Supporting Information *for*

Synthesis of 2-trifluoromethyl chromenes *via* double carbonyl-ene reaction

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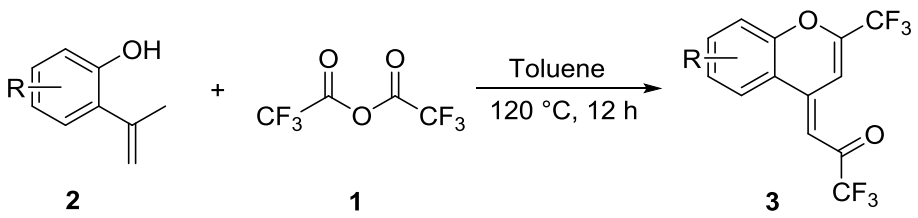
General information

^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.0), ^{1}H NMR (DMSO-d_6 δ 2.50) and ^{13}C NMR (DMSO-d_6 δ 39.50). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. *o*-Isopropenylphenols were prepared according to the published procedures.[1] Other 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. Single-crystal X-ray diffraction data was collected on a Bruker AXS APEX diffractometer. IR spectra were recorded using an FT-IR spectrometer and are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded on Waters GC-TOF instrument using EI techniques and on THERMO SCIENTIFIC Q Exactive Hybrid quadrupole orbitrap mass spectrometer using ESI-Orbitrap techniques. Melting points were determined using a melting range apparatus and are uncorrected.

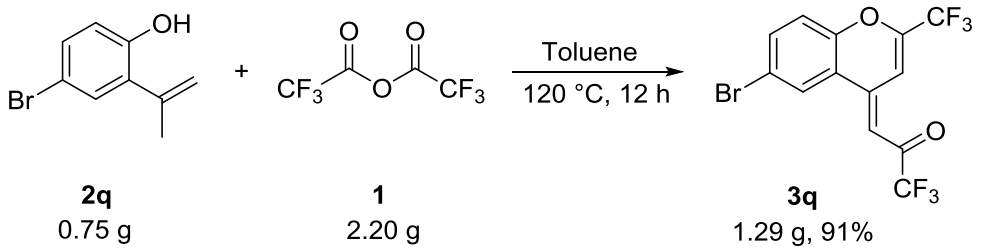
General procedure of the synthesis of 2-trifluoromethyl chromenes 3



2 **1** **3**

Under air atmosphere, to a 5 mL pressure tube equipped with a stir bar was added *o*-Isopropenylphenol **2** (0.50 mmol, 1.0 equiv), trifluoroacetic anhydride **1** (315 mg, 1.50 mmol, 3.0 equiv) and toluene (2.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 12 h. After cooling down to room temperature, the crude mixture was diluted with water (5 mL × 3) and diethyl ether (15 mL × 3). The organic phase was combined and dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The resulting 2-trifluoromethyl chromenes product **3** was purified by column chromatography on silica gel with petroleum ether and ethyl ether.

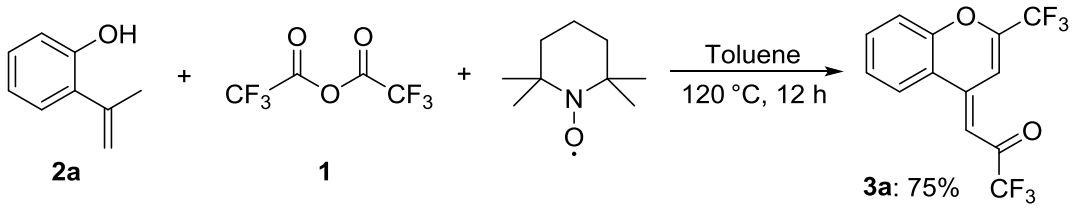
Procedure for gram scale reaction for synthesis of (*E*)-3-(6-bromo-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3q)



2q 0.75 g | **1** 2.20 g | **3q** 1.29 g, 91%

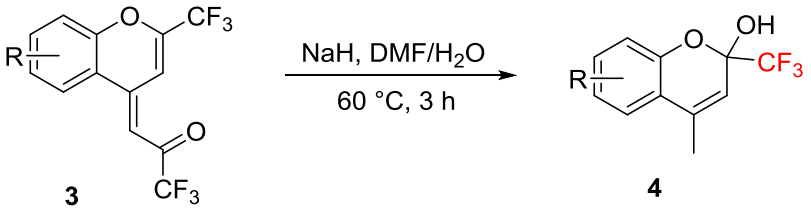
Under air atmosphere, to a 25 mL pressure tube equipped with a stir bar was added 4-bromo-2-(prop-1-en-2-yl)phenol **2q** (0.75 g, 3.5 mmol, 1.0 equiv), trifluoroacetic anhydride **1** (2.20 g, 10.5 mmol, 3 equiv) and toluene (10 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 12 h. After cooling down to room temperature, the crude mixture was diluted with water (30 mL × 3) and diethyl ether (30 mL× 3). The organic phase was combined and dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel with petroleum ether to give 1.29 g of product **3q** (91% yield).

Procedure of inhibition experimentals



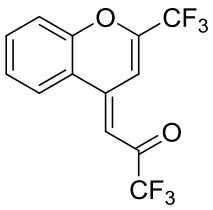
Under air atmosphere, to a 5 mL pressure tube equipped with a stir bar was added *o*-isopropenylphenol **2a** (67 mg, 0.50 mmol, 1.0 equiv), trifluoroacetic anhydride 1 (315 mg, 1.50 mmol, 3.0 equiv), 2,2,6,6-tetramethylpiperidinooxy (156 mg, 1.00 mmol, 2.0 equiv), and toluene (2.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 12 h. After cooling down to room temperature, the crude mixture was diluted with water (5 mL × 3) and diethyl ether (15 mL × 3). The organic phase was combined and dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The resulting 2-trifluoromethyl chromenes product **3a** was purified by column chromatography on silica gel with petroleum ether and ethyl ether to give 116 mg of product **3a** (75% yield).

Procedure of synthetic transformation of 3 to 4



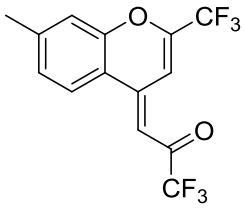
Under air atmosphere, to a 25 mL flask equipped with a stir bar was added trifluoromethyl chromenes **3** (0.50 mmol, 1.0 equiv), NaH (180 mg, 6.0 equiv). To this mixture at 0 ℃ (ice bath) was added solvent mixture of DMF and H_2O (3.0 mL : 3.0 mL) portionwise. The resulting solution was stirred at 60 °C for 3 h. After cooling down to room temperature, the crude mixture was diluted with 3M HCl (10 mL) and ethyl acetate (25 mL). The organic layer was separated and washed with water (10 mL) and then brine (10 mL). The organic solution was then dried over anhydrous $MgSO_4$ and filtered over a sintered funnel, and the filtrate was evaporated to dryness. The crude products **4** was purified by column chromatography on silica gel with petroleum ether and ethyl acetate.

Data for compounds 3 and 4



(*E*)-1,1,1-trifluoro-3-(2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3a)

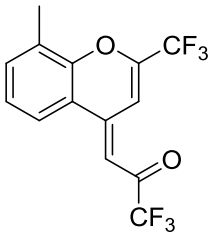
Obtained as a pale yellow solid in 88% yield (136 mg). Mp: 100–103 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.8 Hz, 1H), 7.53 – 7.43 (m, 2H), 6.75 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.1 Hz), 152.2 (s), 146.7 (q, *J* = 38.5 Hz), 144.6 (s), 134.0 (s), 126.8 (s), 123.6 (s), 119.0 (s), 118.9 (s), 118.7 (q, *J* = 273.3 Hz), 116.5 (q, *J* = 291.7 Hz), 105.7 (q, *J* = 3.8 Hz), 101.4 (s). IR (ATR): ν 3114, 2922, 1649, 1551, 1467, 1367, 1271, 1201, 1131, 1083, 1019, 907, 732 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_6F_6O_2$: 308.0272; found: 308.0267.



(*E*)-1,1,1-trifluoro-3-(7-methyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3b)

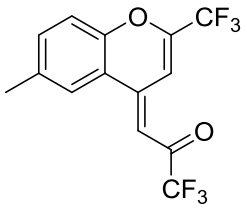
Obtained as a pale yellow solid in 92% yield (148 mg). Mp: 109–112 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.34 – 7.22 (m, 2H), 6.70 (s, 1H), 2.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 33.8 Hz), 152.2 (s), 146.6 (q, *J* = 38.4 Hz), 145.8 (s), 144.9 (s), 128.2 (s), 123.4 (s), 118.8 (q, *J* = 273.2 Hz), 118.7 (s), 116.6 (q, *J* = 291.8 Hz), 116.5 (s), 105.7 (q, *J* = 3.7 Hz), 100.6 (s), 21.6 (s). IR (ATR): ν 2961, 2926, 1645, 1540, 1269, 1194,

1131, 1032, 904, 809, 726, 706 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_8F_6O_2$: 322.0428; found: 322.0417.



(*E*)-1,1,1-trifluoro-3-(8-methyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3c)

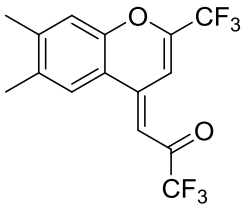
Obtained as a pale yellow solid in 90% yield (145 mg). Mp: 142–145 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.58. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 6.73 (s, 1H), 2.49 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 33.8 Hz), 150.7 (s), 146.6 (q, *J* = 38.5 Hz), 145.3 (s), 135.1 (s), 128.6 (s), 126.3 (s), 121.2 (s), 118.8 (q, *J* = 273.3 Hz), 118.7 (s), 116.5 (q, *J* = 291.7 Hz), 105.6 (q, *J* = 3.6 Hz), 101.3 (s), 15.6 (s). IR (ATR): ν 2253, 1657, 1553, 1381, 1365, 1095, 903, 722, 649, 543 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_8F_6O_2$: 322.0428; found: 322.0421.



(*E*)-1,1,1-trifluoro-3-(6-methyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3d)

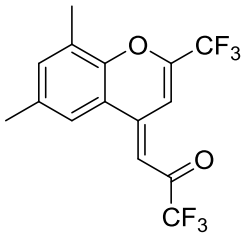
Obtained as a pale yellow solid in 95% yield (153 mg). Mp: 125–128 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.74 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 1H), 6.72 (s, 1H), 2.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 33.7 Hz), 150.5 (s), 146.5 (q, *J* = 38.6 Hz), 144.8 (s),

137.0 (s), 135.3 (s), 123.2 (s), 122.9 (s), 118.8 (q, J = 273.3 Hz), 118.7 (s), 116.5 (q, J = 291.7 Hz), 105.6 (q, J = 3.6 Hz), 100.9 (s), 21.2 (s). IR (ATR): ν 2253, 1657, 1553, 1381, 1365, 1095, 903, 722, 649, 543 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_8F_6O_2$: 322.0428; found: 322.0419.



(*E*)-3-(6,7-dimethyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3e)

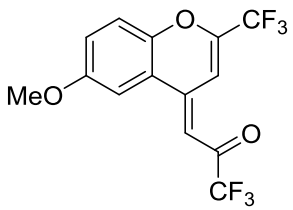
Obtained as a pale yellow solid in 96% yield (161 mg). Mp: 139–141 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.67 (s, 1H), 7.26 (s, 1H), 6.67 (s, 1H), 2.42 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -77.9 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (q, J = 33.6 Hz), 150.7 (s), 146.5 (q, J = 38.5 Hz), 145.0 (s), 144.9 (s), 136.3 (s), 123.4 (s), 119.1 (s), 118.4 (q, J = 273.4 Hz), 116.6 (s), 116.4 (q, J = 291.6 Hz), 105.6 (q, J = 3.7 Hz), 100.1 (s), 20.3 (s), 19.7 (s). IR (ATR): ν 2954, 2925, 1683, 1647, 1545, 1202, 1150, 1090, 1021, 903, 823, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{15}H_{10}F_6O_2$: 336.0585; found: 336.0578.



(*E*)-3-(6,8-dimethyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3f)

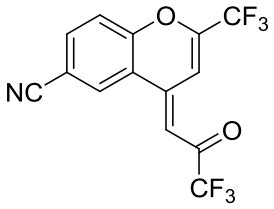
Obtained as a pale yellow solid in 85% yield (143 mg). Mp: 129–133 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s,

1H), 7.55 (s, 1H), 7.36 (s, 1H), 6.68 (s, 1H), 2.47 (s, 3H), 2.44 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (q, *J* = 33.8 Hz), 149.0 (s), 146.5 (q, *J* = 38.5 Hz), 145.4 (s), 136.5 (s), 136.3 (s), 128.2 (s), 120.7 (s), 118.4 (s), 118.9 (q, *J* = 273.3 Hz), 116.6 (q, *J* = 291.8 Hz), 105.4 (q, *J* = 3.6 Hz), 100.7 (s), 21.1 (s), 15.4 (s). IR (ATR): ν 2928, 1647, 1265, 1190, 1148, 1083, 898, 824, 737 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{15}H_{10}F_6O_2$: 336.0585; found: 336.0579.



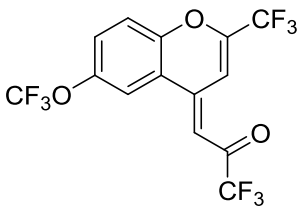
(*E*)-1,1,1-trifluoro-3-(6-methoxy-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3g)

Obtained as a pale yellow solid in 99% yield (167 mg). Mp: 123–127 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.35 – 7.20 (m, 2H), 6.62 (s, 1H), 3.96 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.1 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (q, *J* = 33.8 Hz), 157.9 (s), 146.9 (s), 146.5 (q, *J* = 38.5 Hz), 144.8 (s), 122.7 (s), 120.2 (s), 119.7 (s), 118.8 (q, *J* = 273.3 Hz), 116.6 (q, *J* = 291.8 Hz), 105.0 (q, *J* = 3.7 Hz), 104.7 (s), 100.7 (s), 56.0 (s). IR (ATR): ν 2848, 1646, 1548, 1486, 1369, 1273, 1199, 1139, 1089, 1036, 905, 727, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_8F_6O_3$: 338.0378; found: 338.0383.



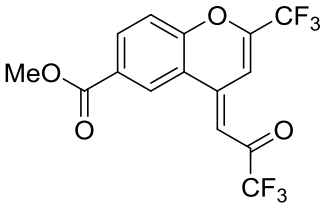
(*E*)-4-(3,3,3-trifluoro-2-oxopropylidene)-2-(trifluoromethyl)-4*H*-chromene-6-carbonitrile (3h)

Obtained as a pale yellow solid in 75% yield (125 mg). Mp: 156–159 ℃. R_f (petroleum ether : ethyl ether =5 : 1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.30 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 6.77 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.5 (s, 3F), -78.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3 (q, *J* = 34.7 Hz), 154.1 (s), 146.4 (q, *J* = 39.2 Hz), 141.7 (s), 136.1 (s), 128.8 (s), 120.5 (s), 119.9 (s), 118.4 (q, *J* = 273.3 Hz), 117.0 (s), 116.4 (q, *J* = 291.7 Hz), 111.1 (s), 106.3 (q, *J* = 3.8 Hz), 103.7 (s). IR (ATR): ν 2924, 2237, 1692, 1563, 1482, 1271, 1206, 1155, 1089, 1039, 904, 840, 732 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_5F_6NO_2$: 333.0224; found: 333.0217.



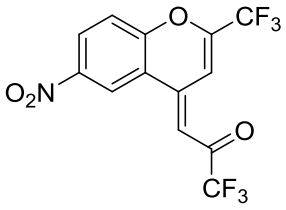
(*E*)-1,1,1-trifluoro-3-(6-(trifluoromethoxy)-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3i)

Obtained as a pale yellow solid in 98% yield (191 mg). Mp: 88–91 ℃. R_f (petroleum ether) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.77 (s, 1H), 7.64 – 7.49 (m, 2H), 6.67 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.1 (s, 3F), -71.4 (s, 3F), -78.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.2 (q, *J* = 34.6 Hz), 150.2 (s), 147.0 (q, *J* = 2.0 Hz), 146.77 (q, *J* = 38.9 Hz), 143.1 (s), 126.9 (s), 120.8 (s), 120.3 (q, *J* = 259.1 Hz), 120.2 (s), 118.6 (q, *J* = 273.4 Hz), 116.3 (q, *J* = 291.4 Hz), 115.9 (s), 105.4 (q, *J* = 3.7 Hz), 102.6 (s). IR (ATR): ν 2254, 1696, 1653, 1559, 1483, 1262, 1210, 1158, 1087, 1040, 903, 723, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{14}H_5F_9O_3$: 392.0095; found: 392.0089.



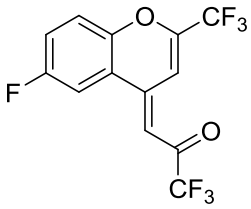
methyl (*E*)-4-(3,3,3-trifluoro-2-oxopropylidene)-2-(trifluoromethyl)-4*H*-chromene-6-carboxylate (3j)

Obtained as a pale yellow solid in 63% yield (115 mg). Mp: 116–118 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.40. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.44 (s, 1H), 8.28 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 6.79 (s, 1H), 4.01 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.6 (s, 3F), -78.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.5 Hz), 165.0 (s), 154.5 (s), 146.4 (q, *J* = 38.8 Hz), 143.3 (s), 134.4 (s), 128.6 (s), 125.6 (s), 119.1 (s), 118.8 (s), 118.5 (q, *J* = 273.3 Hz), 116.3 (q, *J* = 291.5 Hz), 106.0 (q, *J* = 3.7 Hz), 102.8 (s), 52.7 (s). IR (ATR): ν 2924, 1728, 1656, 1555, 1450, 1369, 1268, 1197, 1126, 1035, 880, 745 cm^{-1}. HR-MS (ESI) m/z: calcd. for $C_{15}H_9F_6O_4$ $[M+H]^+$: 367.0395; found: 367.0399.



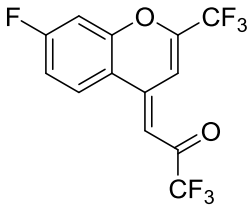
(*E*)-1,1,1-trifluoro-3-(6-nitro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3k)

Obtained as a pale yellow solid in 72% yield (127 mg). Mp: 113–115 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.41. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.67 – 8.34 (m, 2H), 7.64 (d, *J* = 9.1 Hz, 1H), 6.88 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.5 (s, 3F), -78.3 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3 (q, *J* = 35.2 Hz), 155.2 (s), 146.4 (q, *J* = 39.2 Hz), 145.5 (s), 141.9 (s), 128.1 (s), 120.5 (s), 120.0 (s), 119.6 (s), 118.4 (q, *J* = 273.4 Hz), 116.1 (q, *J* = 292.9 Hz), 106.1 (q, *J* = 3.6 Hz), 104.3 (s). IR (ATR): ν 3085, 2927, 1654, 1546, 1464, 1353, 1198, 1144, 1079, 912, 844, 732 cm^{-1}. HR-MS (ESI) m/z: calcd. for $C_{13}H_6NF_6O_4$ $[M+H]^+$: 354.0195; found: 354.0170.



(*E*)-1,1,1-trifluoro-3-(6-fluoro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3l)

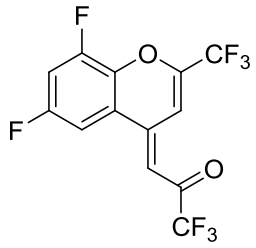
Obtained as a pale yellow solid in 85% yield (139 mg). Mp: 89–91 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.52. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.39 (m, 2H), 6.64 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.2 (s, 3F), -112.2 (dd, *J* = 12.7, 7.9 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 34.4 Hz), 160.2 (d, *J* = 249.5 Hz), 148.5 (d, *J* = 5.8 Hz), 146.7 (q, *J* = 38.8 Hz), 143.7 (d, *J* = 10.1 Hz), 122.0 (d, *J* = 25.2 Hz), 121.0 (d, *J* = 9.1 Hz), 120.3 (d, *J* = 8.1 Hz), 118.6 (q, *J* = 273.4 Hz), 116.4 (q, *J* = 291.4 Hz), 109.2 (d, *J* = 24.7 Hz), 105.0 (q, *J* = 3.7 Hz), 102.1 (s). IR (ATR): ν 2254, 1693, 1653, 1556, 1482, 1273, 1208, 1155, 1085, 903, 722, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5F_7O_2$: 326.0178; found: 326.0170.



(*E*)-1,1,1-trifluoro-3-(7-fluoro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3m)

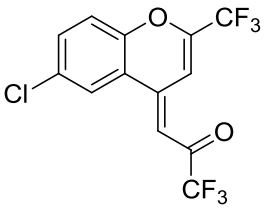
Obtained as a pale yellow solid in 93% yield (151 mg). Mp: 86–89 ℃. R_f (petroleum ether) = 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.00 (dd, *J* = 8.9, 5.8 Hz, 1H), 7.28 – 7.11 (m, 2H), 6.70 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.2 (s, 3F), -101.8 (dd, *J* = 13.9, 7.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 34.3 Hz), 165.5 (d, *J* = 258.6 Hz), 153.2 (d, *J* = 13.0 Hz), 146.6 (q, *J* = 38.9 Hz), 143.6 (s), 125.9 (d, *J* = 10.2 Hz), 118.6 (q, *J* = 273.2 Hz), 116.4 (q, *J* = 291.5 Hz), 115.6 (s), 115.5 (d, *J* = 23.2 Hz), 105.9 (q, *J* = 4.3 Hz), 105.8 (d, *J* = 25.2 Hz), 101.6

(s). IR (ATR): ν 2254, 1694, 1654, 1618, 1556, 1207, 1156, 1032, 903, 722, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5F_7O_2$: 326.0178; found: 326.0171.



(*E*)-3-(6,8-difluoro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3n)

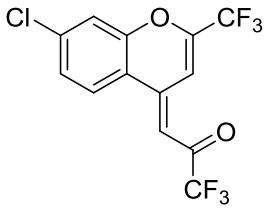
Obtained as a pale yellow solid in 89% yield (153 mg). Mp: 94–98 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.28 (t, *J* = 9.2 Hz, 1H), 6.64 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.4 (s, 3F), -109.2 – -109.3 (m, 1F), -123.6 – -130.0 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 34.8 Hz), 159.2 (dd, *J* = 251.5, 10.5 Hz), 151.9 (dd, *J* = 260.6, 13.1 Hz), 146.2 (q, *J* = 39.3 Hz), 142.1 (t, *J* = 2.8 Hz), 138.1 (dd, *J* = 12.3, 3.0 Hz), 121.5 (d, *J* = 9.4 Hz), 118.5 (q, *J* = 273.4 Hz), 116.2 (q, *J* = 291.4 Hz), 109.2 (dd, *J* = 28.1, 20.3 Hz), 105.3 (q, *J* = 3.7 Hz), 104.4 (dd, *J* = 24.2, 4.0 Hz), 103.3 (s). IR (ATR): ν 2257, 1698, 1656, 1562, 1269, 1079, 904, 724, 649, 622 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_4F_8O_2$: 344.0084; found: 344.0078.



(*E*)-3-(6-chloro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3o)

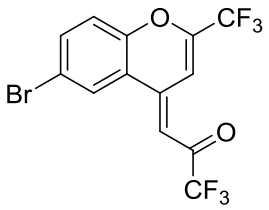
Obtained as a pale yellow solid in 99% yield (169 mg). Mp: 118–120 ℃. R_f (petroleum ether : ethyl ether =20 : 1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.92 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.68 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ

179.1 (q, *J* = 34.5 Hz), 150.6 (s), 146.6 (q, *J* = 39.0 Hz), 143.1 (s), 134.1 (s), 132.7 (s), 123.2 (s), 120.5 (s), 120.2 (s), δ 118.6 (q, *J* = 273.4 Hz), 116.3 (q, *J* = 291.5 Hz), 105.6 (q, *J* = 3.7 Hz), 102.2 (s). IR (ATR): ν 2258, 1690, 1578, 1382, 1287, 1215, 1158, 1089, 903, 656 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5ClF_6O_2$: 341.9882; found: 341.9878.



(*E*)-3-(7-chloro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3p)

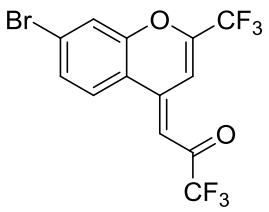
Obtained as a pale yellow solid in 99% yield (169 mg). Mp: 106–108 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.59. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.49 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 1H), 6.72 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.5 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.2 Hz), 152.3 (s), 146.5 (q, *J* = 38.8 Hz), 143.4 (s), 140.1 (s), 127.5 (s), 124.8 (s), 119.0 (s), 118.6 (q, *J* = 273.3 Hz), 117.6 (s), 116.4 (q, *J* = 291.6 Hz), 105.9 (q, *J* = 3.7 Hz), 101.9 (s). IR (ATR): ν 2278, 1658, 1590, 1437, 1398, 1277, 1239, 1212, 913, 742, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5ClF_6O_2$: 341.9882; found: 341.9885.



(*E*)-3-(6-bromo-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3q)

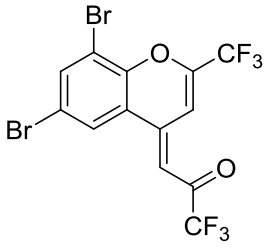
Obtained as a pale yellow solid in 93% yield (180 mg). Mp: 130–133 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s,

1H), 8.07 (s, 1H), 7.79 (d, *J* = 8.9 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.68 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.4 Hz), 151.0 (s), 146.5 (q, *J* = 38.8 Hz), 142.9 (s), 136.9 (s), 126.3 (s), 120.7 (q, *J* = 4.2 Hz), 120.6 (s), 120.1 (s), 118.9 (q, *J* = 273.3 Hz), 116.5 (q, *J* = 291.7 Hz), 105.7 (q, *J* = 3.7 Hz), 102.2 (s). IR (ATR): ν 3072, 1692, 1650, 1554, 1464, 1272, 1196, 1144, 1033, 904, 830, 728 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5BrF_6O_2$: 385.9377; found: 385.9372.



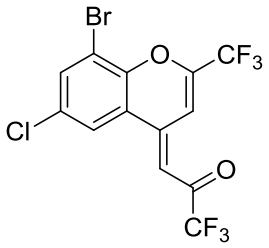
(*E*)-3-(7-bromo-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3r)

Obtained as a pale yellow solid in 97% yield (188 mg). Mp: 110–113 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.67 (s, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 6.73 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.3 Hz), 152.2 (s), 146.4 (q, *J* = 39.0 Hz), 143.5 (s), 130.3 (s), 128.1 (s), 124.8 (s), 122.1 (s), 118.5 (q, *J* = 273.5 Hz), 116.4 (q, *J* = 291.6 Hz), 118.0 (s), 105.9 (q, *J* = 3.7 Hz), 102.0 (s). IR (ATR): ν 2254, 1654, 1557, 1438, 1400, 1365, 1272, 1239, 1198, 1101, 903, 723, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_5BrF_6O_2$: 385.9377; found: 385.9372.



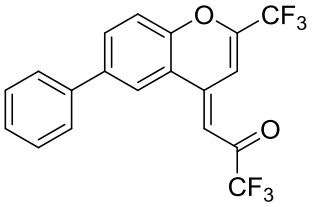
(*E*)-3-(6,8-dibromo-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3s)

Obtained as a pale yellow solid in 86% yield (200 mg). Mp: 93–96 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.04 – 8.00 (m, 2H), 6.68 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.7 Hz), 148.0 (s), 146.5 (q, *J* = 39.4 Hz), 142.3 (s), 139.6 (s), 125.4 (s), 121.6 (s), 119.8 (s), 118.4 (q, *J* = 273.5 Hz), 116.2 (q, *J* = 291.5 Hz), 114.2 (s), 106.0 (q, *J* = 3.6 Hz), 103.4 (s). IR (ATR): ν 2254, 1656, 1560, 1453, 1388, 1361, 1298, 1269, 1204, 1160, 1084, 903, 722, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_4Br_2F_6O_2$: 463.8482; found: 463.8485.



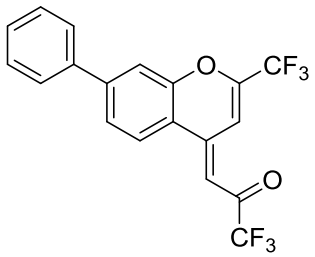
(*E*)-3-(8-bromo-6-chloro-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3t)

Obtained as a pale yellow solid in 89% yield (187 mg). Mp: 86–89 ℃. R_f (petroleum ether) = 0.37. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 7.90 (s, 1H), 7.86 (s, 1H), 6.68 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.2 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.9 Hz), 147.6 (s), 146.6 (q, *J* = 39.3 Hz), 142.4 (s), 137.0 (s), 132.6 (s), 122.3 (s), 121.2 (s), 118.4 (q, *J* = 273.5 Hz), 116.2 (q, *J* = 291.4 Hz), 114.0 (s), 105.9 (q, *J* = 3.7 Hz), 103.4 (s). IR (ATR): ν 3113, 2925, 1556, 1453, 1359, 1267, 1197, 1047, 904, 728, 647 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{13}H_4BrClF_6O_2$: 419.8987; found: 419.8985.



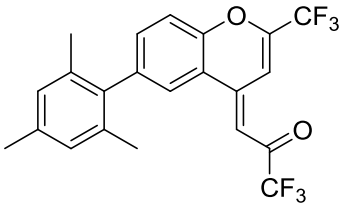
(*E*)-1,1,1-trifluoro-3-(6-phenyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3u)

Obtained as a pale yellow solid in 99% yield (190 mg). Mp: 127–130 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.08 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.73 – 7.45 (m, 6H), 6.81 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.1 Hz), 151.6 (s), 146.5 (q, *J* = 38.8 Hz), 144.6 (s), 140.3 (s), 139.0 (s), 133.2 (s), 129.2 (s), 128.4 (s), 127.3 (s), 121.6 (s), 119.4 (s), 119.2 (s), 118.8 (q, *J* = 273.3 Hz), 116.5 (q, *J* = 291.6 Hz), 105.8 (q, *J* = 3.6 Hz), 101.5 (s). IR (ATR): ν 2922, 1644, 1541, 1474, 1390, 1270, 1202, 1142, 1010, 903, 828, 723, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{19}H_{10}F_6O_2$: 384.0585; found: 384.0577.



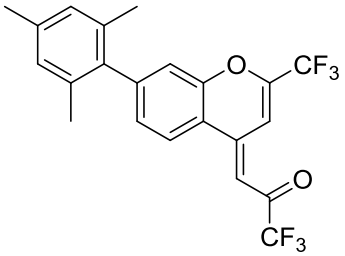
(*E*)-1,1,1-trifluoro-3-(7-phenyl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3v)

Obtained as a pale yellow solid in 99% yield (190 mg). Mp: 132–135 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.55. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.80 – 7.62 (m, 4H), 7.59 – 7.45 (m, 3H), 6.77 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 33.9 Hz), 152.6 (s), 147.2 (s), 146.8 (q, *J* = 38.5 Hz), 144.4 (s), 138.0 (s), 129.3 (s), 129.2 (s), 127.2 (s), 125.6 (s), 124.1 (s), 118.8 (q, *J* = 273.3 Hz), 117.8 (s), 116.6 (s), 116.5 (q, *J* = 291.7 Hz), 105.8 (q, *J* = 3.7 Hz), 101.2 (s). IR (ATR): ν 2254, 1690, 1651, 1551, 1268, 1206, 1153, 1018, 903, 824, 723, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{19}H_{10}F_6O_2$: 384.0585; found: 384.0574.



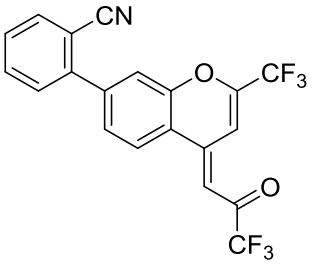
(*E*)-1,1,1-trifluoro-3-(6-mesityl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3w)

Obtained as a pale yellow solid in 89% yield (189 mg). Mp: 157–159 ℃. R_f (petroleum ether) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.02 (s, 1H), 7.77 – 7.70 (m, 2H), 7.20 (s, 2H), 6.95 (s, 1H), 2.55 (s, 3H), 2.27 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 33.9 Hz), 151.3 (s), 146.8 (q, *J* = 38.5 Hz), 144.7 (s), 140.6 (s), 137.7 (s), 136.8 (s), 135.9 (s), 135.7 (s), 128.7 (s), 124.3 (s), 119.4 (s), 119.2 (s), 119.1 (q, *J* = 273.2 Hz), 116.7 (q, *J* = 291.8 Hz), 105.9 (q, *J* = 3.7 Hz), 101.6 (s), 21.0 (s), 20.7 (s). IR (ATR): ν 2254, 1692, 1651, 1553, 1469, 1273, 1030, 903, 832, 723, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{22}H_{16}F_6O_2$: 426.1054; found: 426.1052.



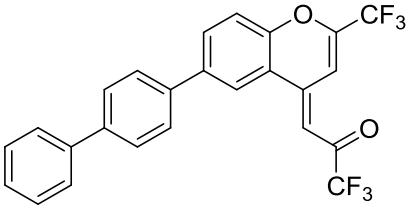
(*E*)-1,1,1-trifluoro-3-(7-mesityl-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3x)

Obtained as a pale yellow solid in 87% yield (185 mg). Mp: 171–173 ℃. R_f (petroleum ether) = 0.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.01 (s, 2H), 6.80 (s, 1H), 2.38 (s, 3H), 2.06 (s, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 34.1 Hz), 152.3 (s), 148.3 (s), 146.8 (q, *J* = 38.5 Hz), 144.6 (s), 137.9 (s), 136.2 (s), 135.3 (s), 128.6 (s), 128.5 (s), 119.5 (s), 118.8 (q, *J* = 273.4 Hz), 117.6 (s), 116.6 (q, *J* = 291.8 Hz), 105.9 (q, *J* = 3.8 Hz), 102.0 (s), 101.2 (s), 21.0 (s), 20.6 (s). IR (ATR): ν 2958, 2253, 1651, 1553, 1272, 1205, 1151, 1020, 904, 824, 727, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{22}H_{16}F_6O_2$: 426.1054; found: 426.1055.



(*E*)-2-(4-(3,3,3-trifluoro-2-oxopropylidene)-2-(trifluoromethyl)-4*H*-chromen-7-yl)benzonitrile (3y)

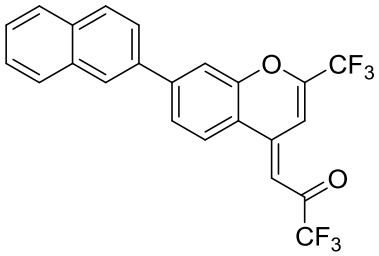
Obtained as a pale yellow solid in 77% yield (157 mg). Mp: 168–171 ℃. R_f (petroleum ether : ethyl ether = 5 : 1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.65 – 7.57 (m, 2H), 6.82 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.3 Hz), 152.1 (s), 146.8 (q, *J* = 38.8 Hz), 142.4 (s), 134.1 (s), 133.3 (s), 133.1 (s), 132.9 (s), 130.6 (s), 129.9 (s), 129.2 (q, *J* = 7.1 Hz), 127.3 (s), 124.2 (s), 121.7 (s), 119.1 (q, *J* = 7.0 Hz), 118.4 (q, *J* = 273.5 Hz), 117.9 (s), 116.4 (q, *J* = 291.8 Hz), 115.0 (s), 111.3 (s). IR (ATR): ν 2254, 1656, 1406, 1368, 1158, 1097, 1018, 903, 824, 722, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{20}H_9F_6NO_2$: 409.0537; found: 409.0533.



(*E*)-3-(6-([1,1'-biphenyl]-4-yl)-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)-1,1,1-trifluoropropan-2-one (3z)

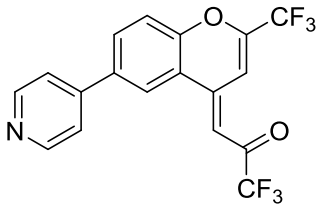
Obtained as a pale yellow solid in 99% yield (228 mg). Mp: 138–141 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.13 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.86 – 7.64 (m, 6H), 7.63 – 7.48 (m, 3H), 7.43 (t, *J* = 6.8 Hz, 1H), 6.84 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.2 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.3 (q, *J* = 34.9 Hz), 151.7 (s), 146.8 (s), 146.4 (s), 144.6 (s), 141.4 (s), 140.2 (s), 139.9 (s), 137.8 (s), 133.1 (s), 129.0 (s), 127.9 (s), 127.7 (q, *J* = 6.5 Hz), 127.1 (s), 121.5 (s), 119.4 (s), 119.2 (s), 118.2 (q, *J* =

273.5 Hz), 116.2 (q, *J* = 291.4 Hz), 105.8 (q, *J* = 3.7 Hz), 101.5 (s). IR (ATR): ν 2257, 1691, 1648, 1550, 1478, 1368, 1271, 1198, 1143, 1101, 905, 825, 729 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{25}H_{14}F_6O_2$: 460.0898; found: 460.0889.



(*E*)-1,1,1-trifluoro-3-(7-(naphthalen-2-yl)-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3aa)

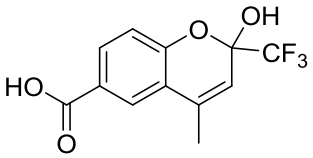
Obtained as a pale yellow solid in 85% yield (184 mg). Mp: 198–201 ℃. R_f (petroleum ether : ethyl ether = 20 : 1) = 0.44. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.15 (s, 1H), 8.10 – 7.88 (m, 4H), 7.85 – 7.78 (m, 3H), 7.65 – 7.53 (m, 2H), 6.78 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.3 (s, 3F), -78.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0 (q, *J* = 33.5 Hz), 152.7 (s), 147.1 (s), 146.8 (q, *J* = 38.6 Hz), 144.4 (s), 135.3 (s), 133.4 (q, *J* = 5.6 Hz), 129.2 (s), 128.5 (s), 127.8 (s), 127.1 (s), 126.9 (s), 126.7 (s), 125.8 (s), 124.5 (s), 124.2 (s), 118.3 (q, *J* = 273.5 Hz), 118.0 (s), 117.9 (s), 116.8 (s), 116.2 (q, *J* = 291.4 Hz), 105.9 (q, *J* = 3.7 Hz), 101.2 (s). IR (ATR): ν 2957, 2925, 1650, 1550, 1449, 1270, 1201, 1142, 1100, 904, 723, 650 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{23}H_{12}F_6O_2$: 434.0741; found: 434.0739.



(*E*)-1,1,1-trifluoro-3-(6-(pyridin-4-yl)-2-(trifluoromethyl)-4*H*-chromen-4-ylidene)propan-2-one (3ab)

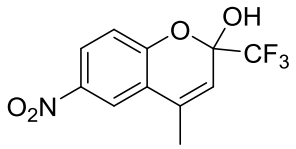
Obtained as a pale yellow solid in 78% yield (150 mg). Mp: 155–158 ℃. R_f (ethyl ether) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 5.6 Hz, 2H), 8.53 (s, 1H), 8.13 (d, *J* = 2.0 Hz, 1H), 7.95 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.63 – 7.53 (m, 3H), 6.81 (s,

1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.4 (s, 3F), -78.1 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.1 (q, *J* = 34.3 Hz), 152.5 (s), 150.6 (s), 146.6 (q, *J* = 38.7 Hz), 146.1 (s), 143.9 (s), 137.2 (s), 132.7 (s), 122.0 (s), 121.7 (s), 119.9 (s), 119.5 (s), 118.7 (q, *J* = 273.3 Hz), 116.4 (q, *J* = 291.6 Hz), 105.8 (q, *J* = 3.7 Hz), 102.0 (s). IR (ATR): ν 2254, 1652, 1556, 1273, 1239, 1202, 1153, 1111, 903, 723, 649 cm^{-1}. HR-MS (EI) m/z: calcd. for $C_{18}H_9F_6NO_2$: 385.0537; found: 385.0532.



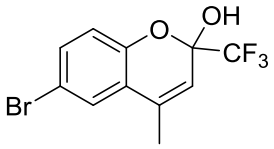
2-hydroxy-4-methyl-2-(trifluoromethyl)-2*H*-chromene-6-carboxylic acid (4j)

Obtained as a pale yellow solid in 38% yield (52 mg). Mp: 47–50 ℃. R_f (petroleum ether : ethyl ether = 1 : 2) = 0.53. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (br s, 1H), 8.63 (br s, 1H), 7.97 (d, J = 2.0 Hz, 1H), 7.91 (dd, J = 8.4, 2.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 1H), 5.89 (s, 1H), 2.22 (d, J = 1.2 Hz, 3H). ^{19}F NMR (376 MHz, DMSO-d_6) δ -83.8 (s). ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.2 (s), 153.9 (s), 134.6 (s), 132.0 (s), 126.1 (s), 125.1 (s), 122.6 (q, J = 280.7 Hz), 120.2 (s), 116.7 (s), 115.2 (s), 94.5 (q, J = 33.1 Hz), 17.9 (s). IR (ATR): ν 3393, 1656, 1530, 1395, 1152, 1035, 968, 912, 747, 624, 535 cm^{-1}. HR-MS (ESI) m/z: calcd. for $C_{12}H_{10}F_3O_4$ $[M+H]^+$: 275.0525; found: 275.0523.



4-methyl-6-nitro-2-(trifluoromethyl)-2*H*-chromen-2-ol (4k)

Obtained as a pale yellow solid in 51% yield (71 mg). Mp: 146–148 ℃. R_f (petroleum ether : ethyl ether = 5 : 1) = 0.33. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.29 (d, J = 2.4 Hz, 1H), 8.22 (dd, J = 8.8, 2.4 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 5.92 (s, 1H), 4.15 (br s, 1H), 2.32 (d, J = 1.6 Hz, 3H). ^{19}F NMR (376 MHz, CD_2Cl_2) δ -85.4 (s). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.6 (s), 144.8 (s), 137.3 (s), 127.8 (s), 123.5 (q, J = 286.6 Hz), 122.2 (s), 122.1 (s), 119.2 (s), 116.3 (s), 96.3 (q, J = 34.5 Hz), 19.8 (s). IR (ATR): ν 3388, 3113, 2926, 1661, 1612, 1511, 1338, 1172, 1114, 955, 737 cm^{-1}. HR-MS (ESI) m/z: calcd. for $C_{11}H_9F_3NO_4$ $[M+H]^+$: 276.0478; found: 276.0477.



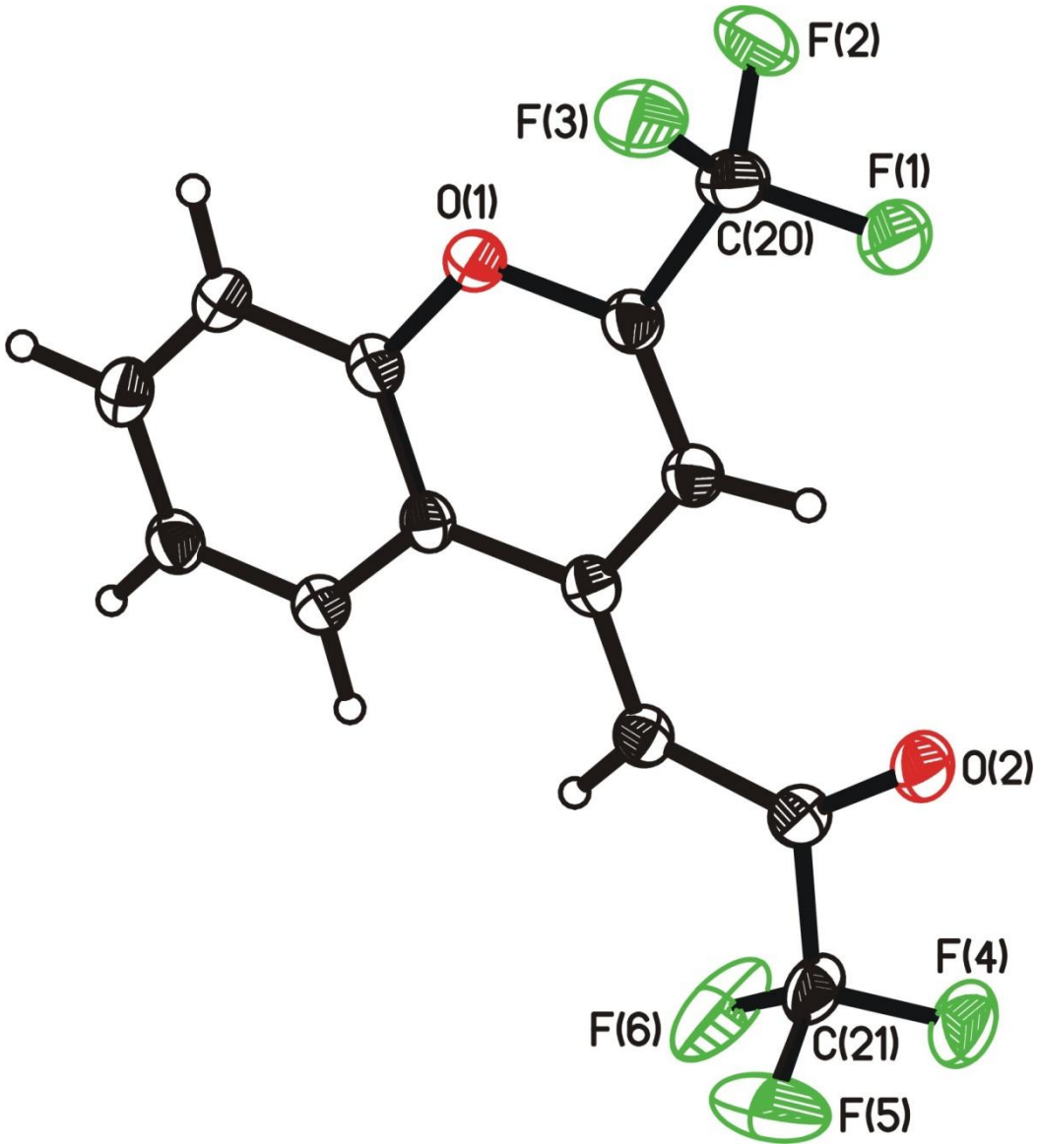
6-bromo-4-methyl-2-(trifluoromethyl)-2*H*-chromen-2-ol (4q)

Obtained as a pale yellow oil in 54% yield (82 mg). R_f (petroleum ether : ethyl ether = 5 : 1) = 0.62. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.3 Hz, 1H), 7.40 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 5.76 (d, *J* = 0.9 Hz, 1H), 3.77 (br s, 1H), 2.19 (d, *J* = 1.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (s, 3F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8 (s), 135.4 (s), 133.0 (s), 126.9 (s), 121.8 (s), 121.7 (q, *J* = 285.6 Hz), 118.4 (s), 114.8 (s), 113.5 (s), 93.7 (q, *J* = 34.2 Hz), 18.0 (s). IR (ATR): ν 3115, 2922, 1650, 1553, 1467, 1271, 1202, 1144, 1033, 904, 728 cm^{-1}. HR-MS (ESI) m/z: calcd. for $C_{11}H_9BrF_3O_2$ $[M+H]^+$: 309.9422; found: 309.9419.

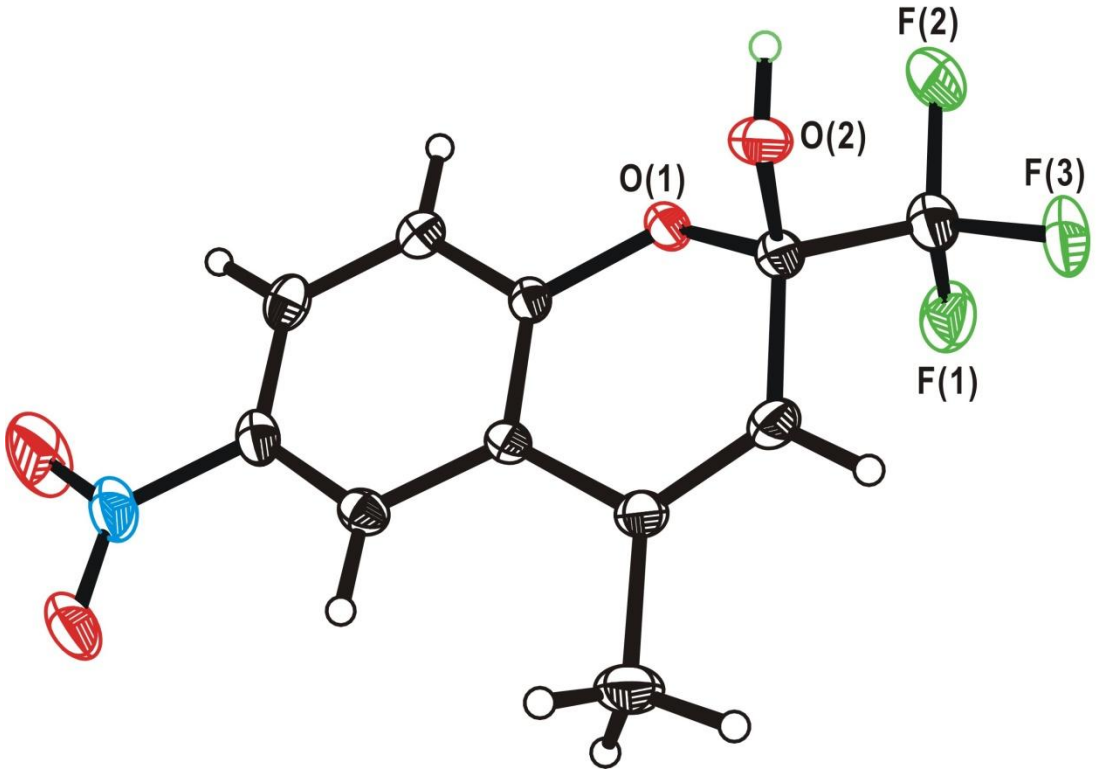
Crystal structure analyses

The crystal samples of **3a** and **4k** were prepared by slow volatilization in diethyl ether. The suitable crystals of **3a** (CCDC 1966094) and **4k** (CCDC 2122313) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ℃, using CuKα radiation (λ 1.54178 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 3a with thermal ellipsoids at the 40% probability level



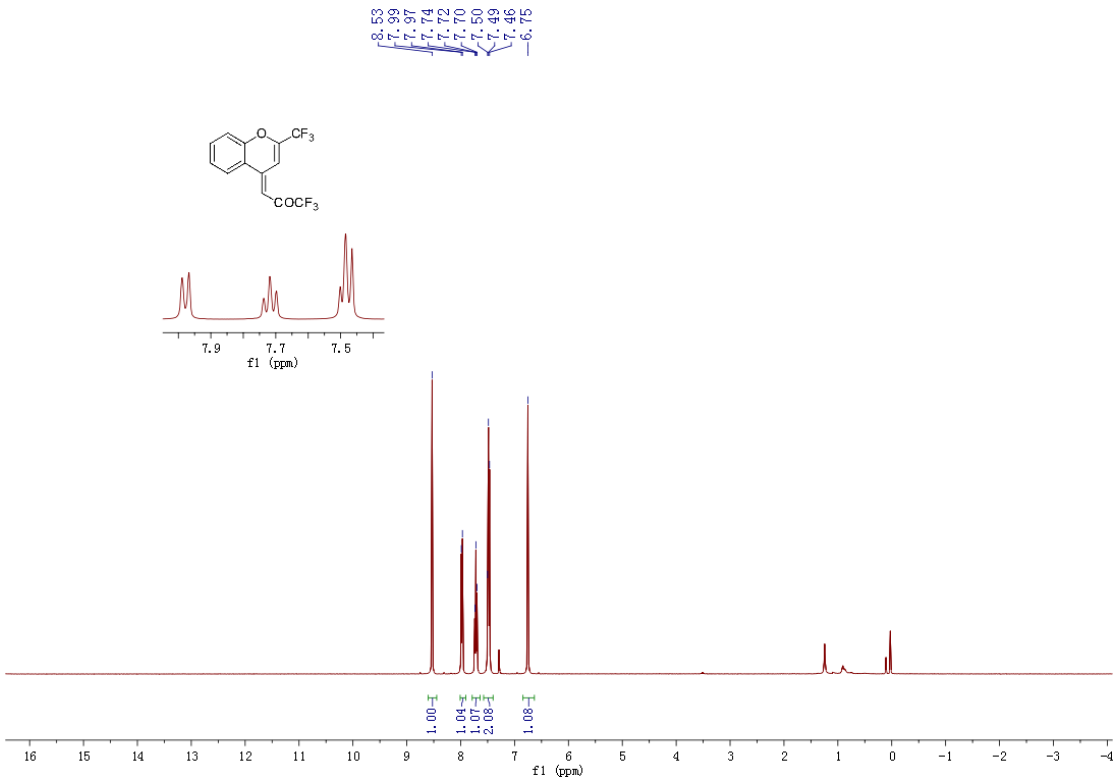
ORTEP diagram of 4k with thermal ellipsoids at the 40% probability level

References:

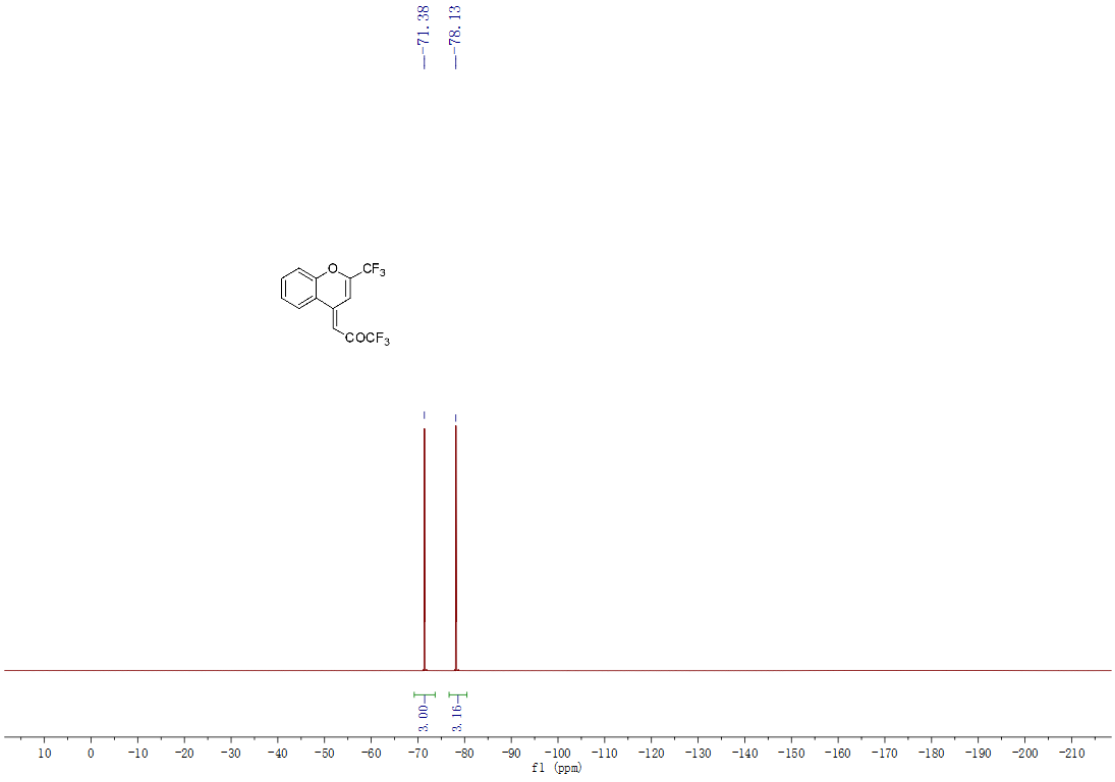
1. A. Seoane, N. Casanova, N. Quiñones, J. L. Mascareñas and M. Gulías, Rhodium(III)-Catalyzed Dearomatizing (3 + 2) Annulation of 2-Alkenylphenols and Alkynes, *J. Am. Chem. Soc.*, 2014, **136**, 7607-7610.
2. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

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

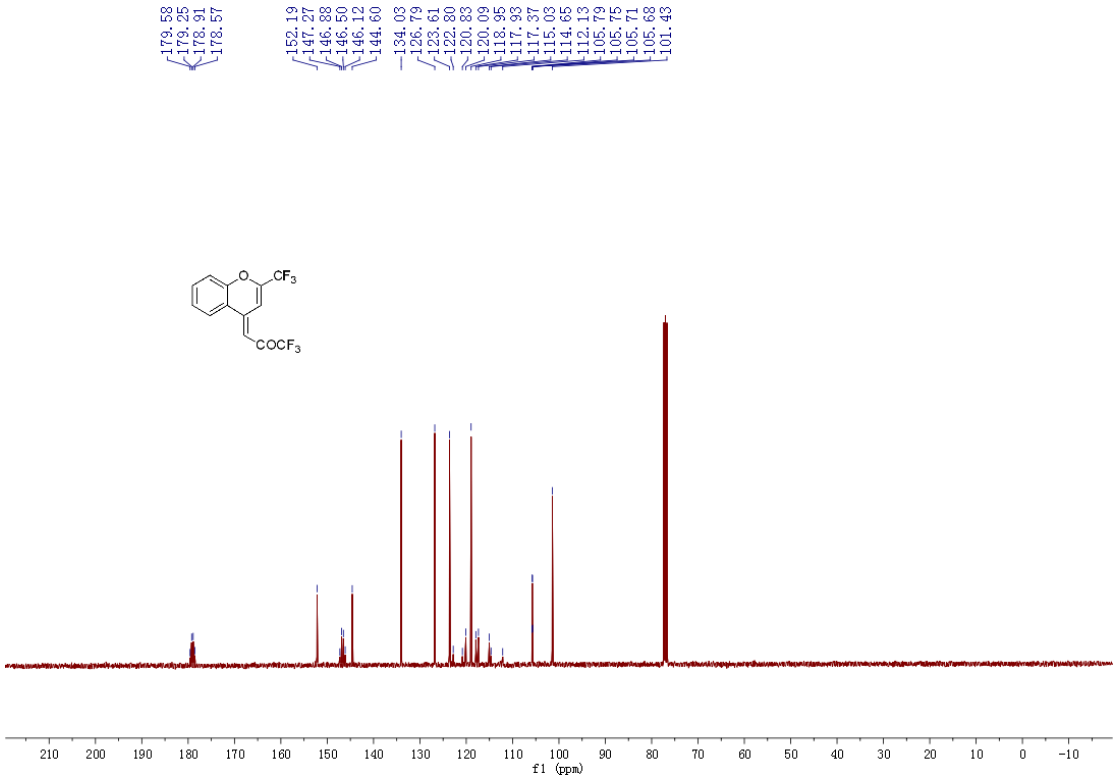
^{1}H NMR spectra of **3a** in $CDCl_3$



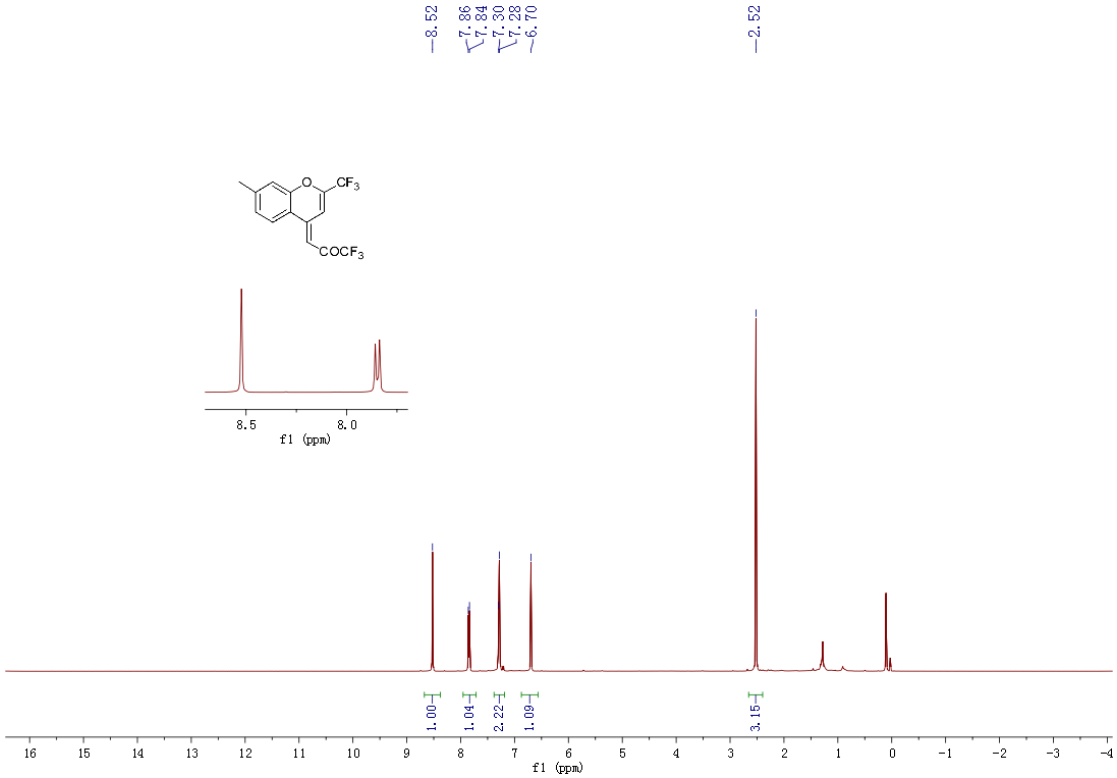
^{19}F NMR spectra of **3a** in $CDCl_3$



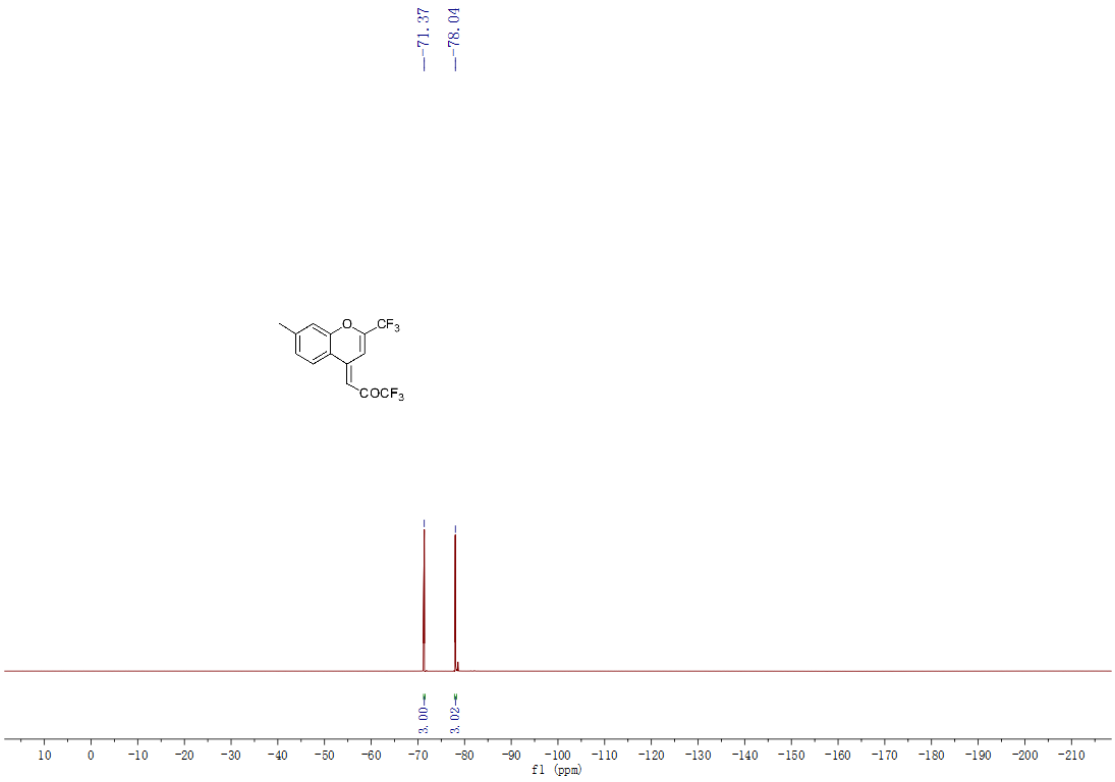
^{13}C NMR spectra of **3a** in $CDCl_3$



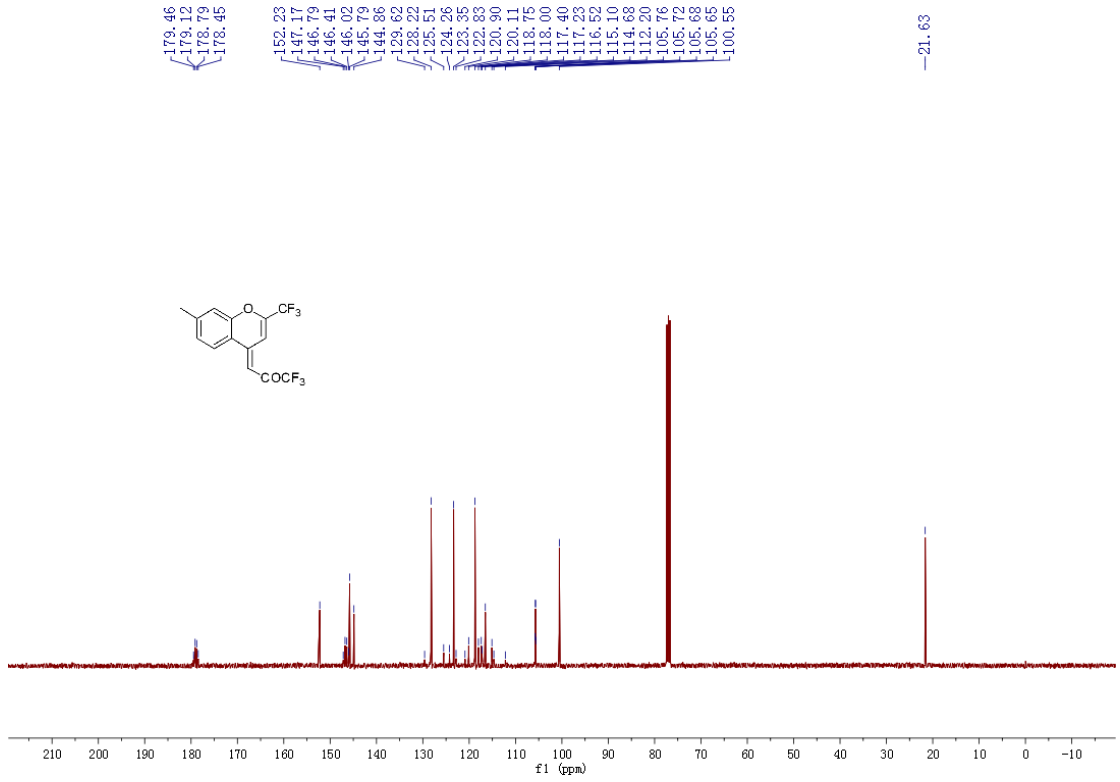
^{1}H NMR spectra of **3b** in $CDCl_3$



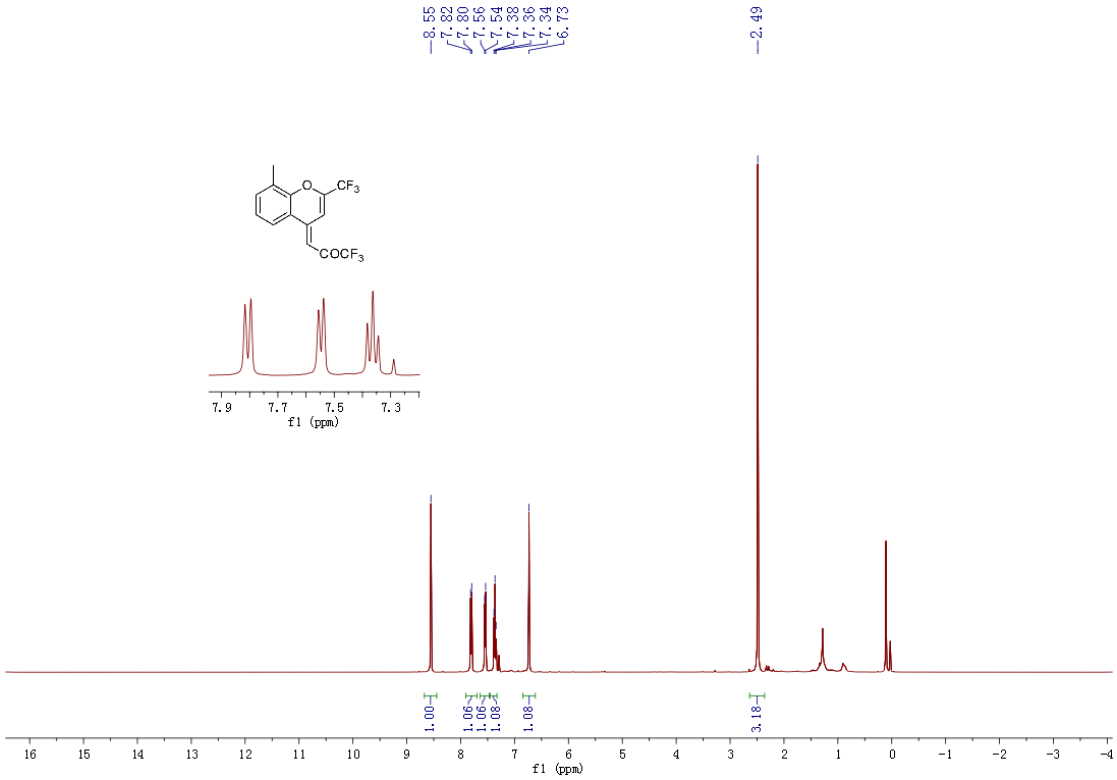
^{19}F NMR spectra of **3b** in $CDCl_3$



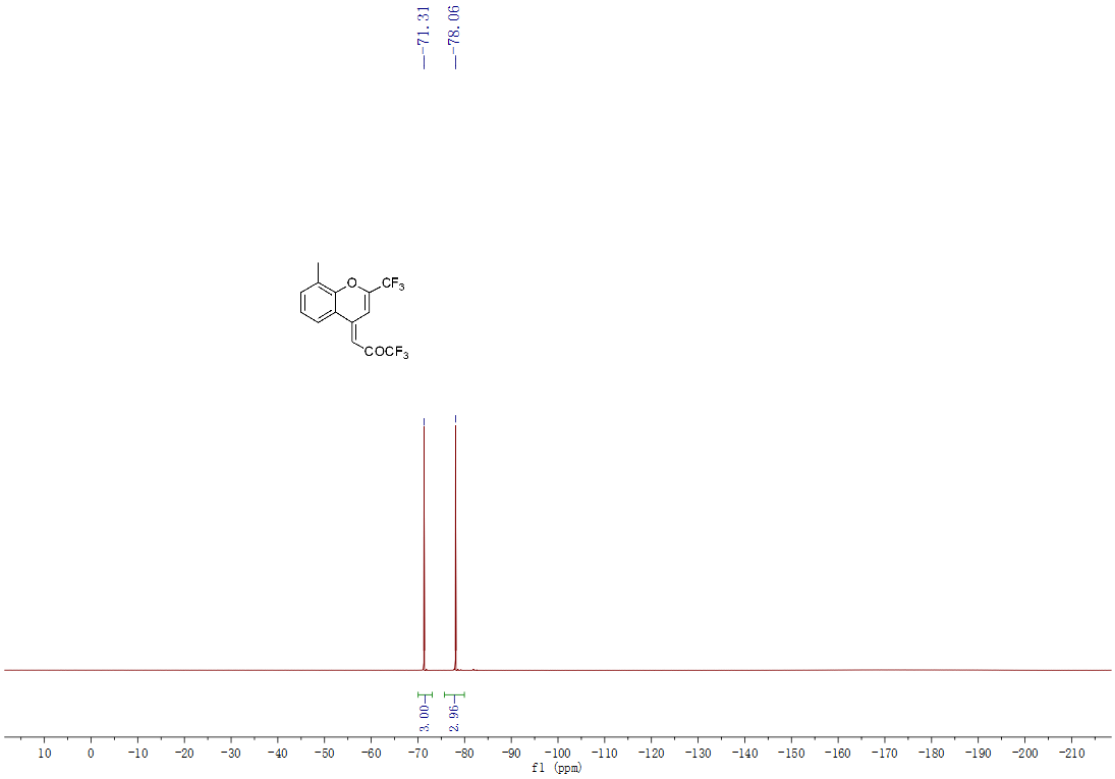
^{13}C NMR spectra of **3b** in $CDCl_3$



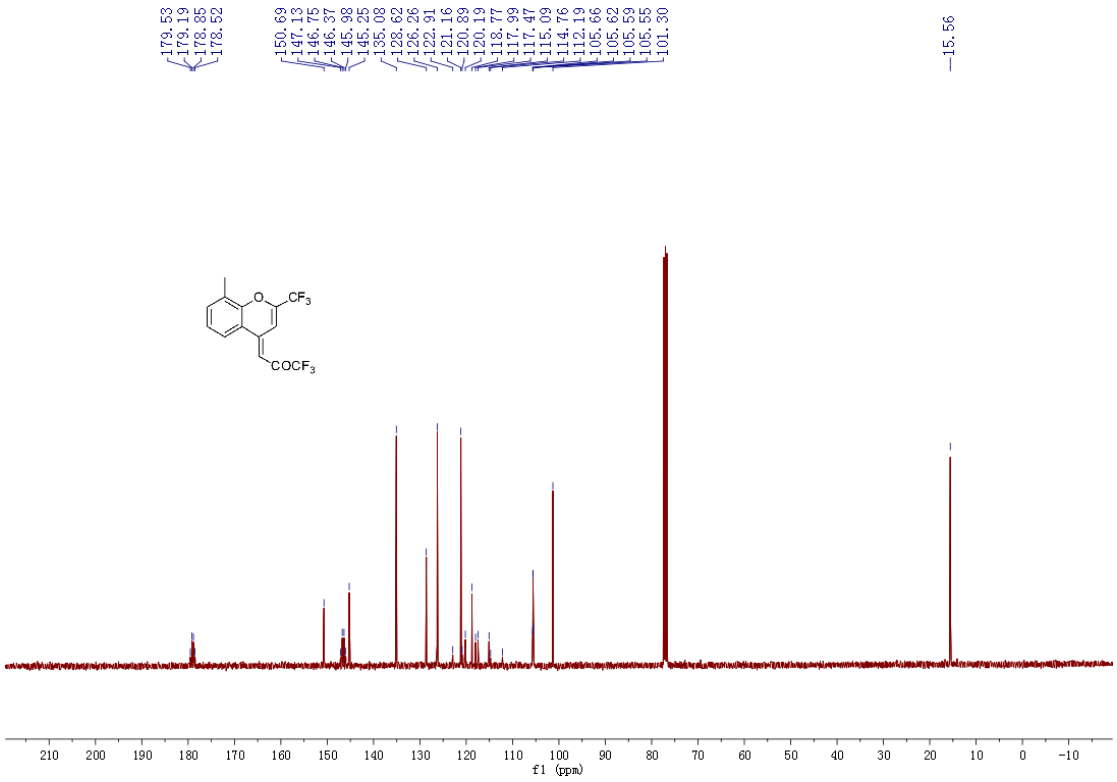
^{1}H NMR spectra of **3c** in $CDCl_3$



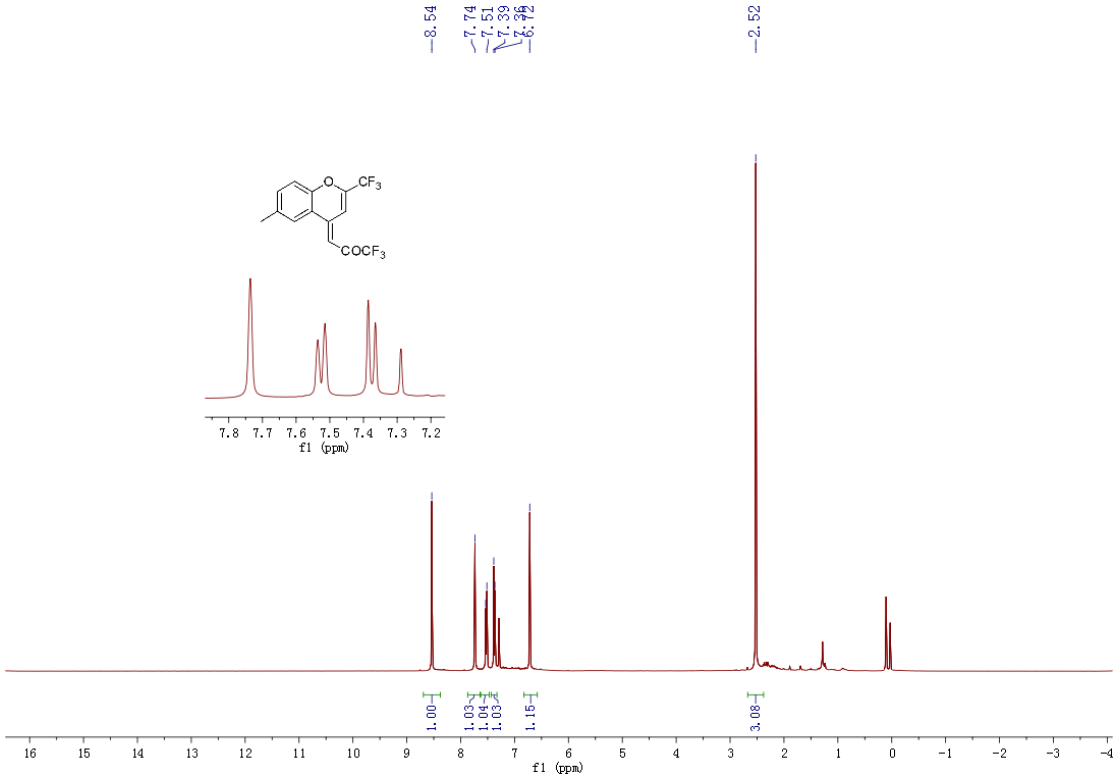
^{19}F NMR spectra of **3c** in $CDCl_3$



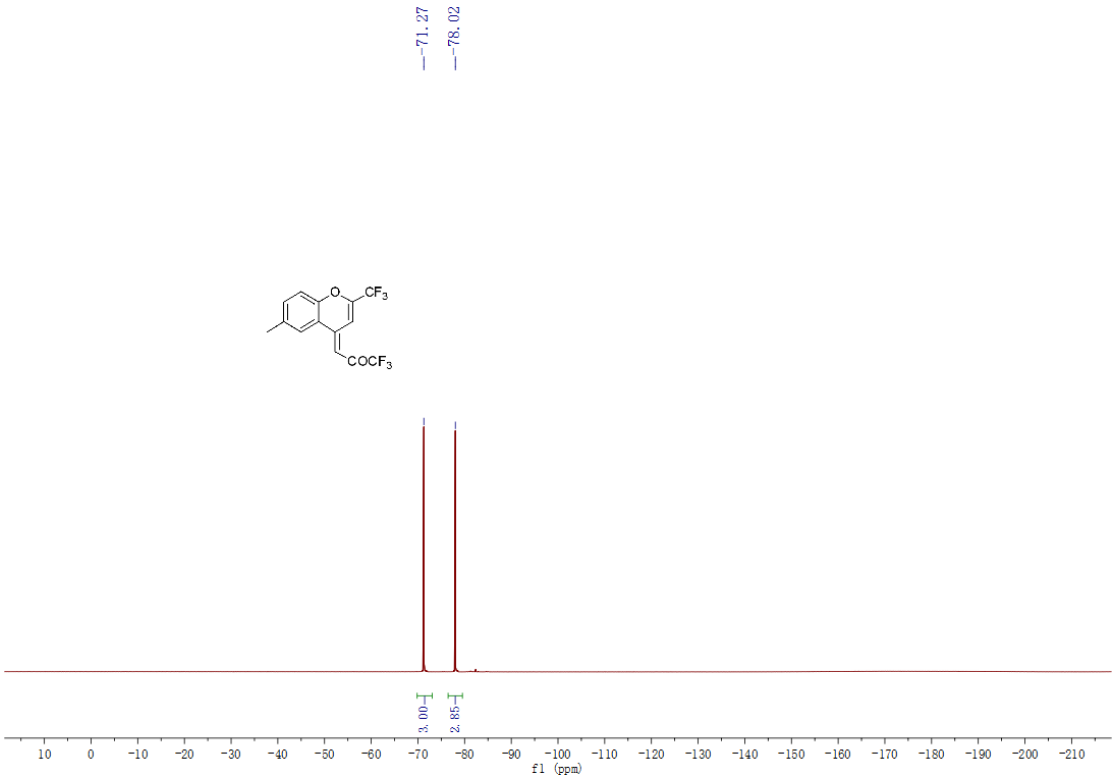
^{13}C NMR spectra of **3c** in $CDCl_3$



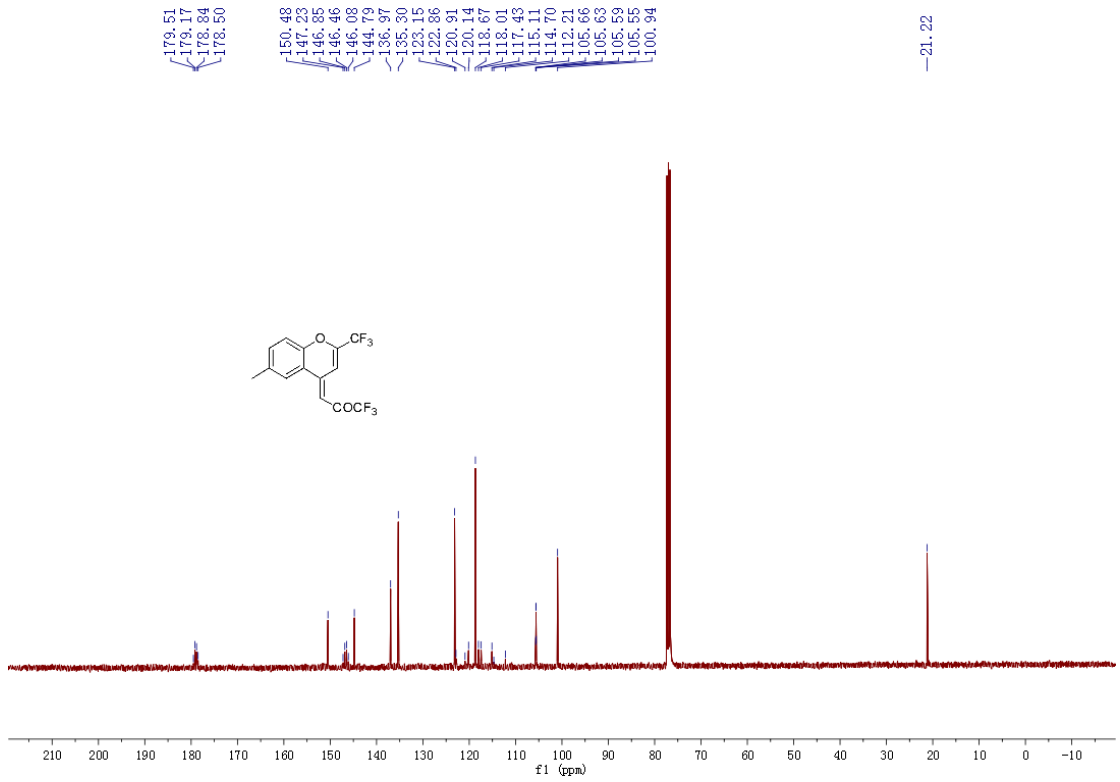
^{1}H NMR spectra of **3d** in $CDCl_3$



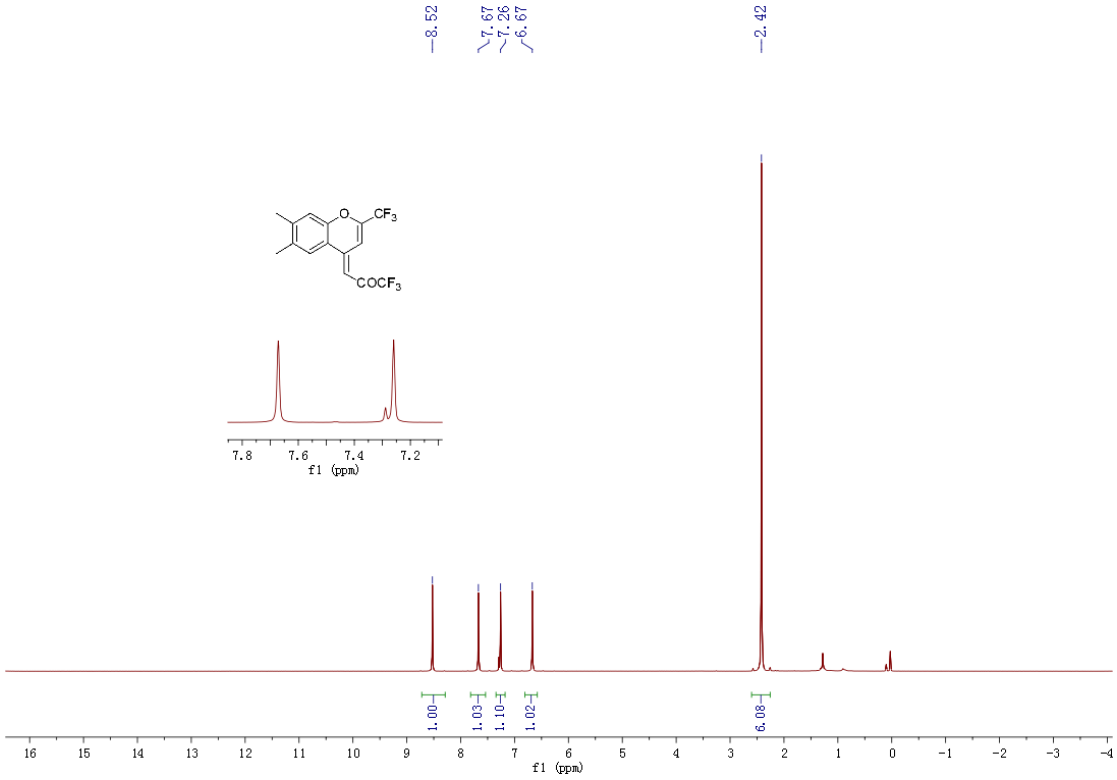
^{19}F NMR spectra of **3d** in $CDCl_3$



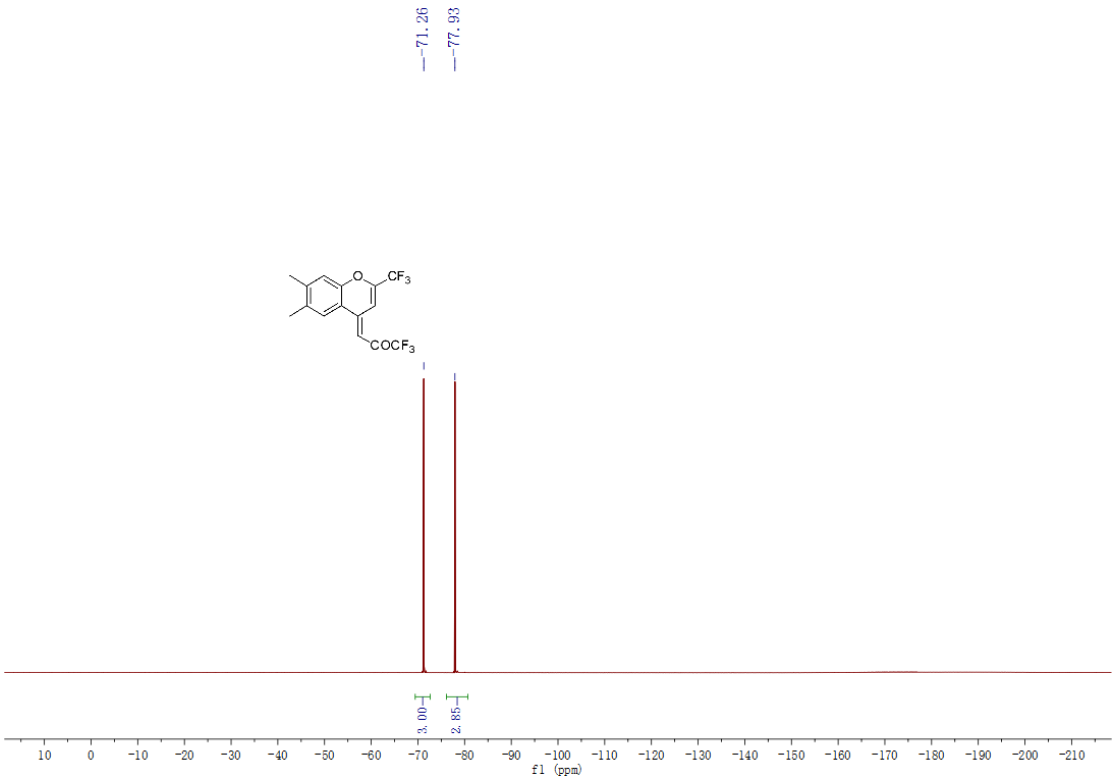
^{13}C NMR spectra of **3d** in $CDCl_3$



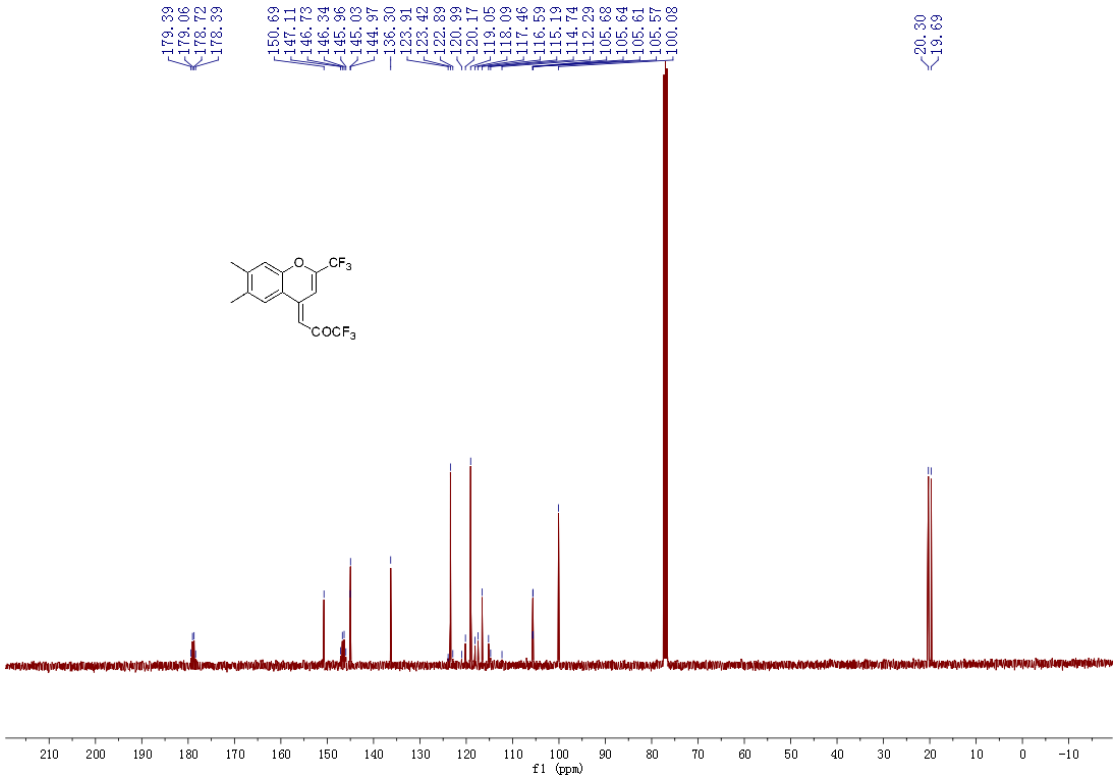
^{1}H NMR spectra of **3e** in $CDCl_3$



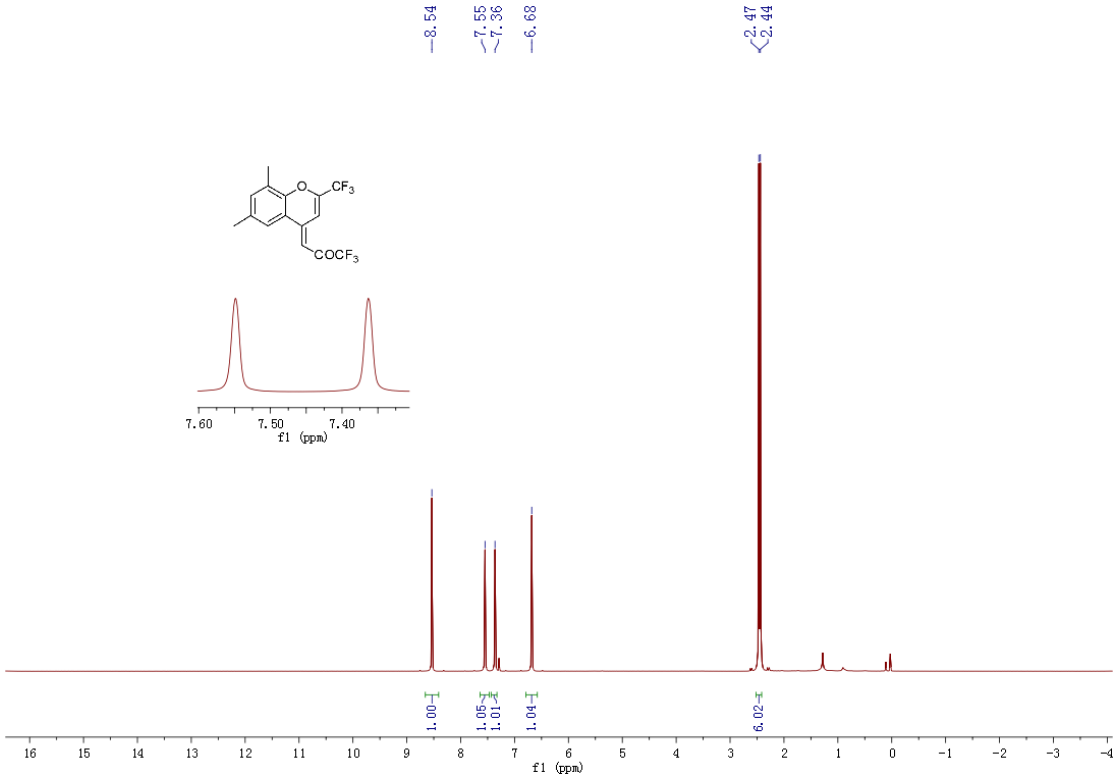
^{19}F NMR spectra of **3e** in $CDCl_3$



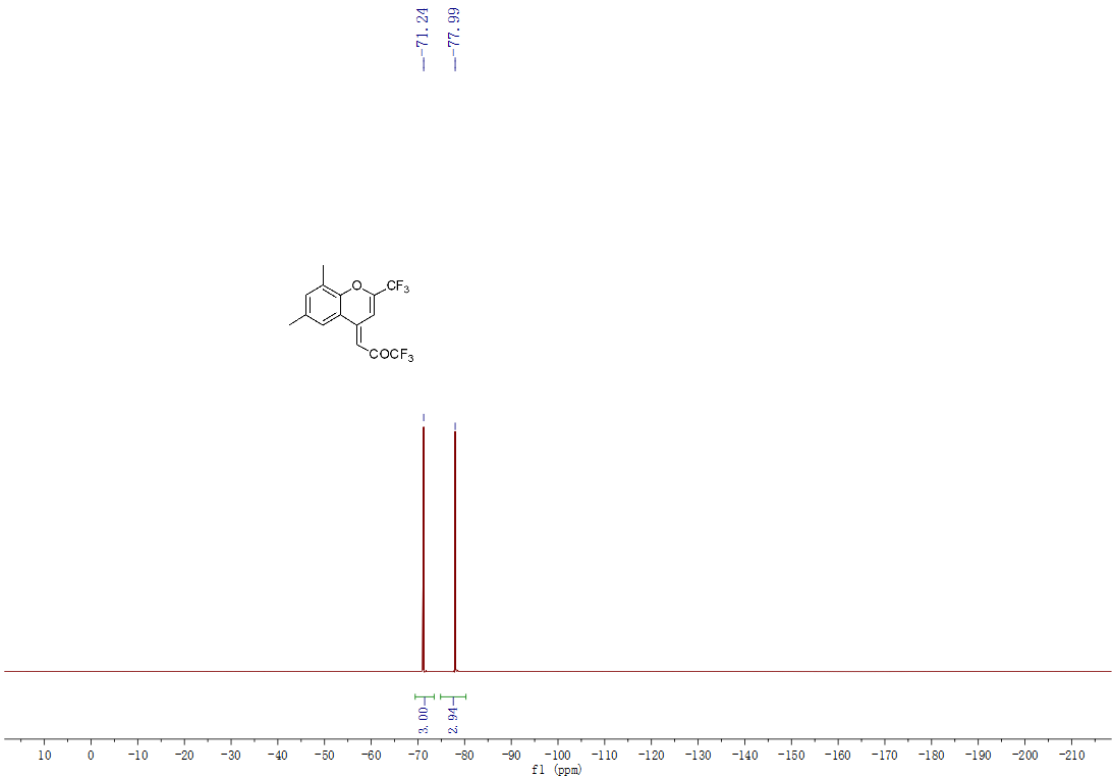
^{13}C NMR spectra of **3e** in $CDCl_3$



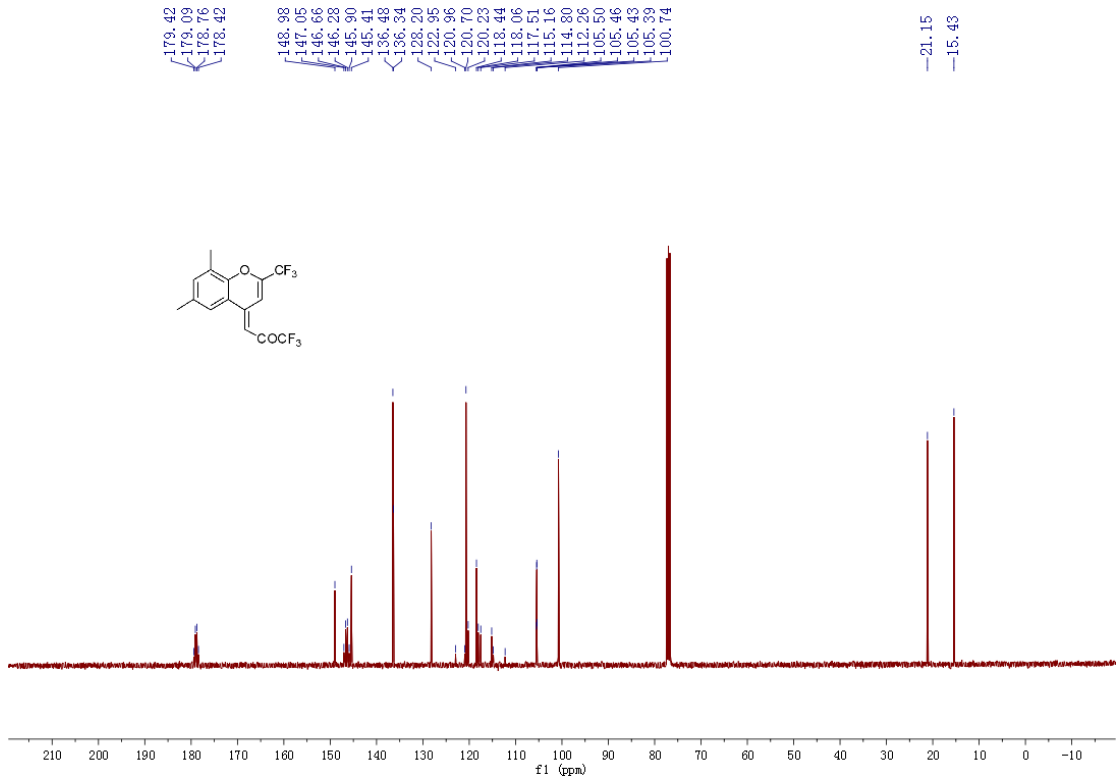
^{1}H NMR spectra of **3f** in $CDCl_3$



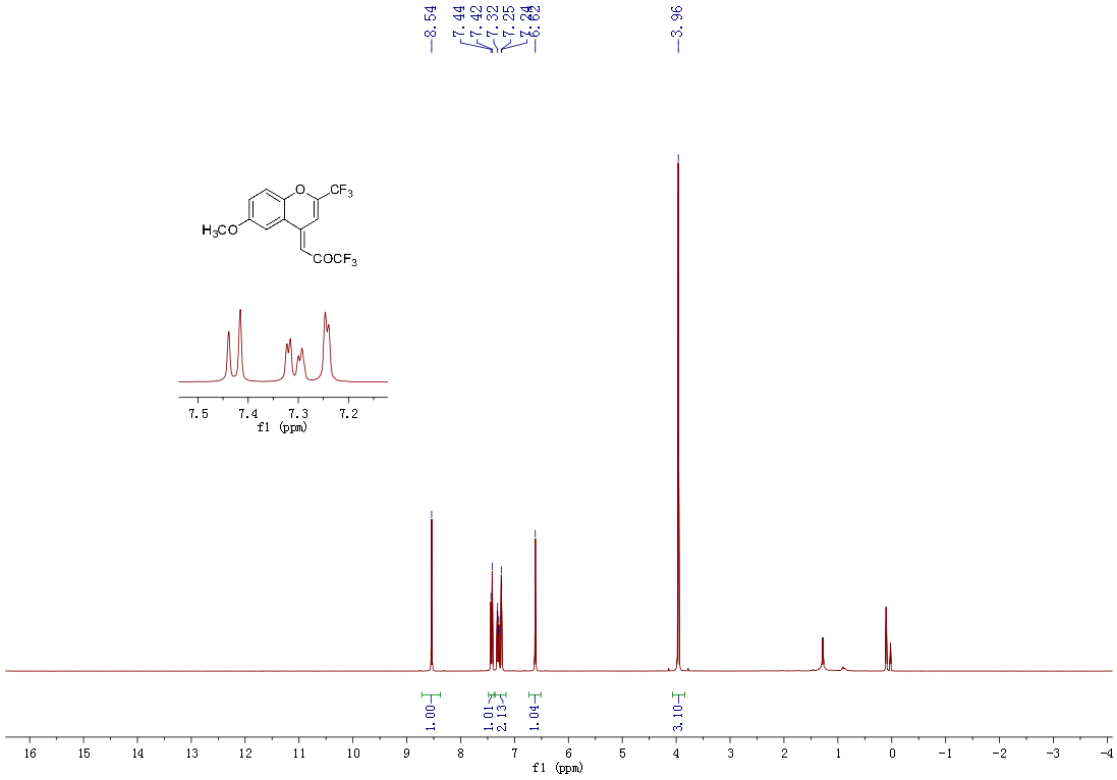
^{19}F NMR spectra of **3f** in $CDCl_3$



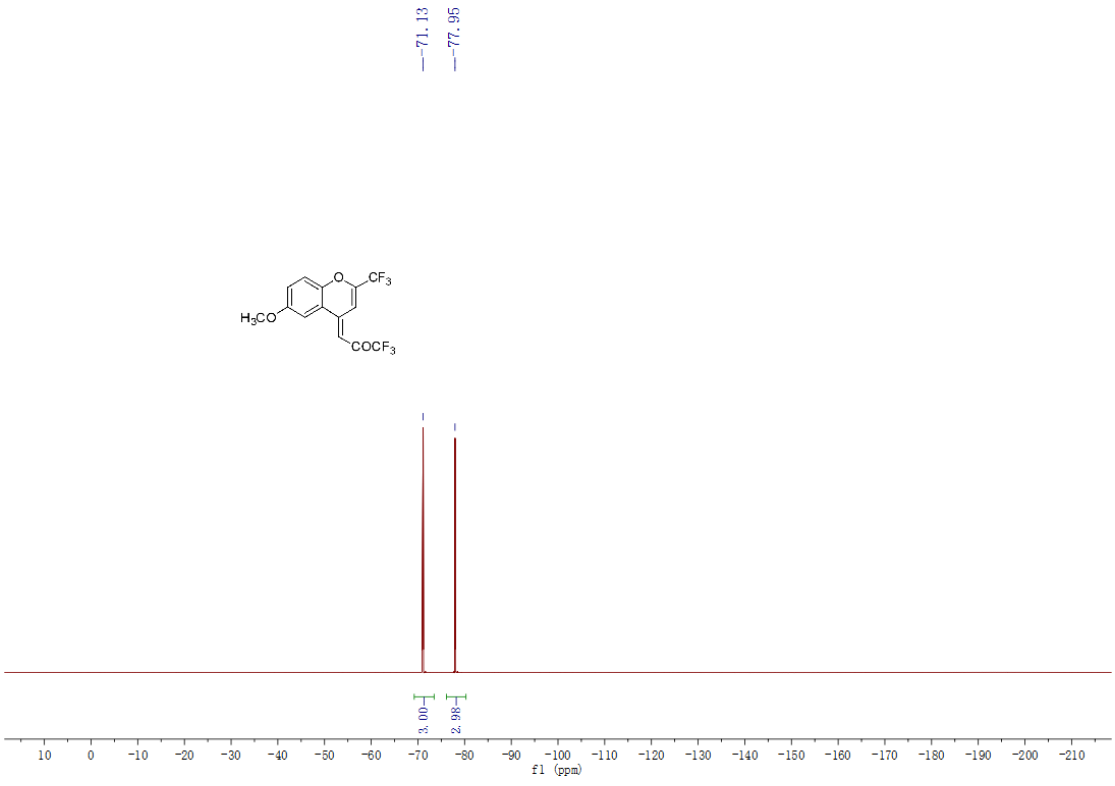
^{13}C NMR spectra of **3f** in $CDCl_3$



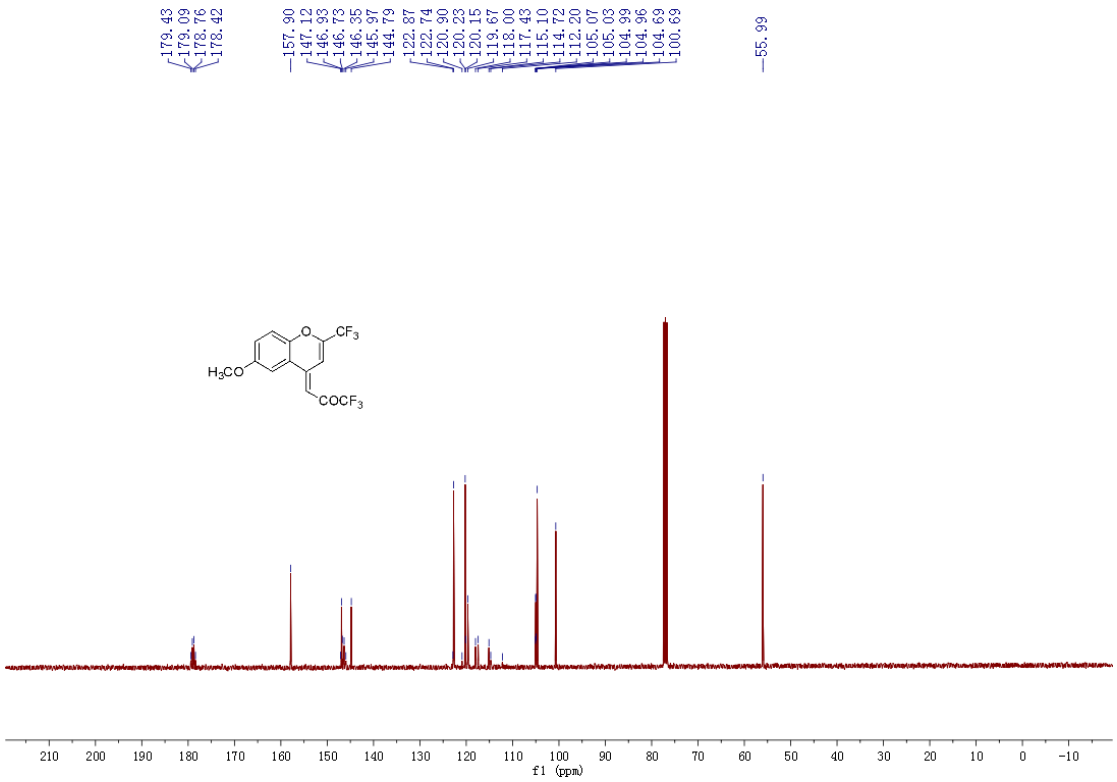
^{1}H NMR spectra of **3g** in $CDCl_3$



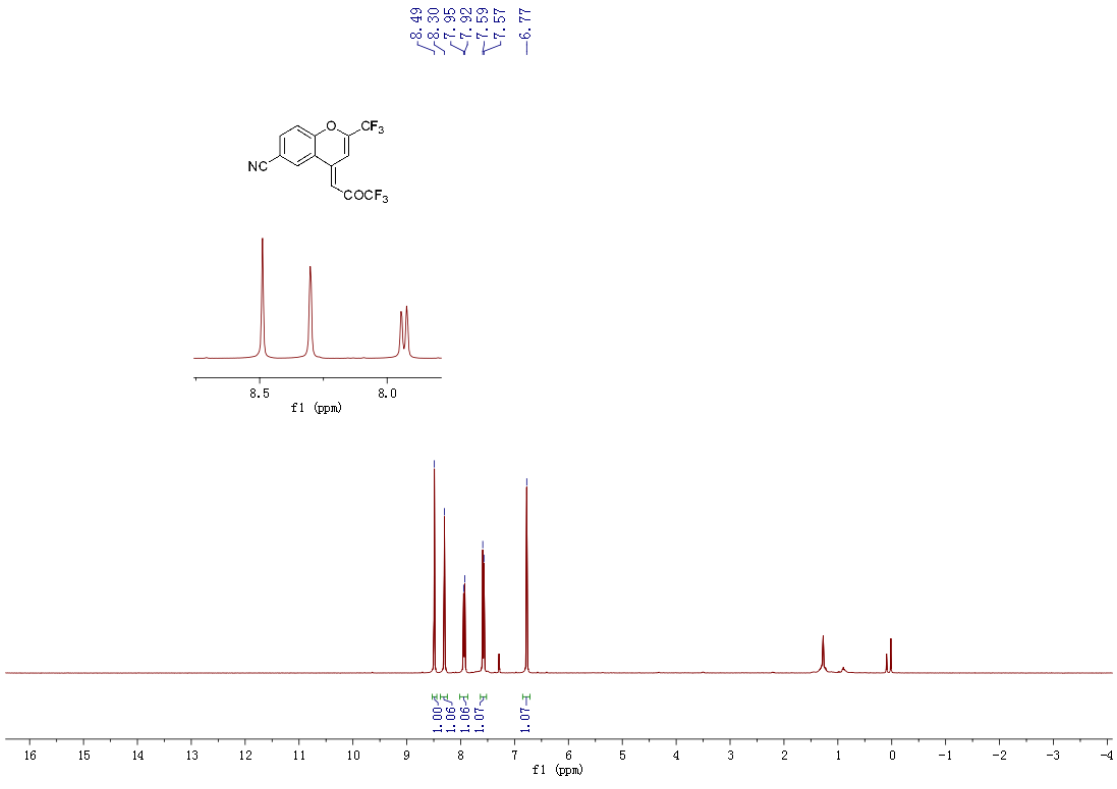
^{19}F NMR spectra of **3g** in $CDCl_3$



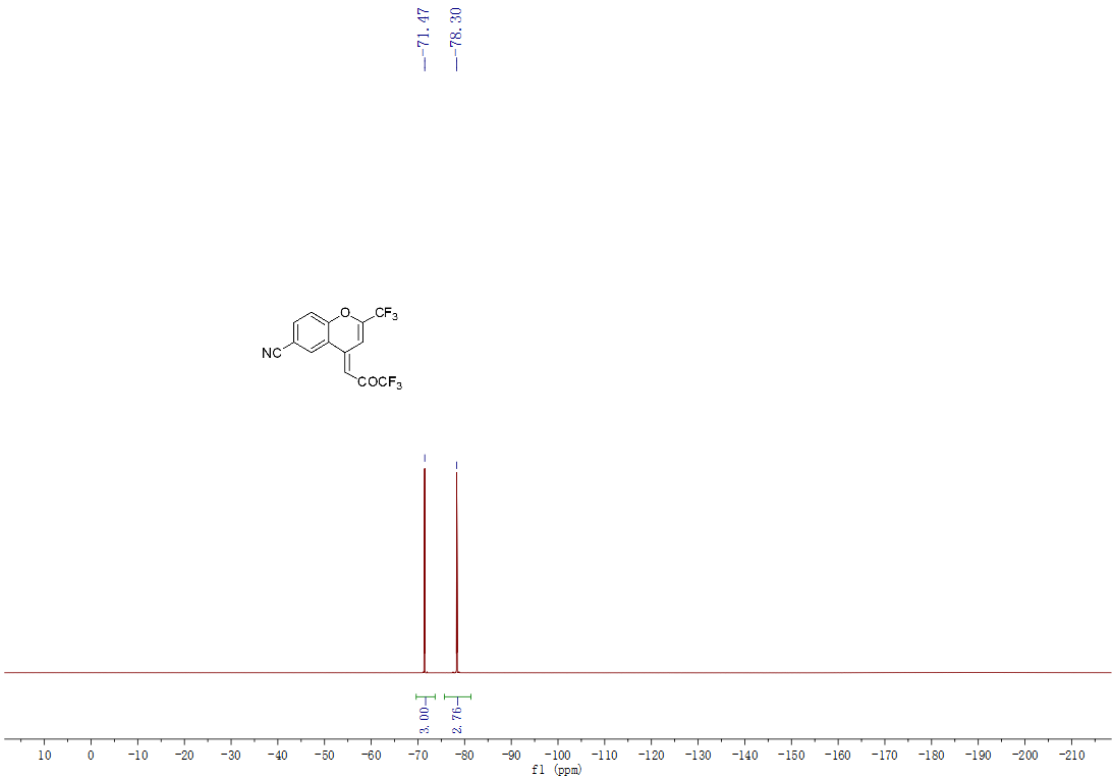
^{13}C NMR spectra of **3g** in $CDCl_3$



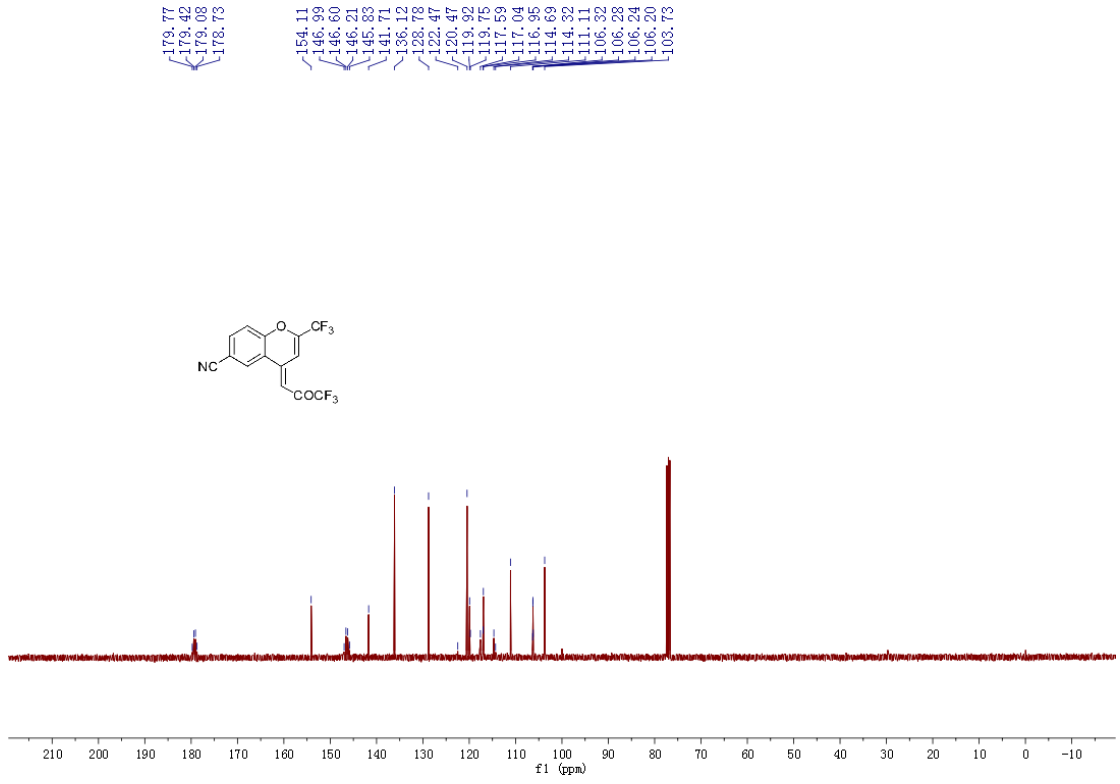
^{1}H NMR spectra of **3h** in $CDCl_3$



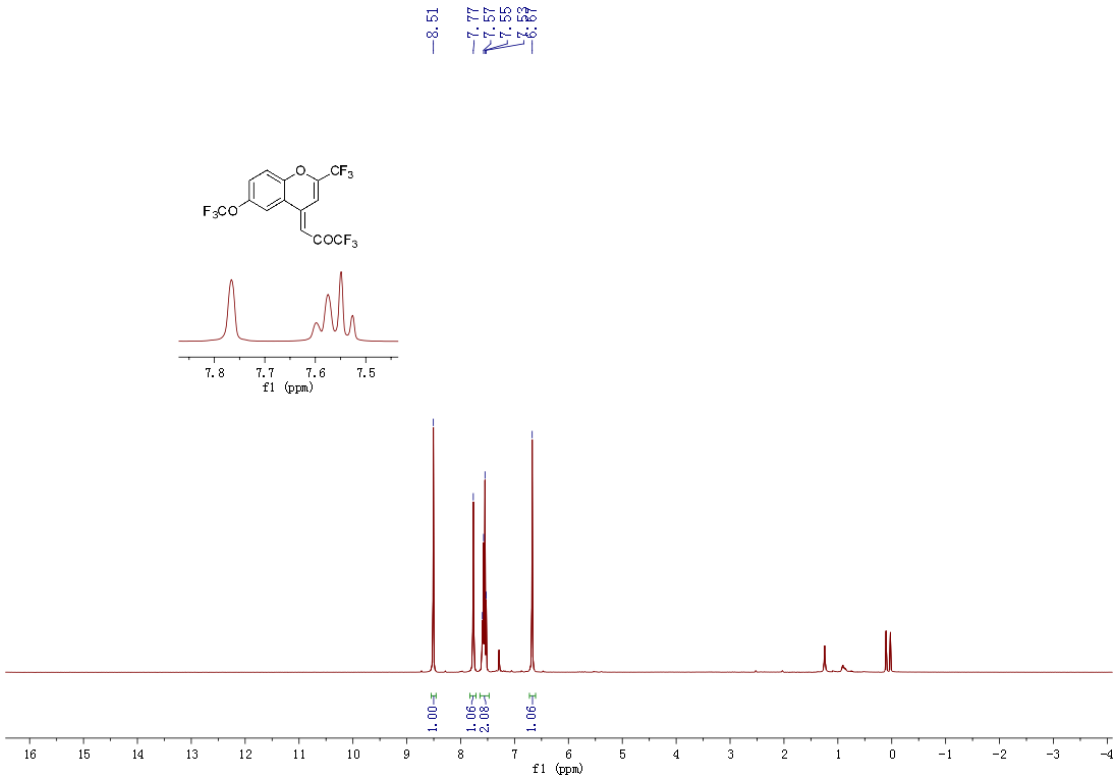
^{19}F NMR spectra of **3h** in $CDCl_3$



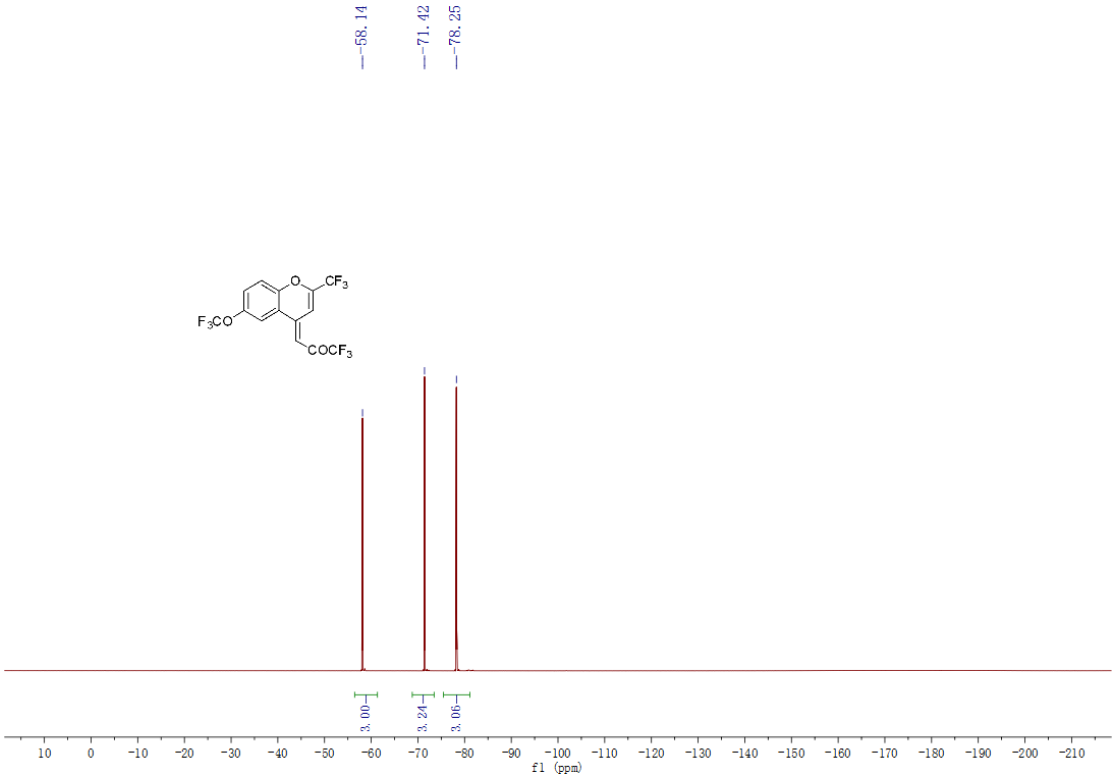
^{13}C NMR spectra of **3h** in $CDCl_3$



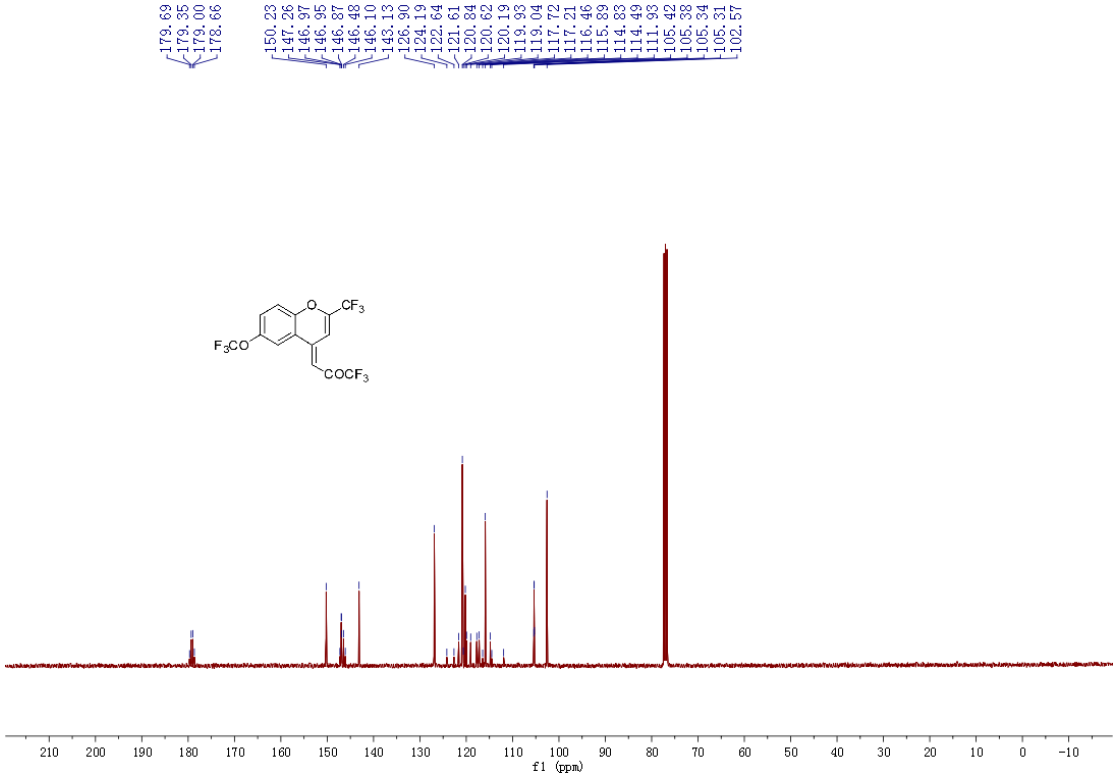
^{1}H NMR spectra of **3i** in $CDCl_3$



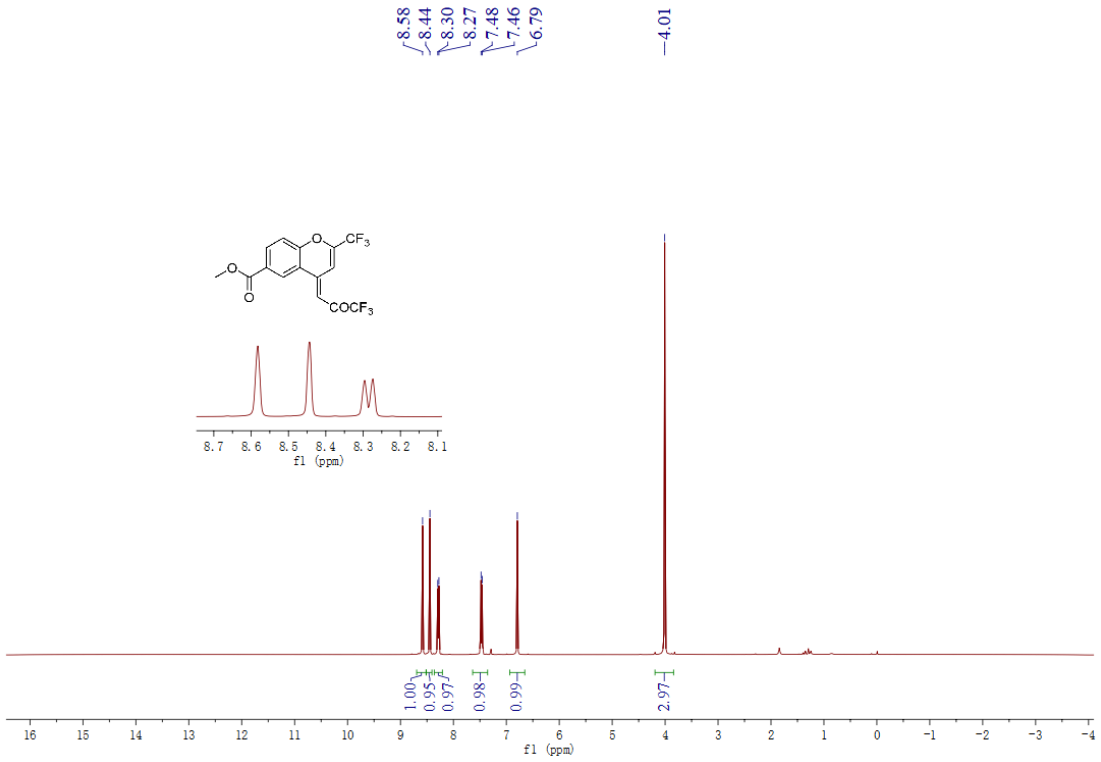
^{19}F NMR spectra of **3i** in $CDCl_3$



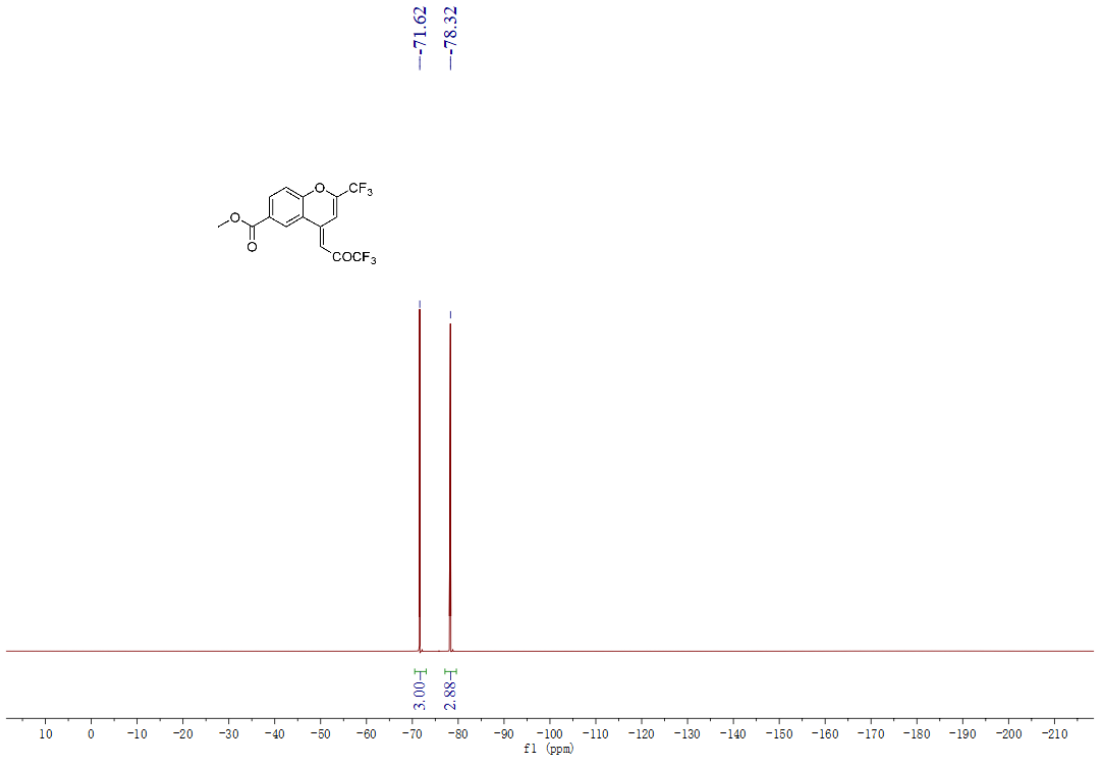
^{13}C NMR spectra of **3i** in $CDCl_3$



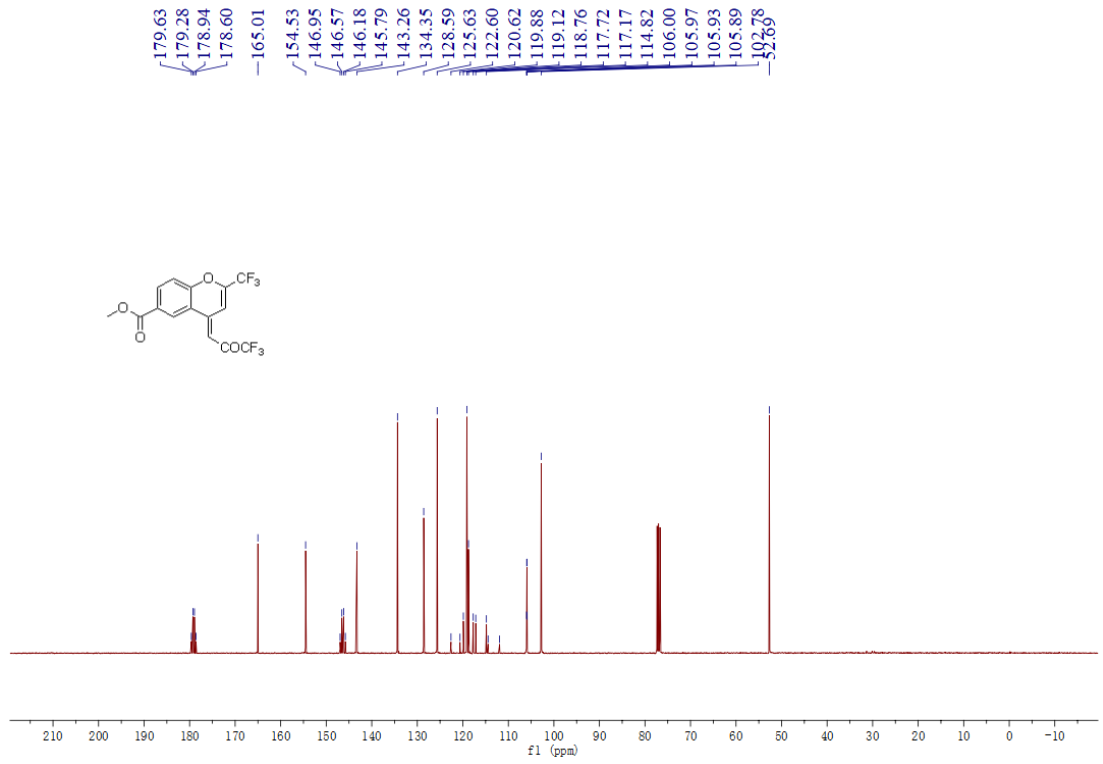
^{1}H NMR spectra of **3j** in $CDCl_3$



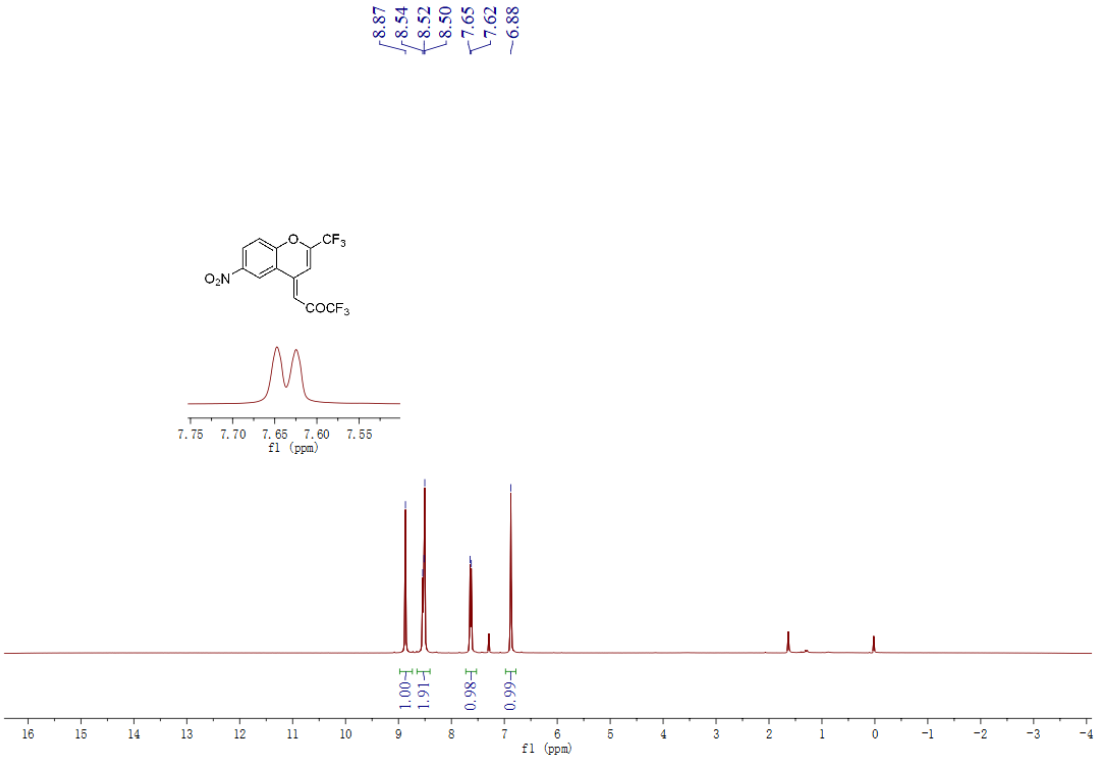
^{19}F NMR spectra of **3j** in $CDCl_3$



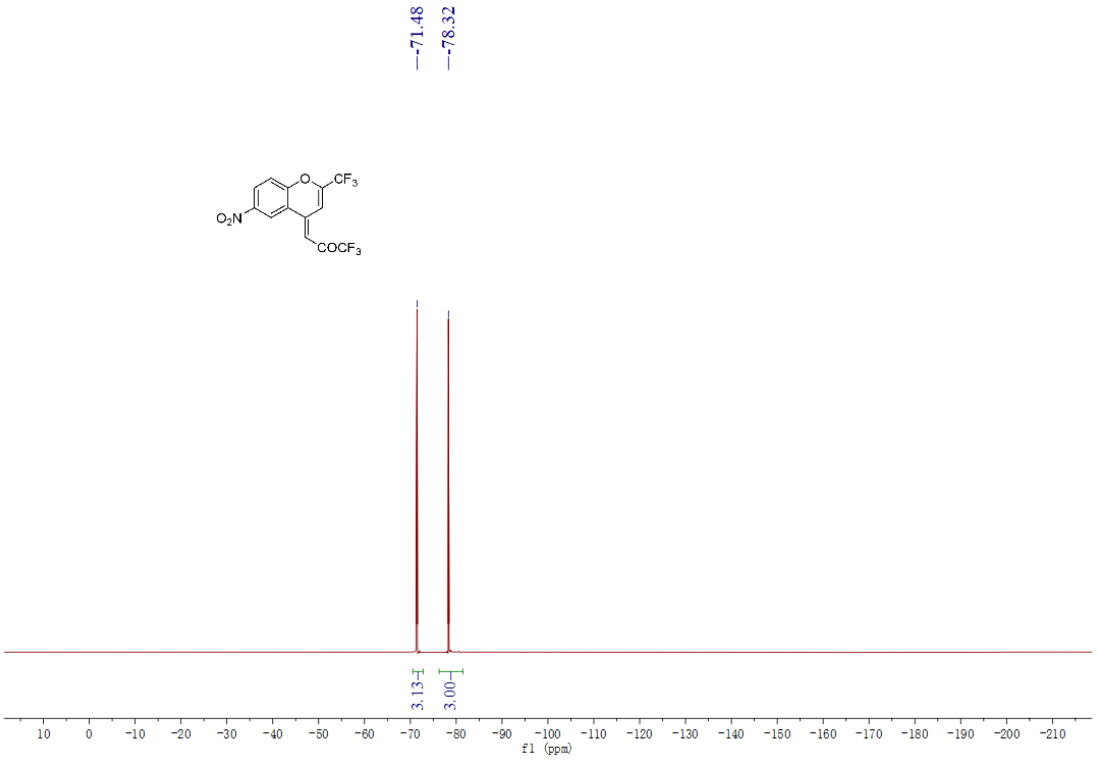
^{13}C NMR spectra of **3j** in $CDCl_3$



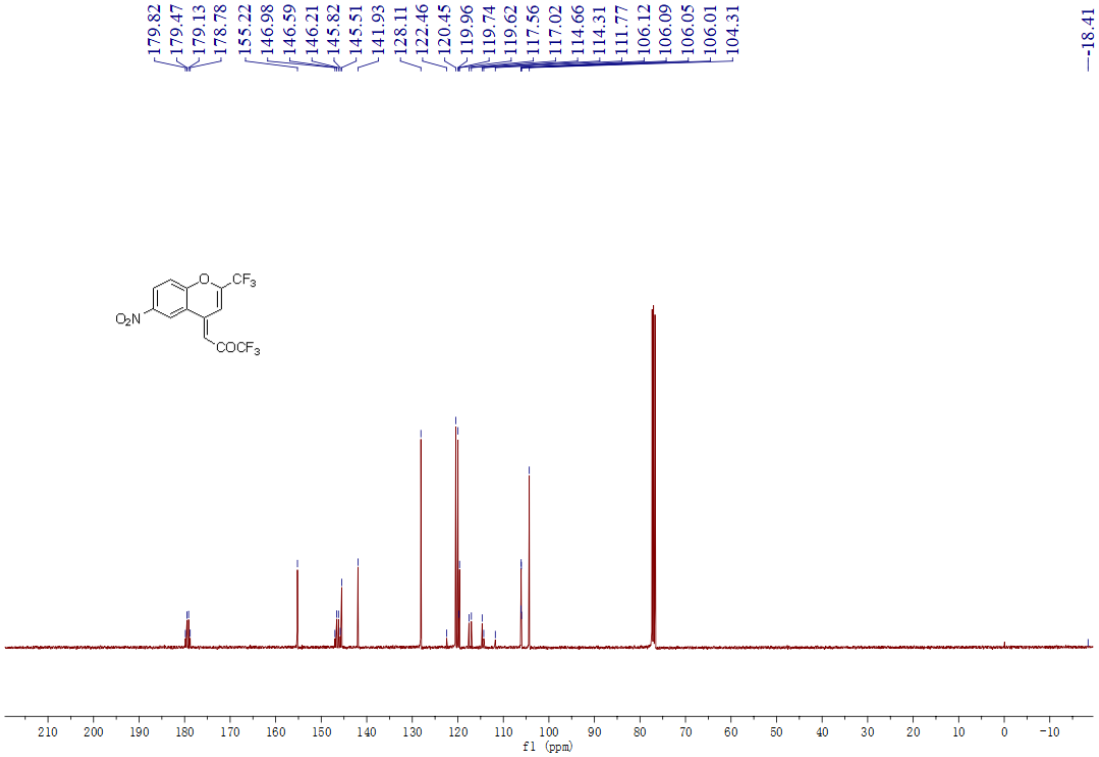
^{1}H NMR spectra of **3k** in $CDCl_3$



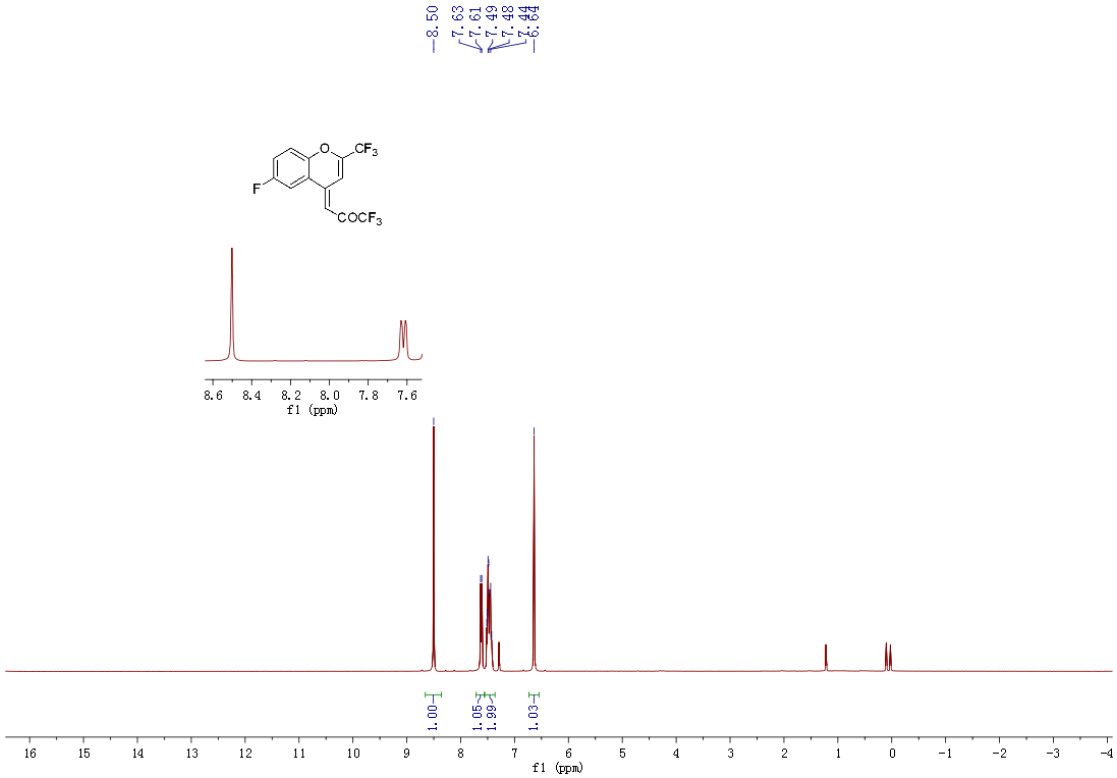
^{19}F NMR spectra of **3k** in $CDCl_3$



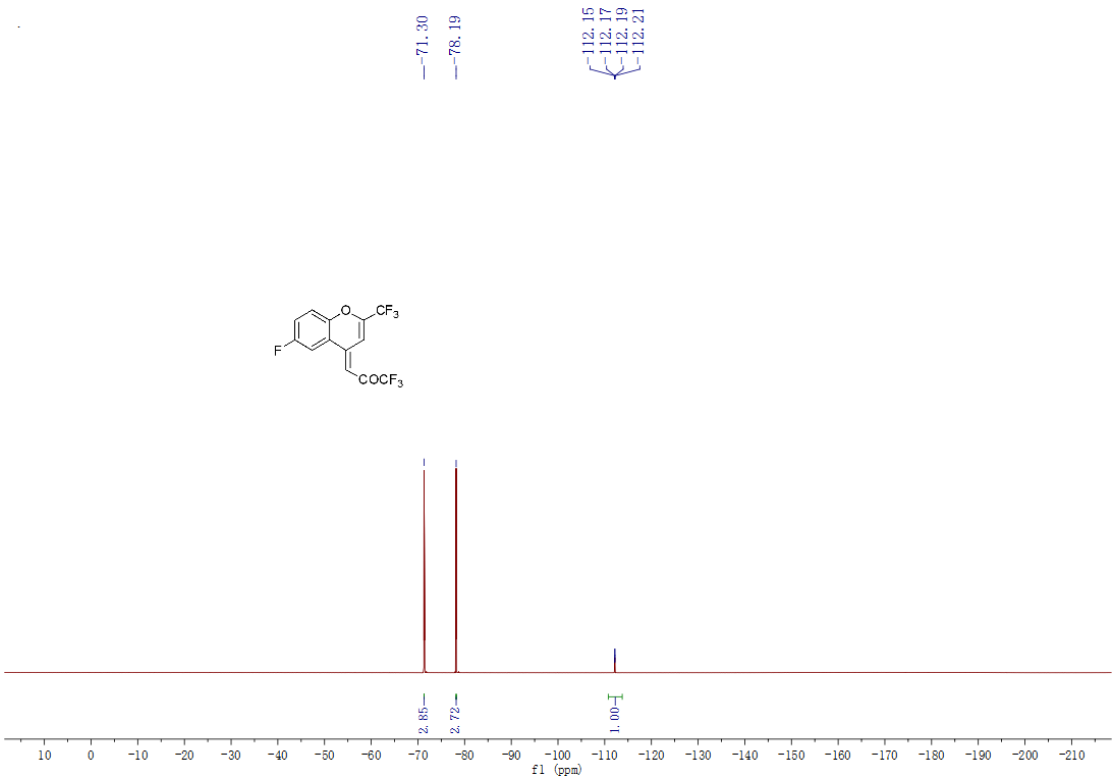
^{13}C NMR spectra of **3k** in $CDCl_3$



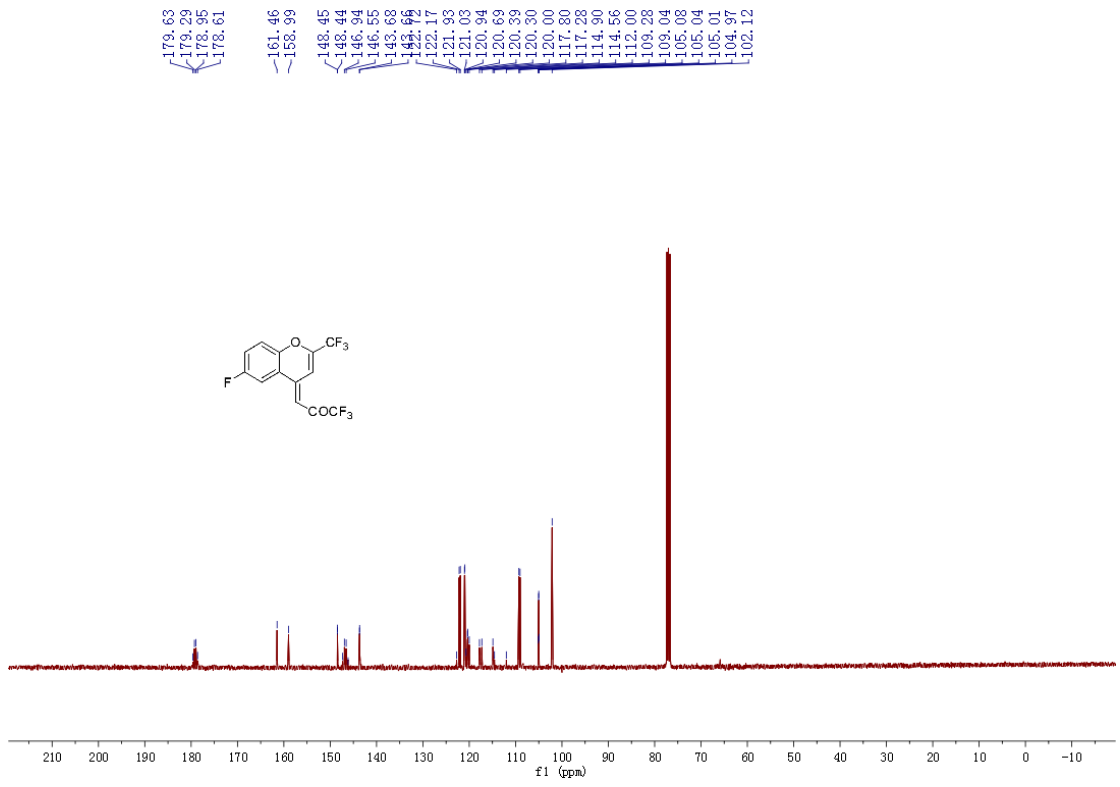
^{1}H NMR spectra of **3l** in $CDCl_3$



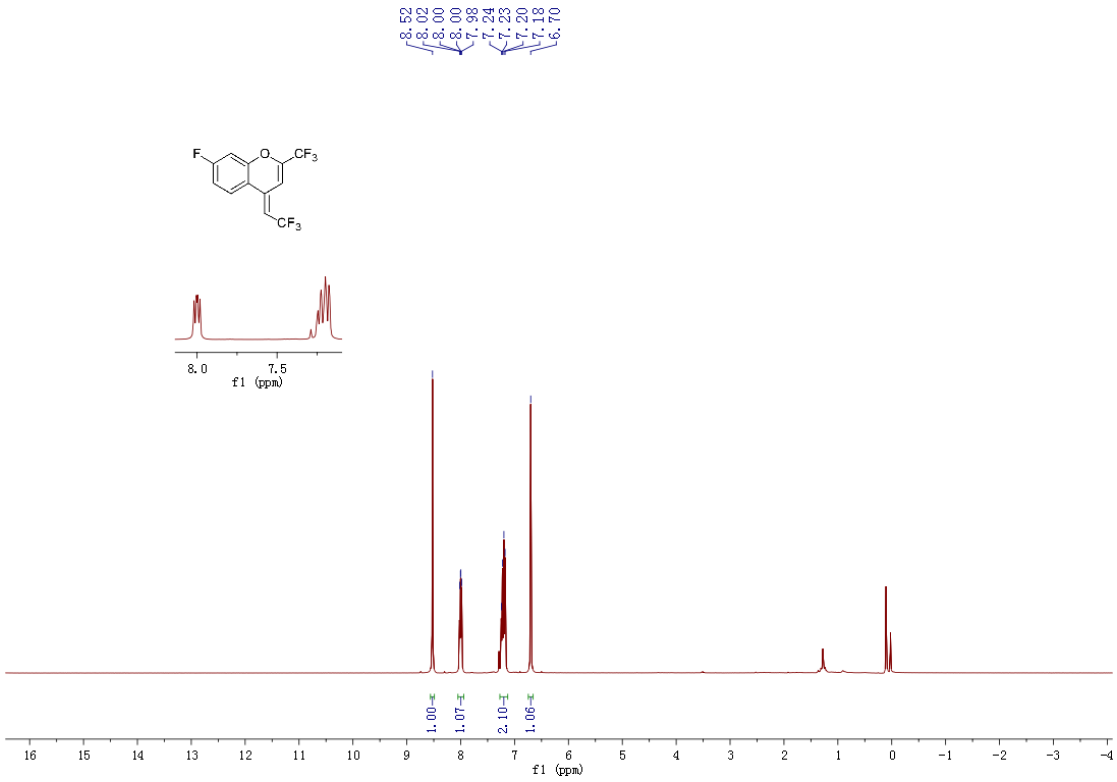
^{19}F NMR spectra of **3l** in $CDCl_3$



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

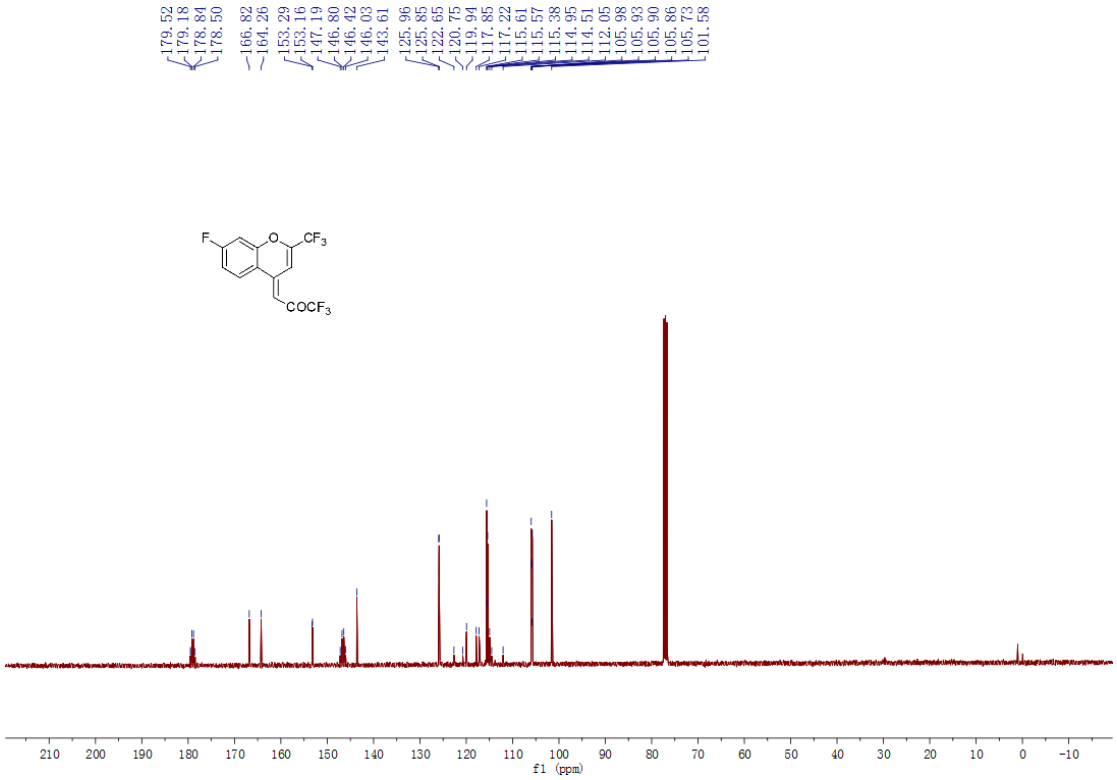


^{1}H NMR spectra of **3m** in $CDCl_3$

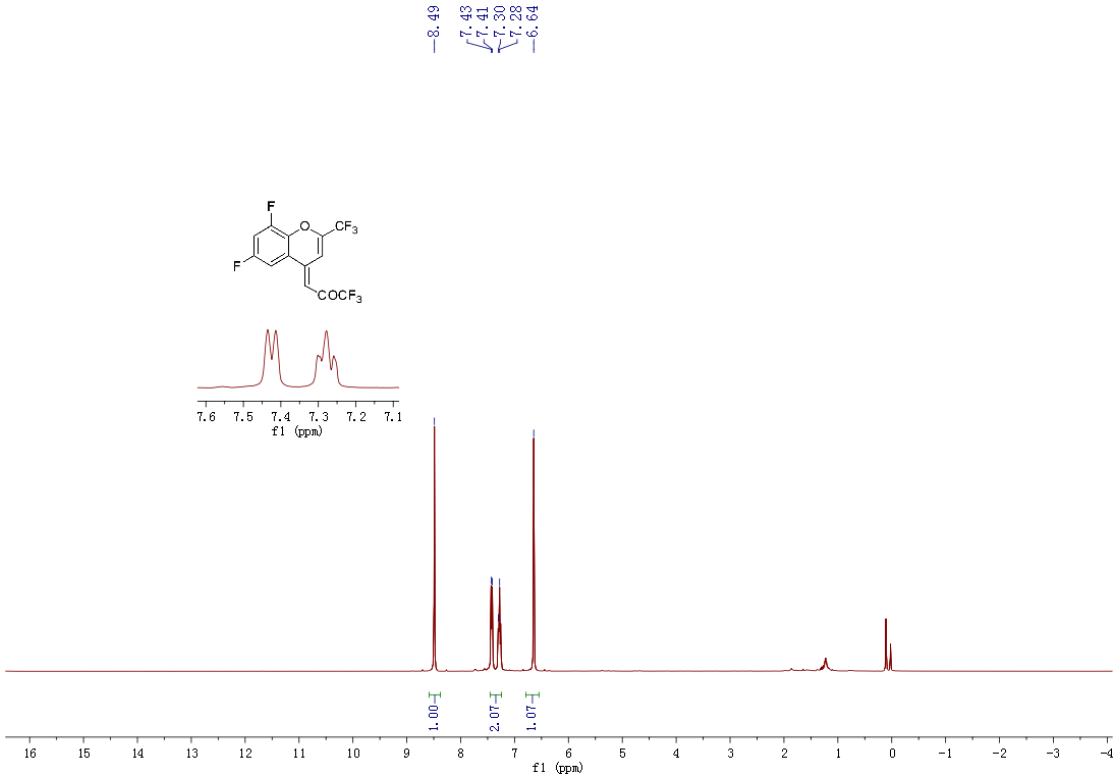


^{19}F NMR spectra of **3m** in $CDCl_3$

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

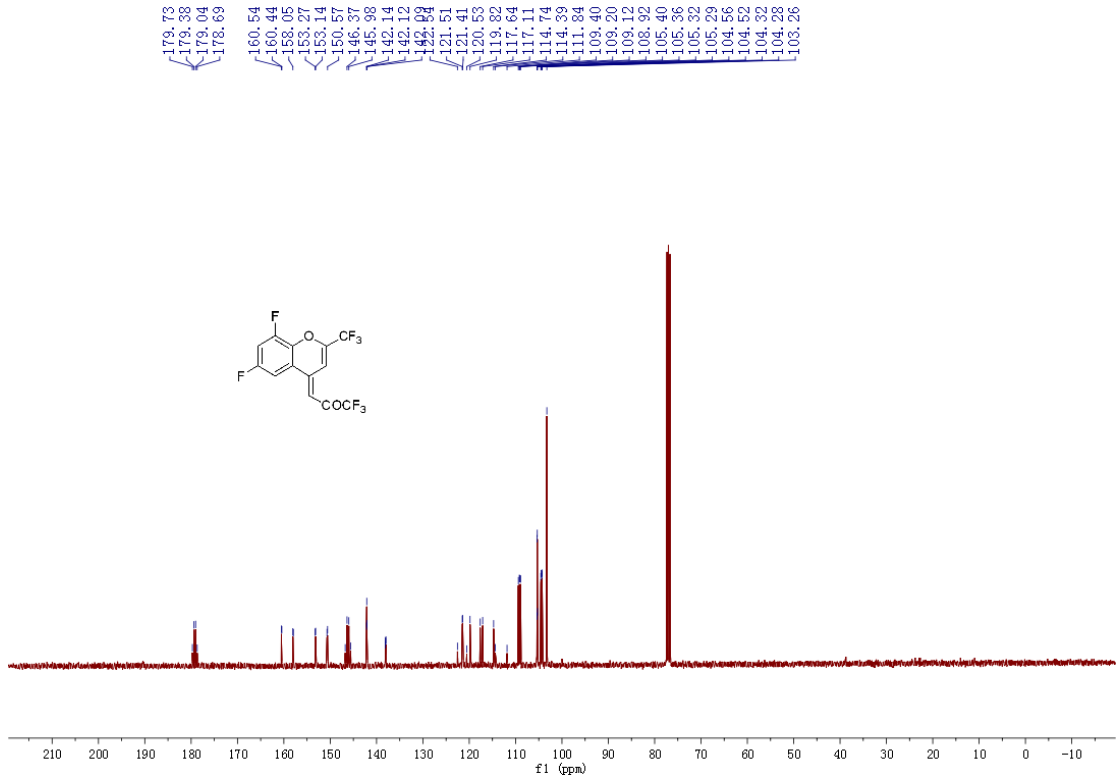


^{1}H NMR spectra of **3n** in $CDCl_3$

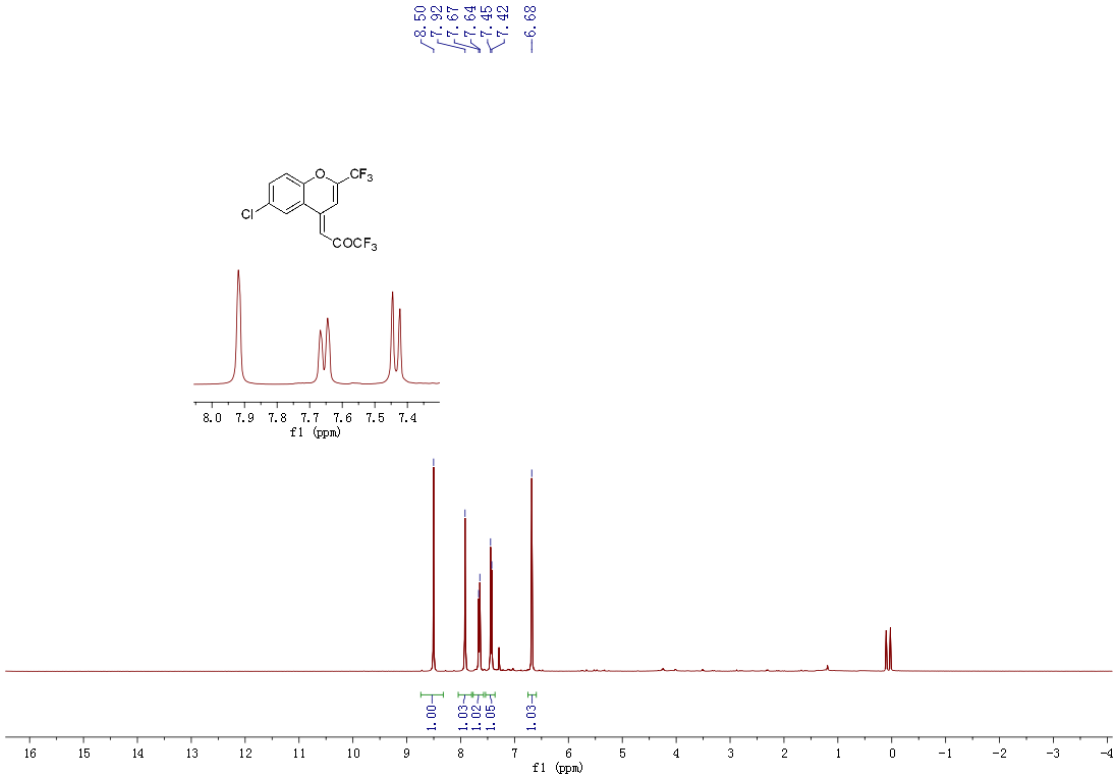


^{19}F NMR spectra of **3n** in $CDCl_3$

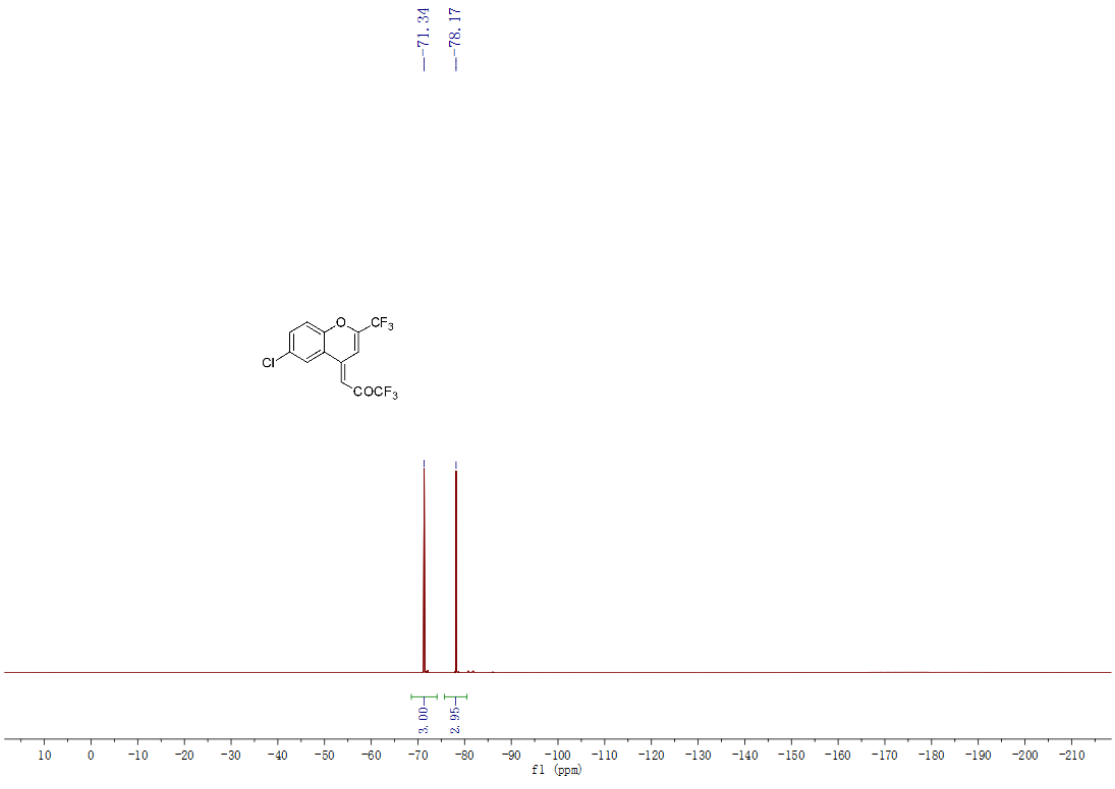
^{13}C NMR spectra of **3n** in $CDCl_3$



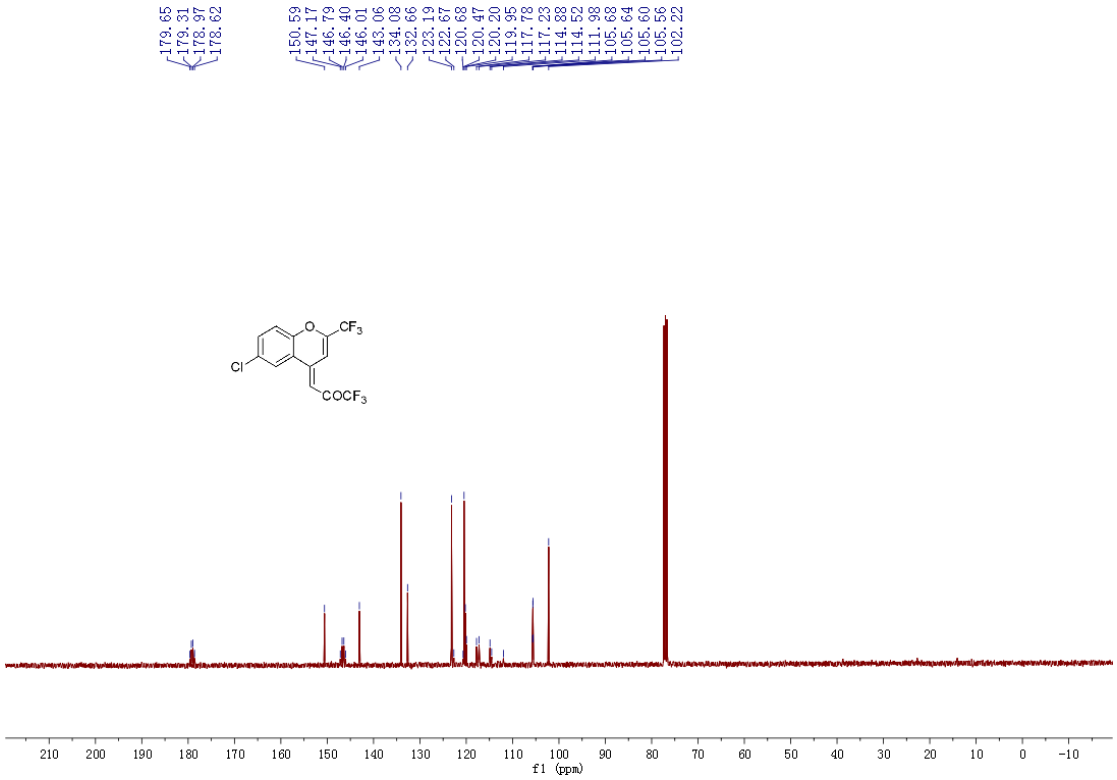
^{1}H NMR spectra of **3o** in $CDCl_3$



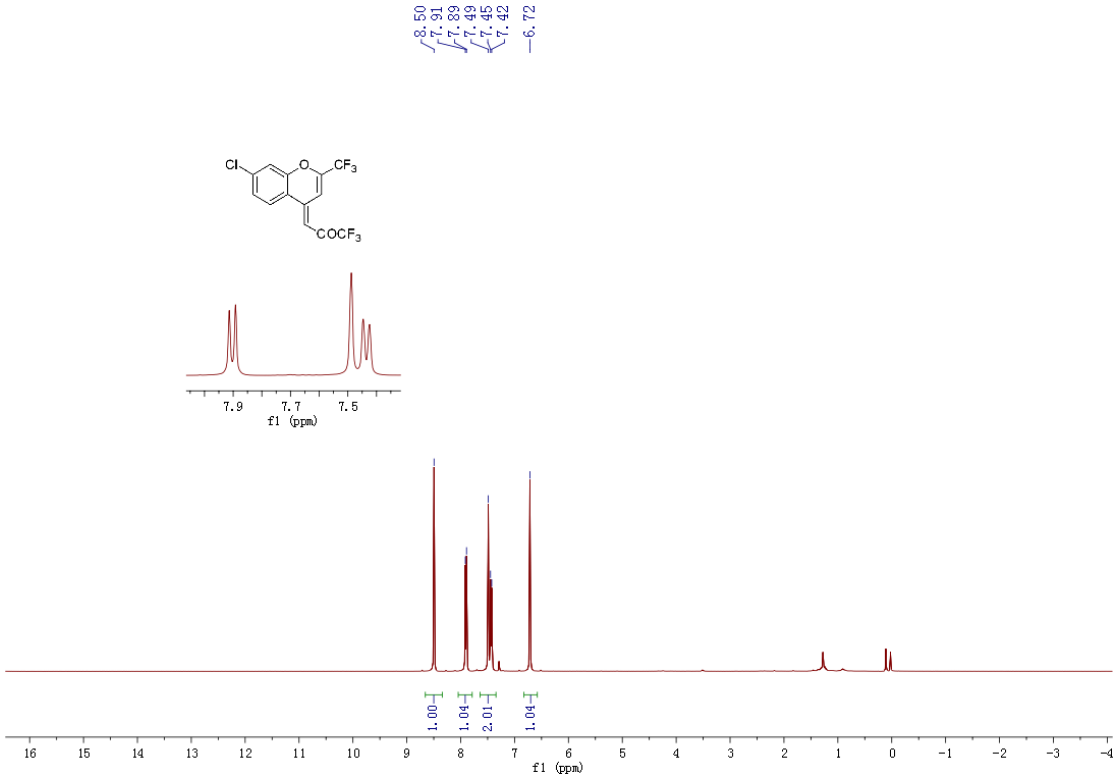
^{19}F NMR spectra of **3o** in $CDCl_3$



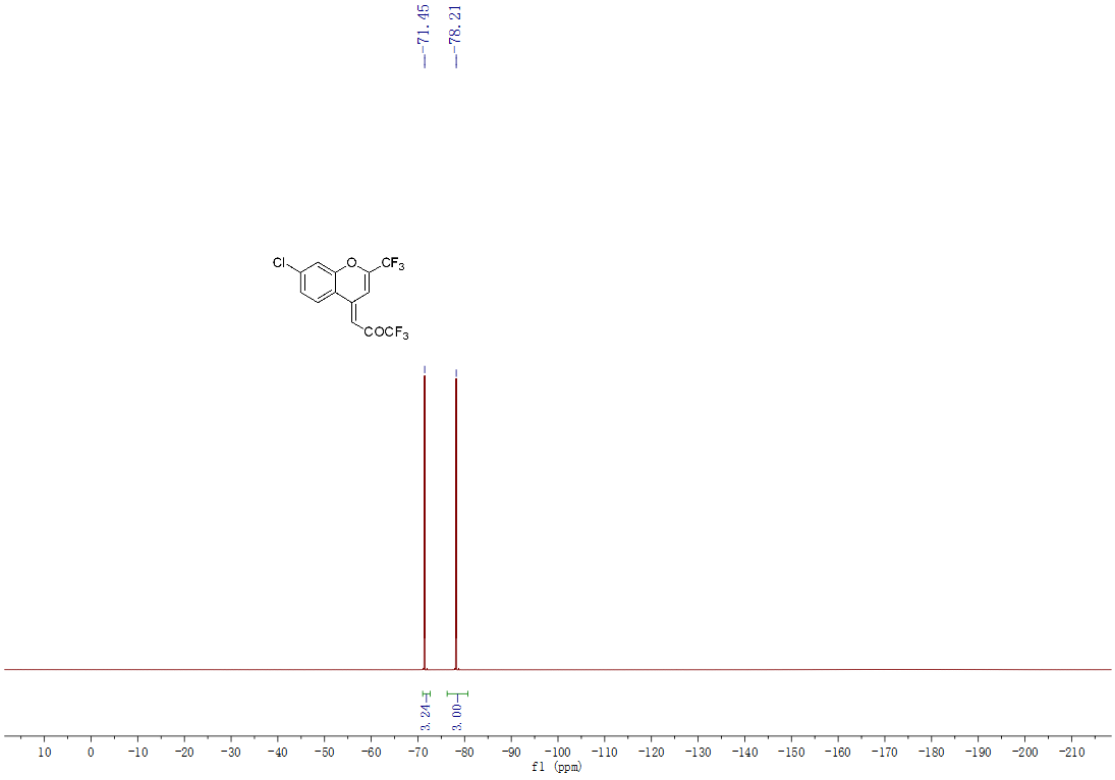
^{13}C NMR spectra of **3o** in $CDCl_3$



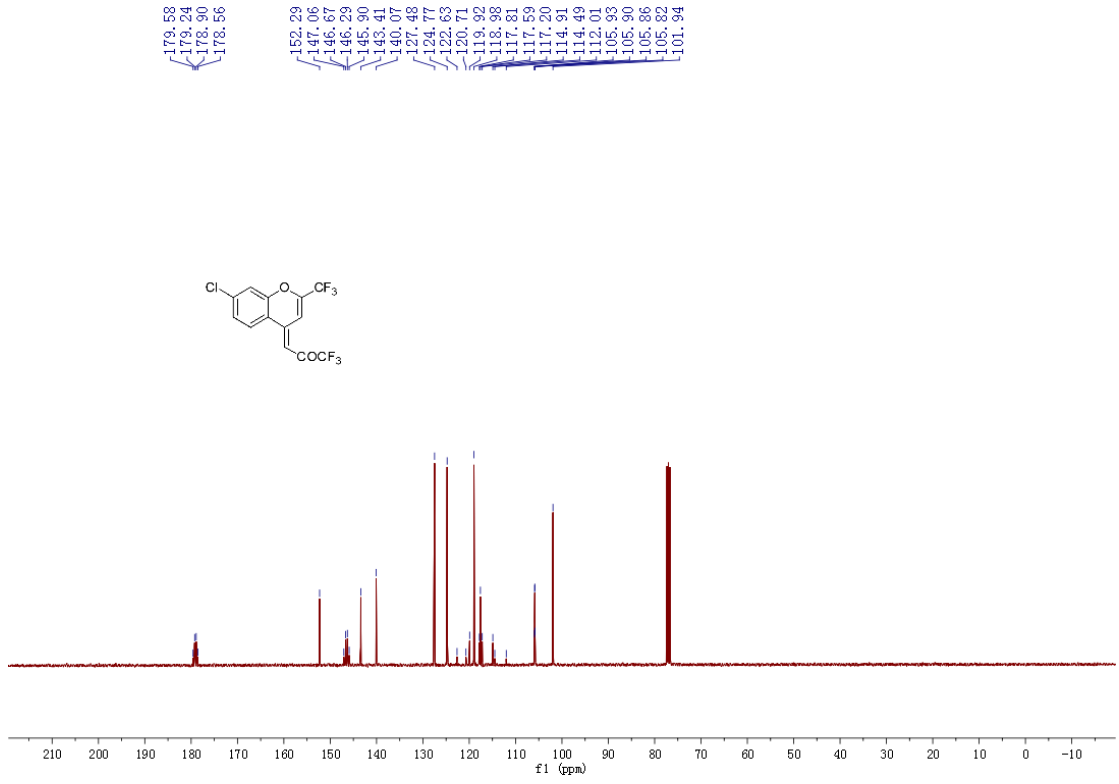
^{1}H NMR spectra of **3p** in $CDCl_3$



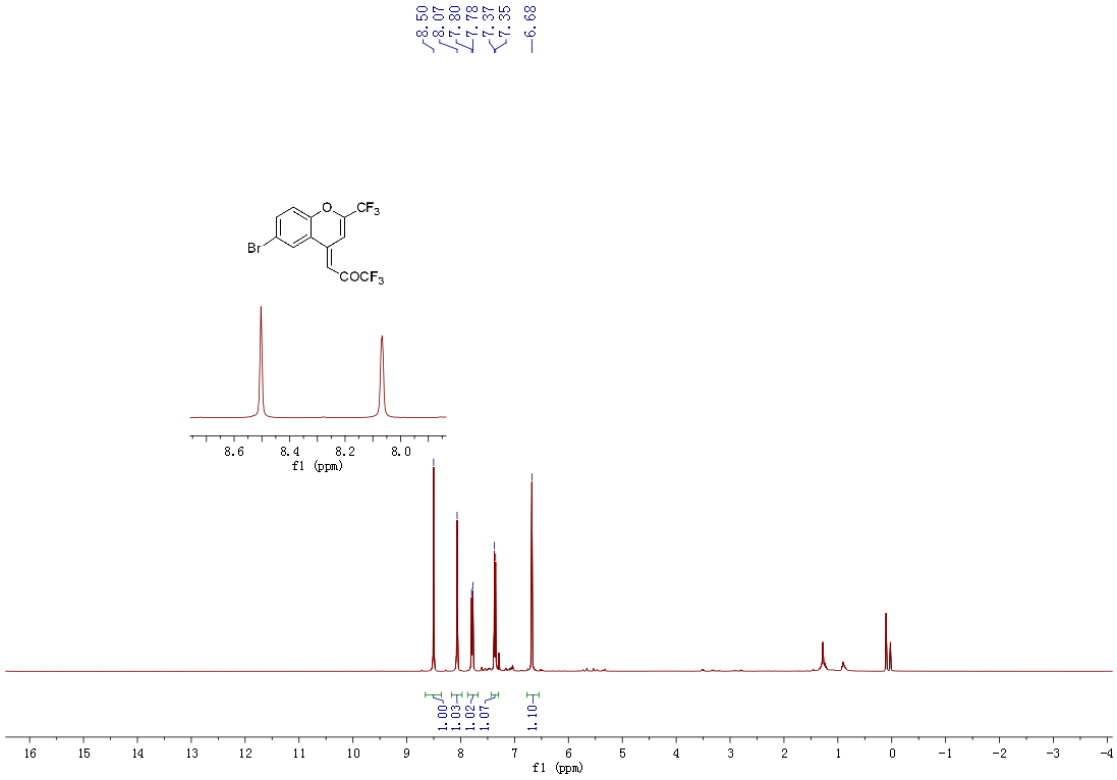
^{19}F NMR spectra of **3p** in $CDCl_3$



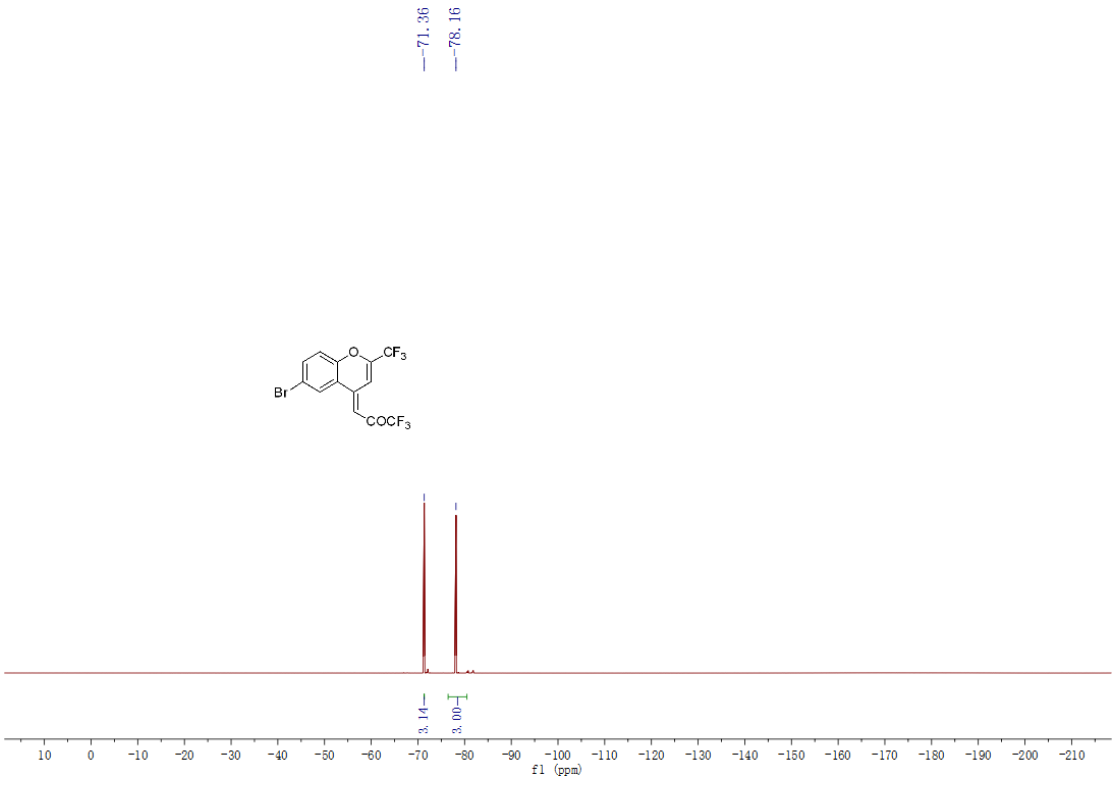
^{13}C NMR spectra of **3p** in $CDCl_3$



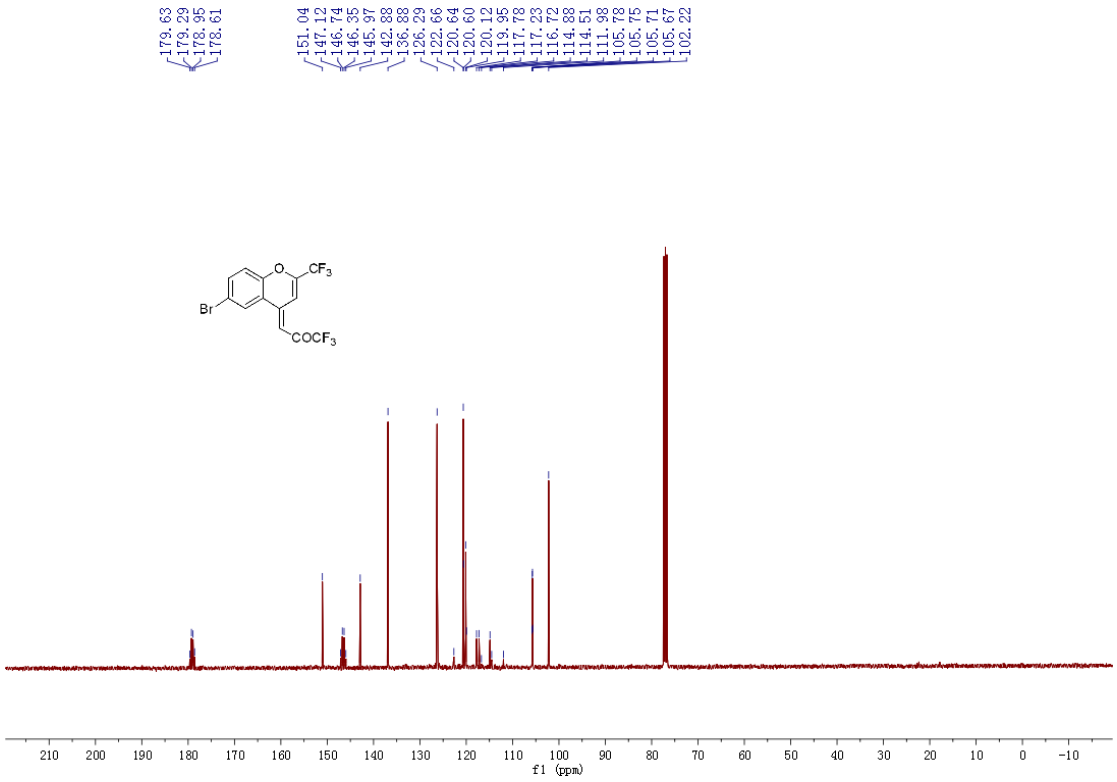
^{1}H NMR spectra of **3q** in $CDCl_3$



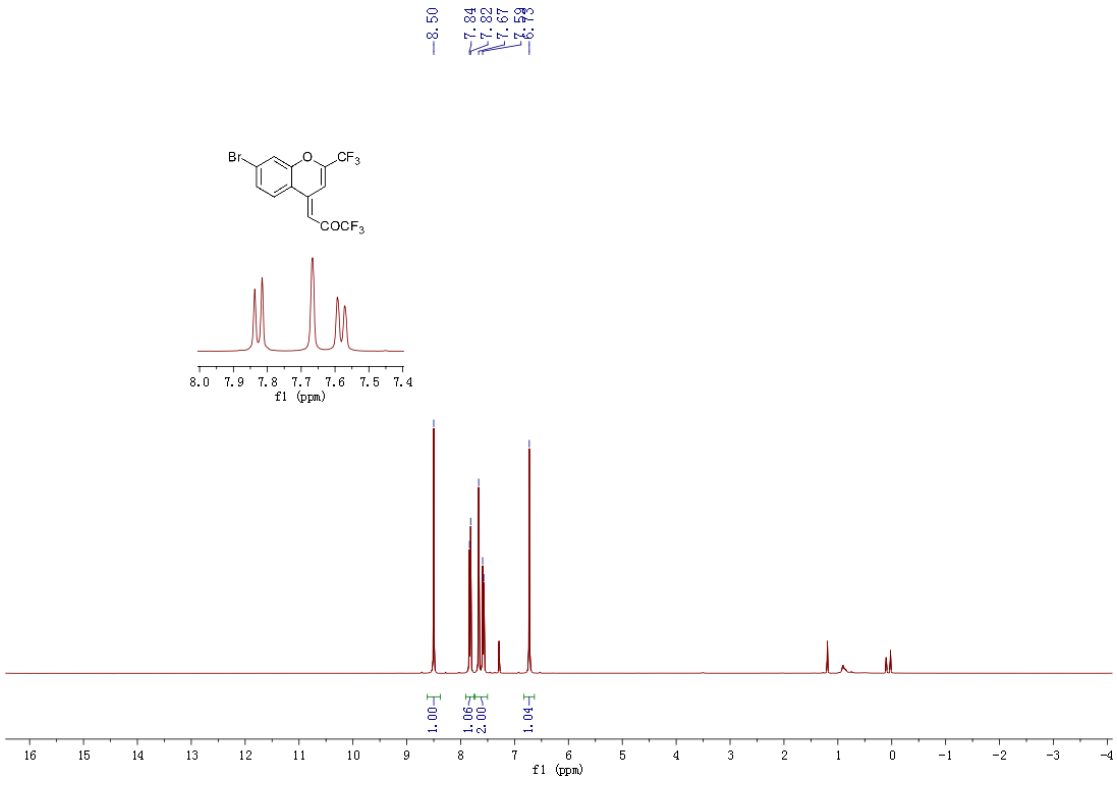
^{19}F NMR spectra of **3q** in $CDCl_3$



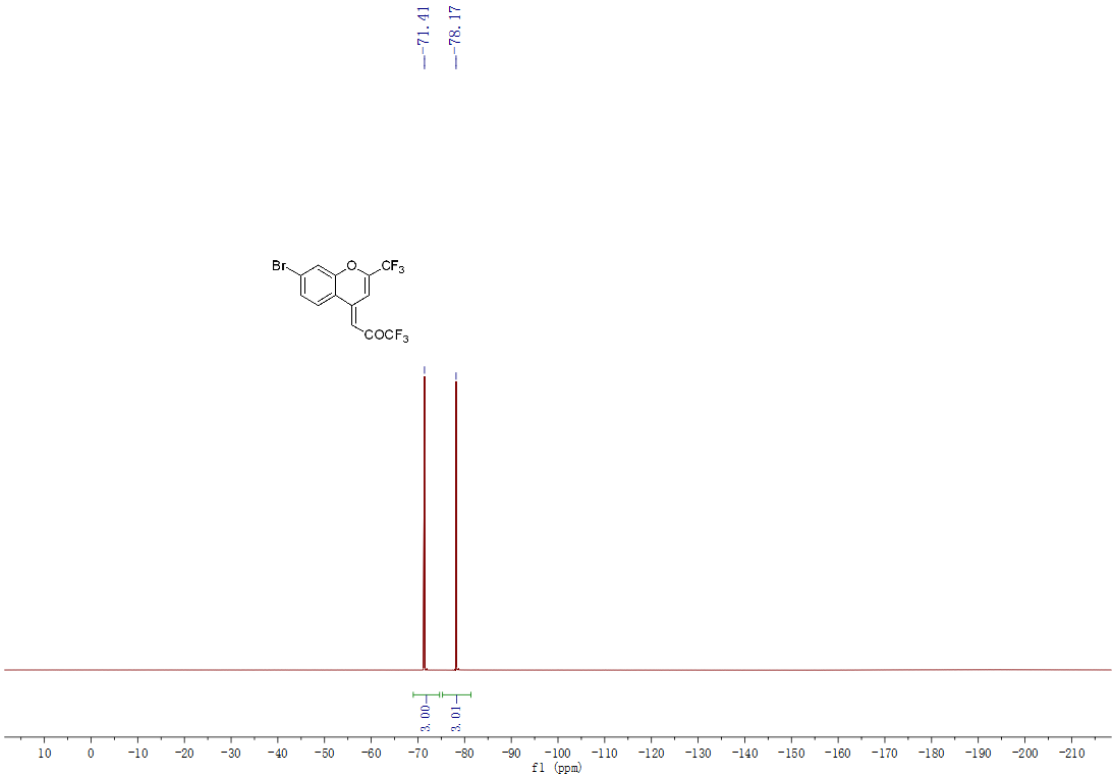
^{13}C NMR spectra of **3q** in $CDCl_3$



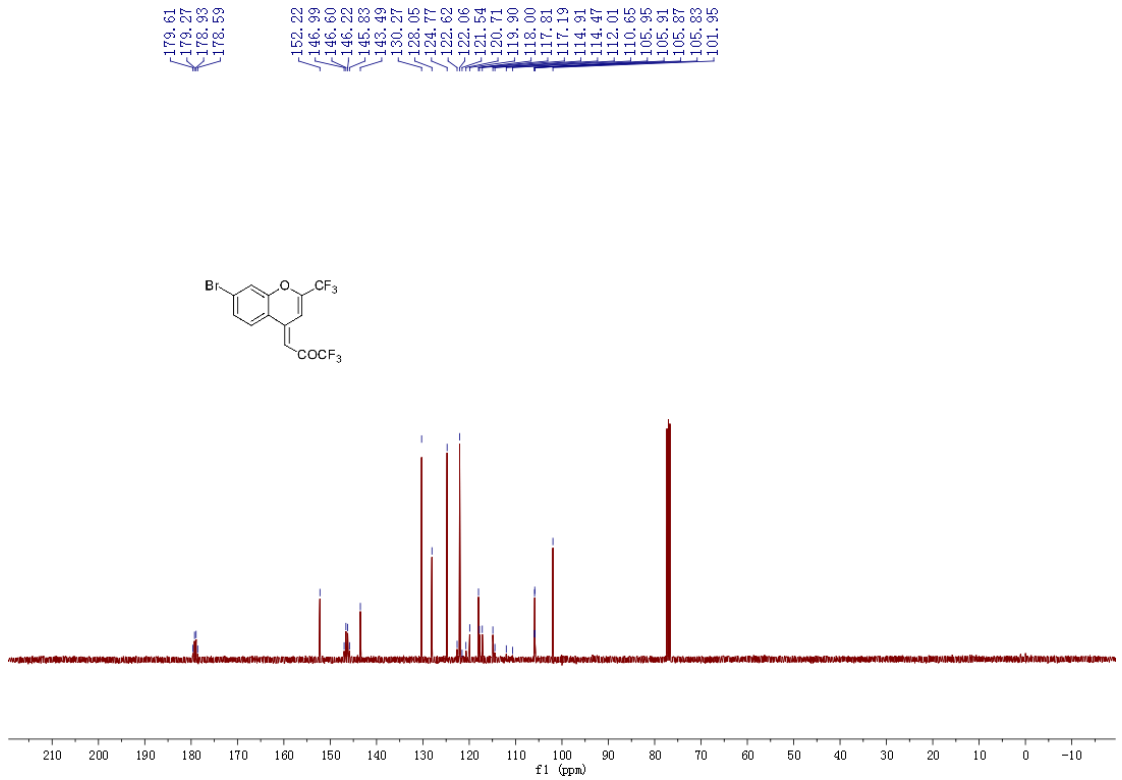
^{1}H NMR spectra of **3r** in $CDCl_3$



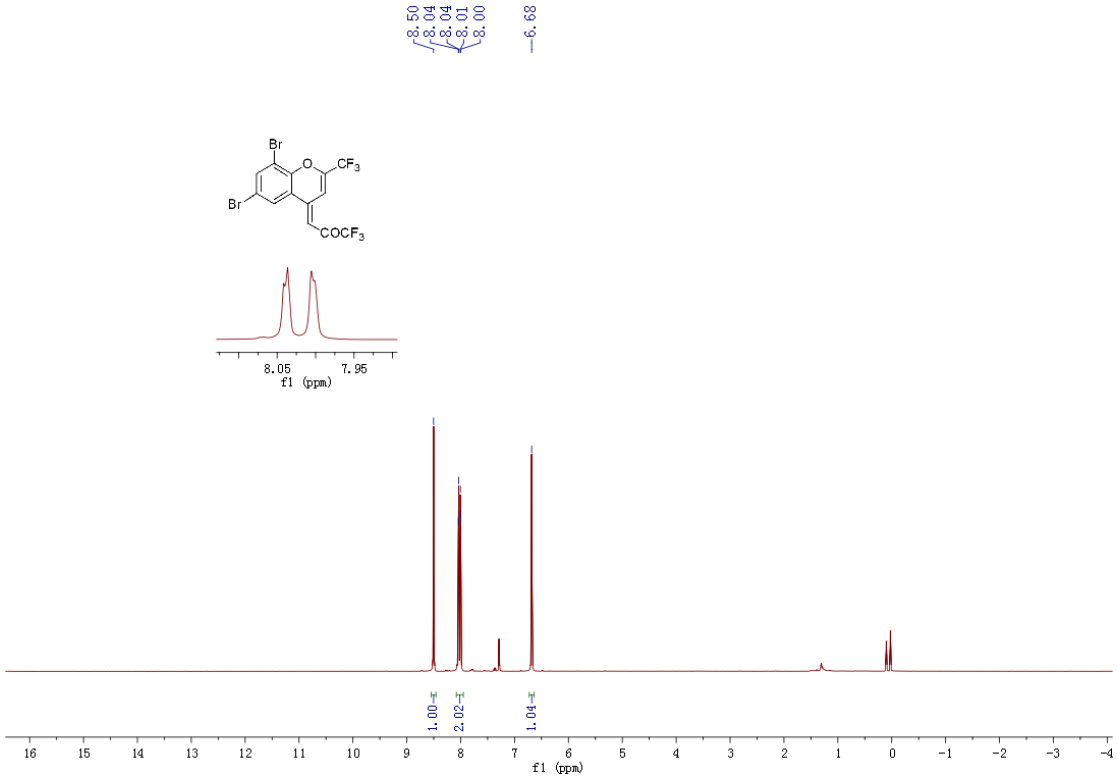
^{19}F NMR spectra of **3r** in $CDCl_3$



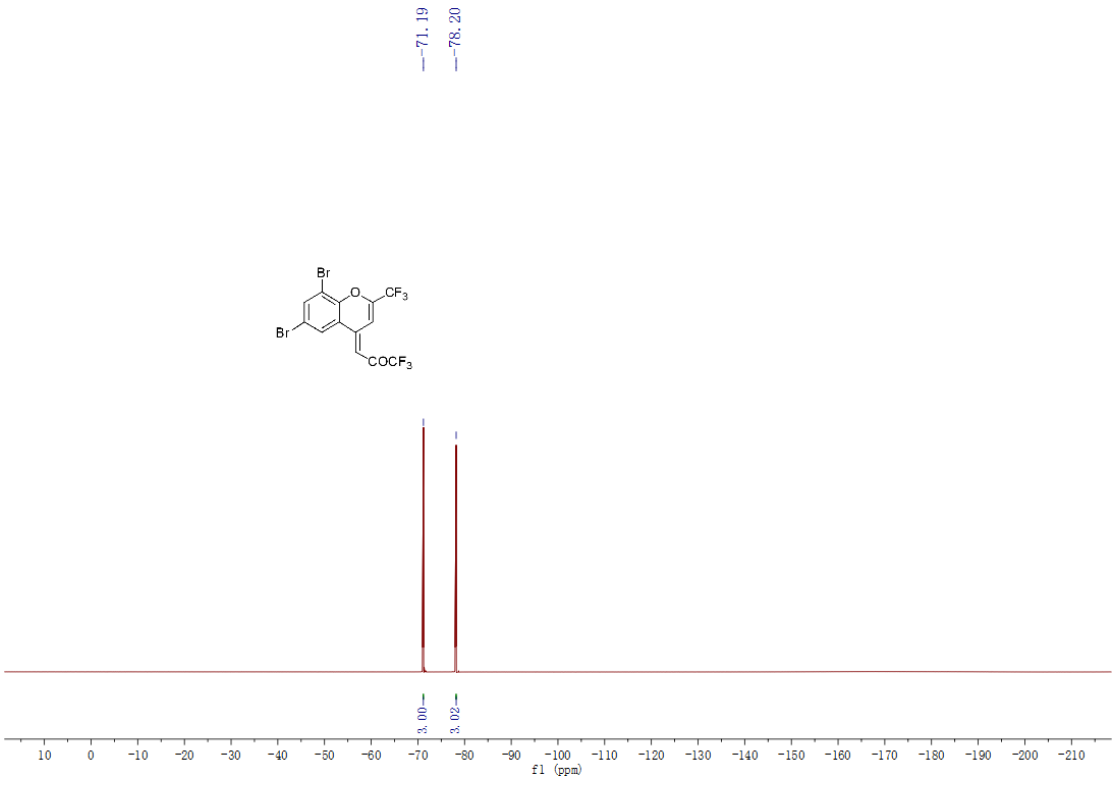
^{13}C NMR spectra of **3r** in $CDCl_3$



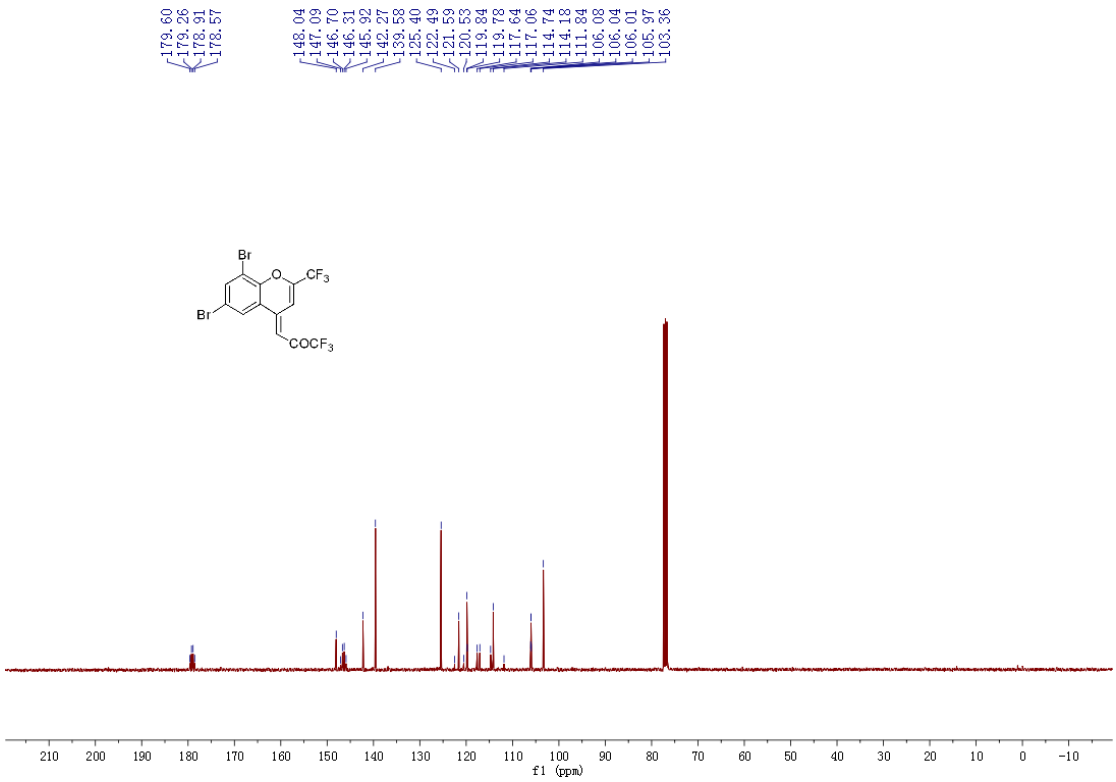
^{1}H NMR spectra of **3s** in $CDCl_3$



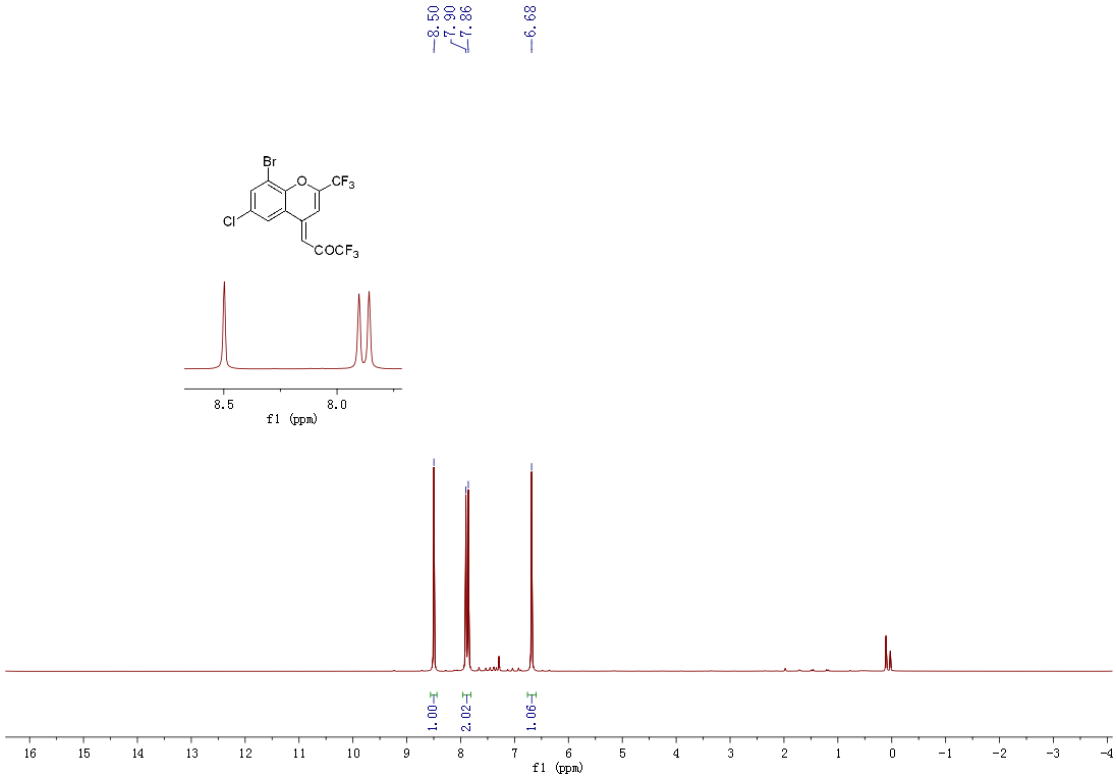
^{19}F NMR spectra of **3s** in $CDCl_3$



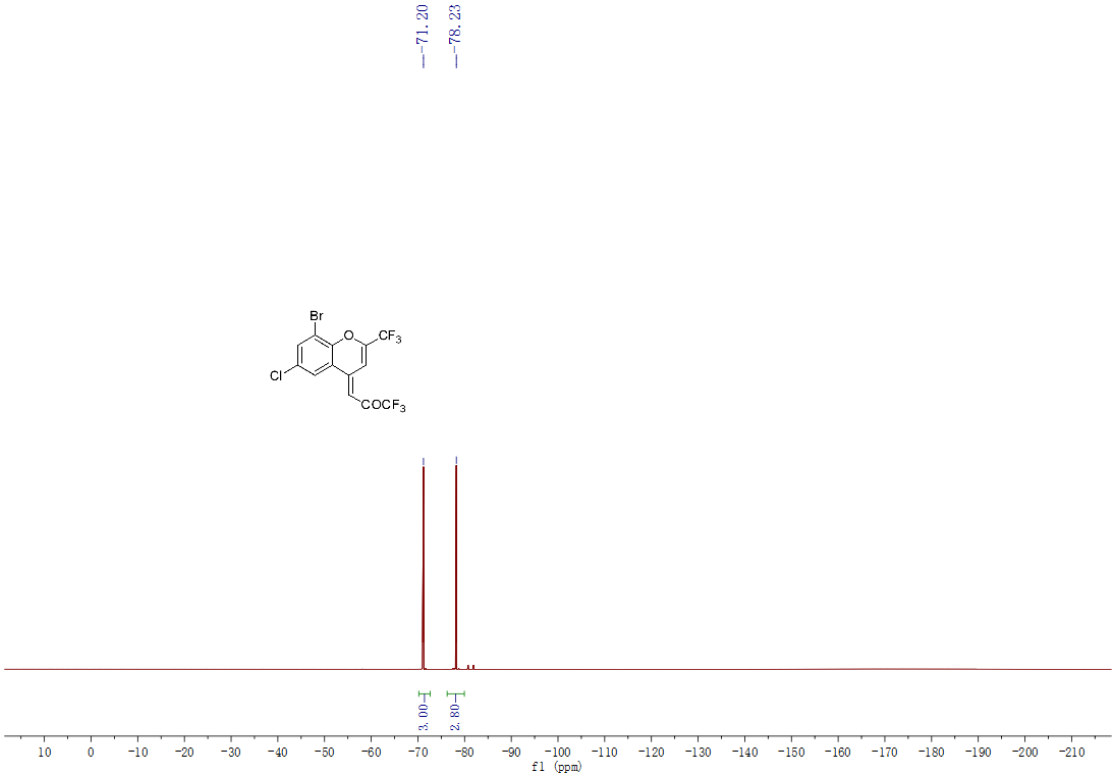
^{13}C NMR spectra of **3s** in $CDCl_3$



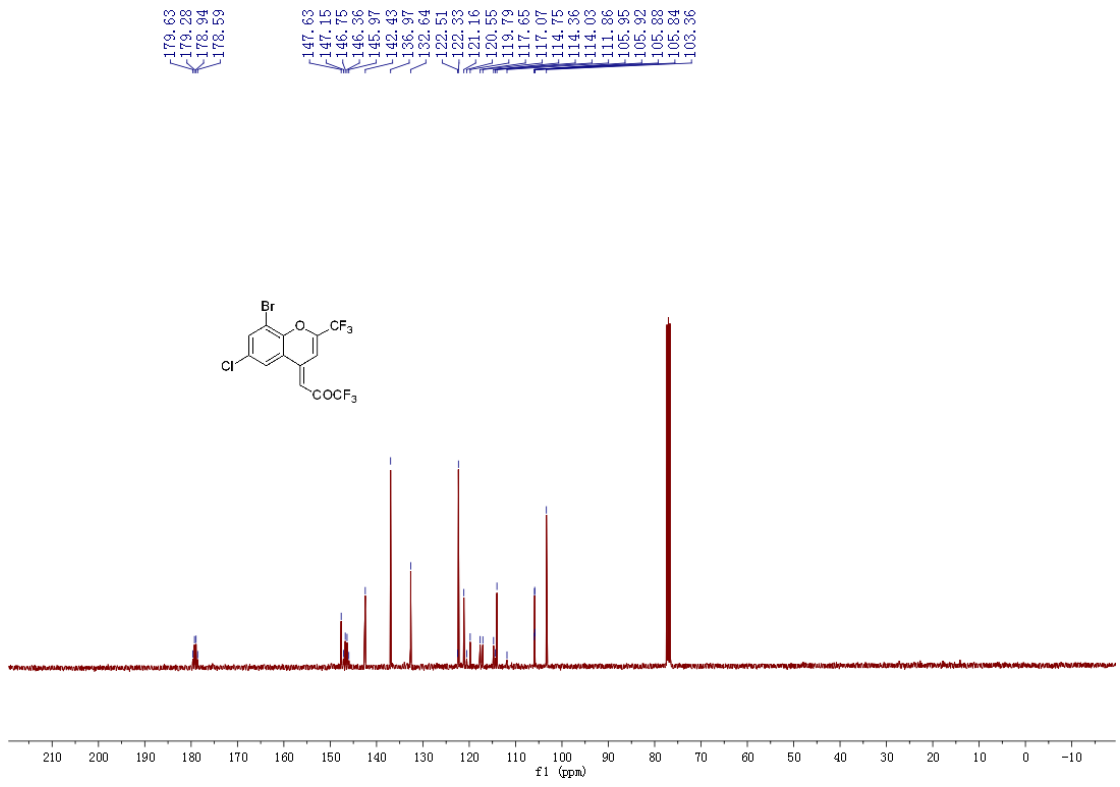
^{1}H NMR spectra of **3t** in $CDCl_3$



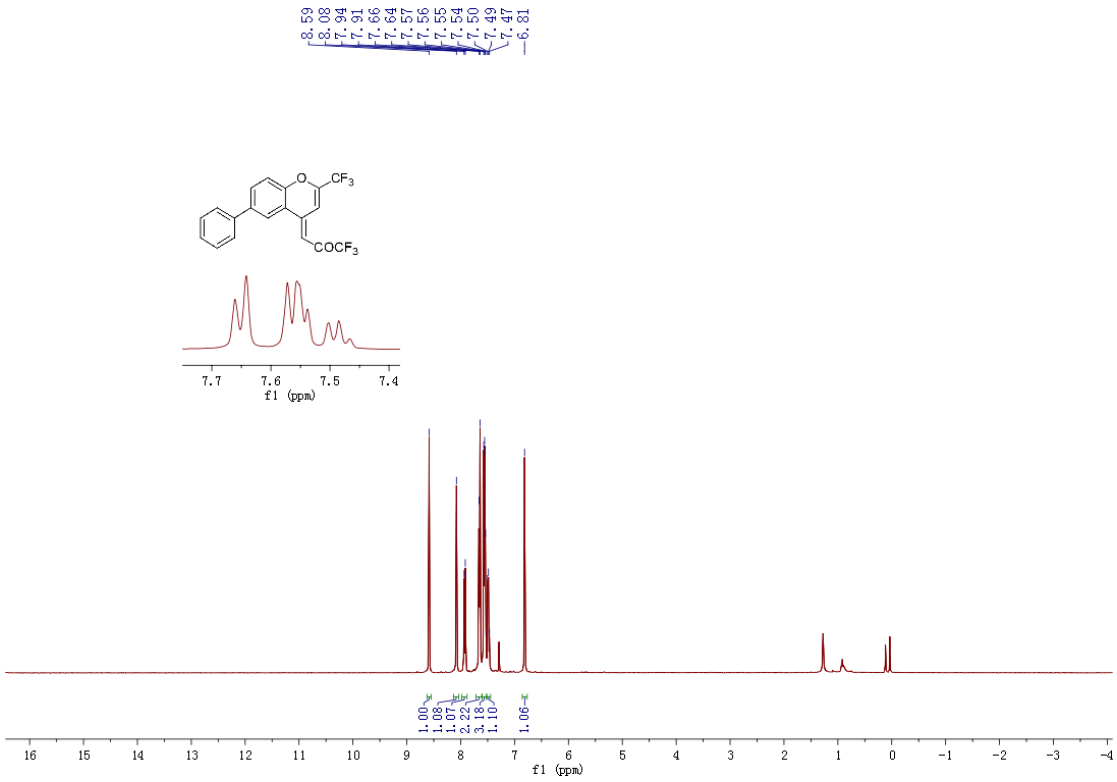
^{19}F NMR spectra of **3t** in $CDCl_3$



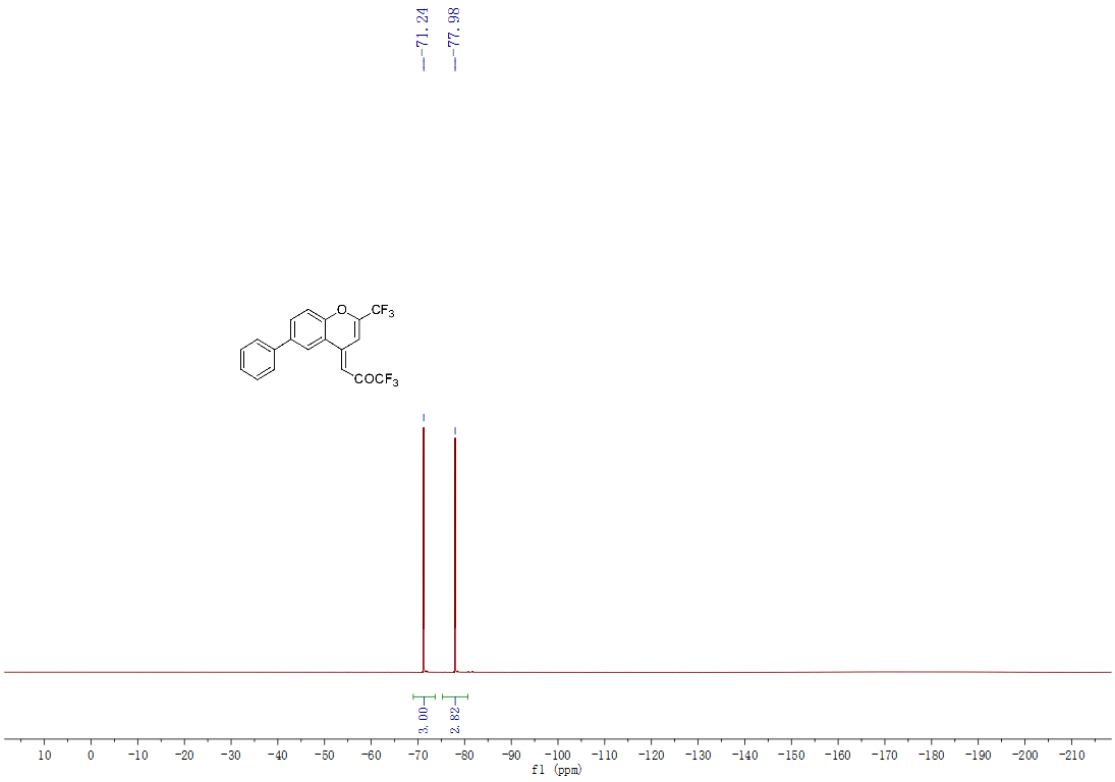
^{13}C NMR spectra of **3t** in $CDCl_3$



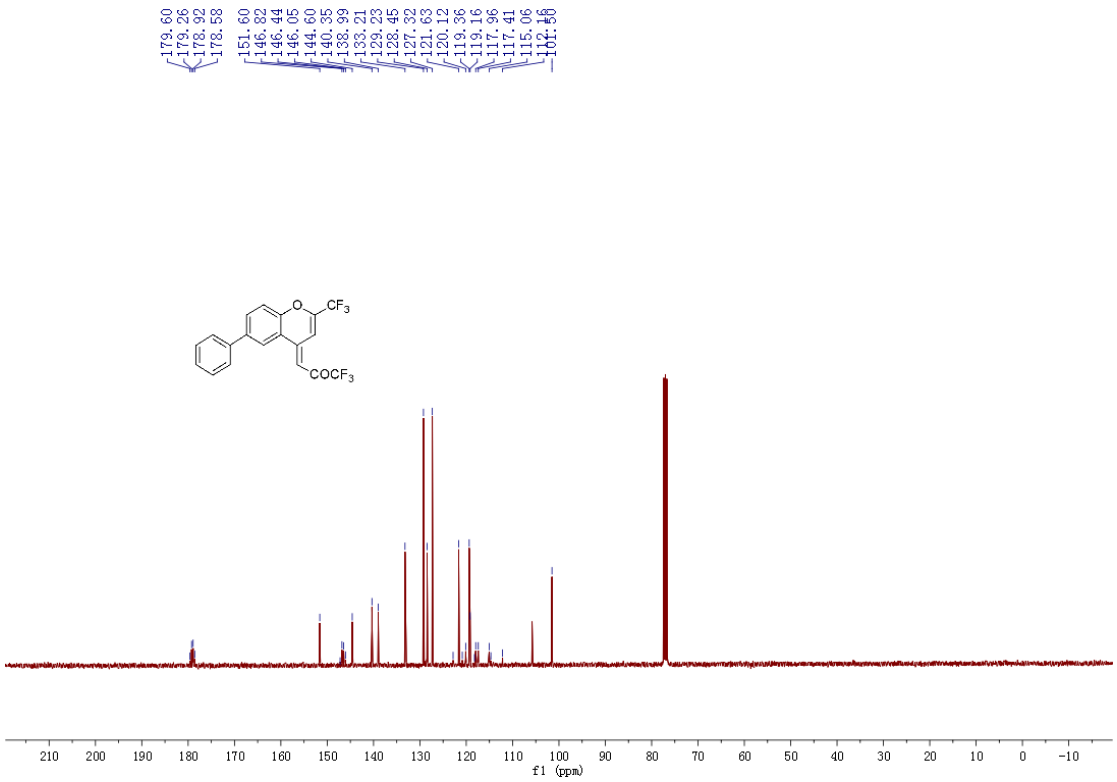
^{1}H NMR spectra of **3u** in $CDCl_3$



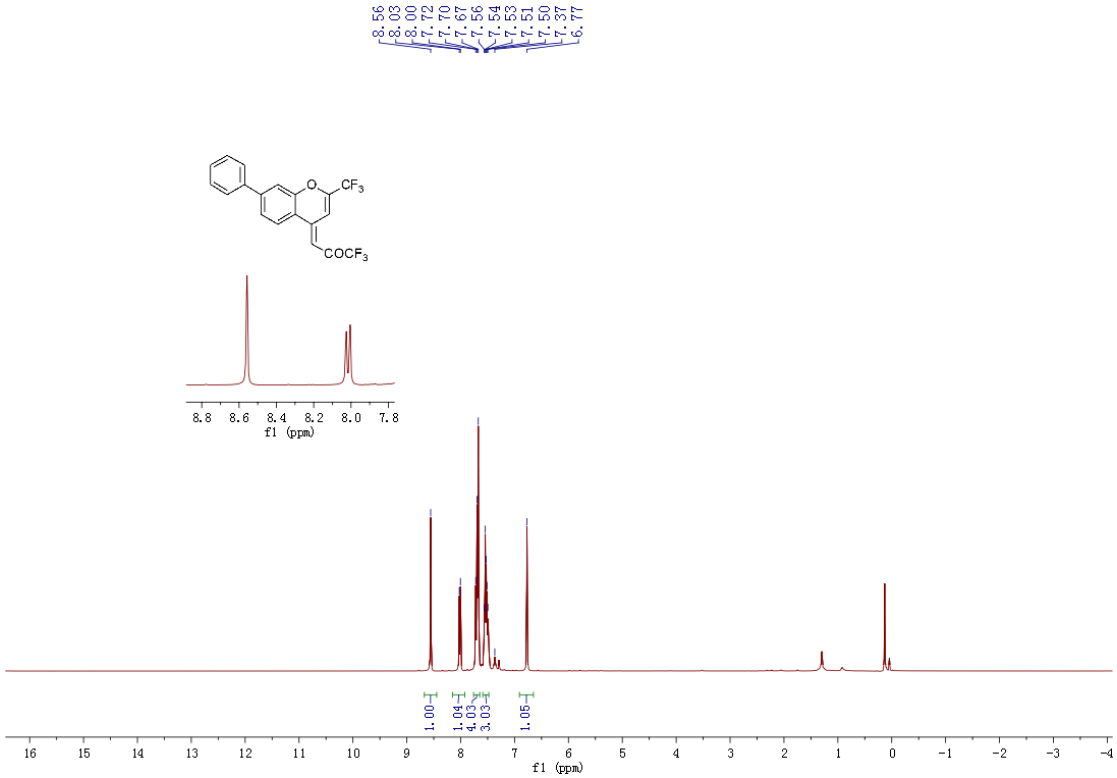
^{19}F NMR spectra of **3u** in $CDCl_3$



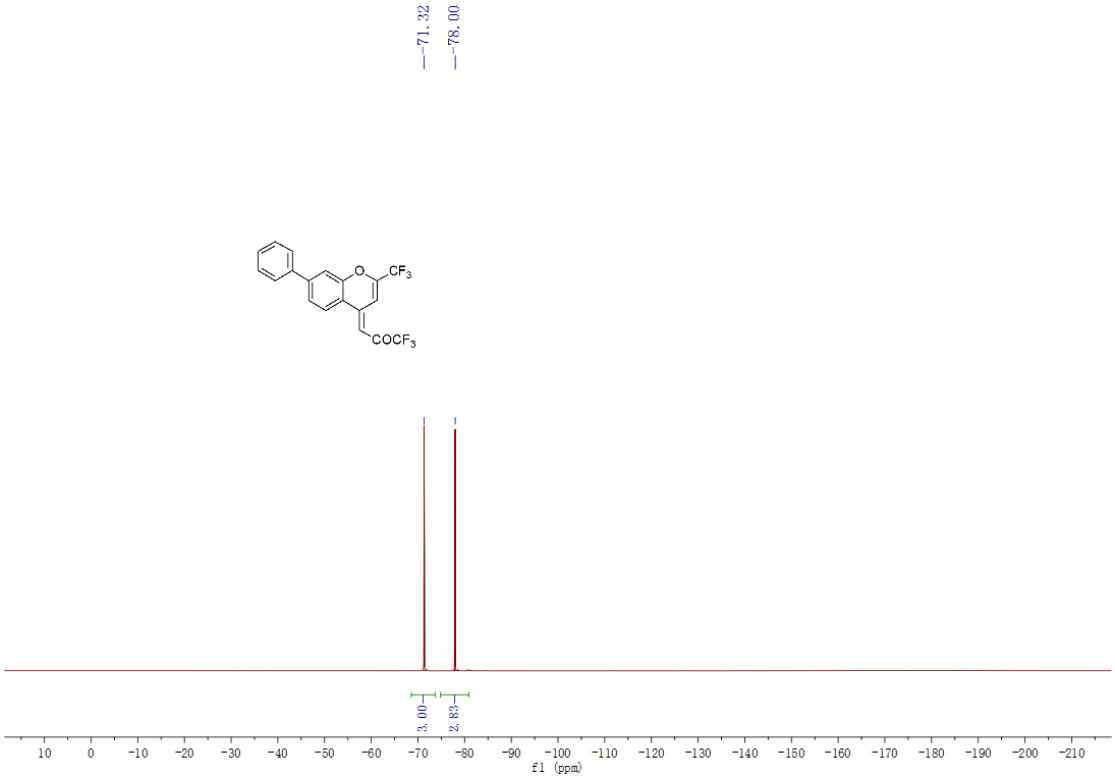
^{13}C NMR spectra of **3u** in $CDCl_3$



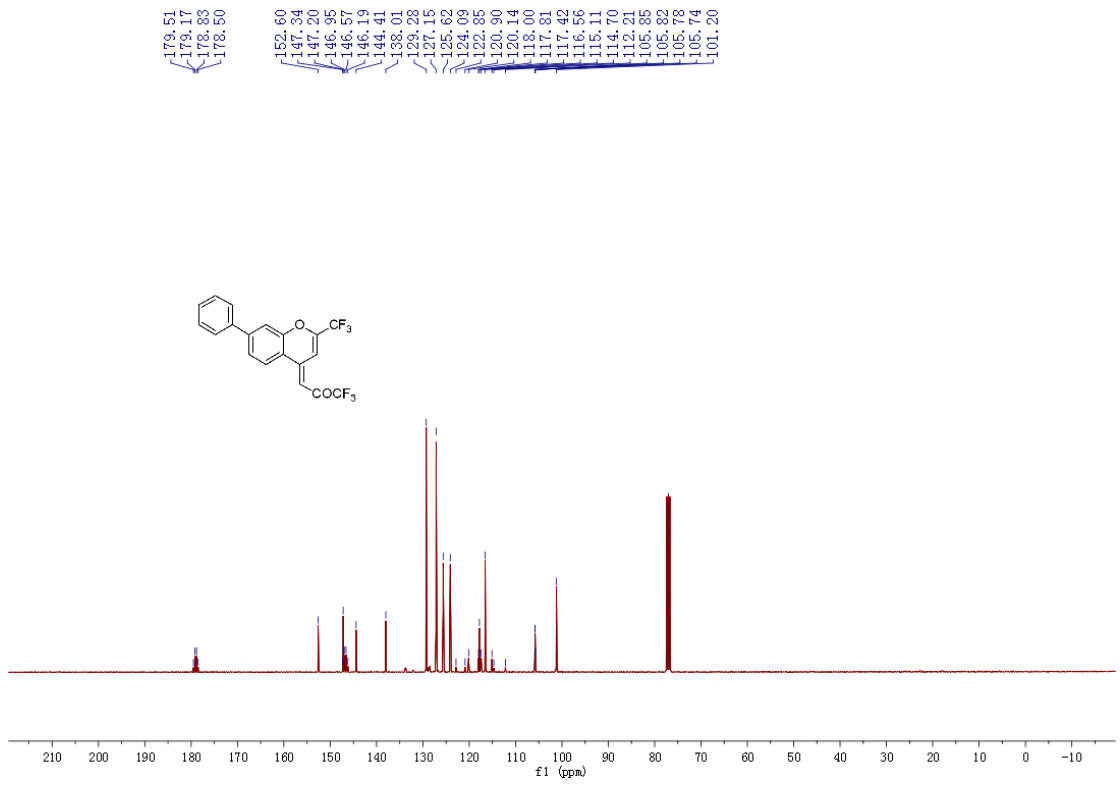
^{1}H NMR spectra of **3v** in $CDCl_3$



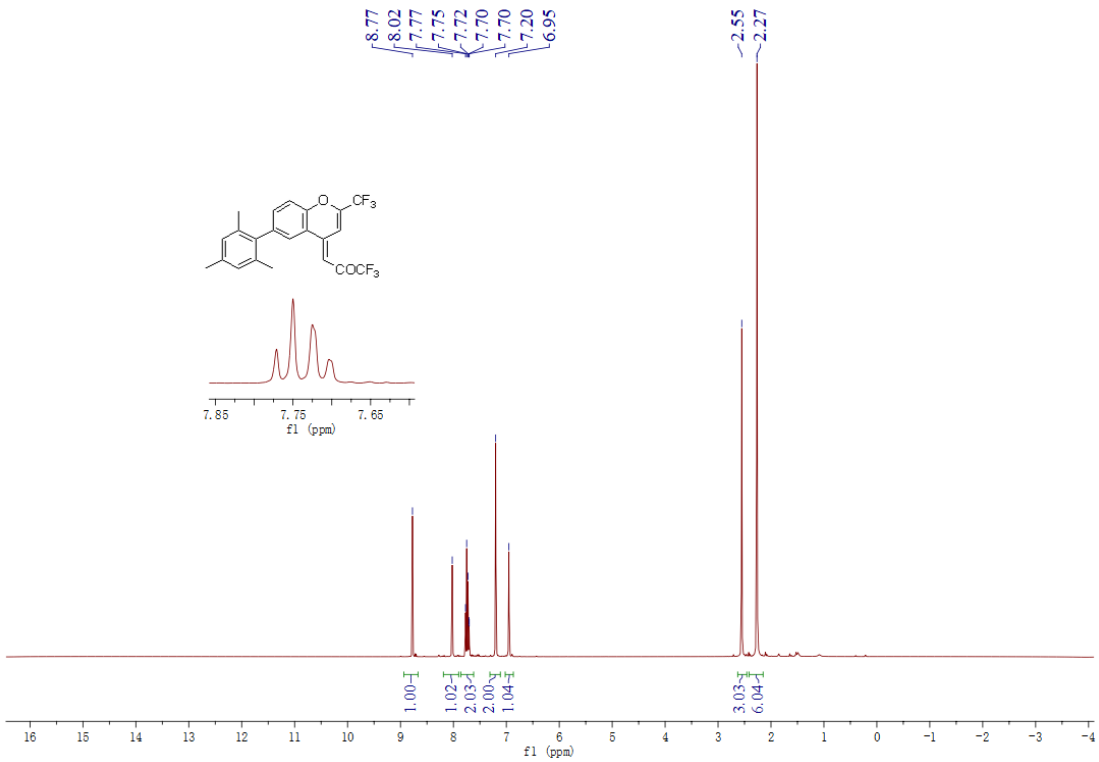
^{19}F NMR spectra of **3v** in $CDCl_3$



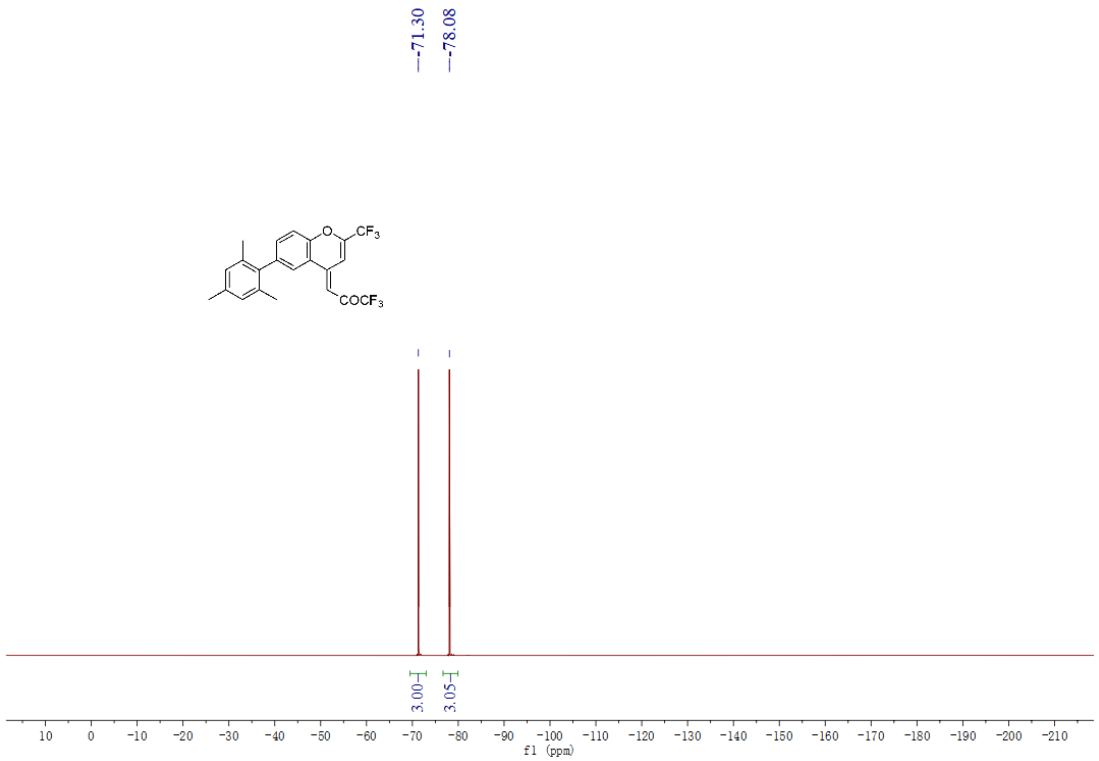
^{13}C NMR spectra of **3v** in $CDCl_3$



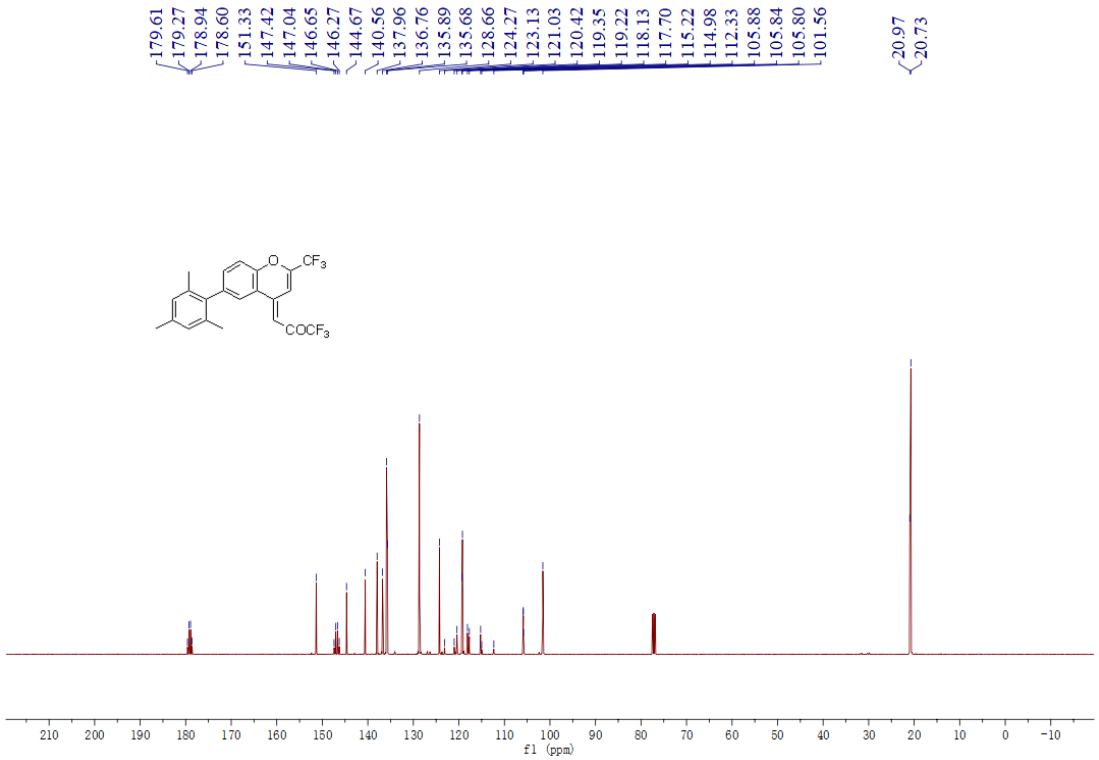
^{1}H NMR spectra of **3w** in $CDCl_3$



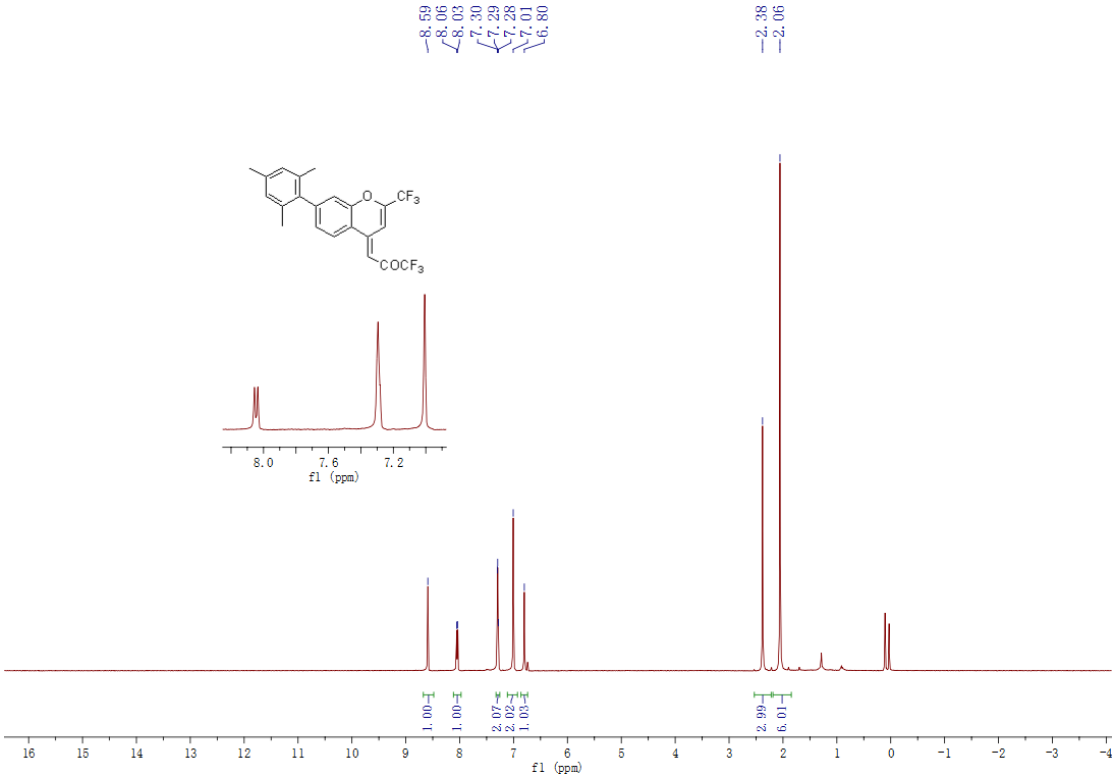
^{19}F NMR spectra of **3w** in $CDCl_3$



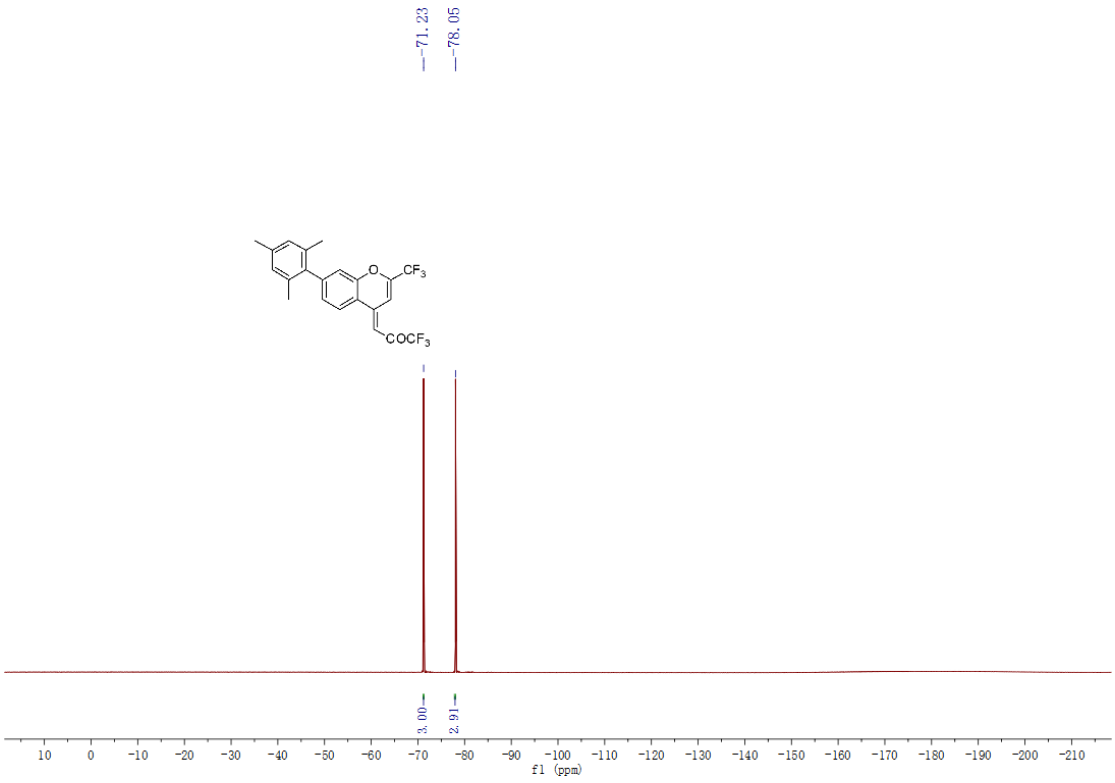
^{13}C NMR spectra of **3w** in $CDCl_3$



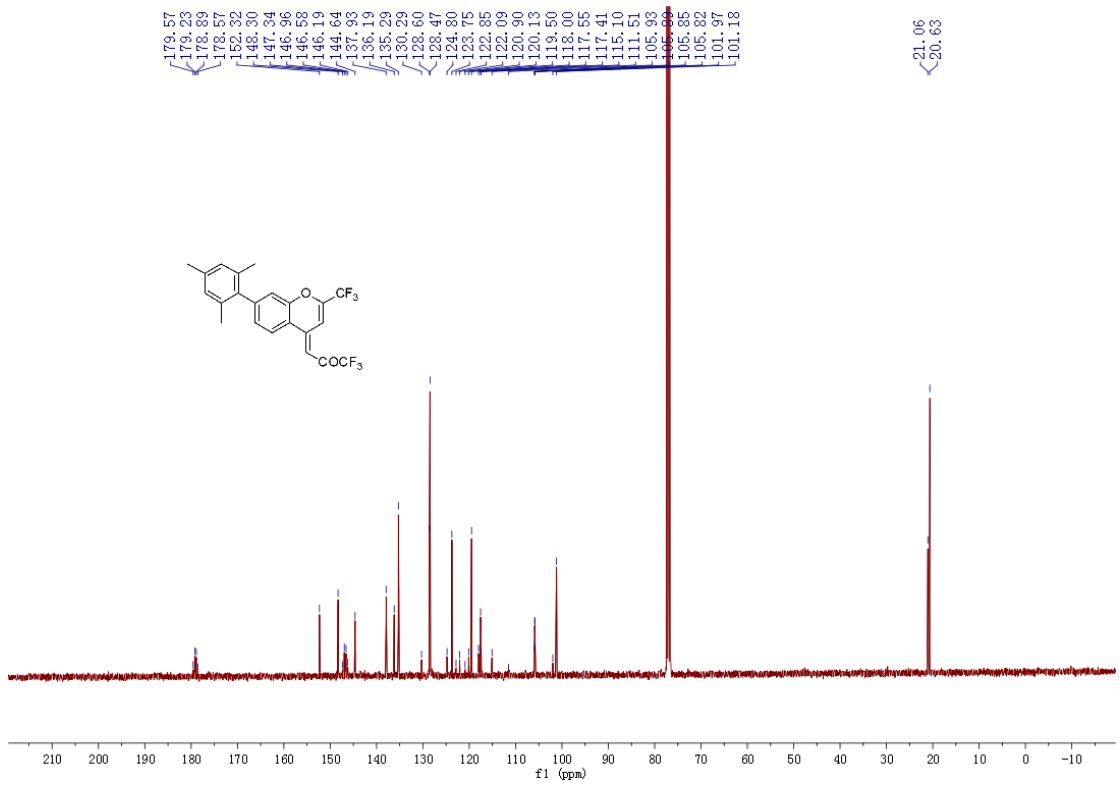
^{1}H NMR spectra of **3x** in $CDCl_3$



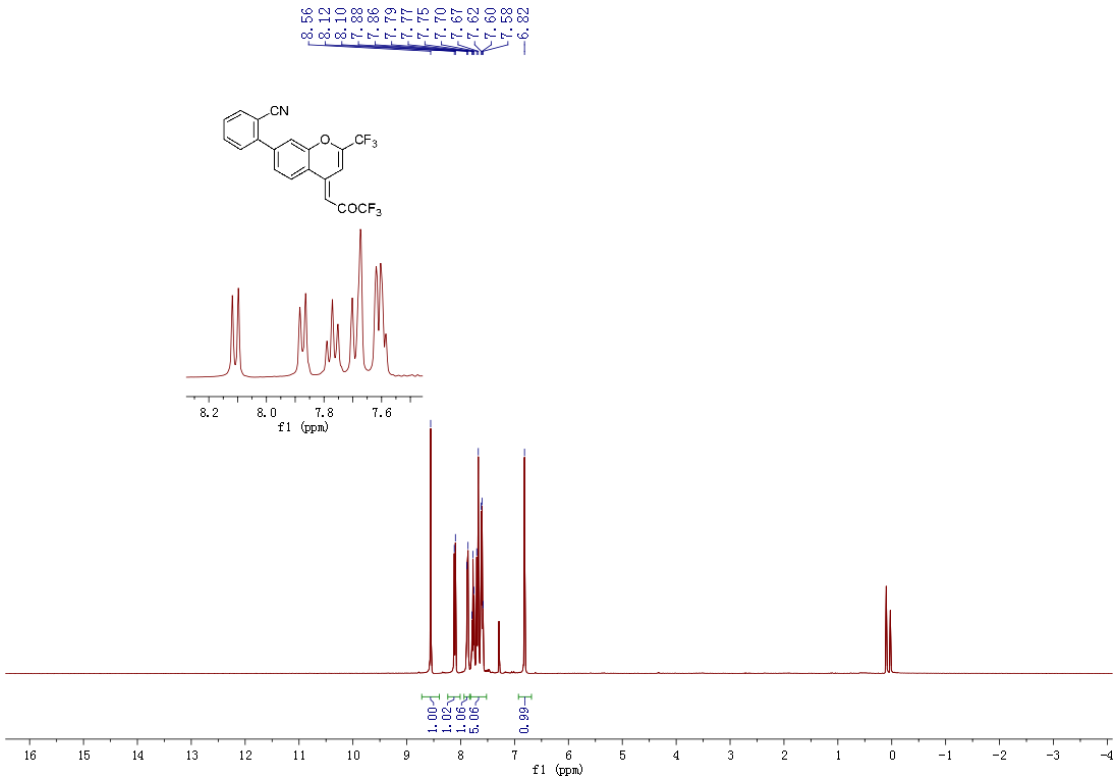
^{19}F NMR spectra of **3x** in $CDCl_3$



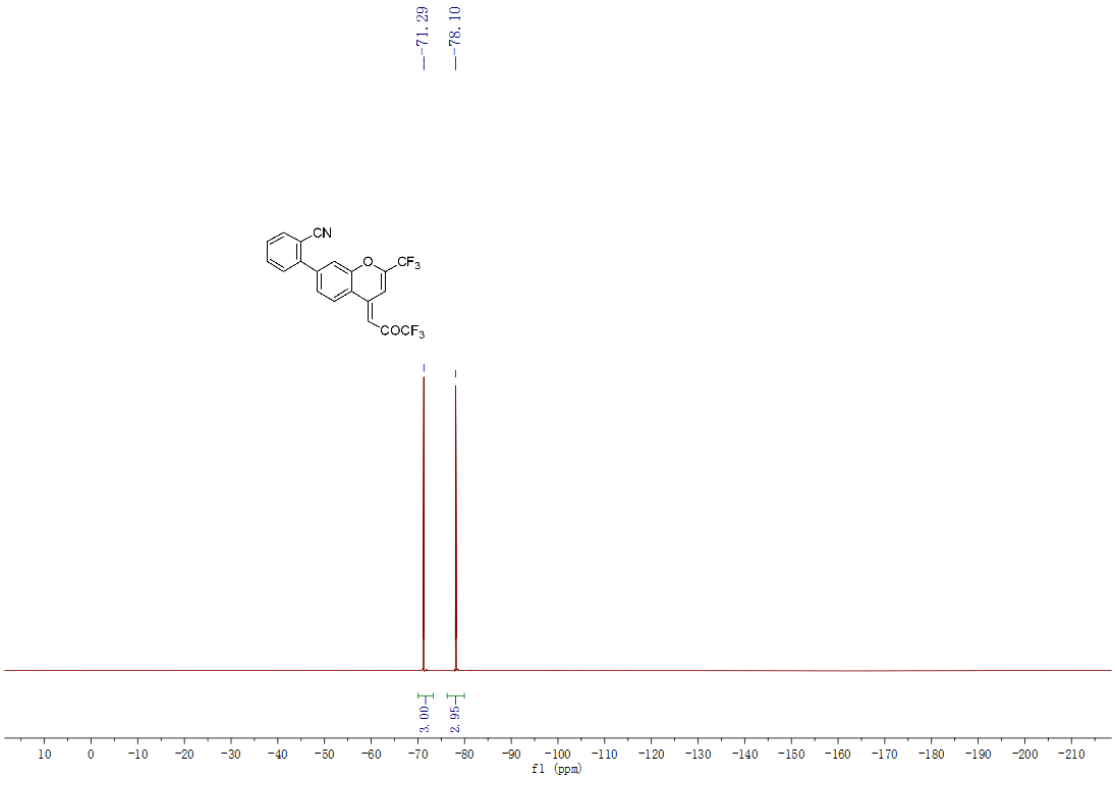
^{13}C NMR spectra of **3x** in $CDCl_3$



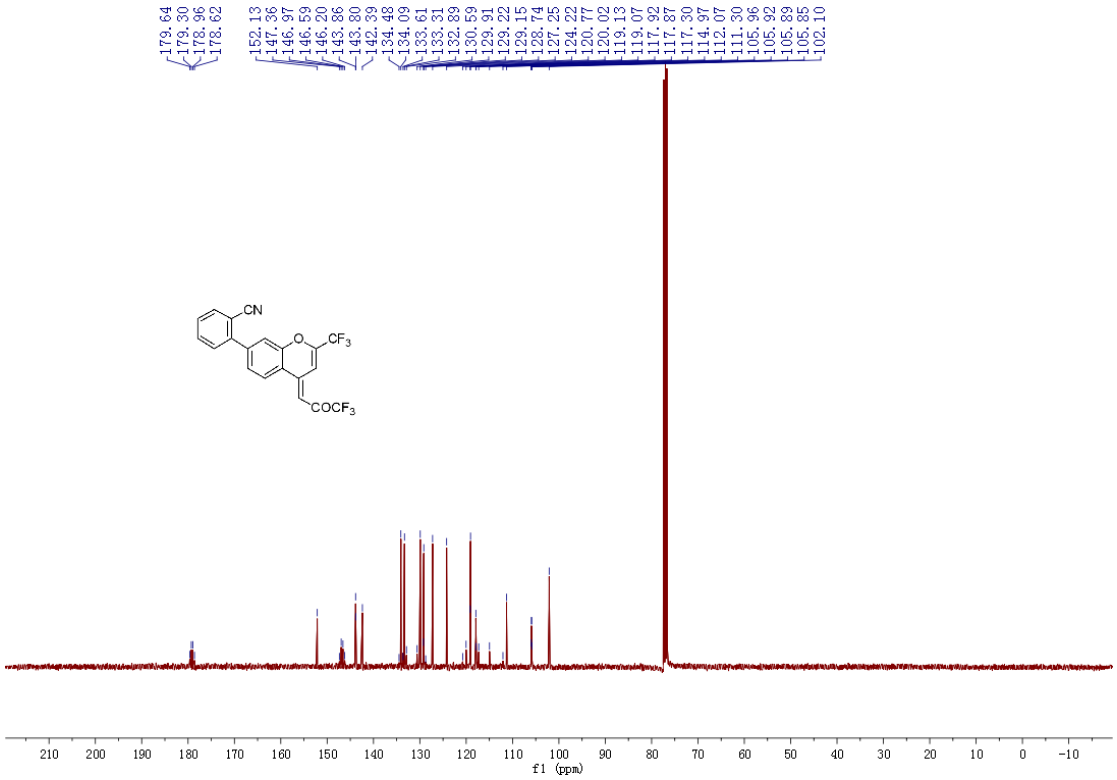
^{1}H NMR spectra of **3y** in $CDCl_3$



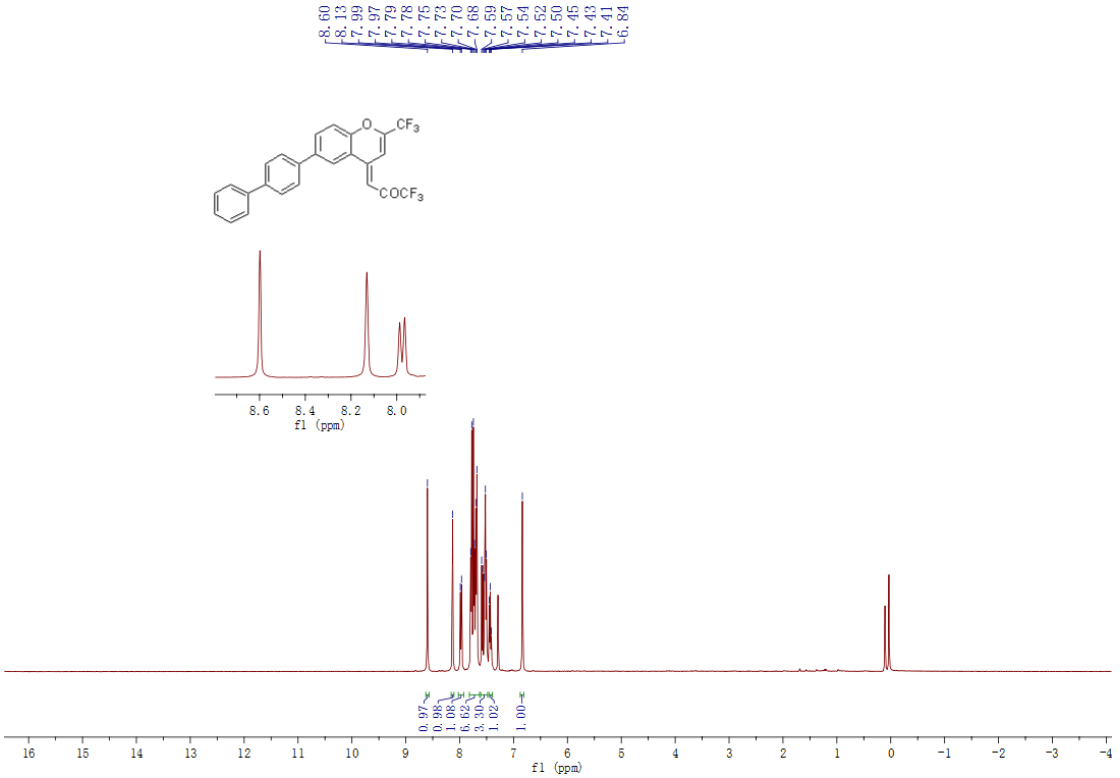
^{19}F NMR spectra of **3y** in $CDCl_3$



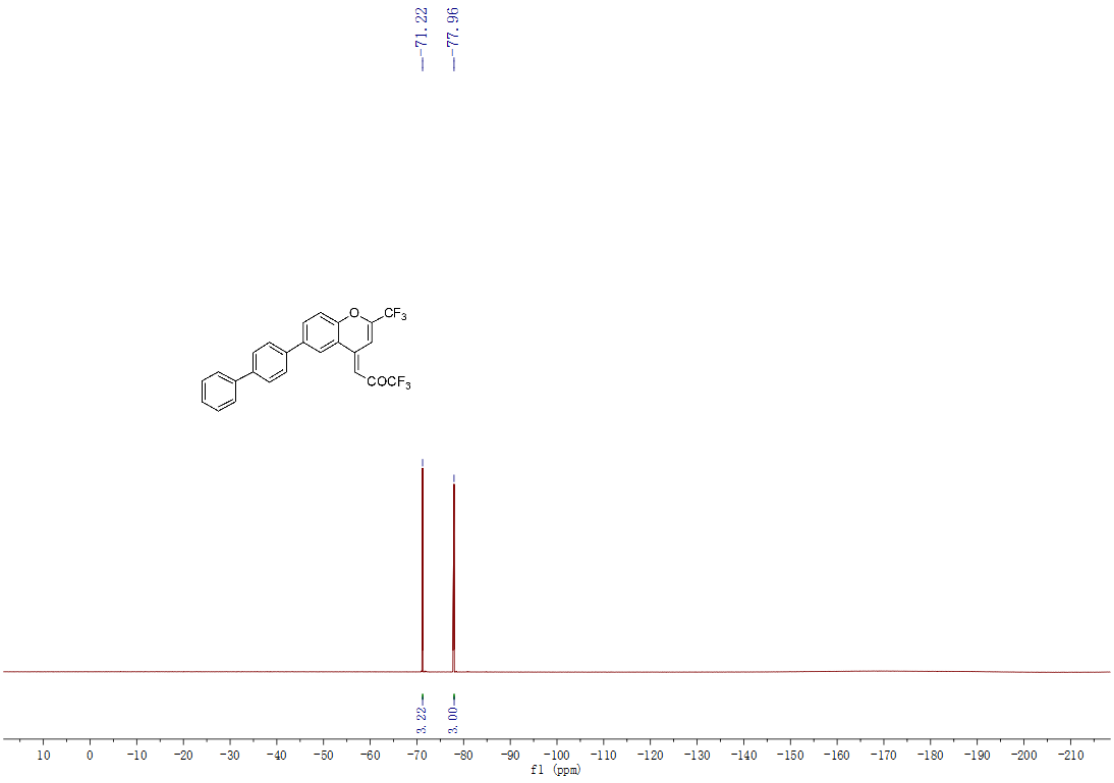
^{13}C NMR spectra of **3y** in $CDCl_3$



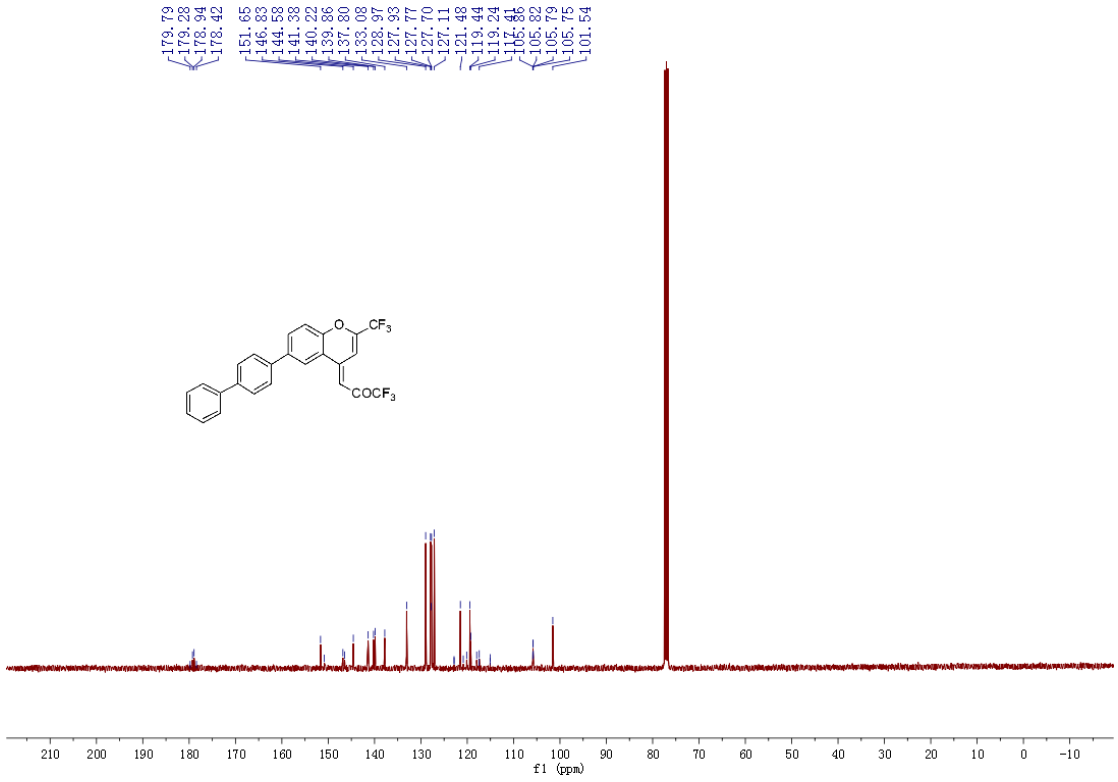
^{1}H NMR spectra of **3z** in $CDCl_3$



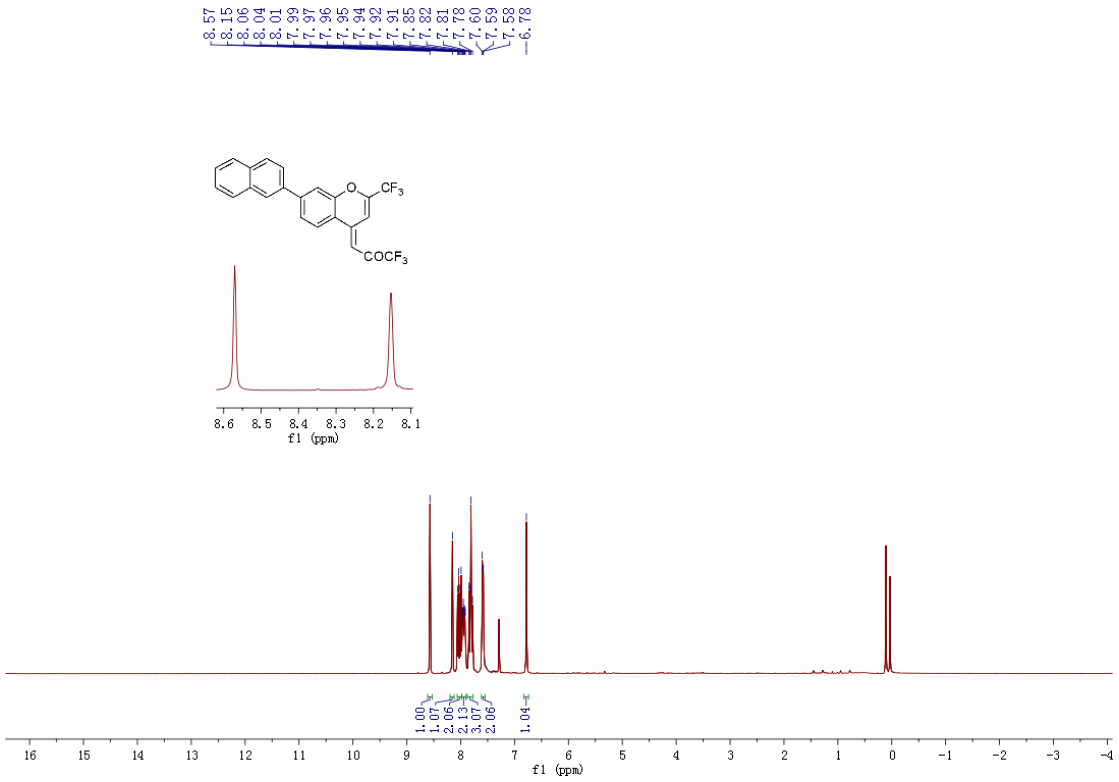
^{19}F NMR spectra of **3z** in $CDCl_3$



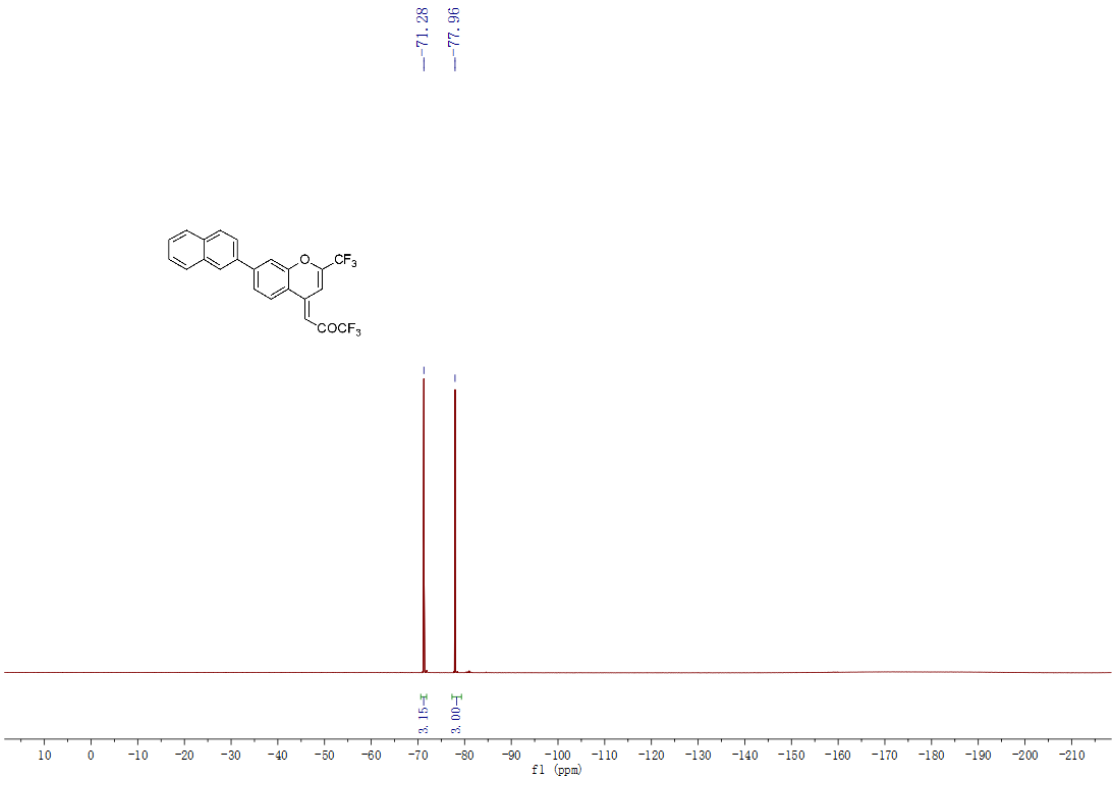
^{13}C NMR spectra of **3z** in $CDCl_3$



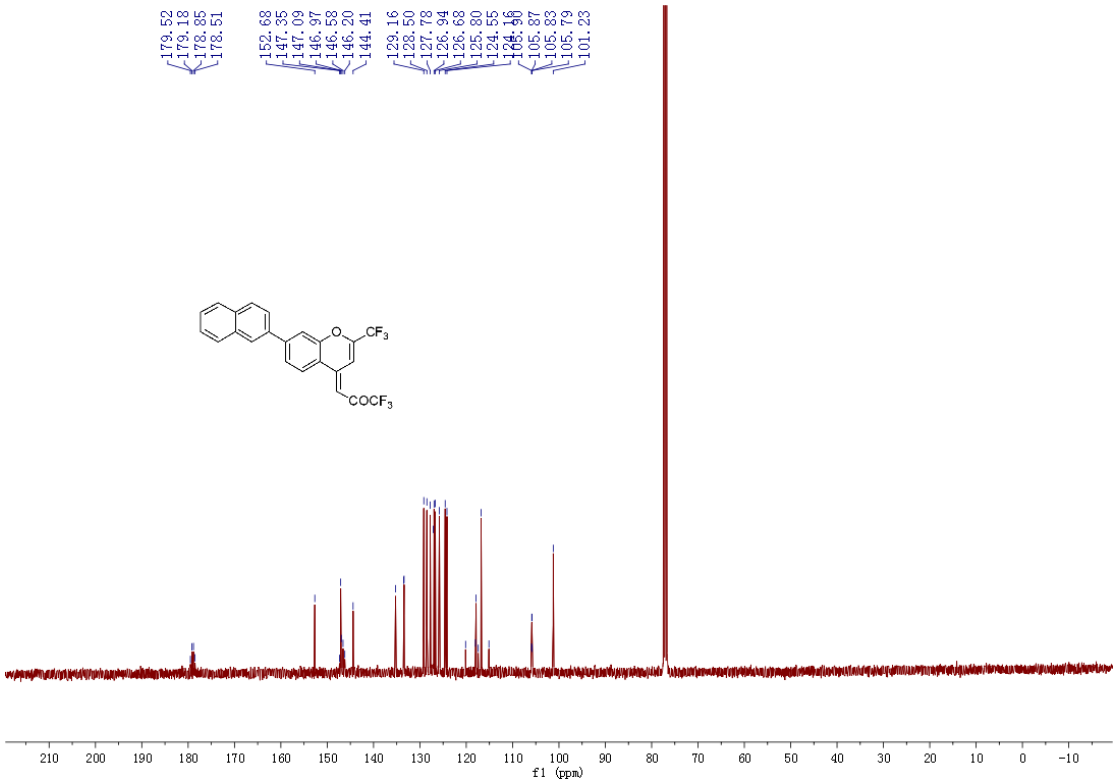
^{1}H NMR spectra of **3aa** in $CDCl_3$



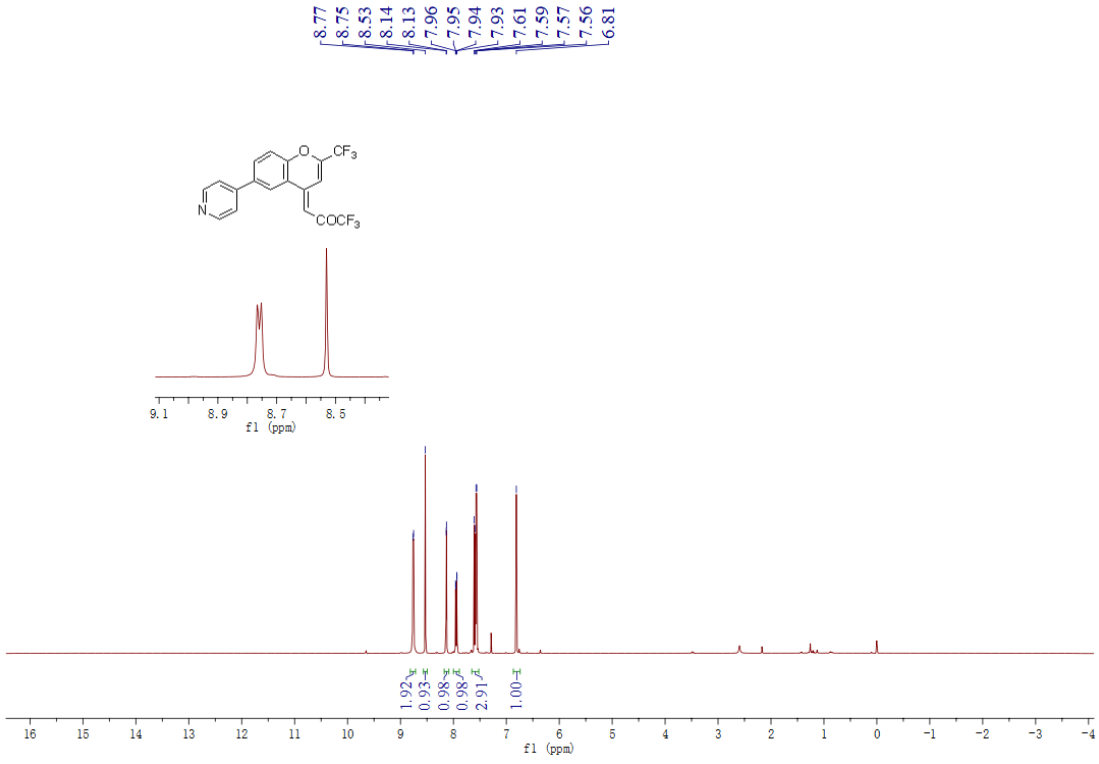
^{19}F NMR spectra of **3aa** in $CDCl_3$



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

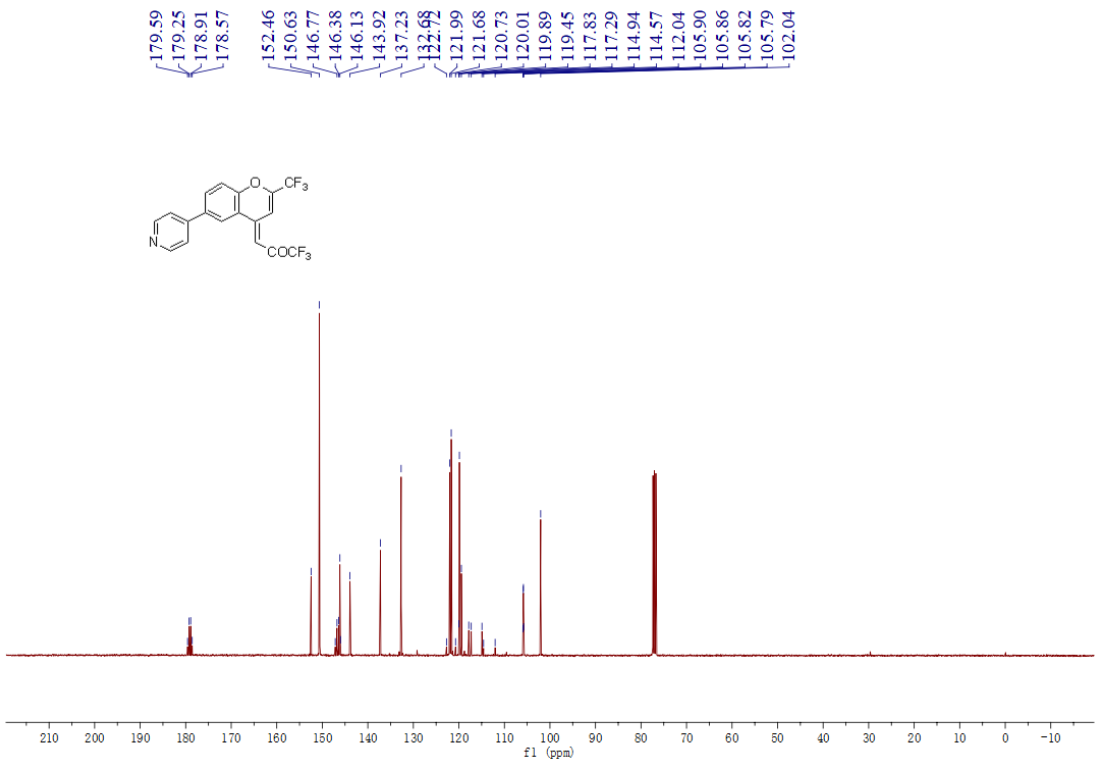


^{1}H NMR spectra of **3ab** in $CDCl_3$

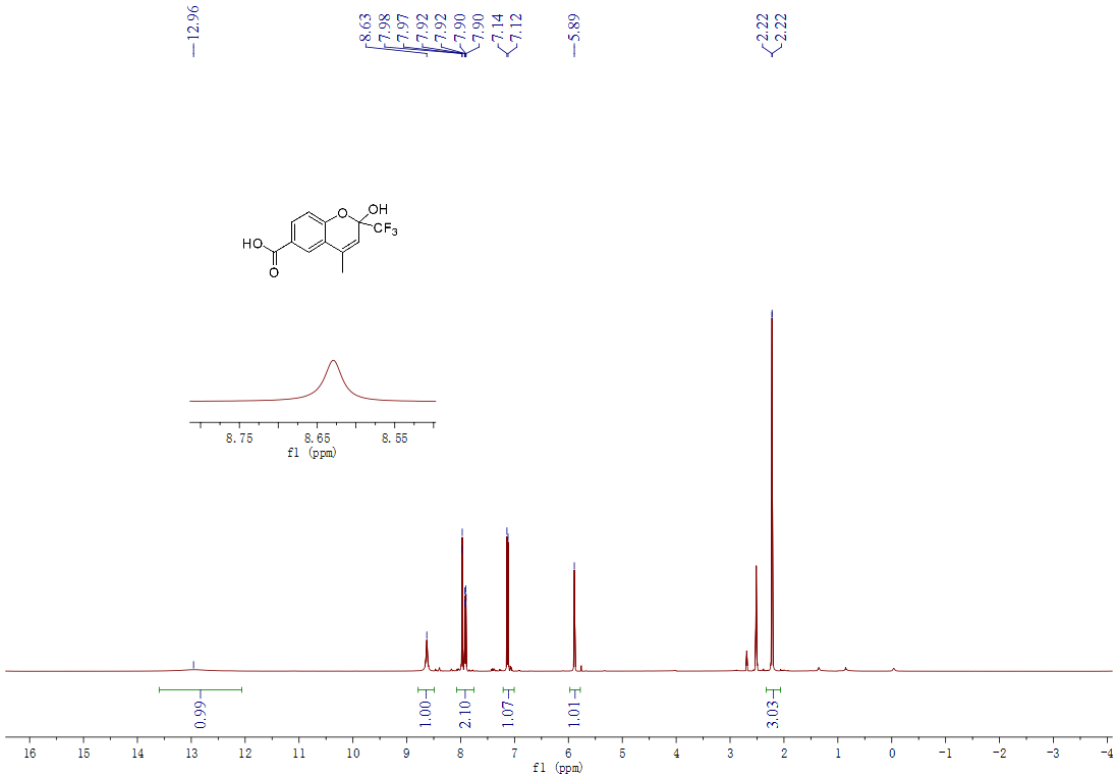


^{19}F NMR spectra of **3ab** in $CDCl_3$

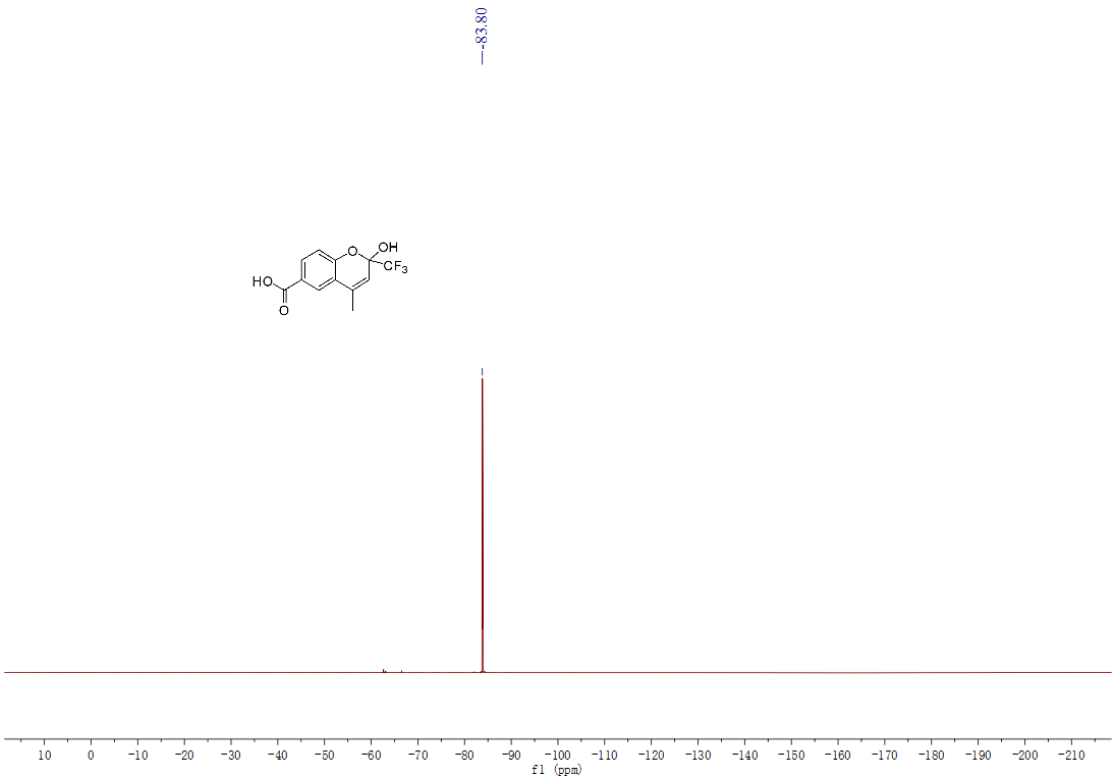
^{13}C NMR spectra of **3ab** in $CDCl_3$



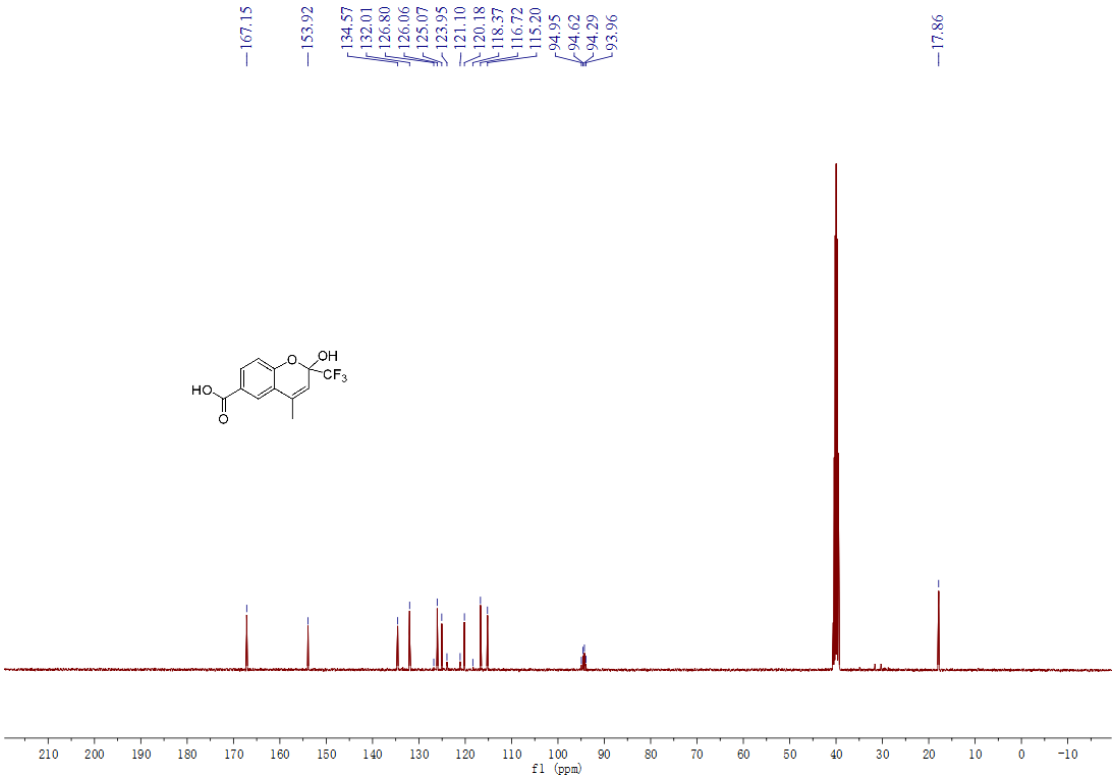
^{1}H NMR spectra of **4j** in DMSO-d_6



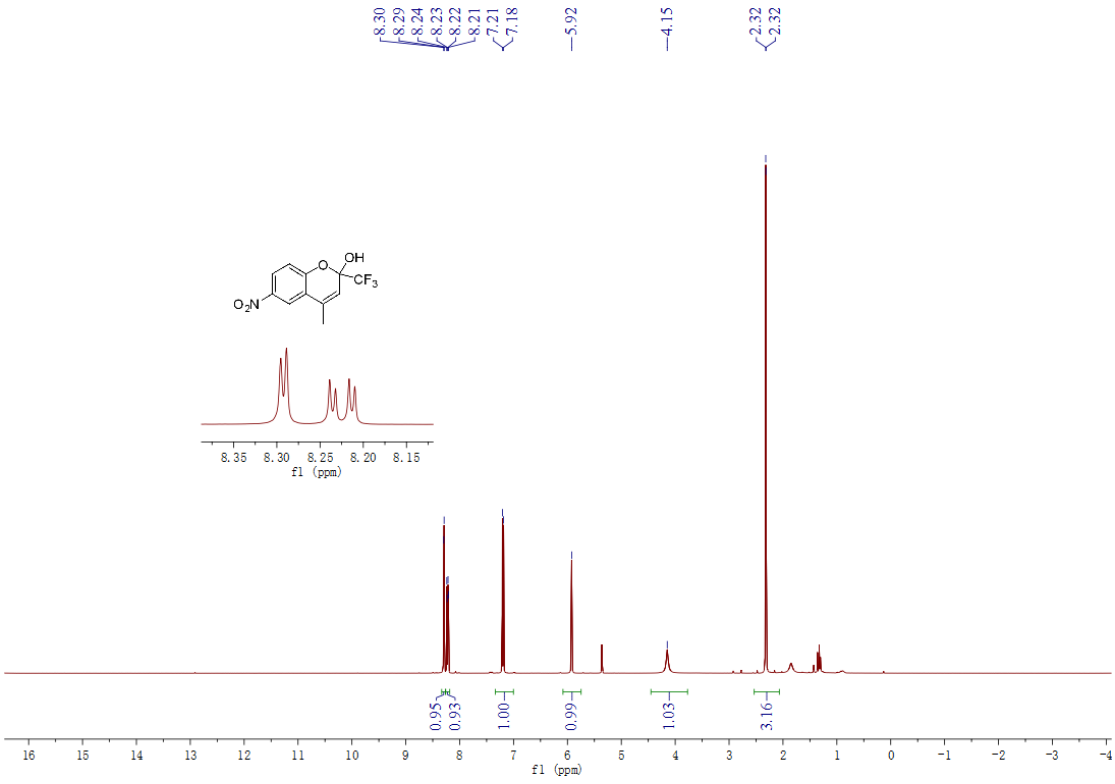
^{19}F NMR spectra of **4j** in DMSO-d_6



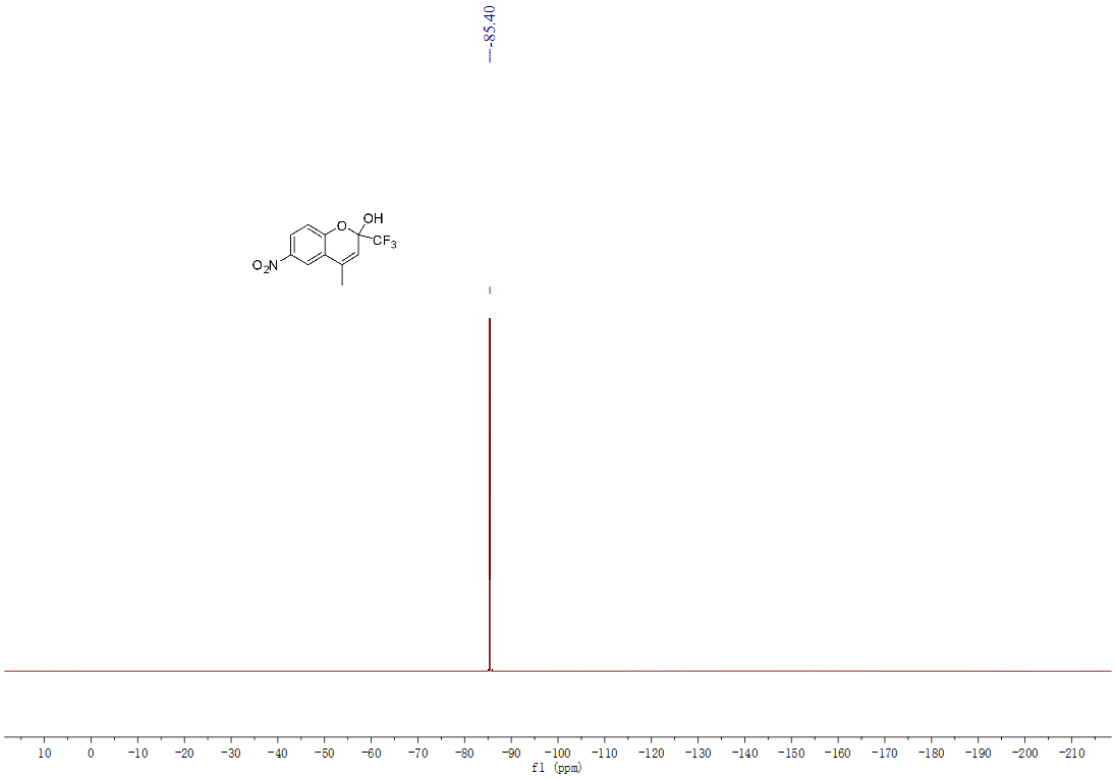
^{13}C NMR spectra of **4j** in DMSO-d_6



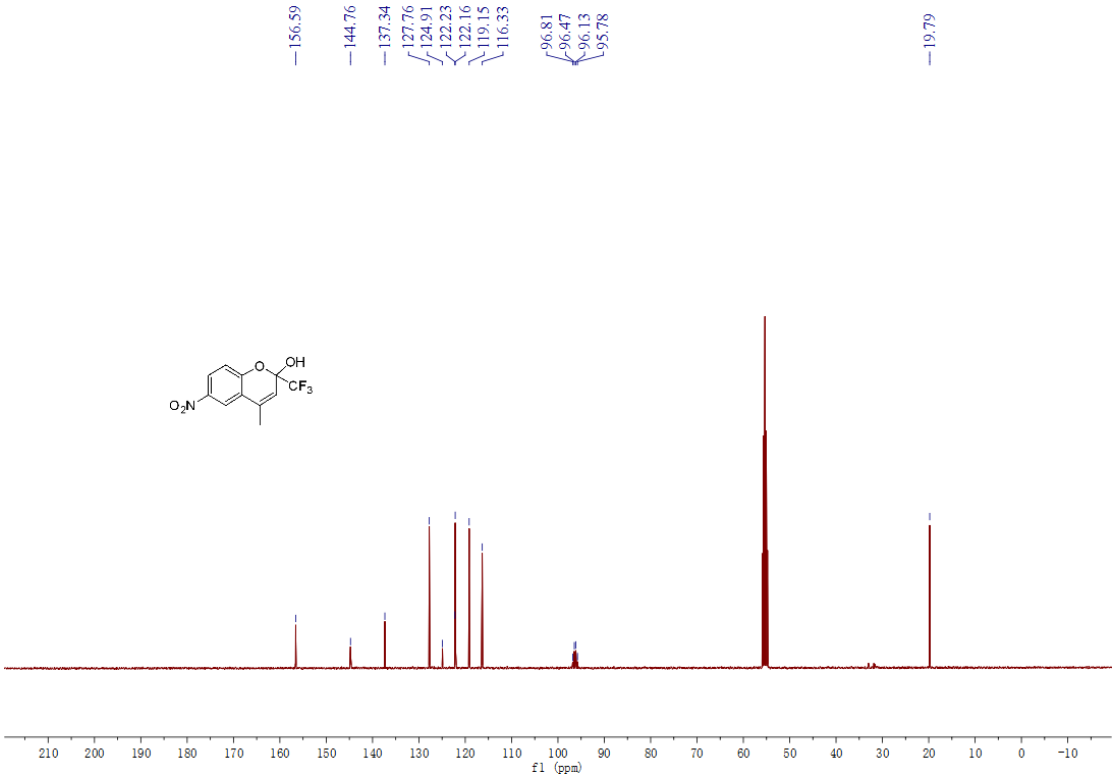
^{1}H NMR spectra of **4k** in CD_2Cl_2



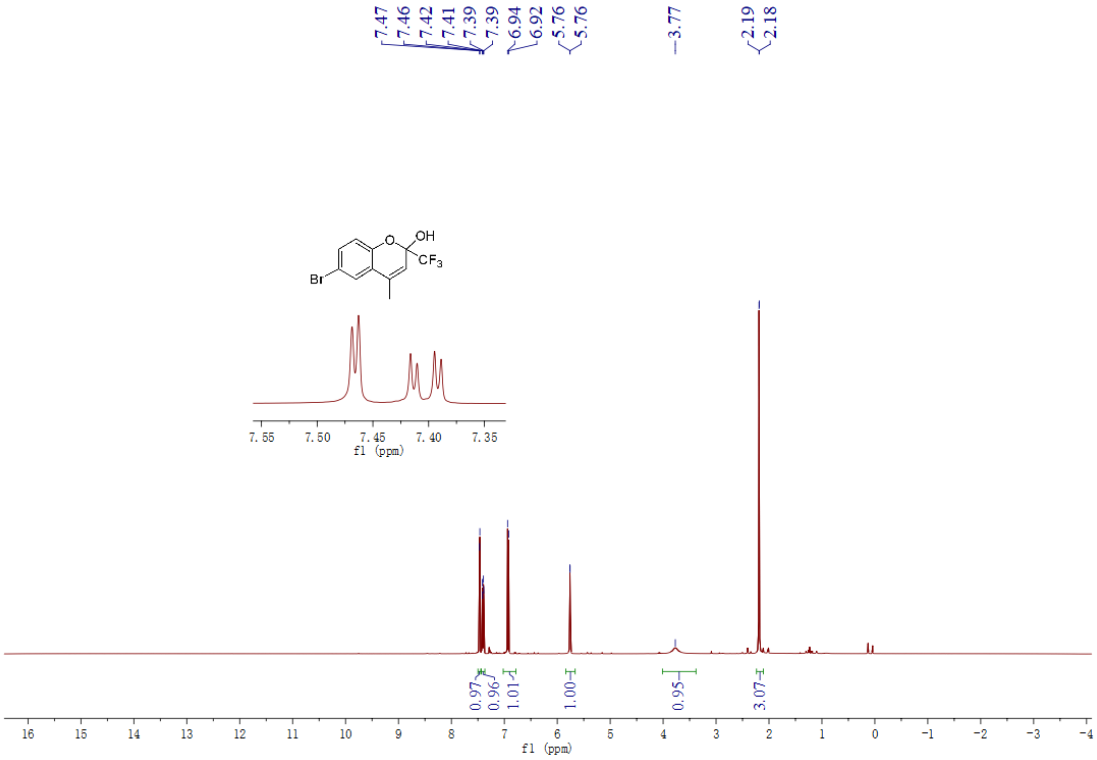
^{19}F NMR spectra of **4k** in CD_2Cl_2



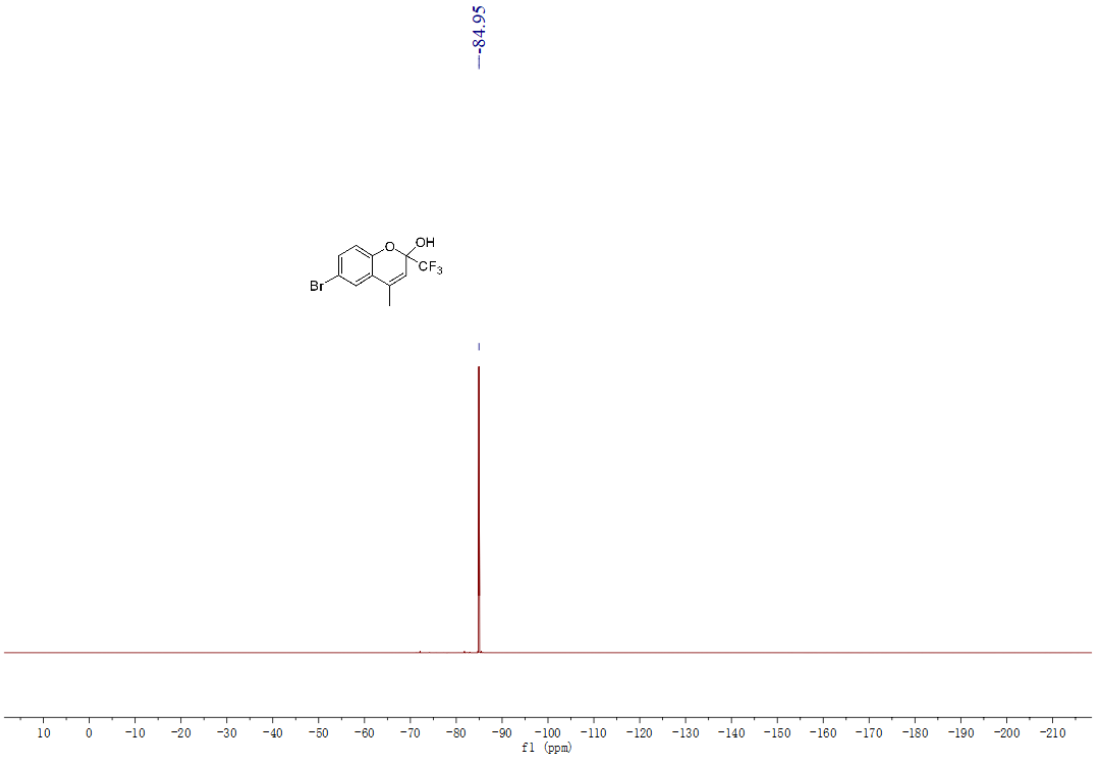
^{13}C NMR spectra of **4k** in CD_2Cl_2



^{1}H NMR spectra of **4q** in $CDCl_3$



^{19}F NMR spectra of **4q** in $CDCl_3$



^{13}C NMR spectra of **4q** in $CDCl_3$