

Supporting Information

Synthesis of 2-Trifluoromethyl Indoles via Visible-Light Induced Intramolecular Radical Cyclization

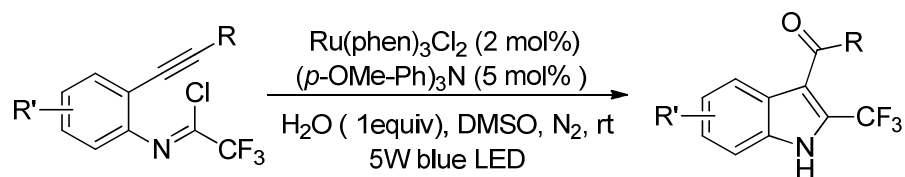
Xichang Dong, Yumin Hu, Tiebo Xiao and Lei Zhou^{*[a]}

*School of Chemistry and Chemical Engineering, Sun Yat-Sen University, 135 Xingang
West Road, Guangzhou 510275, China*

E-mail: zhoul39@mail.sysu.edu.cn

General All reactions were performed under a nitrogen atmosphere in a 10 mL schlenk tube. DMSO and MeCN were dried over CaH₂ before use. Photoirradiation was carried out with a 5W blue LED. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ¹H NMR and ¹³C NMR spectra were measured in CDCl₃ or DMSO and recorded on Varian 300spectrometer. Mass spectra were obtained on Thermo Trace GC Ultra-DCQ, and HRMS were performed on Bruker Daltonics ESI-Q-TOF at Lenh Insititute of Functional Materials or Thermo MAT95XP mass spectrometer at analytical center of Sun Yat-Sen University. Compounds described in the literature were characterized by comparing their ¹H NMR and ¹³C NMR to the reported values. *N*-[2-(alkynyl)phenyl]trifluoroacetimidoyl chlorides were prepared from CF₃CO₂H, CCl₄, and *o*-alkynylaniline according to the reported procedure.^[1] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

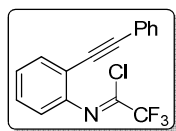
General procedure for synthesis of 2-trifluoromethyl-3-acylindoles



A 10 mL snap vial under nitrogen atmosphere was charged with $\text{Ru(phen)}_3\text{Cl}_2$ catalyst (2.6 mg, 2 mol%), *N*-[2-(alkynyl)phenyl]trifluoroacetimidoyl chloride **1** (0.2 mmol), $(p\text{-OMe-Ph})_3\text{N}$ (3.4 mg, 5 mol%) and dry DMSO (0.5 mL). The solution was stirred at room temperature with the irradiation of a 5 W blue LED. After the reaction was completed, as monitored by TLC, the resulting mixture was filtered through a short path of silica gel, eluting with ethyl acetate. The volatile compounds were removed in vacuo and the residue was purified by column chromatography (SiO_2) with hexane/ethyl acetate.

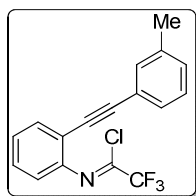
Characterization data:

2, 2, 2-trifluoro-*N*-(2-(phenylethynyl)phenyl)acetimidoyl chloride^[2] (1a):



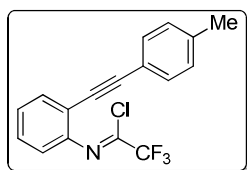
Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.63 (d, *J* = 7.8Hz, 2H), 7.52-7.49 (m, 2H), 7.43-7.40 (m, 4H), 7.29-7.24 (m, 1H), 6.99 (d, *J* = 7.8Hz, 1H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 146.9, 136.2 (q, *J* = 43.2Hz), 134.0, 132.9, 130.4, 130.0, 129.8, 127.8, 124.2, 120.1, 118.2 (q, *J* = 278.5Hz), 115.6, 96.4, 86.2; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -72.1 (s, 3F); MS (EI): *m/z* (%): 307 [M]⁺(90), 272(32), 252(100), 202(34), 176(44), 150(20), 126(10).

2,2,2-trifluoro-*N*-(2-(*m*-tolylethynyl)phenyl)acetimidoyl chloride (1b):



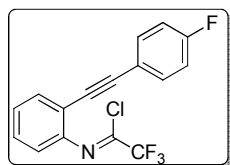
Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.68-7.65 (m, 1H), 7.45-7.39 (m, 3H), 7.31-7.26 (m, 2H), 7.22-7.20 (m, 1H), 7.03-7.00 (m, 1H), 2.42 (s, 3H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 147.0, 139.5, 136.2 (q, *J* = 43.2Hz), 134.0, 133.6, 131.0, 130.3, 130.1, 129.8, 127.8, 124.1, 120.1, 118.4 (q, *J* = 278.6Hz), 115.8, 96.8, 86.0, 22.5; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -72.0 (s, 3F); MS (EI): *m/z* (%): 321 [M]⁺(88), 286(58), 266(100), 252(30), 216(66), 189(76), 163(24). HRMS(EI) calcd. For C₁₇H₁₁F₃N₁Cl₁ [M]⁺: 321.0527, found: 321.0522.

2,2,2-trifluoro-*N*-(2-(*p*-tolylethynyl)phenyl)acetimidoyl chloride^[3] (1c):



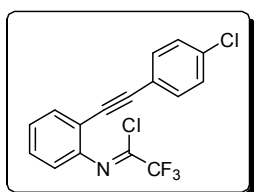
Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.64 (d, *J* = 7.8Hz, 1H), 7.44-7.38 (m, 3H), 7.30-7.38 (m, 3H), 7.30-7.25 (m, 1H), 7.29 (d, *J* = 7.8Hz, 2H), 6.99 (d, *J* = 8.1 Hz); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 146.9, 140.3, 136.1 (q, *J* = 43.2Hz), 134.0, 132.9, 130.6, 130.2, 127.8, 121.2, 120.1, 118.3 (q, *J* = 278.5Hz), 115.9, 96.7, 85.7, 22.9; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -72.1 (s, 3F); MS (EI): *m/z* (%): 321 [M]⁺(80), 285(74), 262(100), 252(16), 216(44), 189(40), 176(12), 126(10).

2,2,2-trifluoro-*N*-(2-((4-fluorophenyl)ethynyl)phenyl)acetimidoyl chloride (1d):



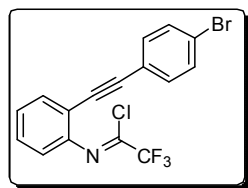
Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.60 (d, $J = 7.5\text{Hz}$, 1H), 7.49-7.44 (m, 2H), 7.39 (t, $J = 7.8\text{Hz}$, 1H), 7.25 (t, $J = 7.8\text{Hz}$, 1H), 7.04 (t, $J = 8.1\text{Hz}$, 2H), 6.98 (d, $J = 7.8\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 164.1 (d, $J = 251.2\text{Hz}$), 146.9, 136.2 (q, $J = 43.2\text{Hz}$), 134.8 (d, $J = 8.5\text{Hz}$), 133.9, 130.4, 127.8, 120.3 (q, $J = 3.2\text{Hz}$), 120.1, 118.2 (q, $J = 278.5\text{Hz}$), 117.1 (d, $J = 22.2\text{Hz}$), 115.5, 95.3, 85.9; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.1 (s, 3F), -110.5 (m, 1H); MS (EI): m/z (%): 325 $[\text{M}]^+$ (60), 290(34), 270(100), 256(20), 221(50), 194(58), 168(24), 149(10). HRMS(EI) calcd. For $\text{C}_{16}\text{H}_8\text{F}_3\text{N}_1\text{Cl}_1$ $[\text{M}]^+$: 325.0276, found: 325.0272.

***N*-(2-((4-chlorophenyl)ethynyl)phenyl)-2,2,2-trifluoroacetimidoyl chloride^[3] (1e):**



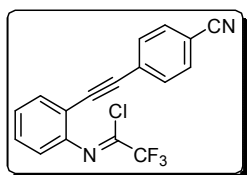
White solid; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.60 (d, $J = 7.5\text{Hz}$, 1H), 7.42-7.36 (m, 3H), 7.33-7.30 (m, 3H), 7.24 (t, $J = 7.8\text{Hz}$, 1H), 6.98 (d, $J = 8.1\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 146.9, 136.2 (q, $J = 43.3\text{Hz}$), 136.2 134.1, 134.0, 130.6, 130.2, 127.9, 120.2, 118.4 (q, $J = 278.6\text{Hz}$), 115.4, 95.2, 87.2; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.1 (s, 3F); MS (EI): m/z (%): 341 $[\text{M}]^+$ (76), 306(44), 286(50), 271(100), 237(40), 201(26), 176(68), 150(24).

***N*-(2-((4-bromophenyl)ethynyl)phenyl)-2,2,2-trifluoroacetimidoyl chloride (1f):**



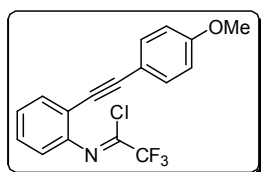
White solid; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.61 (d, $J = 7.8\text{Hz}$, 1H), 7.49 (d, $J = 8.1\text{Hz}$, 2H), 7.41 (t, $J = 7.5\text{Hz}$, 1H), 7.34 (d, $J = 8.1\text{Hz}$, 2H), 7.26 (t, $J = 7.5\text{Hz}$, 1H), 6.99 (d, $J = 7.8\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 146.9, 136.2 (q, $J = 43.3\text{Hz}$), 134.3, 134.0, 133.1, 130.6, 127.9, 124.4, 123.1, 120.2, 118.2 (q, $J = 278.6\text{Hz}$), 115.3, 95.2, 87.3; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.1 (s, 3F); MS (EI): m/z (%): 387 $[\text{M}]^+$ (32), 350(8), 286(8), 271(100), 237(18), 202(20), 176(42), 150(22). HRMS(EI) calcd. For $\text{C}_{16}\text{H}_8\text{F}_3\text{N}_1\text{Br}_1\text{Cl}_1$ $[\text{M}]^+$: 384.9475, found: 384.9469.

***N*-(2-((4-cyanophenyl)ethynyl)phenyl)-2,2,2-trifluoroacetimidoyl chloride (1g):**



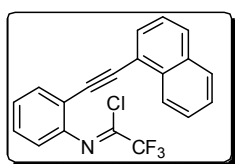
Yellow solid; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.64-7.61 (m, 3H), 7.54-7.52(m, 2H), 7.45 (t, $J = 7.8\text{Hz}$, 1H), 7.29 (t, $J = 7.8\text{Hz}$, 1H), 7.00 (d, $J = 8.1\text{Hz}$, 1H) ; $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 147.1, 136.4 (q, $J = 43.4\text{Hz}$), 134.2, 133.5, 133.3, 131.3, 129.0, 128.0, 120.3, 119.7, 118.1 (q, $J = 278.7\text{Hz}$), 114.7, 113.3, 94.4, 90.4; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -76.8 (s, 3F); MS (EI): m/z (%): 332 $[\text{M}]^+$ (92), 297(16), 277(100), 263(50), 228(74), 201(82), 175(76), 151(32). HRMS(EI) calcd. For $\text{C}_{17}\text{H}_8\text{F}_3\text{N}_2\text{Cl}$ $[\text{M}]^+$: 332.0323, found: 332.0316.

2,2,2-trifluoro-*N*-(2-((4-methoxyphenyl)ethynyl)phenyl)acetimidoyl chloride (1h)



Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.64-7.60 (m, 1H), 7.50-7.45 (m, 2H), 7.38 (t, $J = 7.8\text{Hz}$, 1H), 7.26 (t, $J = 7.8\text{Hz}$, 1H), 7.00-6.97 (m, 1H), 6.92-6.89 (m, 2H), 3.82 (s, 3H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 161.5, 146.7, 136.0 (q, $J = 43.2\text{Hz}$), 134.4, 133.8, 130.0, 127.8, 120.1, 118.4 (q, $J = 278.5\text{Hz}$), 116.3, 116.0, 115.5, 96.7, 85.1, 56.5; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.1 (s, 3F); MS (EI): m/z (%): 337 $[\text{M}]^+$ (46), 302(100), 282(50), 239(30), 218(10), 190(22), 163(36). HRMS(EI) calcd. For $\text{C}_{17}\text{H}_{11}\text{F}_3\text{N}_1\text{Cl}_1\text{O}_1$ $[\text{M}]^+$: 337.0476, found: 337.0471.

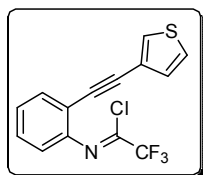
2,2,2-trifluoro-*N*-(2-(naphthalen-1-ylethynyl)phenyl)acetimidoyl chloride (1i):



Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 8.46 (d, $J = 7.8\text{Hz}$, 1H), 7.90-7.89 (m, 2H), 7.79-7.77 (m, 2H), 7.67-7.55 (m, 2H), 7.52-7.42 (m, 2H), 7.33 (d, $J = 7.8\text{Hz}$, 1H), 7.06 (d, $J = 7.8\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 146.8, 136.1 (q, $J = 43.3\text{Hz}$), 134.6, 134.6, 134.4, 132.0, 130.6, 130.4, 129.7, 128.3, 128.1, 128.0, 127.6, 126.7, 121.9, 120.3, 118.4 (q, $J = 278.7\text{Hz}$), 116.5, 94.7, 91.2; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -76.6 (s, 3F); MS (EI): m/z (%): 357 $[\text{M}]^+$ (52), 302(68), 282(38), 252(56), 226(28), 200(12), 151(10), 126(32), 113(100). HRMS(EI) calcd. For $\text{C}_{20}\text{H}_{11}\text{F}_3\text{N}_1\text{Cl}_1$

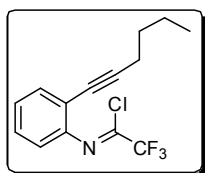
$[M]^+$: 357.0527, found: 357.0533.

2,2,2-trifluoro-*N*-(2-(thiophen-3-ylethynyl)phenyl)acetimidoyl chloride (1j):



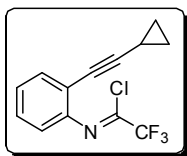
Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.60 (d, $J = 7.8\text{Hz}$, 1H), 7.52-7.51 (m, 1H), 7.36 (d, $J = 7.8\text{Hz}$, 1H), 7.29-7.27 (m, 1H), 7.23 (t, $J = 7.8\text{Hz}$, 1H), 7.17 (d, $J = 7.8\text{Hz}$, 1H), 6.97 (d, $J = 8.1\text{Hz}$, 1H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 146.9, 136.136.2 (q, $J = 43.2\text{Hz}$), 133.9, 131.1, 130.5, 130.3, 127.9, 127.0, 123.3, 120.2, 118.3 (q, $J = 278.5\text{Hz}$), 115.6, 91.7, 85.9; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.0 (s, 3F); MS (EI): m/z (%): 313 $[M]^+$ (50), 278(50), 258(100), 209(32), 182(20), 139(70). HRMS(EI) calcd. For $\text{C}_{14}\text{H}_7\text{F}_3\text{N}_1\text{Cl}_1\text{S}_1$ $[M]^+$: 312.9934, found: 312.9929.

2,2,2-trifluoro-*N*-(2-(hex-1-yn-1-yl)phenyl)acetimidoyl chloride^[2] (1k):



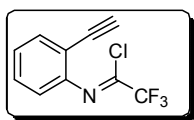
Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.46 (d, $J = 7.5\text{Hz}$, 1H), 7.31 (t, $J = 7.8\text{Hz}$, 1H), 7.18 (t, $J = 7.5\text{Hz}$, 1H), 6.88 (d, $J = 7.8\text{Hz}$, 1H), 2.41 (t, $J = 6.7\text{Hz}$, 2H), 1.62-1.41 (m, 4H), 0.95 (t, $J = 6.9\text{Hz}$, 3H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 147.1, 135.8 (q, $J = 43.2\text{Hz}$), 134.0, 129.5, 127.5, 119.8, 118.2 (q, $J = 278.4\text{Hz}$), 116.3, 97.8, 77.4, 31.9, 23.3, 20.5, 14.8; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -77.1 (s, 3F); MS (EI): m/z (%): 287 $[M]^+$ (50), 252(28), 236(36), 210(99), 183(100), 140(64), 113(74).

***N*-(2-(cyclopropylethynyl)phenyl)-2,2,2-trifluoroacetimidoyl chloride (1l):**



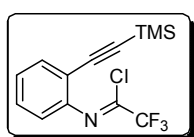
Pale yellow oil; $^1\text{H-NMR}$ (300MHz, CDCl_3): δ (ppm): 7.46 (d, $J = 7.8\text{Hz}$, 1H), 7.31 (t, $J = 7.8\text{Hz}$, 1H), 7.17 (t, $J = 7.8\text{Hz}$, 1H), 6.89 (d, $J = 7.8\text{Hz}$, 1H), 1.49-1.40 (m, 1H), 0.92-0.84 (m, 2H), 0.82-0.77 (m, 2H); $^{13}\text{C-NMR}$ (101MHz, CDCl_3): δ (ppm): 147.1, 135.7 (q, $J = 43.2\text{Hz}$), 134.0, 129.4, 127.6, 119.8, 118.2 (q, $J = 278.4\text{Hz}$), 116.1, 101.0, 72.5, 10.0, 1.5; $^{19}\text{F-NMR}$ (282MHz, CDCl_3): δ (ppm): -72.3 (s, 3F); MS (EI): m/z (%): 271 $[M]^+$ (14), 236(34), 216(62), 202(24), 167(100), 139(60), 113(42). HRMS(EI) calcd. For $\text{C}_{13}\text{H}_9\text{F}_3\text{N}_1\text{Cl}_1$ $[M]^+$: 271.0370, found: 271.0368.

***N*-(2-ethynylphenyl)-2,2,2-trifluoroacetimidoyl chloride^[4] (1m):**



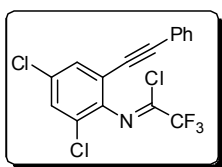
Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.58 (d, *J* = 7.8Hz, 1H), 7.41 (t, *J* = 7.8Hz, 1H), 7.23 (d, *J* = 7.8Hz, 1H), 6.93 (d, *J* = 7.8Hz, 1H), 3.26 (s, 1H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 147.6, 136.6 (q, *J* = 43.5Hz), 134.8, 130.9, 127.7, 120.0, 118.1 (q, *J* = 278.6Hz), 114.4, 83.9, 80.3; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -77.1 (s, 3F); MS (EI): *m/z* (%): 231 [M]⁺(36), 196(100), 176(26), 146(44), 127(26), 101(96).

2,2,2-trifluoro-*N*-(2-((trimethylsilyl)ethynyl)phenyl)acetimidoyl chloride^[2] (1n):



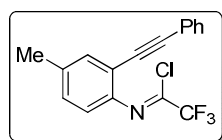
Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.53 (d, *J* = 7.5Hz, 1H), 7.37 (t, *J* = 7.8Hz, 1H), 7.20 (t, *J* = 7.5Hz, 1H), 6.90 (d, *J* = 7.8Hz, 1H), 0.24 (s, 9H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 147.5, 136.1 (q, *J* = 42.6Hz), 134.2, 130.5, 127.5, 119.9, 118.1 (q, *J* = 278.5Hz), 115.2, 101.9, 101.3, 0.96; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -77.0 (s, 3F); MS (EI): *m/z* (%): 303 [M]⁺(44), 192(40), 172(46), 152(100), 115(80).

***N*-(2,4-dichloro-6-(phenylethynyl)phenyl)-2,2,2-trifluoroacetimidoyl chloride (1o)**



White solid; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.51-7.50 (m, 1H), 7.46-7.45 (m, 3H), 7.38-7.36 (m, 3H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 141.9, 138.9 (q, *J* = 42.4Hz), 131.7, 130.6, 129.6, 129.3, 128.5, 124.3, 121.8, 116.6 (q, *J* = 279.1Hz), 115.9, 96.7, 82.7 ; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -76.8 (s, 3F); MS (EI): *m/z* (%): 375 [M]⁺(60), 340(20), 320(100), 306(40), 271(50), 235(30), 201(74), 174(72), 135(22), 122(26). HRMS(EI) calcd. For C₁₆H₇F₃N₁Cl₃ [M]⁺: 374.9591, found: 374.9596.

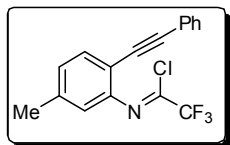
2,2,2-trifluoro-*N*-(4-methyl-2-(phenylethynyl)phenyl)acetimidoyl chloride (1p):



Pale yellow oil; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 7.48-7.43 (m, 3H), 7.34-7.32 (m, 3H), 7.20-7.17 (m, 1H), 6.90 (d, *J* = 8.1Hz, 1H), 2.38 (s, 3H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 144.3, 137.9, 135.4 (q, *J* = 43.2Hz), 134.4, 132.9, 131.1, 129.9, 129.8, 124.3, 120.2, 118.2 (q, *J* = 278.4Hz), 115.8, 96.0, 86.5, 22.2; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -76.8 (s,

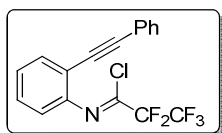
3F); MS (EI): m/z (%): $[M]^+$ 321, 286, 266, 252, 216, 189, 165, 94. HRMS(EI) calcd. For $C_{17}H_{11}F_3N_1Cl_1$ $[M]^+$ 321.0527, found: 321.0526.

2,2,2-trifluoro-*N*-(5-methyl-2-(phenylethynyl)phenyl)acetimidoyl chloride (1q):



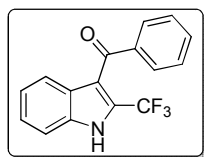
Pale yellow oil; 1H -NMR (300MHz, $CDCl_3$): δ (ppm): 7.58-7.56 (m, 3H), 7.41-7.39(m, 3H), 7.11(d, $J = 7.8$ Hz, 1H), 6.83 (s, 1H), 2.45(s, 3H); ^{13}C -NMR (101MHz, $CDCl_3$): δ (ppm): 147.0, 141.1, 136.0 (q, $J = 43.1$ Hz), 133.9, 132.9, 129.9, 129.8, 128.7, 124.5, 120.6, 118.4 (q, $J = 278.5$ Hz), 112.5, 95.7, 86.5, 22.8; ^{19}F -NMR (282MHz, $CDCl_3$): δ (ppm): -76.8 (s, 3F). MS (EI): m/z (%): $[M]^+$ 321, 286, 266, 252, 216, 189, 165, 150, 126, 94. HRMS(EI) calcd. For $C_{17}H_{11}F_3N_1Cl_1$ $[M]^+$: 321.0527, found: 321.0525.

2,2,3,3,3-pentafluoro-*N*-(2-(phenylethynyl)phenyl)propanimidoyl chloride (1r):



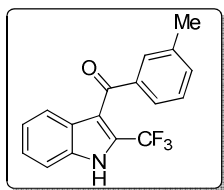
Pale yellow oil; 1H -NMR (300MHz, $CDCl_3$): δ (ppm): 7.64 (d, $J = 7.8$ Hz, 1H), 7.51-7.49 (m, 2H), 7.43-7.37 (m, 4H), 7.30-7.25 (m, 1H), 6.99 (d, $J = 7.8$ Hz, 1H); ^{13}C -NMR (101MHz, $CDCl_3$): δ (ppm): 146.8, 136.6 (t, $J = 33.4$ Hz), 134.3, 132.9, 130.3, 130.0, 129.8, 129.0, 124.2, 120.1, 119.4 (tq, $J = 35.1$ Hz, $J = 288.1$ Hz), 116.0, 109.3 (qt, $J = 38.6$ Hz, $J = 261.2$ Hz), 96.3, 86.1; ^{19}F -NMR (282MHz, $CDCl_3$): δ (ppm): -86.3 (s, 3F), -118.8 (s, 2F); MS (EI): m/z (%): 357 $[M]^+$ (80), 322(38), 302(14), 268(30), 252(60), 238(54), 203(64), 176(82), 151(40). HRMS(EI) calcd. For $C_{17}H_9F_5N_1Cl_1$ $[M]^+$: 357.0338, found: 357.0335.

phenyl(2-(trifluoromethyl)-1H-indol-3-yl)methanone^[5] (2a):



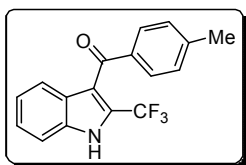
White solid; 1H -NMR (300MHz, d_6 -DMSO): δ (ppm): 13.11 (br, 1H), 7.75 (d, $J = 7.5$ Hz, 2H), 7.65-7.60 (m, 2H), 7.49 (t, $J = 7.5$ Hz, 2H), 7.34-7.29 (m, 1H), 7.16 (d, $J = 8.1$ Hz, 1H), 7.11-7.06 (m, 1H); ^{13}C -NMR (101MHz, d_6 -DMSO): δ (ppm): 190.9, 139.2, 135.5, 133.6, 129.5, 129.0, 126.5 (q, $J = 38.5$ Hz), 126.1, 125.3, 122.4, 121.4, 121.4 (q, $J = 270.9$ Hz), 116.2, 113.5; ^{19}F -NMR (282MHz, d_6 -DMSO): δ (ppm): -57.6 (s, 3F); MS (EI): m/z (%): 289 $[M]^+$ (46), 220(10), 212(100), 164(14), 134(10), 105(26).

***m*-tolyl(2-(trifluoromethyl)-1H-indol-3-yl)methanone (2b):**



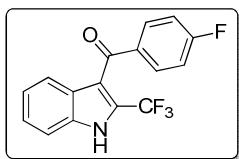
White solid; ^1H -NMR (300MHz, CDCl_3): δ (ppm): 10.00 (br, 1H), 7.75 (s, 1H), 6.68 (d, $J = 7.5\text{Hz}$, 1H), 7.50-7.30 (m, 5H), 7.16 (t, $J = 7.8\text{Hz}$, 1H), 2.41 (s, 3H); ^{13}C -NMR (101MHz, CDCl_3): δ (ppm): 192.1, 134.6, 134.0, 130.1, 128.3, 127.2, 127.1 (q, $J = 39.1\text{Hz}$), 126.4, 125.2, 122.4, 121.8, 120.6 (q, $J = 271.1\text{Hz}$), 117.0, 112.3, 21.2; ^{19}F -NMR (282MHz, CDCl_3): δ (ppm): -59.0 (s, 3F); MS (EI): m/z (%): 303 $[\text{M}]^+$ (60), 288(10), 234(10), 212(100), 192(12), 164(20), 144(12), 119(16). HRMS (EI) calcd. For $\text{C}_{17}\text{H}_{12}\text{F}_3\text{N}_1\text{O}_1$ $[\text{M}]^+$: 303.0866, found: 303.0871.

***p*-tolyl(2-(trifluoromethyl)-1H-indol-3-yl)methanone^[5] (2c):**



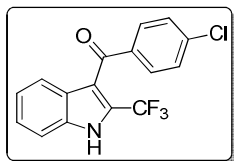
White solid; ^1H -NMR (300MHz, CDCl_3): δ (ppm): 10.17 (br, 1H), 7.83 (d, $J = 7.5\text{Hz}$, 2H), 7.48 (d, $J = 8.4\text{Hz}$, 1H), 7.40 (d, $J = 8.1\text{Hz}$, 1H), 7.33-7.26 (m, 3H), 7.15 (t, $J = 7.5\text{Hz}$, 1H), 2.46 (s, 3H); ^{13}C -NMR (101MHz, CDCl_3): δ (ppm): 193.2, 145.7, 137.6, 136.1, 131.5, 130.6, 128.4 (q, $J = 39.0\text{Hz}$), 127.8, 126.6, 123.7, 123.2, 122.1 (q, $J = 271.1\text{Hz}$), 118.4, 113.8, 23.1; ^{19}F -NMR (282MHz, CDCl_3): δ (ppm): -59.0 (s, 3F); MS (EI): m/z (%): 303 $[\text{M}]^+$ (70), 288(12), 234(8), 212(100), 184(14), 164(24), 144(16), 119(46).

(4-fluorophenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methanone^[5] (2d):



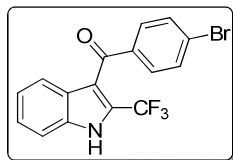
White solid; ^1H -NMR (300MHz, d_6 -DMSO): δ (ppm): 13.12 (br, 1H), 7.83-7.74 (m, 2H), 7.68 (d, $J = 8.1\text{Hz}$, 1H), 7.34-7.28 (m, 3H), 7.19-7.08 (m, 2H); ^{13}C -NMR (101MHz, d_6 -DMSO): δ (ppm): 190.8, 166.9 (d, $J = 253.1\text{Hz}$), 137.1, 136.9, 133.9 (d, $J = 9.5\text{Hz}$), 127.9 (q, $J = 38.5\text{Hz}$), 127.4, 126.7, 123.9, 122.7, 122.7 (q, $J = 270.7\text{Hz}$), 117.5 (d, $J = 22.1\text{Hz}$), 117.3, 114.9; ^{19}F -NMR (282MHz, d_6 -DMSO): δ (ppm): -59.1 (s, 3F), -105.1 (m, 1F); MS (EI): m/z (%): 307 $[\text{M}]^+$ (60), 286(10), 238(8), 212(100), 164(14), 123(58).

(4-chlorophenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methanone^[5] (2e):



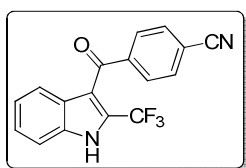
White solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 13.15 (br, 1H), 7.75-7.73 (m, 2H), 7.61-7.55 (m, 3H), 7.35-7.30 (m, 1H), 7.19-7.09 (m, 2H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 191.1, 140.0, 139.2, 136.9, 132.8, 130.1, 128.1 (q, *J* = 38.5Hz), 127.4, 126.8, 124.0, 122.7, 122.6 (q, *J* = 271.0Hz), 117.1, 115.0; ¹⁹F-NMR (282MHz, *d*₆-DMSO): δ (ppm): -59.1 (s, 3F); MS (EI): *m/z* (%): 323 [M]⁺(40), 212(100), 192(18), 164(26), 139(28), 111(66).

(4-bromophenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methanone (2f):



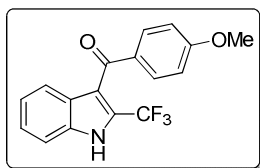
White solid; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 9.79 (br, 1H), 7.75 (d, *J* = 8.4Hz, 2H), 7.61 (d, *J* = 8.4Hz, 2H), 7.50 (d, *J* = 8.1Hz, 1H), 7.38-7.32 (m, 2H), 7.18 (t, *J* = 7.8Hz, 1H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 191.8, 138.9, 135.9, 133.2, 132.6, 129.8, 128.6 (q, *J* = 39.1Hz), 127.6, 126.9, 124.1, 123.1, 121.9 (q, *J* = 271.1Hz), 117.8, 113.7; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -59.1 (s, 3F); MS (EI): *m/z* (%): 367 [M]⁺(14), 319(22), 212(100), 192(20), 164(32), 135(48), 107(20). HRMS (EI) calcd. For C₁₆H₉F₃N₁O₁Br₁ [M]⁺: 366.9814, found: 366.9807.

4-(2-(trifluoromethyl)-1H-indole-3-carbonyl)benzonitrile (2g):



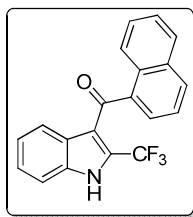
White solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 13.27 (br, 1H), 7.99 (d, *J* = 8.1Hz, 2H), 7.60 (d, *J* = 8.1Hz, 1H), 7.37-7.33 (m, 1H), 7.14-7.12 (m, 1H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 191.1, 144.2, 136.9, 134.6, 131.4, 128.9 (q, *J* = 38.6Hz), 127.3, 126.9, 124.4, 122.8, 122.5 (q, *J* = 271.4Hz), 119.9, 116.9, 116.5, 115.1; ¹⁹F-NMR (282MHz, *d*₆-DMSO): δ (ppm): -53.0 (s, 3F); MS (EI): *m/z* (%): 314 [M]⁺(46), 212(100), 192(10), 164(30), 144(20), 102(92). HRMS(ESI) calcd. For C₁₇H₉F₃N₂O₁ [M+H]⁺: 314.0661, found: 314.0666.

(4-methoxyphenyl)(2-(trifluoromethyl)-1H-indol-3-yl)methanone^[5] (2h):



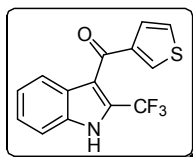
White solid; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 10.20 (br, 1H), 7.91 (d, *J* = 8.7Hz, 2H), 7.48-7.40 (m, 2H), 7.30 (t, *J* = 7.8Hz, 1H), 7.17-7.12 (m, 1H), 6.95 (d, *J* = 8.7Hz, 2H), 3.89 (s, 3H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 192.1, 165.4, 136.2, 133.8, 132.9, 128.0 (q, *J* = 40.0Hz), 127.7, 126.6, 126.2, 123.6, 123.1, 122.2 (q, *J* = 271.1Hz), 118.5, 115.2, 113.8, 56.9; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -59.0 (s, 3F); MS (EI): *m/z* (%): 319 [M]⁺(16), 276(100), 212(30), 194(14), 164(24), 135(92).

naphthalen-1-yl(2-(trifluoromethyl)-1H-indol-3-yl)methanone (2i):



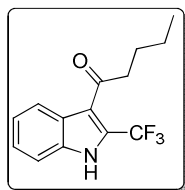
White solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 13.3 (br, 1H), 8.18-8.11 (m, 2H), 8.03-8.00 (m, 1H), 7.65-7.52 (m, 5H), 6.97 (t, *J* = 7.8Hz, 1H), 6.78 (d, *J* = 8.1Hz, 1H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 193.1, 139.6, 136.8, 135.1, 133.5, 131.6, 130.3, 129.9, 129.4, 129.3 (q, *J* = 38.6Hz), 128.3, 127.6, 126.7, 126.6, 124.3, 122.7, 122.7 (q, *J* = 271.2Hz), 118.7, 115.1; ¹⁹F-NMR (282MHz, *d*₆-DMSO): δ (ppm): -53.4 (s, 3F); MS (EI): *m/z* (%): 339 [M]⁺(24), 270(90), 241(14), 212(36), 192(12), 164(24), 127(100). HRMS (EI) calcd. For C₂₀H₁₂F₃N₁O₁[M]⁺: 339.0866, found: 339.0859.

thiophen-3-yl(2-(trifluoromethyl)-1H-indol-3-yl)methanone (2j):



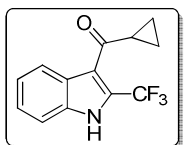
Colorless solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 12.99 (br, 1H), 8.12-8.11 (m, 1H), 7.67-7.64 (m, 1H), 7.58 (d, *J* = 8.4Hz, 1H), 7.37-7.31 (m, 2H), 7.17-7.12 (m, 1H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 185.8, 137.2, 136.9, 129.5, 129.0, 127.2, 127.0 (q, *J* = 38.4Hz), 126.7, 124.1, 123.7, 122.7, 120.1 (q, *J* = 271.1Hz), 118.6, 114.8; ¹⁹F-NMR (282MHz, *d*₆-DMSO): δ (ppm): -58.9 (s, 3F); MS (EI): *m/z* (%): 295 [M]⁺(70), 262(18), 225(10), 212(68), 192(12), 164(20), 144(12), 111(100). HRMS (EI) calcd. For C₁₄H₈F₃N₁O₁S₁ [M]⁺: 295.0273, found: 295.0270.

1-(2-(trifluoromethyl)-1H-indol-3-yl)pentan-1-one^[6] (2k):



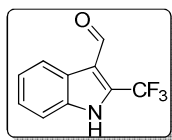
White solid; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 12.76 (br, 1H), 7.96 (d, *J* = 7.8Hz, 1H), 7.52 (d, *J* = 8.1Hz, 1H), 7.31-7.21 (m, 2H), 2.96 (t, *J* = 7.2Hz, 2H), 1.70-1.60 (m, 2H), 1.43-1.30 (m, 2H), 0.90 (t, *J* = 7.5Hz, 3H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 198.4, 135.5, 128.6 (q, *J* = 38.7Hz), 127.2, 126.7, 124.7, 123.8, 122.2 (q, *J* = 271.0Hz), 118.9, 113.7, 44.0, 27.6, 23.7, 15.3; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -57.6 (s, 3F); MS (EI): *m/z* (%): 269[M]⁺(5), 227(50), 212(100), 192(20).

cyclopropyl(2-(trifluoromethyl)-1H-indol-3-yl)methanone (2l):



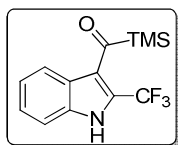
White solid; ¹H-NMR (300MHz, CDCl₃): δ (ppm): 13.00 (br, 1H), 8.05 (d, *J* = 8.1Hz, 1H), 7.58 (d, *J* = 8.1Hz, 1H), 7.38 (t, *J* = 7.2Hz, 1H), 7.29 (t, *J* = 7.2Hz, 1H), 2.65-2.57 (m, 1H), 1.12-1.10 (m, 4H); ¹³C-NMR (101MHz, CDCl₃): δ (ppm): 197.3, 136.7, 127.4 (q, *J* = 38.7Hz), 127.0, 126.7, 124.5, 123.3, 122.8 (q, *J* = 271.1Hz), 118.9, 115.0, 23.1, 12.8; ¹⁹F-NMR (282MHz, CDCl₃): δ (ppm): -63.0 (s, 3F); MS (EI): *m/z* (%): 253[M]⁺(55), 212(100); HRMS(EI) calcd. For C₁₃H₁₀F₃N₁O₁[M]⁺: 253.0709, found: 253.0705.

2-(trifluoromethyl)-1H-indole-3-carbaldehyde^[7] (2m):



White solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 13.39 (br, 1H), 10.20 (br, 1H), 8.23 (d, *J* = 8.1Hz, 1H), 7.58 (d, *J* = 8.1Hz, 1H), 7.43-7.38 (m, 1H), 7.35-7.30 (m, 1H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 186.0, 137.2, 132.7 (q, *J* = 39.2Hz), 127.6, 126.2, 125.6, 123.8, 122.6 (q, *J* = 271.8Hz), 117.3, 115.0; ¹⁹F-NMR (282MHz, *d*₆-DMSO): δ (ppm): -51.6 (s, 3F); MS (EI): *m/z* (%): 213 [M]⁺(100), 192(18), 134(20), 113(22)

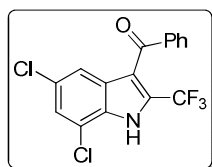
(2-(trifluoromethyl)-1H-indol-3-yl)(trimethylsilyl)methanone (2n):



White solid; ¹H-NMR (300MHz, *d*₆-DMSO): δ (ppm): 7.68 (d, *J* = 8.1Hz, 1H), 7.53 (d, *J* = 8.4Hz, 1H), 7.37-7.32 (m, 1H), 7.26-7.21 (m, 1H), 0.24 (s, 9H); ¹³C-NMR (101MHz, *d*₆-DMSO): δ (ppm): 184.15, 135.2, 130.9 (q, *J* = 36.2Hz), 125.8, 124.9, 124.0, 122.0, 121.1 (q, *J* = 270.4Hz),

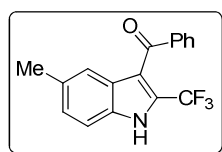
120.9, 112.9, -2.6. ^{19}F -NMR (282MHz, *d6*-DMSO): δ (ppm): -57.3 (s, 3F); MS (EI): *m/z* (%): 285[M]⁺(15), 284(25), 242(25), 216(70), 212(48), 165(47). HRMS (EI) calcd. For C₁₃H₁₄F₃N₁Si₁ [M]⁺: 285.0791, found: 285.0781.

(5,7-dichloro-2-(trifluoromethyl)-1H-indol-3-yl)(phenyl)methanone (2o):



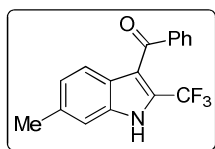
Pale yellow solid; ^1H -NMR (300MHz, *d6*-DMSO): δ (ppm): 13.6 (br, 1H), 7.75 (d, *J* = 7.5Hz, 2H), 7.67 (t, *J* = 7.8Hz, 1H), 7.58 (s, 1H), 7.53 (t, *J* = 7.5Hz, 2H), 7.21 (s, 1H); ^{13}C -NMR (101MHz, *d6*-DMSO): δ (ppm): 191.7, 139.8, 135.6, 133.3, 131.1, 130.6, 129.7 (q, *J* = 39.2Hz), 129.4, 128.3, 126.5, 122.1 (q, *J* = 271.6Hz), 121.0, 120.4, 118.4; ^{19}F -NMR (282MHz, *d6*-DMSO): δ (ppm): -63.9 (s, 3F); MS (EI): *m/z* (%): 356 [M]⁺(78), 280(98), 262(20), 217(22), 197(18), 161(16), 105(100). HRMS(EI) calcd. For C₁₆H₈F₃N₁O₁Cl₂ [M]⁺: 356.9930, found: 352.9932.

(5-methyl-2-(trifluoromethyl)-1H-indol-3-yl)(phenyl)methanone^[5] (2p):



Pale yellow solid; ^1H -NMR (300MHz, *d6*-DMSO): δ (ppm): 12.95 (br, 1H), 7.74-7.72(m, 2H), 7.68-7.63(m, 1H), 7.54-7.46(m, 3H), 7.16(d, *J* = 8.4Hz, 1H), 6.95 (s, 1H), 2.25 (s, 3H); ^{13}C -NMR (101MHz, *d6*-DMSO): δ (ppm): 191.1, 139.2, 133.9, 133.7, 131.5, 129.6, 129.1, 127.2, 126.3, 126.3 (q, *J* = 38.3Hz), 121.4 (q, *J* = 270.7Hz), 115.7, 113.2, 21.6; ^{19}F -NMR (282MHz, *d6*-DMSO): δ (ppm): -57.5 (s, 3F); MS (EI): *m/z* (%): [M]⁺ 303, 226, 206, 151, 105, 77. HRMS(EI) calcd. For C₁₇H₁₂F₃N₁O₁ [M]⁺: 303.0866, found: 303.0864.

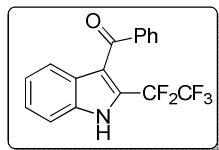
(6-methyl-2-(trifluoromethyl)-1H-indol-3-yl)(phenyl)methanone (2q):



Pale yellow solid; ^1H -NMR (300MHz, *d6*-DMSO): δ (ppm): 12.93 (br, 1H), 7.73-7.71 (m, 2H), 7.64 (dt, *J* = 7.5Hz, *J* = 7.2Hz, 1H), 7.49 (dt, *J* = 7.8Hz, *J* = 7.2Hz, 1H), 7.37 (s, 1H), 7.00 (d, 8.4Hz, 1H), 6.91(d, *J* = 8.4Hz, 1H), 2.39 (s, 3H); ^{13}C -NMR (101MHz, *d6*-DMSO): δ (ppm): 190.9, 139.2, 135.9, 135.0, 133.6, 129.6, 129.0, 126.0 (q, *J* = 36.6Hz), 124.5, 124.1, 121.4 (q, *J* = 270.5Hz), 116.1, 112.9, 21.7; ^{19}F -NMR (282MHz, *d6*-DMSO): δ (ppm): -57.5 (s, 3F); MS (EI): *m/z* (%): [M]⁺ 303, 282, 234, 226, 206, 178, 151, 117, 105.

HRMS(EI) calcd. For C₁₇H₁₂F₃N₁O₁ [M]⁺: 303.0866 , found: 303.0864.

(2-(perfluoroethyl)-1H-indol-3-yl)(phenyl)methanone (2r):



White solid; ¹H-NMR (300MHz, *d6*-DMSO): δ (ppm): 12.95 (br, 1H), 7.72 (d, *J* = 7.5Hz, 2H), 7.63-7.60 (m, 2H), 7.46 (t, *J* = 7.5Hz, 2H), 7.34-7.28 (m, 1H), 7.05-7.04 (m, 2H) ; ¹³C-NMR (101MHz, *d6*-DMSO): δ (ppm): 191.2, 138.8, 136.3, 133.8, 129.7, 129.1, 126.4, 125.4, 123.0 (t, *J* = 29.5Hz), 122.2, 121.1, 119.0 (qt, *J* = 288.3Hz, *J* = 39.5Hz), 118.6, 113.4, 111.6 (qt, *J* = 40.2Hz, *J* = 255.7Hz); ¹⁹F-NMR (282MHz, *d6*-DMSO): δ (ppm): -79.1 (s, 3F), -104.9 (s, 2F); MS (EI): *m/z* (%): 339 [M]⁺(58), 262(100), 220(10), 165(16), 119(10), 105(30). HRMS(EI) calcd. For C₁₇H₁₀F₅N₁O₁ [M]⁺: 339.0677, found: 339.0683.

Reference:

- [1] K. Tamura, H. Mizukami, K. Maeda, H. Watanabe and K. Uneyama, *J. Org. Chem.* 1993, **58**, 32.
- [2] Y. Li, J. Zhu, L. Zhang, Y. Wu, Y. Gong, *Chem.-Eur. J.* **2013**, *19*, 8294.
- [3] J. Zhu, H. Xie, Z. Chen, S. Li, Y. Wu, *Org. Biomol. Chem.* **2012**, *10*, 516.
- [4] A. Isobe, J. Takagi, T. Katagiri, K. Uneyama, *Org. lett.* *10*, 2657.
- [5] Z. Chen, J. Zhu, H. Xie, S. Li, Y. Wu, Y. Gong, *Synlett* **2010**, *9*, 1418.
- [6] Y. Ueda, H. Watanabe, J. Uemura, K. Uneyama, *Tetrahedron lett.* **1993**, *34*, 7933.
- [7] J. Tessier, J. Demasse, J. Demoute, Eur. Pat. Appl. 1988, EP 261035 A1 19880323.

¹H and ¹³C NMR Spectra:

