Visible Light-Promoted Metal-Free C–H Activation: Diarylketone-Catalyzed Selective Benzylic Mono- and Difluorination

Ji-Bao Xia, Chen Zhu, and Chuo Chen*

Supporting Information

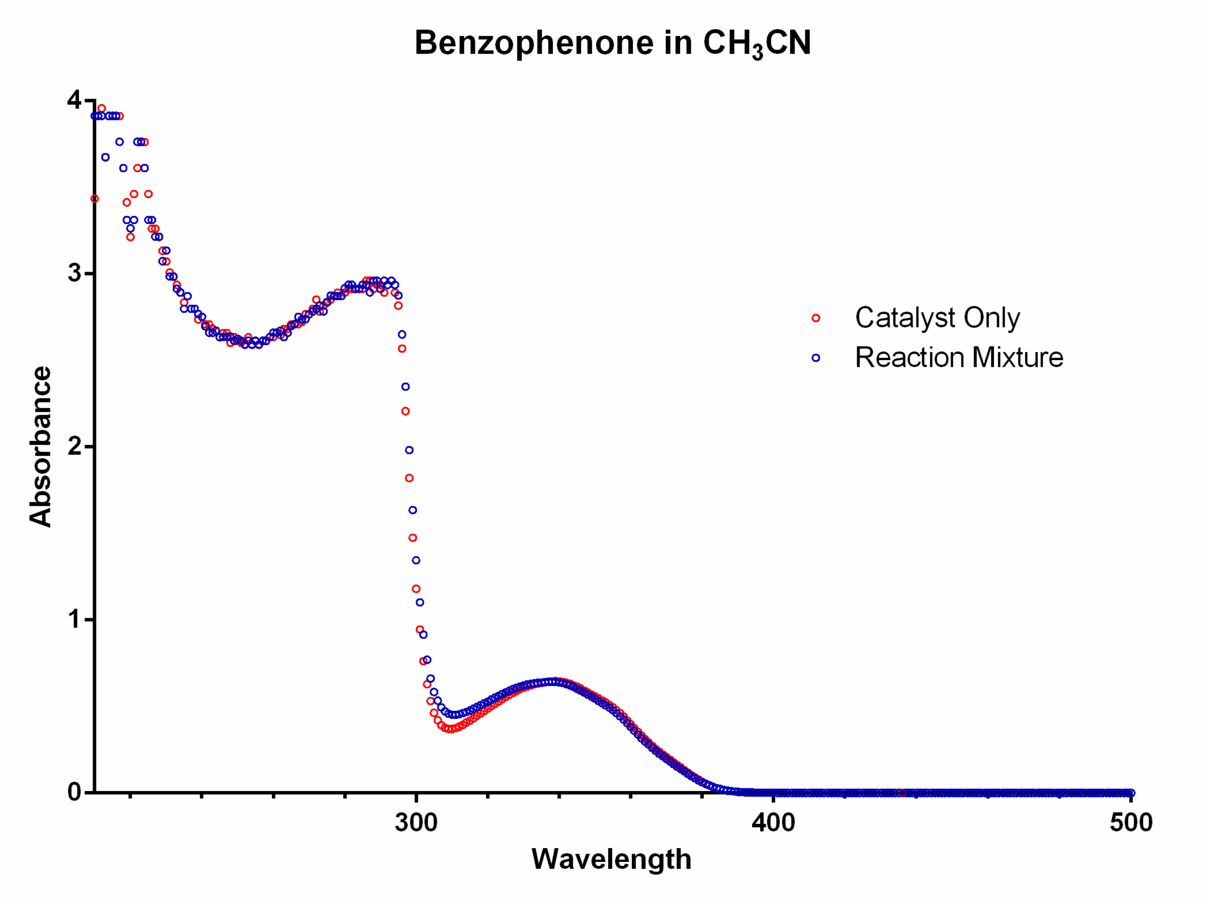

Figure S1. The UV-vis spectrum of 5 mol % benzophenone catalyst in CH_3CN (4 mM) (red), and of the reaction mixture (5 mol% benzophenone, 1.0 equiv ethylbenzene, 2.0 equiv Selectfluor) in CH_3CN (blue).

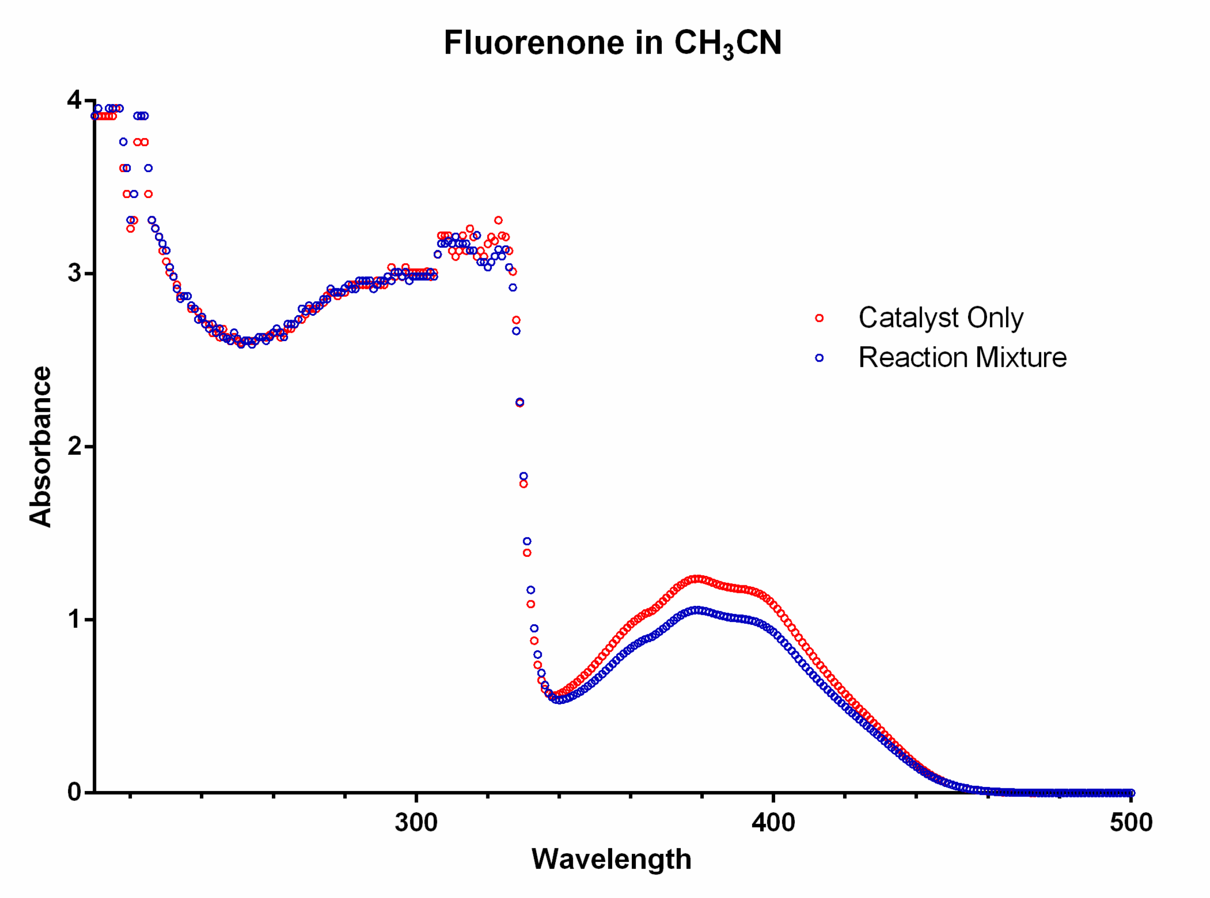

Figure S2. The UV-vis spectrum of 5 mol % 9-fluorenone catalyst in CH_3CN (4 mM) (red), and of the reaction mixture (5 mol% 9-fluorenone, 1.0 equiv ethylbenzene, 2.0 equiv Selectfluor) in CH_3CN (blue).

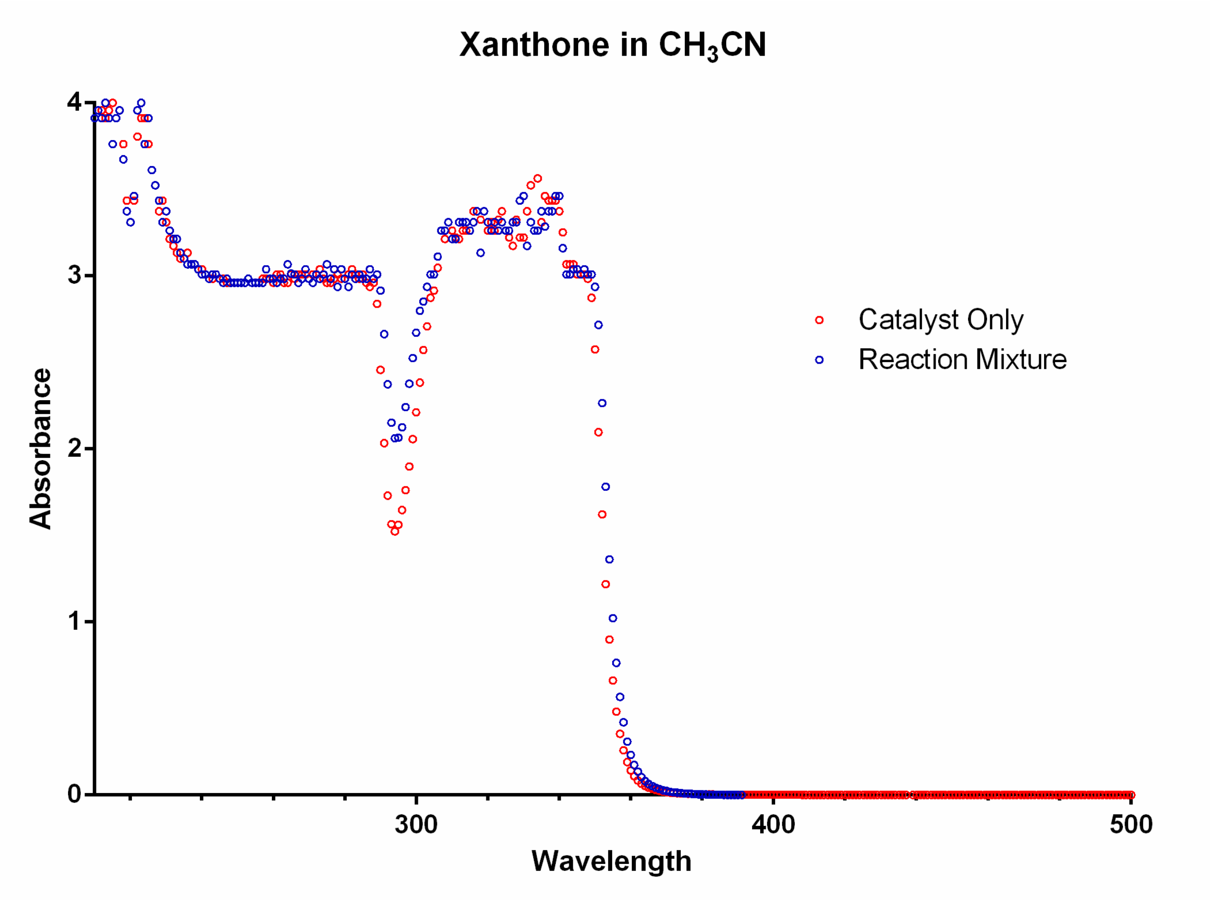

Figure S3. The UV-vis spectrum of 5 mol % xanthone catalyst in CH_3CN (2 mM) (red), and of the reaction mixture (5 mol% xanthone, 1.0 equiv ethylbenzene, 3.0 equiv Selectfluor II) in CH_3CN (blue).

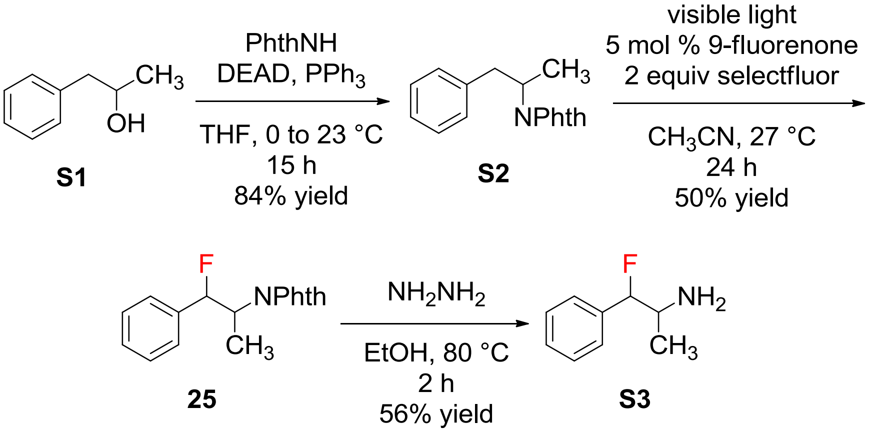

Figure S4. Synthesis of β-fluoroamphetamine (S3). A 100 mL round-bottom flask equipped with a magnetic stir bar was charged with triphenylphosphine (1.31 g, 5 mmol, 1.25 equiv) and phthalimide (PhthNH) (976.2 mg, 5 mmol, 1.25 equiv). After evacuating with vacuum and backfilling with argon for three times, anhydrous THF (40 mL) was added and the mixture was cooled to 0 °C. 1-Phenyl-2-propanol (**S1**) (545.0 mg, 4 mmol) followed by diethyl diazenedicarboxylate (DEAD) (870.8 mg, 5 mmol, 1.25 equiv) were then added. The reaction was stirred at room temperature overnight. After **S1** was consumed (monitored by TLC), the reaction mixture was concentrated and purified by flash column chromatography (5% ethyl acetate/hexanes) to give **S2** (895.0 mg, 84% yield) as a white solid[1]: R_f = 0.3 (5% ethyl acetate/hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 5.4, 3.0 Hz, 2H), 7.66 (dd, J = 5.4, 3.0 Hz, 2H), 7.11-7.26 (m, 5H), 4.61-4.68 (m, 1H), 3.32 (dd, J = 13.7, 9.3 Hz, 1H), 3.10 (dd, J = 13.7, 6.8 Hz, 1H), 1.53 (d, J = 6.9 Hz, 3H); MS(ESI) calcd for $C_{17}H_{16}NO_2$ $(M+H)^+$ 266.1, found 266.1.

To a 4 mL clear vial charged with Selectfluor (141.7 mg, 0.4 mmol, 2.0 equiv) was added anhydrous acetonitrile (2.1 mL), 9-fluorenone (0.01 mmol, 1.8 mg in 0.4 mL acetonitrile), and **S2** (53.1 mg, 0.2 mmol, 1.0 equiv) in a glovebox. The vial was then taken out of the glovebox and irradiated with a 19 W CFL 2–5 cm away from the reaction at room temperature. The temperature of the reaction mixture increased slightly to 27±2 °C. The reaction was monitored by NMR using fluorobenzene (18.75 μL, 0.2 mmol) as an external standard. The reaction mixture was then poured into diethyl ether (20 mL), filtrated, concentrated and purified by flash column chromatography (3% ethyl acetate/hexanes) to give **25** (28.5 mg, 50% yield) as a 1:1 mixture of diastereomers: R_f = 0.3 (3% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.5, 3.0 Hz, 2H), 7.74 (dd, J = 5.4, 3.1 Hz, 2H), 7.23-7.50 (m, 5H), 5.94 (dd, J = 47.8, 9.9 Hz, 1H), 4.68-4.78 (m, 1H), 1.27 (d, J = 7.2 Hz, 3H); 7.71 (dd, J = 5.6, 3.1 Hz, 2H), 7.64 (dd, J = 5.3, 3.1 Hz, 2H), 7.32-7.34 (m, 2H), 7.18-7.25 (m, 3H), 5.93 (dd, J = 47.2, 9.2 Hz, 1H), 4.73 (ddq, J = 11.7, 9.2, 6.8 Hz, 1H), 1.71 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3, 167.6, 136.9 (d, J = 19.3 Hz), 136.6 (d, J = 18.9 Hz), 134.0, 133.9, 131.9, 131.4, 129.4 (d, J = 2.3 Hz), 129.1 (d, J = 2.3 Hz), 128.7, 128.4, 127.0 (d, J = 5.7 Hz), 126.6 (d, J = 5.7 Hz), 123.3, 123.2, 93.9 (d, J = 173.9 Hz), 93.2 (d, J = 175.9 Hz), 51.2 (d, J = 22.9 Hz), 50.5 (d, J = 35.7 Hz), 15.2, 14.4 (d, J = 5.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.84 (dd, J = 47.8, 9.2 Hz, 1F); -175.74 (dd, J = 47.2, 11.7 Hz, 1F); MS(ESI) calcd for $C_{17}H_{15}FNO_2$ $(M+H)^+$ 284.1, found 284.1; HRMS(ESI) calcd for $C_{17}H_{15}FNO_2$ $(M+H)^+$ 284.1087, found 284.1084.

To a 4 mL clear vial charged with **25** (10 mg, 0.035 mmol, 1.0 equiv) was added ethanol (0.5 mL) and hydrazine hydrate (0.022 mL, 0.35 mmol). After stirring at 80 °C for 2 h, the reaction mixture was

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[1] Suau, R.; Garćia-Segura, R.; Sánchez-Sánchez, C.; Pérez-Inestrosa, E.; Pedraza, A. M. *Tetrahedron*, **2003**, *59*, 2913.

cooled to room temperature, filtrated, concentrated, and purified by flash column chromatography (1% dichloromethane/methanol) to give β-fluoroamphetamine (**S3**) (2.7 mg, 56% yield) as a 1:1 mixture of diastereomers[2]: R_f = 0.3 (1% dichloromethane/methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.41 (m, 5H), 7.31-7.41 (m, 5H), 5.19 (dd, *J* = 41.8, 5.5 Hz, 1H), 5.07 (dd, *J* = 43.1, 5.8 Hz, 1H), 3.19-3.32 (m, 1H), 3.19-3.32 (m, 1H), 1.50 (brs, 4H), 1.13 (d, *J* = 6.5 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -183.40 (dd, *J* = 47.6, 15.9 Hz, 1F); -184.12 (dd, *J* = 47.6, 14.2 Hz, 1F); MS(EI) calcd for $C_9H_{12}FN$ $(M)^+$ 153.1, found 153.1.

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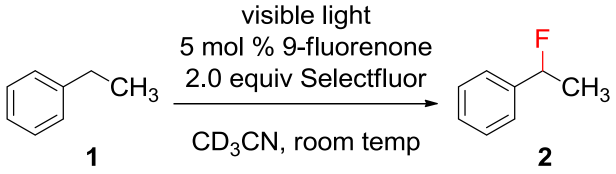
[2] Hamman, S.; Beguin, C.G. *J. Fluorine Chem.* **1987**, *37*, 191.



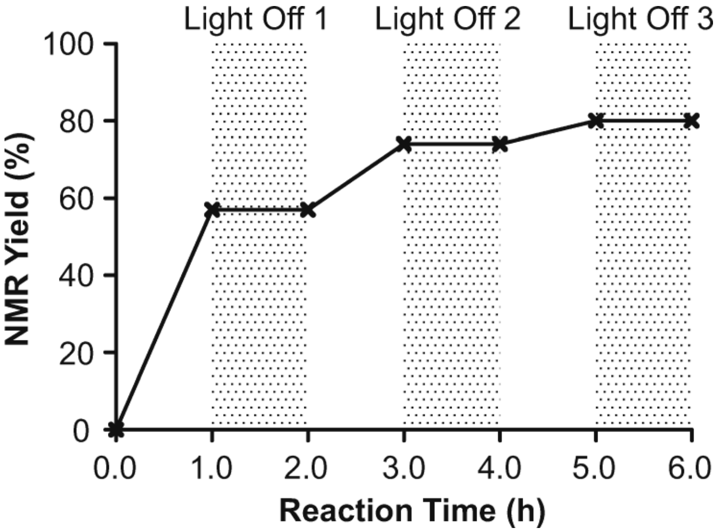


Figure S5. The light-dark cycle experiment: no reaction occurred in the dark period. To a 4 mL clear vial charged with Selectfluor (35.5 mg, 0.1 mmol, 2.0 equiv) was added acetonitrile-*d*3 (0.525 mL, redistilled from calcium hydride and degassed three times by *freeze-pump-thaw* cycles), 9-fluorenone (0.0025 mmol, 0.45 mg in 0.1 mL acetonitrile-*d*3), and ethylbenzene **1** (5.3 mg, 0.05 mmol, 1.0 equiv) in a glovebox. The reaction solution was transfer to a NMR tube (Wilmad-LabGlass, 527PP, 5mm OD), taken out from the glovebox, and irradiated with a 19 W CFL at room temperature. The reaction was monitored by NMR on a Varian Inova-400 NMR instrument.

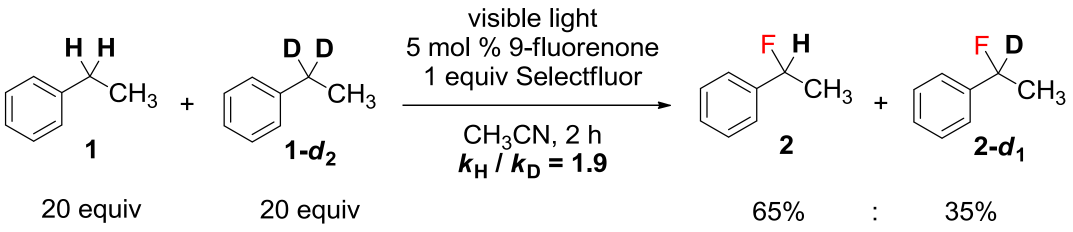


Figure S6. The intermolecular kinetic isotope effect study. To a 4 mL clear vial charged with Selectfluor (17.7 mg, 0.05 mmol, 1.0 equiv) and 9-fluorenone (0.5 mg, 0.0025 mmol) was added acetonitrile-*d*3 (0.5 mL), ethylbenzene **1** (106.2 mg, 1.0 mmol, 20.0 equiv), and (ethyl-1,1-d_2)benzene **1-**d_2 (108.2 mg, 1.0 mmol, 20.0 equiv). The vial was then degassed three times by *freeze-pump-thaw* cycles and irradiated with a 19 W CFL at room temperature for 2 h. The ratio of **2**:**2**-d_1 was determined by ^{19}F NMR on a Varian Inova-400 NMR instrument to be 65:35.

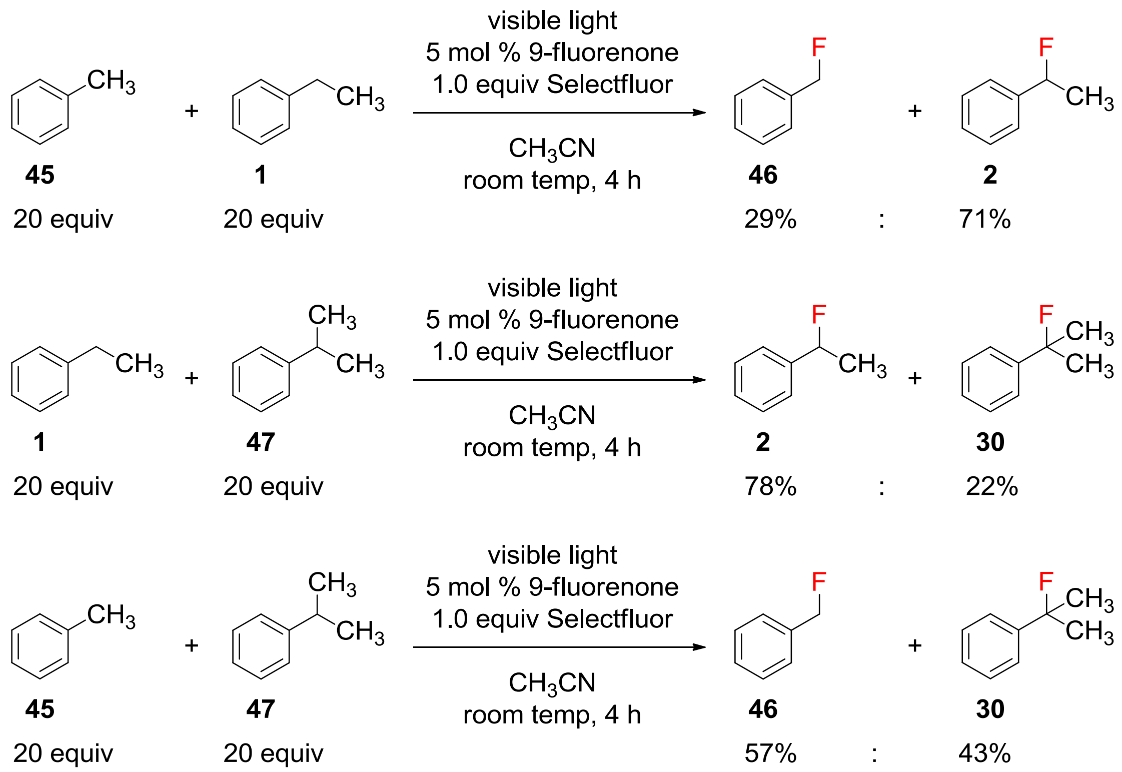


Figure S7. Site-selectivity studies. To a 4 mL clear vial charged with Selectfluor (70.9 mg, 0.1 mmol, 1.0 equiv) and 9-fluorenone (1.8 mg, 0.005 mmol) was added anhydrous acetonitrile (2.0 mL), and the reaction substrates (4.0 mmol, 20.0 equiv). The reaction mixture was then degassed three times by *freeze-pump-thaw* cycles and irradiated with a 19 W CFL at room temperature for 4 h. The ratio of the products was determined by ^{19}F NMR on a Varian Inova-400 NMR instrument.

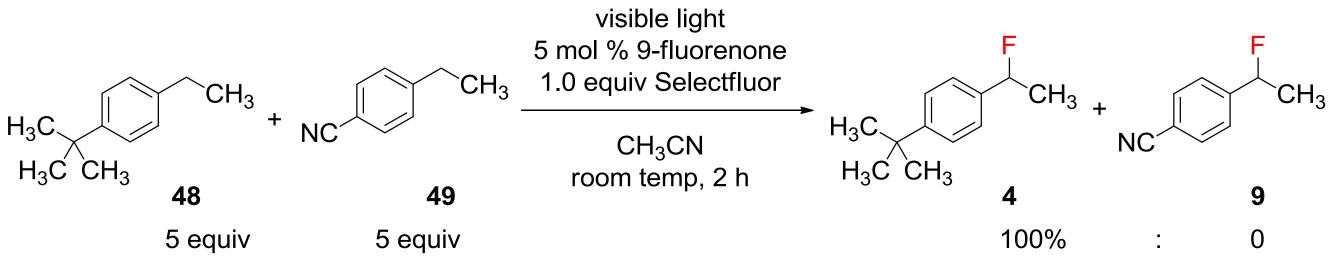


Figure S8. The electronic effect study. To a 4 mL clear vial charged with Selectfluor (14.2 mg, 0.04 mmol, 1.0 equiv) and 9-fluorenone (0.4 mg, 0.002 mmol) was added anhydrous acetonitrile (0.5 mL), 1-(*tert*-butyl)-4-ethylbenzene **48** (32.5 mg, 0.2 mmol, 5.0 equiv), and 4-ethylbenzonitrile **49** (26.2 mg, 0.2 mmol, 5.0 equiv). The reaction mixture was then degassed three times by *freeze-pump-thaw* cycles and irradiated with a 19 W CFL at room temperature for 2 h. The crude ^{19}F NMR spectra indicated that 1-(*tert*-butyl)-3-(1-fluoroethyl)benzene **4** was the only product.

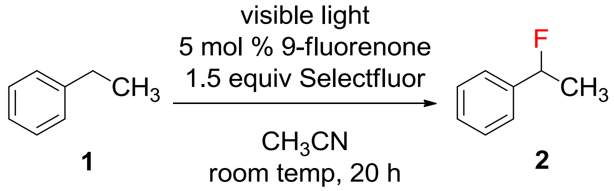


Figure S9. Gram-scale synthesis of (1-fluoroethyl)benzene. A 500 mL round-bottom flask equipped with a magnetic stir bar was charged with Selectfluor (10.63 g, 30 mmol, 1.5 equiv) and 9-fluorenone (180.0 mg, 1 mmol). After evacuating with vacuum and backfilling with argon for three times, anhydrous acetonitrile (225 mL) was added, followed by ethylbenzene (**1**) (2.12 g, 20 mmol, 1.0 equiv). The reaction mixture was degassed three times by *freeze-pump-thaw* cycles, and irradiated with a 19 W CFL at room temperature for 20 h. The temperature of the reaction mixture increased slightly from 22 °C to 27±2 °C during the reaction. Ethyl trifluoroacetate (2.38 mL, 20 mmol) was added as an external standard to determine the NMR yield. The ^{1}H NMR spectrum indicated that (1-fluoroethyl)benzene was formed in 90% yield. Diethyl ether (100 mL) was then added to crush out the remaining Selectfluor and its byproduct. After filtration, the solvent was removed by distillation. The residue was purified by silica gel flash column chromatography using pentane as the eluent and concentrated by rotary evaporator at ca. 200 mmHg to give **2** (2.11 g, 85% yield) as a colorless oil[3]: R_f = 0.5 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.40 (m, 5H), 5.63 (dq, J = 47.8, 6.4 Hz, 1H), 1.65 (dd, J = 23.9, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 142.2 (d, J = 19.6 Hz), 128.7, 128.3 (d, J = 1.4 Hz), 125.4 (d, J = 6.7 Hz), 90.8 (d, J = 169.0 Hz), 23.1 (d, J = 25.4 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -167.07 (dq, J = 47.8, 23.9 Hz, 1F); MS(EI) calcd for C_8H_9F $(M)^+$ 124.1, found 124.1.

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[3] Cazorla, C.; Metay, E.; Andrioletti, B.; Lemaire, M. *Tetrahedron Lett.* **2009**, *50*, 3936.

Materials and Methods

General Information. All reactions were performed in glassware under argon. Organic solutions were concentrated by rotary evaporator at ca. 30 mmHg unless otherwise noted. Flash column chromatography was performed as described by Still[4], employing EMD silica gel 60 (230–400 mesh ASTM). TLC analyses were performed on EMD 250 μm Silica Gel 60 F_{254} plates and visualized by quenching of UV fluorescence (λ_{max}= 254 nm), or by staining ceric ammonium molybdate. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-500 or Inova-400. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to the ^{1}H and ^{13}C signals in the solvent ($CDCl_3$: 7.26, 77.00 ppm; C_6D_6: δ 7.16, 128.06 ppm; CD_3CN: δ 1.94, 1.32 ppm) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet. Crude ^{1}H and ^{19}F NMR spectra were recorded on an Inova-400 in CD_3CN using fluorobenzene (^{19}F NMR δ -114.930) as an external standard. Mass spectra were acquired on an Agilent 6120 Single Quadrupole LC/MS, Agilent 7820A GC/5975 MSD, or VG 70-VSE. Data collection on 70-VSE (purchased in part with a grant from the Division of Research Resources, National Institutes of Health RR 04648) was serviced by the Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign. UV-vis spectra were collected on Shimadzu UV-Visible Spectrophotometer (UV-1601).

Materials. Acetonitrile (anhydrous, 99.8%), 9-fluorenone (98%), xanthone (97%) and Selectfluor II were purchased from Sigma-Aldrich. Selectfluor (98+%) and benzophenone (99%) were purchased from Alfa Aesar. Fluorobenzene (≥99.5%) was purchased from Fluka. Acetonitrile-*d*3 (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. An EcoSmart 19 W Daylight CFL Bulb, an 11 W IKEA E26 CFL Bulb, or a Philips 10.5-watt A19 LED Bright White Bulb was used for the photoreaction.

General procedure for the photolytic benzylic monofluorination reaction. To a 4 mL clear vial charged with Selectfluor (141.7 mg, 0.4 mmol, 2.0 equiv) was added anhydrous acetonitrile (2.1 mL), 9-fluorenone (0.01 mmol, 1.8 mg in 0.4 mL acetonitrile), and the reaction substrate (0.2 mmol, 1.0 equiv) under nitrogen. For convenience, the reactions were typically setup in a batch in a glovebox, but can also be performed on the bench. The reaction mixture was irradiated with an 11 W or a 19 W CFL 2–5 cm away from the reaction at room temperature (27±2 °C). The crude yield was determined by NMR using fluorobenzene (18.75 μL, 0.2 mmol) as an external standard. The reaction mixture was then poured into diethyl ether (20 mL), filtrated, concentrated and purified by silica gel flash column chromatography using diethyl ether/pentane as the eluent.

General procedure for the photolytic benzylic difluorination reaction. To a 4 mL clear vial charged with Selectfluor II (95.9 mg, 0.3 mmol, 3.0 equiv) and xanthone (1.0 mg, 0.005 mmol) was added anhydrous acetonitrile (2.5 mL), and the reaction substrate (0.1 mmol, 1.0 equiv). The reaction mixture was degassed three times by *Freeze-Pump-Thaw* cycles and irradiated with an 11 W or a 19 W CFL 2–5 cm away from the reaction at room temperature (27±2 °C). The crude yield was determined by NMR using fluorobenzene (9.38 μL, 0.1 mmol) as an external standard. The reaction mixture was then poured into diethyl ether (20 mL), filtrated, concentrated and purified by silica gel flash column chromatography using diethyl ether/pentane as the eluent.

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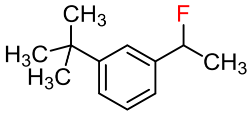
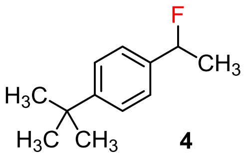
[4] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Characterization Data



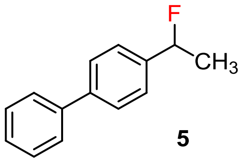
3

1-(*tert*-Butyl)-3-(1-fluoroethyl)benzene (3). Prepared from 1-(*tert*-butyl)-3-ethylbenzene (32.5 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (6 h) and purified by flash column chromatography (1% diethyl ether/pentane) to give **3** (30.7 mg, 85% yield) as a colorless oil: R_f = 0.3 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.38 (m, 2H), 7.29-7.34 (m, 1H), 7.16-7.18 (m, 1H), 5.62 (dq, *J* = 47.8, 6.4 Hz, 1H), 1.65 (dd, *J* = 23.9, 6.4 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 151.5, 142.0 (d, *J* = 19.5 Hz), 128.6, 125.4 (d, *J* = 1.9 Hz), 122.7 (d, *J* = 6.4 Hz), 122.4 (d, *J* = 6.9 Hz), 91.2 (d, *J* = 168.7 Hz), 34.7, 31.4, 23.3 (d, *J* = 25.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -165.93 (dq, *J* = 47.8, 23.9 Hz, 1F); MS(EI) calcd for $C_{12}H_{17}F$ $(M)^+$ 180.1, found 180.1; HRMS(EI) calcd for $C_{12}H_{17}F$ $(M)^+$ 180.1314, found 180.1315.



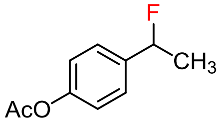
4

1-(*tert*-Butyl)-4-(1-fluoroethyl)benzene (4). [5] Prepared from 1-(*tert*-butyl)-4-ethylbenzene (32.5 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (6 h) and purified by preparative TLC (2% ethyl acetate/hexanes) to give **4** (29.6 mg, 82% yield) as a colorless oil: R_f = 0.5 (2.5% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.37 (dq, *J* = 47.7, 6.4 Hz, 1H), 1.40 (dd, *J* = 23.4, 6.4 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 151.1 (d, *J* = 2.0 Hz), 139.2 (d, *J* = 19.7 Hz), 125.6, 125.4 (d, *J* = 6.4 Hz), 90.8 (d, *J* = 168.2 Hz), 34.6, 31.4, 23.1 (d, *J* = 25.7 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -166.33 (dq, *J* = 47.7, 23.4 Hz, 1F); MS(EI) calcd for $C_{12}H_{17}F$ $(M)^+$ 180.1, found 180.2.



5

4-(1-Fluoroethyl)biphenyl (5).[6] Prepared from 4-ethylbiphenyl (36.4 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (3 h) and purified by preparative TLC (2.5% ethyl acetate/hexanes) to give **5** (35.4 mg, 88% yield) as a white solid: R_f = 0.3 (2.5% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.41-7.46 (m, 4H), 7.12-7.24 (m, 5H), 5.36 (dq, *J* = 47.4, 6.4 Hz, 1H), 1.38 (dd, *J* = 23.4, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 141.5 (d, *J* = 2.0 Hz), 141.2, 141.0 (d, *J* = 19.7 Hz), 129.1, 127.6, 127.5, 127.5, 126.0 (d, *J* = 6.6 Hz), 90.6 (d, *J* = 168.9 Hz), 23.1 (d, *J* = 25.5 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -167.57 (dq, *J* = 47.4, 23.4 Hz, 1F); MS(EI) calcd for $C_{14}H_{13}F$ $(M)^+$ 200.1, found 200.1.



6

4-(1-Fluoroethyl)phenyl acetate (6).[6] Prepared from 4-ethylphenyl acetate (32.8 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by preparative TLC (5% ethyl acetate/hexanes) to give **6** (17.8 mg, 49% yield) as a colorless oil: R_f = 0.2 (5% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.06 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.23 (dq, *J* = 47.4, 6.4 Hz, 1H), 1.73 (s, 3H), 1.27 (dd, *J* = 23.5, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 168.4, 151.1 (d, *J* = 2.3 Hz), 139.4 (d, *J* = 19.8 Hz), 126.5 (d, *J* = 6.6 Hz), 121.9, 90.3 (d, *J* = 169.0 Hz), 22.9 (d, *J* = 25.2 Hz), 20.5; ^{19}F NMR (376 MHz, C_6D_6) δ -166.89 (dq, *J* = 47.4, 23.5 Hz, 1F); MS(EI) calcd for $C_{10}H_{11}FO_2$ $(M)^+$ 182.1, found 182.1.

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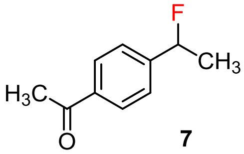
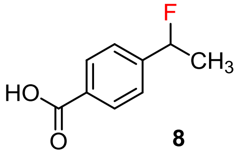
[5] Olah, G. A.; Kuhn, S. J.; Barnes, D. G. *J. Org. Chem.* **1964**, *29*, 2685.

[6] Liu, W.; Groves, J. T. *Angew. Chem. Int. Ed.* **2013**, *52*, 6024.



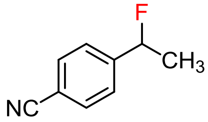
7

1-(4-(1-Fluoroethyl)phenyl)ethanone (7).[7] Prepared from 1-(4-ethylphenyl)ethanone (29.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by flash column chromatography (5% diethyl ether/pentane) to give **7** (25.1 mg, 76% yield) as a colorless oil: R_f = 0.3 (5% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.68 (dq, J = 47.6, 6.4 Hz, 1H), 2.61 (s, 3H), 1.65 (dd, J = 24.0, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 146.6 (d, J = 19.5 Hz), 136.7 (d, J = 1.6 Hz), 128.5, 125.0 (d, J = 7.3 Hz), 90.2 (d, J = 170.2 Hz), 26.5, 22.9 (d, J = 24.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -171.39 (dq, J = 47.6, 24.0 Hz, 1F); MS(ESI) calcd for $C_{10}H_{12}FO$ $(M+H)^+$ 167.1, found 167.1.



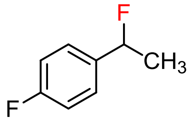
8

4-(1-Fluoroethyl)benzoic acid (8). Prepared from 4-ethylbenzoic acid (30.0 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (30% ethyl acetate/hexanes) to give **8** (25.6 mg, 76% yield) as a colorless oil: R_f = 0.3 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 8.08 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 5.15 (dq, J = 47.5, 6.5 Hz, 1H), 1.19 (dd, J = 23.8, 6.5 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 172.6, 147.9 (d, J = 19.7 Hz), 130.8, 129.3 (d, J = 1.5 Hz), 125.2 (d, J = 7.4 Hz), 90.1 (d, J = 170.9 Hz), 22.9 (d, J = 24.6 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -172.17 (dq, J = 47.5, 23.8 Hz, 1F); MS(EI) calcd for $C_9H_9FO_2$ $(M)^+$ 168.1, found 168.0; HRMS(EI) calcd for $C_9H_9FO_2$ $(M)^+$ 168.0587, found 168.0584.



9

4-(1-Fluoroethyl)benzonitrile (9).[8] Prepared from 4-ethylbenzonitrile (26.2 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (96 h) and purified by flash column chromatography (3% diethyl ether/pentane) to give **9** (19.5 mg, 65% yield) as a colorless oil: R_f = 0.3 (3% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 5.67 (dq, J = 47.6, 6.5 Hz, 1H), 1.64 (dd, J = 24.0, 6.5 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 146.3 (d, J = 20.0 Hz), 132.2, 125.4 (d, J = 7.6 Hz), 118.6, 112.4 (d, J = 1.8 Hz), 89.7 (d, J = 171.6 Hz), 22.7 (d, J = 24.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -172.71 (dq, J = 47.6, 24.0 Hz, 1F); MS(ESI) calcd for C_9H_9FN $(M+H)^+$ 150.1, found 150.2.



10

1-Fluoro-4-(1-fluoroethyl)benzene (10).[9] Prepared from 1-ethyl-4-fluorobenzene (24.8 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% diethyl ether/pentane) and concentrated by rotary evaporator at ca. 200 mmHg to give **10** (20.2 mg, 71% yield) as a colorless oil: R_f = 0.5 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 6.88-6.91 (m, 2H), 6.71-6.76 (m, 2H), 5.16 (dq, J = 46.8, 6.4 Hz, 1H), 1.23 (dd, J = 23.2, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 162.9 (dd, J = 245.8, 2.2 Hz), 137.8 (dd, J = 20.2, 3.1 Hz), 127.3 (dd, J = 8.0, 6.5 Hz), 115.5 (d, J = 21.5 Hz), 90.0 (d, J = 168.9 Hz), 22.9 (d, J = 25.3 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -114.14 (m, 1F), -165.83 (dq, J = 46.8, 23.2 Hz, 1F); MS(EI) calcd for $C_8H_8F_2$ $(M)^+$ 142.1, found 142.1.

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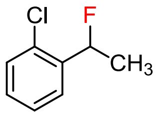
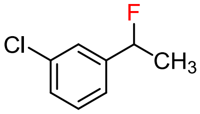


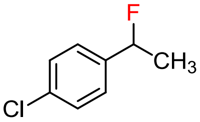
11

1-Chloro-2-(1-fluoroethyl)benzene (11). Prepared from 1-chloro-2-ethylbenzene (28.1 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% ethyl acetate/hexanes) and concentrated by rotary evaporator at ca. 150 mmHg to give **13** (22.8 mg, 72% yield): R_f = 0.6 (1% ethyl acetate/hexanes) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6) δ 7.42 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.87 (dd, *J* = 7.7, 7.6 Hz, 1H), 6.72 (ddd, *J* = 7.9, 7.6, 1.6 Hz, 1H), 5.86 (dq, *J* = 47.2, 6.3 Hz, 1H), 1.36 (dd, *J* = 23.8, 6.3 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 140.1 (d, *J* = 21.3 Hz), 131.0 (d, *J* = 5.8 Hz), 129.5 (d, *J* = 0.7 Hz), 129.2 (d, *J* = 1.5 Hz), 127.4 (d, *J* = 0.6 Hz), 126.4 (d, *J* = 10.1 Hz), 88.0 (d, *J* = 170.4 Hz), 22.0 (d, *J* = 25.4 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -175.38 (dq, *J* = 47.2, 23.8 Hz); MS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0, found 158.0; HRMS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0299, found 158.0295.



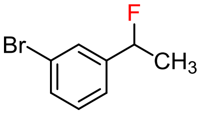
12

1-Chloro-3-(1-fluoroethyl)benzene (12). Prepared from 1-chloro-3-ethylbenzene (28.1 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by preparative TLC (1% ethyl acetate/hexanes) and concentrated by rotary evaporator at ca. 150 mmHg to give **12** (15.0 mg, 46% yield) as a colorless oil: R_f = 0.5 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.16 (s, 1H), 7.08-6.97 (m, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 6.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 5.06 (dq, *J* = 47.4, 6.4 Hz, 1H), 1.15 (dd, *J* = 23.6, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 143.8 (d, *J* = 20.1 Hz), 134.3, 129.6, 127.9, 125.2 (d, *J* = 7.4 Hz), 122.9 (d, *J* = 7.1 Hz), 89.4 (d, *J* = 170.6 Hz), 22.4 (d, *J* = 24.9 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -169.86 (dq, *J* = 47.4, 23.6 Hz); MS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0, found 158.0; HRMS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0299, found 158.0296.



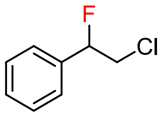
13

1-Chloro-4-(1-fluoroethyl)benzene (13).[6] Prepared from 1-chloro-4-ethylbenzene (28.1 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% ethyl acetate/hexanes) and concentrated by rotary evaporator at ca. 150 mmHg to give **11** (11.4 mg, 36% yield) as a colorless oil: R_f = 0.5 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.04 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 5.10 (dq, *J* = 47.4, 6.4 Hz, 1H), 1.19 (dd, *J* = 23.5, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 140.5 (d, *J* = 20.1 Hz), 134.1 (d, *J* = 2.3 Hz), 128.8, 126.8 (d, *J* = 6.8 Hz), 90.0 (d, *J* = 169.6 Hz), 22.8 (d, *J* = 25.1 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -168.31 (dq, *J* = 47.4, 23.5 Hz); MS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0, found 158.0.



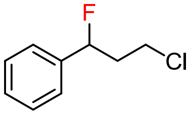
14

1-Bromo-3-(1-fluoroethyl)benzene (14). Prepared from 1-bromo-3-ethylbenzene (37.0 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% ethyl acetate/hexanes) and concentrated by rotary evaporator at ca. 150 mmHg to give **14** (19.1 mg, 47% yield) as a colorless oil: R_f = 0.5 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.32 (s, 1H), 7.16-7.18 (m, 1H), 6.98-6.85 (m, 1H), 6.69 (dd, *J* = 7.9, 7.9 Hz, 1H), 5.04 (dq, *J* = 47.5, 6.4 Hz, 1H), 1.14 (dd, *J* = 23.6, 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 144.4 (d, *J* = 20.0 Hz), 131.3 (d, *J* = 1.7 Hz), 130.3, 128.6 (d, *J* = 7.3 Hz), 123.8 (d, *J* = 7.0 Hz), 122.9, 89.8 (d, *J* = 170.7 Hz), 22.8 (d, *J* = 24.9 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -169.75 (dq, *J* = 47.5, 23.6 Hz); MS(EI) calcd for C_8H_8BrF $(M)^+$ 202.0, found 201.9; HRMS(EI) calcd for C_8H_8BrF $(M)^+$ 201.9793, found 201.9790.



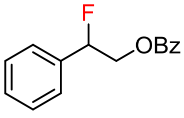
15

(2-Chloro-1-fluoroethyl)benzene (15).[10] Prepared from (2-chloroethyl)benzene (28.1 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by flash column chromatography (1% diethyl ether/pentane) to give **15** (11.0 mg, 35% yield) as a colorless oil: R_f = 0.3 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 6.99-7.02 (m, 3H), 6.92-6.95 (m, 2H), 5.16 (ddd, J = 47.2, 7.7, 3.7 Hz, 1H), 3.32 (ddd, J = 16.2, 12.2, 7.7 Hz, 1H), 3.15 (ddd, J = 25.5, 12.2, 3.7 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 137.1 (d, J = 20.1 Hz), 129.1 (d, J = 1.2 Hz), 128.7, 126.0 (d, J = 6.7 Hz), 93.0 (d, J = 178.9 Hz), 46.9 (d, J = 27.7 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -179.04 (ddd, J = 47.2, 25.5, 16.2 Hz, 1F); MS(EI) calcd for C_8H_8ClF $(M)^+$ 158.0, found 158.0.



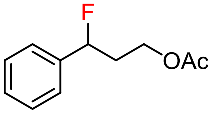
16

(3-Chloro-1-fluoropropyl)benzene (16). Prepared from (3-chloropropyl)benzene (30.9 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% ethyl acetate/hexanes) to give **16** (21.8 mg, 63% yield) as a colorless oil: R_f = 0.4 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.03-7.09 (m, 5H), 5.42 (ddd, J = 47.9, 9.1, 3.9 Hz, 1H), 3.29 (ddd, J = 11.1, 8.5, 5.8 Hz, 1H), 3.07 (ddd, J = 11.1, 5.9, 5.9 Hz, 1H), 1.92-2.04 (m, 1H), 1.64-1.80 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 139.7 (d, J = 19.5 Hz), 128.8, 128.6 (d, J = 1.9 Hz), 125.7 (d, J = 6.8 Hz), 91.3 (d, J = 172.0 Hz), 40.4 (d, J = 4.8 Hz), 40.3 (d, J = 24.4 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -179.53 (ddd, J = 47.9, 31.0, 13.7 Hz, 1F); MS(EI) calcd for $C_9H_{10}ClF$ $(M)^+$ 172.0, found 172.0; HRMS(EI) calcd for $C_9H_{10}ClF$ $(M)^+$ 172.0455, found 172.0458.



17

2-Fluoro-2-phenylethyl benzoate (17). Prepared from phenethyl benzoate (45.2 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by preparative TLC (10% ethyl acetate/hexanes) to give **17** (29.5 mg, 60% yield) as a colorless oil: R_f = 0.5 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 8.14-8.17 (m, 2H), 7.01-7.14 (m, 8H), 5.48 (ddd, J = 48.6, 7.2, 3.5 Hz, 1H), 4.41-4.48 (m, 1H), 4.37-4.39 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 166.0, 136.6 (d, J = 19.8 Hz), 133.2, 130.4, 130.1, 129.0 (d, J = 1.7 Hz), 128.8, 128.6, 126.1 (d, J = 6.8 Hz), 91.9 (d, J = 176.6 Hz), 67.4 (d, J = 24.4 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -184.52 (ddd, J = 48.6, 26.7, 21.8 Hz, 1F); MS(ESI) calcd for $C_{15}H_{13}FO_2Na$ $(M+Na)^+$ 267.1, found 267.1; HRMS(ESI) calcd for $C_{15}H_{13}FO_2Na$ $(M+Na)^+$ 267.0797, found 267.0797.



18

3-Fluoro-3-phenylpropyl acetate (18).[11] Prepared from 3-phenylpropyl acetate (35.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by preparative TLC (10% ethyl acetate/hexanes) to give **18** (29.5 mg, 75% yield) as a colorless oil: R_f= 0.3 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.04-7.12 (m, 5H), 5.34 (ddd, J = 47.8, 8.8, 4.3 Hz, 1H), 4.11 (ddd, J = 11.3, 7.8, 5.8 Hz, 1H), 4.03 (ddd, J = 11.3, 6.0, 5.8 Hz, 1H), 1.99 (ddddd, J = 14.8, 8.8, 8.8, 5.8, 5.8 Hz, 1H), 1.73-1.89 (m, 1H), 1.63 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.9, 140.2 (d, J = 19.6 Hz), 128.7, 128.6 (d, J = 1.9 Hz), 125.8 (d, J = 6.8 Hz), 91.5 (d, J = 171.7 Hz), 60.4 (d, J = 4.9 Hz), 36.6 (d, J = 24.0 Hz), 20.4; ^{19}F NMR (376 MHz, C_6D_6) δ -177.55 (ddd, J = 47.8, 30.0, 14.8 Hz, 1F); MS(ESI) calcd for $C_{11}H_{13}FO_2Na$ $(M+Na)^+$ 219.1, found 219.1.

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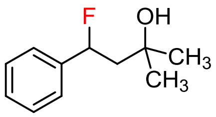
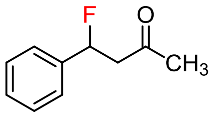
[11] Bloom, S.; Pitts, C. R.; Woltornist, R., Griswold, A., Holl, M. G., Lectka, T. *Org. Lett.* **2013**, *15*, 1722.



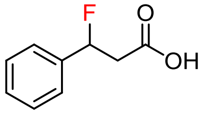
19

4-Fluoro-2-methyl-4-phenylbutan-2-ol (19). Prepared from 2-methyl-4-phenylbutan-2-ol (32.8 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (10% ethyl acetate/hexanes) to give **19** (26.8 mg, 74% yield) as a colorless oil: R_f = 0.3 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.20 (d, *J* = 8.1 Hz, 2H), 7.05-7.14 (m, 3H), 5.70 (ddd, *J* = 49.0, 9.8, 2.2 Hz, 1H), 2.02 (ddd, *J* = 17.4, 15.2, 9.8 Hz, 1H), 1.60 (ddd, *J* = 39.6, 15.2, 2.2 Hz, 1H), 1.21 (s, 3H), 1.07 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 141.7 (d, *J* = 20.1 Hz), 128.7, 128.3, 125.8 (d, *J* = 6.9 Hz), 92.4 (d, *J* = 169.2 Hz), 69.6, 50.9 (d, *J* = 22.0 Hz), 30.2, 29.2; ^{19}F NMR (376 MHz, C_6D_6) δ -173.11 (ddd, *J* = 49.0, 39.6, 17.4 Hz, 1F); MS(EI) calcd for $C_{11}H_{15}FO$ $(M)^+$ 182.1, found 182.1; HRMS(EI) calcd for $C_{11}H_{15}FO$ $(M)^+$ 182.1107, found 182.1106.



20

4-Fluoro-4-phenylbutan-2-one (20).[11] Prepared from 4-phenylbutan-2-one (29.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) to give crude reaction mixture. A 3:1 mixture of **20** and *trans*-4-phenyl-3-buten-2-one (elimination product) was obtained when purified by preparative TLC (10% ethyl acetate/hexanes): R_f = 0.3 (10% ethyl acetate/hexanes). The crude product **20** was reduced by $NaBH_4$ to give 4-fluoro-4-phenylbutan-2-ol **20s** (27.5 mg, 82% yield, two steps) as a colorless oil: R_f = 0.3 (20% ethyl acetate/hexanes). **20**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.02-7.16 (m, 5H), 5.90 (ddd, *J* = 46.7, 8.5, 4.2 Hz, 1H), 2.67 (ddd, *J* = 16.8, 14.9, 8.5 Hz, 1H), 2.19 (ddd, *J* = 31.0, 16.8, 4.2 Hz, 1H), 1.59 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 202.8 (d, *J* = 3.5 Hz), 140.0 (d, *J* = 19.8 Hz), 128.7, 128.6 (d, *J* = 2.0 Hz), 125.9 (d, *J* = 6.6 Hz), 90.3 (d, *J* = 170.7 Hz), 50.4 (d, *J* = 25.9 Hz), 30.1; ^{19}F NMR (376 MHz, C_6D_6) δ -174.39 (ddd, *J* = 46.7, 31.0, 14.9 Hz, 1F); MS(EI) calcd for $C_{10}H_{11}FO$ $(M)^+$ 166.1, found 166.1; **20s**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.21-7.23 (m, 4H), 7.03-7.14 (m, 6H), 5.73 (ddd, *J* = 48.6, 10.3, 2.3 Hz, 1H), 5.51 (ddd, *J* = 48.0, 7.9, 5.8 Hz, 1H), 3.96 (dqd, *J* = 9.3, 6.2, 2.9 Hz, 1H), 3.61 (dq, *J* = 12.4, 6.2 Hz, 1H), 2.08 (dddd, *J* = 14.0, 14.0, 7.9, 7.9 Hz, 1H), 1.75-1.88 (m, 1H), 1.75 (s, 2H), 1.49-1.68 (m, 2H), 0.96 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 141.3 (d, *J* = 19.7 Hz), 140.6 (d, *J* = 19.7 Hz), 128.7, 128.5 (d, *J* = 2.1 Hz), 126.1 (d, *J* = 6.6 Hz), 125.7 (d, *J* = 6.9 Hz), 93.5 (d, *J* = 168.4 Hz), 91.7 (d, *J* = 169.8 Hz), 65.2 (d, *J* = 5.6 Hz), 64.0 (d, *J* = 2.2 Hz), 47.2 (d, *J* = 22.9 Hz), 46.4 (d, *J* = 22.5 Hz), 24.2, 23.6; ^{19}F NMR (376 MHz, C_6D_6) δ -173.98 (ddd, *J* = 48.0, 27.4, 13.5 Hz, 1F), -178.99 (ddd, *J* = 48.6, 38.5, 14.9 Hz, 1F); MS(EI) calcd for $C_{10}H_{13}FO$ $(M)^+$ 168.1, found 168.1; HRMS(EI) calcd for $C_{10}H_{13}FO$ $(M)^+$ 168.0950, found 168.0952.



21

3-Fluoro-3-phenylpropanoic acid (21).[12] Prepared from 3-phenylpropanoic acid (30.0 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (72 h) and purified by preparative TLC (30% ethyl acetate/hexanes) to give **21** (27.1 mg, 81% yield) as a colorless oil: R_f = 0.2 (30% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 6.99-7.05 (m, 5H), 5.77 (ddd, *J* = 46.9, 9.2, 3.9 Hz, 1H), 2.74 (ddd, *J* = 16.4, 13.2, 9.2 Hz, 1H), 2.32 (ddd, *J* = 33.0, 16.4, 3.9 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 176.7 (d, *J* = 4.1 Hz), 138.8 (d, *J* = 19.6 Hz), 129.0 (d, *J* = 1.2 Hz), 128.8, 126.0 (d, *J* = 6.3 Hz), 90.4 (d, *J* = 172.9 Hz), 42.2 (d, *J* = 27.2 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -172.80 (ddd, *J* = 46.9, 33.0, 13.2 Hz, 1F); MS(ESI) calcd for $C_9H_8FO_2$ $(M-H)^-$ 167.1, found 167.0.

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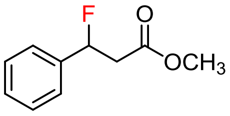
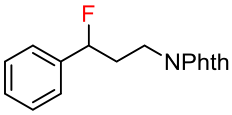
[12] Watanabe, S.; Fujita, T.; Sakamoto, M.; Endo, H.; Kitazume, T. *J. Am. Oil Chem. Soc.* **1987**, *64*, 874.



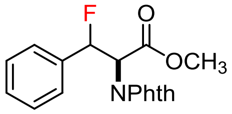
22

Methyl 3-fluoro-3-phenylpropanoate (22).[11] Prepared from methyl 3-phenylpropanoate (32.8 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (72 h) and purified by preparative TLC (10% ethyl acetate/hexanes) to give **22** (27.2 mg, 75% yield) as a colorless oil: R_f = 0.3 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.01-7.10 (m, 5H), 5.89 (ddd, *J* = 46.7, 9.2, 4.2 Hz, 1H), 3.26 (s, 3H), 2.81 (ddd, *J* = 16.0, 13.4, 9.2 Hz, 1H), 2.39 (ddd, *J* = 32.4, 16.0, 4.2 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 169.7 (d, *J* = 4.8 Hz), 139.3 (d, *J* = 19.6 Hz), 128.8 (d, *J* = 1.4 Hz), 128.8, 125.9 (d, *J* = 6.4 Hz), 90.9 (d, *J* = 172.4 Hz), 51.4, 42.3 (d, *J* = 27.1 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -173.08 (ddd, *J* = 46.7, 32.4, 13.4 Hz, 1F); MS(ESI) calcd for $C_{10}H_{11}FO_2Na$ $(M+Na)^+$ 205.1, found 205.0.



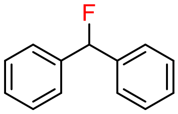
23

***N*-Phthaloyl 3-fluoro-3-phenylpropylamine (23).**[6] Prepared from 2-(3-phenylpropyl)isoindoline-1,3-dione (53.0 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (48 h) and purified by preparative TLC (20% ethyl acetate/hexanes) to give **23** (46.2 mg, 82% yield) as a colorless oil: R_f = 0.4 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.43-7.46 (m, 2H), 6.99-7.11 (m, 5H), 6.88-6.91 (m, 2H), 5.28 (ddd, *J* = 47.8, 8.8, 3.9 Hz, 1H), 3.61-3.76 (m, 2H), 2.12-2.25 (m, 1H), 1.86-2.02 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 167.8, 140.0 (d, *J* = 19.6 Hz), 133.5, 132.6, 128.6, 128.4 (d, *J* = 2.0 Hz), 125.9 (d, *J* = 6.8 Hz), 123.0, 92.6 (d, *J* = 172.0 Hz), 36.0 (d, *J* = 23.6 Hz), 34.7 (d, *J* = 4.5 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -176.12 (ddd, *J* = 47.8, 30.8, 16.2 Hz, 1F); MS(ESI) calcd for $C_{17}H_{14}FNO_2Na$ $(M+Na)^+$ 306.1, found 306.1.



24

(2*R*)-*N*-Phthaloyl-3-fluorophenylalanine methyl ester (24).[13] Prepared from methyl (*S*)-*N*-phthaloylphenylalanine methyl ester[14] (61.8 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (84 h) to give **24** (34.1 mg, 52% yield) as a 1:1 mixture of diastereomers: R_f = 0.3 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.42-7.46 (m, 2H), 7.40 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.33-7.36 (m, 2H), 7.20 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.00-7.07 (m, 3H), 6.82-6.89 (m, 3H), 6.80 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.68 (dd, *J* = 46.6, 8.3 Hz, 1H), 6.65 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.46 (dd, *J* = 46.9, 8.2 Hz, 1H), 5.52-5.59 (m, 1H), 5.52-5.59 (m, 1H), 3.31 (s, 3H), 3.11 (s, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 167.6, 167.3, 166.7, 166.6 (d, *J* = 7.8 Hz), 137.4 (d, *J* = 19.5 Hz), 136.1 (d, *J* = 19.4 Hz), 134.0, 133.9, 132.0, 131.5, 129.5 (d, *J* = 2.2 Hz), 129.3 (d, *J* = 2.4 Hz), 128.7, 128.6, 127.7 (d, *J* = 6.3 Hz), 127.4 (d, *J* = 5.6 Hz), 123.6, 123.4, 91.18 (d, *J* = 177.6 Hz), 90.19 (d, *J* = 178.6 Hz), 56.1 (d, *J* = 24.7 Hz), 55.3 (d, *J* = 36.6 Hz), 52.6, 52.3; ^{19}F NMR (376 MHz, C_6D_6) δ -169.58 (dd, *J* = 46.7, 15.5 Hz, 1F), -177.24 (dd, *J* = 47.0, 11.0 Hz, 1F); MS(ESI) calcd for $C_{18}H_{14}FNO_4Na$ $(M+Na)^+$ 350.1, found 350.1.



26

(Fluoromethylene)dibenzene (26).[15] Prepared from diphenylmethane (33.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) to give **26** (74% NMR yield). ^{1}H NMR (400 MHz, C_6D_6) δ 7.22 (d, *J* = 7.7 Hz, 4H), 7.01-7.13 (m, 6H), 6.24 (d, *J* = 47.5 Hz, 1H); ^{19}F NMR (376 MHz, C_6D_6) δ -166.87 (d, *J* = 47.5 Hz, 1F).

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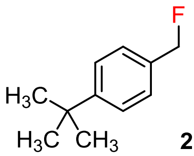
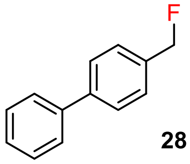
[13] Bergmann, E. D.; Cohen, A. M. *Isr. J. Chem.* **1970**, *8*, 925.

[14] Ito, M.; Sakaguchi, A.; Kobayashi, C.; Ikariya, T. *J. Am. Chem. Soc.* **2007**, *129*, 290.

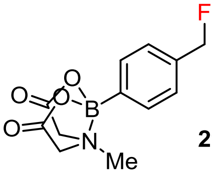
[15] Bellavance, G.; Dubé, P.; Nguyen, B. *Synlett* **2012**, 569.


27

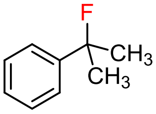
1-(*tert*-Butyl)-4-(fluoromethyl)benzene (27).[16] Prepared from 1-(*tert*-butyl)-4-methylbenzene (29.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (6 h) and purified by preparative TLC (1% ethyl acetate/hexanes) to give **27** (28.6 mg, 86% yield) as a colorless oil: R_f = 0.3 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.21 (d, *J* = 7.9 Hz, 2H), 7.12-7.15 (m, 2H), 5.02 (d, *J* = 48.2 Hz, 2H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6): δ 151.7 (d, *J* = 3.2 Hz), 134.0 (d, *J* = 17.3 Hz), 127.9, 125.7 (d, *J* = 1.6 Hz), 84.3 (d, *J* = 166.5 Hz), 34.6, 31.4; ^{19}F NMR (376 MHz, C_6D_6) δ -205.10 (t, *J* = 48.2 Hz, 1F); MS(EI) calcd for $C_{11}H_{15}F$ $(M)^+$ 166.1, found 166.1.


28

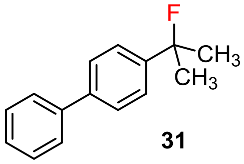
4-(Fluoromethyl)-1,1'-biphenyl (28).[17] Prepared from 4-methyl-1,1'-biphenyl (33.6 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (6 h) and purified by flash column chromatography (1% diethyl ether/pentane) to give **28** (33.7 mg, 93% yield) as a white solid: R_f = 0.3 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.64 (m, 4H), 7.44-7.47 (m, 4H), 7.35-7.38 (m, 1H), 5.43 (d, *J* = 47.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7 (d, *J* = 3.4 Hz) , 140.5, 135.1 (d, *J* = 17.1 Hz), 128.8, 128.0 (d, *J* = 5.7 Hz), 127.5, 127.3, 127.1, 84.4 (d, *J* = 166.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -206.23 (t, *J* = 47.9 Hz, 1F); MS(EI) calcd for $C_{13}H_{11}F$ $(M)^+$ 186.1, found 186.1.


29

(4-(Fluoromethyl)phenyl)boronic *N*-methyliminodiacetate (29). Prepared from 4-tolylboronic *N*-methyliminodiacetate (49.4 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (12 h) and purified by flash column chromatography (95% ethyl acetate/hexane) to give **29** (45.0 mg, 84% yield) as a white solid: R_f = 0.3 (95% ethyl acetate/hexane). ^{1}H NMR (400 MHz, CD_3CN) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.42 (dd, *J* = 7.7, 1.8, 2H), 5.41 (d, *J* = 47.8 Hz, 2H), 4.07 (d, *J* = 17.1, 2H), 3.90 (d, *J* = 17.1, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN) δ 169.5, 138.4 (d, *J* = 16.6 Hz), 133.8 (d, *J* = 1.4 Hz), 133.5, 128.2 (d, *J* = 5.7 Hz), 85.6 (d, *J* = 162.2 Hz), 62.8, 48.5; ^{19}F NMR (376 MHz, CD_3CN) δ -206.91 (t, *J* = 47.8 Hz, 1F); MS(ESI) calcd for $C_{12}H_{14}BFNO_4$ $(M+H)^+$ 266.1, found 266.1; HRMS(ESI) calcd for $C_{12}H_{14}BFNO_4$ $(M+H)^+$ 266.1000, found 266.0998.


30

(2-Fluoropropan-2-yl)benzene (30).[18] Prepared from cumene (24.0 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (12 h) to give **30** (72% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ -136.82 (hept, *J* = 22.3 Hz, 1F).


31

4-(2-Fluoropropan-2-yl)-1,1'-biphenyl (31). Prepared from 4-isopropyl-1,1'-biphenyl (39.2 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (6 h) give **31** (64% NMR yield). ^{1}H NMR (400 MHz, C_6D_6) δ 7.43-7.54 (m, 4H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.21-7.26 (m, 2H), 7.13-7.16 (m, 1H), 1.51 (d, *J* = 21.6 Hz, 1H); ^{19}F NMR (376 MHz, CD_3CN) δ -137.88 (hept, *J* = 21.6 Hz, 1F).

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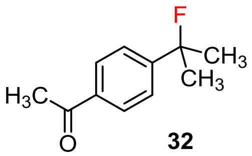
[16] Yokoyama, T.; Wiley, G. R.; Miller, S. I. *J. Org. Chem.* **1969**, *34*, 1859.

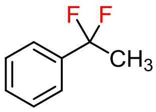
[17] Blessley, G.; Holden, P.; Walker, M.; Brown, J. M.; Gouverneur, V. *Org. Lett.* **2012**, *14*, 2754.

[18] Lai, C.; Kim, Y. I.; Wang, C. M.; Mallouk, T. E. *J. Org. Chem.* **1993**, *58*, 1393.



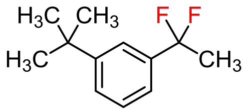
32

1-(4-(2-Fluoropropan-2-yl)phenyl)ethanone (32). Prepared from 1-(4-isopropylphenyl)ethanone (32.4 mg, 0.2 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by flash column chromatography (5% diethyl ether/pentane) to give **32** (29.7 mg, 83% yield) as a colorless oil: R_f = 0.3 (5% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.6 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 2.61 (s, 3H), 1.70 (d, J = 21.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.6, 151.0 (d, J = 21.8 Hz), 136.1 (d, J = 1.2 Hz), 128.4 (d, J = 1.3 Hz), 124.0 (d, J = 9.3 Hz), 95.4 (d, J = 170.8 Hz), 29.1 (d, J = 25.5 Hz), 26.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.03 (hept, J = 21.6 Hz, 1F); MS(EI) calcd for $C_{11}H_{13}FO$ $(M)^+$ 180.1, found 180.1; HRMS(EI) calcd for $C_{11}H_{13}FO$ $(M)^+$ 180.0950, found 180.0947.



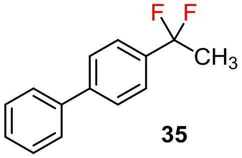
33

(1,1-Difluoroethyl)benzene (33).[19] Prepared from ethylbenzene (10.6 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24h) to give **33** (83% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ -87.16 (q, J = 18.6 Hz, 2F).



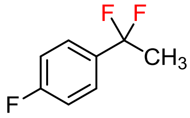
34

1-(*tert*-Butyl)-3-(1,1-difluoroethyl)benzene (34). Prepared from 1-(*tert*-butyl)-3-ethylbenzene (16.2 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% diethyl ether/pentane) and concentrated by rotary evaporator at ca. 200 mgHg to give **34** (6.5 mg, 33% yield) as a colorless oil: R_f = 0.9 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 7.68 (s, 1H), 7.22-7.26 (m, 2H), 7.09 (dd, J = 7.8, 7.8 Hz, 1H), 1.63 (t, J = 18.1 Hz, 3H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 151.7, 138.6 (t, J = 26.1 Hz), 128.6, 127.0 (t, J = 1.7 Hz), 122.5 (t, J = 238.9 Hz), 122.3 (t, J = 6.0 Hz), 121.6 (t, J = 6.1 Hz), 34.8, 31.2, 26.0 (t, J = 30.1 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -86.97 (d, J = 18.1 Hz, 2F); MS(EI) calcd for $C_{12}H_{16}F_2$ $(M)^+$ 198.1, found 198.1; HRMS(EI) calcd for $C_{12}H_{16}F_2$ $(M)^+$ 198.1220, found 198.1218.



35

4-(1,1-Difluoroethyl)-1,1'-biphenyl (35). Prepared from 4-ethyl-1,1'-biphenyl (18.2 mg, 0.1 mmol, 1.0 equiv) according to the general procedure using 3.0 equiv Selectfluor and 5 mol% 9-fluorenone (20 h) and purified by flash column chromatography (1% diethyl ether/pentane) to give **35** (19.8 mg, 91% yield) as a white solid: R_f = 0.3 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.58-7.61 (m, 4H), 7.47 (dd, J = 7.3, 7.8 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 1.97 (t, J = 18.1 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 143.0 (t, J = 1.7 Hz), 140.7, 137.5 (t, J = 26.8 Hz), 129.1, 128.0, 127.5, 127.5, 125.5 (t, J = 5.9 Hz), 122.2 (t, J = 238.7 Hz), 25.7 (t, J = 30.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.29 (q, J = 18.1 Hz, 2F); MS(EI) calcd for $C_{14}H_{12}F_2$ $(M)^+$ 218.1, found 218.1; HRMS(EI) calcd for $C_{14}H_{12}F_2$ $(M)^+$ 218.0907, found 218.0903.



36

1-(1,1-Difluoroethyl)-4-fluorobenzene (36).[20] Prepared from 1-ethyl-4-fluorobenzene (12.4 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) to give **36** (>95% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ -86.08 (q, J = 19.0 Hz, 2F), -113.17 (m, 1F).

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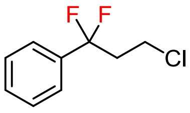
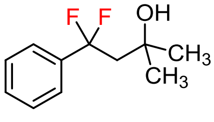
[19] Rozen, S.; Zamir, D. *J. Org. Chem.* **1991**, *56*, 4695.

[20] Volz, H.; Streicher, H.-J. *Tetrahedron*, **1977**, *33*, 3133.



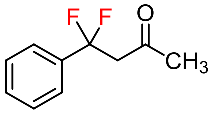
37

(3-Chloro-1,1-difluoropropyl)benzene (37). Prepared from (3-chloropropyl)benzene (15.4 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (pentane) and concentrated by rotary evaporator at ca. 200 mmHg to give 3**7** (12.2 mg, 64% yield) as a colorless oil: R_f = 0.6 (pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 7.15-7.17 (m, 2H), 6.96-7.03 (m, 3H), 3.21 (t, *J* = 7.8 Hz, 2H), 2.20 (tt, *J* = 15.7, 7.8 Hz, 2H); ^{13}C NMR (101 MHz, C_6D_6) δ 136.6 (t, *J* = 26.1 Hz), 130.1 (t, *J* = 1.7 Hz), 128.7, 125.0 (t, *J* = 6.3 Hz), 121.6 (t, *J* = 243.4 Hz), 42.4 (t, *J* = 27.9 Hz), 37.0 (t, *J* = 5.1 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -95.63 (t, *J* = 15.7 Hz, 1F); MS(EI) calcd for $C_9H_9ClF_2$ $(M)^+$ 190.0, found 190.0; HRMS(EI) calcd for $C_9H_9ClF_2$ $(M)^+$ 190.0361, found 190.0364.



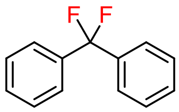
38

4,4-Difluoro-2-methyl-4-phenylbutan-2-ol (38). Prepared from 2-methyl-4-phenylbutan-2-ol (16.4 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (10% ethyl acetate/hexanes) to give **38** (8.2 mg, 40% yield) as a colorless oil: R_f = 0.3 (10% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.51 (m, 2H), 7.42-7.44 (m, 3H), 2.39 (t, *J* = 18.5 Hz, 2H), 1.35 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.0 (t, *J* = 26.3 Hz), 129.8 (t, *J* = 1.8 Hz), 128.5, 124.7 (t, *J* = 6.5 Hz), 123.2 (t, *J* = 243.5 Hz), 67.0, 50.7 (t, *J* = 25.2 Hz), 30.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.58 (t, *J* = 18.5 Hz, 2F); MS(EI) calcd for $C_{11}H_{14}F_2O$ $(M)^+$ 200.1, found 200.1; HRMS(EI) calcd for $C_{11}H_{14}F_2O$ $(M)^+$ 200.1013, found 200.1017.



39

4,4-Difluoro-4-phenylbutan-2-one (39). Prepared from 4-phenylbutan-2-one (14.8 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) to give crude prodtct **39**. The crude product **39** was reduced by $NaBH_4$ to give 4,4-difluoro-4-phenylbutan-2-ol **39s** (10.1 mg, 54% yield, two steps) as a colorless oil: R_f = 0.3 (25% ethyl acetate/hexanes). **39**: ^{19}F NMR (376 MHz, CD_3CN) -91.33 (t, *J* = 16.1 Hz, 2F). **39s**: ^{1}H NMR (400 MHz, C_6D_6) δ 7.31-7.34 (m, 2H), 7.03-7.04 (m, 3H), 3.89-3.96 (m, 1H), 2.17 (tdd, *J* = 16.6, 15.0, 7.7 Hz, 1H), 1.93 (tdd, *J* = 17.5, 15.0, 4.0 Hz, 1H), 1.41 (s, 1H), 0.96 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 137.8 (t, *J* = 26.3 Hz), 129.8 (t, *J* = 1.7 Hz), 128.6, 125.2 (t, *J* = 6.3 Hz), 123.1 (d, *J* = 242.4 Hz), 63.1 (t, *J* = 3.7 Hz), 48.1 (t, *J* = 25.6 Hz), 23.9; ^{19}F NMR (376 MHz, C_6D_6) δ -93.58 (t, *J* = 17.0 Hz, 2F); MS(ESI) calcd for $C_{10}H_{12}F_2ONa$ $(M+Na)^+$ 209.1, found 209.1; HRMS(ESI) calcd for $C_{10}H_{12}F_2ONa$ $(M+Na)^+$ 209.0754, found 209.0756.



40

Difluorodiphenylmethane (40).[21] Prepared from diphenylmethane (16.8 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24 h) and purified by preparative TLC (1% ethyl acetate/hexanes) to give **40** (10.5 mg, 51% yield) as a colorless oil: R_f = 0.5 (1% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 7.43-7.48 (m, 4H), 6.98-7.03 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 138.3 (t, *J* = 28.3 Hz), 130.0 (t, *J* = 1.8 Hz), 128.6, 126.2 (t, *J* = 5.6 Hz), 121.3 (t, *J* = 241.5 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ -88.23 (s, 2F); MS(EI) calcd for $C_{13}H_{10}F_2$ $(M)^+$ 204.1, found 204.1.

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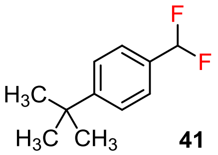
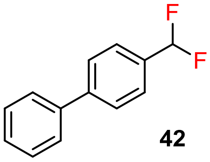
[21] Hara, S.; Monoi, M.; Umemura, R.; Fuse, C. *Tetrahedron*, **2012**, *68*, 10145.



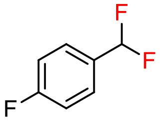
41

1-(*tert*-Butyl)-4-(difluoromethyl)benzene (41).[22] Prepared from 1-(*tert*-butyl)-4-methylbenzene (14.8 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (16 h) and purified by preparative TLC (1% diethyl ether/pentane) and concentrated by rotary evaporator at ca. 200 mmHg to give **41** (13.3 mg, 72% yield) as a colorless oil: R_f = 0.8 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.22 (t, *J* = 56.5 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (101 MHz, C_6D_6) δ 153.8 (t, *J* = 2.0 Hz), 132.2 (t, *J* = 22.5 Hz), 125.8, 125.7 (t, *J* = 5.9 Hz), 115.4 (t, *J* = 237.6 Hz), 34.7, 31.2; ^{19}F NMR (376 MHz, C_6D_6) δ -109.12 (d, *J* = 56.5 Hz, 2F); MS(EI) calcd for $C_{11}H_{14}F_2$ $(M)^+$ 184.1, found 184.1.



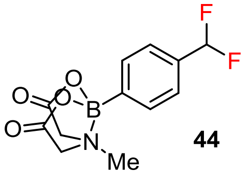
42

4-(Difluoromethyl)-1,1'-biphenyl (42).[22] Prepared from 4-methyl-1,1'-biphenyl (16.8 mg, 0.1 mmol, 1.0 equiv) according to the general procedure using 4.0 equiv Selectfluor and 5 mol% 9-fluorenone (20 h) and purified by flash column chromatography (1% diethyl ether/pentane) to give **42** (19.0 mg, 93% yield) as a white solid: R_f = 0.3 (1% diethyl ether/pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.58-7.62 (m, 4H), 7.45-7.49 (m, 2H), 7.37-7.41 (m, 1H), 6.70 (t, *J* = 56.6 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6) δ 143.9 (t, *J* = 2.0 Hz), 140.5, 133.6 (t, *J* = 22.4 Hz), 129.1, 127.6, 127.5, 126.3 (t, *J* = 5.9 Hz), 115.3 (t, *J* = 237.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.42 (d, *J* = 56.6 Hz, 2F); MS(EI) calcd for $C_{13}H_{10}F_2$ $(M)^+$ 204.1, found 204.1.



43

1-(Difluoromethyl)-4-fluorobenzene (43).[23] Prepared from 1-fluoro-4-methylbenzene (11.0 mg, 0.1 mmol, 1.0 equiv) according to the general procedure (24h) to give **43** (74% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ -110.23 (d, *J* = 56.1 Hz, 2F), -111.42 (m, 1F).



44

(4-(Difluoromethyl)phenyl)boronic *N*-methyliminodiacetate (44). Prepared from 4-tolylboronic *N*-methyliminodiacetate (24.7 mg, 0.1 mmol, 1.0 equiv) according to the general procedure using 4.0 equiv Selectfluor and 5 mol% 9-fluorenone (96 h) and purified by flash column chromatography (95% ethyl acetate/hexane) to give **44** (22.6 mg, 80% yield) as a white solid: R_f = 0.3 (95% ethyl acetate/hexane). ^{1}H NMR (400 MHz, CD_3CN) δ 7.63 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 6.80 (t, *J* = 56.2 Hz, 1H), 4.09 (d, *J* = 17.0 Hz, 2H), 3.91 (d, *J* = 17.0 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (101 MHz, CD_3CN) δ 170.1, 136.8 (t, *J* = 22.0 Hz), 136.0, 134.6, 126.6 (t, *J* = 6.0 Hz), 116.8 (t, *J* = 236.0 Hz), 63.5, 49.2; ^{19}F NMR (376 MHz, CD_3CN) δ -111.31 (d, *J* = 56.2 Hz); MS(ESI) calcd for $C_{12}H_{13}BF_2NO_4$ $(M+H)^+$ 284.1, found 284.1; HRMS(ESI) calcd for $C_{12}H_{13}BF_2NO_4$ $(M+H)^+$ 284.0906, found 284.0907.

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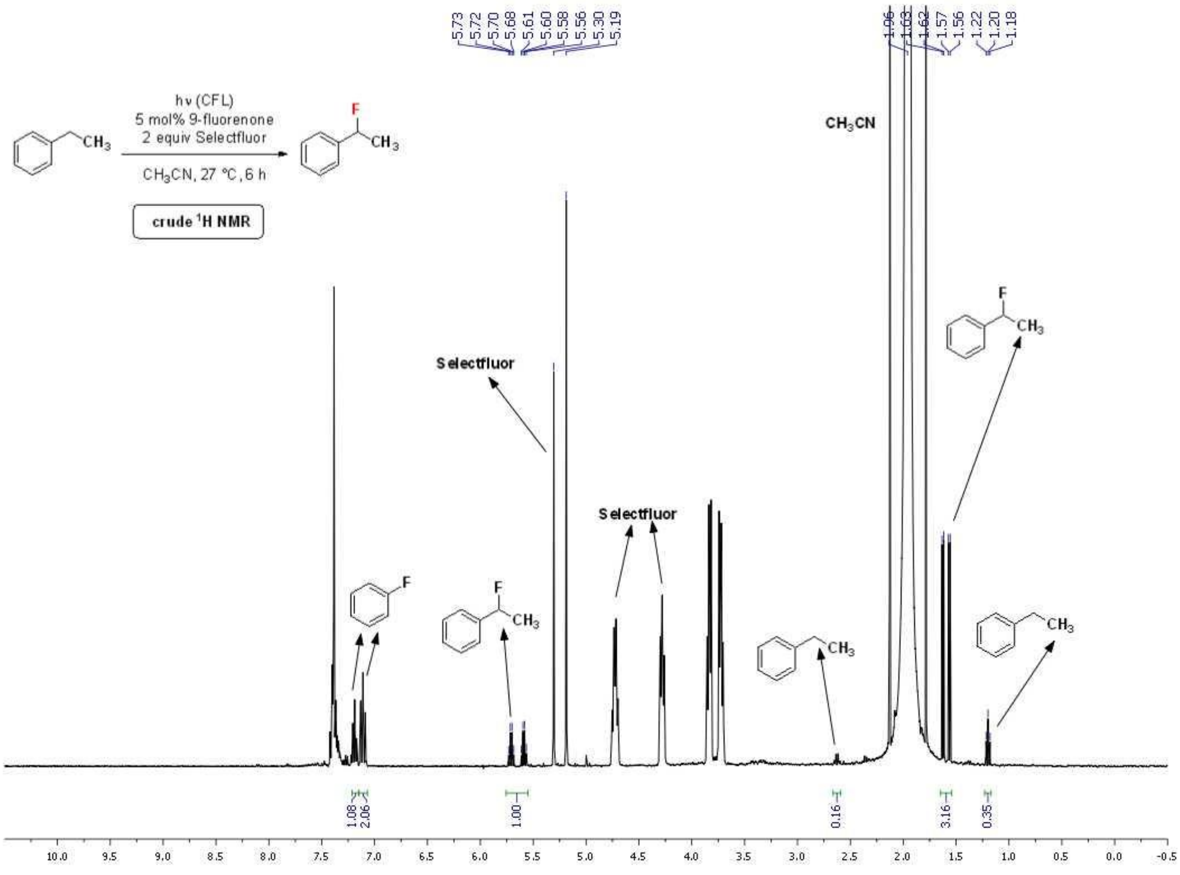
[22] Fier, P. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2012**, *134*, 5524.

[23] Ilayaraja, N.; Manivel, A.; Velayutham, D.; Noel, M. *J. Fluorine Chem.* **2008**, 129, 185.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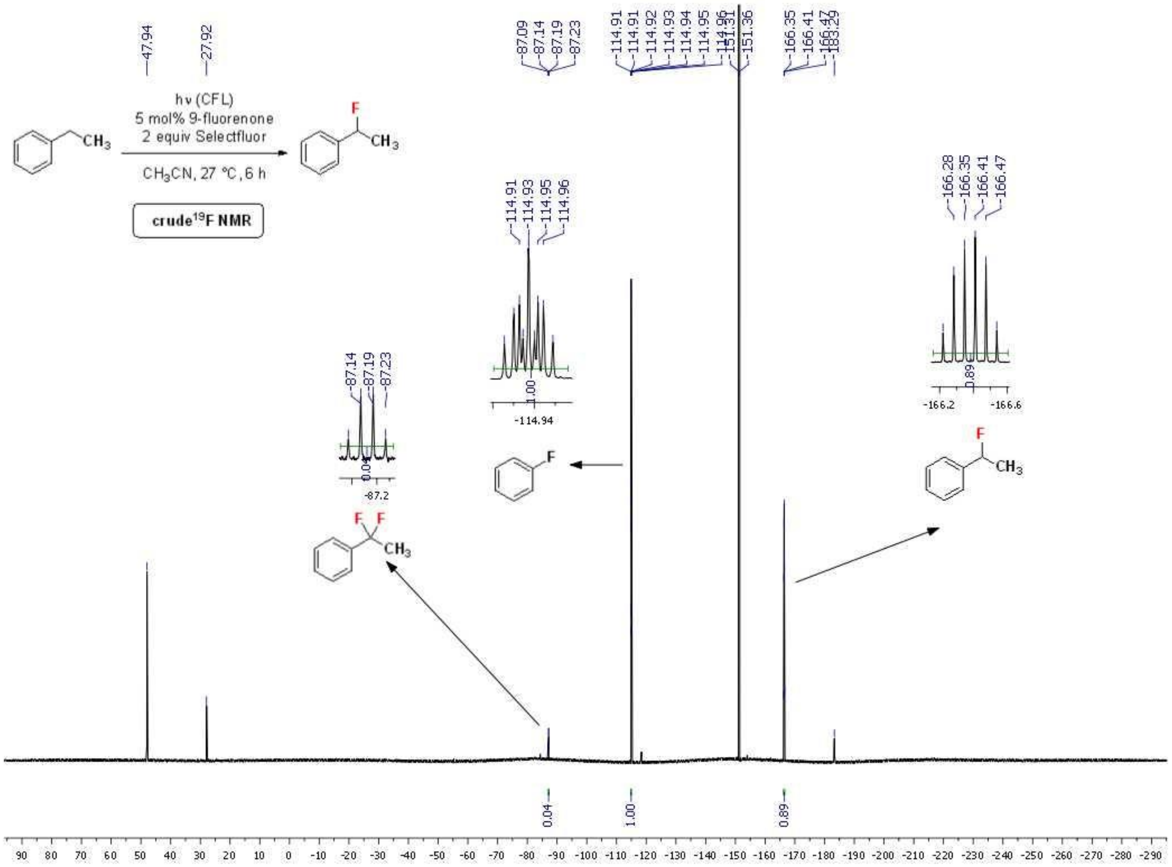
5 mol% 9-fluorenone
2 equiv Selectfluor
CH3CN, 27 °C, 6 h
crude 1H NMR
CH3CN
Selectfluor
Selectfluor
5.73 5.72 5.70 5.68 5.61 5.60 5.58 5.56 5.30 5.19
1.96 1.63 1.62 1.57 1.56 1.22 1.20 1.18
1.08 2.06 1.00 0.16 3.16 0.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


hν (CFL)
5 mol% 9-fluorenone
2 equiv Selectfluor
CH3CN, 27 °C, 6 h
crude 19F NMR
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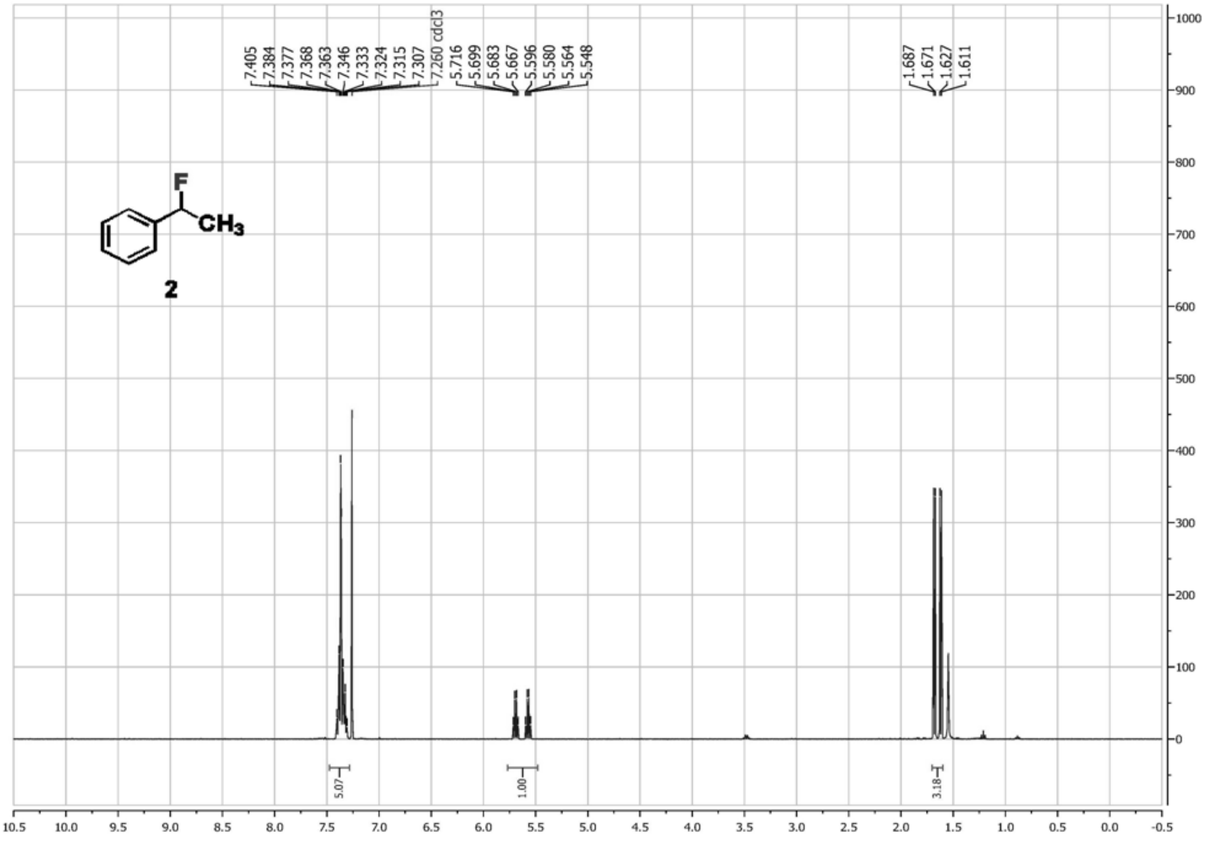
-87.09 -87.14 -87.19 -87.23
-114.91 -114.91 -114.92 -114.93 -114.94 -114.95 -114.96 -151.31 -151.36
-166.35 -166.41 -166.47 -183.29
-114.91 -114.93 -114.95 -114.96
1.00
-114.94
-166.28 -166.35 -166.41 -166.47
0.89
-166.2 -166.6
-87.14 -87.19 -87.23
0.04
-87.2
0.04 1.00 0.89
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290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7.346
7.333
7.324
7.315
7.307
7.260 cdcl3
5.716
5.699
5.683
5.667
5.596
5.580
5.564
5.548
1.687
1.671
1.627
1.611
F
CH3
2
5.07
1.00
3.18
10.5 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
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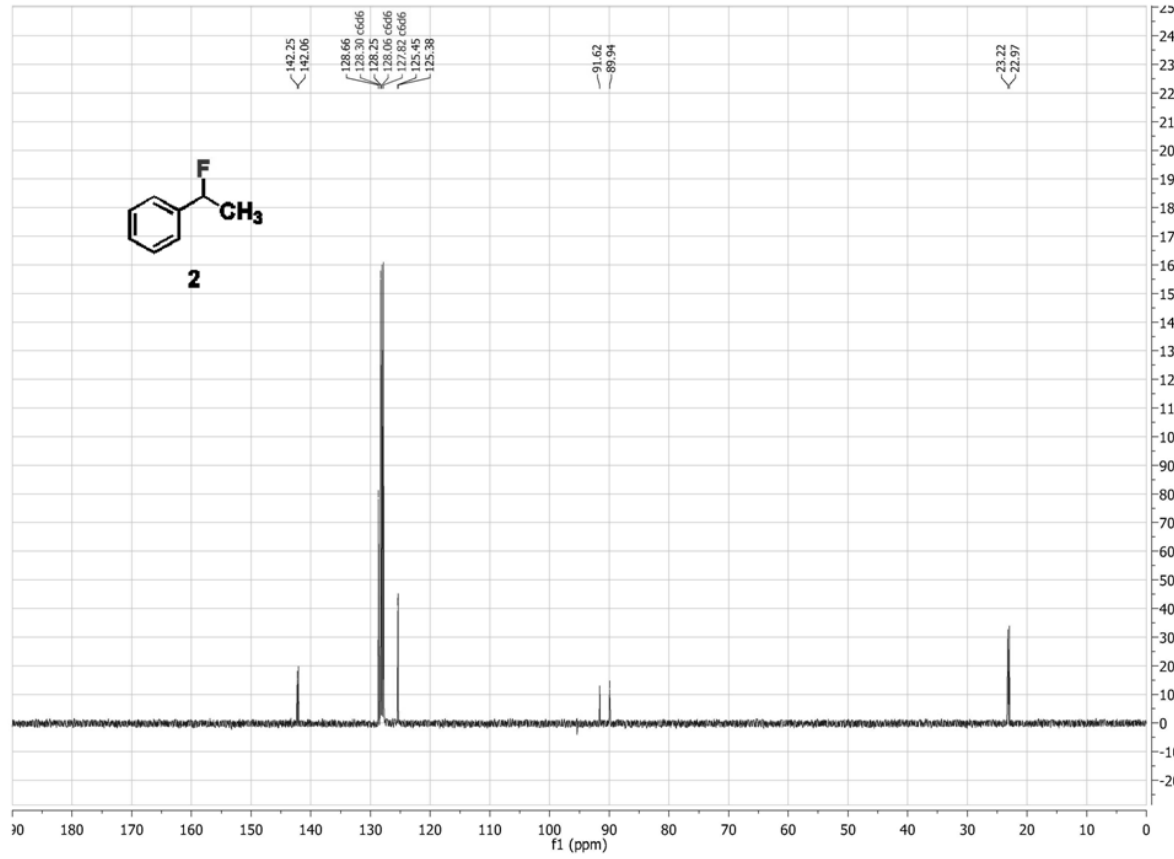
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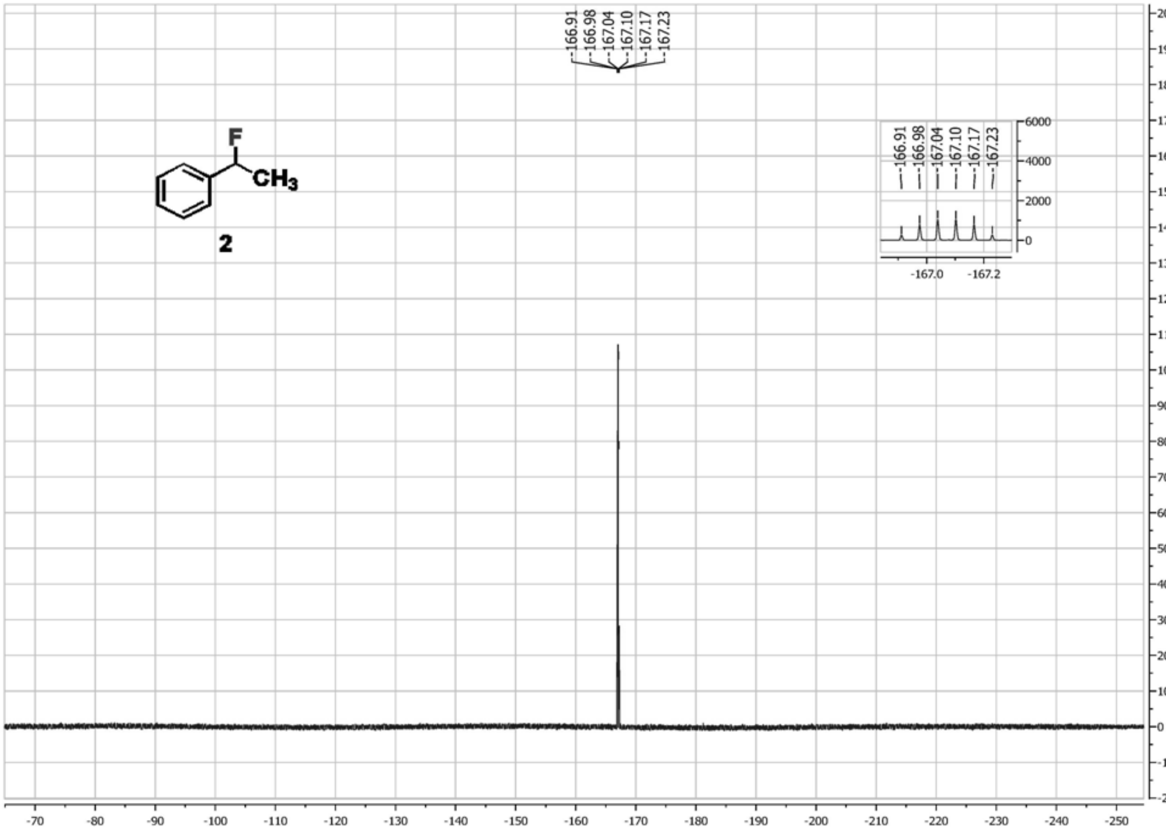
128.25
128.06 c6d6
127.82 c6d6
125.45
125.38
91.62
89.94
23.22
22.97
F
CH3
2
f1 (ppm)
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
2500 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200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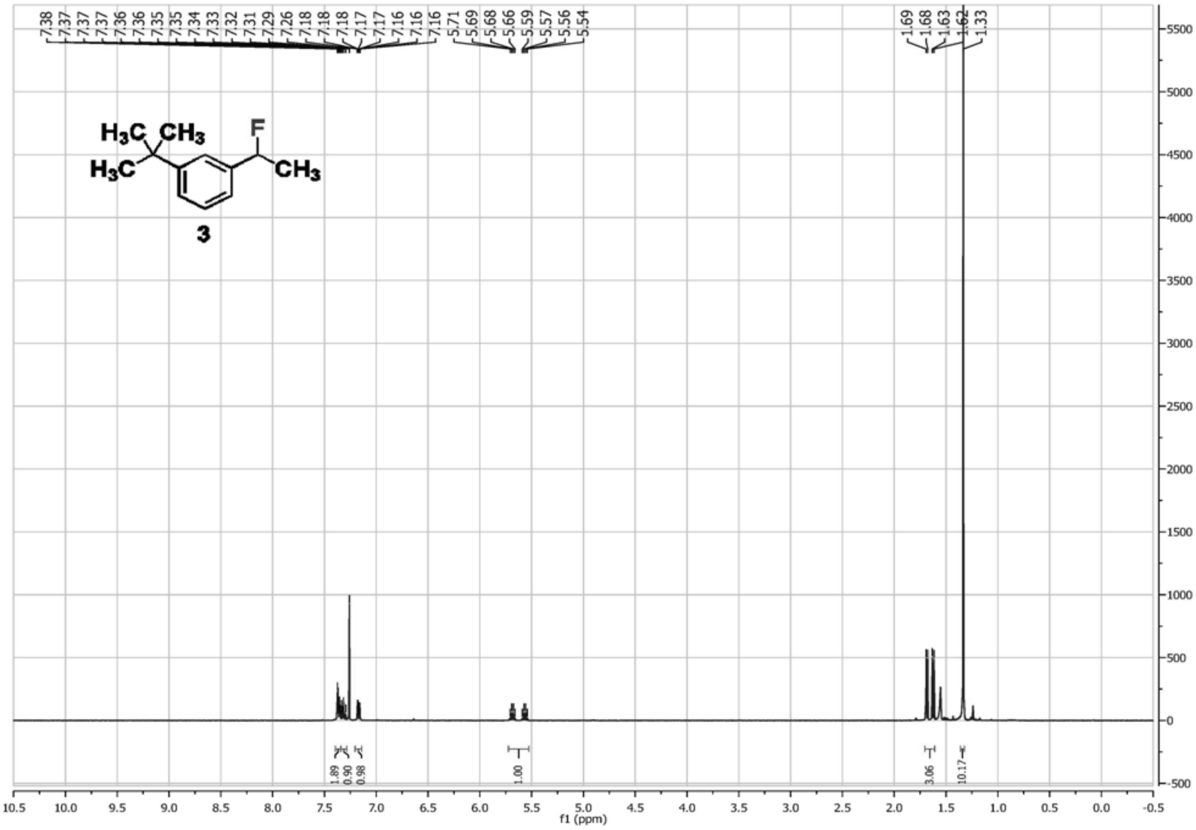
-166.98
-167.04
-167.10
-167.17
-167.23
F
CH3
2
-167.0
-167.2
6000
4000
2000
0
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250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7.37
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7.36
7.35
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7.34
7.33
7.32
7.31
7.29
7.26
7.18
7.18
7.17
7.17
7.16
7.16
7.16
5.71
5.69
5.68
5.66
5.59
5.57
5.56
5.54
1.69
1.68
1.63
1.62
1.33
H3C
CH3
H3C
F
CH3
3
1.89
0.90
0.98
1.00
3.06
10.17
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
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
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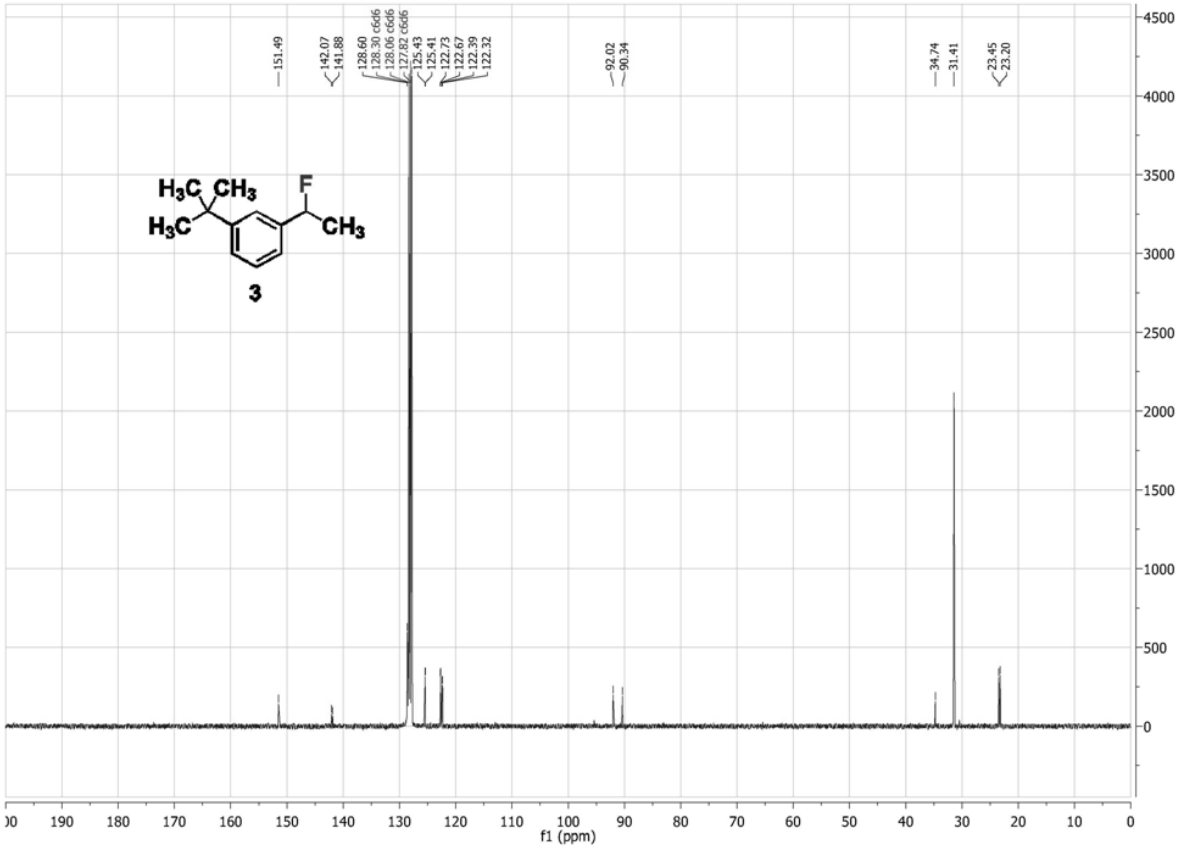
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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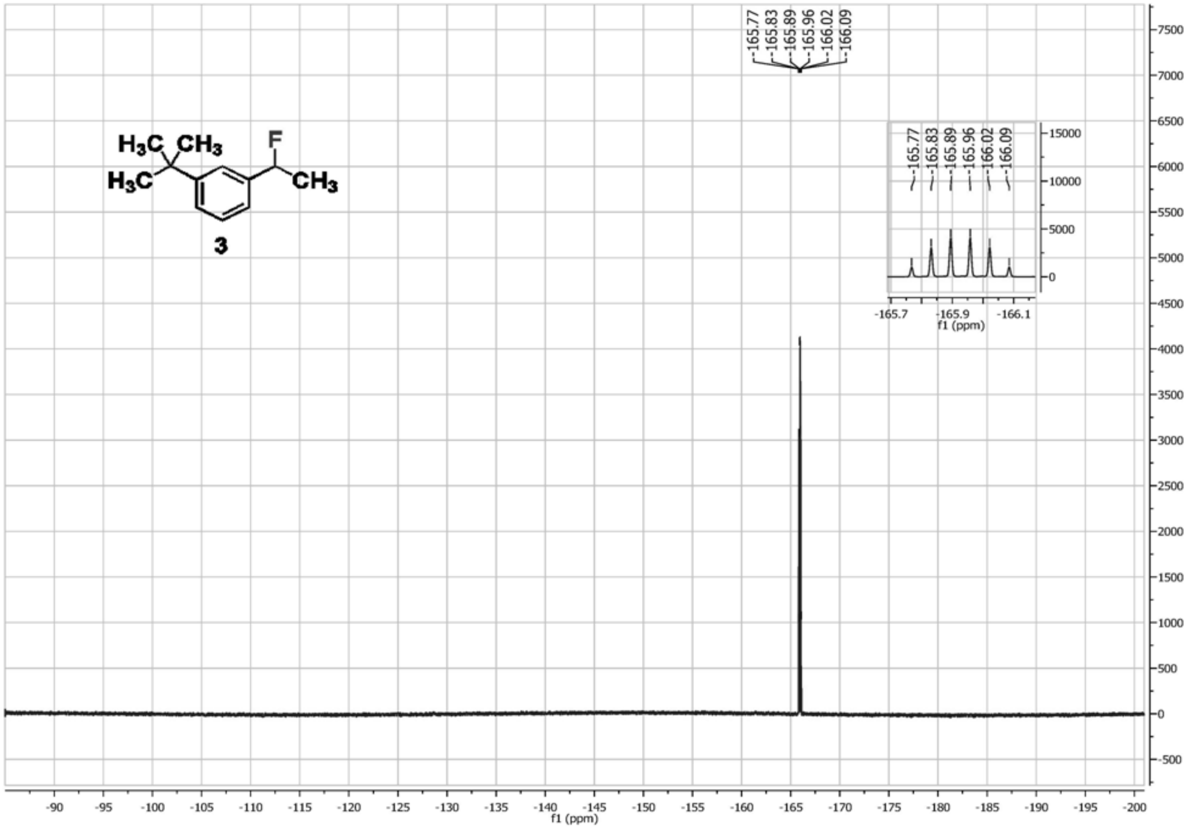
128.06 c6d6
127.82 c6d6
125.43
125.41
122.73
122.67
122.39
122.32
92.02
90.34
34.74
31.41
23.45
23.20
3
f1 (ppm)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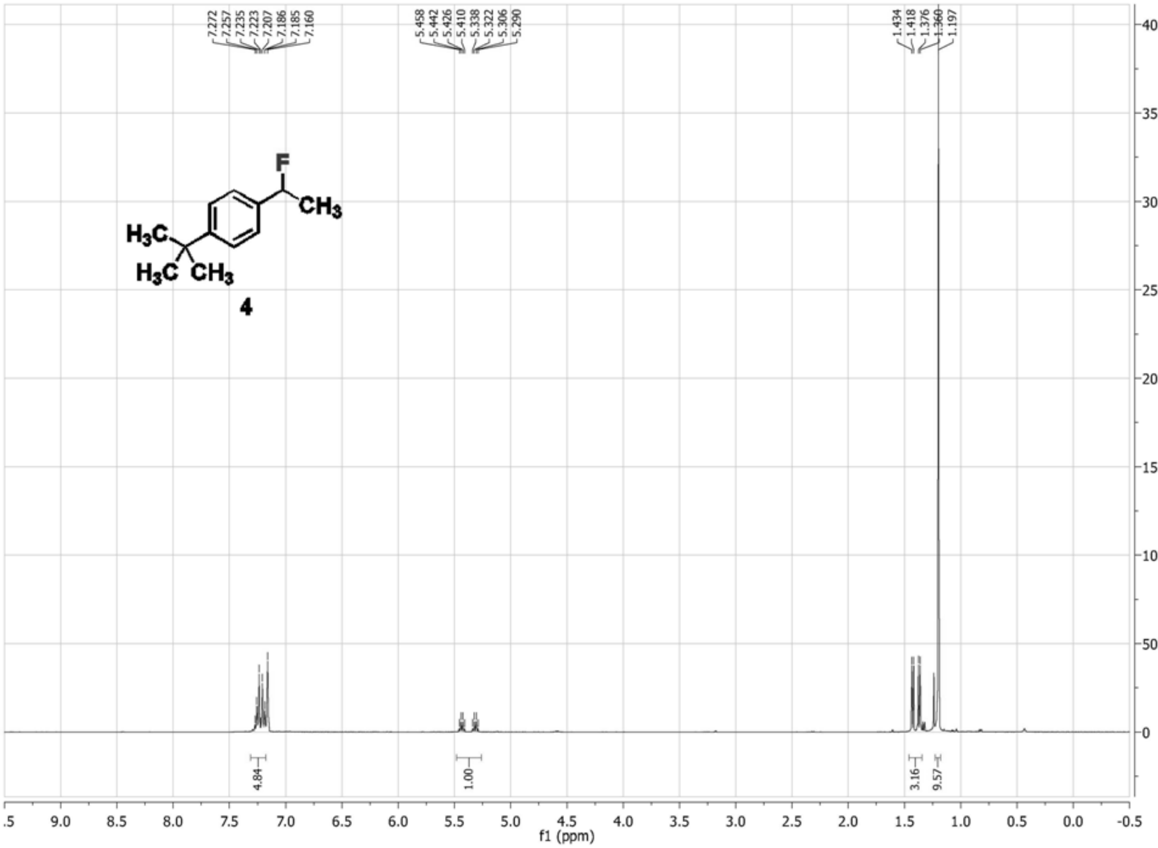
-165.89
-165.96
-166.02
-166.09
3
f1 (ppm)



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7.235
7.223
7.207
7.186
7.185
7.160
5.458
5.442
5.426
5.410
5.338
5.322
5.306
5.290
1.434
1.418
1.376
1.360
1.197
F
CH3
H3C
H3C
CH3
4
4.84
1.00
3.16
9.57
4000
3500
3000
2500
2000
1500
1000
500
0
.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
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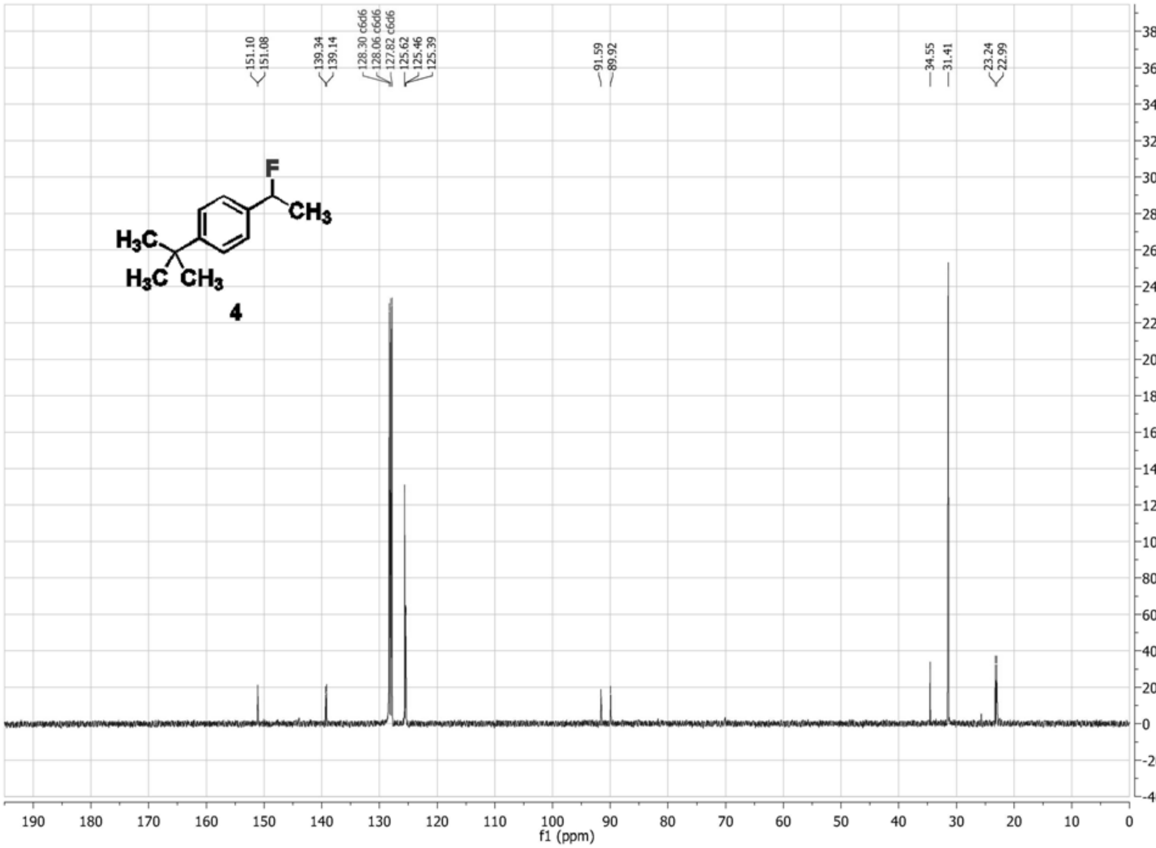
1.0
0.5
0.0
-0.5
f1 (ppm)



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151.08
139.34
139.14
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.62
125.46
125.39
91.59
89.92
34.55
31.41
23.24
22.99
F
CH3
H3C
H3C
CH3
4
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
190
180
170
160
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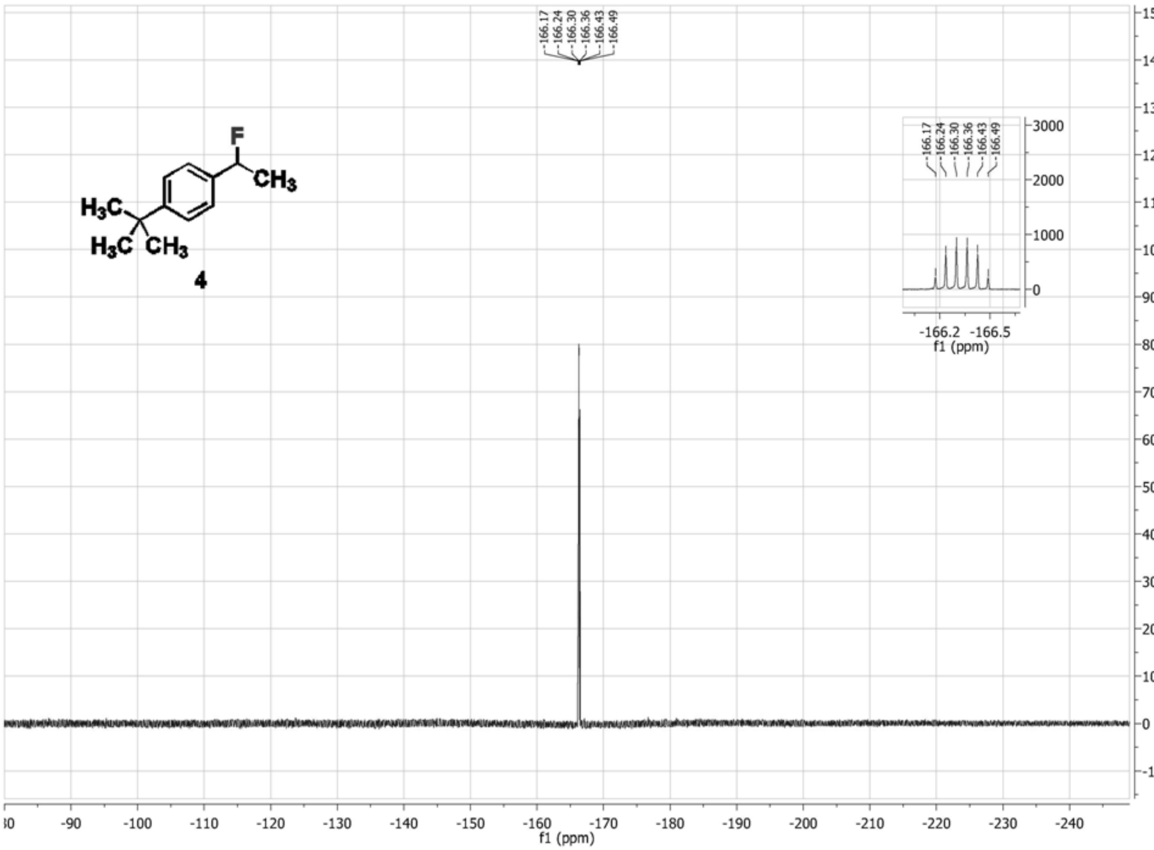
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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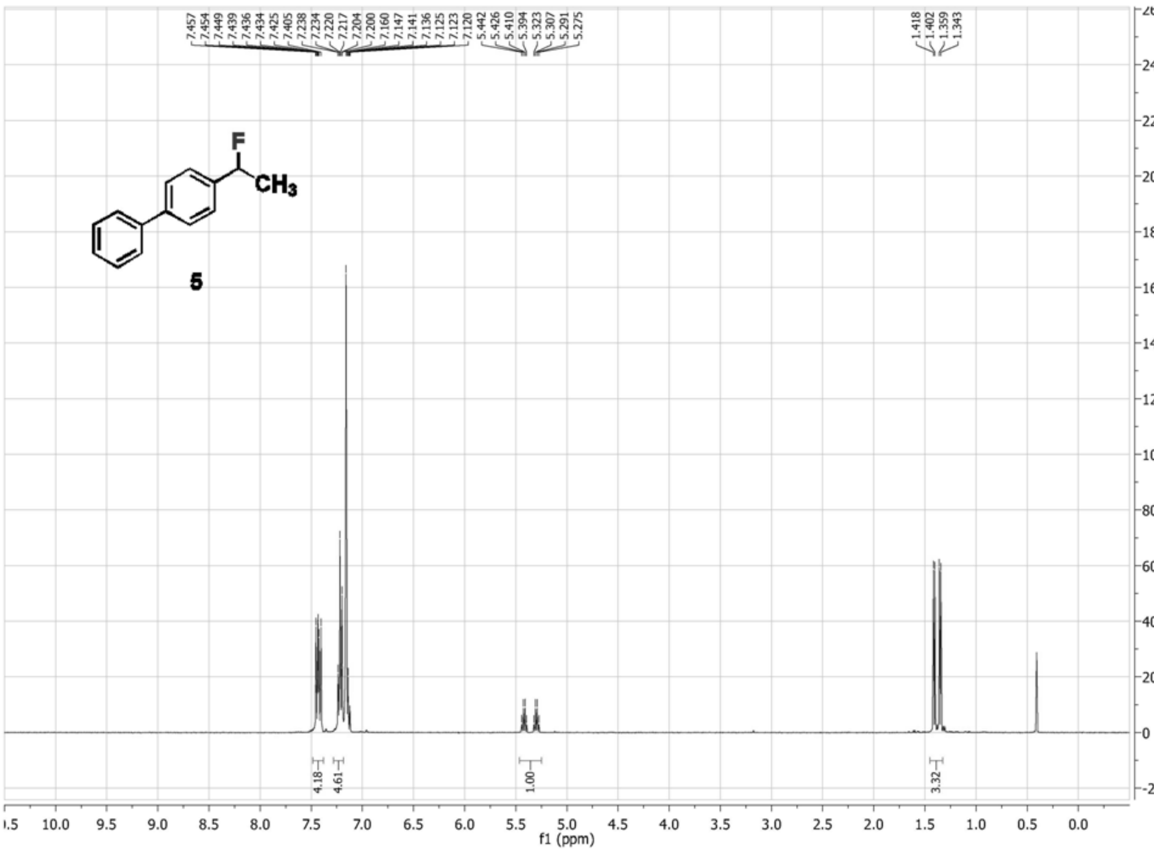
-166.24
-166.30
-166.36
-166.43
-166.49
F
CH3
H3C
H3C
CH3
4
3000
2000
1000
0
-166.2 -166.5
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)



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7.405
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7.220
7.217
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7.160
7.147
7.141
7.136
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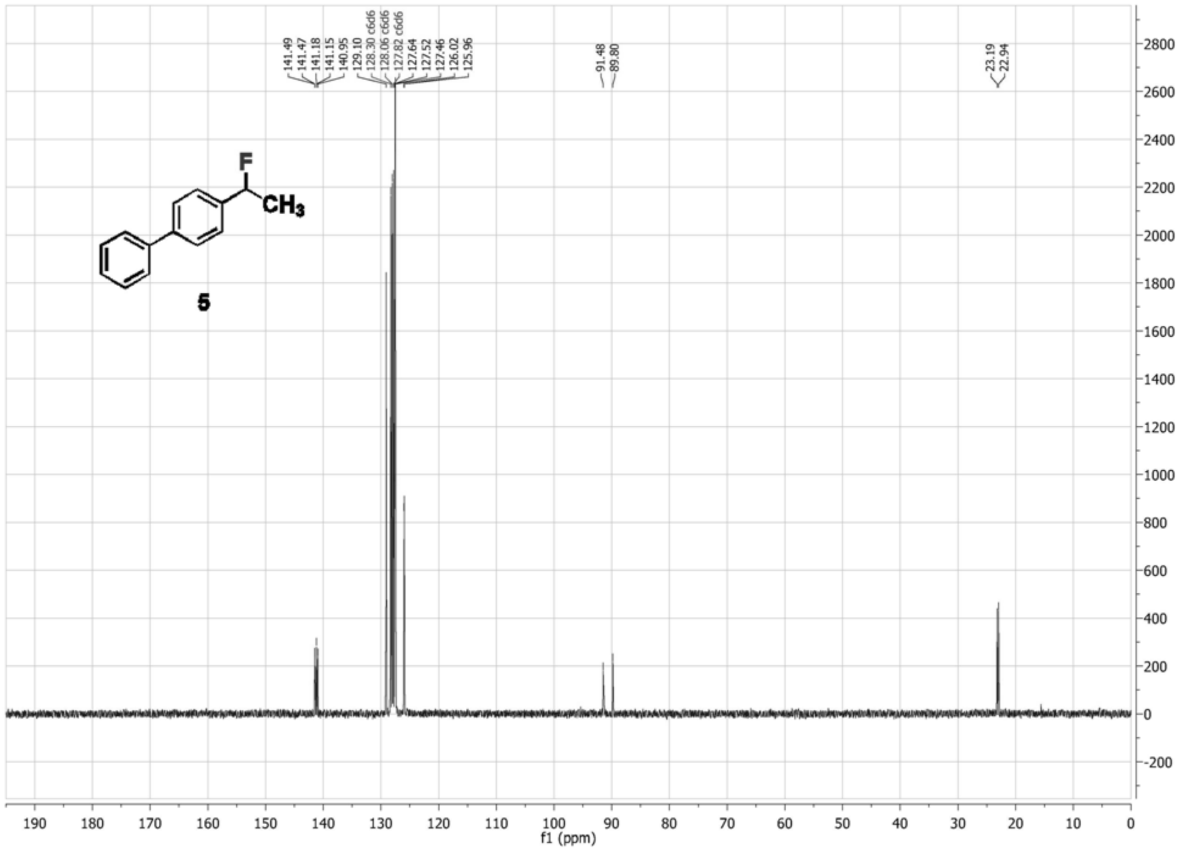
5.442
5.426
5.410
5.394
5.323
5.307
5.291
5.275
1.418
1.402
1.359
1.343
F
CH3
5
4.18
4.61
1.00
3.32
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



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141.18
141.15
140.95
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128.06 c6d6
127.82 c6d6
127.64
127.52
127.46
126.02
125.96
91.48
89.80
23.19
22.94
F
CH3
5
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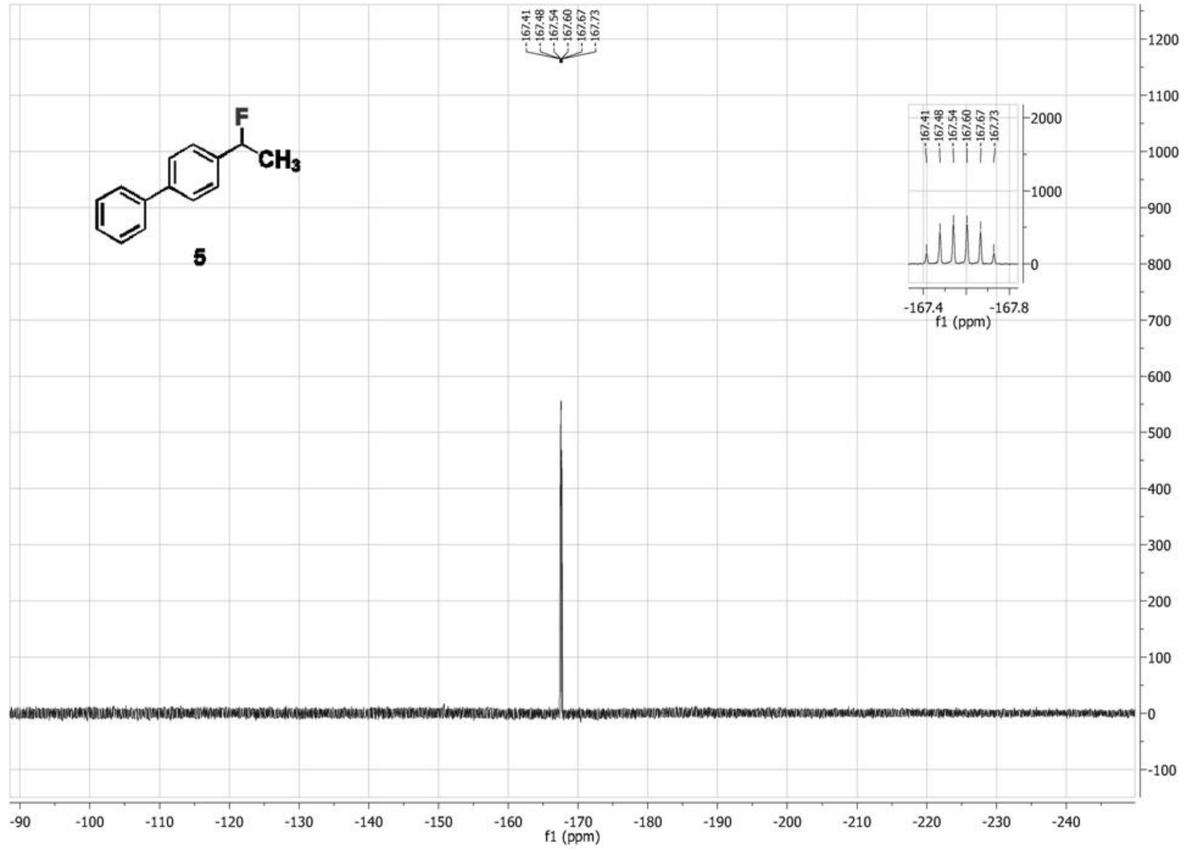
f1 (ppm)
2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200



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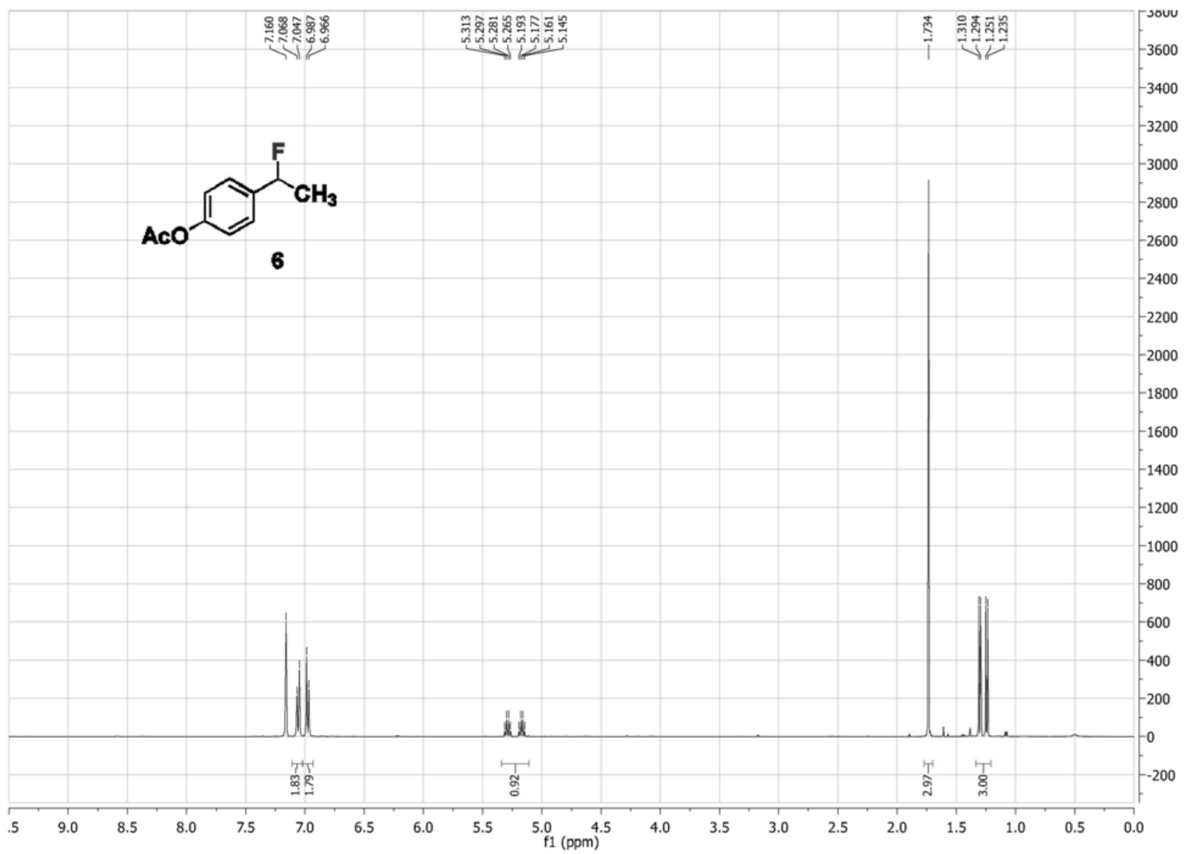
-167.54
-167.60
-167.67
-167.73
F
CH3
5
2000
1000
0
-167.4
-167.8
f1 (ppm)
-90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)
1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100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6.966
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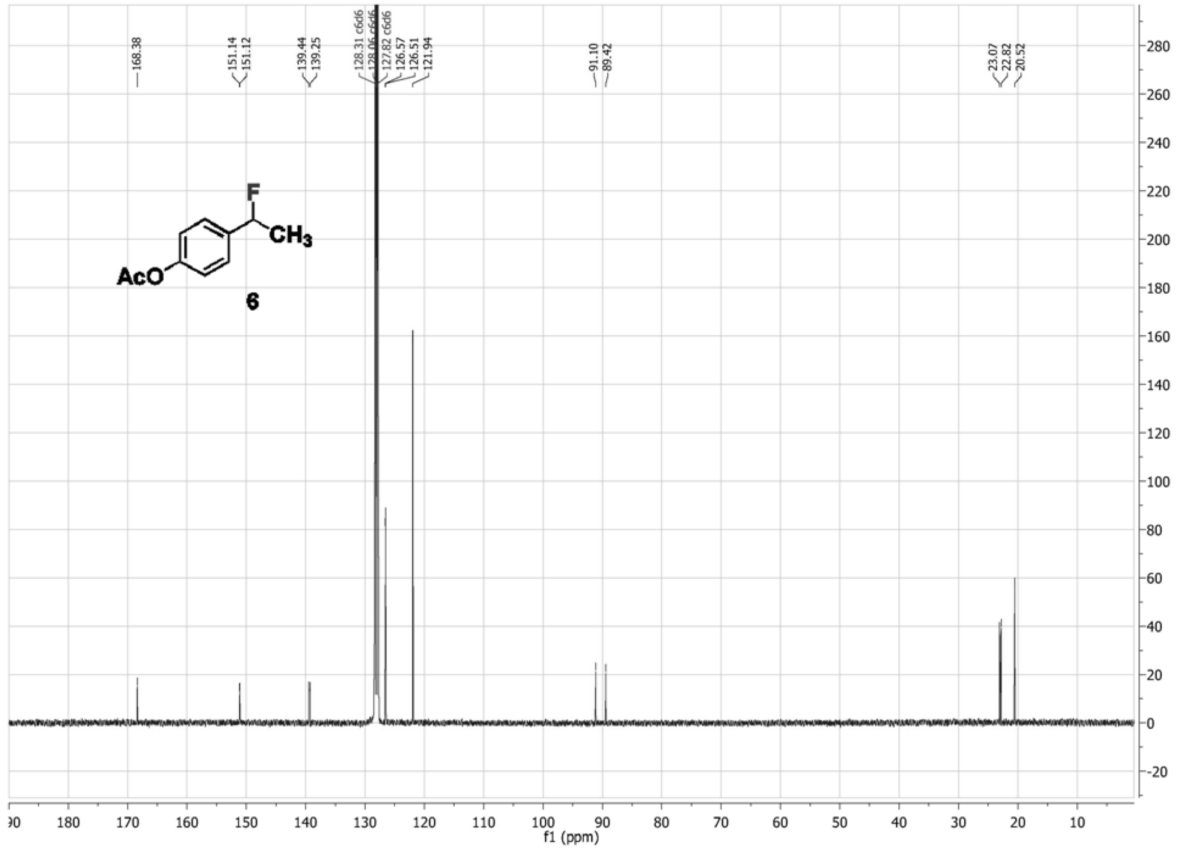
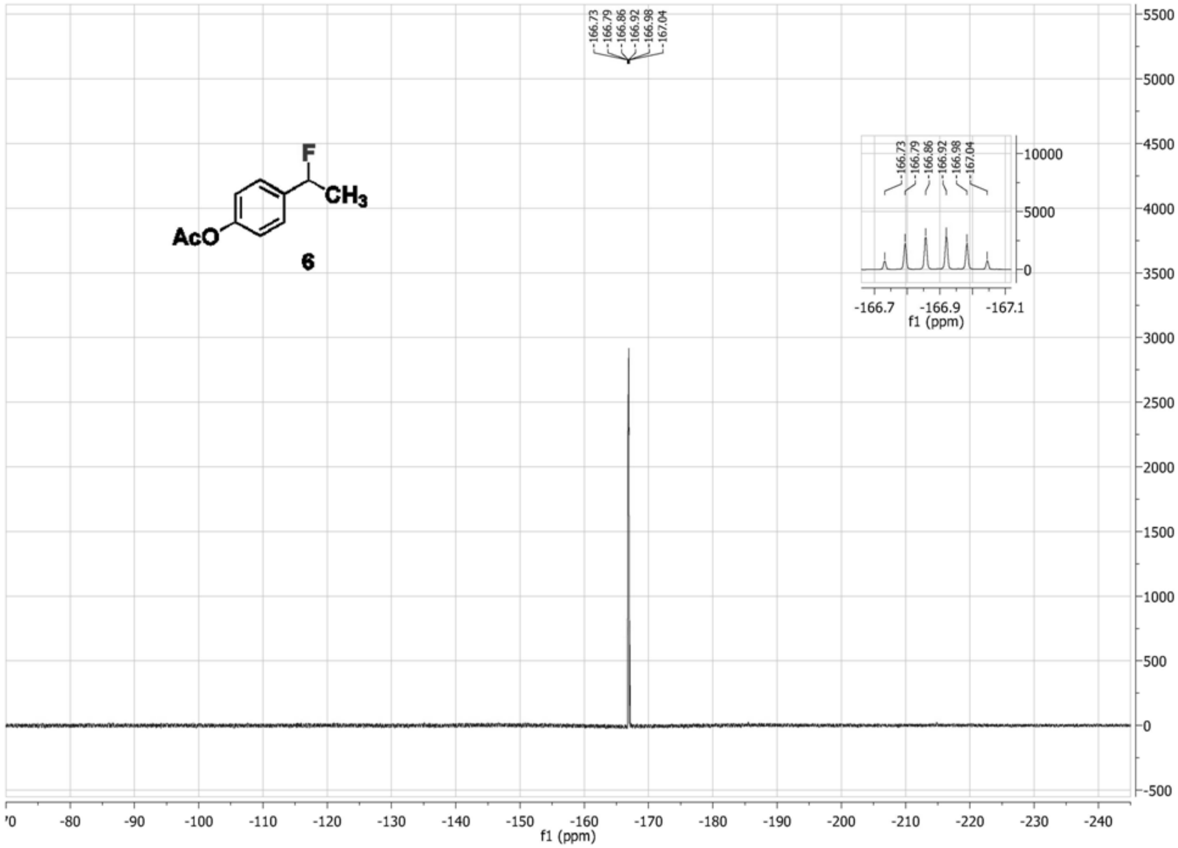
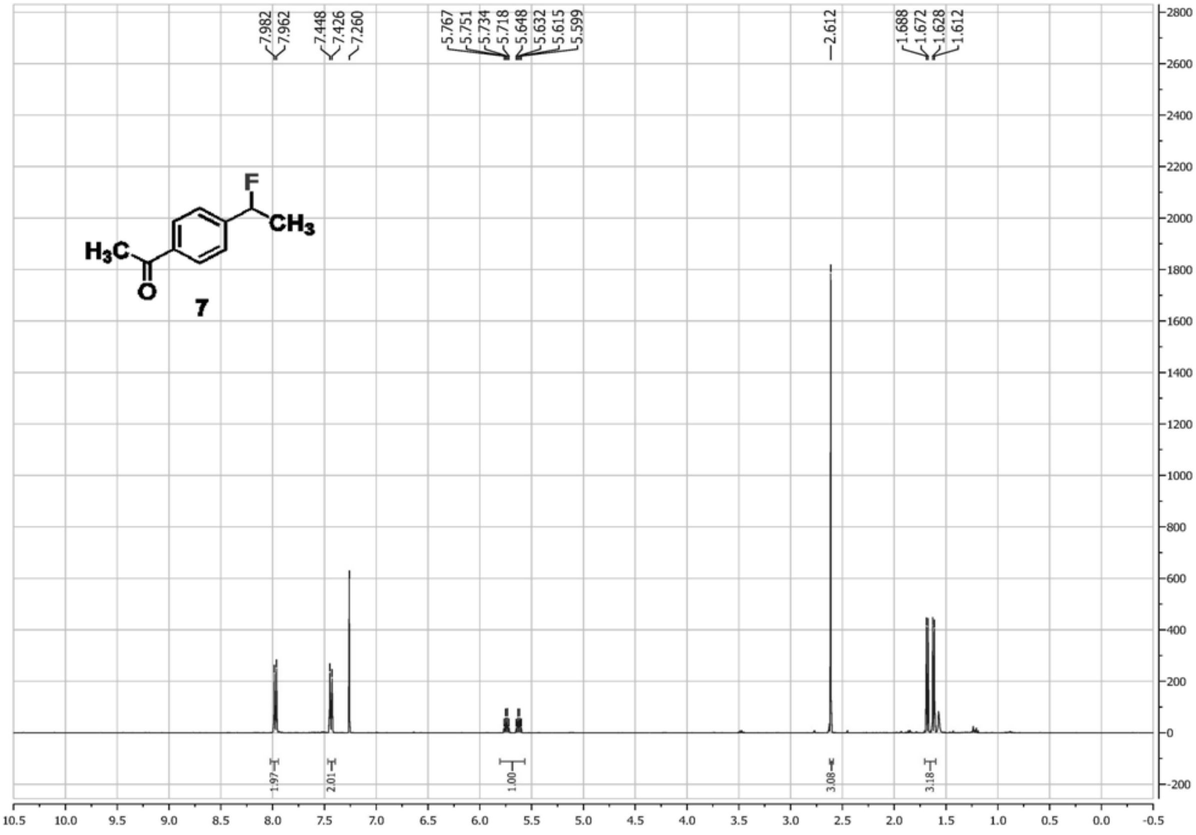
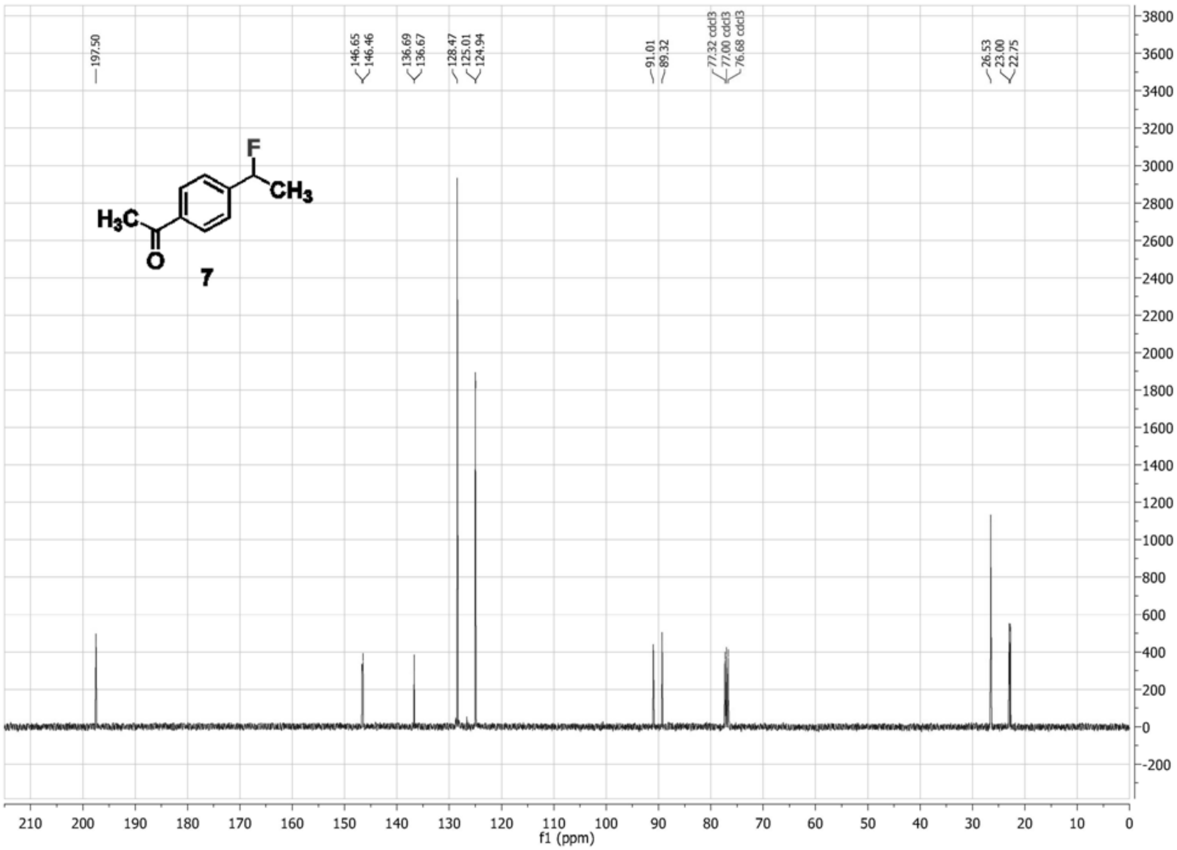
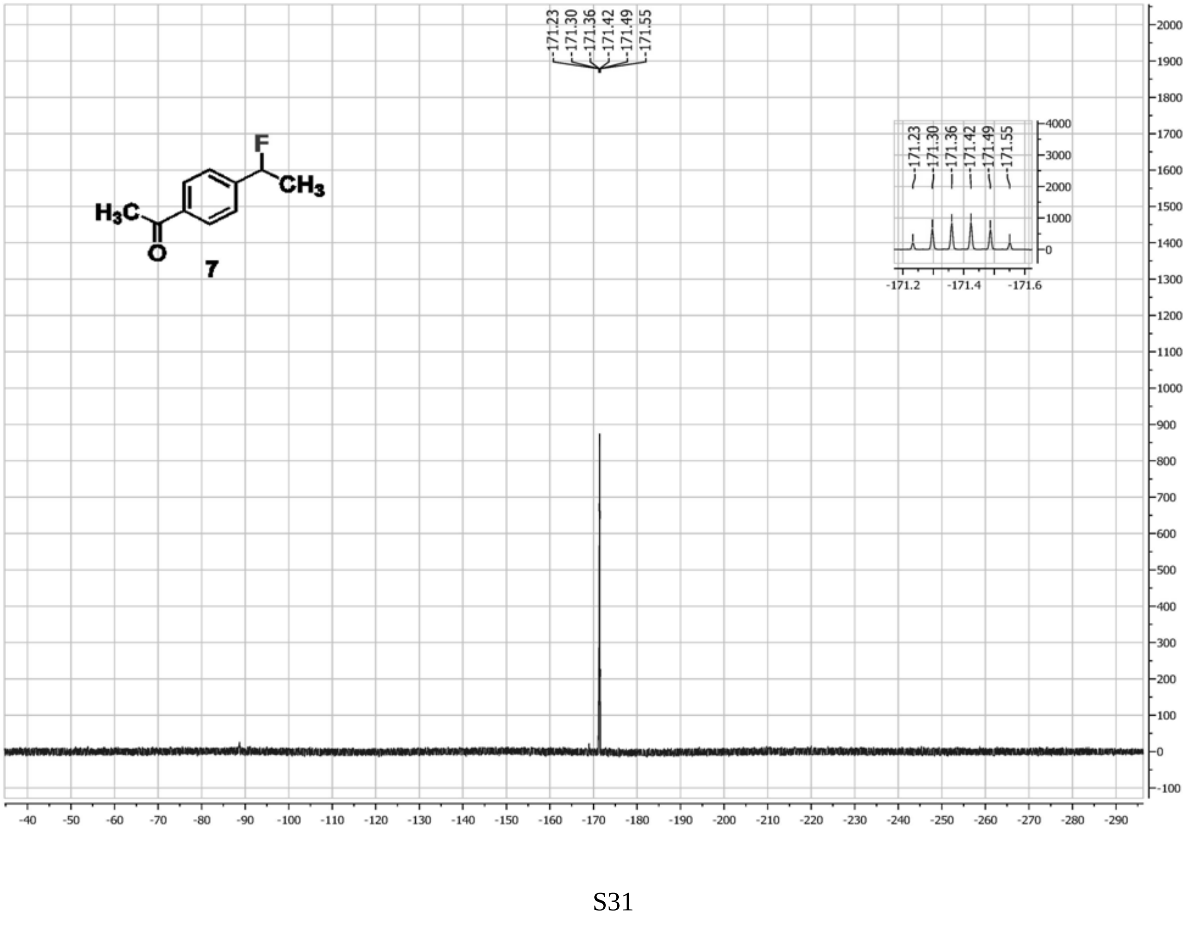
5.193
5.177
5.161
5.145
1.734
1.310
1.294
1.251
1.235
F
CH3
AcO
6
1.83
1.79
0.92
2.97
3.00
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

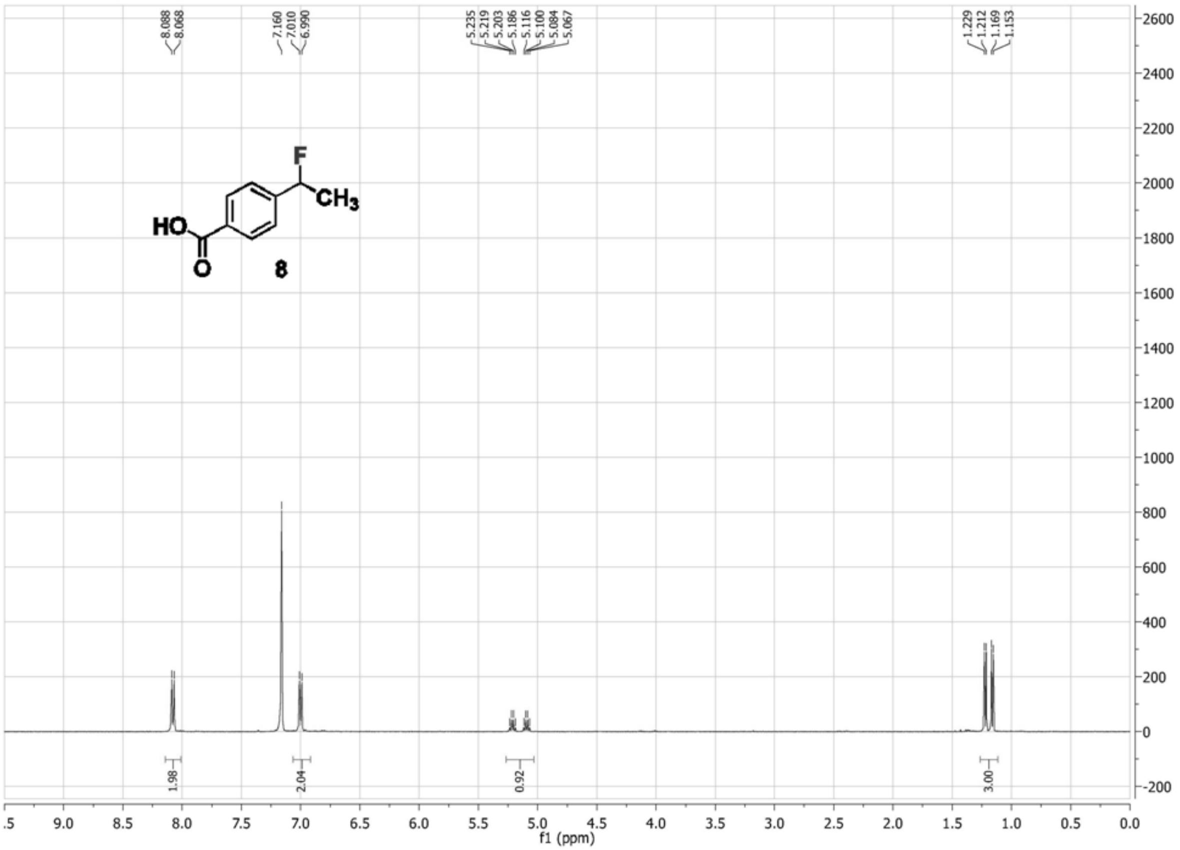

168.38
151.14
151.12
139.44
139.25
128.31 c6d6
128.06 c6d6
127.82 c6d6
126.57
126.51
121.94
91.10
89.42
23.07
22.82
20.52
F
CH3
AcO
6
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

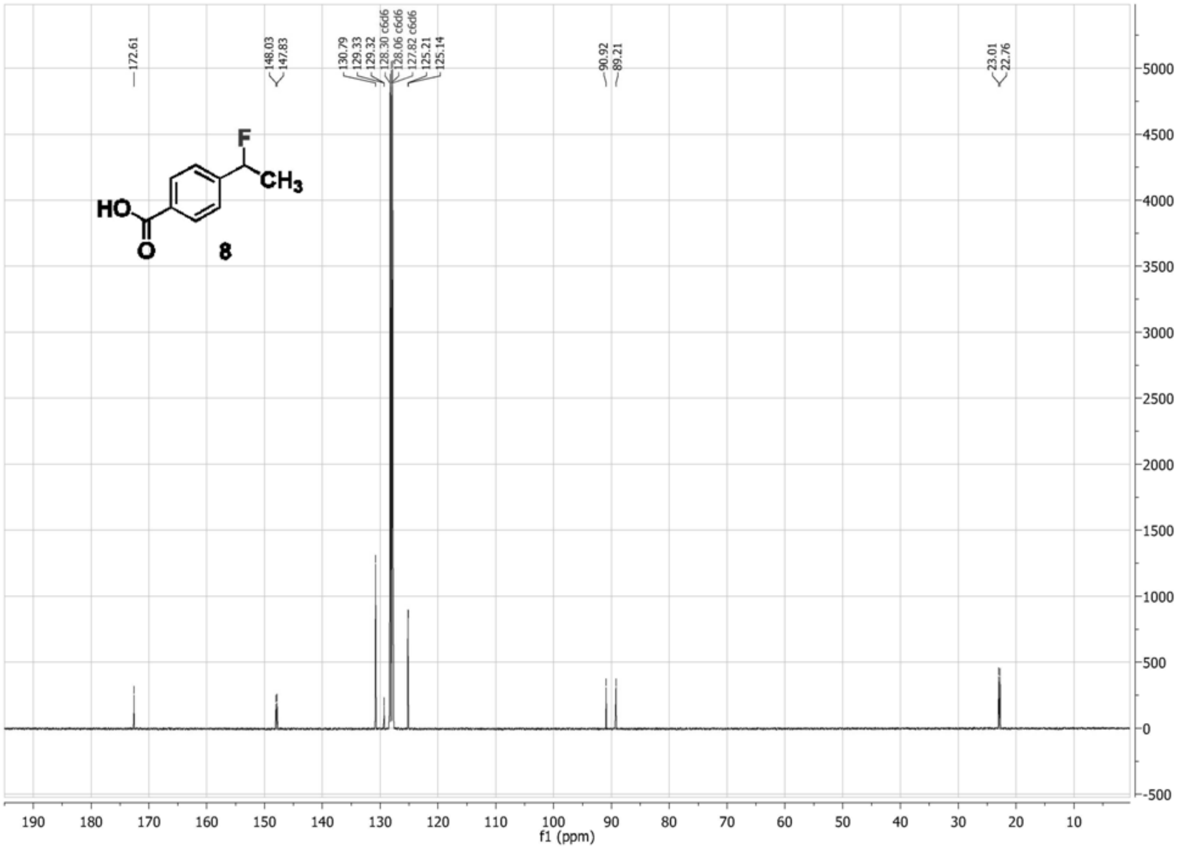

-166.73
-166.79
-166.86
-166.92
-166.98
-167.04
AcO
F
CH3
6
10000
5000
0
-166.7
-166.9
-167.1
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

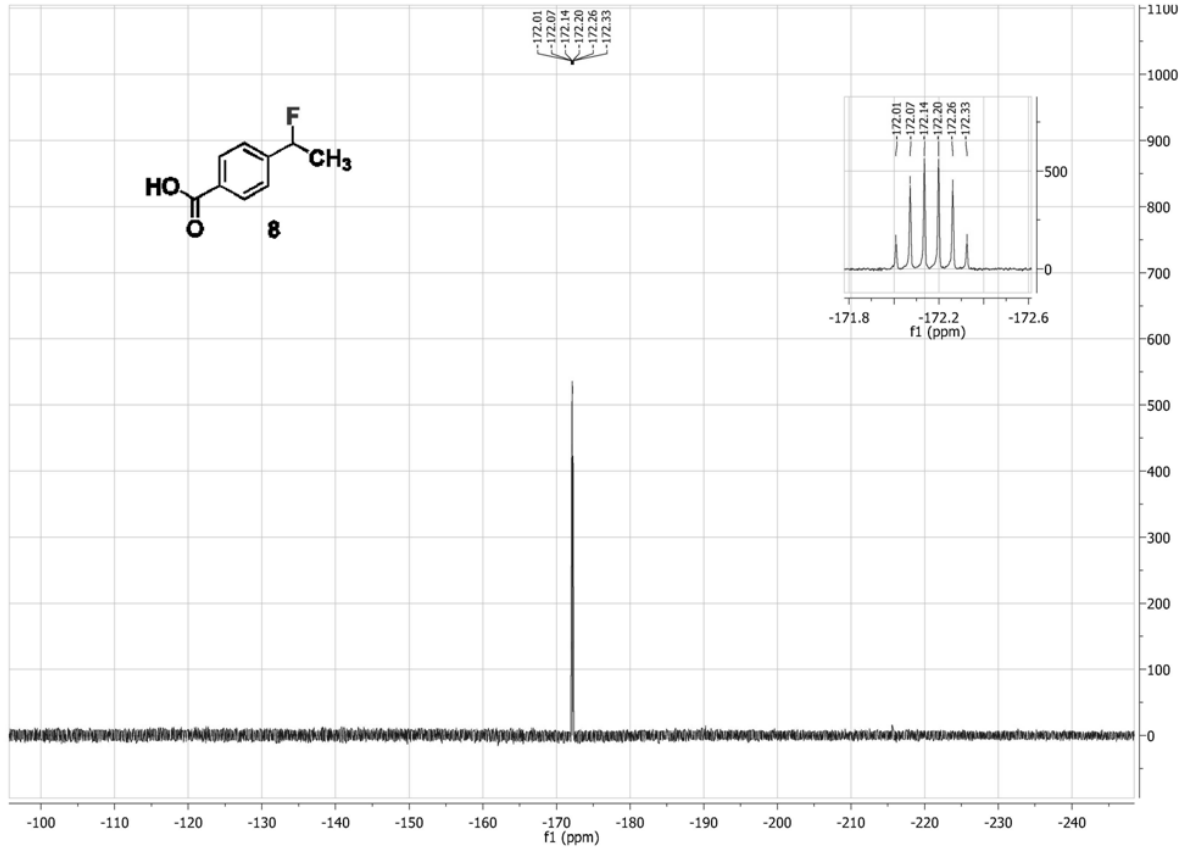

7.982
7.962
7.448
7.426
7.260
5.767
5.751
5.734
5.718
5.648
5.632
5.615
5.599
2.612
1.688
1.672
1.628
1.612
F
CH3
H3C
O
7
1.97
2.01
1.00
3.08
3.18
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

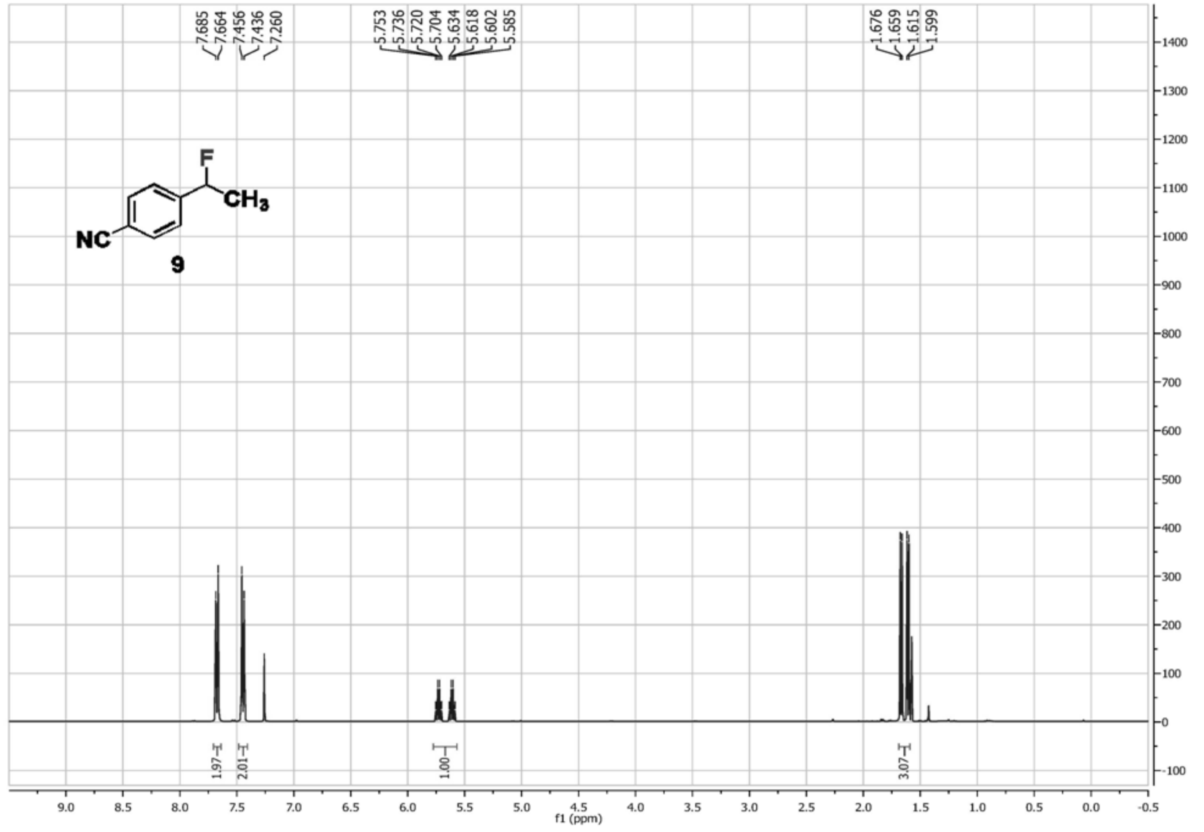

197.50
146.65
146.46
136.69
136.67
128.47
125.01
124.94
91.01
89.32
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
26.53
23.00
22.75
F
CH3
H3C
O
7
f1 (ppm)

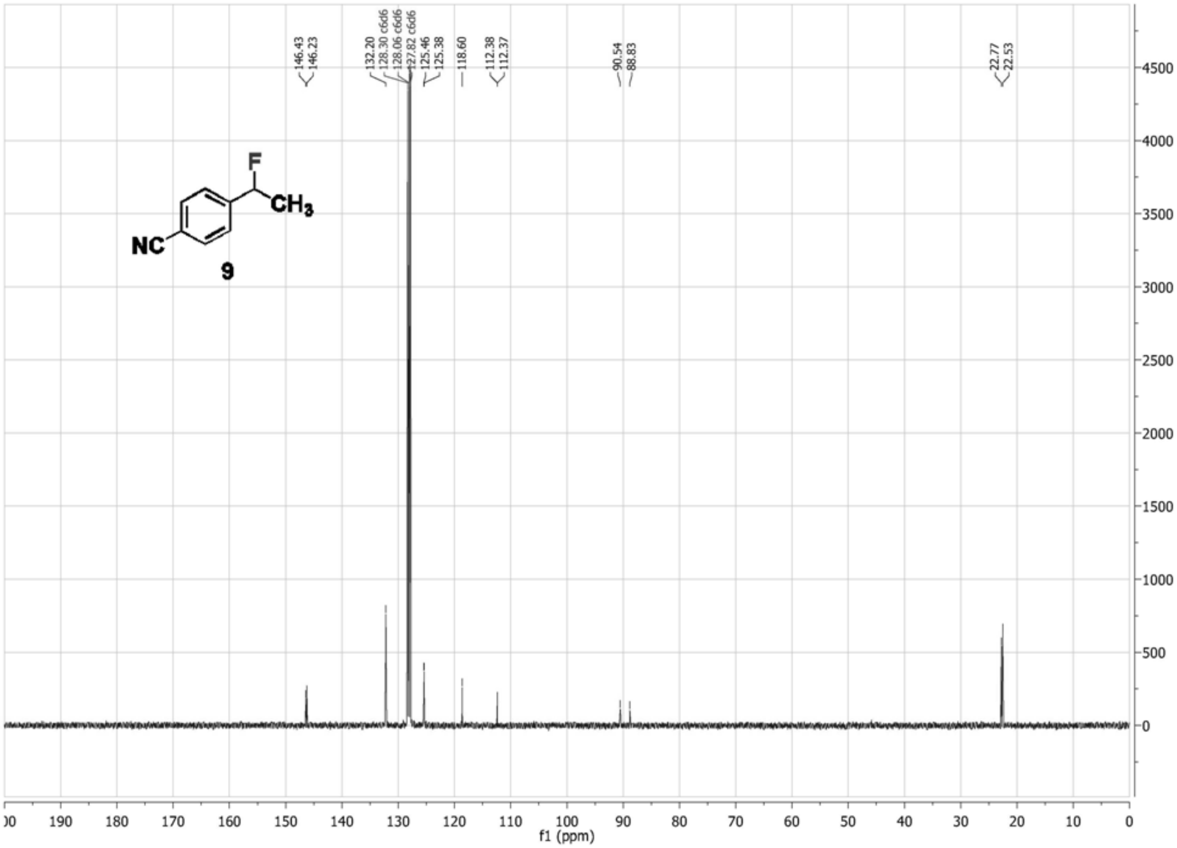

-171.23
-171.30
-171.36
-171.42
-171.49
-171.55
F
CH3
H3C
O
7

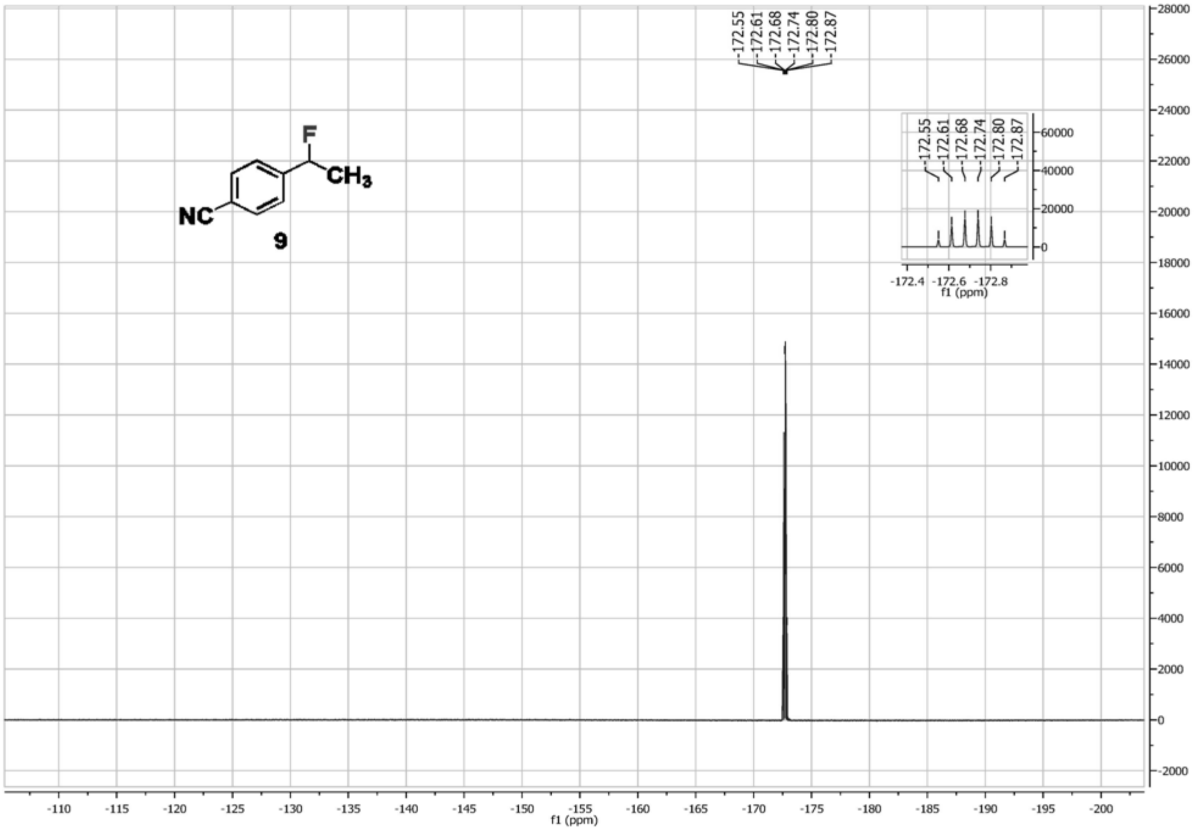

8.088
8.068
7.160
7.010
6.990
5.235
5.219
5.203
5.186
5.116
5.100
5.084
5.067
1.229
1.212
1.169
1.153
F
CH3
HO
O
8
1.98
2.04
0.92
3.00
f1 (ppm)

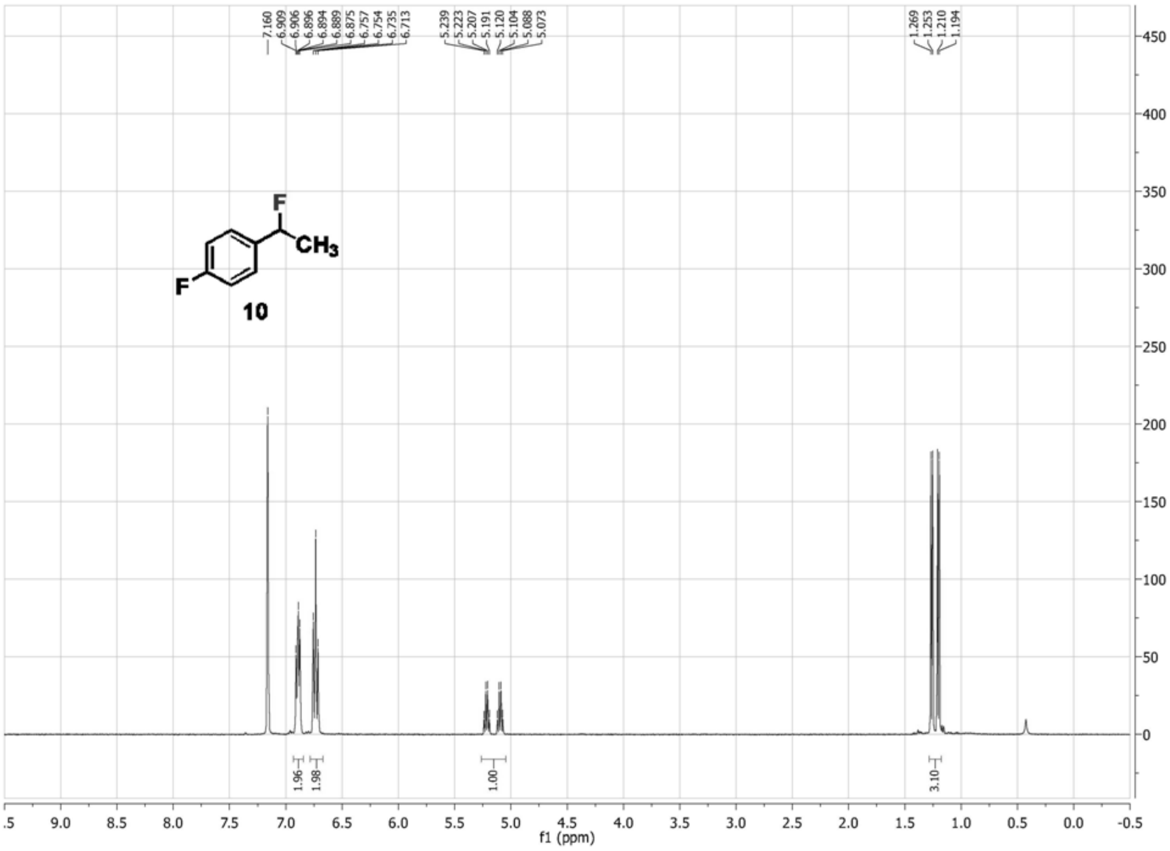

172.61
148.03
147.83
130.79
129.33
129.32
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.21
125.14
90.92
89.21
23.01
22.76
F
CH3
HO
O
8
f1 (ppm)

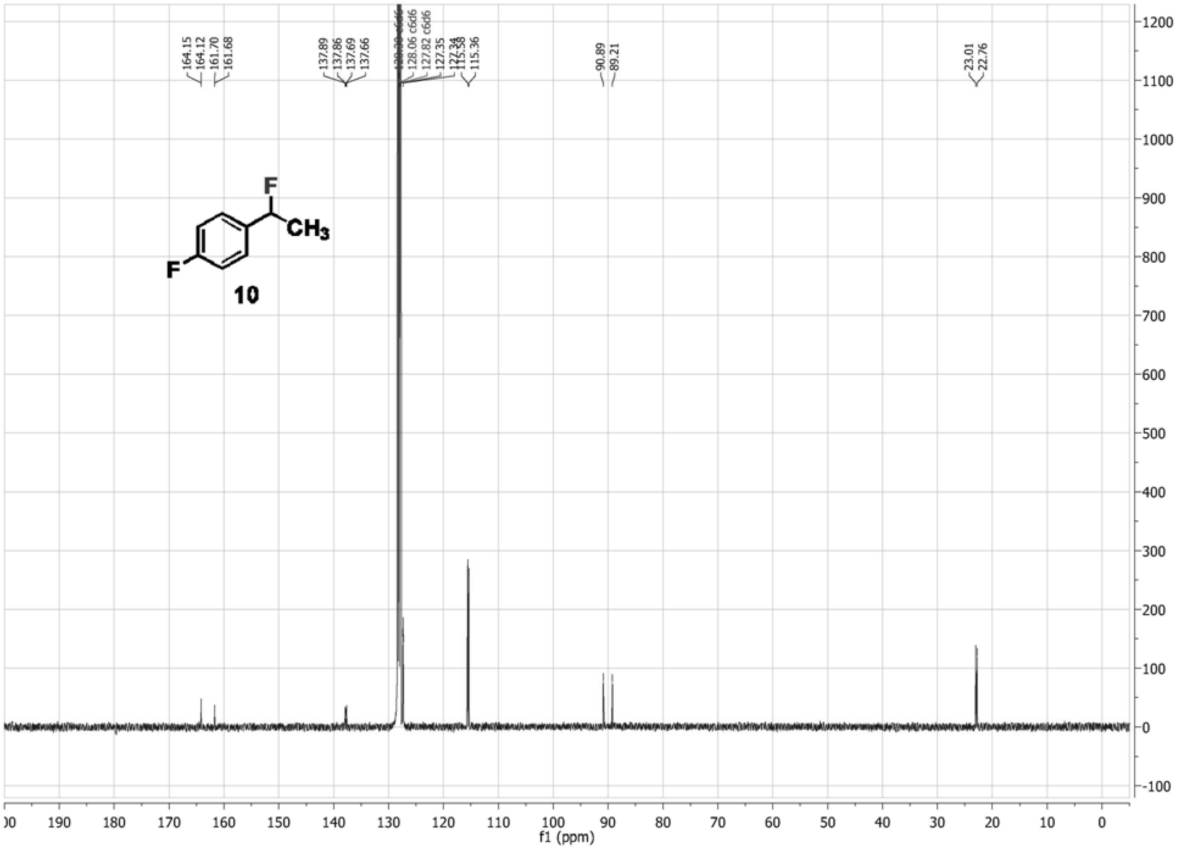

-172.01
-172.07
-172.14
-172.20
-172.26
-172.33
HO
F
CH3
O
8
-171.8
-172.2
-172.6
f1 (ppm)
500
0
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

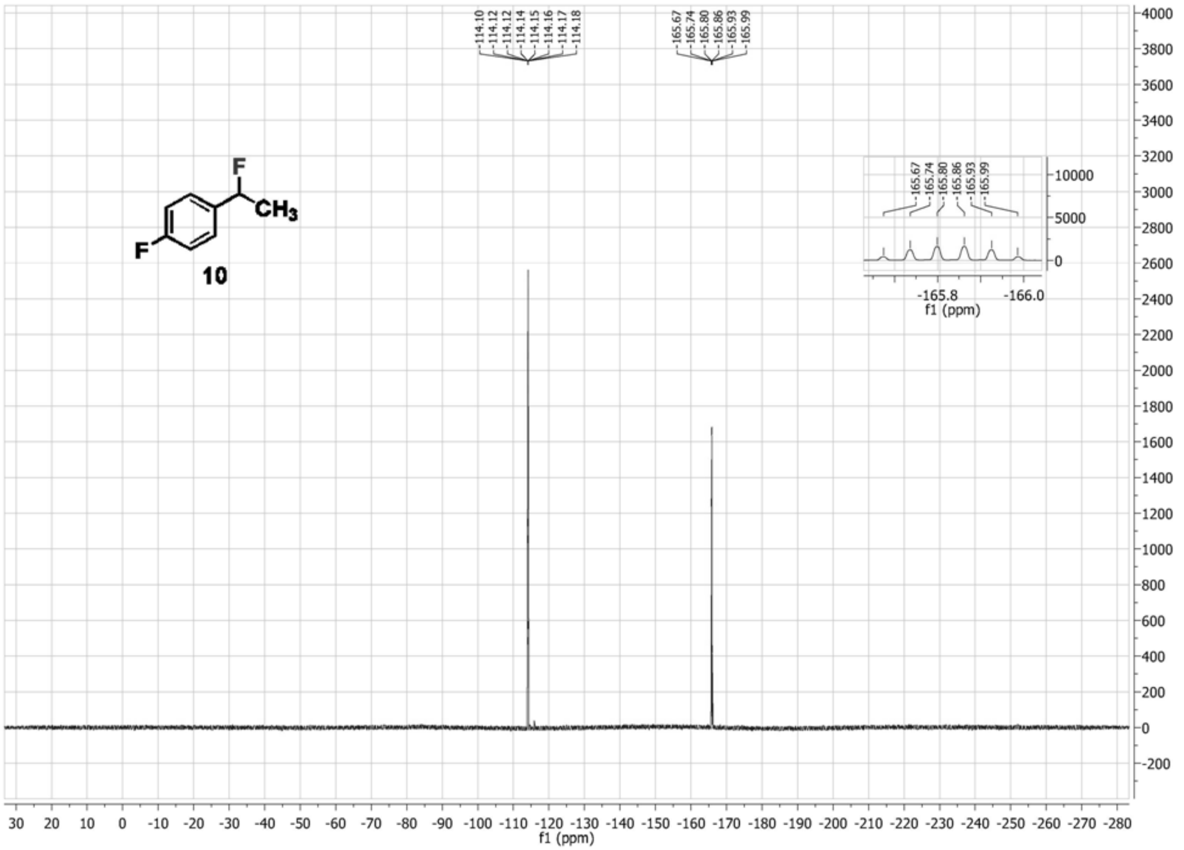

7.685
7.664
7.456
7.436
7.260
5.753
5.736
5.720
5.704
5.634
5.618
5.602
5.585
1.676
1.659
1.615
1.599
F
CH3
NC
9
1.97
2.01
1.00
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

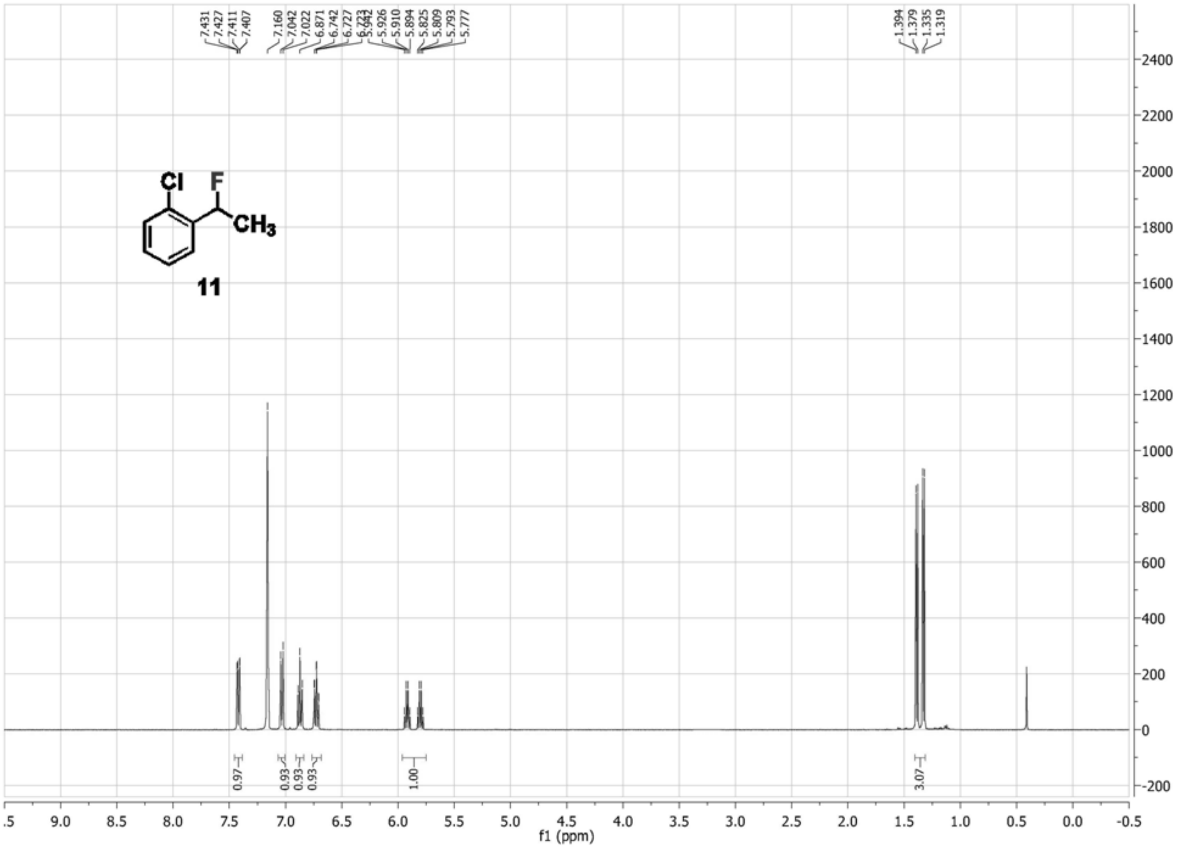

146.43
146.23
132.20
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.46
125.38
118.60
112.38
112.37
90.54
88.83
22.77
22.53
F
CH3
NC
9
4500
4000
3500
3000
2500
2000
1500
1000
500
0
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

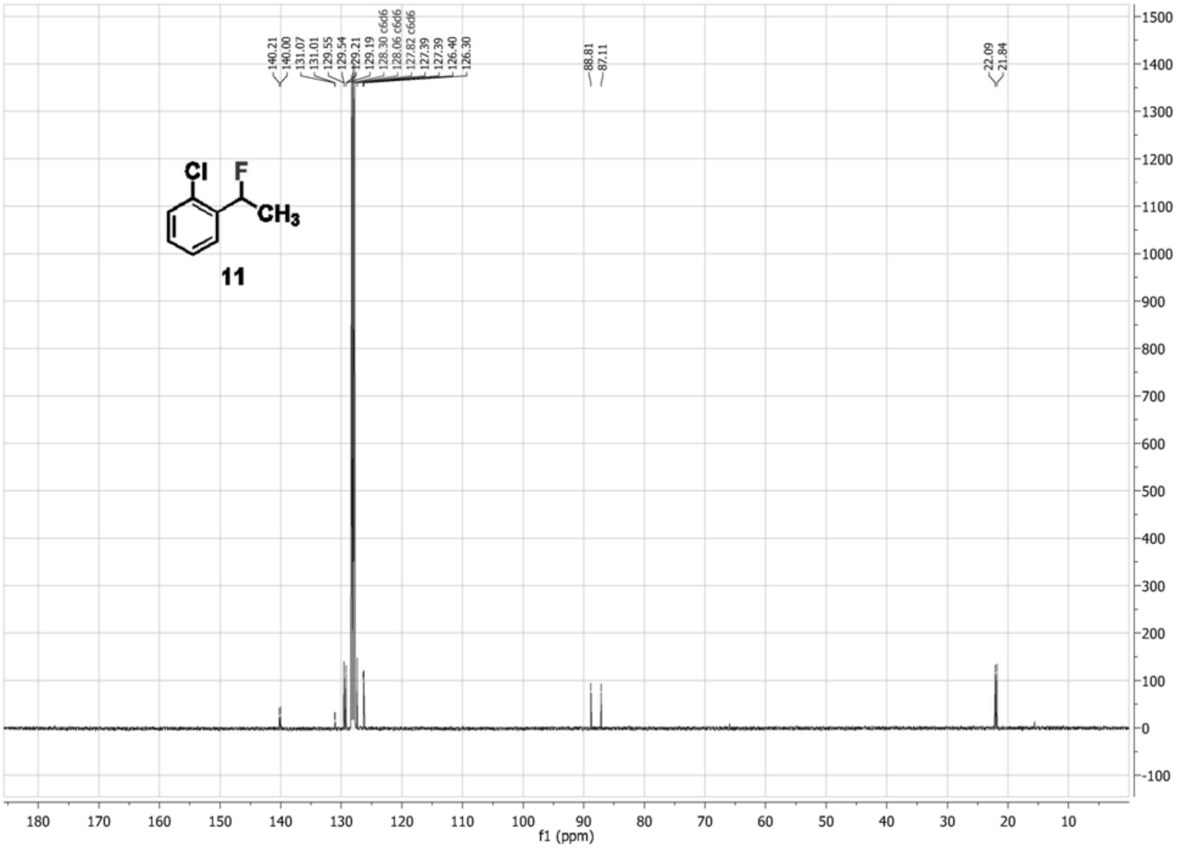

-172.55
-172.61
-172.68
-172.74
-172.80
-172.87
F
CH3
NC
9
60000
40000
20000
0
-172.4
-172.6
-172.8
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
-190
-195
-200
f1 (ppm)

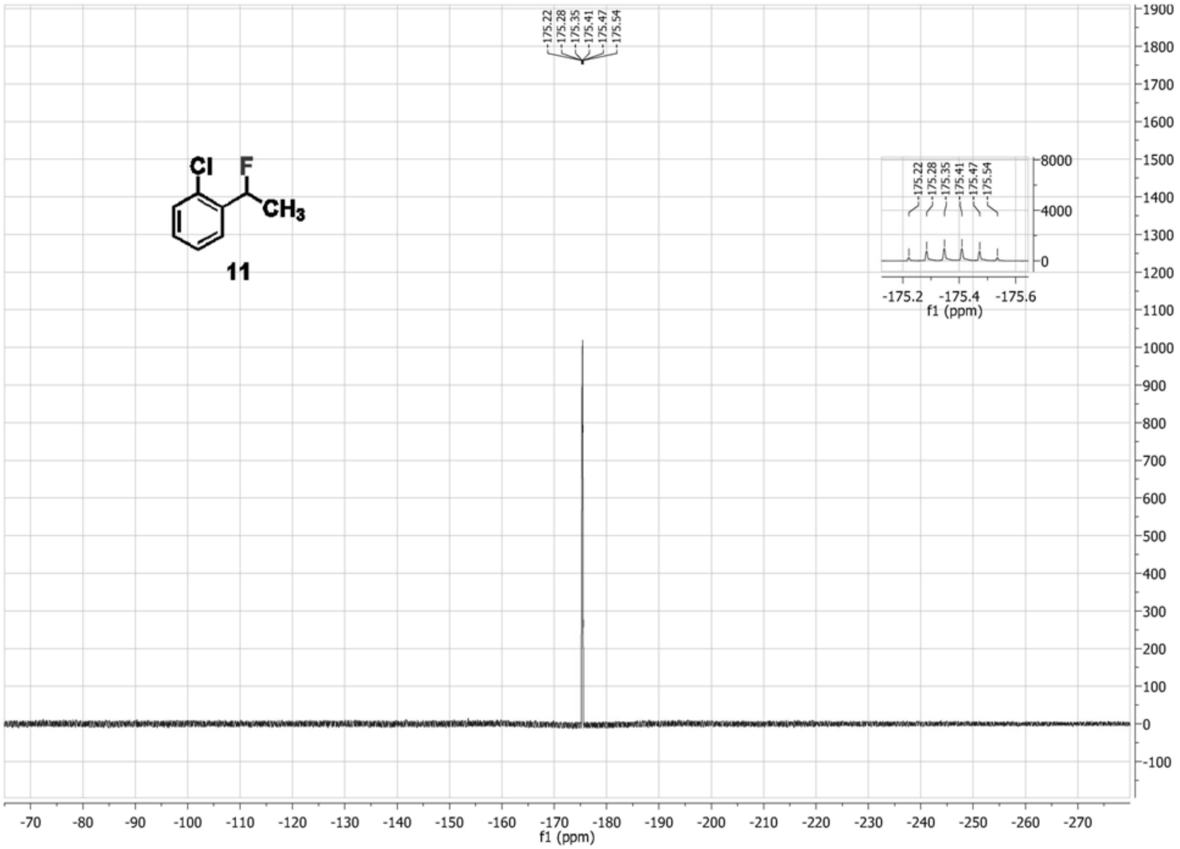

7.160
6.909
6.906
6.896
6.894
6.889
6.875
6.757
6.754
6.735
6.713
5.239
5.223
5.207
5.191
5.120
5.104
5.088
5.073
1.269
1.253
1.210
1.194
F
CH3
F
10
1.96
1.98
1.00
3.10
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
450
400
350
300
250
200
150
100
50
0

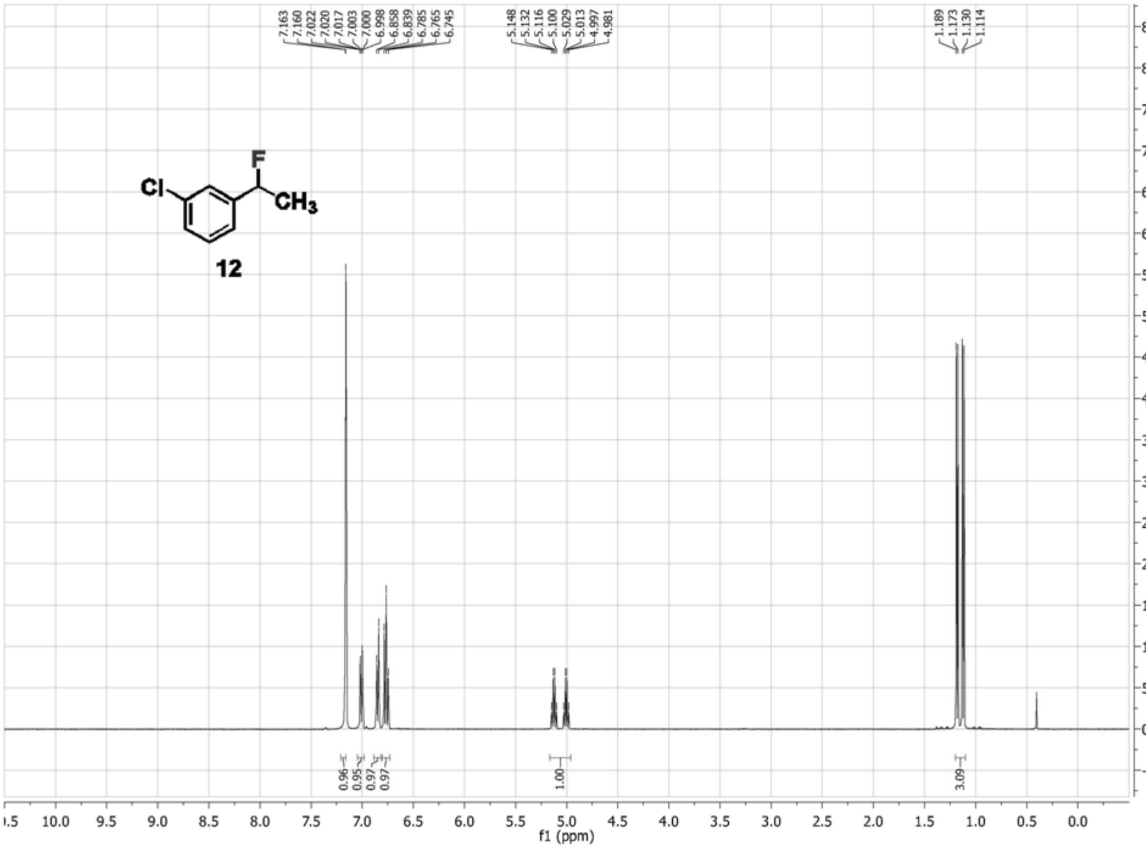

164.15
164.12
161.70
161.68
137.89
137.86
137.69
137.66
128.30 c6d6
128.06 c6d6
127.82 c6d6
127.35
127.34
115.58
115.36
90.89
89.21
23.01
22.76
F
CH3
F
10
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

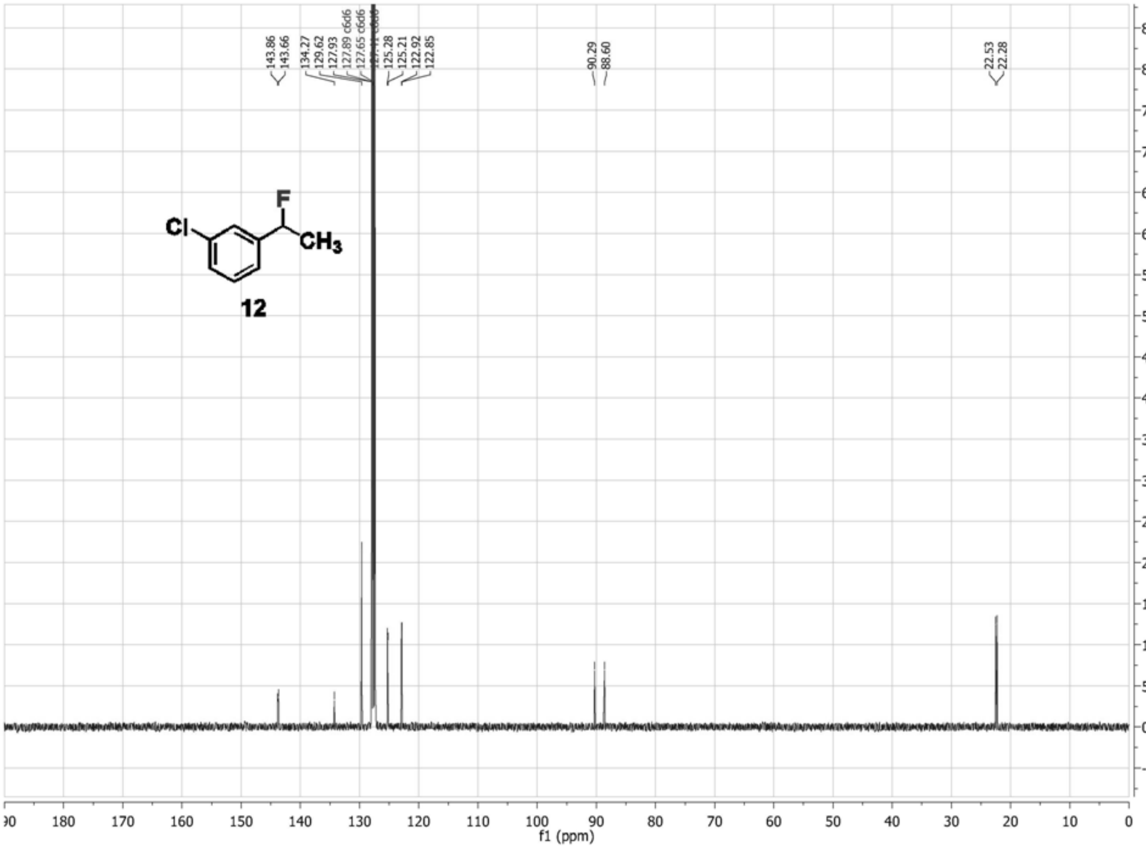

-114.10
-114.12
-114.12
-114.14
-114.15
-114.16
-114.17
-114.18
-165.67
-165.74
-165.80
-165.86
-165.93
-165.99
F
CH3
F
10
-165.8
-166.0
f1 (ppm)
10000
5000
0
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280
f1 (ppm)

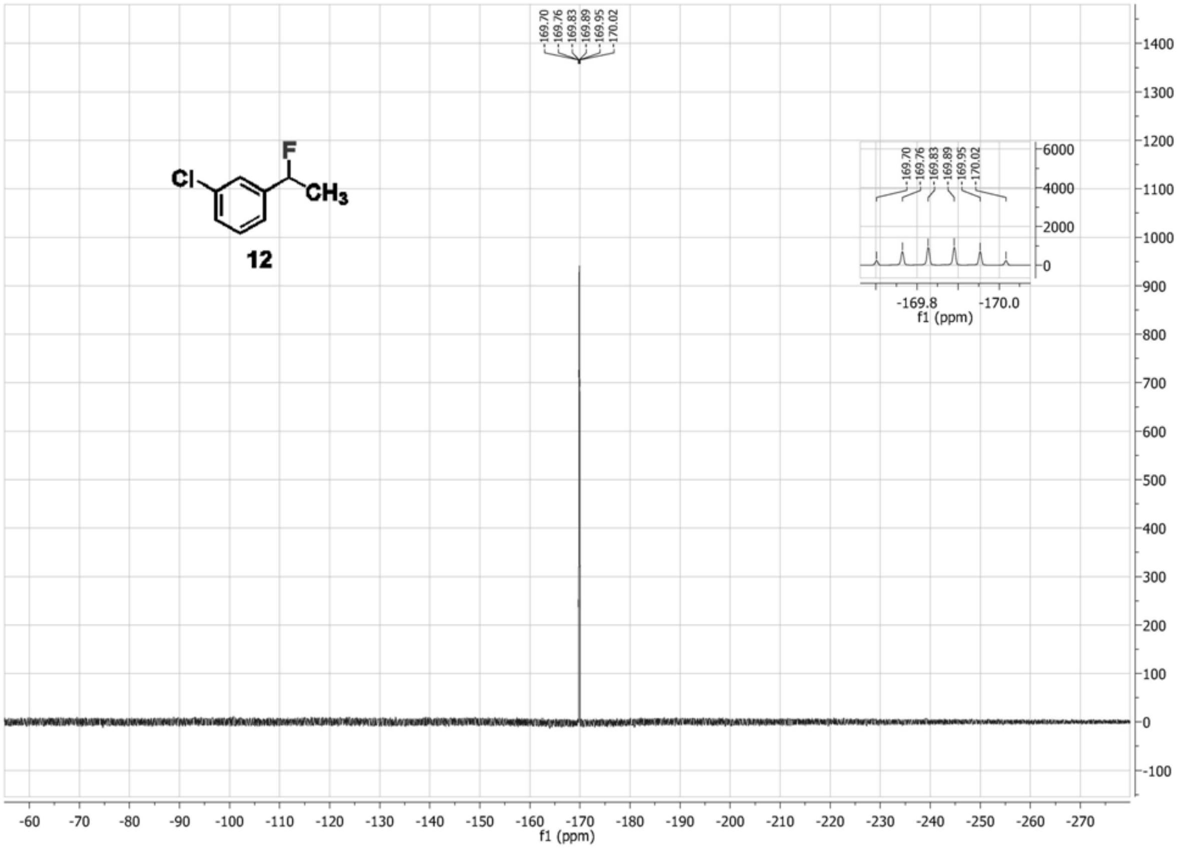

7.431
7.427
7.411
7.407
7.160
7.042
7.022
6.871
6.742
6.727
6.723
5.942
5.926
5.910
5.894
5.825
5.809
5.793
5.777
1.394
1.379
1.335
1.319
Cl
F
CH3
11
0.97
0.93
0.93
0.93
1.00
3.07
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


140.21
140.00
131.07
131.01
129.55
129.54
129.21
129.19
128.30 c6d6
128.06 c6d6
127.82 c6d6
127.39
127.39
126.40
126.30
88.81
87.11
22.09
21.84
Cl
F
CH3
11
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

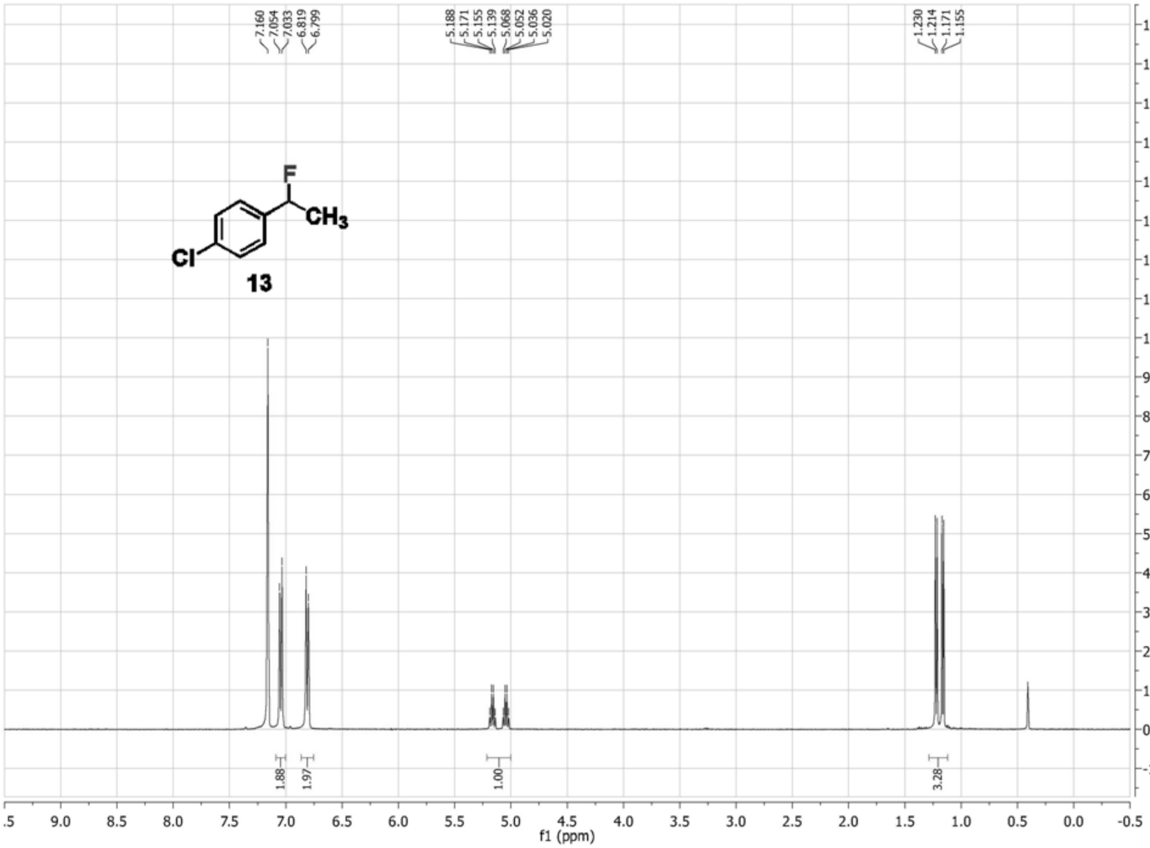

-175.22
-175.28
-175.35
-175.41
-175.47
-175.54
Cl
F
CH3
11
8000
4000
0
-175.2
-175.4
-175.6
f1 (ppm)
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
f1 (ppm)


7.163
7.160
7.022
7.020
7.017
7.003
7.000
6.998
6.858
6.839
6.785
6.765
6.745
5.148
5.132
5.116
5.100
5.029
5.013
4.997
4.981
1.189
1.173
1.130
1.114
Cl
F
CH3
12
0.96
0.95
0.97
0.97
1.00
3.09
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
f1 (ppm)
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

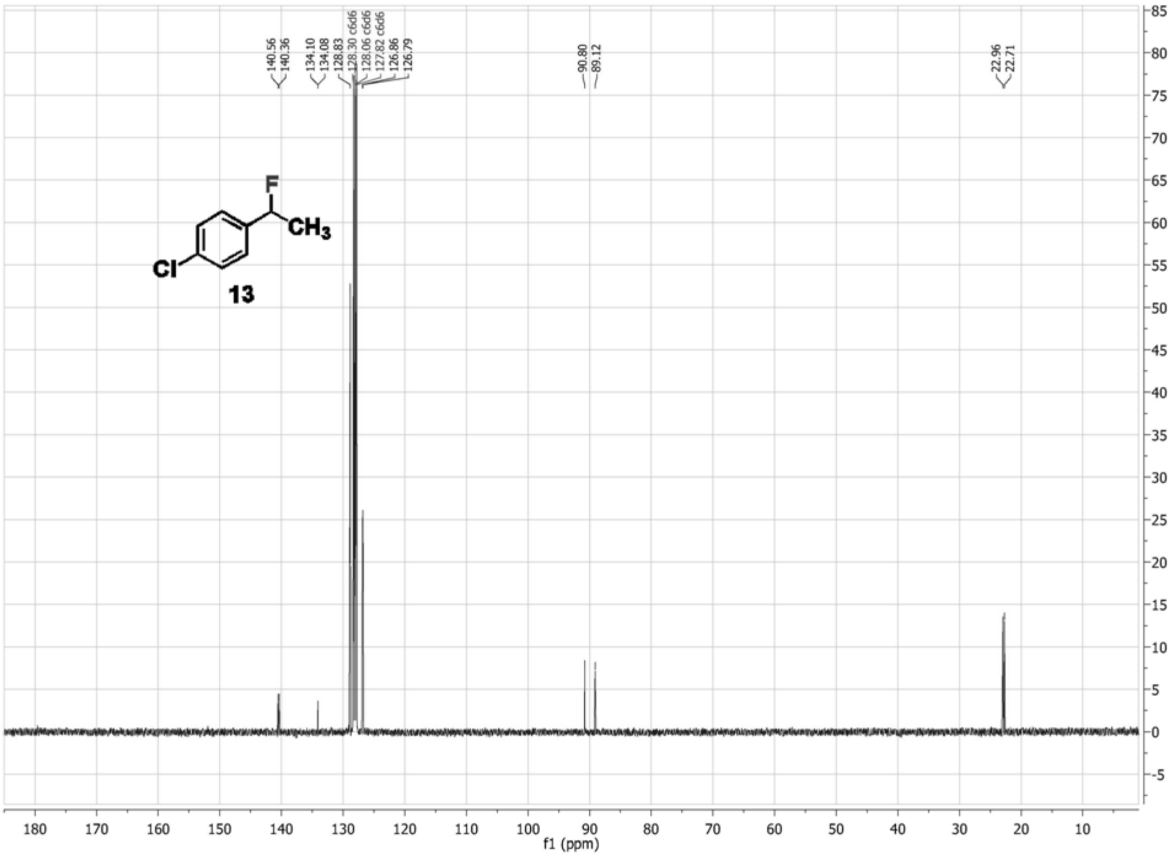

143.86
143.66
134.27
129.62
127.93
127.89 c6d6
127.65 c6d6
127.41 c6d6
125.28
125.21
122.92
122.85
90.29
88.60
22.53
22.28
Cl
F
CH3
12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

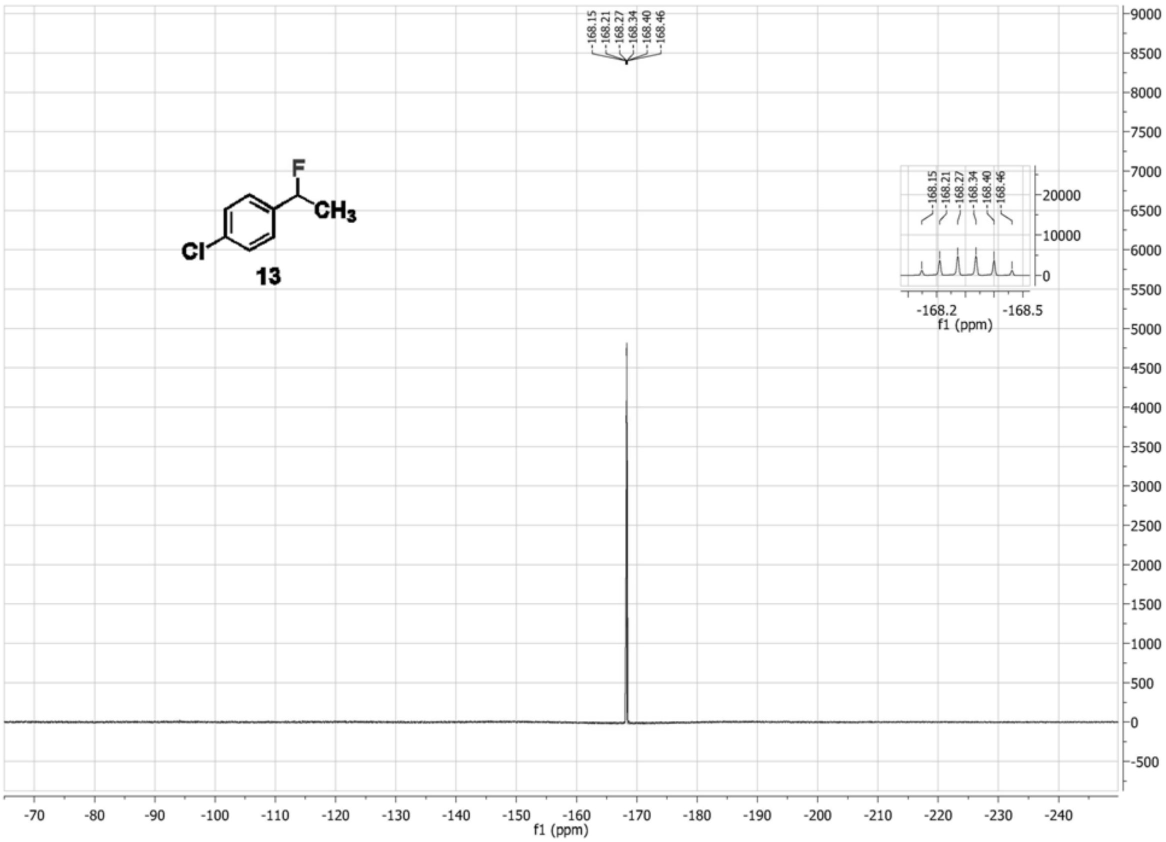


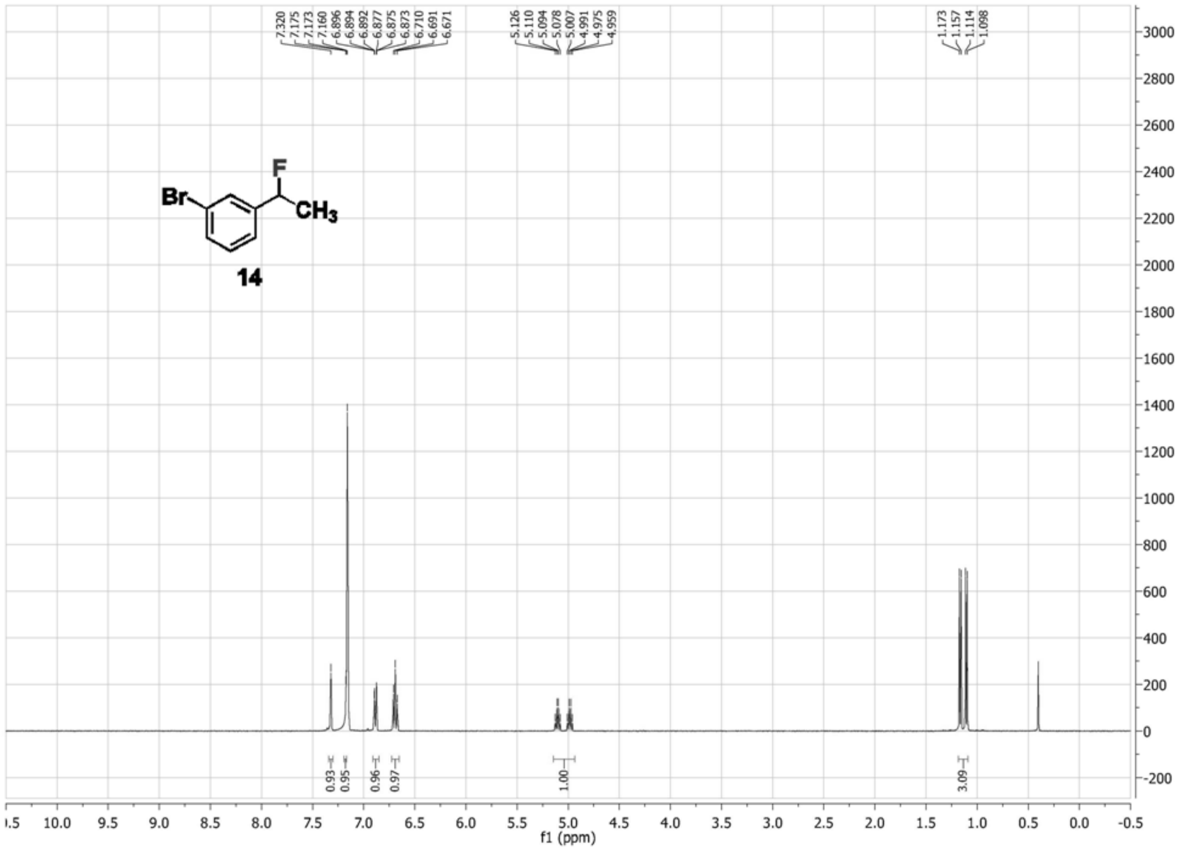
-169.70
-169.76
-169.83
-169.89
-169.95
-170.02
Cl
F
CH3
12
-169.8
-170.0
f1 (ppm)
6000
4000
2000
0
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
f1 (ppm)

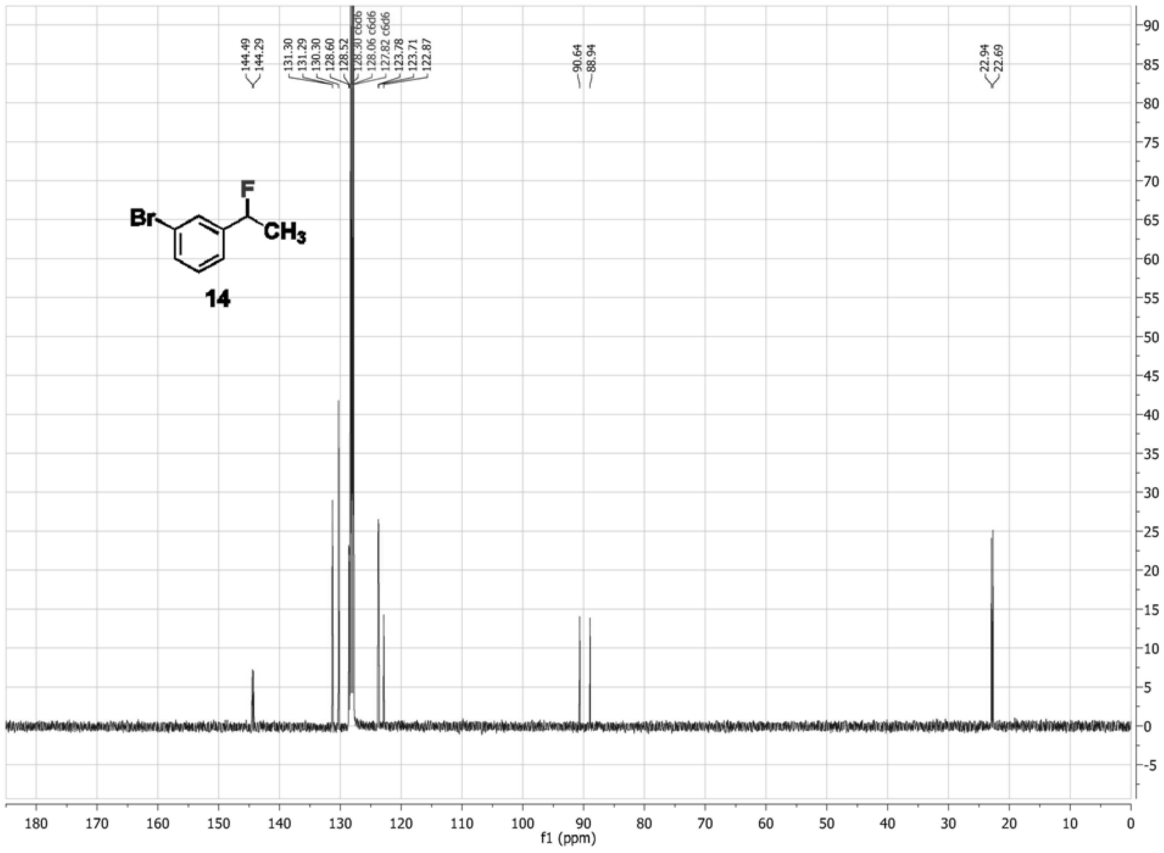


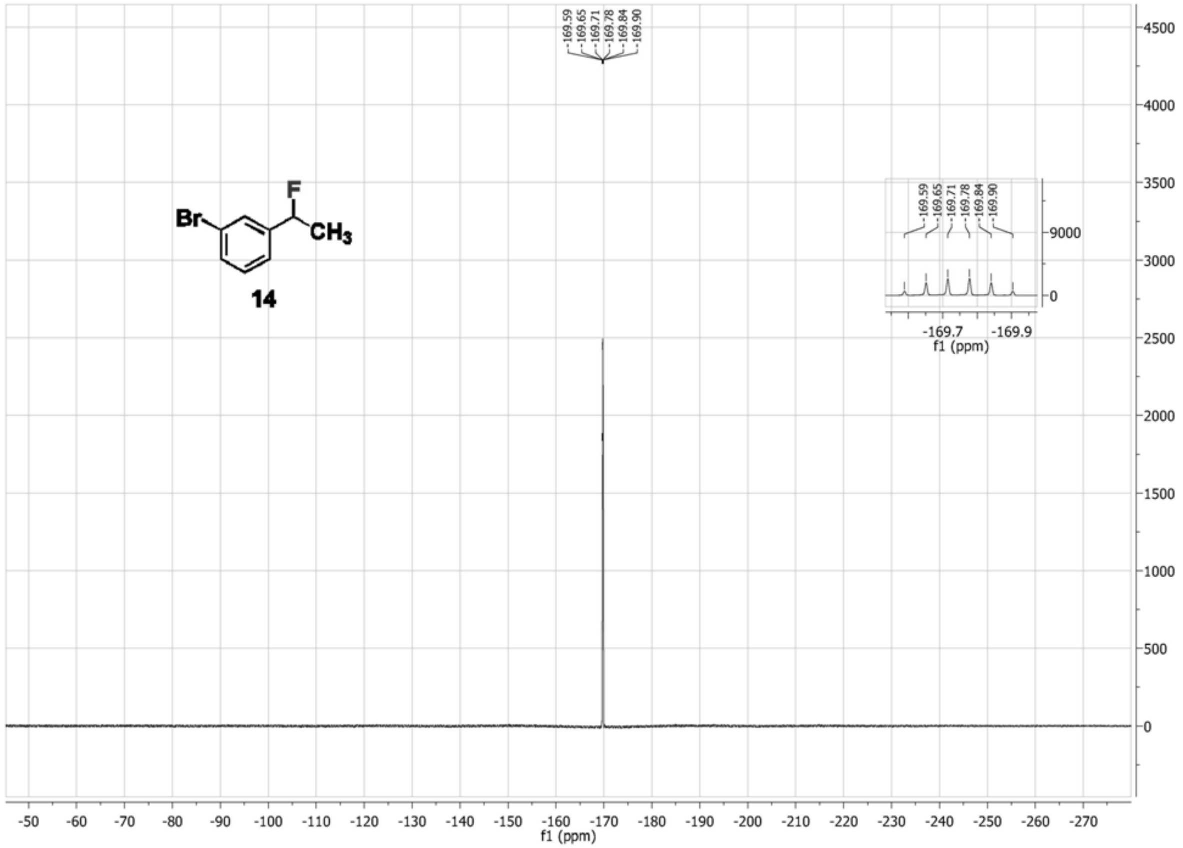
7.160
7.054
7.033
6.819
6.799
5.188
5.171
5.155
5.139
5.068
5.052
5.036
5.020
1.230
1.214
1.171
1.155
F
CH3
Cl
13
1.88
1.97
1.00
3.28
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

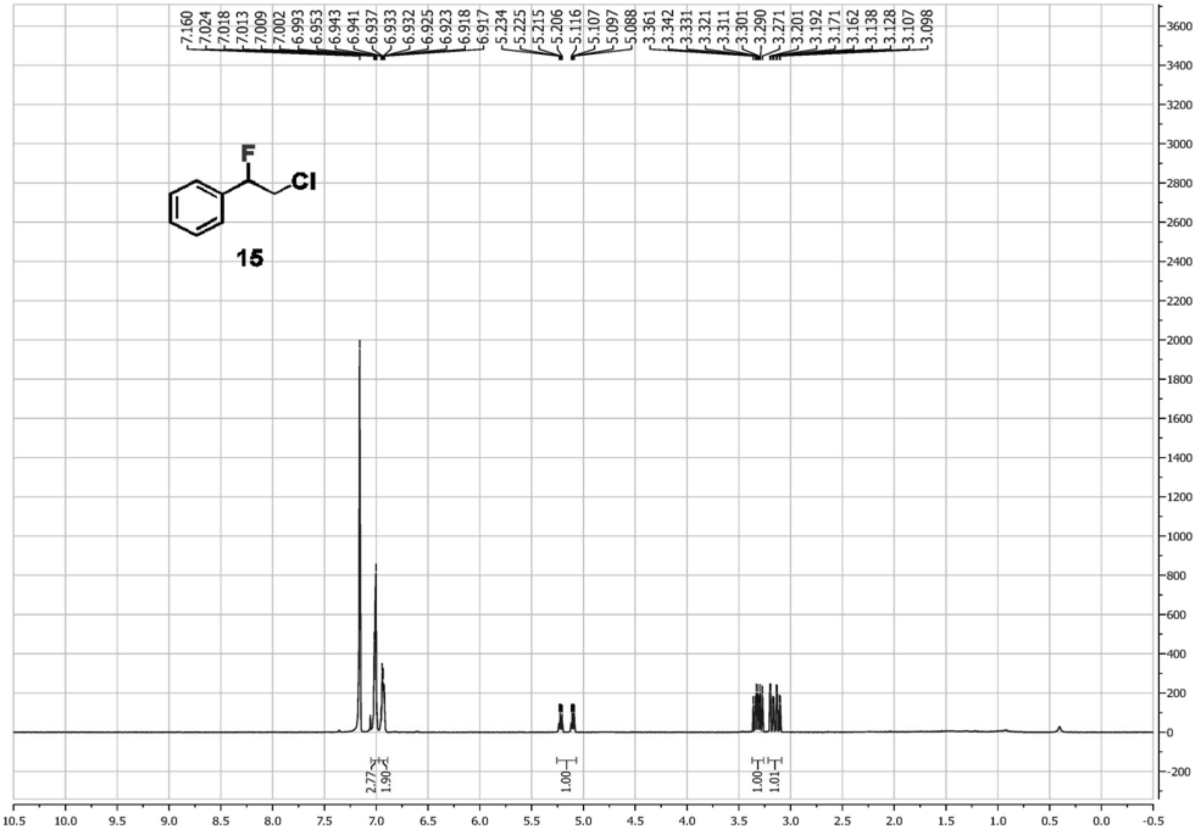

140.56
140.36
134.10
134.08
128.83
128.30 c6d6
128.06 c6d6
127.82 c6d6
126.86
126.79
90.80
89.12
22.96
22.71
F
CH3
Cl
13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5

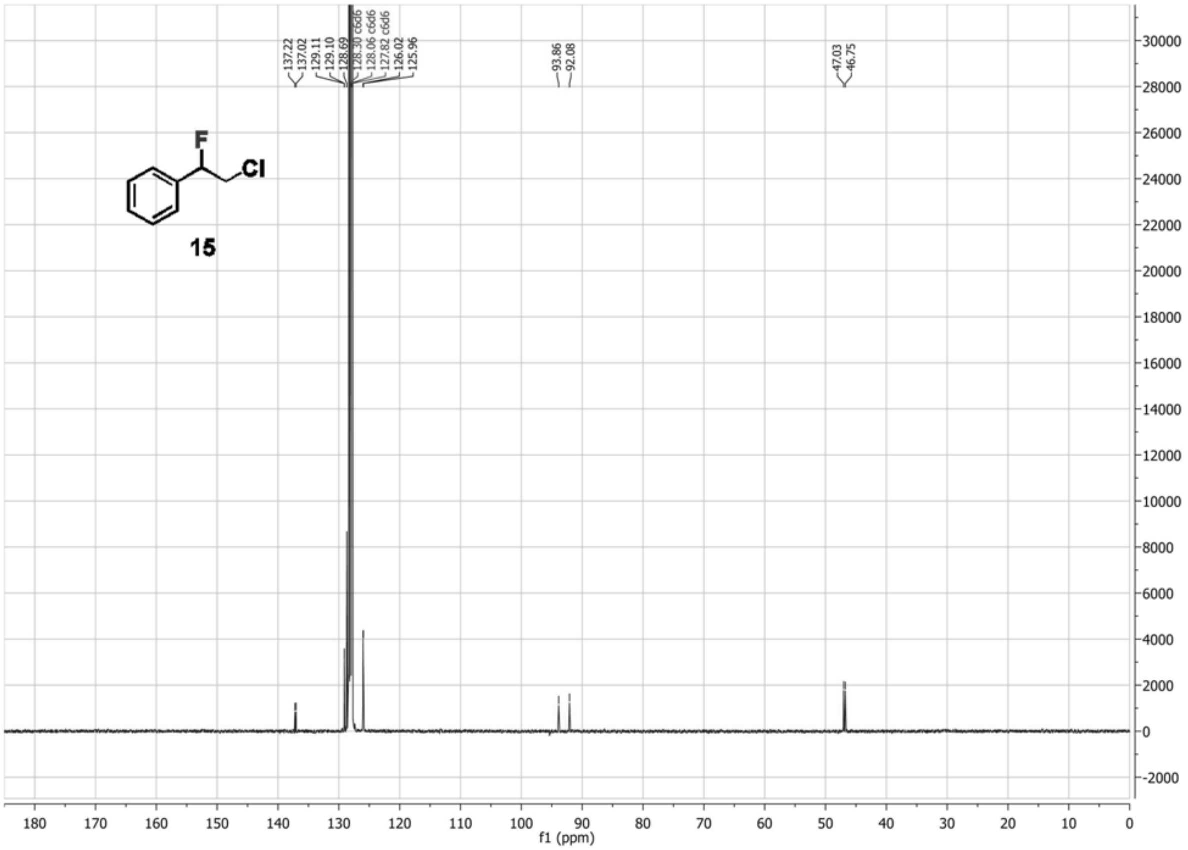

-168.15
-168.21
-168.27
-168.34
-168.40
-168.46
F
CH3
Cl
13
-168.2
-168.5
f1 (ppm)
20000
10000
0
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

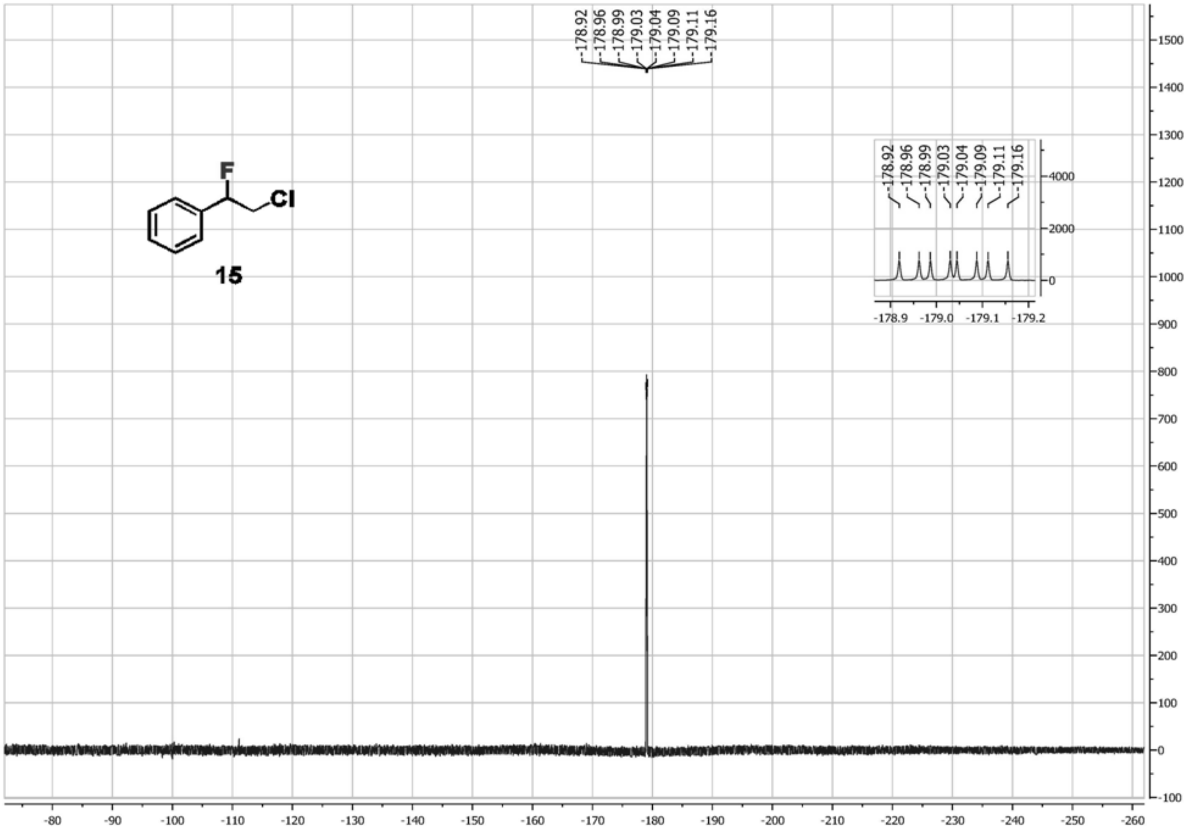

7.320
7.175
7.173
7.160
6.896
6.894
6.892
6.877
6.875
6.873
6.710
6.691
6.671
5.126
5.110
5.094
5.078
5.007
4.991
4.975
4.959
1.173
1.157
1.114
1.098
Br
F
CH3
14
0.93
0.95
0.96
0.97
1.00
3.09
f1 (ppm)

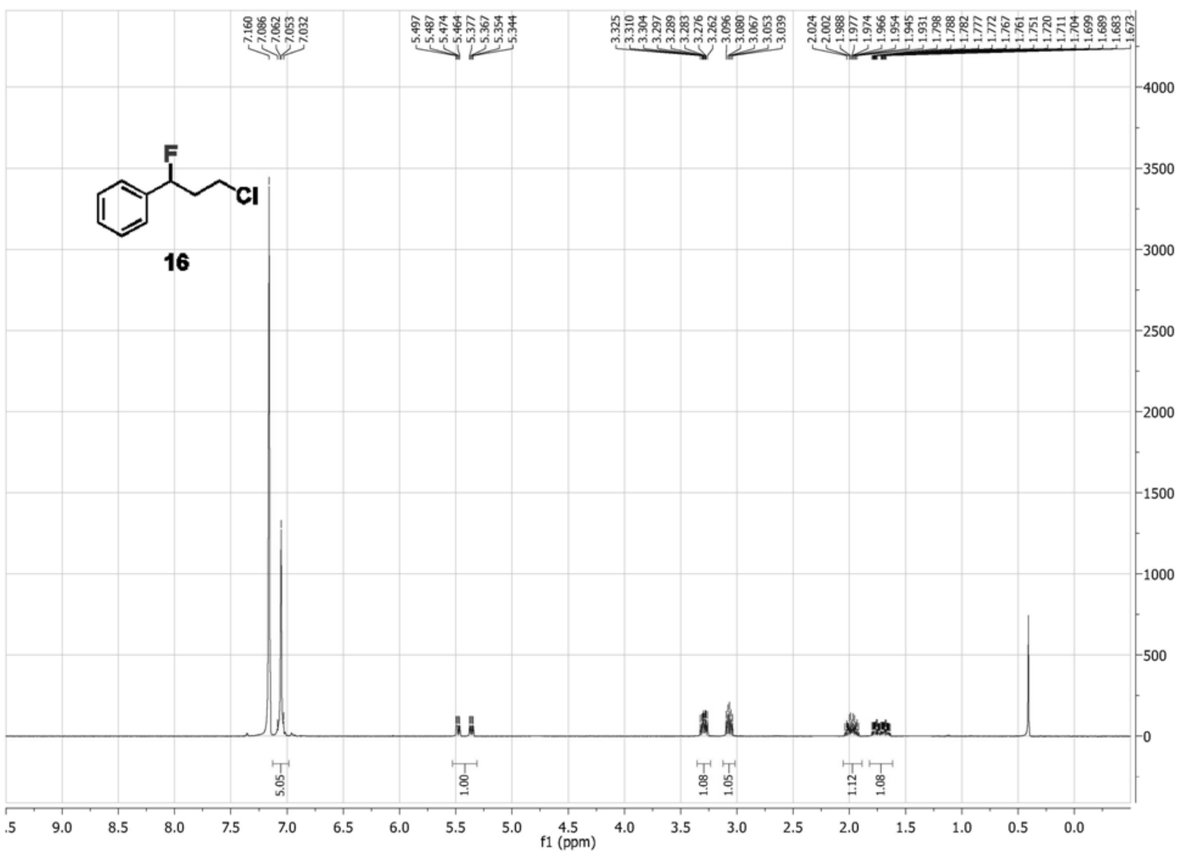

144.49
144.29
131.30
131.29
130.30
128.60
128.52
128.30 c6d6
128.06 c6d6
127.82 c6d6
123.78
123.71
122.87
90.64
88.94
22.94
22.69
Br
F
CH3
14
f1 (ppm)

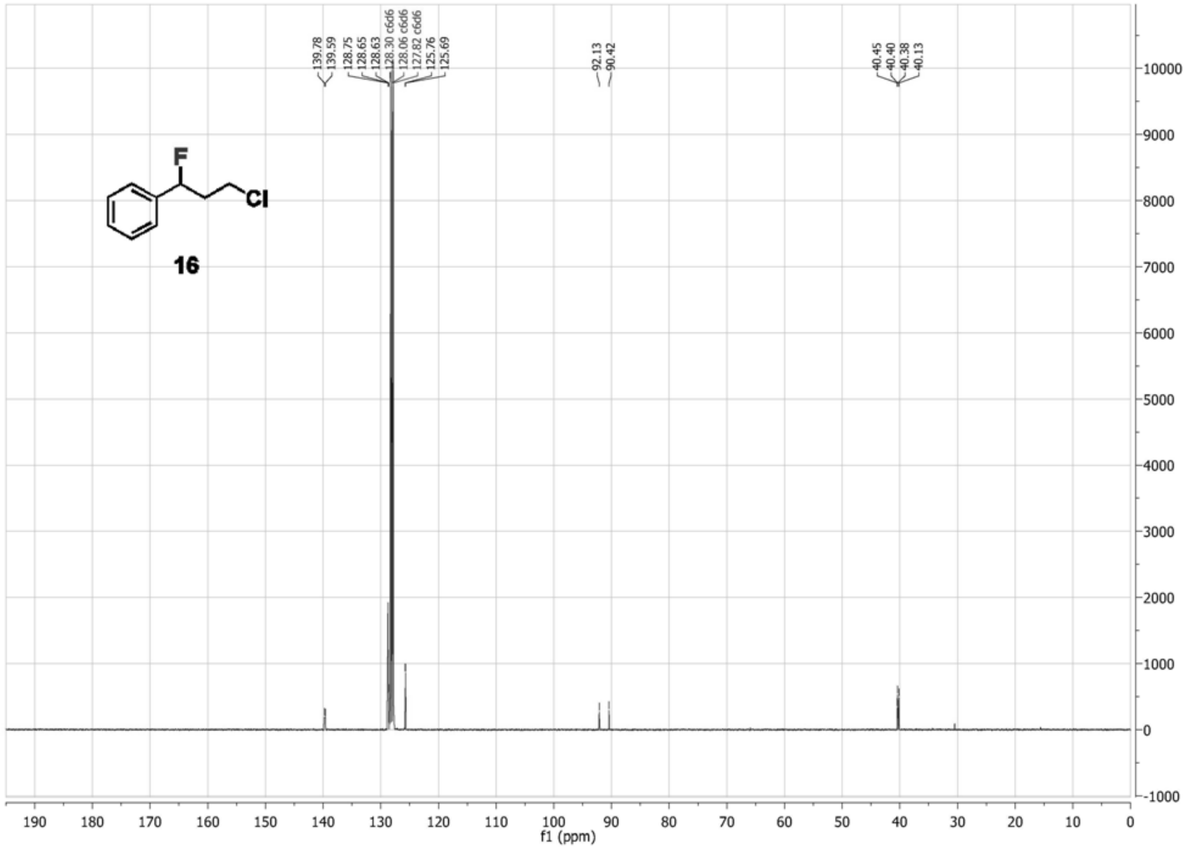

-169.59
-169.65
-169.71
-169.78
-169.84
-169.90
Br
F
CH3
14
-169.7
-169.9
f1 (ppm)
9000
0
4500
4000
3500
3000
2500
2000
1500
1000
500
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270
f1 (ppm)

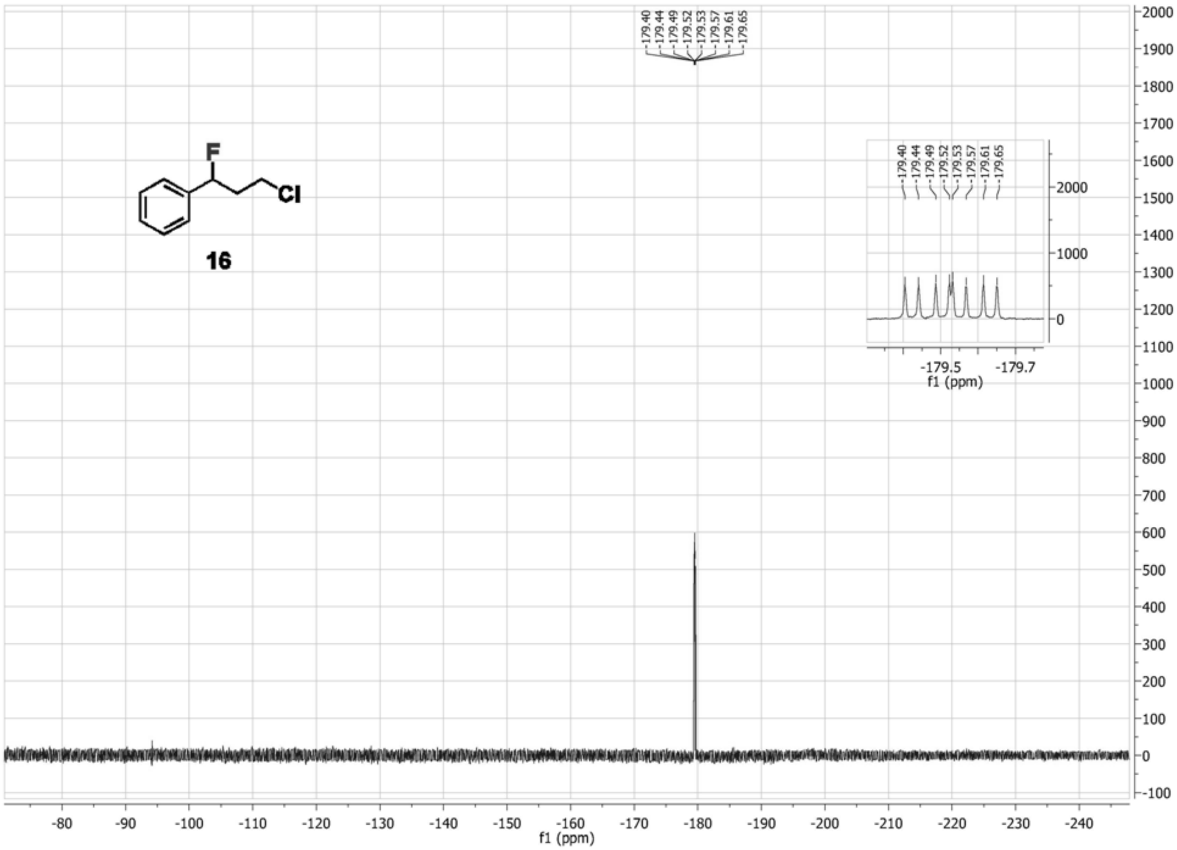

7.160
7.024
7.018
7.013
7.009
7.002
6.993
6.953
6.943
6.941
6.937
6.933
6.932
6.925
6.923
6.918
6.917
5.234
5.225
5.215
5.206
5.116
5.107
5.097
5.088
3.361
3.342
3.331
3.321
3.311
3.301
3.290
3.271
3.201
3.192
3.171
3.162
3.138
3.128
3.107
3.098
F
Cl
15
2.77
1.90
1.00
1.00
1.01
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5 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

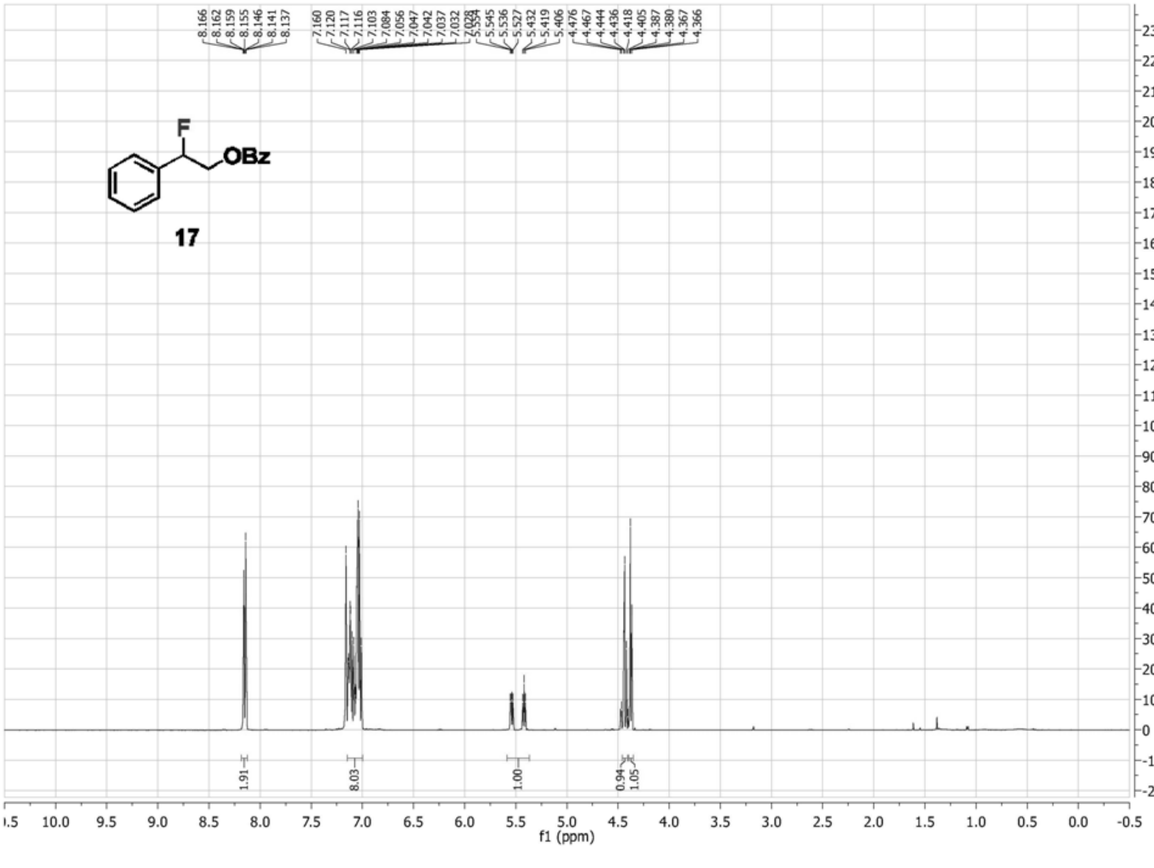

137.22
137.02
129.11
129.10
128.69
128.30 c6d6
128.06 c6d6
127.82 c6d6
126.02
125.96
93.86
92.08
47.03
46.75
F
Cl
15
f1 (ppm)

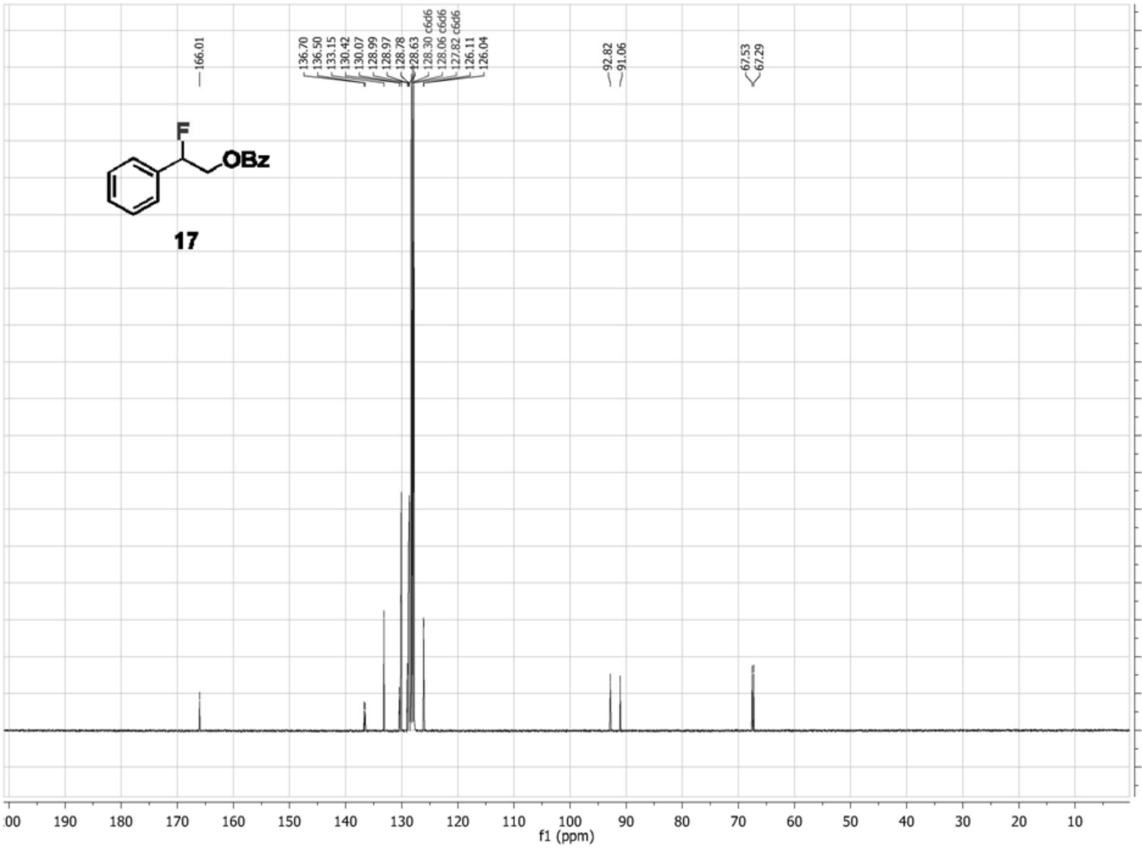

-178.92
-178.96
-178.99
-179.03
-179.04
-179.09
-179.11
-179.16
F
Cl
15


7.160
7.086
7.062
7.053
7.032
5.497
5.487
5.474
5.464
5.377
5.367
5.354
5.344
3.325
3.310
3.304
3.297
3.289
3.283
3.276
3.262
3.096
3.080
3.067
3.053
3.039
2.024
2.002
1.988
1.977
1.974
1.966
1.954
1.945
1.931
1.798
1.788
1.782
1.777
1.772
1.767
1.761
1.751
1.720
1.711
1.704
1.699
1.689
1.683
1.673
F
Cl
16
5.05
1.00
1.08
1.05
1.12
1.08
f1 (ppm)

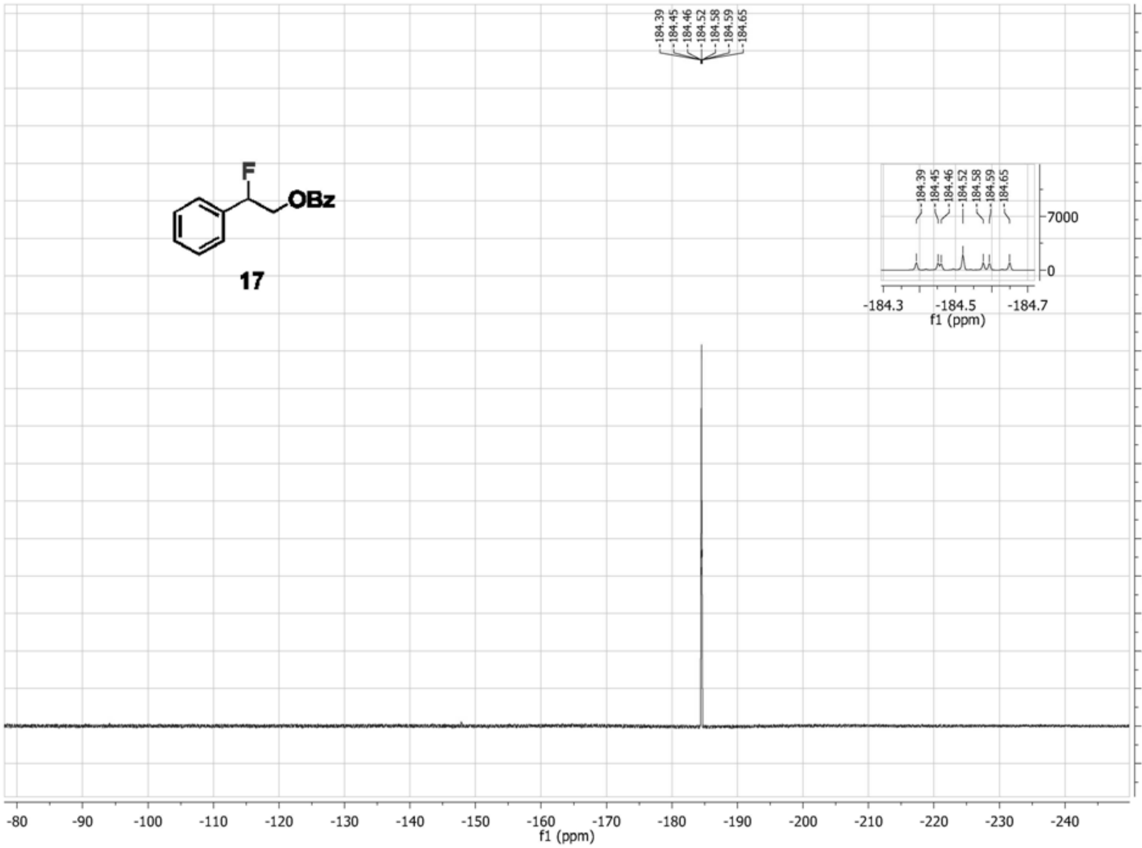

139.78
139.59
128.75
128.65
128.63
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.76
125.69
92.13
90.42
40.45
40.40
40.38
40.13
F
Cl
16
f1 (ppm)


16
-179.40
-179.44
-179.49
-179.52
-179.53
-179.57
-179.61
-179.65
F
Cl
-179.5
-179.7
f1 (ppm)
2000
1000
0
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

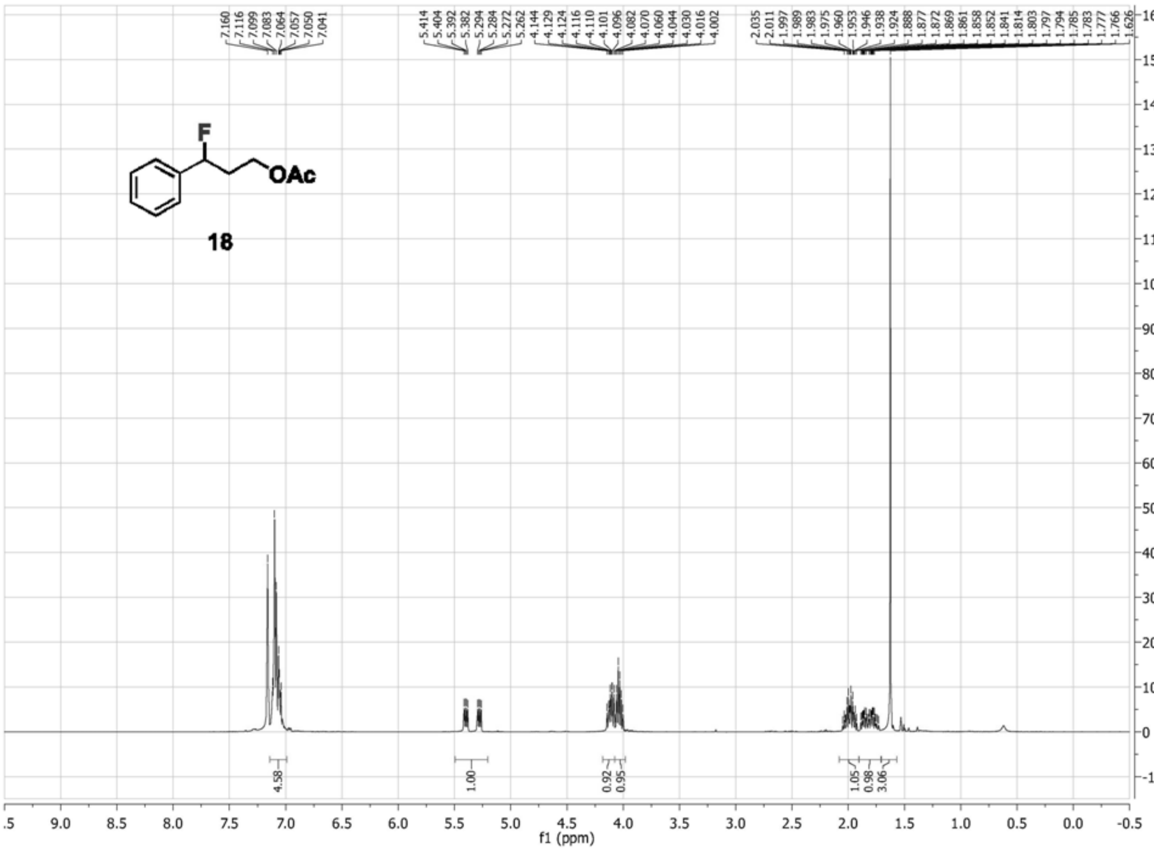

17
8.166
8.162
8.159
8.155
8.146
8.141
8.137
7.160
7.120
7.117
7.116
7.103
7.084
7.056
7.047
7.042
7.037
7.032
7.028
5.554
5.545
5.536
5.527
5.432
5.419
5.406
4.476
4.467
4.444
4.436
4.418
4.405
4.387
4.380
4.367
4.366
F
OBz
1.91
8.03
1.00
0.94
1.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

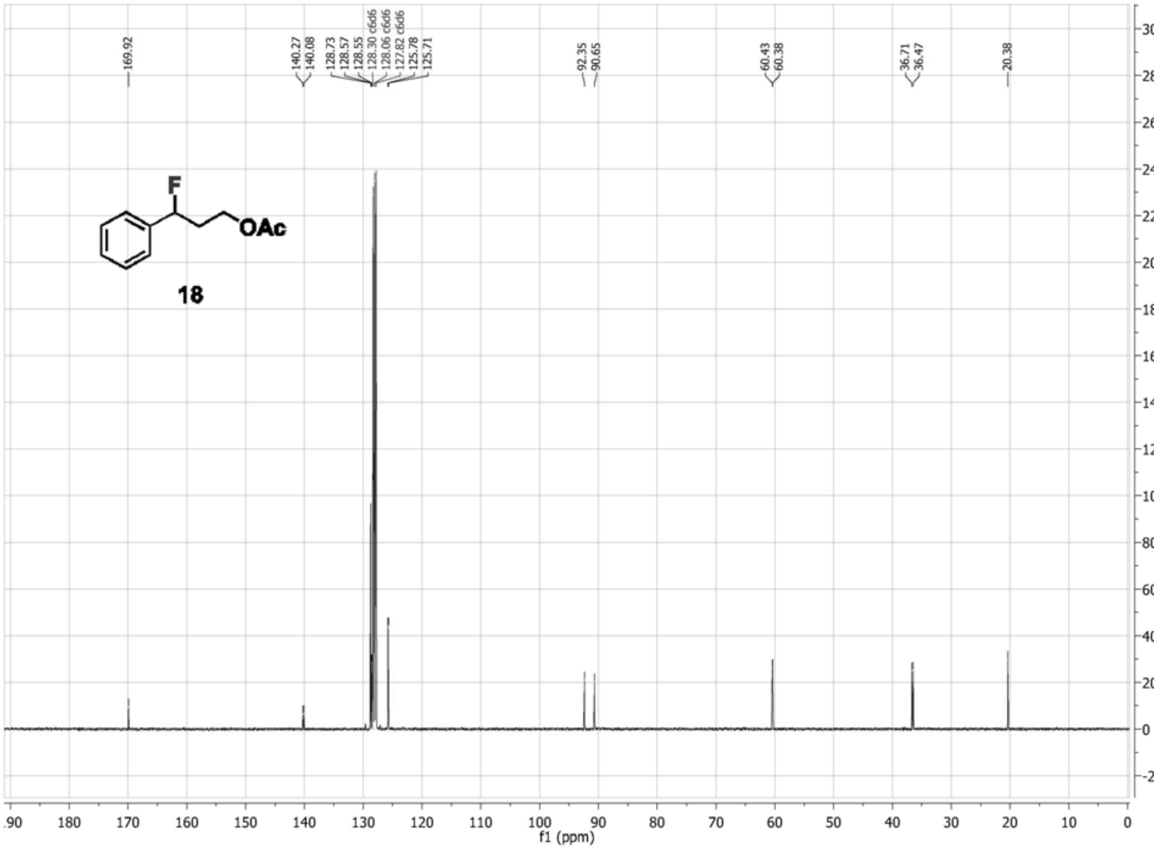


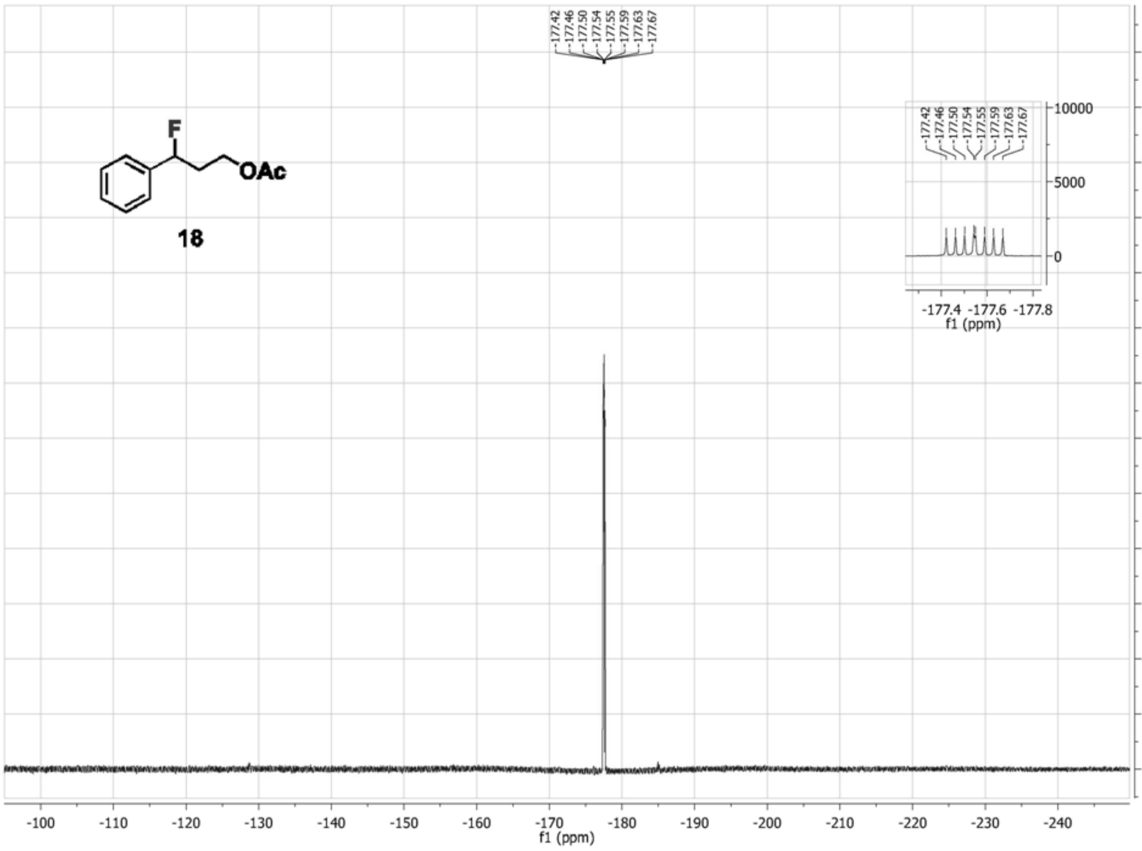
166.01
136.70
136.50
133.15
130.42
130.07
128.99
128.97
128.78
128.63
128.30 c6d6
128.06 c6d6
127.82 c6d6
126.11
126.04
92.82
91.06
67.53
67.29
F
OBz
17
f1 (ppm)

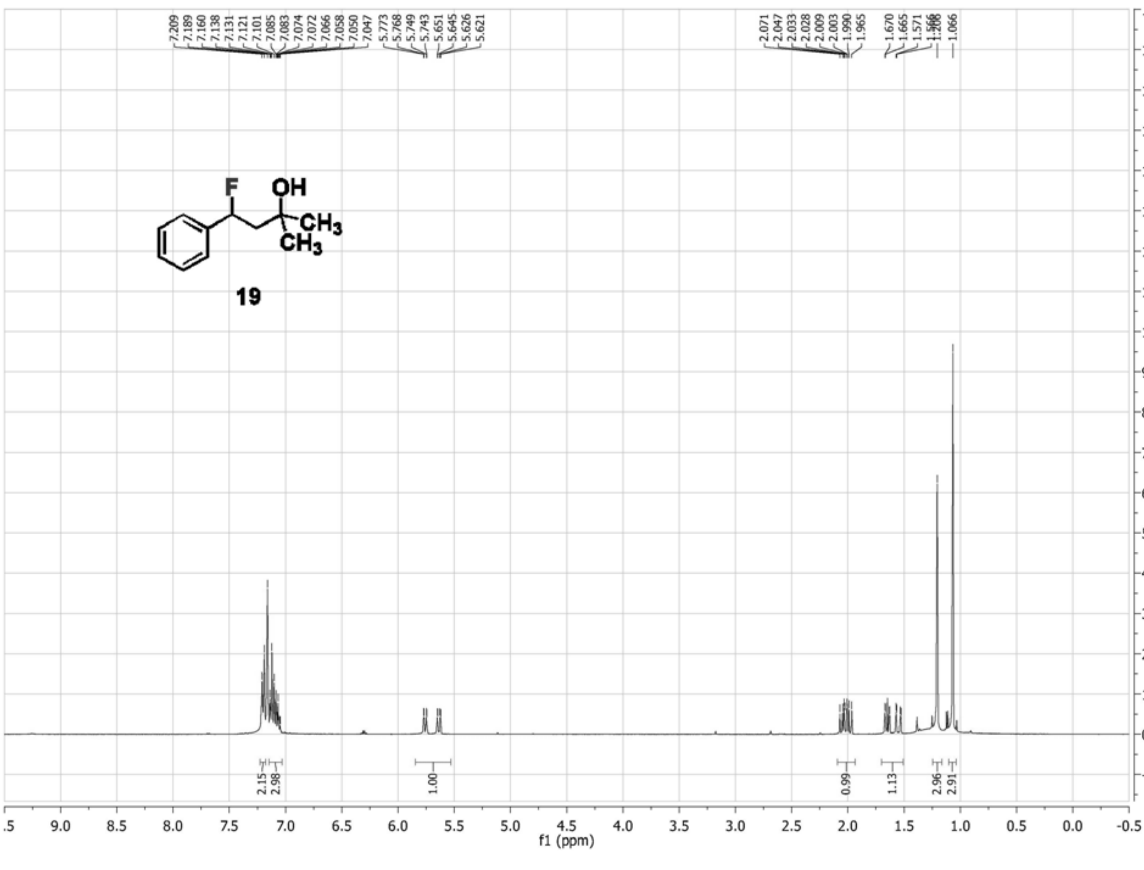


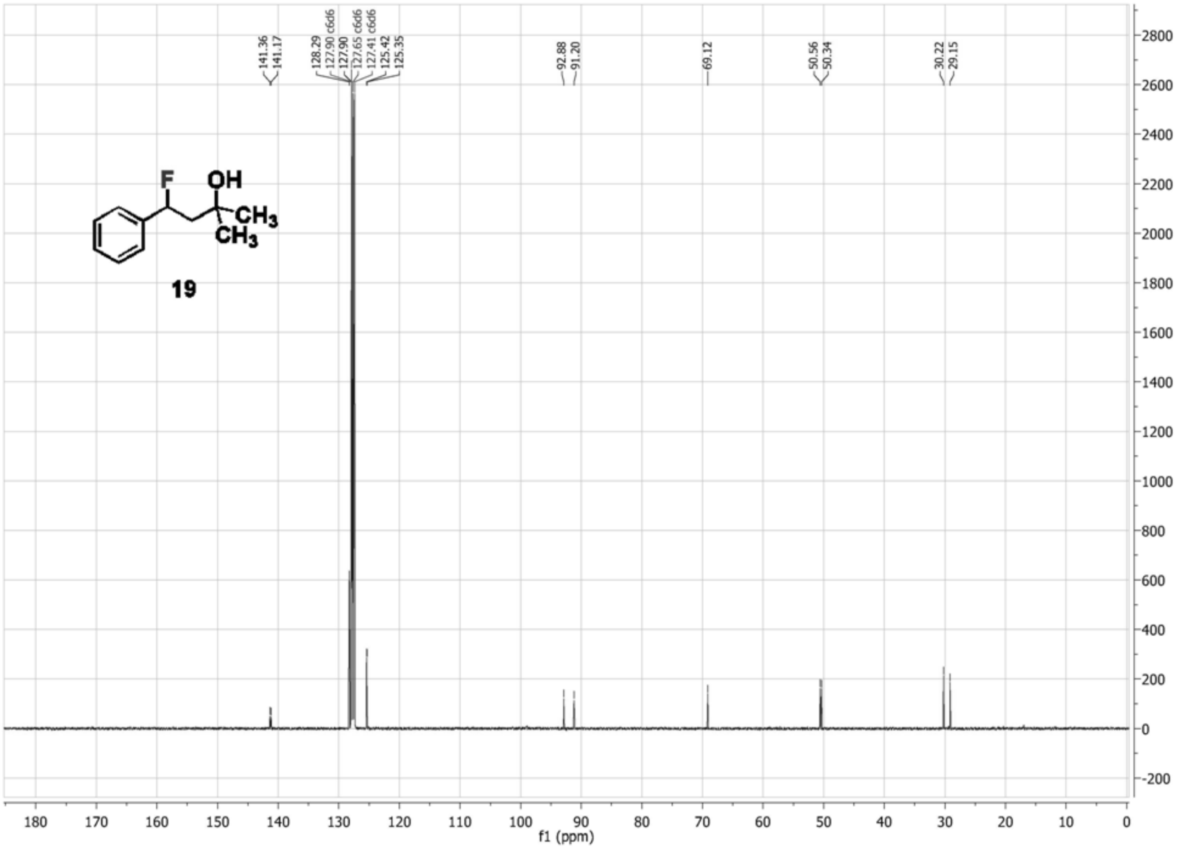
-184.39
-184.45
-184.46
-184.52
-184.58
-184.59
-184.65
F
OBz
17
-184.3
-184.5
-184.7
7000
0
f1 (ppm)

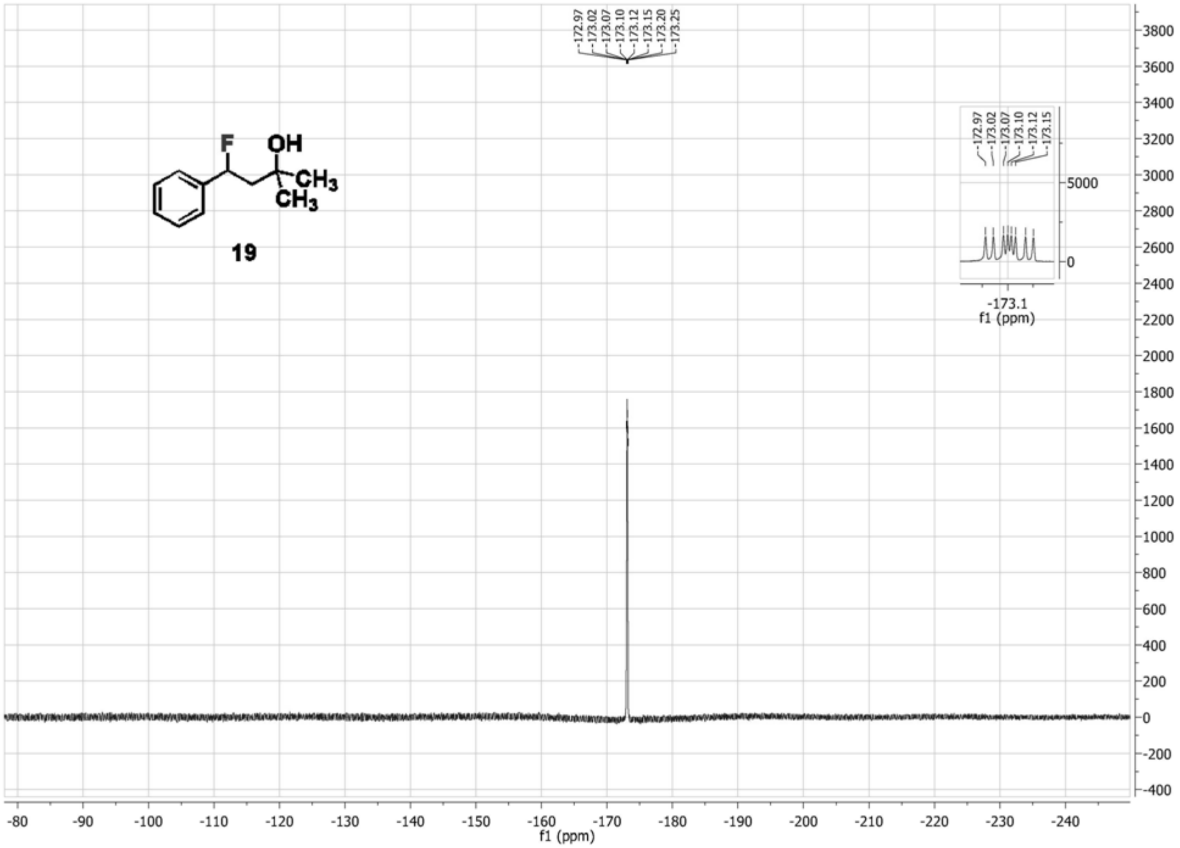

7.160
7.116
7.099
7.083
7.064
7.057
7.050
7.041
5.414
5.404
5.392
5.382
5.294
5.284
5.272
5.262
4.144
4.129
4.124
4.116
4.110
4.101
4.096
4.082
4.070
4.060
4.044
4.030
4.016
4.002
2.035
2.011
1.997
1.989
1.983
1.975
1.960
1.953
1.946
1.938
1.924
1.888
1.877
1.872
1.869
1.861
1.858
1.852
1.841
1.814
1.803
1.797
1.794
1.785
1.783
1.777
1.766
1.626
F
OAc
18
4.58
1.00
0.92
0.95
1.05
0.98
3.06
f1 (ppm)

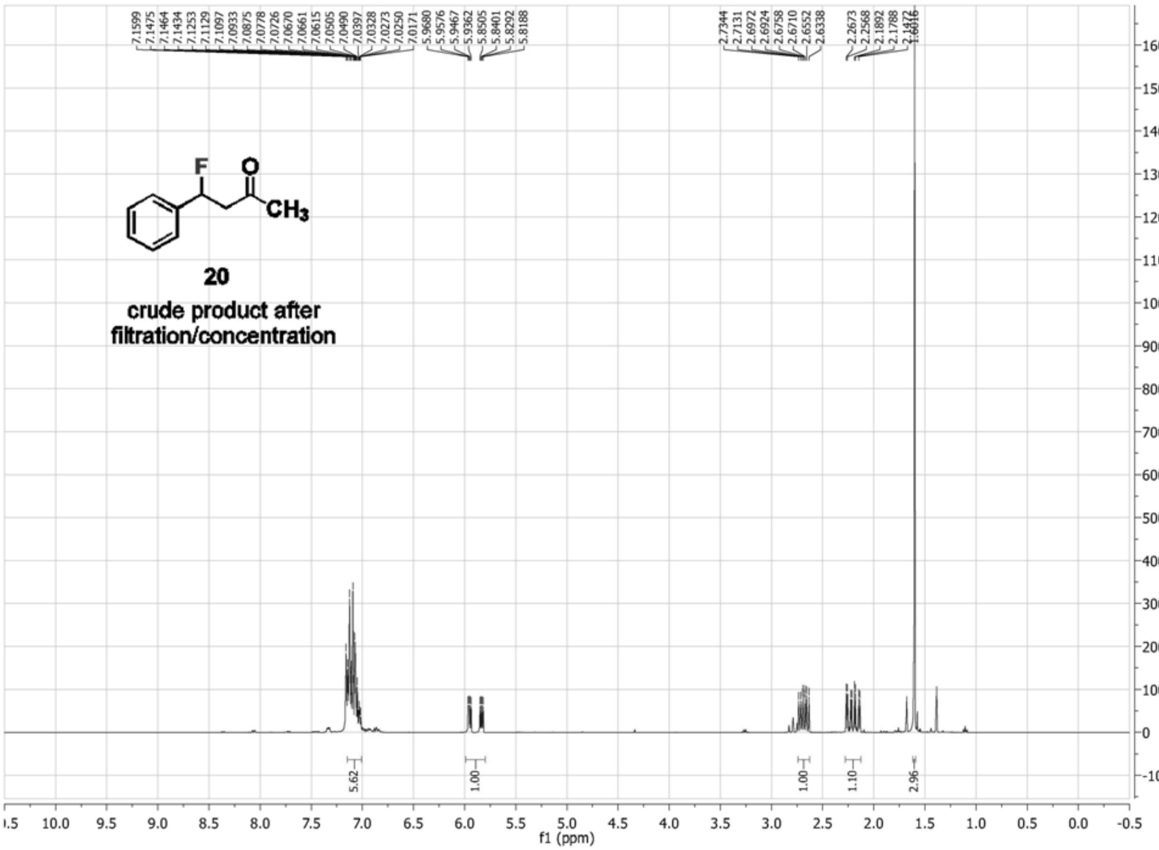

169.92
140.27
140.08
128.73
128.57
128.55
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.78
125.71
92.35
90.65
60.43
60.38
36.71
36.47
20.38
F
OAc
18
f1 (ppm)

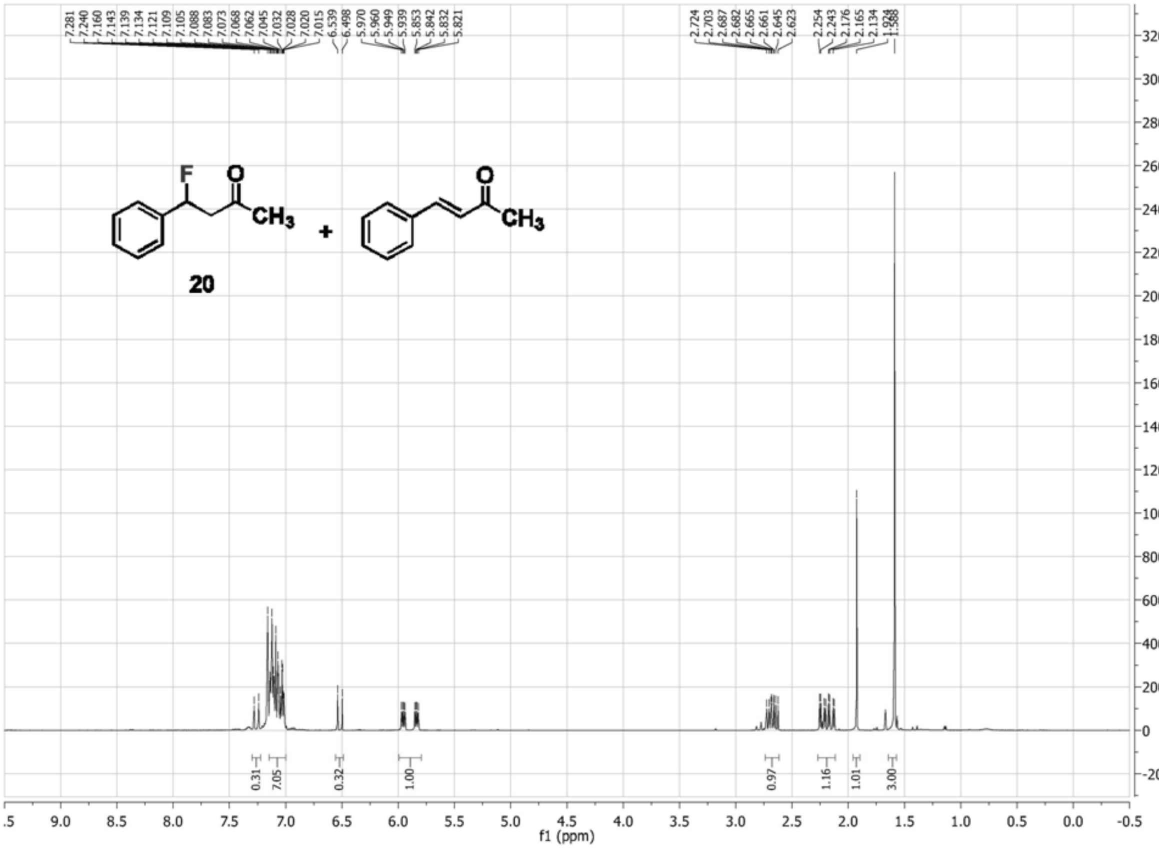

-177.42
-177.46
-177.50
-177.54
-177.55
-177.59
-177.63
-177.67
F
OAc
18
-177.4 -177.6 -177.8
f1 (ppm)
10000
5000
0
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

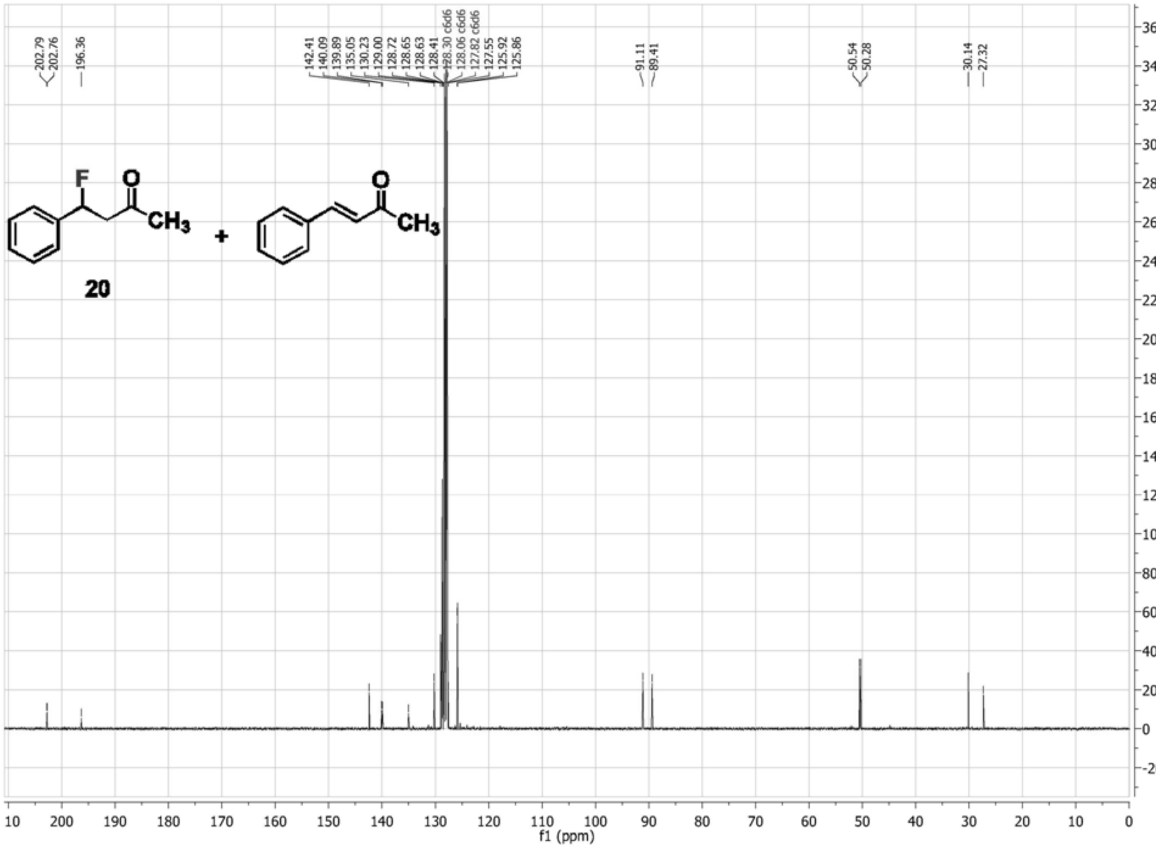

7.209
7.189
7.160
7.138
7.131
7.121
7.101
7.085
7.083
7.074
7.072
7.066
7.058
7.050
7.047
5.773
5.768
5.749
5.743
5.651
5.645
5.626
5.621
2.071
2.047
2.033
2.028
2.009
2.003
1.990
1.965
1.670
1.665
1.571
1.206
1.066
F
OH
CH3
CH3
19
2.15
2.98
1.00
0.99
1.13
2.96
2.91
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.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)

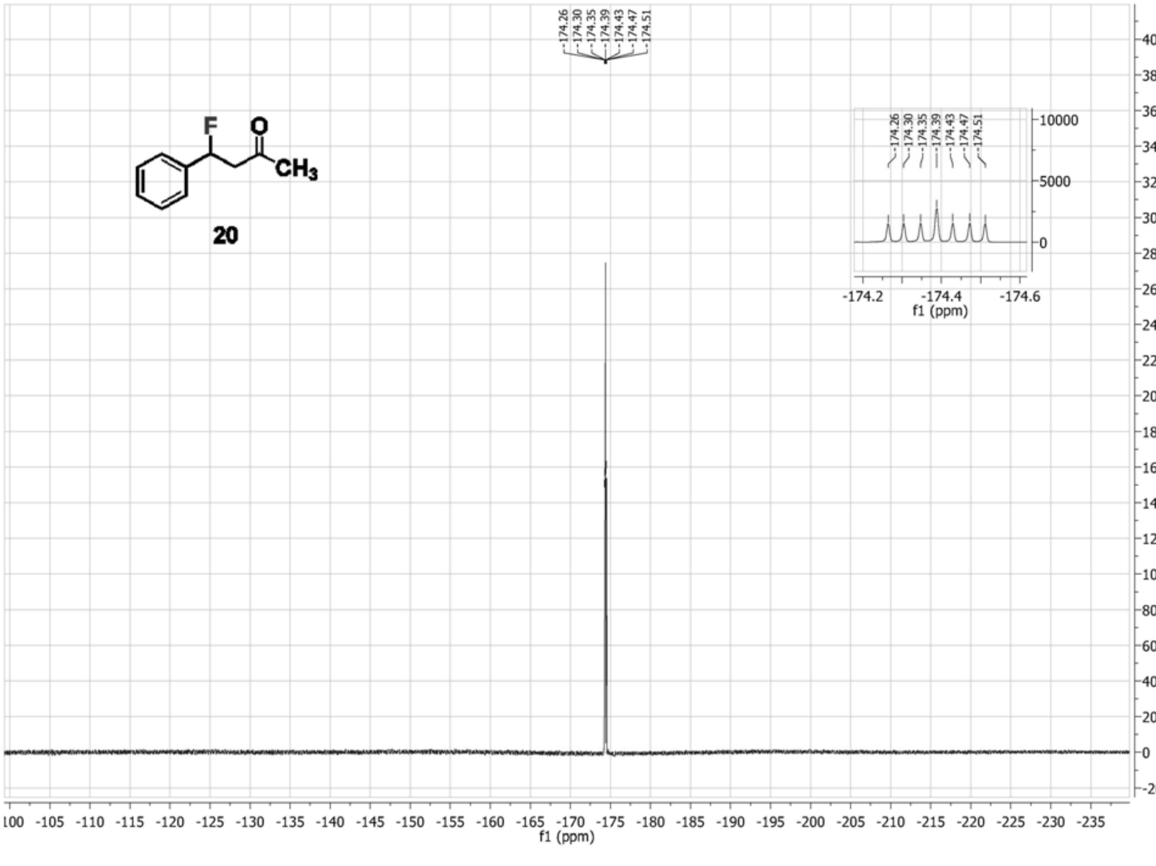

141.36
141.17
128.29
127.90 c6d6
127.90
127.65 c6d6
127.41 c6d6
125.42
125.35
92.88
91.20
69.12
50.56
50.34
30.22
29.15
F
OH
CH3
CH3
19
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

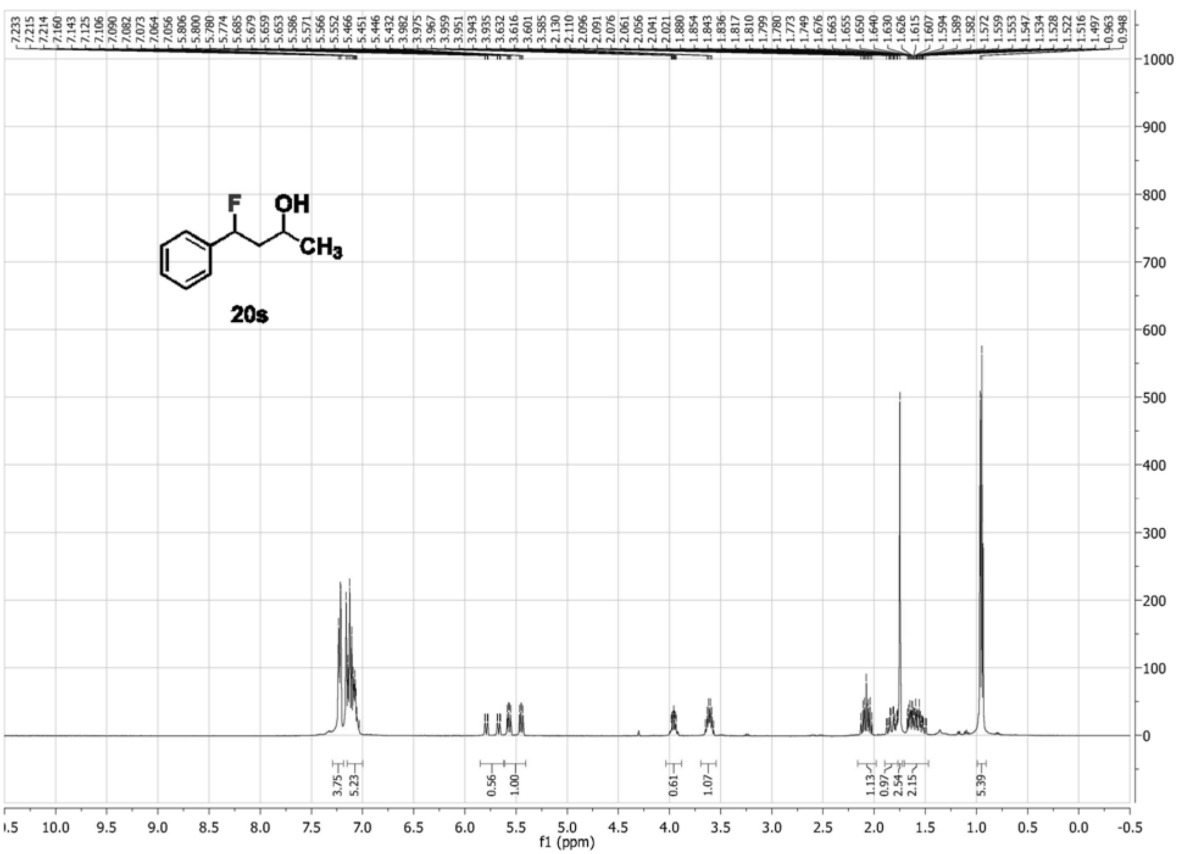

-172.97
-173.02
-173.07
-173.10
-173.12
-173.15
-173.20
-173.25
F
OH
CH3
CH3
19
5000
0
-173.1
f1 (ppm)
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

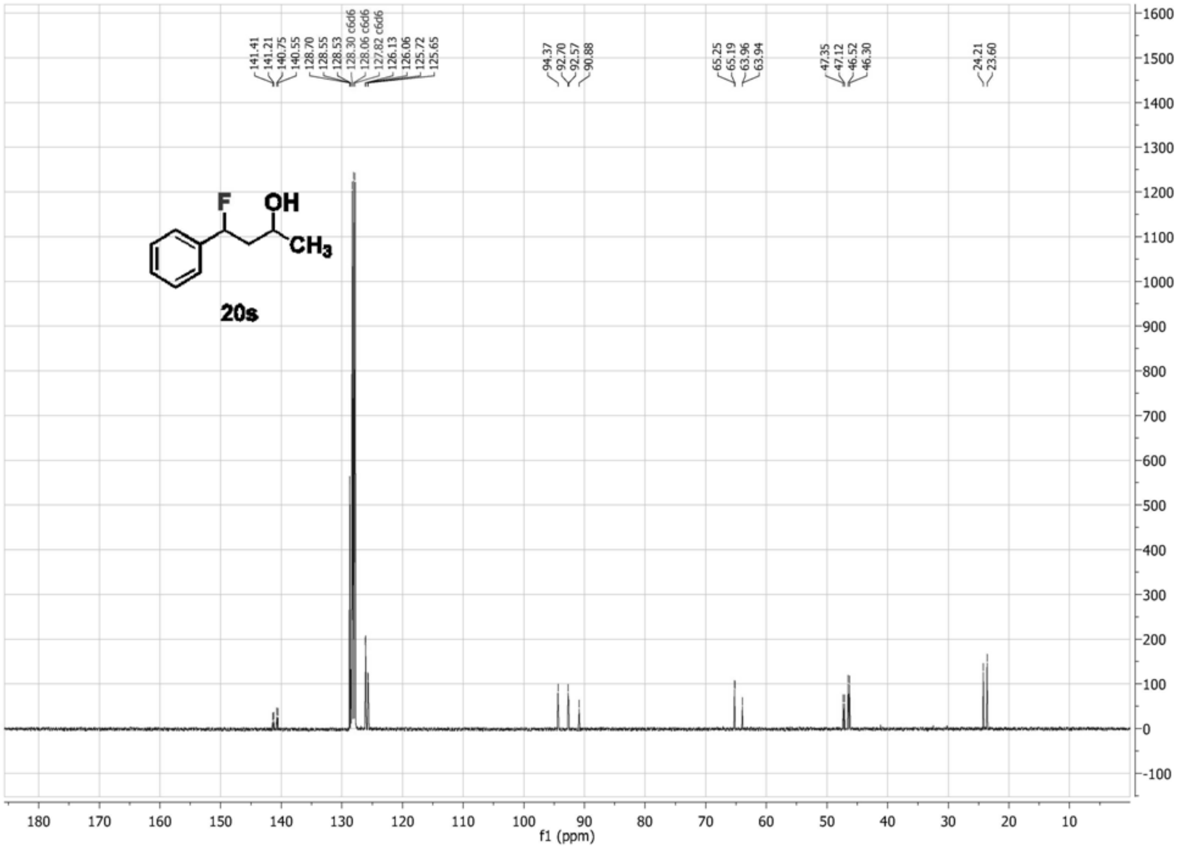

7.1599
7.1475
7.1464
7.1434
7.1253
7.1129
7.1097
7.0933
7.0875
7.0778
7.0726
7.0670
7.0661
7.0615
7.0505
7.0490
7.0397
7.0328
7.0273
7.0250
7.0171
5.9680
5.9576
5.9467
5.9362
5.8505
5.8401
5.8292
5.8188
2.7344
2.7131
2.6972
2.6924
2.6758
2.6710
2.6552
2.6338
2.2673
2.2568
2.1892
2.1788
1.6016
F
O
CH3
20
crude product after
filtration/concentration
5.62
1.00
1.00
1.10
2.96
f1 (ppm)

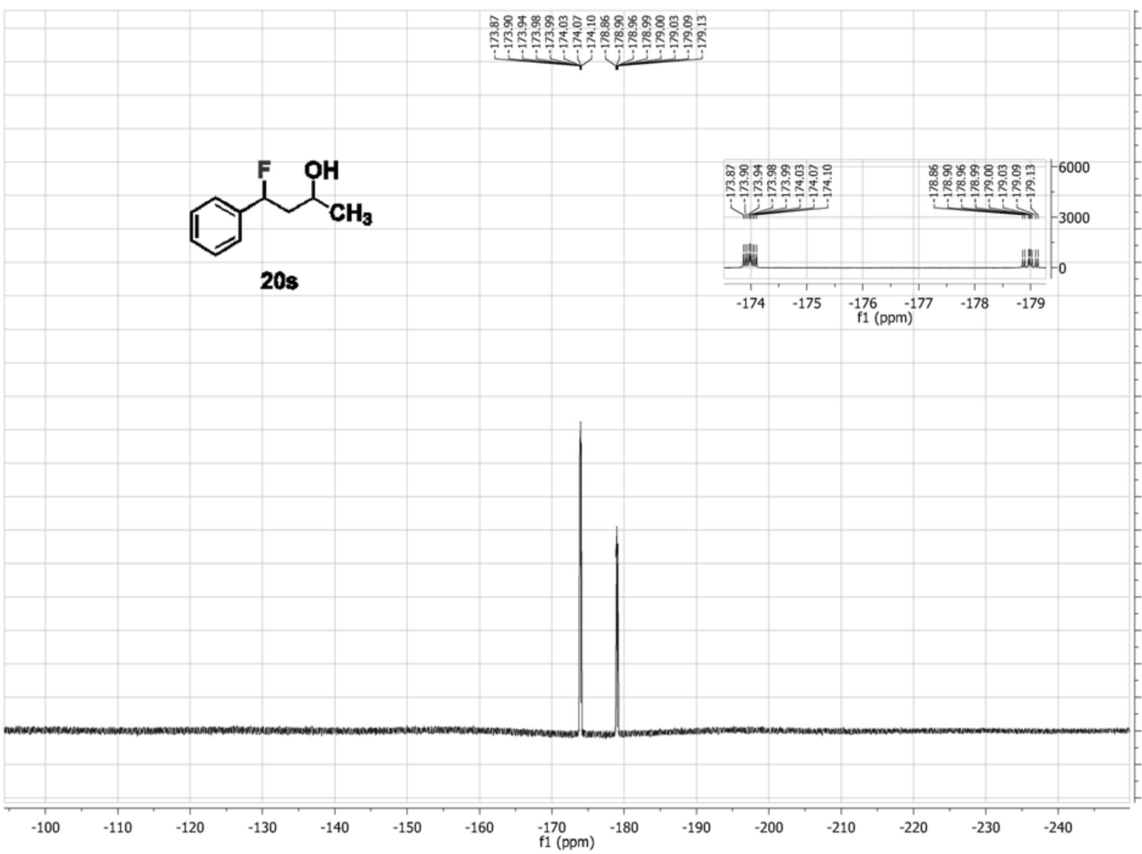

7.281
7.240
7.160
7.143
7.139
7.134
7.121
7.109
7.105
7.088
7.083
7.073
7.068
7.062
7.045
7.032
7.028
7.020
7.015
6.539
6.498
5.970
5.960
5.949
5.939
5.853
5.842
5.832
5.821
2.724
2.703
2.687
2.682
2.665
2.661
2.645
2.623
2.254
2.243
2.176
2.165
2.134
1.588
F
O
CH3
+
O
CH3
20
0.31
7.05
0.32
1.00
0.97
1.16
1.01
3.00
f1 (ppm)


202.79
202.76
196.36
142.41
140.09
139.89
135.05
130.23
129.00
128.72
128.65
128.63
128.41
128.30 c6d6
128.06 c6d6
127.82 c6d6
127.55
125.92
125.86
91.11
89.41
50.54
50.28
30.14
27.32
F
O
CH3
+
O
CH3
20
f1 (ppm)

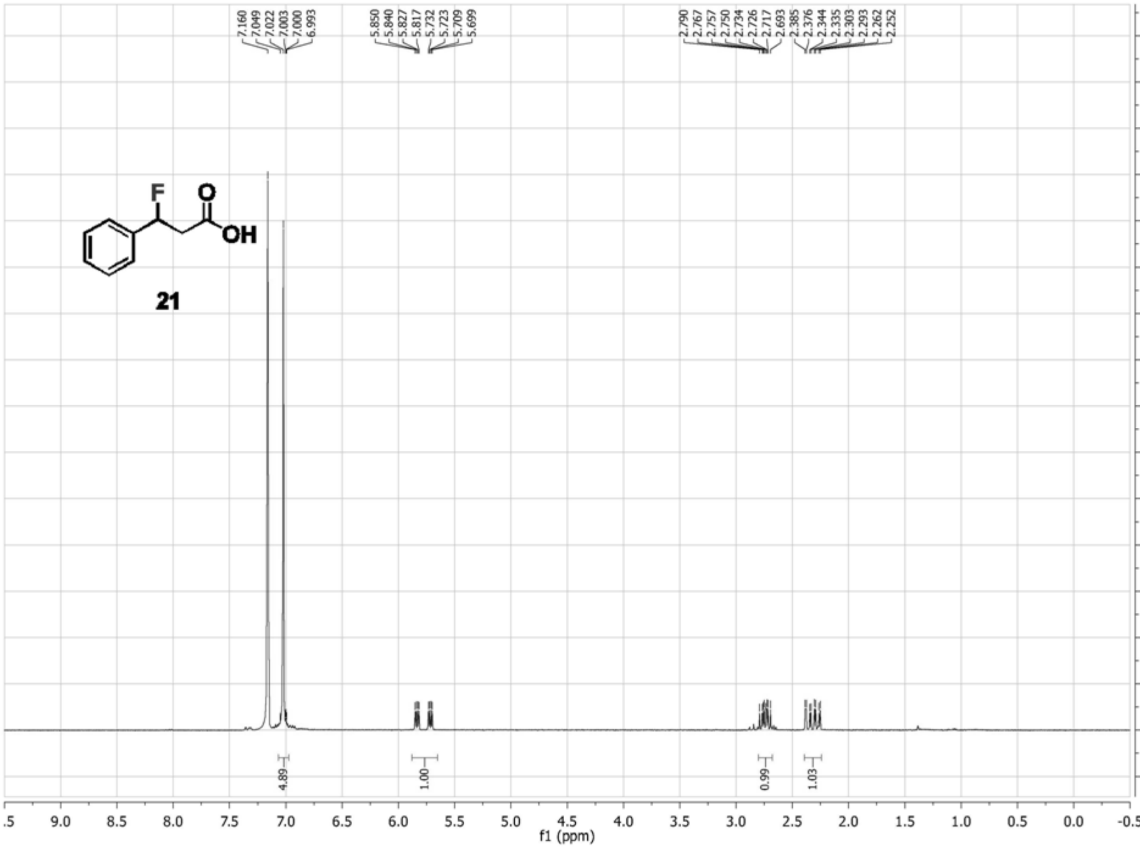

-174.26
-174.30
-174.35
-174.39
-174.43
-174.47
-174.51
F
O
CH3
20
f1 (ppm)


7.233
7.215
7.214
7.160
7.143
7.125
7.106
7.090
7.082
7.073
7.064
7.056
5.806
5.800
5.780
5.774
5.685
5.679
5.659
5.653
5.586
5.571
5.566
5.552
5.466
5.451
5.446
5.432
3.982
3.975
3.967
3.959
3.951
3.943
3.935
3.632
3.616
3.601
3.585
2.130
2.110
2.096
2.091
2.076
2.061
2.056
2.041
2.021
1.880
1.854
1.843
1.836
1.817
1.810
1.799
1.780
1.773
1.749
1.676
1.663
1.655
1.650
1.640
1.630
1.626
1.615
1.607
1.594
1.589
1.582
1.572
1.559
1.553
1.547
1.534
1.528
1.522
1.516
1.497
0.963
0.948
F
OH
CH3
20s
3.75
5.23
0.56
1.00
0.61
1.07
1.13
0.97
2.54
2.15
5.39
f1 (ppm)

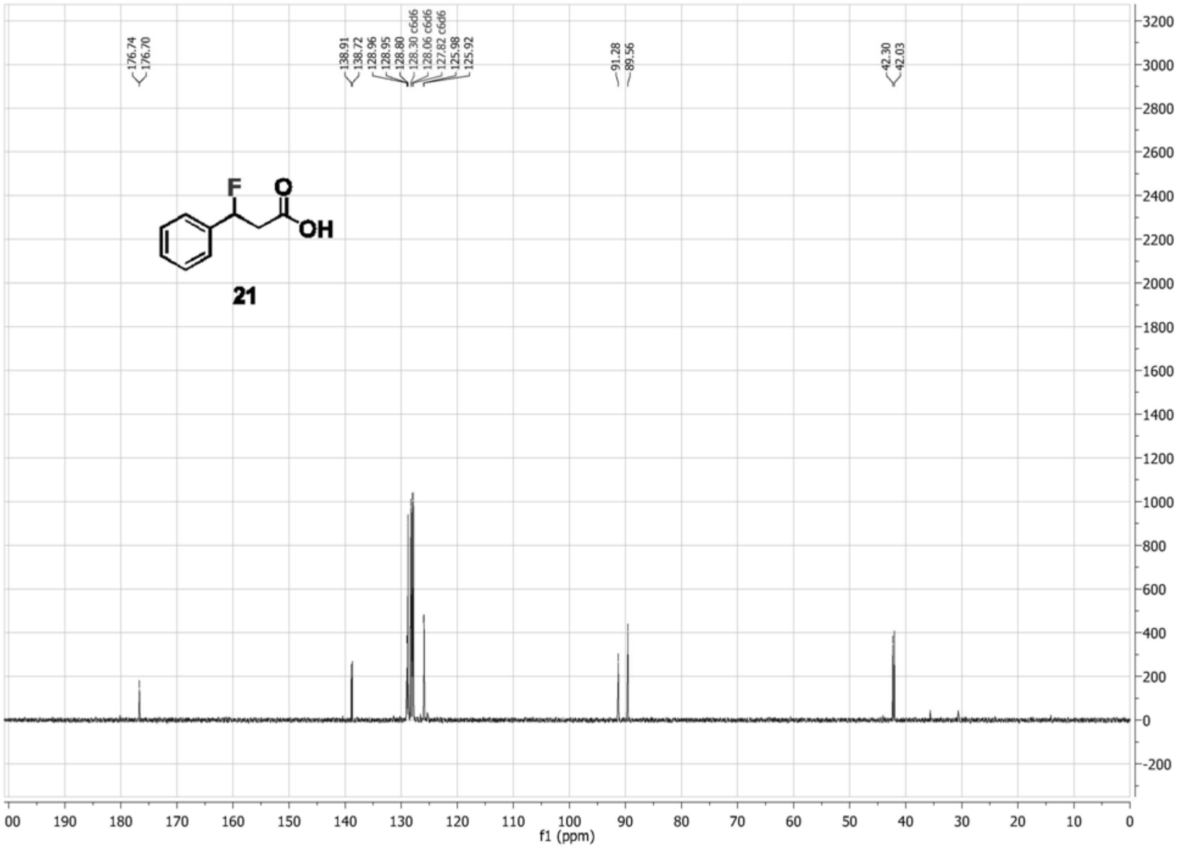

141.41
141.21
140.75
140.55
128.70
128.55
128.53
128.30 c6d6
128.06 c6d6
127.82 c6d6
126.13
126.06
125.72
125.65
94.37
92.70
92.57
90.88
65.25
65.19
63.96
63.94
47.35
47.12
46.52
46.30
24.21
23.60
F
OH
CH3
20s
f1 (ppm)

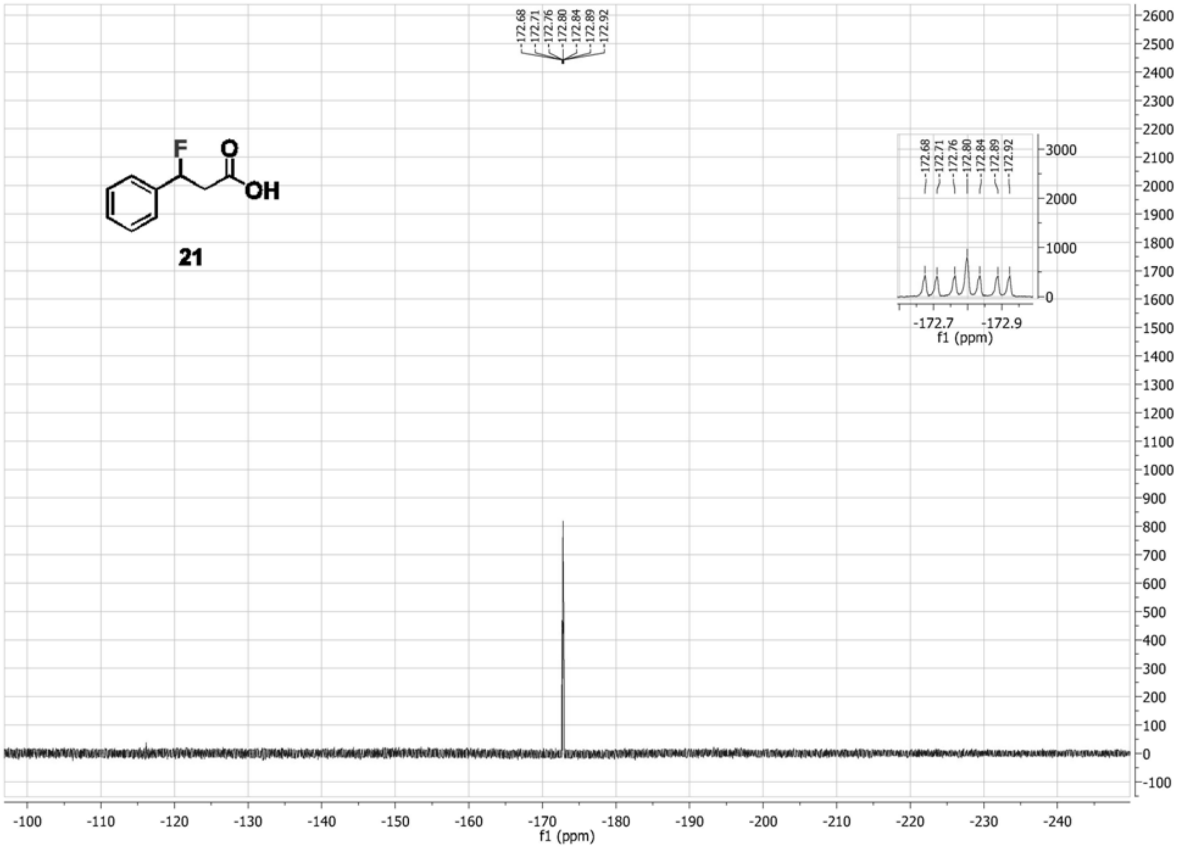

173.87
173.90
173.94
173.98
173.99
174.03
174.07
174.10
178.86
178.90
178.96
178.99
179.00
179.03
179.09
179.13
F
OH
CH3
-174
-175
-176
-177
-178
-179
f1 (ppm)
6000
3000
0
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
-200

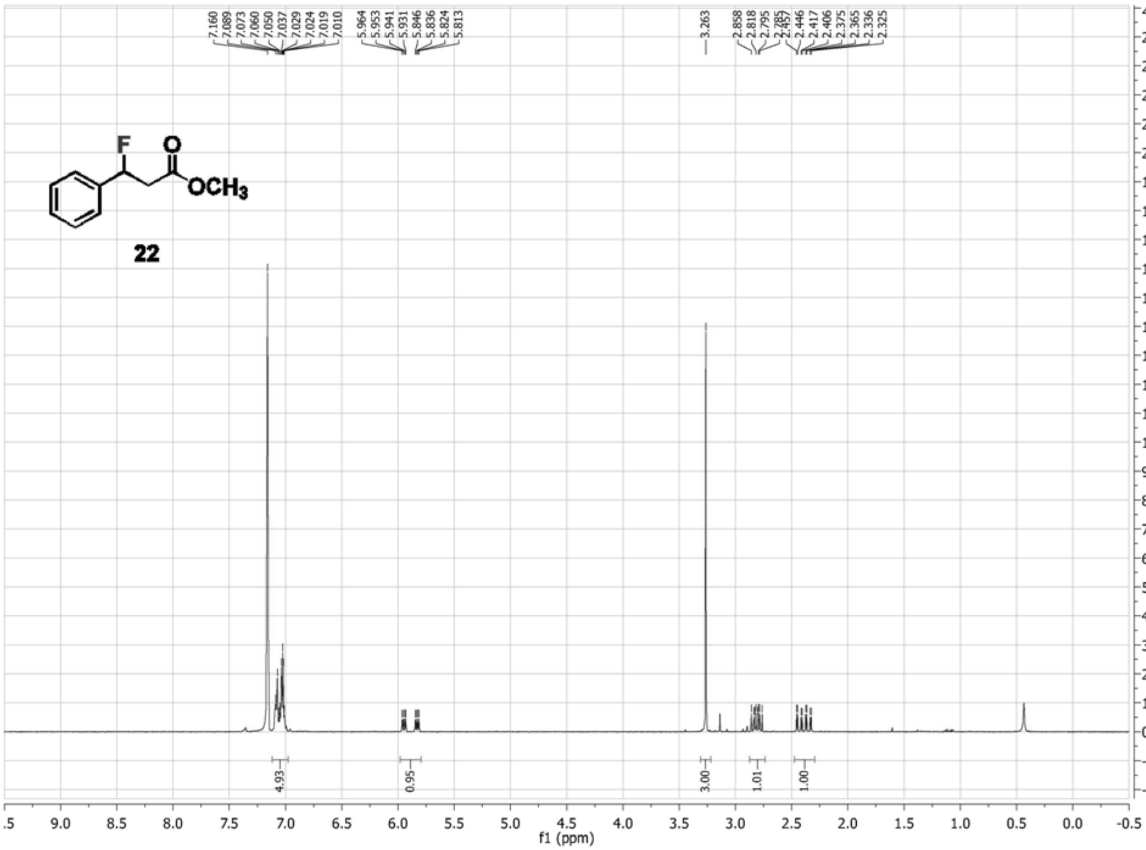
20s

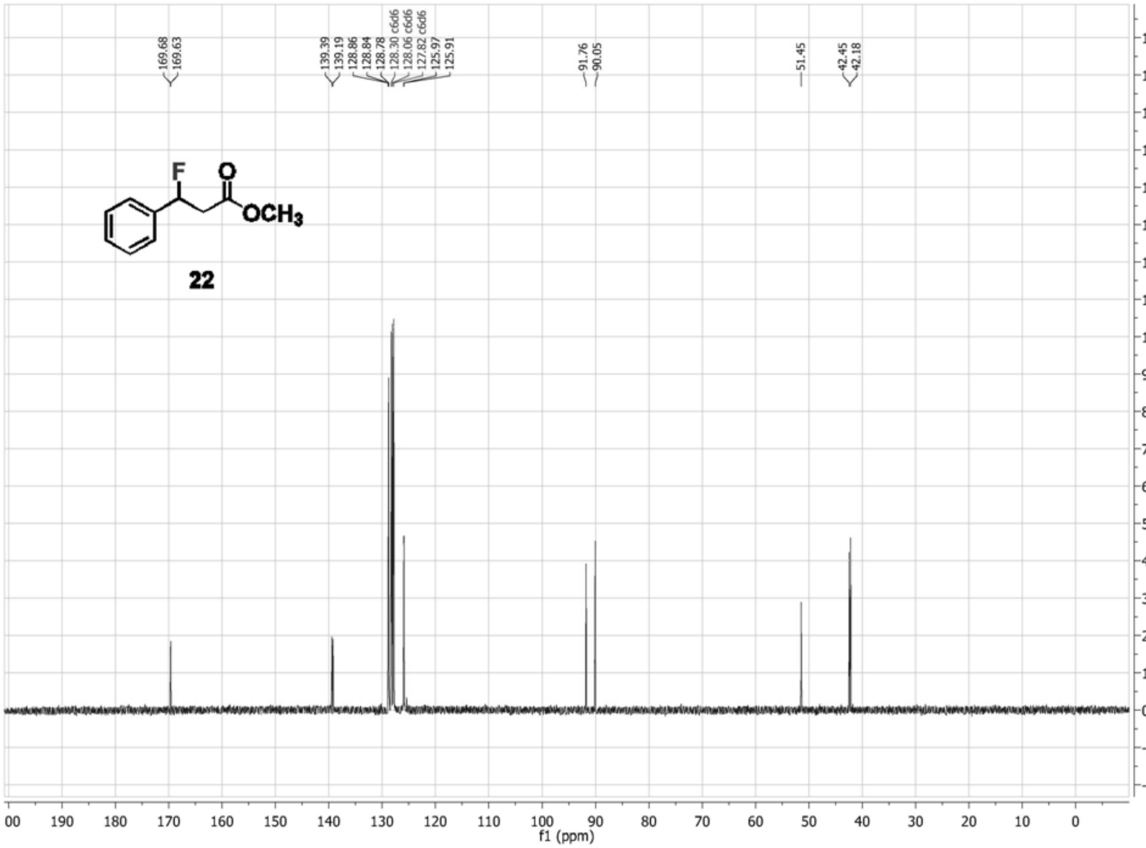

7.160
7.049
7.022
7.003
7.000
6.993
5.850
5.840
5.827
5.817
5.732
5.723
5.709
5.699
2.790
2.767
2.757
2.750
2.734
2.726
2.717
2.693
2.385
2.376
2.344
2.335
2.303
2.293
2.262
2.252
F
O
OH
4.89
1.00
0.99
1.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

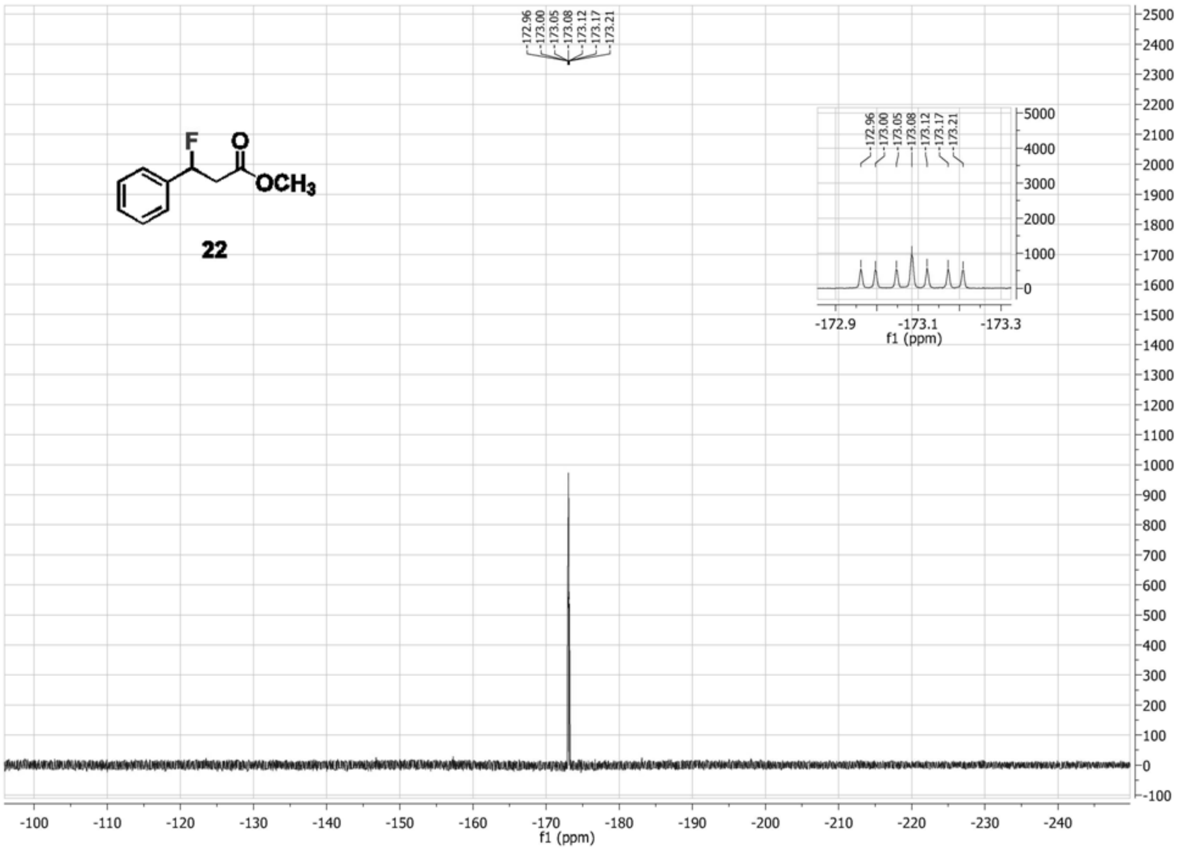
21


176.74
176.70
138.91
138.72
128.96
128.95
128.80
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.98
125.92
91.28
89.56
42.30
42.03
F
O
OH
21
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-172.68
-172.71
-172.76
-172.80
-172.84
-172.89
-172.92
F
O
OH
21
3000
2000
1000
0
-172.7
-172.9
f1 (ppm)
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

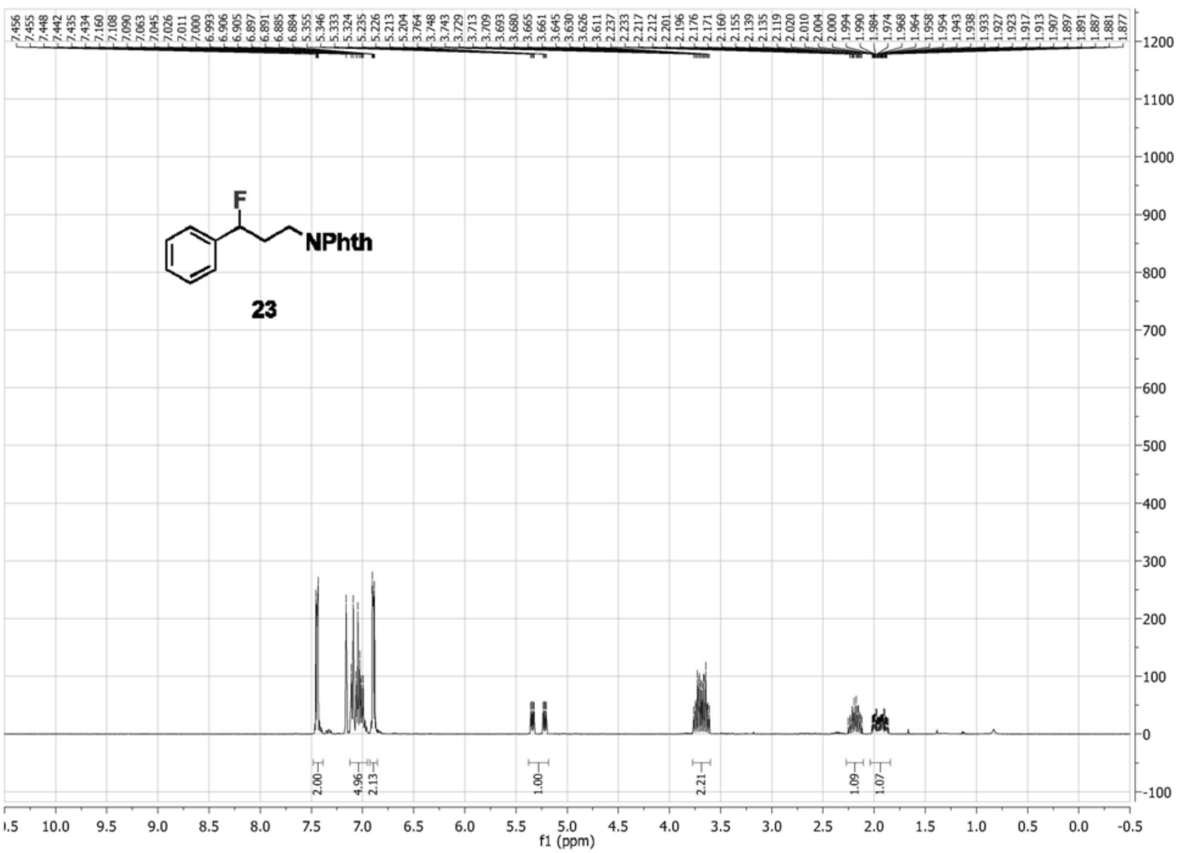

7.160
7.089
7.073
7.060
7.050
7.037
7.029
7.024
7.019
7.010
5.964
5.953
5.941
5.931
5.846
5.836
5.824
5.813
3.263
2.858
2.818
2.795
2.785
2.457
2.446
2.417
2.406
2.375
2.365
2.336
2.325
F
O
OCH3
22
4.93
0.95
3.00
1.01
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


169.68
169.63
139.39
139.19
128.86
128.84
128.78
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.97
125.91
91.76
90.05
51.45
42.45
42.18
F
O
OCH3
22
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200



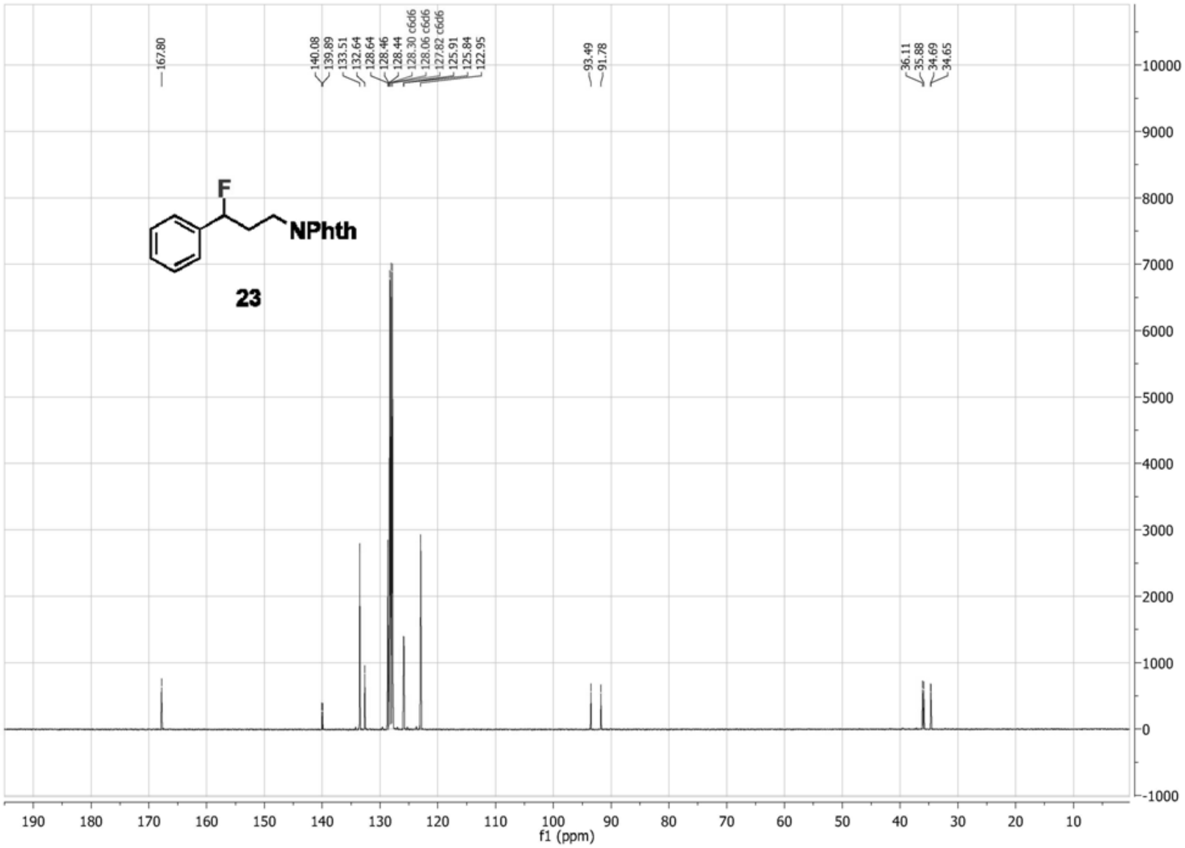
-172.96
-173.00
-173.05
-173.08
-173.12
-173.17
-173.21
F
O
OCH3
-172.9
-173.1
-173.3
f1 (ppm)
5000
4000
3000
2000
1000
0
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

22

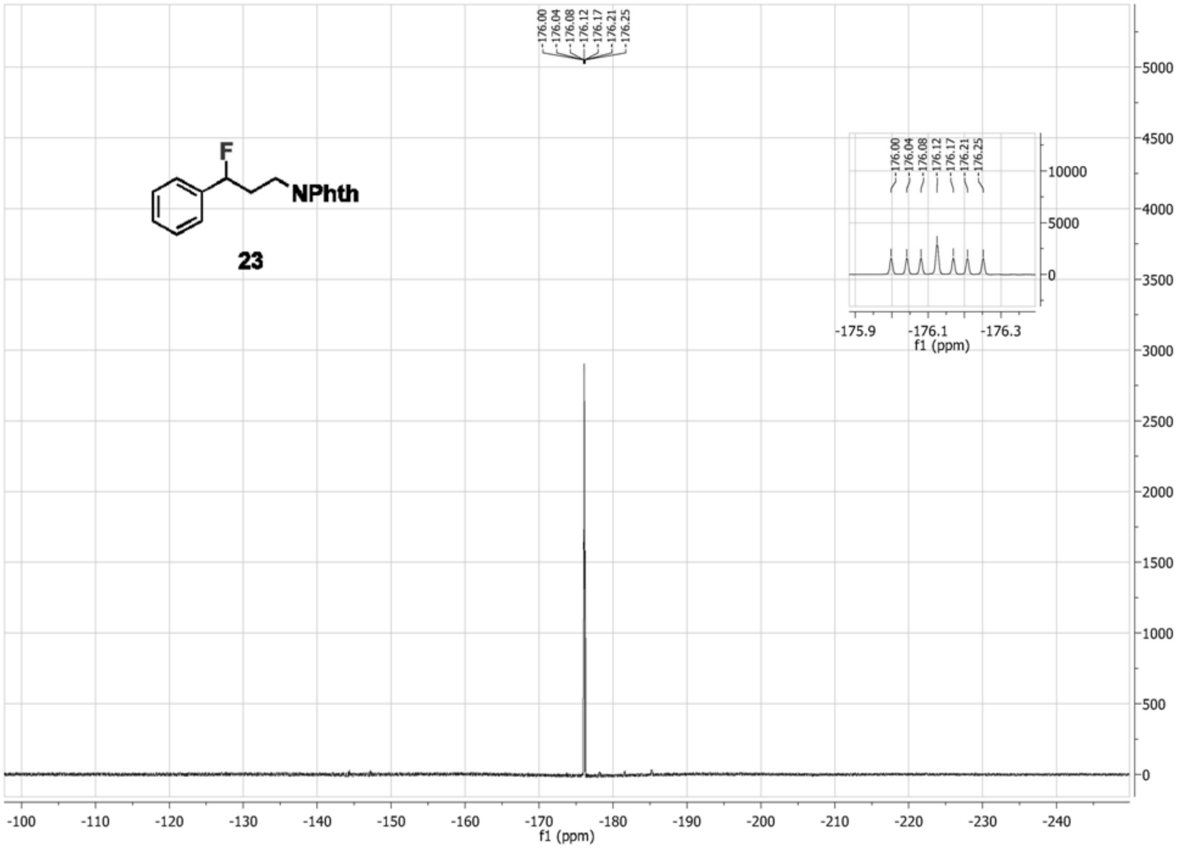


7.456
7.455
7.448
7.442
7.435
7.434
7.160
7.108
7.090
7.063
7.045
7.026
7.011
7.000
6.993
6.906
6.905
6.897
6.891
6.885
6.884
5.355
5.346
5.333
5.324
5.235
5.226
5.213
5.204
3.764
3.748
3.743
3.729
3.713
3.709
3.693
3.680
3.665
3.661
3.645
3.630
3.626
3.611
2.237
2.233
2.217
2.212
2.201
2.196
2.176
2.171
2.160
2.155
2.139
2.135
2.119
2.020
2.010
2.004
2.000
1.994
1.990
1.984
1.974
1.968
1.964
1.958
1.954
1.943
1.938
1.933
1.927
1.923
1.917
1.913
1.907
1.897
1.891
1.887
1.881
1.877
F
NPhth
2.00
4.96
2.13
1.00
2.21
1.09
1.07
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
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
f1 (ppm)

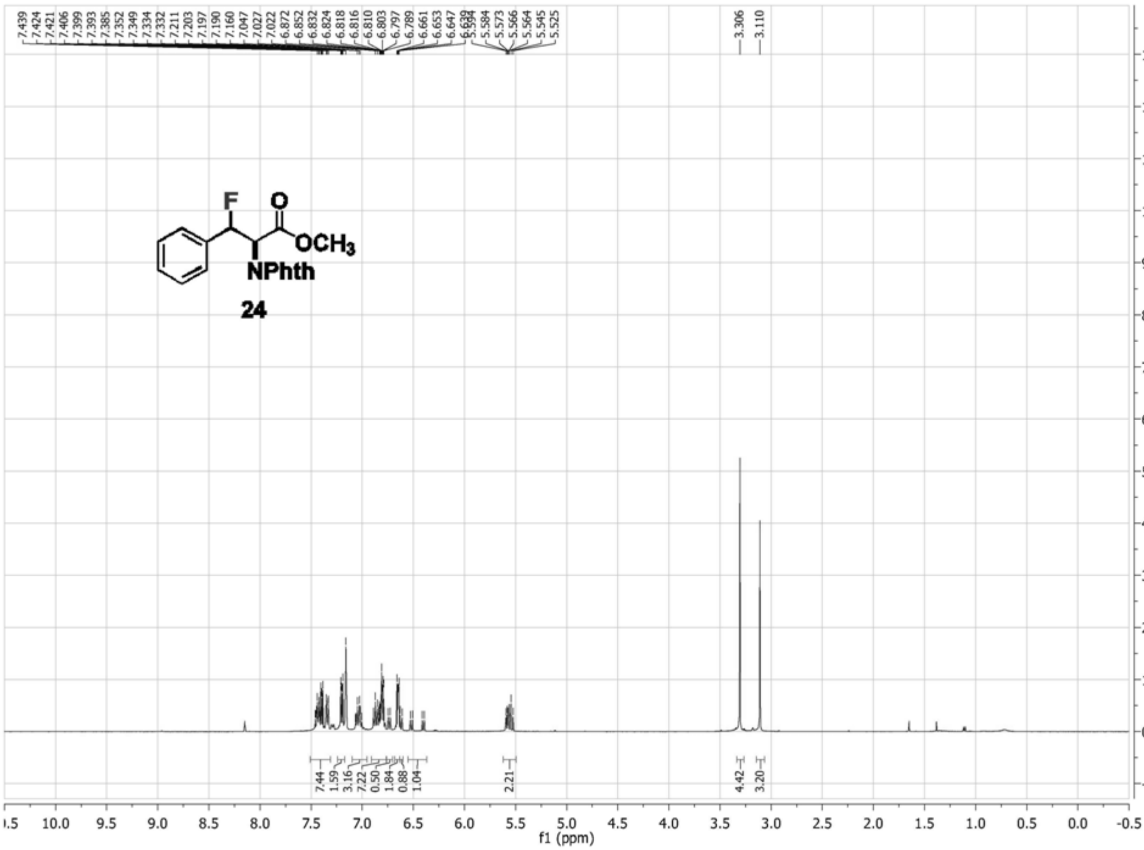
23

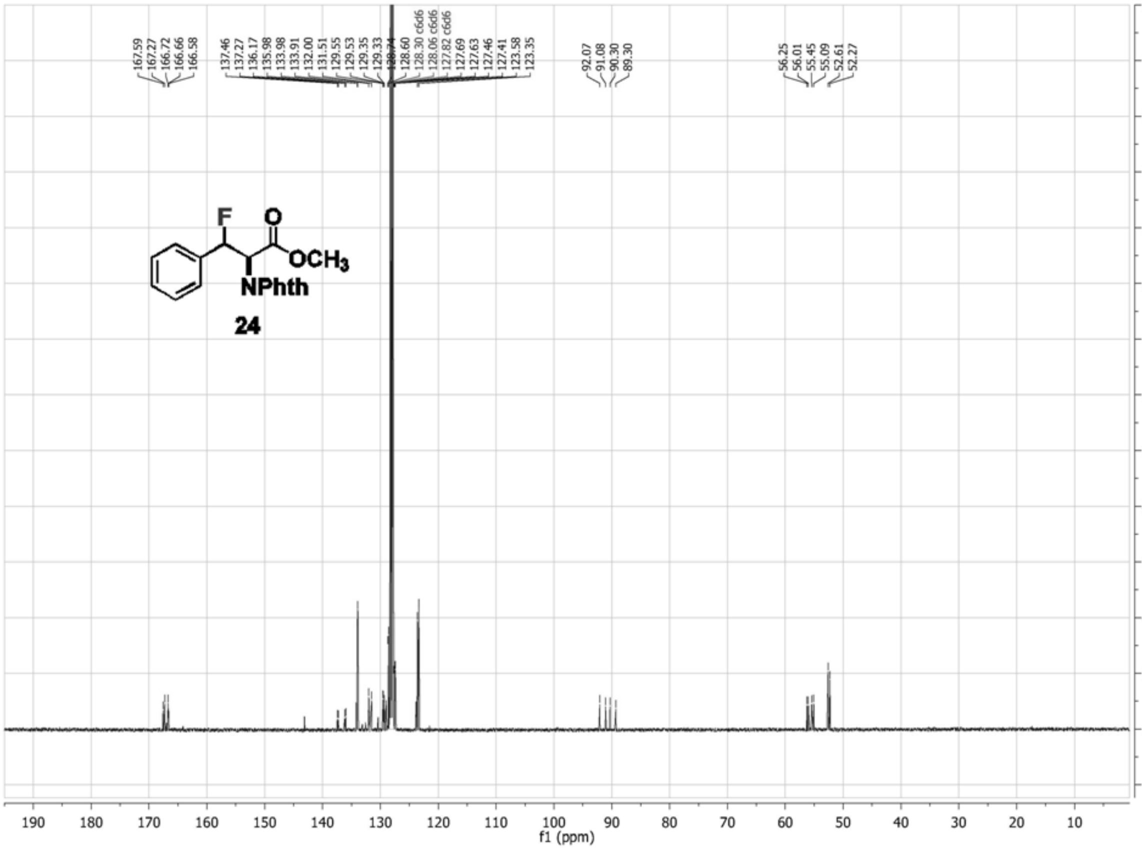


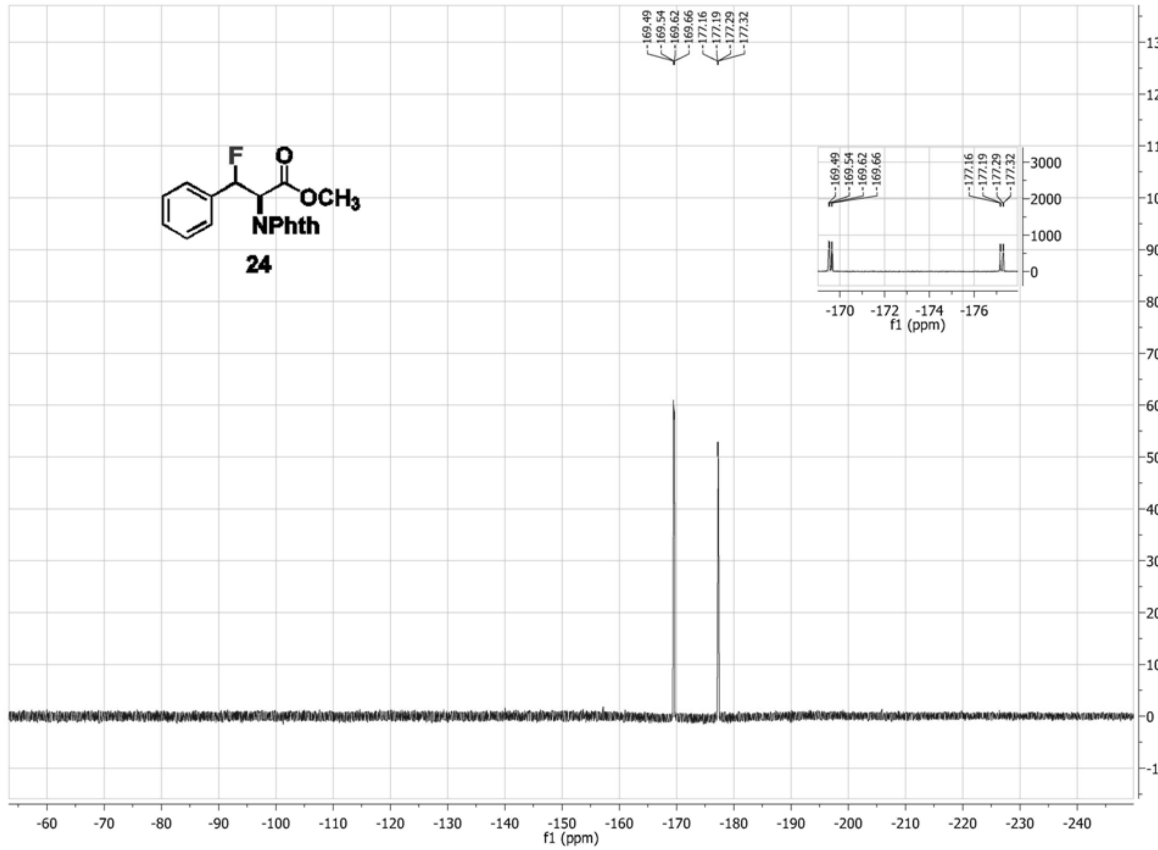
167.80
140.08
139.89
133.51
132.64
128.64
128.46
128.44
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.91
125.84
122.95
93.49
91.78
36.11
35.88
34.69
34.65
F
NPhth
23
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

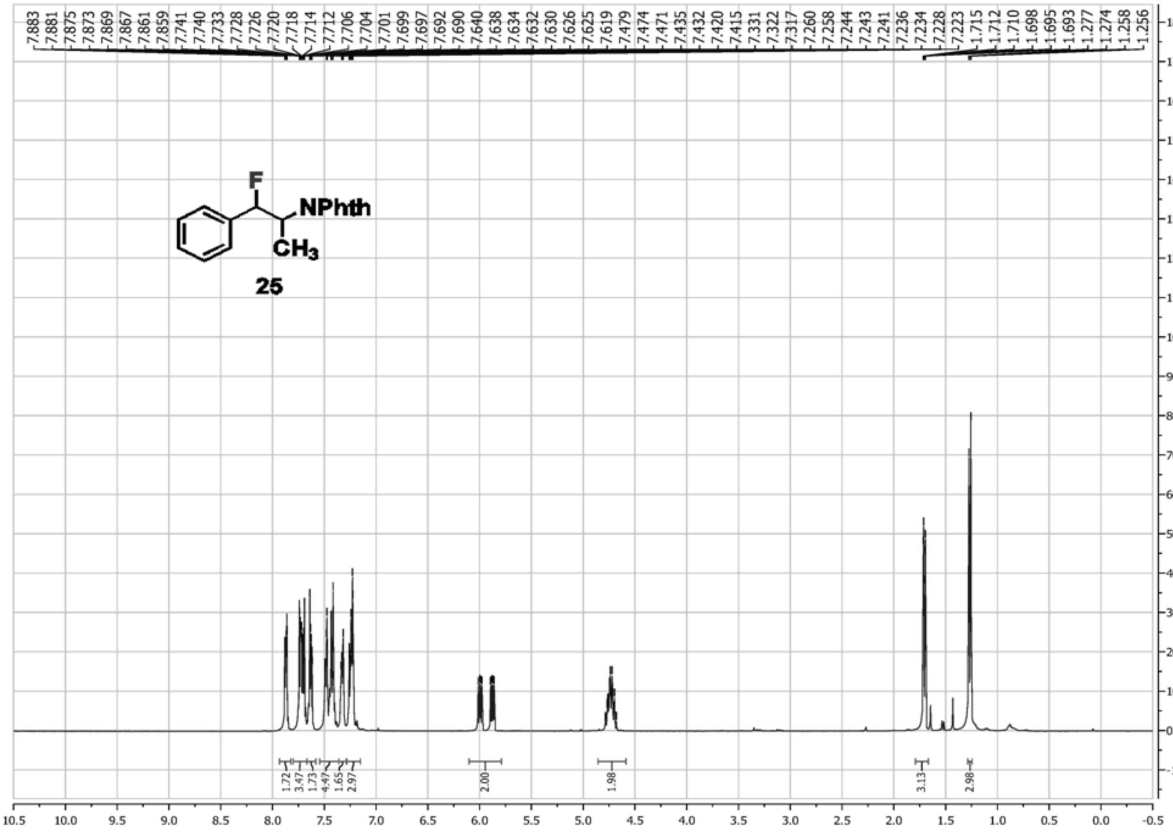


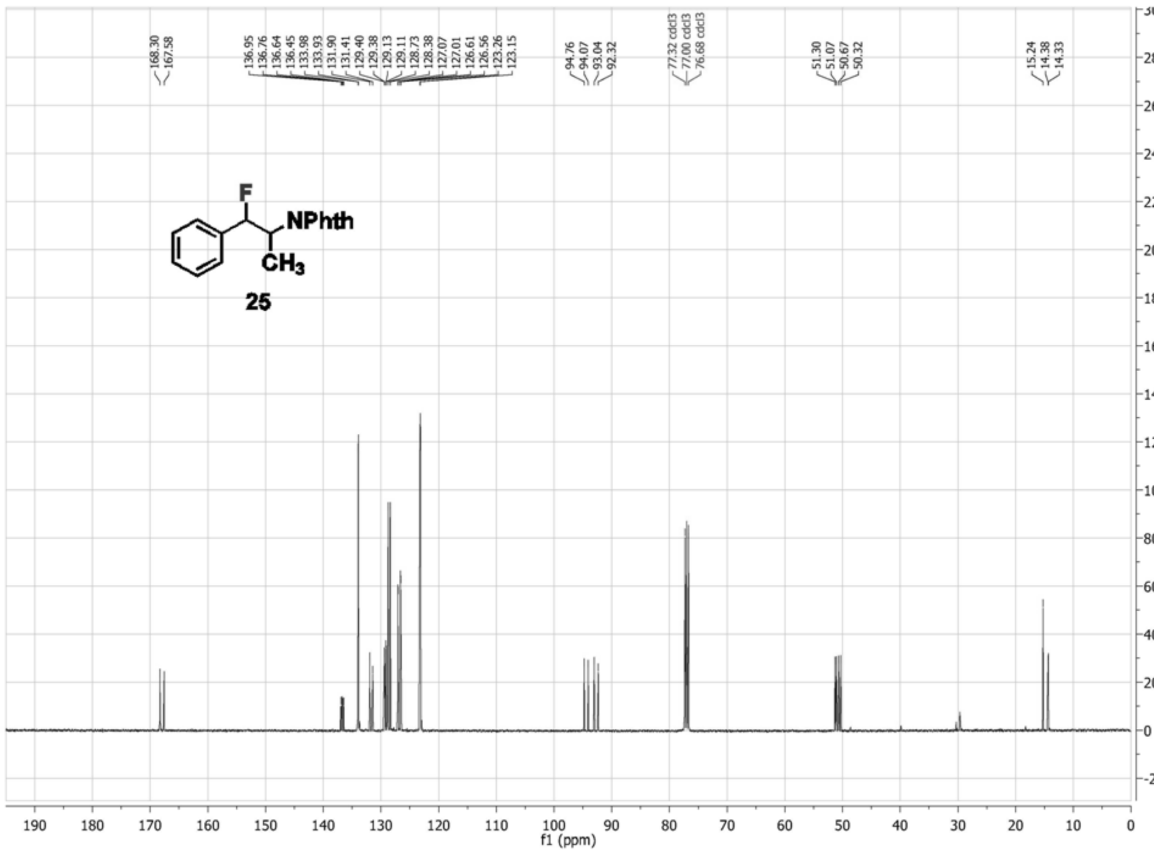
-176.00
-176.04
-176.08
-176.12
-176.17
-176.21
-176.25
F
NPhth
23
10000
5000
0
-175.9
-176.1
-176.3
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

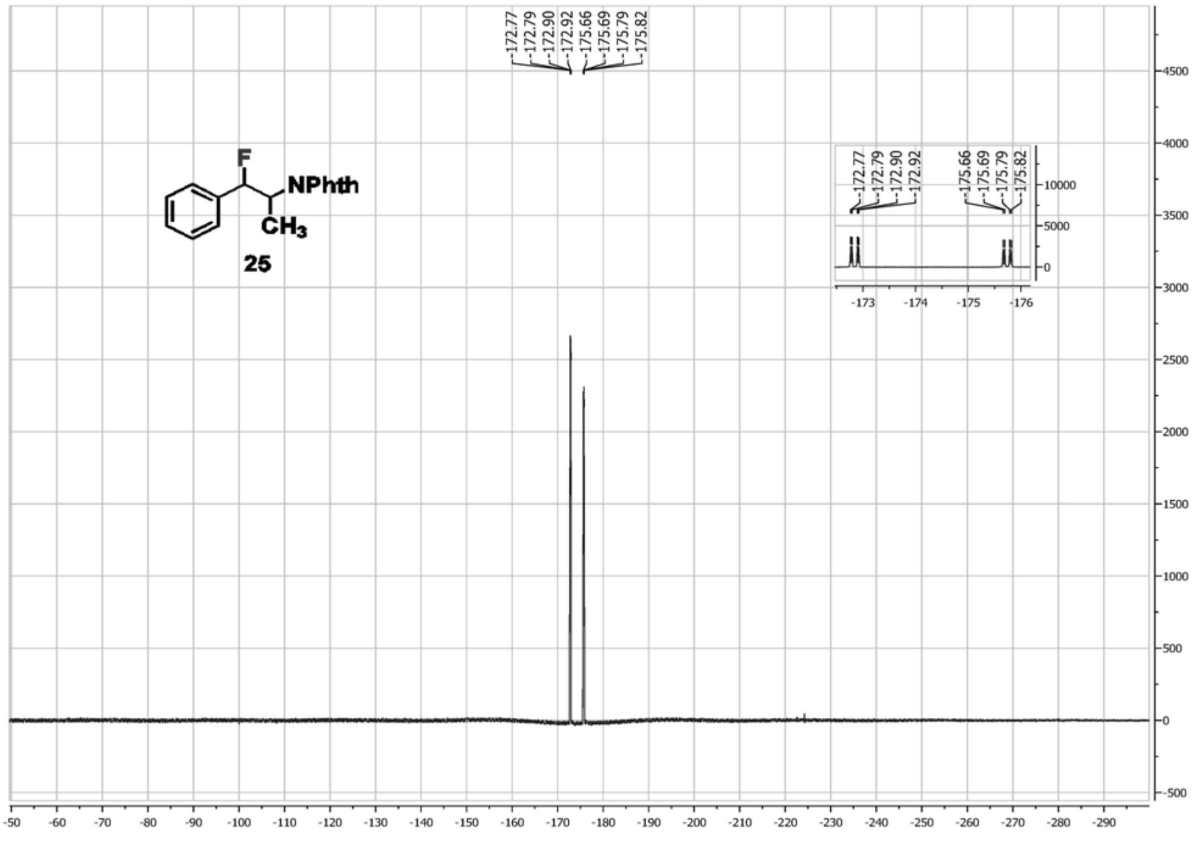

7.439 7.424 7.421 7.406 7.399 7.393 7.385 7.352 7.349 7.334 7.332 7.211 7.203 7.197 7.190 7.160 7.047 7.027 7.022 6.872 6.852 6.832 6.824 6.818 6.816 6.810 6.803 6.797 6.789 6.661 6.653 6.647 6.639 5.594 5.584 5.573 5.566 5.564 5.545 5.525
3.306
3.110
F
O
OCH3
NPhth
24
7.44 1.59 3.16 7.22 0.50 1.84 0.88 1.04
2.21
4.42
3.20
f1 (ppm)


167.59 167.27 166.72 166.66 166.58
137.46 137.27 136.17 135.98 133.98 133.91 132.00 131.51 129.55 129.53 129.35 129.33 128.74 128.60 128.30 c6d6 128.06 c6d6 127.82 c6d6 127.69 127.63 127.46 127.41 123.58 123.35
92.07 91.08 90.30 89.30
56.25 56.01 55.45 55.09 52.61 52.27
F
O
OCH3
NPhth
24
f1 (ppm)


-169.49
-169.54
-169.62
-169.66
-177.16
-177.19
-177.29
-177.32
F
O
OCH3
NPhth
24
-170
-172
-174
-176
f1 (ppm)
3000
2000
1000
0
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)


7.883
7.881
7.875
7.873
7.869
7.867
7.861
7.859
7.741
7.740
7.733
7.728
7.726
7.720
7.718
7.714
7.712
7.706
7.704
7.701
7.699
7.697
7.692
7.690
7.640
7.638
7.634
7.632
7.630
7.626
7.625
7.619
7.479
7.474
7.471
7.435
7.432
7.420
7.415
7.331
7.322
7.317
7.260
7.258
7.244
7.243
7.241
7.236
7.234
7.228
7.223
1.715
1.712
1.710
1.698
1.695
1.693
1.277
1.274
1.258
1.256
F
NPhth
CH3
25
1.72
3.47
1.73
4.47
1.65
2.97
2.00
1.98
3.13
2.98
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
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


168.30
167.58
136.95
136.76
136.64
136.45
133.98
133.93
131.90
131.41
129.40
129.38
129.13
129.11
128.73
128.38
127.07
127.01
126.61
126.56
123.26
123.15
94.76
94.07
93.04
92.32
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
51.30
51.07
50.67
50.32
15.24
14.38
14.33
F
NPhth
CH3
25
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-172.77
-172.79
-172.90
-172.92
-175.66
-175.69
-175.79
-175.82
F
NPhth
CH3
25
-172.77
-172.79
-172.90
-172.92
-175.66
-175.69
-175.79
-175.82
10000
5000
0
-173
-174
-175
-176
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
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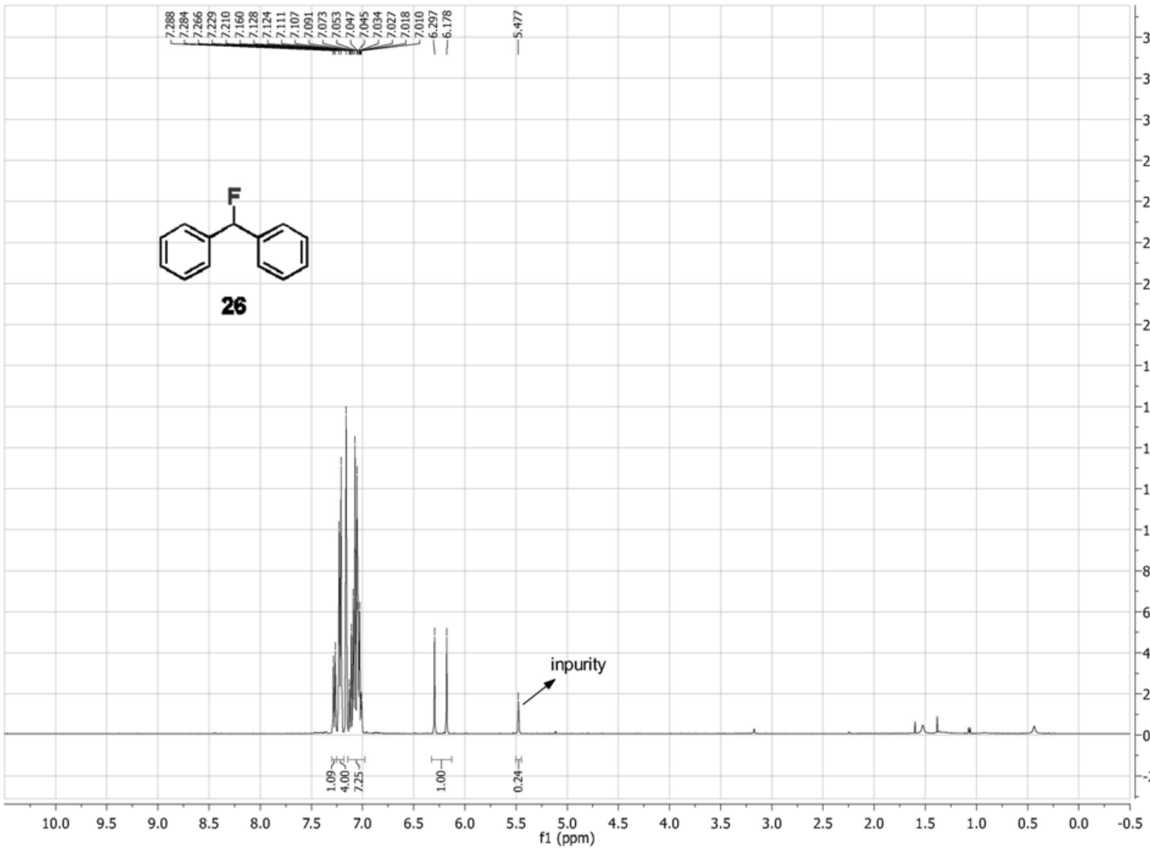
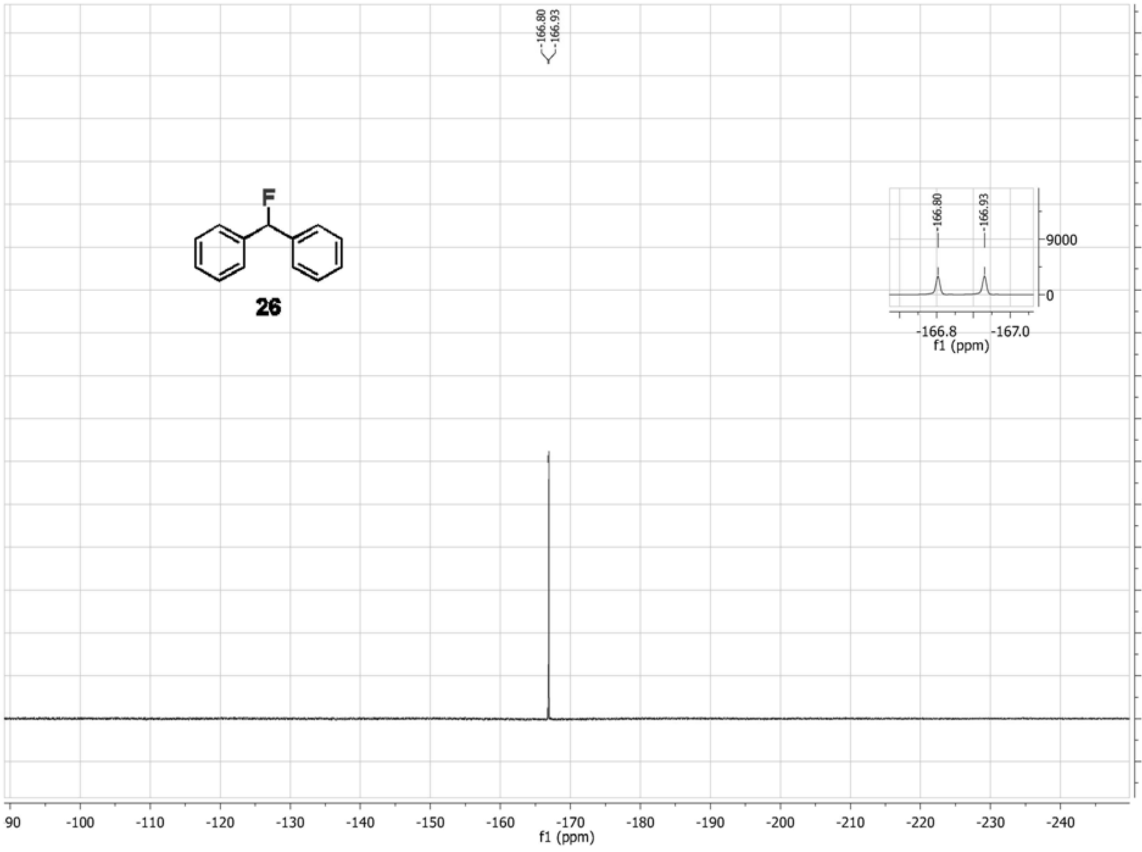
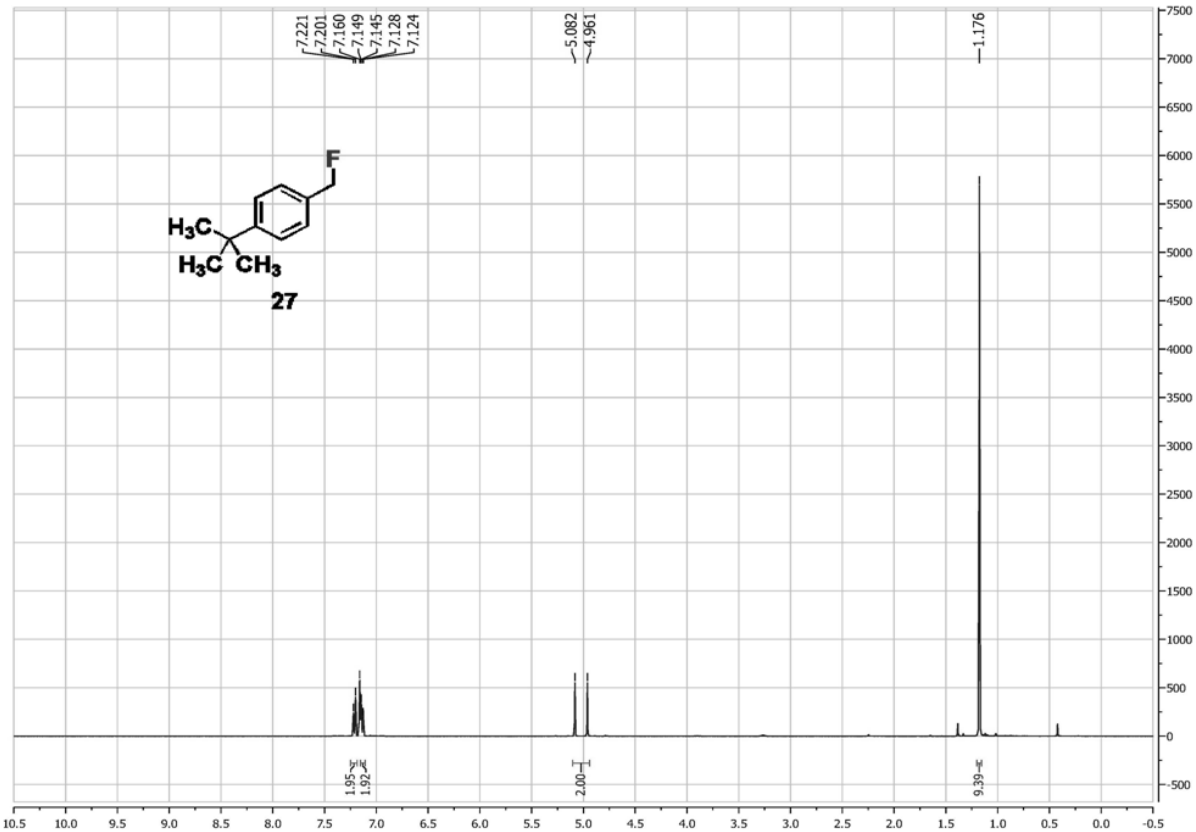
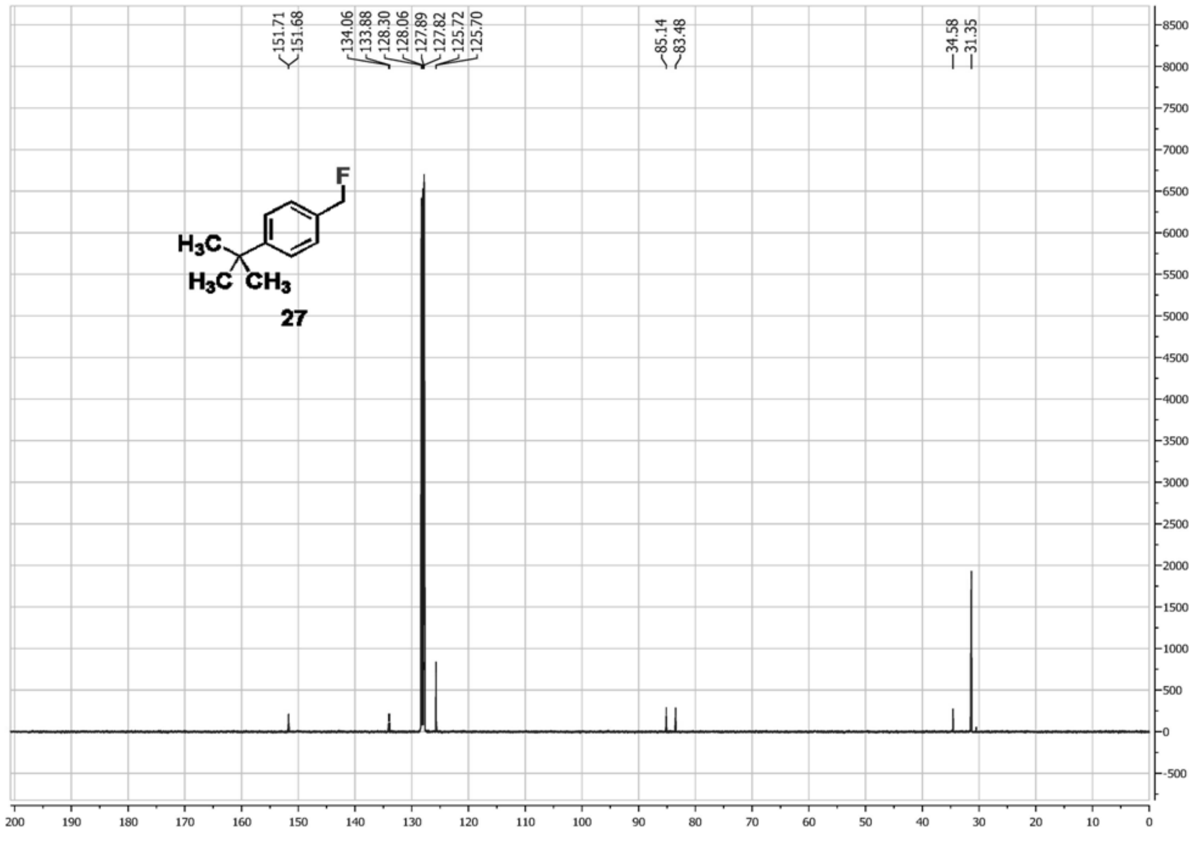
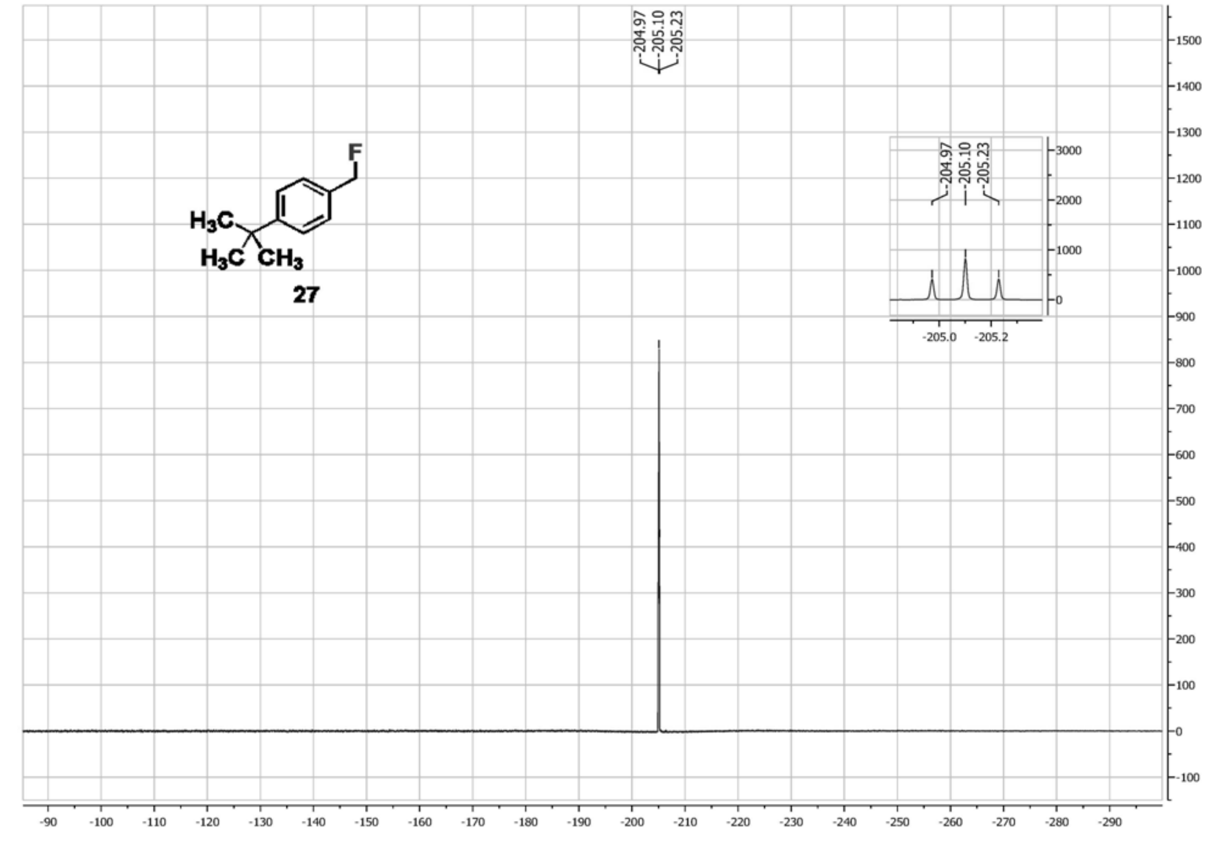
-250
-260
-270
-280
-290


7.288
7.284
7.266
7.229
7.210
7.160
7.128
7.124
7.111
7.107
7.091
7.073
7.053
7.047
7.045
7.034
7.027
7.018
7.010
6.297
6.178
5.477
F
26
inpurity
1.09
4.00
7.25
1.00
0.24
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
f1 (ppm)
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

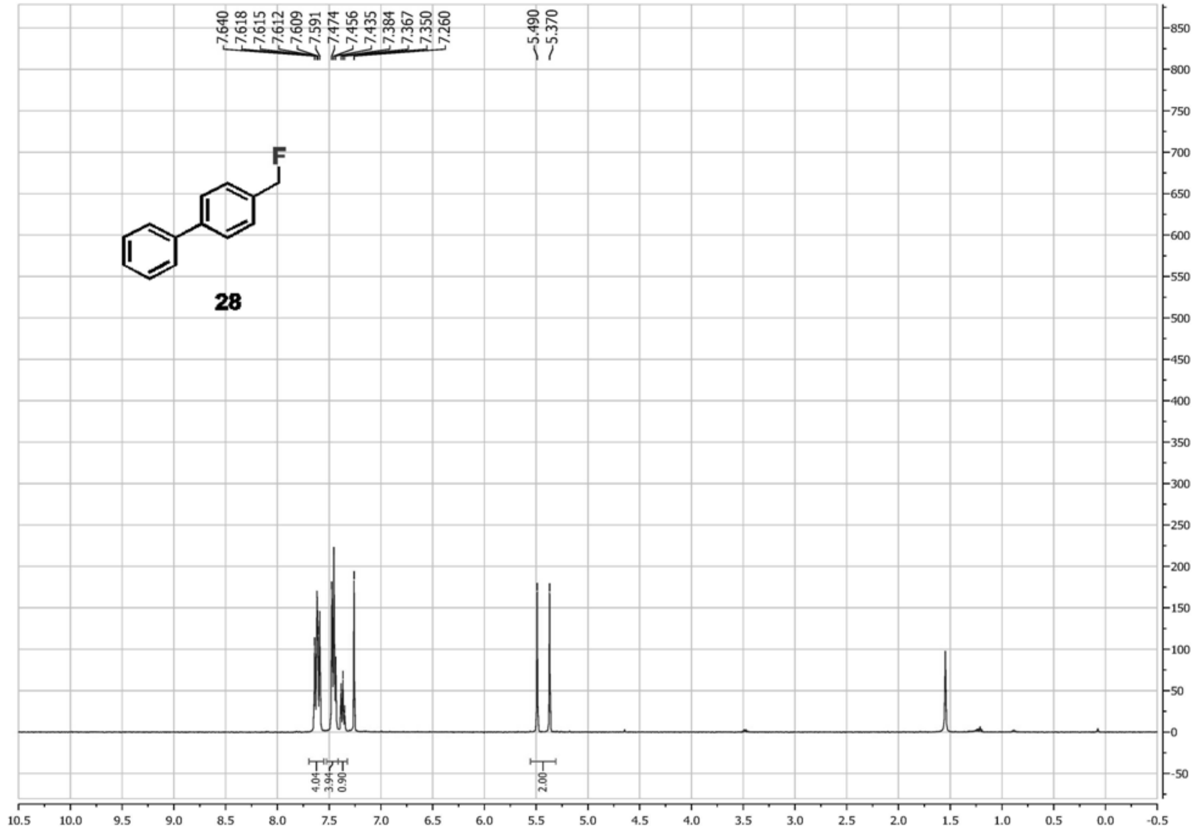

-166.80
-166.93
F
26
-166.80
-166.93
9000
0
-166.8
-167.0
f1 (ppm)
90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500


7.221
7.201
7.160
7.149
7.145
7.128
7.124
5.082
4.961
1.176
H_3C
H_3C
CH_3
F
27
1.95
1.92
2.00
9.39
10.5 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
7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

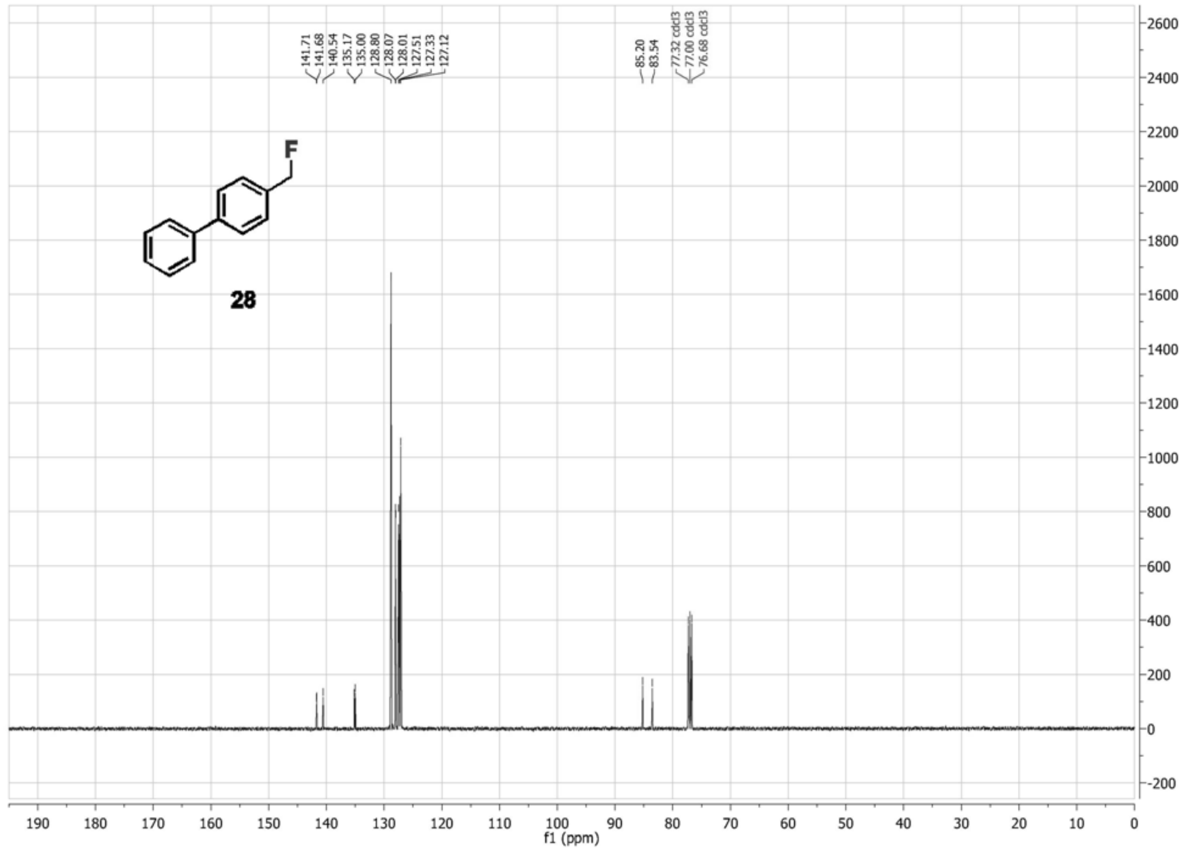

151.71
151.68
134.06
133.88
128.30
128.06
127.89
127.82
125.72
125.70
85.14
83.48
34.58
31.35
H_3C
H_3C
CH_3
F
27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

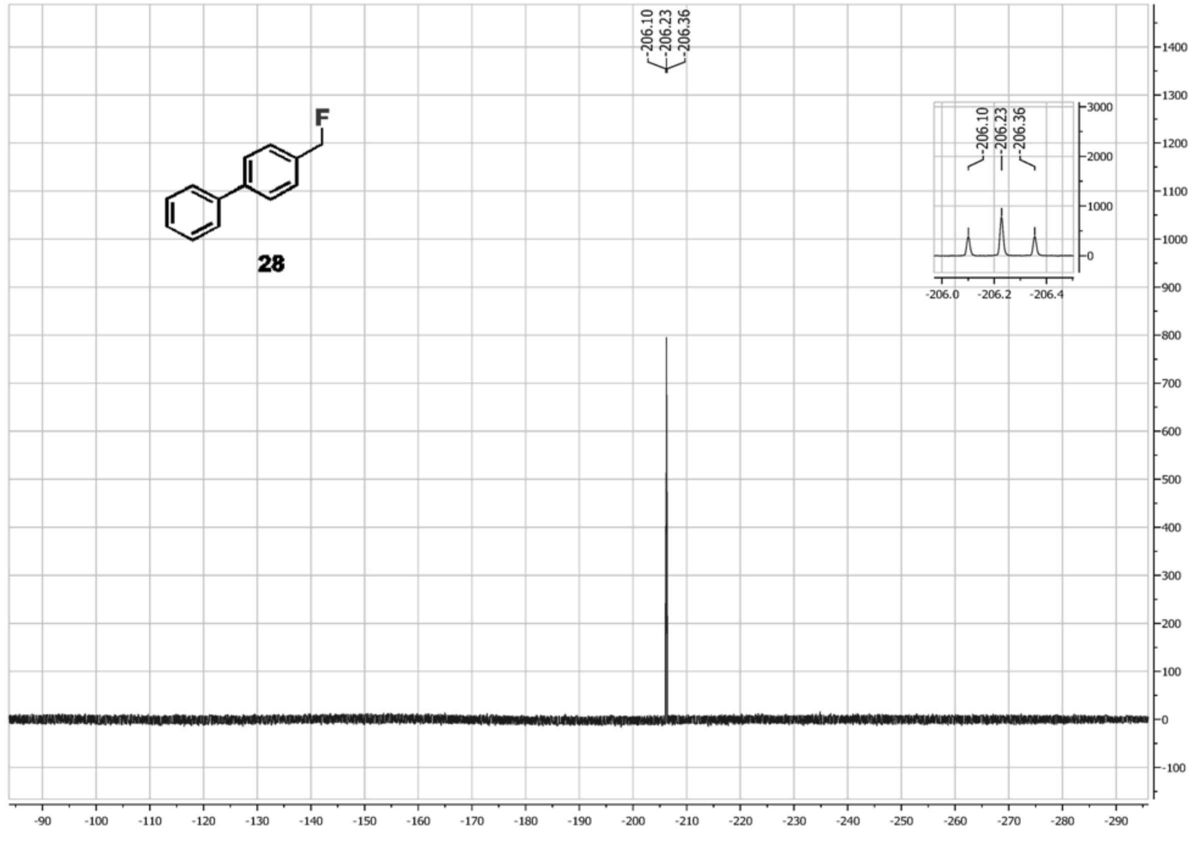

-204.97
-205.10
-205.23
H3C
H3C
CH3
F
-205.0
-205.2
3000
2000
1000
0
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
-280
-290

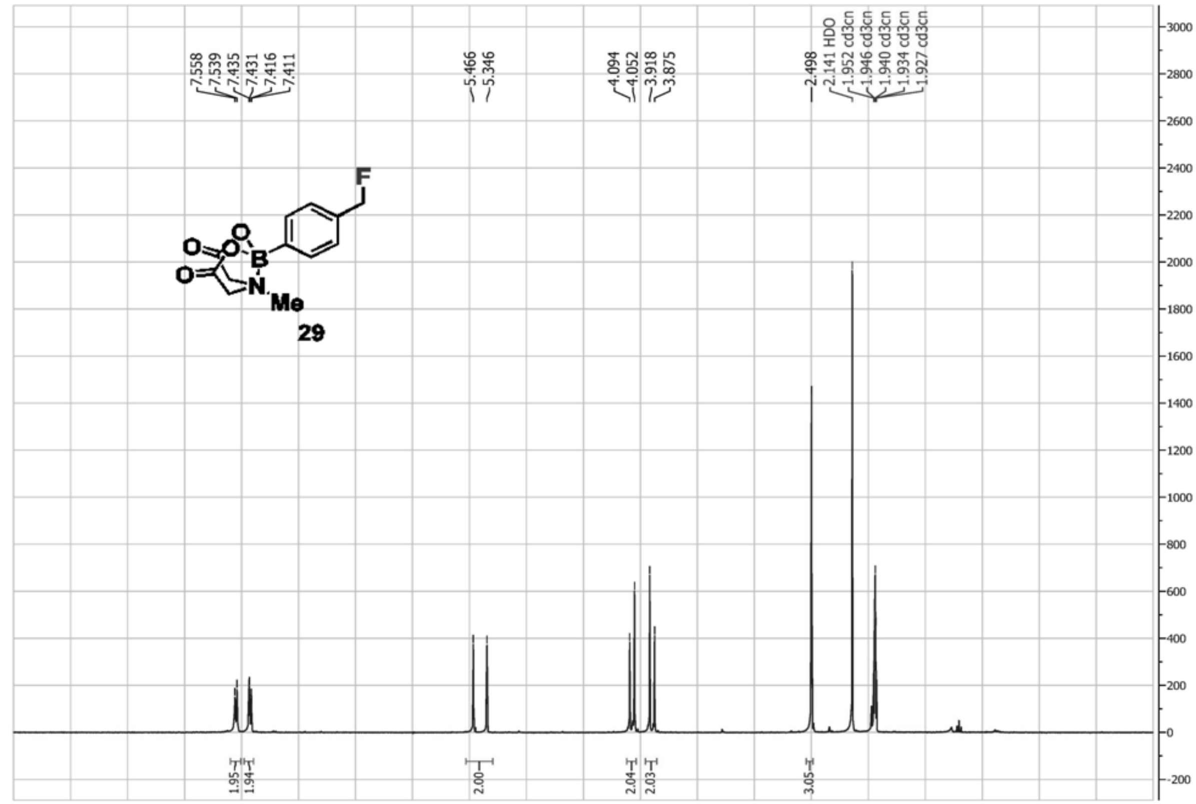
27


7.640
7.618
7.615
7.612
7.609
7.591
7.474
7.456
7.435
7.384
7.367
7.350
7.260
5.490
5.370
F
4.04
3.94
0.90
2.00
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
10.5
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

28


141.71
141.68
140.54
135.17
135.00
128.80
128.07
128.01
127.51
127.33
127.12
85.20
83.54
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
F
28
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-206.10
-206.23
-206.36
F
28
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
3000
2000
1000
0
-206.0
-206.2
-206.4
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
-250
-260
-270
-280
-290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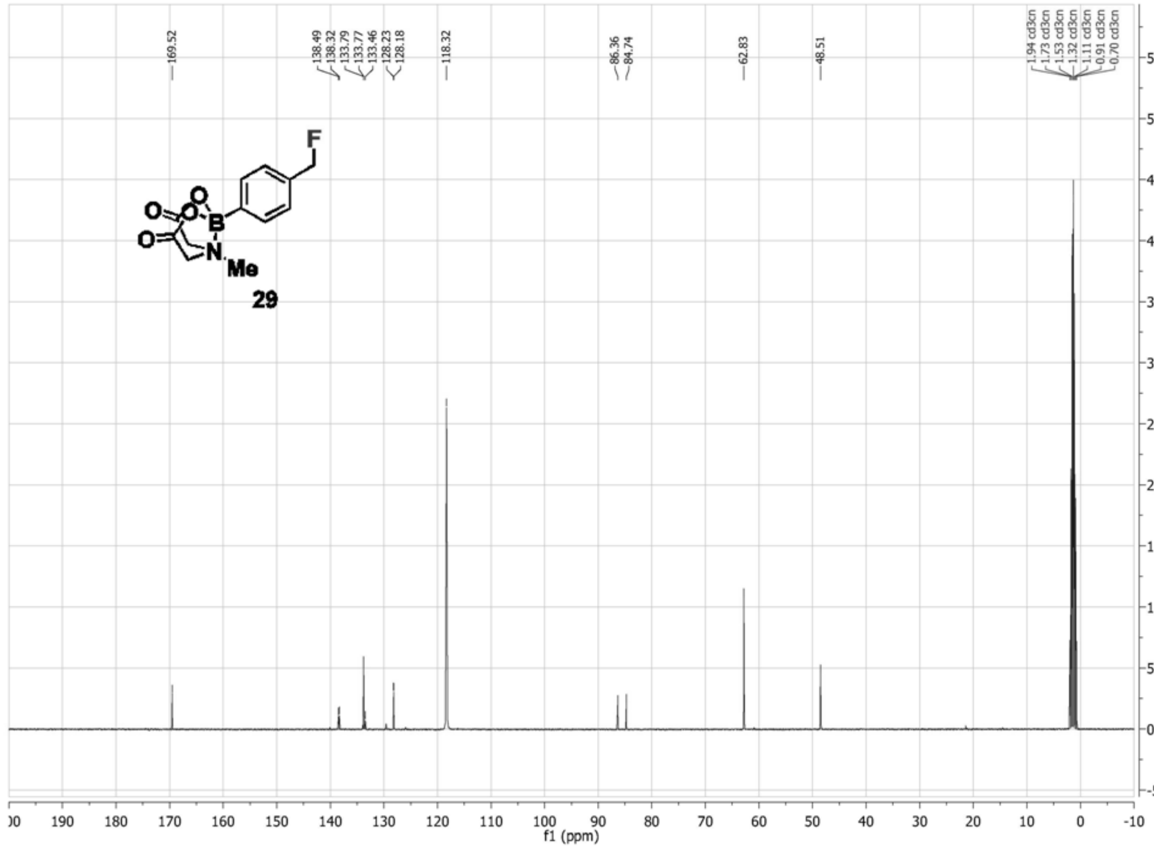
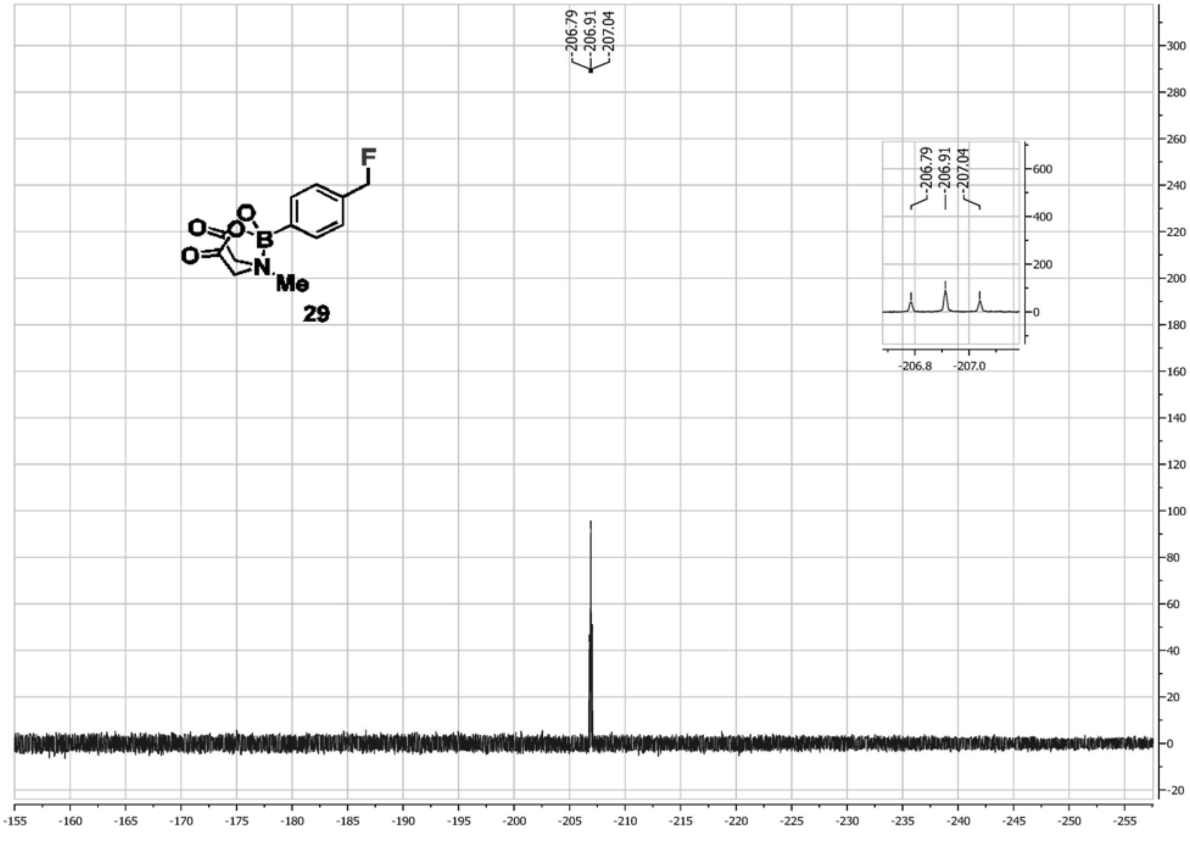
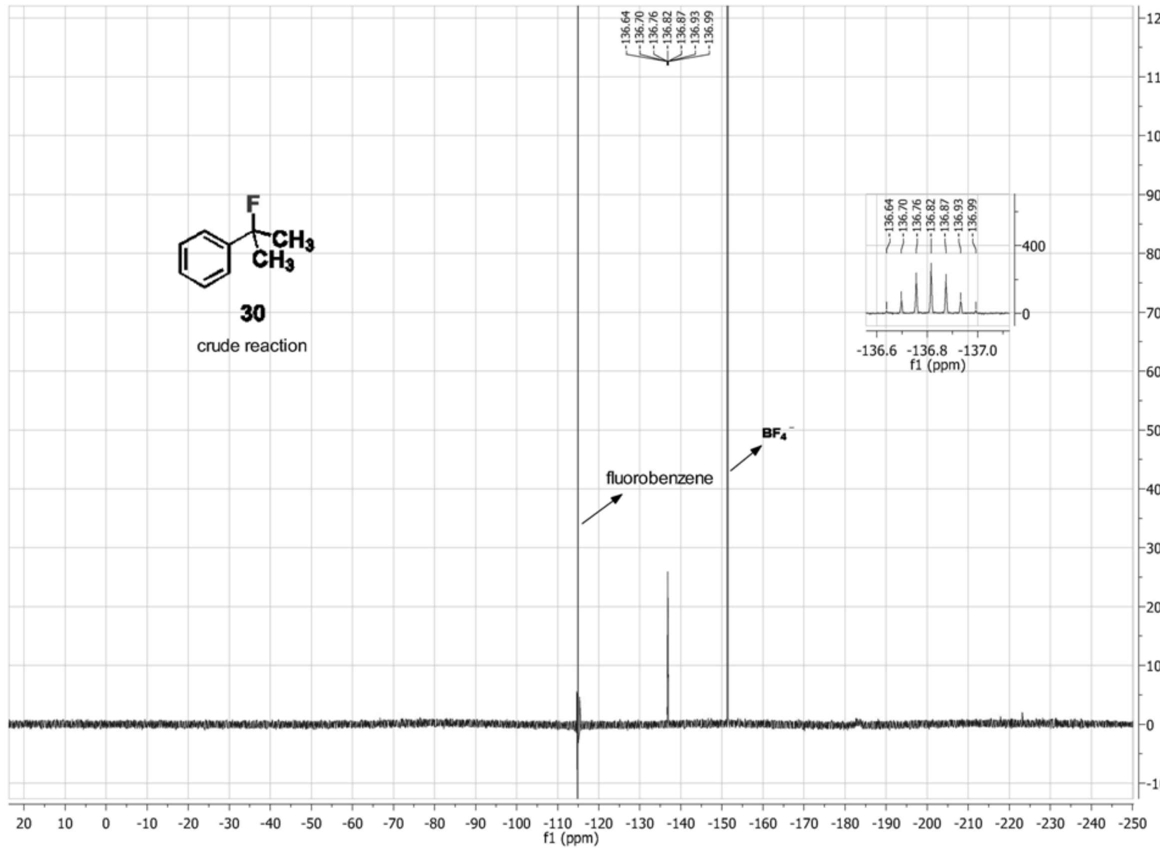
7.539
7.435
7.431
7.416
7.411
5.466
5.346
4.094
4.052
3.918
3.875
2.498
2.141 HDO
1.952 cd3cn
1.946 cd3cn
1.940 cd3cn
1.934 cd3cn
1.927 cd3cn
F
O
O
O
O
B
N
Me
29
1.95
1.94
2.00
2.04
2.03
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200

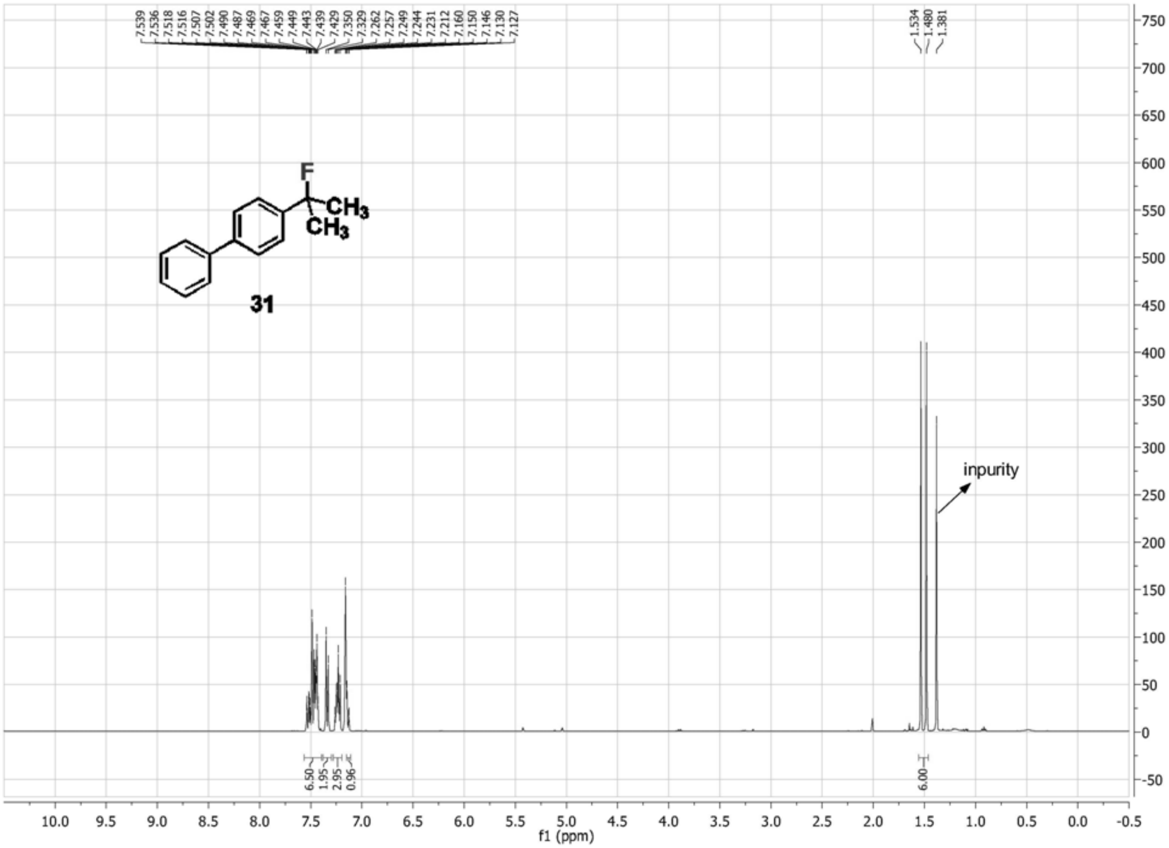

169.52
138.49
138.32
133.79
133.77
133.46
128.23
128.18
118.32
86.36
84.74
62.83
48.51
1.94 cd3cn
1.73 cd3cn
1.53 cd3cn
1.32 cd3cn
1.11 cd3cn
0.91 cd3cn
0.70 cd3cn
F
O
O
O
O
B
N
Me
29
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

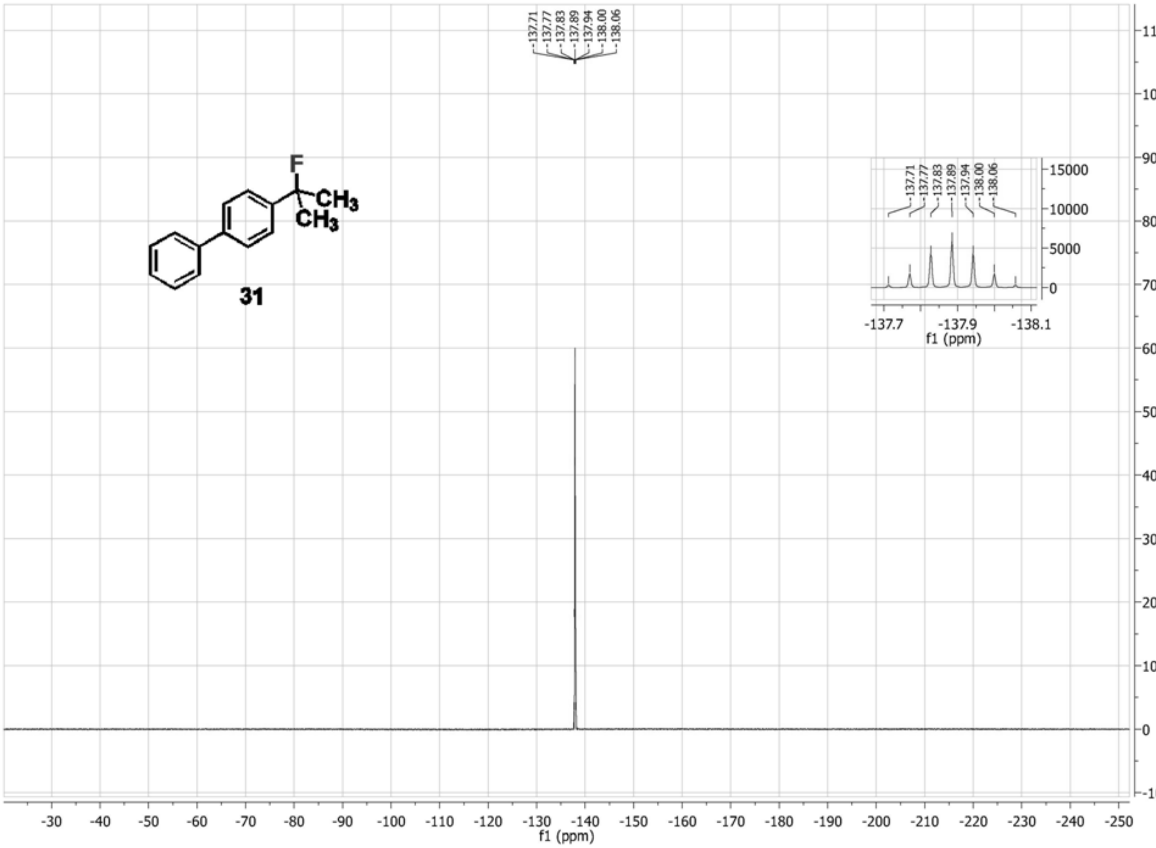


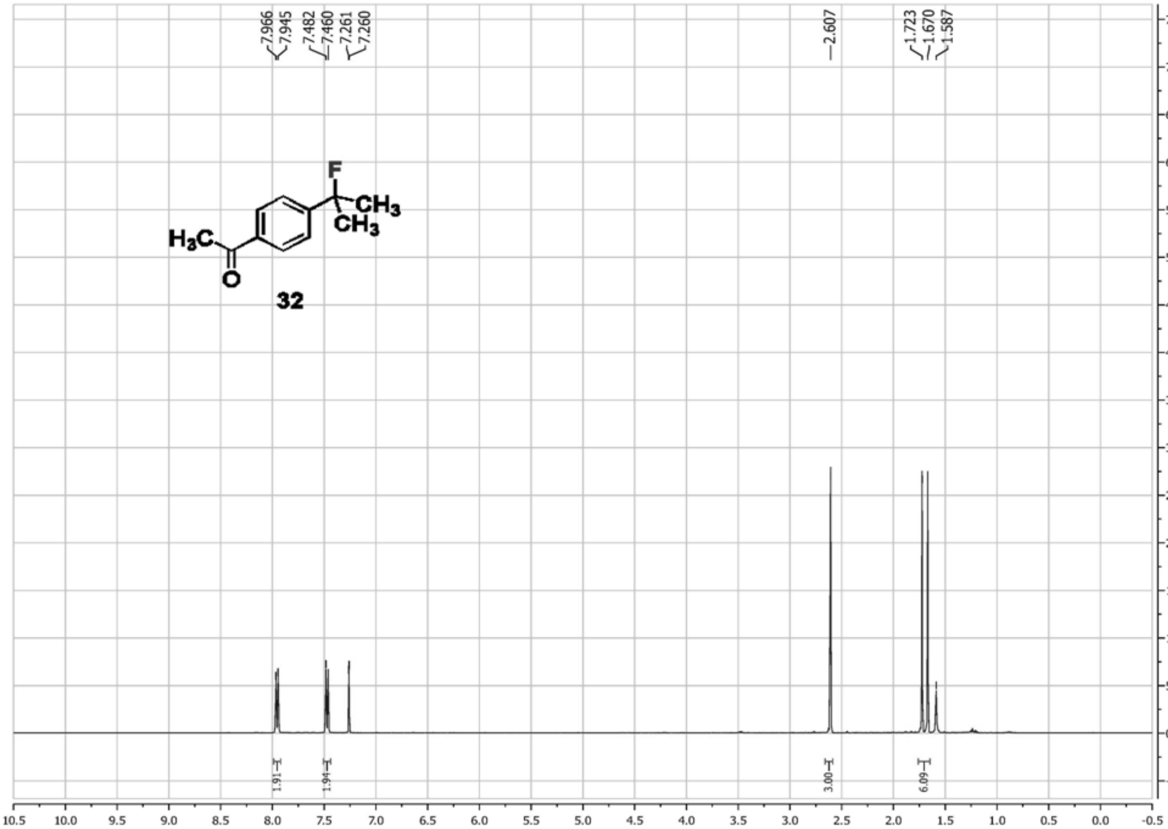
-206.79
-206.91
-207.04
29
-206.8
-207.0
-155 -160 -165 -170 -175 -180 -185 -190 -195 -200 -205 -210 -215 -220 -225 -230 -235 -240 -245 -250 -255
300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20

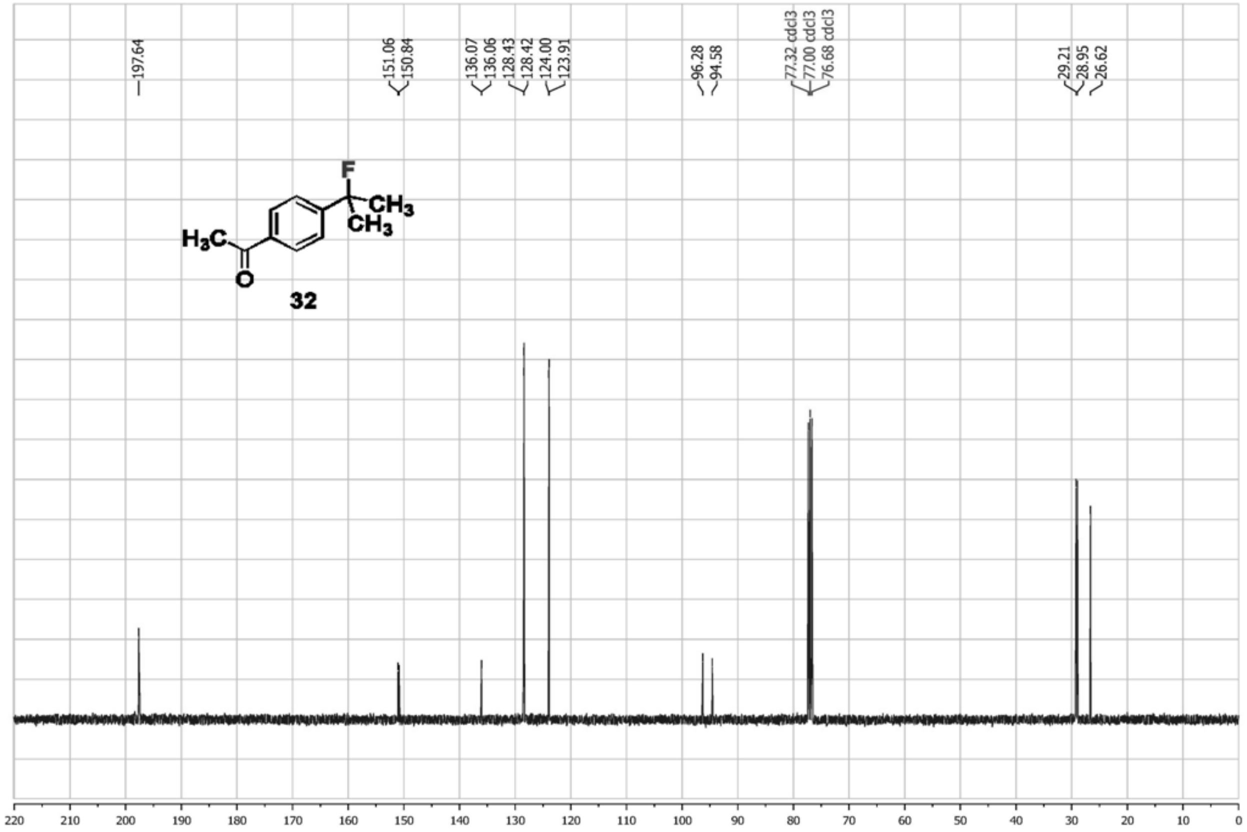


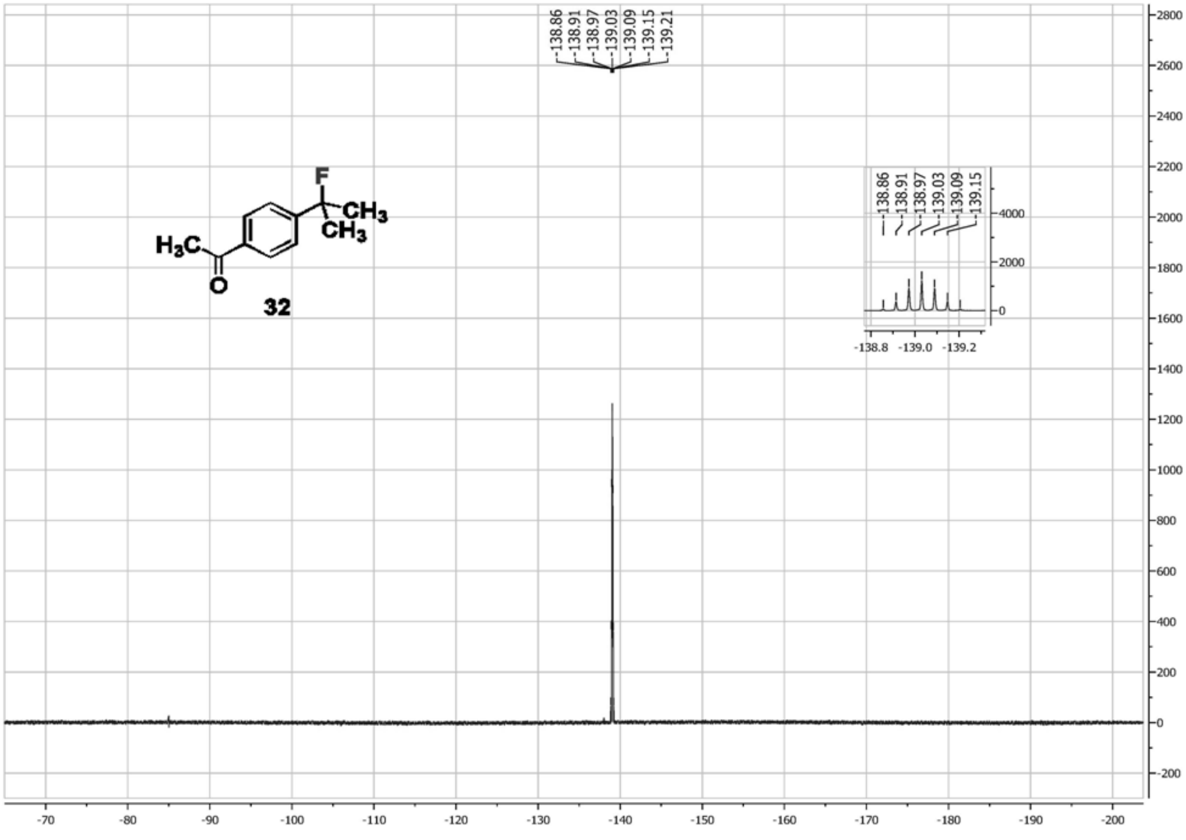
-136.64
-136.70
-136.76
-136.82
-136.87
-136.93
-136.99
30
crude reaction
fluorobenzene
BF4⁻
-136.6 -136.8 -137.0
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)
1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

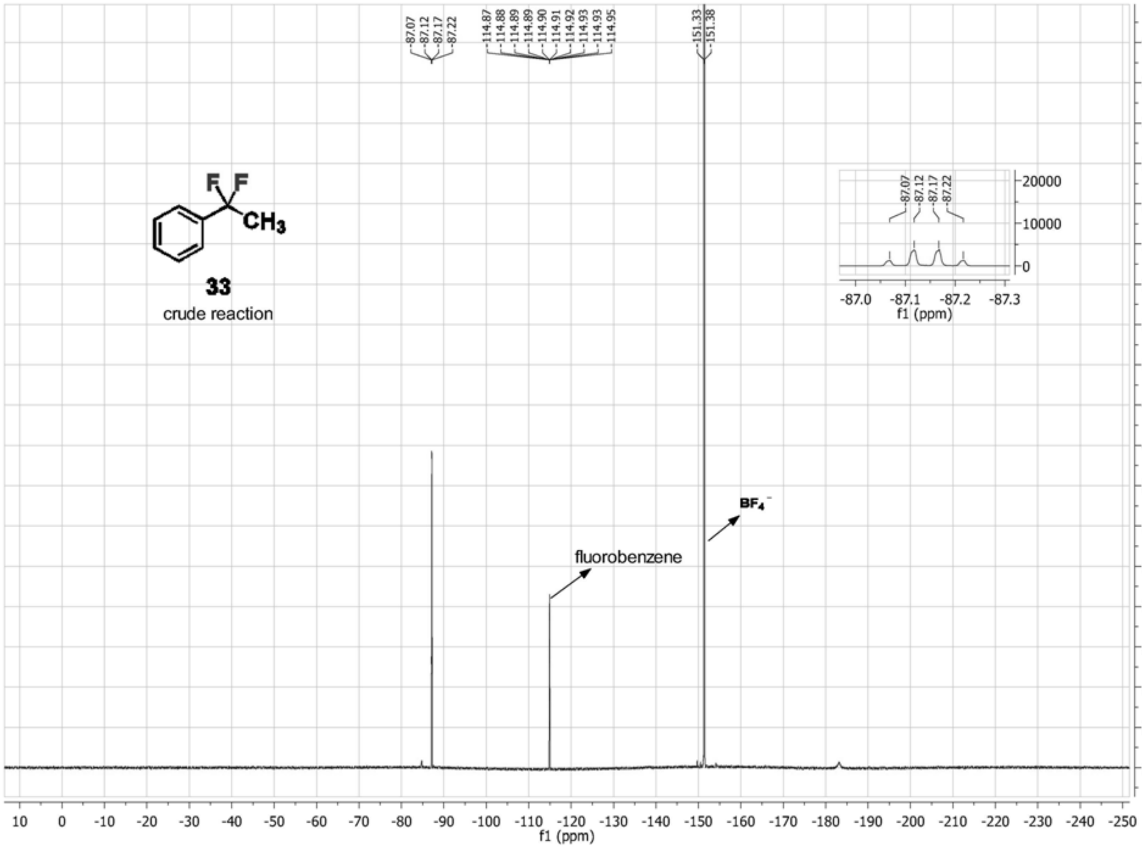

7.539
7.536
7.518
7.516
7.507
7.502
7.490
7.487
7.469
7.467
7.459
7.449
7.443
7.439
7.429
7.350
7.329
7.262
7.257
7.249
7.244
7.231
7.212
7.160
7.150
7.146
7.130
7.127
1.534
1.480
1.381
F
CH3
CH3
31
inpurity
6.50
1.95
2.95
0.96
6.00
f1 (ppm)

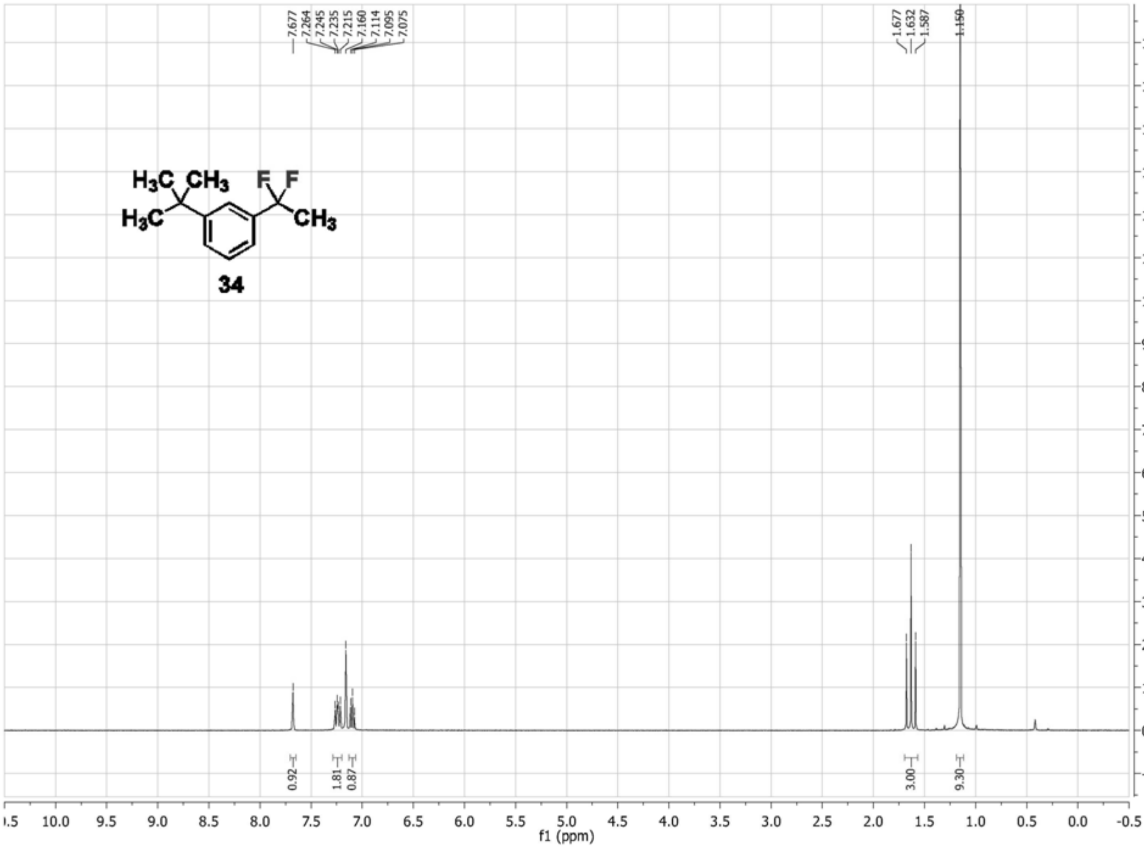

-137.71
-137.77
-137.83
-137.89
-137.94
-138.00
-138.06
F
CH3
CH3
31
-137.7
-137.9
-138.1
f1 (ppm)

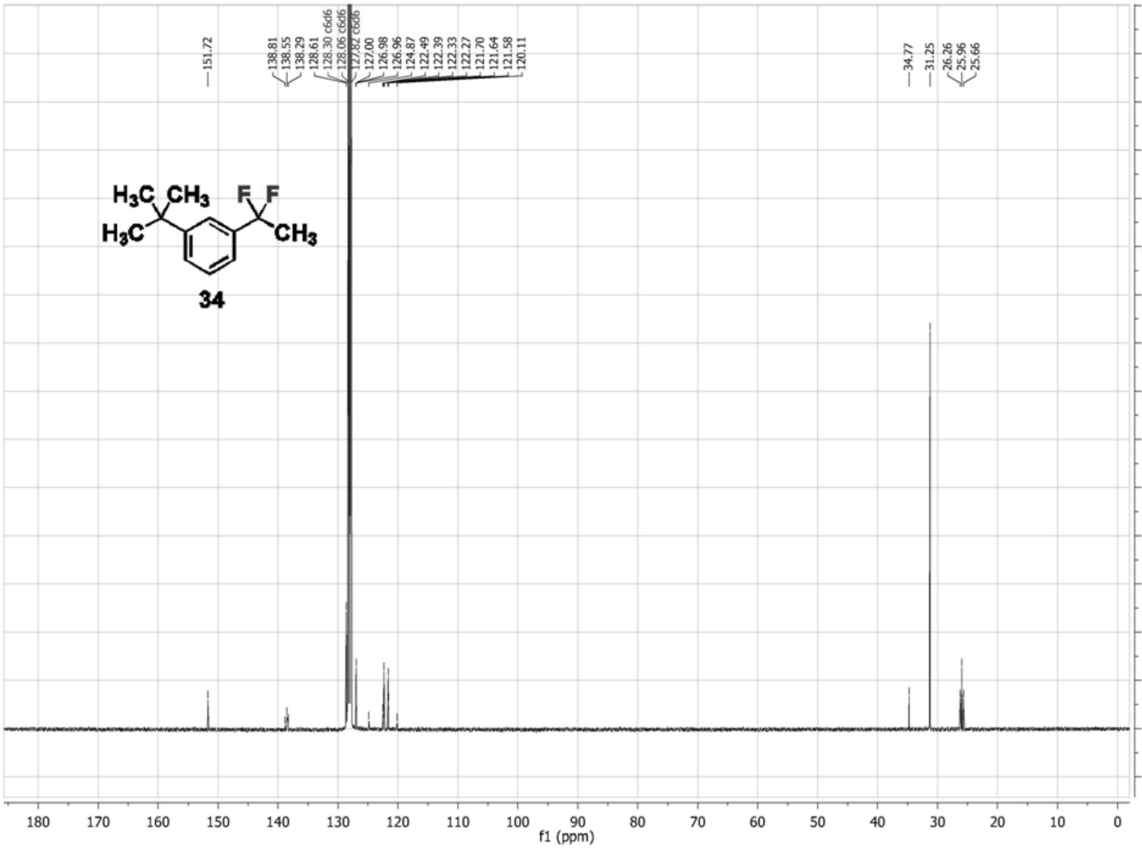

7.966
7.945
7.482
7.460
7.261
7.260
2.607
1.723
1.670
1.587
F
CH3
CH3
H3C
O
32
1.91
1.94
3.00
6.09
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

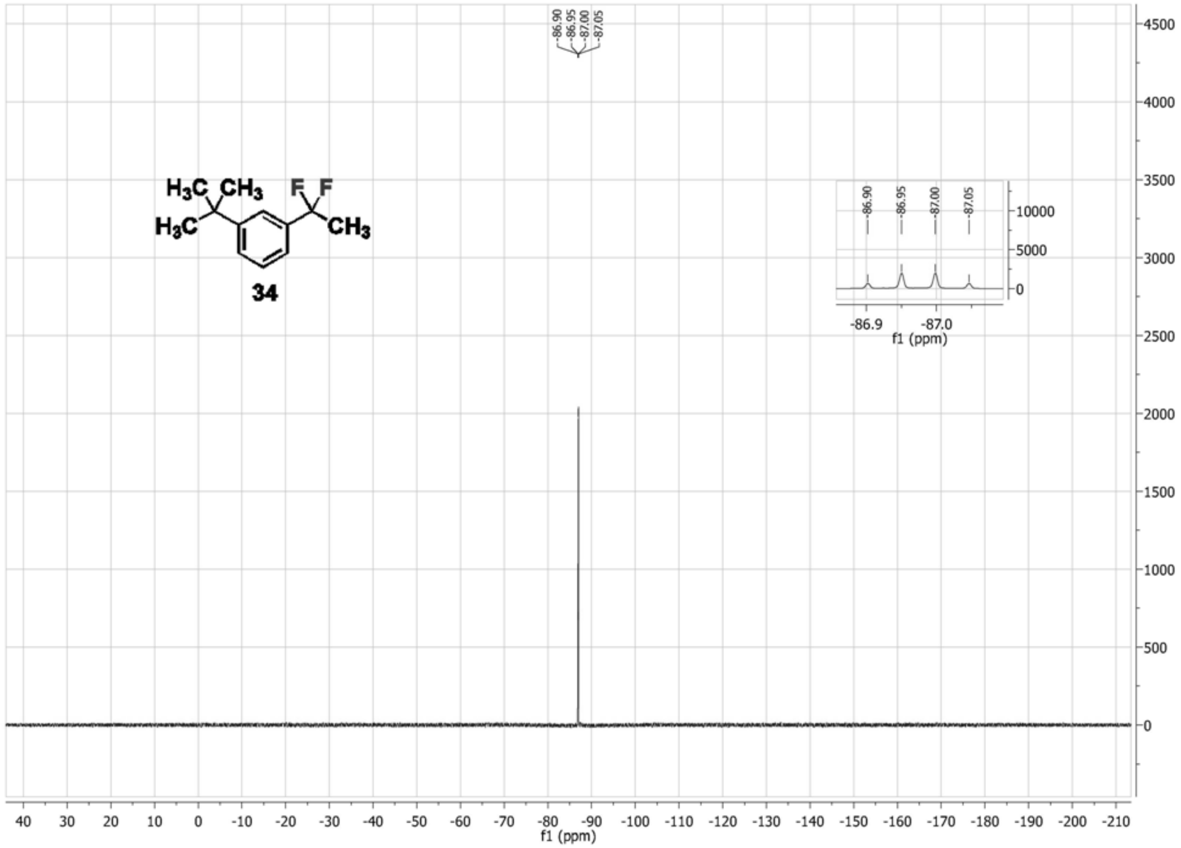

197.64
151.06
150.84
136.07
136.06
128.43
128.42
124.00
123.91
96.28
94.58
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
29.21
28.95
26.62
F
CH3
CH3
H3C
O
32
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

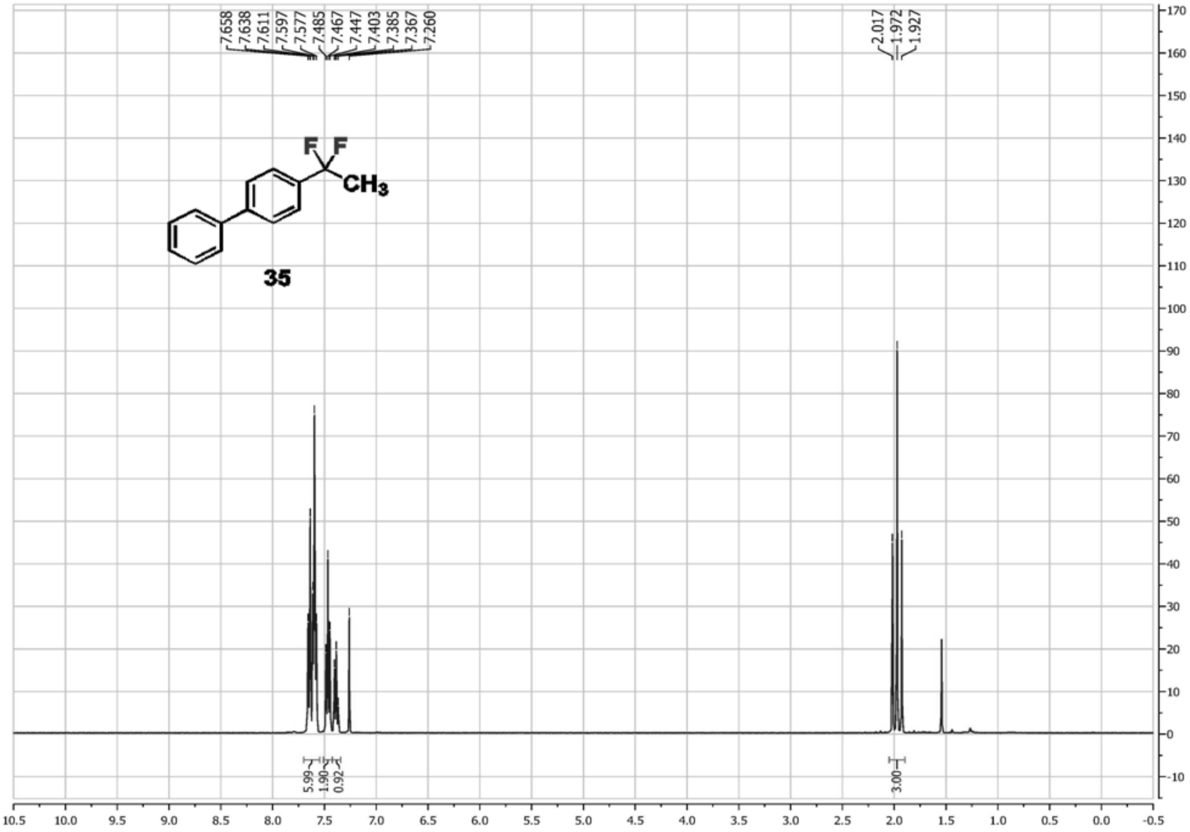

-138.86
-138.91
-138.97
-139.03
-139.09
-139.15
-139.21
F
CH3
CH3
H3C
O
32
-138.8 -139.0 -139.2
4000
2000
0
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200

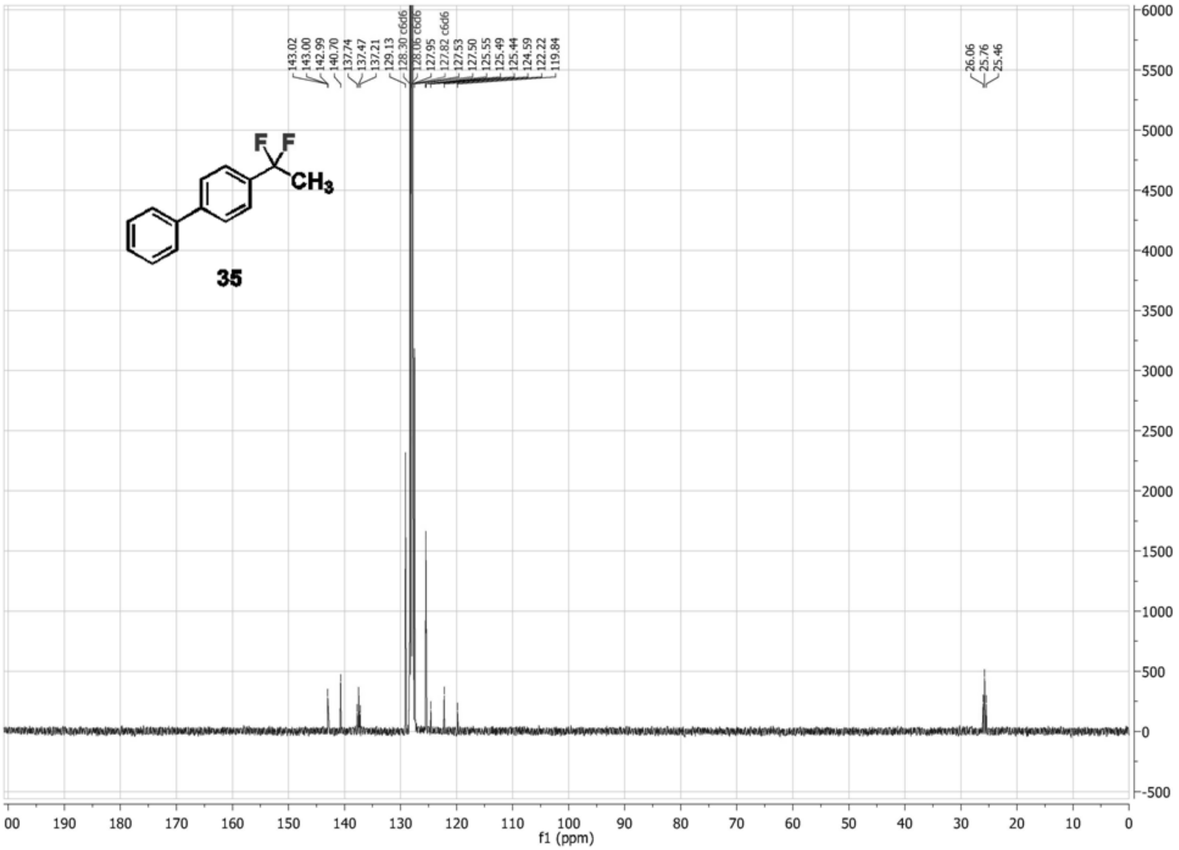

-87.07
-87.12
-87.17
-87.22
-114.87
-114.88
-114.89
-114.89
-114.90
-114.91
-114.92
-114.93
-114.93
-114.95
-151.33
-151.38
F F
CH3
33
crude reaction
20000
10000
0
-87.0 -87.1 -87.2 -87.3
f1 (ppm)
fluorobenzene
BF4⁻
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

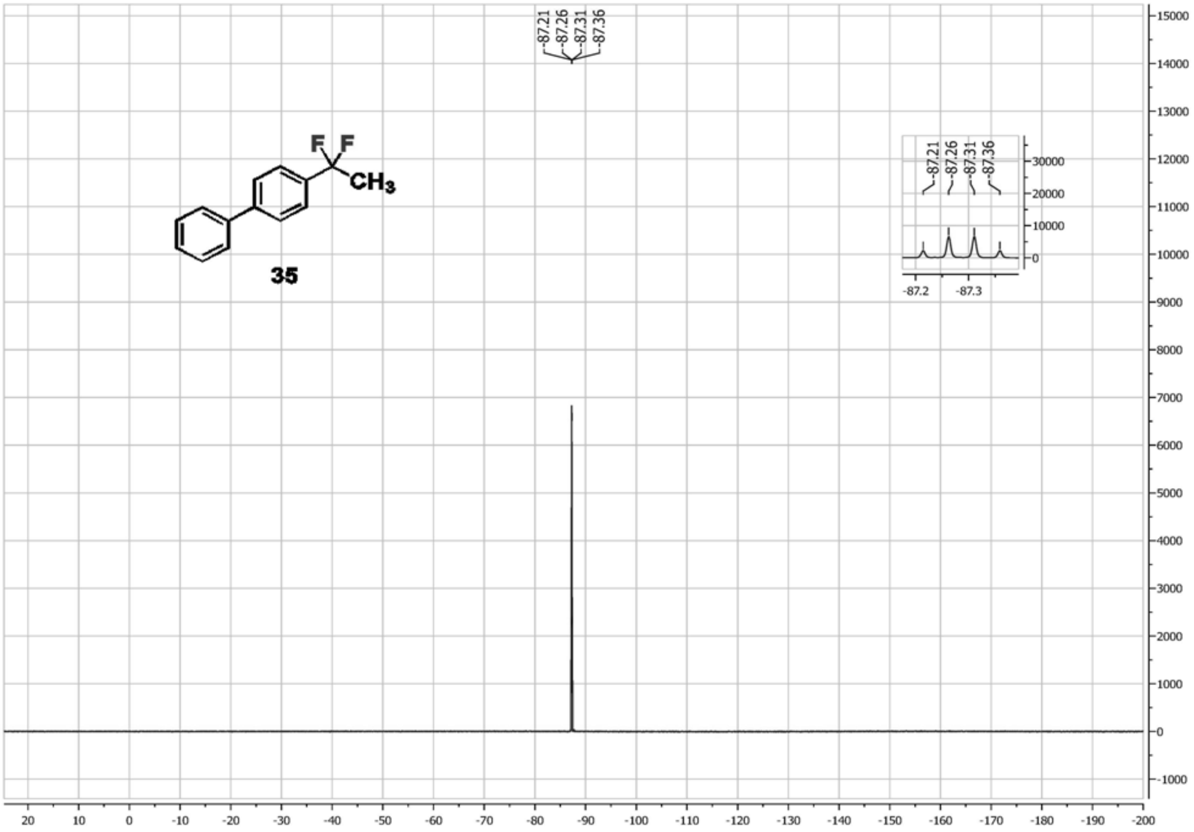

34
7.677
7.264
7.245
7.235
7.215
7.160
7.114
7.095
7.075
1.677
1.632
1.587
1.150
0.92
1.81
0.87
3.00
9.30
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

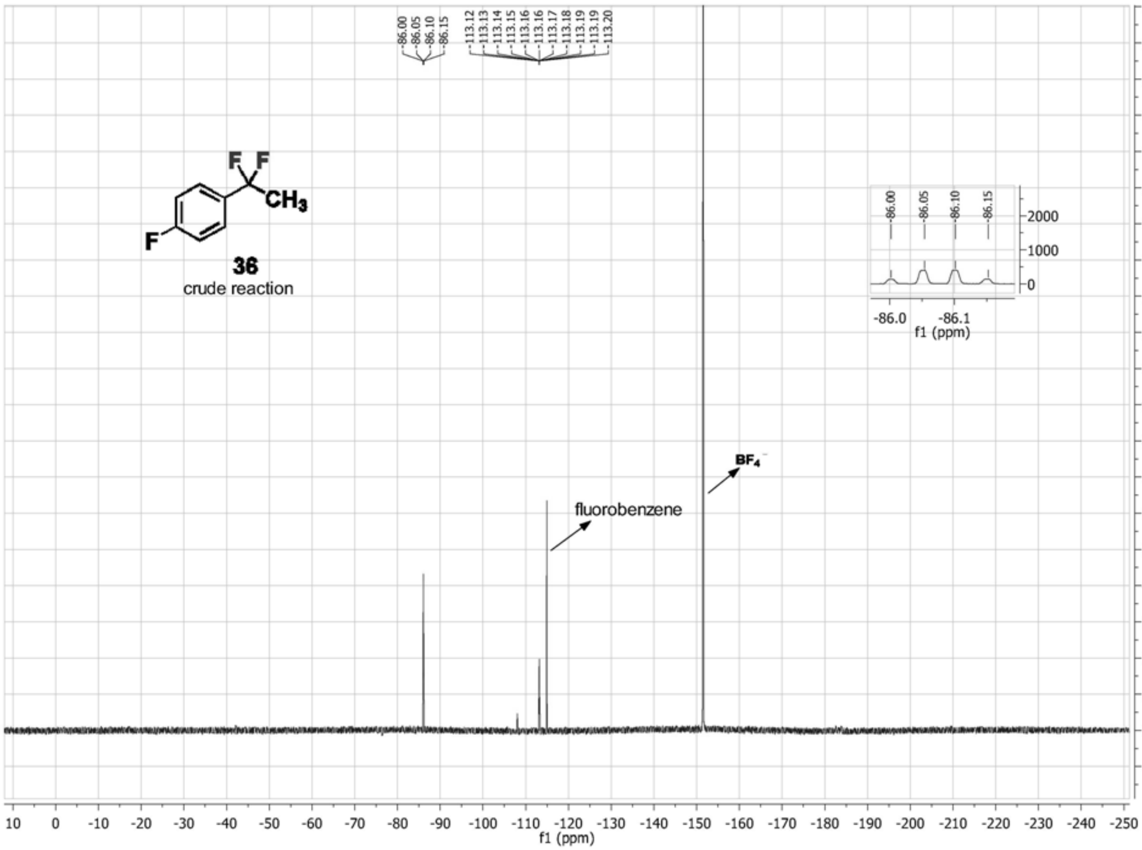

34
151.72
138.81
138.55
138.29
128.61
128.30 c6d6
128.06 c6d6
127.82 c6d6
127.00
126.98
126.96
124.87
122.49
122.39
122.33
122.27
121.70
121.64
121.58
120.11
34.77
31.25
26.26
25.96
25.66
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-86.90
-86.95
-87.00
-87.05
H3C CH3
H3C
F F
CH3
34
-86.9
-87.0
f1 (ppm)
10000
5000
0
4500
4000
3500
3000
2500
2000
1500
1000
500
0
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.658
7.638
7.611
7.597
7.577
7.485
7.467
7.447
7.403
7.385
7.367
7.260
2.017
1.972
1.927
F F
CH3
35
5.99
1.90
0.92
3.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
10.5 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


143.02
143.00
142.99
140.70
137.74
137.47
137.21
129.13
128.30 c6d6
128.06 c6d6
127.95
127.82 c6d6
127.53
127.50
125.55
125.49
125.44
124.59
122.22
119.84
26.06
25.76
25.46
F
F
CH3
35
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-87.21
-87.26
-87.31
-87.36
F
F
CH3
35
-87.21
-87.26
-87.31
-87.36
30000
20000
10000
0
-87.2
-87.3
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200



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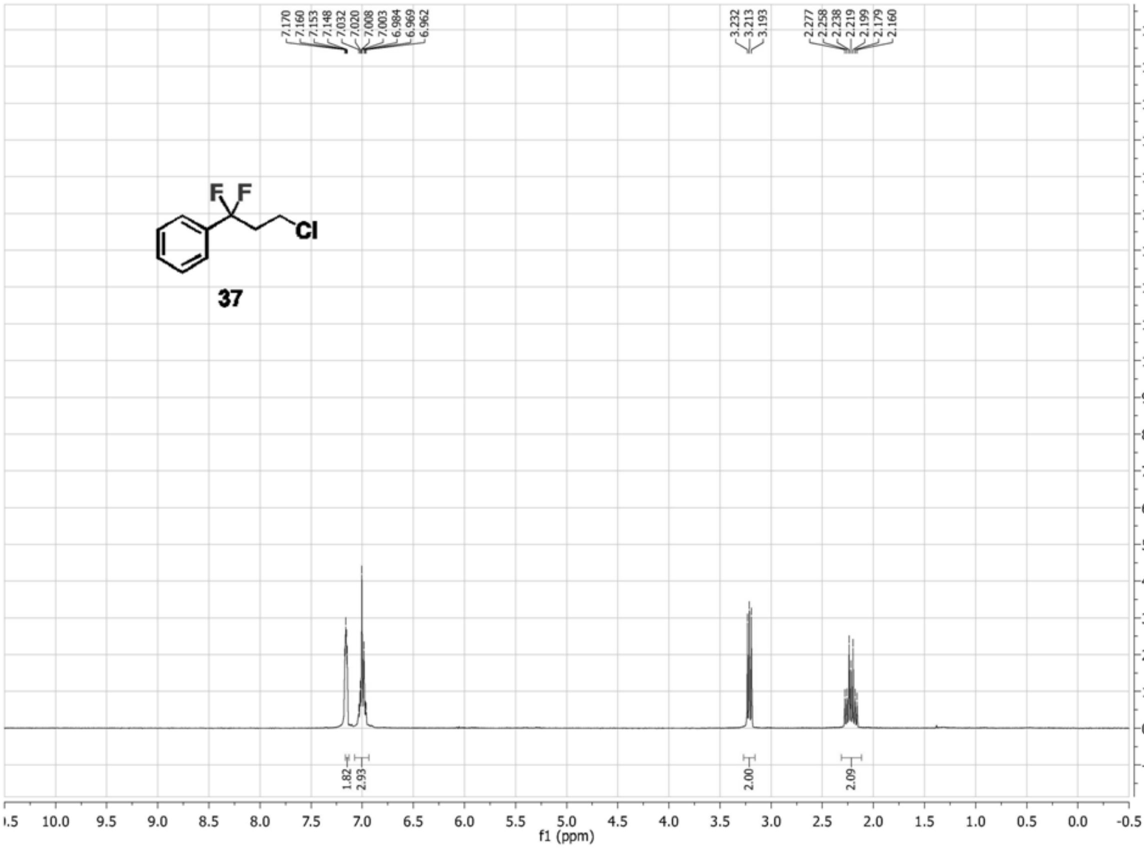
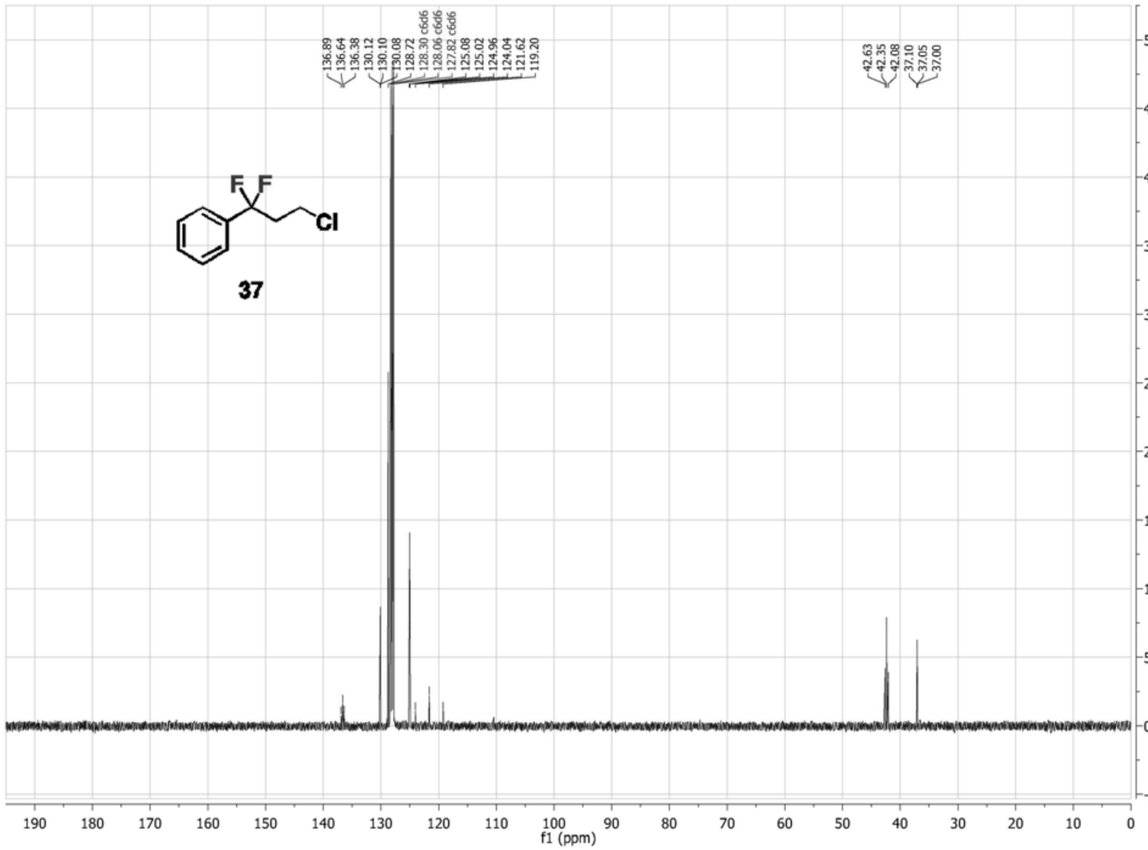
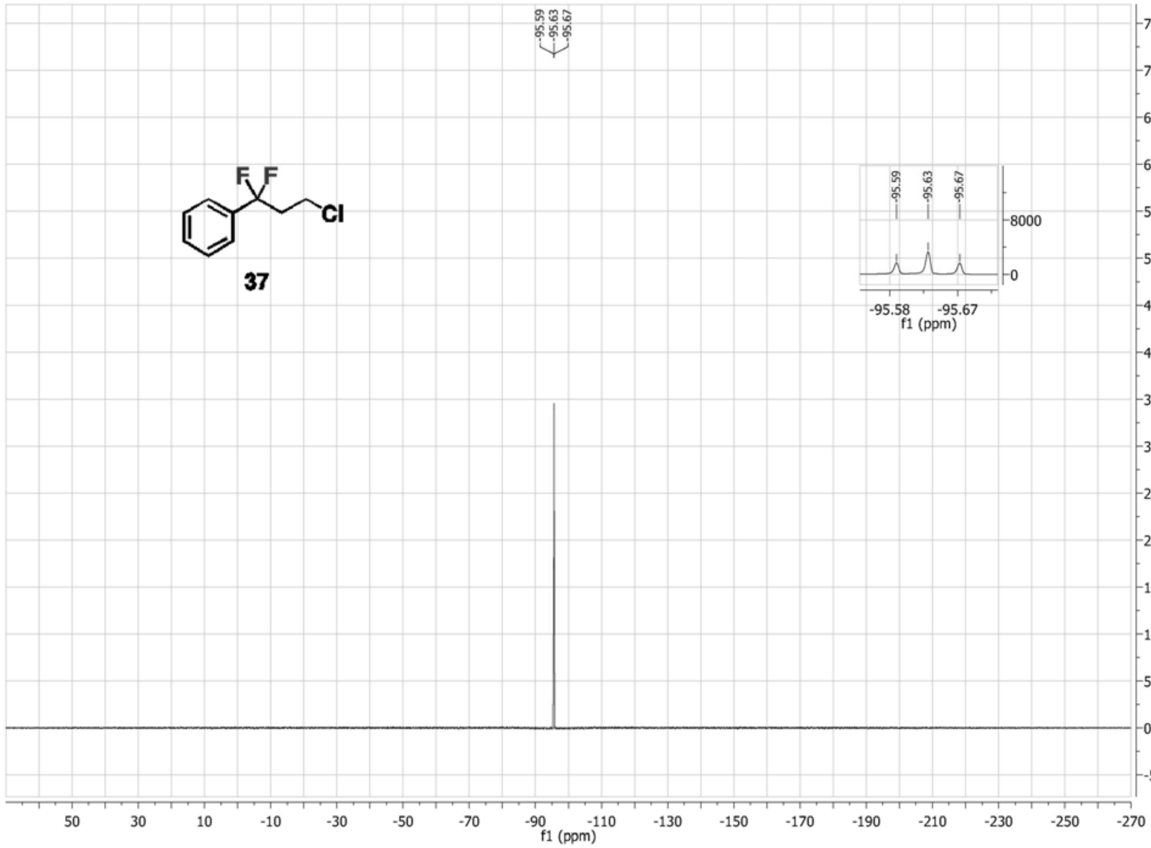
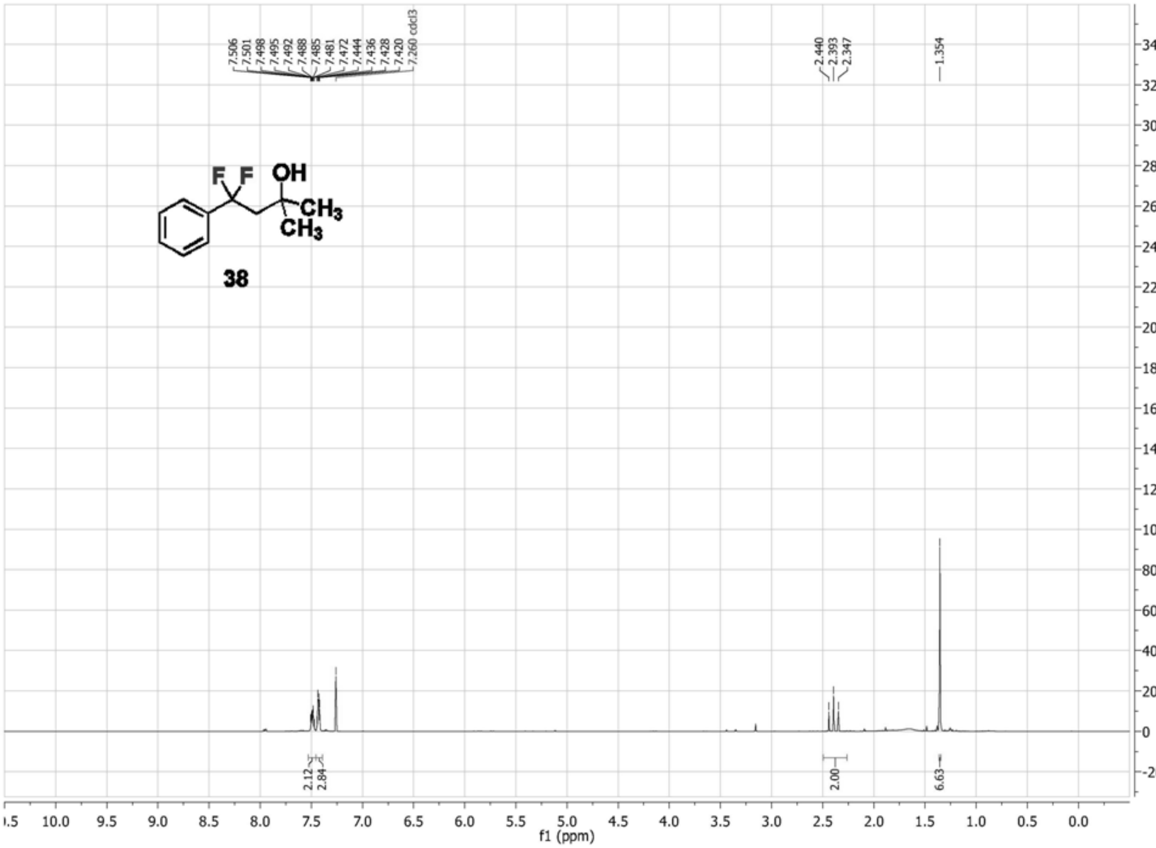
crude reaction

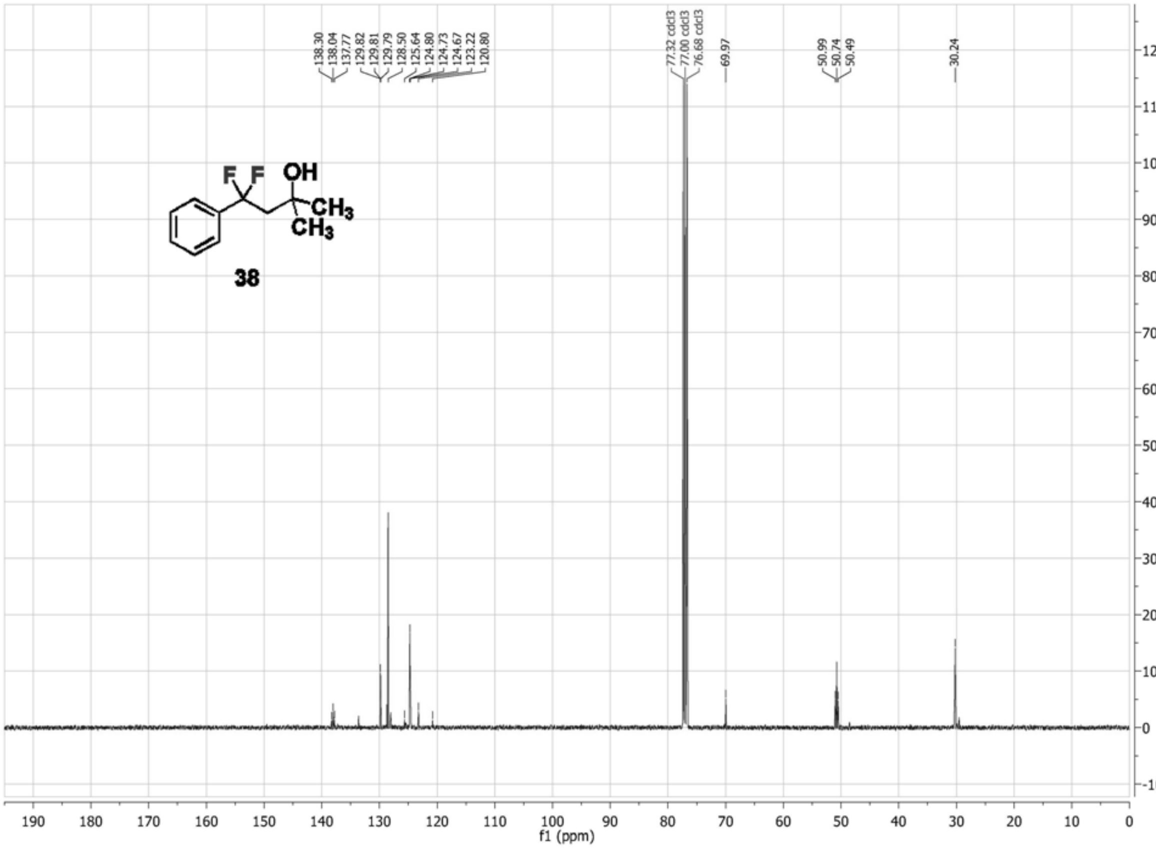


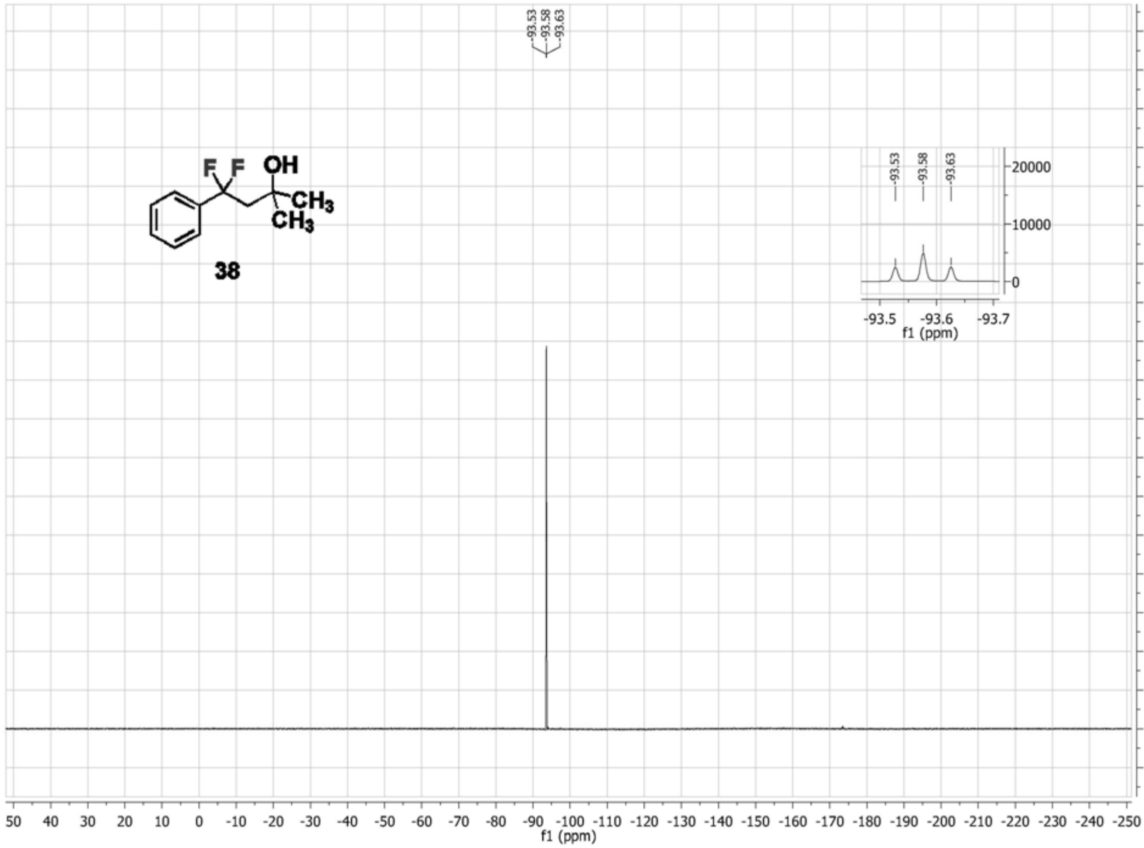
37


136.89
136.64
136.38
130.12
130.10
130.08
128.72
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.08
125.02
124.96
124.04
121.62
119.20
42.63
42.35
42.08
37.10
37.05
37.00
F
F
Cl
37
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-95.59
-95.63
-95.67
F
F
Cl
37
-95.59
-95.63
-95.67
8000
0
-95.58
-95.67
f1 (ppm)
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
f1 (ppm)

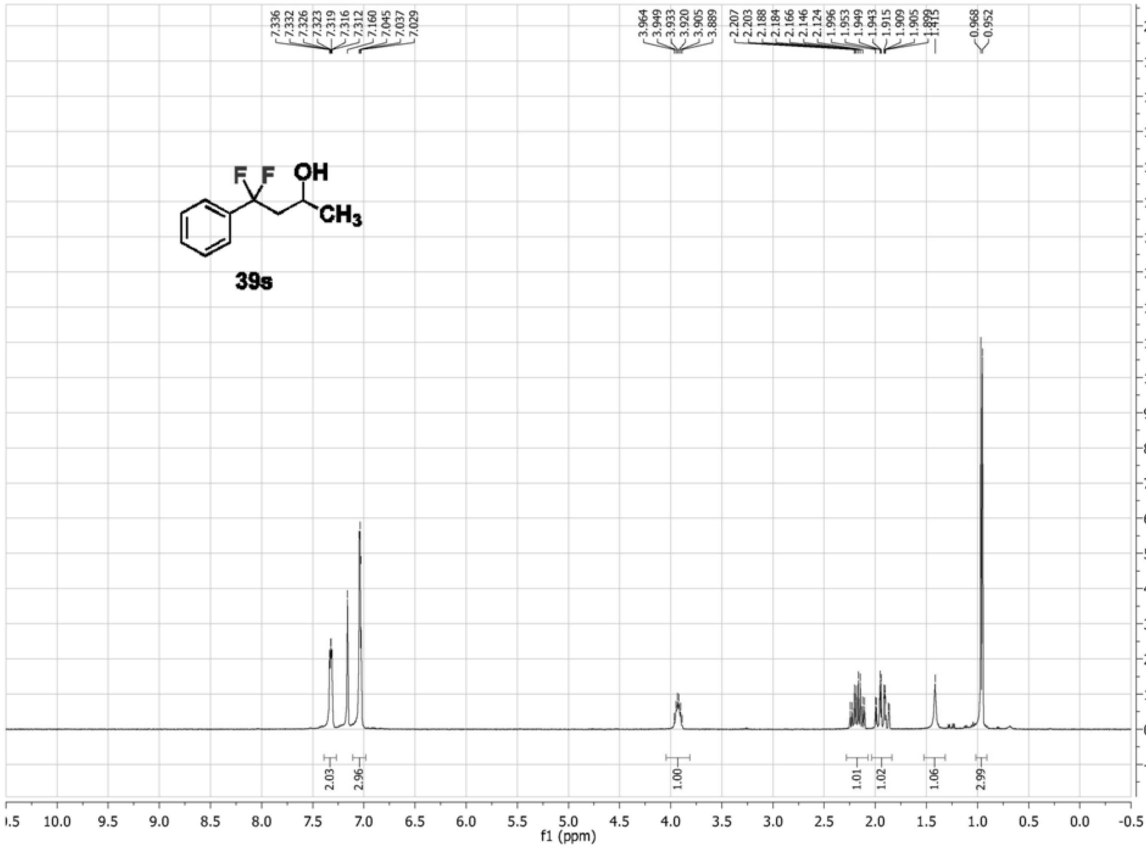

7.506
7.501
7.498
7.495
7.492
7.488
7.485
7.481
7.472
7.444
7.436
7.428
7.420
7.260 cdcl3
2.440
2.393
2.347
1.354
F F OH
CH3
CH3
38
2.12
2.84
2.00
6.63
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200


138.30
138.04
137.77
129.82
129.81
129.79
128.50
125.64
124.80
124.73
124.67
123.22
120.80
77.32 cdcl3
77.00 cdcl3
76.68 cdcl3
69.97
50.99
50.74
50.49
30.24
F F OH
CH3
CH3
38
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000



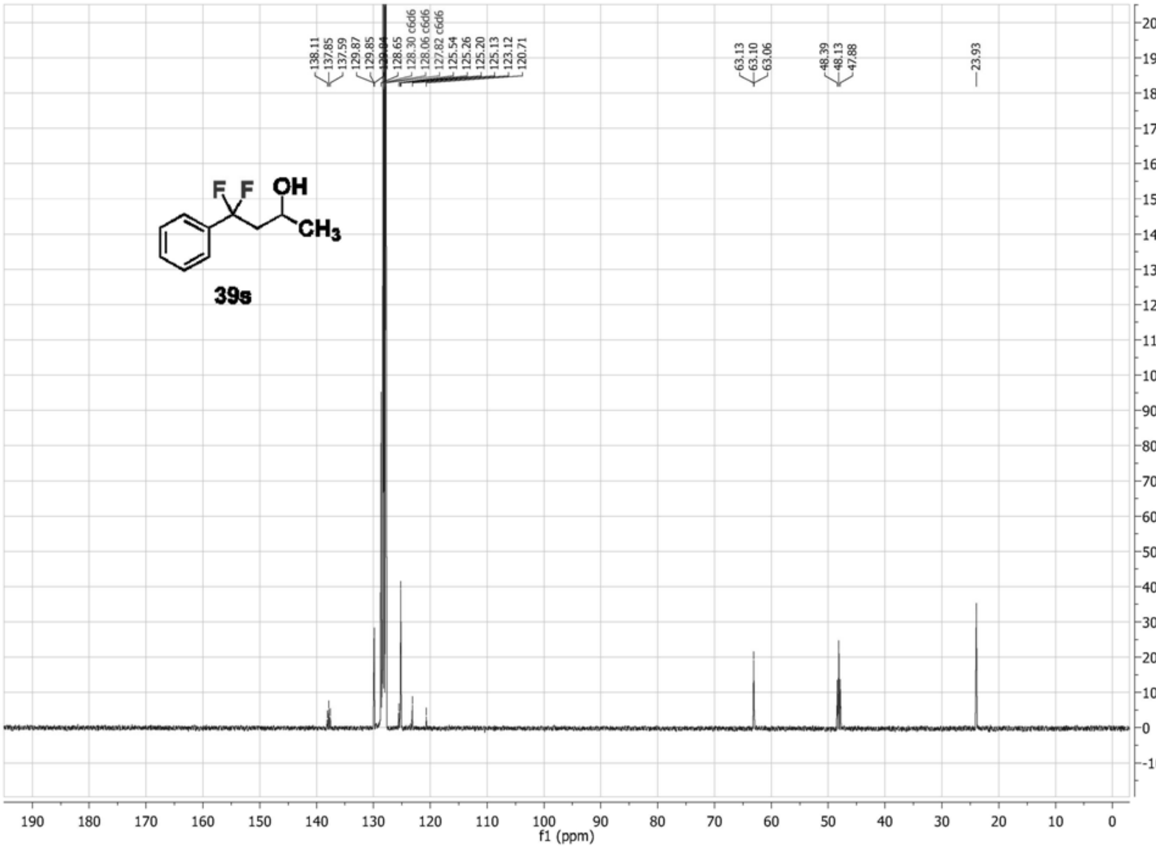
-93.53
-93.58
-93.63
F F OH
CH3
CH3
-93.5 -93.6 -93.7
f1 (ppm)
20000 10000 0
9000 8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250
f1 (ppm)

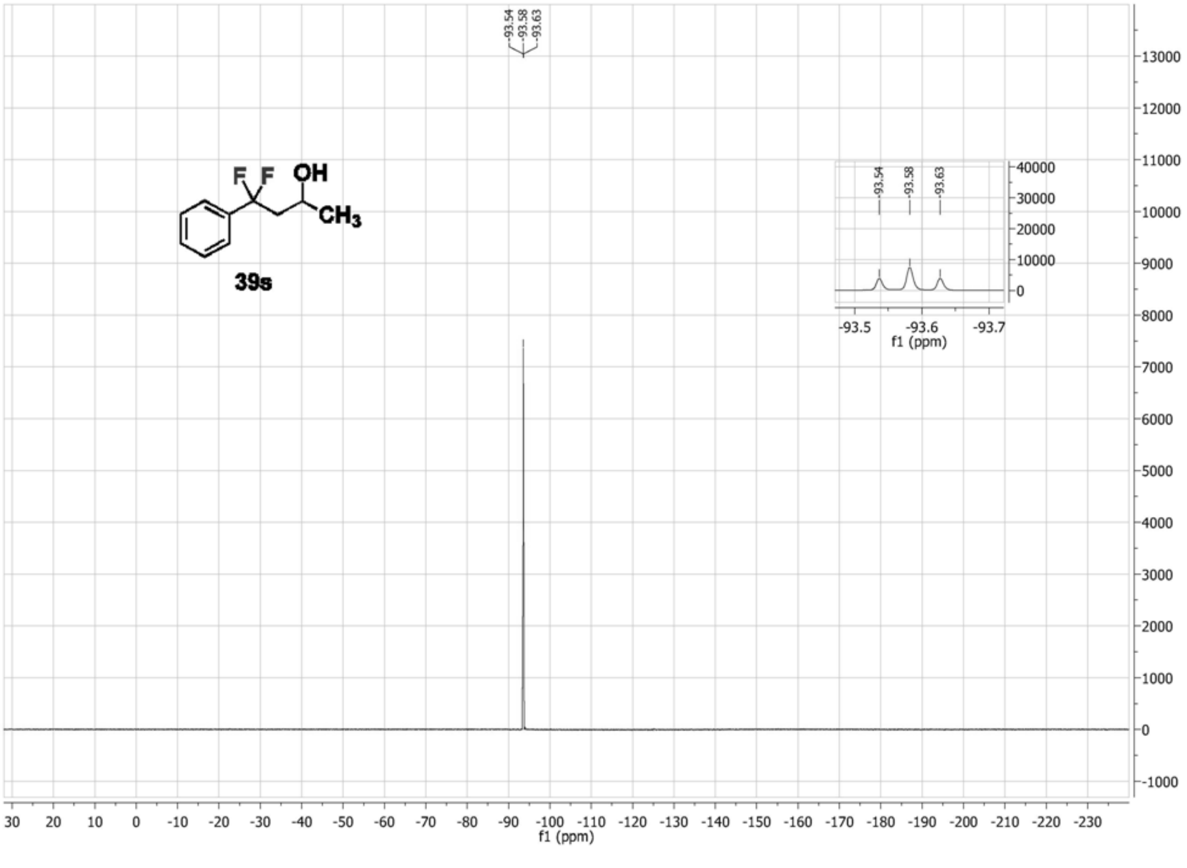
38

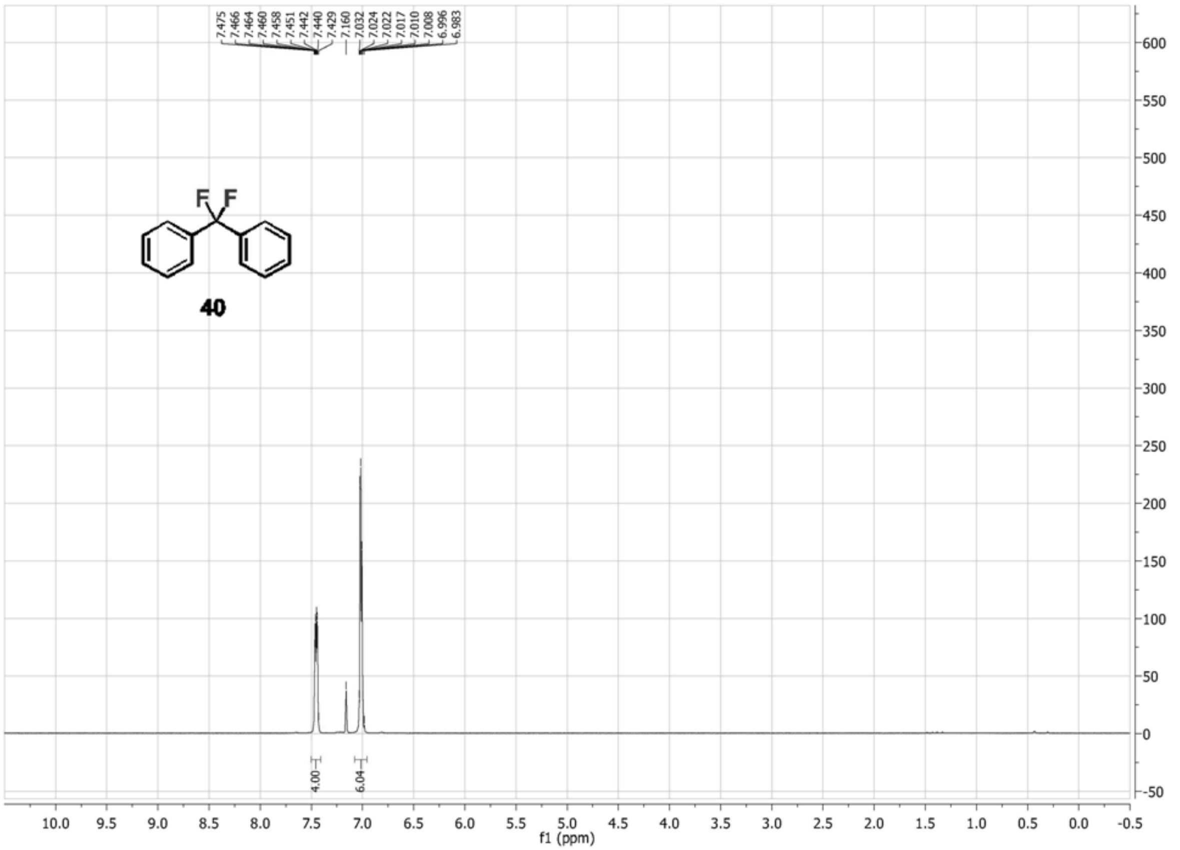


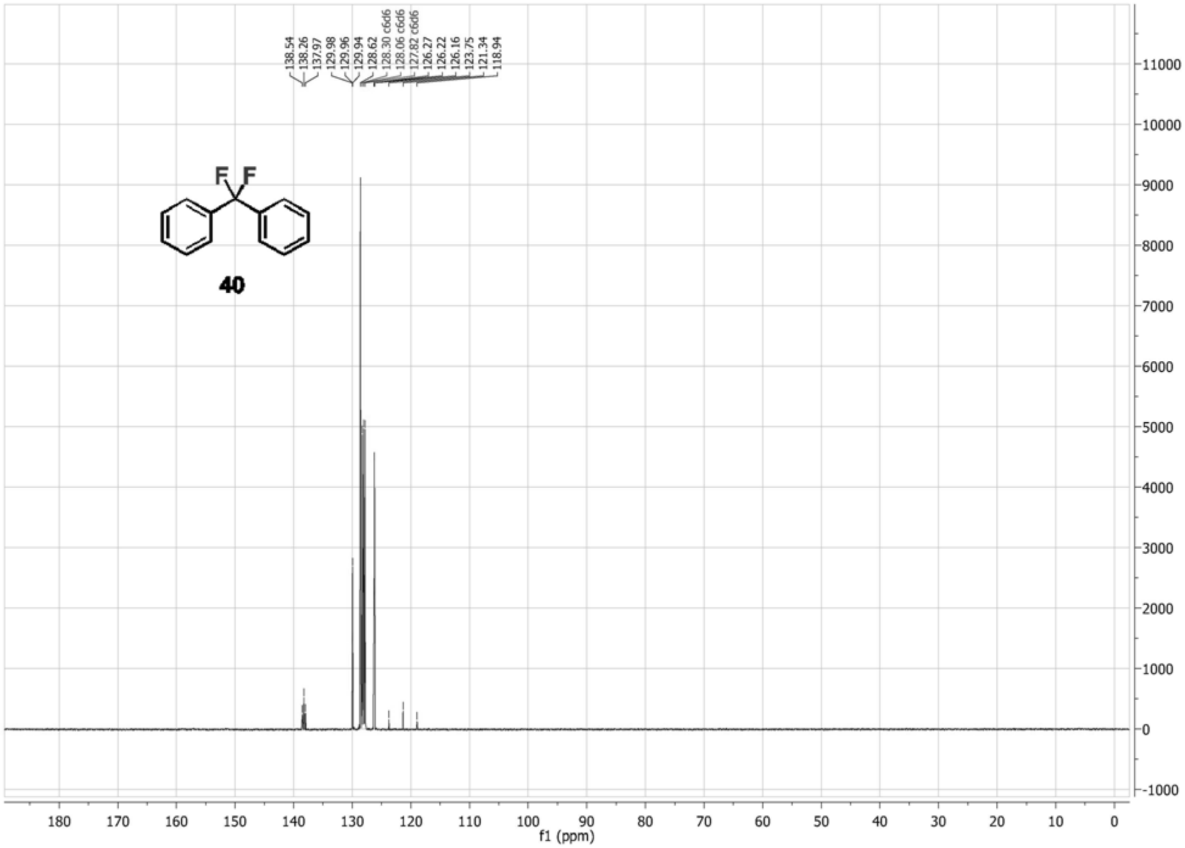
7.336 7.332 7.326 7.323 7.319 7.316 7.312 7.160 7.045 7.037 7.029
3.964 3.949 3.933 3.920 3.905 3.889
2.207 2.203 2.188 2.184 2.166 2.146 2.124 1.996 1.953 1.949 1.943 1.915 1.909 1.905 1.899 1.415
0.968 0.952
F F OH
CH3
2.03 2.96 1.00 1.01 1.02 1.06 2.99
2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100
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
f1 (ppm)

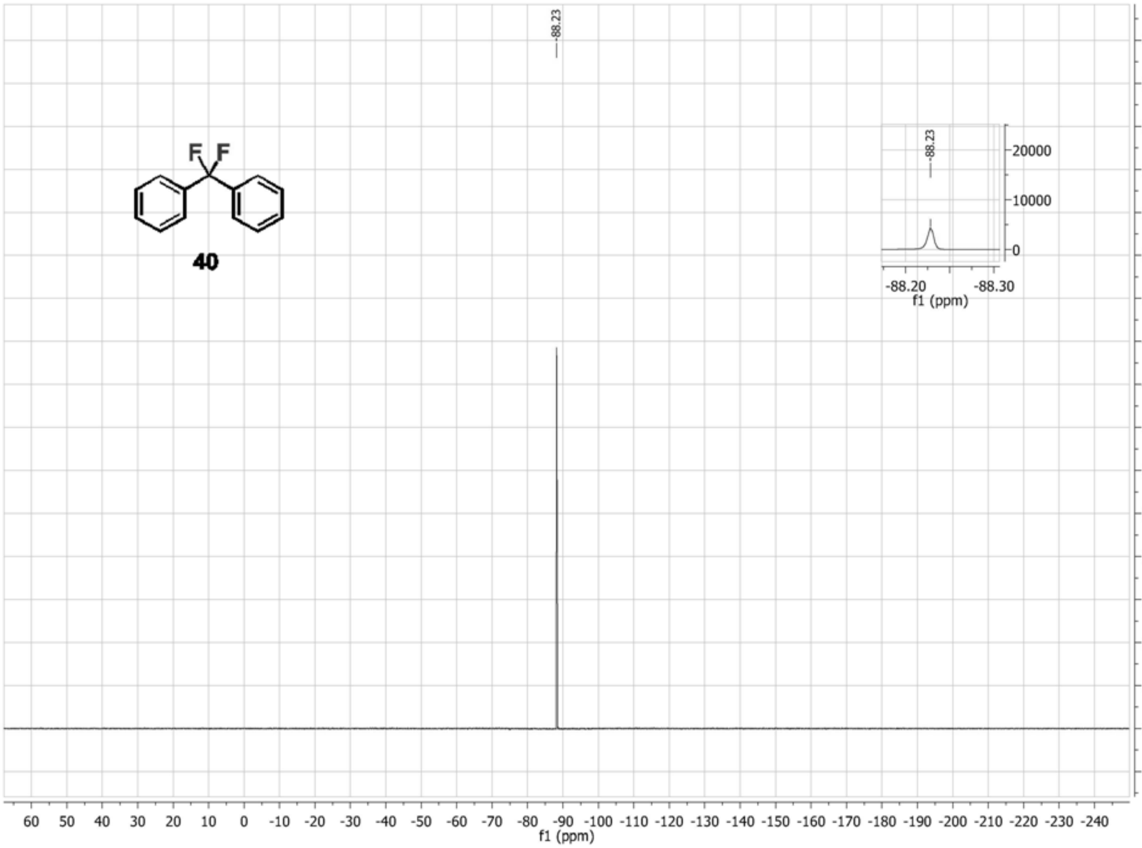
39s

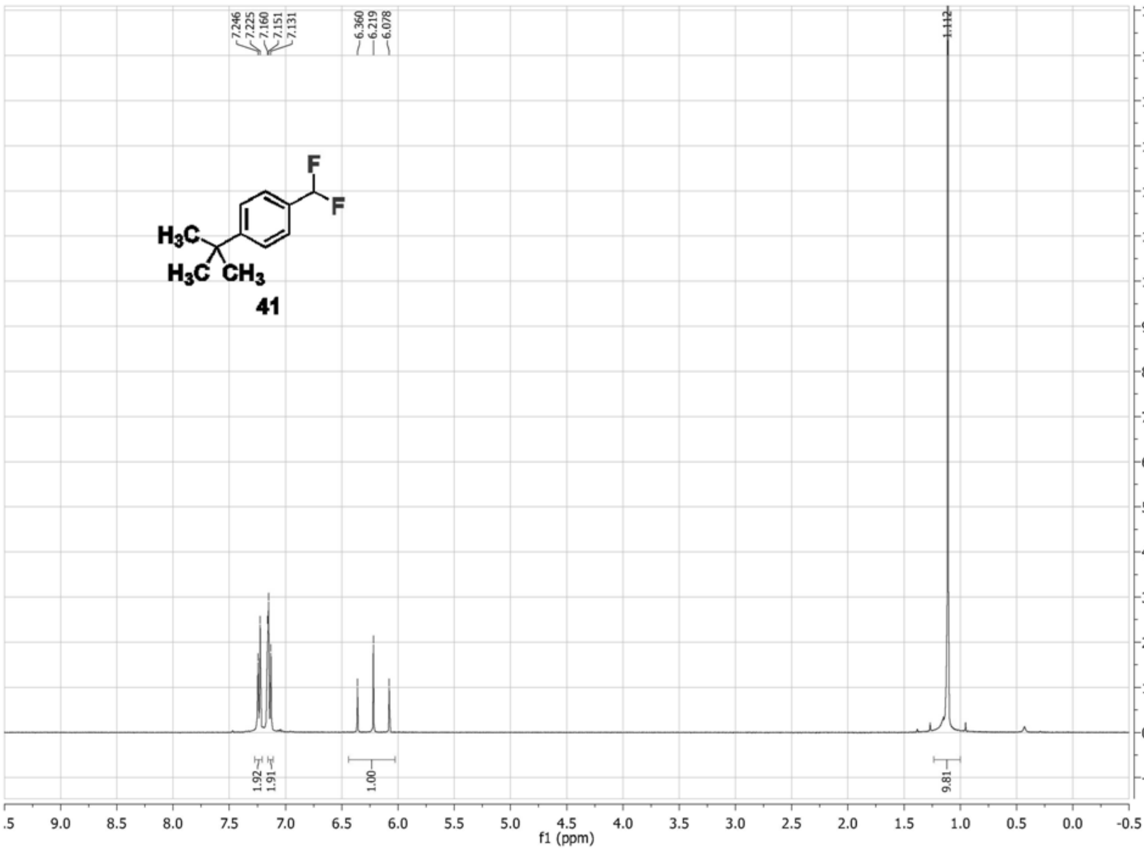

138.11
137.85
137.59
129.87
129.85
129.84
128.65
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.54
125.26
125.20
125.13
123.12
120.71
63.13
63.10
63.06
48.39
48.13
47.88
23.93
F F OH
CH3
39s
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

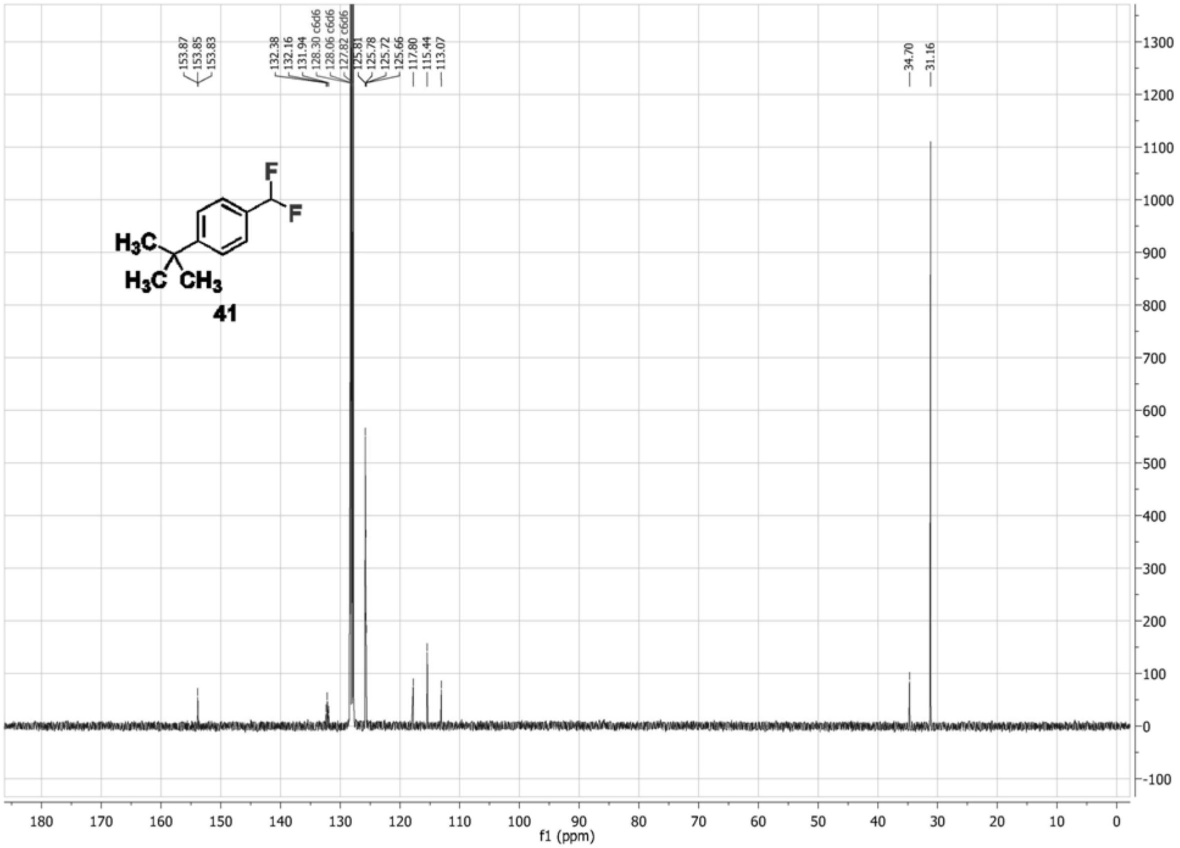

-93.54
-93.58
-93.63
F F OH
CH3
39s
40000
30000
20000
10000
0
-93.5 -93.6 -93.7
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

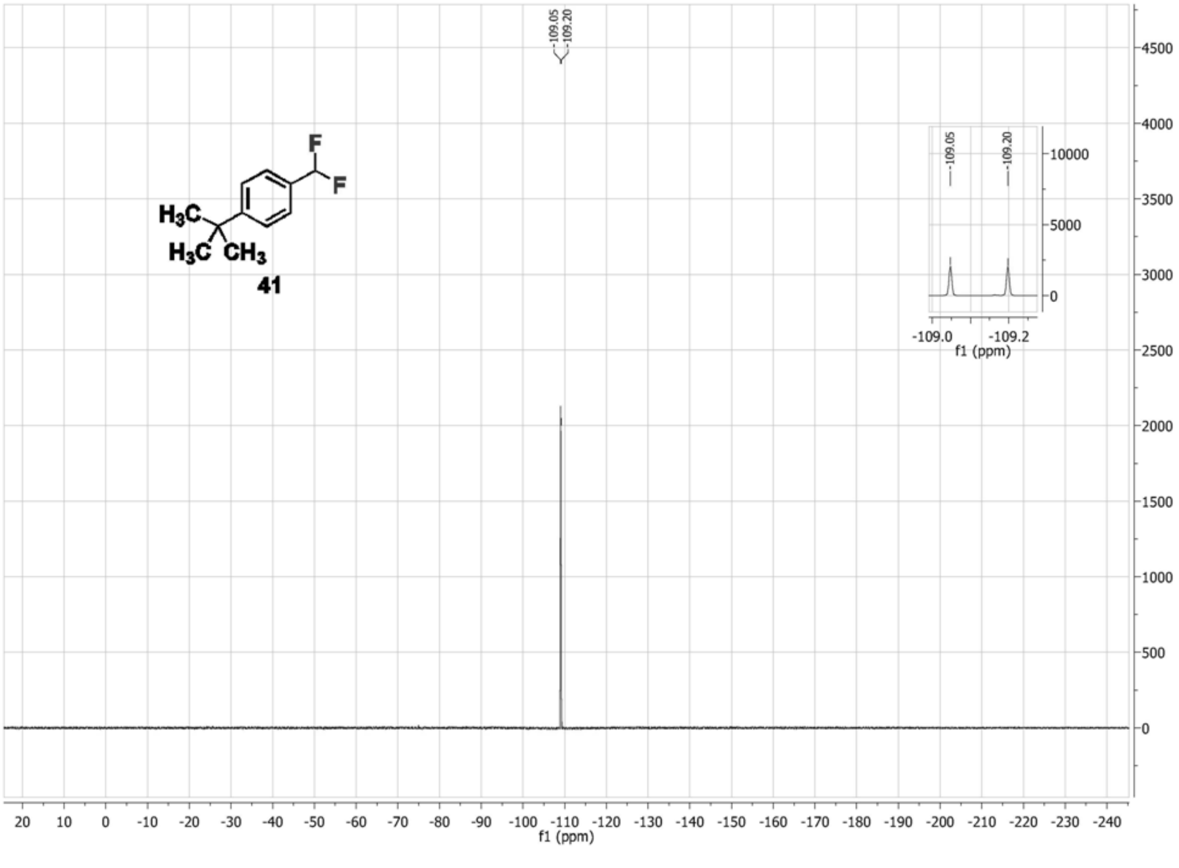

7.475
7.466
7.464
7.460
7.458
7.451
7.442
7.440
7.429
7.160
7.032
7.024
7.022
7.017
7.010
7.008
6.996
6.983
F
F
40
4.00
6.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
600 550 500 450 400 350 300 250 200 150 100 50 0 -50

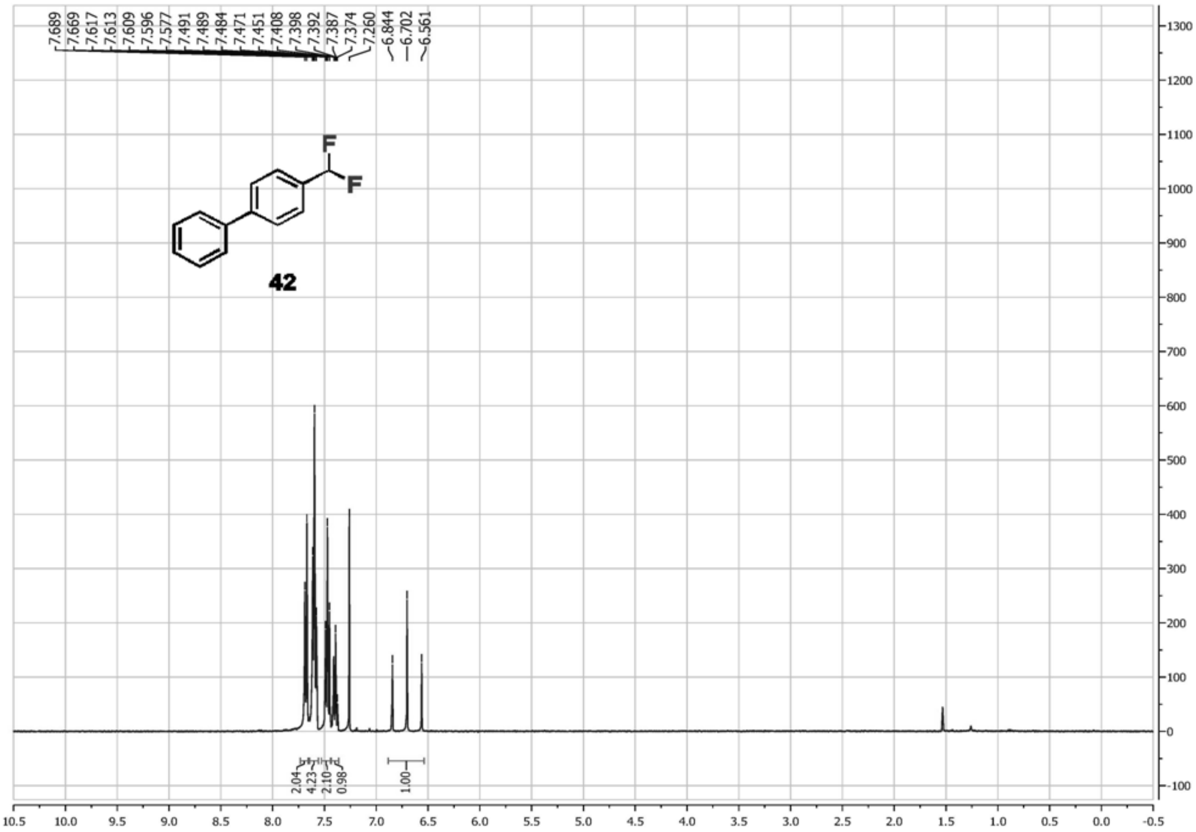

138.54
138.26
137.97
129.98
129.96
129.94
128.62
128.30 c6d6
128.06 c6d6
127.82 c6d6
126.27
126.22
126.16
123.75
121.34
118.94
F
F
40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

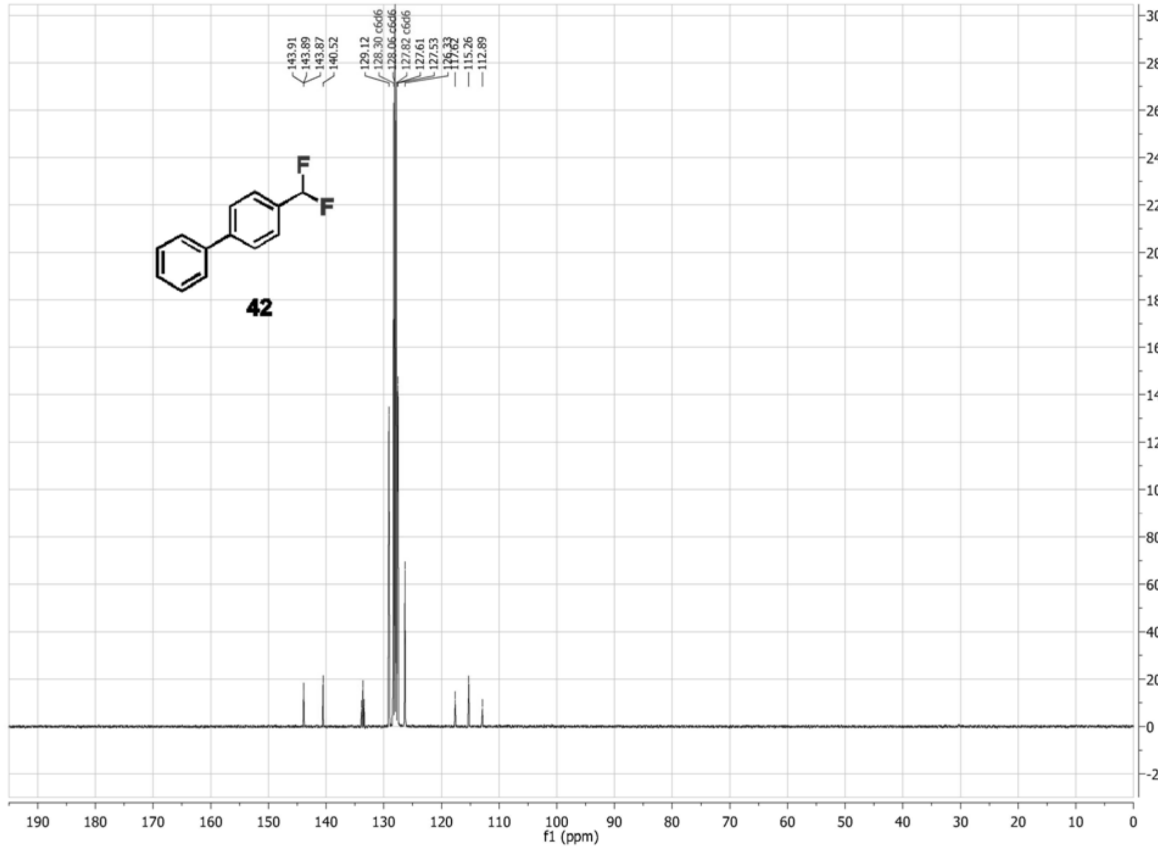

-88.23
F
F
40
-88.23
20000
10000
0
-88.20
-88.30
f1 (ppm)
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

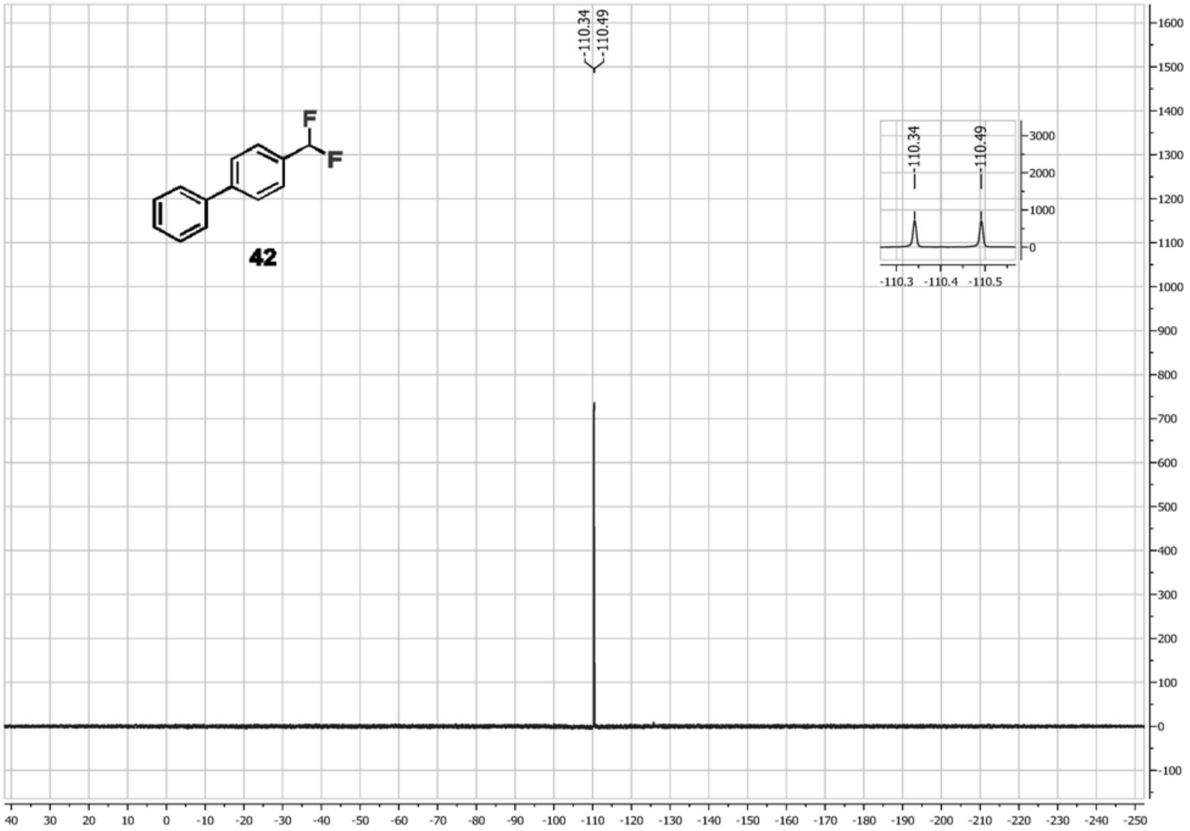

7.246
7.225
7.160
7.151
7.131
6.360
6.219
6.078
1.112
F
F
H3C
H3C
CH3
41
1.92
1.91
1.00
9.81
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

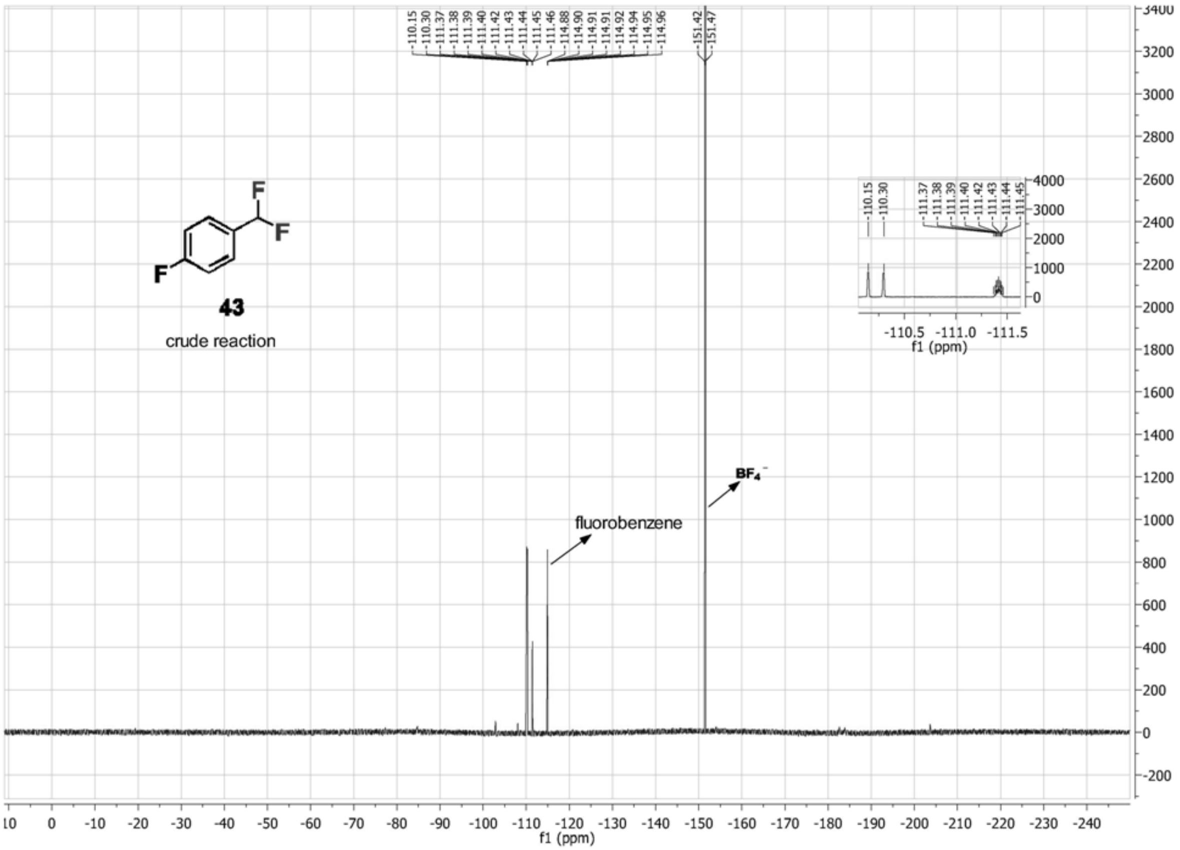

153.87
153.85
153.83
132.38
132.16
131.94
128.30 c6d6
128.06 c6d6
127.82 c6d6
125.81
125.78
125.72
125.66
117.80
115.44
113.07
34.70
31.16
F
F
H_3C
H_3C
CH_3
41
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

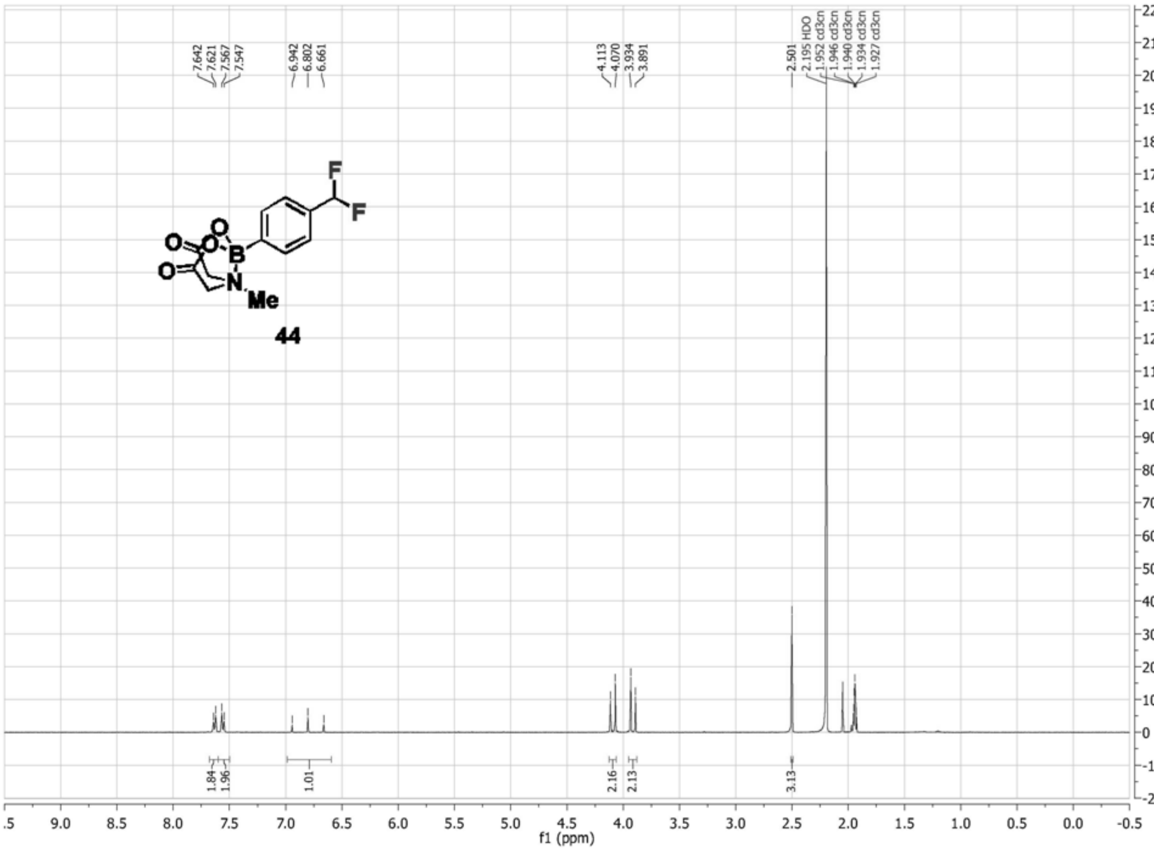

-109.05
-109.20
F
F
H_3C
H_3C
CH_3
41
-109.05
-109.20
10000
5000
0
-109.0
-109.2
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)

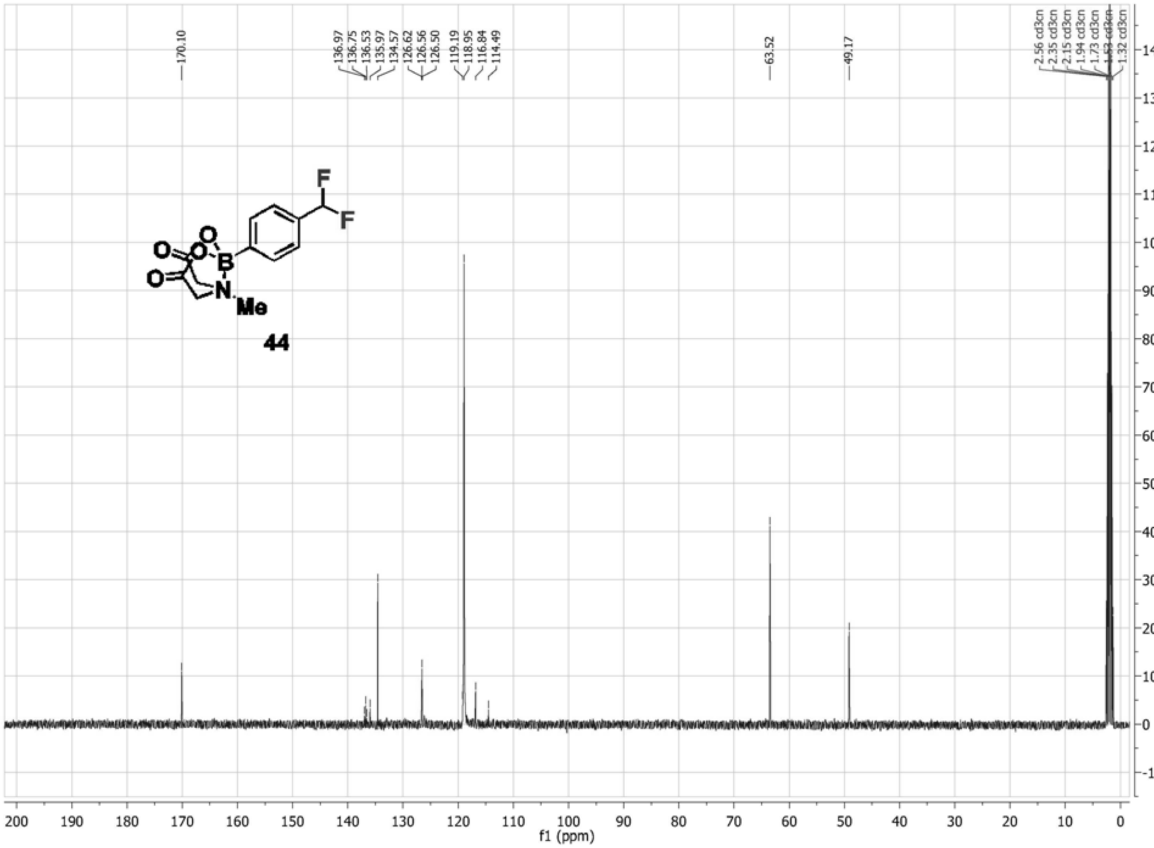

7.689
7.669
7.617
7.613
7.609
7.596
7.577
7.491
7.489
7.484
7.471
7.451
7.408
7.398
7.392
7.387
7.374
7.260
6.844
6.702
6.561
F
F
42
2.04
4.23
2.10
0.98
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

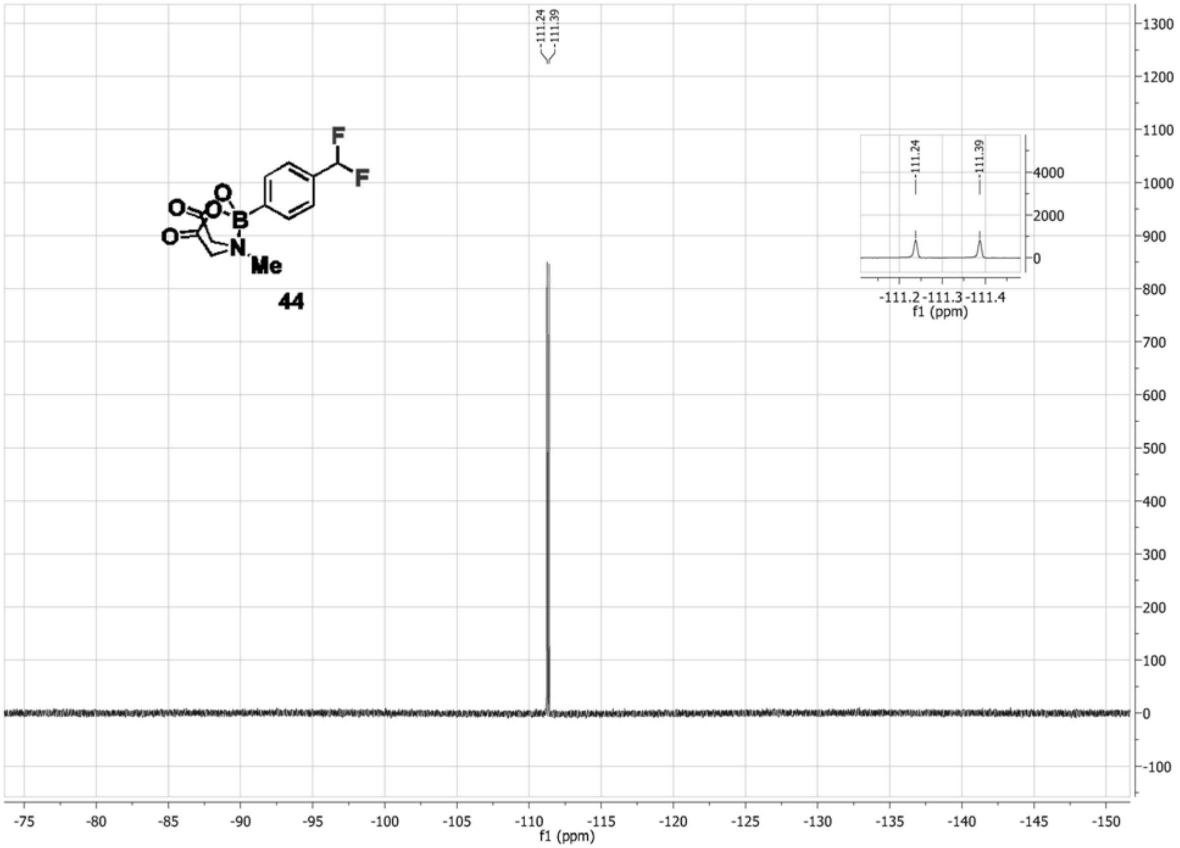

143.91
143.89
143.87
140.52
129.12
128.30 c6d6
128.06 c6d6
127.82 c6d6
127.61
127.53
126.33
117.62
115.26
112.89
F
F
42
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000


-110.34
-110.49
F
F
42
-110.34
-110.49
3000
2000
1000
0
-110.3 -110.4 -110.5
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250


-110.15
-110.30
-111.37
-111.38
-111.39
-111.40
-111.42
-111.43
-111.44
-111.45
-111.46
-114.88
-114.90
-114.91
-114.91
-114.92
-114.94
-114.95
-114.96
-151.42
-151.47
F
F
F
43
crude reaction
-110.15
-110.30
-111.37
-111.38
-111.39
-111.40
-111.42
-111.43
-111.44
-111.45
4000
3000
2000
1000
0
-110.5 -111.0 -111.5
f1 (ppm)
fluorobenzene
BF₄⁻
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10 0 -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)


7.642
7.621
7.567
7.547
6.942
6.802
6.661
4.113
4.070
3.934
3.891
2.501
2.195 HDO
1.952 cd3cn
1.946 cd3cn
1.940 cd3cn
1.934 cd3cn
1.927 cd3cn
F
F
O
O
O
O
B
N
Me
44
1.84
1.96
1.01
2.16
2.13
3.13
f1 (ppm)
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
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200


170.10
136.97
136.75
136.53
135.97
134.57
126.62
126.56
126.50
119.19
118.95
116.84
114.49
63.52
49.17
2.56 cd3cn
2.35 cd3cn
2.15 cd3cn
1.94 cd3cn
1.73 cd3cn
1.53 cd3cn
1.32 cd3cn
F
F
O
O
O
O
B
N
Me
44
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100



-111.24
-111.39
F
F
O
O
O
B
O
N
Me
44
-111.24
-111.39
4000
2000
0
-111.2 -111.3 -111.4
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)