

Supporting Information *for*

Copper-catalyzed chemoselective synthesis of 4-trifluoromethyl pyrazoles

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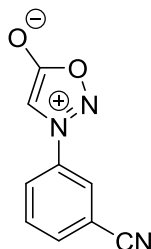
General information

^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^1H 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: ^1H 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. HRMS were obtained on Waters GCT-TOF. Reagents were received from commercial sources. Solvents were freshly dried and degassed according to the published procedures prior to use. Column chromatography purifications were performed by flash chromatography using silica gel 60.

Synthesis of sydnone substrates

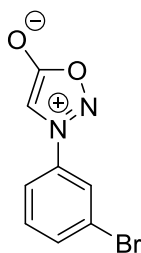
Sydnone substrates were prepared according to the published procedures.¹

Data for the new synthesized sydnone substrates.



3-(3-Cyanophenyl)-1,2,3-oxadiazol-3-ium-5-olate (2l)

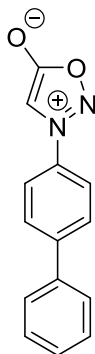
Following the published procedure and workup, **2l** was isolated as a white solid in 73% yield (682 mg). mp: 149-151 °C. R_f (dichloromethane) = 0.71. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.51 (s, 1H), 8.28 (d, $J = 7.7$ Hz, 1H), 8.20 (d, $J = 7.2$ Hz, 1H), 7.91 (t, $J = 7.7$ Hz, 1H), 7.85 (s, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 168.8 (s), 136.4 (s), 135.4 (s), 131.9 (s), 126.7 (s), 126.0 (s), 117.6 (s), 113.5 (s), 95.8 (s). IR (ATR): ν 3137, 3097, 2231, 1728, 1583, 1464, 1346, 1249, 1169, 1092, 1027, 952, 870, 795, 685, 600, 556, 530, 469 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_9\text{H}_6\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 188.0455; found: 188.0453.



3-(3-Bromophenyl)-1,2,3-oxadiazol-3-ium-5-olate (2t)

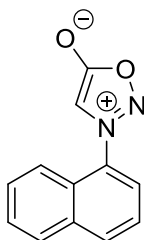
Following the published procedure and workup, **2t** was isolated as a white solid in 70% yield (840 mg). mp: 149-151 °C. R_f (dichloromethane) = 0.89. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 8.19 (s, 1H), 7.93 (dd, $J = 15.2, 8.0$ Hz, 2H), 7.82 (s, 1H), 7.64 (t, $J = 7.8$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 168.8 (s), 135.9 (s), 135.6 (s), 132.4 (s), 124.9 (s), 123.0 (s), 121.1 (s), 95.7 (s). IR (ATR): ν 3136, 3093, 3048, 1726, 1586, 1462, 1424, 1344, 1220, 1167, 1092, 999, 952, 868, 795, 724, 689, 625, 554,

527, 432 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_8\text{H}_6\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 240.9607; found: 240.9604



3-([1,1'-Biphenyl]-4-yl)-1,2,3-oxadiazol-3-ium-5-olate (2w)

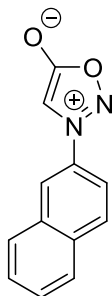
Following the published procedure and workup, **2w** was isolated as a white solid in 65% yield (773 mg). mp: 162-163 °C. R_f (dichloromethane) = 0.67. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.98 (dd, $J = 22.3, 7.9$ Hz, 4H), 7.83 (s, 1H), 7.75 (d, $J = 7.1$ Hz, 2H), 7.51 (t, $J = 6.8$ Hz, 2H), 7.46 (d, $J = 6.6$ Hz, 1H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 169.0 (s), 144.4 (s), 138.6 (s), 134.0 (s), 129.6 (s), 129.0 (s), 128.6 (s), 127.5 (s), 122.3 (s), 95.1 (s). IR (ATR): ν 3054, 2985, 1700, 1603, 1485, 1421, 1263, 1157, 1055, 895, 840, 705, 504, 459 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 239.0815; found: 239.0812.



3-(Naphthalen-1-yl)-1,2,3-oxadiazol-3-ium-5-olate (2x)

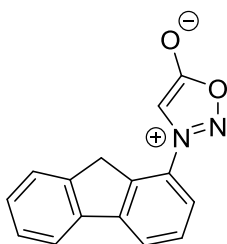
Following the published procedure and workup, **2x** was isolated as a light yellow solid in 60% yield (636 mg). mp: 146-147 °C. R_f (dichloromethane) = 0.89. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 8.2$ Hz, 1H), 8.10 – 7.97 (m, 1H), 7.78 (d, $J = 4.7$ Hz, 1H), 7.73 (d, $J = 7.3$ Hz, 1H), 7.71 – 7.63 (m, 3H), 6.72 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.8 (s), 134.1 (s), 132.9 (s), 131.2 (s), 129.1 (s), 128.7 (s), 127.9 (s), 126.8 (s), 124.8 (s), 123.4 (s), 120.9 (s), 98.4 (s). IR (ATR): ν 3120, 1731, 1591, 1510, 1445, 1385, 1337, 1261, 1217, 1164, 1124, 1050, 1021, 973, 929, 859, 797, 760, 728, 690,

645, 573, 530, 496 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 213.0659; found: 213.0656.



3-(Naphthalen-2-yl)-1,2,3-oxadiazol-3-ium-5-olate (2y)

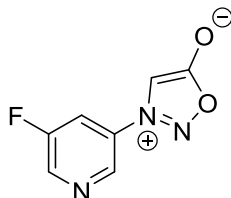
Following the published procedure and workup, **2y** was isolated as a white solid in 66% yield (699 mg). mp: 159-161 °C. R_f (dichloromethane) = 0.73. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 8.01 (s, 2H), 7.80 (d, $J = 8.4$ Hz, 1H), 7.71 (s, 2H), 6.89 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.1 (s), 134.6 (s), 132.6 (s), 132.1 (s), 130.8 (s), 128.9 (s), 128.9 (s), 128.4 (s), 128.2 (s), 120.9 (s), 117.9 (s), 93.8 (s). IR (ATR): ν 3055, 2985, 1750, 1600, 1512, 1424, 1379, 1263, 1170, 1078, 1016, 959, 894, 861, 811, 731, 584, 549, 474 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_9\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 213.0659; found: 213.0657.



3-(9H-Fluoren-1-yl)-1,2,3-oxadiazol-3-ium-5-olate (2z)

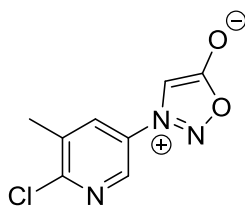
Following the published procedure and workup, **2z** was isolated as a deep red solid in 70% yield (875 mg). mp: 195-198 °C. R_f (dichloromethane) = 0.72. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.09 (s, 1H), 8.00 (s, 1H), 7.92 (s, 1H), 7.78 (s, 1H), 7.63 (s, 1H), 7.42 (s, 1H), 4.01 (s, 2H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 169.0 (s), 145.3 (s), 145.1 (s), 144.4 (s), 139.7 (s), 133.3 (s), 128.7 (s), 127.6 (s), 125.8 (s), 121.6 (s), 121.5 (s), 120.7 (s), 118.5 (s), 95.1 (s), 37.1 (s). IR (ATR): ν 3169, 3054, 2898, 1732,

1682, 1614, 1577, 1497, 1442, 1397, 1365, 1334, 1287, 1257, 1177, 1132, 1075, 1014, 951, 868, 827, 806, 766, 725, 584, 544, 470 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 251.0815; found: 251.0813.



3-(5-Fluoropyridin-3-yl)-4,5-dihydro-1,2,3-oxadiazol-3-ium-5-olate (**2aa**)

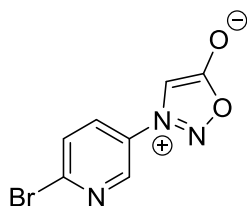
Following the published procedure and workup, **2aa** was isolated as a white solid in 30% yield (271 mg). mp: 97-98 °C. R_f (dichloromethane/ethyl acetate = 5:1) = 0.72. ^1H NMR (400 MHz, CDCl_3) δ 8.93 (s, 1H), 8.82 (s, 1H), 7.98 (d, $J = 7.3$ Hz, 1H), 6.99 (s, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -121.4 (d, $J = 7.0$ Hz, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 168.4 (s), 158.9 (d, $J = 265.3$ Hz), 142.3 (d, $J = 22.9$ Hz), 138.1 (d, $J = 4.6$ Hz), 131.9 (s), 116.7 (d, $J = 22.9$ Hz), 94.4 (s). IR (ATR): ν 3132, 3072, 2916, 2849, 1739, 1592, 1491, 1419, 1342, 1302, 1228, 1171, 1075, 1019, 953, 898, 814, 728, 690, 592, 455 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_7\text{H}_5\text{FN}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 182.0366; found: 182.0360.



3-(6-Chloro-5-methylpyridin-3-yl)-4,5-dihydro-1,2,3-oxadiazol-3-ium-5-olate (**2ac**)

Following the published procedure and workup, **2ac** was isolated as a white solid in 70% yield (738 mg). mp: 117-118 °C. R_f (dichloromethane/ethyl acetate = 5:1) = 0.70. ^1H NMR (400 MHz, CDCl_3) δ 8.64 (s, 1H), 8.06 (s, 1H), 7.01 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.6 (s), 155.1 (s), 139.3 (s), 135.1 (s), 132.0 (s), 130.7 (s), 94.5 (s), 19.8 (s). IR (ATR): ν 3116, 3062, 2918, 2850, 1727, 1567, 1448, 1394, 1339, 1282, 1233, 1172, 1072, 964, 899, 814, 725, 691, 569, 510, 447 cm^{-1} .

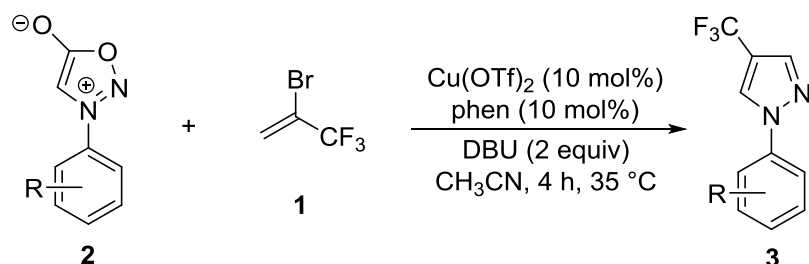
HR-MS (ESI): m/z calcd. for $C_8H_7ClN_3O_2$ $[M+H]^+$: 212.0221; found: 212.0222.



3-(6-Bromopyridin-3-yl)-4,5-dihydro-1,2,3-oxadiazol-3-ium-5-olate (2ad)

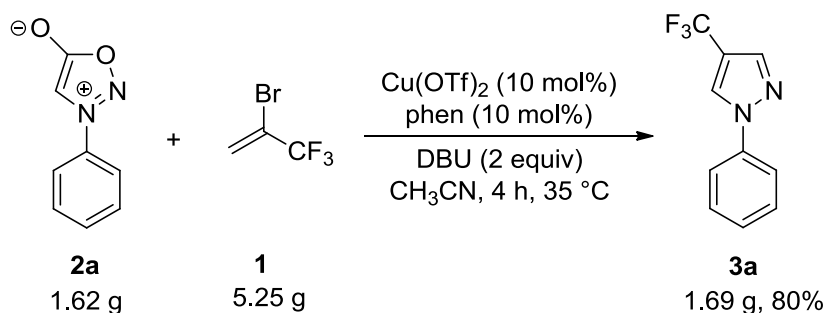
Following the published procedure and workup, **2ae** was isolated as a white solid in 80% yield (964 mg). mp: 160-162 °C. R_f (dichloromethane/ethyl acetate = 5:1) = 0.70. 1H NMR (400 MHz, $DMSO-d_6$) δ 9.02 (s, 1H), 8.35 (d, J = 8.3 Hz, 1H), 8.06 (d, J = 8.3 Hz, 1H), 7.88 (s, 1H). ^{13}C NMR (101 MHz, $DMSO-d_6$) δ 168.7 (s), 144.9 (s), 144.0 (s), 133.2 (s), 131.9 (s), 129.8 (s), 96.2 (s). IR (ATR): ν 3151, 3047, 2995, 1745, 1574, 1482, 1333, 1284, 1171, 1031, 941, 845, 723, 658, 557, 499 cm^{-1} . HR-MS (ESI): m/z calcd. for $C_7H_5BrN_3O_2$ $[M+H]^+$: 241.9560; found: 241.9561.

General procedure of copper-catalyzed synthesis of 4-trifluoromethyl pyrazoles



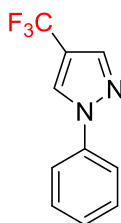
In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added 2-bromo-3,3,3-trifluoroprop-1-ene (**1**) (262 mg, 1.5 mmol, 3.0 equiv), sydnone (**2**) (0.50 mmol), DBU (152 mg, 1.0 mmol, 2.0 equiv), Cu(OTf)₂ (18 mg, 0.050 mmol, 10 mol%), phen (9.0 mg, 0.050 mmol, 10 mol%), and CH₃CN (5.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 35 °C for 4 h. The reaction mixture was filtered through a layer of Celite, eluted with ethyl acetate. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with *n*-pentane/dichloromethane.

Procedure for gram scale reaction for synthesis of 1-phenyl-4-(trifluoromethyl)-1H-pyrazole (3a)



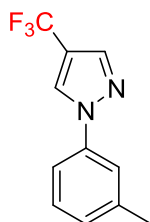
In a glove box filled with nitrogen, to an oven-dried 100 mL pressure tube equipped with a stir bar were added 2-bromo-3,3,3-trifluoroprop-1-ene (**1**) (5.25 g, 30 mmol, 3.0 equiv), *N*-phenylsydnone (**2a**) (1.62 g, 10 mmol), DBU (3.04 g, 20 mmol, 2.0 equiv), Cu(OTf)₂ (362 mg, 1.0 mmol, 10 mol%), phen (156 mg, 1.0 mmol, 10 mol%), and CH₃CN (30 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 35 °C for 4 h. The reaction mixture was filtered through a layer of Celite, eluted with ethyl acetate. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with *n*-pentane/dichloromethane.

Data for compounds 3



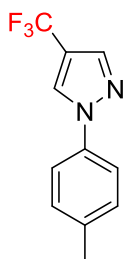
1-Phenyl-4-(trifluoromethyl)-1H-pyrazole (3a)

Following the general procedure and workup, **3a** was isolated as a white solid in 95% yield (101 mg). mp: 56-57 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.85. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 7.93 (s, 1H), 7.70 (d, $J = 7.9$ Hz, 2H), 7.50 (t, $J = 7.3$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.7 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 139.3 (s), 138.2 (q, $J = 2.7$ Hz), 129.6 (s), 127.7 (s), 126.3 (q, $J = 3.6$ Hz), 122.5 (q, $J = 266.2$ Hz), 119.7 (s), 115.5 (q, $J = 38.3$ Hz). IR (ATR): ν 3143, 3121, 2922, 2852, 1738, 1643, 1577, 1503, 1407, 1264, 1145, 1091, 1036, 963, 870, 754, 739, 675, 554, 504, 484, 429 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_8\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 213.0634; found: 213.0631.



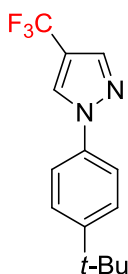
1-(*m*-Tolyl)-4-(trifluoromethyl)-1H-pyrazole (3b)

Following the general procedure and workup, **3b** was isolated as a pale yellow oil in 90% yield (102 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.74. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.92 (s, 1H), 7.53 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 7.8$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 1H), 2.42 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.7 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 139.8 (s), 139.2 (s), 138.0 (q, $J = 2.7$ Hz), 129.4 (s), 128.5 (s), 126.3 (q, $J = 3.6$ Hz), 122.6 (q, $J = 266.2$ Hz), 120.4 (s), 116.7 (s), 115.3 (q, $J = 38.3$ Hz), 21.2 (s). IR (ATR): ν 3126, 3056, 2924, 2860, 1729, 1577, 1502, 1403, 1269, 1185, 1113, 968, 867, 845, 781, 738, 682, 593, 548, 485, 438 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 227.0791; found: 227.0791.



1-(*p*-Tolyl)-4-(trifluoromethyl)-1*H*-pyrazole (**3c**)

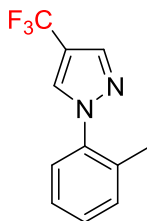
Following the general procedure and workup, **3c** was isolated as a white solid in 70% yield (79 mg). mp: 61-62 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.61. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.92 (s, 1H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.31 (d, $J = 7.8$ Hz, 2H), 2.43 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.6 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 138.0 (q, $J = 2.7$ Hz), 137.8 (s), 137.1 (s), 130.2 (s), 126.2 (q, $J = 3.6$ Hz), 122.5 (q, $J = 266.0$ Hz), 119.7 (s), 115.2 (q, $J = 38.9$ Hz), 21.0 (s). IR (ATR): ν 3132, 2926, 2251, 1576, 1522, 1402, 1262, 1120, 969, 867, 815, 680, 587, 521, 473 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 227.0791; found: 227.0790.



1-(4-(*tert*-Butyl)phenyl)-4-(trifluoromethyl)-1*H*-pyrazole (**3d**)

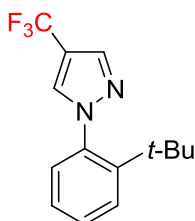
Following the general procedure and workup, **3d** was isolated as a white solid in 92% yield (123 mg). mp: 63-64 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.82. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 7.92 (s, 1H), 7.62 (d, $J = 8.3$ Hz, 2H), 7.53 (d, $J = 8.3$ Hz, 2H), 1.39 (s, 9H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.6 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 151.1 (s), 138.0 (q, $J = 2.6$ Hz), 136.9 (s), 126.5 (s), 126.2 (q, $J = 3.5$ Hz), 122.6 (q, $J = 266.1$ Hz), 119.5 (s), 115.2 (q, $J = 38.4$ Hz), 34.7 (s), 31.3 (s). IR (ATR): ν 3133, 2964, 2907, 2871, 1574, 1521, 1400, 1365, 1262, 1192, 1116, 1034, 968, 866, 836, 821, 746, 680, 557, 494, 436 cm^{-1} . HR-MS (ESI): m/z calcd. for

C₁₄H₁₆F₃N₂ [M+H]⁺: 269.1260; found: 269.1261.



1-(*o*-Tolyl)-4-(trifluoromethyl)-1*H*-pyrazole (3e)

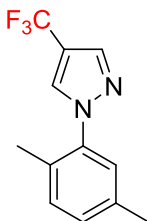
Following the general procedure and workup, **3e** was isolated as a white liquid in 58% yield (66 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.67. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.90 (s, 1H), 7.46 – 7.30 (m, 4H), 2.27 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.4 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 139.0 (s), δ 137.6 (q, J = 2.6 Hz), 133.9 (s), 131.5 (s), 129.9 (q, J = 3.5 Hz), 129.4 (s), 126.8 (s), 126.1 (s), 122.6 (q, J = 266.0 Hz), 114.4 (q, J = 38.2 Hz), 17.9 (s). IR (ATR): ν 3124, 2961, 2928, 2855, 1577, 1505, 1401, 1259, 1189, 1126, 969, 867, 763, 735, 682, 662, 590, 549 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₁H₁₀F₃N₂ [M+H]⁺: 227.0791; found: 227.0791.



1-(2-(*tert*-Butyl)phenyl)-4-(trifluoromethyl)-1*H*-pyrazole (3f)

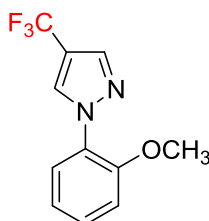
Following the general procedure and workup, **3f** was isolated as a white liquid in 21% yield (28 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.61. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 7.85 (s, 1H), 7.64 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.34 – 7.26 (m, 1H), 7.13 (d, J = 7.7 Hz, 1H), 1.20 (s, 9H). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.2 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 147.1 (s), 138.3 (s), 136.8 (q, J = 2.6 Hz), 131.8 (q, J = 3.5 Hz), 130.2 (s), 130.1 (s), 128.3 (s), 126.6 (s), 122.6 (q, J = 265.9 Hz), 114.3 (q, J = 38.3 Hz), 35.8 (s), 31.3 (s). IR (ATR): ν 3155, 2966, 2926, 2872, 1576, 1497, 1399, 1259, 1148, 1123, 969, 730, 591, 537 cm⁻¹. HR-MS (ESI):

m/z calcd. for C₁₄H₁₆F₃N₂ [M+H]⁺: 269.1260; found: 269.1260.



1-(2,5-Dimethylphenyl)-4-(trifluoromethyl)-1H-pyrazole (3g)

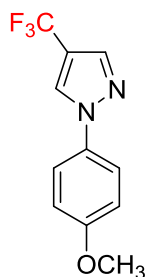
Following the general procedure and workup, **3g** was isolated as a pale yellow liquid in 65% yield (78 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.62. ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.89 (s, 1H), 7.29 – 7.15 (m, 3H), 2.39 (s, 3H), 2.22 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.3 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 138.7 (s), 137.5 (q, J = 2.6 Hz), 136.8 (s), 131.3 (s), 130.4 (s), 130.0 (s), 129.8 (q, J = 3.5 Hz), 126.6 (s), 122.7 (q, J = 266.0 Hz), 114.3 (q, J = 38.4 Hz), 20.7 (s), 17.4 (s). IR (ATR): ν 3126, 2926, 2865, 1575, 1514, 1467, 1400, 1261, 1182, 1122, 968, 865, 815, 681, 601, 552, 499, 463 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₂H₁₂F₃N₂ [M+H]⁺: 241.0947; found: 241.0941.



1-(2-Methoxyphenyl)-4-(trifluoromethyl)-1H-pyrazole (3h)

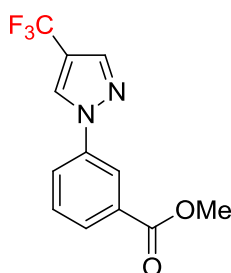
Following the general procedure and workup, **3h** was isolated as a pale yellow liquid in 60% yield (73 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.41. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H), 7.91 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.15 – 7.04 (m, 2H), 3.89 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.4 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 151.1 (s), 137.2 (q, J = 2.7 Hz), 131.0 (q, J = 3.7 Hz), 129.0 (s), 128.6 (s), 125.1 (s), 122.8 (q, J = 266.1 Hz), 121.2 (s), 114.1 (q, J = 38.0 Hz), 112.2 (s), 55.8 (s). IR (ATR): ν 3138, 2939, 2842, 1577, 1508, 1473, 1406, 1264, 1241, 1114, 1023, 968, 867, 679, 593, 552, 481, 445 cm⁻¹. HR-MS (ESI): m/z calcd.

for $C_{11}H_{10}F_3N_2O$ $[M+H]^+$: 243.0740; found: 243.0739.



1-(4-Methoxyphenyl)-4-(trifluoromethyl)-1H-pyrazole (**3i**)

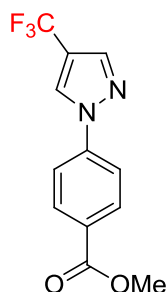
Following the general procedure and workup, **3i** was isolated as a white solid in 83% yield (100 mg). mp: 53-54 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.56. 1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.90 (s, 1H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.6 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (s), 137.8 (q, $J = 2.7$ Hz), 133.0 (s), 126.3 (q, $J = 3.6$ Hz), 122.6 (q, $J = 266.1$ Hz), 121.5 (s), 115.1 (q, $J = 38.3$ Hz), 114.9 (s), 55.6 (s). IR (ATR): ν 3129, 3008, 2963, 2939, 2839, 1576, 1519, 1402, 1259, 1120, 1039, 1023, 969, 867, 831, 680, 533, 475 cm^{-1} . HR-MS (ESI): m/z calcd. for $C_{11}H_{10}F_3N_2O$ $[M+H]^+$: 243.0740; found: 243.0740.



Methyl 3-(4-(trifluoromethyl)-1H-pyrazol-1-yl)benzoate (**3j**)

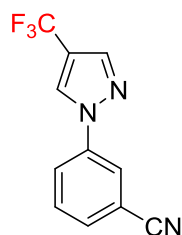
Following the general procedure and workup, **3j** was isolated as a white solid in 55% yield (74 mg). mp: 107-109 °C. R_f (*n*-pentane/dichloromethane = 3:1) = 0.51. 1H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.28 (s, 1H), 8.04 (d, $J = 7.6$ Hz, 1H), 8.00 – 7.86 (m, 2H), 7.58 (t, $J = 7.5$ Hz, 1H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.8 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9 (s), 139.4 (s), 138.5 (s), 131.8 (s), 129.9 (s), 128.6 (s), 126.4 (q, $J = 3.7$ Hz), 123.9 (s), 122.3 (q, $J = 266.3$ Hz), 120.3 (s),

115.9 (q, $J = 38.8$ Hz), 52.5 (s). IR (ATR): ν 3114, 2959, 2851, 1715, 1596, 1482, 1411, 1288, 1236, 1107, 1047, 966, 864, 840, 753, 679, 592, 465 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 271.0689; found: 271.0688.



Methyl 4-(4-(trifluoromethyl)-1H-pyrazol-1-yl)benzoate (**3k**)

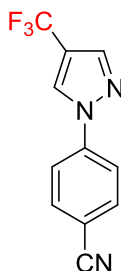
Following the general procedure and workup, **3k** was isolated as a white solid in 45% yield (61 mg). mp: 94-95 °C. R_f (*n*-pentane/dichloromethane = 3:1) = 0.49. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 8.19 (d, $J = 7.5$ Hz, 2H), 7.96 (s, 1H), 7.81 (d, $J = 7.6$ Hz, 2H), 3.97 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.9 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 166.0 (s), 142.3 (s), 138.9 (q, $J = 2.6$ Hz), 131.3 (s), 129.2 (s), 126.4 (q, $J = 3.8$ Hz), 122.2 (q, $J = 266.4$ Hz), 119.0 (s), 116.2 (q, $J = 38.6$ Hz), 52.4 (s). IR (ATR): ν 3110, 2960, 2925, 1708, 1579, 1522, 1403, 1300, 1142, 1105, 972, 868, 769, 735, 695, 521, 456 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{12}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 271.0689; found: 271.0688.



3-(4-(Trifluoromethyl)-1H-pyrazol-1-yl)benzonitrile (**3l**)

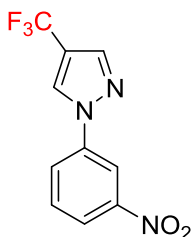
Following the general procedure and workup, **3l** was isolated as a white solid in 23% yield (27 mg). mp: 111-112 °C. R_f (*n*-pentane/dichloromethane = 3:1) = 0.43. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1H), 8.08 (s, 1H), 8.02 – 7.93 (m, 2H), 7.73 – 7.60 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.0 (s, 3F). ^{13}C NMR (101 MHz,

CDCl₃) δ 139.8 (s), 139.0 (q, $J = 2.5$ Hz), 131.0 (s), 130.7 (s), 126.3 (q, $J = 3.6$ Hz), 123.4 (s), 122.9 (s), 122.1 (q, $J = 266.5$ Hz), 117.6 (s), 116.6 (q, $J = 38.6$ Hz), 114.1 (s). IR (ATR): ν 3113, 3082, 2236, 1611, 1580, 1503, 1405, 1274, 1122, 1101, 970, 889, 866, 830, 793, 679, 602, 547, 470 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₁H₇F₃N₃ [M+H]⁺: 238.0587; found:238.0583.



4-(4-(Trifluoromethyl)-1H-pyrazol-1-yl)benzonitrile (3m)

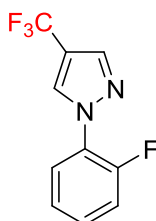
Following the general procedure and workup, **3m** was isolated as a white solid in 25% yield (30 mg). mp: 91-92 °C. R_f (*n*-pentane/dichloromethane = 3:1) = 0.40. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.98 (s, 1H), 7.89 (d, $J = 7.6$ Hz, 2H), 7.83 (d, $J = 7.6$ Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.1 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 142.0 (s), 139.3 (q, $J = 2.5$ Hz), 133.9 (s), 126.4 (q, $J = 3.7$ Hz), 122.1 (q, $J = 266.4$ Hz), 119.7 (s), 117.9 (s), 116.8 (q, $J = 38.8$ Hz), 111.3 (s). IR (ATR): ν 3136, 2952, 2253, 1610, 1519, 1403, 1268, 1121, 969, 680, 548, 481 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₁H₇F₃N₃ [M+H]⁺: 238.0587; found: 238.0582.



1-(3-Nitrophenyl)-4-(trifluoromethyl)-1H-pyrazole (3n)

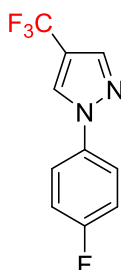
Following the general procedure and workup, **3n** was isolated as a white solid in 14% yield (18 mg). mp: 81-82 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.36. ¹H NMR (400 MHz, CDCl₃) δ 8.60 (s, 1H), 8.35 (s, 1H), 8.25 (d, $J = 8.1$ Hz, 1H), 8.12 (d, $J = 7.8$ Hz, 1H), 7.99 (s, 1H), 7.73 (t, $J = 8.1$ Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ

-57.0 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 149.0 (s), 140.0 (s), 139.1 (q, $J = 2.3$ Hz), 130.8 (s), 126.5 (q, $J = 3.7$ Hz), 124.9 (s), 122.2 (s), 122.1 (q, $J = 266.5$ Hz), 116.7 (q, $J = 38.9$ Hz), 114.5 (s). IR (ATR): ν 3125, 2924, 2852, 1772, 1580, 1533, 1496, 1405, 1348, 1268, 1248, 1207, 1116, 1042, 969, 890, 870, 801, 680, 593, 434 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{F}_3\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 258.0485; found: 258.0481.



1-(2-Fluorophenyl)-4-(trifluoromethyl)-1H-pyrazole (3o)

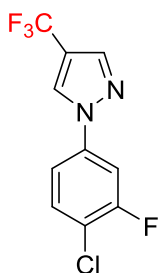
Following the general procedure and workup, **3o** was isolated as a white liquid in 25% yield (29 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.77. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.95 (s, 1H), 7.91 (t, $J = 7.9$ Hz, 1H), 7.43 – 7.25 (m, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.7 (s, 3F), -125.0 – -125.2 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 153.6 (d, $J = 249.7$ Hz), 138.0 (q, $J = 2.6$ Hz), 130.2 (dq, $J = 10.6, 3.7$ Hz), 129.0 (d, $J = 7.9$ Hz), 127.5 (d, $J = 9.2$ Hz), 125.2 (d, $J = 3.8$ Hz), 124.6 (s), 122.4 (q, $J = 266.2$ Hz), 117.0 (d, $J = 20.3$ Hz), 115.5 (q, $J = 39.8$ Hz). IR (ATR): ν 3135, 2919, 2850, 1599, 1579, 1510, 1472, 1406, 1285, 1258, 1223, 1118, 1037, 968, 955, 869, 818, 755, 680, 555, 449 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{F}_4\text{N}_2$ $[\text{M}+\text{H}]^+$: 231.0540; found: 231.0539.



1-(4-Fluorophenyl)-4-(trifluoromethyl)-1H-pyrazole (3p)

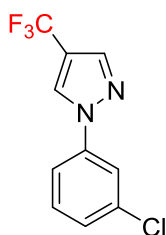
Following the general procedure and workup, **3p** was isolated as a white liquid in 80% yield (92 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.77. ^1H NMR (400 MHz,

CDCl₃) δ 8.13 (s, 1H), 7.90 (s, 1H), 7.74 – 7.48 (m, 2H), 7.17 (t, J = 7.9 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.8 (s, 3F), -113.9 – -114.0 (m, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 161.8 (d, J = 247.8 Hz), 138.2 (q, J = 2.7 Hz), 135.6 (d, J = 2.7 Hz), 126.4 (q, J = 3.6 Hz), 122.4 (q, J = 266.2 Hz), 121.6 (d, J = 8.5 Hz), 116.5 (d, J = 23.2 Hz), 115.6 (q, J = 38.5 Hz). IR (ATR): ν 3133, 2918, 2849, 1611, 1579, 1517, 1447, 1420, 1401, 1265, 1230, 1117, 1030, 968, 869, 835, 819, 739, 679, 625, 586, 524, 481 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₀H₇F₄N₂ [M+H]⁺: 231.0540; found: 231.0539.



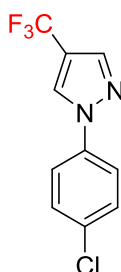
1-(4-Chloro-3-fluorophenyl)-4-(trifluoromethyl)-1H-pyrazole (3q)

Following the general procedure and workup, **3q** was isolated as a pale yellow liquid in 22% yield (29 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.81. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (s, 1H), 7.94 (s, 1H), 7.62 (d, J = 9.6 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 7.46 (d, J = 9.7 Hz, 1H). ¹⁹F NMR (376 MHz, CDCl₃) δ -57.0 (s, 3F), -111.4 (t, J = 8.6 Hz, 1F). ¹³C NMR (101 MHz, CDCl₃) δ 158.5 (d, J = 250.7 Hz), 138.9 (s), 138.7 (q, J = 2.7 Hz), 131.5 (s), 126.3 (q, J = 3.7 Hz), 122.1 (q, J = 266.4 Hz), 120.2 (d, J = 17.9 Hz), 116.3 (q, J = 38.7 Hz), 115.3 (d, J = 3.8 Hz), 108.6 (d, J = 26.0 Hz). IR (ATR): ν 3134, 2926, 2853, 1579, 1503, 1463, 1406, 1281, 1261, 1215, 1190, 1123, 1073, 1031, 972, 876, 815, 735, 705, 680, 580, 489 cm⁻¹. HR-MS (ESI): m/z calcd. for C₁₀H₆ClF₄N₂ [M+H]⁺: 265.0150; found: 265.0146.



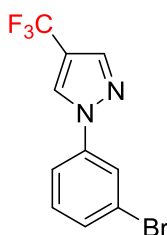
1-(3-Chlorophenyl)-4-(trifluoromethyl)-1H-pyrazole (3r)

Following the general procedure and workup, **3r** was isolated as a white liquid in 40% yield (49 mg). R_f (*n*-pentane) = 0.71. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.93 (s, 1H), 7.76 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 7.9$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.9 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.1 (s), 138.6 (q, $J = 2.6$ Hz), 135.6 (s), 130.7 (s), 127.8 (s), 126.3 (q, $J = 3.6$ Hz), 122.3 (q, $J = 266.2$ Hz), 120.0 (s), 117.5 (s), 116.0 (q, $J = 38.5$ Hz). IR (ATR): ν 3132, 2924, 2851, 1593, 1577, 1493, 1404, 1264, 1236, 1121, 1076, 1038, 969, 871, 820, 777, 735, 680, 594, 547, 495 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{ClF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 247.0244; found: 247.0249.



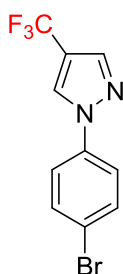
1-(4-Chlorophenyl)-4-(trifluoromethyl)-1H-pyrazole (3s)

Following the general procedure and workup, **3s** was isolated as a pale yellow liquid in 50% yield (62 mg). R_f (*n*-pentane) = 0.71. ^1H NMR (400 MHz, CDCl_3) δ 8.15 (s, 1H), 7.90 (s, 1H), 7.60 (d, $J = 7.4$ Hz, 2H), 7.41 (d, $J = 7.4$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.8 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 138.4 (q, $J = 2.6$ Hz), 137.7 (s), 133.3 (s), 129.7 (s), 126.2 (q, $J = 3.7$ Hz), 122.4 (q, $J = 266.2$ Hz), 120.7 (s), 115.8 (q, $J = 38.5$ Hz). IR (ATR): ν 3232, 2923, 1576, 1503, 1405, 1262, 1193, 1118, 1094, 1029, 968, 955, 869, 827, 679, 516, 471 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{ClF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 247.0244; found: 247.0251.



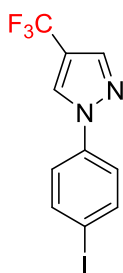
1-(3-Bromophenyl)-4-(trifluoromethyl)-1H-pyrazole (3t)

Following the general procedure and workup, **3t** was isolated as a white solid in 36% yield (52 mg). mp: 41-42 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.75. ^1H NMR (400 MHz, CDCl_3) δ 8.20 (s, 1H), 7.93 (s, 2H), 7.65 (d, $J = 7.5$ Hz, 1H), 7.52 (d, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 8.0$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.8 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.2 (s), 138.6 (q, $J = 2.6$ Hz), 130.9 (s), 130.7 (s), 126.3 (q, $J = 3.7$ Hz), 123.3 (s), 122.9 (s), 122.3 (q, $J = 266.3$ Hz), 118.0 (s), 116.0 (q, $J = 38.7$ Hz). IR (ATR): ν 3130, 2923, 1574, 1490, 1459, 1404, 1263, 1195, 1120, 1035, 969, 871, 820, 779, 679, 592, 546, 488, 434 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{BrF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 290.9739; found: 290.9740.



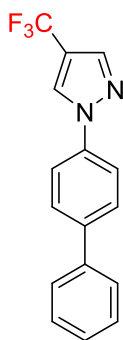
1-(4-Bromophenyl)-4-(trifluoromethyl)-1H-pyrazole (3u)

Following the general procedure and workup, **3u** was isolated as a white liquid in 45% yield (65 mg). R_f (*n*-pentane/dichloromethane = 5:1) = 0.73. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (s, 1H), 7.93 (s, 1H), 7.65 (d, $J = 8.1$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.8 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 138.5 (q, $J = 2.5$ Hz), 138.3 (s), 132.8 (s), 126.2 (q, $J = 3.5$ Hz), 122.3 (q, $J = 266.2$ Hz), 121.3 (s), 121.2 (s), 115.9 (q, $J = 38.6$ Hz). IR (ATR): ν 3129, 2927, 1574, 1500, 1407, 1264, 1122, 969, 823, 666, 624, 518, 463 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{BrF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 290.9739; found: 290.9741.



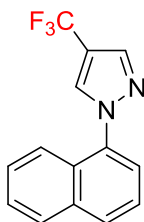
1-(4-Iodophenyl)-4-(trifluoromethyl)-1H-pyrazole (3v)

Following the general procedure and workup, **3v** was isolated as a white solid in 67% yield (113 mg). mp: 52-53 °C. R_f (*n*-pentane/dichloromethane = 20:1) = 0.82. ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.91 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.7 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 138.9 (s), 138.7 (s), 138.5 (q, $J = 2.6$ Hz), 126.1 (q, $J = 3.7$ Hz), 122.3 (q, $J = 266.4$ Hz), 121.2 (s), 115.9 (q, $J = 38.5$ Hz), 92.3 (s). IR (ATR): ν 3130, 2846, 2676, 1572, 1495, 1406, 1263, 1193, 1121, 1061, 968, 953, 869, 817, 679, 591, 514, 455 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_7\text{F}_3\text{IN}_2$ $[\text{M}+\text{H}]^+$: 338.9601; found: 338.9592.



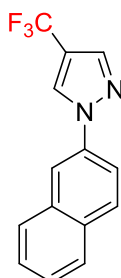
1-([1,1'-Biphenyl]-4-yl)-4-(trifluoromethyl)-1H-pyrazole (3w)

Following the general procedure and workup, **3w** was isolated as a white solid in 88% yield (127 mg). mp: 159-160 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.71. ^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 7.98 (s, 1H), 7.78 (d, $J = 7.7$ Hz, 2H), 7.74 (d, $J = 7.7$ Hz, 2H), 7.65 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.3$ Hz, 2H), 7.46 – 7.39 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.6 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7 (s), 139.7 (s), 138.4 (s), 138.3 (q, $J = 2.6$ Hz), 129.0 (s), 128.2 (s), 127.8 (s), 127.0 (s), 126.2 (q, $J = 3.7$ Hz), 122.5 (q, $J = 266.3$ Hz), 120.0 (s), 115.6 (q, $J = 38.4$ Hz). IR (ATR): ν 3136, 3085, 2923, 2849, 1566, 1528, 1491, 1400, 1266, 1149, 1093, 1039, 964, 871, 826, 759, 674, 599, 545, 484 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 289.0947; found: 289.0942.



1-(Naphthalen-1-yl)-4-(trifluoromethyl)-1H-pyrazole (**3x**)

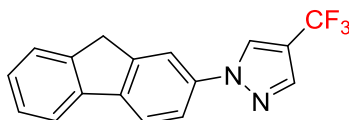
Following the general procedure and workup, **3x** was isolated as a white solid in 15% yield (20 mg). mp: 110-111 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.57. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 8.07 (s, 1H), 8.04 – 7.96 (m, 2H), 7.75 (d, J = 7.5 Hz, 1H), 7.63 – 7.56 (m, 4H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.3 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 138.1 (q, J = 2.6 Hz), 136.2 (s), 134.3 (s), 131.0 (q, J = 3.3 Hz), 130.0 (s), 128.8 (s), 128.3 (s), 127.7 (s), 127.0 (s), 125.0 (s), 123.5 (s), 122.6 (q, J = 266.1 Hz), 122.5 (s), 114.7 (q, J = 38.2 Hz). IR (ATR): ν 3125, 3059, 2926, 2852, 1577, 1514, 1472, 1401, 1385, 1260, 1182, 1120, 1019, 995, 968, 940, 867, 800, 771, 682, 589, 567, 460 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 263.0791; found: 263.0786.



1-(Naphthalen-2-yl)-4-(trifluoromethyl)-1H-pyrazole (**3y**)

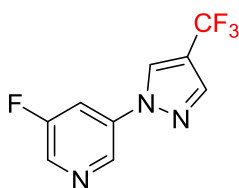
Following the general procedure and workup, **3y** was isolated as a white solid in 70% yield (92 mg). mp: 106-107 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.68. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.28 (s, 1H), 8.42 (s, 1H), 8.23 (s, 1H), 8.14 – 7.85 (m, 4H), 7.59 – 7.46 (m, 2H). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -55.2 (s, 3F). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 138.6 (q, J = 2.5 Hz), 136.8 (s), 133.4 (s), 132.3 (s), 130.0 (s), 128.9 (q, J = 3.7 Hz), 128.5 (s), 128.1 (s), 127.6 (s), 126.8 (s), 123.3 (q, J = 266.1 Hz), 118.5 (s), 117.1 (s), 114.5 (q, J = 37.7 Hz). IR (ATR): ν 3084, 2925, 2840, 2250, 1632, 1575, 1516, 1408, 1277, 1230, 1118, 1053, 1025, 1006, 970, 865, 819, 757, 682, 621,

476 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 263.0791; found: 263.0792.



1-(9H-fluoren-2-yl)-4-(trifluoromethyl)-1H-pyrazole (**3z**)

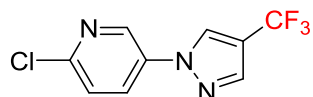
Following the general procedure and workup, **3z** was isolated as a white solid in 63% yield (95 mg). mp: 172-173 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.58. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.23 (s, 1H), 8.23 (s, 1H), 8.13 (s, 1H), 8.05 (d, $J = 8.2$ Hz, 1H), 7.94 (t, $J = 7.7$ Hz, 2H), 7.62 (d, $J = 7.3$ Hz, 1H), 7.42 (t, $J = 7.3$ Hz, 1H), 7.35 (t, $J = 7.3$ Hz, 1H), 4.02 (s, 2H). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -54.9 (s, 3F). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 145.0 (s), 143.8 (s), 140.9 (s), 140.6 (s), 138.5 (q, $J = 2.7$ Hz), 138.1 (s), 128.8 (q, $J = 3.6$ Hz), 127.6 (s), 127.4 (s), 125.7 (s), 123.3 (q, $J = 265.6$ Hz), 121.3 (s), 120.8 (s), 118.6 (s), 116.7 (s), 114.2 (q, $J = 37.6$ Hz), 37.1 (s). IR (ATR): ν 3137, 3111, 2958, 2919, 2850, 1577, 1500, 1405, 1297, 1272, 1222, 1100, 1037, 965, 865, 824, 766, 626, 582, 526, 448 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{17}\text{H}_{12}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 301.0947; found: 301.0941.



3-Fluoro-5-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine (**3aa**)

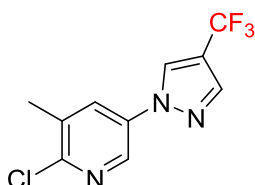
Following the general procedure and workup, **3aa** was isolated as a white solid in 5% yield (5 mg). mp: 55-56 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.31. ^1H NMR (400 MHz, CDCl_3) δ 8.91 (s, br, 1H), 8.61 (s, br, 1H), 8.29 (s, 1H), 8.00 (s, 1H), 7.92 (d, $J = 8.6$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.0 (s, 3F), -123.8 – -124.1 (m, 1F). ^{13}C NMR (101 MHz, CDCl_3) δ 139.4 (q, $J = 2.5$ Hz), 137.2 (s), 137.0 (s), 135.9 (s), 126.6 (q, $J = 3.5$ Hz), 121.7 (q, $J = 283.7$ Hz), 116.6 (q, $J = 19.9$ Hz), 114.8 (s), 114.6 (s). IR (ATR): ν 3062, 2922, 2849, 1567, 1482, 1394, 1282, 1121, 1072, 941,

899, 814, 723, 679, 569, 447 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_9\text{H}_6\text{F}_4\text{N}_3$ $[\text{M}+\text{H}]^+$: 232.0498; found: 232.0492.



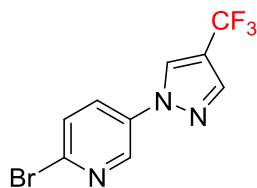
2-Chloro-5-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine (3ab)

Following the general procedure and workup, **3ab** was isolated as a white solid in 36% yield (44 mg). mp: 79-80 $^{\circ}\text{C}$. R_f (*n*-pentane/dichloromethane = 5:1) = 0.69. ^1H NMR (400 MHz, CDCl_3) δ 8.75 (s, 1H), 8.25 (s, 1H), 8.05 (d, $J = 8.6$ Hz, 1H), 7.95 (s, 1H), 7.47 (d, $J = 8.6$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.0 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 150.0 (s), 140.4 (s), 139.2 (q, $J = 2.2$ Hz), 134.9 (s), 130.0 (s), 126.5 (q, $J = 3.7$ Hz), 125.0 (s), 122.1 (q, $J = 266.5$ Hz), 116.6 (q, $J = 39.0$ Hz). IR (ATR): ν 3130, 3075, 2926, 1587, 1570, 1484, 1404, 1380, 1302, 1267, 1193, 1152, 1125, 1107, 1034, 1009, 969, 953, 910, 872, 842, 734, 678, 629, 526, 480 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_9\text{H}_6\text{ClF}_3\text{N}_3$ $[\text{M}+\text{H}]^+$: 248.0197; found: 248.0192.



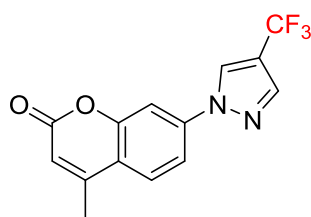
2-Chloro-3-methyl-5-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine (3ac)

Following the general procedure and workup, **3ac** was isolated as a white solid in 30% yield (39 mg). mp: 101-104 $^{\circ}\text{C}$. R_f (*n*-pentane/dichloromethane = 5:1) = 0.32. ^1H NMR (400 MHz, CDCl_3) δ 8.60 (s, 1H), 8.23 (s, 1H), 7.98 (d, $J = 9.8$ Hz, 1H), 2.51 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.9 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 150.3 (s), 139.1 (q, $J = 2.5$ Hz), 137.5 (s), 135.0 (s), 133.9 (s), 130.5 (s), 126.5 (q, $J = 3.7$ Hz), 122.1 (q, $J = 266.5$ Hz), 116.5 (q, $J = 38.8$ Hz), 19.8 (s). IR (ATR): ν 3116, 3062, 2918, 2850, 1727, 1567, 1448, 1394, 1339, 1282, 1233, 1172, 1072, 964, 899, 814, 725, 691, 569, 510, 447 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{10}\text{H}_8\text{ClF}_3\text{N}_3$ $[\text{M}+\text{H}]^+$: 262.0353; found: 262.0354.



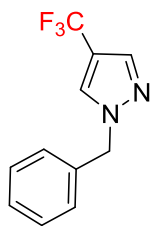
2-Bromo-5-(4-(trifluoromethyl)-1H-pyrazol-1-yl)pyridine (3ad)

Following the general procedure and workup, **3ad** was isolated as a white solid in 33% yield (48 mg). mp: 99-100 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.32. ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 8.25 (s, 1H), 7.97 (s, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3) δ -57.0 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8 (s), 140.3 (s), 139.3 (q, $J = 2.6$ Hz), 135.3 (s), 129.7 (s), 128.8 (s), 126.4 (q, $J = 3.7$ Hz), 122.0 (q, $J = 266.7$ Hz), 116.7 (q, $J = 38.6$ Hz). IR (ATR): ν 3129, 3074, 2919, 1581, 1485, 1403, 1376, 1260, 1119, 1031, 967, 871, 841, 731, 675, 626, 549, 466 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_9\text{H}_6\text{BrF}_3\text{N}_3$ $[\text{M}+\text{H}]^+$: 291.9692; found: 291.9694.



4-Methyl-7-(4-(trifluoromethyl)-1H-pyrazol-1-yl)-2H-chromen-2-one (3ae)

Following the general procedure and workup, **3ae** was isolated as a white solid in 41% yield (60 mg). mp: 195-198 °C. R_f (*n*-pentane/dichloromethane = 5:1) = 0.30. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 9.37 (s, 1H), 8.30 (s, 1H), 7.94 (s, 3H), 6.43 (s, 1H), 2.47 (s, 3H). ^{19}F NMR (376 MHz, $\text{DMSO}-d_6$) δ -55.2 (s, 3F). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 160.0 (s), 154.1 (s), 153.3 (s), 141.3 (s), 139.5 (q, $J = 2.0$ Hz), 129.6 (q, $J = 3.5$ Hz), 127.5 (s), 123.0 (q, $J = 266.1$ Hz), 119.0 (s), 115.1 (s), 115.0 (q, $J = 37.7$ Hz), 114.7 (s), 106.9 (s), 18.6 (s). IR (ATR): ν 3116, 3071, 2921, 2852, 1709, 1619, 1587, 1461, 1278, 1216, 1100, 1027, 971, 864, 822, 765, 707, 678, 624, 576, 533, 487, 441 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 295.0694; found: 295.0689.



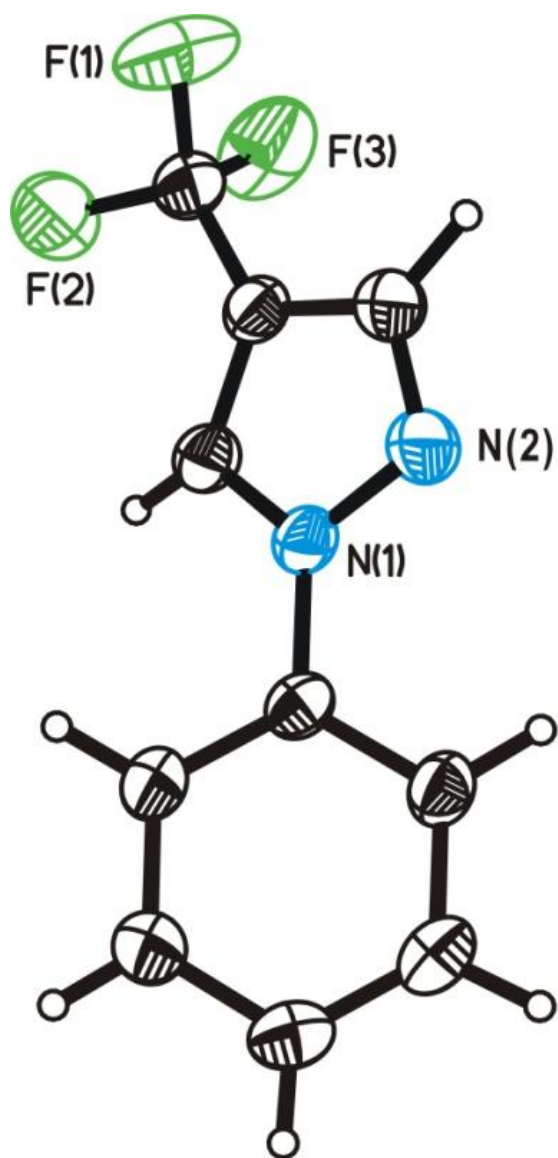
1-Benzyl-4-(trifluoromethyl)-1H-pyrazole (3af)

Following the general procedure and workup, **3af** was isolated as a white solid in 40% yield (45 mg). R_f (*n*-pentane/dichloromethane = 20:1) = 0.32. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (s, 1H), 7.66 (s, 1H), 7.47 – 7.35 (m, 3H), 7.29 (d, J = 6.9 Hz, 2H), 5.34 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3) δ -56.3 (s, 3F). ^{13}C NMR (101 MHz, CDCl_3) δ 137.1 (q, J = 2.7 Hz), 135.2 (s), 129.1 (s), 128.6 (s), 128.5 (q, J = 3.4 Hz), 128.0 (s), 122.6 (q, J = 265.8 Hz), 114.0 (q, J = 38.0 Hz), 56.5 (s). IR (ATR): ν 3034, 2922, 2852, 2251, 1576, 1498, 1463, 1399, 1233, 1126, 995, 682, 581, 473 cm^{-1} . HR-MS (ESI): m/z calcd. for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 227.0791; found: 227.0785.

Crystal structure analyses

The suitable crystals of **3a** (CCDC 1934789) 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 MoK α 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.² Structure solution and refinement were carried out with the SHELXTL suite of programs.² The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

ORTEP diagrams



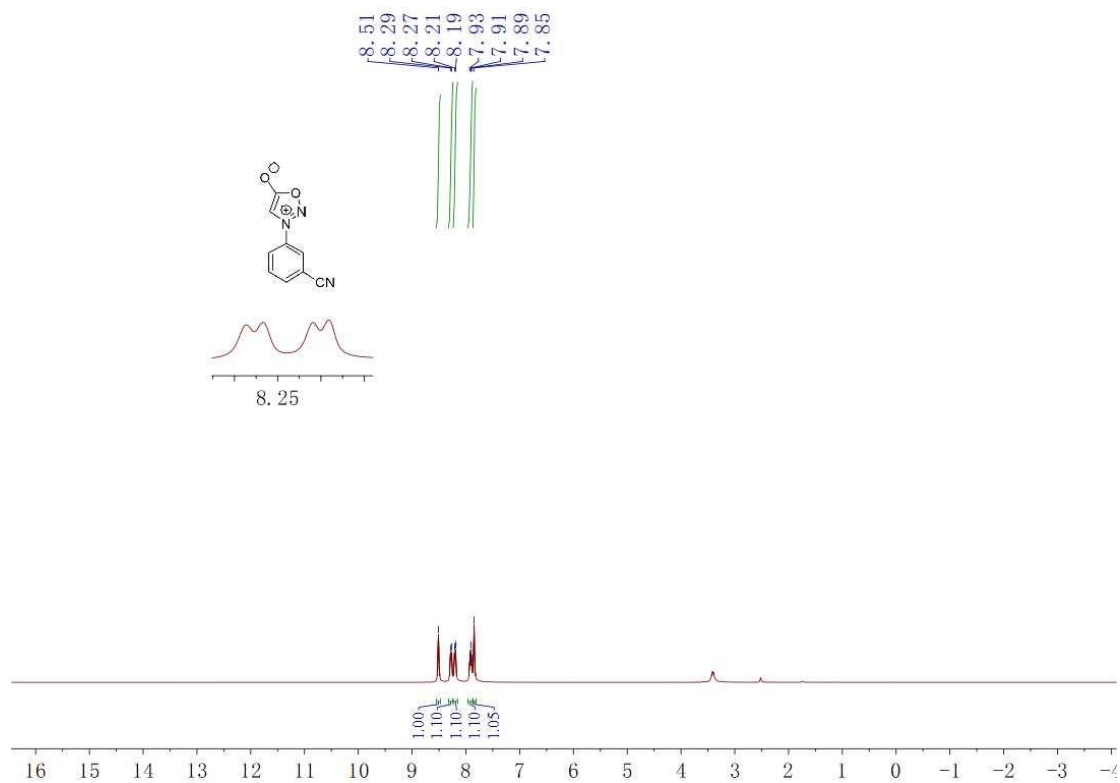
ORTEP diagram of compound 3a. Thermal ellipsoids are drawn at 40% probability

References:

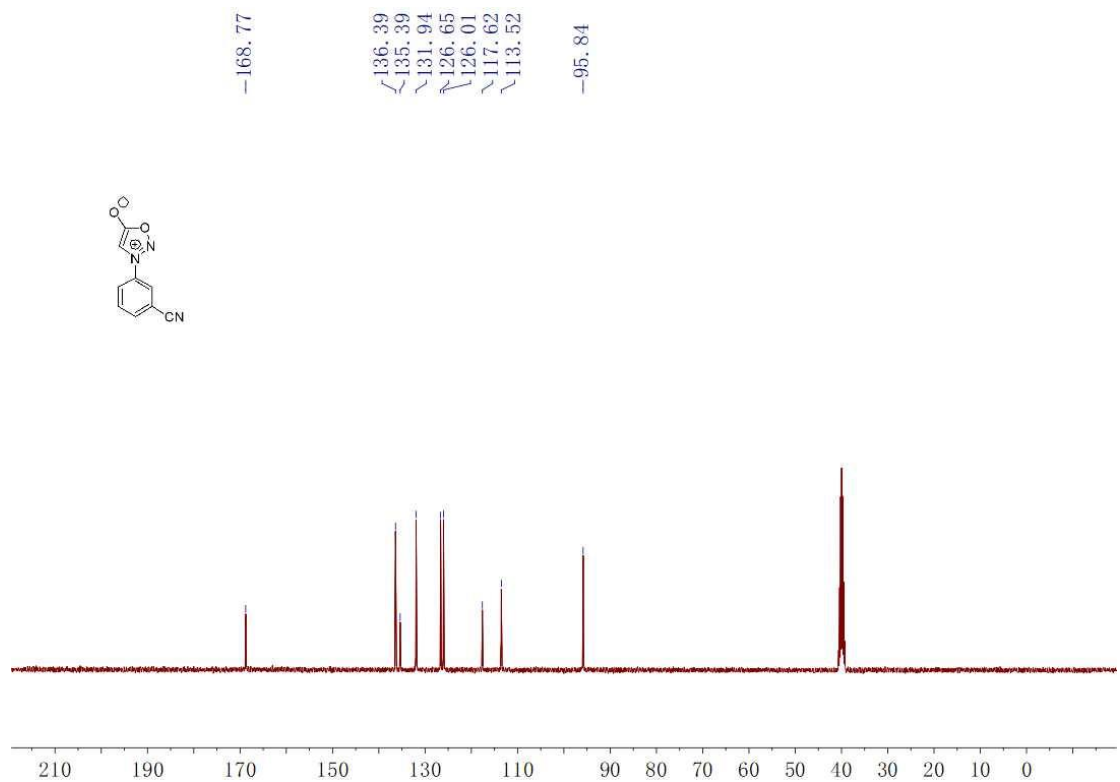
- (1) Liu, H.; Audisio, D.; Plougastel, L.; Decuypere, E.; Buisson, D.-A.; Koniev, O.; Kolodych, S.; Wagner, A.; Elhabiri, M.; Krzyczmonik, A.; Forsback, S.; Solin, O.; Gouverneur, V.; Taran, F. *Angew. Chem. Int. Ed.* **2016**, *55*, 12073.
- (2) SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

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

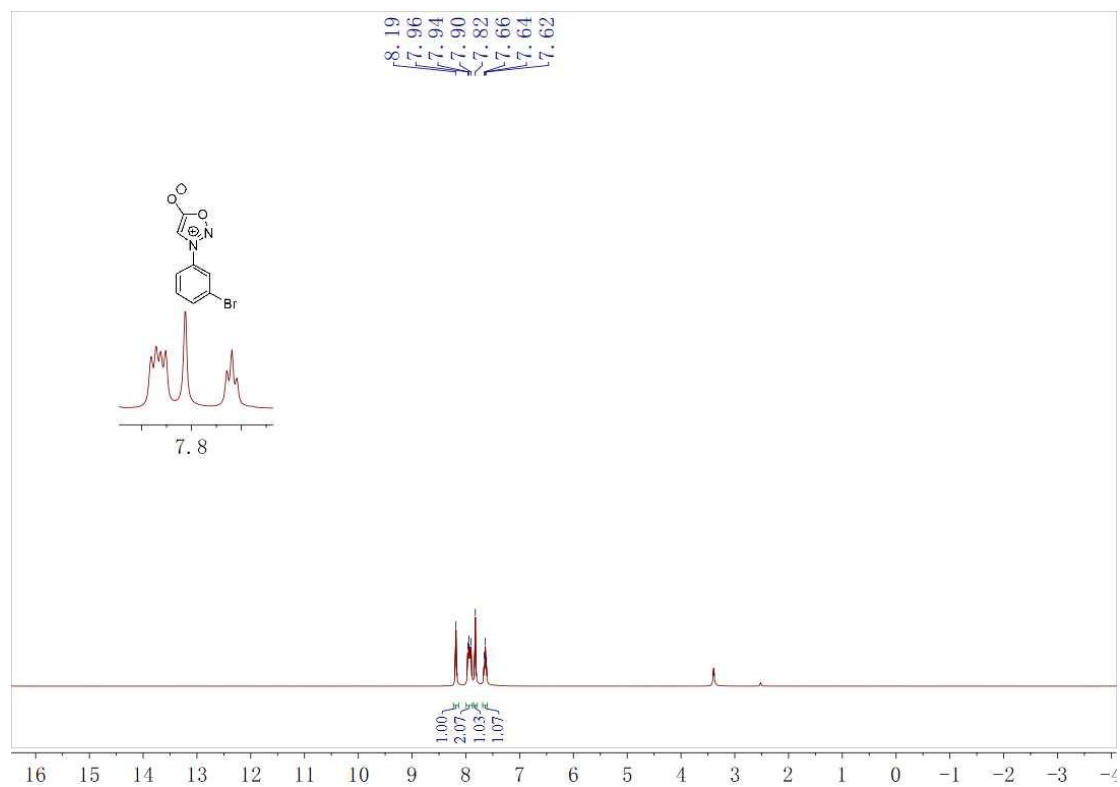
^1H NMR spectrum of **21** in $\text{DMSO-}d_6$



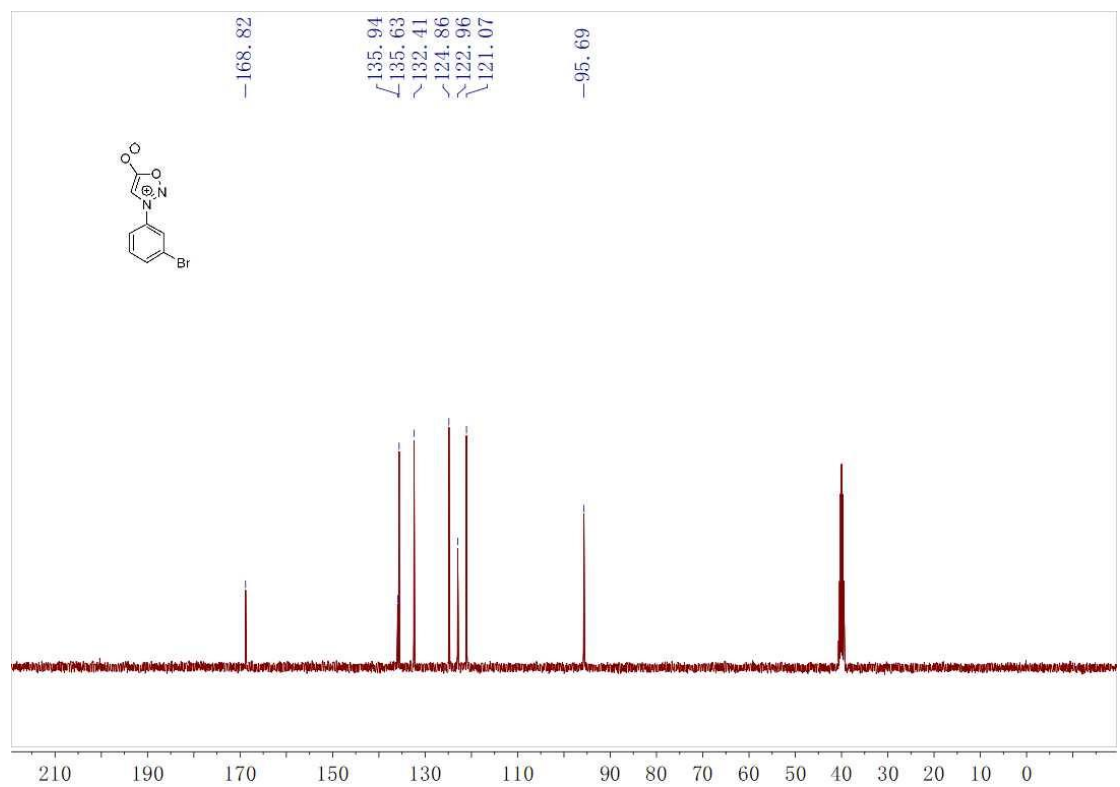
^{13}C NMR spectrum of **21** in $\text{DMSO-}d_6$



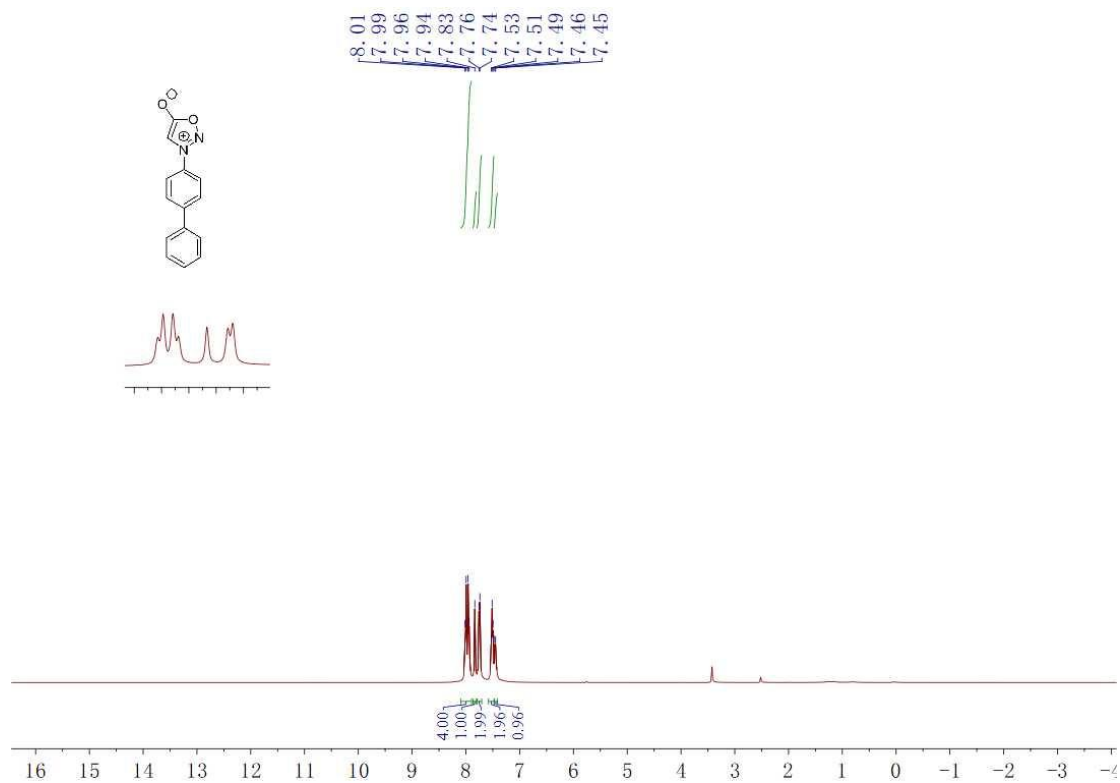
^1H NMR spectrum of **2t** in $\text{DMSO-}d_6$



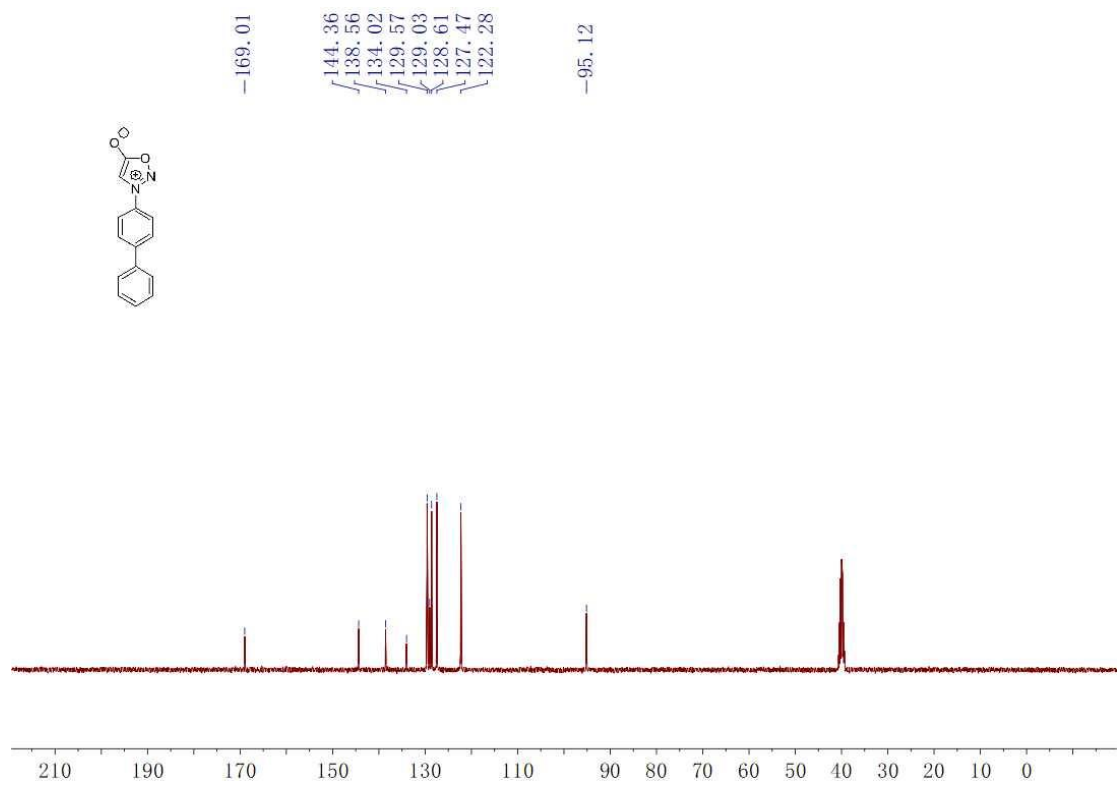
^{13}C NMR spectrum of **2t** in $\text{DMSO-}d_6$



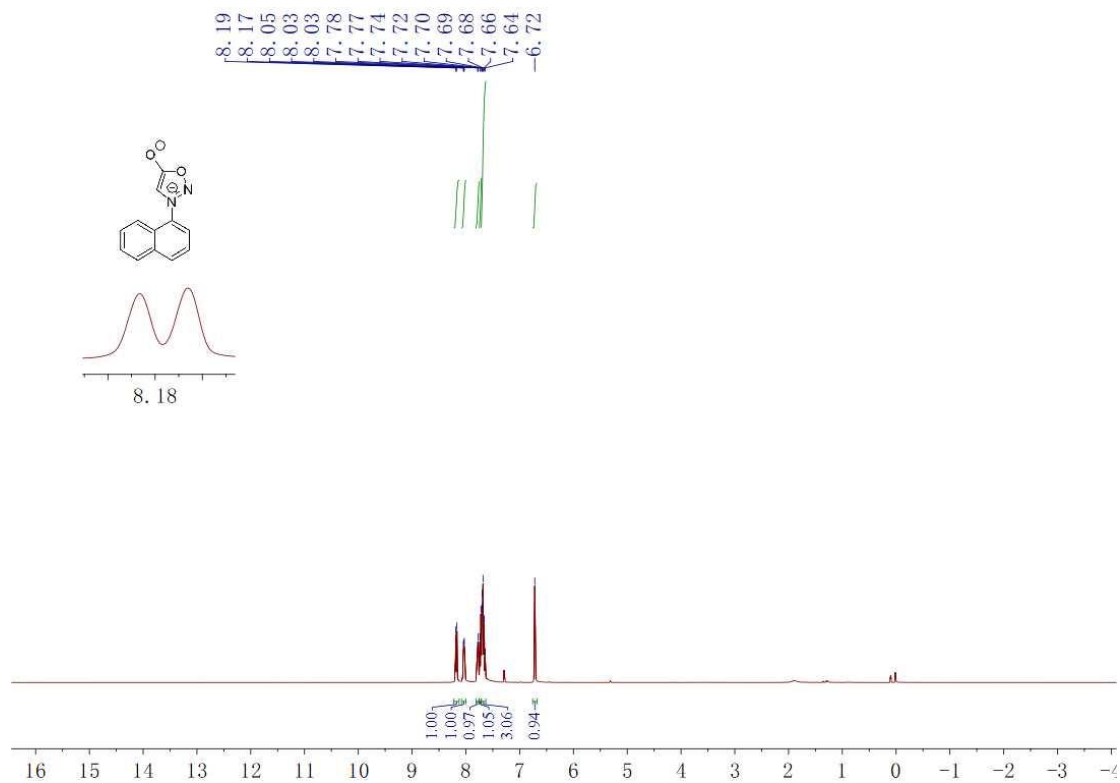
^1H NMR spectrum of **2w** in $\text{DMSO-}d_6$



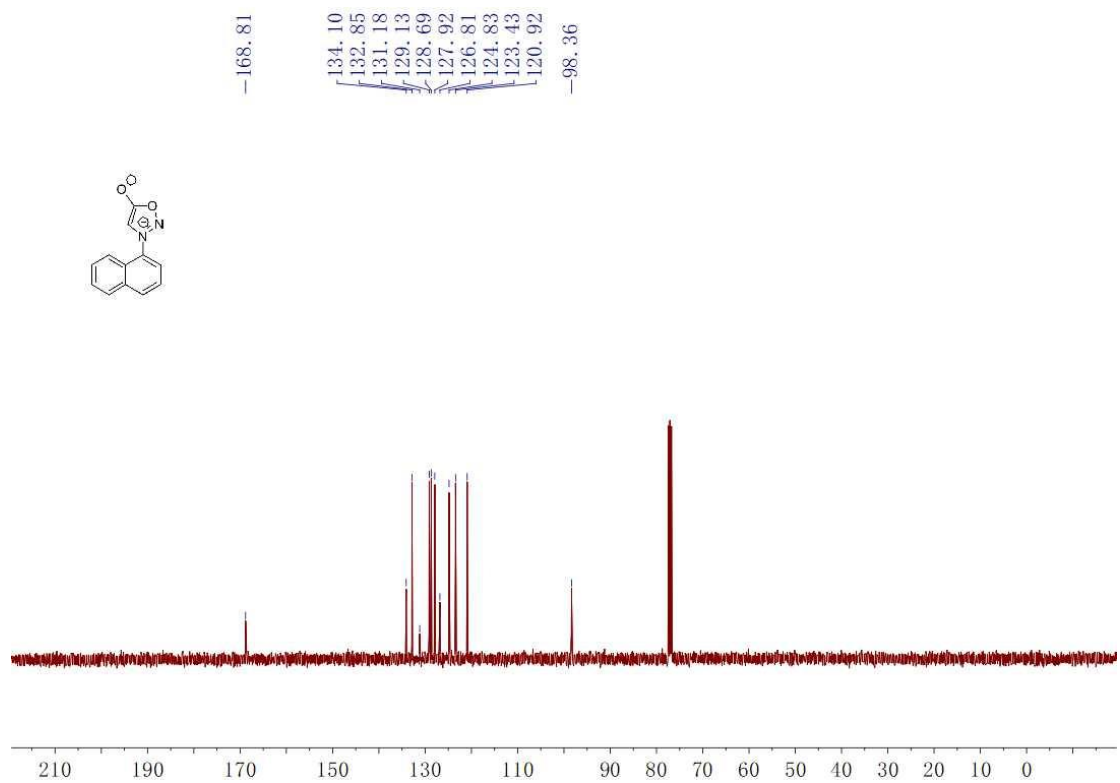
^{13}C NMR spectrum of **2w** in $\text{DMSO-}d_6$



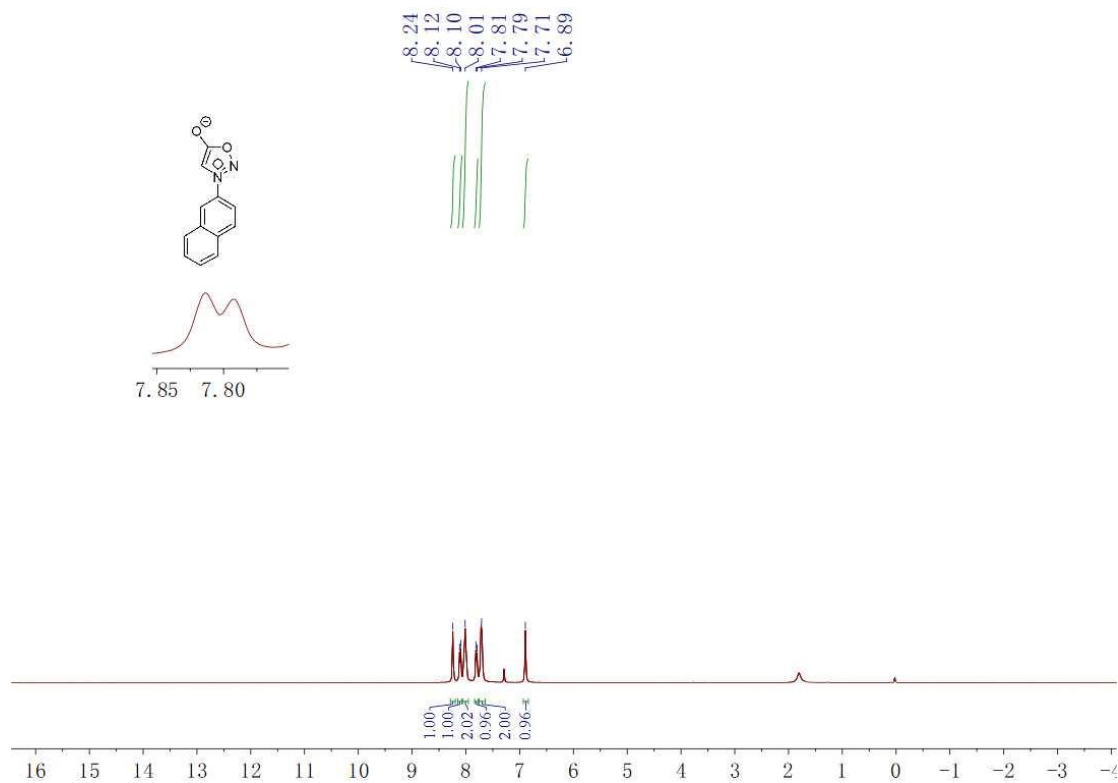
^1H NMR spectrum of **2x** in CDCl_3



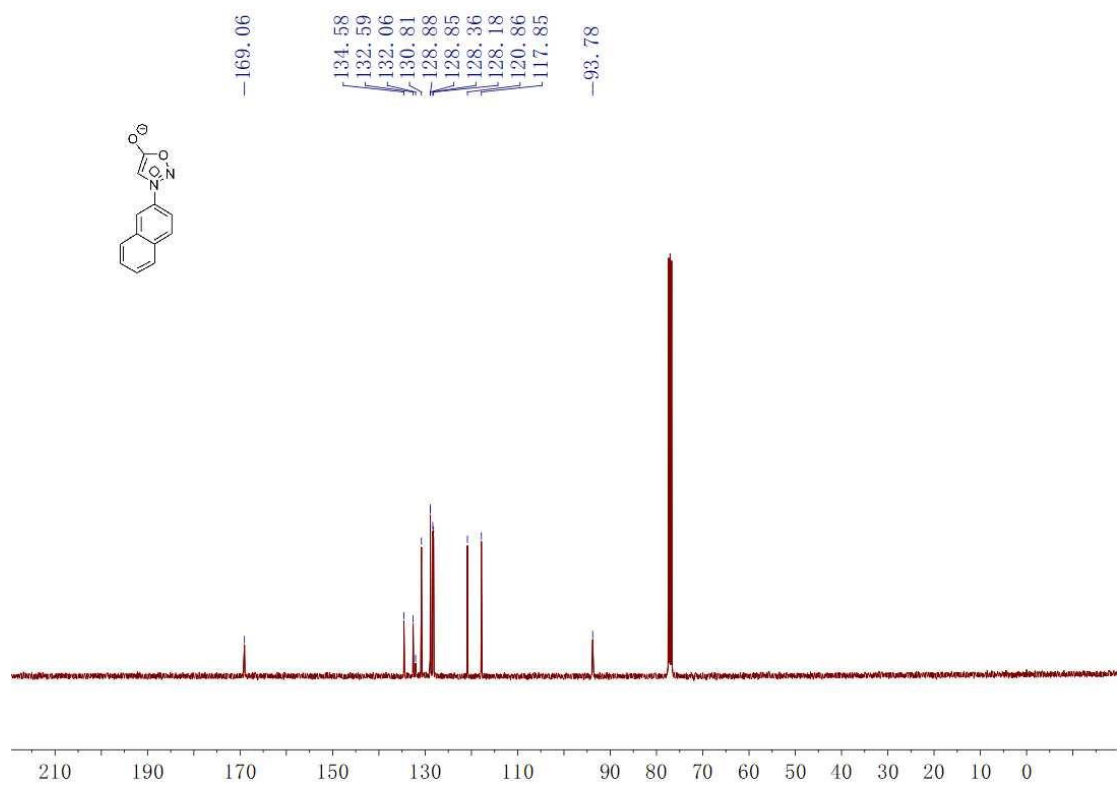
^{13}C NMR spectrum of **2x** in CDCl_3



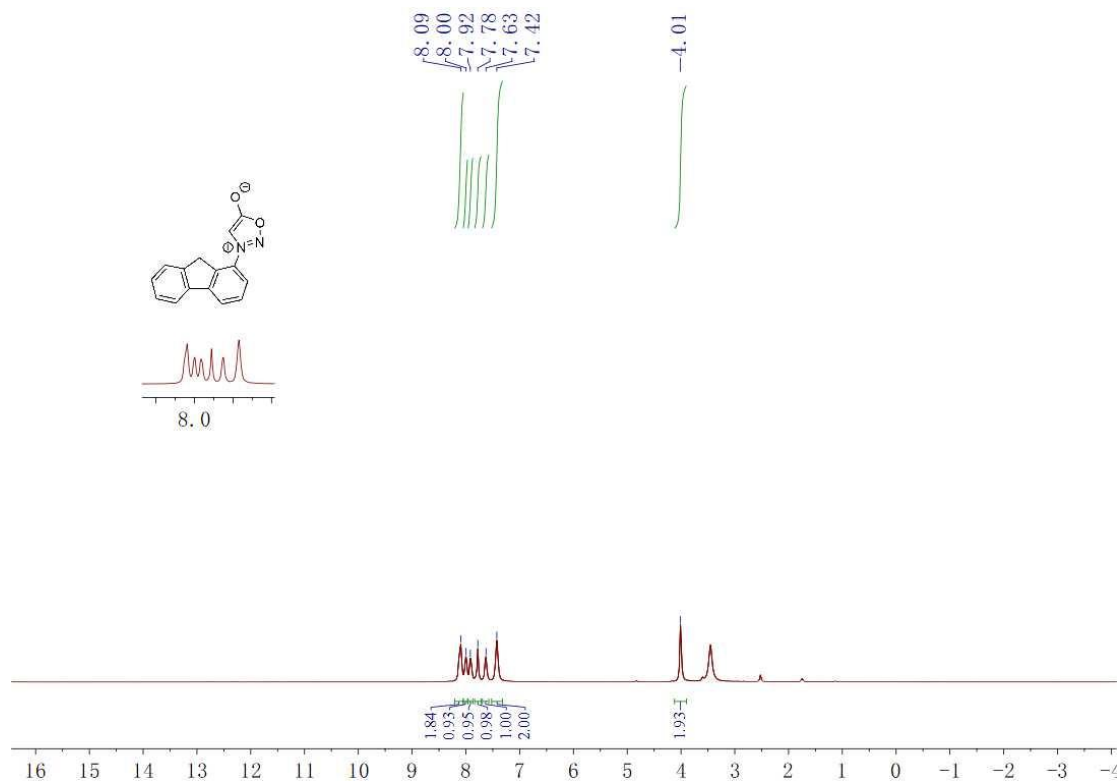
^1H NMR spectrum of **2y** in CDCl_3



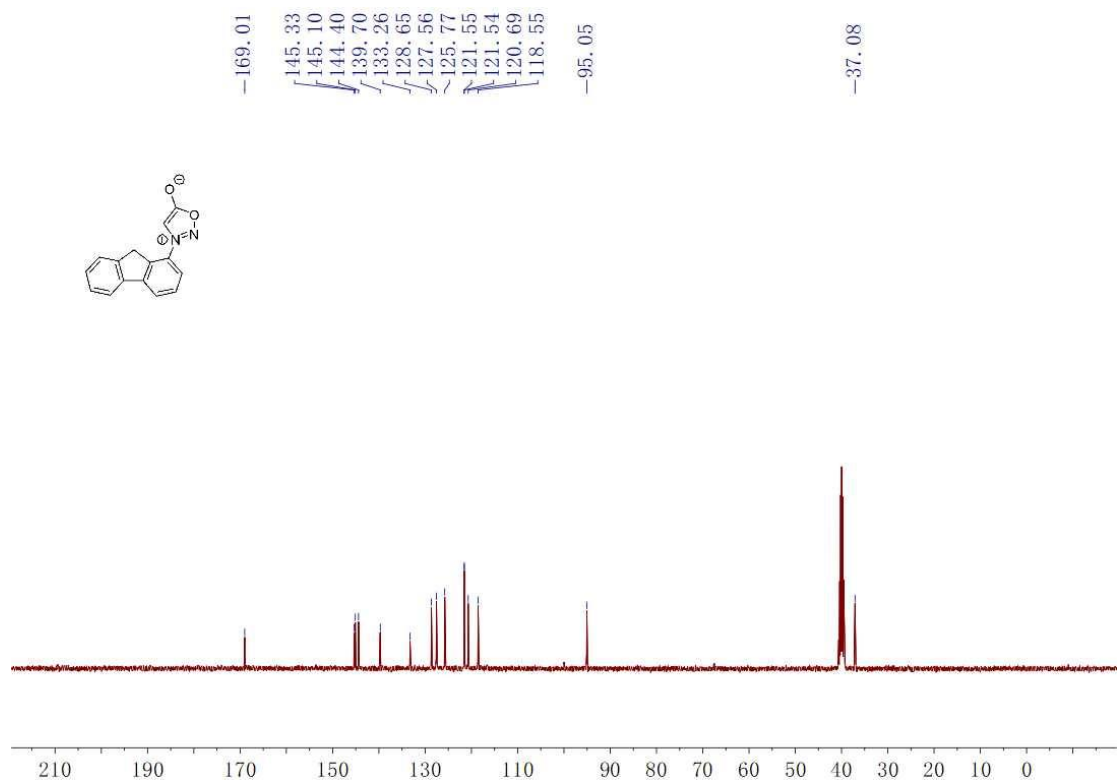
^{13}C NMR spectrum of **2y** in CDCl_3



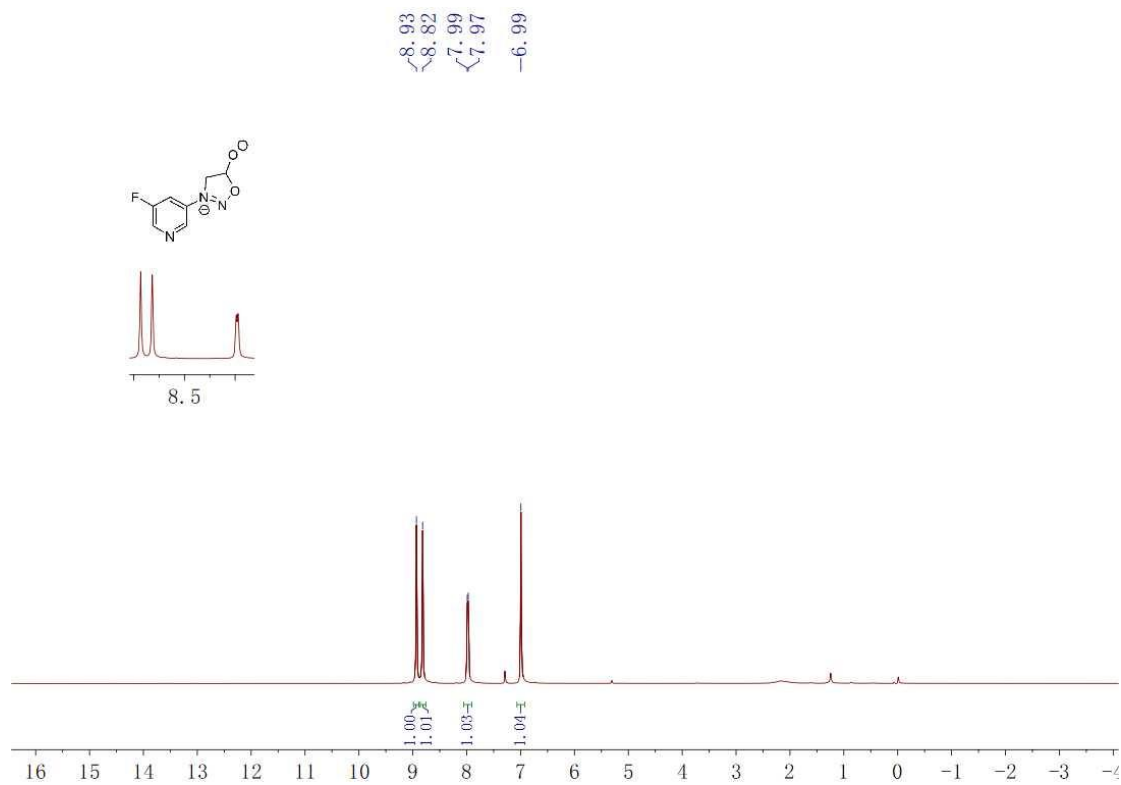
^1H NMR spectrum of **2z** in $\text{DMSO-}d_6$



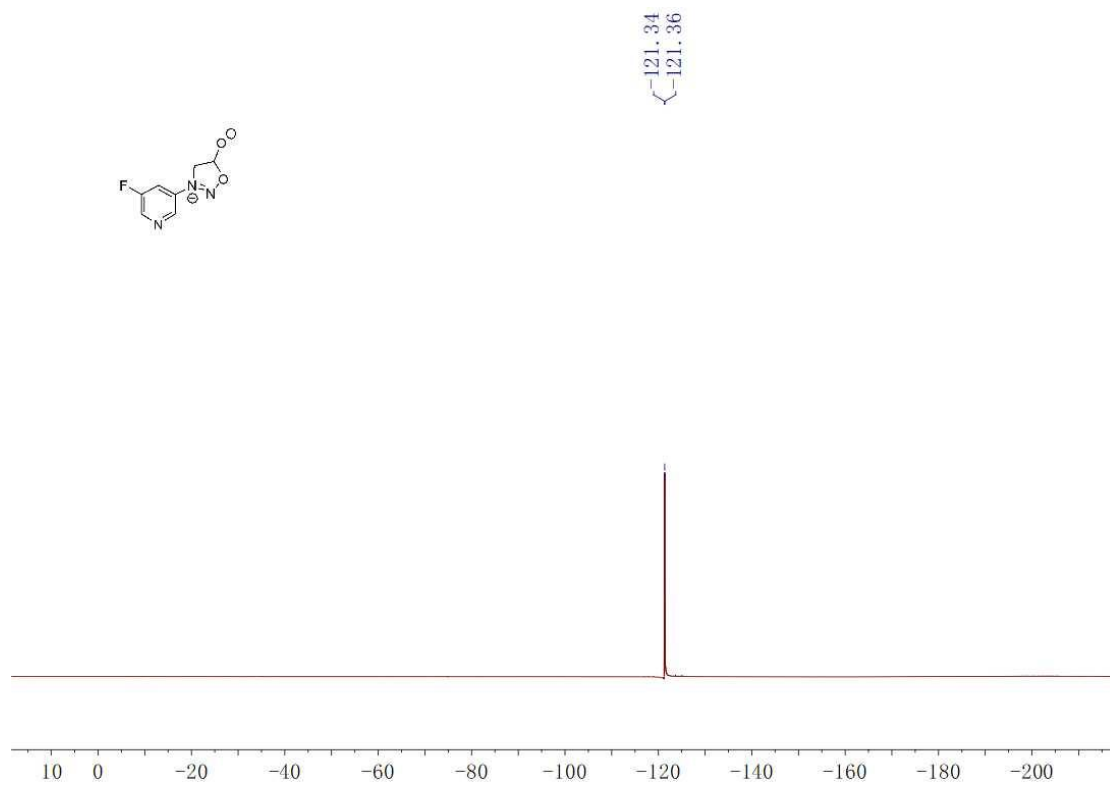
^{13}C NMR spectrum of **2z** in $\text{DMSO-}d_6$



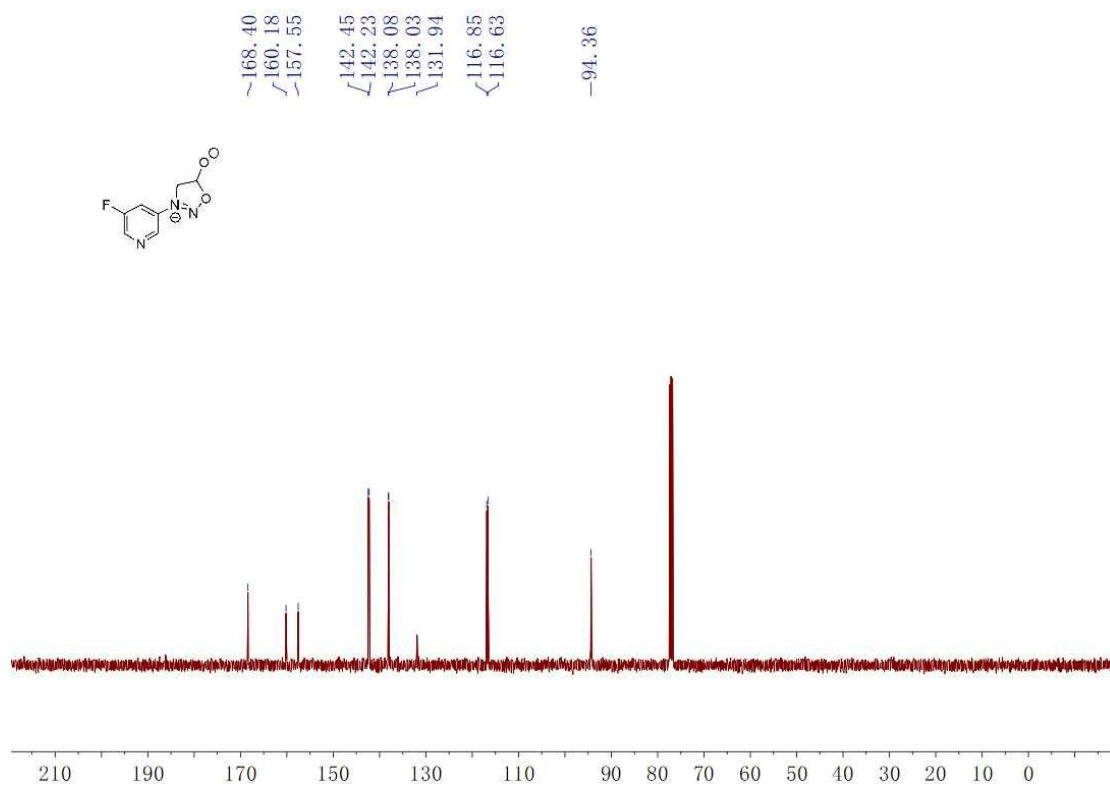
^1H NMR spectrum of **2aa** in CDCl_3



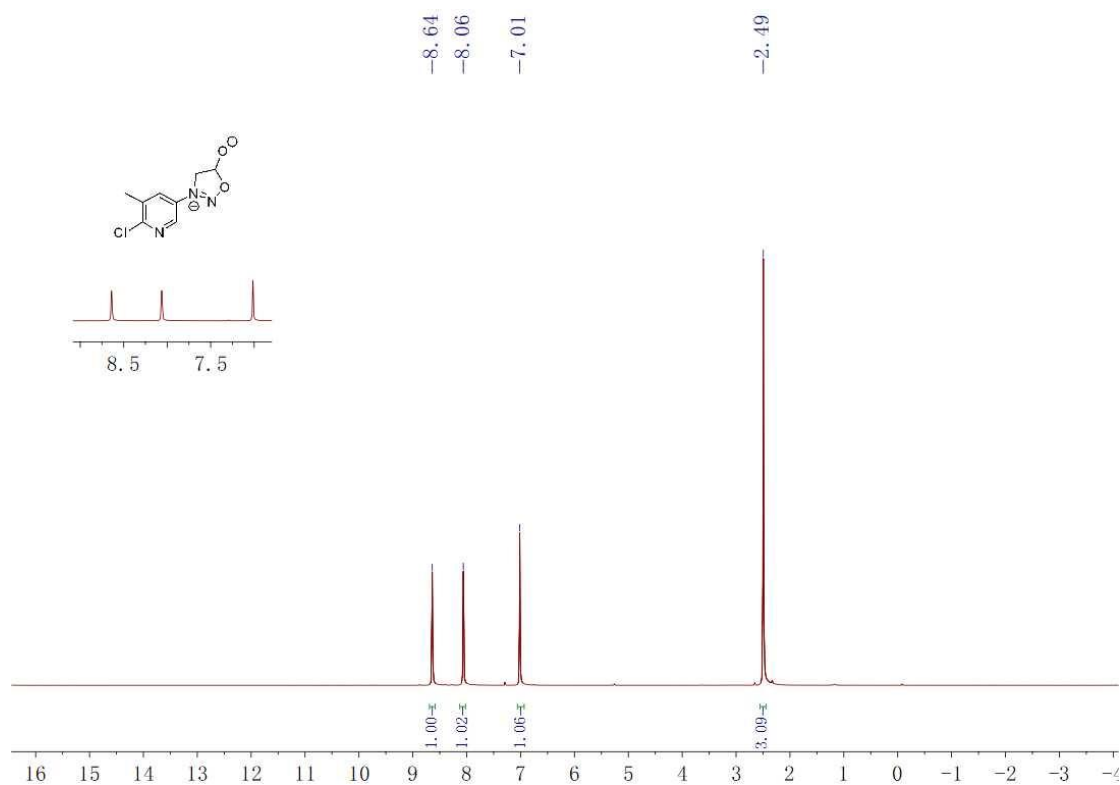
^{19}F NMR spectrum of **2aa** in CDCl_3



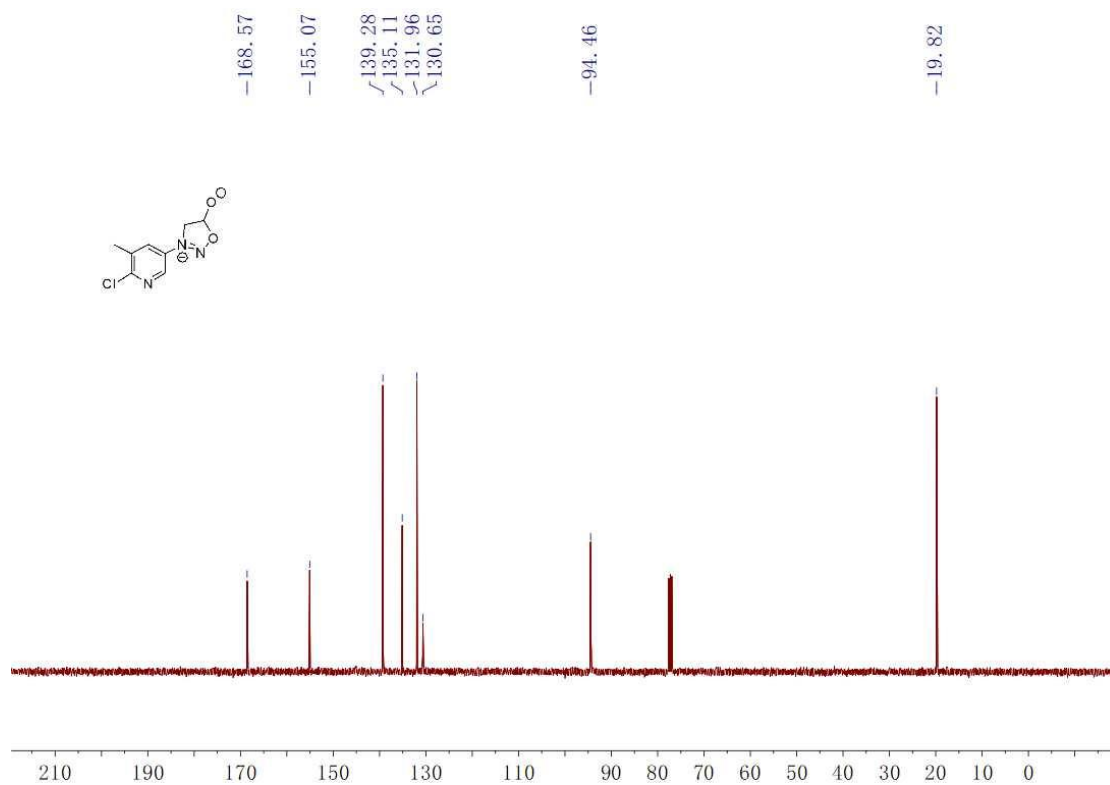
^{13}C NMR spectrum of **2aa** in CDCl_3



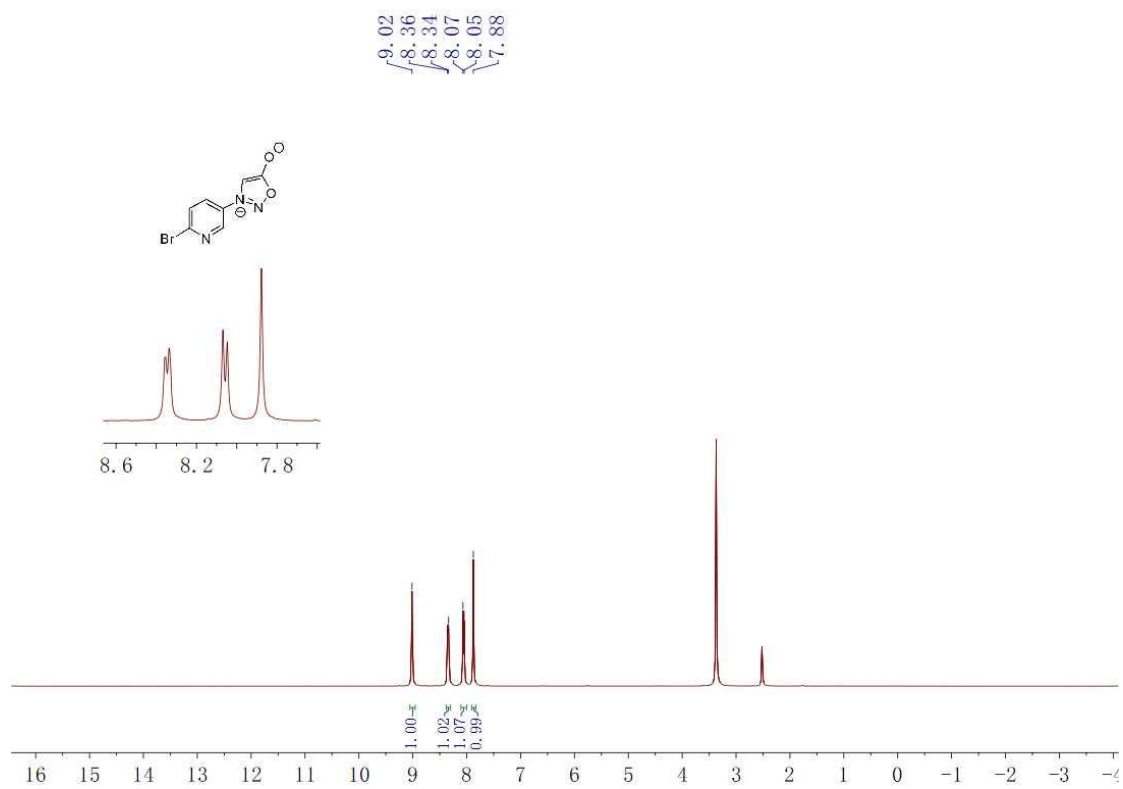
^1H NMR spectrum of **2ac** in CDCl_3



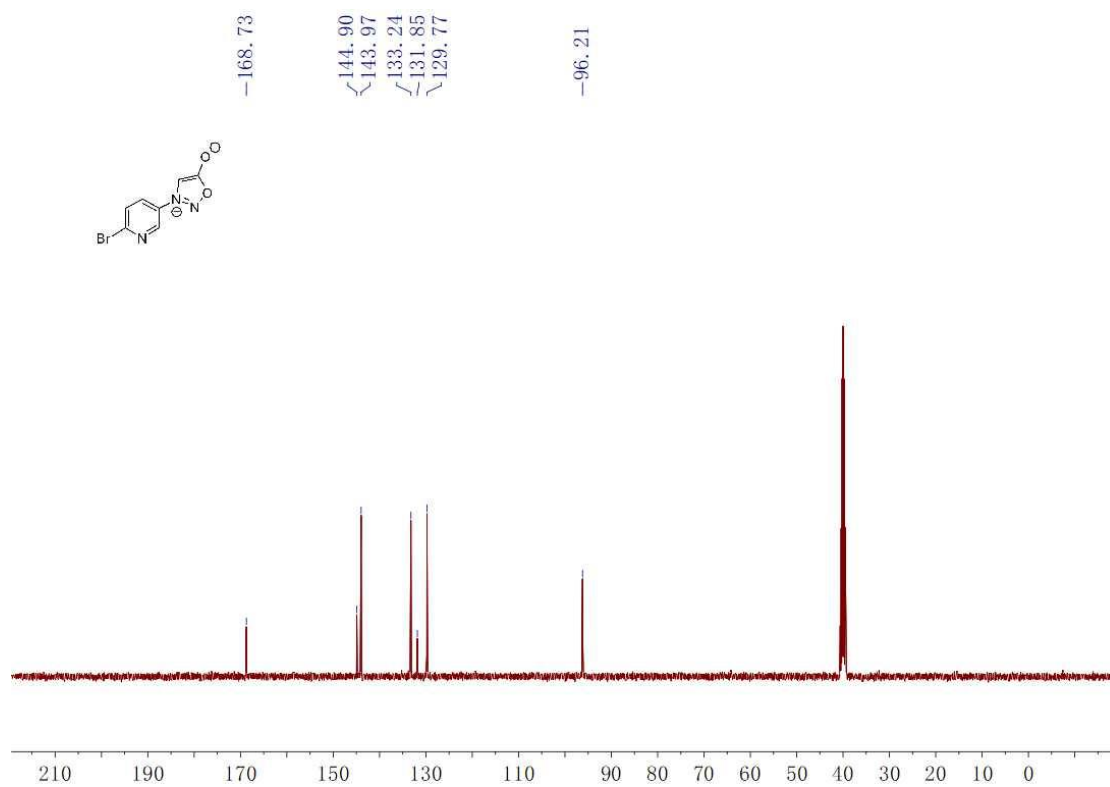
^{13}C NMR spectrum of **2ac** in CDCl_3



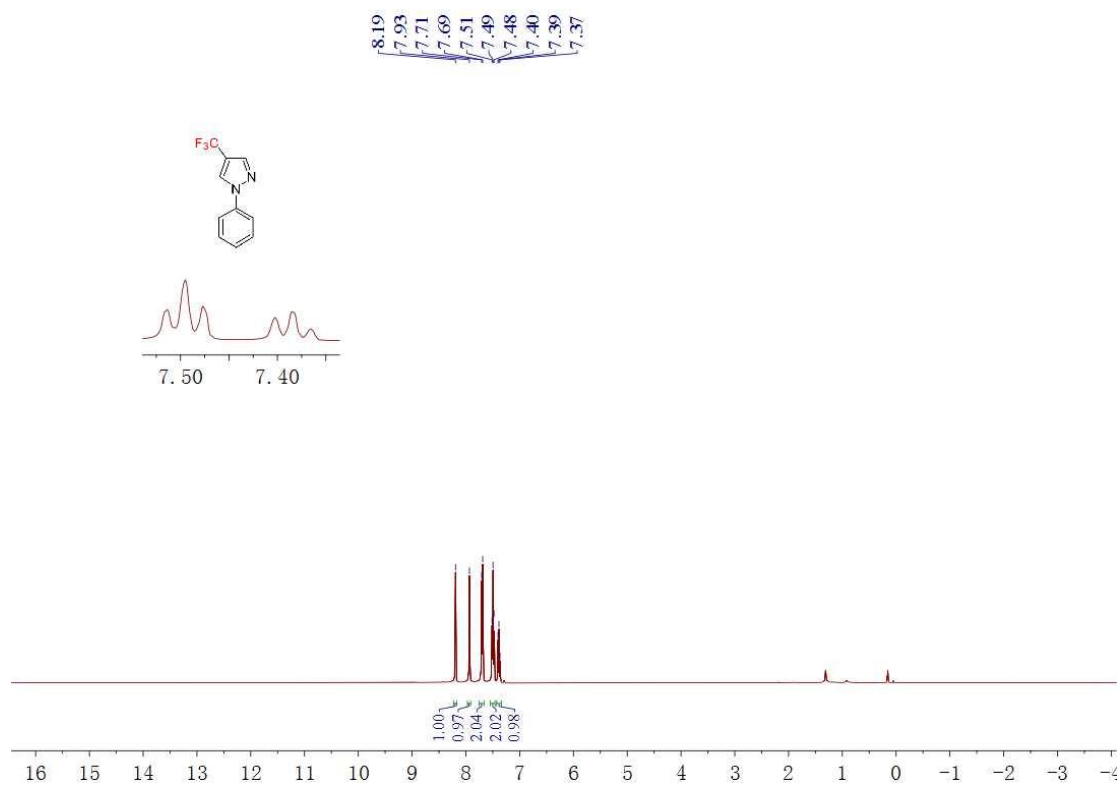
^1H NMR spectrum of **2ad** in $\text{DMSO-}d_6$



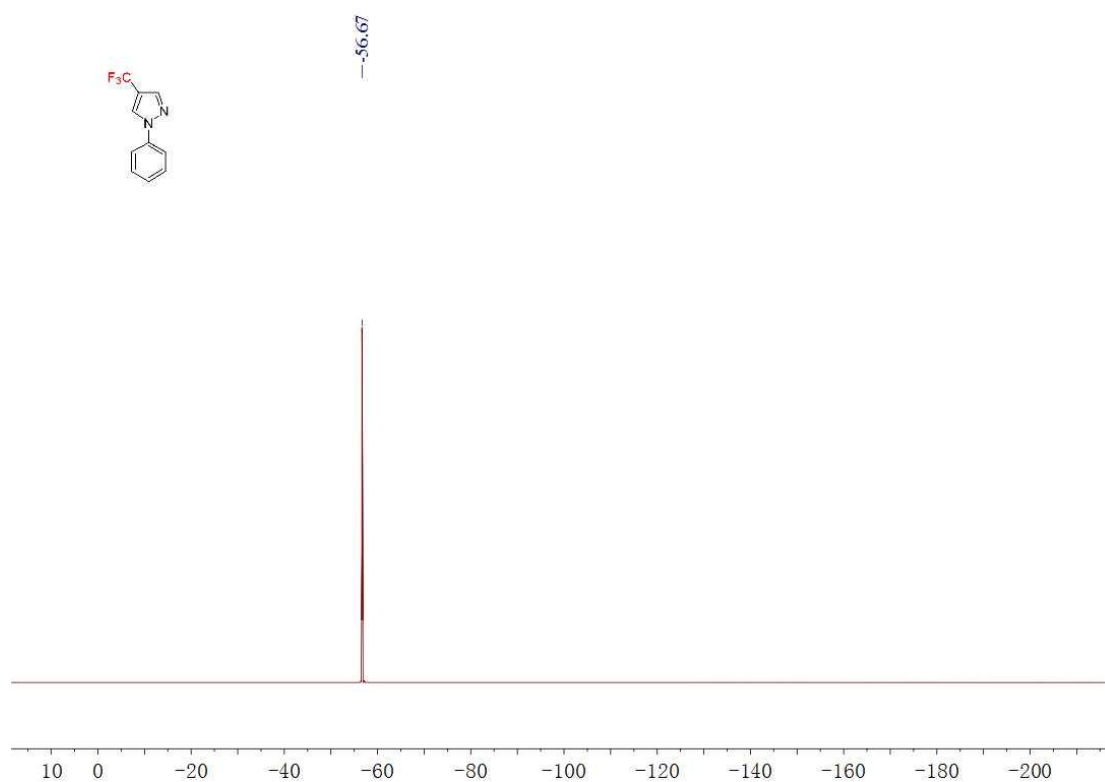
^{13}C NMR spectrum of **2ad** in $\text{DMSO-}d_6$



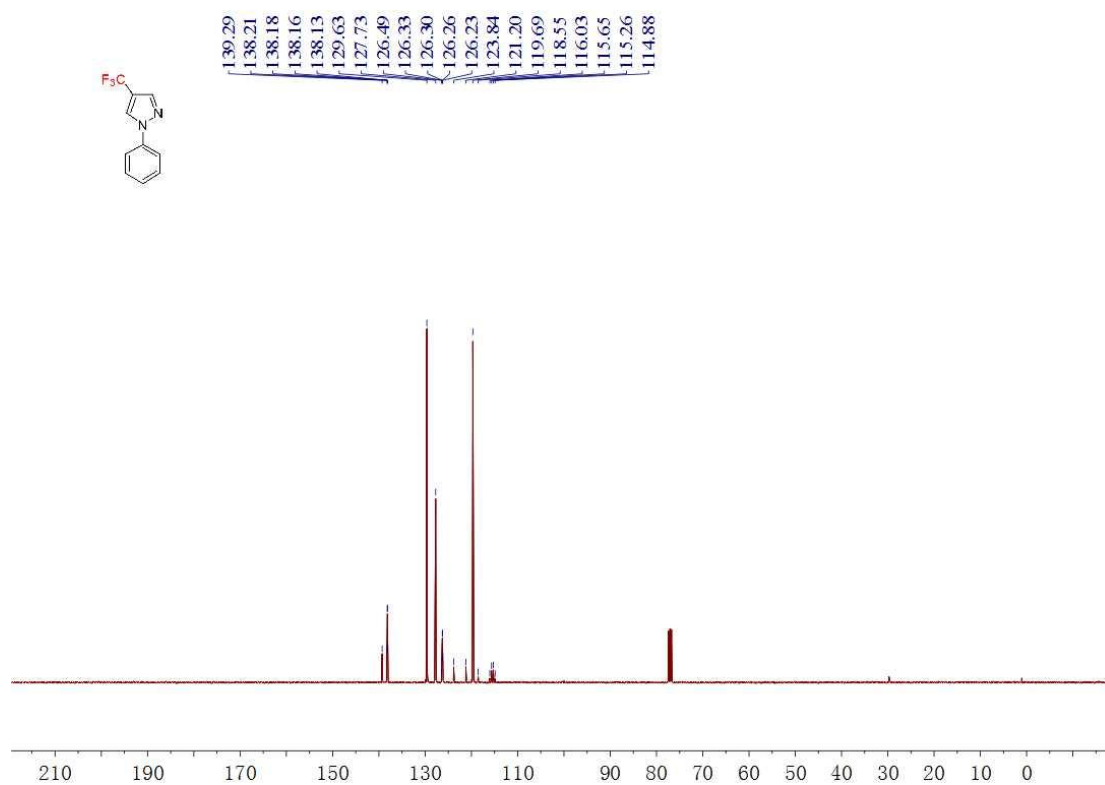
^1H NMR spectrum of **3a** in CDCl_3



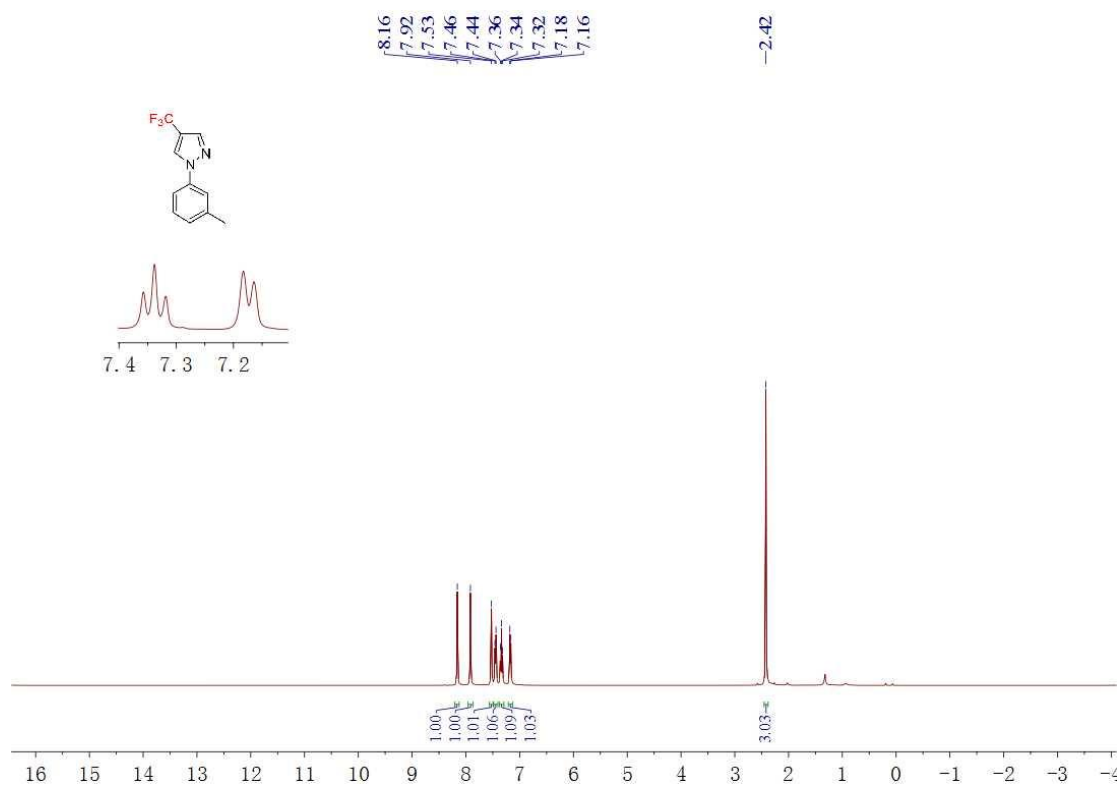
¹⁹F NMR spectrum of **3a** in CDCl₃



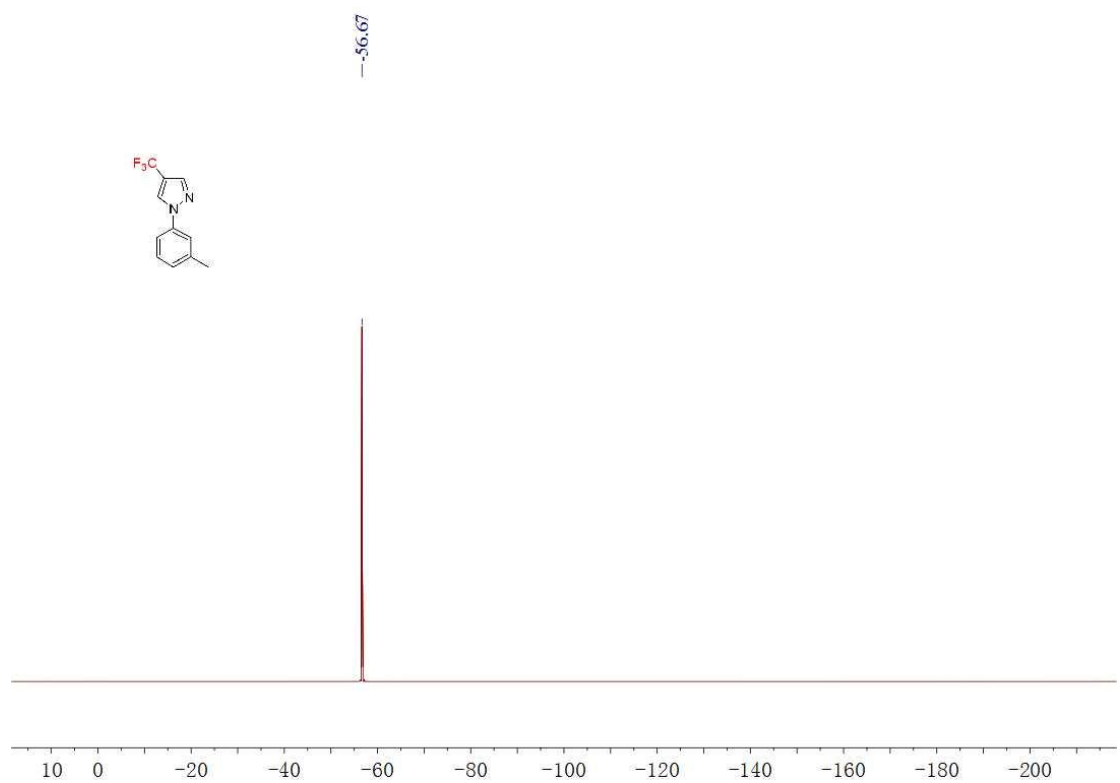
¹³C NMR spectrum of **3a** in CDCl₃



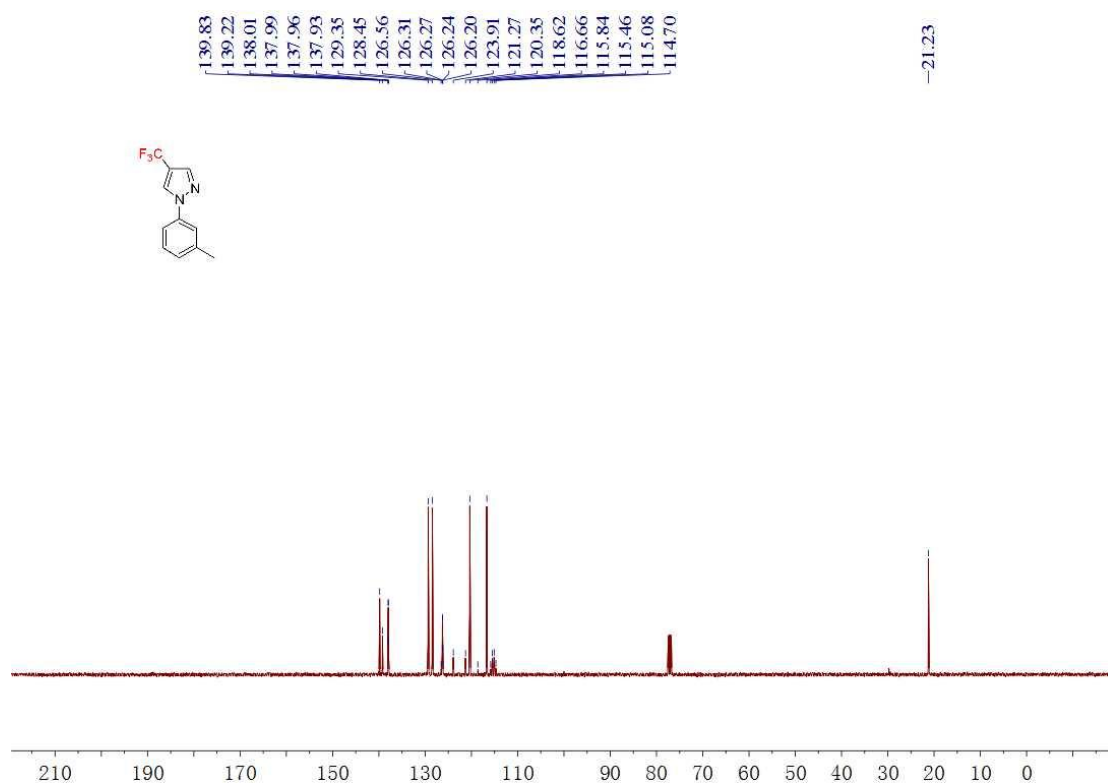
^1H NMR spectrum of **3b** in CDCl_3



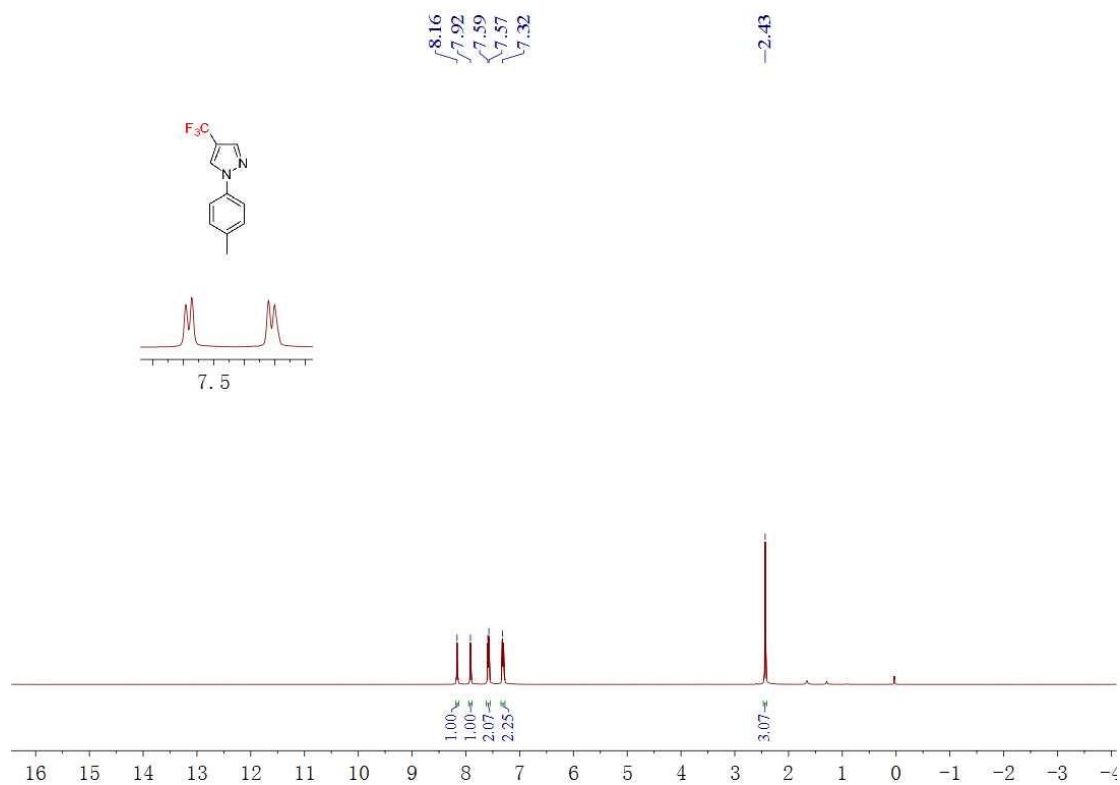
^{19}F NMR spectrum of **3b** in CDCl_3



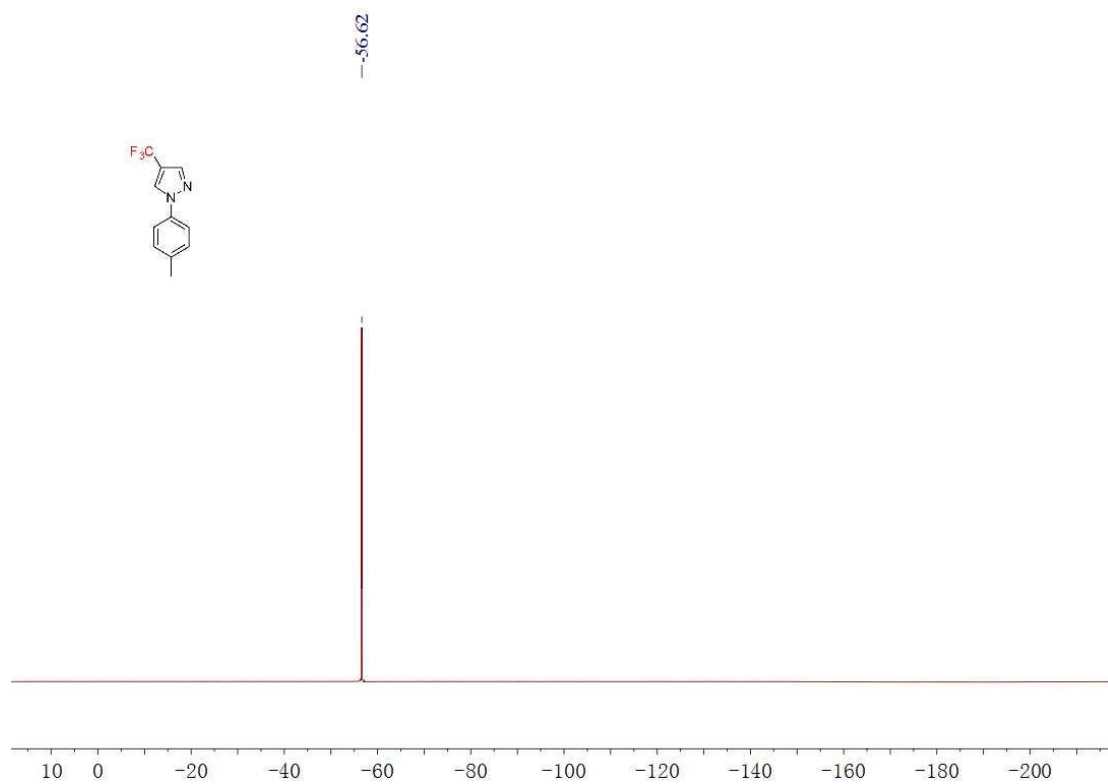
^{13}C NMR spectrum of **3b** in CDCl_3



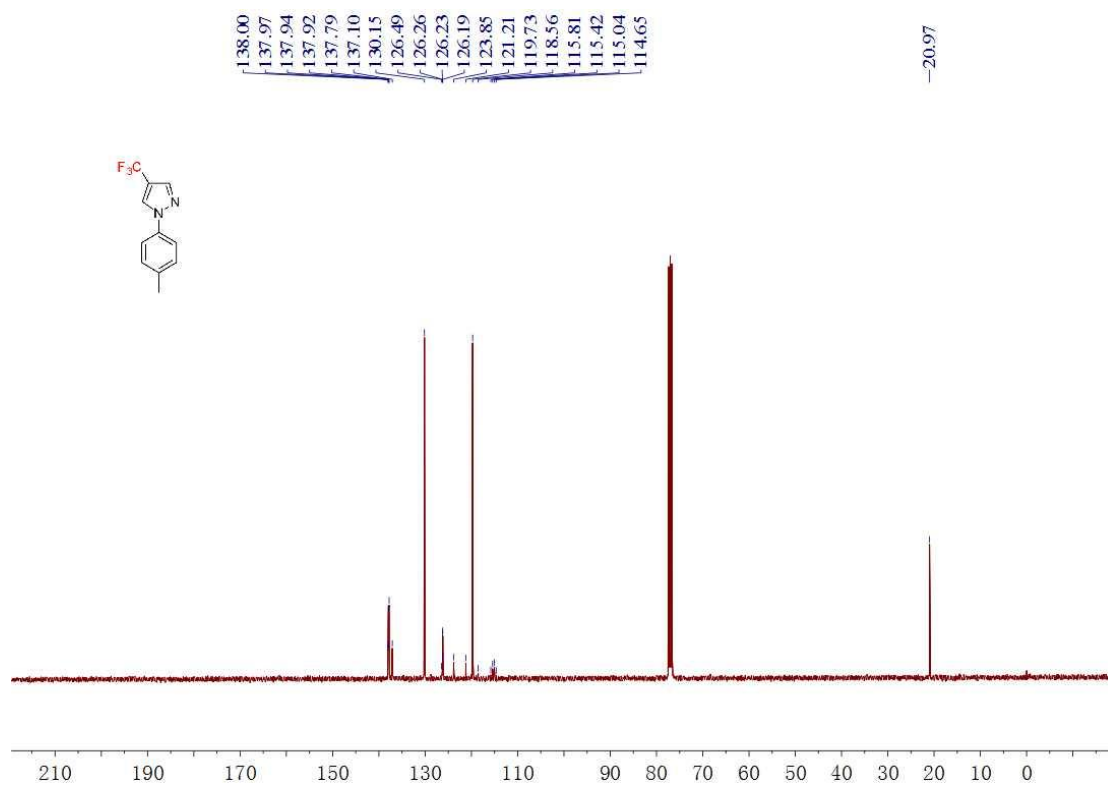
^1H NMR spectrum of **3c** in CDCl_3



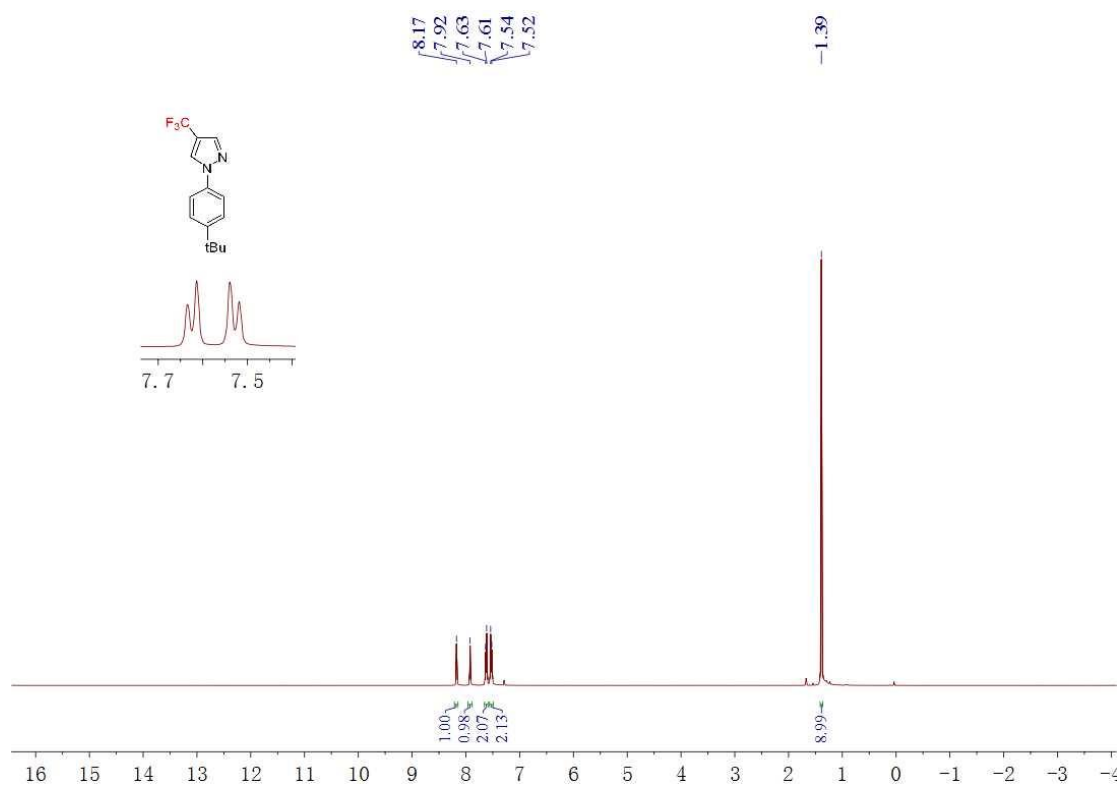
^{19}F NMR spectrum of **3c** in CDCl_3



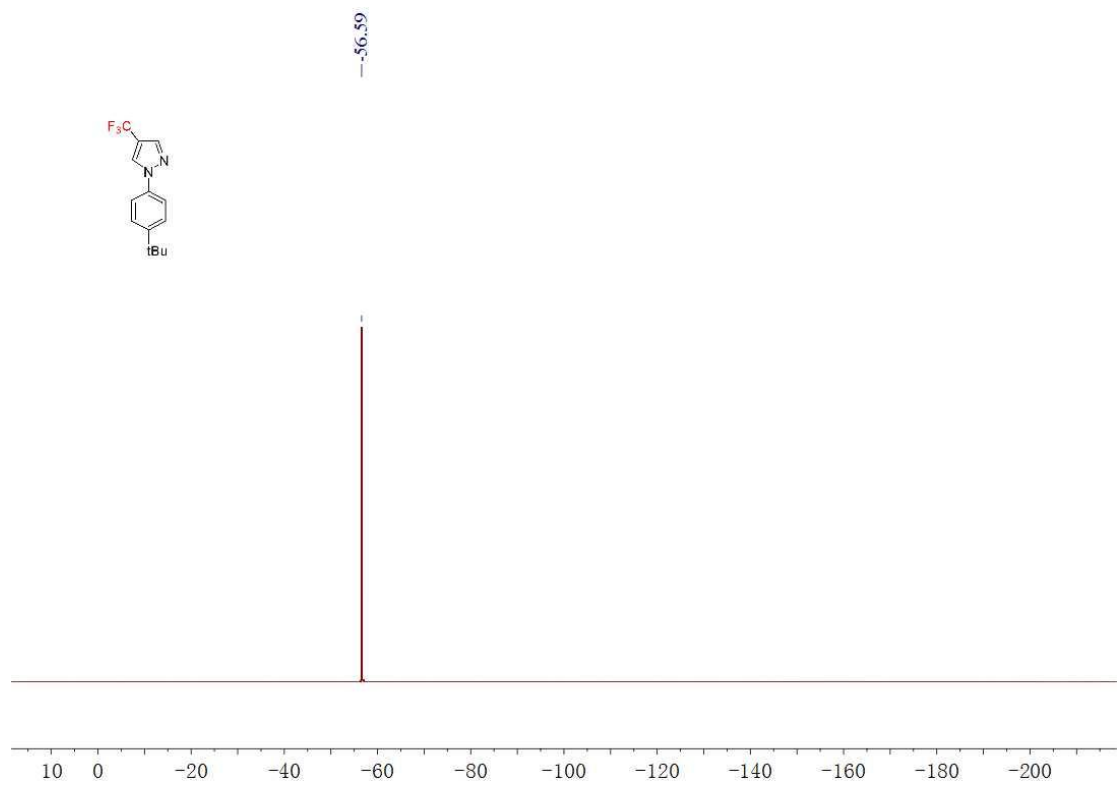
^{13}C NMR spectrum of **3c** in CDCl_3



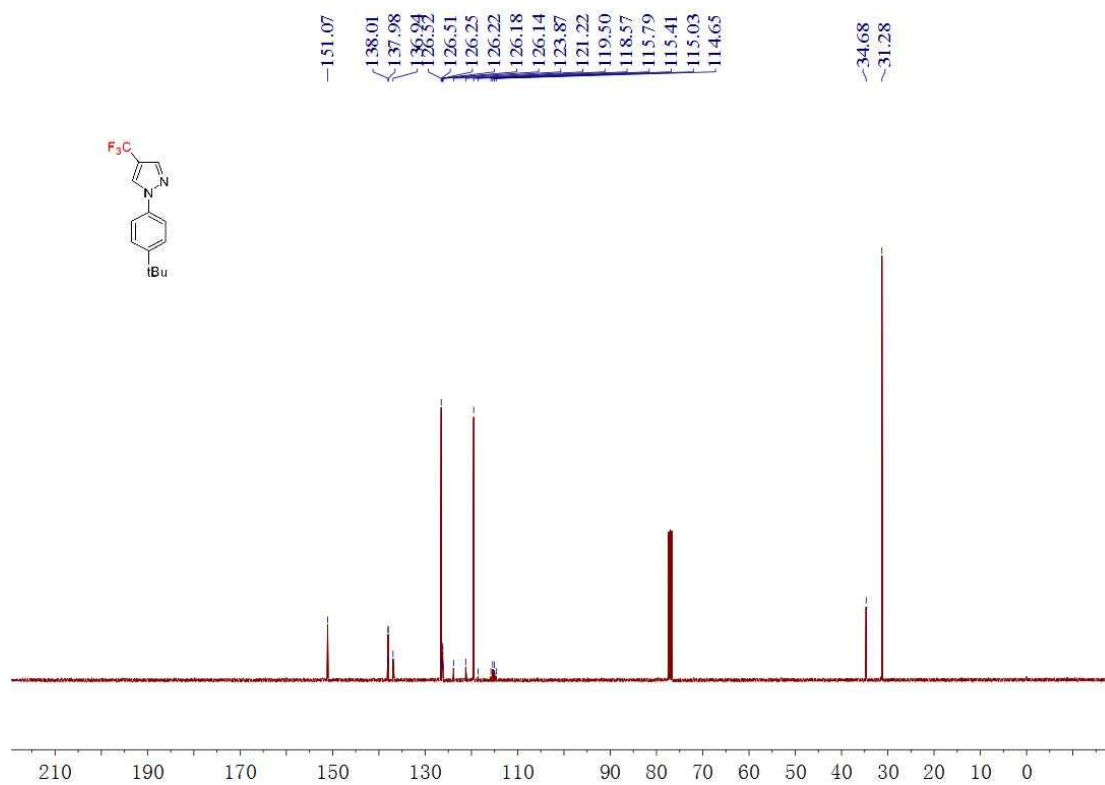
^1H NMR spectrum of **3d** in CDCl_3



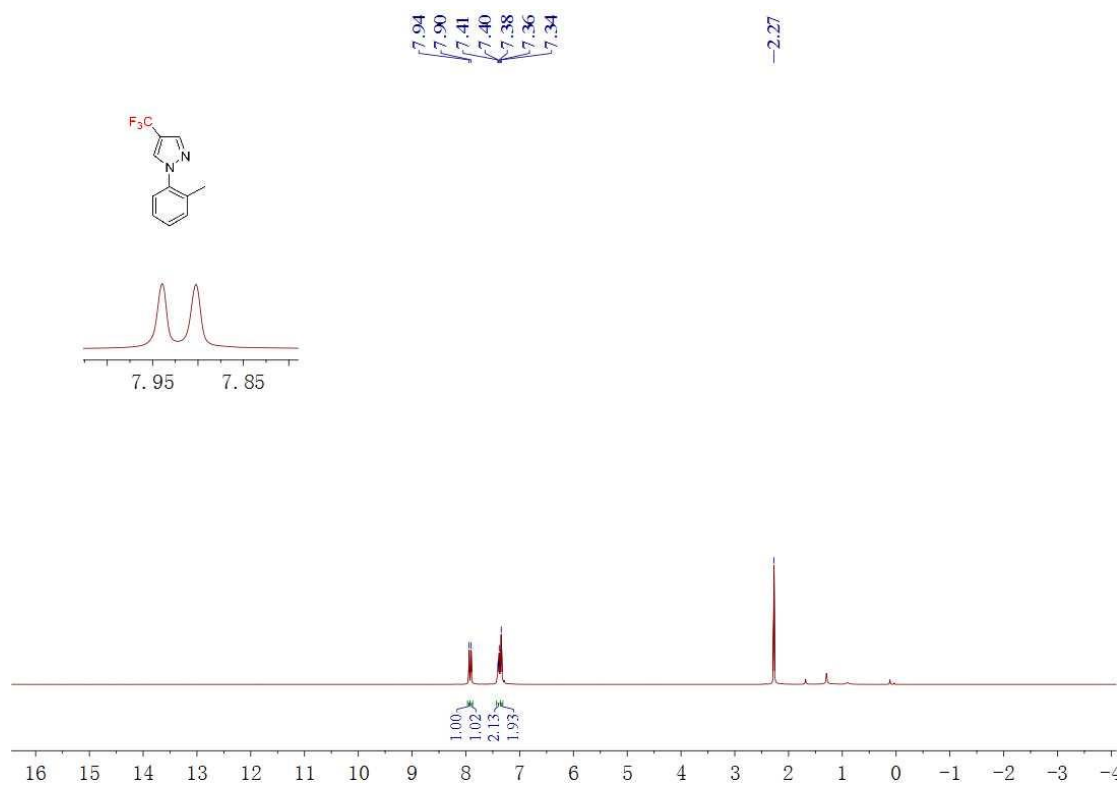
^{19}F NMR spectrum of **3d** in CDCl_3



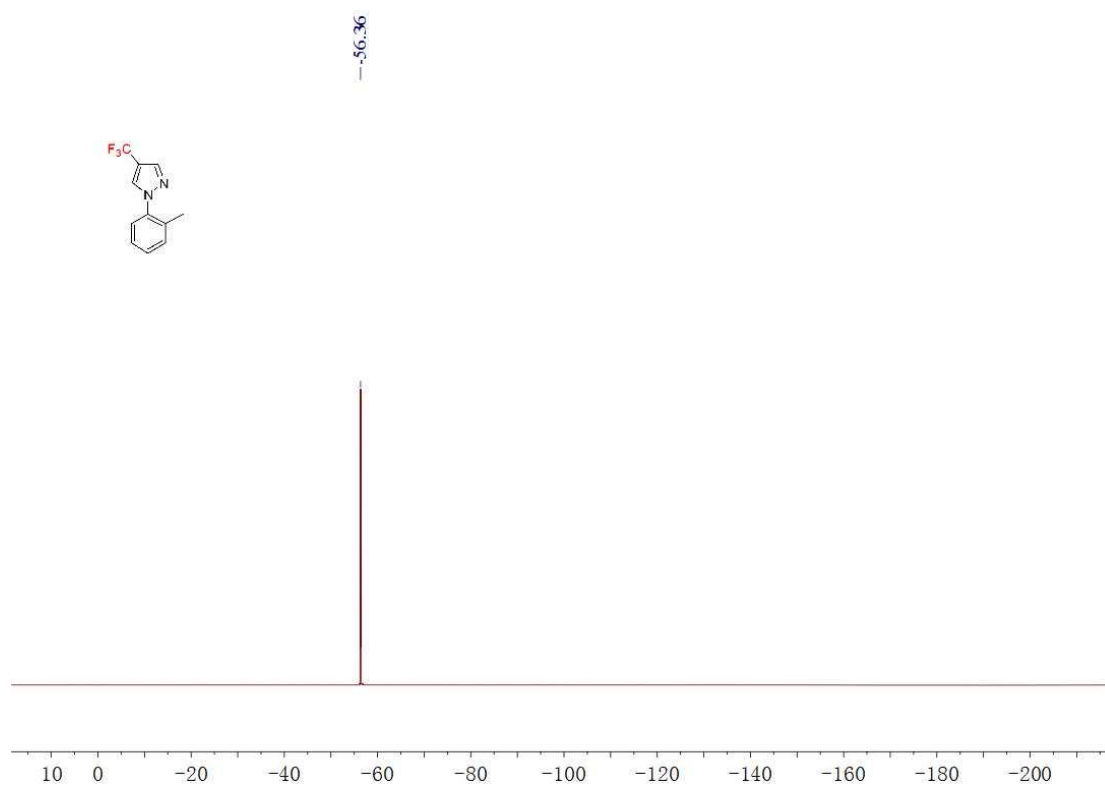
^{13}C NMR spectrum of **3d** in CDCl_3



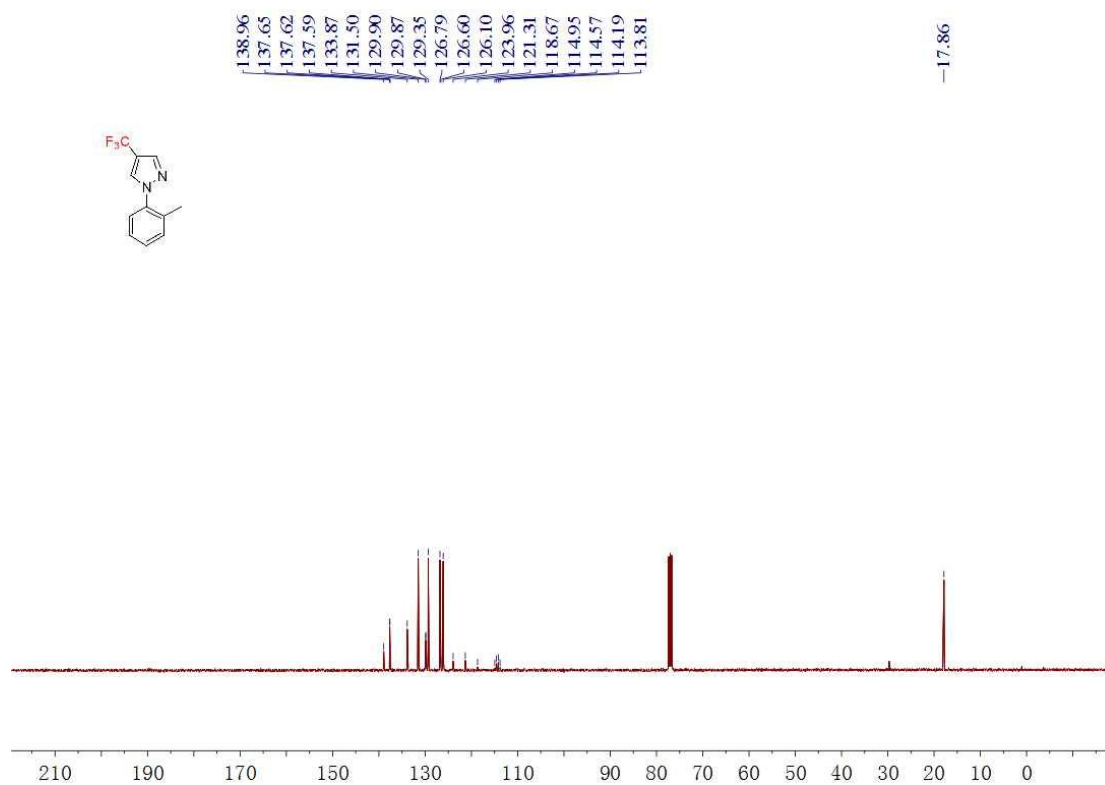
^1H NMR spectrum of **3e** in CDCl_3



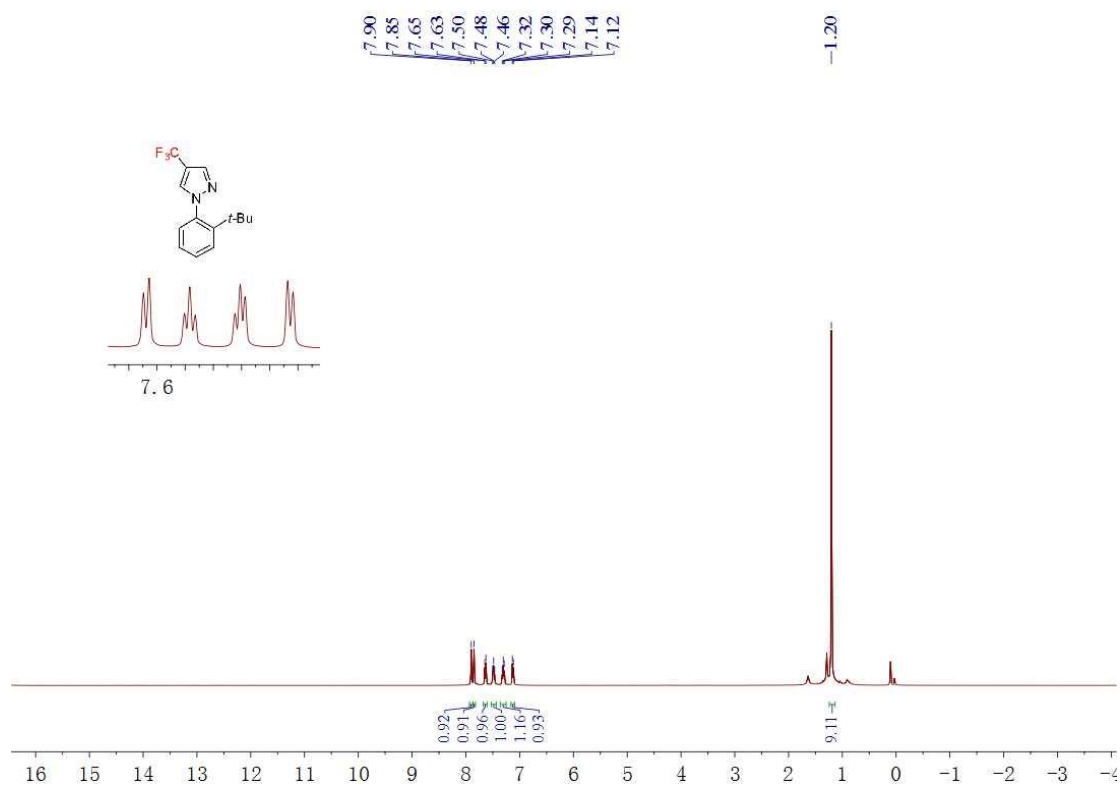
^{19}F NMR spectrum of **3e** in CDCl_3



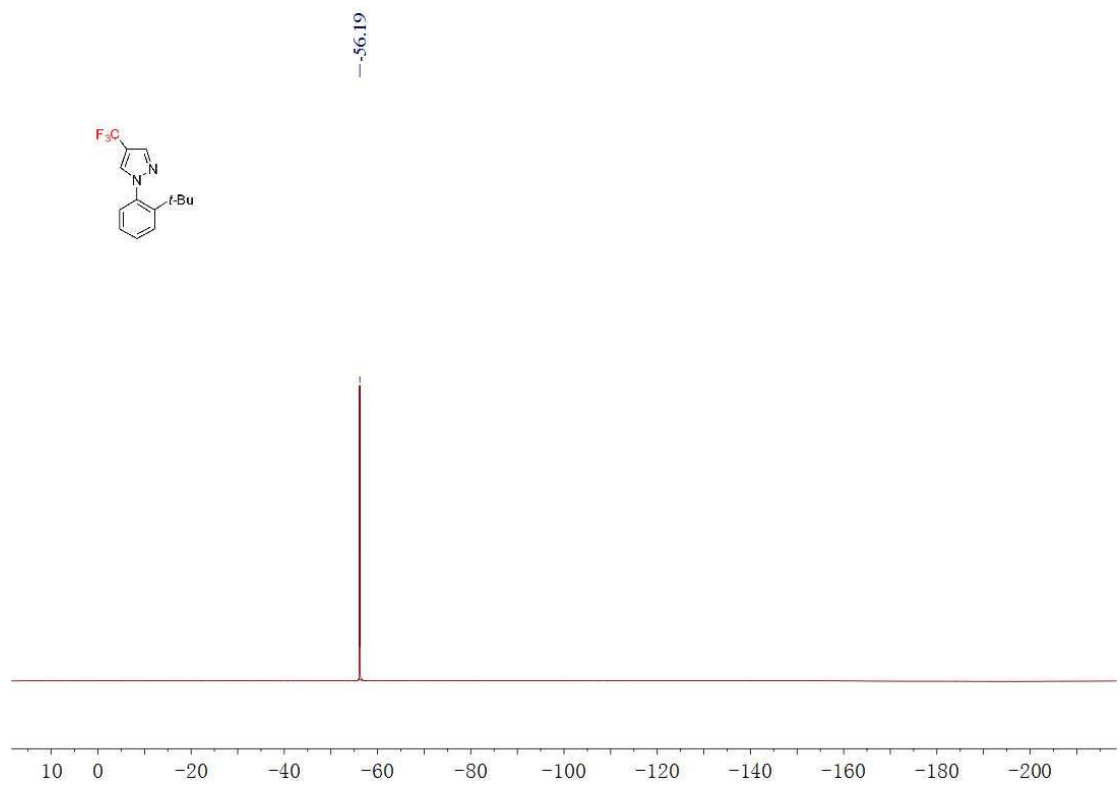
^{13}C NMR spectrum of **3e** in CDCl_3



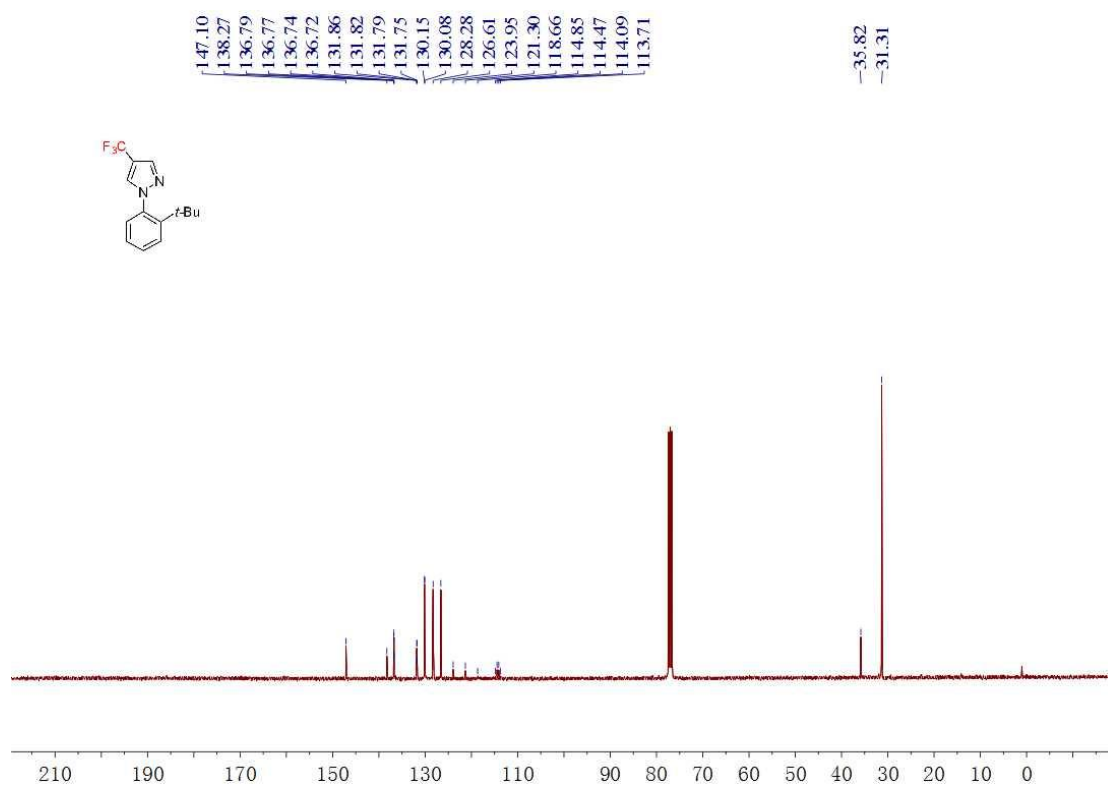
^1H NMR spectrum of **3f** in CDCl_3



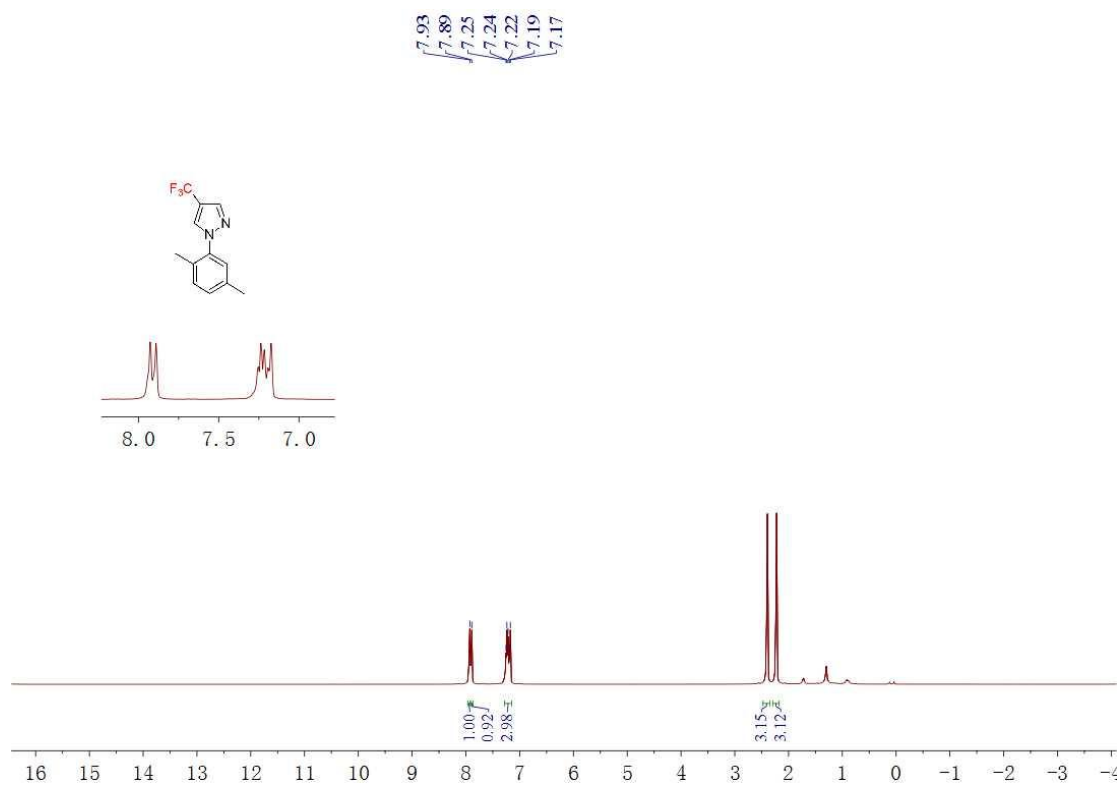
^{19}F NMR spectrum of **3f** in CDCl_3



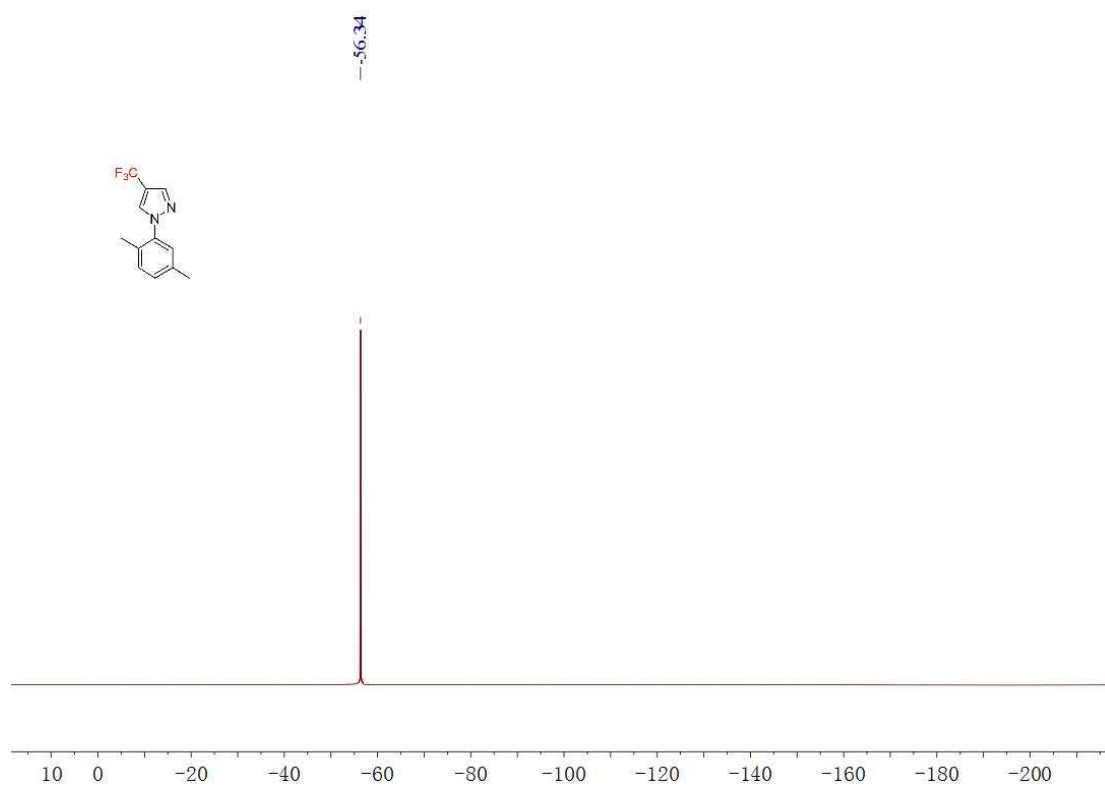
^{13}C NMR spectrum of **3f** in CDCl_3



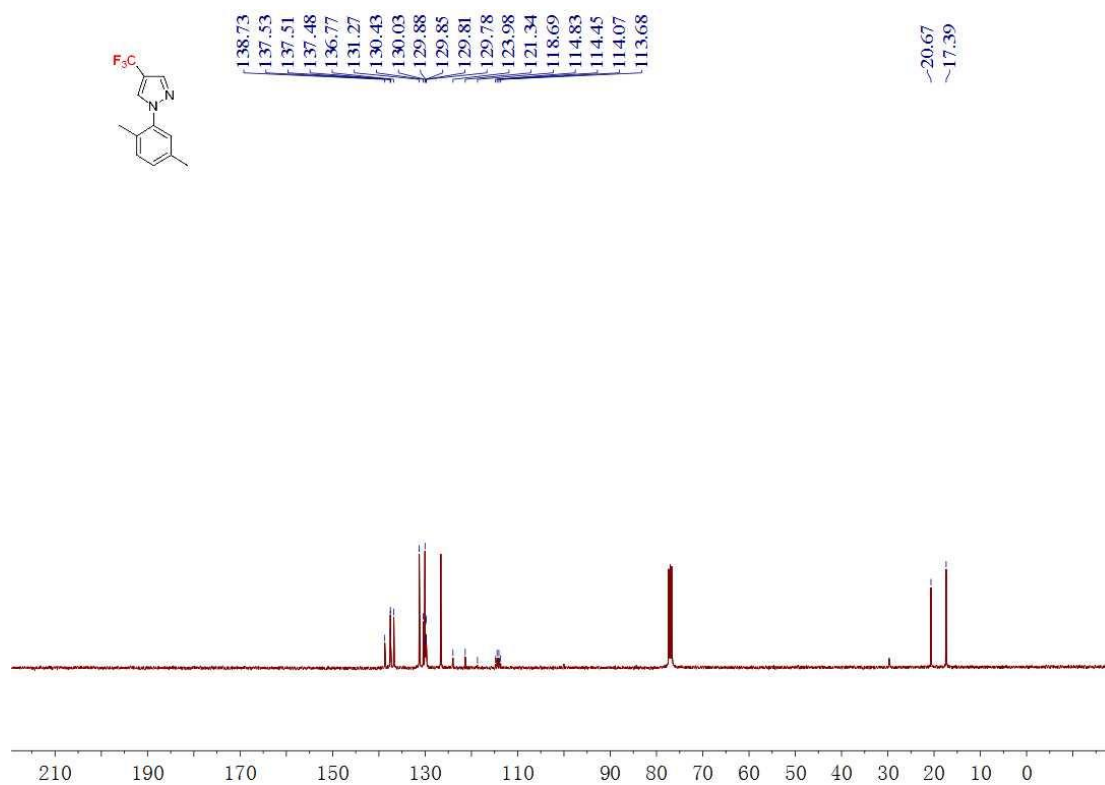
^1H NMR spectrum of **3g** in CDCl_3



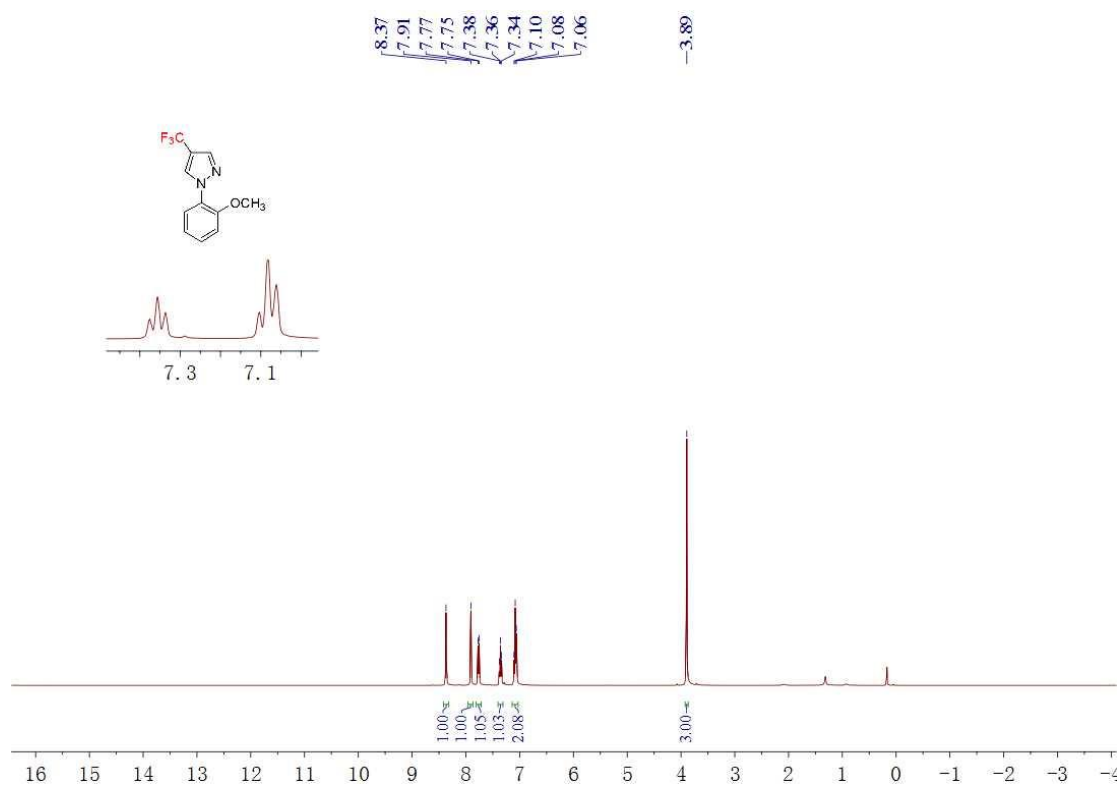
^{19}F NMR spectrum of **3g** in CDCl_3



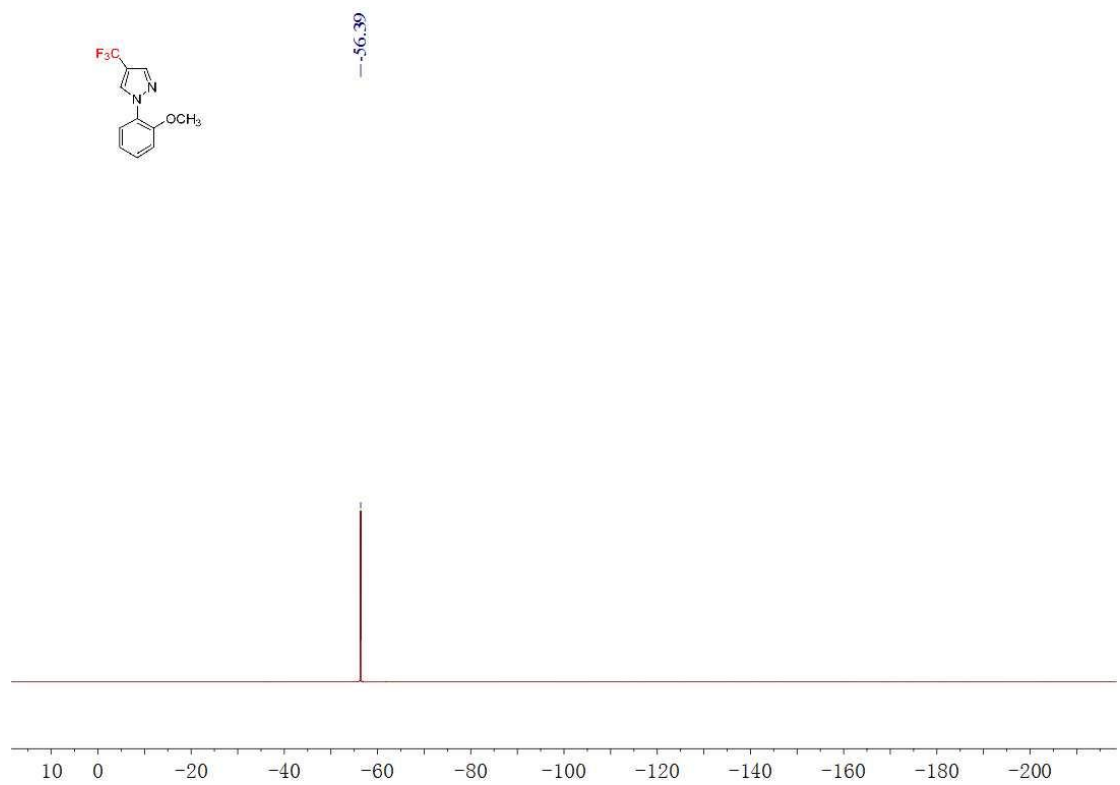
^{13}C NMR spectrum of **3g** in CDCl_3



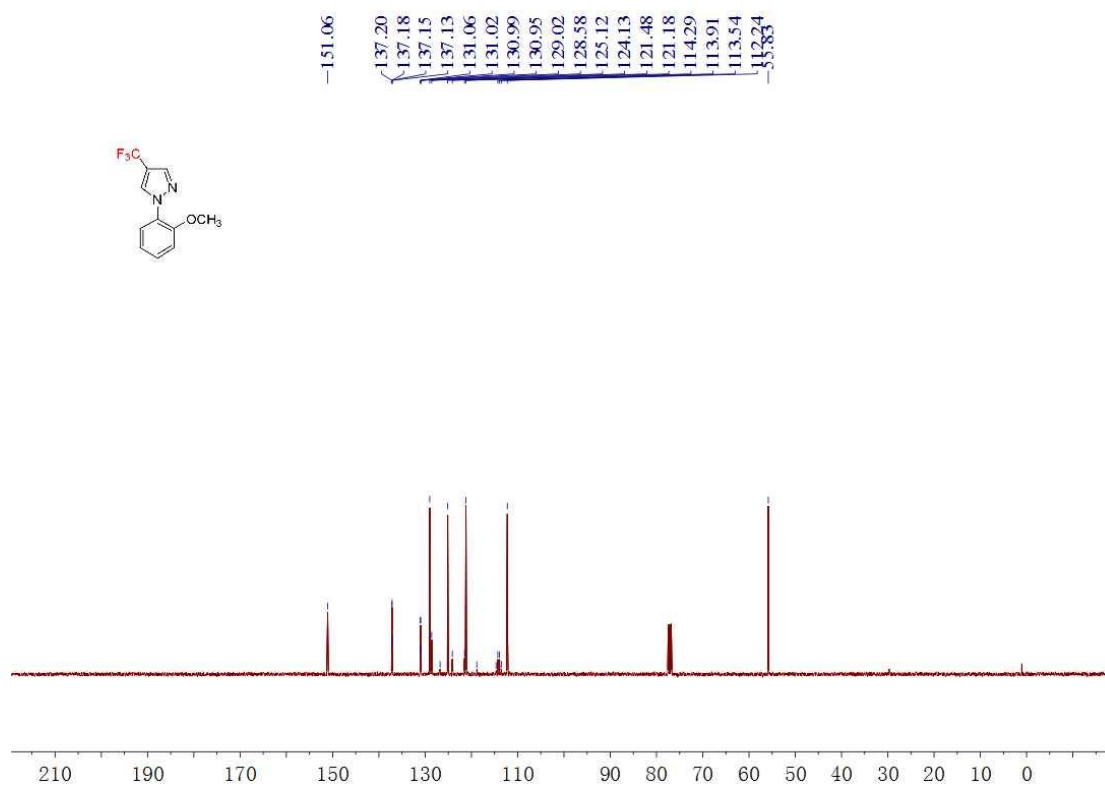
^1H NMR spectrum of **3h** in CDCl_3



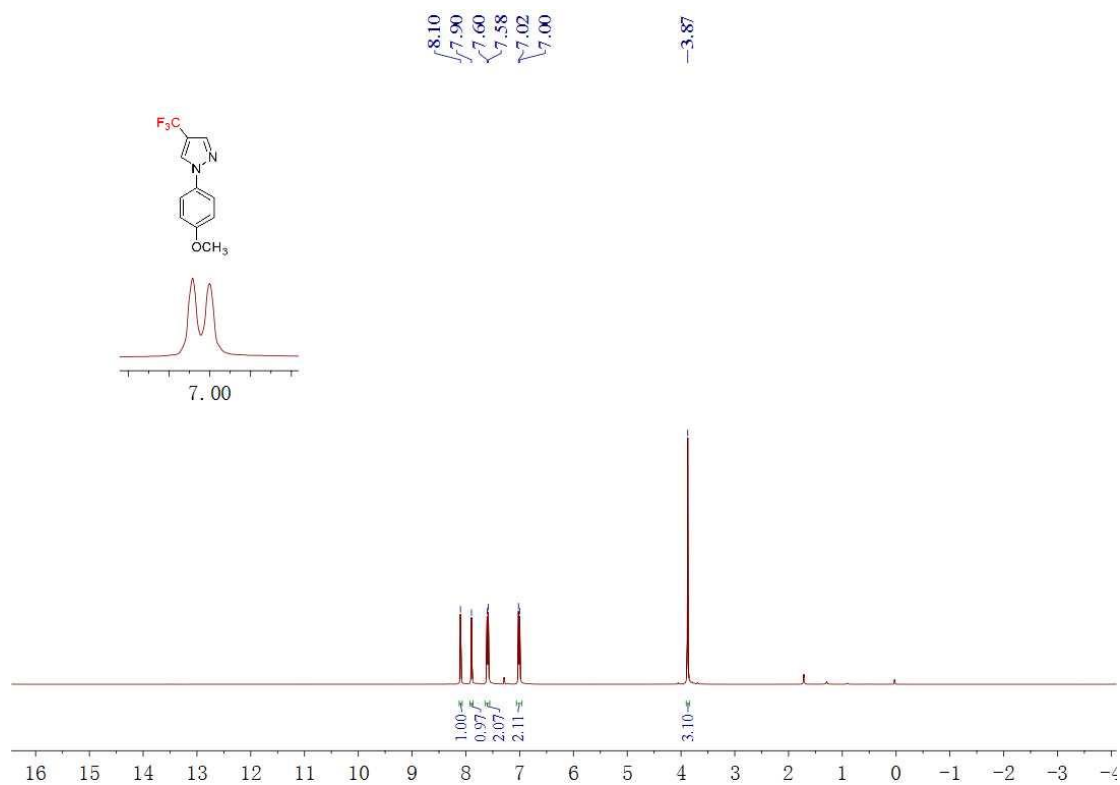
^{19}F NMR spectrum of **3h** in CDCl_3



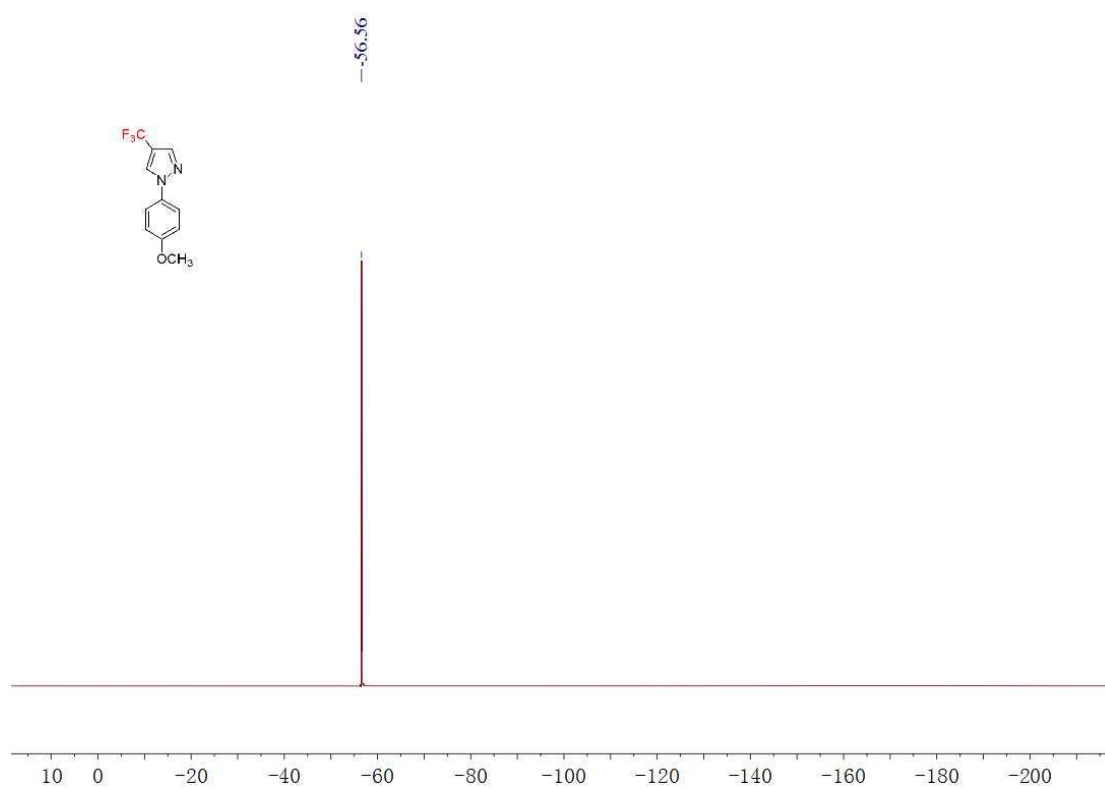
^{13}C NMR spectrum of **3h** in CDCl_3



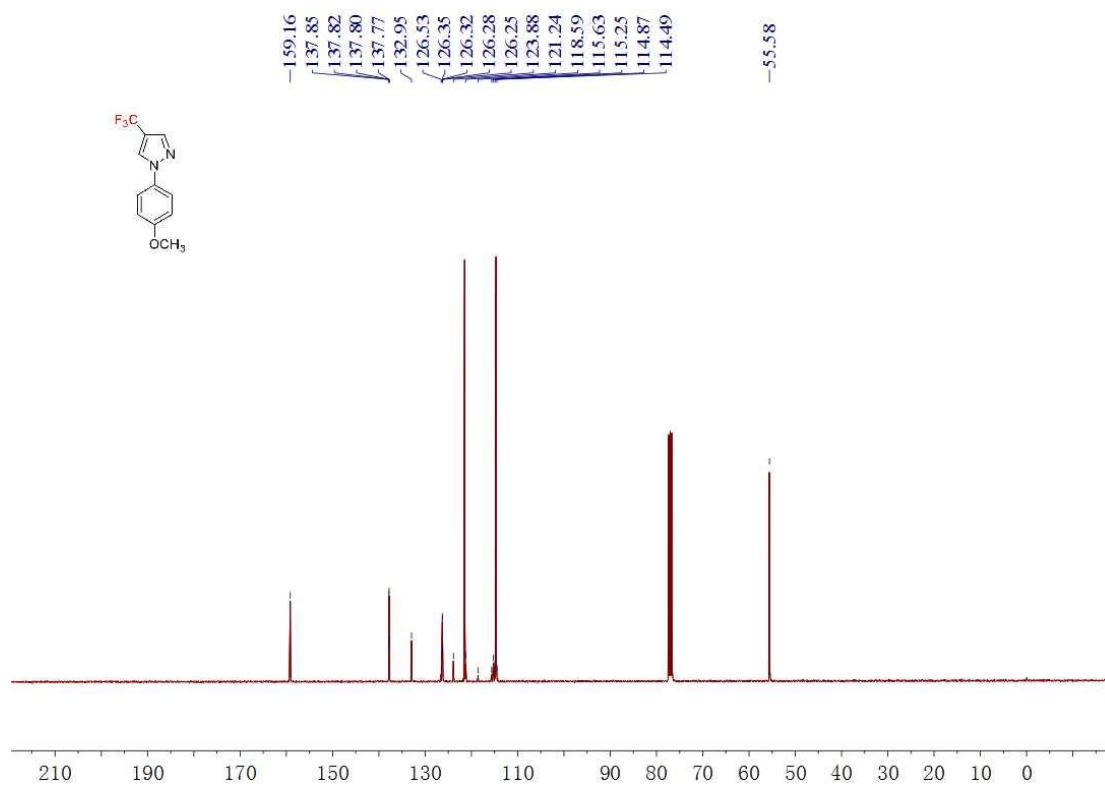
^1H NMR spectrum of **3i** in CDCl_3



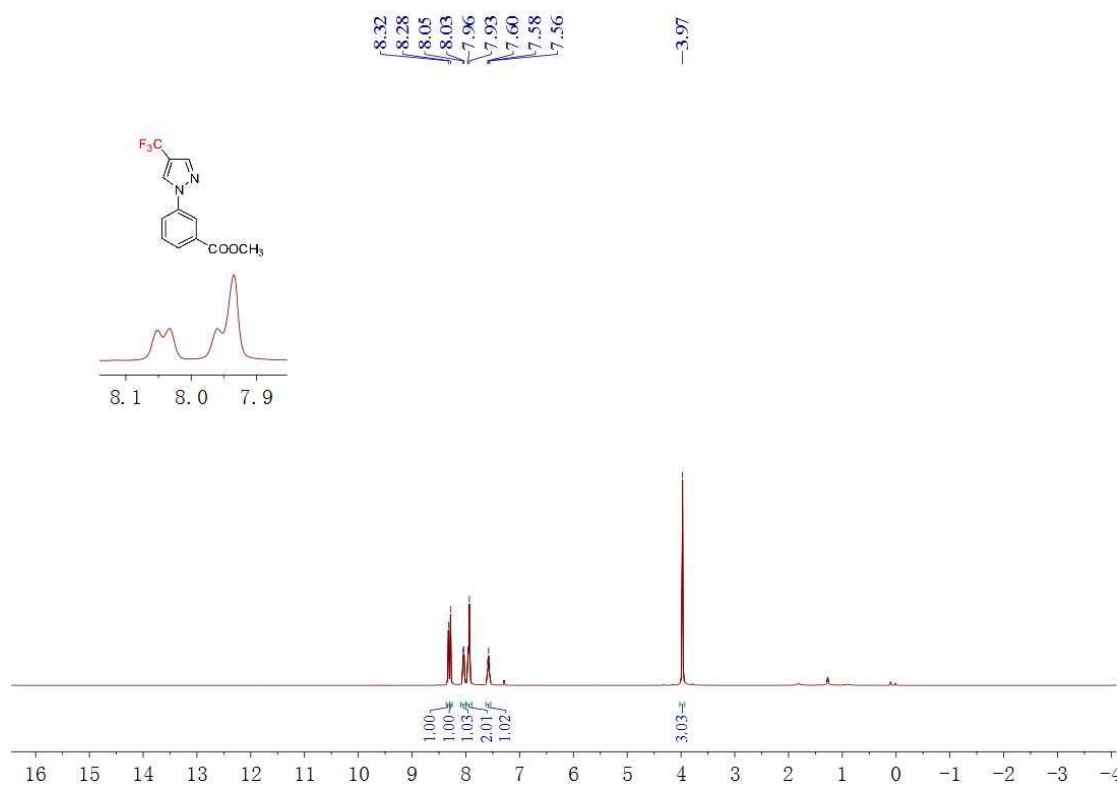
^{19}F NMR spectrum of **3i** in CDCl_3



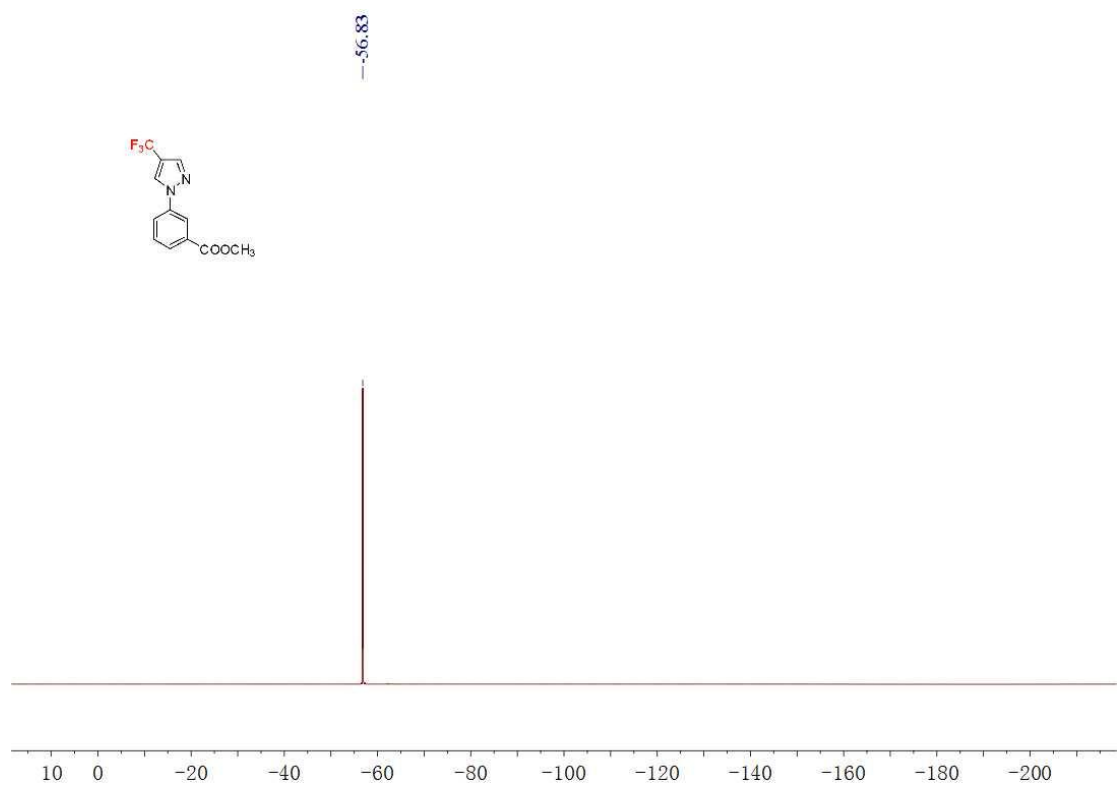
^{13}C NMR spectrum of **3i** in CDCl_3



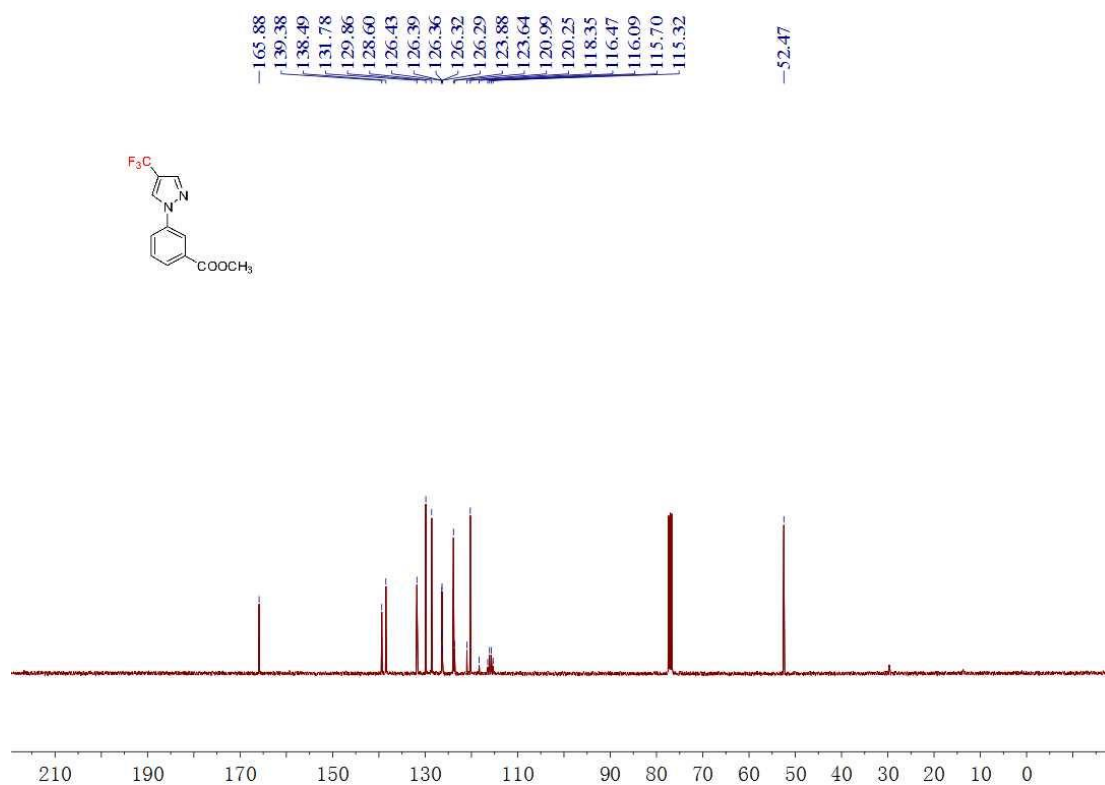
^1H NMR spectrum of **3j** in CDCl_3



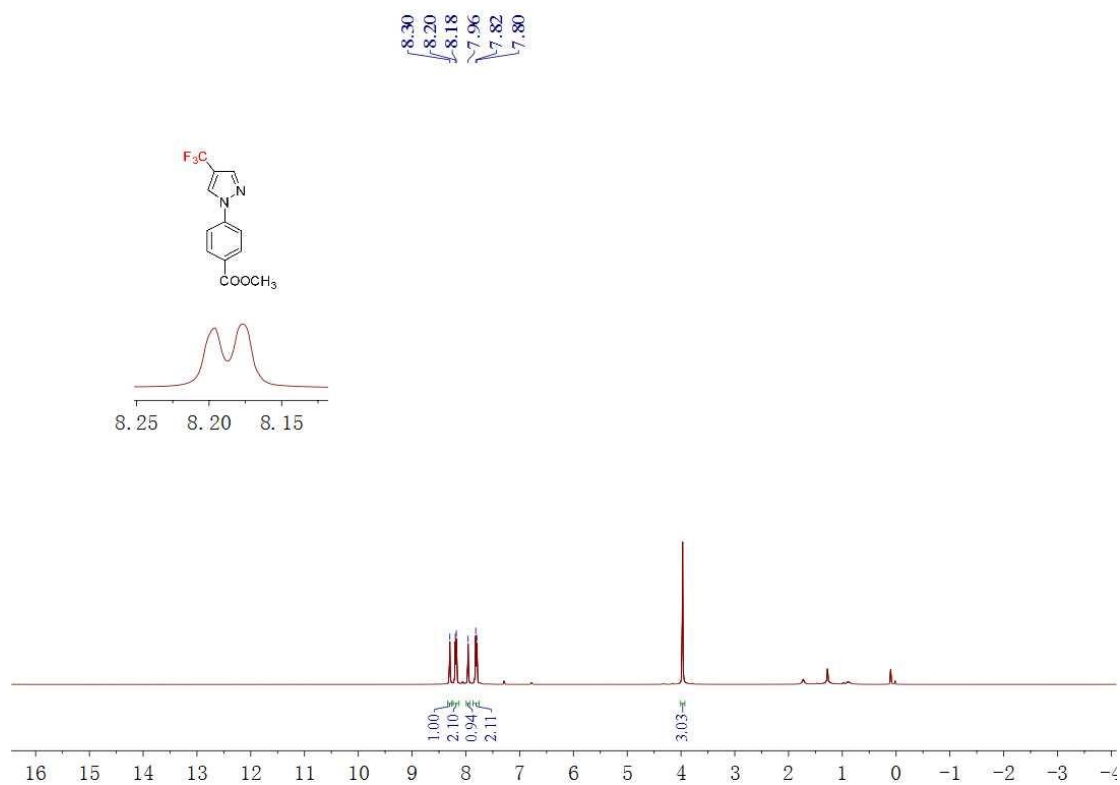
^{19}F NMR spectrum of **3j** in CDCl_3



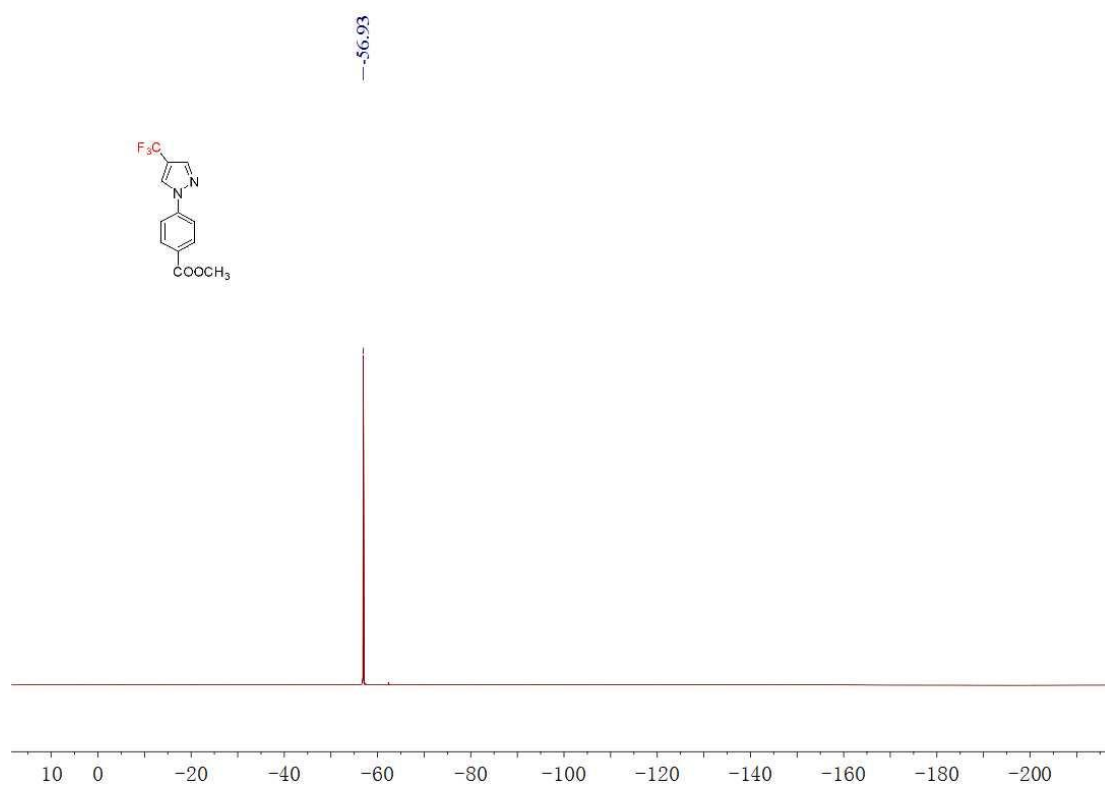
^{13}C NMR spectrum of **3j** in CDCl_3



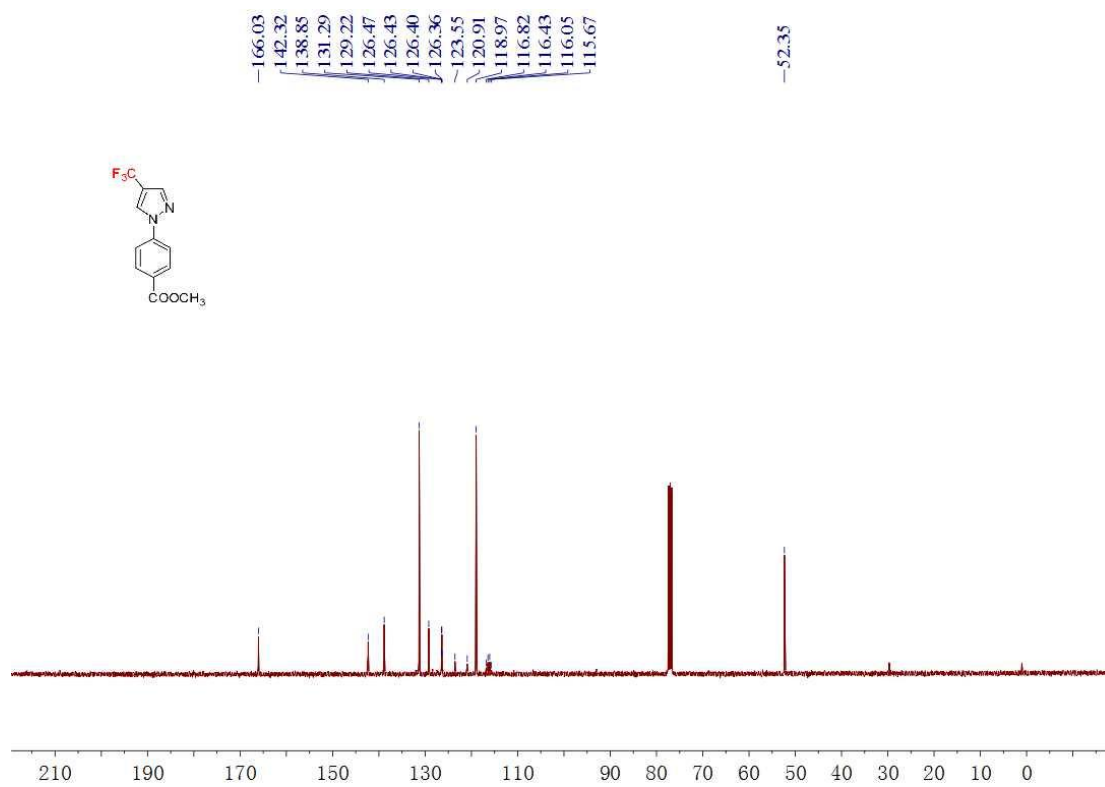
^1H NMR spectrum of **3k** in CDCl_3



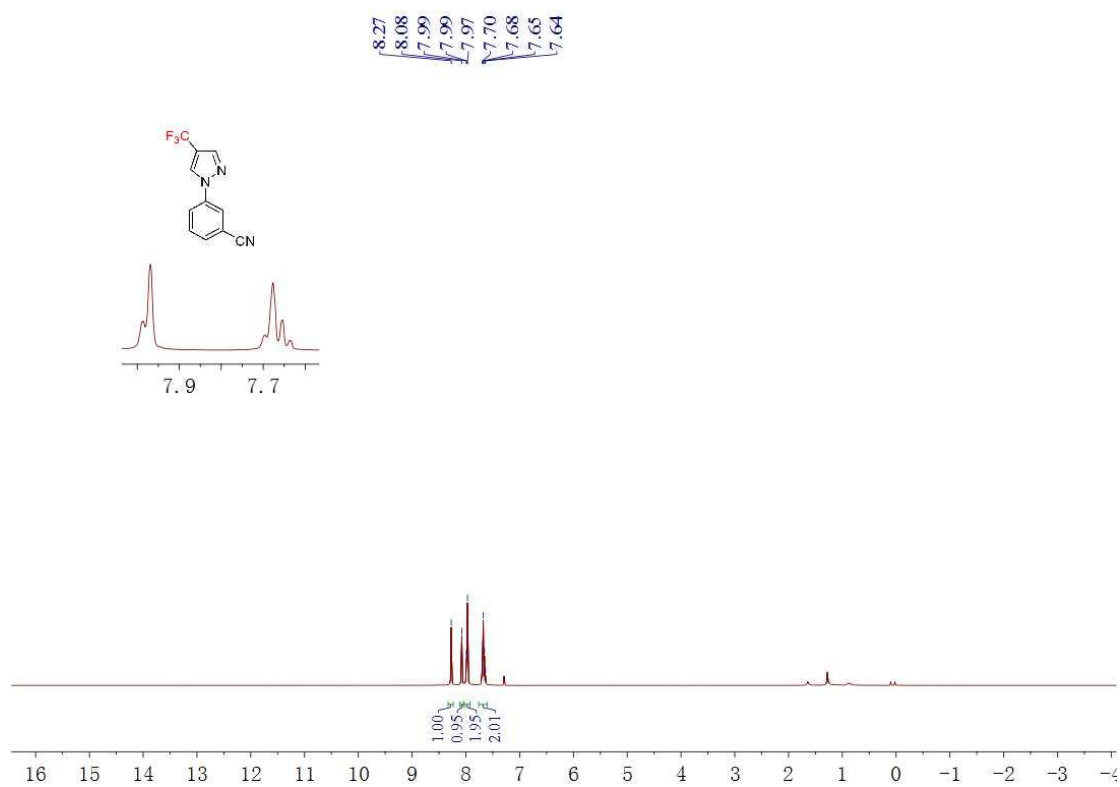
^{19}F NMR spectrum of **3k** in CDCl_3



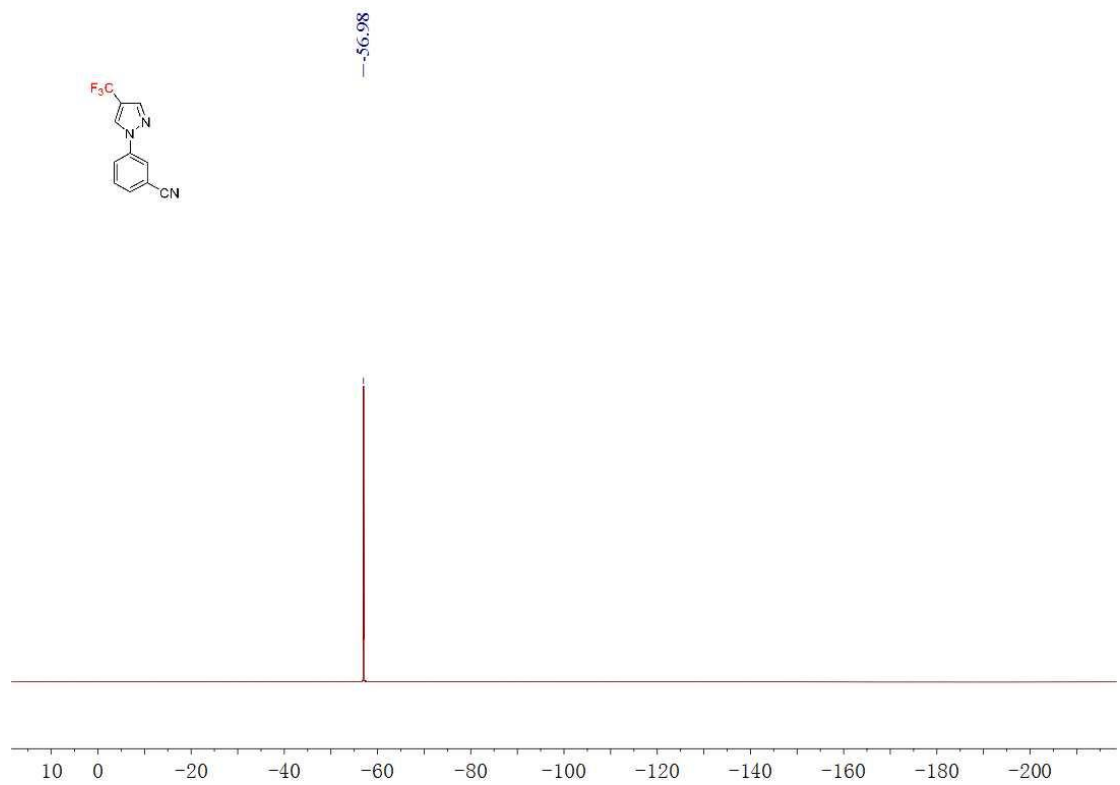
^{13}C NMR spectrum of **3k** in CDCl_3



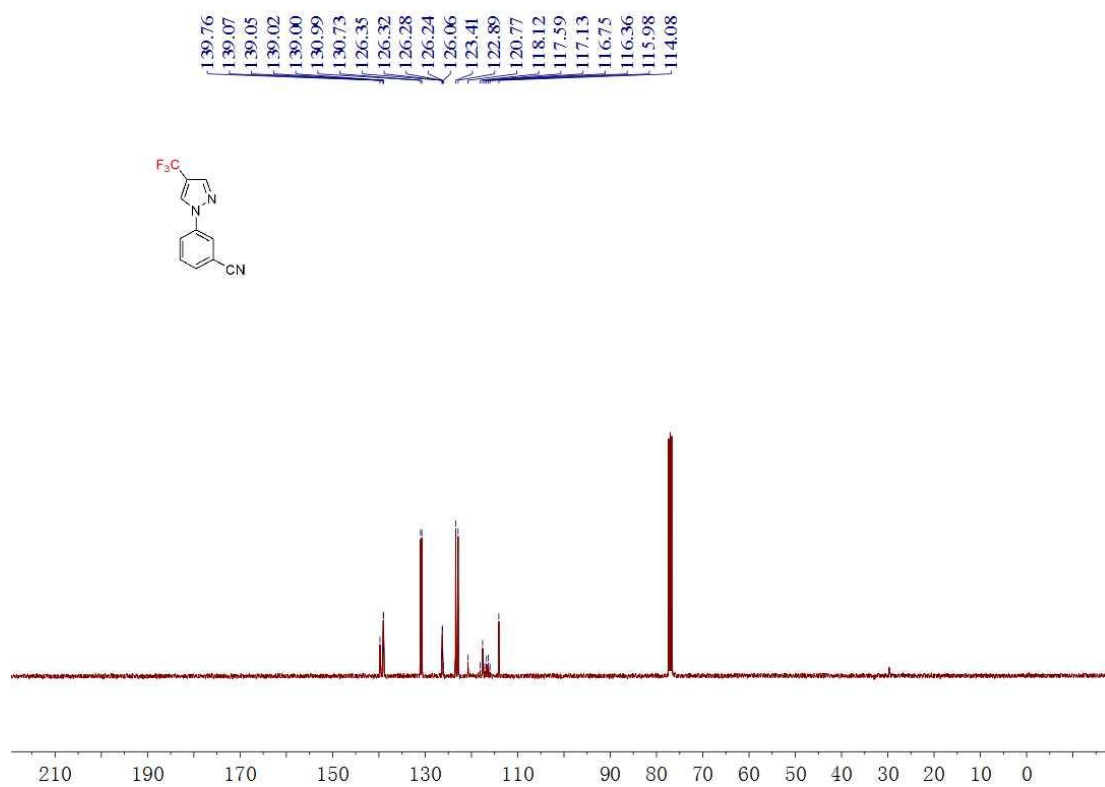
^1H NMR spectrum of **31** in CDCl_3



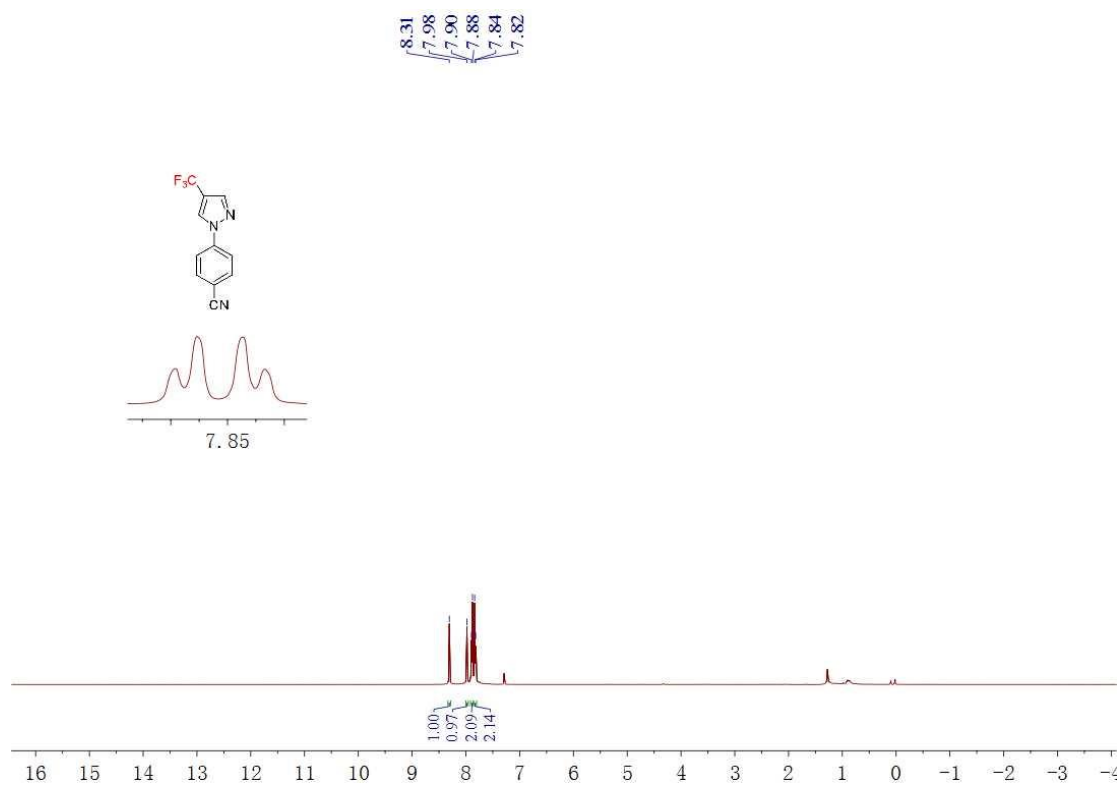
^{19}F NMR spectrum of **31** in CDCl_3



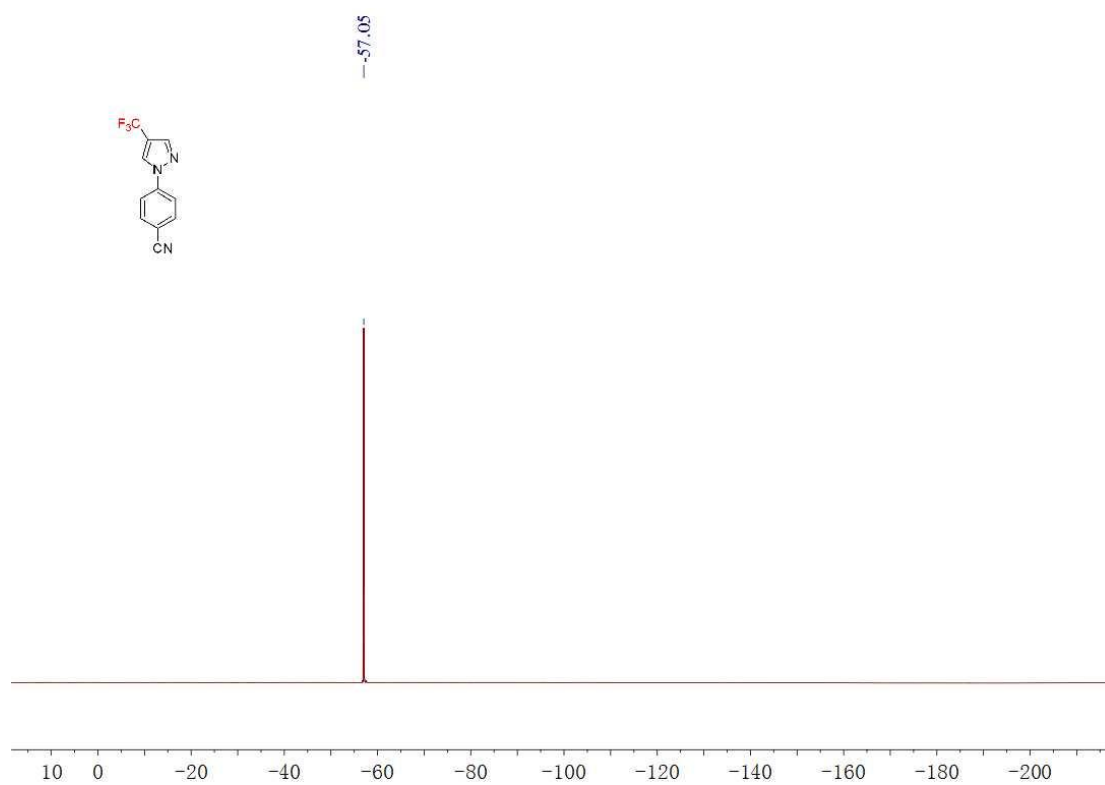
^{13}C NMR spectrum of **3l** in CDCl_3



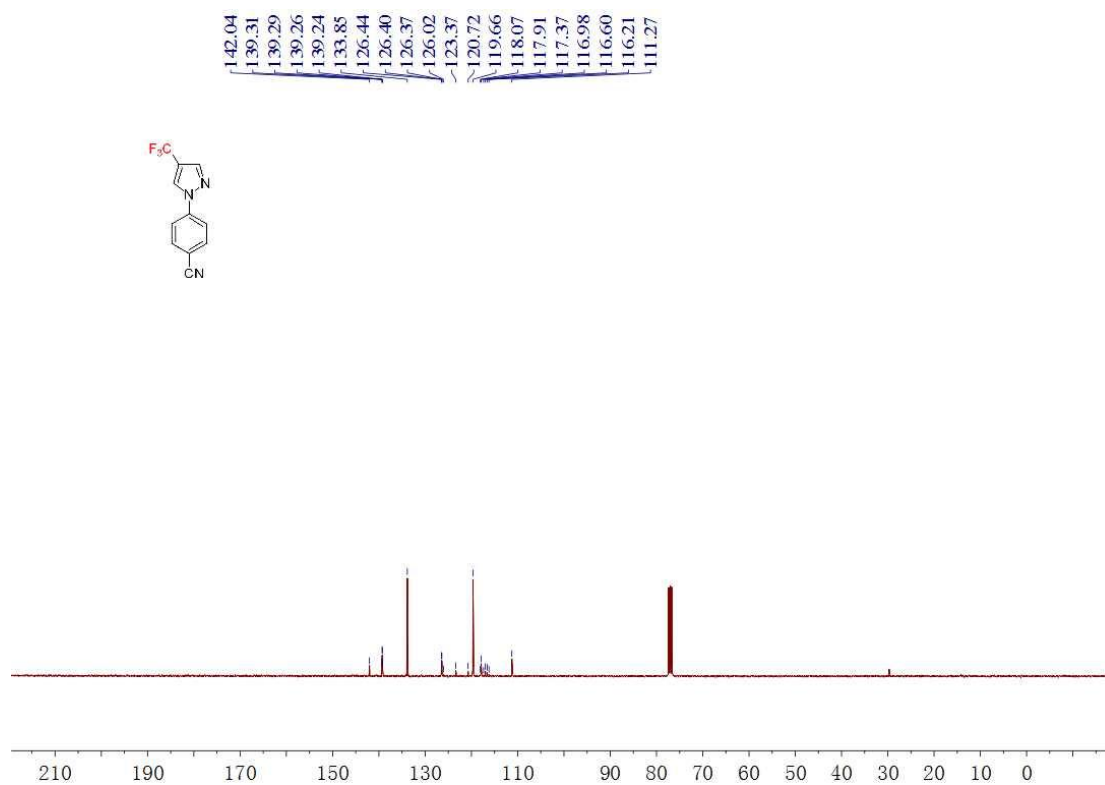
^1H NMR spectrum of **3m** in CDCl_3



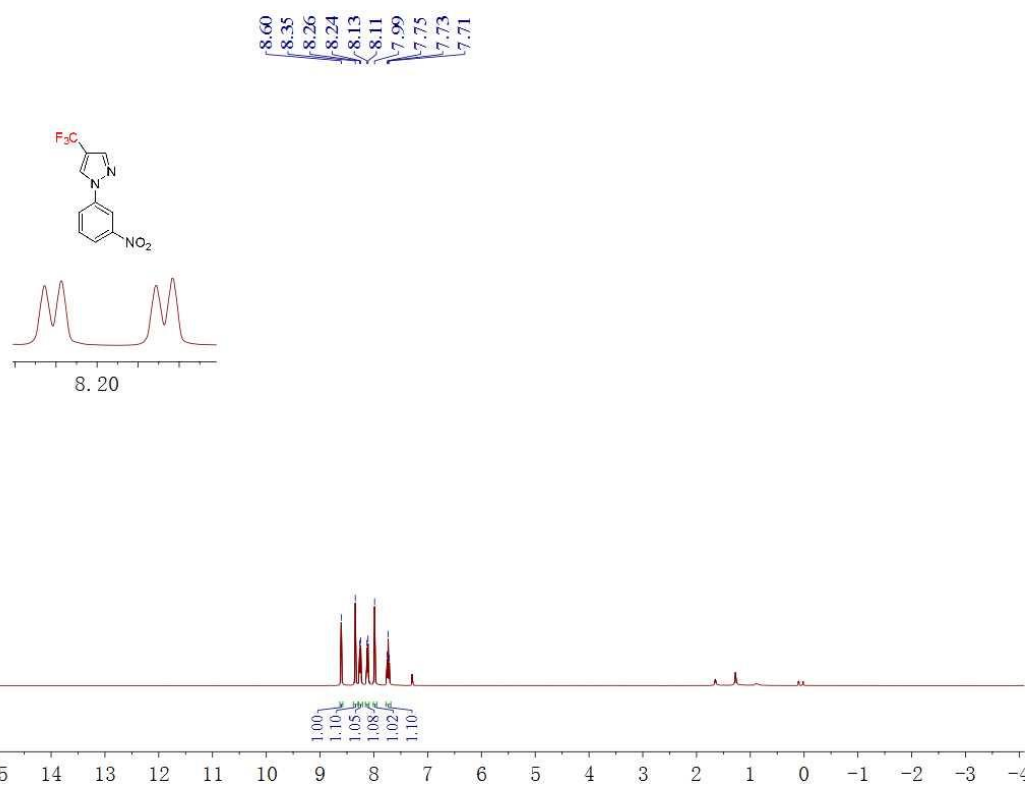
^{19}F NMR spectrum of **3m** in CDCl_3



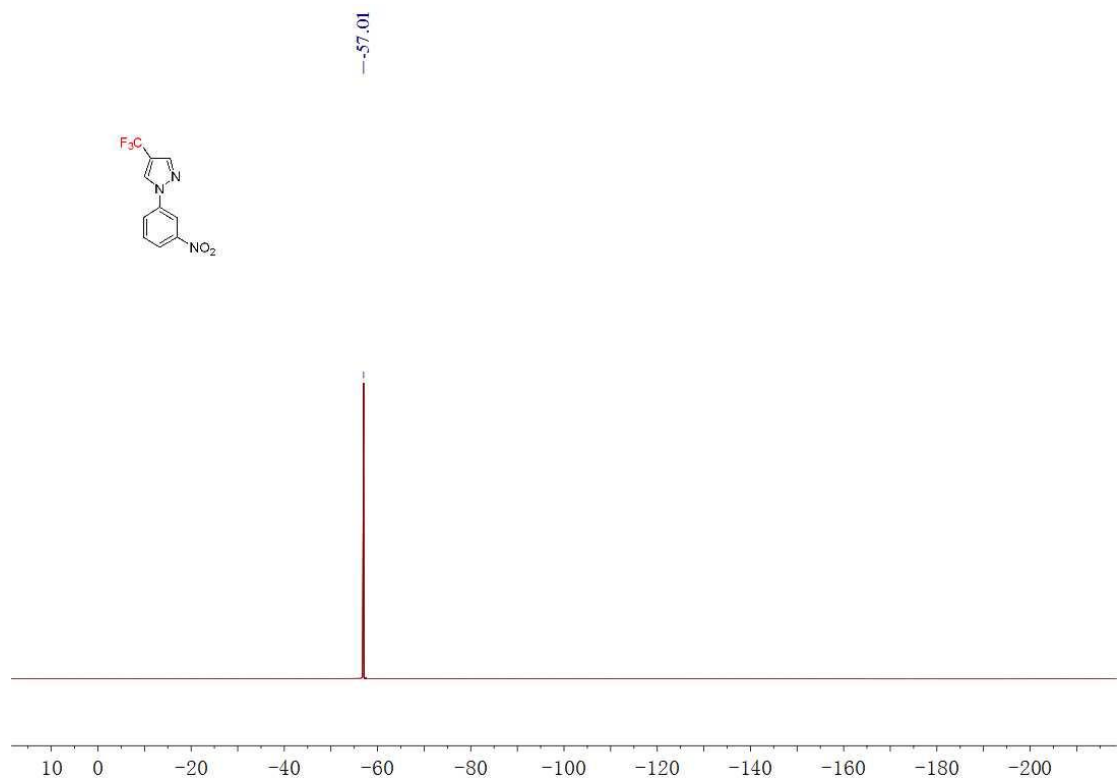
^{13}C NMR spectrum of **3m** in CDCl_3



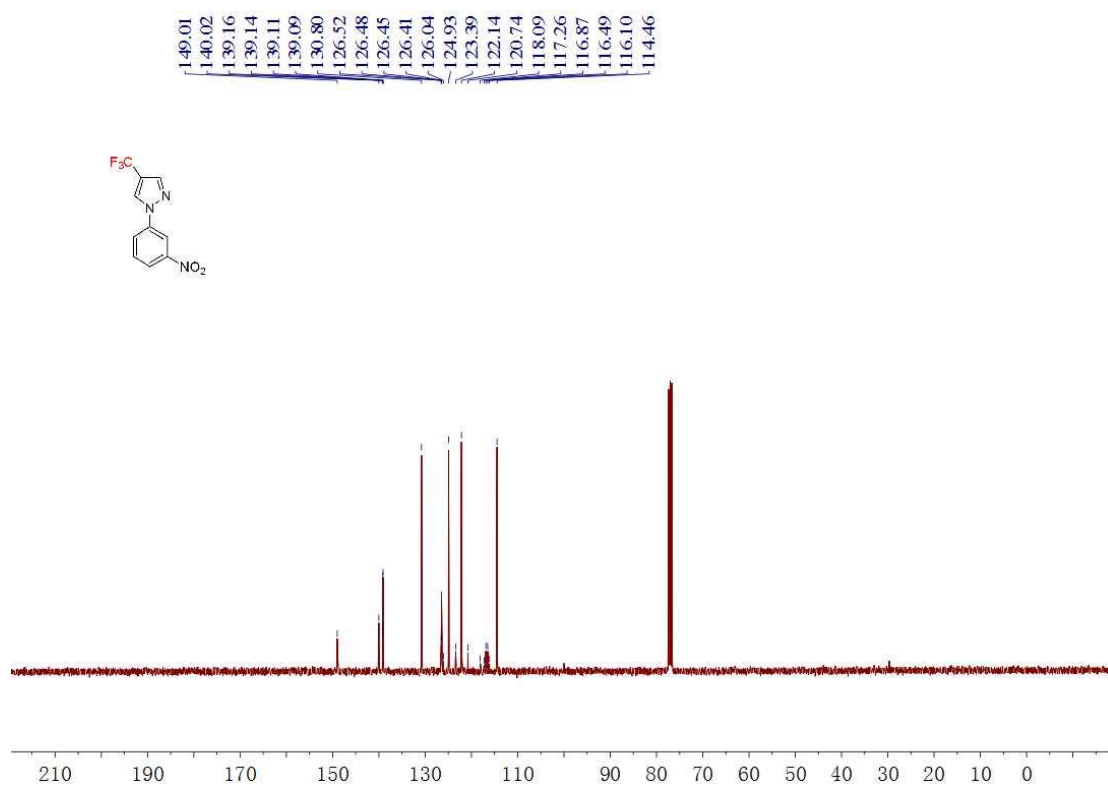
^1H NMR spectrum of **3n** in CDCl_3



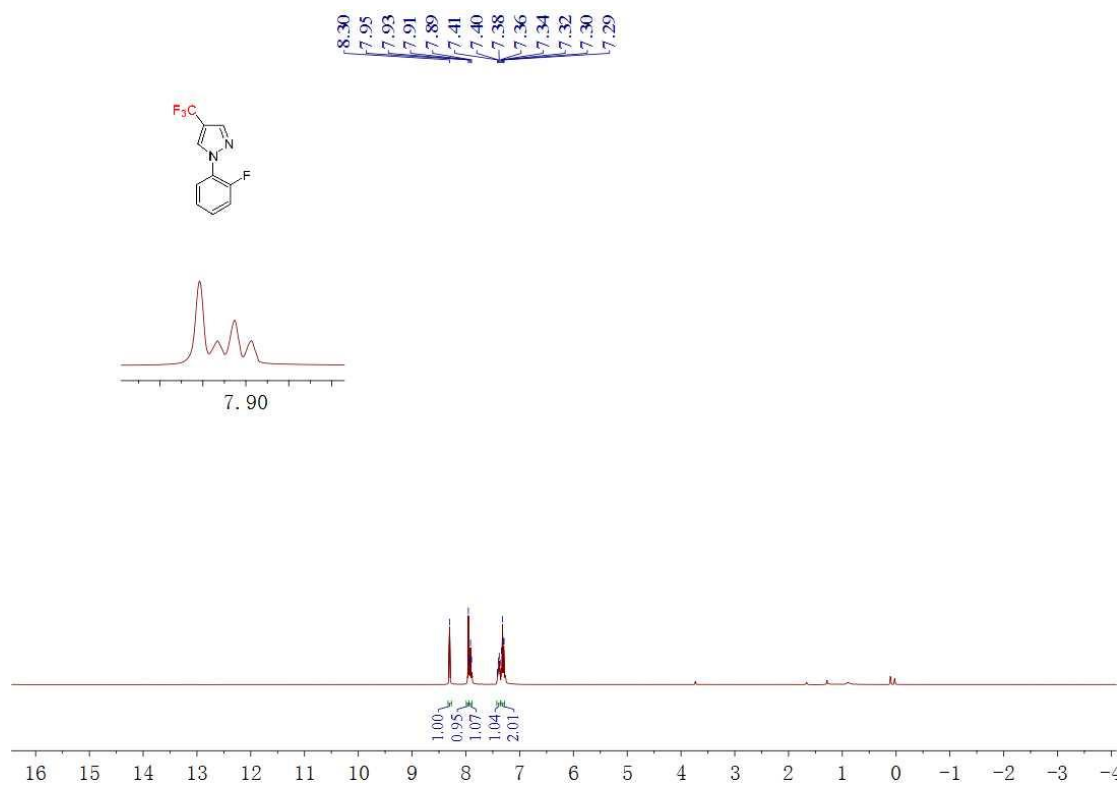
^{19}F NMR spectrum of **3n** in CDCl_3



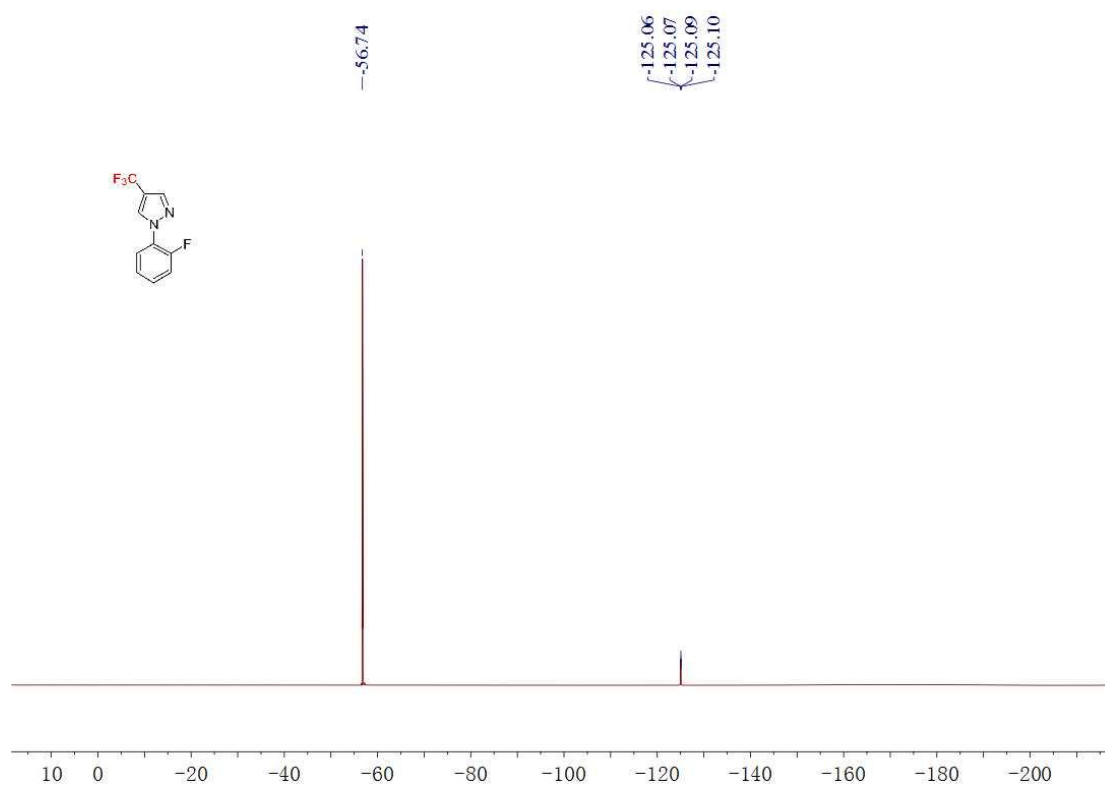
^{13}C NMR spectrum of **3n** in CDCl_3



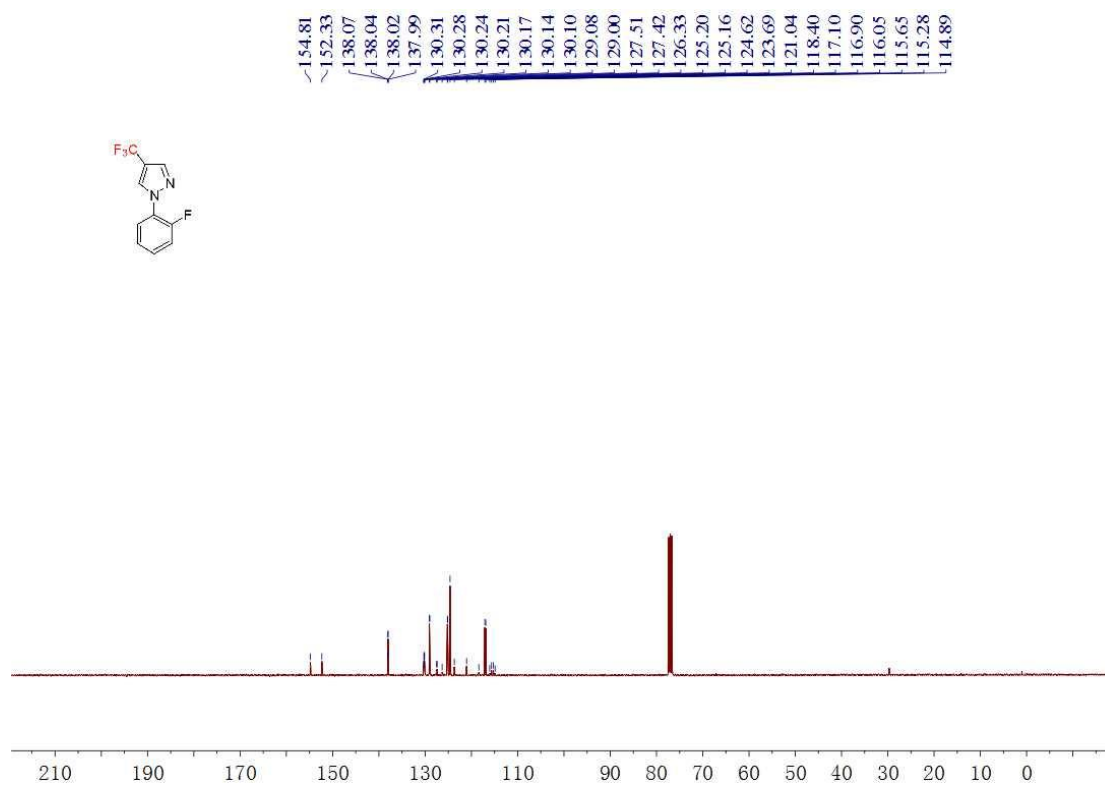
^1H NMR spectrum of **3o** in CDCl_3



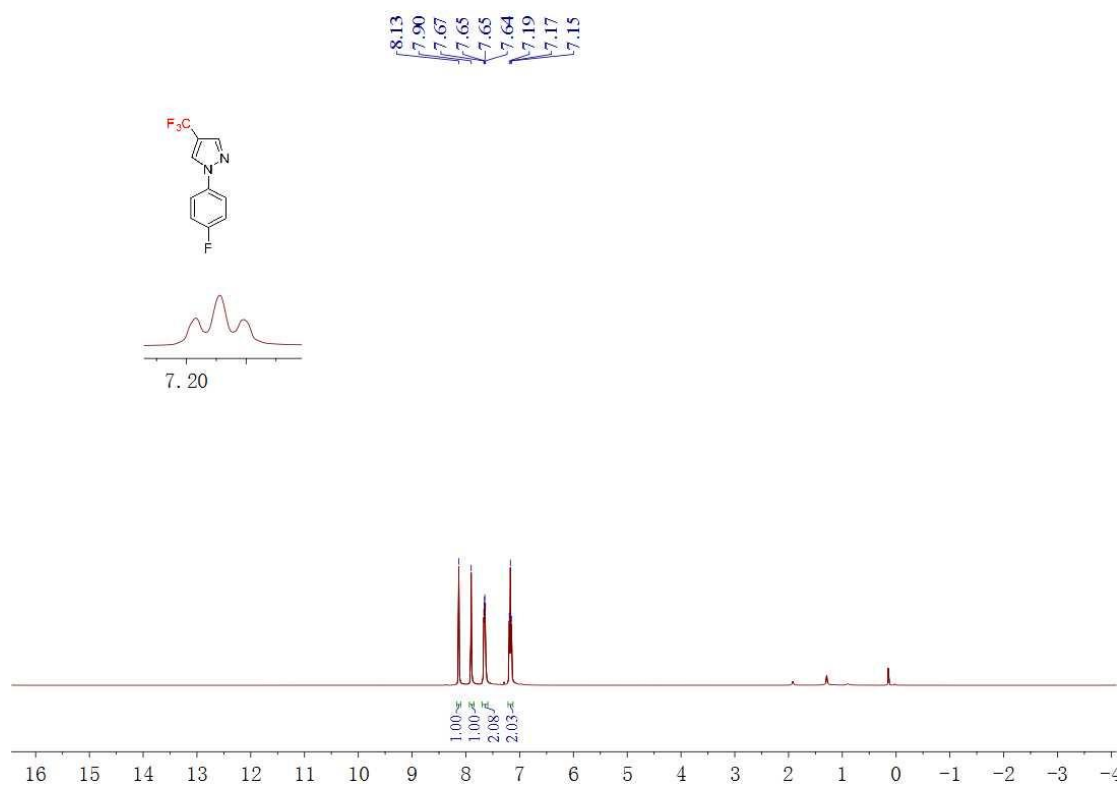
^{19}F NMR spectrum of **3o** in CDCl_3



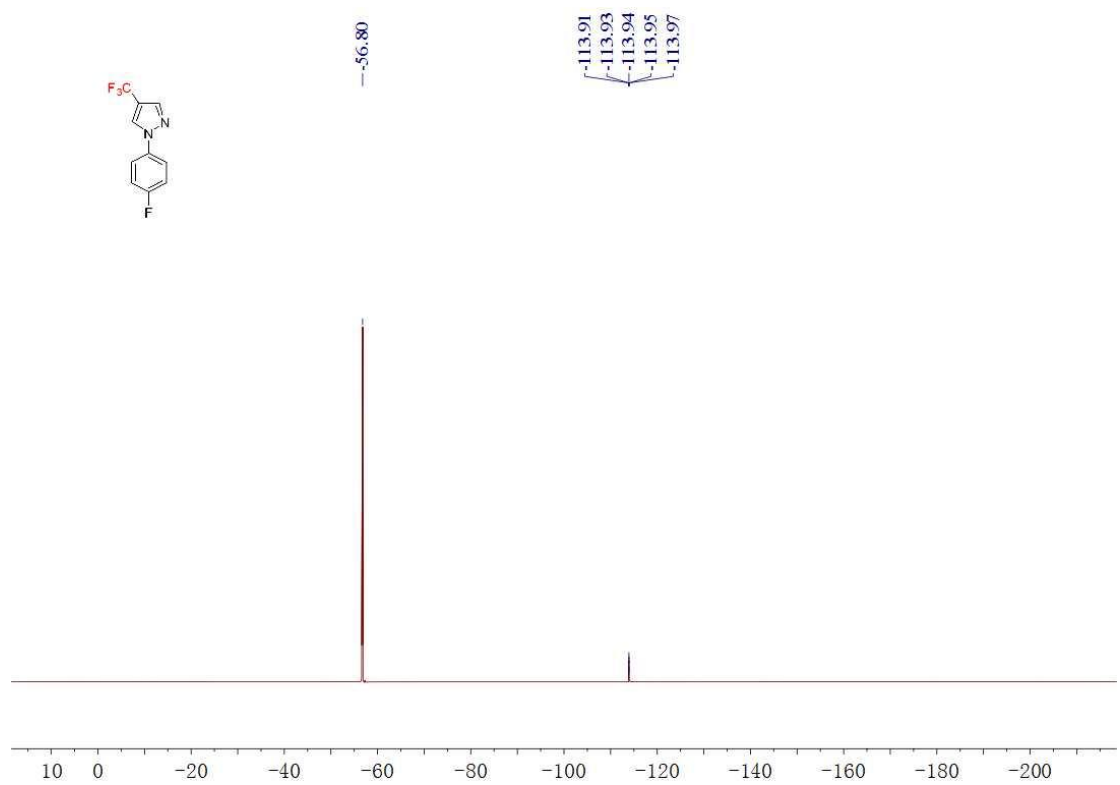
^{13}C NMR spectrum of **3o** in CDCl_3



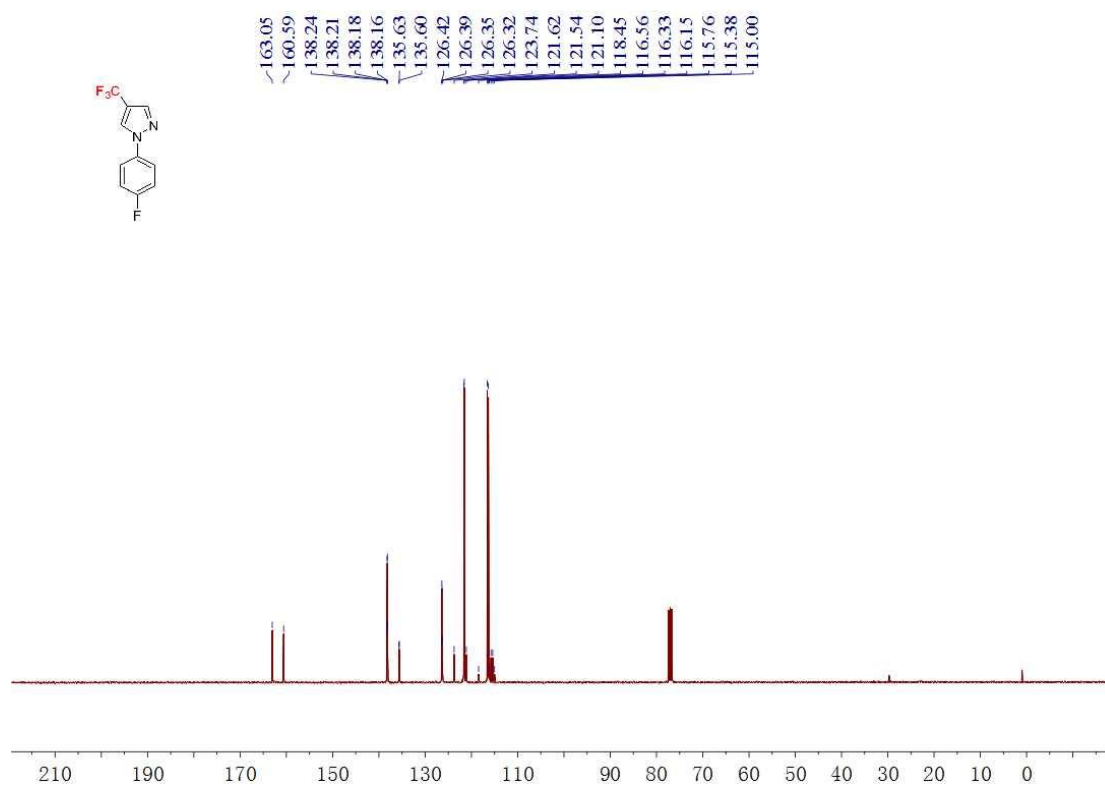
^1H NMR spectrum of **3p** in CDCl_3



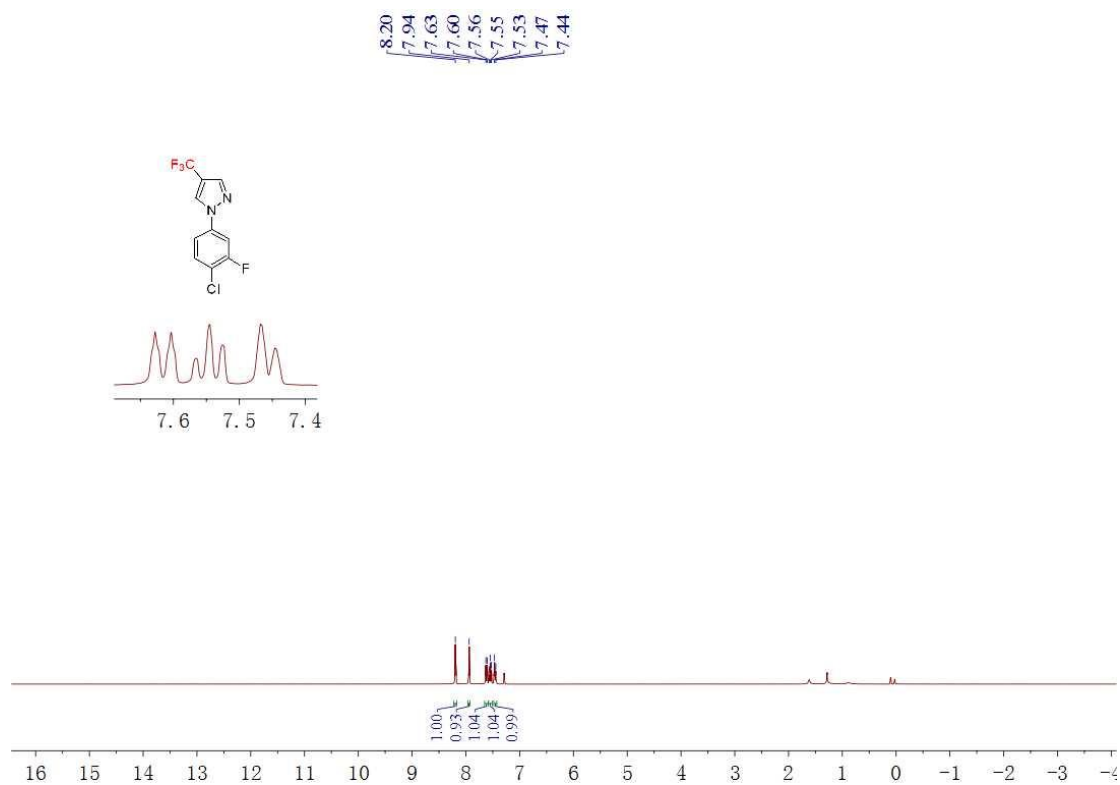
^{19}F NMR spectrum of **3p** in CDCl_3



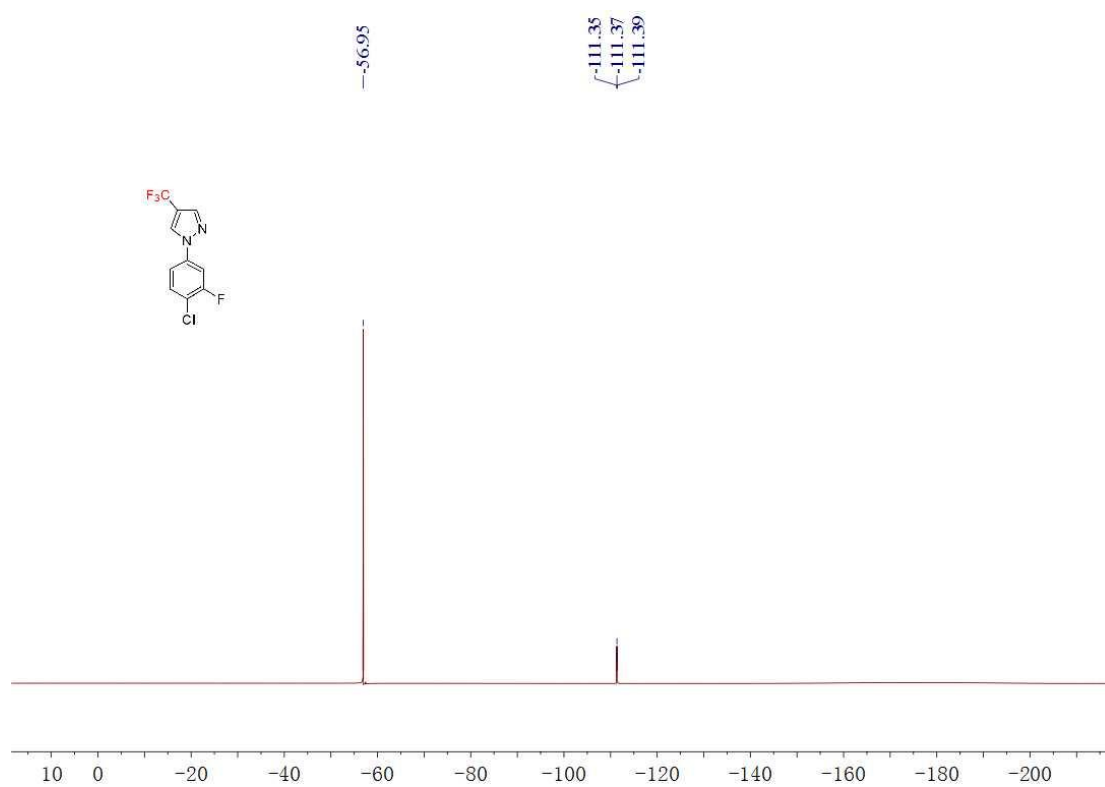
^{13}C NMR spectrum of **3p** in CDCl_3



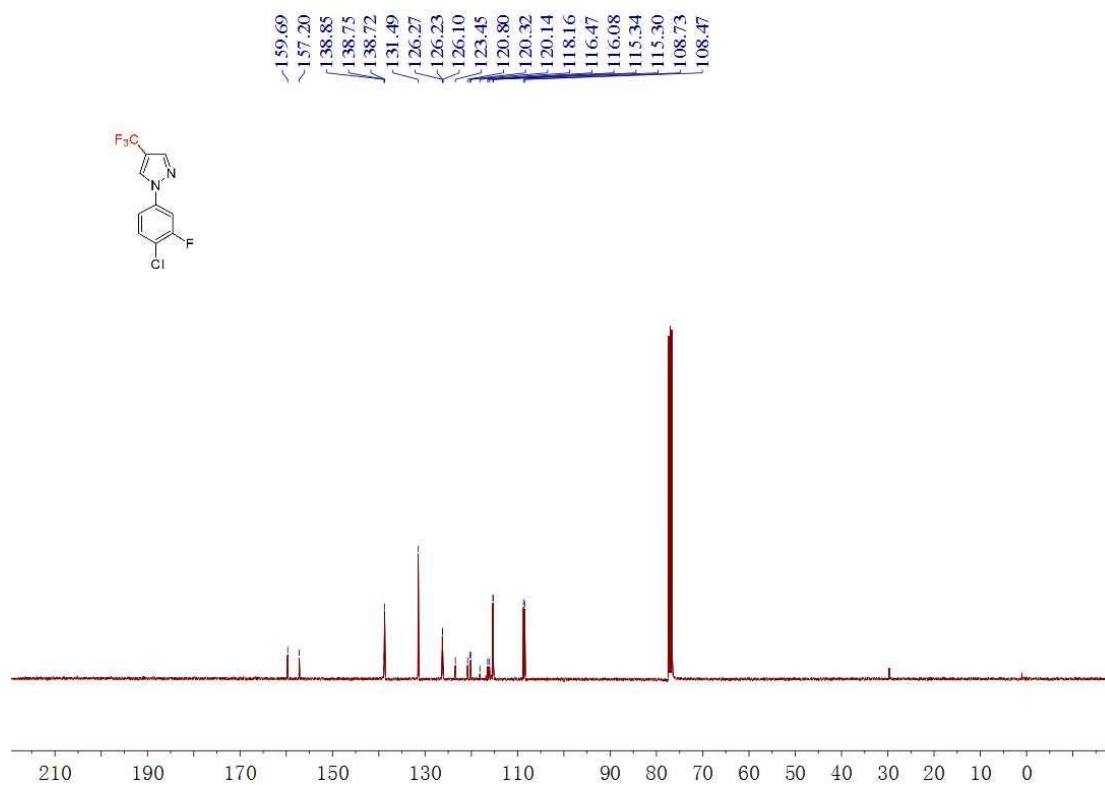
^1H NMR spectrum of **3q** in CDCl_3



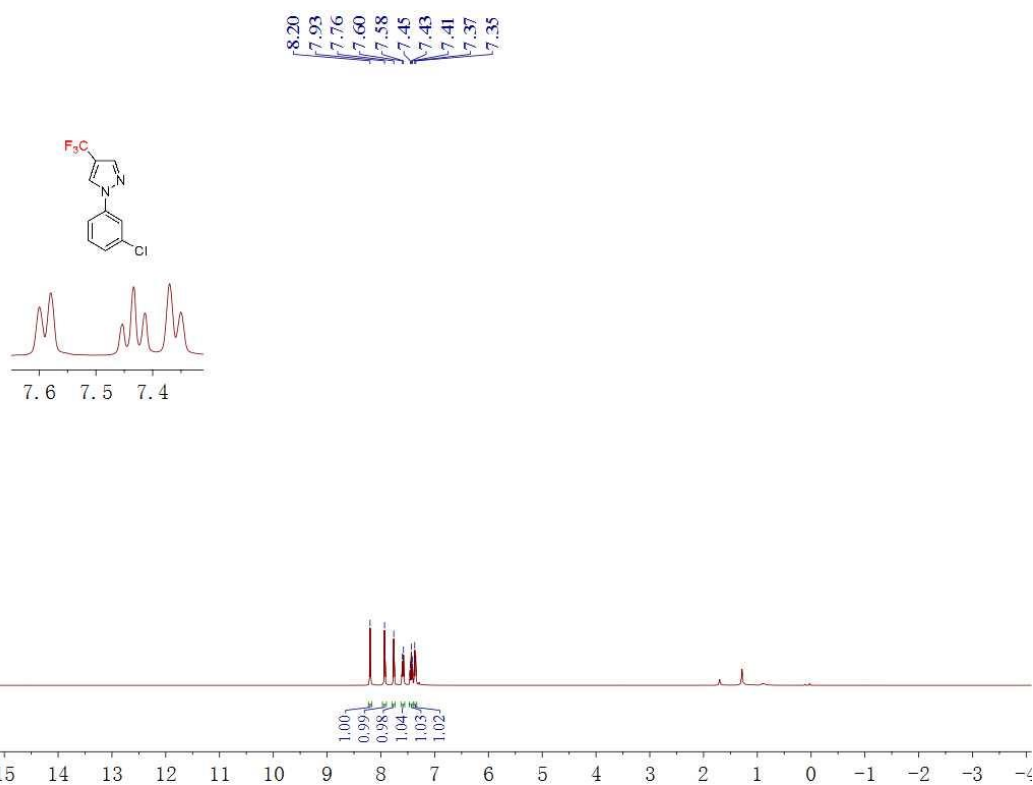
^{19}F NMR spectrum of **3q** in CDCl_3



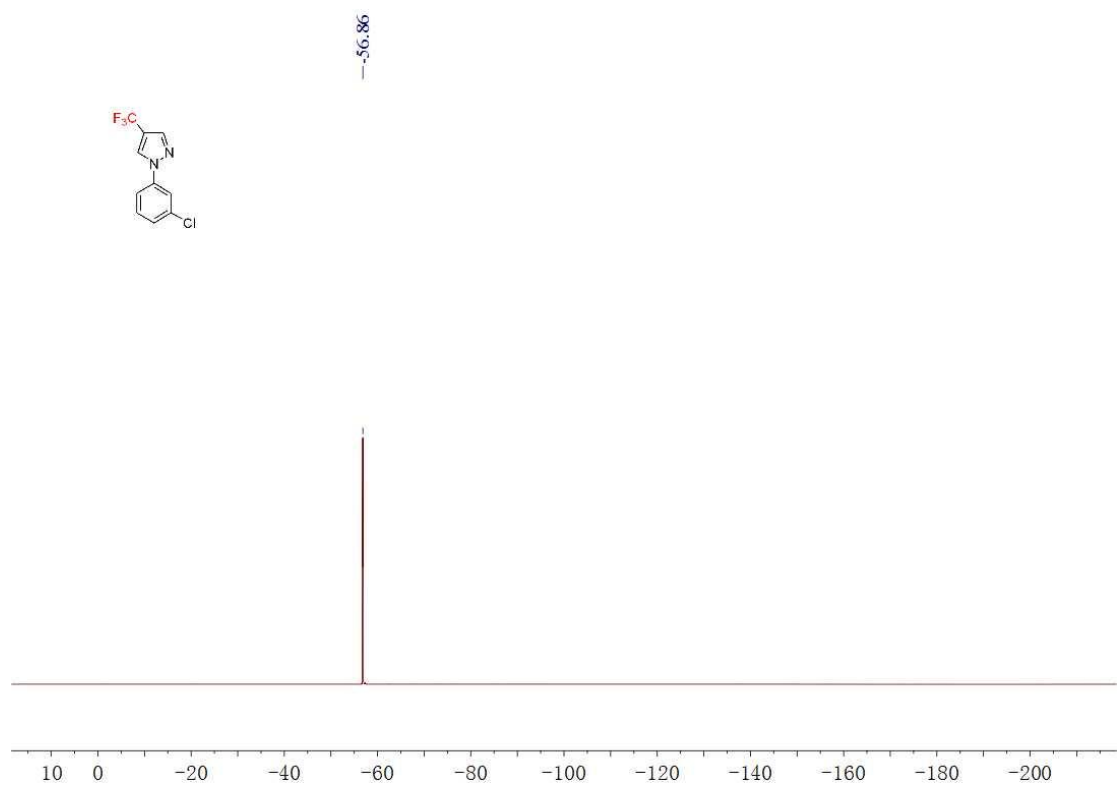
^{13}C NMR spectrum of **3q** in CDCl_3



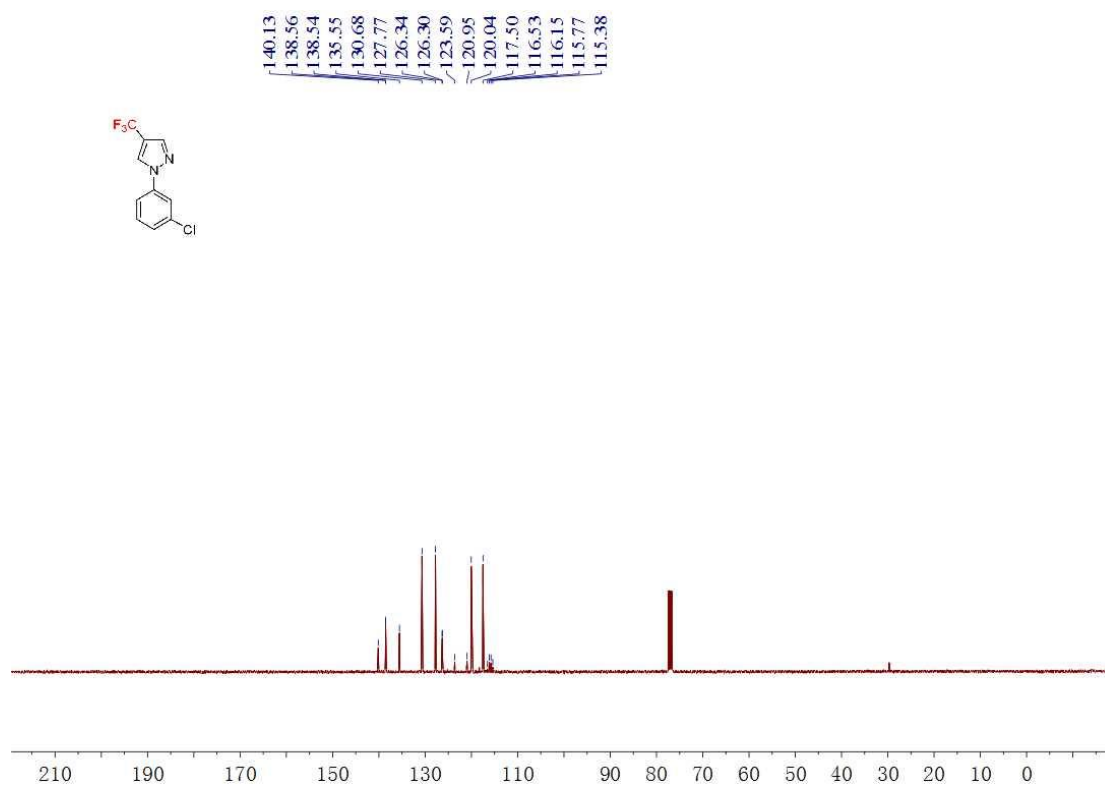
^1H NMR spectrum of **3r** in CDCl_3



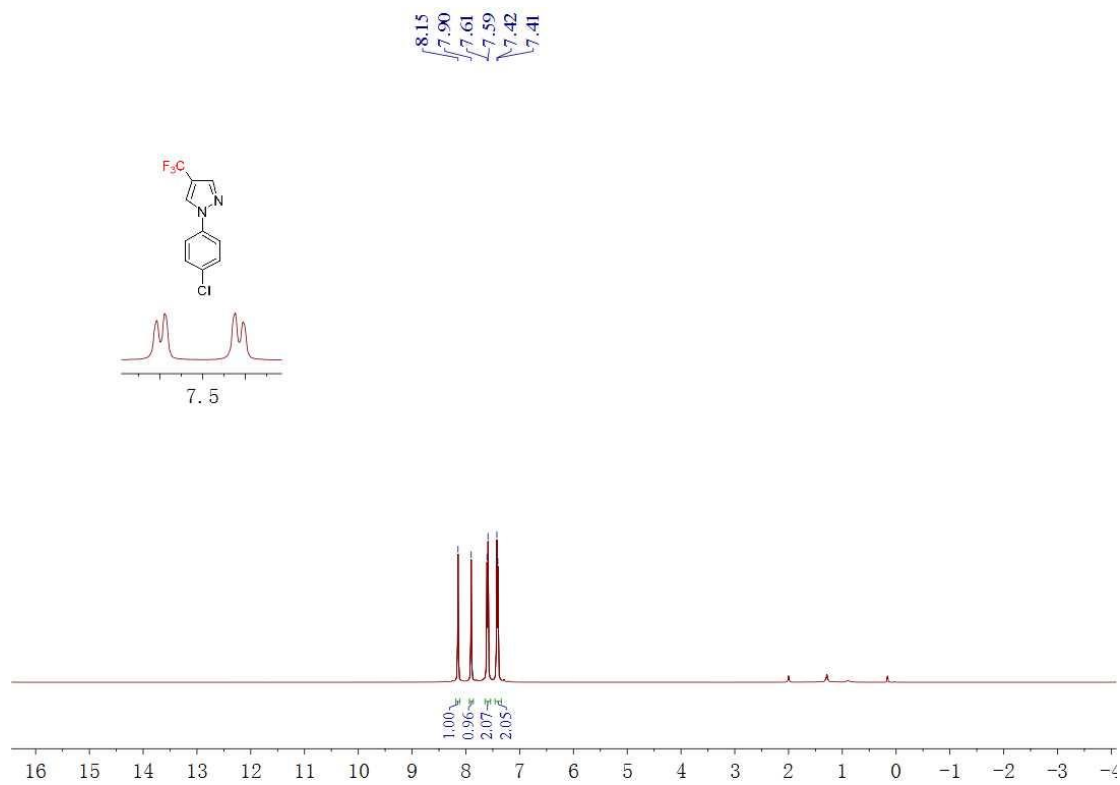
^{19}F NMR spectrum of **3r** in CDCl_3



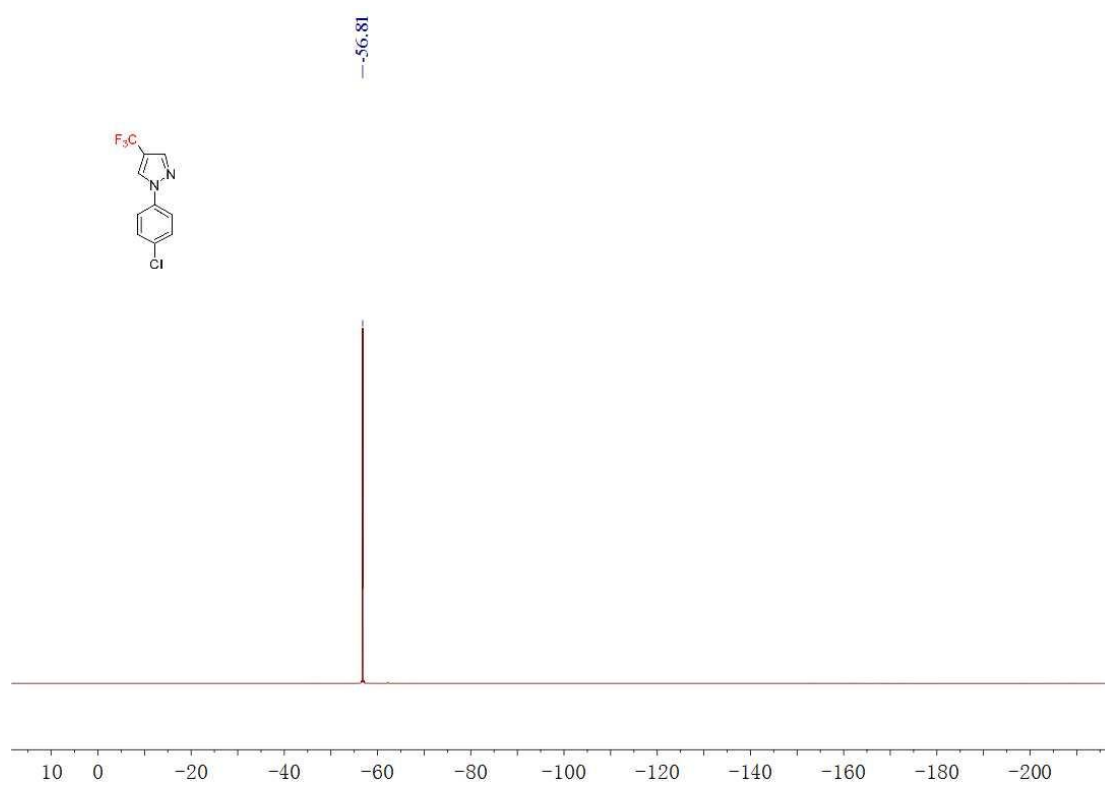
^{13}C NMR spectrum of **3r** in CDCl_3



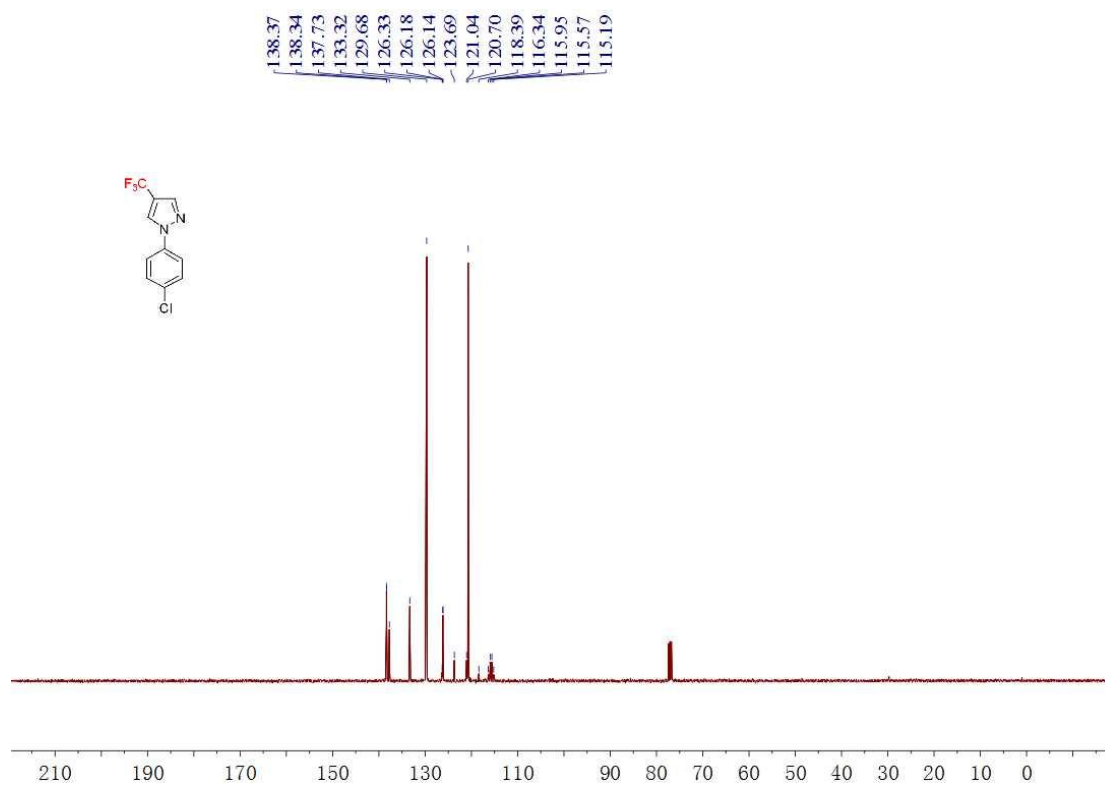
^1H NMR spectrum of **3s** in CDCl_3



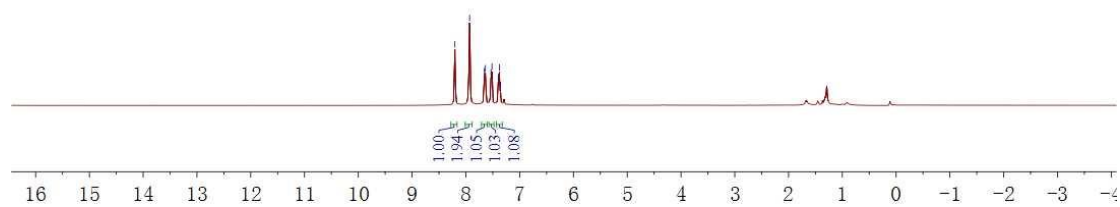
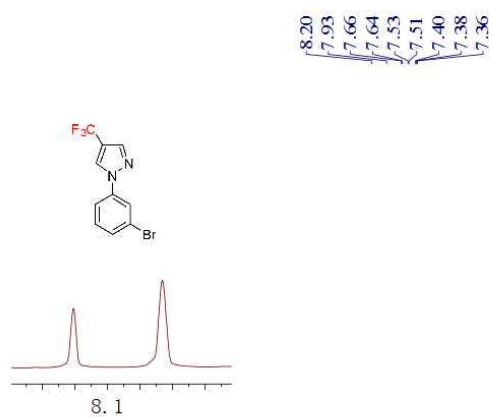
^{19}F NMR spectrum of **3s** in CDCl_3



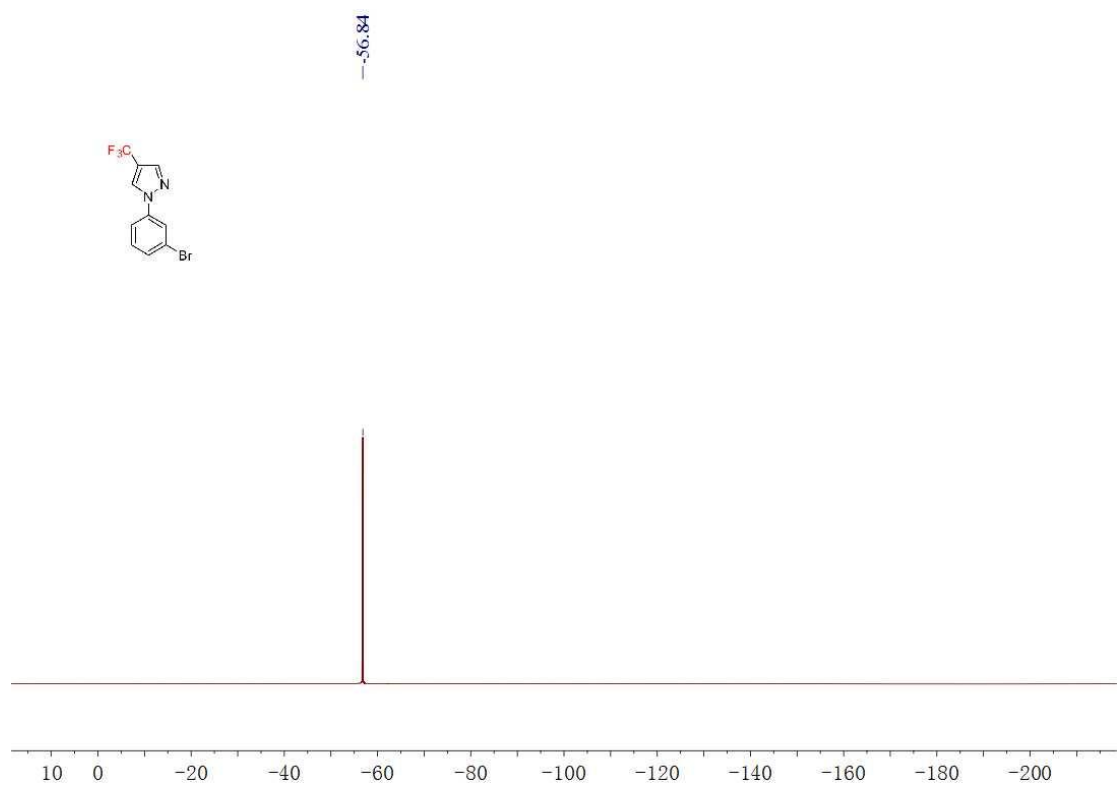
^{13}C NMR spectrum of **3s** in CDCl_3



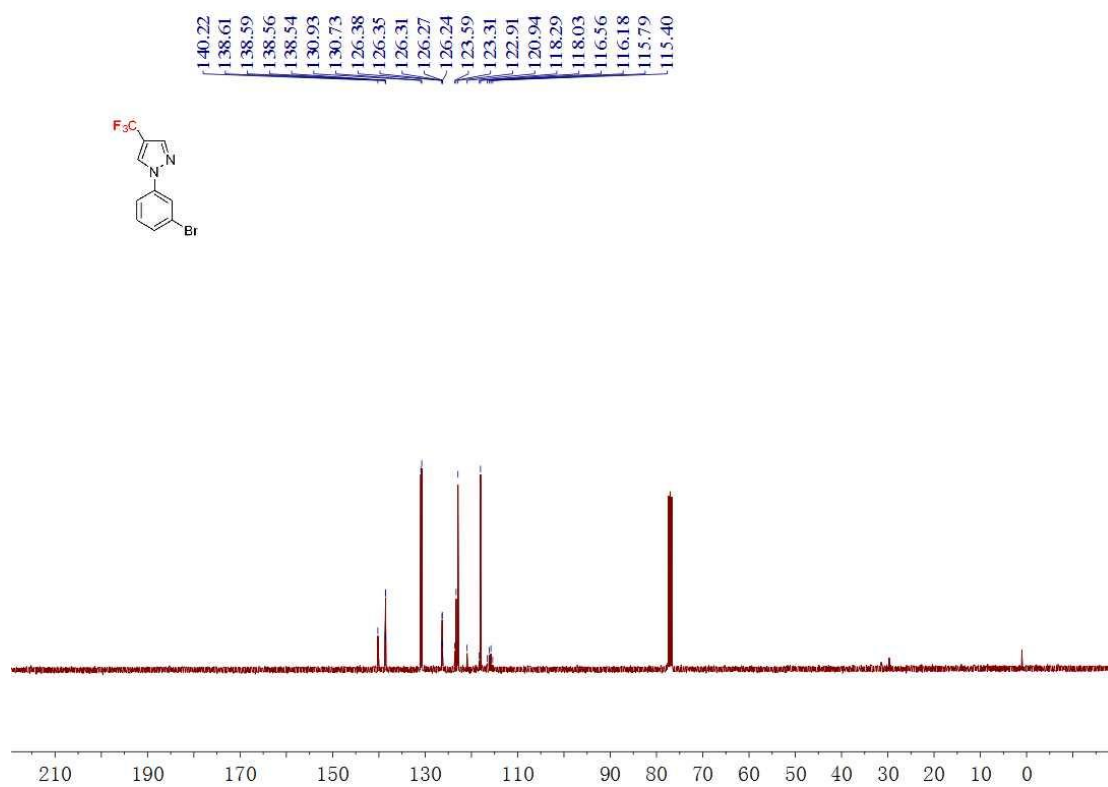
^1H NMR spectrum of **3t** in CDCl_3



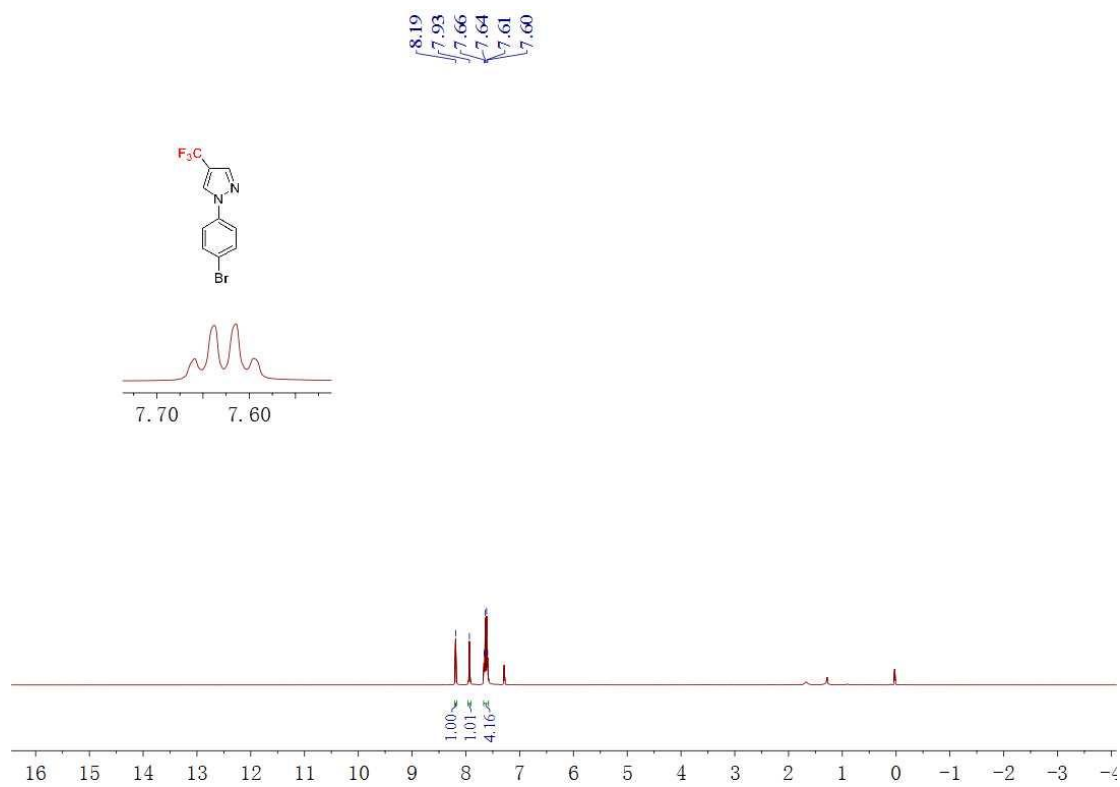
^{19}F NMR spectrum of **3t** in CDCl_3



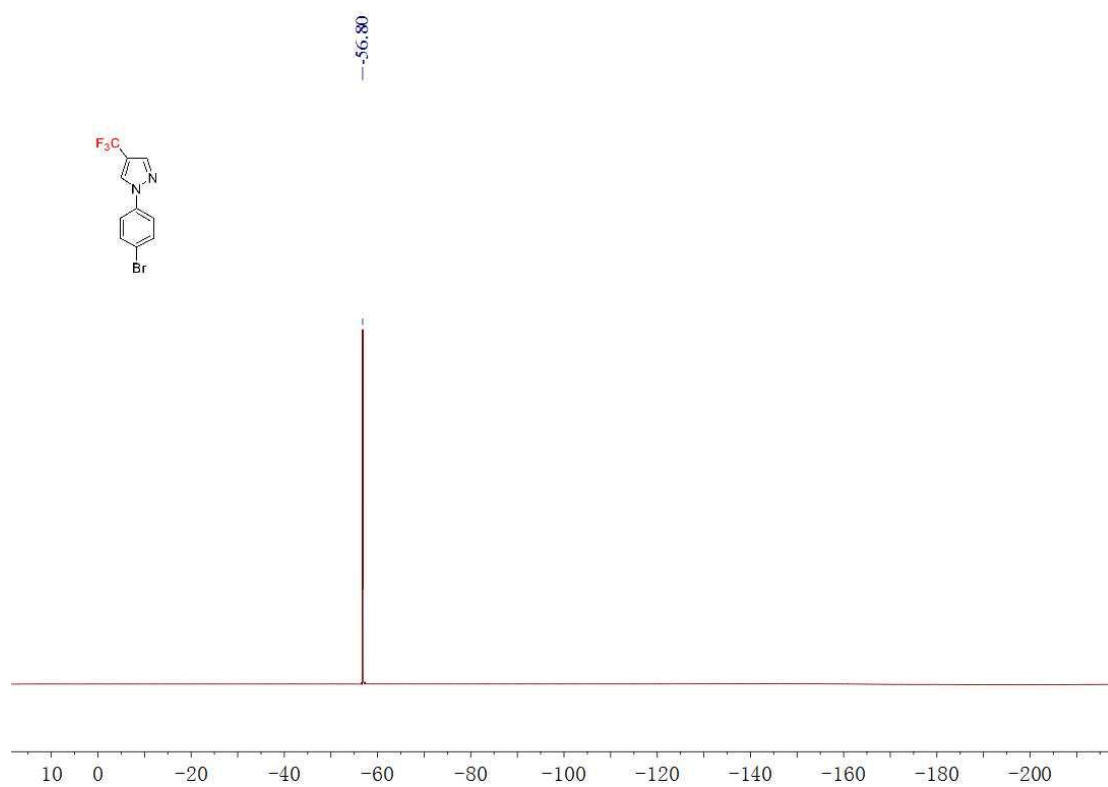
^{13}C NMR spectrum of **3t** in CDCl_3



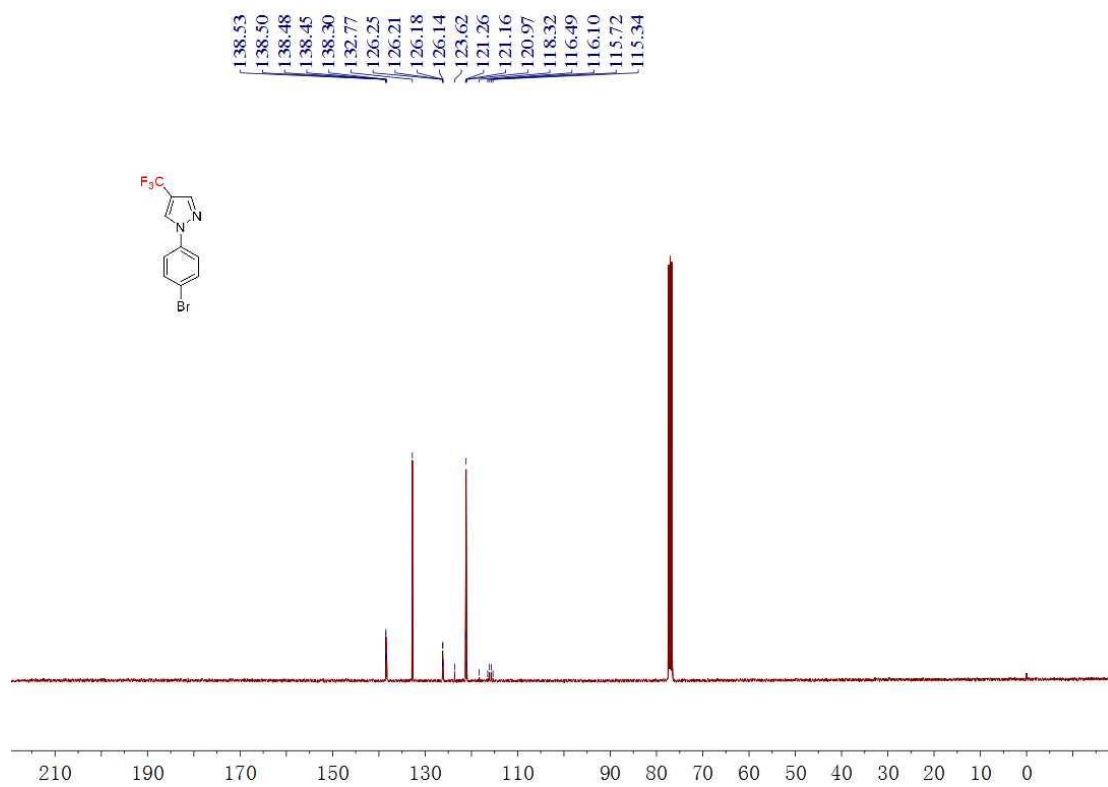
^1H NMR spectrum of **3u** in CDCl_3



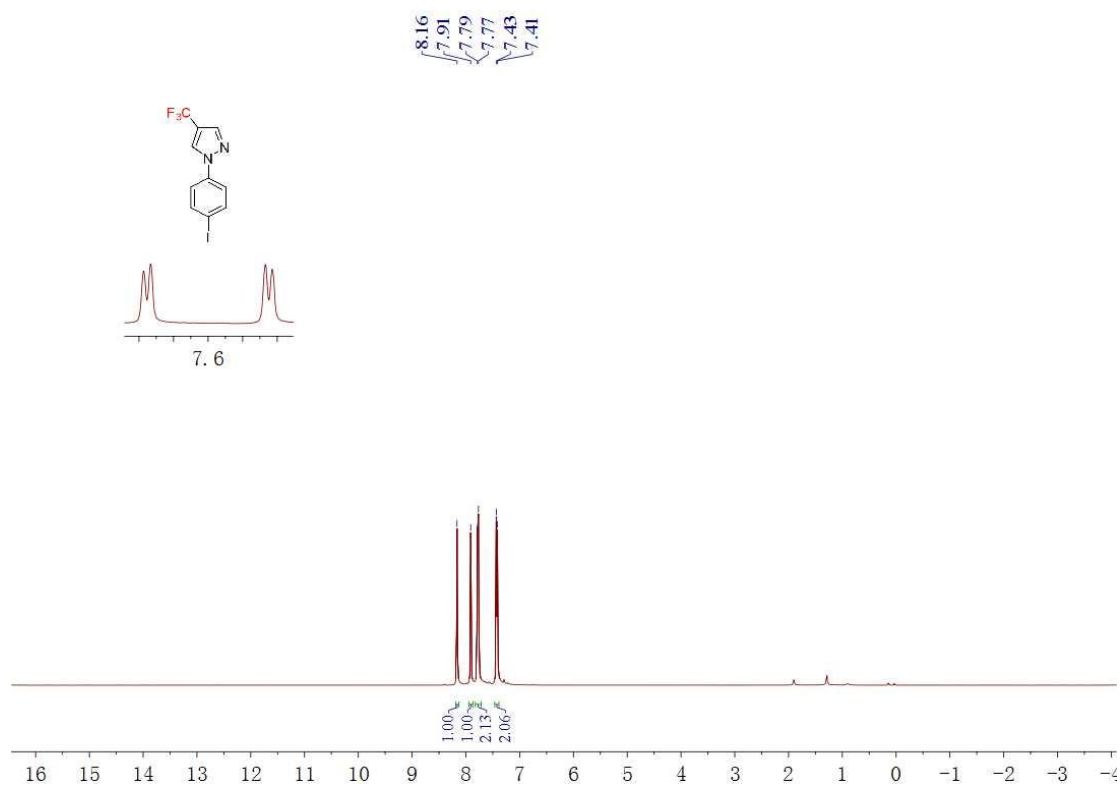
^{19}F NMR spectrum of **3u** in CDCl_3



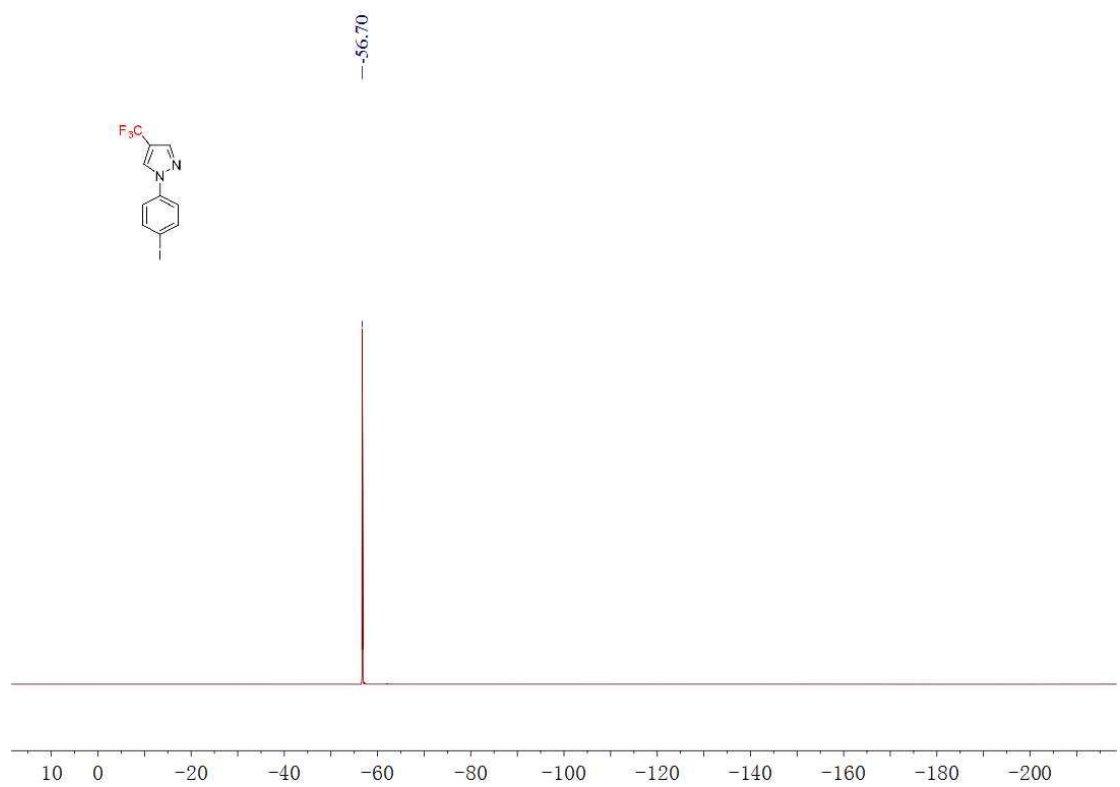
^{13}C NMR spectrum of **3u** in CDCl_3



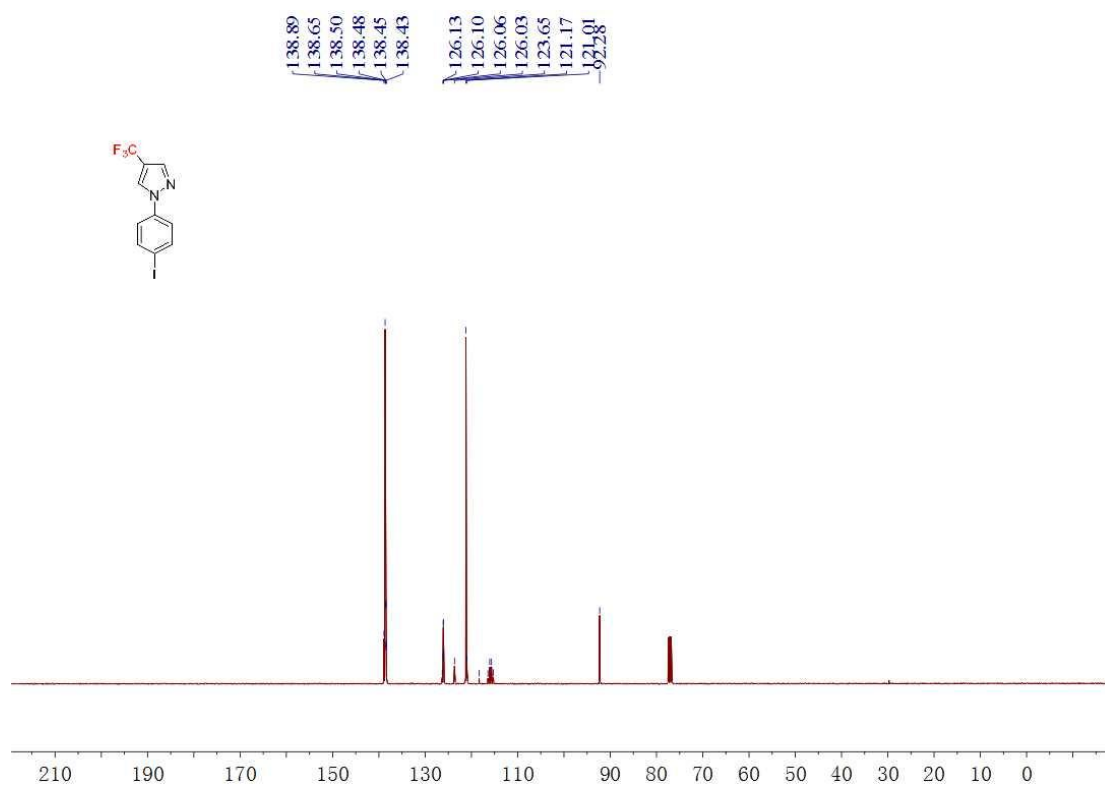
^1H NMR spectrum of **3v** in CDCl_3



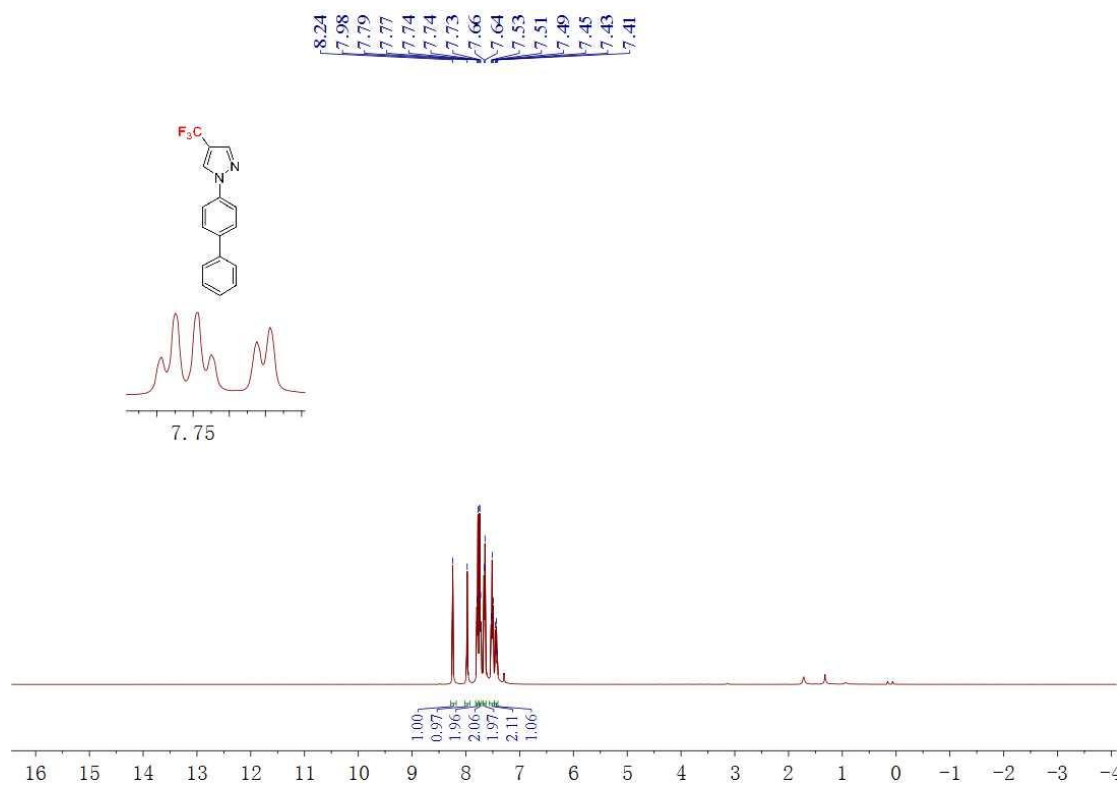
^{19}F NMR spectrum of **3v** in CDCl_3



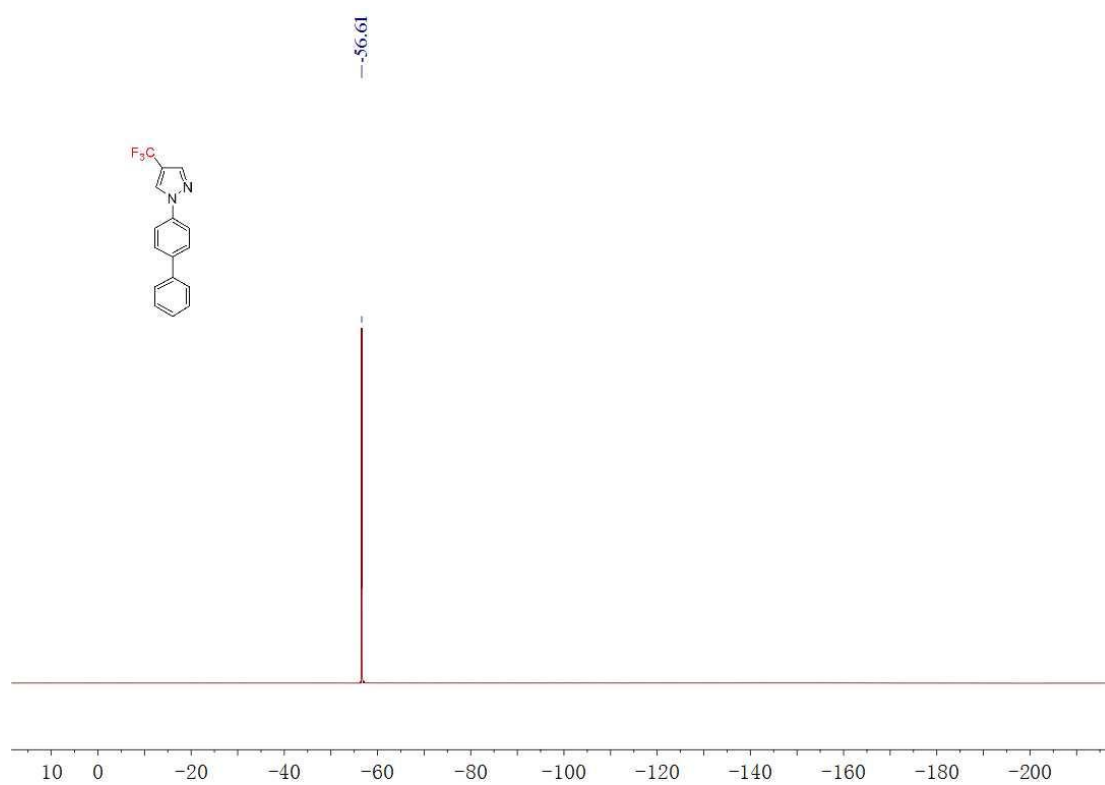
^{13}C NMR spectrum of **3v** in CDCl_3



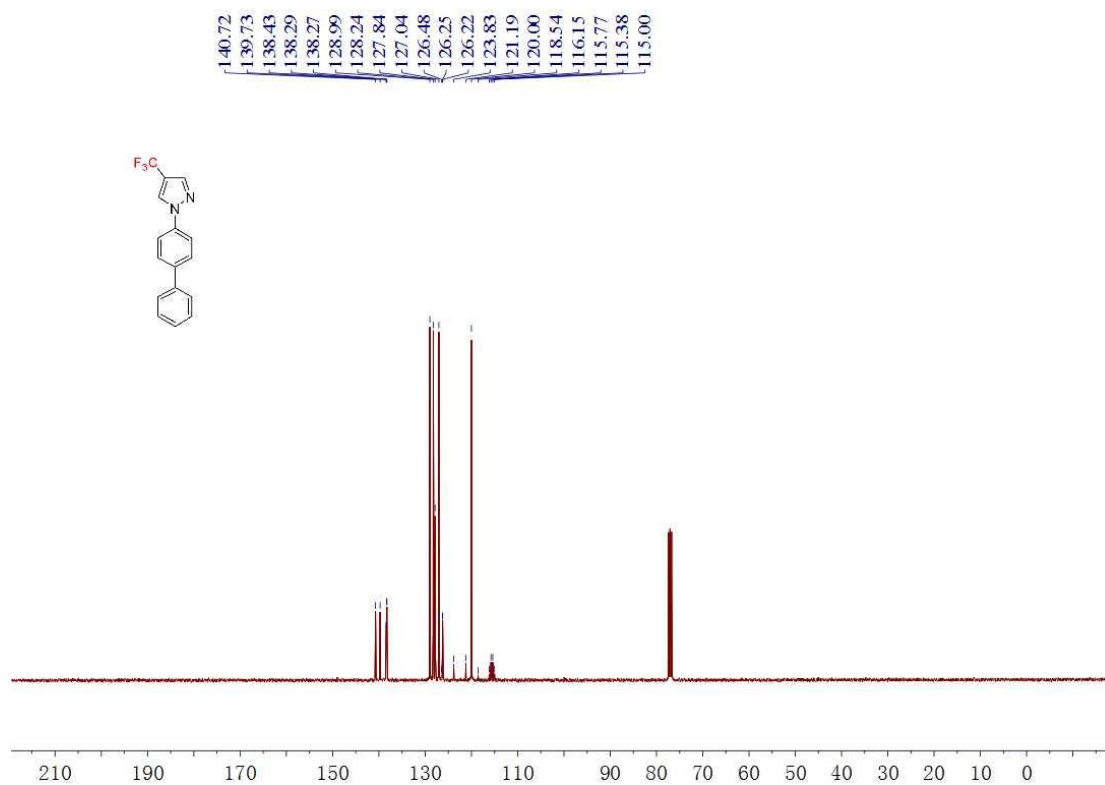
^1H NMR spectrum of **3w** in CDCl_3



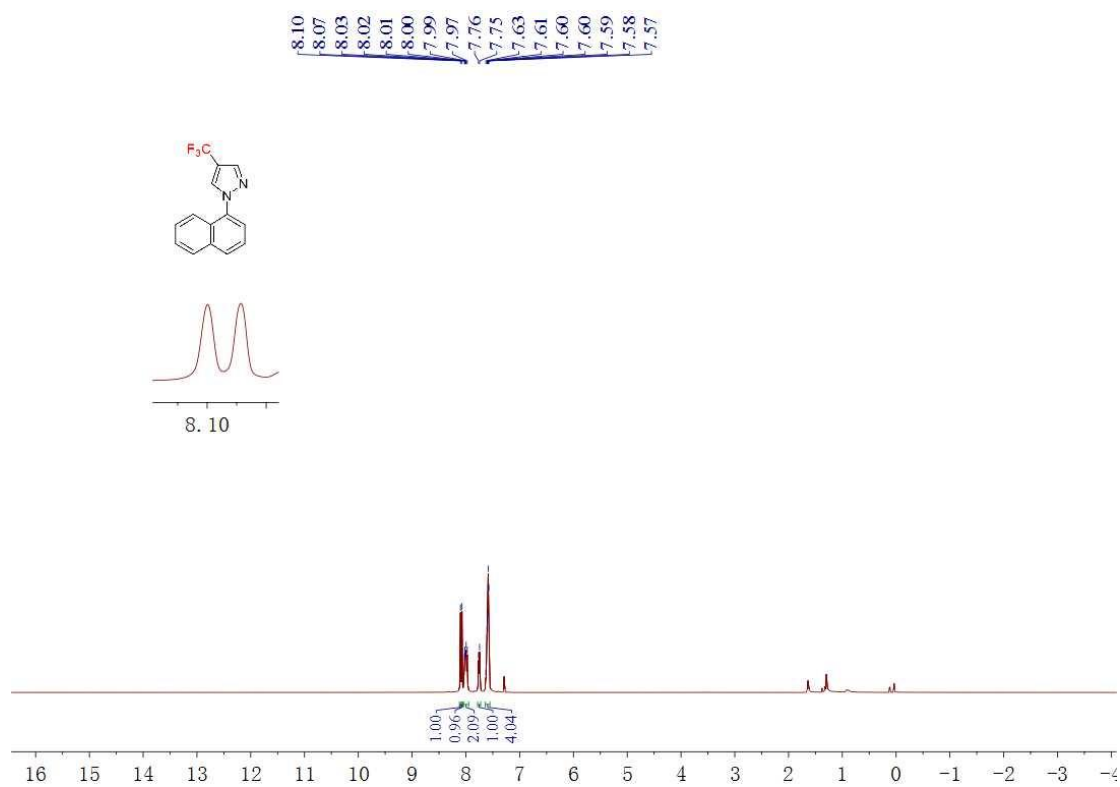
^{19}F NMR spectrum of **3w** in CDCl_3



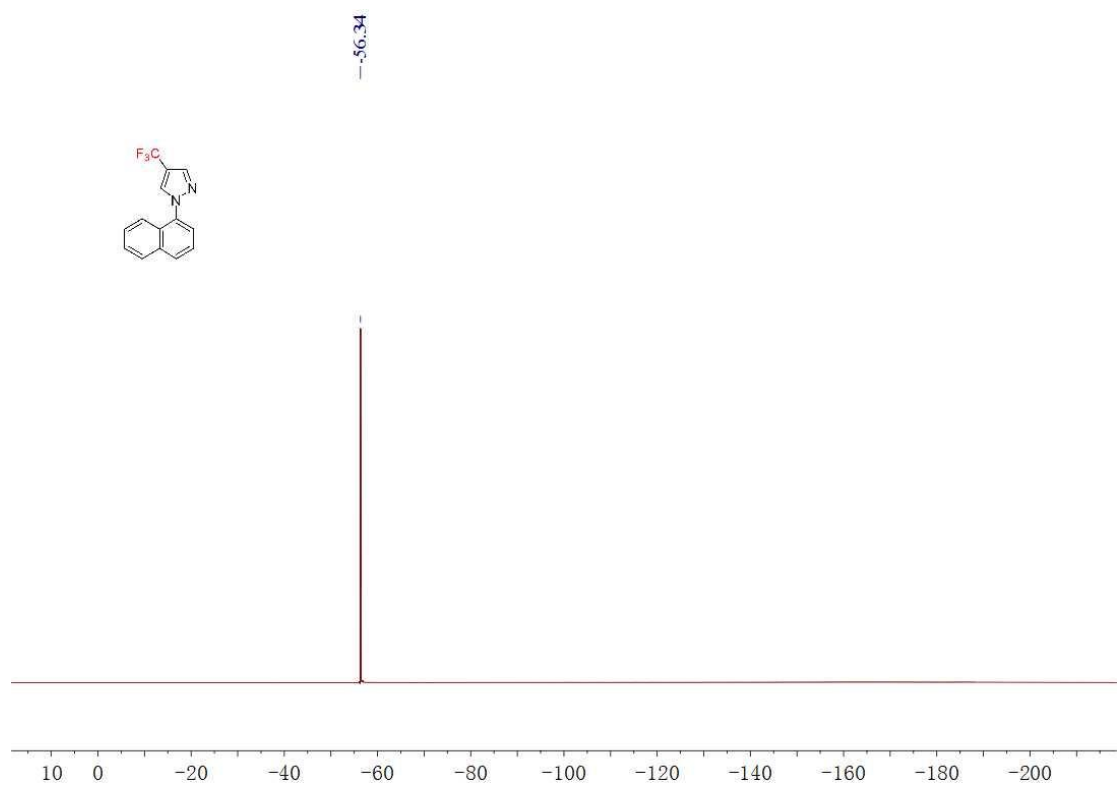
^{13}C NMR spectrum of **3w** in CDCl_3



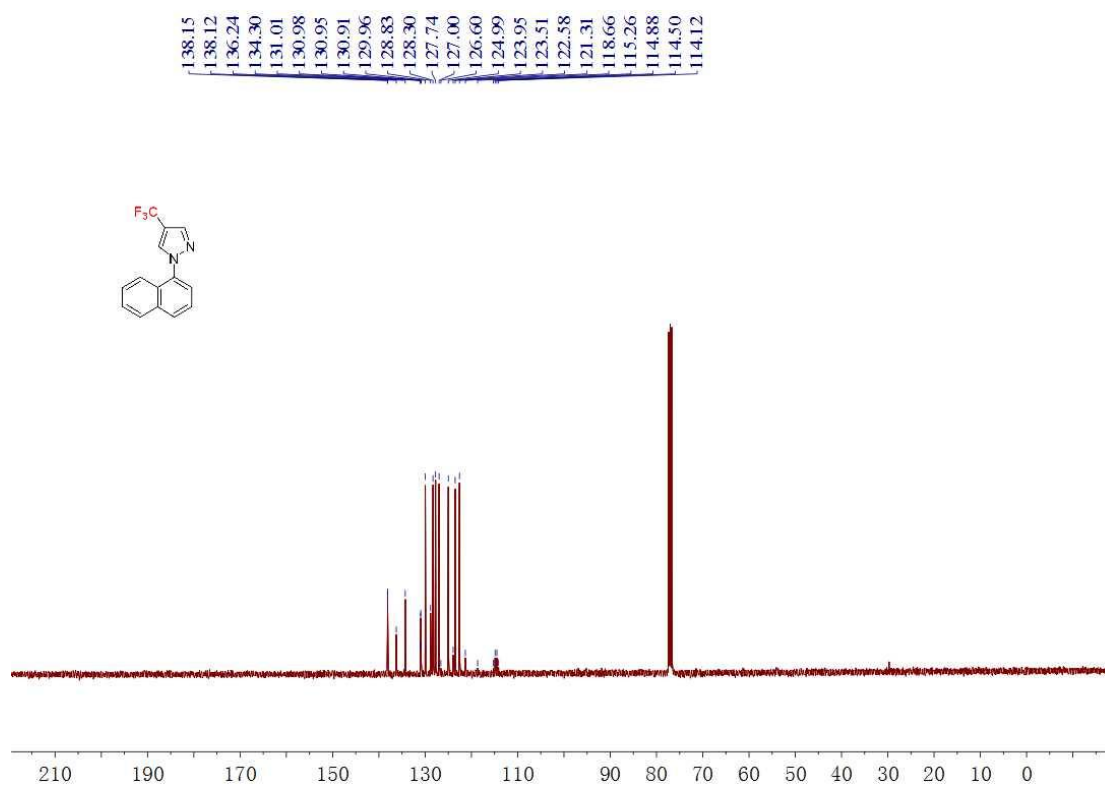
^1H NMR spectrum of **3x** in CDCl_3



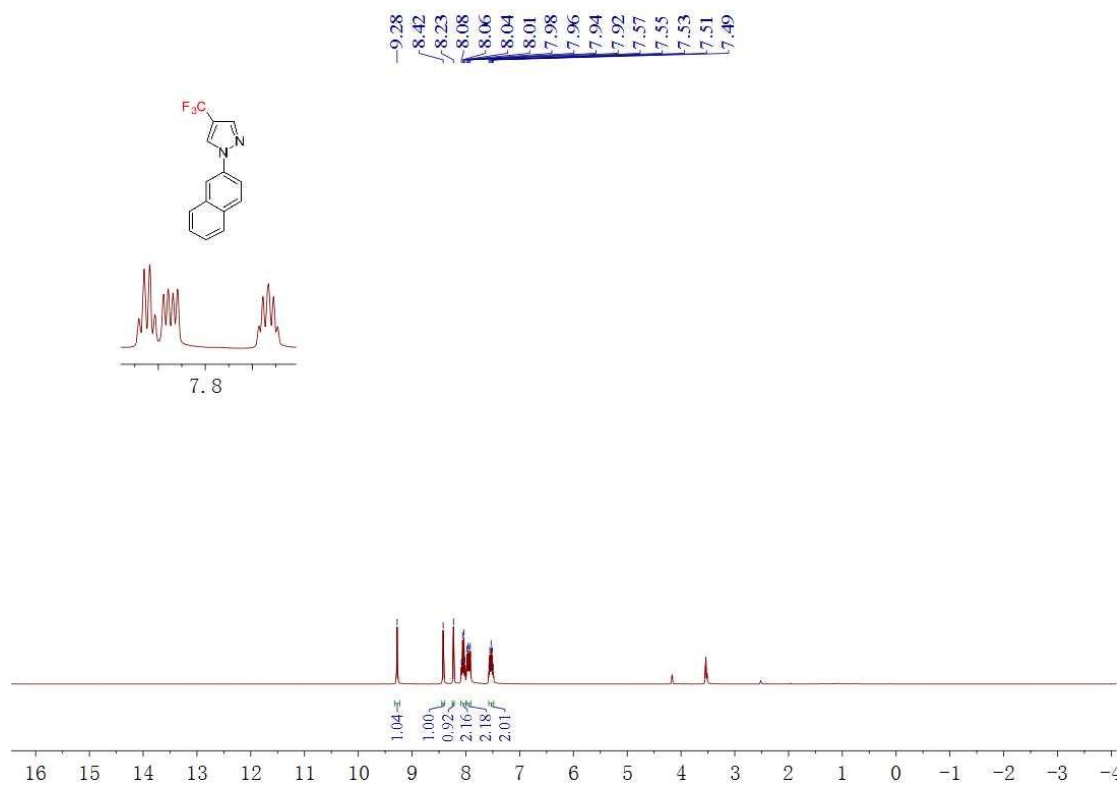
^{19}F NMR spectrum of **3x** in CDCl_3



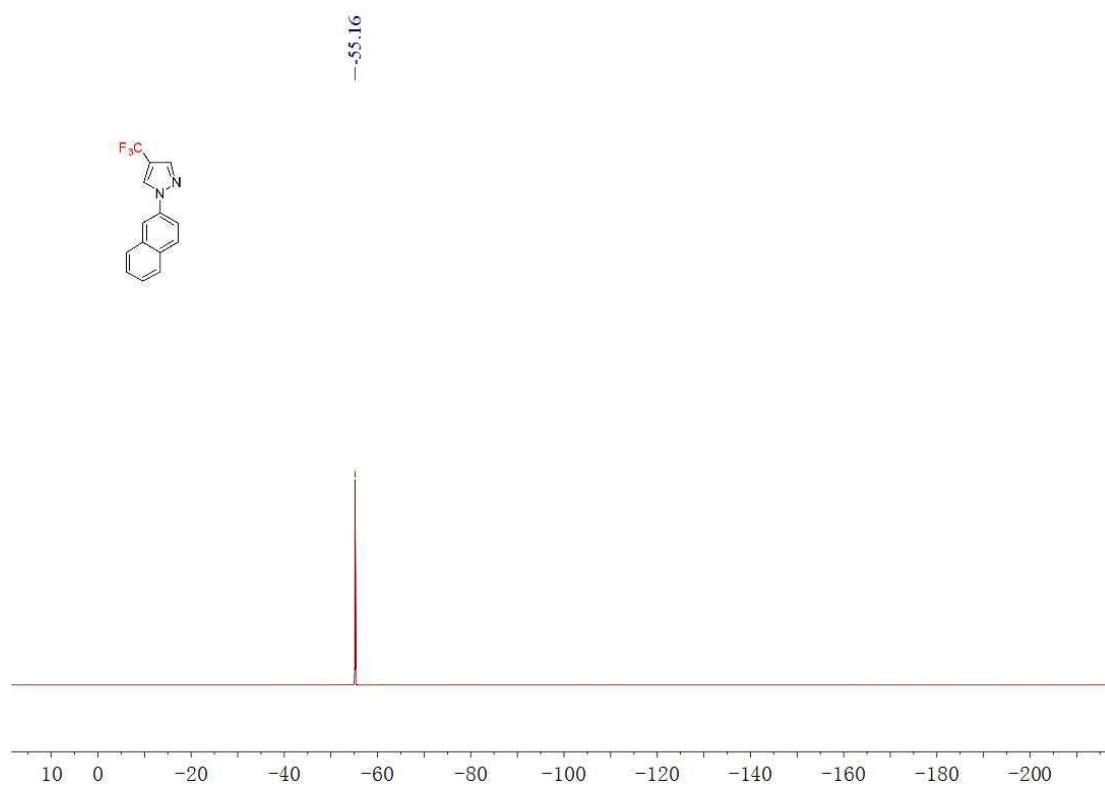
^{13}C NMR spectrum of **3x** in CDCl_3



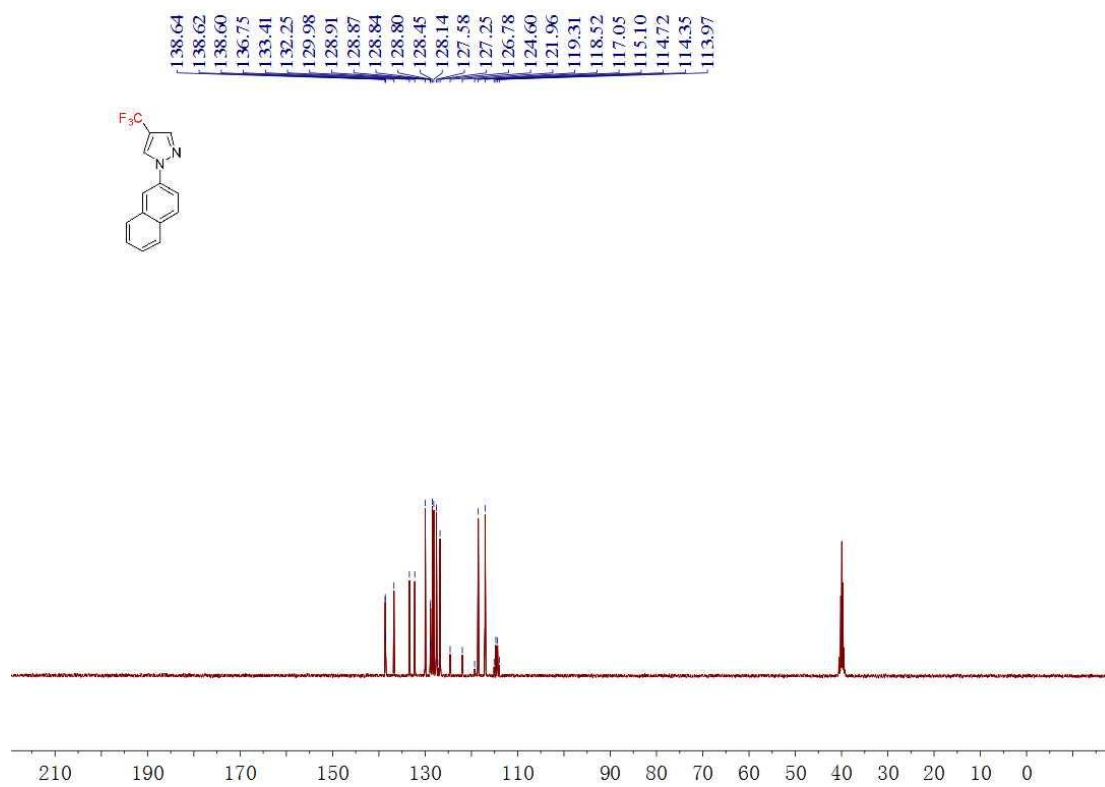
^1H NMR spectrum of **3y** in $\text{DMSO-}d_6$



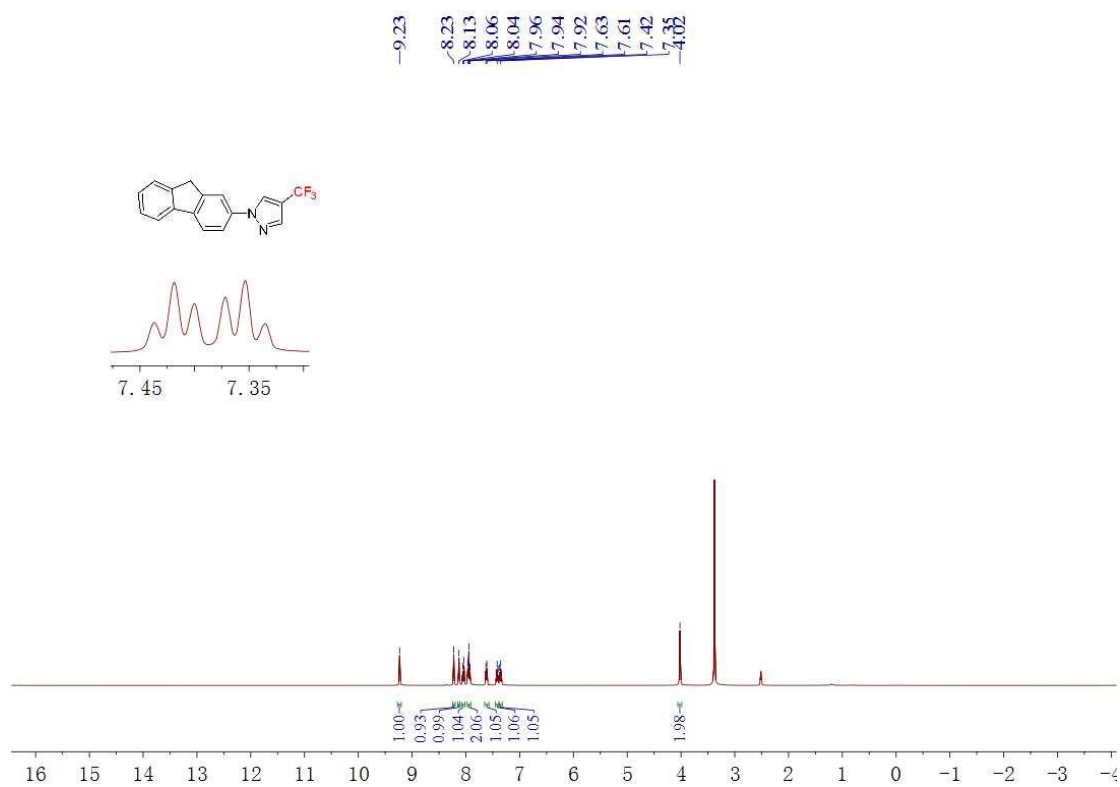
^{19}F NMR spectrum of **3y** in $\text{DMSO-}d_6$



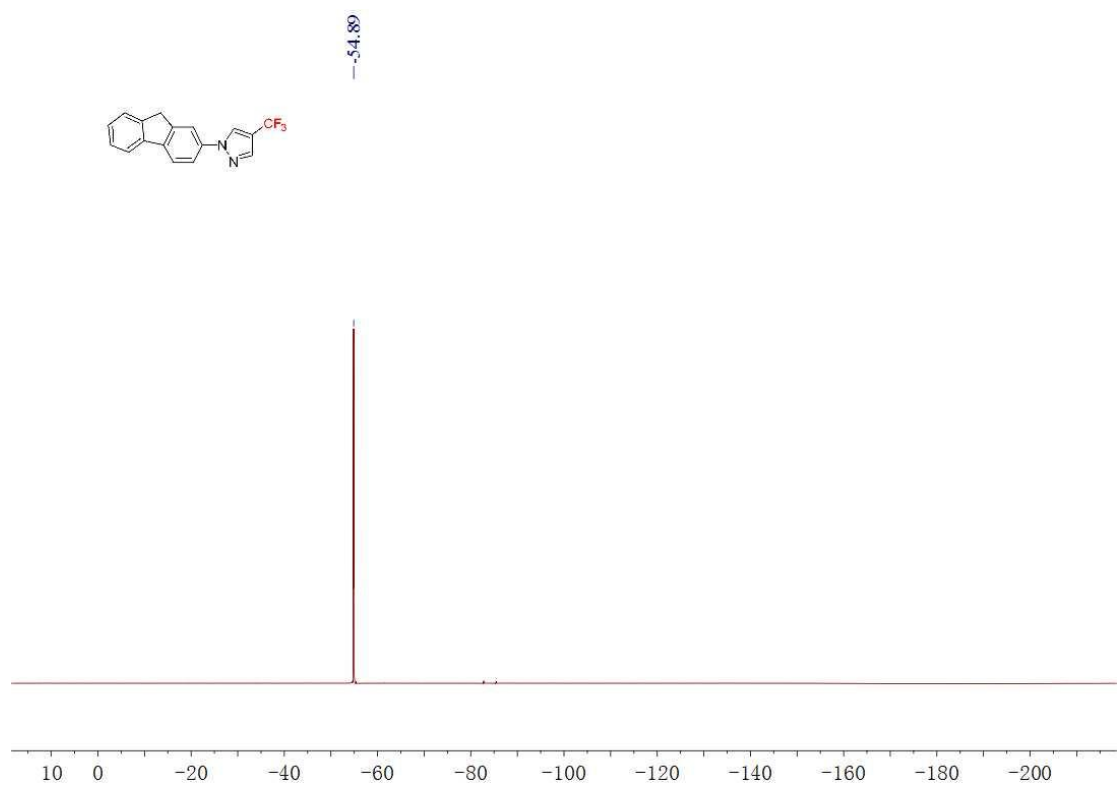
^{13}C NMR spectrum of **3y** in $\text{DMSO-}d_6$



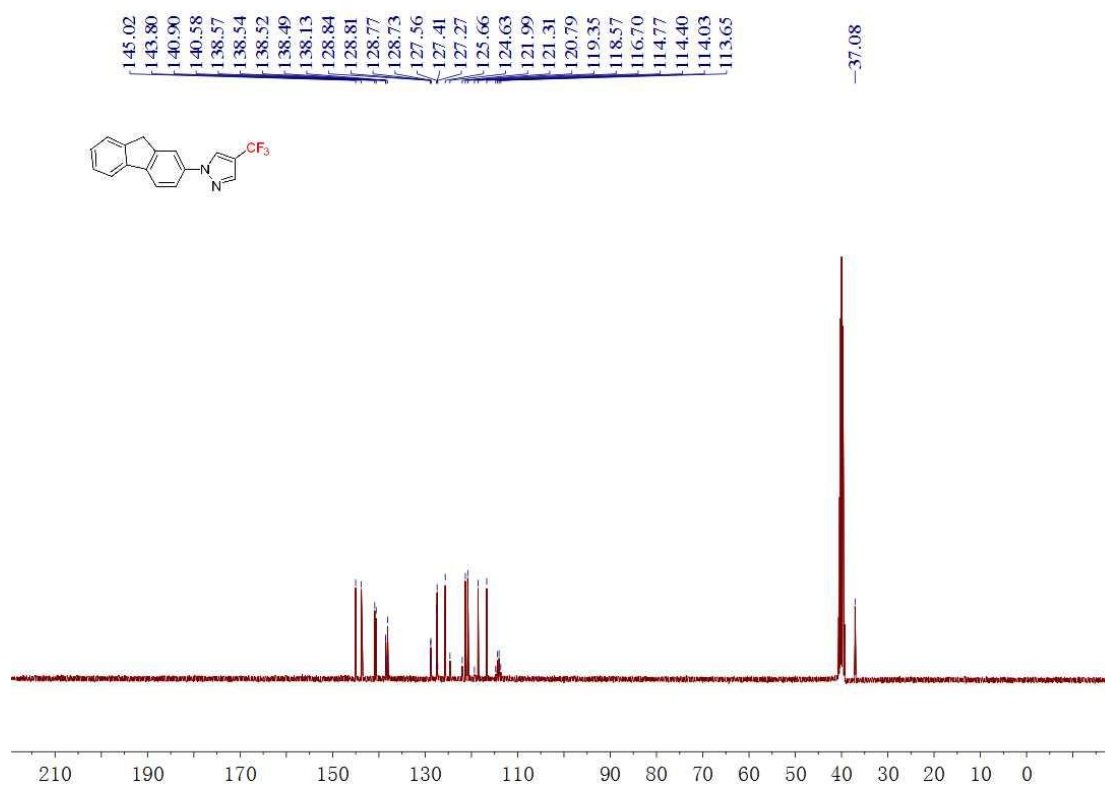
^1H NMR spectrum of **3z** in $\text{DMSO-}d_6$



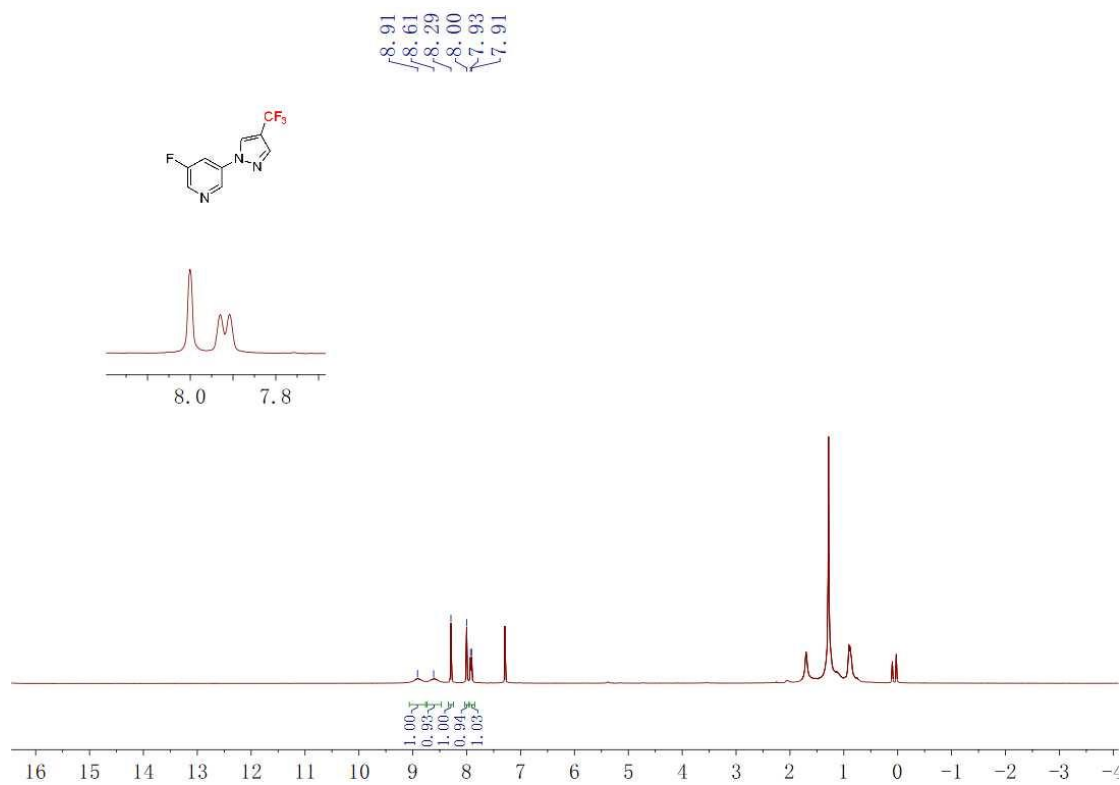
^{19}F NMR spectrum of **3z** in $\text{DMSO-}d_6$



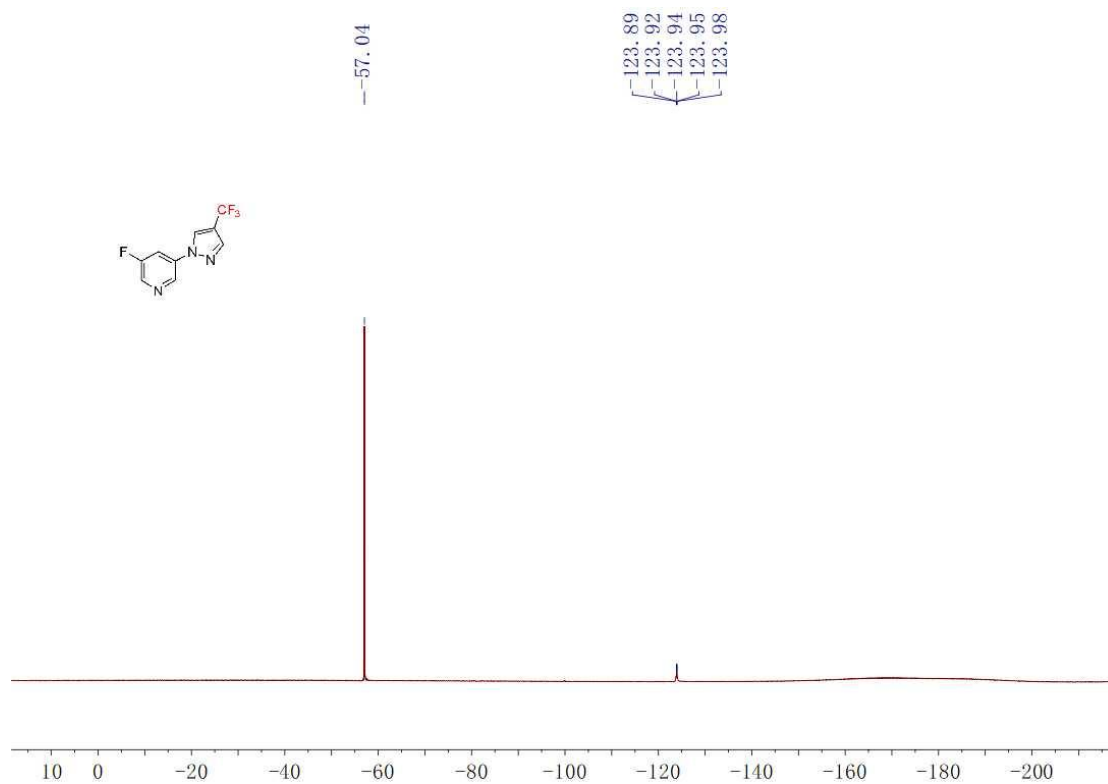
^{13}C NMR spectrum of **3z** in $\text{DMSO-}d_6$



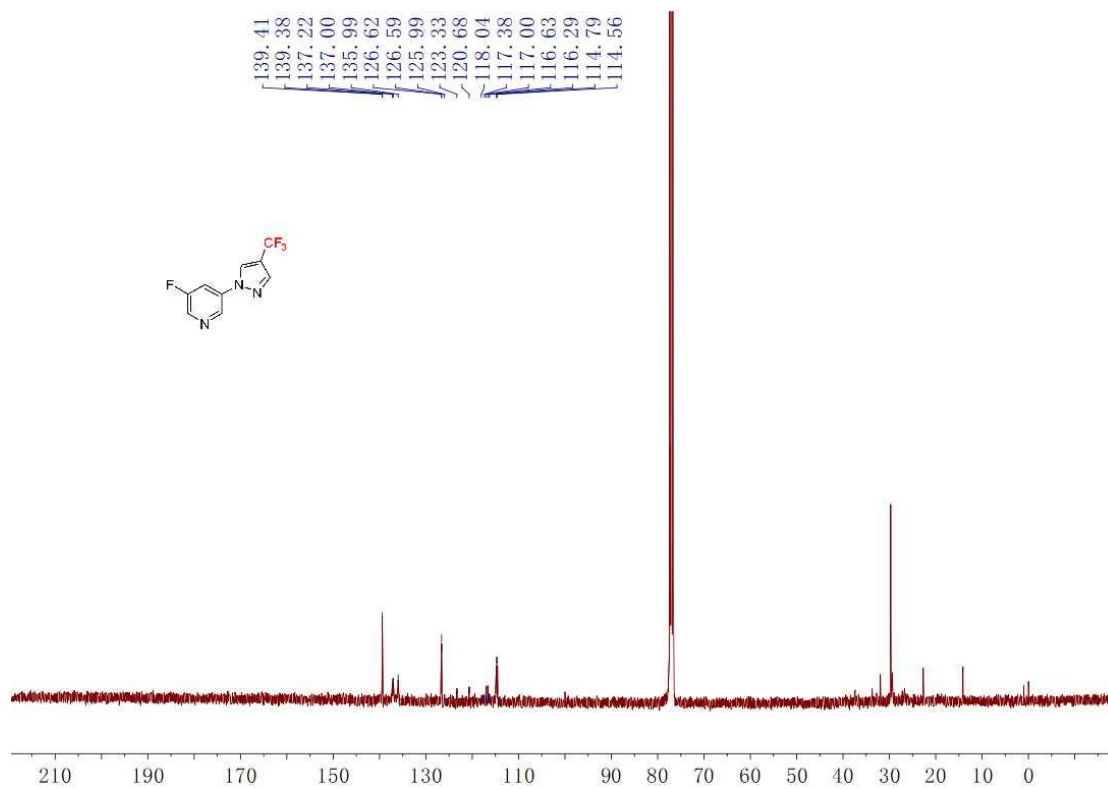
^1H NMR spectrum of **3aa** in CDCl_3



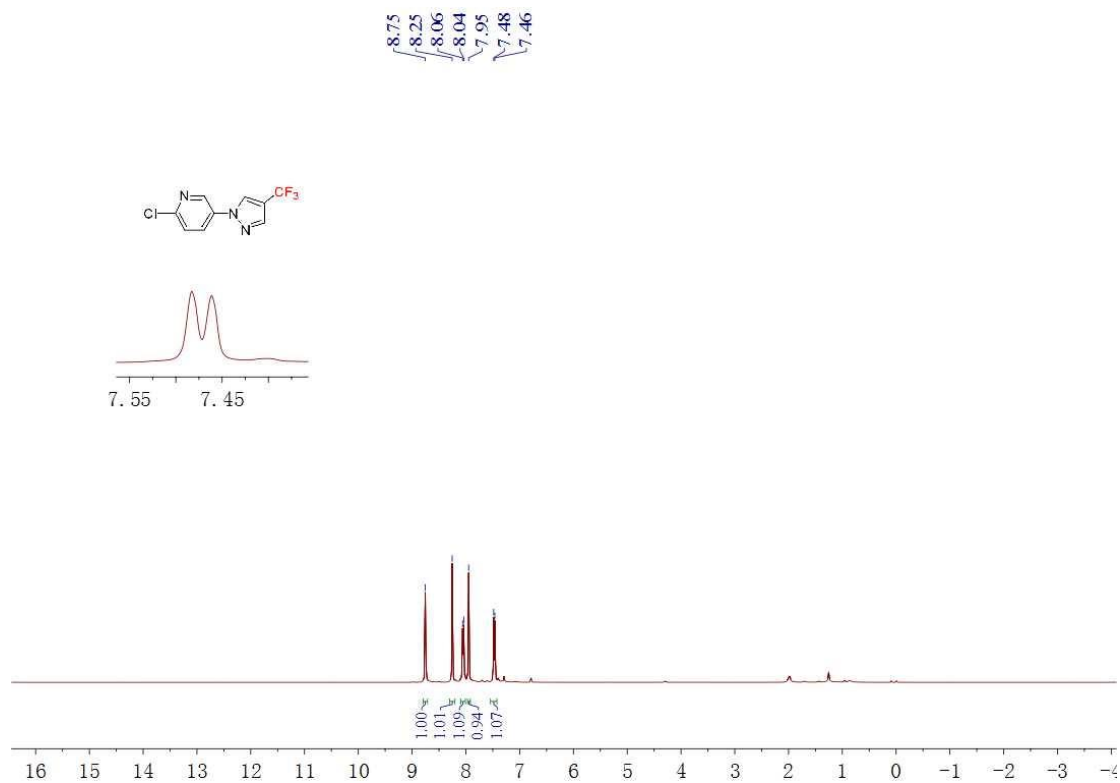
^{19}F NMR spectrum of **3aa** in CDCl_3



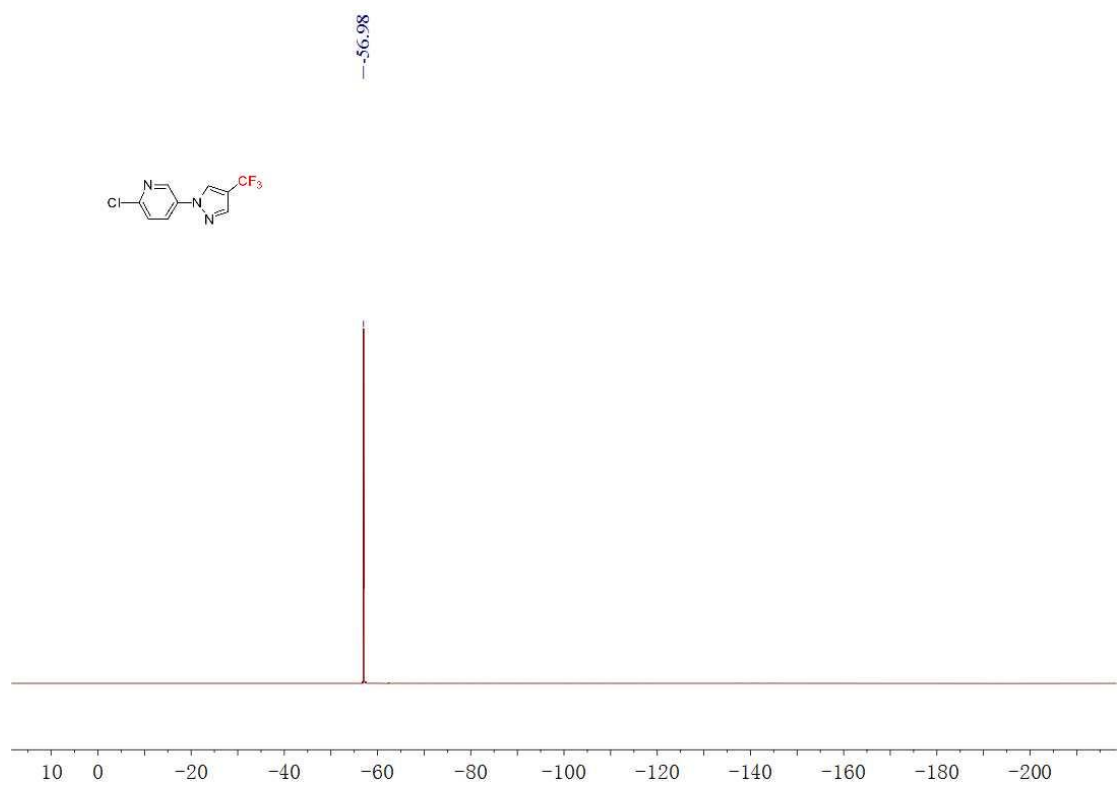
^{13}C NMR spectrum of **3aa** in CDCl_3



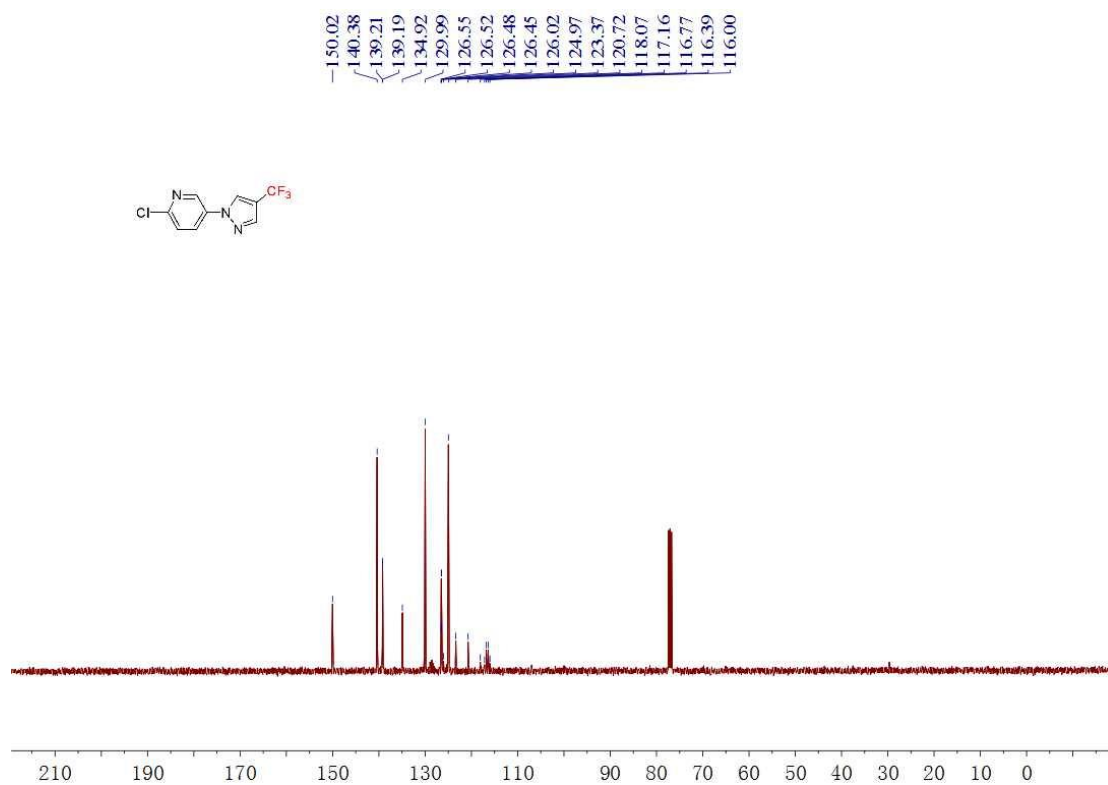
^1H NMR spectrum of **3ab** in CDCl_3



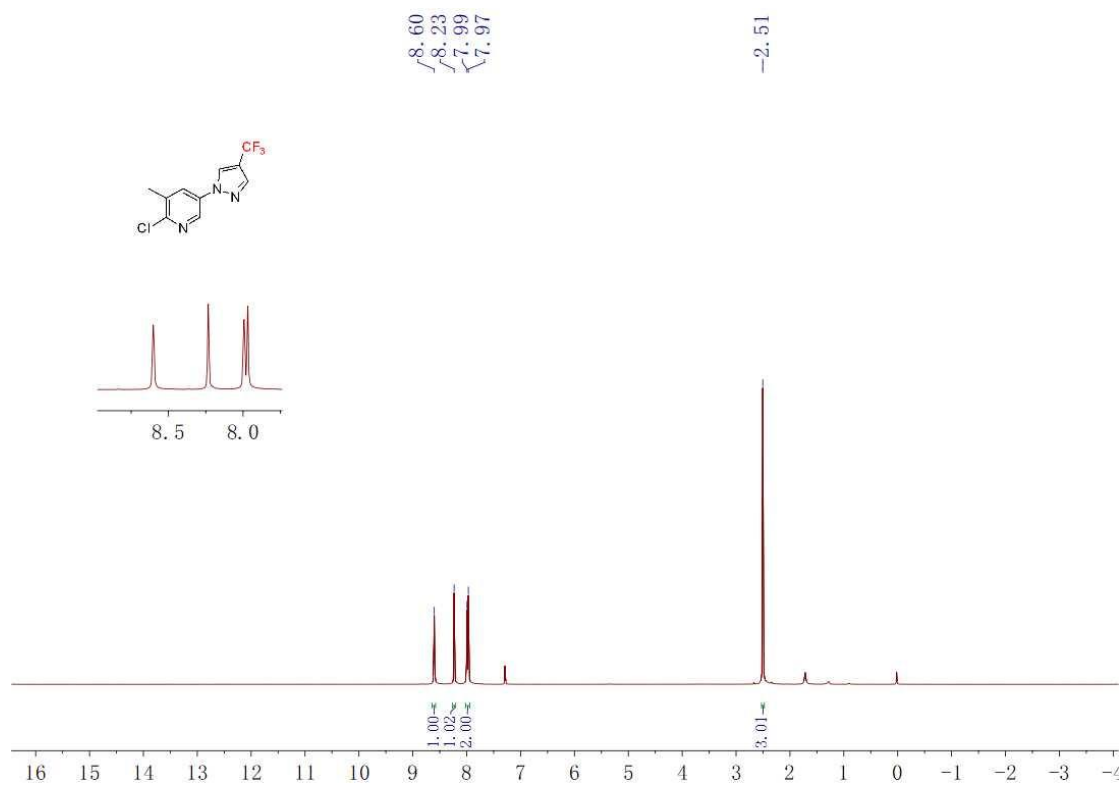
^{19}F NMR spectrum of **3ab** in CDCl_3



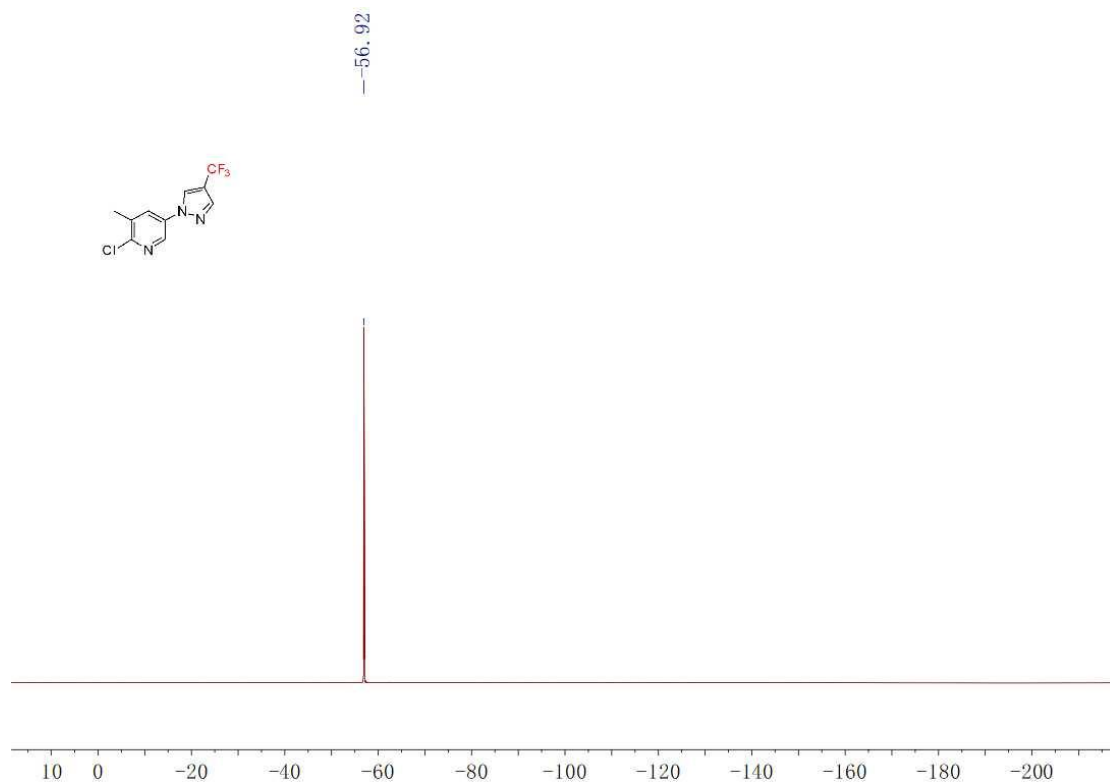
^{13}C NMR spectrum of **3ab** in CDCl_3



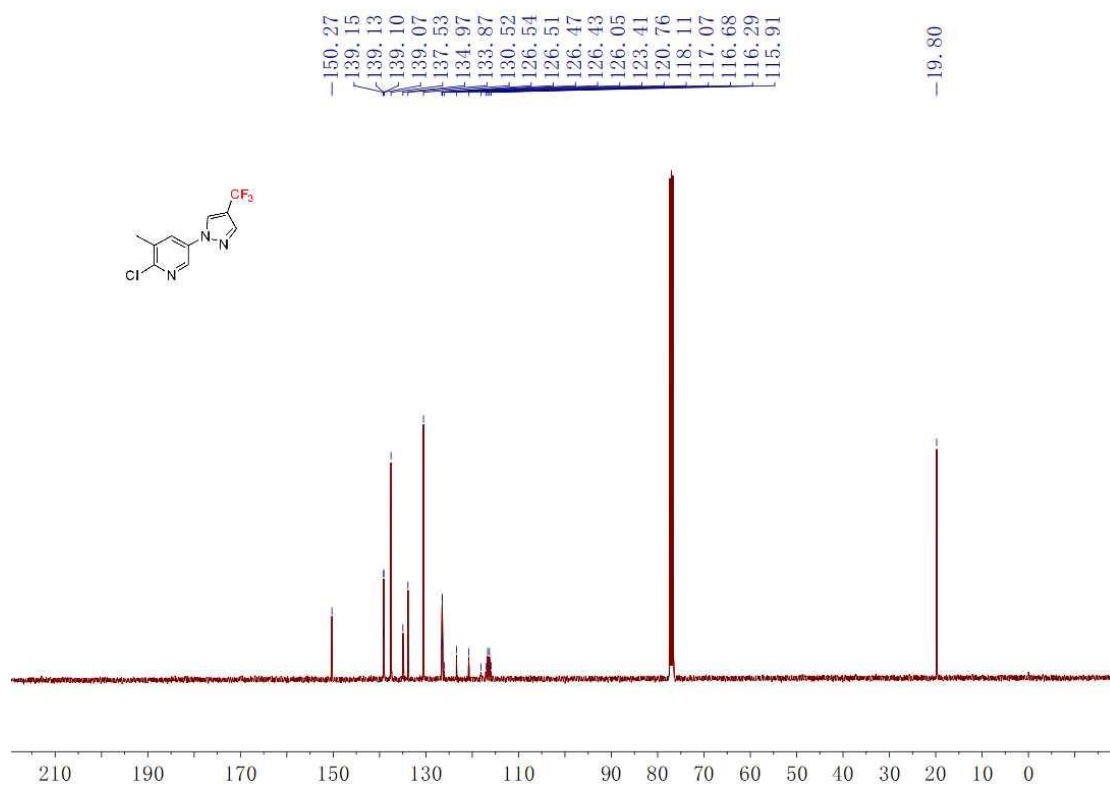
^1H NMR spectrum of **3ac** in CDCl_3



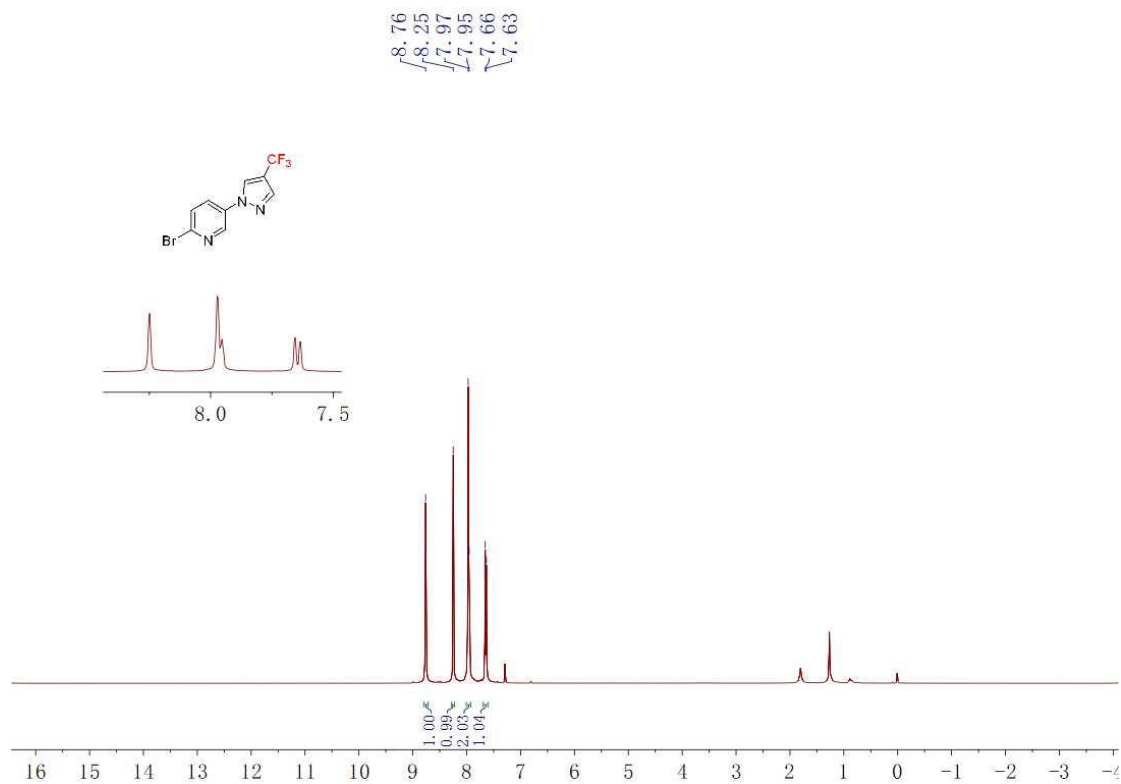
^{19}F NMR spectrum of **3ac** in CDCl_3



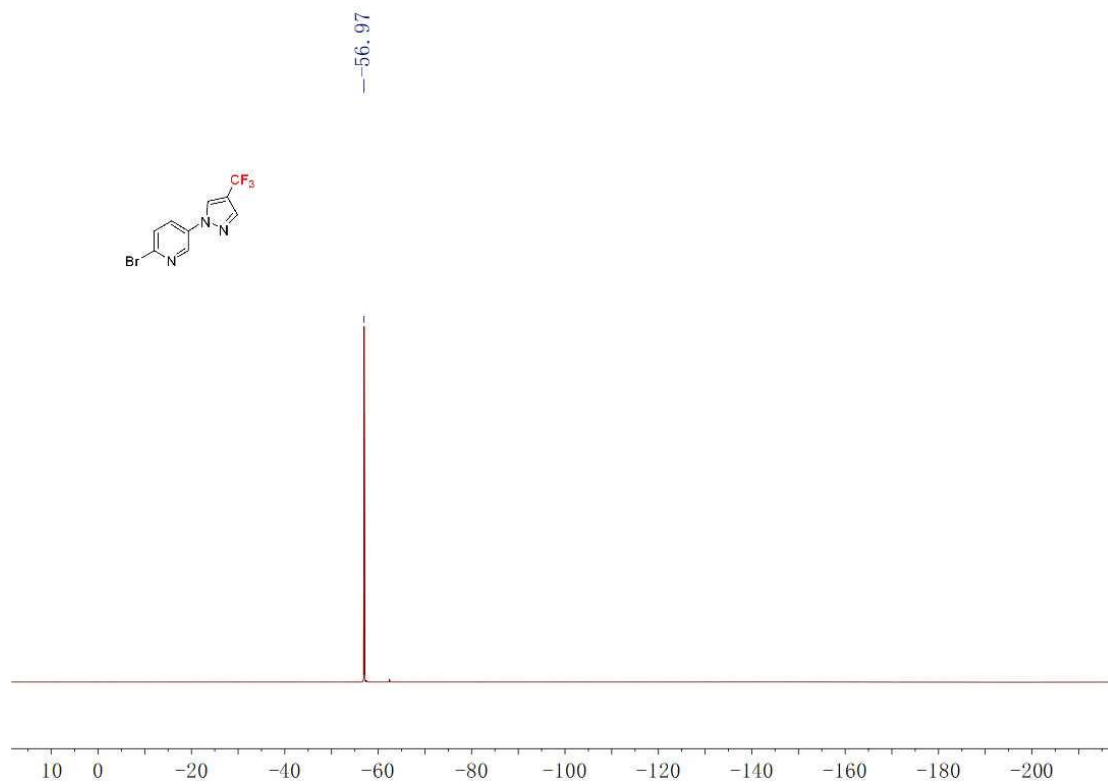
^{13}C NMR spectrum of **3ac** in CDCl_3



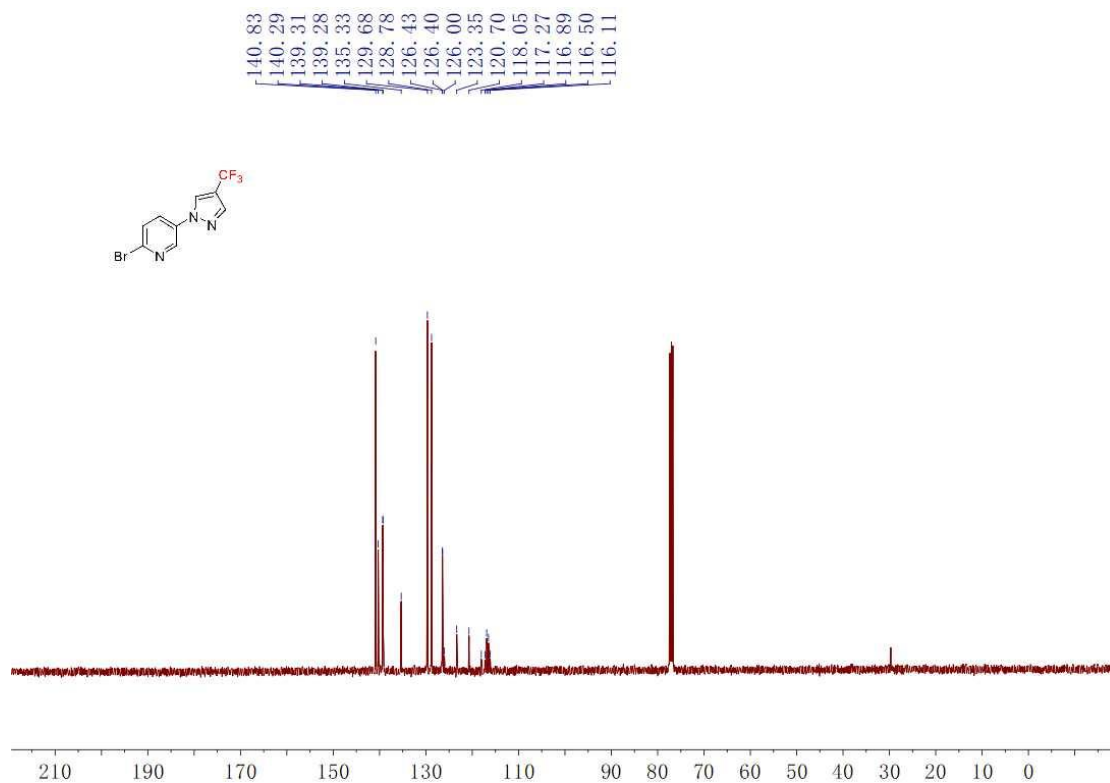
^1H NMR spectrum of **3ad** in CDCl_3



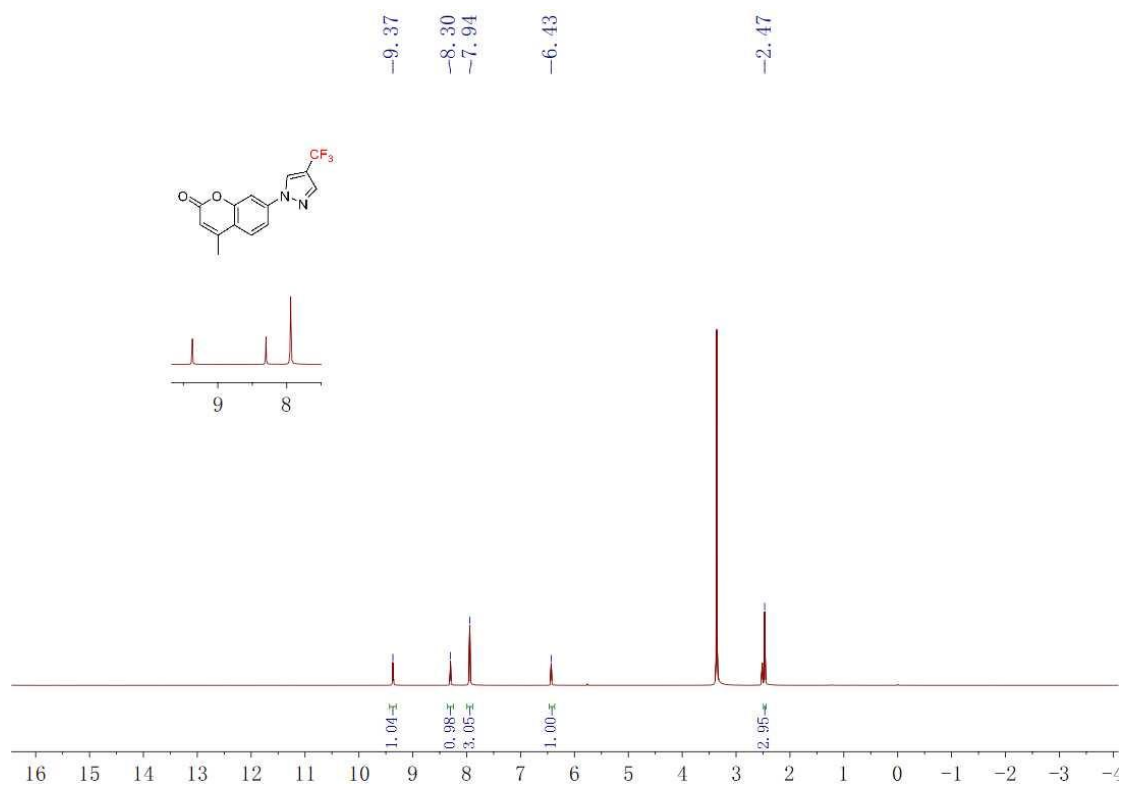
^{19}F NMR spectrum of **3ad** in CDCl_3



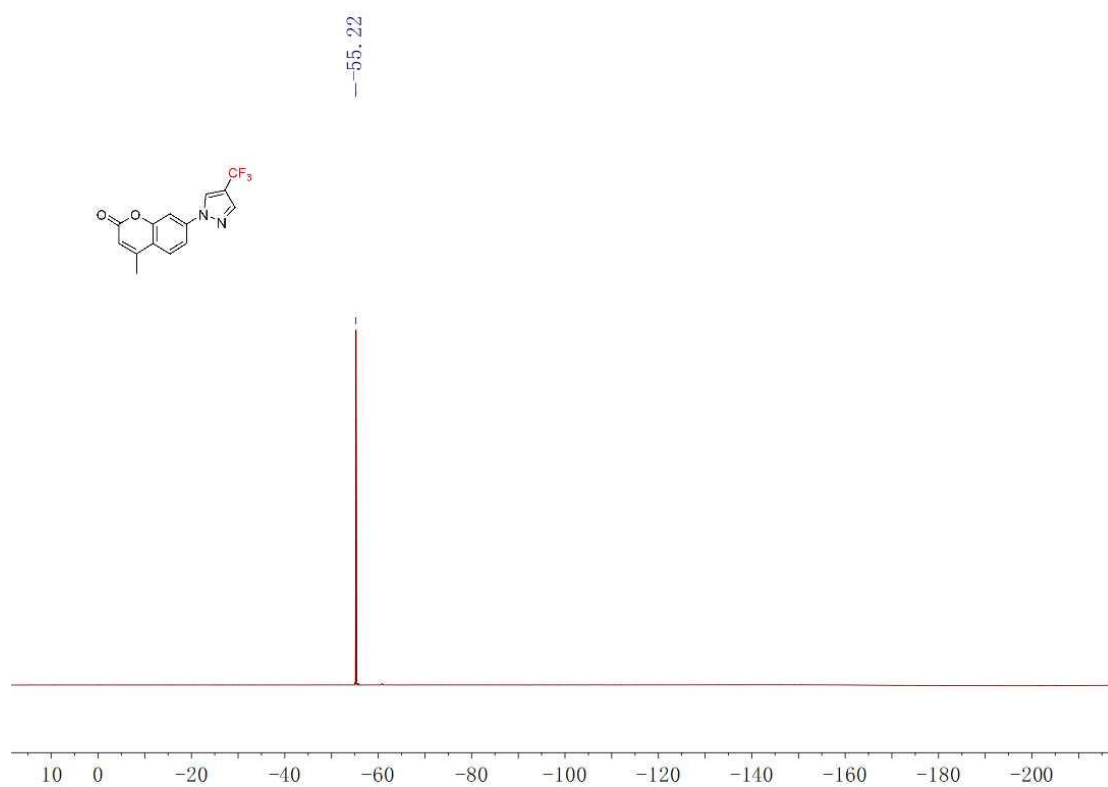
^{13}C NMR spectrum of **3ad** in CDCl_3



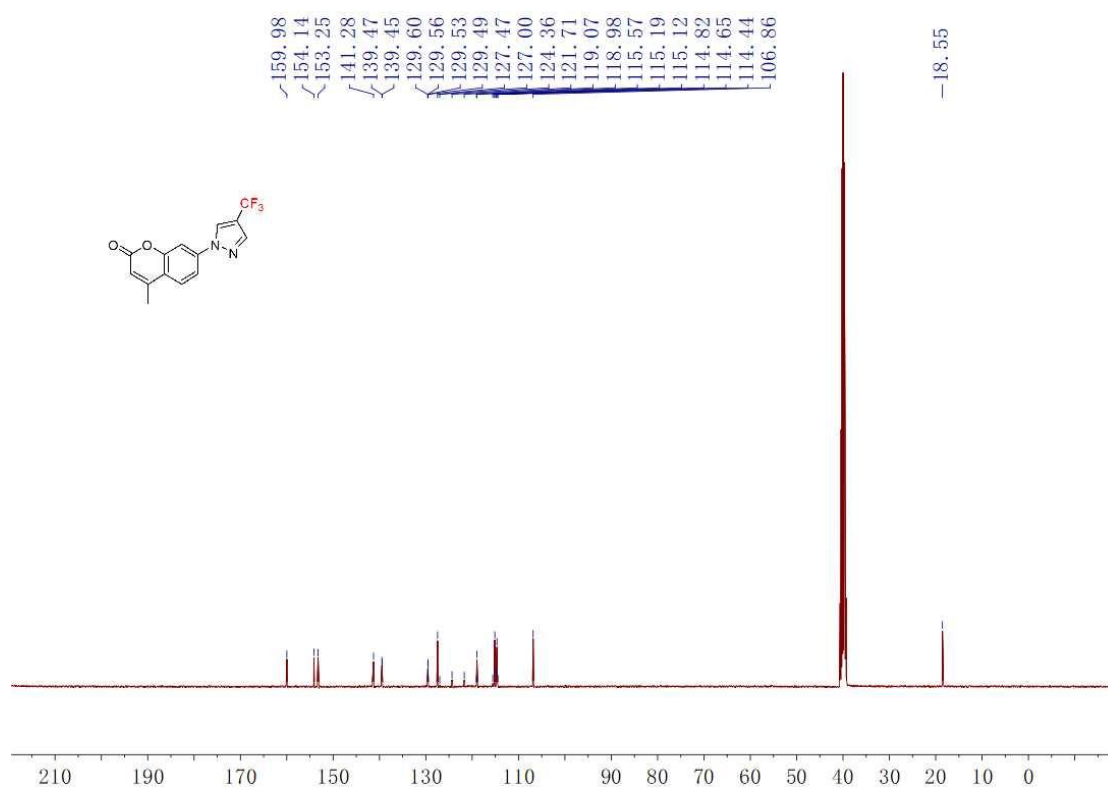
^1H NMR spectrum of **3ae** in $\text{DMSO-}d_6$



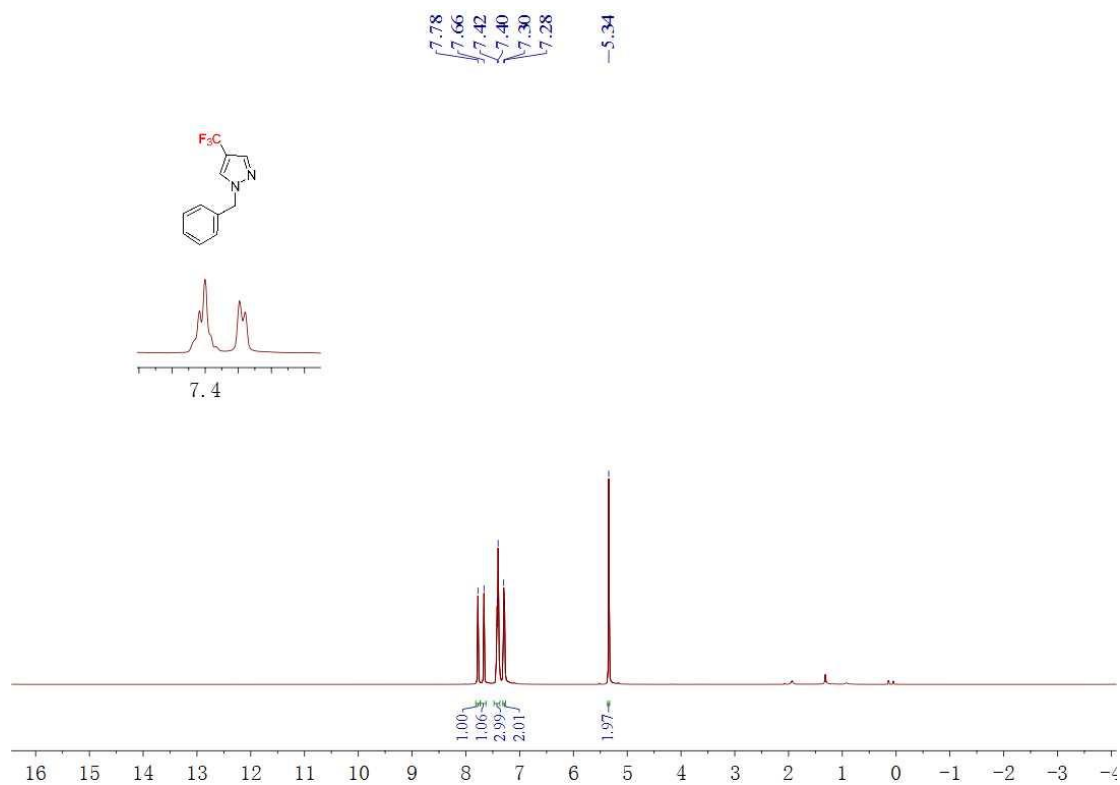
^{19}F NMR spectrum of **3ae** in $\text{DMSO-}d_6$



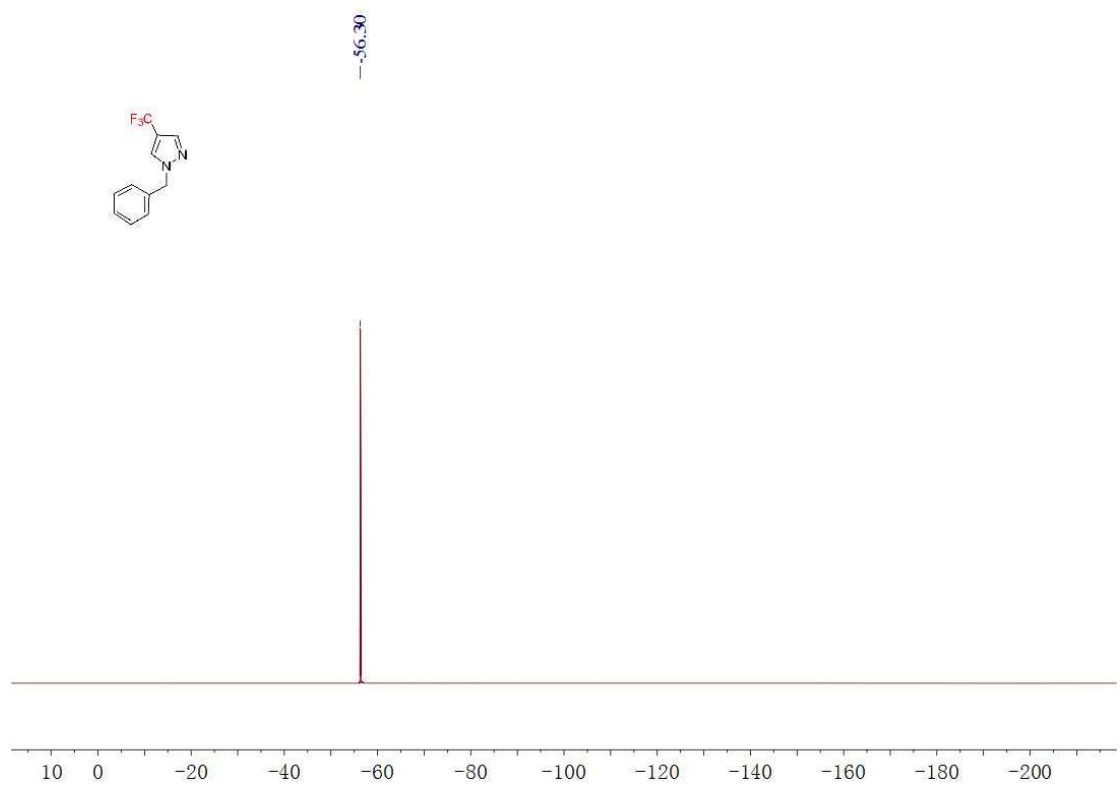
^{13}C NMR spectrum of **3ae** in $\text{DMSO-}d_6$



^1H NMR spectrum of **3af** in CDCl_3



^{19}F NMR spectrum of **3af** in CDCl_3



¹³C NMR spectrum of **3af** in CDCl₃

