Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Visible light-induced monofluoromethylenation of heteroarenes with ethyl bromofluoroacetate

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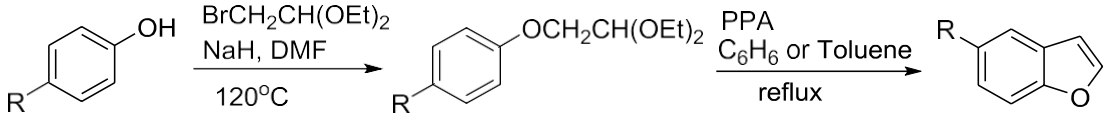
Experimental Section

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. ^{1}H and ^{19}F NMR ($CFCl_3$ as outside standard and low field is positive) spectra were recorded on a Agilent AM 400 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction.

Experimental procedures:

Preparation of substrates

Compounds **1a-c** and **1r** were purchased from commercial sources. Compounds **1d-q** were prepared according to the following procedure.[1]

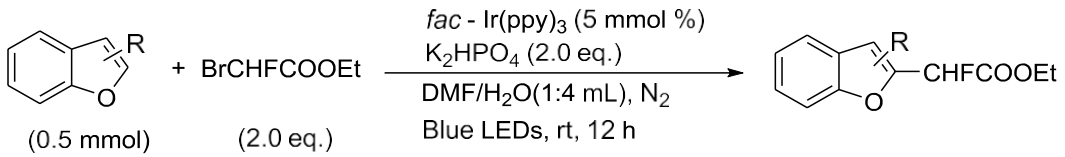


To a solution of phenol (30.0 mmol, 1.0 equiv.) in DMF (60 mL) at 0 ^{o}C, the NaH (1.32 g, 33 mmol, 1.1 equiv.) was added in the mixture slowly. Then 2-bromoacetaldehyde diethyl acetal (7.9 g, 36.0 mmol, 1.2 equiv.) was added dropwise to the reaction mixture and the reaction mixture was heated at 120 ^{o}C for 5 hours. After cooled to room temperature, ice-water was added and extracted by Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced vacuum. The residue was purified by silica gel column chromatography to provide the aryl ether intermediate. Then the aryl ether (15 mmol) and polyphosphoric acid (3.36 g) were combined in 100 mL of benzene and brought to reflux for 5 hours. The reaction mixture was cooled to room temperature, decanted from the polyphosphoric acid, concentrated under reduced pressure. The residue was purified by silica gel column chromatography to provide the desired product

Reference:

[1] W. L. Cody, D. D. Holsworth, N. L. Powell, M. Jalaie, E.-L. Zhang, W. Wang, B. Samas, J. Bryant, R. Ostroski, M. J. Ryan and J. J. Edmunds, *Bio. Med. Chem.*, 2005, **13**, 59.

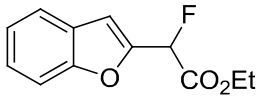
General experimental procedure for preparation of α-fluoro-α-heteroarylacetates:



A 50 mL Schlenk flask equipped with a rubber septum and a magnetic stir bar was charged with *fac*-Ir(ppy)$_3$ (16.4 mg, 0.025 mmol, 5 mol %), K_2HPO_4 (174.1 mg, 1.0 mmol, 2.0 equiv), ethyl bromofluoroacetate (184.9 mg, 1.0 mmol, 2.0 equiv), and heteroarene (0.5 mmol, 1.0 equiv). DMF (1.0 mL) and H_2O (4.0 mL) were added to the mixture. Then, the reaction mixture was degassed three times by the freeze-pump-thaw procedure. The flask was placed at a distance of 2 cm from the blue LEDs. The mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 12 h. After the reaction was complete, the reaction mixture was extracted by Et_2O, and the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel to give the corresponding product.

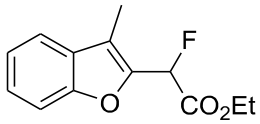
Characterization Data of Products

Ethyl 2-(benzofuran-2-yl)-2-fluoroacetate (2a)



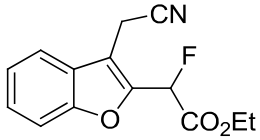
Yield = 62% (69.8 mg); Colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.62-7.60 (m, 1H), 7.52-7.50 (m, 1H), 7.38-7.34 (m, 1H), 7.28-7.25 (m, 1H), 6.95 (d, *J* = 4.3 Hz, 1H), 5.93 (d, *J* = 48.3 Hz, 1H), 4.39-4.29 (m, 2H), 1.31 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -177.01 (dd, *J* = 48.8 Hz, *J* = 5.6 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$):** δ 166.1 (d, *J* = 27.8 Hz), 155.4 (d, *J* = 1.1 Hz), 127.2 (d, *J* = 2.3 Hz), 125.8 (d, *J* =1.8 Hz), 123.8, 121.8 (d, *J* = 1.8 Hz), 111.8, 108.6 (d, *J* = 6.9 Hz), 82.6 (d, *J* = 185.5 Hz), 62.4, 14.0; **IR (thin film)** ***v*** 2930, 1764, 1475, 1452, 752 cm^{-1}; **Ms (EI)**: *m/z* 222 [M^+]; **HRMS EI**: [M^+], $C_{12}H_{11}FO_3$; Calculated for 222.0692; Found: 222.0688.

Ethyl 2-fluoro-2-(3-methylbenzofuran-2-yl)acetate (2b)



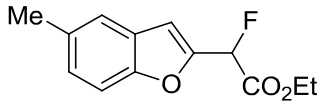
Yield: 76% (89.6 mg); Pale yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.56-7.54 (m, 1H), 7.48-7.45 (m, 1H), 7.38-7.34 (m, 1H), 7.29-7.25 (m, 1H), 5.98 (d, *J* = 47.9 Hz, 1H), 4.40-4.26 (m, 2H), 2.34 (d, *J* = 4.3 Hz, 3H), 1.29 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.88 (m, 1F), **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.4 (d, *J* = 29.3 Hz), 154.4 (d, *J* = 2.0 Hz), 144.3 (d, *J* = 19.9 Hz), 129.9 (d, *J* = 2.9 Hz), 125.9 (d, *J* = 2.5 Hz), 122.8. 120.1 (d, *J* = 2.4 Hz), 118.0 (d, *J* = 6.8 Hz), 111.7 (d, *J* = 1.4 Hz), 81.0 (d, *J* = 185.1 Hz), 62.3, 14.0, 7.8 (d, *J* = 1.2 Hz); **IR (thin film)** ***v*** 2983, 1765, 1613, 1453, 749 cm^{-1}; **Ms (EI)**: *m/z* 236 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{13}H_{13}FO_3$ 236.0849; Found: 236.0843.

Ethyl 2-(3-(cyanomethyl)benzofuran-2-yl)-2-fluoroacetate (2c)



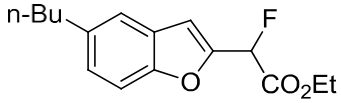
Yield: 77% (101.0 mg); Yellow liquid; **^{1}H NMR(400 MHz, $CDCl_3$)**: δ 7.73-7.71 (m, 1H), 7.55-7.53 (m, 1H), 7.46-7.42 (m, 1H), 7.39-7.35 (m, 1H), 6.03 (d, *J* = 46.7 Hz, 1H), 4.43-4.27 (m, 2H), 3.90 (d, *J* = 2.3 Hz, 2H), 1.31 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -181.06 (d, *J* = 45.8 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 165.6 (d, *J* = 28.8 Hz), 154.3 (d, *J* = 1.3 Hz), 145.8 (d, *J* = 22.7 Hz), 126.8 (d, *J* = 1.6 Hz), 126.5 (d, *J* = 1.8 Hz), 123.9, 119.8 (d, *J* = 1.7 Hz), 115.4 (d, *J* = 2.4 Hz), 112.1, 110.5 (d, *J* = 4.5 Hz), 81.6 (d, *J* = 186.1 Hz), 62.9, 14.0, 12.4; **IR (thin film)** ***v*** 2983, 1763, 1613, 1453, 750 cm^{-1}; **Ms (EI)**: *m/z* 261 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{14}H_{12}FNO_3$ 261.0801; Found: 261.0806.

Ethyl 2-fluoro-2-(5-methylbenzofuran-2-yl)acetate (2d)



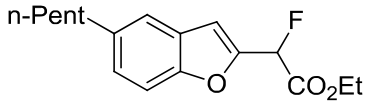
Yield: 60% (71.3 mg); Pale yellow liquid; **^{1}H NMR(400 MHz, $CDCl_3$)**: δ 7.40-7.38 (m, 2 H), 7.18-7.15 (m, 1H), 6.87 (d, *J* = 4.7 Hz, 1H), 5.90 (d, *J* = 48.3 Hz, 1H), 4.38-4.29 (m, 2H), 2.4 (s, 3H), 1.31 (t, *J* = 7.5 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -176.67 (dd, *J* = 49.6 Hz, *J* = 4.8 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)** δ 166.2 (d, *J* = 28.0 Hz), 153.8 (d, *J* = 1.1 Hz), 149.0 (d, *J* = 21.0 Hz), 132.8, 127.3 (d, *J* = 1.9 Hz), 127.2 (d, *J* = 2.7 Hz), 121.5 (d, *J* = 1.4 Hz), 111.2 (d, *J* = 1.5 Hz), 108.4 (d, *J* = 7.0 Hz), 82.7 (d, *J* = 185.3 Hz), 62.3, 21.2, 14.0; **IR (thin film) *v*** 2924, 2924, 1765, 1475, 731 cm^{-1}; **Ms (EI)**: *m/z* 236 [M$^+$]; **HRMS EI**: [M$^+$], Calculated for $C_{13}H_{13}FO_3$ 236.0849; Found: 236.0852.

Ethyl 2-fluoro-2-(5-pentylbenzofuran-2-yl)acetate (2e)



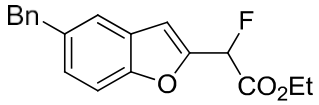
Yield: 68% (94.9 mg); Pale yellow liquid; **^{1}H NMR(400 MHz, $CDCl_3$):** δ 7.42-7.39 (m, 2H), 7.19-7.17 (m, 1H), 6.88 (d, *J* = 4.3 Hz, 1H), 4.40-4.27 (m, 2H), 2.71 (t, *J* = 7.5 Hz, 2H), 1.66-1.58 (m, 2H), 1.38-1.29 (m, 5H), 0.93 (t, *J* = 7.5 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.58 (dd, *J* = 48.5 Hz, *J* = 5.2 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.2 (d, *J* = 27.6 Hz), 154.0 (d, *J* = 1.8 Hz), 149.5 (d, *J* = 21.1 Hz), 138.1, 127.3 (d, *J* = 2.6 Hz), 126.6 (d, *J* = 2.3 Hz), 120.9 (d, *J* = 1.5 Hz), 111.3 (d, *J* = 1.6 Hz), 108.5 (d, *J* = 5.3 Hz), 82.7 (d, *J* = 184.8 Hz), 62.3, 35.4, 24.1, 22.0, 14.0, 13.9; **IR (thin film) *v*** 2930, 1766, 1471, 1445, 729 cm^{-1}; **Ms (EI)**: *m/z* 278 [M$^+$]; **HRMS EI**: [M$^+$], Calculated for $C_{16}H_{19}FO_3$ 278.1318; Found: 278.1310.

Ethyl 2-fluoro-2-(5-pentylbenzofuran-2-yl)acetate (2f)



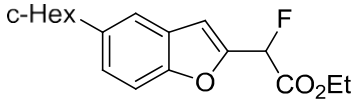
Yield: 63% (91.5 mg); Yellow liquid; **^{1}H NMR(400 MHz, $CDCl_3$)** δ 7.41-7.39 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.88 (d, *J* = 3.9 Hz, 1H), 5.90 (d, *J* = 48.3 Hz, 2H), 4.35-4.31 (m, 2H), 2.70-2.66 (m, 2H), 1.65-1.60 (m, 3H), 1.32-1.29 (m, 7H), 0.89 (t, *J* = 6.3 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.57 (dd, *J* = 46.6 Hz, *J* = 3.3 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.2 (d, *J* = 27.6 Hz), 154.0 (d, *J* = 1.4 Hz), 149.0 (d, *J* = 21.6 Hz), 138.1, 127.3 (d, *J* = 2.8 Hz), 126.6 (d, *J* = 2.7 Hz), 120.9 (d, *J* = 1.9 Hz), 111.3, 108.5 (d, *J* = 5.9 Hz), 82.7 (d, *J* = 185.4 Hz), 62.3, 35.7, 31.6, 31.4, 22.5, 14.0; **IR (thin film) *v*** 2929, 2857, 1766, 1445, 730 cm^{-1}; **Ms (EI)**: *m/z* 292 [M$^+$]; **HRMS EI**: [M$^+$], Calculated for $C_{17}H_{21}FO_3$, 292.1475; Found: 292.1474.

Ethyl 2-(5-benzylbenzofuran-2-yl)-2-fluoroacetate (2g)



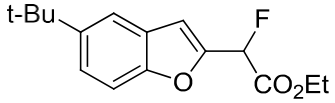
Yield: 68% (105.4 mg); White solid; M.P.: 82-84 ^{o}C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.73-7.40 (m, 2H), 7.30-7.25 (m, 2H), 7.20-7.18 (m, 4H), 6.87 (d, *J* = 4.7 Hz, 1H), 5.89 (d, *J* = 47.9 Hz, 1H), 4.37-4.28 (m, 2H), 4.06 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.85 (dd, *J* = 49.6 Hz, *J* = 5.6 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.1 (d, *J* = 27.8 Hz), 154.2 (d, *J* = 2.6 Hz), 149.2 (d, *J* = 20.8 Hz), 141.3, 136.4, 128.8, 128.5, 127.4 (d, *J* = 4.4 Hz), 127.1 (d, *J* = 2.0 Hz), 126.1, 121.7 (d, *J* = 1.3 Hz), 111.6 (d, *J* = 1.6 Hz), 108.6 (d, *J* = 6.0 Hz), 82.6 (d, *J* = 185.5 Hz), 62.4, 41.7, 14.0; **IR (thin film) *v*** 2983, 1764, 1602, 1494, 734 cm^{-1}; **Ms (EI)**: *m/z* 312 [M$^+$]; **HRMS EI**: [M$^+$], Calculated for $C_{19}H_{17}FO_3$ 312.1162; Found: 312.1157.

Ethyl 2-(5-cyclohexylbenzofuran-2-yl)-2-fluoroacetate (2h)



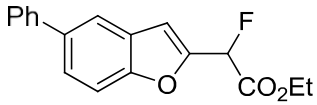
Yield: 50% (76.8 mg); Pale yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43-7.41 (m, 2H), 7.25-7.20 (m, 1H), 6.90 (d, *J* = 3.9 Hz, 1H), 5.90 **(**d, *J* = 47.9 Hz, 1H**),** 4.39-4.26 (m, 2H), 2.61-2.55 (m, 2H), 1.90-1.84 (m, 5H), 1.49-1.36 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$):** δ -176.47 (dd, *J* = 49.2 Hz, *J* = 6.0 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.2 (d, *J* = 28.1 Hz), 154.0 (d, *J* = 1.6 Hz), 149.0 (d, *J* = 21.2 Hz), 143.5, 127.2 (d, *J* = 2.7 Hz), 125.3 (d, *J* = 1.4 Hz), 119.2 (d, *J* = 1.2 Hz), 111.3 (d, *J* = 1.5 Hz), 108.7 (d, *J* = 6.4 Hz), 82.7 (d, *J* = 185.9 Hz), 62.3, 44.5, 35.0, 26.9, 26.1, 14.0; **IR (thin film)** ***ν*** 2925, 2851, 1766, 1471, 1447 cm^{-1}; **Ms (EI)**: *m/z* 304 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{18}H_{21}FO_3$ 304.1475; Found: 304.1483.

Ethyl 2-(5-(tert-butyl)benzofuran-2-yl)-2-fluoroacetate (2i)



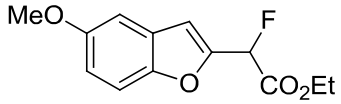
Yield: 77% (106.6 mg); Pale Yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (s, 1H), 7.43 (s, 2H), 6.90 (s, 1H), 5.91 (d, *J* = 47.9 Hz, 1H), 4.37-4.28 (m, 2H), 1.36 (s, 9H), 1.30 (t, *J* = 6.3 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.47 (dd, *J* = 47.7 Hz, *J* = 3.3 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.2 (d, *J* = 28.8 Hz), 153.7 (d, *J* = 1.5 Hz), 149.1 (d, *J* = 20.7 Hz), 146.5, 127.0 (d, *J* = 3.4 Hz), 123.9 (d, *J* = 1.6 Hz), 108.9 (d, *J* = 6.7 Hz), 82.7 (d, *J* = 185.2 Hz), 62.3, 34.7, 31.7, 14.0; **IR (thin film)** ***ν*** 2963, 1766, 1478, 1366, 751 cm^{-1}; **Ms (EI)**: *m/z* 278 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{16}H_{19}FO_3$ 278.1318; Found: 278.1313.

Ethyl 2-fluoro-2-(5-phenylbenzofuran-2-yl)acetate (2j)



Yield: 70% (104.3 mg); White solid; M.P.: 78-80 ^oC; **^{1}H NMR(400 MHz, $CDCl_3$)**: δ 7.79 (s, 1H), 7.61-7.57 (m, 4H), 7.47-7.43 (m, 2H), 7.37-7.33 (m, 1H), 6.99 (d, *J* = 4.3 Hz, 1H), 5.96 (d, *J* = 48.3 Hz, 1H), 4.42-4.29 (m, 2H), 1.33 (t, *J* = 7.5 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -177.25 (dd, *J* = 47.0 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.8 (d, *J* = 27.1 Hz), 154.9 (d, *J* = 1.8 Hz), 149.6 (d, *J* = 16.8 Hz), 141.2. 137.2, 128.8, 127.8 (d, *J* = 2.0 Hz), 127.4, 127.1, 125.6 (d, *J* = 1.7 Hz), 120.2 (d, *J* = 1.4 Hz), 111.9, 108.8 (d, *J* = 5.6 Hz), 82.6 (d, *J* = 185.2 Hz), 62.4, 14.0; **IR (thin film)** ***ν*** 2982, 1764, 1600, 1465, 1454, 763 cm^{-1}; **Ms (EI)**: *m/z* 298 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{18}H_{15}FO_3$ 298.1005; Found: 292.1011.

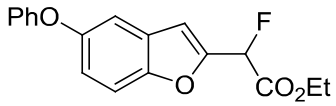
Ethyl 2-fluoro-2-(5-phenylbenzofuran-2-yl)acetate (2k)



Yield: 50% (62.4 mg); Pale yellow liquid; **^{1}H NMR(400 MHz, $CDCl_3$)**: δ 7.41-7.38 (m, 1H), 7.04-7.03 (m, 1H), 6.98-6.95 (m, 2H), 6.88 (d, *J* = 4.3 Hz, 1H), 5.90 (d, *J* = 47.9 Hz, 1H), 4.38-4.29 (m, 2H), 3.83 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -176.69 (dd, *J* = 48.1 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.1 (d, *J* = 27.7 Hz), 156.3, 150.4 (d, *J* = 2.1 Hz), 149.7 (d, *J* = 21.5 Hz), 127.8 (d, *J* = 3.0 Hz), 115.0 (d, *J* = 1.3 Hz), 112.3,

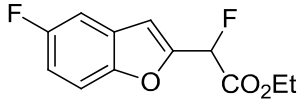
108.7 (d, *J* = 6.3 Hz), 103.7, 82.6 (d, *J* = 185.7 Hz), 62.4, 55.8, 14.0; **IR (thin film)** ***ν*** 2937, 1763, 1604, 1447, 733 cm^{-1}; **Ms (EI)**: *m/z* 252 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{13}H_{13}FO_4$ 252.0798; Found: 252.0795.

Ethyl 2-fluoro-2-(5-phenoxybenzofuran-2-yl)acetate (2l)



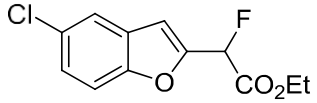
Yield: 55% (87 mg); Pale yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.49-7.47 (m, 1H), 7.34-7.32 (m, 2H), 7.22 (d, *J* = 1.9 Hz, 1H), 7.10-7.06 (m, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 4.3 Hz, 1H), 5.91 (d, *J* = 47.9 Hz, 1H), 4.40-4.30 (m, 2H), 1.33 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -177.44 (dd, *J* = 47.3 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 166.0 (d, *J* = 27.8 Hz), 158.2, 153.1, 151.8 (d, *J* = 2.3 Hz), 150.2 (d, *J* = 21.4 Hz), 129.7, 128.4 (d, *J* = 1.9 Hz), 122.9, 118.6 (d, *J* = 1.5 Hz), 118.1, 112.6, 111.6, 108.6 (d, *J* = 5.6 Hz), 82.6 (d, *J* = 186.4 Hz), 62.5, 14.0; **IR (thin film)** ***ν*** 2983, 1765, 1587, 1490, 750 cm^{-1}; **Ms (EI)**: *m/z* 314 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{18}H_{15}FO_4$ 314.0954; Found: 314.0959.

Ethyl 2-fluoro-2-(5-fluorobenzofuran-2-yl)acetate (2m)



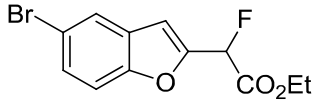
Yield: 48% (57.5 mg); Brown liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.46-7.43 (m, 1H), 7.28-7.25 (m, 1H), 7.11-7.06 (m, 1H), 6.92 (d, *J* = 3.9 Hz, 1H), 5.91 (d, *J* = 48.3 Hz, 1H), 4.41-4.28 (m, 2H), 1.32 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -119.94 (m, 1F), -177.99 (dd, *J* = 47.7 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.9 (d, *J* = 27.2 Hz), 159.3 (d, *J* = 238.2 Hz), 151.6, 150.7 (d, *J* = 21.3 Hz), 128.0 (d, *J* = 13.0 Hz), 113.9 (d, *J* = 2.4 Hz), 113.7 (d, *J* = 1.9 Hz), 112.6 (d, *J* = 9.5 Hz), 108.6 (m), 107.3 (d, *J* = 1.5 Hz), 107.1 (d, *J* = 1.5 Hz), 82.5 (d, *J* = 186.1 Hz), 62.5, 14.0; **IR (thin film)** ***ν*** 2923, 1765, 1473, 1447, 765 cm^{-1}; **Ms (EI)**: *m/z* 240 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{12}H_{10}F_2O_3$ 240.0598; Found: 240.0602.

Ethyl 2-(5-chlorobenzofuran-2-yl)-2-fluoroacetate (2n)



Yield: 70% (89.8 mg); Colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.45-7.43 (m, 1H), 7.33-7.30 (m, 1H), 6.90 (d, *J* = 4.3 Hz, 1H), 5.91 (d, *J* = 47.9 Hz, 1H), 4.39-4.30 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -178.28 (dd, *J* = 47.7 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)** δ 167.8 (d, *J* = 27.0 Hz), 153.6 (d, *J* = 1.2 Hz), 150.5 (d, *J* = 21.3 Hz), 129.0, 128.5 (d, *J* = 2.0 Hz), 126.1 (d, *J* = 1.7 Hz), 121.4 (d, *J* = 1.8 Hz), 112.8, 108.0 (d, *J* = 6.0 Hz), 83.4 (d, *J* = 186.4 Hz), 62.5, 14.0; **IR (thin film)** ***ν*** 2923, 1765, 1602, 1447, 732 cm^{-1}; **Ms (EI)**: *m/z* 256 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{12}H_{10}ClFO_3$ 256.0303; Found: 256.0296.

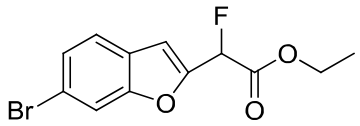
Ethyl 2-(5-bromobenzofuran-2-yl)-2-fluoroacetate (2o)



Yield: 74% (111.2 mg); Pale yellow liquid; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.75 (d, *J* = 2.3 Hz,

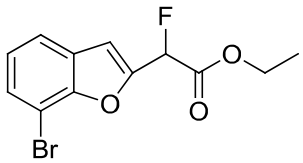
2H), 7.47-7.44 (m, 1H), 7.40-7.38 (m, 1H), 6.90 (d, *J* = 4.3 Hz, 1H), 5.91 (d , *J* = 47.9 Hz, 1H), 4.36-4.33 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -178.35 (dd, *J* = 48.1 Hz, *J* = 4.1 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.8 (d, *J* = 27.8 Hz), 154.1 (d, *J* = 1.5 Hz); 150.3 (d, *J* = 21.1 Hz), 129.1 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 1.6 Hz), 124.4 (d, *J* = 1.5 Hz), 116.4, 113.2, 107.9 (d, *J* = 5.8 Hz), 82.4 (d, *J* = 186.4 Hz), 62.5, 14.0; **IR (thin film)** ***v*** 2922, 2849, 1765, 1444, 731 cm^{-1}; **Ms (EI)**: *m/z* 300 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{12}H_{10}BrFO_3$ 299.9797; Found: 299.9796.

Ethyl 2-(6-bromobenzofuran-2-yl)-2-fluoroacetate (2p)



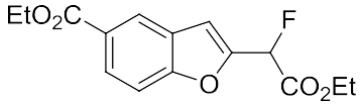
Yield: 51% (76.9 mg); Pale yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 7.39-7.30 (m, 2H), 6.84 (d, *J* = 3.9 Hz, 1H), 5.83 (d, *J* = 47.9 Hz, 1H), 4.33-4.20 (m, 2H), 1.25-1.21 (t, *J* = 7.19 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -177.7 (dd, *J* = 47.7 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.8 (d, *J* = 27.4 Hz), 153.5 (d, *J* = 1.5 Hz), 149.6 (d, *J* = 21.3 Hz), 126.9, 126.2 (d, *J* = 2.2 Hz), 122.7 (d, *J* = 1.4 Hz), 119.2 (d, *J* = 2.3 Hz), 115.2 (d, *J* = 1.3 Hz), 108.5 (d, *J* = 6.1 Hz), 82.4 (d, *J* = 186.1 Hz), 62.5, 14.0; **IR (thin film)** ***v*** 2983, 1765, 1610, 1462, 731 cm^{-1}; **Ms (EI)**: 300 (M^+); **HRMS** Calculated for : $C_{12}H_{10}BrFO_3$: 299.9797; Found: 299.9788.

Ethyl 2-(7-bromobenzofuran-2-yl)-2-fluoroacetate (2q)



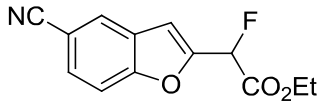
Yield: 36% (53.9 mg); Pale yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.09-7.05 (m, 1H), 6.92 (d, *J* = 4.3 Hz, 1H), 5.90 (d, *J* = 48.3 Hz, 1H), 4.32-4.25 (m, 2H), 1.26 (t, *J* = 7.19 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -177.4 (dd, *J* = 46.8 Hz, *J* = 4.1 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.8 (d, *J* = 27.4 Hz), 152.5, 149.9 (d, *J* = 22.3 Hz), 128.9 (d, *J* = 1.50 Hz), 128.4 (d, *J* = 3.2 Hz), 124.6, 121.0 (d, *J* = 1.0 Hz), 109.0 (d, *J* = 6.5 Hz), 104.4 (d, *J* = 1.6 Hz), 82.3 (d, *J* = 185.8 Hz), 62.5, 14.0; **IR (thin film)** ***v*** 2983, 1764, 1473, 1420, 734 cm^{-1}; **Ms (EI)**: 300(M^+); **HRMS** Calculated for : $C_{12}H_{10}BrFO_3$ 299.9797; Found: 299.9800.

Ethyl 2-(2-ethoxy-1-fluoro-2-oxoethyl)benzofuran-5-carboxylate (2r)



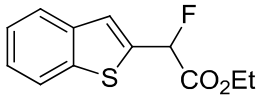
Yield: 40% (59.4 mg); Colorless liquid; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36 (s, 1H), 8.11-8.08 (m, 1H), 7.55-7.53 (m, 1H), 7.02 (d, *J* = 3.9 Hz, 1H), 5.96 (d, *J* = 47.5 Hz, 1H), 4.43-4.32 (m, 4H), 1.42 (t, *J* = 6.7 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -178.25 (dd, *J* = 47.7 Hz, *J* = 4.1 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 166.4, 165.8 (d, *J* = 26.8 Hz), 157.7, 150.4 (d, *J* = 21.3 Hz), 127.4 (d, *J* = 1.5 Hz), 127.2 (d, *J* = 2.9 Hz), 126.2, 124.3 (d, *J* = 2.3 Hz), 111.6, 108.9 (d, *J* = 5.6 Hz), 82.4 (d, *J* = 186.2 Hz), 62.6, 61.1, 14.3, 14.0; **IR (thin film)** ***v*** 2982, 1766, 1716, 1443, 768 cm^{-1}; **Ms (EI)**: *m/z* 294 [M^+]; **HRMS EI**: [M^+], Calculated for $C_{15}H_{15}FO_5$ 294.0904; Found: 294.0910.

Ethyl 2-(5-cyanobenzofuran-2-yl)-2-fluoroacetate (2s)



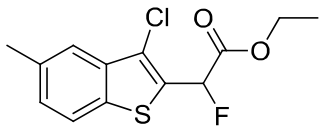
Yield: 31% (38.6 mg); Pale yellow solid; M.P.: 48-50 ^{o}C;**^{1}H NMR(400 MHz, $CDCl_3$)**: δ 7.98 (s, 1H), 7.66-7.60 (m, 2H), 7.02 (d, *J* = 3.9 Hz, 1H), 5.95 (d, *J* = 47.9 Hz, 1H), 4.43-4.30 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -179.73 (dd, *J* = 48.1 Hz, *J* = 4.5 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 165.4 (d, *J* = 27.2 Hz); 156.8, 151.5 (d, *J* = 21.7 Hz), 129.3 (d, *J* = 1.4 Hz); 127.9 (d, *J* = 2.4 Hz), 127.0 (d, *J* = 1.3 Hz), 118.8, 113.1, 108.1 (d, *J* = 5.5 Hz), 107.6, 82.2 (d, *J* = 187.3 Hz), 62.7, 14.0; **IR (thin film) *ν*** 2923, 1763, 1615, 1466, 731 cm^{-1}; **Ms (EI)**: *m/z* 247 [M^{+}]; **HRMS EI**: [M^{+}], Calculated for $C_{13}H_{10}FNO_3$ 247.0645; Found: 247.0647.

Ethyl 2-(benzo[b]thiophen-2-yl)-2-fluoroacetate (2t)



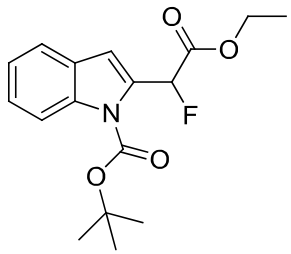
Yield: 34% (40.3 mg); Orange solid; M.P.: 77-90 ^{o}C; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.85-7.78 (m, 1H), 7.46 (d, *J* = 2.7 Hz, 1H), 7.40-7.35 (m, 2H), 6.07 (d, *J* = 47.9 Hz, 1H), 4.38-4.25 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)**: δ -170.40 (dd, *J* = 51.8 Hz, *J* = 3.7 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)**: δ 167.2 (d, *J* = 26.9 Hz), 140.4 (d, *J* = 1.4 Hz), 138.7 (d, *J* = 1.7 Hz), 136.0 (d, *J* = 21.6 Hz), 125.4, 124.9 (d, *J* = 6.3 Hz), 124.7, 124.3, 122.50 85.6 (d, *J* = 184.5 Hz), 62.3, 14.0; **IR (thin film) *ν*** cm^{-1} 2980, 1736, 1458, 1435, 748; **Ms (EI)**: *m/z* 238.2 [M^{+}]; **HRMS EI**: [M^{+}], Calculated for $C_{12}H_{11}FO_2S$ 238.0464; Found: 238.0468.

Ethyl 2-(3-chloro-5-methylbenzo[b]thiophen-2-yl)-2-fluoroacetate (2u)



Yield: 51% (72.9 mg); Pale yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.28-7.26 (m, 1H), 6.09 (d, *J* = 47.1 Hz, 1H), 4.29-4.14 (m, 2H), 2.39 (d, *J* = 2.3 Hz, 3H), 1.21 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -171.5 (d, *J* = 46.2 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.3 (d, *J* = 28.8 Hz), 140.9 (d, *J* = 1.4 Hz) , 137.4 (d, *J* = 1.5 Hz), 132.4 (d, *J* = 5.3 Hz), 131.7, 130.7, 125.9 (d, *J* = 1.5 Hz), 123.6, 122.2 (d, *J* = 2.1 Hz), 83.8 (d, *J* = 185.4 Hz), 62.3, 14.0, 11.9; **IR (thin film) *ν*** 2983, 1761, 1438, 1383, 802 cm^{-1}; **Ms (EI)**: (M^{+}): 286; **HRMS** Calculated for: $C_{13}H_{12}ClFO_2S$: 286.0231; Found: 286.0230.

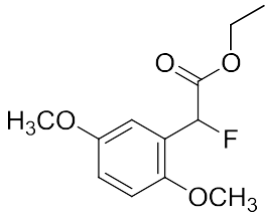
***Tert*-butyl 2-(2-ethoxy-1-fluoro-2-oxoethyl)-1H-indole-1-carboxylate (2v)**



Yield: 47% (76.0 mg); Pale yellow liquid;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.30-7.26 (m, 1H), 7.20-7.16 (m, 1H), 6.72 (d, *J* = 2.7 Hz, 1H), 6.35

(d, *J* = 46.3, 1H), 1.60 (s, 9H), 1.24 (t, *J* = 7.19); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -176.3 (d, *J* = 47.0 Hz, 1F); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 167.3 (d, *J* = 24.8 Hz), 150.0, 136.7, 132.7 (d, *J* = 23.8 Hz), 128.2 (d, *J* = 2.6 Hz), 125.4, 123.1, 121.3, 115.8, 111.6 (d, *J* = 7.4 Hz), 84.4 (d, *J* = 183.6 Hz), 85.1, 61.9, 28.1, 14.0; **IR (thin film)** ***v*** 2980, 1738, 1453, 1392, 747 cm^{-1}; **Ms (EI)**: (M^+): 321; **HRMS** Calculated for: $C_{17}H_{20}FNO_4$: 321.1376; Found: 321.1376.

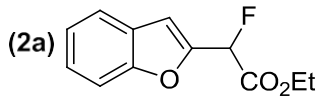
Ethyl 2-(2,5-dimethoxyphenyl)-2-fluoroacetate (2w)

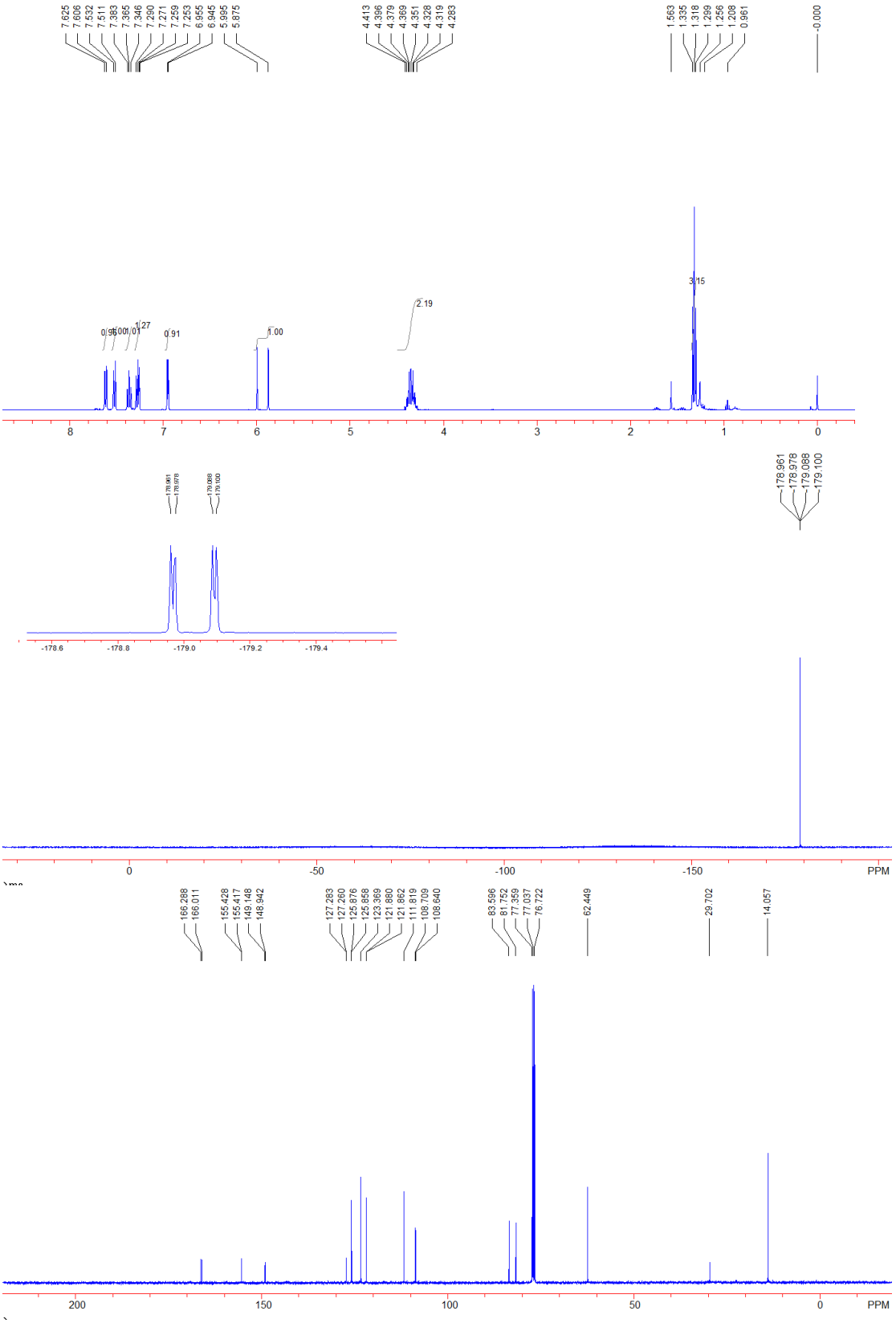


Yield: 22% (26.4 mg). Pale yellow liquid; ^{1}H NMR(400 MHz, $CDCl_3$) δ 6.88-6.79 (m, 3H), 6.51 (d, *J* = 47.5 Hz, 1H), 4.26-4.21 (m, 2H), 3.75 (s, 3H), 3.70 (s, 3H), 1.20 (t, *J* = 6.7 Hz, 3H); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -178.9 (d, *J* = 46.2 Hz, 1F); **^{13}C NMR(100 MHz, $CDCl_3$)** δ 168.9 (d, *J* = 27.4 Hz), 153.7 (d, *J* = 1.8 Hz), 151.5 (d, *J* = 4.2 Hz), 123.8 (d, *J* = 19.3 Hz), 116.4 (d, *J* = 3.3 Hz), 114.17 (d, *J* = 4.5 Hz), 112.6 (d, *J* = 1.4 Hz), 84.7 (d, *J* = 182.3 Hz), 61.6, 56.4, 56.8, 14.1; **IR (thin film)** ***v*** 2917, 1754, 1502, 1463, 808 cm^{-1}; **Ms (EI)**: (M^+): 242; **HRMS** Calculated for $C_{12}H_{15}FO_4$: 242.0954 ; Found: 242.0954.

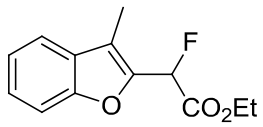
Copies of ^{1}H NMR, ^{19}F NMR, ^{13}C NMR:

(2a)





(2b)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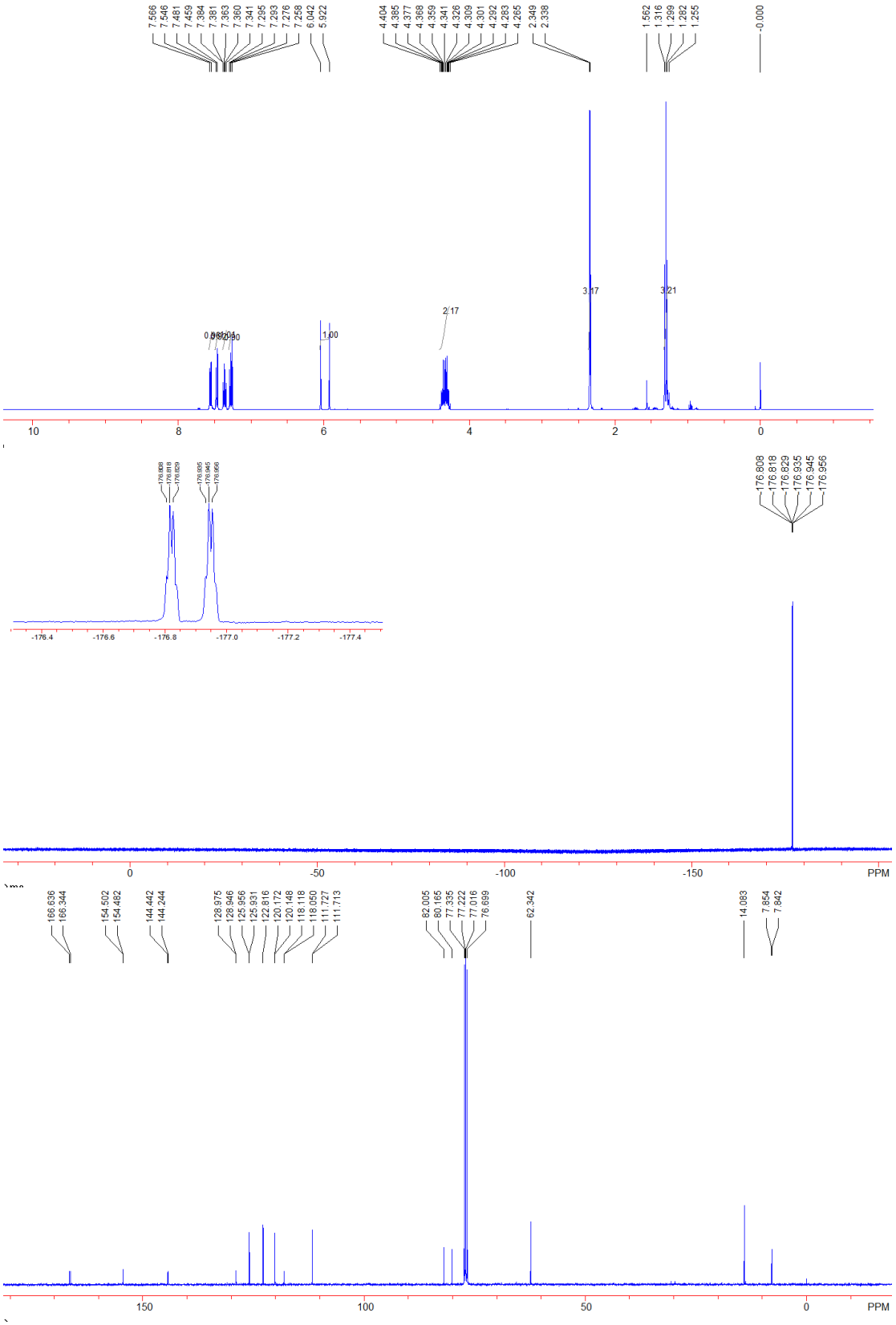
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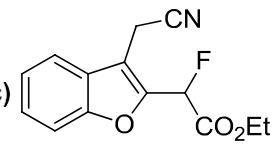
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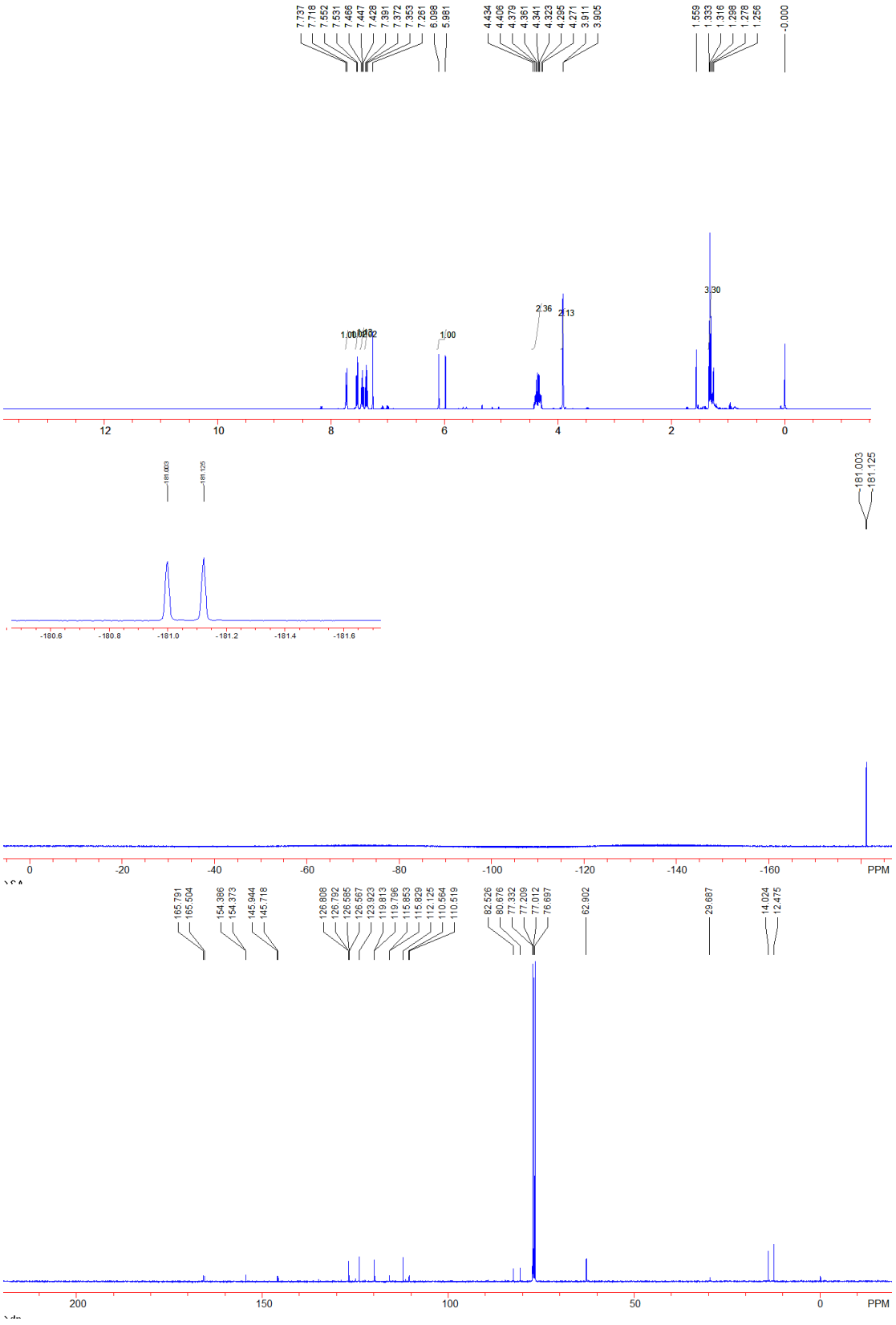
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-181.6
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-120
-140
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126.567
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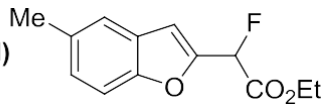
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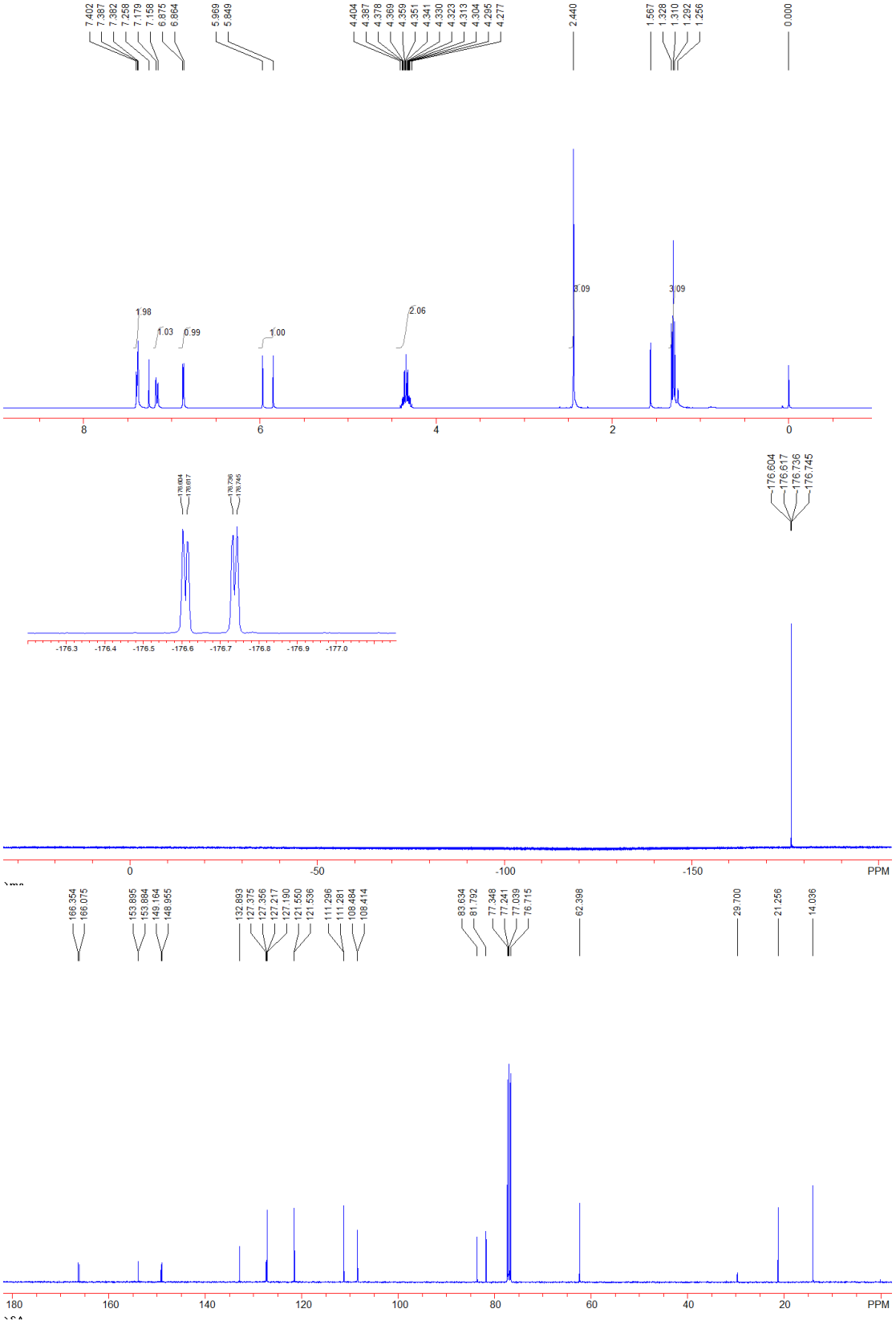
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1.292
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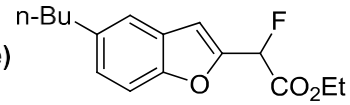
(2e)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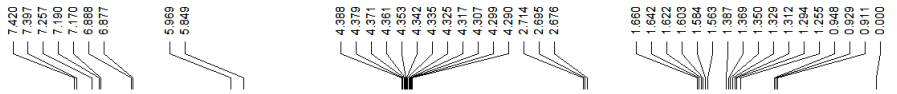
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4.299
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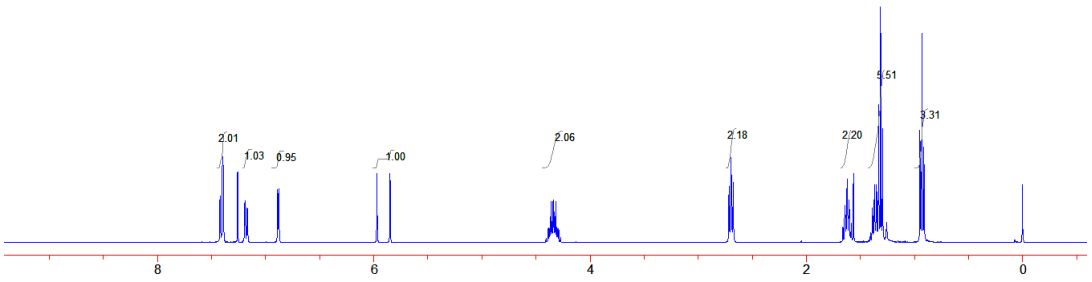
0.000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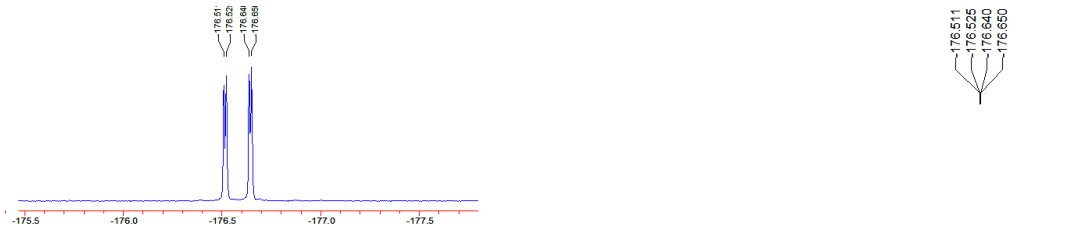
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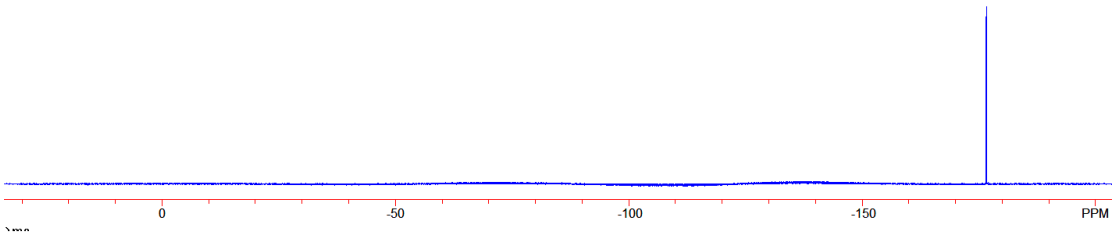
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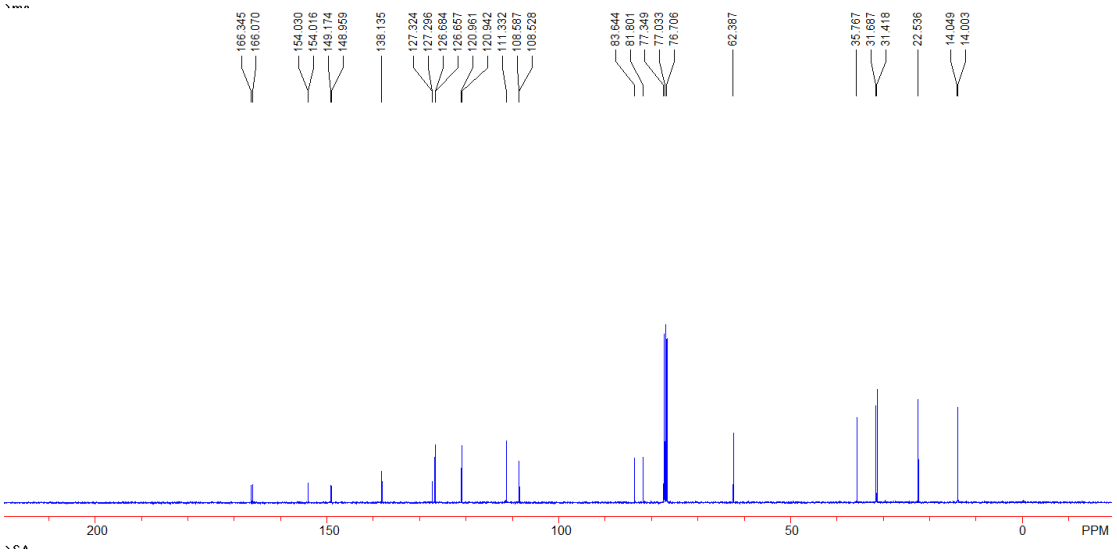
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81.801
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77.033
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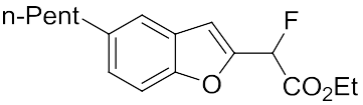
(2f)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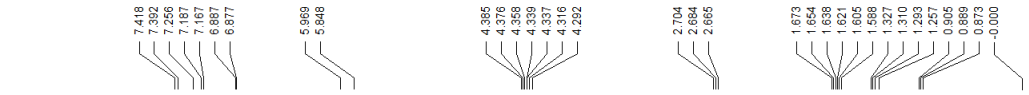
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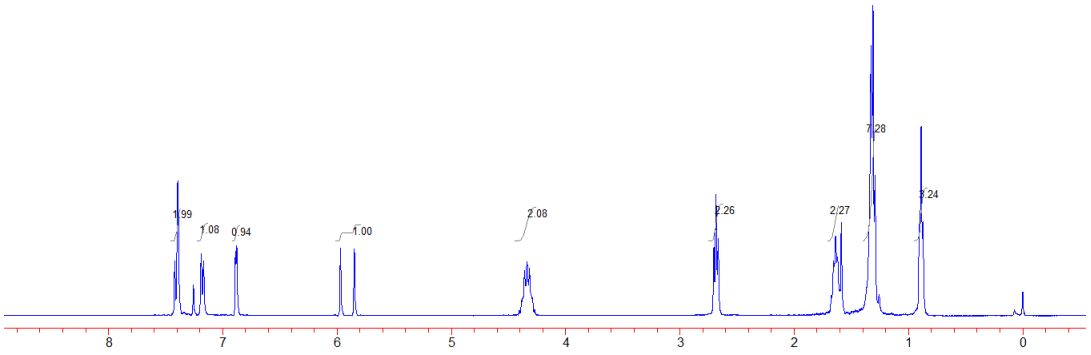
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3
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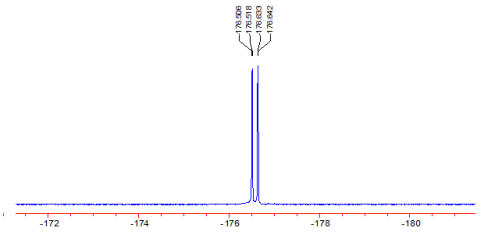
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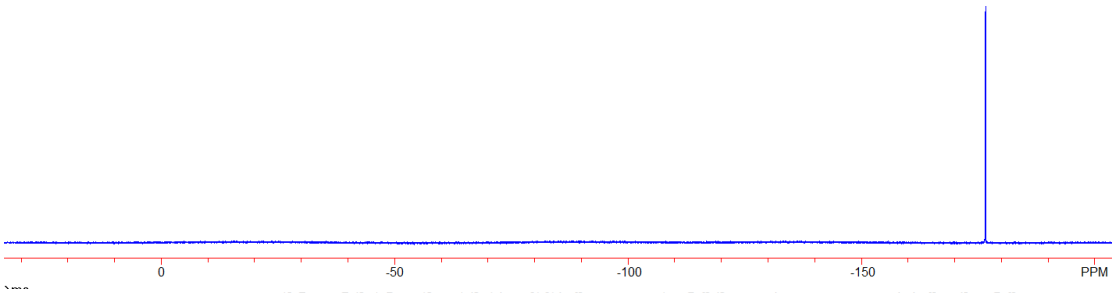
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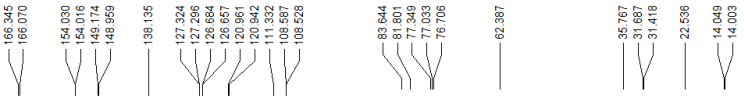
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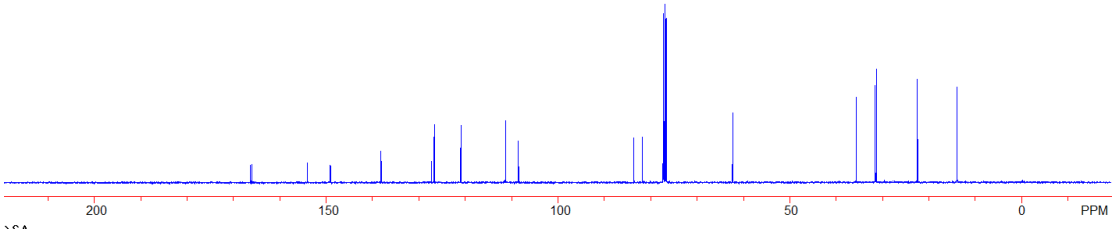
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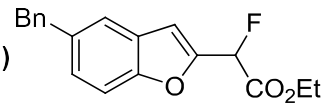
(2g)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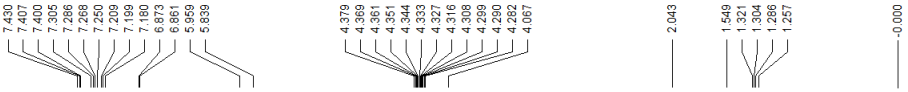
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4.344
4.333
4.327
4.316
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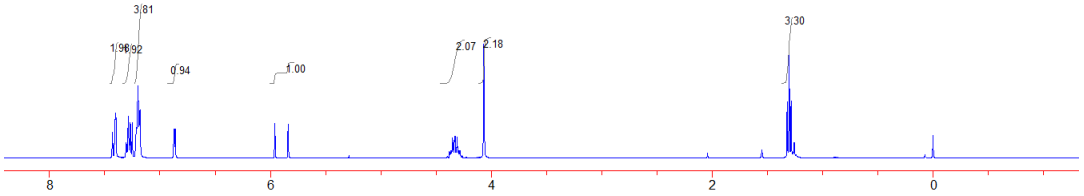
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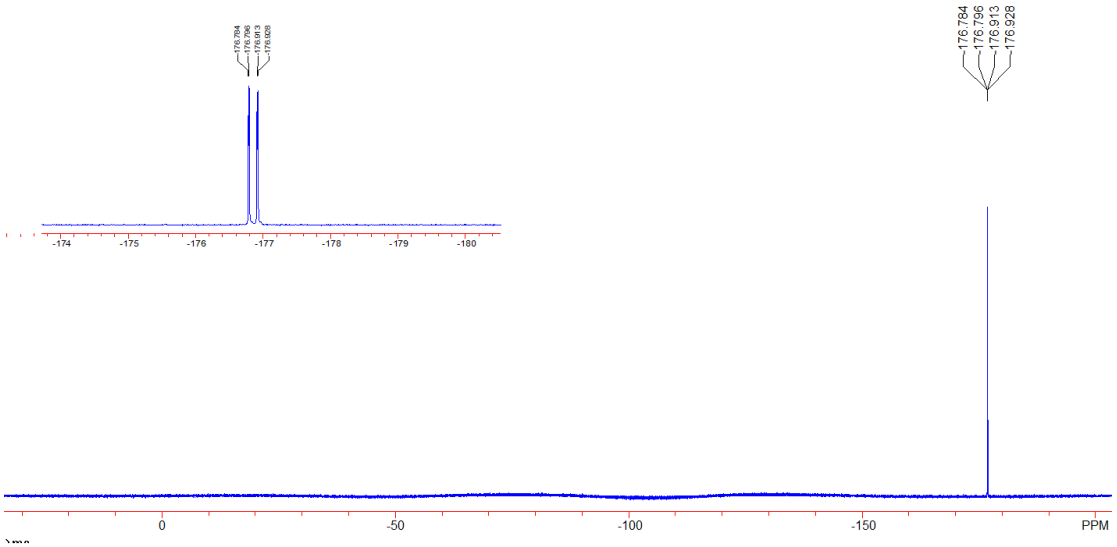
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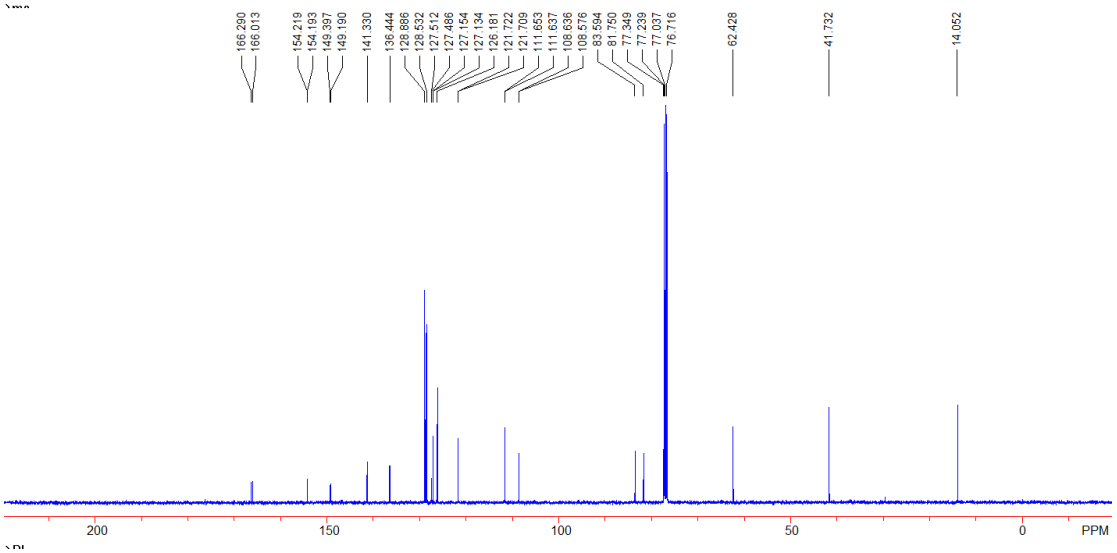
PPM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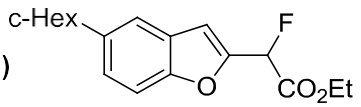
(2h)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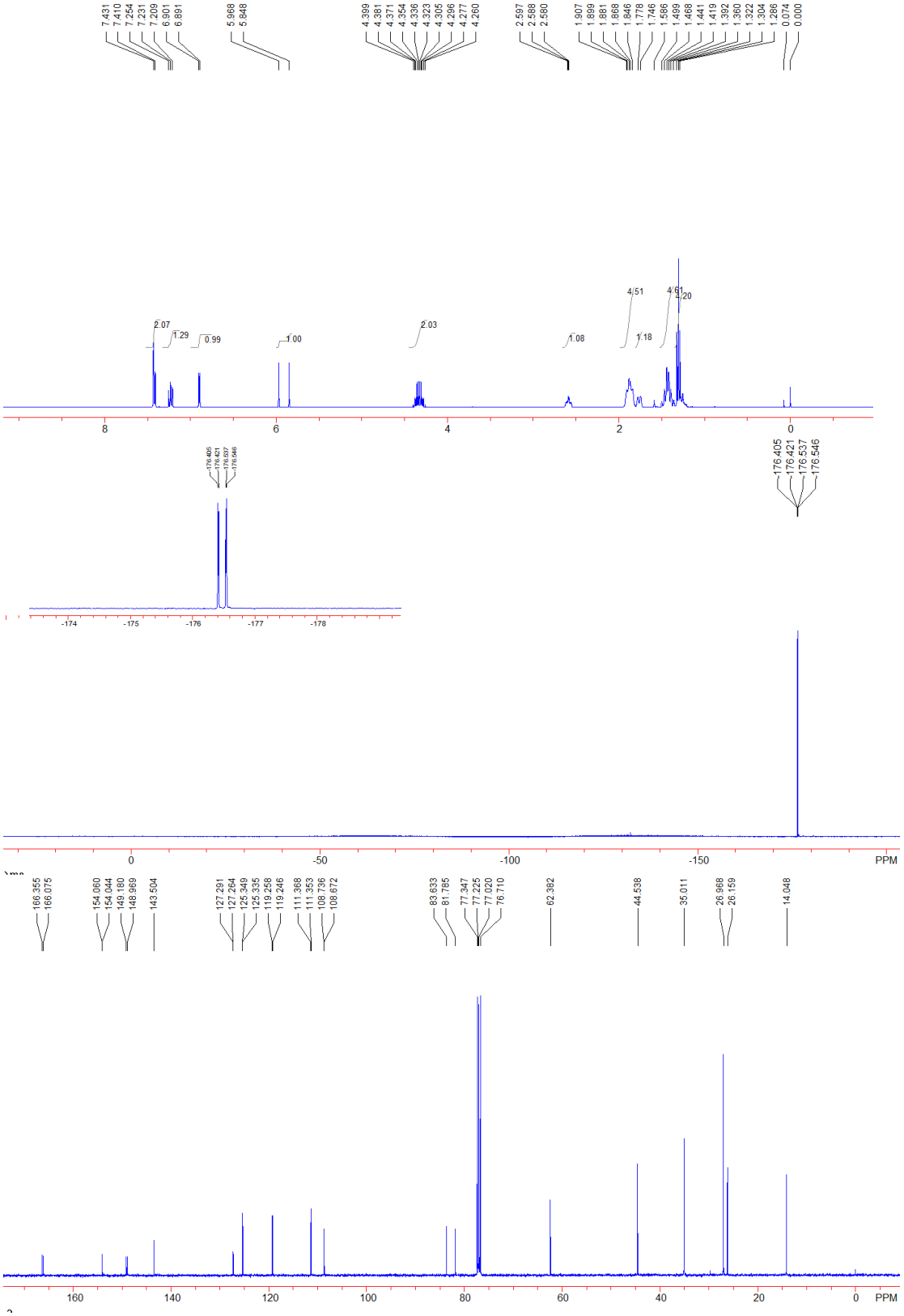
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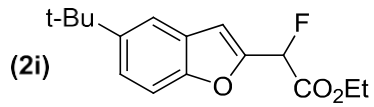
(2i)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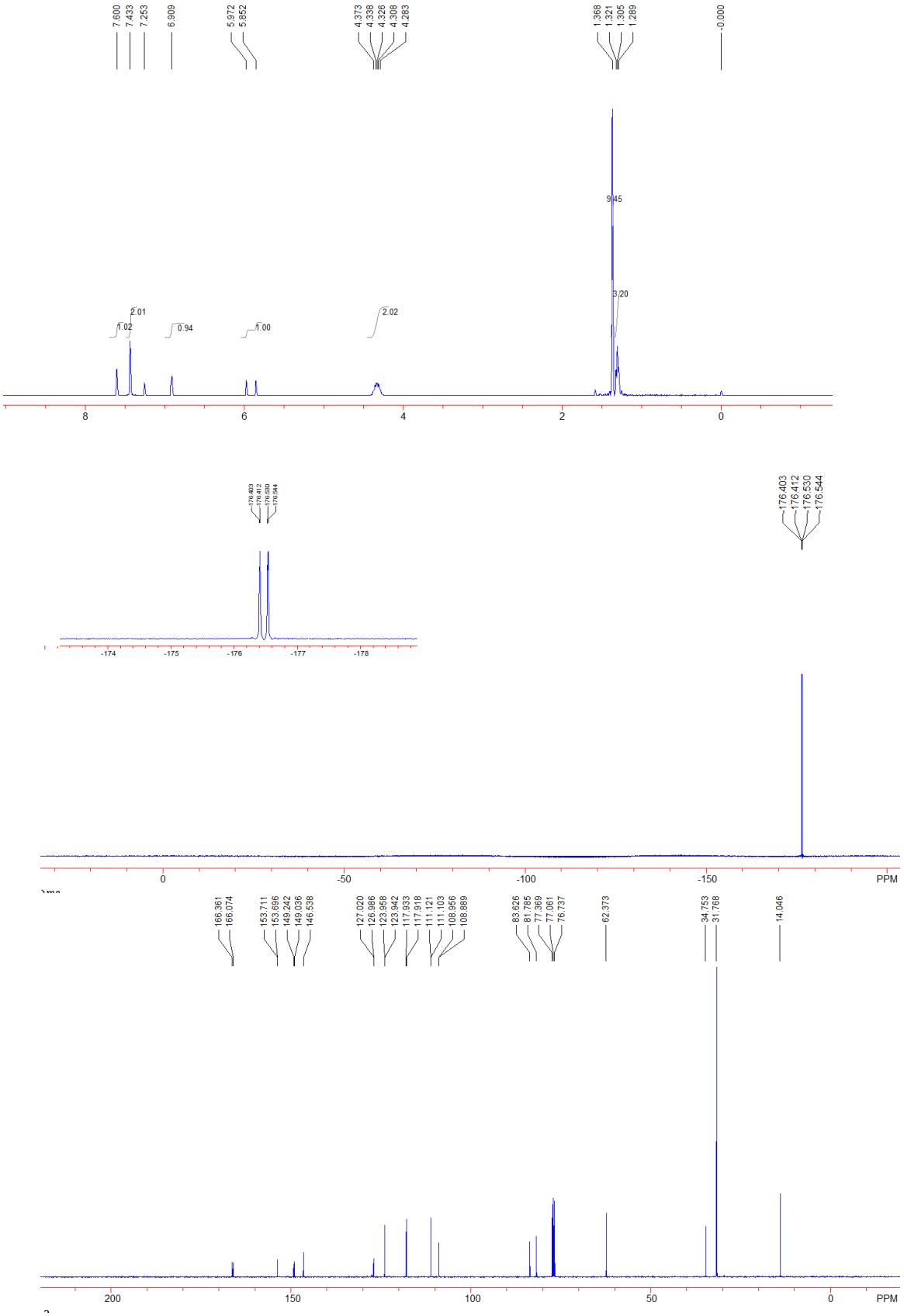
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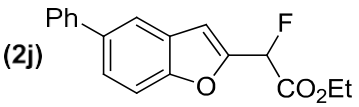
(2j)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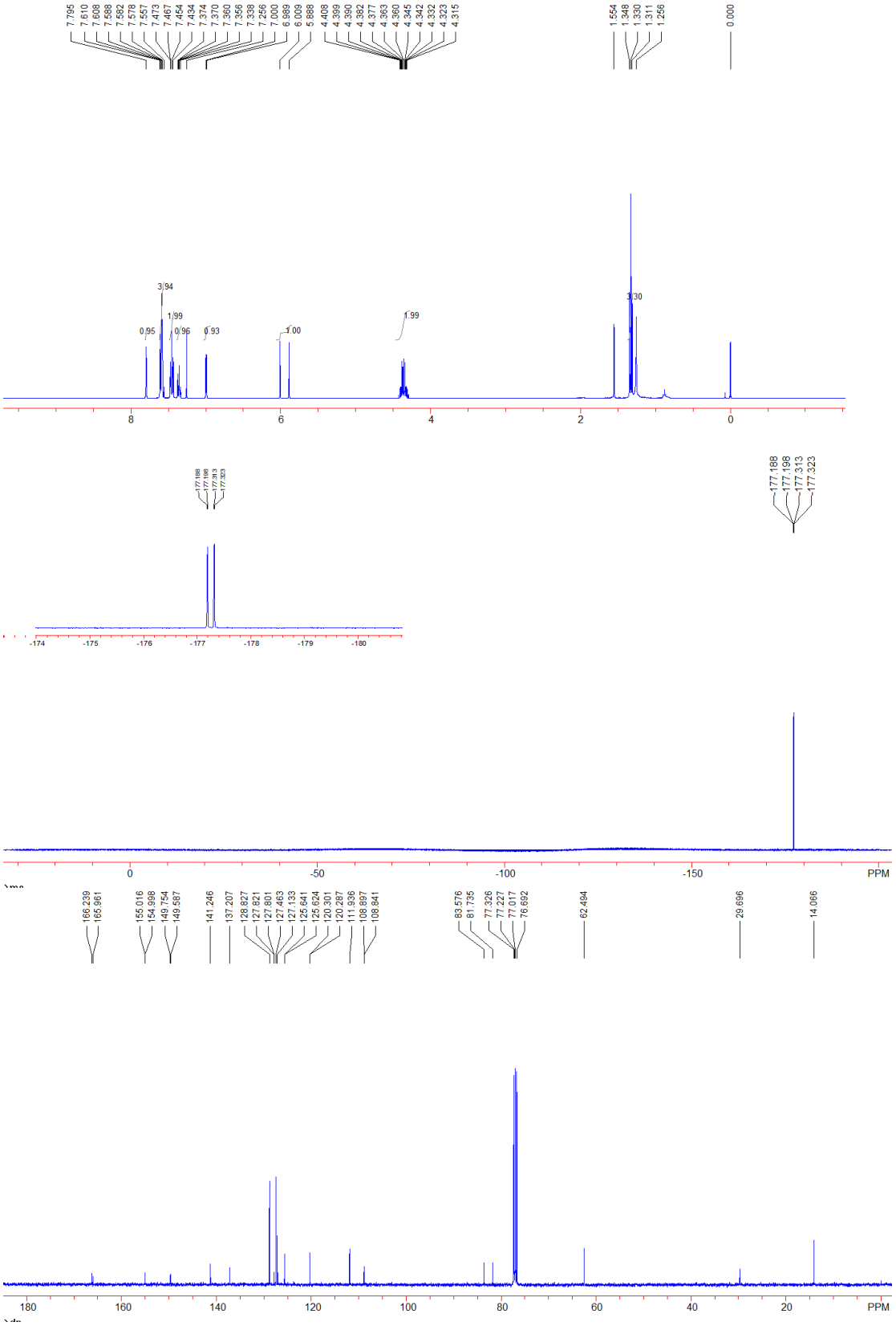
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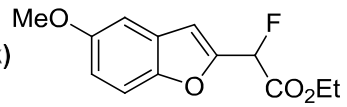
(2k)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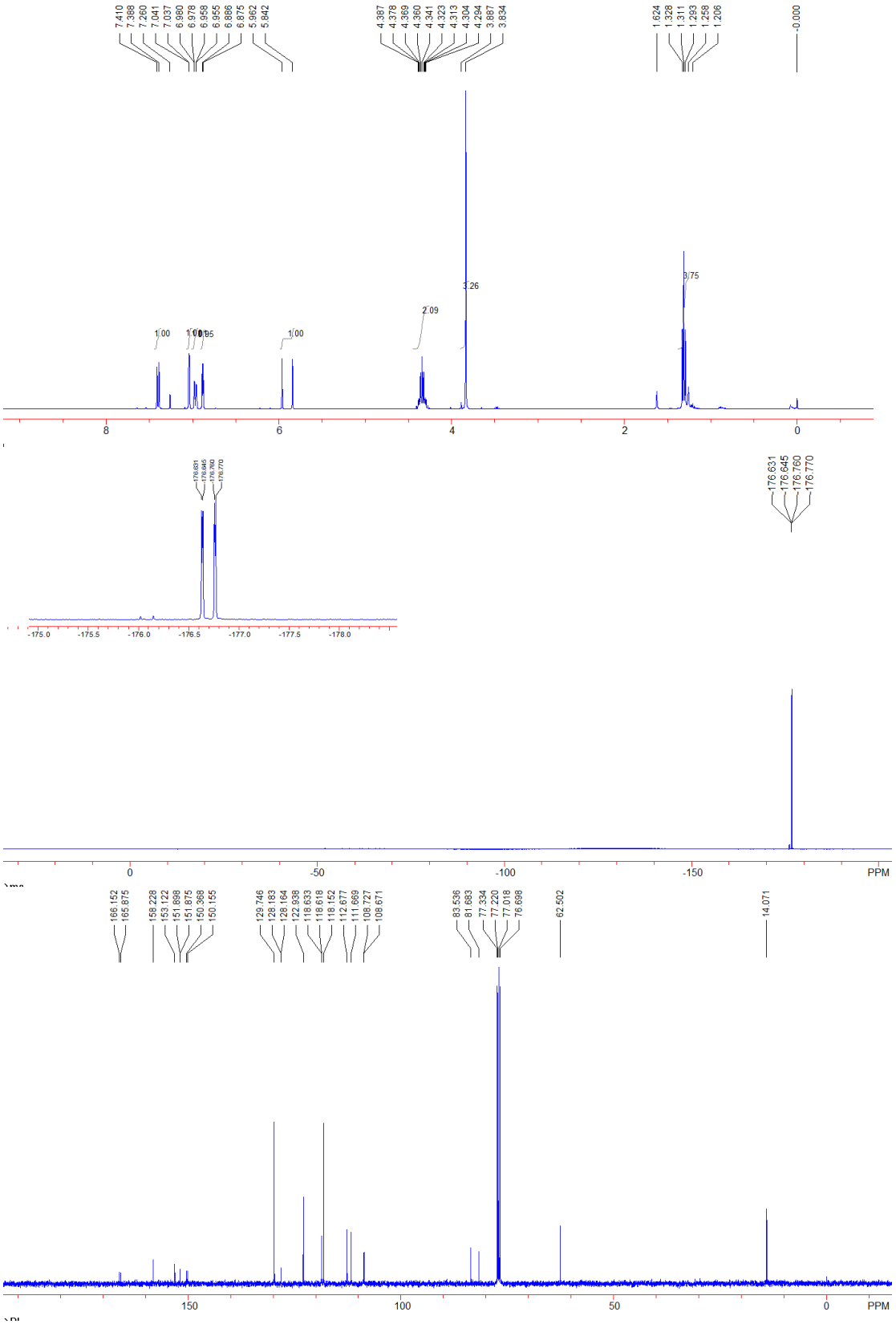
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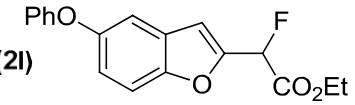
(2l)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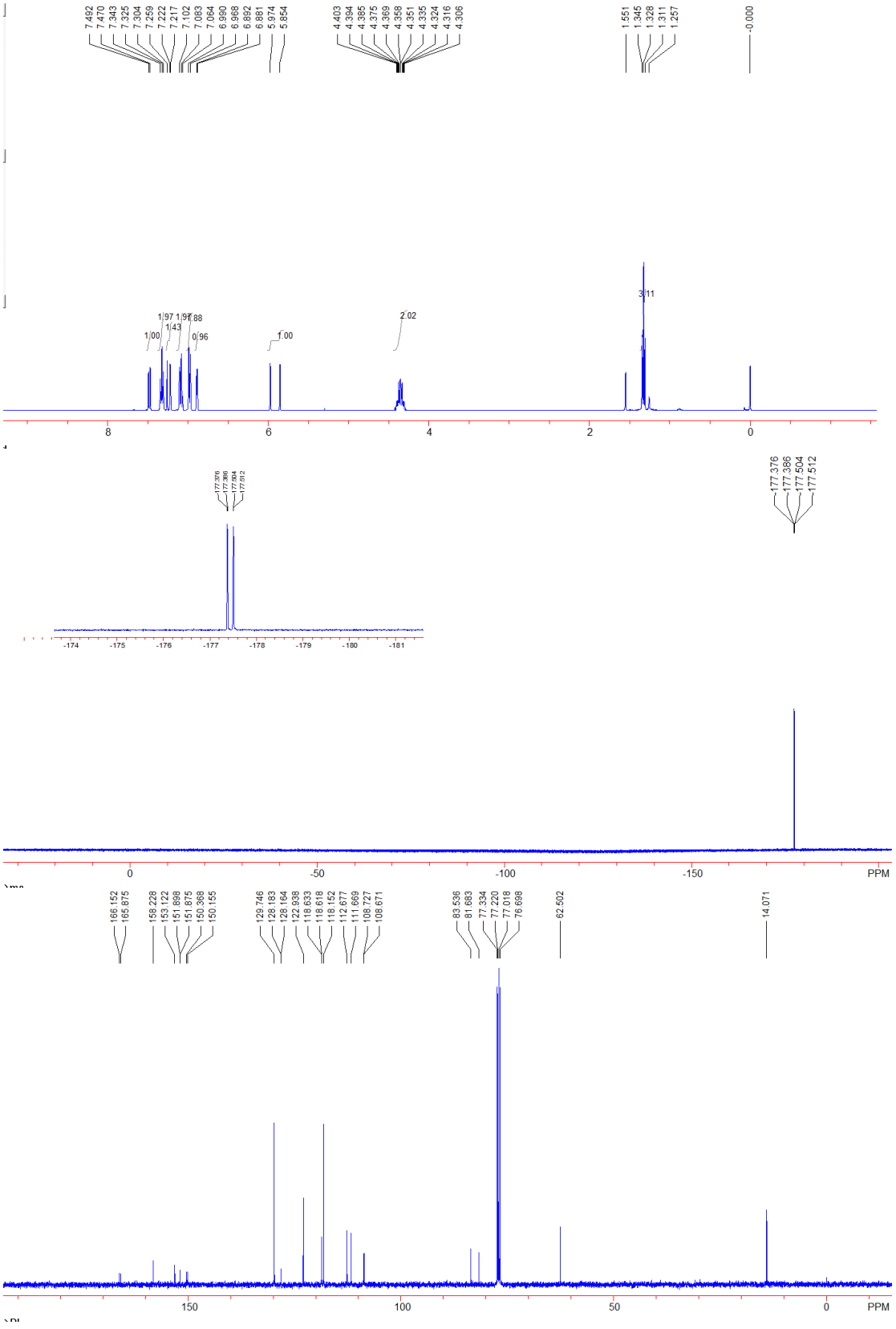
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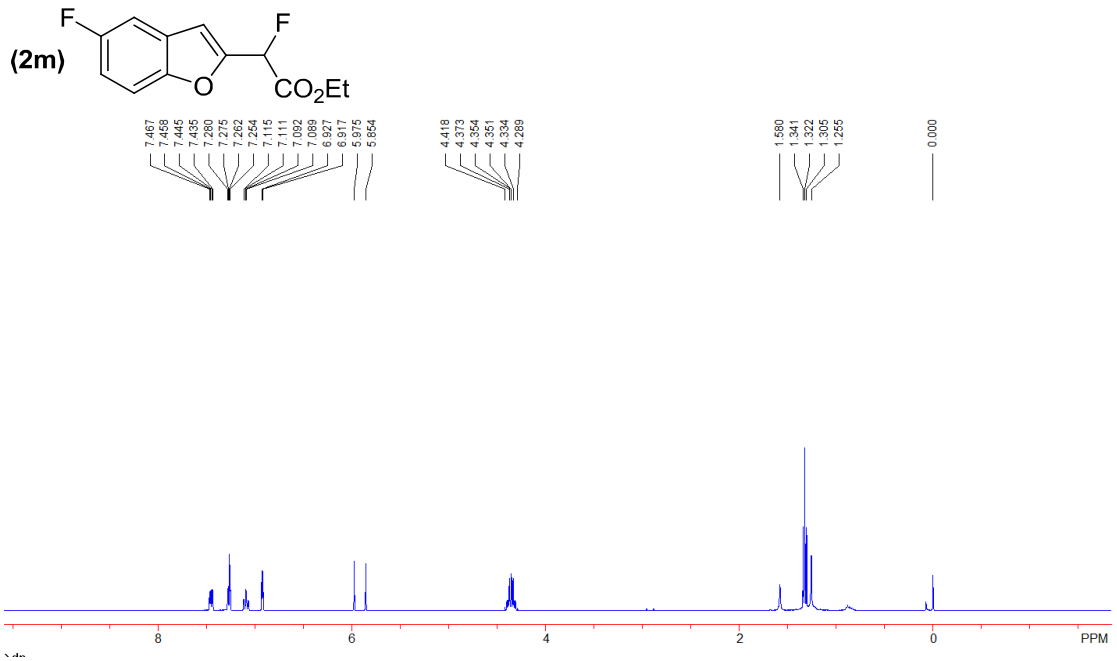
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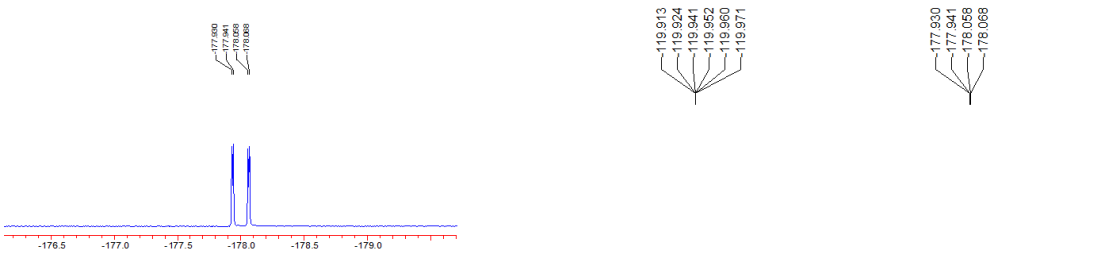
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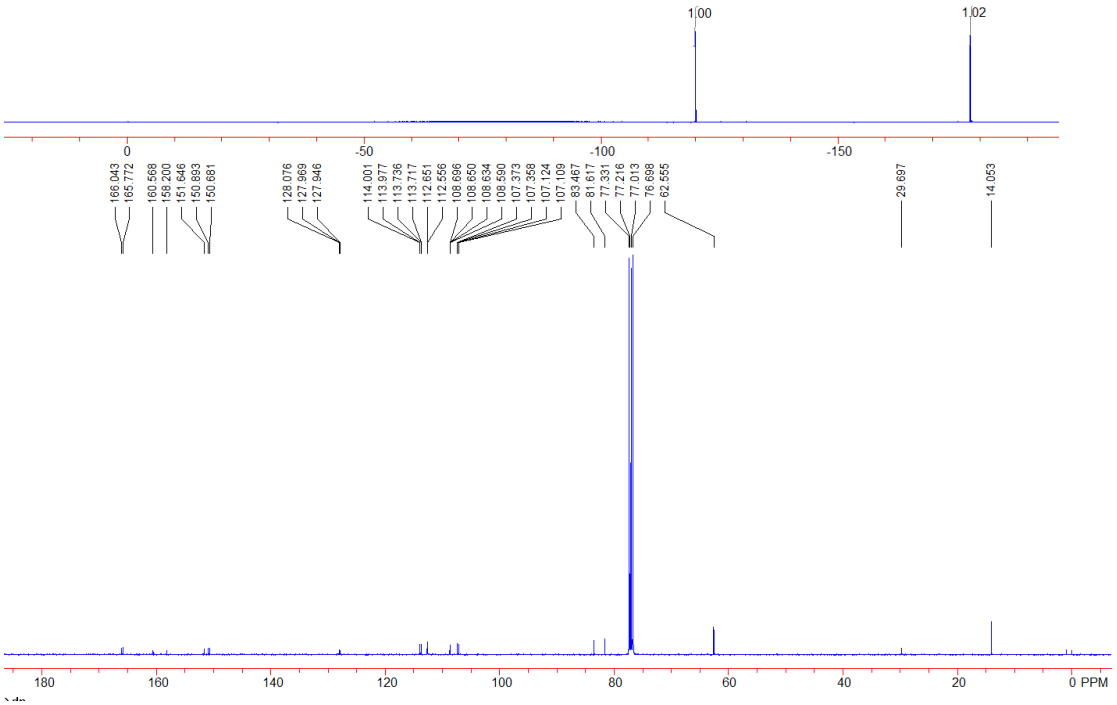
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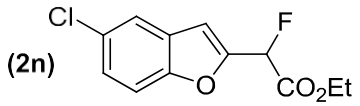
0 PPM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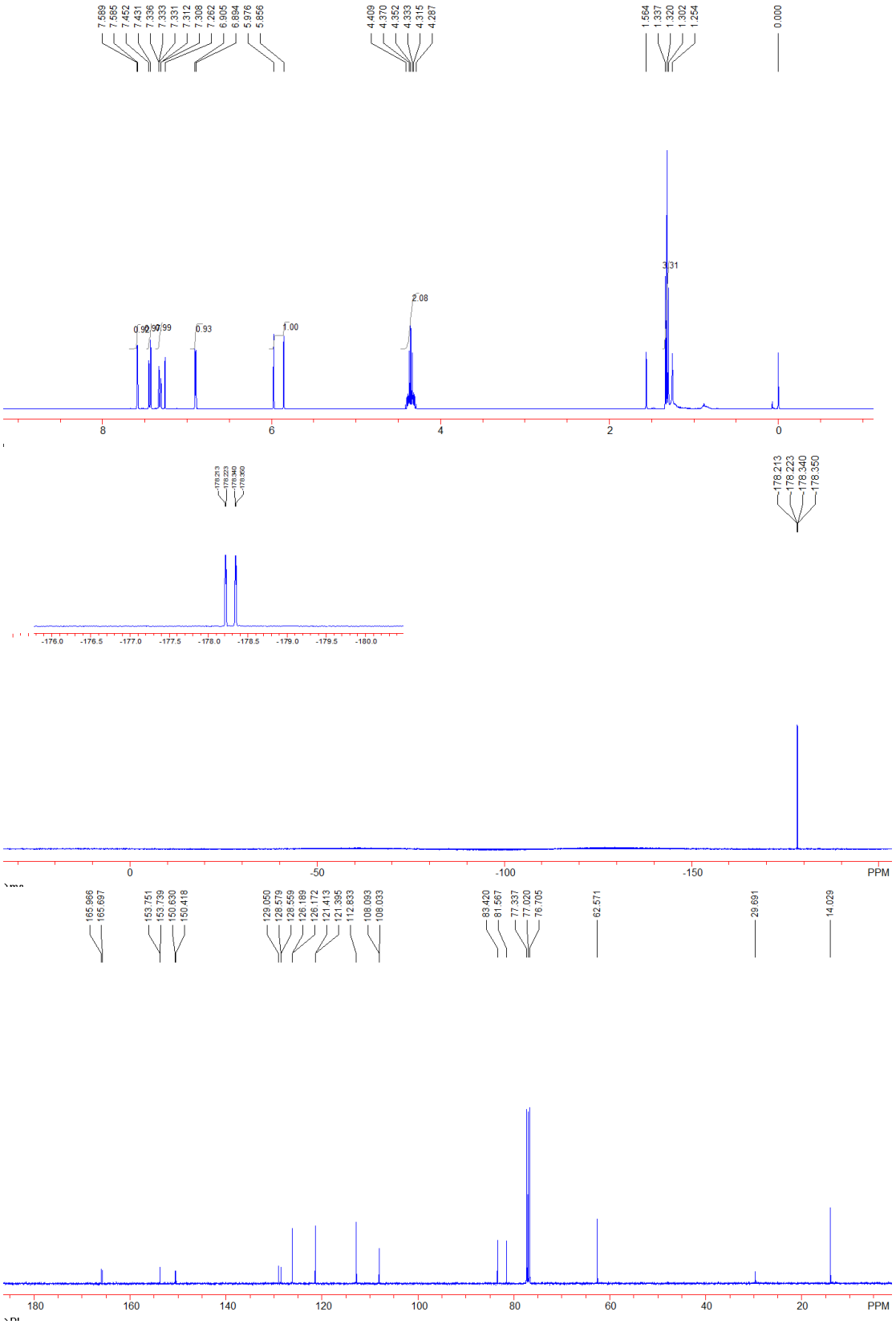
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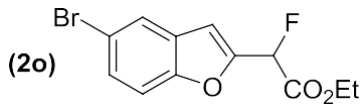
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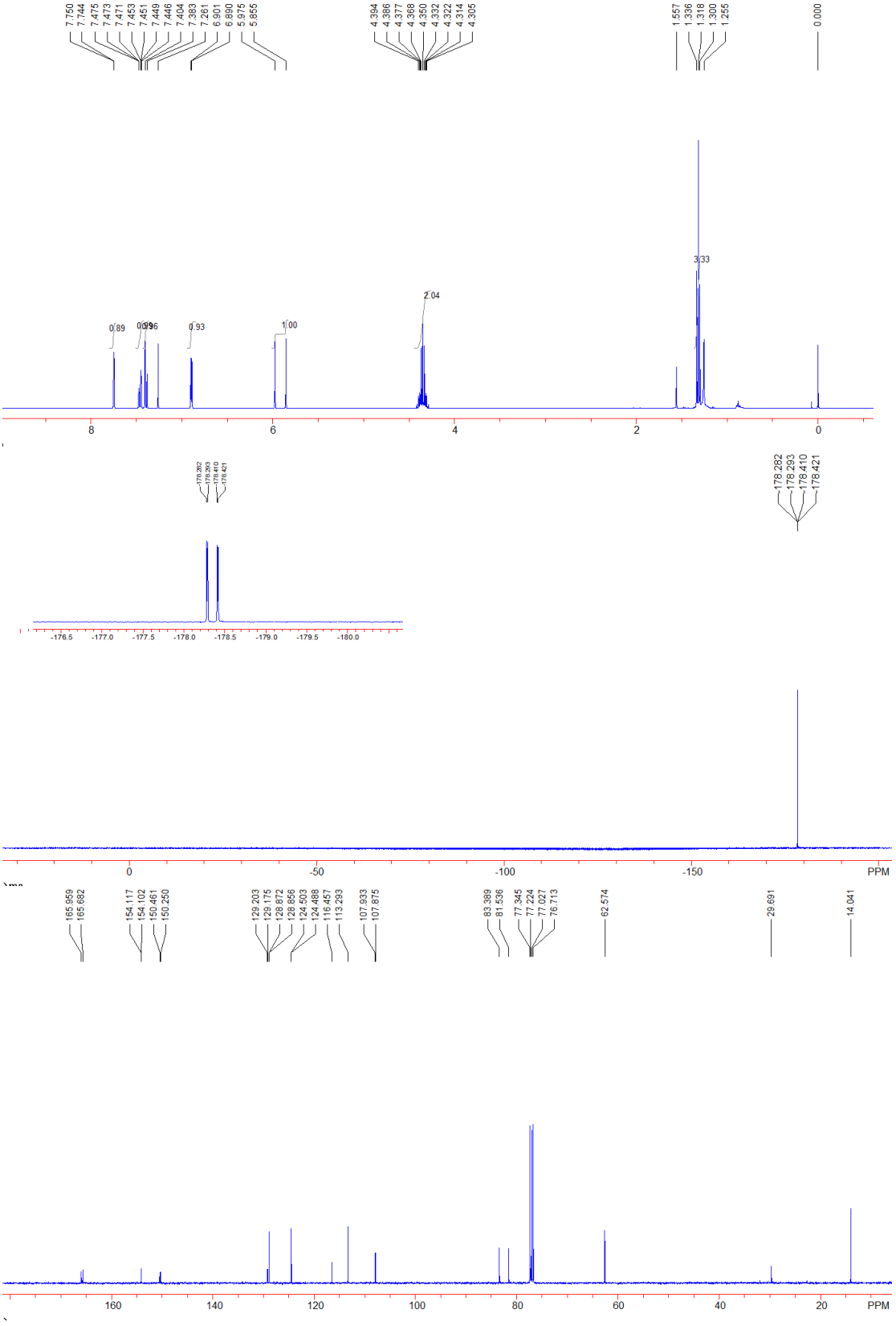
CO2Et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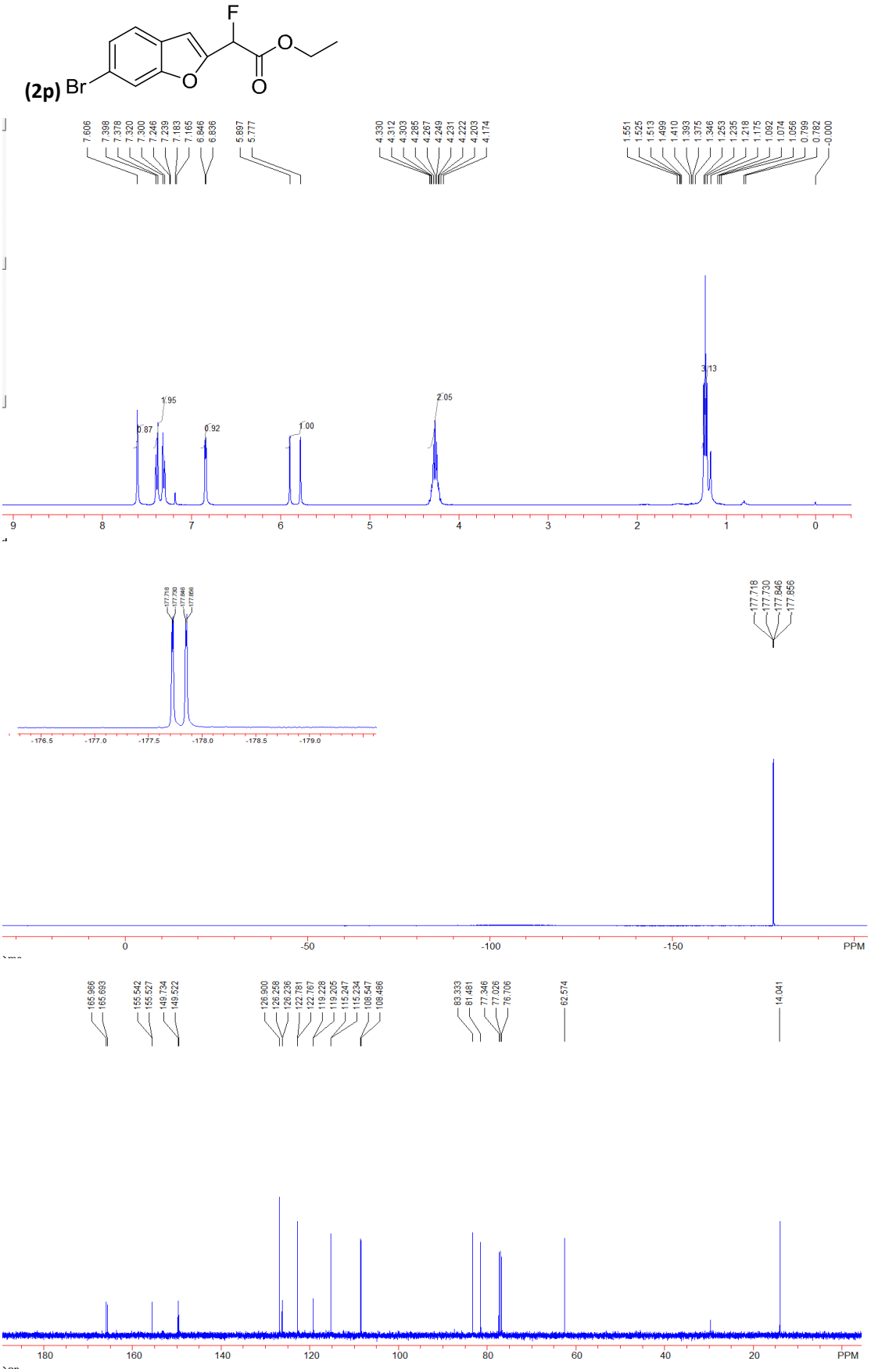
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4.203
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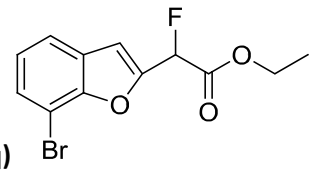
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O
O
Br

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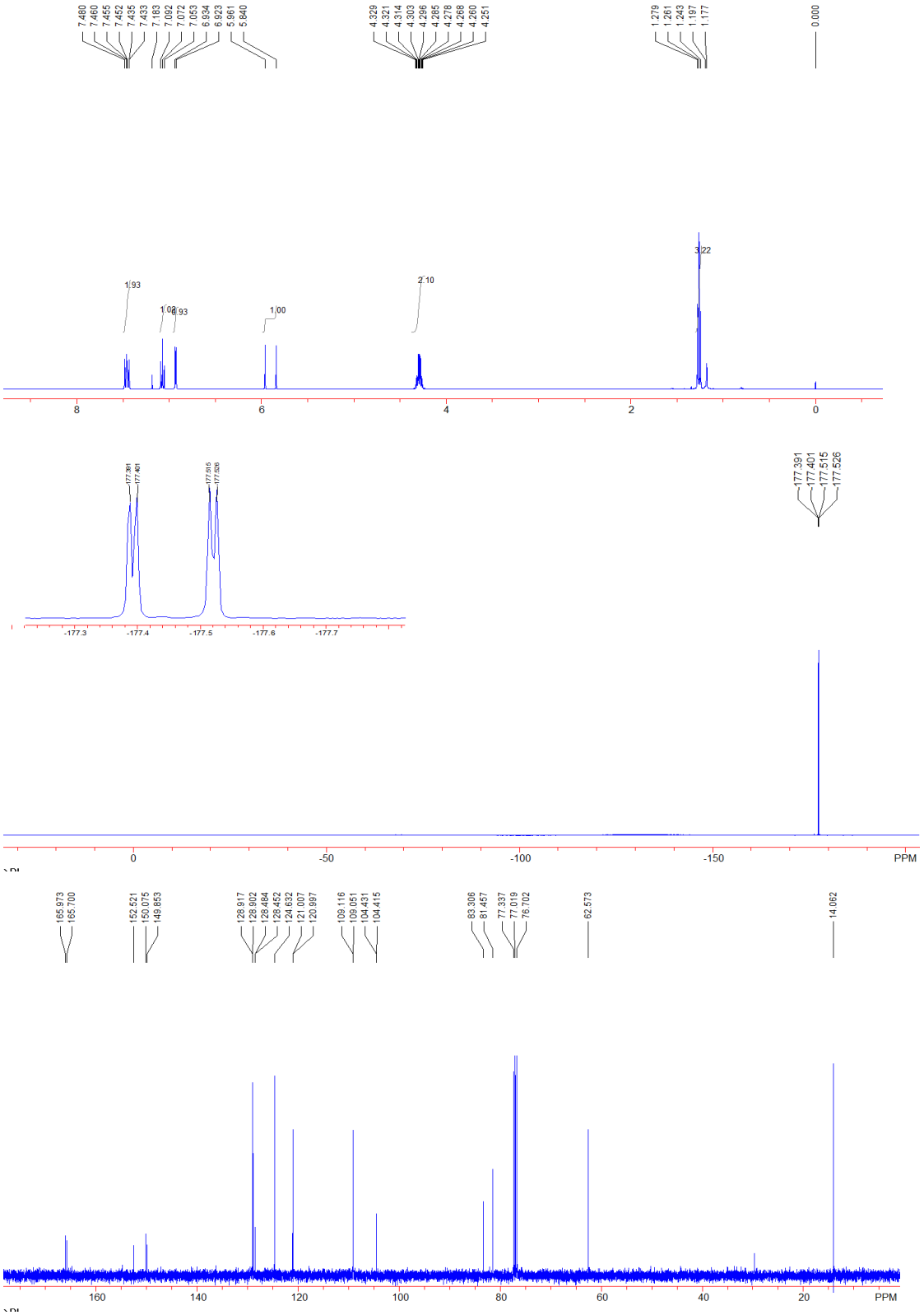
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20
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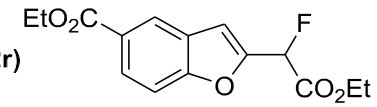
(2r)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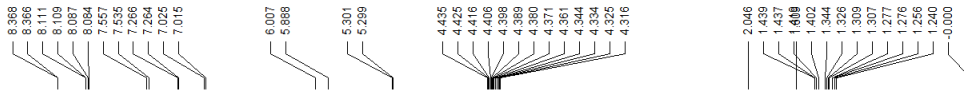
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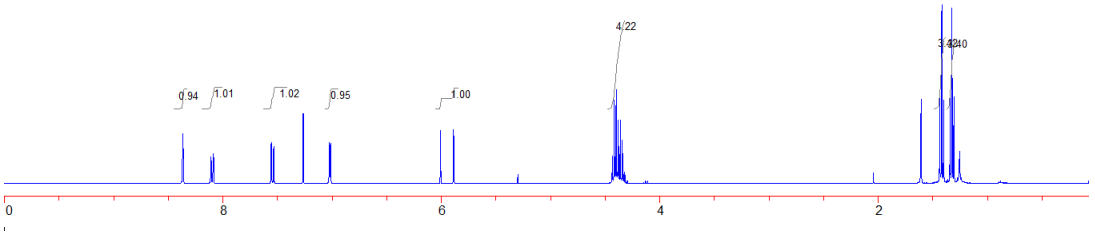
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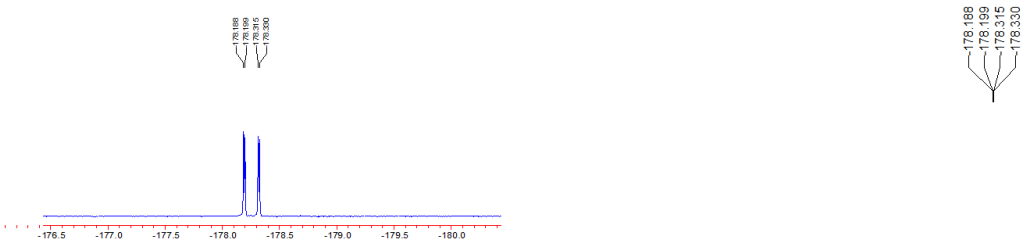
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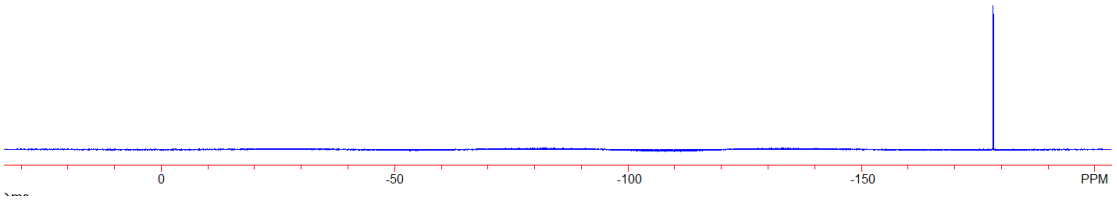
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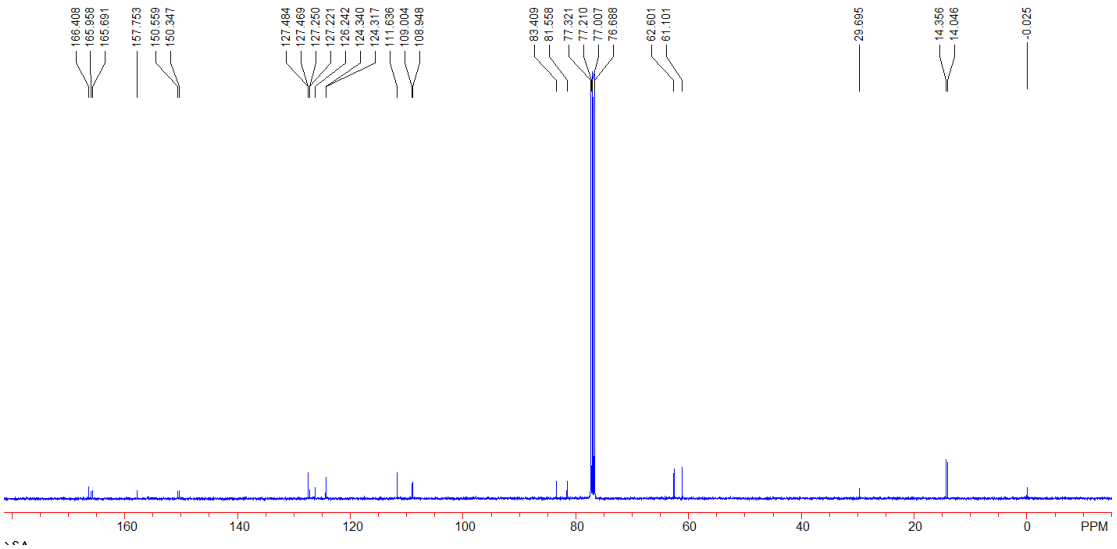
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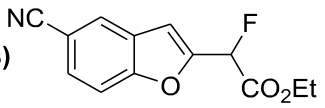
(2s)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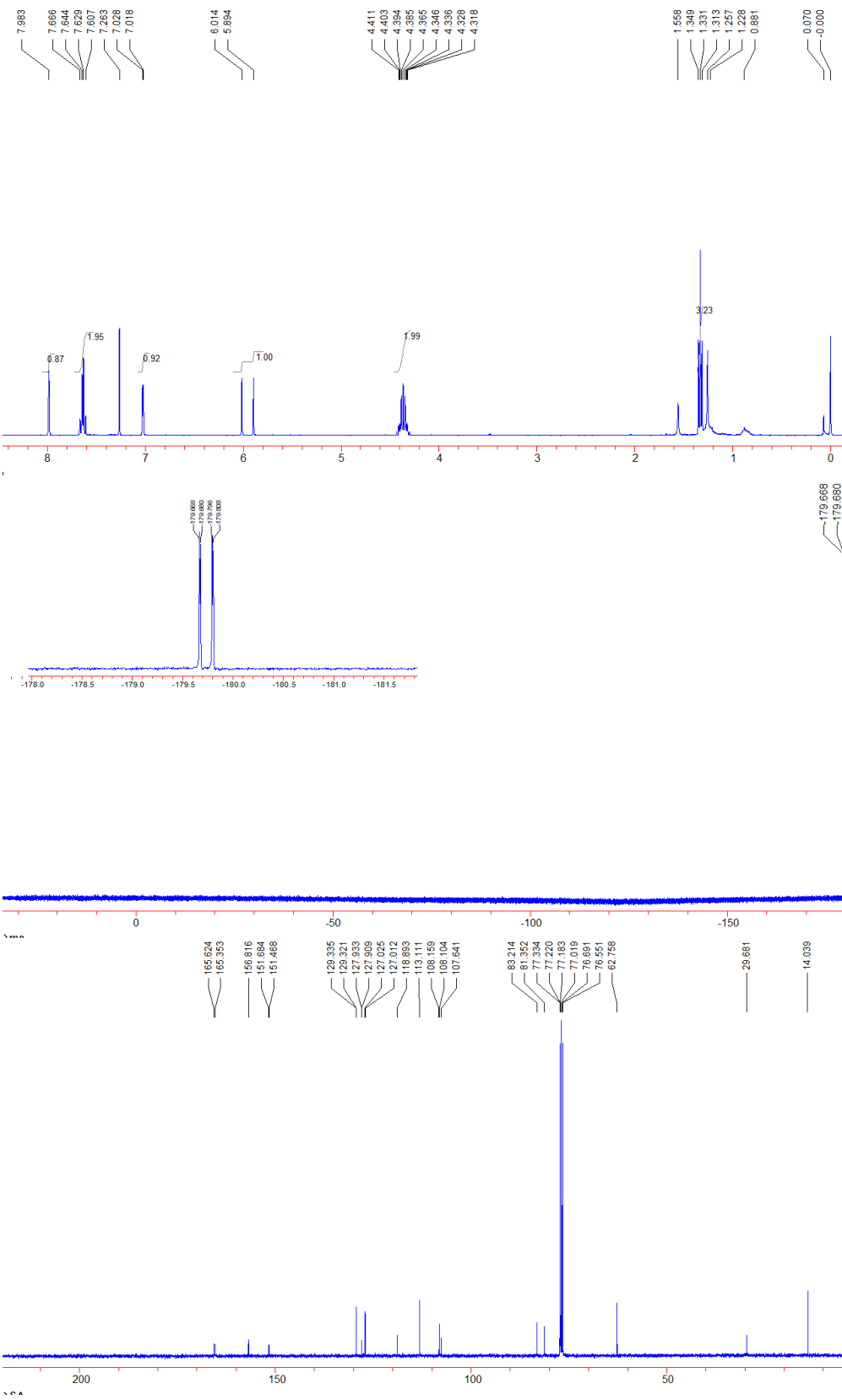
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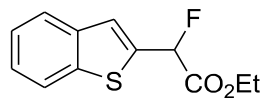
(2t)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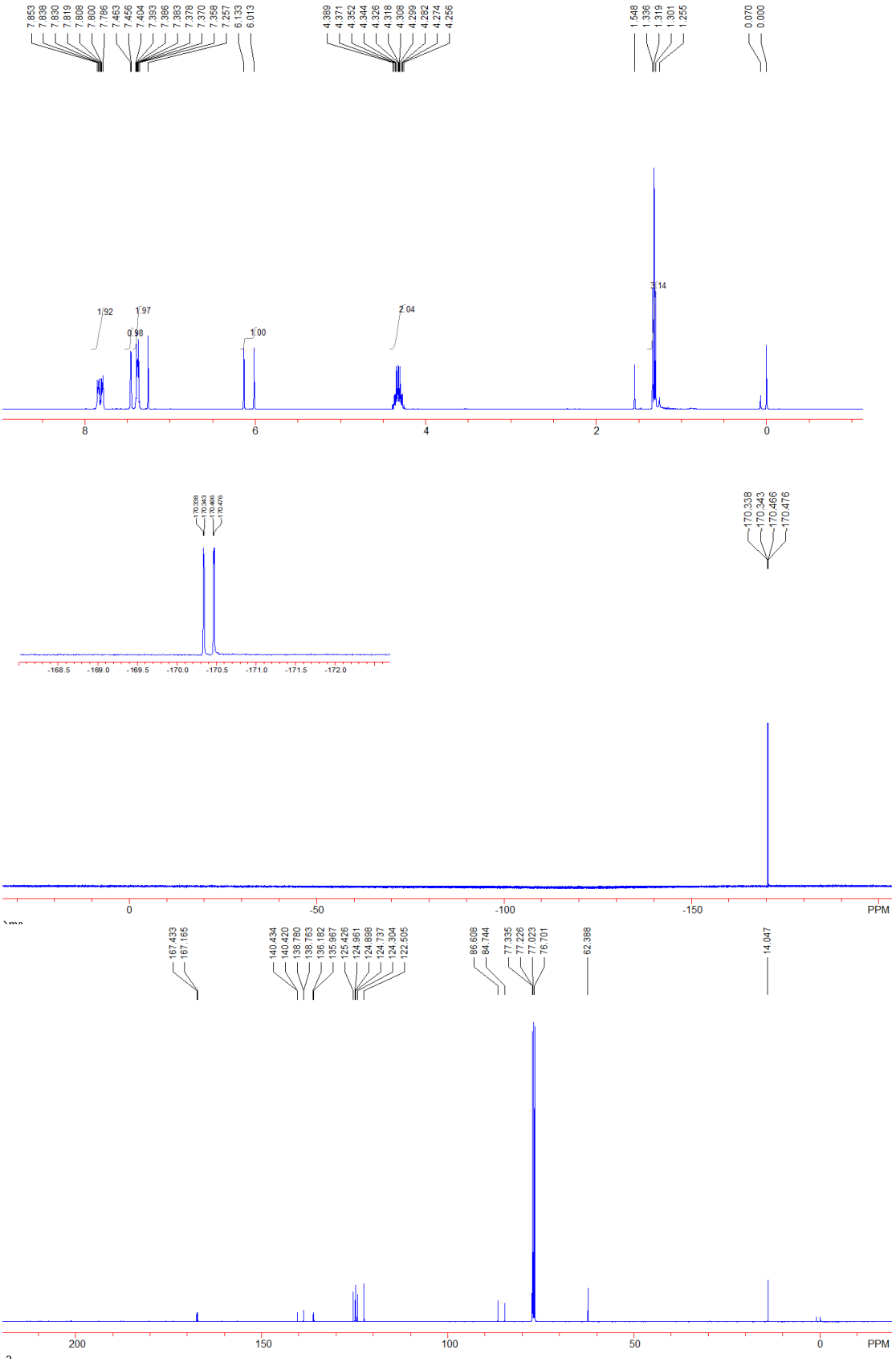
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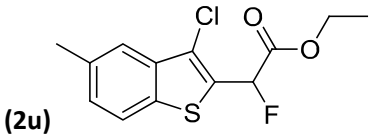
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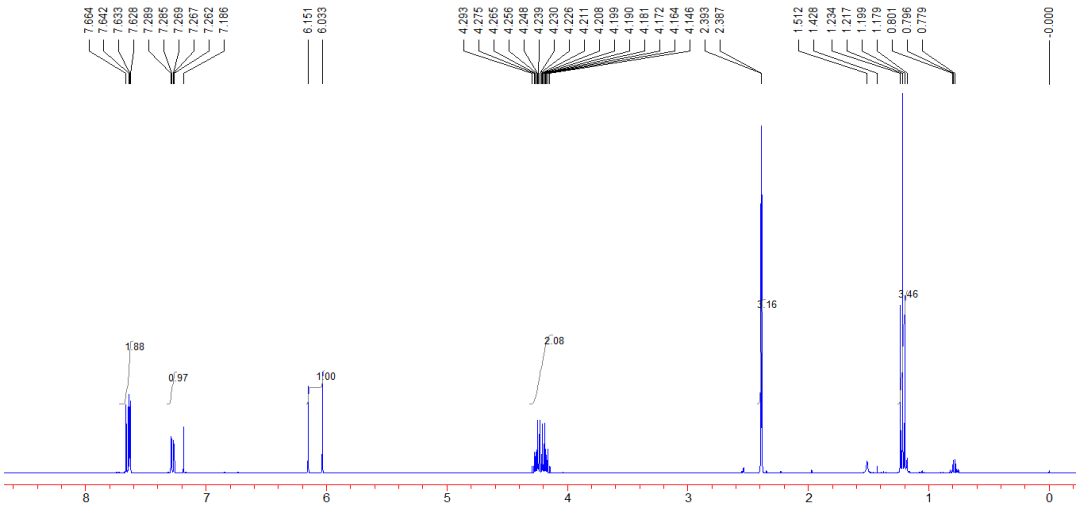
O
S
F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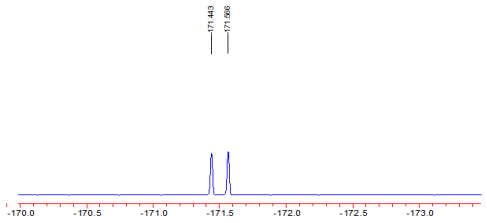
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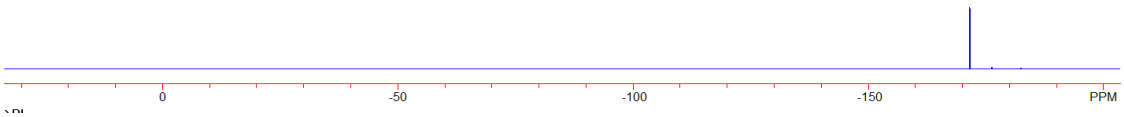
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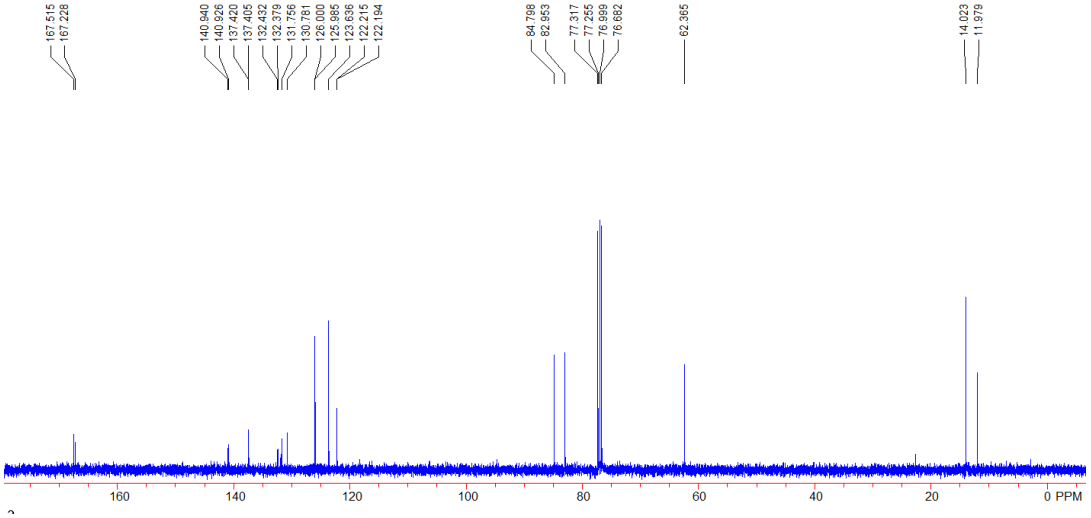
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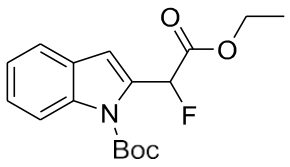
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Boc

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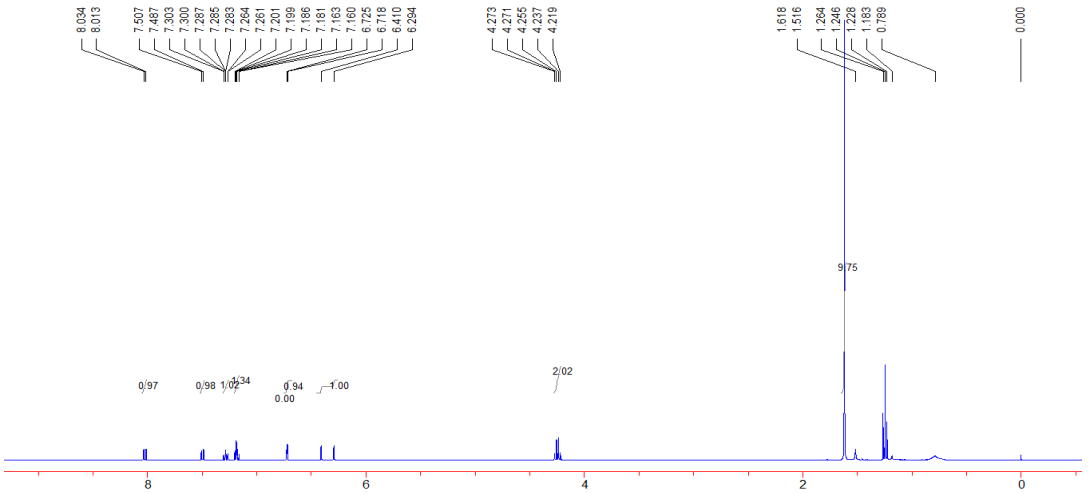
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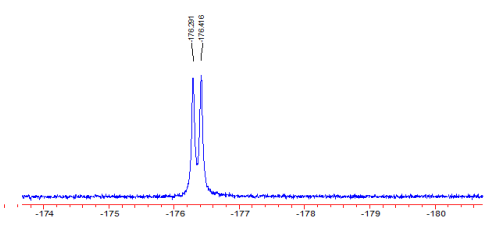
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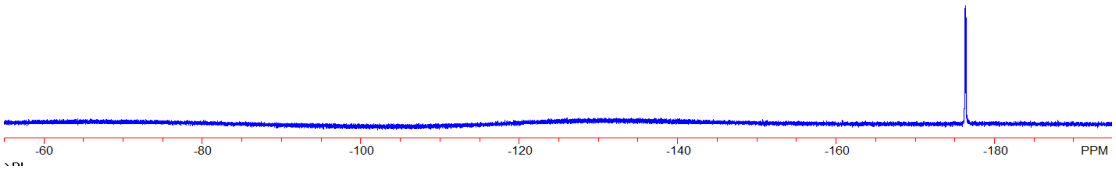
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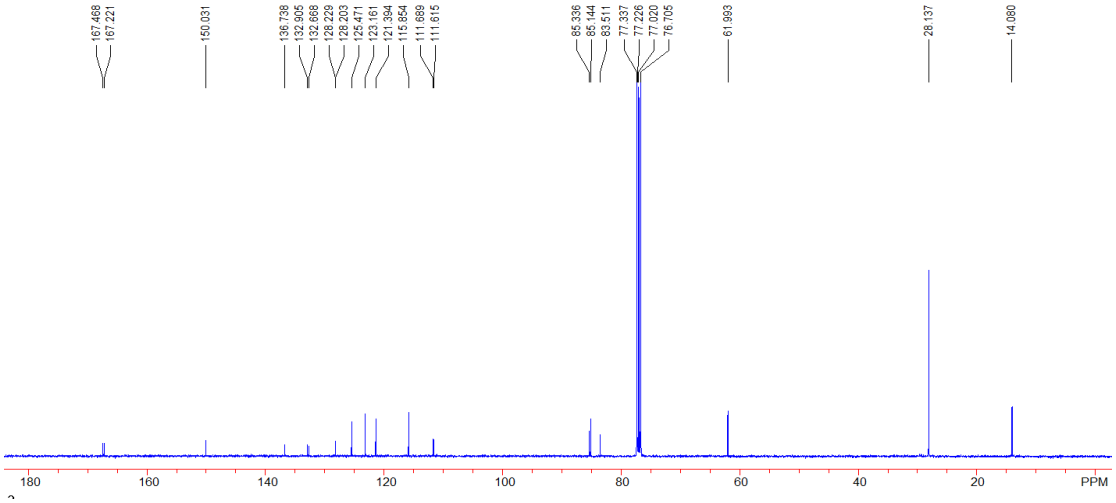
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111.689
111.615
85.336
85.144
83.911
77.337
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14.080
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160
140
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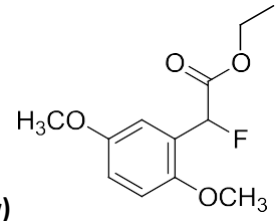
60
40
20
PPM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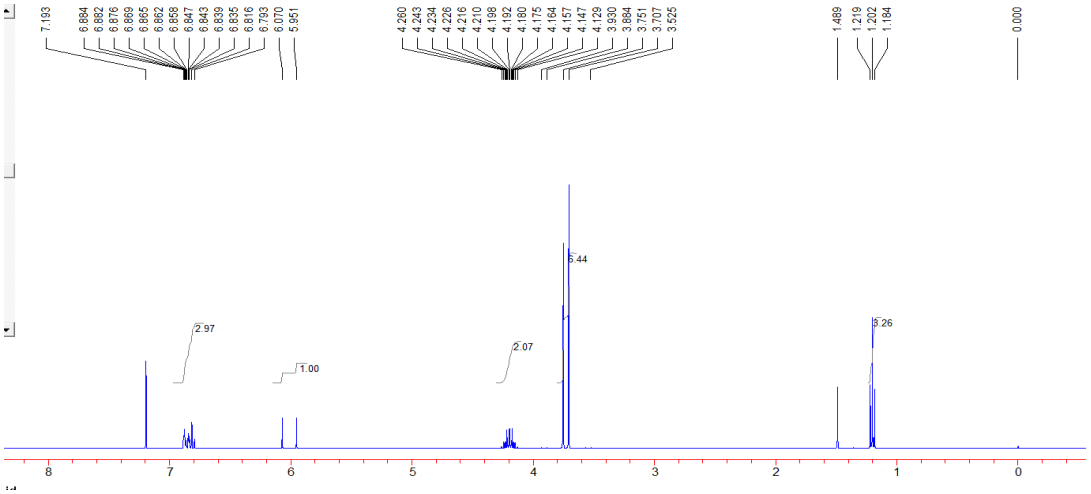
O
H3CO
F
OCH3

(2w)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6.816
6.793
6.070
5.951
4.260
4.243
4.234
4.226
4.216
4.210
4.198
4.192
4.180
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4.164
4.157
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3.884
3.751
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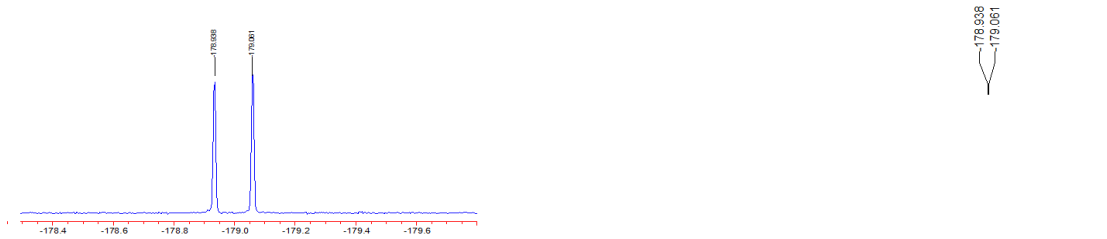
5.26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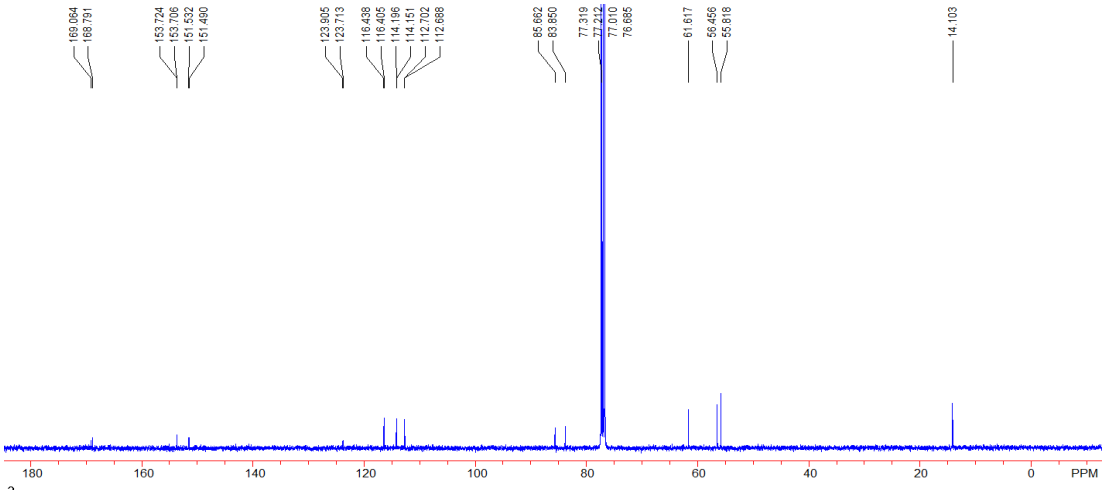
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77.319
77.212
77.010
76.685
61.617
56.456
55.818
14.103
PPM