Supporting Information *for*

Synthesis of 3-(tri/difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-ones *via* the cyclization of the hydrazinecarboxamides with tri/difluoroacetic anhydride

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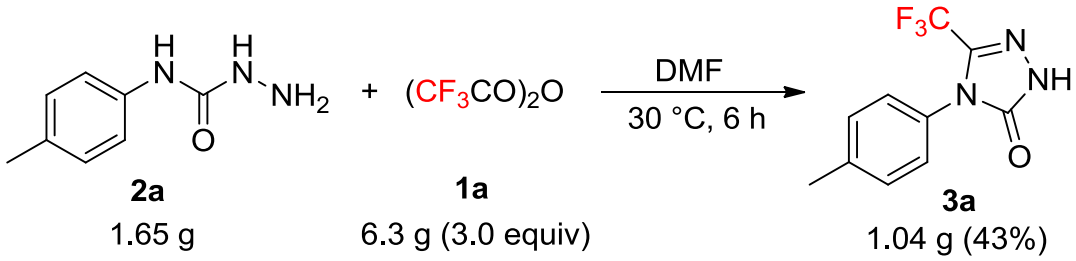
Procedure for gram scale reaction for synthesis of 4-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3a)



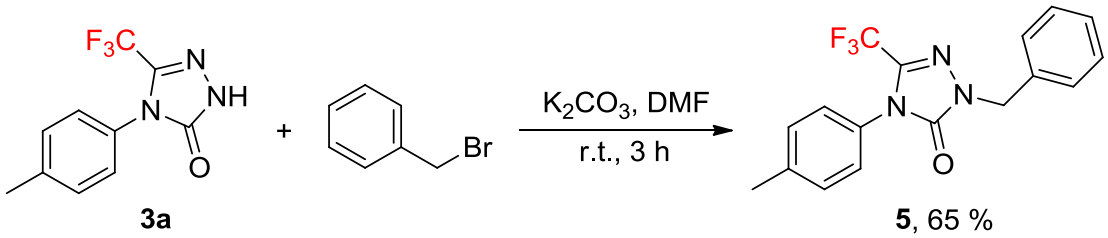
2a 1.65 g

1a 6.3 g (3.0 equiv)

3a 1.04 g (43%)

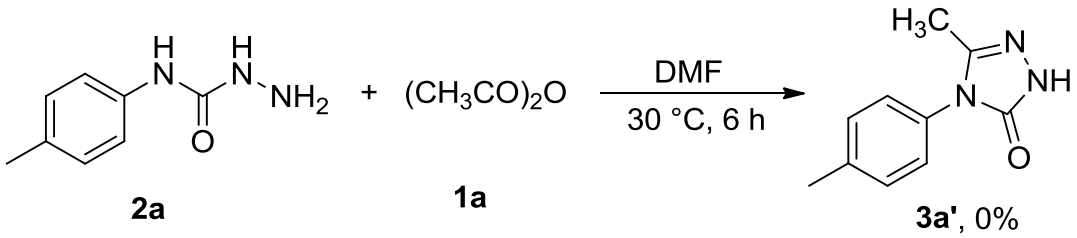
The *N*-(*p*-Tolyl)hydrazinecarboxamide (**2a**) (1.65 g, 10.0 mmol), trifluoroacetic anhydride (**1a**) (6.3 g, 30.0 mmol, 3.0 equiv), and dry *N*,*N*-dimethylformamide (30 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 30 ^{o}C for 6 h under nitrogen atmosphere. The reaction mixture was diluted with ethyl acetate (80 mL), washed with saturated ammonium chloride solution (100 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting product **3a** was purified by column chromatography over silica gel (*n*-pentane/ethyl acetate = 5:1).

The procedure for the *N*-Alkylation of compound 3a



4-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (**3a**) (121.0 mg, 0.50 mmol), benzyl bromide (128 mg, 0.75 mmol, 1.5 equiv), potassium carbonate (138.0 mg, 1.5 mmol, 3.0 equiv), *N*,*N*-dimethylformamide (5 mL) were added to a reaction tube equipped with a stir bar a reaction tube equipped. The mixture was stirred at room temperature for 6 h. The reaction mixture was then diluted with ethyl acetate (30 mL), washed with saturated ammonium chloride solution (100 mL), dried over $MgSO_4$. The solvent was removed by rotary evaporation and the crude product **5** was washed by petroleum ether three times. Compound **5** was purified by recrystallization (65%).

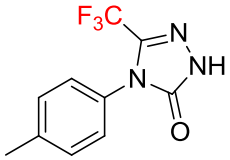
The procedure for the attempted reaction of *N*-(*p*-tolyl)hydrazinecarboxamide (2a) with acetic anhydride (the nonfluorinated version of the reaction)



2a **1a** **3a'**, 0%

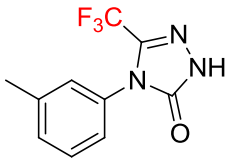
The *N*-(*p*-tolyl)hydrazinecarboxamide (**2a**) (83 mg, 0.50 mmol), acetic anhydride (153 mg, 1.50 mmol, 3.0 equiv), and dry *N*,*N*-dimethylformamide (3.0 mL) were added to a reaction tube equipped with a stir bar. The mixture was stirred at 30 ℃ for 6 h. The resulting reaction mixture was analyzed by GC-MS, and no trace of 1,2,4-triazol-3-one product **3a′** was detected.

Data for compounds 3–5.



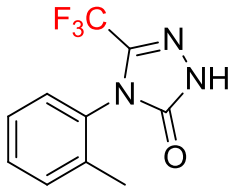
4-(*p*-Tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3a)

Obtained as a pale white solid in 87% yield (105 mg). Mp: 151–152 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 7.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 140.6 (s), 137.1 (q, *J* = 40.9 Hz), 130.4 (s), 128.3 (s), 127.1 (s), 117.0 (q, *J* = 271.1 Hz), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.2 (s, 3F). IR (KBr): ν 3195, 2253, 1721, 1581, 1468, 1210, 1176, 1099, 1039, 983, 828, 795, 545, 500 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O$ $[M+H]^+$: 244.0692; found: 244.0689.



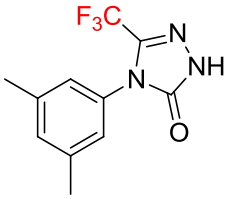
4-(*m*-Tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3b)

Obtained as a pale white solid in 63% yield (76 mg). Mp: 144–146 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.11 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 140.1 (s), 137.0 (q, *J* = 41.1 Hz), 131.1 (s), 130.8 (s), 129.6 (s), 127.9 (s), 124.4 (s), 117.0 (q, *J* = 270.9 Hz), 21.3 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1 (s, 3F). IR (KBr): ν 3021, 2253, 2189, 2025, 1721, 1469, 1380, 1213, 1164, 1101, 544 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O$ $[M+H]^+$: 244.0692; found: 244.0689.



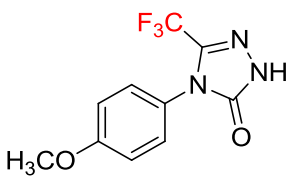
4-(*o*-Tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3c)

Obtained as a pale white solid in 85% yield (103 mg). Mp: 187–190 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.32 – 7.23 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (s), 137.2 (q, *J* = 41.1 Hz), 136.7 (s), 131.4 (s), 130.9 (s), 129.7 (s), 128.5 (s), 127.3 (s), 116.8 (q, *J* = 271.0 Hz), 17.4 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (KBr): ν 3024, 2949, 2123, 1736, 1535, 1352, 1206, 1147, 684, 470 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O$ $[M+H]^+$: 244.0692; found: 244.0689.



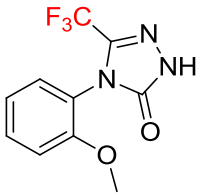
4-(3,5-Dimethylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3d)

Obtained as a pale white solid in 68% yield (87 mg). Mp: 190–192 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.18 (s, 1H), 6.99 (s, 2H), 2.41 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (s), 139.8 (s), 137.1 (q, *J* = 41.0 Hz), 132.1 (s), 130.6 (s), 124.9 (s), 117.0 (q, *J* = 270.9 Hz), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.2 (s, 3F). IR (KBr): ν 3155, 2253, 1720, 1580, 1477, 1381, 1209, 1169, 1098, 984, 856, 801, 624, 569, 532 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{11}H_{11}F_3N_3O$ $[M+H]^+$: 258.0849; found: 258.0845.



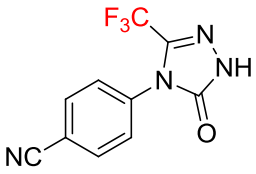
4-(4-Methoxyphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3e)

Obtained as a pale white solid in 72% yield (93 mg). Mp: 145–148 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (s), 155.0 (s), 137.4 (q, *J* = 41.4 Hz), 128.7 (s), 123.2 (s), 117.0 (q, *J* = 270.9 Hz), 115.0 (s), 55.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.4 (s, 3F). IR (KBr): ν 2253, 2192, 2039, 1971, 1793, 1470, 1382, 1166, 1095, 624, 543 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O_2$ $[M+H]^+$: 260.0641; found: 260.0637.



5-(2-Methoxyphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3f)

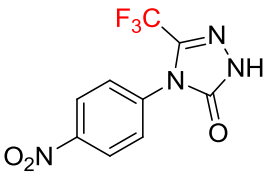
Obtained as a pale white solid in 40% yield (51 mg). Mp: 140–143 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 8.6 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5 (s), 155.1 (s), 137.7 (q, *J* = 40.8 Hz), 132.1 (s), 129.6 (s), 121.0 (s), 119.4 (s), 117.0 (q, *J* = 271.1 Hz), 112.2 (s), 55.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.7 (s, 3F). IR (KBr): ν 3030, 2949, 2254, 2106, 1992, 1794, 1562, 1394, 1360, 1184, 1067, 862, 543, 482 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O_2$ $[M+H]^+$: 260.0641; found: 260.0638.



3-(5-Oxo-3-(trifluoromethyl)-1*H*-1,2,4-triazol-4(5*H*)-yl)benzonitrile (3g)

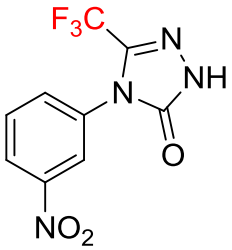
Obtained as a pale white solid in 30% yield (38 mg). Mp: 171–173 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.66 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6 (s), 136.6 (q, *J* = 40.4 Hz), 134.8 (s), 133.7 (s), 128.0 (s), 117.3 (s), 116.8 (q, *J*

= 271.5 Hz), 114.4 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.8 (s, 3F). IR (KBr): ν 3103, 2949, 2253, 1731, 1511, 1468, 1213, 1105, 985, 849, 804, 553 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_6F_3N_4O$ $[M+H]^+$: 255.0488; found: 255.0487.



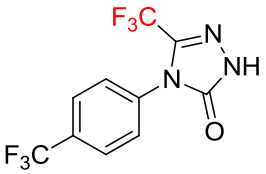
4-(4-Nitrophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3h)

Obtained as a pale white solid in 43% yield (58 mg). Mp: 171–172 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), N*H* was not observed. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1 (s), 148.5 (s), 136.4 (q, *J* = 41.4 Hz), 136.3 (s), 128.2 (s), 125.2 (s), 116.8 (q, *J* = 271.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.6 (s, 3F). IR (KBr): ν 3155, 2253, 2050, 1996, 1793, 1469, 1381, 1216, 1169, 1095, 624, 544 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_3N_4O_3$ $[M+H]^+$: 275.0387; found: 275.0386.



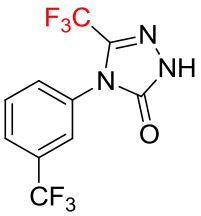
5-(3-Nitrophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3i)

Obtained as a pale white solid in 30% yield (41 mg). Mp: 164–167 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.37. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.95 (s, 1H), 8.53 (s, 1H), 8.42 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.89 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.1 (s), 148.6 (s), 135.5 (t, *J* = 60.1 Hz), 135.2 (s), 133.1 (s), 131.5 (s), 125.2 (s), 123.8 (s), 117.5 (q, *J* = 270.3 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -63.3 (s, 3F). IR (KBr): ν 3002, 2248, 2169, 2123, 1998, 1736, 1535, 1492, 1351, 1206, 1145, 682 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_3N_4O_3$ $[M+H]^+$: 275.0387; found: 275.0386.



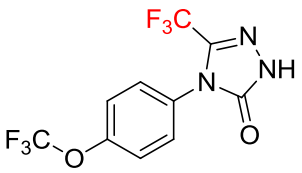
3-(Trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3j)

Obtained as a pale white solid in 60% yield (89 mg). Mp: 128–130 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (s), 136.6 (q, *J* = 41.4 Hz), 134.0 (s), 132.5 (q, *J* = 33.4 Hz), 127.8 (s), 127.1 (q, *J* = 3.5 Hz), 123.3 (q, *J* = 274.6 Hz), 116.8 (q, *J* = 271.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.1 (s, 3F), -64.0 (s, 3F). IR (KBr): ν 3154, 2253, 2197, 2104, 1986, 1727, 1465, 1380, 1324, 1215, 1175, 1049, 1010, 981, 543 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_6F_6N_3O$ $[M+H]^+$: 298.0410; found: 298.0408.



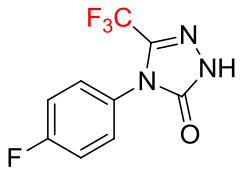
4-(Trifluoromethyl)-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3k)

Obtained as a pale white solid in 62% yield (92 mg). Mp: 128–130 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.62 (d, *J* = 7.9 Hz, 1H), N*H* was not observed. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (s), 136.6 (q, *J* = 41.4 Hz), 132.6 (q, *J* = 33.6 Hz), 131.5 (s), 130.8 (s), 130.6 (s), 127.2 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 3.5 Hz), 123.1 (q, *J* = 272.0 Hz), 116.8 (q, *J* = 271.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F), -64.1 (s, 3F). IR (KBr): ν 3030, 2949, 2914, 2253, 2165, 2091, 1976, 1729, 1583, 1472, 1395, 1346, 1289, 1216, 1178, 858, 624, 545 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_6F_6N_3O$ $[M+H]^+$: 298.0410; found: 298.0409.



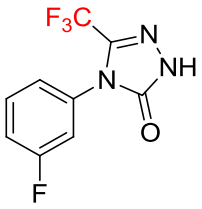
4-(4-(Trifluoromethoxy)phenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3l)

Obtained as a pale white solid in 60% yield (93 mg). Mp: 182–185 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (s), 150.3 (s), 136.8 (q, *J* = 41.3 Hz), 129.2 (s), 129.1 (s), 122.0 (s), 120.3 (q, *J* = 258.7 Hz), 116.8 (q, *J* = 270.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.1 (s, 3F), -64.3 (s, 3F). IR (KBr): ν 3157, 2880, 2821, 2564, 2374, 2254, 2048, 1971, 1728, 1513, 1468, 1262, 1212, 1177, 1099, 983, 801, 562 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_6F_6N_3O_2$ $[M+H]^+$: 314.0359; found: 314.0355.



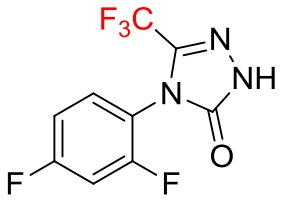
5-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3m)

Obtained as a pale white solid in 30% yield (37 mg). Mp: 121–122 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.44 – 7.33 (m, 2H), 7.26 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 251.5 Hz), 154.8 (s), 137.0 (q, *J* = 40.9 Hz), 129.5 (d, *J* = 9.1 Hz), 126.8 (d, *J* = 3.3 Hz), 117.0 (d, *J* = 23.3 Hz), 116.9 (q, *J* = 270.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.2 (s, 3F), -109.38 – -109.6 (m, 1F). IR (KBr): ν 3154, 2635, 2254, 2158, 1970, 1794, 1513, 1469, 1381, 1216, 1160, 1095, 624, 544 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_4N_3O$ $[M+H]^+$: 248.0442; found: 248.0440.



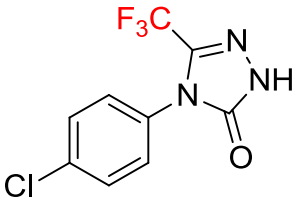
5-(3-Fluorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3n)

Obtained as a pale white solid in 20% yield (25 mg). Mp: 158–160 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.80. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 249.9 Hz), 154.4 (s), 136.8 (q, *J* = 40.4 Hz), 132.1 (d, *J* = 10.6 Hz), 131.1 (d, *J* = 8.9 Hz), 123.2 (s), 117.6 (d, *J* = 20.7 Hz), 116.8 (q, *J* = 271.0 Hz), 115.2 (d, *J* = 24.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1 (s, 3F), -109.5 (d, *J* = 6.1 Hz, 1F). IR (KBr): ν 3066, 2248, 2189, 2123, 1996, 1736, 1611, 1497, 1204, 1149, 757, 693, 539 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_4N_3O$ $[M+H]^+$: 248.0442; found: 248.0443.



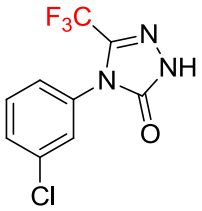
6-(2,4-Difluorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3o)

Obtained as a pale white solid in 50% yield (66 mg). Mp: 180–183 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.73. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.48 – 7.35 (m, 1H), 7.14 – 7.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (ddd, *J* = 270.0, 256.0, 12.1 Hz), 154.5 (s), 136.9 (q, *J* = 41.4 Hz), 131.1 (d, *J* = 10.5 Hz), 116.7 (q, *J* = 271.0 Hz), 114.8 (dd, *J* = 13.5, 4.2 Hz), 112.6 (dd, *J* = 23.0, 3.9 Hz), 105.8 (d, *J* = 23.0 Hz), 105.6 (d, *J* = 23.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.6 (s, 3F), -103.7 – -103.8 (m, 1F), -114.9 (d, *J* = 5.2 Hz, 1F). IR (KBr): ν 3032, 2949, 2662, 2253, 1730, 1605, 1520, 1467, 984, 962, 856, 802, 539 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_5F_5N_3O$ $[M+H]^+$: 266.0347; found: 266.0346.



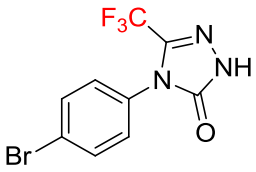
5-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3p)

Obtained as a pale white solid in 42% yield (55 mg). Mp: 139–141 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.62 – 7.47 (m, 2H), 7.43 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.6 (s), 136.7 (q, *J* = 41.6 Hz), 135.5 (s), 131.9 (s), 130.8 (s), 130.7 (s), 127.7 (s), 125.6 (s), 116.8 (q, *J* = 271.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (s, 3F). IR (KBr): ν 3156, 2253, 2188, 2038, 1995, 1794, 1471, 1382, 1215, 1161, 1097, 624, 541 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6ClF_3N_3O$ $[M+H]^+$: 264.0146; found: 264.0149.



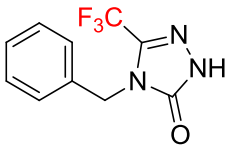
4-(3-Chlorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3q)

Obtained as a pale white solid in 39% yield (51 mg). Mp: 135–138 °C R_f (*n*-pentane/ethyl acetate = 5:1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.46 (m, 2H), 7.43 (s, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), N*H* was not observed. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (s), 136.7 (q, *J* = 41.3 Hz), 135.5 (s), 131.9 (s), 130.8 (s), 130.7 (s), 127.7 (s), 125.6 (s), 116.9 (q, *J* = 271.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (s, 3F). IR (KBr): ν 3191, 2816, 2253, 2181, 2127, 2024, 1725, 1587, 1485, 1381, 1213, 1155, 1102, 1045, 990, 813, 711, 545 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6ClF_3N_3O$ $[M+H]^+$: 264.0146; found: 264.0144.



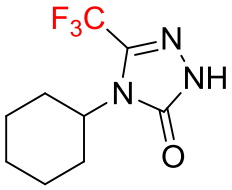
7-(4-Bromophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3r)

Obtained as a pale white solid in 55% yield (85 mg). Mp: 178–181 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7 (s), 136.7 (q, *J* = 41.3 Hz), 133.2 (s), 129.8 (s), 128.9 (s), 124.6 (s), 116.8 (q, *J* = 271.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.0 (s, 3F). IR (KBr): ν 3023, 2989, 2253, 2160, 2101, 2036, 1724, 1589, 1493, 1401, 1339, 1272, 1156, 1100, 1072, 801, 561 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6BrF_3N_3O$ $[M+H]^+$: 309.9620; found: 309.9620.



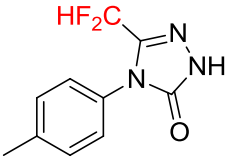
6-Benzyl-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3s)

Obtained as a pale white solid in 67% yield (81 mg). Mp: 150–153 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.45 – 7.30 (m, 5H), 5.00 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (s), 136.6 (q, *J* = 41.4 Hz), 134.4 (s), 128.9 (s), 128.6 (s), 127.6 (s), 117.2 (q, *J* = 270.7 Hz), 45.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0 (s, 3F). IR (KBr): ν 3036, 2253, 2172, 2024, 1957, 1719, 1580, 1438, 1209, 1148, 1103, 811, 629, 577 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_9F_3N_3O$ $[M+H]^+$: 244.0692; found: 244.0691.



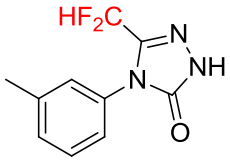
4-Cyclohexyl-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (3t)

Obtained as a pale white solid in 60% yield (67 mg). Mp: 145–148 °C. R_f (*n*-pentane/ethyl acetate = 5:1) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 3.86 (t, *J* = 10.4 Hz, 1H), 2.30 (q, *J* = 12.1 Hz, 2H), 1.92 (d, *J* = 11.9 Hz, 2H), 1.82 (d, *J* = 12.0 Hz, 2H), 1.71 (d, *J* = 10.2 Hz, 1H), 1.44 – 1.09 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4 (s), 136.7 (q, *J* = 40.5 Hz), 117.4 (q, *J* = 270.2 Hz), 56.5 (s), 29.4 (s), 25.7 (s), 24.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.8 (s, 3F). IR (KBr): ν 2939, 2860, 2253, 1712, 1658, 1580, 1472, 1381, 1257, 1211, 1147, 1097, 822, 625, 563 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_{13}F_3N_3O$ $[M+H]^+$: 236.1005; found: 236.1004.



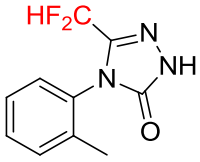
3-(Difluoromethyl)-4-(*p*-tolyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4a)

Obtained as a pale white solid in 85% yield (95 mg). Mp: 174–176 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.63. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.42 – 7.21 (m, 4H), 6.94 (t, *J* = 51.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.5 (s), 140.1 (t, *J* = 27.6 Hz), 139.3 (s), 130.3 (s), 129.8 (s), 127.7 (s), 108.9 (t, *J* = 235.9 Hz), 21.2 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.6 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3065, 2818, 2123, 1727, 1619, 1581, 1517, 1466, 1370, 1125, 728, 679, 561 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O$ $[M+H]^+$: 226.0786; found: 226.0784.



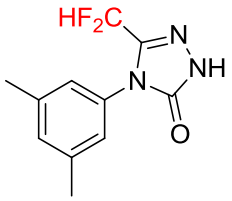
3-(Difluoromethyl)-4-(*m*-tolyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4b)

Obtained as a pale white solid in 78% yield (87 mg). Mp: 206–207 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.71. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.52 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.18 (m, 2H), 6.96 (t, *J* = 51.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.5 (s), 140.0 (t, *J* = 27.6 Hz), 139.4 (s), 132.4 (s), 130.3 (s), 129.6 (s), 128.3 (s), 124.9 (s), 108.7 (t, *J* = 236.0 Hz), 21.2 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.6 (d, *J* = 51.4 Hz, 2F). IR (KBr): ν 3034, 2949, 2915, 2778, 2124, 1995, 1727, 1612, 1494, 1362, 1296, 1219, 1126, 729, 696 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O$ $[M+H]^+$: 226.0786; found: 226.0784.



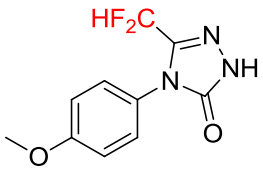
4-(Difluoromethyl)-4-(*o*-tolyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4c)

Obtained as a pale white solid in 80% yield (90 mg). Mp: 223–225 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.57. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (s, 1H), 7.43 (s, 2H), 7.37 (s, 2H), 6.91 (t, *J* = 51.4 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.2 (s), 140.1 (t, *J* = 27.6 Hz), 136.9 (s), 131.3 (s), 131.2 (s), 130.4 (s), 129.4 (s), 127.4 (s), 108.9 (t, *J* = 235.5 Hz), 17.4 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -119.4 (ddd, *J* = 478.7, 85.3, 13.1 Hz, 2F). IR (KBr): ν 3006, 2800, 2160, 2123, 1991, 1726, 1620, 1583, 1500, 1465, 1314, 1219, 678, 590 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O$ $[M+H]^+$: 226.0786; found: 226.0785.



5-(Difluoromethyl)-4-(3,5-dimethylphenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4d)

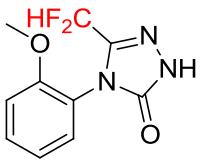
Obtained as a pale white solid in 78% yield (93 mg). Mp: 222–224 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.93. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 7.14 (s, 1H), 7.05 (s, 2H), 6.96 (t, *J* = 51.4 Hz, 1H), 2.33 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.5 (s), 140.1 (t, *J* = 27.7 Hz), 139.2 (s), 132.3 (s), 131.0 (s), 125.3 (s), 108.8 (t, *J* = 236.1 Hz), 21.1 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.8 (d, *J* = 51.4 Hz, 2F). IR (KBr): ν 3007, 2803, 2178, 2123, 1727, 1480, 1370, 1312, 1204, 1125, 857, 693, 566 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{11}H_{12}F_2N_3O$ $[M+H]^+$: 240.0943; found: 240.0940.



3-(Difluoromethyl)-4-(4-methoxyphenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4e)

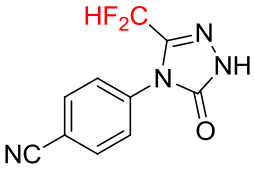
Obtained as a pale white solid in 42% yield (50 mg). Mp: 189–190 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.54. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.46 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 51.4 Hz, 1H), 3.82

(s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.1 (s), 154.7 (s), 140.3 (t, J = 27.5 Hz), 129.4 (s), 124.9 (s), 115.0 (s), 108.9 (t, J = 235.7 Hz), 55.9 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.7 (d, J = 51.4 Hz, 2F). IR (KBr): ν 3037, 3004, 2836, 2167, 2125, 1992, 1955, 1726, 1661, 1587, 1466, 1371, 1298, 1252, 1176, 1126, 729, 588 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O_2$ $[M+H]^+$: 242.0736; found: 242.0733.



4-(Difluoromethyl)-4-(2-methoxyphenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4f)

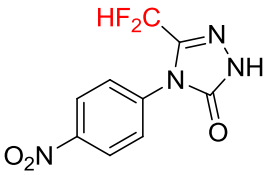
Obtained as a pale white solid in 97% yield (116 mg). Mp: 177–178 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.43. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.44 (s, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 8.3 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.84 (t, J = 51.4 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.5 (s), 154.4 (s), 140.7 (t, J = 27.6 Hz), 131.8 (s), 130.3 (s), 121.0 (s), 120.6 (s), 113.0 (s), 108.7 (t, J = 236.1 Hz), 56.4 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -119.9 (d, J = 51.4 Hz), -120.1 (d, J = 51.5 Hz, 2F). IR (KBr): ν 3253, 3006, 2817, 2123, 1728, 1603, 1509, 1470, 1371, 1285, 1254, 679, 591 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O_2$ $[M+H]^+$: 242.0736; found: 242.0733.



3-(3-(Difluoromethyl)-5-oxo-1*H*-1,2,4-triazol-4(5*H*)-yl)benzonitrile (4g)

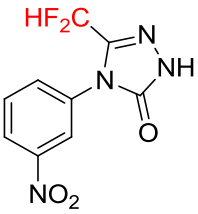
Obtained as a pale white solid in 74% yield (87 mg). Mp: 214–216 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.47. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.06 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.05 (t, J = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.7 (s), 144.3 (t, J = 27.9 Hz), 141.4 (s), 138.8 (s), 133.5 (s), 123.3 (s), 117.1 (s), 113.7 (t, J = 236.2 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.3 (d, J = 51.3 Hz, 2F). IR (KBr): ν 2898, 2822, 2190, 2128, 2023, 1729, 1657,

1511, 1461, 1371, 1321, 1129, 608, 550 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_7F_2N_4O$ $[M+H]^+$: 237.0582; found: 237.0579.



6-(Difluoromethyl)-4-(4-nitrophenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4h)

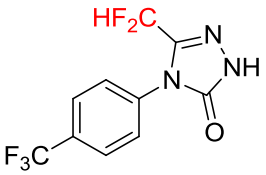
Obtained as a pale white solid in 46% yield (58 mg). Mp: 220–221 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.54. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.41 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.07 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.9 (s), 147.8 (s), 139.5 (t, *J* = 28.0 Hz), 138.2 (s), 128.9 (s), 125.1 (s), 108.9 (t, *J* = 236.2 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.2 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3029, 2948, 2204, 2122, 1731, 1576, 1348, 1216, 1132, 855, 690, 582 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7F_2N_4O_3$ $[M+H]^+$: 257.0481; found: 257.0478.



3-(Difluoromethyl)-4-(3-nitrophenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4i)

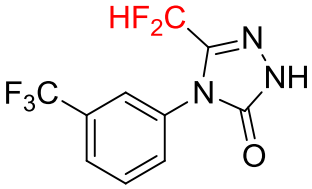
Obtained as a pale white solid in 56% yield (71 mg). Mp: 184–186 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.53. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.66 (s, 1H), 8.44 (s, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.2 (s), 148.6 (s), 139.6 (t, *J* = 27.9 Hz), 134.6 (s), 133.6 (s), 131.4 (s), 124.5 (s), 123.0 (s), 109.0 (t, *J* = 236.0 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.3 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3070, 2123, 1731, 1662, 1619, 1534, 1490, 1353, 1243, 1126, 875, 716, 680,

561 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_2N_4O_3$ $[M+H]^+$: 257.0481; found: 257.0478.



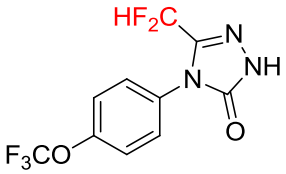
4-(Difluoromethyl)-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4j)

Obtained as a pale white solid in 40% yield (55 mg). Mp: 168–171 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.67. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.64 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.04 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.1 (s), 139.6 (t, *J* = 27.9 Hz), 136.2 (s), 129.9 (q, *J* = 32.0 Hz), 128.8 (s), 127.0 (s), 124.3 (q, *J* = 272.7 Hz), 108.9 (t, *J* = 236.0 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.2 (s, 3F), -118.3 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3068, 3005, 2789, 2123, 1985, 1730, 1615, 1582, 1522, 1466, 1326, 1169, 857, 731, 571 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_7F_5N_3O$ $[M+H]^+$: 280.0504; found: 280.0500.



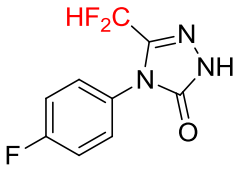
3-(Difluoromethyl)-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4k)

Obtained as a pale white solid in 40% yield (55 mg). Mp: 165–168 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.73. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.61 (s, 1H), 7.99 – 7.70 (m, 4H), 7.02 (t, *J* = 51.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.3 (s), 139.7 (t, *J* = 27.9 Hz), 133.4 (s), 132.2 (s), 131.2 (s), 130.6 (q, *J* = 32.8 Hz), 126.7 (q, *J* = 272.0 Hz), 126.4 (s), 125.0 (s), 109.0 (t, *J* = 235.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.2 (s, 3F), -118.4 (d, *J* = 51.2 Hz, 2F). IR (KBr): ν 3024, 2948, 2193, 1996, 1938, 1730, 1616, 1584, 1397, 1304, 1230, 1170, 1130, 852, 584 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_7F_5N_3O$ $[M+H]^+$: 280.0504; found: 280.0499.



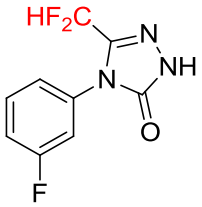
3-(Difluoromethyl)-4-(4-(trifluoromethoxy)phenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4l)

Obtained as a pale white solid in 52% yield (76 mg). Mp: 176–178 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.71. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.00 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.3 (s), 148.9 (s), 139.8 (t, *J* = 27.7 Hz), 131.5 (s), 130.2 (s), 122.4 (s), 120.5 (q, *J* = 257.0 Hz), 108.9 (t, *J* = 235.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.9 (s, 3F), -118.5 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3068, 3005, 2800, 2174, 2123, 1729, 1619, 1583, 1511, 1467, 1372, 1259, 1168, 1128, 678, 587 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_7F_5N_3O_2$ $[M+H]^+$: 296.0453; found: 296.0451.



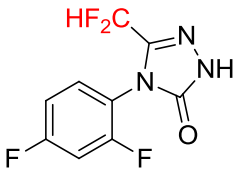
4-(Difluoromethyl)-4-(4-fluorophenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4m)

Obtained as a pale white solid in 83% yield (95 mg). Mp: 192–194 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.67. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.52 (s, 1H), 7.63 – 7.47 (m, 2H), 7.40 (t, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.5 (d, *J* = 246.3 Hz), 154.5 (s), 140.0 (t, *J* = 27.4 Hz), 130.4 (d, *J* = 9.1 Hz), 128.8 (d, *J* = 2.8 Hz), 116.7 (d, *J* = 23.1 Hz), 108.9 (t, *J* = 235.7 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.2 (d, *J* = 4.3 Hz, 1F), -118.6 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3008, 2185, 2124, 1986, 1729, 1604, 1513, 1468, 1295, 1221, 1161, 1125, 930, 730, 680, 587 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7F_3N_3O$ $[M+H]^+$: 230.0536; found: 230.0534.



3-(Difluoromethyl)-4-(3-fluorophenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4n)

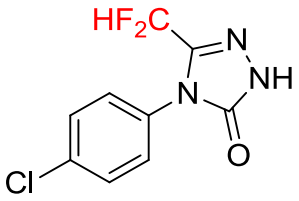
Obtained as a pale white solid in 87% yield (99 mg). Mp: 188–190 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.60. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 7.67 – 7.54 (m, 1H), 7.49 – 7.27 (m, 3H), 7.01 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.1 (d, *J* = 245.2 Hz), 158.9 (s), 144.5 (t, *J* = 27.9 Hz), 138.7 (d, *J* = 10.6 Hz), 136.2 (d, *J* = 9.1 Hz), 129.0 (s), 121.5 (d, *J* = 20.8 Hz), 120.2 (d, *J* = 24.1 Hz), 113.6 (t, *J* = 236.1 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -111.7 (dd, *J* = 15.9, 8.7 Hz, 1F), -118.7 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 2898, 2190, 2128, 1729, 1657, 1511, 1461, 1371, 1321, 1129, 608, 550 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7F_3N_3O$ $[M+H]^+$: 230.0536; found: 230.0534.



5-(Difluoromethyl)-4-(2,4-difluorophenyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4o)

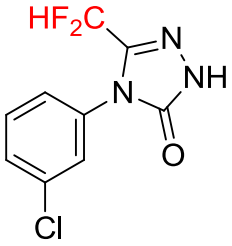
Obtained as a pale white solid in 91% yield (112 mg). Mp: 189–190 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.67. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.68 (s, 1H), 7.80 – 7.65 (m, 1H), 7.59 (t, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 51.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.8 (ddd, *J* = 266.8, 251.7, 12.6 Hz), 154.1 (s), 140.0 (t, *J* = 27.9 Hz), 132.7 (d, *J* = 10.5 Hz), 116.6 (dd, *J* = 13.2, 3.9 Hz), 113.0 (d, *J* = 22.6 Hz), 108.8 (t, *J* = 235.4 Hz), 106.0 (s), 105.6 (d, *J* = 24.6 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -106.3 (s, 1F), -116.5 (s, 1F), -119.5 (dd, *J* = 342.6, 82.6 Hz). IR (KBr): ν 3069, 3009, 2787, 2125, 1734, 1661, 1614, 1520, 1461, 1436,

1368, 1272, 1224, 1150, 963, 580 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_6F_4N_3O$ $[M+H]^+$: 248.0442; found: 248.0439.



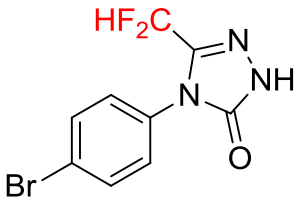
5-(4-Chlorophenyl)-3-(difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4p)

Obtained as a pale white solid in 41% yield (50 mg). Mp: 226–228 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.46 – 12.27 (m, 3H), 12.26 – 12.15 (m, 1H), 11.76 (t, *J* = 51.3 Hz, 1H), N*H* was not observed. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0 (s), 144.5 (t, *J* = 27.8 Hz), 138.6 (s), 136.2 (s), 134.5 (s), 132.8 (s), 131.6 (s), 113.6 (t, *J* = 236.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8 (dd, *J* = 51.3, 5.8 Hz, 2F). IR (KBr): ν 3072, 2251, 2213, 2126, 1729, 1658, 1591, 1486, 1225, 1126, 878, 720, 685, 567 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7ClF_2N_3O$ $[M+H]^+$: 246.0240; found: 246.0239.



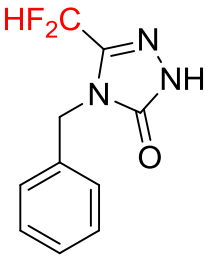
4-(3-Chlorophenyl)-3-(difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4q)

Obtained as a pale white solid in 23% yield (28 mg). Mp: 201–203 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.82. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 7.82 – 7.50 (m, 3H), 7.47 (d, *J* = 6.0 Hz, 1H), 7.01 (t, *J* = 51.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.2 (s), 139.7 (t, *J* = 27.5 Hz), 133.8 (s), 131.4 (s), 129.8 (s), 128.0 (s), 126.8 (s), 108.9 (t, *J* = 235.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.6 (d, *J* = 51.3 Hz, 2F). IR (KBr): ν 3057, 2656, 2304, 2248, 2092, 2028, 1737, 1590, 1491, 1204, 1179, 1105, 980, 926, 796, 687 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7ClF_2N_3O$ $[M+H]^+$: 246.0240; found: 246.0240.



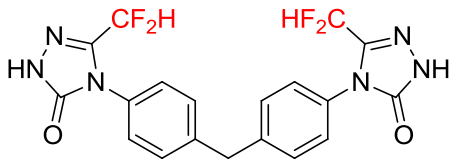
5-(4-Bromophenyl)-3-(difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4r)

Obtained as a pale white solid in 70% yield (101 mg). Mp: 204–206 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.47. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.57 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.99 (t, *J* = 51.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.2 (s), 139.8 (t, *J* = 27.7 Hz), 132.8 (s), 131.8 (s), 130.1 (s), 122.8 (s), 108.9 (t, *J* = 235.8 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.5 (d, *J* = 51.2 Hz, 2F). IR (KBr): ν 3452, 3270, 2323, 2050, 1654, 1590, 1495, 1223, 713, 679 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_9H_7F_2N_3O$ $[M+H]^+$: 289.9735; found: 289.9733.



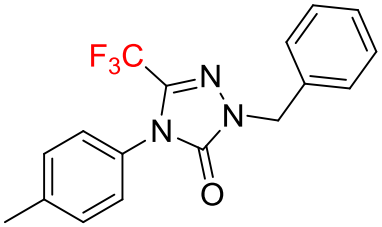
4-Benzyl-3-(difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (4s)

Obtained as a pale white solid in 31% yield (35 mg). Mp: 120.7–123.6 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.47. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.49 (s, 1H), 7.42 – 7.20 (m, 5H), 7.04 (t, *J* = 51.2 Hz, 1H), 4.92 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.2 (s), 140.3 (t, *J* = 28.0 Hz), 136.6 (s), 129.0 (s), 128.1 (s), 127.4 (s), 109.1 (t, *J* = 234.9 Hz), 44.7 (s). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.6 (d, *J* = 51.2 Hz, 2F). IR (KBr): ν 3439, 2186, 2124, 1667, 1581, 1223, 711, 680 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{10}H_{10}F_2N_3O$ $[M+H]^+$: 226.0786; found: 226.0785.



4,4'-(Methylenebis(4,1-phenylene))bis(3-(difluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one) (4u)

Obtained as a pale white solid in 65% yield (141 mg). Mp: 197–199 °C. R_f (*n*-pentane/ethyl acetate = 2:1) = 0.67. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.50 (s, 1H), 10.70 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.32 (m, 4H), 7.29 (d, *J* = 7.3 Hz, 2H), 6.95 (t, *J* = 51.3 Hz, 1H), 6.37 (t, *J* = 53.6 Hz, 1H), 4.01 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.9 (t, *J* = 25.8 Hz), 154.5 (s), 143.0 (s), 140.1 (t, *J* = 29.0 Hz), 137.6 (s), 136.0 (s), 130.4 (s), 129.9 (s), 129.7 (s), 127.9 (s), 120.9 (s), 108.9 (t, *J* = 240.4 Hz), 108.8 (t, *J* = 242.1 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.6 (d, *J* = 51.4 Hz, 2F), -125.1 (d, *J* = 53.8 Hz, 2F). IR (KBr): ν 3065, 3004, 2809, 2167, 2123, 1992, 1727, 1613, 1552, 1513, 1467, 1370, 1258, 1223, 679, 565 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{19}H_{13}F_4N_6O_2$ $[M+H]^+$: 435.1187; found: 435.1185.



1-Benzyl-4-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazol-5(4*H*)-one (5)

Obtained as a pale white solid in 65% yield (108 mg). Mp: 123–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.37 (m, 3H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 2H), 5.11 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8 (s), 140.3 (s), 135.3 (s), 135.2 (q, *J* = 40.8 Hz), 130.3 (s), 128.9 (s), 128.8 (s), 128.7 (s), 128.4 (s), 127.1 (s), 117.2 (q, *J* = 271.0 Hz), 50.1 (s), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.7 (s, 3F). IR (KBr): ν 2252, 1732, 1515, 1468, 1381, 1208, 1153, 984, 815, 545 cm^{-1}. HR-MS (ESI): m/z calcd. for $C_{17}H_{15}F_3N_3O$ $[M+H]^+$: 334.1162; found: 334.1163.

Crystal structure analyses

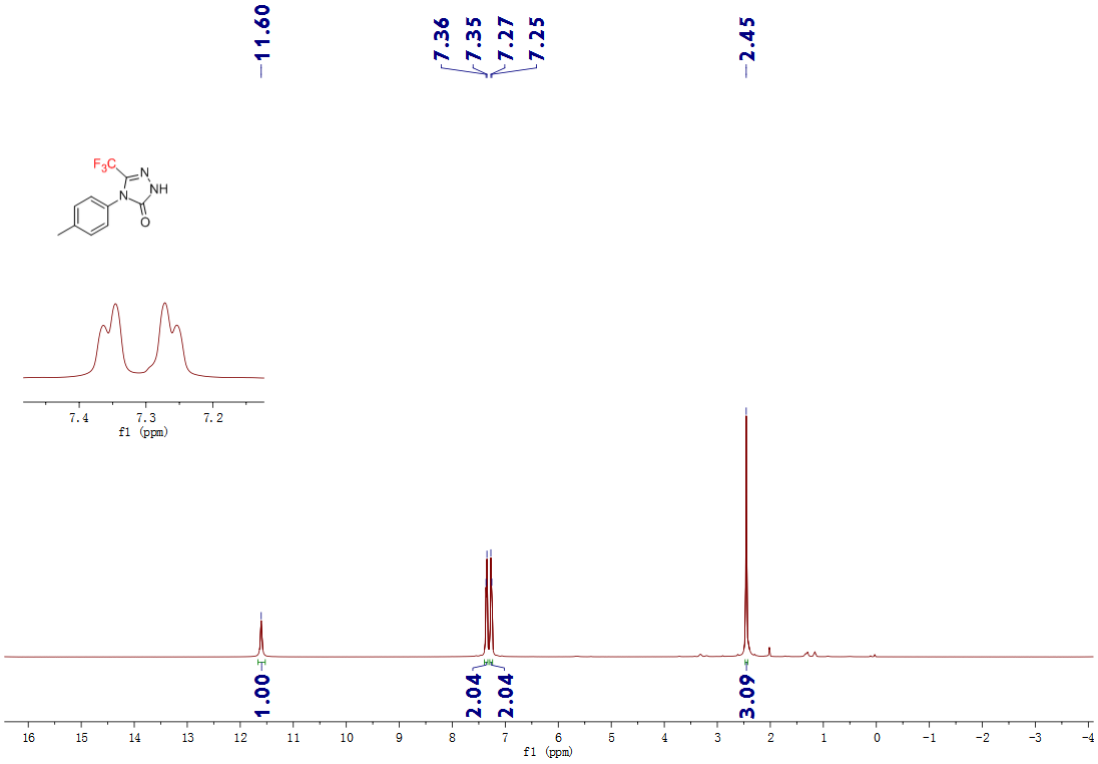
The suitable crystals of **3a** (CCDC 1914002), and **4a** (CCDC 1910663) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the **SMART** suite of programs and for absorption effects with SADABS.[1] Structure solution and refinement were carried out with the SHELXTL suite of programs.[1] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.

References:

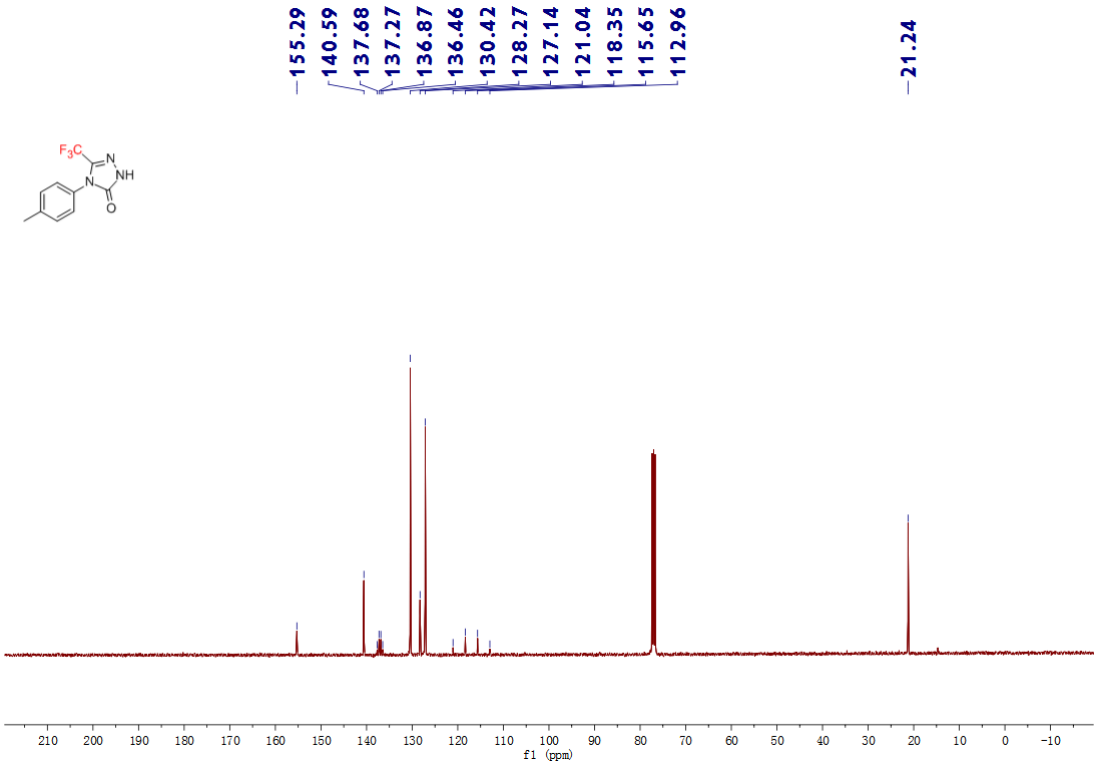
[1] SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

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

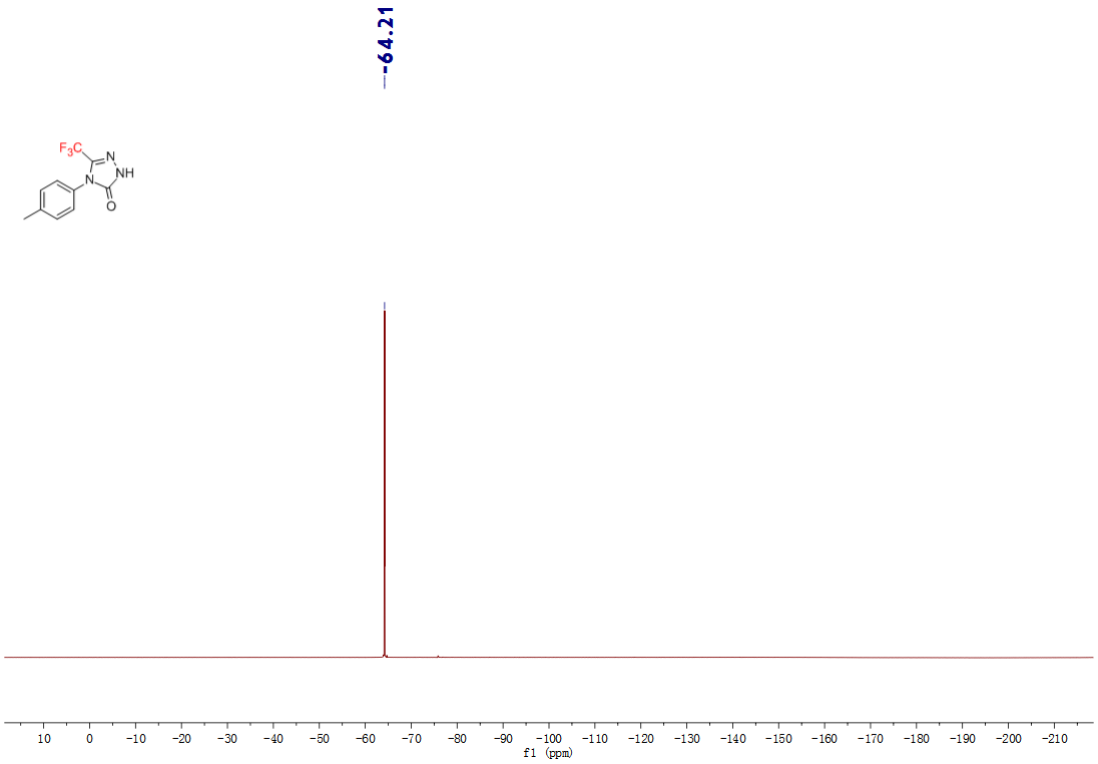
^{1}H-NMR spectrum of **3a** in $CDCl_3$



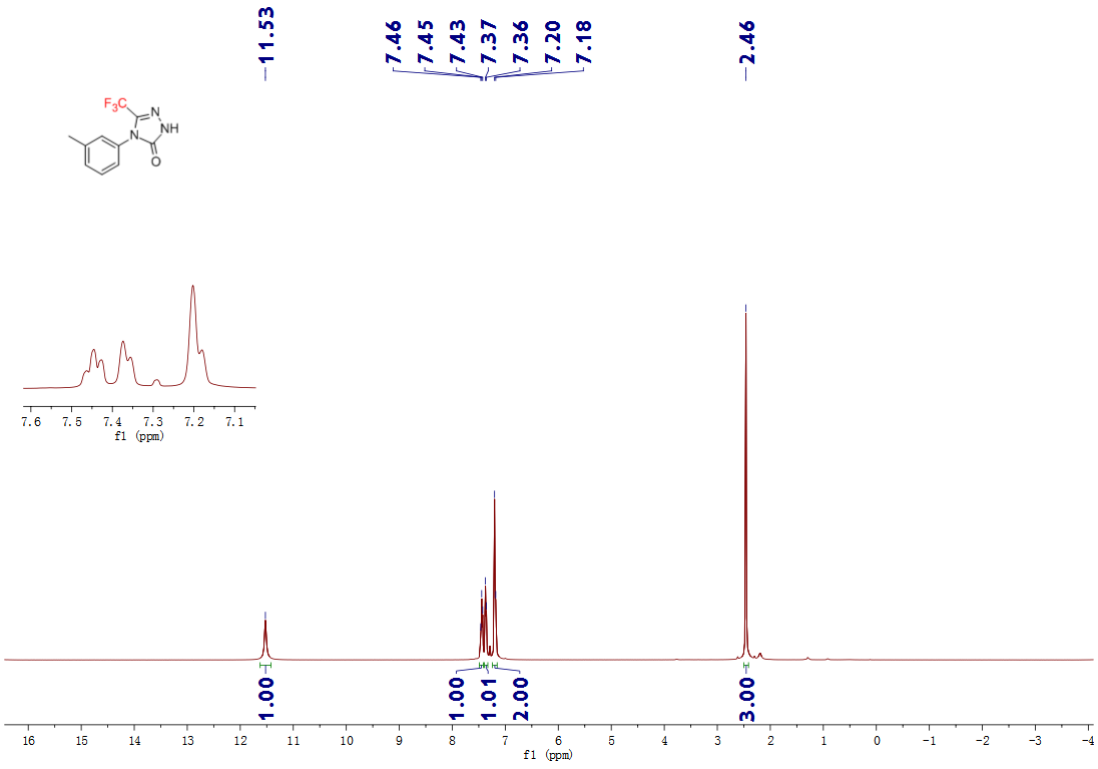
^{13}C-NMR spectrum of **3a** in $CDCl_3$



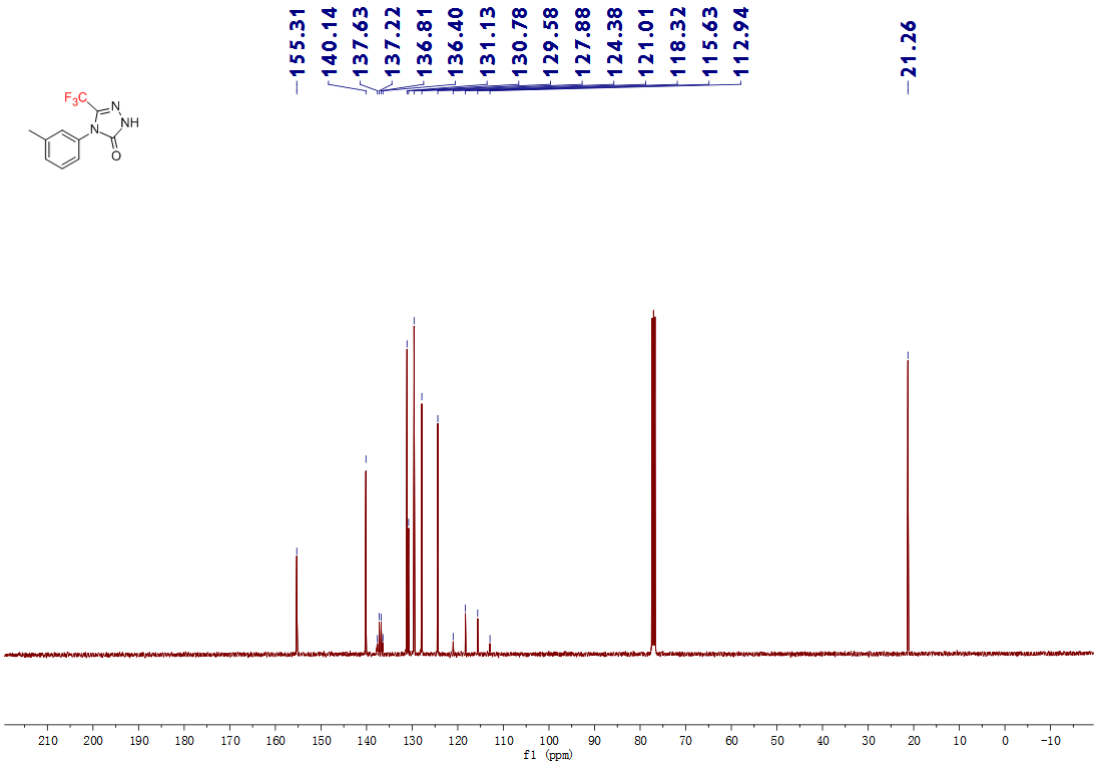
^{19}F-NMR spectrum of **3a** in $CDCl_3$



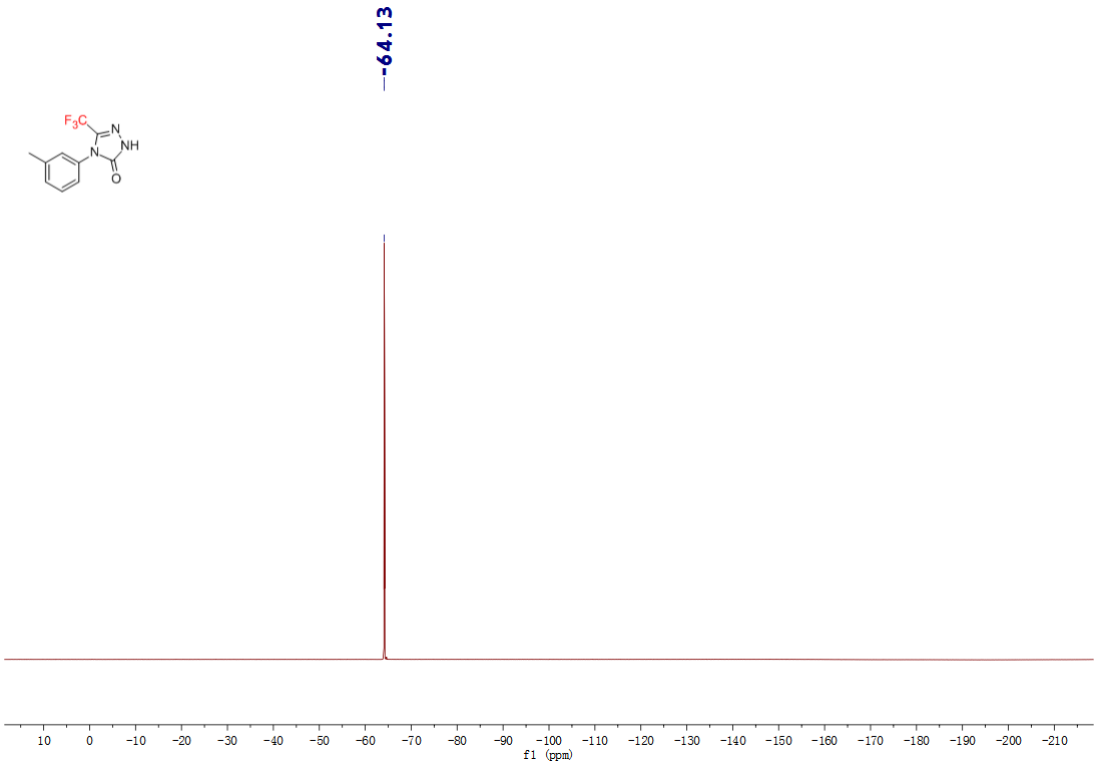
^{1}H-NMR spectrum of **3b** in $CDCl_3$



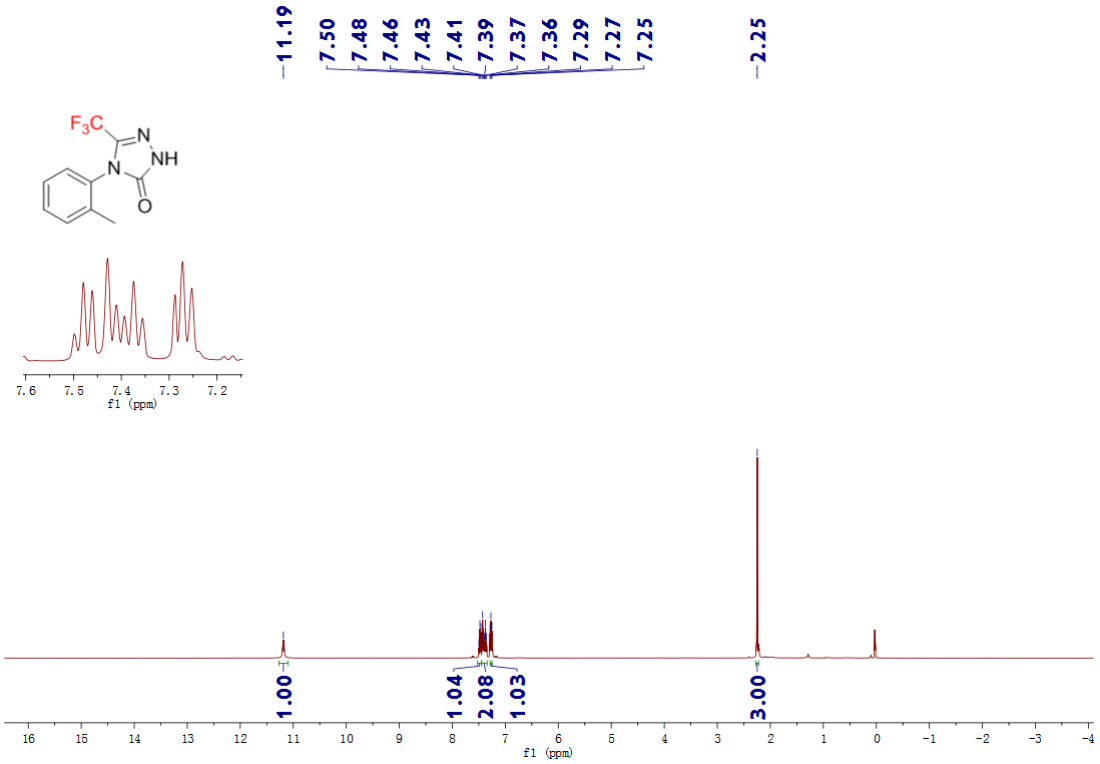
^{13}C-NMR spectrum of **3b** in $CDCl_3$



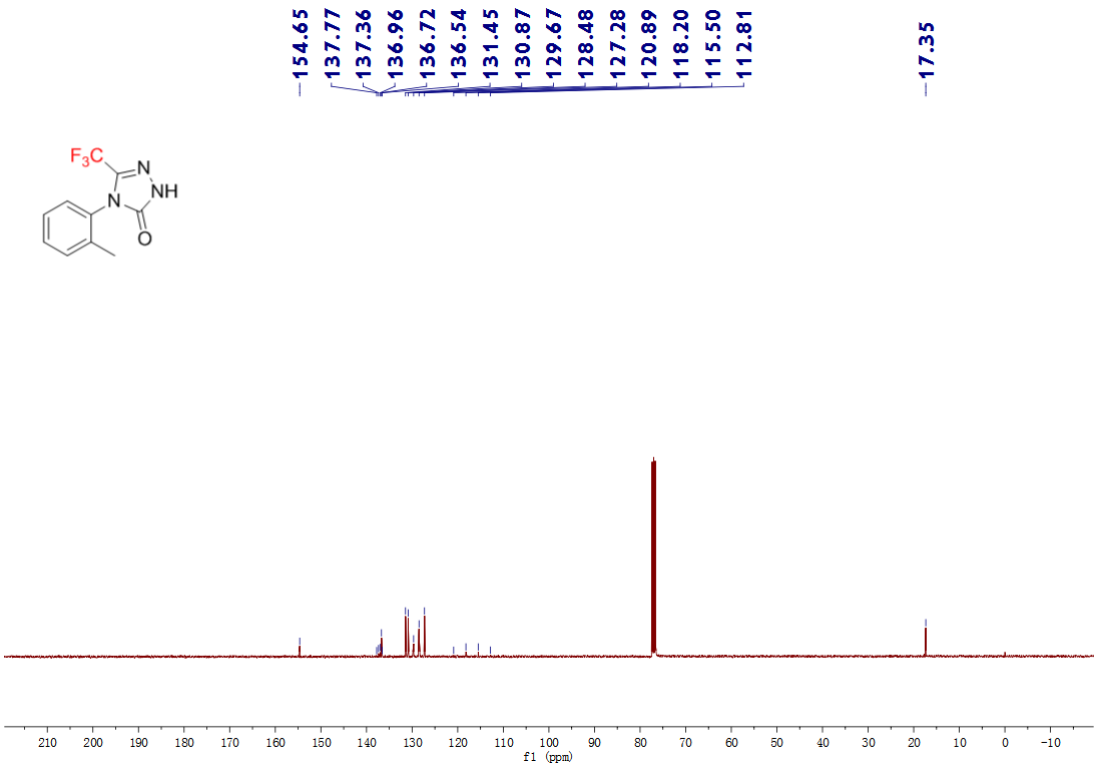
^{19}F-NMR spectrum of **3b** in $CDCl_3$



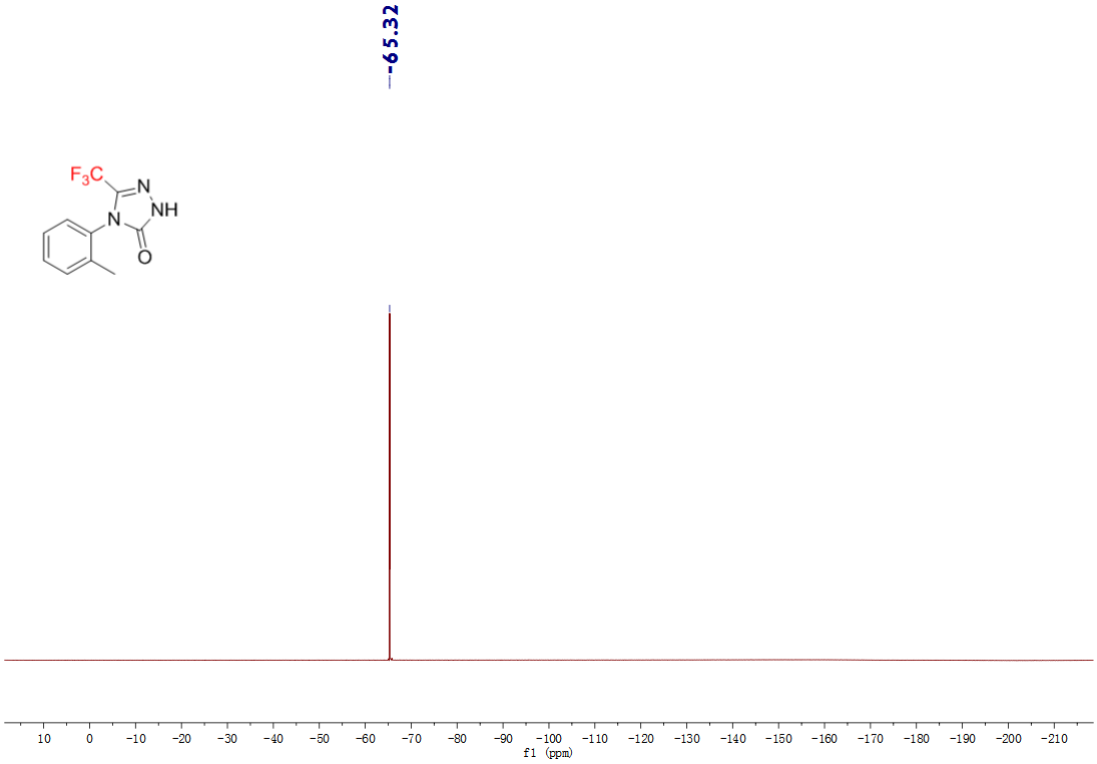
^{1}H-NMR spectrum of **3c** in $CDCl_3$



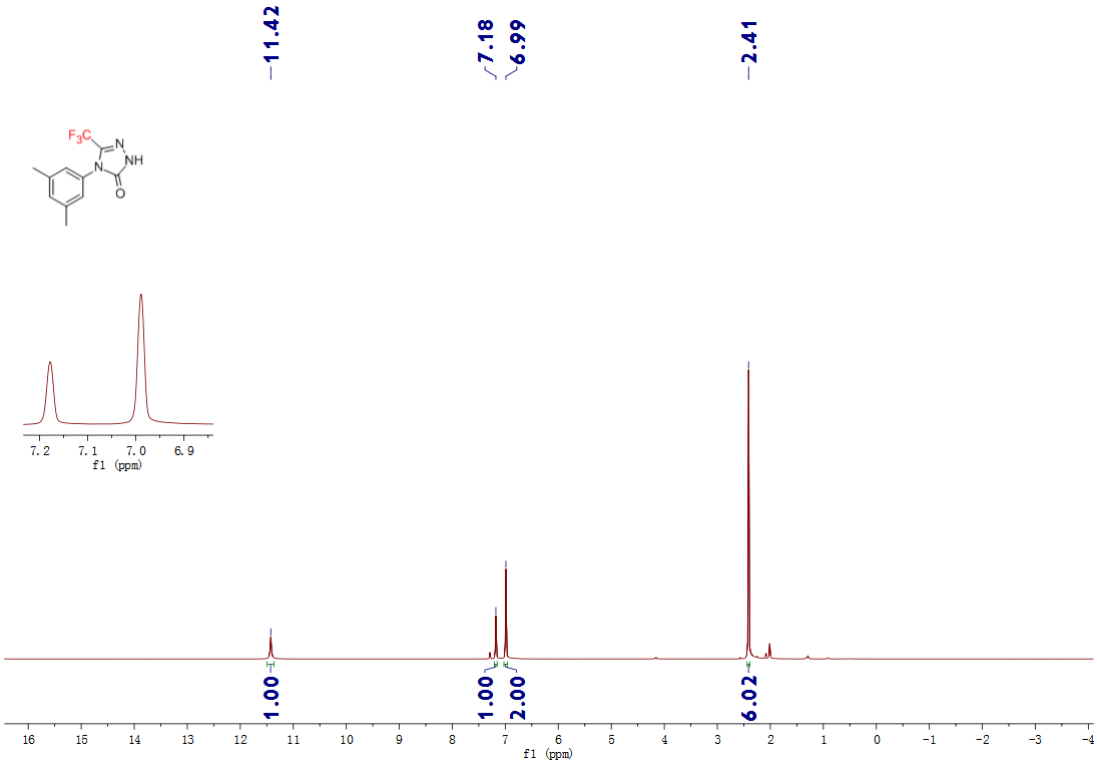
^{13}C-NMR spectrum of **3c** in $CDCl_3$



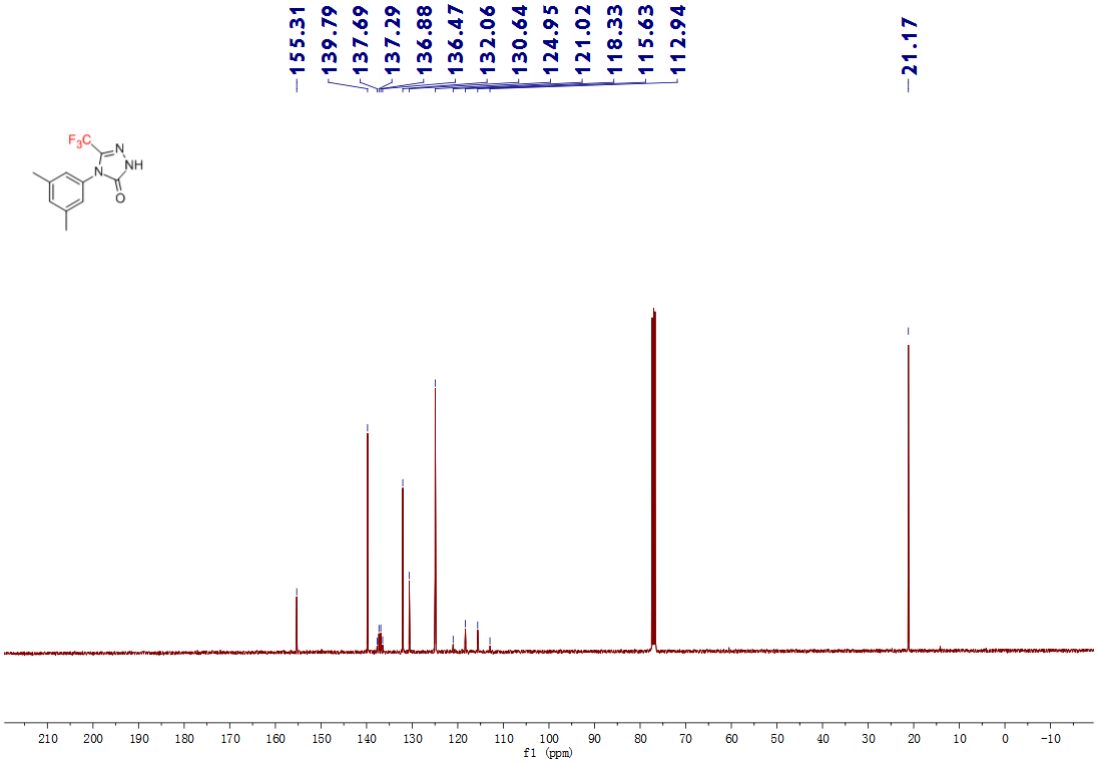
^{19}F-NMR spectrum of **3c** in $CDCl_3$



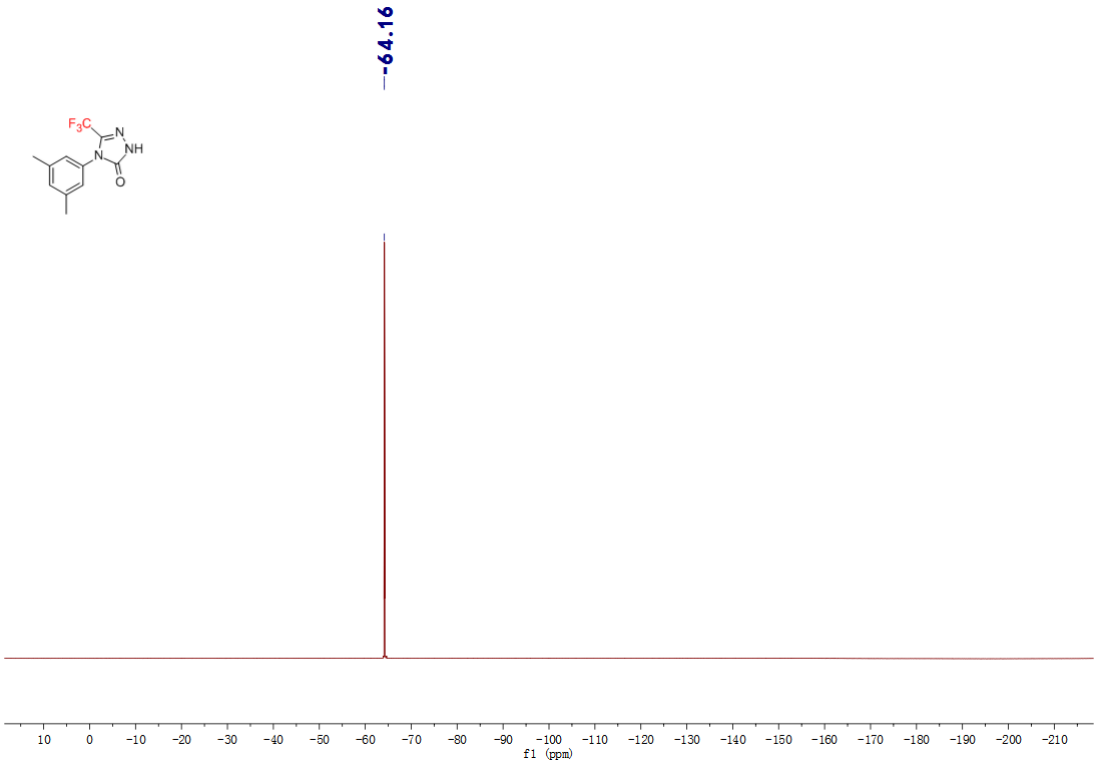
^{1}H-NMR spectrum of **3d** in $CDCl_3$



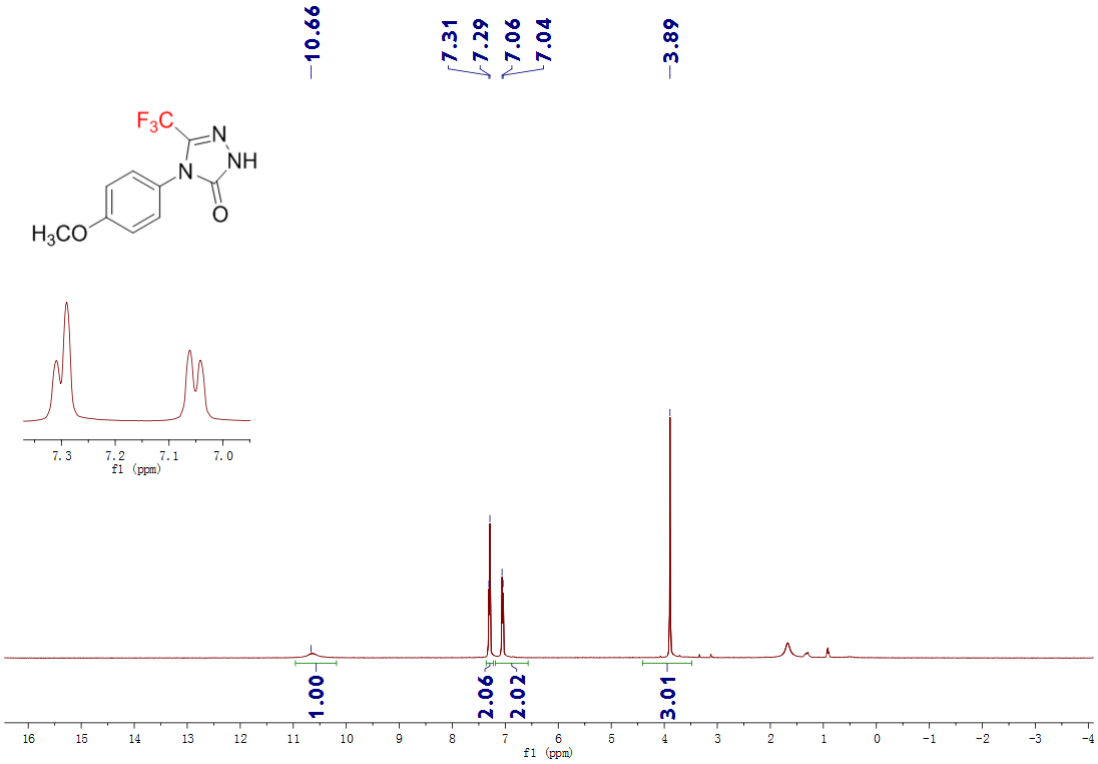
^{13}C-NMR spectrum of **3d** in $CDCl_3$



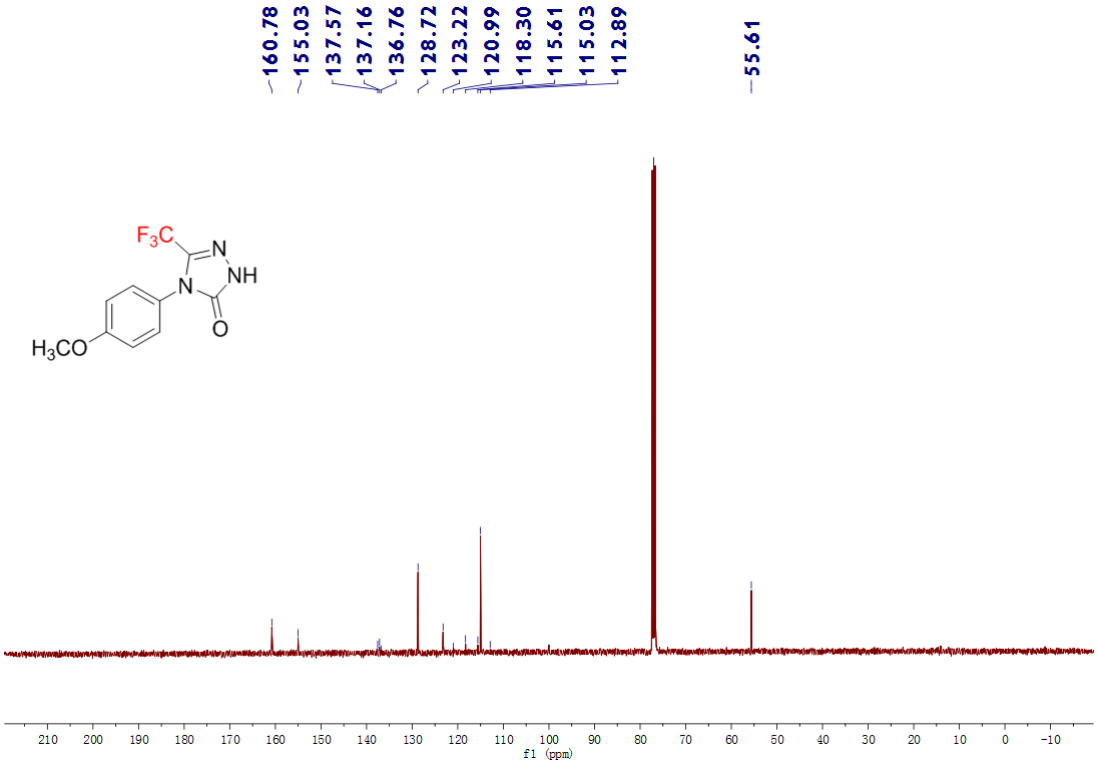
^{19}F-NMR spectrum of **3d** in $CDCl_3$



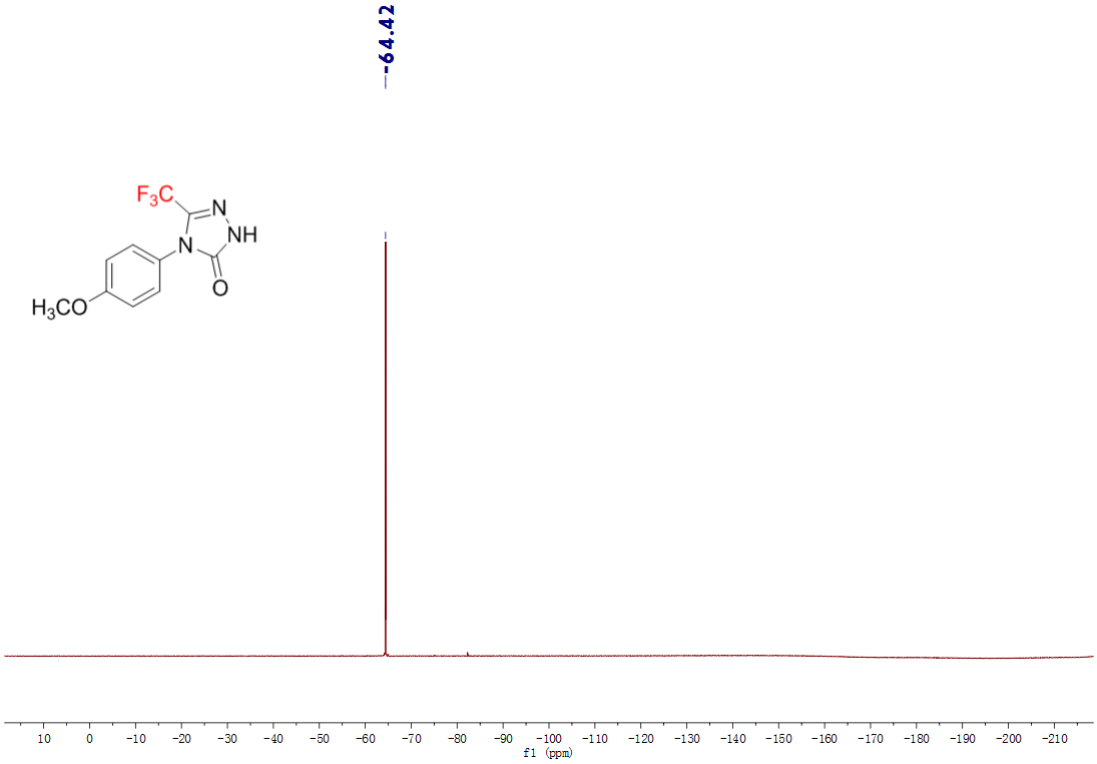
^{1}H-NMR spectrum of **3e** in $CDCl_3$



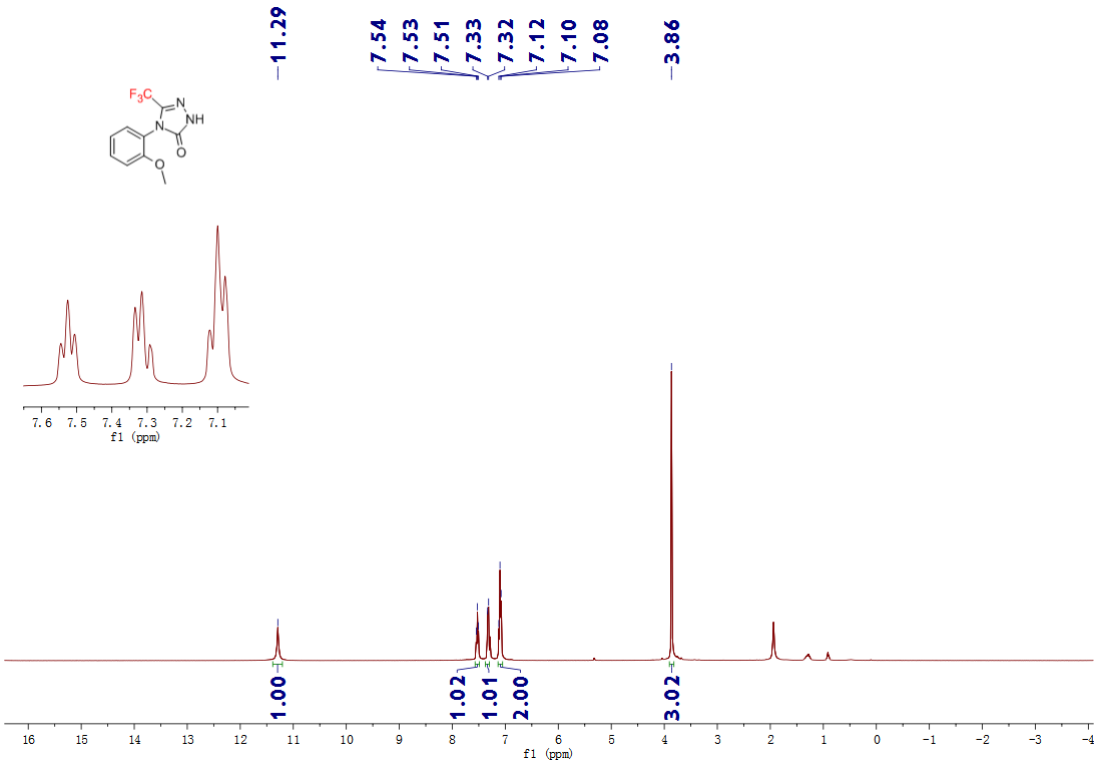
^{13}C-NMR spectrum of **3e** in $CDCl_3$



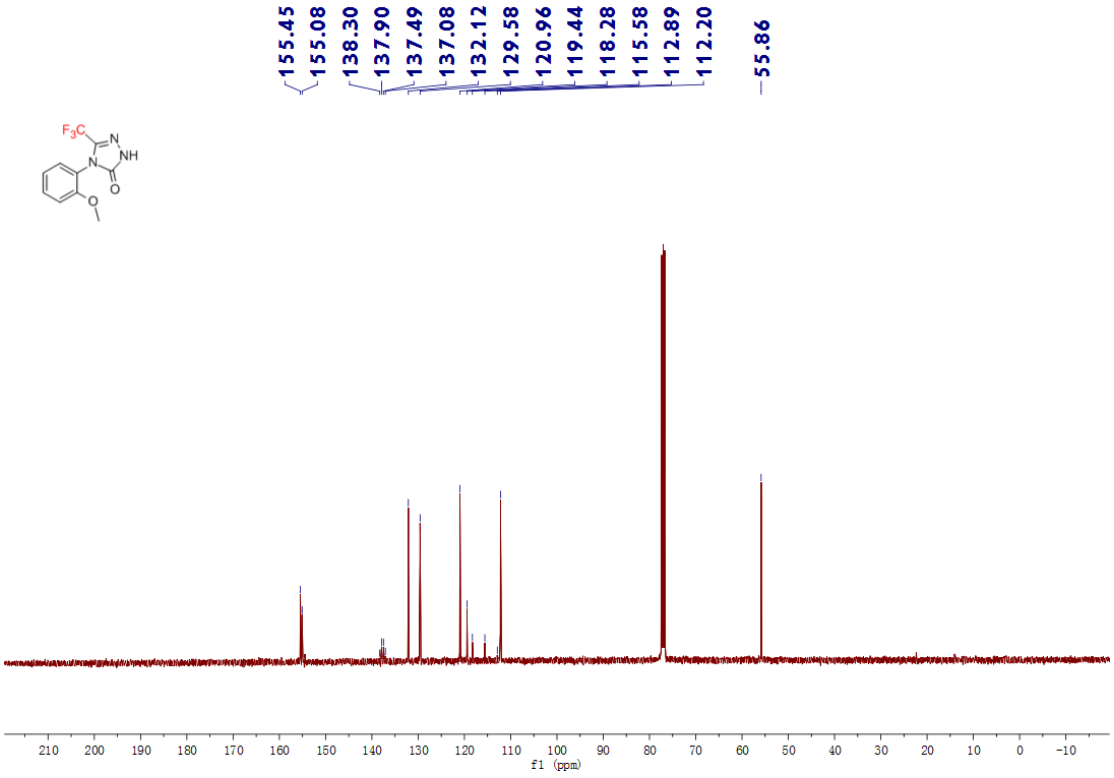
^{19}F-NMR spectrum of **3e** in $CDCl_3$



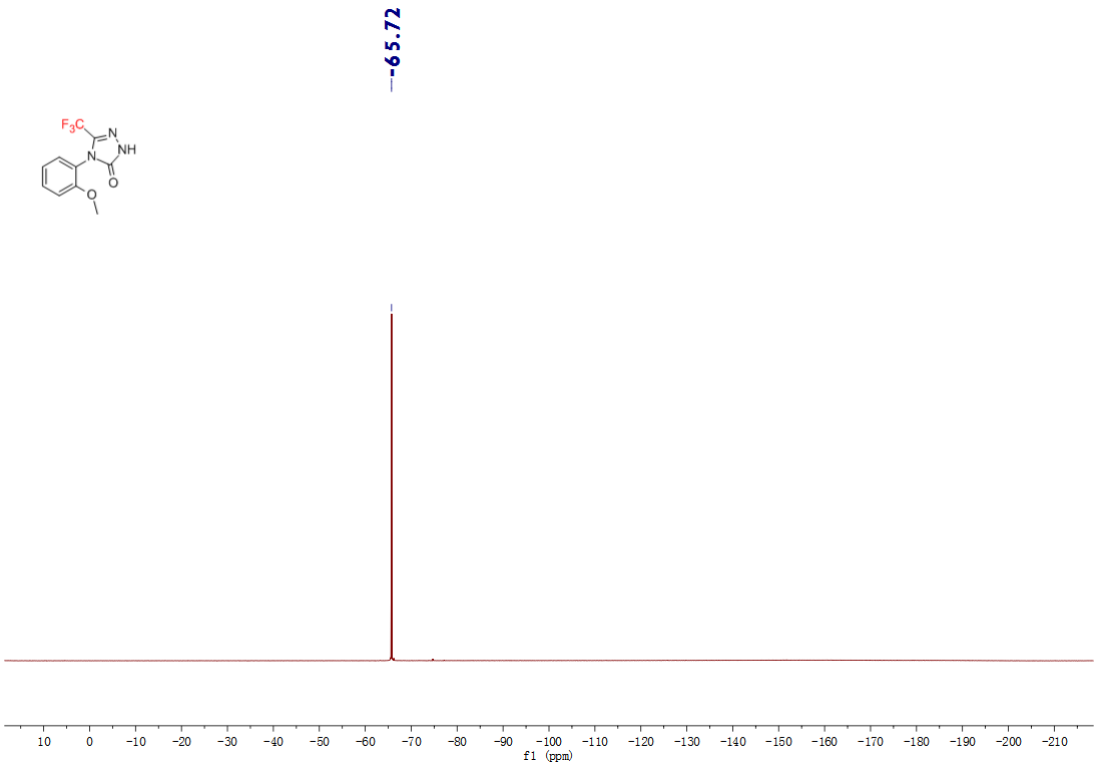
^{1}H-NMR spectrum of **3f** in $CDCl_3$



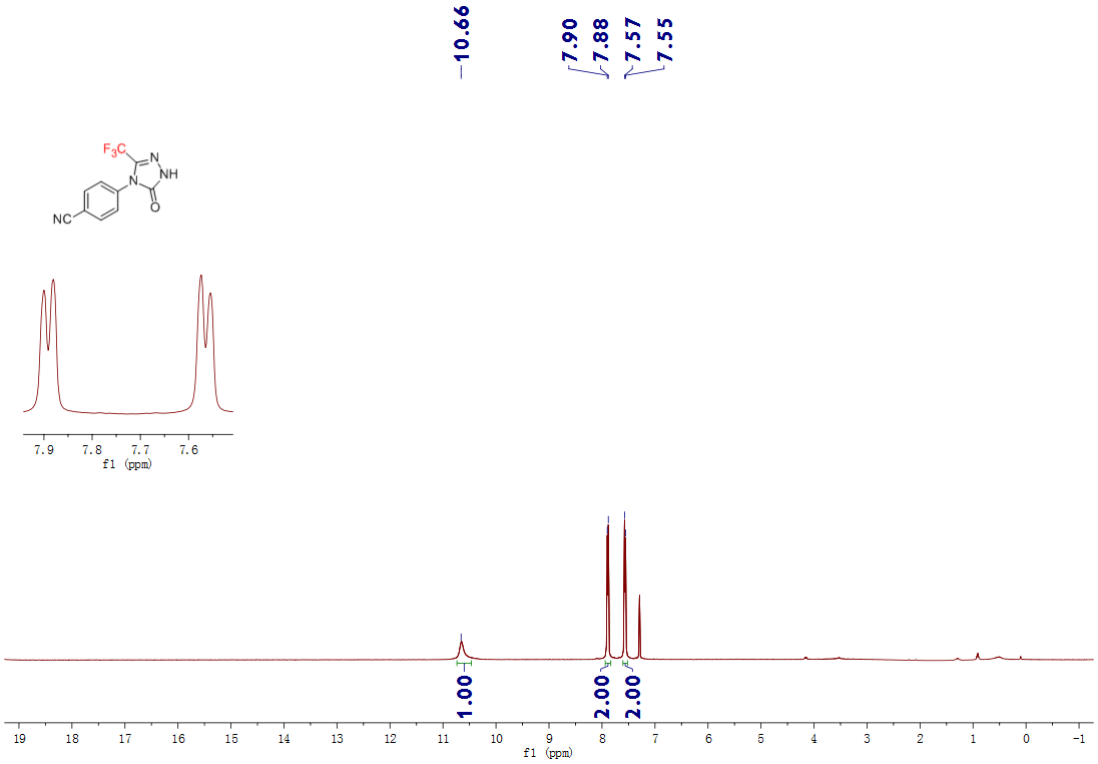
^{13}C-NMR spectrum of **3f** in $CDCl_3$



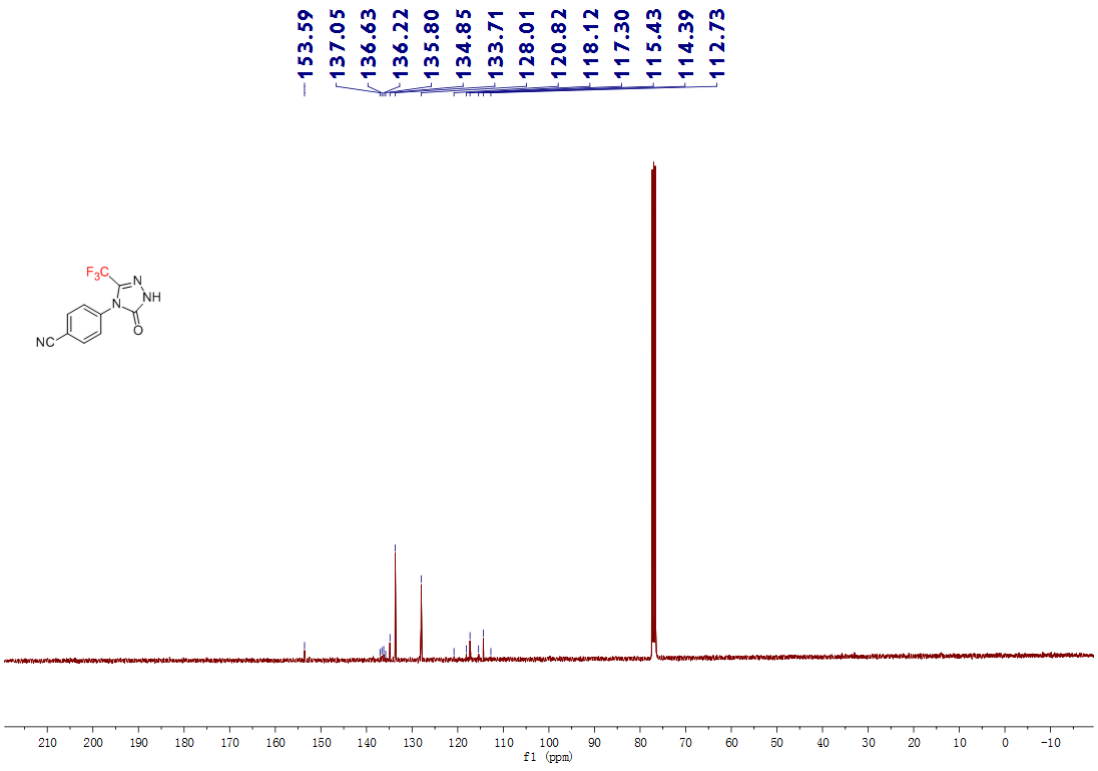
^{19}F-NMR spectrum of **3f** in $CDCl_3$



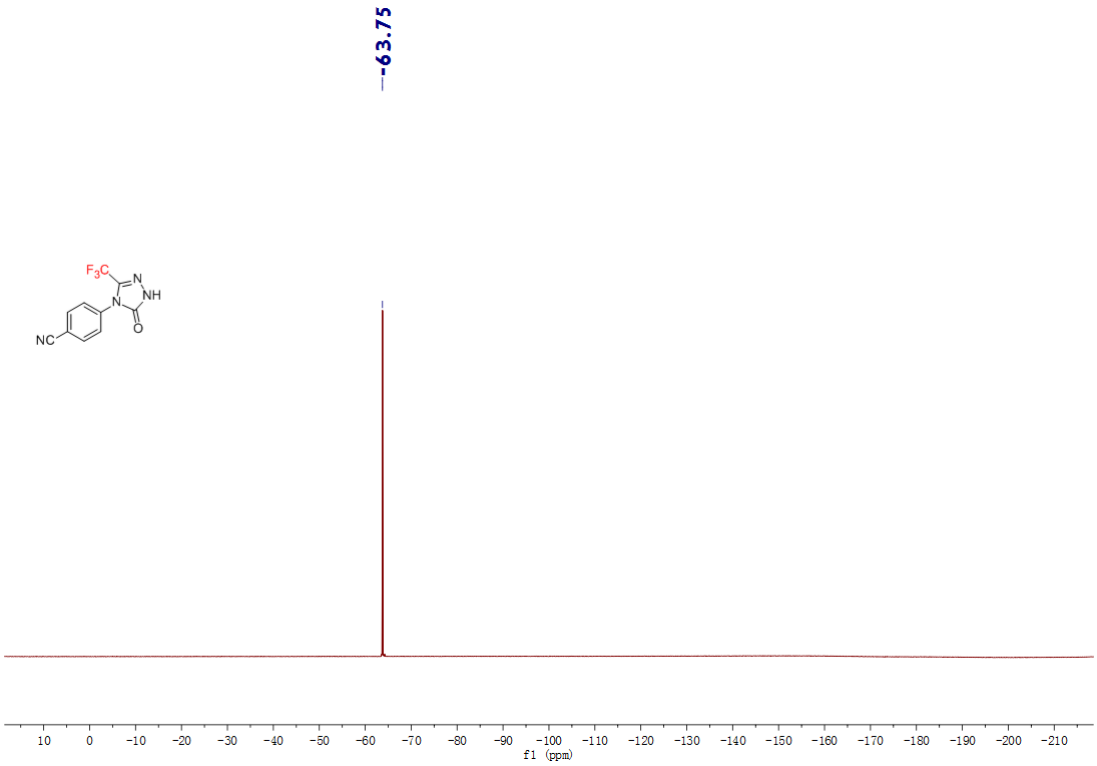
^{1}H-NMR spectrum of **3g** in $CDCl_3$



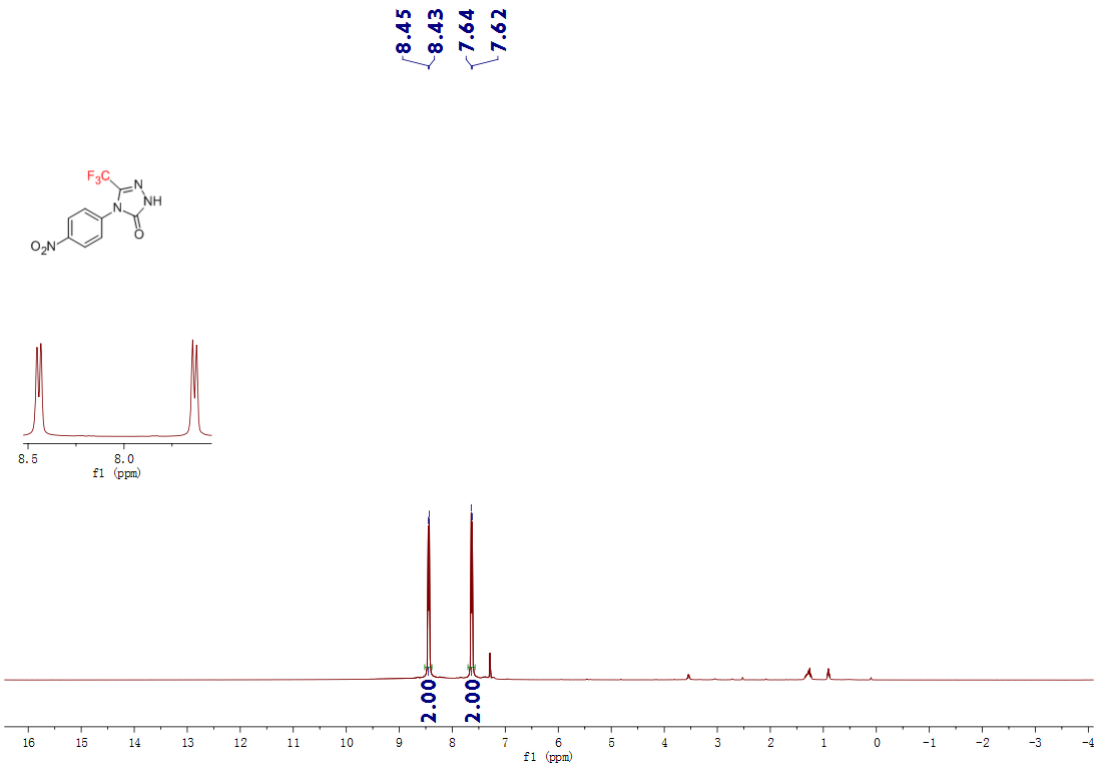
^{13}C-NMR spectrum of **3g** in $CDCl_3$



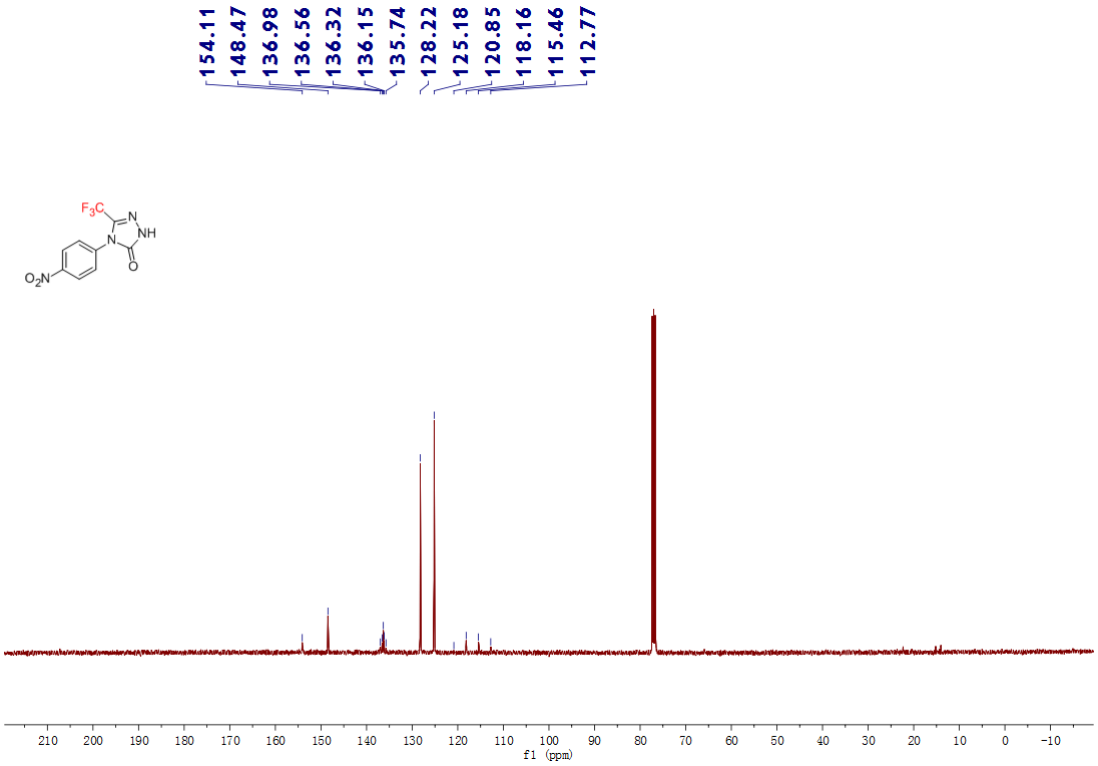
^{19}F-NMR spectrum of **3g** in $CDCl_3$



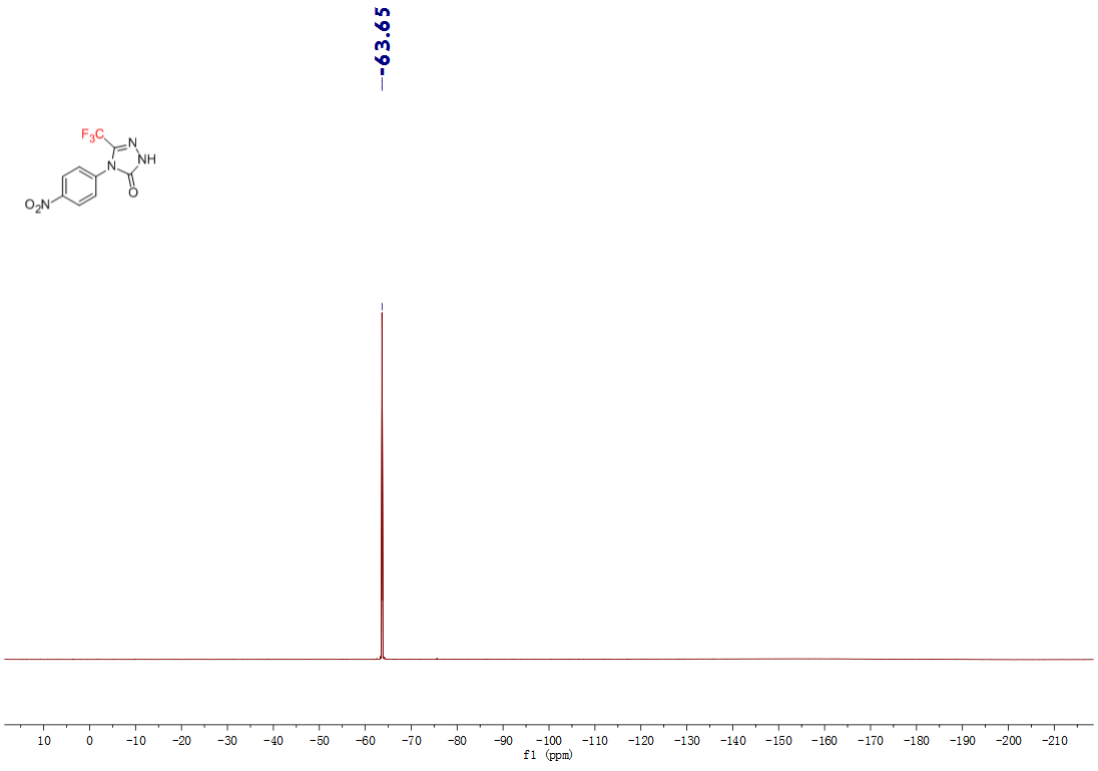
^{1}H-NMR spectrum of **3h** in $CDCl_3$



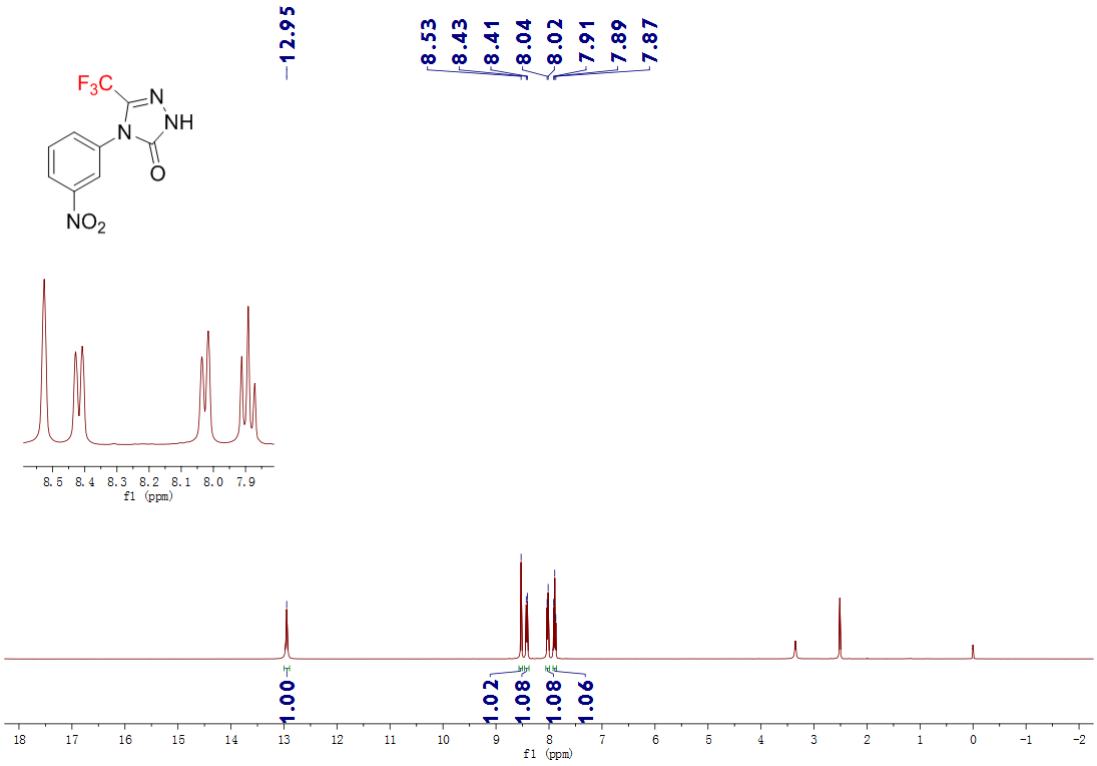
^{13}C-NMR spectrum of **3h** in $CDCl_3$



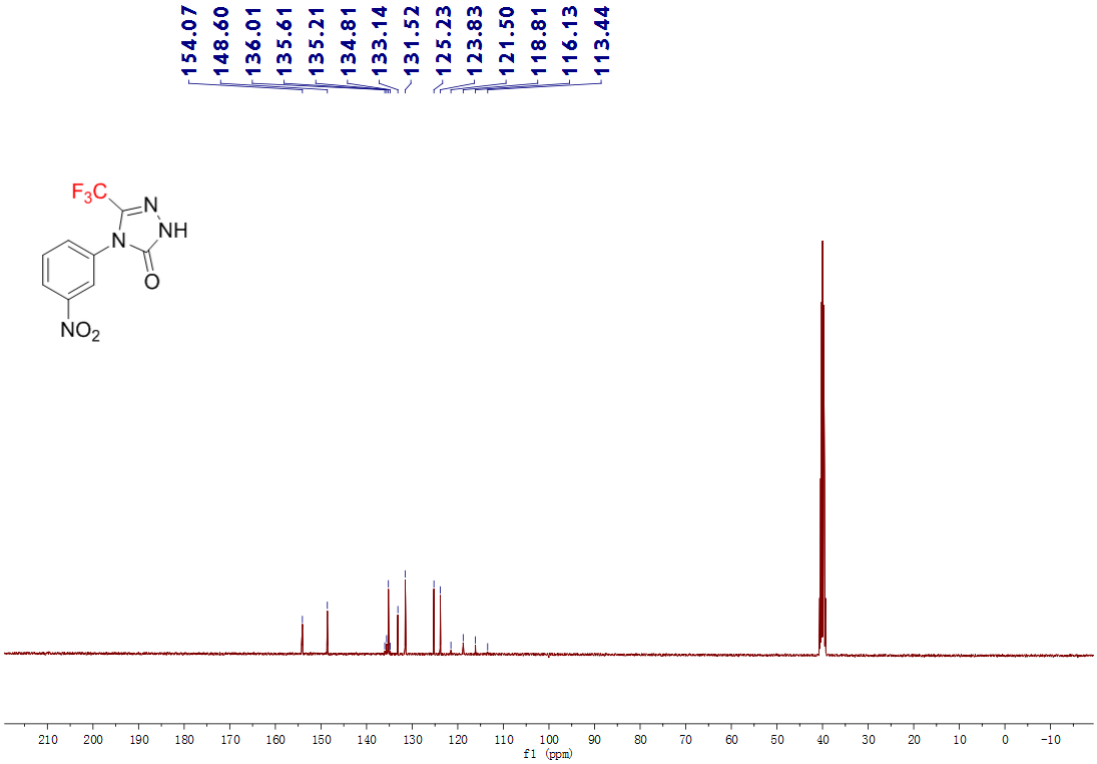
^{19}F-NMR spectrum of **3h** in $CDCl_3$



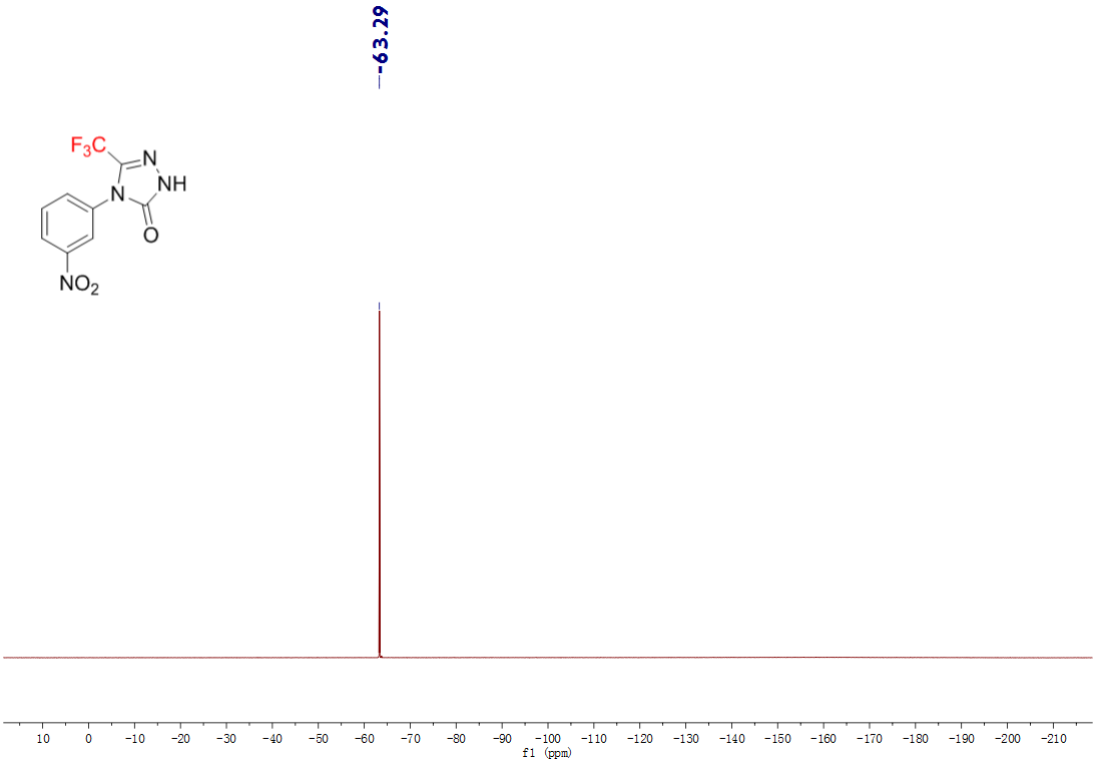
^{1}H-NMR spectrum of **3i** in DMSO-*d6*



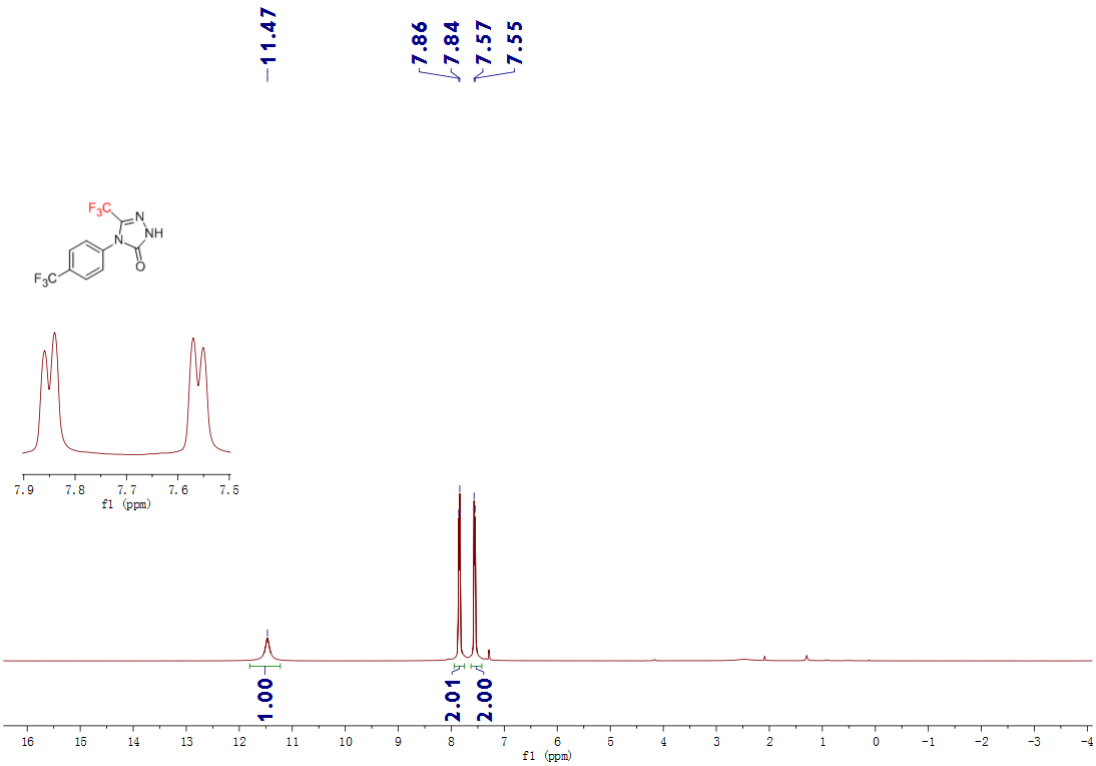
^{13}C-NMR spectrum of **3i** in DMSO-*d6*



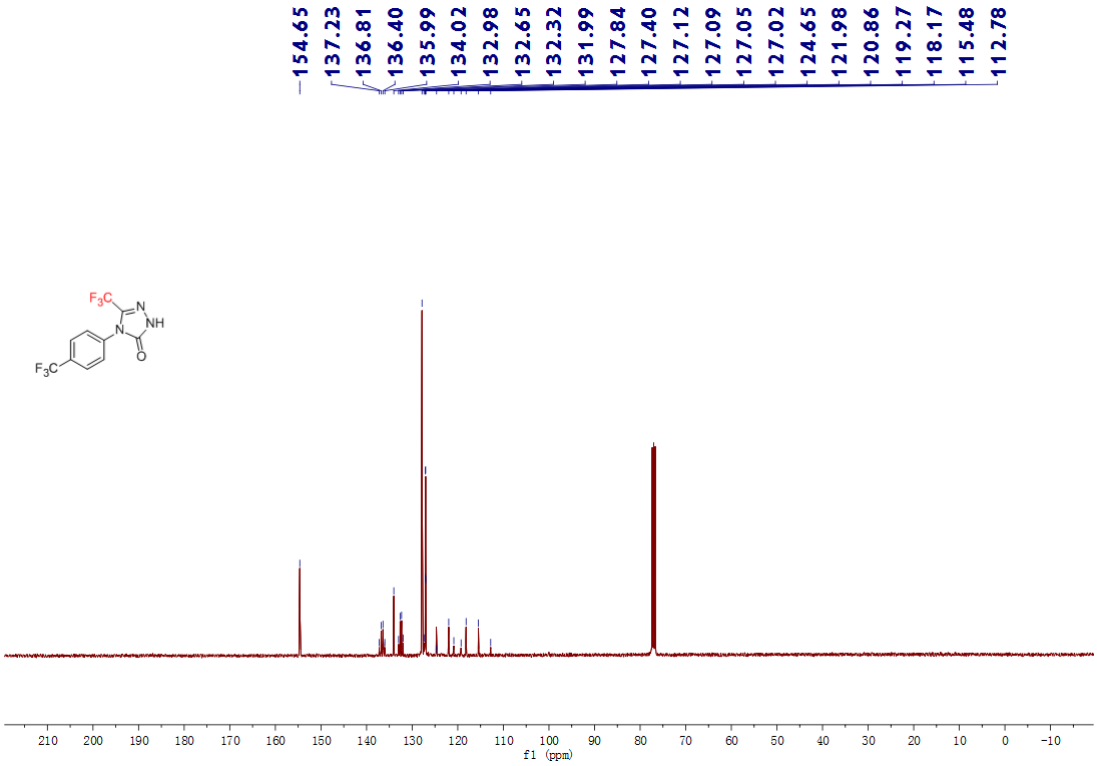
^{19}F-NMR spectrum of **3i** in DMSO-*d6*



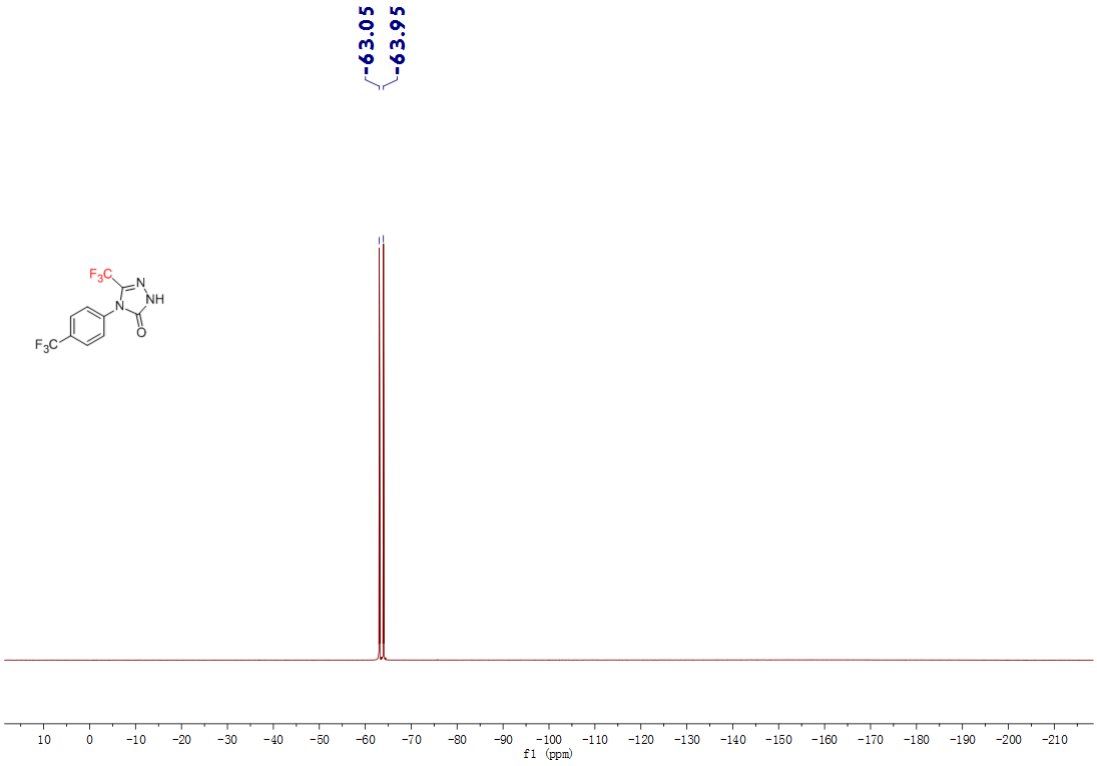
^{1}H-NMR spectrum of **3j** in $CDCl_3$



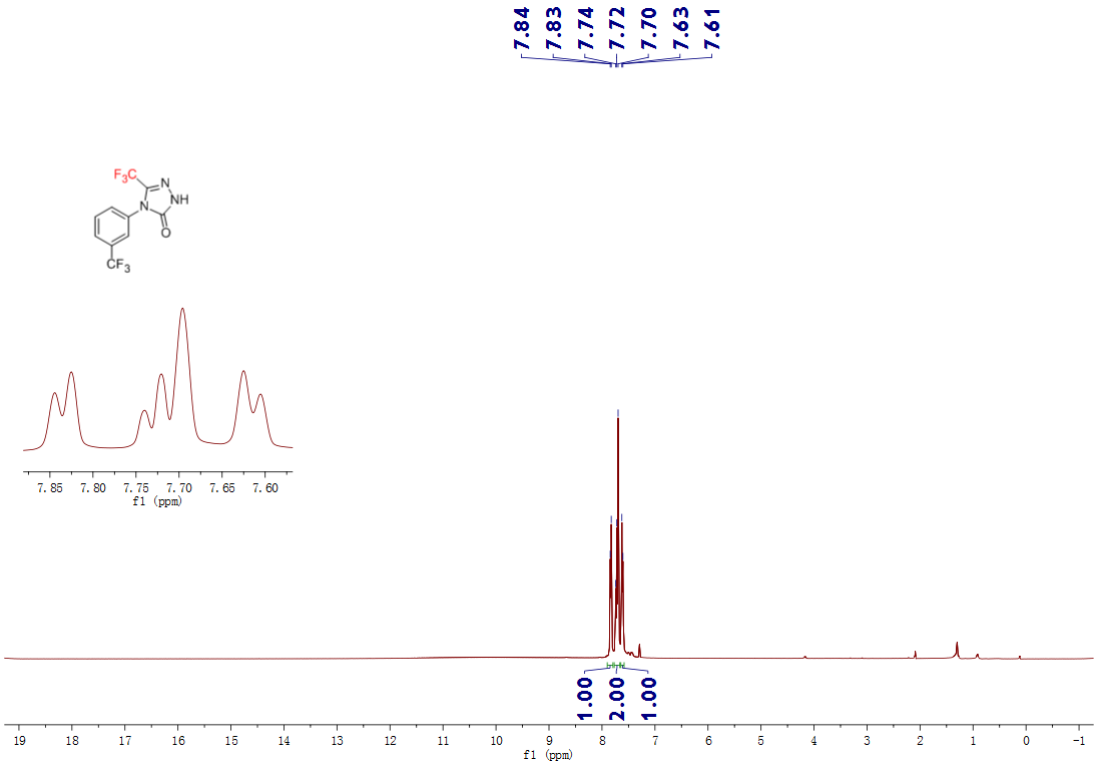
^{13}C-NMR spectrum of **3j** in $CDCl_3$



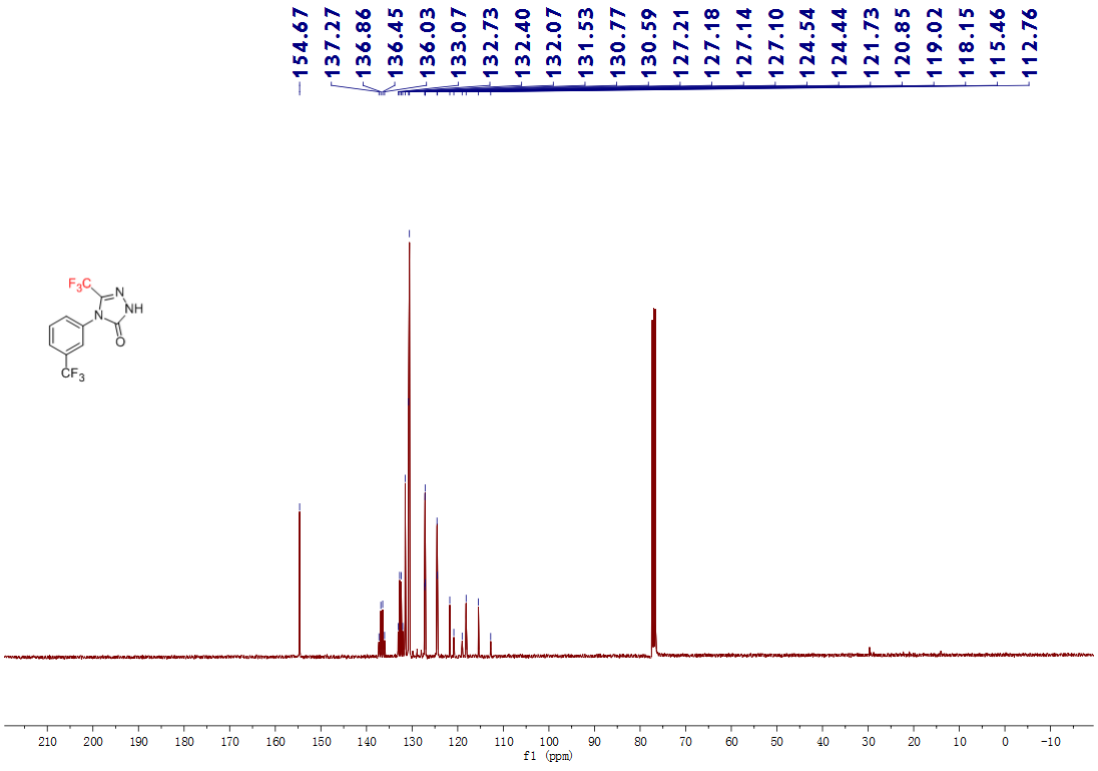
^{19}F-NMR spectrum of **3j** in $CDCl_3$



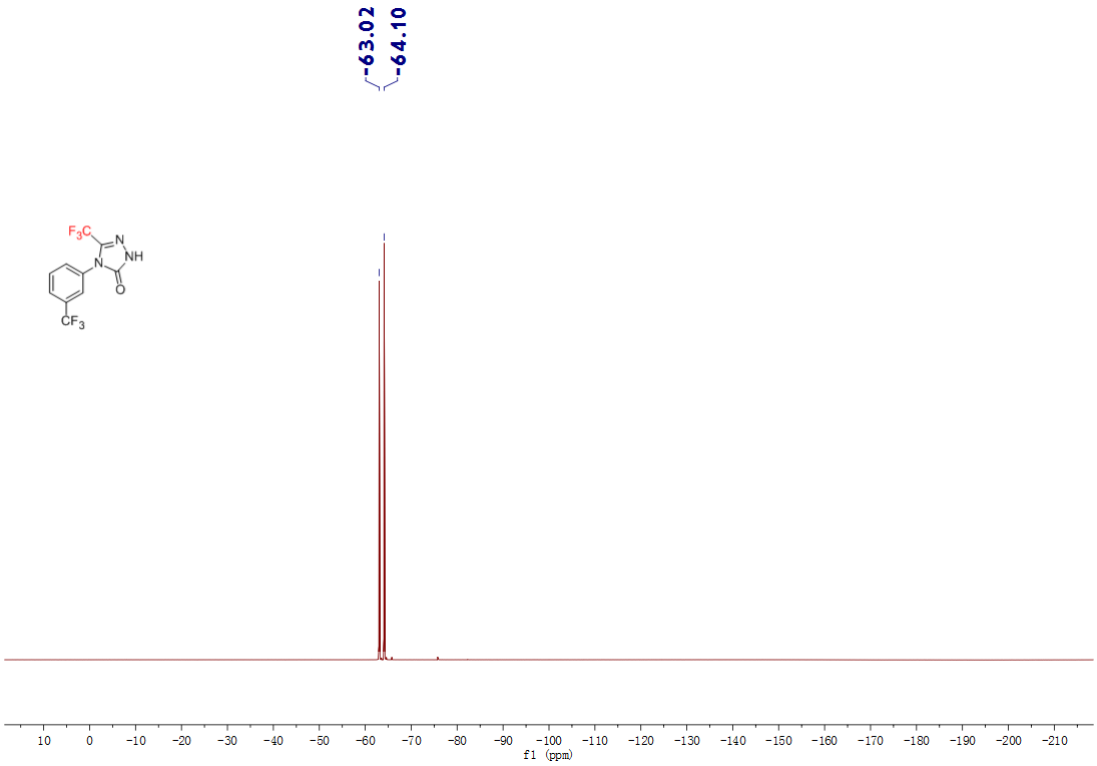
^{1}H-NMR spectrum of **3k** in $CDCl_3$



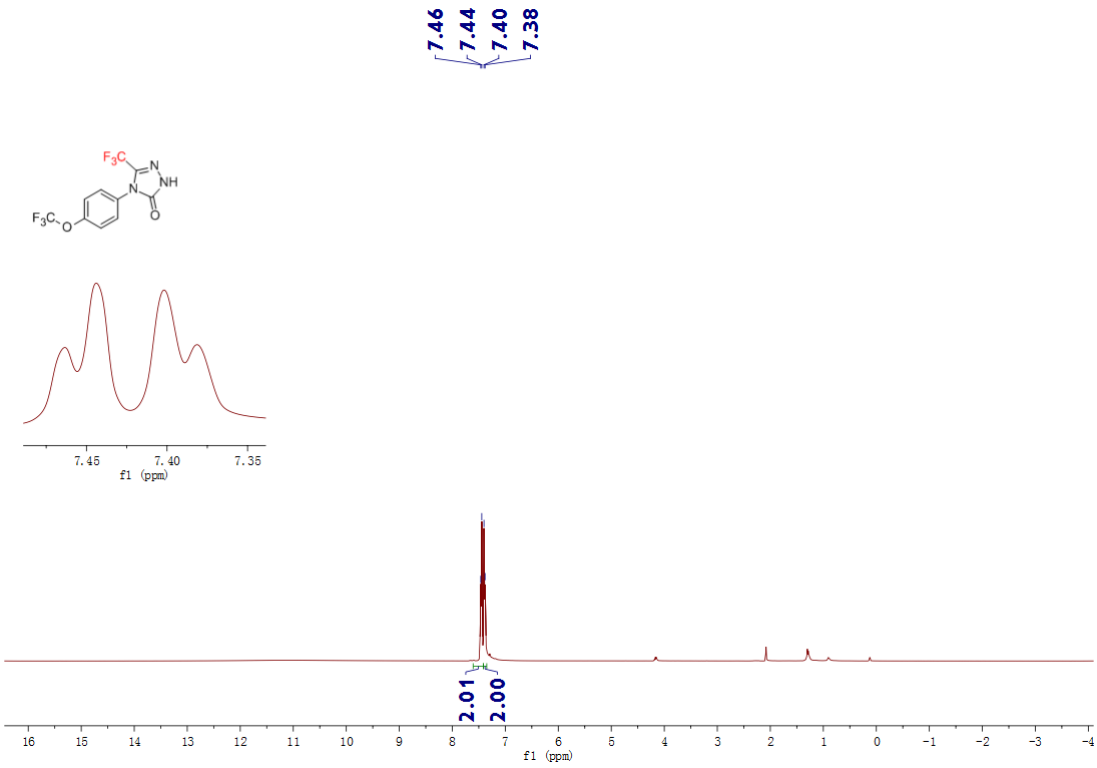
^{13}C-NMR spectrum of **3k** in $CDCl_3$



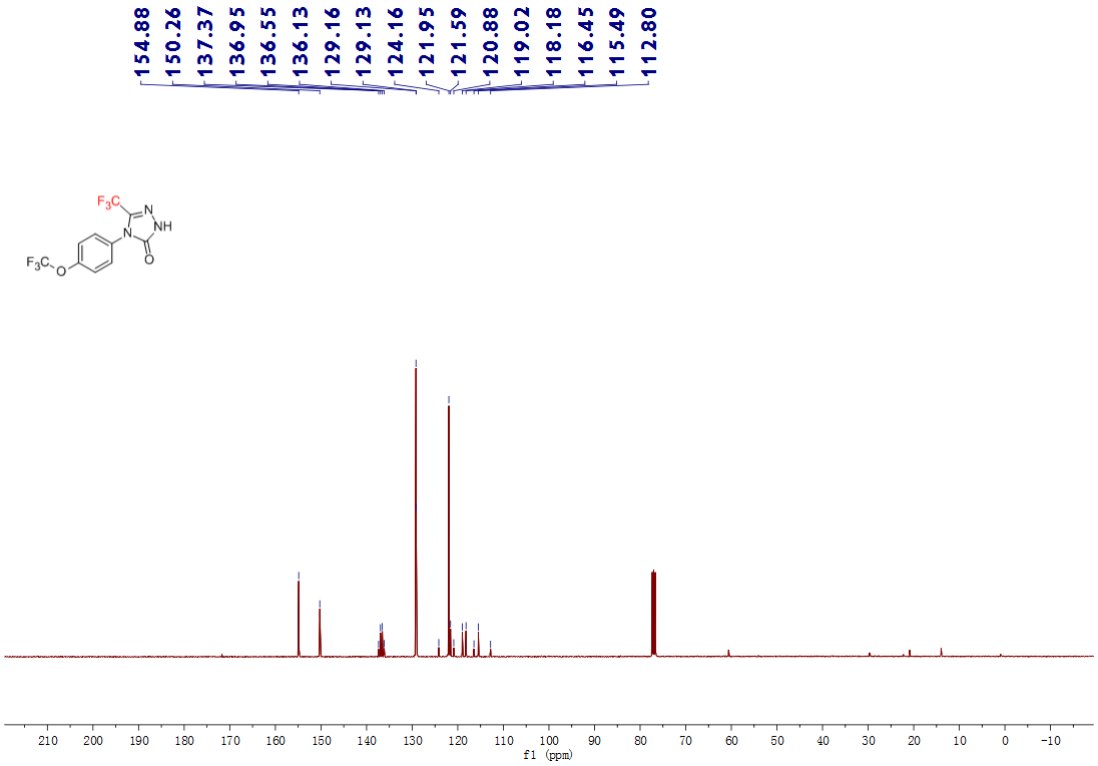
^{19}F-NMR spectrum of **3k** in $CDCl_3$



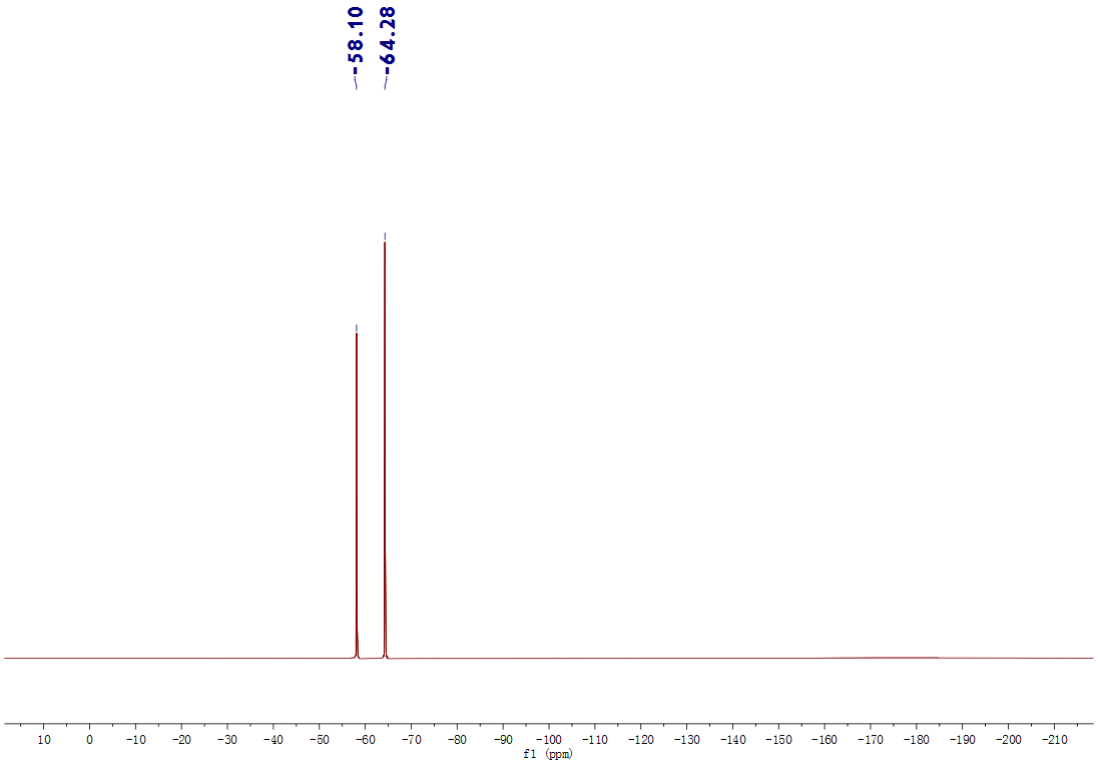
^{1}H-NMR spectrum of **3l** in $CDCl_3$



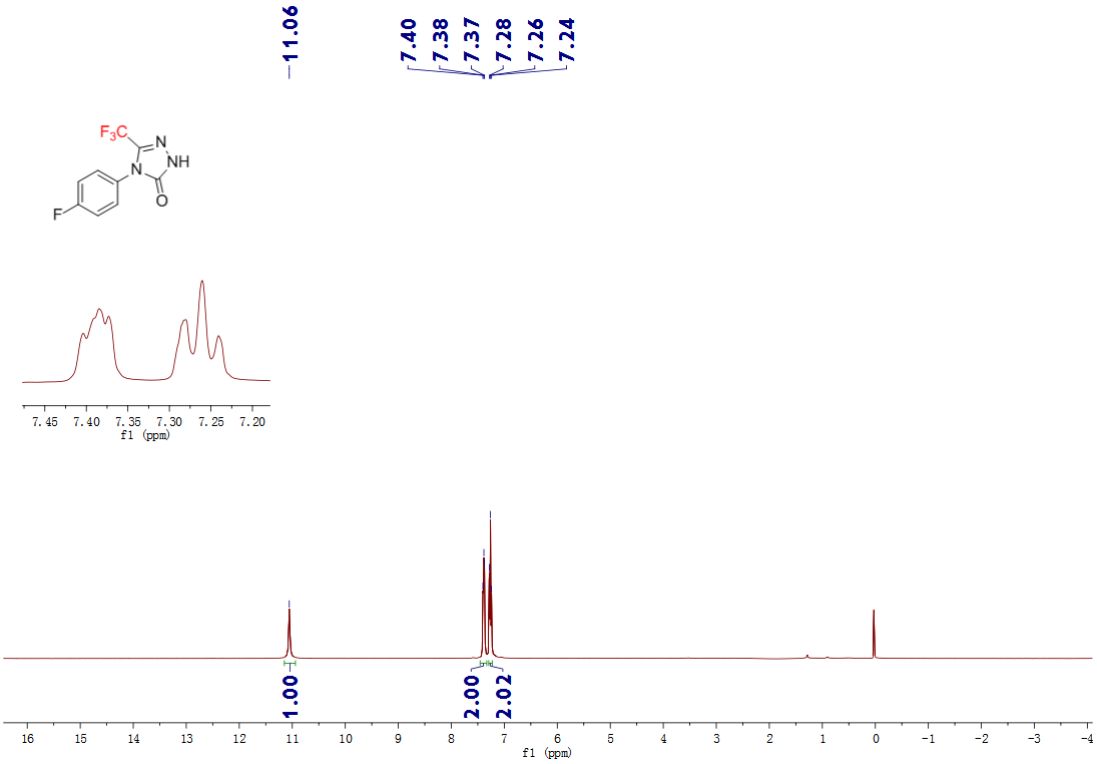
^{13}C-NMR spectrum of **3l** in $CDCl_3$



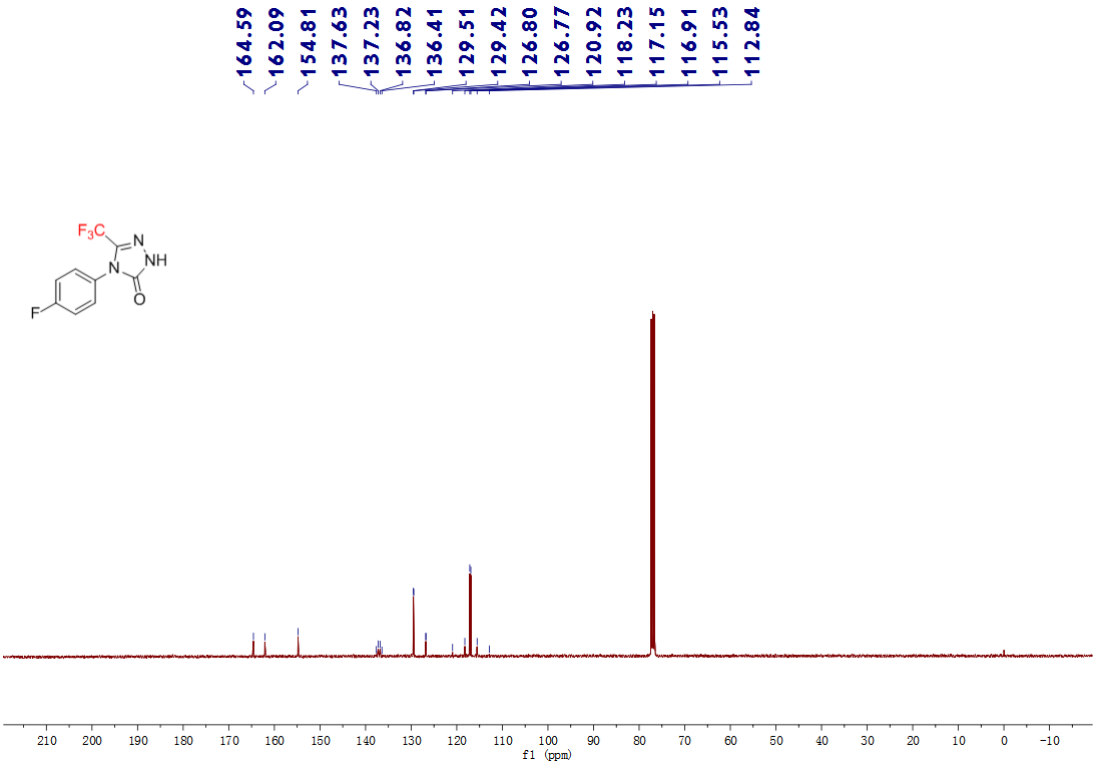
^{19}F-NMR spectrum of **3l** in $CDCl_3$



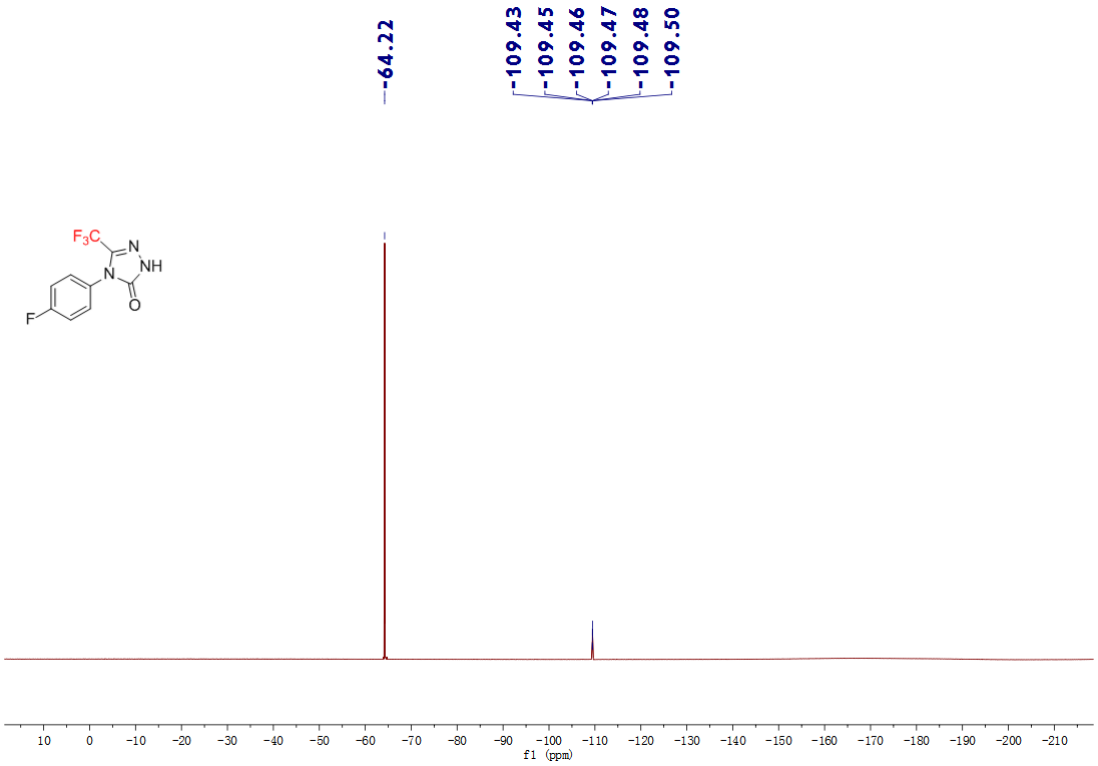
^{1}H-NMR spectrum of **3m** in $CDCl_3$



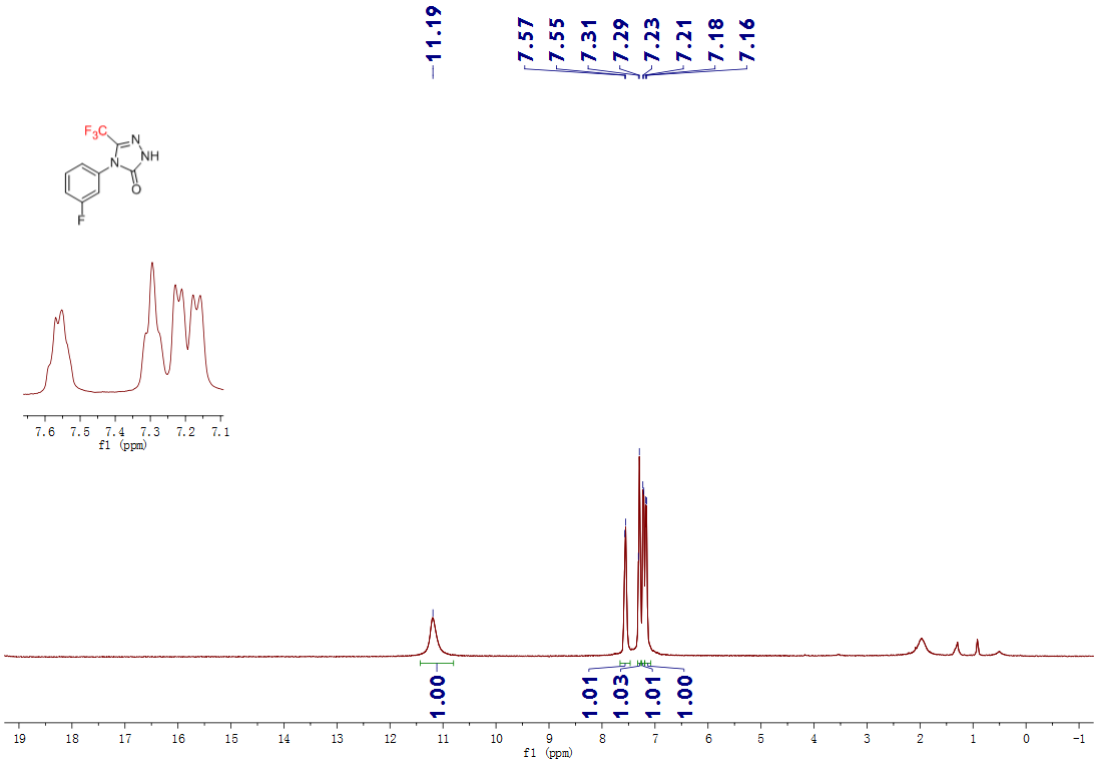
^{13}C-NMR spectrum of **3m** in $CDCl_3$



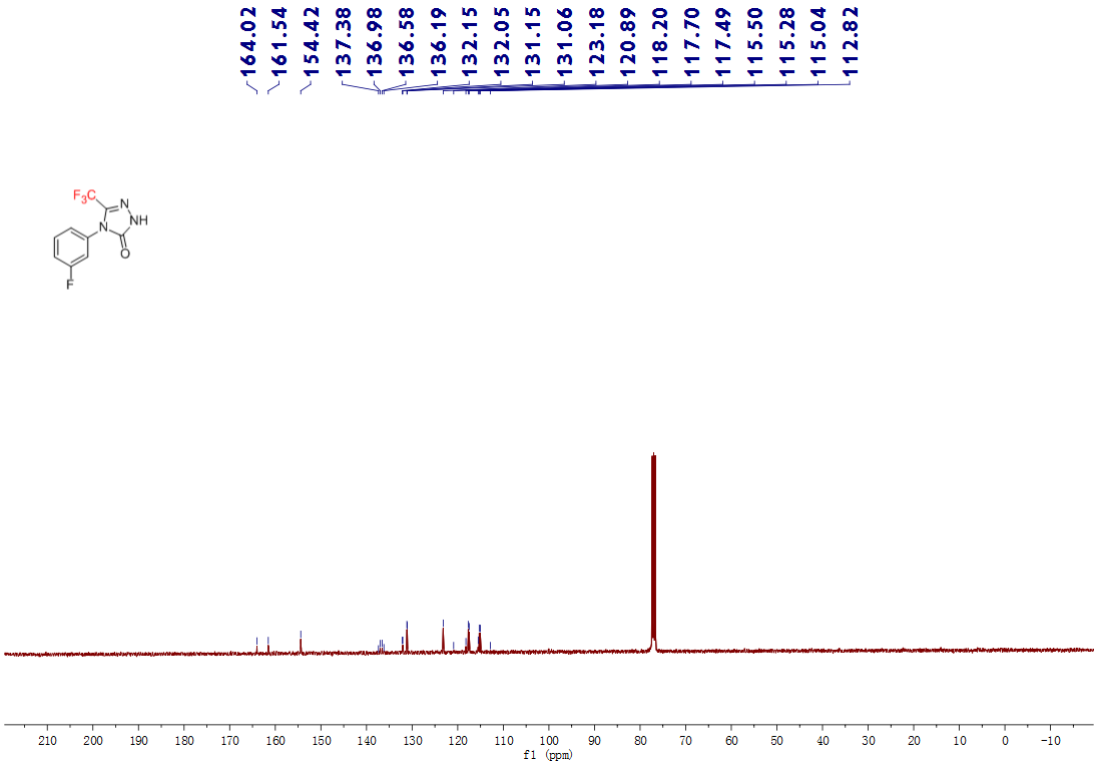
^{19}F-NMR spectrum of **3m** in $CDCl_3$



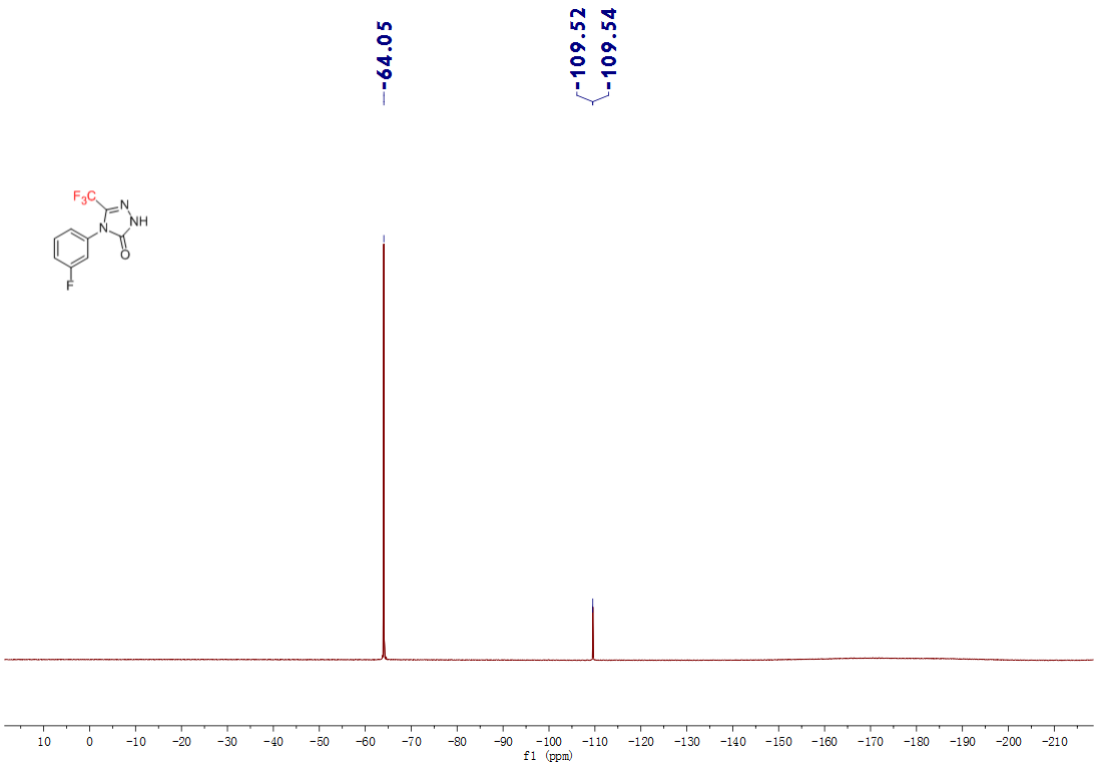
^{1}H-NMR spectrum of **3n** in $CDCl_3$



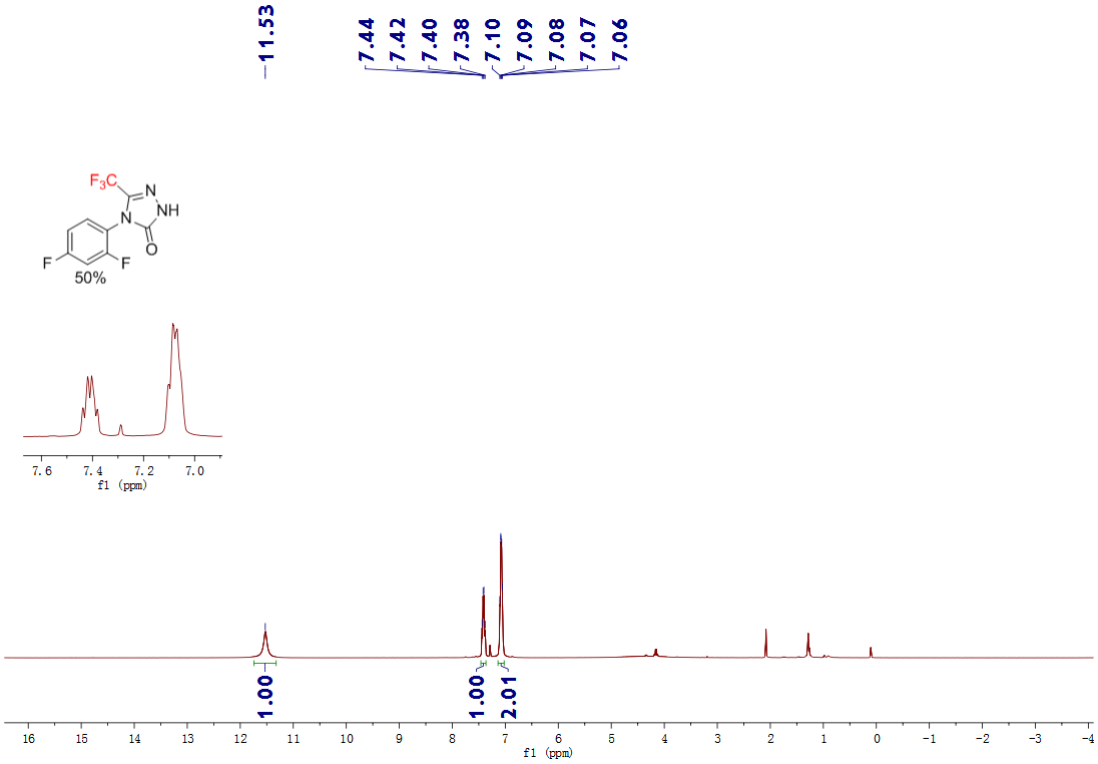
^{13}C-NMR spectrum of **3n** in $CDCl_3$



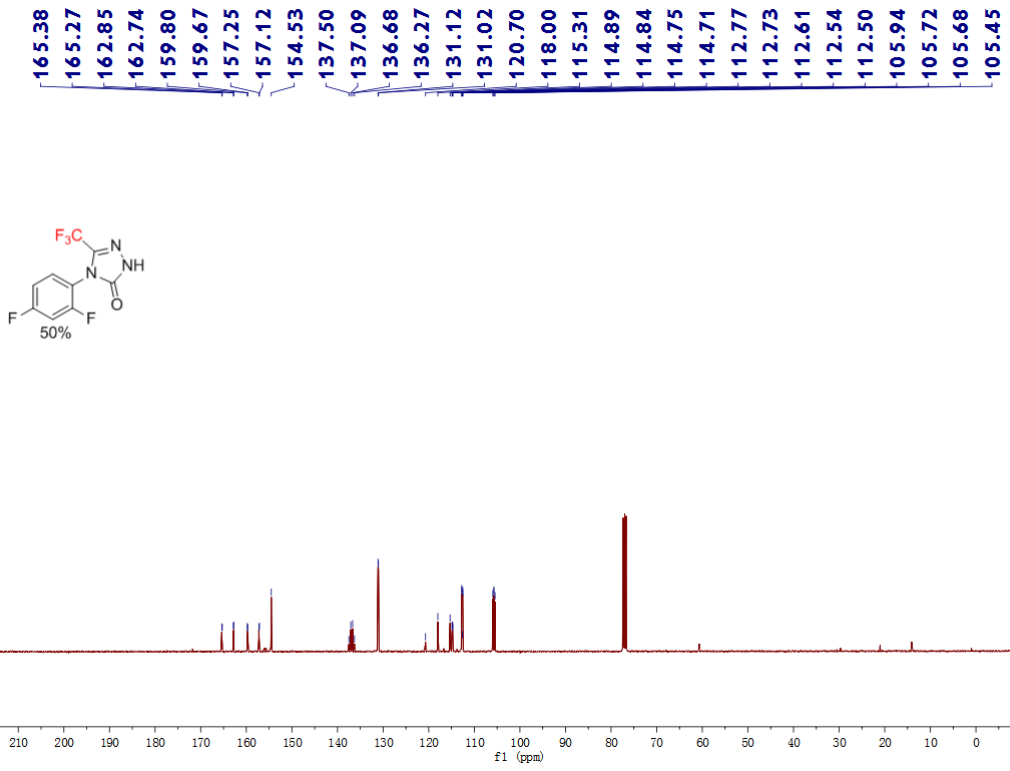
^{19}F-NMR spectrum of **3n** in $CDCl_3$



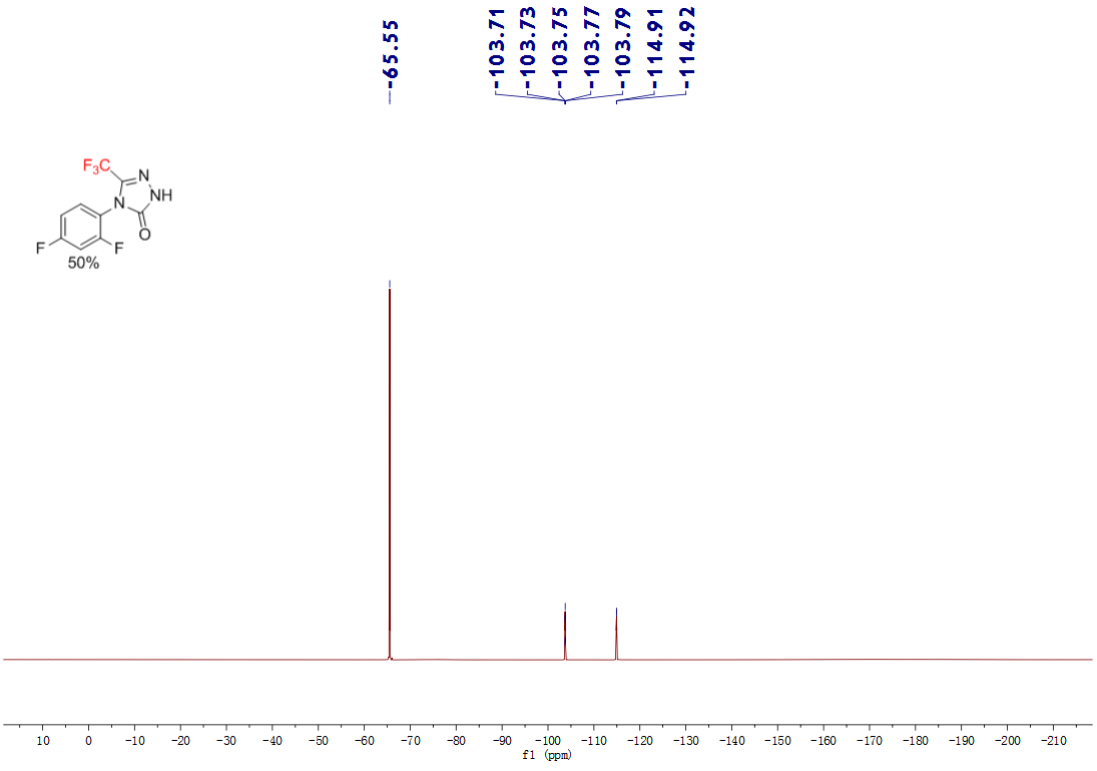
^{1}H-NMR spectrum of **3o** in $CDCl_3$



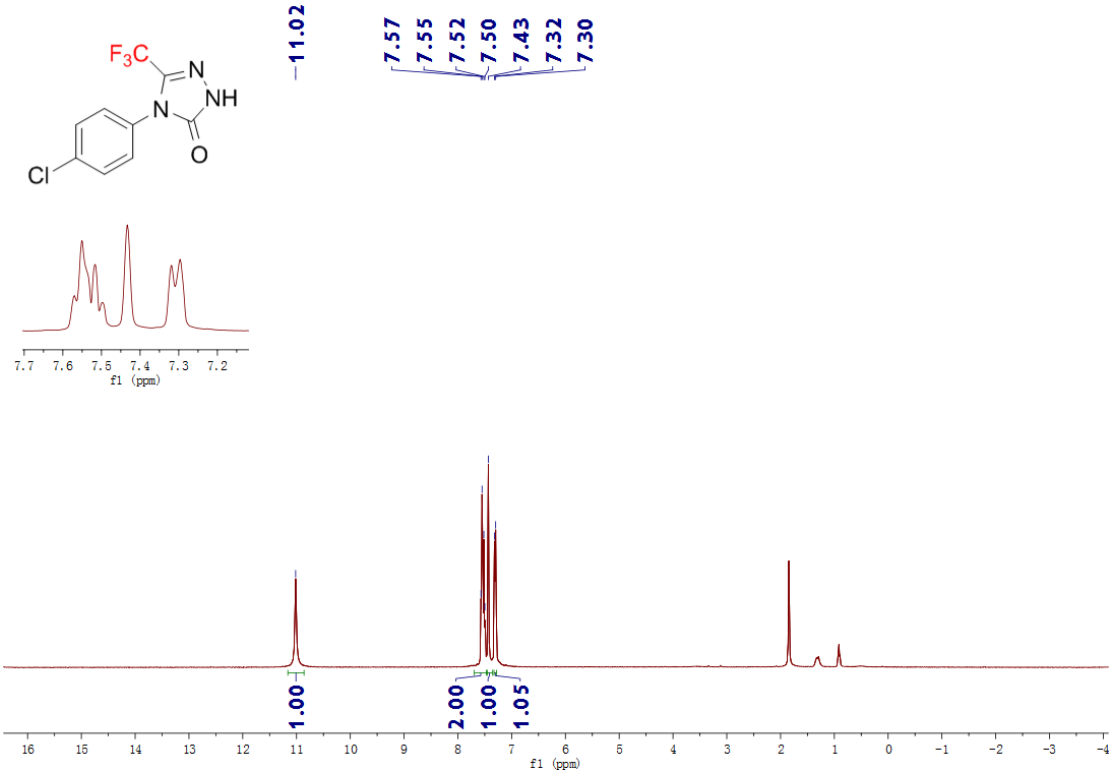
^{13}C-NMR spectrum of **3o** in $CDCl_3$



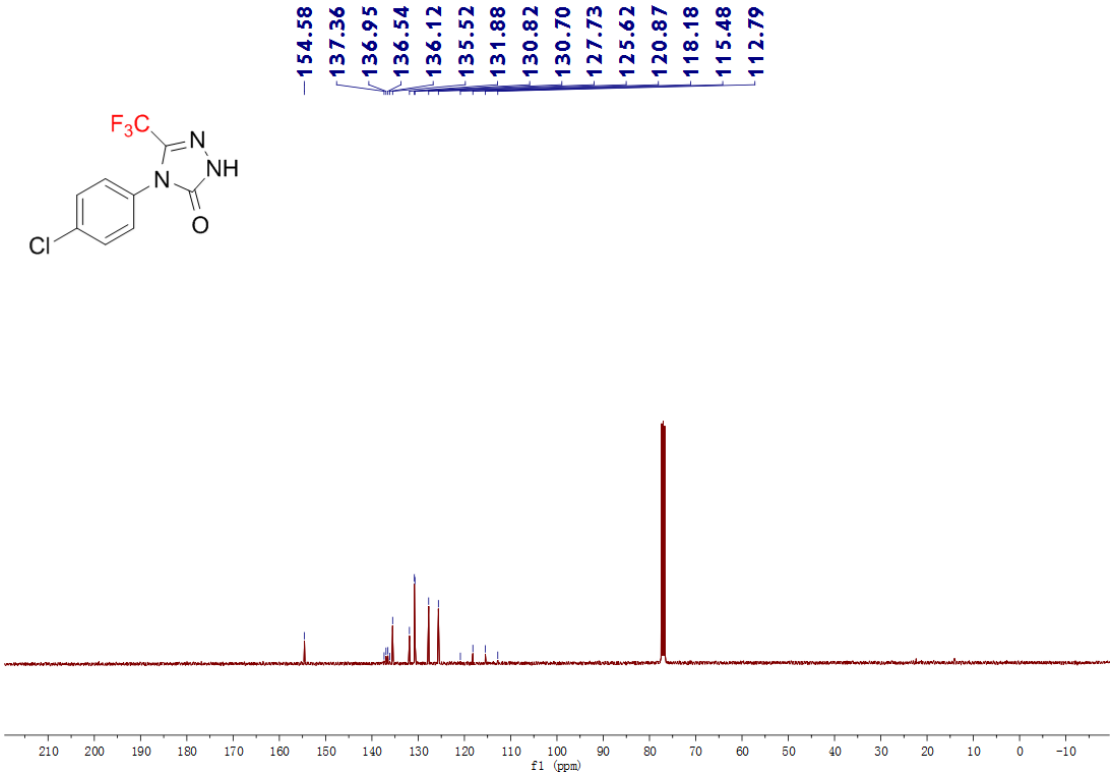
^{19}F-NMR spectrum of **3o** in $CDCl_3$



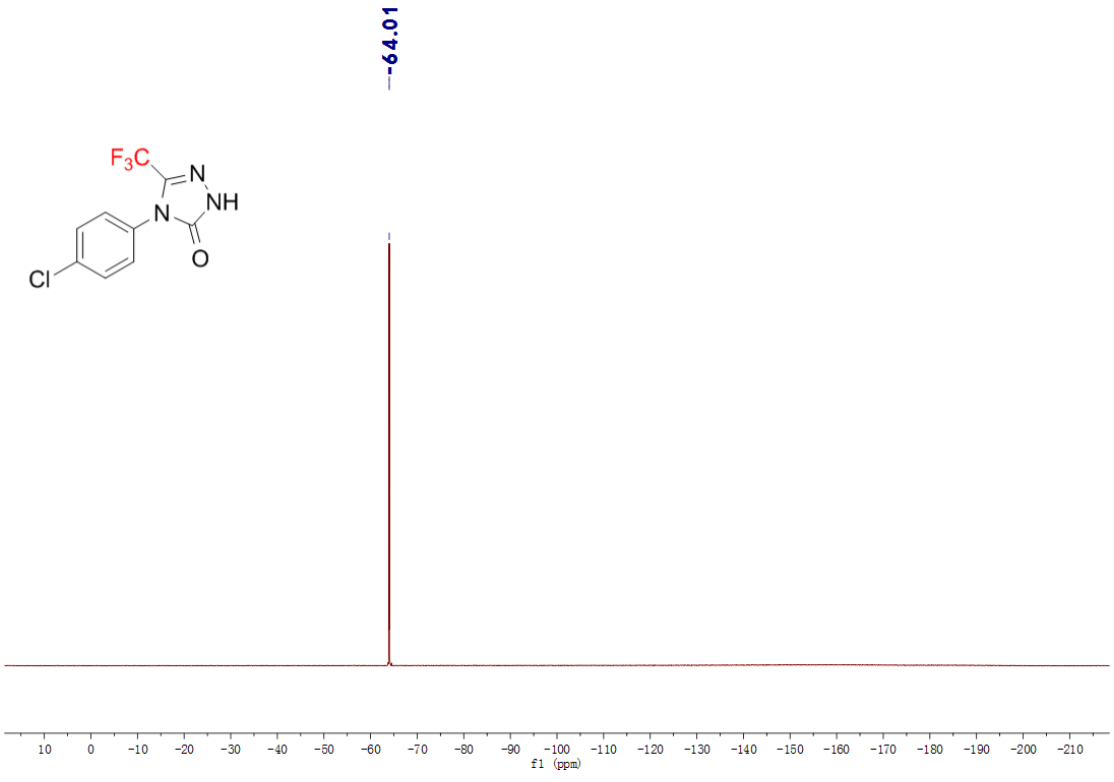
^{1}H-NMR spectrum of **3p** in $CDCl_3$



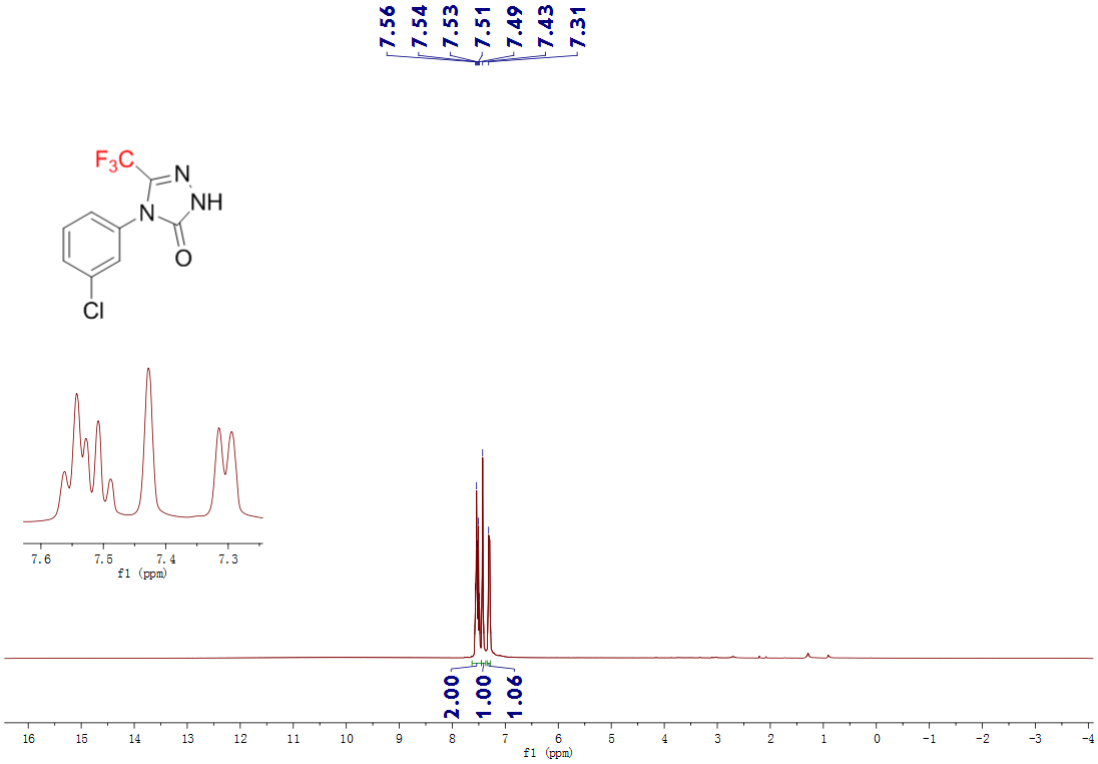
^{13}C-NMR spectrum of **3p** in $CDCl_3$



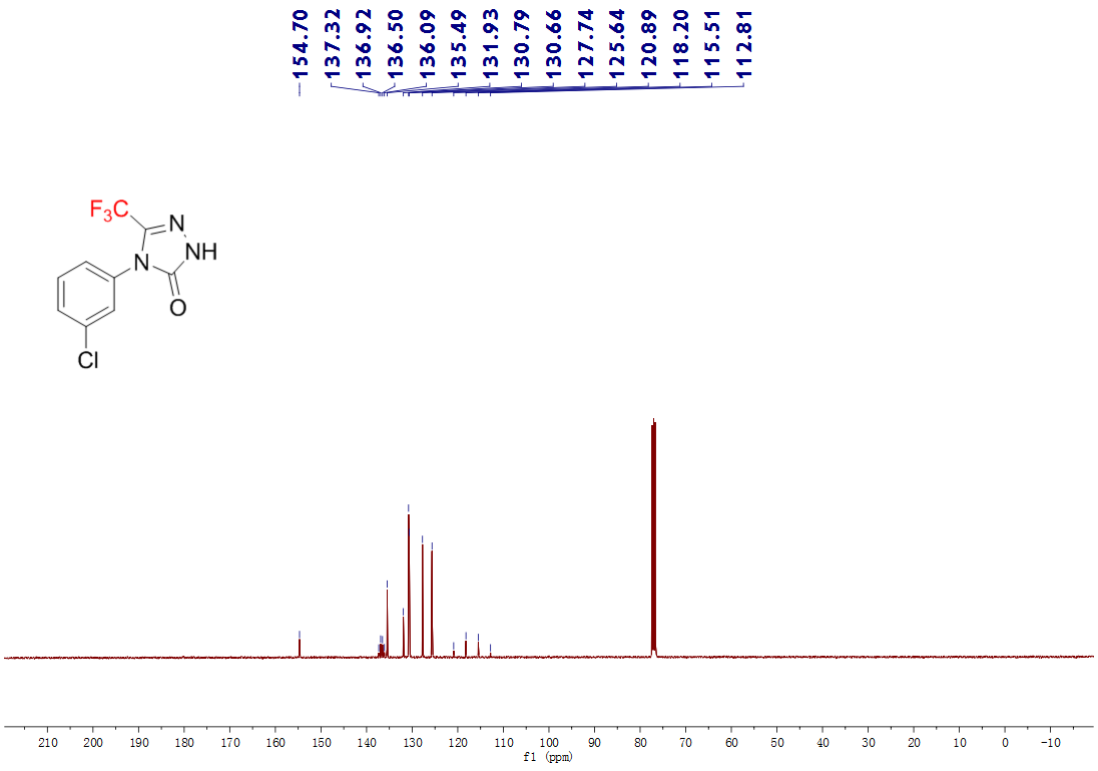
^{19}F-NMR spectrum of **3p** in $CDCl_3$



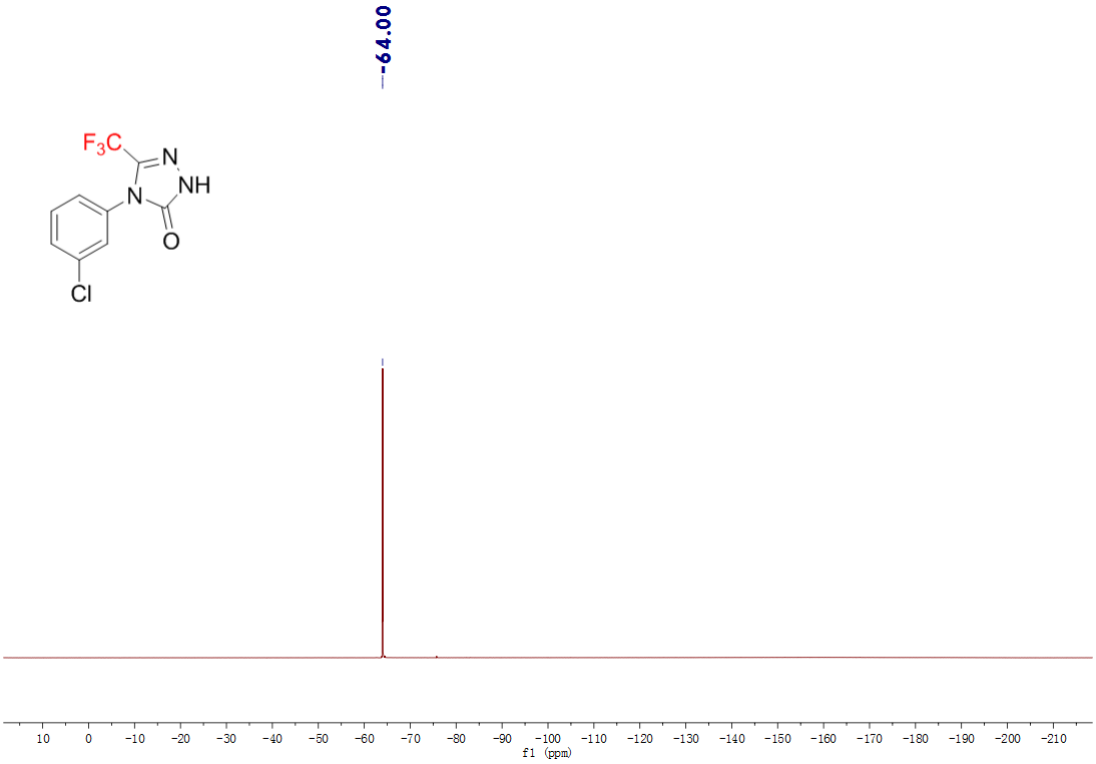
^{1}H-NMR spectrum of **3q** in $CDCl_3$



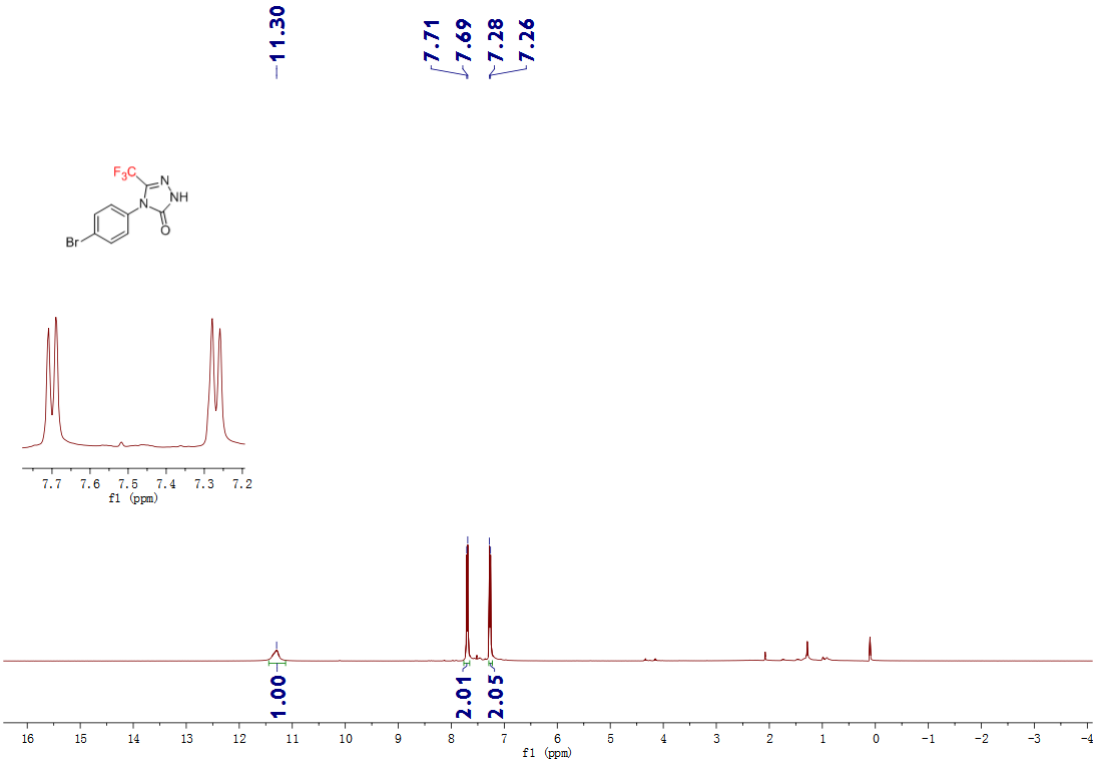
^{13}C-NMR spectrum of **3q** in $CDCl_3$



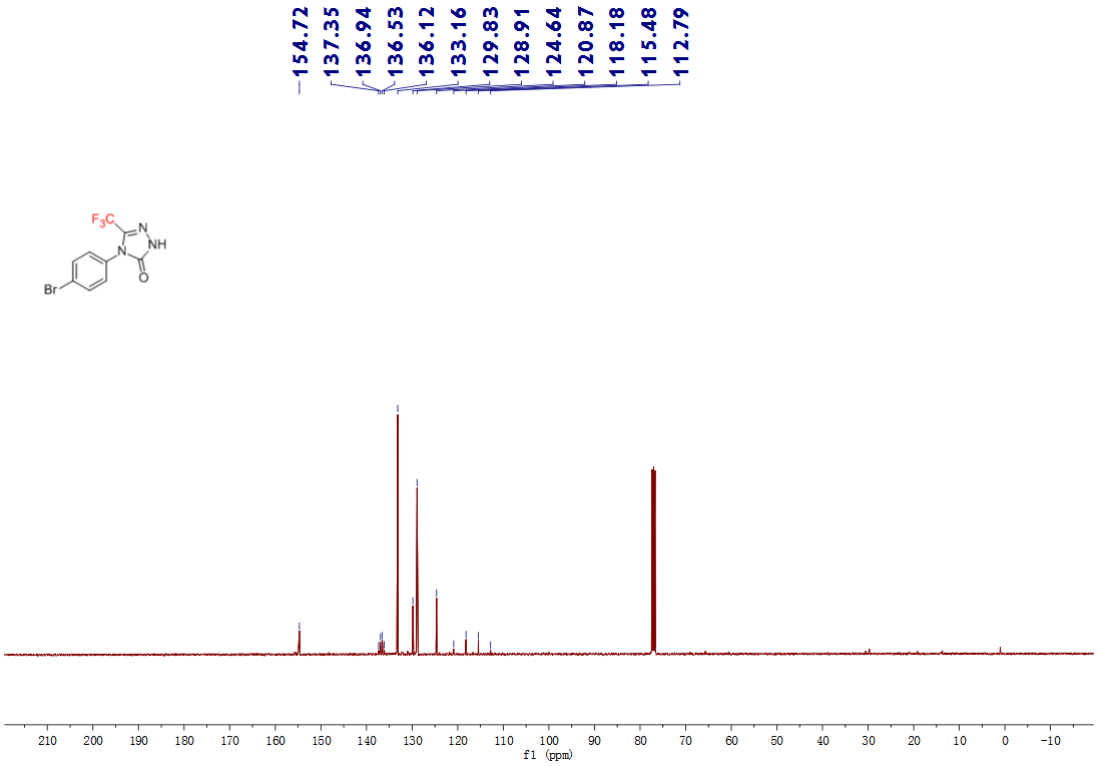
^{19}F-NMR spectrum of **3q** in $CDCl_3$



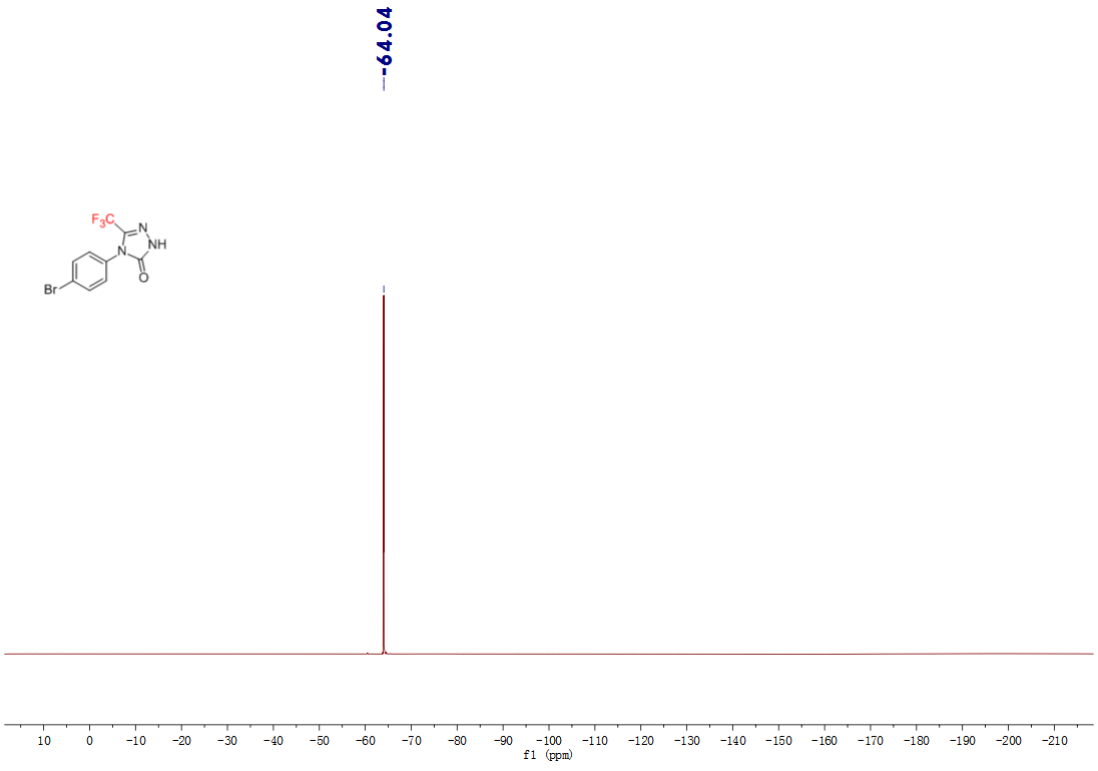
^{1}H-NMR spectrum of **3r** in $CDCl_3$



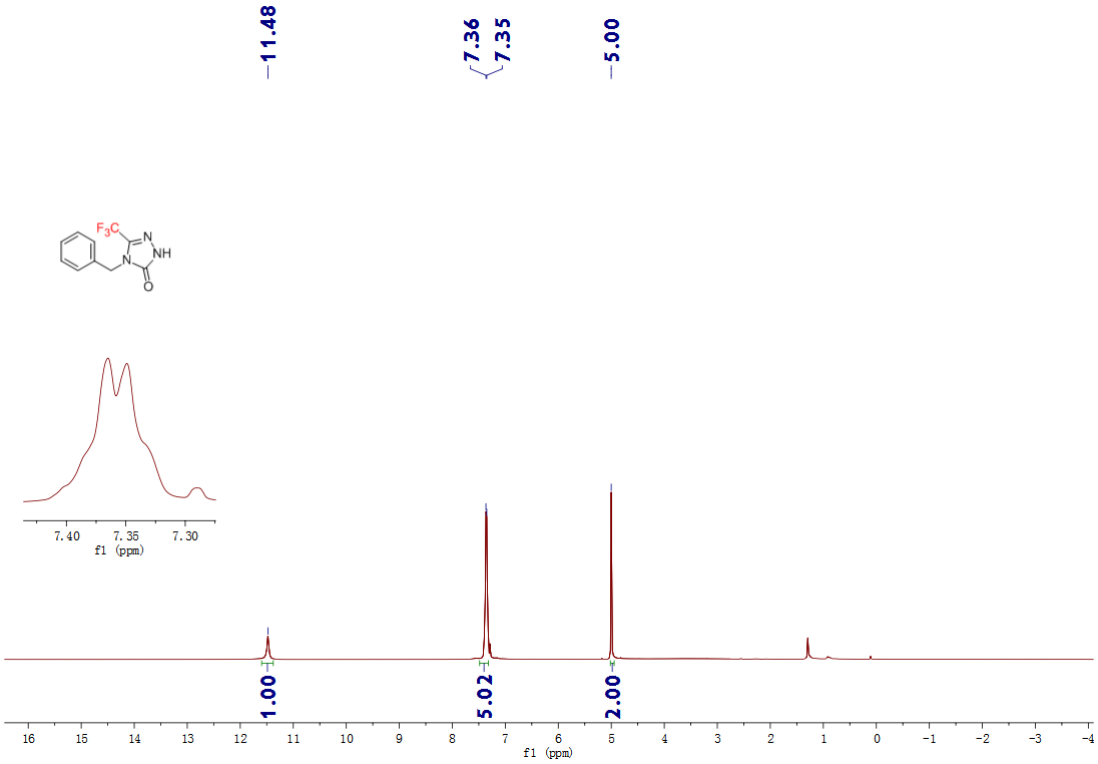
^{13}C-NMR spectrum of **3r** in $CDCl_3$



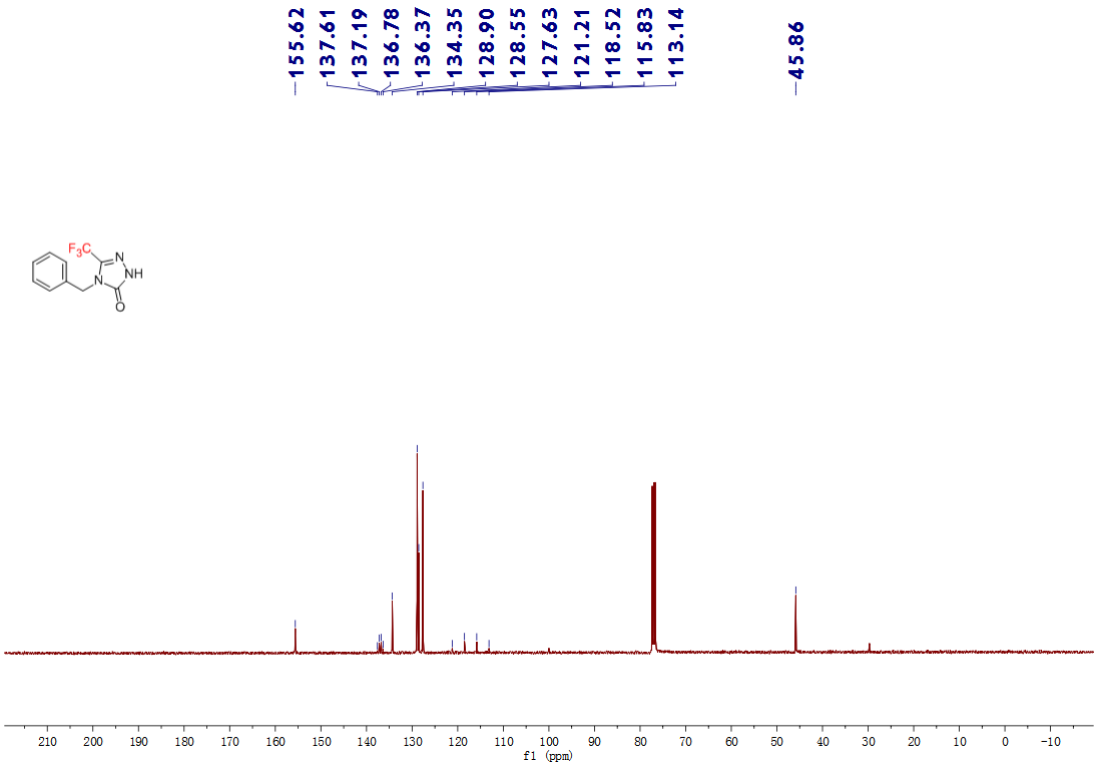
^{19}F-NMR spectrum of **3r** in $CDCl_3$



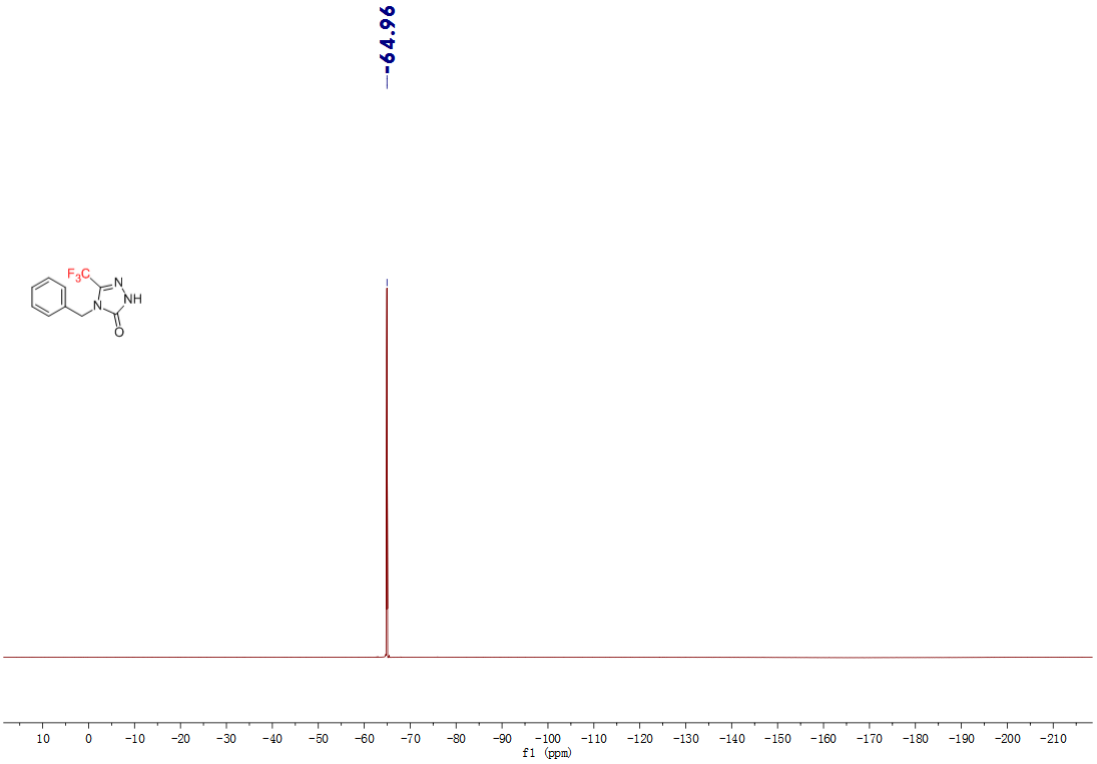
^{1}H-NMR spectrum of **3s** in $CDCl_3$



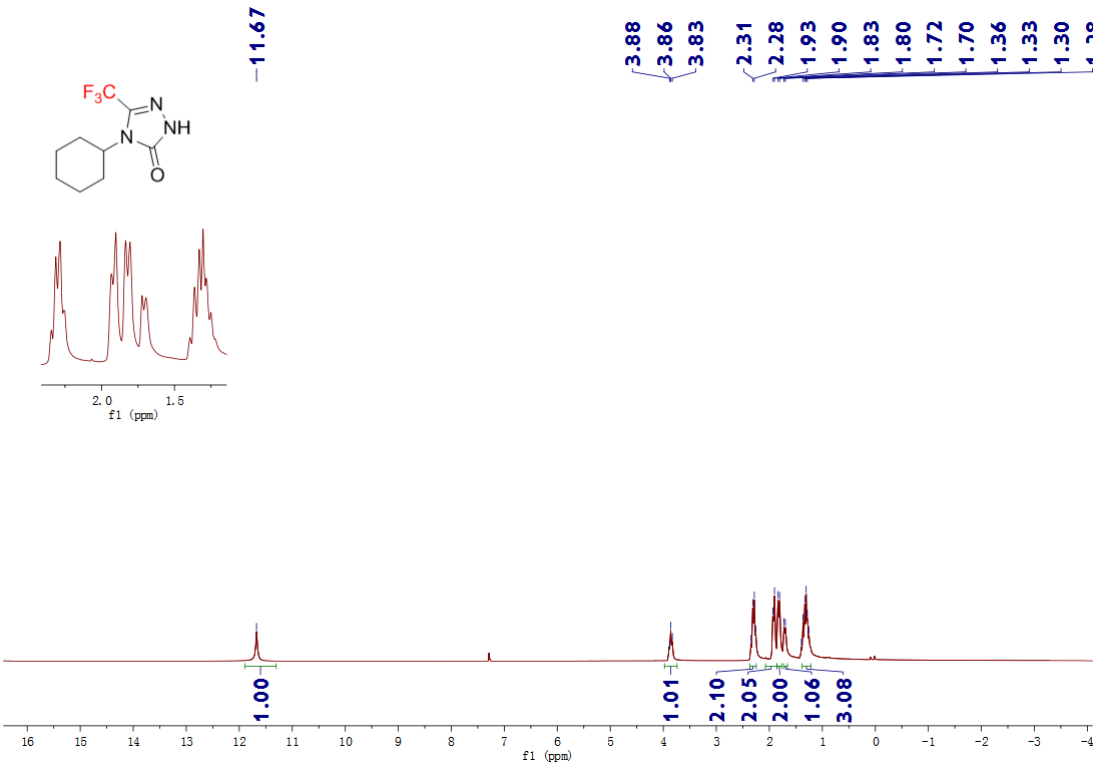
^{13}C-NMR spectrum of **3s** in $CDCl_3$



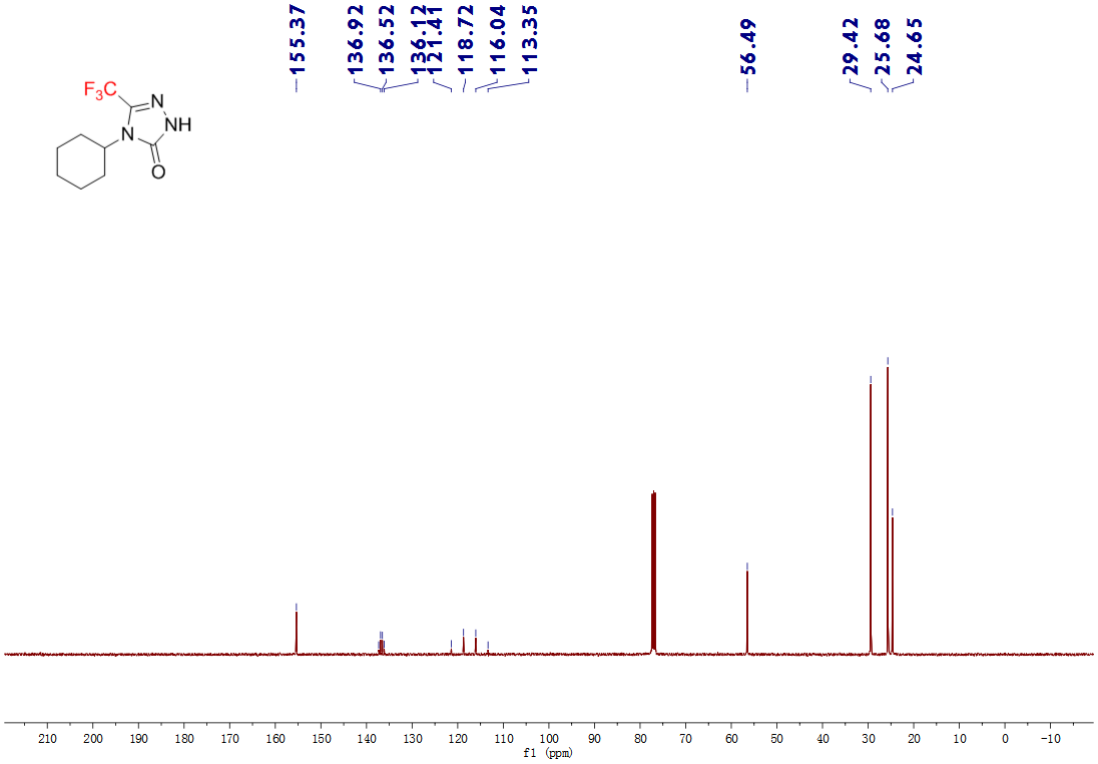
^{19}F-NMR spectrum of **3s** in $CDCl_3$



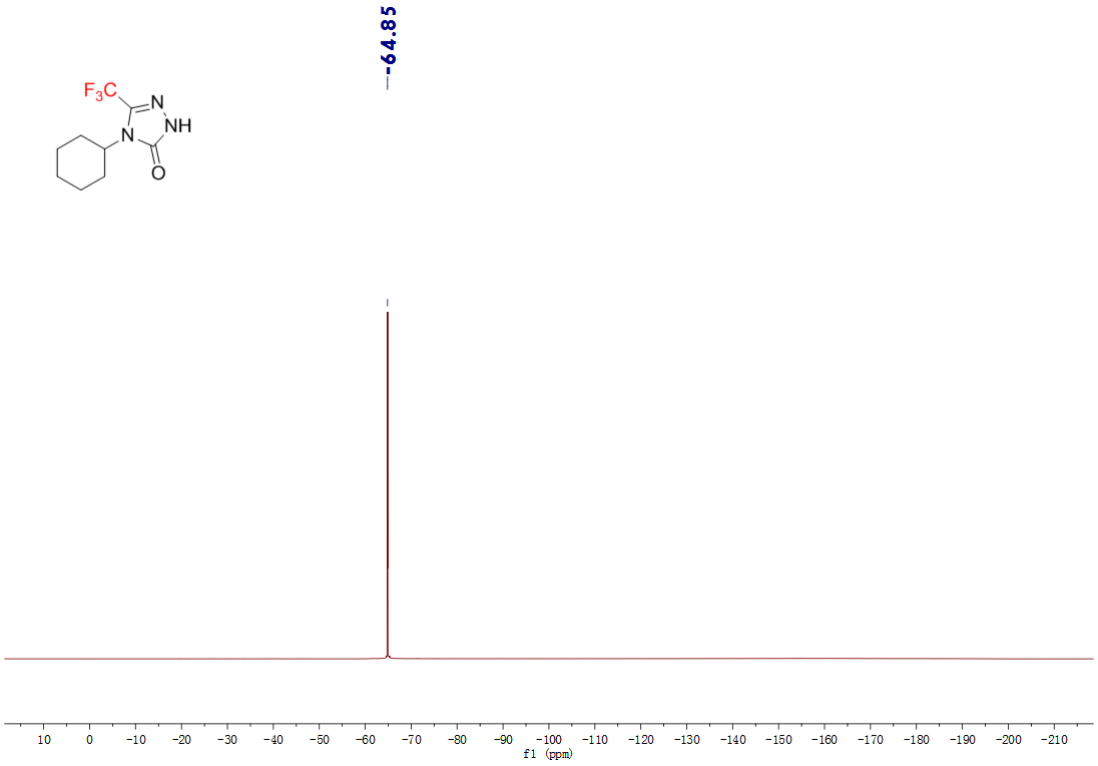
^{1}H-NMR spectrum of **3t** in $CDCl_3$



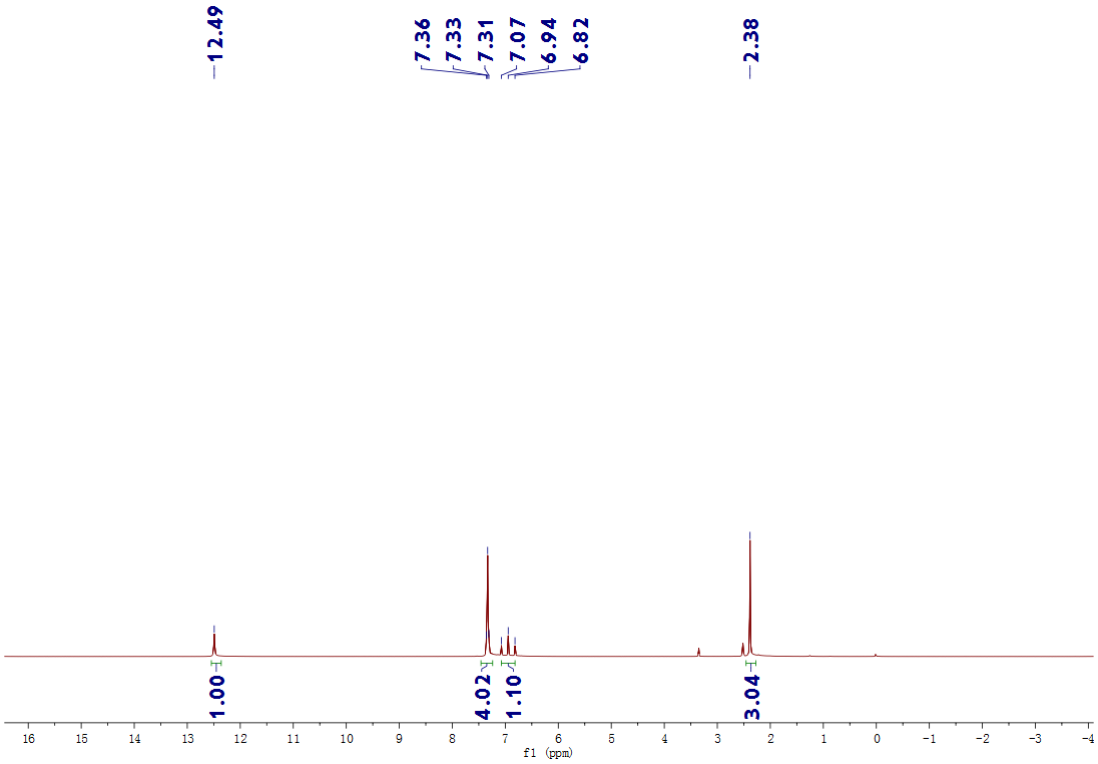
^{13}C-NMR spectrum of **3t** in $CDCl_3$



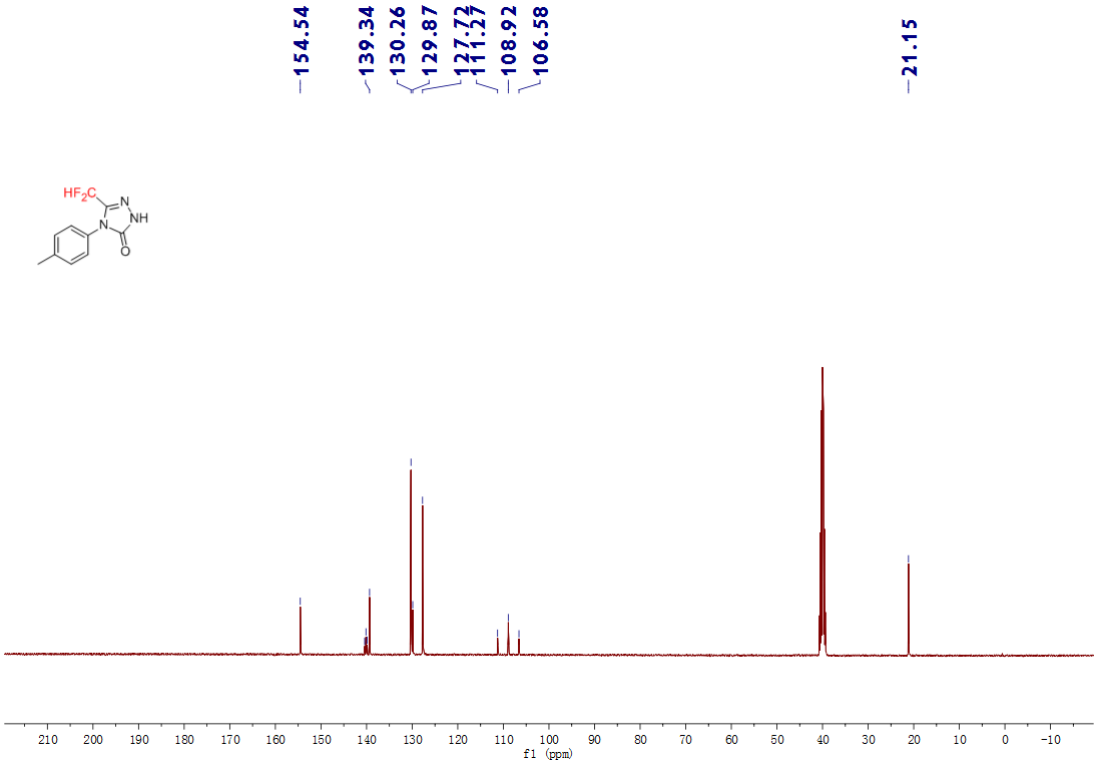
^{19}F-NMR spectrum of **3t** in CDCl



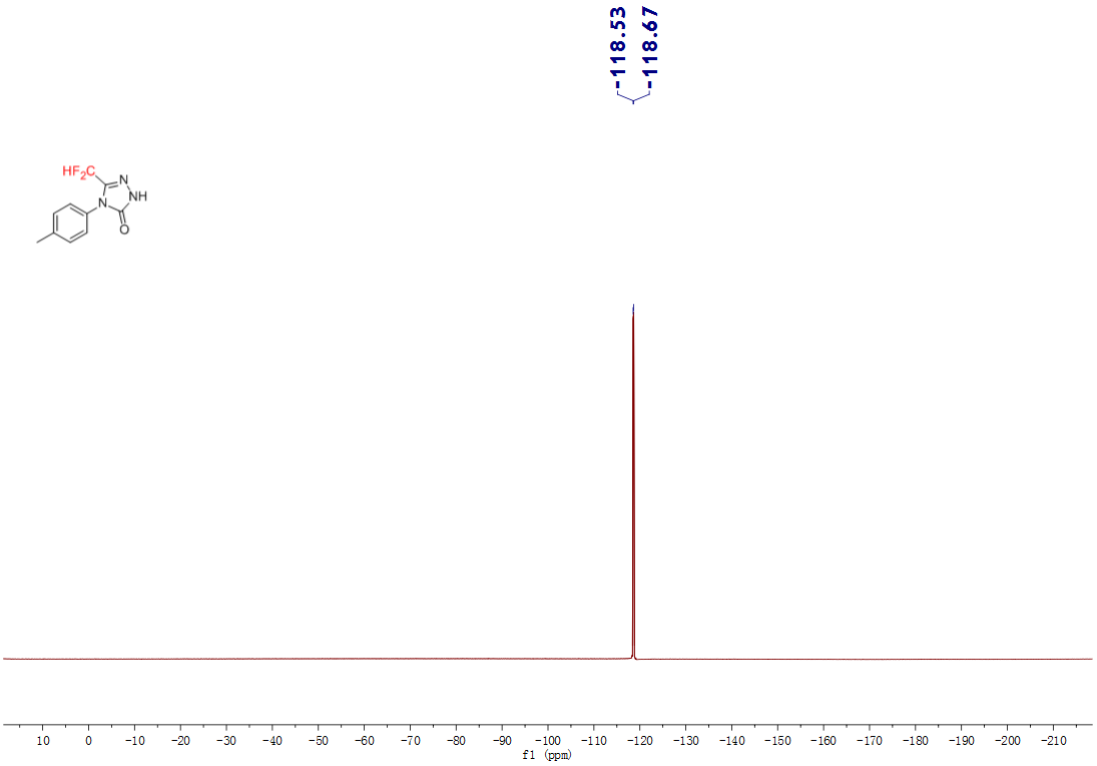
^{1}H-NMR spectrum of **4a** in DMSO-d_6



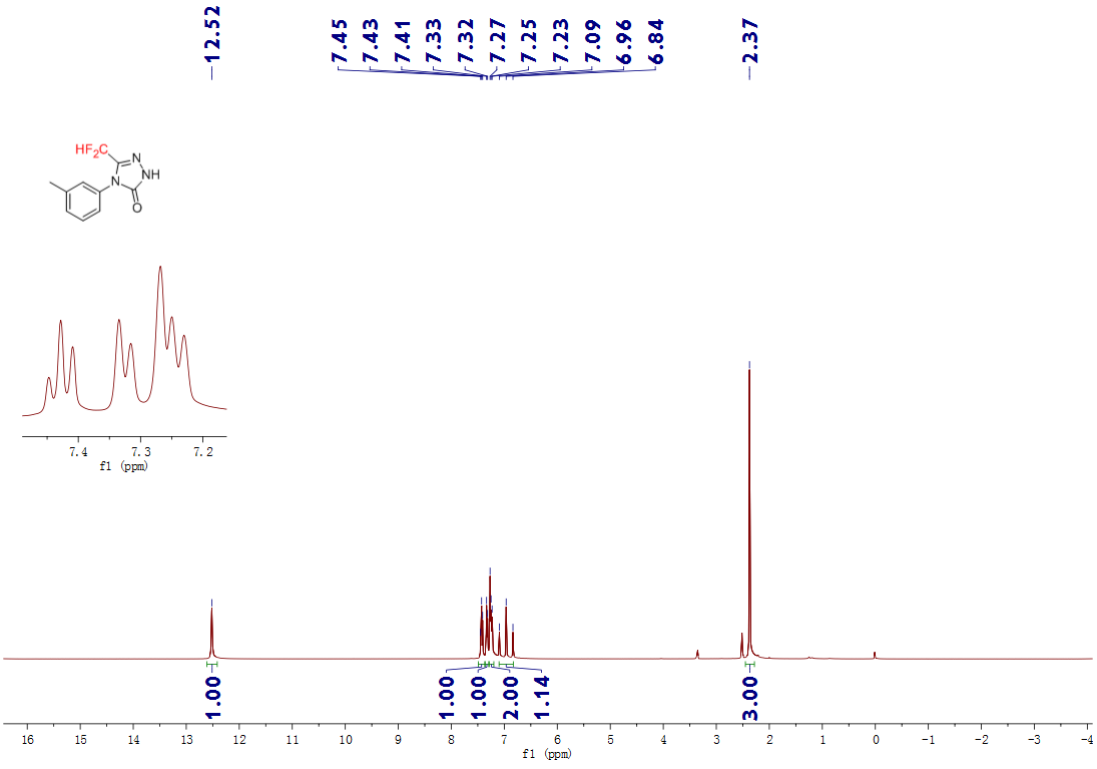
^{13}C-NMR spectrum of **4a** in DMSO-d_6



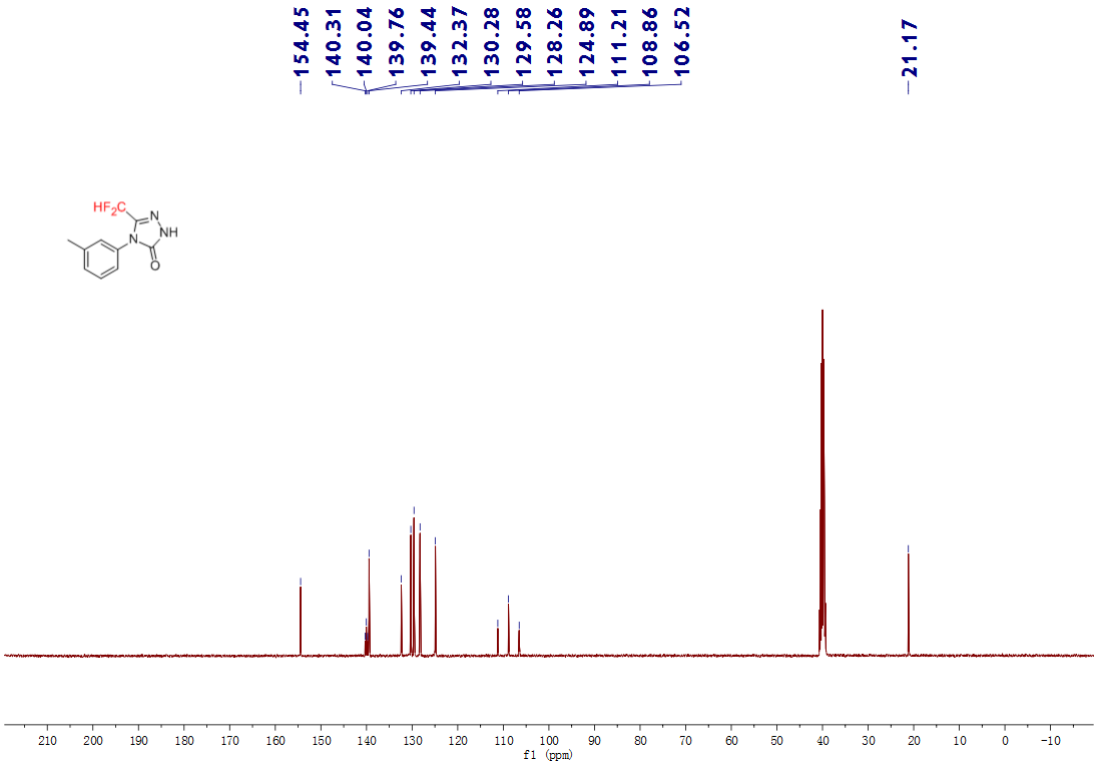
^{19}F-NMR spectrum of **4a** in DMSO-d_6



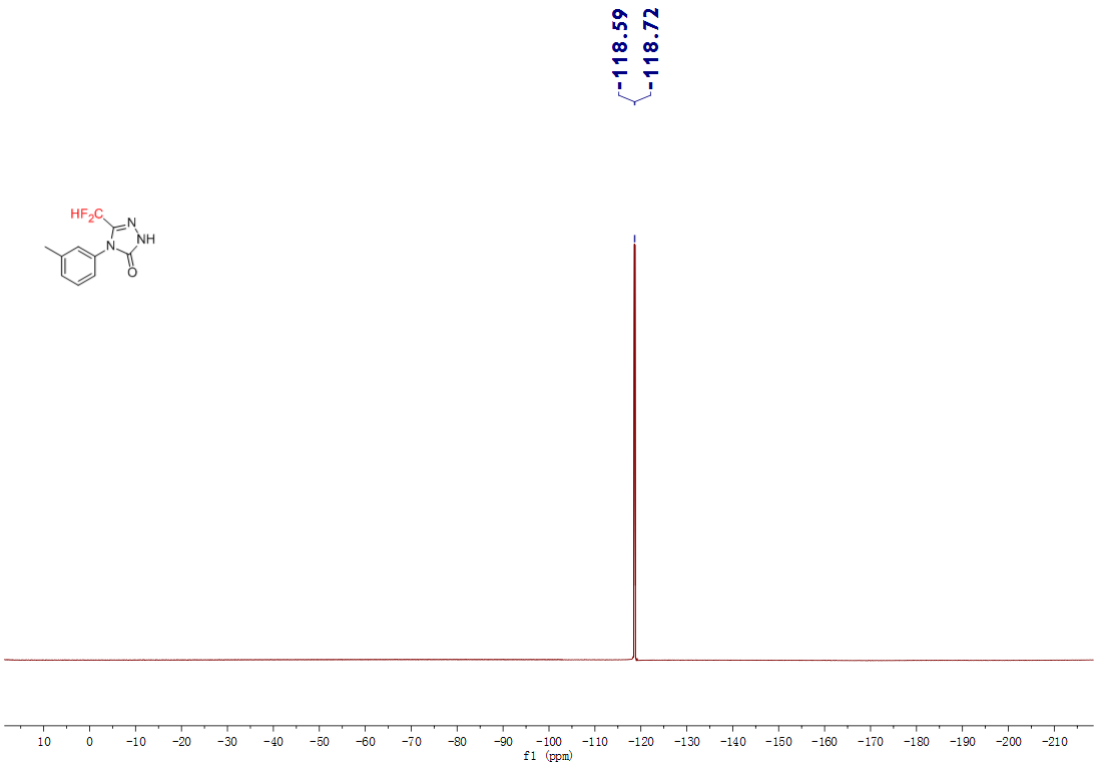
^{1}H-NMR spectrum of **4b** in DMSO-d_6



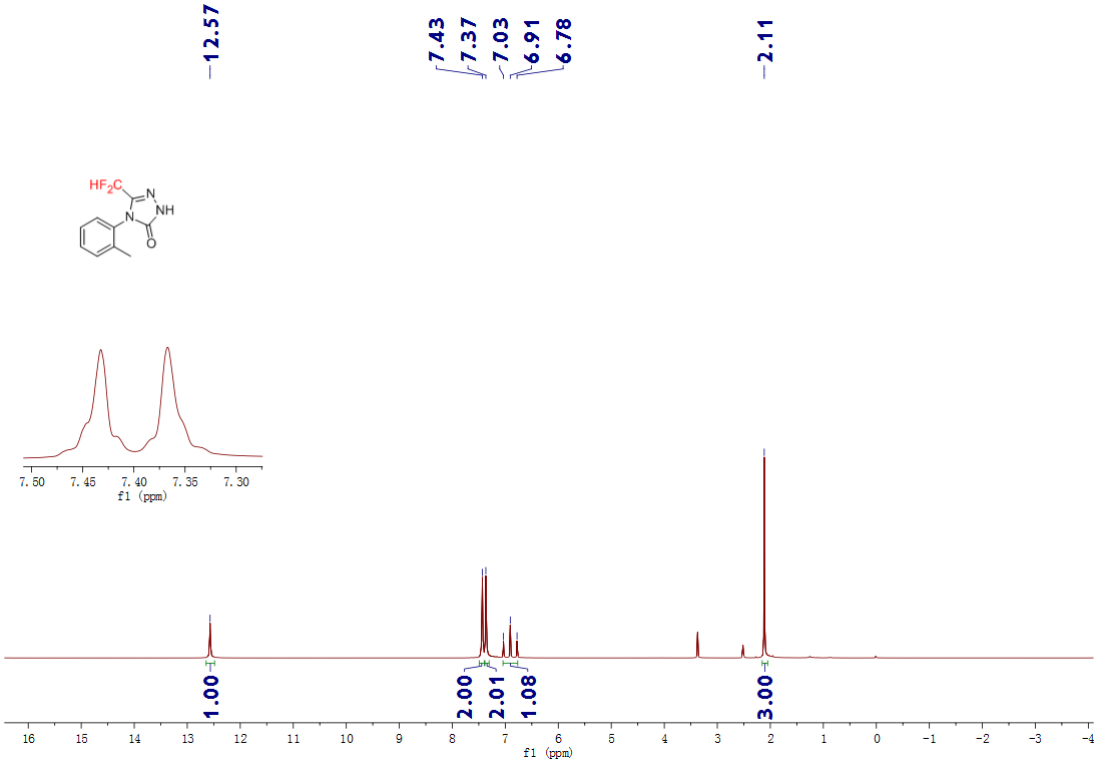
^{13}C-NMR spectrum of **4b** in DMSO-d_6



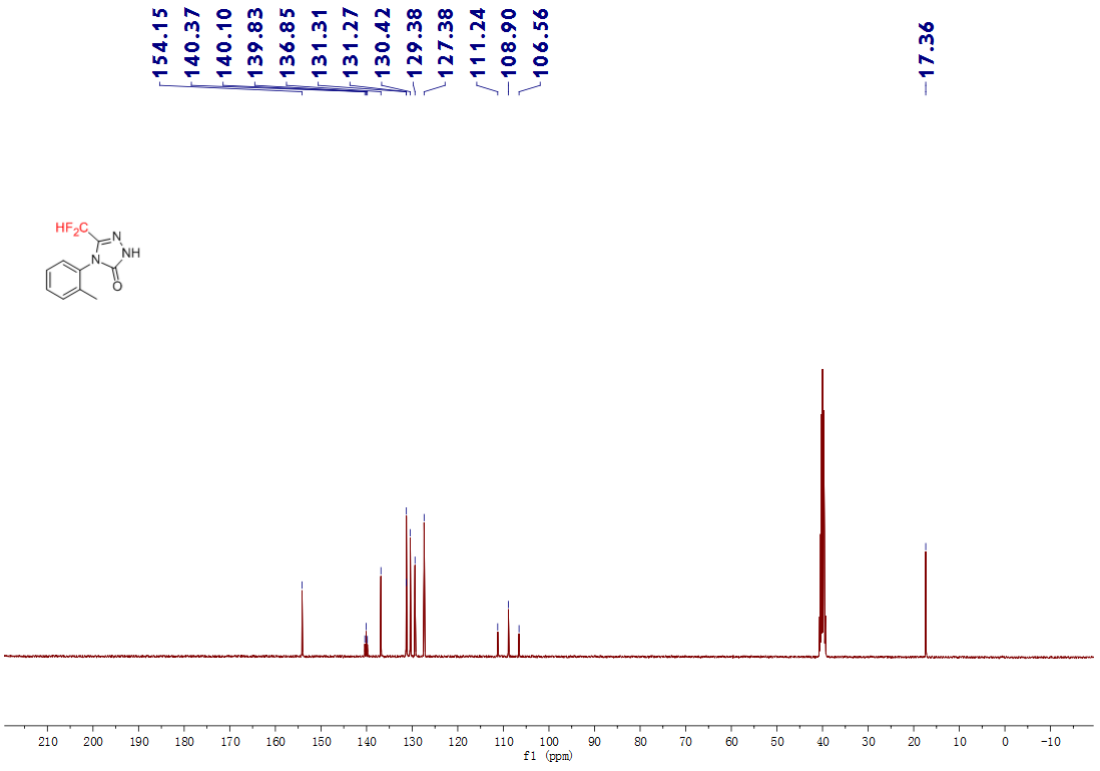
^{19}F-NMR spectrum of **4b** in DMSO-d_6



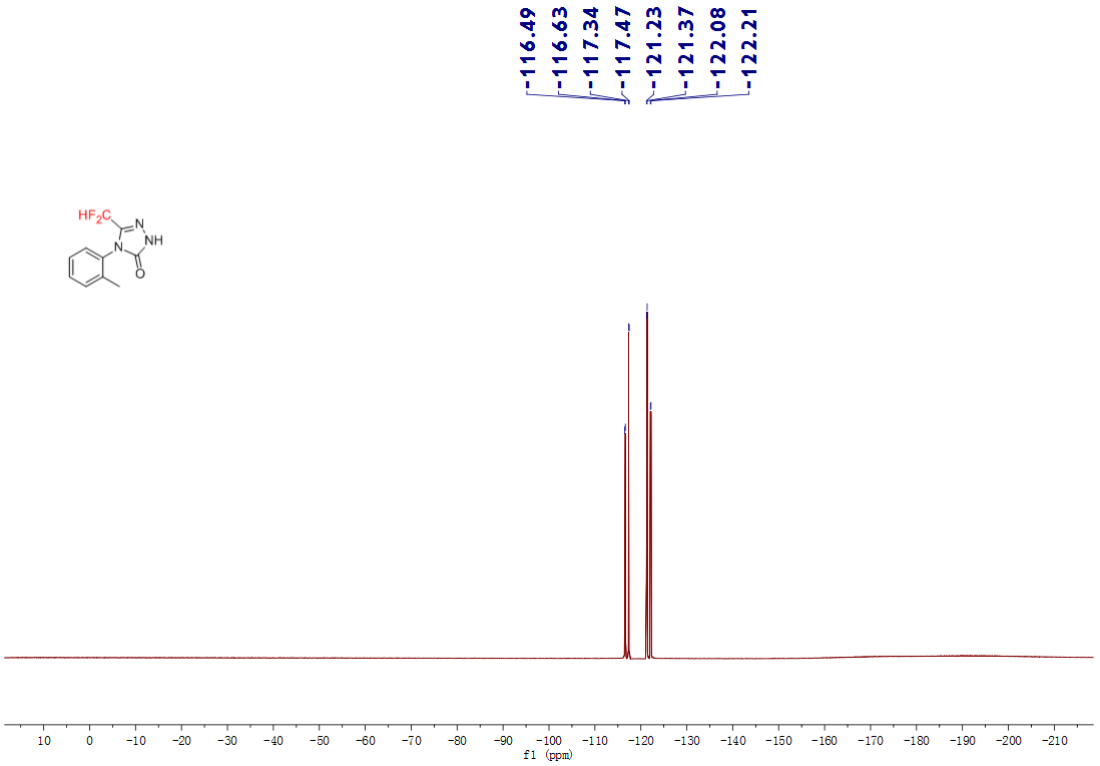
^{1}H-NMR spectrum of **4c** in DMSO-d_6



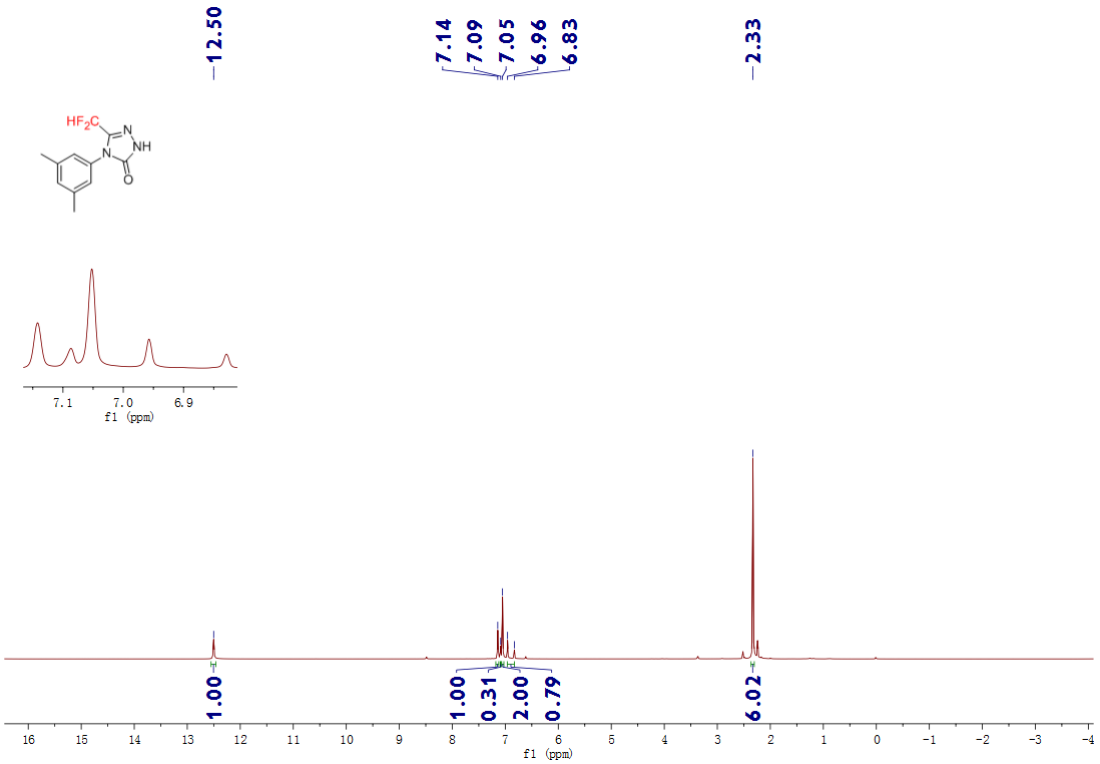
^{13}C-NMR spectrum of **4c** in DMSO-d_6



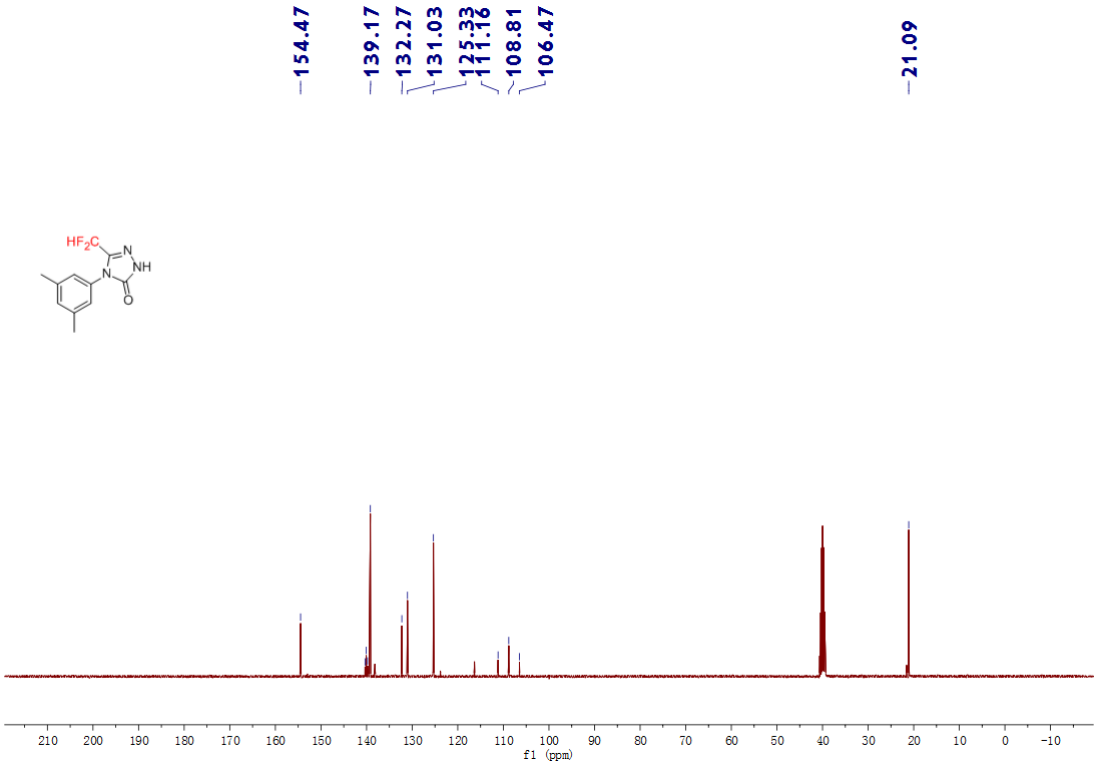
^{19}F-NMR spectrum of **4c** in DMSO-d_6



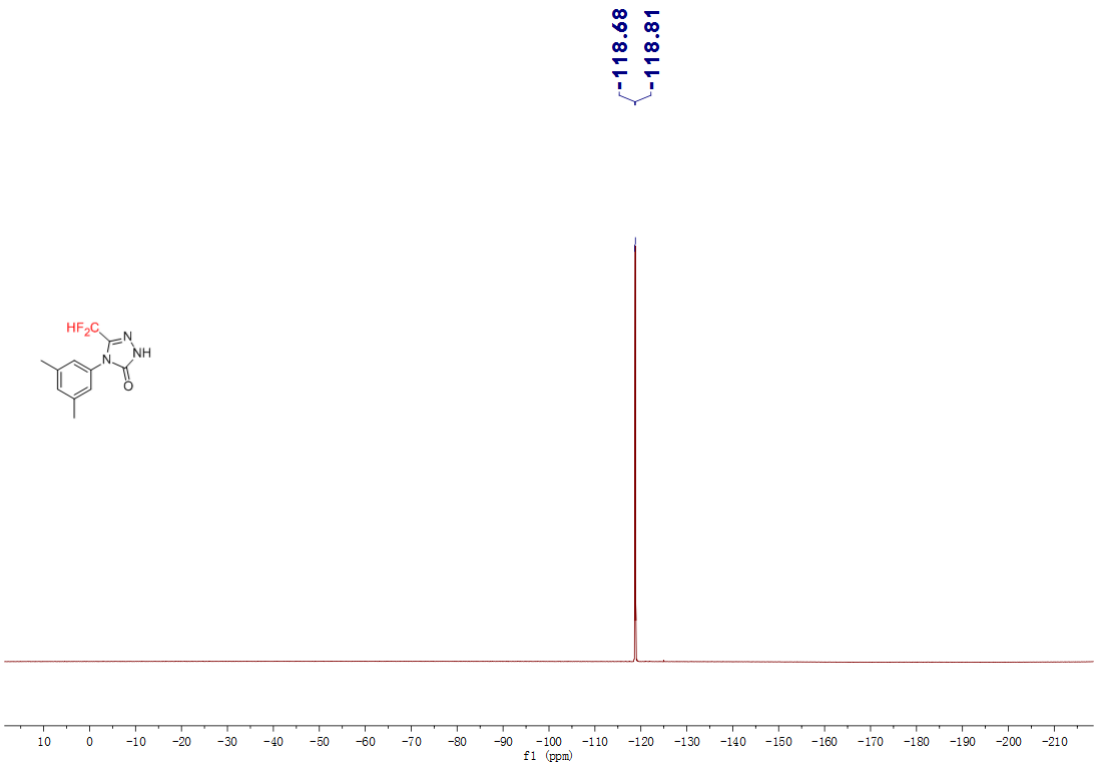
^{1}H-NMR spectrum of **4d** in DMSO-d_6



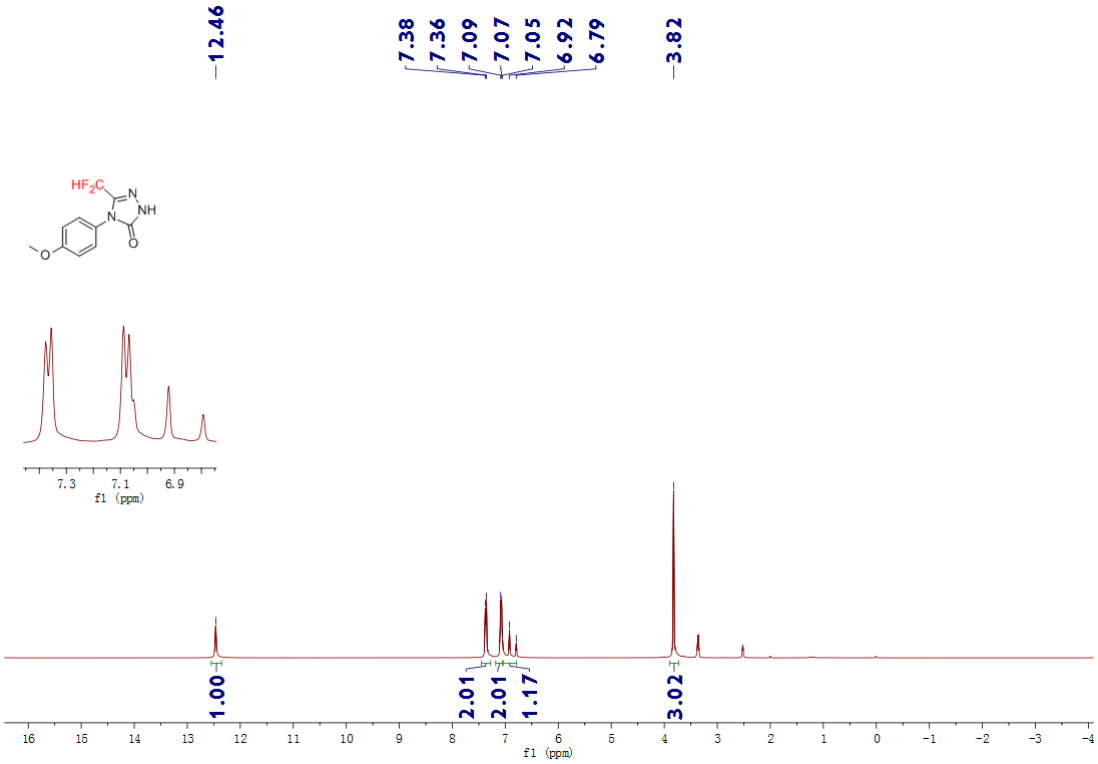
^{13}C-NMR spectrum of **4d** in DMSO-d_6



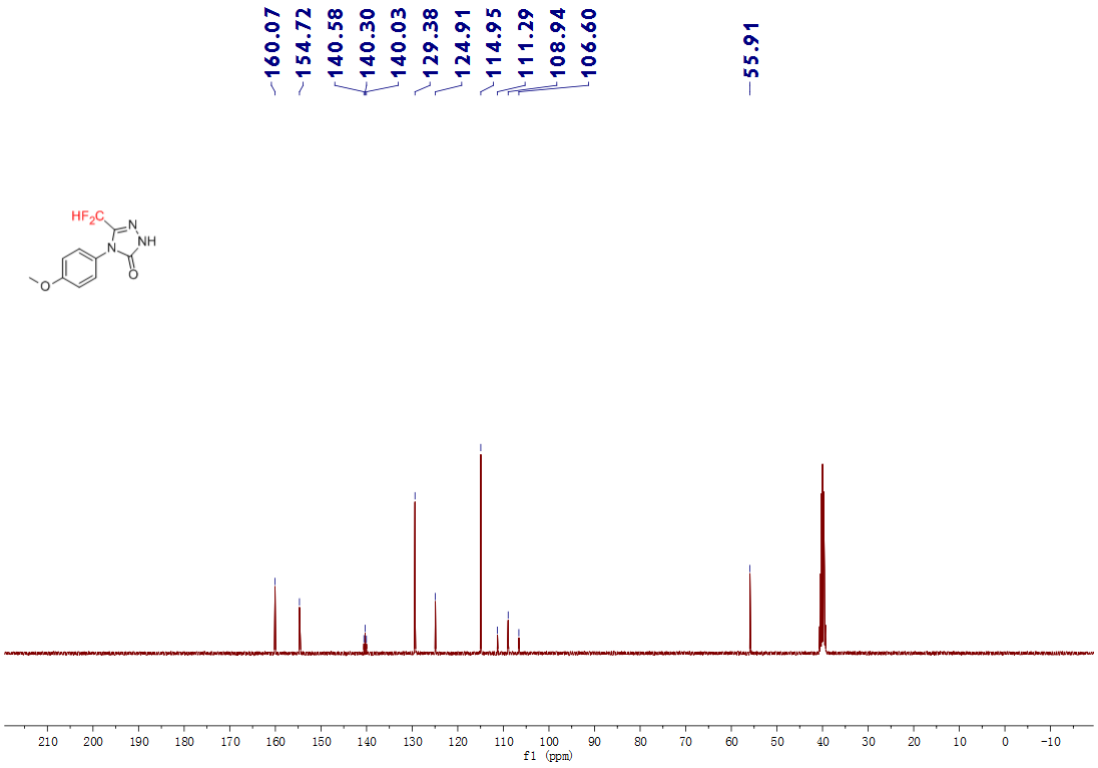
^{19}F-NMR spectrum of **4d** in DMSO-d_6



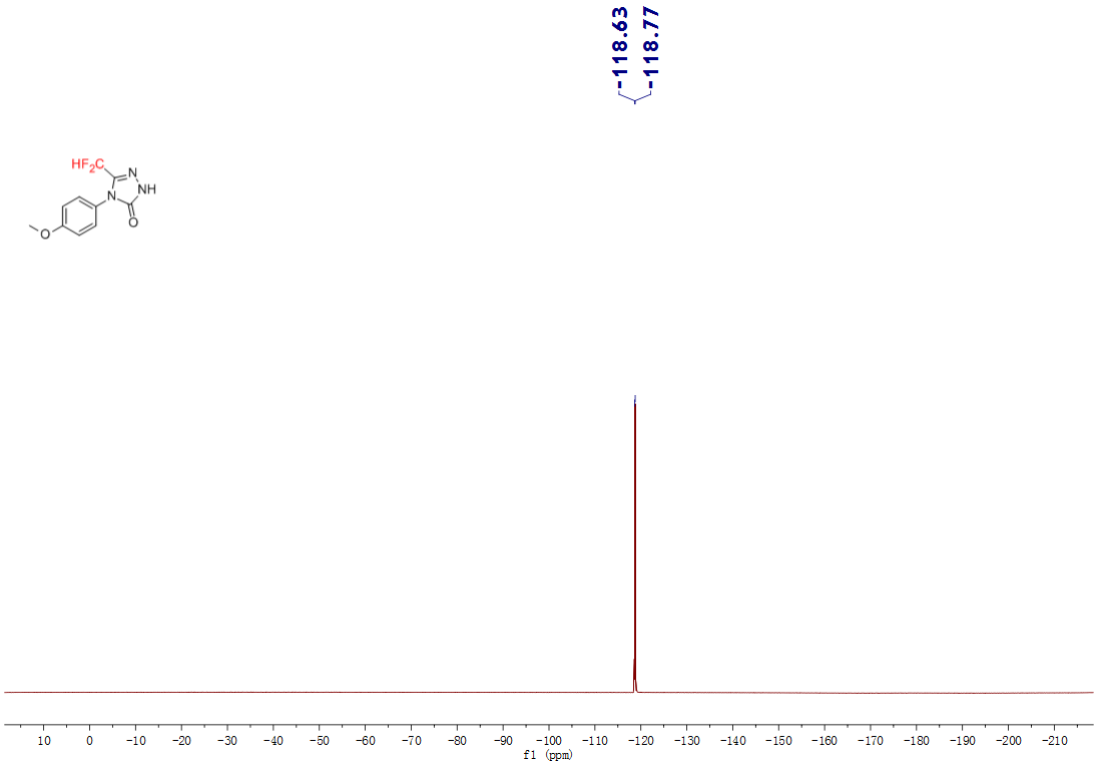
^{1}H-NMR spectrum of **4e** in DMSO-d_6



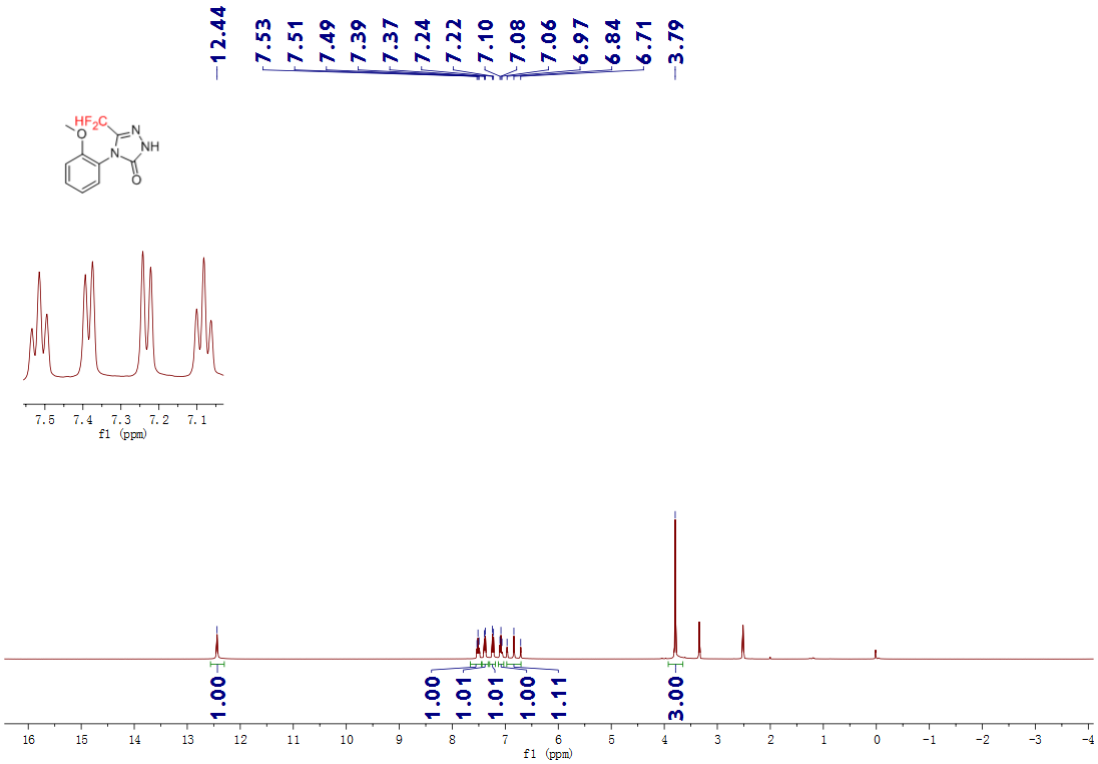
^{13}C-NMR spectrum of **4e** in DMSO-d_6



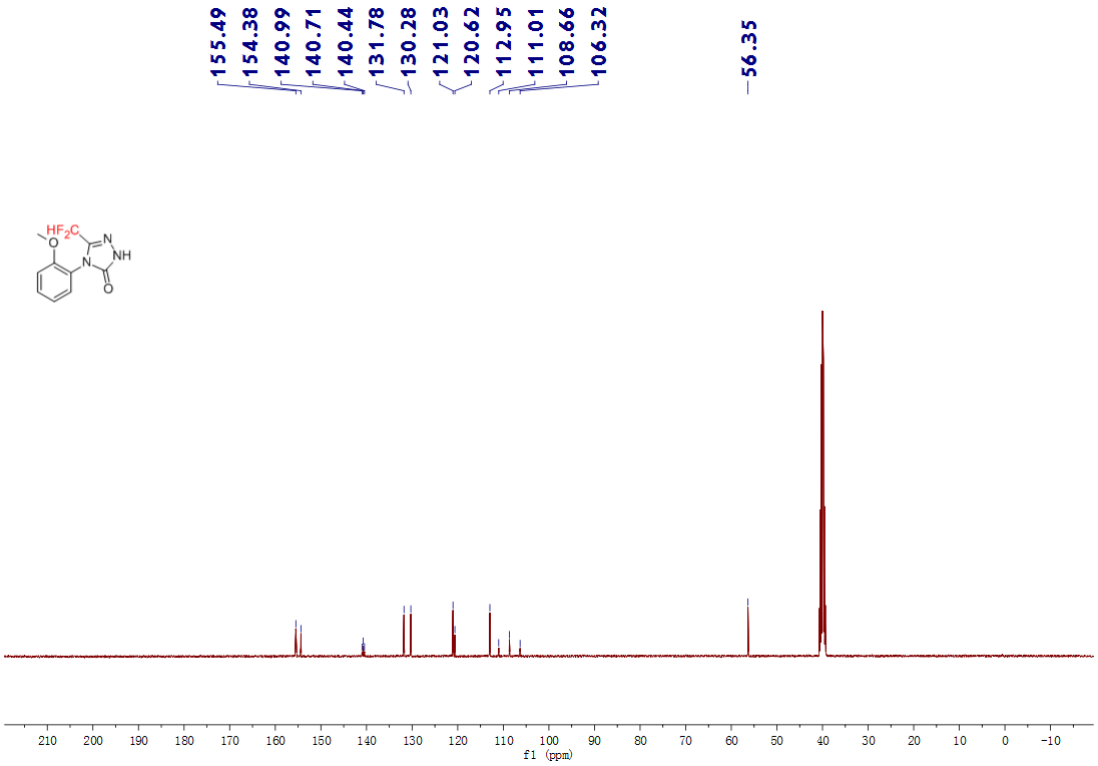
^{19}F-NMR spectrum of **4e** in DMSO-d_6



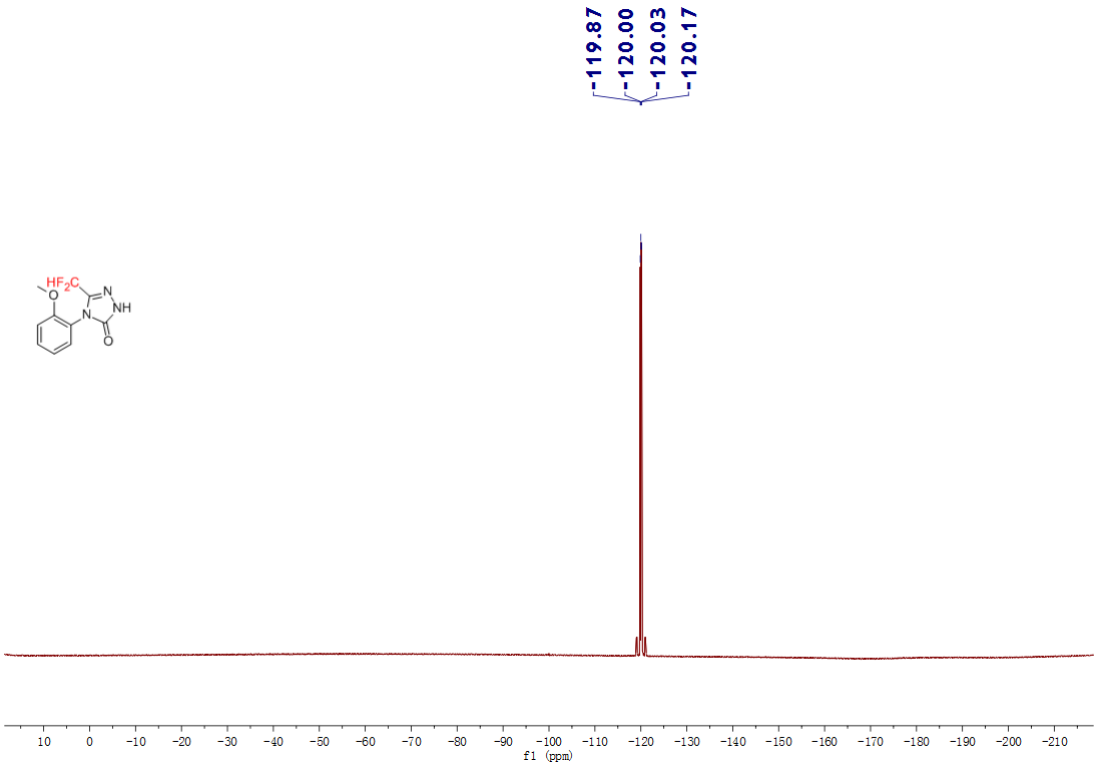
^{1}H-NMR spectrum of **4f** in DMSO-d_6



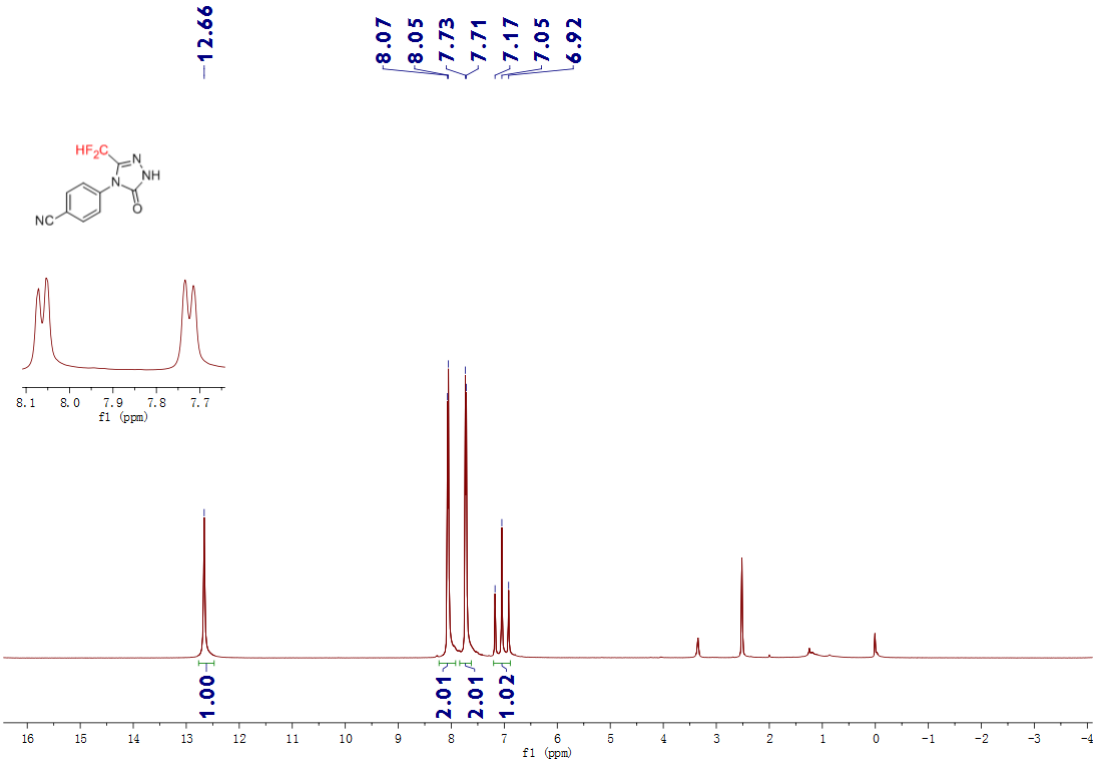
^{13}C-NMR spectrum of **4f** in DMSO-d_6



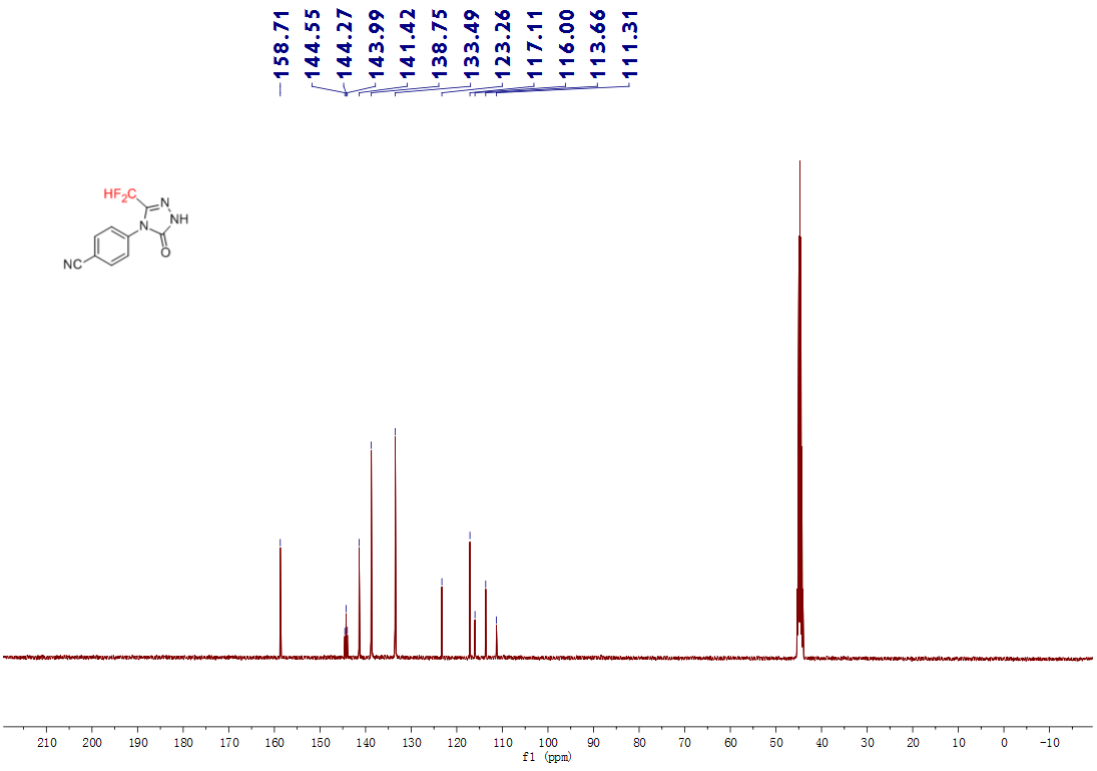
^{19}F-NMR spectrum of **4f** in DMSO-d_6



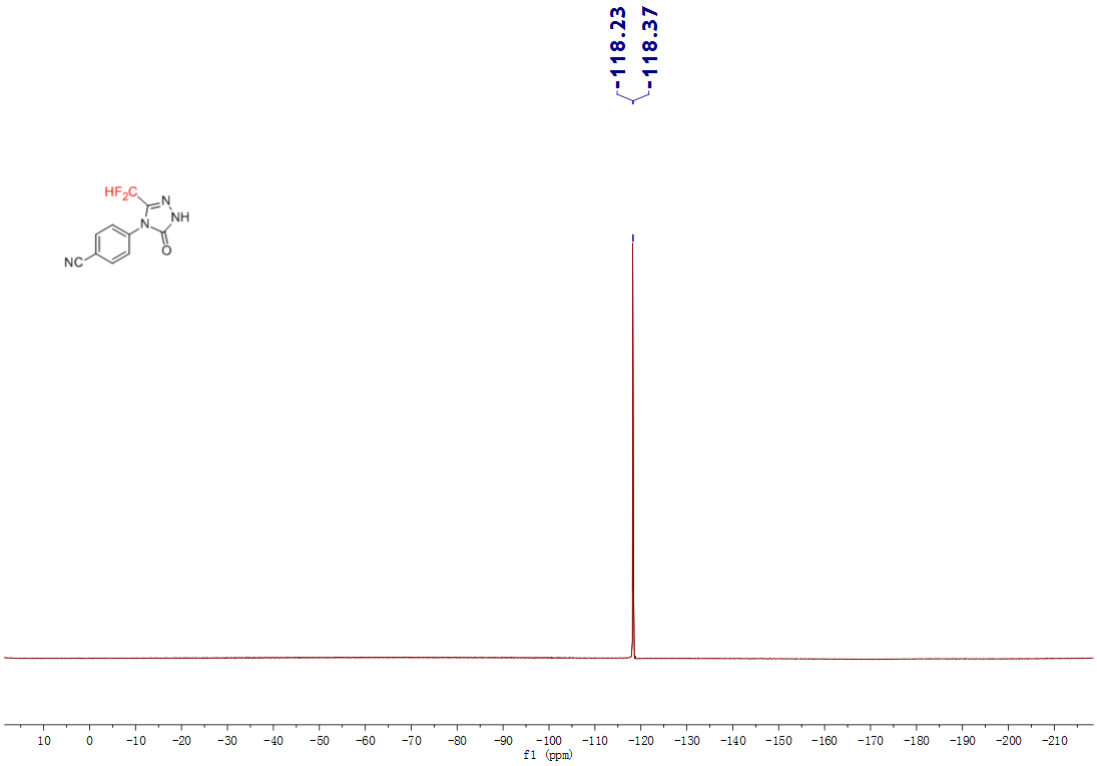
^{1}H-NMR spectrum of **4g** in DMSO-d_6



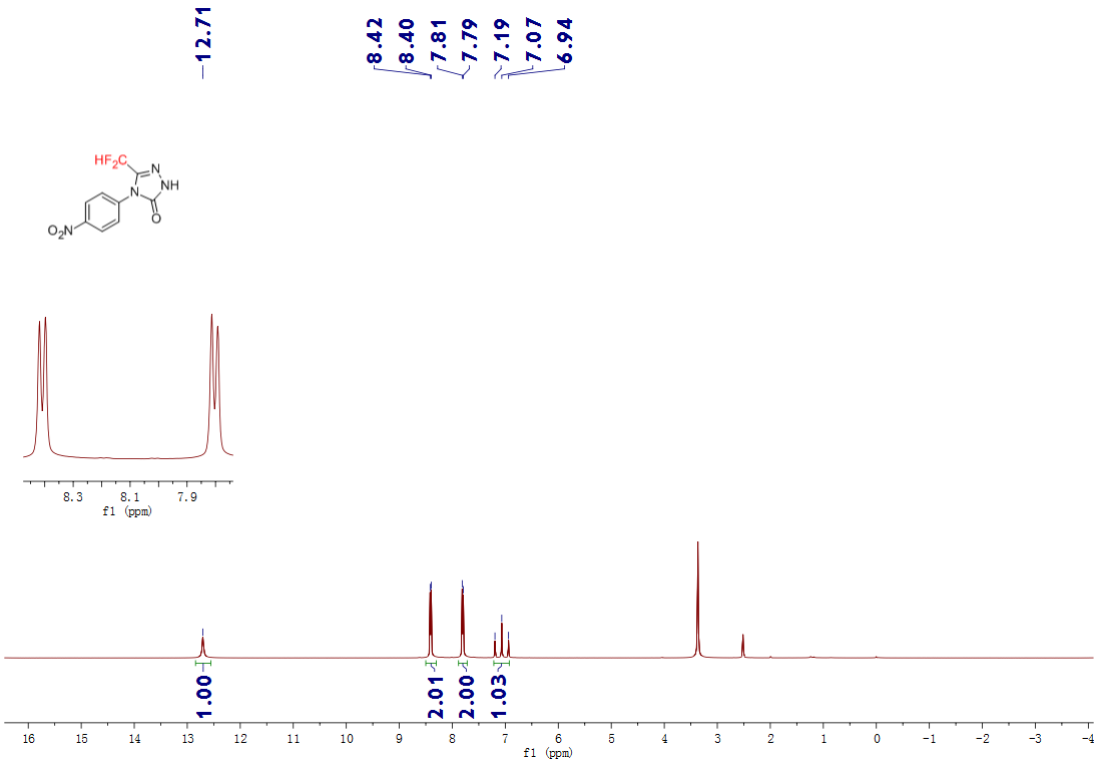
^{13}C-NMR spectrum of **4g** in DMSO-d_6



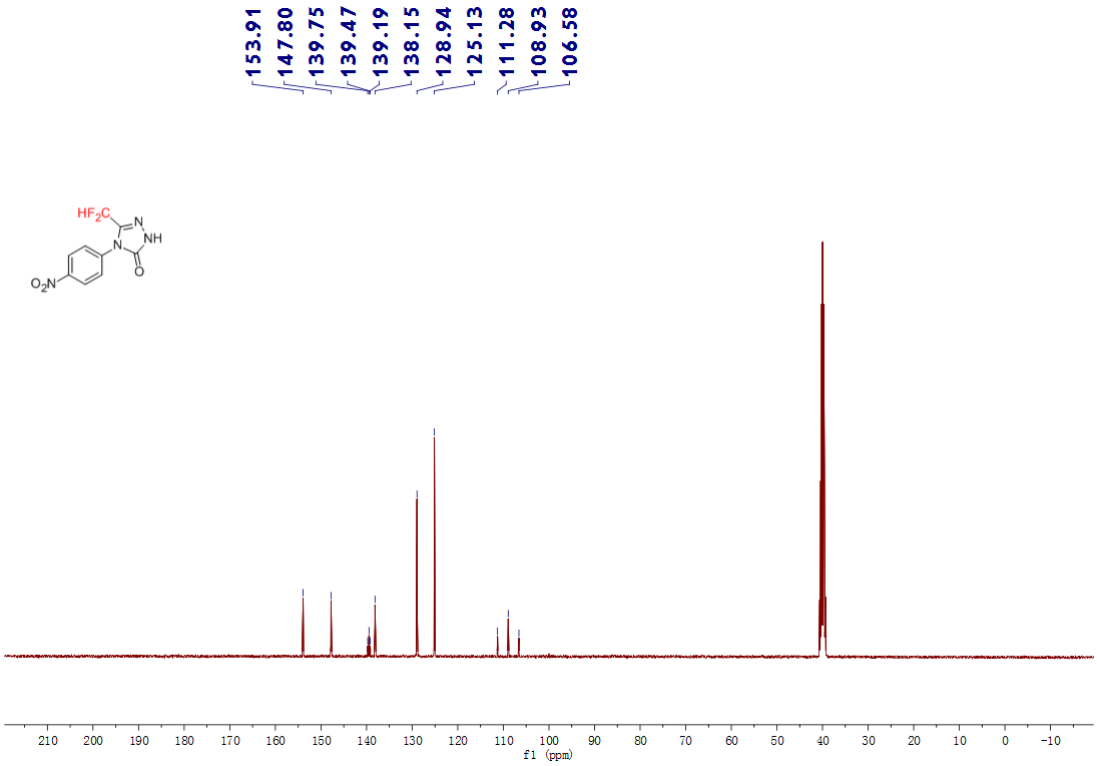
^{19}F-NMR spectrum of **4g** in DMSO-d_6



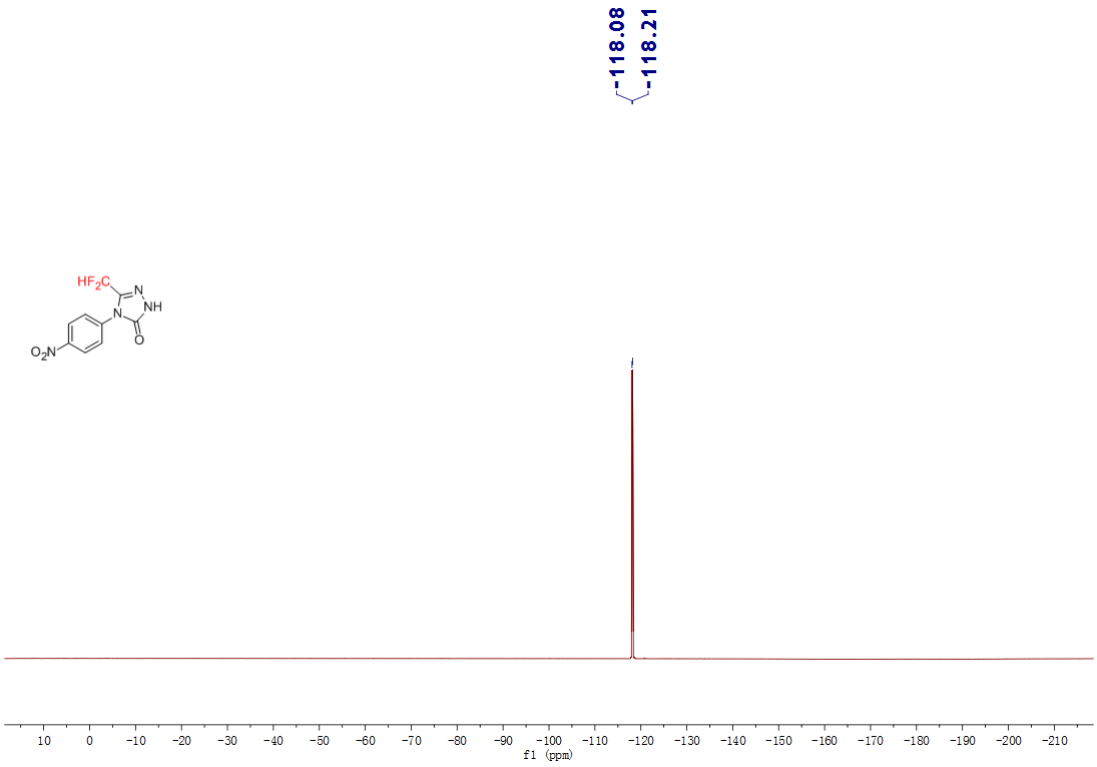
^{1}H-NMR spectrum of **4h** in DMSO-d_6



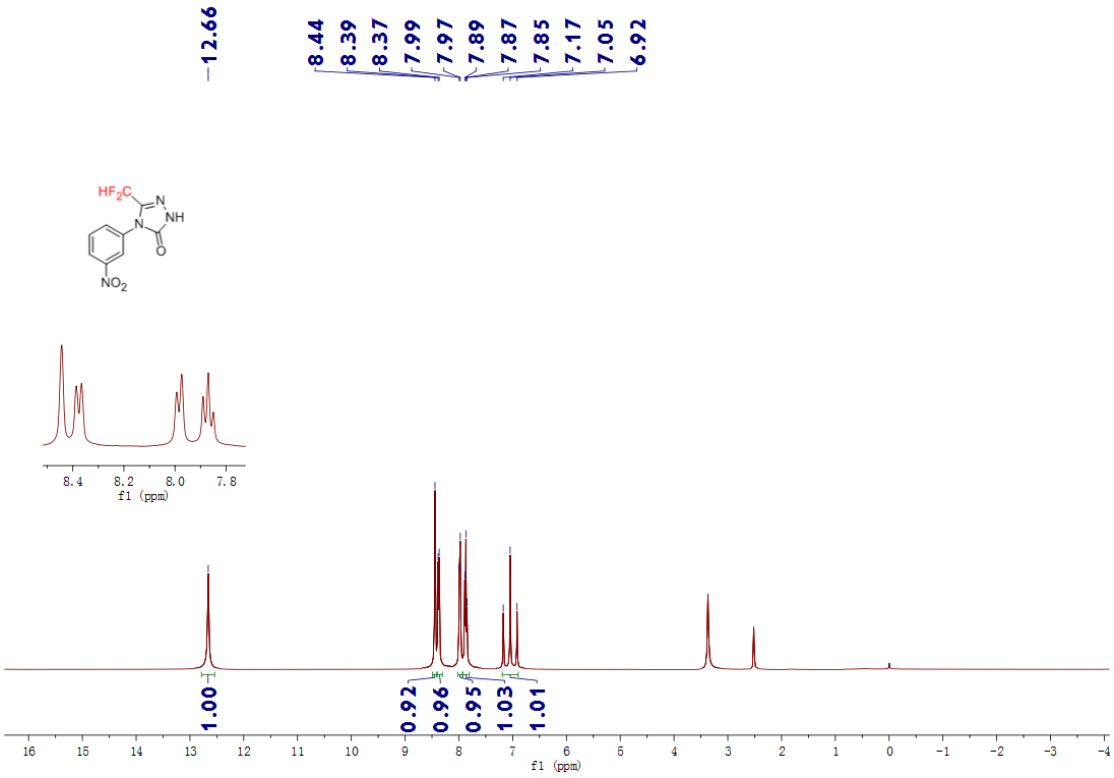
^{13}C-NMR spectrum of **4h** in DMSO-d_6



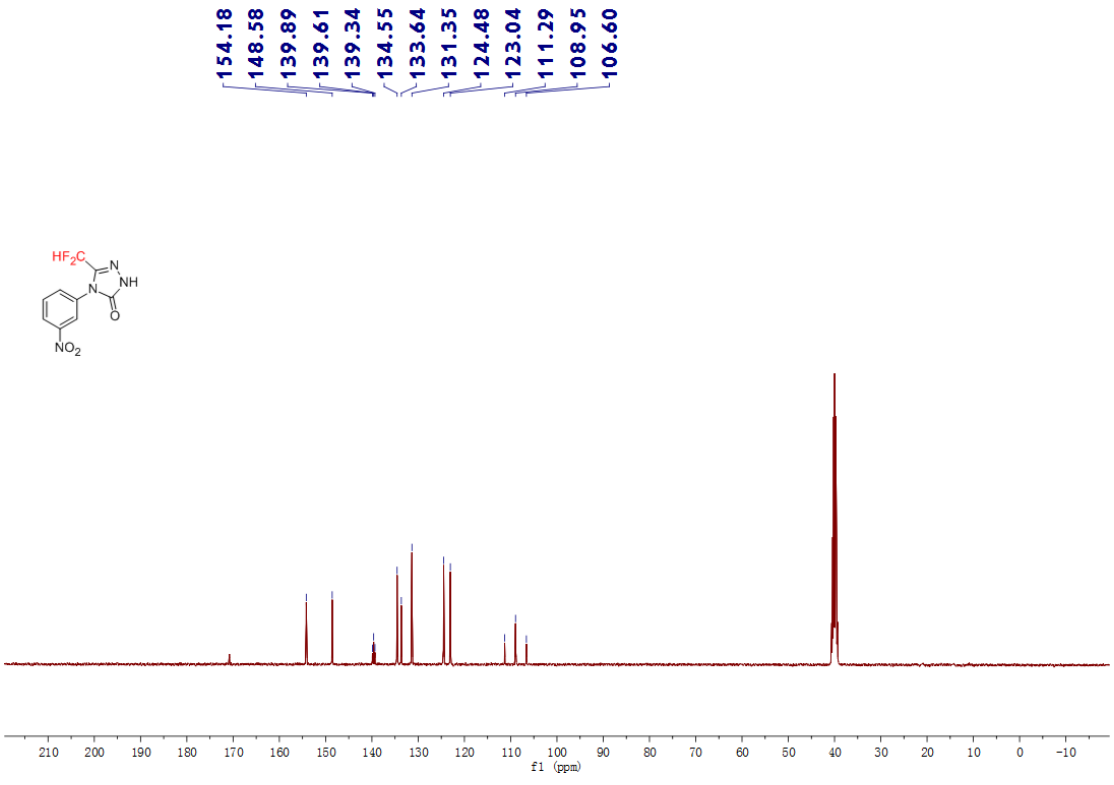
^{19}F-NMR spectrum of **4h** in DMSO-d_6



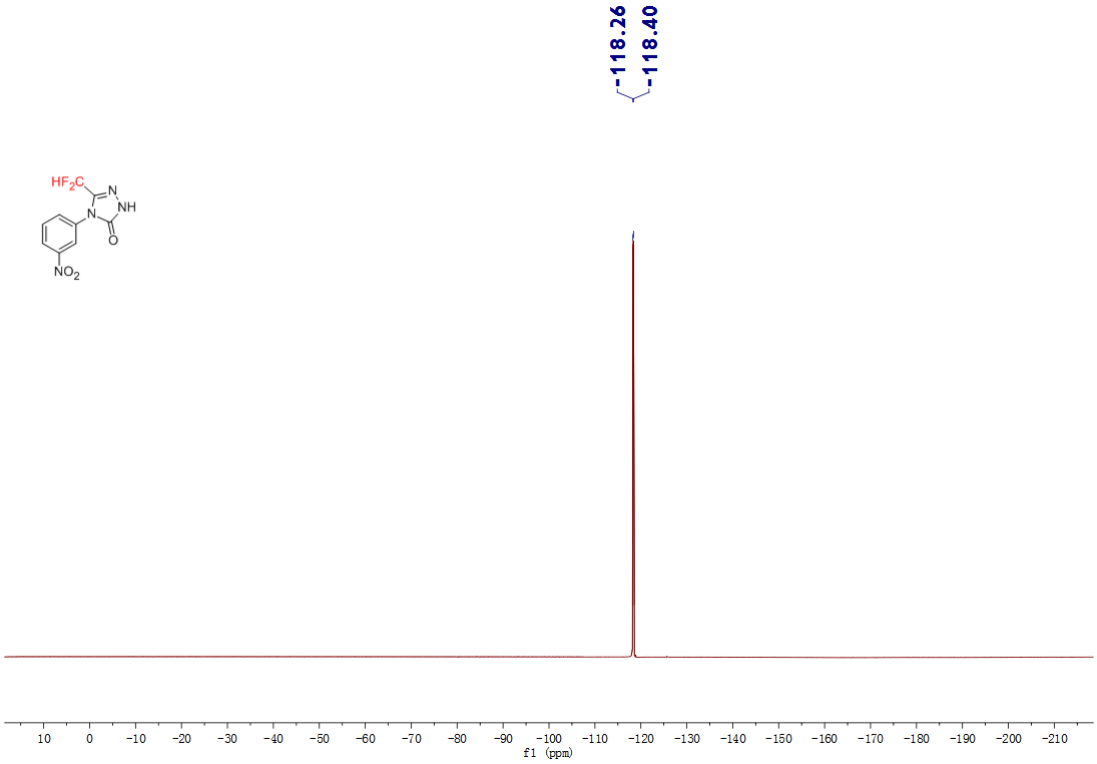
^{1}H-NMR spectrum of **4i** in DMSO-d_6



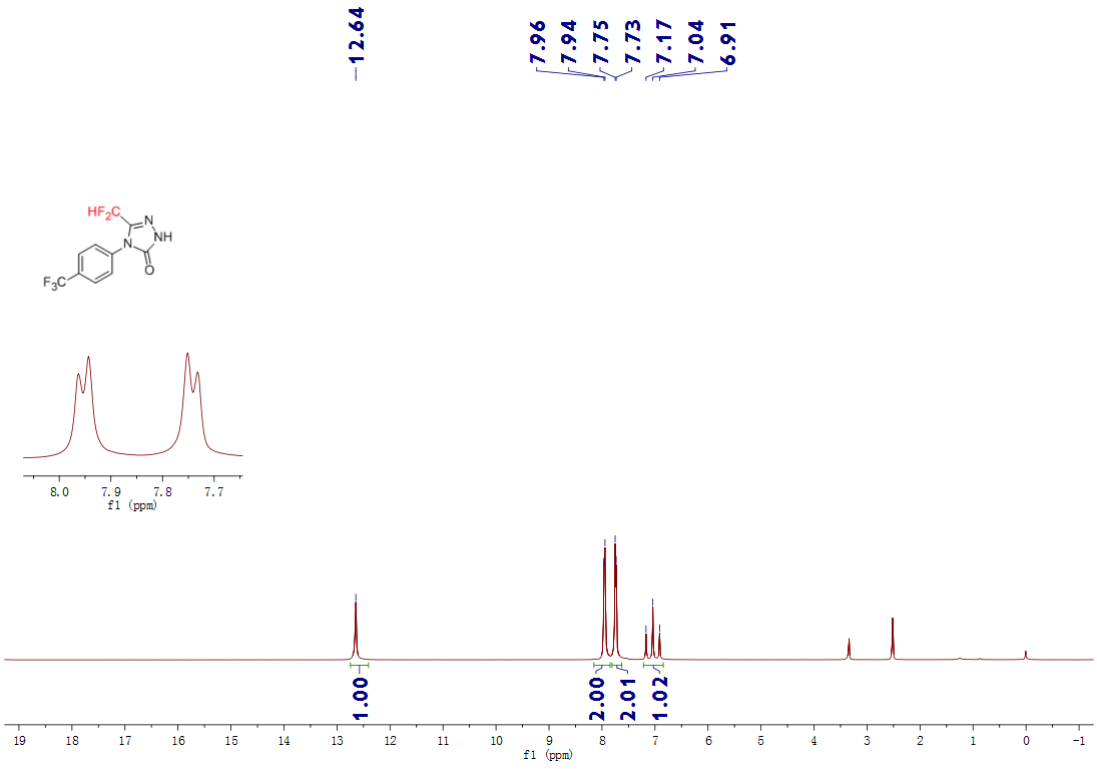
^{13}C-NMR spectrum of **4i** in DMSO-d_6



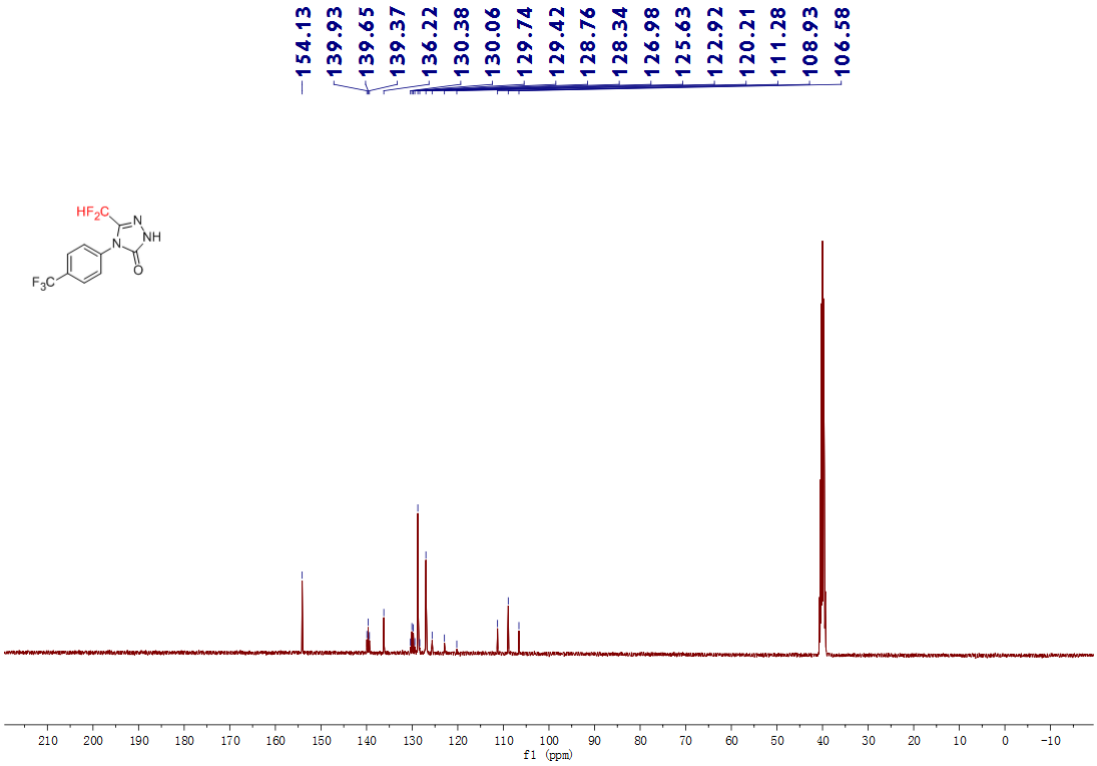
^{19}F-NMR spectrum of **4i** in DMSO-d_6



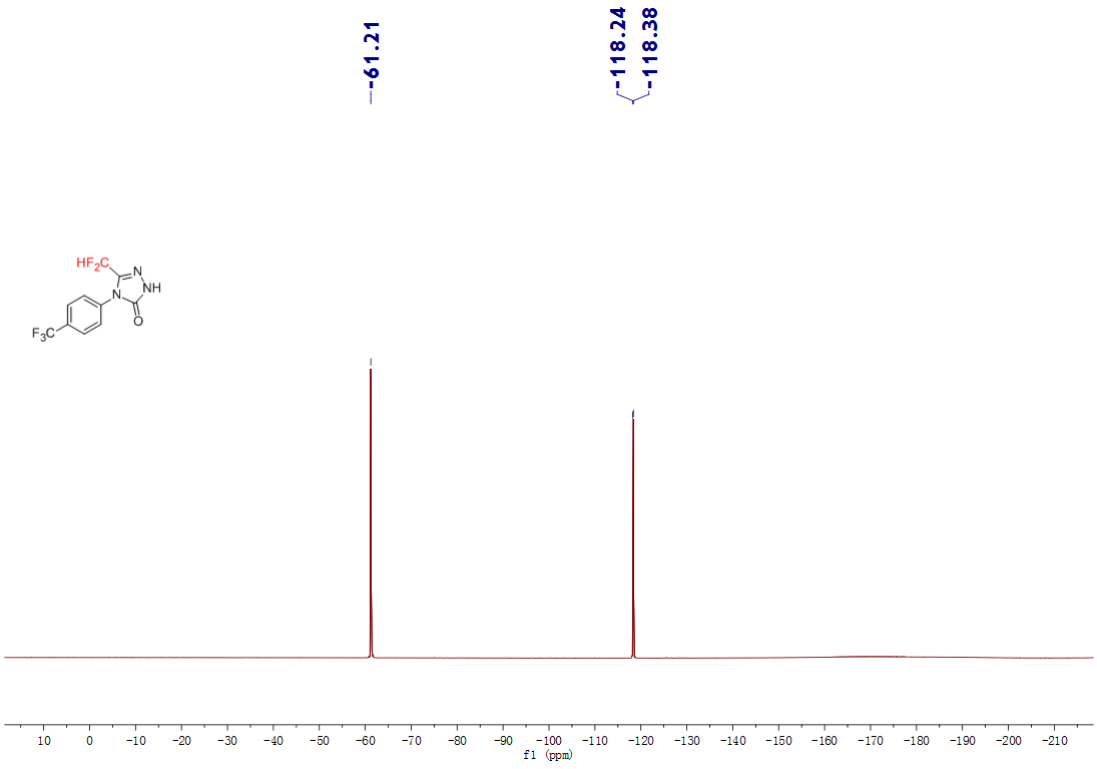
^{1}H-NMR spectrum of **4j** in DMSO-d_6



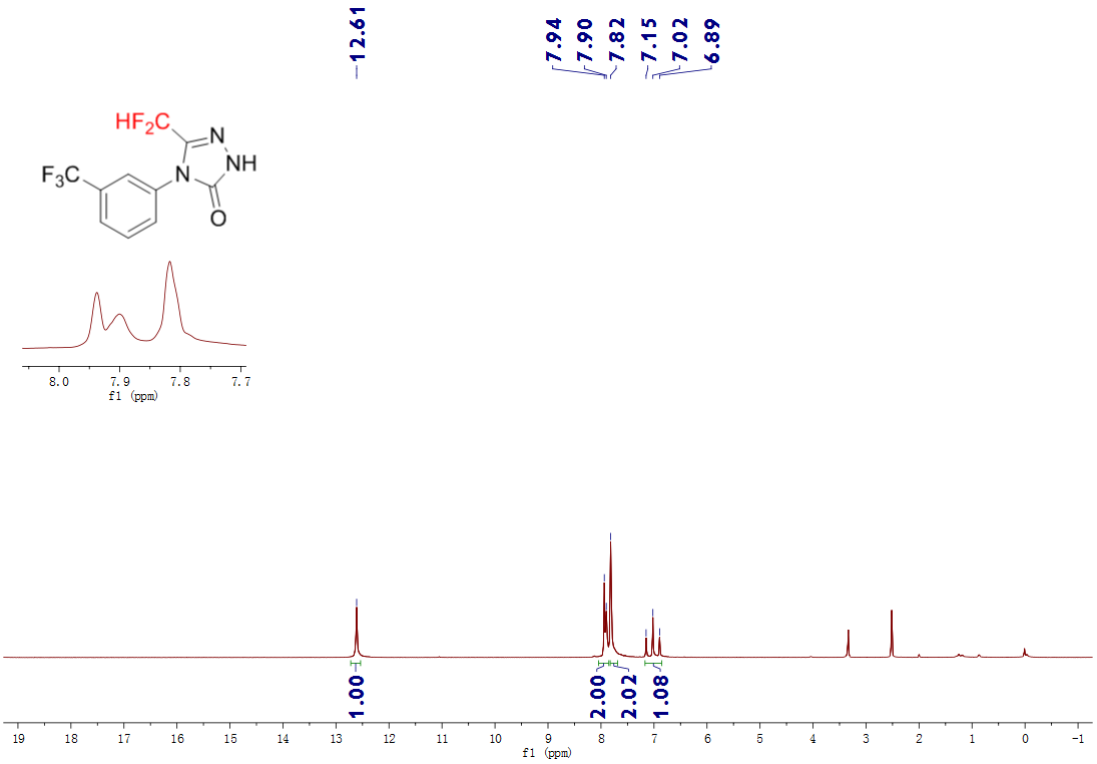
^{13}C-NMR spectrum of **4j** in DMSO-d_6



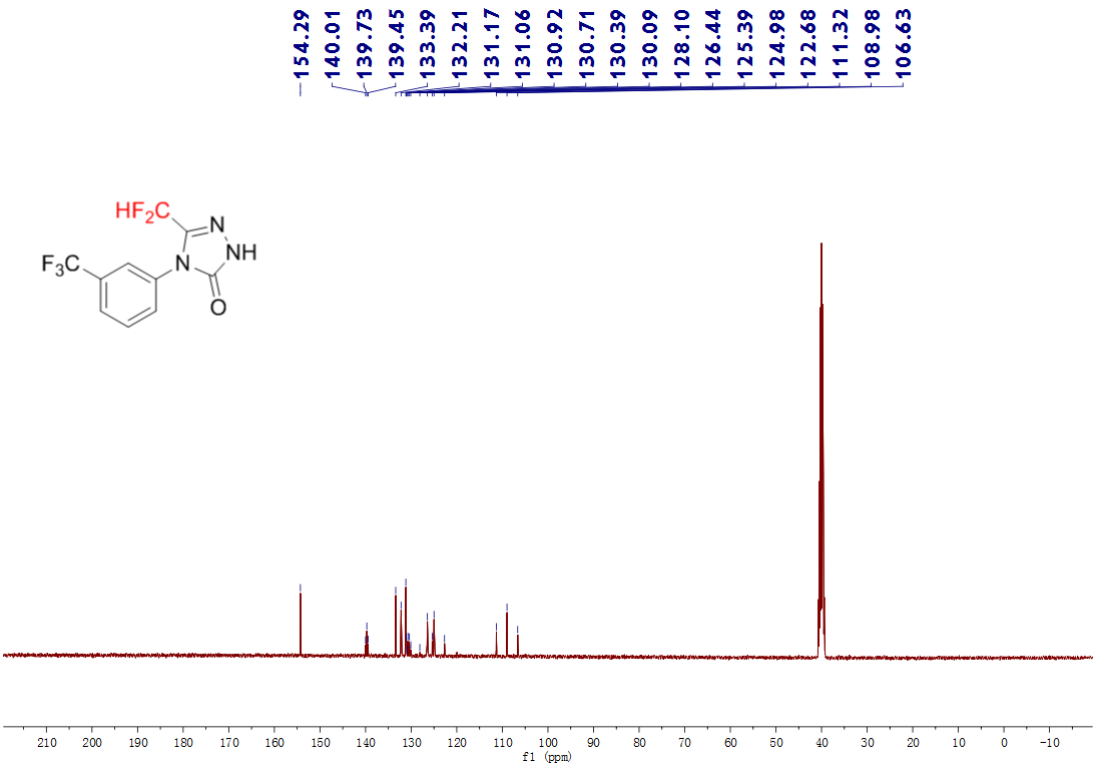
^{19}F-NMR spectrum of **4j** in DMSO-d_6



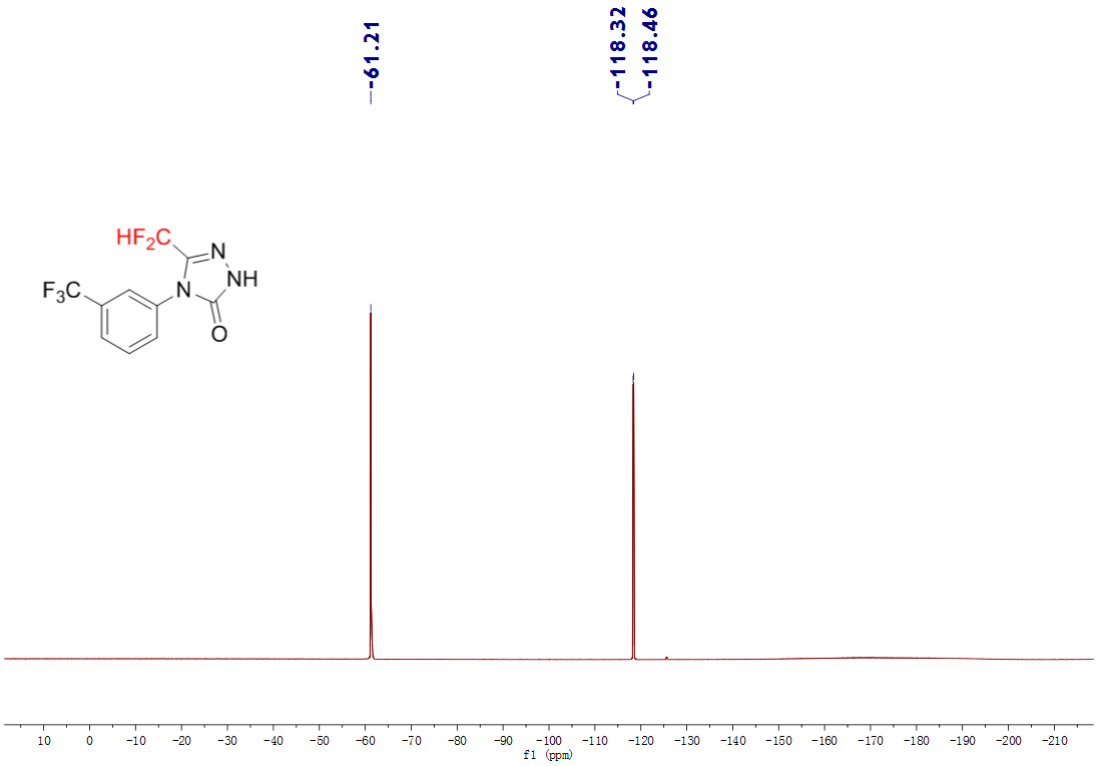
^{1}H-NMR spectrum of **4k** in DMSO-d_6



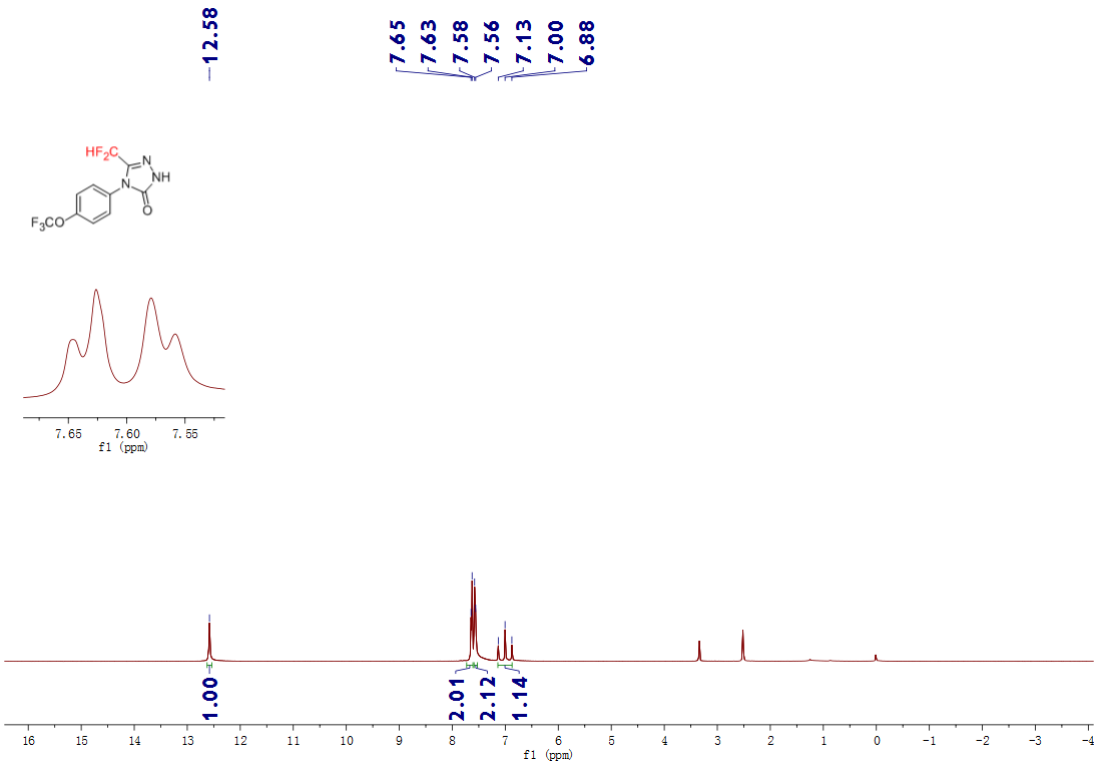
^{13}C-NMR spectrum of **4k** in DMSO-d_6



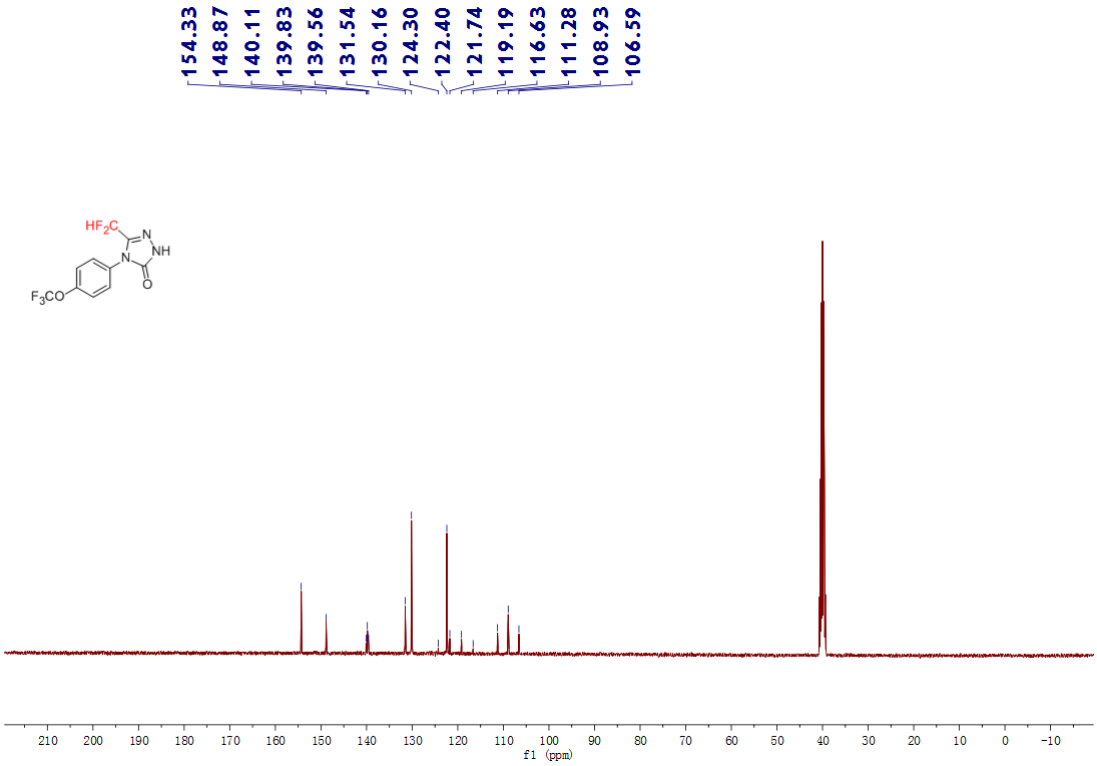
^{19}F-NMR spectrum of **4k** in DMSO-d_6



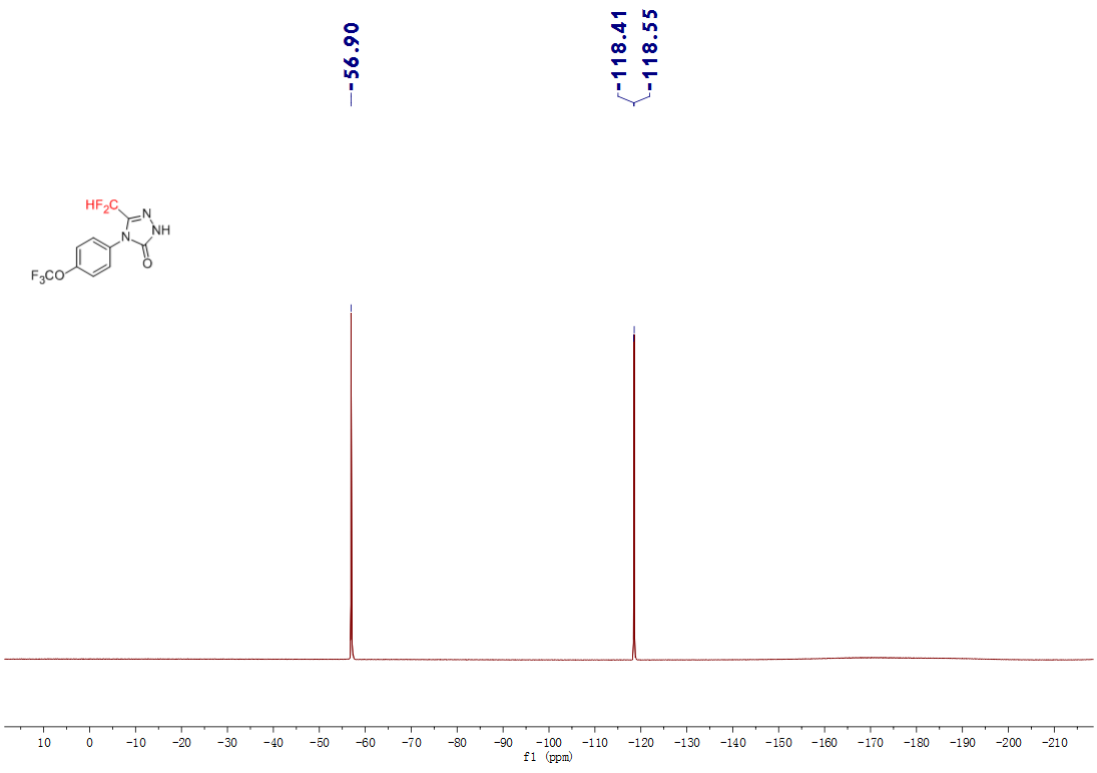
^{1}H-NMR spectrum of **4l** in DMSO-d_6



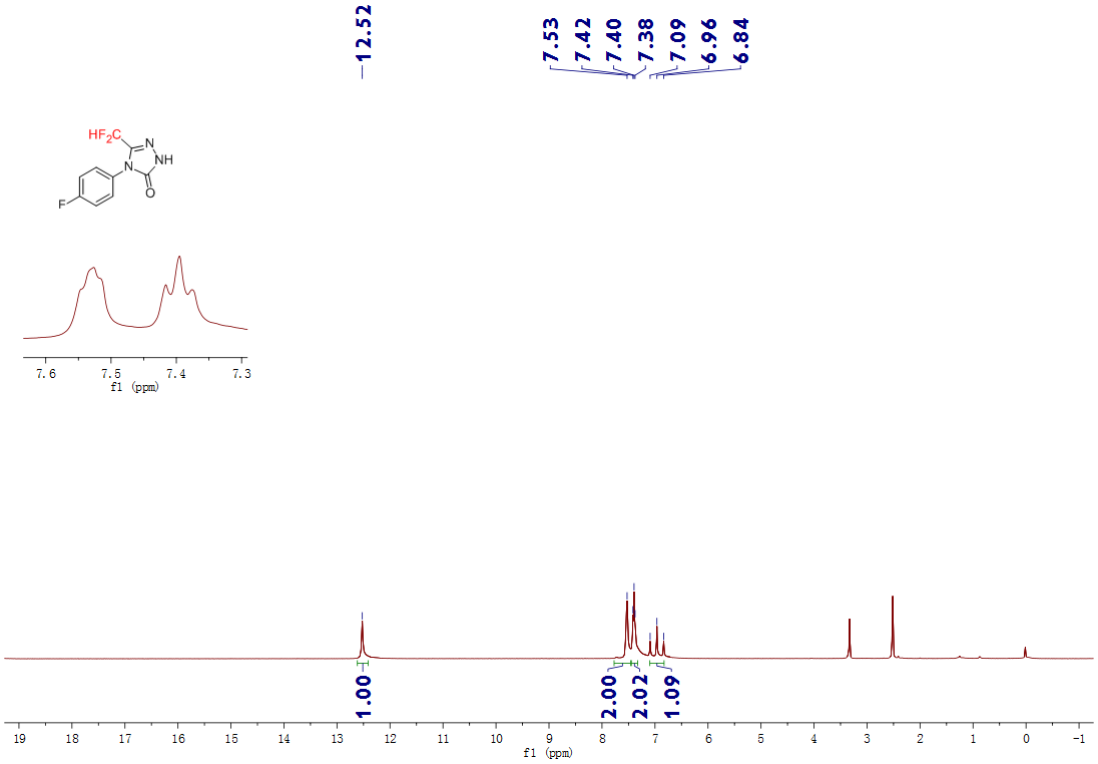
^{13}C-NMR spectrum of **4l** in DMSO-d_6



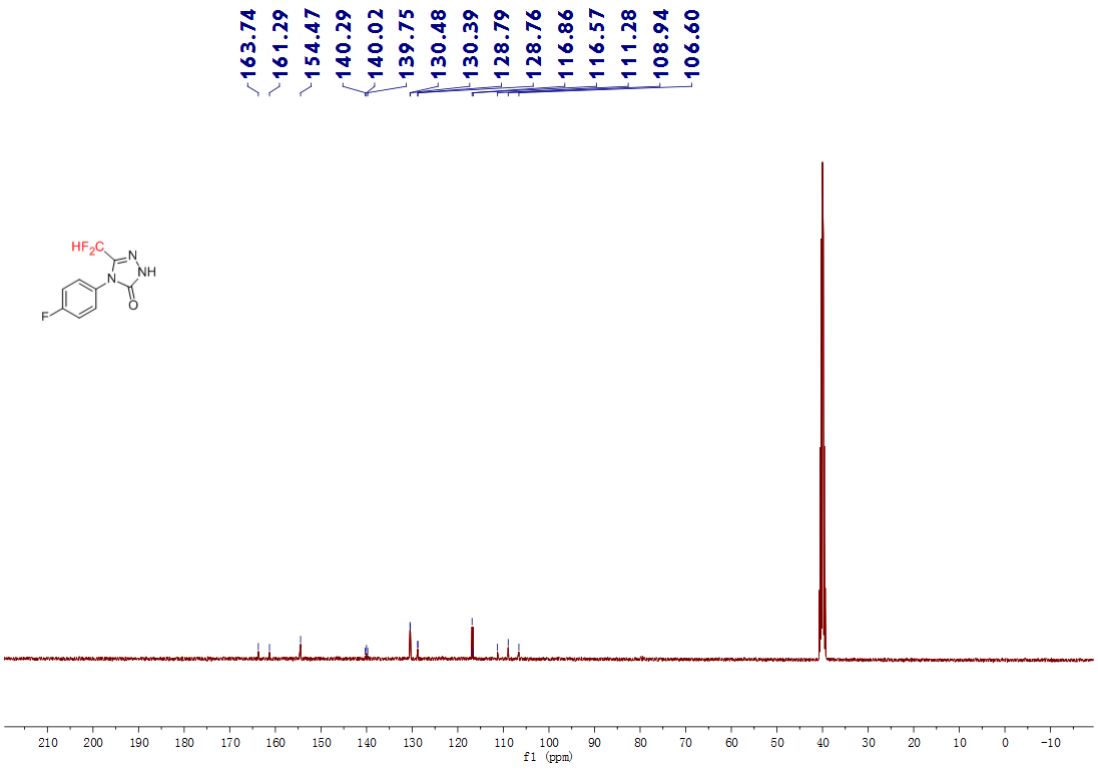
^{19}F-NMR spectrum of **4l** in DMSO-d_6



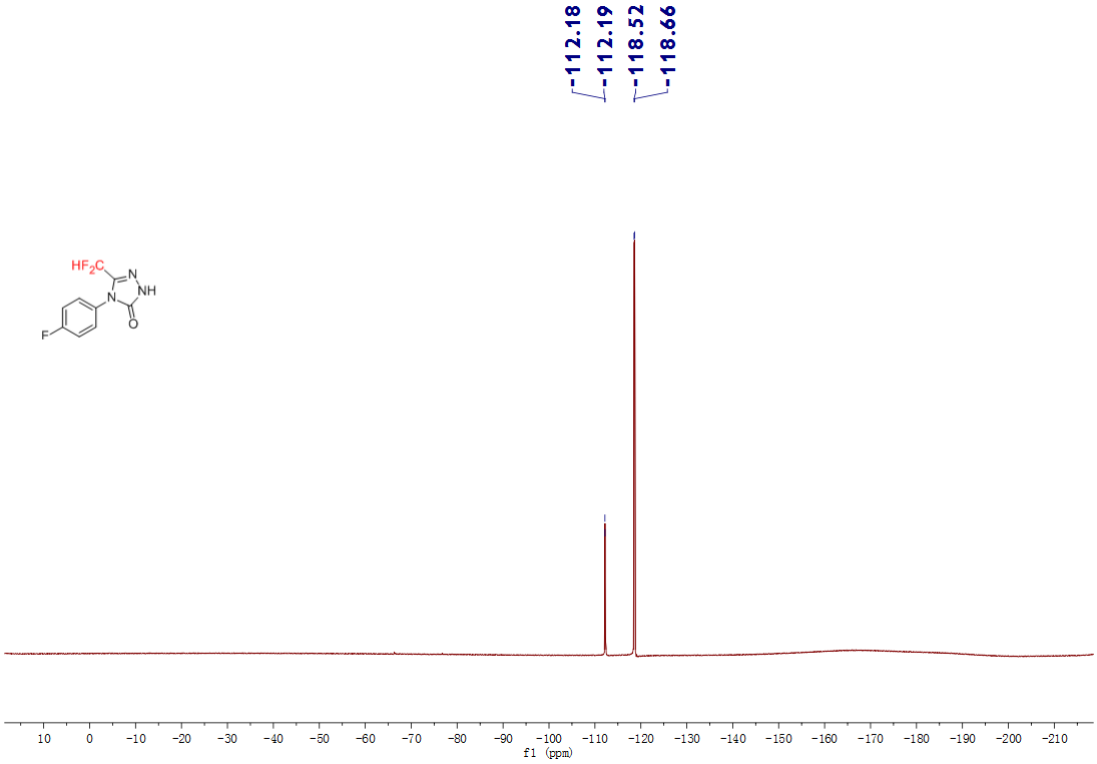
^{1}H-NMR spectrum of **4m** in DMSO-d_6



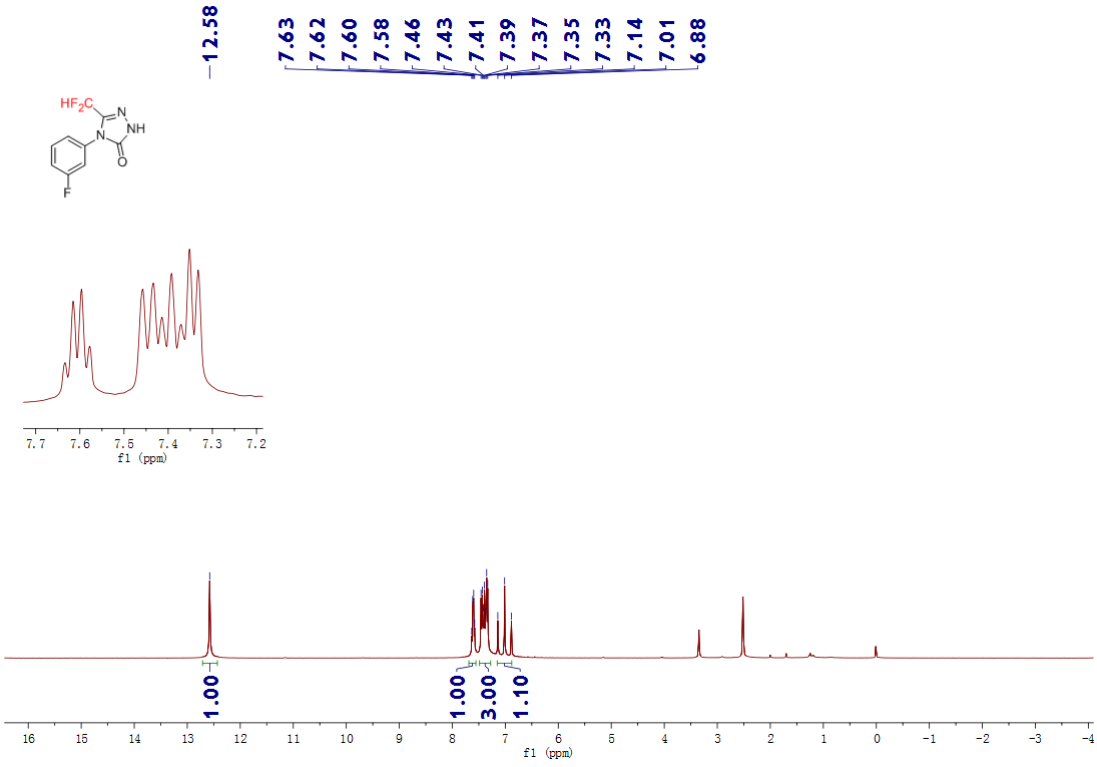
^{13}C-NMR spectrum of **4m** in DMSO-d_6



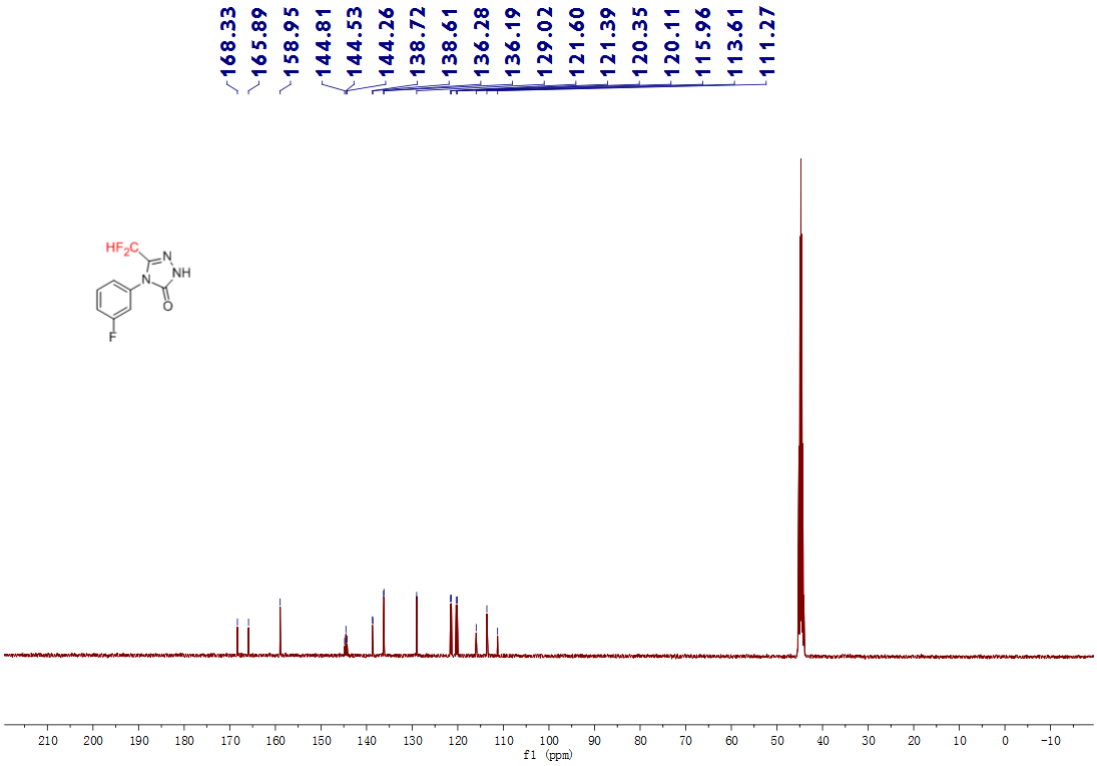
^{19}F-NMR spectrum of **4m** in DMSO-d_6



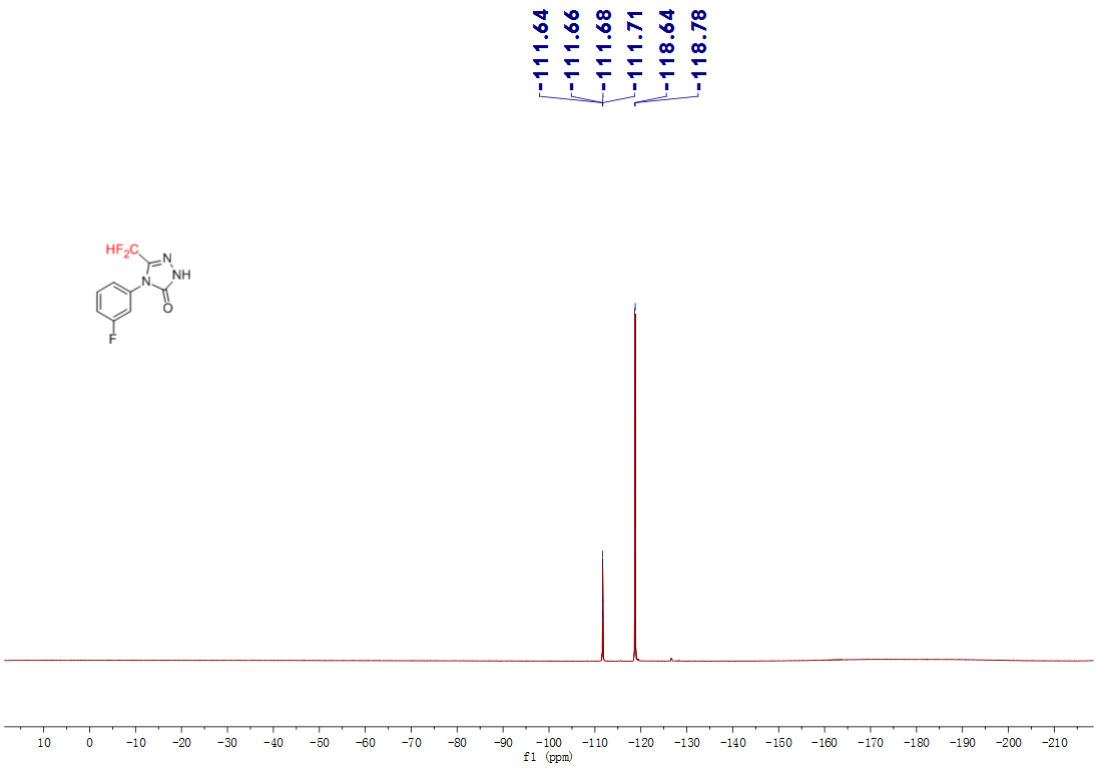
^{1}H-NMR spectrum of **4n** in DMSO-d_6



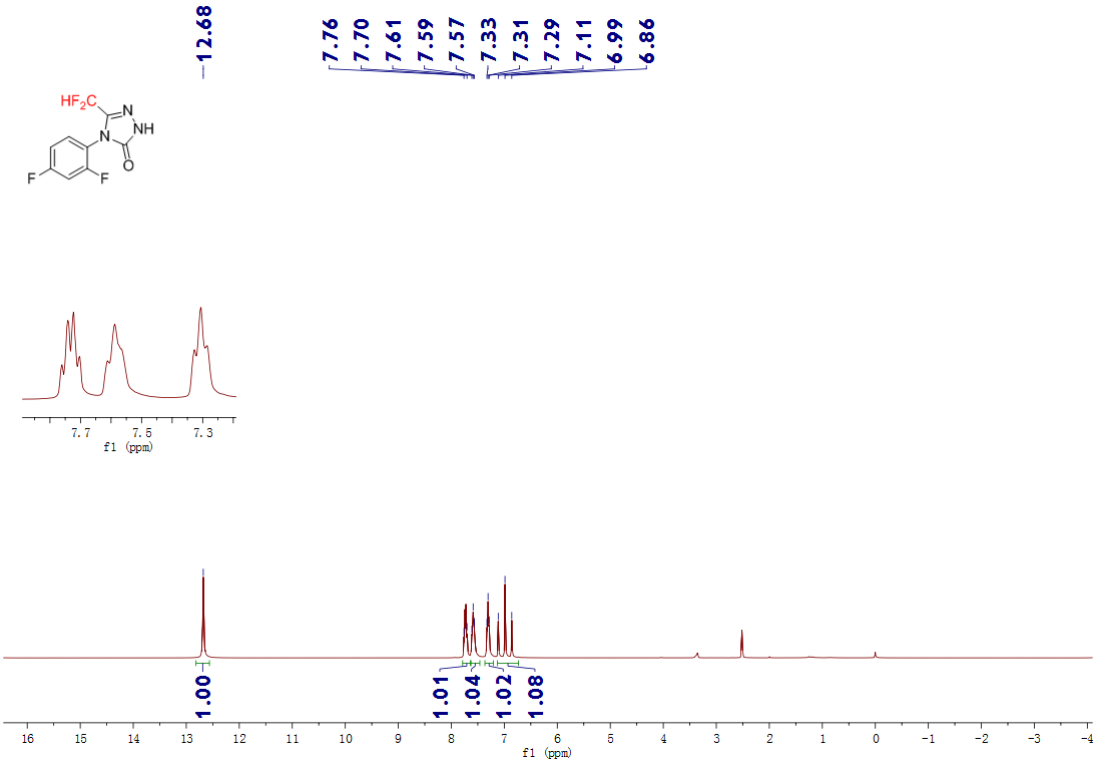
^{13}C-NMR spectrum of **4n** in DMSO-d_6



^{19}F-NMR spectrum of **4n** in DMSO-d_6



^{1}H-NMR spectrum of **4o** in DMSO-d_6



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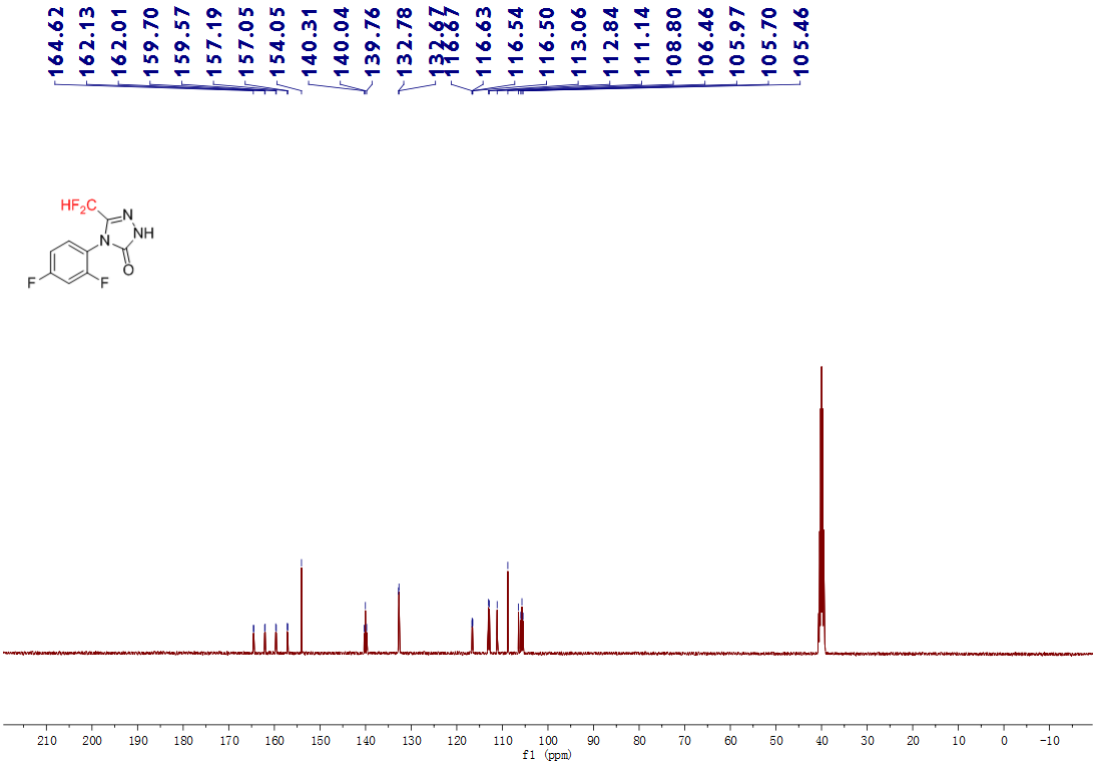

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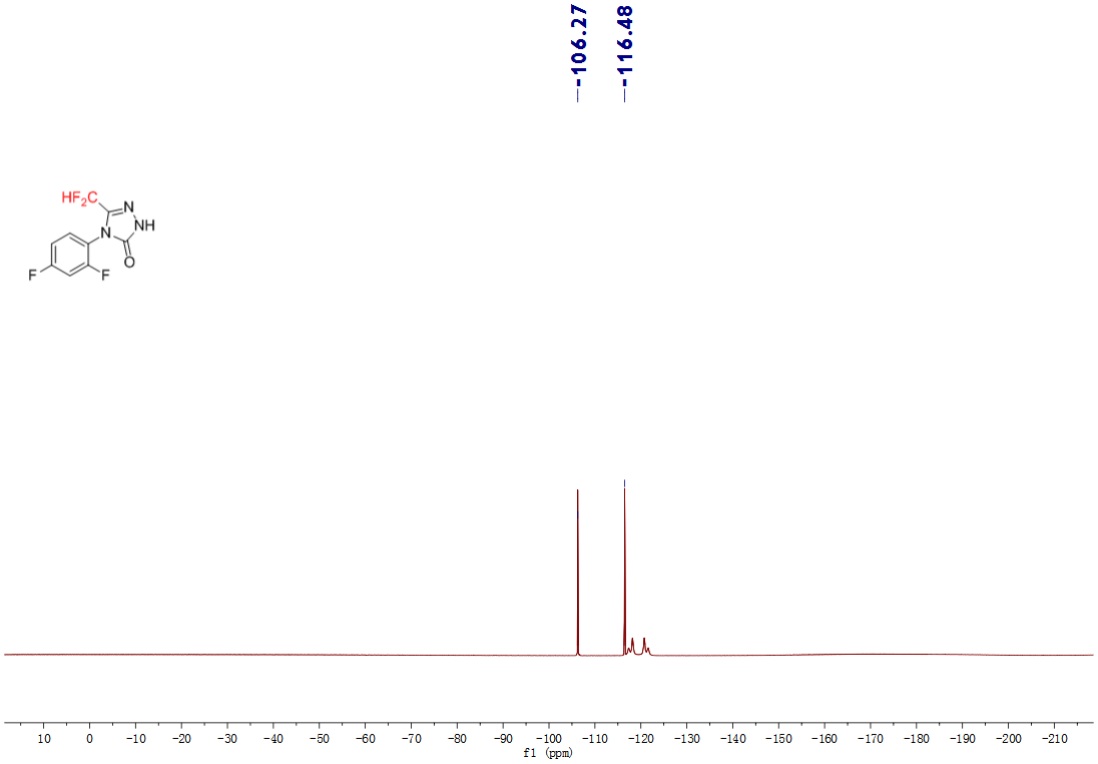
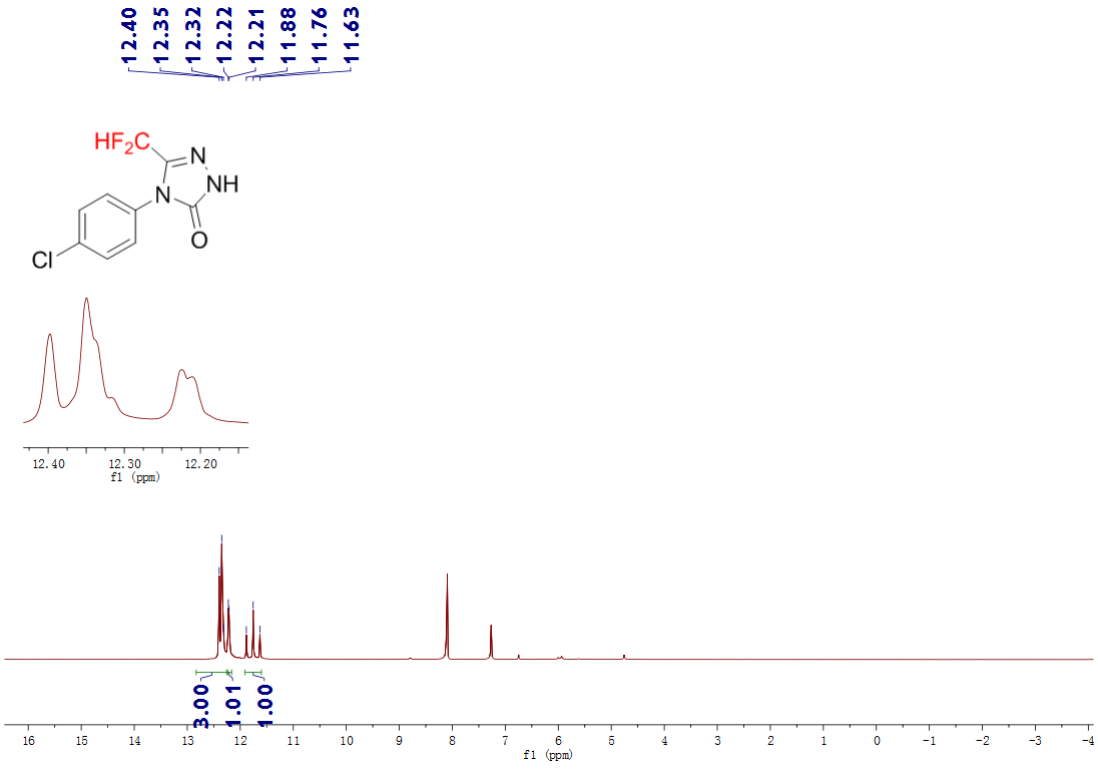
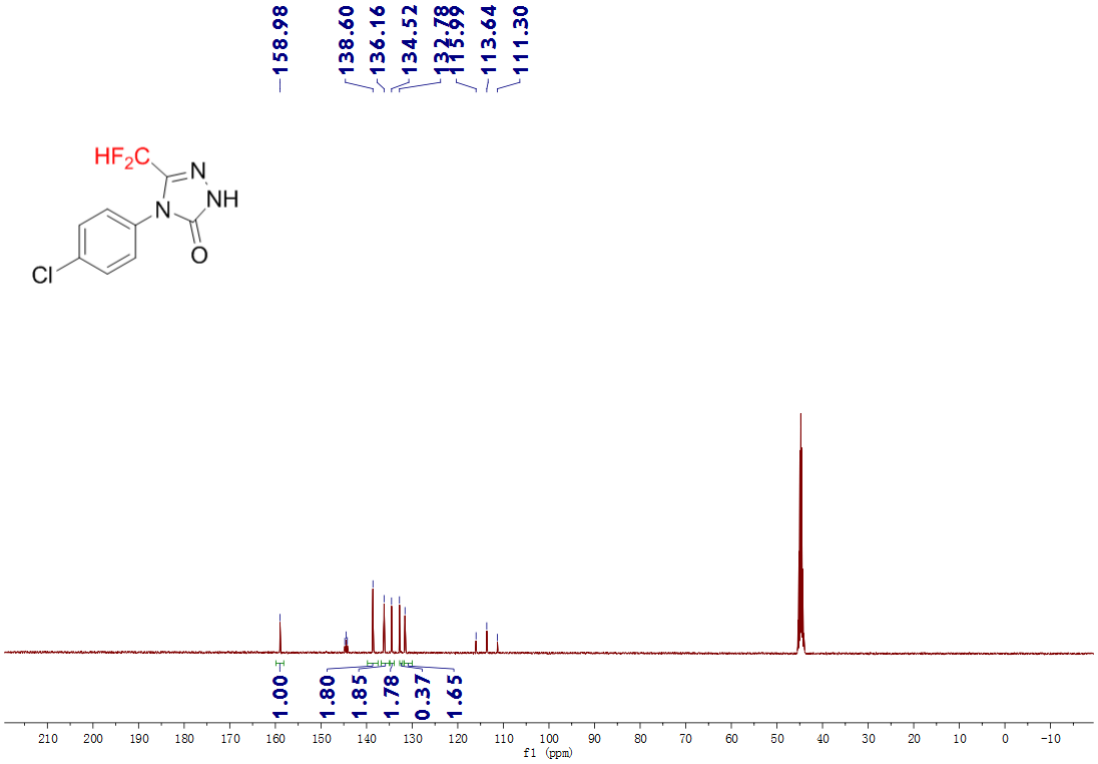


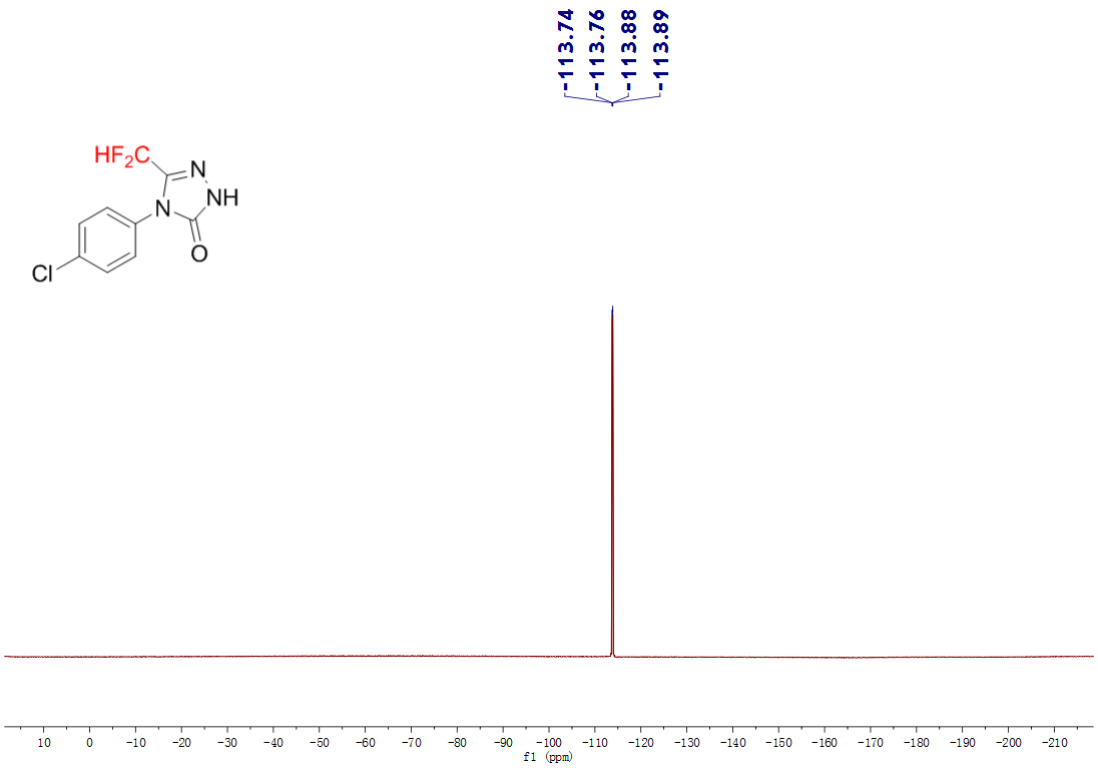
^{1}H-NMR spectrum of **4p** in DMSO-d_6



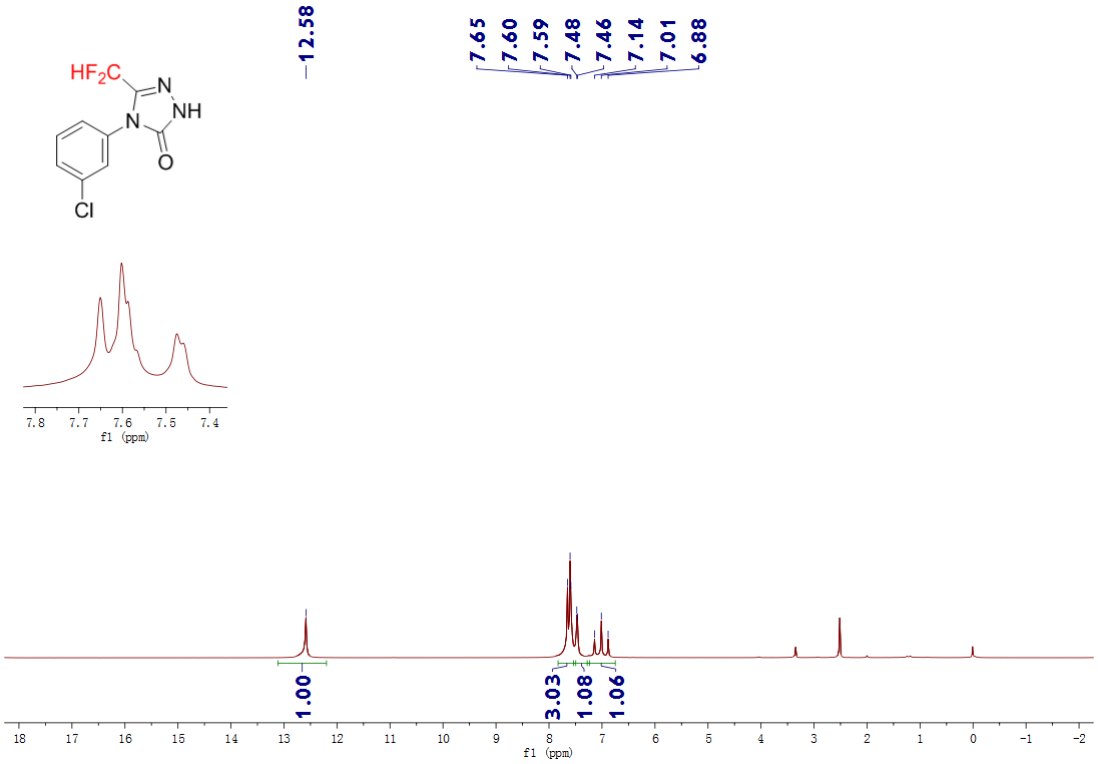
^{13}C-NMR spectrum of **4p** in DMSO-d_6



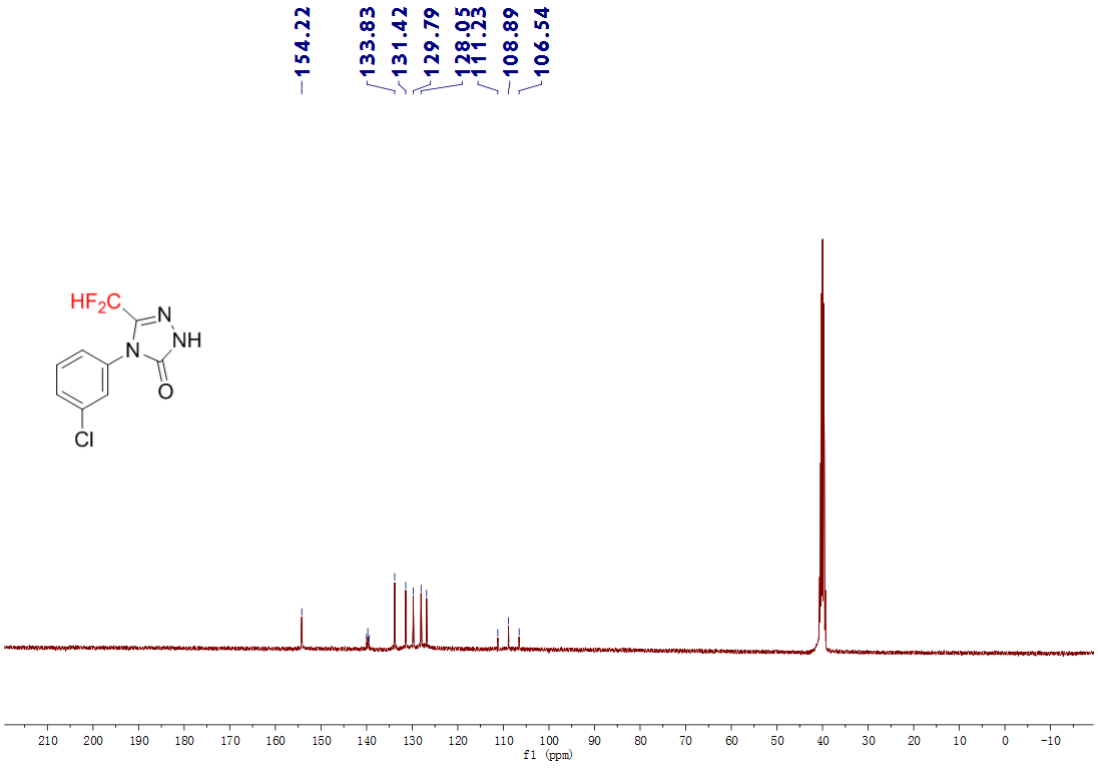
^{19}F-NMR spectrum of **4p** in DMSO-d_6



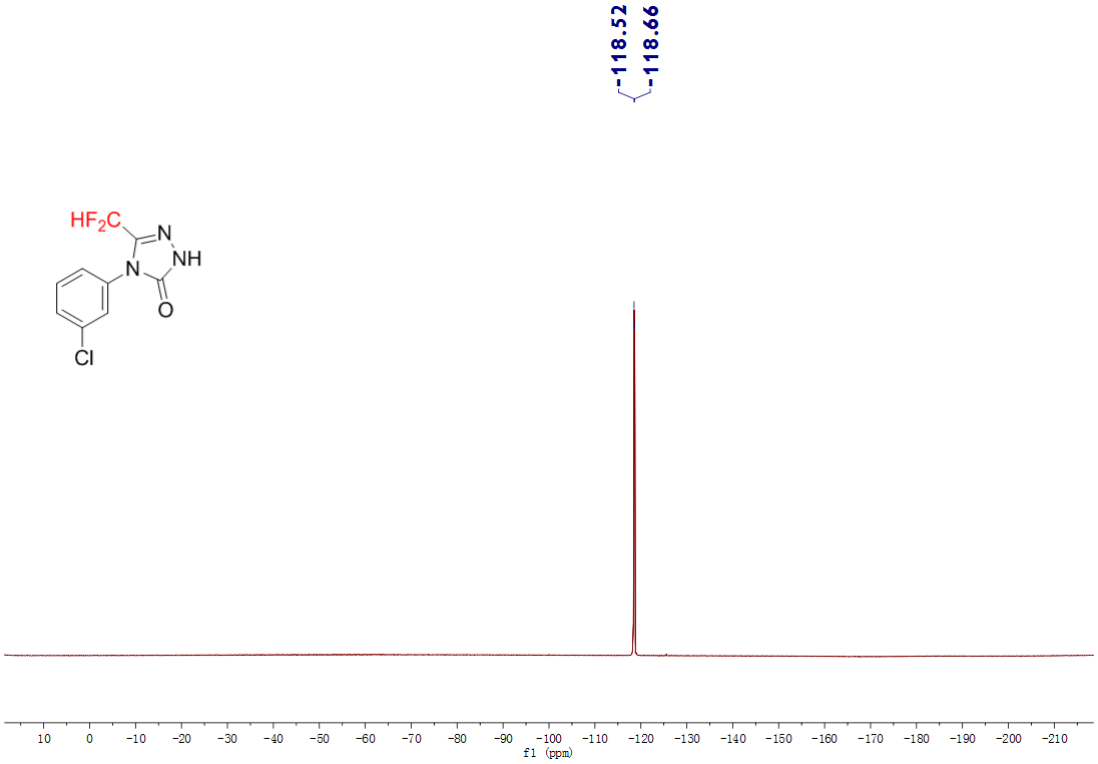
^{1}H-NMR spectrum of **4q** in DMSO-d_6



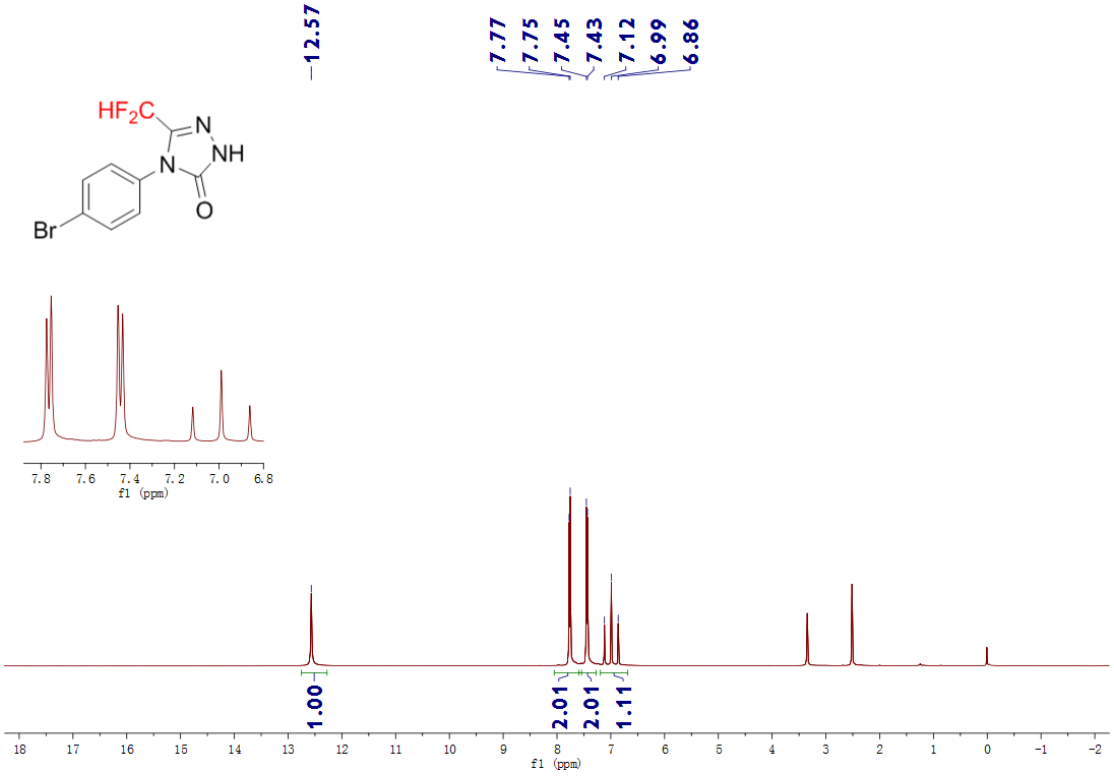
^{13}C-NMR spectrum of **4q** in DMSO-d_6



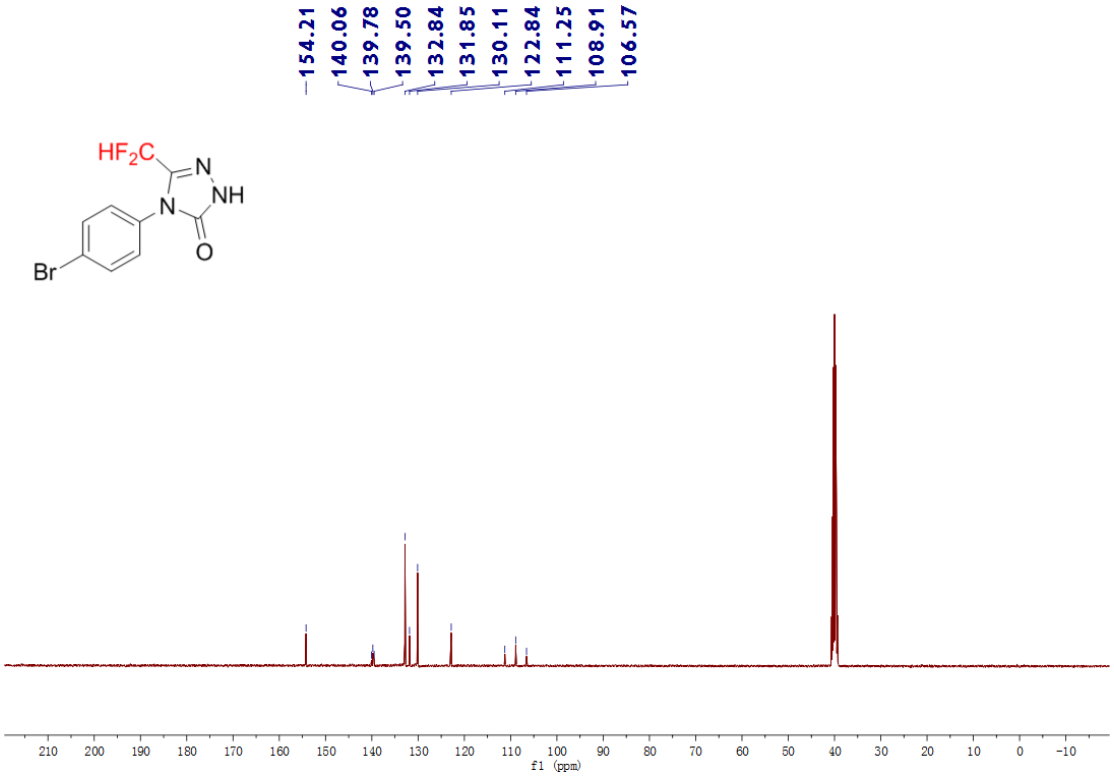
^{19}F-NMR spectrum of **4q** in DMSO-d_6



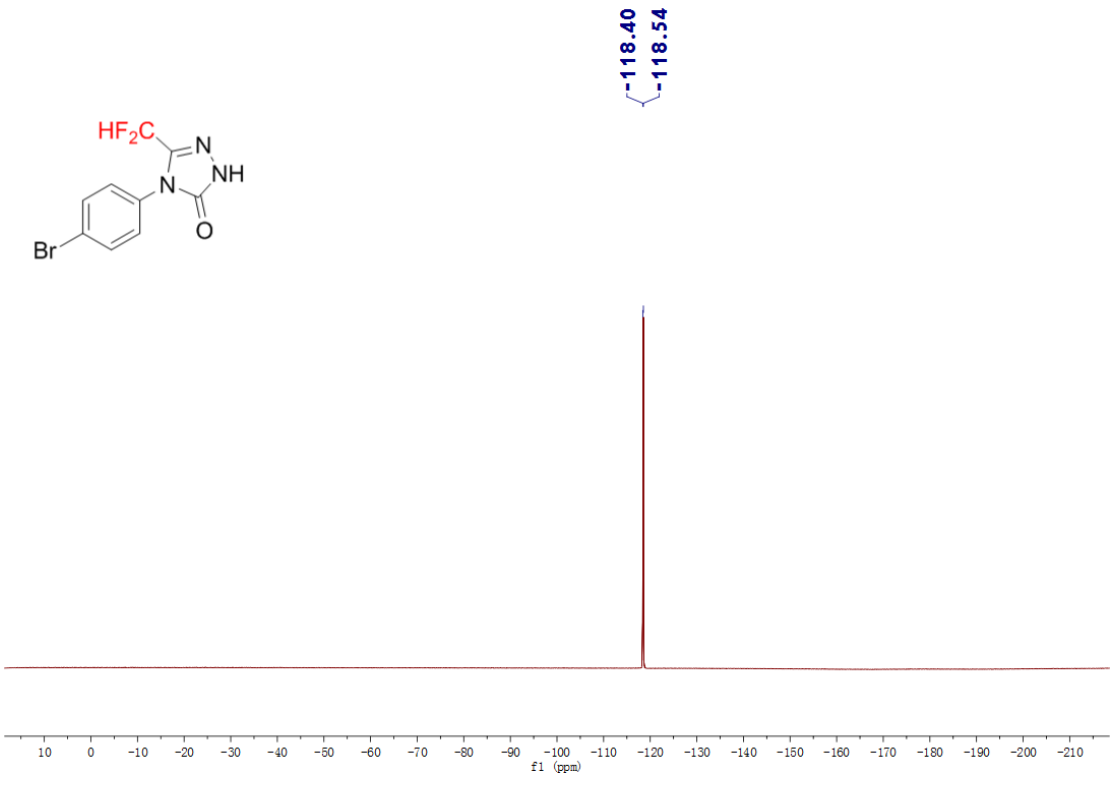
^{1}H-NMR spectrum of **4r** in DMSO-d_6



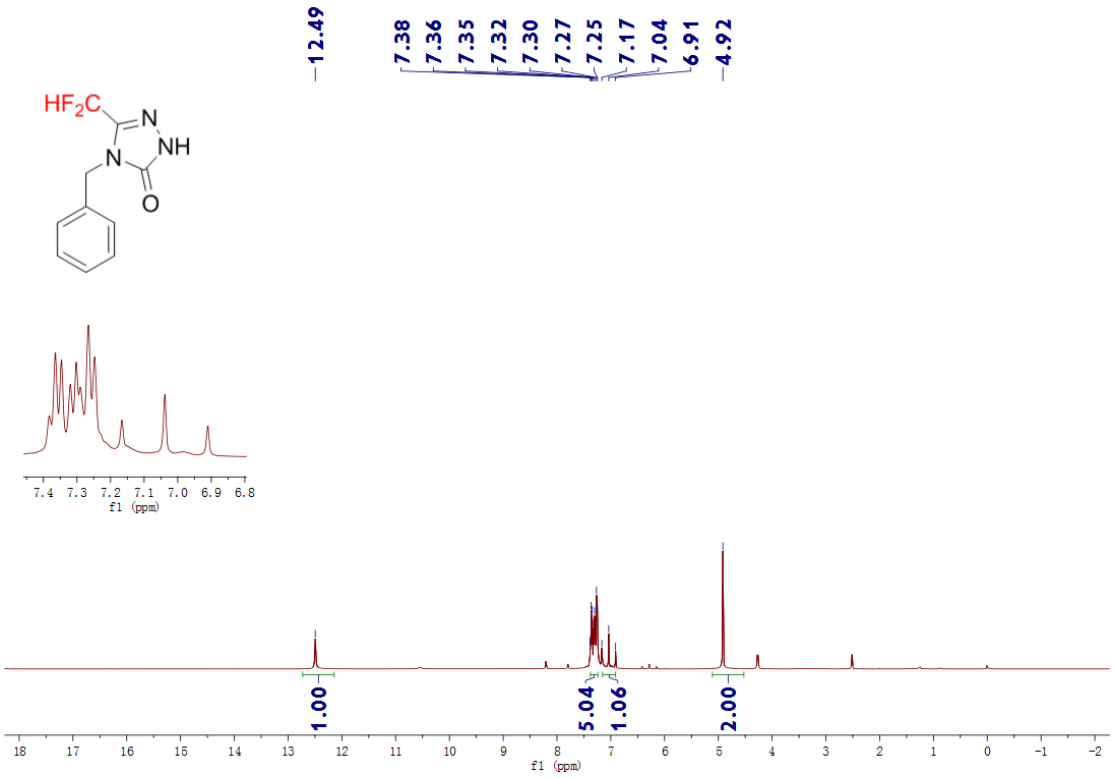
^{13}C-NMR spectrum of **4r** in DMSO-d_6



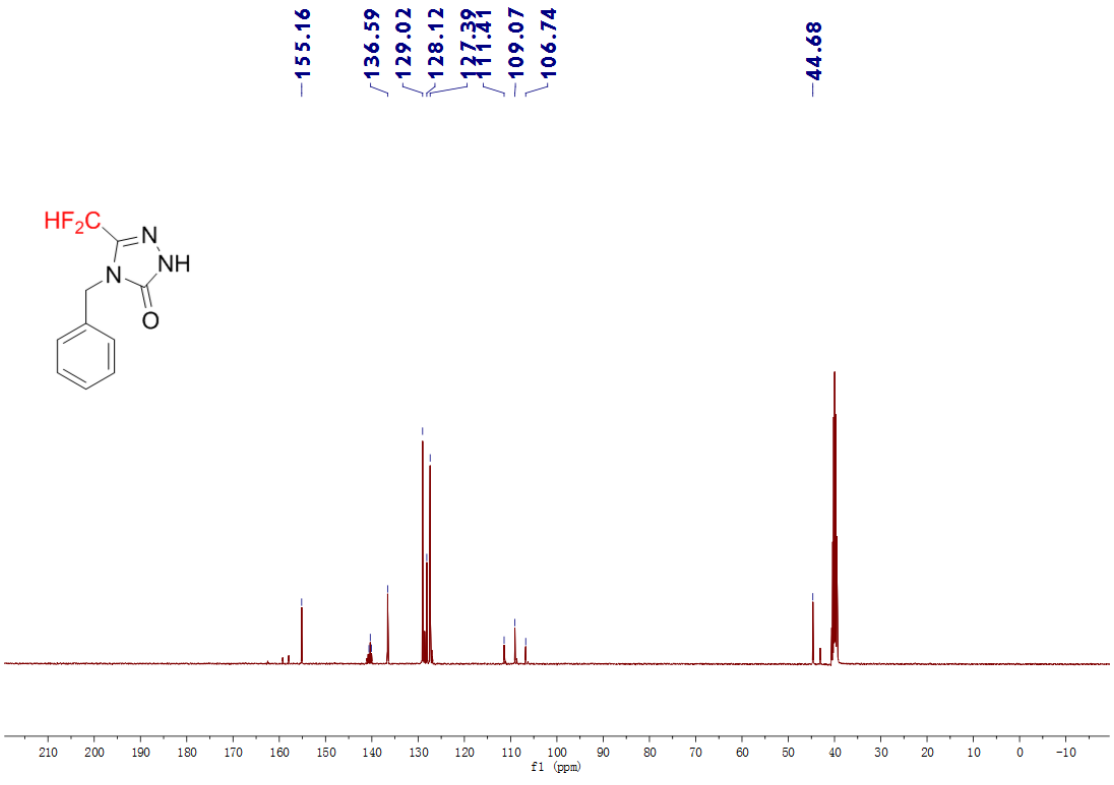
^{19}F-NMR spectrum of **4r** in DMSO-d_6



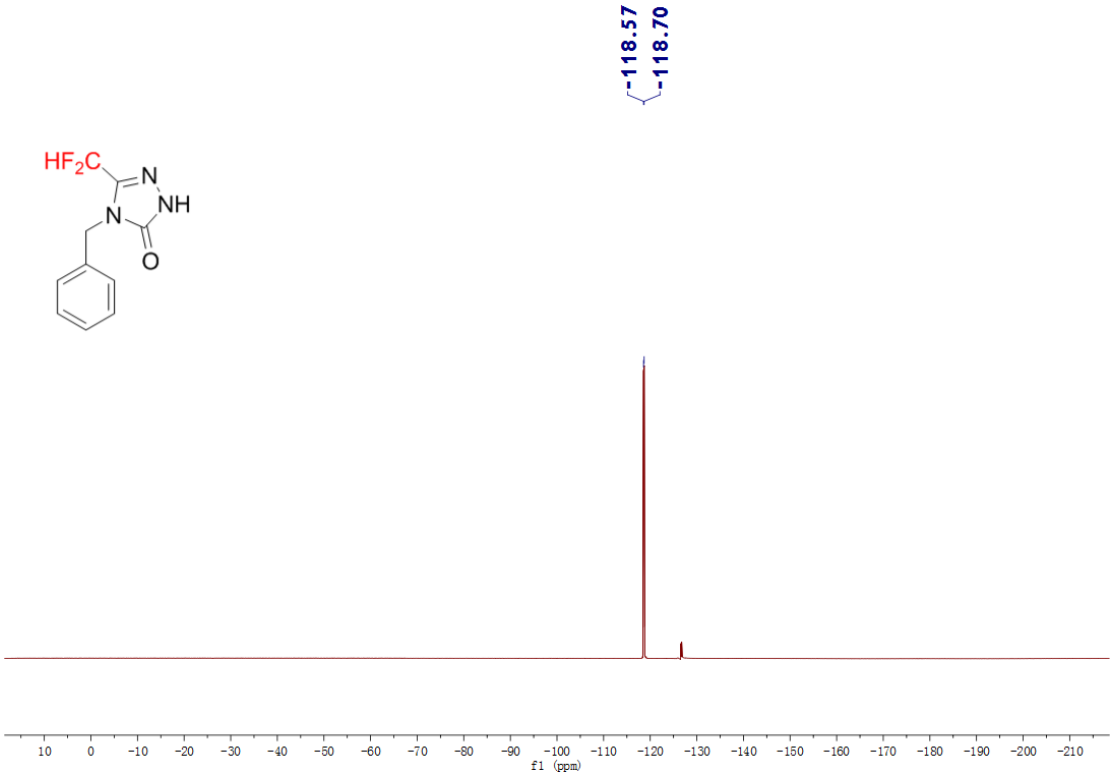
^{1}H-NMR spectrum of **4s** in DMSO-d_6



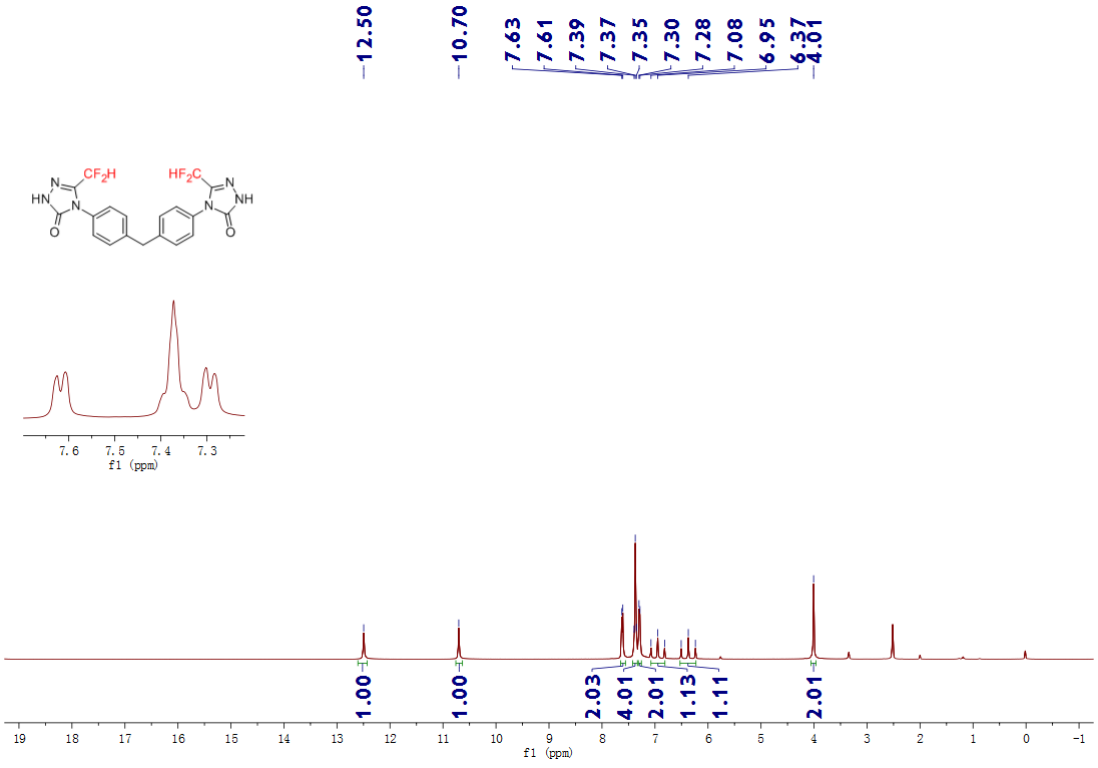
^{13}C-NMR spectrum of **4s** in DMSO-d_6



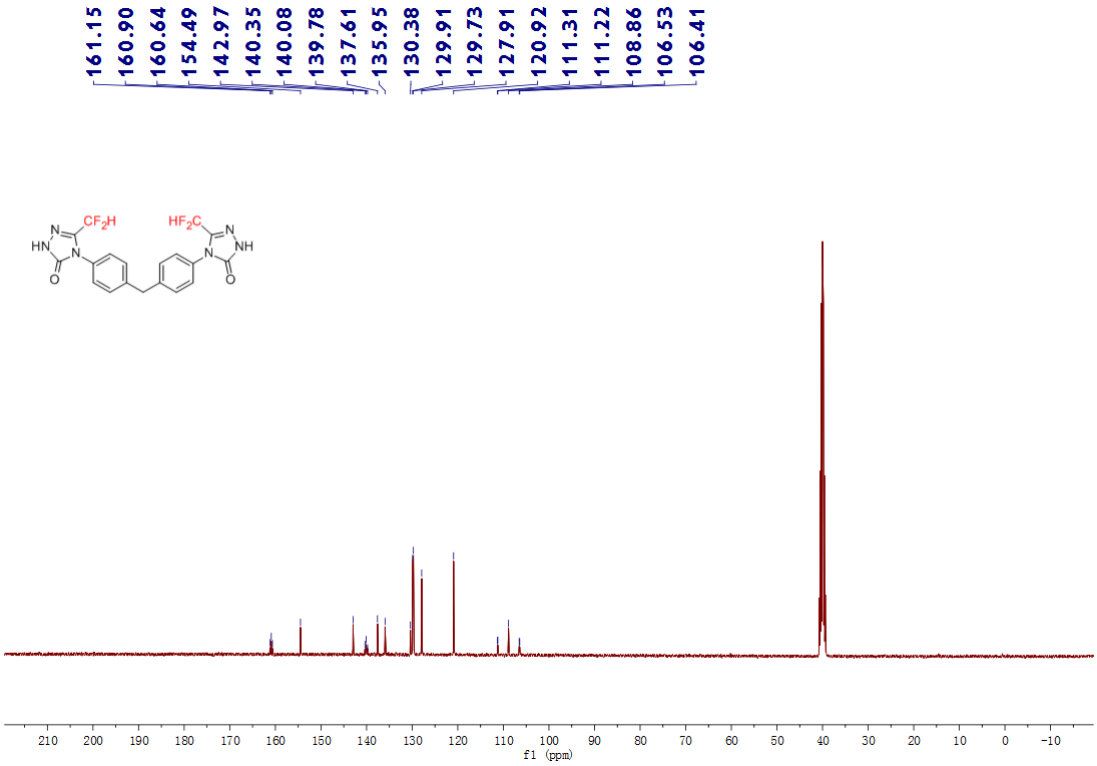
^{19}F-NMR spectrum of **4s** in DMSO-d_6



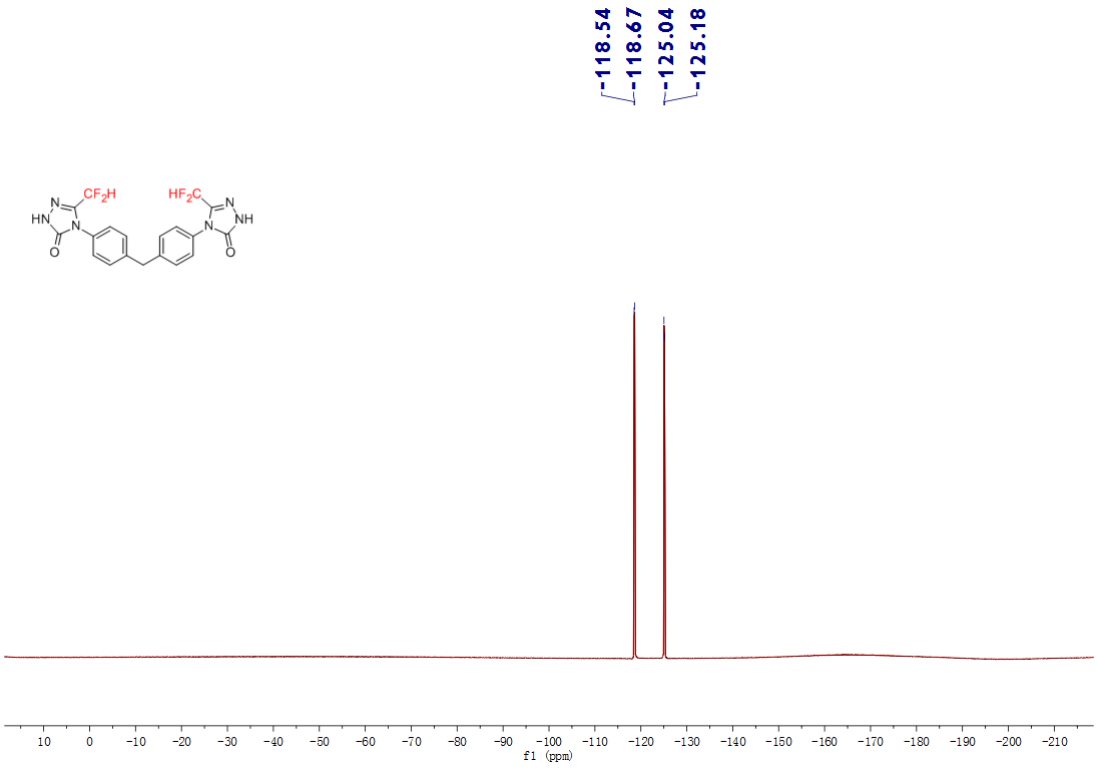
^{1}H-NMR spectrum of **4u** in DMSO-d_6



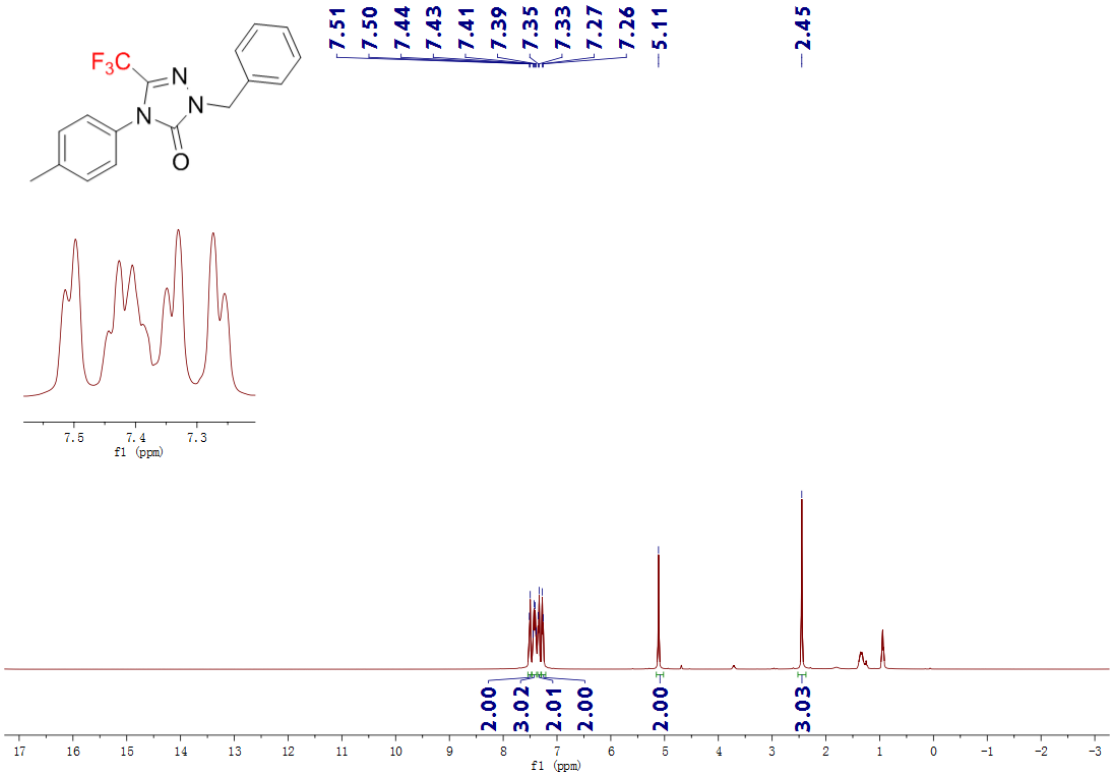
^{13}C-NMR spectrum of **4u** in DMSO-d_6



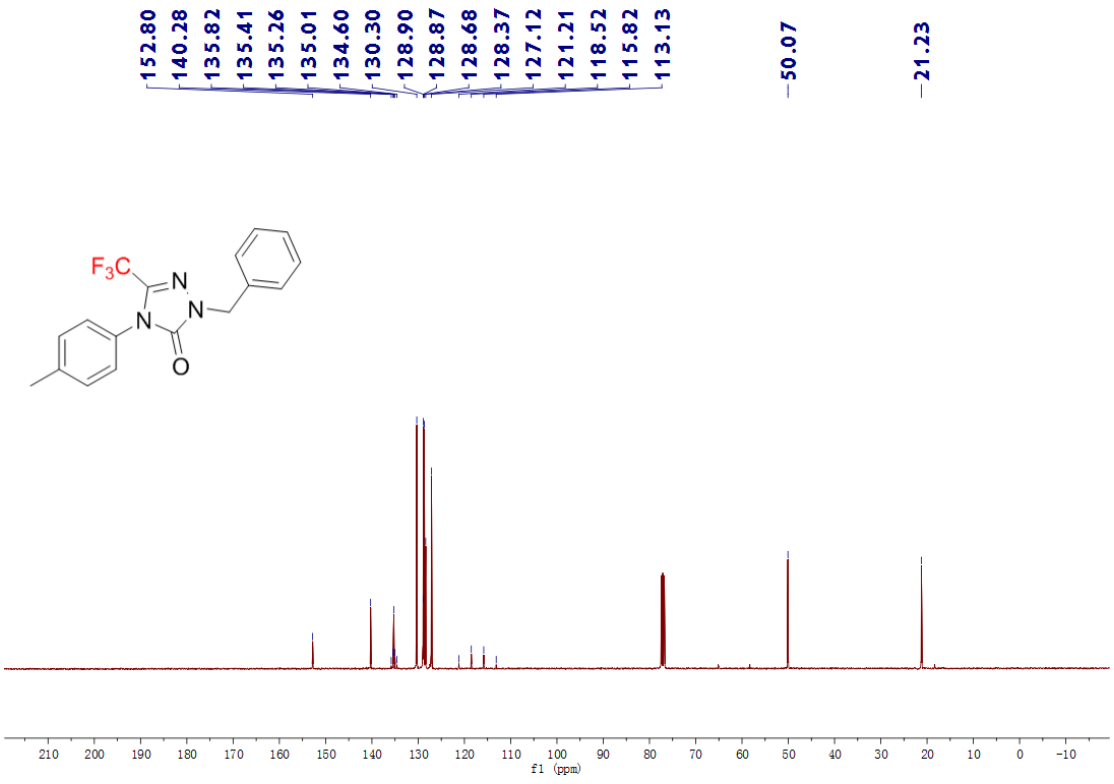
^{19}F-NMR spectrum of **4u** in DMSO-d_6



^{1}H-NMR spectrum of **5** in $CDCl_3$



^{13}C-NMR spectrum of **5** in $CDCl_3$



^{19}F-NMR spectrum of **5** in $CDCl_3$