Supporting Information

Silver-catalyzed decarboxylative acylfluorination of styrenes in aqueous media

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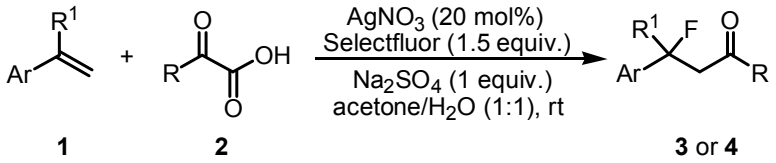
General Information

All reactions were carried out under an atmosphere of nitrogen with strict exclusion of air. Column chromatography was carried out on silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance III-400 in solvents as indicated. Chemical shift are reported in ppm from $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm^{-1}. HRMS were obtained on a Q-TOF micro spectrometer.

Starting Materials

Styrenes **1** were purchased from TCI, Alfa or Acros. Phenylglyoxylic acid **2a** was purchased from Sigma-Aldrich. Other α-oxocarboxylic acids **2** were prepared from the corresponding methyl ketones according to the reported procedure.[1] All of other commercially available compounds were used without further purification.

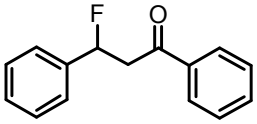
General Procedure for the Decarboxylative Acylfluorination of Styrenes with α-Oxocarboxylic Acids



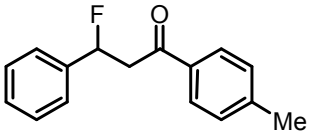
1 **2** **3** or **4**

A 10 mL oven-dried Schlenk-tube was charged with $AgNO_3$ (6.8 mg, 20 mol %), α-Oxocarboxylic Acids (**2**, 0.3 mmol, 1.5 equiv.), Selectfluor (0.3 mmol, 1.5 equiv.), and Na_2SO_4 (0.2 mmol, 1.0 equiv.). The tube was evacuated and backfilled with nitrogen (three times). Styrenes (**1**, 0.2 mmol, 1.0 equiv.) in acetone/H_2O (1:1, 1 mL) were added by syringe under nitrogen. The tube was then sealed and the mixture was stirred for 12 h at room temperature. The resulting mixture was diluted with EtOAc (15 mL). The organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/100 to 1/50) to give the corresponding products **3** or **4** in yields listed in Table 2 and Table 3.

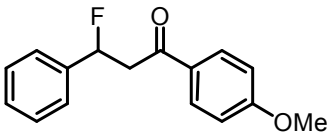
Characterization of Products 3



3a: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (d, *J* = 7.6 Hz, 2H), 7.61-7.57 (m, 1H), 7.50-7.36 (m, 7H), 6.27-6.12 (ddd, *J* = 46.8, 8.4, 4.4 Hz, 1H), 3.87-3.77 (ddd, *J* = 16.8, 14.8, 8.0 Hz, 1H), 3.39-3.27 (ddd, *J* = 30.0, 17.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1 (d, *J* = 3.6 Hz), 139.5 (d, *J* = 19.6 Hz), 136.7, 133.5, 128.7, 128.6, 128.2, 125.6 (d, *J* = 6.6 Hz), 90.3 (d, *J* = 169.8 Hz), 45.9 (d, *J* = 25.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.5 (ddd, *J* = 45.2, 30.1, 18.8 Hz, 1F); IR (KBr): υmax 1686, 1449, 1205 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{13}FNaO$ $[M+Na]^+$ 251.0843, found 251.0840.

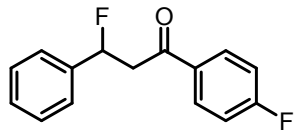


3b: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.86 (d, *J* = 8.4 Hz, 2H), 7.45-7.35 (m, 5H), 7.28-7.26 (m, 2H), 6.26-6.11 (ddd, *J* = 46.4, 8.0, 4.0 Hz, 1H), 3.84-3.74 (ddd, *J* = 17.2, 15.2, 8.4 Hz, 1H), 3.36-3.23 (ddd, *J* = 30.2, 17.2, 4.4 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.7, 144.4, 139.6 (d, *J* = 19.6 Hz), 134.2, 129.4, 128.6, 128.3, 125.6 (d, *J* = 6.8 Hz), 90.4 (d, *J* = 169.7 Hz), 45.8 (d, *J* = 26.0 Hz), 21.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, *J* = 48.9, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1683, 1004 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.0999, found 265.0999.

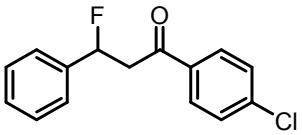


3c: R_f 0.3 (EtOAc/petroleum ether = 1:20); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.45-7.33 (m, 5H), 6.96-6.92 (m, 2H), 6.25-6.10 (ddd, *J* = 46.8, 8.4, 4.0 Hz, 1H), 3.90 (s, 3H), 3.81-3.71 (ddd, *J* = 16.8, 14.8, 8.4 Hz, 1H), 3.33-3.20 (ddd, *J* = 30.0, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.6 (d, *J* = 3.6 Hz), 163.8, 139.6 (d, *J* = 19.6 Hz), 130.5, 129.8, 128.6, 125.6 (d, *J* = 6.8 Hz), 113.8, 90.5 (d, *J* =

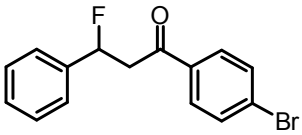
169.8 Hz), 55.5, 45.6 (d, J = 26.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, J = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1676, 1600, 1261, 1169 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{15}FNaO_2$ $[M+Na]^+$ 281.0948, found 281.0949.



3d: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.98 (m, 2H), 7.44-7.36 (m, 5H), 7.17-7.12 (m, 2H), 6.24-6.09 (ddd, J = 46.4, 8.0, 4.0 Hz, 1H), 3.83-3.73 (ddd, J = 16.8, 14.8, 8.4 Hz, 1H), 3.35-3.22 (ddd, J = 30.0, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5 (d, J = 3.6 Hz), 160.0 (d, J = 254.0 Hz), 139.3 (d, J = 19.6 Hz), 133.2, 130.9 (d, J = 9.4 Hz), 128.7, 128.5, 125.6 (d, J = 6.6 Hz), 115.8 (d, J = 21.8 Hz), 90.3 (d, J = 170.1 Hz), 45.9 (d, J = 26.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.3 (m, 1F), -174.1 (ddd, J = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1687, 1597, 1206, 1156 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}F_2NaO$ $[M+Na]^+$ 269.0748, found 269.0751.

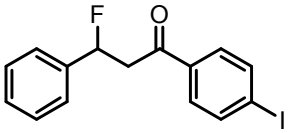


3e: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.89 (d, J = 8.8 Hz, 2H), 7.46-7.36 (m, 7H), 6.23-6.09 (ddd, J = 46.8, 8.4, 4.0 Hz, 1H), 3.82-3.72 (ddd, J = 16.8, 14.8, 8.4 Hz, 1H), 3.35-3.22 (ddd, J = 30.2, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9 (d, J = 3.6 Hz), 140.0, 139.2 (d, J = 19.6 Hz), 135.0, 129.6, 129.0, 128.7, 128.6, 125.6 (d, J = 6.6 Hz), 90.2 (d, J = 170.1 Hz), 45.9 (d, J = 26.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, J = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1687, 1589, 911, 740 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}ClFNaO$ $[M+Na]^+$ 285.0453, found 285.0450.

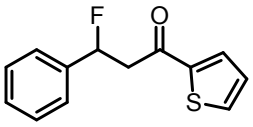


3f: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.81

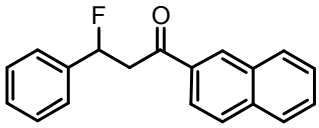
(d, *J* = 8.8 Hz, 2H), 7.63-7.60 (d, *J* = 8.8 Hz, 2H), 7.41-7.36 (m, 5H), 6.23-6.09 (ddd, *J* = 46.8, 8.4, 4.0 Hz, 1H), 3.82-3.72 (ddd, *J* = 16.8, 14.4, 8.0 Hz, 1H), 3.34-3.21 (ddd, *J* = 30.0, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1 (d, *J* = 3.6 Hz), 145.4, 139.2 (d, *J* = 19.6 Hz), 135.4, 132.0, 131.9, 129.7, 128.8, 128.7, 125.6 (d, *J* = 6.6 Hz), 90.2 (d, *J* = 170.3 Hz), 45.9 (d, *J* = 26.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1688, 1584, 1397, 1069, 1008 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}BrFNaO$ $[M+Na]^+$ 328.9948, found 328.9963.



3g: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.83 (d, *J* = 8.4 Hz, 2H), 7.68-7.65 (d, *J* = 8.4 Hz, 2H), 7.43-7.36 (m, 5H), 6.23-6.08 (ddd, *J* = 46.4, 8.4, 4.0 Hz, 1H), 3.81-3.71 (ddd, *J* = 16.8, 14.8, 8.4 Hz, 1H), 3.33-3.20 (ddd, *J* = 30.0, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.4, 139.2 (d, *J* = 19.7 Hz), 138.0, 135.9, 129.6, 128.7, 125.6 (d, *J* = 6.6 Hz), 101.7, 90.1 (d, *J* = 170.4 Hz), 45.8 (d, *J* = 26.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1680, 1603, 1004 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}FINaO$ $[M+Na]^+$ 376.9809, found 376.9824.

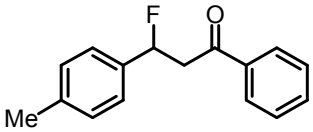


3h: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 3.2 Hz, 1H), 7.69-7.67 (d, *J* = 4.8 Hz, 1H), 7.44-7.36 (m, 5H), 7.15-7.13 (dd, *J* = 4.0, 4.4 Hz, 1H), 6.22-6.07 (ddd, *J* = 46.8, 8.4, 4.0 Hz, 1H), 3.78-3.68 (ddd, *J* = 23.2, 14.8, 4.8Hz, 1H), 3.31-3.18 (ddd, *J* = 31.2, 16.4, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.8 (d, *J* = 3.6 Hz), 144.0, 139.2 (d, *J* = 19.6 Hz), 134.5, 132.6, 128.7, 128.6, 128.2, 125.5 (d, *J* = 6.6 Hz), 90.2 (d, *J* = 171.1 Hz), 46.7 (d, *J* = 26.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.0 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1658, 1415, 1212 cm^{-1}; HRMS(ESI) calcd for $C_{13}H_{11}FNaOS$ $[M+Na]^+$ 257.0407, found 257.0416.

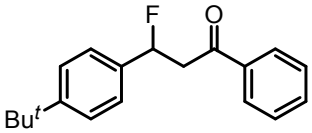


3i: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.06-7.87 (m, 4H), 7.64-7.37 (m, 7H), 6.33-6.19 (ddd, *J* = 46.4, 8.0, 4.0 Hz, 1H), 4.02-3.91 (ddd, *J* = 16.8, 14.8, 8.4 Hz, 1H), 3.52-3.40 (ddd, *J* = 30.0, 16.8, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 139.5 (d, *J* = 19.5 Hz), 135.7, 134.0, 132.4, 130.1, 129.6, 128.7, 128.6, 127.8, 126.9, 125.6 (d, *J* = 6.6 Hz), 123.7, 90.4 (d, *J* = 169.9 Hz), 46.0 (d, *J* = 26.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -174.1 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1681, 1374, 1283, 1183 cm^{-1}; HRMS(ESI) calcd for $C_{19}H_{15}FNaO$ $[M+Na]^+$ 301.0999, found 301.1011.

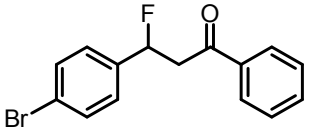
Characterization of Products 4



4a: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (d, *J* = 7.6 Hz, 2H), 7.59-7.57 (m, 1H), 7.50-7.46 (m, 2H), 7.34-7.33 (d, *J* = 7.6 Hz, 2H), 7.22-7.20 (d, *J* = 8.0 Hz, 2H), 6.22-6.07 (ddd, *J* = 46.4, 8.0, 4.0 Hz, 1H), 3.86-3.76 (ddd, *J* = 16.8, 14.4, 8.0 Hz, 1H), 3.38-3.25 (ddd, *J* = 29.2, 16.8, 4.0 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 138.5, 136.7, 136.4 (d, *J* = 19.8 Hz), 133.4, 129.3, 128.7, 128.2, 125.7 (d, *J* = 6.4 Hz), 90.3 (d, *J* = 169.1 Hz), 45.8 (d, *J* = 26.4 Hz), 21.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -172.1 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1687, 1598, 1208, 1014 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.0999, found 265.1003.

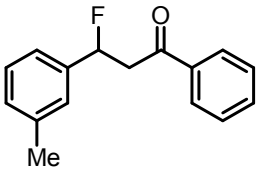


4b: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (d, *J* = 8.4 Hz, 2H), 7.61-7.57 (t, *J* = 7.6 Hz, 1H), 7.50-7.37 (m, 6H), 6.24-6.09 (ddd, *J* = 46.4, 8.0, 4.0 Hz, 1H), 3.88-3.78 (ddd, *J* = 16.8, 14.4, 8.4 Hz, 1H), 3.39-3.26 (ddd, *J* = 30.0, 17.2, 4.0 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2 (d, *J* = 3.6 Hz), 151.8, 136.7, 136.4 (d, *J* = 19.5 Hz), 133.5, 128.7, 128.2, 125.6, 125.5 (d, *J* = 6.4 Hz), 90.2 (d, *J* = 168.7 Hz), 45.8 (d, *J* = 26.3 Hz), 34.6, 31.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -172.4 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1688, 1445, 1207, 1017 cm^{-1}; HRMS(ESI) calcd for $C_{19}H_{21}FNaO$ $[M+Na]^+$ 307.1469, found 307.1477.

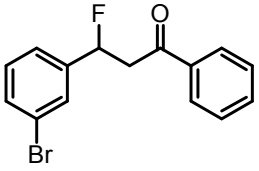


4c: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.94 (m, 2H), 7.60-7.46 (m, 5H), 7.33-7.31 (d, *J* = 8.0 Hz, 2H), 6.22-6.08 (ddd, *J* = 46.4,

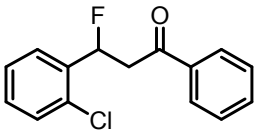
8.0, 4.8 Hz, 1H), 3.83-3.73 (ddd, *J* = 17.2, 14.8, 8.0 Hz, 1H), 3.38-3.26 (ddd, *J* = 27.6, 16.8, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 138.5 (d, *J* = 20.0 Hz), 136.5, 133.6, 131.8, 129.8, 128.7, 128.5, 128.2, 127.4 (d, *J* = 6.6 Hz), 122.6, 89.7 (d, *J* = 170.1 Hz), 45.8 (d, *J* = 26.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -175.0 (m, 1F); IR (KBr): υmax 1685, 1208, 1008 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}BrFNaO$ $[M+Na]^+$ 328.9948, found 328.9954.



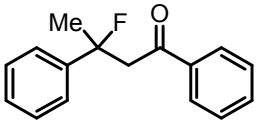
4d: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.96 (m, 2H), 7.61-7.46 (m, 3H), 7.31-7.16 (m, 4H), 6.23-6.09 (ddd, *J* = 46.8, 8.4, 4.0 Hz, 1H), 3.86-3.76 (ddd, *J* = 17.2, 15.2, 8.4 Hz, 1H), 3.37-3.24 (ddd, *J* = 30.4, 17.2, 4.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 139.3, 138.4, 136.7, 133.5, 129.4, 128.7, 128.5, 128.2, 126.3 (d, *J* = 6.5 Hz), 122.7 (d, *J* = 6.8 Hz), 90.3 (d, *J* = 169.6 Hz), 45.9 (d, *J* = 26.1 Hz), 21.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -173.7 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1688, 1370, 1001 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.0999, found 265.1010.



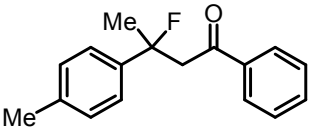
4e: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.95 (d, *J* = 7.2 Hz, 2H), 7.62-7.58 (m, 2H), 7.50-7.46 (m, 3H), 7.37-7.35 (d, *J* = 7.6 Hz, 1H), 7.29-7.25 (t, *J* = 7.6 Hz, 1H), 6.23-6.09 (ddd, *J* = 46.0, 8.0, 4.4 Hz, 1H), 3.84-3.74 (ddd, *J* = 17.2, 15.2, 8.0 Hz, 1H), 3.37-3.25 (ddd, *J* = 28.8, 17.2, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6 (d, *J* = 3.6 Hz), 141.8 (d, *J* = 19.9 Hz), 136.4, 133.7, 131.7, 130.2, 128.7, 128.6 (d, *J* = 7.2 Hz), 128.2, 124.3 (d, *J* = 6.6 Hz), 122.7, 89.4 (d, *J* = 171.5 Hz), 45.8 (d, *J* = 25.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -175.8 (ddd, *J* = 45.1, 30.1, 15.0 Hz, 1F); IR (KBr): υmax 1686, 1207, 689 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}BrFNaO$ $[M+Na]^+$ 328.9948, found 328.9953.



4f: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.98 (d, *J* = 7.2 Hz, 2H), 7.60-7.58 (d, *J* = 7.6 Hz, 2H), 7.50-7.47 (m, 2H), 7.40-7.28 (m, 3H), 6.60-6.46 (ddd, *J* = 46.4, 9.2, 2.4 Hz, 1H), 3.67-3.76 (m, 1H), 3.49-3.35 (ddd, *J* = 31.6, 17.2, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 137.4 (d, *J* = 21.1 Hz), 136.5, 133.5, 130.7 (d, *J* = 5.6 Hz), 129.6, 129.5, 128.7, 128.2, 127.2, 126.6 (d, *J* = 10.4 Hz), 87.3 (d, *J* = 172.8 Hz), 44.5 (d, *J* = 25.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -182.9 (m, 1F); IR (KBr): υmax 1688, 1367, 1207, 1017 cm^{-1}; HRMS(ESI) calcd for $C_{15}H_{12}ClFNaO$ $[M+Na]^+$ 285.0453, found 285.0456.

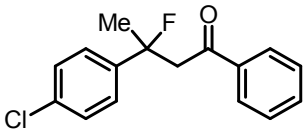


4g: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92-7.90 (d, *J* = 7.6 Hz, 2H), 7.56-7.53 (t, *J* = 7.6 Hz, 1H), 7.45-7.43 (m, 4H), 7.38-7.34 (m, 2H), 7.31-7.29 (d, *J* = 7.6 Hz, 1H), 3.72-3.65 (t, *J* = 14.8 Hz, 1H), 3.54-3.44 (dd, *J* = 23.6, 14.8 Hz, 1H), 1.91-1.85 (d, *J* = 23.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6 (d, *J* = 4.9 Hz), 144.1 (d, *J* = 21.8 Hz), 137.5, 133.2, 128.6, 128.5, 128.3, 127.7, 124.1 (d, *J* = 9.1 Hz), 95.9 (d, *J* = 173.5 Hz), 49.9 (d, *J* = 25.2 Hz), 26.7 (d, *J* = 24.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -139.7 (m, 1F); IR (KBr): υmax 1677, 1448, 1216 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{15}FNaO$ $[M+Na]^+$ 265.0999, found 265.0998.

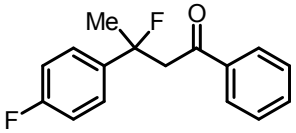


4h: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.91 (d, *J* = 7.6 Hz, 2H), 7.57-7.53 (t, *J* = 7.6 Hz, 1H), 7.45-7.41 (m, 2H), 7.33-7.31 (d, *J* = 8.4 Hz, 2H), 7.18-7.16 (d, *J* = 8.0 Hz, 2H), 3.71-3.63 (t, *J* = 14.8 Hz, 1H), 3.53-3.44 (dd, *J* = 23.2, 15.2 Hz, 1H), 2.34 (s, 3H), 1.89-1.83 (d, *J* = 23.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.6 (d, *J* = 4.6 Hz), 141.1 (d, *J* = 21.7 Hz), 137.4 (d, *J* = 9.8 Hz), 133.1, 129.1, 129.0, 128.6, 128.4, 125.7, 124.1 (d, *J* = 8.7 Hz), 96.0 (d, *J* = 172.6

Hz), 49.9 (d, J = 25.3 Hz), 26.7 (d, J = 24.1 Hz), 21.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -138.7 (m, 1F); IR (KBr): υmax 1678, 1213, 1079, 1005 cm^{-1}; HRMS(ESI) calcd for $C_{17}H_{17}FNaO$ $[M+Na]^+$ 279.1156, found 279.1166.

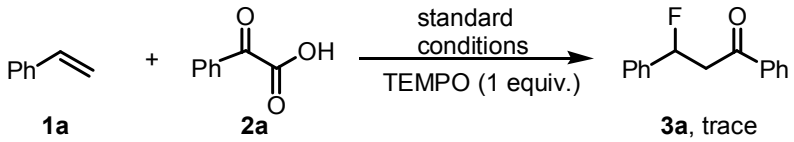


4i: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.88 (d, J = 7.6 Hz, 2H), 7.58-7.54 (t, J = 7.6 Hz, 1H), 7.46-7.42 (t, J = 8.0 Hz, 2H), 7.38-7.31 (m, 4H), 3.68-3.49 (m, 2H), 1.89-1.83 (d, J = 23.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1 (d, J = 5.5 Hz), 142.4 (d, J = 21.9 Hz), 137.2, 133.6, 133.3, 128.5, 128.4, 125.8 (d, J = 9.2 Hz), 95.6 (d, J = 173.6 Hz), 49.7 (d, J = 25.1 Hz), 26.8 (d, J = 24.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -138.9 (m, 1F); IR (KBr): υmax 1677, 1089, 1008, 746 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{14}ClFNaO$ $[M+Na]^+$ 299.0609, found 299.0619.



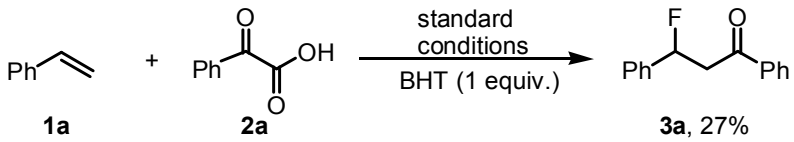
4j: R_f 0.4 (EtOAc/petroleum ether = 1:50); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.88 (d, J = 7.6 Hz, 2H), 7.57-7.54 (t, J = 7.6 Hz, 1H), 7.45-7.38 (m, 4H), 7.05-7.01 (t, J = 8.8 Hz, 2H), 3.68-3.49 (m, 2H), 1.90-1.84 (d, J = 23.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3 (d, J = 5.9 Hz), 162.1 (d, J = 244.9 Hz), 139.7 (d, J = 22.0 Hz), 137.3, 133.3, 128.5, 126.2, 126.1, 115.1 (d, J = 21.3 Hz), 95.7 (d, J = 172.9 Hz), 49.9 (d, J = 25.6 Hz), 26.8 (d, J = 23.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ -114.9 (m, 1F), -137.3 (m, 1F); IR (KBr): υmax 1679, 1511, 1219 cm^{-1}; HRMS(ESI) calcd for $C_{16}H_{14}F_2NaO$ $[M+Na]^+$ 283.0905, found 283.0914.

Investigation of the Reaction Mechanism



1a **2a** **3a**, trace

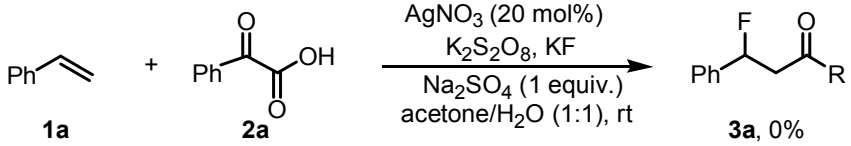
When the TEMPO was added to the reaction of **1a** and **2a** with Selectfluor under the standard conditions, only trace amount of the desired product **3a** was detected. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.



1a **2a** **3a**, 27%

When the BHT was added to the reaction of **1a** and **2a** with Selectfluor under the standard conditions, the desired product **3a** was only isolated in 27% yield. The result indicates that the radical intermediate should be involved in the catalytic cycle of the reaction.

Investigation of the Reaction Mechanism



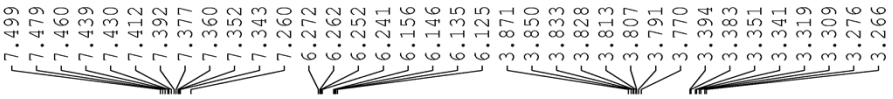
When the reaction of **1a** and **2a** was conducted with $AgNO_3$ (20 mol%), $K_2S_2O_8$ (2 equiv.), Na_2SO_4 (1 equiv.) and KF (2 equiv.) in acetone/H_2O at room temperature for 12 h, no desired product **3a** was detected, suggesting that a reaction pathway other than a common Ag(II) intermediate might also be involved.

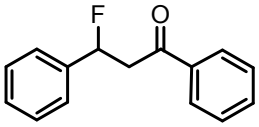
When the reaction of **1a** and **2a** was conducted with $AgNO_3$ (20 mol%), $K_2S_2O_8$ (2 equiv.), Na_2SO_4 (1 equiv.) and AgF (2 equiv.) in acetone/H_2O at room temperature for 12 h, no desired product **3a** was detected, suggesting that a reaction pathway other than a common Ag(II) intermediate might also be involved.

References

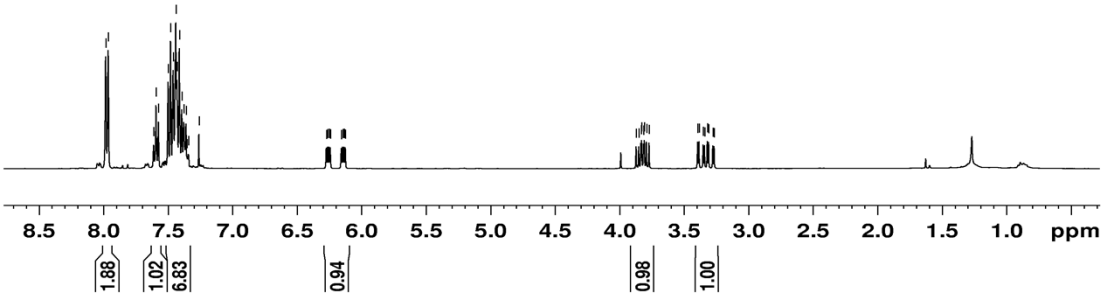
(1) K. Wadhwa, C.Yang, P. R. West, K. C. Deming, S. R. Chemburkar and R. E. Reddy, *Synth. Commun.*, 2008, **38**, 4434.

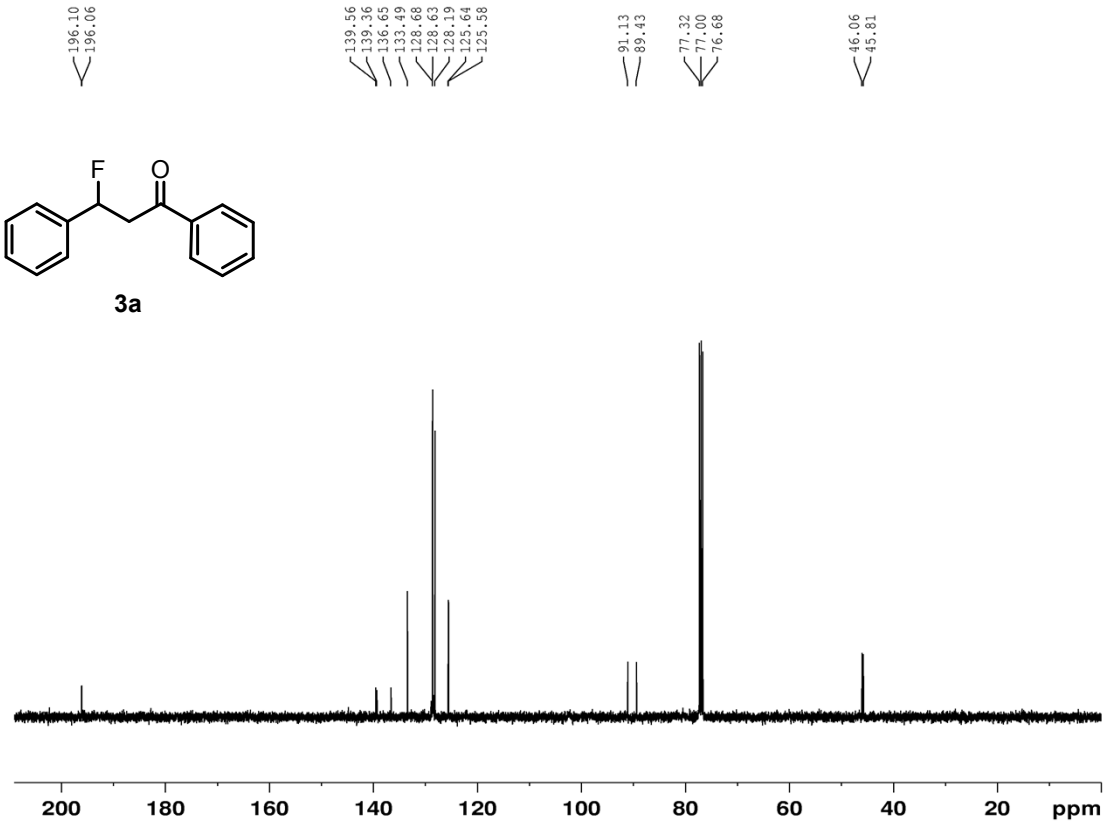
^{1}H NMR and ^{13}C NMR Spectra of the Products 3





3a

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89.43
77.32
77.00
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F
O
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160
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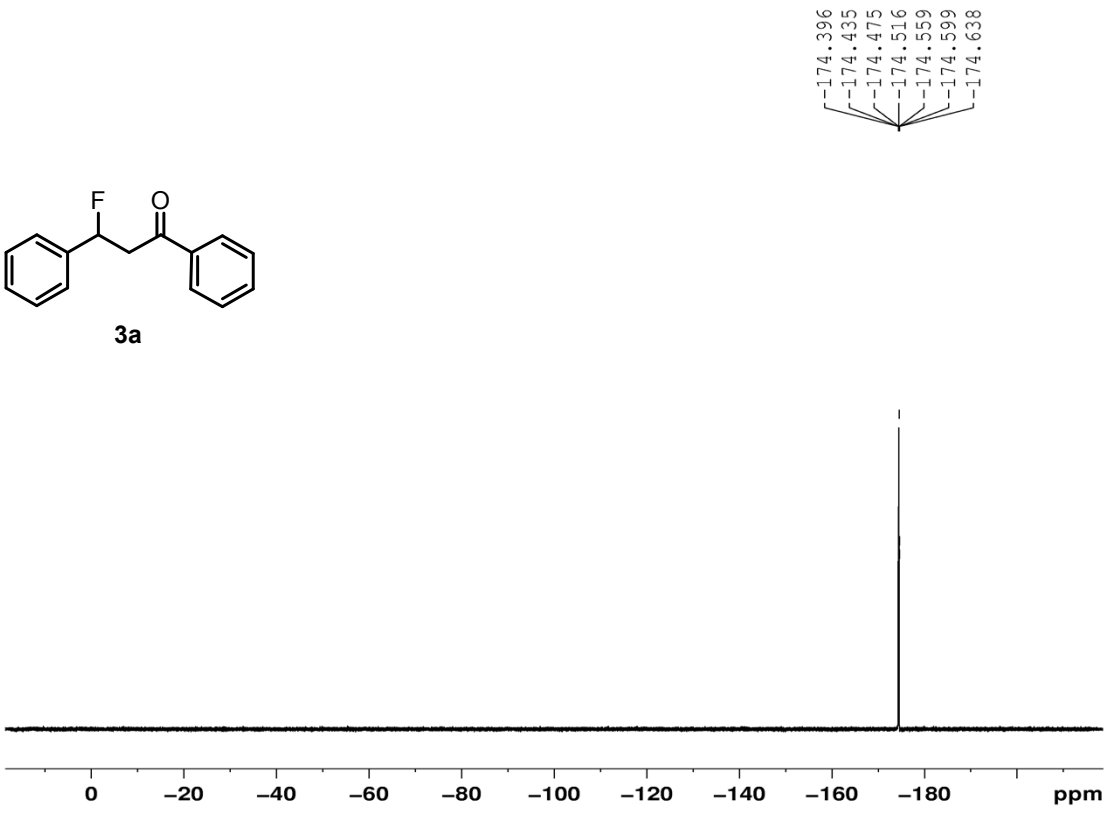
120
100
80
60
40
20
ppm

3a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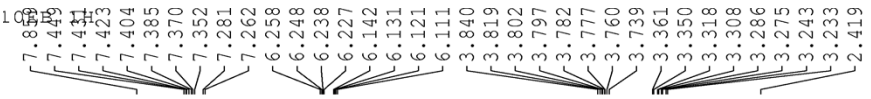
ppm

3a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6.227
6.142
6.131
6.121
6.111
3.840
3.819
3.802
3.797
3.782
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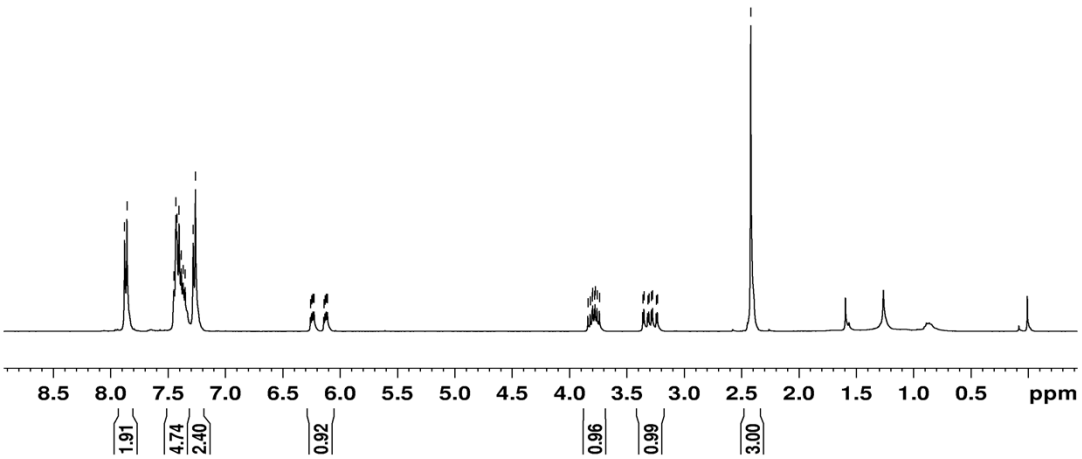
3.286
3.275
3.243
3.233
2.419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3.0
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1.0
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ppm
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4.74
2.40
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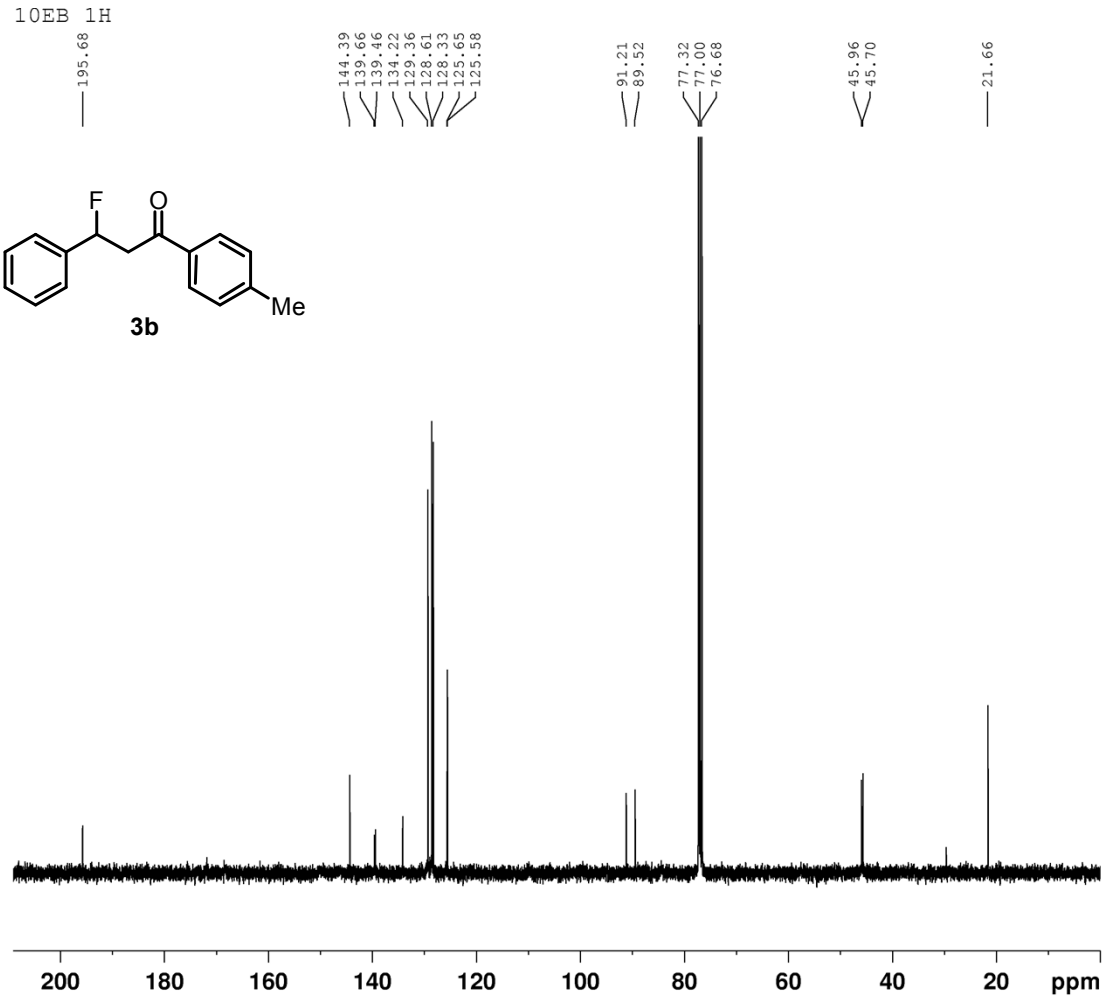
0.96
0.99
3.00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76.68
45.96
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Me
3b
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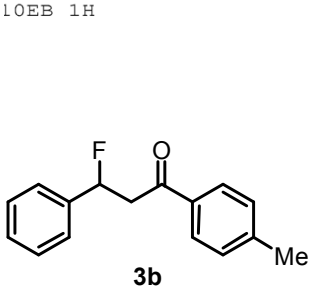
20
ppm

l0EB 1H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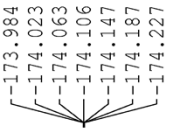
O
Me

3b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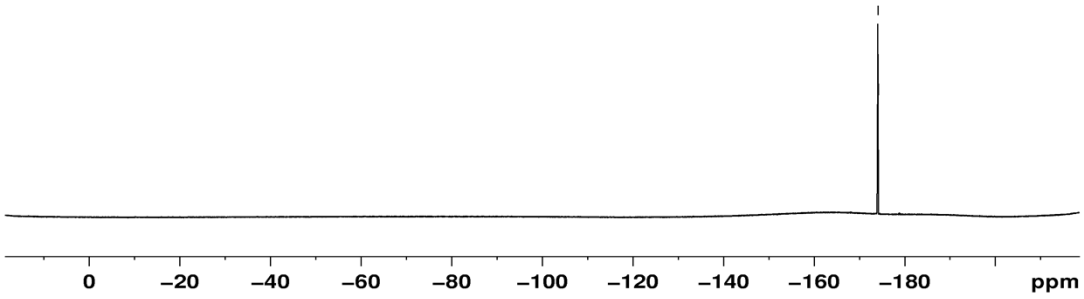
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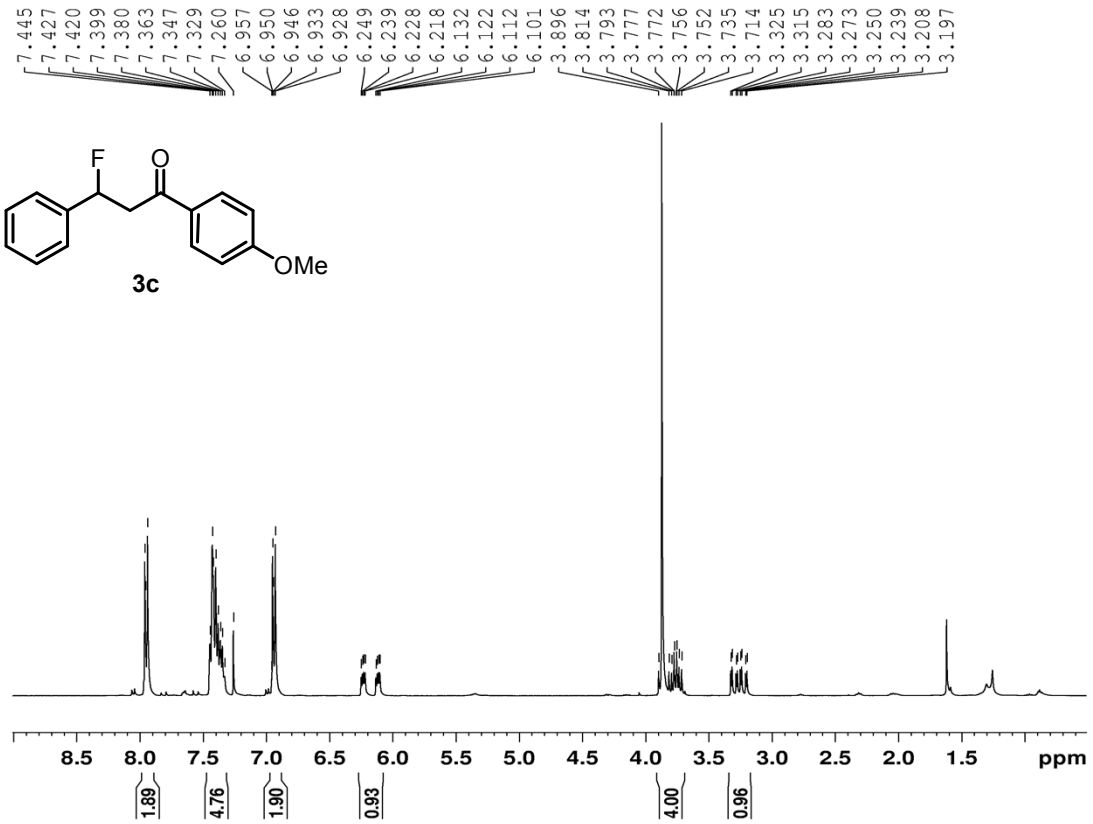
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3.283
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3.250
3.239
3.208
3.197
F
O
OMe
3c
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7.5
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6.5
6.0
5.5
5.0
4.5
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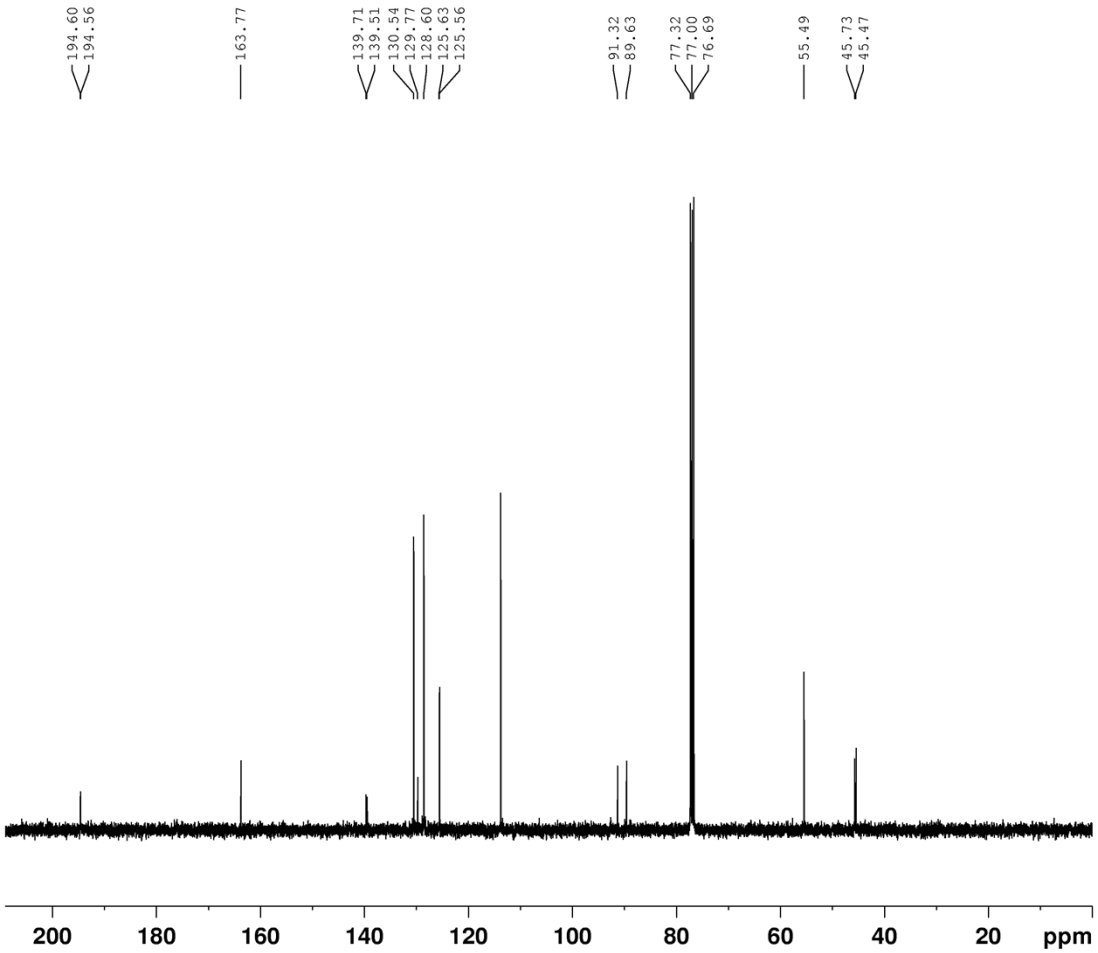
0.96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129.77
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45.47
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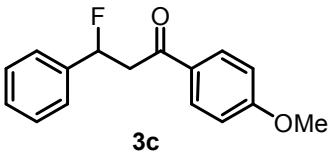
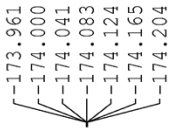

F
O
OMe

3c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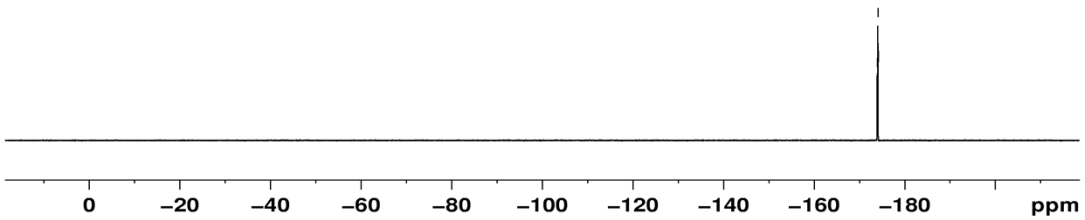
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6.229
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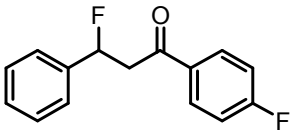
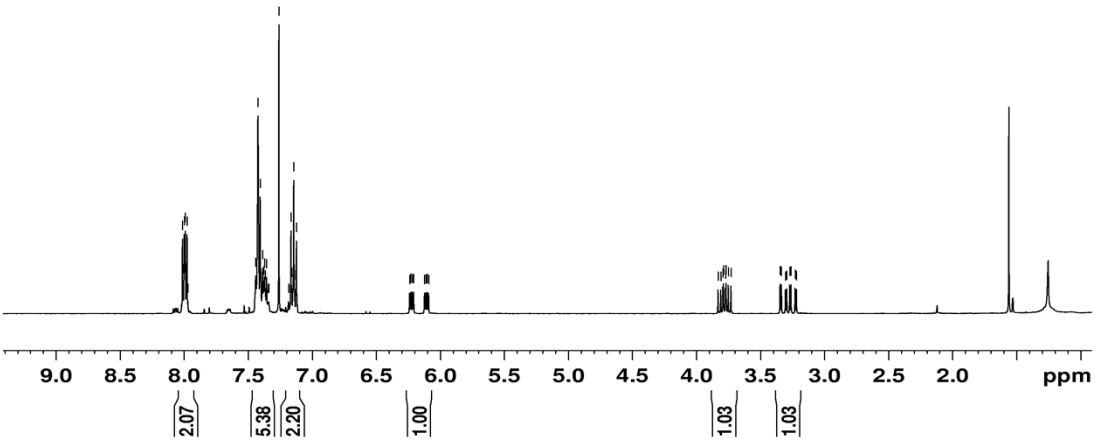
3.773
3.768
3.752
3.731
3.347
3.337
3.305
3.294
3.272
3.262
3.230
3.219


F
O
F

3d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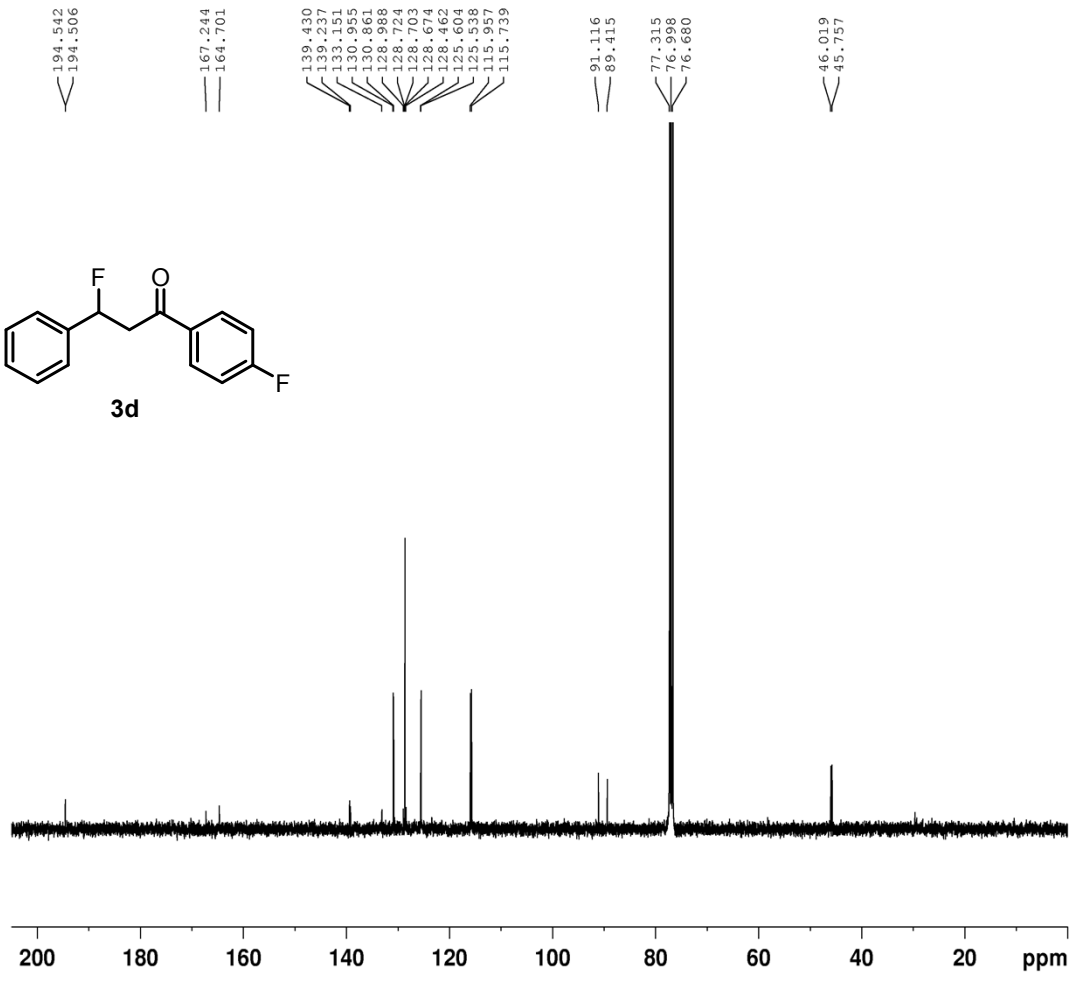
1.03
1.03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128.674
128.462
125.604
125.538
115.957
115.739
91.116
89.415
77.315
76.998
76.680
46.019
45.757
F
O
F
200
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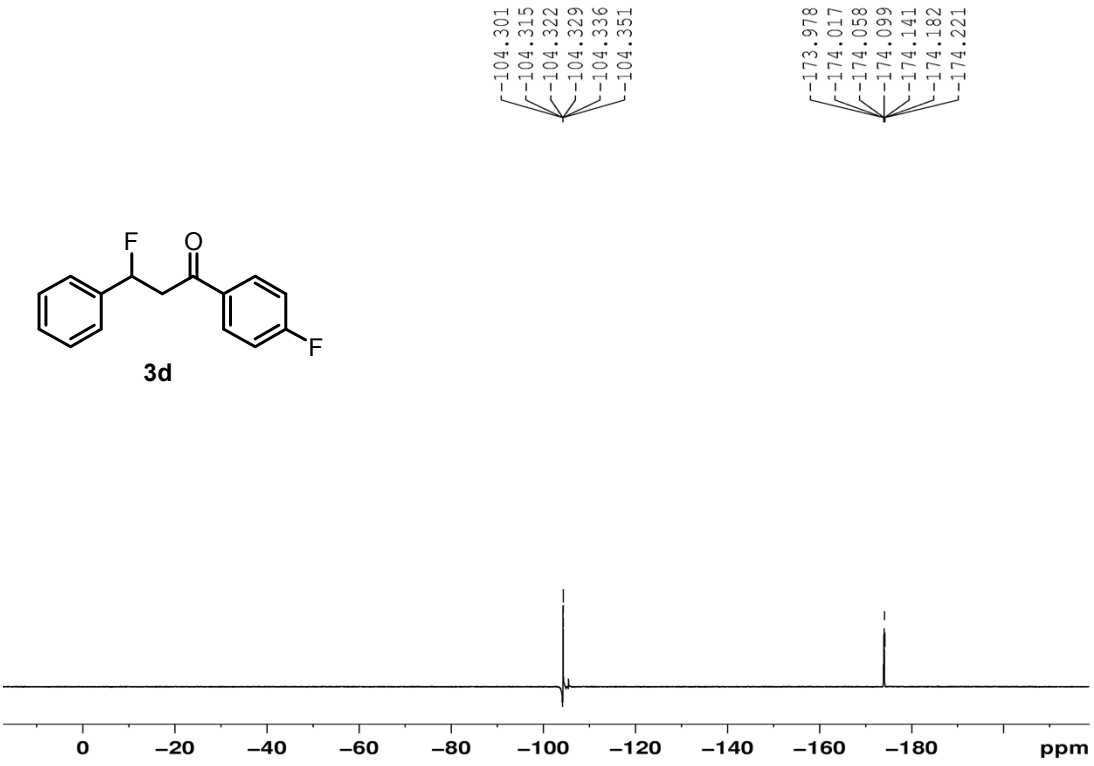
160
140
120
100
80
60
40
20
ppm

3d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-104.322
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-104.351
-173.978
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-174.058
-174.099
-174.141
-174.182
-174.221
F
O
F
3d
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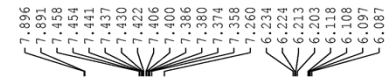
−160
−180
ppm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7.422
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7.400
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7.380
7.374
7.358
7.260
6.234
6.224
6.213
6.203
6.118
6.108
6.097
6.087
3.823
3.803
3.787
3.781
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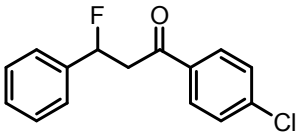
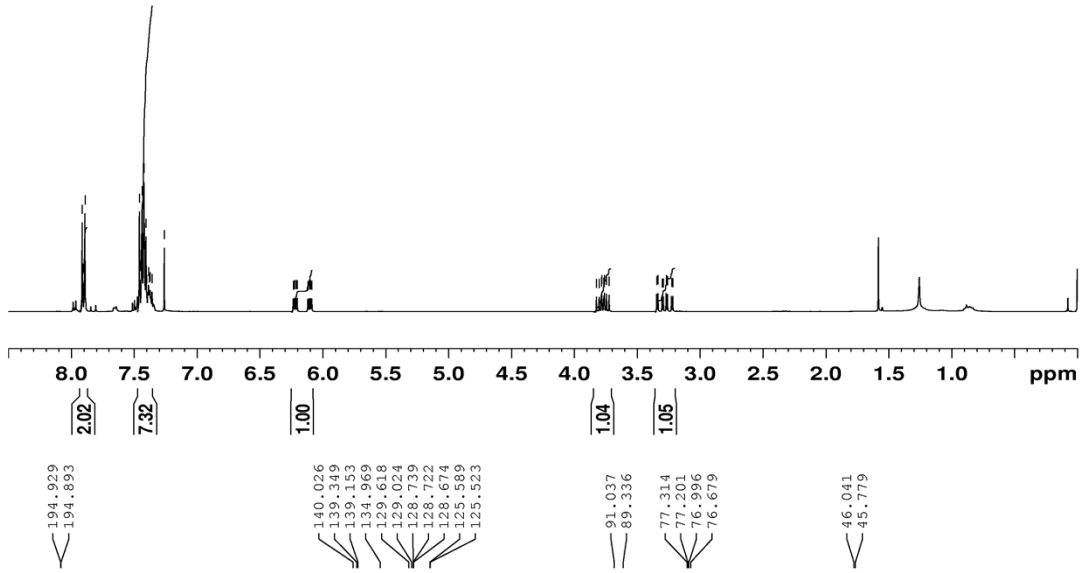
3.270
3.259
3.227
3.217


F
O
Cl

3e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1.5
1.0
ppm
2.02
7.32
1.00
1.04
1.05

194.929
194.893
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139.349
139.153
134.969
129.618
129.024
128.739
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89.336
77.314
77.201
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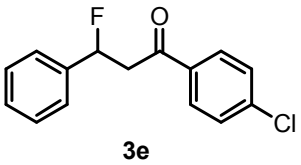
46.041
45.779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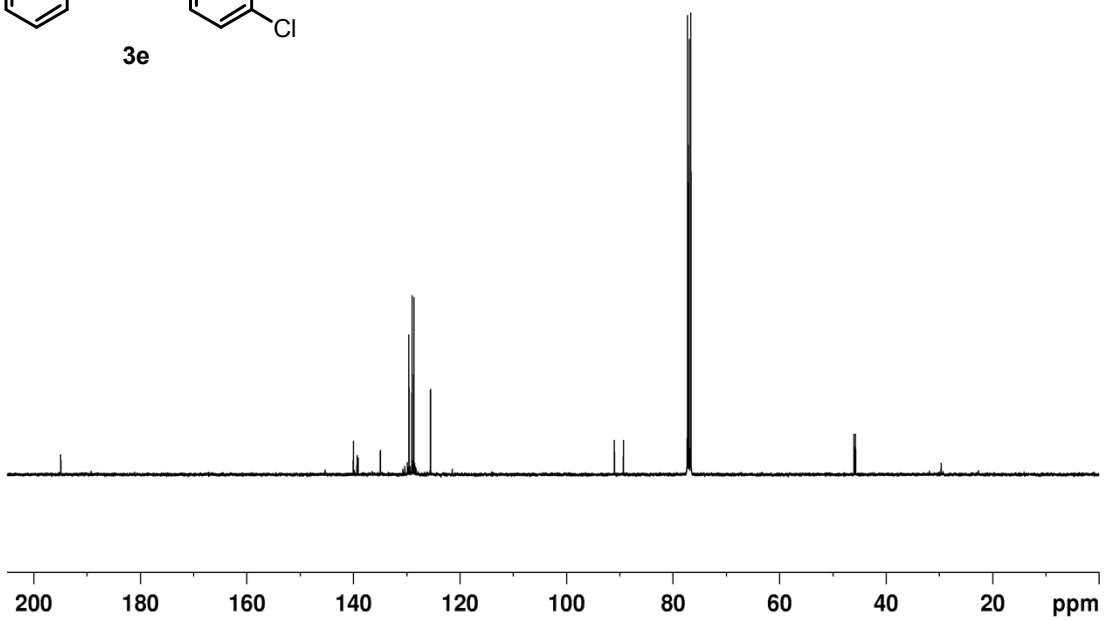
O
Cl

3e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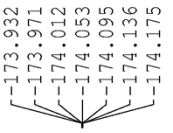
160
140
120
100
80
60
40
20
ppm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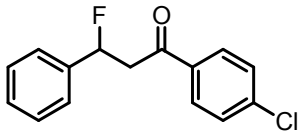
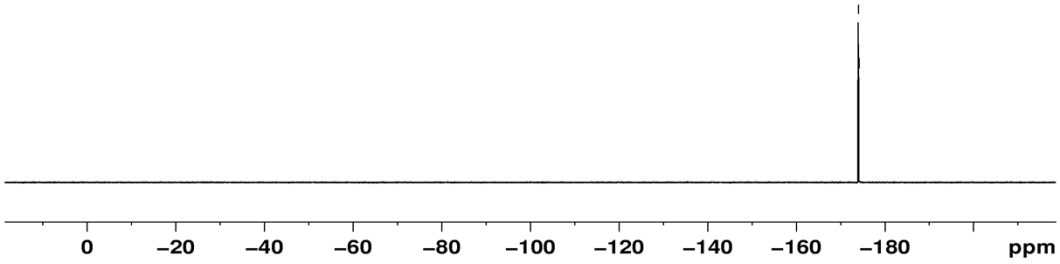
-174.053
-174.095
-174.136
-174.175


F
O
Cl

3e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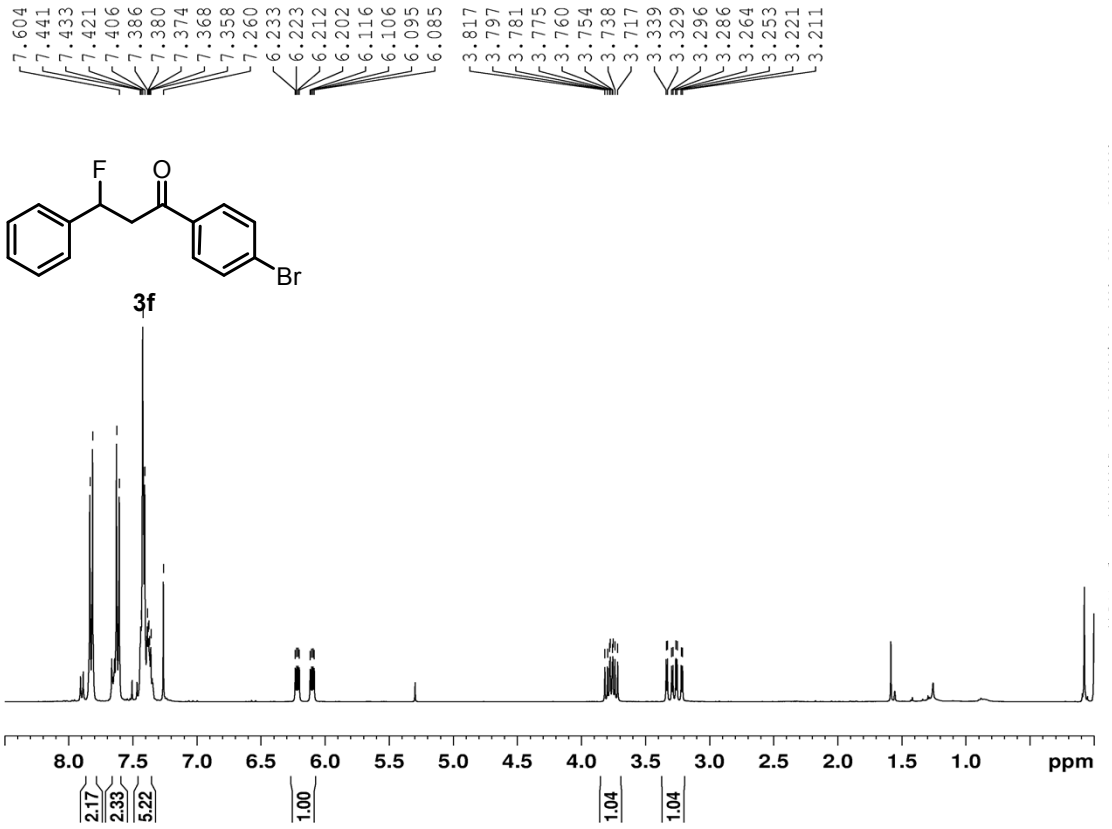
−100
−120
−140
−160
−180
ppm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7.433
7.421
7.406
7.386
7.380
7.374
7.368
7.358
7.260
6.233
6.223
6.212
6.202
6.116
6.106
6.095
6.085
3.817
3.797
3.781
3.775
3.760
3.754
3.738
3.717
3.339
3.329
3.296
3.286
3.264
3.253
3.221
3.211
F
O
Br
3f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.0
1.5
1.0
ppm
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2.33
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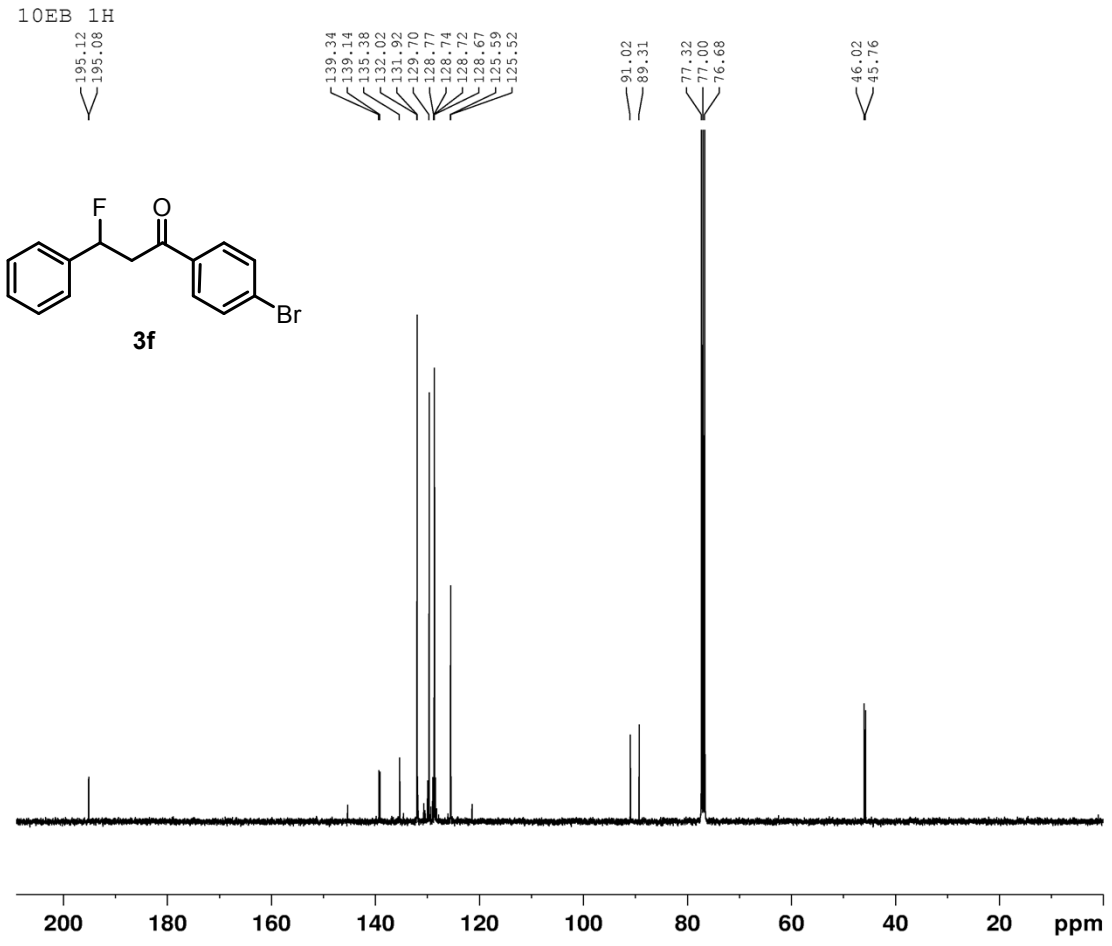
1.00
1.04
1.04


10EB 1H
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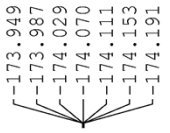
195.08
139.34
139.14
135.38
132.02
131.92
129.70
128.77
128.74
128.72
128.67
125.59
125.52
91.02
89.31
77.32
77.00
76.68
46.02
45.76
F
O
Br
3f
200
180
160
140
120
100
80
60
40
20
ppm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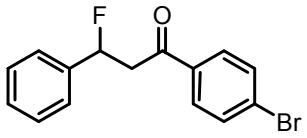
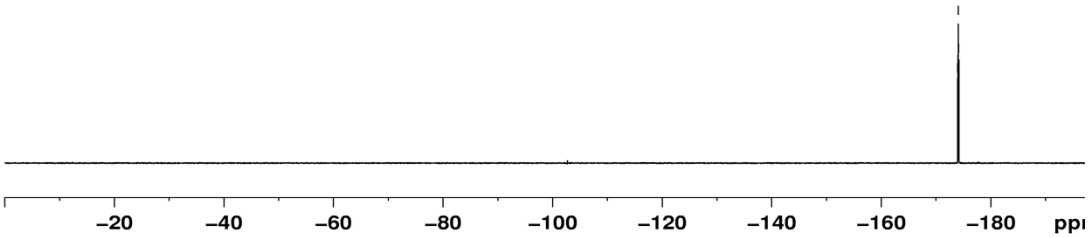

F
O
Br

3f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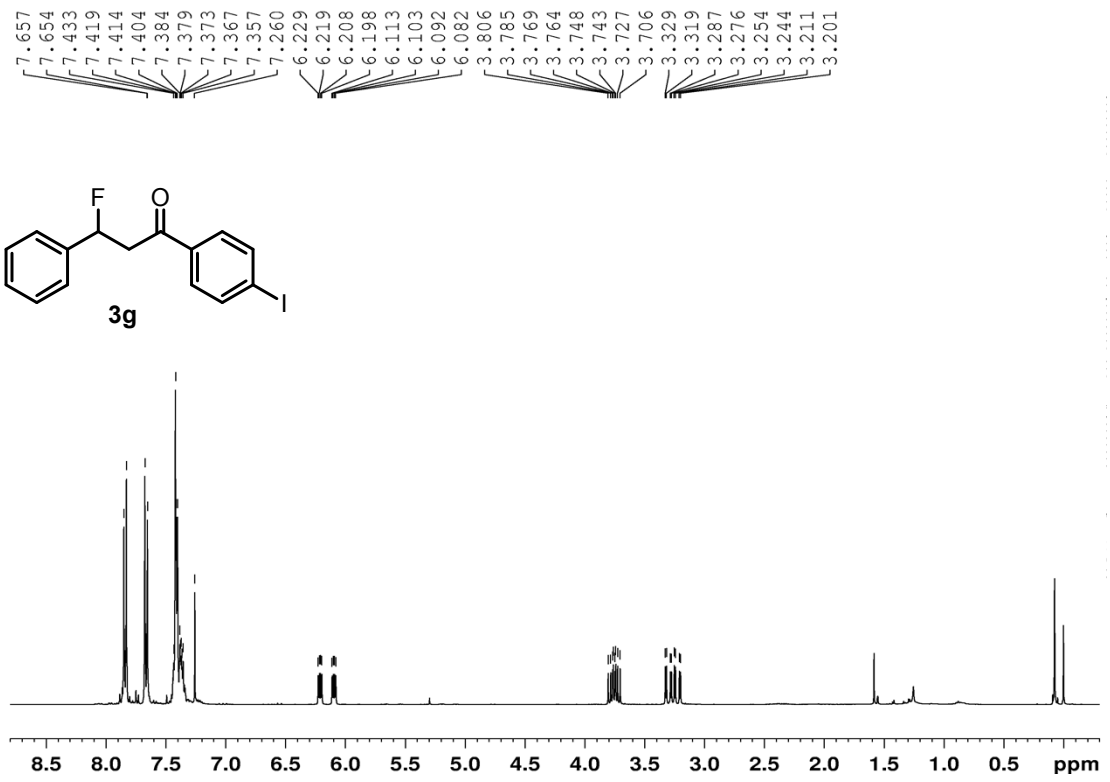
-40
-60
-80
-100
-120
-140
-160
-180
ppm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7.357
7.260
6.229
6.219
6.208
6.198
6.113
6.103
6.092
6.082
3.806
3.785
3.769
3.764
3.748
3.743
3.727
3.706
3.329
3.319
3.287
3.276
3.254
3.244
3.211
3.201
F
O
I
3g
8.5
8.0
7.5
7.0
6.5
6.0
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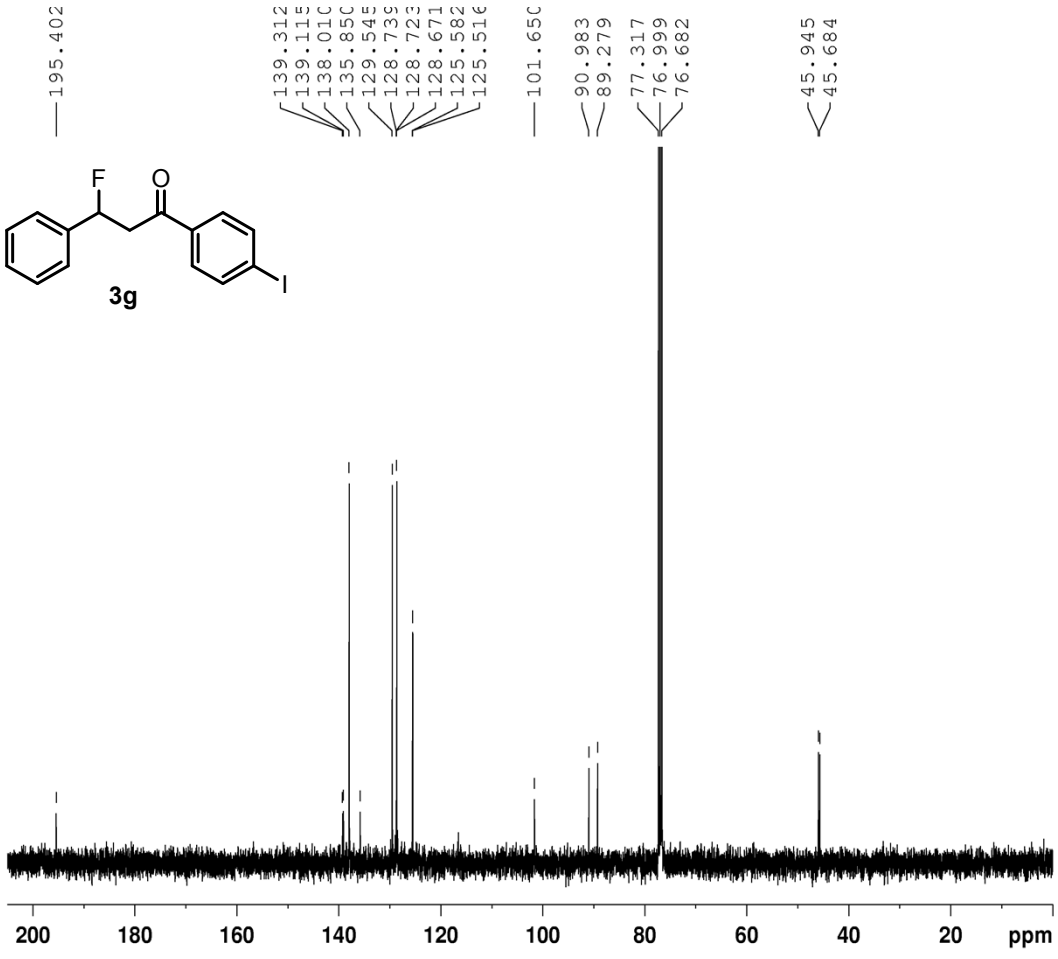
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm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139.115
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135.850
129.545
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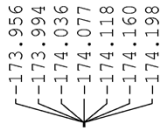
128.723
128.671
125.582
125.516
101.650
90.983
89.279
77.317
76.999
76.682
45.945
45.684
F
O
I
3g
200
180
160
140
120
100
80
60
40
20
ppm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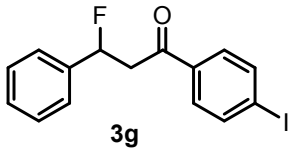
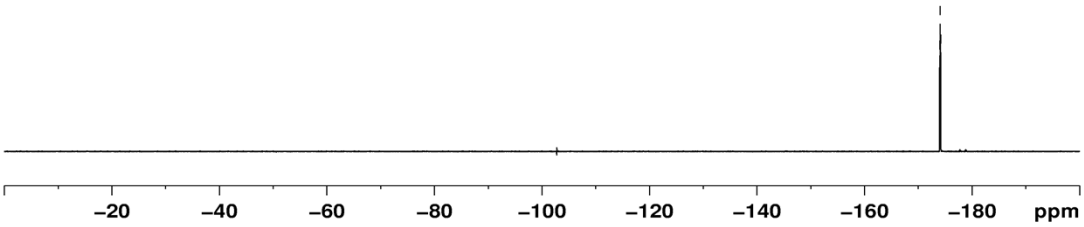

F
O
I

3g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-100
-120
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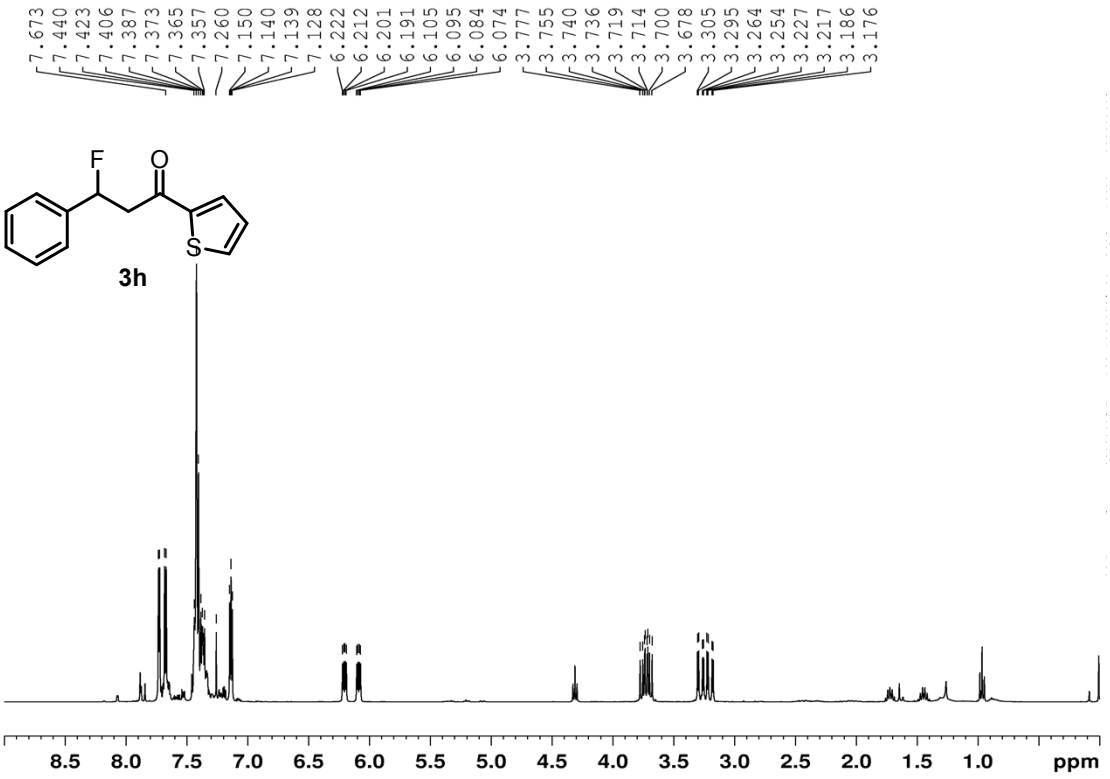
-160
-180
ppm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7.140
7.139
7.128
6.222
6.212
6.201
6.191
6.105
6.095
6.084
6.074
3.777
3.755
3.740
3.736
3.719
3.714
3.700
3.678
3.305
3.295
3.264
3.254
3.227
3.217
3.186
3.176
F
O
S
3h
8.5
8.0
7.5
7.0
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5.0
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4.0
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2.5
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1.5
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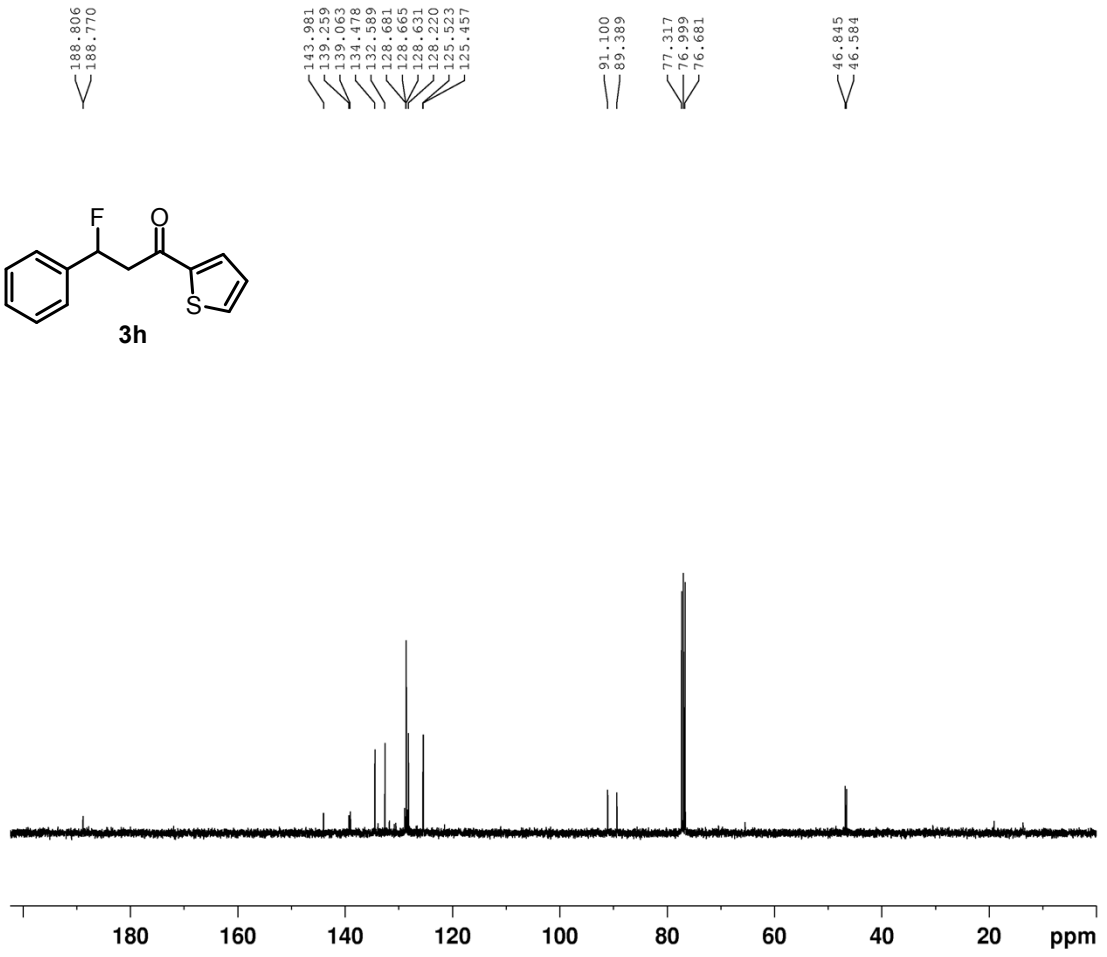
ppm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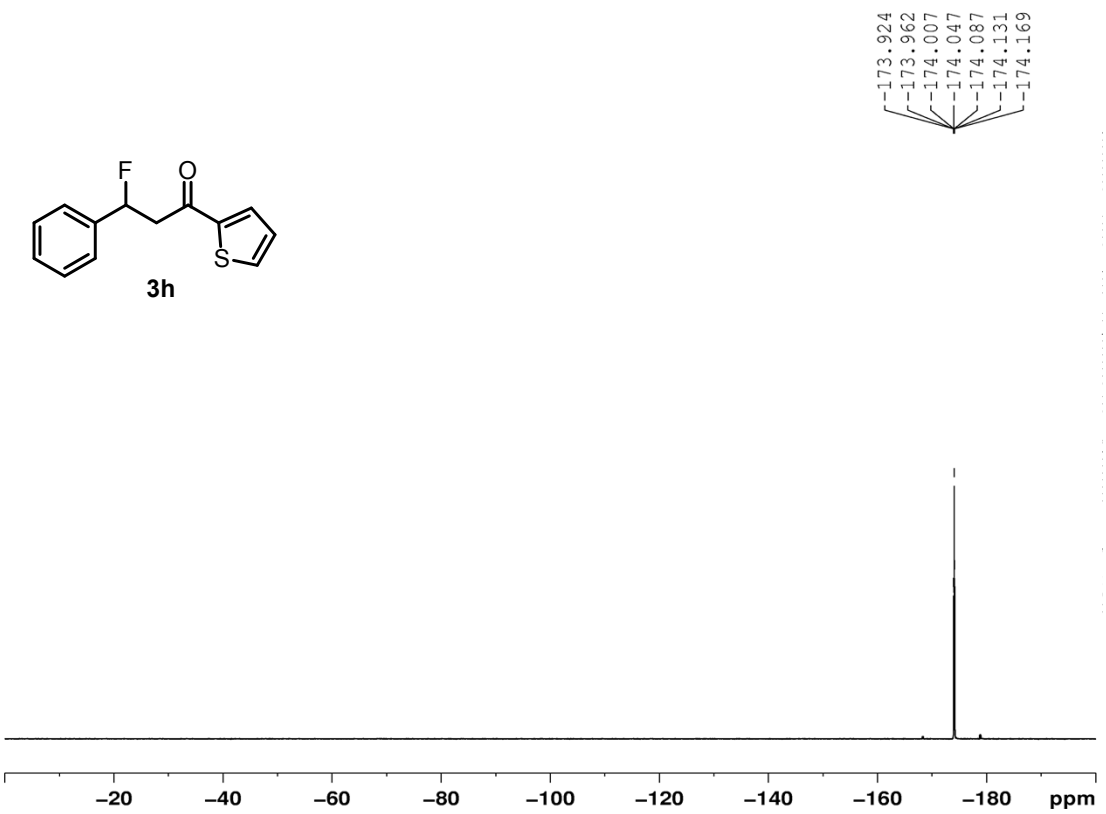
128.681
128.665
128.631
128.220
125.523
125.457
91.100
89.389
77.317
76.999
76.681
46.845
46.584
F
O
S
3h
180
160
140
120
100
80
60
40
20
ppm

F
O
S

3h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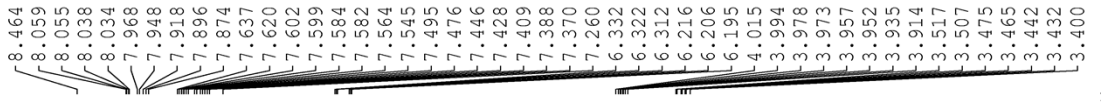
-174.169
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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8.055
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8.034
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7.918
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7.874
7.637
7.620
7.602
7.599
7.584
7.582
7.564
7.545
7.495
7.476
7.446
7.428
7.409
7.388
7.370
7.260
6.332
6.322
6.312
6.216
6.206
6.195
4.015
3.994
3.978
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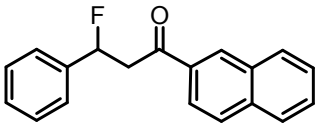
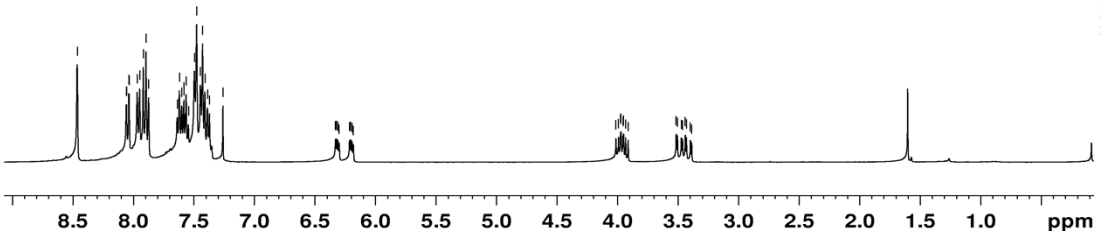
3.442
3.432
3.400


F
O

3i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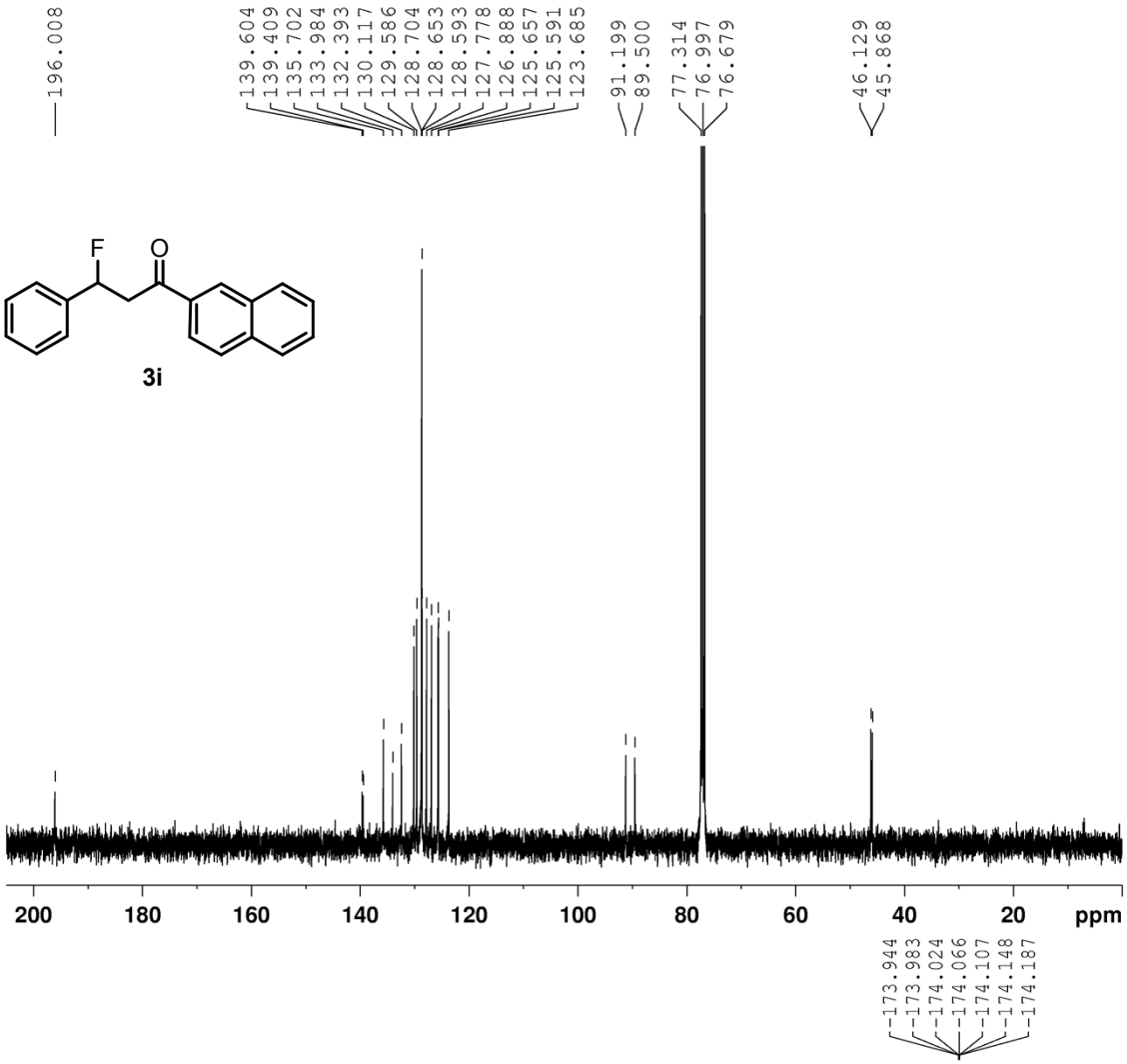
1.5
1.0
ppm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128.593
127.778
126.888
125.657
125.591
123.685
91.199
89.500
77.314
76.997
76.679
46.129
45.868
F
O
3i
200
180
160
140
120
100
80
60
40
20
ppm
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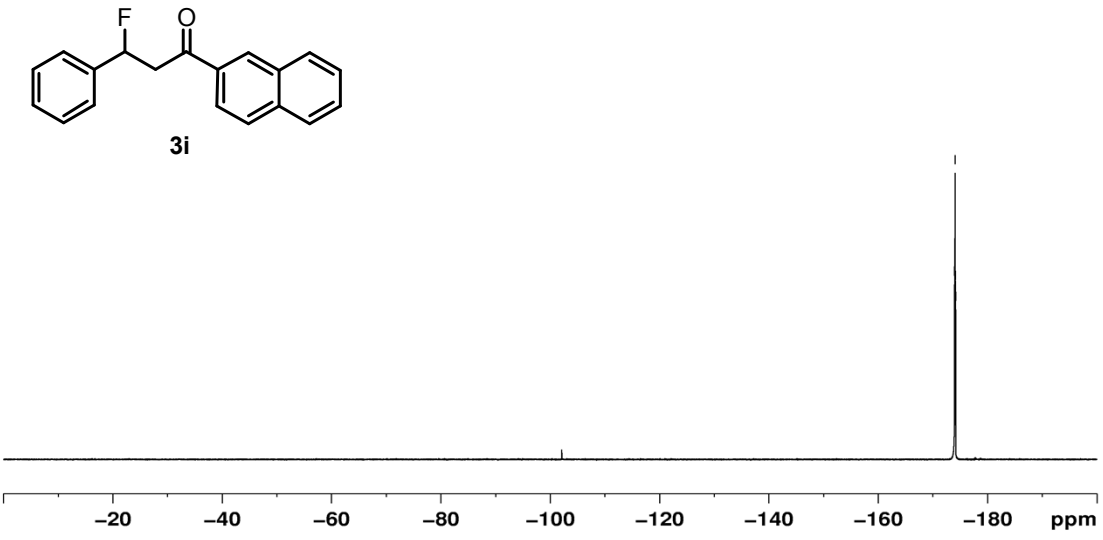
174.148
174.187


F
O
3i
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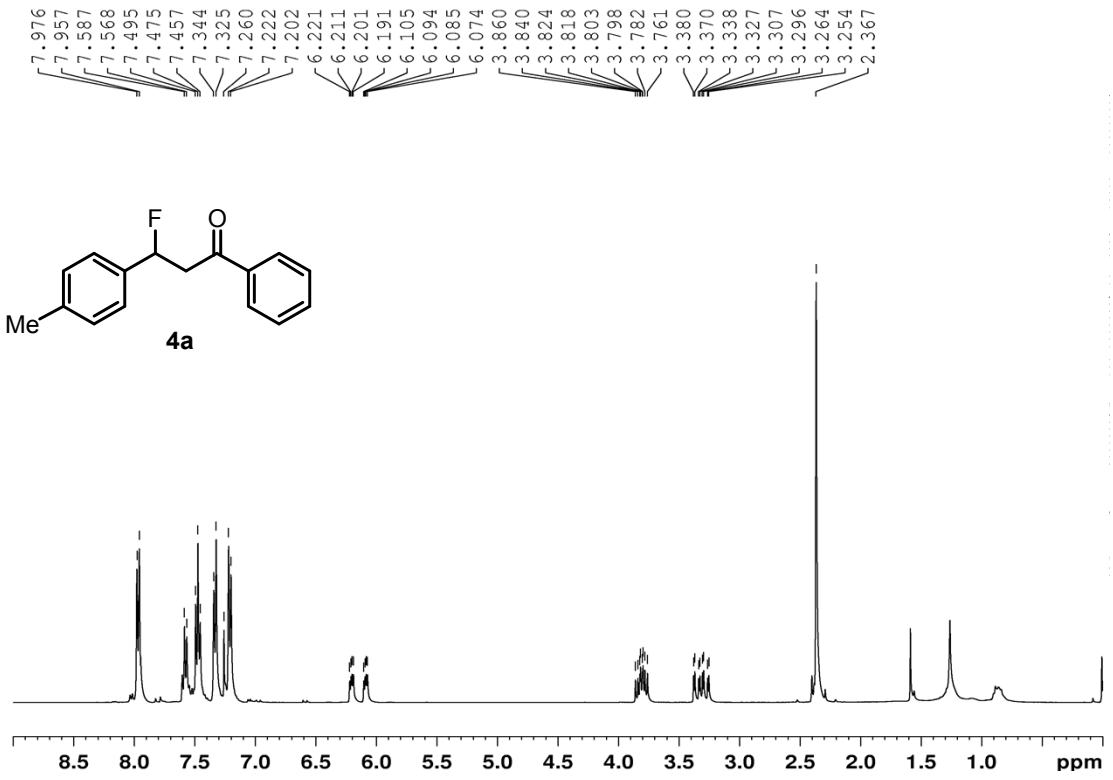
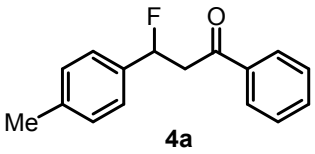
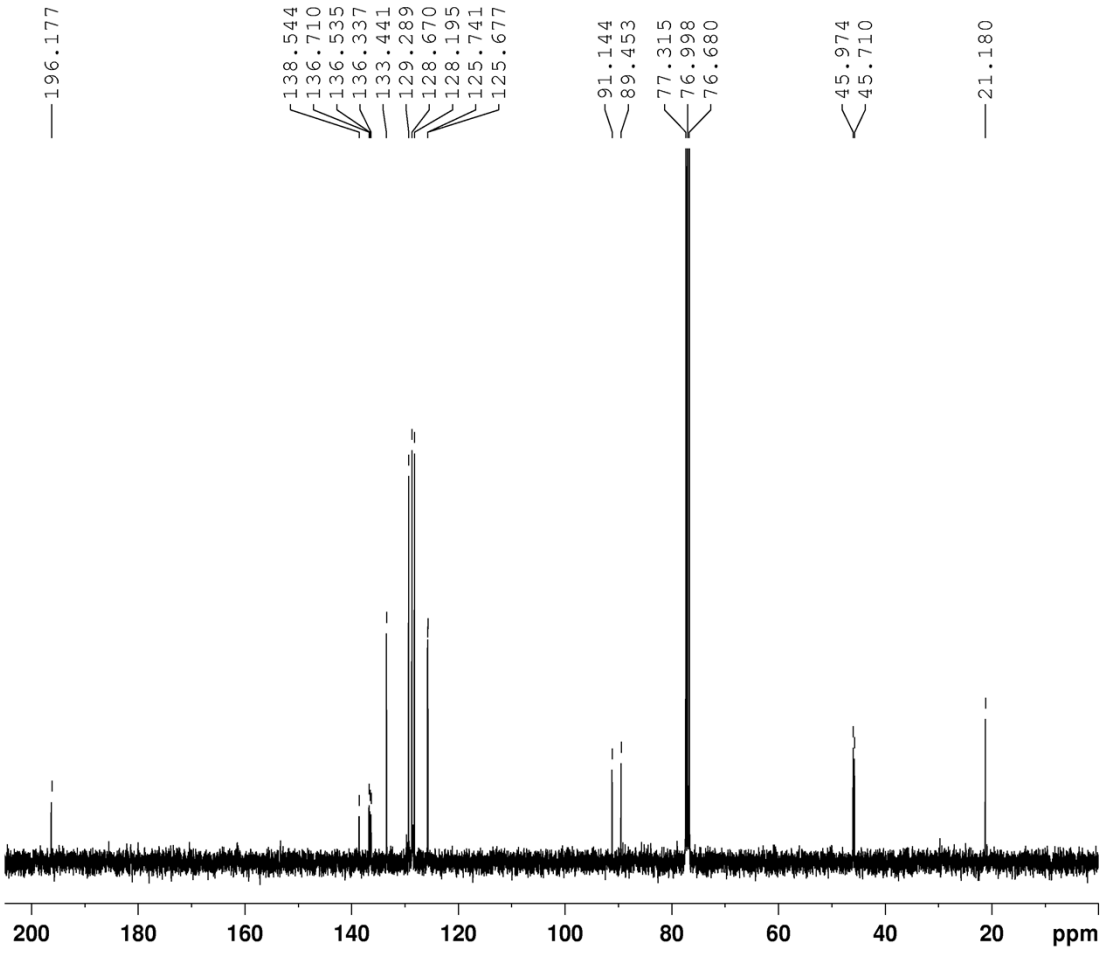
−60
−80
−100
−120
−140
−160
−180
ppm

^{1}H NMR and ^{13}C NMR Spectra of the Products 4



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136.337
133.441
129.289
128.670
128.195
125.741
125.677
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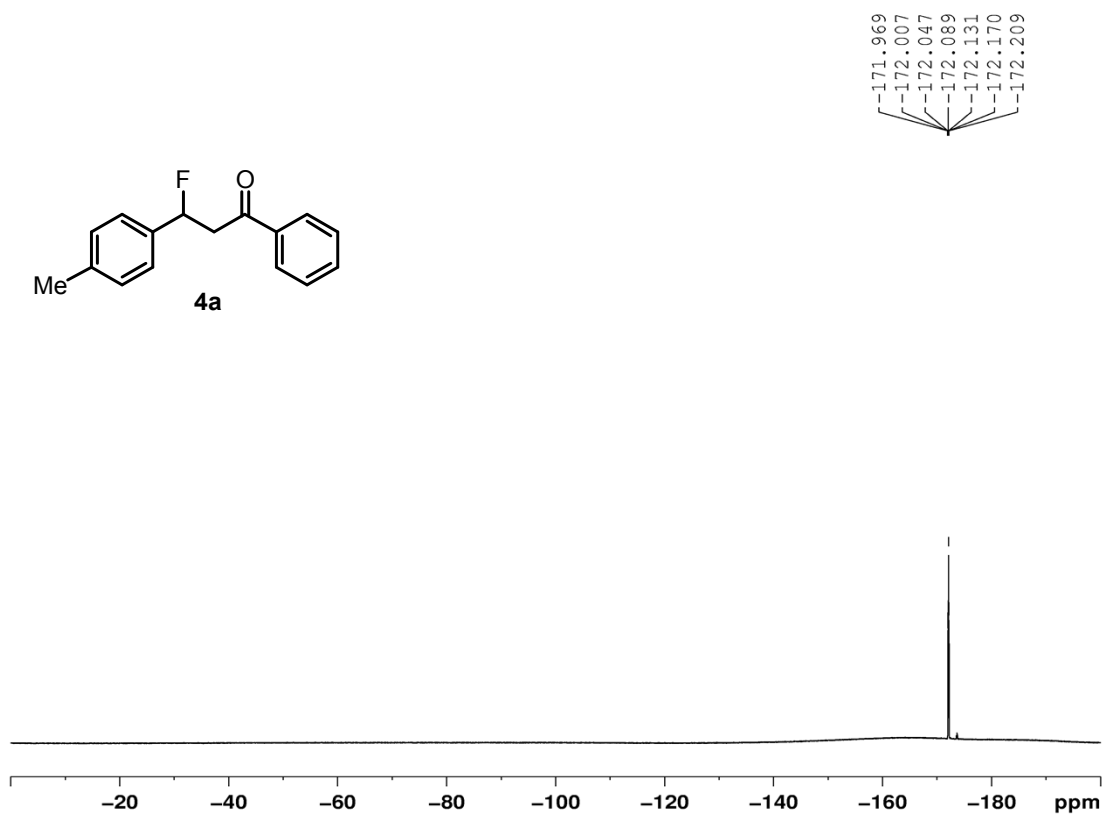
89.453
77.315
76.998
76.680
45.974
45.710
21.180
200
180
160
140
120
100
80
60
40
20
ppm

F
O
Me

4a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172.089
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−20
−40
−60
−80
−100
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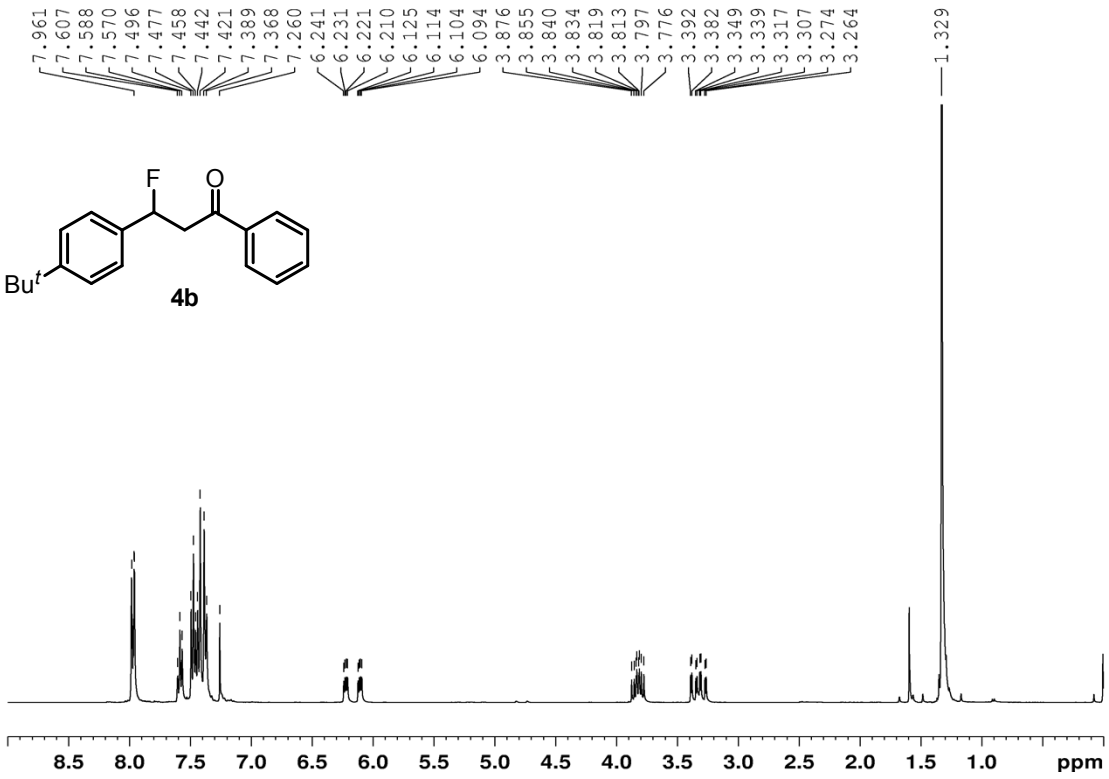
−160
−180
ppm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7.389
7.368
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6.241
6.231
6.221
6.210
6.125
6.114
6.104
6.094
3.876
3.855
3.840
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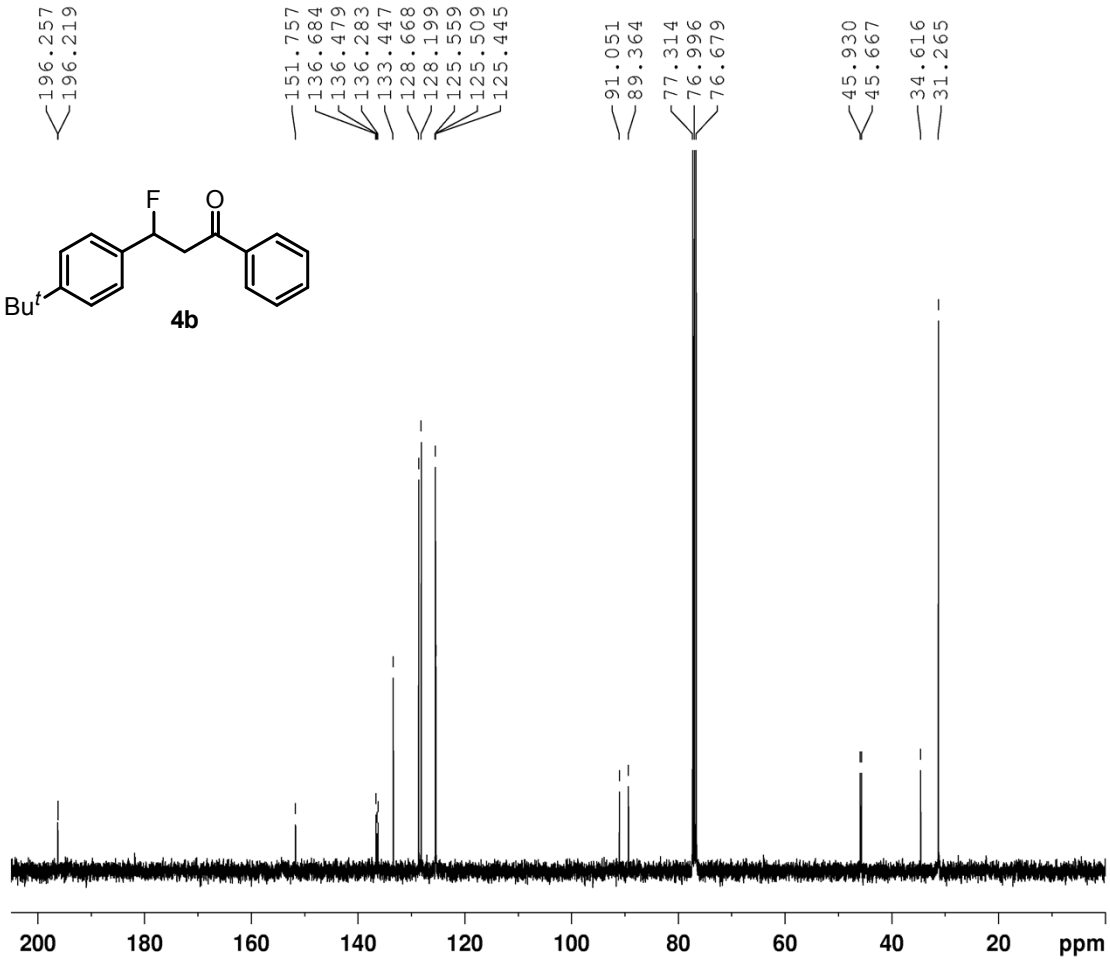
3.819
3.813
3.797
3.776
3.392
3.382
3.349
3.339
3.317
3.307
3.274
3.264
1.329
F
O
Bu^t
4b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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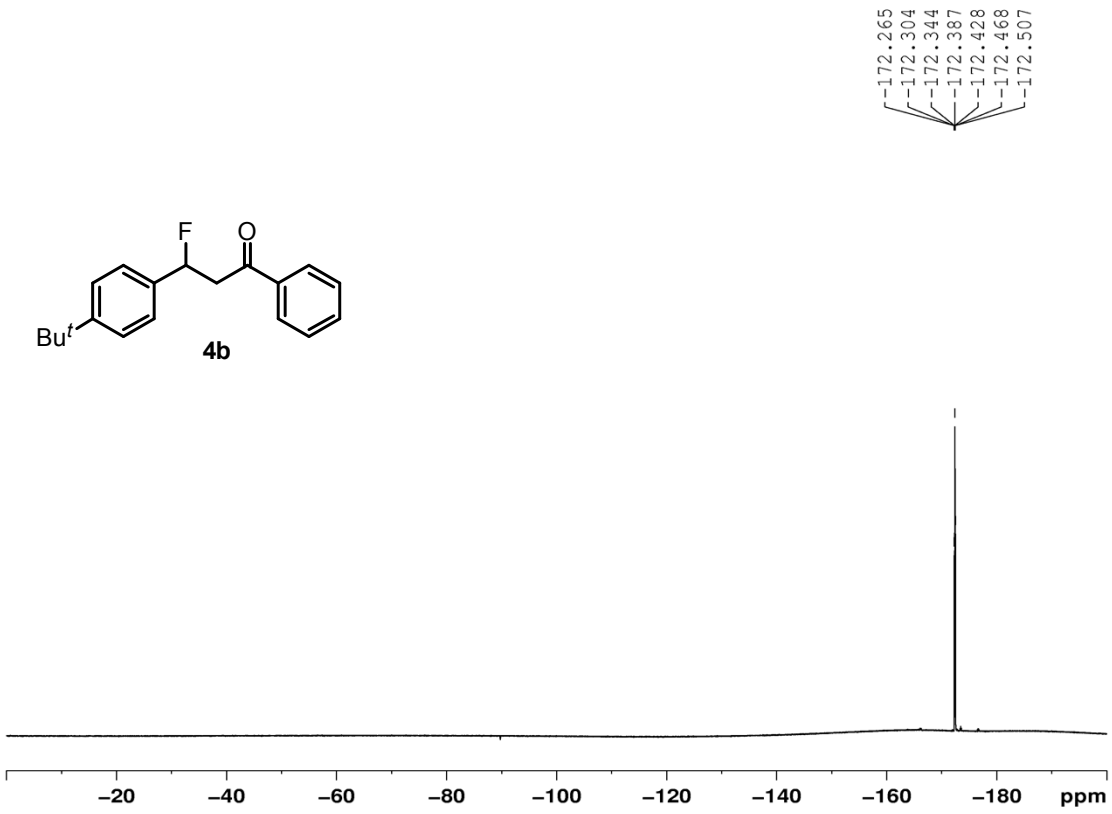
128.199
125.559
125.509
125.445
91.051
89.364
77.314
76.996
76.679
45.930
45.667
34.616
31.265
F
O
Bu^t
4b
200
180
160
140
120
100
80
60
40
20
ppm

F
O
Bu^t

4b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-180
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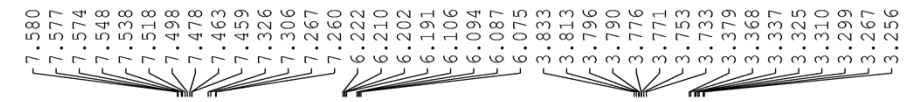
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7.478
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7.459
7.326
7.306
7.267
7.260
6.222
6.210
6.202
6.191
6.106
6.094
6.087
6.075
3.833
3.813
3.796
3.790
3.776
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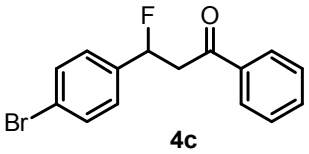
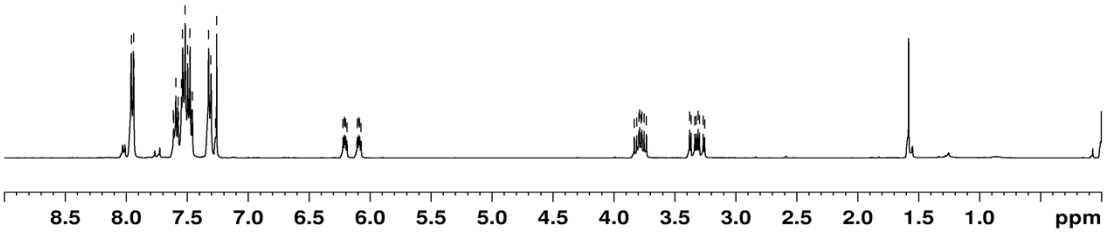
3.325
3.310
3.299
3.267
3.256


F
O
Br

4c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5.0
4.5
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2.5
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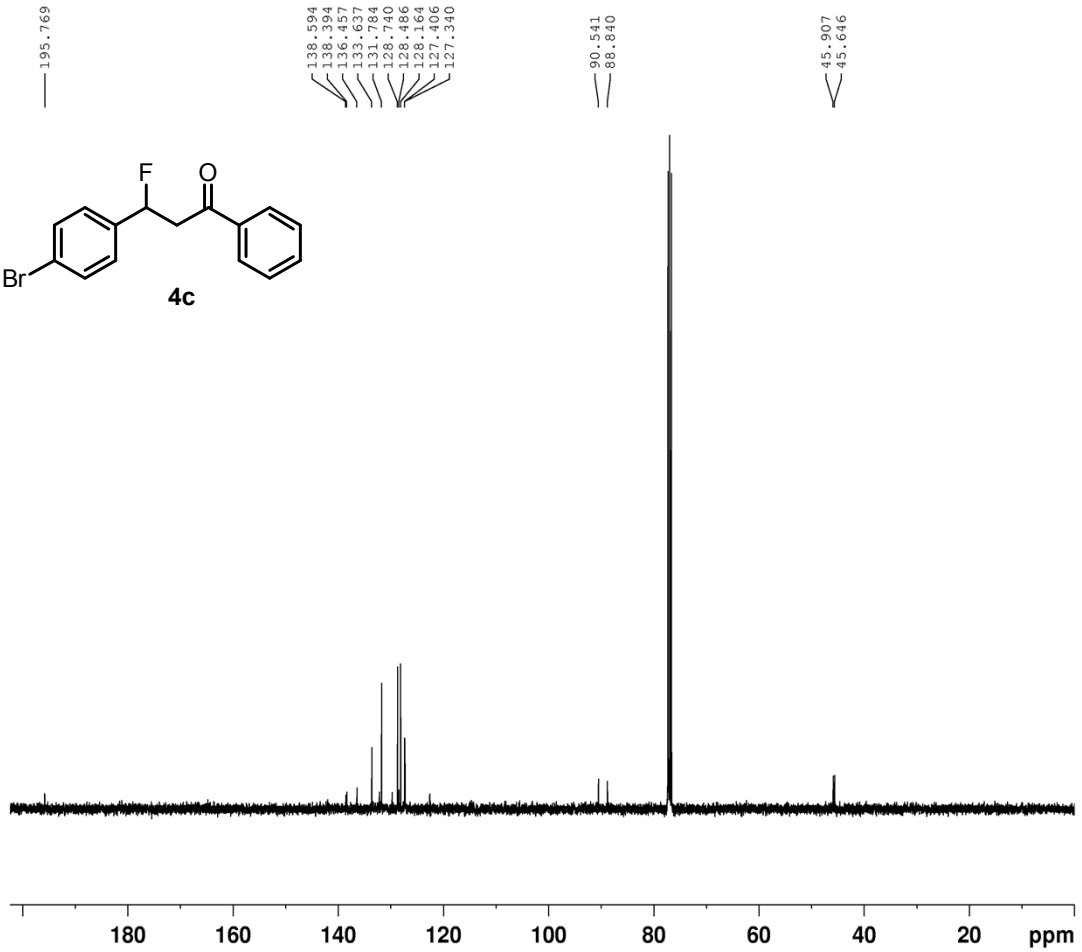
1.5
1.0
ppm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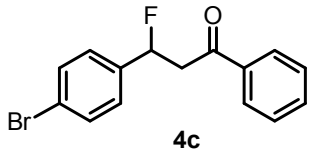
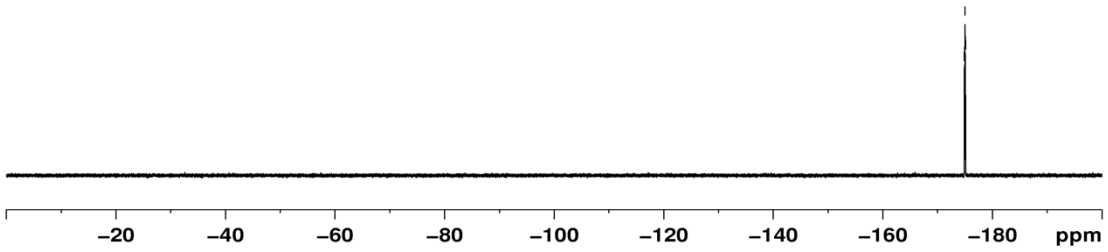
136.457
133.637
131.784
128.740
128.486
128.164
127.406
127.340
90.541
88.840
45.907
45.646
F
O
Br
180
160
140
120
100
80
60
40
20
ppm

4c


F
O
Br

4c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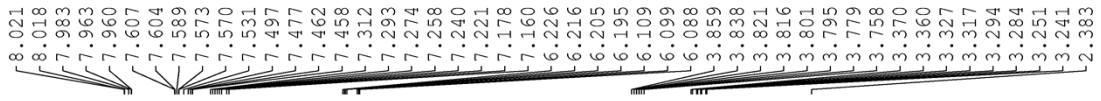
-60
-80
-100
-120
-140
-160
-180
ppm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8.018
7.983
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7.960
7.607
7.604
7.589
7.573
7.570
7.531
7.497
7.477
7.462
7.458
7.312
7.293
7.274
7.258
7.240
7.221
7.178
7.160
6.226
6.216
6.205
6.195
6.109
6.099
6.088
3.859
3.838
3.821
3.816
3.801
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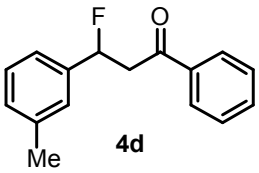
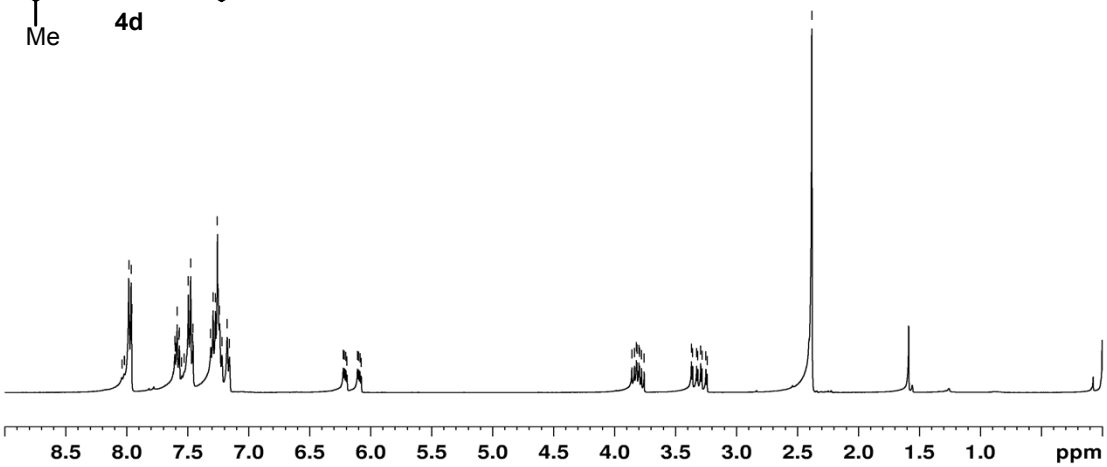
3.370
3.360
3.327
3.317
3.294
3.284
3.251
3.241
2.383


F
O
Me

4d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5.0
4.5
4.0
3.5
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2.5
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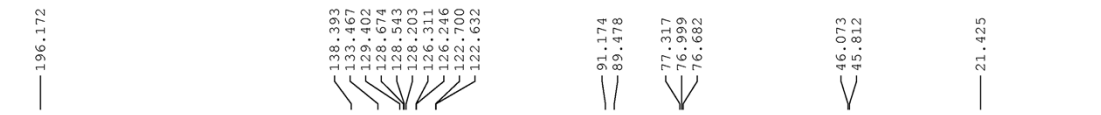
1.5
1.0
ppm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129.402
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128.543
128.203
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126.246
122.700
122.632
91.174
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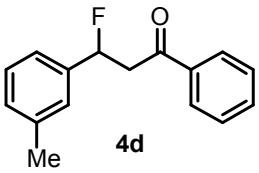
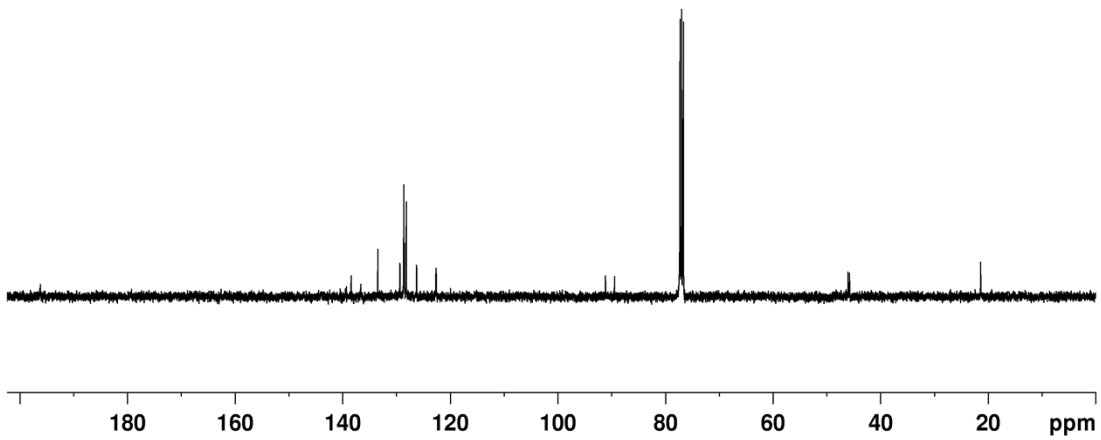
77.317
76.999
76.682
46.073
45.812
21.425


F
O
Me

4d


180
160
140
120
100
80
60
40
20
ppm

F
O
Me

4d


-173.555
-173.594
-173.636
-173.677
-173.718
-173.760
-173.799
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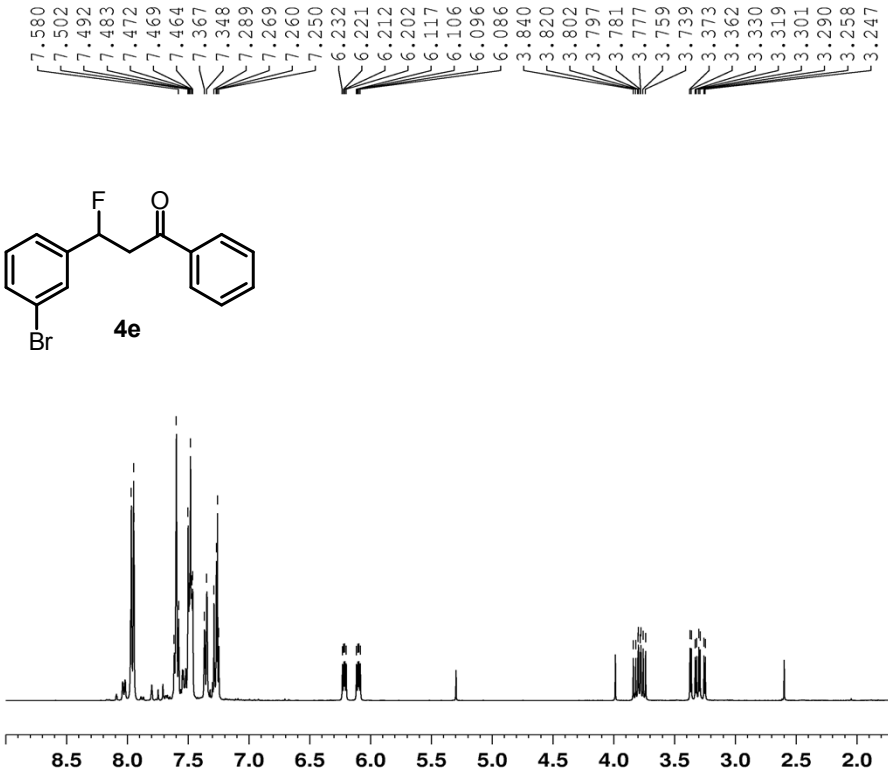
−40
−60
−80
−100
−120
−140
−160
−180
ppm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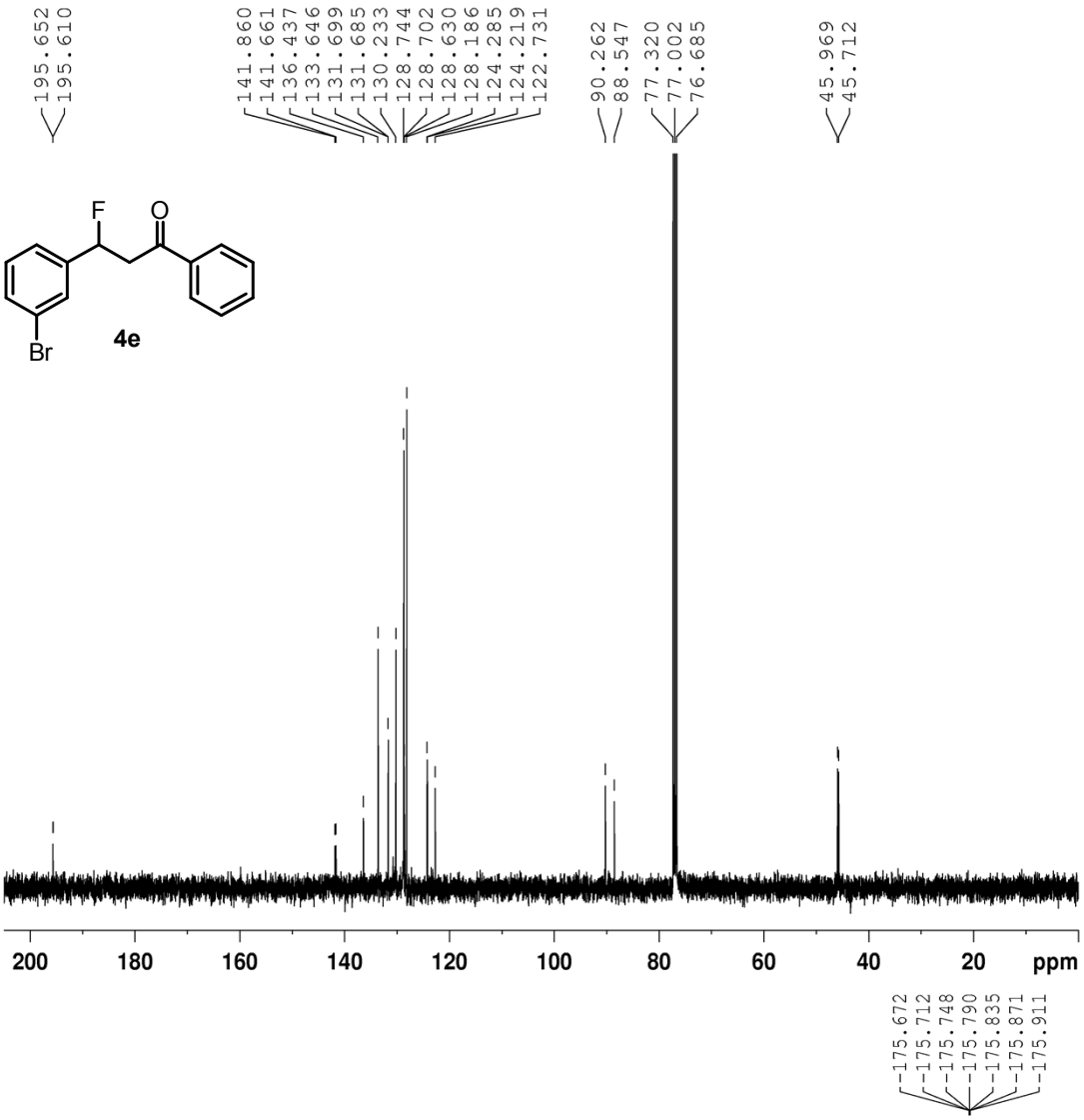
7.483
7.472
7.469
7.464
7.367
7.348
7.289
7.269
7.260
7.250
6.232
6.221
6.212
6.202
6.117
6.106
6.096
6.086
3.840
3.820
3.802
3.797
3.781
3.777
3.759
3.739
3.373
3.362
3.330
3.319
3.301
3.290
3.258
3.247
F
O
Br
4e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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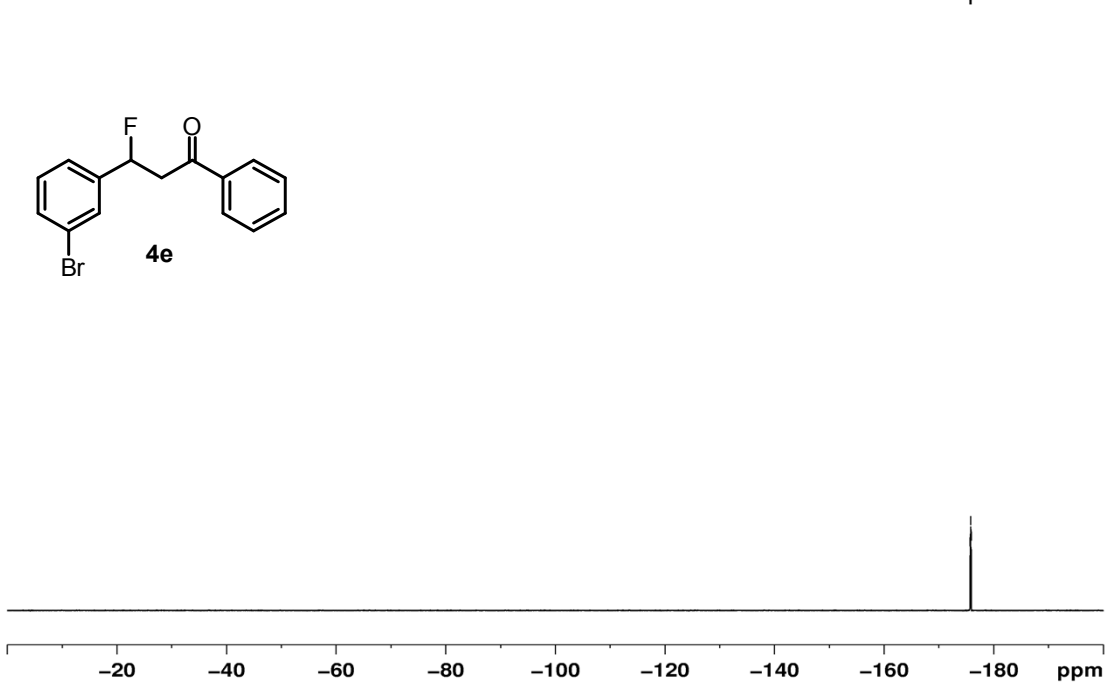
141.860
141.661
136.437
133.646
131.699
131.685
130.233
128.744
128.702
128.630
128.186
124.285
124.219
122.731
90.262
88.547
77.320
77.002
76.685
45.969
45.712
F
O
Br
4e
200
180
160
140
120
100
80
60
40
20
ppm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-175.712
-175.748
-175.790
-175.835
-175.871
-175.911
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O
Br
4e
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−40
−60
−80
−100
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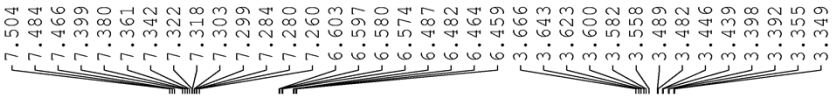
−180
ppm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7.322
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7.303
7.299
7.284
7.280
7.260
6.603
6.597
6.580
6.574
6.487
6.482
6.464
6.459
3.666
3.643
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3.558
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3.482
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3.439
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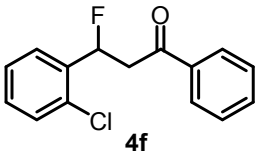
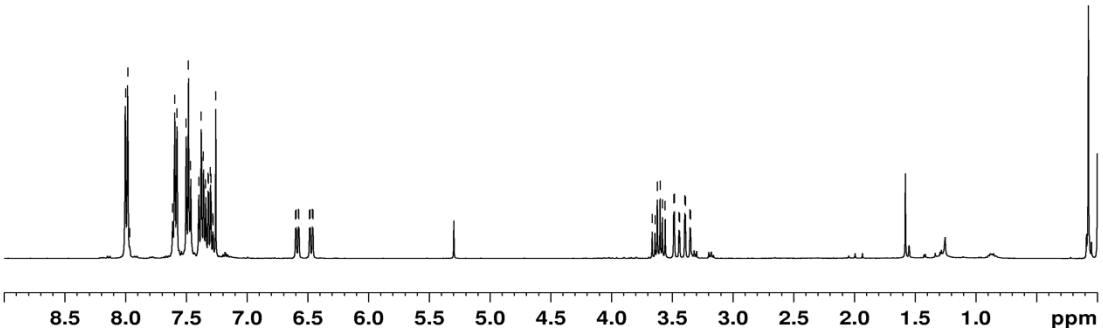
3.355
3.349


F
O
Cl

4f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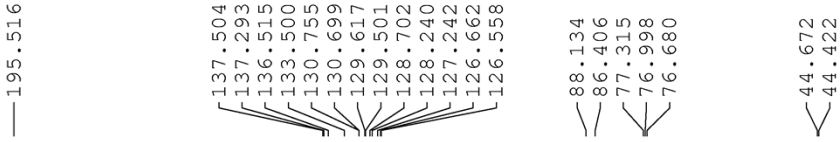
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm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129.501
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127.242
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77.315
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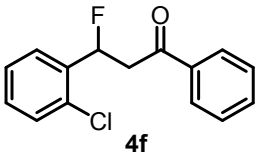
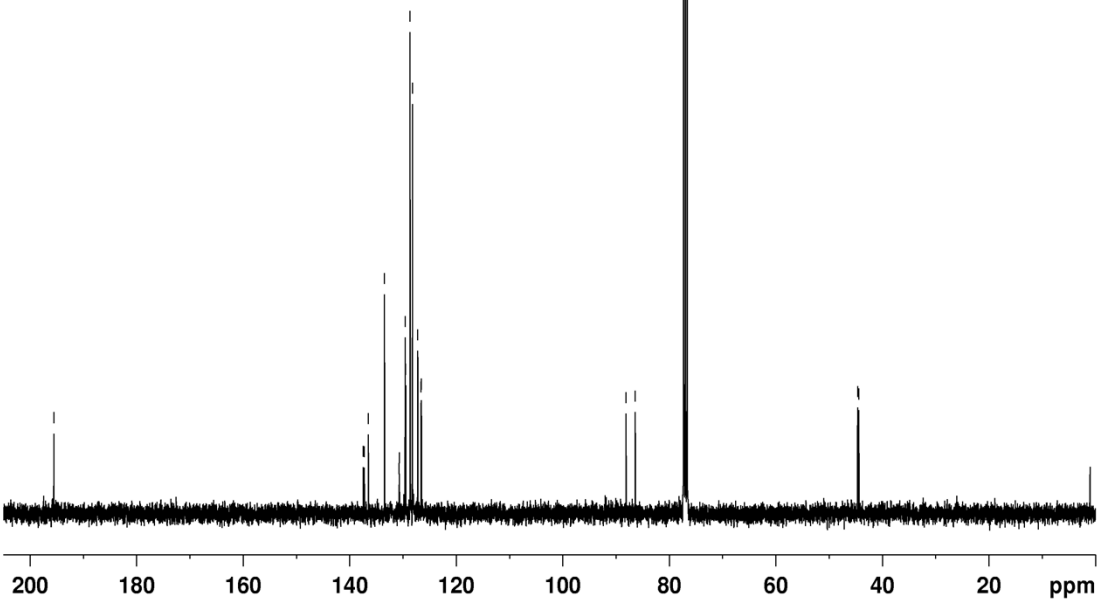
44.422


F
O
Cl

4f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180
160
140
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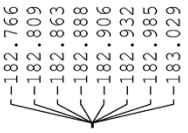
100
80
60
40
20
ppm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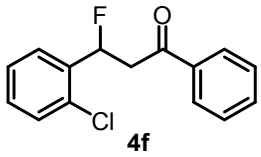
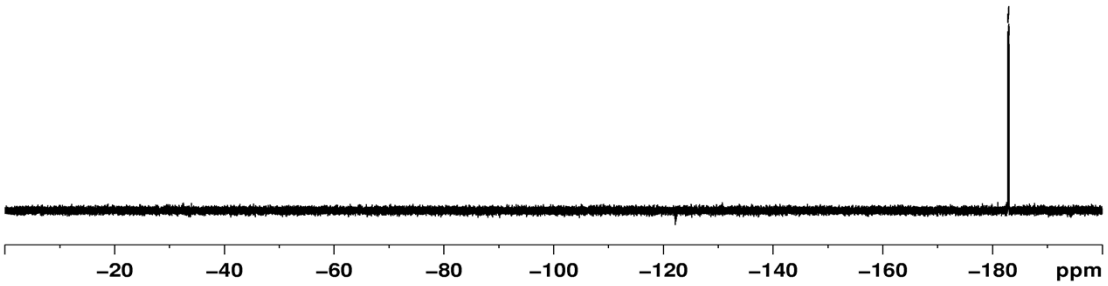

F
O
Cl

4f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-100
-120
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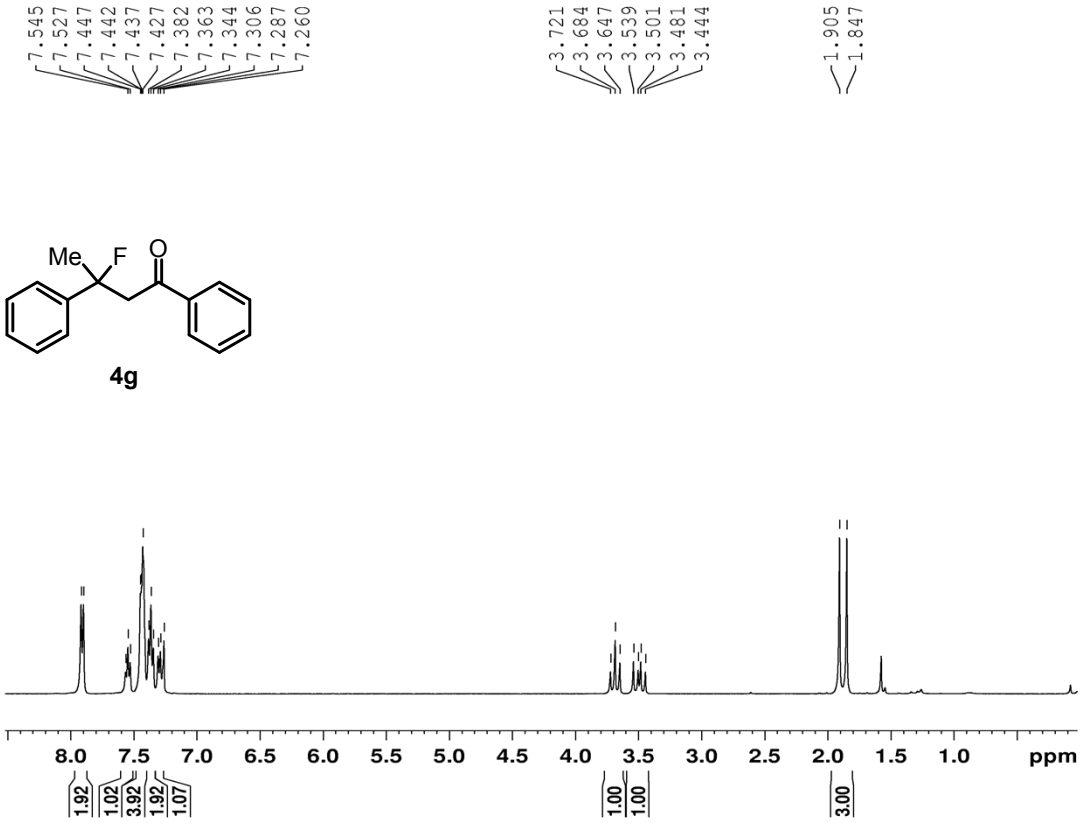
-160
-180
ppm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7.447
7.442
7.437
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7.344
7.306
7.287
7.260
3.721
3.684
3.647
3.539
3.501
3.481
3.444
1.905
1.847
Me
F
O
4g
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.92
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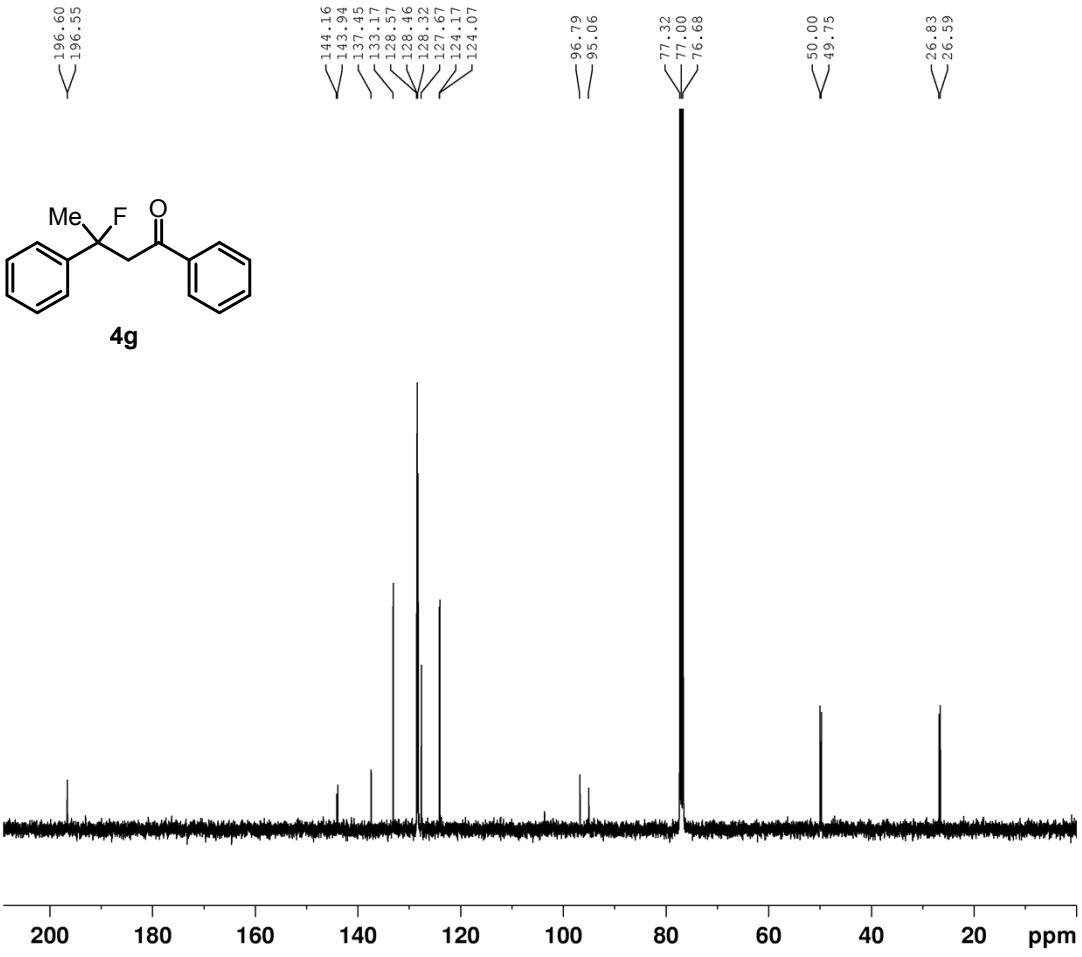
1.00
3.00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128.46
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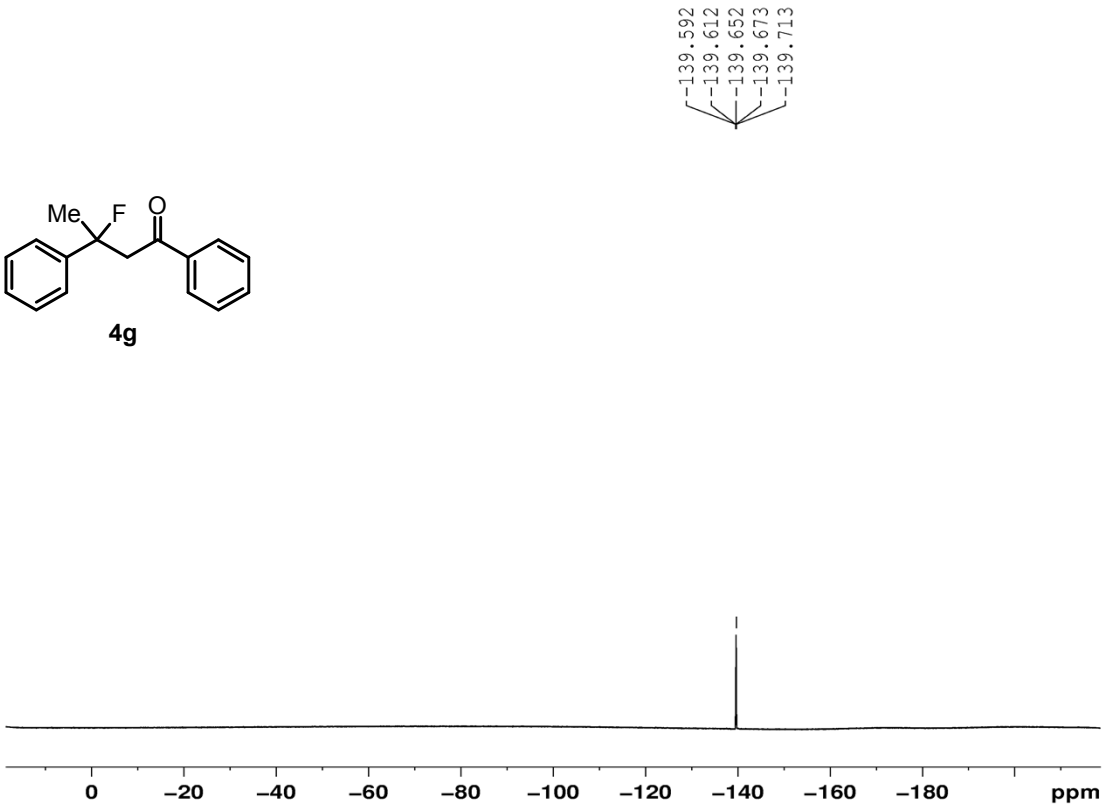
127.67
124.17
124.07
96.79
95.06
77.32
77.00
76.68
50.00
49.75
26.83
26.59
Me
F
O
4g
200
180
160
140
120
100
80
60
40
20
ppm

Me
F
O

4g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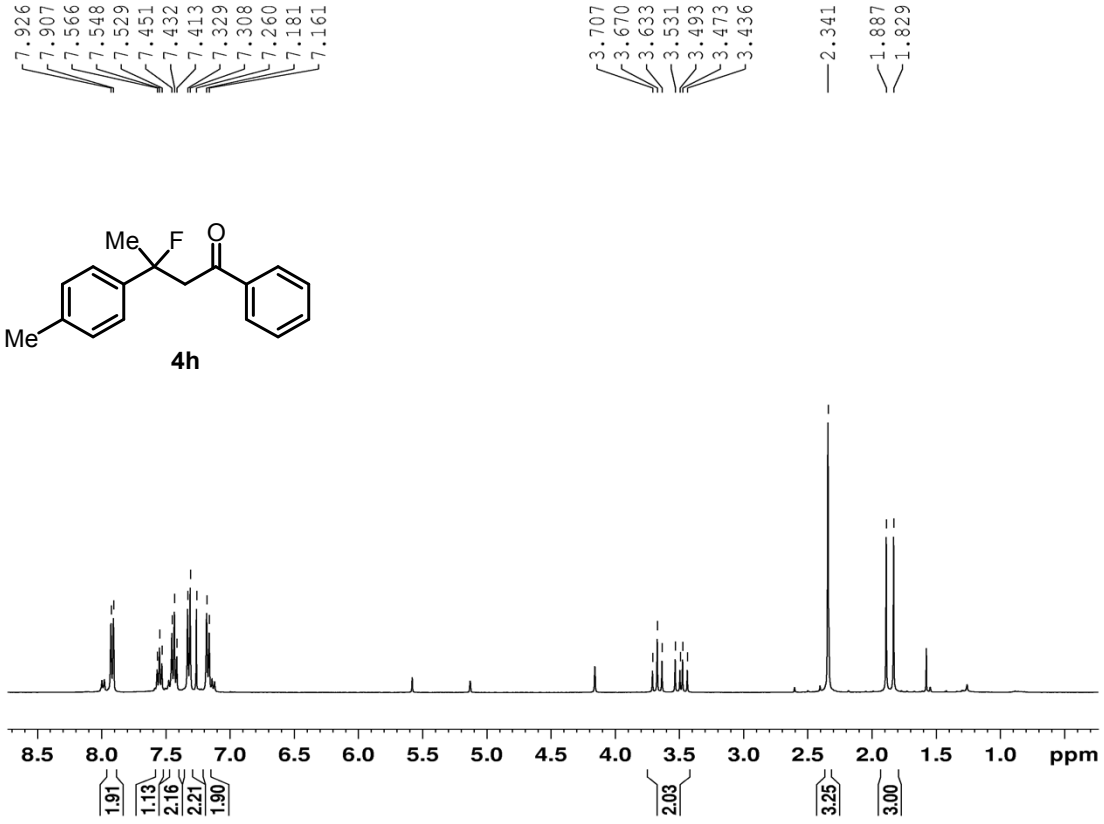
−140
−160
−180
ppm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7.308
7.260
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7.161
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3.670
3.633
3.531
3.493
3.473
3.436
2.341
1.887
1.829
Me
F
O
Me
4h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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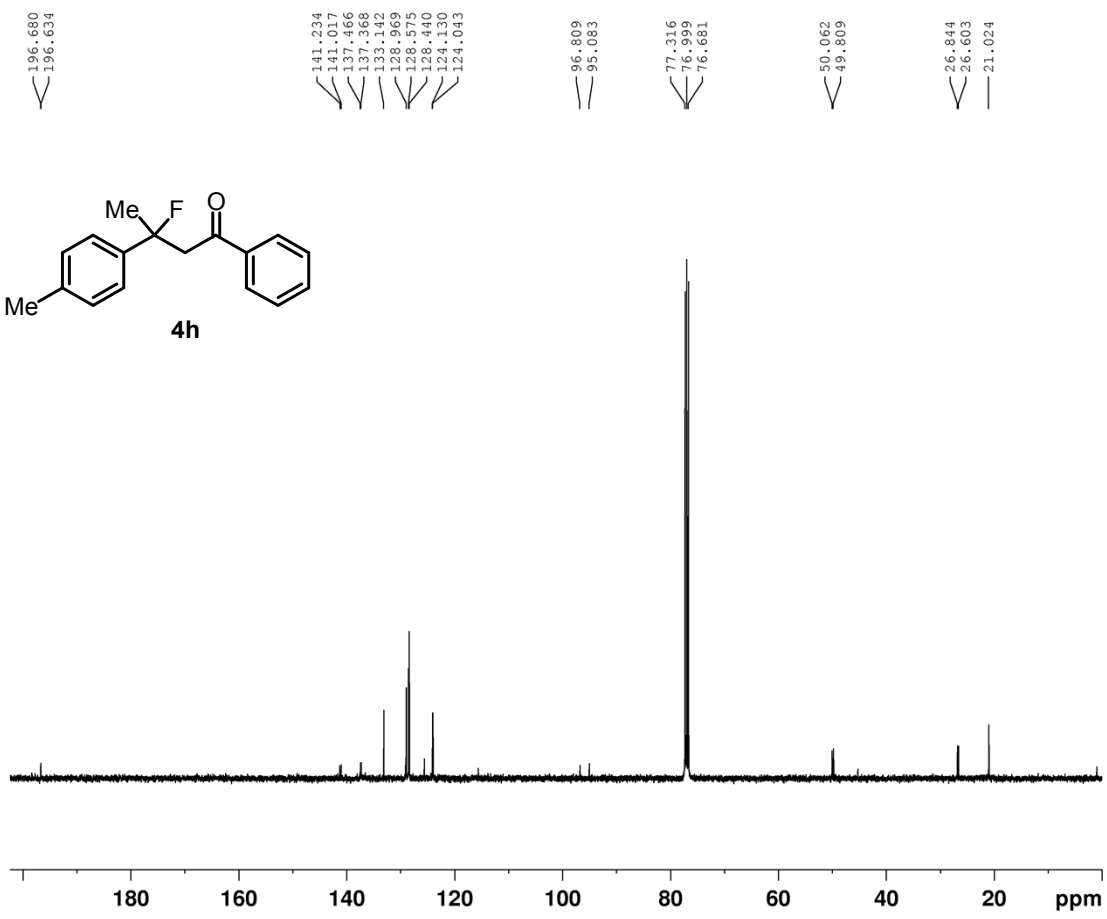
3.25
3.00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128.969
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128.440
124.130
124.043
96.809
95.083
77.316
76.999
76.681
50.062
49.809
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Me
F
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Me
4h
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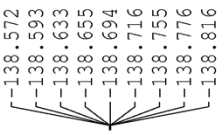
140
120
100
80
60
40
20
ppm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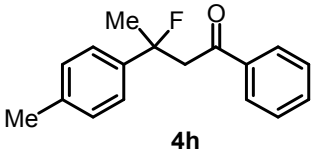
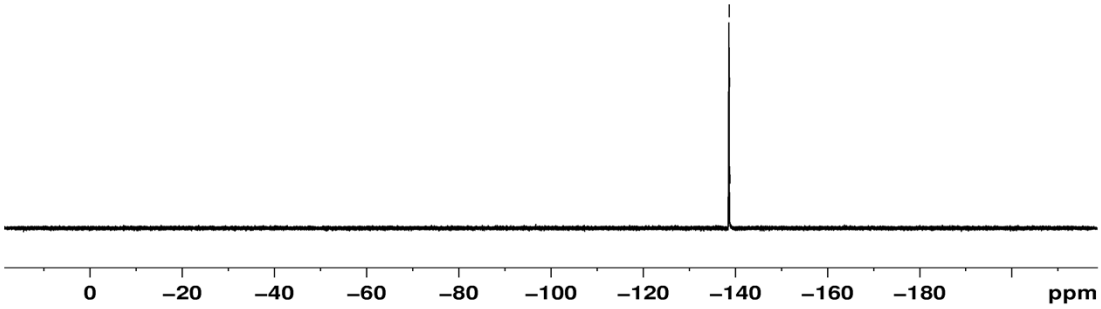
-138.816


Me
F
O
Me

4h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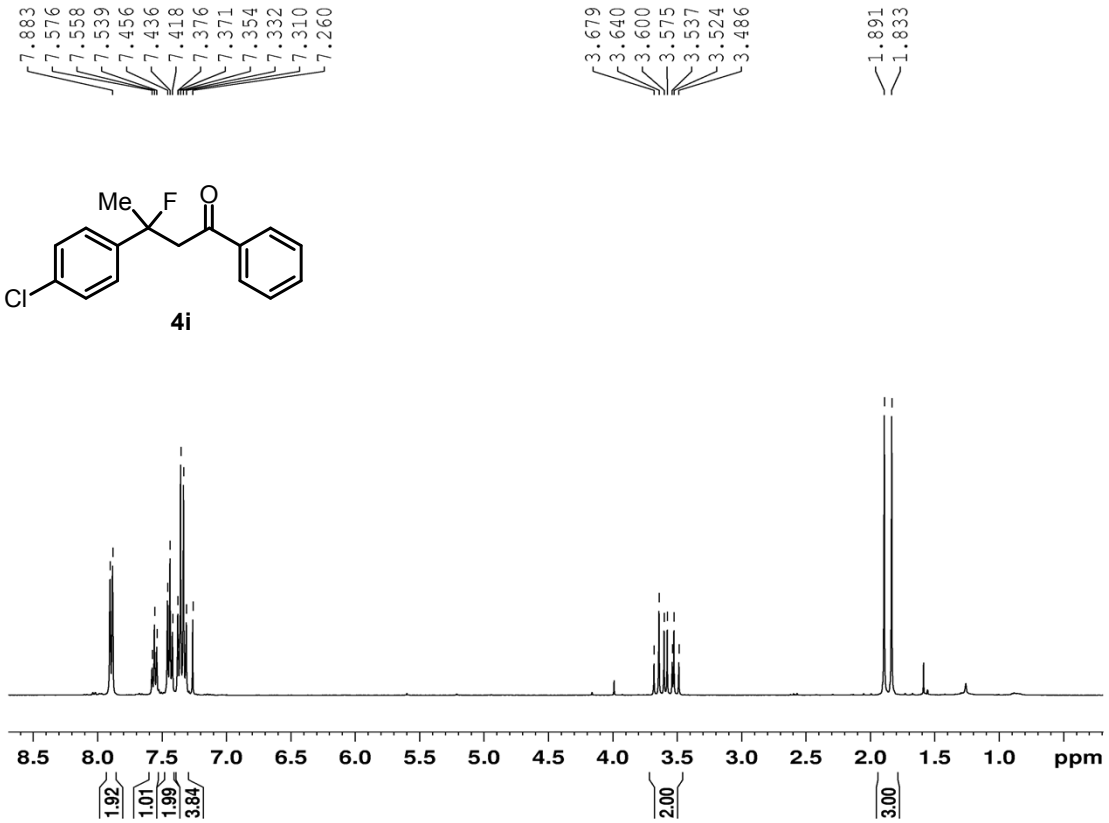
ppm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7.310
7.260
3.679
3.640
3.600
3.575
3.537
3.524
3.486
1.891
1.833
Me
F
O
Cl
4i
8.5
8.0
7.5
7.0
6.5
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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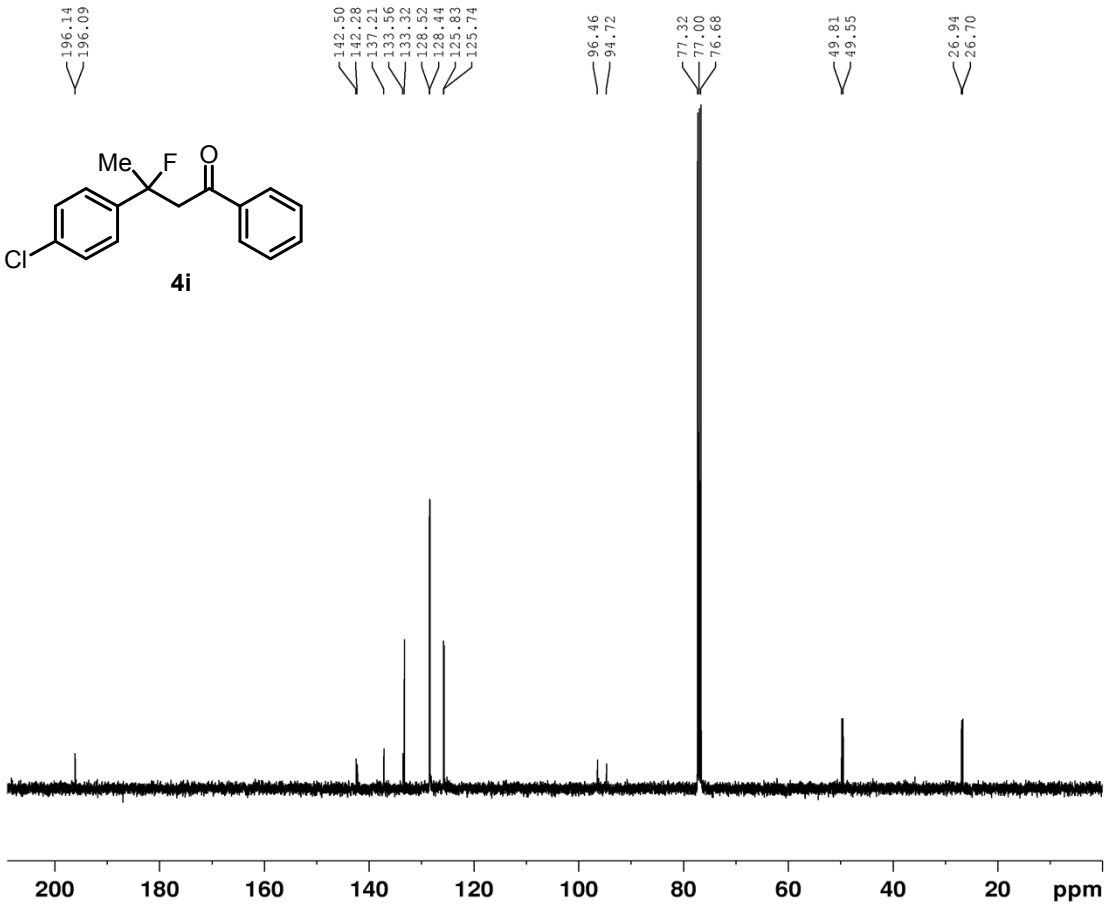
1.01
1.99
3.84
2.00
3.00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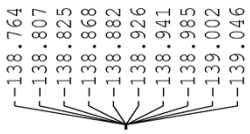
196.09
142.50
142.28
137.21
133.56
133.32
128.52
128.44
125.83
125.74
96.46
94.72
77.32
77.00
76.68
49.81
49.55
26.94
26.70
Me
F
O
Cl
4i
200
180
160
140
120
100
80
60
40
20
ppm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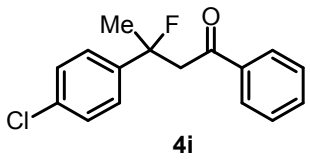
-139.002
-139.046


Me
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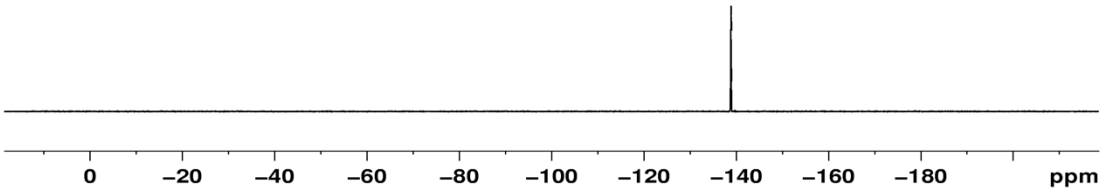
O
Cl

4i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-120
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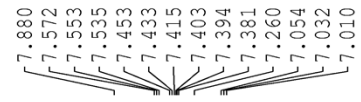
-160
-180
ppm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7.403
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7.381
7.260
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7.010
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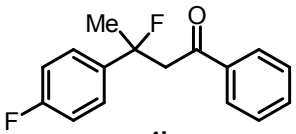
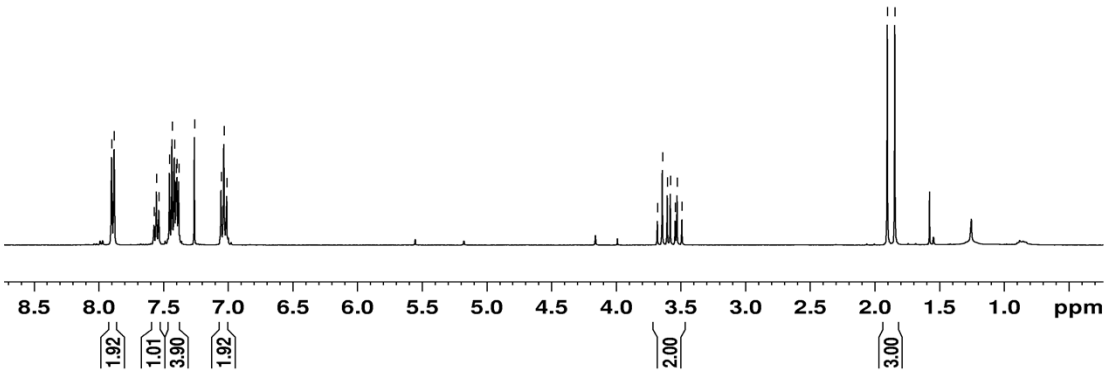
3.642
3.604
3.580
3.542
3.528
3.491
1.902
1.844


Me
F
O
F

4j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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
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2.0
1.5
1.0
ppm
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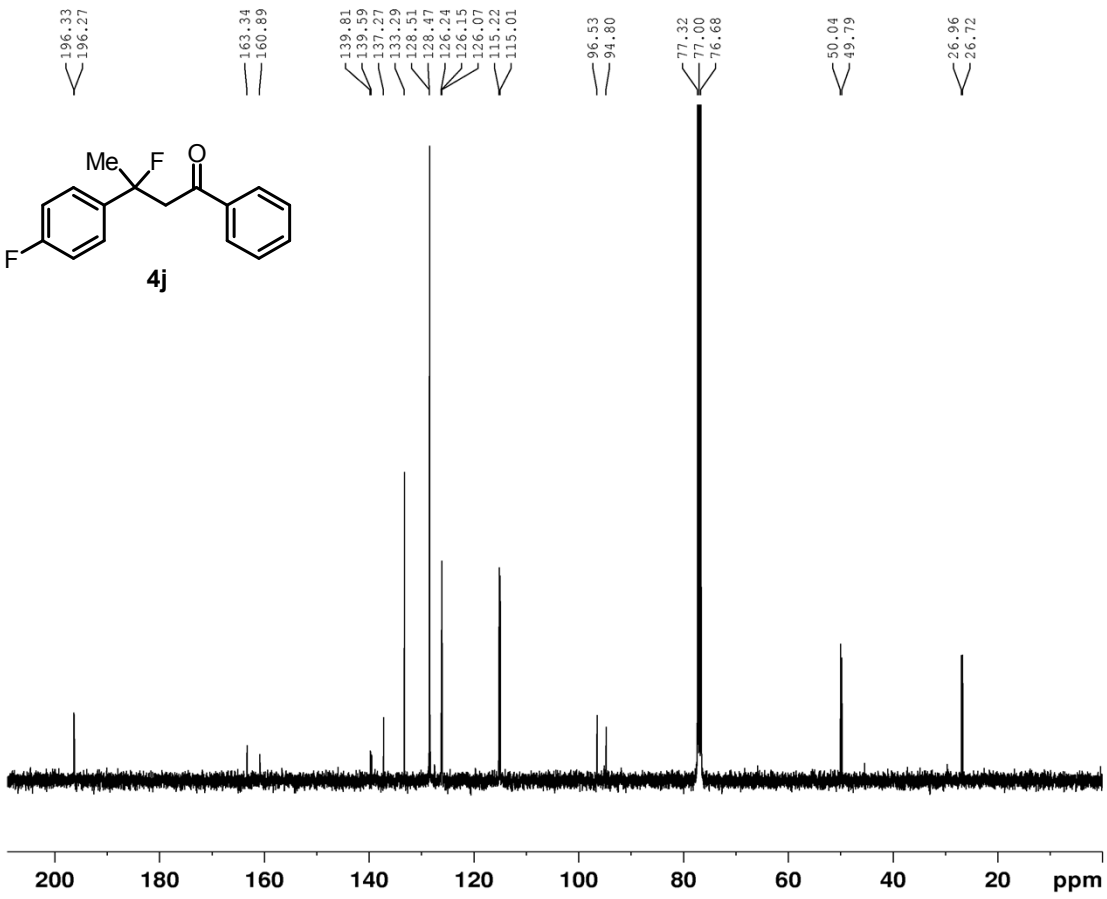
1.01
3.90
1.92
2.00
3.00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163.34
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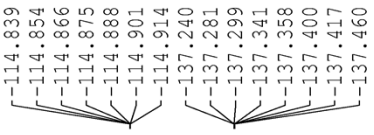
139.59
137.27
133.29
128.51
128.47
126.24
126.15
126.07
115.22
115.01
96.53
94.80
77.32
77.00
76.68
50.04
49.79
26.96
26.72
Me
F
O
F
200
180
160
140
120
100
80
60
40
20
ppm

4j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-137.240
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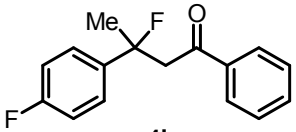
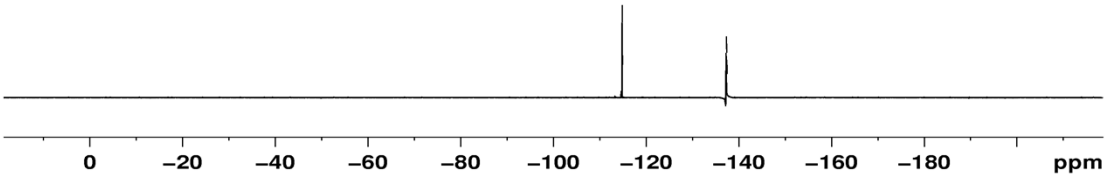
-137.358
-137.400
-137.417
-137.460


Me
F
O
F

4j


0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm