Supporting Information for

Copper-catalyzed synthesis of trifluoromethylated bis(indolyl)arylmethanes from 2-arylindoles and 2,2,2-trifluoroacetohydrazide

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General remarks

$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were recorded using Bruker AVIII 400 spectrometer. $^1$H NMR and $^{13}$C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and $^{19}$F NMR chemical shifts were determined relative to CFCl$_3$ as the external standard and low field is positive. Coupling constants ($J$) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: $^1$H NMR (chloroform δ 7.26) and $^{13}$C NMR (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

2,2,2-Trifluoroacetohydrazide$^1$, the 2-arynildoles,$^2$ 2-phenyl-3-(2,2,2-trifluoroacetyl) indole $^5$ and 2,2,2-trifluoro-1-(2-phenyl-1H-indol-3-yl)-1-ethanol $^6$ were prepared according to the published procedures. Other reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use.
General procedure for the synthesis of trifluoromethylated bis(indolyl)arylmethanes 3

The 2-arylindoles (2) (1.0 mmol), trifluoroacetyl hydrazine (1) (153 mg, 1.2 mmol, 1.2 equiv), DTBP (276 μL, 1.5 mmol, 1.5 equiv), KOt-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)₂ (322 mg, 1.0 mmol, 1.0 equiv), Cu₂S (7.9 mg, 0.050 mmol, 5.0 mol%) and DCE (4.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. The tube was removed from the oil bath and cooled to r.t. The reaction mixture was diluted with ethyl acetate (15 mL × 3), washed with saturated sodium bicarbonate (30 mL), and water (20 mL), dried over MgSO₄. The solvent was removed by rotary evaporation and the resulting crude product 3 was purified by column chromatography over silica gel (n-pentanes/ethyl acetate).
Reaction with the C2-unsubstituent of indole

The indole (1.0 mmol), trifluoroacetyl hydrazine (153 mg, 1.2 mmol, 1.2 equiv), DTBP (276 µL, 1.5 mmol, 1.5 equiv), KOt-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)$_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu$_2$S (7.9 mg, 0.050 mmol, 5.0 mol%) and DCE (4.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. The tube was removed from the oil bath and cooled to r.t. A $^{19}$F NMR spectrum was acquired, and no trace of trifluoromethylated bis(indolyl)arylmethane was detected.
Mechanistic study

(a) Reaction of 2a with 1 in the presence of TEMPO

The 2-phenyl-1H-indole (2a) (193 mg, 1.0 mmol), trifluoroacetyl hydrazine (1) (153 mg, 1.2 mmol, 1.2 equiv), DTBP (276 µL, 1.5 mmol, 1.5 equiv), KOt-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)$_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu$_2$S (7.9 mg, 0.050 mmol, 0.050 equiv), TEMPO (312 mg, 2.0 mmol, 2.0 equiv), and DCE (3.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. 10 µL (Trifluoromethoxy)benzene was then added as an internal standard. The reaction mixture was filtered through a layer of celite. The filtrate was analyzed by $^{19}$F NMR and GC-MS, and no trace of 3,3′-(2,2,2-trifluoroethane-1,1-diyl)bis(2-phenyl-1H-indole) (3a) was detected. The adduct 2,2,6,6-tetramethylpiperidin-1-yl 2,2,2-trifluoroacetate (4) was formed in ca. 4% GC yield.
(b) Reaction of 2a with trifluoroacetaldehyde hydrate

The 2-phenyl-1H-indole (2a) (193 mg, 1.0 mmol), trifluoroacetaldehyde hydrate (99 µL, 1.2 mmol, 1.2 equiv), DTBP (276 µL, 1.5 mmol, 1.5 equiv), KOt-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)$_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu$_2$S (7.9 mg, 0.050 mmol, 0.050 equiv), and DCE (4.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. 10 µL (Trifluoromethoxy)benzene was then added as an internal standard. The reaction mixture was filtered through a layer of celite. The filtrate was analyzed by $^{19}$F NMR and GC-MS, and no trace of 3,3'-((2,2,2-trifluoroethane-1,1-diyl)bis(2-phenyl-1H-indole) (3a) was detected.
(c) Reaction of trifluoroacetylated indole with 2-arylidole under standard conditions

\[
\begin{align*}
\text{F}_3\text{C} - \text{O} & \quad + \\
\text{N} & \quad \text{HN}
\end{align*}
\]

\[
\text{Cu}_2\text{S} (5.0 \text{ mol\%}) \quad \text{Mg(OTf)}_2 (1.0 \text{ equiv})
\]

\[
\text{DTBP} (1.5 \text{ equiv}) \quad \text{KOr-Bu} (3.5 \text{ equiv})
\]

\[
\text{DCE, 120 °C, 12 h}
\]

The 2-(p-tolyl)-1H-indole 2f (207 mg, 1.0 mmol), 2,2,2-trifluoro-1-(2-phenyl-1H-indol-3-yl)-1-ethanone 5 (303 mg, 1.0 mmol), DTBP (276 µL, 1.5 mmol, 1.5 equiv), KOr-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)_2 (322 mg, 1.0 mmol, 1.0 equiv), Cu_2S (7.9 mg, 0.050 mmol, 0.050 equiv), and DCE (4.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. The tube was removed from the oil bath and cooled to r.t. A $^{19}$F NMR spectrum was acquired, and no trace of trifluoromethylated bis(indolyl)arylmethane 3f was detected.
(d) Reaction of 2,2,2-trifluoro-1-(2-phenyl-1H-indol-3-yl)ethanol 6 with 2-arylidene 2a under standard conditions

The 2-arylidene 2a (193 mg, 1.0 mmol), 2,2,2-trifluoro-1-(2-phenyl-1H-indol-3-yl)-1-ethanol 6 (291 mg, 1.0 mmol), DTBP (0.276 mL, 1.5 mmol, 1.5 equiv), KOr-Bu (392 mg, 3.5 mmol, 3.5 equiv), Mg(OTf)₂ (322 mg, 1.0 mmol, 1.0 equiv), Cu₂S (7.9 mg 0.050 mmol, 0.050 equiv) and DCE (4.0 mL) were added to a oven-dried 25.0 mL test tube with Teflon screw cap. The tube was sealed and the mixture solution was placed into a preheated 120 °C oil bath for 12 h. The tube was removed from the oil bath and cooled to r.t. A $^{19}$F NMR spectrum was acquired, and only 2% yield of trifluoromethylated bis(indolyl)aryl methane 3a was detected.
Data for compounds 3.

3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-phenyl-1H-indole) (3a)
Obtained as a white solid in 99% yield (231 mg). M.p. 248.1–249.2 °C. Rf (n-pentane/ethyl acetate = 7:1) = 0.40. ¹H NMR (400 MHz, DMSO-d₆) δ 11.44 (s, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.43 – 7.24 (m, 8H), 7.21 – 7.06 (m, 6H), 7.00 (t, J = 7.5 Hz, 2H), 5.57 (q, J = 11.5 Hz, 1H). ¹³F NMR (376 MHz, DMSO-d₆) δ -61.9 (d, J = 11.5 Hz, 3F). ¹³C NMR (101 MHz, DMSO-d₆) δ 138.2 (s), 136.3 (s), 132.7 (s), 129.3 (s), 128.9 (s), 128.6 (q, J = 280.7 Hz), 128.5 (s), 126.9 (s), 121.7 (s), 120.7 (s), 119.7 (s), 111.9 (s), 106.5 (s), δ 39.6 (q, J = 29.2 Hz; overlapped with carbon signal of DMSO-d₆). IR (ATR): 3425, 3389, 1646, 1486, 1454, 1423, 1325, 1309, 1250, 1163, 998, 684, 518, 471 cm⁻¹. HRMS (ESI) m/z: calcd. for C₃₀H₂₁F₃N₂: 466.1651; found: 466.1652.

3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-methyl-2-phenyl-1H-indole) (3b)
Obtained as a white solid in 76% yield (188 mg). M.p. 251.8–253.6 °C. Rf (n-pentane/ethyl acetate = 9:1) = 0.42. ¹H NMR (400 MHz, DMSO-d₆) δ 11.30 (s, 2H), 7.58 (s, 2H), 7.44 – 7.08 (m, 12H), 6.96 (d, J = 7.7 Hz, 2H), 5.53 (q, J = 11.5 Hz, 1H), 2.33 (s, 6H). ¹³F NMR (376 MHz, DMSO-d₆) δ -61.8 (d, J = 11.5 Hz, 3F). ¹³C NMR (101 MHz, DMSO-d₆) δ 138.2 (s), 134.7 (s), 133.0 (s), 129.5 (s), 128.9 (s), 128.6 (d, J = 278.2 Hz), 128.4 (s), 127.7 (s), 127.2 (s), 123.2 (s), 120.7 (s), 111.5 (s), 106.2 (s), 39.4 (q, J = 29.8 Hz; overlapped with carbon signal of DMSO-d₆), 21.9 (s).

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-fluoro-2-phenyl-1H-indole) (3c)

Obtained as a white solid in 95% yield (253 mg). M.p. 203.5–204.8 °C. \(R_f\) (n-pentane/ethyl acetate = 4:1) = 0.50. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.64 (s, 2H), 7.47 – 7.23 (m, 10H), 7.16 (d, \(J = 7.4\) Hz, 4H), 7.02 (t, \(J = 8.9\) Hz, 2H), 5.56 (q, \(J = 11.5\) Hz, 1H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -62.2 (d, \(J = 11.5\) Hz, 3F), -123.7 (td, \(J = 10.5, 5.2\) Hz, 2F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 157.5 (d, \(J = 232.0\) Hz), 140.4 (s), 133.0 (s), 132.3 (s), 129.3 (s), 128.9 (s), 128.8 (s), 128.4 (q, \(J = 279.7\) Hz), 127.0 (d, \(J = 10.2\) Hz), 113.0 (d, \(J = 10.0\) Hz), 110.0 (d, \(J = 26.0\) Hz), 106.4 (s), 105.1 (d, \(J = 25.2\) Hz), \(\delta\) 39.19 (q, \(J = 29.4\) Hz; overlapped with carbon signal of DMSO-\(d_6\)).


3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-phenyl-1H-indole) (3d)

Obtained as a white solid in 83% yield (222 mg). M.p. 223.4–224.6 °C. \(R_f\) (n-pentane/ethyl acetate = 9:1) = 0.43. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.70 (s, 2H), 7.59 (s, 2H), 7.36 (t, \(J = 9.2\) Hz, 4H), 7.29 (t, \(J = 6.9\) Hz, 4H), 7.14 (d, \(J = 7.2\) Hz, 6H), 5.52 (q, \(J = 11.5\) Hz, 1H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -62.2 (d, \(J = 11.5\) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 140.1 (s), 134.7 (s), 132.0 (s), 129.3 (s), 128.9 (s), 128.2 (q, \(J = 282.7\) Hz), 127.8 (s), 124.5 (s), 121.8 (s), 119.5 (s), 113.5 (s),
105.9 (s), δ 39.42 (q, \(J = 29.4\) Hz; overlapped with carbon signal of DMSO-\(d_6\)). IR (ATR): 3416, 2253, 2167, 2127, 1656, 1475, 1161, 1048, 1023, 1001, 822, 760, 610 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{30}\)H\(_{19}\)Cl\(_2\)F\(_3\)N\(_2\): 534.0872; found: 534.0869.

### 3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-bromo-2-phenyl-1H-indole) (3e)

Obtained as a white solid in 83% yield (258 mg). M.p. 269.8–270.7 °C. \(R_f\) (n-pentane/ethyl acetate = 5:1) = 0.57. \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)) δ 11.43 (s, 2H), 7.81 (d, \(J = 8.0\) Hz, 2H), 7.44 (d, \(J = 7.7\) Hz, 4H), 7.35 (d, \(J = 8.0\) Hz, 2H), 7.18 – 6.95 (m, 8H), 5.57 (q, \(J = 11.5\) Hz, 1H). \(^1^9^F\) NMR (376 MHz, DMSO-\(d_6\)) δ -61.4 (d, \(J = 11.5\) Hz, 3F). \(^1^3^C\) NMR (101 MHz, DMSO-\(d_6\)) δ 136.8 (s), 136.4 (s), 131.8 (s), 131.6 (s), 131.0 (s), 128.7 (d, \(J = 280.3\) Hz), 126.5 (s), 122.2 (s), 122.0 (s), 120.8 (s), 119.9 (s), 112.0 (s), 107.1 (s), δ 39.3 (q, \(J = 29.9\) Hz; overlapped with carbon signal of DMSO-\(d_6\)). IR (ATR): 3418, 3377, 1641, 1597, 1484, 1456, 1254, 1158, 1091, 1008, 826, 740, 490 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{30}\)H\(_{15}\)Br\(_2\)F\(_3\)N\(_2\) [M–H\(^+\): 620.9799; found: 620.9794.

### 3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(p-tolyl)-1H-indole) (3f)

Obtained as a white solid in 86% yield (212 mg). M.p. 201.5–202.8 °C. \(R_f\) (n-pentane/ethyl acetate = 6:1) = 0.51. \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)) δ 11.34 (s, 2H), 7.81 (d, \(J = 8.0\) Hz, 2H), 7.35 (d, \(J = 7.9\) Hz, 2H), 7.15 – 6.94 (m, 12H), 5.59 (q, \(J = 11.6\) Hz, 1H), 2.36 (s, 6H). \(^1^9^F\) NMR (376 MHz, DMSO-\(d_6\)) δ -61.8 (d, \(J = 11.6\) Hz, 3F). \(^1^3^C\) NMR (101 MHz, DMSO-\(d_6\)) δ 138.4 (s), 137.8 (s), 136.2 (s), 129.8 (s),
129.4 (s), 129.0 (s), 128.7 (q, \( J = 280.3 \) Hz), 126.8 (s), 121.5 (s), 120.7 (s), 119.6 (s), 111.8 (s), 106.4 (s), 39.41 (q, \( J = 29.2 \) Hz; overlapped with carbon signal of DMSO-\( d_6 \)), 21.3 (s). IR (ATR): 3372, 2924, 1639, 1501, 1456, 1096, 1023, 1007, 876, 819, 612, 527 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{32}\)H\(_{26}\)F\(_3\)N\(_2\) [M+H]\(^+\): 495.2042; found: 495.2041.

3,3′-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3,5-dimethylphenyl)-1H-indole) (3g)

Obtained as a white solid in 71% yield (196 mg). M.p. 246.0–247.5 \(^\circ\)C. \( R_f \) (\( n \)-pentane/ethyl acetate = 10:1) = 0.43. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 11.30 (s, 2H), 7.68 (d, \( J = 7.6 \) Hz, 2H), 7.34 (d, \( J = 7.7 \) Hz, 2H), 7.09 (t, \( J = 7.0 \) Hz, 2H), 6.96 (t, \( J = 7.0 \) Hz, 2H), 6.92 (s, 2H), 6.70 (s, 4H), 5.59 (q, \( J = 11.7 \) Hz, 1H), 2.17 (s, 12H). \(^19\)F NMR (376 MHz, DMSO-\( d_6 \)) \( \delta \) -61.9 (d, \( J = 11.7 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 138.5 (s), 137.5 (s), 136.2 (s), 132.6 (s), 129.8 (s), 128.6 (q, \( J = 280.6 \) Hz), 127.0 (s), 126.9 (s), 121.4 (s), 120.5 (s), 119.6 (s), 111.7 (s), 106.5 (s), 39.4 (q, \( J = 29.6 \) Hz; overlapped with carbon signal of DMSO-\( d_6 \)), 21.4 (s). IR (ATR): 3438, 3385, 3045, 2918, 2860, 2644, 1602, 1457, 1324, 1251, 1152, 1097, 744, 530 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{34}\)H\(_{29}\)F\(_3\)N\(_2\): 522.2277; found: 522.2273.

3,3′-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-methoxyphenyl)-1H-indole) (3h)

Obtained as a white solid in 76% yield (199 mg). M.p. 189.1–190.8 \(^\circ\)C. \( R_f \) (\( n \)-pentane/ethyl acetate = 4:1) = 0.45. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 11.40 (s,
2H), 7.79 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.23 – 7.05 (m, 4H), 7.00 (t, J = 6.8 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 6.75 (d, J = 6.9 Hz, 2H), 6.69 (s, 2H), 5.68 (q, J = 11.5 Hz, 1H), 3.70 (s, 6H). 

19F NMR (376 MHz, DMSO-d6) δ -61.7 (d, J = 10.5 Hz, 3F). 

13C NMR (101 MHz, DMSO-d6) δ 159.4 (s), 138.2 (s), 136.3 (s), 133.9 (s), 129.8 (s), 128.7 (q, J = 280.7 Hz), 126.8 (s), 121.7 (s), 121.4 (s), 120.8 (s), 119.8 (s), 114.6 (s), 114.3 (s), 111.9 (s), 106.7 (s), 55.3 (s), 39.4 (q, J = 30.3 Hz; overlapped with carbon signal of DMSO-d6). IR (ATR): 3394, 3063, 3016, 1609, 1579, 1458, 1250, 1151, 1040, 740, 688, 506 cm⁻¹. HRMS (ESI) m/z: calcd. for C32H26F3N2O2 [M+H]+: 527.1941; found: 527.1945.

3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-fluorophenyl)-1H-indole) (3i)

Obtained as a white solid in 73% yield (183 mg). M.p. 250.6 – 251.9 °C. Rf (n-pentane/ethyl acetate = 8:1) = 0.39. 

1H NMR (400 MHz, DMSO-d6) δ 11.43 (s, 2H), 7.83 (d, J = 5.0 Hz, 2H), 7.35 (d, J = 5.7 Hz, 2H), 7.28 – 6.79 (m, 12H), 5.52 (q, J = 10.5 Hz, 1H). 

19F NMR (376 MHz, DMSO-d6) δ -61.7 (d, J = 10.5 Hz, 3F), -113.7 (s, 2F). 

13C NMR (101 MHz, DMSO-d6) δ 162.4 (d, J = 245.6 Hz), 137.2 (s), 136.3 (s), 131.3 (d, J = 8.4 Hz), 128.9 (d, J = 3.0 Hz), 128.7 (q, J = 280.8 Hz), 126.5 (s), 121.8 (s), 120.7 (s), 119.8 (s), 115.8 (d, J = 21.6 Hz), 111.9 (s), 106.8 (s), 39.4 (q, J = 30.3 Hz; overlapped with carbon signal of DMSO-d6). IR (ATR): 3458, 3392, 3258, 3065, 1609, 1558, 1500, 1456, 1431, 1324, 1220, 1154, 746, 701 cm⁻¹. HRMS (ESI) m/z: calcd. for C30H19F3N2: 502.1463; found: 502.1462.
3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-fluorophenyl)-1H-indole) (3j)

Obtained as a white solid in 66% yield (176 mg). M.p. 245.8–246.9 °C. R_f (n-pentane/ethyl acetate = 4:1) = 0.49. ^1H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 2H), 7.80 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 14.5, 7.3 Hz, 2H), 7.13 (t, J = 7.7 Hz, 4H), 7.02 (d, J = 6.8 Hz, 4H), 6.90 (d, J = 9.8 Hz, 2H), 5.62 (q, J = 11.6 Hz, 1H). ^19F NMR (376 MHz, DMSO-d_6) δ -61.6 (d, J = 11.6 Hz, 3F), -112.4 (dd, J = 15.8, 9.1 Hz, 2F). ^13C NMR (101 MHz, DMSO-d_6) δ 162.2 (d, J = 244.3 Hz), 136.5 (d, J = 34.4 Hz), 134.7 (d, J = 8.3 Hz), 130.8 (d, J = 8.7 Hz), 128.6 (q, J = 280.6 Hz), 126.0 (d, J = 128.2 Hz), 121.0 (d, J = 209.7 Hz), 120.8 (s), 116.0 (d, J = 22.1 Hz), 115.4 (d, J = 20.9 Hz), 112.0 (s), 107.2 (s), 39.3 (q, J = 29.5 Hz; overlapped with carbon signal of DMSO-d_6). IR (ATR): 3428, 3394, 1615, 1587, 1455, 1321, 1139, 1095, 872, 682, 500 cm^{-1}. HRMS (ESI) m/z: calcd. for C_{30}H_{20}F_{5}N_{2} [M+H]^+: 503.1541; found: 503.1542.

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-chlorophenyl)-1H-indole) (3k)

Obtained as a white solid in 76% yield (203 mg). M.p. 247.2–248.0 °C. R_f (n-pentane/ethyl acetate = 6:1) = 0.61. ^1H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 7.8 Hz, 4H), 7.19 – 7.08 (m, 6H), 7.02 (t, J = 7.4 Hz, 2H), 5.58 (q, J = 11.5 Hz, 1H). ^19F NMR (376 MHz, DMSO-d_6) δ -61.5 (d, J = 11.5 Hz, 3F). ^13C NMR (101 MHz, DMSO-d_6) δ 136.8 (s), 136.4 (s), 133.5 (s), 131.2 (s), 130.8 (s), 128.8 (s), 128.7 (q, J = 280.9 Hz), 126.5 (s), 121.9 (s), 120.8 (s), 119.9 (s), 112.0 (s), 107.1 (s), 39.3 (q, J = 30.0 Hz; overlapped
with carbon signal of DMSO-\(d_6\). IR (ATR): 3431, 3379, 1643, 1485, 1456, 1256, 1160, 1092, 1013, 829, 699, 462 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{30}\)H\(_{20}\)Cl\(_2\)F\(_3\)N\(_2\) [M+H]\(^+\): 535.0775; found: 535.0781.

![Chemical structure of compound 3l](image)

3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-chlorophenyl)-1H-indole) (3l)
Obtained as a white solid in 79% yield (215 mg). M.p. 215.4–216.3 °C. \(R_f\) (n-pentane/ethyl acetate = 8:1) = 0.46. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.48 (s, 2H), 7.76 (d, \(J = 8.1\) Hz, 2H), 7.35 (d, \(J = 7.7\) Hz, 4H), 7.27 (t, \(J = 7.8\) Hz, 2H), 7.13 (t, \(J = 7.1\) Hz, 4H), 7.07 (s, 2H), 7.01 (t, \(J = 7.5\) Hz, 2H), 5.55 (q, \(J = 11.6\) Hz, 1H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -61.6 (d, \(J = 11.6\) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 136.5 (s), 136.4 (s), 134.5 (s), 133.6 (s), 130.5 (s), 128.9 (s), 128.6 (q, \(J = 280.9\) Hz), 128.5 (s), 127.7 (s), 126.5 (s), 122.1 (s), 120.7 (s), 120.0 (s), 112.0 (s), 107.2 (s), 39.4 (q, \(J = 30.4\) Hz; overlapped with carbon signal of DMSO-\(d_6\)). IR (ATR): 3444, 3378, 3062, 1639, 1599, 1453, 1258, 1154, 1092, 787, 733, 455 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{30}\)H\(_{20}\)Cl\(_2\)F\(_3\)N\(_2\) [M+H]\(^+\): 535.0775; found: 535.0778.

![Chemical structure of compound 3m](image)

3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-bromophenyl)-1H-indole) (3m)
Obtained as a white solid in 72% yield (221 mg). M.p. 123.3–124.6 °C. \(R_f\) (n-pentane/ethyl acetate = 4:1) = 0.48. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.71 (s, 2H), 7.76 (s, 2H), 7.42 – 7.20 (m, 10H), 7.15 (d, \(J = 7.0\) Hz, 4H), 5.50 (q, \(J = 11.5\) Hz, 1H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)) \(\delta\) -62.1 (d, \(J = 11.5\) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 139.9 (s), 134.8 (s), 131.9 (s), 129.3 (s), 128.9 (s), 128.4 (s), 128.2
(q, $J = 280.6$ Hz), 124.3 (s), 122.5 (s), 113.9 (s), 112.5 (s), 105.7 (s), 39.4 (q, $J = 29.3$ Hz; overlapped with carbon signal of DMSO-$d_6$). IR (ATR): 3410, 3061, 1709, 1604, 1564, 1343, 1312, 1251, 1158, 1099, 764, 496 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{30}$H$_{18}$Br$_2$F$_3$N$_2$ [M–H]$^+$: 620.9794; found: 620.9793.

$3,3'$-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-bromophenyl)-1H-indole) (3n)

Obtained as a white solid in 81% yield (503 mg). M.p. 201.2–202.3 °C. $R_f$ (n-pentane/ethyl acetate = 6:1) = 0.41. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 11.48 (s, 2H), 7.75 (d, $J = 7.8$ Hz, 2H), 7.50 (d, $J = 7.1$ Hz, 2H), 7.35 (d, $J = 7.8$ Hz, 2H), 7.28 – 7.08 (m, 8H), 7.01 (t, $J = 7.2$ Hz, 2H), 5.55 (q, $J = 11.5$ Hz, 1H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -61.6 (d, $J = 11.5$ Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 136.4 (d, $J = 8.6$ Hz), 134.7 (s), 131.7 (s), 131.4 (s), 130.7 (s), 128.5 (d, $J = 280.7$ Hz), 128.0 (s), 126.4 (s), 122.1 (d, $J = 14.1$ Hz), 120.7 (s), 120.0 (s), 112.0 (s), 107.2 (s), 39.3 (q, $J = 30.3$ Hz; overlapped with carbon signal of DMSO-$d_6$). IR (ATR): 3388, 3057, 1598, 1453, 1254, 1155, 1099, 1020, 996, 878, 741, 620 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{30}$H$_{20}$Br$_2$F$_3$N$_2$ [M+H]$^+$: 622.9940; found: 622.9933.

$3,3'$-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(naphthalen-2-yl)-1H-indole) (3o)

Obtained as a white solid in 91% yield (258 mg). M.p. 139.7–140.3 °C. $R_f$ (n-pentane/ethyl acetate = 5:1) = 0.62. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 11.49 (s, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.59 (s, 2H), 7.50 (t, $J = 7.1$ Hz, 3H), 7.47 – 7.35 (m, 7H), 7.20 – 7.06 (m, 4H), 7.01 (t, $J = 7.5$ Hz, 2H), 5.82 (q, $J$
= 11.6 Hz, 1H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -61.8 (d, $J = 11.6$ Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 138.2 (s), 136.5 (s), 132.8 (s), 132.6 (s), 130.1 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (s), 126.9 (s), 126.8 (s), 126.7 (s), 121.8 (s), 120.8 (s), 119.8 (s), 111.9 (s), 107.1 (s), 39.4 (q, $J = 29.8$ Hz; overlapped with carbon signal of DMSO-$d_6$). IR (ATR): 3440, 2250, 2124, 1660, 1325, 1154, 1052, 1024, 1003, 820, 757, 620, 479 cm$^{-1}$. HRMS (ESI) m/z: calcd. for $C_{38}H_{26}F_{3}N_{2}$ [M+H]$^+$: 567.1964; found: 567.1965.

\[ \text{3,3\textsuperscript{'}-(2,2,2-}	ext{Trifluoroethane-1,1-diyli)b}i\text{(2-(4-isopropylphenyl)-5-methyl-1H-indole)} \]

\( \text{(3p)} \)

Obtained as a white solid in 59% yield (199 mg). M.p. 235.1–236.4 °C. $R_f$ (n-pentane/ethyl acetate = 8:1) = 0.48. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 11.23 (s, 2H), 7.52 (s, 2H), 7.33 – 7.07 (m, 10H), 6.93 (d, $J = 7.6$ Hz, 2H), 5.44 (q, $J = 11.5$ Hz, 1H), 2.99 – 2.83 (m, 2H), 2.30 (s, 6H), 1.25 (s, 12H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -61.8 (d, $J = 11.5$ Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 148.5 (s), 138.1 (s), 134.6 (s), 130.6 (s), 129.5 (s), 128.5 (q, $J = 280.3$ Hz), 127.6 (s), 127.4 (s), 126.8 (s), 123.1 (s), 120.6 (s), 111.4 (s), 105.9 (s), 39.4 (q, $J = 29.8$ Hz; overlapped with carbon signal of DMSO-$d_6$), 33.7 (s), 24.2 (s), 21.9 (s). IR (ATR): 3386, 2960, 2927, 1636, 1481, 1438, 1315, 1252, 1157, 1096, 1019, 837, 793, 540 cm$^{-1}$. HRMS (ESI) m/z: calcd. for $C_{38}H_{38}F_{3}N_{2}$ [M+H]$^+$: 579.2906; found: 579.2903.
3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-chlorophenyl)-5-methyl-1H-indole)  
(3q)

Obtained as a white solid in 78% yield (219 mg). M.p. 275.1–275.9 °C. \( R_f \) (n-pentane/ethyl acetate = 6:1) = 0.43. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 11.30 (s, 2H), 7.65 (s, 2H), 7.30 (d, \( J = 7.8 \) Hz, 4H), 7.23 (d, \( J = 8.2 \) Hz, 2H), 7.15 (d, \( J = 8.0 \) Hz, 4H), 6.95 (d, \( J = 8.2 \) Hz, 2H), 5.51 (q, \( J = 11.7 \) Hz, 1H), 2.35 (s, 6H). \(^19\)F NMR (376 MHz, DMSO-\(d_6\)) \( \delta \) -61.5 (d, \( J = 11.7 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \( \delta \) 136.8 (s), 134.8 (s), 133.5 (s), 131.4 (s), 130.9 (s), 128.8 (s), 128.7 (q, \( J = 280.8 \) Hz), 127.9 (s), 126.8 (s), 123.5 (s), 120.7 (s), 111.5 (s), 106.8 (s), 39.3 (q, \( J = 30.2 \) Hz; overlapped with carbon signal of DMSO-\(d_6\)), 21.9 (s). IR (ATR): 3455, 3388, 1640, 1474, 1436, 1315, 1158, 1093, 831, 793, 494 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{33}\)H\(_{24}\)Cl\(_2\)F\(_3\)N\(_2\) [M+H\(^+\)]: 563.1263; found: 563.1262.

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\]

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-bromophenyl)-5-methyl-1H-indole)  
(3r)

Obtained as a white solid in 68% yield (221 mg). M.p. 263.2–263.9 °C. \( R_f \) (n-pentane/ethyl acetate = 8:1) = 0.42. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \( \delta \) 11.28 (s, 2H), 7.61 (s, 2H), 7.43 (d, \( J = 7.5 \) Hz, 4H), 7.21 (d, \( J = 8.1 \) Hz, 2H), 7.08 (d, \( J = 7.5 \) Hz, 4H), 6.95 (d, \( J = 8.2 \) Hz, 2H), 5.48 (q, \( J = 11.7 \) Hz, 1H), 2.34 (s, 6H). \(^19\)F NMR (376 MHz, DMSO-\(d_6\)) \( \delta \) -61.4 (d, \( J = 11.7 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \( \delta \) 136.8 (s), 134.7 (s), 131.7 (s), 131.1 (s), 128.6 (q, \( J = 279.0 \) Hz), 127.9 (s), 126.8 (s), 123.5 (s), 122.1 (s), 120.6 (s), 111.6 (s), 106.7 (s), 39.2 (q, \( J = 24.8 \) Hz; overlapped with carbon signal of DMSO-\(d_6\)), 21.9 (s). IR (ATR): 3447, 3390, 1479, 1437, 1316, 1253, 1148, 1091, 1007, 883, 827, 793, 492 cm\(^{-1}\) HRMS (ESI) m/z: calcd. for C\(_{33}\)H\(_{24}\)Br\(_2\)F\(_3\)N\(_2\) [M+H\(^+\)]: 651.0252; found: 651.0253.
3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-chlorophenyl)-6-methyl-1H-indole) (3s)

Obtained as a white solid in 65% yield (183 mg). M.p. 238.5–239.2 °C. Rf (n-pentane/ethyl acetate = 6:1) = 0.42. 1H NMR (400 MHz, DMSO-d6) δ 11.24 (s, 2H), 7.68 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.0 Hz, 4H), 7.18 – 7.04 (m, 6H), 6.84 (d, J = 8.0 Hz, 2H), 5.50 (q, J = 11.5 Hz, 1H), 2.38 (s, 6H). 19F NMR (376 MHz, DMSO-d6) δ -61.6 (d, J = 11.5 Hz, 3F). 13C NMR (101 MHz, DMSO-d6) δ 136.8 (s), 136.1 (s), 133.3 (s), 131.4 (s), 131.1 (s), 130.7 (s), 128.8 (s), 128.7 (q, J = 281.6 Hz), 124.4 (s), 121.7 (s), 120.6 (s), 111.6 (s), 107.1 (s), 39.4 (q, J = 16.9 Hz; overlapped with carbon signal of DMSO-d6), 21.6 (s). IR (ATR): 3456, 3389, 1476, 1459, 1437, 1394, 1345, 1124, 1013, 883, 725, 530 cm⁻¹ HRMS (ESI) m/z: calcd. for C32H24Cl2F3N2 [M+H]^+: 563.1259; found: 563.1263.

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-ethylphenyl)-5-fluoro-1H-indole) (3t)

Obtained as a white solid in 71% yield (198 mg). M.p. 221.3–222.1 °C. Rf (n-pentane/ethyl acetate = 8:1) = 0.38. 1H NMR (400 MHz, DMSO-d6) δ 11.53 (s, 2H), 7.40 – 7.33 (m, 2H), 7.29 (d, J = 7.5 Hz, 2H), 7.10 (d, J = 7.5 Hz, 4H), 7.05 (d, J = 7.2 Hz, 4H), 6.97 (t, J = 8.9 Hz, 2H), 5.49 (q, J = 11.5 Hz, 1H), 2.63 (q, J = 7.2 Hz, 4H), 1.22 (t, J = 7.2 Hz, 6H). 19F NMR (376 MHz, DMSO-d6) δ -62.1 (d, J = 11.6 Hz, 3F), -123.9 (dd, J = 16.6, 7.7 Hz, 2F). 13C NMR (101 MHz, DMSO-d6) δ 157.4 (d, J = 230.9 Hz), 144.3 (s), 140.5 (s), 132.9 (s), 129.6 (s), 129.2 (s), 128.4 (q, J = 280.7 Hz), 128.2 (s), 127.0 (d, J = 10.2 Hz), 112.9 (d, J = 10.0 Hz), 109.8 (d, J = 26.0 Hz), 106.3
(s), 105.0 (d, $J = 25.2$ Hz), 39.2 (q, $J = 32.9$ Hz; overlapped with carbon signal of DMSO-$d_6$), 28.4 (s), 15.8 (s). IR (ATR): 3449, 3406, 3085, 3026, 2969, 2932, 1576, 1485, 1450, 1249, 1161, 1093, 798, 616 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{34}$H$_{28}$F$_3$N$_2$[M+H]$^+$: 559.2054; found: 559.2050.

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-(p-tolyl)-1H-indole) (3u)

Obtained as a white solid in 77% yield (228 mg). M.p. 257.5–258.4 °C. $R_f$ (n-pentane/ethyl acetate = 4:1) = 0.38. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.62 (s, 2H), 7.63 (s, 2H), 7.37 (d, $J = 8.6$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 4H), 7.02 (d, $J = 7.7$ Hz, 4H), 5.55 (q, $J = 11.6$ Hz, 1H), 2.35 (s, 6H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -62.0 (d, $J = 11.6$ Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 140.2 (s), 138.3 (s), 134.6 (s), 129.4 (s), 129.2 (s), 129.1 (s), 128.4 (q, $J = 280.7$ Hz), 127.8 (s), 124.4 (s), 121.6 (s), 119.5 (s), 113.4 (s), 105.9 (s), 39.4 (q, $J = 29.0$ Hz; overlapped with carbon signal of DMSO-$d_6$), 21.3 (s). IR (ATR): 3412, 3028, 2921, 2864, 1640, 1465, 1430, 1318, 1250, 1160, 1095, 797, 598, 516 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{32}$H$_{24}$Cl$_2$F$_3$N$_2$[M+H]$^+$: 563.1263; found: 563.1260.
3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-(3-methoxyphenyl)-1H-indole) (3v)

Obtained as a white solid in 77% yield (229 mg). M.p. 226.5–228.1 °C. 

\[ R_f (n\text{-pentane/ethyl acetate} = 9:2) = 0.47. \]

\[ ^{1}H \text{ NMR (400 MHz, DMSO-}d_6\text{)} \delta 11.59 (s, 2H), 7.64 (s, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.18 – 6.98 (m, 6H), 6.82 (d, J = 8.1 Hz, 4H), 5.48 (q, J = 11.6 Hz, 1H), 3.80 (s, 6H). \]

\[ ^{19}F \text{ NMR (376 MHz, DMSO-}d_6\text{)} \delta -62.0 (d, J = 11.6 \text{ Hz, 3F}). \]

\[ ^{13}C \text{ NMR (101 MHz, DMSO-}d_6\text{)} \delta 159.7 (s), 140.1 (s), 134.6 (s), 130.5 (s), 128.4 (q, J = 281.0 Hz), 127.8 (s), 124.4 (s), 124.1 (s), 121.5 (s), 119.4 (s), 114.3 (s), 113.3 (s), 105.7 (s), 55.5 (s), 39.2 (q, J = 34.9 Hz; overlapped with carbon signal of DMSO-}d_6\text{). IR (ATR): 3417, 2944, 2837, 1611, 1501, 1464, 1440, 1246, 1159, 1098, 1025, 927, 831, 597 \text{ cm}^{-1}. \]

\[ \text{HRMS (ESI) m/z: calcd. for C}_{32}\text{H}_{24}\text{Cl}_{2}\text{F}_{3}\text{N}_{2}\text{[M+H]}^+: 595.1161; \text{ found: 595.1169}. \]

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-(4-fluorophenyl)-1H-indole) (3w)

Obtained as a white solid in 70% yield (201 mg). M.p. 237.5–238.6 °C. 

\[ R_f (n\text{-pentane/ethyl acetate} = 5:1) = 0.63. \]

\[ ^{1}H \text{ NMR (400 MHz, DMSO-}d_6\text{)} \delta 11.61 (s, 2H), 7.36 (d, J = 11.8 Hz, 4H), 7.29 (d, J = 7.6 Hz, 4H), 7.12 (d, J = 7.7 Hz, 4H), 7.00 (t, J = 9.0 Hz, 2H), 5.55 (q, J = 11.6 Hz, 1H). \]

\[ ^{19}F \text{ NMR (376 MHz, DMSO-}d_6\text{)} \delta -61.7 (d, J = 11.6 \text{ Hz, 3F}), -123.6 (td, J = 10.0, 4.9 Hz, 2F). \]

\[ ^{13}C \text{ NMR (101 MHz, DMSO-}d_6\text{)} \delta 157.5 (d, J = 231.5 Hz), 138.9 (s), 133.4 (d, J = 79.3 Hz), 130.7 (d, J = 4.8 Hz), \]
128.8 (s), 128.4 (q, $J = 280.3$ Hz), 126.6 (d, $J = 10.2$ Hz), 113.1 (d, $J = 9.9$ Hz), 110.3 (d, $J = 26.1$ Hz), 107.0 (s), 105.0 (d, $J = 25.1$ Hz), $\delta$ 39.3 (q, $J = 30.2$ Hz; overlapped with carbon signal of DMSO-$d_6$). IR (ATR): 3430, 3405, 1628, 1602, 1579, 1479, $1450$, 1253, 1093, 834, 618, 528, 487 cm$^{-1}$. HRMS (ESI) m/z: calcd. for $C_{30}H_{18}Cl_2F_5N_2$ [M+H]$^+$: 571.0772; found: 571.0772.

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(6-chloro-2-phenyl-1H-indole) (3x)

Obtained as a white solid in 75% yield (200 mg). M.p. 163.6–164.6 °C. $R_f$ ($n$-pentane/ethyl acetate = 5:1) = 0.57. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.63 (s, 2H), 7.61 (d, $J = 8.6$ Hz, 2H), 7.41 – 7.30 (m, 4H), 7.27 (t, $J = 7.2$ Hz, 4H), 7.11 (d, $J = 7.2$ Hz, 4H), 7.03 (d, $J = 8.6$ Hz, 2H), 5.53 (q, $J = 11.5$ Hz, 1H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -62.1 (d, $J = 11.5$ Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 139.4 (s), 136.7 (s), 132.1 (s), 129.2 (s), 128.9 (s), 128.8 (s), 128.3 (q, $J = 281.1$ Hz), 126.4 (s), 125.6 (s), 121.7 (s), 120.3 (s), 111.4 (s), 106.4 (s), 39.2 (q, $J = 33.7$ Hz; overlapped with carbon signal of DMSO-$d_6$). IR (ATR): 3401, 1618, 1457, 1446, 1326, 1255, 1160, 1098, 1024, 870, 764, 695, 494 cm$^{-1}$. HRMS (ESI) m/z: calcd. for $C_{30}H_{20}Cl_2F_3N_2$ [M+H]$^+$: 535.0950; found: 535.0946.

3,3’-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-methyl-1H-indole) (3y)

Obtained as a white solid in 73% yield (124 mg). M.p. 202.1–203.5 °C. $R_f$ ($n$-pentane/ethyl acetate = 6:1) = 0.61. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.01 (s,
2H), 7.44 (d, \( J = 7.7 \) Hz, 2H), 7.27 (d, \( J = 7.8 \) Hz, 2H), 6.99 (t, \( J = 7.1 \) Hz, 2H), 6.88 (t, \( J = 7.0 \) Hz, 2H), 5.39 (q, \( J = 12.2 \) Hz, 1H), 2.35 (s, 6H). \(^{19}\)F NMR (376 MHz, DMSO-\( d_6 \)) \( \delta \) -63.4 (d, \( J = 12.2 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 135.4 (s), 134.2 (s), 128.6 (q, \( J = 279.3 \) Hz), 127.6 (s), 120.5 (s), 119.1 (s), 118.8 (s), 111.1 (s), 105.3 (s), 38.9 (q, \( J = 29.9 \) Hz), 12.3 (s). IR (ATR): 3374, 3062, 1621, 1461, 1331, 1258, 1154, 1112, 1085, 1022, 875, 741, 481 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( C_{20}H_{18}F_3N_2 [M+H]^+ \): 343.1417; found: 343.1418.

3,3'-[(2,2,2-Trifluoroethane-1,1-diyl)bis(5-methoxy-2-methyl-1H-indole) (3z)

Obtained as a white solid in 72% yield (145 mg). M.p. 233.4–234.9 °C. \( R_f \) (\( n \)-pentane/ethyl acetate = 4:1) = 0.35. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 10.85 (s, 2H), 7.16 (d, \( J = 8.5 \) Hz, 2H), 6.98 (s, 2H), 6.64 (d, \( J = 8.4 \) Hz, 2H), 5.31 (q, \( J = 12.2 \) Hz, 1H), 3.57 (s, 6H), 2.34 (s, 6H). \(^{19}\)F NMR (376 MHz, DMSO-\( d_6 \)) \( \delta \) -63.4 (d, \( J = 12.2 \) Hz, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 153.5 (s), 134.9 (s), 130.6 (s), 128.7 (q, \( J = 280.3 \) Hz), 128.0 (s), 111.6 (s), 109.8 (s), 105.2 (s), 101.7 (s), 55.5 (s), 38.9 (q, \( J = 29.8 \) Hz), 12.3 (s). IR (ATR): 3382, 2993, 2952, 2833, 1626, 1586, 1484, 1452, 1262, 1213, 1152, 1027, 494 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( C_{22}H_{22}F_3N_2O_2 [M+H]^+ \): 403.1628; found: 403.1633.

3,3'-[(2,2,2-Trifluoroethane-1,1-diyl)bis(5-fluoro-2-methyl-1H-indole) (3aa)

Obtained as a white solid in 75% yield (142 mg). M.p. 241.8–242.8 °C. \( R_f \) (\( n \)-pentane/ethyl acetate = 4:1) = 0.55. \(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 11.20 (s,
2H), 7.28 (dd, J = 7.8, 4.6 Hz, 2H), 7.10 (d, J = 10.7 Hz, 2H), 6.85 (t, J = 8.7 Hz, 2H), 5.43 (q, J = 12.1 Hz, 1H), 2.33 (s, 6H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -63.6 (d, J = 12.1 Hz, 3F), -124.8 (td, J = 10.0, 5.0 Hz, 2F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 157.3 (d, J = 230.2 Hz), 136.8 (s), 132.1 (s), 128.5 (q, J = 280.1 Hz), 127.7 (d, J = 10.1 Hz), 112.1 (d, J = 9.9 Hz), 108.4 (d, J = 25.9 Hz), 105.4 (d, J = 1.8 Hz), 103.5 (d, J = 24.1 Hz), 38.6 (q, J = 29.9 Hz), 12.4 (s). IR (ATR): 3418, 1579, 1482, 1453, 1261, 1151, 1089, 895, 801, 598, 499, 434 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{20}$H$_{15}$F$_3$N$_2$: 378.1150; found: 378.1151.

3,3'-((2,2,2-trifluoroethane-1,1-diyl)bis(1-methyl-2-phenyl-1H-indole) (3ab)

Obtained as a white solid in 65% yield (161 mg). M.p. 190.5–191.7 °C. $R_f$ (n-pentane/ethyl acetate = 10:1) = 0.47. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.69 (d, J = 8.0 Hz, 2H), 7.56 – 7.26 (m, 9H), 7.19 (t, J = 7.6 Hz, 3H), 7.02 (t, J = 7.5 Hz, 2H), 6.39 (s, 2H), 5.10 (q, J = 11.7 Hz, 1H), 3.36 (s, 6H). $^{19}$F NMR (376 MHz, DMSO-$d_6$) $\delta$ -62.9 (d, J = 11.7 Hz, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$) $\delta$ 140.7 (s), 136.9 (s), 131.2 (s), 130.9 (s), 129.2 (d, J = 7.7 Hz), 128.2 (q, J = 281.0 Hz), 126.1 (s), 121.8 (s), 120.5 (s), 120.1 (s), 110.6 (s), 106.5 (s), 39.4 (q, J = 29.2 Hz; overlapped with carbon signal of DMSO-$d_6$), 30.9 (s). IR (ATR): 3035, 2911, 2845, 2322, 1467, 1441, 1365, 1325, 1252, 1151, 1169, 1101, 1059, 740, 697 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{32}$H$_{25}$F$_3$N$_2$: 494.1964; found: 494.1960.
Crystal structure analyses

The suitable crystals of 3a (CCDC 1917454) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.
References:


5. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.
Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

$^1$H NMR spectrum of $3a$ in DMSO-$d_6$

$^{19}$F NMR spectrum of $3a$ in DMSO-$d_6$
$^{13}$C NMR spectrum of $3a$ in DMSO-$d_6$

$^1$H NMR spectrum of $3b$ in DMSO-$d_6$
$^{19}$F NMR spectrum of 3b in DMSO-$d_6$

$^{13}$C NMR spectrum of 3b in DMSO-$d_6$
$^1$H NMR spectrum of 3c in DMSO-$d_6$

$^{19}$F NMR spectrum of 3c in DMSO-$d_6$
$^{13}$C NMR spectrum of 3c in DMSO-$d_6$

$^1$H NMR spectrum of 3d in DMSO-$d_6$
$^{19}$F NMR spectrum of 3d in DMSO-$d_6$

$^{13}$C NMR spectrum of 3d in DMSO-$d_6$
$^1$H NMR spectrum of 3e in DMSO-$d_6$

$^{19}$F NMR spectrum of 3e in DMSO-$d_6$
$^{13}$C NMR spectrum of 3e in DMSO-$d_6$

$^1$H NMR spectrum of 3f in DMSO-$d_6$
$^{19}$F NMR spectrum of 3f in DMSO-$d_6$ 

$^{13}$C NMR spectrum of 3f in DMSO-$d_6$
$^1$H NMR spectrum of 3g in DMSO-$d_6$
$^{13}$C NMR spectrum of $3g$ in DMSO-$d_6$

$^1$H NMR spectrum of $3h$ in DMSO-$d_6$
$^{19}$F NMR spectrum of 3h in DMSO-$d_6$

$^{13}$C NMR spectrum of 3h in DMSO-$d_6$
$^1$H NMR spectrum of 3i in DMSO-$d_6$

$^{19}$F NMR spectrum of 3i in DMSO-$d_6$
$^{13}$C NMR spectrum of 3i in DMSO-$d_6$

$^1$H NMR spectrum of 3i in DMSO-$d_6$
$^{19}$F NMR spectrum of 3j in DMSO-$d_6$

$^{13}$C NMR spectrum of 3j in DMSO-$d_6$
$^1$H NMR spectrum of 3k in DMSO-$d_6$

$^{19}$F NMR spectrum of 3k in DMSO-$d_6$
$^{13}$C NMR spectrum of 3k in DMSO-$d_6$

$^1$H NMR spectrum of 3l in DMSO-$d_6$
$^{19}$F NMR spectrum of 3l in DMSO-$d_6$

$^{13}$C NMR spectrum of 3l in DMSO-$d_6$
$^1$H NMR spectrum of 3m in DMSO-$d_6$

$^{19}$F NMR spectrum of 3m in DMSO-$d_6$
$^{13}$C NMR spectrum of 3m in DMSO-$d_6$

$^1$H NMR spectrum of 3n in DMSO-$d_6$
$^{19}$F NMR spectrum of 3n in DMSO-$d_6$

$^{13}$C NMR spectrum of 3n in DMSO-$d_6$
$^{1}$H NMR spectrum of 3o in DMSO-d$_6$

$^{19}$F NMR spectrum of 3o in DMSO-d$_6$
$^{13}$C NMR spectrum of 3o in DMSO-$d_6$

$^1$H NMR spectrum of 3p in DMSO-$d_6$
\(^{19}\)F NMR spectrum of 3p in DMSO-\(d_6\)

\(^{13}\)C NMR spectrum of 3p in DMSO-\(d_6\)
$^1$H NMR spectrum of 3q in DMSO-$d_6$

$^{19}$F NMR spectrum of 3q in DMSO-$d_6$
$^{13}$C NMR spectrum of 3q in DMSO-$d_6$

$^1$H NMR spectrum of 3r in DMSO-$d_6$
$^{19}$F NMR spectrum of 3r in DMSO-$d_6$

$^{13}$C NMR spectrum of 3r in DMSO-$d_6$
$^1$H NMR spectrum of 3s in DMSO-$d_6$.

$^{19}$F NMR spectrum of 3s in DMSO-$d_6$. 

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$^{12}$C NMR spectrum of 3s in DMSO-$d_6$

$^1$H NMR spectrum of 3t in DMSO-$d_6$
$^{19}$F NMR spectrum of $3t$ in DMSO-$d_6$

$^{13}$C NMR spectrum of $3t$ in DMSO-$d_6$
$^1$H NMR spectrum of 3u in DMSO-$d_6$

$^{19}$F NMR spectrum of 3u in DMSO-$d_6$
$^{13}$C NMR spectrum of 3u in DMSO-$d_6$
$^{19}$F NMR spectrum of 3v in DMSO-$d_6$

$^{13}$C NMR spectrum of 3v in DMSO-$d_6$
$^1$H NMR spectrum of 3w in DMSO-$d_6$

$^{19}$F NMR spectrum of 3w in DMSO-$d_6$
$^{13}$C NMR spectrum of 3w in DMSO-$d_6$

$^1$H NMR spectrum of 3x in DMSO-$d_6$
$^{19}$F NMR spectrum of 3x in DMSO-$d_6$

$^{13}$C NMR spectrum of 3x in DMSO-$d_6$
$^1$H NMR spectrum of $3y$ in DMSO-$d_6$

$^{19}$F NMR spectrum of $3y$ in DMSO-$d_6$
$^{13}$C NMR spectrum of 3y in DMSO-$d_6$

$^1$H NMR spectrum of 3z in DMSO-$d_6$
$^{19}F$ NMR spectrum of 3z in DMSO-$d_6$

$^{13}C$ NMR spectrum of 3z in DMSO-$d_6$
$^1$H NMR spectrum of 3aa in DMSO-$d_6$

$^{19}$F NMR spectrum of 3aa in DMSO-$d_6$
$^{13}$C NMR spectrum of 3aa in DMSO-$d_6$

$^1$H NMR spectrum of 3ab in DMSO-$d_6$
$^{19}$F NMR spectrum of 3ab in DMSO-$d_6$

$^{13}$C NMR spectrum of 3ab in DMSO-$d_6$