8.1, 3.1 Hz, 1H), 3.05 (ddd, *J* = 11.2, 7.7, 3.5 Hz, 1H), 2.85–2.63 (m, 2H), 1.94–1.79 (m, 1H), 1.68–1.54 (m, 1H). ¹³C{¹H} NMR (75 MHz, CDCl₃), δ: 159.7, 144.9, 130.7 (dd, *J* = 2.9 Hz, 1.7 Hz), 130.0, 127.3, 125.5 (t, *J* = 2.3 Hz), 123.8, 117.8, 114.1, 112.1 (d, *J* = 2.3 Hz), 106.0 (dd, *J* = 324.7, 322.4 Hz), 71.6 (dd, *J* = 20.7, 18.4 Hz), 55.4, 44.8 (t, *J* = 2.0 Hz), 28.3, 21.8. ¹⁹F NMR (282 MHz, CDCl₃), δ: –41.4 (dd, *J* = 180.1, 12.4 Hz, 1F), –44.8 (dd, *J* = 178.0, 17.4 Hz, 1F). HRMS (ESI): calcd for C₁₈H₁₉F₂INO (M+H) 430.0474; found 430.0463.

Synthesis of indoles 3 (General procedure 3). A test tube containing sodium acetate (82 mg, 1 mmol) and triphenylphosphine (26.2 mg, 0.1 mmol) was evacuated and filled with argon. Then, a solution of iodide **1** (0.5 mmol) in acetonitrile (2 mL) was injected, and Ru(bpy)₃(BF₄)₂ (2 mg) was added, and the mixture was irradiated with a strip of blue LED during 12–16 h (since diodes provide heat when working, the reaction tube was immersed into a glass vessel cooled with circulating room temperature water; the cooling vessel was wrapped with the LED strip). For the work-up, water (2 mL) was added, and the mixture was washed with EtOAc/hexane (1/2, 3×5 mL). The organic phases were combined, silica gel (5 g) was added, and the mixture was stirred for 4–14 h at room temperature (TLC control). The solvent was evaporated to dryness under vacuum, the residual silica gel was transferred onto packed chromatography column followed by elution.

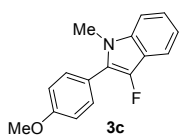


2-(4-Chlorophenyl)-3-fluoro-1-methyl-1H-indole (3a). Reaction time 12 h; treatment with silica gel 4 h; yield 126 mg (97%). White crystals. Mp 112–114 °C. Chromatography: hexanes/EtOAc, 15/1. R_f 0.35 (hexanes/EtOAc). ¹H NMR (300 MHz, CDCl₃) δ: 7.66 (d, *J* = 7.8 Hz, 1H), 7.57–7.41 (m, 4H), 7.40–7.24 (m, 2H), 7.24–7.14 (m, 1H), 3.68 (s, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ:

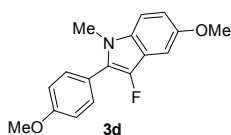
142.2 (d, $J = 245.5$ Hz), 134.3 (d, $J = 3.4$ Hz), 131.1 (d, $J = 2.3$ Hz), 127.5 (d, $J = 3.4$ Hz), 125.2, 122.5 (d, $J = 20.7$ Hz), 121.5 (d, $J = 15.0$ Hz), 120.1, 117.1 (d, $J = 2.3$ Hz), 116.8, 109.8 (d, $J = 2.3$ Hz), 31.2. ^{19}F NMF (282 MHz, CDCl_3) δ : -175.6 (s, 1F). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{12}\text{FCIN}$ (M+H) 260.0623; found 260.0637.



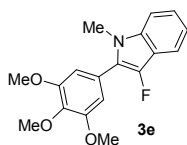
3-Fluoro-1-methyl-2-phenyl-1H-indol (3b). Reaction time 12 h; treatment with silica gel 4 h; yield 110 mg (98%). White crystals. Mp 73–75 °C. Chromatography: hexanes/EtOAc, 15/1. R_f 0.33 (hexanes/EtOAc, 15/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.88–7.12 (m, 9H), 3.73 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 141.9 (d, $J = 245.5$ Hz), 134.0 (d, $J = 5.7$ Hz), 129.9, 129.0 (d, $J = 3.4$ Hz), 128.8, 128.2, 123.7 (d, $J = 20.7$ Hz), 122.8, 119.9, 117.1, 116.8 (d, $J = 3.4$ Hz), 109.7 (d, $J = 2.3$ Hz), 31.1. ^{19}F NMF (282 MHz, CDCl_3) δ : -176.3 (s, 1F). HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{FN}$ (M+H) 226.1017; found 226.1027.



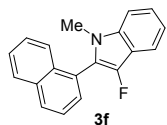
3-Fluoro-2-(4-methoxyphenyl)-1-methyl-1H-indole (3c). Reaction time 12 h; treatment with silica gel 4 h; yield 114 mg (89%). White crystals. Mp 110–112 °C. Chromatography: hexanes/EtOAc, 20/1. R_f 0.46 (hexanes/EtOAc, 20/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.65 (d, $J = 8.5$ Hz, 1H), 7.47 (d, $J = 8.9$ Hz, 2H), 7.39–7.12 (m, 3H), 7.06 (d, $J = 8.2$ Hz, 2H), 3.89 (s, 3H), 3.67 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 159.7, 141.4 (d, $J = 243.2$ Hz), 133.7 (d, $J = 5.7$ Hz), 131.3 (d, $J = 2.3$ Hz), 123.6 (d, $J = 21.8$ Hz), 122.5, 121.4 (d, $J = 3.4$ Hz), 119.8, 117.0 (d, $J = 16.1$ Hz), 116.7 (d, $J = 3.5$ Hz), 114.4, 109.6, 55.5, 31.0. ^{19}F NMF (282 MHz, CDCl_3) δ : -177.3 (s, 1F). Calcd for $\text{C}_{16}\text{H}_{14}\text{FNO}$ (255.29) C, 75.28; H, 5.53; N, 5.49. Found: C, 75.39; H, 5.53; N, 5.50.



3-Fluoro-5-methoxy-2-(4-methoxyphenyl)-1-methyl-1H-indole (3d). Reaction time 12 h; treatment with silica gel 4 h; yield 128 mg (90%). White crystals. Mp 99–100 °C. Chromatography: hexanes/EtOAc, 10/1. R_f 0.26 (hexanes/EtOAc, 10/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.46 (d, J = 8.2 Hz, 2H), 7.29–7.18 (m, 1H), 7.13–7.00 (m, 3H), 6.88 (d, J = 9.0 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.64 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (50 MHz, CDCl_3) δ : 159.6, 154.4, 141.6 (d, J = 241.3 Hz), 131.2, 129.3 (d, J = 5.7 Hz), 124.3 (d, J = 21.3 Hz), 121.5 (d, J = 4.3 Hz), 116.9 (d, J = 15.6 Hz), 114.3, 113.2, 110.7, 97.8 (d, J = 2.8 Hz), 56.0, 55.4, 31.0. ^{19}F NMF (282 MHz, CDCl_3) δ : –177.6 (s, 1F). Calcd for $\text{C}_{17}\text{H}_{16}\text{FNO}_2$ (285.31) C, 71.56; H, 5.65; N, 4.91; Found: C, 71.62; H, 5.63; N, 5.00.

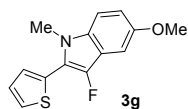


3-Fluoro-1-methyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (3e). Reaction time 12 h; treatment with silica gel 4 h; yield 153 mg (97%). White crystals. Mp 136–137 °C. Chromatography: hexanes/EtOAc, 5/1. R_f 0.34 (hexanes/EtOAc, 5/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.65 (d, J = 8.6 Hz, 1H), 7.39–7.24 (m, 2H), 7.21–7.14 (m, 1H), 6.74 (s, 2H), 3.94 (s, 3H), 3.93 (s, 6H), 3.70 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (50 MHz, CDCl_3) δ : 153.5, 141.6 (d, J = 244.4 Hz), 124.3 (d, J = 3.5 Hz), 123.9, 123.6 (d, J = 20.7 Hz), 122.8, 116.8 (d, J = 16.1 Hz), 116.6 (d, J = 2.3 Hz), 109.6 (d, J = 2.3 Hz), 109.1, 107.4, 105.8, 61.0, 56.3, 31.0. ^{19}F NMF (282 MHz, CDCl_3) δ : –175.9 (s, 1F). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{19}\text{FNO}_3$ (M+H) 316.1343; found 316.1338.

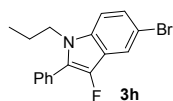


3-Fluoro-1-methyl-2-(naphthalen-1-yl)-1H-indole (3f). Reaction time 16 h; treatment with silica gel 14 h; yield 110 mg (80%). Light yellow crystals. Mp 111–112 °C. Chromatography: hexanes/ CH_2Cl_2 , 10/1. R_f 0.32 (hexanes/ CH_2Cl_2 , 10/1). ^1H NMR (300 MHz, CDCl_3) δ : 8.11–7.89 (m, 2H), 7.77 (d, J = 7.5 Hz, 2H), 7.71–7.19 (m, 7H), 3.50 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 142.3 (d, J = 245.5 Hz), 133.9, 133.8, 132.9, 130.0, 129.7, 128.6, 127.0, 126.4 (d, J = 2.3 Hz), 126.3, 126.0, 125.4, 122.7, 121.9 (d, J = 23.0 Hz), 119.9, 117.0 (d, J = 2.3 Hz), 116.9 (d, J = 16.1

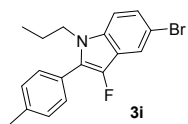
Hz), 109.7, 30.7. ^{19}F NMF (282 MHz, CDCl_3) δ : -174.3 (s, 1F). HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{15}\text{FN}$ (M+H) 276.1186; found 276.1183.



3-Fluoro-5-methoxy-1-(thiophen-2-yl)-1H-indole (3g). Reaction time 12 h; treatment with silica gel 4 h; yield 111 mg (85%). Yellow crystals. Mp 80–81 °C. Chromatography: hexanes/EtOAc, 15/1. R_f 0.30 (hexanes/EtOAc, 15/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.49 (d, J = 5.1 Hz, 1H), 7.31 (d, J = 3.3 Hz, 1H), 7.25–7.18 (m, 2H), 7.08 (d, J = 1.8 Hz, 1H), 6.96 (dd, J = 9.0, 2.5 Hz, 1H), 3.91 (s, 3H), 3.76 (s, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (50 MHz, CDCl_3) δ : 154.4, 142.2 (d, J = 245.5 Hz), 129.8 (d, J = 5.0 Hz), 129.5 (d, J = 5.7 Hz), 127.9 (d, J = 3.4 Hz), 127.6, 126.8, 118.0 (d, J = 20.7 Hz), 116.4 (d, J = 14.9 Hz), 114.2, 110.7, 97.8 (d, J = 2.3 Hz), 55.9, 31.1. ^{19}F NMF (282 MHz, CDCl_3) δ : -172.0 (s, 1F). HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{13}\text{FNOS}$ (M+H); 262.0696; found 262.0692.

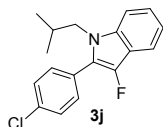


5-Bromo-3-fluoro-2-phenyl-1-propyl-1H-indole (3h). Reaction time 12 h; treatment with silica gel 4 h; yield 163 mg (98%). Yellow oil. Chromatography: hexanes/ CH_2Cl_2 , 20/1. R_f 0.32 (hexanes/ CH_2Cl_2 , 20/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.81 (d, J = 1.9 Hz, 1H), 7.63–7.42 (m, 5H), 7.35 (dd, J = 8.0 Hz, 2.2 Hz, 1H), 7.25 (dd, J = 9.2, 2.8 Hz, 1H), 4.06 (t, J = 7.2 Hz, 2H), 1.65 (sext, J = 7.8 Hz, 2H), 0.75 (t, J = 7.2 Hz, 3H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 141.0 (d, J = 245.5 Hz), 131.8 (d, J = 4.6 Hz), 139.9, 128.9, 128.8, 128.6, 125.5, 124.8 (d, J = 19.5 Hz), 119.4 (d, J = 3.4 Hz), 118.6 (d, J = 16.1 Hz), 113.0, 111.8, 45.7, 23.3, 11.3. ^{19}F NMF (282 MHz, CDCl_3) δ : -175.8 (s, 1F). HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{16}\text{FNBr}$ (M+H) 334.0425; found 334.0420.

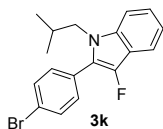


5-Bromo-3-fluoro-1-propyl-2-(p-tolyl)-1H-indole (3i). Reaction time 12 h; treatment with silica gel 4 h; yield 159 mg (92%). Yellow oil. Chromatography: hexanes/ CH_2Cl_2 , 20/1. R_f 0.36

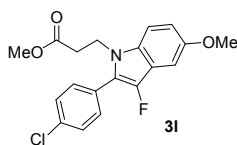
(hexanes/CH₂Cl₂, 20/1). ¹H NMR (300 MHz, CDCl₃) δ: 7.83 (d, *J* = 2.4 Hz, 1H), 7.48–7.31 (m, 5H), 7.25 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H), 4.07 (t, *J* = 7.7 Hz, 2H), 2.49 (s, 3H), 1.67 (sext, *J* = 7.4 Hz, 2H), 0.78 (t, *J* = 6.8 Hz, 3H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 140.6 (d, *J* = 244.4 Hz), 138.6, 131.7 (d, *J* = 5.7 Hz), 129.8, 129.6, 125.8 (d, *J* = 3.4 Hz), 125.3, 124.9 (d, *J* = 20.7 Hz), 119.2 (d, *J* = 3.4 Hz), 118.7 (d, *J* = 14.9 Hz), 112.9, 111.7, 45.6, 23.3, 21.4, 11.2. ¹⁹F NMF (282 MHz, CDCl₃) δ: –176.0 (s, 1F). HRMS (ESI): calcd for C₁₈H₁₈FNBr (M+H) 346.0601; found 346.0599.



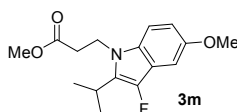
2-(4-Chlorophenyl)-3-fluoro-1-isobutyl-1H-indole (3j). Reaction time 14 h; treatment with silica gel 4 h; yield 122 mg (81%). Pale yellow oil. Chromatography: hexanes. R_f 0.25 (hexanes). ¹H NMR (300 MHz, CDCl₃) δ: 7.75 (d, *J* = 8.3 Hz, 1H), 7.62–7.16 (m, 7H), 4.01 (d, *J* = 7.6 Hz, 2H), 2.11–1.93 (m, 1H), 0.73 (d, *J* = 6.6 Hz, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 142.3 (d, *J* = 245.5 Hz), 134.2, 133.7 (d, *J* = 5.7 Hz), 131.3, 129.1, 128.0 (d, *J* = 3.4 Hz), 122.9, 122.5 (d, *J* = 19.5 Hz), 120.0, 117.0 (d, *J* = 16.1 Hz), 116.9 (d, *J* = 2.3 Hz), 110.6, 51.2, 29.2, 20.1. ¹⁹F NMF (282 MHz, CDCl₃) δ: –175.7 (s, 1F). HRMS (ESI): calcd for C₁₈H₁₇FCIN (M) 301.1028; found 301.1029.



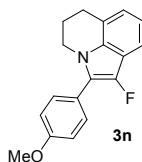
2-(4-Bromophenyl)-3-fluoro-1-isobutyl-1H-indole (3k). Reaction time 15 h; treatment with silica gel 4 h; yield 156 mg (90%). Yellow oil. Chromatography: hexanes/CH₂Cl₂, 20/1. R_f 0.38 (hexanes/CH₂Cl₂, 20/1). ¹H NMR (300 MHz, CDCl₃) δ: 7.78–7.62 (m, 3H), 7.48–7.38 (m, 3H), 7.33 (t, *J* = 6.7 Hz, 1H), 6.23 (t, *J* = 7.7 Hz, 1H), 4.00 (d, *J* = 7.4 Hz, 2H), 2.10–1.91 (m, 1H), 0.71 (d, *J* = 6.0 Hz, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃) δ: 142.3 (d, *J* = 245.5 Hz), 133.7 (d, *J* = 5.7 Hz), 132.0, 131.4, 128.5 (d, *J* = 3.4 Hz), 122.9, 122.4 (d, *J* = 20.6 Hz), 122.4, 120.0, 117.0 (d, *J* = 16.1 Hz), 116.9 (d, *J* = 2.3 Hz), 110.6, 51.1, 29.1, 20.0. ¹⁹F NMF (282 MHz, CDCl₃) δ: –175.6 (s, 1F). HRMS (ESI): calcd for C₁₈H₁₈FNBr (M+H) 346.0601; found 346.0607.



Methyl 3-[2-(chlorophenyl)-3-fluoro-5-methoxy-1H-indol-1-yl]propanoate (3l). Reaction time 12 h; treatment with silica gel 4 h; yield 157 mg (87%). Yellow crystals. Mp 66–67 °C. Chromatography: hexanes/EtOAc, 5/1. R_f 0.27 (hexanes/EtOAc, 5/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.40–7.28 (m, 4H), 7.16 (dd, $J = 9.2, 2.7$ Hz, 1H), 6.95 (d, $J = 2.8$ Hz, 1H), 6.83 (dd, $J = 9.2, 2.8$ Hz, 1H), 4.27 (t, $J = 7.3$ Hz, 2H), 3.75 (s, 3H), 3.44 (s, 3H), 2.37 (t, $J = 7.3$ Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 171.1, 154.6, 142.6 (d, $J = 246.7$ Hz), 134.4, 130.8 (d, $J = 2.3$ Hz), 129.2, 128.8 (d, $J = 5.7$ Hz), 127.3 (d, $J = 3.4$ Hz), 122.3 (d, $J = 19.5$ Hz), 117.7 (d, $J = 15.0$ Hz), 114.2, 111.2, 98.1 (d, $J = 2.3$ Hz), 55.7, 51.8, 39.8, 34.1. ^{19}F NMR (282 MHz, CDCl_3) δ : –174.4 (s, 1F). HRMS (ESI): calcd for $\text{C}_{19}\text{H}_{18}\text{ClFNO}_3$ (M+H) 362.0954; found 362.0943.



Methyl 3-(3-fluoro-2-isopropyl-5-methoxy-1H-indol-1-yl)propanoate (3m). Reaction time 12 h; treatment with silica gel was omitted since the indole was formed directly after the reaction; yield 126 mg (86%). Yellow oil. Chromatography: hexanes/EtOAc, 10/1. R_f 0.28 (hexanes/EtOAc, 10/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.16 (dd, $J = 9.1, 2.3$ Hz, 1H), 6.76 (d, $J = 2.3$ Hz, 1H), 6.71 (dd, $J = 9.1, 2.6$ Hz, 1H), 4.35 (t, $J = 7.3$ Hz, 2H), 3.85 (s, 3H), 3.69 (s, 3H), 3.15–3.99 (m, 1H), 2.69 (t, $J = 7.8$ Hz, 2H), 1.43 (d, $J = 7.5$ Hz, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 171.5, 154.2, 141.7 (d, $J = 239.8$ Hz), 128.2, 127.9, 126.8 (d, $J = 5.7$ Hz), 117.8 (d, $J = 16.1$ Hz), 112.3, 110.2 (d, $J = 2.3$ Hz), 97.8, 55.9, 52.0, 39.0, 25.2 (d, $J = 3.4$ Hz), 21.8 (d, $J = 3.4$ Hz). ^{19}F NMR (282 MHz, CDCl_3) δ : –175.5 (s, 1F). HRMS (ESI): calcd for $\text{C}_{16}\text{H}_{20}\text{FNO}_3\text{Na}$ (M+Na) 316.1319; found 316.1317.



1-Fluoro-2-(4-methoxyphenyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quimoline (3n). Reaction time 12 h; treatment with silica gel 4 h; yield 124 mg (88%). White crystals. Mp 126–127 °C. Chromatography: hexanes/EtOAc, 15/1. R_f 0.35 (hexanes/EtOAc, 15/1). ^1H NMR (300 MHz, CDCl_3) δ : 7.57–7.40 (m, 3H), 7.14–7.00 (m, 3H), 6.95 (d, J = 7.1 Hz, 1H), 4.09 (t, J = 5.5 Hz, 2H), 3.89 (s, 3H), 3.03 (t, J = 6.0 Hz, 2H), 2.23 (quint, J = 6.0 Hz, 2H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3) δ : 159.5, 141.3 (d, J = 244.2 Hz), 130.5 (d, J = 2.3 Hz), 122.3 (d, J = 21.3 Hz), 121.7 (d, J = 2.3 Hz), 121.6, 119.9, 119.3, 114.4, 114.2 (d, J = 2.3 Hz), 55.5, 43.1, 25.1, 23.1. ^{19}F NMR (282 MHz, CDCl_3) δ : –177.0 (s, 1F). HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{17}\text{FNO}$ ($\text{M}+\text{H}$) 282.1289; found 282.1299.

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Supporting Information

Copies of NMR spectra for all compounds and CV curves for **1a-I**, $\text{Ru}(\text{bpy})_3(\text{BF}_4)_2$ and PPh_3 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, 37, 320–330. (b) Wang, J.; Sanchez-Roselló, M.; Aceña, J. L.; del Pozo, C.; Sorochinsky, A. E.; Fustero, S.; Soloshonok, V. A.; Liu, H. *Chem. Rev.* **2014**, 114, 2432–2506. (c) Zhou, Y.; Wang, J.; Gu, Z.; Wang, S.; Zhu, W.; Aceña, J. L.; Soloshonok, V. A.; Izawa, K.; Liu, H. *Chem. Rev.* **2016**, 116, 422–518.
- (2) (a) Liang, T.; Neumann, C. N.; Ritter, T. *Angew. Chem. Int. Ed.* **2013**, 52, 8214–8264. (b) Shimizu, M.; Hiyama, T. *Angew. Chem. Int. Ed.* **2005**, 44, 214–231. (c) See special issue of *Chem. Rev.* devoted to fluorine chemistry: *Chem. Rev.* **2015**, 115, 563–1306.
- (3) Campbell, M. G.; Ritter, T. *Org. Proc. Res. Dev.* **2014**, 18, 474–480.

- (4) (a) *Fluorine in Heterocyclic Chemistry*, Volumes 1,2; Nenajdenko, V., Ed.; Springer International Publishing: Cham, 2014. (b) Petrov, V. A. *Fluorinated Heterocyclic Compounds. Synthesis, Chemistry and Applications*; John Wiley & Sons: Hoboken, 2009.
- (5) (a) Lin, R.; Ding, S.; Shi, Z.; Jiao, N. *Org. Lett.* **2011**, *13*, 4498–4501. (b) Alcaide, B.; Almendros, P.; Cembellin, S.; Martinez del Campo, T.; Munoz, A. *Chem. Commun.* **2016**, *52*, 6813–6816. (c) Nguyen, T. M.; Duong, H. A.; Richard, J.-A.; Johannes, C. W.; Pincheng, F.; Kwong Jia Ye, D.; Shuying, E. L. *Chem. Commun.* **2013**, *49*, 10602–10604. (d) Fong, J. Z. M.; Choo, S. S. S.; Richard, J.-A.; Garland, M. V.; Guo, L.; Johannes, C. W.; Nguyen, T. M. *Eur. J. Org. Chem.* **2015**, *2015*, 995–1006.
- (6) Hodson, H. F.; Madge, D. J.; Slawin, A. N. Z.; Widdowson, D. A.; Williams, D. J. *Tetrahedron* **1994**, *50*, 1899–1906.
- (7) (a) Yang, L.; Ma, Y.; Song, F.; You, J. *Chem. Commun.* **2014**, *50*, 3024–3026. (b) Arcadi, A.; Pietropaolo, E.; Alvino, A.; Michelet, V. r. *Beilstein J. Org. Chem.* **2014**, *10*, 449–458.
- (8) For use of difluorocarbene as a building block, see: Ni, C.; Hu, J. *Synthesis* **2014**, *46*, 842–863.
- (9) (a) Kosobokov, M. D.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2014**, *16*, 3784–3787. (b) Tsymbal, A. V.; Kosobokov, M. D.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2014**, *79*, 7831–7835. (c) Levin, V. V.; Smirnov, V. O.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2015**, *80*, 9349–9353. (d) Levin, V. V.; Trifonov, A. L.; Zemtsov, A. A.; Struchkova, M. I.; Arkhipov, D. E.; Dilman, A. D. *Org. Lett.* **2014**, *16*, 6256–6259. (e) Trifonov, A. L.; Zemtsov, A. A.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2016**, *18*, 3458–3461.
- (10) For recent reports from our group on nucleophilic fluoroalkylation, see (a) Fedorov, O. V.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2016**, *81*, 9455–9460. (b) Maslov, A. S.; Smirnov, V. O.; Struchkova, M. I.; Arkhipov, D. E.; Dilman, A. D. *Tetrahedron Lett.* **2015**, *56*, 5048–5050. (c) Dilman, A. D.; Levin, V. V. *Mendeleev Commun.* **2015**, *25*, 239–244.

- (11) (a) Pham, P. V.; Nagib, D. A.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2011**, *50*, 6119–6122. (b) Nagib, D. A.; Scott, M. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2009**, *131*, 10875–10877. (c) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875–8884. (d) Koike, T.; Akita, M. *Top. Catal.* **2014**, *57*, 967–974. (e) Barata-Vallejo, S.; Bonesi, S. M.; Postigo, A. *Org. Biomol. Chem.* **2015**, *13*, 11153–11183. (f) Chatterjee, T.; Iqbal, N.; You, Y.; Cho, E. J. *Acc. Chem. Res.* **2016**, *49*, 2284–2294. (g) Koike, T.; Akita, M. *Acc. Chem. Res.* **2016**, *49*, 1937–1945.
- (12) (a) Panferova, L. I.; Tsymbal, A. V.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *Org. Lett.* **2016**, *18*, 996–999. (b) Lin, Q.-Y.; Xu, X.-H.; Zhang, K.; Qing, F.-L. *Angew. Chem. Int. Ed.* **2016**, *55*, 1479–1483. (c) Lin, Q.-Y.; Ran, Y.; Xu, X.-H.; Qing, F.-L. *Org. Lett.* **2016**, *18*, 2419–2422. (d) Ran, Y.; Lin, Q.-Y.; Xu, X.-H.; Qing, F.-L. *J. Org. Chem.* **2016**, *81*, 7001–7007.
- (13) (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322–5363. (b) Shaw, M. H.; Twilton, J.; MacMillan, D. W. C. *J. Org. Chem.* **2016**, *81*, 6898–6926. (c) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, *77*, 1617–1622.
- (14) For examples of synthesis of oxindoles via photoredox mediated cyclizations, see: (a) Ju, X.; Liang, Y.; Jia, P.; Li, W.; Yu, W. *Org. Biomol. Chem.* **2012**, *10*, 498–501. (b) Tang, X.-J.; Thomason, C. S.; Dolbier, W. R. *Org. Lett.* **2014**, *16*, 4594–4597.
- (15) (a) Narayanam, J. M. R.; Tucker, J. W.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2009**, *131*, 8756–8757. (b) Tucker, J. W.; Nguyen, J. D.; Narayanam, J. M. R.; Krabbe, S. W.; Stephenson, C. R. J. *Chem. Commun.* **2010**, *46*, 4985–4987.
- (16) (Bromodifluoromethyl)silane ($\text{Me}_3\text{SiCF}_2\text{Br}$) is available from Aldrich. For its preparation, see: (a) Kosobokov, M. D.; Dilman, A. D.; Levin, V. V.; Struchkova, M. I. *J. Org. Chem.* **2012**, *77*, 5850–5855. (b) Li, L.; Wang, F.; Ni, C.; Hu, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 12390–12394.
- (17) Cano-Yelo, H.; Deronzier, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 3011–3019.