Supporting Information

Transition-Metal-Free Visible-Light Photoredox Catalysis at Room-Temperature for Decarboxylative Fluorination of Aliphatic Carboxylic Acids by Organic Dyes

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A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H-NMR) spectra and carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane or referenced to residual solvent. ^{19}F-NMR spectra were recorded on a Bruker AV-400 spectrometer (376 MHz). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). High resolution mass spectrometry (ESI) were carried out using a Waters Quatro Macro triple quadrupole mass spectrometer Mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. Melting points were measured on a XT3A apparatus.

Starting Materials. All reactions were performed under nitrogen atmosphere in Schlenk-tube unless otherwise noted. Distilled water was sparged with nitrogen and used in the photoredox reactions. All other solvents, including those for NMR analysis, were used without further purification. All chemicals were purchased from commercial sources and used as received. **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1j**, **1k**, **1l** were prepared following the literature procedures.[1] **1r**, **1x** were prepared following the literature procedures.[2] **1u**, **1v**, **1w** were prepared following the literature procedures.[3]

References

[1] C. Tie, J. C. Gallucci, J. R. Parquette, *J. Am. Chem. Soc.* **2006** *128*, 1162-1171.

[2] L. R. Jefferies, S. P. Cook, *Org. Lett.* ***2014****, 16,* 2026-2029.

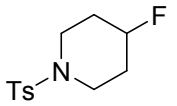
[3] M. R. Becerril, O. Mahé, M. Drouin, M. B. Majewski, J. G. West, M. O. Wolf, G. M. Sammis, J.-F. Paquin, *J. Am. Chem. Soc.* **2014**, *136*, 2637-2641.

B: Synthesis and Characterizations of Products.

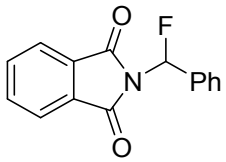
Typical Procedure for Transition-Metal-Free, Room-Temperature, Decarboxylative Fluorination of Aliphatic Carboxylic Acids through Visible-Light Photoredox Catalysis. Aliphatic carboxylic acids (**1**, 0.4 mmol, 1.0 equiv), Cs_2CO_3 (130.3 mg, 0.4 mmol, 1.0 equiv), 9-mesityl-10-methylacridinium perchlorate or Riboflavin (0.02 mmol, 0.05 equiv) and Selectfluor (283.4 mg, 0.8 mmol, 2.0 equiv) were placed in a Schlenk-tube. The reaction vessel was evacuated and filled with nitrogen. A 1:1 mixture of H_2O:CH_3CN (3.0 mL) degassed with N_2 was then added. The reaction mixture was irradiated with a 23 W CFL (at approximately 5 cm from the light source) at room temperature. Upon completion of the reaction, the resulting mixture was extracted with dichloromethane (20 mL × 3). The combined organics were died over anhydrous Na_2SO_4, filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography on silica gel

with petroleum/ethyl acetate (15:1, v:v) as the eluent to give the corresponding product.

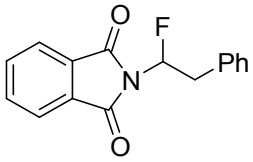
Characterization of Fluorinated Products:



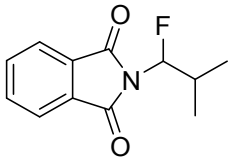
4-fluoro-1-tosylpiperidine (2a). White solid, mp 121-123 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.82-4.66 (m, 1H), 3.35-3.30 (m, 2H), 2.91-2.85 (m, 2H), 2.44 (s, 3H), 1.98-1.84 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 133.1, 129.7, 127.7, 86.3 (d, *J* = 170.0 Hz), 41.8, 41.7, 30.6, 30.4, 21.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -185.5 (s, 1F); HRMS (EI) calcd for $C_{12}H_{16}FNO_2S$ $(M)^+$ 257.0886, found 257.0891.



2-(fluoro(phenyl)methyl)isoindoline-1,3-dione (2b). White solid, mp 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.86 (m, 2H), 7.79-7.75 (m, 2H), 7.52-7.50 (m, 2H), 7.43-7.36 (m, 3H), 7.22 (d, *J* = 46.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.2, 134.8, 131.6, 129.1, 128.4, 125.4, 125.3, 124.0, 88.4 (d, *J* = 204.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -156.5 (d, *J* = 46.6 Hz, 1F); HRMS (EI) calcd for $C_{15}H_{10}FNO_2$ $(M)^+$ 255.0696, found 255.0698.

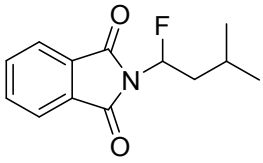


2-(1-fluoro-2-phenylethyl)isoindoline-1,3-dione (2c). White solid, mp 93-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.32 (m, 2H), 7.65-7.61 (m, 2H), 7.19-7.10 (m, 5H), 6.34-6.19 (m, 1H), 3.75-3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 133.8, 133.7, 133.6, 130.3, 128.2, 127.7, 126.2, 122.8, 89.3 (d, *J* = 203.0 Hz), 36.4 (d, *J* = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -144.9 (s, 1F); HRMS (EI) calcd for $C_{16}H_{12}FNO_2$ $(M)^+$ 269.0852, found 269.0851.

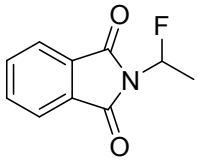


2-(1-fluoro-2-methylpropyl)isoindoline-1,3-dione (2d). White solid, mp 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.82 (m, 2H), 7.73-7.70 (m, 2H), 5.63 (dd, *J* =

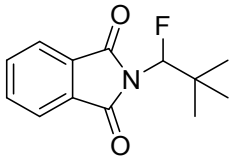
10.0, 37.2 Hz, 1H), 3.11-3.03 (m, 1H), 1.11 (d, J = 6.4 Hz, 3H), 0.77 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9 (d, J = 1.0 Hz), 134.7, 131.4, 123.9, 95.0 (d, J = 203.0 Hz), 29.2 (d, J = 24.0 Hz), 18.9 (d, J = 1.0 Hz), 17.4 (d, J = 7.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -150.5 (s, 1F); HRMS (EI) calcd for $C_{12}H_{12}FNO_2$ $(M)^+$ 221.0852, found 221.0854.



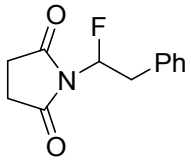
2-(1-fluoro-3-methylbutyl)isoindoline-1,3-dione (2e). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.82 (m, 2H), 7.72-7.70 (m, 2H), 6.16 (dt, J = 14.4, 48.0 Hz, 1H), 2.40-2.30 (m, 1H), 2.17-2.04 (m, 1H), 1.73-1.60 (m, 1H), 0.91 (dd, J = 2.0, 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (d, J = 1.0 Hz), 133.7, 130.5, 122.9, 88.3 (d, J = 199.0 Hz), 38.7, 38.5, 23.8 (d, J = 5.0 Hz), 21.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.6 (m, 1F); HRMS (EI) calcd for $C_{13}H_{14}FNO_2$ $(M)^+$ 235.1009, found 235.1008.



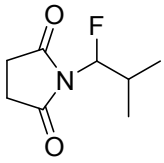
2-(1-fluoroethyl)isoindoline-1,3-dione (2f). White solid, mp 129-131 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (m, 2H), 7.81-7.77 (m, 2H), 6.44-6.27 (m, 1H), 2.00 (dd, J = 16.0, 20.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (d, J = 1.0 Hz), 134.7, 131.5, 123.9, 87.1 (d, J = 197.0 Hz), 18.1 (d, J = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -139.8 (s, 1F); HRMS (EI) calcd for $C_{10}H_8FNO_2$ $(M)^+$ 193.0539, found 193.0541.



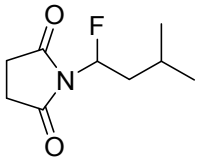
2-(1-fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (2g). White solid, mp 78-80 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 2H), 7.81-7.77 (m, 2H), 5.82 (d, J = 43.2 Hz, 1H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 133.5, 130.5, 122.7, 97.3 (d, J = 210.0 Hz), 36.1 (d, J = 24.0 Hz), 24.6 (d, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -173.0 (s, 1F); HRMS (EI) calcd for $C_{13}H_{14}FNO_2$ $(M)^+$ 235.1009, found 235.1008.



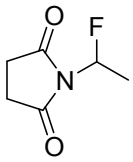
1-(1-fluoro-2-phenylethyl)pyrrolidine-2,5-dione (2h). White solid, mp 110-112 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 2H), 7.17-7.12 (m, 3H), 6.08 (dt, J = 8.0, 48.0 Hz, 1H), 3.64-3.56 (m, 1H), 3.51-3.40 (m, 1H), 2.57-2.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 134.5 (d, J = 7.0 Hz), 129.2, 128.8, 127.4, 90.7 (d, J = 203.0 Hz), 36.7 (d, J = 26 Hz), 27.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ -151.6 (s, 1F); HRMS (EI) calcd for $C_{12}H_{12}FNO_2$ $(M)^+$ 221.0852, found 221.0855.



1-(1-fluoro-2-methylpropyl)pyrrolidine-2,5-dione (2i). White solid, mp 50-51 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.52 (dd, J = 8.0, 48.0 Hz, 1H), 3.06-2.95 (m, 1H), 2.76(s, 4H), 1.13 (d, J = 6.8 Hz, 3H), 0.78 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 95.3 (d, J = 203.0 Hz), 28.5, 28.3, 27.92, 18.6 (d, J = 2.0 Hz), 17.1 (d, J = 7.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -156.4 (dd, J = 7.5, 45.1 Hz, 1F); HRMS (EI) calcd for $C_8H_{12}FNO_2$ $(M)^+$ 173.0852, found 173.0850.

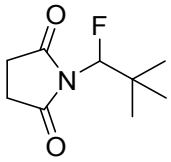


1-(1-fluoro-3-methylbutyl)pyrrolidine-2,5-dione (2j). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13-5.98 (m, 1H), 2.74 (s, 4H), 2.42-2.32 (m, 1H), 2.01-1.89 (m, 1H), 1.74-1.64 (m, 1H), 0.97 (dd, J = 24.0, 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 89.8 (d, J = 199.0 Hz), 39.1, 38.9, 28.0, 24.7 (d, J = 5.0 Hz), 22.4, 22.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -153.1 (s, 1F); HRMS (EI) calcd for $C_9H_{14}FNO_2$ $(M)^+$ 187.1009, found 187.1004.

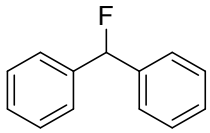


1-(1-fluoroethyl)pyrrolidine-2,5-dione (2k). White solid, mp 55-56 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24-6.09 (m, 1H), 2.74 (s, 4H), 1.87 (dd, J = 6.4, 20.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.7, 87.6 (d, J = 197.0 Hz), 28.0, 17.4 (d, J = 27.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.4 (m, 1F); HRMS (EI) calcd for $C_6H_8FNO_2$

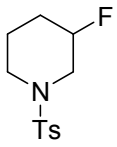
$(M)^+$ 145.0539, found 145.0540.



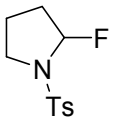
1-(1-fluoro-2,2-dimethylpropyl)pyrrolidine-2,5-dione (2l). White solid, mp 95-96 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 5.72 (d, J = 43.2 Hz, 1H), 2.78-2.73 (m, 4H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 98.3 (d, J = 210.0 Hz), 37.1 (d, J = 23.0 Hz), 28.2, 25.5 (d, J = 4.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.5 (s, 1F); HRMS (EI) calcd for $C_9H_{14}FNO_2$ $(M)^+$ 187.1009, found 187.1011.



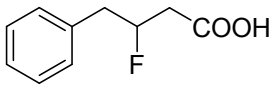
(fluoromethylene)dibenzene (2m). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 10H), 6.46 (d, J= 47.6 Hz, 1H); ^{19}F NMR (376 MHz, $CDCl_3$): δ -166.7 (d, J = 48.9 Hz, 1F); HRMS (EI) calcd for $C_{13}H_{11}F$ $(M)^+$ 186.0845, found 186.0844.



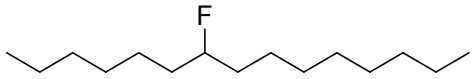
3-fluoro-1-tosylpiperidine (2n). White solid, mp 101-103 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 14.0 Hz, 2H), 4.75-4.59 (m, 1H), 3.37-3.28 (m, 1H), 3.09-3.00 (m, 2H), 2.95-2.89 (m, 1H), 2.44 (s, 3H), 1.88-1.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 133.3, 129.8, 127.6, 86.1 (d, J = 176.0 Hz), 49.7 (d, J = 26.0 Hz), 45.8, 29.3 (d, J = 20.0 Hz), 21.6, 21.1 (d, J = 7.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -182.8 (m, 1F); HRMS (EI) calcd for $C_{12}H_{16}FNO_2S$ $(M)^+$ 257.0886, found 257.0889.



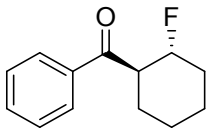
2-fluoro-1-tosylpyrrolidine (2o). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.78 (d, J = 5.2 Hz, 1H), 3.51-3.47 (m, 1H), 3.05-2.98 (m, 1H), 2.43 (s, 3H), 2.05-1.89 (m, 2H), 1.74-1.67 (m, 1H), 1.48-1.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 135.4, 129.8, 127.4, 89.2, 47.9, 33.7, 23.1, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ -188.2 (s, 1F); HRMS (EI) calcd for $C_{11}H_{14}FNO_2S$ $(M)^+$ 243.0729, found 243.0730.



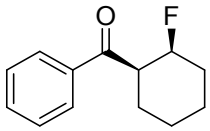
3-fluoro-4-phenylbutanoic acid (2p). White solid. mp 58-60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.26-7.22 (m, 2H), 7.20-7.13 (m, 3H), 5.16-4.98 (m, 1H), 3.02-2.83 (m, 2H), 2.68-2.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 135.8 (d, J = 5.0 Hz), 129.5, 128.7, 127.0, 90.1 (d, J = 173.0 Hz), 40.9 (d, J = 21.0 Hz), 39.3 (d, J = 24.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -177.8 (s, 1F); HRMS (EI) calcd for $C_{10}H_{11}FO_2$ $(M)^+$ 182.0743, found 182.0746.



7-fluoropentadecane (2q). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.48-4.30 (m, 1H), 1.58-1.36 (m, 5H), 1.28-1.16 (m, 20H), 0.83-0.79 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 94.63 (d, J = 166.0 Hz), 35.19 (d, J = 21.0 Hz), 31.82 (d, J = 11.0 Hz), 29.72, 29.68, 29.54, 29.52, 29.38, 29.26, 29.20, 29.17, 29.13, 25.09, 22.64 (d, J = 8.0 Hz), 14.09 (d, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -179.9 (s, 1F); HRMS (EI) calcd for $C_{15}H_{31}F$ $(M)^+$ 230.2410, found 230.2411.

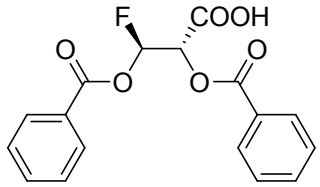


(*trans*-2-fluorocyclohexyl)(phenyl)methanone (2r). White solid, mp 97-98 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.93 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 5.03-4.85 (m, 1H), 3.60-3.52 (m, 1H), 2.29-2.23 (m, 1H), 2.00-1.94 (m, 2H), 1.76-1.72 (m, 1H), 1.66-1.53 (m, 1H), 1.49-1.24 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.3, 136.8, 133.2, 128.6, 128.4, 92.4 (d, J = 172.3 Hz), 50.8 (d, J = 18.9 Hz), 31.8 (d, J = 18.1 Hz), 29.0 (d, J = 7.9 Hz), 24.6 (d, J = 2.0 Hz), 23.7 (d, J = 5.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -171.0 (s, 1F); HRMS (EI) calcd for $C_{13}H_{15}FO$ $(M)^+$ 206.1107, found 206.1108.

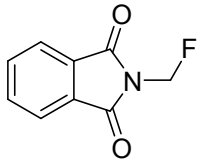


(*cis*-2-fluorocyclohexyl)(phenyl)methanone (2r'). White solid, mp 103-104 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.86 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.45 (m, 2H), 5.18-5.05 (m, 1H), 3.48-3.45 (m, 1H), 2.17-2.01 (m, 2H), 2.92-1.87 (m, 1H), 1.80-1.72 (m, 1H), 1.73-1.54 (m, 3H), 1.46-1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 136.3, 132.8, 128.7, 128.1, 89.2 (d, J = 175.0 Hz), 48.8 (d, J = 21.0 Hz), 31.0

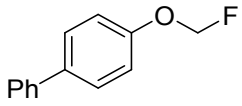
(d, J = 21.0 Hz), 24.3, 22.2 (d, J = 2.0 Hz), 19.9 (d, J = 1.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -193.3 (s, 1F); HRMS (EI) calcd for $C_{13}H_{15}FO$ $(M)^+$ 206.1107, found 206.1108.



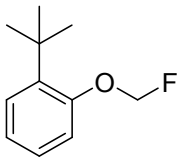
2,3-bis(benzoyloxy)-3-fluoropropanoic acid (2s). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 8.16-7.95 (m, 4H), 7.68-7.58 (m, 2H), 7.50-7.41 (m, 4H), 7.12-6.97 (m, 1H), 5.80-5.76 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 163.8, 163.7, 134.4 (d, J = 4.4 Hz), 134.1 (J = 2.7 Hz), 130.4, 130.3, 130.25, 130.2, 128.9, 128.8, 128.7, 128.5, 127.8 (d, J = 5.6 Hz), 99.5, 71.3 (d, J = 25.9); ^{19}F NMR (376 MHz, $CDCl_3$): δ -139.3 (d, J = 383.5 Hz, 1F); HRMS (ESI) calcd for $C_{17}H_{13}FO_6Na$ $[M+Na]^+$ 355.0594, found 355.0600.



2-(fluoromethyl)isoindoline-1,3-dione (2t). White solid, mp 93-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.77-7.73 (m, 2H), 5.70 (d, J = 52.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.5 (d, J = 3.0 Hz), 134.9, 131.6, 124.2, 74.9 (d, J = 197.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.2 (t, J = 52.6 Hz, 1F); HRMS (EI) calcd for $C_9H_6FNO_2$ $(M)^+$ 179.0383, found 179.0384.

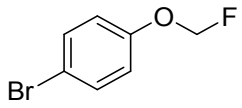


4-(fluoromethoxy)-1,1'-biphenyl (2u). White solid, mp 68-69 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (m, 4H), 7.37-7.36 (m, 2H), 7.27-7.23 (m, 1H), 7.09-7.06 (m, 2H), 5.66 (d, J = 54.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2 (d, J = 3.0 Hz), 139.3, 135.6, 127.7, 127.3, 126.1, 125.8, 115.8 (d, J = 1.2 Hz), 99.7 (d, J = 217.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -148.4 (s, 1F); HRMS (EI) calcd for $C_{13}H_{11}FO$ $(M)^+$ 202.0794, found 202.0795.

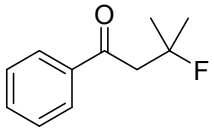


1-tert-butyl-2-(fluoromethoxy)benzene (2v). Colorless oil; ^{1}H NMR (400 MHz,

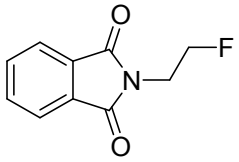
$CDCl_3$): δ 7.32 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.22-7.18 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.05-7.10 (m, 1H), 5.76 (d, *J* = 54.4 Hz, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1 (d, *J* = 3.5 Hz), 139.0 (d, *J* = 2.7 Hz), 127.5, 127.0, 123.2, 115.5 (d, *J* = 1.3 Hz), 100.8 (d, *J* = 216.2), 34.8, 30.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -146.7 (s, 1F); HRMS (EI) calcd for $C_{11}H_{15}FO$ $(M)^+$ 182.1107, found 182.1108.



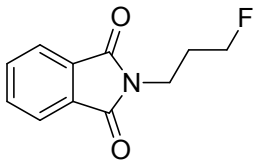
1-bromo-4-(fluoromethoxy)benzene (2w). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.42 (m, 2H), 6.97-6.92 (m, 2H), 5.68 (d, *J* = 54.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9 (d, *J* = 3.0 Hz), 132.6, 118.5 (d, *J* = 1.0 Hz), 116.1, 100.7 (d, *J* = 218.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -149.1 (t, *J* = 52.6 Hz, 1F); HRMS (EI) calcd for C_7H_6BrFO $(M)^+$ 203.9586, found 203.9585.



3-fluoro-3-methyl-1-phenylbutan-1-one (2x). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.87 (m, 2H), 7.50-7.46 (m, 1H), 7.40-7.36 (m, 2H), 3.24 (d, *J* = 15.6 Hz, 2H), 1.48 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2 (d, *J* = 9.0 Hz), 137.5 (d, *J* = 2.0 Hz), 133.3, 128.6, 128.5, 94.5 (d, *J* = 166.0 Hz), 49.0 (d, *J* = 24.0 Hz), 27.2, 26.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ -129.1 (m, 1F); HRMS (EI) calcd for $C_{11}H_{13}FO$ $(M)^+$ 180.0950, found 180.0951.

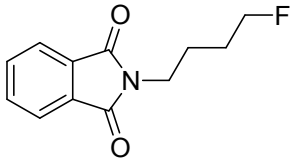


2-(2-fluoroethyl)isoindoline-1,3-dione (2ya). White solid, mp 99-100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.64 (dt, *J* = 46.9, 5.2 Hz, 2H), 4.02 (dt, *J* = 24.0, 5.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 134.1, 131.9, 123.4, 80.4 (d, *J* = 171.8 Hz), 38.2 (d, *J* = 21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -224.7 (m, 1F).

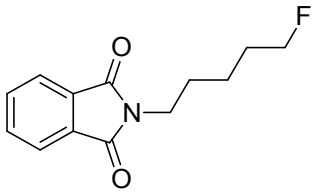


2-(3-fluoropropyl)isoindoline-1,3-dione (2yb). White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.48 (dt, *J* =

47.0, 5.7 Hz, 2H), 3.81 (t, *J* = 6.9 Hz, 2H), 2.18-1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 134.0, 132.0, 123.2, 81.6 (d, *J* = 165.8 Hz), 34.6 (d, *J* = 5.3 Hz), 29.4 (d, *J* = 19.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -220.8 (m, 1F).



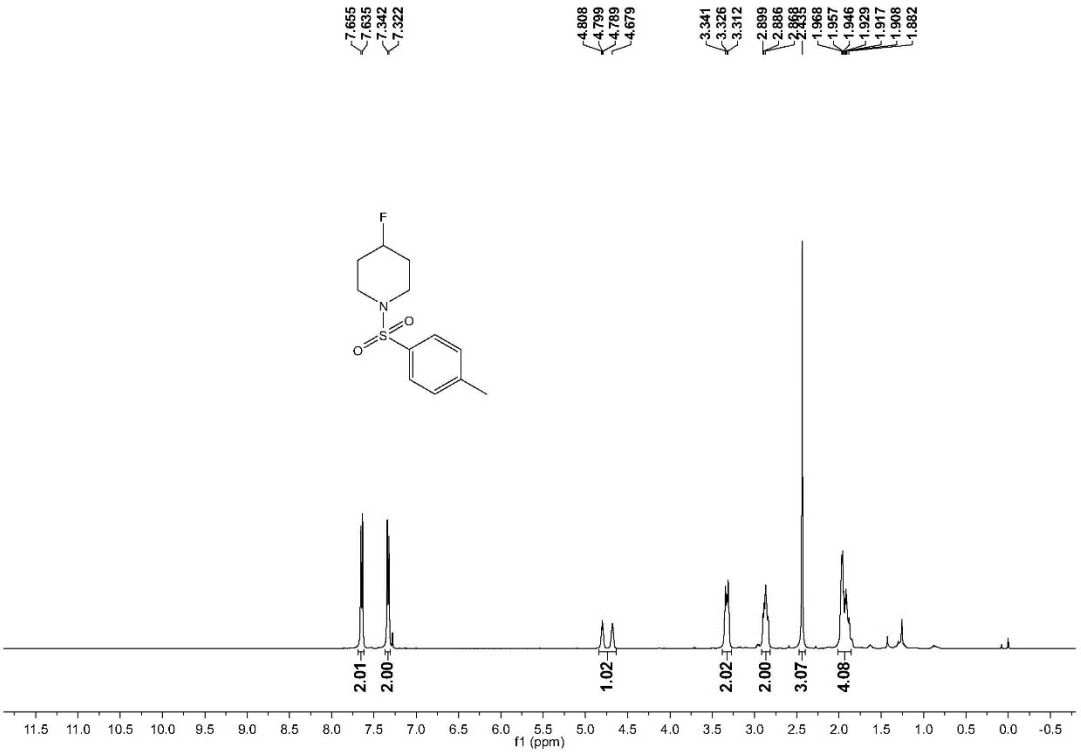
2-(4-fluorobutyl)isoindoline-1,3-dione (2yc). White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.44 (dt, *J* = 47.4, 5.7 Hz, 2H), 3.71 (t, *J* = 6.9 Hz, 2H), 1.82-1.65 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 133.9, 132.0, 123.2, 83.3 (d, *J* = 165.2 Hz), 37.4, 27.7 (d, *J* = 20.1 Hz), 24.6 (d, *J* = 4.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -218.9 (m, 1F).



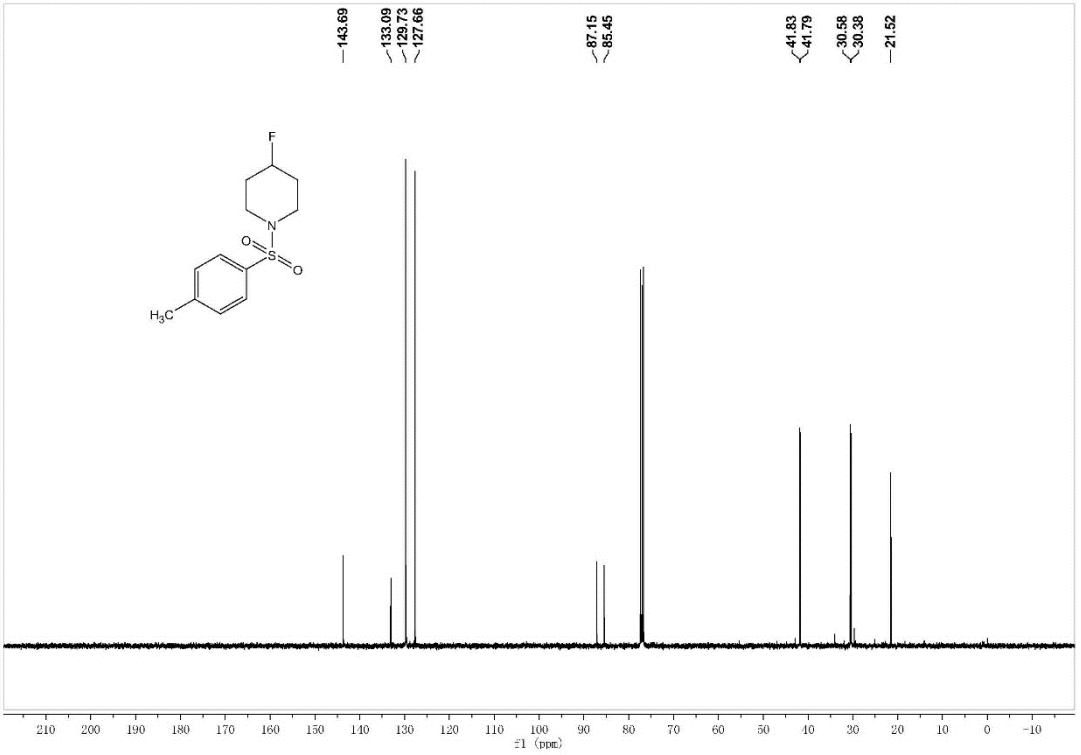
2-(5-fluoropentyl)isoindoline-1,3-dione (2yd). White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.67 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.39 (dt, *J* = 47.3, 6.0 Hz, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 1.80-1.61 (m, 4H), 1.43 (d, *J* = 7.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 133.9, 132.1, 123.1, 83.7 (d, *J* = 164.7 Hz), 37.7, 29.9 (d, *J* = 19.7 Hz), 28.2, 22.5 (d, *J* = 5.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -218.5 (m, 1F).

C: ^{1}H, ^{13}C and ^{19}F NMR Spectra of Products.

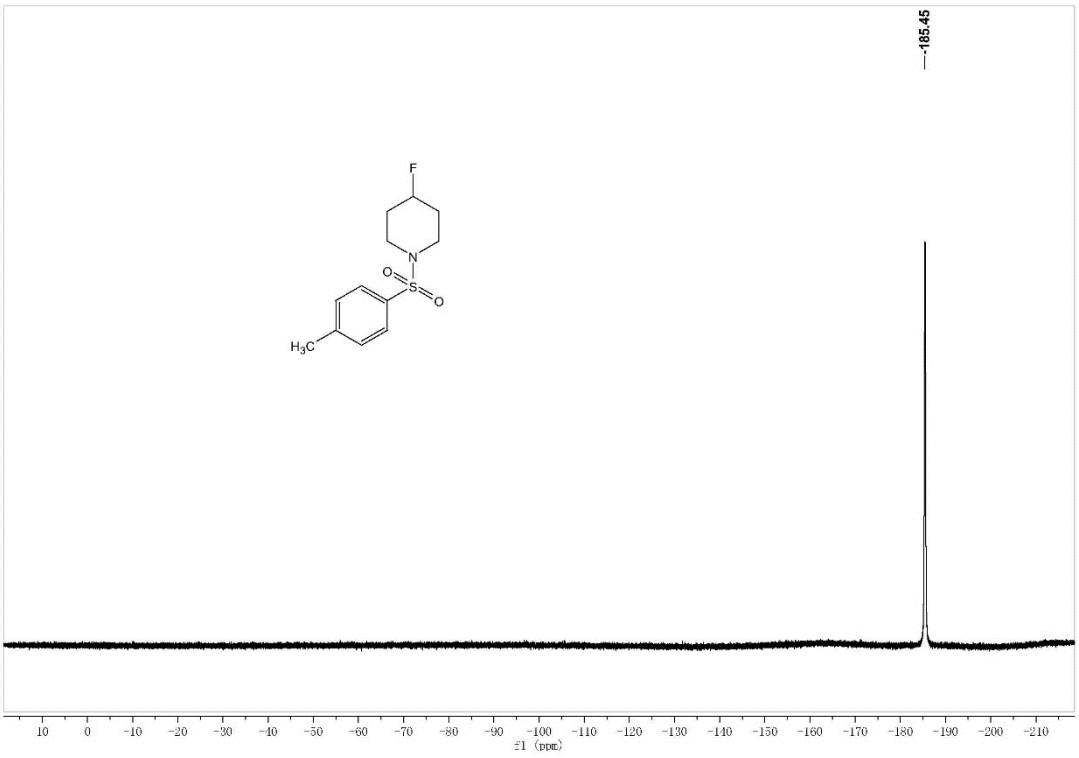
^{1}H NMR of 4-fluoro-1-tosylpiperidine (**2a**)



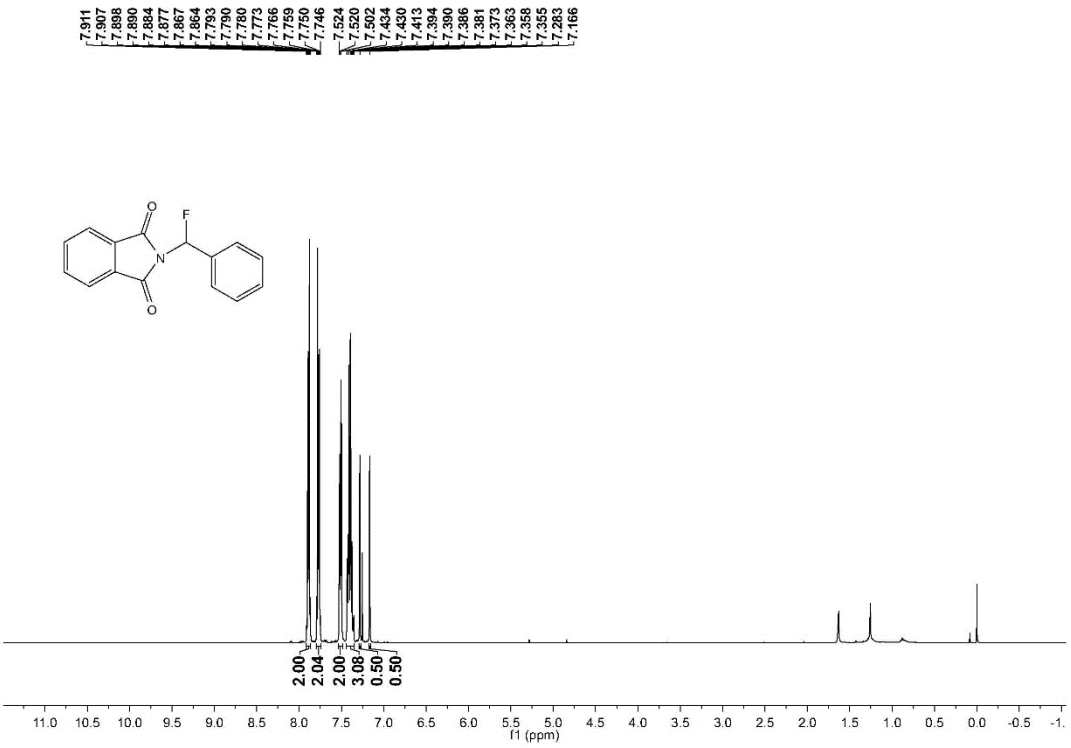
^{13}C NMR of 4-fluoro-1-tosylpiperidine (**2a**)



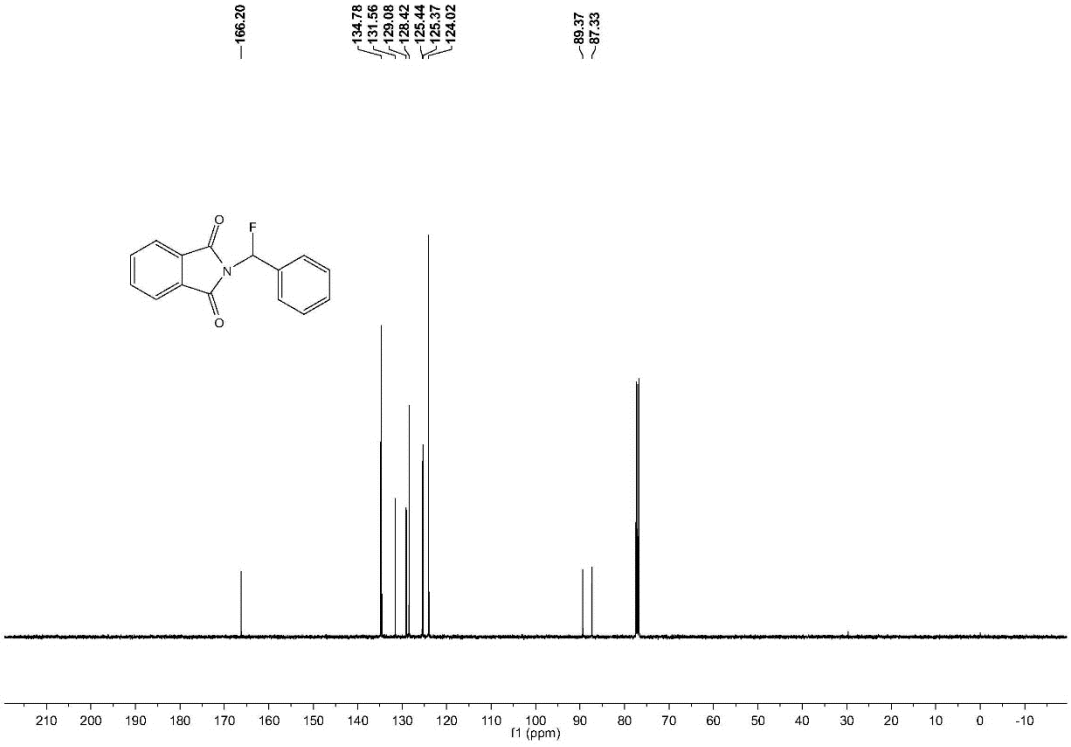
^{19}F NMR of 4-fluoro-1-tosylpiperidine (**2a**)



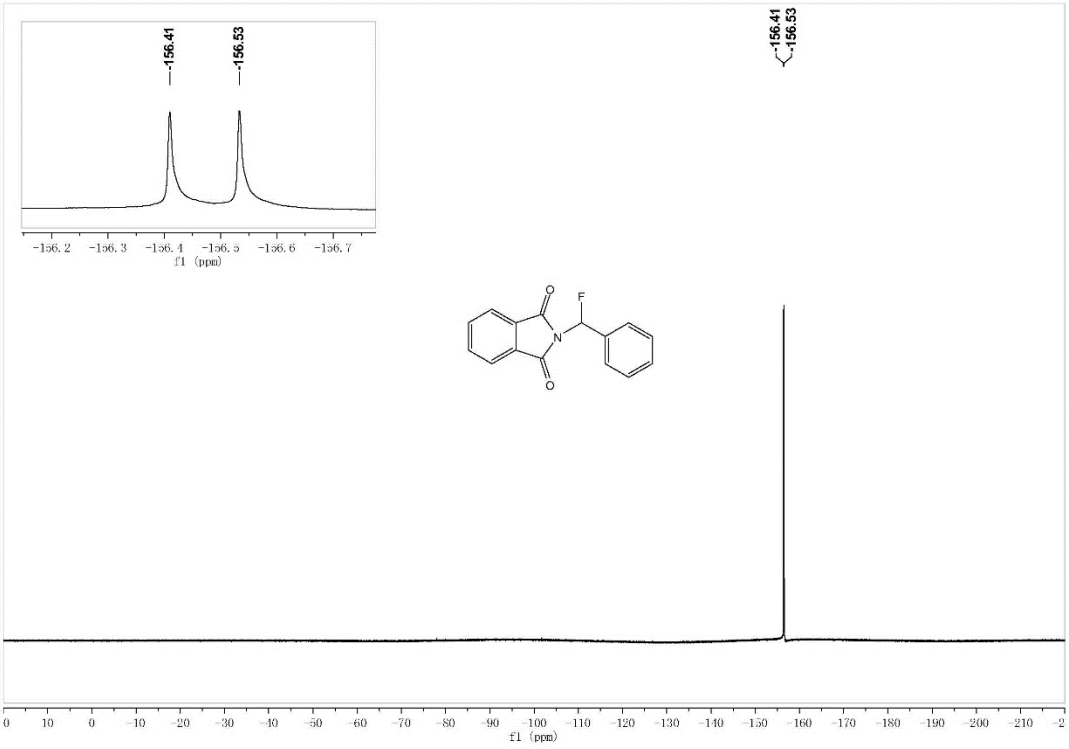
^{1}H NMR of 2-(fluoro(phenyl)methyl)isoindoline-1,3-dione (**2b**)



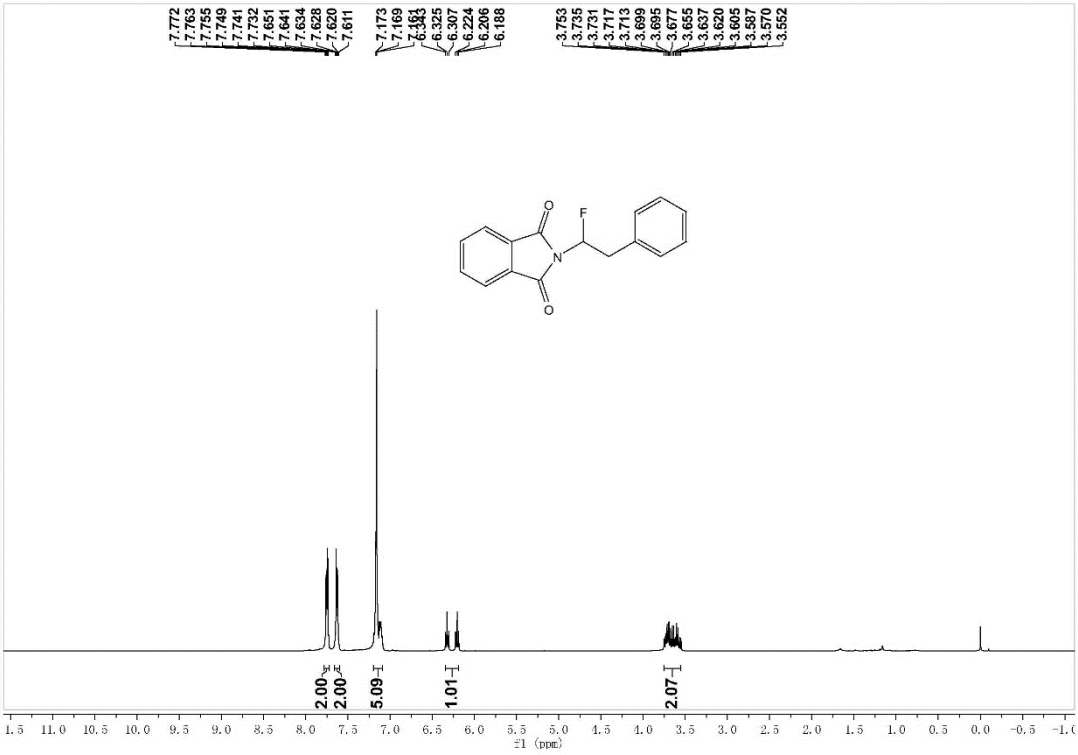
^{13}C NMR of 2-(fluoro(phenyl)methyl)isoindoline-1,3-dione (**2b**)



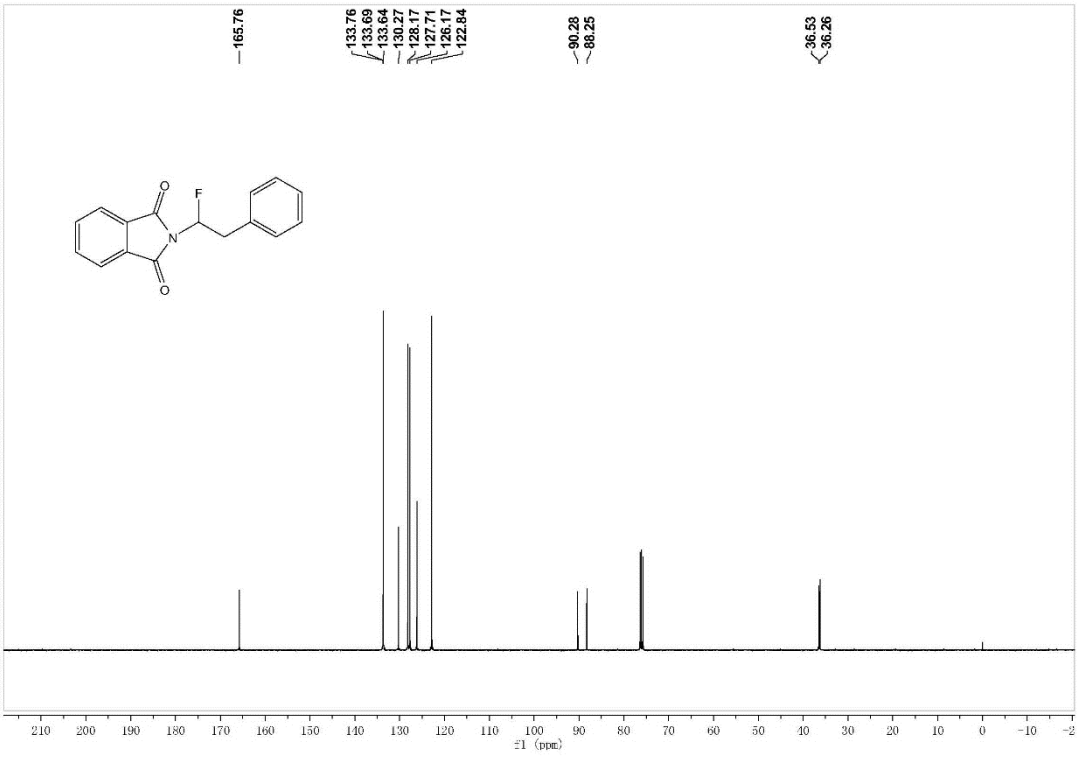
^{19}F NMR of 2-(fluoro(phenyl)methyl)isoindoline-1,3-dione (**2b**)



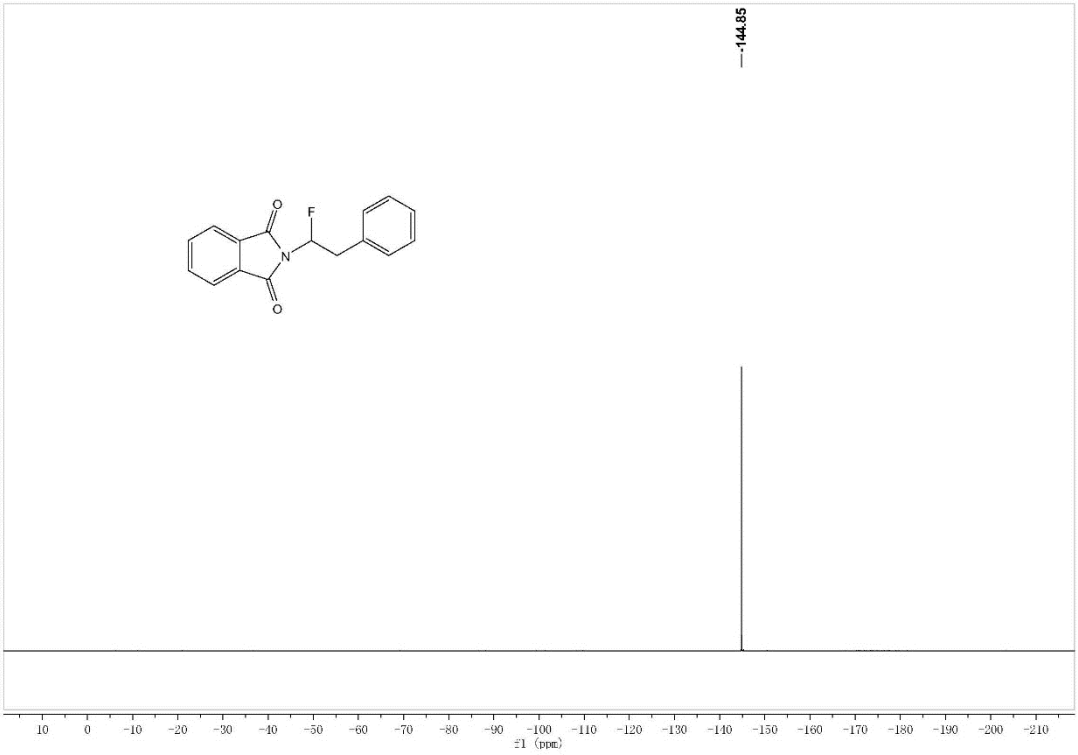
^{1}H NMR of 2-(1-fluoro-2-phenylethyl)isoindoline-1,3-dione (**2c**)



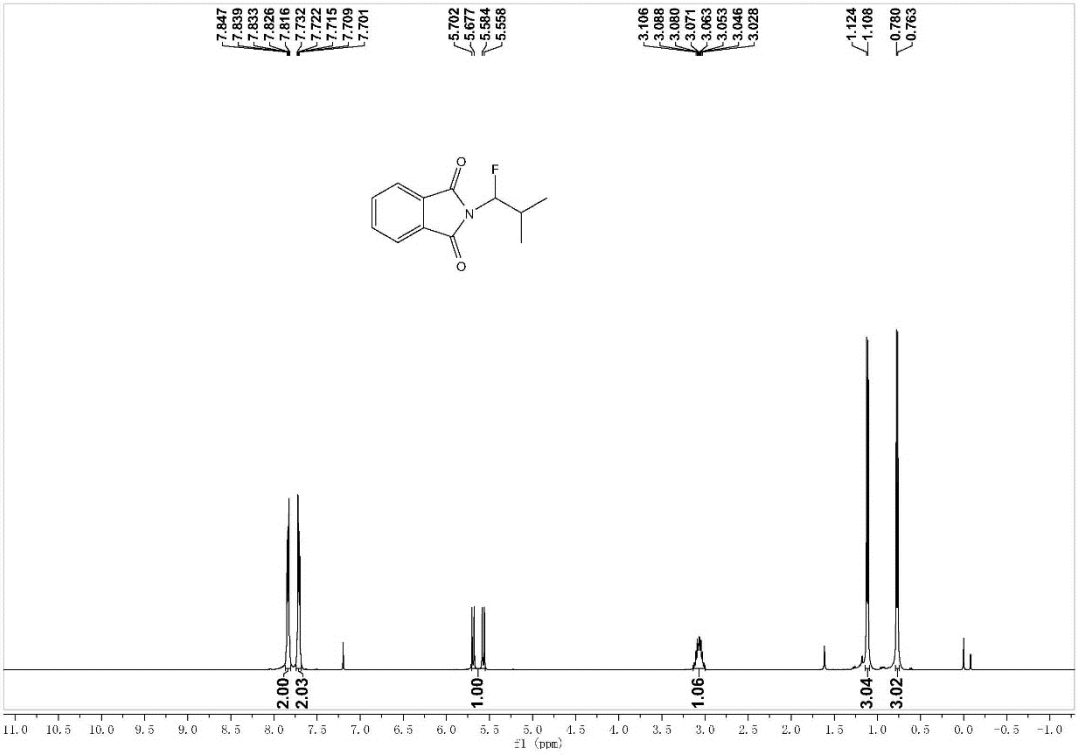
^{13}C NMR of 2-(1-fluoro-2-phenylethyl)isoindoline-1,3-dione (**2c**)



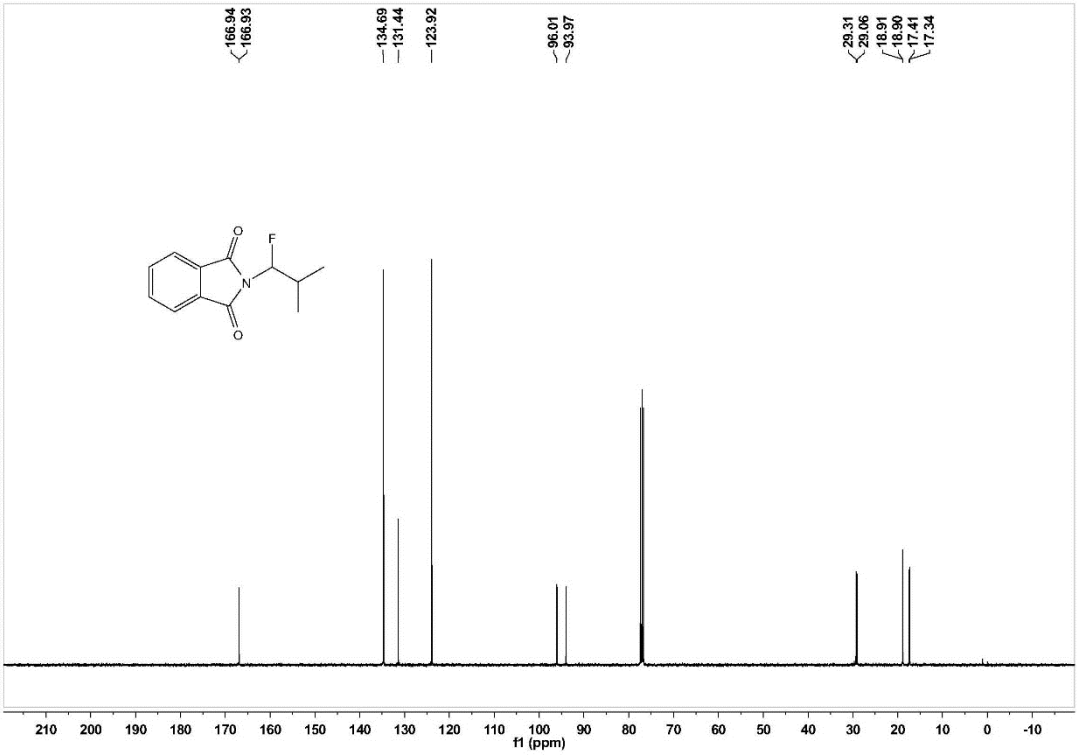
^{19}F NMR of 2-(1-fluoro-2-phenylethyl)isoindoline-1,3-dione (**2c**)



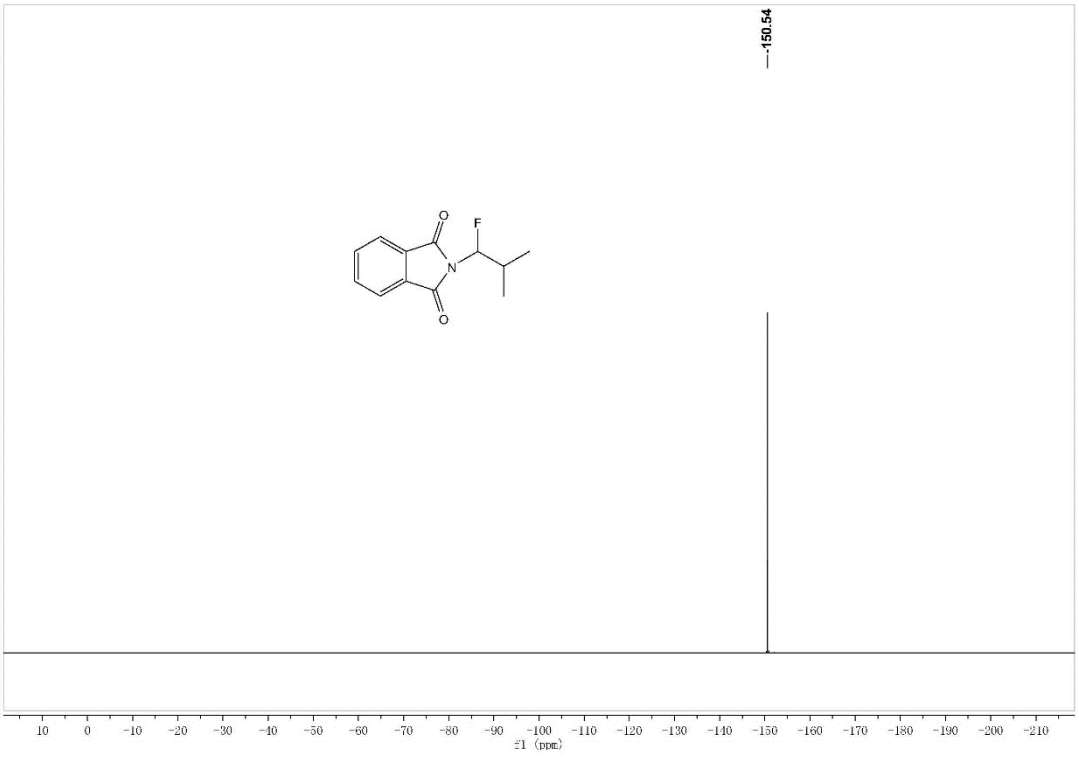
^{1}H NMR of 2-(1-fluoro-2-methylpropyl)isoindoline-1,3-dione (**2d**)



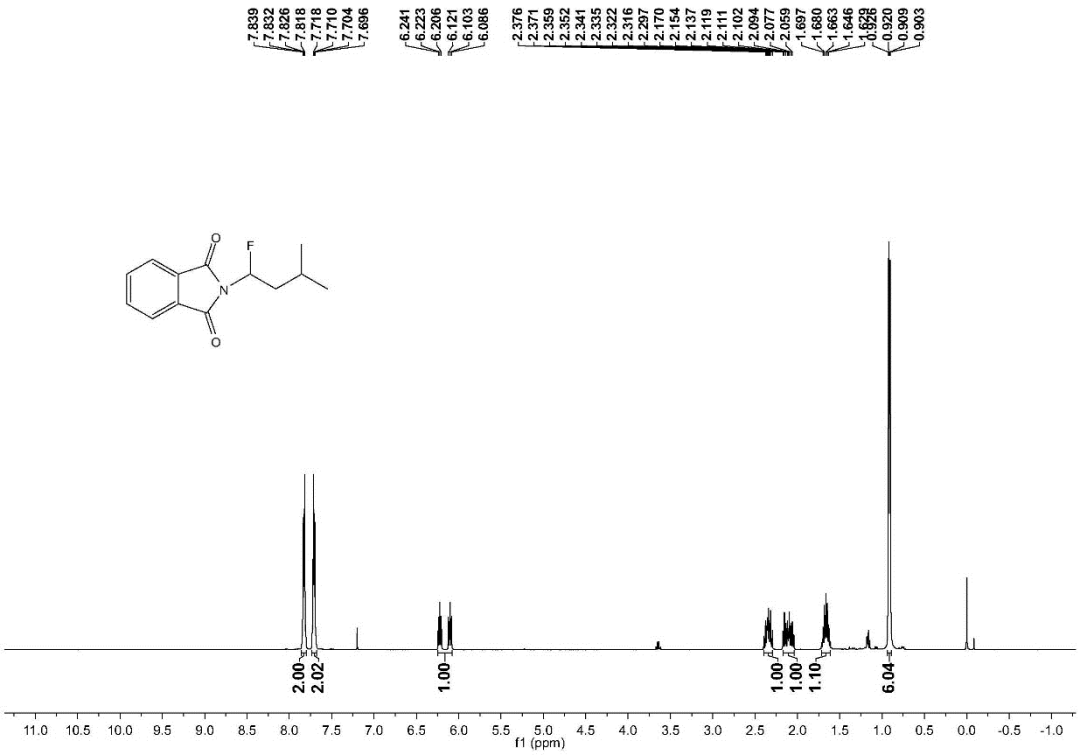
^{13}C NMR of 2-(1-fluoro-2-methylpropyl)isoindoline-1,3-dione (**2d**)



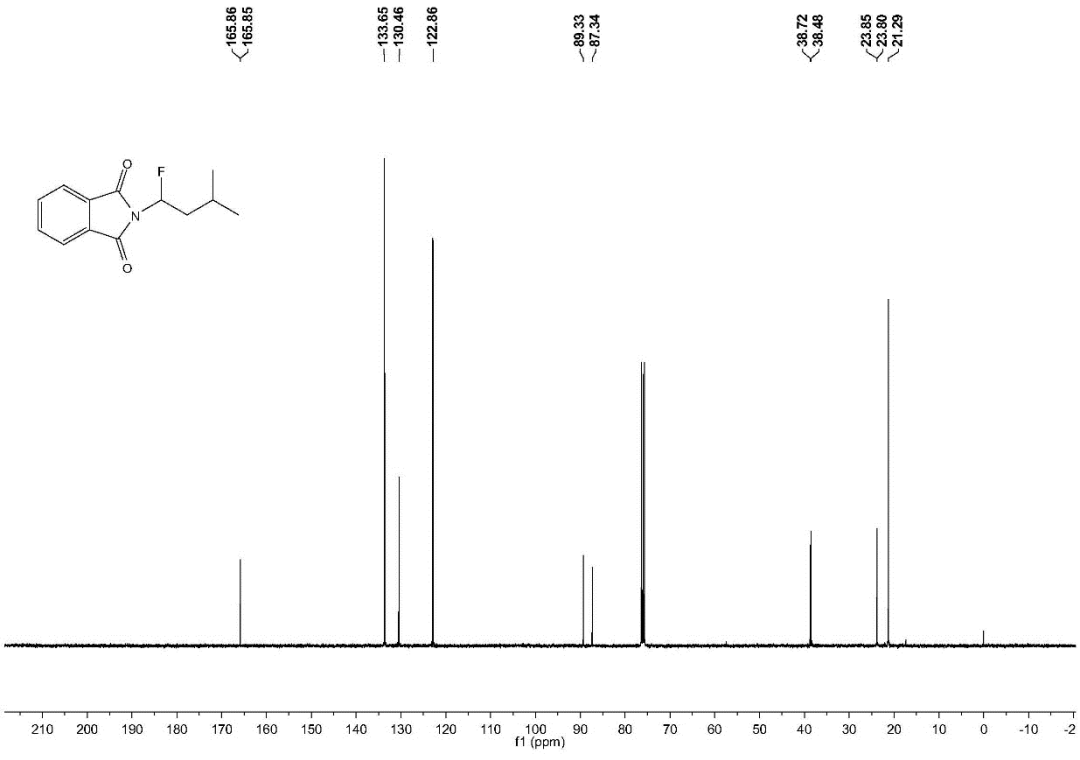
^{19}F NMR of 2-(1-fluoro-2-methylpropyl)isoindoline-1,3-dione (**2d**)



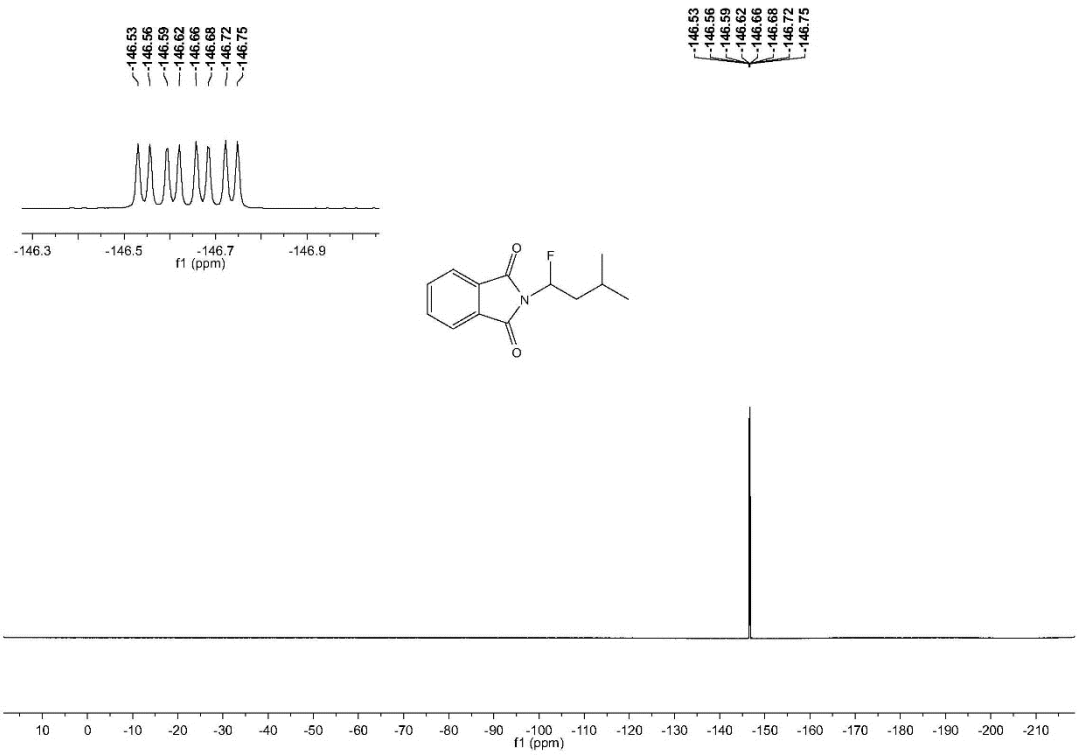
^{1}H NMR of 2-(1-fluoro-3-methylbutyl)isoindoline-1,3-dione (**2e**)



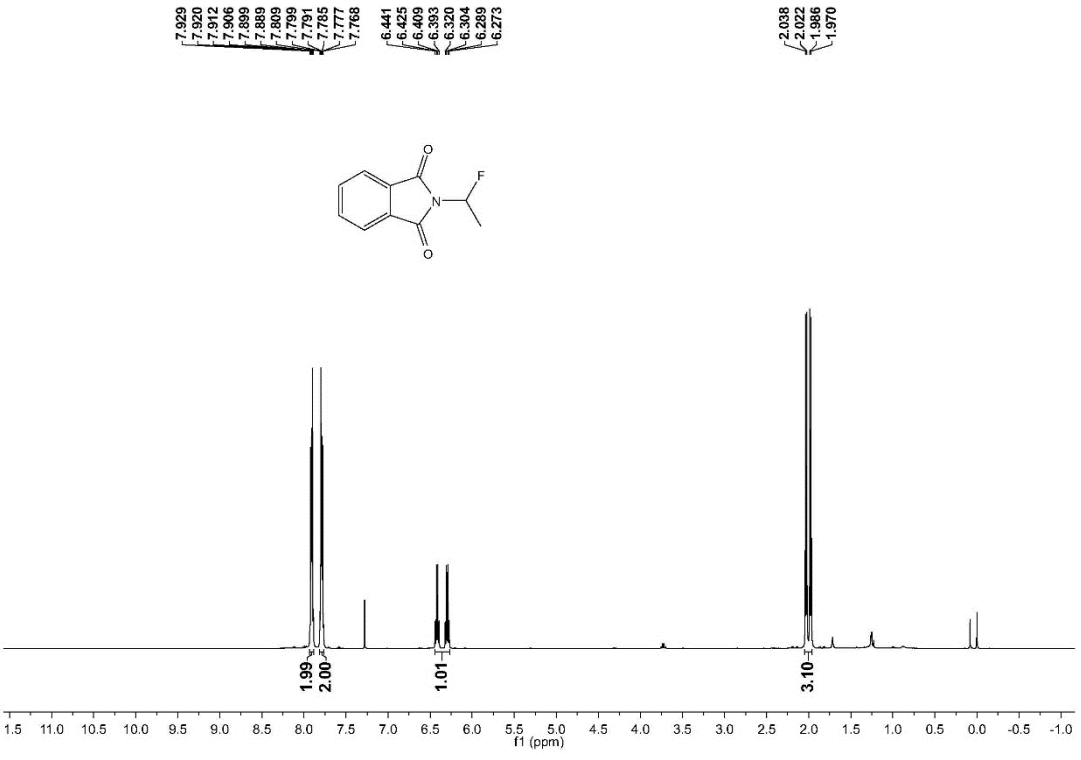
^{13}C NMR of 2-(1-fluoro-3-methylbutyl)isoindoline-1,3-dione (**2e**)



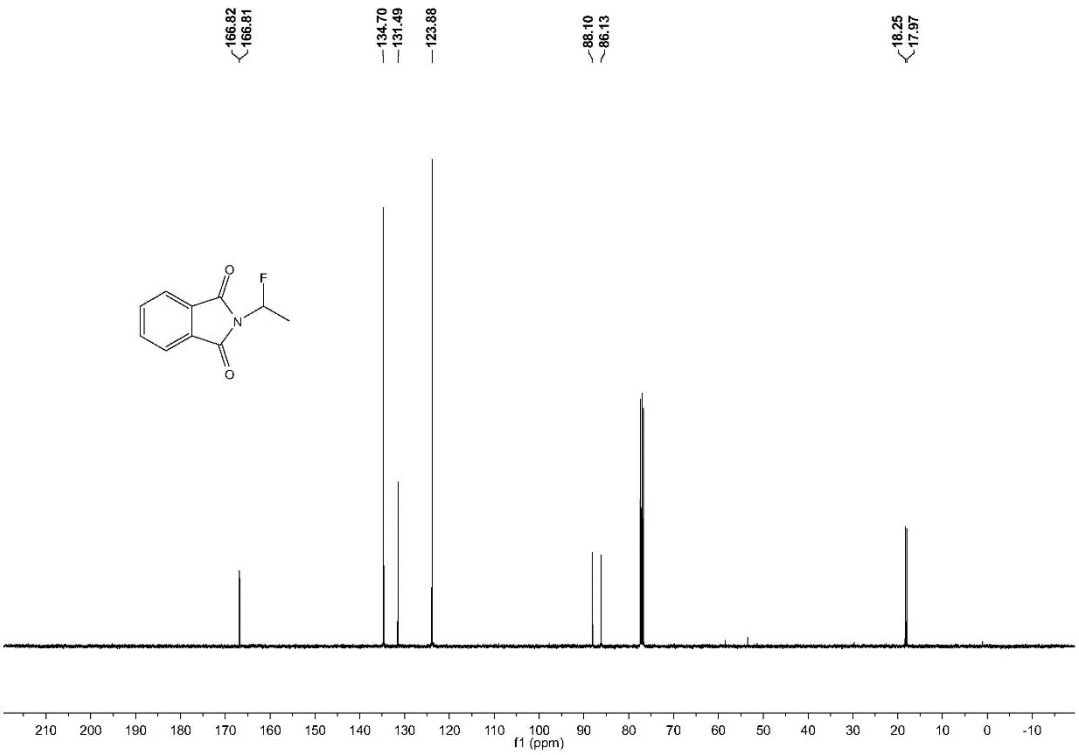
^{19}F NMR of 2-(1-fluoro-3-methylbutyl)isoindoline-1,3-dione (**2e**)



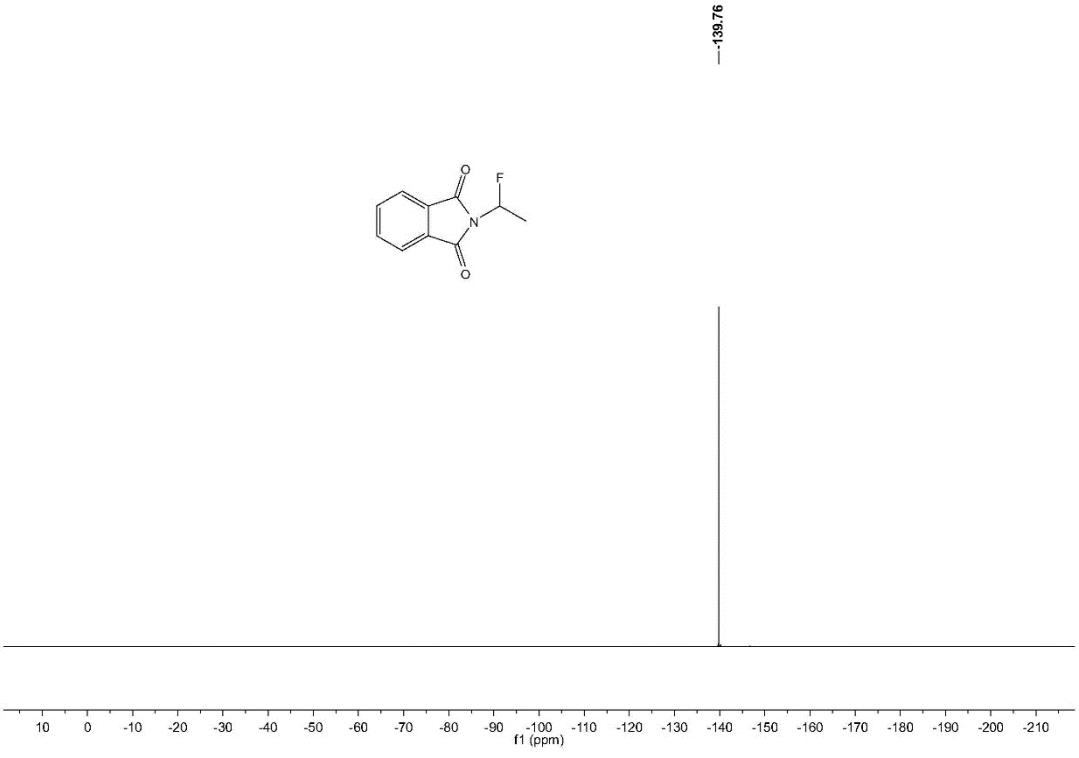
^{1}H NMR of 2-(1-fluoroethyl)isoindoline-1,3-dione (**2f**)



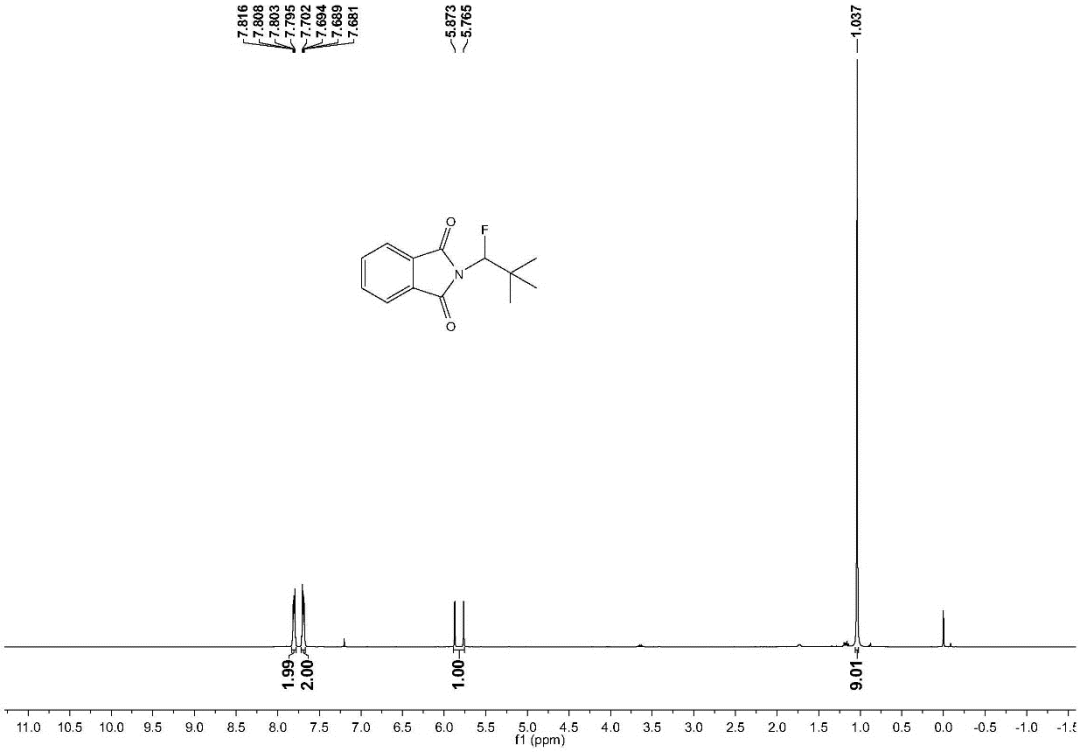
^{13}C NMR of 2-(1-fluoroethyl)isoindoline-1,3-dione (**2f**)



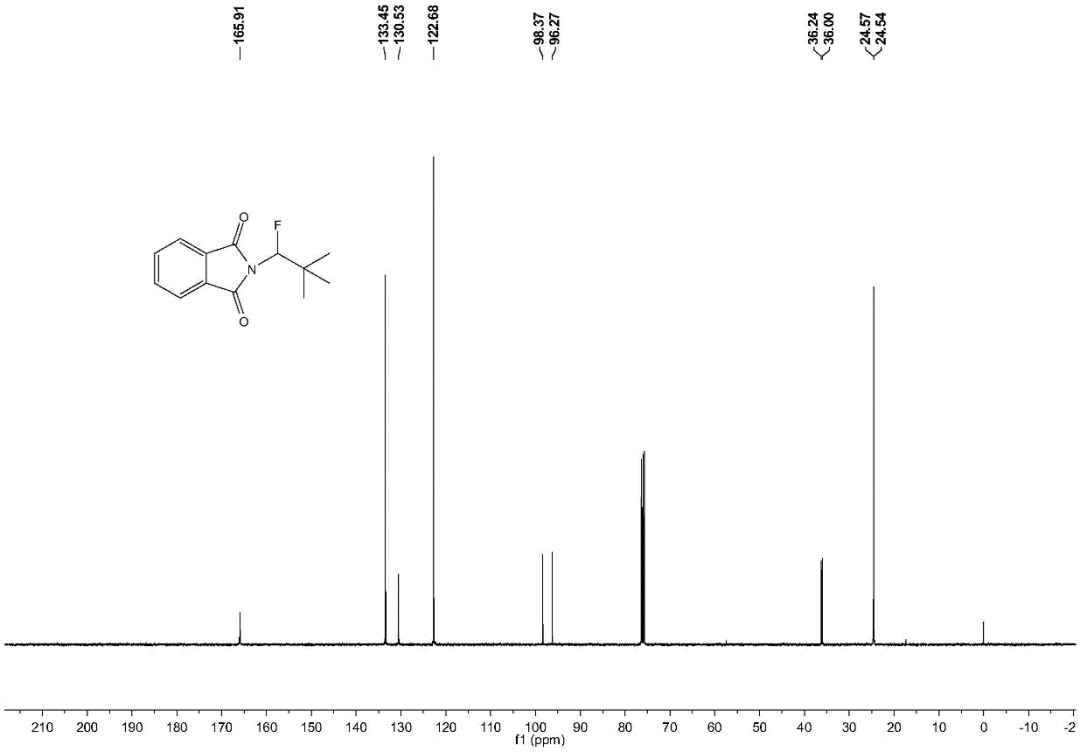
^{19}F NMR of 2-(1-fluoroethyl)isoindoline-1,3-dione (**2f**)



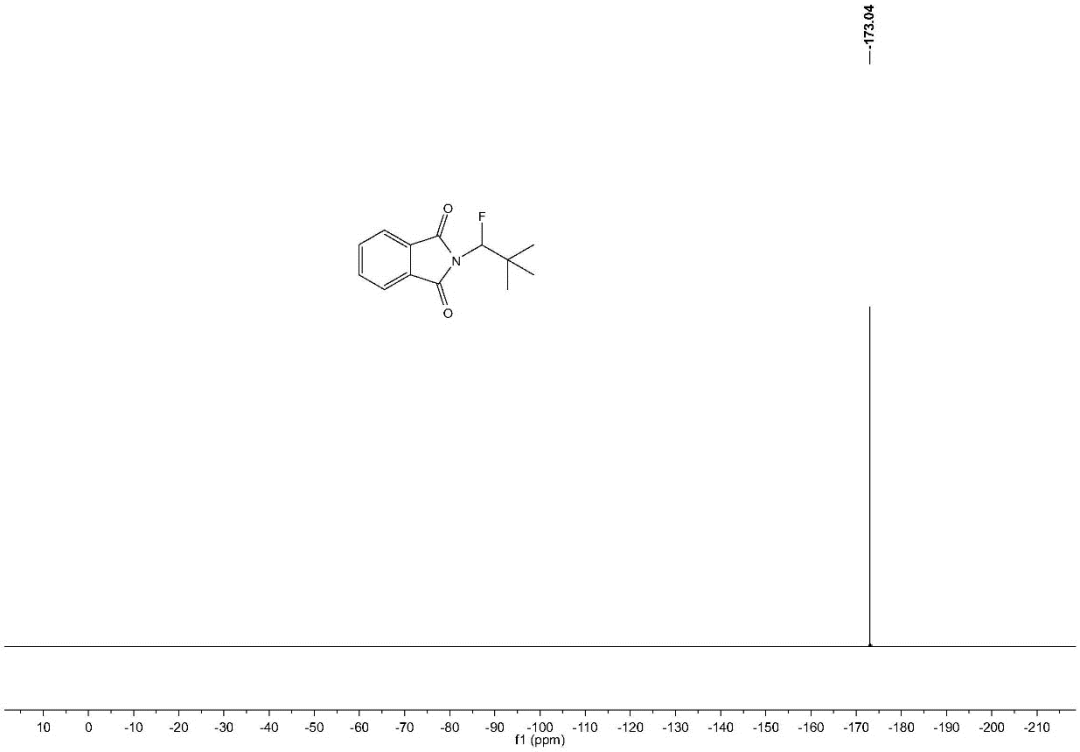
^{1}H NMR of 2-(1-fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (**2g**)



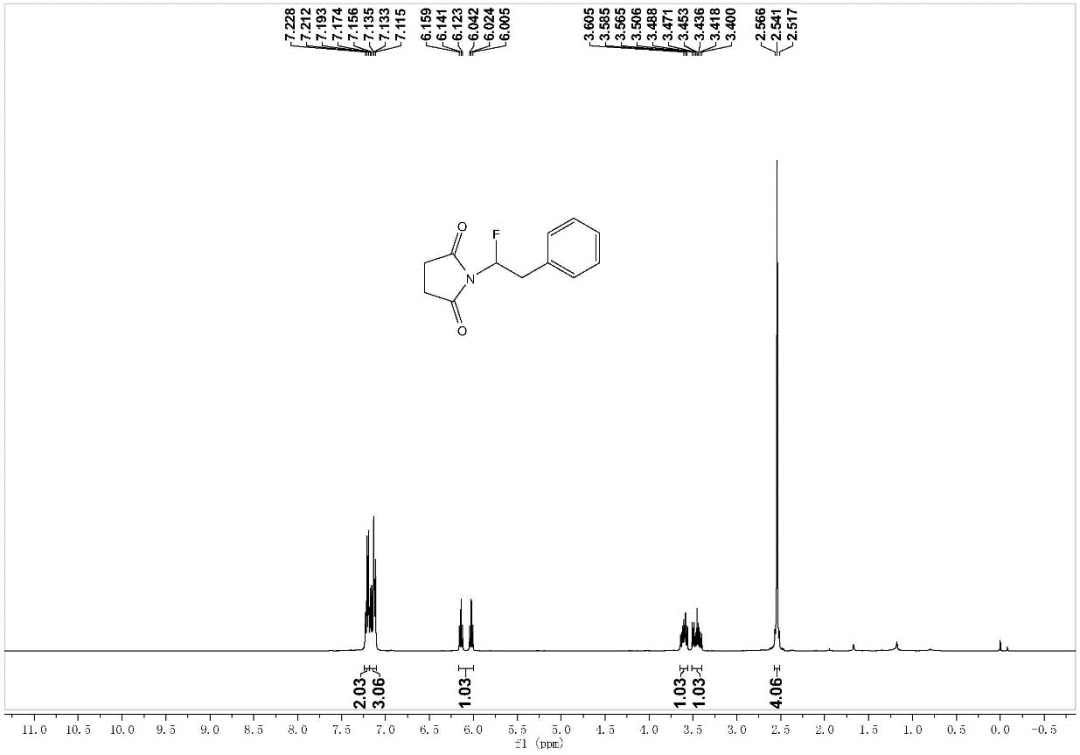
^{13}C NMR of 2-(1-fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (**2g)**



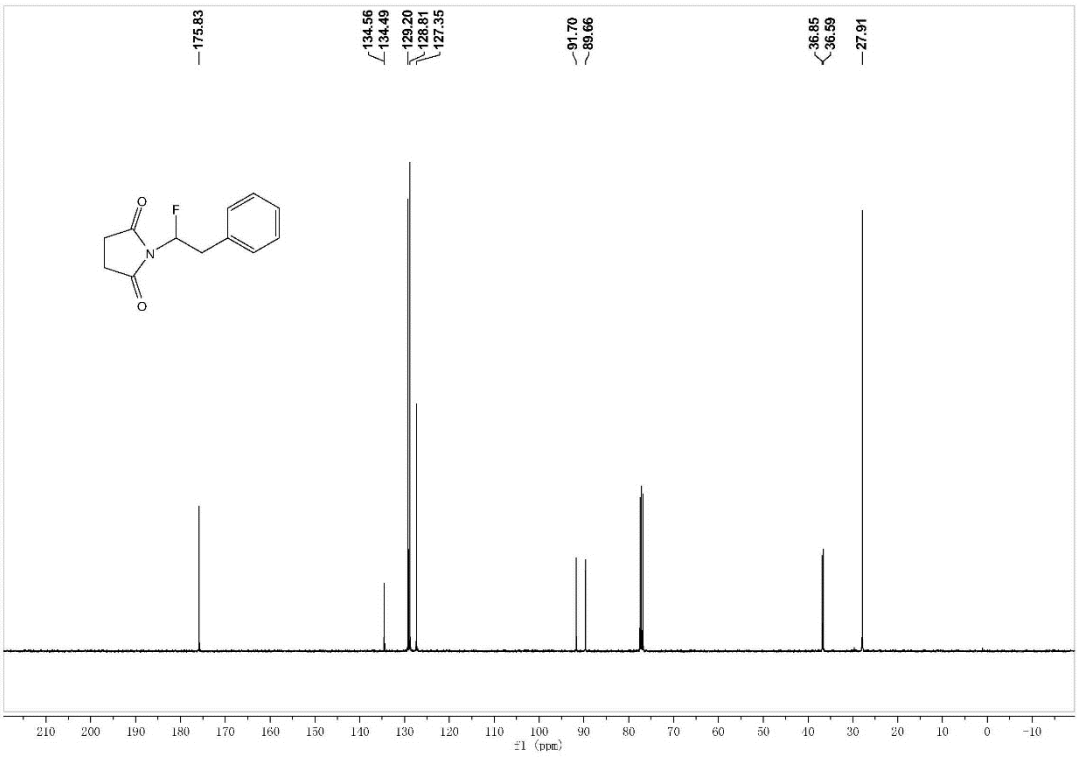
^{19}F NMR of 2-(1-fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (**2g**)



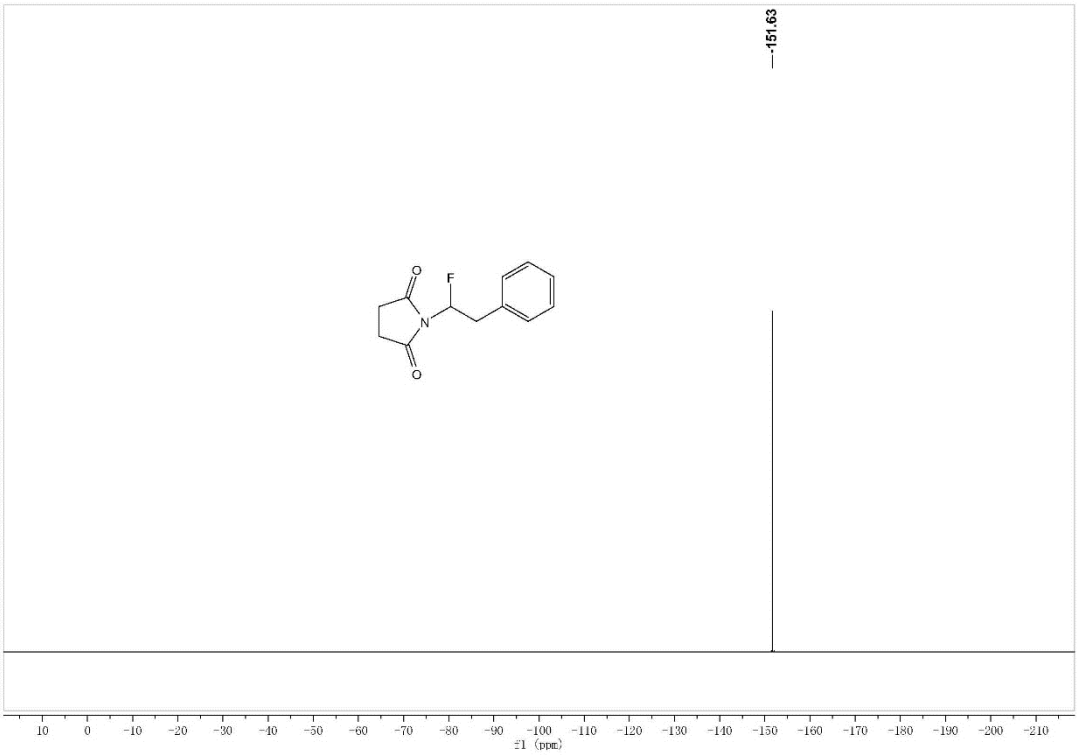
^{1}H NMR of 1-(1-fluoro-2-phenylethyl)pyrrolidine-2,5-dione (**2h**)



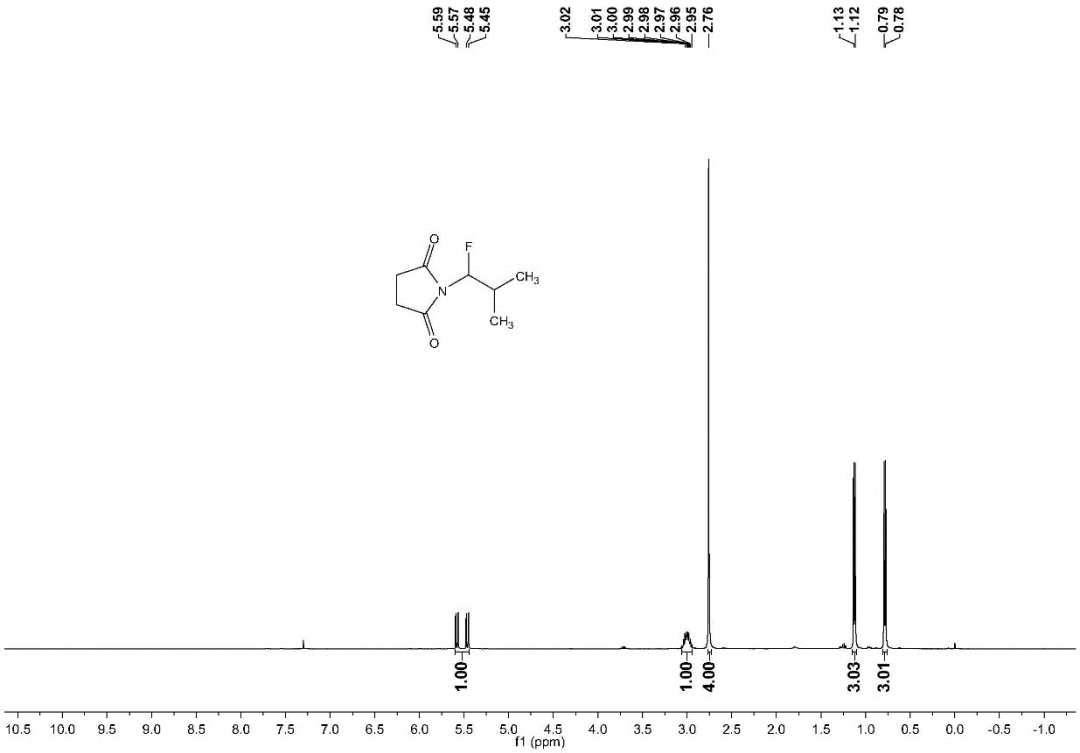
^{13}C NMR of 1-(1-fluoro-2-phenylethyl)pyrrolidine-2,5-dione (**2h**)



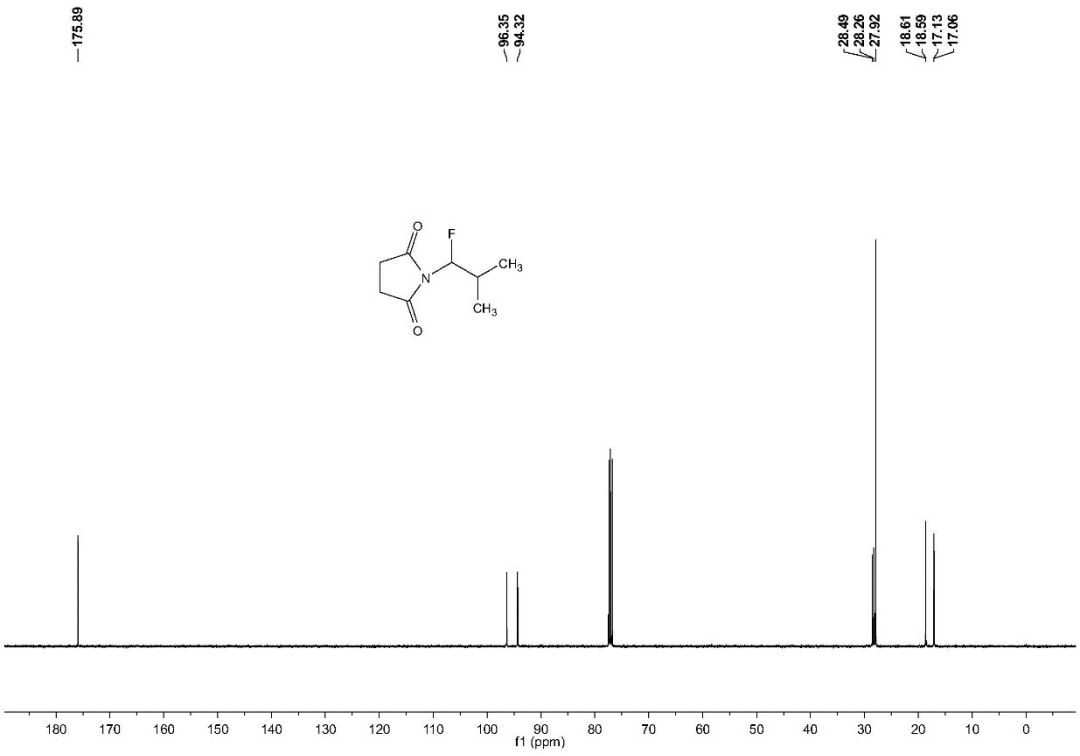
^{19}F NMR of 1-(1-fluoro-2-phenylethyl)pyrrolidine-2,5-dione (**2h**)



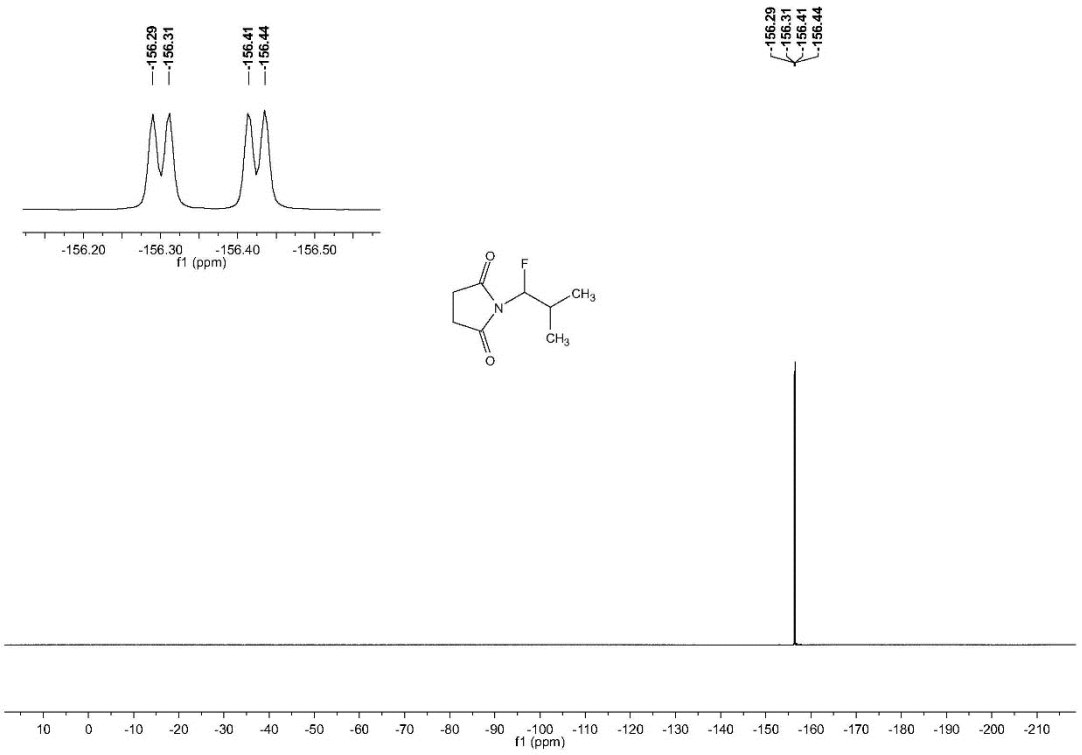
^{1}H NMR of 1-(1-fluoro-2-methylpropyl)pyrrolidine-2,5-dione (**2i**)



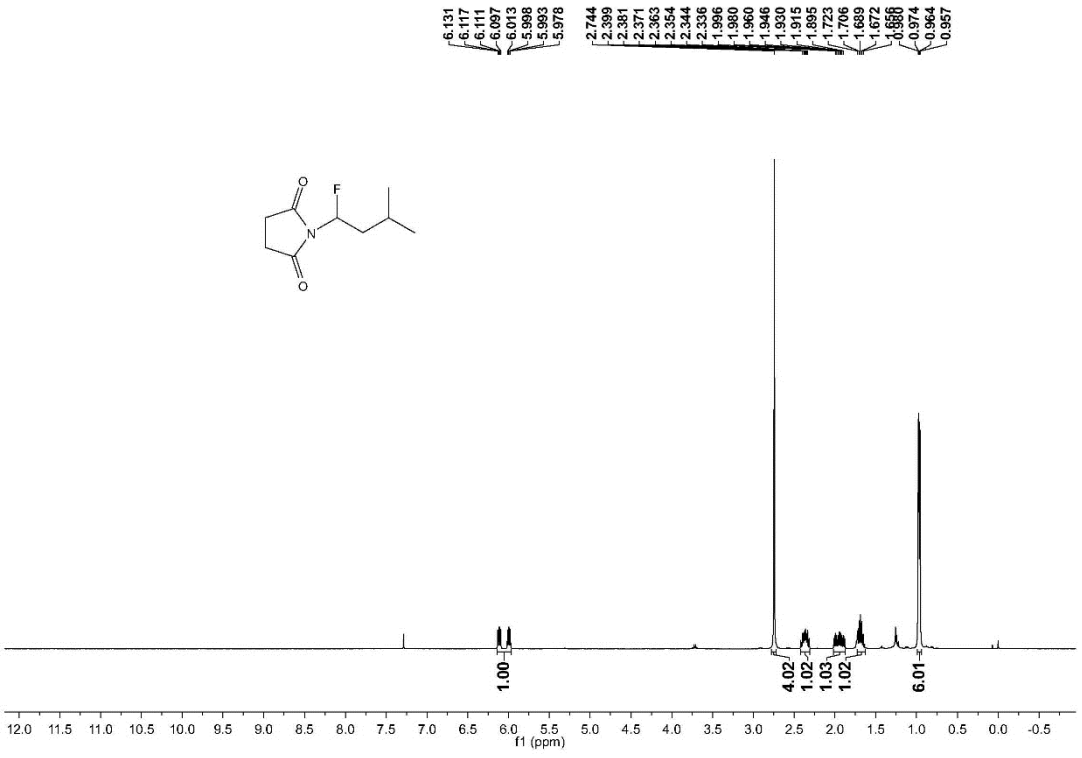
^{13}C NMR of 1-(1-fluoro-2-methylpropyl)pyrrolidine-2,5-dione (**2i**)



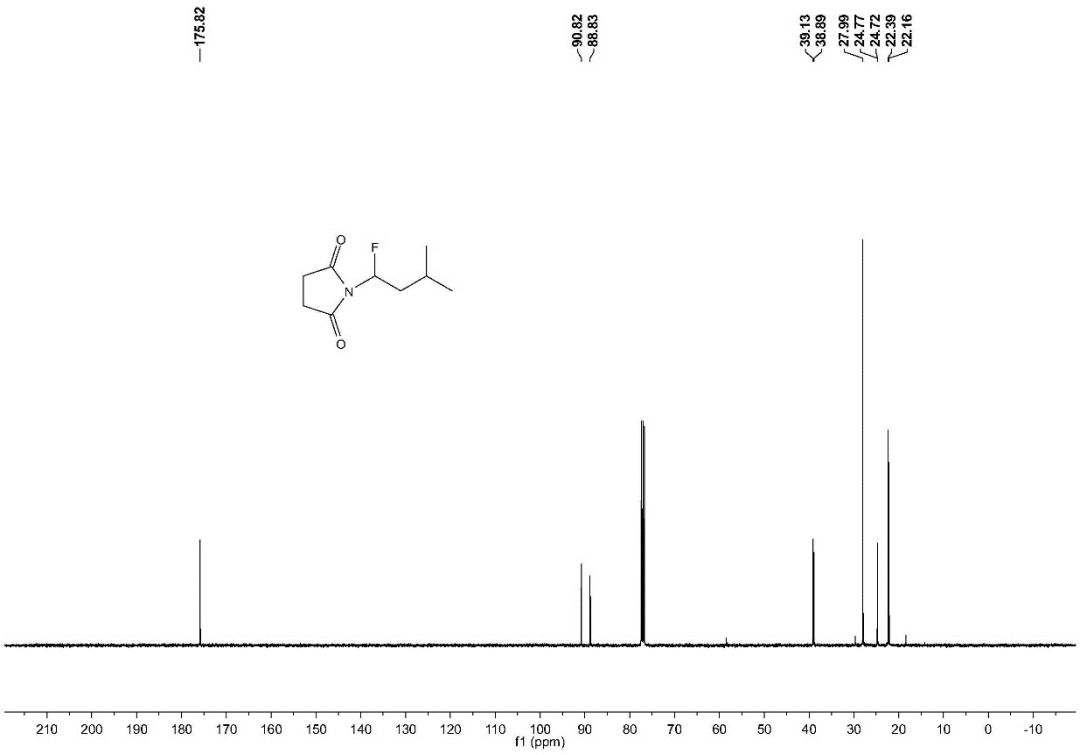
^{19}F NMR of 1-(1-fluoro-2-methylpropyl)pyrrolidine-2,5-dione (**2i**)



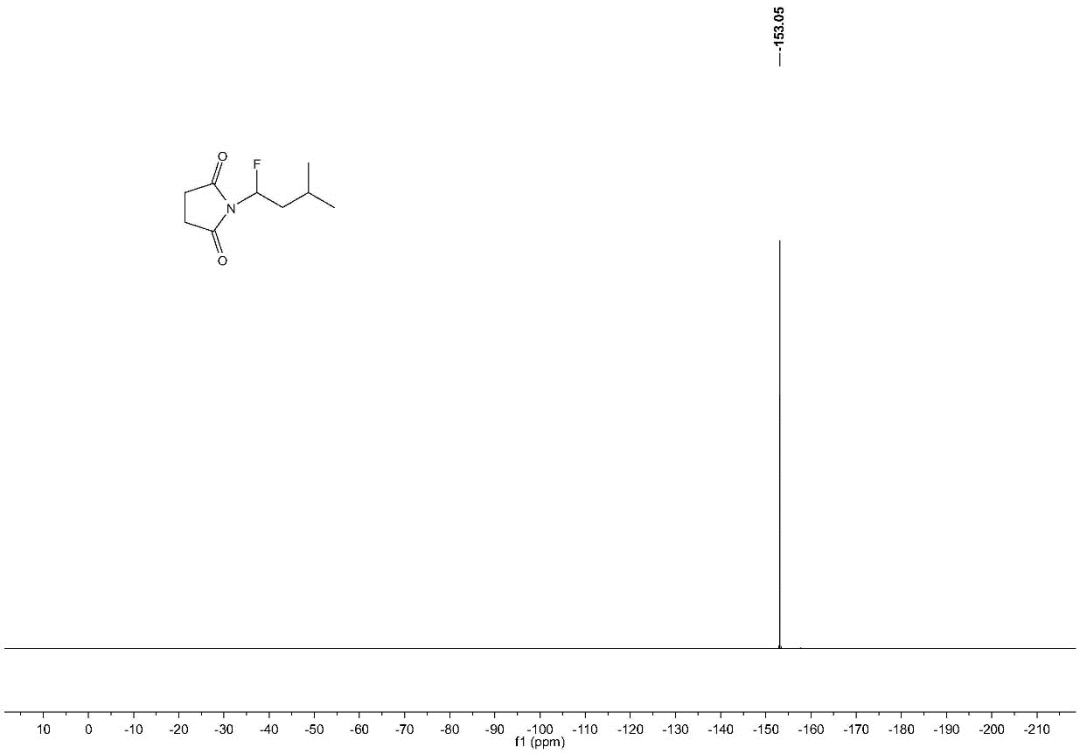
^{1}H NMR of 1-(1-fluoro-3-methylbutyl)pyrrolidine-2,5-dione (**2j**)



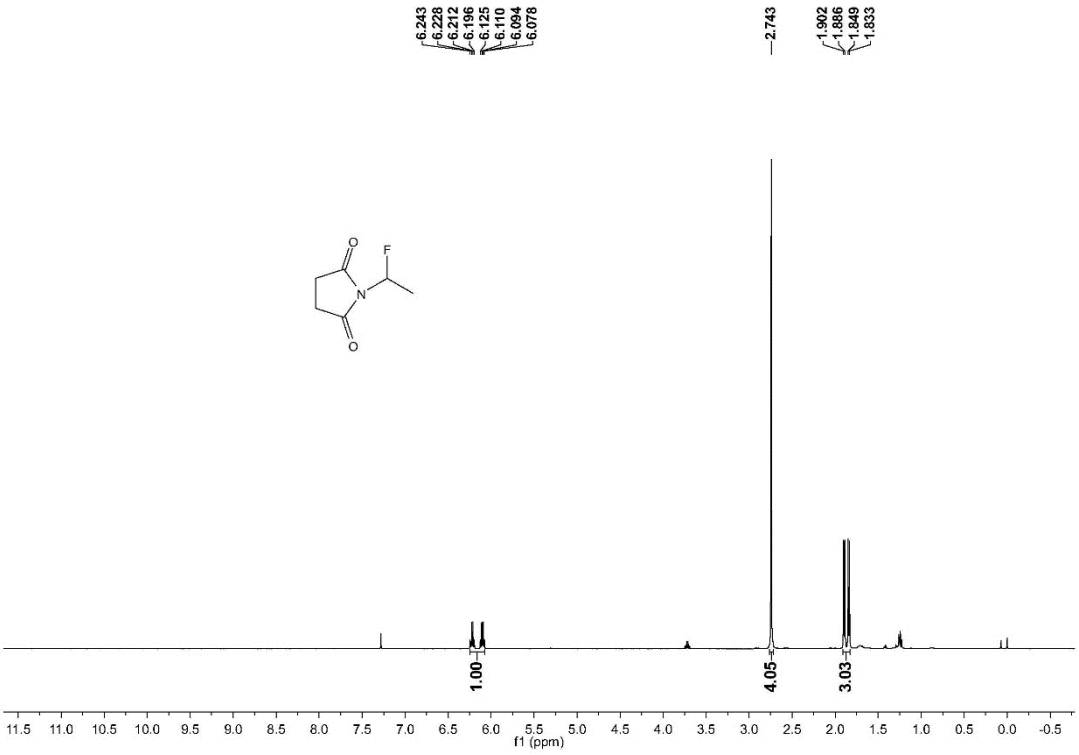
^{13}C NMR of 1-(1-fluoro-3-methylbutyl)pyrrolidine-2,5-dione (**2j**)



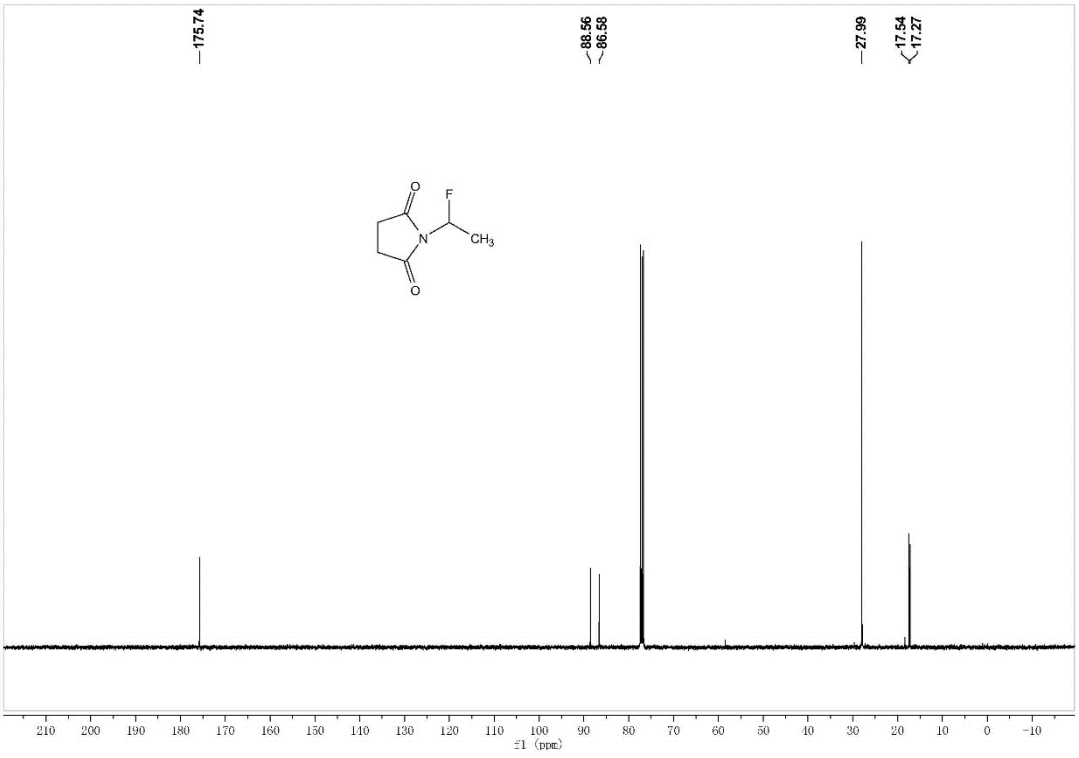
^{19}F NMR of 1-(1-fluoro-3-methylbutyl)pyrrolidine-2,5-dione (**2j**)



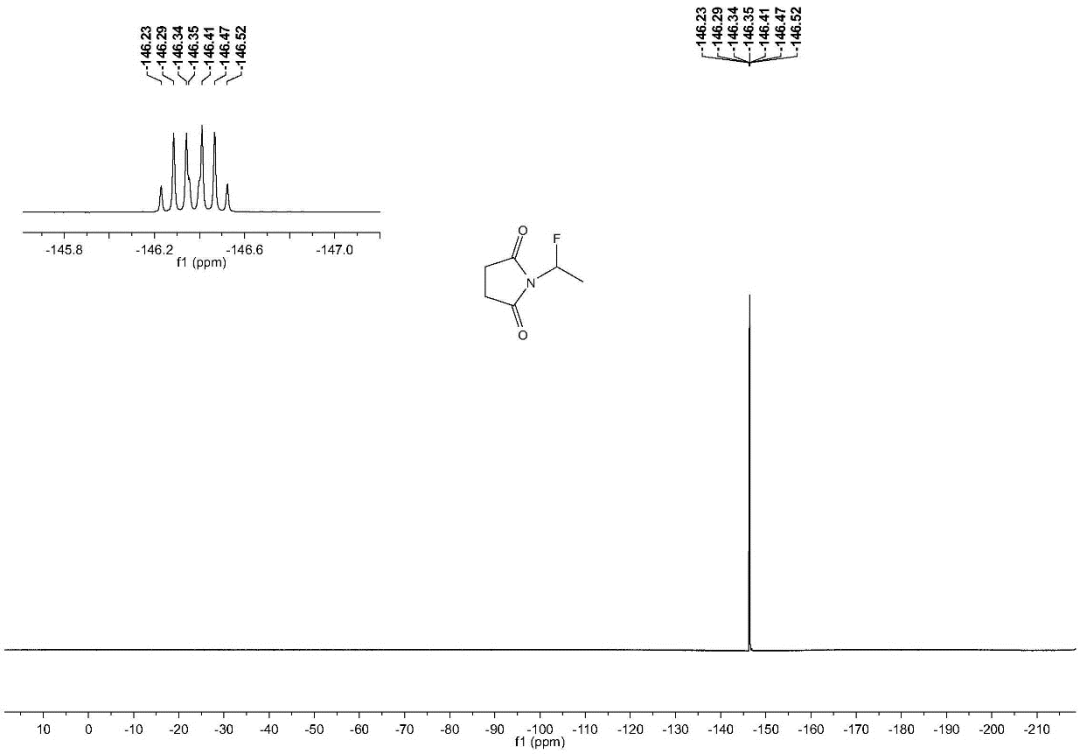
^{1}H NMR of 1-(1-fluoroethyl)pyrrolidine-2,5-dione (2**k**)



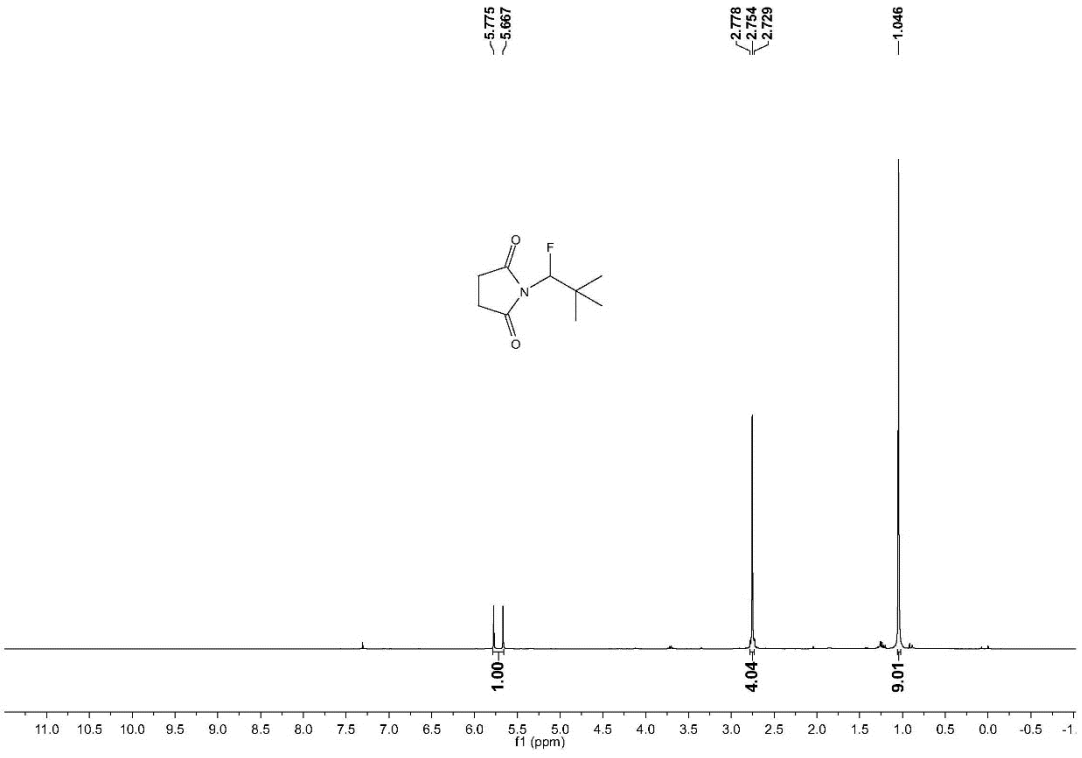
^{13}C NMR of 1-(1-fluoroethyl)pyrrolidine-2,5-dione (2**k**)



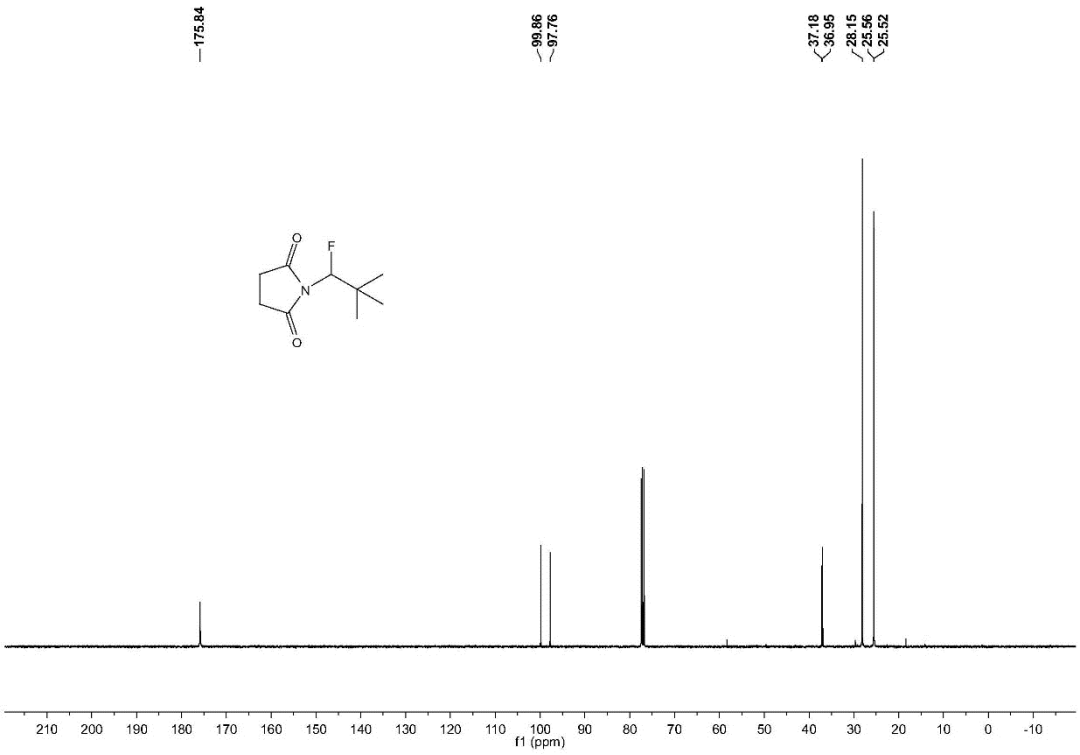
^{19}F NMR of 1-(1-fluoroethyl)pyrrolidine-2,5-dione (2**k**)



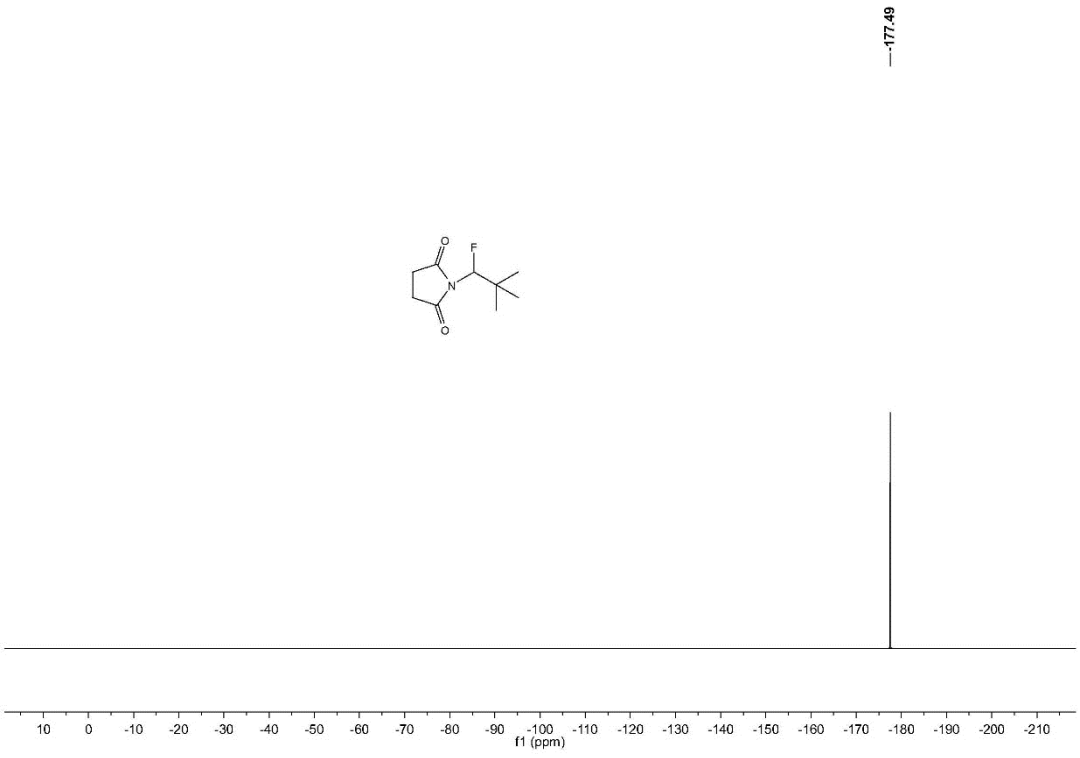
^{1}H NMR of 1-(1-fluoro-2,2-dimethylpropyl)pyrrolidine-2,5-dione (**2l**)



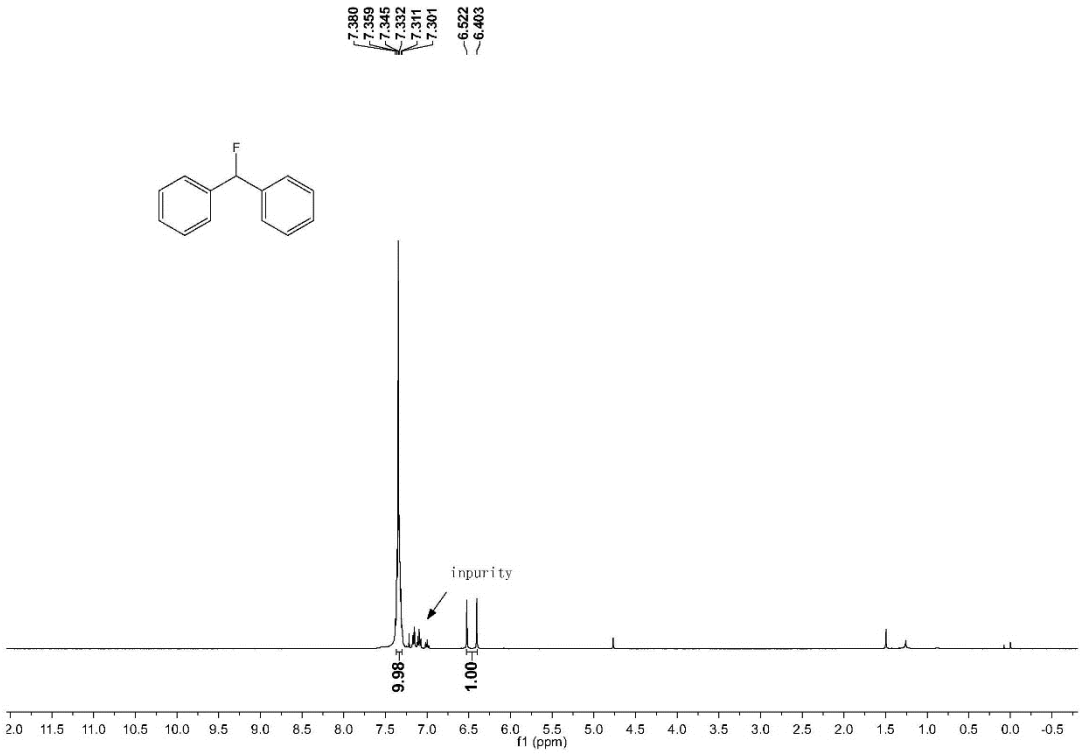
^{13}C NMR of 1-(1-fluoro-2,2-dimethylpropyl)pyrrolidine-2,5-dione (**2l**)



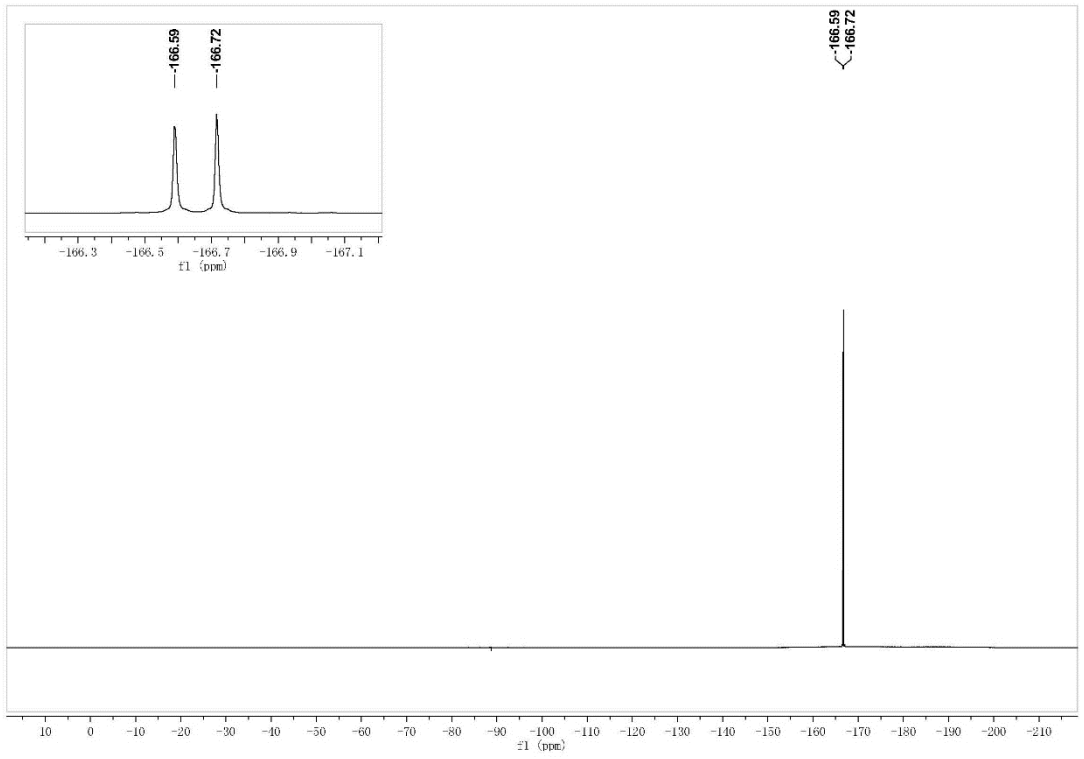
^{19}F NMR of 1-(1-fluoro-2,2-dimethylpropyl)pyrrolidine-2,5-dione (**2l**)



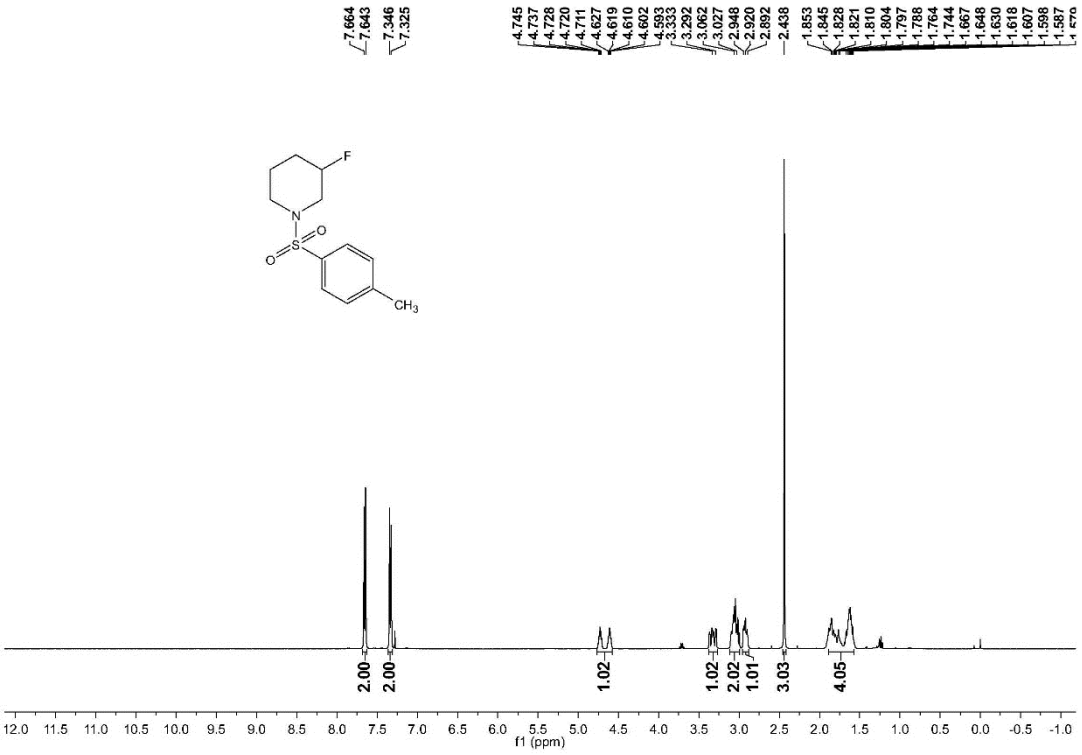
^{1}H NMR of (fluoromethylene)dibenzene (**2m**)



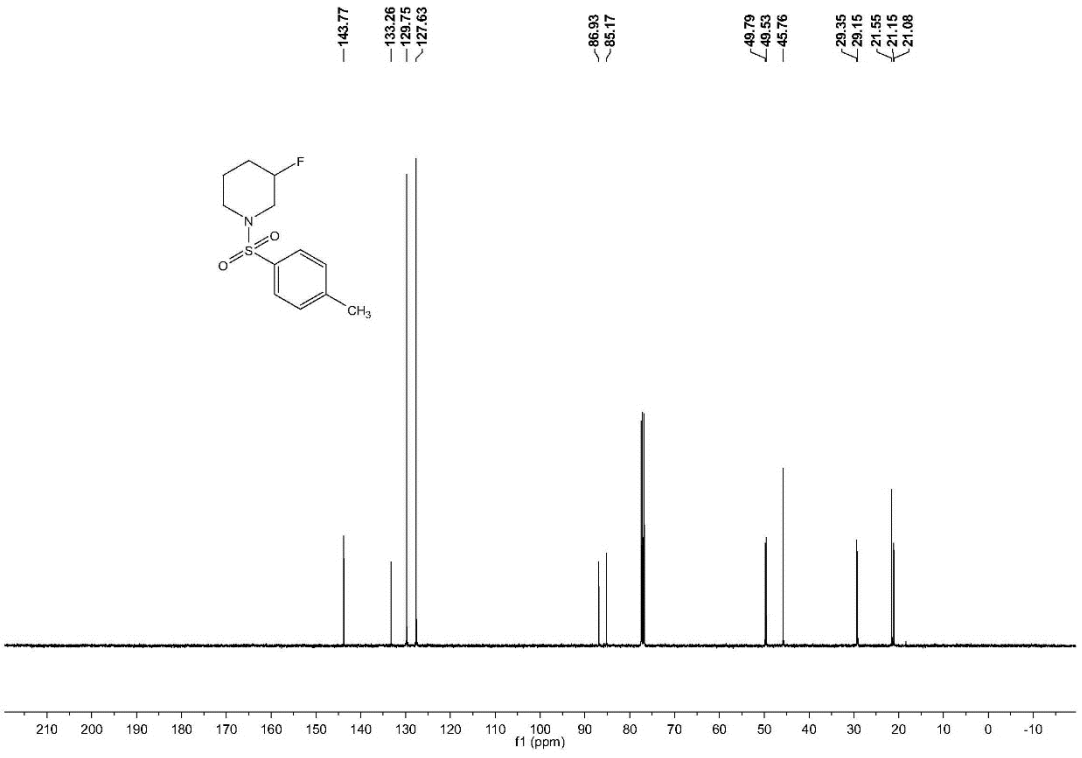
^{19}F NMR of (fluoromethylene)dibenzene (**2m**)



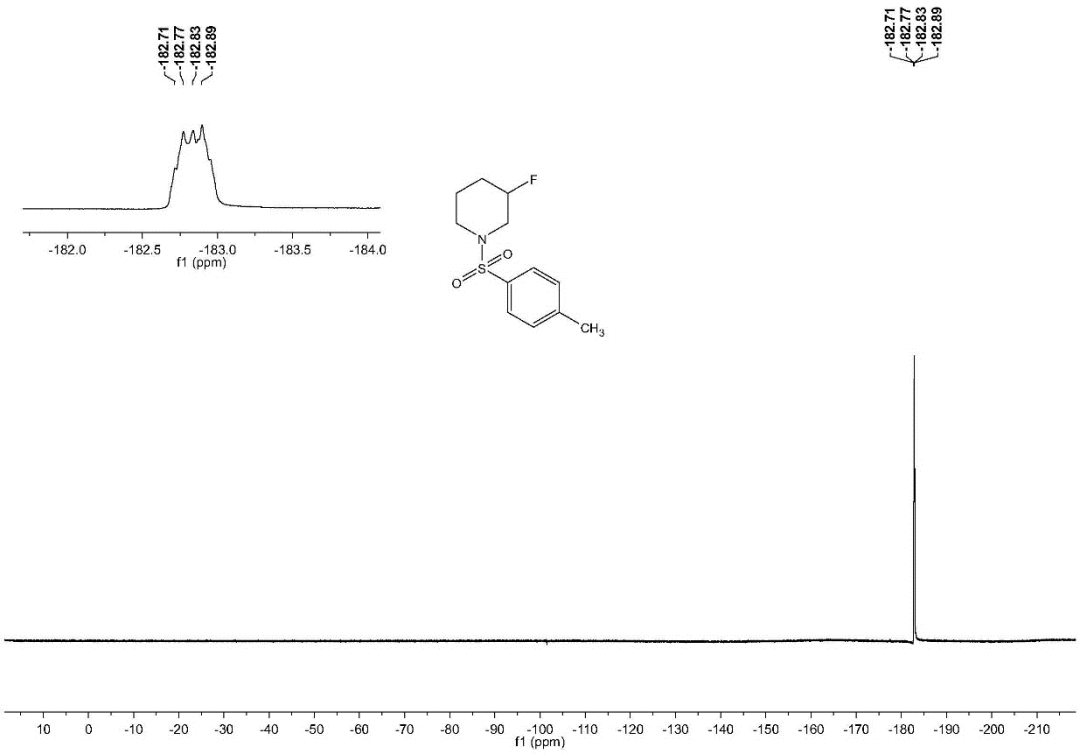
^{1}H NMR of 3-fluoro-1-tosylpiperidine (**2n**)



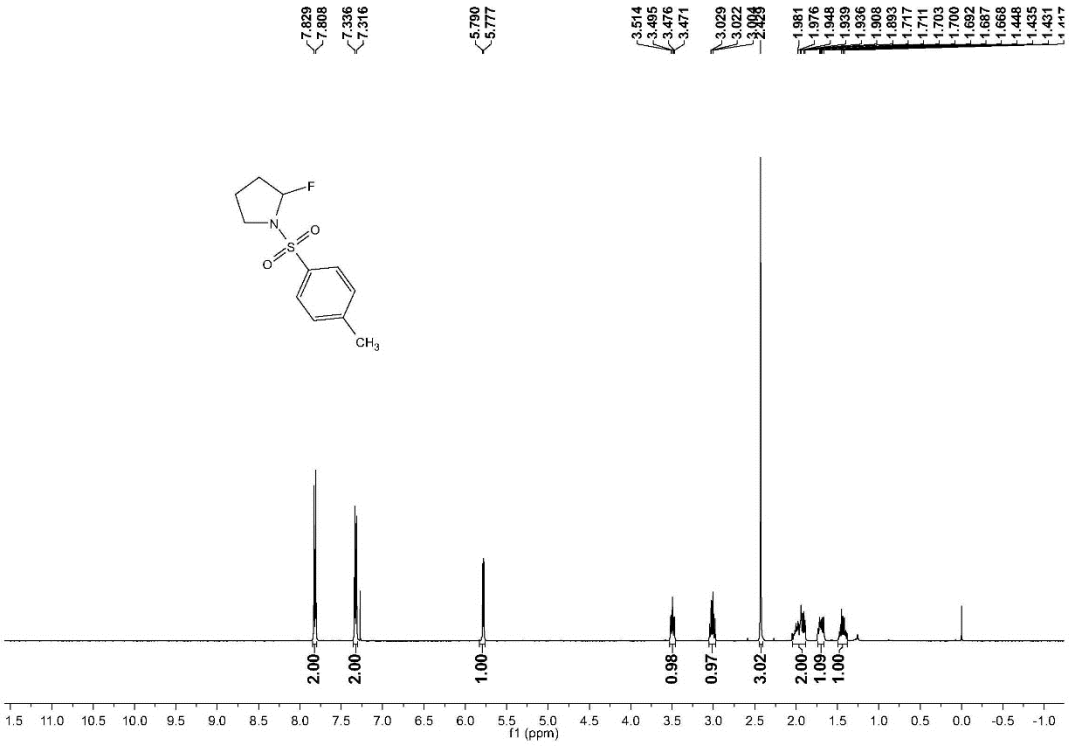
^{13}C NMR of 3-fluoro-1-tosylpiperidine (**2n**)



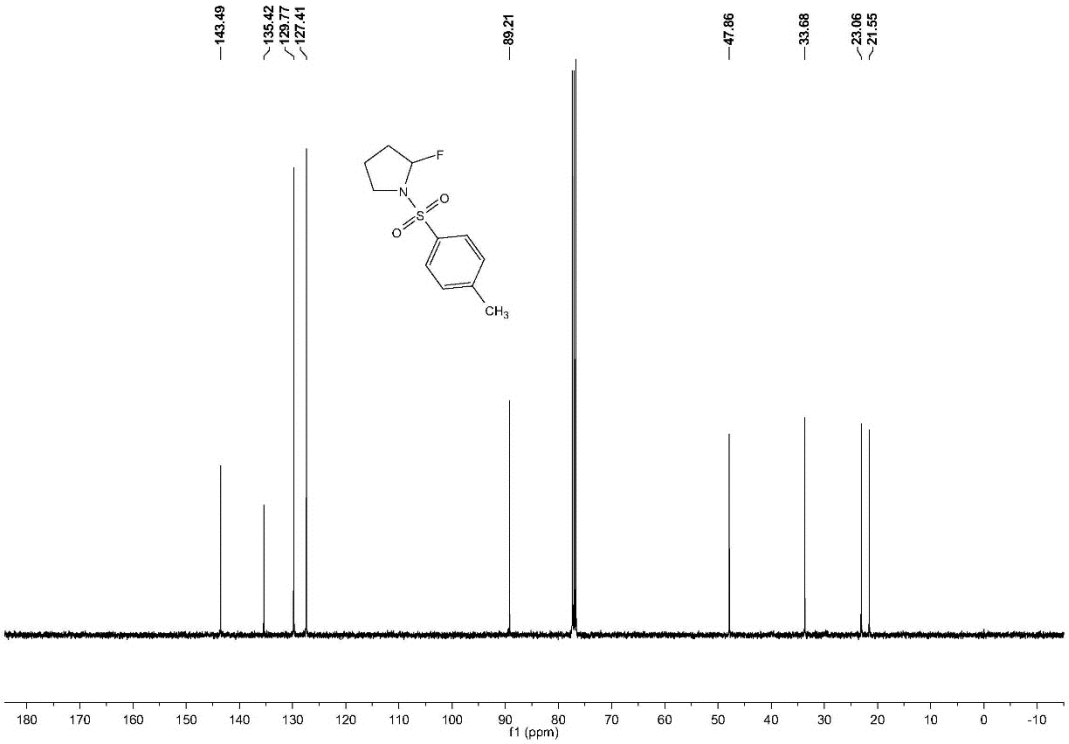
^{19}F NMR of 3-fluoro-1-tosylpiperidine (**2n**)



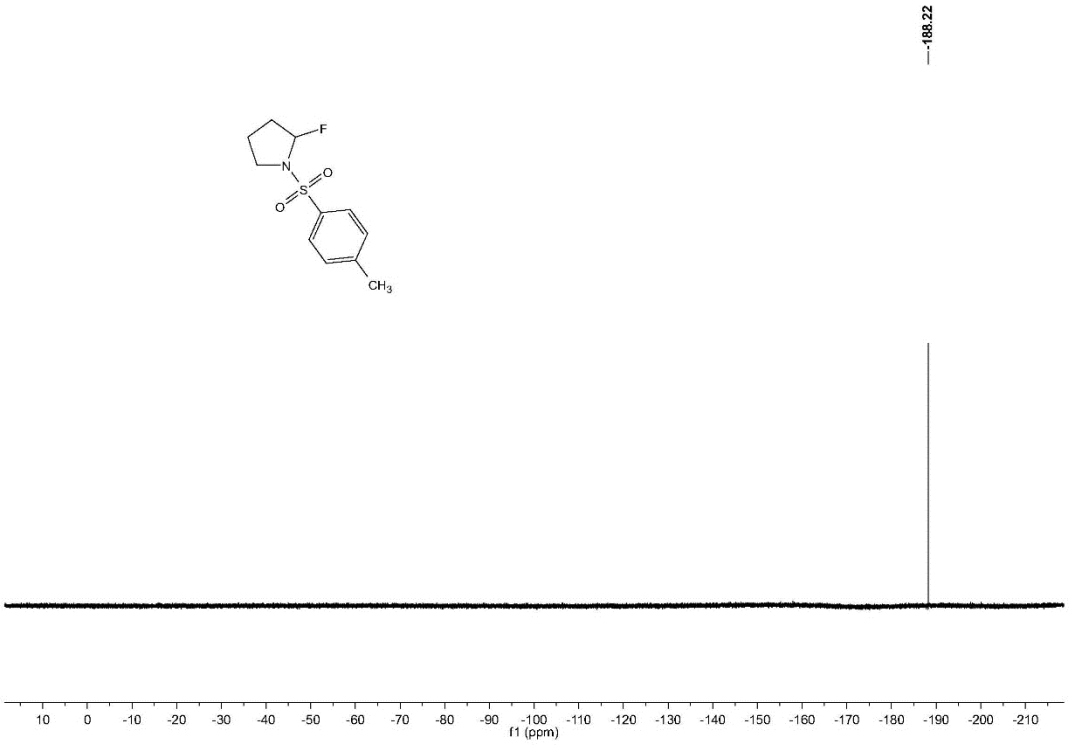
^{1}H NMR of 2-fluoro-1-tosylpyrrolidine (**2o**)



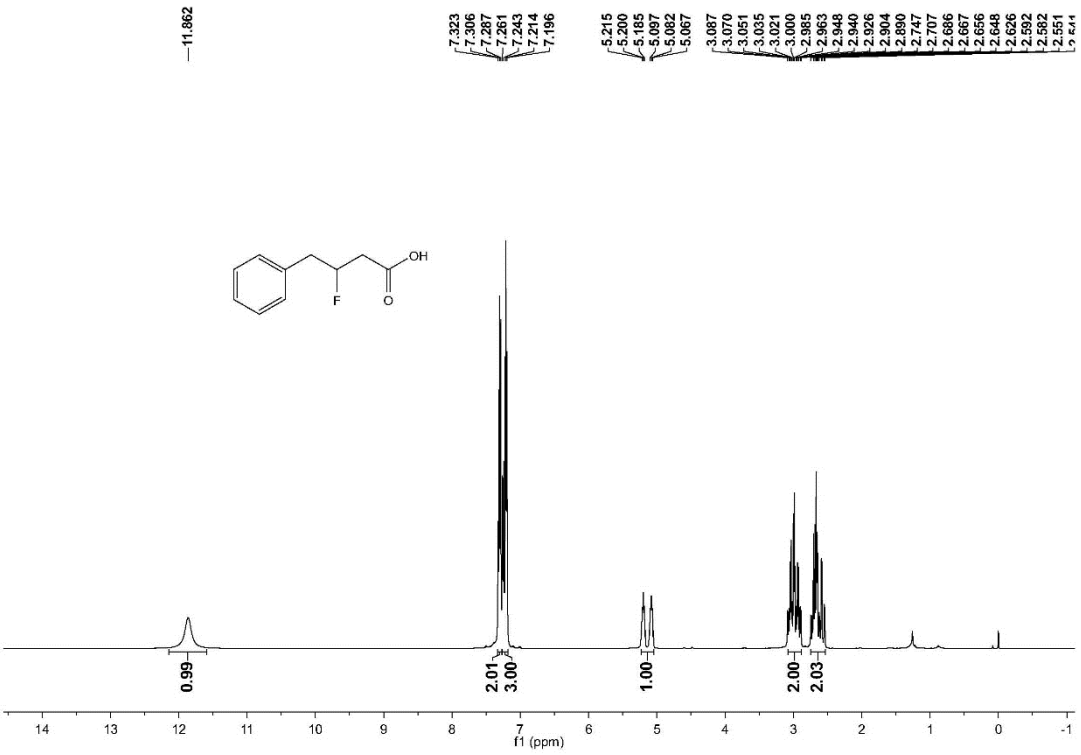
^{13}C NMR of 2-fluoro-1-tosylpyrrolidine (**2o**)



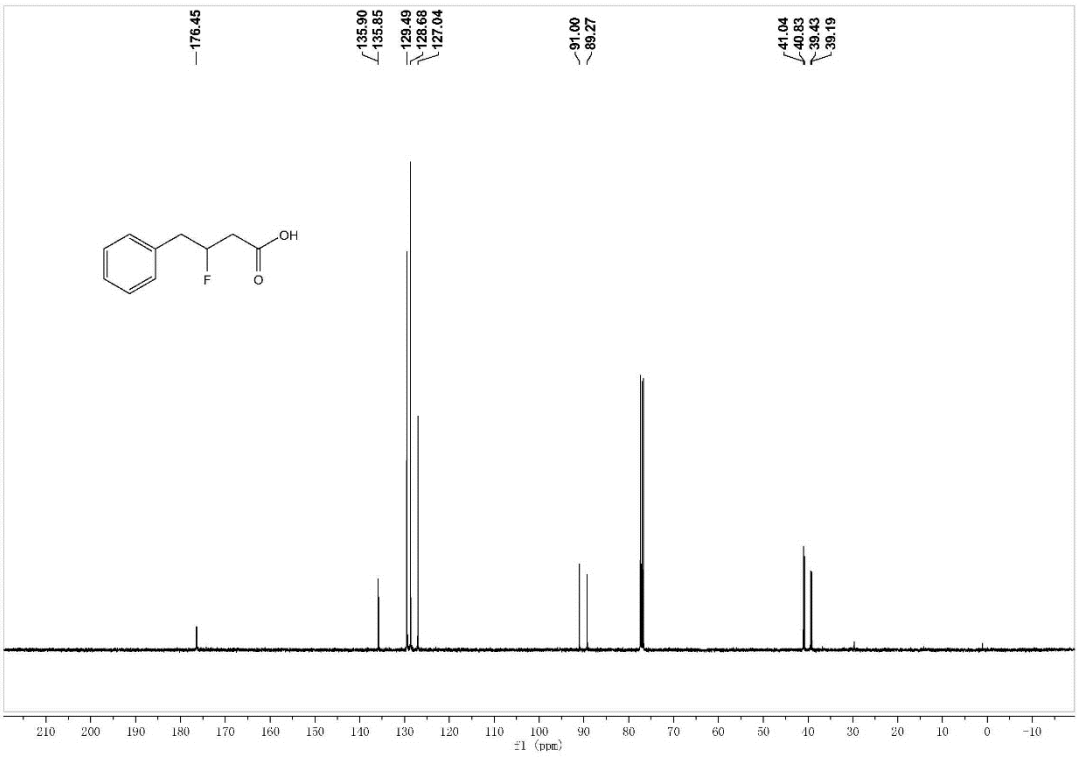
^{19}F NMR of 2-fluoro-1-tosylpyrrolidine (**2o**)



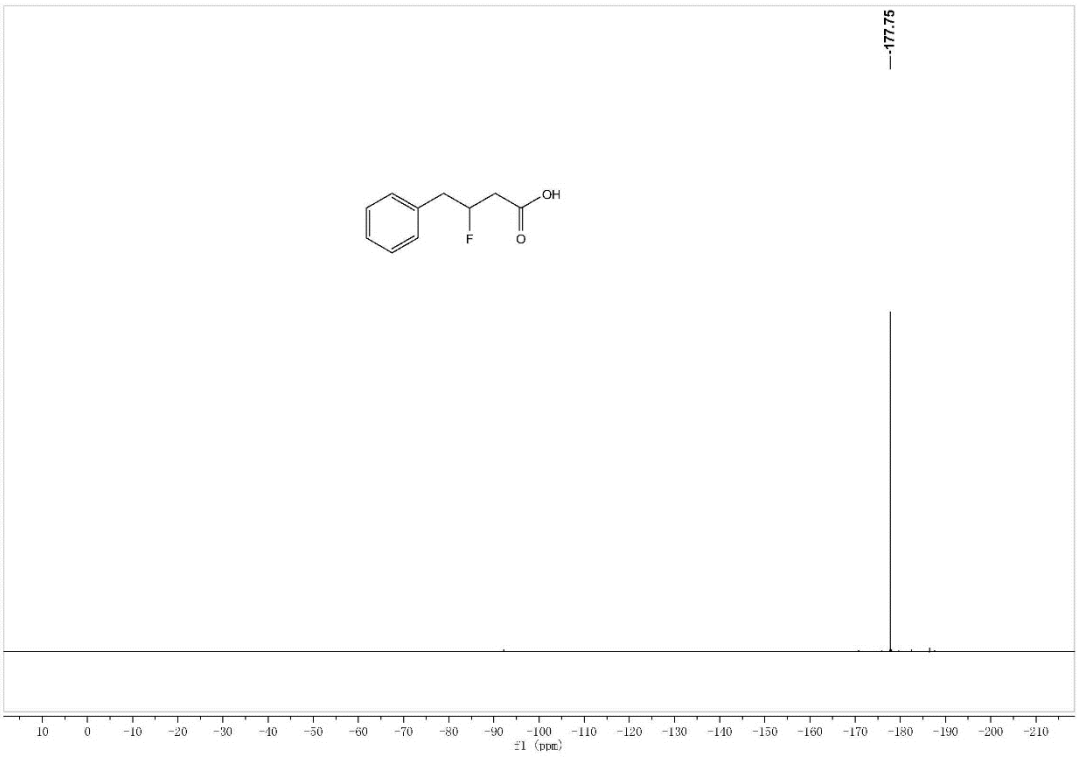
^{1}H NMR of 3-fluoro-4-phenylbutanoic acid (**2p**)



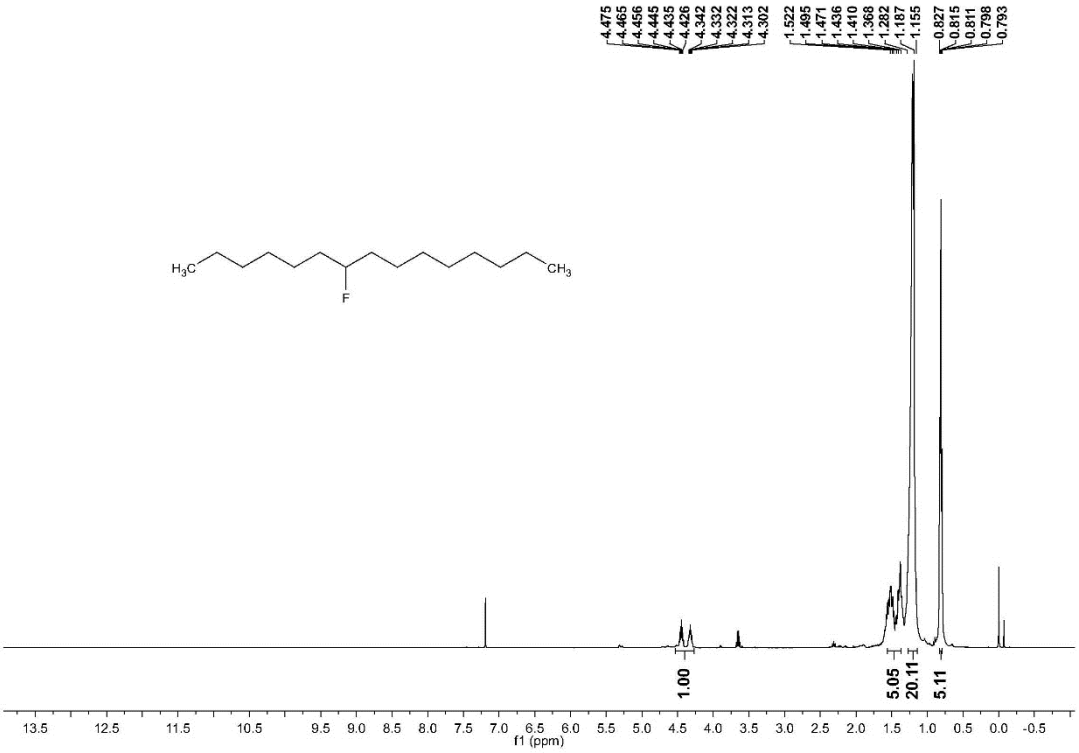
^{13}C NMR of 3-fluoro-4-phenylbutanoic acid (**2p**)



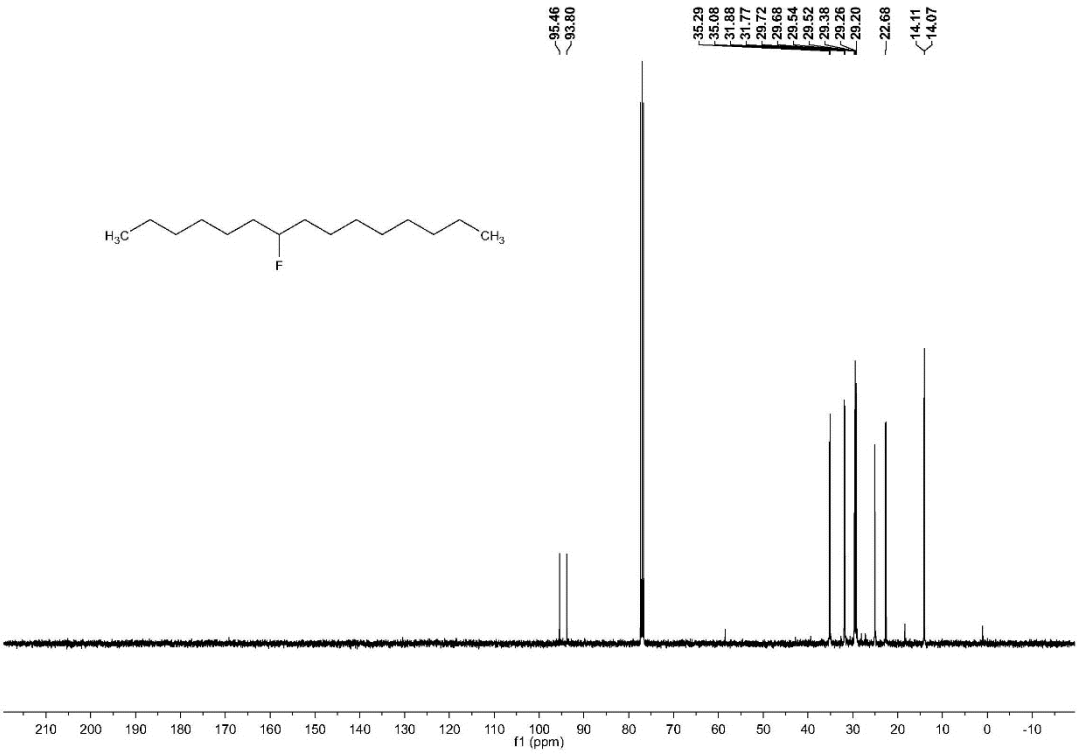
^{19}F NMR of 3-fluoro-4-phenylbutanoic acid (**2p**)



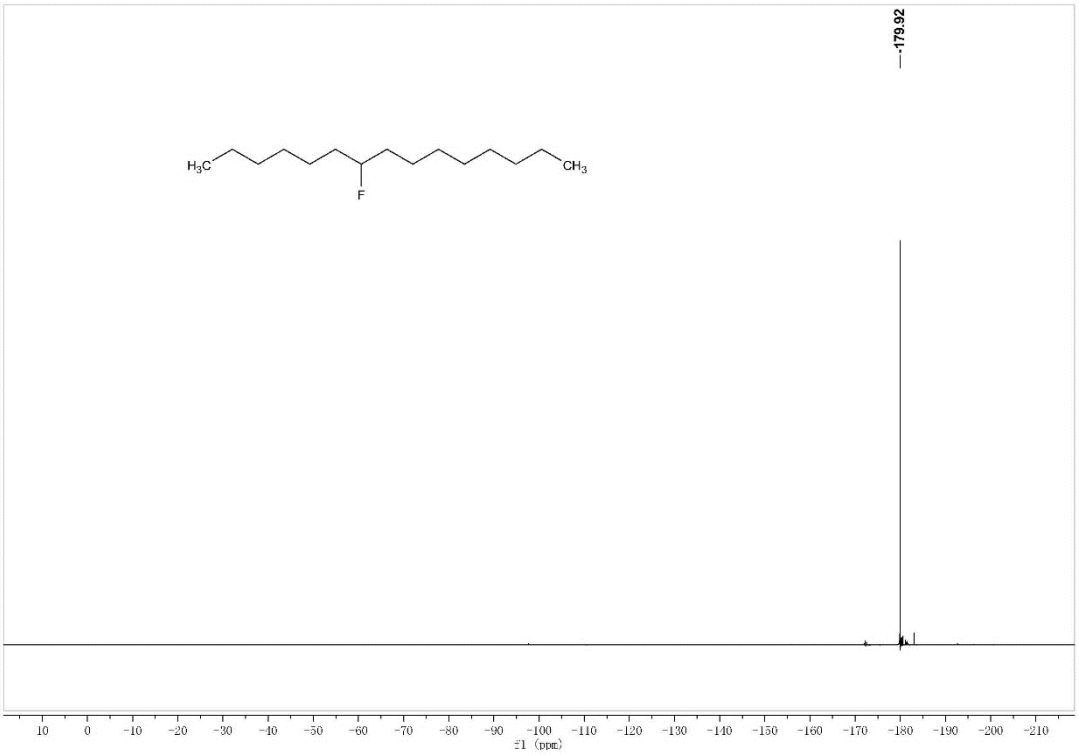
^{1}H NMR of 7-fluoropentadecane (**2q**)



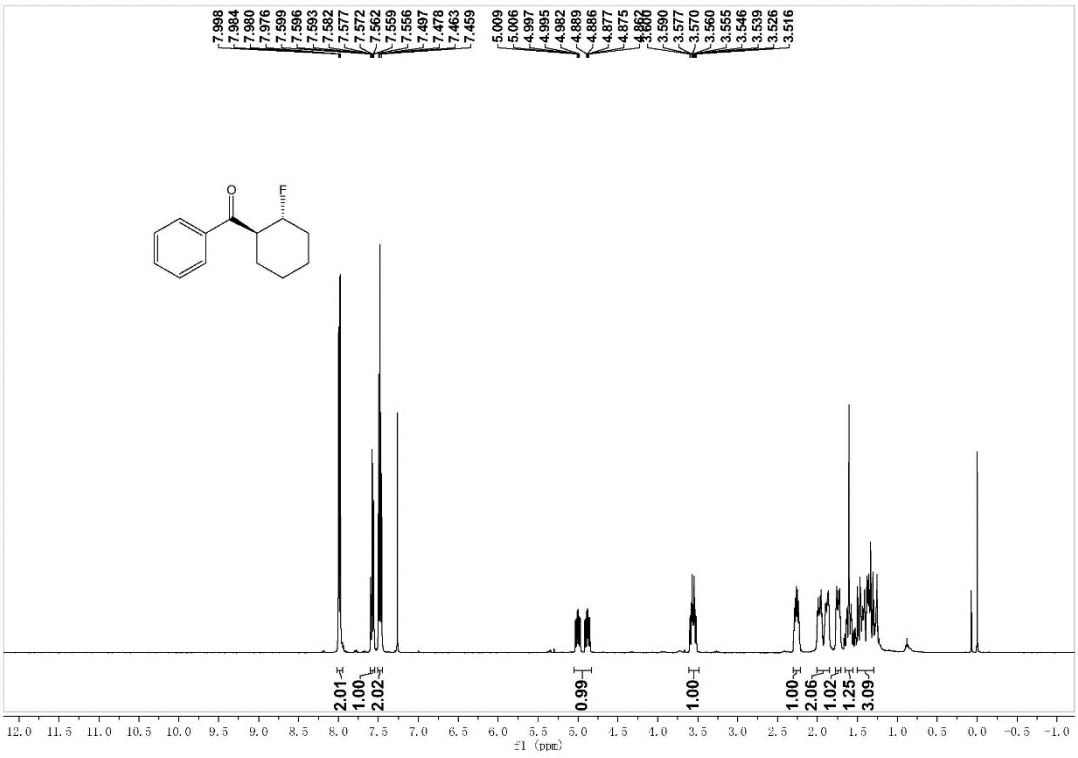
^{13}C NMR of 7-fluoropentadecane (**2q**)



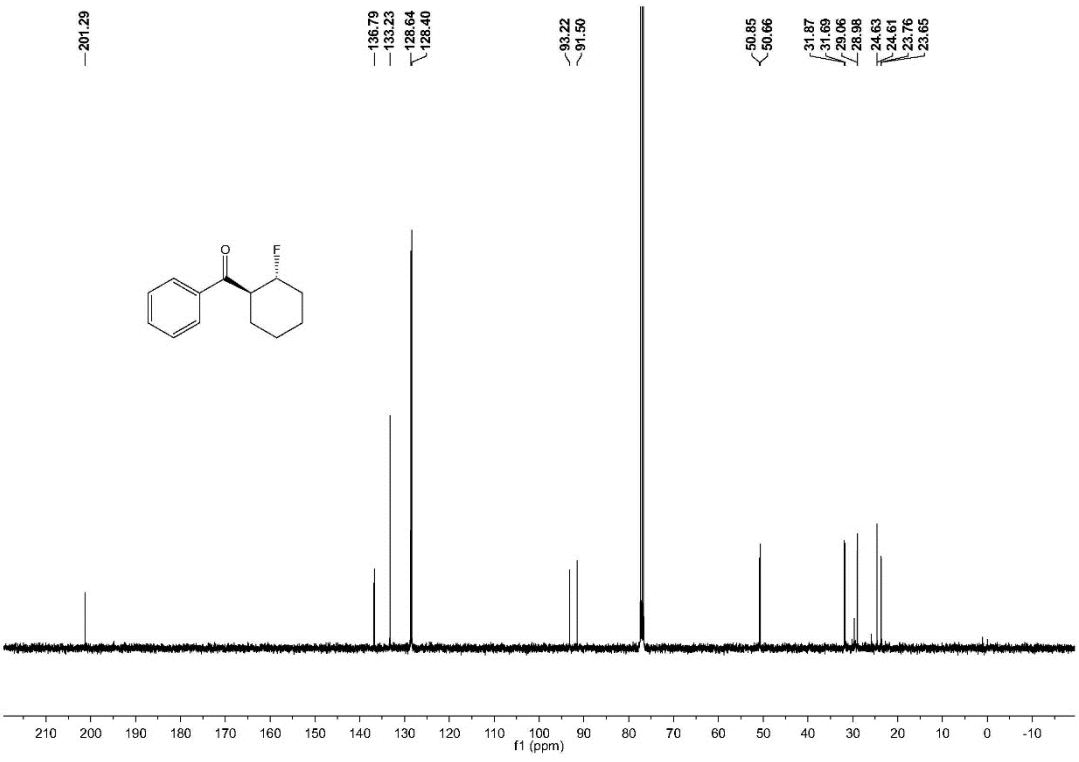
^{19}F NMR of 7-fluoropentadecane (**2q**)



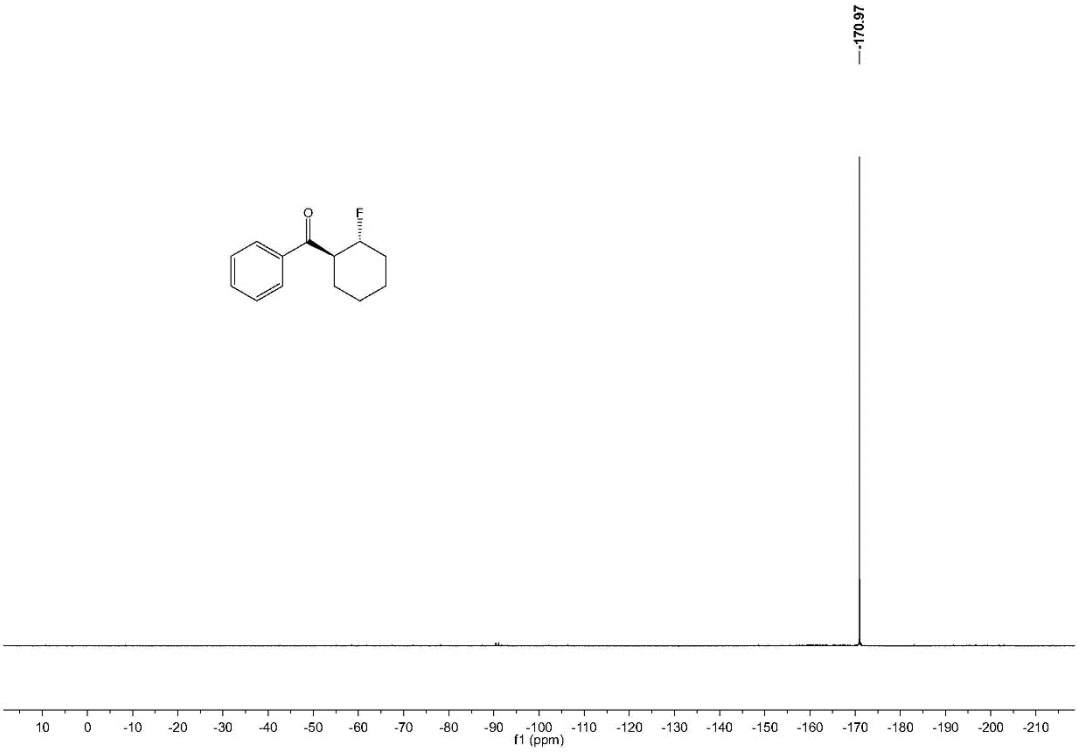
^{1}H NMR of (*trans*-2-fluorocyclohexyl)(phenyl)methanone (**2r**)



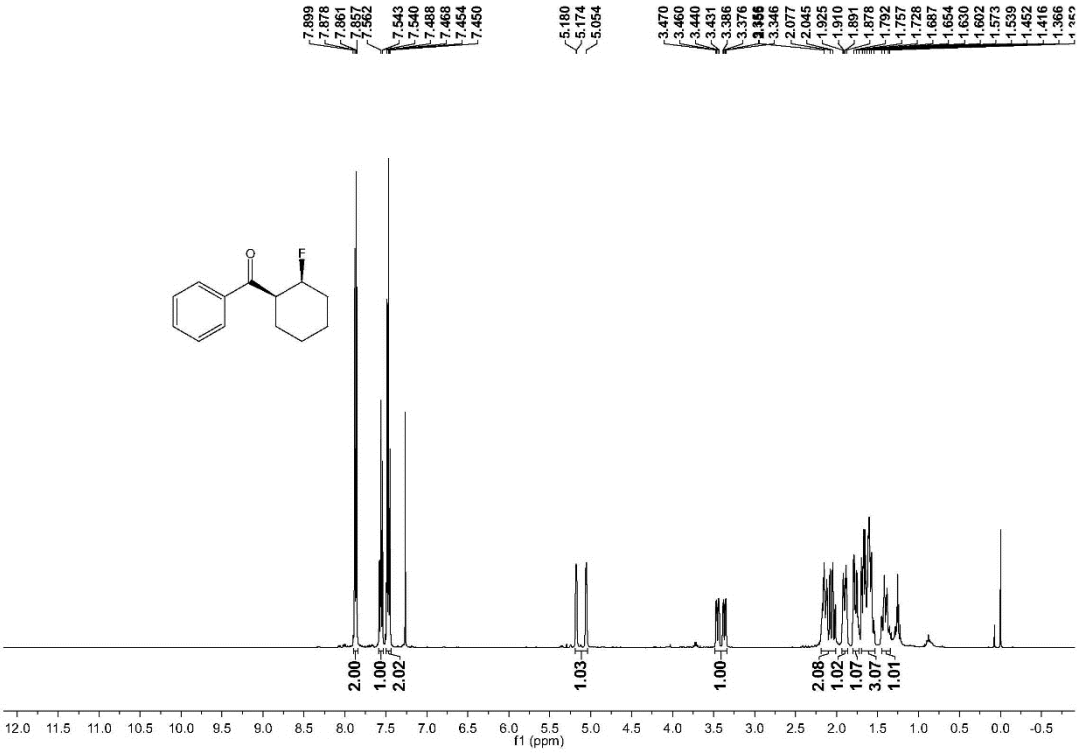
^{13}C NMR of (*trans*-2-fluorocyclohexyl)(phenyl)methanone (**2r**)



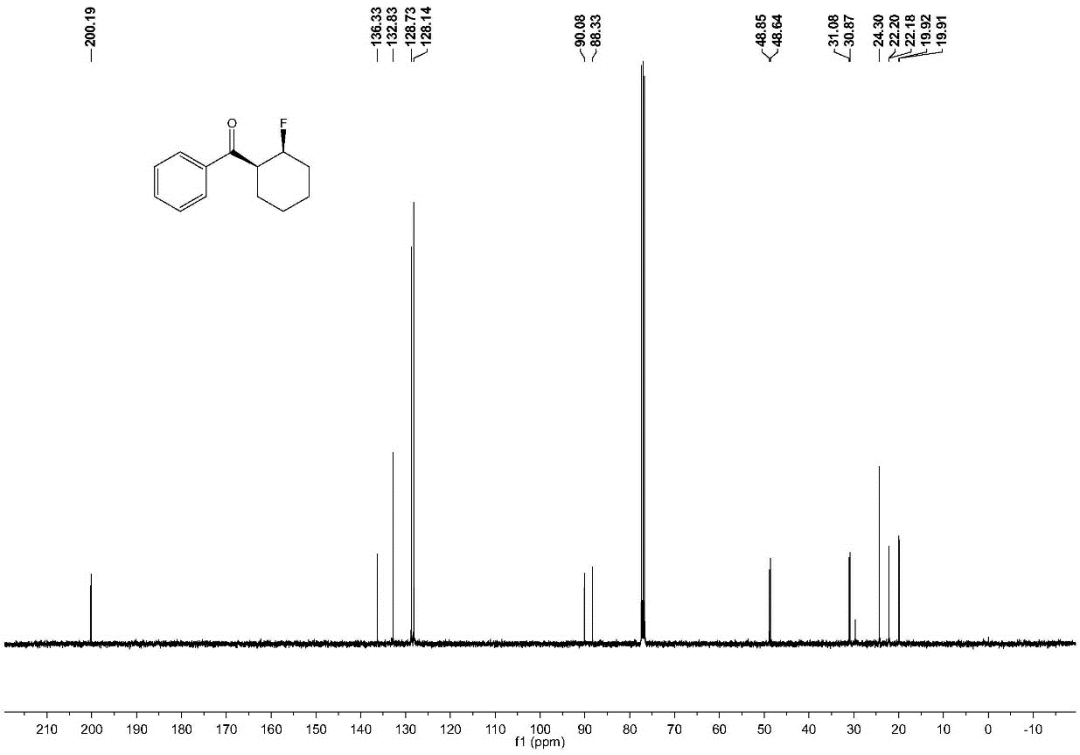
^{19}F NMR of (*trans*-2-fluorocyclohexyl)(phenyl)methanone (**2r**)



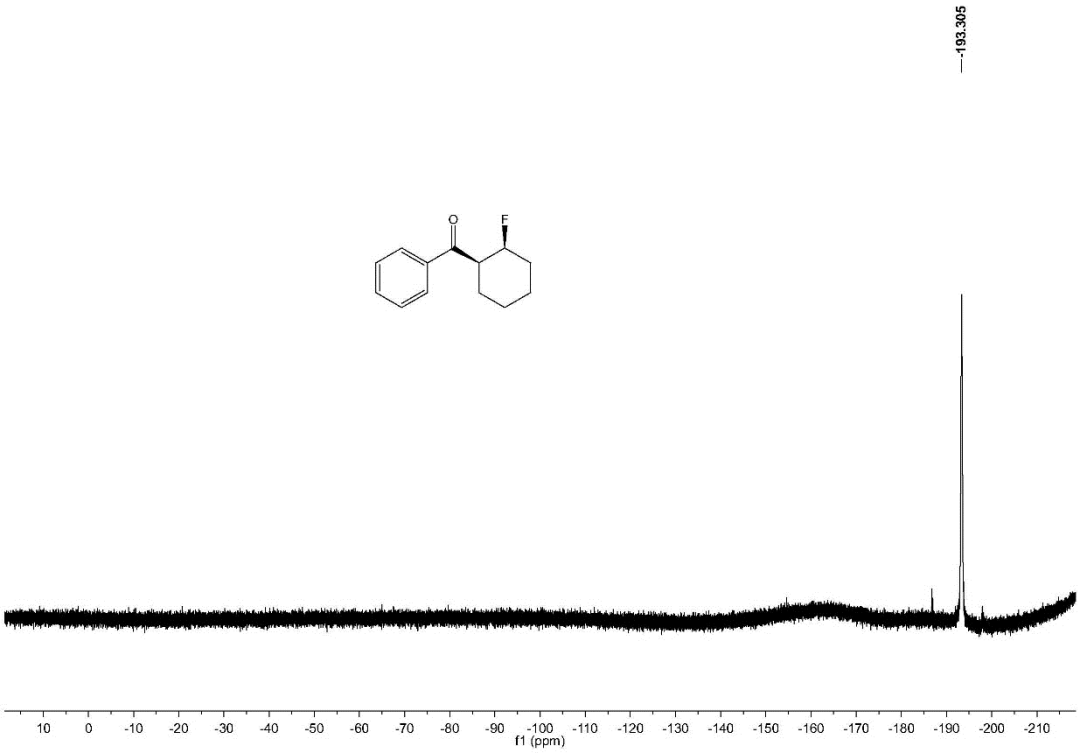
^{1}H NMR of (*cis*-2-fluorocyclohexyl)(phenyl)methanone (**2r'**)



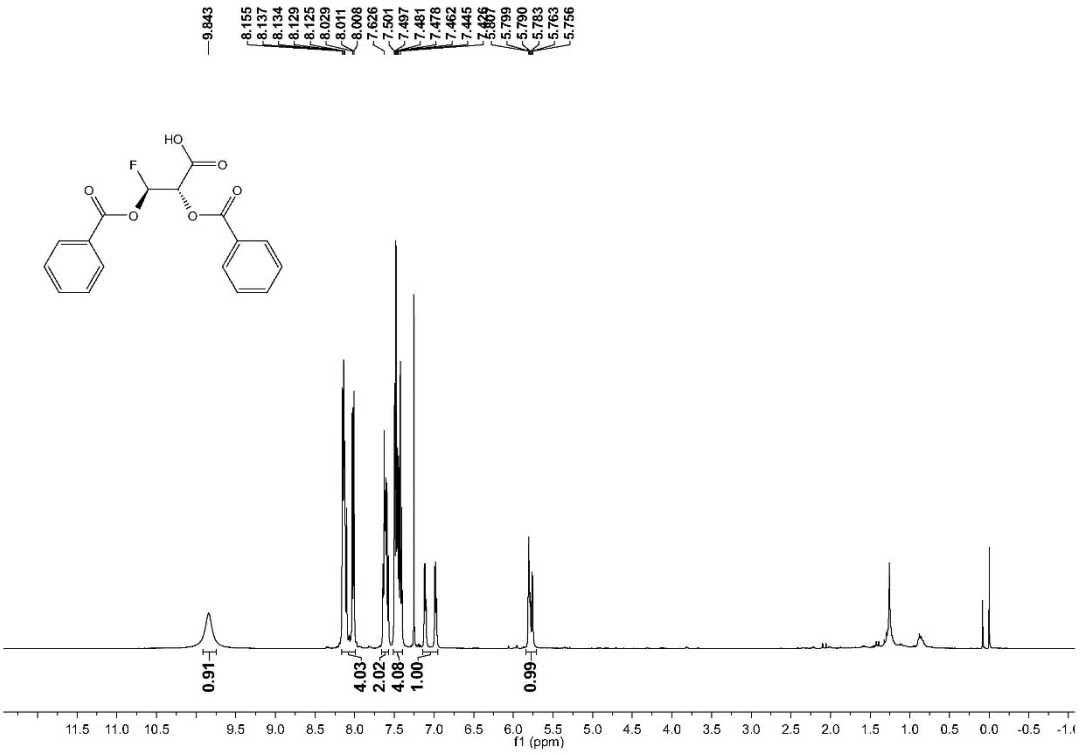
^{13}C NMR of (*cis*-2-fluorocyclohexyl)(phenyl)methanone (**2r'**)



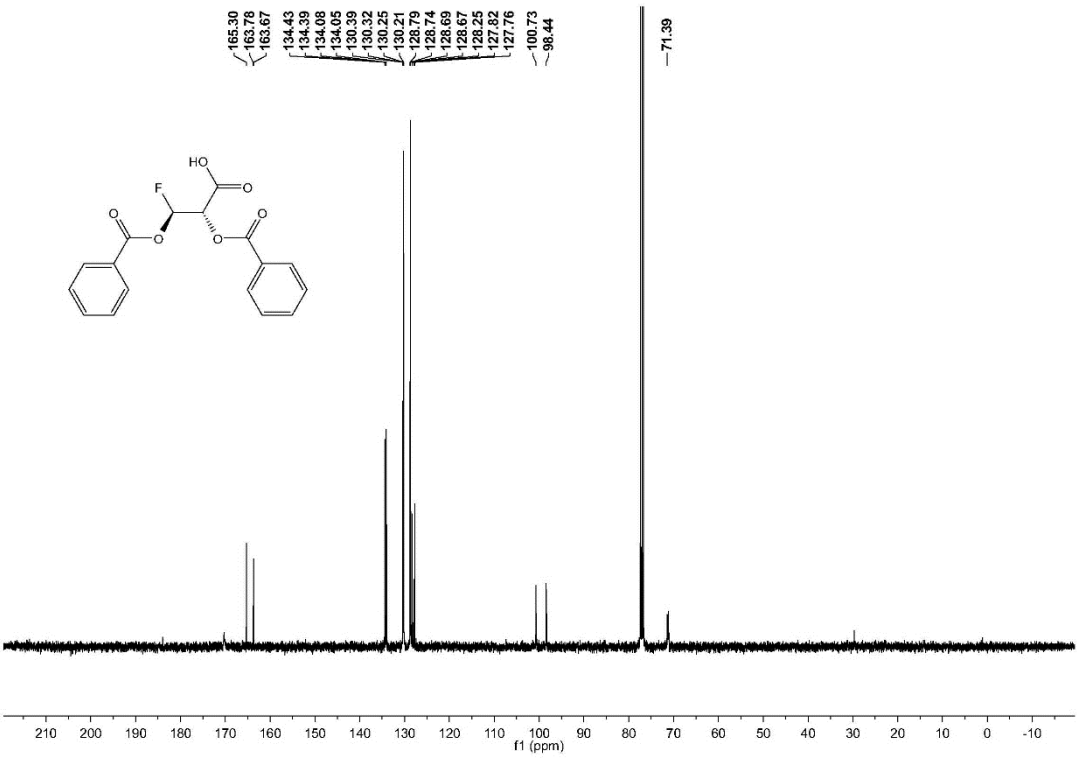
^{19}F NMR of (*cis*-2-fluorocyclohexyl)(phenyl)methanone (**2r'**)



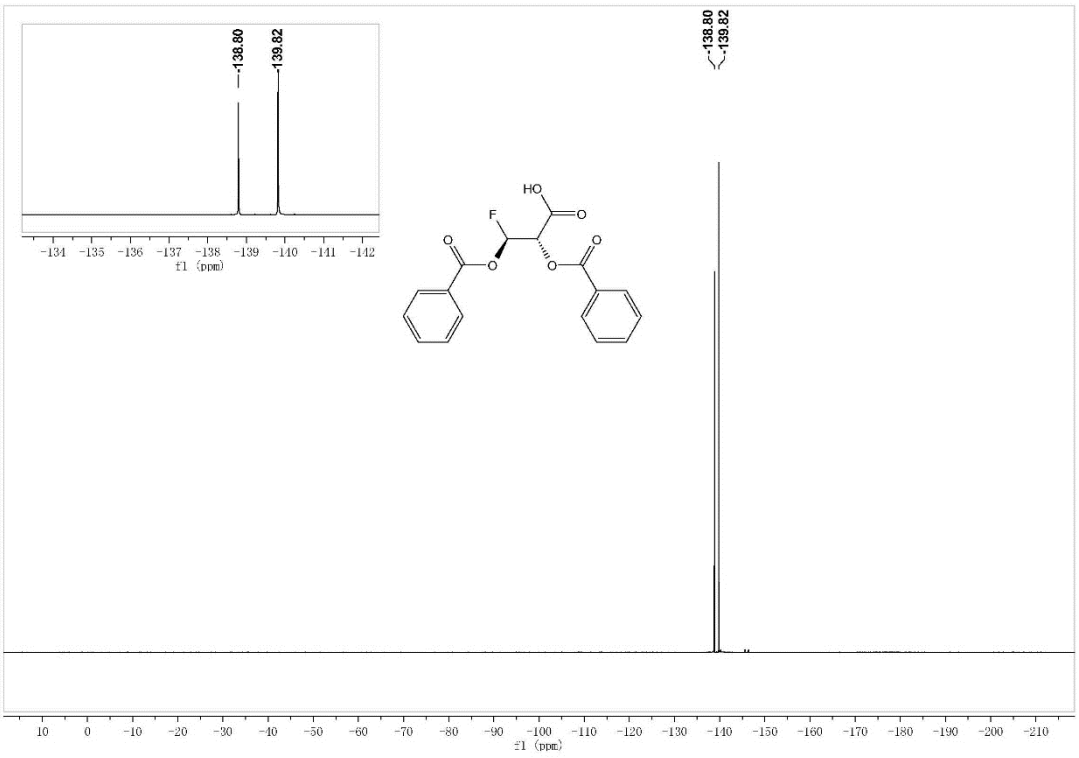
^{1}H NMR of 2,3-bis(benzoyloxy)-3-fluoropropanoic acid (**2s**)



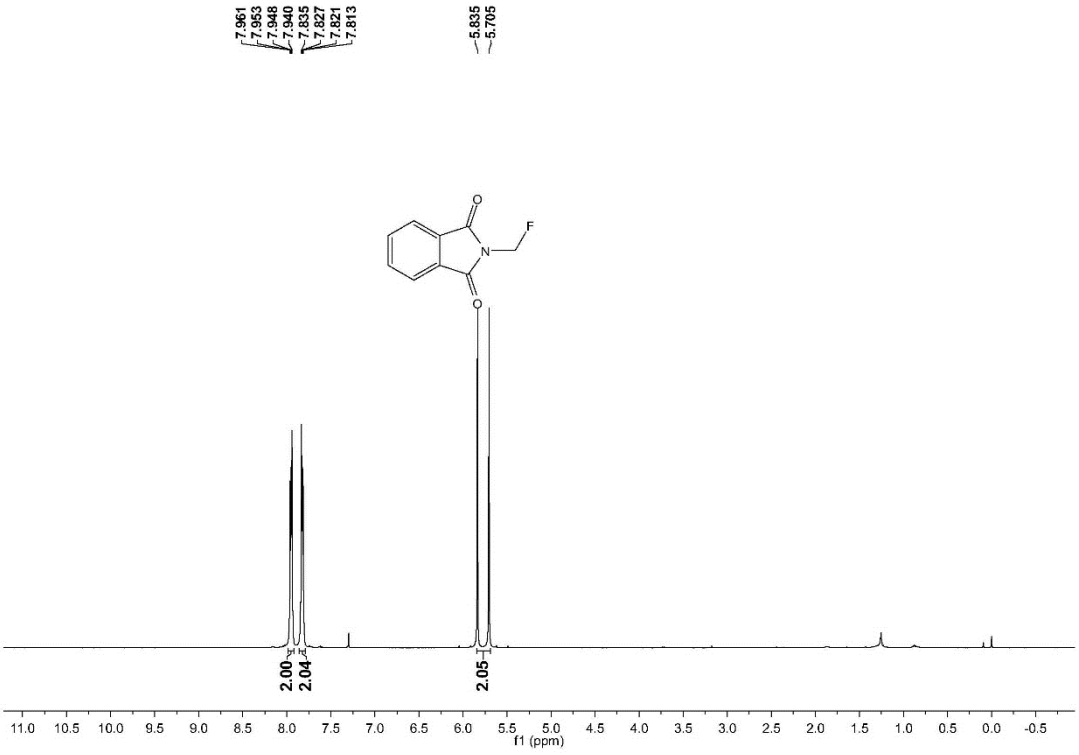
^{13}C NMR of 2,3-bis(benzoyloxy)-3-fluoropropanoic acid (**2s**)



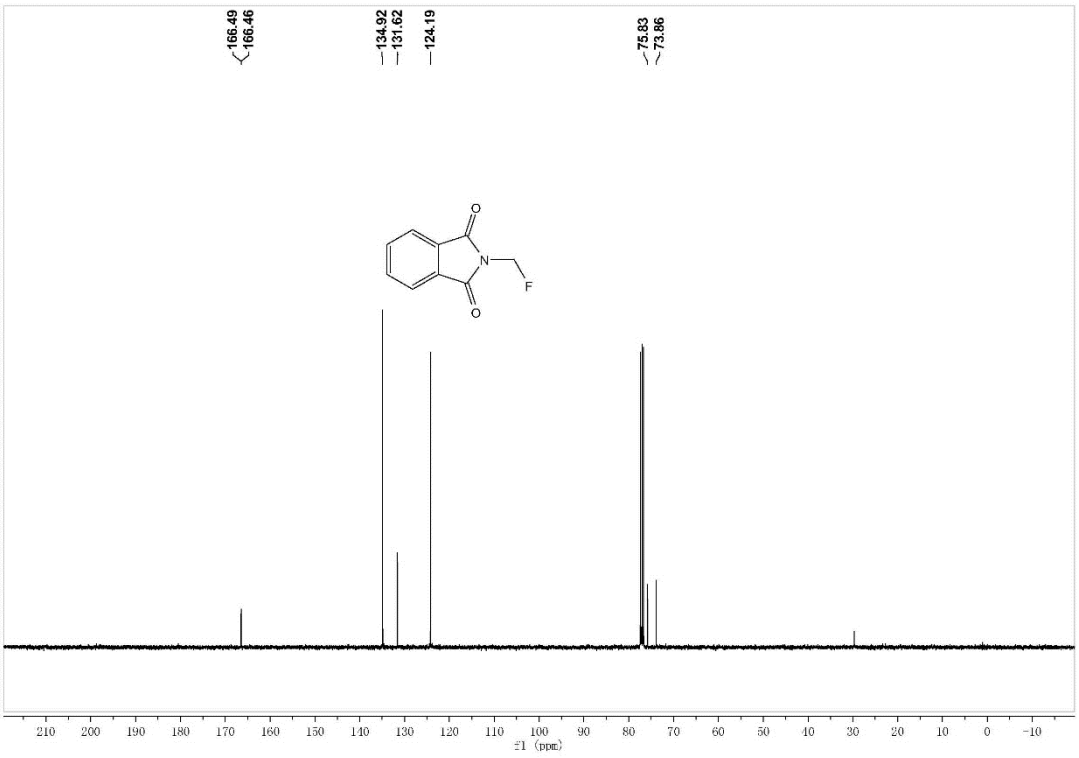
^{19}F NMR of 2,3-bis(benzoyloxy)-3-fluoropropanoic acid (**2s**)



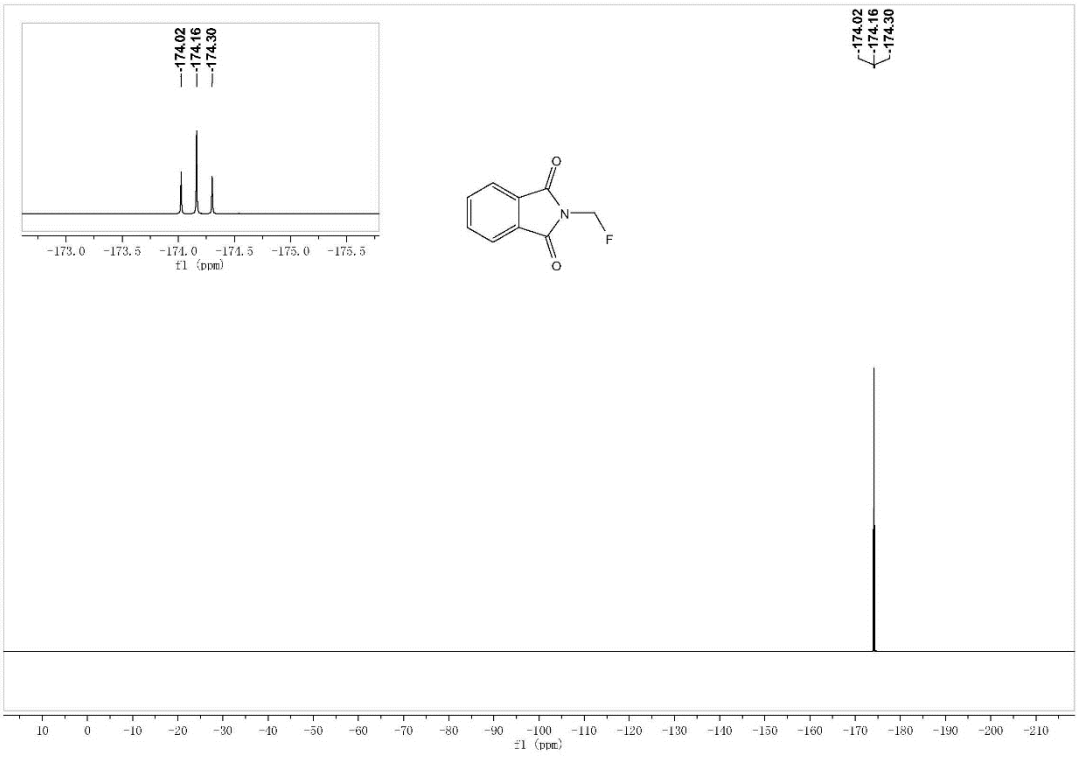
^{1}H NMR of 2-(fluoromethyl)isoindoline-1,3-dione (**2t**)



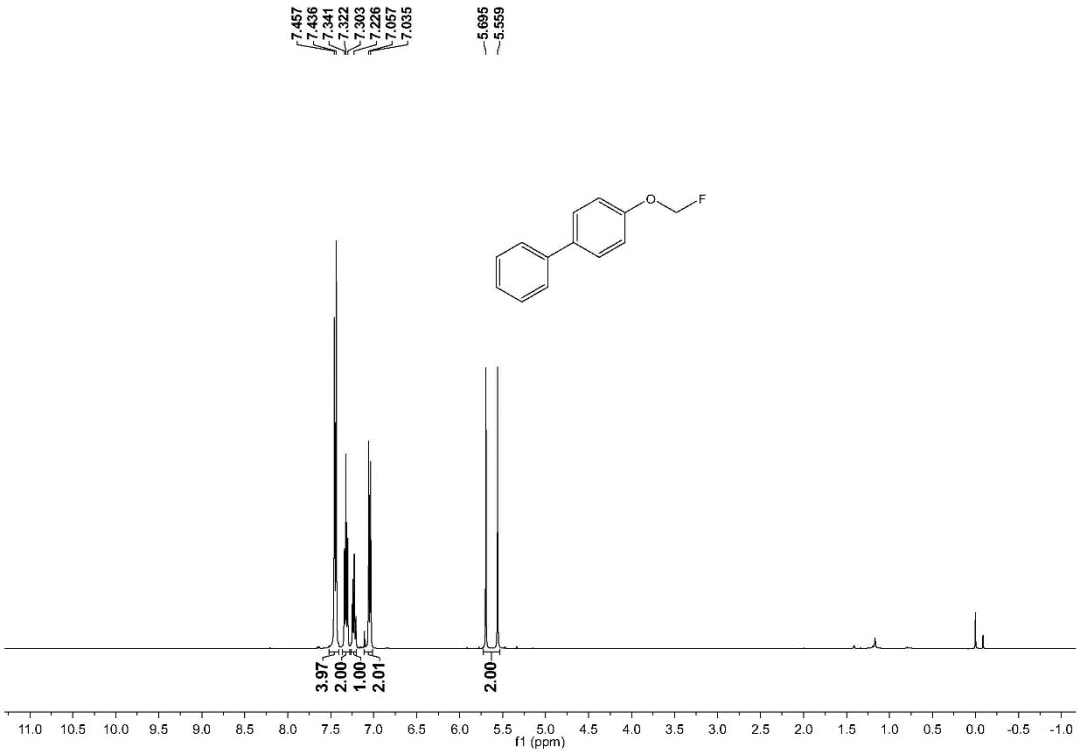
^{13}C NMR of 2-(fluoromethyl)isoindoline-1,3-dione (**2t**)



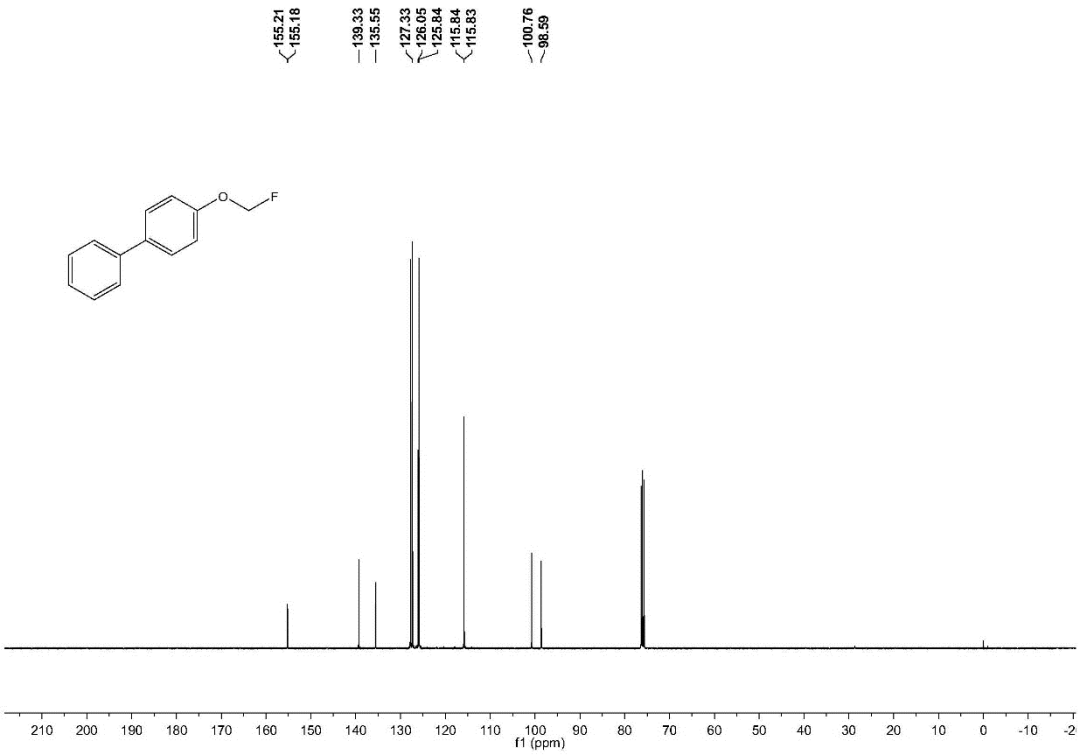
^{19}F NMR of 2-(fluoromethyl)isoindoline-1,3-dione (**2t**)



^{1}H NMR of 4-(fluoromethoxy)-1,1'-biphenyl (**2u**)

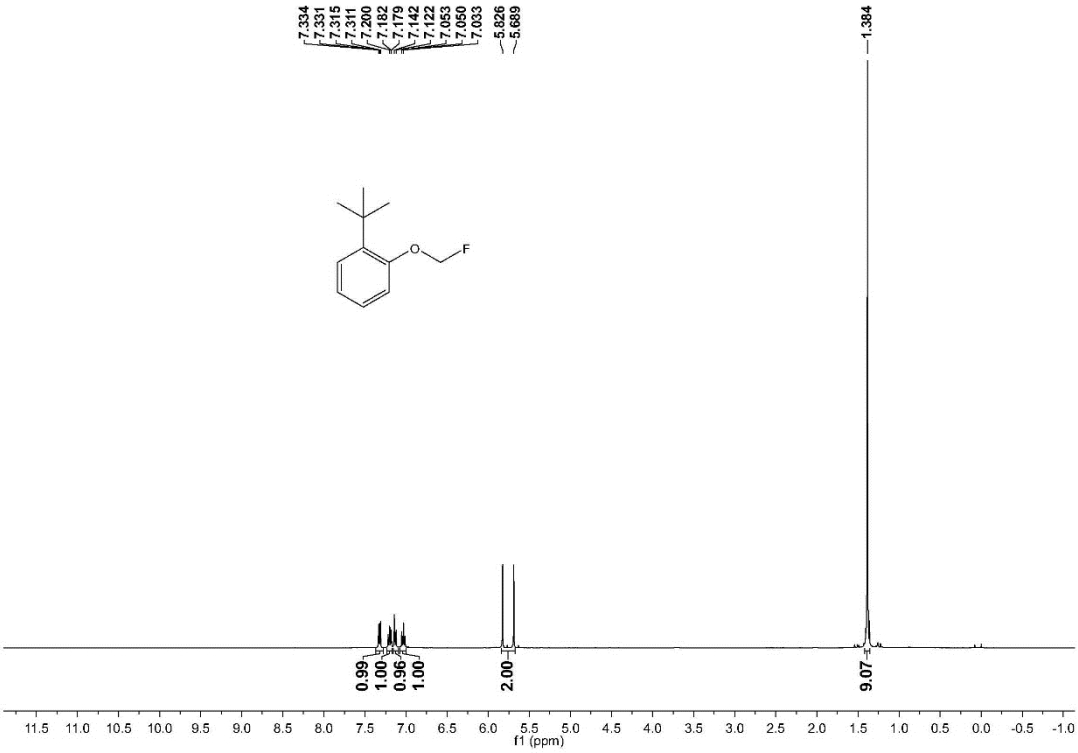


^{13}C NMR of 4-(fluoromethoxy)-1,1'-biphenyl (**2u**)

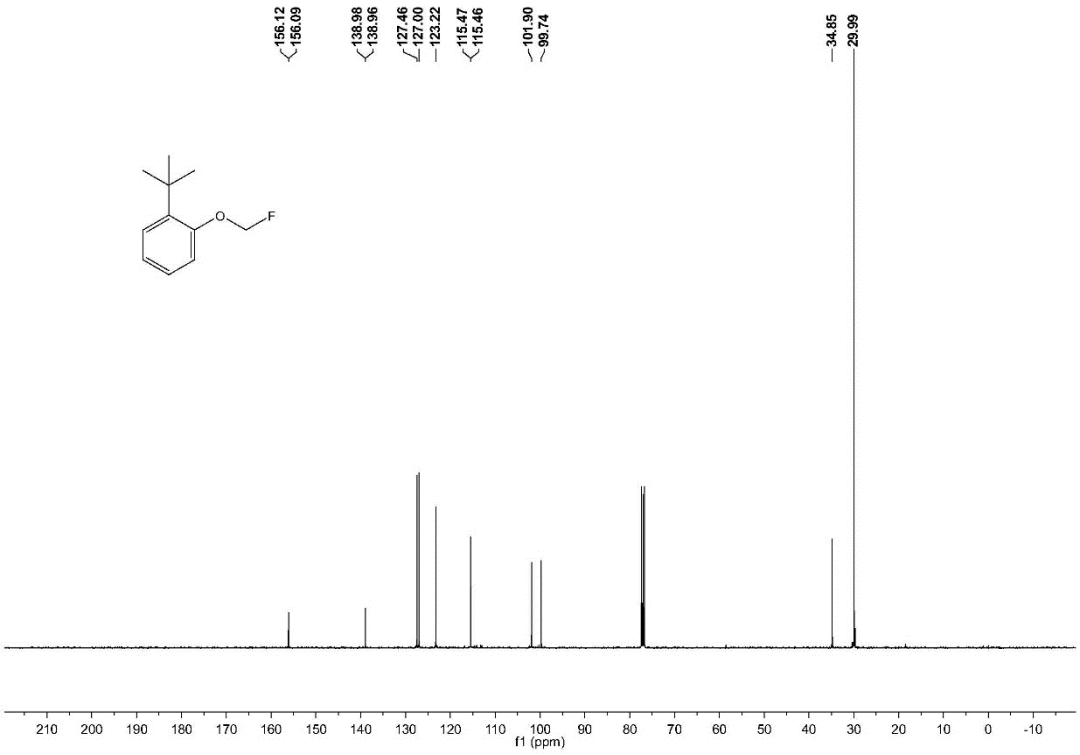


^{19}F NMR of 4-(fluoromethoxy)-1,1'-biphenyl (**2u**)

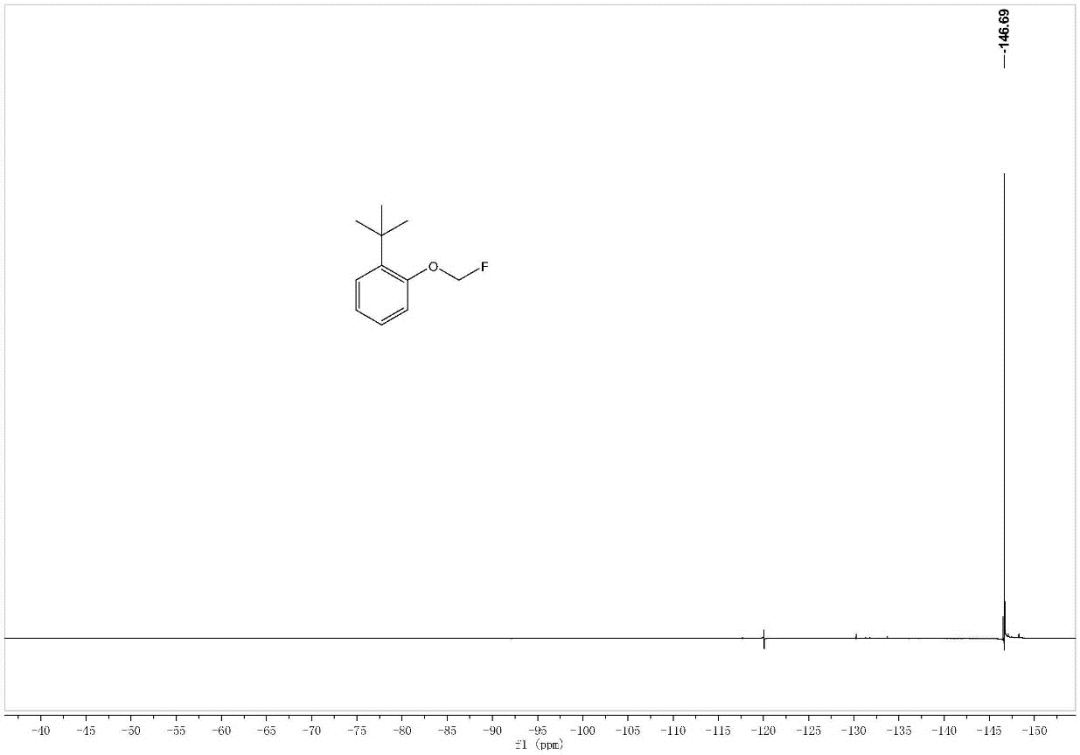
^{1}H NMR of 1-tert-butyl-2-(fluoromethoxy)benzene (**2v**)



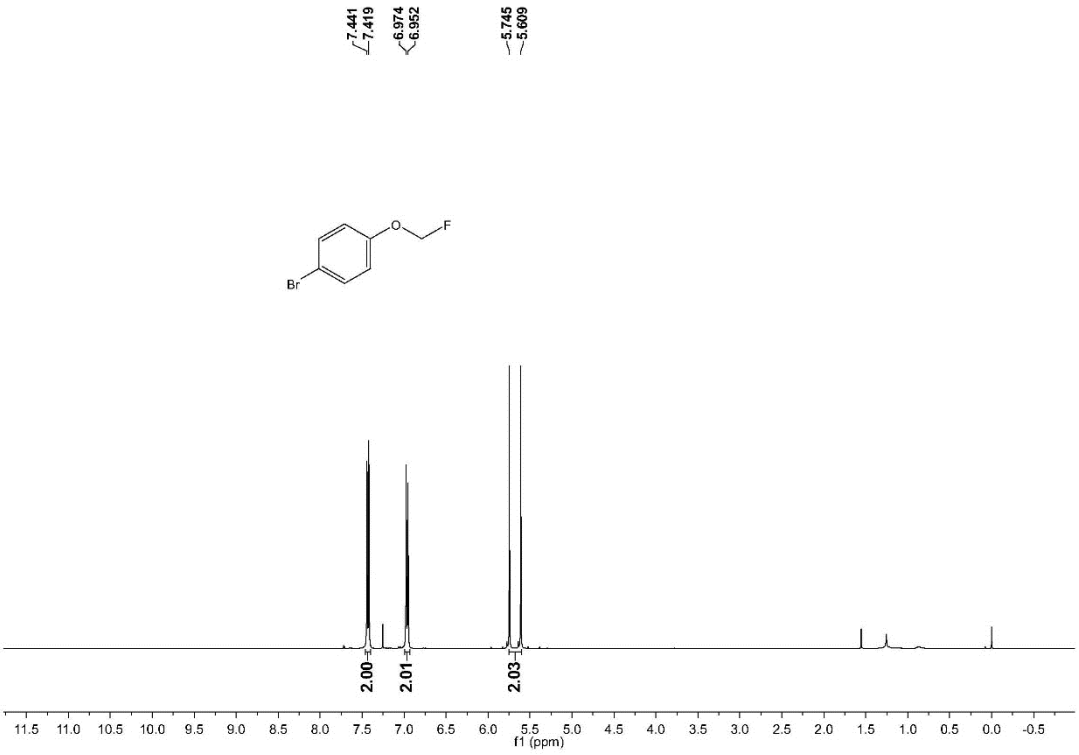
^{13}C NMR of 1-tert-butyl-2-(fluoromethoxy)benzene (**2v**)



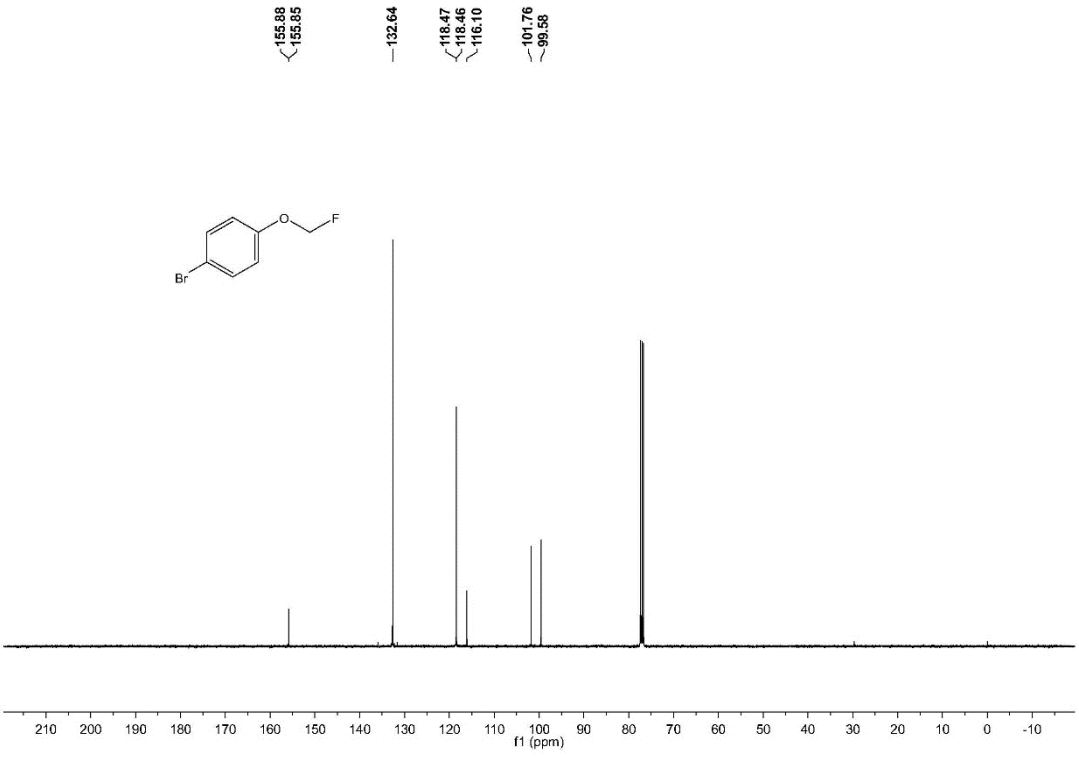
^{19}F NMR of 1-tert-butyl-2-(fluoromethoxy)benzene (**2v**)



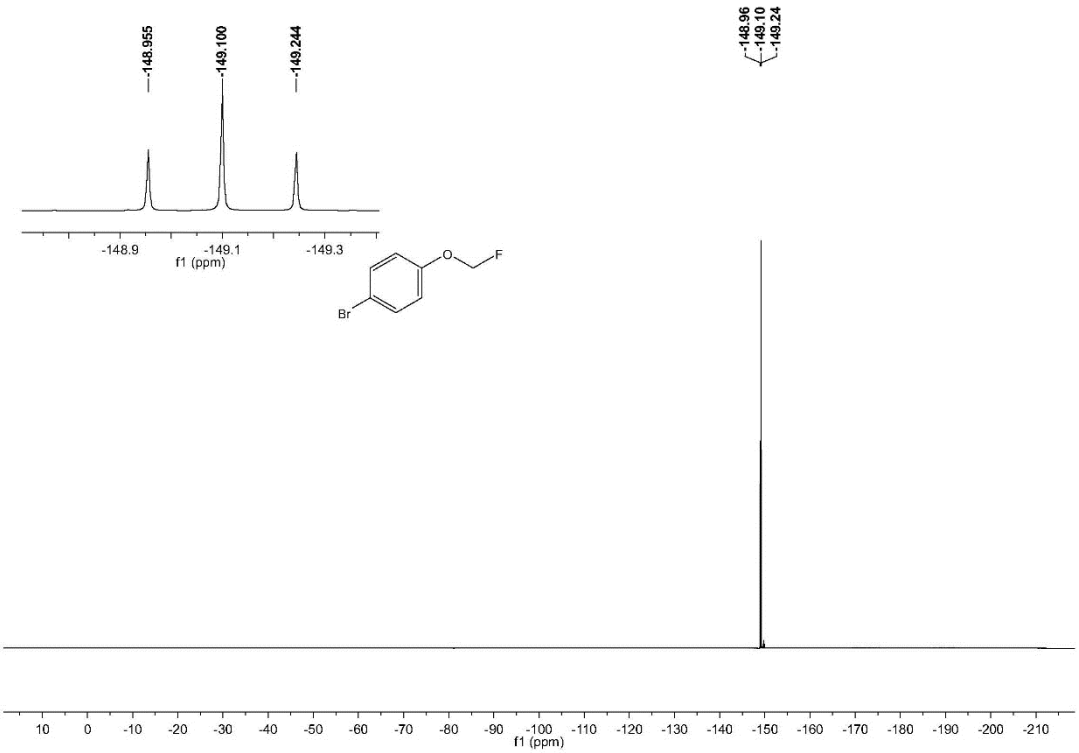
^{1}H NMR of 1-bromo-4-(fluoromethoxy)benzene (2**w**)



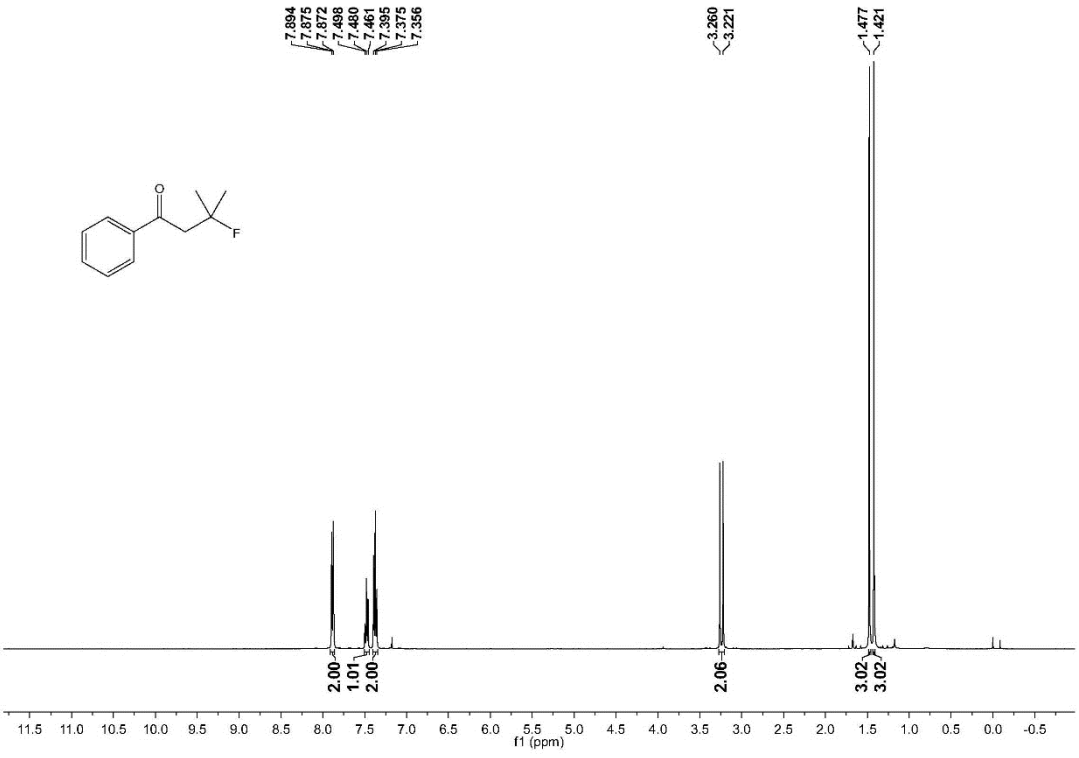
^{13}C NMR of 1-bromo-4-(fluoromethoxy)benzene (2**w**)



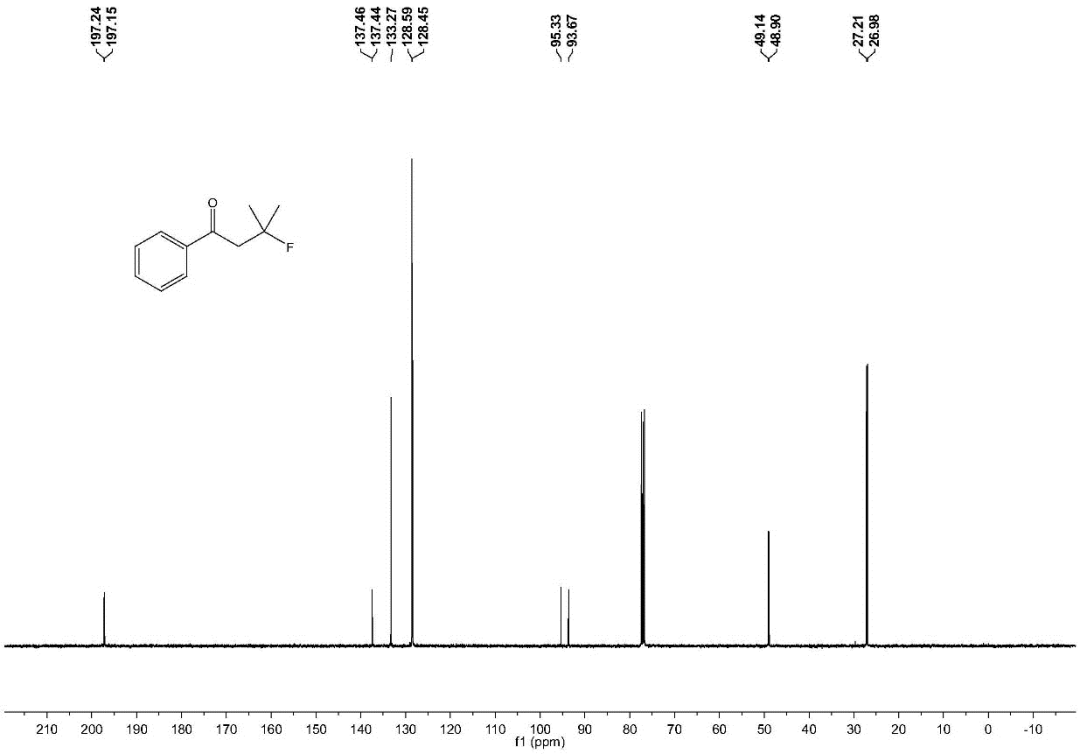
^{19}F NMR of 1-bromo-4-(fluoromethoxy)benzene (2**w**)



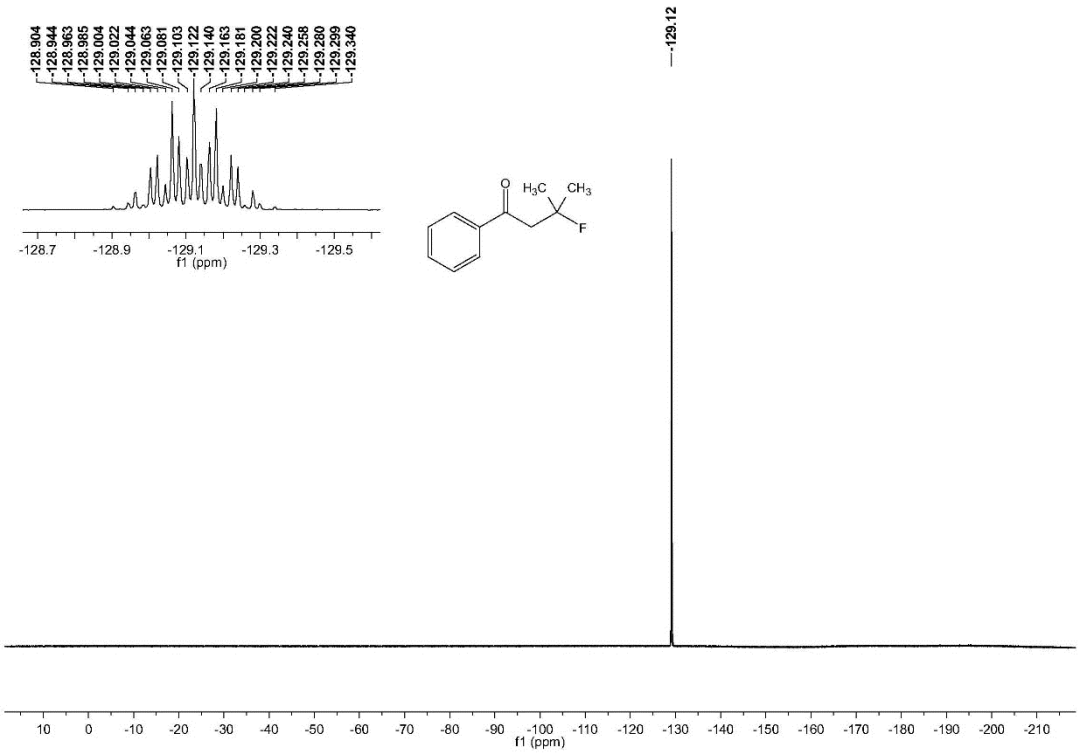
^{1}H NMR of 3-fluoro-3-methyl-1-phenylbutan-1-one (**2x**)



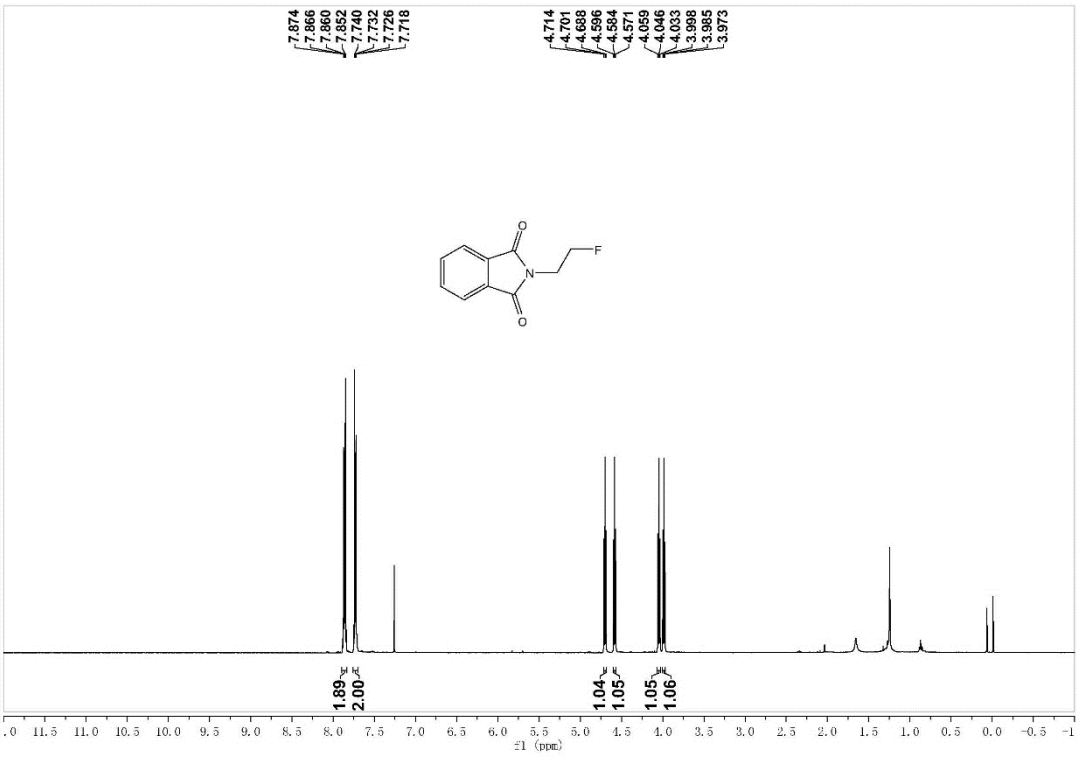
^{13}C NMR of 3-fluoro-3-methyl-1-phenylbutan-1-one (**2x**)



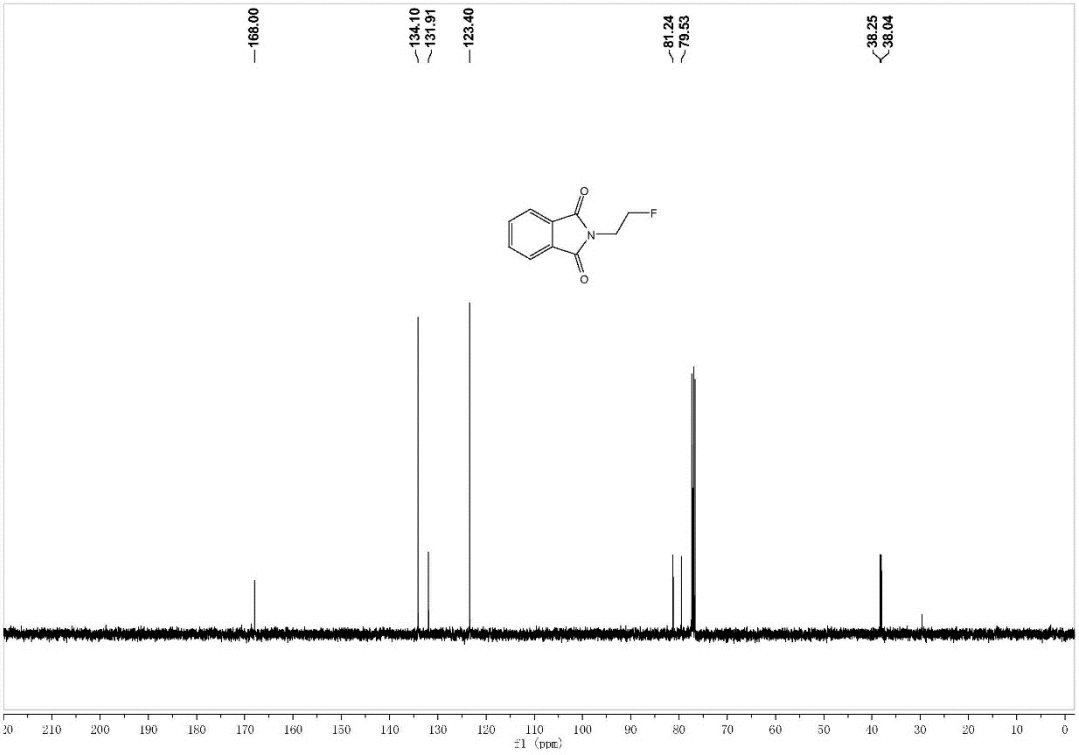
^{19}F NMR of 3-fluoro-3-methyl-1-phenylbutan-1-one (**2x**)



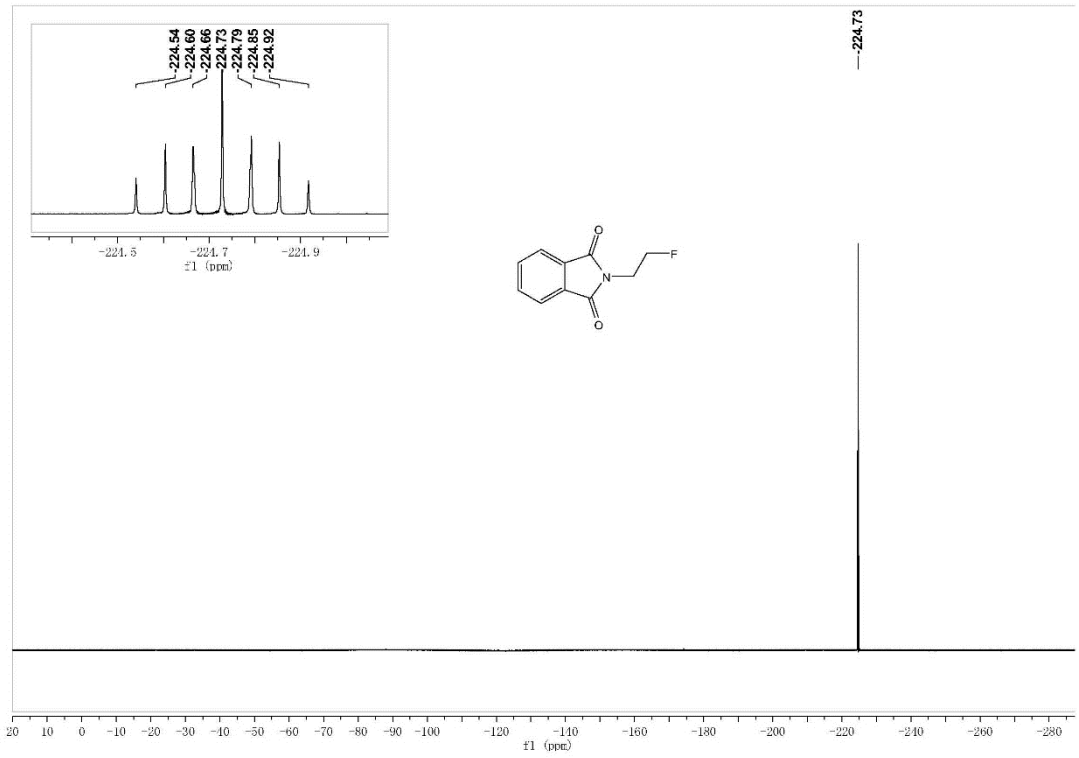
^{1}H NMR of 2-(2-fluoroethyl)isoindoline-1,3-dione (**2ya**)



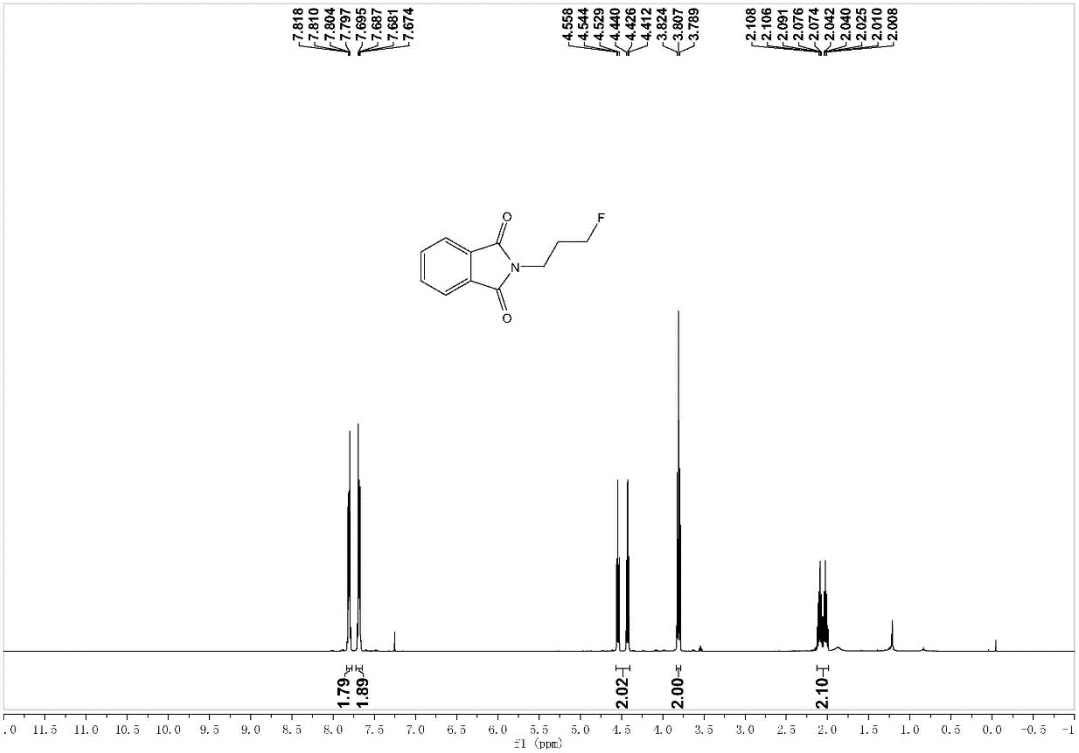
^{13}C NMR of 2-(2-fluoroethyl)isoindoline-1,3-dione (**2ya**)



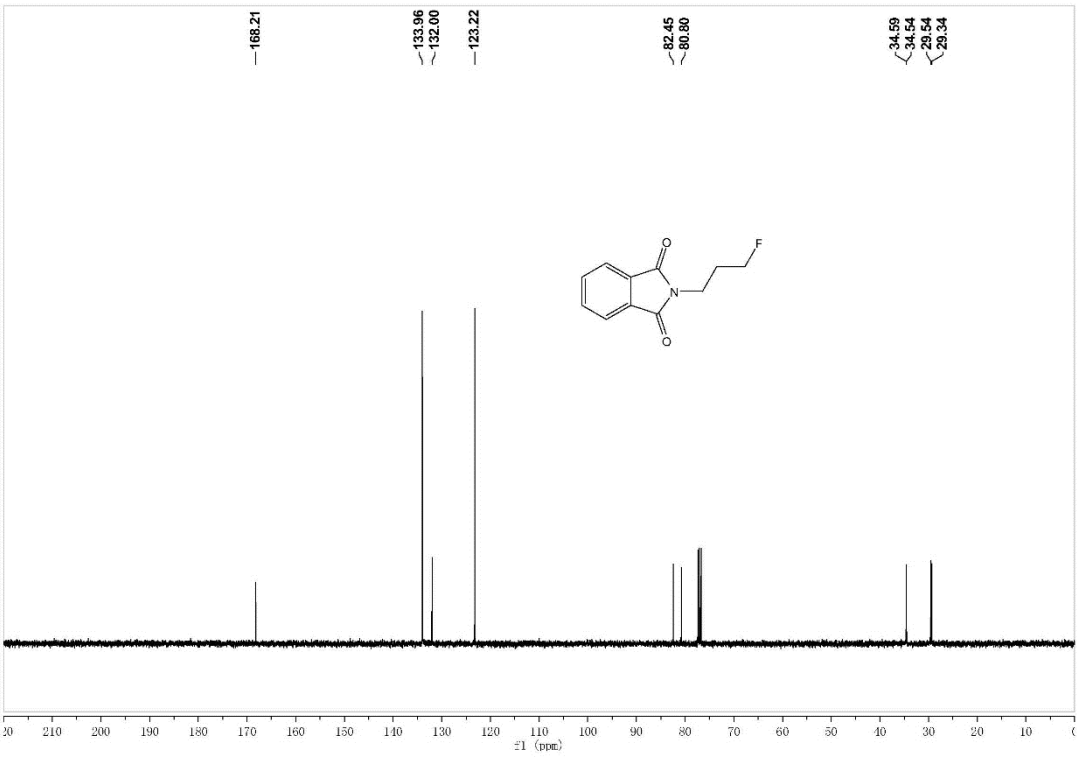
^{19}F NMR of 2-(2-fluoroethyl)isoindoline-1,3-dione (**2ya**)



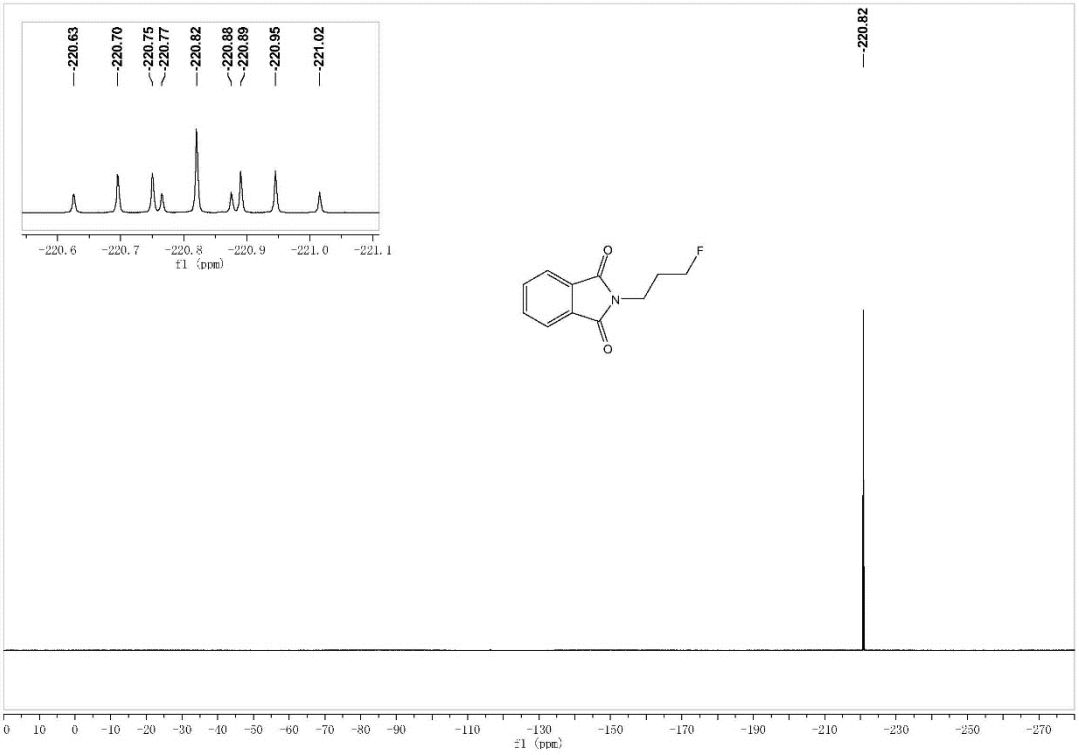
^{1}H NMR of 2-(3-fluoropropyl)isoindoline-1,3-dione (**2yb**)



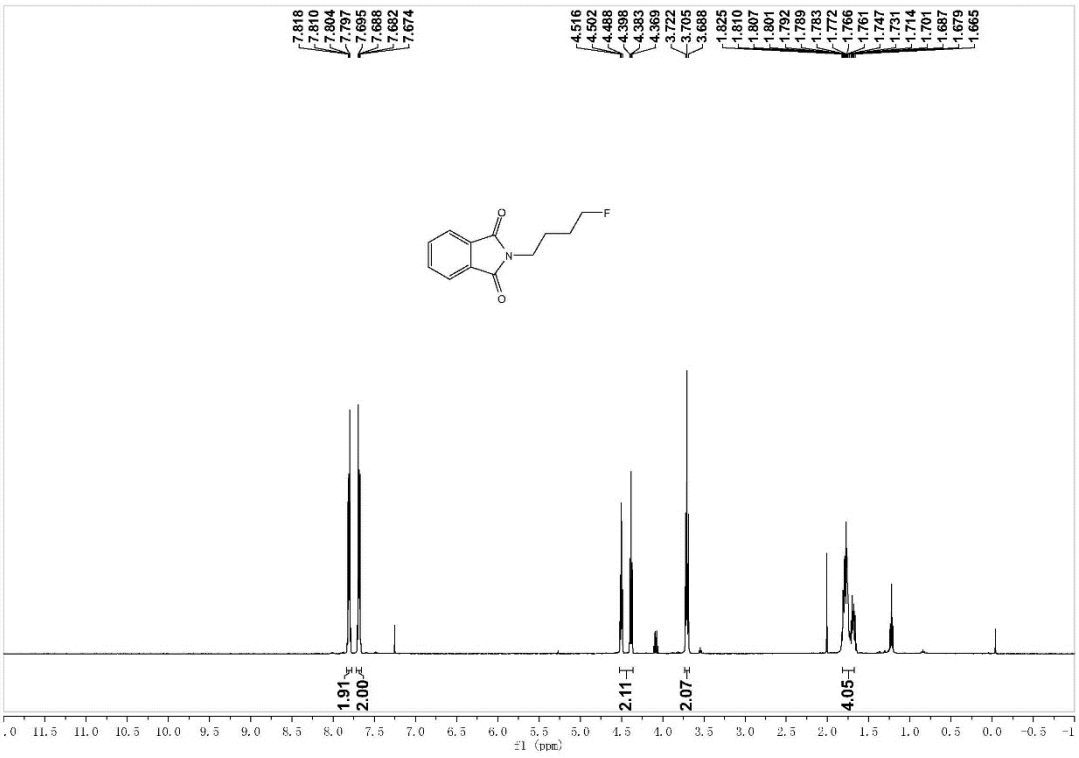
^{13}C NMR 2-(3-fluoropropyl)isoindoline-1,3-dione (**2yb**)



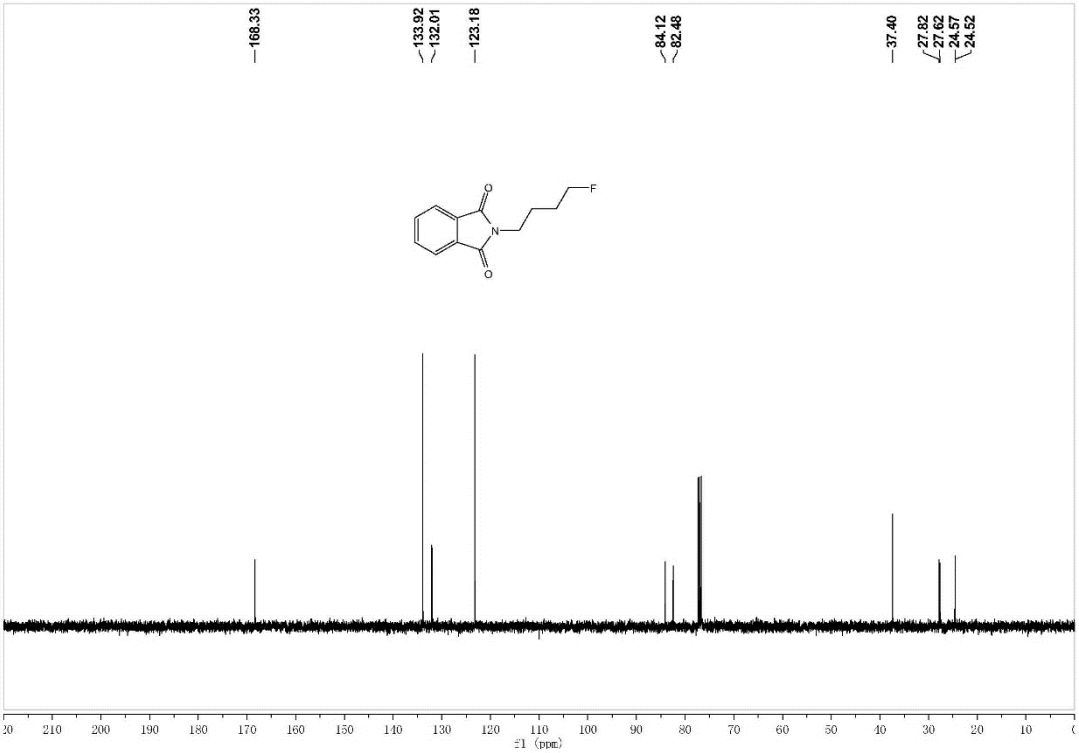
^{19}F NMR of 2-(3-fluoropropyl)isoindoline-1,3-dione (**2yb**)



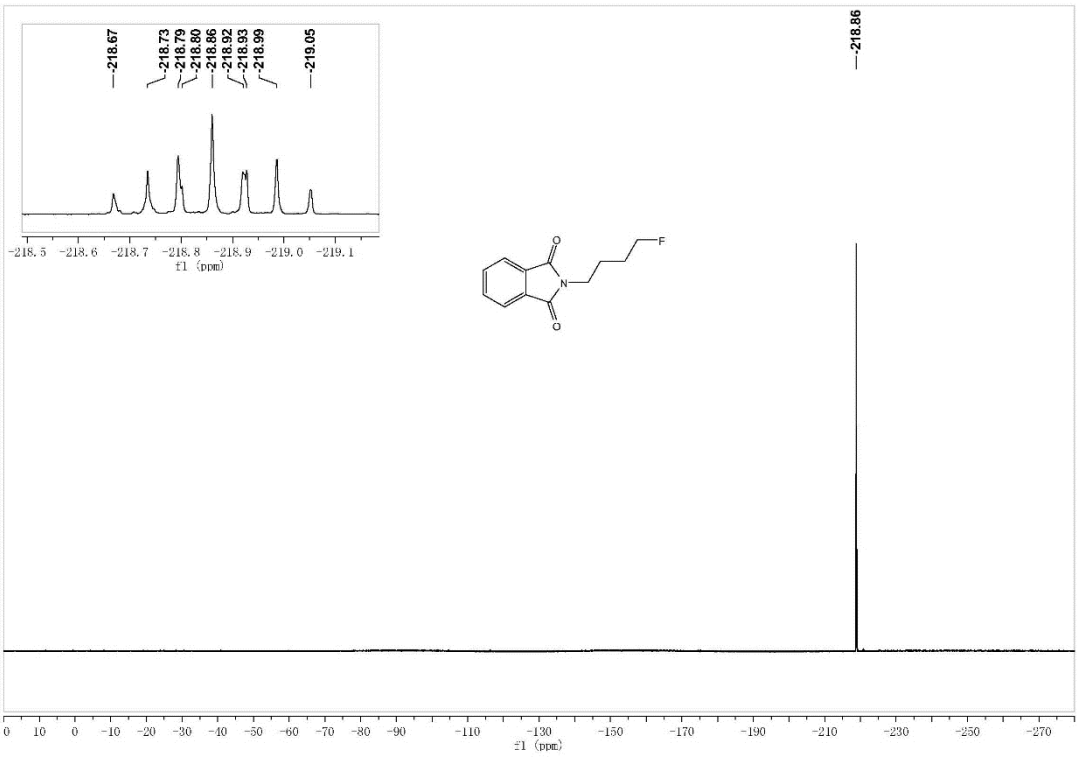
^{1}H NMR of 2-(4-fluorobutyl)isoindoline-1,3-dione (**2yc**)



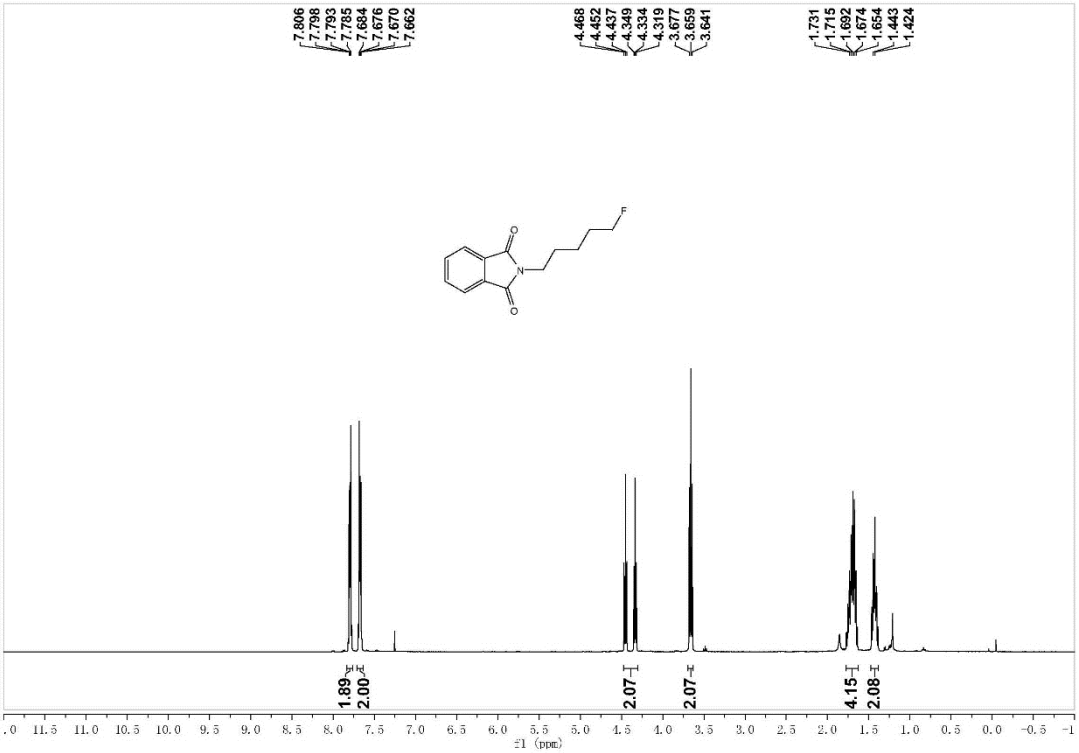
^{13}C NMR of 2-(4-fluorobutyl)isoindoline-1,3-dione (**2yc**)



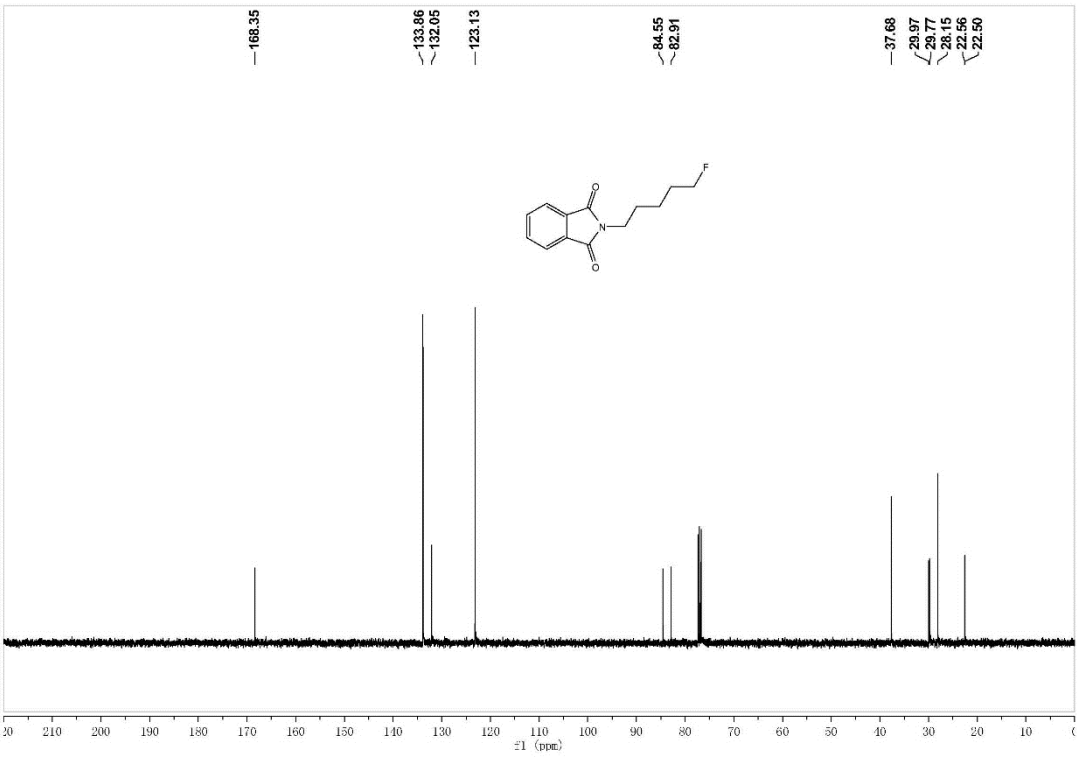
^{19}F NMR of 2-(4-fluorobutyl)isoindoline-1,3-dione (**2yc**)



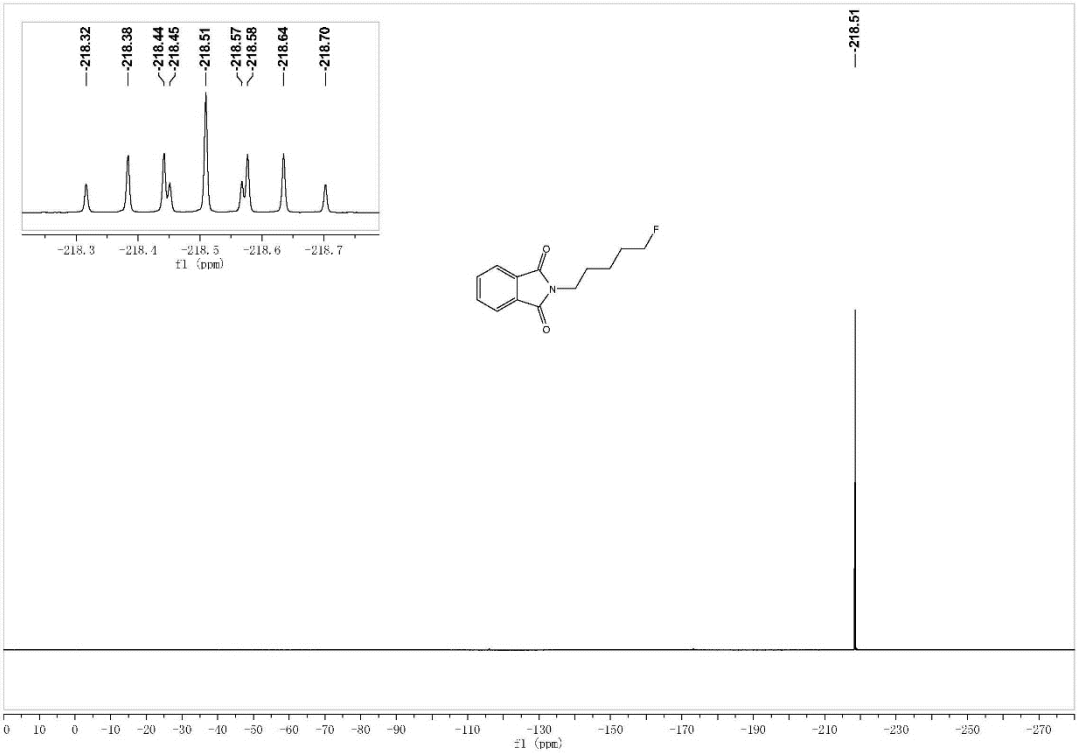
^{1}H NMR of 2-(5-fluoropentyl)isoindoline-1,3-dione (**2yd**)



^{13}C NMR of 2-(5-fluoropentyl)isoindoline-1,3-dione (**2yd**)

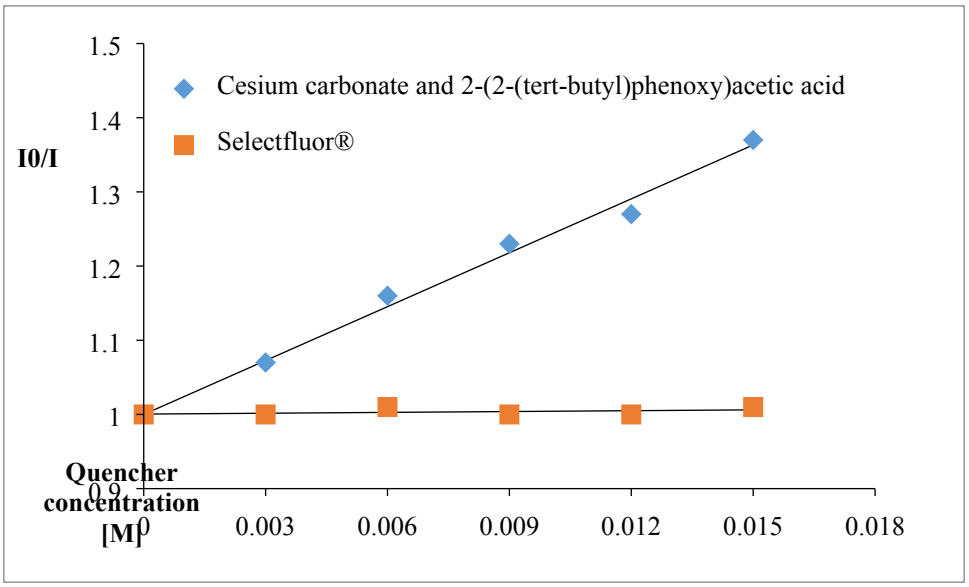


^{19}F NMR of 2-(5-fluoropentyl)isoindoline-1,3-dione (**2yd**)



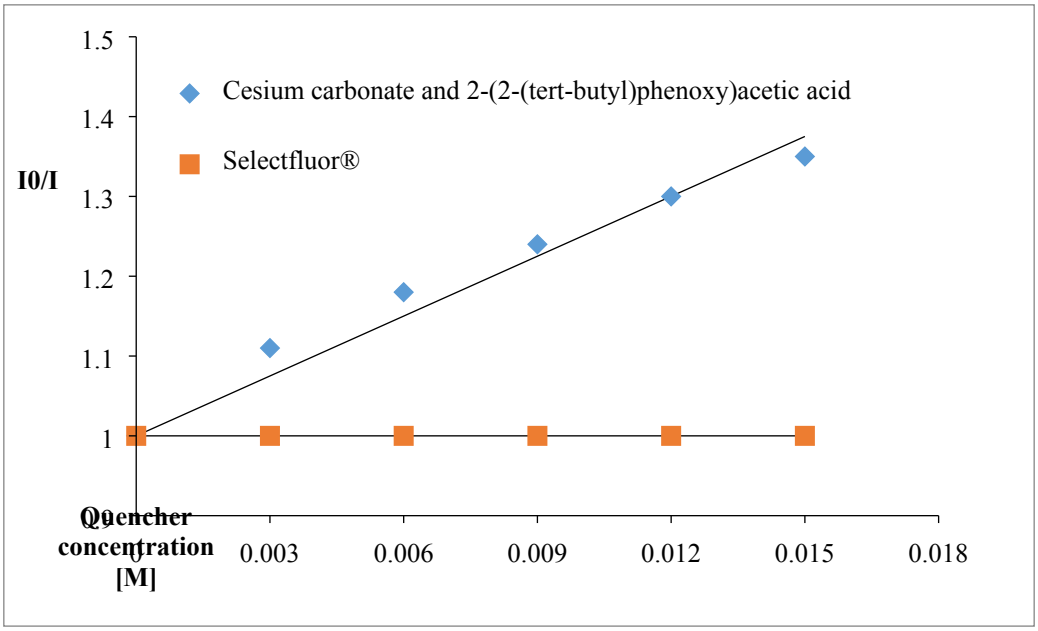
D: Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a Xenon flash lamp. All 9-mesityl-10-methylacridinium perchlorate solutions were excited at 430 nm and the emission intensity was collected at 550 nm. In a typical experiment, to a 9×10^{-5} M solution of 9-mesityl-10-methylacridinium perchlorate in CH_3CN/H_2O (1:1) was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



Scheme S1. 9-mesityl-10-methylacridinium perchlorate Emission Quenching by carboxylate and Selectfluor

Emission intensities were recorded using a Cary Eclipse Fluorescence Spectrophotometer. All Riboflavin solutions were excited at 440 nm and the emission intensity was collected at 520 nm. In a typical experiment, to a 3×10^{-5} M solution of Riboflavin in CH_3CN/H_2O (1:1) was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.



Scheme S2. Riboflavin Emission Quenching by carboxylate and Selectfluor