

Supporting Information

Visible-light-mediated direct difluoromethylation of alkynoates: Synthesis of 3-difluoromethylated coumarins

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R. China.*

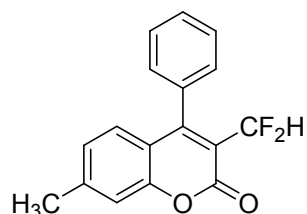
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General: Solvents were purified or dried in a standard manner. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ¹H NMR, ¹³C NMR and ¹⁹F{¹H} NMR spectra were recorded on a 500 MHz NMR spectrometers with TMS as an internal standard. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. HRMS analyses was recorded on Waters Q-TOF Global mass spectrometer. All of alkynoates **1** were synthesized according to the literature.¹

General experimental details

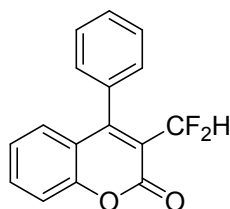
To a mixture of alkynoates **1** (0.20 mmol), 2-((difluoromethyl)sulfonyl)benzo[d]thiazole (0.30 mmol) and Na₂CO₃ (0.30 mmol) in 2.0 mL of DMSO was added *fac*-Ir(ppy)₃ (0.004 mmol, 2.0 mol%) under N₂ atmosphere. The solution was stirred at room temperature under 5 W blue LED irradiation for 24 h. Then the reaction mixture was diluted by adding EtOAc and brine. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over MgSO₄, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate 20:1 as the eluant) on silica gel to give the desired products **3**.



3-(difluoromethyl)-6-methyl-4-phenyl-2H-chromen-2-one (3a):

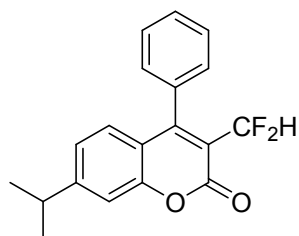
¹H NMR (500 MHz, CDCl₃): δ 7.58-7.56 (m, 3 H), 7.34-7.33 (m, 2 H), 7.23 (s, 1 H), 7.05-6.99 (m, 2 H), 6.52 (t, 1 H, *J* = 53.5 Hz), 2.48 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ 158.19, 156.47 (t, *J* = 4.3 Hz), 153.76, 145.21, 131.89, 129.65, 128.70,

128.37, 128.28, 125.93, 117.11, 116.60 (t, $J = 22.1$ Hz), 111.90 (t, $J = 237.0$ Hz), 21.77. ^{19}F NMR (470 MHz, CDCl_3): δ -114.56. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_2$: 287.0883, found: 287.0880.



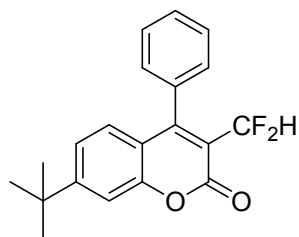
3-(difluoromethyl)-4-phenyl-2H-chromen-2-one (3b):

^1H NMR (500 MHz, CDCl_3): δ 7.64-7.61 (m, 1 H), 7.60-7.57 (m, 3 H), 7.43 (dd, 1 H, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz), 7.36-7.34 (m, 2 H), 7.25-7.22 (m, 1 H), 7.13 (dd, 1 H, $J_1 = 8.0$ Hz, $J_2 = 1.5$ Hz), 6.53 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 157.89, 156.39 (t, $J = 4.1$ Hz), 153.68, 133.46, 131.70, 129.74, 128.75, 128.58, 128.38, 124.66, 119.53, 117.82 (t, $J = 22.1$ Hz), 117.02, 111.73 (t, $J = 237.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -114.82. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{11}\text{F}_2\text{O}_2$: 273.0727, found: 273.0733.



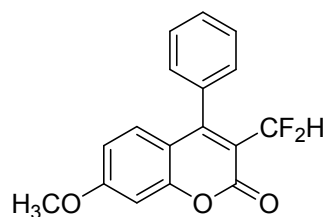
3-(difluoromethyl)-7-isopropyl-4-phenyl-2H-chromen-2-one (3c):

^1H NMR (500 MHz, CDCl_3): δ 7.58-7.55 (m, 3 H), 7.36-7.33 (m, 2 H), 7.27 (d, 1 H, $J = 2.0$ Hz), 7.10 (dd, 1 H, $J_1 = 10.0$ Hz, $J_2 = 2.0$ Hz), 7.04 (d, 1 H, $J = 10.5$ Hz), 6.53 (t, 1 H, $J = 66.5$ Hz), 3.05-2.99 (m, 1 H), 1.30 (d, 6 H, $J = 9.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 158.24, 156.44 (t, $J = 4.3$ Hz), 156.00, 153.96, 131.95, 129.62, 128.67, 128.47, 128.36, 124.42, 117.41, 116.67 (t, $J = 22.1$ Hz), 114.56, 111.90 (t, $J = 237.0$ Hz), 34.29, 23.50. ^{19}F NMR (470 MHz, CDCl_3): δ -114.54. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{19}\text{H}_{17}\text{F}_2\text{O}_2$: 315.1196, found: 315.1190.



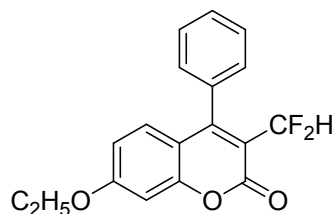
7-(tert-butyl)-3-(difluoromethyl)-4-phenyl-2H-chromen-2-one (3d):

^1H NMR (500 MHz, CDCl_3): δ 7.58-7.56 (m, 3 H), 7.43 (d, 1 H, $J = 2.0$ Hz), 7.36-7.33 (m, 2 H), 7.27 (dd, 1 H, $J_1 = 10.5$ Hz, $J_2 = 2.5$ Hz), 7.05 (d, 1 H, $J = 10.5$ Hz), 6.55 (t, 1 H, $J = 66.5$ Hz), 1.37 (s, 9 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.35, 156.29 (t, $J = 4.0$ Hz), 153.75, 131.96, 129.60, 128.65, 128.36, 128.10, 122.26, 117.05, 116.84, 116.66, 113.78, 111.87 (t, $J = 237.1$ Hz), 35.38, 30.92. ^{19}F NMR (470 MHz, CDCl_3): δ -114.52. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{20}\text{H}_{19}\text{F}_2\text{O}_2$: 329.1353, found: 329.1359.



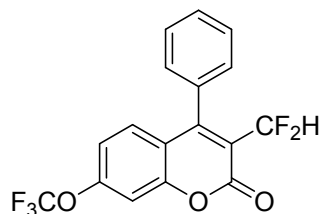
3-(difluoromethyl)-7-methoxy-4-phenyl-2H-chromen-2-one (3e):

^1H NMR (500 MHz, CDCl_3): δ 7.55-7.53 (m, 3 H), 7.32-7.30 (m, 2 H), 6.99 (d, 1 H, $J = 11.0$ Hz), 6.87 (d, 1 H, $J = 3.0$ Hz), 6.76 (dd, 1 H, $J_1 = 11.0$ Hz, $J_2 = 3.0$ Hz), 6.49 (t, 1 H, $J = 67.0$ Hz), 3.89 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 164.12, 158.36, 156.58 (t, $J = 4.0$ Hz), 155.69, 132.08, 129.69, 129.60, 128.67, 128.34, 114.46 (t, $J = 22.1$ Hz), 113.05, 112.99, 112.07 (t, $J = 236.0$ Hz), 100.66, 55.96. ^{19}F NMR (470 MHz, CDCl_3): δ -114.18. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_3$: 303.0883, found: 303.0876.



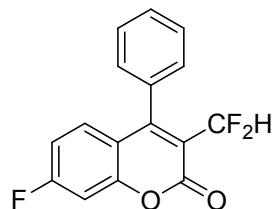
3-(difluoromethyl)-7-ethoxy-4-phenyl-2H-chromen-2-one (3f):

^1H NMR (500 MHz, CDCl_3): δ 7.55-7.53 (m, 3 H), 7.32-7.30 (m, 2 H), 6.98 (d, 1 H, $J = 11.5$ Hz), 6.85 (d, 1 H, $J = 3.0$ Hz), 6.74 (dd, 1 H, $J_1 = 11.0$ Hz, $J_2 = 3.0$ Hz), 6.49 (t, 1 H, $J = 67.0$ Hz), 4.11 (q, 2 H, $J = 9.0$ Hz), 1.46 (t, 3 H, $J = 9.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 163.51, 158.43, 156.59, 155.70, 132.15, 129.64, 129.55, 128.65, 128.34, 114.33 (t, $J = 22.1$ Hz), 113.40, 112.84, 112.09 (t, $J = 236.6$ Hz), 101.09, 64.44, 14.47. ^{19}F NMR (470 MHz, CDCl_3): δ -114.12. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_3$: 317.0989, found: 317.0981.



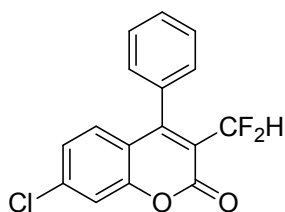
3-(difluoromethyl)-4-phenyl-7-(trifluoromethoxy)-2H-chromen-2-one (3g):

^1H NMR (500 MHz, CDCl_3): δ 7.61-7.59 (m, 3 H), 7.36-7.34 (m, 2 H), 7.293-7.289 (m, 1 H), 7.18 (d, 1 H, $J = 9.0$ Hz), 7.08 (dd, 1 H, $J_1 = 9.0$ Hz, $J_2 = 1.0$ Hz), 6.53 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 157.22, 155.53 (t, $J = 4.1$ Hz), 154.38, 152.46, 131.27, 130.23, 130.02, 128.92, 128.28, 120.20 (q, $J = 258.6$ Hz), 117.93, 117.83 (t, $J = 22.3$ Hz), 116.72, 111.47 (t, $J = 237.9$ Hz), 108.85. ^{19}F NMR (470 MHz, CDCl_3): δ -57.74 (s, 3 F), -114.88 (s, 2 F). HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{10}\text{F}_5\text{O}_3$: 357.0550, found: 357.0555.



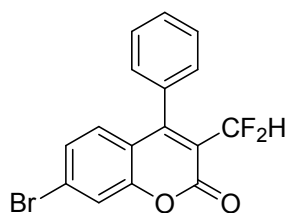
3-(difluoromethyl)-7-fluoro-4-phenyl-2H-chromen-2-one (3h):

^1H NMR (500 MHz, CDCl_3): δ 7.60-7.58 (m, 3 H), 7.35-7.33 (m, 2 H), 7.15-7.12 (m, 2 H), 6.97 (td, 1 H, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz), 6.50 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 165.42 (d, $J = 255.6$ Hz), 157.48, 155.95 (t, $J = 4.1$ Hz), 154.93 (d, $J = 13.1$ Hz), 131.50, 130.62 (d, $J = 10.4$ Hz), 129.93, 128.88, 128.29, 116.73 (td, $J_1 = 22.4$ Hz, $J_2 = 2.9$ Hz), 116.30 (d, $J = 2.5$ Hz), 112.91 (d, $J = 22.5$ Hz), 111.65 (t, $J = 237.5$ Hz), 104.50 (t, $J = 25.5$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -102.34 (s, 1 F), -114.81 (s, 2 F). HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{10}\text{F}_3\text{O}_2$: 291.0633, found: 291.0637.



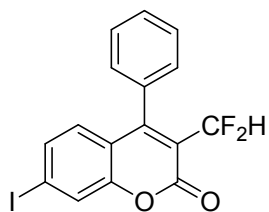
7-chloro-3-(difluoromethyl)-4-phenyl-2H-chromen-2-one (3i):

^1H NMR (500 MHz, CDCl_3): δ 7.61-7.58 (m, 3 H), 7.44 (d, 1 H, $J = 2.0$ Hz), 7.34-7.33 (m, 2 H), 7.20 (dd, 1 H, $J_1 = 9.0$ Hz, $J_2 = 2.5$ Hz), 7.07 (d, 1 H, $J = 9.0$ Hz), 6.52 (t, 1 H, $J = 54.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 157.26, 155.73 (t, $J = 4.3$ Hz), 153.87, 139.67, 131.32, 129.96, 129.50, 128.89, 128.30, 125.30, 118.19, 117.75 (t, $J = 22.3$ Hz), 117.27, 111.52 (t, $J = 237.8$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -114.79. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{10}\text{ClF}_2\text{O}_2$: 307.0337, found: 307.0332.



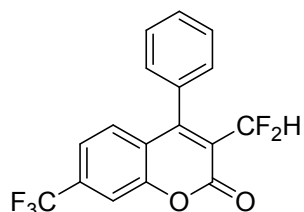
7-bromo-3-(difluoromethyl)-4-phenyl-2H-chromen-2-one (3j):

^1H NMR (500 MHz, CDCl_3): δ 7.61-7.59 (m, 4 H), 7.37-7.32 (m, 3 H), 6.99 (d, 1 H, $J = 8.5$ Hz), 6.52 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 157.20, 155.79 (t, $J = 4.3$ Hz), 153.75, 131.27, 129.96, 129.55, 128.89, 128.30, 128.16, 127.83, 120.26, 118.56, 117.98 (t, $J = 22.3$ Hz), 111.52 (t, $J = 237.9$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -114.84. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{10}\text{BrF}_2\text{O}_2$: 350.9832, found: 350.9837.



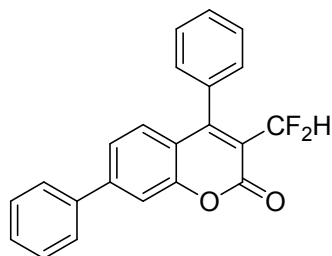
3-(difluoromethyl)-7-iodo-4-phenyl-2H-chromen-2-one (3k):

^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, 1 H, $J = 1.0$ Hz), 7.57-7.53 (m, 4 H), 7.31-7.30 (m, 2 H), 6.79 (d, 1 H, $J = 8.5$ Hz), 6.49 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 157.11, 155.91 (t, $J = 4.4$ Hz), 153.33, 134.02, 131.22, 129.95, 129.40, 128.89, 128.30, 126.16, 119.08, 118.26 (t, $J = 22.3$ Hz), 111.53 (t, $J = 237.8$ Hz), 99.75. ^{19}F NMR (470 MHz, CDCl_3): δ -114.86. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{16}\text{H}_{10}\text{F}_2\text{IO}_2$: 398.9693, found: 398.9698.



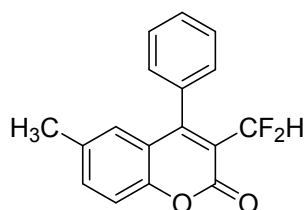
3-(difluoromethyl)-4-phenyl-7-(trifluoromethyl)-2H-chromen-2-one (3l):

^1H NMR (500 MHz, CDCl_3): δ 7.68 (s, 1 H), 7.62-7.60 (m, 3 H), 7.47 (dd, 1 H, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz), 7.36-7.35 (m, 2 H), 7.29 (s, 1 H), 6.56 (t, 1 H, $J = 53.0$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 156.93, 155.21 (t, $J = 4.0$ Hz), 153.29, 134.88 (q, $J = 33.5$ Hz), 130.96, 130.15, 129.51, 129.01, 128.29, 122.89 (q, $J = 271.4$ Hz), 122.17, 121.89 (q, $J = 3.4$ Hz), 119.79 (t, $J = 22.4$ Hz), 114.46 (q, $J = 4.0$ Hz), 111.26 (t, $J = 238.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -63.17 (s, 3 F), -115.16 (s, 2 F). HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{10}\text{F}_5\text{O}_2$: 341.0601, found: 341.0594.



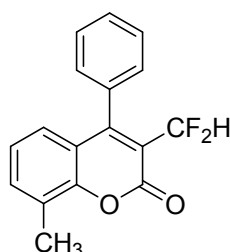
3-(difluoromethyl)-4,7-diphenyl-2H-chromen-2-one (3m):

^1H NMR (500 MHz, CDCl_3): δ 7.66-7.59 (m, 6 H), 7.54-7.45 (m, 4 H), 7.40-7.38 (m, 2 H), 7.19 (d, 1 H, $J = 10.5$ Hz), 6.57 (t, 1 H, $J = 66.5$ Hz). ^{13}C NMR (125 MHz, CDCl_3): δ 158.08, 156.20, 154.10, 146.65, 138.64, 131.80, 129.74, 129.21, 128.97, 128.93, 128.77, 128.40, 127.27, 123.47, 118.42, 117.33 (t, $J = 22.1$ Hz), 115.03, 111.79 (t, $J = 237.4$ Hz). ^{19}F NMR (470 MHz, CDCl_3): δ -114.55. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{22}\text{H}_{15}\text{F}_2\text{O}_2$: 349.1040, found: 349.1046.



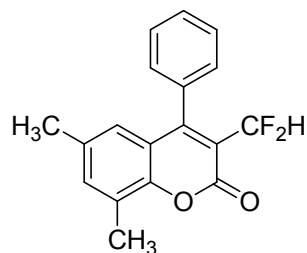
3-(difluoromethyl)-6-methyl-4-phenyl-2H-chromen-2-one (3n):

^1H NMR (500 MHz, CDCl_3): δ 7.60-7.57 (m, 3 H), 7.43 (dd, 1 H, $J_1 = 10.5$ Hz, $J_2 = 2.0$ Hz), 7.35-7.31 (m, 3 H), 6.87 (s, 1 H), 6.52 (t, 1 H, $J = 67.0$ Hz), 2.31 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.11, 156.39 (t, $J = 4.1$ Hz), 151.84, 134.54, 134.49, 131.82, 129.66, 128.72, 128.36, 128.15, 119.20, 117.68 (t, $J = 22.0$ Hz), 116.77, 111.81 (t, $J = 237.4$ Hz), 20.89. ^{19}F NMR (470 MHz, CDCl_3): δ -114.78. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_2$: 287.0883, found: 287.0881.



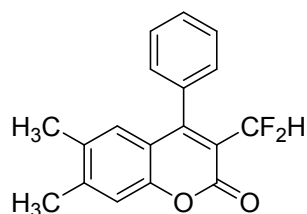
3-(difluoromethyl)-8-methyl-4-phenyl-2H-chromen-2-one (3n'):

^1H NMR (500 MHz, CDCl_3): δ 7.58-7.56 (m, 3 H), 7.47 (d, 1 H, $J = 9.5$ Hz), 7.35-7.33 (m, 2 H), 7.12 (t, 1 H, $J = 10.0$ Hz), 6.95 (d, 1 H, $J = 9.5$ Hz), 6.55 (t, 1 H, $J = 66.5$ Hz), 2.54 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.11, 156.70, 152.04, 134.70, 132.08, 129.58, 128.64, 128.39, 126.54, 126.31, 124.07, 119.32, 117.47 (t, $J = 22.1$ Hz), 111.84 (t, $J = 237.1$ Hz), 15.59. ^{19}F NMR (470 MHz, CDCl_3): δ -114.78. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_2$: 287.0883, found: 287.0889.



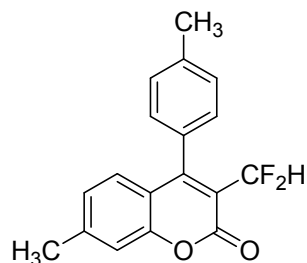
3-(difluoromethyl)-6,8-dimethyl-4-phenyl-2H-chromen-2-one (3o):

^1H NMR (500 MHz, CDCl_3): δ 7.56-7.55 (m, 3 H), 7.32-7.27 (m, 2 H), 7.19 (s, 1 H), 6.79 (s, 1 H), 6.49 (t, 1 H, $J = 53.5$ Hz), 2.36 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.40, 156.43, 152.13, 144.09, 133.59, 132.05, 129.55, 128.65, 128.36, 128.35, 117.52, 117.17, 116.60 (t, $J = 22.1$ Hz), 111.95 (t, $J = 236.9$ Hz), 20.33, 19.30. ^{19}F NMR (470 MHz, CDCl_3): δ -114.77. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_2$: 300.1040, found: 300.1046.



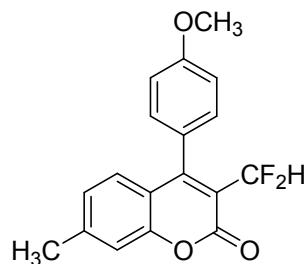
3-(difluoromethyl)-6,7-dimethyl-4-phenyl-2H-chromen-2-one (3p):

^1H NMR (500 MHz, CDCl_3): δ 7.56-7.55 (m, 3 H), 7.31-7.26 (m, 3 H), 6.67 (s, 1 H), 6.50 (t, 1 H, $J = 53.5$ Hz), 2.47 (s, 3 H), 2.24 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.22, 156.69, 150.23, 135.93, 133.77, 132.19, 129.51, 128.61, 128.38, 126.18, 125.87, 119.03, 117.33 (t, $J = 22.0$ Hz), 111.93 (t, $J = 237.0$ Hz), 20.81, 15.49. ^{19}F NMR (470 MHz, CDCl_3): δ -114.49. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_2$: 300.1040, found: 300.1033.



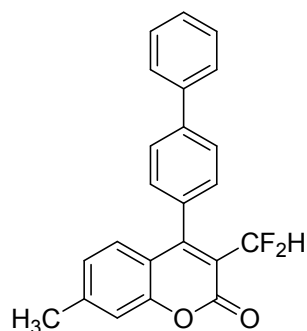
3-(difluoromethyl)-7-methyl-4-(p-tolyl)-2H-chromen-2-one (3s):

^1H NMR (500 MHz, CDCl_3): δ 7.43 (t, 1 H, $J = 7.5$ Hz), 7.36 (d, 1 H, $J = 7.5$ Hz), 7.20 (s, 1 H), 7.10 (d, 1 H, $J = 7.5$ Hz), 7.03-6.99 (m, 2 H), 6.46 (t, 1 H, $J = 53.5$ Hz), 2.46 (s, 3 H), 2.45 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.06, 156.73 (t, $J = 4.5$ Hz), 153.76, 145.13, 138.65, 131.76, 130.41, 128.82, 128.62, 128.37, 125.89, 125.47, 117.10, 117.06, 116.42 (t, $J = 22.1$ Hz), 112.01 (t, $J = 236.9$ Hz), 21.76, 21.46. ^{19}F NMR (470 MHz, CDCl_3): δ -114.98. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_2$: 300.1040, found: 300.1049.



3-(difluoromethyl)-4-(4-methoxyphenyl)-7-methyl-2H-chromen-2-one (3t):

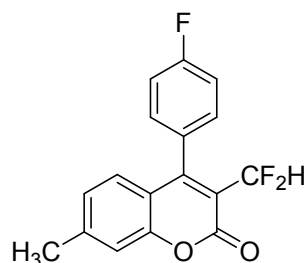
^1H NMR (500 MHz, CDCl_3): δ 7.26 (d, 2 H, $J = 8.5$ Hz), 7.20 (s, 1 H), 7.09-7.07 (m, 3 H), 7.04 (d, 1 H, $J = 8.5$ Hz), 6.52 (t, 1 H, $J = 53.5$ Hz), 3.91 (s, 3 H), 2.47 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 160.66, 158.20, 156.54 (t, $J = 4.3$ Hz), 153.77, 145.05, 129.77, 128.32, 125.85, 123.79, 117.32, 117.08, 116.56 (t, $J = 22.0$ Hz), 114.19, 112.10 (t, $J = 236.9$ Hz), 55.42, 21.71. ^{19}F NMR (470 MHz, CDCl_3): δ -114.54. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_3$: 317.0989, found: 317.0996.



4-([1,1'-biphenyl]-4-yl)-3-(difluoromethyl)-7-methyl-2H-chromen-2-one (3u):

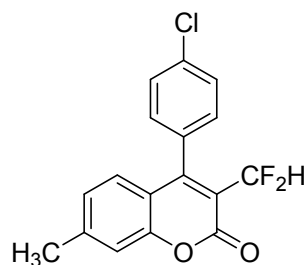
^1H NMR (500 MHz, CDCl_3): δ 7.76 (d, 2 H, $J = 8.0$ Hz), 7.67 (d, 2 H, $J = 8.0$ Hz), 7.50 (t, 2 H, $J = 7.5$ Hz), 7.43-7.38 (m, 3 H), 7.21 (s, 1 H), 7.08 (d, 1 H, $J = 8.0$ Hz), 7.04 (d, 1 H, $J = 8.0$ Hz), 6.57 (t, 1 H, $J = 53.0$ Hz), 2.47 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.21, 156.30 (t, $J = 4.0$ Hz), 153.81, 145.24, 145.56, 139.86,

130.72, 129.03, 128.96, 128.30, 128.06, 127.31, 127.17, 125.96, 117.17, 117.12, 116.70 (t, $J = 22.1$ Hz), 111.95 (t, $J = 237.1$ Hz), 21.78. ^{19}F NMR (470 MHz, CDCl_3): δ -114.29. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{23}\text{H}_{17}\text{F}_2\text{O}_2$: 363.1196, found: 363.1203.



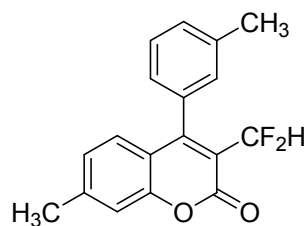
3-(difluoromethyl)-4-(4-fluorophenyl)-7-methyl-2H-chromen-2-one (3v):

^1H NMR (500 MHz, CDCl_3): δ 7.35-7.32 (m, 2 H), 7.29-7.23 (m, 3 H), 7.06 (dd, 1 H, $J_1 = 10.0$ Hz, $J_2 = 1.0$ Hz), 7.15-7.12 (m, 2 H), 6.98 (d, 1 H, $J = 10.5$ Hz), 6.61 (t, 1 H, $J = 66.5$ Hz), 2.49 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 163.33(d, $J = 248.4$ Hz), 158.40, 155.44 (t, $J = 3.4$ Hz), 153.71, 145.37, 130.40 (d, $J = 8.3$ Hz), 128.02, 127.92 (d, $J = 3.5$ Hz), 126.03, 117.21, 117.10 (t, $J = 22.1$ Hz), 115.90 (d, $J = 21.8$ Hz), 111.65 (t, $J = 237.3$ Hz), 21.76. ^{19}F NMR (470 MHz, CDCl_3): δ -110.79 (s, 1 F), -113.71 (s, 2 F). HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}_2$: 305.0789, found: 305.0782.



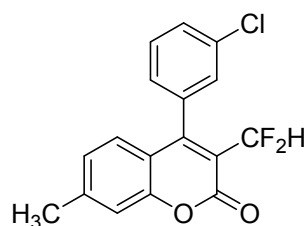
4-(4-chlorophenyl)-3-(difluoromethyl)-7-methyl-2H-chromen-2-one (3w):

^1H NMR (500 MHz, CDCl_3): δ 7.55 (d, 2 H, $J = 8.5$ Hz), 7.29 (d, 2 H, $J = 8.0$ Hz), 7.05 (d, 1 H, $J = 8.5$ Hz), 6.97 (d, 1 H, $J = 8.0$ Hz), 6.63 (t, 1 H, $J = 53.5$ Hz), 2.49 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.41, 155.15 (t, $J = 3.1$ Hz), 153.71, 145.44, 135.86, 130.46, 129.78, 128.95, 127.95, 126.06, 117.24, 117.05 (t, $J = 22.1$ Hz), 117.00, 111.56 (t, $J = 237.5$ Hz), 21.77. ^{19}F NMR (470 MHz, CDCl_3): δ -113.45. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{12}\text{ClF}_2\text{O}_2$: 321.0494, found: 321.0488.



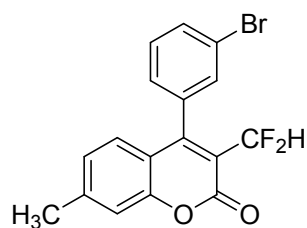
3-(difluoromethyl)-7-methyl-4-(m-tolyl)-2H-chromen-2-one (3x):

^1H NMR (500 MHz, CDCl_3): δ 7.45 (t, 1 H, $J = 8.0$ Hz), 7.37 (d, 2 H, $J = 8.0$ Hz), 7.21 (s, 1 H), 7.12 (d, 2 H, $J = 7.5$ Hz), 7.05-7.01 (m, 2 H), 6.48 (t, 1 H, $J = 53.0$ Hz), 2.48 (s, 3 H), 2.46 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.04, 156.73 (t, $J = 4.6$ Hz), 153.76, 145.14, 138.66, 131.75, 130.42, 128.82, 128.63, 128.37, 125.89, 125.47, 117.08, 117.05, 116.41 (t, $J = 22.0$ Hz), 112.02 (t, $J = 236.8$ Hz), 21.76, 21.47. ^{19}F NMR (470 MHz, CDCl_3): δ -114.99. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{18}\text{H}_{15}\text{F}_2\text{O}_2$: 301.1040, found: 301.1033.



4-(3-chlorophenyl)-3-(difluoromethyl)-7-methyl-2H-chromen-2-one (3y):

^1H NMR (500 MHz, CDCl_3): δ 7.54-7.48 (m, 2 H), 7.33 (t, 1 H, $J = 1.5$ Hz), 7.23-7.22 (m, 2 H), 7.05 (dd, 1 H, $J_1 = 8.5$ Hz, $J_2 = 1.0$ Hz), 6.94 (d, 1 H, $J = 8.5$ Hz), 6.59 (t, 1 H, $J = 53.5$ Hz), 2.47 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.30, 154.62 (t, $J = 3.3$ Hz), 153.69, 145.53, 134.80, 133.76, 129.99, 129.77, 128.32, 127.97, 126.61, 126.13, 117.23, 117.03, 116.84, 111.51 (t, $J = 237.6$ Hz), 21.79. ^{19}F NMR (470 MHz, CDCl_3): δ -113.66. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{12}\text{ClF}_2\text{O}_2$: 321.0494, found: 321.0499.



4-(3-bromophenyl)-3-(difluoromethyl)-7-methyl-2H-chromen-2-one (3z):

^1H NMR (500 MHz, CDCl_3): δ 7.69 (dd, 1 H, $J_1 = 8.0$ Hz, $J_2 = 0.5$ Hz), 7.48 (s, 1 H), 7.43 (t, 1 H, $J = 8.0$ Hz), 7.28-7.27 (m, 1 H), 7.22 (s, 1 H), 7.05 (d, 1 H, $J = 8.5$ Hz), 6.95 (d, 1 H, $J = 8.5$ Hz), 6.59 (t, 1 H, $J = 53.0$ Hz), 2.47 (s, 3 H). ^{13}C NMR (125 MHz, CDCl_3): δ 158.28, 154.51 (t, $J = 3.1$ Hz), 153.68, 145.55, 134.00, 132.70, 131.09, 130.19, 127.98, 127.07, 126.15, 122.74, 117.22, 117.01, 116.84, 111.51 (t, $J = 237.5$ Hz), 21.79. ^{19}F NMR (470 MHz, CDCl_3): δ -113.60. HRMS (ESI): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{17}\text{H}_{12}\text{BrF}_2\text{O}_2$: 364.9988, found: 364.9981.

Reference :

- (1) C. E. Song, D.-U. Jung, S. Y. Choung, E. J. Roh and S.-G. Lee, *Angew. Chem., Int. Ed.*, 2004, **43**, 6183.

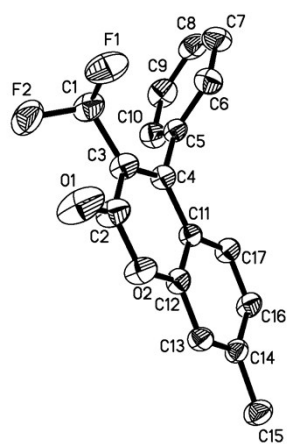
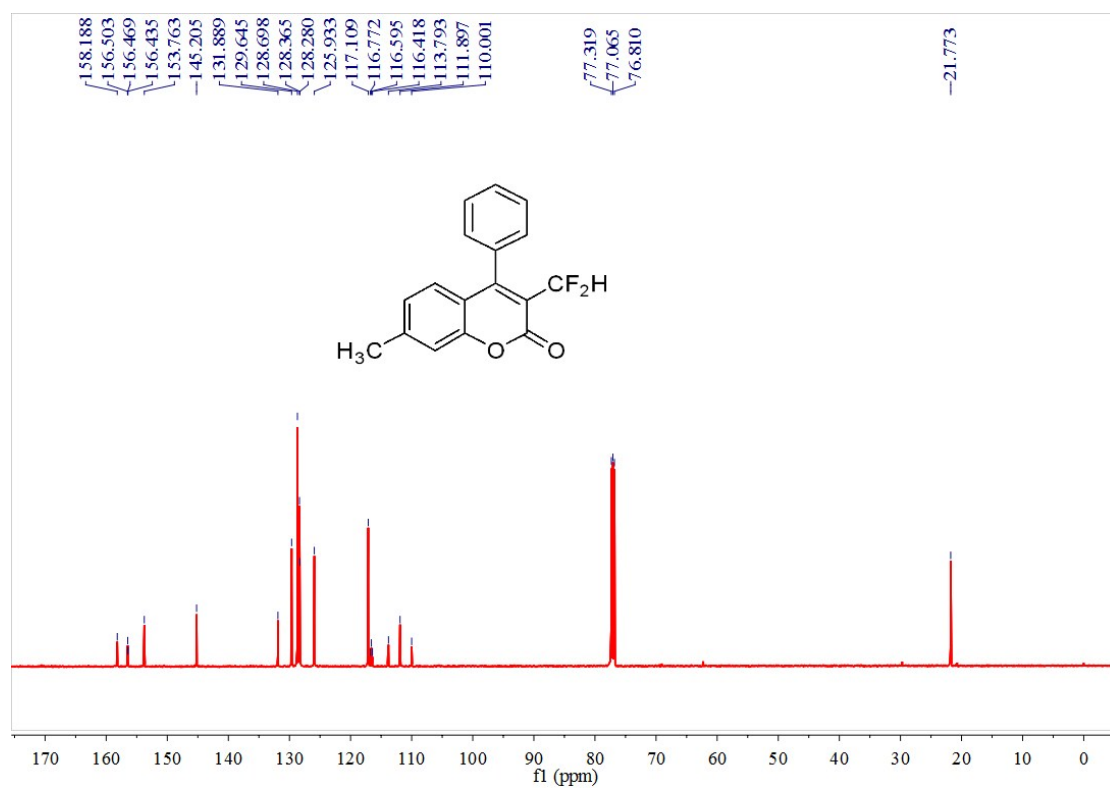
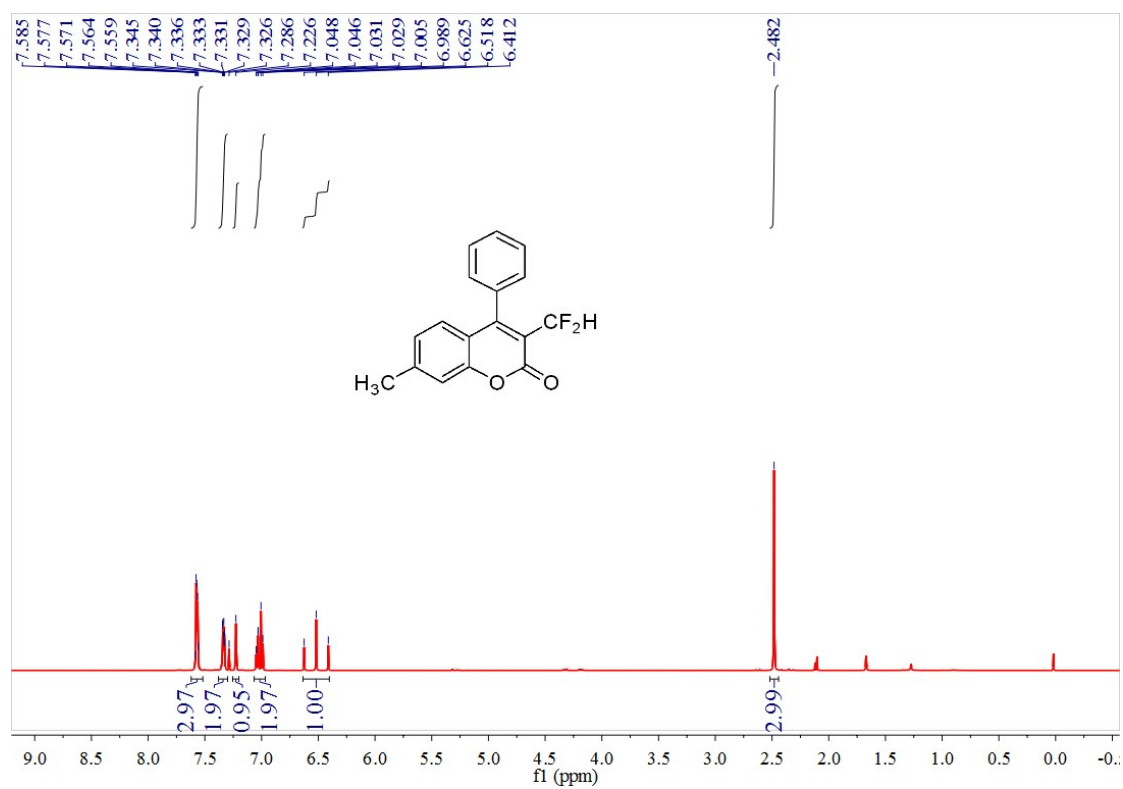
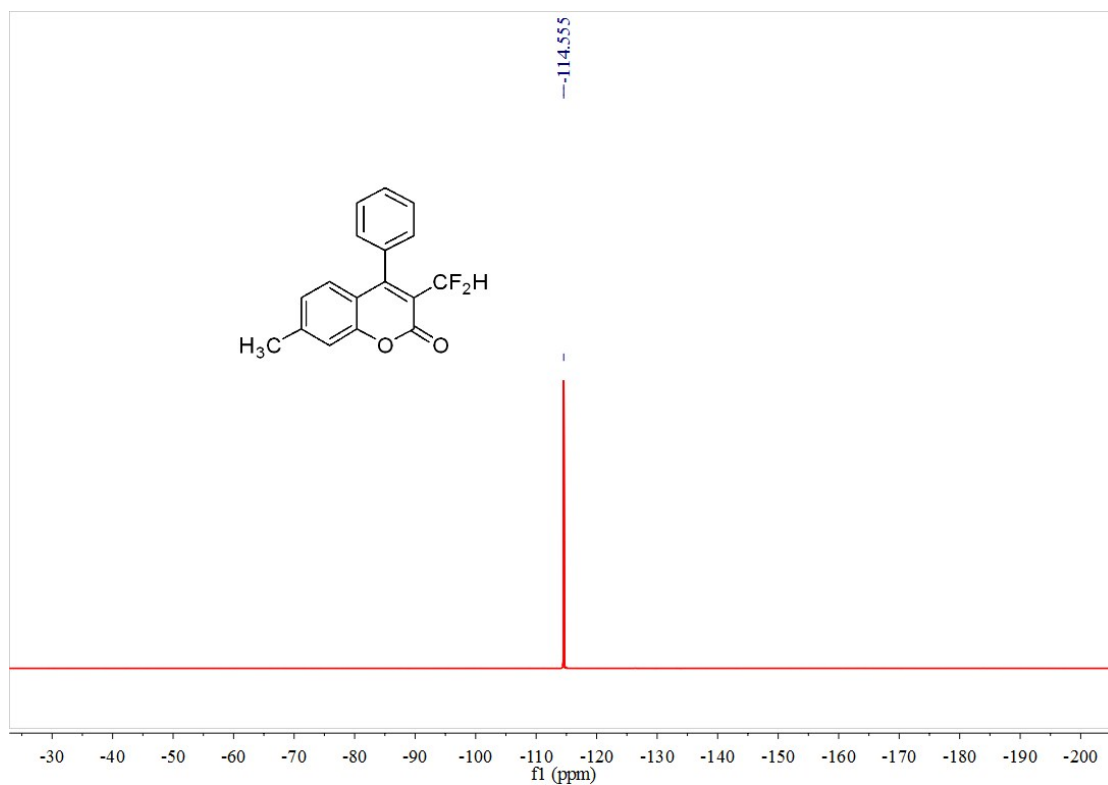


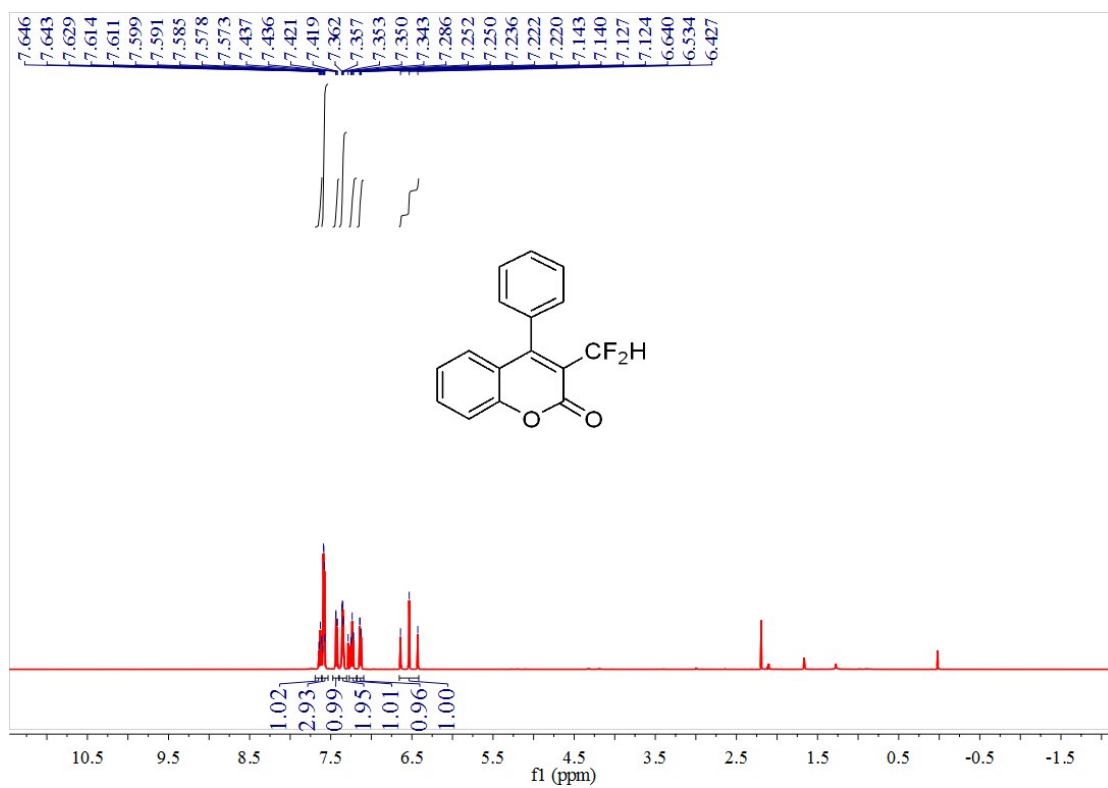
Figure 1 The ORTEP drawing of **3a**

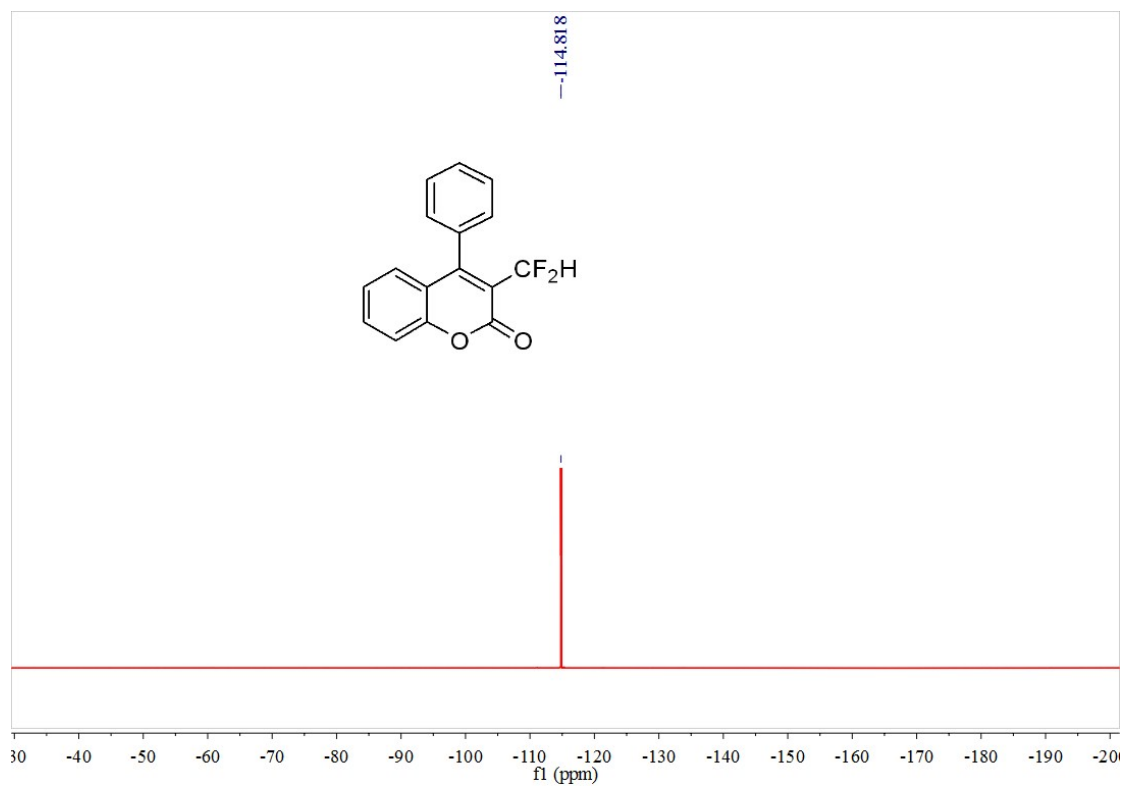
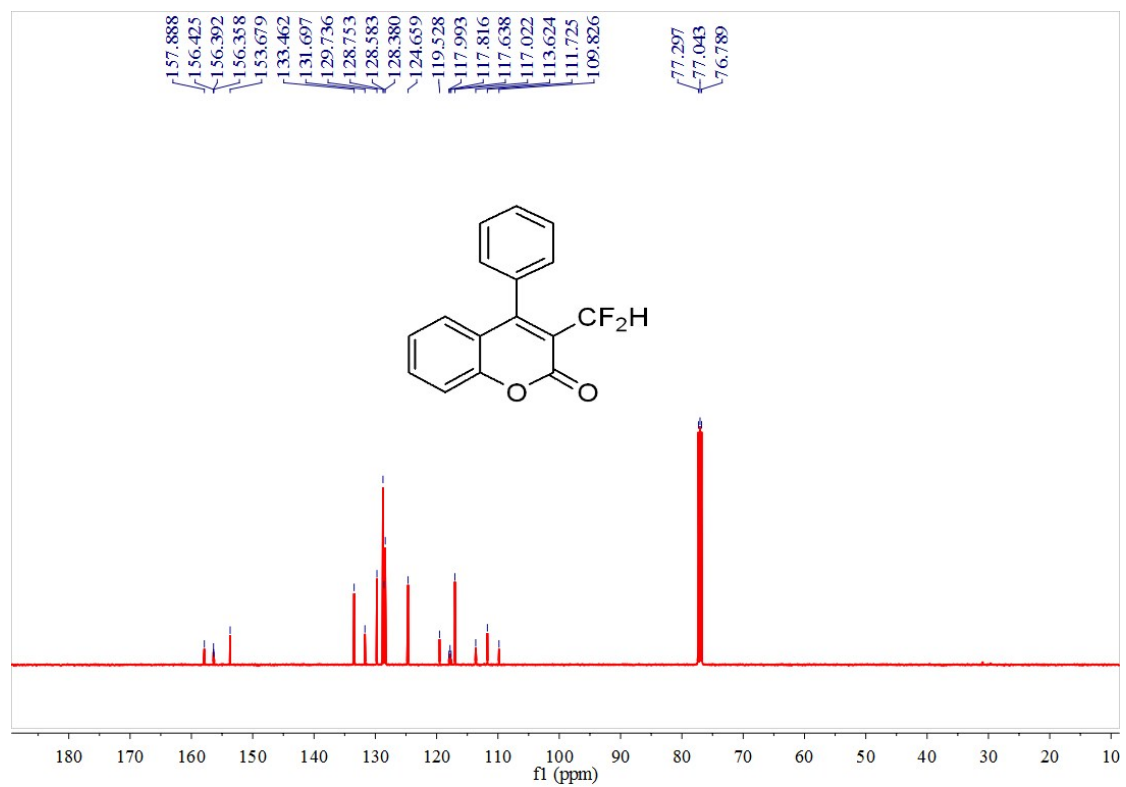
¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of compound **3a**:



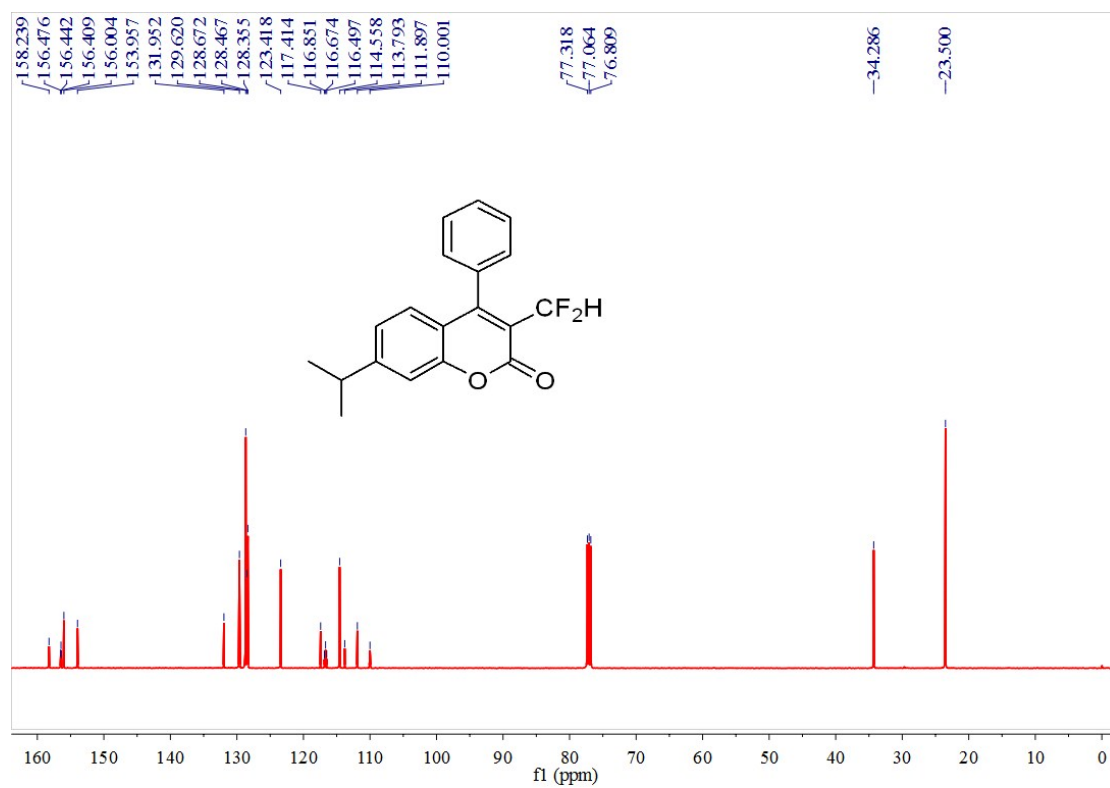
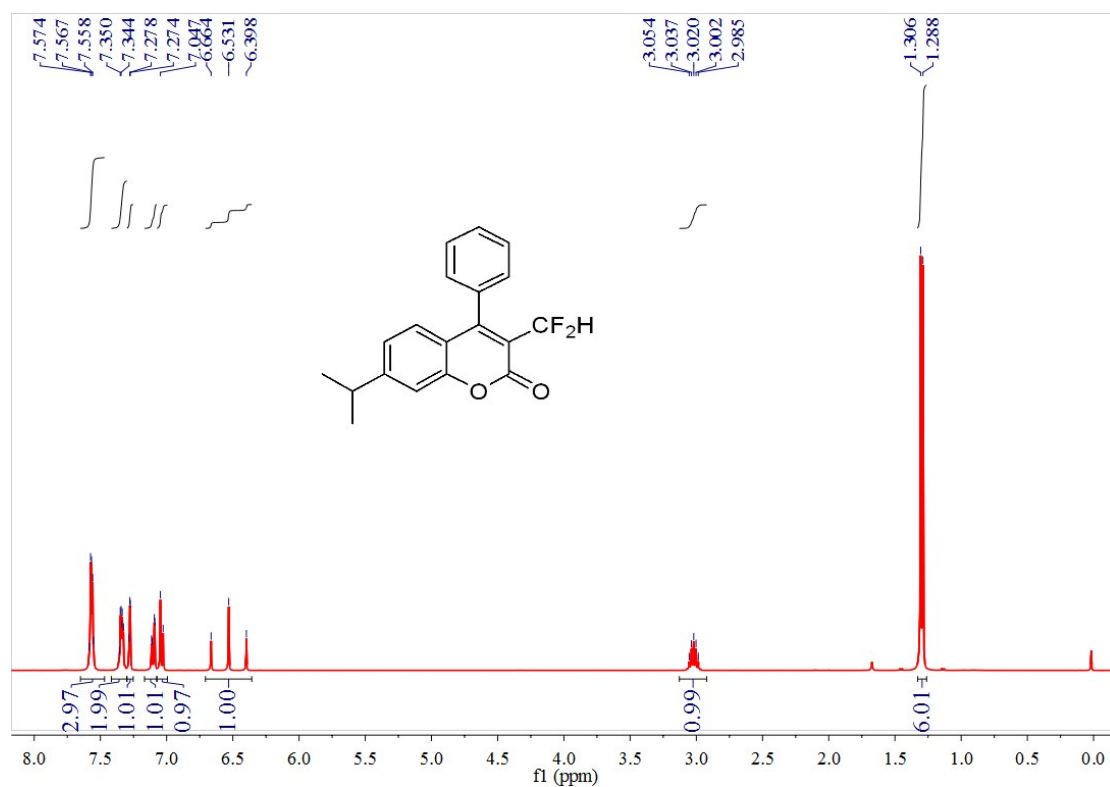


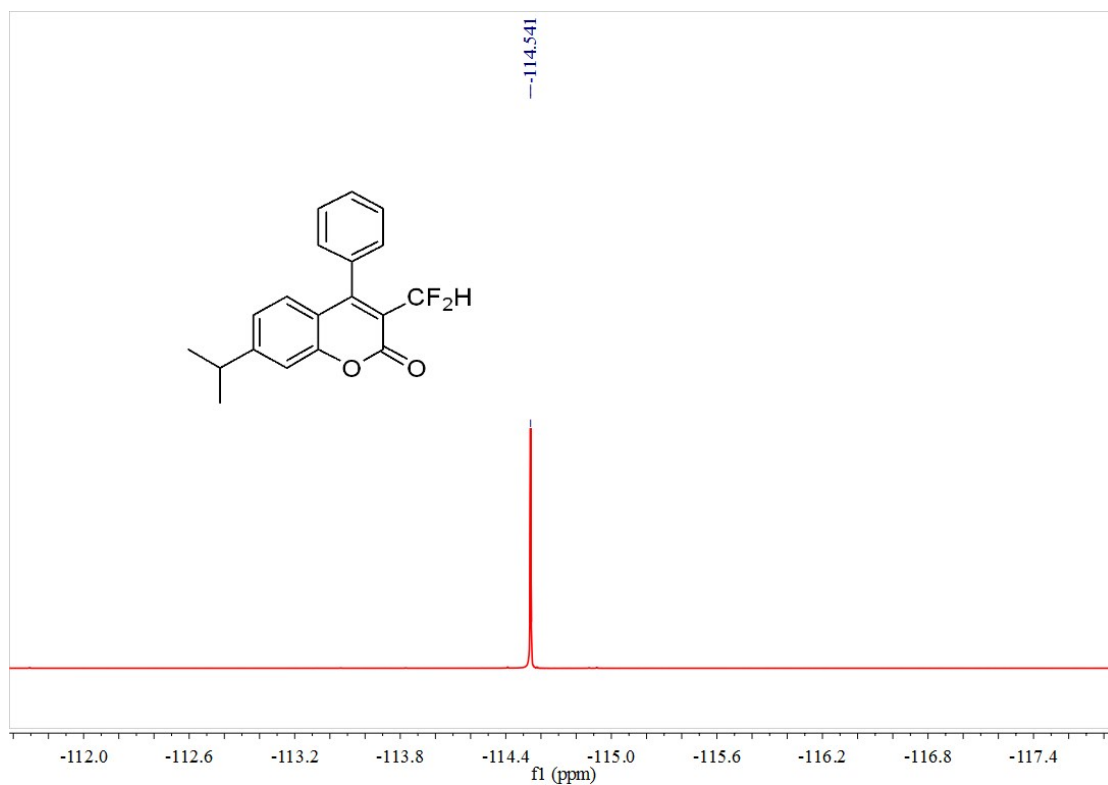
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3b**:



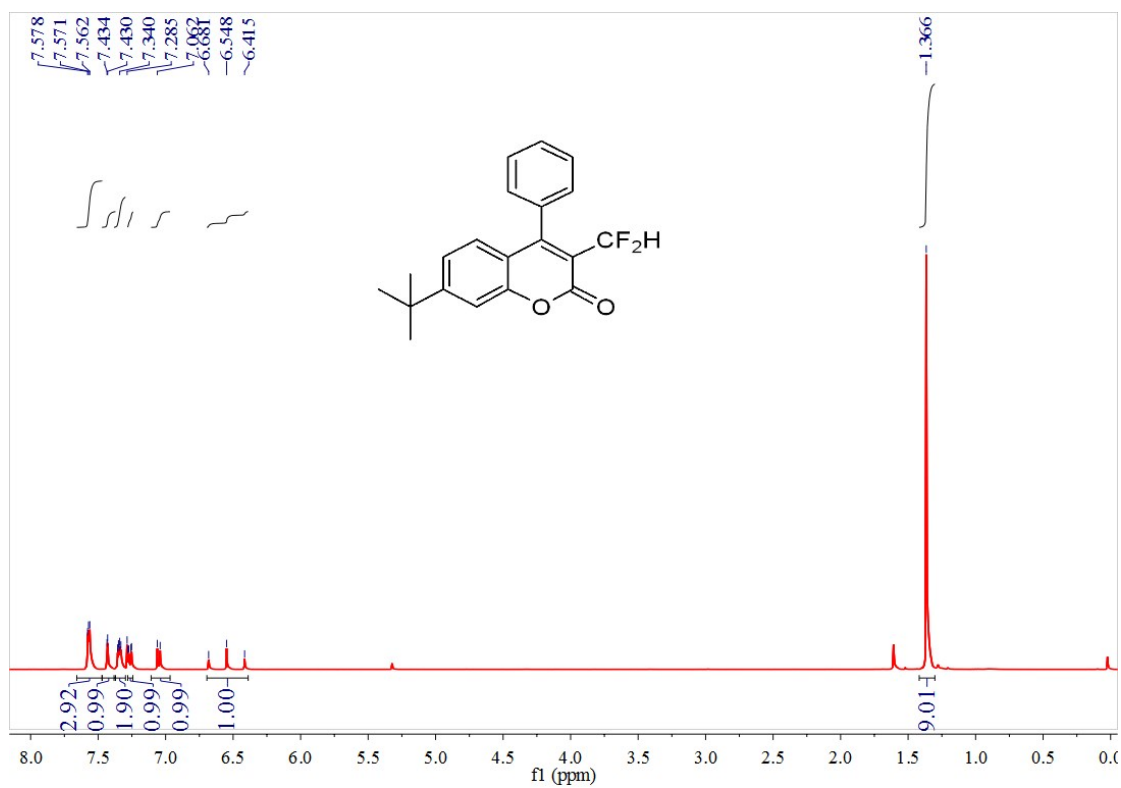


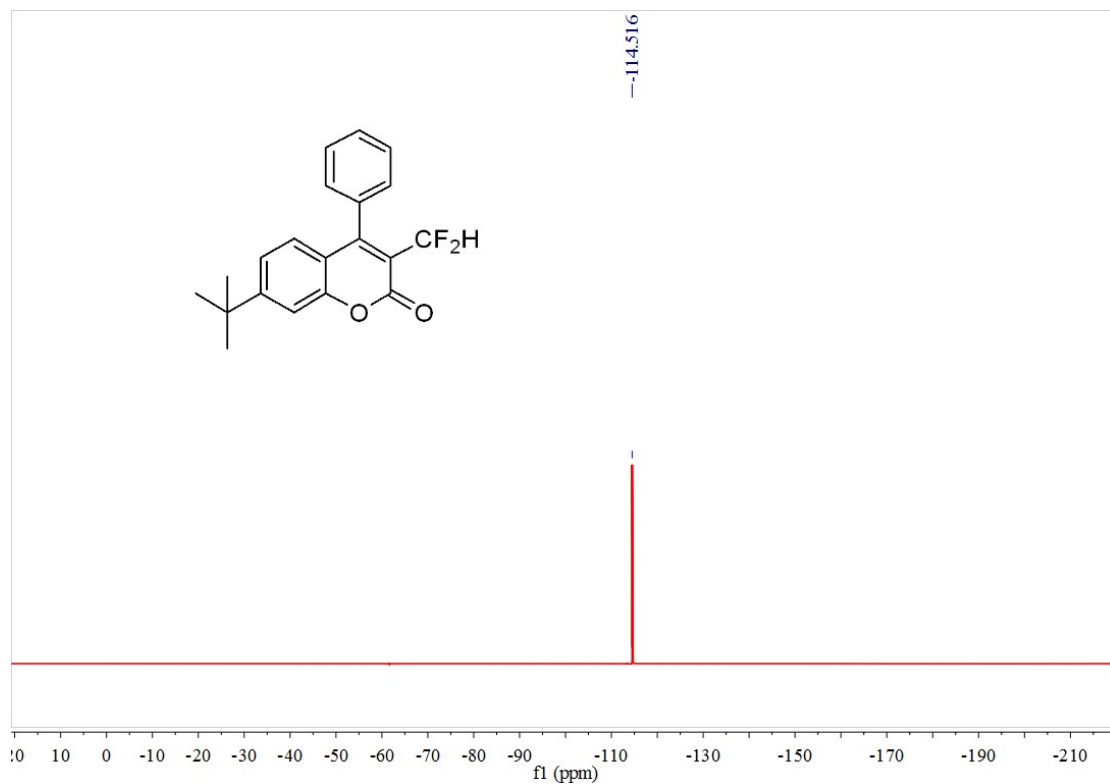
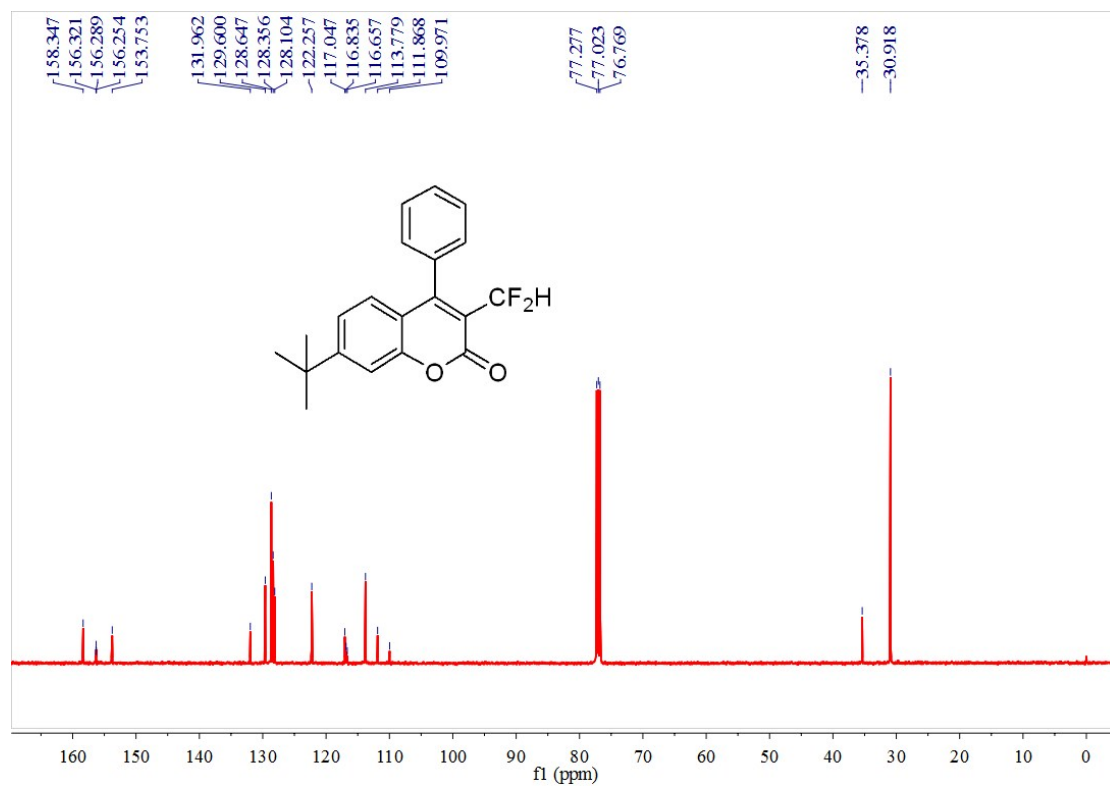
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3c**:



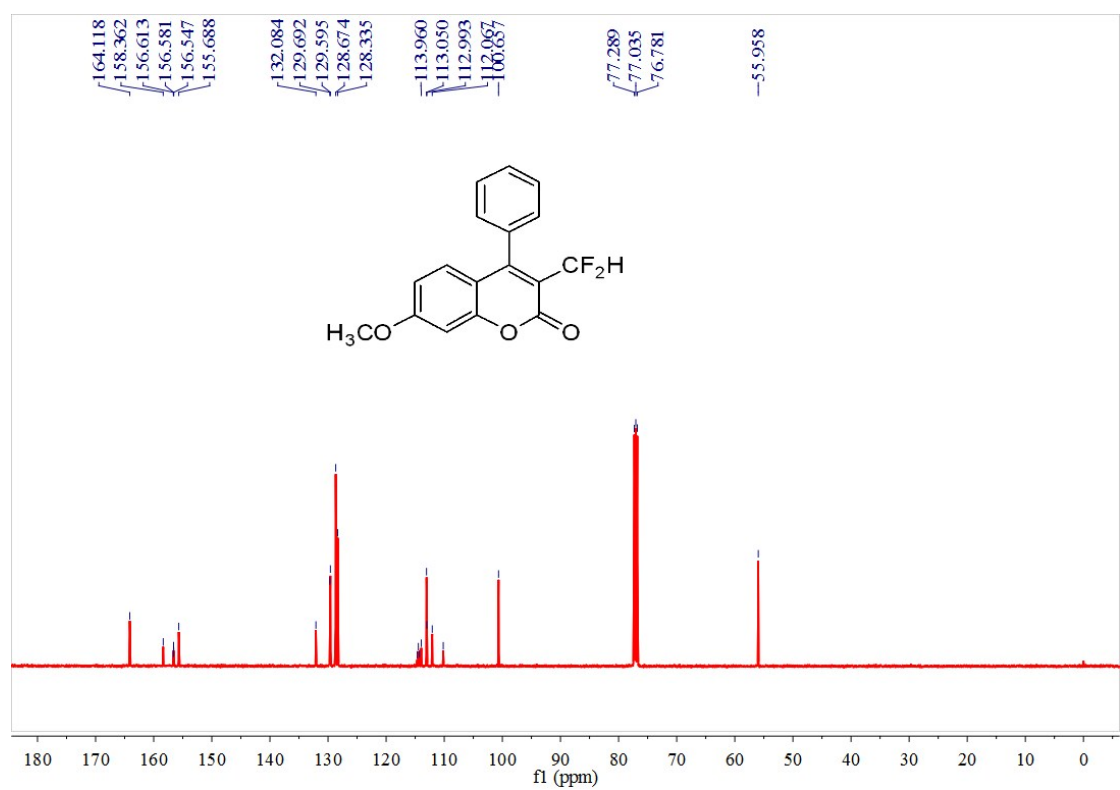
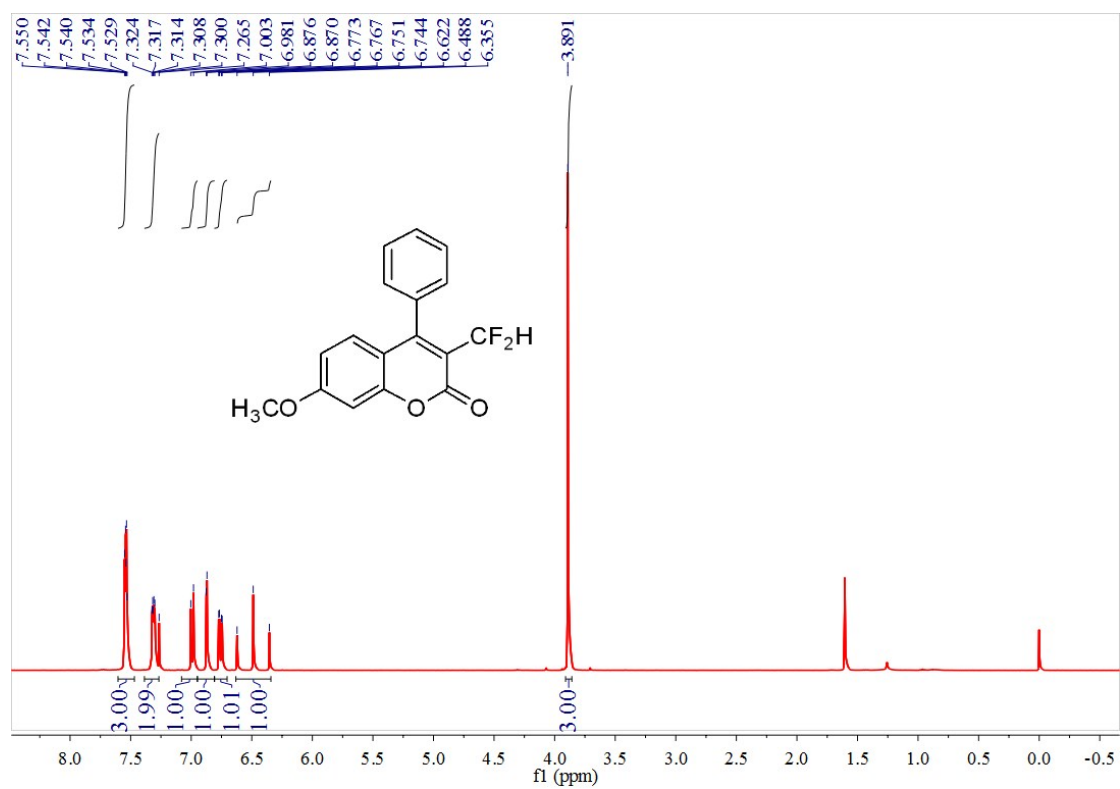


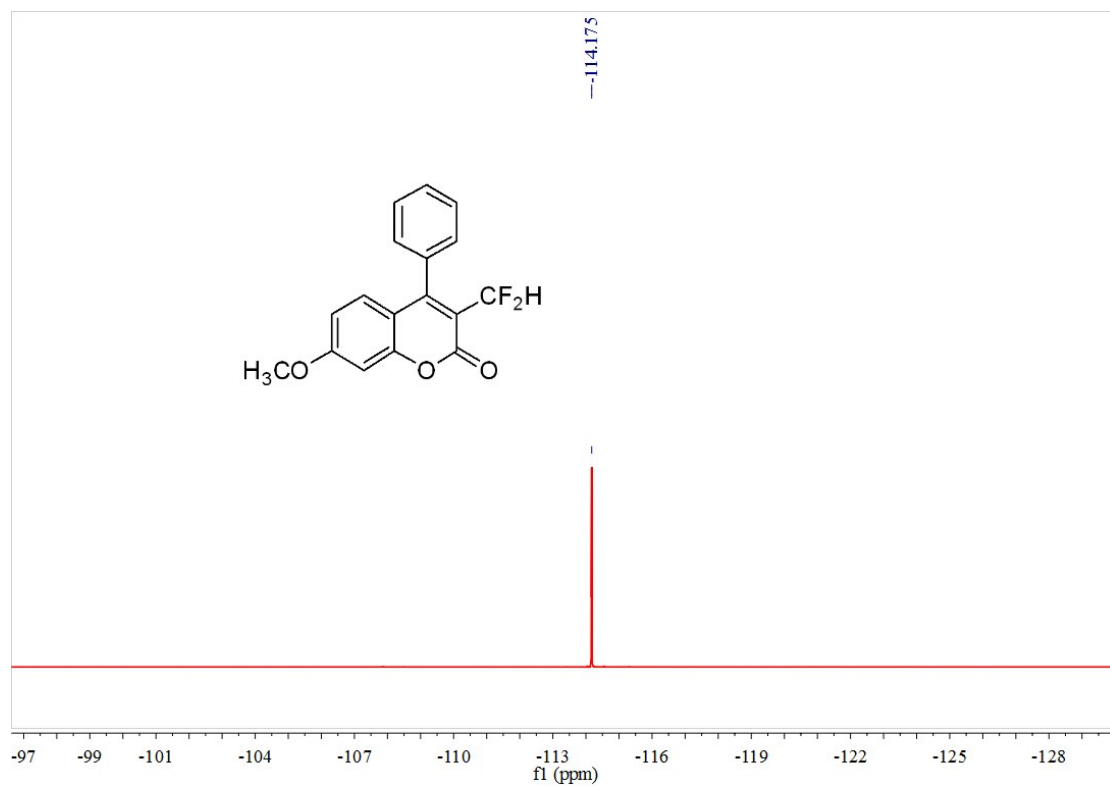
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3d**:



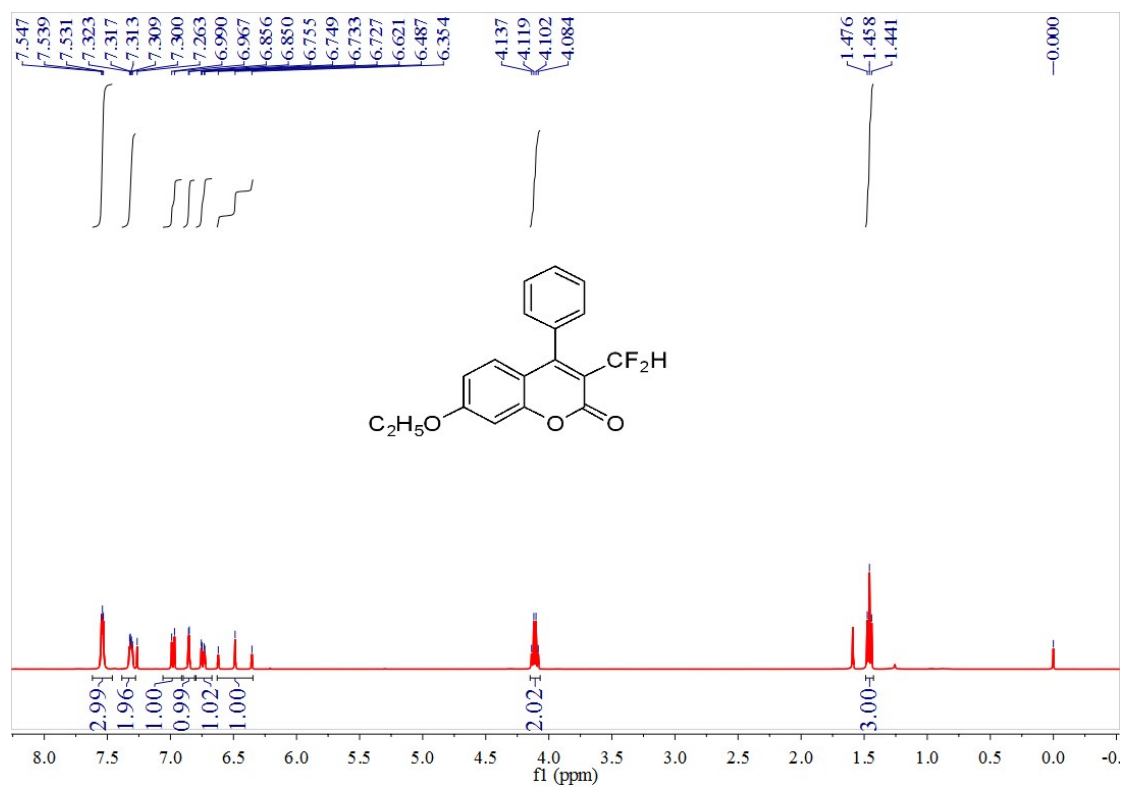


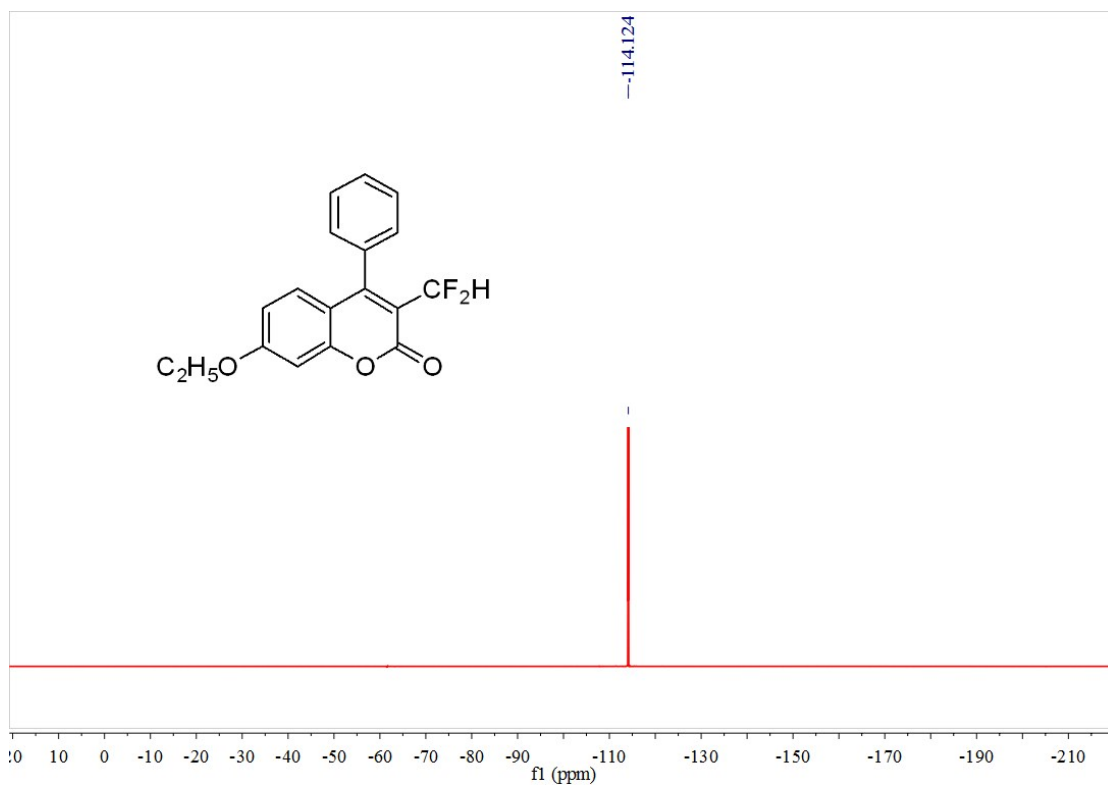
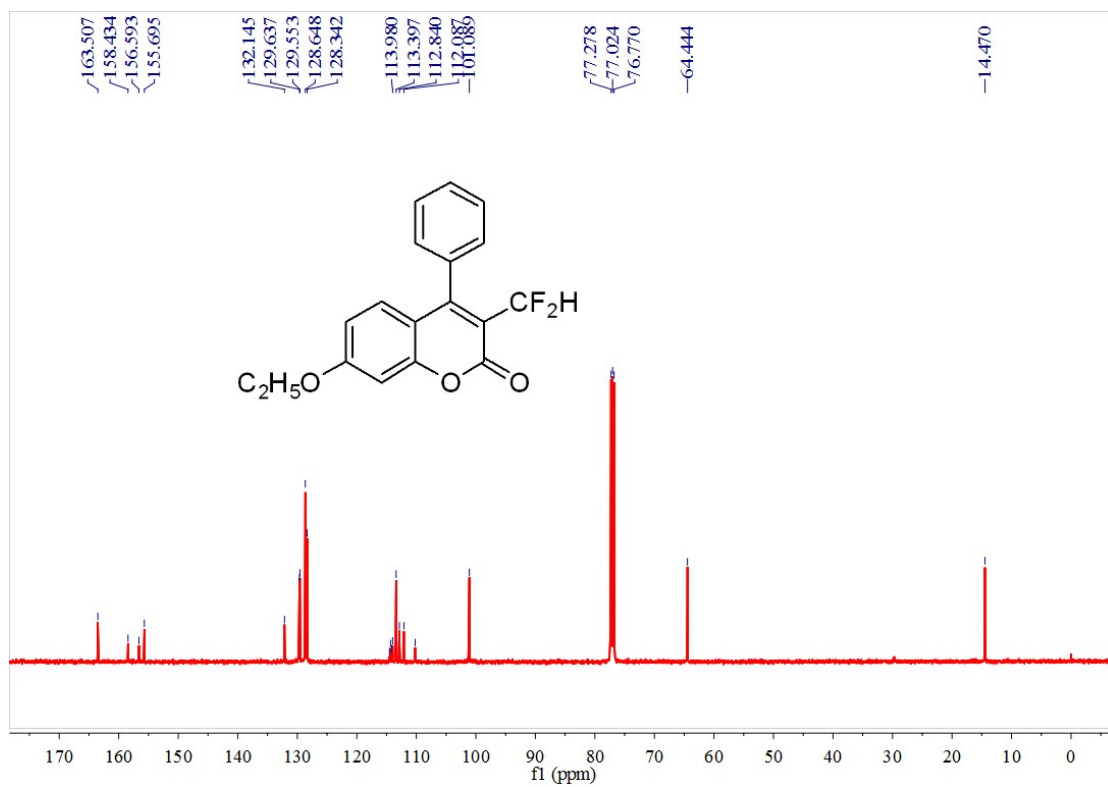
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3e**:



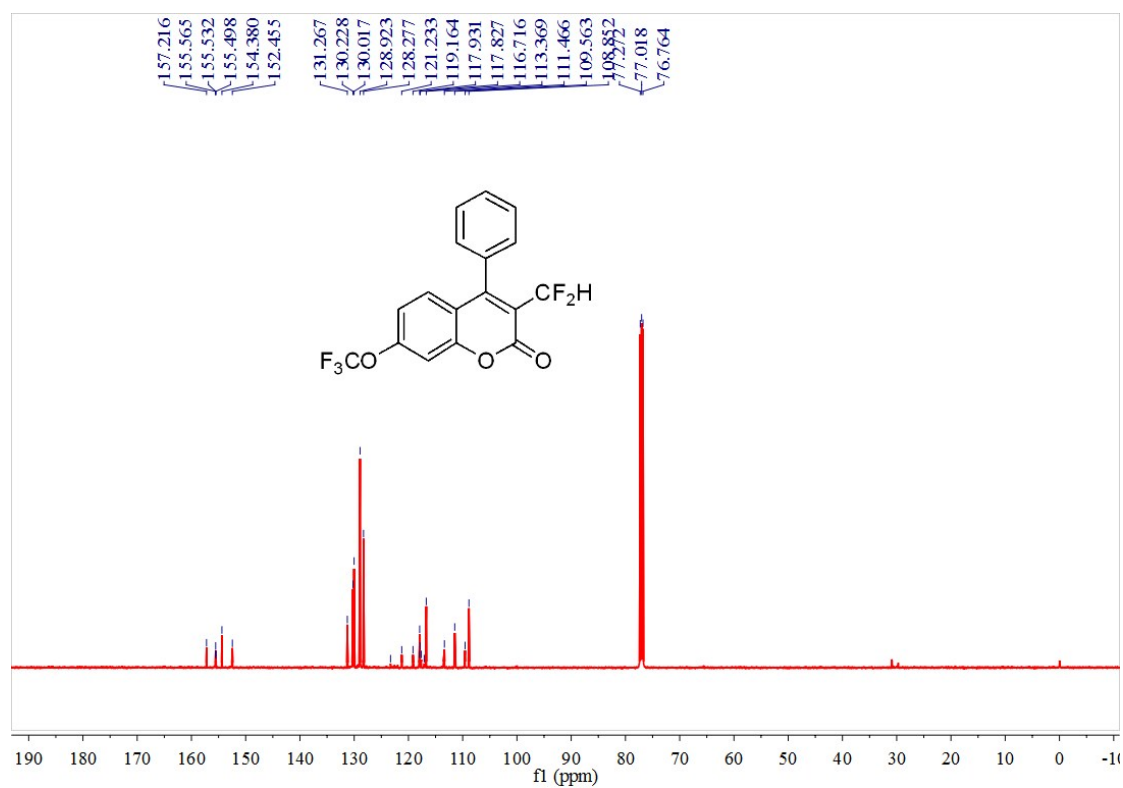
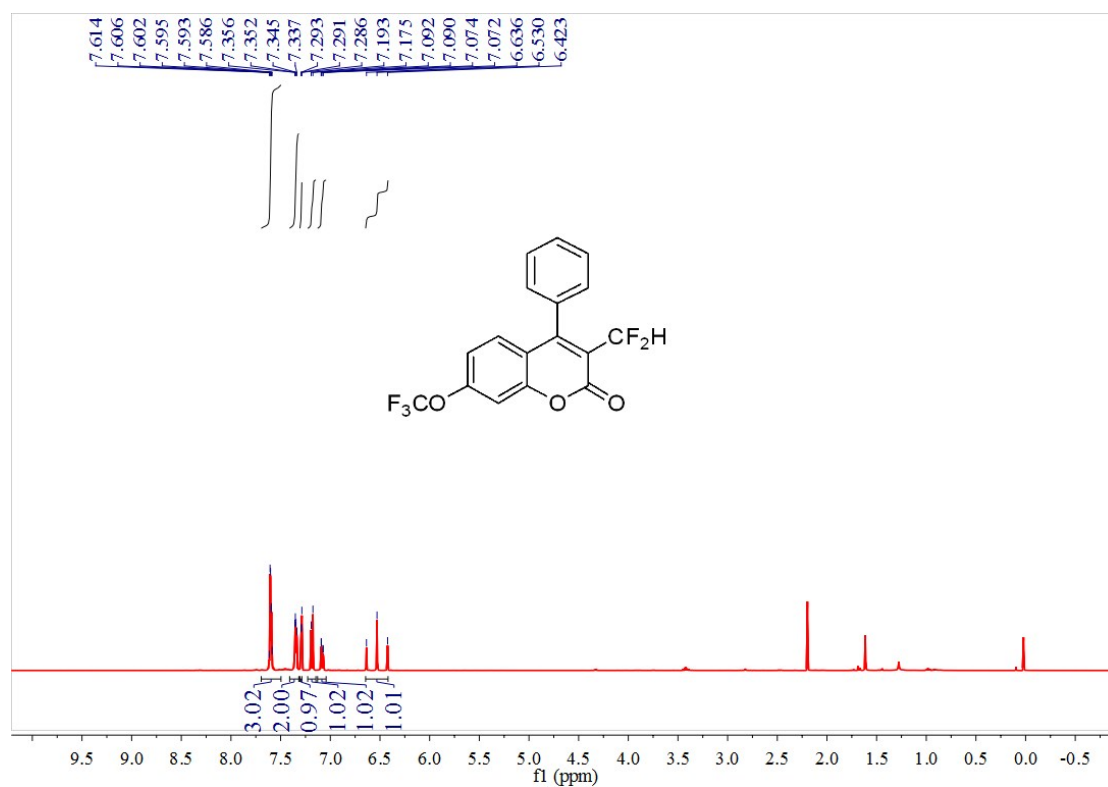


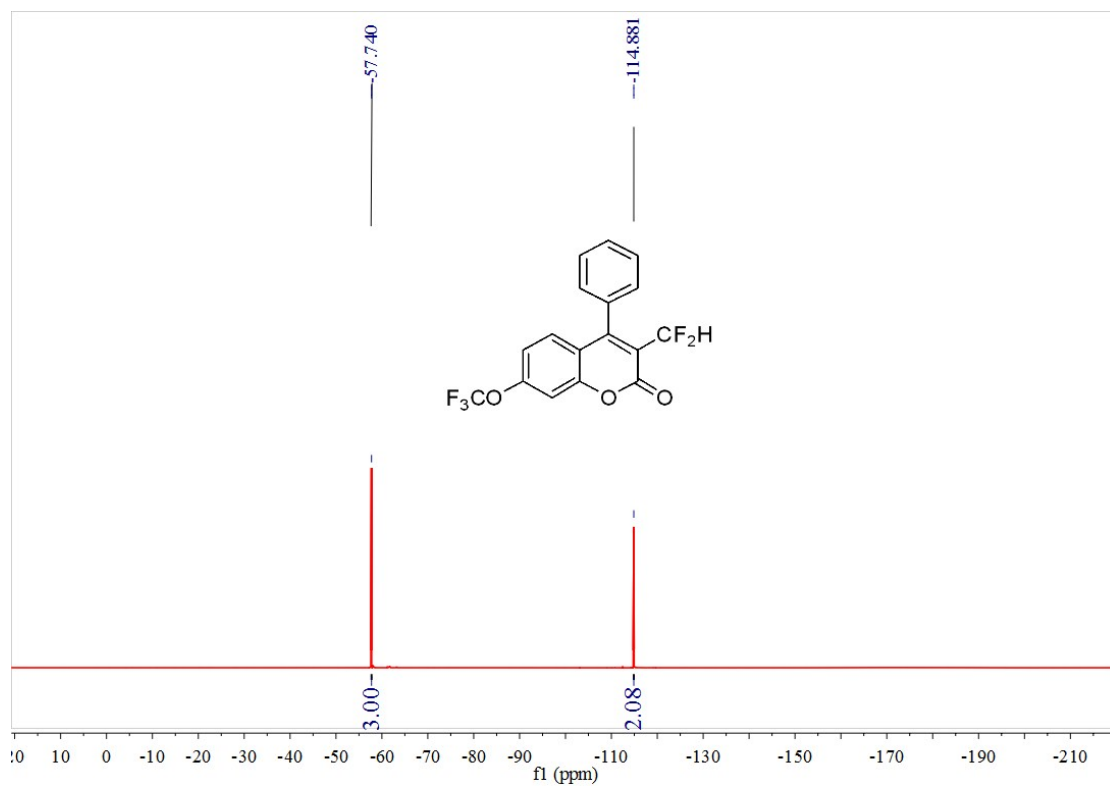
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3f**:



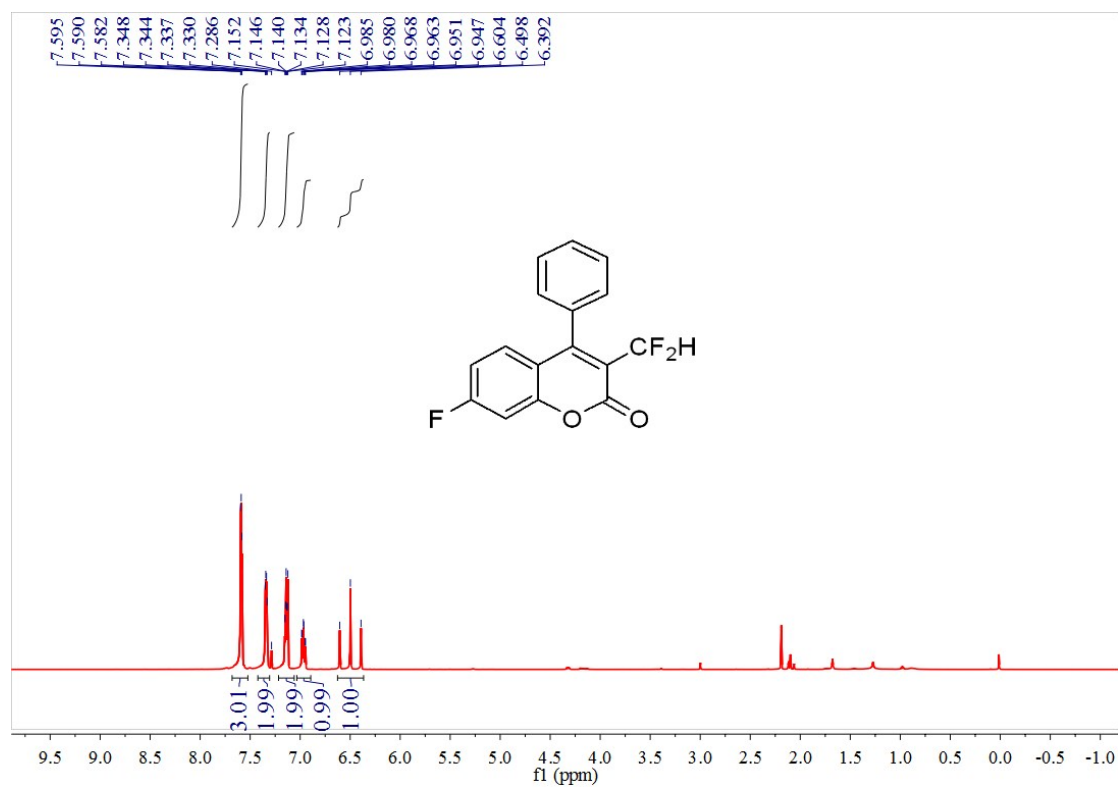


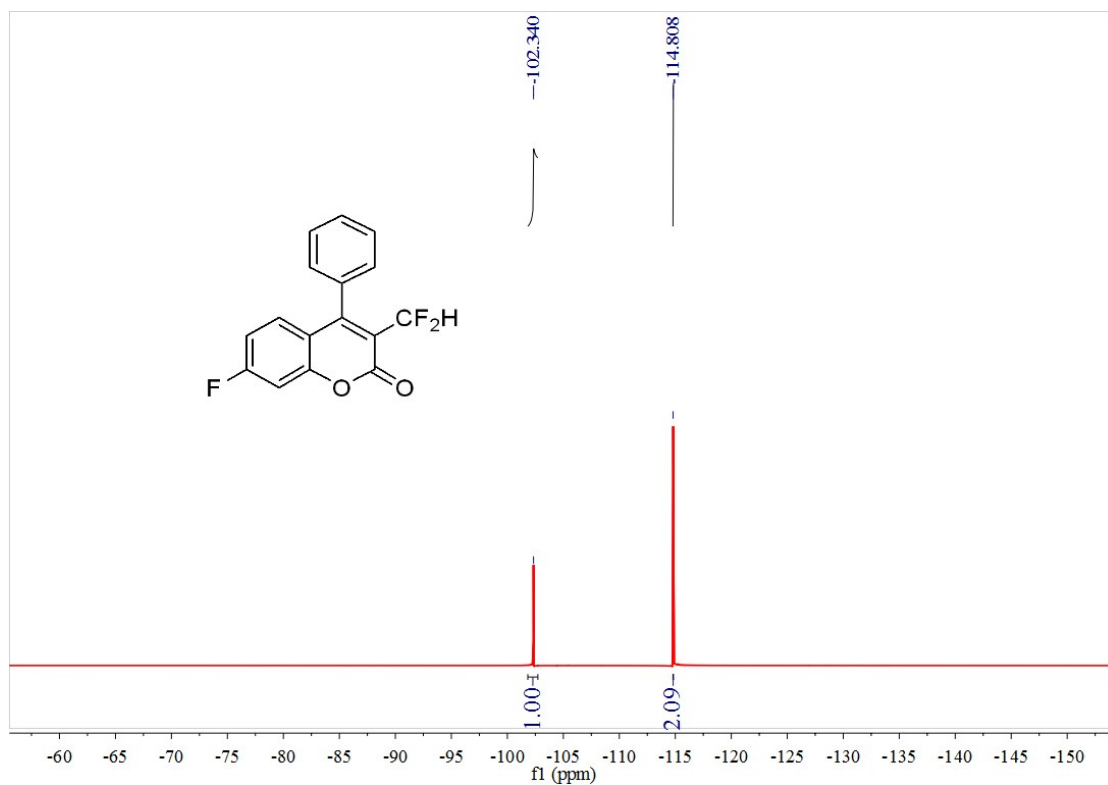
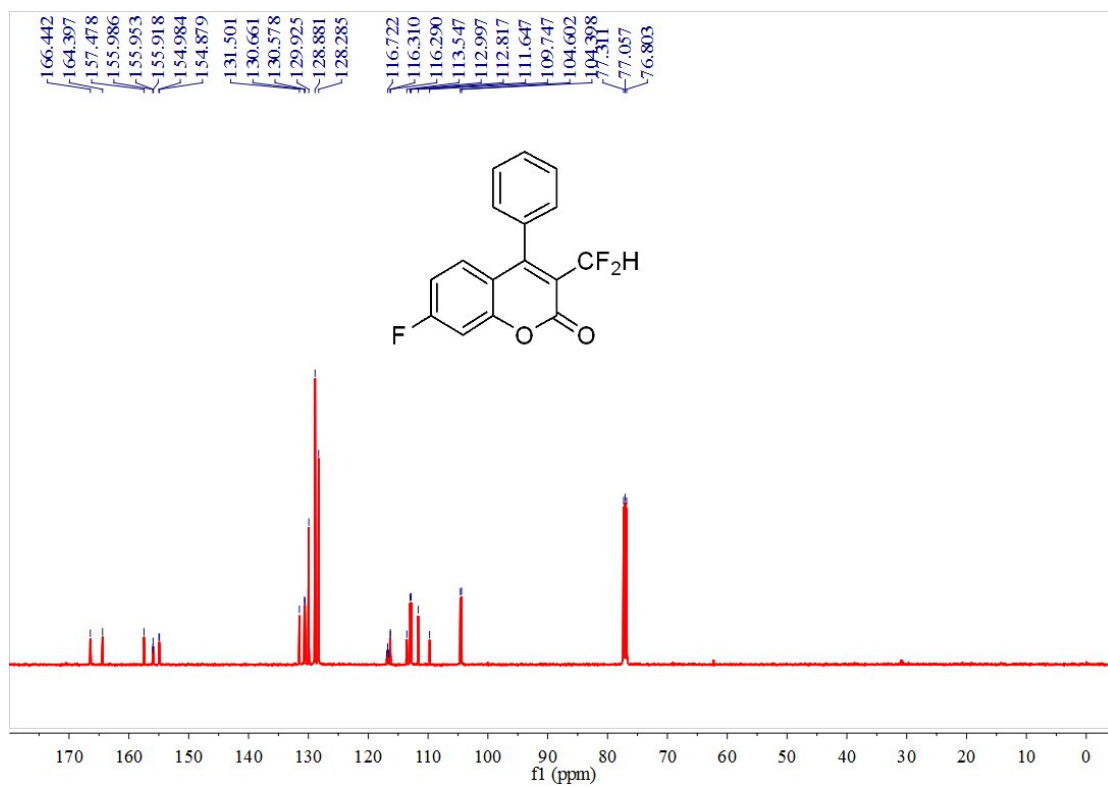
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3g**:



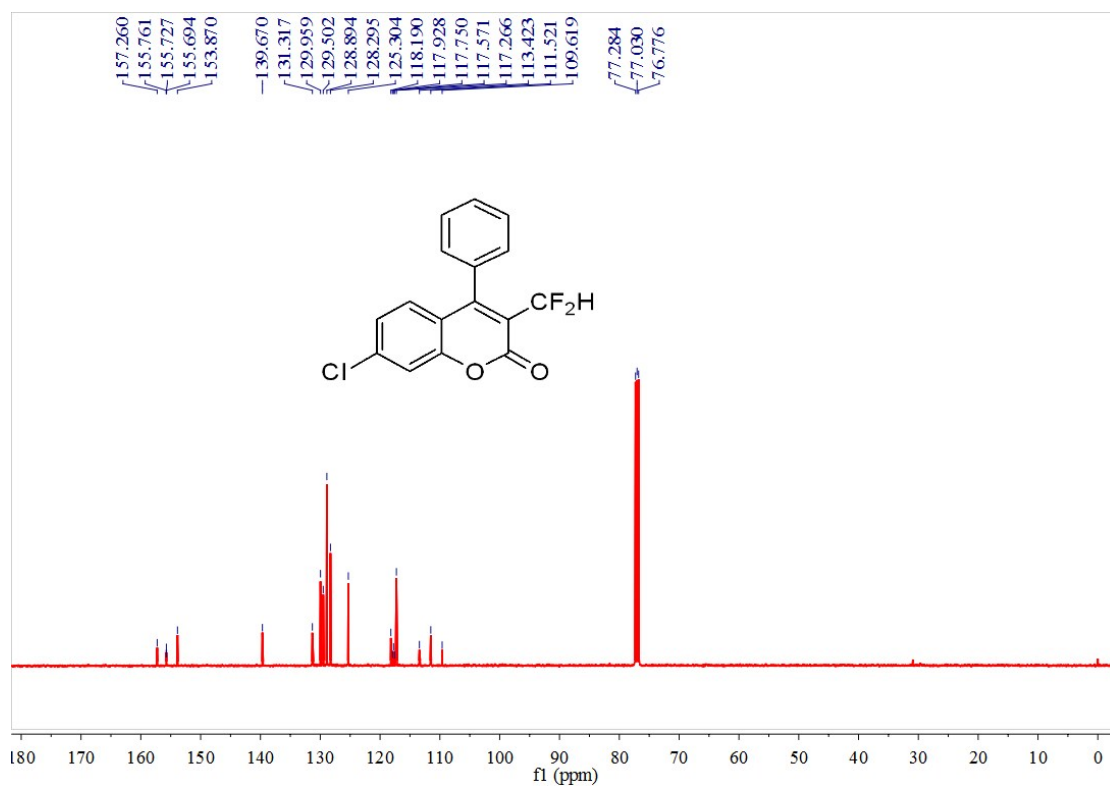
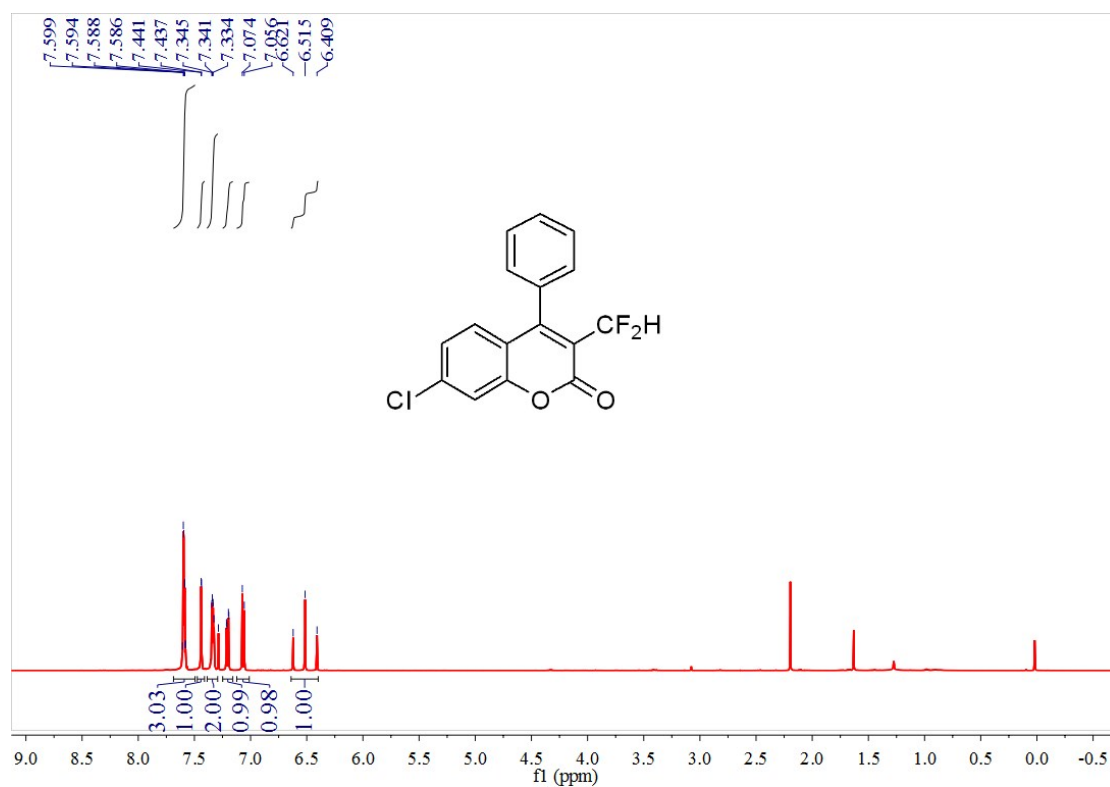


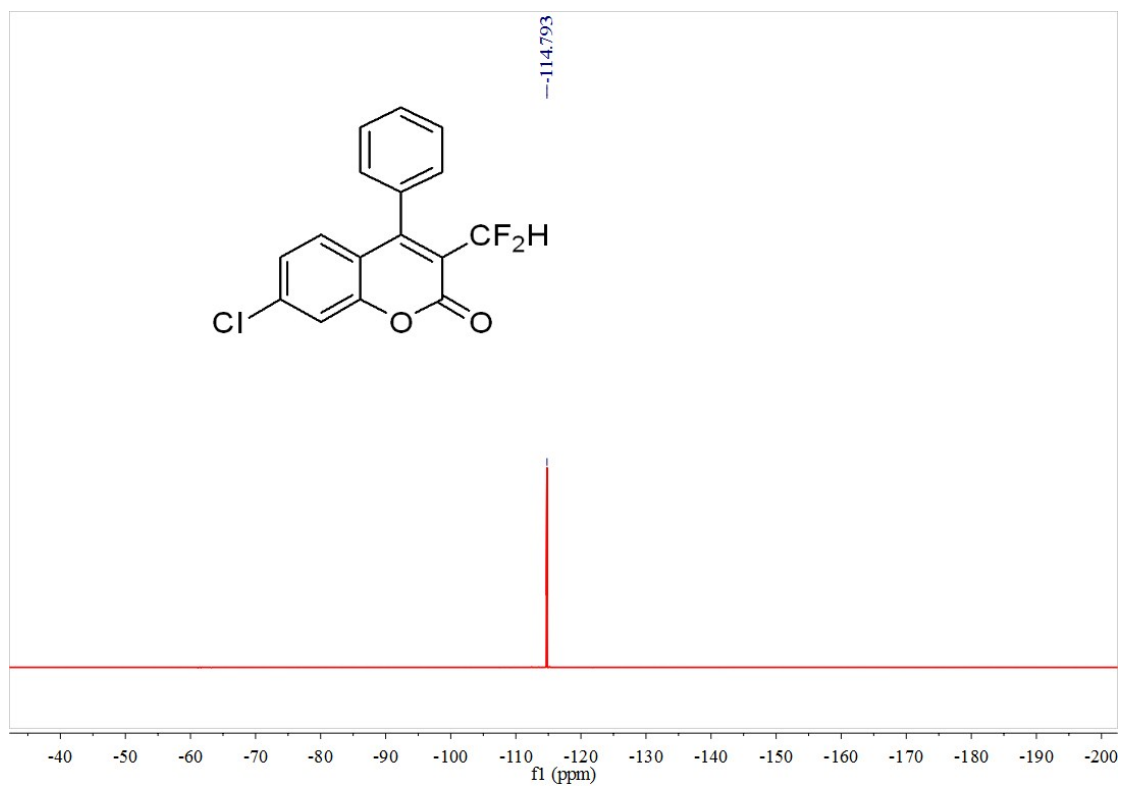
¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of compound **3h**:



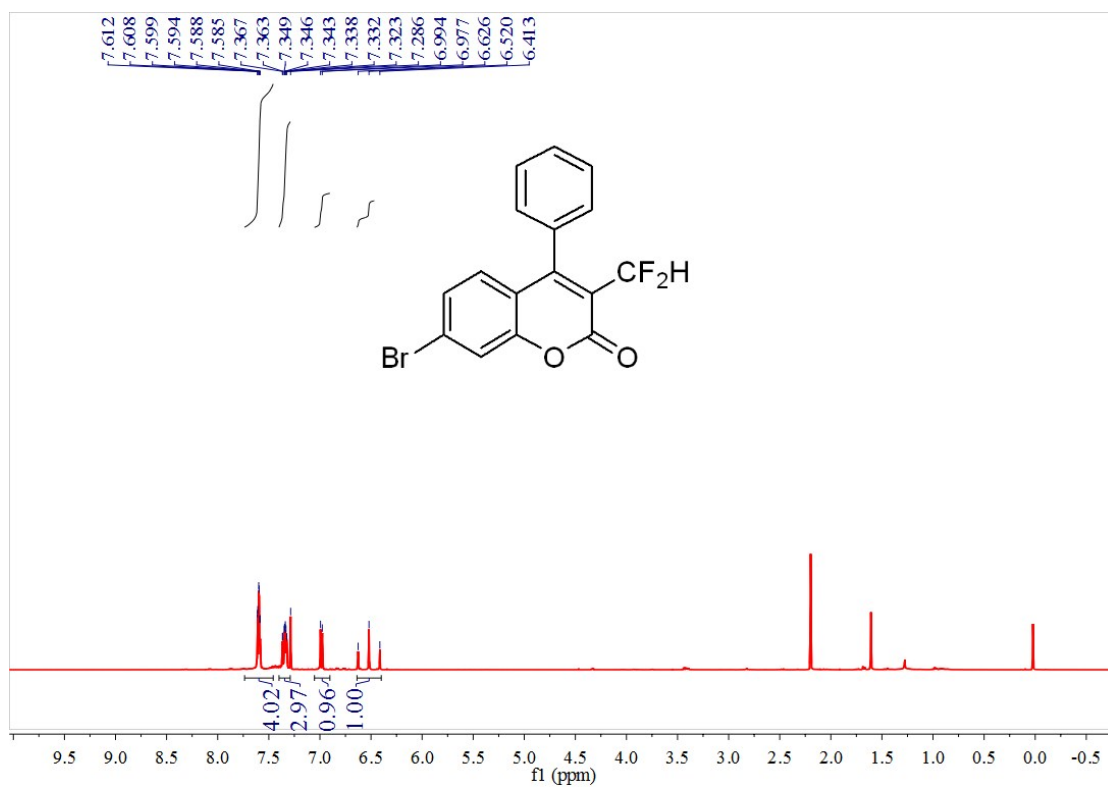


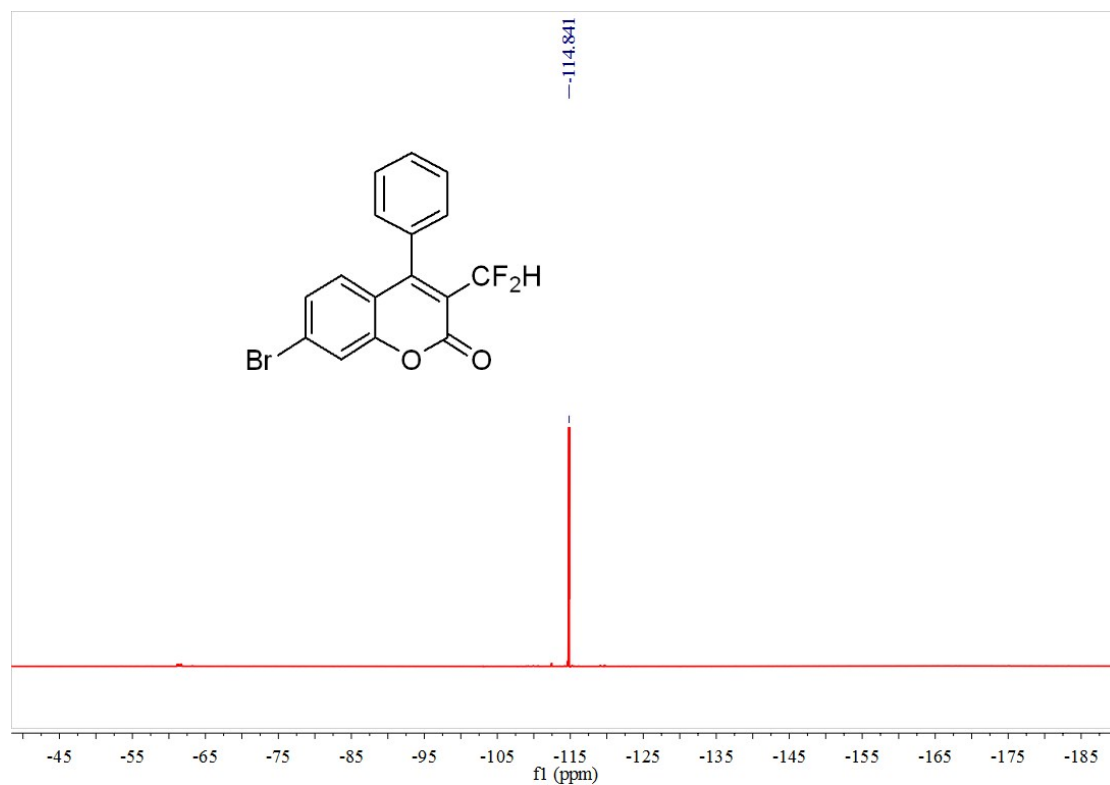
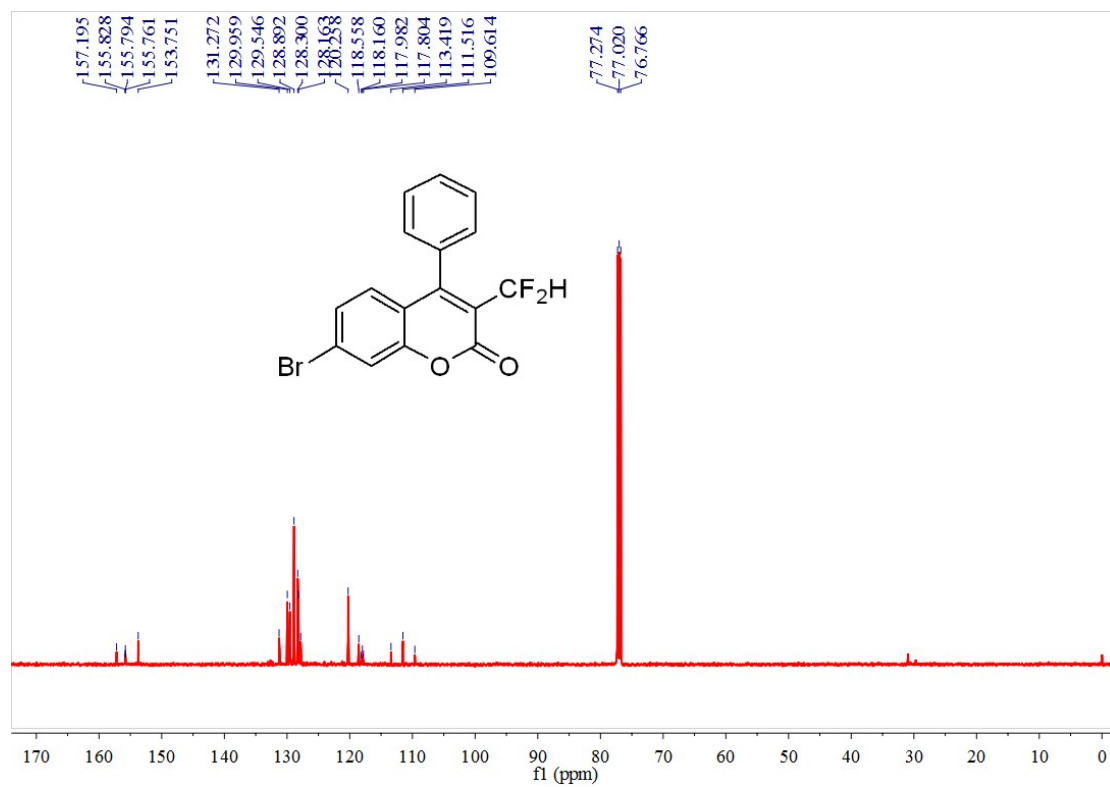
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3i**:



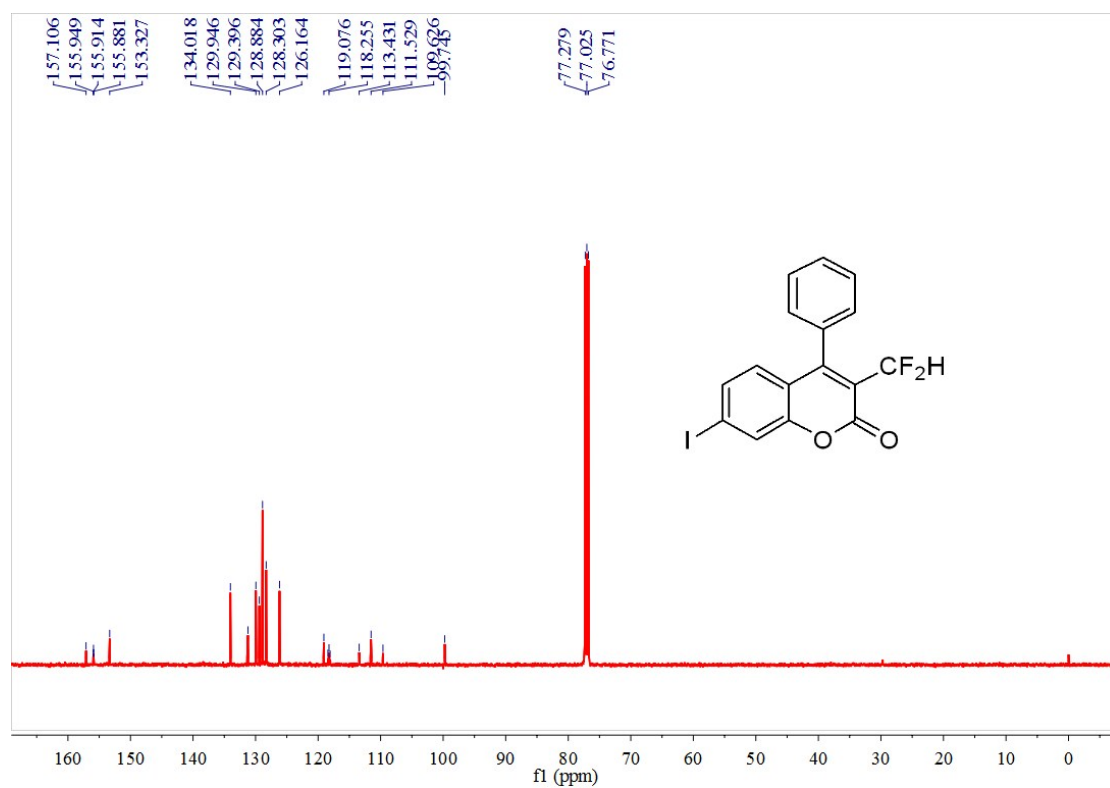
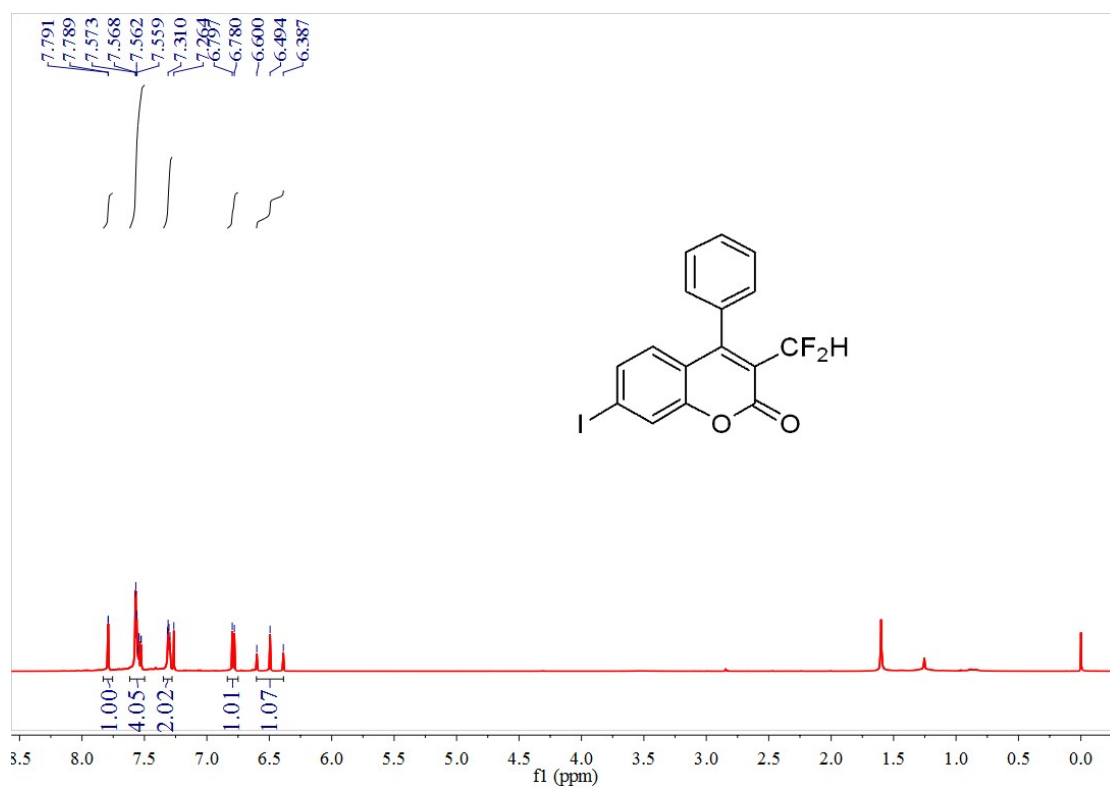


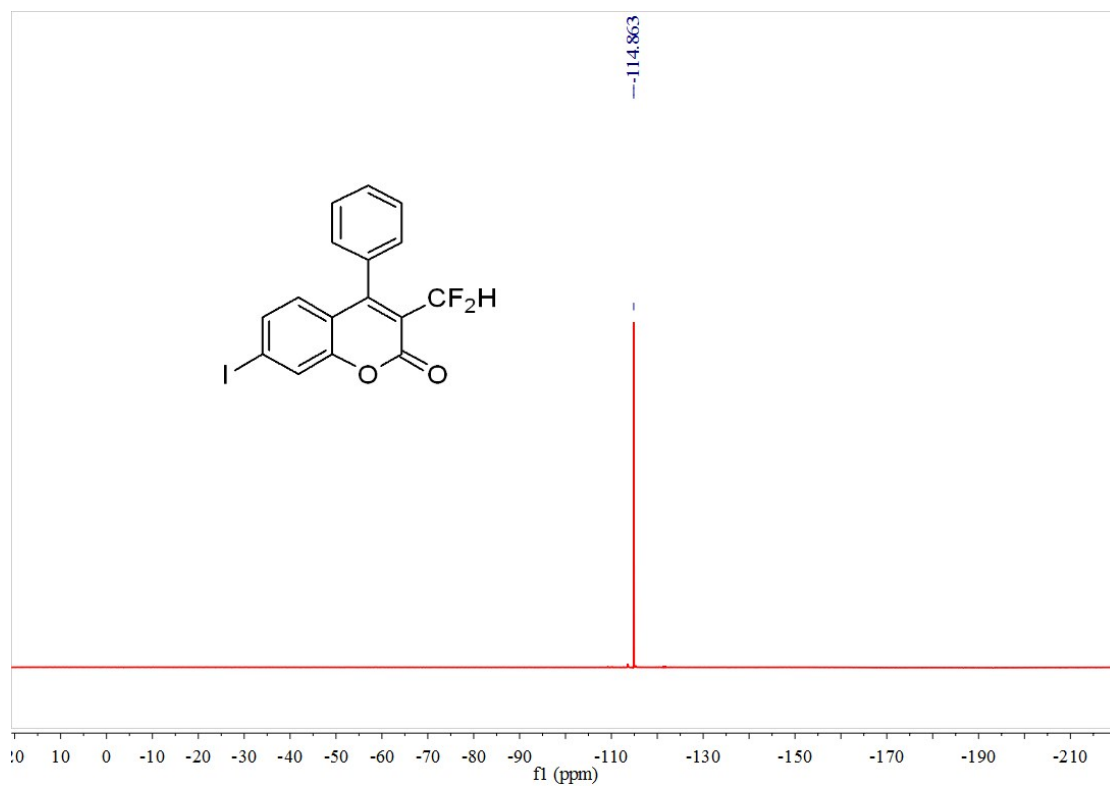
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3j**:



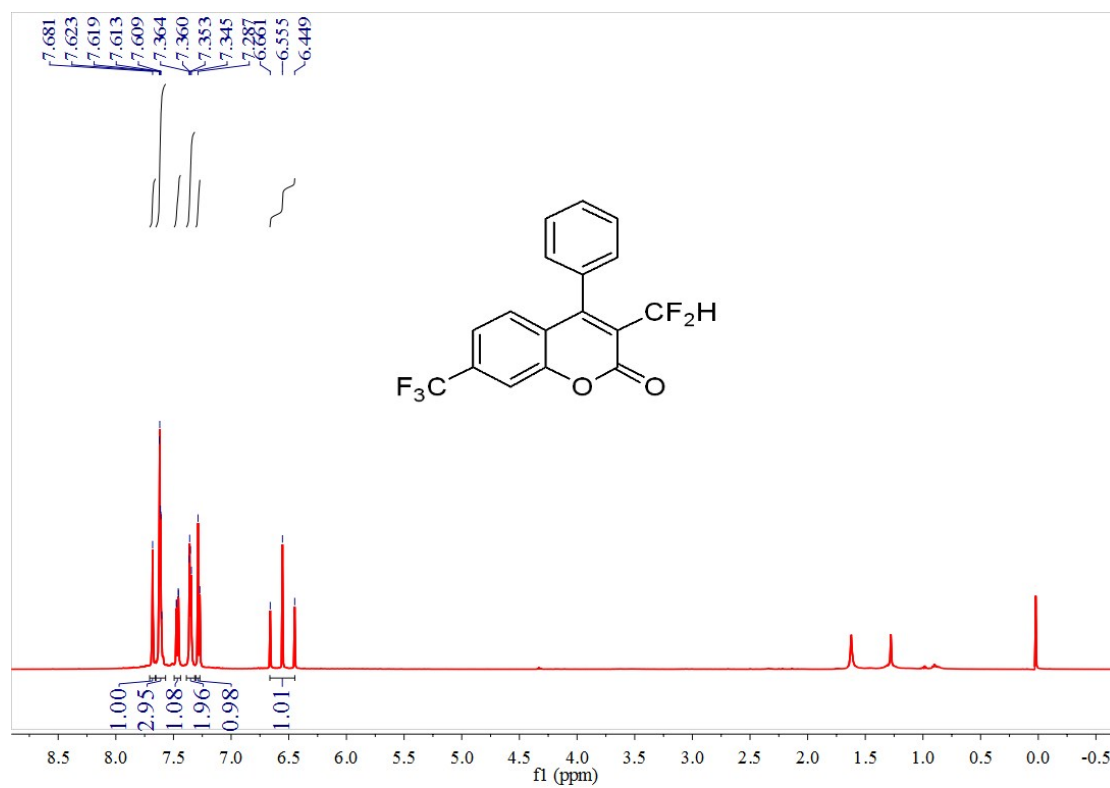


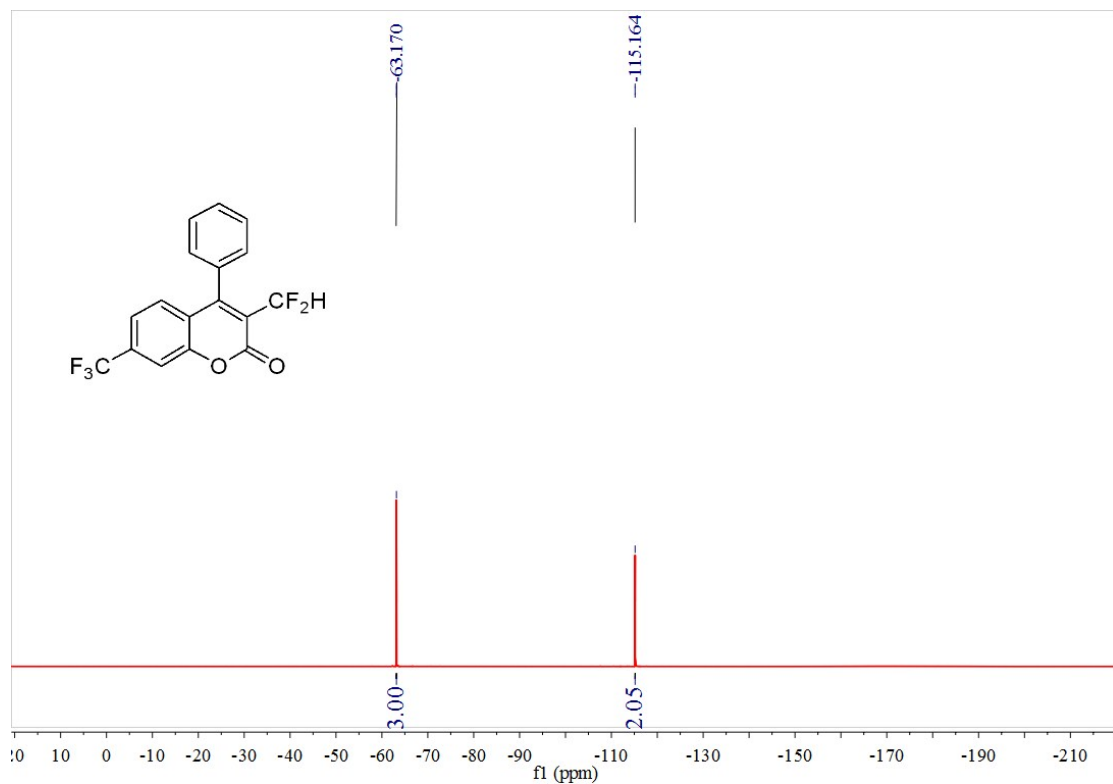
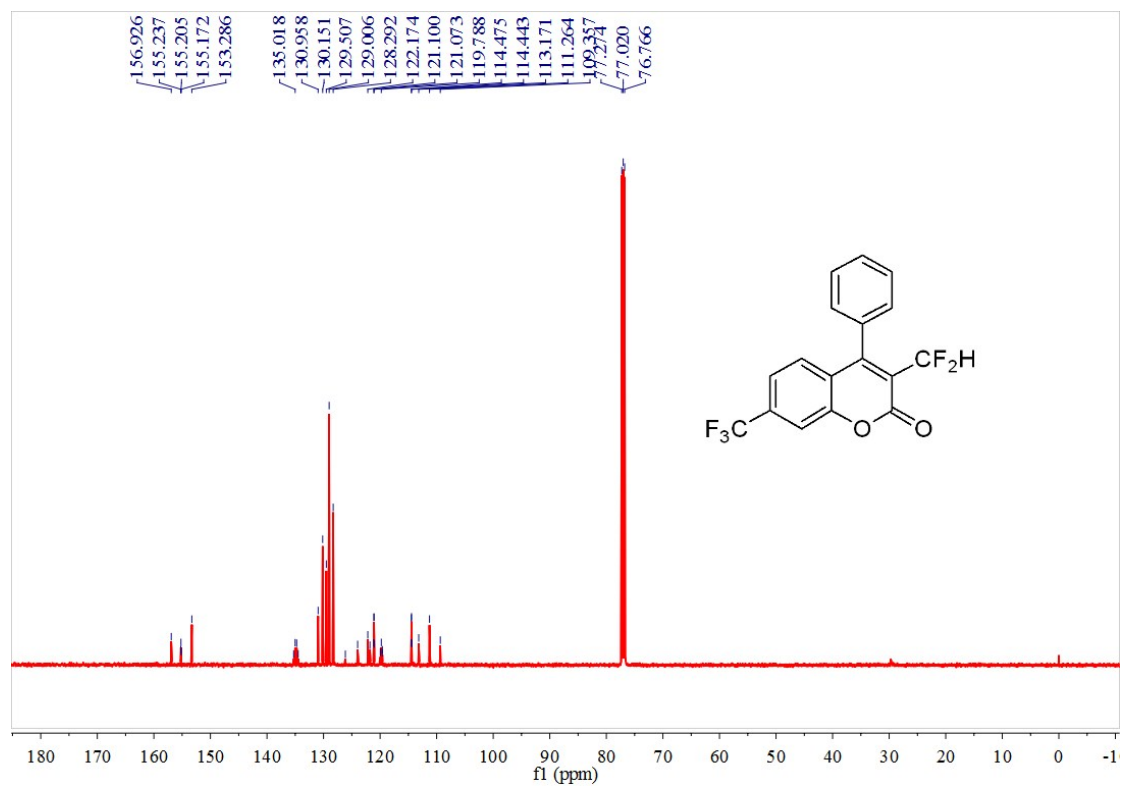
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3k**:



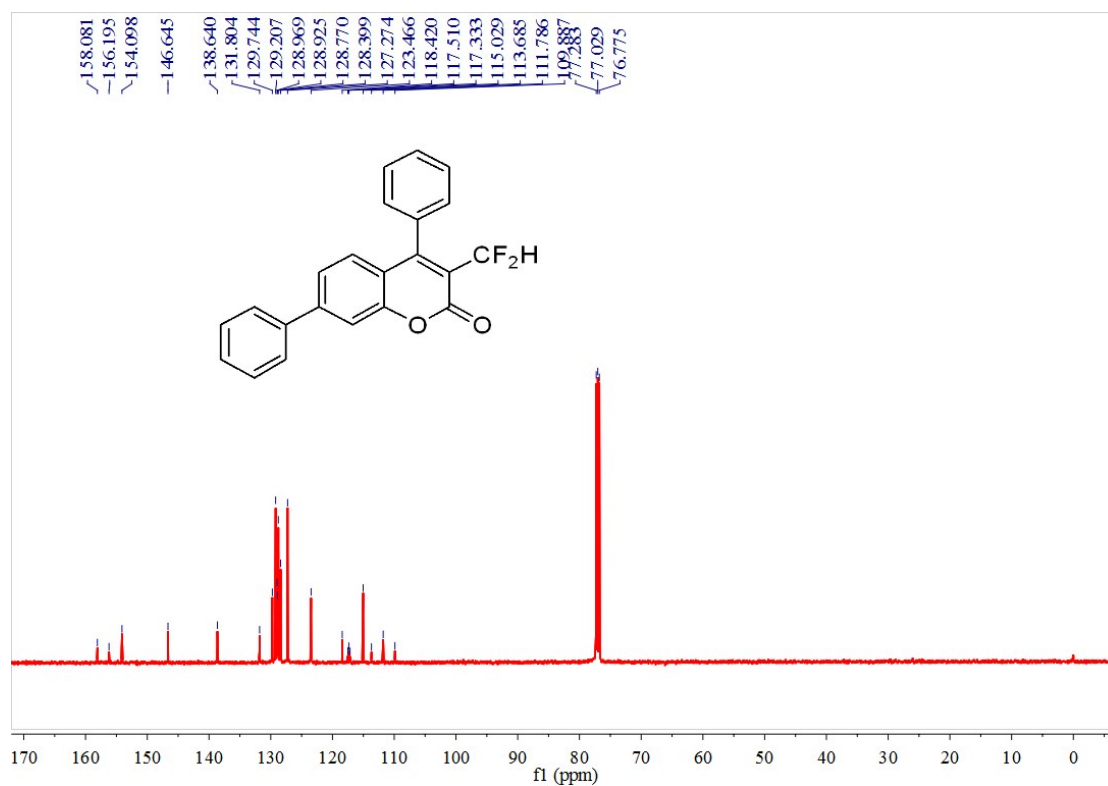
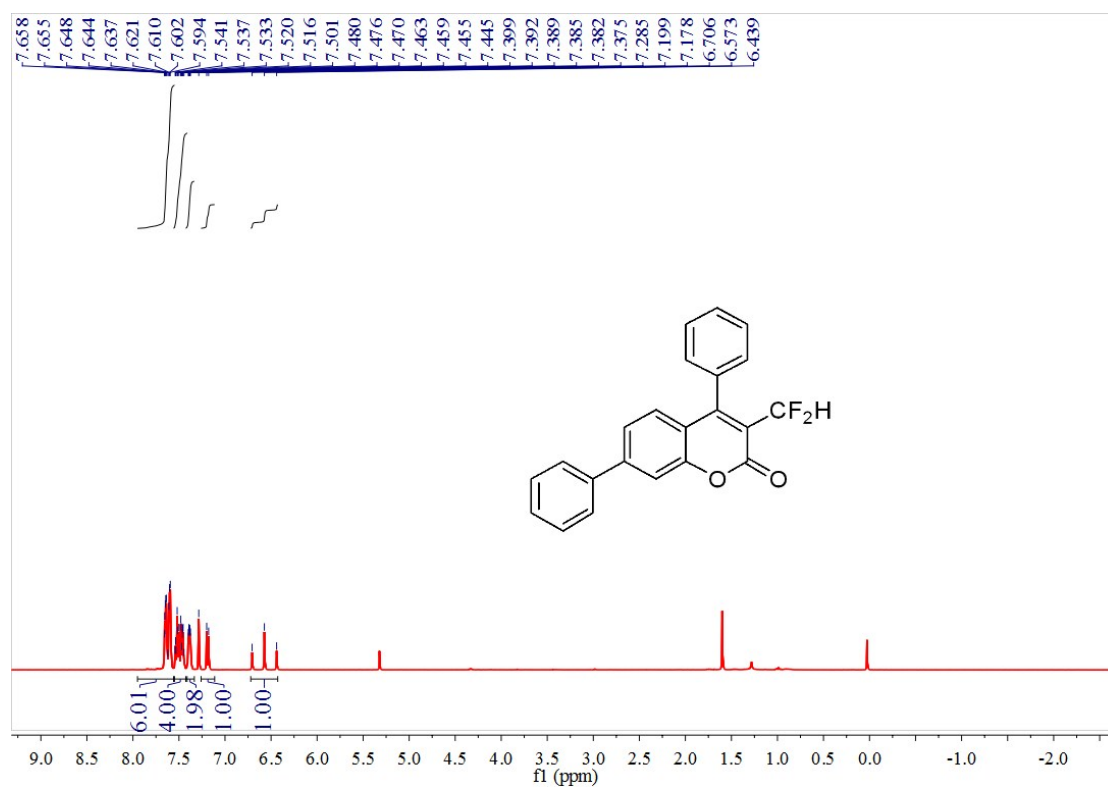


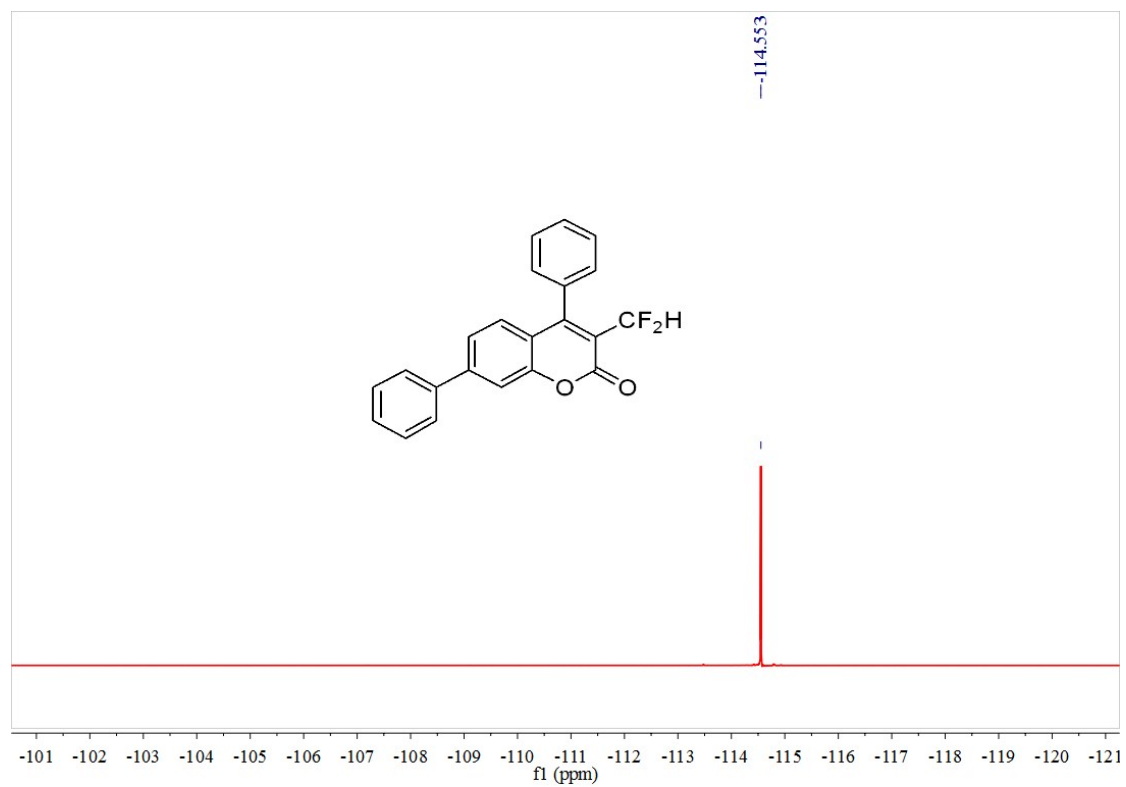
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3I**:



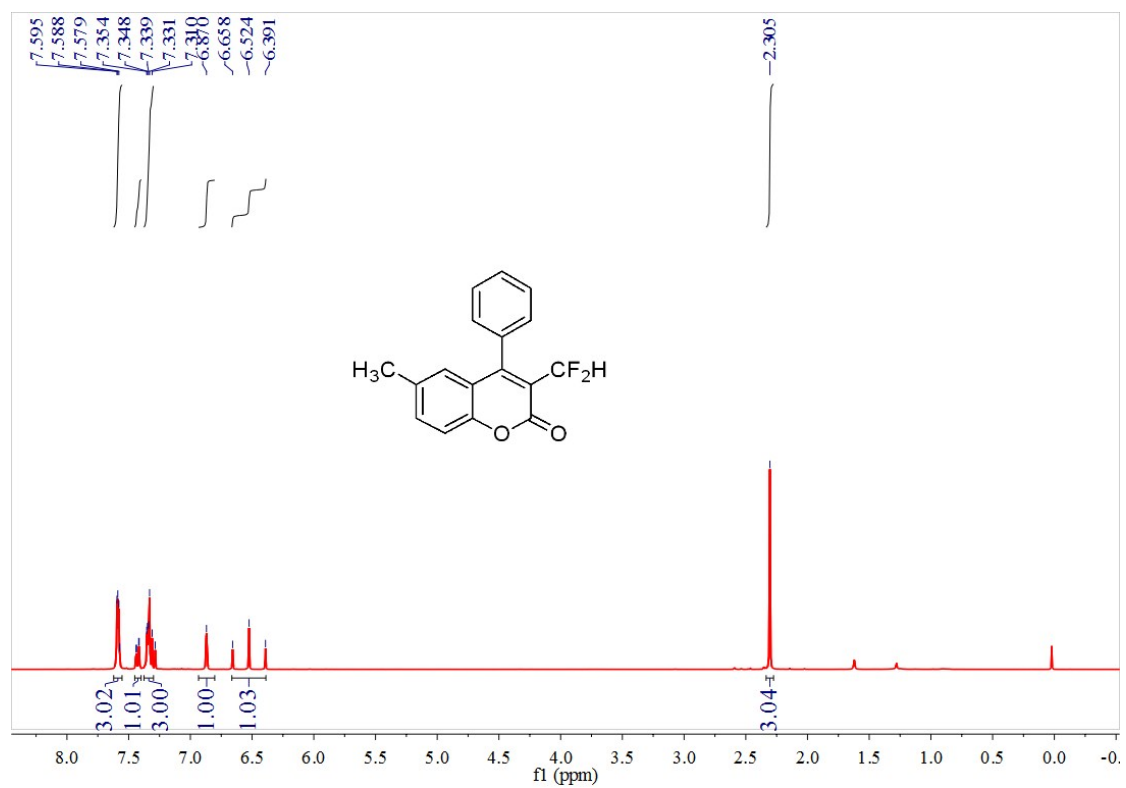


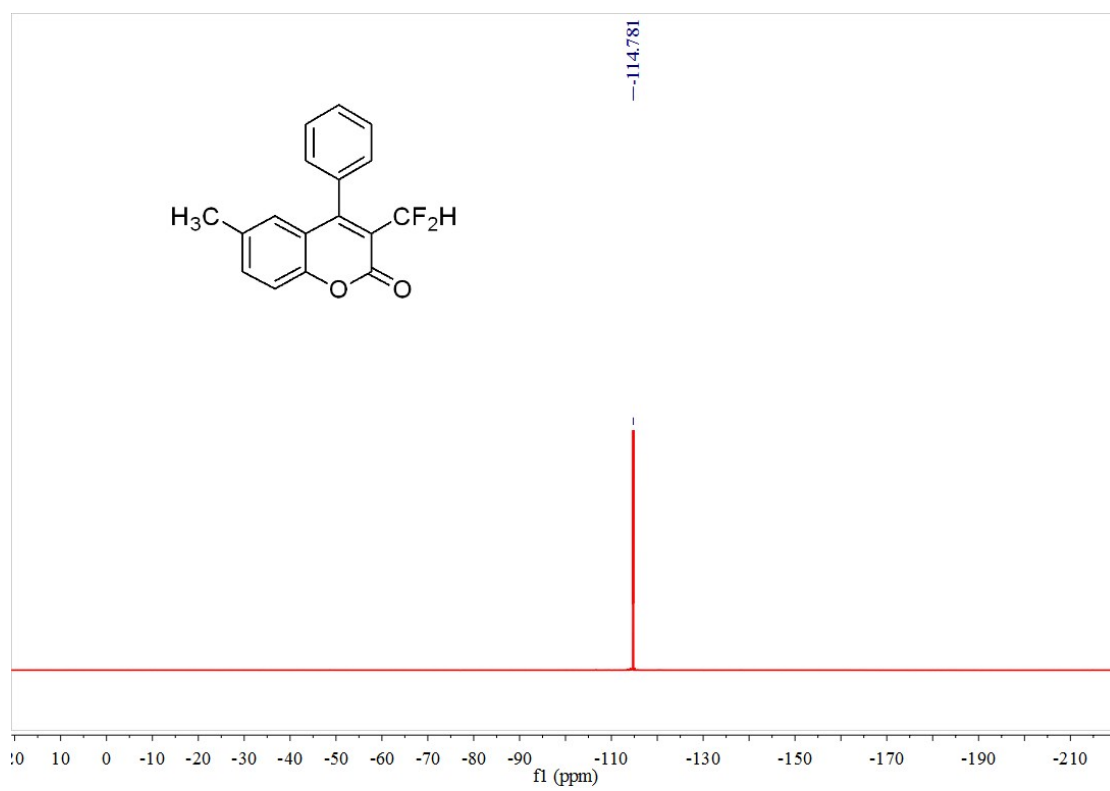
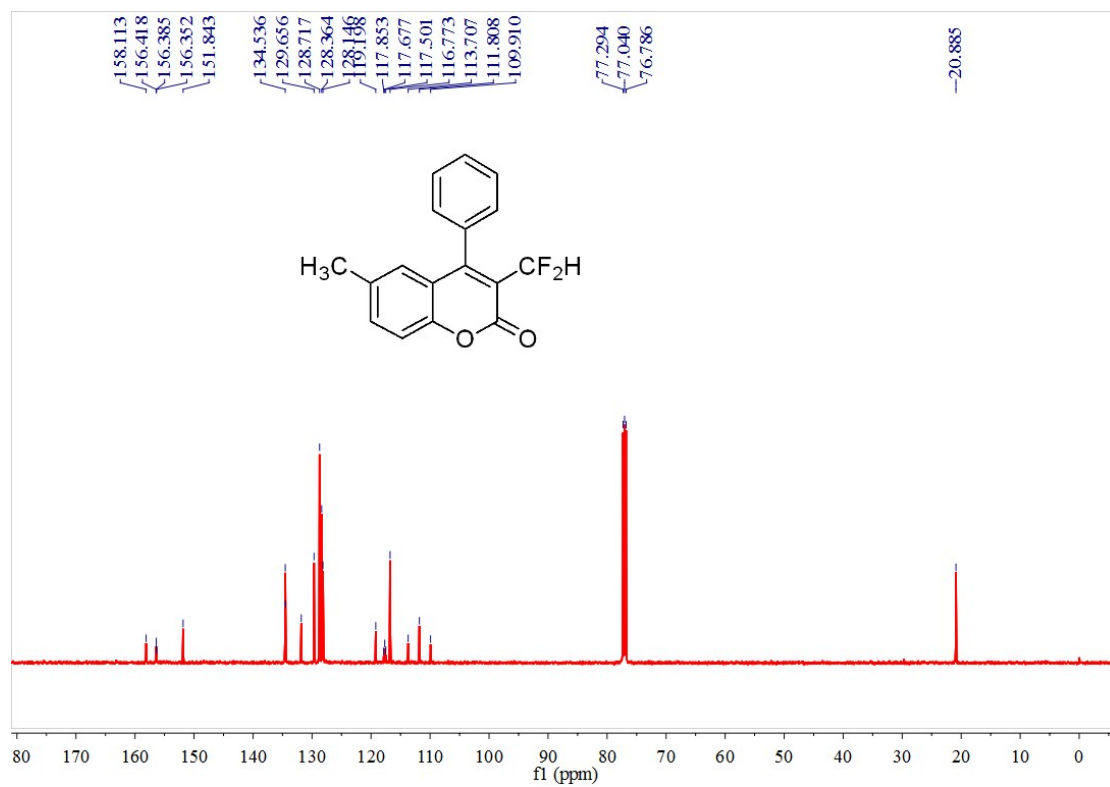
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3m**:



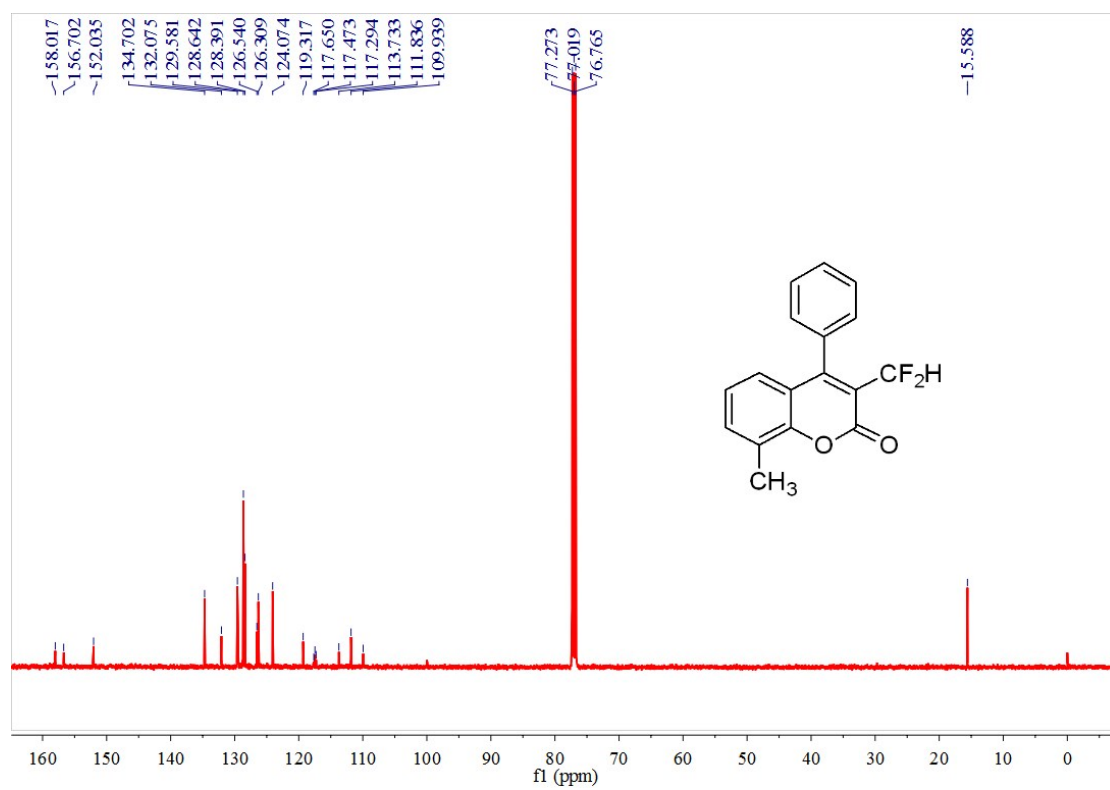
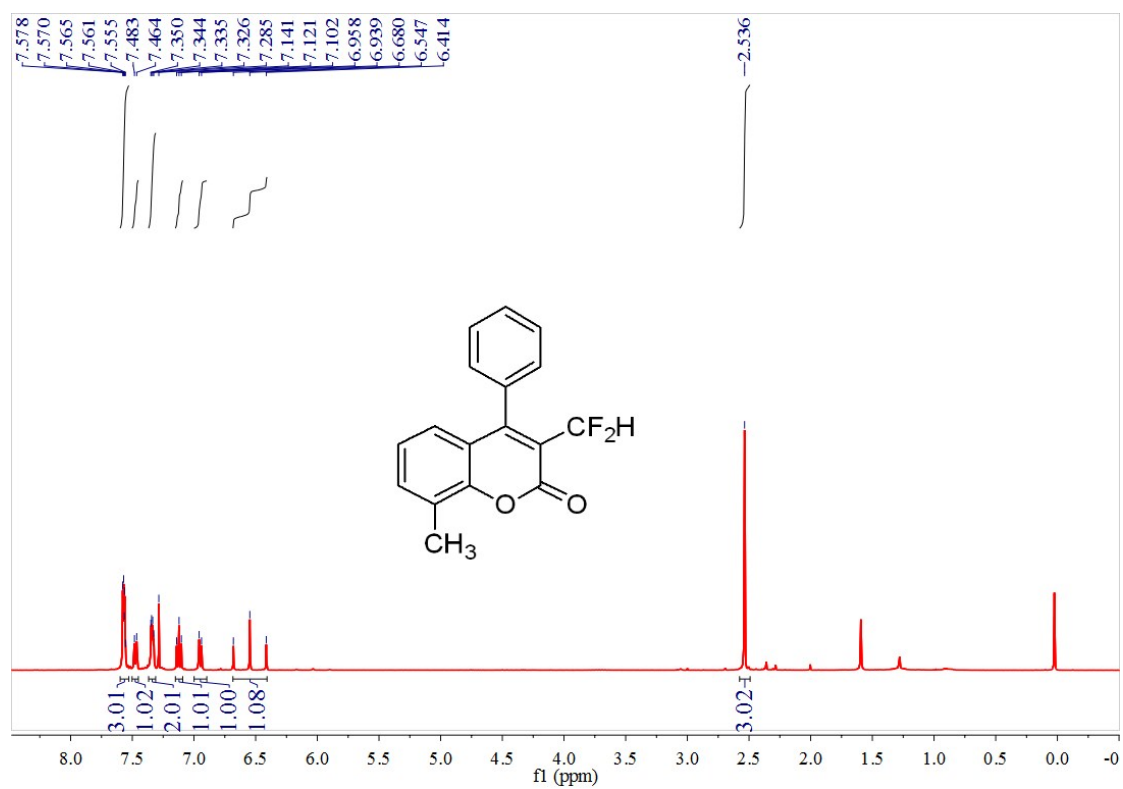


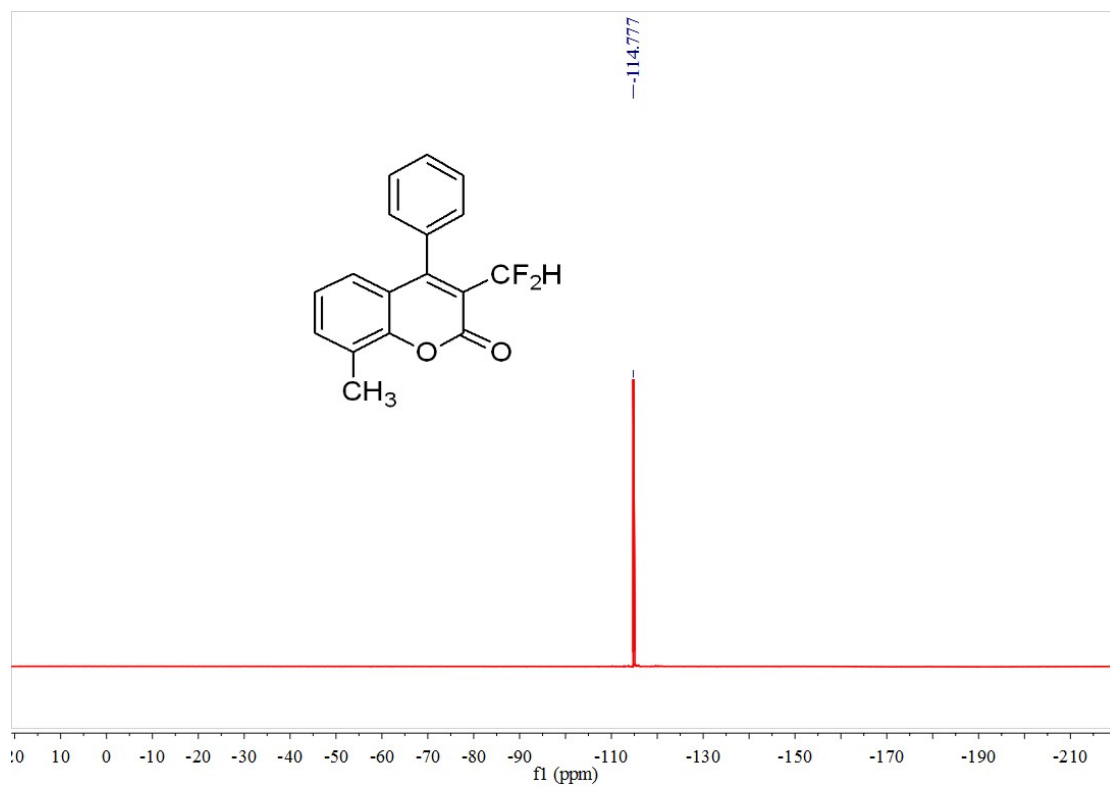
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3n**:



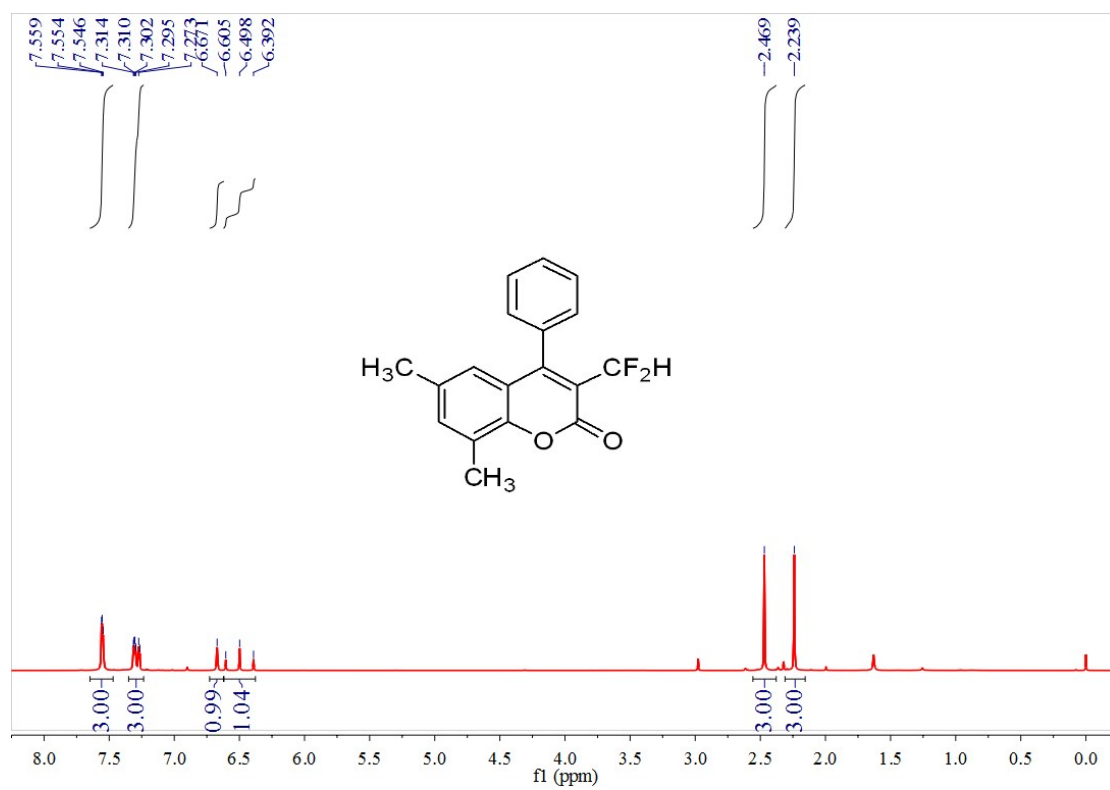


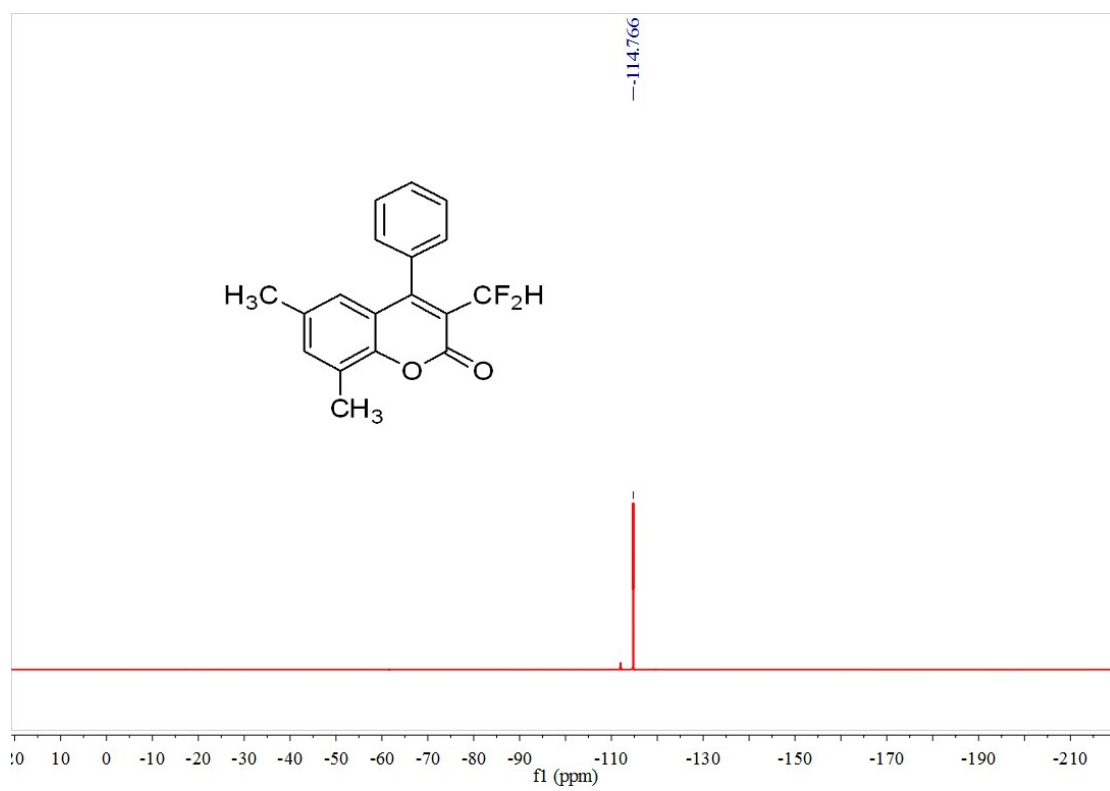
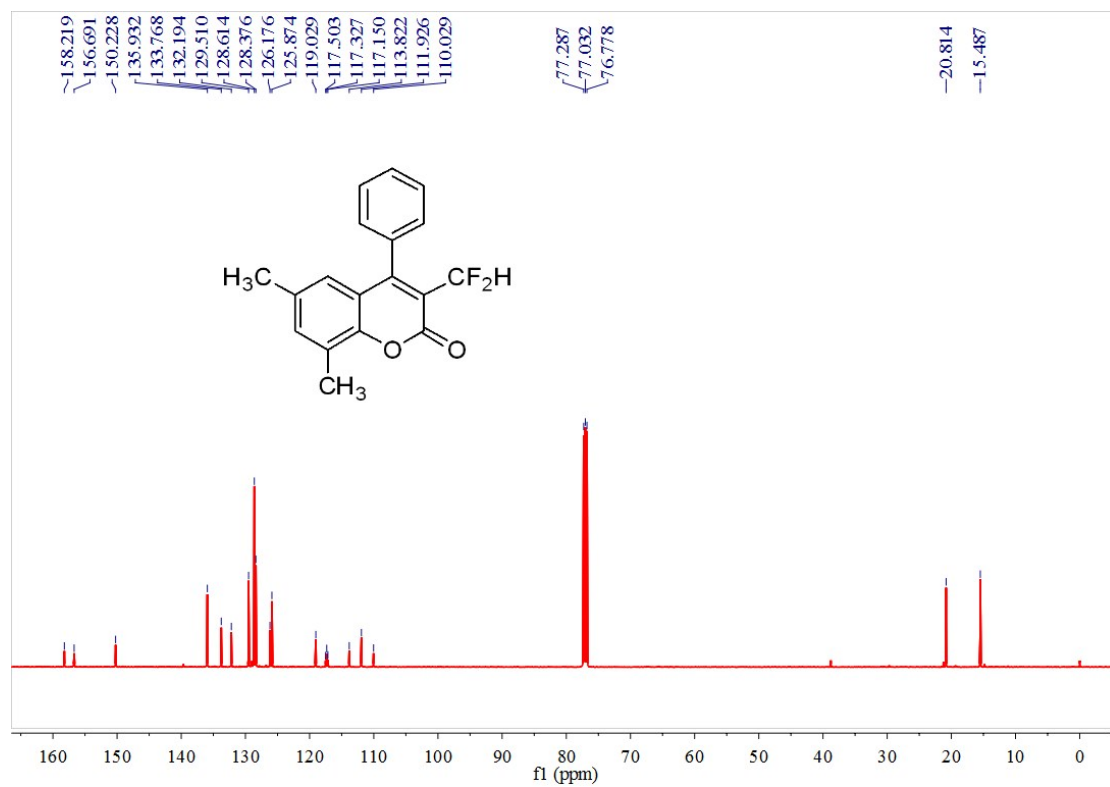
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3n'**:



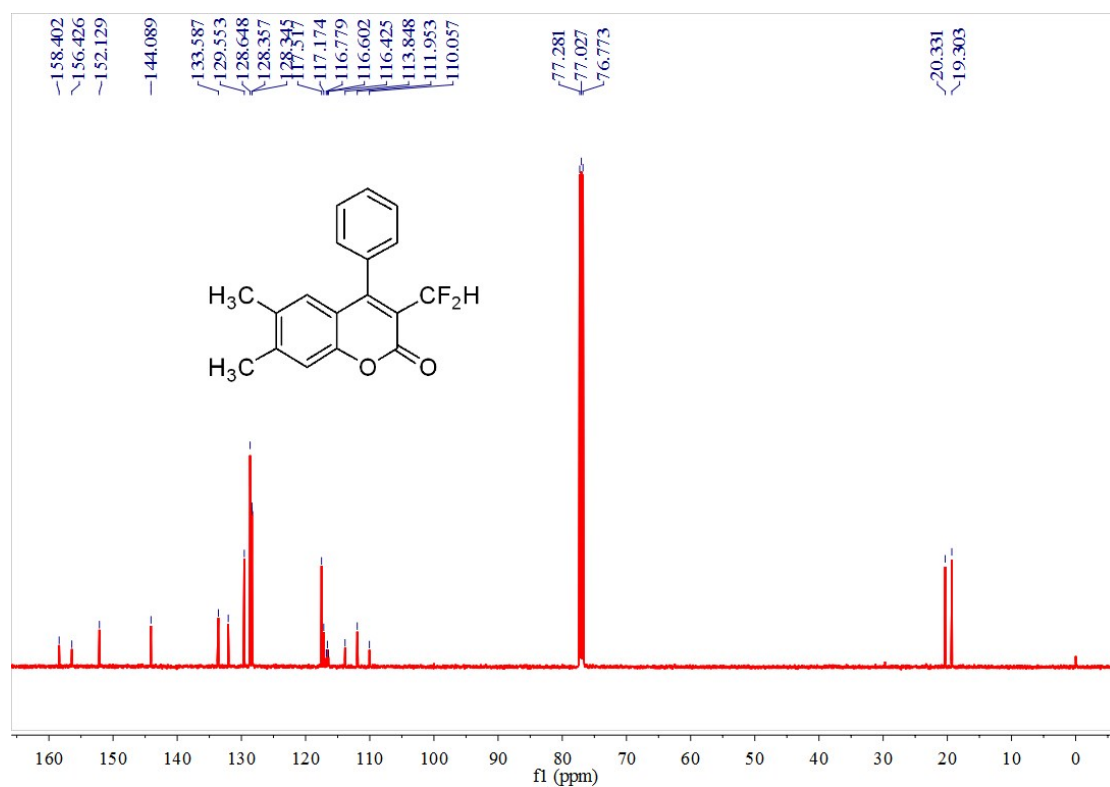
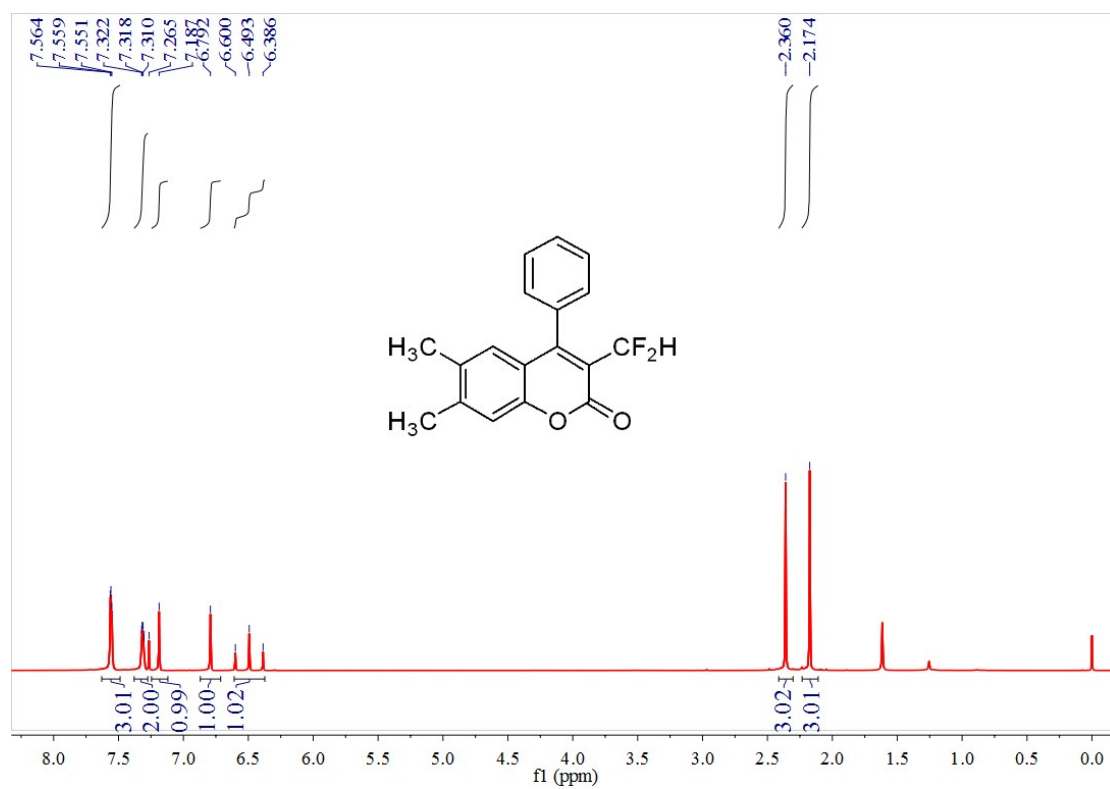


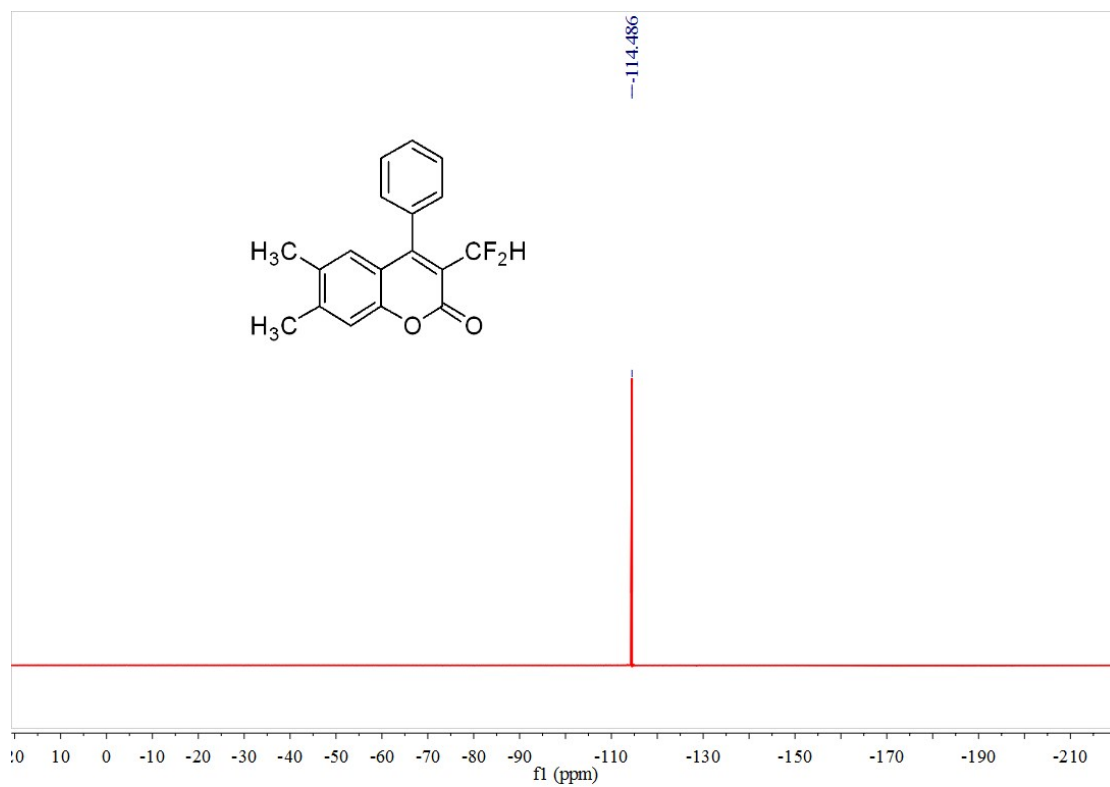
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3o**:



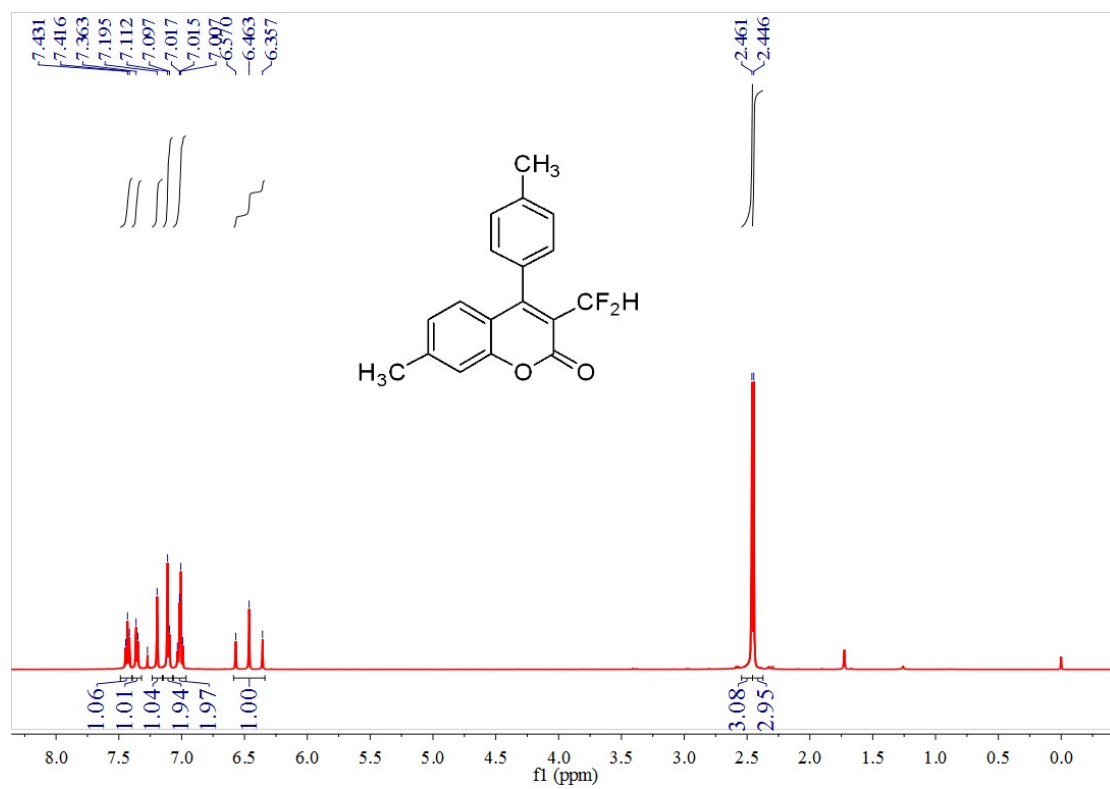


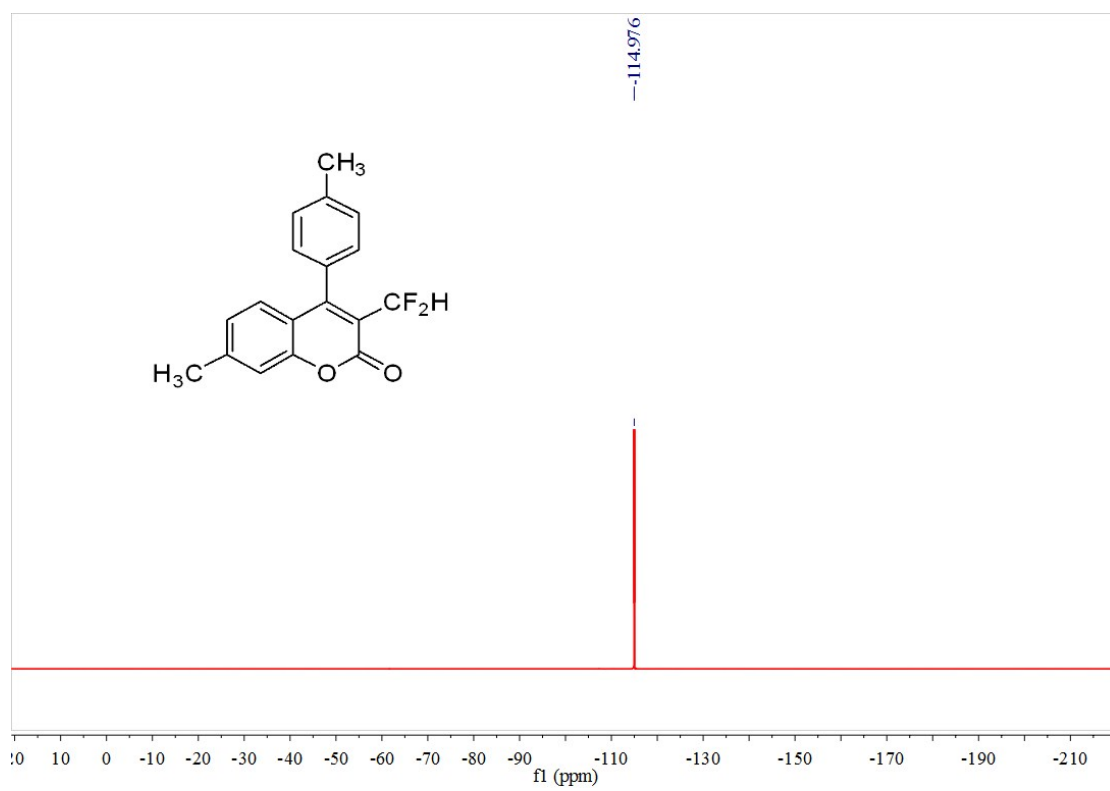
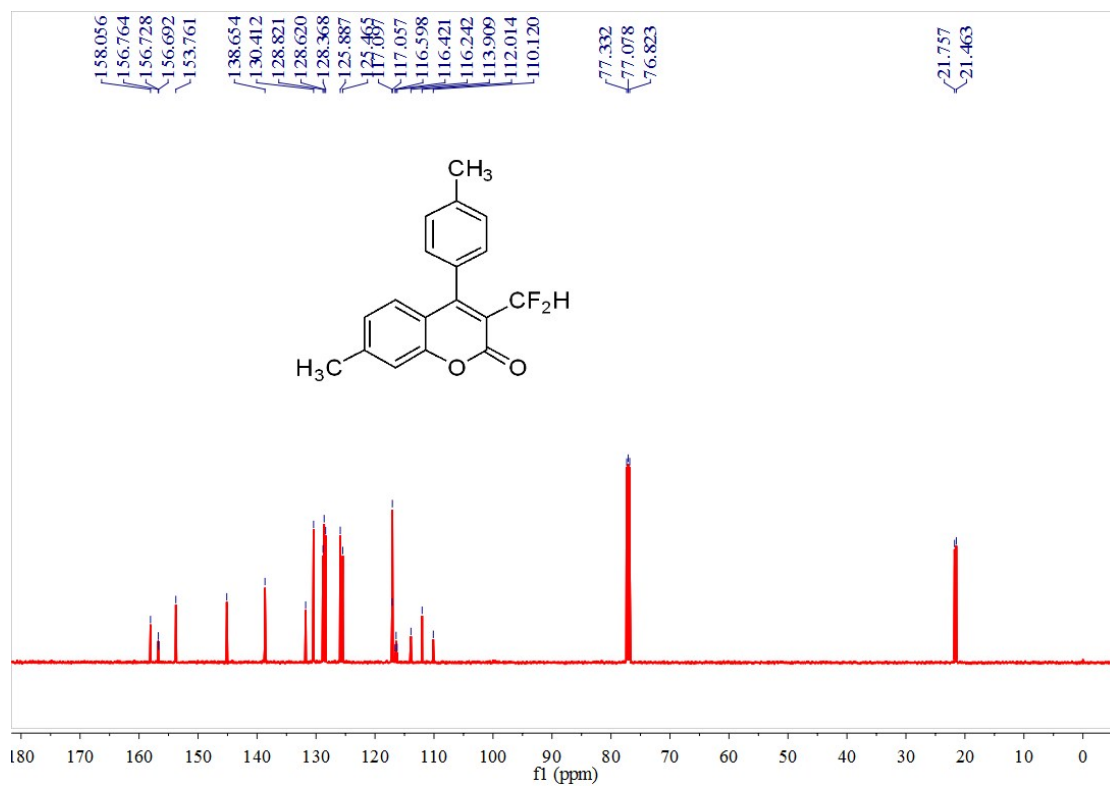
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3p**:



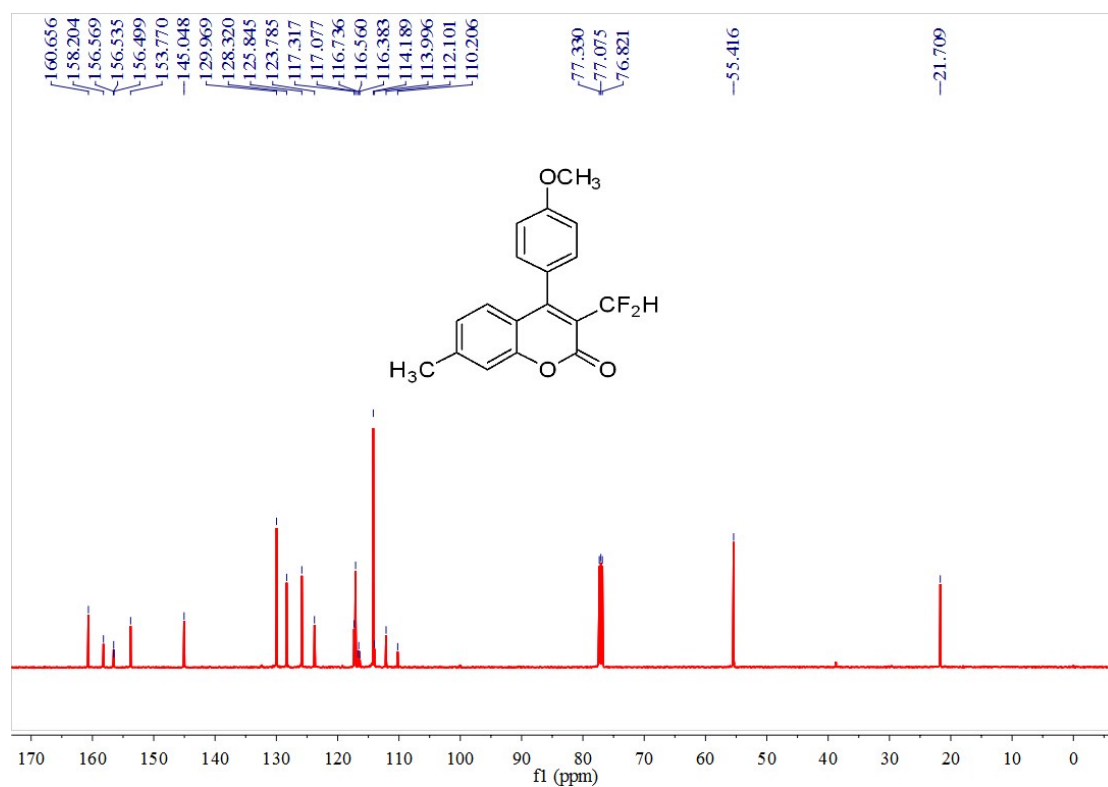
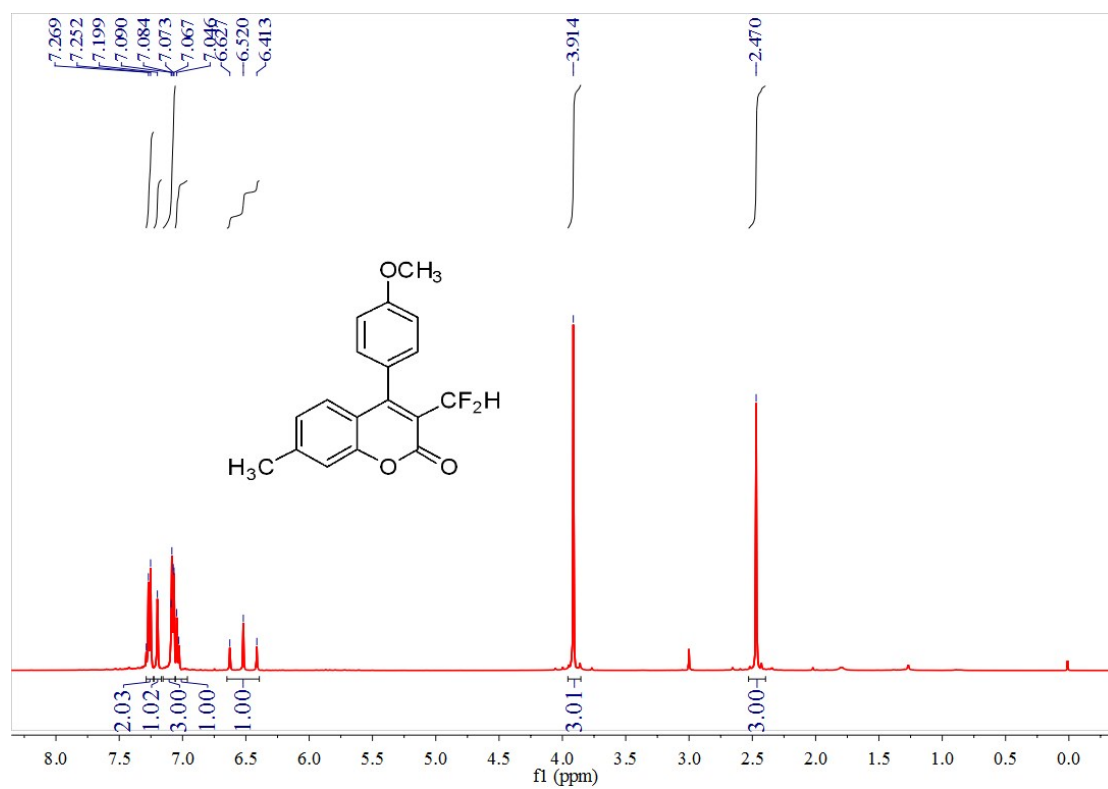


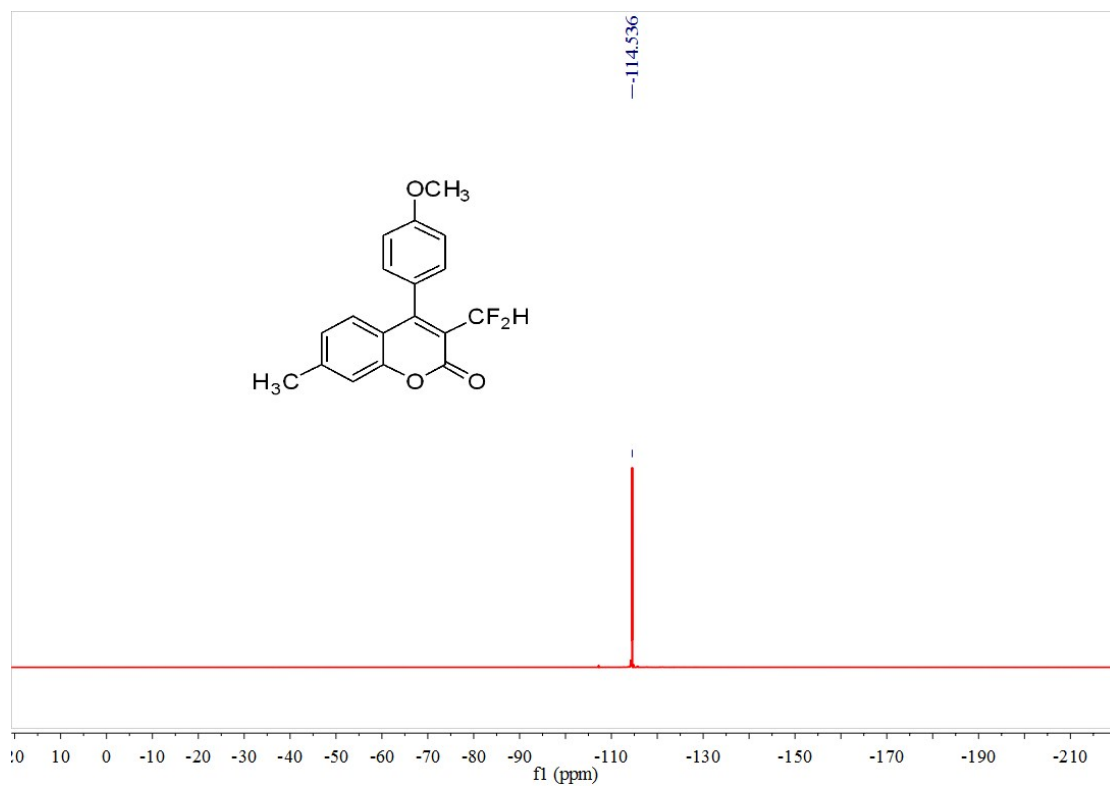
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3s**:



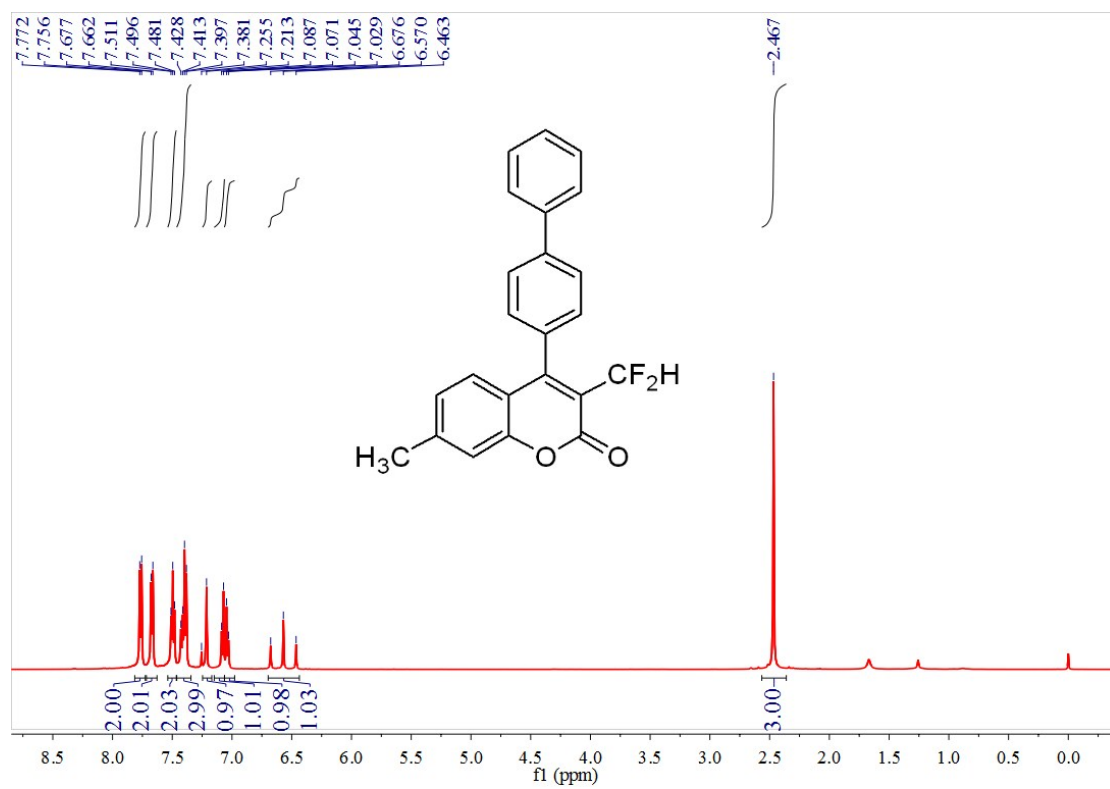


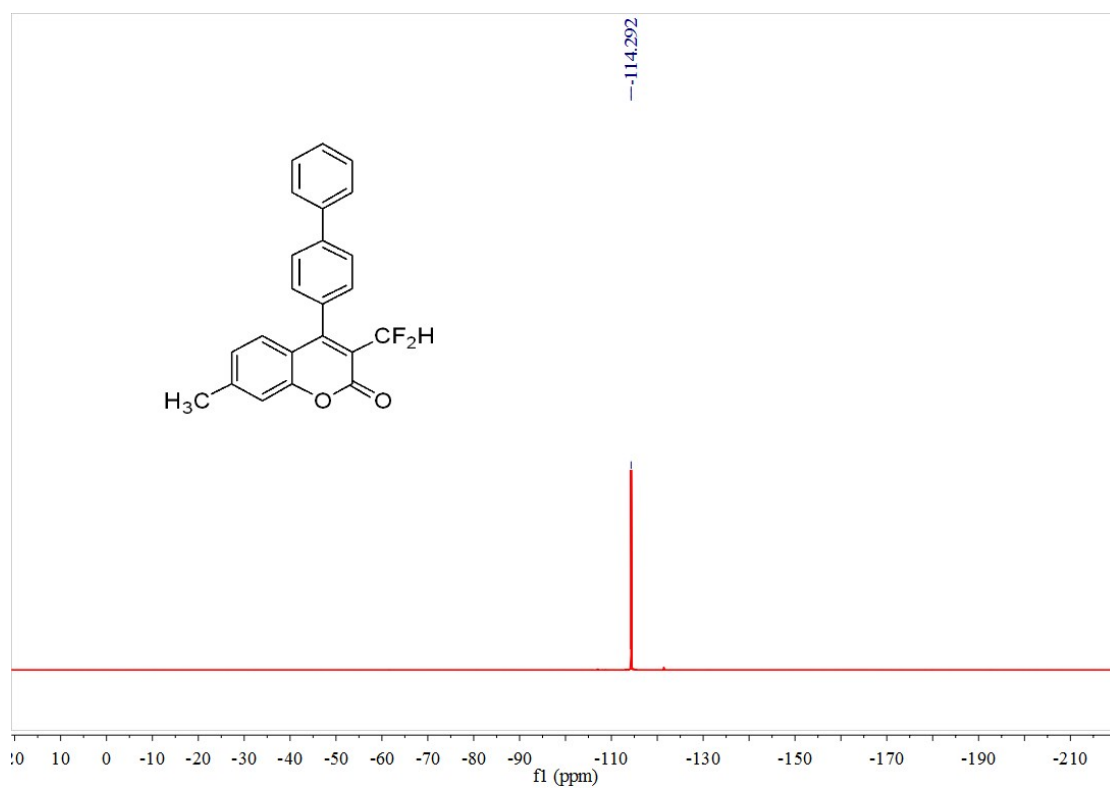
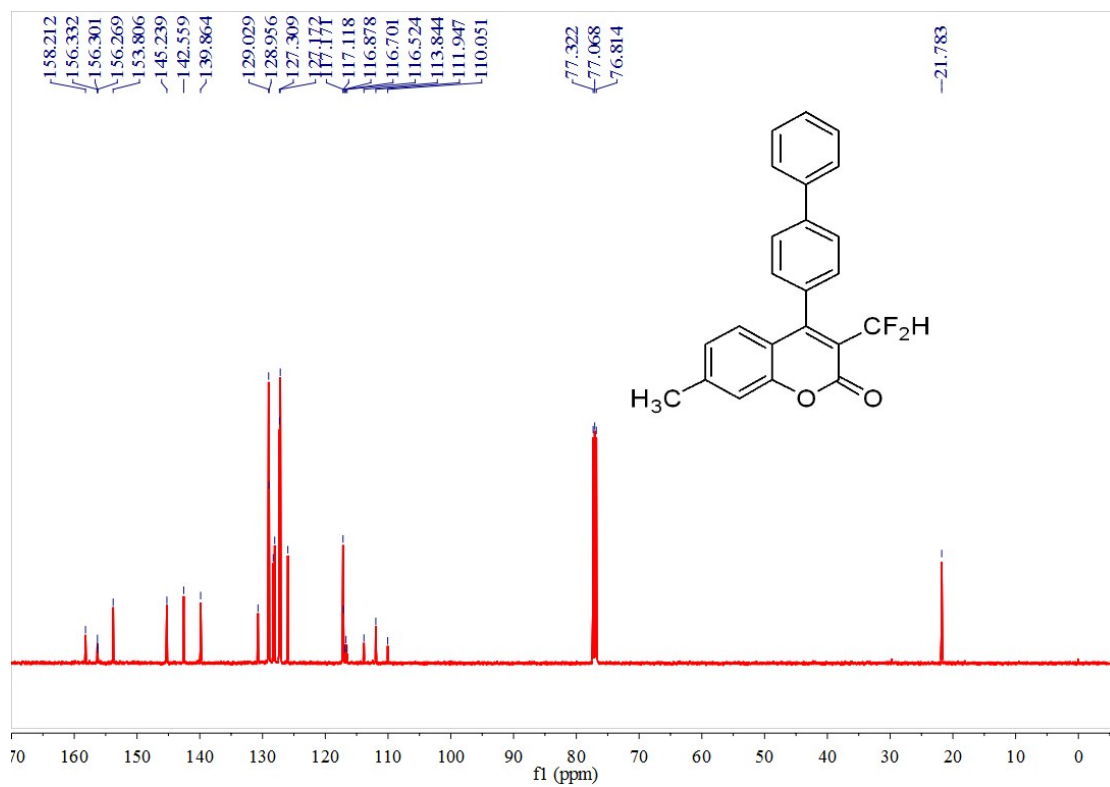
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3t**:



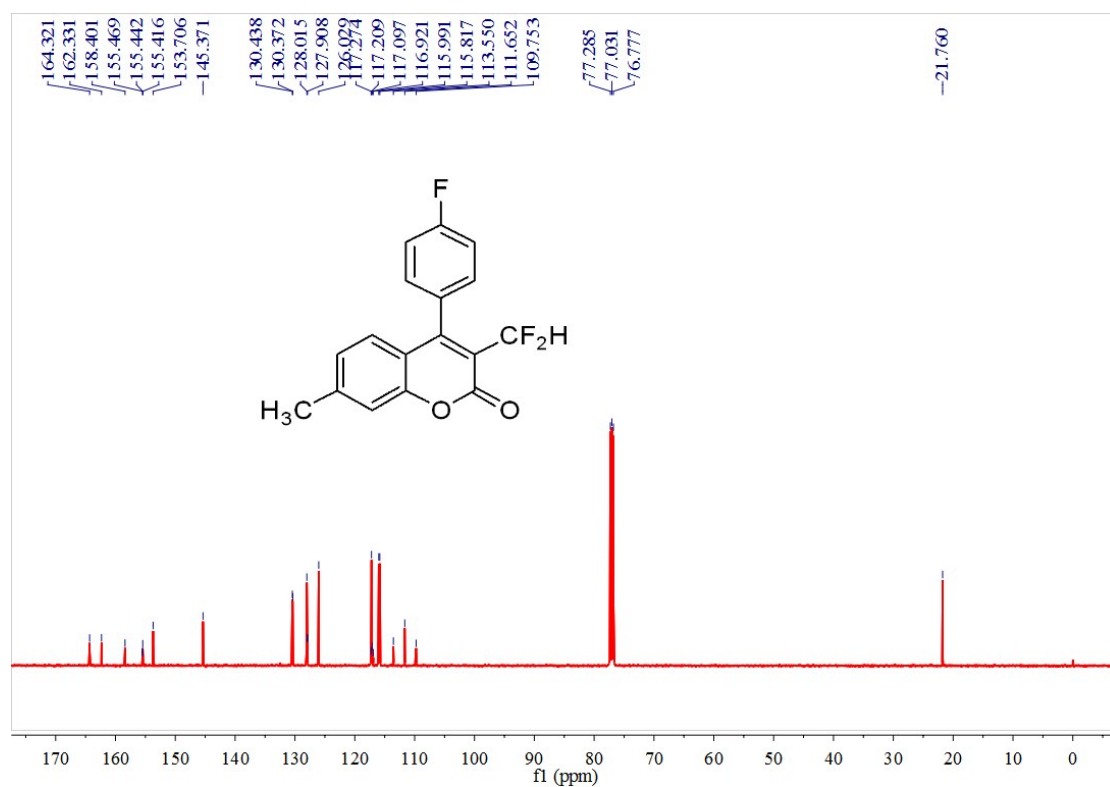
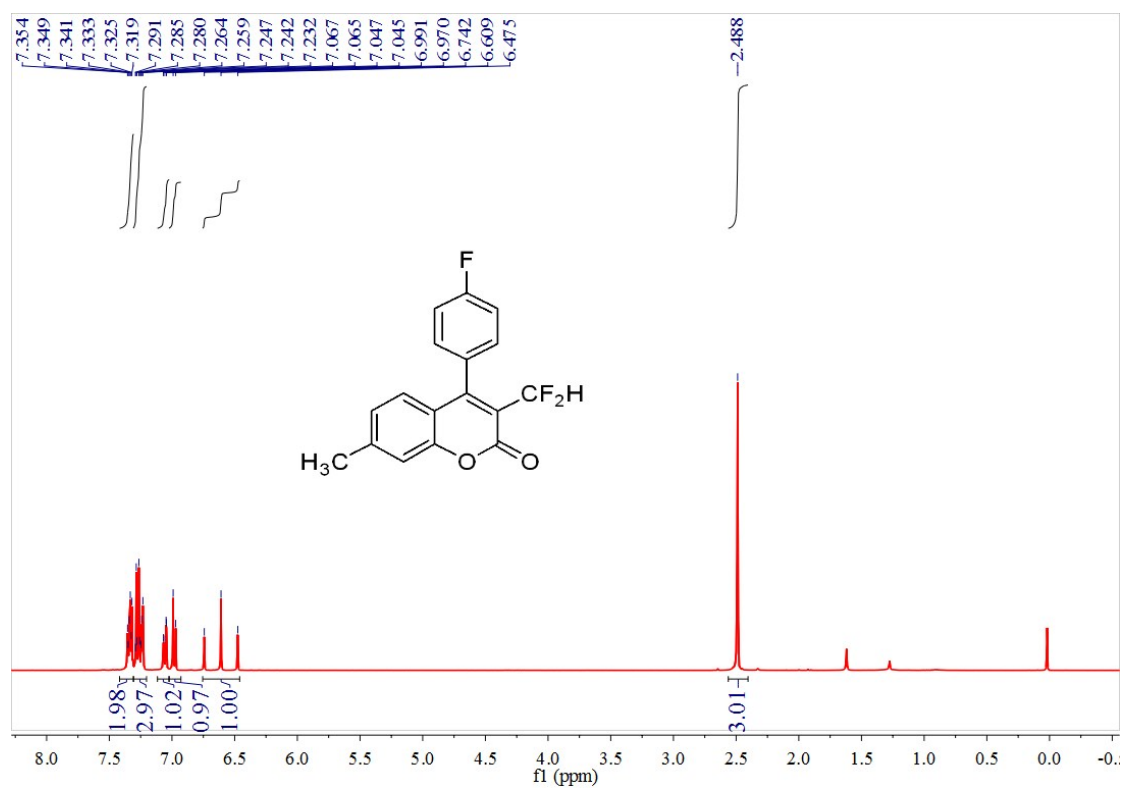


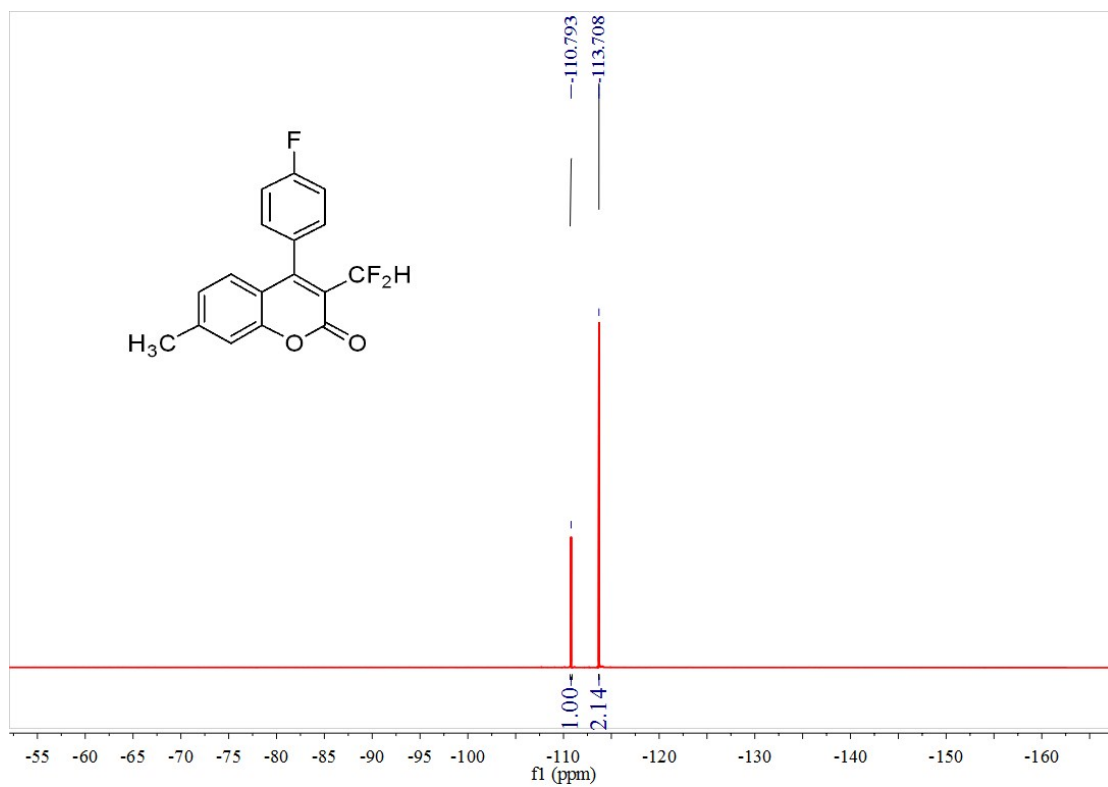
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3u**:



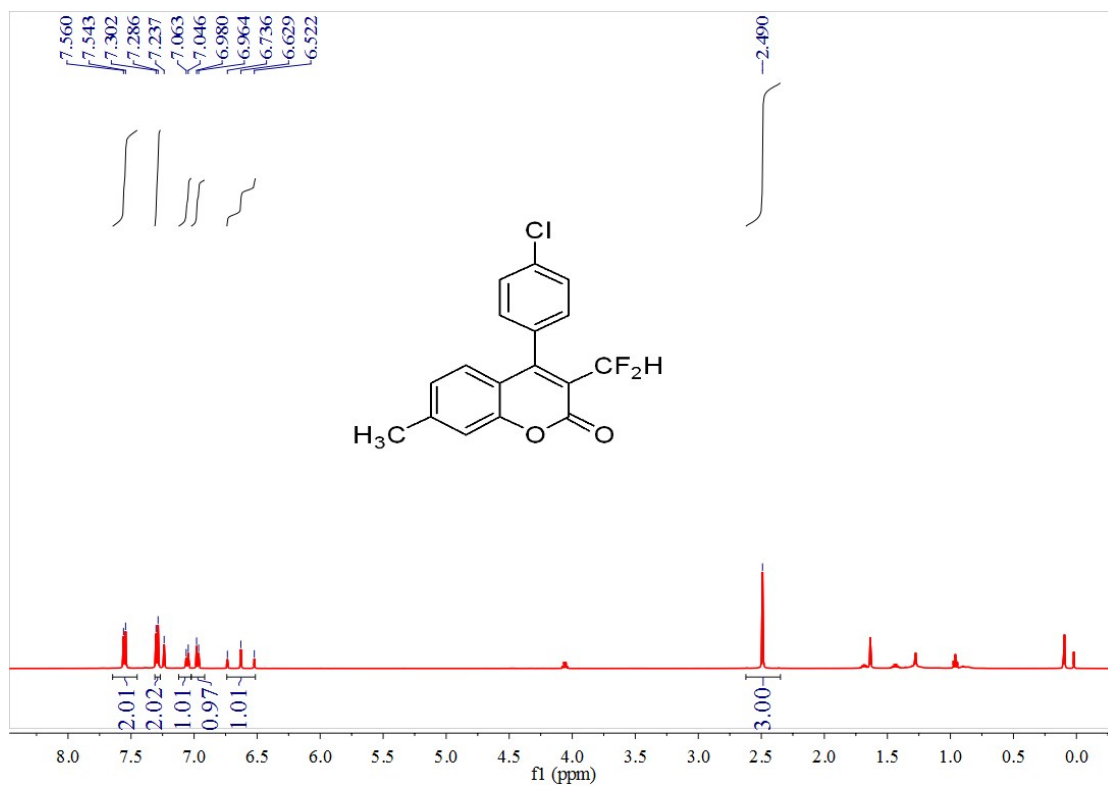


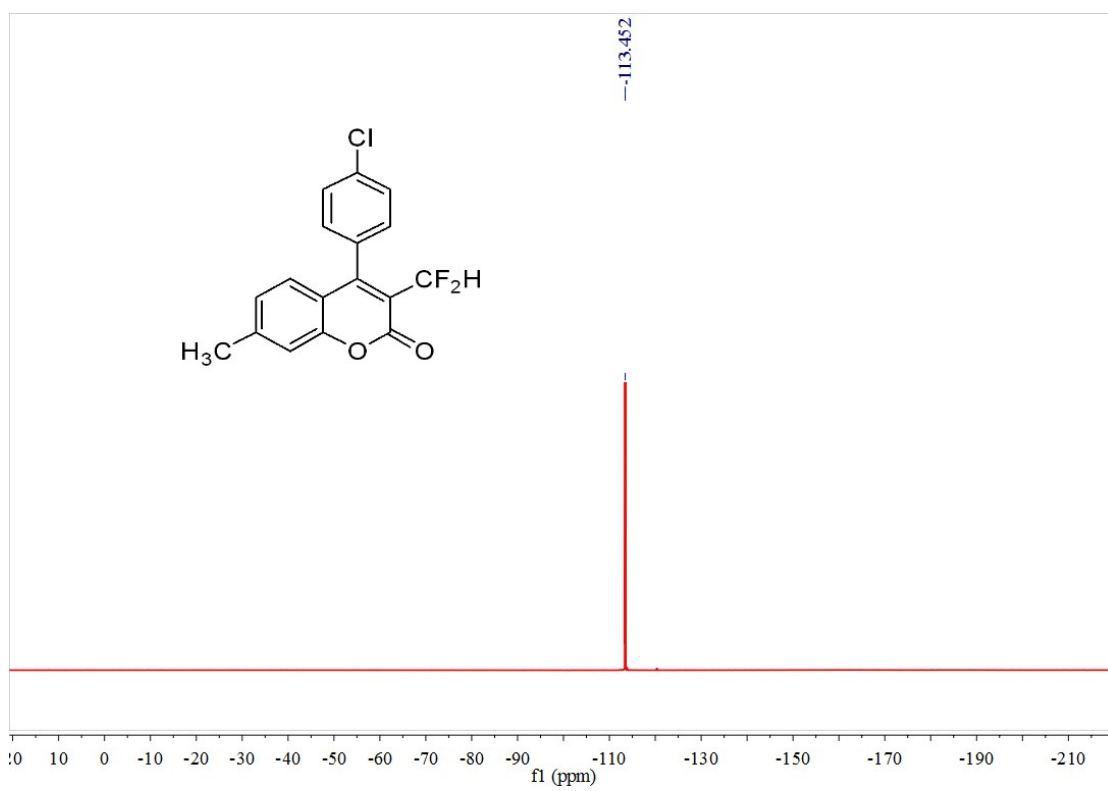
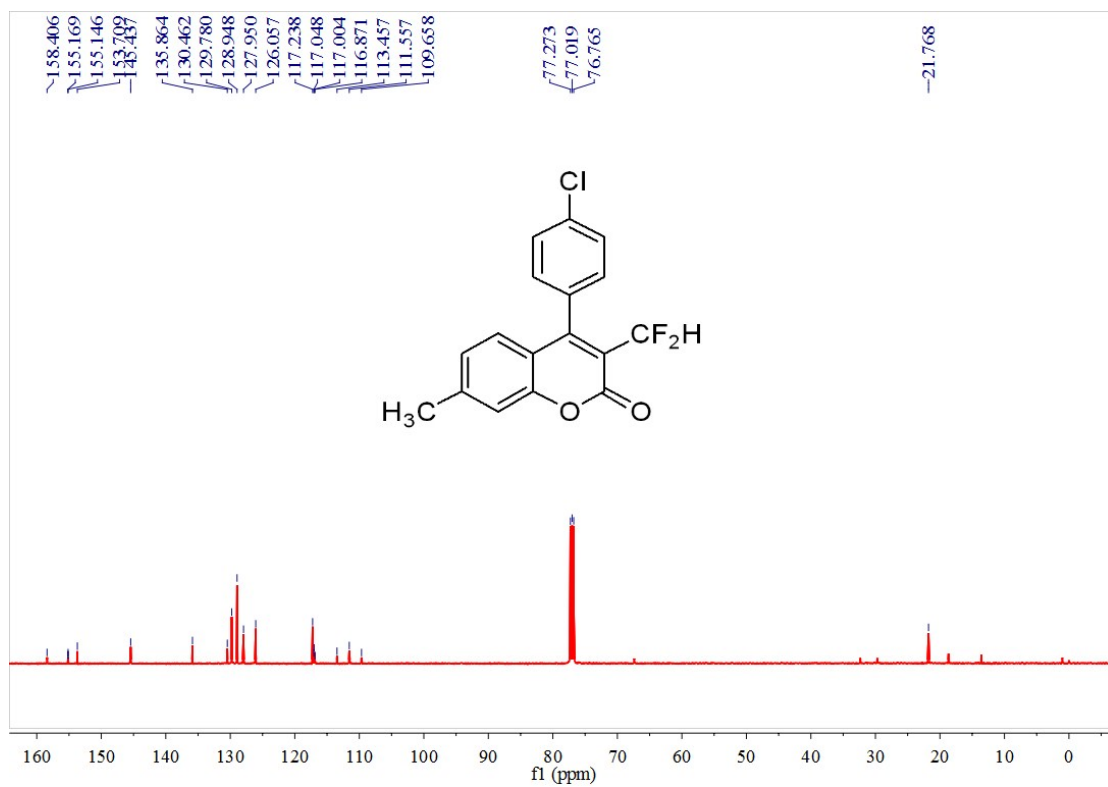
¹H NMR, ¹³C NMR and ¹⁹F NMR spectra of compound **3v**:



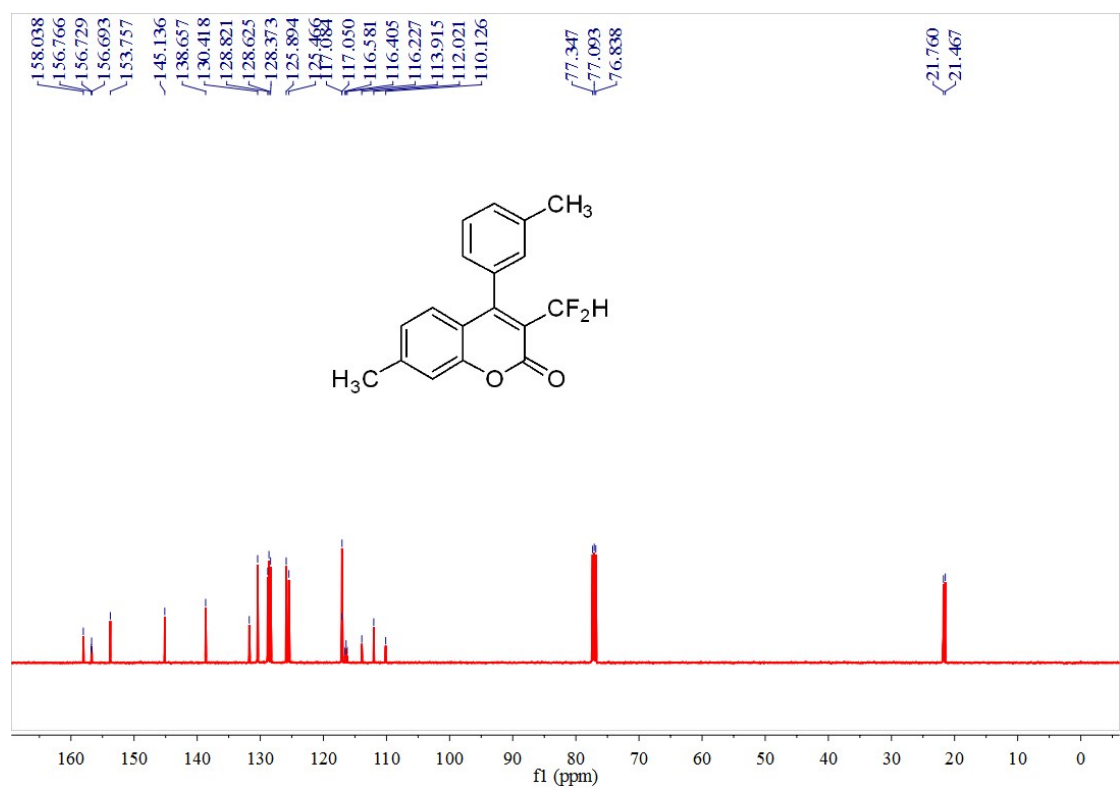
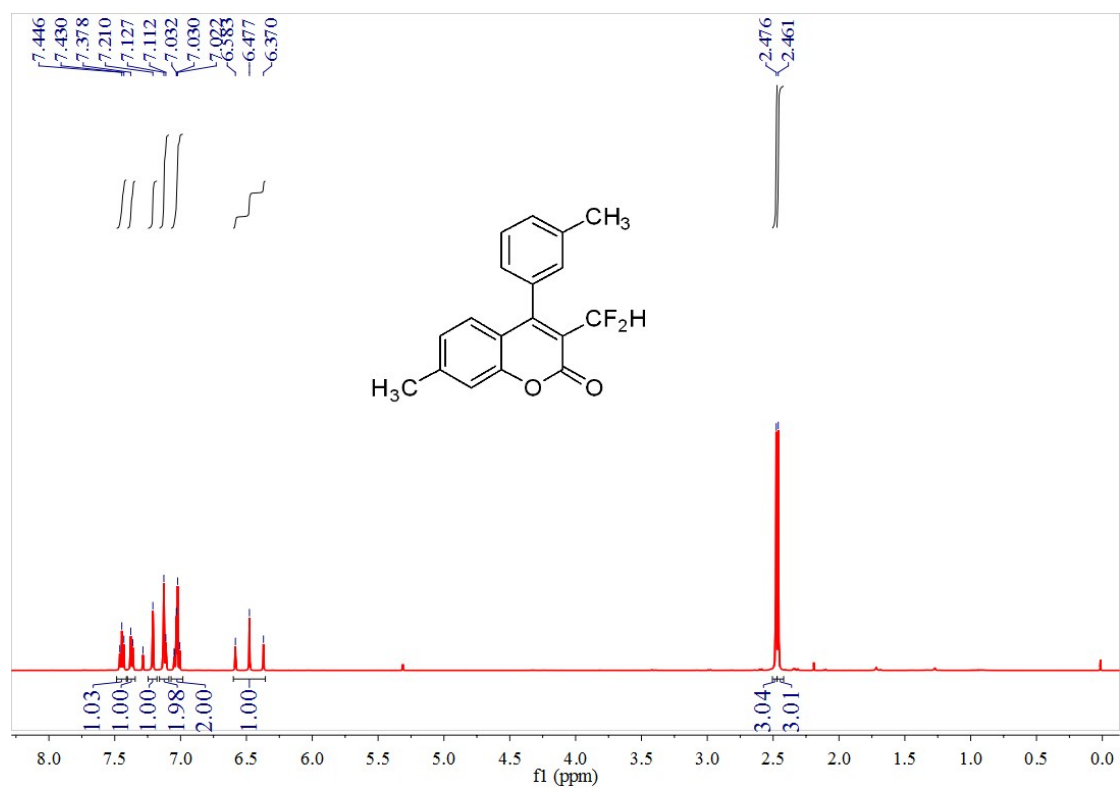


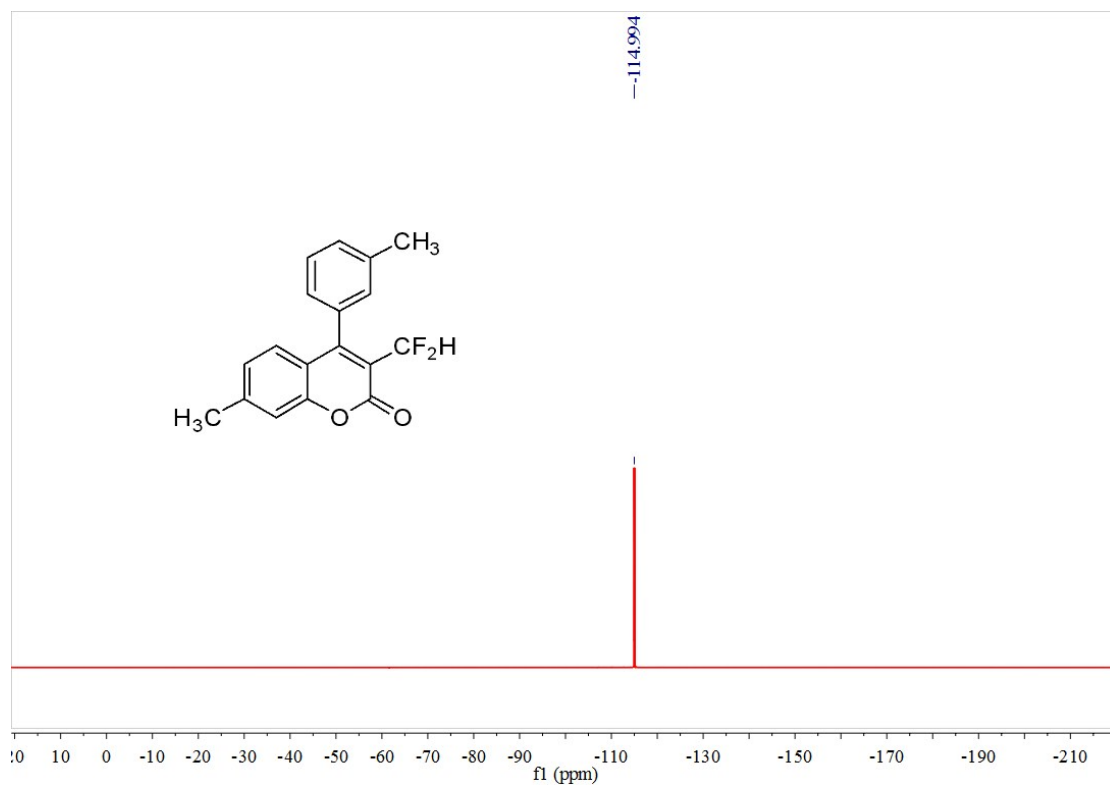
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3w**:



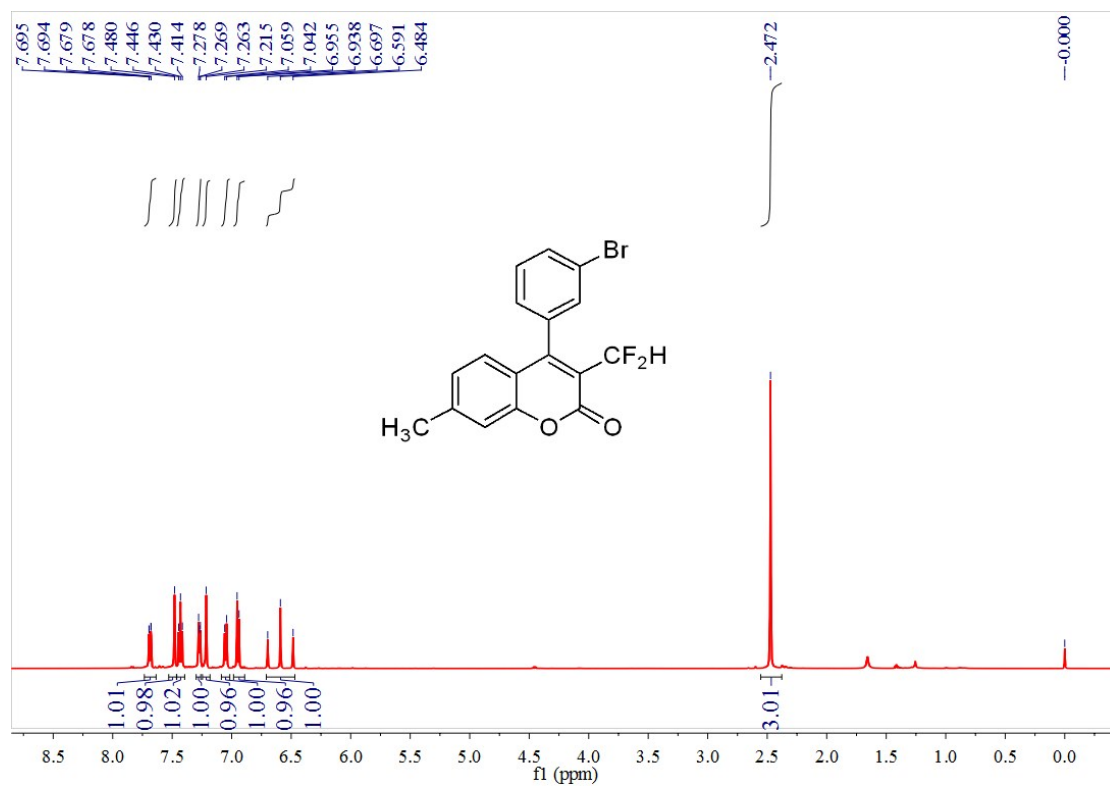


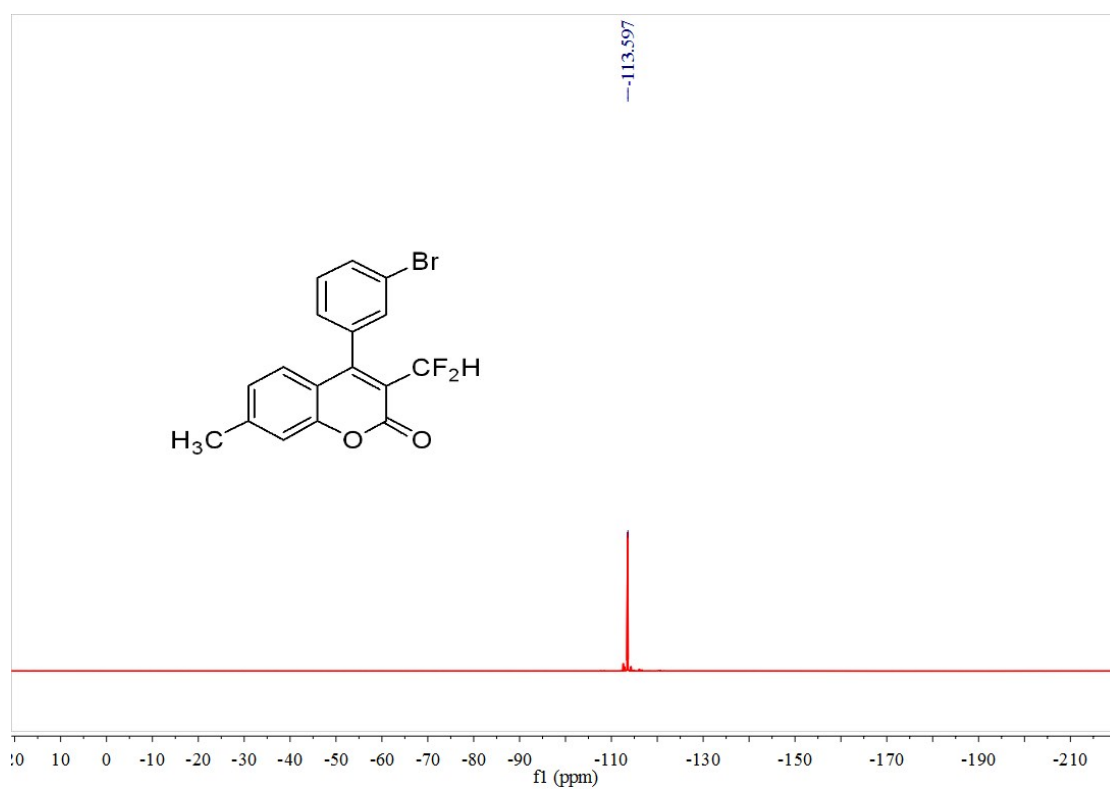
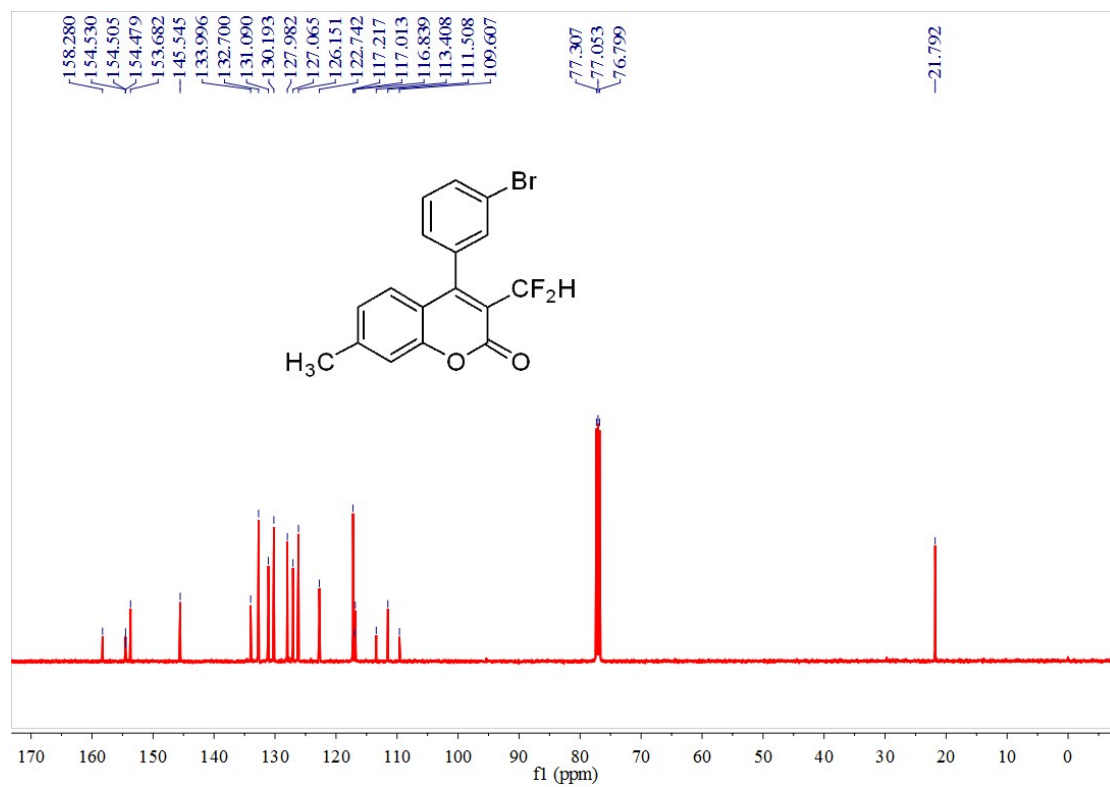
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3x**:





^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3y**:





^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of compound **3z**:

