Decarboxylative Fluorination of Aliphatic Carboxylic Acids via Photoredox Catalysis

Sandrine Ventre, Filip R. Petronijević, and David W. C. MacMillan*

Merck Center for Catalysis at Princeton University, Princeton, New Jersey 08544

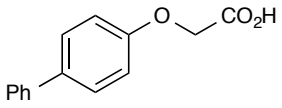
Supporting Information

Contents:

1. General Information. Commercial reagents were purchased from Sigma Aldrich and purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using an acetone-dry ice bath. Chromatographic purification of products was accomplished using forced-flow chromatography according to the method of Still[3] on ICN 60 32-64 mesh silica gel 63. Thin-layer chromatography (TLC) was performed on Silicycle 250 mm silica gel F-254 plates. Visualization of the developed plates was performed by fluorescence quenching, potassium permanganate or ceric ammonium molybdate stain. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 (500 and 125 MHz), and are internally referenced to residual protio solvent signals (for $CDCl_3$, δ 7.27 and 77.0 ppm, respectively). ^{19}F NMR spectra were recorded on Bruker 300 (282 MHz) and are referenced to $CFCl_3$ at δ = 0 ppm. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C spectra were reported as chemical shifts in ppm and multiplicity where appropriate. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of wavenumber of absorption (cm^{-1}). High Resolution Mass spectra were obtained from the Princeton University Mass Spectral Facility.

2. Experimental Procedures and Spectral Characterization of the Starting Materials

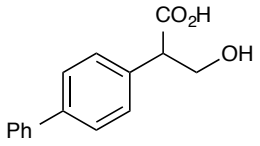
The following acids were commercially available: 4-benzoylbutanoic acid (precursor to **11**), 3,3'-(1,4-phenylene)dipropionic acid (precursor to **12**), 3-([1,1'-biphenyl]-4-yl)propanoic acid (precursor to **13**), 2-([1,1'-biphenyl]-4-yl)acetic acid (precursor to **14**), 3-phenylbutanoic acid (precursor to **16**), 3,3,3-triphenylpropanoic acid (precursor to **17**), cis-2-((*tert*-butoxycarbonyl)amino)cyclopentane-1-carboxylic acid (precursor to **19**), trans-4-(*tert*-butyl)cyclohexane-1-carboxylic acid (precursor to **20**), 2,3-dihydro-1*H*-indene-2-carboxylic acid (precursor to **22**), 2-methyl-4-oxo-4-phenylbutanoic acid (precursor to **25**), 2-butyloctanoic acid (precursor to **27**), and (3*S*,4*S*,6*R*,6*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carboxylic acid (precursor to **28**). The rest of the substrates were prepared according to the following procedures or literature methods.



4-Phenylphenoxyacetic acid (precursor to **18**).[4]

^{1}H NMR (500 MHz, DMSO-d_6): d 13.06 (bs, 1 H), 7.60 (t, J = 7.6 Hz, 4 H), 7.43 (t, J = 5.6 Hz, 2 H), 7.31 (t, J = 7.6 Hz, 1 H), 6.99 (d, J = 8.3 Hz, 2 H), 4.70 (s, 2 H);

^{13}C NMR (125 MHz, DMSO-d_6): δ 171.1, 158.3, 140.6, 133.9, 129.8 (2 C), 128.6 (2 C), 127.7, 127.1 (2 C), 115.8 (2 C), 65.4.



2-([1,1'-Biphenyl]-4-yl)-3-hydroxypropanoic acid (precursor to **21**).

To a stirred solution of *n*-BuLi (2.5 M in solution in hexanes, 10.6 mL, 26.5 mmol, 3 equiv.) in THF (45 mL) was added dropwise 2,2,6,6-tetramethylpiperidine (4.50 mL, 26.5 mmol, 3 equiv.) at –10 °C over 30 minutes, cooled to –78 °C, treated with a solution of methyl 2-([1,1'-biphenyl]-4-yl)acetate[5] (2.00 g, 8.84 mmol, 1 equiv.) in THF (70 mL) over 30 minutes, and stirred at this temperature for 1 h. To this mixture was then added dropwise a solution of 1*H*-benzotriazole-1-methanol (2.64 g, 17.7 mmol, 2 equiv.) in THF (60 ml). The reaction was quenched with water (20 mL), extracted with diethyl ether (60 mL), and then washed successively with 4 M NaOH (20 mL) and brine (20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude ester, which was used in the next step without any further purification.

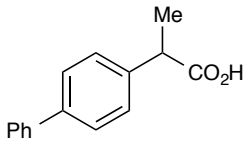
To a solution of the crude ester (1.15 g, 4.49 mmol, 1 equiv.) in a mixture of methanol (10 mL) and tetrahydrofuran (10 mL) was added LiOH (215 mg, 8.97 mmol, 2 equiv.) in water (10 mL). The resulting mixture was stired overnight, then acidified to pH 3 (with aqueous 1 M HCl solution), extracted with ethyl acetate, and washed with brine. The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give the crude carboxylic acid. The acid was purified by flash chromatography on SiO_2 (50% EtOAc/hexanes) to obtain 2-([1,1'-Biphenyl]-4-yl)-3-hydroxypropanoic acid as a white solid (782.0 mg, 43% over 2 steps).

^{1}H NMR (500 MHz, DMSO-d_6): δ 12.43 (bs, 1 H), 7.72–7.58 (m, 4 H), 7.51–7.42 (m, 2 H), 7.42–7.32 (m, 3 H), 4.96 (bs, 1 H), 3.94 (t, *J* = 9.5 Hz, 1 H), 3.69 (dd, *J* = 8.6, 5.8 Hz, 1 H), 3.61 (dd, *J* = 10.2, 5.8 Hz, 1 H);

^{13}C NMR (125 MHz, DMSO-d_6): δ 173.7, 139.9, 139.0, 136.3, 128.9 (2 C), 128.7 (2 C), 127.4, 126.8 (2 C), 126.6 (2 C), 63.4, 54.0;

HRMS-EI (*m/z*) calcd for $C_{15}H_{13}O_2$ [$(M–H_2O)^+$] 224.0837, found 224.0858;

IR (film): 3389, 2546, 1949, 1696, 1519, 1485, 1465, 1434, 1334, 1255, 1214, 1172, 1075, 1043, 1018, 830 cm^{-1}.



2-([1,1'-biphenyl]-4-yl)propanoic acid (precursor to **24**)

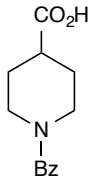
To a solution of LDA (diisopropylamine (2.19 mL, 15.65 mmol, 1.1 equiv.) and *n*-BuLi (2.5 M in solution in hexanes, 6.00 mL, 14.94 mmol, 1.05 equiv.)), was added dropwise methyl 2-([1,1′-biphenyl]-4-yl)acetate[6] (3.22 g, 14.2 mmol, 1.0 equiv.) in THF (10 mL) at –78 °C. After stirring the reaction mixture at this temperature for 30 minutes, iodomethane (0.980 mL, 15.65 mmol, 1.1 equiv.) was added. The mixture was then warmed to 0 °C over 1 h, quenched with sat. aq NH_4Cl, and the aqueous layer extracted with Et_2O. The combined organic layers were washed with water, brine, dried ($MgSO_4$), and concentrated *in vacuo* to give the crude ester as a colorless oil, which was used in the next step without any further purification.

To a solution of the crude ester (1.46 g, 6.08 mmol, 1 equiv.) in a mixture of methanol (15 mL) and tetrahydrofuran (15 mL) was added a solution of LiOH (291 mg, 8.97 mmol, 2 equiv.) in water (10 mL). The resulting mixture was stired overnight, then acidified to

pH 3 (with aqueous 1 M HCl solution), extracted with EtOAc, and washed with brine. The organic layer was dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give the crude carboxylic acid. Purification by flash chromatography on SiO_2 (40% EtOAc in hexanes) to obtain 2-([1,1'-biphenyl]-4-yl)propanoic acid as a white solid (1.29 g, 94%). Spectral data of the acid were in agreement with the previously reported literature data.[7]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.51 (m, 4 H), 7.48–7.37 (m, 4 H), 7.37–7.30 (m, 1 H), 3.80 (q, *J* = 7.2 Hz, 1 H), 1.56 (d, *J* = 7.2 Hz, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.8, 140.8, 140.6, 138.9, 128.9 (2 C), 128.2 (2 C), 127.6 (2 C), 127.5, 127.2 (2 C), 45.0, 18.3.



1-Benzoylpiperidine-4-carboxylic acid (precursor to **26**).

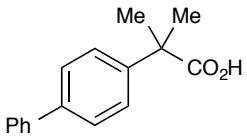
To a solution of isonipecotic acid (3.00 g, 23.2 mmol) in 2 M aqueous NaOH (20 mL) was added a solution of benzoyl chloride (2.7 mL, 23 mmol) in DCM (20 mL), stirred for 10 h, and the layers were separated. The organic layer was acidified with 1 M HCl to pH 2, and the aqueous layer extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The crude material was recrystallized from hexane/EtOAc mixture.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.04 (br s, 1 H), 7.44–7.39 (m, 5 H), 4.53–4.50 (m, 1 H), 3.76–3.73 (m, 1 H), 3.11–3.06 (m, 2 H), 2.62 (tt, *J* = 10.6, 4.0 Hz), 2.09–2.06 (m, 1 H), 1.88–1.70 (m, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): 178.9, 170.7, 135.5, 129.7, 128.5, 126.8, 46.9, 41.5, 40.6;

HRMS-EI (*m/z*) calcd for $C_{13}H_{13}NO_3$ [$M^{\bullet+}$] 233.1052, found 233.1050;

IR (film): 2950, 1730, 1594, 1448, 1213 cm^{-1}.



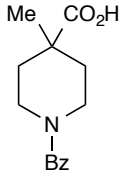
2-([1,1'-biphenyl]-4-yl)-2-methylpropanoic acid (precursor to **31**)

To a solution of LDA (diisopropylamine (1.15 mL, 8.24 mmol, 1.1 equiv.) and *n*-BuLi (2.5 M in solution in hexanes, 3.15 mL, 7.87 mmol, 1.05 equiv.)) was added dropwise a solution of methyl 2-([1,1'-biphenyl]-4-yl)-2-methylpropanoate (1.80 g, 7.49 mmol, 1.0 equiv.) in THF (10 mL) at –78 °C. After stirring the reaction mixture at this temperature for 30 minutes, methyliodide (0.515 mL, 8.24 mmol, 1.1 equiv.) was added. The mixture was then warmed to 0 °C over 1 h, and quenched with sat. aq NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic extracts were washed with water, brine, dried ($MgSO_4$), and concentrated *in vacuo* to give the crude ester as a colorless oil, which was used in the hydrolysis step without any further purification.

To a solution of the crude ester (1.90 g, 6.08 mmol, 1 equiv.) in methanol (50 mL) was added a solution of NaOH (1.49 g, 37.4 mmol, 5 equiv.) in water (30 mL). The resulting mixture was stired for 48 h, acidified to pH 3 (with aqueous 1 M HCl). The reaction was extracted with ethyl acetate, washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the crude carboxylic acid. Purification by flash chromatography on SiO_2 (30% EtOAc in hexanes) provided 2-([1,1'-biphenyl]-4-yl)propanoic acid as a white solid (1.29 g, 94%). Spectral data of the acid were in agreement with the previously reported literature data.[8]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66–7.55 (m, 4 H), 7.51–7.47 (m, 2 H), 7.46–7.41 (m, 2 H), 7.39–7.31 (m, 1 H), 1.66 (s, 6 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 182.9, 143.0, 140.8, 140.1, 128.9 (2 C), 127.4, 127.3 (2 C), 127.2 (2 C), 126.4 (2 C), 46.2, 26.4 (2 C).



1-Benzoyl-4-methylpiperidine-4-carboxylic acid (precursor to **32**).

To a suspension of 1-benzoylpiperidine-4-carboxylic acid (precursor to **29**) (2.00 g, 8.57 mmol) and K_2CO_3 (2.40 g, 17.0 mmol) in DMF (210 mL) was added iodomethane (2.0 mL, 34 mmol), the resulting mixture was stirred for 12 h at room temperature, and then partitioned between EtOAc and water. The aqueous layer was extracted with EtOAc (3 x 45 mL), the combined organic layers washed with water (3 x 30 mL), brine, filtered, and concetrated *in vacuo* to obtain methyl 1-benzoylpiperidine-4-carboxylate, which was used in the next step without further purification or characterization.

To a solution of diisopropyl amine (1.28 mL, 9.10 mmol) in THF (10 mL) at 0 °C was treated with *n*-BuLi (2.5 M solution in hexane, 3.6 mL, 9.1 mmol), stirred for 15 min at room temperature, and cooled to –78 °C. To this solution was added a solution of the previously made methyl ester (1.5 g, 6.1 mmol) in THF (5 mL) dropwise, stirred at –78 °C for 1 h, treated with iodomethane (3.6 mL, 9.1 mmol), and stirred for next 3 h at –78 °C. After quenching the reaction with sat. aq NH_4Cl, the reaction mixture was partitioned between EtOAc and water, and the layers separated. The aqueous layer was extracted with EtOAc (3 x 20 mL), the combined organic layers washed with brine, dried

(Na_2SO_4), filtered, and concentrated *in vacuo* to obtained crude methyl 1-benzoyl-4-methylpiperidine-4-carboxylate (1.51 g, 98%).

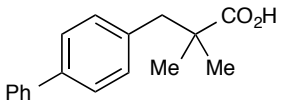
A solution of 1-benzoyl-4-methylpiperidine-4-carboxylate (1.40 g, 5.36 mmol) and LiOH•H_2O (257 mg, 10.7 mmol) in a mixture of water and THF (1:1 v/v, 20 mL) was heated to reflux for 12 h, cooled to room temperature, acidified to pH 2 (with aqueous 1 M HCl), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by chromatography on SiO_2 (30% EtOAc in hexanes) provided 1-benzoyl-4-methylpiperidine-4-carboxylic acid (1.32 g, 99%) in the form of white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.39 (m, 5 H), 4.37–4.35 (m, 1 H), 3.57 (br s, 1 H), 3.25–3.16 (m, 1 H), 2.23–2.04 (m, 2 H), 1.53 (br s, 1 H), 1.36 (br s, 1 H), 1.29 (s, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): 181.6, 170.6, 135.8, 129.7, 128.4, 126.8, 45.3, 41.9, 39.8, 26.0;

HRMS-EI (*m/z*) calcd for $C_{14}H_{17}NO_3$ [$M^{\bullet+}$] 247.1208, found 247.1211;

IR (film): 2947, 2927, 2876, 1630, 1432, 1264, 967, 708 cm^{-1}.



3-(4-Biphenyl)-2,2-dimethylpropanoic acid (precursor to **33**).

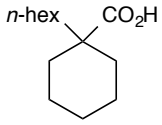
To a solution of LDA (diisopropylamine (970 mL, 6.88 mmol, 1 equiv.) and *n*-BuLi (2.5 M in solution in hexanes, 2.75 mL, 6.88 mmol, 1 equiv.)), was added methyl isobutyrate (790 mL, 6.88 mmol, 1 equiv.) dropwise at –78 °C. After stirring the reaction mixture at this temperature for 1 h, 4-(bromomethyl)-1,1'-biphenyl (1.70 g, 6.88 mmol, 1 equiv.) was added, the reaction mixture warmed to room temperature, stirred for 16 h, and

quenched with water at 0 °C. The mixture was extracted with Et_2O, and the combined organic layers washed with brine, dried ($MgSO_4$), and concentrated *in vacuo* to give the crude ester, which was used in the next step without any further purification.

To a solution of the crude ester in MeOH (10 mL) was added a solution of NaOH (1.60 g, 34.4 mmol) in water (10 mL), and the mixture was stirred at 60 °C overnight. The reaction mixture was then acidified to pH 2 (with conc. aq HCl). The reaction was extracted with EtOAc, and the aqueous layer was saturated with NaCl and extracted with EtOAc again. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated *in vacuo* to give the crude carboxylic acid. The acid was purified by flash chromatography on SiO_2 (20% EtOAc in hexanes) to obtain 3-(4-biphenyl)-2,2-dimethylpropanoic acid as a white solid (1.32 g, 75%). Spectral data of the acid were in agreement with the previously reported literature data.[9]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.56 (m, 2 H), 7.56–7.50 (m, 2 H), 7.47–7.40 (m, 2 H), 7.38–7.31 (m, 1 H), 7.30–7.22 (m, 2 H), 2.97 (s, 2 H), 1.27 (s, 6 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 183.3, 140.9, 139.4, 130.7 (2 C), 128.7 (2 C), 127.1, 127.0 (2 C), 126.8 (2 C), 45.6, 43.5, 24.9 (2 C).



1-Hexylcyclohexane-1-carboxylic acid (precursor to **34**).

To a solution of diisopropyl amine (3.0 mL, 21 mmol) in THF (20 mL) at 0 °C was treated with *n*-BuLi (2.5 M solution in hexane, 8.5 mL, 21 mmol), stirred for 15 min at room temperature, and cooled to –78 °C. To this solution was added a solution of methyl cyclohexanecarboxylate (2.00 g, 14.1 mmol) in THF (15 mL) dropwise, stirred at –78 °C

for 1 h, treated with 1-bromohexane (2.0 mL, 14 mmol), and stirred for next 10 h at room temperature. After quenching the reaction with sat. aq NH_4Cl, the reaction mixture was partitioned between EtOAc and water, and the layers separated. The aqueous layer was extracted with EtOAc (3 x 20 mL), the combined organic layers washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to obtained crude methyl methyl 1-hexyl-1-cyclohexanecarboxylate (2.2 g, 69%).

A solution of methyl 1-hexyl-1-cyclohexanecarboxylate (1.00 g, 4.42 mmol) and KOH (500 mg, 9.1 mmol) in ethanol (15 mL) was heated to reflux for 48 h, cooled to room temperature, acidified to pH 2 (with aqueous 1 M HCl), and extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by chromatography on SiO_2 (10 to 30 to 50% EtOAc in hexanes) provided 1-hexyl-1-cyclohexanecarboxylic acid (0.58 g, 62%) in the form of white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 11.39 (br s, 1 H), 2.06–2.04 (m, 2 H), 1.61–1.57 (m, 3 H), 1.53–1.50 (m, 2 H), 1.41 (dt, J = 14.9, 10.6 Hz), 1.31–1.21 (m, 11 H), 0.88 (t, J = 6.6 Hz, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): 183.9, 46.8, 40.4, 33.9, 31.7, 29.7, 25.9, 23.9, 23.2, 22.6, 14.1;

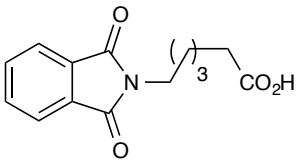
HRMS-EI (*m/z*) calcd for $C_{13}H_{24}O_2$ [$(M+H)^+$] 213.1854, found 213.1857;

IR (film): 2928, 2856, 1695, 1454, 1245 cm^{-1}.

General procedure for phthalimide protected amino acids.

A mixture of phthalic anhydride (20.0 mmol, 1 equiv.) and an amino acid (20.0 mmol, 1 equiv.) was melted in a round bottom flask at 170 °C. The mixture was stirred at this

temperature for 2 h, open to air in order to evaporate water. After cooling the reaction to room temperature, the crude mixture was dissolved in dichlorometane and filtrate though a pad of silica gel. The filtrate was then concentrated *in vacuo* to yield the desired compound which was used without any further purification.

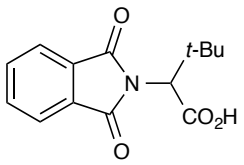


6-(1,3-Dioxo-1,3- dihydroisoindol-2-yl)-hexanoic acid (precursor to **15**).

According to the general procedure for phthalimide protected amino acids, 6-aminohexanoic acid (2.62 g, 20.0 mmol, 1 equiv.) and phthalic anhydride (2.96 g, 20.0 mmol, 1 equiv.) yielded 6-(1,3-dioxoisoindolin-2-yl)-hexanoic acid as a white solid (4.30 g, 92%). Spectral data for the desired product were in agreement with the previously reported literature data.[10]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2 H), 7.71 (dd, *J* = 5.4, 3.1 Hz, 2 H), 3.69 (t, *J* = 7.3 Hz, 2 H), 2.35 (t, *J* = 7.4 Hz, 2 H), 1.73–1.65 (m, 4 H), 1.45–1.30 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 178.3, 168.6 (2 C), 134,1 (2 C), 132,3 (2 C), 123, 4 (2 C), 37.9, 34.0, 28.9, 26.44, 24.4.



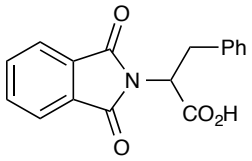
2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-3,3-dimethylbutanoic acid (precursor to **29**).

According to the general procedure for phthalimide protected amino acids, DL-*tert*-Leucine (2.62 g, 20.0 mmol, 1 equiv.) and phthalic anhydride (2.96 g, 20.0 mmol, 1

equiv.) yielded 2-(1,3-dioxoisoindolin-2-yl)-3,3-dimethylbutanoic acid as a white solid (4.9 g, 94%). Spectral data for the desired product were in agreement with the previously reported literature data.[11]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.82 (m, 2 H), 7.77–7.69 (m, 2 H), 4.65 (s, 1 H), 1.14 (s, 9 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.6, 168.4 (2 C), 134.3 (2 C), 131.8 (2 C), 123.7 (2 C), 60.3, 35.8, 28.1 (3 C).



2-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)-3-phenylpropionic acid (precursor to **30**).

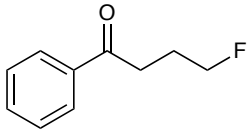
According to the general procedure for phthalimide protected amino acids, DL-phenylalanine (3.30 g, 20.0 mmol, 1 equiv.) and phthalic anhydride (2.96 g, 20.0 mmol, 1 equiv.) yielded 2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanoic acid as a white solid (5.8 g, 98%). Spectral data for the desired product were in agreement with the previously reported literature data.[12]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79–7.73 (m, 2 H), 7.70–7.64 (m, 2 H), 7.22–7.09 (m, 5 H), 5.23 (t, J = 8.5 Hz, 1 H), 3.59 (d, J = 8.5 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173, 167.5 (2 C), 136.5 (2 C), 134.1 (2 C), 131.5 (2 C), 128.8 (2 C), 128.6 (2 C), 126.9, 123.5, 53.2, 34.5.

3. Experimental Procedures and Spectral Characterization of the Isolated Fluorinated Products

General Procedure for Photoredox-Catalyzed Decarboxylative Fluorination of Carboxylic Acid: A solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), carboxylic acid (0.7 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in a mixture of acetonitrile/water (7.0 mL, 1:1 v/v) was degassed by sparging argon for 10 min, then irradiated with two 34 W blue LEDs (at approximately 4 cm from the light source). After the reaction completion, the crude reaction mixture was extracted with Et_2O (3 x 10 mL), the combined organic extracts were dried (Na_2SO_4), and concentrated *in vacuo*. Purification by flash chromatography on SiO_2 (5–10% Et_2O in pentane) afforded the desired fluorinated product.



3-Fluoro-1-phenylpropan-1-one (11): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 4-benzoylbutanoic acid (124.7 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 15 h to obtain **11** as a colorless oil (82 mg, 77%).

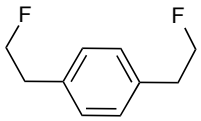
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.98 (m, 2 H), 7.80–7.57 (m, 1 H), 7.48 (t, J = 7.8 Hz, 2 H), 4.57 (dt, J = 47.3, 5.7 Hz, 2 H), 3.16 (t, J = 7.1 Hz, 2 H), 2.24–2.06 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 199.1, 136.7, 133.2, 128.6, 128.0, 83.3 (d, *J* = 164.4 Hz), 34.0 (d, *J* = 4.2 Hz), 24.8 (d, *J* = 20.1 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -219.9 – -220.3 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{10}H_{11}FO$ [$M^{\bullet+}$] 166.0794, found 166.0799;

IR (film): 2969, 2905, 1683, 1598, 1449, 740 cm^{-1}.



1,4-Bis(2-fluoroethyl)benzene (12): A mixture of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7.8 mg, 7.0 μmol, 1 mol%), disodium 3,3'-(1,4-phenylene)dipropionate (186 mg, 0.700 mmol, 1 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 6 h to obtain **12** as a colorless oil (84.5 mg, 71%).

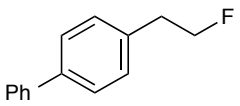
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (s, 4 H), 4.63 (dt, *J* = 47.1, 6.6 Hz, 4 H), 3.02 (dd, *J* = 23.2, 6.6 Hz, 4 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 135.4 (d, *J* = 6.8 Hz, 2 C), 129.1 (4 C), 84.1 (d, *J* = 169.0 Hz, 2 C), 36.5 (d, *J* = 20.6 Hz, 2 C);

^{19}F NMR (282 MHz, $CDCl_3$): δ -215.1 – -215.6 (m, 2 F);

HRMS-EI (*m/z*) calcd for $C_{10}H_{12}F_2$ [$M^{\bullet+}$] 170.0907, found 170.0912;

IR (film): 2966, 2903, 1516, 1479, 1234, 810 cm^{-1}.



4-(2-Fluoroethyl)-1,1'-biphenyl (13): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (7.8 mg, 7.0 μmol, 1 mol%), 3-([1,1'-biphenyl]-4-

yl)propanoic acid (158 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 6 h to obtain **13** as a colorless oil (114 mg, 81%).

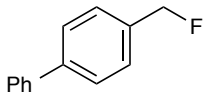
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.53 (m, 4 H), 7.47–7.42 (m, 2 H), 7.37–7.30 (m, 3 H), 4.68 (dt, *J* = 47.0, 6.5 Hz, 2 H), 3.07 (dt, *J* = 23.4, 6.6 Hz, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0, 139.8, 136.3 (d, *J* = 6.2 Hz), 129.5 (2 C), 128.9 (2 C), 127.5 (2 C), 127.3, 127.2 (2 C), 84.2 (d, *J* = 169.0 Hz), 36.7 (d, *J* = 20.4 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -215.1– -215.6 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{14}H_{13}F$ [$M^{\bullet+}$] 200.0996, found 200.0989;

IR (film): 2923, 1709, 1683, 1604, 1487, 1409, 1358, 1220, 1091, 1021, 1007, 973, 916, 886, 841, 764 cm^{-1}.



4-(Fluoromethyl)-1,1'-biphenyl (14): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-([1,1'-biphenyl]-4-yl)acetic acid (148 mg, 0.70 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **14** as a colorless oil (113.4 mg, 87%).

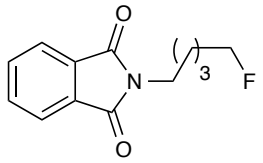
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67–7.61 (m, 4 H), 7.49–7.46 (m, 4 H), 7.40–7.37 (m, 1 H), 5.45 (d, *J* = 47.9 Hz, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.7, 140.6, 135.1, 128.8 (2 C), 128.0 (d, *J* = 5.7 Hz, 2 C), 127.5, 127.3 (2 C), 127.1 (2 C), 84.4 (d, *J* = 165.9 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -206.1 – 206.4 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{13}H_{11}F$ [$(M–F)^{\bullet+}$]167.0861, found 167.0855;

IR (film): 3027, 1488, 1401, 1007, 909, 762, 697 cm^{-1}.



2-(3-Fluoropentyl)isoindoline-1,3-dione (15): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 4-(1,3-dioxoisoindolin-2-yl)butanoic acid (183 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 12 h to obtain **15** as a white solid (145 mg, 79%).

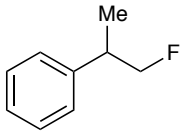
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.80 (m, 2 H), 7.76–7.65 (m, 2 H), 4.44 (dt, *J* = 47.2, 6.0 Hz, 2 H), 3.70 (t, *J* = 7.2 Hz, 2 H), 1.84–1.61 (m, 4 H), 1.53–1.40 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.6 (2 C), 134.0 (2 C), 132.2 (2 C), 123.4 (2 C), 83.9 (d, *J* = 164.6 Hz), 37.9, 30.0 (d, *J* = 19.7 Hz), 28.4, 22.7 (d, *J* = 5.32 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -218.5 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{13}H_{14}FNO_2$ [$M^{\bullet+}$] 235.1003, found 235.1001;

IR (film): 2942, 2866, 1772, 1704, 1614, 1466, 1437, 1394, 1364, 1337, 1187, 1171, 1153, 1053, 958, 880, 845, 793, 715 cm^{-1}.



(1-Fluoropropan-2-yl)benzene (16): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 3-phenylbutanoic acid (114.9 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 6 h to obtain **16** as a colorless oil (89.0 mg, 92%).

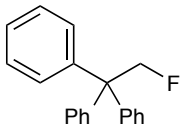
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 2 H), 7.29–7.27 (m, 3 H), 4.49 (dddd, *J* = 47.4, 42.8, 8.8, 6.6 Hz, 2 H), 3.17 (dq, *J* = 16.5, 6.9 Hz, 1H), 1.38 (dd, *J* = 7.3, 1.3 Hz, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 142.2 (d, *J* = 6.3 Hz), 128.6, 127.4, 126.9, 88.1 (d, *J* = 173.1 Hz), 40.4 (d, *J* = 18.9 Hz), 16.9 (d, *J* = 5.6 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -216.7 – -216.2 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_9H_{11}F$ [$M^{\bullet+}$] 138.0845, found 138.0847;

IR (film): 2967, 2896, 1479, 1233, 1000, 760, 698 cm^{-1}.



(2-Fluoroethane-1,1,1-triyl)tribenzene (17): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 3,3,3-triphenylpropanoic acid (212 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and

Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **17** as a white solid (159 mg, 82%).

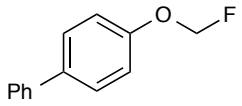
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55–7.45 (m, 4 H), 7.44–7.37 (m, 4 H), 7.37–7.32 (m, 2 H), 7.30–7.27 (m, 2 H), 7.20–7.13 (m, 1 H), 6.80–6.74 (m, 2 H), 3.68 (d, *J* = 23.5 Hz, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 150.56, 142.3, 142.1, 129.4 (2 C), 128.6 (2 C), 128.3 (2 C), 126.0 (2 C), 125.6 (2 C), 125.5 (2 C), 121.5 (2 C), 97.0 (d, *J* = 182.1 Hz), 45.8 (d, *J* = 24.3 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -144.3 (t, *J* = 23.5 Hz, 1 F);

HRMS-EI (*m/z*) calcd for $C_{20}H_{16}$ [$(M–HF)^{\bullet+}$] 256.1247, found 256.1261;

IR (film): 2921, 1852, 1592, 1492, 1449, 1360, 1227, 1192, 1161, 1134 cm^{-1}.



4-(Fluoromethoxy)-1,1'-biphenyl (18): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-([1,1'-biphenyl]-4-yloxy)acetic acid (160 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **18** as a white solid (140 mg, 99%).

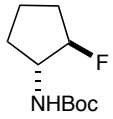
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.53 (m, 4 H), 7.43 (t, *J* = 7.2 Hz, 2 H), 7.37–7.31 (m, 1 H), 7.21–7.13 (m, 2 H), 5.76 (d, *J* = 54.7 Hz, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4, 156.4, 140.6, 136.8, 128.9 (2 C), 128.5 (2 C), 127.2, 127.0 (2 C), 117.0, 100.9 (d, *J* = 218.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -148.8 (t, *J* = 54.6 Hz, 1 F);

HRMS-EI (*m/z*) calcd for $C_{13}H_{11}FO$ [$M^{\bullet+}$] 202.0788, found 202.0788;

IR (film): 3032, 2933, 2178, 1895, 1712, 1608, 1587, 1518, 1483, 1452, 1413, 1361, 1316, 1292, 1277, 1223, 1190, 1180, 1155, 1091, 1038, 949, 836 cm^{-1}.



Trans-*tert*-butyl (2-fluorocyclopentyl)carbamate (19): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), cis-2-((*tert*-butoxycarbonyl)amino)cyclopentane-1-carboxylic acid (160.5 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 15 h to obtain **19** as a white solid (116.7 mg, 82%).

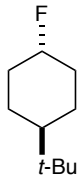
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.90 (dd, *J* = 52.5, 4.3 Hz, 1 H), 4.41 (br s, 1 H), 4.00 (d, *J* = 17.5 Hz, 1 H), 2.27–2.08 (m, 1 H), 1.99–1.66 (m, 3 H), 1.45 (s, 9 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 98.7 (d, *J* = 178.0 Hz), 79.7, 57.5, 30.8, 30.6, 28.3 (3 C), 21.3;

^{19}F NMR (282 MHz, $CDCl_3$): δ -175.7 (s, 1 F);

HRMS-EI (*m/z*) calcd for $C_6H_{11}NO_2$ [$(M–Boc+H)^{\bullet+}$] 103.0797, found 103.0793;

IR (film): 3342, 2973, 1681, 1524, 1366, 1251, 1167, 954 cm^{-1}.



Trans-1-(*tert*-butyl)-4-fluorocyclohexane (20): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), trans-4-(*tert*-butyl)cyclohexane-1-carboxylic acid (129 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 15 h to obtain **20** as a colorless liquid (77.5 mg, 70%), as a mixture of trans/cis isomers (2.5:1 trans:cis ratio).

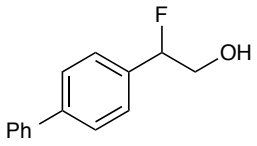
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.82 (dt, *J* = 47.9, 2.3 Hz, 1 H), 4.42 (dm, *J* = 49.5 Hz, 0.4 H), 2.15–2.06 (m, 2.9 H), 1.85–1.82 (m, 0.9 H), 1.60–1.58 (m, 2.1 H), 1.52–1.33 (m, 5.1 H), 1.06–0.97 (m, 2.2 H), 0.91–0.88 (m, 0.9 H), 0.87 (s, 9 H), 0.86 (s, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 92.9 (d, *J* = 171.1 Hz), 88.8 (d, *J* = 166.2 Hz), 47.4, 46.9 (d, *J* = 1.9 Hz), 33.1, 33.0, 32.5, 31.5, 31.3, 27.6, 27.4, 25.0, 24.9, 21.2;

^{19}F NMR (282 MHz, $CDCl_3$): δ -168.8 – -169.1 (m, 0.4 F), -184.8 – -185.1 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{10}H_{18}$ $[(M–HF)^{\bullet+}]$ 138.1409, found 138.1403;

IR (film): 2942, 2869, 1479, 1441, 1367, 1179, 937, 823 cm^{-1}.



2-([1,1'-Biphenyl]-4-yl)-2-fluoroethan-1-ol (21): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-([1,1'-biphenyl]-4-yl)-3-

hydroxypropanoic acid (169.6 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 2.10 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **21** as a white solid (121 mg, 80%).

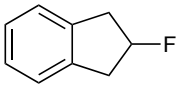
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–7.51 (m, 4 H), 7.48–7.41 (m, 4 H), 7.39–7.35 (m, 1 H), 5.62 (ddd, *J* = 48.6, 7.7, 3.1 Hz, 1 H), 4.18–3.58 (m, 2 H), 2.01–1.96 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.98, 140.6, 135.4 (d, *J* = 19.8 Hz), 129.0 (2 C), 127.7, 127.5 (2 C), 127.3 (2 C), 126.4 (d, *J* = 6.8 Hz, 2 C), 94.8 (d, *J* = 171.8 Hz), 66.7 (d, *J* = 24.8 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -186.6 – -187.1 (m, 1 F);

HRMS-EI (*m/z*) calcd for $C_{14}H_{12}O$ $[(M–HF)^{\bullet+}]$ 196.0883, found 196.0887;

IR (film): 3362, 3058, 3033, 2928, 1947, 1693, 1666, 1603, 1487, 1450, 1408, 1355, 1315, 1234, 1167, 1086, 1046, 978 cm^{-1}.



2-Fluoro-2,3-dihydro-1*H*-indene (22): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ru(bpz)_3(PF_6)_2$ (5.9 mg, 7.0 μmol, 1 mol%), 2,3-dihydro-1*H*-indene-2-carboxylic acid (114 mg, 0.70 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **22** as a white solid (88 mg, 92%).

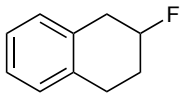
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.24 (m, 2 H), 7.23–7.18 (m, 2 H), 5.56–5.40 (m, 1 H), 3.31–3.23 (m, 2 H), 3.22–3.16 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.1 (2 C), 127.9 (2 C), 127.0 (2 C), 94.9 (d, *J* = 176.7 Hz), 40.7 (d, *J* = 23.14 Hz, 2 C);

^{19}F NMR (282 MHz, $CDCl_3$): δ -173.5 – -173.8 (m, 1 F);

HRMS (*m/z*): calcd for C_9H_9F [$M^{\bullet+}$] 136.0683, found 136.0683;

IR (film): 2959, 1479, 1417, 1346, 1233, 1215, 1193, 1016, 941, 808, 739 cm^{-1}.



2-Fluoro-1,2,3,4-tetrahydronaphthalene (23): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ru(bpz)_3(PF_6)_2$ (5.9 mg, 7.0 μmol, 1 mol%), 1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (114 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **23** as a colorless liquid (74 mg, 71%).

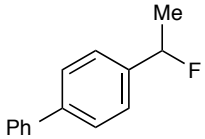
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16–7.11 (m, 4 H), 5.09 (m, 1 H), 3.19–2.99 (m, 3 H), 2.82 (dt, *J* = 16.8, 6.5 Hz, 1 H), 2.16–2.09 (m, 1 H), 2.08–2.04 (m, 1 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 135.4 (d, *J* = 1.5 Hz), 132.9 (d, *J* = 6.1 Hz), 129.4, 128.5, 126.1, 126.0, 88.8 (d, *J* = 169.9 Hz), 35.3 (d, *J* = 22.3 Hz), 28.5 (d, *J* = 20.0 Hz), 25.6 (d, *J* = 8.2 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -177.3 – -177.7 (m, 1 F);

HRMS (*m/z*): calcd for $C_{10}H_{11}F$ [$M^{\bullet+}$] 150.0845, found 150.0843;

IR (film): 2939, 1496, 1455, 1343, 1052, 1014, 955, 928, 835, 744 cm^{-1}.



4-(1-Fluoroethyl)-1,1'-biphenyl (24): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-([1,1'-biphenyl]-4-yl)propanoic acid (158 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **24** as a colorless oil (119.0 mg, 85%).

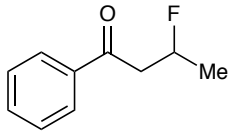
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67–7.56 (m, 4 H), 7.50–7.41 (m, 4 H), 7.40–7.34 (m, 1 H), 5.69 (dq, *J* = 47.7, 6.4 Hz, 1 H), 1.71 (dd, *J* = 23.9, 6.4 Hz, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.4, 140.8, 140.5 (d, *J* = 19.6 Hz), 128.9 (2 C), 127.6, 127.4 (2 C), 127.3 (2 C), 125.9 (d, *J* = 6.6 Hz, 2 C), 90.9 (d, *J* = 167.4 Hz), 23.0 (d, *J* = 25.3 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -166.6 (dq, *J* = 47.7, 23.9 Hz, 1 F);

HRMS-EI (*m/z*) calcd for $C_{14}H_{12}$ $[(M–HF)^{\bullet+}]$ 180.0934, found 180.0928;

IR (film): 3027, 2971, 2926, 2871, 1600, 1485, 1449, 1404, 1367, 1300, 1182, 1089, 1076, 1007, 908 cm^{-1}.



3-Fluoro-1-phenylbutan-1-one (25): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ru(bpz)_3(PF_6)_2$ (5.9 mg, 7.0 μmol, 1 mol%), 2-methyl-4-oxo-4-phenylbutanoic acid (134.5 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **25** as a colorless oil (112 mg, 96%).

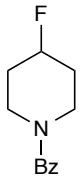
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.10–7.91 (m, 2 H), 7.64–7.57 (m, 1 H), 7.49 (t, *J* = 7.8 Hz, 2 H), 5.33 (dq, *J* = 47.5, 6.2 Hz, 1 H), 3.62–3.42 (m, 1 H), 3.10 (ddd, *J* = 23.6, 16.7, 5.5 Hz, 1 H), 1.49 (dd, *J* = 24.2 Hz, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.8 (d, *J* = 6.7 Hz), 136.8 (d, *J* = 1.5 Hz), 133.4, 128.7 (2 C), 128.1 (2 C), 87.2 (d, *J* = 165.3 Hz), 45.4 (d, *J* = 23.0 Hz), 21.2 (d, *J* = 22.2 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -172.4 – -172.9 (1 F, m);

HRMS-EI (*m/z*): calcd for $C_{11}H_{22}$ [$M^{\bullet+}$] 166.0794, found 166.0802;

IR (film): 2984, 1684, 1598, 1385, 1214, 1134, 839, 753 cm^{-1}.



(4-Fluoropiperidin-1-yl)(phenyl)methanone (26): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 1-benzoylpiperidine-4-carboxylic acid (163.3 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 6 h to obtain **26** as a colorless oil (131.0 mg, 90%).

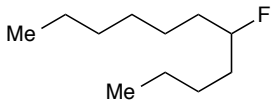
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.41 (m, 5 H), 4.98–4.86 (m, 1 H), 4.04–4.00 (m, 1 H), 3.68–3.44 (m, 3 H), 1.98–1.81 (m, 4 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.5, 135.8, 129.7, 128.6, 126.8, 87.6 (d, *J* = 171.5 Hz), 43.5, 38.0;

^{19}F NMR (282 MHz, $CDCl_3$): δ -183.0 – -183.4 (m, 1 F);

HRMS (*m/z*): calcd for $C_{12}H_{14}FNO$ [$M^{\bullet+}$] 207.1059, found 207.1051;

IR (film): 2951, 1632, 1433, 1283, 1027, 710 cm^{-1}.



5-Fluoroundecane (27): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-butyloctanoic acid (140 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 6 h to obtain **27** as a colorless oil (100 mg, 83%).

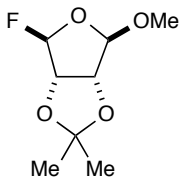
^{1}H NMR (500 MHz, $CDCl_3$): δ 4.54–4.37 (m, 1 H), 1.65–1.40 (m, 6 H), 1.37–1.26 (m, 10 H), 0.90 (t, *J* = 6.9 Hz, 6 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 94.8 (d, *J* = 166.4 Hz), 35.3 (d, *J* = 20.9 Hz), 35.0 (d, *J* = 20.8 Hz), 31.9, 29.4, 27.5 (d, *J* = 4.5 Hz), 26.3 (d, *J* = 4.5 Hz), 22.8 (2 C), 14.2, 14.2;

^{19}F NMR (282 MHz, $CDCl_3$): δ -185.1 – -185.5 (1 F, m);

HRMS-EI (*m/z*): calcd for $C_{11}H_{22}$ [$(M–HF)^{\bullet+}$] 154.1716, found 154.1719;

IR (film): 2931, 2860, 1463, 1379, 1129, 980 cm^{-1}.



(3*S*,4*R*,6*R*,6*R*)-4-Fluoro-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (28): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%),

(3*S*,4*S*,6*R*,6*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carboxylic acid (172.7 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **28** as a white solid (123.8 mg, 92%).

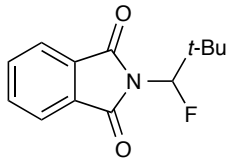
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (d, *J* = 60.5 Hz, 1 H), 5.17 (d, *J* = 2.9 Hz, 1 H), 4.82 (t, *J* = 6.0 Hz, 1 H), 4.67 (d, *J* = 5.7 Hz, 1 H), 3.43 (s, 3 H), 1.45 (s, 3 H), 1.32 (s, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 115.7 (d, *J* = 226.5 Hz), 112.9 (d, *J* = 1.2 Hz), 111.4 (d, *J* = 1.9 Hz), 83.9 (40.0 Hz), 83.2, 55.4, 26.2, 24.8;

^{19}F NMR (282 MHz, $CDCl_3$): δ -119.4 (m, 1 F);

HRMS (*m/z*): calcd for $C_8H_{12}O_4$ [$(M–HF)^{\bullet+}$] 172.0736, found 172.0746;

IR (film): 2990, 1377, 1202, 1101, 1060, 995, 867, 785 cm^{-1}.



2-(1-Fluoro-2,2-dimethylpropyl)isoindoline-1,3-dione (29): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-(1,3-dioxoisoindolin-2-yl)-3,3-dimethylbutanoic acid (183 mg, 0.700 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 3 h to obtain **29** as a white solid (148 mg, 90%).

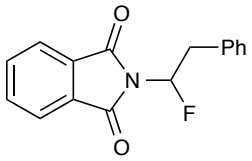
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91–7.87 (m, 2 H), 7.79–7.74 (m, 2 H), 5.91 (d, *J* = 43.0 Hz, 1 H), 1.12 (s, 9 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 167.0 (2 C), 134.5 (2 C), 133.6 (2 C), 123.7 (2 C), 98.4 (d, J = 211.3 Hz), 37.2 (d, J = 23.4 Hz), 23.6 (3 C);

^{19}F NMR (282 MHz, $CDCl_3$): δ -173.0 (d, J = 42.8 Hz);

HRMS-EI (*m/z*): calcd for $C_{13}H_{14}FNO_2$ $[(M–HF)^{\bullet+}]$ 235.1003, found 235.0997;

IR (film): 2968, 1781, 1721, 1612, 1480, 1468, 1392, 1353, 1327, 1269, 1216, 1124, 1088, 1050, 1011, 987, 898 cm^{-1}.



2-(1-Fluoro-2-phenylethyl)isoindoline-1,3-dione (30): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-(1,3-dioxoisoindolin-2-yl)-3-phenylpropanoic acid (207 mg, 0.70 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **30** as a white solid (170 mg, 90%).

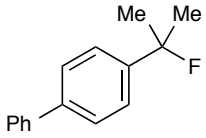
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–7.88 (m, 2 H), 7.78–7.76 (m, 2 H), 7.29–7.22 (m, 5 H), 6.26 (dt, J = 47.3, 7.4 Hz, 1 H), 3.85–3.67 (m, 2 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.9 (2 C), 134.7 (2 C), 131.4, 129.2 (2 C), 128.8 (2 C), 127.2 (2 C), 124.0 (3 C), 90.3 (d, J = 206.0 Hz), 37.5 (d, J = 27.5 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -144.9 (ddd, J = 47.7, 19.7, 9.4 Hz, 1 F);

HRMS (*m/z*): calcd for $C_{16}H_{12}NO_2$ $[(M–HF+H)^{+}]$ 249.07898, found 249.07895;

IR (film): 1784, 1724, 1609, 1495, 1469, 1456, 1363, 1087, 998, 967, 875, 847 cm^{-1}.



4-(2-fluoropropan-2-yl)-1,1'-biphenyl (31): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 2-([1,1'-biphenyl]-4-yl)-2-methylpropanoic acid (168 mg, 0.70 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **31** as a colorless oil (135.0 mg, 90%).

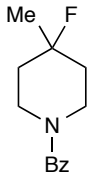
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.55 (m, 4 H), 7.50–7.41 (m, 4 H), 7.37–7.33 (m, 1 H), 1.73 (d, *J* = 21.9 Hz, 6 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 145.0 (d, *J* = 22.1 Hz), 140.9, 140.4, 128.9 (2 C), 127.5, 127.3 (2 C), 127.2 (2 C), 124.4 (d, *J* = 8.8 Hz, 2 C), 95.8 (d, *J* = 168.9 Hz), 29.5 (d, *J* = 25.8 Hz, 2 C);

^{19}F NMR (282 MHz, $CDCl_3$): δ -137.0 (hept, *J* = 22.0 Hz, 1 F);

HRMS-EI (*m/z*) calcd for $C_{15}H_{14}$ $[(M–HF)^{\bullet+}]$ 194.1090, found 194.1094;

IR (film): 3034, 2985, 2937, 1714, 1682, 1600, 1486, 1451, 1402, 1367, 1287, 1203, 1165, 1155, 1155, 1103, 1005, 937 cm^{-1}.



(4-Fluoro-4-methylpiperidin-1-yl)(phenyl)methanone (32): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 1-benzoyl-4-methylpiperidine-

4-carboxylic acid (173.1 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 15 h to obtain **32** as a white solid (111.5 mg, 72%).

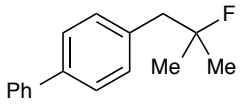
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.40 (m, 5 H), 4.55–4.52 (m, 1 H), 3.62–3.59 (m, 1 H), 3.40–3.34 (m, 1 H), 3.20–3.15 (m, 1 H), 1.99–1.96 (m, 1 H), 1.81–1.78 (m, 1 H), 1.69–1.54 (m, 2 H), 1.41 (d, *J* = 21.5 Hz, 3 H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.4, 135.9, 129.6, 128.5 (2 C), 126.8 (2 C), 92.3 (d, *J* = 168.8 Hz), 43.7, 38.2, 36.5 (dd, *J* = 122.9, 21.1 Hz, 2 C), 27.0 (d, *J* = 24.1 Hz);

^{19}F NMR (282 MHz, $CDCl_3$): δ -153.55 – -153.96 (m, 1 F);

HRMS (*m/z*): calcd for $C_{13}H_{17}FNO$ $[(M+H)^+]$ 222.1294, found 222.1293;

IR (film): 2935, 1632, 1435, 1290, 1264, 1149, 1114, 968, 709 cm^{-1}.



4-(2-Fluoro-2-methylpropyl)-1,1'-biphenyl (33): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 3-([1,1'-biphenyl]-4-yl)-2,2-dimethylpropanoic acid (178.0 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (496 mg, 1.40 mmol, 2 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 1 h to obtain **33** as a colorless oil (140.6 mg, 88%).

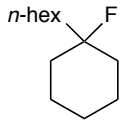
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2 H), 7.56–7.51 (m, 2 H), 7.45–7.40 (m, 2 H), 7.36–7.31 (m, 1 H), 7.31–7.27 (m, 2 H), 2.95 (d, *J* = 20.5 Hz, 2 H), 1.38 (d, *J* = 21.3 Hz, 6 H);

^{13}C NMR (125 MHz, CDCl3): δ 140.9, 139.4, 136.1 (d, *J* = 3.9 Hz), 130.8 (2 C), 128.7 (2 C), 127.1, 127.0 (2 C), 126.8 (2 C), 95.3 (d, J = 168.0 Hz), 47.2 (d, J = 22.9 Hz), 26.7 (d, J = 24.4 Hz, 2 C);

^{19}F NMR (282 MHz, CDCl3): δ -137.0 (hept, *J* = 21.2 Hz, 1 F);

HRMS (m/z): calcd for $C_{16}H_{16}$ $[(M–HF)^{\bullet+}]$ 209.1332, found 209.1325;

IR (film): 3032, 2980, 2918, 1487, 1408, 1372, 1225, 1185, 1130 cm^{-1}.



1-Fluoro-1-hexylcyclohexane (34): According to the general procedure for the photoredox-catalyzed decarboxylative fluorination, a mixture of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (7.8 mg, 7.0 μmol, 1 mol%), 1-hexylcyclohexane-1-carboxylic acid (148.6 mg, 0.7000 mmol, 1 equiv.), Na_2HPO_4 (199 mg, 1.40 mmol, 2 equiv.), and Selectfluor® (744 mg, 2.10 mmol, 3 equiv.) in acetonitrile/water (7.0 mL, 1:1 v/v) was irradiated for 15 h to obtain **34** as a colorless oil (103.0 mg, 79%).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.80–1.76 (m, 2 H), 1.63–1.28 (m, 18 H), 0.94–0.87 (m, 3 H);

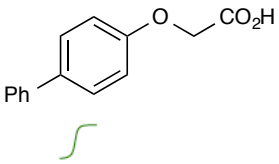
^{13}C NMR (125 MHz, CD_2Cl_2): δ 40.4, 40.2, 35.2, 35.0, 31.9, 29.8, 25.5, 22.9 (d, *J* = 4.5 Hz), 22.7, 22.2 (d, *J* = 3.6 Hz);

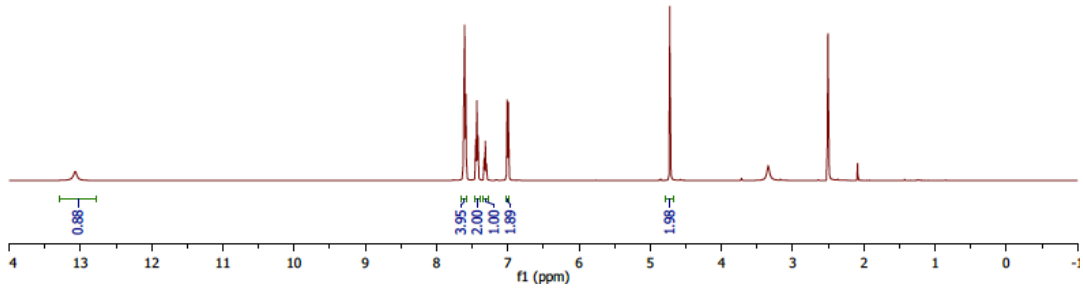
^{19}F NMR (282 MHz, CD_2Cl_2): δ -155.4 (s, 1 F);

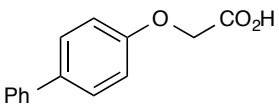
HRMS (*m/z*): calcd for $C_{12}H_{23}$ $[(M–F)^{\bullet+}]$ 167.1800, found 167.1794;

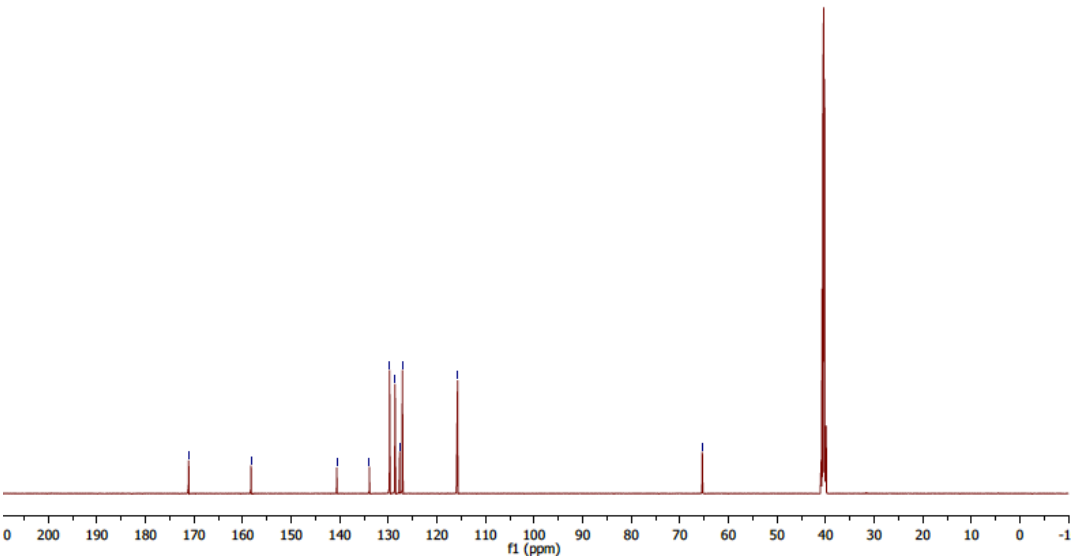
IR (film): 2932, 2859, 1449, 1375, 1149, 960, 928, 829 cm^{-1}.

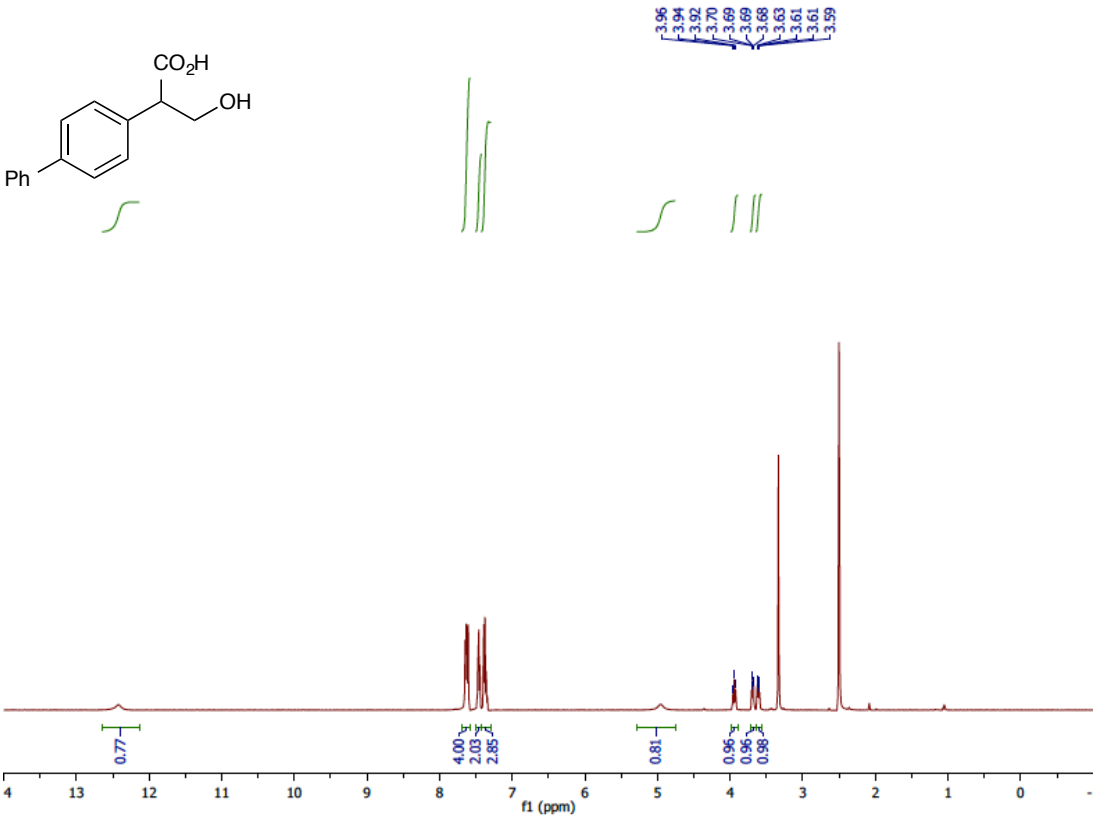
4. Spectral Data

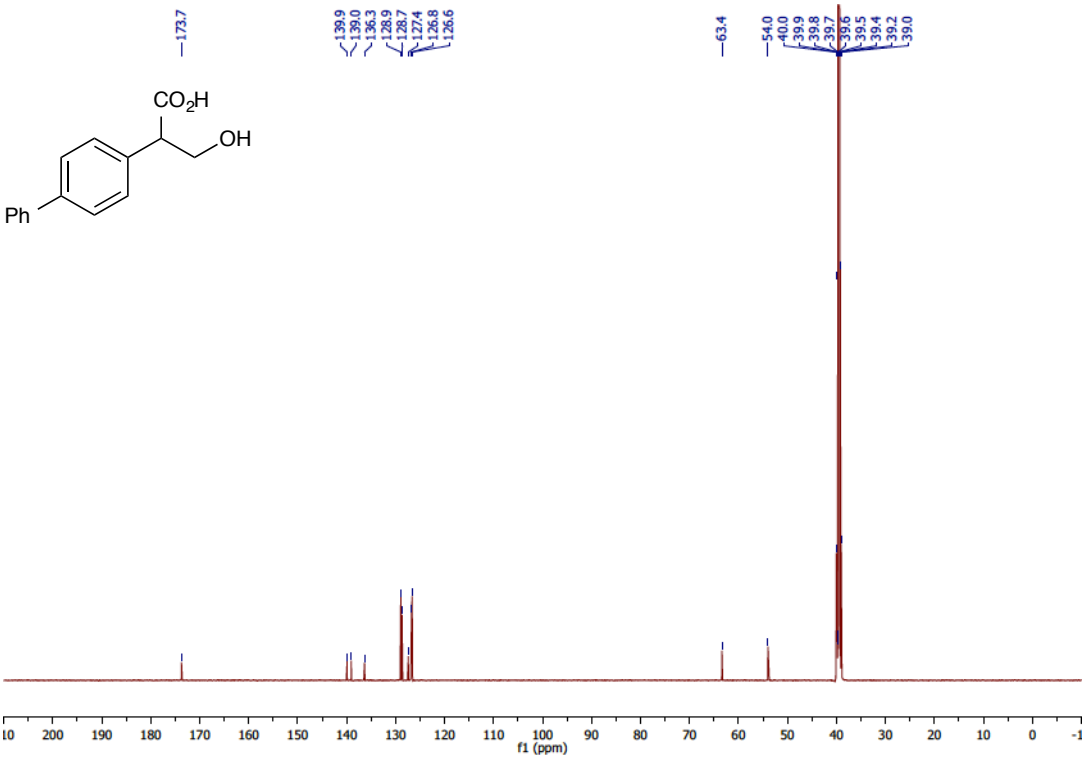


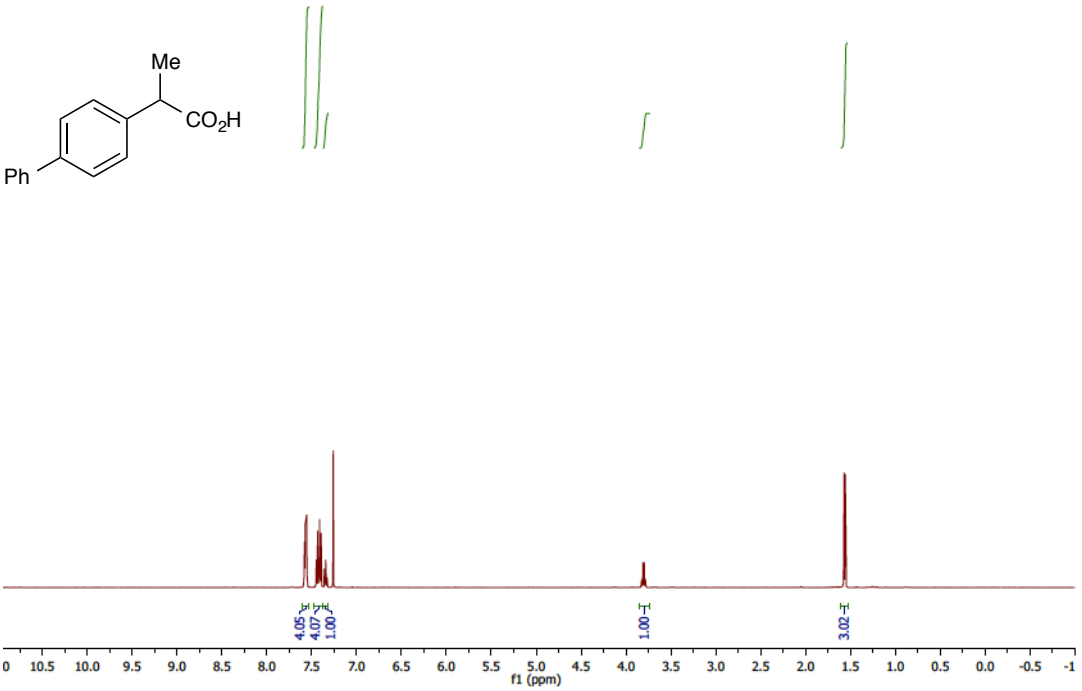


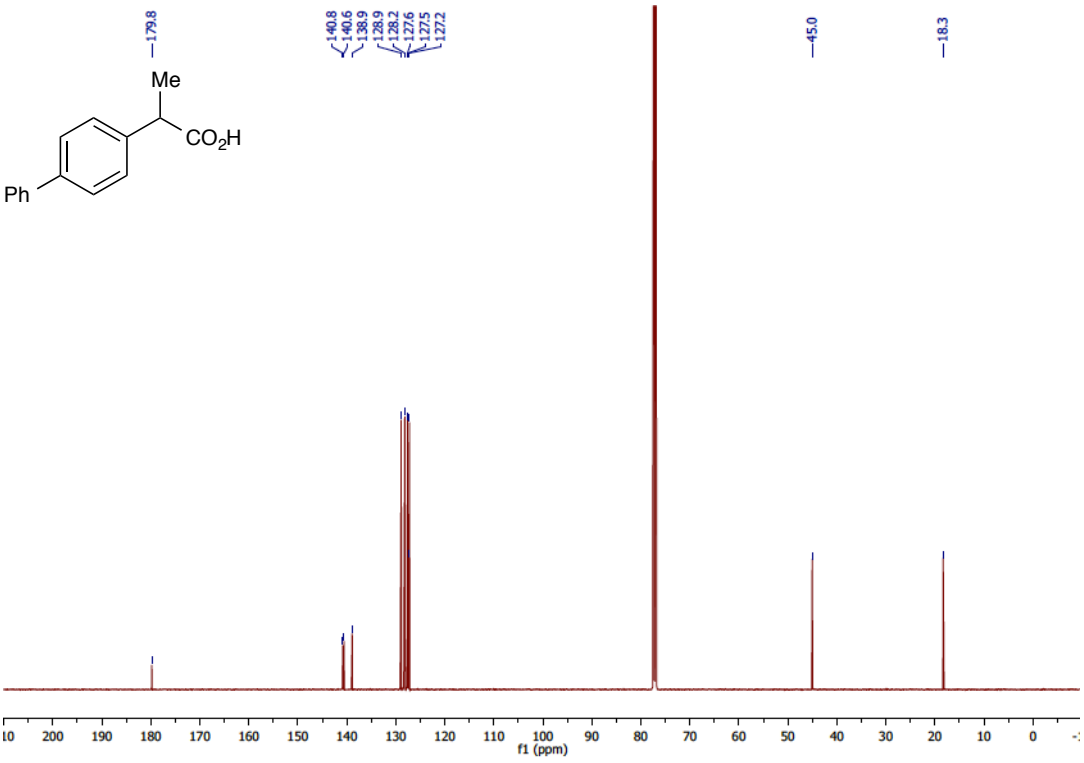


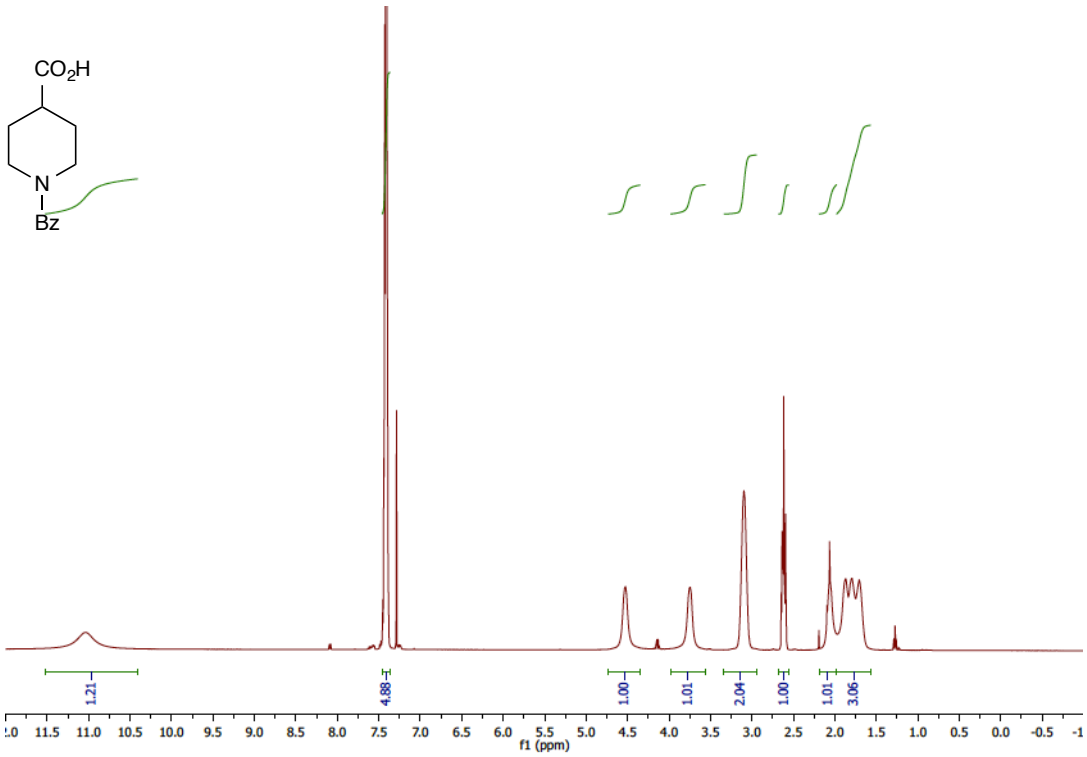



CO2H
OH
Ph
3.96
3.94
3.92
3.70
3.69
3.69
3.68
3.63
3.61
3.61
3.59
0.77
4.00
2.03
2.85
0.81
0.96
0.96
0.98
f1 (ppm)

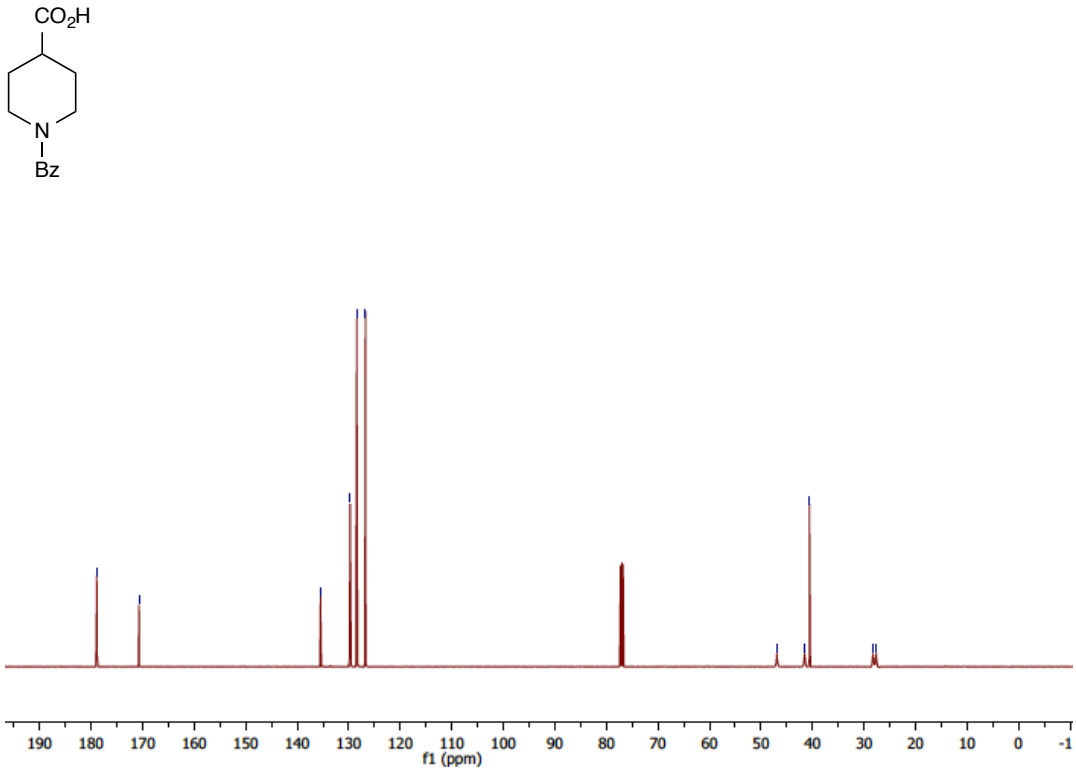

173.7
139.9
139.0
136.3
128.9
128.7
127.4
126.8
126.6
63.4
54.0
40.0
39.9
39.8
39.7
39.6
39.5
39.4
39.2
39.0
CO2H
OH
Ph
f1 (ppm)

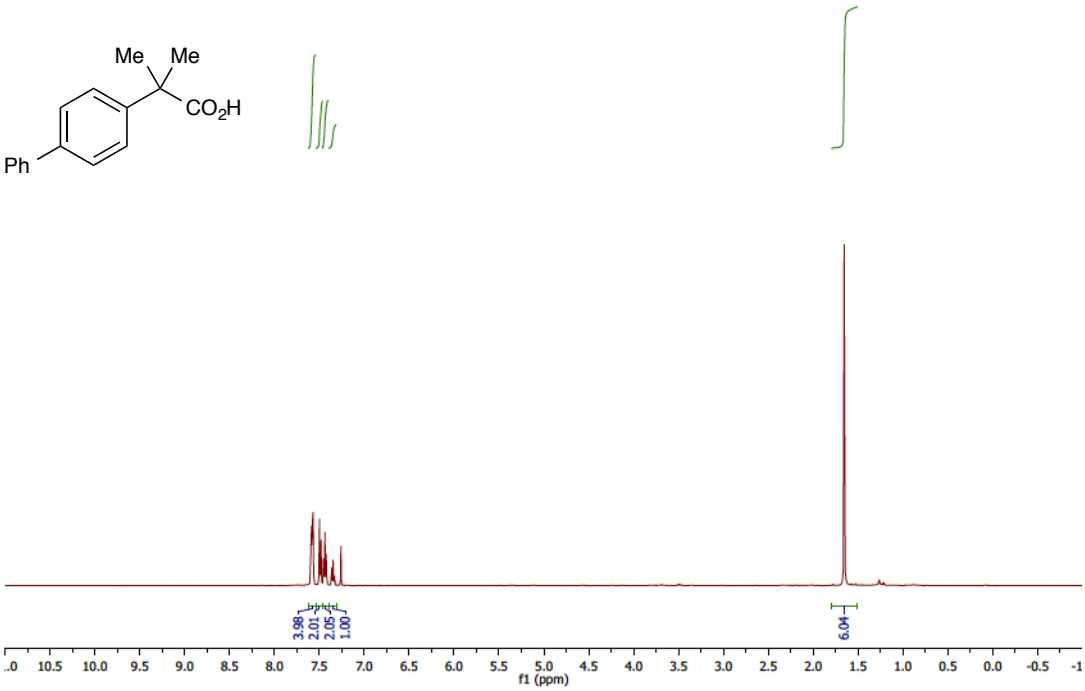

Me
CO2H
Ph
4.05
4.07
1.00
1.00
3.02
f1 (ppm)

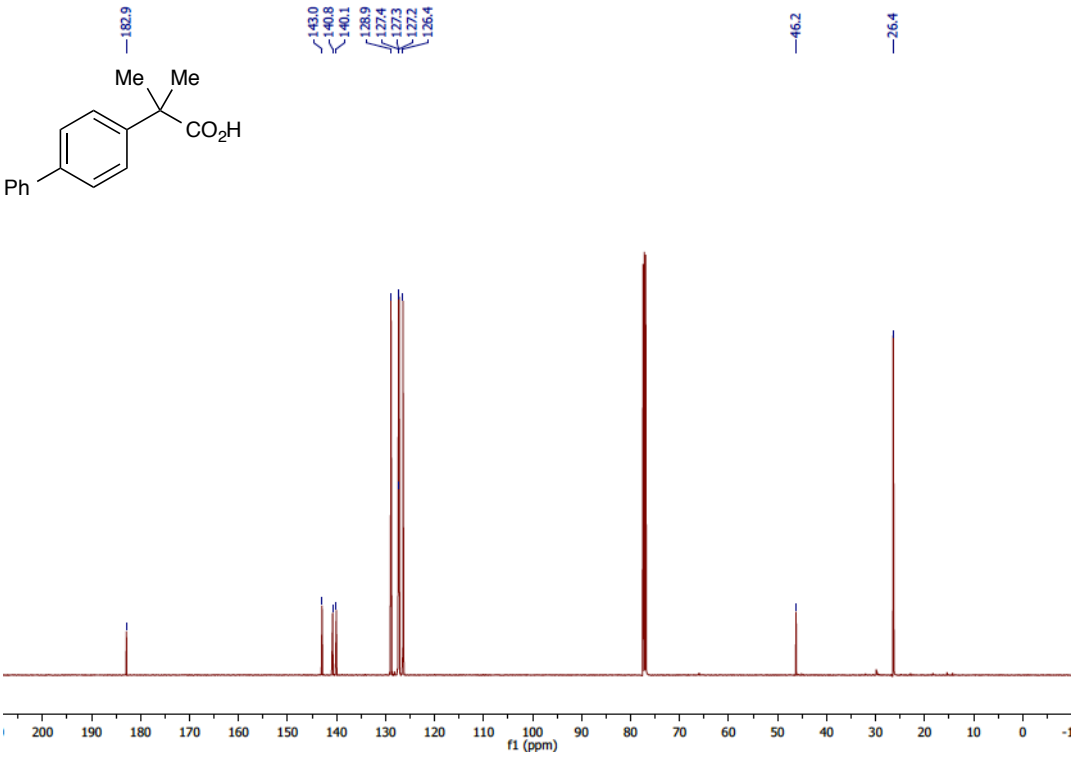

179.8
140.8
140.6
138.9
128.9
128.2
127.6
127.5
127.2
45.0
18.3
Me
CO2H
Ph
f1 (ppm)

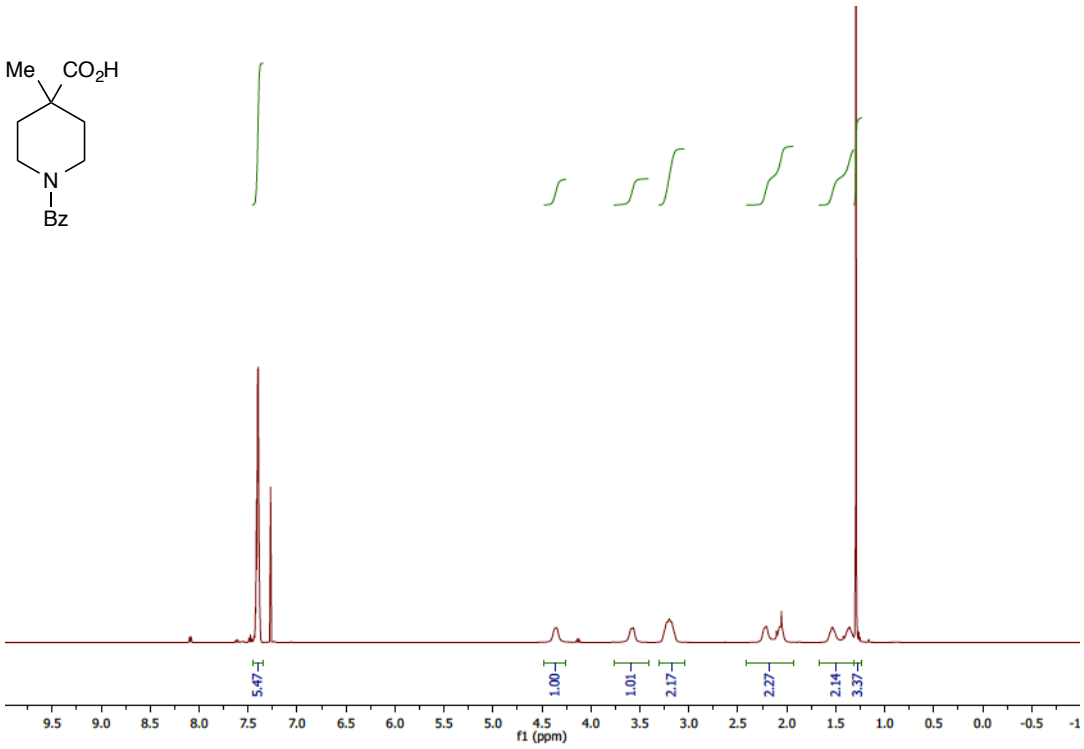

CO2H
N
Bz
1.21
4.88
1.00
1.01
2.04
1.00
1.01
3.06
f1 (ppm)

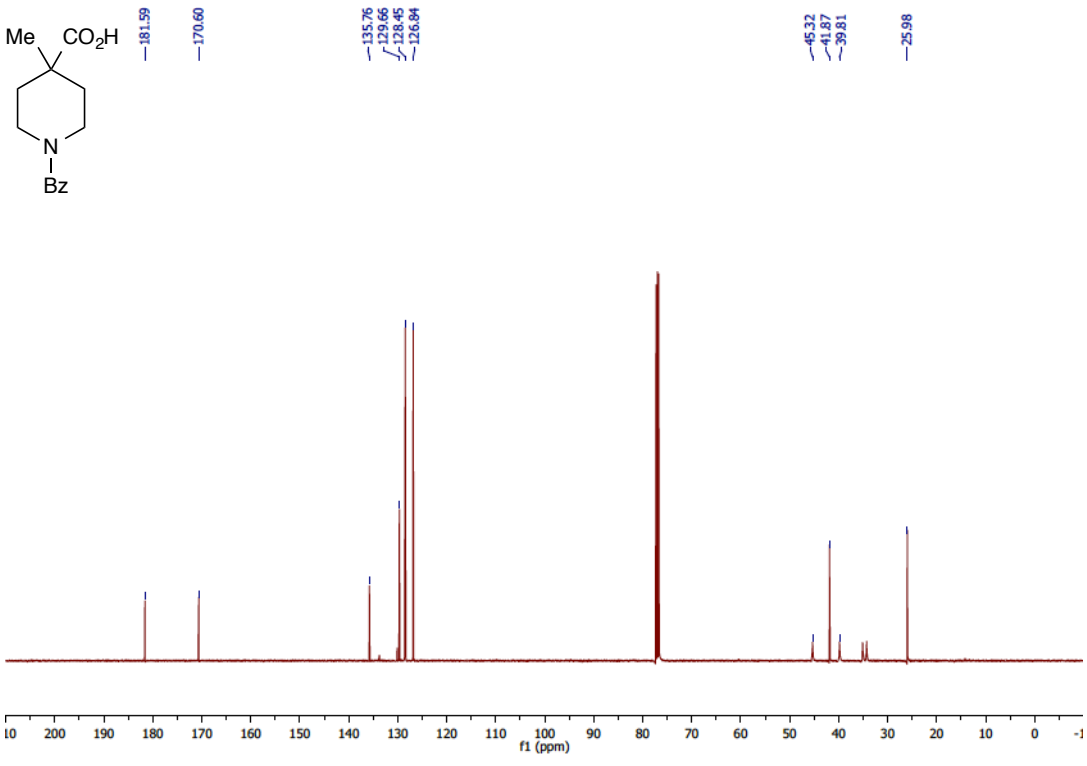

178.90
170.71
135.48
129.73
128.45
126.77
46.90
41.51
40.59
28.24
27.64

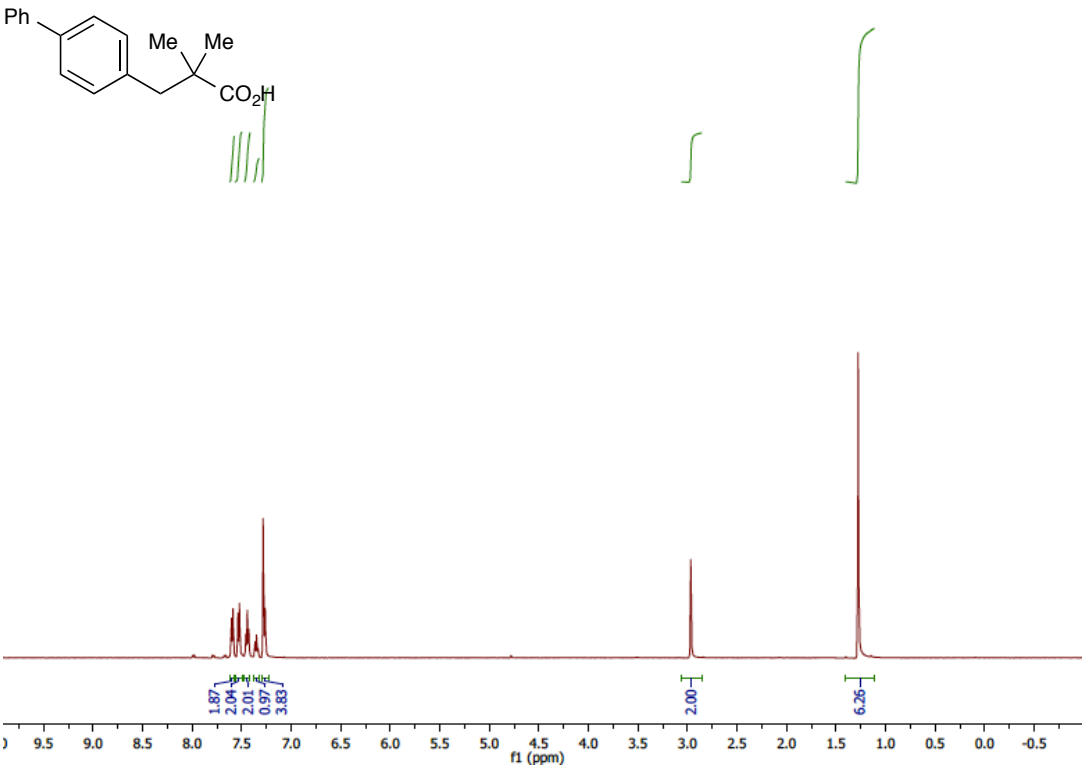

CO2H
N
Bz
f1 (ppm)

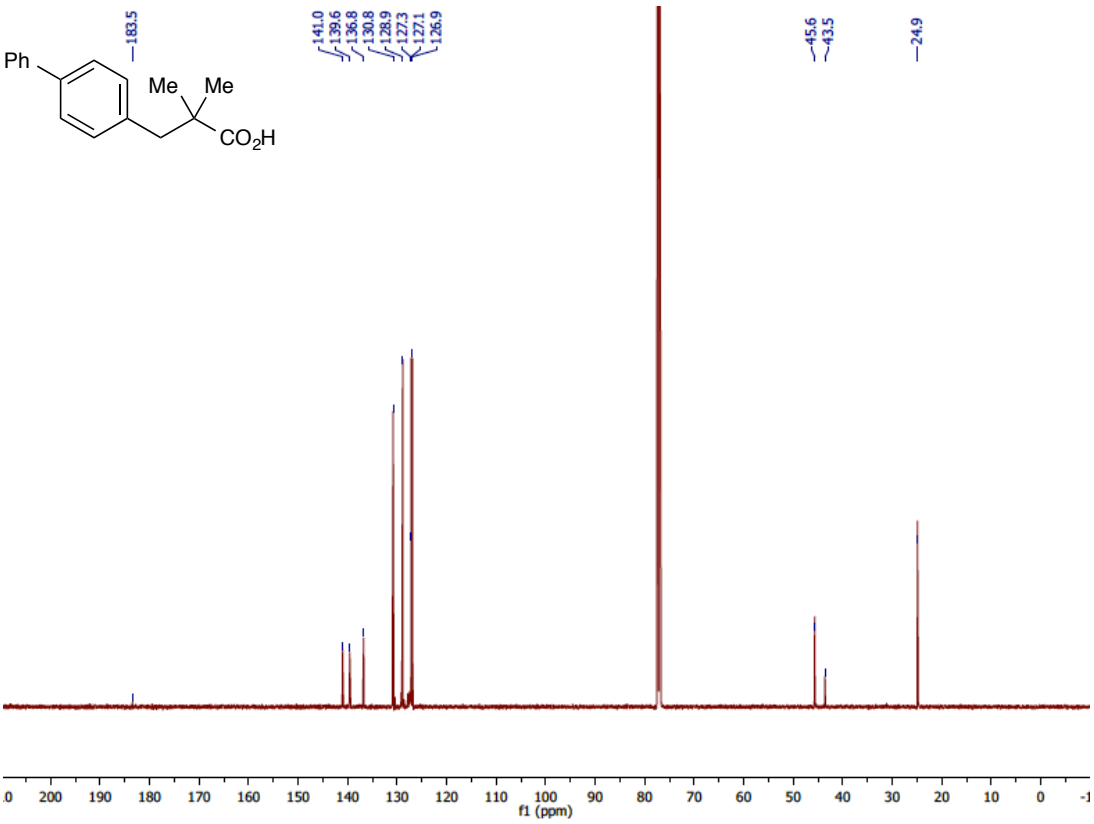

Me
Me
CO2H
Ph
3.98
2.01
2.05
1.00
6.04
f1 (ppm)

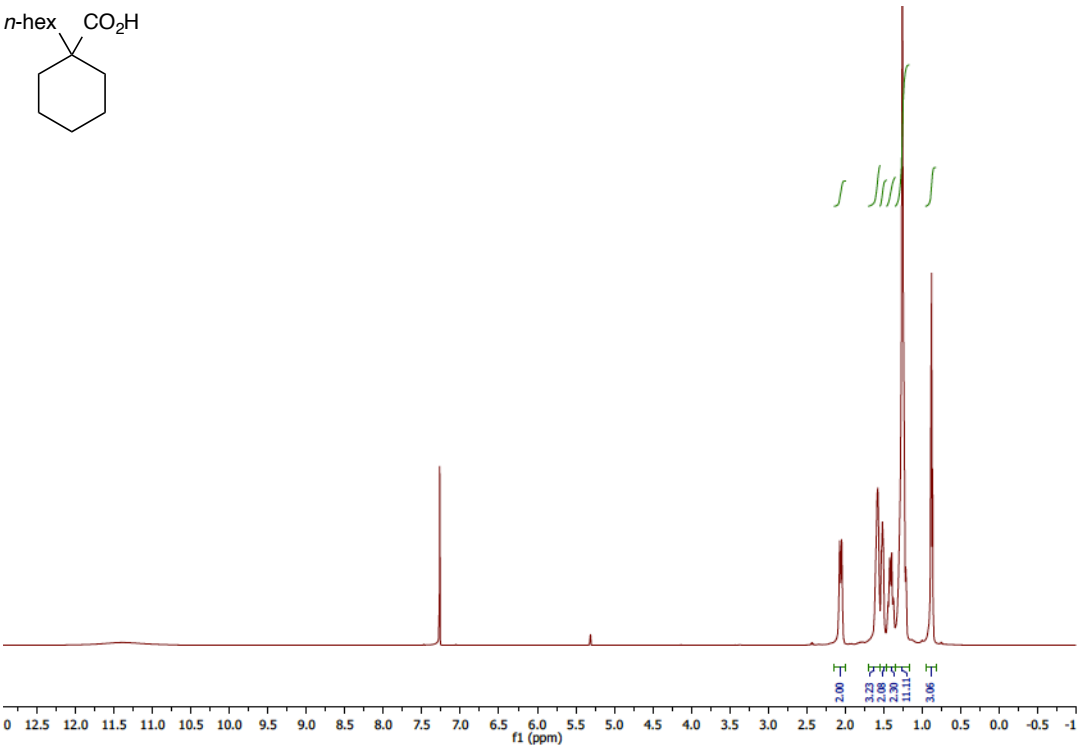

182.9
143.0
140.8
140.1
128.9
127.4
127.3
127.2
126.4
46.2
26.4
Me
Me
CO2H
Ph
f1 (ppm)

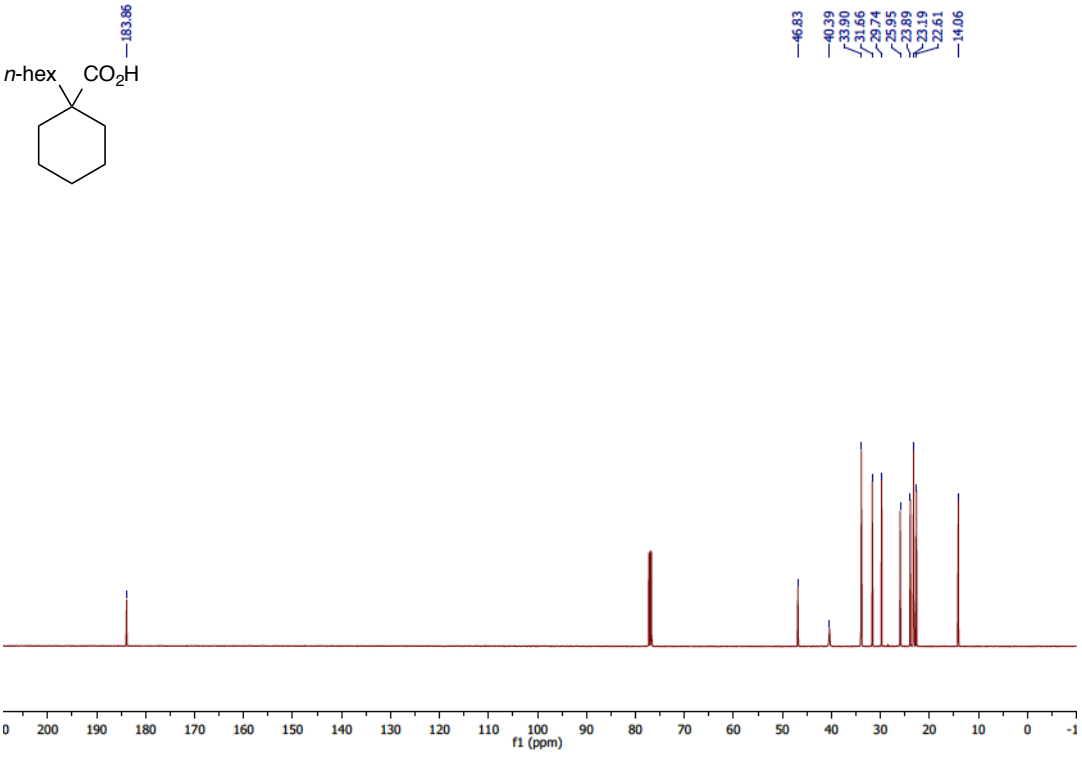

Me
CO2H
N
Bz
5.47
1.00
1.01
2.17
2.27
2.14
3.37
f1 (ppm)

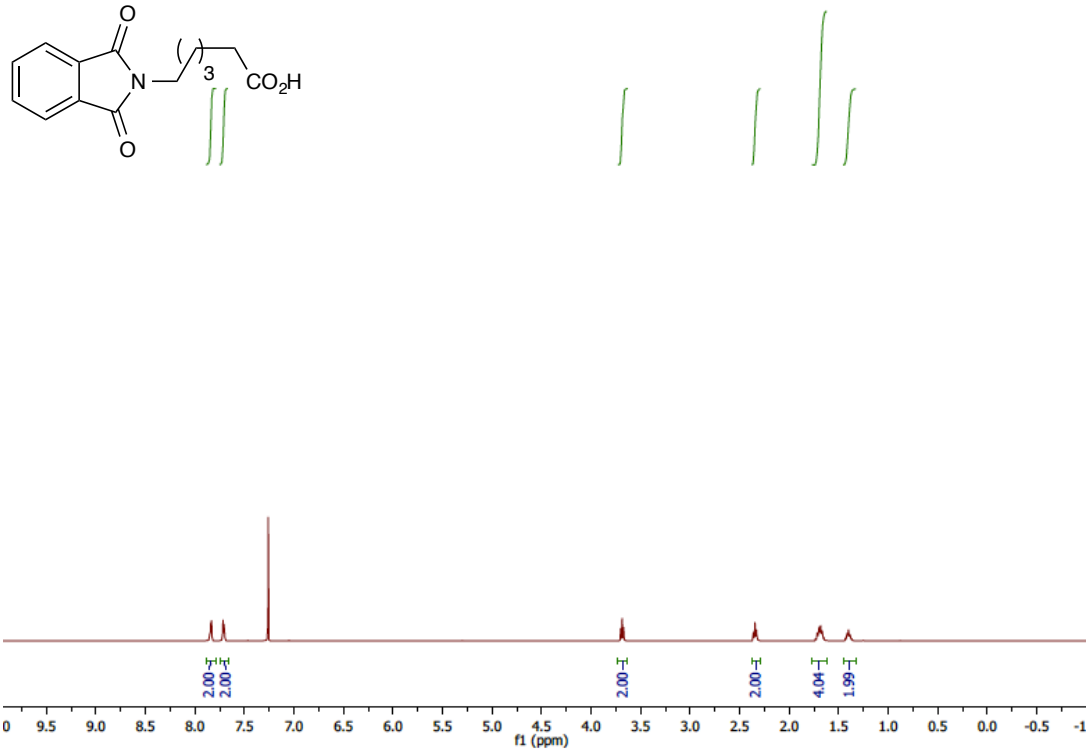

Me
CO2H
N
Bz
181.59
170.60
135.76
129.66
128.45
126.84
45.32
41.87
39.81
25.98
f1 (ppm)

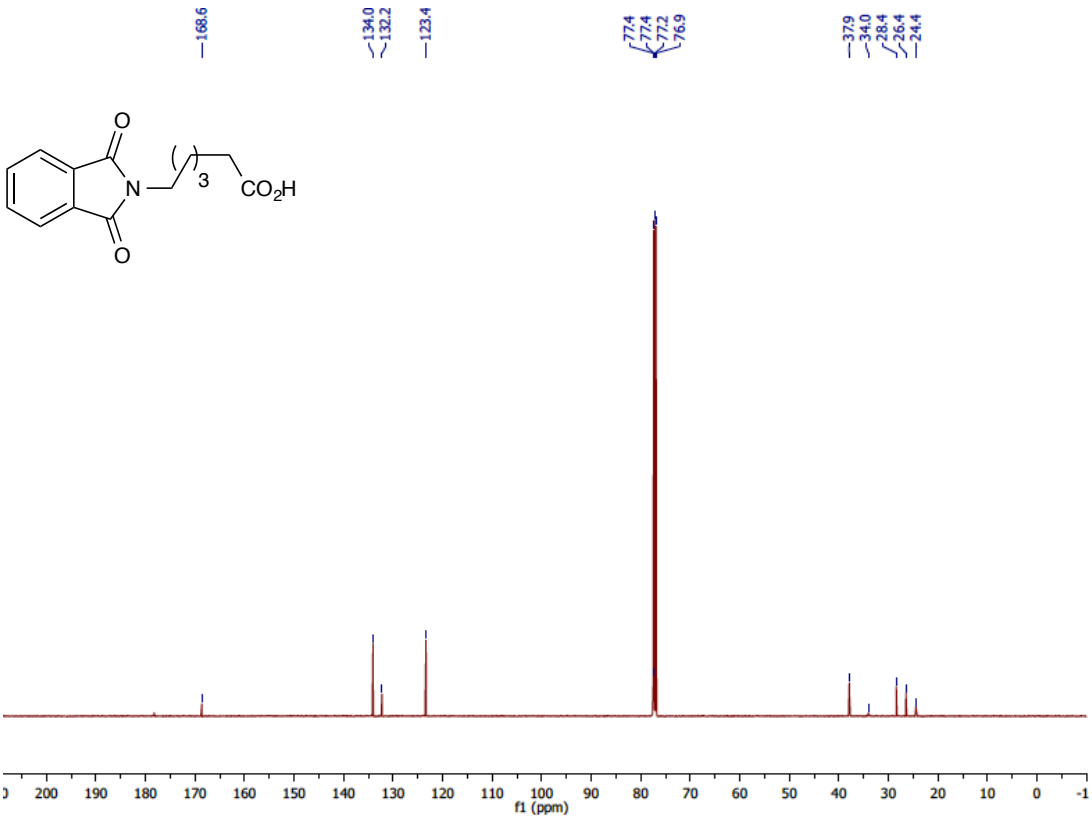

Ph
Me
Me
CO2H
1.87
2.04
2.01
0.97
3.83
2.00
6.26
f1 (ppm)

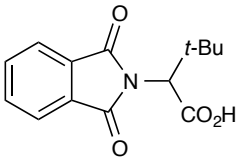

Ph
Me
Me
CO2H
183.5
141.0
139.6
136.8
130.8
128.9
127.3
127.1
126.9
45.6
43.5
24.9
f1 (ppm)


n-hex
CO2H
2.00
3.23
2.08
2.30
11.11
3.06
f1 (ppm)

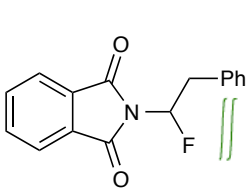

183.86
n-hex
CO2H
46.83
40.39
33.90
31.66
29.74
25.95
23.89
23.19
22.61
14.06
f1 (ppm)

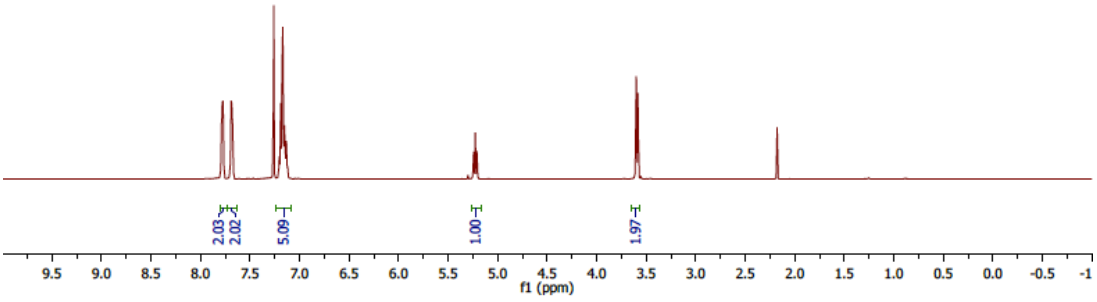

O
N
3
CO2H
O
2.00
2.00
2.00
2.00
4.04
1.99
f1 (ppm)

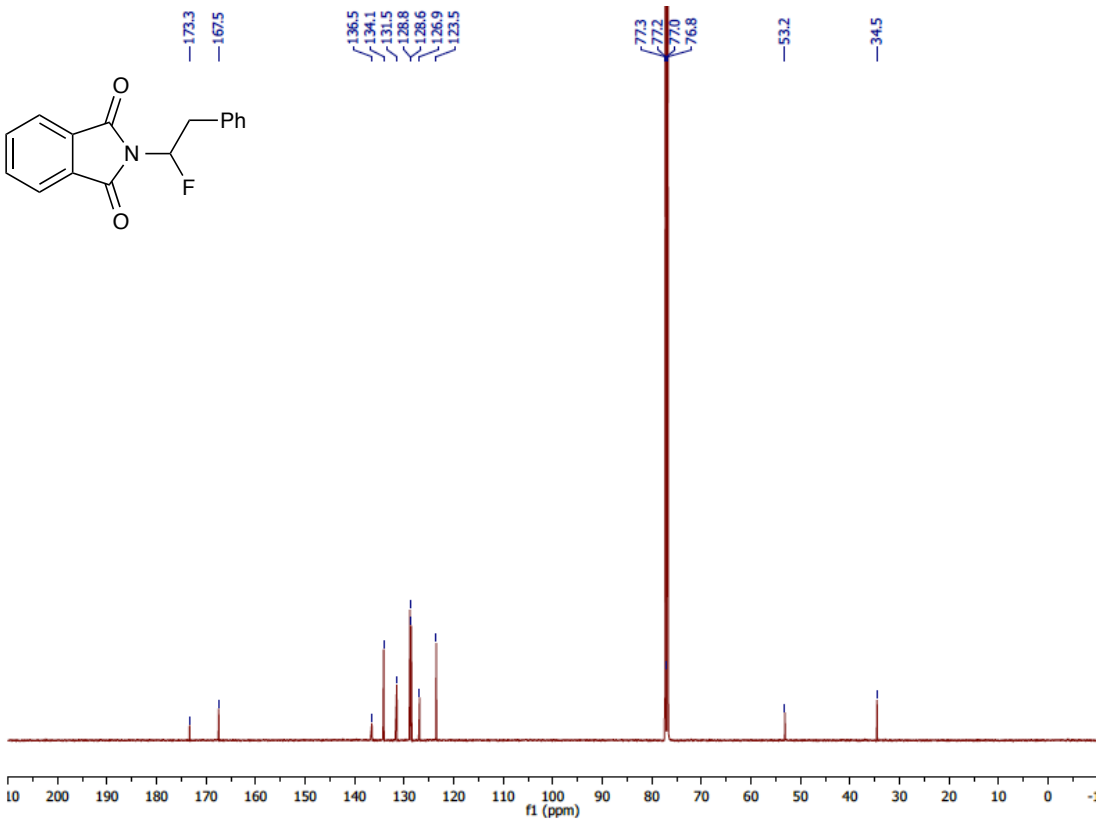

168.6
134.0
132.2
123.4
77.4
77.4
77.2
76.9
37.9
34.0
28.4
26.4
24.4
O
N
3
CO2H
O
f1 (ppm)

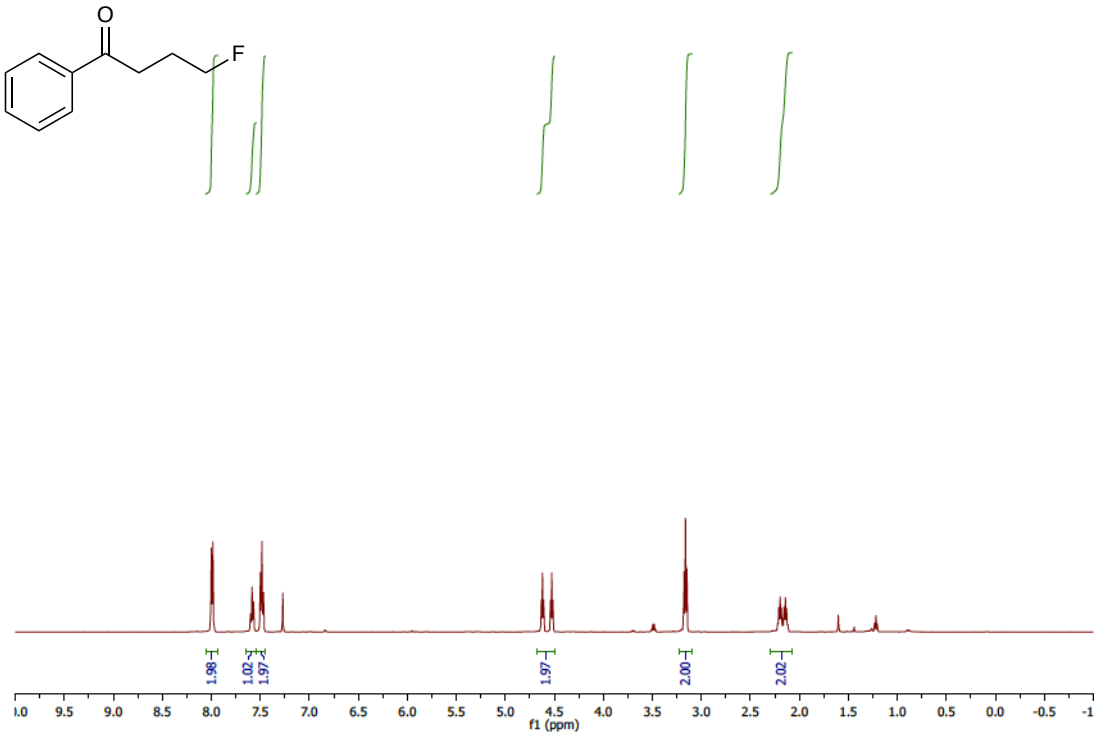

O
t-Bu
N
CO2H
O

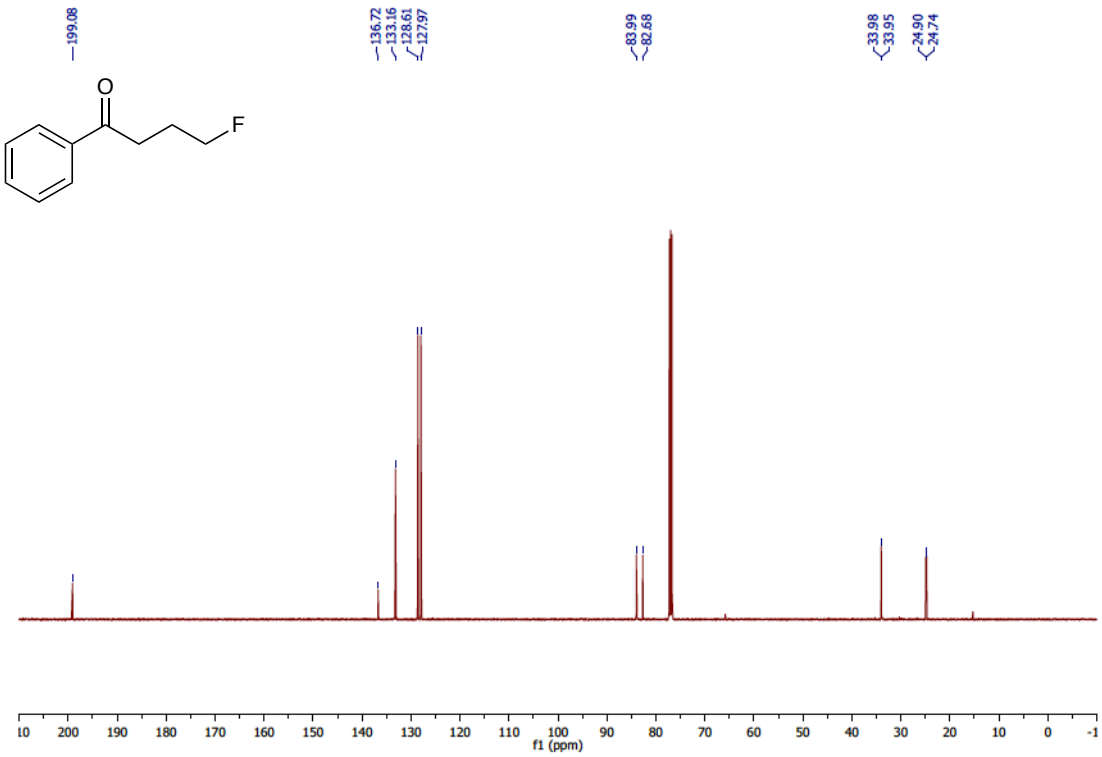
2.09
2.10
1.00
9.20
f1 (ppm)

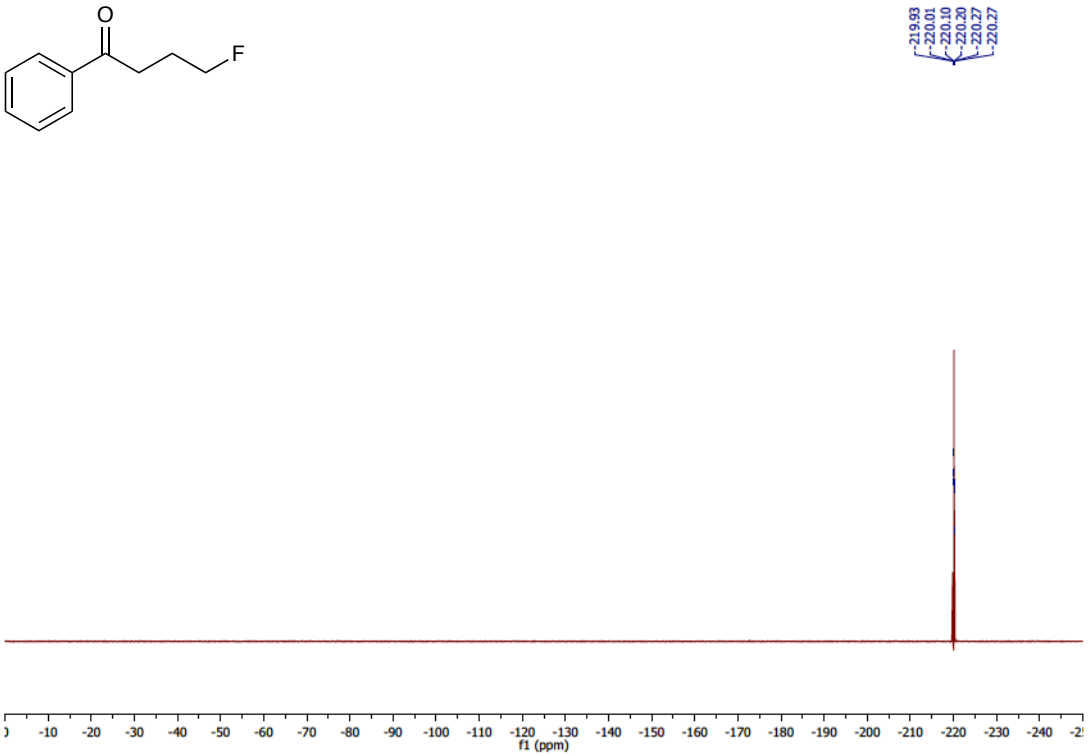

O
Ph
N
F
O

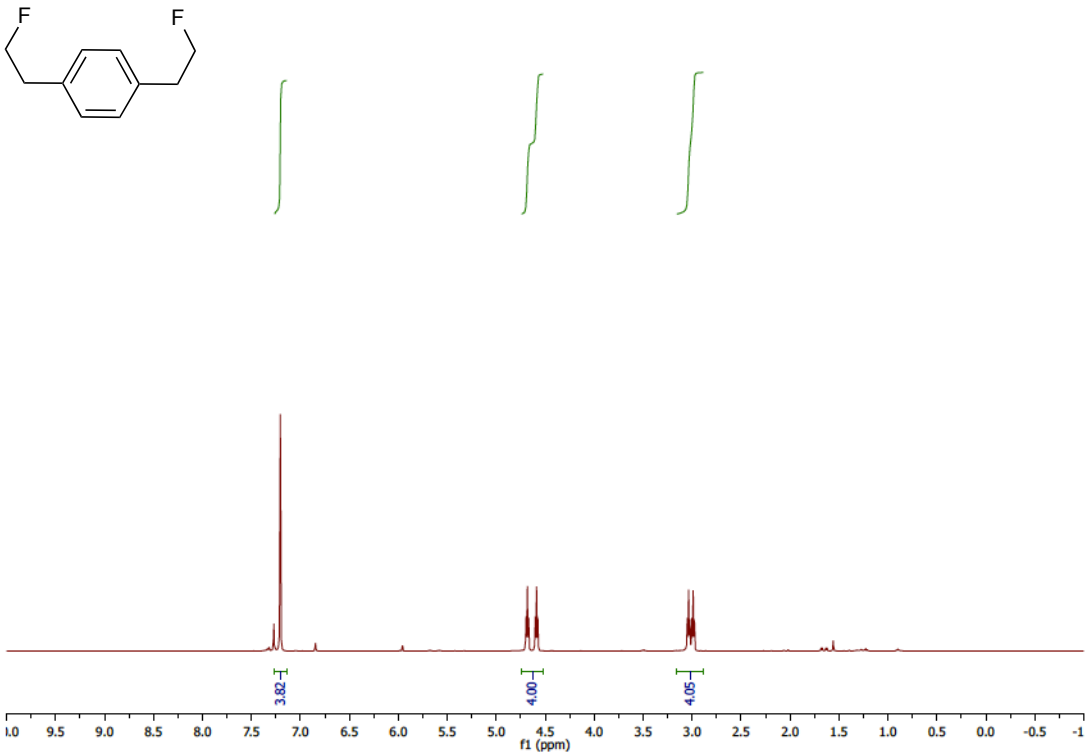

2.03
2.02
5.09
1.00
1.97
f1 (ppm)

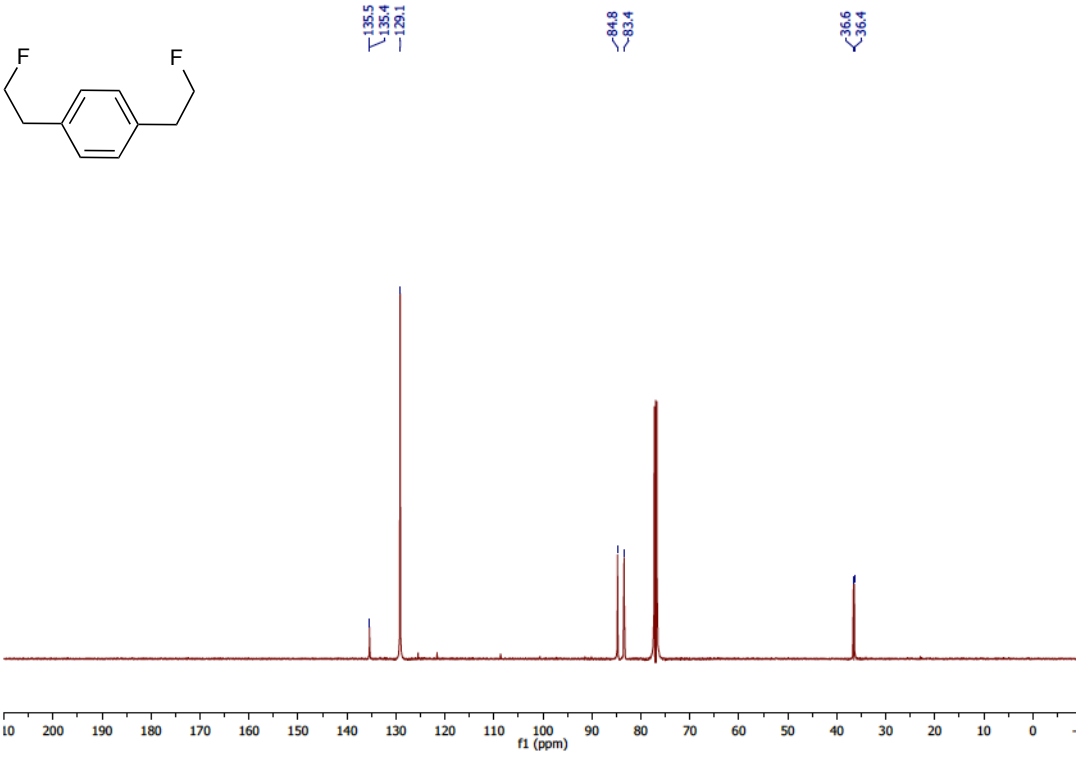

173.3
167.5
136.5
134.1
131.5
128.8
128.6
126.9
123.5
77.3
77.2
77.0
76.8
53.2
34.5
O
N
Ph
F
O
f1 (ppm)

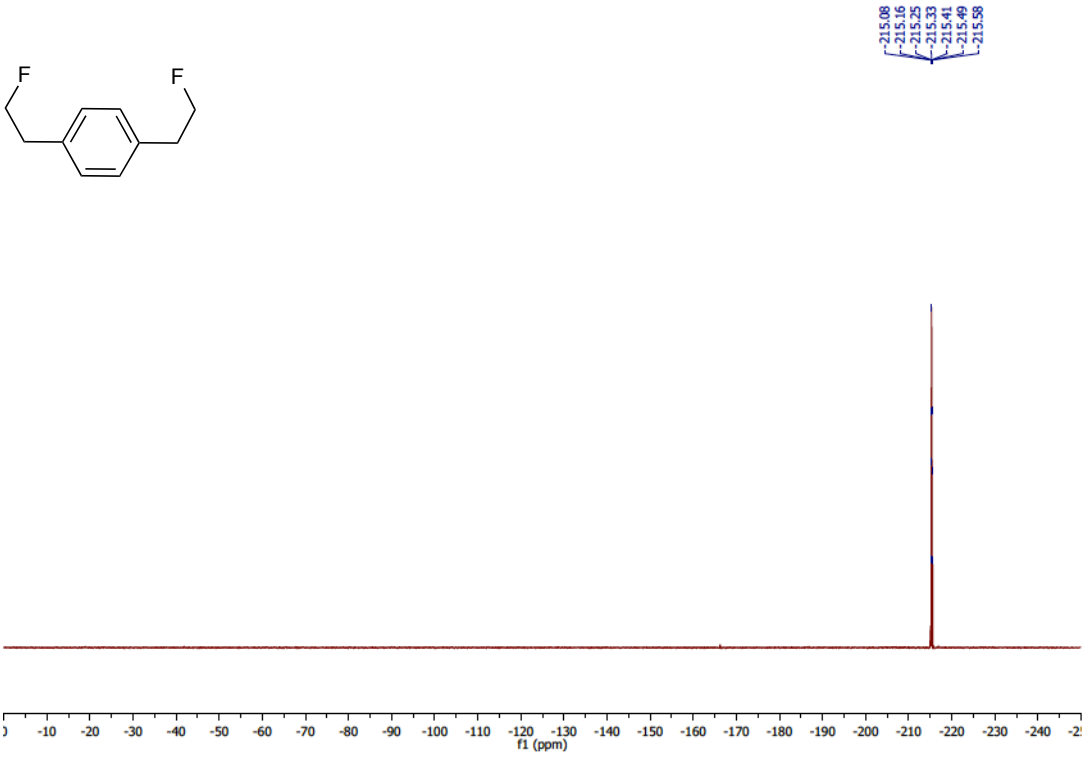

O
F
1.98
1.02
1.97
1.97
2.00
2.02
f1 (ppm)

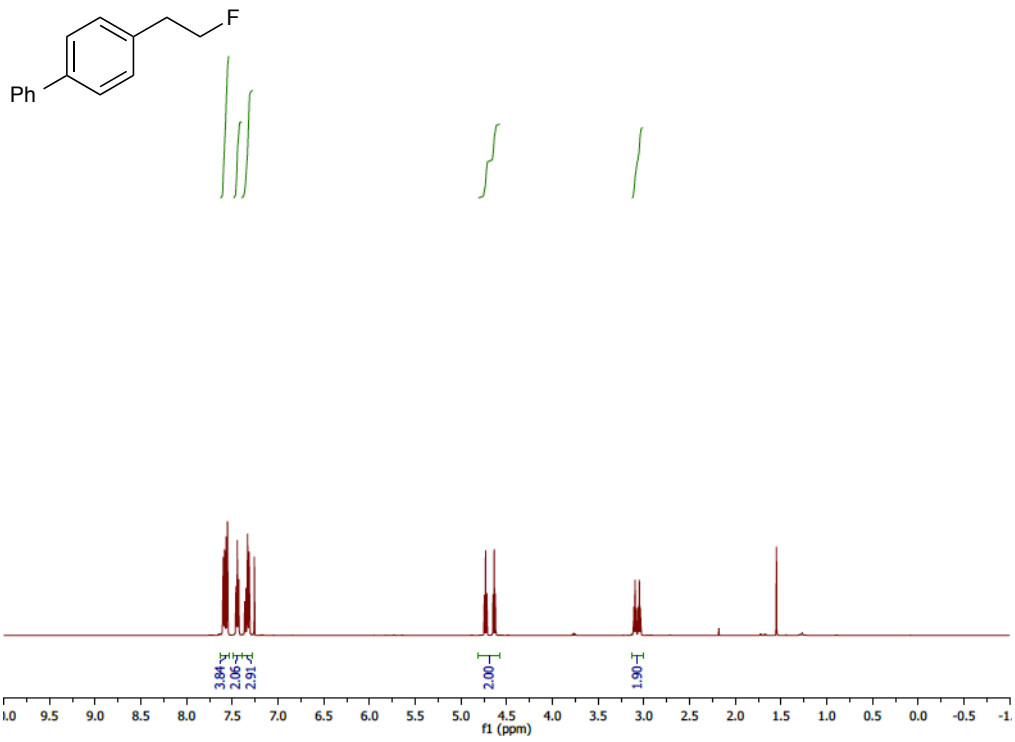

199.08
136.72
133.16
128.61
127.97
83.99
82.68
33.98
33.95
24.90
24.74
O
F
f1 (ppm)

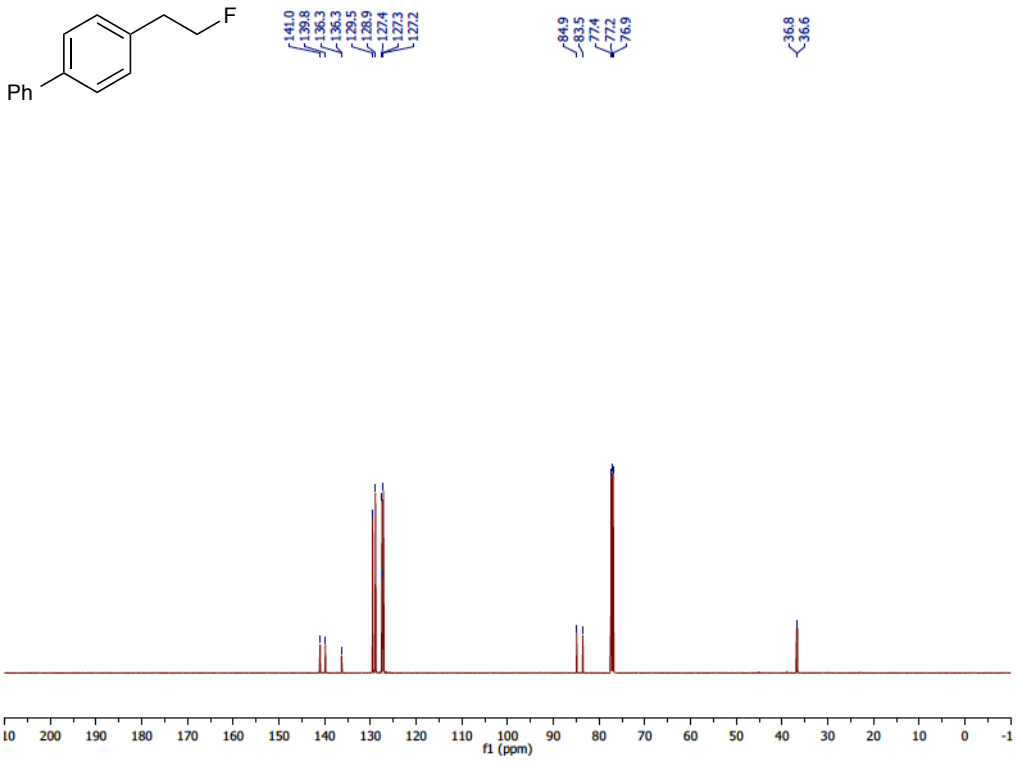

219.93
220.01
220.10
220.20
220.27
220.27
O
F
f1 (ppm)

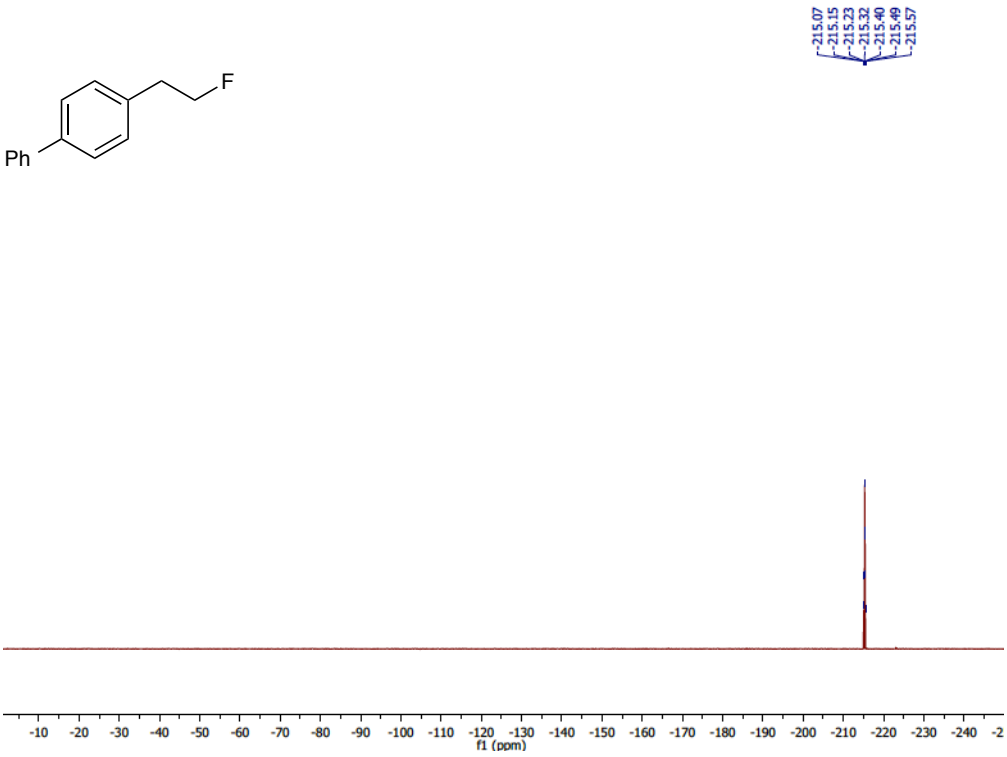

F
F
3.82
4.00
4.05
f1 (ppm)

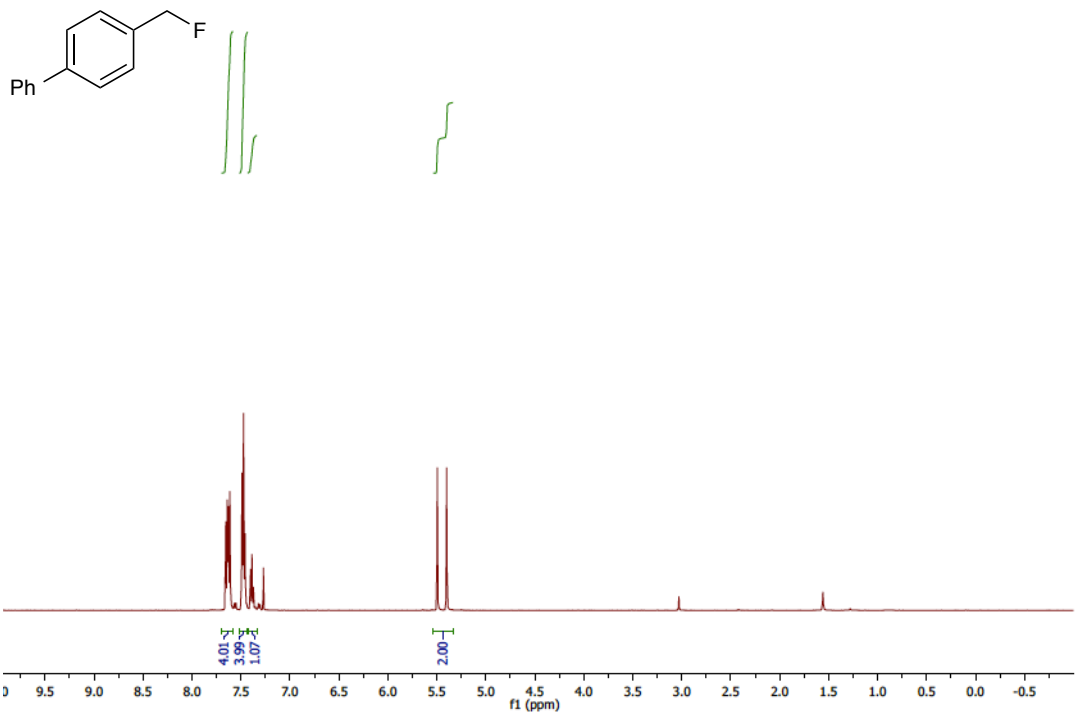

F
F
135.5
135.4
129.1
84.8
83.4
36.6
36.4
f1 (ppm)

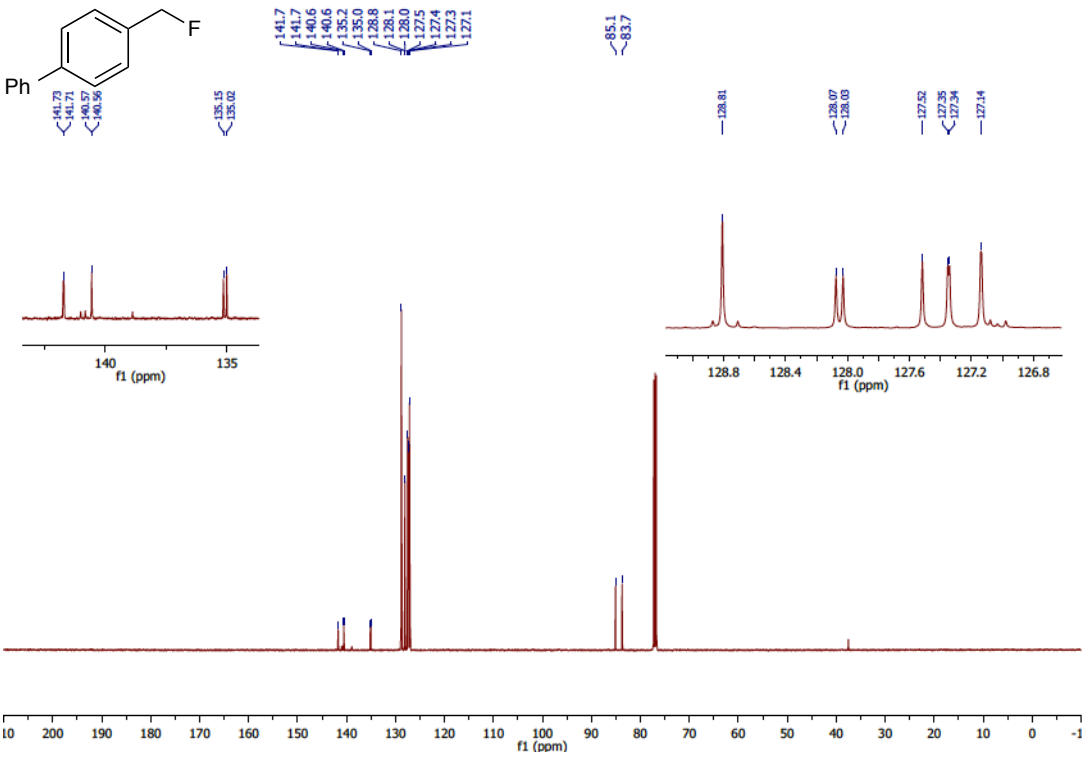

F
F
-215.08
-215.16
-215.25
-215.33
-215.41
-215.49
-215.58
f1 (ppm)

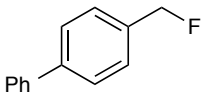

F
Ph
3.94
2.06
2.91
2.00
1.90
f1 (ppm)


F
Ph
141.0
139.8
136.3
136.3
129.5
128.9
127.4
127.3
127.2
84.9
83.5
77.4
77.2
76.9
36.8
36.6
f1 (ppm)

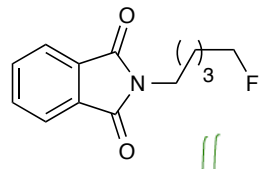

F
Ph
215.07
215.15
215.23
215.32
215.40
215.49
215.57
f1 (ppm)

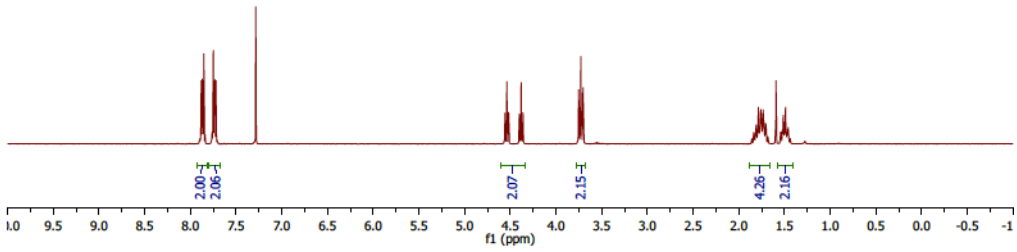

F
Ph
4.01
3.99
1.07
2.00
f1 (ppm)

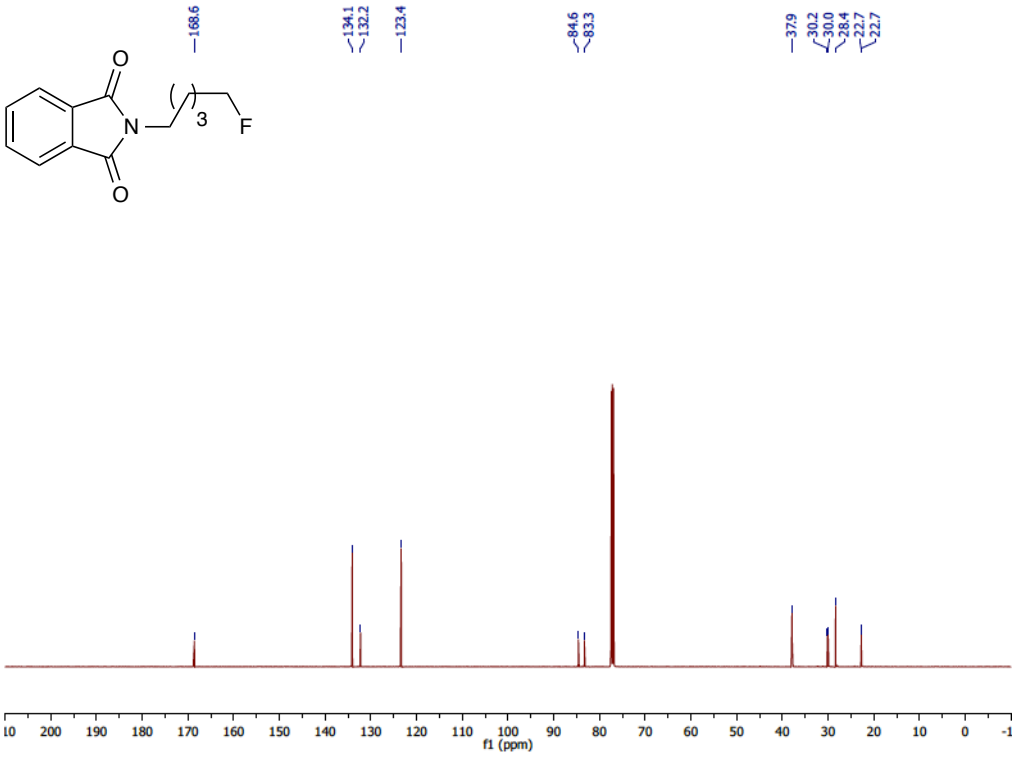

F
Ph
141.7
141.7
140.6
140.6
135.2
135.0
128.8
128.1
128.0
127.5
127.4
127.3
127.1
85.1
83.7
141.73
141.71
140.57
140.56
135.15
135.02
128.81
128.07
128.03
127.52
127.35
127.34
127.14
140
135
f1 (ppm)
128.8
128.4
128.0
127.6
127.2
126.8
f1 (ppm)
f1 (ppm)

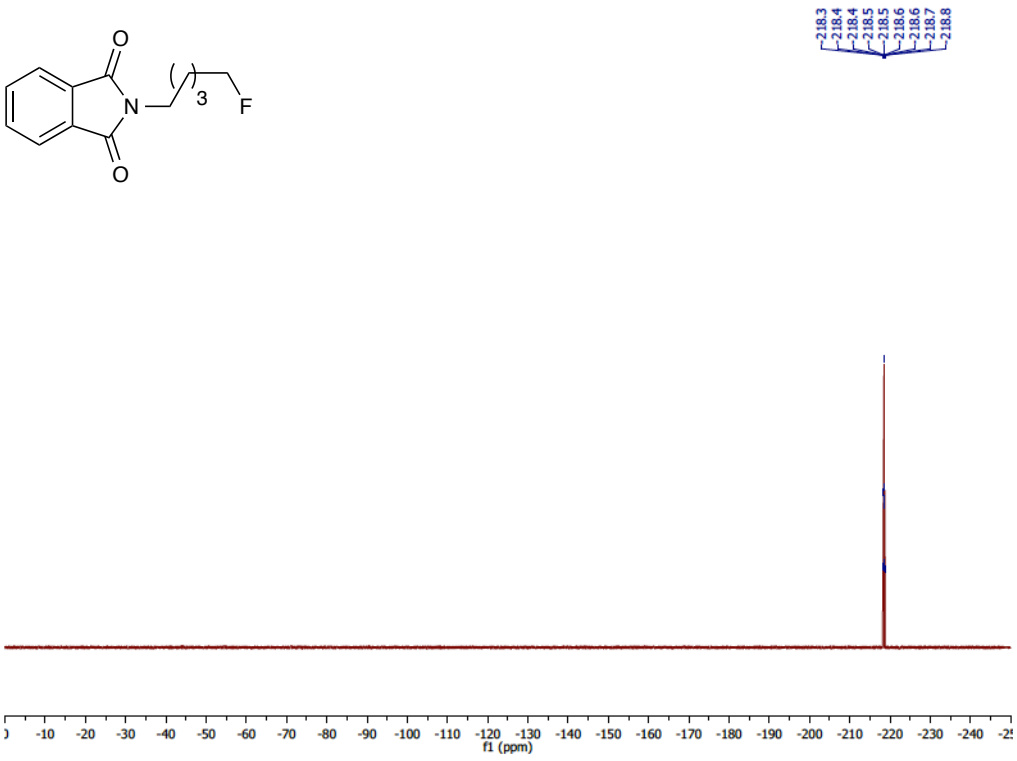

F
Ph

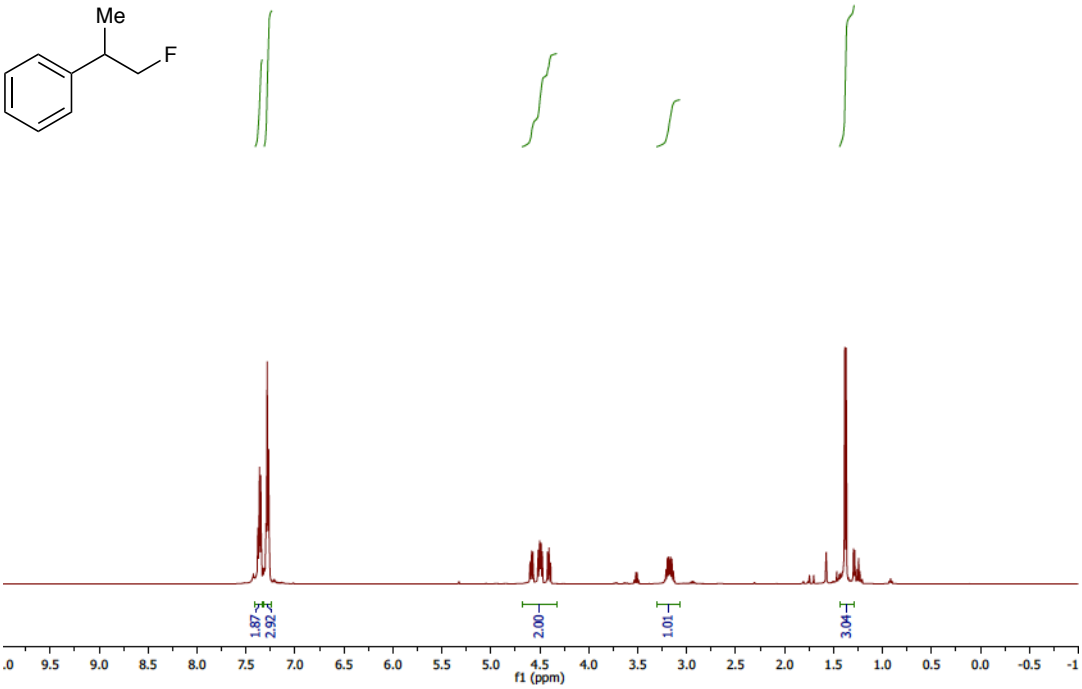
-206.10
-206.27
-206.44
f1 (ppm)

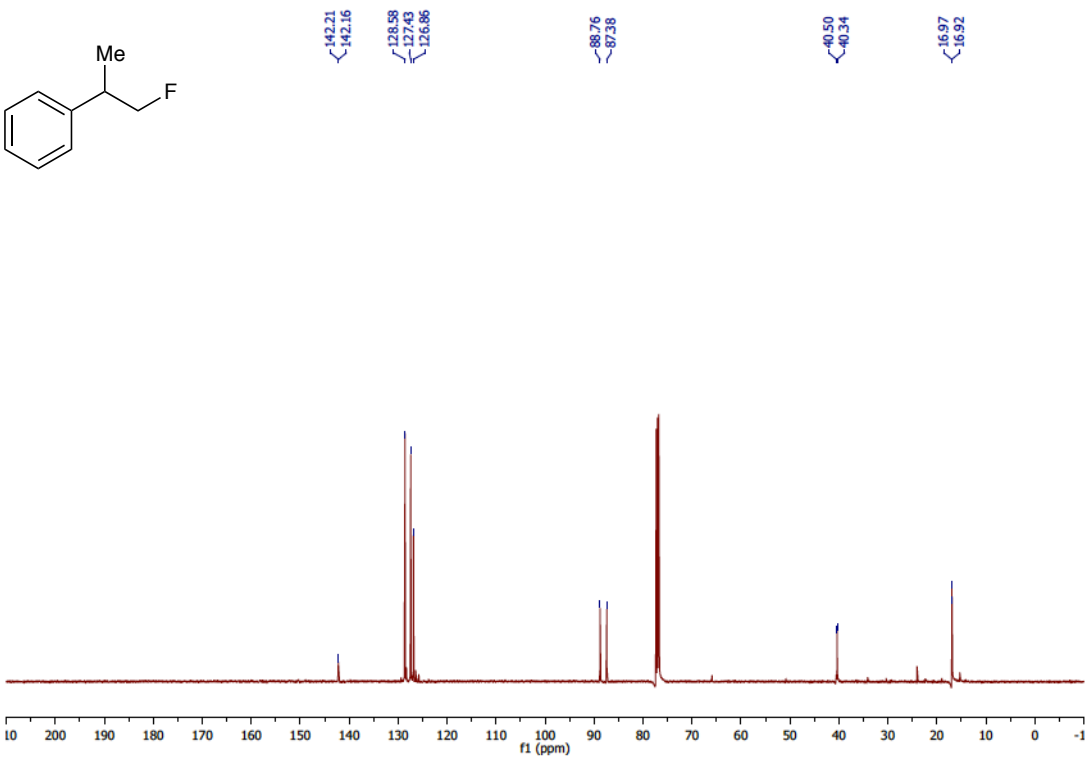

O
N
3
F
O

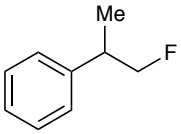

2.00
2.06
2.07
2.15
4.26
2.16
f1 (ppm)


168.6
134.1
132.2
123.4
84.6
83.3
37.9
30.2
30.0
28.4
22.7
22.7
O
N
3
F
O
f1 (ppm)

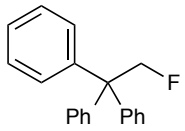

218.3
218.4
218.4
218.5
218.5
218.6
218.6
218.7
218.8
O
N
3
F
O
f1 (ppm)

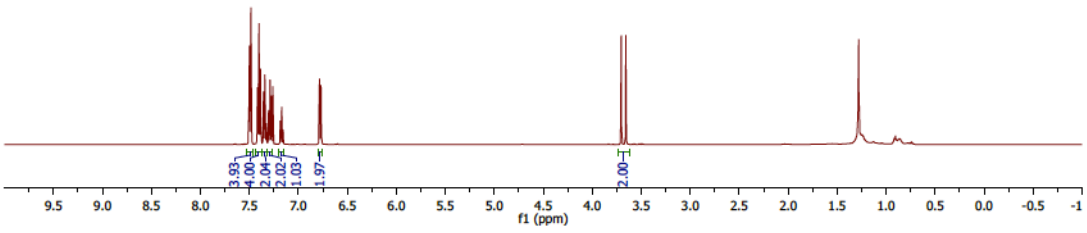

Me
F
1.87
2.92
2.00
1.01
3.04
f1 (ppm)

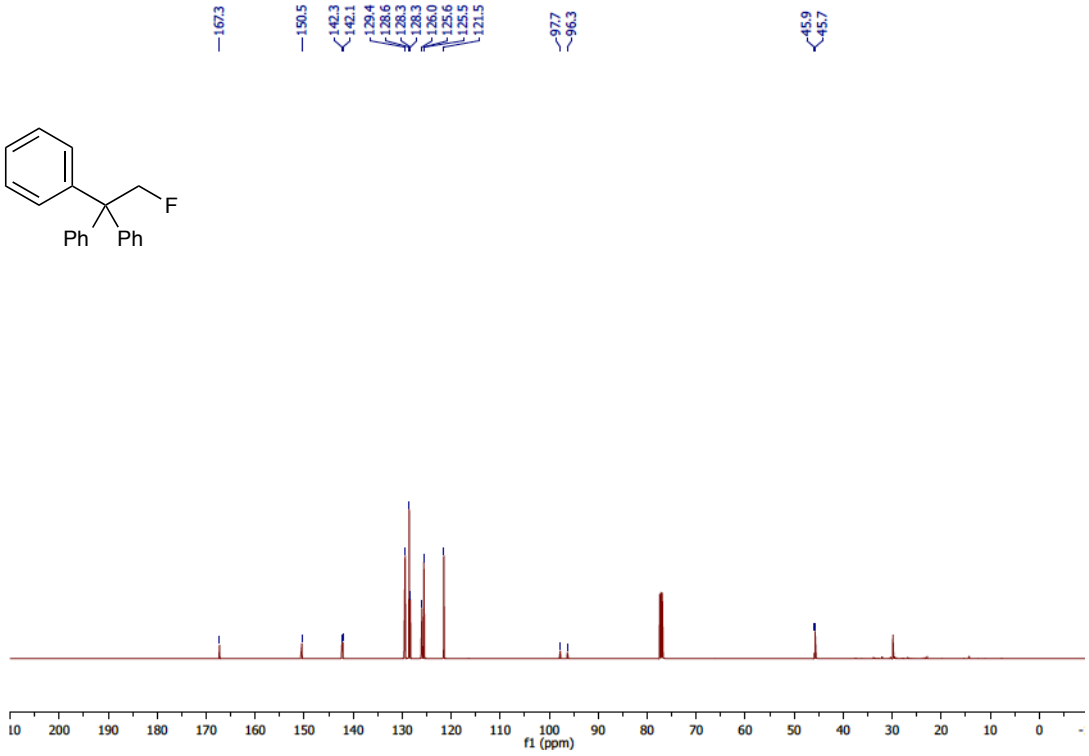

142.21
142.16
128.58
127.43
126.86
88.76
87.38
40.50
40.34
16.97
16.92
Me
F
f1 (ppm)

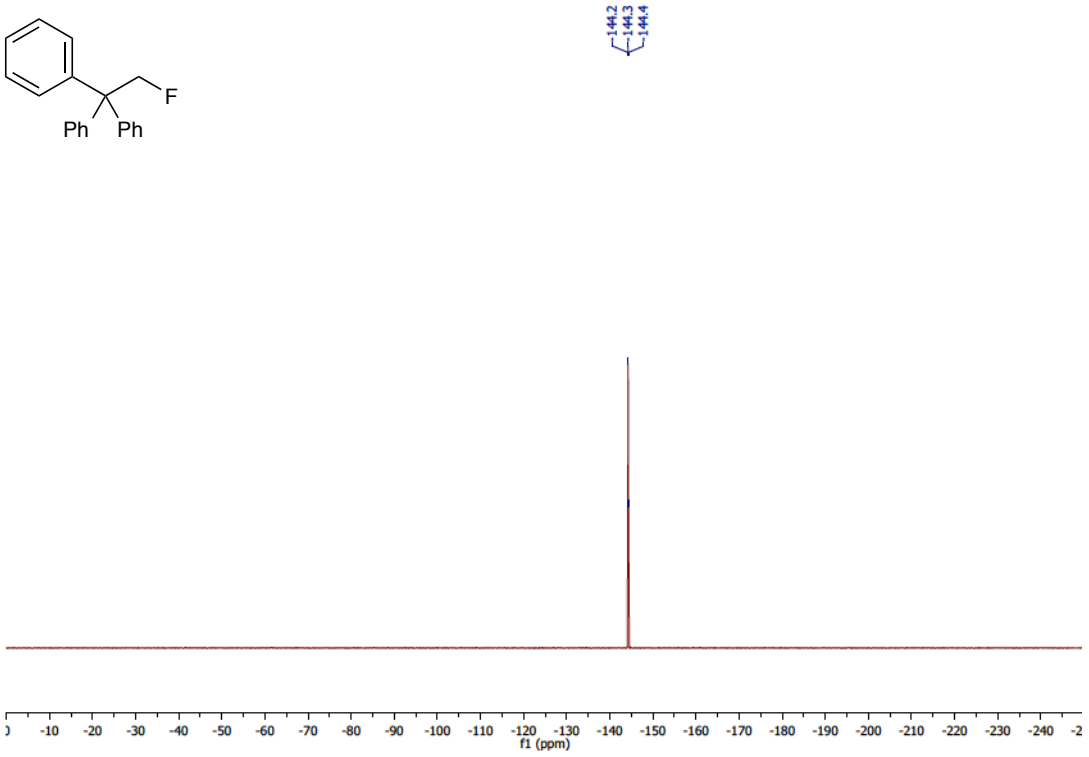

Me
F

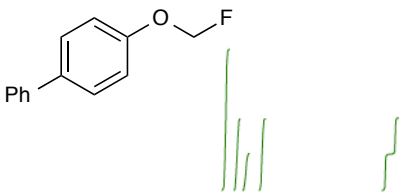
216.77
216.82
216.93
216.99
217.10
217.16
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

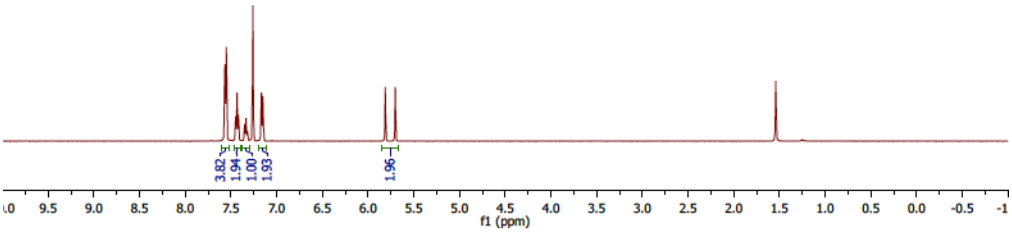

F
Ph
Ph

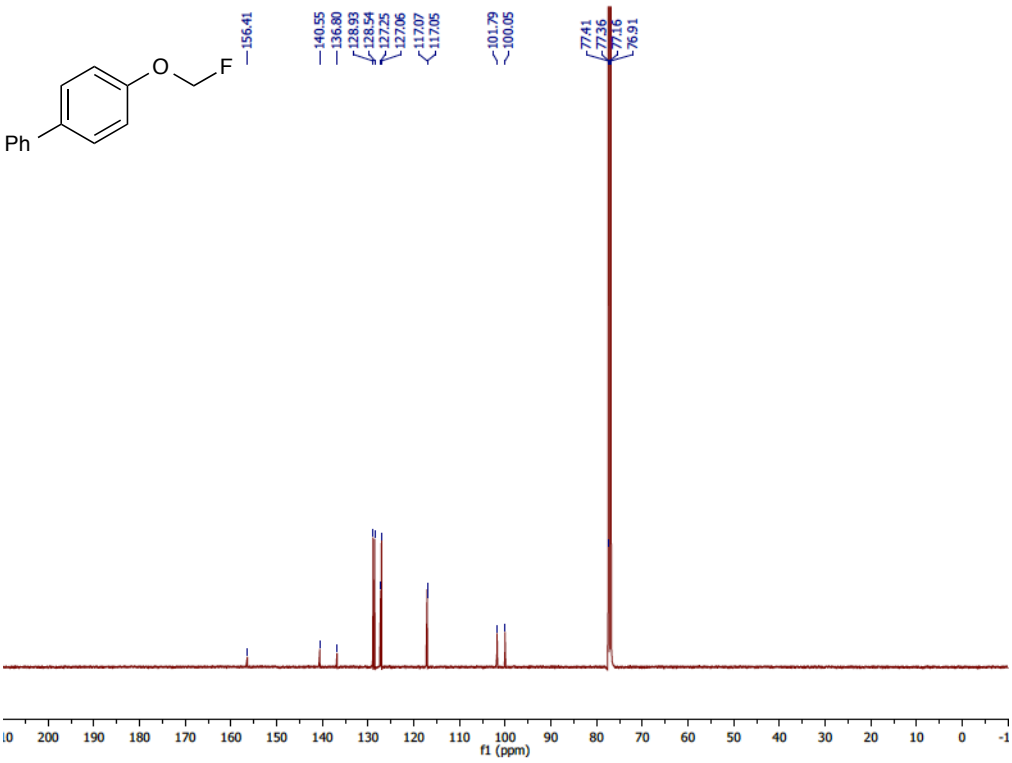

3.93
4.00
2.04
2.02
1.03
1.97
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

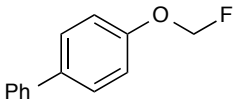

167.3
150.5
142.3
142.1
129.4
128.6
128.3
128.3
126.0
125.6
125.5
121.5
97.7
96.3
45.9
45.7
F
Ph
Ph
f1 (ppm)


144.2
144.3
144.4
F
Ph
Ph
f1 (ppm)


O
F
Ph


3.82
1.94
1.00
1.93
1.96
f1 (ppm)

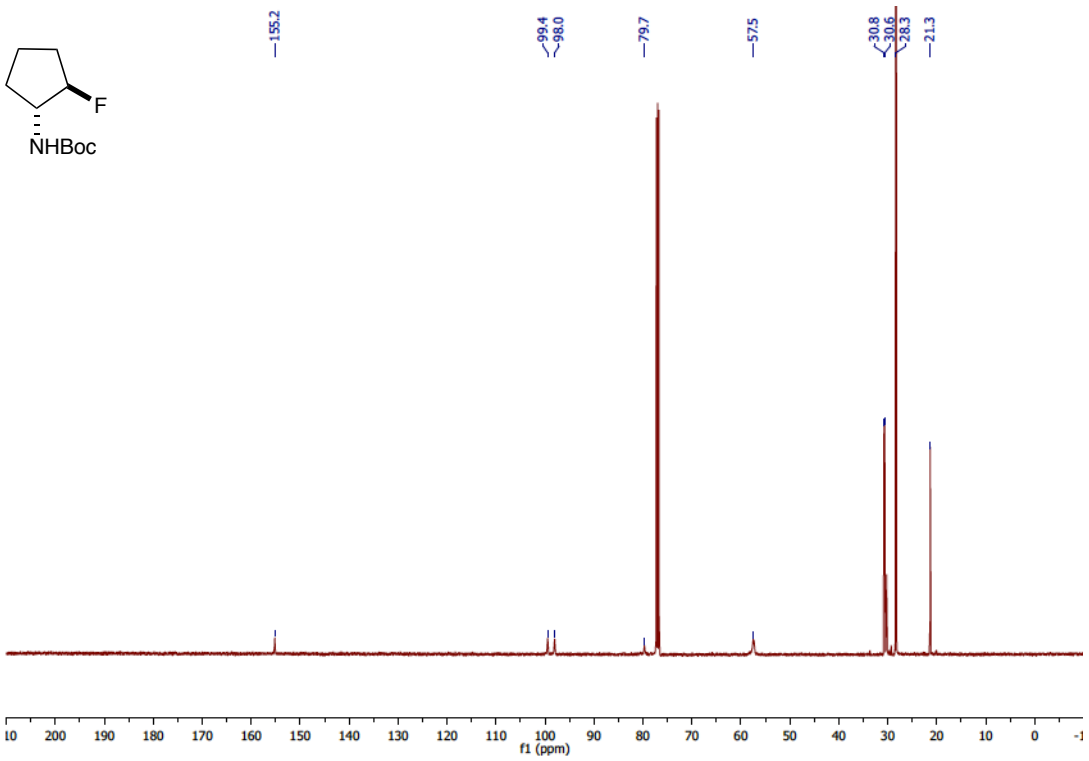

156.41
140.55
136.80
128.93
128.54
127.25
127.06
117.07
117.05
101.79
100.05
77.41
77.36
77.16
76.91
O
F
Ph
f1 (ppm)

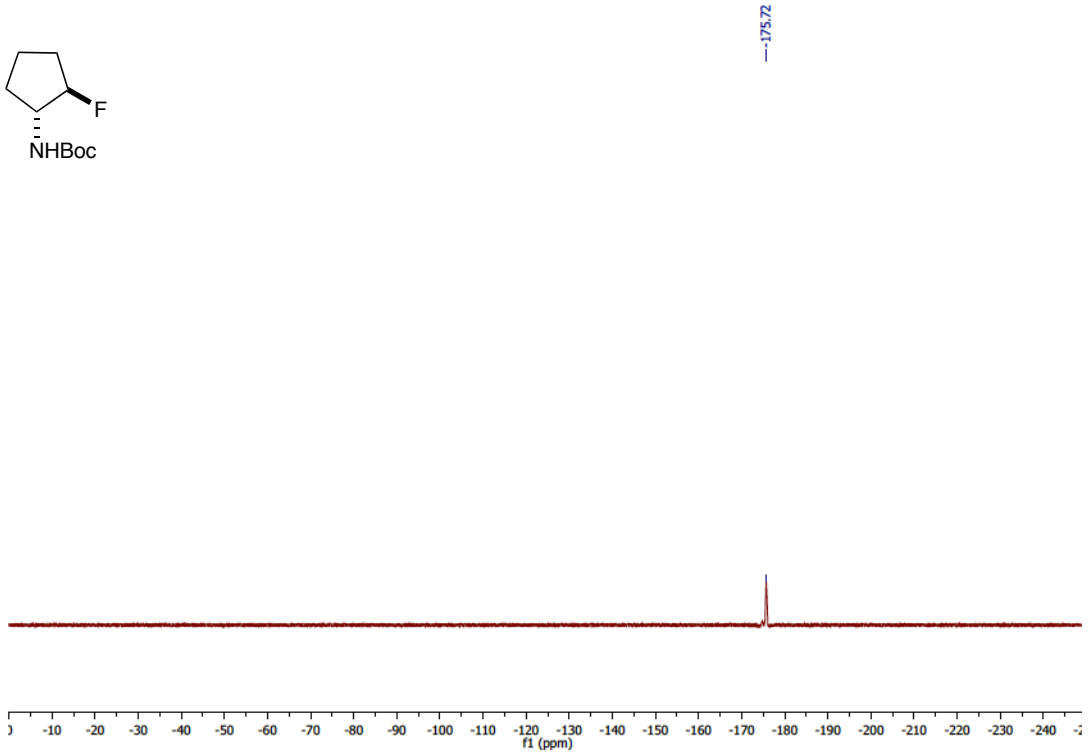

O
F
Ph

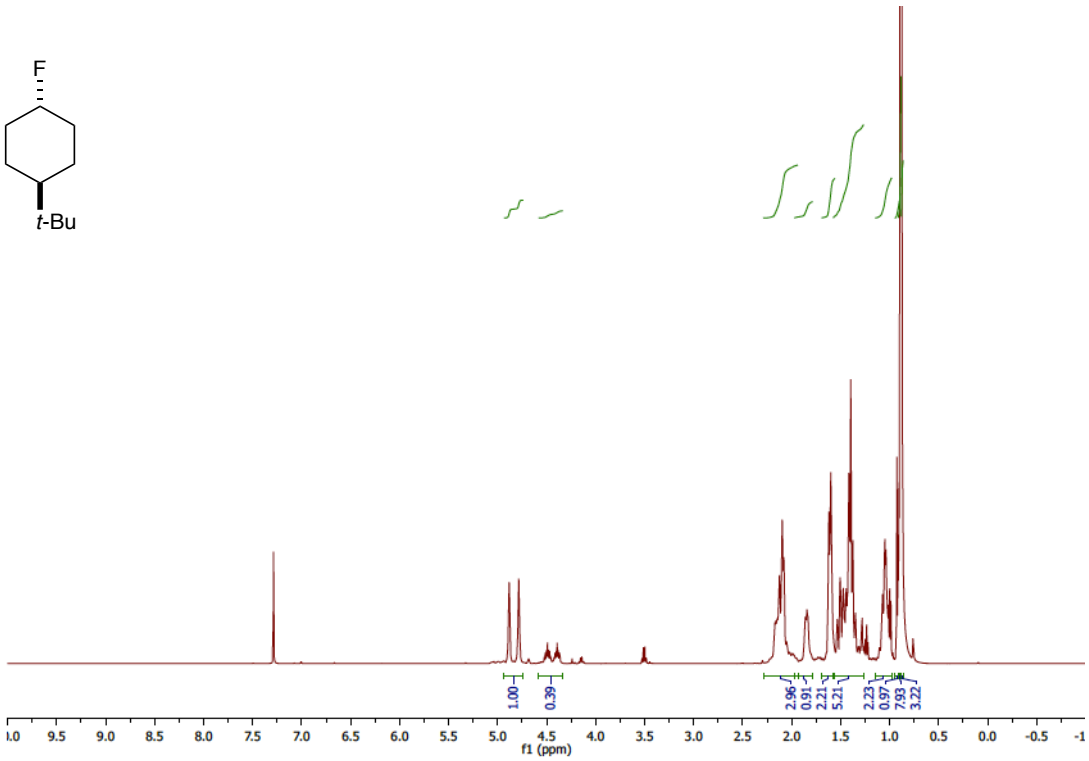
-148.3
-148.5
-148.7
f1 (ppm)

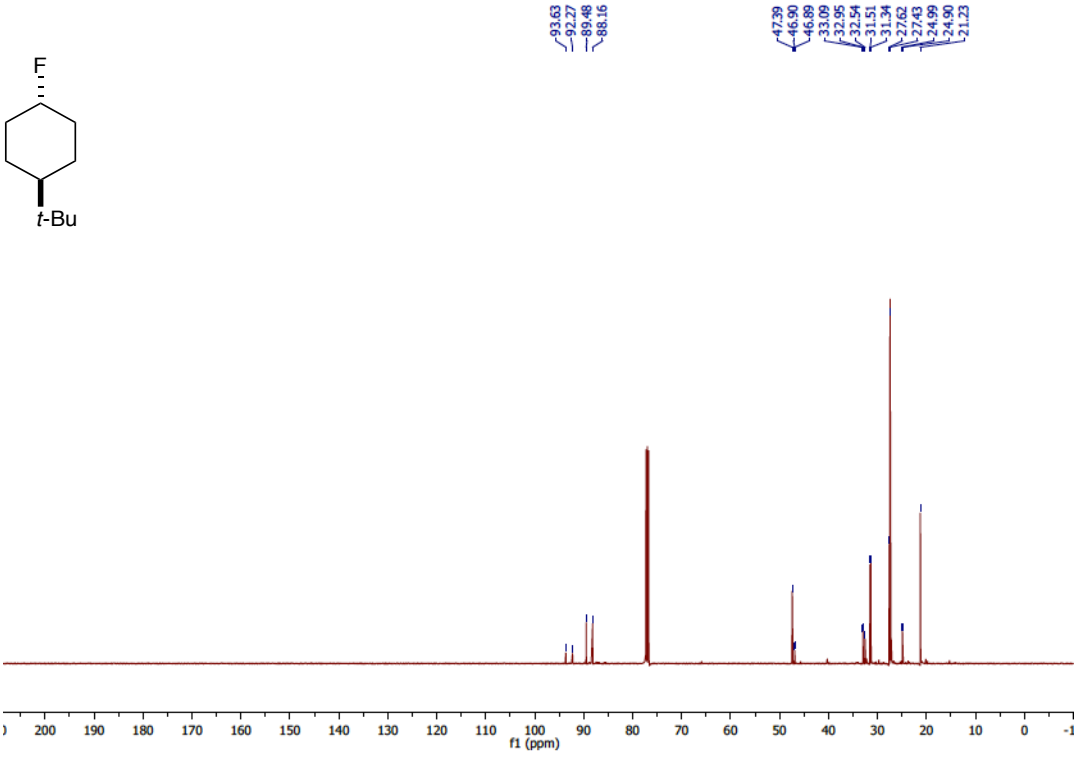

F
NHBoc

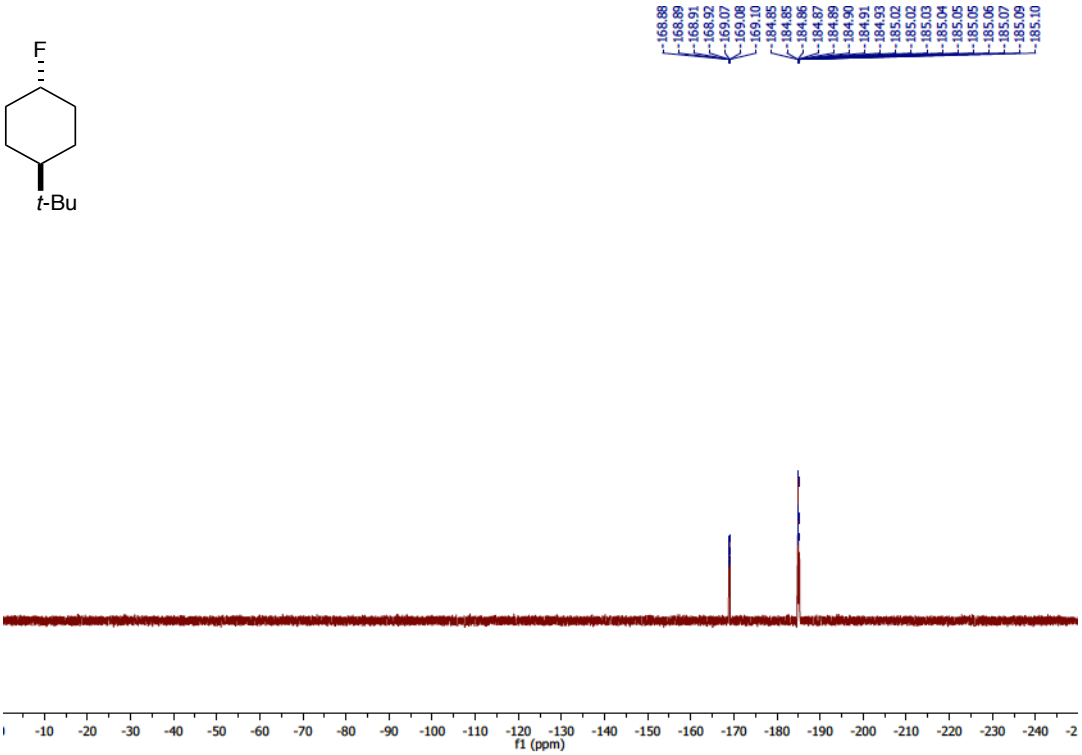
1.00
0.95
0.99
0.98
0.97
2.97
9.26
f1 (ppm)

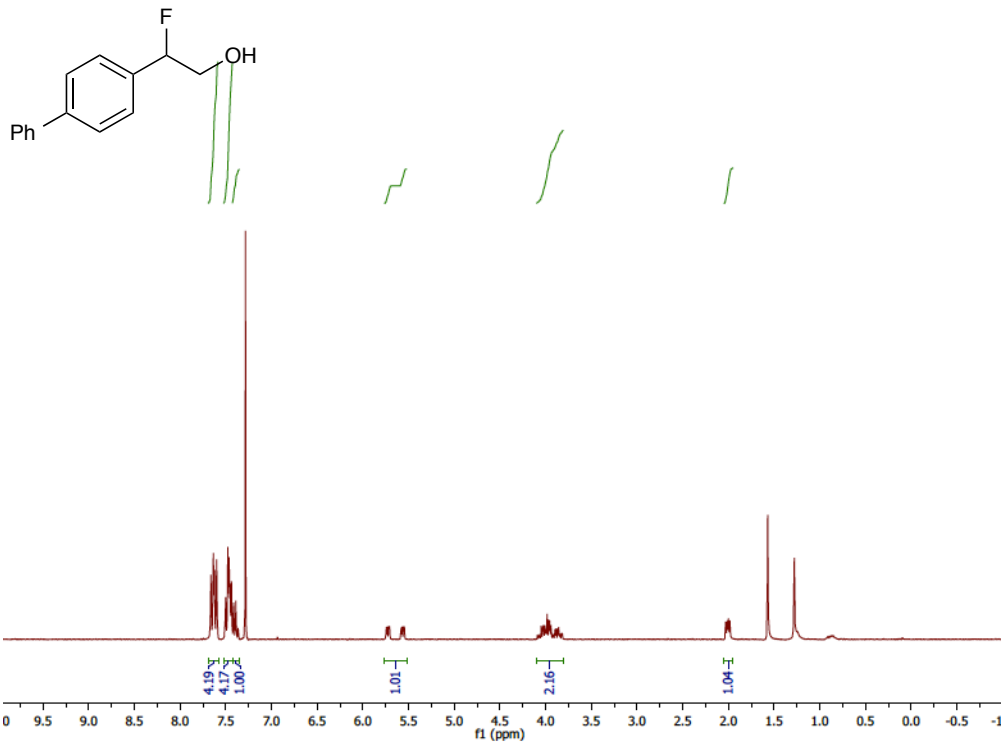

F
NHBoc
155.2
99.4
98.0
79.7
57.5
30.8
30.6
28.3
21.3
f1 (ppm)

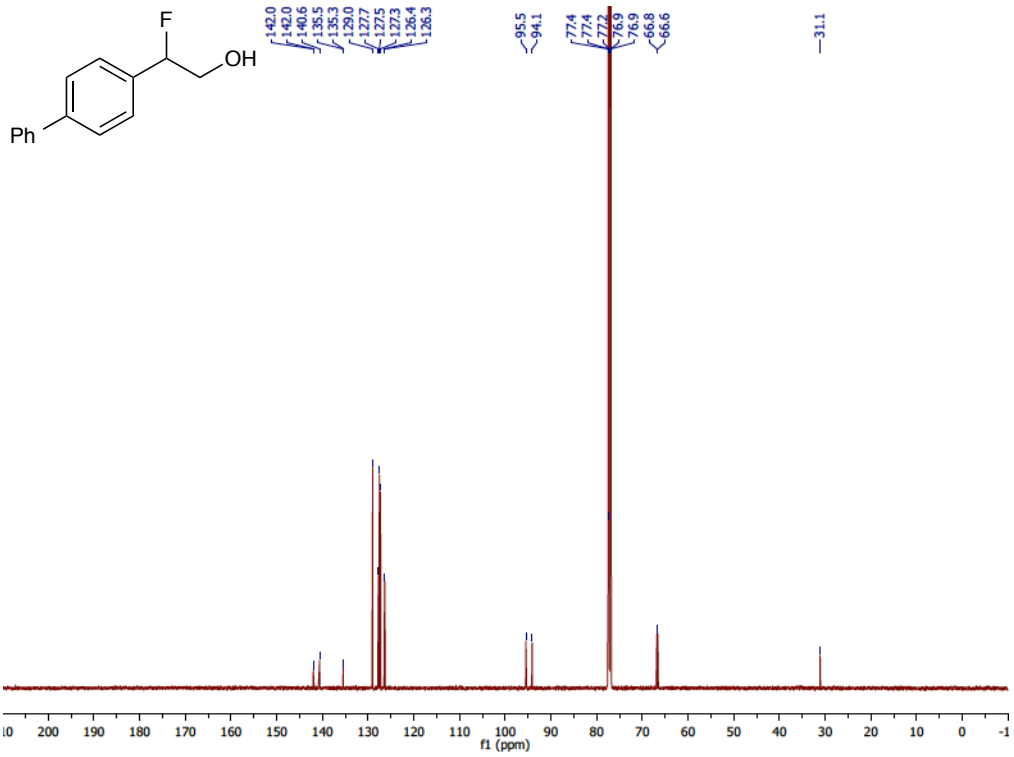

F
NHBoc
175.72
f1 (ppm)

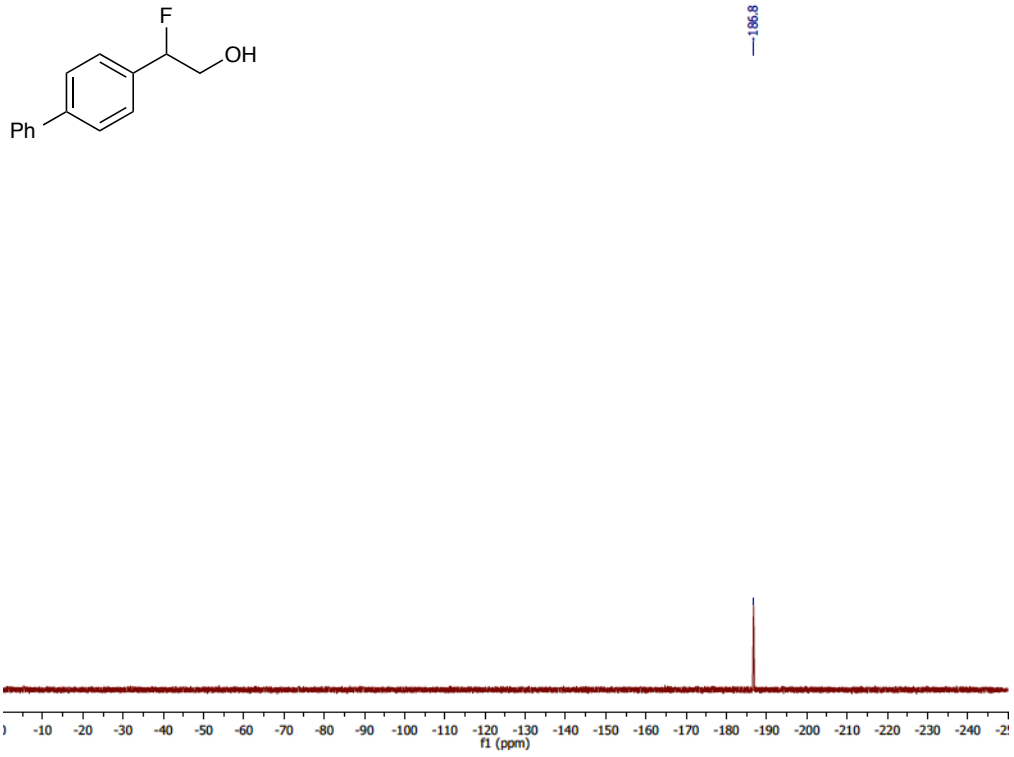

F
t-Bu
1.00
0.39
2.96
0.91
2.21
5.21
2.23
0.97
7.93
3.22
f1 (ppm)

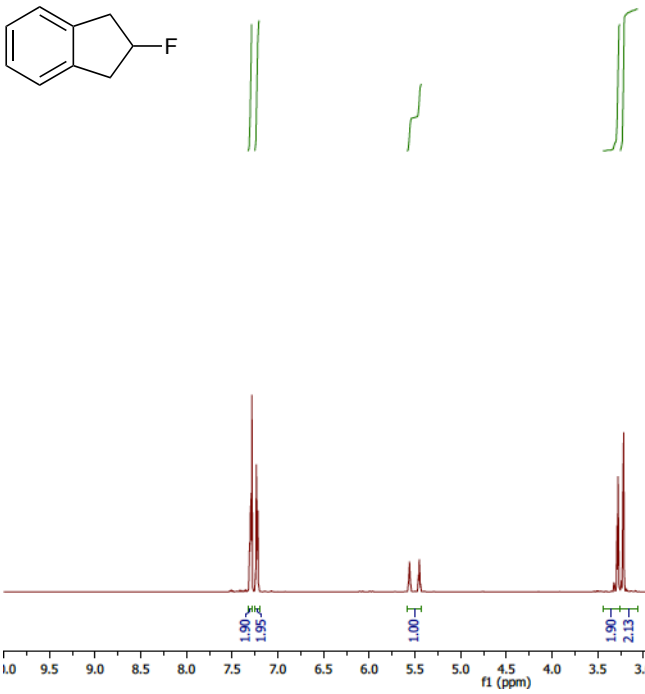

93.63
92.27
89.48
88.16
47.39
46.90
46.89
33.09
32.95
32.54
31.51
31.34
27.62
27.43
24.99
24.90
21.23
F
t-Bu
f1 (ppm)

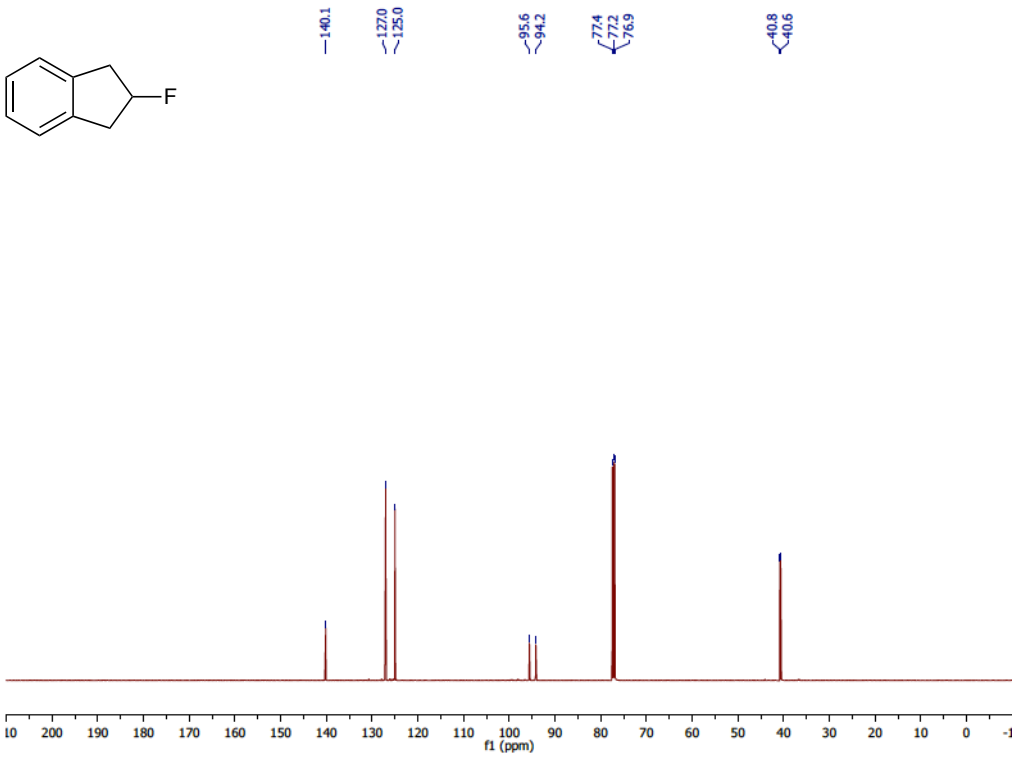

F
t-Bu
168.88
168.89
168.91
168.92
169.07
169.08
169.10
184.85
184.85
184.86
184.87
184.89
184.90
184.91
184.93
185.02
185.03
185.04
185.05
185.05
185.06
185.07
185.09
185.10
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -2
f1 (ppm)

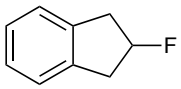

F
OH
Ph
4.19
4.17
1.00
1.01
2.16
1.04
0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


F
OH
Ph
142.0
142.0
140.6
135.5
135.3
129.0
127.7
127.5
127.3
126.4
126.3
95.5
94.1
77.4
77.4
77.2
76.9
76.9
66.8
66.6
31.1
f1 (ppm)

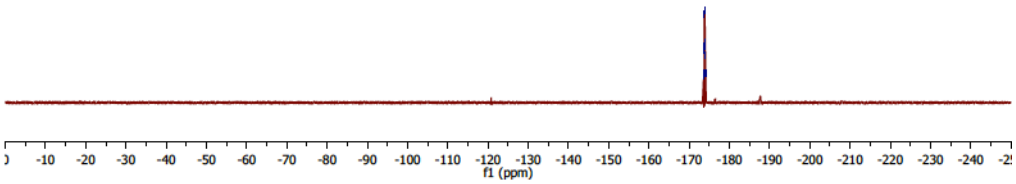

F
OH
Ph
186.8
f1 (ppm)

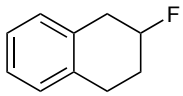

F
1.90
1.95
1.00
1.90
2.13
f1 (ppm)

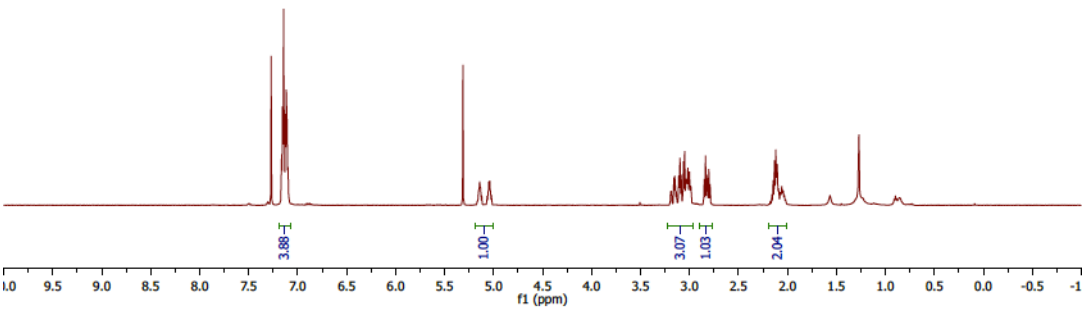

140.1
127.0
125.0
95.6
94.2
77.4
77.2
76.9
40.8
40.6
F
f1 (ppm)

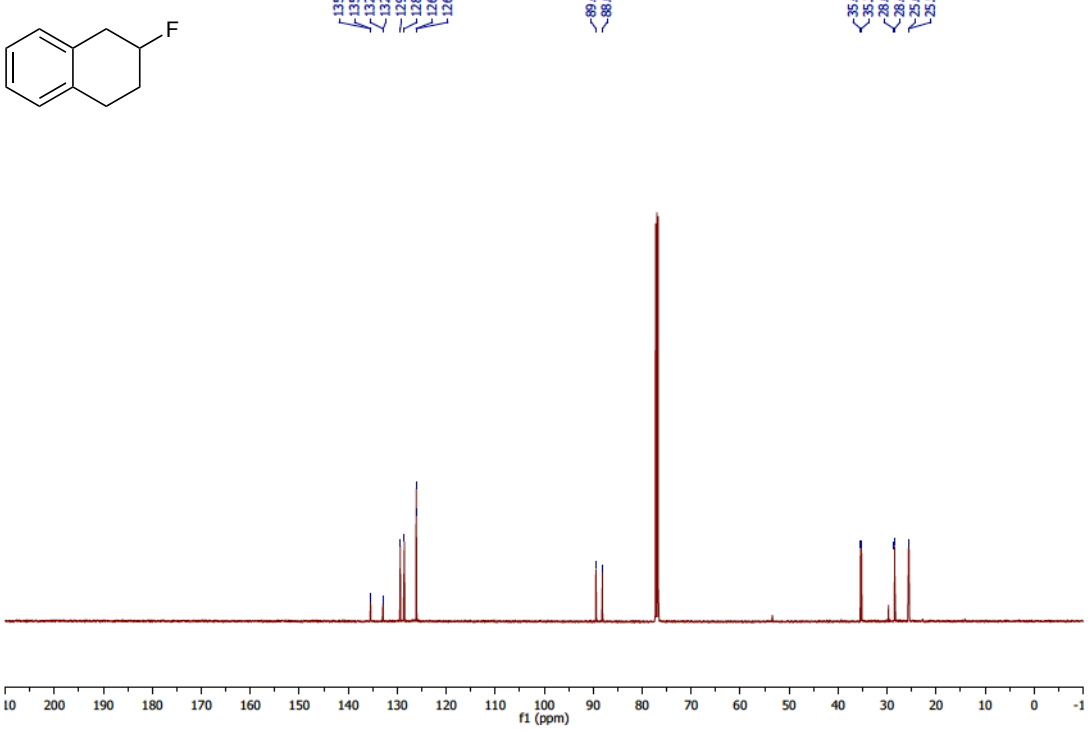

F

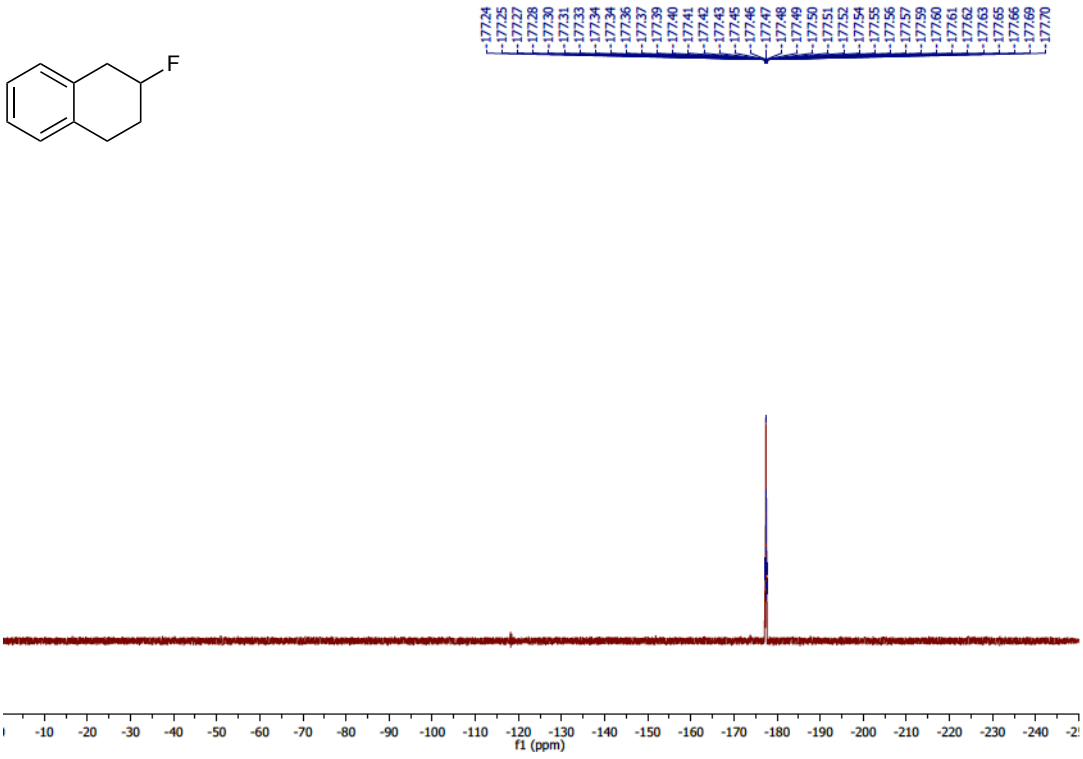

173.5
173.6
173.6
173.7
173.8
173.8
173.8
173.9
174.0
174.0
174.0
174.1


-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

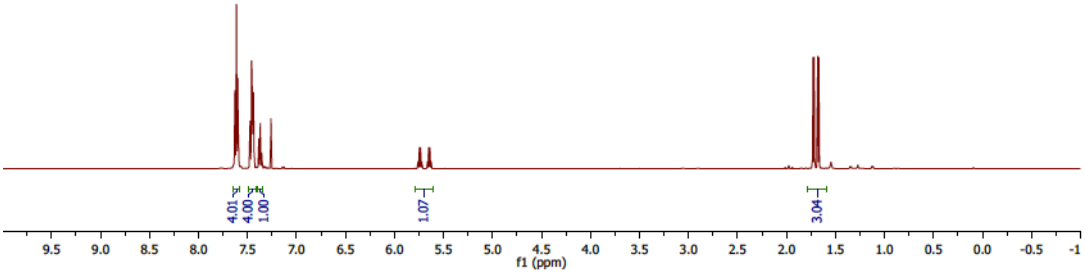

F

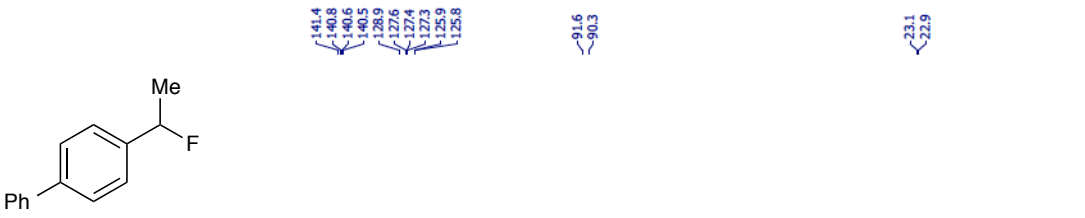

3.88
1.00
3.07
1.03
2.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


F
135.44
135.43
132.92
132.87
129.37
128.53
126.11
126.04
89.44
88.09
35.41
35.23
28.60
28.45
25.61
25.54
f1 (ppm)

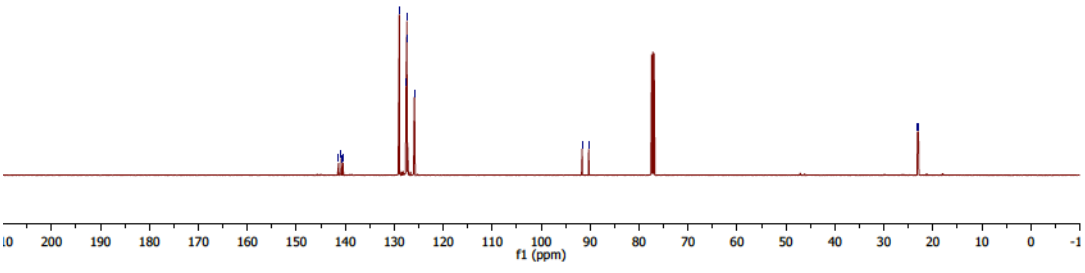

F
f1 (ppm)

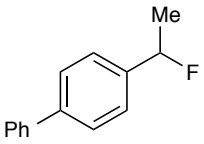

Me
F
Ph


4.01
4.00
1.00
1.07
3.04
f1 (ppm)

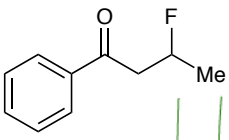

141.4
140.8
140.6
140.5
128.9
127.6
127.4
127.3
125.9
125.8
91.6
90.3
23.1
22.9

Me
F
Ph

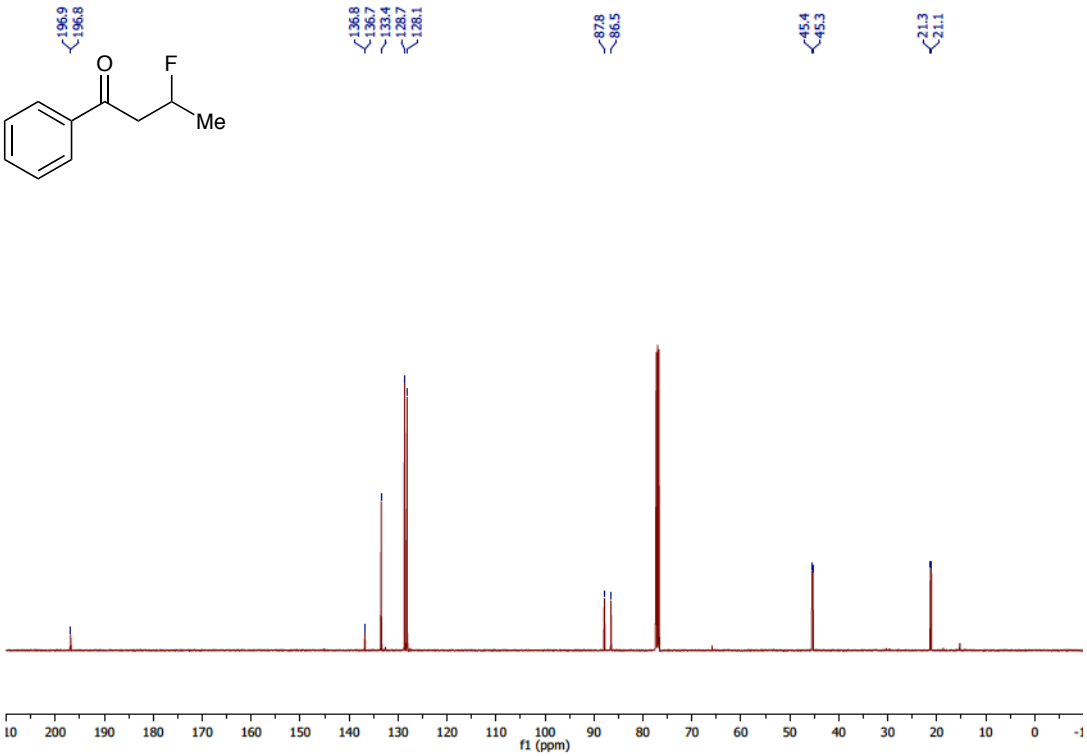

f1 (ppm)

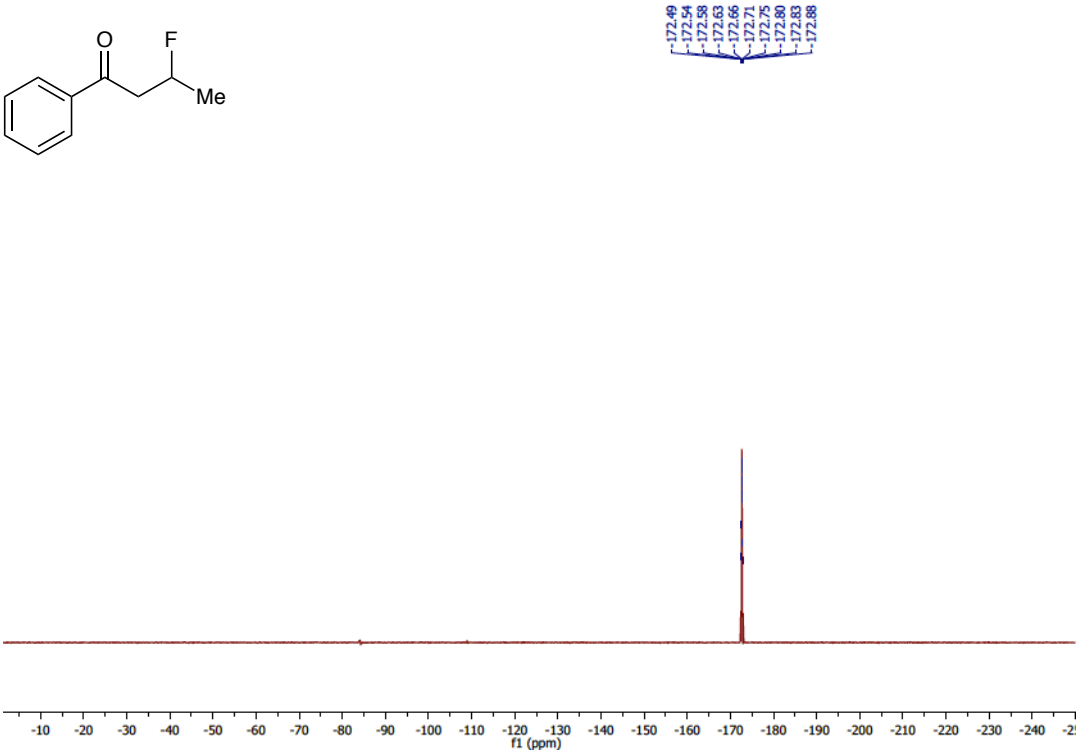

Me
F
Ph

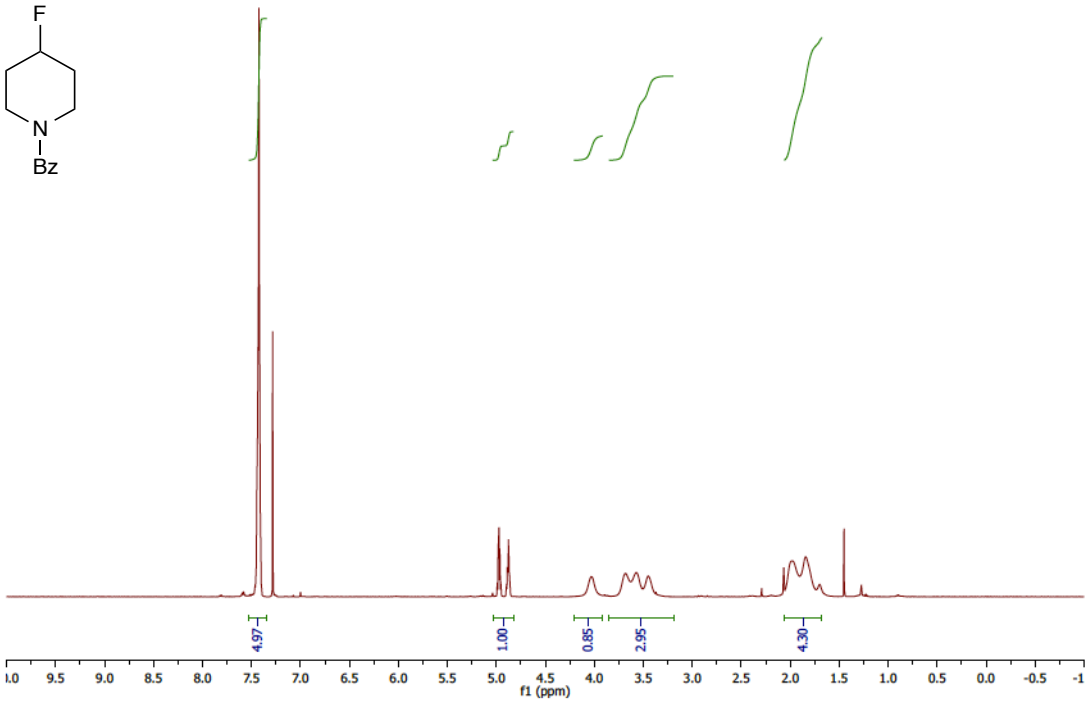
166.4
166.5
166.6
166.7
166.7
166.8
f1 (ppm)

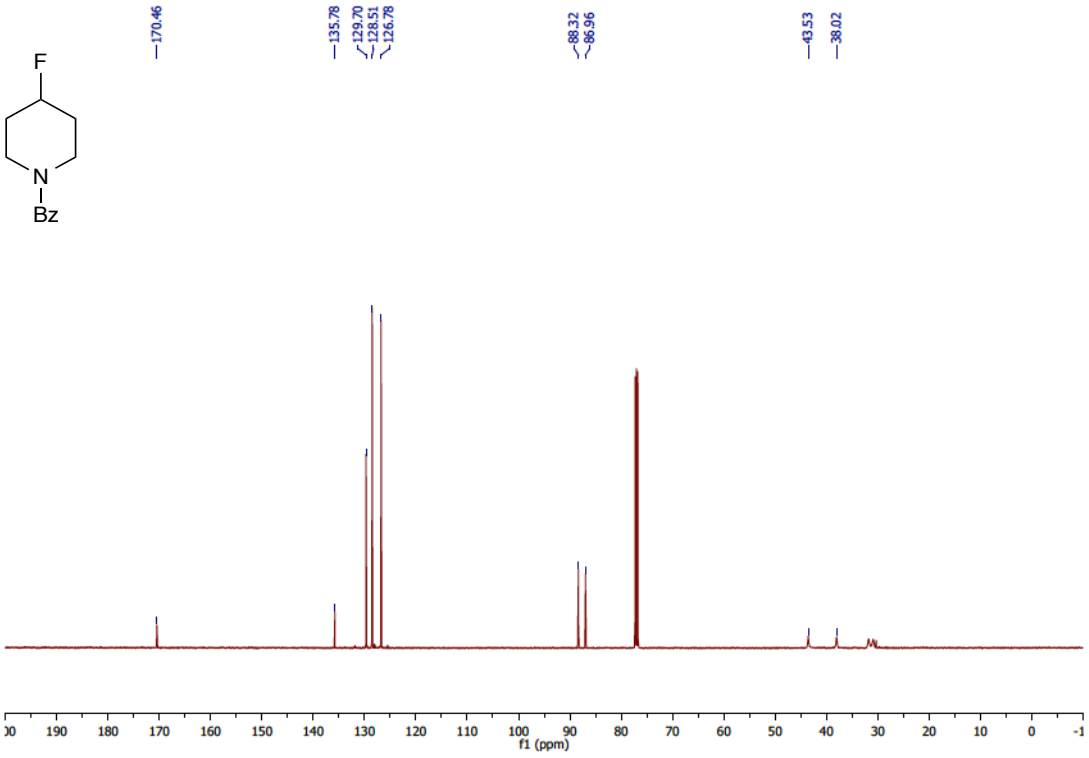

O
F
Me

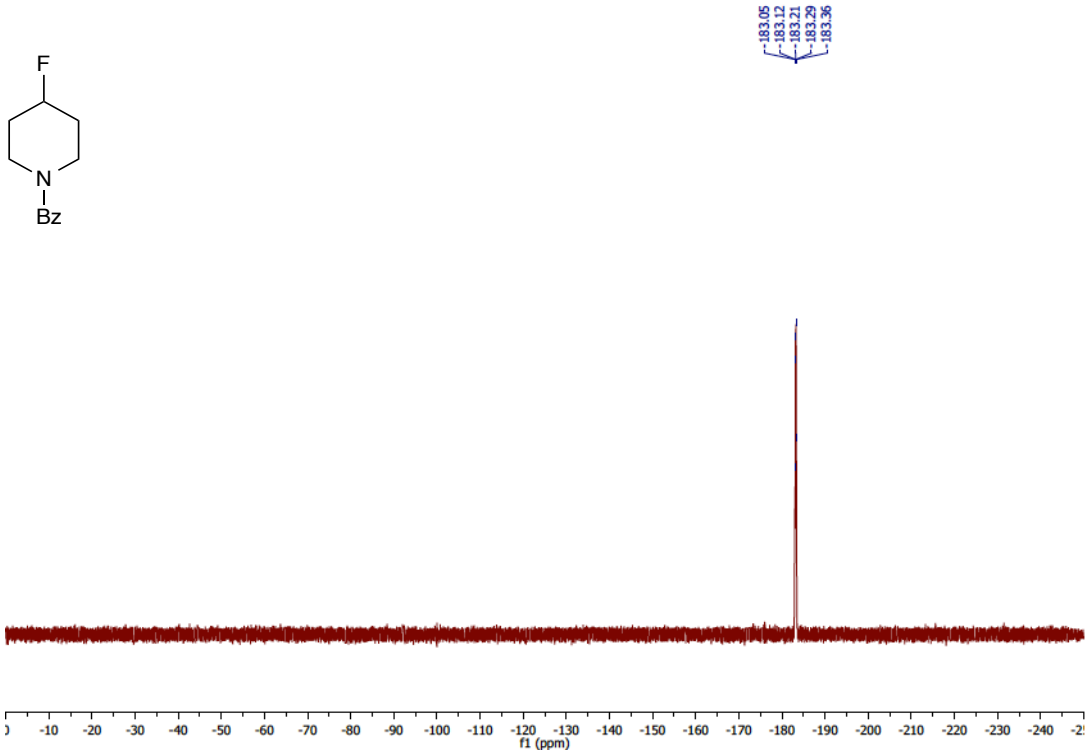
2.00
1.00
2.04
0.99
1.16
1.01
3.07
f1 (ppm)

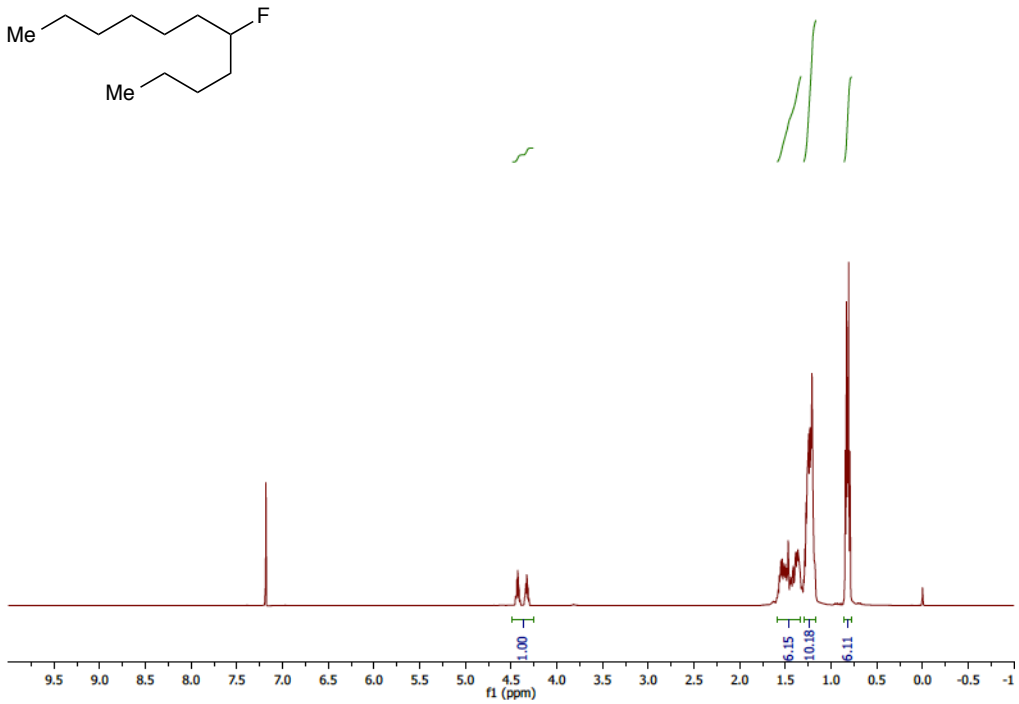

196.9
196.8
136.8
136.7
133.4
128.7
128.1
87.8
86.5
45.4
45.3
21.3
21.1
O
F
Me
f1 (ppm)

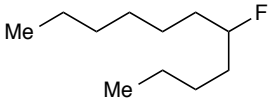

172.49
172.54
172.58
172.63
172.66
172.71
172.75
172.80
172.83
172.88
O
F
Me
f1 (ppm)

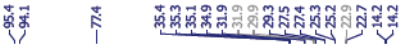

F
N
Bz
4.97
1.00
0.85
2.95
4.30
f1 (ppm)

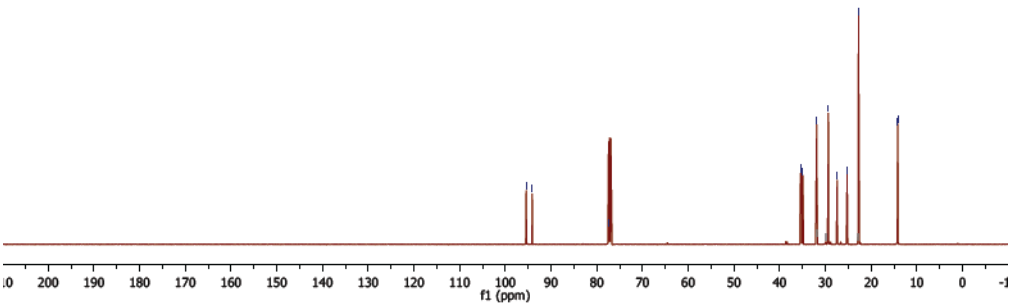

170.46
135.78
129.70
128.51
126.78
88.32
86.96
43.53
38.02
F
N
Bz
f1 (ppm)

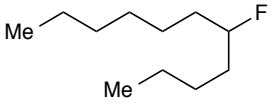

F
N
Bz
183.05
183.12
183.21
183.29
183.36
f1 (ppm)


Me
F
Me
1.00
6.15
10.18
6.11
f1 (ppm)

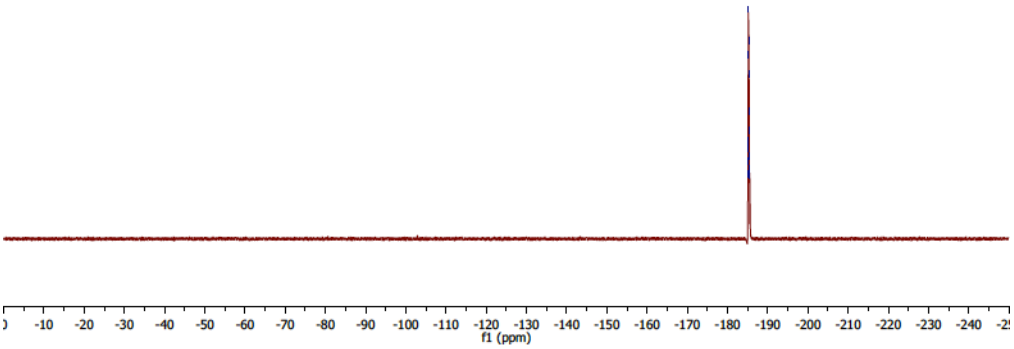

Me
F
Me

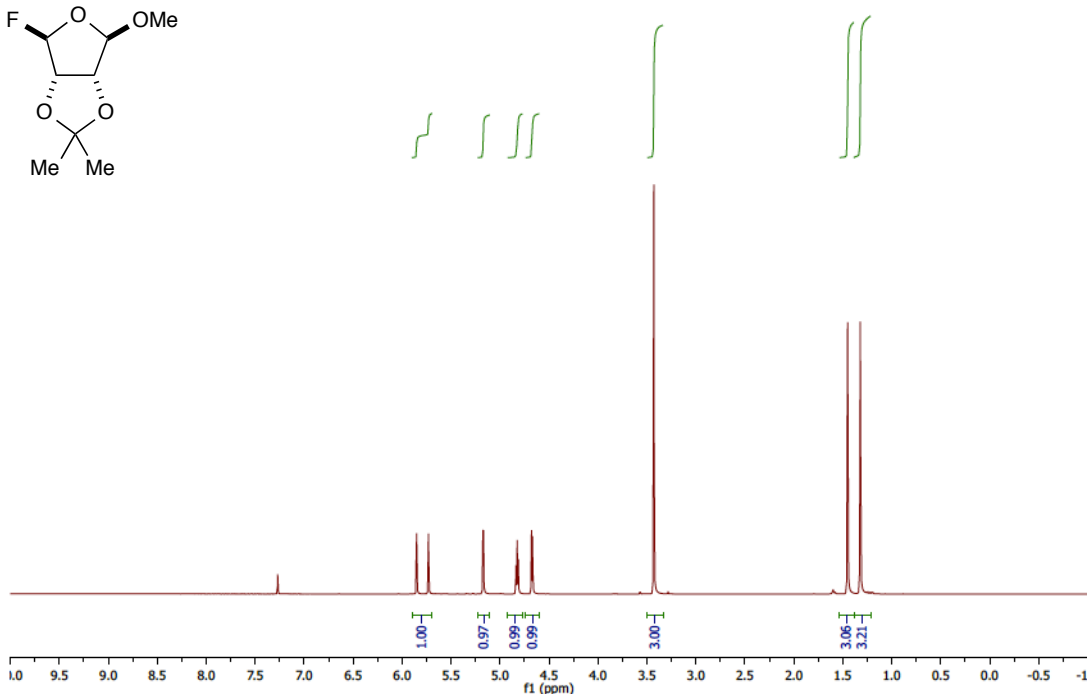

95.4
94.1
77.4
35.4
35.3
35.1
34.9
31.9
31.9
29.9
29.3
27.5
27.4
25.3
25.2
22.9
22.7
14.2
14.2

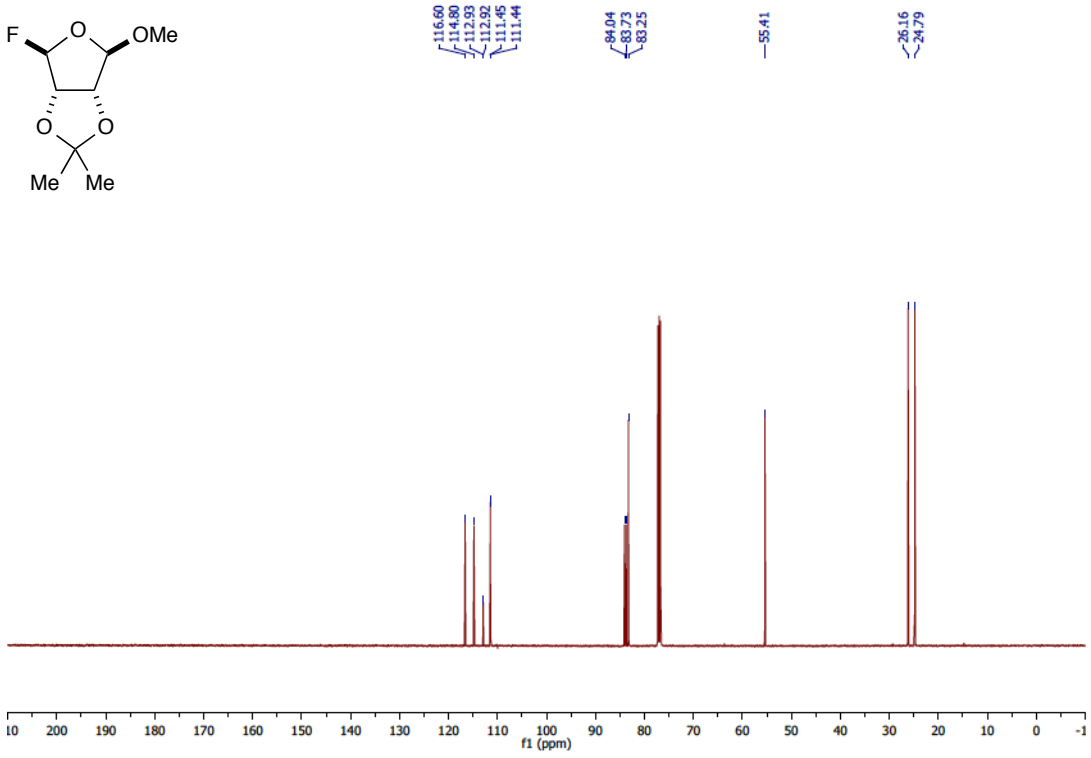

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

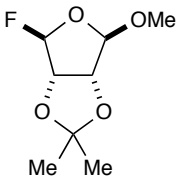

Me
F
Me


185.1
185.1
185.1
185.2
185.2
185.2
185.3
185.3
185.4
185.4
185.4
185.5
185.5

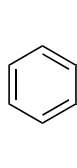

-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


F
O
OMe
O
O
Me
Me
1.00
0.97
0.99
0.99
3.00
3.06
3.21
f1 (ppm)

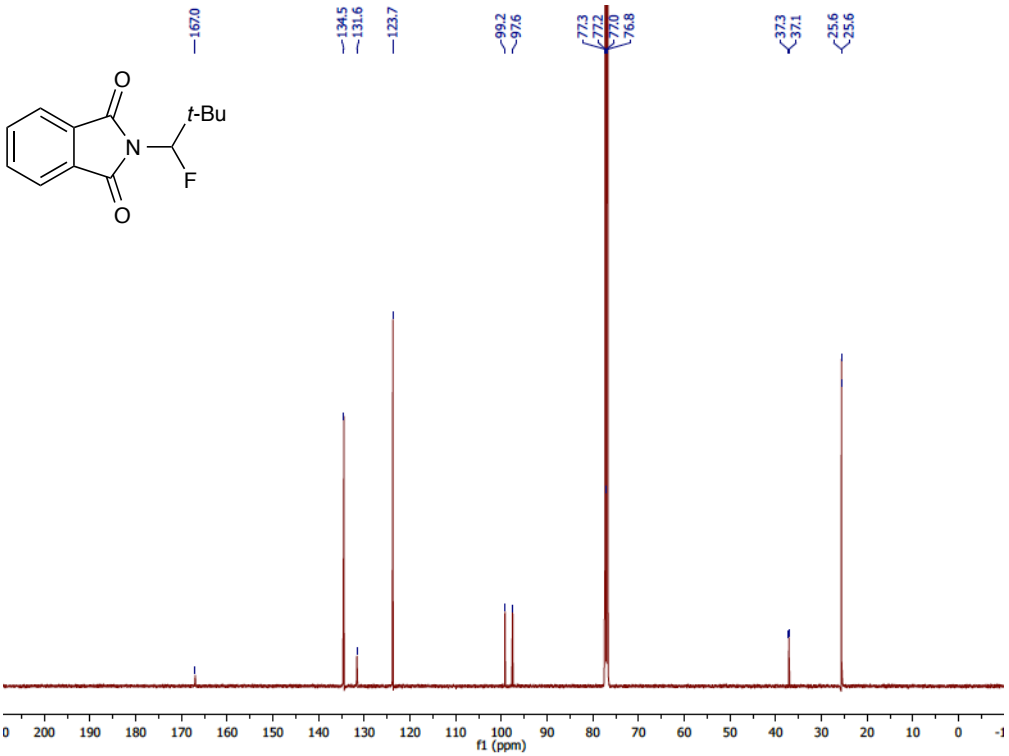

F
O
OMe
O
O
Me
Me
116.60
114.80
112.93
112.92
111.45
111.44
84.04
83.73
83.25
55.41
26.16
24.79
f1 (ppm)

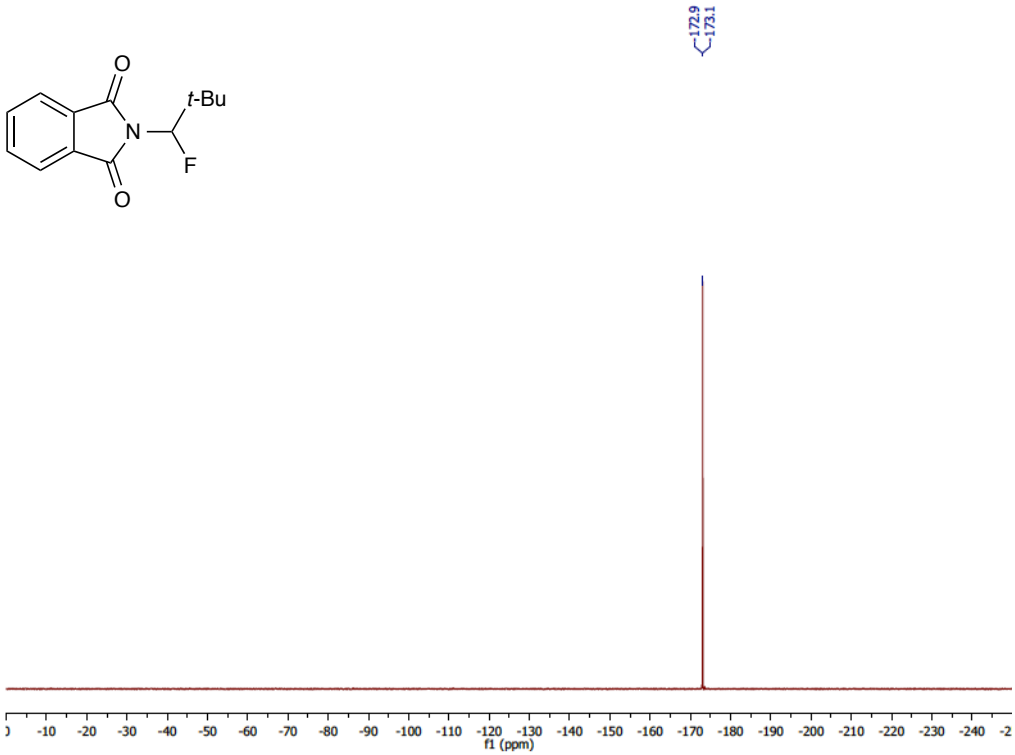

F
O
OMe
O
O
Me
Me

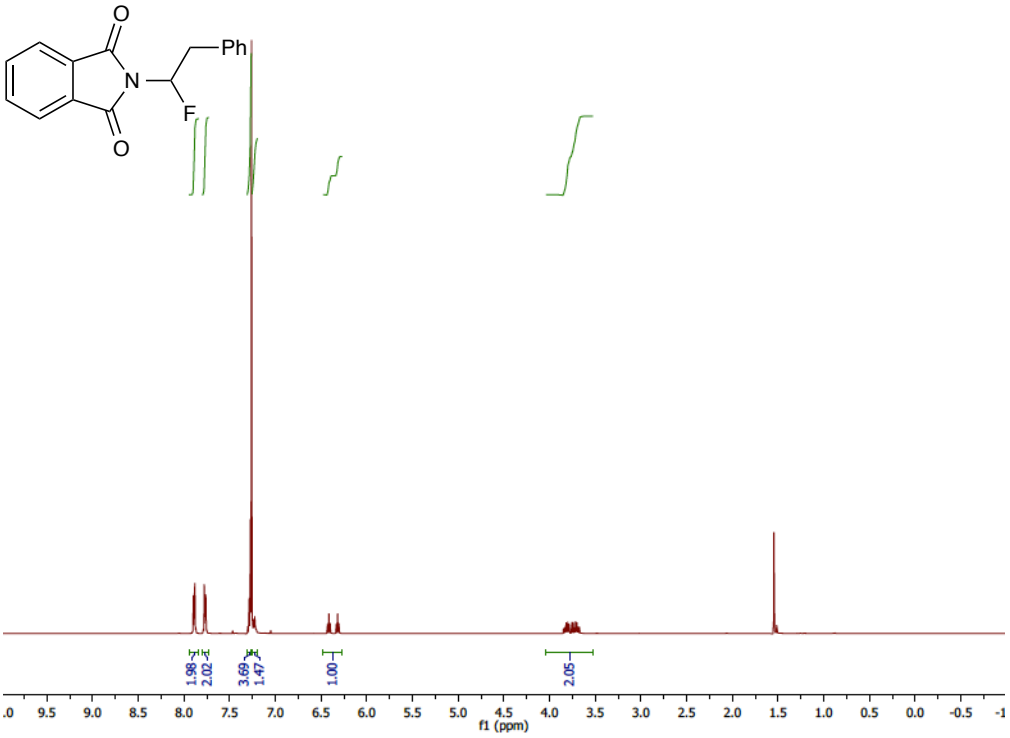
119.32
119.34
119.54
119.55
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

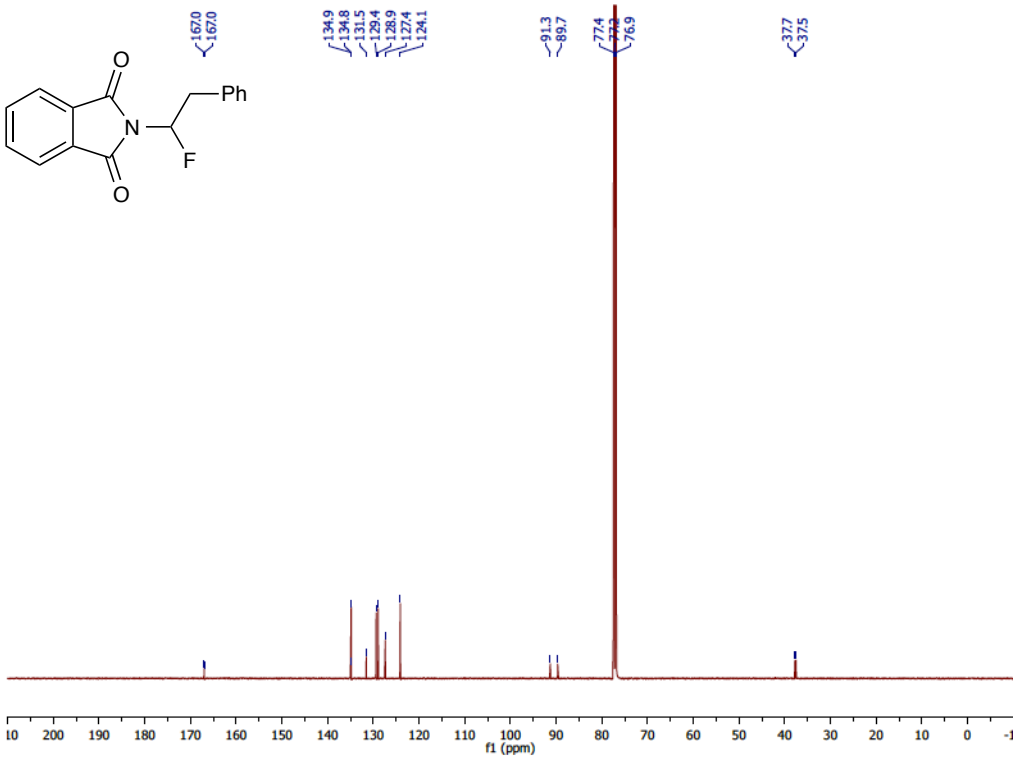

O
N
t-Bu
F
O

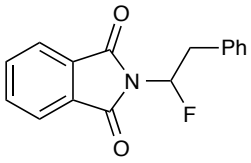
2.02
2.04
1.00
9.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


167.0
134.5
131.6
123.7
99.2
97.6
77.3
77.2
77.0
76.8
37.3
37.1
25.6
25.6
O
N
t-Bu
F
O
f1 (ppm)

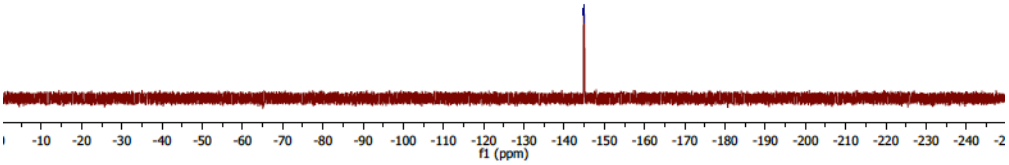

172.9
173.1
O
N
t-Bu
F
O
f1 (ppm)

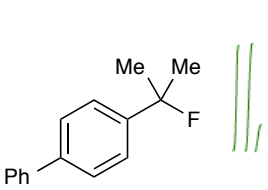

O
N
Ph
F
O
1.98
2.02
3.69
1.47
1.00
2.05
f1 (ppm)

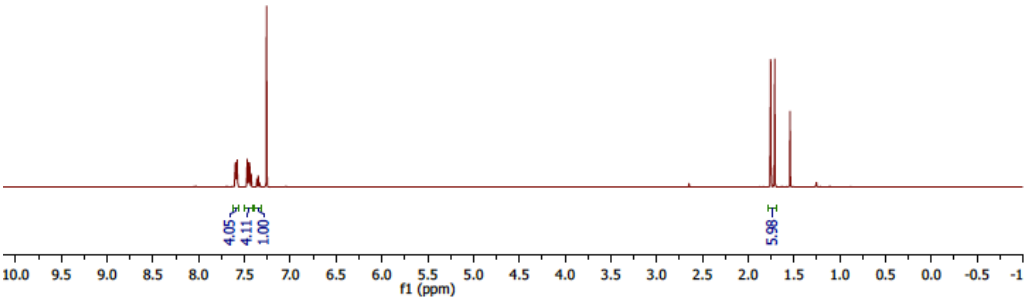

167.0
167.0
134.9
134.8
131.5
129.4
128.9
127.4
124.1
91.3
89.7
77.4
77.3
76.9
37.7
37.5
O
N
Ph
F
O
f1 (ppm)

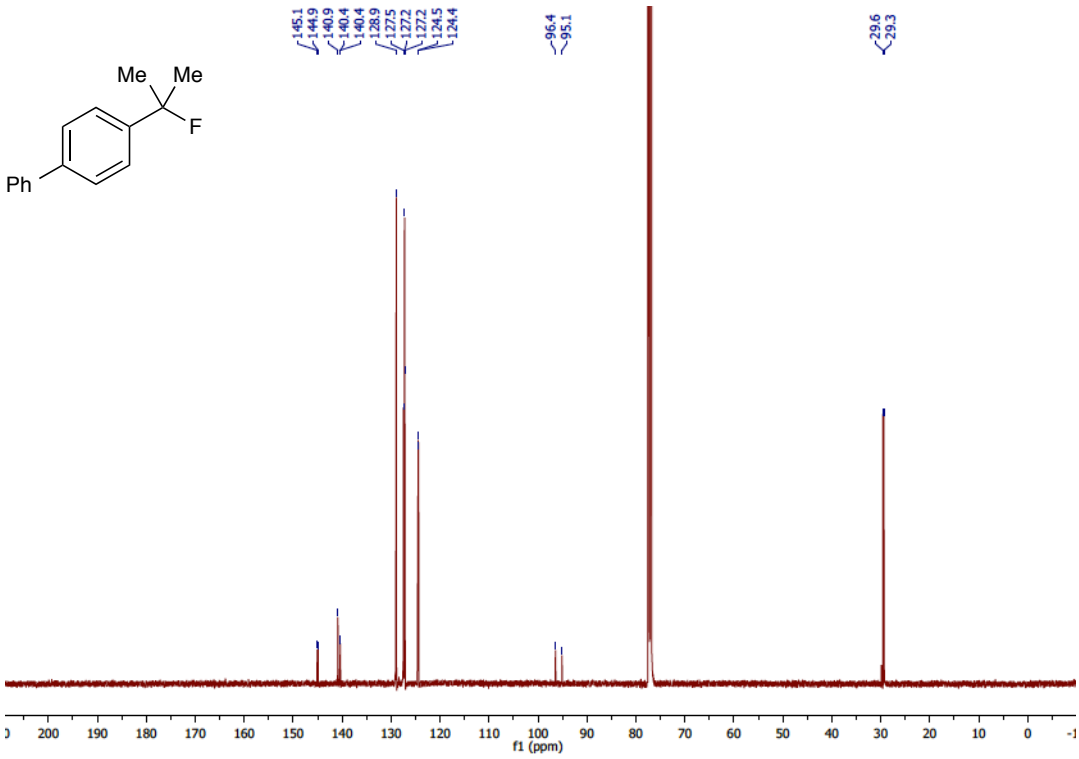

O
N
Ph
F
O

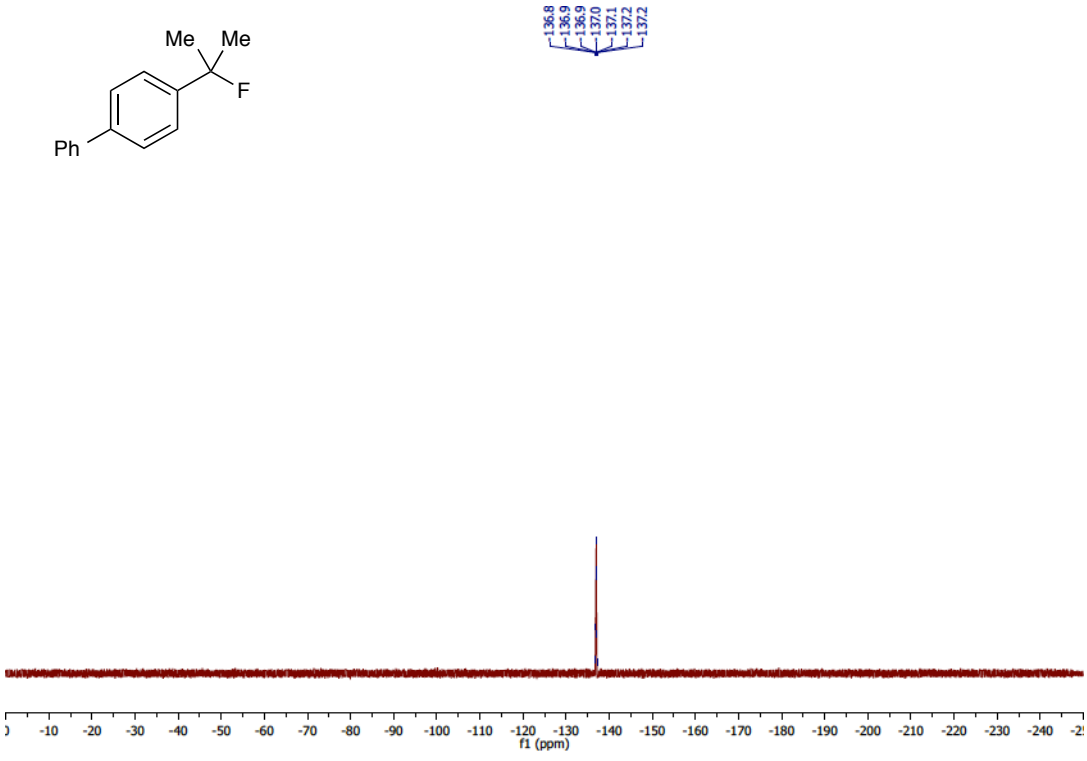

144.78
144.81
144.85
144.88
144.95
144.98
145.02
145.05

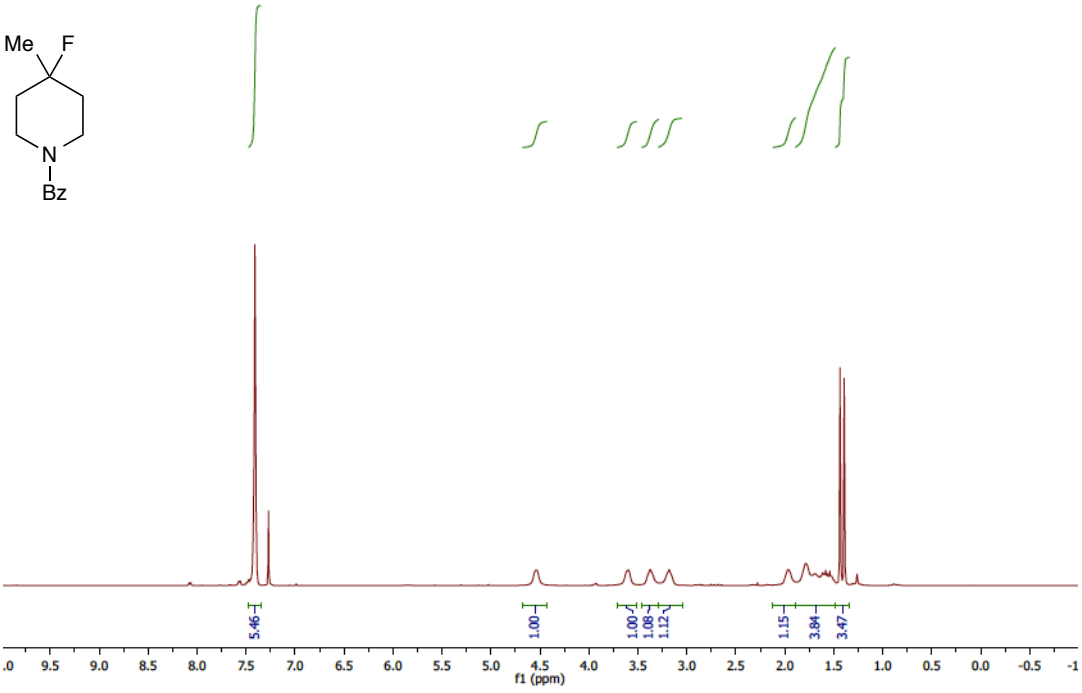

-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

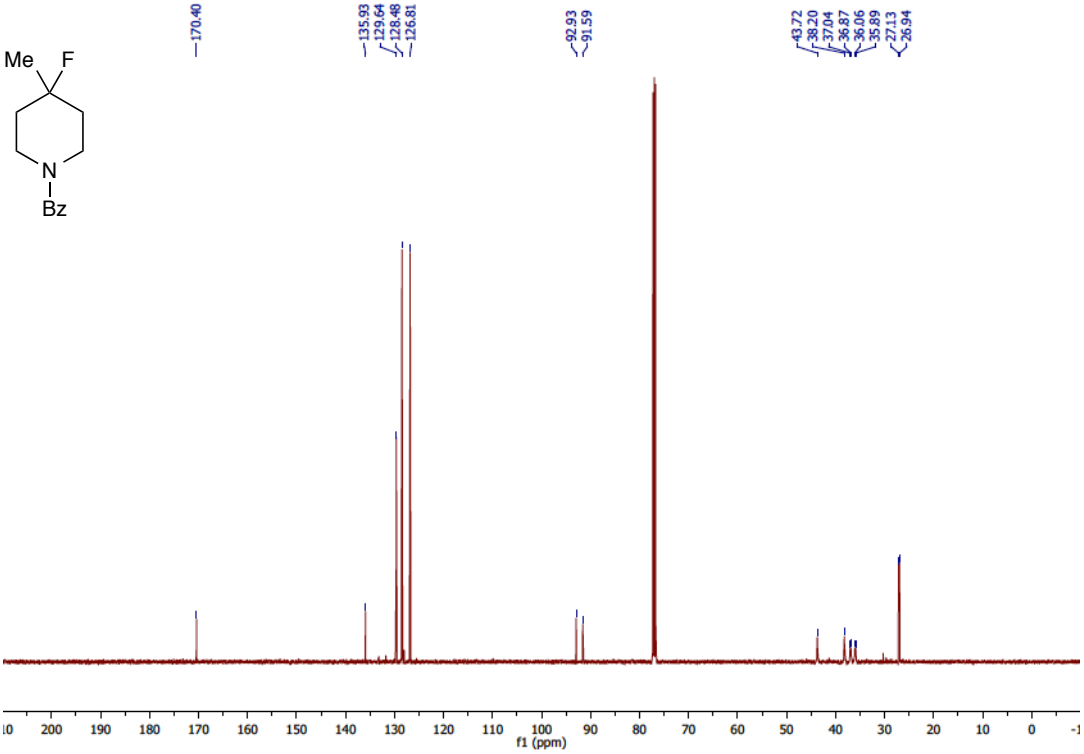

Me
Me
F
Ph

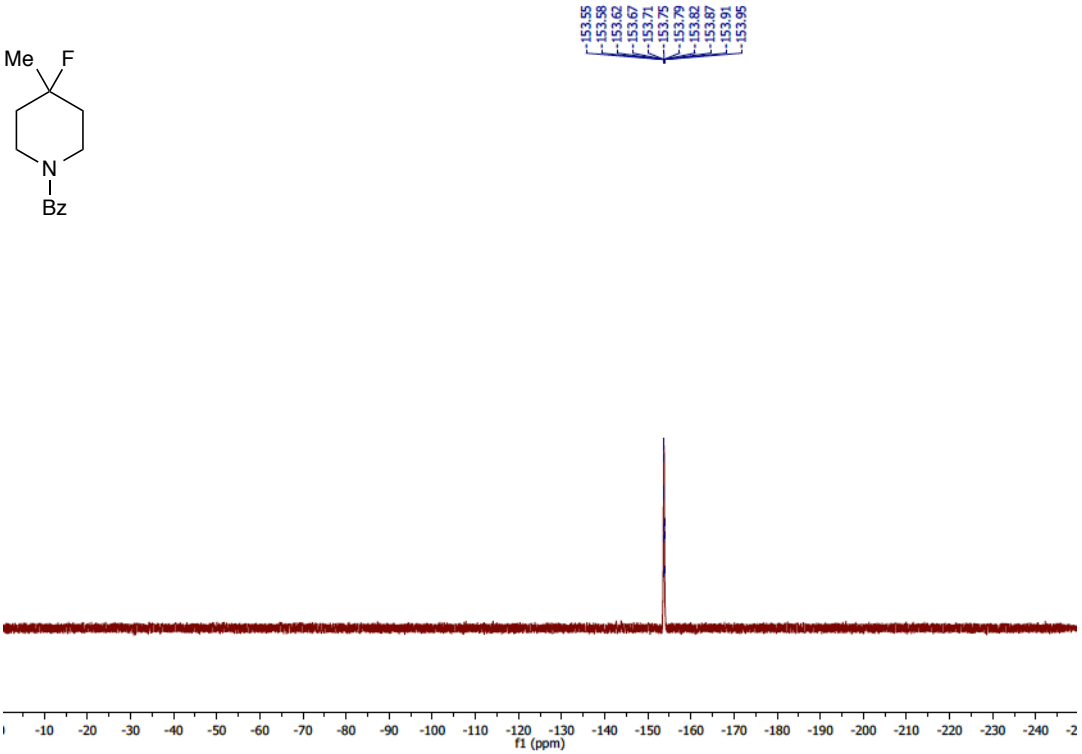

4.05
4.11
1.00
5.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

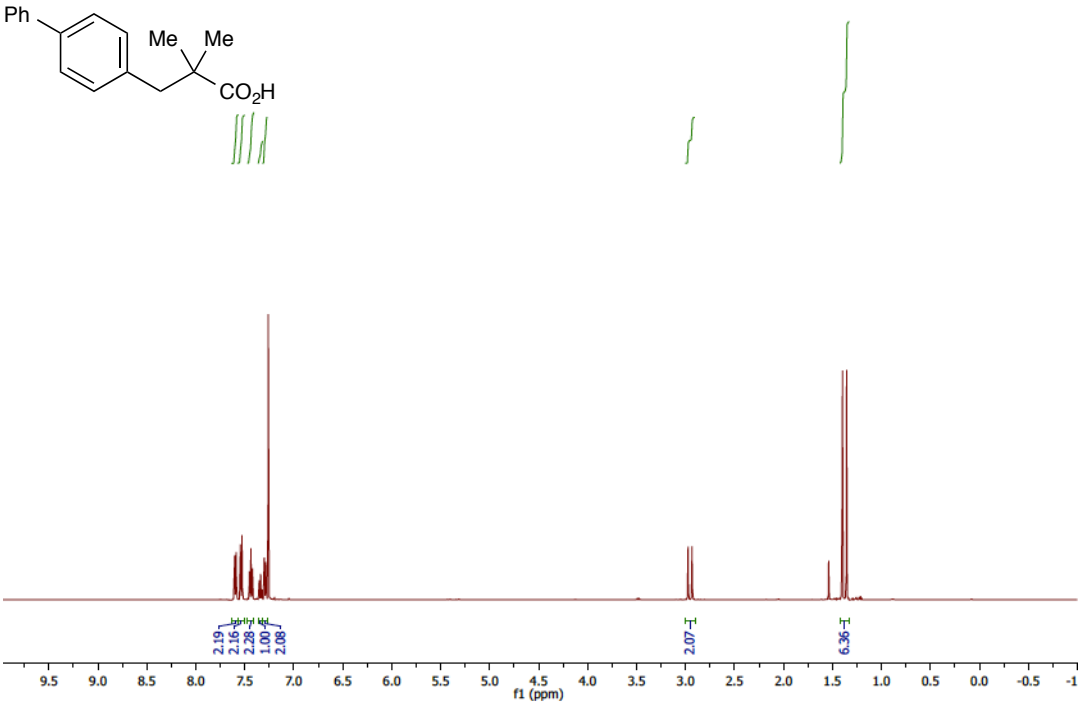

Me
Me
F
Ph
145.1
144.9
140.9
140.4
140.4
128.9
127.5
127.2
127.2
124.5
124.4
96.4
95.1
29.6
29.3
f1 (ppm)

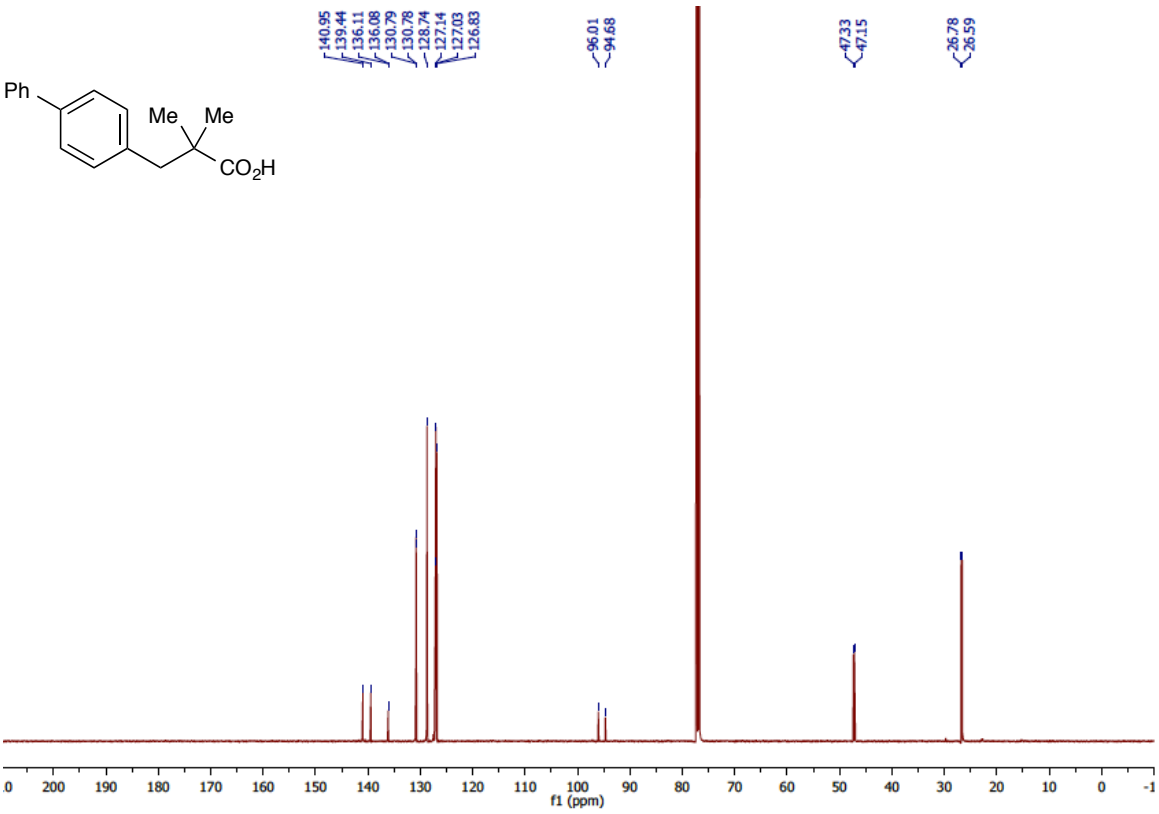

Me
Me
F
Ph
136.8
136.9
136.9
137.0
137.1
137.2
137.2
f1 (ppm)

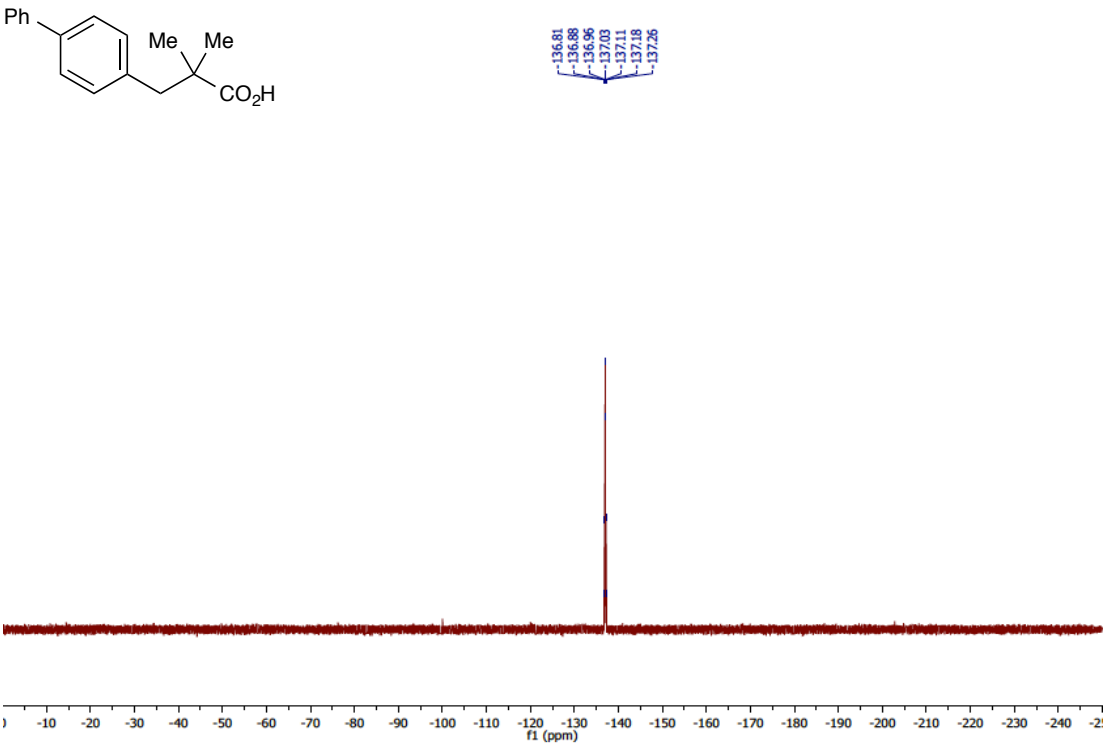

Me
F
N
Bz
5.46
1.00
1.00
1.08
1.12
1.15
3.84
3.47
f1 (ppm)

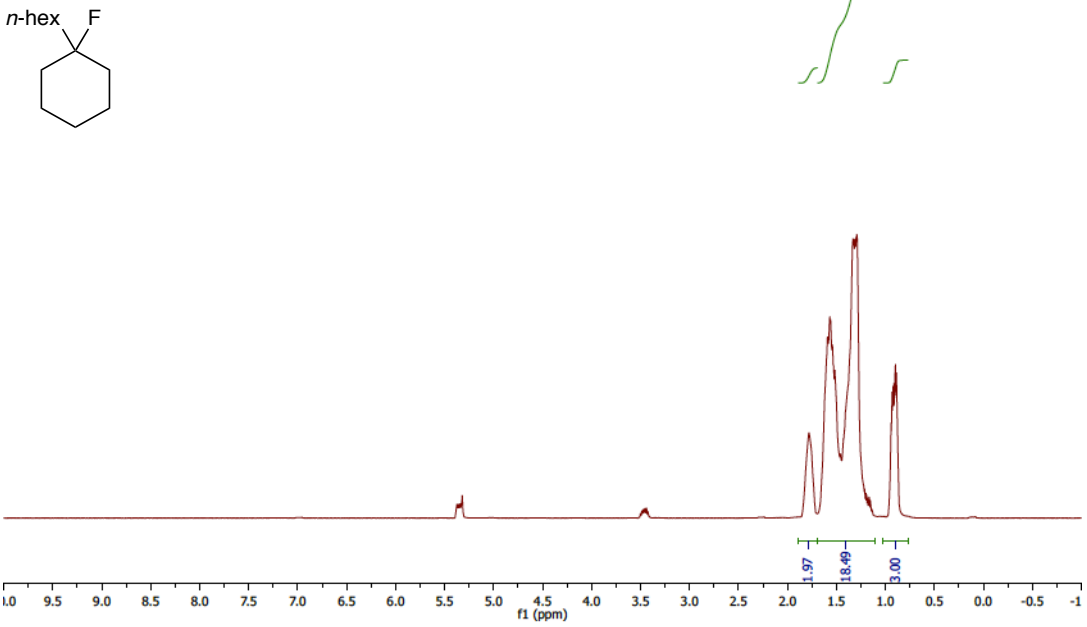

Me
F
N
Bz
170.40
135.93
129.64
128.48
126.81
92.93
91.59
43.72
38.20
37.04
36.87
36.06
35.89
27.13
26.94
f1 (ppm)

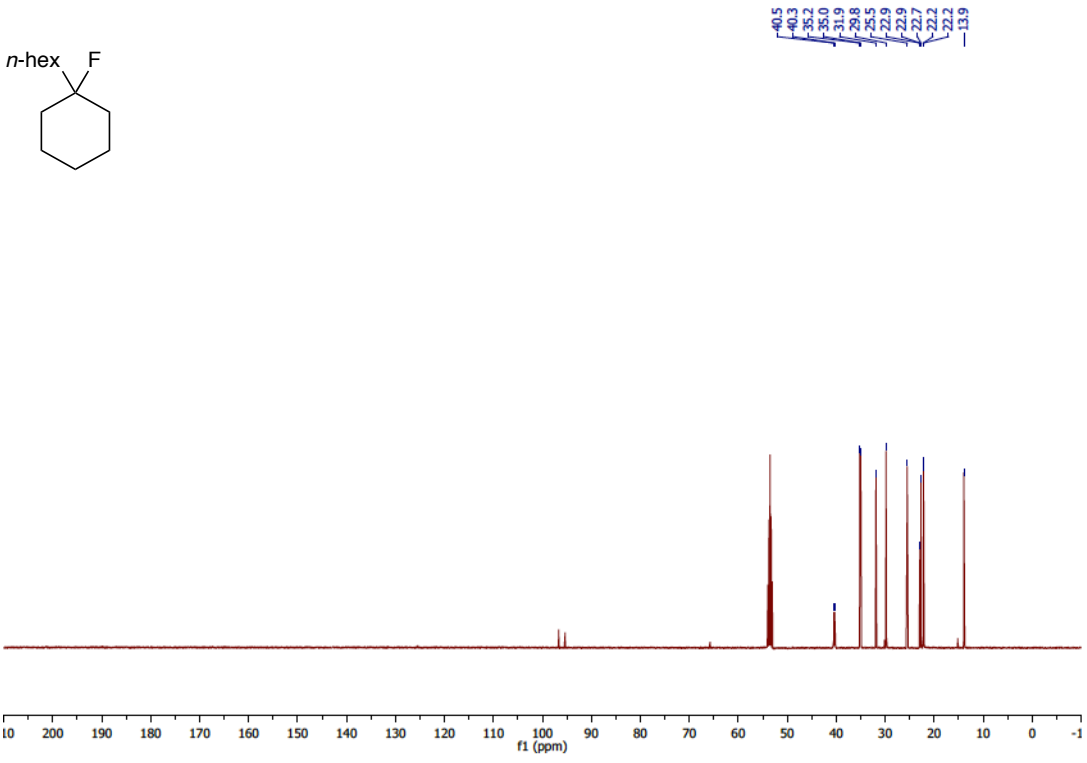

Me
F
N
Bz
153.55
153.58
153.62
153.67
153.71
153.75
153.79
153.82
153.87
153.91
153.95
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

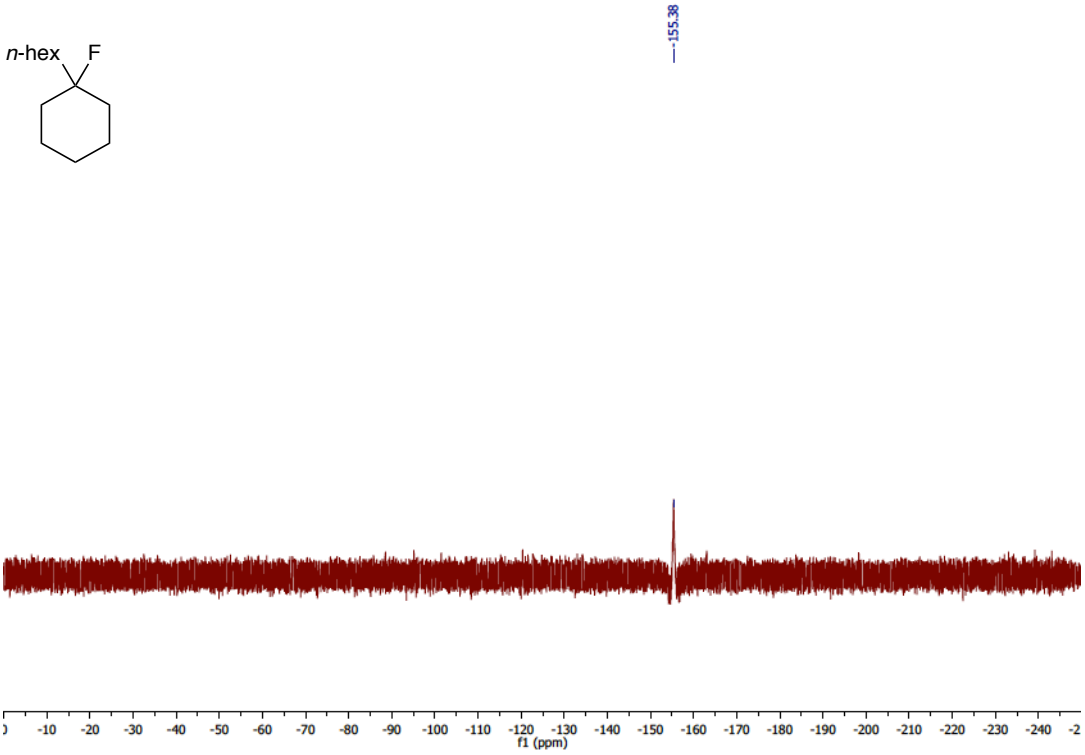

Ph
Me
Me
CO2H
2.19
2.16
2.28
1.00
2.08
2.07
6.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Ph
Me
Me
CO2H
140.95
139.44
136.11
136.08
130.79
130.78
128.74
127.14
127.03
126.83
96.01
94.68
47.33
47.15
26.78
26.59
f1 (ppm)


Ph
Me
Me
CO2H
136.81
136.88
136.96
137.03
137.11
137.18
137.26
f1 (ppm)


n-hex
F
1.97
18.49
3.00
f1 (ppm)


40.5
40.3
35.2
35.0
31.9
29.8
25.5
22.9
22.9
22.7
22.2
22.2
13.9
n-hex
F
f1 (ppm)


n-hex
F
-155.38
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

5. Emission Quenching Experiments (Stern–Volmer Studies)

Emission intensities were recorded using a Perkin Elmer LS50 luminescence spectrophotometer. All $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ solutions were excited at 350 nm and the emission intensity was collected at 475 nm. In a typical experiment, to a $3 \cdot 10^{-6}$ M solution of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ in CH_3CN/H_2O (1:1) was added the appropriate amount of a quencher in a screw-top quartz cuvette. After degassing the sample with a stream of argon for 10 minutes, the emission of the sample was collected.

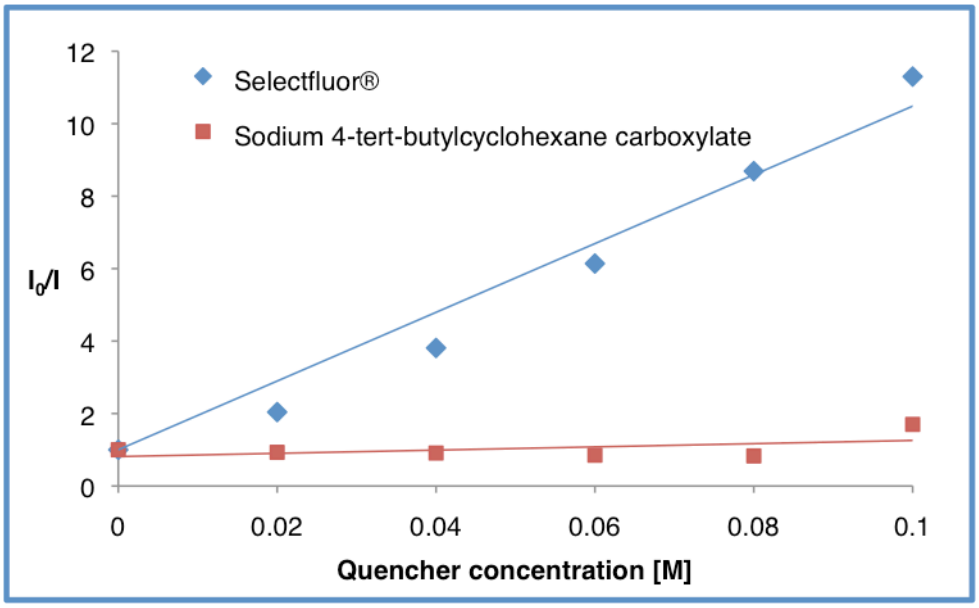


Figure 1. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ emission quenching with Selectfluor® or sodium *tert*-butylcyclohexylcarboxylate.

6. References

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