Supporting Information *for*

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

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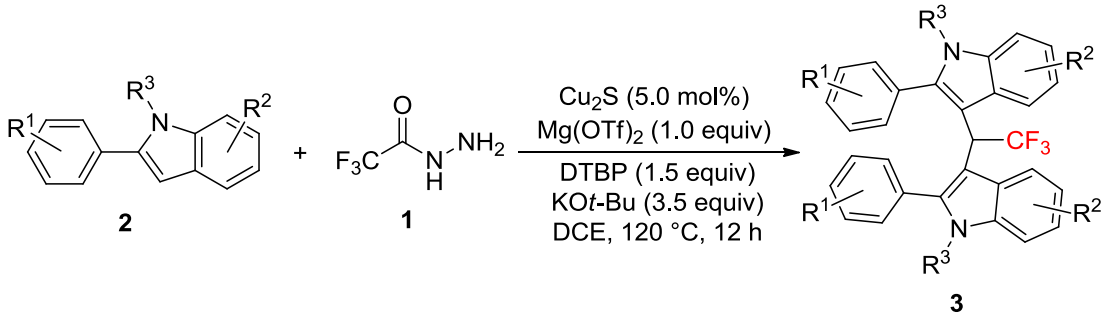
General remarks

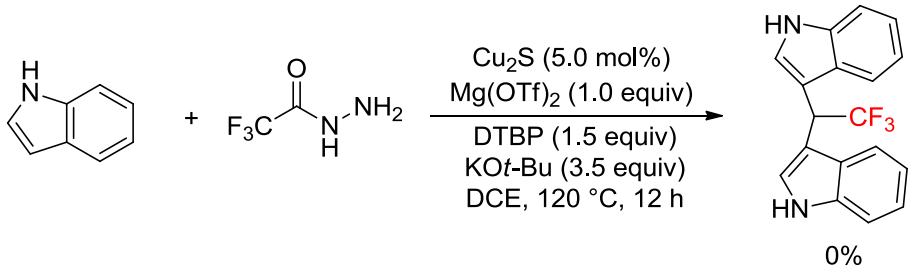
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard 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-arylindoles,[2] 2-phenyl-3-(2,2,2-trifluoroacetyl) indole **5**[3] and 2,2,2-trifluoro-1-(2-phenyl-1*H*-indol-3-yl)-1-ethanol **6**[4] 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), KO*t*-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, 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 $MgSO_4$. 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

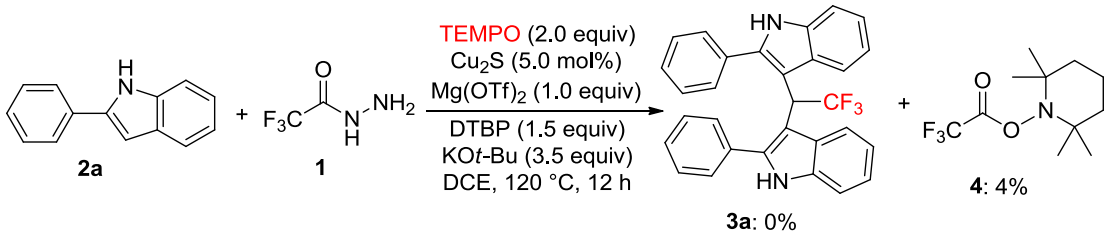


0%

The indole (1.0 mmol), trifluoroacetyl hydrazine (153 mg, 1.2 mmol, 1.2 equiv), DTBP (276 μL, 1.5 mmol, 1.5 equiv), KO*t*-Bu (392 mg, 3.5 mmol, 3.5 equiv), $Mg(OTf)_2$ (322 mg, 1.0 mmol, 1. equiv), Cu_2S (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.

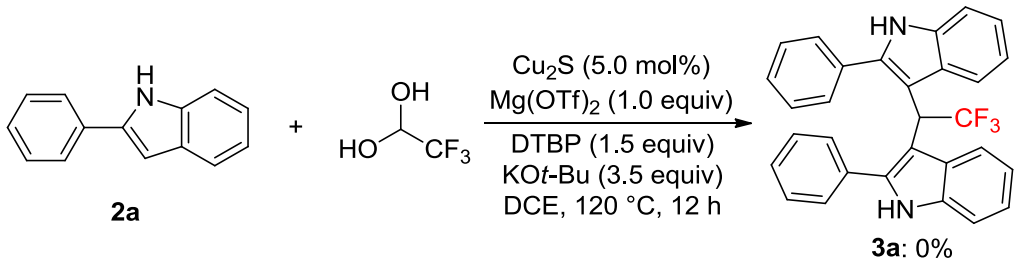
Mechanistic study

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



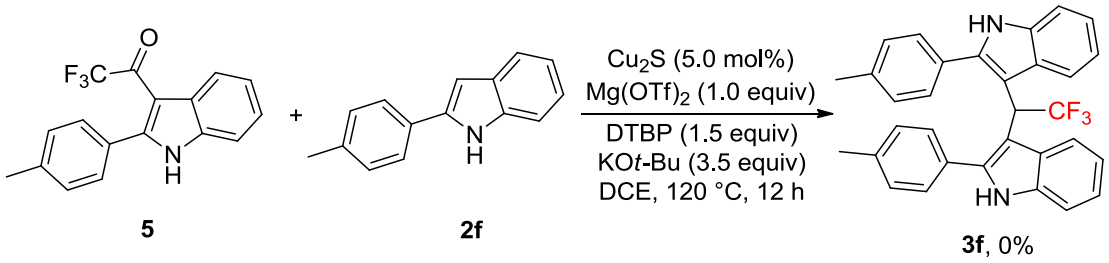
The 2-phenyl-1*H*-indole (**2a**) (193 mg, 1.0 mmol), trifluoroacetyl hydrazine (**1**) (153 mg, 1.2 mmol, 1.2 equiv), DTBP (276 μL, 1.5 mmol, 1.5 equiv), KO*t*-Bu (392 mg, 3.5 mmol, 3.5 equiv), $Mg(OTf)_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu_2S (7.9 mg, 0.050 mmol, 0.050 equiv), TEMPO (312 mg, 2.0 mmol, 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-1*H*-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



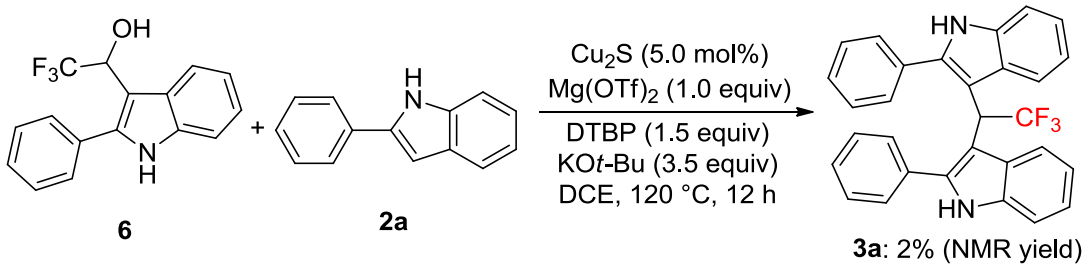
The 2-phenyl-1*H*-indole (**2a**) (193 mg, 1.0 mmol), trifluoroacetaldehyde hydrate (99 μL, 1.2 mmol, 1.2 equiv), DTBP (276 μL, 1.5 mmol, 1.5 equiv), KO*t*-Bu (392 mg, 3.5 mmol, 3.5 equiv), $Mg(OTf)_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu_2S (7.9 mg, 0.050 mmol, 0.050 equiv), and DCE (4.0 mL) were added 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. 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-1*H*-indole) (**3a**) was detected.

(c) Reaction of trifluoroacetylated indole with 2-arylindole under standard conditions



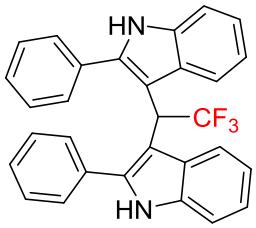
The 2-(*p*-tolyl)-1*H*-indole **2f** (207 mg, 1.0 mmol), 2,2,2-trifluoro-1-(2-phenyl-1*H*-indol-3-yl)-1-ethanone **5** (303 mg, 1.0 mmol), DTBP (276 μL, 1.5 mmol, 1.5 equiv), KO*t*-Bu (392 mg, 3.5 mmol, 3.5 equiv), $Mg(OTf)_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu_2S (7.9 mg, 0.050 mmol, 0.050 equiv), and 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-1*H*-indol-3-yl)ethanol 6 with 2-arylindole 2a under standard conditions



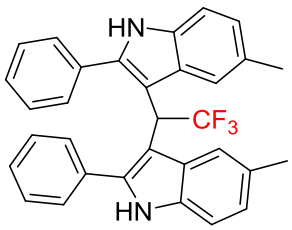
The 2-arylindole **2a** (193 mg, 1.0 mmol), 2,2,2-trifluoro-1-(2-phenyl-1*H*-indol-3-yl)-1-ethanol **6** (291 mg, 1.0 mmol), DTBP (0.276 mL, 1.5 mmol, 1.5 equiv), KO*t*-Bu (392 mg, 3.5 mmol, 3.5 equiv), $Mg(OTf)_2$ (322 mg, 1.0 mmol, 1.0 equiv), Cu_2S (7.9 mg 0.050 mmol, 0.050 equiv) and DCE (4.0 mL) 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 only 2% yield of trifluoromethylated bis(indolyl)arylmethane **3a** was detected.

Data for compounds 3.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-phenyl-1*H*-indole) (3a)

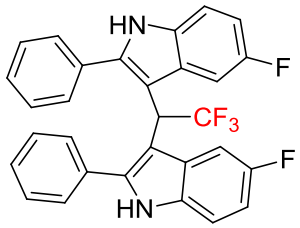
Obtained as a white solid in 99% yield (231 mg). M.p. 248.1–249.2 °C. R_f (*n*-pentane/ethyl acetate = 7:1) = 0.40. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 2H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.24 (m, 8H), 7.21 – 7.06 (m, 6H), 7.00 (t, *J* = 7.5 Hz, 2H), 5.57 (q, *J* = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.9 (d, *J* = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) 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-d_6). IR (ATR): 3425, 3389, 1646, 1486, 1454, 1423, 1325, 1309, 1250, 1163, 998, 684, 518, 471 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{30}H_{21}F_3N_2$: 466.1651; found: 466.1652.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-methyl-2-phenyl-1*H*-indole) (3b)

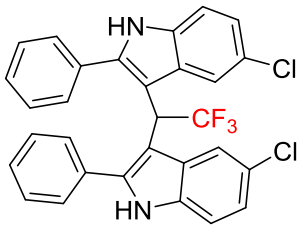
Obtained as a white solid in 76% yield (188 mg). M.p. 251.8–253.6 °C. R_f (*n*-pentane/ethyl acetate = 9:1) = 0.42. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.30 (s, 2H), 7.58 (s, 2H), 7.44 – 7.08 (m, 12H), 6.96 (d, *J* = 7.7 Hz, 2H), 5.53 (q, *J* = 11.5 Hz, 1H), 2.33 (s, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.8 (d, *J* = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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-d_6), 21.9 (s).

IR (ATR): 3445, 3394, 3061, 2920, 1578, 1446, 1343, 1311, 1159, 1093, 1060, 1026, 881, 507 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{32}H_{25}F_3N_2$: 494.1964; found: 494.1960.



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

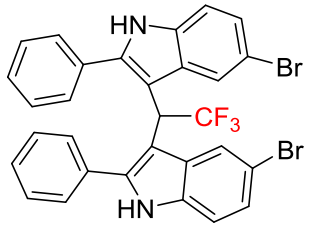
Obtained as a white solid in 95% yield (253 mg). M.p. 203.5–204.8 °C. R_f (*n*-pentane/ethyl acetate = 4:1) = 0.50. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.64 (s, 2H), 7.47 – 7.23 (m, 10H), 7.16 (d, *J* = 7.4 Hz, 4H), 7.02 (t, *J* = 8.9 Hz, 2H), 5.56 (q, *J* = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -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) δ 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), δ 39.19 (q, *J* = 29.4 Hz; overlapped with carbon signal of DMSO-d_6). IR (ATR): 3388, 2256, 2128, 2014, 1981, 1652, 1046, 1023, 992, 824, 762, 537 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{30}H_{18}F_5N_2$ $[M-H]^+$: 501.1396; found: 501.1397.



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

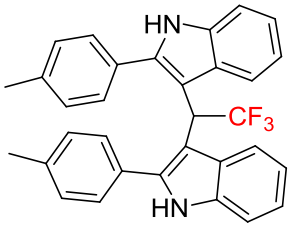
Obtained as a white solid in 83% yield (222 mg). M.p. 223.4–224.6 °C. R_f (*n*-pentane/ethyl acetate = 9:1) = 0.43. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 2H), 7.59 (s, 2H), 7.36 (t, *J* = 9.2 Hz, 4H), 7.29 (t, *J* = 6.9 Hz, 4H), 7.14 (d, *J* = 7.2 Hz, 6H), 5.52 (q, *J* = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.2 (d, *J* = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{30}H_{19}Cl_2F_3N_2$: 534.0872; found: 534.0869.



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

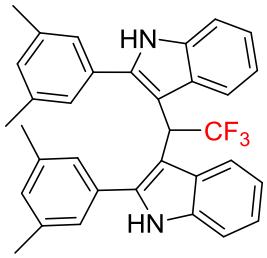
Obtained as a white solid in 83% yield (258 mg). M.p. 269.8–270.7 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.57. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.43 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 7.7 Hz, 4H), 7.35 (d, J = 8.0 Hz, 2H), 7.18 – 6.95 (m, 8H), 5.57 (q, J = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.4 (d, J = 11.5 Hz, 3F). ^{13}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 $C_{30}H_{18}Br_2F_3N_2$ $[M–H]^+$: 620.9799; found: 620.9794.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(*p*-tolyl)-1*H*-indole) (3f)

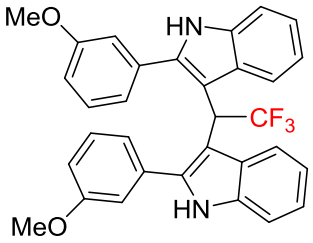
Obtained as a white solid in 86% yield (212 mg). M.p. 201.5–202.8 °C. R_f (*n*-pentane/ethyl acetate = 6:1) = 0.51. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 7.9 Hz, 2H), 7.15 – 6.94 (m, 12H), 5.59 (q, J = 11.6 Hz, 1H), 2.36 (s, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.8 (d, J = 11.6 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.4 (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 $C_{32}H_{26}F_3N_2$ $[M+H]^+$: 495.2042; found: 495.2041.



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

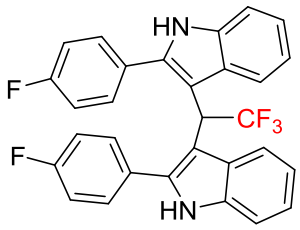
Obtained as a white solid in 71% yield (196 mg). M.p. 246.0–247.5 °C. R_f (*n*-pentane/ethyl acetate = 10:1) = 0.43. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.30 (s, 2H), 7.68 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.09 (t, J = 7.0 Hz, 2H), 6.96 (t, J = 7.0 Hz, 2H), 6.92 (s, 2H), 6.70 (s, 4H), 5.59 (q, J = 11.7 Hz, 1H), 2.17 (s, 12H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.9 (d, J = 11.7 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{34}H_{29}F_3N_2$: 522.2277; found: 522.2273.



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

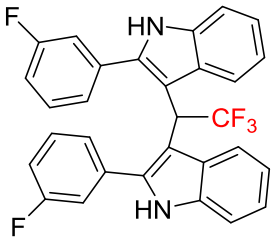
Obtained as a white solid in 76% yield (199 mg). M.p. 189.1–190.8 °C. R_f (*n*-pentane/ethyl acetate = 4:1) = 0.45. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.40 (s,

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). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7 (d, *J* = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) 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-d_6). IR (ATR): 3394, 3063, 3016, 1609, 1579, 1458, 1250, 1151, 1040, 740, 688, 506 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{32}H_{26}F_3N_2O_2$ $[M+H]^+$: 527.1941; found: 527.1945.



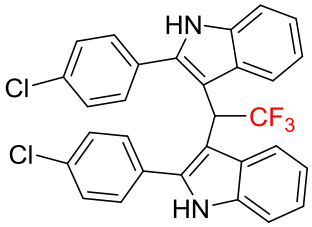
3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-fluorophenyl)-1*H*-indole) (3i)

Obtained as a white solid in 73% yield (183 mg). M.p. 250.6–251.9 °C. R_f (*n*-pentane/ethyl acetate = 8:1) = 0.39. ^{1}H NMR (400 MHz, DMSO-d_6) 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). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7 (d, *J* = 10.5 Hz, 3F), -113.7 (s, 2F). ^{13}C NMR (101 MHz, DMSO-d_6) 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-d_6). IR (ATR): 3458, 3392, 3258, 3065, 1609, 1558, 1500, 1456, 1431, 1324, 1220, 1154, 746, 701 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{30}H_{19}F_5N_2$: 502.1463; found: 502.1462.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-fluorophenyl)-1*H*-indole) (3j)

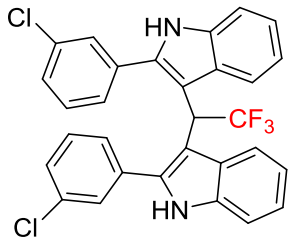
Obtained as a white solid in 66% yield (176 mg). M.p. 245.8–246.9 °C. R_f (*n*-pentane/ethyl acetate = 4:1) = 0.49. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 2H), 7.80 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 14.5, 7.3 Hz, 2H), 7.13 (t, *J* = 7.7 Hz, 4H), 7.02 (d, *J* = 6.8 Hz, 4H), 6.90 (d, *J* = 9.8 Hz, 2H), 5.62 (q, *J* = 11.6 Hz, 1H). ^{19}F 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). ^{13}C 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 $C_{30}H_{20}F_5N_2$ $[M+H]^+$: 503.1541; found: 503.1542.



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

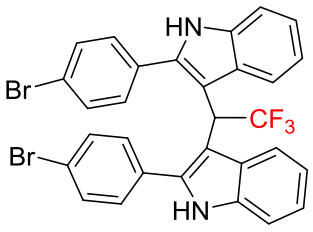
Obtained as a white solid in 76% yield (203 mg). M.p. 247.2–248.0 °C. R_f (*n*-pentane/ethyl acetate = 6:1) = 0.61. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.44 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 4H), 7.19 – 7.08 (m, 6H), 7.02 (t, *J* = 7.4 Hz, 2H), 5.58 (q, *J* = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.5 (d, *J* = 11.5 Hz, 3F). ^{13}C 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 $C_{30}H_{20}Cl_2F_3N_2$ $[M+H]^+$: 535.0775; found: 535.0781.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(3-chlorophenyl)-1*H*-indole) (3l)

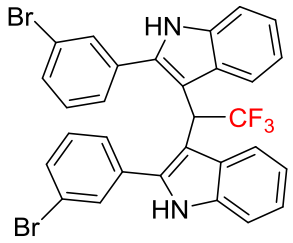
Obtained as a white solid in 79% yield (215 mg). M.p. 215.4–216.3 °C. R_f (*n*-pentane/ethyl acetate = 8:1) = 0.46. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 2H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 4H), 7.27 (t, *J* = 7.8 Hz, 2H), 7.13 (t, *J* = 7.1 Hz, 4H), 7.07 (s, 2H), 7.01 (t, *J* = 7.5 Hz, 2H), 5.55 (q, *J* = 11.6 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.6 (d, *J* = 11.6 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{30}H_{20}Cl_2F_3N_2$ $[M+H]^+$: 535.0775; found: 535.0778.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-bromophenyl)-1*H*-indole) (3m)

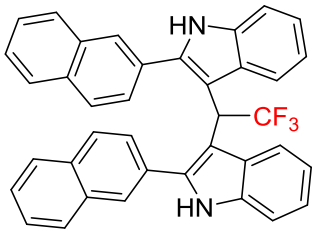
Obtained as a white solid in 72% yield (221 mg). M.p. 123.3–124.6 °C. R_f (*n*-pentane/ethyl acetate = 4:1) = 0.48. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.71 (s, 2H), 7.76 (s, 2H), 7.42 – 7.20 (m, 10H), 7.15 (d, *J* = 7.0 Hz, 4H), 5.50 (q, *J* = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.1 (d, *J* = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{30}H_{18}Br_2F_3N_2$ $[M–H]^+$: 620.9794; found: 620.9793.



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

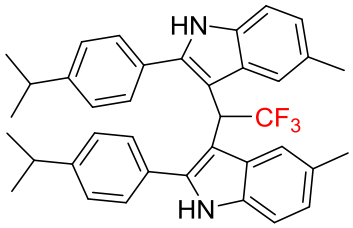
Obtained as a white solid in 81% yield (503 mg). M.p. 201.2–202.3 °C. R_f (*n*-pentane/ethyl acetate = 6:1) = 0.41. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 2H), 7.75 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.1 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.28 – 7.08 (m, 8H), 7.01 (t, J = 7.2 Hz, 2H), 5.55 (q, J = 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 $C_{30}H_{20}Br_2F_3N_2$ $[M+H]^+$: 622.9940; found: 622.9933.



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

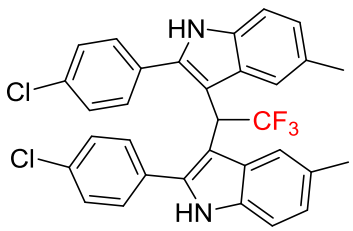
Obtained as a white solid in 91% yield (258 mg). M.p. 139.7–140.3 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.62. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.49 (s, 2H), 7.82 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.59 (s, 2H), 7.50 (t, J = 7.1 Hz, 3H), 7.47 – 7.35 (m, 7H), 7.20 – 7.06 (m, 4H), 7.01 (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 $C_{38}H_{26}F_3N_2$ $[M+H]^+$: 567.1964; found: 567.1965.



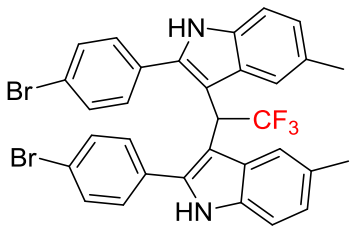
3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-isopropylphenyl)-5-methyl-1*H*-indole) (3p)

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 $C_{38}H_{38}F_3N_2$ $[M+H]^+$: 579.2906; found: 579.2903.



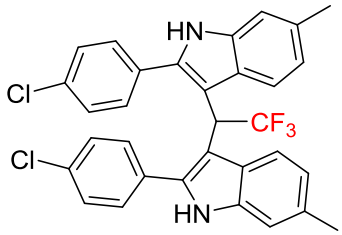
3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-chlorophenyl)-5-methyl-1*H*-indole) (3q)

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) δ 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) δ -61.5 (d, *J* = 11.7 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{32}H_{24}Cl_2F_3N_2$ $[M+H]^+$: 563.1263; found: 563.1262.



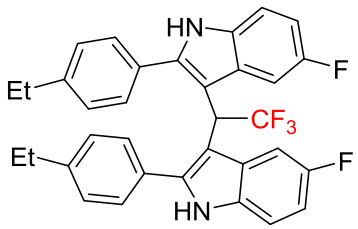
3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-bromophenyl)-5-methyl-1*H*-indole) (3r)

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) δ 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) δ -61.4 (d, *J* = 11.7 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{32}H_{24}Br_2F_3N_2$ $[M+H]^+$: 651.0252; found: 651.0253.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(2-(4-chlorophenyl)-6-methyl-1*H*-indole) (3s)

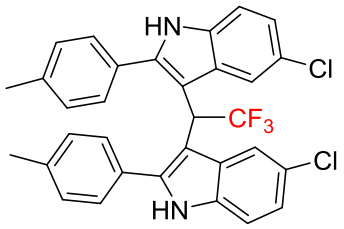
Obtained as a white solid in 65% yield (183 mg). M.p. 238.5–239.2 °C. R_f (*n*-pentane/ethyl acetate = 6:1) = 0.42. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.24 (s, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 4H), 7.18 – 7.04 (m, 6H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.50 (q, *J* = 11.5 Hz, 1H), 2.38 (s, 6H). ^{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 136.8 (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-d_6), 21.6 (s). IR (ATR): 3456, 3389, 1476, 1459, 1437, 1394, 1345, 1124, 1013, 883, 725, 617, 530 cm^{-1} HRMS (ESI) m/z: calcd. for $C_{32}H_{24}Cl_2F_3N_2$ $[M+H]^+$: 563.1259; found: 563.1263.



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

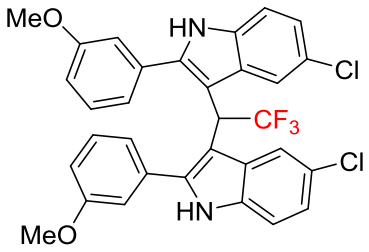
Obtained as a white solid in 71% yield (198 mg). M.p. 221.3–222.1 °C. R_f (*n*-pentane/ethyl acetate = 8:1) = 0.38. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (s, 2H), 7.40 – 7.33 (m, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 4H), 7.05 (d, *J* = 7.2 Hz, 4H), 6.97 (t, *J* = 8.9 Hz, 2H), 5.49 (q, *J* = 11.5 Hz, 1H), 2.63 (q, *J* = 7.2 Hz, 4H), 1.22 (t, *J* = 7.2 Hz, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.1 (d, *J* = 11.6 Hz, 3F), -123.9 (dd, *J* = 16.6, 7.7 Hz, 2F). ^{13}C NMR (101 MHz, DMSO-d_6) 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 $C_{34}H_{28}F_5N_2$ $[M+H]^+$: 559.2054; found: 559.2050.



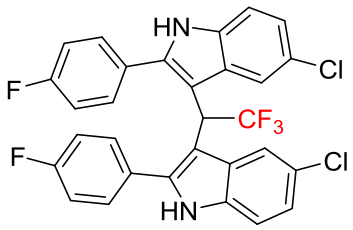
3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-(*p*-tolyl)-1*H*-indole) (3u)

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) δ 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) δ -62.0 (d, *J* = 11.6 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{32}H_{24}Cl_2F_3N_2$ $[M+H]^+$: 563.1263; found: 563.1260.



3,3'-(2,2,2-Trifluoroethane-1,1-diyl)bis(5-chloro-2-(3-methoxyphenyl)-1*H*-indole) (3v)

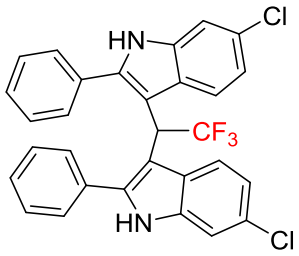
Obtained as a white solid in 77% yield (229 mg). M.p. 226.5–228.1 °C. R_f (*n*-pentane/ethyl acetate = 9:2) = 0.47. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.59 (s, 2H), 7.64 (s, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.18 – 6.98 (m, 6H), 6.82 (d, *J* = 8.1 Hz, 4H), 5.48 (q, *J* = 11.6 Hz, 1H), 3.80 (s, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.0 (d, *J* = 11.6 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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). IR (ATR): 3417, 2944, 2837, 1611, 1501, 1464, 1440, 1246, 1159, 1098, 1025, 927, 831, 597 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{32}H_{24}Cl_2F_3N_2$ $[M+H]^+$: 595.1161; found: 595.1169.



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

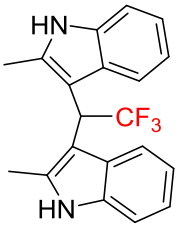
Obtained as a white solid in 70% yield (201 mg). M.p. 237.5–238.6 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.63. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.61 (s, 2H), 7.36 (d, *J* = 11.8 Hz, 4H), 7.29 (d, *J* = 7.6 Hz, 4H), 7.12 (d, *J* = 7.7 Hz, 4H), 7.00 (t, *J* = 9.0 Hz, 2H), 5.55 (q, *J* = 11.6 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.7 (d, *J* = 11.6 Hz, 3F), -123.6 (td, *J* = 10.0, 4.9 Hz, 2F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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), δ 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-1*H*-indole) (3x)

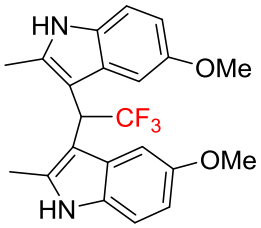
Obtained as a white solid in 75% yield (200 mg). M.p. 163.6–164.6 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.57. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.63 (s, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.41 – 7.30 (m, 4H), 7.27 (t, J = 7.2 Hz, 4H), 7.11 (d, J = 7.2 Hz, 4H), 7.03 (d, J = 8.6 Hz, 2H), 5.53 (q, J = 11.5 Hz, 1H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -62.1 (d, J = 11.5 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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)

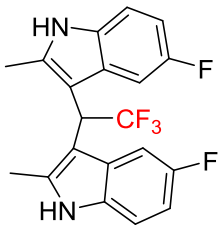
Obtained as a white solid in 73% yield (124 mg). M.p. 202.1–203.5 °C. R_f (*n*-pentane/ethyl acetate = 6:1) = 0.61. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.01 (s,

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) δ -63.4 (d, *J* = 12.2 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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-1*H*-indole) (3z)

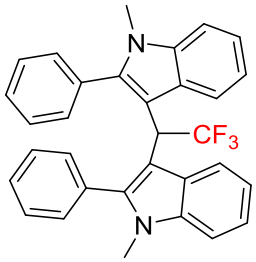
Obtained as a white solid in 72% yield (145 mg). M.p. 233.4–234.9 °C. R_f (*n*-pentane/ethyl acetate = 4:1) = 0.35. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.98 (s, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 5.31 (q, *J* = 12.2 Hz, 1H), 3.57 (s, 6H), 2.34 (s, 6H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.4 (d, *J* = 12.2 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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-1*H*-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) δ 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) δ -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) δ 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, 1109, 1071, 1008, 895, 801, 598, 499, 434 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{20}H_{15}F_5N_2$: 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) δ 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) δ -62.9 (d, *J* = 11.7 Hz, 3F). ^{13}C NMR (101 MHz, DMSO-d_6) δ 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 $C_{32}H_{25}F_3N_2$: 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 ºC, 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.[5] 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:

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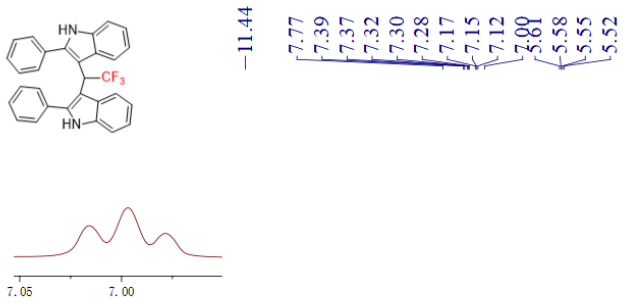
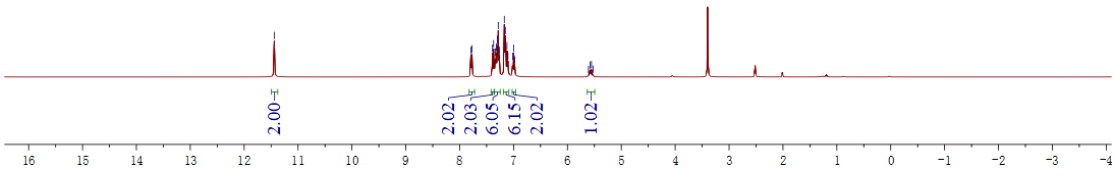
4. E. Vitaku, D. T. Smith and J. T. Njardarson, Metal-free synthesis of fluorinated indoles enabled by oxidative dearomatization, *Angew. Chem. Int. Ed.*, 2016, **55**, 2243-2247.
5. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

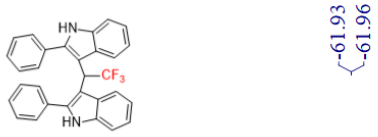
Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

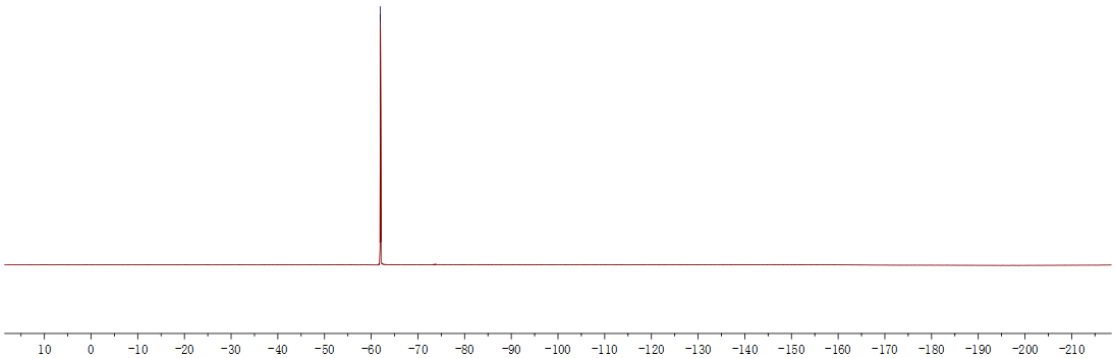
^{1}H NMR spectrum of **3a** in DMSO-d_6



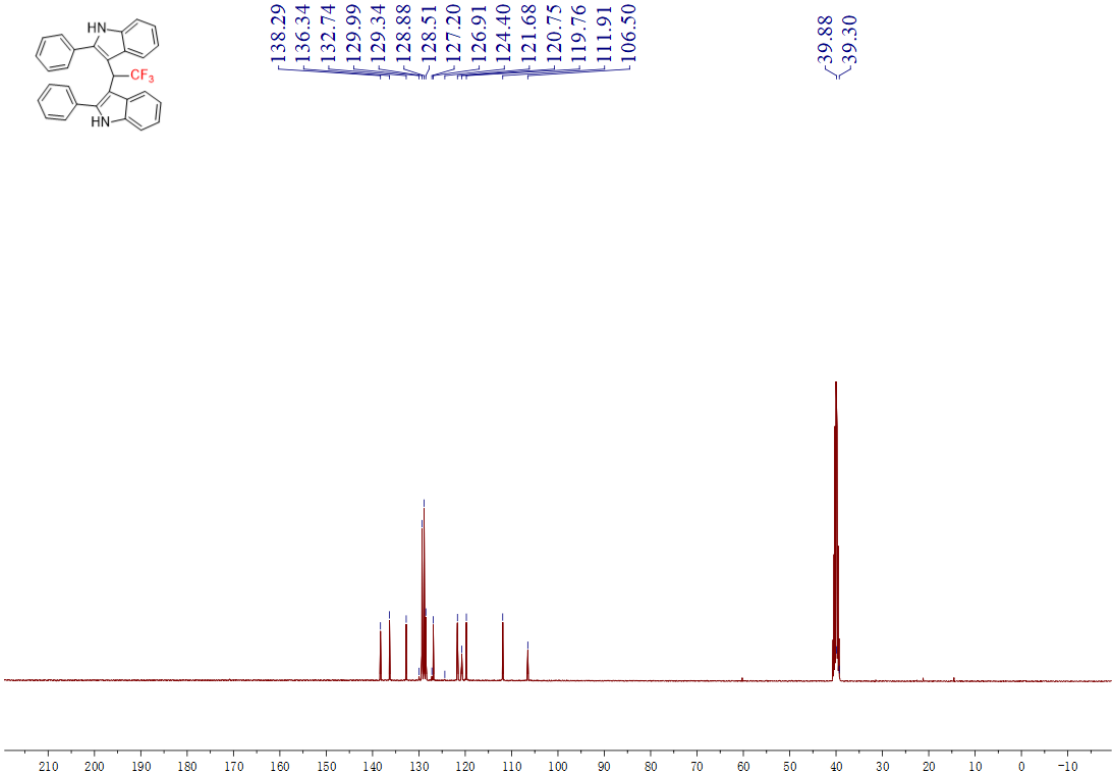


^{19}F NMR spectrum of **3a** in DMSO-d_6

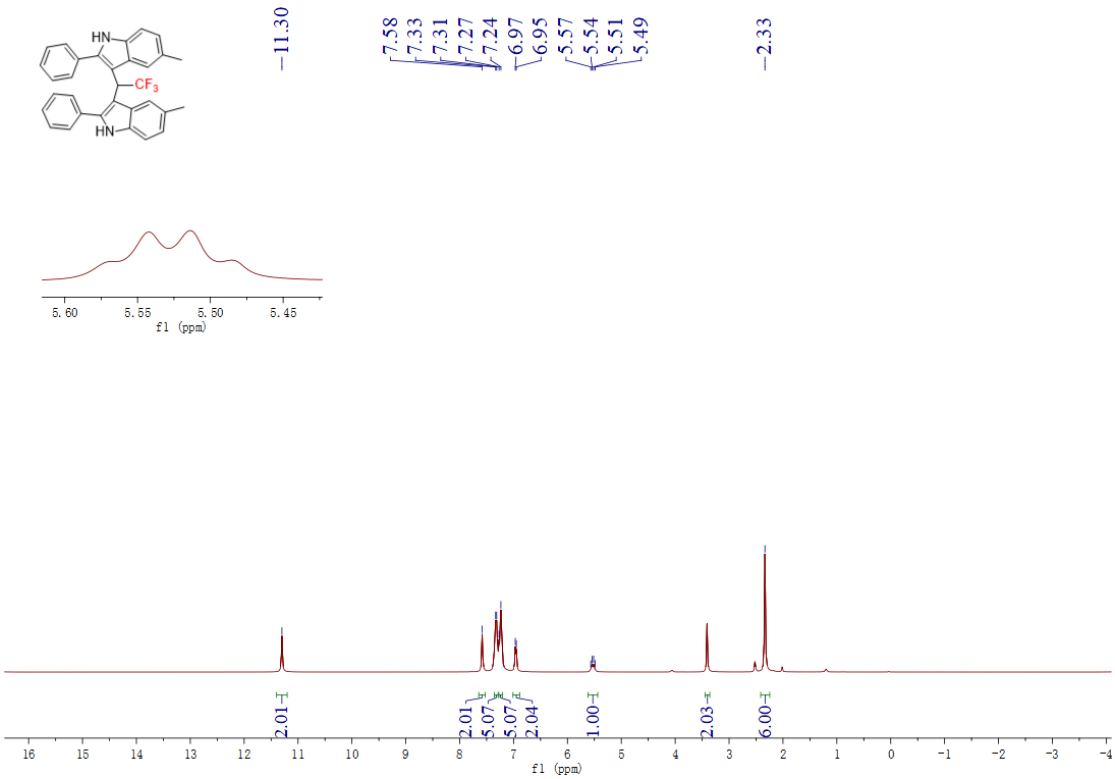




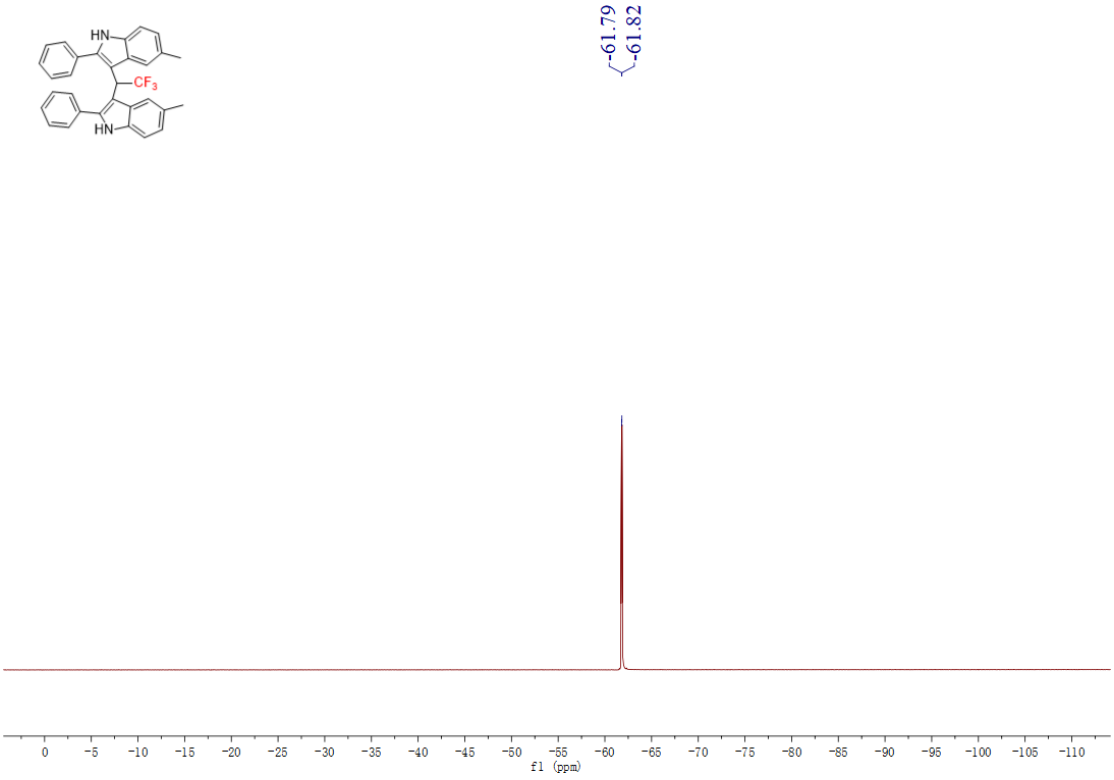
^{13}C NMR spectrum of **3a** in DMSO-d_6



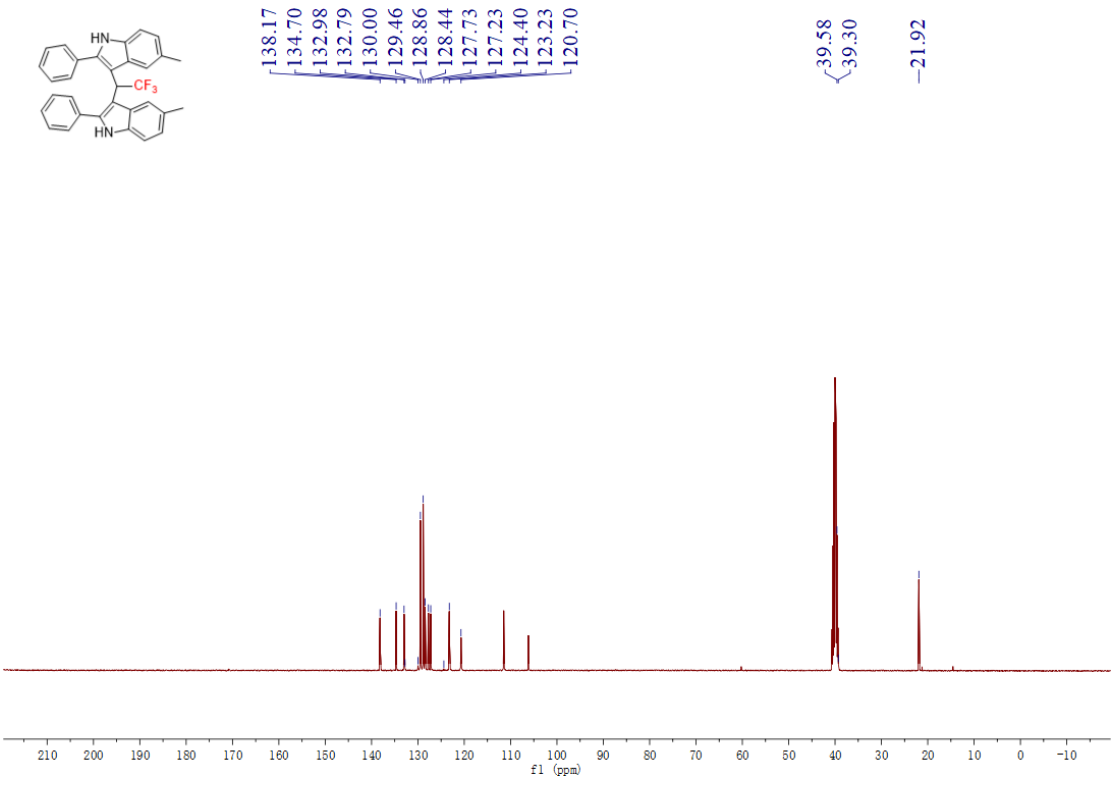
^{1}H NMR spectrum of **3b** in DMSO-d_6



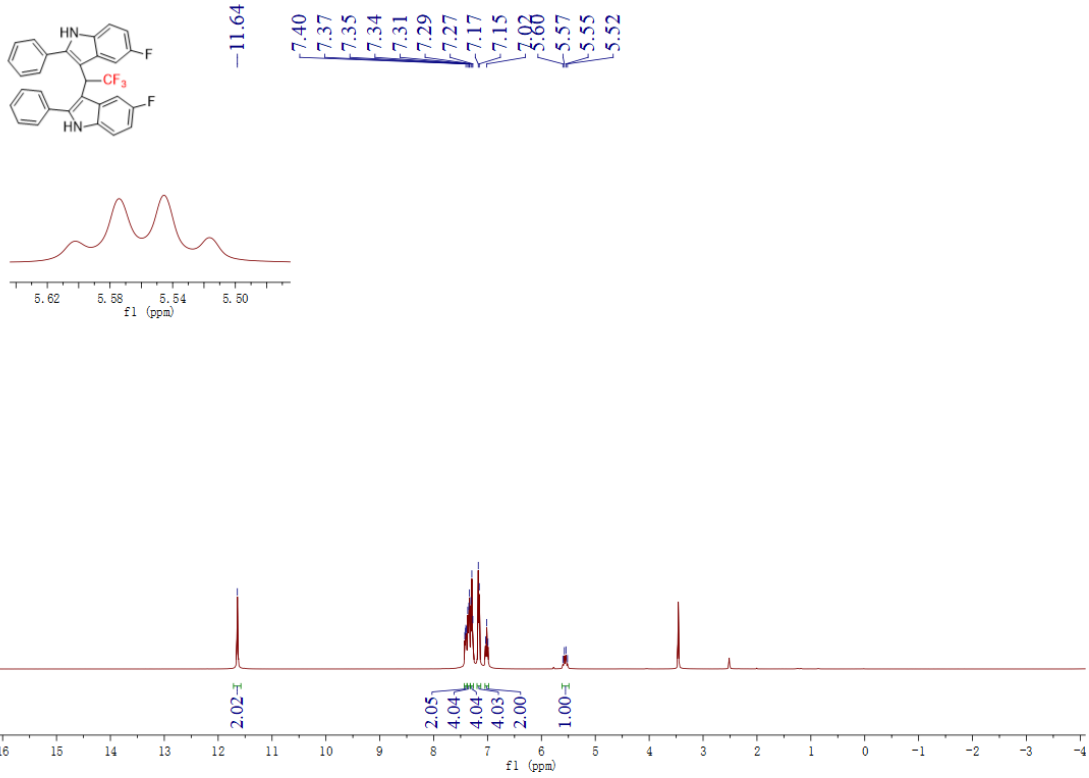
^{19}F NMR spectrum of **3b** in DMSO-d_6



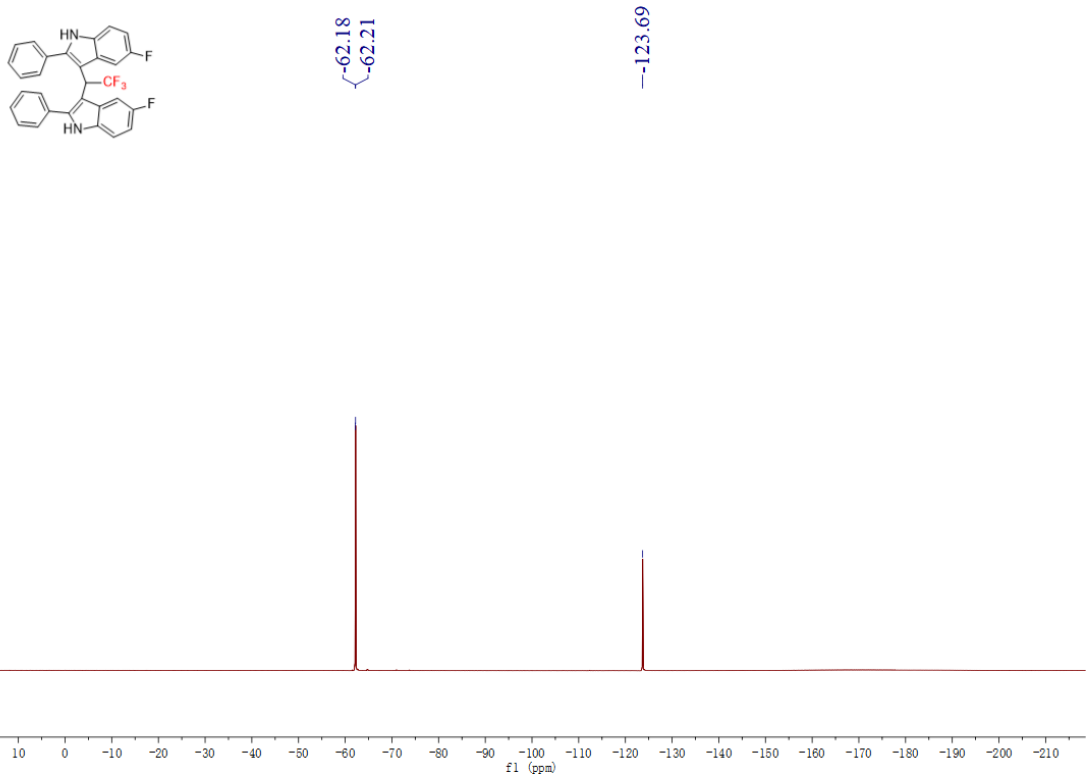
^{13}C NMR spectrum of **3b** in DMSO-d_6



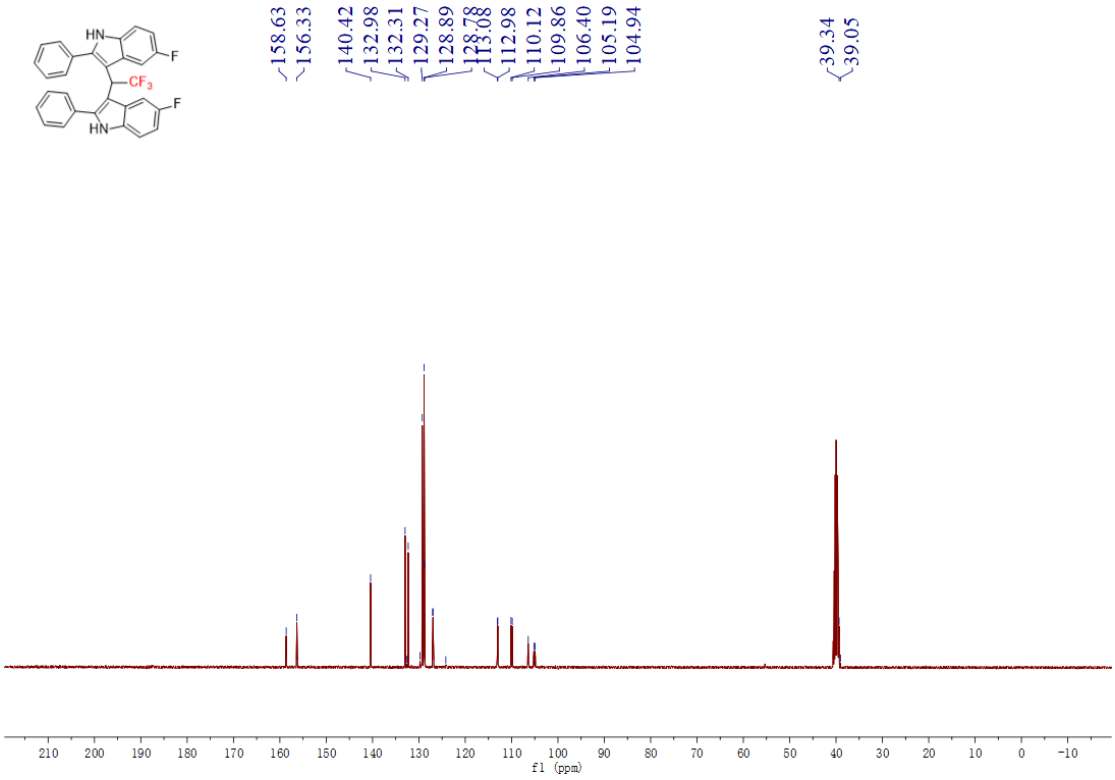
^{1}H NMR spectrum of **3c** in DMSO-d_6



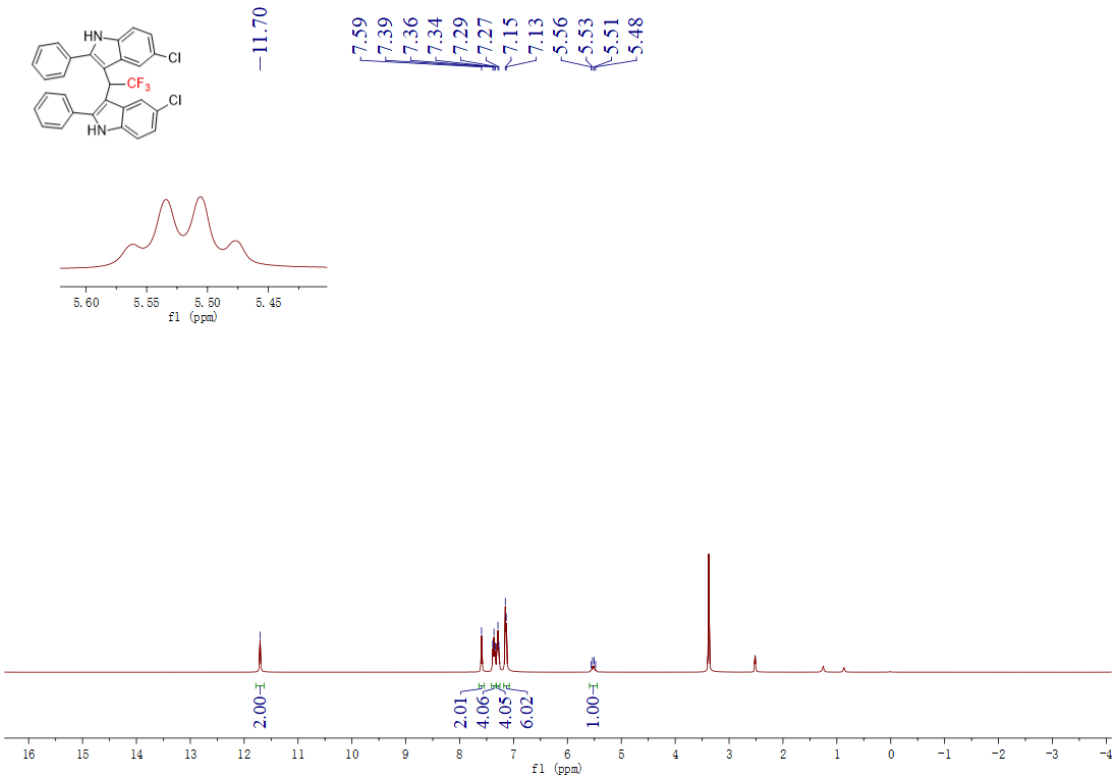
^{19}F NMR spectrum of **3c** in DMSO-d_6



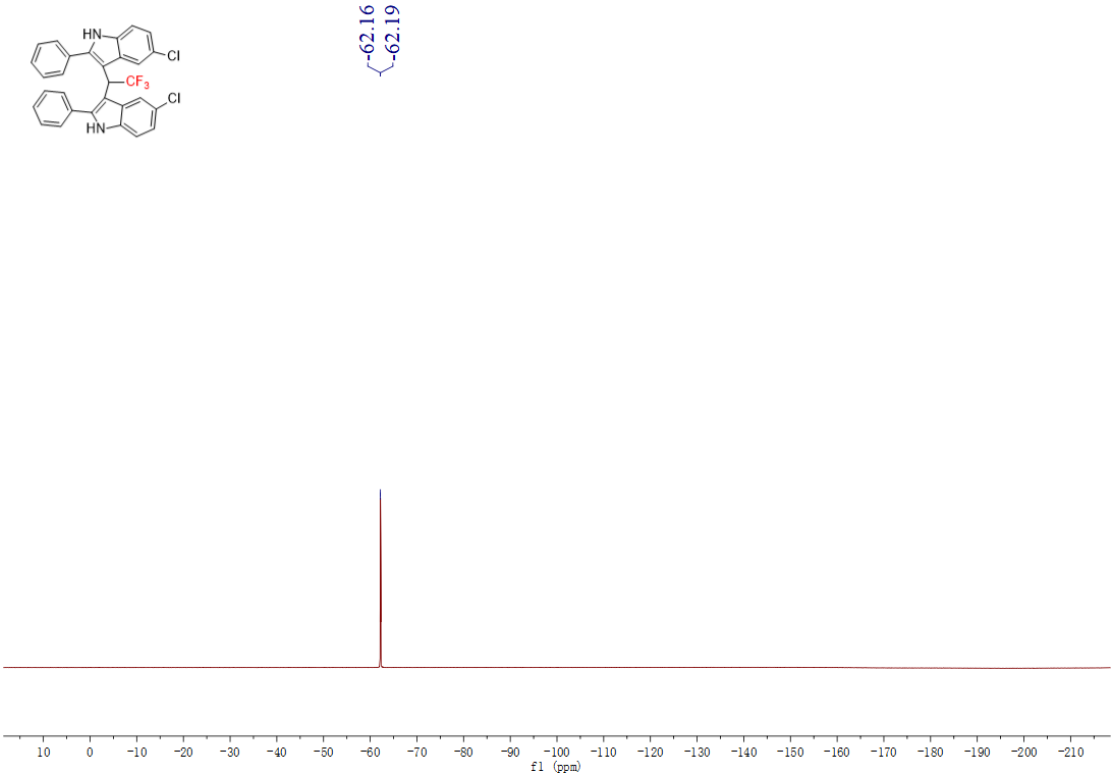
^{13}C NMR spectrum of **3c** in DMSO-d_6



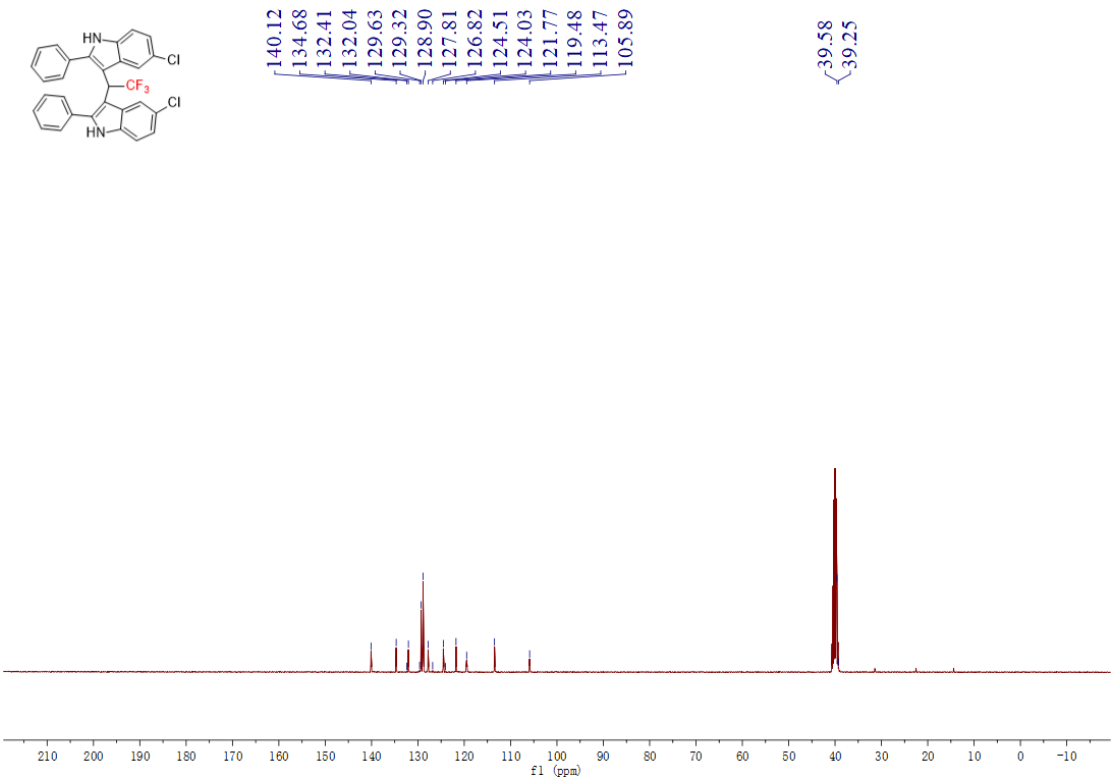
^{1}H NMR spectrum of **3d** in DMSO-d_6



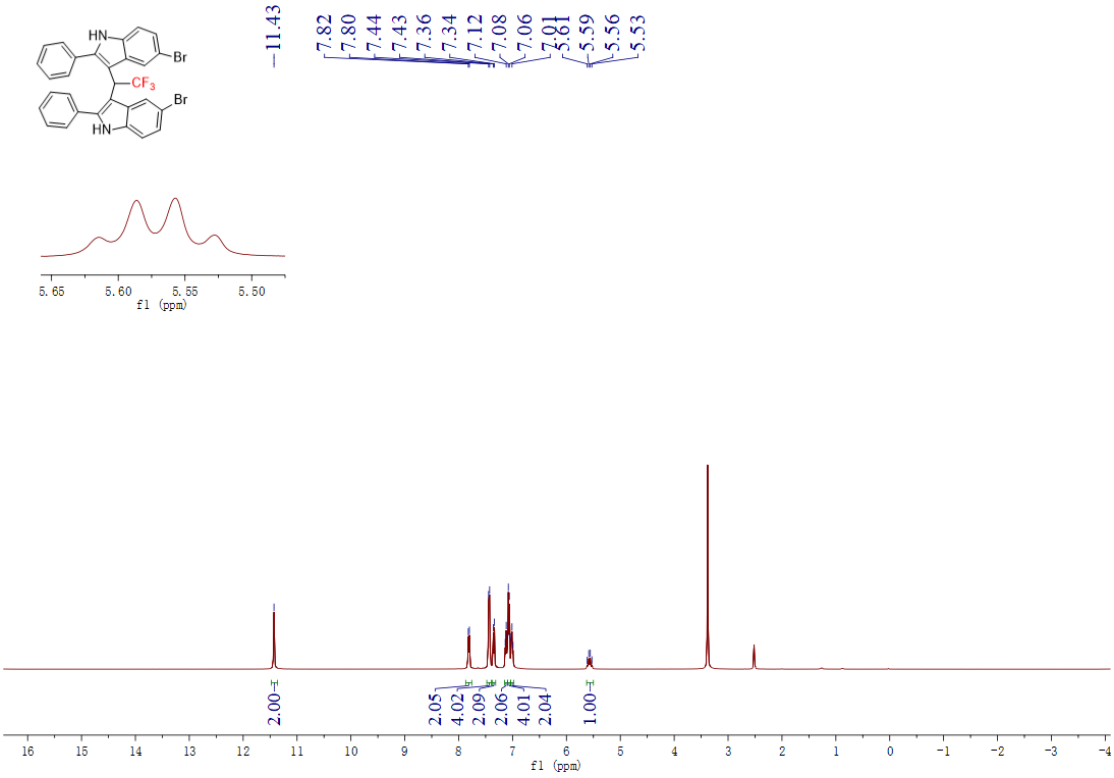
^{19}F NMR spectrum of **3d** in DMSO-d_6



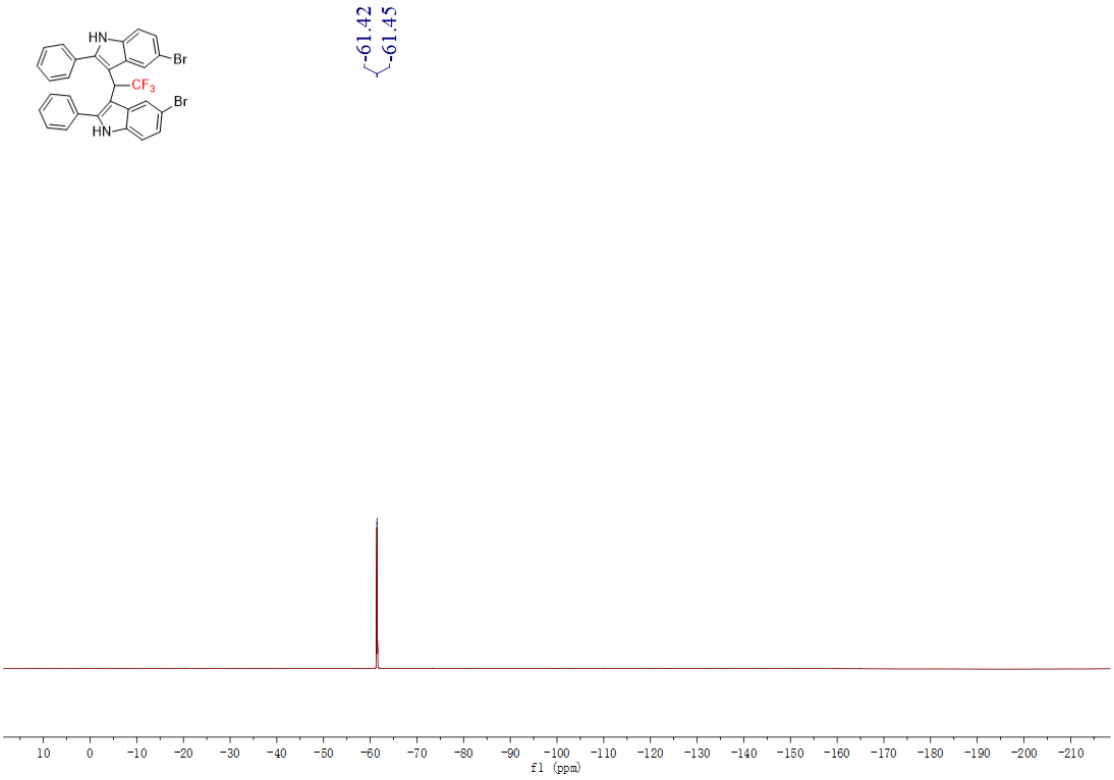
^{13}C NMR spectrum of **3d** in DMSO-d_6



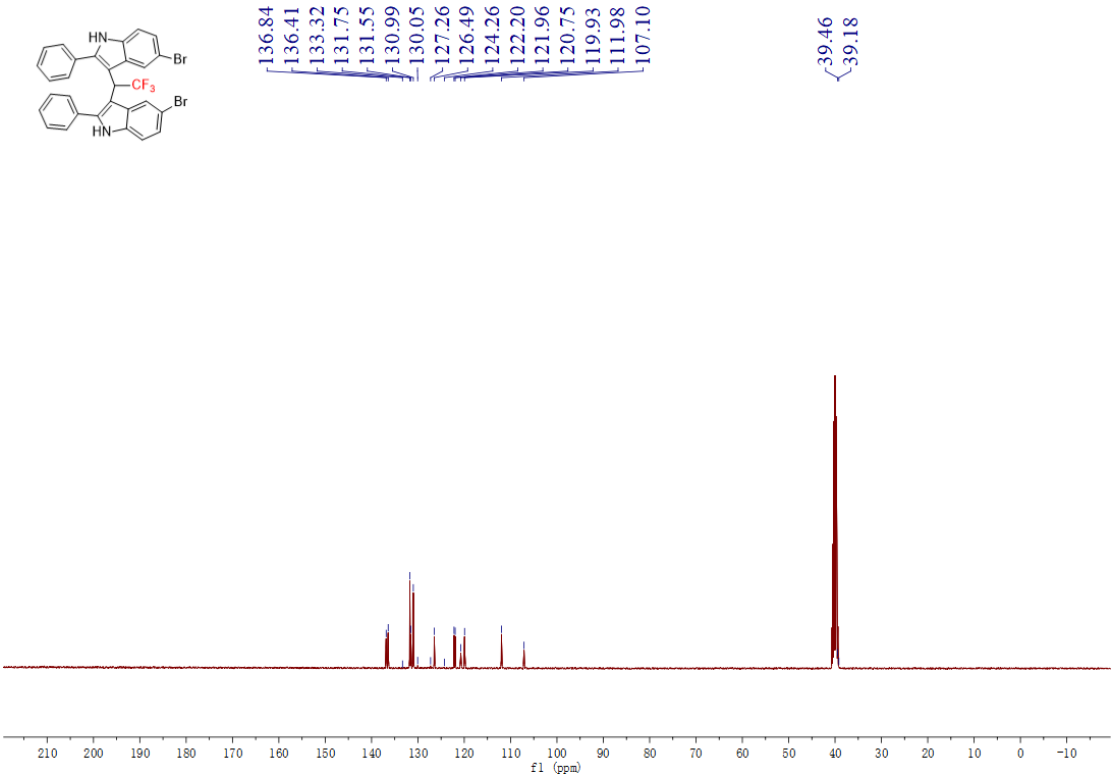
^{1}H NMR spectrum of **3e** in DMSO-d_6



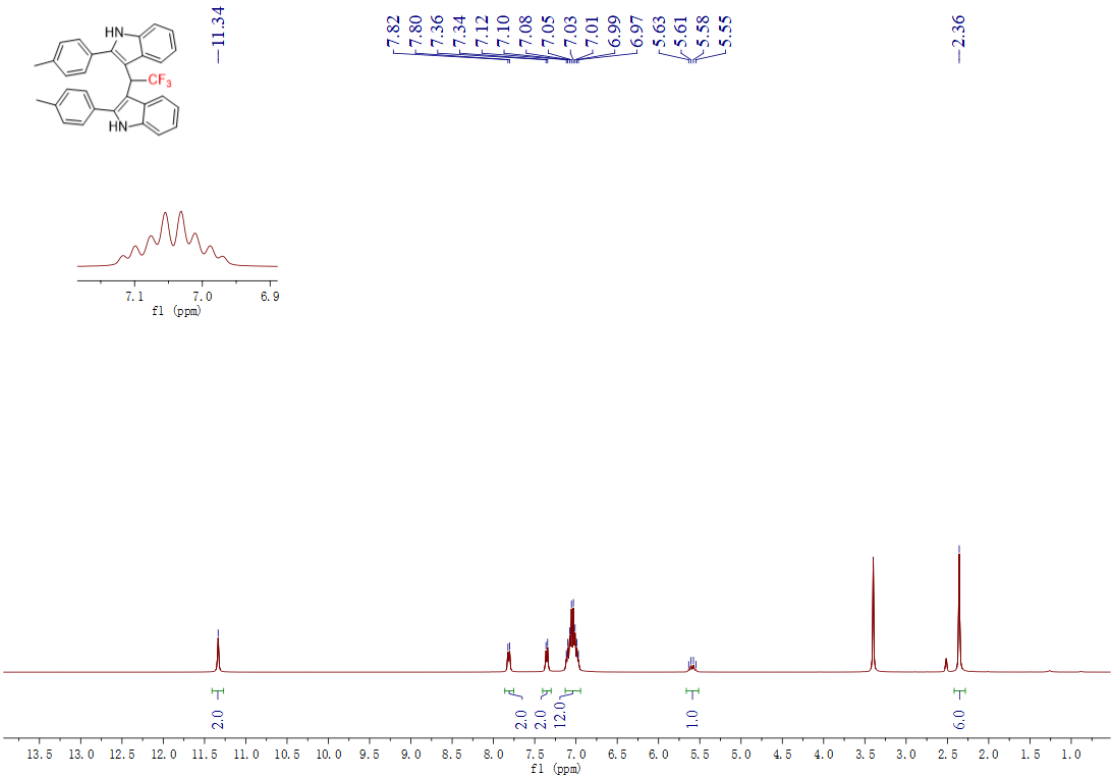
^{19}F NMR spectrum of **3e** in DMSO-d_6



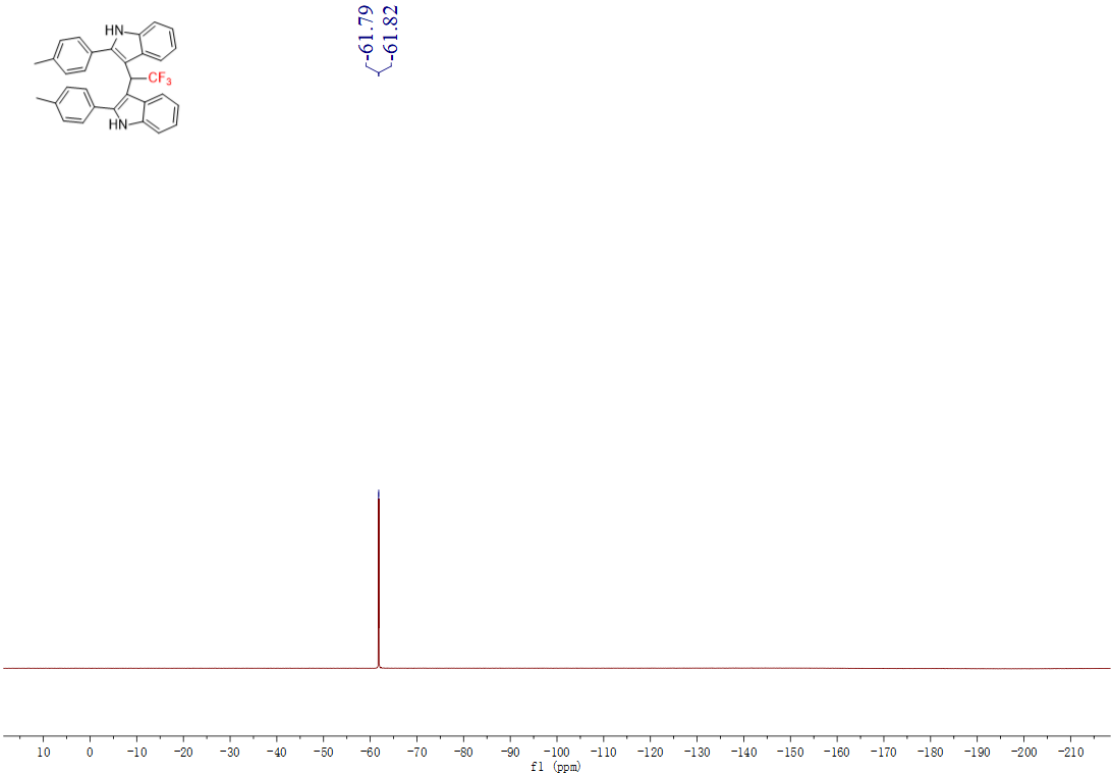
^{13}C NMR spectrum of **3e** in DMSO-d_6



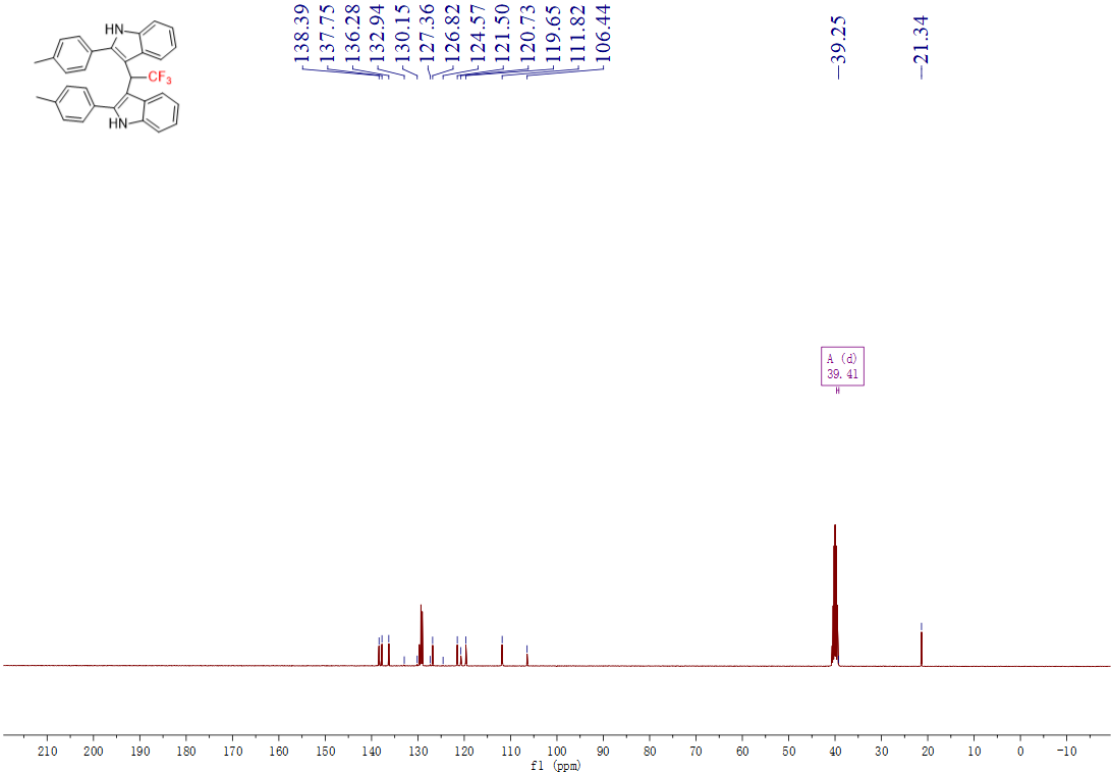
^{1}H NMR spectrum of **3f** in DMSO-d_6



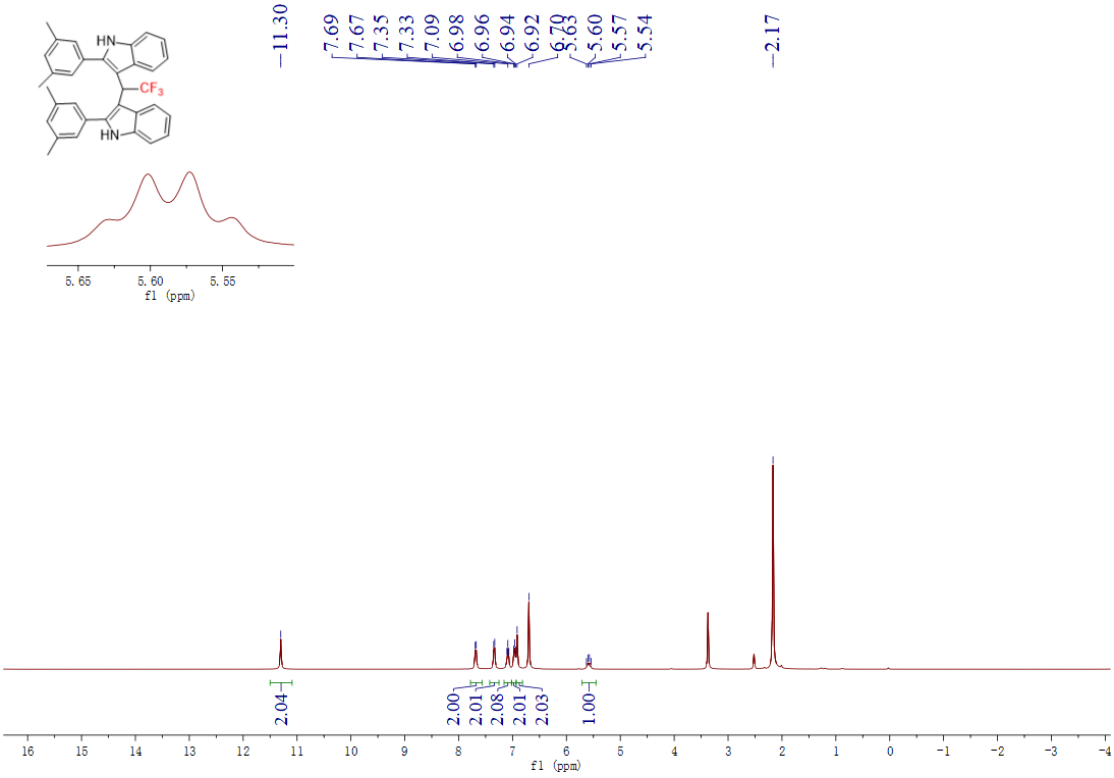
^{19}F NMR spectrum of **3f** in DMSO-d_6



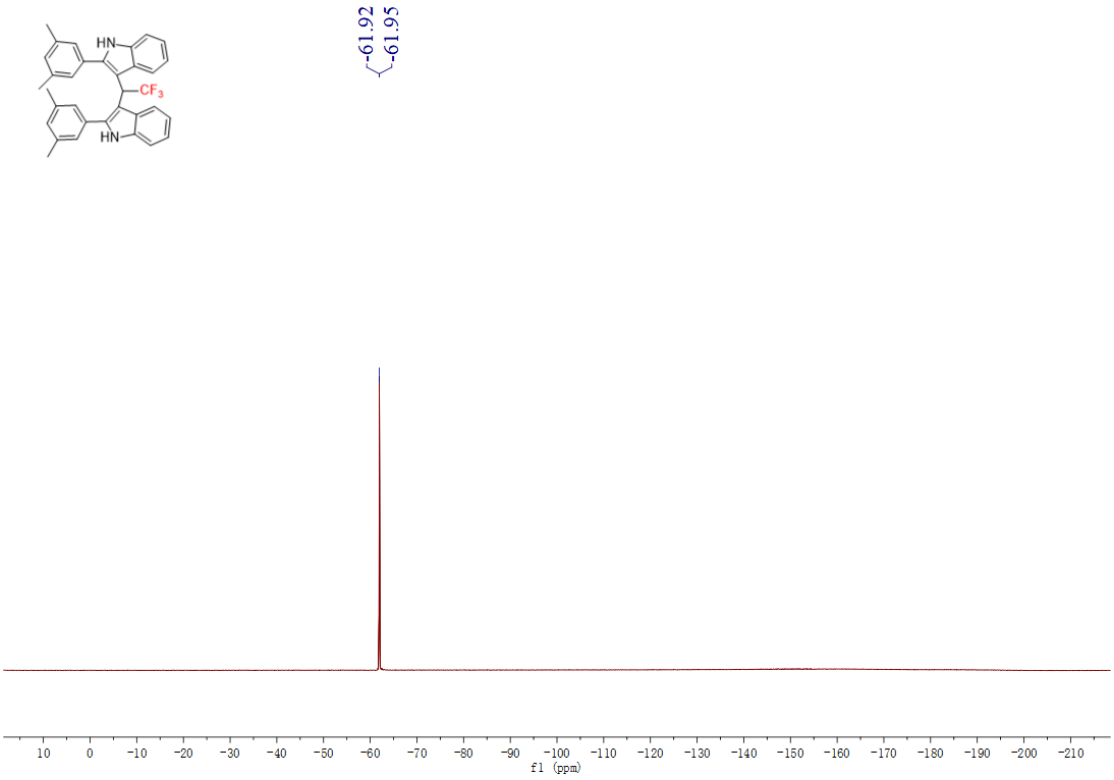
^{13}C NMR spectrum of **3f** in DMSO-d_6



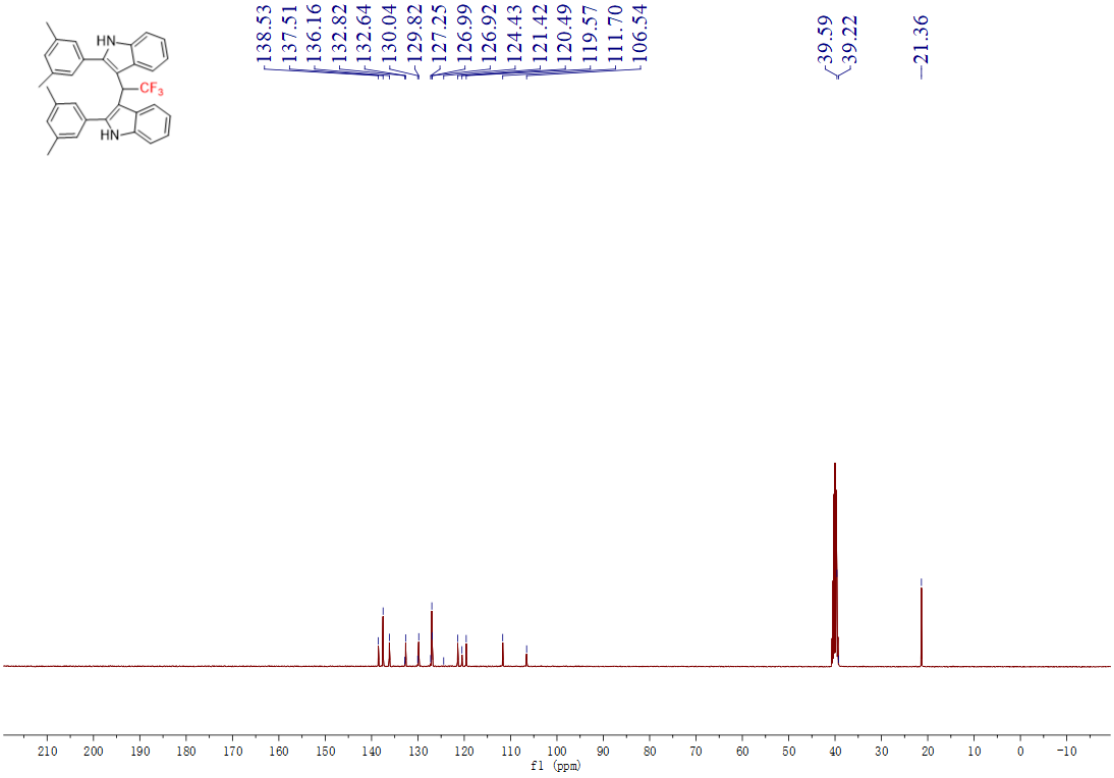
^{1}H NMR spectrum of **3g** in DMSO-d_6



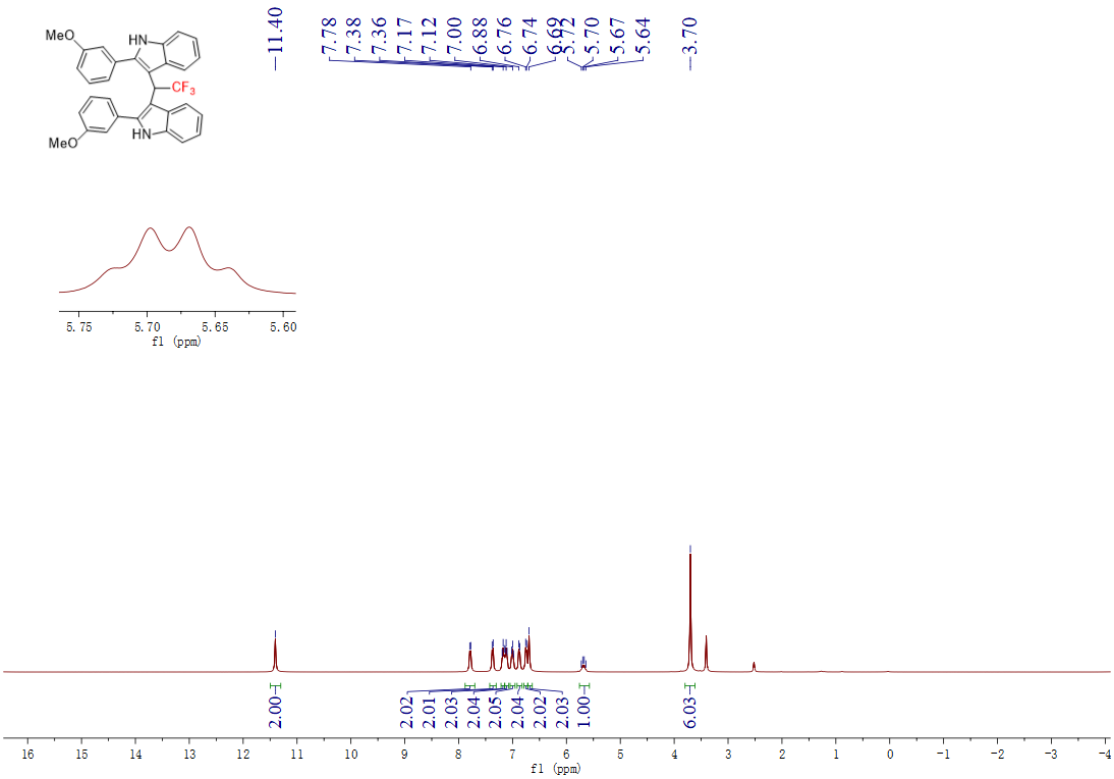
^{19}F NMR spectrum of **3g** in DMSO-d_6



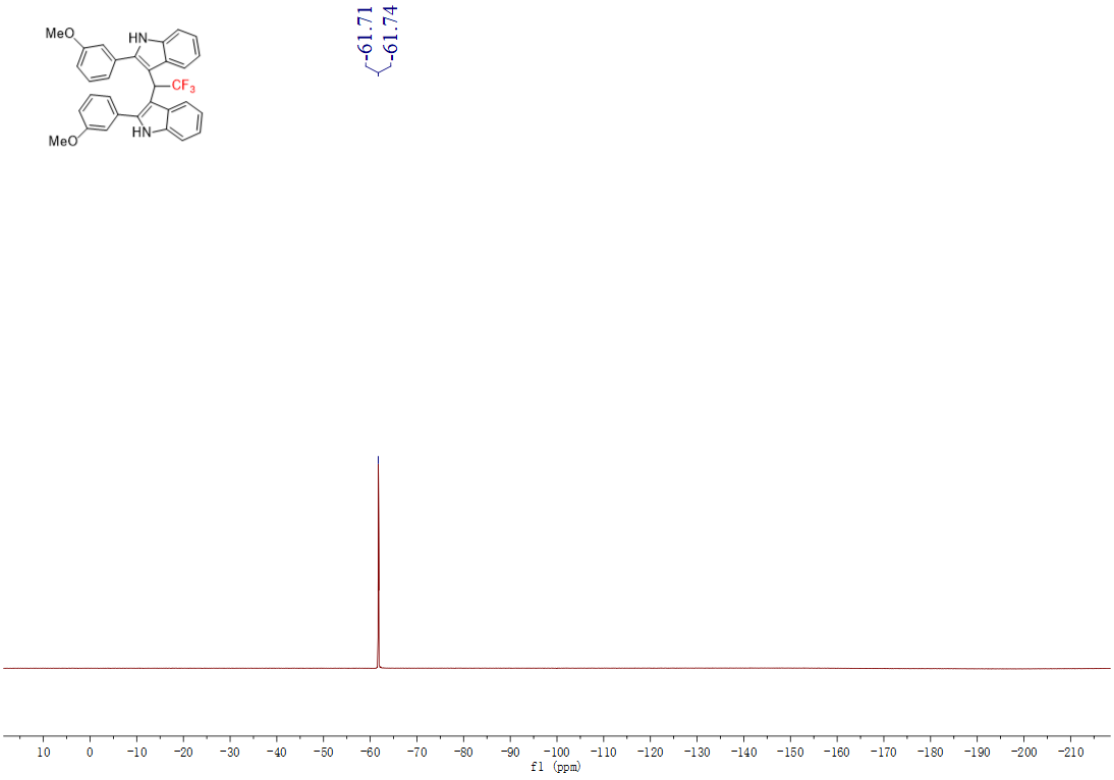
^{13}C NMR spectrum of **3g** in DMSO-d_6



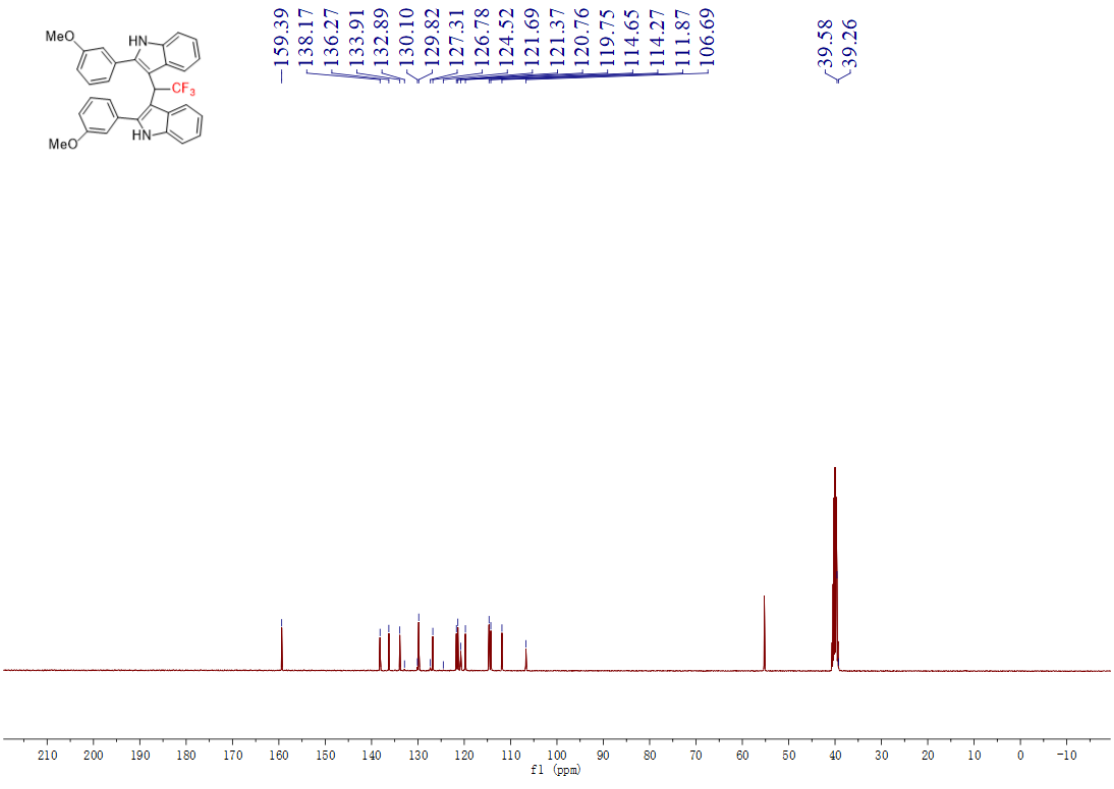
^{1}H NMR spectrum of **3h** in DMSO-d_6



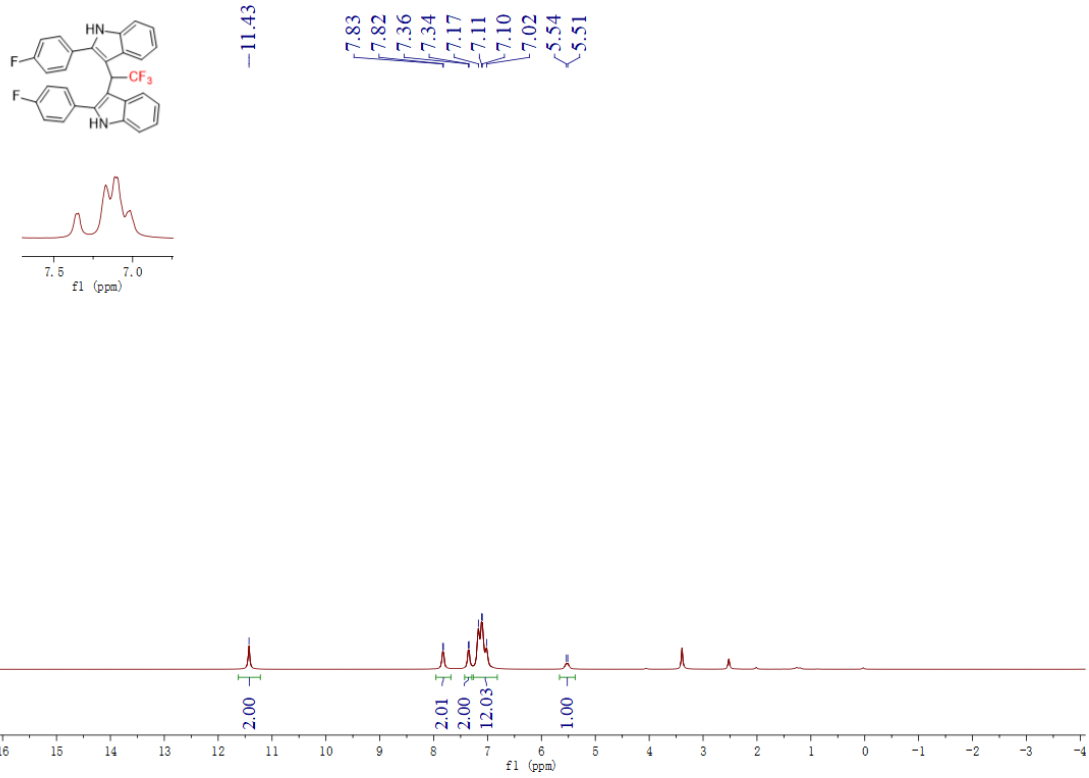
^{19}F NMR spectrum of **3h** in DMSO-d_6



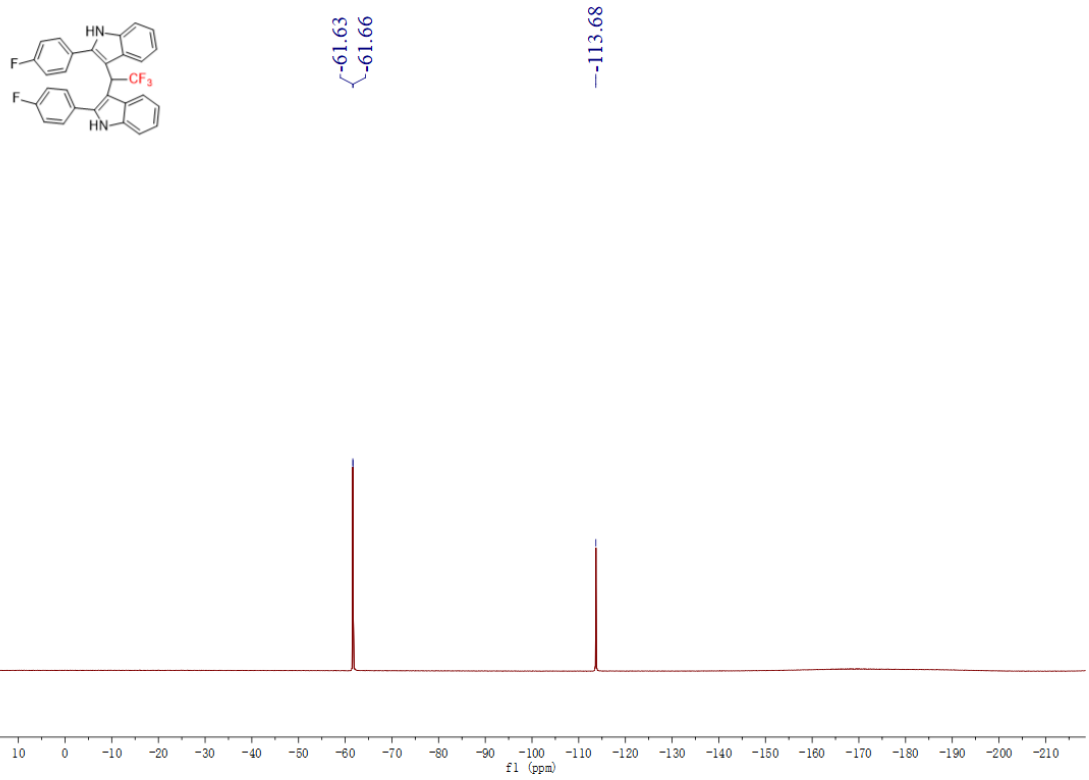
^{13}C NMR spectrum of **3h** in DMSO-d_6



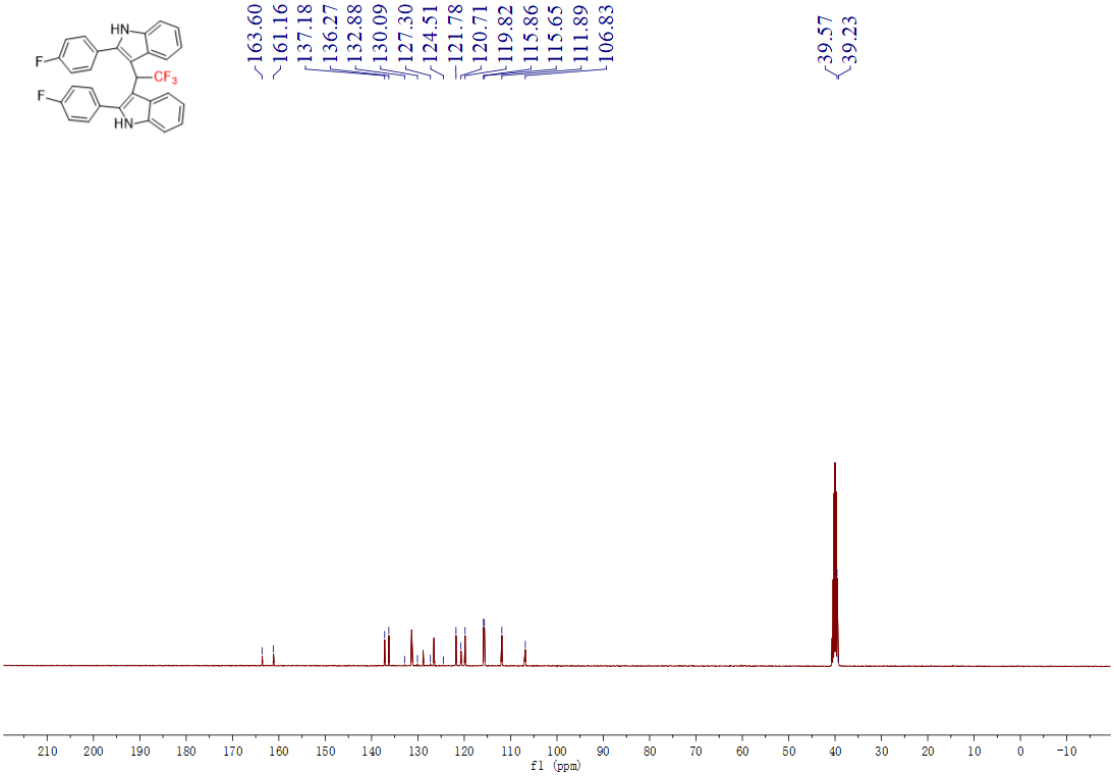
^{1}H NMR spectrum of **3i** in DMSO-d_6



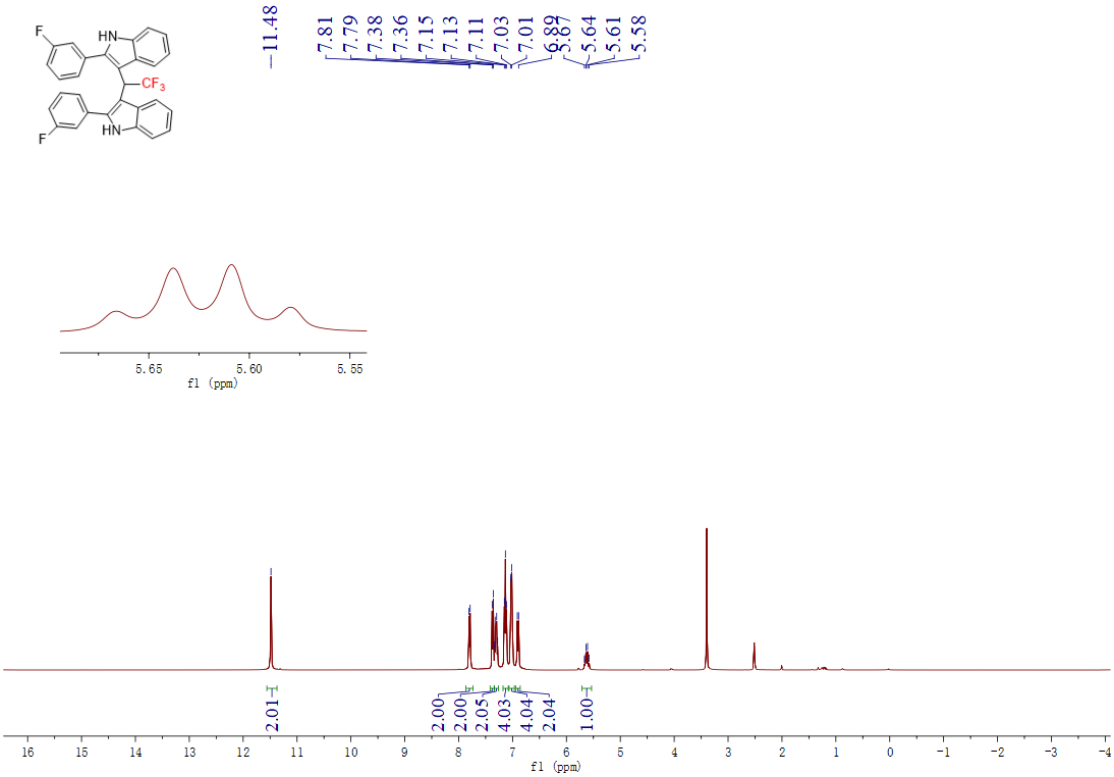
^{19}F NMR spectrum of **3i** in DMSO-d_6



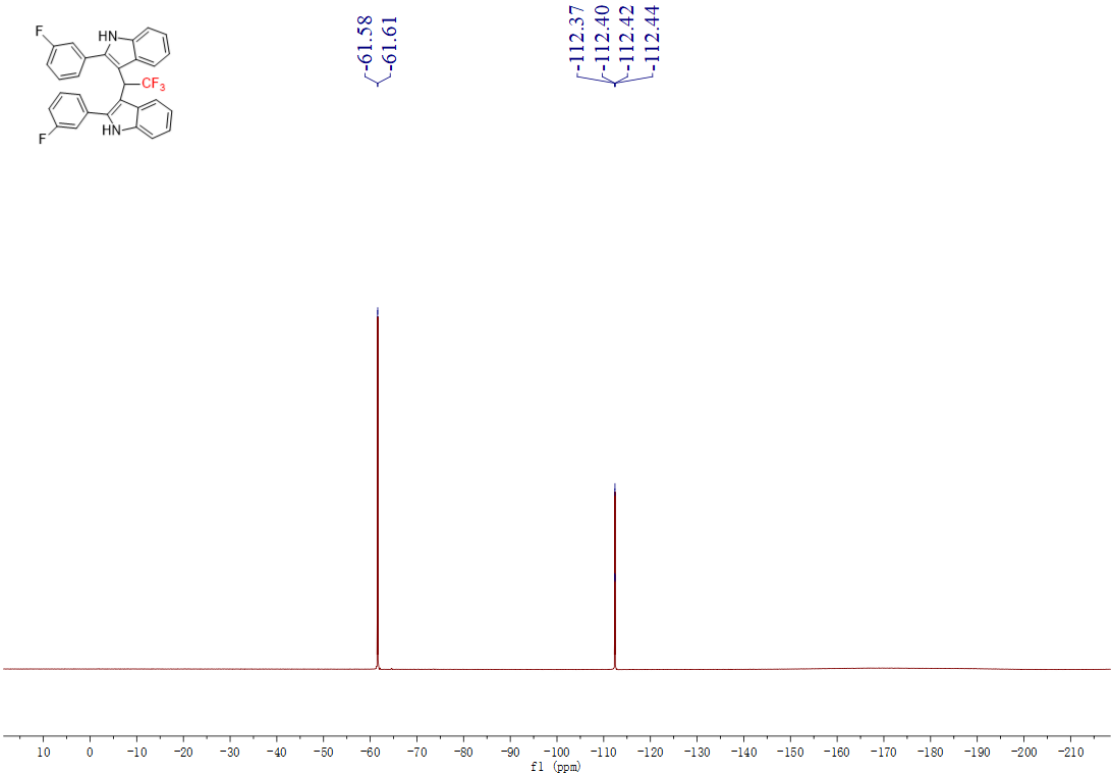
^{13}C NMR spectrum of **3i** in DMSO-d_6



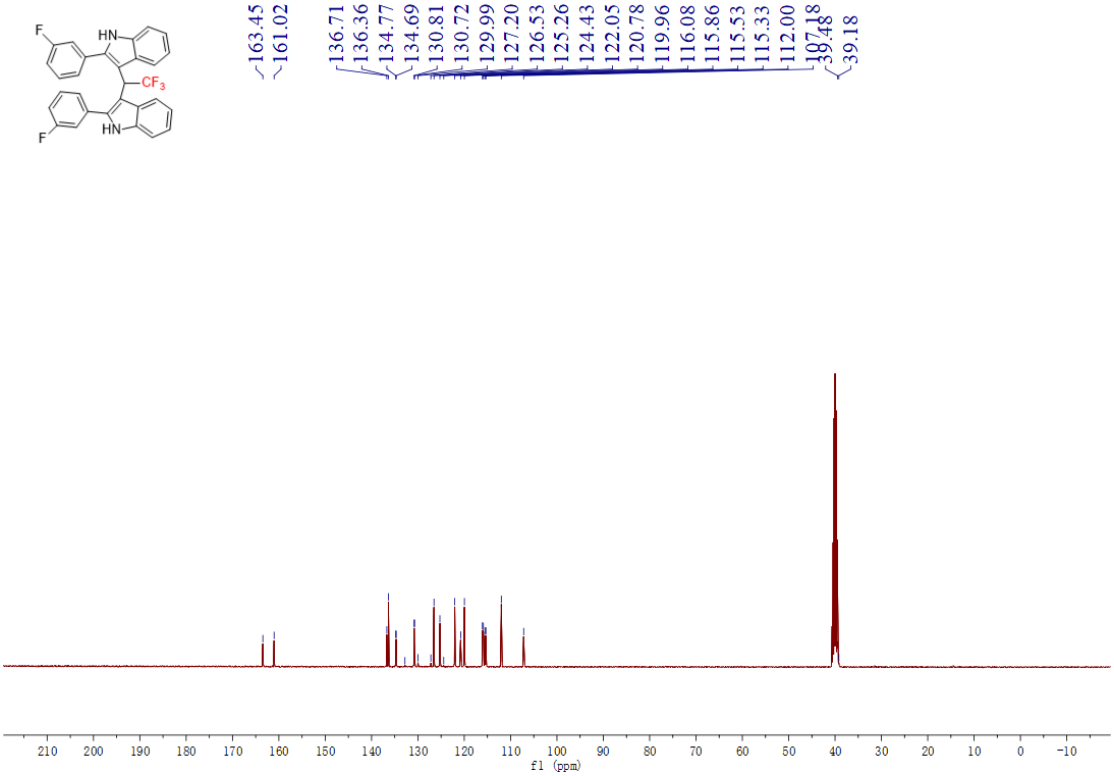
^{1}H NMR spectrum of **3i** in DMSO-d_6



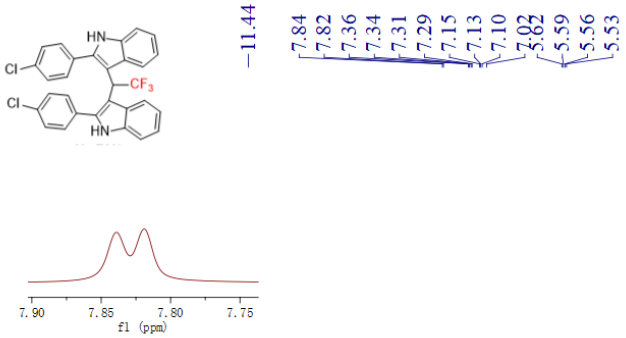
^{19}F NMR spectrum of **3j** in DMSO-d_6

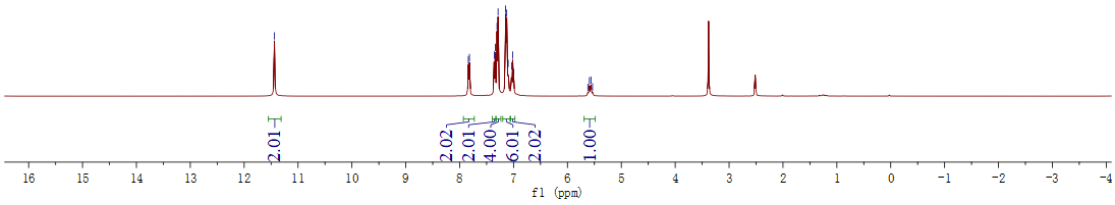


^{13}C NMR spectrum of **3j** in DMSO-d_6

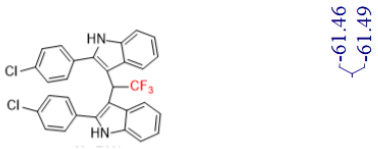


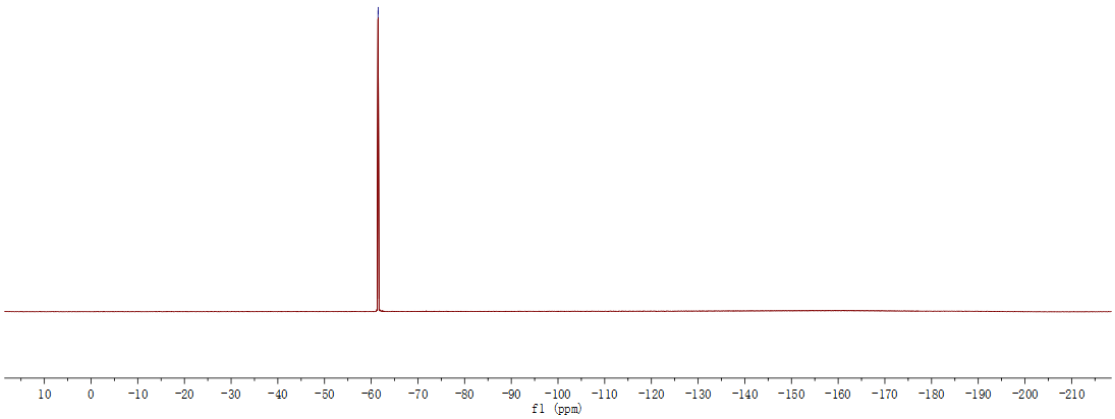
^{1}H NMR spectrum of **3k** in DMSO-d_6



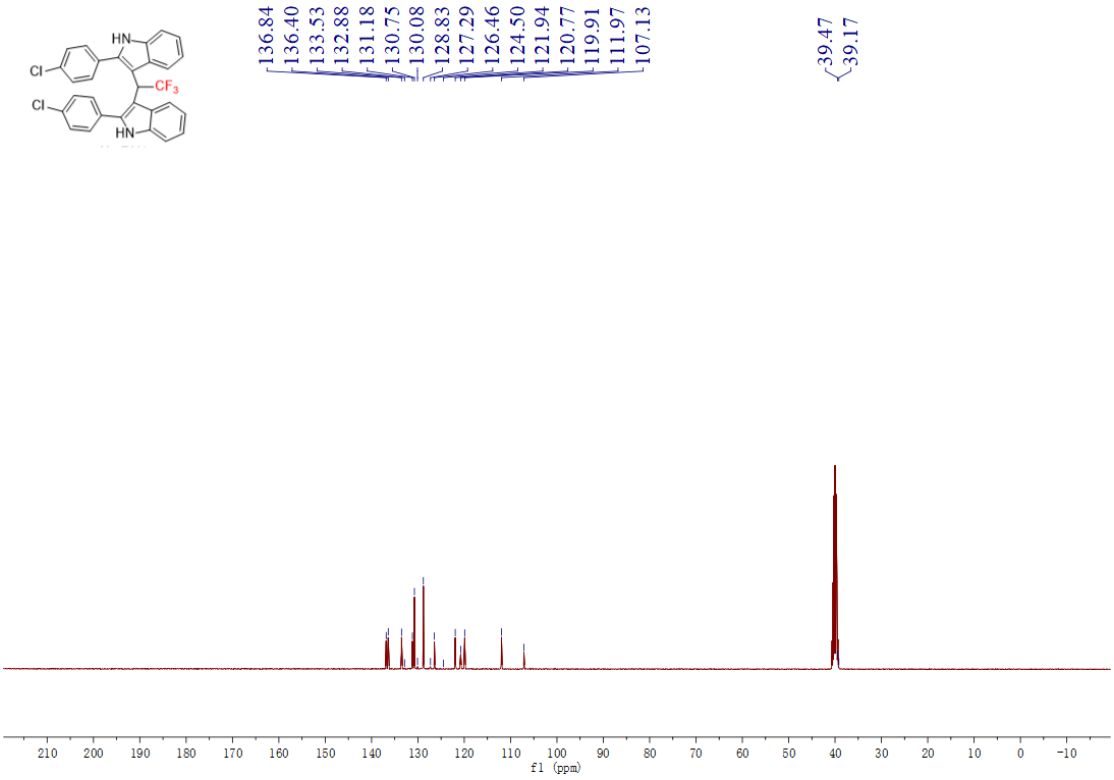


^{19}F NMR spectrum of **3k** in DMSO-d_6

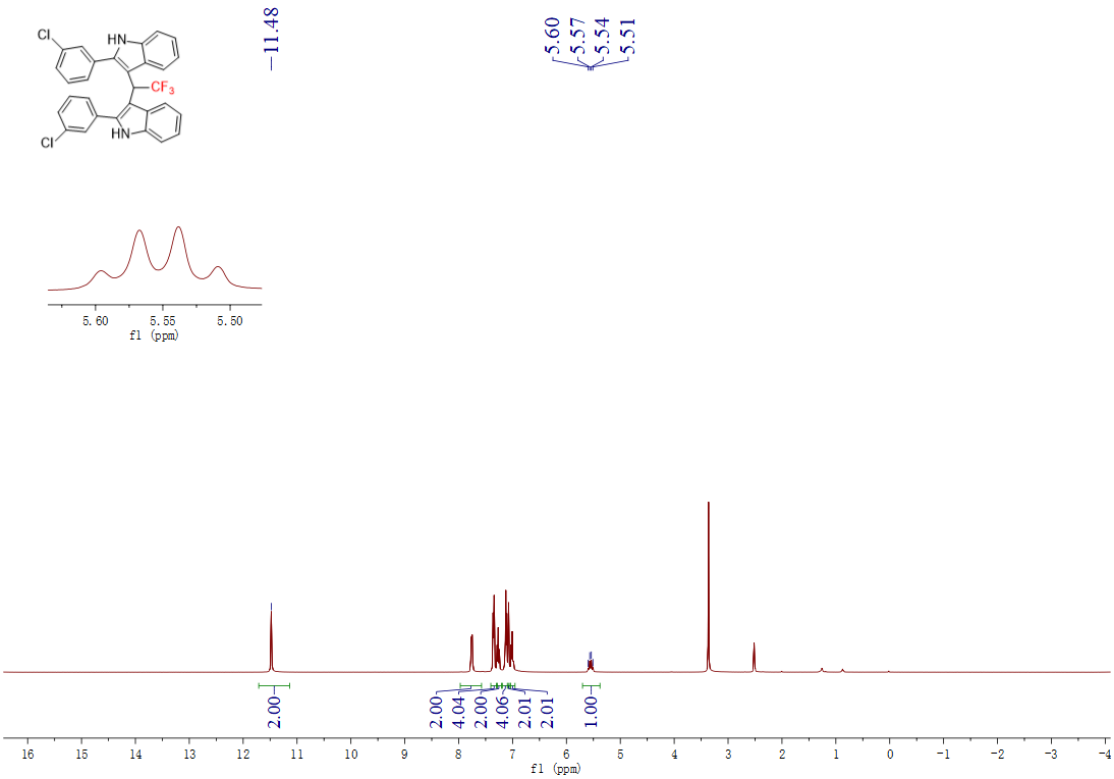




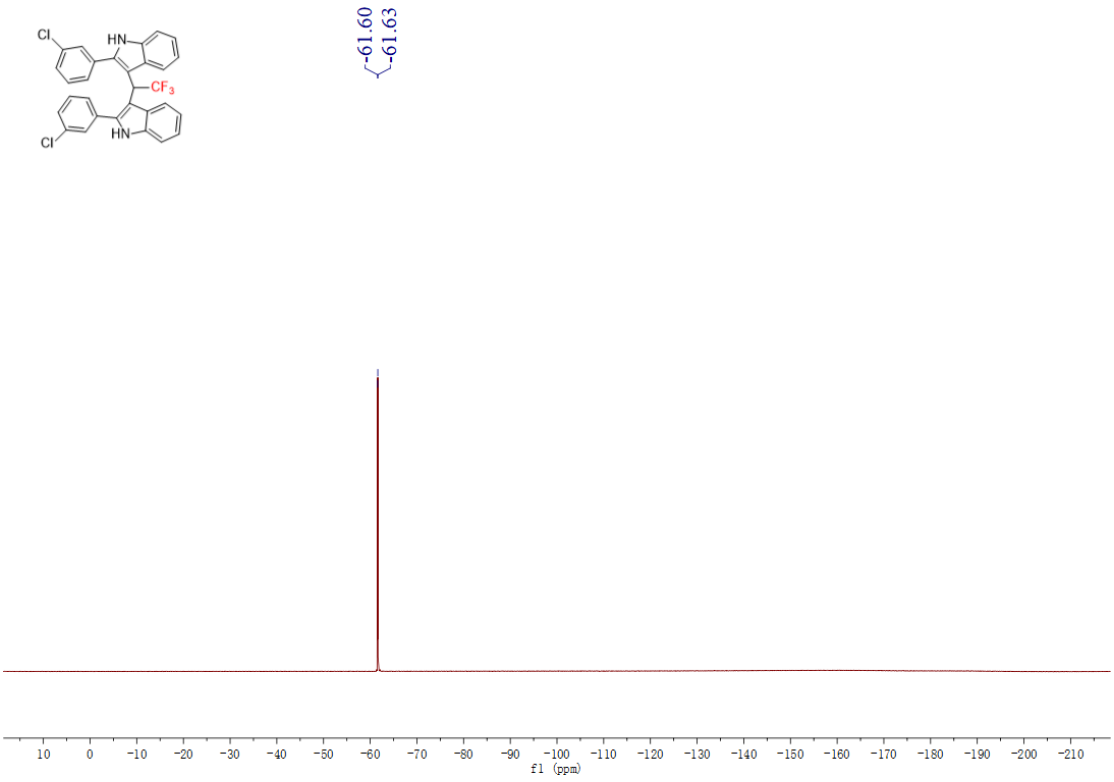
^{13}C NMR spectrum of **3k** in DMSO-d_6



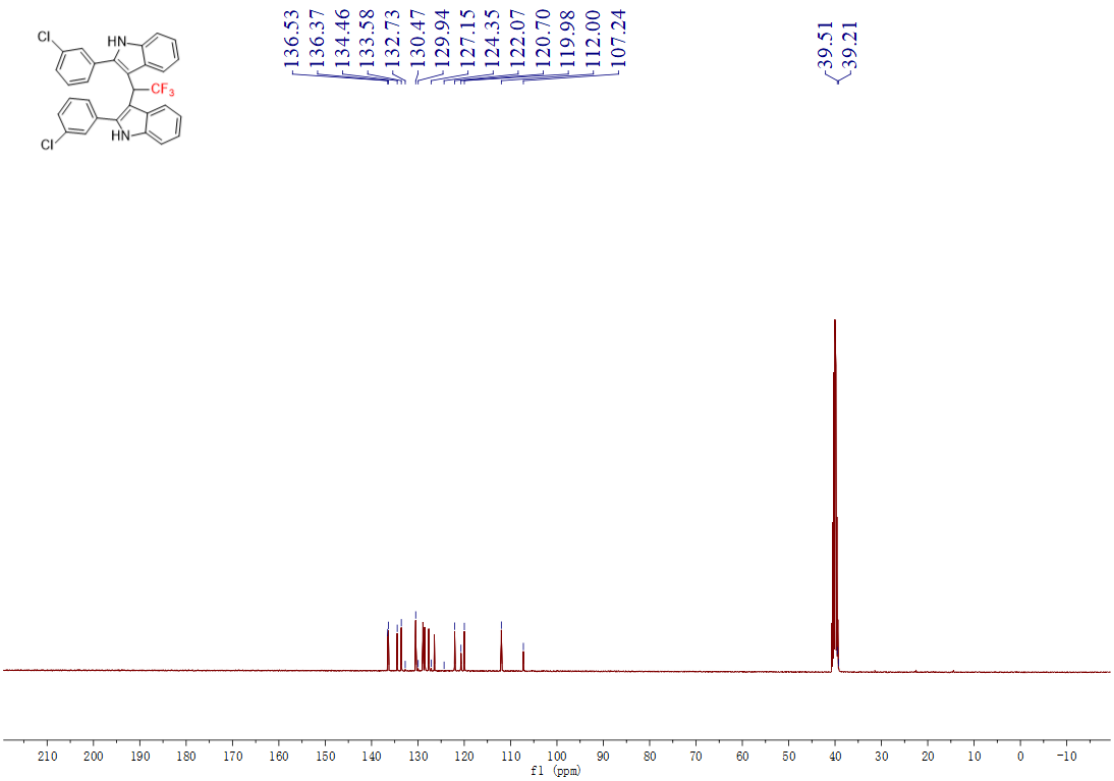
^{1}H NMR spectrum of **3l** in DMSO-d_6



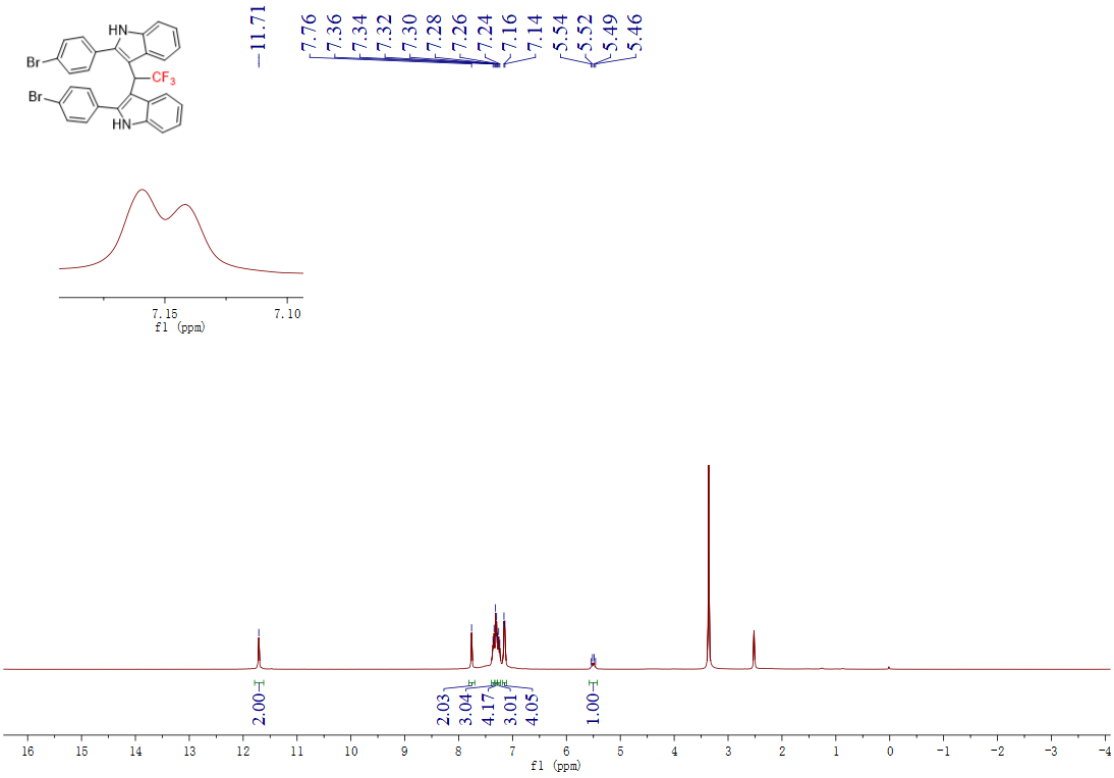
^{19}F NMR spectrum of **3l** in DMSO-d_6



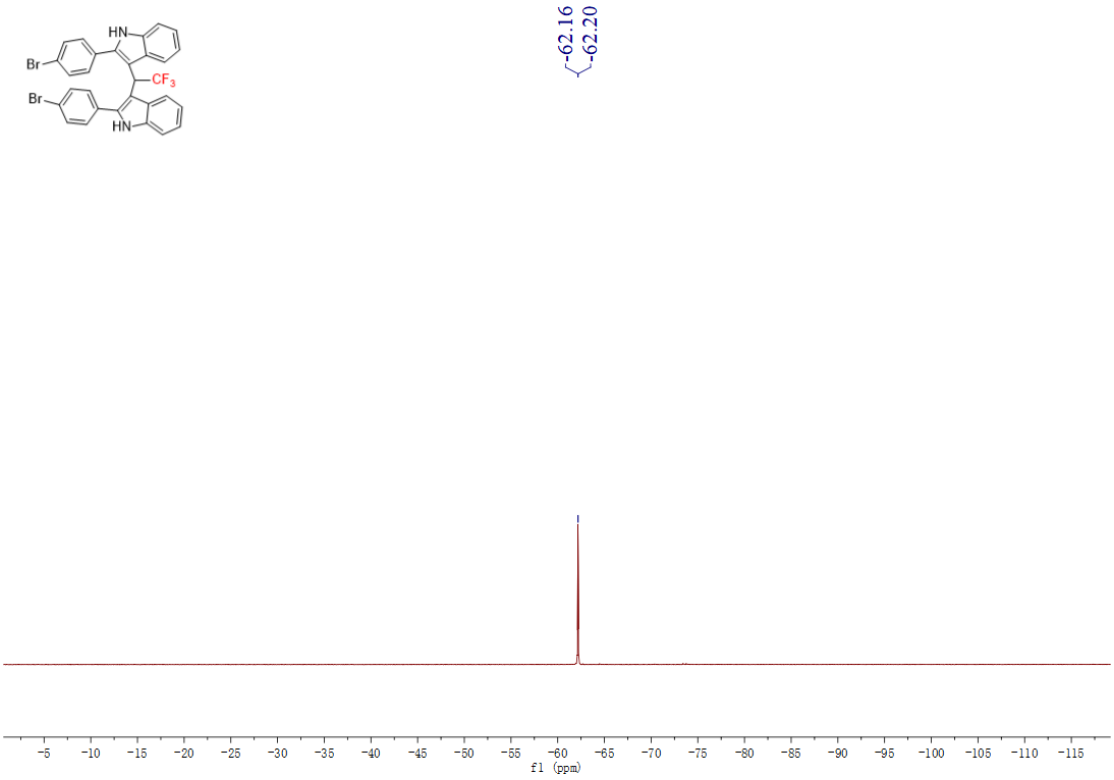
^{13}C NMR spectrum of **3l** in DMSO-d_6



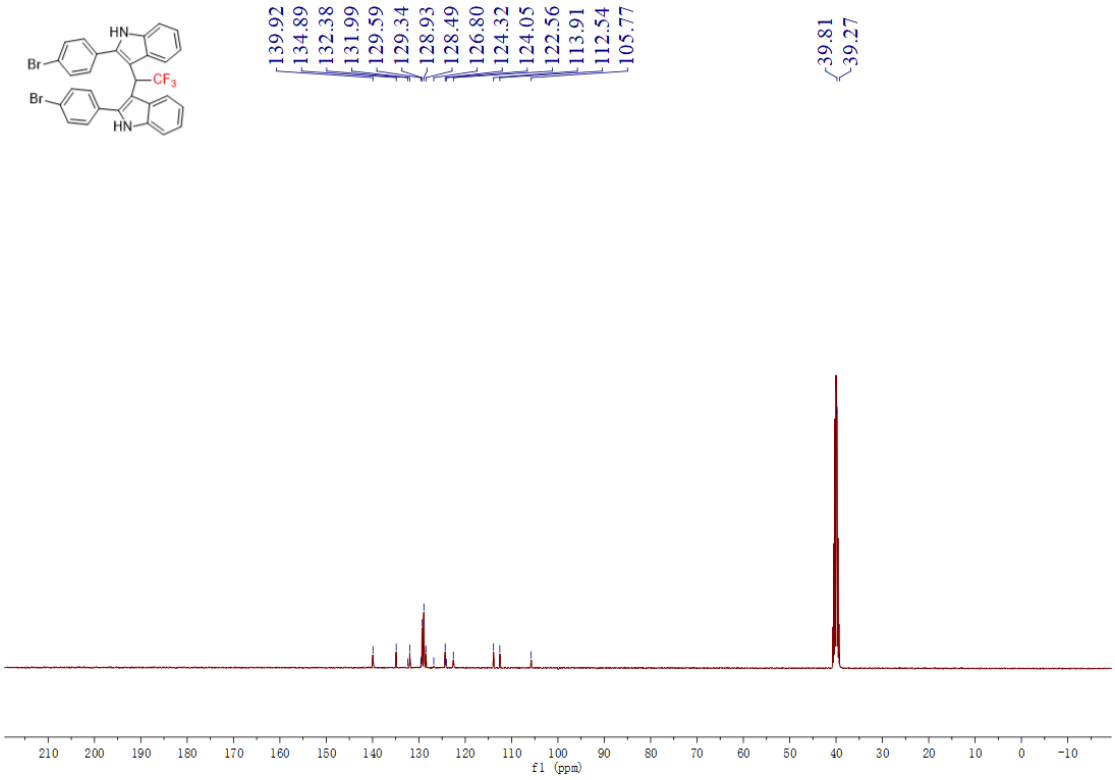
^{1}H NMR spectrum of **3m** in DMSO-d_6



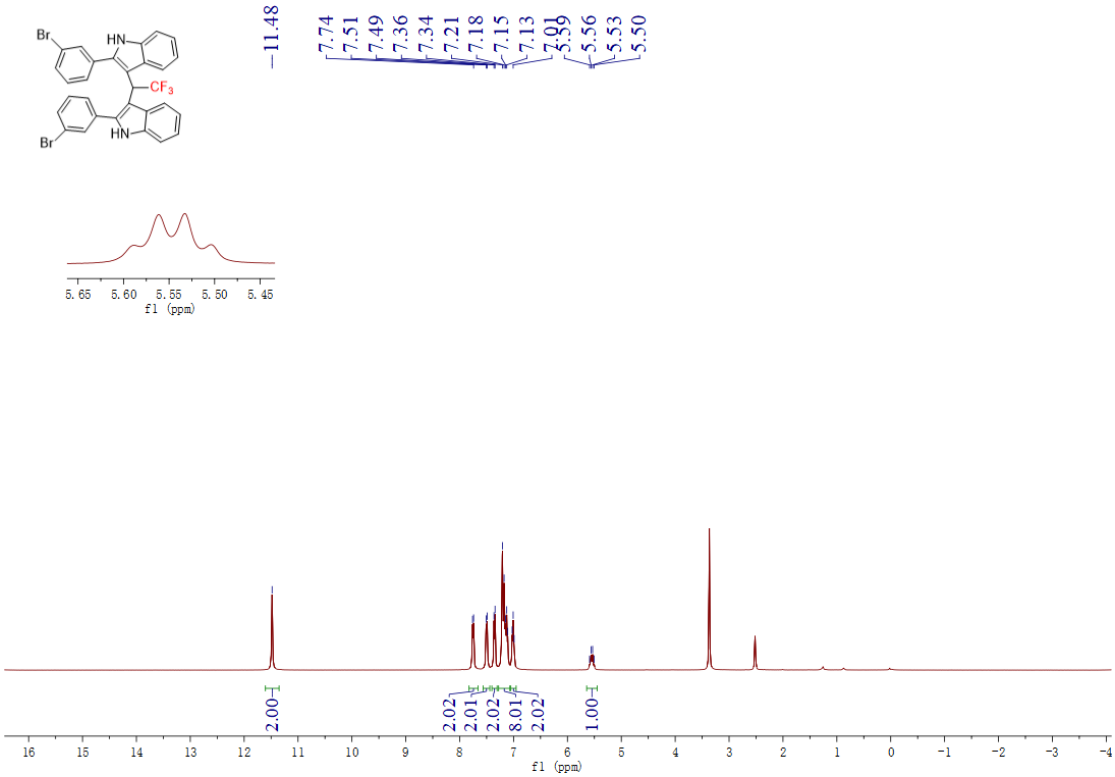
^{19}F NMR spectrum of **3m** in DMSO-d_6



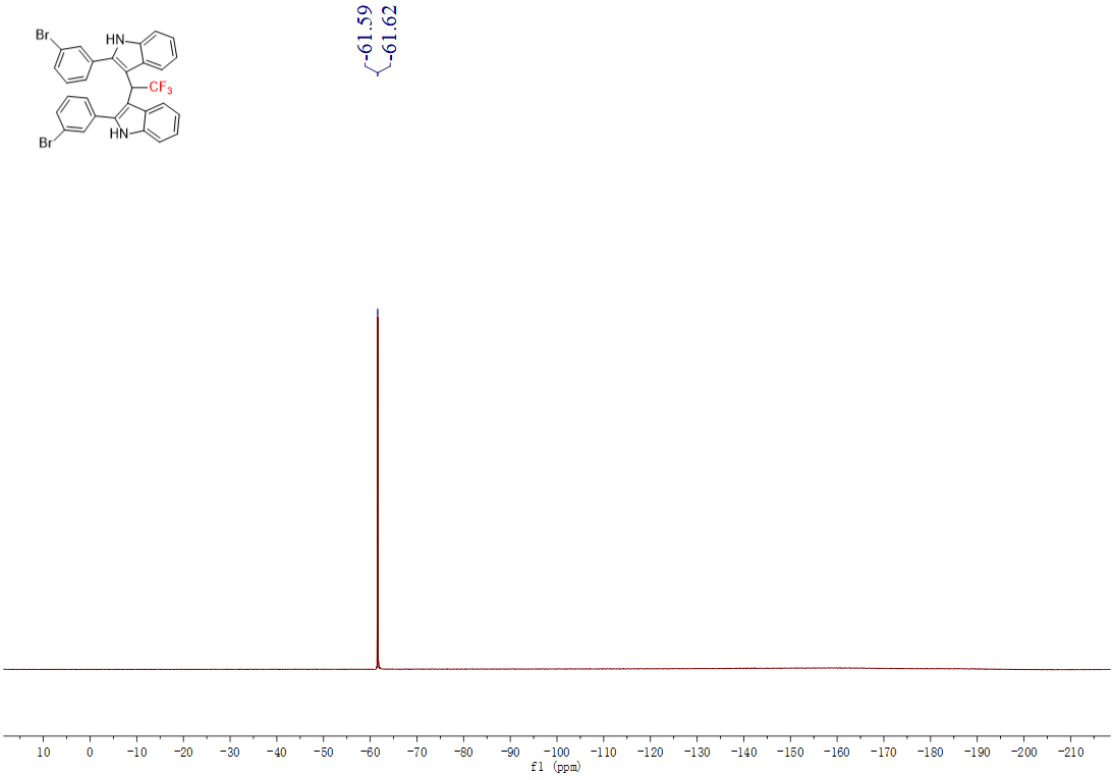
^{13}C NMR spectrum of **3m** in DMSO-d_6



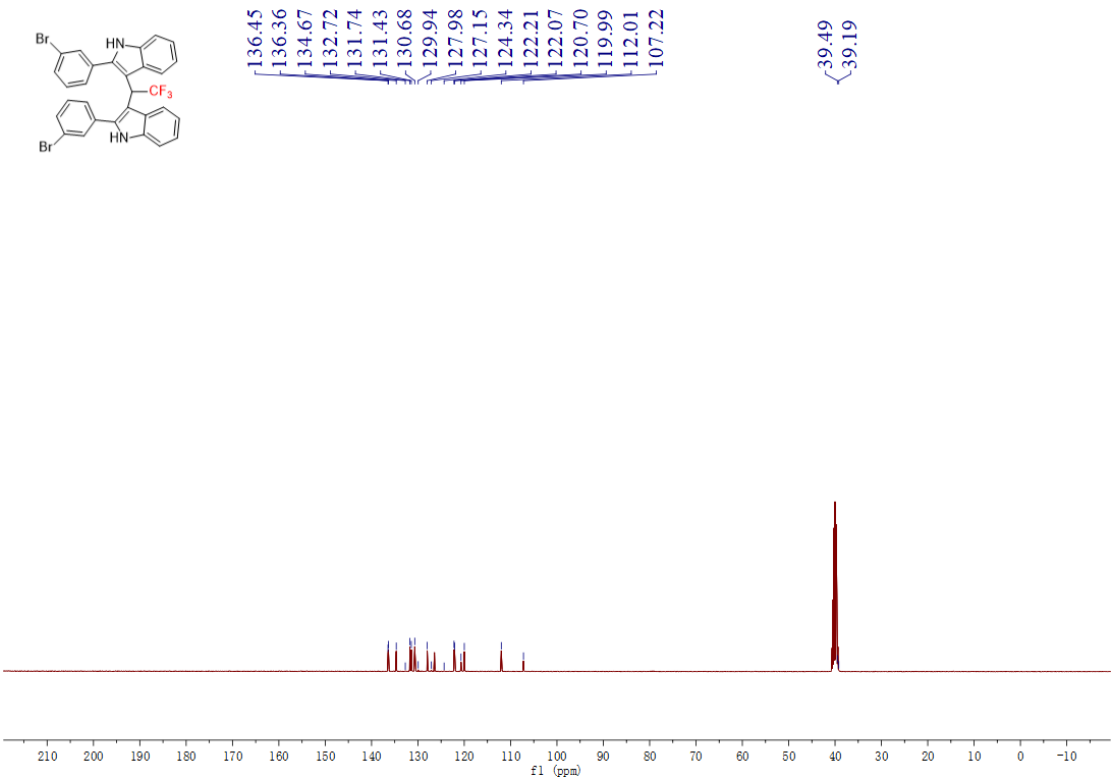
^{1}H NMR spectrum of **3n** in DMSO-d_6



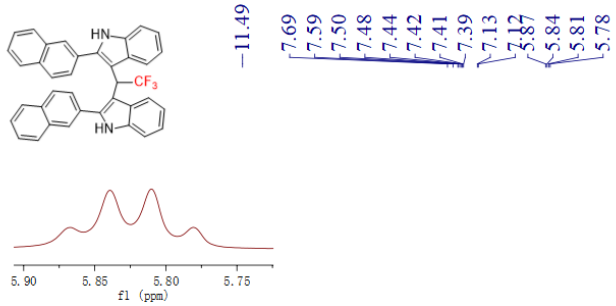
^{19}F NMR spectrum of **3n** in DMSO-d_6

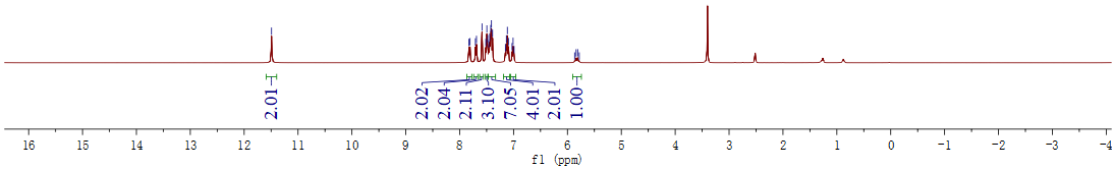


^{13}C NMR spectrum of **3n** in DMSO-d_6

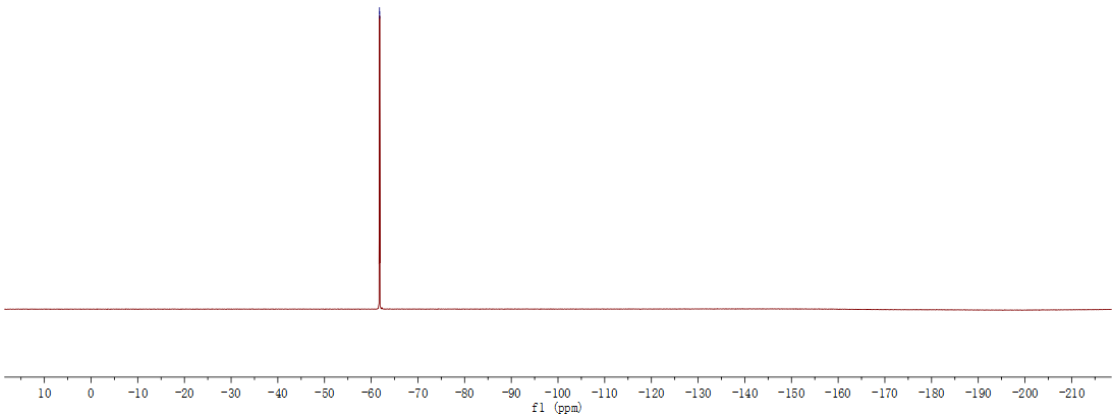


^{1}H NMR spectrum of **3o** in DMSO-d_6

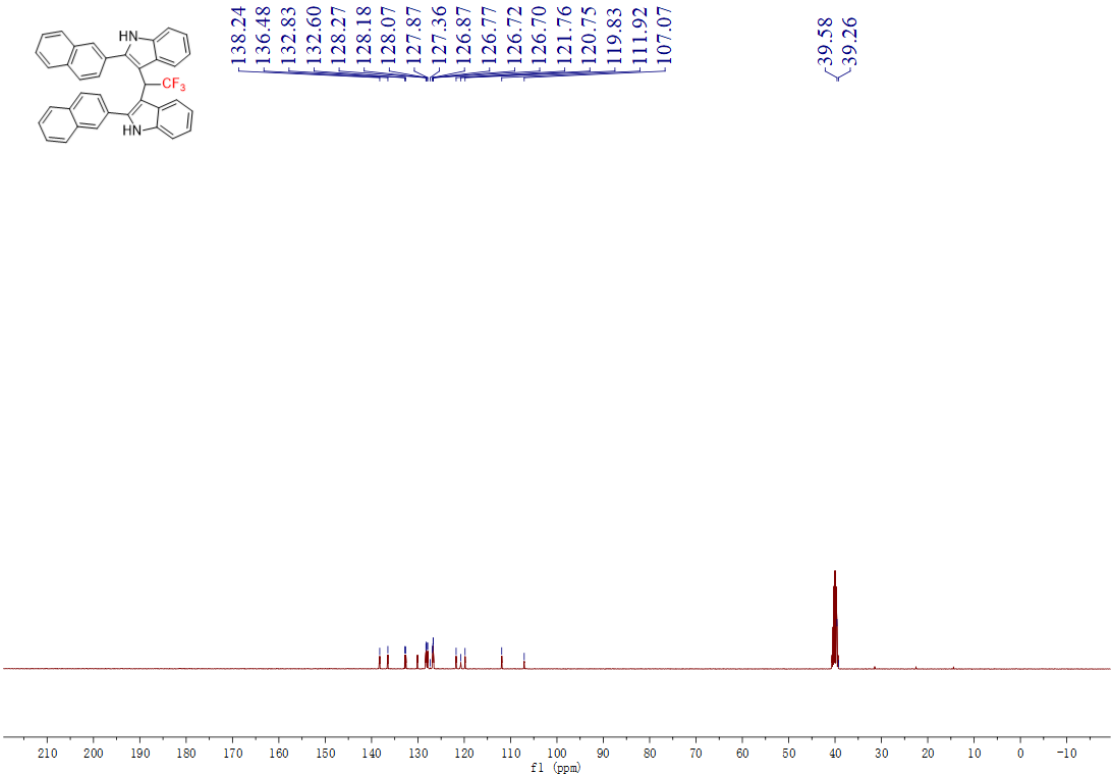




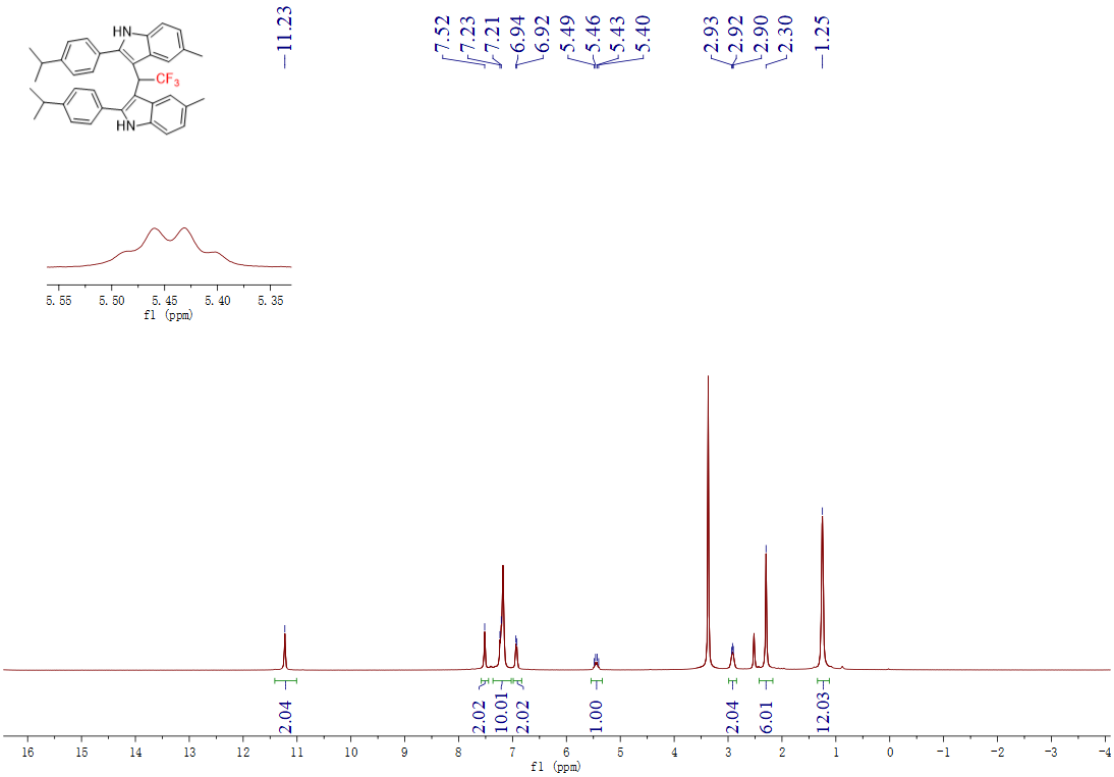
^{19}F NMR spectrum of **3o** in DMSO-d_6



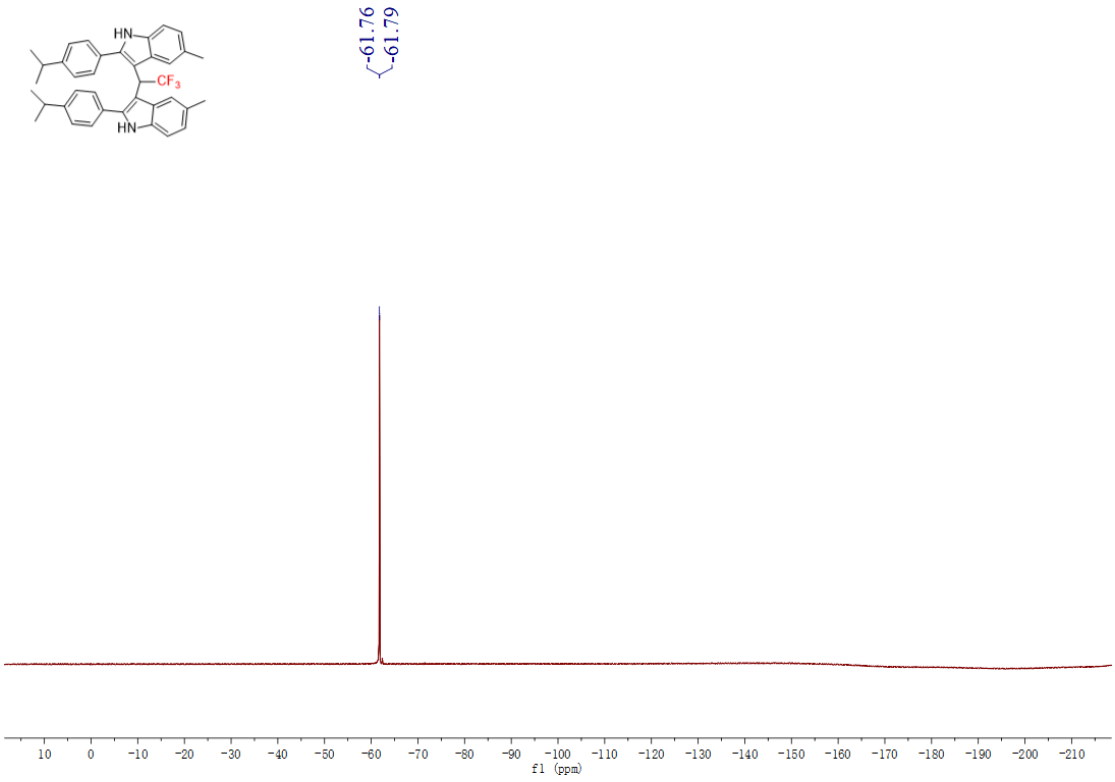
^{13}C NMR spectrum of **3o** in DMSO-d_6



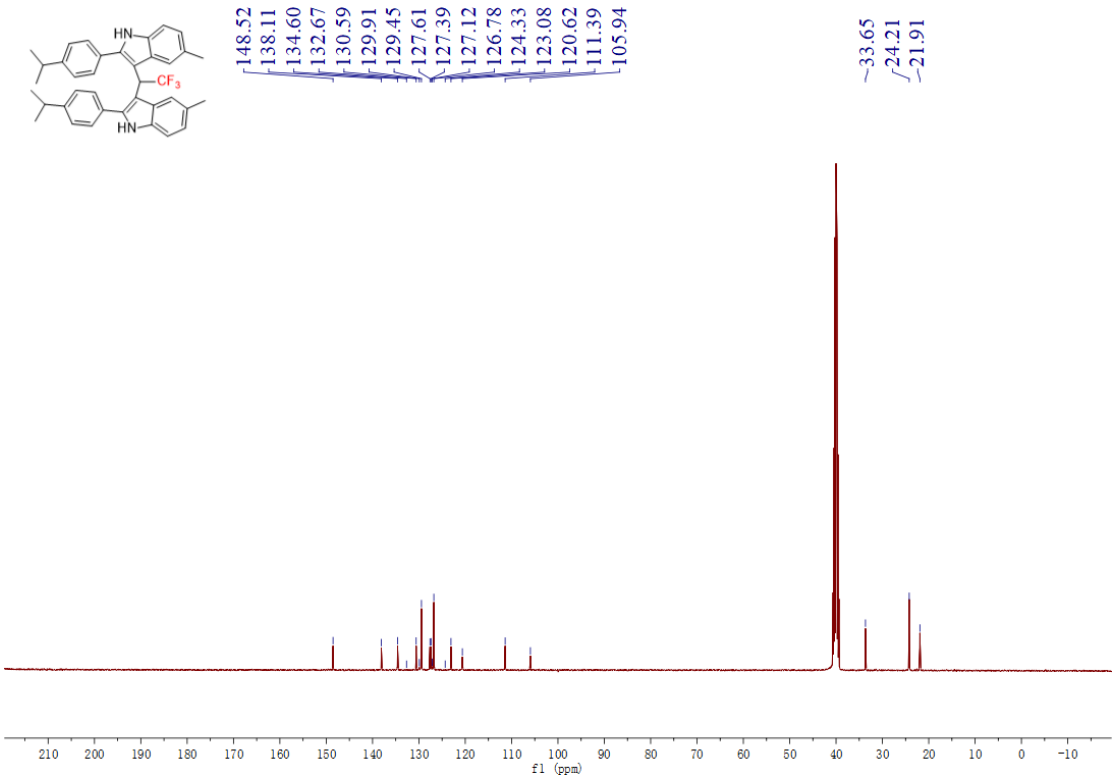
^{1}H NMR spectrum of **3p** in DMSO-d_6



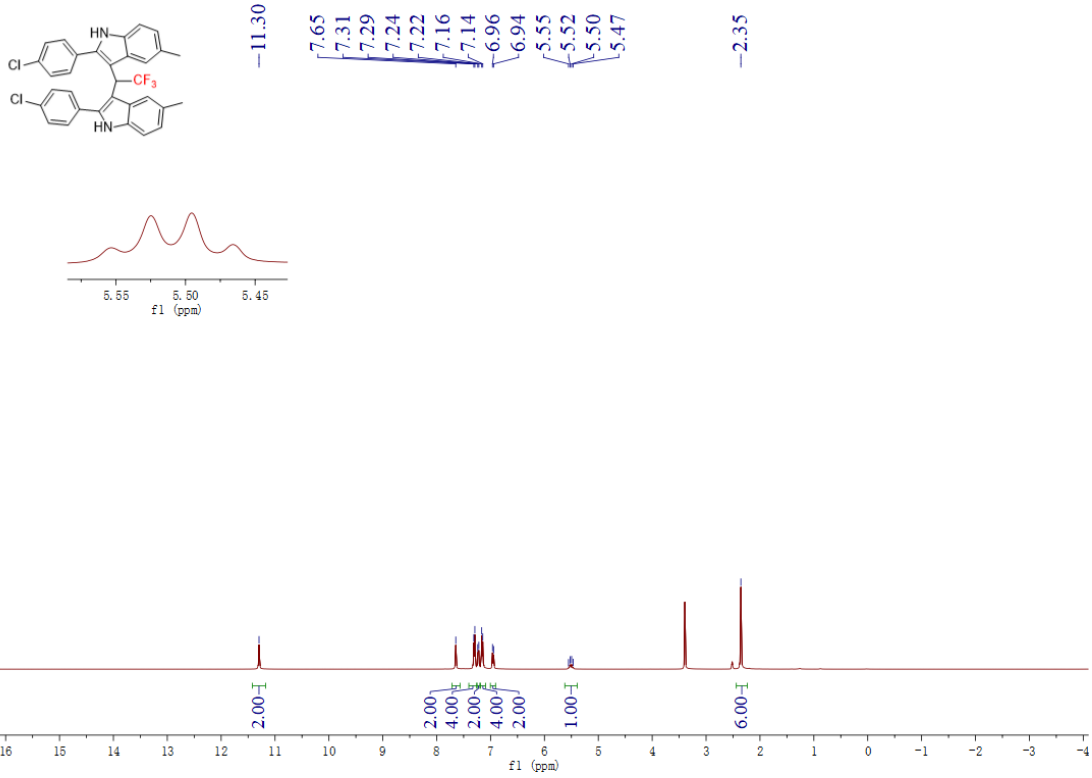
^{19}F NMR spectrum of **3p** in DMSO-d_6



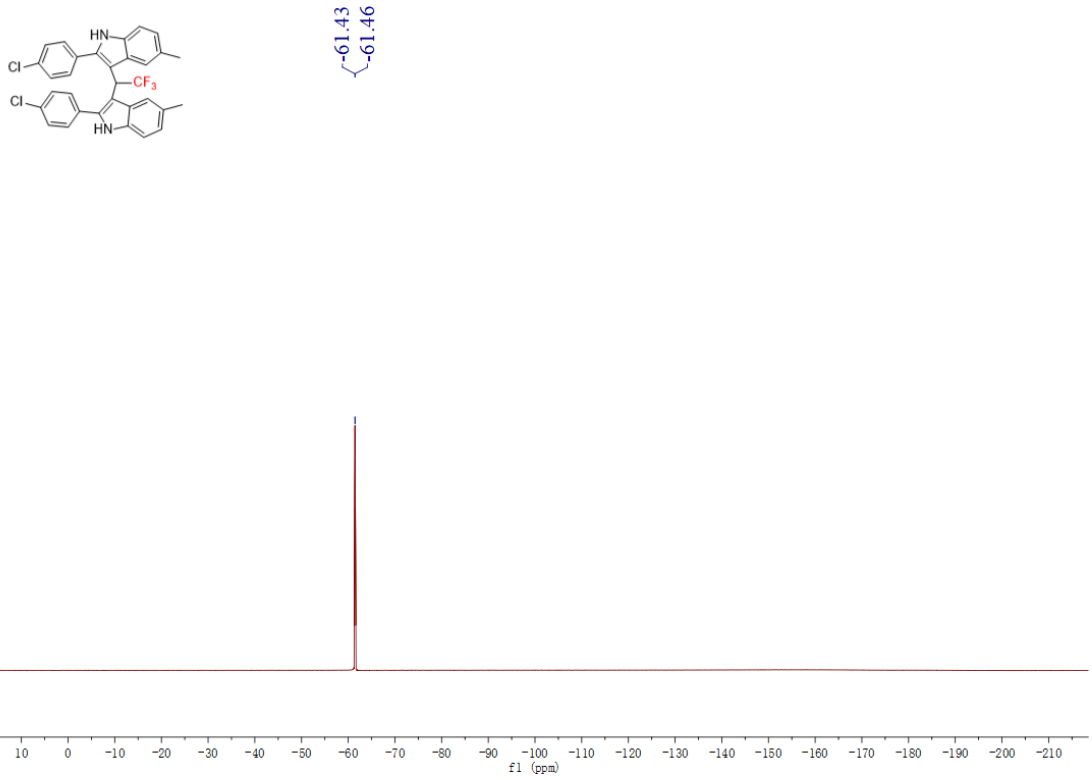
^{13}C NMR spectrum of **3p** in DMSO-d_6



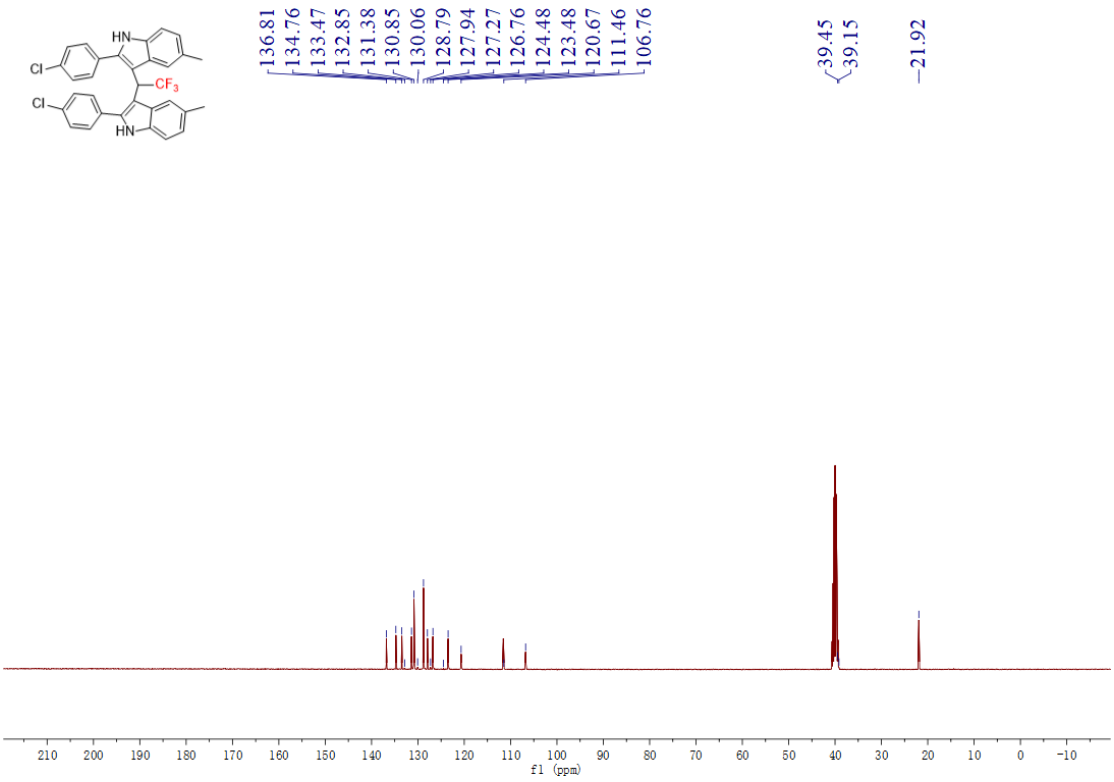
^{1}H NMR spectrum of **3q** in DMSO-d_6



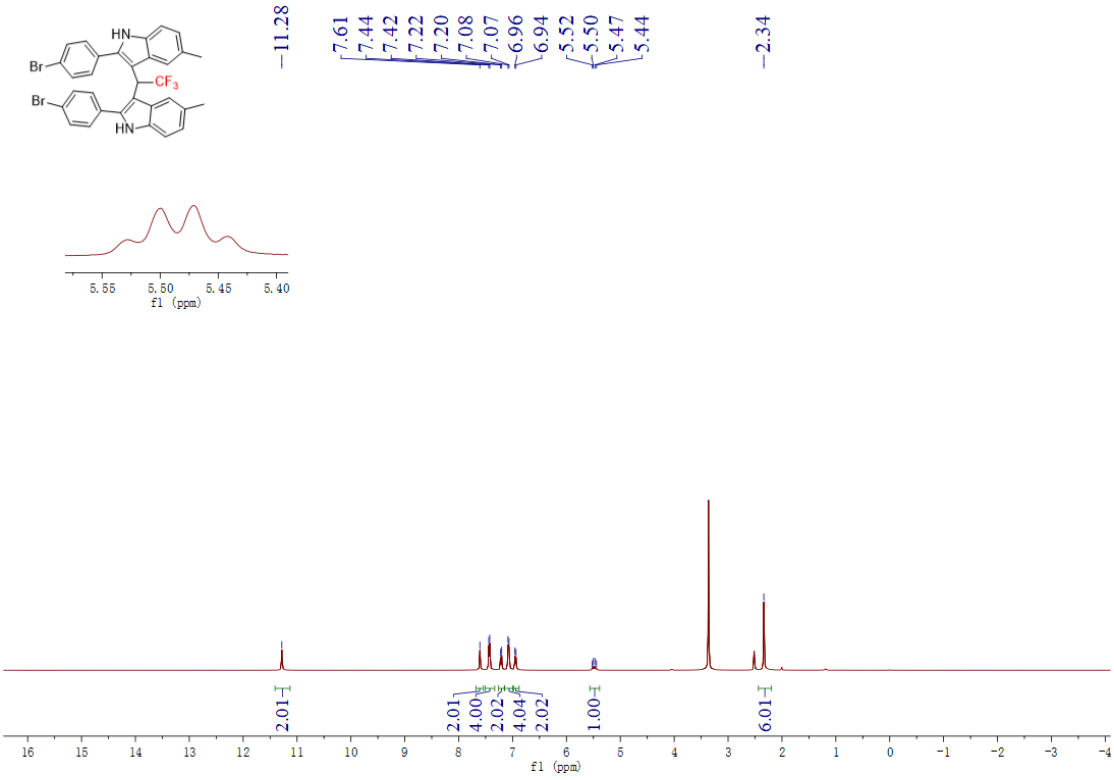
^{19}F NMR spectrum of **3q** in DMSO-d_6



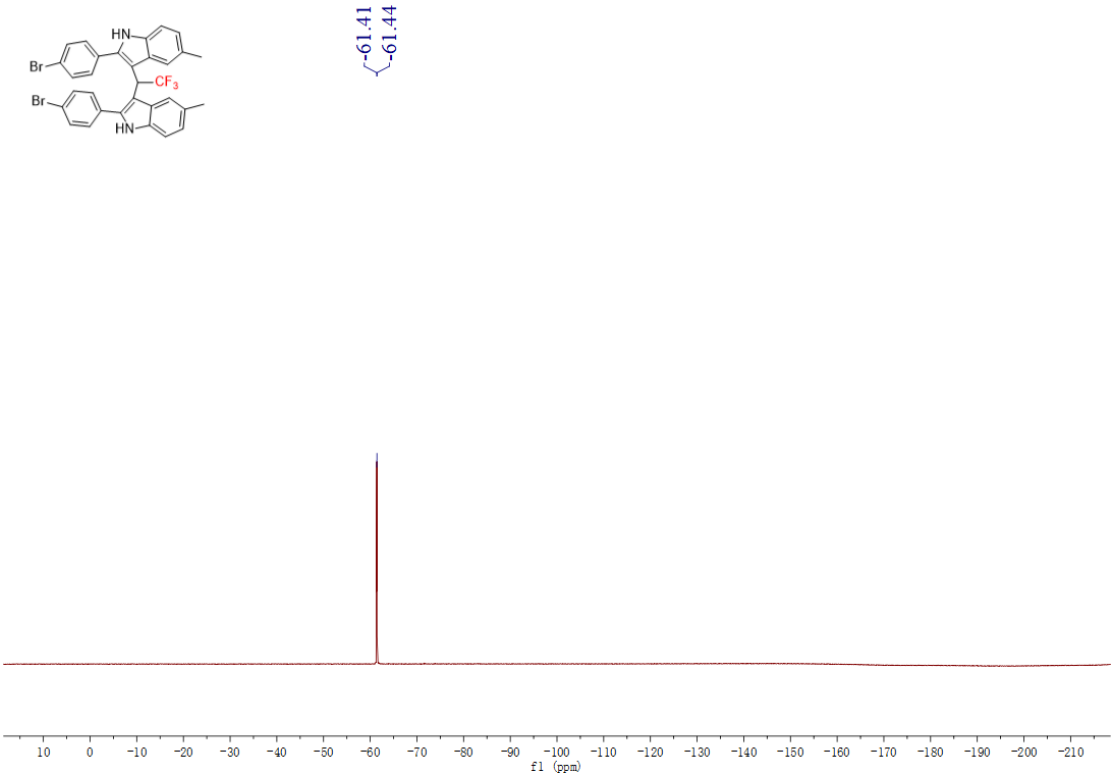
^{13}C NMR spectrum of **3q** in DMSO-d_6



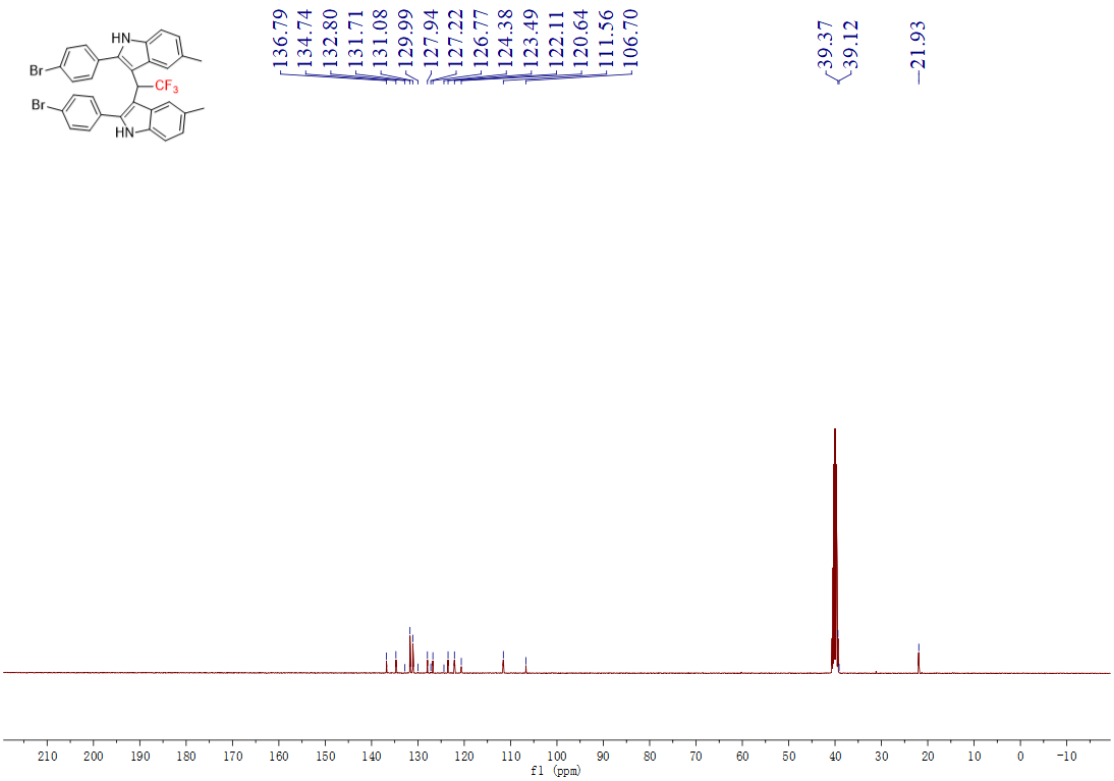
^{1}H NMR spectrum of **3r** in DMSO-d_6



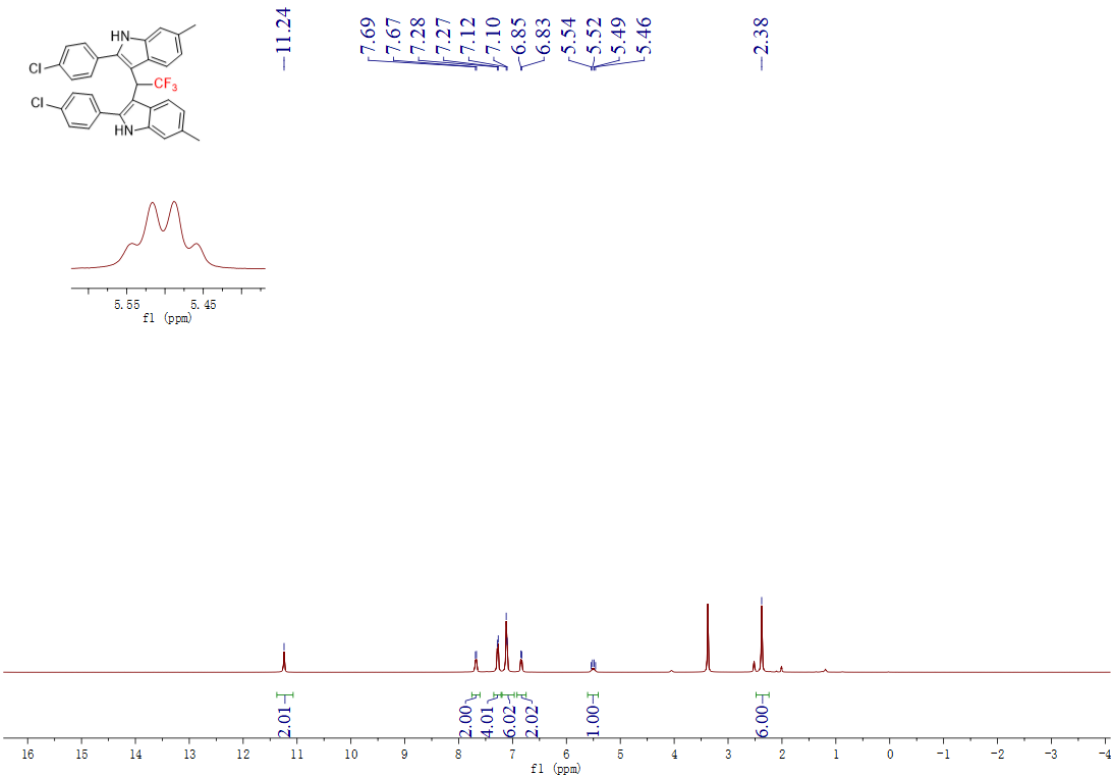
^{19}F NMR spectrum of **3r** in DMSO-d_6



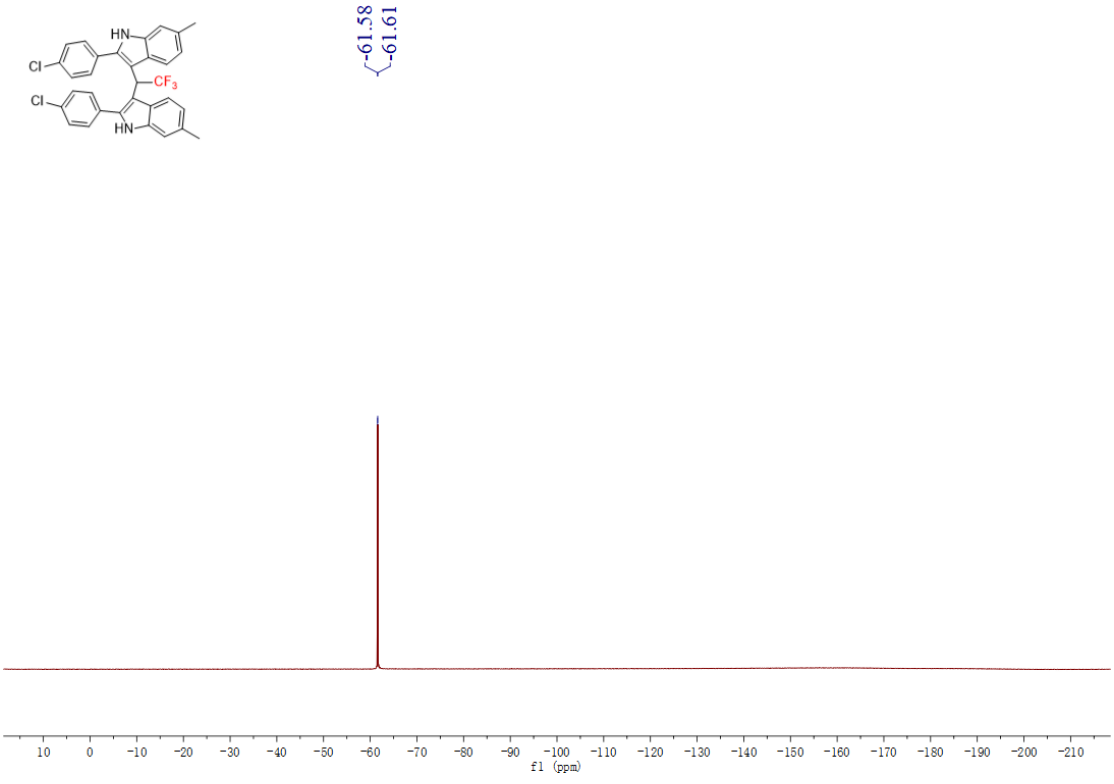
^{13}C NMR spectrum of **3r** in DMSO-d_6



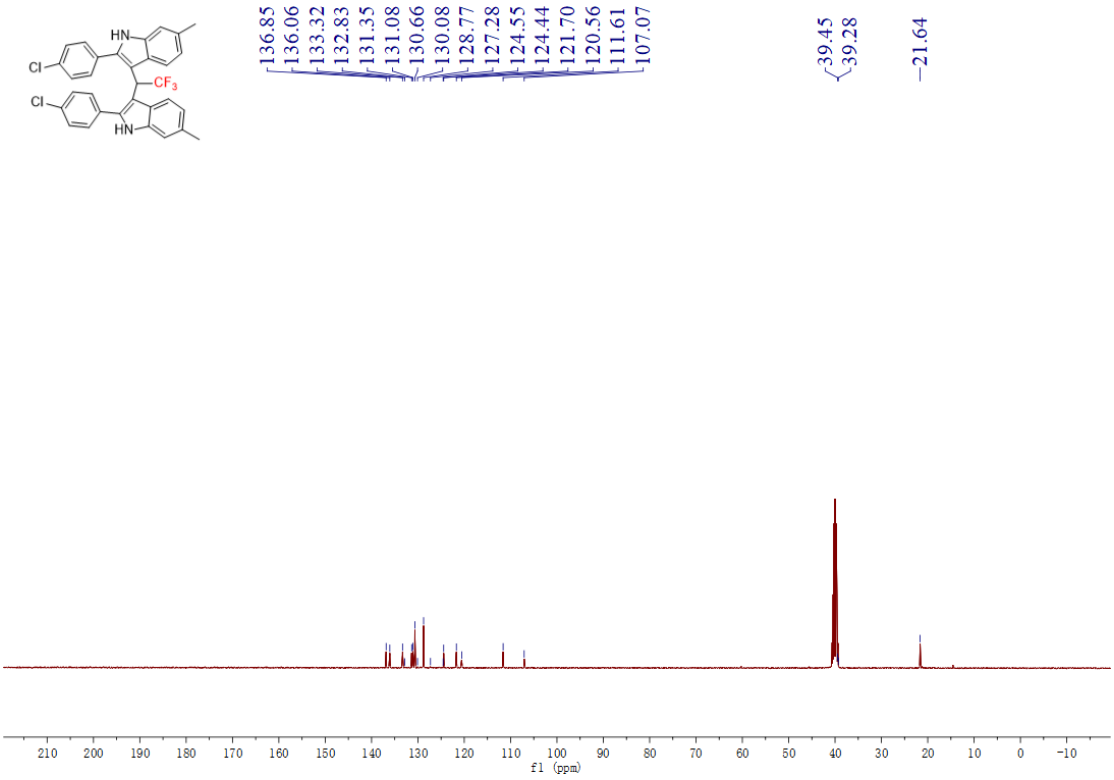
^{1}H NMR spectrum of **3s** in DMSO-d_6



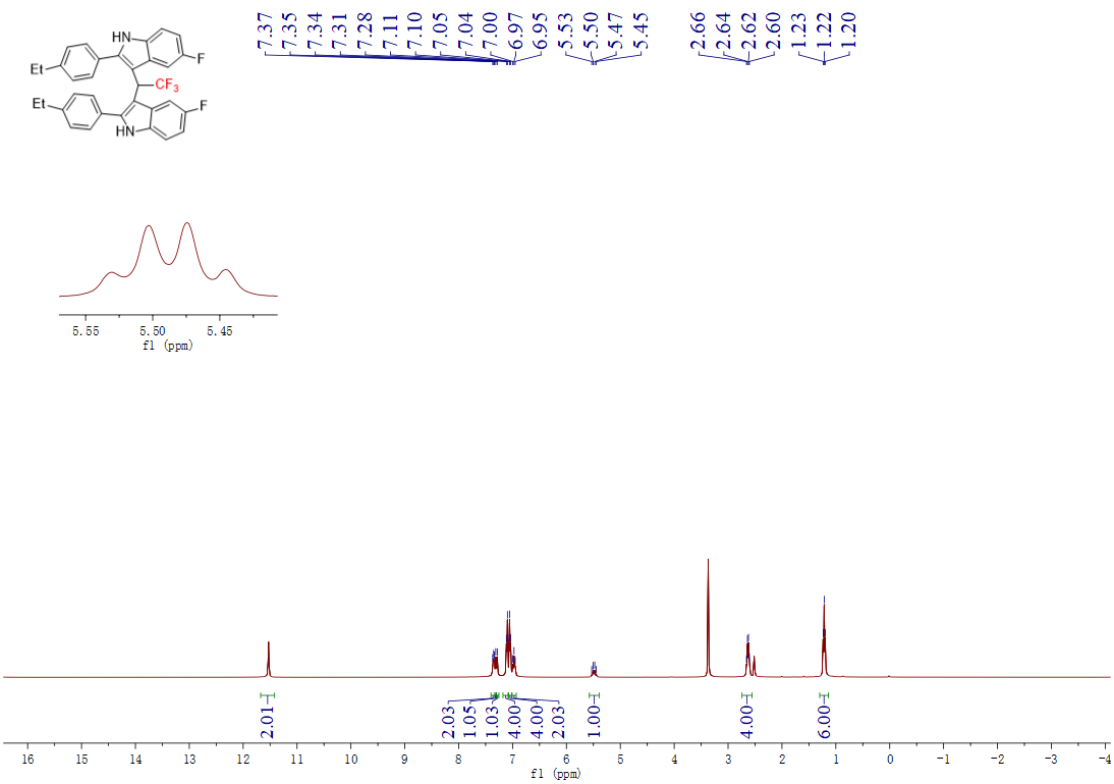
^{19}F NMR spectrum of **3s** in DMSO-d_6



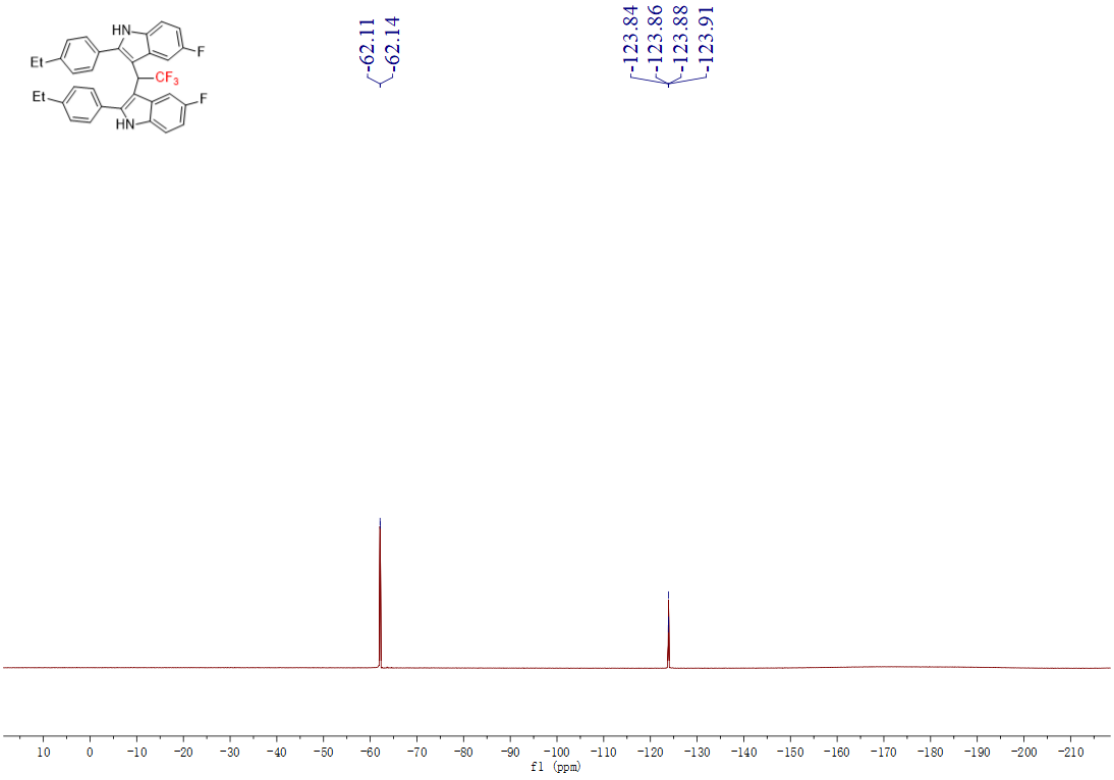
^{13}C NMR spectrum of **3s** in DMSO-d_6



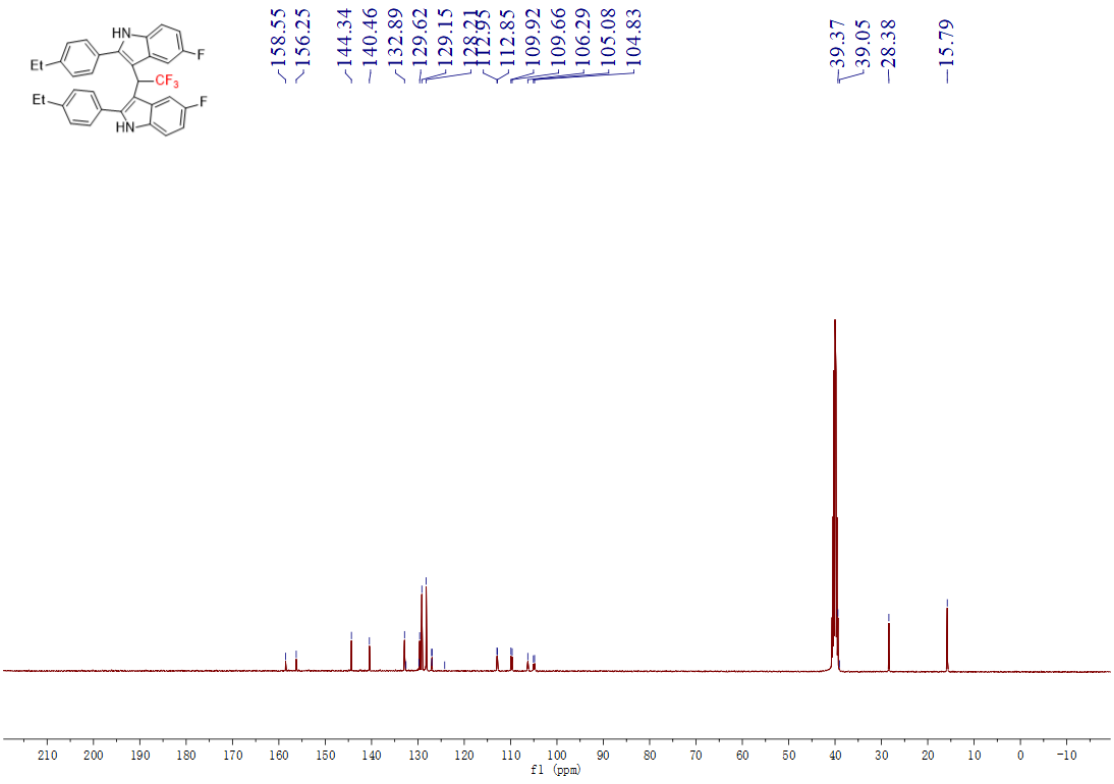
^{1}H NMR spectrum of **3t** in DMSO-d_6



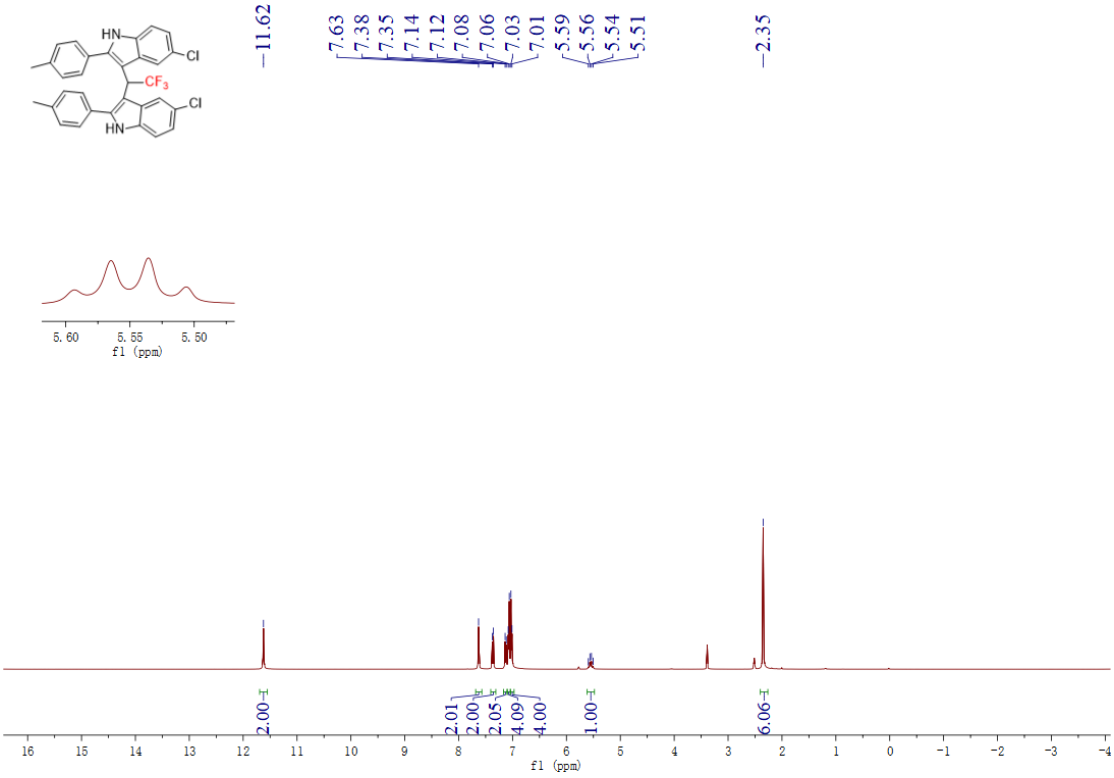
^{19}F NMR spectrum of **3t** in DMSO-d_6



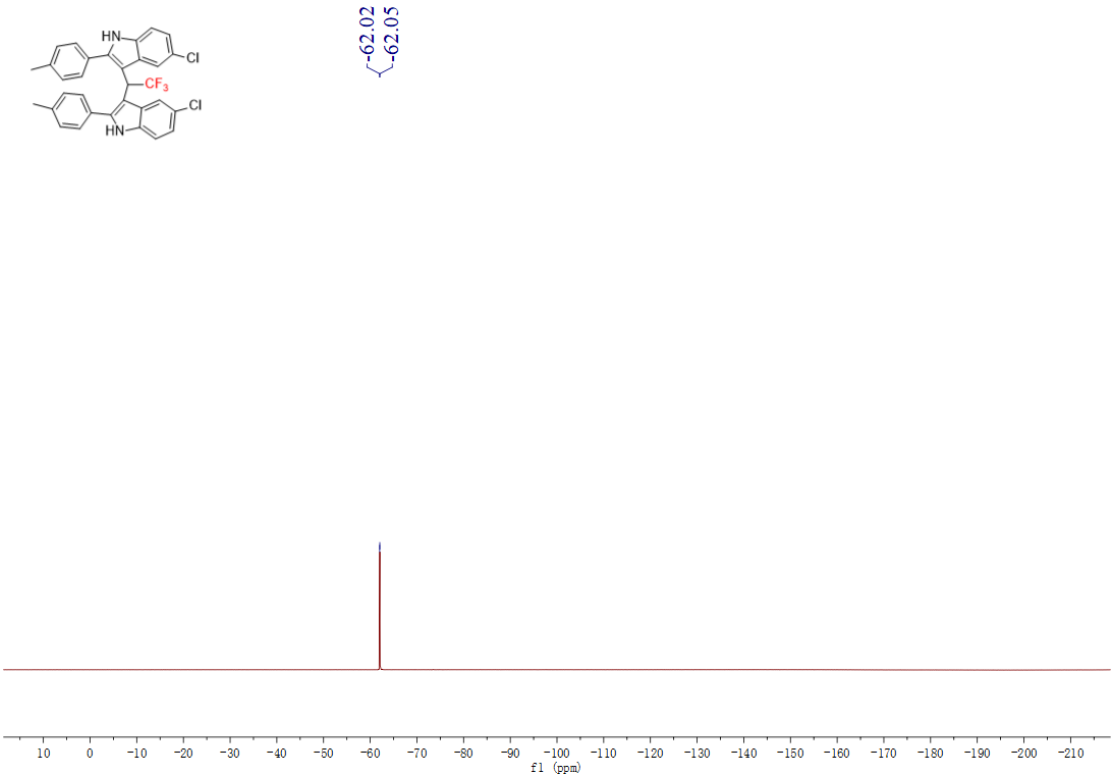
^{13}C NMR spectrum of **3t** in DMSO-d_6



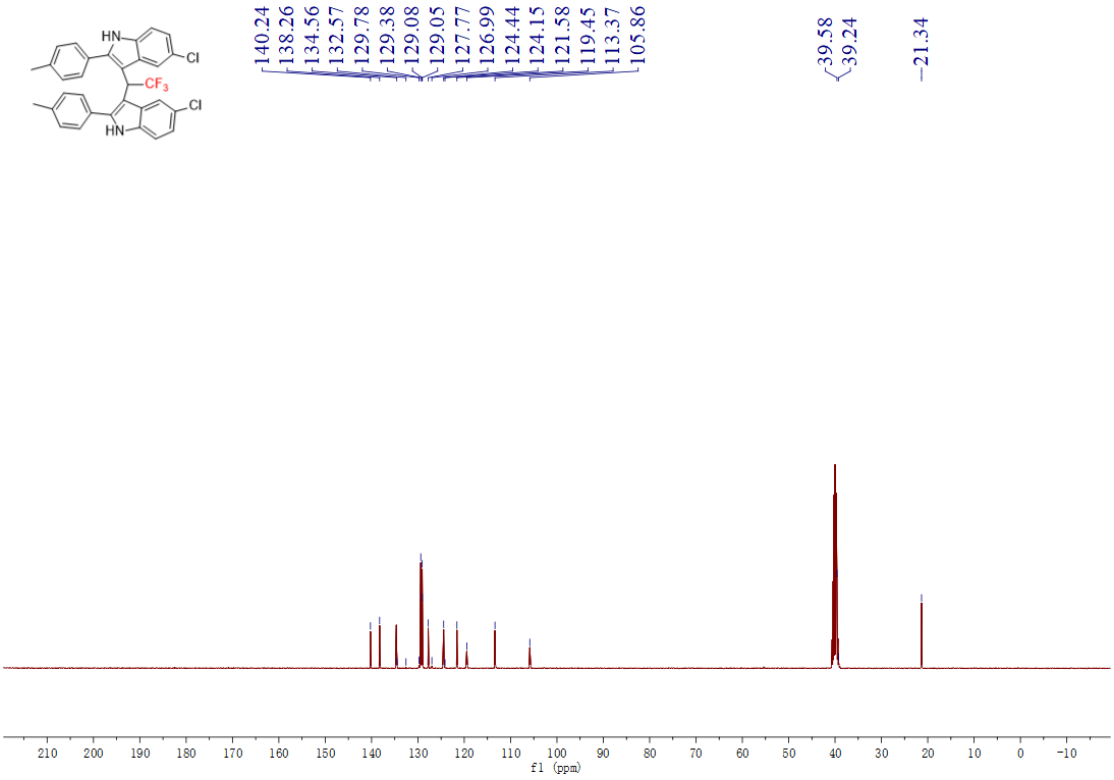
^{1}H NMR spectrum of **3u** in DMSO-d_6



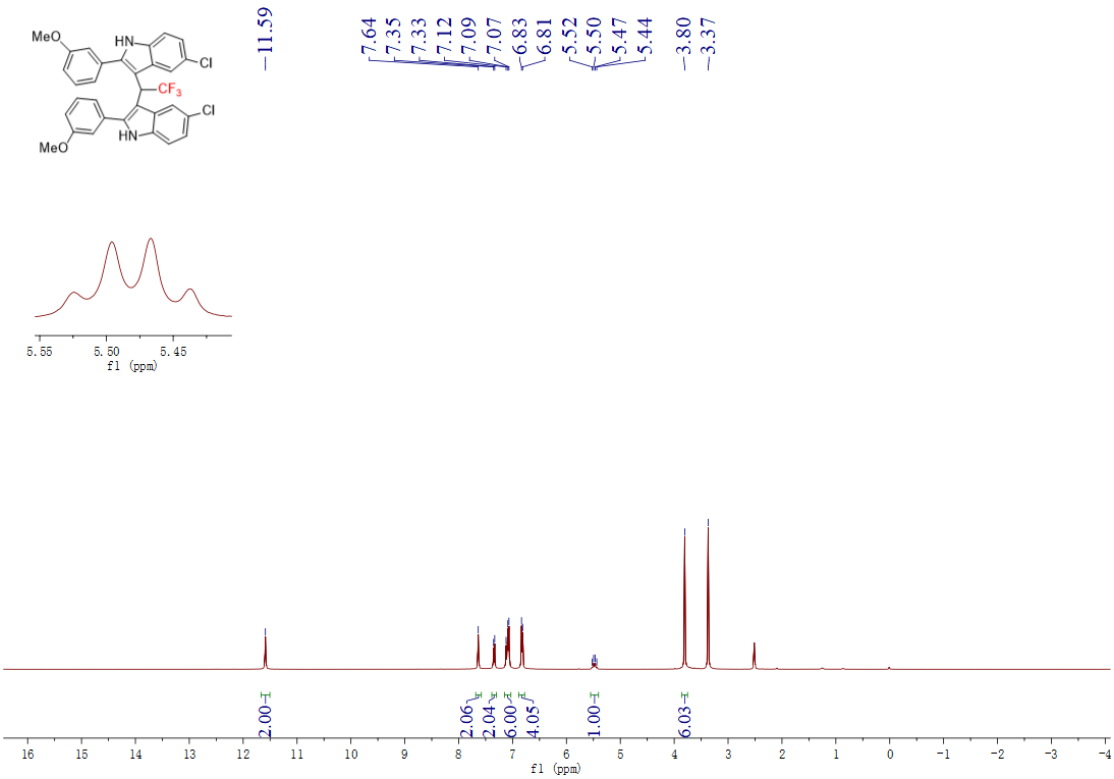
^{19}F NMR spectrum of **3u** in DMSO-d_6



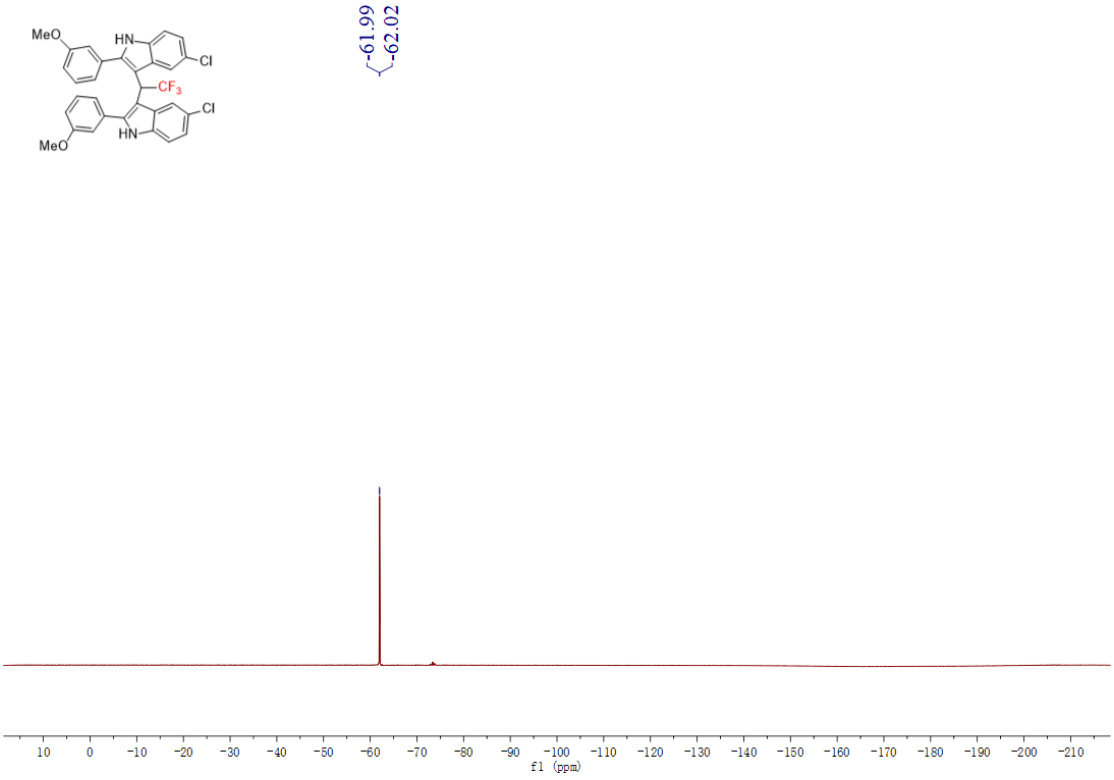
^{13}C NMR spectrum of **3u** in DMSO-d_6



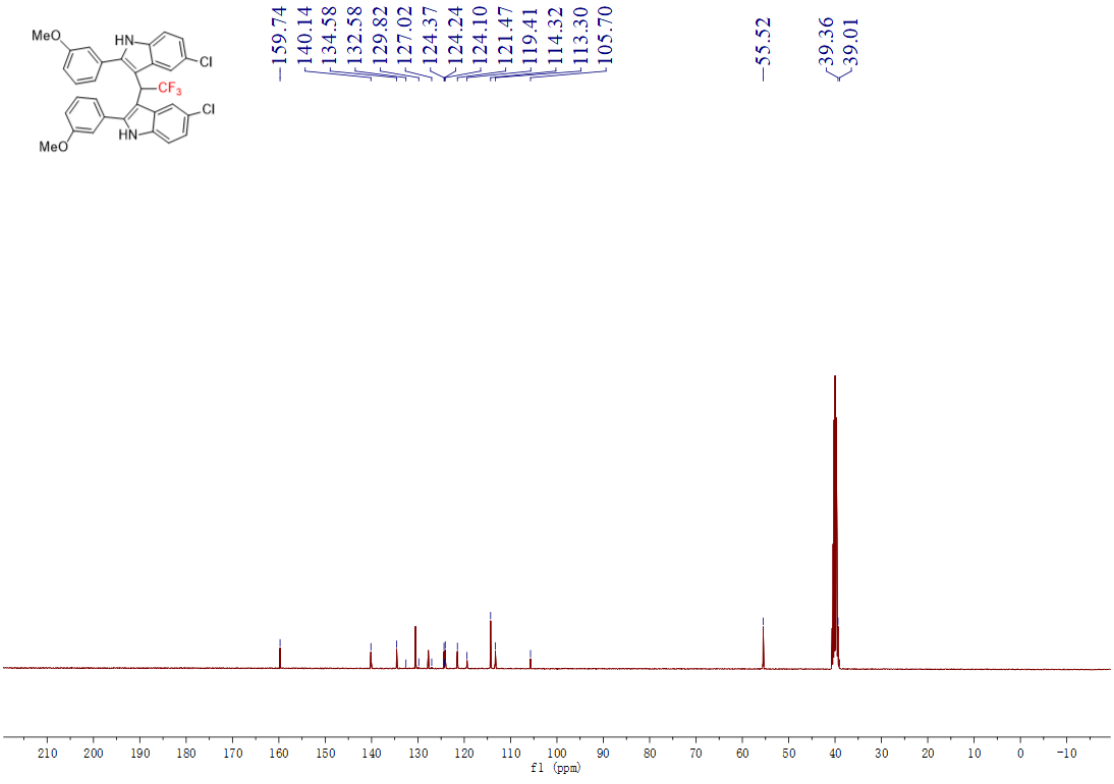
^{1}H NMR spectrum of **3v** in DMSO-d_6



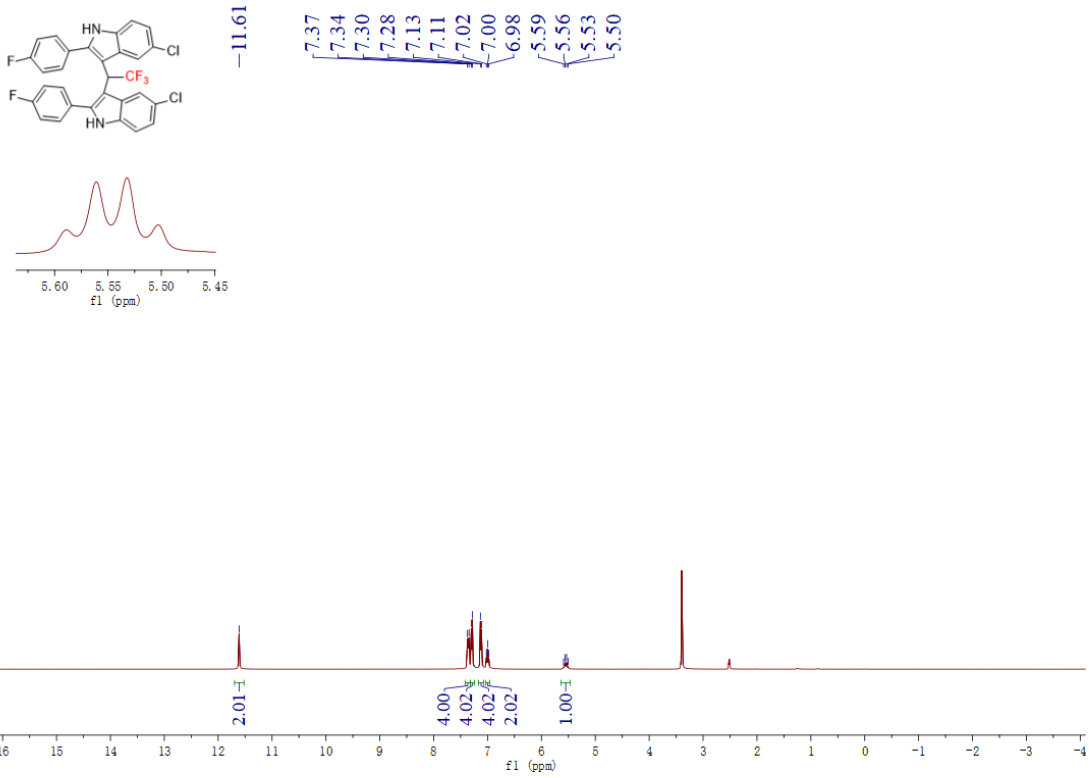
^{19}F NMR spectrum of **3v** in DMSO-d_6



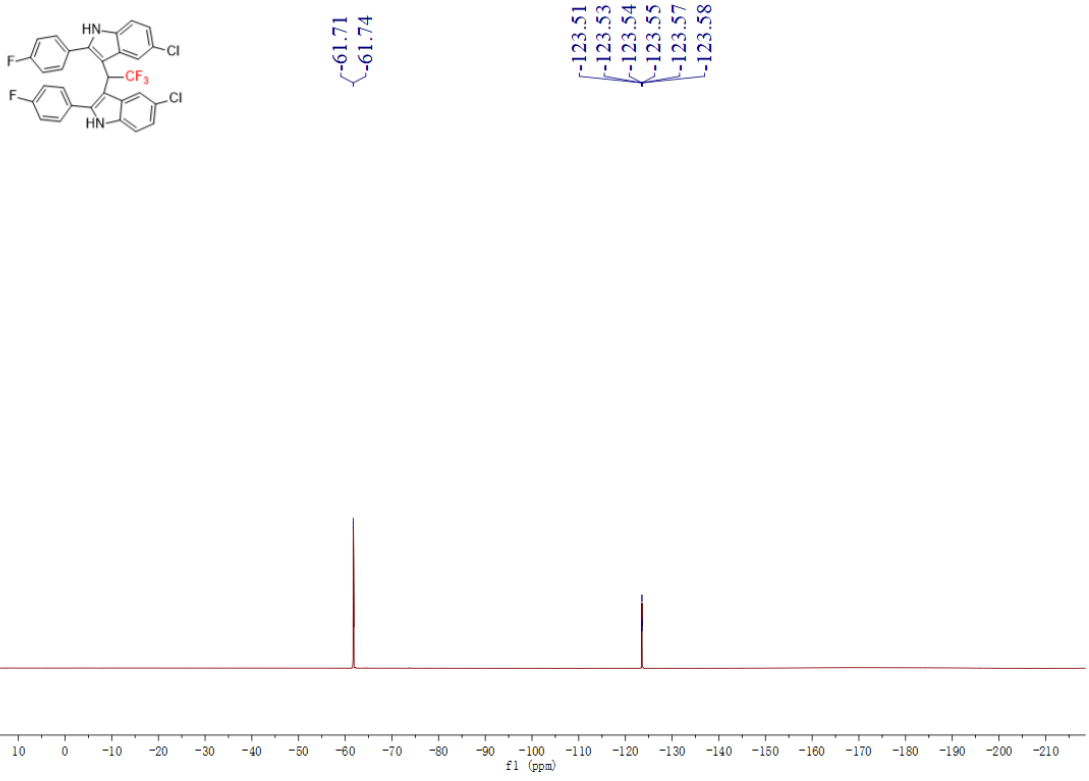
^{13}C NMR spectrum of **3v** in DMSO-d_6



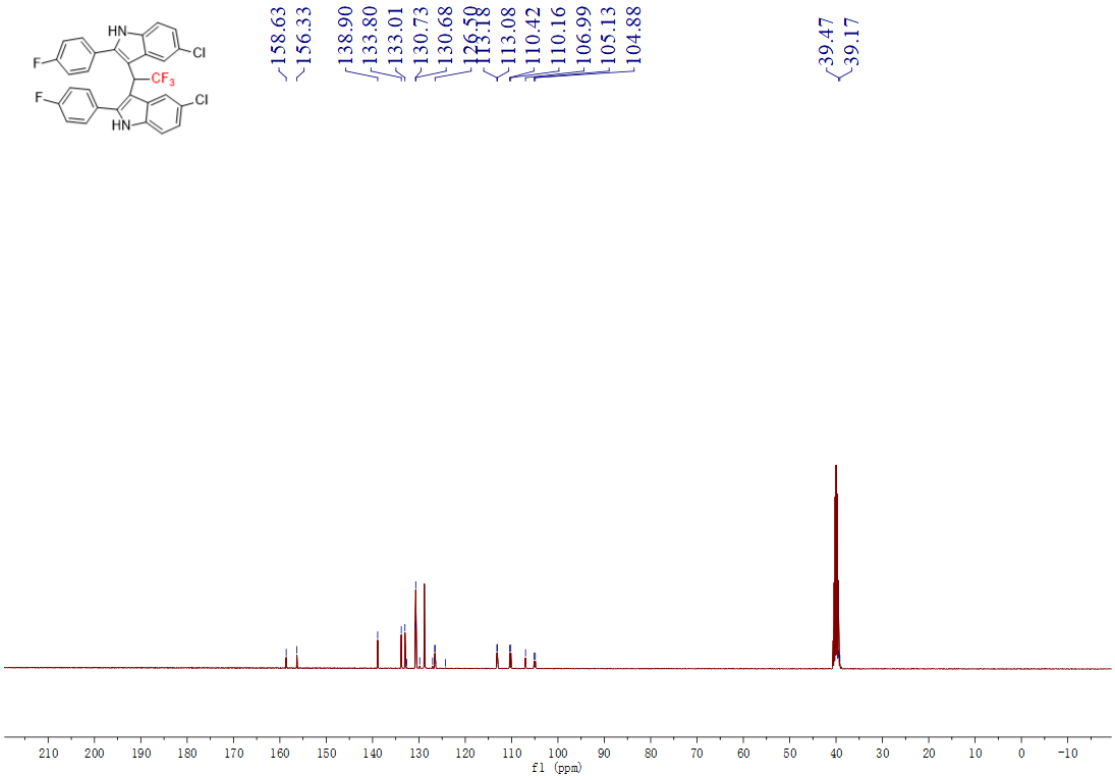
^{1}H NMR spectrum of **3w** in DMSO-d_6



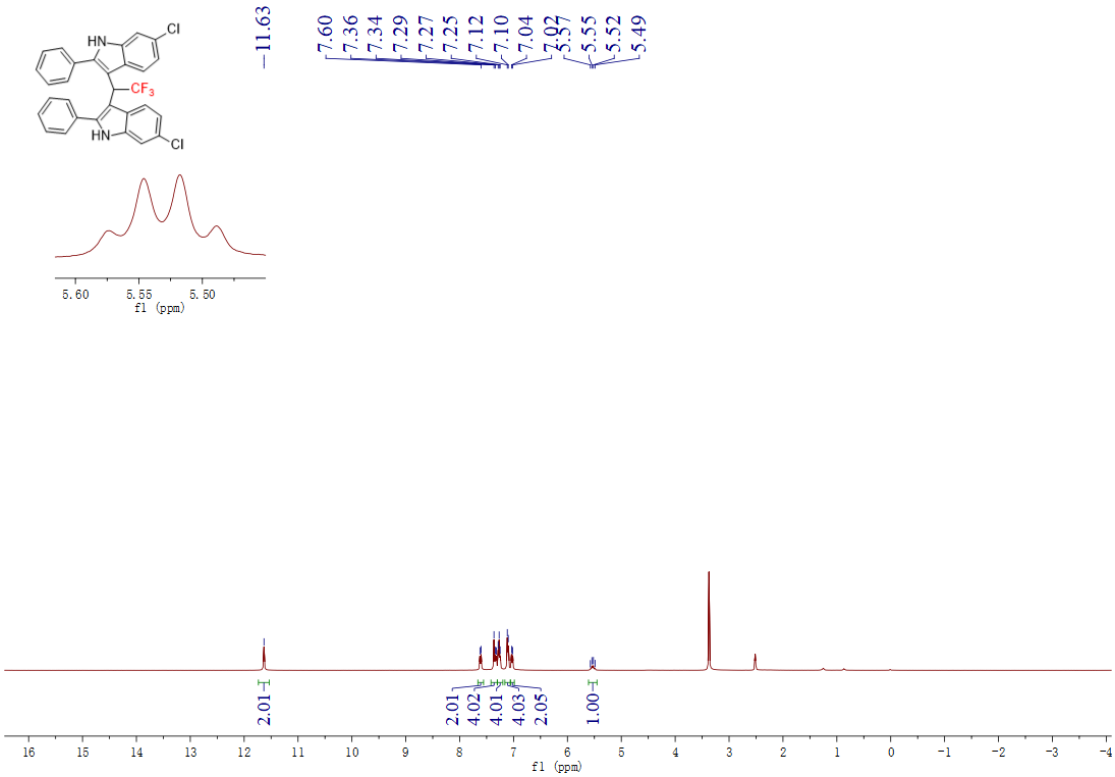
^{19}F NMR spectrum of **3w** in DMSO-d_6



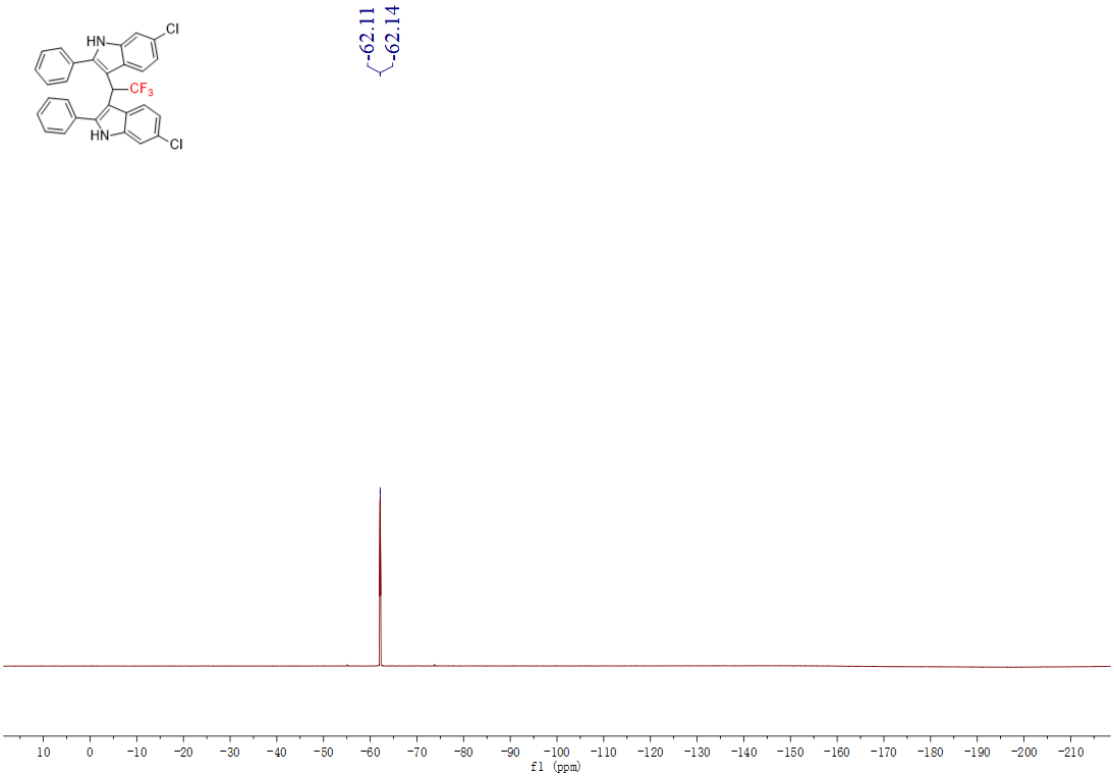
^{13}C NMR spectrum of **3w** in DMSO-d_6



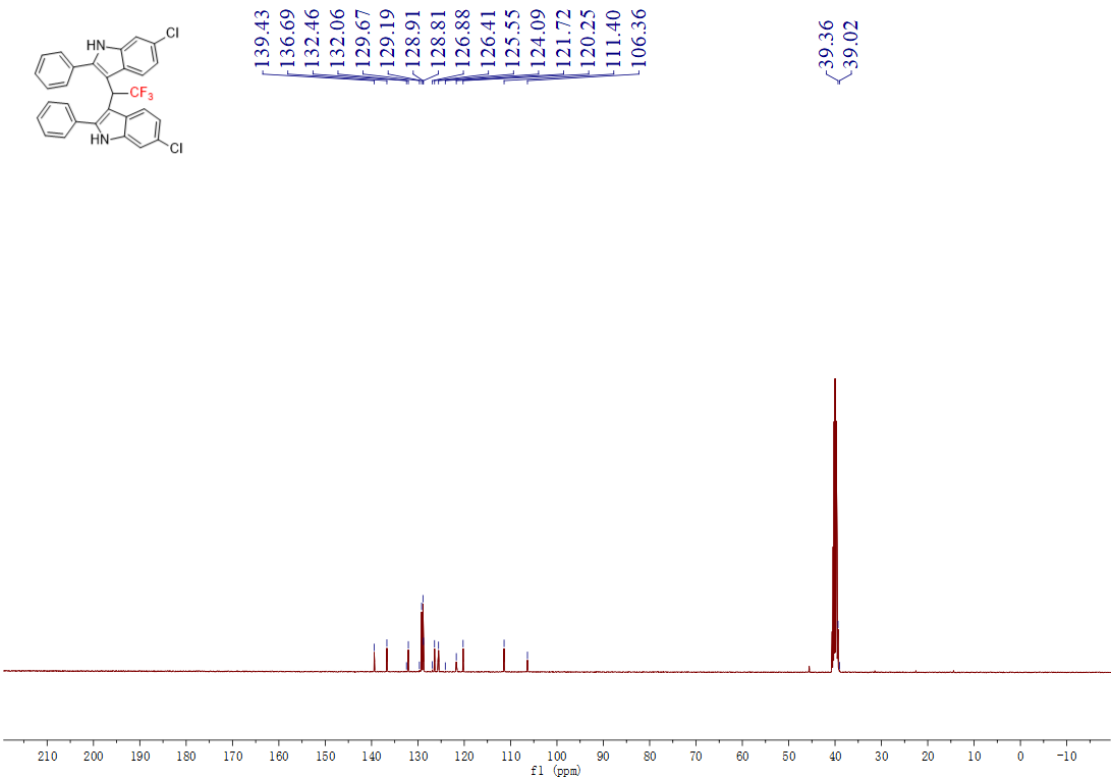
^{1}H NMR spectrum of **3x** in DMSO-d_6



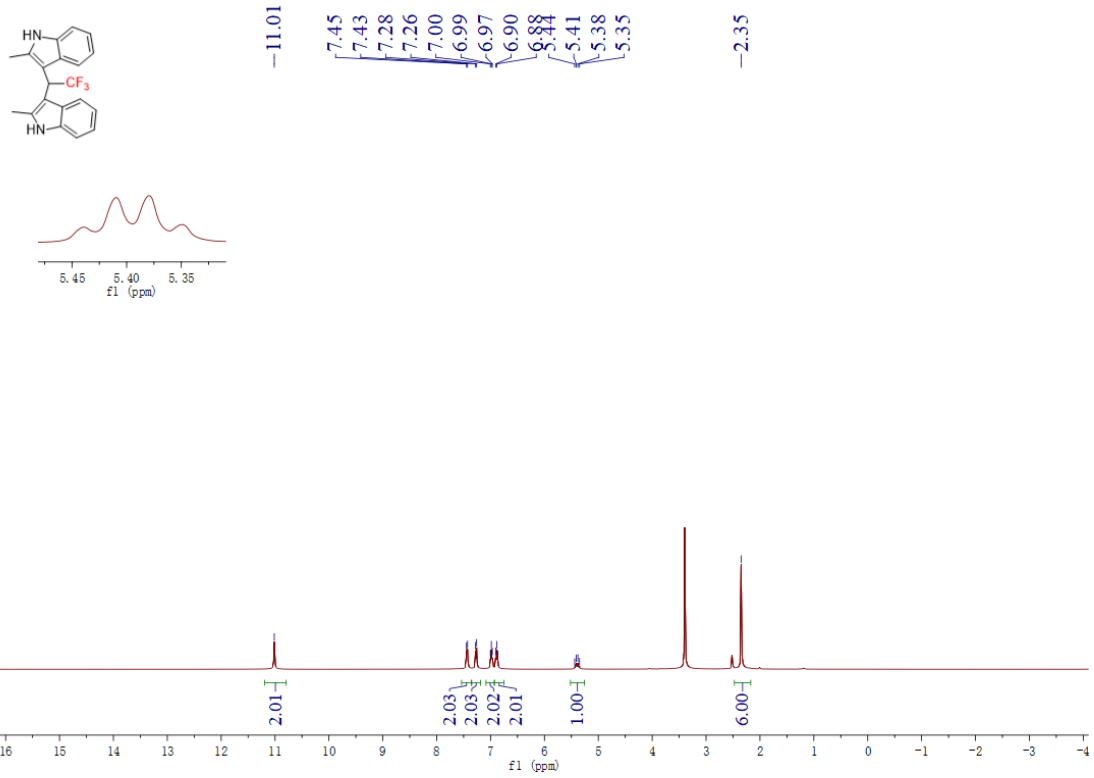
^{19}F NMR spectrum of **3x** in DMSO-d_6



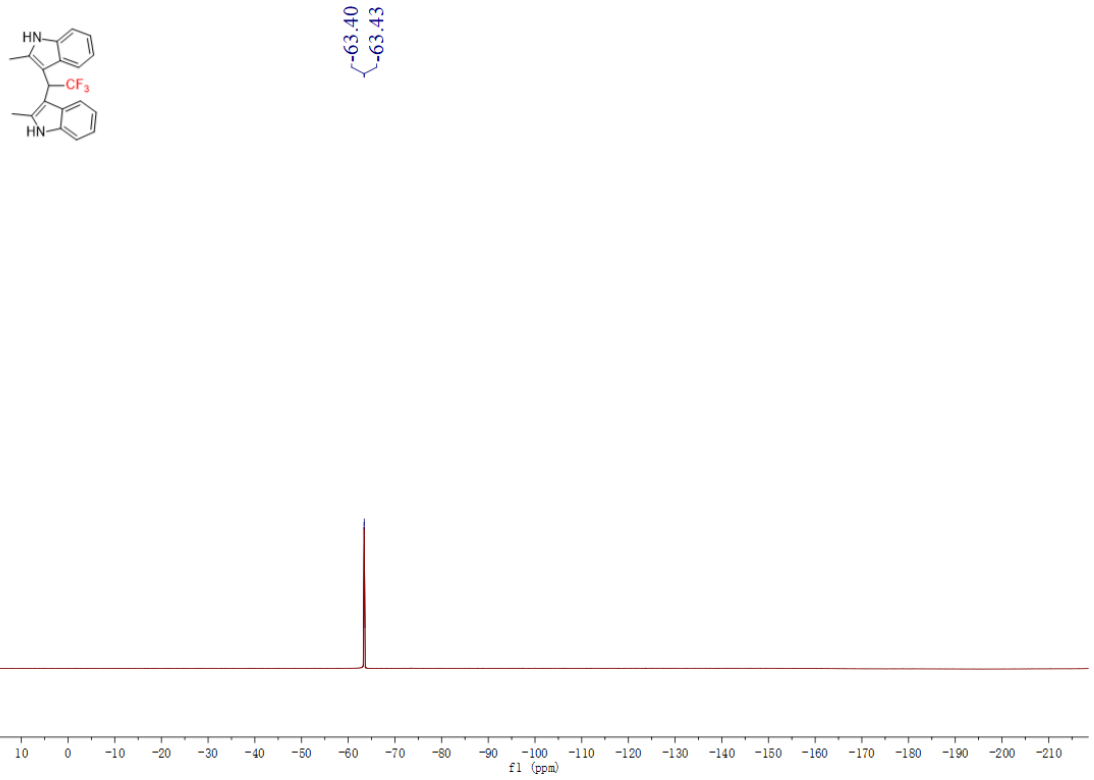
^{13}C NMR spectrum of **3x** in DMSO-d_6



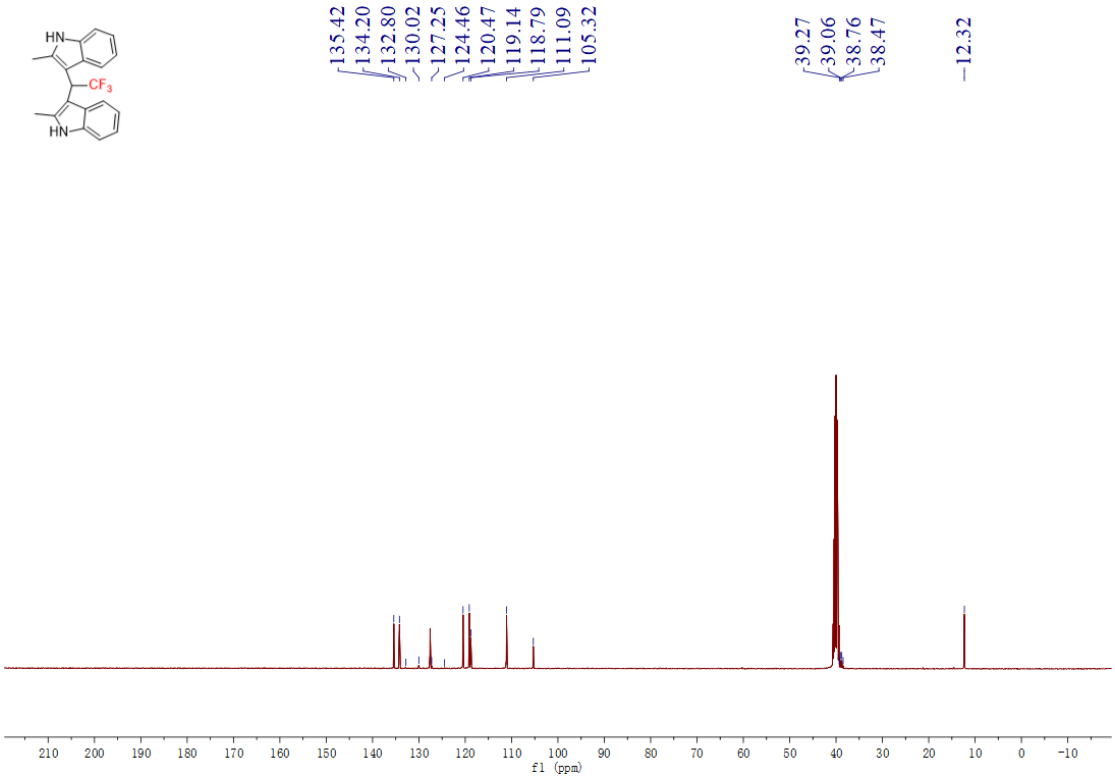
^{1}H NMR spectrum of **3y** in DMSO-d_6



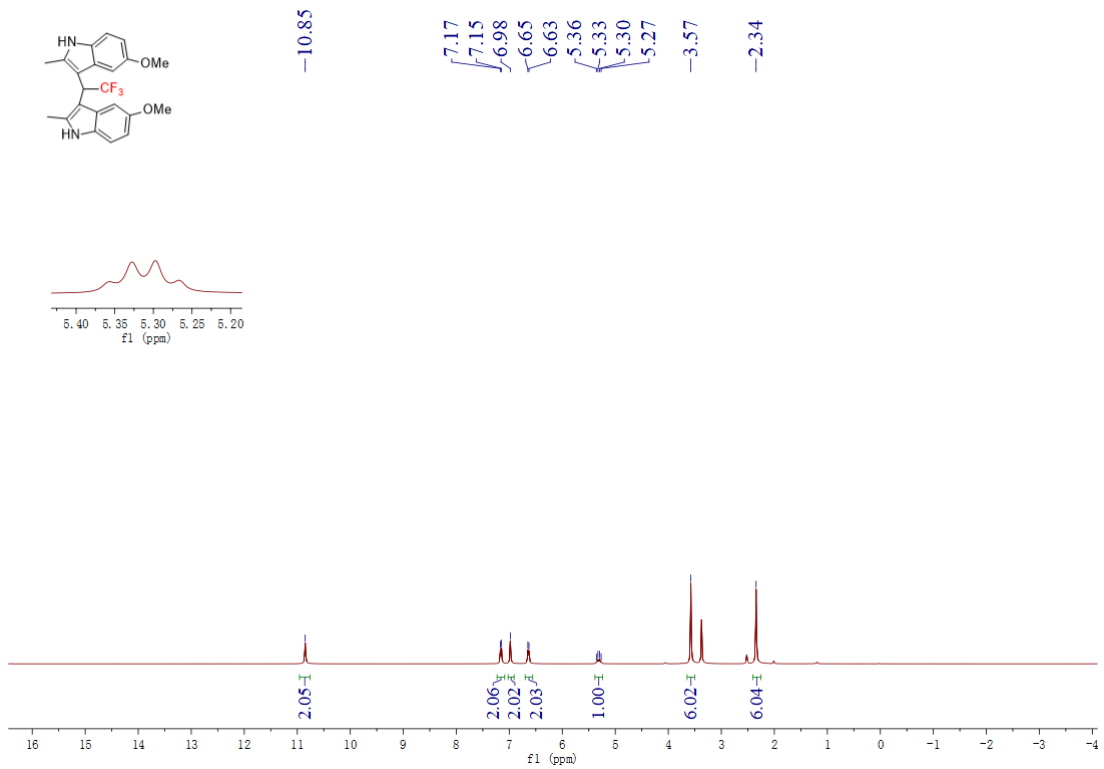
^{19}F NMR spectrum of **3y** in DMSO-d_6



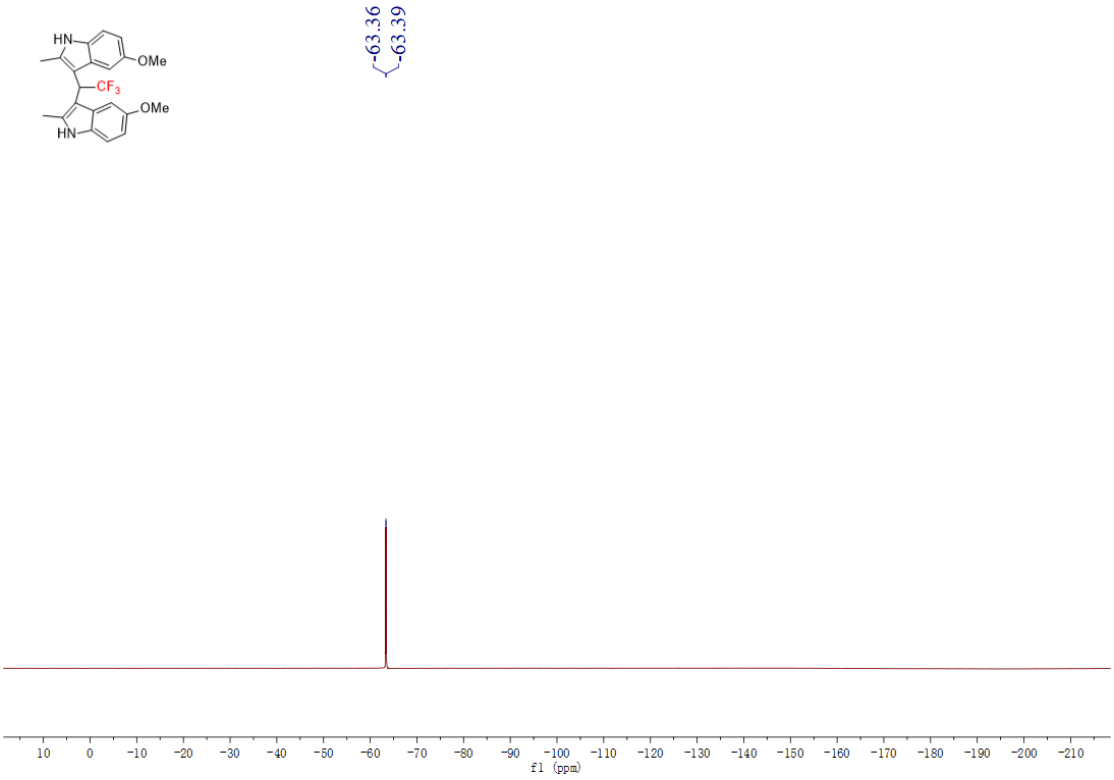
^{13}C NMR spectrum of **3y** in DMSO-d_6



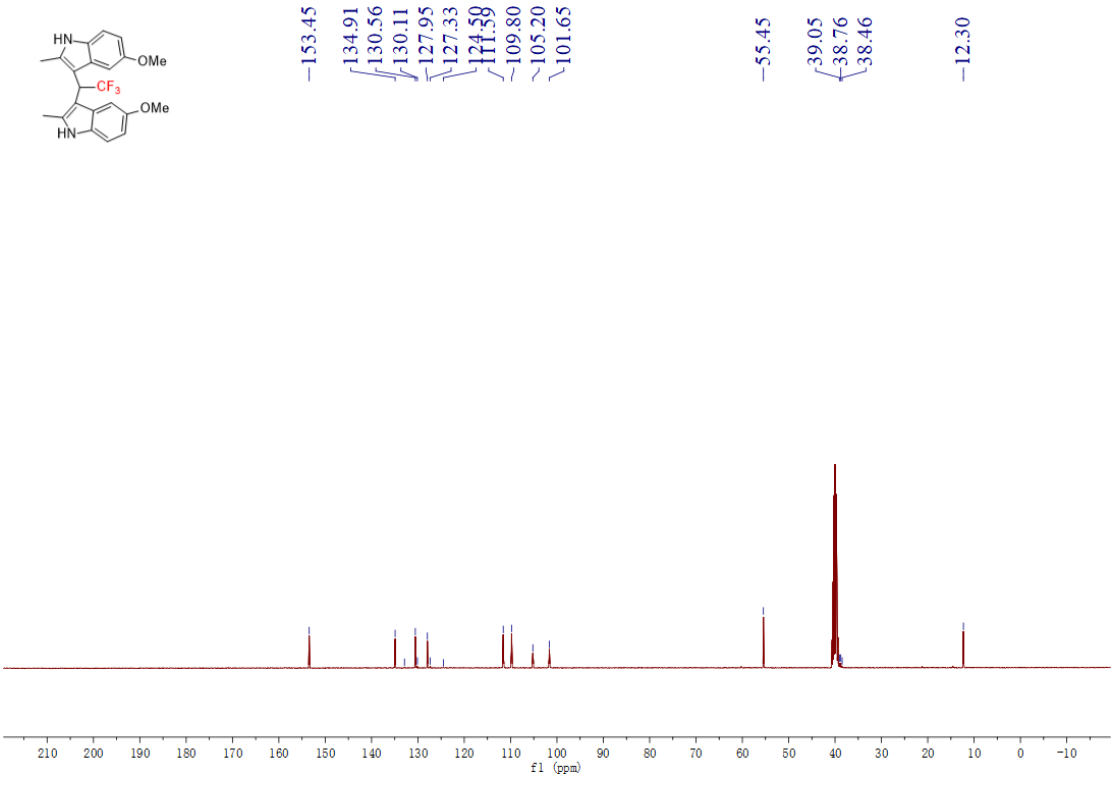
^{1}H NMR spectrum of **3z** in DMSO-d_6



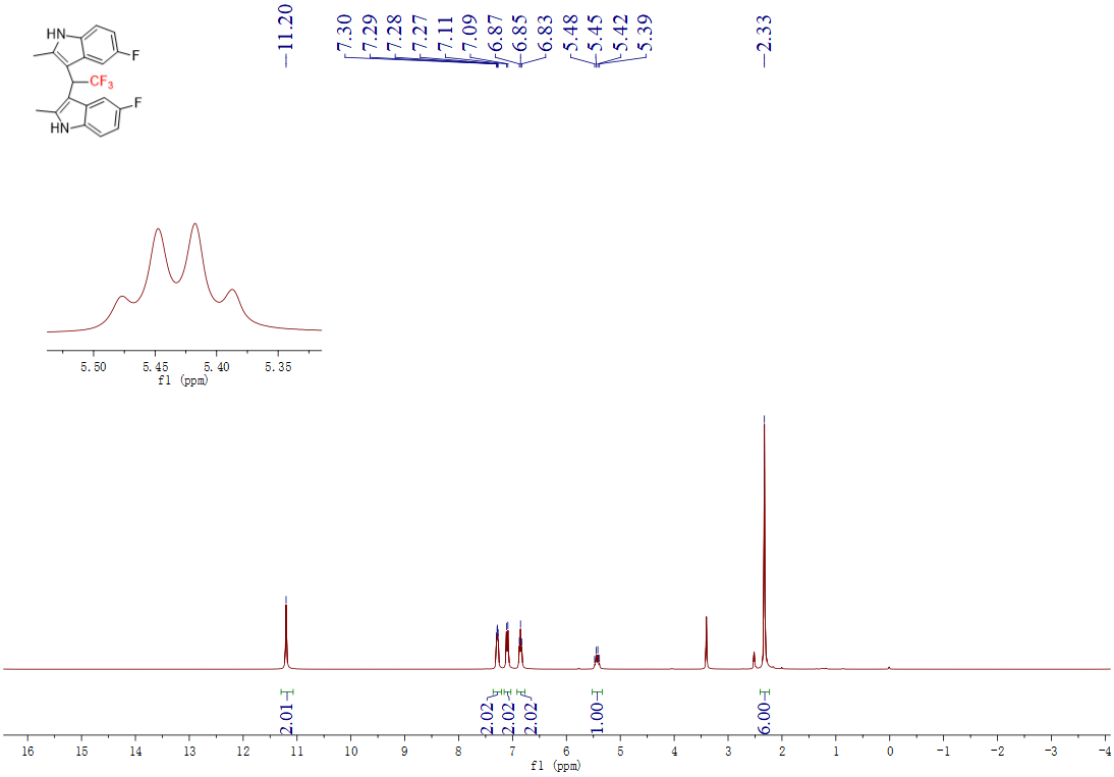
^{19}F NMR spectrum of **3z** in DMSO-d_6



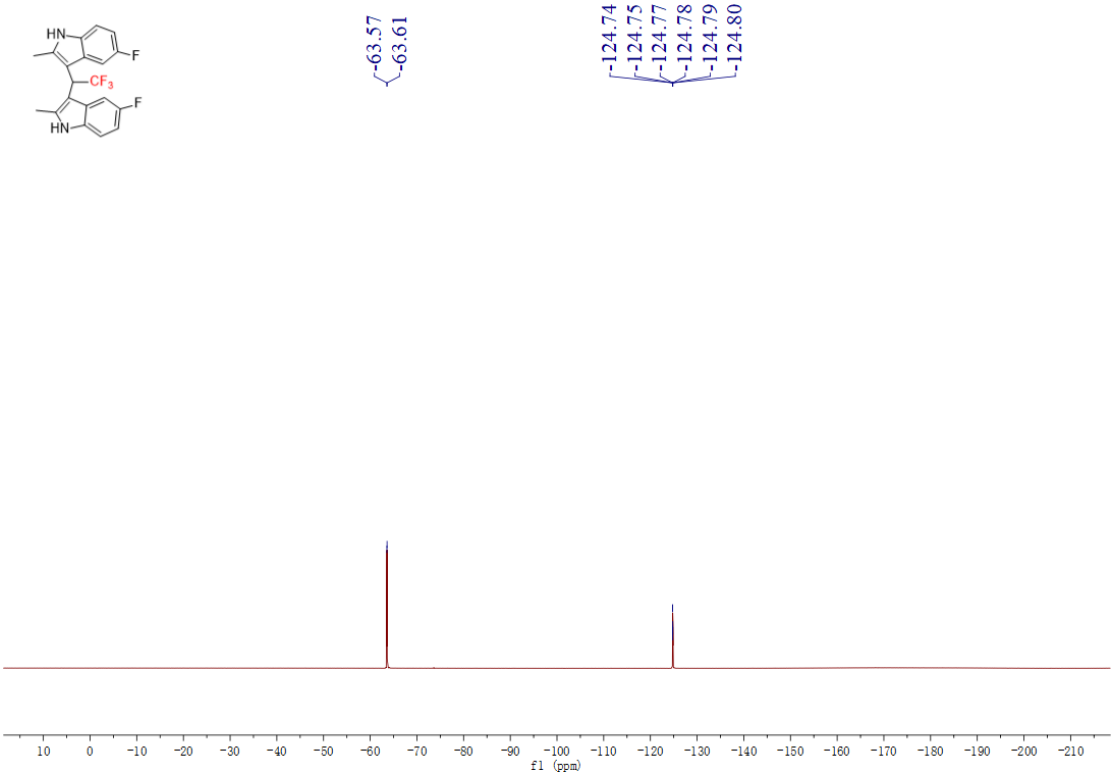
^{13}C NMR spectrum of **3z** in DMSO-d_6



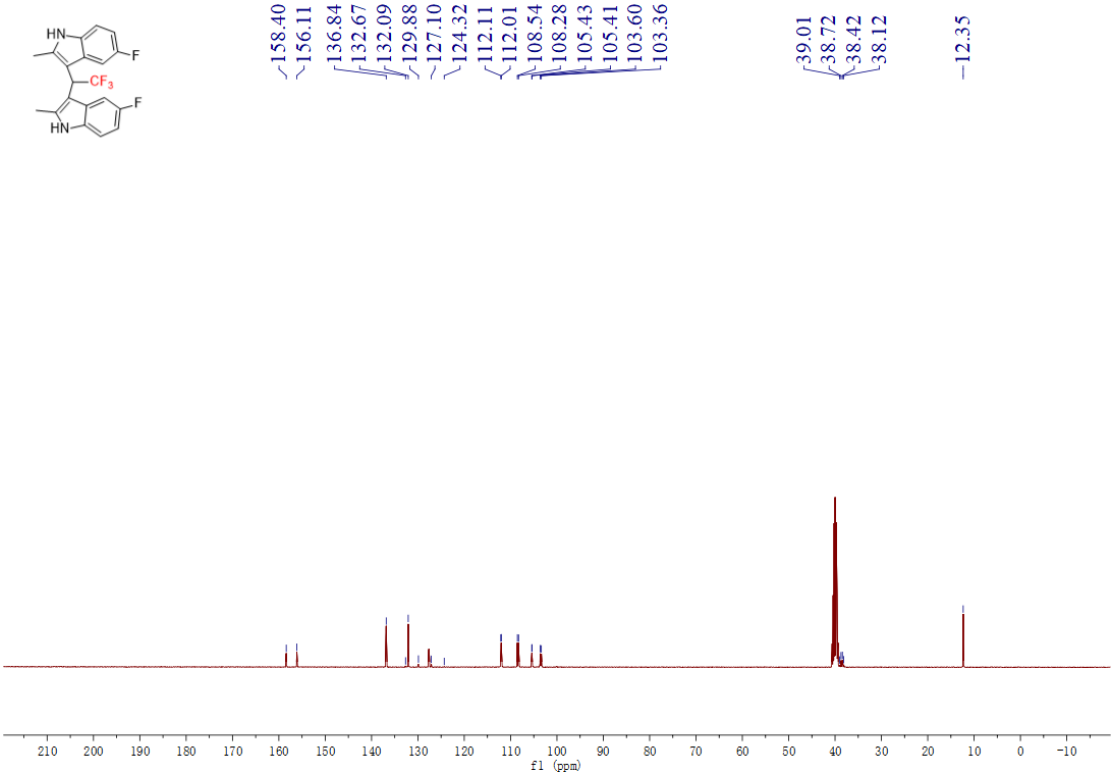
^{1}H NMR spectrum of **3aa** in DMSO-d_6



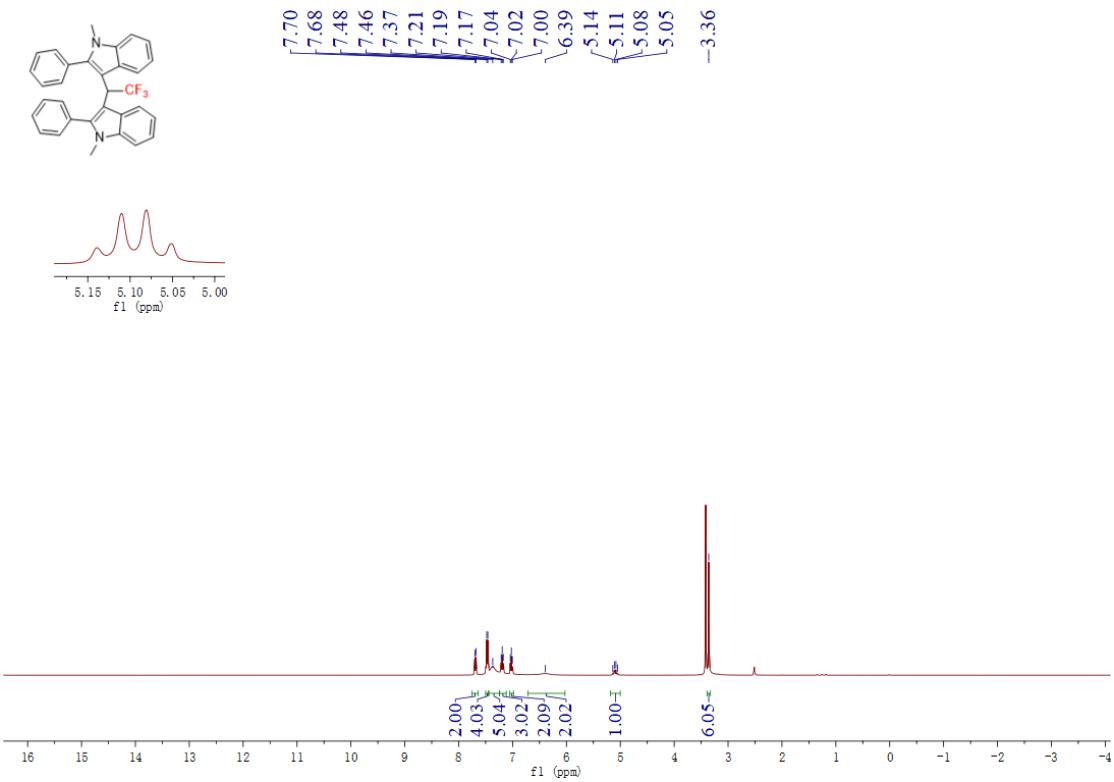
^{19}F NMR spectrum of **3aa** in DMSO-d_6



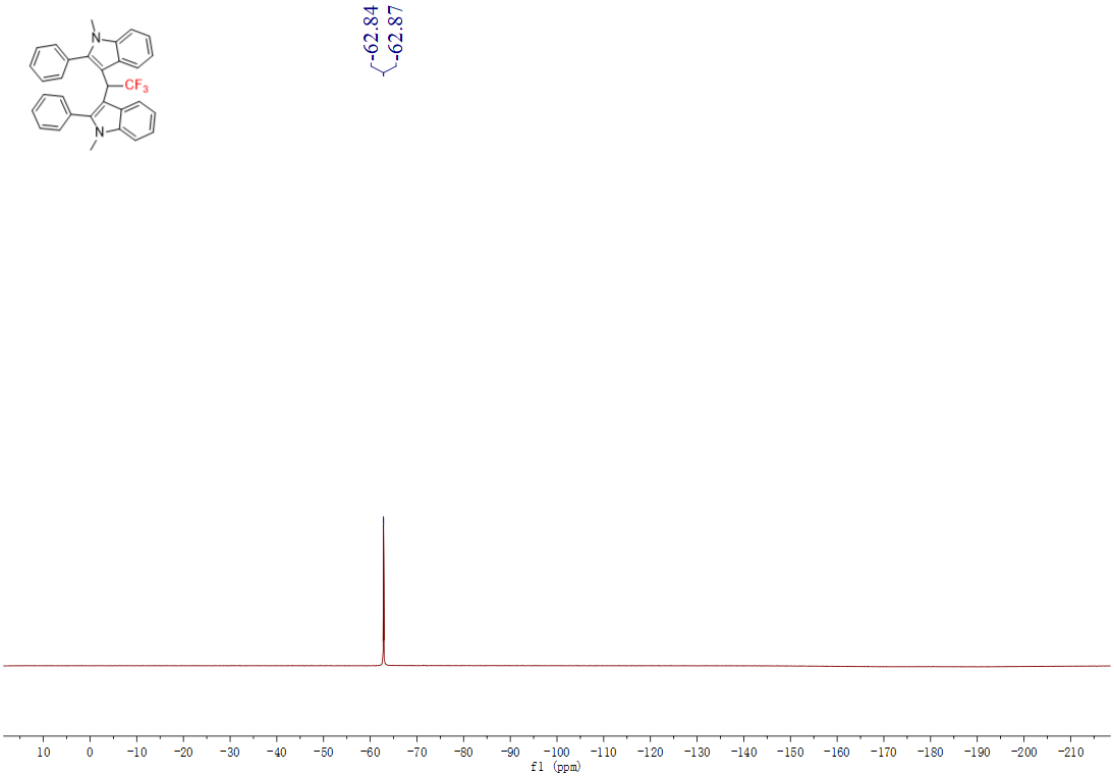
^{13}C NMR spectrum of **3aa** in DMSO-d_6



^{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