Supporting Information
for

Aminofluorination of 2-alkynylanilines: a Au-catalyzed entry to fluorinated indoles

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Experimental

All manipulations were carried out under an argon atmosphere. 1H NMR and 13C NMR spectra were recorded on a Bruker AV 300 instrument. All signals were expressed as ppm (δ) and internally referenced to residual protio solvent signals. Coupling constants (J) are reported in Hz and refer to apparent peak
multiplicities. $^1$H, $^{13}$C NMR and mass spectroscopy data for compounds 2a–e were described elsewhere [1].

**2-((1H-Pyrazol-4-yl)ethynyl)aniline (1f):** To a solution of 4-iodopyrazole (0.365 g, 3.12 mmol) in THF (1 mL) and triethylamine (1.5 mL) were added Pd(PPh$_3$)$_2$Cl$_2$ (0.027 g, 0.039 mmol), copper(I) iodide (0.007 g, 0.039 mmol) and 2-ethynylaniline (0.500 g, 2.60 mmol). After 8 h of stirring at 50 °C under N$_2$, 100 mL of H$_2$O and 100 mL of EtOAc were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Purification of the residue by flash chromatography (eluent: hexane/EtOAc 70:30) afforded 1f (0.211 g, 37% yield): Molecular formula: C$_{11}$H$_9$N$_3$; Mol. Wt.: 183.21 g/mol; purified by flash chromatography (Hexane/EtOAc 70:30); (0.211 g, 37 %); IR: (neat) $\nu_{\text{max}}$ 3182 (b), 2213, 1613, 1488, 749; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.79 (s, 2 H), 7.38-7.35 (m, 1 H), 7.18-7.13 (m, 1 H), 6.76-6.72 (m, 3 H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 147.6, 136.4, 132.0, 129.6, 118.0, 114.4, 108.2, 103.2, 86.7, 85.4; MS (El): $m/z$(%) = 182.8 (100) [M-1]$^+$, 183.8 (34).

**Ethyl 4-((2-amino-3,5-dichlorophenyl)ethynyl)benzoate (1h):** To a solution of ethyl 4-iodobenzoate (0.266 g, 0.97 mmol) in THF (9.0 mL) was added Pd(PPh$_3$)$_2$Cl$_2$ (0.017 g, 0.024 mmol), copper(I) iodide (0.015 g, 0.012 mmol) and 2,4-dichloro-6-ethynylbenzenamine (0.150 g, 0.81 mmol). After 4 h of stirring at 60 °C under N$_2$, 100 mL of H$_2$O and 100 mL of EtOAc were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over

sodium sulfate, and concentrated. Purification of the residue by flash chromatography (hexane/EtOAc 95:5) afforded 1h (0.227 g, 84%): Molecular formula: C$_{17}$H$_{13}$Cl$_2$NO$_2$; Mol. Wt.: 334.20 g/mol; purified by flash chromatography IR: (neat) $\nu_{\text{max}}$ 3315, 2193, 1721, 1604, 1462, 1272, 765; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05-8.03 (m, 2 H), 7.58-7.56 (m, 2H), 7.28-7.26 (m, 2 H), 4.39 (q, J = 7.13 Hz, 2 H), 3.95 (bs, 2 H), 1.41 (t, J = 7.13 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.9, 143.3, 131.4, 130.4, 130.1, 129.8, 129.6, 126.8, 121.7, 119.2, 109.2, 95.4, 86.6, 61.2, 14.3; MS (EI): $m/z$ (%) = 334.5 (62) and 332.4 (100) [M$^+$].

2,4-Dichloro-6-(oct-1-ynyl)aniline (1j): To a solution of 2-bromo-4,6-dichloroaniline (1.000 g, 4.16 mmol) in DMF (1 mL) and triethylamine (4.0 mL) were added Pd(PPh$_3$)$_2$Cl$_2$ (0.058 g, 0.083 mmol), copper(I) iodide (0.008 g, 0.042 mmol) and 1-octyne (0.550 g, 4.99 mmol). After 7 h of stirring at 50 °C under N$_2$, 100 mL of H$_2$O and 100 mL of EtOAc were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Purification of the residue by flash chromatography (eluent: hexane/EtOAc 99:1) afforded 1j (0.774 g, 70% yield): Molecular formula: C$_{14}$H$_{17}$Cl$_2$N; Mol. Wt.: 270.20 g/mol; IR: (neat) $\nu_{\text{max}}$ 3489, 3387, 2219, 1610, 1464, 731; $^1$H-NMR: (400 MHz, CDCl$_3$) $\delta$ 7.19 (d, J = 2.35 Hz, 1 H), 7.16 (d, J = 2.35 Hz, 1 H), 4.55 (bs, 2 H), 2.48 (t, J = 7.10 Hz, 2 H), 1.67-1.57 (m, 2 H), 1.51-1.44 (m, 2 H), 1.36-1.33 (m, 4 H), 0.93 (t, J = 7.00 Hz, 3 H); $^{13}$C-NMR: (100 MHz, CDCl$_3$) $\delta$ 143.0, 129.9, 128.4, 121.4, 118.8, 110.9, 97.9, 75.5, 31.3, 28.7, 28.6, 22.5, 19.6, 14.0; MS (EI): $m/z$ (%) = 270.8 (27) and 268.9 (44) [M$^+$], 198.2 (96), 165.2 (99).
3,3-Difluoro-2-(1H-pyrazol-4-yl)-3H-indole (2f): PPh₃AuNTf₂ (0.038 g, 0.049 mmol) and Selectfluor (0.520 g, 1.47 mmol) were added to a solution of 2-((1H-pyrazol-4-yl)ethynyl)aniline 1f (0.090 g, 0.49 mmol) in EtOH 4.9 mL/H₂O (0.87 mL). The mixture was stirred at reflux for 2.0 h. Then, the mixture was evaporated. Column chromatographic purification of the crude on silica gel (eluent: hexane/EtOAc 70:30) afforded the 3,3-difluoro-2-(1H-pyrazol-4-yl)-3H-indole (2f) (0.070 g, 65 %). Molecular formula: C₁₁H₇F₂N₃; Mol. Wt.: 219.19 g/mol; IR: (neat) νₓ = 3500, 1579, 1261, 754 cm⁻¹; ¹H NMR: (400 MHz, acetone-d₆) δ 12.89 (bs, 1 H), 8.35 (s, 2 H), 7.68-7.49 (m, 3 H), 7.37-7.34 (m, 1 H); ¹³C NMR: (100 MHz, acetone-d₆) δ 164.4 (t, J = 26.1 Hz), 154.0 (t, J = 9.5), 133.7 (t, J = 1.5 Hz), 129.9 (d, J = 237.6), 126.8 (t, J = 1.7 Hz), 123.0, 121.1, 111.6; ¹⁹F NMR: (376 MHz, acetone-d₆) δ -118.0; MS (EI): m/z (%) = 218.9 [M]+ (100), 126.0 (88).

Ethyl 4-(5,7-dichloro-3,3-difluoro-3H-indol-2-yl)benzoate (2h): NaAuCl₄·2H₂O (0.004 g, 0.009 mmol) was added to a solution of ethyl 4-((2-amino-3,5-dichlorophenyl)ethynyl)benzoate (1h, 0.060 g, 0.18 mmol) in EtOH 1.8 mL/H₂O (0.32 mL). The mixture was stirred at reflux under N₂ atmosphere for 2.0 h until the complete conversion of the starting 1h into the corresponding ethyl 4-(5,7-dichloro-1H-indol-2-yl)benzoate as monitored by GC-MS. Then, Selectfluor (0.191 g, 0.54 mmol) was added and the mixture after stirring under reflux for 22 h was evaporated. Column chromatographic purification of the crude on silica gel (eluent: hexane/EtOAc 95:5) afforded the ethyl 4-(5,7-dichloro-3,3-difluoro-3H-indol-2-yl)benzoate (2h, 0.010 g, 12%) and the ethyl 4-(5,7-dichloro-2-ethoxy-3,3-difluoroidolin-2-yl)benzoate (3h, 0.080 g, 56%).
**2h**: Molecular formula: C$_{17}$H$_{11}$Cl$_2$F$_2$NO$_2$; Mol. Wt.: 370.18 g/mol; IR: (neat) $\nu_{\text{max}}$ 1713, 1256, 706 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 8.28 (d, $J = 8.84$ Hz, 2 H), 8.18 (d, $J = 8.84$ Hz, 2 H), 7.54 (s, 1 H), 7.48 (s, 1 H), 4.43 (q, $J = 7.13$ Hz, 2 H), 1.43 (t, $J = 7.13$ Hz, 3 H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 168.8 (t, $J = 24.4$ Hz), 165.6, 147.6 (t, $J = 9.0$ Hz), 134.5, 134.2, 133.6, 131.8, 129.9, 128.7, 128.4, 122.4 (t, $J = 259.0$ Hz), 122.3, 61.4, 14.2; $^{19}$F NMR: (376 MHz, CDCl$_3$) $\delta$ -115.6; HRMS m/z (ESI) calcd for C$_{17}$H$_{12}$Cl$_2$F$_2$NO$_2$ (M H)$^+$ 372.0184 and 370.0213, found 372.0190 and 370.0688.

**Ethyl 4-(5,7-dichloro-2-ethoxy-3,3-difluoroindolin-2-yl)benzoate (3h):**

Molecular formula: C$_{19}$H$_{17}$Cl$_2$F$_2$NO$_3$; Mol. Wt.: 416.25 g/mol; IR: (neat) $\nu_{\text{max}}$ 3351, 2981, 1716, 1277, 865 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 8.08 (dd, $J_1 = 8.26$ Hz, $J_2 = 1.87$ Hz, 2 H), 7.75 (dd, $J_1 = 8.26$ Hz, $J_2 = 1.87$ Hz, 2 H), 7.38 (s, 1 H), 7.33 (s, 1 H), 5.29 (s, 1 H), 4.39 (q, $J = 7.11$ Hz, 2 H), 3.48-3.34 (m, 2 H), 1.39 (t, $J = 7.11$ Hz, 3 H), 1.21 (t, $J = 6.98$ Hz 3 H); $^{13}$C NMR: (100 MHz, CDCl$_3$) $\delta$ 166.1, 148.0, 144.4 (t, $J = 5.9$ Hz), 139.3, 132.0, 131.6, 130.0, 129.6, 127.6, 125.8 (t, $J = 296.8$ Hz), 122.9, 116.1, 96.6 (dd, $J_1 = 20.1$, $J_2 = 13.8$ Hz), 61.19, 59.2, 15.3, 14.20.

**4-Methyl-N-(2-(p-tolylethynyl)phenyl)benzenesulfonamide (4c):** 2-(p-Tolylethynyl)aniline (1c, 0.144 g, 0.69 mmol), THF (1.8 mL), pyridine (0.545 g, 6.90 mmol) and tosyl chloride (0.263 g, 1.38 mmol) were stirred for 15 h. The crude was purified by column chromatography (hexane/EtOAc 95:5) to give the title compound 4c (0.150 g, 60%); Molecular formula: C$_{22}$H$_{19}$NO$_2$S; Mol. Wt.: 361.46 g/mol; purified by flash chromatography (hexane/EtOAc 95:5); (0.150 g, 60%); IR: (neat) $\nu_{\text{max}}$ 3242, 2213, 1403, 1166, 1091, 754 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) $\delta$ 7.67-7.60 (m, 3 H), 7.37-7.15 (m, 9 H), 7.07-7.03
(m, 1 H), 2.40 (s, 3 H), 2.33 (s, 3 H); $^{13}$C NMR: (100 MHz, CDCl$_3$) δ 143.9, 139.4, 137.4, 136.1, 131.9, 129.6, 129.4, 129.3, 127.2, 124.5, 120.2, 118.9, 114.8, 96.4, 83.0, 21.6, 21.5; HRMS m/z (ESI) calcld for C$_{22}$H$_{20}$NO$_2$S (M-H)$^+$ 362.1215 found 362.1215.

2-Ethoxy-3,3-difluoro-2-phenyl-1-tosyl-3H-indole 5a: NaAuCl$_4$·2H$_2$O (0.004 g, 0.009 mmol) was added to a solution of 4-methyl-N-(2-phenylethynyl) phenylbenzenesulfonamide 4a (0.065 g, 0.19 mmol) in EtOH 1.9 mL)/H$_2$O (0.33 mL). The mixture was stirred at reflux under N$_2$ atmosphere for 2 h until the complete conversion of the starting 4a. Then, Selectfluor (0.202 g, 0.57 mmol) was added and the mixture after stirring under reflux for 5 h was evaporated. Column chromatographic purification of the crude on silica gel (eluent: hexane/EtOAc 95:5) afforded the 2-ethoxy-3,3-difluoro-2-phenyl-1-tosyl-3H-indole (5a, 0.034 g, 42%) and the 2-ethoxy-2-phenyl-1-tosylindolin-3-one (6a, 0.011 g, 14%). 5a: Molecular formula: C$_{23}$H$_{21}$F$_2$NO$_3$S; Mol. Wt.: 429.12 g/mol; IR: (neat) $\nu_{\text{max}}$ 2982, 1609, 1466, 704 cm$^{-1}$; $^1$H NMR: (400 MHz, CDCl$_3$) δ 7.84-7.82 (m, 1H), 7.57-7.52 (m, 2 H), 7.38-7.11 (m, 10 H), 3.80-3.59 (m, 2 H), 2.36 (s, 3 H), 1.32 (t, $J = 6.50$ Hz, 3 H); $^{13}$C NMR: (100 MHz, CDCl$_3$) δ 144.2, 143.3 (t, $J = 6.6$ Hz), 136.8, 133.8, 133.6, 129.2, 128.7, 128.0, 127.7, 127.5, 127.4, 127.2, 126.5 (t, $J = 34.2$ Hz), 124.2, 123.6, 121.0 (t, $J = 254.1$ Hz), 113.5, 99.5 (dd, $J_1 = 21.8$ Hz, $J_2 = 8.9$ Hz), 61.5, 21.5, 14.8; $^{19}$F NMR: (376 MHz, CDCl$_3$) δ -83.0 (d, $J = 253.3$), -107.1 (d, $J = 253.3$); HRMS m/z (ESI) calcld for C$_{23}$H$_{21}$F$_2$NO$_3$SNa (M-Na)$^+$ 452.1086, found 452.1108.

2-Ethoxy-3,3-difluoro-2-p-tolyl-1-tosyl-3H-indole 5c: NaAuCl$_4$·2H$_2$O (0.008 g, 0.019 mmol) was added to a solution of 4-methyl-N-(2-($p$-
tolylethynyl)phenyl)benzenesulfonamide (4c, 0.140 g, 0.39 mmol) in EtOH 3.9 mL/H2O (0.66 mL). The mixture was stirred at reflux under N2 atmosphere for 3 h until the complete conversion of the starting 4c. Then, Selectfluor (0.414 g, 1.17 mmol) was added and the mixture after stirring under reflux for 4 h was evaporated. Column chromatographic purification of the crude on silica gel (eluent: hexane/EtOAc = 95:5) afforded the 2-ethoxy-3,3-difluoro-2-p-tolyl-1-tosyl-3H-indole (5c, 0.093 g, 54%). 5c: Molecular formula: C24H23F2NO3S; Mol. Wt.: 443.51 g/mol; purified by flash chromatography (hexane/EtOAc 95:5); (0.044 g, 54 %); IR: (neat) νmax 2981, 2926, 1609, 1465, 748 cm⁻¹; 1H NMR: (400 MHz, CDCl3) δ 7.83-7.81 (m, 1H), 7.56-7.52 (m, 2 H), 7.43-7.41 (m, 2 H), 7.27-7.24 (m, 2 H), 7.18-7.11 (m, 3 H), 6.99-6.97 (m, 2 H), 3.76-3.57 (m, 2 H), 2.37 (s, 3 H), 2.34 (s, 3 H), 1.30 (t, J = 6.90 Hz, 3 H); 13C NMR: (100 MHz, CDCl3) δ 144.1, 143.3 (t, J = 6.4 Hz), 138.6, 137.0, 133.5, 131.0, 129.2, 127.9, 127.5, 126.0, 125.8 (t, J = 25.5 Hz), 118.4, 113.5, 99.7 (dd, J1 = 21.8 Hz, J2 = 8.6 Hz) 61.5, 21.5, 21.2, 14.7; 19F NMR: (376 MHz, CDCl3) δ -83.5 (d, J = 257.8), -107.5 (d, J = 254.4); HRMS m/z (ESI) calcd for C24H23F2NO3SNa (M-Na)+ 466.1259, found 466,1264.

2-Ethoxy-2-phenyl-1-tosylindolin-3-one (6a): Molecular formula: C23H23NO4S; Mol. Wt.: 409.50 g/mol; IR: (neat) νmax 2981, 1730, 1604, 1366, 658 cm⁻¹; 1H NMR: (400 MHz, CDCl3) δ 8.04 (d, J = 8.20, 1H), 7.75-7.61 (m, 2 H), 7.39-7.06 (m, 10 H), 3.57-3.43 (m, 2 H), 2.34 (s, 3 H), 1.29 (t, J = 6.96 Hz, 3 H); 13C NMR: (100 MHz, CDCl3) δ 196.5, 153.2, 144.2, 138.4, 136.7, 135.6, 129.3, 128.8, 128.2, 127.1, 126.1, 125.2, 123.4, 121.1, 114.3, 96.9, 60.6, 21.5, 14.8; HRMS m/z (ESI) calcd for C23H23NNaO4S (M-Na)+ 430.1089, found 430,1012.
Synthesis of \((E)-2-\text{(1-fluorohexylidene)indolin-3-one}\ (7)\): \(\text{NaAuCl}_4\cdot2\text{H}_2\text{O}\ (0.009\ \text{g},\ 0.020\ \text{mmol})\) was added to a solution of \(2-\text{(oct-1-ynyl)aniline (1i, 0.095\ \text{g},\ 0.47\ \text{mmol})}\) in \(\text{EtOH}\ 1.9\ \text{mL}/\text{H}_2\text{O}\ (0.33\ \text{mL})\). The mixture was stirred at room temperature under \(\text{N}_2\) atmosphere for 4 h until the complete conversion of the starting \(1i\). Then, \(\text{Selectfluor (0.418\ g,\ 1.18\ mmol)}\) was added and the mixture after stirring for 20 h was evaporated. Column chromatographic purification of the crude on silica gel (eluent: hexane/EtOAc 90:10) afforded the \((E)-2-\text{(1-fluorohexylidene)indolin-3-one 7a}\ (0.044\ \text{g},\ 39\%)\); Molecular formula: \(\text{C}_{14}\text{H}_{16}\text{FNO}\); Mol. Wt.: 233.28 g/mol; IR: (neat) \(\nu_{\text{max}}\) 3296, 1650, 1466, 743 cm\(^{-1}\); \(^1\text{H NMR: (400 MHz, CDCl}_3\) \(\delta\ 8.86\ (s,\ 1\ H),\ 7.71-7.69\ (m,\ 1\ H),\ 7.36-7.34\ (m,\ 2\ H),\ 7.17-7.13\ (m,\ 1\ H),\ 3.00-2.95\ (m,\ 2\ H),\ 1.81-1.77\ (m,\ 2\ H),\ 1.42-1.37\ (m,\ 4\ H),\ 0.92\ (t,\ J = 7.14,\ 3\ H); \(^{13}\text{C NMR: (100 MHz, CDCl}_3\) \(\delta\ 191.9,\ 148.8,\ 146.2,\ 133.6,\ 127.3,\ 120.8,\ 119.4,\ 112.4,\ 40.4,\ 31.5,\ 24.2,\ 22.5,\ 13.9; \(^{19}\text{F-NMR: (376 MHz, CDCl}_3\) \(\delta\ -154.6;\) time-dependent NOESY (Nuclear Overhauser Effect Spectroscopy) and HOESY (Heteronuclear Overhauser Enhancement Spectroscopy) experiments were used to provide experimental measures of the conformation. NH exhibited a NOE with the aliphatic hydrogen of methylene 13 and with the aromatic hydrogen 6. Moreover a HOESY peak was observed between the fluorine and the methylene 13. The \(^{19}\text{F-}^{1}\text{H}-\text{HOESY NMR (}^{1}\text{H, 400.13 MHz) experiment was carried out with a mixing time of 400 ms and 32 scans were taken for each of the 256-}^{t1}\) increments recorded. \(^{1}\text{H-}^{1}\text{H NOESY, NMR (}^{1}\text{H, 400.13 MHz): The duration of the mixing time was 600 ms and 128 scans were taken for each of the 256-}^{t1}\) increments recorded. In all experiments, the recycle time was set to 2 s.
Typical procedure for a two-step one-pot gold(III)-catalyzed synthesis of 3-fluorinoindoles a–j: Synthesis of 3-fluoro-2-(4-methoxyphenyl)-1H-indole (8a): NaAuCl₄·2H₂O (0.008 g, 0.020 mmol) was added to a solution of 2-[(4-methoxy)ethynyl]aniline (1a, 0.090 g, 0.40 mmol) in CH₃CN (4 mL). The mixture was stirred at reflux for 1.5 h until complete disappearance of the starting material 1a. The solution was cooled to 0 °C. DMSO (4 mL) and Selectfluor (0.142 g, 0.40 mmol) were added to the mixture. The reaction was allowed to stir at 0 °C for one hour, then gradually warmed up to room temperature. Then, 100 mL of H₂O and 100 mL of EtOAc were added. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over sodium sulfate, and concentrated. Purification of the residue by flash chromatography (eluent: hexane/EtOAc 98:3) afforded 3-fluoro-2-(4-methoxyphenyl)-1H-indole (8a, 0.040 g, 41%). Molecular formula: C₁₅H₁₂FNO; Mol. Wt.: 241.09 g/mol; IR: (neat) ν max 3432, 1599, 1252, 742 cm⁻¹; ¹H NMR: (400 MHz, acetone-d₆) δ 10.29 (s, 1 H), 7.82 (d, J = 8.9 Hz, 2 H), 7.57-7.53 (m, 2 H), 7.19-7.15 (m, 1 H), 7.03-7.01 (m, 3 H), 3.86 (s, 3 H); ¹³C NMR: (100 MHz, acetone-d₆) δ 159.1, 131.1, 129.9 (d, J = 238.8), 129.7 (d, J = 245.4), 126.8 (d, J = 5.2 Hz), 124.5, 122.5, 119.5 (d, J = 29.0 Hz), 115.7, 114.3, 112.9 (d, J = 44.4), 111.5, 54.7; ¹⁹F NMR: (376 MHz,acetone-d₆) δ -174.9; MS (El): m/z (%) = 241.2 [M⁺] (100).

3-Fluoro-2-(2-methoxyphenyl)-1H-indole (8b): Molecular formula: C₁₅H₁₂FNO; Mol. Wt.: 241.09 g/mol; purified by flash chromatography (hexane/EtOAc 95:5); (0.040 g, 37 %); IR: (neat) ν max 3447, 1464, 1243, 744 cm⁻¹; ¹H NMR: (400 MHz, CDCl₃) δ 9.22 (s, 1 H). 8.09 (dd, J₁ = 6.10 Hz, J₂ =
1.70 Hz, 1 H), 7.66 (dd, \( J_1 = 6.10 \) Hz, \( J_2 = 1.70 \) Hz, 1 H), 7.37-7.05 (m, 6 H), 4.03 (s, 3 H); \(^{13}\text{C} \) NMR: (100 MHz, CDCl\(_3\)) \( \delta \) 155.3, 142.3 (d, \( J = 247.0 \) Hz), 131.3 (d, \( J = 6.8 \) Hz), 128.9 (d, \( J = 12.1 \) Hz), 128.3, 127.3 (d \( J = 246.8 \) Hz), 122.8, 121.7, 119.7, 118.5, 116.4 (d, \( J = 1.8 \) Hz), 111.7, 111.3 (d, \( J = 65.4 \) Hz), 111.1, 55.9; \(^{19}\text{F} \) NMR: (376 MHz, CDCl\(_3\)) \( \delta \) -168.6; MS (EI): \( m/z \) (%) = 241.3 [M]\(^+\) (100).

**3-Fluoro-2-p-tolyl-1H-indole 8c:** Molecular formula: C\(_{15}\)H\(_{12}\)FN; Mol. Wt.: 225.26 g/mol; purified by flash chromatography (hexane/EtOAc 95:5); (0.060 g, 55%); IR: (neat) \( \nu_{\max} \) 3431, 1599, 1456, 1347, 1238, 740 cm\(^{-1}\); \(^1\text{H} \) NMR: (400 MHz, acetone-\( \text{d}_6 \)) \( \delta \) 10.36 (s, 1 H), 7.77 (d, \( J = 8.31 \) Hz, 2 H), 7.58-7.56 (m, 1 H), 7.40-7.32 (m, 3 H), 7.20-7.16 (m, 1 H), 7.12-7.08 (m, 1 H), 2.38 (s, 3 H); \(^{13}\text{C} \) NMR: (100 MHz, acetone-\( \text{d}_6 \)) \( \delta \) 142.7 (d, \( J = 244.2 \) Hz), 138.2, 131.0 (d, \( J = 239.0 \) Hz), 130.6, 126.4 (d, \( J = 5.3 \) Hz), 126.0, 125.7 (d, \( J = 57.3 \) Hz), 123.8, 120.8, 116.9 (d, \( J = 1.7 \) Hz), 112.6 (d, \( J = 5.2 \) Hz), 111.9 (d, \( J = 16.2 \) Hz), 21.3; \(^{19}\text{F} \) NMR: (376 MHz, acetone-\( \text{d}_6 \)) \( \delta \) -173.6; MS (EI): \( m/z \) (%) = 225.0 [M]\(^+\) (100).

**3-Fluoro-2-(1H-pyrazol-4-yl)-1H-indole 8f:** Molecular formula: C\(_{11}\)H\(_8\)FN\(_3\); Mol. Wt.: 201.20 g/mol; purified by flash chromatography (Hexane/EtOAc 70:30); (0.020 g, 20%); IR: (neat) \( \nu_{\max} \) 3418, 3158, 744 cm\(^{-1}\); \(^1\text{H} \) NMR: (400 MHz, acetone-\( \text{d}_6 \)) \( \delta \) 10.71 (s, 1 H), 10.27 (s, 1 H), 8.09 (s, 2 H), 7.78-7.76 (m, 1 H), 7.67-7.65 (m, 1 H), 7.15-7.06 (m, 1 H); \(^{13}\text{C} \) NMR: (100 MHz, acetone-\( \text{d}_6 \)) \( \delta \) 140.2 (d, \( J = 240.0 \) Hz), 132.4 (d, \( J = 6.1 \) Hz), 131.1, 128.7, 121.9, 121.1 (d, \( J = 223.2 \) Hz), 119.6, 115.3 (d, \( J = 2.0 \) Hz), 114.6 (d, \( J = 22.4 \) Hz); \(^{19}\text{F} \) NMR: (376 MHz, acetone-\( \text{d}_6 \)) \( \delta \) -176.1; MS (EI): \( m/z \) (%) = 201.1 [M]\(^+\) (100).
3-Fluoro-2-hexyl-1H-indole (8i): Molecular formula: C_{14}H_{18}FN; Mol. Wt.: 219.30 g/mol; purified by flash chromatography (hexane/EtOAc 98:2); (0.044 g, 40 %); IR: (neat) ν_{max} 3387, 1459, 1260, 741 cm^{-1}; ^1H NMR: (400 MHz, acetone-d$_6$) δ 9.80 (s, 1 H), 7.46-7.01 (m, 4 H), 2.90-2.80 (m, 2 H), 2.07-2.05 (m, 2 H), 1.35-1.30 (m, 6 H), 0.89 (t, J = 7.10 Hz, 3 H); ^13C NMR: (100 MHz, acetone-d$_6$) δ; 134.5 (d, J = 243.8 Hz), 132.1, 122.1, 120.6 (d, J = 277.6 Hz), 119.9, 116.9 (d, J = 1.9 Hz), 111.9 (d, J = 5.2 Hz), 111.2 (d, J = 5.5 Hz), 32.2, 24.7, 24.6, 23.3, 23.2, 14.2; ^19F NMR: (376 MHz, acetone-d$_6$) δ - 181.5; MS (EI): m/z (%) = 219.0 [M]^+ (23), 148.1 (100).

5,7-Dichloro-3-fluoro-2-hexyl-1H-indole (8j): Molecular formula: C_{14}H_{16}Cl$_2$FN; Mol. Wt.: 288.18 g/mol; purified by flash chromatography (hexane/EtOAc 99:1); (0.097 g, 85 %); IR: (neat) ν_{max} 3387, 1459, 1260, 741 cm^{-1}; ^1H NMR: (400 MHz, acetone-d$_6$) δ 10.39 (s, 1 H), 7.30 (s, 1 H), 7.06 (s, 1 H), 2.79 (t, J = 7.90 Hz, 2 H), 1.57-1.52 (m, 2 H), 1.24-1.20 (m, 6 H), 0.85 (t, J = 6.76 Hz, 3 H); ^13C NMR: (100 MHz, acetone-d$_6$) δ 132.1 (d, J = 179.3 Hz), 132.0 (d, J = 191.8 Hz), 123.6, 119.6 (d, J = 233.6), 119.3, 116.4, 116.0, 110.6 (d, J = 4.5 Hz), 31.4, 29.5, 26.2, 22.3, 18.8, 13.4; ^19F NMR: (376 MHz, acetone-d$_6$) δ - 178.1; MS (EI): m/z (%) = 288.8 [M]^+ (7), 286.8 [M]^+ (13), 218.1 (76), 216.3 (100).
Time-dependent NOESY (Nuclear Overhauser Effect Spectroscopy) and HOESY (Heteronuclear Overhauser Enhancement Spectroscopy) experiments of compound 7.