Supporting Information

Simple generation of various α-monofluoroalkyl radicals by organic photoredox catalysis: modular synthesis of β-monofluoroketones

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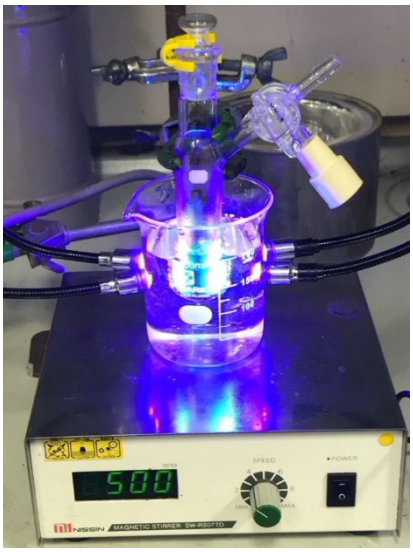
Materials and methods

All the chemicals for synthesis of the substrates and the catalysts were commercially available. All vinyl acetates were prepared according to the reported procedures.[1] All the reactions were carried out with standard Schlenk techniques unless otherwise noted. Anhydrous acetone, acetonitrile, benzene and methanol were purchased from Kanto Chemical Co., Inc. Thin-layer chromatography was performed on TLC plates with 60 F_{254} (Merck). Purification was performed by flash column chromatography on silica gel (Aldrich, silica gel 60 Å). Automated column chromatography was performed using silica gel cartridges (Biotage SNAP Ultra, particle size 25 μm) on a Biotage Isolera One.

Experiments and measurements were carried out with the following apparatuses:

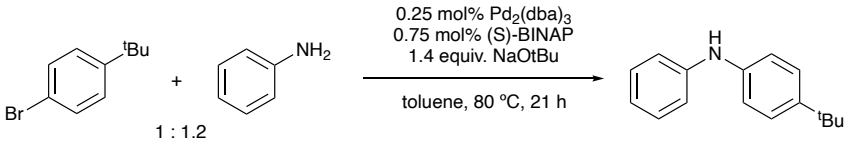
Visible light irradiation: Relyon LED lamp (3 W × 2 or 4: λ = 425 nm, 3 W × 2: λ = 380 nm). NMR spectra: Bruker AVANCE-400 (400 MHz for ^{1}H NMR) and Bruker AVANCE-500 (500 MHz for ^{1}H NMR) (Reference of ^{1}H NMR spectra: Residual protio impurities in the deuterated solvents. Reference of ^{19}F NMR spectra: Trifluoroacetic acid (–76.55 ppm)). EPR spectra: Brucker E-500. HRMS (ESI-TOF): Bruker micrOTOF II. Recycling preparative HPLC: Japan Analytical Industry Co., Ltd. (JAI) LC-9225. (Column: JAIGEL-1H-40 and JAIGEL-2H-40), and Japan Analytical Industry Co., Ltd. (JAI) LC-9201. (Column: JAIGEL-1H-20 and JAIGEL-2H-20). UV-vis: JASCO V-670DS. Fluorescence: HITACHI F-7000. Absolute PL quantum yield: Hamamatsu Photonics C9920-02G with an integration sphere. Excited-state lifetime: Hamamatsu Photonics C7700-ABS-N. Laser flash photolysis was performed with UNISOKU TSP-1000M. CV & DPV: Hokutodenkou HZ-5000. GC-MS(EI): SHIMADZU GC-2010/PARVUM2 (Column: Rxi-5ms). Single-crystal X-ray measurements were made on a Rigaku XtaLAB Synergy R, DW system. The crystallographic data were deposited at Cambridge Crystallographic Data Centre: CCDC 2047104 (**1d**), 2047105 (**1b**), 2047106 (2^{t}Bu-BDN) and 2047107 (**3bl**).

Reaction apparatus



Preparation of organic photoredox catalyst (2^{t}Bu-BDN)

4-(*tert*-Butyl)-*N*-phenylaniline

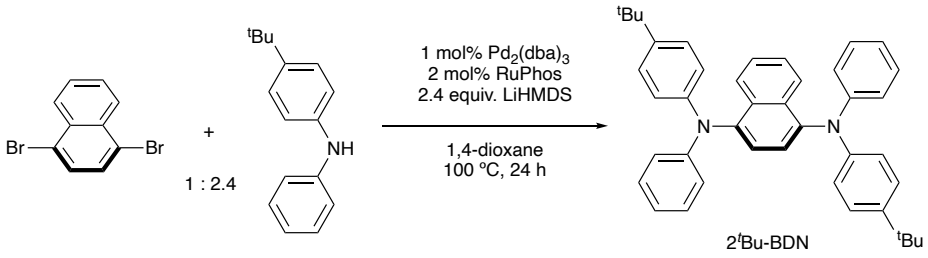


4-(*tert*-Butyl)-*N*-phenylaniline was synthesized according to the reported procedures.[2a] To a mixture of 1-bromo-4-*tert*-butylbenzene (2.13g, 10.0 mmol), aniline (1.14 g, 12.2 mmol), sodium *tert*-butoxide (NaO^{t}Bu) (1.39 g, 14.4 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (22.9 mg, 0.0250 mmol) and (*S*)-BINAP (46.7 mg, 0.0750 mmol) in a two-neck flask was added toluene (20 mL) under N_2 atmosphere. The reaction mixture was stirred at 80 ºC for 21 hours. The solution was then allowed to cool to room temperature, taken up in ether (150 mL), filtered, and concentrated. The desired product was obtained as a brown solid (2.02 g, 8.96 mmol, 95%) after purification by flash column chromatography on silica-gel (hexane/ethyl acetate = 20/1).

The data is in accordance with the reported literature.[2a]

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.31-7.23 (4H), 7.04 (d, 4H, *J* = 8.6 Hz), 6.89 (t, 1H, *J* = 7.3 Hz), 5.63 (brs, 1H), 1.31 (s, 9H).

N^1,*N*^{4}-Bis(4-(*tert*-butyl)phenyl)-*N*^{1},*N*^{4}-diphenylnaphthalene-1,4-diamine (2^{t}Bu-BDN)



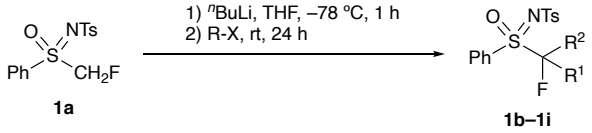
2^{t}Bu-BDN was synthesized according to the reported procedures.[2b] To a mixture of 1,4-dibromonaphthalene (0.428 g, 1.50 mmol), amine (0.827 g, 3.67 mmol), LiHMDS (0.602 g, 3.60 mmol), $Pd_2(dba)_3$ (13.7 mg, 0.0150 mmol) and RuPhos (14.0 mg, 0.0300 mmol) in a two-neck flask was added 1,4-dioxane under N_2 atmosphere. The mixture was stirred at 100 ºC for 24 h. After cooling it to room temperature, precipitates were filtered off and washed with CH_2Cl_2, and the volatiles were evaporated under reduced pressure. The desired product was obtained (0.735 g, 1.28 mmol, 85%) as a pale yellow solid after purification by flash column chromatography on alumina and reprecipitation (methanol/CH_2Cl_2). Recrystallization from CH_2Cl_2 and methanol afforded crystals, which are suitable for single-crystal X-ray structure analysis.

^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ 8.01 (dd, *J* = 6.5 Hz, 3.3 Hz, 2H; naphthalene's *Ar*), 7.34 (dd, *J* = 6.5 Hz,

3.3 Hz, 2H; naphthalene's *Ar*), 7.32 (s, 2H; naphthalene's *Ar*), 7.28-7.17 (8H; *Ar*), 7.04-6.98 (8H; *Ar*), 6.91 (t, *J* = 7.3 Hz, 2H; *Ar*), 1.30 (s, 18H; C*H*$_3$). **^{13}C NMR** (126 MHz, CD_2Cl_2, rt): δ 149.1, 146.0, 145.5, 142.3, 133.3, 129.4, 128.1, 126.8, 126.4, 125.3, 122.5, 121.4, 121.3, 34.5, 31.5. **HRMS** (ESI-TOF) calcd m/z for $[C_{42}H_{42}N_2]^+$ 574.3344, found 574.3345.

Preparation of monofluoroalkylating reagents 1 (Scheme 2)

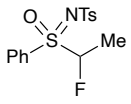
N-((fluoromethyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1a**) was synthesized according to the reported procedures.[2b]



1a **1b–1i**

The synthesis of CR^1FR^2 reagent (**1b**–**1i**) was referred to the reported procedures.[3a] To a solution of **1a** (1.0 equiv.) in THF was added ^{n}BuLi (1.57 M in hexane, 1.2 equiv.) at –78 ºC under N_2 atmosphere. After the mixture was stirred at the same temperature for 1 hour, alkyl halide or tosylate (R-X) (3.0 equiv.) was added at –78 ºC. The mixture was stirred at room temperature for 24 hours. Then, saturated NH_4Cl aq. was added and the water phase was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and removed under reduced pressure. The desired product was obtained after purification by flash column chromatography on silica-gel and reprecipitation (hexane/ethyl acetate) or recycling preparative HPLC.

N-((1-Fluoroethyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1b**)



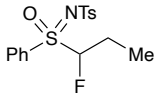
1b

According to the above procedures, **1a** (7.07 g, 21.6 mmol), ^{n}BuLi (1.57 M in hexane, 16.5 mL, 25.9 mmol), iodomethane (9.11 g, 64.2 mmol) and THF (140 mL) afforded **1b** as a white solid (3.69 g, 10.8 mmol, 50%). Eluent: Hexane/ethyl acetate = 2/1. Recrystallization from pentane and Et_2O afforded crystals, which are suitable for single-crystal X-ray structure analysis.

The data is in accordance with the reported literature.[3a]

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.97 (dq, *J* = 46.8, 6.3 Hz, 1H), 2.40 (s, 3H), 1.63 (dd, *J* = 23.0, 6.3 Hz, 3H).

N-((1-Fluoropropyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1c**)



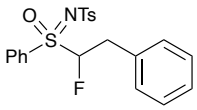
1c

According to the above procedures, **1a** (1.28 g, 3.92 mmol), ^{n}BuLi (1.57 M in hexane, 3.0 mL, 4.71 mmol), iodoethane (1.84 g, 11.8 mmol) and THF (25 mL) afforded **1c** as a white solid (0.212 g, 0.597 mmol, 15%). Eluent: Hexane/ethyl acetate = 3/1.

The data is in accordance with the reported literature.[3b]

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 5.60 (ddd, *J* = 47.3, 10.1, 2.8 Hz, 1H), 2.40 (s, 3H), 2.16 (m, 1H), 1.66 (m, 1H), 1.08 (t, *J* = 7.4 Hz, 3H).

N-((1-Fluoro-2-phenylethyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1d**)



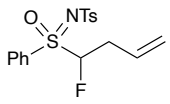
1d

According to the above procedures, **1a** (1.28 g, 3.91 mmol), ^{n}BuLi (1.57 M in hexane, 3.0 mL, 4.71 mmol), benzyl bromide (2.02 g, 11.8 mmol) and THF (25 mL) afforded **1d** as a white solid (0.693 g, 1.66 mmol, 42%). Eluent: Hexane/ethyl acetate = 3/1 → 2/1. Recrystallization from acetone and methanol afforded crystals, which are suitable for single-crystal X-ray structure analysis.

The data is in accordance with the reported literature.[3a]

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 2H), 7.30-7.17 (7H), 5.88 (ddd, *J* = 47.3, 10.5, 1.7 Hz, 1H), 3.48 (m, 1H), 2.89 (m, 1H), 2.41 (s, 3H).

N-((1-Fluorobut-3-en-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1e**)



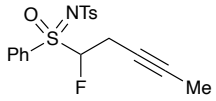
1e

According to the above procedures, **1a** (0.820 g, 2.51 mmol), ^{n}BuLi (1.57 M in hexane, 1.9 mL, 3.02 mmol), allyl iodide (1.26 g, 7.53 mmol) and THF (15 mL) afforded **1e** as a white solid (0.447 g, 1.22 mmol, 49%, diastereomer ratio = 80:20). Eluent: Hexane/ethyl acetate = 3/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.03-7.98 (2H; *Ar* of major and minor), 7.89-7.85 (2H; *Ar* of major and minor), 7.75 (m, 1H; *Ar* of major and minor), 7.64-7.60 (2H; *Ar* of major and minor), 7.27-7.25 (2H; *Ar* of

major and minor), 5.84 (m, 1H; C*H*FCH$_2$CH=CH$_2$ of major and minor), 5.71 (m, 1H; CHFCH$_2$C*H*=CH$_2$ of major and minor), 5.21-5.17 (2H; CHFCH$_2$CH=C*HH* of major and minor), 2.96 (m, 1H; CHFC*H*HCH=CH$_2$ of major and minor), 2.41 (m, 1H; CHFCH*H*CH=CH$_2$ of major and minor), 2.40 (s, 3H; ArC*H*$_3$ of major and minor). **^{13}C NMR** (126 MHz, CDCl$_3$, rt): δ 128.9 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 2.2 Hz), 121.0 (2C), 104.6 (d, *J* = 229.4 Hz), 102.5 (d, *J* = 227.8 Hz), 33.8 (d, *J* = 19.0 Hz), 32.8 (d, *J* = 19.0 Hz), 21.7, Aromatic signals of major and minor diastereomers were overlapped around (143.4, 143.3, 140.5, 135.5, 135.3, 132.2, 132.0, 130.3, 130.0, 129.7, 129.5, 129.4, 126.8). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ −177.4 (m, 1F; major), −177.7 (m, 1F; minor). **HRMS** (ESI-TOF) calcd m/z for [C$_{17}$H$_{18}$FNO$_3$S$_2$+Na]$^+$ 390.0604, found 390.0603.

N-((1-Fluoropent-3-yn-1-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1f**)

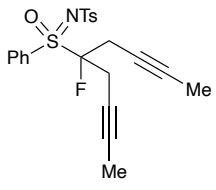


1f

According to the above procedures, **1a** (0.819 g, 2.50 mmol), ^{n}BuLi (1.57 M in hexane, 1.9 mL, 3.02 mmol), 1-bromo-2-butyne (1.00 g, 7.52 mmol) and THF (15 mL) afforded **1f** as a white solid (0.218 g, 0.575 mmol, 23%, diastereomeric ratio = 73:27). Eluent: Hexane/ethyl acetate = 3/1 → 2/1.

^{1}H NMR (400 MHz, CDCl$_3$, rt): δ 8.04-7.98 (2H; *Ar* of major and minor), 7.88-7.84 (2H; *Ar* of major and minor), 7.75 (m, 1H; *Ar* of major and minor), 7.64-7.60 (2H; *Ar* of major and minor), 7.28-7.26 (2H; *Ar* of major and minor), 5.93 (ddd, *J* = 46.4, 8.8, 3.1 Hz, 1H; C*H*FCH$_2$C≡CCH$_3$ of major), 5.83 (ddd, *J* = 46.4, 8.8, 3.2 Hz, 1H; C*H*FCH$_2$C≡CCH$_3$ of minor), 3.19-2.53 (2H; CHFC*HH*C≡CCH$_3$ of major and minor), 2.40 (s, 3H; ArC*H*$_3$ of major and minor), 1.69 (s, 3H; CHFCH$_2$C≡CC*H*$_3$ of major and minor). **^{13}C NMR** (126 MHz, CDCl$_3$, rt): δ 103.0 (d, *J* = 232.3 Hz), 101.0 (d, *J* = 230.8 Hz), 80.7, 80.6, 69.5, 69.4, 21.7, 21.3 (d, *J* = 20.7 Hz), 20.4 (d, *J* = 20.6 Hz), 3.60, 3.57, Aromatic signals of major and minor diastereomers were overlapped around (143.4, 143.3, 140.4, 135.5, 135.4, 131.9, 130.4, 130.1, 129.7, 129.5, 126.8). **^{19}F NMR** (376 MHz, CDCl$_3$, rt): δ −176.2 (m, 1F; major), −176.7 (m, 1F; minor). **HRMS** (ESI-TOF) calcd m/z for [C$_{18}$H$_{18}$FNO$_3$S$_2$+Na]$^+$ 402.0604, found 402.0605.

N-((5-Fluorononona-2,7-diyn-5-yl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1g**)



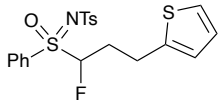
1g

According to the above procedures, **1a** (0.819 g, 2.50 mmol), ^{n}BuLi (1.57 M in hexane, 1.9 mL, 3.02 mmol),

1-bromo-2-butyne (1.00 g, 7.52 mmol) and THF (15 mL) afforded **1g** as a pale yellow solid (0.193 g, 0.447 mmol, 18%). Eluent: Hexane/ethyl acetate = 3/1 → 2/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.06 (d, *J* = 8.2 Hz, 2H; *Ar*), 7.83 (d, *J* = 8.2 Hz, 2H; *Ar*), 7.74 (m, 1H; *Ar*), 7.64-7.60 (2H; *Ar*), 7.24 (d, *J* = 8.2 Hz, 2H; *Ar*), 3.27-2.92 (4H; C*H*$_2$C≡CCH$_3$), 2.40 (s, 3H; ArC*H*$_3$), 1.67-1.64 (6H; CH$_2$C≡CC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 142.9, 140.9, 135.3, 133.5, 131.2, 129.4, 129.3, 126.7, 109.1 (d, *J* = 234.9 Hz), 81.1 (d, *J* = 20.8 Hz), 69.3 (dd, *J* = 9.2, 4.3 Hz), 23.2 (dd, *J* = 123.7, 20.8 Hz), 21.6, 3.6 (d, *J* = 4.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −149.1 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{22}H_{22}FNO_3S_2+Na]^+$ 454.0917, found 454.0917.

N-((1-Fluoro-3-(thiophen-2-yl)propyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1h**)

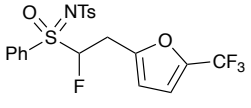


1h

According to the above procedures, **1a** (0.820 g, 2.50 mmol), ^{n}BuLi (1.57 M in hexane, 1.9 mL, 3.02 mmol), 2-(2-thienyl)ethyl *p*-toluenesulfonate (2.13 g, 7.53 mmol) and THF (15 mL) afforded **1h** as a white solid (0.293 g, 0.669 mmol, 27%, diastereomeric ratio = 61:39). Eluent: Hexane/ethyl acetate = 3/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.02-7.97 (2H; *Ar* of major and minor), 7.87-7.83 (2H; *Ar* of major and minor), 7.75 (m, 1H; *Ar* of major and minor), 7.64-7.60 (2H; *Ar* of major and minor), 7.27-7.25 (2H; *Ar* of major and minor), 7.16 (dd, *J* = 5.1, 1.1 Hz, 1H; thiophene's *Ar* of major and minor), 6.92 (m, 1H; thiophene's *Ar* of major and minor), 6.81 (dd, *J* = 10.5, 3.3 Hz, 1H; thiophene's *Ar* of major and minor), 5.74 (m, 1H; C*H*FCH$_2$CH$_2$Ar of major and minor), 3.11-2.95 (2H; CHFCH$_2$C*H*$_2$Ar of major and minor), 2.58 (m, 1H; CHFC*H*HCH$_2$Ar of major and minor), 2.40 (s, 3H; ArC*H*$_3$ of major and minor), 2.01 (m, 1H; CHFCH*H*CH$_2$Ar of major and minor). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 104.5 (d, *J* = 228.0 Hz), 102.5 (d, *J* = 226.3 Hz), 31.1 (d, *J* = 19.3 Hz), 30.5 (d, *J* = 18.9 Hz), 24.8 (d, *J* = 3.7 Hz), 24.8 (d, *J* = 2.6 Hz), 21.7, Aromatic signals of major and minor diastereomers were overlapped around (143.3, 141.1, 141.0, 140.5, 135.4, 135.3, 132.3, 132.2, 130.3, 130.0, 129.8, 129.5, 127.3, 127.2, 126.8, 125.6, 124.3). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −178.5 (m, 1F; major), −178.9 (m, 1F; minor). **HRMS** (ESI-TOF) calcd m/z for $[C_{20}H_{20}FNO_3S_3+Na]^+$ 460.0482, found 460.0482.

N-((1-Fluoro-2-(5-(trifluoromethyl)furan-2-yl)ethyl)(oxo)(phenyl)-λ^6-sulfaneylidene)-4-methylbenzenesulfonamide (**1i**)

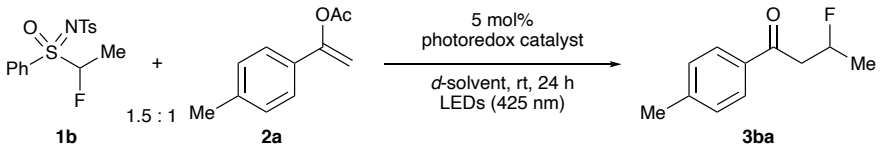


1i

According to the above procedures, **1a** (0.491 g, 1.50 mmol), ^{n}BuLi (1.57 M in hexane, 1.1 mL, 1.80 mmol), 2-(bromomethyl)-5-(trifluoromethyl)furan (1.03 g, 4.50 mmol) and THF (9 mL) afforded **1i** as a white solid (0.221 g, 0.466 mmol, 31%, diastereomeric ratio = 78:22). Eluent: Hexane/ethyl acetate = 3/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.05-8.01 (2H; *Ar* of major and minor), 7.89-7.85 (2H; *Ar* of major and minor), 7.78 (m, 1H; *Ar* of major and minor), 7.67-7.63 (2H; *Ar* of major and minor), 7.29-7.25 (2H; *Ar* of major and minor), 6.68 (d, *J* = 2.9 Hz, 1H; furans's *Ar* of major and minor), 6.25 (d, *J* = 3.2 Hz, 1H; furans's *Ar* of major and minor), 6.05 (m, 1H; C*H*FCH$_2$Ar of major and minor), 3.66 (m, 1H; CHFC*H*HAr of major and minor), 3.11 (m, 1H; CHFCH*H*Ar of major and minor), 2.41 (s, 3H; ArC*H*$_3$ of major and minor). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 149.6 (minor), 149.4 (major), 143.6 (minor), 143.5 (major), 142.01 (q, *J* = 42.8 Hz; major), 141.97 (q, *J* = 42.8 Hz; minor), 140.24 (major), 140.18 (minor), 131.9 (minor), 131.8 (major), 130.2 (minor), 129.93 (major), 129.91 (major), 129.87 (minor), 129.6 (minor), 129.5 (major), 126.82 (minor), 126.77 (major), 118.9 (q, *J* = 266.6 Hz; major and minor), 112.83 (minor), 112.81 (major), 112.79 (major), 112.76 (minor), 110.3 (major), 110.2 (minor), 102.5 (d, *J* = 231.4 Hz), 100.5 (d, *J* = 228.9 Hz), 28.6 (d, *J* = 20.1 Hz), 27.8 (d, *J* = 20.1 Hz), 21.6 (major and minor). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −64.2 (s, 3F; ArC*F*$_3$ of major and minor), −174.8 (m, 1F; minor), −175.8 (m, 1F; major). **HRMS** (ESI-TOF) calcd m/z for $[C_{20}H_{17}F_4NO_4S_2+Na]^+$ 498.0427, found 498.0427.

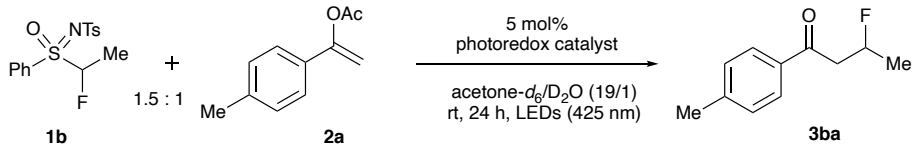
General procedures for NMR experiment (Table 1)

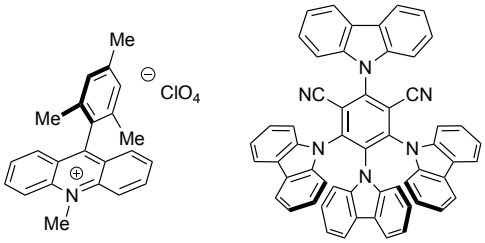


An NMR tube was charged with **2a** (4.4 mg, 25.0 μmol), **1b** (12.8 mg, 37.5 μmol), photoredox catalyst (1.25 μmol) and tetraethylsilane (2 μL) under N_2 atmosphere. Then, deuterated solvent (0.50 mL in total) was added and the mixture was degassed by three freeze-pump-thaw cycles. The NMR tube was placed at 2-3 cm away from blue LED lamps in a water bath. The reaction was carried out under visible light irradiation for 24 hours at room temperature and monitored by NMR spectroscopy.

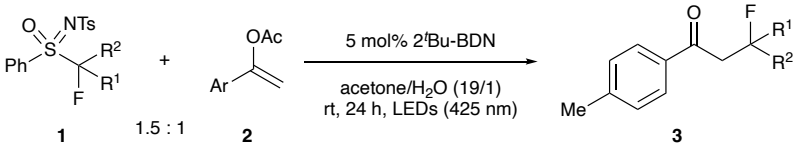
Reactions with other commonly used photocatalysts

We conducted the reactions using Mes-Acr$^+$ (*N*-methyl-9-mesitylacridinium salt) and 4CzIPN (1,2,3,5-tetra(carbazole-9-yl)-4,6-dicyanobenzene) photocatalysts, but the reactions did not proceed at all.



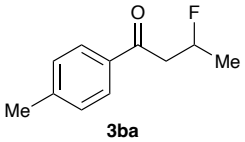


General procedures for fluoroalkylation and characterization (Table 2)



A 20 mL Schlenk tube was charged with vinyl acetate **2** (0.250 mmol), **1** (0.375 mmol), 2^{t}Bu-BDN (12.5–25.0 μmol), acetone (4.75 mL), and H_2O (0.25 mL). The mixture was degassed by three freeze-pump-thaw cycles, and placed at 2-3 cm away from blue LED lamps (λ = 425 nm) in a water bath. The mixture was stirred for 24-72 h at room temperature under visible light irradiation. After the reaction, volatiles were removed *in vacuo*. The desired product was obtained after purification by flash column chromatography on silica-gel and recycling preparative HPLC.

3-Fluoro-1-(4-methylphenyl)butan-1-one (**3ba**)

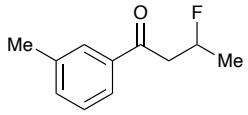


According to the general procedures (reaction time = 24 h), 1-(4-methylphenyl)vinyl acetate **2a** (44.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ba** as a pale yellow oil (33.5 mg, 0.186 mmol, 74%). Eluent: Pentane/diethyl ether = 1/0 → 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.85 (d, *J* = 8.1 Hz, 2H; *Ar*), 7.27 (d, *J* = 8.1 Hz, 2H; *Ar*), 5.30 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.48 (m, 1H; C*H*H), 3.06 (m, 1H; CH*H*), 2.41 (s, 3H, $C_6H_4CH_3$), 1.46 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.6 (d, *J* = 6.7 Hz), 144.4, 134.5, 129.5,

128.4, 87.3 (d, *J* = 165.4 Hz), 45.4 (d, *J* = 22.8 Hz), 21.8, 21.3 (d, *J* = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{11}H_{13}FO+Na]^+$ 203.0843, found 203.0846.

3-Fluoro-1-(3-methylphenyl)butan-1-one (**3bb**)

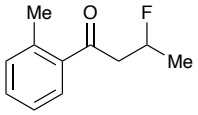


3bb

According to the general procedures (reaction time = 24 h), 1-(3-methylphenyl)vinyl acetate **2b** (44.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bb** as a pale yellow oil (25.9 mg, 0.144 mmol, 58%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.76-7.74 (2H; *Ar*), 7.40-7.34 (2H; *Ar*), 5.30 (dq, *J* = 47.5 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.49 (m, 1H; C*H*H), 3.07 (m, 1H; CH*H*), 2.41 (s, 3H, $C_6H_4CH_3$), 1.47 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 197.2 (d, *J* = 6.7 Hz), 138.6, 137.0, 134.3, 128.8, 128.7, 125.5, 87.4 (d, *J* = 165.5 Hz), 45.5 (d, *J* = 22.9 Hz), 21.5, 21.3 (d, *J* = 22.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.6 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{11}H_{13}FO+Na]^+$ 203.0843, found 203.0843.

3-Fluoro-1-(2-methylphenyl)butan-1-one (**3bc**)

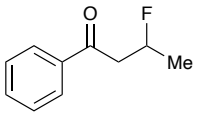


3bc

According to the general procedures (reaction time = 72 h), 1-(2-methylphenyl)vinyl acetate **2c** (44.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (14.4 mg, 25.0 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bc** as a pale yellow oil (17.9 mg, 0.0993 mmol, 40%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.64 (d, *J* = 7.5 Hz, 1H; *Ar*), 7.39 (m, 1H; *Ar*), 7.29-7.25 (2H; *Ar*), 5.27 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.41 (m, 1H; C*H*H), 3.02 (m, 1H; CH*H*), 2.51 (s, 3H, $C_6H_4CH_3$), 1.46 (dd, *J* = 24.0 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 200.8 (d, *J* = 5.8 Hz), 138.5, 137.7, 132.2, 131.8, 128.7, 125.9, 87.5 (d, *J* = 165.3 Hz), 48.4 (d, *J* = 22.9 Hz), 21.4, 21.2 (d, *J* = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.7 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{11}H_{13}FO+Na]^+$ 203.0843, found 203.0842.

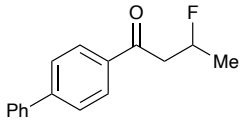
3-Fluoro-1-phenylbutan-1-one (**3bd**)



3bd

According to the general procedures (reaction time = 24 h), 1-phenylvinyl acetate **2d** (40.5 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bd** as a pale yellow oil (31.4 mg, 0.189 mmol, 76%). Eluent: Pentane/diethyl ether = 1/0 → 9/1. **^{1}H NMR** (400 MHz, $CDCl_3$, rt): δ 7.96 (d, *J* = 7.5 Hz, 2H; *Ar*), 7.58 (t, *J* = 7.5 Hz, 1H; *Ar*), 7.47 (t, *J* = 7.5 Hz, 2H; *Ar*), 5.31 (dq, *J* = 47.5 Hz, 6.2 Hz, 1H; C*H*F), 3.51 (m, 1H; C*H*H), 3.09 (m, 1H; CH*H*), 1.47 (dd, *J* = 24.2 Hz, 6.2 Hz, 3H; CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 197.0 (d, *J* = 6.7 Hz), 136.9, 133.5, 128.8, 128.3, 87.3 (d, *J* = 165.3 Hz), 45.5 (d, *J* = 23.0 Hz), 21.3 (d, *J* = 22.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.6 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{10}H_{11}FO+Na]^+$ 189.0686, found 189.0687.

1-([1,1'-Biphenyl]-4-yl)-3-fluorobutan-1-one (**3be**)

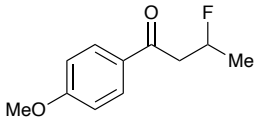


3be

According to the general procedures (reaction time = 24 h), 1-([1,1'-biphenyl]-4-yl)vinyl acetate **2e** (59.6 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3be** as a white solid (44.4 mg, 0.183 mmol, 73%). Eluent: Pentane/diethyl ether = 1/0 → 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.04 (d, *J* = 8.3 Hz, 2H; *Ar*), 7.70 (d, *J* = 8.3 Hz, 2H; *Ar*), 7.63 (d, *J* = 7.4 Hz, 2H; *Ar*), 7.48 (t, *J* = 7.4 Hz, 2H; *Ar*), 7.41 (t, *J* = 7.4 Hz, 1H; *Ar*), 5.34 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*F), 3.55 (m, 1H; C*H*H), 3.12 (m, 1H; CH*H*), 1.50 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.6 (d, *J* = 6.7 Hz), 146.3, 139.9, 135.6, 129.1, 128.9, 128.5, 127.5, 127.4, 87.4 (d, *J* = 165.5 Hz), 45.6 (d, *J* = 22.8 Hz), 21.4 (d, *J* = 22.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{16}H_{15}FO+Na]^+$ 265.0999, found 265.0997.

3-Fluoro-1-(4-methoxyphenyl)butan-1-one (**3bf**)



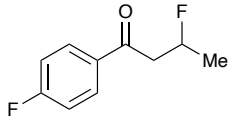
3bf

According to the general procedures (reaction time = 24 h), 1-(4-methoxyphenyl)vinyl acetate **1f** (48.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bf** as a pale yellow oil (37.5 mg, 0.191 mmol, 76%). Eluent: Pentane/diethyl ether = 1/0 →

9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.93 (d, *J* = 8.8 Hz, 2H; *Ar*), 6.93 (d, *J* = 8.8 Hz, 2H; *Ar*), 5.28 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.86 (s, 3H; OC*H*$_3$), 3.45 (m, 1H; C*H*H), 3.02 (m, 1H; CH*H*), 1.45 (dd, *J* = 24.2 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.4 (d, *J* = 6.6 Hz), 163.8, 130.5, 130.0, 113.8, 87.4 (d, *J* = 165.2 Hz), 55.5, 45.1 (d, *J* = 22.8 Hz), 21.2 (d, *J* = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.4 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{11}H_{13}FO_2+Na]^+$ 219.0792, found 219.0792.

3-Fluoro-1-(4-fluorophenyl)butan-1-one (**3bg**)

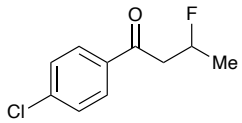


3bg

According to the general procedures (reaction time = 24 h), 1-(4-fluorophenyl)vinyl acetate **2g** (45.0 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bg** as a pale yellow oil (33.7 mg, 0.183 mmol, 73%). Eluent: Pentane/diethyl ether = 1/0 → 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.98 (dd, *J* = 8.7 Hz, 5.5 Hz, 2H; *Ar*), 7.14 (dd, *J* = 8.7 Hz, 8.7 Hz, 2H; *Ar*), 5.29 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*F), 3.47 (m, 1H; C*H*H), 3.04 (m, 1H; CH*H*), 1.47 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; C*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.4 (d, *J* = 6.3 Hz), 166.1 (d, *J* = 255.3 Hz), 133.5, 131.0 (d, *J* = 9.4 Hz), 115.9 (d, *J* = 21.9 Hz), 87.3 (d, *J* = 165.8 Hz), 45.5 (d, *J* = 23.1 Hz), 21.3 (d, *J* = 22.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −105.6 (m, 1F; C_6H_4F), −173.5 (m, 1F; CH*F*). **HRMS** (ESI-TOF) calcd m/z for $[C_{10}H_{10}F_2O+Na]^+$ 207.0592, found 207.0593.

1-(4-Chlorophenyl)-3-fluorobutan-1-one (**3bh**)



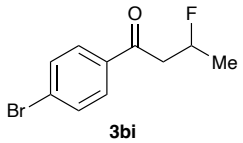
3bh

According to the general procedures (reaction time = 24 h), 1-(4-chlorophenyl)vinyl acetate **2h** (49.2 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bh** as a pale yellow oil (35.5 mg, 0.177 mmol, 71%). Eluent: Pentane/diethyl ether = 1/0 → 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.89 (d, *J* = 8.6 Hz, 2H; *Ar*), 7.44 (d, *J* = 8.6 Hz, 2H; *Ar*), 5.28 (dq, *J* = 47.5 Hz, 6.2 Hz, 1H; C*H*F), 3.46 (m, 1H; C*H*H), 3.04 (m, 1H; CH*H*), 1.47 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; C*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.8 (d, *J* = 6.0 Hz), 140.1, 135.2, 129.7, 129.1, 87.2 (d, *J* = 165.8 Hz), 45.4 (d, *J* = 23.2 Hz), 21.3 (d, *J* = 22.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF)

calcd m/z for $[C_{10}H_{10}ClFO+Na]^+$ 223.0296, found 223.0298.

1-(4-Bromophenyl)-3-fluorobutan-1-one (**3bi**)

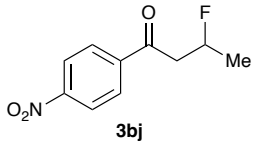


3bi

According to the general procedures (reaction time = 48 h), 1-(4-bromophenyl)vinyl acetate **2i** (60.3 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2*t*Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bi** as a pale yellow solid (40.6 mg, 0.166 mmol, 66%). Eluent: Pentane/diethyl ether = 1/0 → 9/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.82 (d, *J* = 8.5 Hz, 2H; *Ar*), 7.62 (d, *J* = 8.5 Hz, 2H; *Ar*), 5.29 (dq, *J* = 47.4 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.46 (m, 1H; C*H*H), 3.04 (m, 1H; CH*H*), 1.47 (dd, *J* = 24.1 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.0 (d, *J* = 6.1 Hz), 135.6, 132.1, 129.8, 128.8, 87.2 (d, *J* = 165.8 Hz), 45.4 (d, *J* = 23.1 Hz), 21.3 (d, *J* = 22.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{10}H_{10}BrFO+Na]^+$ 266.9791, found 266.9789.

3-Fluoro-1-(4-nitrophenyl)butan-1-one (**3bj**)

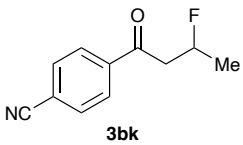


3bj

According to the general procedures (reaction time = 48 h), 1-(4-nitrophenyl)vinyl acetate **2j** (51.8 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2*t*Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bj** as a pale yellow oil (12.2 mg, 0.0578 mmol, 23%). Eluent: Pentane/diethyl ether = 9/1 → 0/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.33 (d, *J* = 8.8 Hz, 2H; *Ar*), 8.11 (d, *J* = 8.8 Hz, 2H; *Ar*), 5.31 (dq, *J* = 47.5 Hz, *J* = 6.2 Hz, 1H; C*H*FCH$_3$), 3.53 (m, 1H; C*H*H), 3.11 (m, 1H; CH*H*), 1.50 (dd, *J* = 24.2 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.6 (d, *J* = 5.8 Hz), 150.6, 141.3, 129.4, 124.1, 87.0 (d, *J* = 166.5 Hz), 46.0 (d, *J* = 23.4 Hz), 21.2 (d, *J* = 22.3 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{10}H_{10}FNO_3+Na]^+$ 234.0537, found 234.0535.

4-(3-Fluorobutanoyl)benzonitrile (**3bk**)

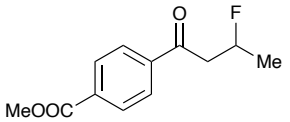


3bk

According to the general procedures (reaction time = 48 h), 1-(4-cyanophenyl)vinyl acetate **2k** (46.8 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bk** as a pale yellow oil (23.5 mg, 0.123 mmol, 49%). Eluent: Pentane/diethyl ether = 9/1 → 0/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.05 (d, *J* = 8.4 Hz, 2H; *Ar*), 7.79 (d, *J* = 8.4 Hz, 2H; *Ar*), 5.30 (dq, *J* = 47.4 Hz, 6.1 Hz, 1H; C*H*FCH$_3$), 3.50 (m, 1 H; C*H*H), 3.08 (m, 1H; CH*H*), 1.49 (dd, *J* = 24.0 Hz, 6.1 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.8 (d, *J* = 5.8 Hz), 139.8, 132.7, 128.7, 117.9, 116.8, 87.0 (d, *J* = 166.3 Hz), 45.7 (d, *J* = 23.0 Hz), 21.2 (d, *J* = 22.5 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{11}H_{10}FNO+Na]^+$ 214.0639, found 214.0640.

Methyl 4-(3-fluorobutanoyl)benzoate (**3bl**)

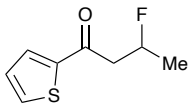


3bl

According to the general procedures (reaction time = 24 h), methyl 4-(1-acetoxyvinyl)benzoate **2l** (55.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bl** as a white solid (35.4 mg, 0.158 mmol, 63%). Eluent: Pentane/diethyl ether = 19/1 → 1/1. Recrystallization from methanol afforded crystals, which are suitable for single-crystal X-ray structure analysis.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.14 (d, *J* = 8.4 Hz, 2H; *Ar*), 8.01 (d, *J* = 8.4 Hz, 2H; *Ar*), 5.31 (dq, *J* = 47.5 Hz, 6.1 Hz, 1H; C*H*FCH$_3$), 3.96 (s, 3H, COOC*H*$_3$), 3.53 (m, 1H; C*H*H), 3.10 (m, 1H; CH*H*), 1.49 (dd, *J* = 24.1 Hz, 6.1 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.5 (d, *J* = 6.0 Hz), 166.2, 140.0, 134.3, 130.0, 128.2, 87.1 (d, *J* = 165.9 Hz), 52.6, 45.8 (d, *J* = 23.0 Hz), 21.3 (d, *J* = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.6 (m, 1F); **HRMS** (ESI-TOF) calcd m/z for $[C_{12}H_{13}FO_3+Na]^+$ 247.0741, found 247.0738.

3-Fluoro-1-(thiophen-2-yl)butan-1-one (**3bm**)



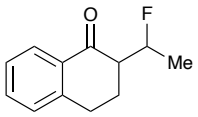
3bm

According to the general procedures (reaction time = 24 h), 1-(thiophen-2-yl)vinyl acetate **2m** (42.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bm** as a pale yellow oil (25.7 mg, 0.149 mmol, 60%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.74 (dd, *J* = 3.9 Hz, 0.7 Hz, 1H; *Ar*), 7.67 (dd, *J* = 4.8 Hz, 0.7 Hz, 1H; *Ar*),

7.15 (dd, *J* = 4.8, 3.9 Hz, 1H; *Ar*), 5.27 (dq, *J* = 47.6 Hz, 6.2 Hz, 1H; C*H*FCH$_3$), 3.42 (m, 1H; C*H*H), 3.02 (m, 1H; CH*H*), 1.47 (dd, *J* = 24.0 Hz, 6.2 Hz, 3H; CHFC*H*$_3$). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 189.7 (d, *J* = 6.5 Hz), 144.4 (d, *J* = 1.3 Hz), 134.5, 132.7, 128.4, 87.3 (d, *J* = 166.7 Hz), 46.3 (d, *J* = 23.2 Hz), 21.3 (d, *J* = 22.4 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −173.0 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_8H_9FOS+Na]^+$ 195.0250, found 195.0248.

2-(1-Fluoroethyl)-3,4-dihydronaphthalen-1(2*H*)-one (**3bn**)

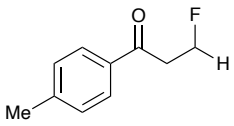


3bn

According to the general procedures (reaction time = 72 h), 3,4-dihydronaphthalen-1-yl acetate **2n** (47.1 mg, 0.250 mmol), **1b** (128 mg, 0.375 mmol), 2^{t}Bu-BDN (14.4 mg, 25.0 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3bn** as a colorless oil (18.0 mg, 0.0936 mmol, 37%, diastereomer ratio = 53:47). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.05–8.00 (1H; *Ar* of major and minor), 7.50–7.46 (1H; *Ar* of major and minor), 7.33–7.25 (2H; *Ar* of major and minor), 5.43 (m, 1H; C*H*FCH$_3$ of major and minor), 3.12-2.47 (2H; C*H*HCH$_2$CH, CH*H*CH$_2$CH of major and minor), 3.03 (m, 1H; CH$_2$CH$_2$C*H* of major and minor), 2.35 (m, 1H; CH$_2$C*H*HCH of major and minor), 2.08 (m, 1H; CH$_2$CH*H*CH of major and minor), 1.48 (dd, *J* = 24.5 Hz, 6.4 Hz, 3H; CHFC*H*$_3$ of major), 1.36 (dd, *J* = 24.7 Hz, 6.4 Hz, 3H; CHFC*H*$_3$ of minor). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 197.2 (d, *J* = 11.3 Hz), 196.9 (d, *J* = 3.5 Hz), 89.8 (d, *J* = 161.3 Hz), 88.2 (d, *J* = 166.7 Hz), 53.0 (d, *J* = 21.4 Hz), 52.4 (d, *J* = 22.4 Hz), 28.9, 28.5, 23.1 (brs), 22.8 (d, *J* = 6.0 Hz), 19.4 (d, *J* = 22.6 Hz), 16.6 (d, *J* = 22.7 Hz). Aromatic signals of major and minor diastereomers were overlapped around (144.2, 144.1, 133.7, 132.8, 132.7, 128.9, 128.8, 127.7, 127.4, 126.8). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ –184.2 (m, 1F; major), −184.8 (m, 1F; minor). **HRMS** (ESI-TOF) calcd m/z for $[C_{12}H_{13}FO+Na]^+$ 215.0843, found 215.0843.

3-Fluoro-1-(*p*-tolyl)propan-1-one (**3aa**)



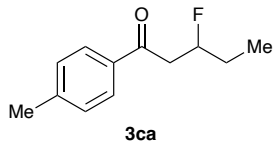
3aa

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1a** (123 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3aa** as a pale yellow oil (33.5 mg, 0.202 mmol, 81%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.87 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 4.90 (dt, *J* = 46.6 Hz, *J*

= 6.1 Hz, 2H), 3.36 (dt, *J* = 22.2 Hz, 6.1 Hz, 2H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.4 (d, *J* = 5.5 Hz), 144.5, 134.3, 129.5, 128.4, 79.5 (d, *J* = 165.0 Hz), 38.9 (d, *J* = 21.5 Hz), 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −222.1 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{10}H_{11}FO+Na]^+$ 189.0686, found 189.0687.

3-Fluoro-1-(*p*-tolyl)pentan-1-one (**3ca**)

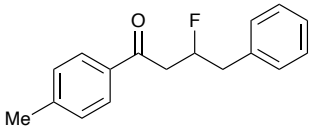


3ca

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1c** (133 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ca** as a pale yellow oil (31.0 mg, 0.160 mmol, 64%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.09 (dquin, *J* = 48.0 Hz, 6.0 Hz, 1H), 3.44 (m, 1H), 3.05 (m, 1H), 2.42 (s, 3H), 1.82-1.69 (2H), 1.04 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.8 (d, *J* = 5.4 Hz), 144.3, 134.7, 129.4, 128.4, 91.7 (d, *J* = 168.4 Hz), 43.4 (d, *J* = 23.0 Hz), 28.4 (d, *J* = 21.1 Hz), 21.7, 9.4 (d, *J* = 5.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −182.2 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{12}H_{15}FO+Na]^+$ 217.0999, found 217.1000.

3-Fluoro-4-phenyl-1-(*p*-tolyl)butan-1-one (**3da**)

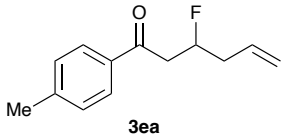


3da

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1d** (157 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3da** as a pale yellow solid (49.4 mg, 0.193 mmol, 77%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.33-7.25 (7H), 5.39 (dquin, *J* = 47.2 Hz, 6.0 Hz, 1H), 3.47-3.03 (2H), 3.14-3.07 (2H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.6 (d, *J* = 6.0 Hz), 144.4, 136.7 (d, *J* = 4.1 Hz), 134.5, 129.7, 129.5, 128.6, 128.4, 126.9, 90.7 (d, *J* = 171.3 Hz), 42.8 (d, *J* = 23.1 Hz), 41.3 (d, *J* = 21.0 Hz), 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −179.6 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{17}H_{17}FO+Na]^+$ 279.1156, found 279.1154.

3-Fluoro-1-(*p*-tolyl)hex-5-en-1-one (**3ea**)

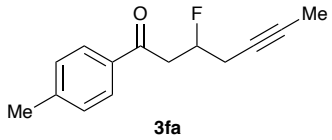


3ea

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1e** (138 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ea** as a colorless oil (31.6 mg, 0.153 mmol, 61%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.87 (m, 1H), 5.23 (m, 1H), 5.21-5.15 (2H), 3.43 (m, 1H), 3.10 (m, 1H), 2.58-2.48 (2H), 2.41 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.4 (d, *J* = 5.8 Hz), 144.3, 134.4, 132.6 (d, *J* = 5.7 Hz), 129.4, 128.3, 118.7, 89.5 (d, *J* = 170.1 Hz), 42.8 (d, *J* = 23.2 Hz), 39.4 (d, *J* = 21.2 Hz), 21.7. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −180.9 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{13}H_{15}FO+Na]^+$ 229.0999, found 229.1001.

3-Fluoro-1-(*p*-tolyl)hept-5-yn-1-one (**3fa**)

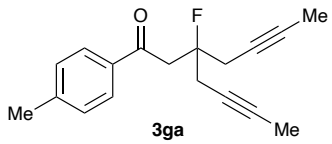


3fa

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1f** (142 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3fa** as a pale yellow oil (34.4 mg, 0.158 mmol, 63%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.24 (dquin, *J* = 47.0 Hz, 5.8 Hz, 1H), 3.53-3.29 (2H), 2.71-2.63 (2H), 2.42 (s, 3H), 1.79 (t, *J* = 2.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.3 (d, *J* = 5.4 Hz), 144.5, 134.4, 129.5, 128.4, 88.3 (d, *J* = 173.3 Hz), 79.1, 73.3 (d, *J* = 10.0 Hz), 42.4 (d, *J* = 22.6 Hz), 25.4 (d, *J* = 24.8 Hz), 21.8, 3.6. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −179.0 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{14}H_{15}FO+Na]^+$ 241.0999, found 241.1000.

3-(But-2-yn-1-yl)-3-fluoro-1-(*p*-tolyl)hept-5-yn-1-one (**3ga**)

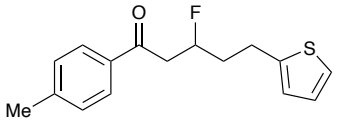


3ga

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1g** (162 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ga** as a pale yellow solid (38.1 mg, 0.141 mmol, 56%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 3.56 (d, *J* = 14.5 Hz, 2H), 2.86-2.79 (4H), 2.42 (s, 3H), 1.77 (t, *J* = 2.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.2 (d, *J* = 9.6 Hz), 144.2, 134.9 (d, *J* = 2.5 Hz), 129.3, 128.5, 95.4 (d, *J* = 180.7 Hz), 79.1, 73.5 (d, *J* = 5.8 Hz), 43.3 (d, *J* = 23.5 Hz), 28.4 (d, *J* = 24.2 Hz), 21.7, 3.6. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −146.5 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{18}H_{19}FO+Na]^+$ 293.1312, found 293.1312.

3-Fluoro-5-(thiophen-2-yl)-1-(*p*-tolyl)pentan-1-one (**3ha**)

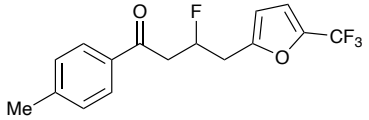


3ha

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1h** (164 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ha** as a white solid (46.3 mg, 0.168 mmol, 67%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 4.2 Hz, 2.2 Hz, 1H), 6.93 (d, *J* = 4.2 Hz, 2.2 Hz, 1H), 6.84 (d, *J* = 4.2 Hz, 2.2 Hz, 1H), 5.21 (dquin, *J* = 48.1 Hz, 6.1 Hz, 1H), 3.54-2.97 (2H), 3.14-2.97 (2H), 2.42 (s, 3H), 2.16-2.03 (2H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 196.4 (d, *J* = 5.8 Hz), 144.5, 143.9, 134.4, 129.5, 128.4, 126.9, 124.7, 123.4, 89.6 (d, *J* = 168.9 Hz), 43.7 (d, *J* = 23.0 Hz), 37.4 (d, *J* = 20.8 Hz), 25.6 (d, *J* = 4.3 Hz), 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −183.2 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{16}H_{17}FOS+Na]^+$ 299.0876, found 299.0877.

3-Fluoro-1-(*p*-tolyl)-4-(5-(trifluoromethyl)furan-2-yl)butan-1-one (**3ia**)



3ia

According to the general procedures (reaction time = 24 h), **2a** (44.1 mg, 0.250 mmol), **1i** (178 mg, 0.375 mmol), 2^{t}Bu-BDN (7.2 mg, 12.5 μmol), acetone (4.75 mL) and H_2O (0.25 mL) afforded **3ia** as a white solid (56.3 mg, 0.179 mmol, 72%). Eluent: Pentane/diethyl ether = 1/0 → 4/1.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 2.6 Hz, 1H), 6.27 (d, *J* = 2.6 Hz, 1H), 5.44 (dquin, *J* = 47.0 Hz, 5.9 Hz, 1H), 3.53-3.09 (2H), 3.26-3.09 (2H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, rt): δ 195.9 (d, *J* = 6.6 Hz), 153.9, 144.7, 141.2 (q, *J* = 42.8 Hz), 134.2 (d, *J* = 1.3 Hz), 129.6, 128.4, 119.2 (q, *J* = 266.6 Hz), 112.7 (q, *J* = 2.7 Hz), 108.9, 88.0 (d, *J* = 172.7 Hz), 42.8 (d, *J* = 22.7 Hz), 33.7 (d, *J* = 22.7 Hz), 21.8. **^{19}F NMR** (376 MHz, $CDCl_3$, rt): δ −65.0 (m, 3F), −180.6 (m, 1F). **HRMS** (ESI-TOF) calcd m/z for $[C_{16}H_{14}F_4O_2+Na]^+$ 337.0822, found 337.0824.

Photo- and electro-chemical measurements

The measurements of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of 2^{t}Bu-BDN were performed in acetone ([2^{t}Bu-BDN] = 1.0 mM, [$(NBu_4)PF_6$] = 0.10 M) with platinum disk(working electrode), wire electrodes (counter electrode) and a $Ag/AgNO_3$ reference electrode. The scan rates were 100 mV/s. Ferrocene was used as a reference.

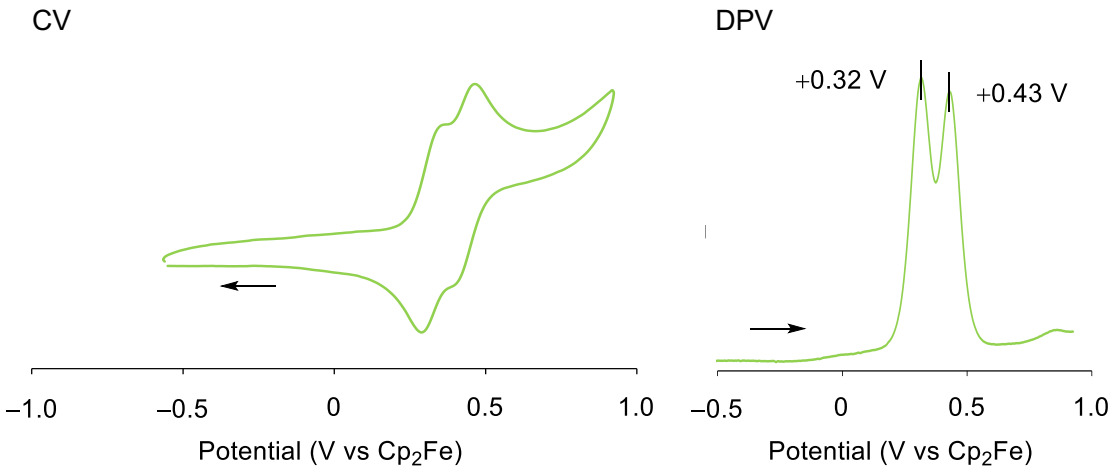


Figure S1. CV and DPV of 2^{t}Bu-BDN.

The measurements of UV-vis spectra of naphthalene-based photoredox catalysts (2^{t}Bu-BDN) were performed in acetone ([2^{t}Bu-BDN] = 1.0 × 10^{-4} M) under air at room temperature.

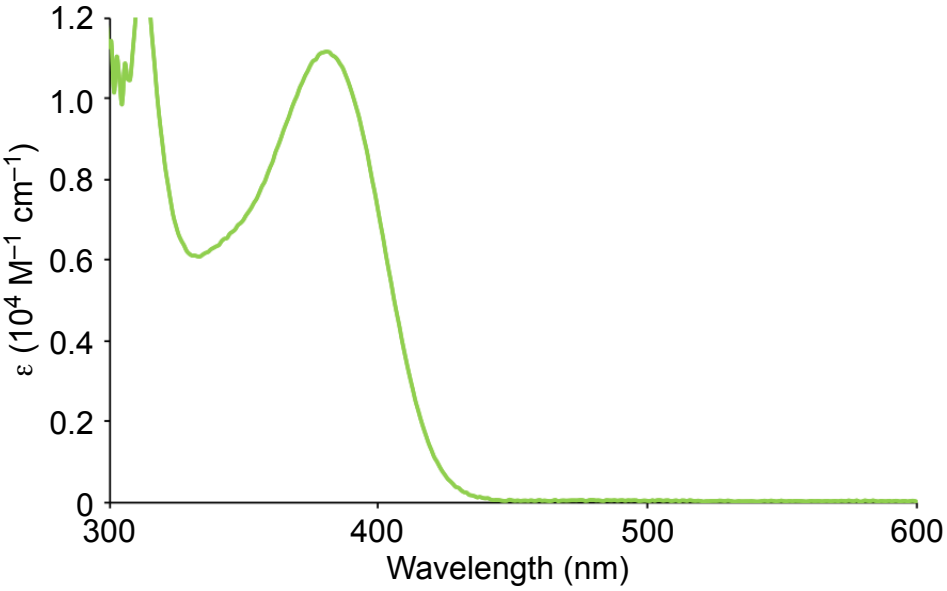


Figure S2. UV-vis spectrum of 2^{t}Bu-BDN.

The luminescence measurement (Ex: 370 nm) of naphthalene-based photoredox catalysts (2^{t}Bu-BDN) was performed in acetone ([2^{t}Bu-BDN] = 1.0 × 10^{-5} M) under N_2 at room temperature.

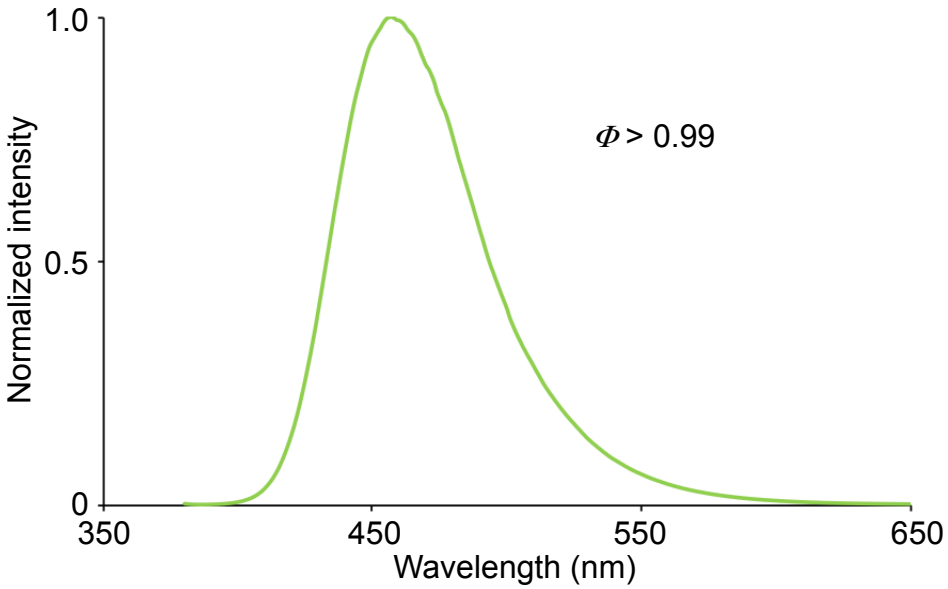


Figure S3. Fluorescence spectrum of 2^{t}Bu-BDN.

The measurements of cyclic voltammetry of CR^1FR^2-reagents (**1b**–**1k**) were performed in acetone ([**1**] = 5.0 mM, $[(NBu_4)PF_6]$ = 0.10 M) with platinum disk (working electrode), wire electrodes (counter electrode) and a $Ag/AgNO_3$ reference electrode. The scan rates were 100 mV/s. Ferrocene was used as a reference.

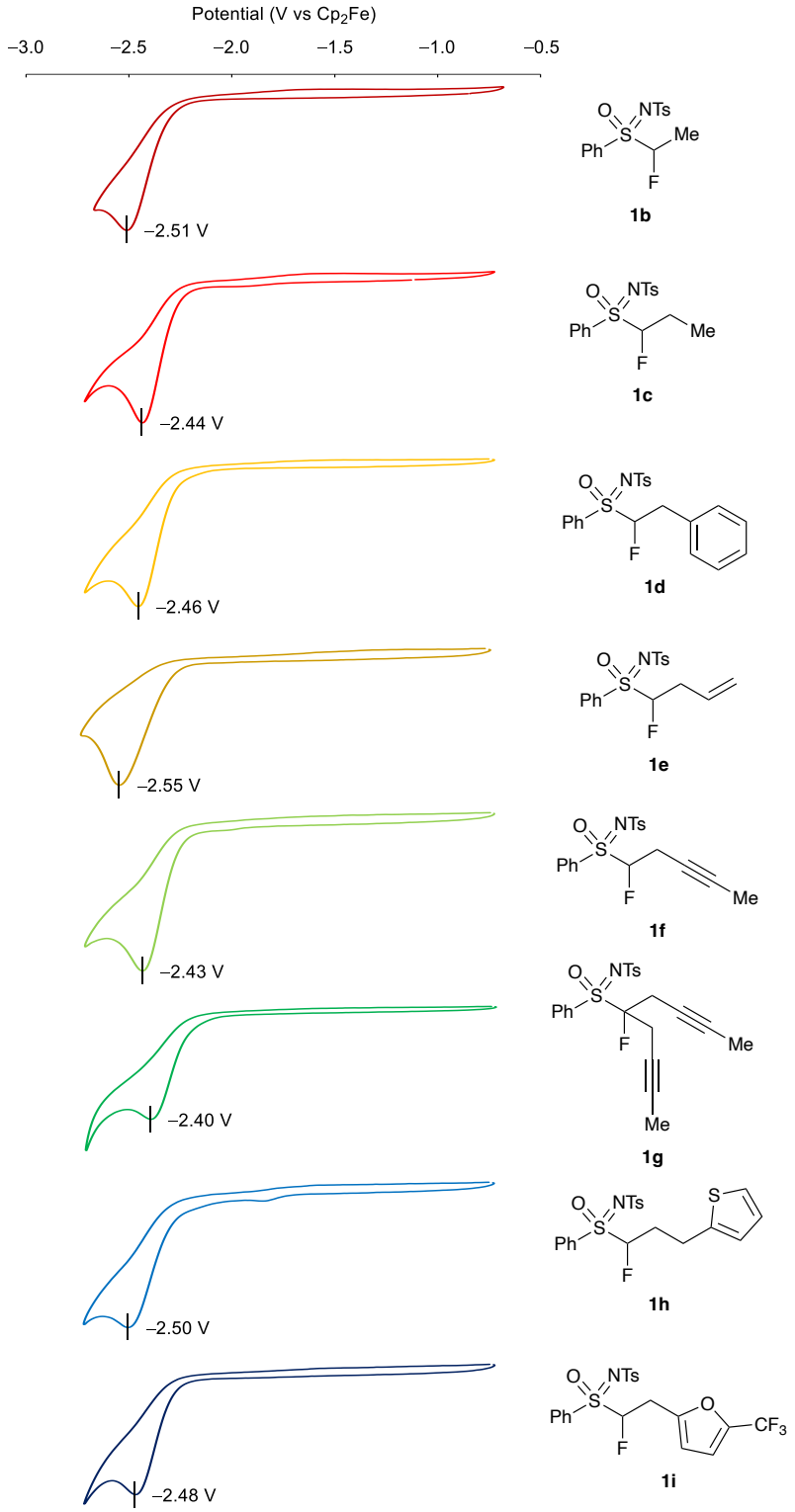


Figure S4. CV of reagents.

Luminescence quenching experiments

Luminescence quenching experiments of 2^{t}Bu-BDN were performed in acetone ([2^{t}Bu-BDN] = 1.0 × 10^{-4} M) at room temperature. The solutions were degassed by three freeze-pump-thaw cycles before the measurements.

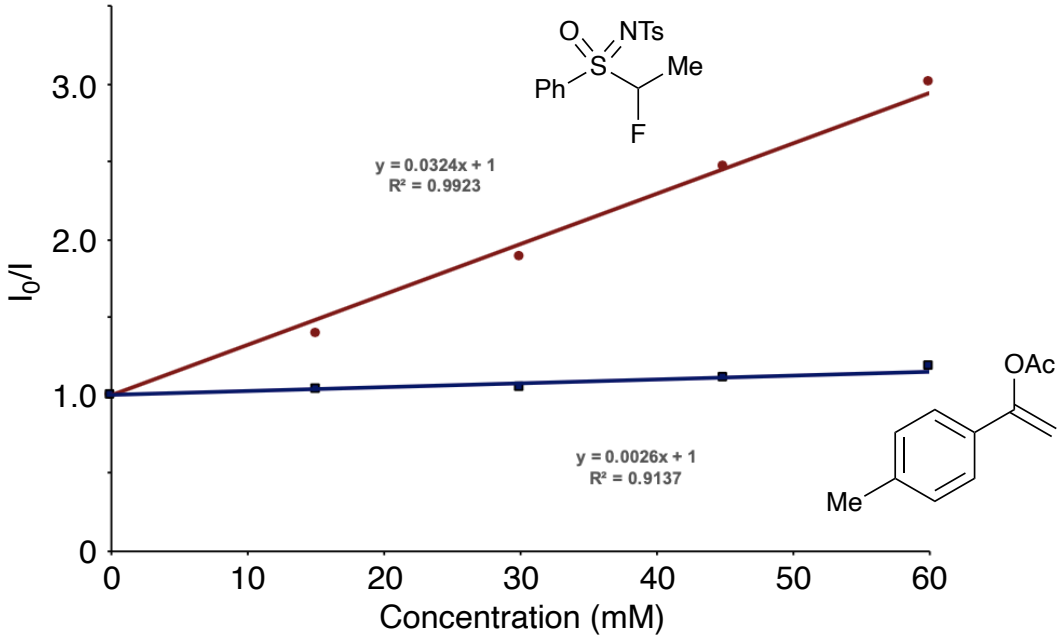
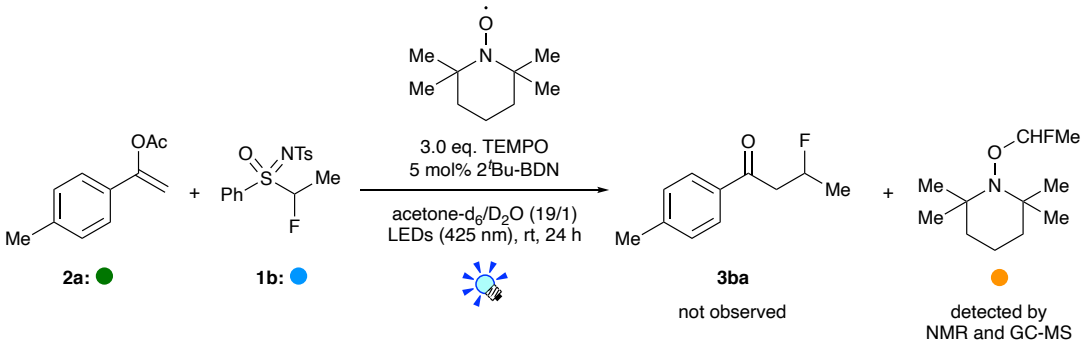


Figure S5. Stern-Volmer plots.

Radical trapping experiment with TEMPO



An NMR tube was charged with **2a** (4.4 mg, 25.0 μmol), **1b** (12.8 mg, 37.5 μmol), 2^{t}Bu-BDN (0.72 mg, 1.25 μmol), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (11.7 mg, 74.9 μmol) and tetraethylsilane (2 μL) under N_2 atmosphere. Then, the mixed solvent (acetone-d_6: 475 μL, D_2O: 25 μL) was added and the mixture was degassed by three freeze-pump-thaw cycles. The NMR tube was placed at 2-3 cm away from blue LED lamps (λ = 425 nm) in a water bath. The reaction was carried out under visible light irradiation for 24 hours at room temperature and monitored by NMR spectroscopy.

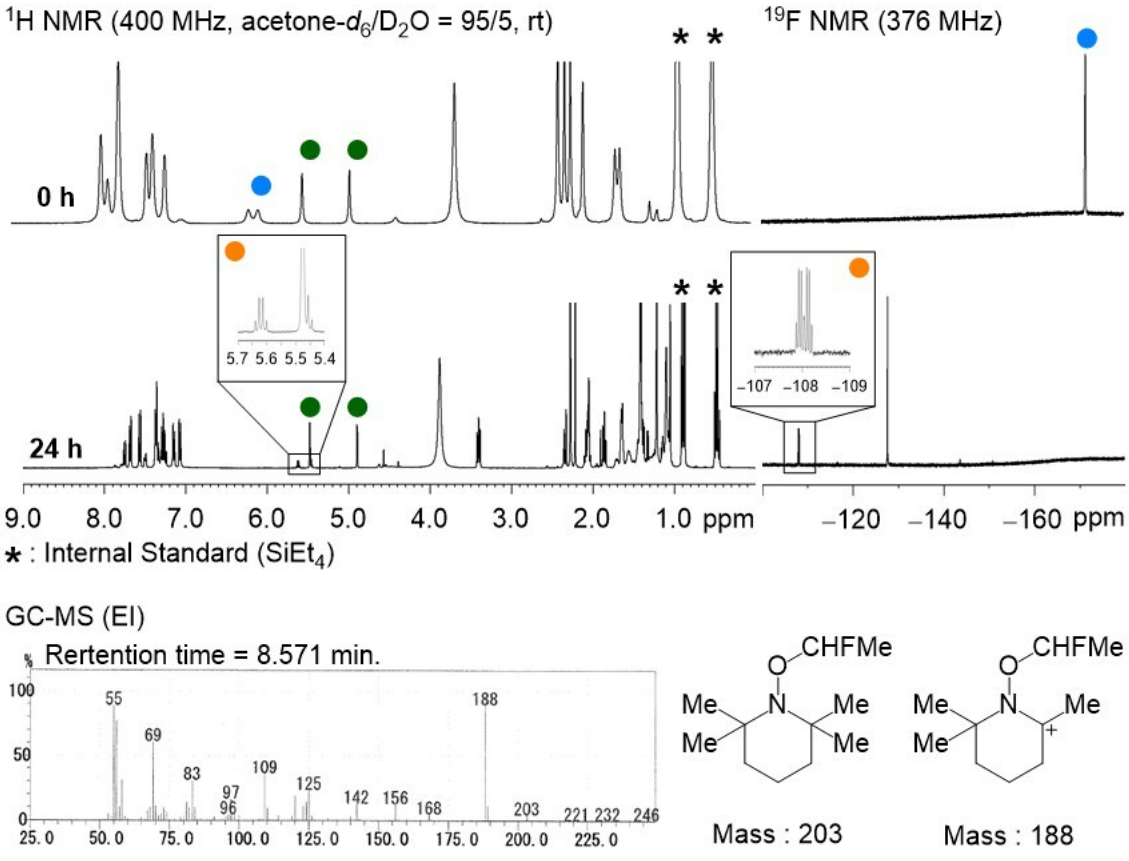
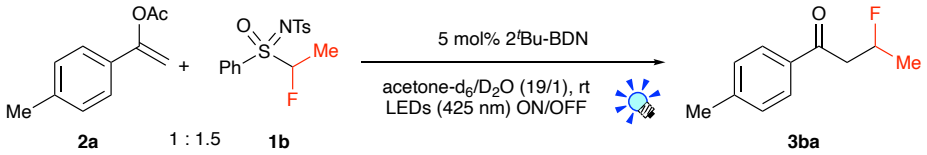


Figure S6. NMR of GC-MS after the reaction.

Light/dark experiment



Preparation of the sample was followed according to the procedures for the above-mentioned NMR experiment. Time profile for the reaction under light and dark conditions is shown below.

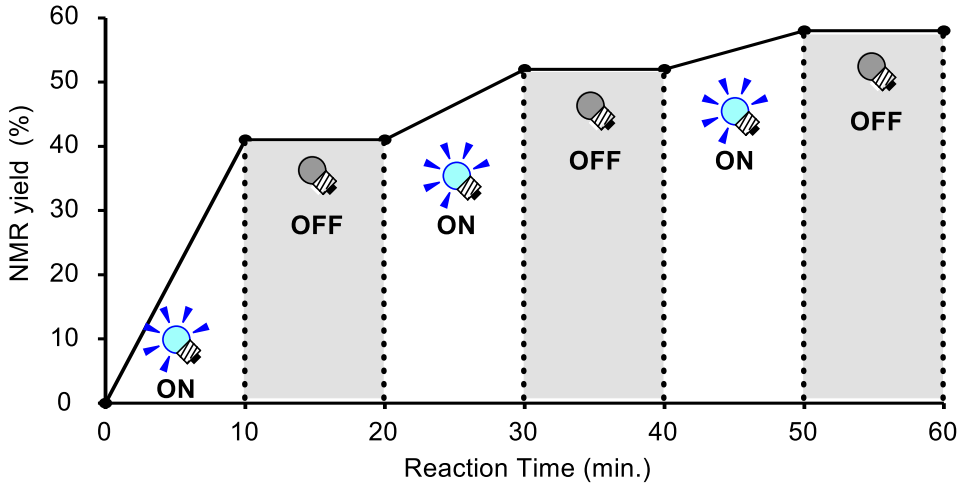


Figure S7. Light/dark experiment.

Quantum yield for photocatalytic reaction

(Photon flux)

Photon flux was calculated according to the equation below. Power of light was measured with Ophir PD300-UV and Ophir StarLite.

Irradiation was carried out with HITACHI F-7000 (λ = 420 nm, emission slit width = 10.0 nm).

Power of light: 243.3 μW (for λ = 420 nm)

$$photon\ flux = \frac{power\ of\ light\ (\mathrm{W}) \times wavelength\ of\ irradiation\ light\ (\mathrm{m})}{Plank\ constant\ (\mathrm{J \cdot s}) \times speed\ of\ light\ (\mathrm{m/s}) \times Avogadro\ constant\ (1/mol)}$$

$$\therefore \frac{243.3 \times 10^{-6} \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 2.998 \times 10^{8} \times 6.022 \times 10^{23}} = 8.54 \times 10^{-10}$$

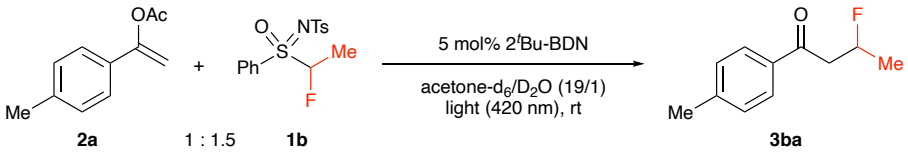
Calculated photon flux: 8.54×10^{-10} einstein·s^{-1}

(Quantum yield)

A cuvette was charged with a solution of **2a** (17.6 mg, 0.100 mmol), **1b** (51.2 mg, 0.150 mmol), 2^{t}Bu-BDN (2.9 mg, 5.0 μmol), α,α,α-trifluorotoluene (1.2 mg, 8.2 μmol) as an internal standared and the mixed solvent (acetone: 1.9 mL, H_2O: 0.1 mL) under N_2 atmosphere. The solution was degassed by three freeze-pump-thaw cycles, and it was irradiated by F-7000 (λ = 420 nm, emission slit width = 10.0 nm). A small portion of the reaction solution was diluted with acetone-d_6, and the reaction was monitored by ^{19}F NMR.

The quantum yield (Φ) was calculated by following formula. (A: Absorbance of catalysts)

$$\phi = \frac{mol\ product}{4.20 \times 10^{-10} \cdot 43200\ \mathrm{s} \cdot f} \qquad (f = 1 - 10^{-A})$$



yield of **3ba** (17 h): 4.4% NMR yield (4.41 x 10^{-6} mol), Φ = 8.4%

yield of **3ba** (27 h): 6.9% NMR yield (6.92 x 10^{-6} mol), Φ = 8.3%

yield of **3ba** (40 h): 11% NMR yield (1.06 x 10^{-5} mol), Φ = 8.6%

average Φ = 8.4%

LFP studies (Figure 1)

The fluorescence emission lifetime of 2^{t}Bu-BDN at 458 nm under N_2 bubbled conditions was quenched at different concentration of quencher **1b** (Figure S8). The fluorescence emission lifetime at 458 nm was affected by increasing the concentration of **1b**. Equation 1, where Q is the quencher, was used to obtain the Stern-Volmer plot of τ^0/τ versus concentration of **1b** (Figure S9). This yielded a straight line with slope of 0.0235 and intercept of 1. From the slope, the rate of quenching, k_q, was determined to be 2.27×10^9 $M^{-1}s^{-1}$.

$$\tau^0/\tau = 1 + k_q\tau^0[Q] \qquad \text{equation 1}$$

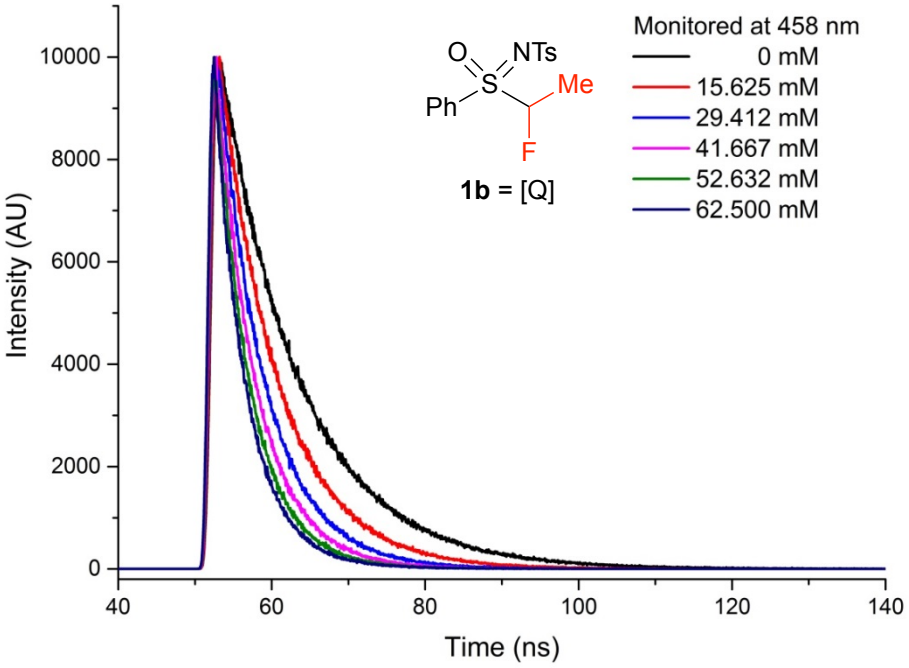


Figure S8. Fluorescence emission decay (excitation wavelength = 390 nm nano-LED) observed at 458 nm under N_2 (10 min) conditions of 0.005 mM solution of 2^{t}Bu-BDN in acetone at room temperature in presence of different concentration of quencher **1b**

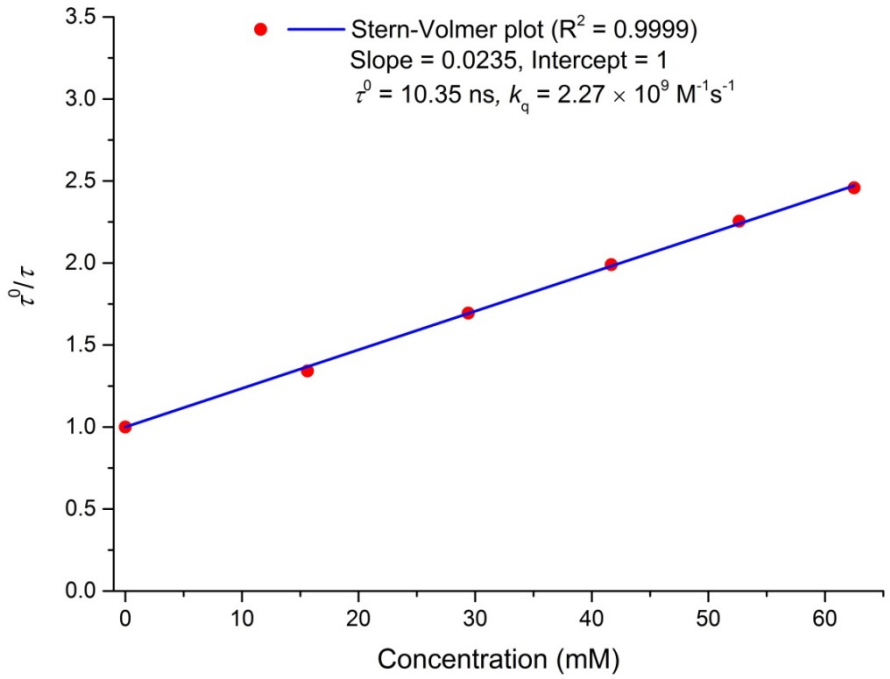


Figure S9. Stern-Volmer plot obtained from fluorescence emission lifetime observed at 458 nm under N_2 (10 min) conditions at different concentration of quencher **1b**. τ^0 is the lifetime in absence of **1**b and τ is the lifetime at various concentrations of **1b**.

EPR experiments

A solution of **1b** (25.6 mg, 15 mM) and 2^{t}Bu-BDN (1.3 mg, 0.5 mM) was prepared in Ar-saturated acetone (4.75 mL) and H_2O (0.25 mL). An EPR flat tube was charged with ~50 μL of the solution. The EPR spectrum was measured under visible light irradiation (430 nm) at room temperature. During irradiation for 4 min (Figure S10b), a broad signal around 3500-3540 G was observed at the resonance frequency of 9.87 GHz, see the difference spectrum in Figure S10c (= Figure S10b – Figure S10a). When irradiation stopped, the signal disappeared. These results suggest that radical species appeared in the photoreaction of **1b** with 2^{t}Bu-BDN, but it was difficult to be assigned due to the weak intensity and transiency.

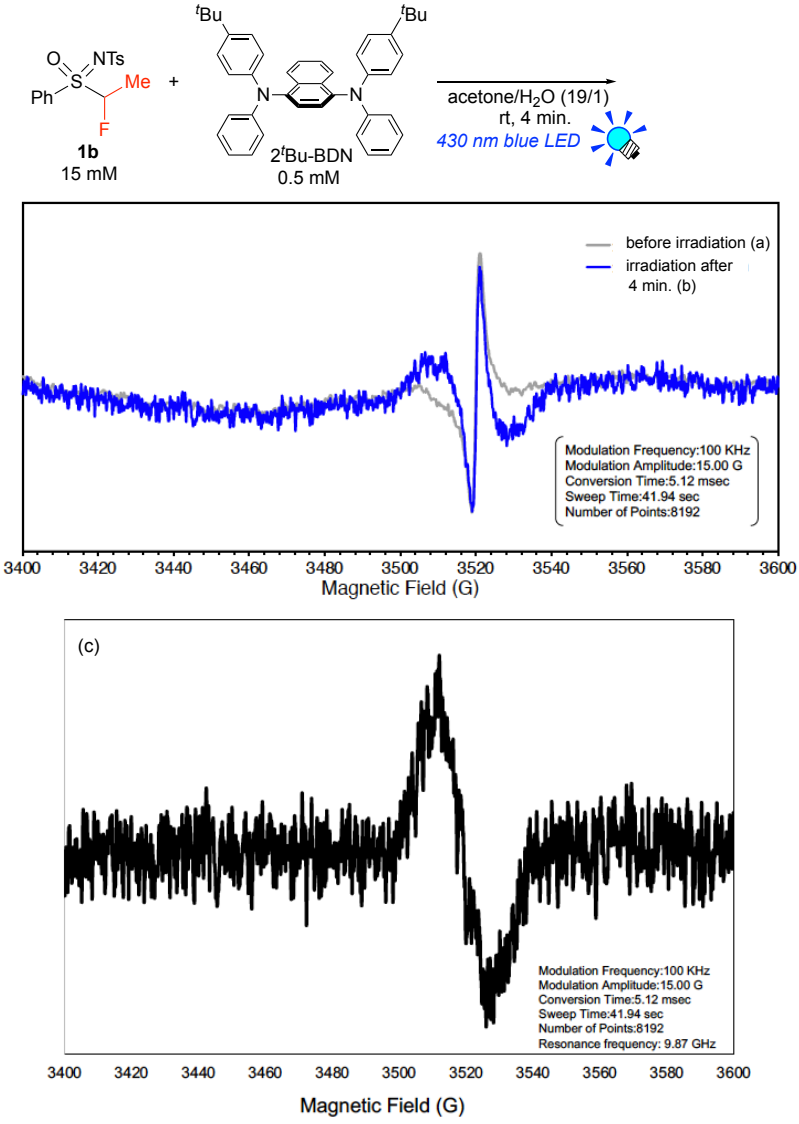


Figure 10. EPR spectra obtained from the acetone/H_2O solution of **1b** and 2^{t}Bu-BDN before (a), after irradiation (b) (430 nm visible light), and (c) a difference spectrum (b)–(a).

To confirm generation of the α-monofluoroethyl radical under these conditions, EPR trapping experiments were conducted in the presence of a spin trapping agent, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) (23.6 mg, 104 mM). As a result, formation of the DMPO spin adduct of α-monofluoroethyl radical was observed by EPR and HRMS (ESI$^+$) (Figure S11). Calcd m/z for $C_6H_{15}ONF$ 160.11322, found 160.11350.

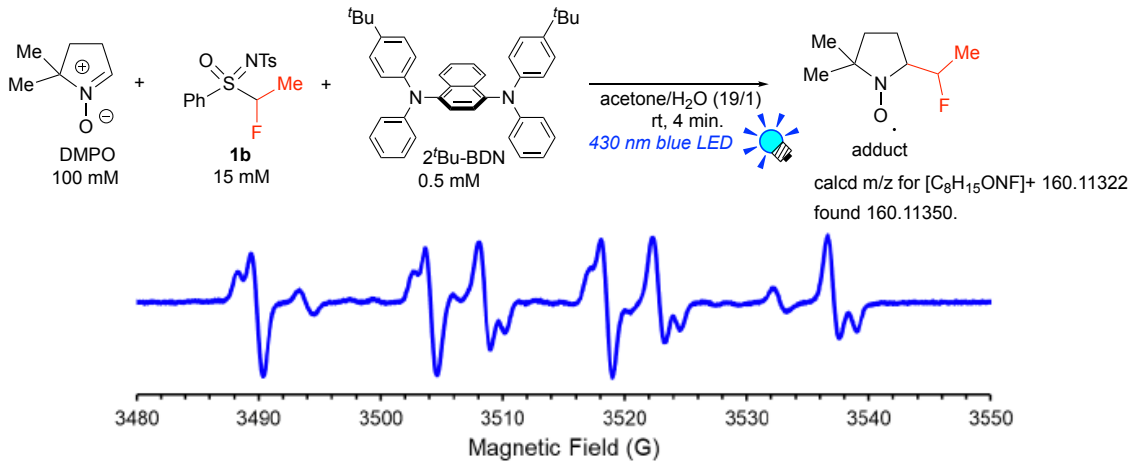


Figure 11. An EPR spectrum obtained from the acetone/H_2O solution of **1b** and 2^{t}Bu-BDN in the presence of DMPO after irradiation (430 nm visible light).

Crystallographic data

• Crystallographic data of 2^{t}Bu-BDN

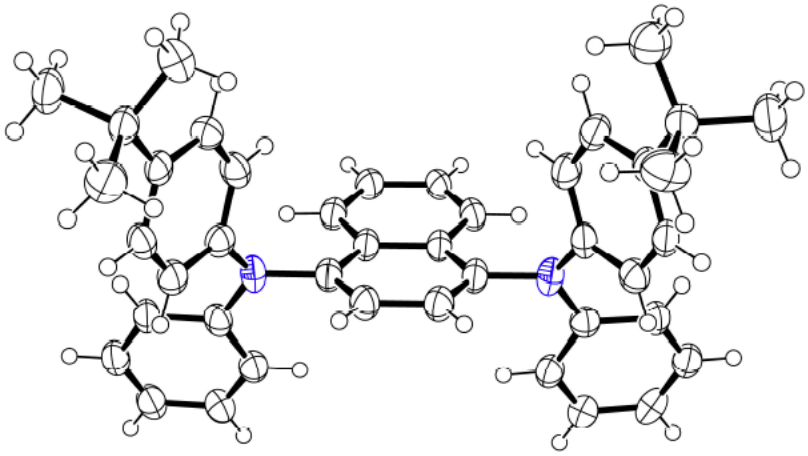


Figure S12. An ORTEP diagram of 2^{t}Bu-BDN with ellipsoids shown at the 50% contour percent probability level.

Table S1. Crystal data and structure refinement for 2^{t}Bu-BDN.

Identification code	RT064
Empirical formula	$C_{42}H_{42}N_2$
Formula weight	574.77
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.060(2)
b/Å	10.1206(8)
c/Å	19.139(2)
α/°	90
β/°	98.606(11)
γ/°	90
Volume/Å^3	3267.2(6)
Z	4
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.508
F(000)	1232.0
Crystal size/mm^3	0.361 × 0.037 × 0.026
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	6.476 to 152.72
Index ranges	-21 ≤ h ≤ 21, -10 ≤ k ≤ 12, -23 ≤ l ≤ 24
Reflections collected	22964
Independent reflections	6521 [R_{int} = 0.1195, R_{sigma} = 0.1034]
Data/restraints/parameters	6521/0/403
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0958, wR_2 = 0.2462
Final R indexes [all data]	R_1 = 0.1681, wR_2 = 0.2998
Largest diff. peak/hole / e $Å^{-3}$	0.52/-0.34

• Crystallographic data of **1b**

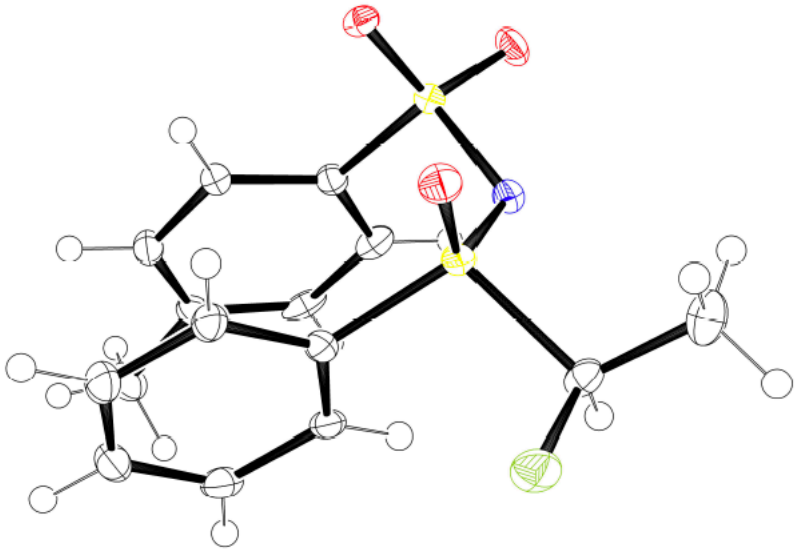


Figure S13. An ORTEP diagram of **1b** with ellipsoids shown at the 50% contour percent probability level.

Table S2. Crystal data and structure refinement for **1b**.

Identification code	RT052
Empirical formula	$C_{30}H_{32}F_2N_2O_6S_4$
Formula weight	682.81
Temperature/K	93.0
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	15.5254(2)
b/Å	5.72610(10)

c/Å	34.5954(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3075.53(8)
Z	4
ρ_{calc}g/cm^3	1.475
μ/mm^{-1}	3.351
F(000)	1424.0
Crystal size/mm^3	0.143 × 0.057 × 0.032
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.228 to 152.482
Index ranges	-19 ≤ h ≤ 19, -7 ≤ k ≤ 6, -43 ≤ l ≤ 43
Reflections collected	75912
Independent reflections	6261 [R_{int} = 0.0379, R_{sigma} = 0.0172]
Data/restraints/parameters	6261/1/401
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0842
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0845
Largest diff. peak/hole / e Å^{-3}	0.42/-0.38
Flack parameter	0.158(6)

• Crystallographic data of **1d**

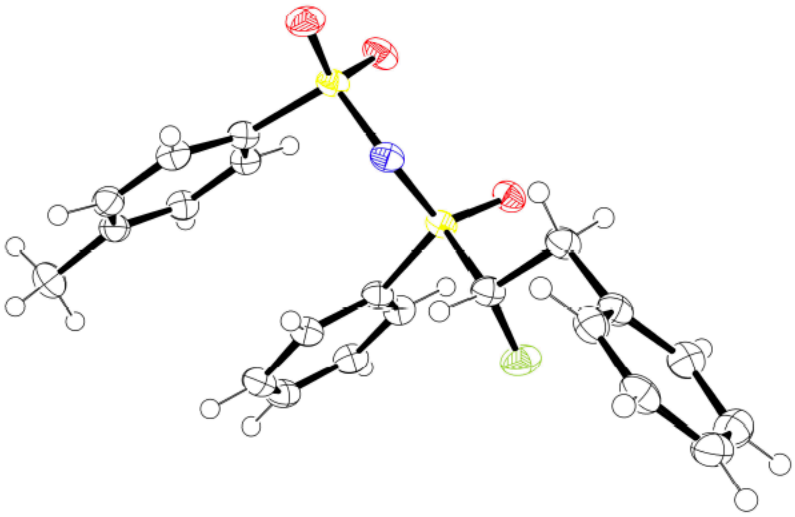


Figure S14. An ORTEP diagram of **1d** with ellipsoids shown at the 50% contour percent probability level.

Table S3. Crystal data and structure refinement for **1d**.

Identification code	RT277
Empirical formula	$C_{21}H_{20}FNO_3S_2$
Formula weight	417.50
Temperature/K	93.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.1286(7)
b/Å	5.7699(2)
c/Å	15.7586(5)
α/°	90
β/°	106.416(3)
γ/°	90
Volume/Å^3	1930.03(11)
Z	4
ρ_{calc}g/cm^3	1.437
μ/mm^{-1}	2.782
F(000)	872.0
Crystal size/mm^3	0.268 × 0.065 × 0.054
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.33 to 152.548
Index ranges	-27 ≤ h ≤ 27, -6 ≤ k ≤ 7, -19 ≤ l ≤ 19
Reflections collected	48671
Independent reflections	3925 [R_{int} = 0.0528, R_{sigma} = 0.0200]
Data/restraints/parameters	3925/0/254
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0347, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0363, wR_2 = 0.0966
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.34

• Crystallographic data of **1d**

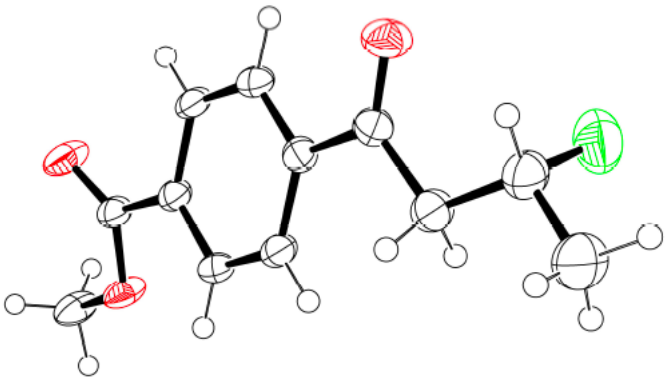


Figure S15. An ORTEP diagram of **3bl** with ellipsoids shown at the 50% contour percent probability level.

Table S4. Crystal data and structure refinement for **3bl**.

Identification code	RT217/
Empirical formula	$C_{12}H_{13}FO_3$
Formula weight	224.22
Temperature/K	93
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	26.0397(16)
b/Å	5.8337(3)
c/Å	7.1864(5)
α/°	90
β/°	95.629(6)
γ/°	90

Volume/Å^3	1086.41(12)
Z	4
ρ_{calc}g/cm^3	1.371
μ/mm^{-1}	0.919
F(000)	472.0
Crystal size/mm^3	0.077 × 0.054 × 0.026
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.822 to 152.924
Index ranges	-32 ≤ h ≤ 31, -7 ≤ k ≤ 7, -9 ≤ l ≤ 8
Reflections collected	23370
Independent reflections	2243 [R_{int} = 0.0548, R_{sigma} = 0.0234]
Data/restraints/parameters	2243/0/147
Goodness-of-fit on F^2	1.161
Final R indexes [I>=2σ (I)]	R_1 = 0.0885, wR_2 = 0.2106
Final R indexes [all data]	R_1 = 0.0971, wR_2 = 0.2161
Largest diff. peak/hole / e Å^{-3}	0.59/-0.45

References

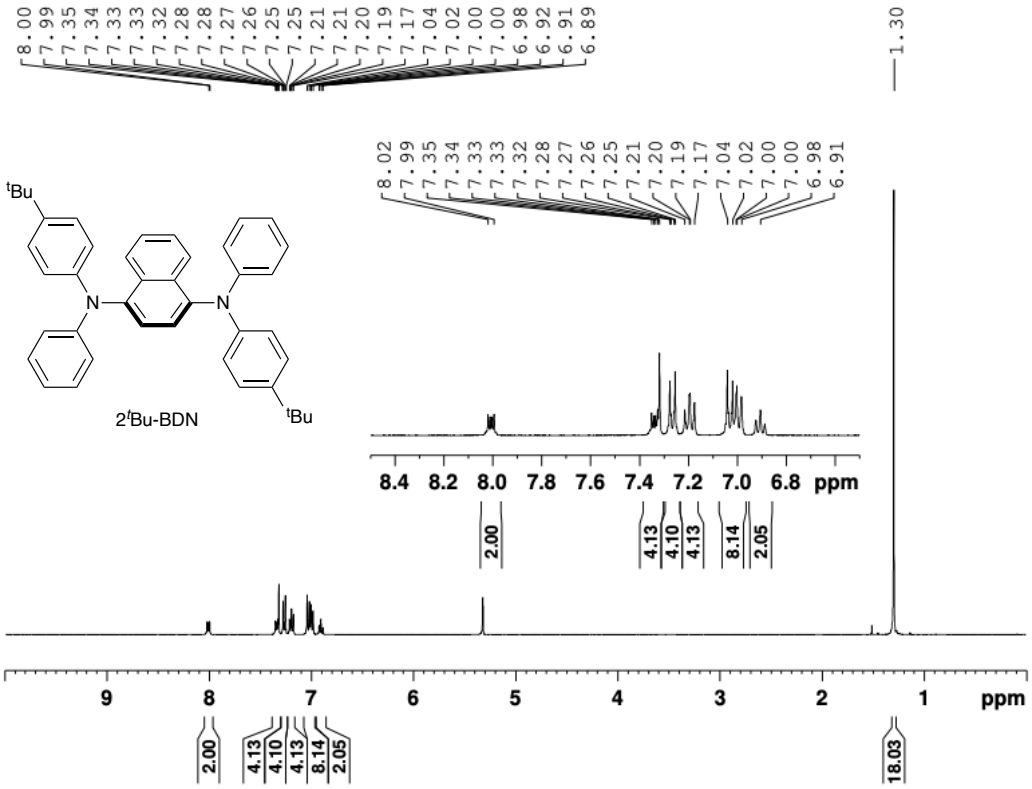
[1] (a) D. Gärtner, A. L. Stein, S. Grupe, J. Arp and A. Wangelin, *Angew. Chem. Int. Ed.,* 2015, **54**, 10545–10549; (b) C.-X. Song, G.-X. Cai, T. R. Farrell, Z.-P. Jiang, H. Li, L.-B. Gan and Z.-J. Shi, *Chem. Commun.,* 2009, 6002–6004; (c) S. Rozen and Y. Menahem, *J. Fluorine Chem.,* 1980, **16**, 19–31; (d) D. Felipe-Blanco and J. C. Gonzalez-Gomez, *Adv. Synth. Catal.,* 2018, **360**, 2773–2778; (e) J. S. Sharley, A. M. C. Pérez, E. E. Ferri, A. F. Miranda and I. R. Baxendale, *Tetrahedron*, 2016, **72**, 2947–2954; (f) I. Geibel and J. Christoffers, *Eur. J. Org. Chem.* 2016, 918–920.

[2] (a) J. P. Wolfe and S. L. Buchwald, *J. Org. Chem.,* 2000, **65,** 1144–1157; (b) N. Noto, T. Koike and M. Akita, *ACS Catal.,* 2019, **9**, 4382–4387.

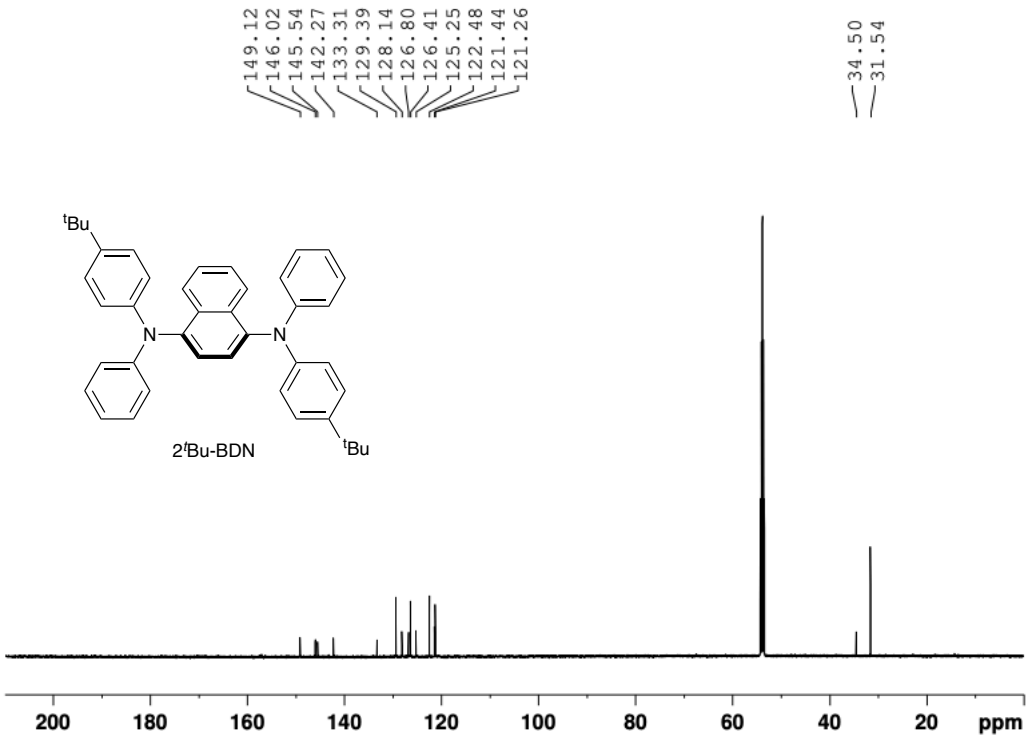
[3] (a) T. Luo, R. Zhang, X. Shen, W. Zhang, C. Nia and J. Hu, *Dalton Trans.,* 2015, **44**, 19636–19641; (b) W. Zhang and J. Hu, *Adv. Synth. Catal.,* 2010, **352**, 2799–2804.

NMR Spectra

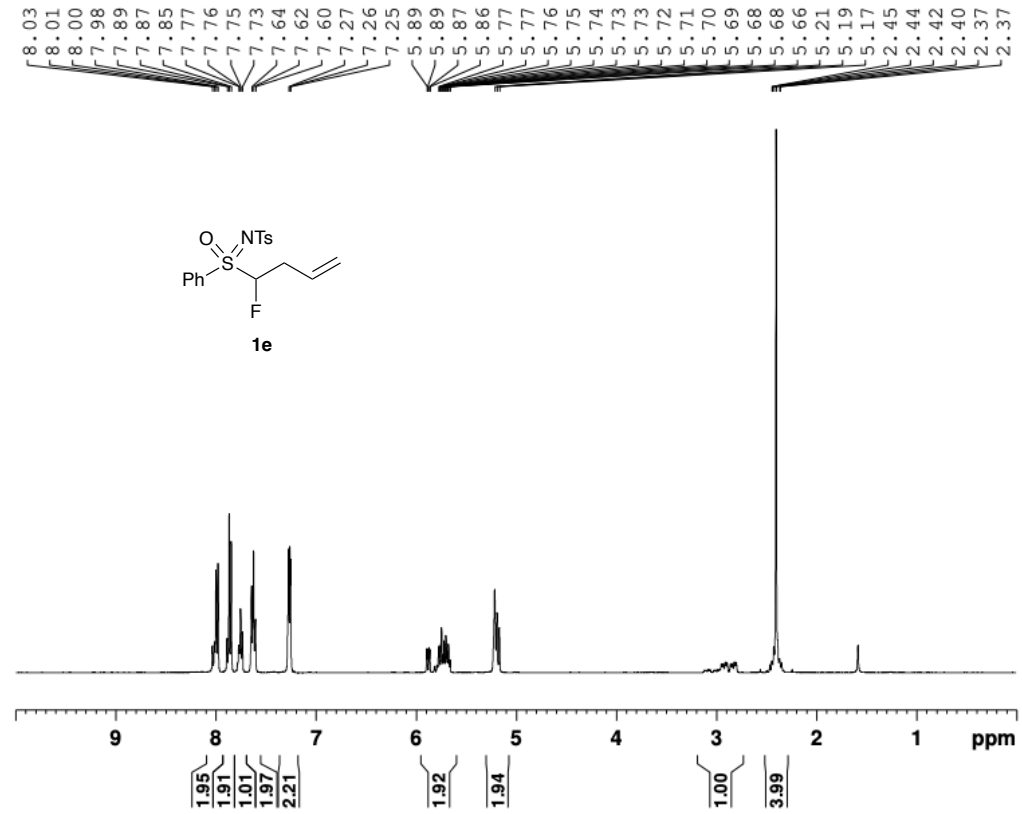
^{1}H NMR



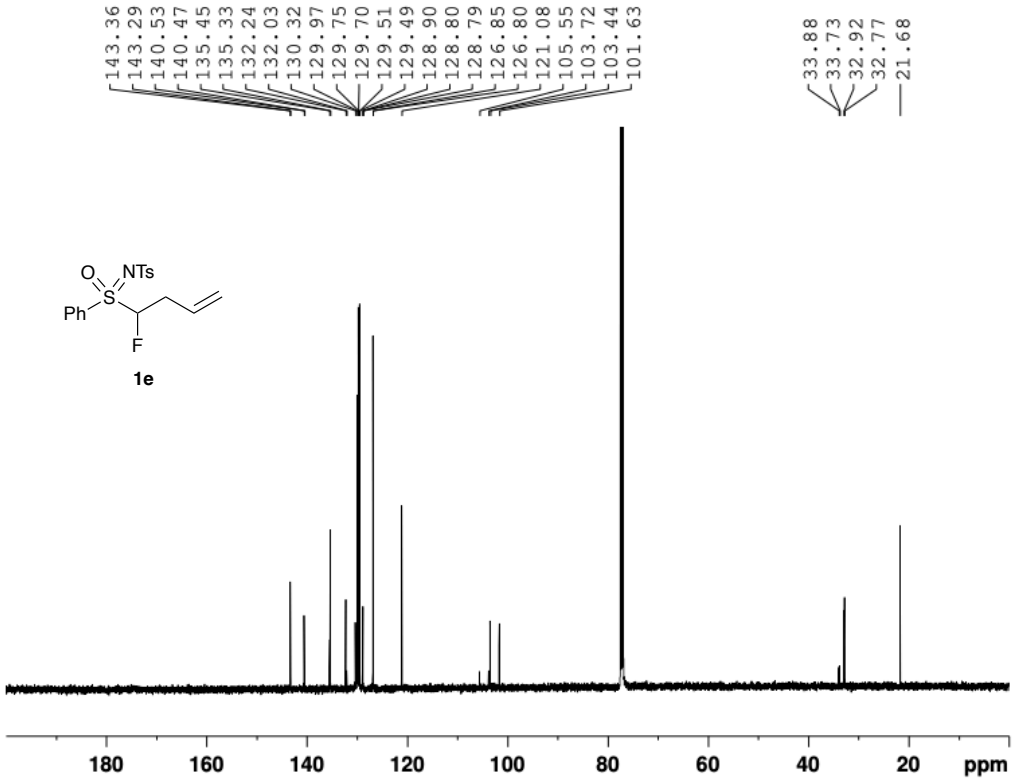
^{13}C NMR



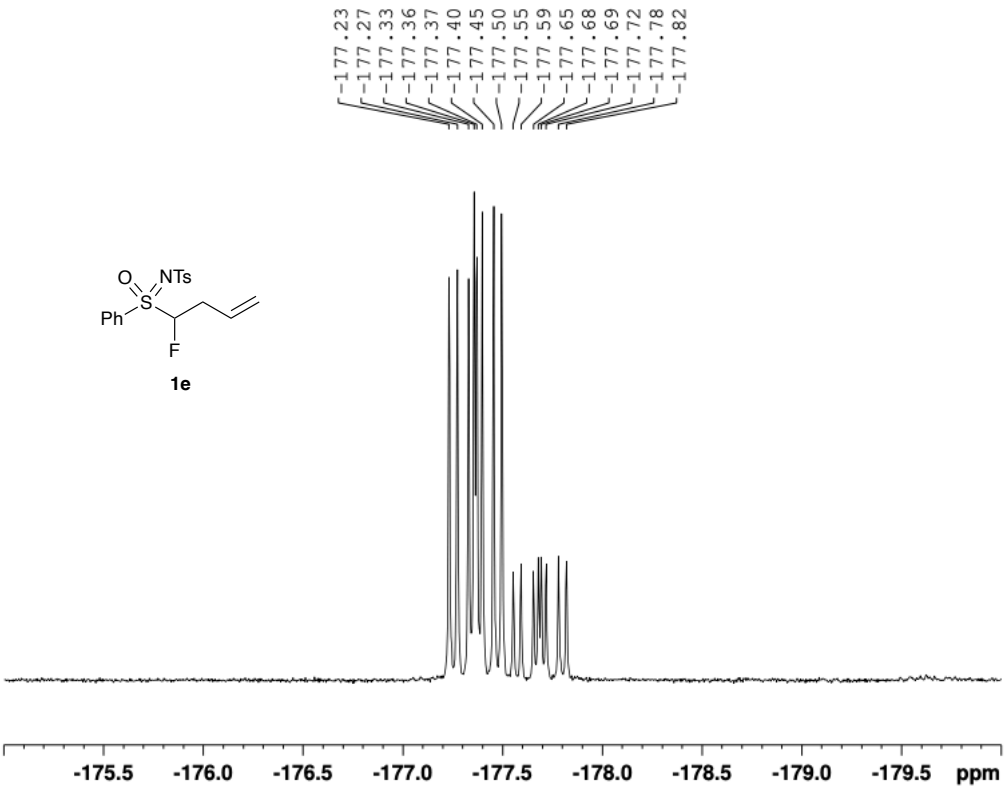
^{1}H NMR



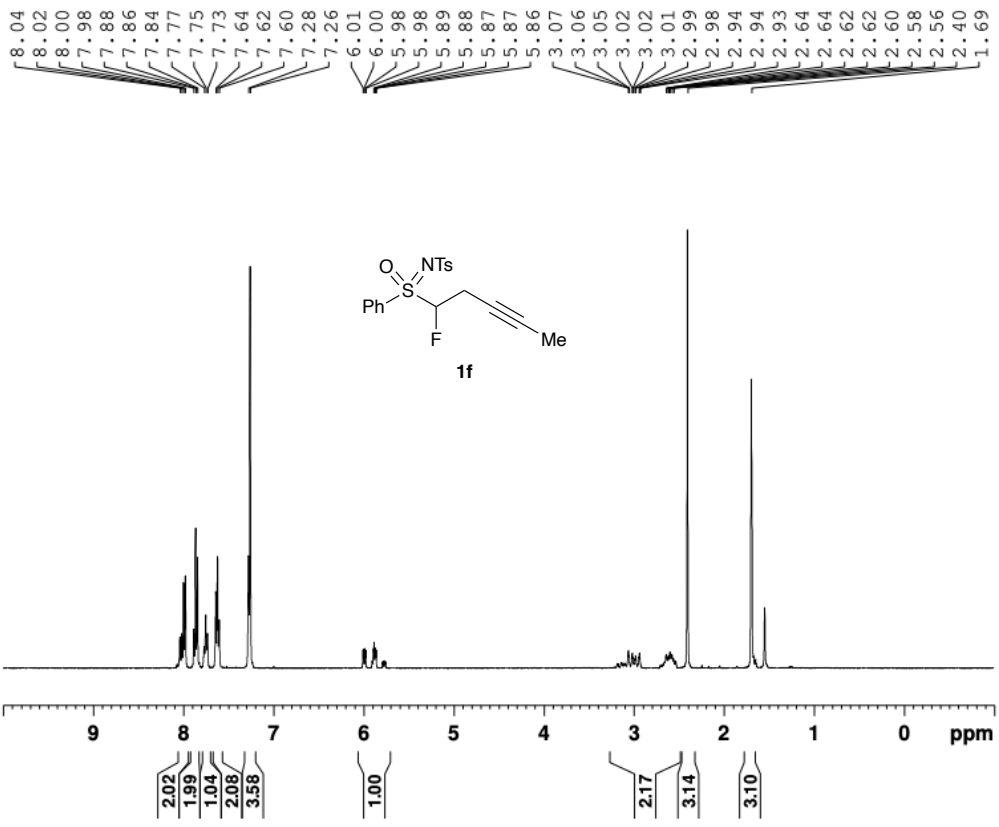
^{13}C NMR



^{19}F NMR



^{1}H NMR



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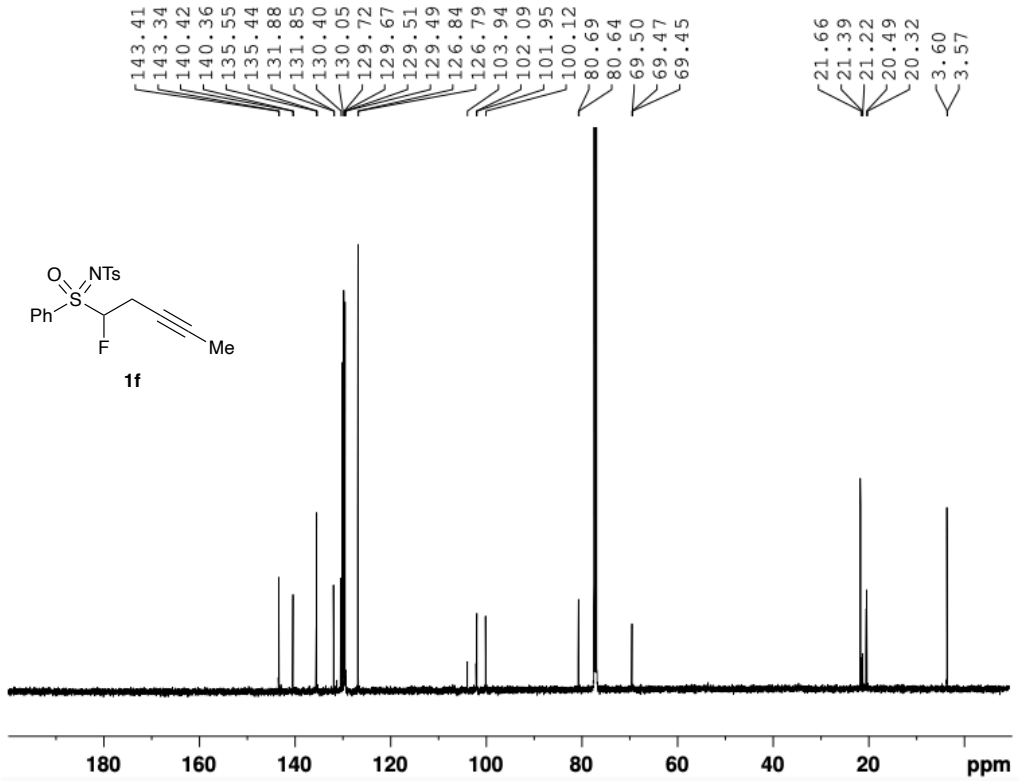

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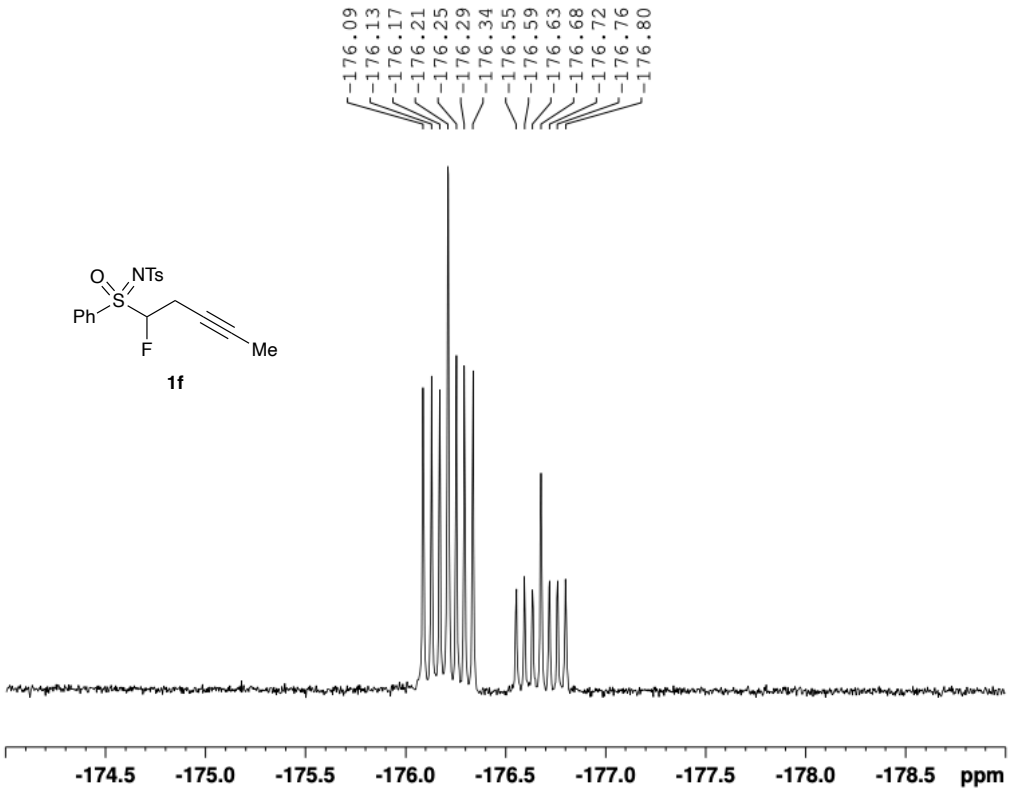

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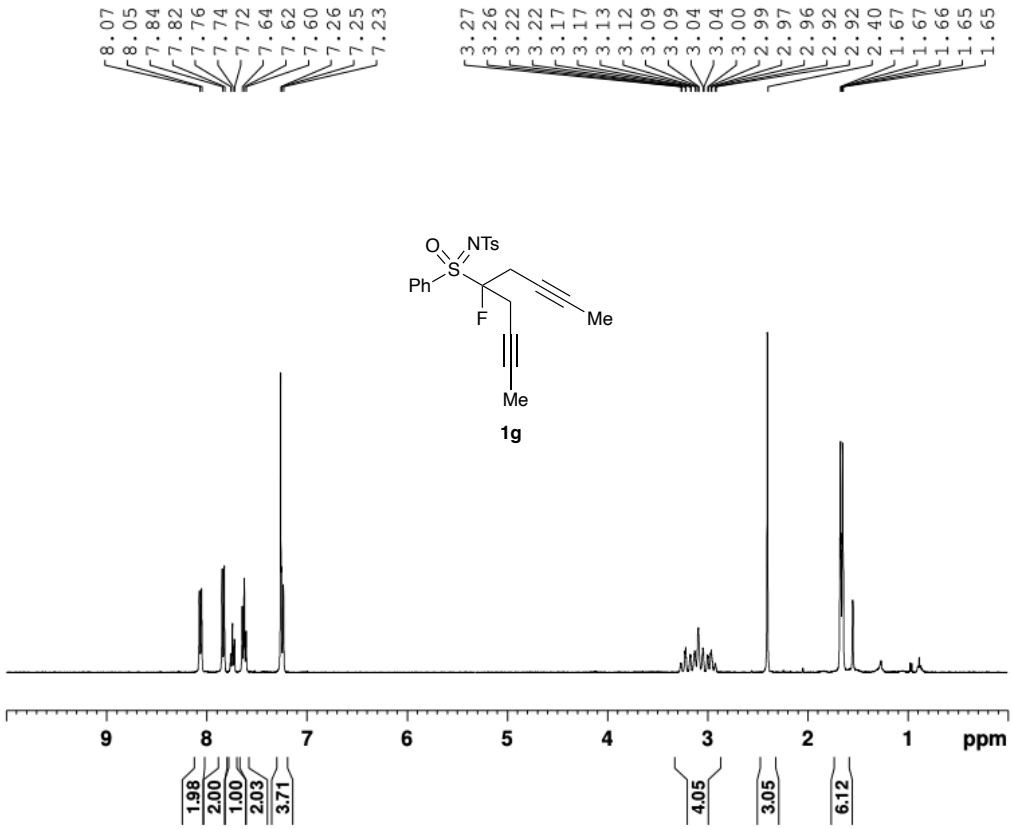

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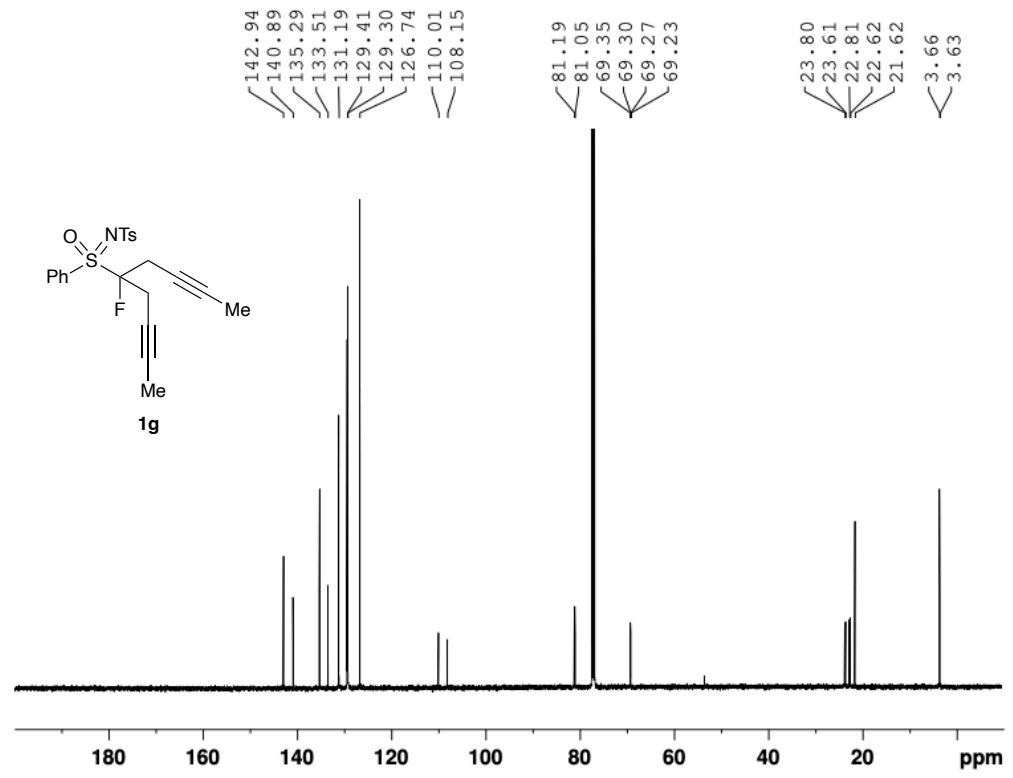

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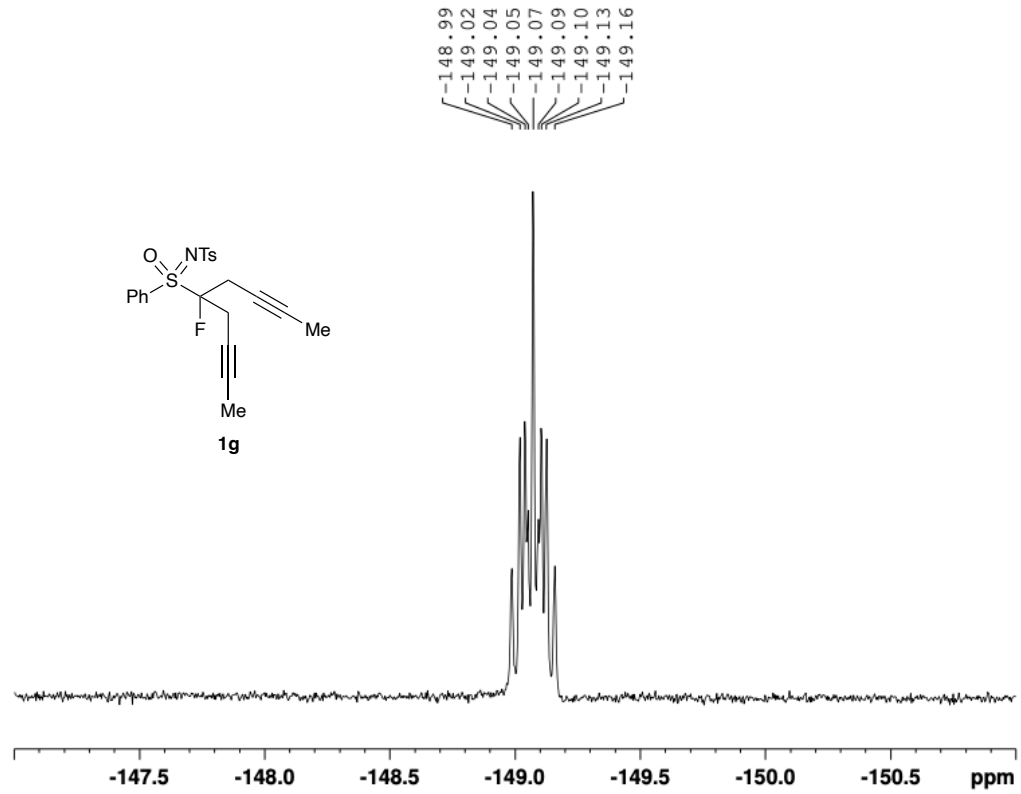

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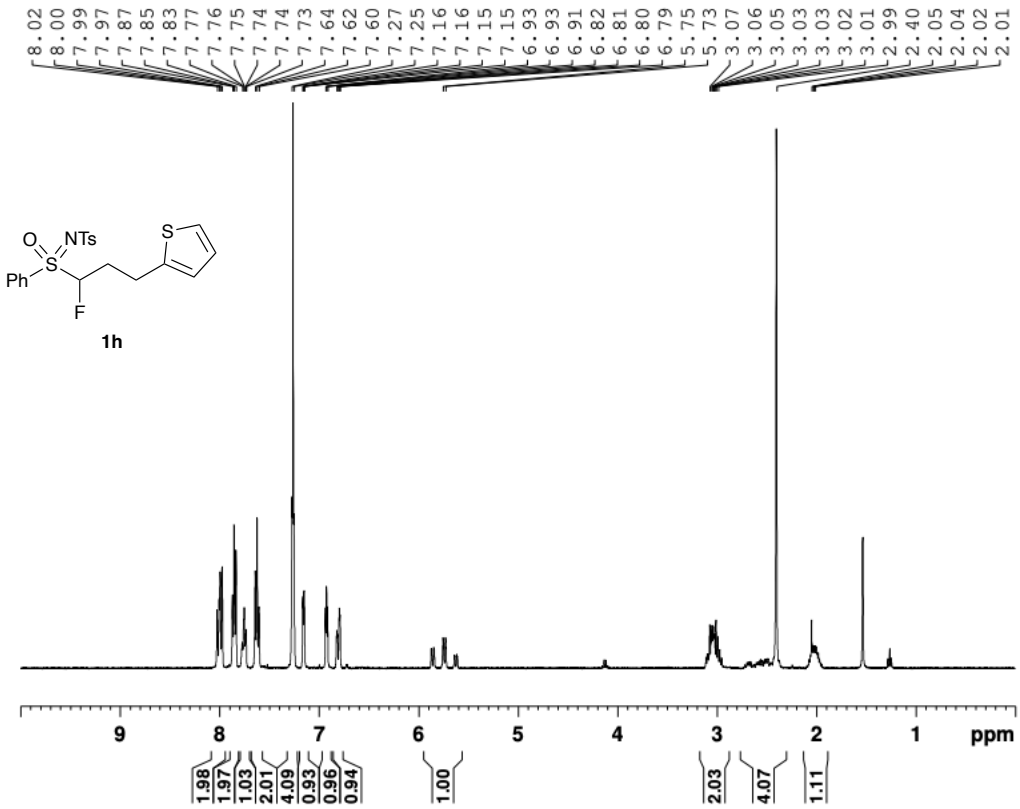

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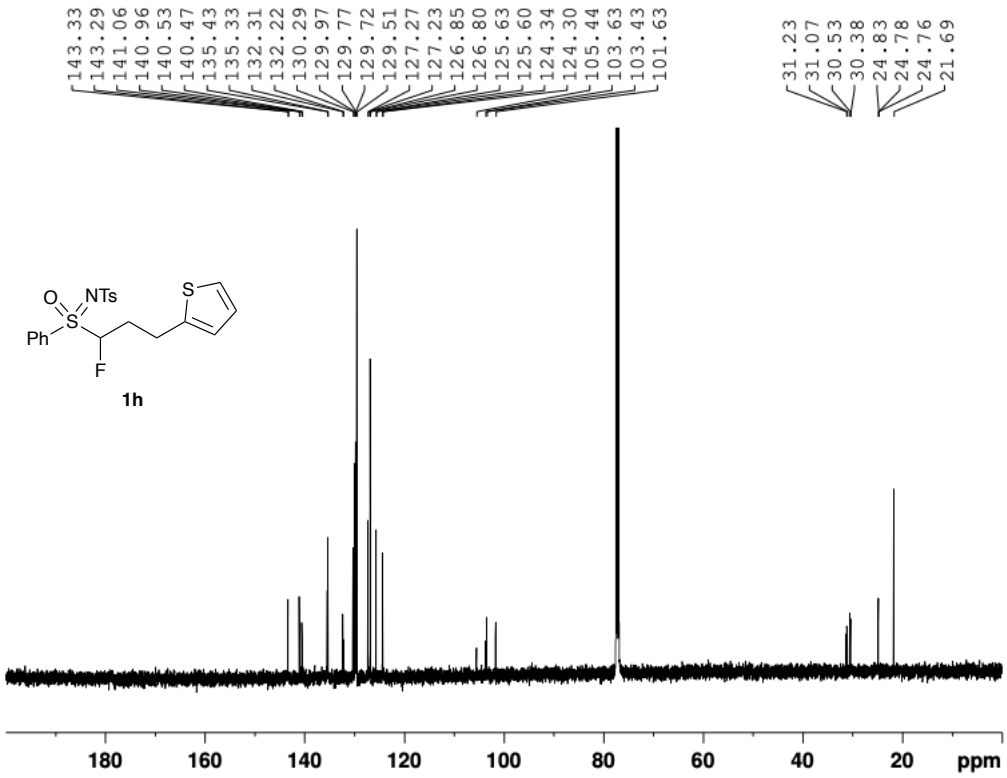

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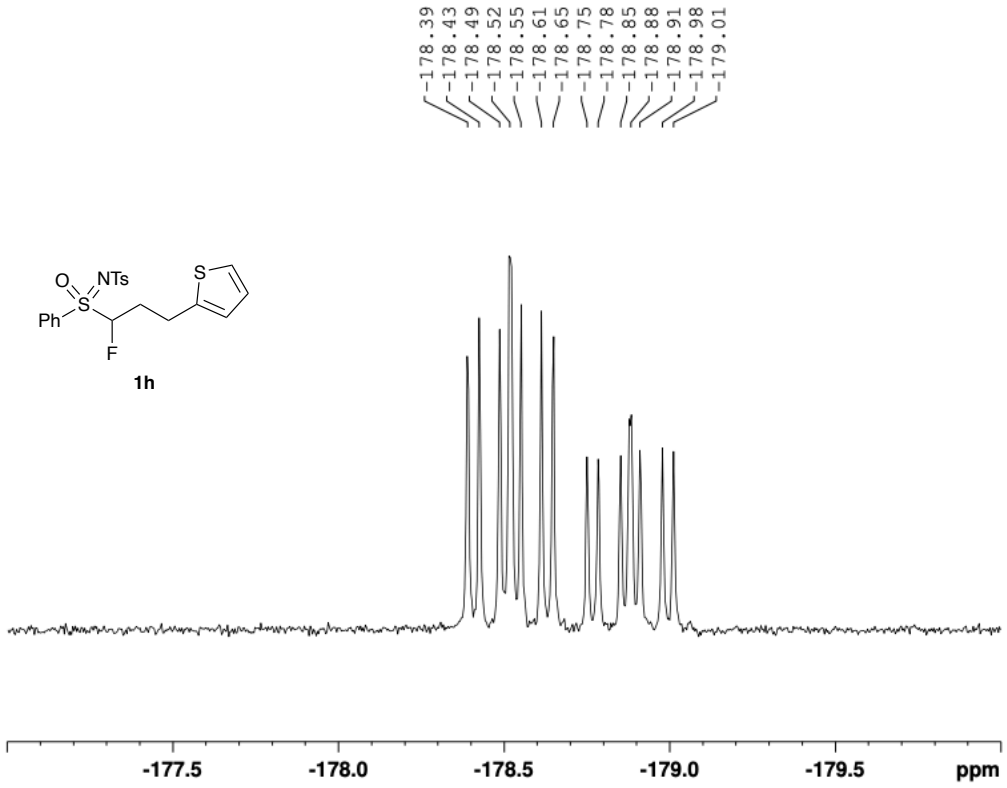

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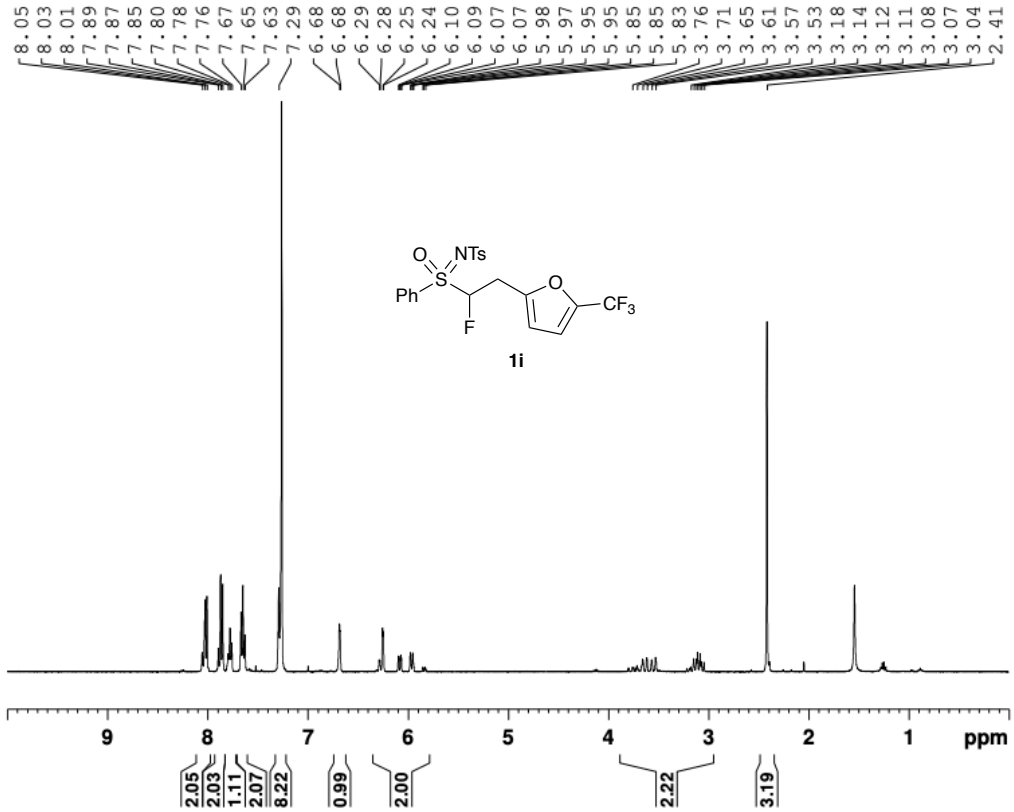

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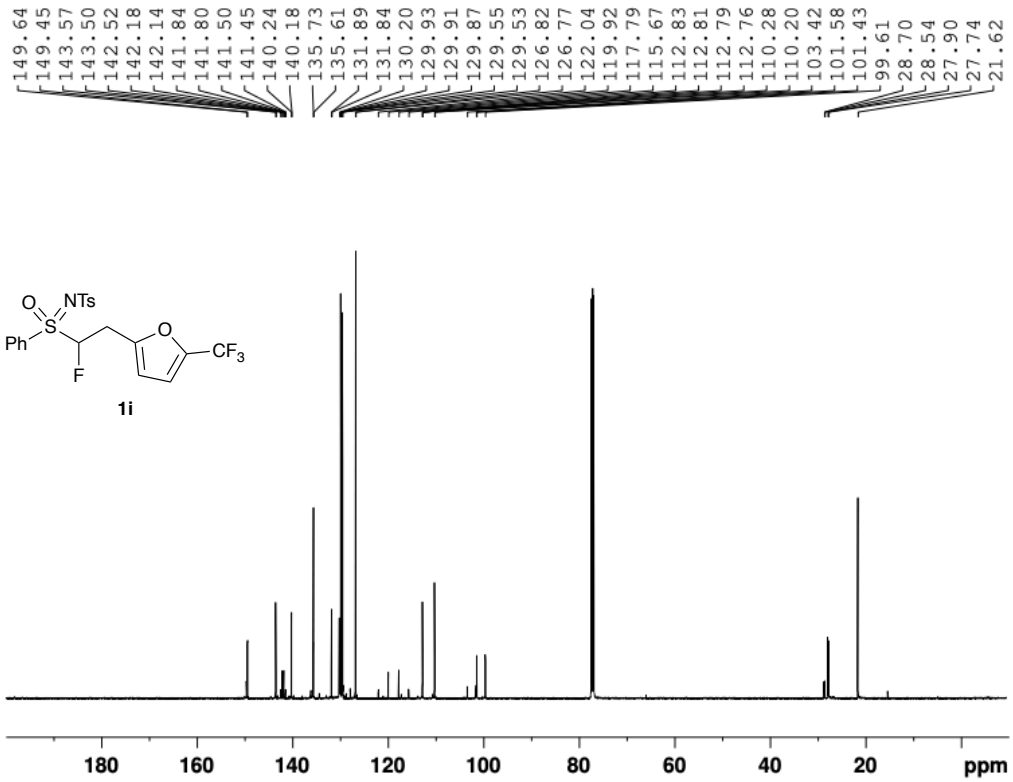

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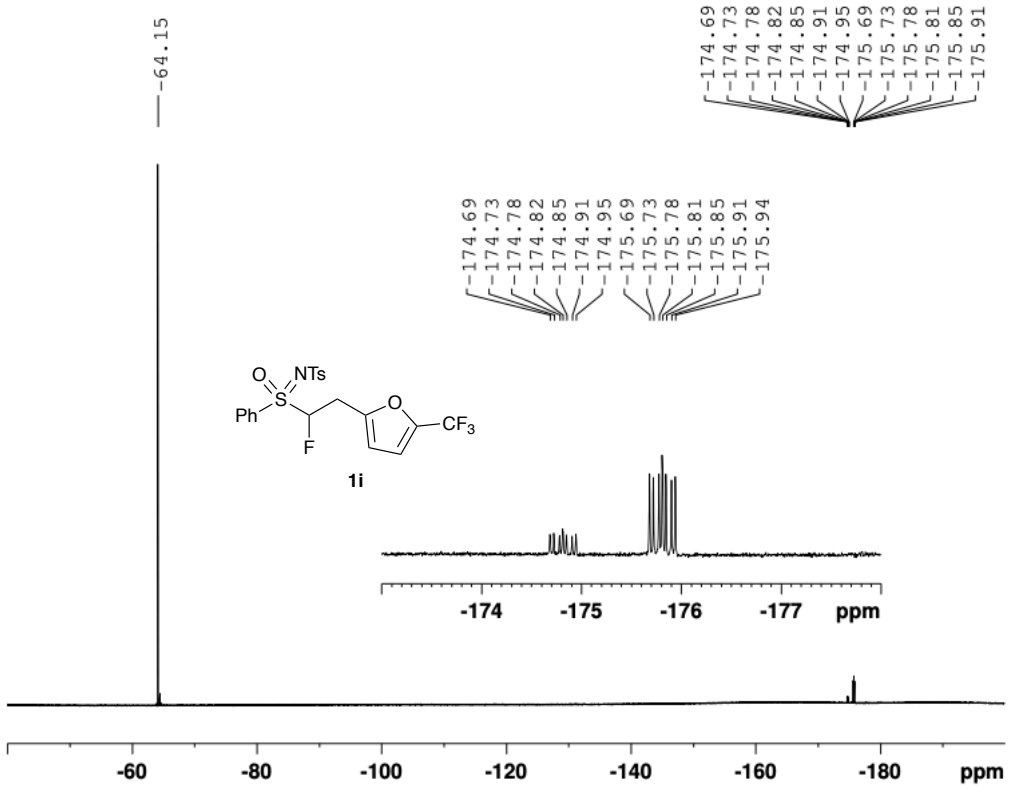

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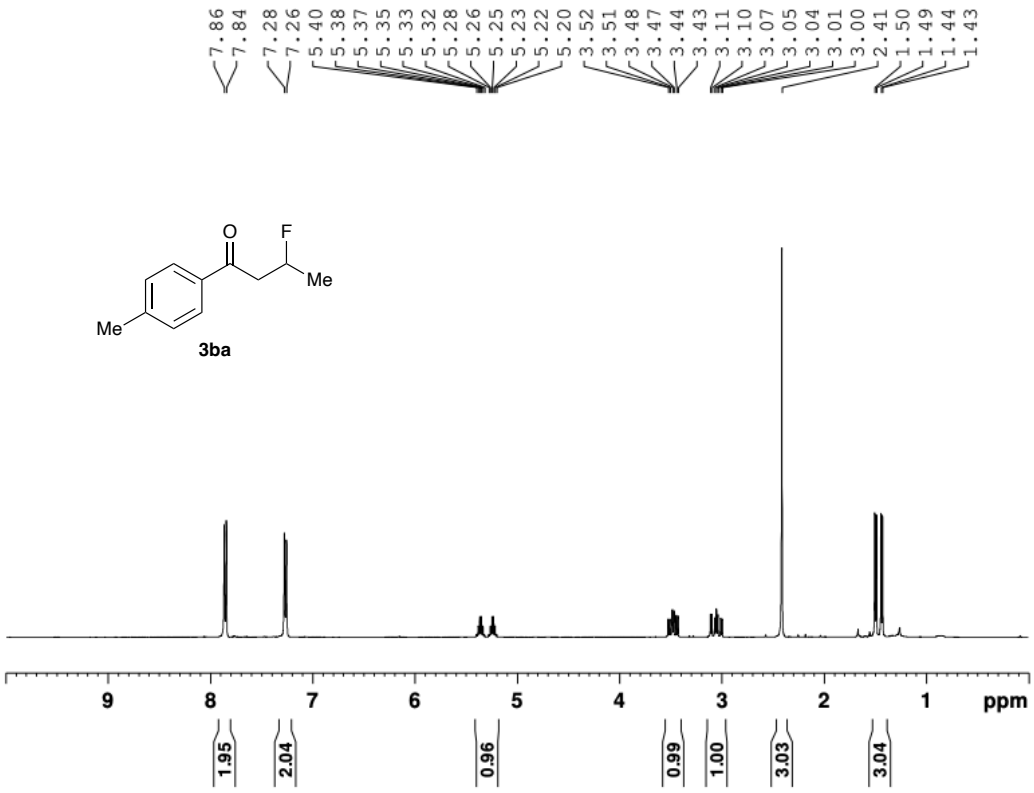

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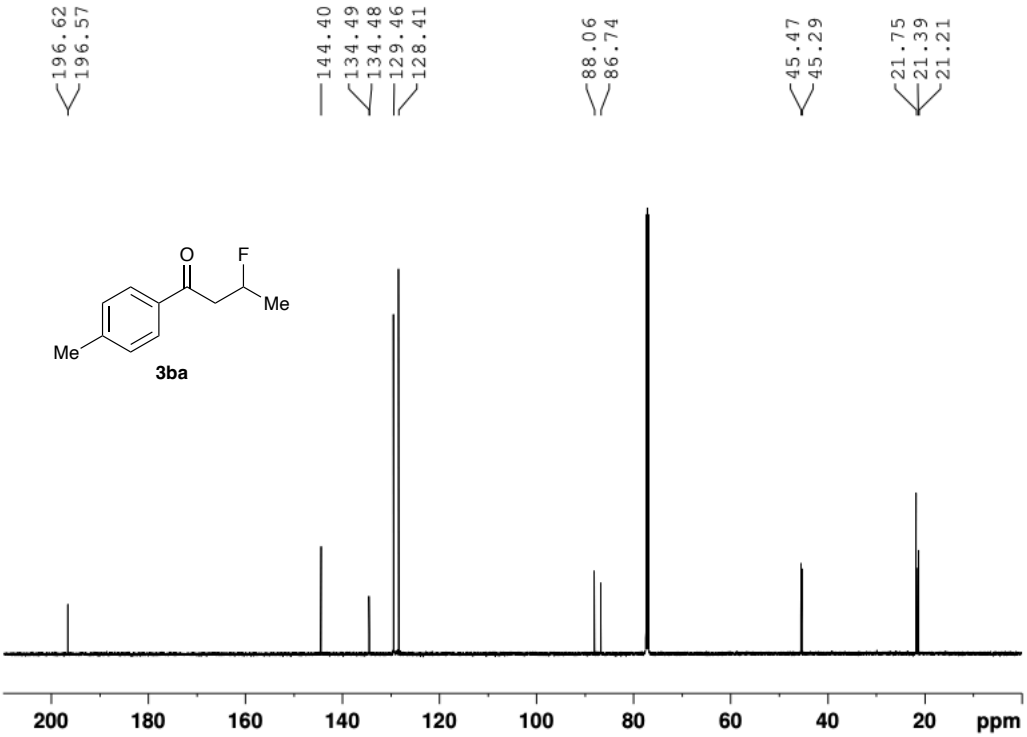

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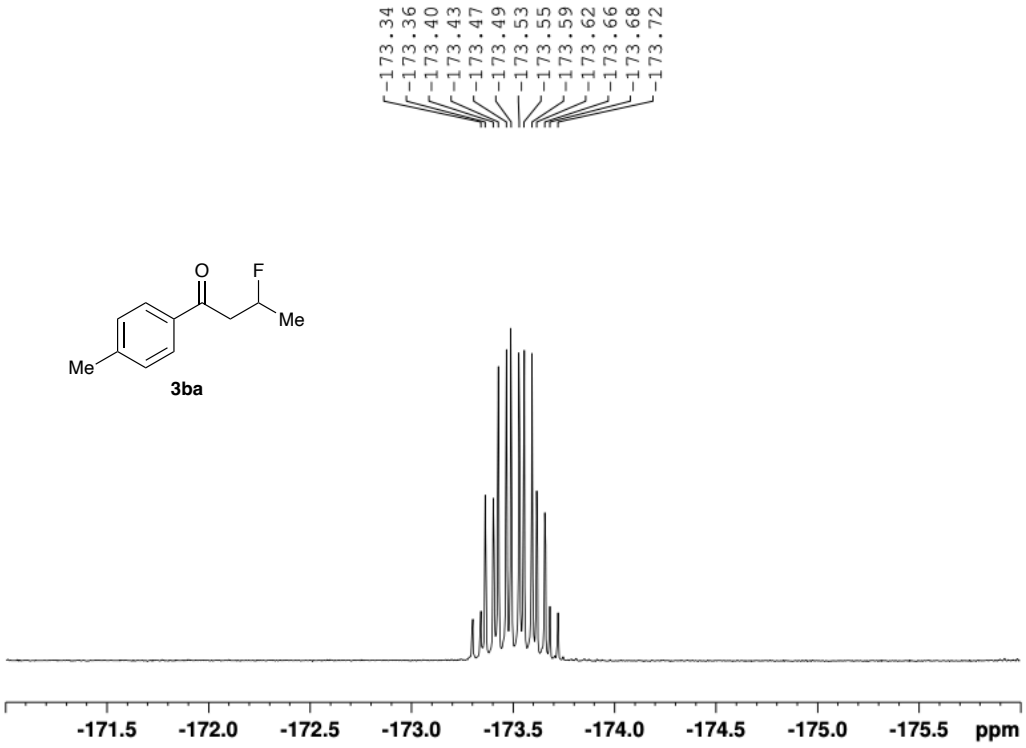

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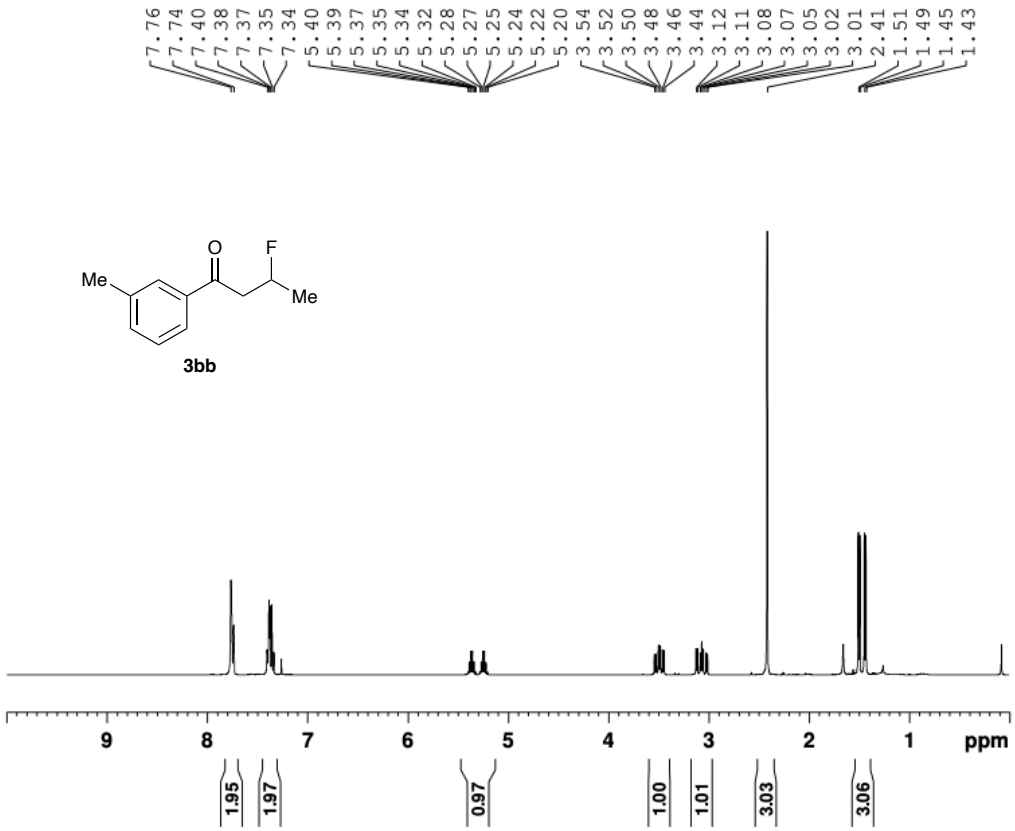

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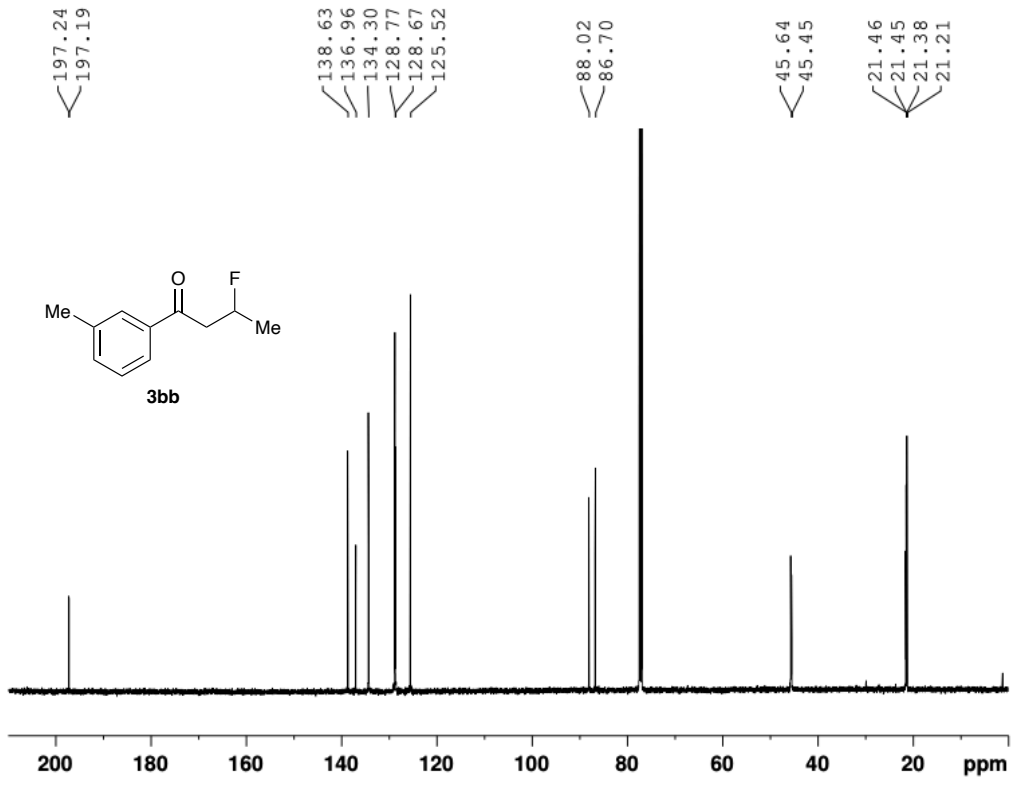

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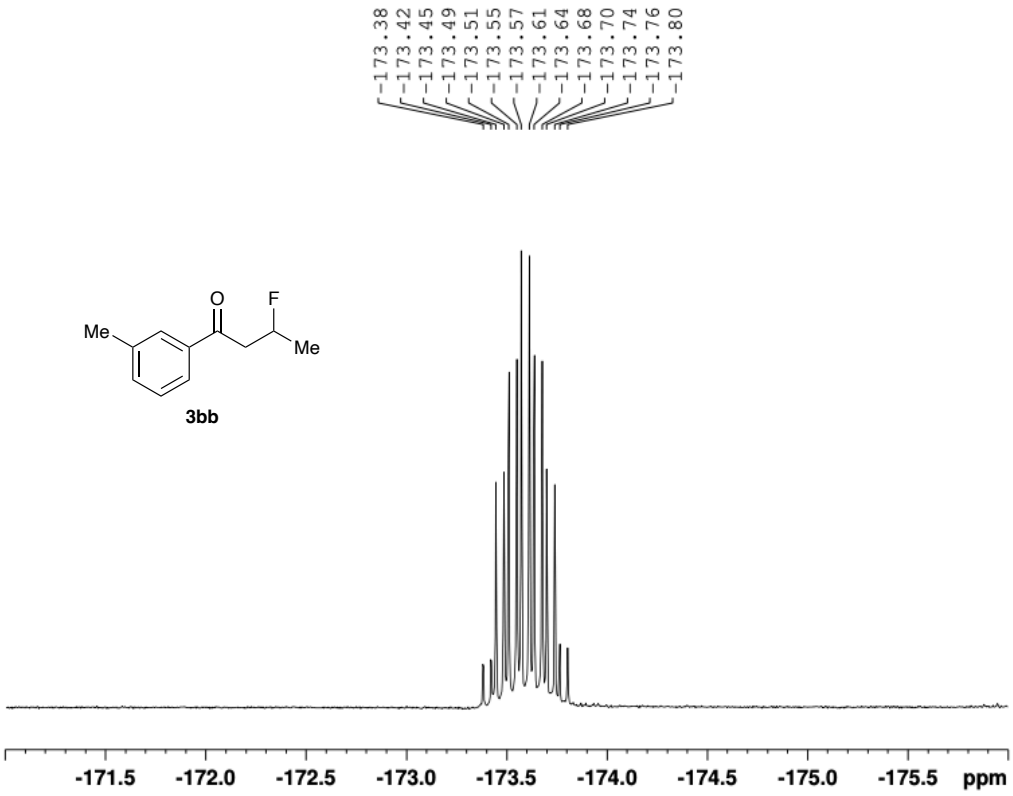

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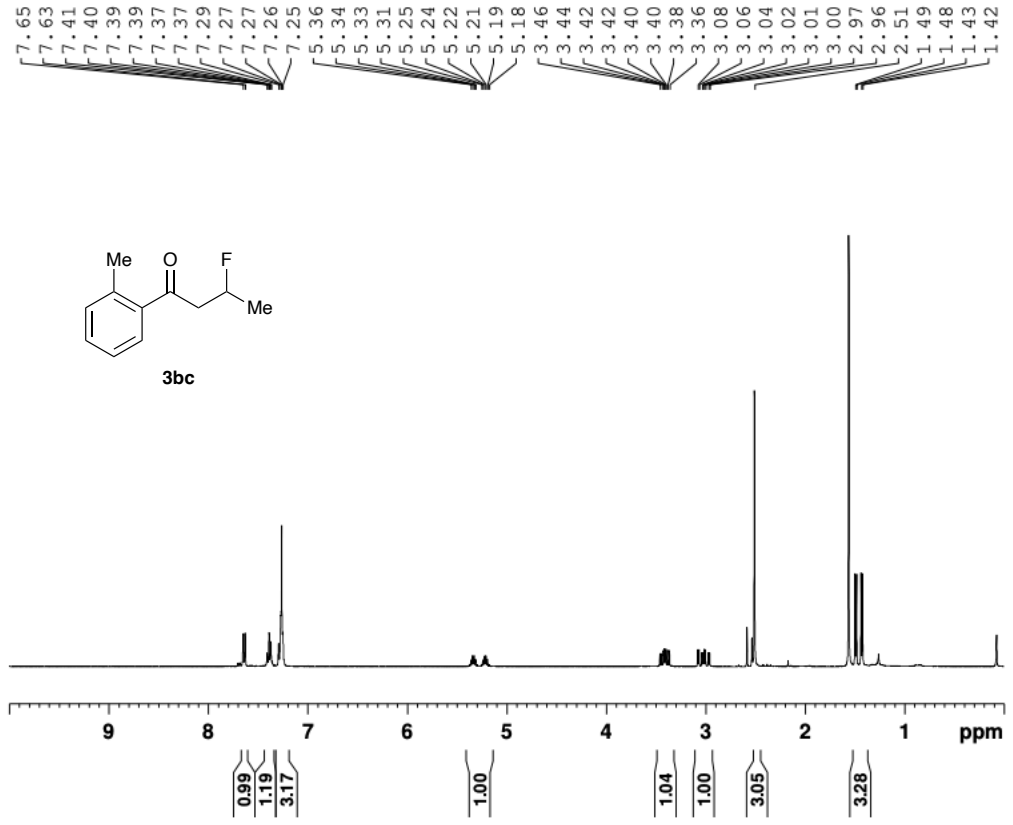

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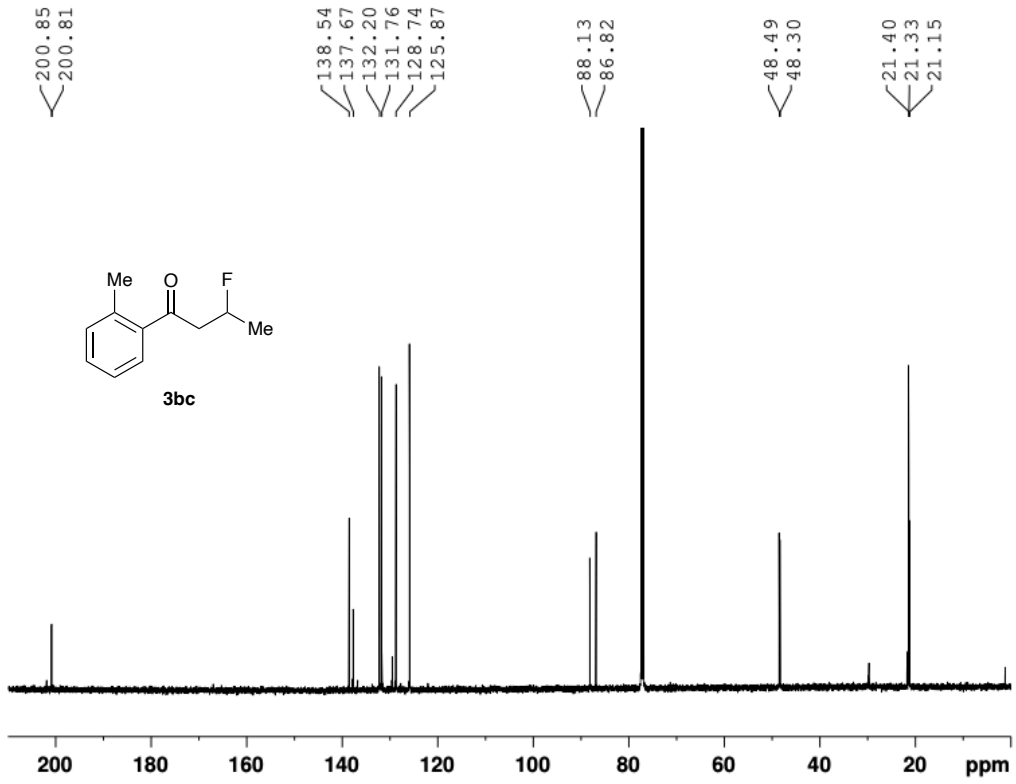

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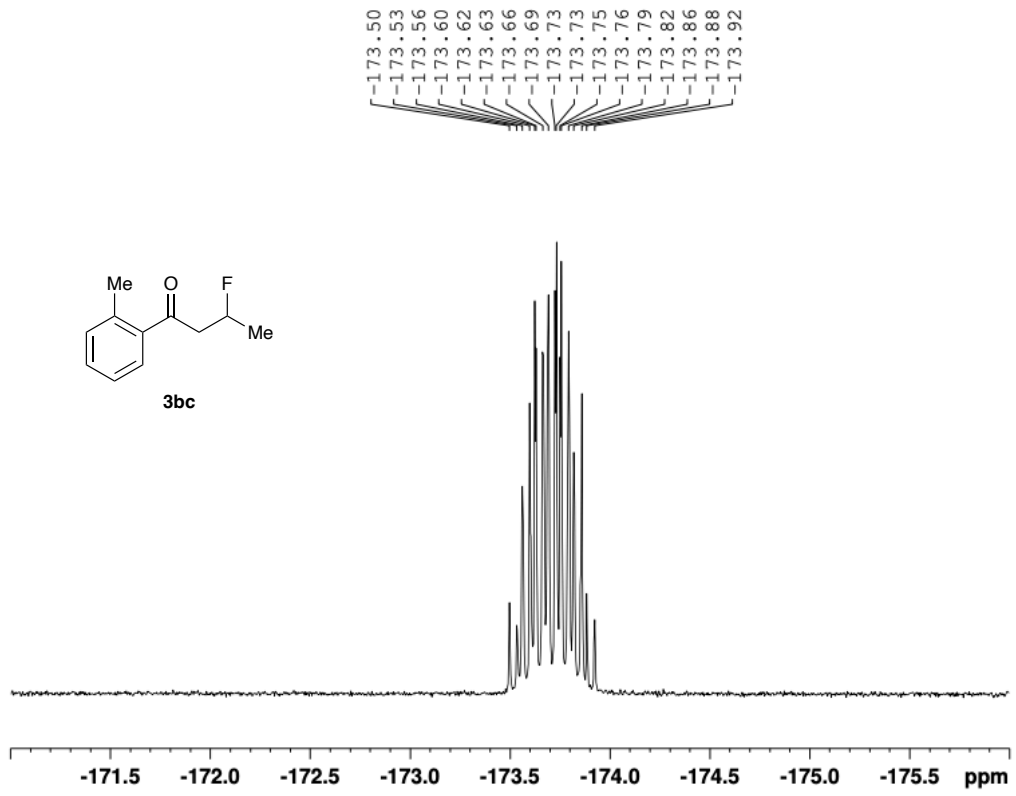

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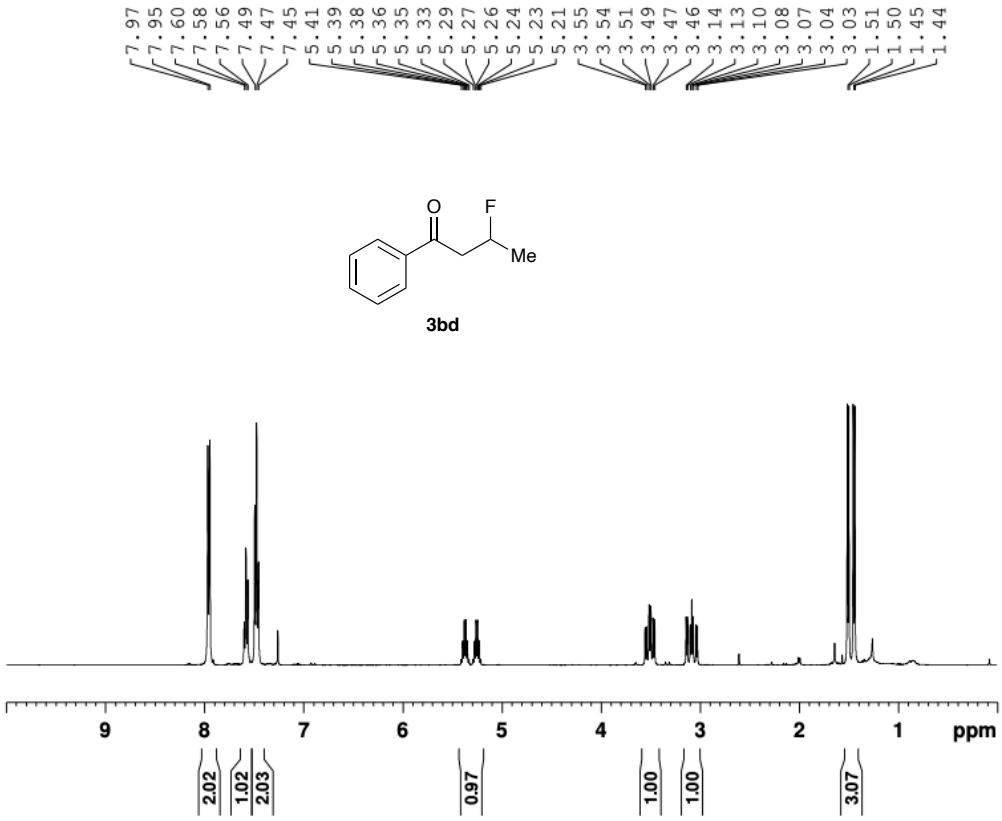

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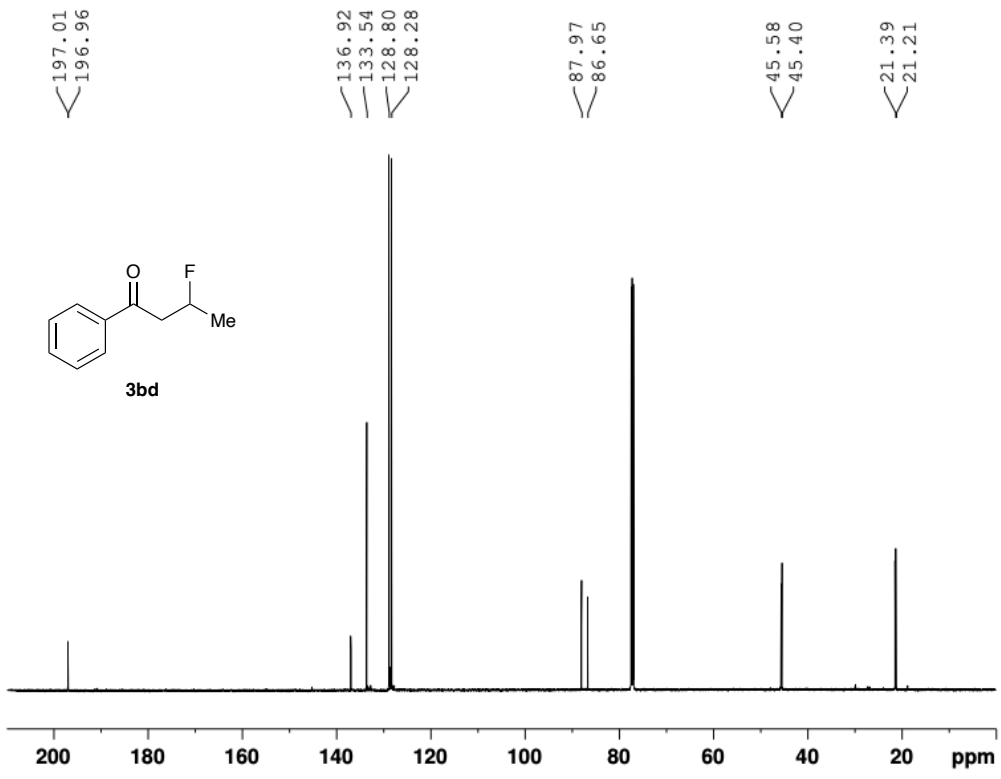

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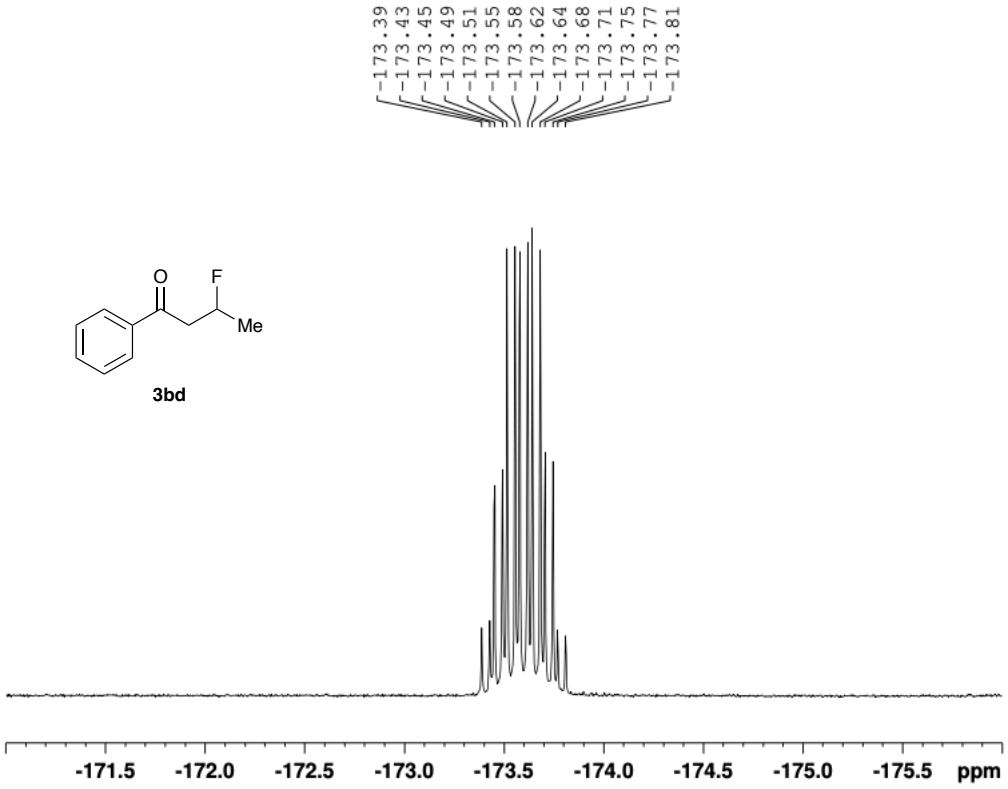

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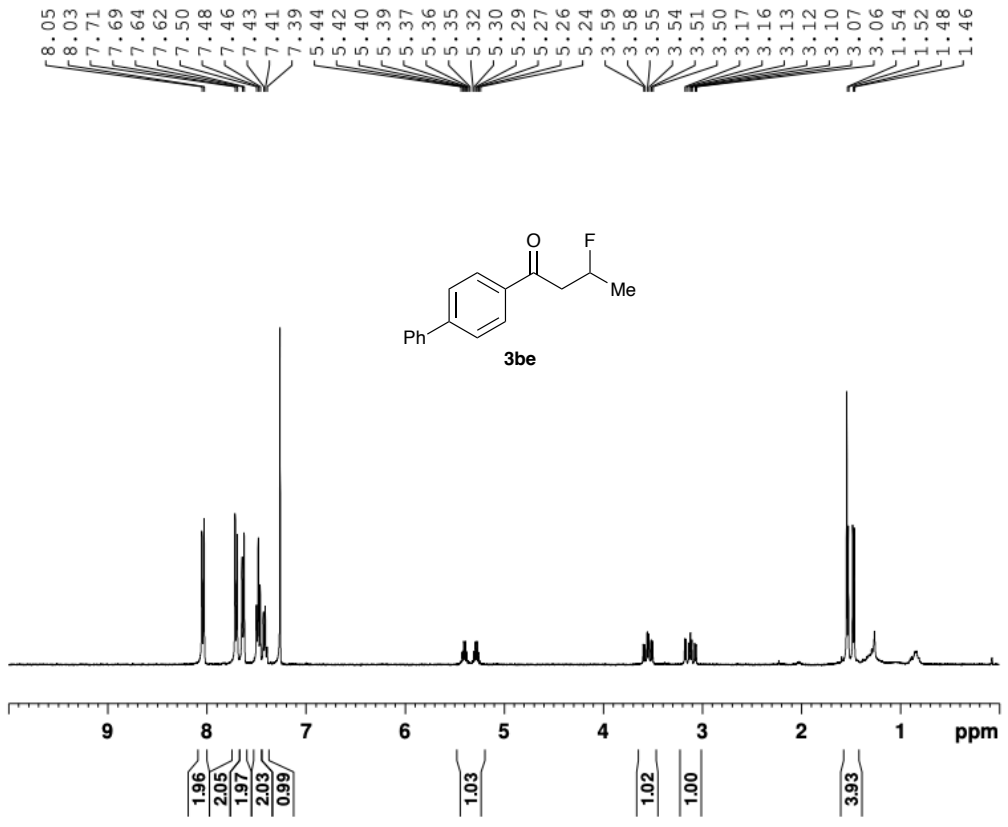

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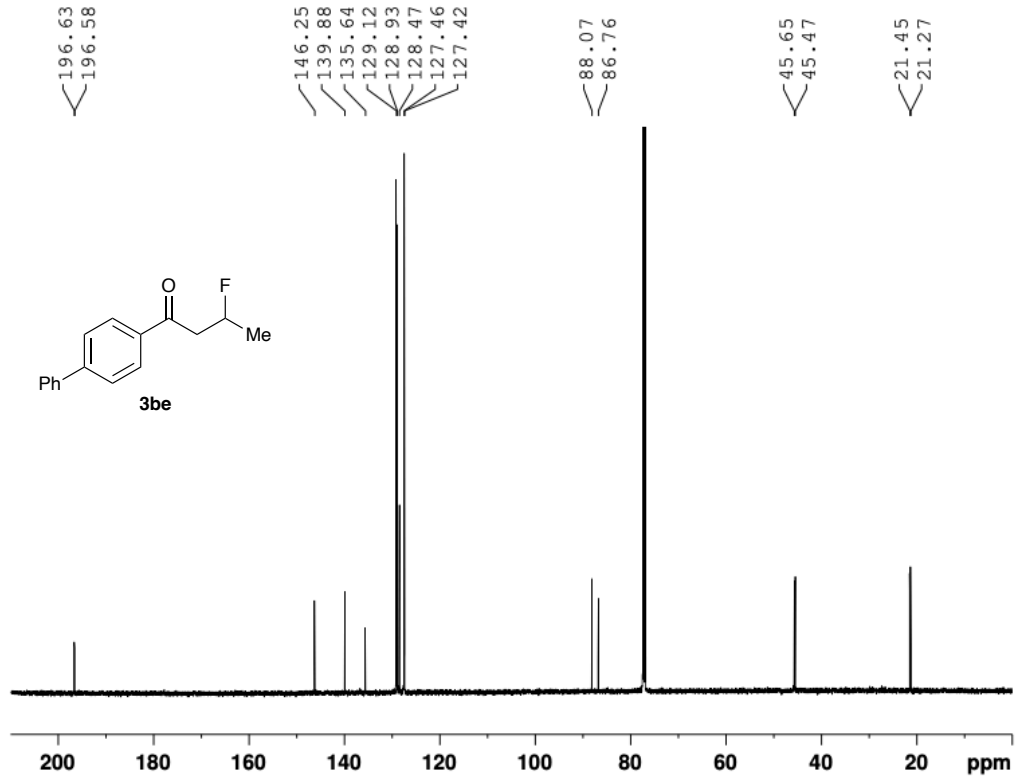

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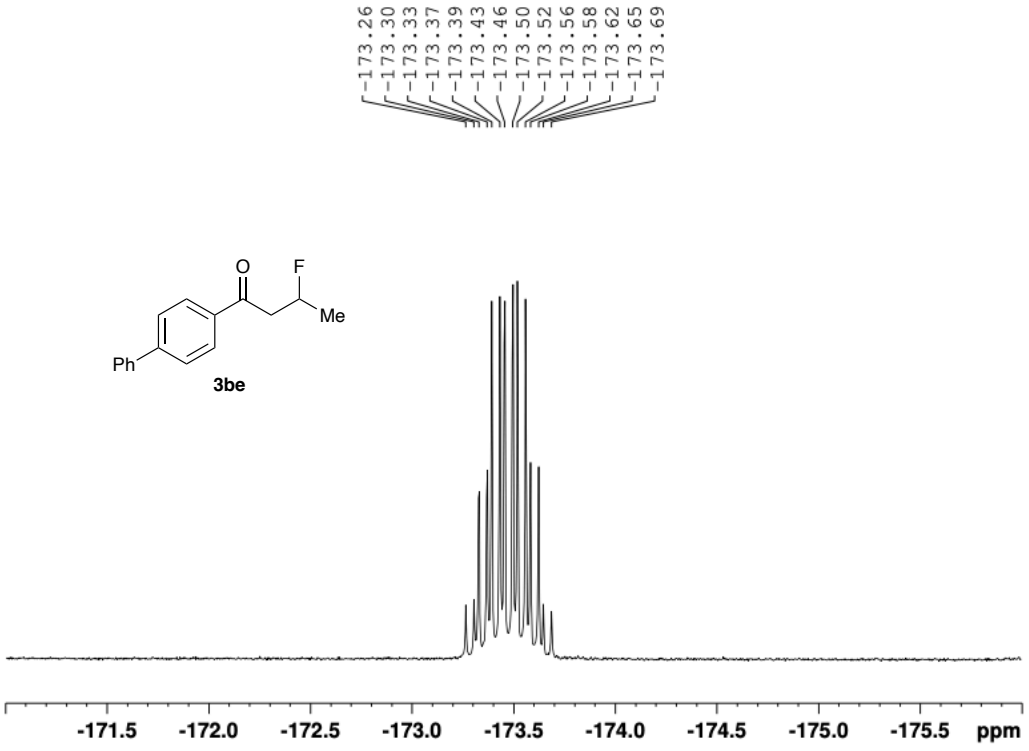

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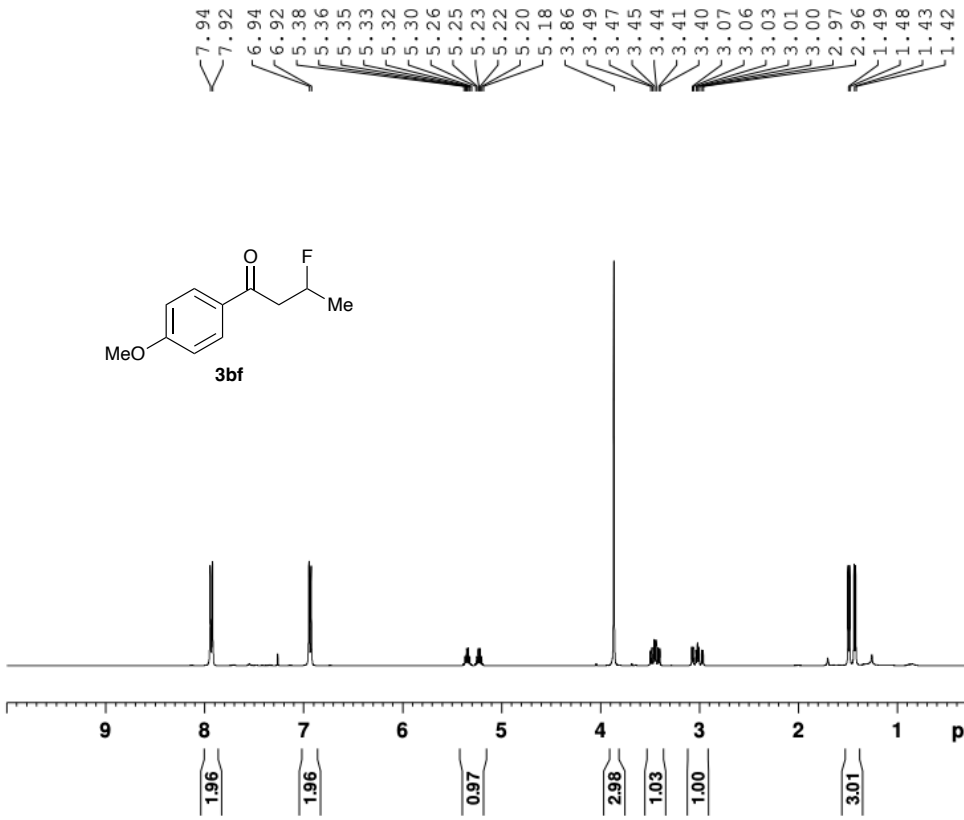

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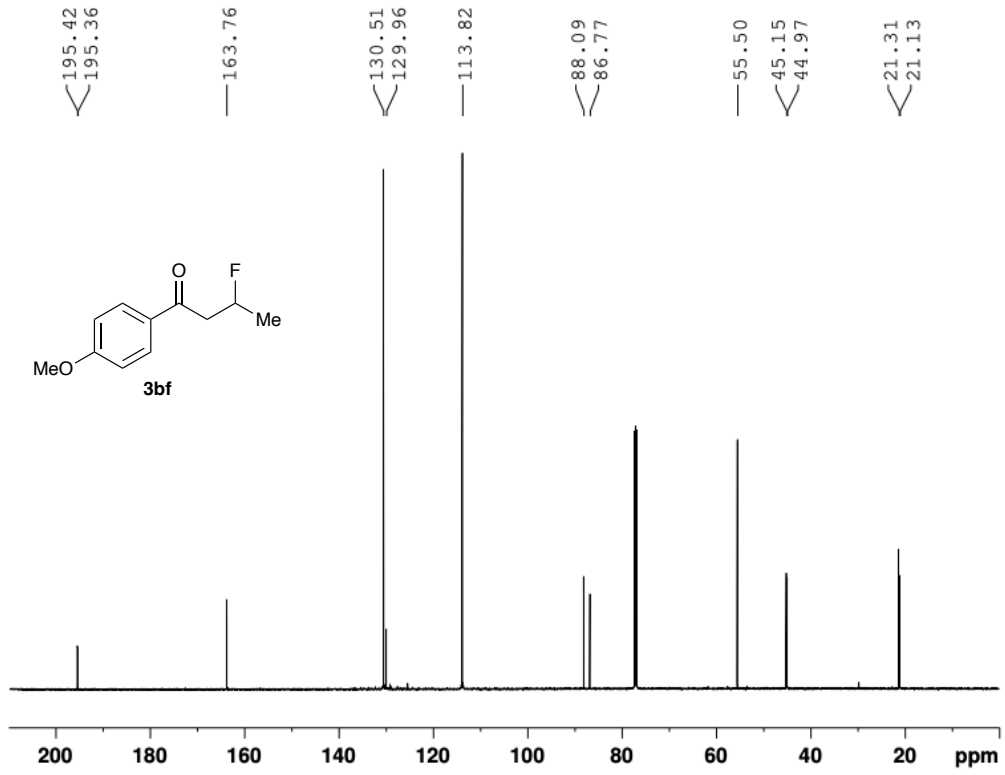

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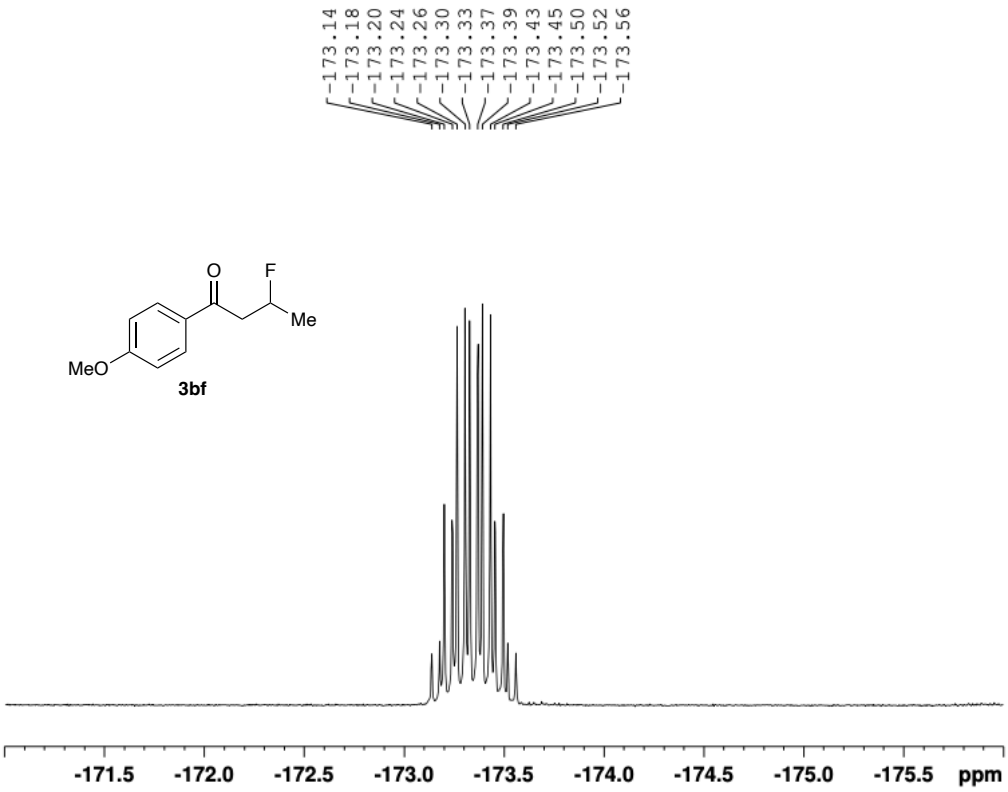

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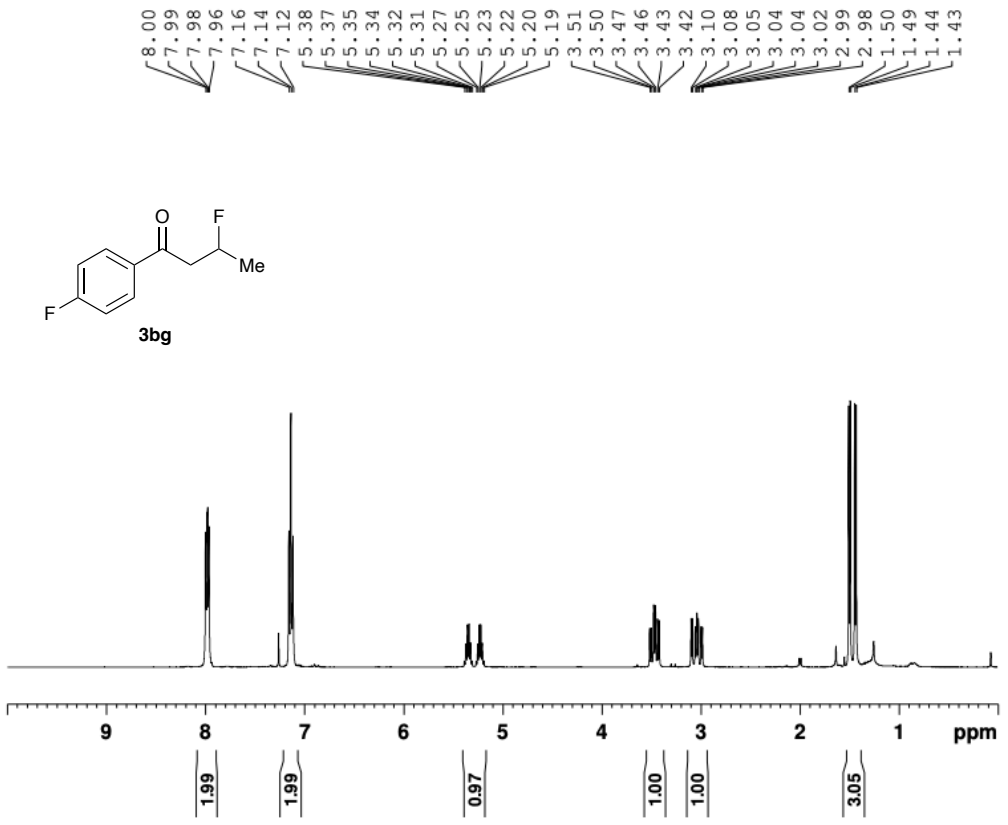

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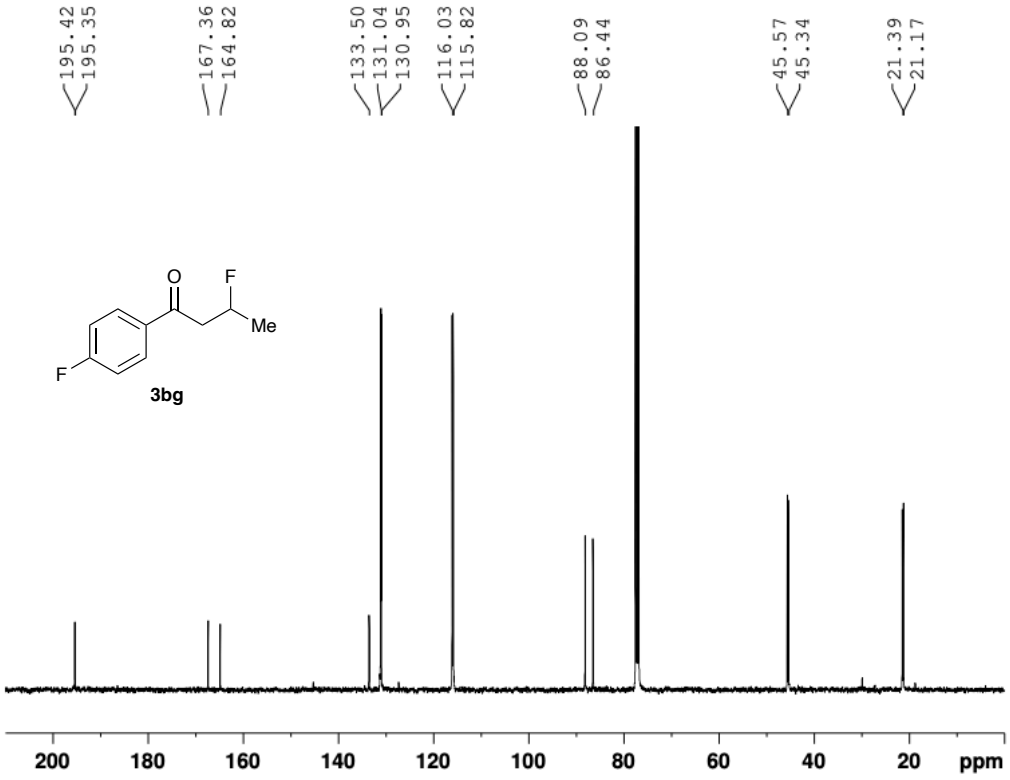

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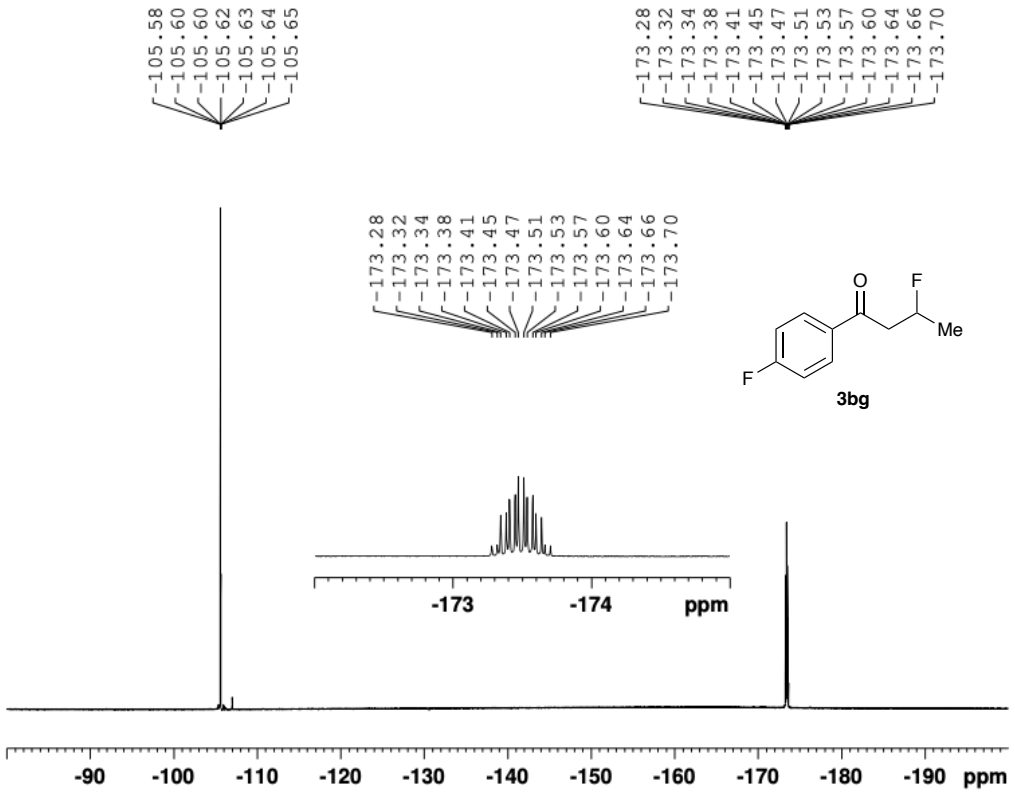

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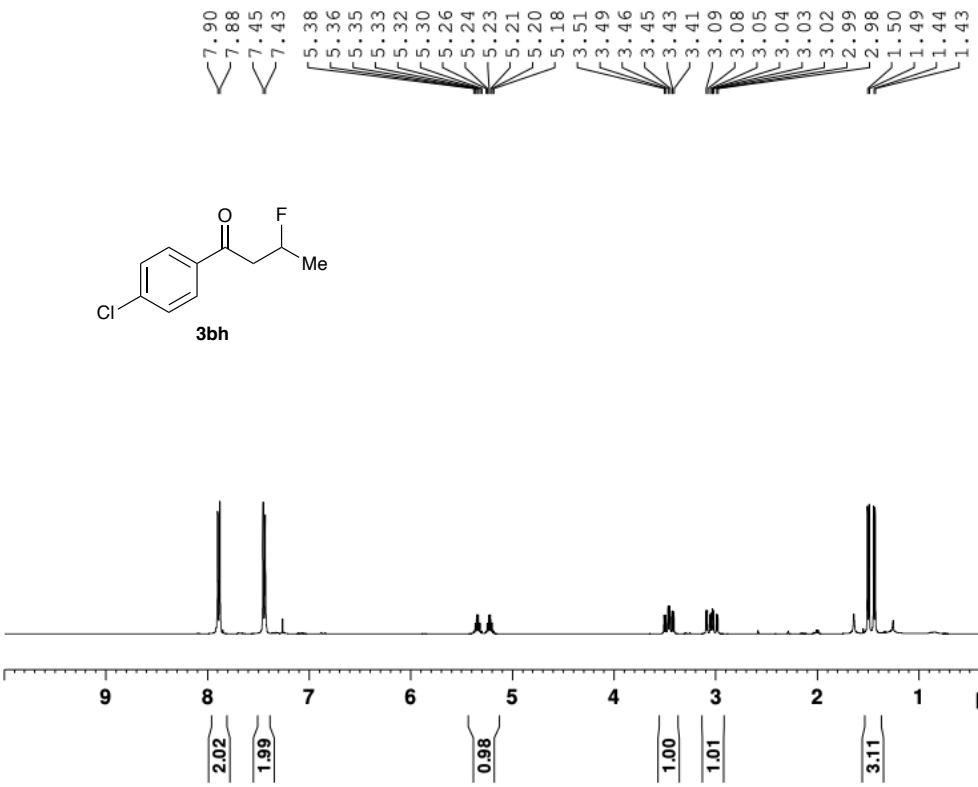

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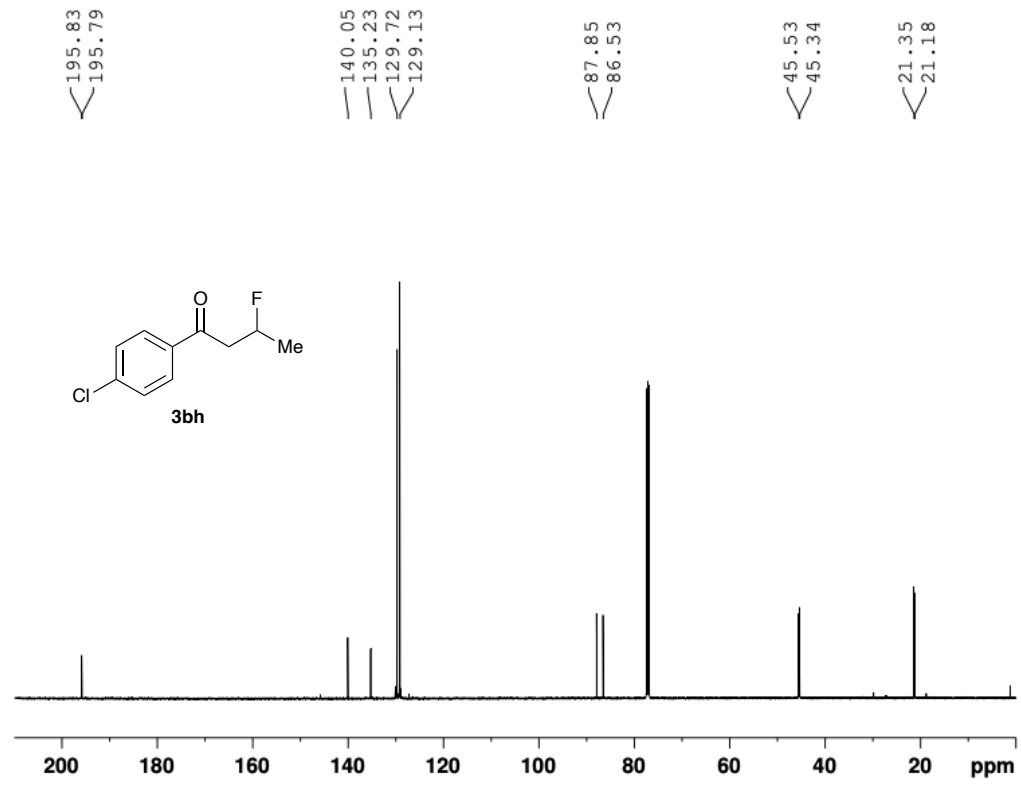

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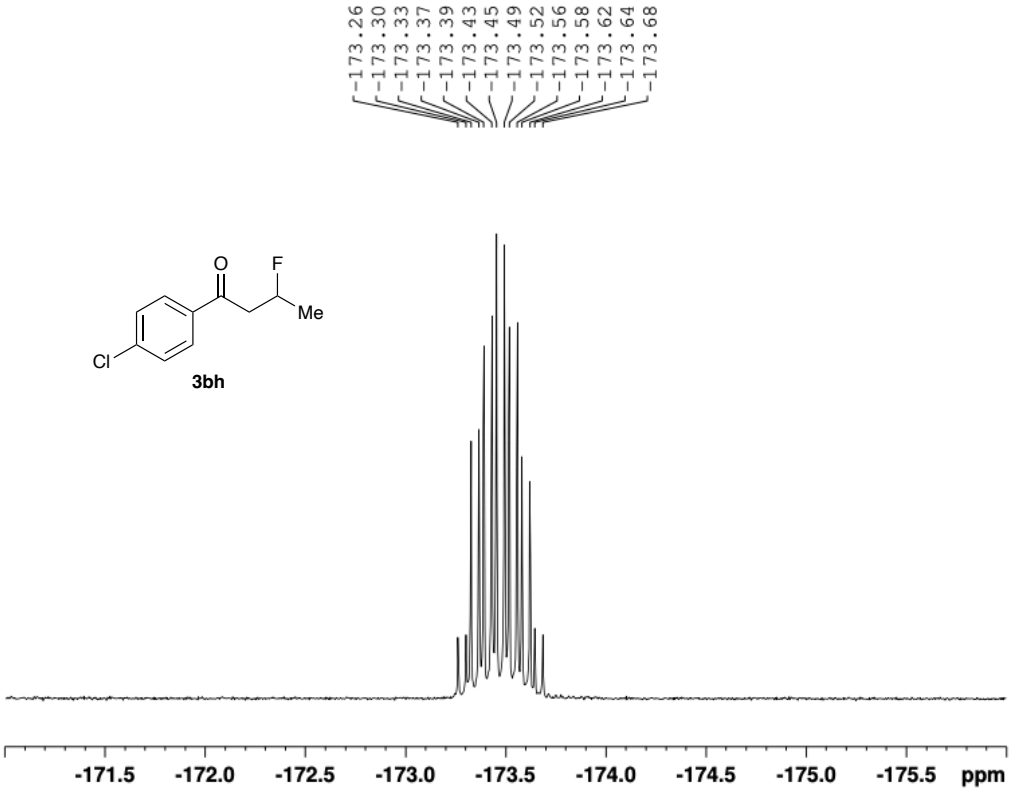

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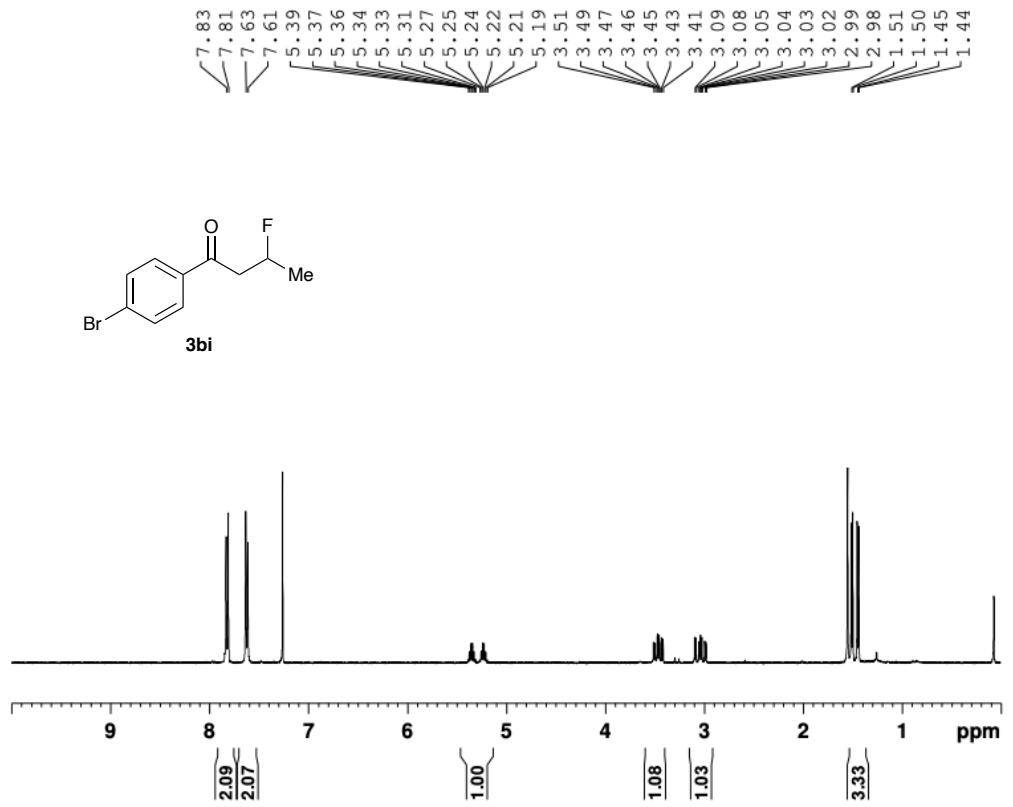

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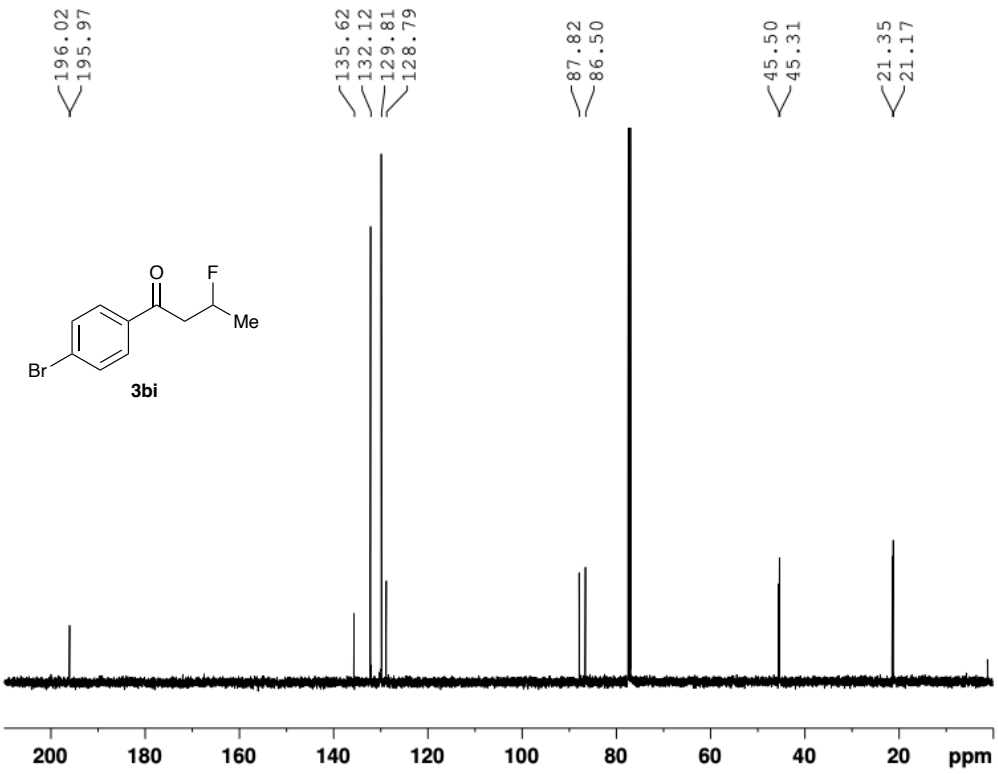

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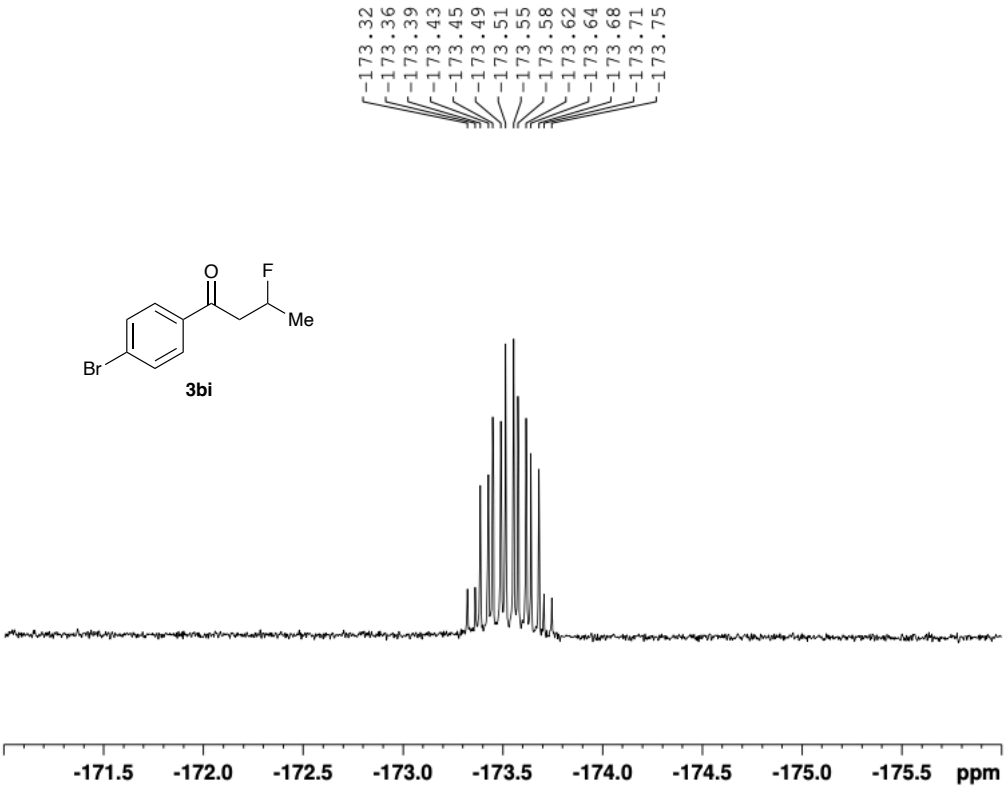

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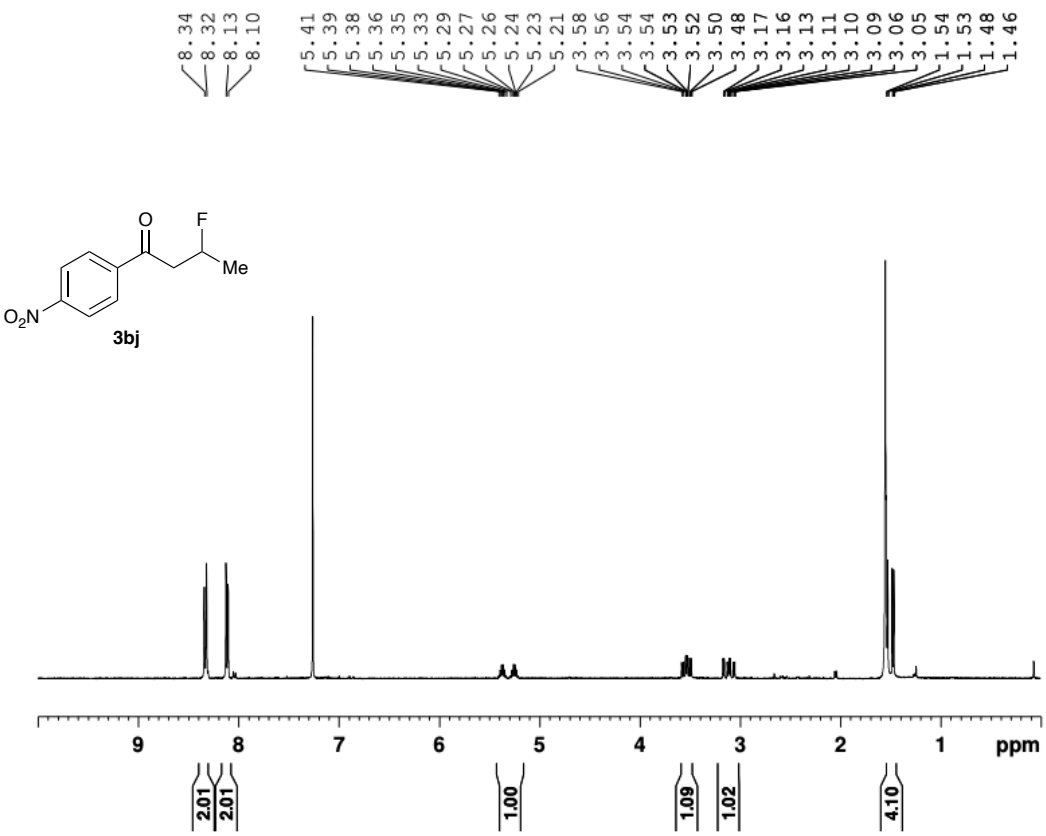

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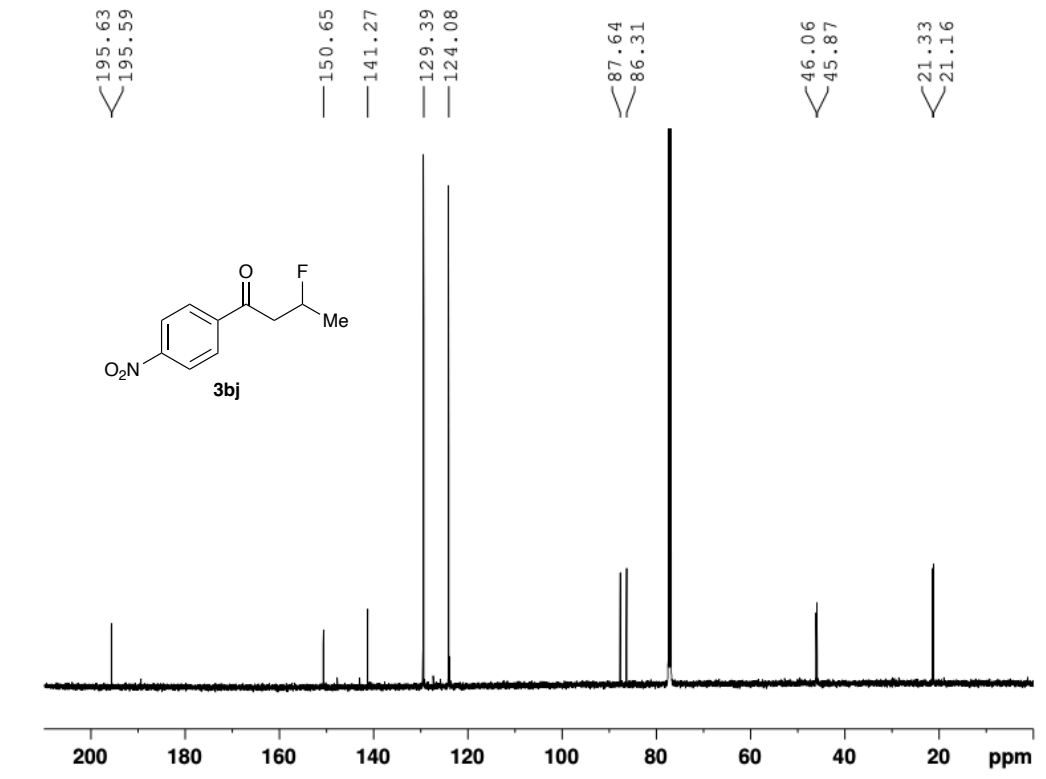

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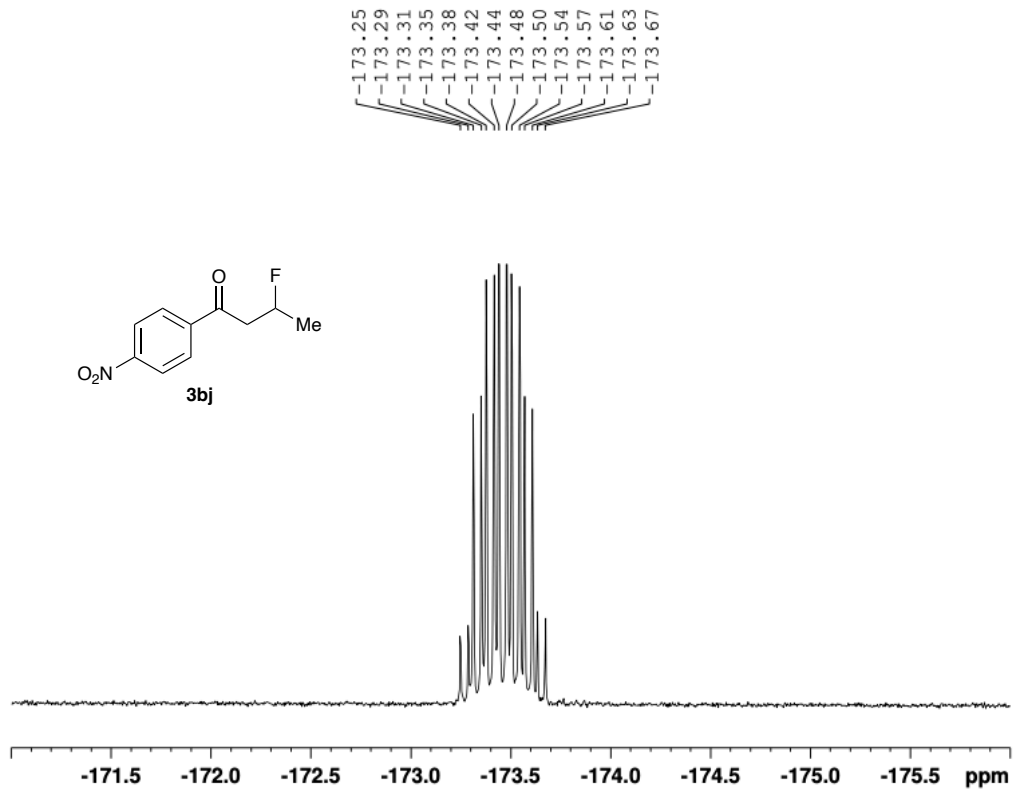

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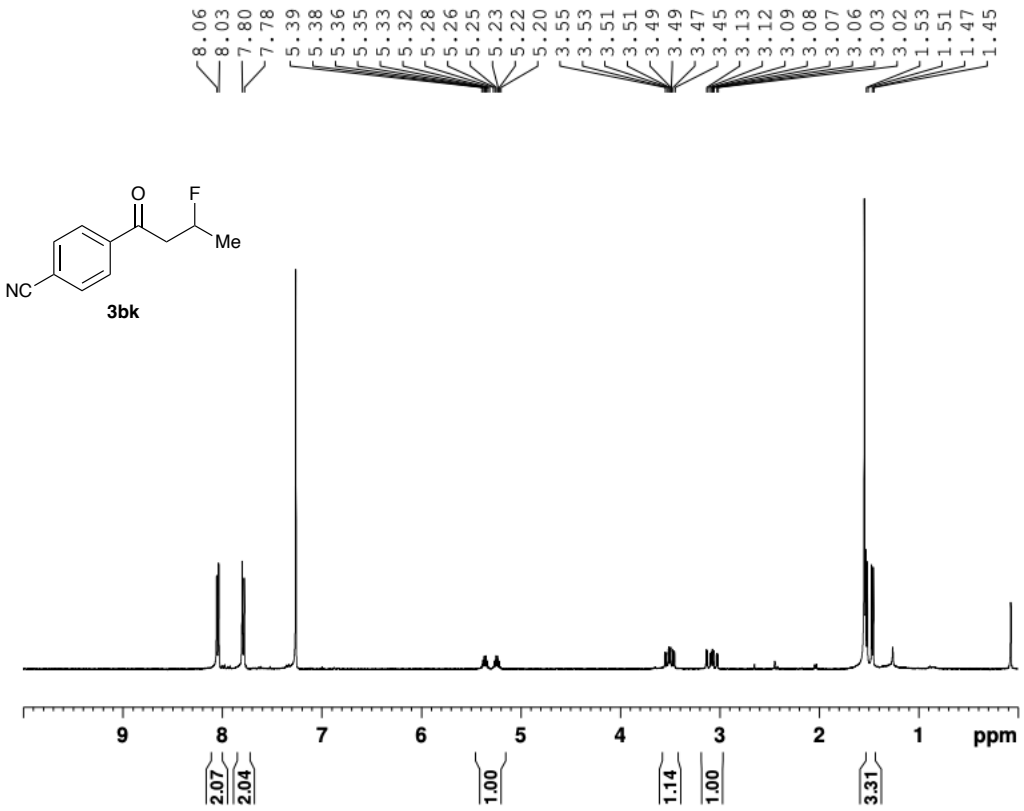

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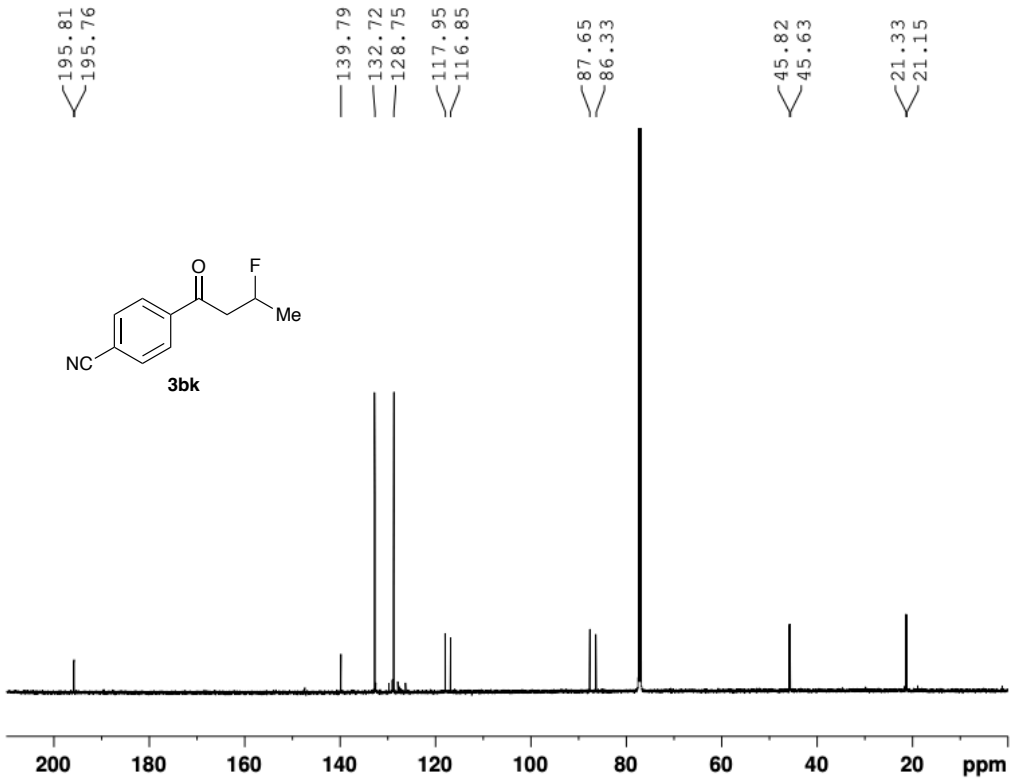

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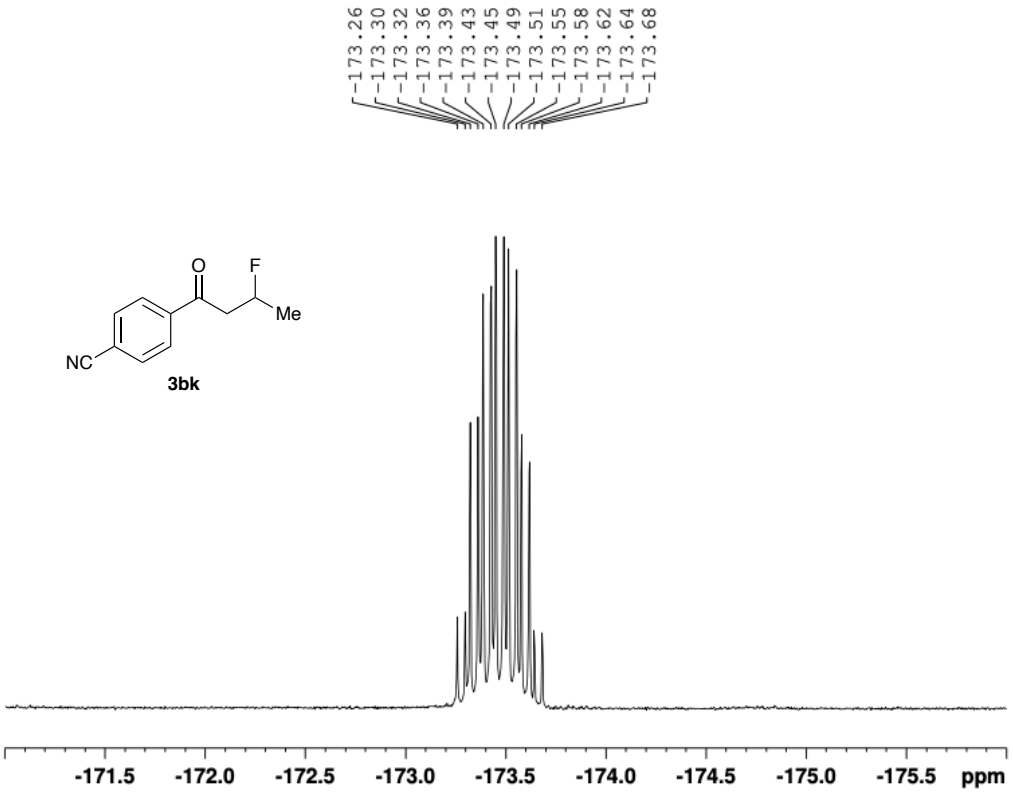

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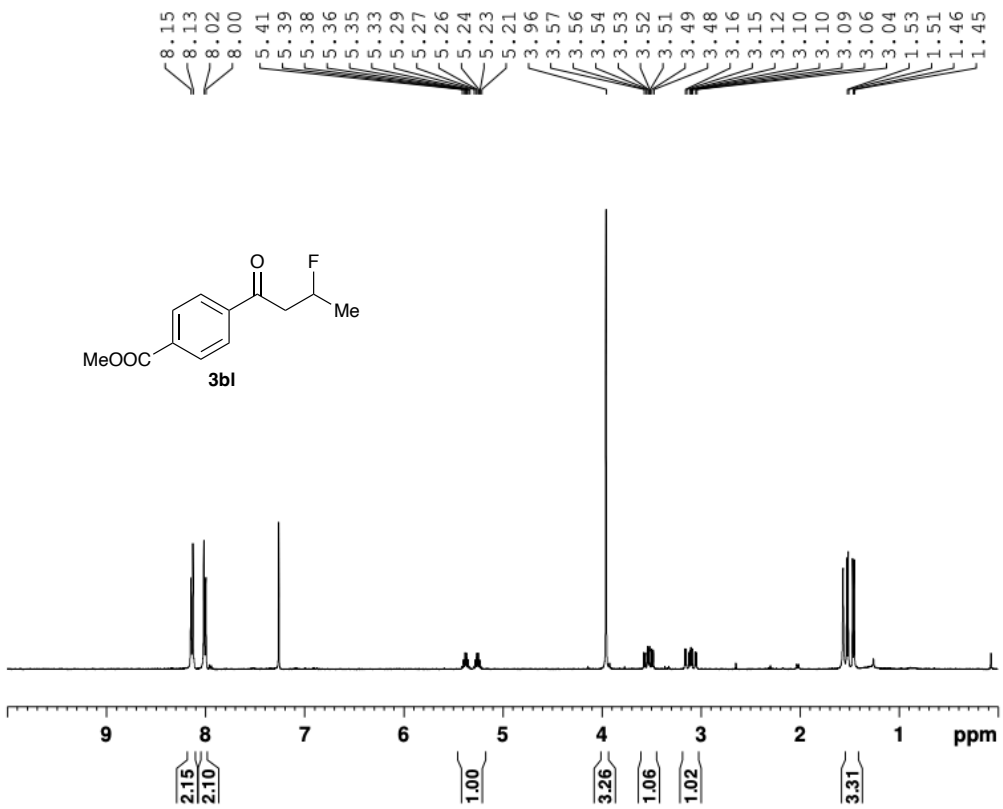

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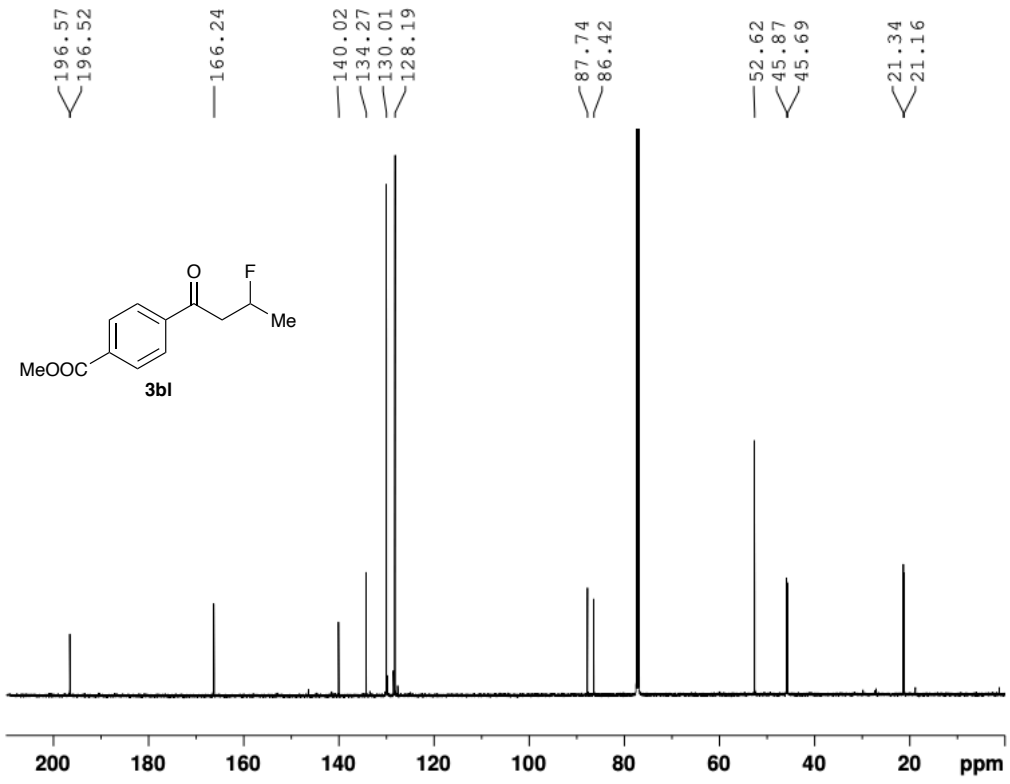

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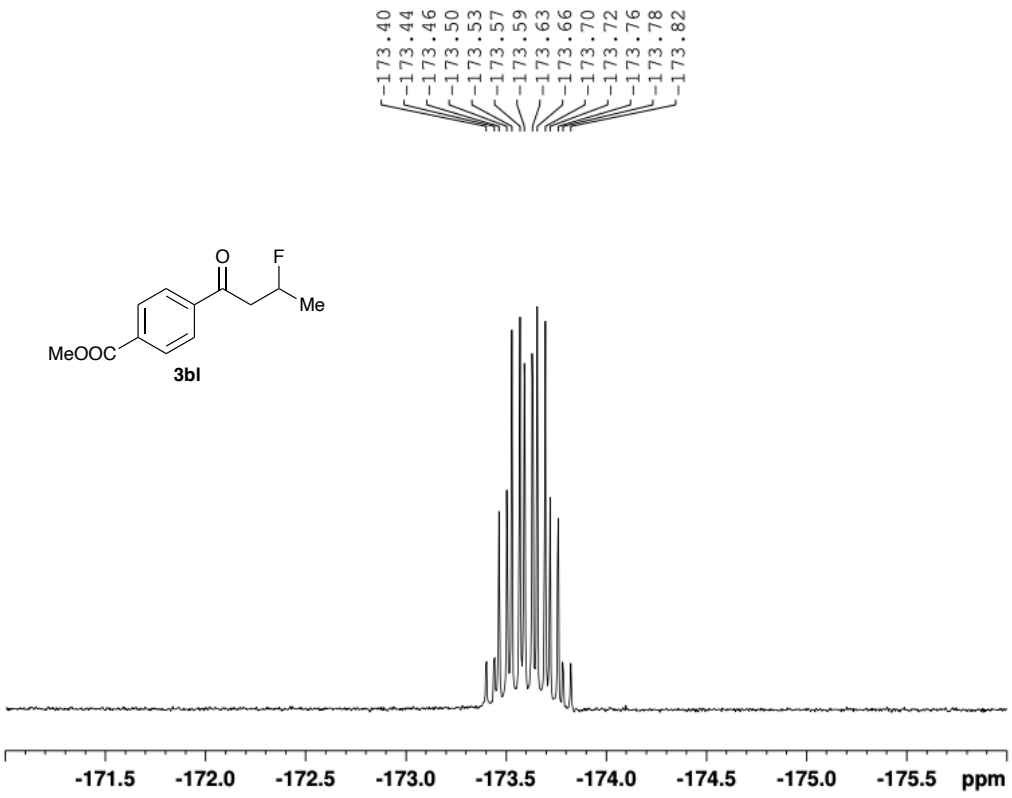

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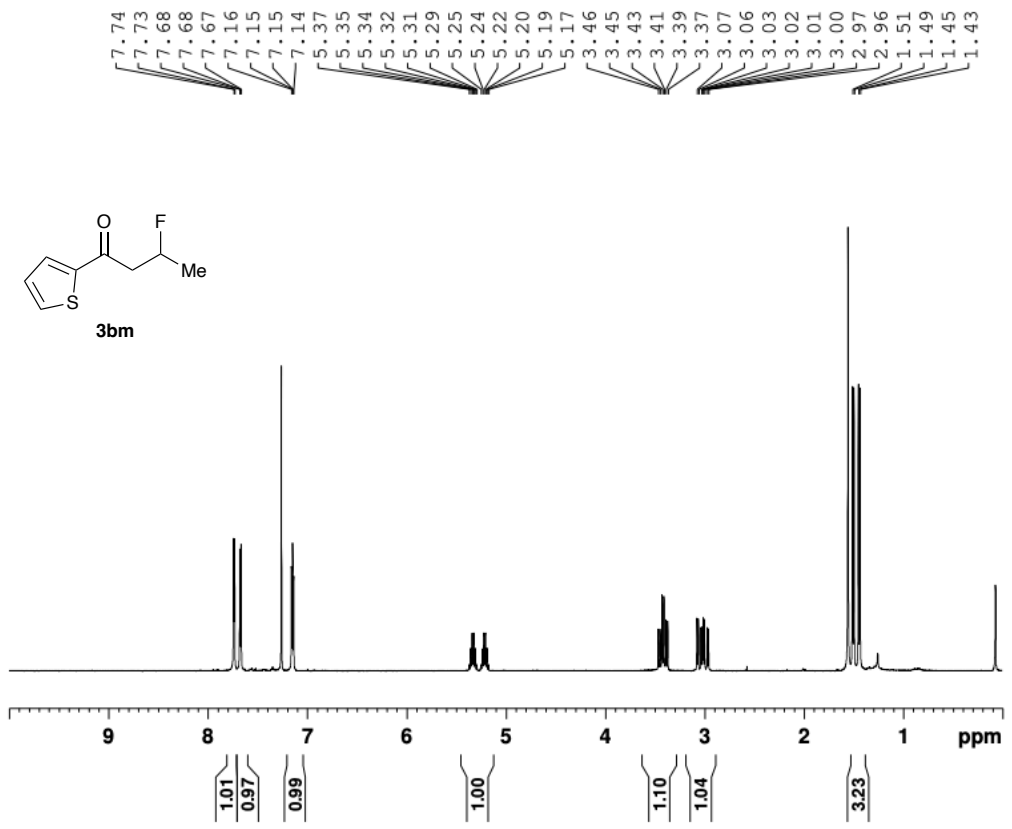

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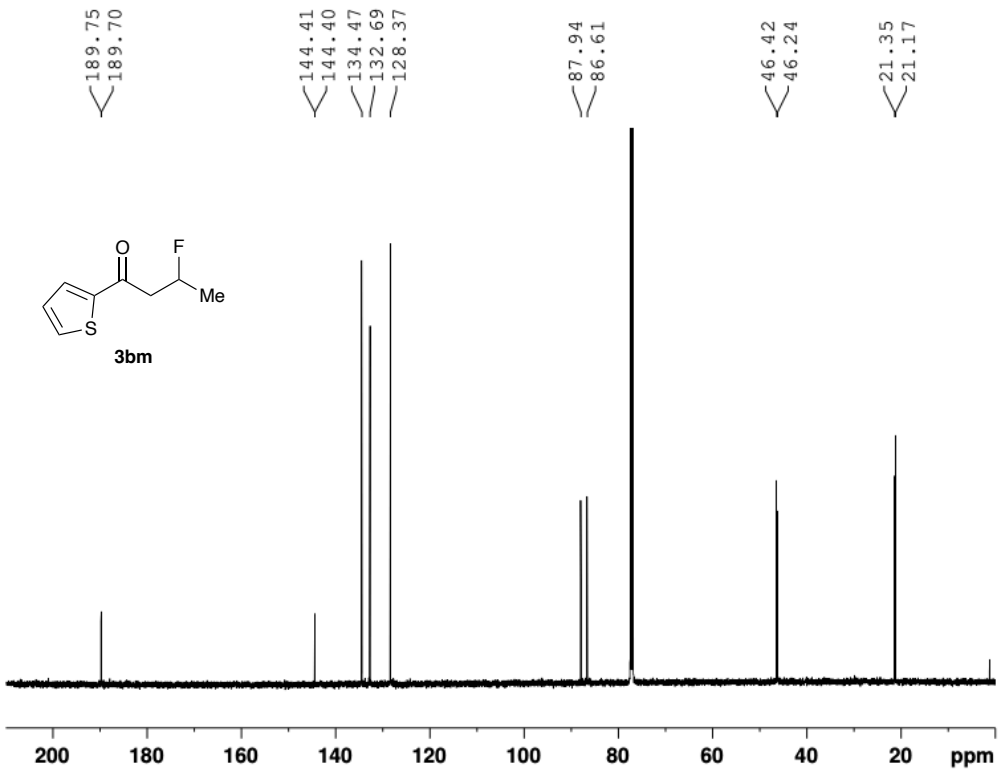

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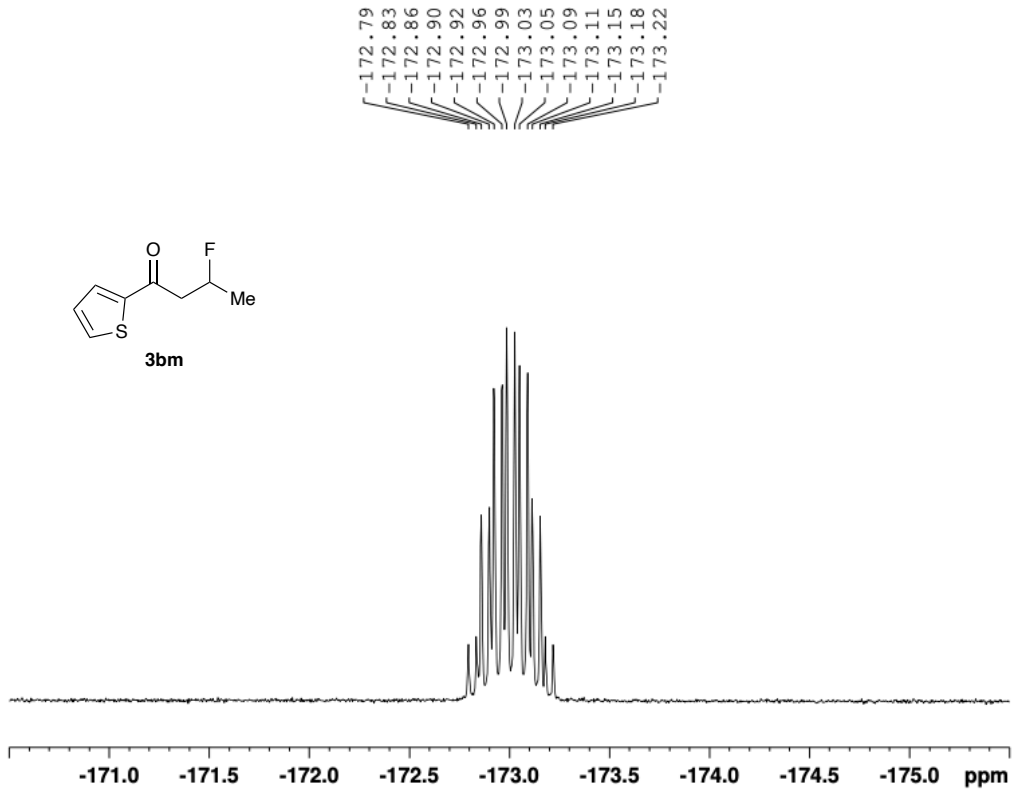

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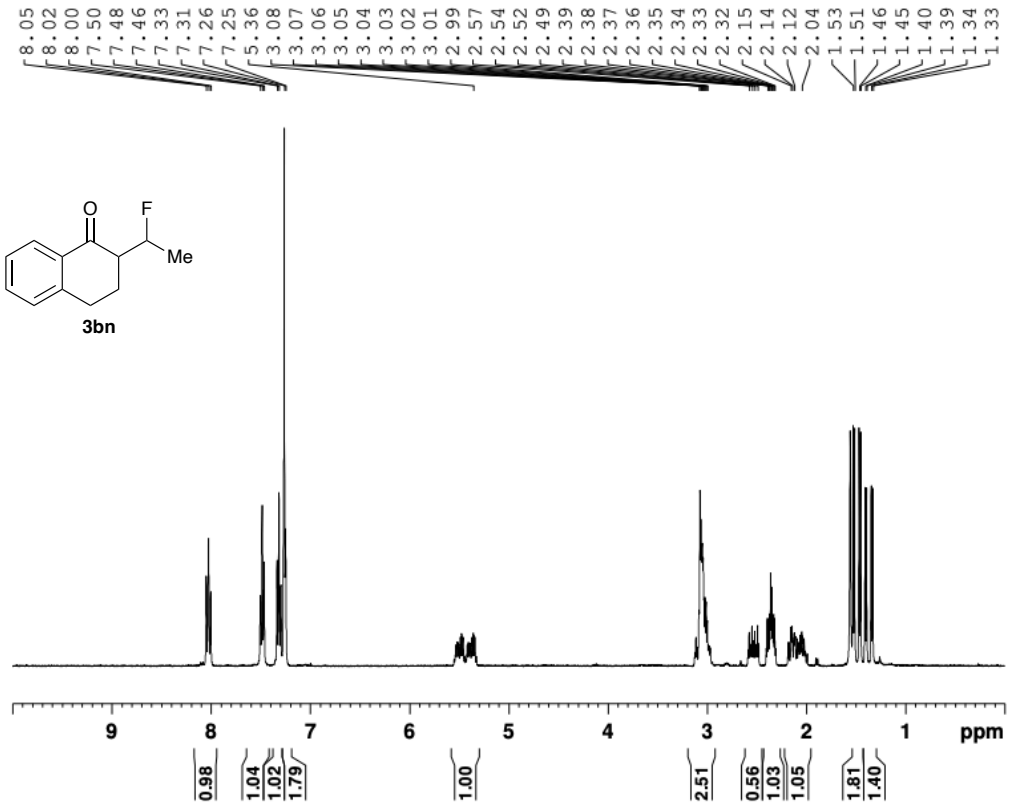

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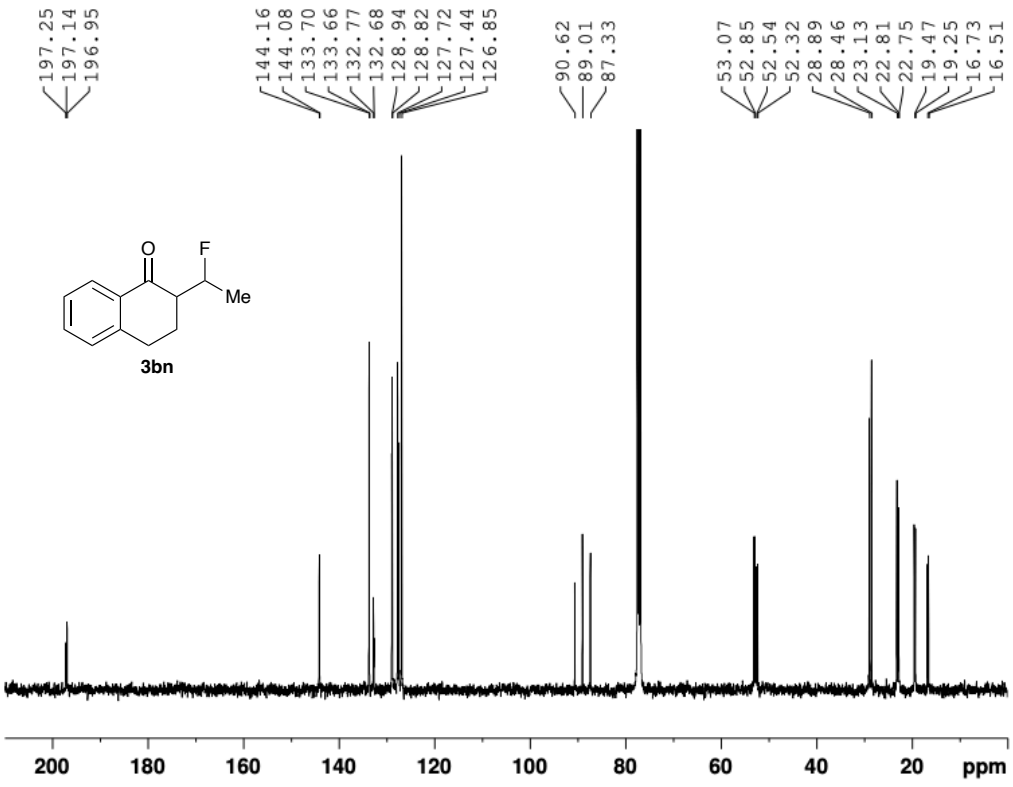

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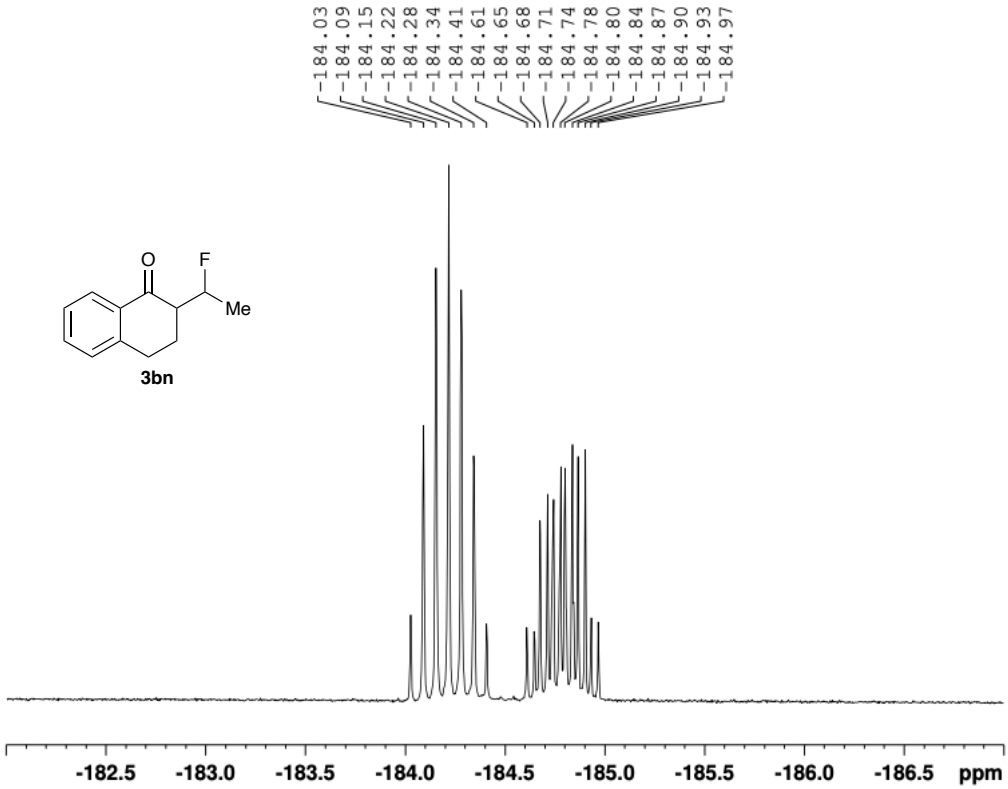

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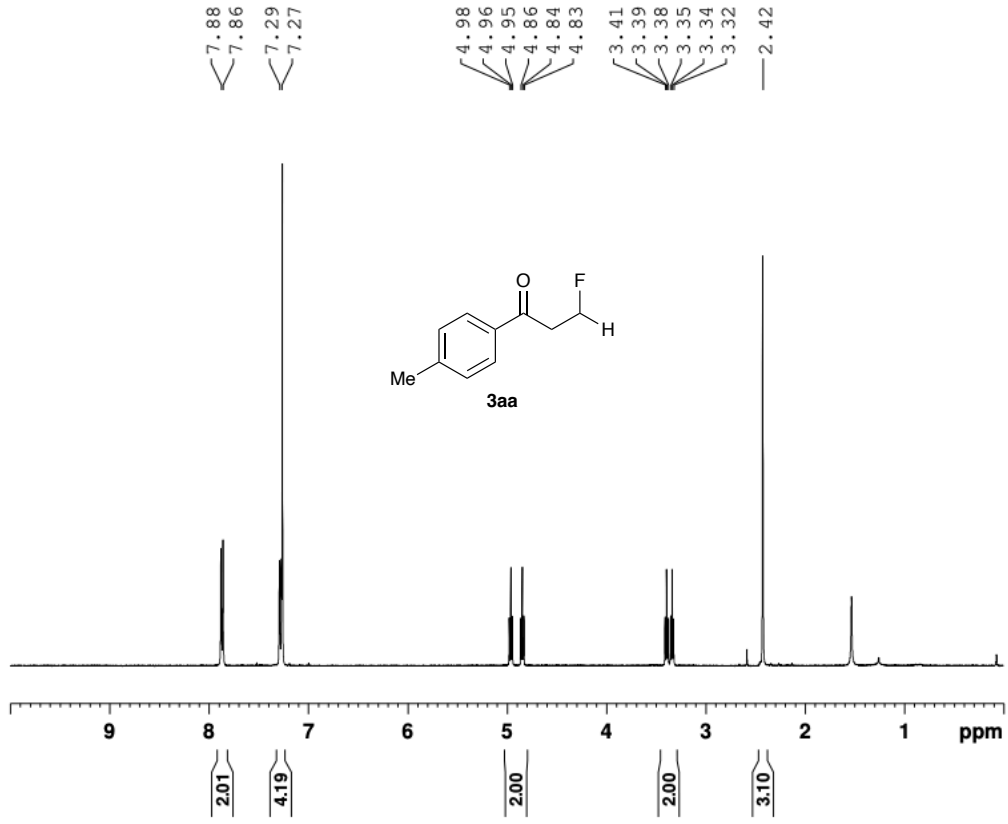

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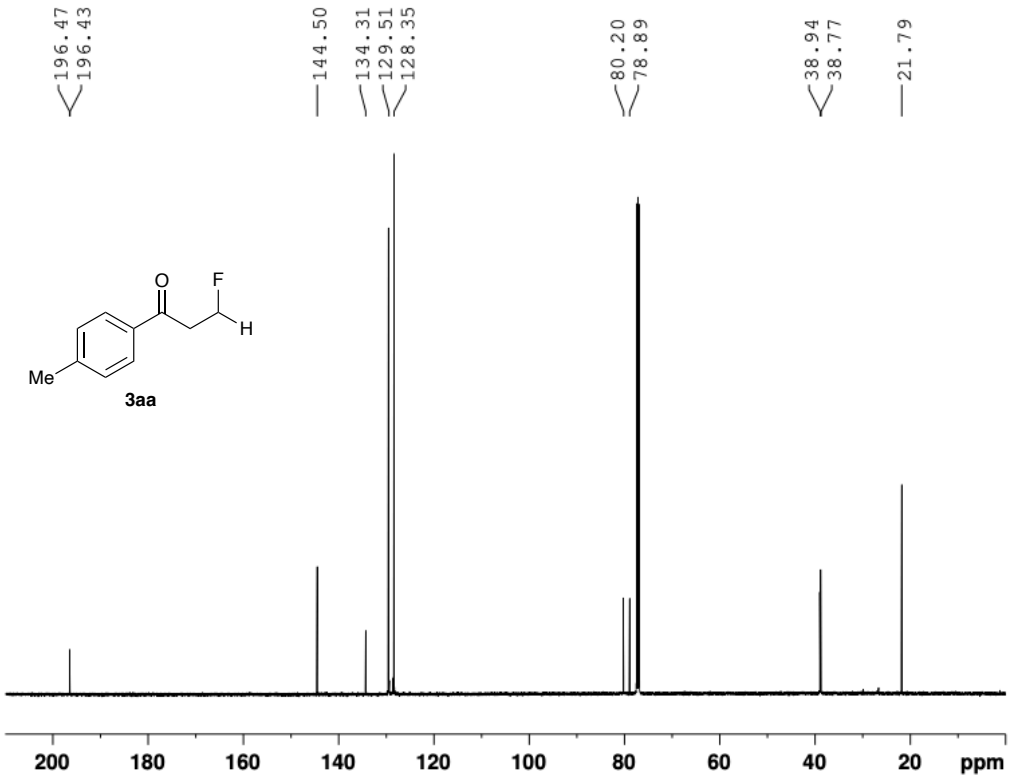

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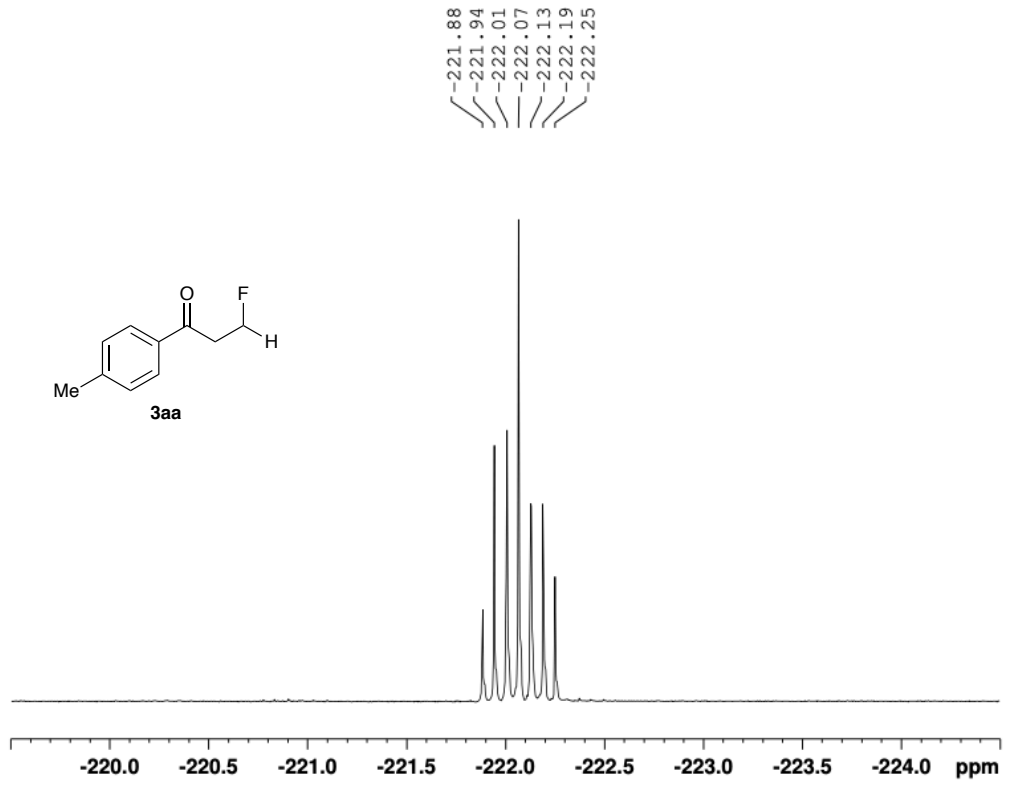

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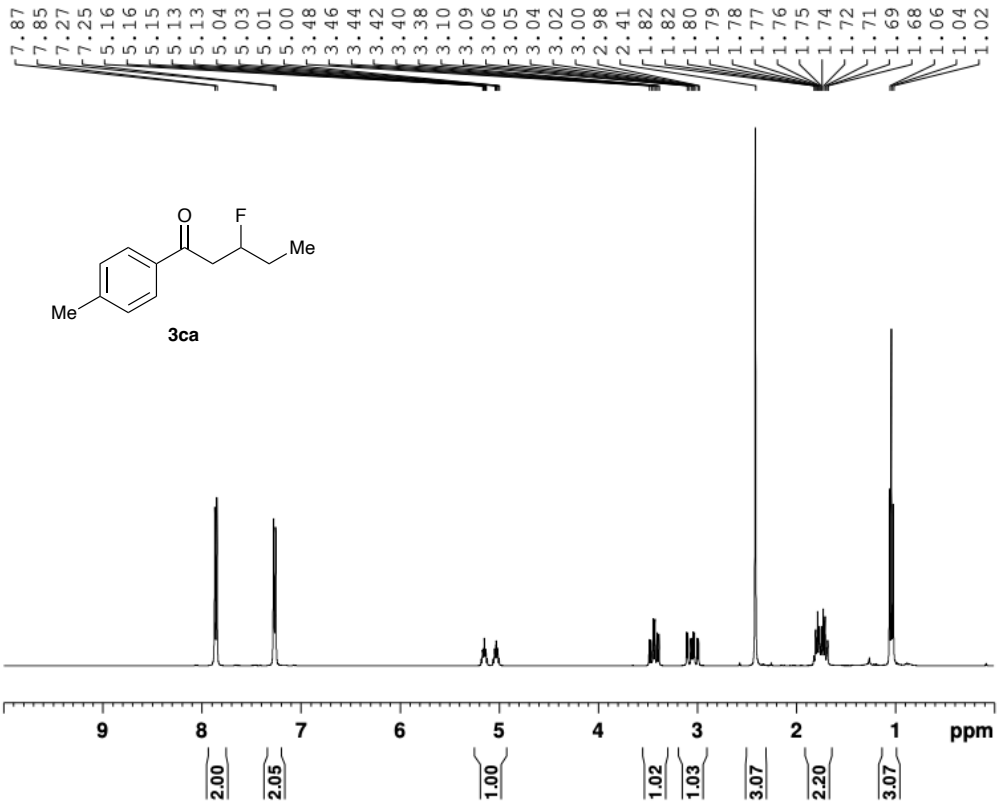
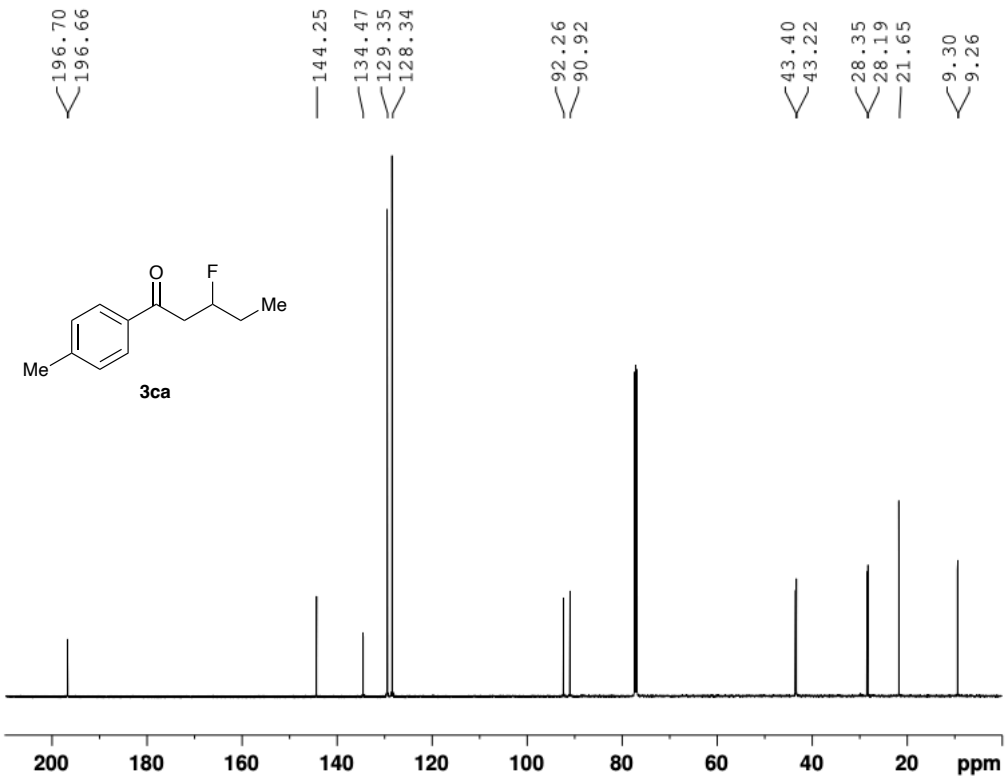
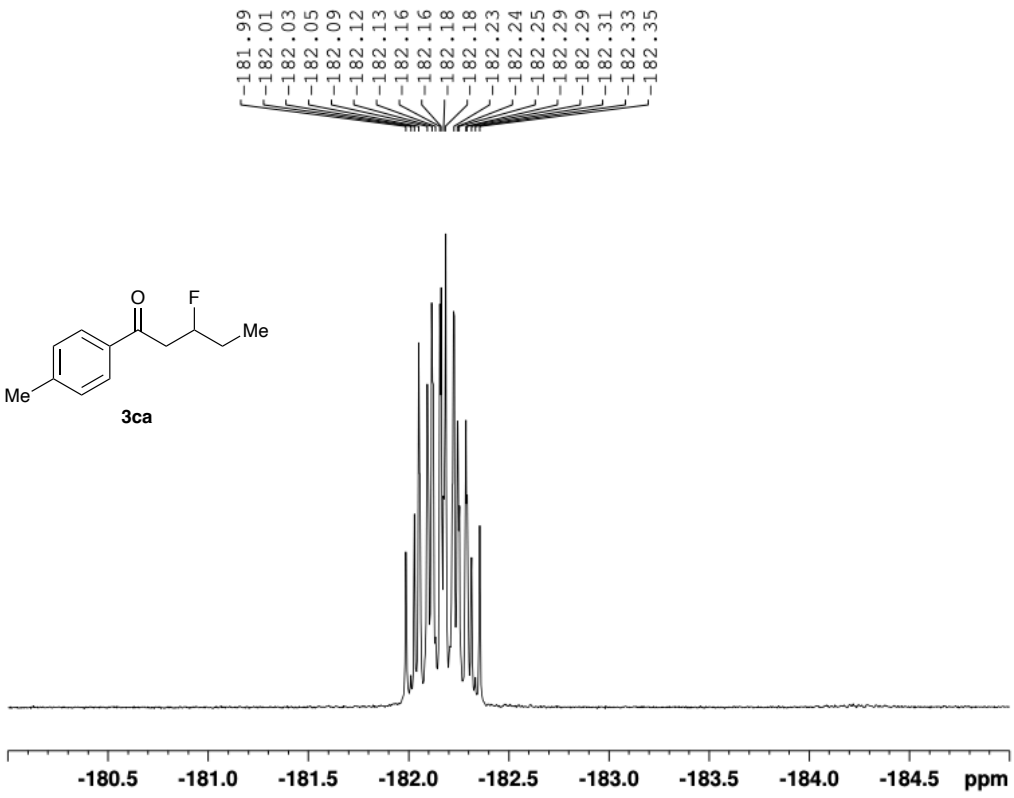


^{13}C NMR



^{19}F NMR



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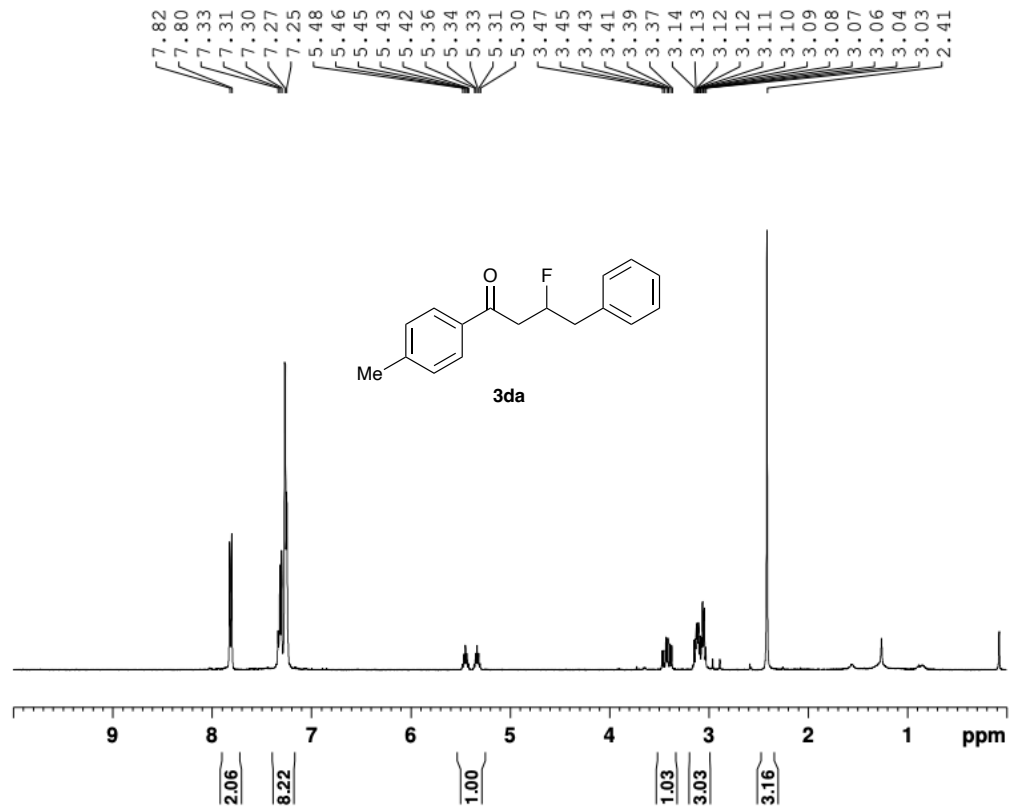

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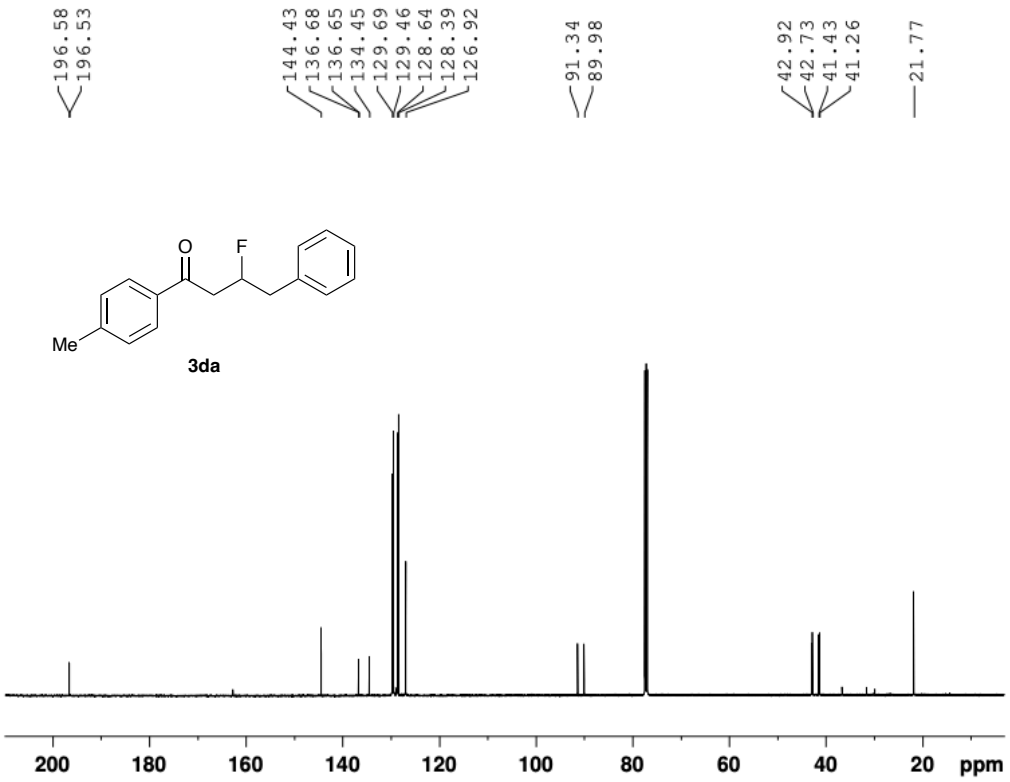

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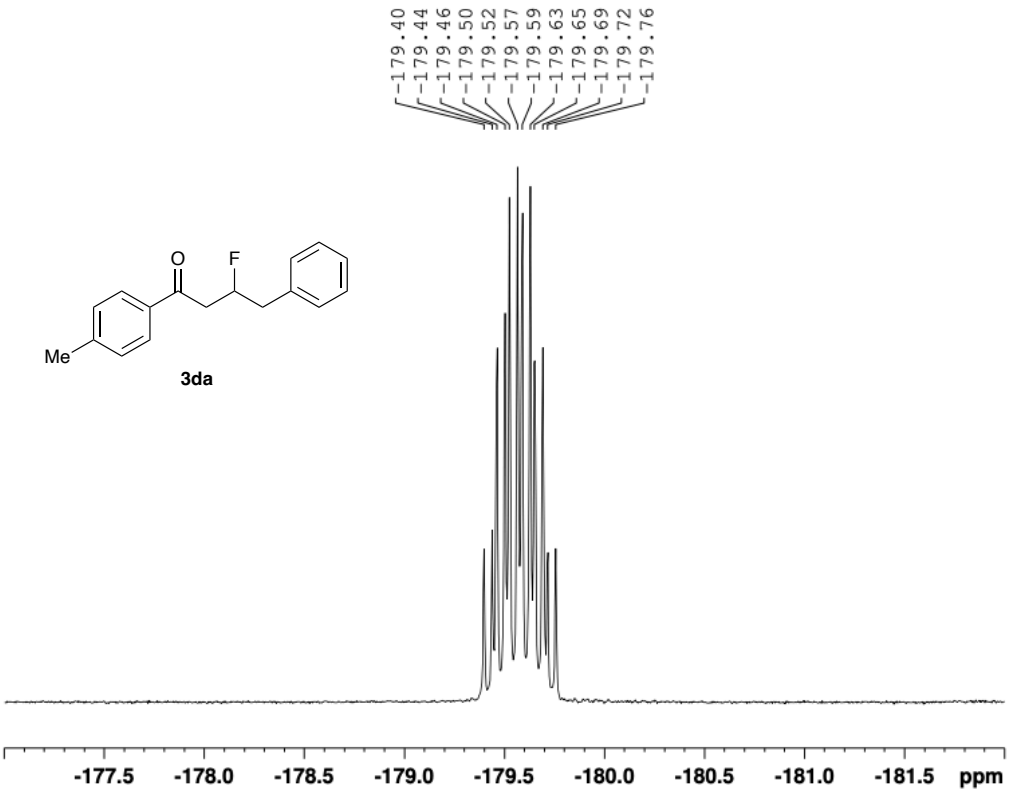

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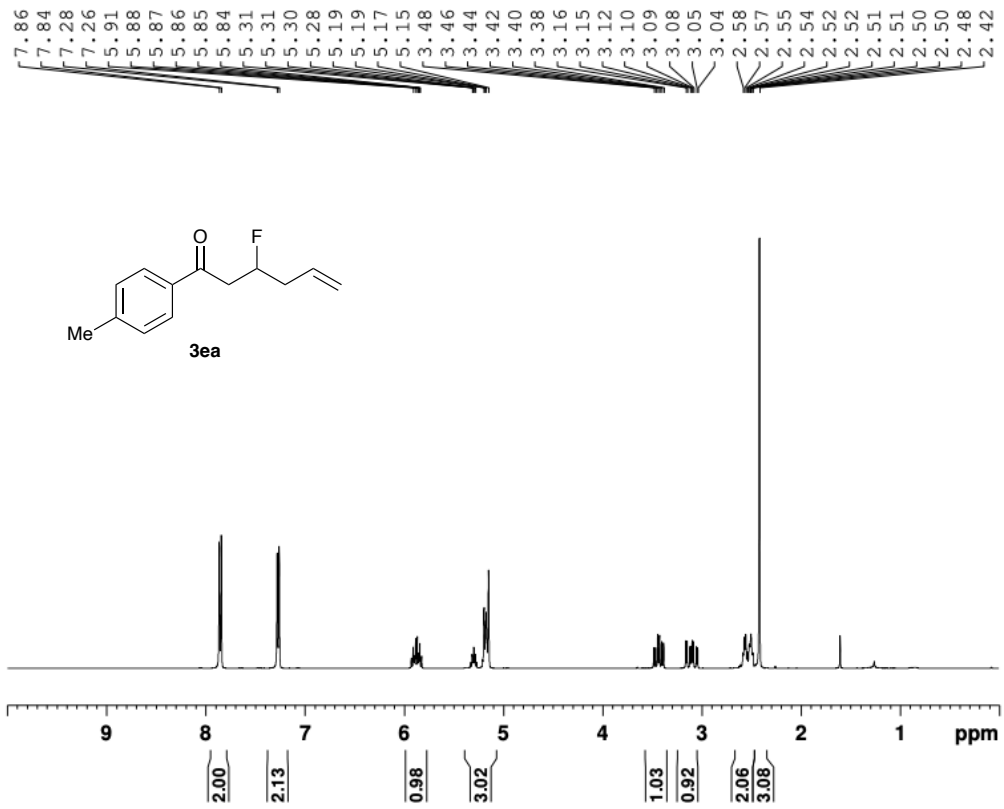

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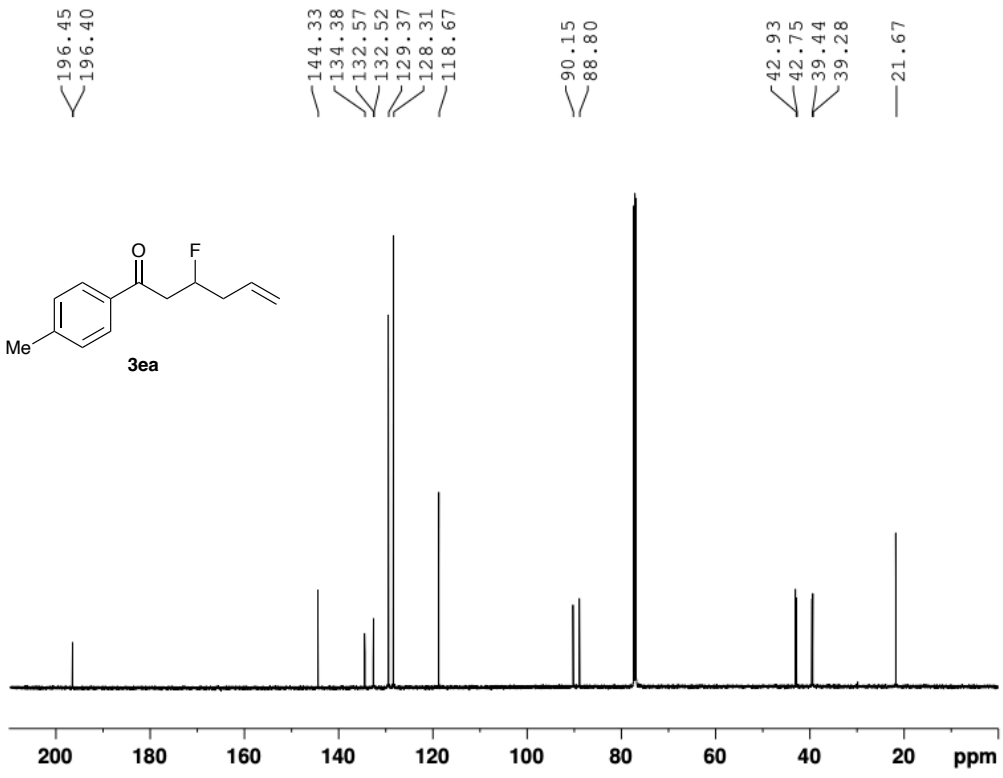

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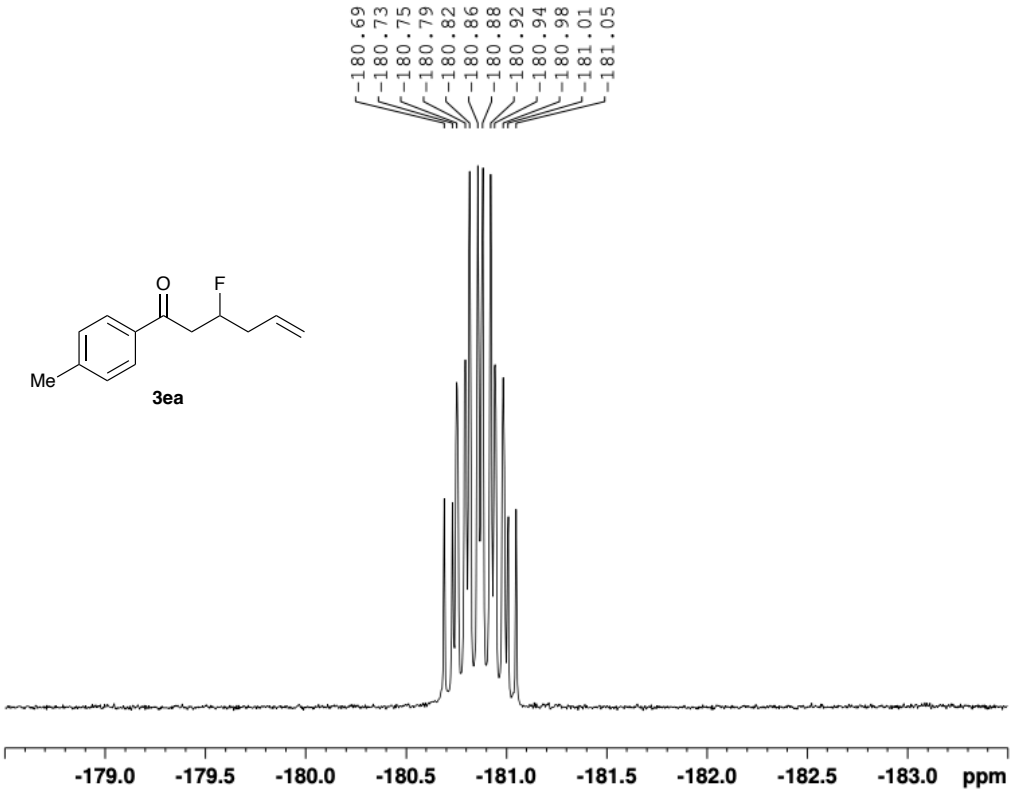

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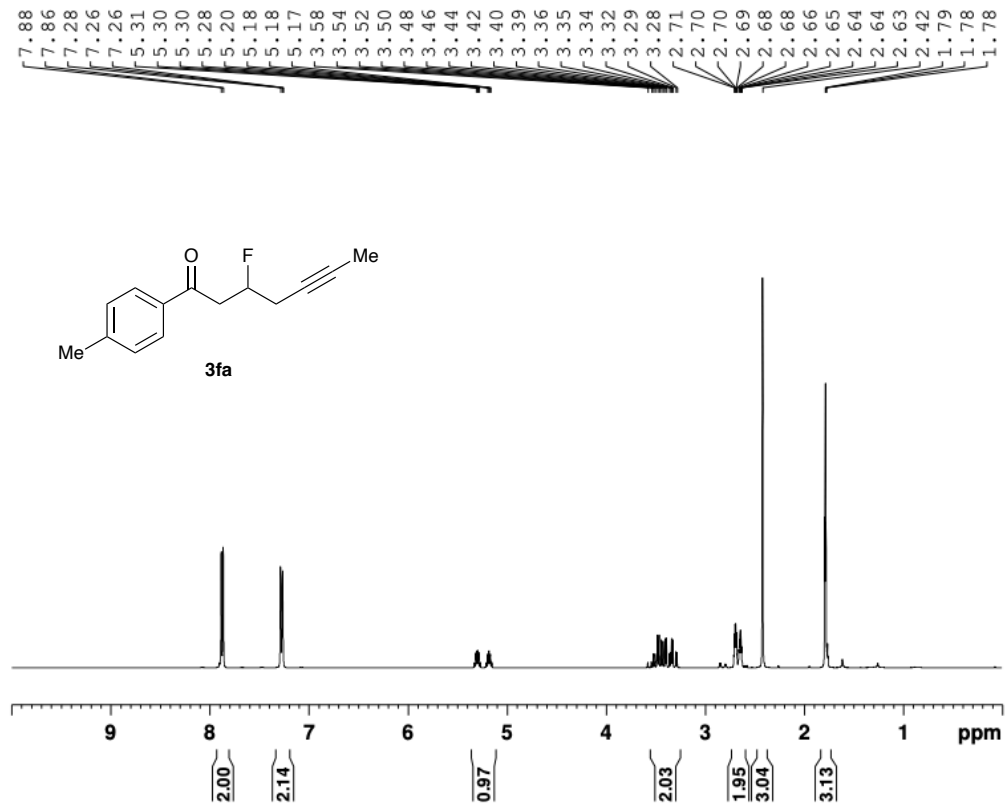

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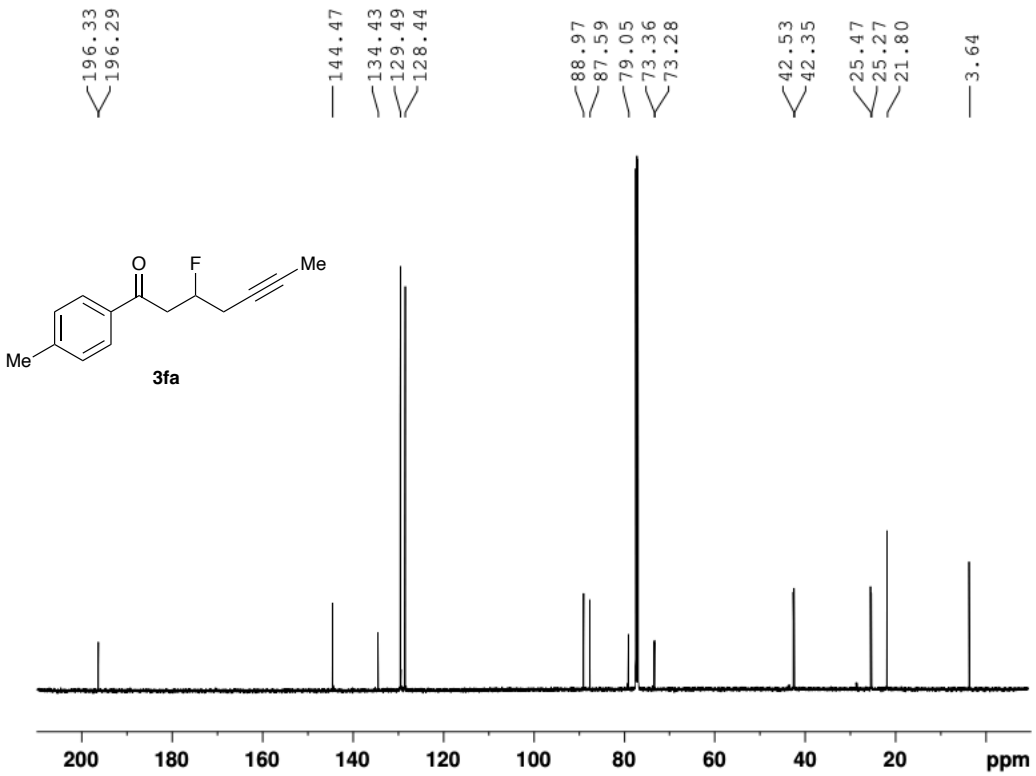

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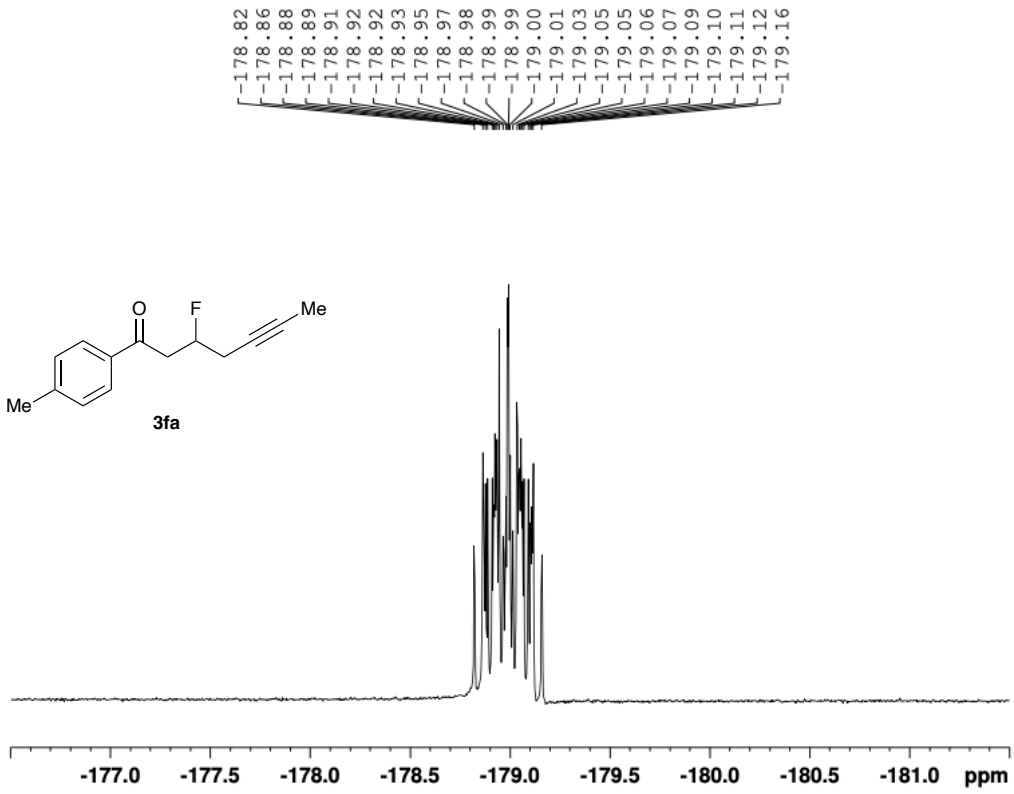

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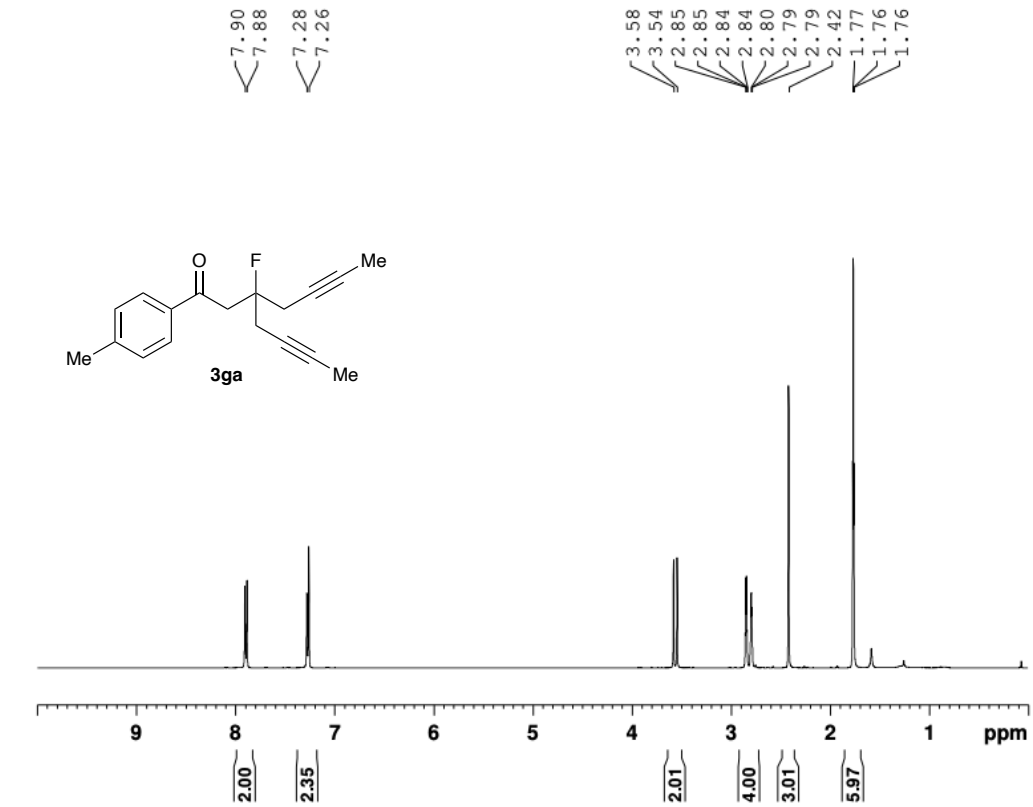

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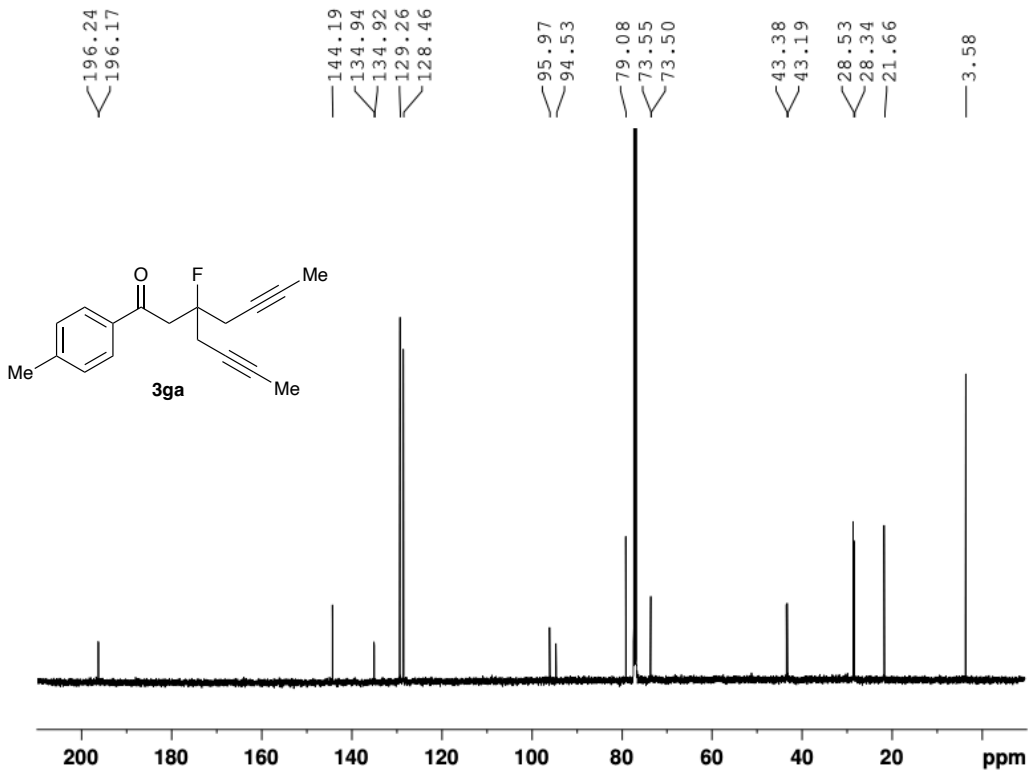

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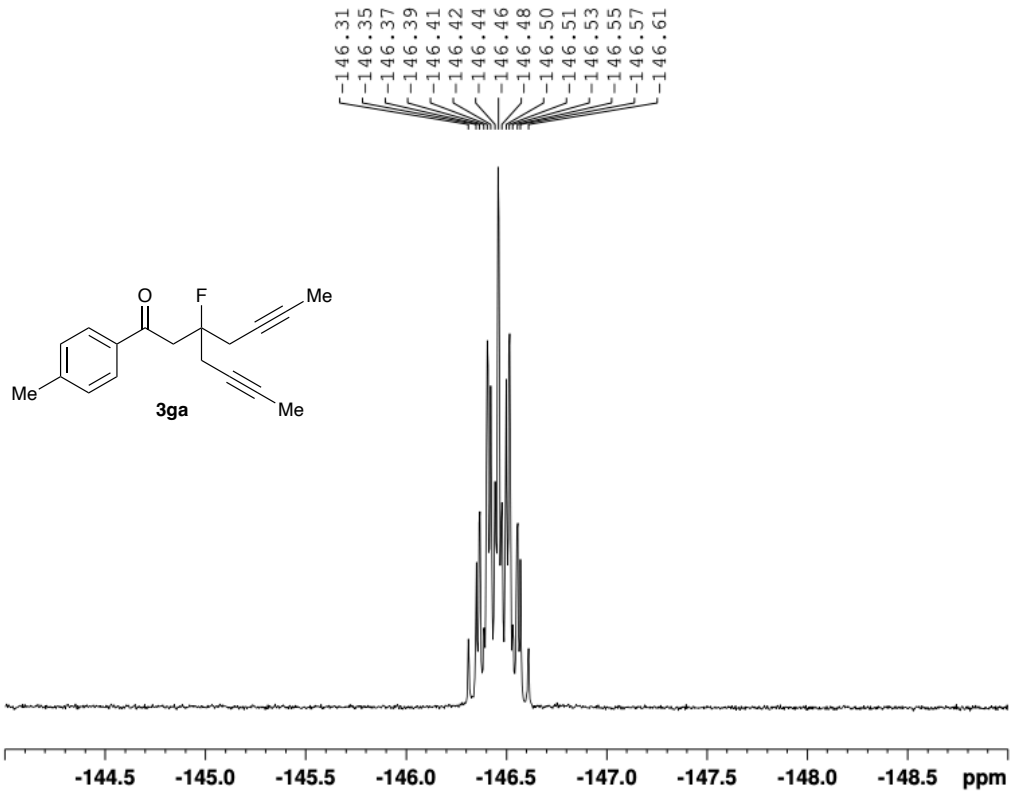

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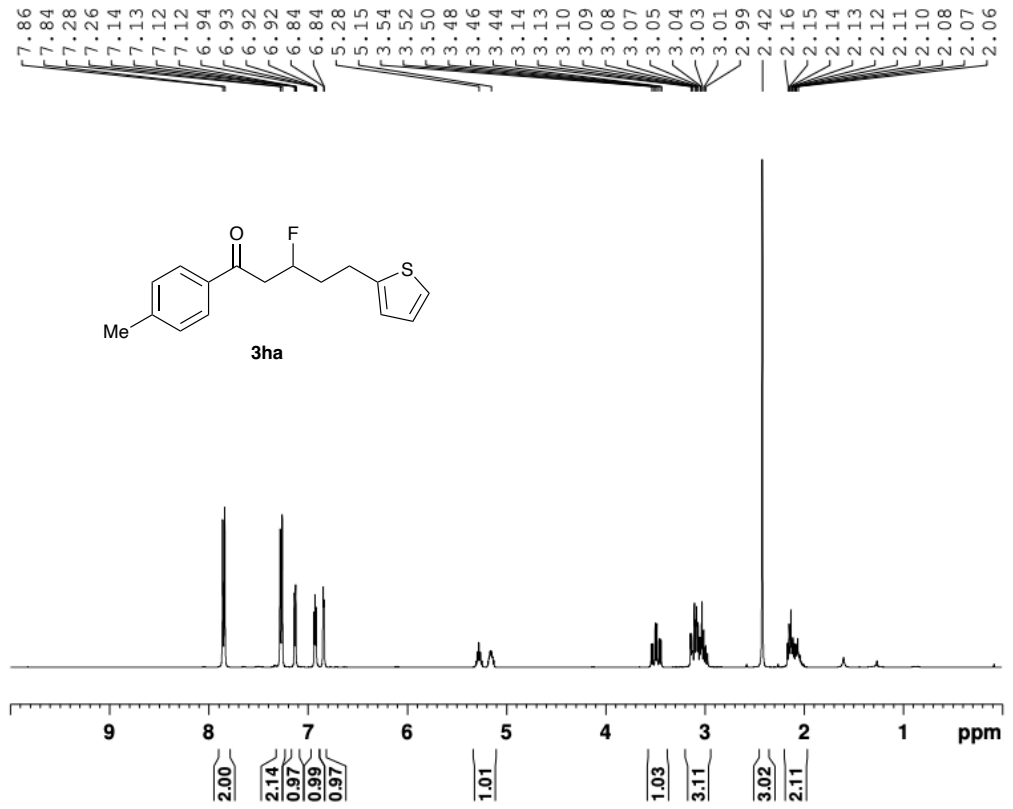

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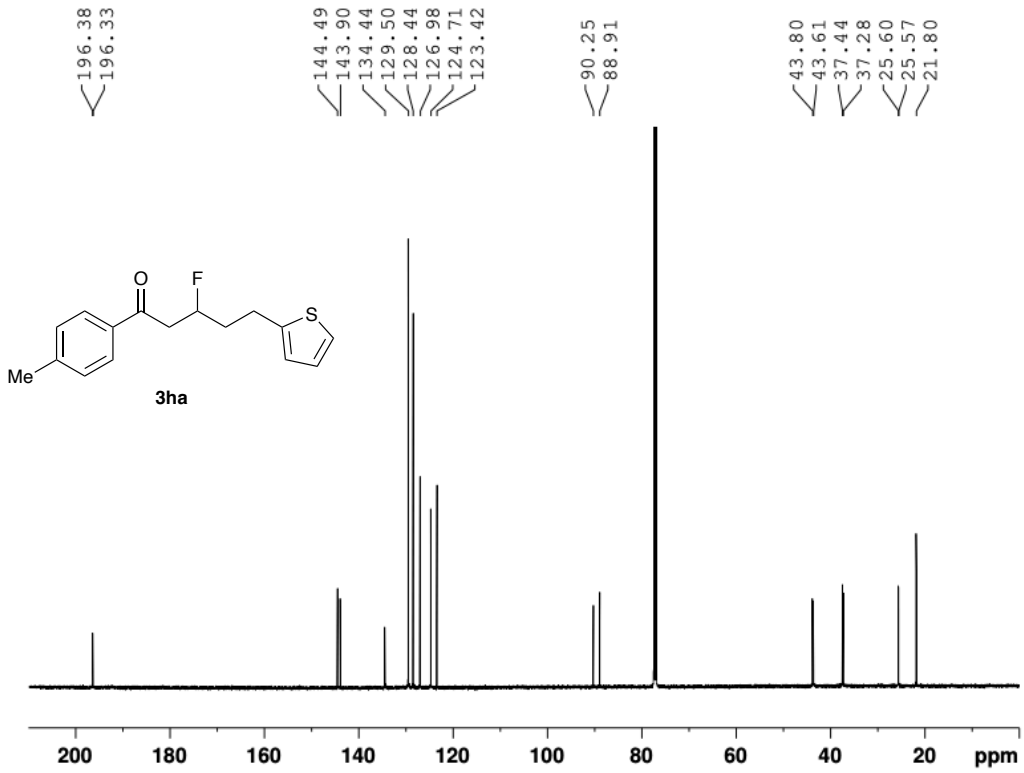

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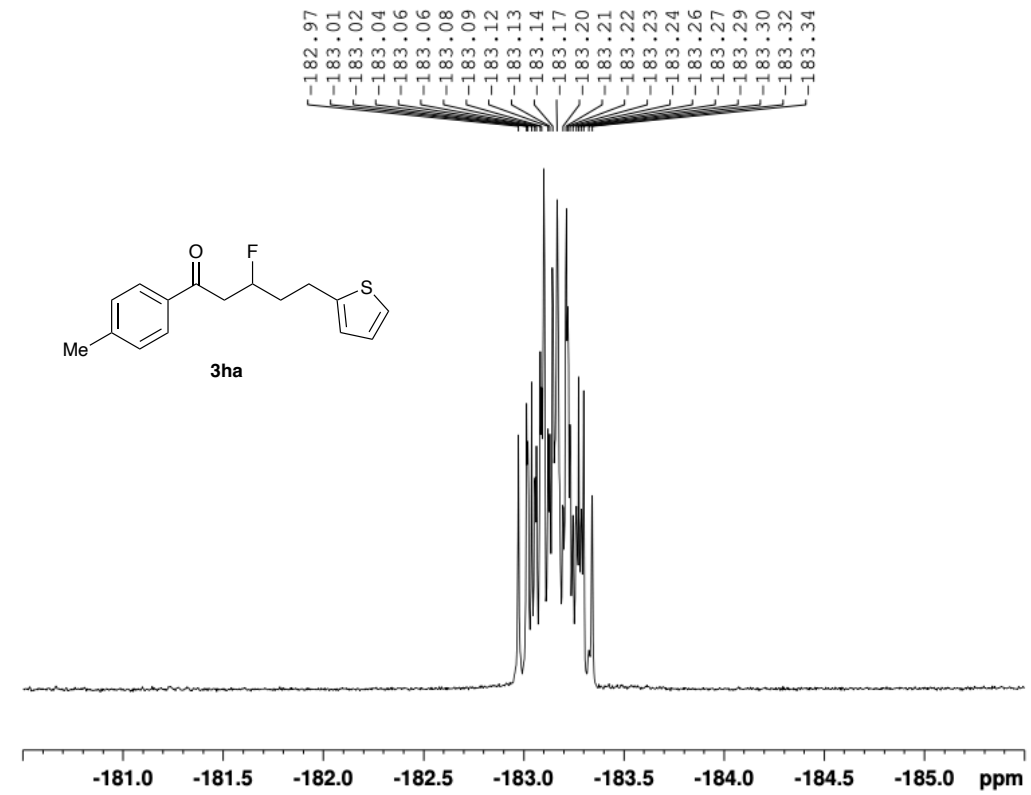

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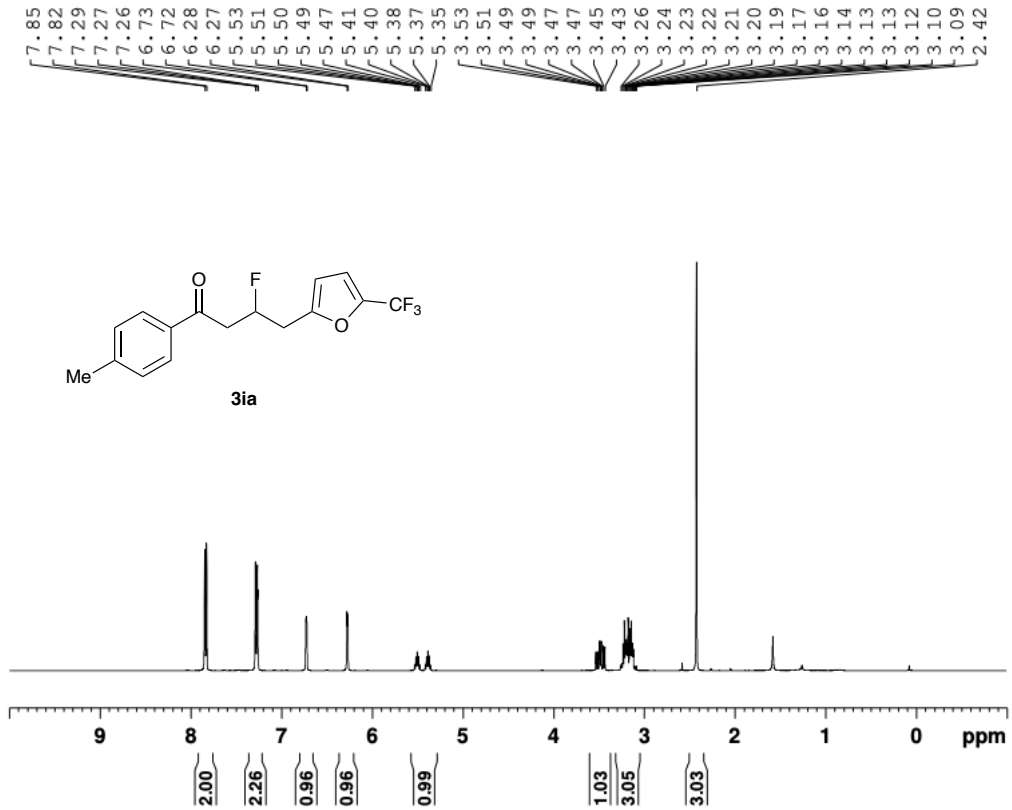

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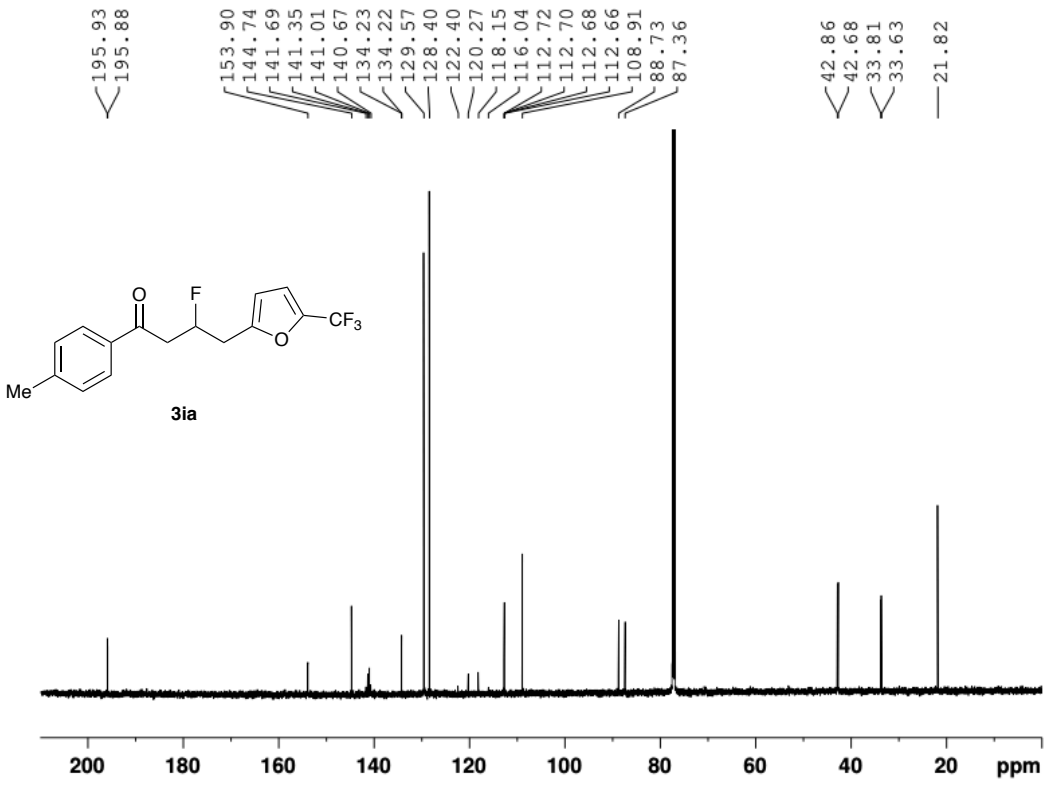

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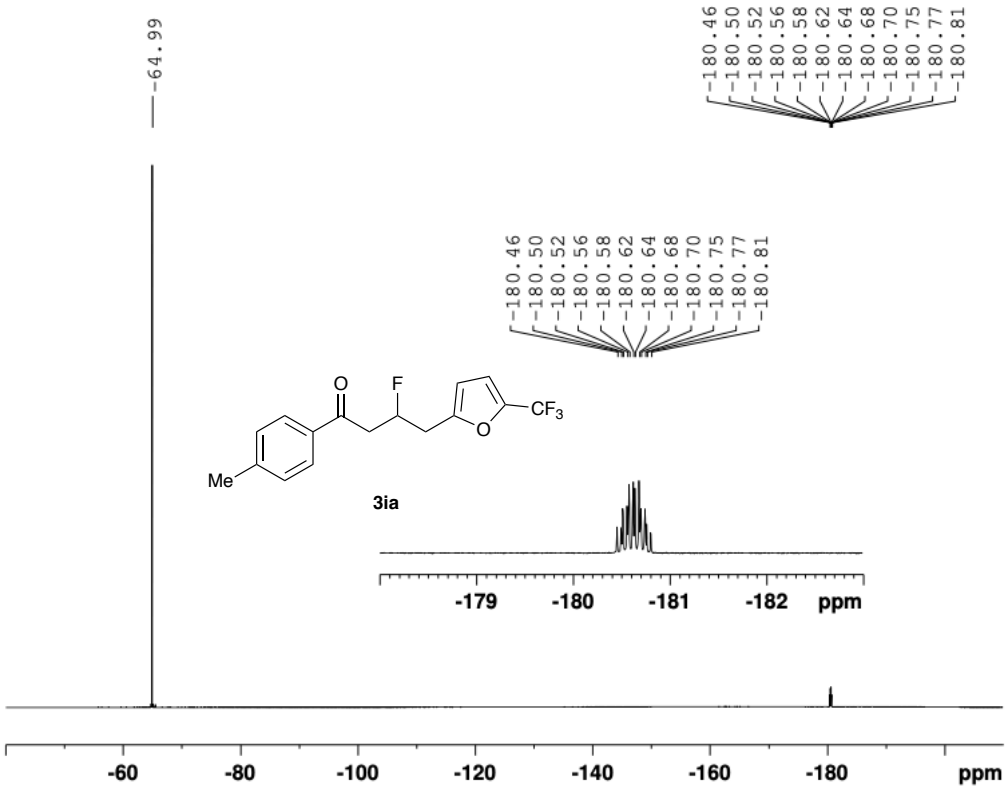
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CF3
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Me
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ppm