

Supporting Information

Electrochemical C-C Bond Cleavage of Cyclopropanes towards the Synthesis of 1,3-Difunctionalized Molecules

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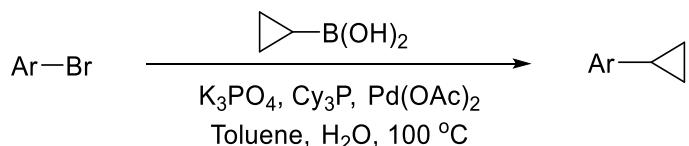
General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. PhCF₃ was purchased from Aladdin. Et₃N·3HF (95%) was purchased from Accela ChemBio Co., Ltd. Phenylcyclopropane, 1-bromo-4-cyclopropylbenzene and 1-fluoronaphthalene (98%) were purchased from Bidepharm. Other Arylcyclopropanes were prepared according to literature report. Carbon cloth was purchased from CeTech Co., Ltd. Nickel foam was purchased from KUNSHAN JIAYISHENG ELECTRONICS CO.,LTD. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel. GC yields were recorded with a Shimadzu GC-2014. GC-MS was recorded by Shimadzu GCMS-QP2010 SE. All new compounds were characterized by ¹H NMR, ¹³C NMR, ¹⁹F NMR and HRMS. The known compounds were characterized by ¹H NMR, ¹³C NMR and ¹⁹F NMR. ¹H and ¹³C NMR data were recorded with ADVANCE III 400 MHz or JNM-ECZ400 400 MHz with tetramethylsilane as an internal standard. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ¹H), and CDCl₃ (77.16 ppm for ¹³C), respectively. High resolution mass spectra (HRMS) were measured with Orbitrap Velos Pro, Thermo Scientific or Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FT Ultra, accurate masses are reported for the molecular ion + proton ([M+H]⁺), molecular ion + NH₄⁺ ([M+NH₄]⁺) or molecular ion + Na⁺ ([M+Na]⁺).

Experimental section

1) General procedure for synthesis of arylcyclopropanes

General procedure A: Suzuki coupling^[1]



General procedure A: Aryl bromide (6 mmol, 1 equiv.), cyclopropylboronic acid (670 mg, 7.8 mmol, 1.3 equiv.), K₃PO₄ (4.46 g, 21.0 mmol, 3.5 equiv.), Cy₃P (168.2 mg, 0.6 mmol, 0.1 equiv.) and Pd(OAc)₂ (67.4 mg, 0.3 mmol, 0.05 equiv.) were added to a three-neck flask equipped with a magnetic stir bar, and the resultant mixture was degassed and filled with argon gas. Toluene (40 mL) and water (2 mL) were added. The resultant mixture was heated at 100 °C until aryl halide was consumed (more than 5 h, detected by GC-MS). The reaction was cooled to room temperature and diluted with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

The following were prepared according to general procedure A: **S6**^[2], **S8**^[1], **S14**^[3], **S15**^[2], **S17**^[4], **S18**^[2], **S19**^[2], **S21**^[1], **S22**^[5] and **S24**^[1] were previously reported.

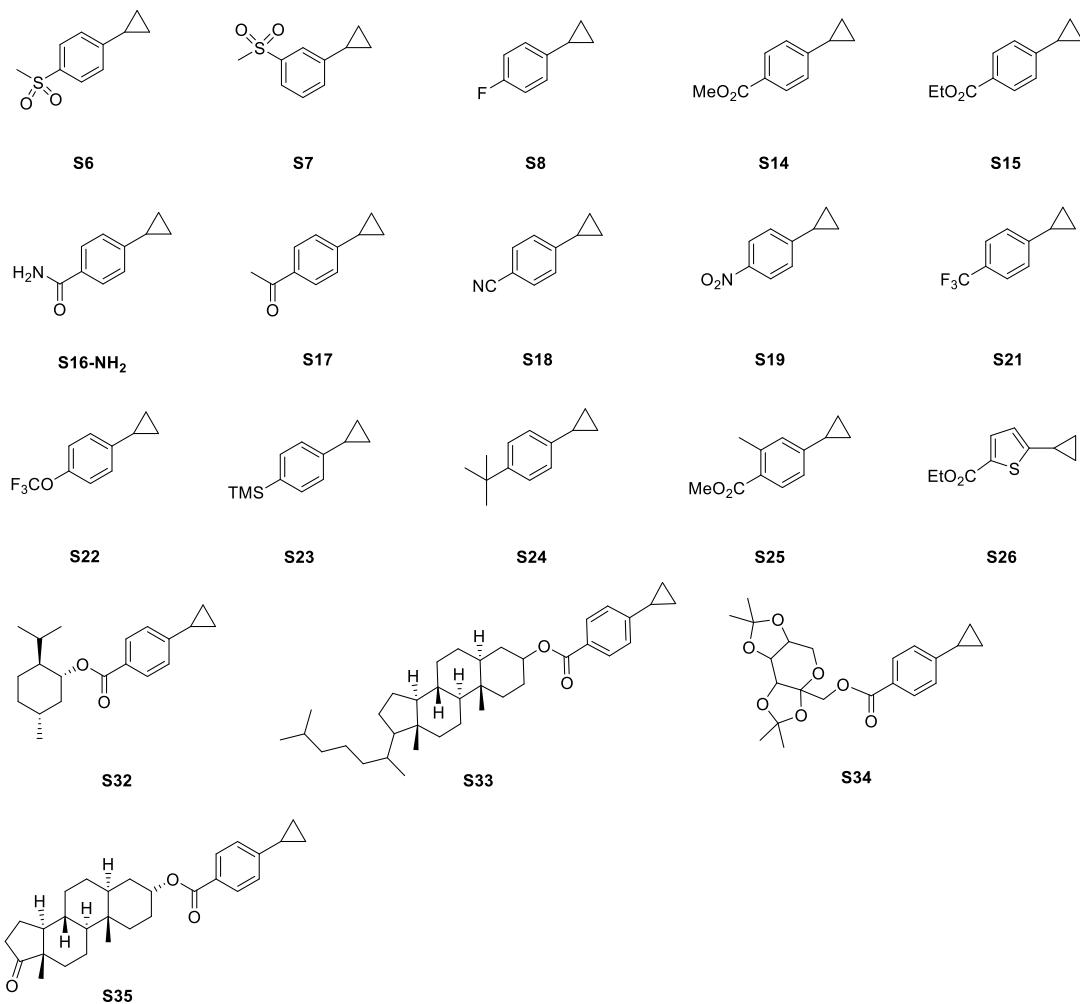
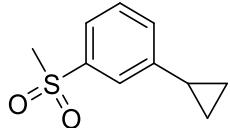
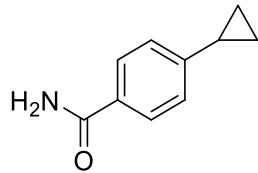


Figure S1

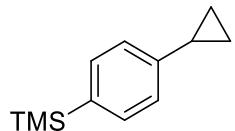
Characterization of unknown product:



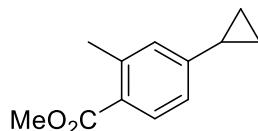
S7. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (ddd, J = 7.7, 1.7, 1.2 Hz, 1H), 7.63 (t, J = 1.8 Hz, 1H), 7.45 (t, J = 7.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 3.05 (s, 3H), 1.99 (tt, J = 8.4, 5.1 Hz, 1H), 1.07 (ddd, J = 8.4, 6.5, 4.8 Hz, 2H), 0.77 (dt, J = 6.6, 4.9 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 146.23, 140.54, 131.05, 129.33, 124.44, 124.29, 44.60, 15.53, 10.00. HRMS (ESI) m/z calculated for C₁₀H₁₃O₂S (M+H)⁺: 197.06308, found: 197.06302.



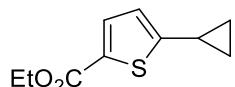
S16-NH₂. ¹H NMR (400 MHz, DMSO) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 1.96 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.06 – 0.95 (m, 2H), 0.78 – 0.67 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 167.84, 147.64, 131.30, 127.63, 125.03, 15.23, 10.23. HRMS (ESI) m/z calculated for C₁₀H₁₂NO (M+H)⁺: 162.09134, found: 162.09075.



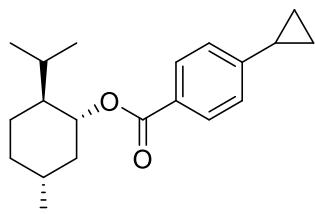
S23. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 1.94 – 1.81 (m, 1H), 0.99 – 0.92 (m, 2H), 0.74 – 0.68 (m, 2H), 0.24 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 144.94, 136.96, 133.49, 125.18, 15.49, 9.53, -0.91. HRMS (EI⁺) m/z calculated for C₁₂H₁₈Si (M⁺): 190.1178, found: 190.1185.



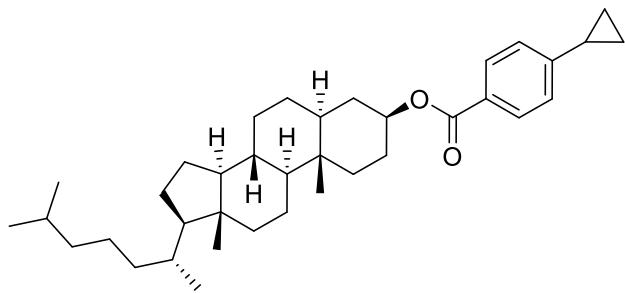
S25. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.1 Hz, 1H), 6.89 (dd, *J* = 11.6, 3.5 Hz, 2H), 3.86 (s, 3H), 2.57 (s, 3H), 1.87 (tt, *J* = 8.4, 5.0 Hz, 1H), 1.04 – 0.98 (m, 2H), 0.77 – 0.71 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 168.00, 148.97, 140.57, 131.01, 128.98, 126.42, 122.64, 51.73, 22.08, 15.52, 10.13. HRMS (ESI) m/z calculated for C₁₂H₁₅O₂ (M+H)⁺: 191.10666, found: 191.10670.



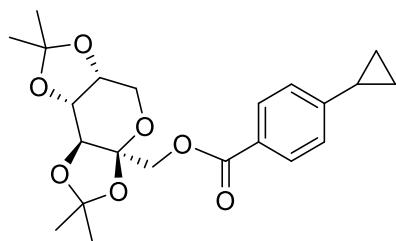
S26. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 3.8 Hz, 1H), 6.73 (dd, *J* = 3.8, 0.5 Hz, 1H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.10 (dq, *J* = 8.4, 5.0 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.07 (ddd, *J* = 8.3, 6.6, 4.6 Hz, 2H), 0.78 (dt, *J* = 6.7, 4.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.21, 157.01, 133.56, 129.58, 123.30, 60.86, 14.38, 11.93, 11.02. HRMS (ESI) m/z calculated for C₁₀H₁₃O₂S (M+H)⁺: 197.06308, found: 197.06308.



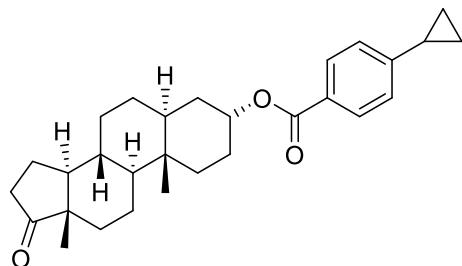
S32. ¹H NMR (400 MHz, CDCl₃) δ 7.97 – 7.87 (m, 2H), 7.15 – 7.04 (m, 2H), 4.91 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 – 2.07 (m, 1H), 2.00 – 1.89 (m, 2H), 1.77 – 1.67 (m, 2H), 1.60 – 1.48 (m, 2H), 1.16 – 1.01 (m, 4H), 0.96 – 0.85 (m, 7H), 0.80 – 0.73 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 166.23, 149.85, 129.74, 128.03, 125.38, 74.64, 47.41, 41.12, 34.47, 31.57, 26.62, 23.77, 22.20, 20.91, 16.67, 15.80, 10.38. HRMS (ESI) m/z calculated for C₂₀H₂₈O₂Na (M+Na)⁺: 323.19815, found: 323.19800.



S33. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 5.05 – 4.77 (m, 1H), 2.01 – 1.88 (m, 3H), 1.87 – 0.80 (m, 42H), 0.78 – 0.73 (m, 2H), 0.71 – 0.61 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.30, 149.78, 129.70, 128.12, 125.32, 74.23, 56.55, 56.38, 54.35, 44.83, 42.72, 40.11, 39.65, 36.94, 36.30, 35.95, 35.65, 35.62, 34.28, 32.15, 28.78, 28.40, 28.16, 27.74, 24.36, 23.98, 22.99, 22.72, 21.36, 18.81, 15.81, 12.45, 12.22, 10.40. HRMS (DART POSITIVE) m/z calculated for $\text{C}_{34}\text{H}_{57}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 533.4353, found: 533.4352.

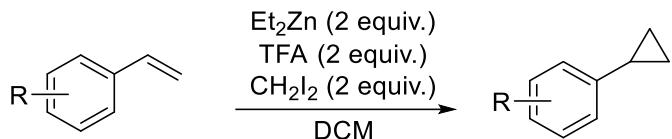


S34. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.09 (d, $J = 8.4$ Hz, 2H), 4.69 – 4.63 (m, 2H), 4.47 (d, $J = 2.6$ Hz, 1H), 4.34 – 4.23 (m, 2H), 4.01 – 3.74 (m, 2H), 1.98 – 1.89 (m, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H), 1.12 – 1.01 (m, 2H), 0.82 – 0.72 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.07, 150.38, 129.95, 126.98, 125.43, 109.29, 108.95, 101.84, 70.94, 70.57, 70.23, 65.08, 61.45, 26.68, 26.02, 25.69, 24.15, 15.85, 10.53. HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{29}\text{O}_7$ ($\text{M}+\text{H}$) $^+$: 405.19078, found: 405.18947.



S35. ^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.87 (m, 2H), 7.09 (d, $J = 8.3$ Hz, 2H), 4.98 – 4.86 (m, 1H), 2.48 – 2.40 (m, 1H), 2.14 – 2.03 (m, 1H), 1.97 – 1.90 (m, 3H), 1.85 – 1.72 (m, 4H), 1.71 – 1.44 (m, 5H), 1.41 – 1.21 (m, 6H), 1.17 – 0.96 (m, 4H), 0.90 (s, 3H), 0.87 (s, 3H), 0.78 – 0.71 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 221.55, 166.29, 149.88, 129.70, 128.01, 125.34, 73.96, 54.43, 51.48, 47.94, 44.83, 36.89, 36.01, 35.84, 35.17, 34.19, 31.65, 30.96, 28.43, 27.67, 21.93, 20.61, 15.81, 13.96, 12.43, 10.42. HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{39}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 435.28937, found: 435.28876.

General procedure B: Simmons-Smith cyclopropanation^[6]



General procedure B: To 15 mL distilled DCM was added 10.0 mL Et₂Zn (10.0 mmol, 2 equiv., 1.0 M in hexanes) under N₂ atmosphere. The solution was cooled in an ice bath and a solution of trifluoroacetic acid (0.8 mL, 10.0 mmol, 2 equiv.) in 5 mL DCM was then dripped very slowly into the reaction mixture via syringe. Upon stirring for 20 min, a solution of CH₂I₂ (0.8 mL, 10.0 mmol, 2 equiv.) in 5 mL DCM was added. After an additional 20 min of stirring, a solution of the respective styrene derivative (5.0 mmol, 1 equiv.) in 5 mL DCM was added, and the ice bath was removed. After starting styrene derivative was consumed (detected by GC-MS, 12 h - 3 d), the reaction mixture was quenched with 1M HCl (10 mL) and the phases were separated. The aqueous layer was extracted with DCM. The combined organic layers were washed with saturated NaHCO₃, and brine and then dried with Na₂SO₄, filtered and concentrated. The residue was purified by column chromatography to give the title compound.

The following were prepared according to general procedure B, **S9^[1]**, **S11^[1]**, **S12^[6]**, **S13^[7]**, **S27^[8]**, **S28^[8]**, **trans-S30^[9]** and **S31^[10]** were previously reported.

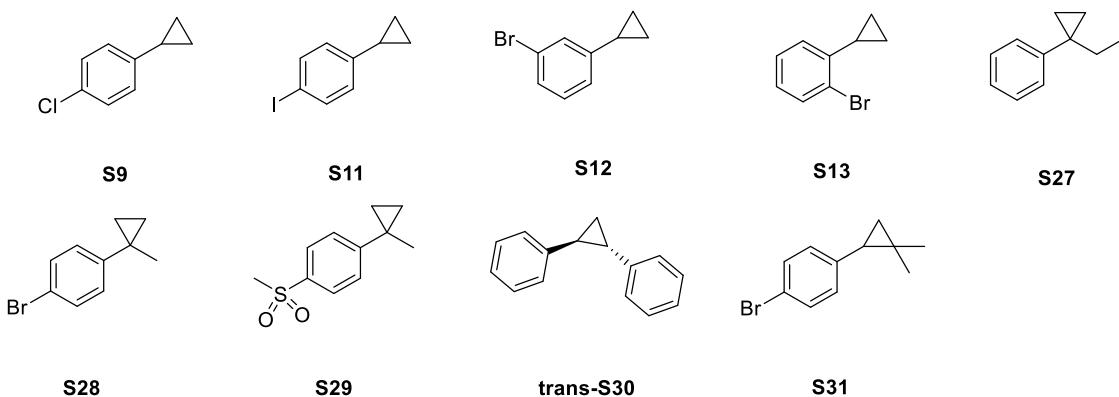
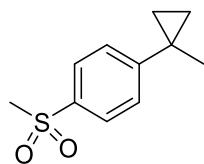
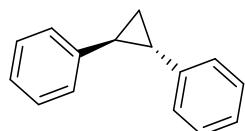


Figure S2

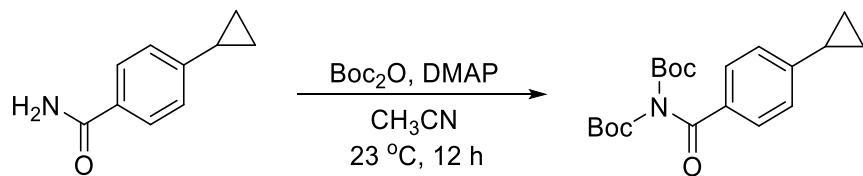


S29. ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.79 (m, 2H), 7.44 – 7.34 (m, 2H), 3.04 (s, 3H), 1.45 (s, 3H), 0.99 – 0.79 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 153.99, 137.38, 127.43, 127.24, 44.74, 24.90, 19.77, 17.10. HRMS (ESI) m/z calcd for C₁₁H₁₅O₂S (M+H)⁺: 211.07873, found: 211.07854.

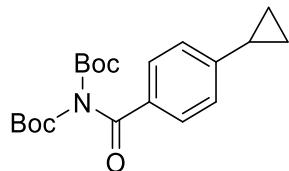


Trans-S30. ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.26 (m, 4H), 7.22 – 7.11 (m, 6H), 2.21 – 2.12 (m, 2H), 1.47 – 1.43 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.61, 128.50, 125.85, 28.18, 18.38. The observed spectral data are in agreement with the reported literature.

2) General procedure for synthesis of protected amide^[11]



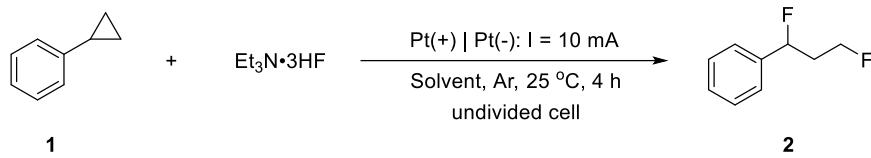
To a flask containing amide (4.6 mmol) was added DMAP (56.7mg, 0.46 mmol, 0.1 equiv.), followed by acetonitrile (23 mL, 0.2 M). Boc_2O (2.03 g, 9.28 mmol, 2.0 equiv.) was added in one portion and the reaction vessel was flushed with N_2 . The reaction mixture was allowed to stir at 23 °C for 12 h. The mixture was washed with 1.0 M HCl (5 mL) and brine (5 mL). After drying over Na_2SO_4 , filtered and the organics were concentrated under reduced pressure.



S16. ^1H NMR (400 MHz, CDCl_3) δ 7.77 – 7.70 (m, 2H), 7.12 (d, J = 8.4 Hz, 2H), 1.96 (ddd, J = 13.4, 8.4, 5.0 Hz, 1H), 1.38 (s, 18H), 1.12 – 1.06 (m, 2H), 0.80 (dt, J = 6.7, 4.8 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.04, 151.38, 149.94, 131.14, 129.63, 125.72, 84.19, 27.78, 16.00, 10.84. HRMS (EI+) m/z calculated for $\text{C}_{20}\text{H}_{27}\text{NO}_5\text{Na}$ ($\text{M}+\text{Na}^+$): 384.17814, found: 384.17697.

3) Optimization of Reaction Parameters for 1,3-difluorination

Evaluation of solvents (Table S1):



Entry	Solvent	Yield [%] ^a
1	CH ₃ CN	11 %
2	DCE	55 %
3	CH ₂ Cl ₂	27 %
4	Acetone	3 %
5	CH ₃ NO ₂	1 %
6	EtOAc	11 %
7	THF	14 %
8	DME	23 %
9	TBME	9 %
10	PhMe	0 %
11	PhCF ₃	72 %

Reaction conditions: undivided cell, Pt anode, Pt cathode, **1** (0.5 mmol), Et₃N•3HF (1.2 mL), solvent (4.8 mL), 10 mA. [a] GC Yield using biphenyl as internal standard.

Evaluation of current (Table S2):

Entry	I, Time	Yield [%] ^a
1	5 mA, 8 h	71 %
2	10 mA, 4 h	72 %
3	16 mA, 2 h	77 %
4	20 mA, 96 min	73 %

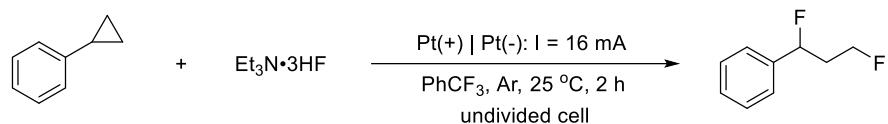
Reaction conditions: undivided cell, Pt anode, Pt cathode, **1** (0.5 mmol), Et₃N•3HF (1.2 mL), PhCF₃ (4.8 mL). [a] GC Yield using biphenyl as internal standard.

Evaluation of reaction temperature (Table S3):

Entry	Temp.	Yield [%] ^a
1	0 °C	49 %
2	25 °C	77 %
3	60 °C	55 %

Reaction conditions: undivided cell, Pt anode, Pt cathode, **1** (0.5 mmol), Et₃N•3HF (1.2 mL), PhCF₃ (4.8 mL). [a] GC Yield using biphenyl as internal standard.

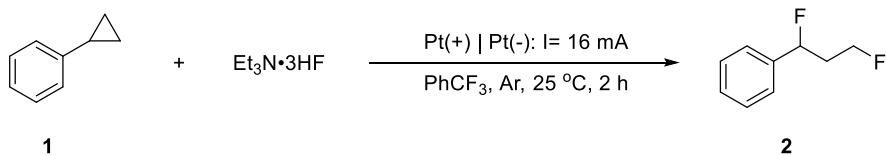
Evaluation of electrode materials (Table S4):



Entry	Electrode	Yield [%] ^a
1	Pt(+) Pt(-)	77 %
2	C cloth(+) Pt(-)	69 %
3	C rod(+) Pt(-)	63 %
4	Pt(+) Ni plate(-)	71 %
5	Pt(+) Ni foam(-)	74 %

Reaction conditions: undivided cell, Pt anode, Pt cathode, **1** (0.5 mmol), Et₃N·3HF (1.2 mL), PhCF₃ (4.8 mL). [a] GC Yield using biphenyl as internal standard.

Evaluation of amount of Et₃N·3HF and electricity (Table S5):



Entry	Variation from standard conditions	Yield [%] ^a
9	0.5 mL Et ₃ N·3HF, 5.5 mL PhCF ₃	64%
10	5 mL Et ₃ N·3HF	66%
11	no electric current	N.R.

Reaction conditions: undivided cell, Pt anode, Pt cathode, **1** (0.5 mmol), Et₃N·3HF (1.2 mL), PhCF₃ (4.8 mL). [a] GC Yield using biphenyl as internal standard.

4) Procedures and analytical data of 1,3-difluorination compounds

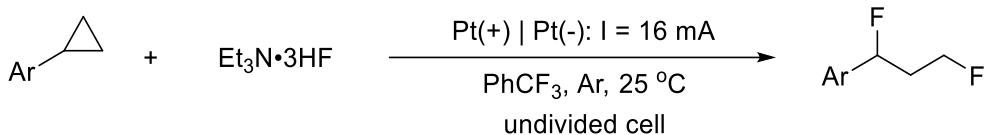
Graphical guide for the set-up: As experiment set-up, a platinum plate electrode anode (15 mm×15 mm×0.3 mm), a platinum plate electrode cathode (15 mm×15 mm×0.3 mm), rubber plugs, an undivided three-necked bottle and a dual display potentiostat (HJS-292B) (made in China) were used.



A) Platinum plate anode and cathode

B) Assembly of electrochemical cell

C) Current control electrosis

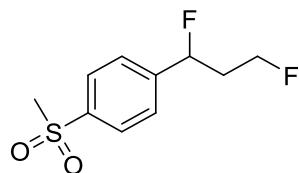


General procedure for the electrolysis: An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped platinum plate (15 mm×15 mm×0.3 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with argon gas by glove box. Arylcyclopropane (0.1 mmol, 0.25 mmol or 0.5 mmol), Et₃N·3HF (1.2 mL) and PhCF₃ (4.8 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 16 mA under room temperature (monitored by TLC). The reaction was diluted with water. The organic layer was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

Analytical data of compounds:



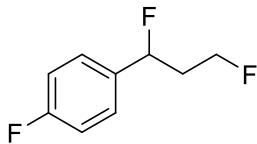
(1,3-Difluoropropyl)benzene (2). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **3** as a colorless oil. NMR Yield = 75% using 1-fluoronaphthalene as internal standard, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.32 (m, 5H), 5.64 (ddd, *J* = 47.8, 9.1, 4.1 Hz, 1H), 4.78 – 4.41 (m, 2H), 2.40 – 2.08 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.54 (d, *J* = 19.5 Hz), 128.72, 128.69 (d, *J* = 2.0 Hz), 125.59 (d, *J* = 6.7 Hz), 90.70 (dd, *J* = 170.7, 4.8 Hz), 80.07 (dd, *J* = 165.0, 4.7 Hz), 38.25 (dd, *J* = 24.1, 19.7 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -178.55, -222.47. HRMS (EI+) m/z calculated for C₉H₁₀F₂ (M⁺): 156.0751, found: 156.0752.



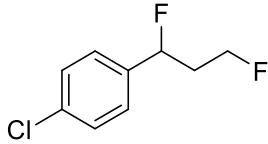
1-(1,3-Difluoropropyl)-4-(methylsulfonyl)benzene (6).^[2] 0.5 mmol scale, 200 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3:1) to give **6** as a yellow solid. Yield = 75%, electricity = 4.0 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 5.84 – 5.68 (m, 1H), 4.81 – 4.48 (m, 2H), 3.08 (s, 3H), 2.34 – 2.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 145.70 (d, *J* = 19.9 Hz), 140.52 (d, *J* = 1.4 Hz), 127.82, 126.15 (d, *J* = 7.6 Hz), 89.61 (dd, *J* = 173.9, 4.4 Hz), 79.50 (dd, *J* = 165.8, 4.4 Hz), 44.45, 38.17 (dd, *J* = 23.3, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -183.72, -222.41.



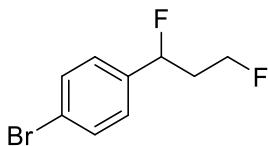
1-(1,3-difluoropropyl)-3-(methylsulfonyl)benzene (7). 0.5 mmol scale, 200 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3:1) to give **7** as a yellow oil. Yield = 75%, electricity = 4.0 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.90 (m, 2H), 7.69 – 7.60 (m, 2H), 5.86 – 5.66 (m, 1H), 4.86 – 4.45 (m, 2H), 3.09 (s, 3H), 2.38 – 2.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.49 (d, *J* = 20.4 Hz), 141.19, 130.68 (d, *J* = 6.9 Hz), 129.92, 127.48 (d, *J* = 1.4 Hz), 124.28 (d, *J* = 7.6 Hz), 89.67 (dd, *J* = 173.6, 4.4 Hz), 79.56 (dd, *J* = 165.9, 4.4 Hz), 44.49, 38.14 (dd, *J* = 23.5, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -181.56, -222.41. HRMS (ESI) m/z calculated for C₁₀H₁₃F₂O₂S (M+H)⁺ : 235.05988, found: 235.05975.



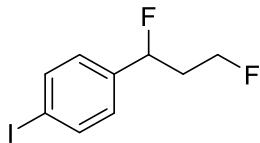
1-(1,3-Difluoropropyl)-4-fluorobenzene (8). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **8** as a colorless oil. Yield = 52%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.30 (m, 2H), 7.17 – 7.03 (m, 2H), 5.63 (ddd, *J* = 47.6, 9.1, 4.1 Hz, 1H), 4.82 – 4.41 (m, 2H), 2.41 – 2.07 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.91 (dd, *J* = 247.2, 2.1 Hz), 135.34 (dd, *J* = 20.0, 3.2 Hz), 127.58 (dd, *J* = 8.2, 6.5 Hz), 115.75 (d, *J* = 21.7 Hz), 90.16 (dd, *J* = 170.8, 4.6 Hz), 80.00 (dd, *J* = 165.2, 4.7 Hz), 38.25 (dd, *J* = 24.5, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -113.17 (d, *J* = 3.3 Hz), -176.45 (d, *J* = 3.2 Hz), -222.61. HRMS (EI+) m/z calculated for C₉H₉F₃ (M<>): 174.0656, found: 174.0659.



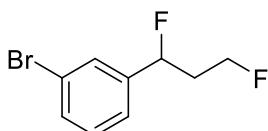
1-chloro-4-(1,3-difluoropropyl)benzene (9). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **9** as a pale yellow oil. Yield = 66%, electricity = 2.4 F mol⁻¹. NMR (400 MHz, CDCl₃) δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 5.62 (ddd, *J* = 47.6, 9.0, 4.1 Hz, 1H), 4.78 – 4.41 (m, 2H), 2.38 – 2.05 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.05 (d, *J* = 19.9 Hz), 134.51 (d, *J* = 2.3 Hz), 128.95, 127.00 (d, *J* = 6.8 Hz), 90.03 (dd, *J* = 171.6, 4.7 Hz), 79.87 (dd, *J* = 165.4, 4.7 Hz), 38.21 (dd, *J* = 24.1, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -178.96, -222.52. HRMS (EI+) m/z calculated for C₉H₉ClF₂ (M<>): 190.0361, found: 190.0368.



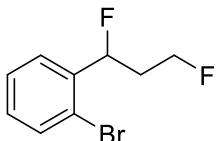
1-Bromo-4-(1,3-difluoropropyl)benzene (10). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **10** as a colorless oil. Yield = 67%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 5.60 (ddd, *J* = 47.6, 9.0, 4.1 Hz, 1H), 4.78 – 4.41 (m, 2H), 2.37 – 2.05 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.57 (d, *J* = 20.0 Hz), 131.90, 127.27 (d, *J* = 6.8 Hz), 122.63 (d, *J* = 2.4 Hz), 90.05 (dd, *J* = 171.8, 4.6 Hz), 79.83 (dd, *J* = 165.5, 4.6 Hz), 38.17 (dd, *J* = 24.0, 19.7 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -179.45, -222.49. HRMS (EI+) m/z calculated for C₉H₉BrF₂ (M<>): 233.9856, found: 233.9860.



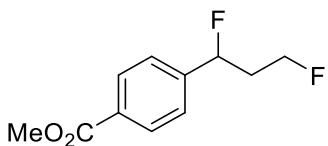
1-(1,3-Difluoropropyl)-4-iodobenzene (11). 0.5 mmol, 140 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **11** as a colorless oil. Yield = 52%, electricity = 2.8 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.70 – 5.48 (m, 1H), 4.79 – 4.40 (m, 2H), 2.36 – 2.05 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.22 (d, *J* = 19.9 Hz), 137.84, 127.41 (d, *J* = 6.8 Hz), 94.32 (d, *J* = 2.5 Hz), 90.09 (dd, *J* = 171.9, 4.6 Hz), 79.82 (dd, *J* = 165.5, 4.6 Hz), 38.15 (dd, *J* = 23.9, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -180.02, -222.44. HRMS (EI+) m/z calculated for C₉H₉F₂I (M⁺): 281.9717, found: 281.9723.



1-bromo-3-(1,3-difluoropropyl)benzene (12). 0.5 mmol scale, add 0.5 mL DCE, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **12** as a colorless oil. Yield = 63%, electricity = 2.4 F·mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.46 (m, 2H), 7.36 – 7.27 (m, 2H), 5.65 (ddd, *J* = 47.7, 8.8, 4.3 Hz, 1H), 4.83 – 4.47 (m, 2H), 2.42 – 2.10 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.83 (d, *J* = 19.9 Hz), 131.73 (d, *J* = 1.7 Hz), 130.36, 128.60 (d, *J* = 7.5 Hz), 124.13 (d, *J* = 6.9 Hz), 122.84, 89.80 (dd, *J* = 172.8, 4.6 Hz), 79.79 (dd, *J* = 165.6, 4.6 Hz), 38.24 (dd, *J* = 23.8, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -180.45, -222.52. HRMS (EI+) m/z calculated for C₉H₉BrF₂ (M⁺): 233.9850, found: 233.9853.

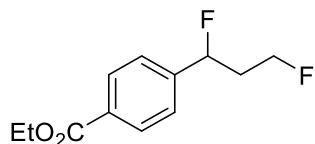


1-Bromo-2-(1,3-difluoropropyl)benzene (13). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **13** as a colorless oil. Yield = 52%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.45 (m, 2H), 7.39 – 7.35 (m, 1H), 7.21 – 7.17 (m, 1H), 5.95 (ddd, *J* = 47.1, 9.5, 2.7 Hz, 1H), 4.85 – 4.48 (m, 2H), 2.51 – 1.97 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.17 (d, *J* = 21.2 Hz), 132.91, 129.87 (d, *J* = 1.4 Hz), 127.95, 126.74 (d, *J* = 10.3 Hz), 120.61 (d, *J* = 5.9 Hz), 89.83 (dd, *J* = 173.1, 5.2 Hz), 79.97 (dd, *J* = 166.1, 2.9 Hz), 37.08 (dd, *J* = 23.6, 20.0 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -185.12, -222.30 (d, *J* = 1.1 Hz). HRMS (EI+) m/z calculated for C₉H₉BrF₂ (M⁺): 233.9856, found: 233.9858.

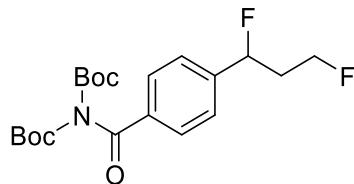


Methyl 4-(1,3-difluoropropyl)benzoate (14). 0.5 mmol scale, 6 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate

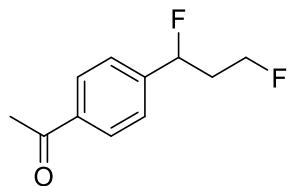
= 100:1) to give **14** as a pale yellow oil. Yield = 56%, electricity = 7.2 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 5.81 – 5.61 (m, 1H), 4.81 – 4.44 (m, 2H), 3.92 (s, 3H), 2.35 – 2.14 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 166.70, 144.51 (d, *J* = 19.6 Hz), 130.33 (d, *J* = 1.6 Hz), 130.02, 125.28 (d, *J* = 7.3 Hz), 90.07 (dd, *J* = 172.7, 4.6 Hz), 79.74 (dd, *J* = 165.6, 4.5 Hz), 52.30, 38.26 (dd, *J* = 23.6, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -182.45, -222.52. HRMS (ESI) m/z calcd for C₁₁H₁₃F₂O₂ (M+H)⁺ : 215.08781, found : 215.08720.



Ethyl 4-(1,3-difluoropropyl)benzoate (15).^[2] 0.5 mmol scale, 6 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give **15** as a pale yellow oil. Yield = 56%, electricity = 7.2 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 5.84 – 5.60 (m, 1H), 4.82 – 4.43 (m, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.39 – 2.10 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.20 (s), 144.38 (d, *J* = 19.5 Hz), 130.68 (d, *J* = 1.5 Hz), 129.96, 125.22 (d, *J* = 7.3 Hz), 90.08 (dd, *J* = 172.7, 4.6 Hz), 79.73 (dd, *J* = 165.6, 4.5 Hz), 61.18, 38.26 (dd, *J* = 23.6, 19.8 Hz), 14.38. ¹⁹F NMR (377 MHz, CDCl₃) δ -182.34, -222.51.

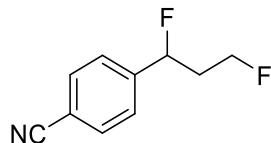


(16). 0.25 mmol scale, add 0.5 mL DCE, 10 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15:1) to give **16** as a white solid. Isolated yield = 52%, 27% starting material was recovered, electricity = 23.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 5.89 – 5.58 (m, 1H), 4.87 – 4.44 (m, 2H), 2.37 – 2.11 (m, 2H), 1.39 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 168.92, 149.79, 145.19 (d, *J* = 19.7 Hz), 134.28 (d, *J* = 1.5 Hz), 129.48, 125.49 (d, *J* = 7.4 Hz), 89.86 (dd, *J* = 173.4, 4.5 Hz), 84.54, 79.60 (dd, *J* = 165.9, 4.4 Hz), 38.26 (dd, *J* = 23.5, 19.8 Hz), 27.65. ¹⁹F NMR (377 MHz, CDCl₃) δ -183.23, -222.45. HRMS (EI+) m/z calculated for C₂₀H₂₇F₂NO₅Na (M+Na⁺): 422.17495, found: 422.17328.

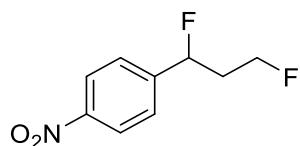


1-(4-(1,3-difluoropropyl)phenyl)ethan-1-one (17).^[2] 0.5 mmol scale, 14 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **17** as a pale yellow oil. Isolated yield = 42%, electricity = 16.7 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 5.81 – 5.62 (m, 1H), 4.82 – 4.44 (m, 2H), 2.62 (s, 3H), 2.35 – 2.15 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 197.71, 144.66 (d, *J* = 19.6 Hz), 137.16 (d, *J* = 1.4 Hz), 128.76, 125.46 (d, *J* = 7.3 Hz), 90.02 (dd, *J* = 172.8,

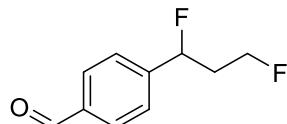
4.6 Hz), 79.71 (dd, J = 165.6, 4.5 Hz), 38.20 (dd, J = 23.5, 19.8 Hz), 26.74. ^{19}F NMR (377 MHz, CDCl_3) δ -182.59, -222.45.



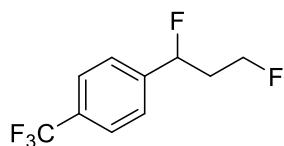
4-(1,3-difluoropropyl)benzonitrile (18).^[2] 0.5 mmol scale, 20 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **18** as a pale yellow oil. Isolated yield = 49%, electricity = 23.9 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 5.72 (ddd, J = 47.7, 7.9, 5.1 Hz, 1H), 4.82 – 4.46 (m, 2H), 2.33 – 2.15 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.79 (d, J = 20.0 Hz), 132.59, 125.95 (d, J = 7.7 Hz), 118.53, 112.43 (d, J = 1.6 Hz), 89.64 (dd, J = 174.1, 4.4 Hz), 79.51 (dd, J = 166.0, 4.4 Hz), 38.19 (dd, J = 23.3, 19.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -183.97, -222.47.



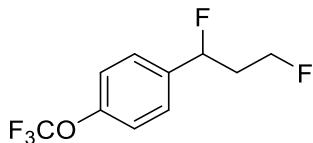
1-(1,3-Difluoropropyl)-4-nitrobenzene (19).^[2] 0.5 mmol scale, 3 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **19** as a yellow oil. Yield = 49%, electricity = 3.6 F·mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, J = 8.3 Hz, 2H), 7.54 (d, J = 8.9 Hz, 2H), 5.94 – 5.64 (m, 1H), 4.83 – 4.48 (m, 2H), 2.38 – 2.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.92, 146.72 (d, J = 19.9 Hz), 126.10 (d, J = 7.7 Hz), 123.96, 89.51 (dd, J = 174.4, 4.4 Hz), 79.47 (dd, J = 166.0, 4.4 Hz), 38.22 (dd, J = 23.2, 19.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -183.95, -222.44.



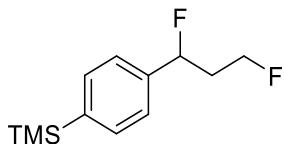
4-(1,3-Difluoropropyl)benzaldehyde (20). 0.5 mmol, 16 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give **20** as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 10.03 (s, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 5.84 – 5.65 (m, 1H), 4.82 – 4.47 (m, 2H), 2.36 – 2.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.85, 146.20 (d, J = 19.6 Hz), 136.46, 130.17, 125.87 (d, J = 7.5 Hz), 89.98 (dd, J = 173.4, 4.5 Hz), 79.67 (dd, J = 165.8, 4.4 Hz), 38.30 (dd, J = 23.5, 19.8 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -183.28, -222.47. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{11}\text{F}_2\text{O}$ ($\text{M}+\text{H}$)⁺ : 185.07725, found : 185.07729.



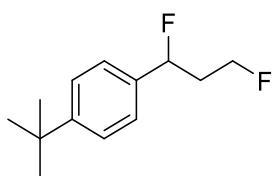
1-(1,3-Difluoropropyl)-4-(trifluoromethyl)benzene (21). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **21** as a colorless oil. Yield = 49%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 5.82 – 5.60 (m, 1H), 4.83 – 4.44 (m, 2H), 2.36 – 2.14 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 143.61 (d, *J* = 21.0 Hz), 130.83 (q, *J* = 32.4 Hz), 125.78 (q, *J* = 3.6 Hz), 125.73 (d, *J* = 7.5 Hz), 124.08 (q, *J* = 272.1 Hz), 89.93 (dd, *J* = 173.0, 4.6 Hz), 79.72 (dd, *J* = 165.7, 4.5 Hz), 38.37 (dd, *J* = 23.5, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -62.66, -182.59, -222.58. HRMS (EI+) m/z calculated for C₁₀H₉F₅ (M⁺): 224.0624, found: 224.0616.



1-(1,3-Difluoropropyl)-4-(trifluoromethoxy)benzene (22). 0.25 mmol scale, add 0.5 mL DCE, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (30–60 °C petroleum ether: ethyl acetate = 200:1) to give **22** as a colorless oil. Isolated yield = 53%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.67 (ddd, *J* = 47.6, 9.0, 4.1 Hz, 1H), 4.83 – 4.40 (m, 2H), 2.43 – 2.08 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 149.38, 138.28 (d, *J* = 20.1 Hz), 127.13 (d, *J* = 6.8 Hz), 121.29, 120.56 (q, *J* = 258.4 Hz), 89.94 (dd, *J* = 171.8, 4.6 Hz), 79.86 (dd, *J* = 165.5, 4.6 Hz), 38.31 (dd, *J* = 24.0, 19.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -57.90, -179.09, -222.64. HRMS (EI+) m/z calculated for C₁₀H₉F₅O (M⁺): 240.0574, found: 240.0581.

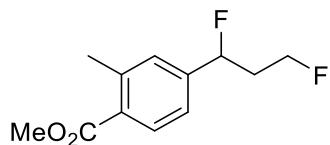


(4-(1,3-Difluoropropyl)phenyl)trimethylsilane (23). 0.25 mmol scale, add 0.5 mL DCE, 110 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **23** as a colorless oil. Yield = 53%, electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 5.63 (ddd, *J* = 47.9, 9.1, 4.1 Hz, 1H), 4.84 – 4.39 (m, 2H), 2.41 – 2.07 (m, 2H), 0.27 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 141.25 (d, *J* = 1.7 Hz), 140.00 (d, *J* = 19.4 Hz), 133.75, 124.90 (d, *J* = 6.7 Hz), 90.69 (dd, *J* = 170.7, 4.8 Hz), 80.13 (dd, *J* = 165.1, 4.6 Hz), 38.23 (dd, *J* = 24.1, 19.7 Hz), -1.04. ¹⁹F NMR (377 MHz, CDCl₃) δ -179.29, -222.45. HRMS (EI+) m/z calculated for C₁₂H₁₈F₂Si (M⁺): 228.1146, found: 228.1150.

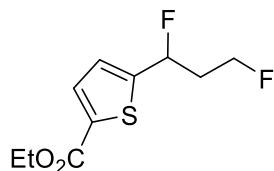


1-(Tert-butyl)-4-(1,3-difluoropropyl)benzene (24). 0.25 mmol, 40 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **24** as a colorless oil. Isolated yield = 40%, electricity = 1.6 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 5.62 (ddd, *J* = 47.9, 9.2, 4.0 Hz, 1H), 4.81 – 4.40 (m, 2H), 2.43 – 2.08 (m, 2H), 1.32 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 151.82 (d, *J* = 2.2 Hz), 136.47 (d, *J* = 19.5 Hz), 125.67, 125.53 (d, *J* = 6.3 Hz), 90.64 (dd, *J* = 169.7, 4.9

Hz), 80.21 (dd, J = 165.0, 4.6 Hz), 38.09 (dd, J = 24.3, 19.7 Hz), 34.75, 31.42. ^{19}F NMR (377 MHz, CDCl_3) δ -176.63, -222.43. HRMS (EI+) m/z calculated for $\text{C}_{13}\text{H}_{18}\text{F}_2$ (M^+): 212.1377, found: 212.1376.



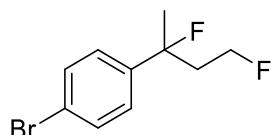
Methyl 4-(1,3-difluoropropyl)-2-methylbenzoate (25). 0.5 mmol scale, 6 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give **25** as a colorless oil. Yield = 54%, electricity = 7.2 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 8.6 Hz, 1H), 7.23 – 7.21 (m, 2H), 5.66 (ddd, J = 47.9, 8.5, 4.5 Hz, 1H), 4.82 – 4.43 (m, 2H), 3.90 (s, 3H), 2.62 (s, 3H), 2.34 – 2.13 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.73, 143.42 (d, J = 19.5 Hz), 140.89, 131.15, 129.72, 128.54 (d, J = 7.1 Hz), 122.61 (d, J = 7.1 Hz), 90.07 (dd, J = 172.4, 4.7 Hz), 79.85 (dd, J = 165.5, 4.5 Hz), 52.06, 38.26 (dd, J = 23.7, 19.8 Hz), 21.95. ^{19}F NMR (377 MHz, CDCl_3) δ -182.34, -222.53. HRMS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{F}_2\text{O}_2$ ($\text{M}+\text{H}$)⁺: 229.10346, found : 229.10347.



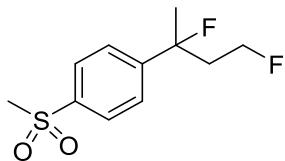
Ethyl 5-(1,3-difluoropropyl)thiophene-2-carboxylate (26). 0.25 mmol scale, 80 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give **26** as a yellow oil. Isolated yield = 56%, electricity = 3.2 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 7.71 – 7.69 (m, 1H), 7.13 – 6.96 (m, 1H), 5.85 (ddd, J = 48.0, 8.9, 4.4 Hz, 1H), 4.84 – 4.45 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 2.78 – 2.20 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.02, 148.51 (d, J = 21.3 Hz), 134.55 (d, J = 2.6 Hz), 133.11 (d, J = 1.4 Hz), 126.23 (d, J = 5.8 Hz), 86.15 (dd, J = 171.5, 4.8 Hz), 79.50 (dd, J = 166.1, 4.4 Hz), 61.51, 37.99 (dd, J = 23.8, 19.9 Hz), 14.41. ^{19}F NMR (377 MHz, CDCl_3) δ -165.87, -222.91. HRMS (ESI) m/z calcd for $\text{C}_{10}\text{H}_{13}\text{F}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$)⁺: 235.05988, found : 235.05981.



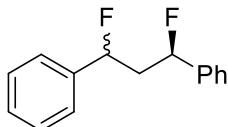
(1,3-Difluoropentan-3-yl)benzene (27).^[8] 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **27** as a colorless oil. Yield = 67%, electricity = 2.4 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 7.63 – 7.24 (m, 5H), 4.64 – 4.23 (m, 2H), 2.52 – 2.21 (m, 2H), 2.12 – 1.85 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.87 (d, J = 22.1 Hz), 128.35 (d, J = 1.9 Hz), 127.32 (d, J = 0.9 Hz), 124.35 (d, J = 10.5 Hz), 98.48 (dd, J = 176.3, 7.1 Hz), 80.05 (dd, J = 163.8, 5.1 Hz), 40.79 (dd, J = 23.1, 19.7 Hz), 33.80 (d, J = 23.9 Hz), 7.46 (d, J = 4.9 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -162.48 (d, J = 1.9 Hz), -220.34 (d, J = 2.1 Hz).



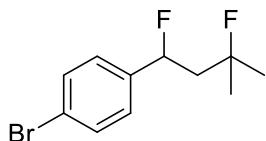
1-Bromo-4-(2,4-difluorobutan-2-yl)benzene (28). [8] 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **28** as a colorless oil. Yield = 65%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.67 – 4.30 (m, 2H), 2.45 – 2.20 (m, 2H), 1.70 (d, *J* = 22.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 143.14 (d, *J* = 22.2 Hz), 131.68 (d, *J* = 1.4 Hz), 125.86 (d, *J* = 9.8 Hz), 121.67 (d, *J* = 1.6 Hz), 95.97 (dd, *J* = 173.7, 5.4 Hz), 79.83 (dd, *J* = 165.0, 5.2 Hz), 42.25 (dd, *J* = 23.8, 19.6 Hz), 27.81 (d, *J* = 24.9 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -148.18 (d, *J* = 2.3 Hz), -219.84 (d, *J* = 2.3 Hz).



1-(2,4-Difluorobutan-2-yl)-4-(methylsulfonyl)benzene (29). 0.25 mmol scale, 100 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3:1) to give **29** as a yellow oil. Yield = 81%, electricity = 4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 4.70 – 4.33 (m, 2H), 3.08 (s, 3H), 2.54 – 2.22 (m, 2H), 1.75 (d, *J* = 22.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 150.23 (d, *J* = 22.0 Hz), 139.81, 127.73 (d, *J* = 1.7 Hz), 125.09 (d, *J* = 10.1 Hz), 95.86 (dd, *J* = 175.7, 4.6 Hz), 79.45 (dd, *J* = 165.7, 5.1 Hz), 44.54, 42.05 (dd, *J* = 23.5, 19.7 Hz), 27.77 (d, *J* = 24.9 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -149.48 (d, *J* = 2.5 Hz), -219.41 (d, *J* = 2.5 Hz). HRMS (ESI) m/z calcd for C₁₁H₁₅F₂O₂S (M+H)⁺ : 249.07553, found : 249.07550.

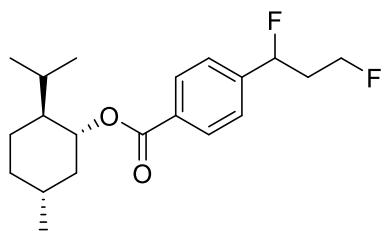


1,3-Difluoro-1,3-diphenylpropane (30). 0.5 mmol scale, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **30** as a colorless oil with 1.3:1 diastereoselectivity. Isolated yield = 61%, electricity = 2.4 F mol⁻¹. ¹H, ¹³C, ¹⁹F spectra are obtained from diastereoisomer mixture. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 23.2 H), 5.89 – 5.71 (m, 2.6 H), 5.43 (ddd, *J* = 47.1, 7.8, 6.2 Hz, 2H), 2.90 – 2.75 (m, 1H), 2.44 – 2.15 (m, 3.8 H). ¹³C NMR (101 MHz, CDCl₃) δ 139.65 (d, *J* = 19.4 Hz), 139.13 (d, *J* = 19.5 Hz), 128.92 (d, *J* = 2.1 Hz), 128.79, 128.74, 128.71 (d, *J* = 1.0 Hz), 125.97 (d, *J* = 6.5 Hz), 125.59 (d, *J* = 6.9 Hz), 91.67 (dd, *J* = 170.2, 6.5 Hz), 90.63 (dd, *J* = 171.1, 2.3 Hz), 45.63 (t, *J* = 23.4 Hz) 44.42 (t, *J* = 24.4 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -174.32, -178.23. HRMS (EI+) m/z calculated for C₁₅H₁₄F₂ (M+): 232.1064, found: 232.1059.

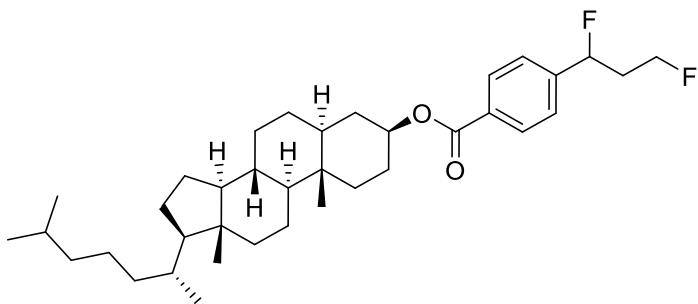


1-Bromo-4-(1,3-difluoro-3-methylbutyl)benzene (31). 0.25 mmol scale, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 200:1) to give **31** as a colorless oil. Isolated yield = 81%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.58 – 7.49 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 5.68 (ddd, *J* = 48.4,

9.5, 2.0 Hz, 1H), 2.59 – 1.93 (m, 2H), 1.52 (dd, J = 21.7, 1.3 Hz, 3H), 1.43 (d, J = 21.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.67 (d, J = 20.4 Hz), 131.82 (d, J = 5.0 Hz), 127.20 (d, J = 6.9 Hz), 122.38 (d, J = 2.4 Hz), 94.38 (d, J = 166.5 Hz), 90.42 (dd, J = 171.8, 5.8 Hz), 48.70 (t, J = 22.8 Hz), 28.55 (dd, J = 24.0, 1.3 Hz), 26.37 (dd, J = 24.8, 3.0 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -136.88 (d, J = 3.6 Hz), -173.34 (d, J = 3.7 Hz). HRMS (EI+) m/z calculated for $\text{C}_{11}\text{H}_{13}\text{BrF}_2$ (M^+): 262.0163, found: 262.0159.

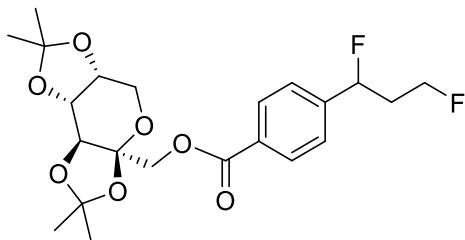


(1R, 2S, 5R)-2-isopropyl-5-methylcyclohexyl 4-(1,3-difluoropropyl)benzoate (32). 0.1 mmol scale, add 0.5 ml DCE, 2 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **32** as yellow oil. Isolated yield = 86%, electricity = 11.9 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 5.71 (ddd, J = 47.8, 8.5, 4.5 Hz, 1H), 4.94 (td, J = 10.9, 4.4 Hz, 1H), 4.81 – 4.44 (m, 2H), 2.40 – 2.15 (m, 2H), 2.15 – 2.09 (m, 1H), 1.99 – 1.91 (m, 1H), 1.79 – 1.70 (m, 2H), 1.63 – 1.50 (m, 2H), 1.18 – 1.05 (m, 2H), 0.94 – 0.91 (m, 7H), 0.80 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.72, 144.31 (d, J = 19.6 Hz), 131.10, 130.03, 125.26 (d, J = 7.2 Hz), 90.13 (dd, J = 172.7, 4.6 Hz), 79.78 (dd, J = 165.6, 4.5 Hz), 75.13, 47.36, 41.06, 38.33 (dd, J = 23.6, 19.8 Hz), 34.41, 31.56, 26.63, 23.73, 22.17, 20.89, 16.63. ^{19}F NMR (377 MHz, CDCl_3) δ -182.26 (d, J = 26.3 Hz), -222.50 (d, J = 2.4 Hz). HRMS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{38}\text{F}_2\text{O}_2\text{Na}$ ($\text{M}+\text{Na}^+$): 361.19496, found : 361.19437.

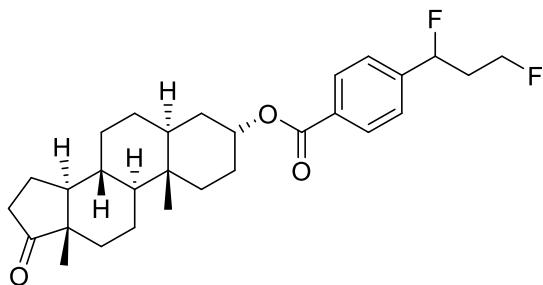


(33). 0.1 mmol scale, add 0.5 mL DCE, 4 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 100:1) to give **33** as white solid. Isolated yield = 65%, 10% starting material was recovered, electricity = 23.8 F mol⁻¹. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 5.71 (ddd, J = 47.7, 8.3, 4.5 Hz, 1H), 5.03 – 4.87 (m, 1H), 4.81 – 4.42 (m, 2H), 2.38 – 2.09 (m, 2H), 2.02 – 1.89 (m, 2H), 1.85 – 0.99 (m, 28H), 0.92 – 0.84 (m, 12H), 0.73 – 0.63 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.73, 144.24 (d, J = 19.5 Hz), 131.19, 130.00, 125.18 (d, J = 7.2 Hz), 90.12 (dd, J = 172.7, 4.5 Hz), 79.78 (dd, J = 165.7, 4.5 Hz), 74.68, 56.52, 56.37, 54.33, 44.80, 42.70, 40.09, 39.64, 38.35 (dd, J = 23.6, 19.8 Hz), 36.90, 36.29, 35.94, 35.63, 35.59, 34.22, 32.12, 28.76, 28.39, 28.14, 27.69, 24.34, 23.97, 22.97, 22.71, 21.35, 18.80, 12.42, 12.20. ^{19}F NMR (377 MHz, CDCl_3) δ -182.32 (d,

$J = 3.3$ Hz), -222.48. HRMS (DART POSITIVE) m/z calcd for $C_{37}H_{60}F_2NO_2$ ($M+NH_4$)⁺ : 588.4587, found : 588.4589.

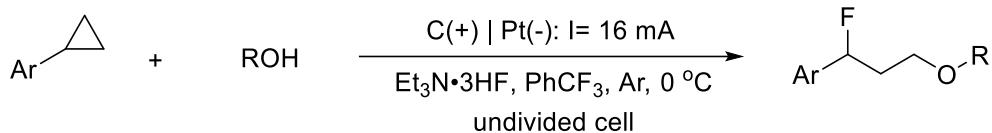


(34). 0.1 mmol scale, add 0.5 mL DCE, 6 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8:1) to give **34** as colorless oil. Isolated yield = 82%, electricity = 35.8 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, $J = 8.1$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 5.83 – 5.60 (m, 1H), 4.81 – 4.44 (m, 5H), 4.36 – 4.26 (m, 2H), 3.99 – 3.79 (m, 2H), 2.40 – 2.12 (m, 2H), 1.55 (s, 3H), 1.47 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.55, 144.74 (d, $J = 19.6$ Hz), 130.20, 130.06, 125.28 (d, $J = 7.3$ Hz), 109.23, 108.93, 101.68, 90.01 (dd, $J = 172.9, 4.6$ Hz), 79.70 (dd, $J = 165.7, 4.5$ Hz), 70.83, 70.61, 70.13, 65.48, 61.41, 38.26 (dd, $J = 23.5, 19.8$ Hz), 26.60, 25.94, 25.59, 24.07. ¹⁹F NMR (377 MHz, CDCl₃) δ -182.69 (d, $J = 8.2$ Hz), -222.51. HRMS (ESI) m/z calcd for $C_{22}H_{29}F_2O_7$ ($M+H$)⁺ : 443.18759, found : 443.18588.

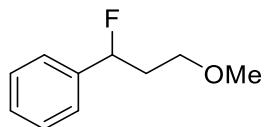


(3R, 5S, 8R, 9S, 10S, 13S, 14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-(1,3-difluoropropyl)benzoate (35). 0.1 mmol scale, add 0.5 mL DCE, 140 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 15:1) to give **35** as white solid. Yield = 30%, 36% starting material was recovered, electricity = 13.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, $J = 8.1$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 5.71 (ddd, $J = 47.7, 8.3, 4.5$ Hz, 1H), 5.01 – 4.89 (m, 1H), 4.82 – 4.43 (m, 2H), 2.48 – 2.41 (m, 1H), 2.35 – 2.14 (m, 2H), 2.13 – 2.02 (m, 1H), 2.00 – 1.90 (m, 2H), 1.85 – 1.73 (m, 4H), 1.72 – 1.47 (m, 5H), 1.36 – 1.23 (m, 6H), 1.17 – 0.98 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H), 0.79 – 0.71 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 221.44, 165.72, 144.30 (d, $J = 19.6$ Hz), 131.07, 129.99, 125.20 (d, $J = 7.2$ Hz), 90.11 (dd, $J = 172.7, 4.6$ Hz), 79.77 (dd, $J = 165.6, 4.5$ Hz), 74.40, 54.39, 51.45, 47.90, 44.79, 38.32 (dd, $J = 23.6, 19.7$ Hz), 36.83, 35.97, 35.81, 35.14, 34.12, 31.62, 30.92, 28.40, 27.61, 21.89, 20.59, 13.93, 12.40. ¹⁹F NMR (377 MHz, CDCl₃) δ -182.32 (d, $J = 3.5$ Hz), -222.50. HRMS (ESI) m/z calcd for $C_{29}H_{39}F_2O_3$ ($M+H$)⁺ : 473.28618, found : 473.28513.

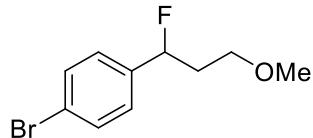
5) Procedures and analytical data of 1,3-oxyfluorination compounds



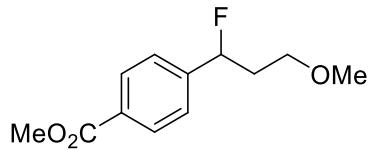
An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped carbon cloth (15 mm×15 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with argon gas by glove box. Arylcyclopropane (0.25 mmol), ROH (0.2-0.75 mL), Et₃N·3HF (0.8 mL) and PhCF₃ (4.8 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 16 mA under 0 °C. The reaction was diluted with water. The organic layer was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.



(1-fluoro-3-methoxypropyl)benzene (33). 0.25 mmol scale, 0.2 mL MeOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **33** as colorless oil. Yield = 76%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.28 (m, 5H), 5.62 (ddd, *J* = 47.9, 9.0, 4.3 Hz, 1H), 3.63 – 3.39 (m, 2H), 3.37 (s, 3H), 2.30 – 1.96 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.22 (d, *J* = 19.6 Hz), 128.62, 128.45 (d, *J* = 2.0 Hz), 125.65 (d, *J* = 6.8 Hz), 91.78 (d, *J* = 169.7 Hz), 68.47 (d, *J* = 4.7 Hz), 58.92, 37.59 (d, *J* = 23.9 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -177.56. HRMS (ESI) m/z calculated for C₁₀H₁₃FONa (M+Na)⁺ : 191.08426, found: 191.08354.

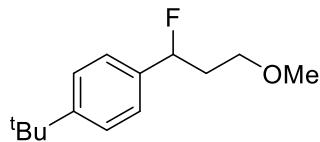


1-Bromo-4-(1-fluoro-3-methoxypropyl)benzene (36). 0.25 mmol scale, 0.2 mL MeOH, 100 min. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **36** as colorless oil. Yield = 50%, electricity = 4.0 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 5.62 (ddd, *J* = 47.7, 8.9, 4.3 Hz, 1H), 3.68 – 3.36 (m, 5H), 2.29 – 1.94 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.26 (d, *J* = 20.0 Hz), 131.76, 127.33 (d, *J* = 6.9 Hz), 122.33 (d, *J* = 2.4 Hz), 91.09 (d, *J* = 170.7 Hz), 68.20 (d, *J* = 4.8 Hz), 58.93, 37.52 (d, *J* = 23.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -178.49. HRMS (ESI) m/z calculated for C₁₀H₁₂BrFONa (M+Na)⁺ : 268.99478, found: 268.99551.

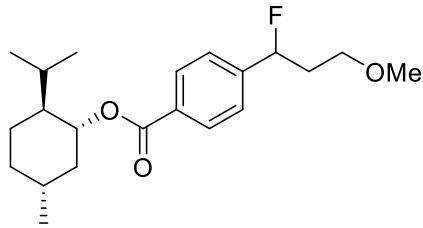


Methyl 4-(1-fluoro-3-methoxypropyl)benzoate (37). 0.25 mmol scale, 0.2 mL MeOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **37** as colorless oil. Yield = 69%, electricity = 2.4 F mol⁻¹. ¹H

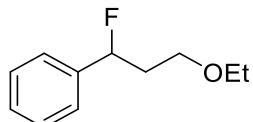
NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 5.70 (ddd, J = 47.9, 8.9, 4.2 Hz, 1H), 3.94 (s, 3H), 3.67 – 3.34 (m, 5H), 2.33 – 1.95 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.80, 145.27 (d, J = 19.7 Hz), 130.04 (d, J = 1.5 Hz), 129.90, 125.32 (d, J = 7.3 Hz), 91.10 (d, J = 171.6 Hz), 68.09 (d, J = 4.6 Hz), 58.90, 52.27, 37.62 (d, J = 23.4 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -181.50. HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{15}\text{FO}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 249.08974, found: 249.08956.



1-(Tert-butyl)-4-(1-fluoro-3-methoxypropyl)benzene (38). 0.25 mmol scale, 0.2 mL MeOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **38** as colorless oil. Yield = 49%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, J = 8.5 Hz, 2H), 7.31 – 7.26 (m, 2H), 5.59 (ddd, J = 48.0, 9.1, 4.2 Hz, 1H), 3.64 – 3.42 (m, 2H), 3.37 (s, 3H), 2.32 – 1.95 (m, 2H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.52 (d, J = 2.1 Hz), 137.17 (d, J = 19.6 Hz), 125.56 (d, J = 3.2 Hz), 125.53 (d, J = 3.2 Hz), 91.70 (d, J = 168.6 Hz), 68.60 (d, J = 4.5 Hz), 58.91, 37.40 (d, J = 24.1 Hz), 34.73, 31.45. ^{19}F NMR (376 MHz, CDCl_3) δ -175.43 – -175.76 (m). HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{21}\text{FONa}$ ($\text{M}+\text{Na}$) $^+$: 247.14686, found: 247.14703.

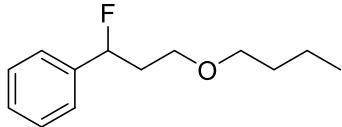


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(1-fluoro-3-methoxypropyl)benzoate (39). 0.25 mmol scale, 0.2 mL MeOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **39**. Yield = 56%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.1 Hz, 2H), 5.69 (ddd, J = 47.9, 8.9, 4.1 Hz, 1H), 4.94 (td, J = 10.9, 4.3 Hz, 1H), 3.69 – 3.14 (m, 5H), 2.27 – 1.91 (m, 4H), 1.73 (d, J = 12.9 Hz, 2H), 1.61 – 1.49 (m, 2H), 1.13 (dd, J = 24.6, 12.4 Hz, 2H), 0.97 – 0.86 (m, 7H), 0.79 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.82, 145.07 (d, J = 19.7 Hz), 130.79 (d, J = 0.9 Hz), 129.90, 125.29 (dd, J = 7.3, 1.6 Hz), 91.16 (d, J = 171.6 Hz), 75.04, 68.15 (d, J = 4.6 Hz), 58.93, 47.35, 41.06, 37.67 (d, J = 23.5 Hz), 34.41, 31.55, 26.60, 23.70, 22.17, 20.89, 16.61. ^{19}F NMR (377 MHz, CDCl_3) δ -181.28 (d, J = 38.0 Hz). HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{31}\text{FO}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 373.21494, found: 373.21467.

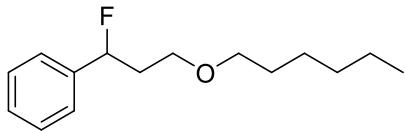


(3-Ethoxy-1-fluoropropyl)benzene (40). 0.25 mmol scale, 0.3 mL EtOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **40** as colorless oil. Yield = 50%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400

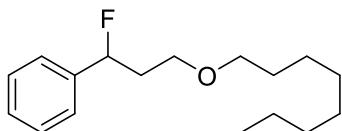
MHz, CDCl_3) δ 7.46 – 7.27 (m, 5H), 5.63 (ddd, J = 47.9, 8.9, 4.4 Hz, 1H), 3.67 – 3.43 (m, 4H), 2.31 – 1.95 (m, 2H), 1.21 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.26 (d, J = 19.5 Hz), 128.57, 128.40 (d, J = 1.9 Hz), 125.67 (d, J = 6.8 Hz), 91.85 (d, J = 169.5 Hz), 66.50, 66.23 (d, J = 4.9 Hz), 37.65 (d, J = 23.8 Hz), 15.30. ^{19}F NMR (377 MHz, CDCl_3) δ -177.37. HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{15}\text{FONa}$ ($\text{M}+\text{Na}$) $^+$: 205.09991, found: 205.09956.



(3-Butoxy-1-fluoropropyl)benzene (41). 0.25 mmol scale, 0.45 mL *n*-BuOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **41** as colorless oil. Yield = 63%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.47 – 7.32 (m, 5H), 5.67 (ddd, J = 47.9, 8.8, 4.4 Hz, 1H), 3.69 – 3.45 (m, 4H), 2.36 – 1.99 (m, 2H), 1.65 – 1.57 (m, 2H), 1.50 – 1.38 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.19 (d, J = 19.6 Hz), 128.48, 128.30 (d, J = 1.9 Hz), 125.60 (d, J = 6.7 Hz), 91.80 (d, J = 169.4 Hz), 70.95, 66.33 (d, J = 5.0 Hz), 37.56 (d, J = 23.8 Hz), 31.82, 19.40, 13.98. ^{19}F NMR (377 MHz, CDCl_3) δ -177.32. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{19}\text{FONa}$ ($\text{M}+\text{Na}$) $^+$: 233.13121, found: 233.13198.

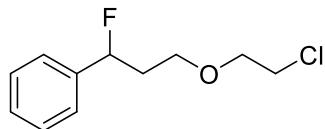


(1-Fluoro-3-(hexyloxy)propyl)benzene (42). 0.25 mmol scale, 0.6 mL 1-hexanol, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **42** as colorless oil. Yield = 69%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.28 (m, 5H), 5.62 (ddd, J = 47.9, 8.8, 4.4 Hz, 1H), 3.65 – 3.39 (m, 4H), 2.31 – 1.95 (m, 2H), 1.63 – 1.53 (m, 2H), 1.36 – 1.26 (m, 6H), 0.93 – 0.87 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.29 (d, J = 19.6 Hz), 128.56, 128.38 (d, J = 1.9 Hz), 125.68 (d, J = 6.7 Hz), 91.88 (d, J = 169.4 Hz), 71.36, 66.42 (d, J = 5.0 Hz), 37.66 (d, J = 23.8 Hz), 31.83, 29.79, 25.99, 22.77, 14.20. ^{19}F NMR (377 MHz, CDCl_3) δ -177.31. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{23}\text{FONa}$ ($\text{M}+\text{Na}$) $^+$: 261.16251, found: 261.16197.

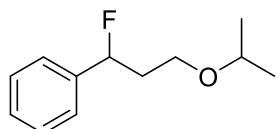


(1-Fluoro-3-(octyloxy)propyl)benzene (43). 0.25 mmol scale, 0.75 mL octanol, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **43** as colorless oil. Yield = 59%, electricity = 2.4 F mol $^{-1}$. ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.31 (m, 5H), 5.68 (ddd, J = 47.9, 8.8, 4.4 Hz, 1H), 3.73 – 3.43 (m, 4H), 2.38 – 2.00 (m, 2H), 1.67 – 1.58 (m, 2H), 1.39 – 1.27 (m, 10H), 0.96 – 0.92 (m, J = 9.0, 4.8 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.30 (d, J = 19.5 Hz), 128.56, 128.38 (d, J = 1.9 Hz), 125.68 (d, J = 6.7 Hz), 91.87 (d, J = 169.5 Hz), 71.36, 66.41 (d, J = 5.0 Hz), 37.66 (d, J = 23.8 Hz),

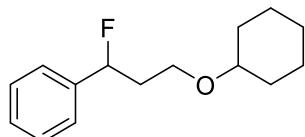
31.98, 29.83, 29.59, 29.42, 26.32, 22.81, 14.25. ^{19}F NMR (377 MHz, CDCl_3) δ -177.33. HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{27}\text{FONa} (\text{M}+\text{Na})^+$:289.19381, found: 289.19352.



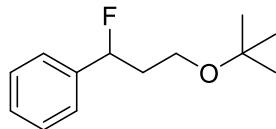
(3-(2-Chloroethoxy)-1-fluoropropyl)benzene (44). 0.25 mmol scale, 0.3 mL $\text{ClCH}_2\text{CH}_2\text{OH}$, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **44** as colorless oil. Yield = 40%, electricity = 2.4 F mol^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.33 (m, 5H), 5.70 (ddd, J = 47.9, 8.9, 4.4 Hz, 1H), 3.81 – 3.55 (m, 6H), 2.37 – 2.03 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.97 (d, J = 19.5 Hz), 128.53, 128.40 (d, J = 2.0 Hz), 125.60 (d, J = 6.8 Hz), 91.55 (d, J = 169.6 Hz), 71.05, 66.84 (d, J = 5.0 Hz), 42.88, 37.39 (d, J = 24.0 Hz). ^{19}F NMR (377 MHz, CDCl_3) δ -177.63. HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{14}\text{FCIONa} (\text{M}+\text{Na})^+$:239.06094, found: 239.06167.



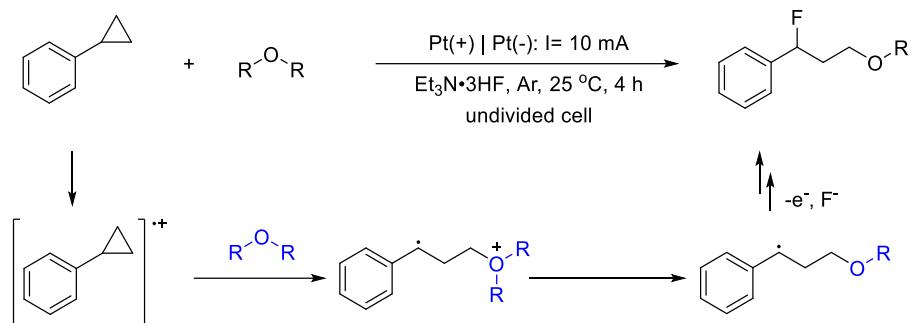
(1-Fluoro-3-isopropoxypropyl)benzene (45). 0.25 mmol scale, 0.3 mL $i\text{-PrOH}$, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **45** as colorless oil. Yield = 47%, electricity = 2.4 F mol^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.27 (m, 5H), 5.63 (ddd, J = 48.0, 8.9, 4.4 Hz, 1H), 3.65 – 3.43 (m, 3H), 2.29 – 1.94 (m, 2H), 1.17 (t, J = 6.1 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.32 (d, J = 19.5 Hz), 128.56, 128.39 (d, J = 2.0 Hz), 125.73 (d, J = 6.8 Hz), 91.92 (d, J = 169.2 Hz), 71.85, 63.77 (d, J = 5.0 Hz), 37.95 (d, J = 23.8 Hz), 22.24, 22.21. ^{19}F NMR (377 MHz, CDCl_3) δ -177.35. HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{17}\text{FONa} (\text{M}+\text{Na})^+$:219.11556, found: 219.11487.



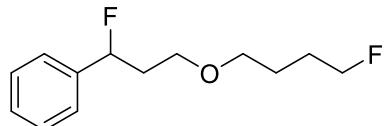
(3-(Cyclohexyloxy)-1-fluoropropyl)benzene (46). 0.25 mmol scale, 0.5 mL cyclohexanol, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **46** as colorless oil. Yield = 62%, electricity = 2.4 F mol^{-1} . ^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.28 (m, 5H), 5.63 (ddd, J = 48.0, 8.8, 4.4 Hz, 1H), 3.69 – 3.45 (m, 2H), 3.25 – 3.19 (m, 1H), 2.31 – 1.97 (m, 2H), 1.94 – 1.88 (m, 2H), 1.75 – 1.73 (m, 2H), 1.55 – 1.52 (m, 1H), 1.36 – 1.07 (m, 5H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.35 (d, J = 19.5 Hz), 128.55, 128.36 (d, J = 2.0 Hz), 125.74 (d, J = 6.8 Hz), 91.95 (d, J = 169.1 Hz), 77.90, 63.48 (d, J = 5.0 Hz), 38.01 (d, J = 23.7 Hz), 32.47, 32.31, 25.95, 24.29. ^{19}F NMR (377 MHz, CDCl_3) δ -177.26. HRMS (ESI) m/z calculated for $\text{C}_{15}\text{H}_{21}\text{FONa} (\text{M}+\text{Na})^+$:259.14686, found: 259.14675.



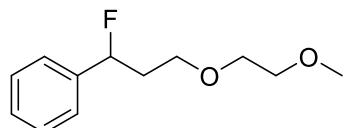
(3-(Tert-butoxy)-1-fluoropropyl)benzene (47). 0.25 mmol scale, 0.45 mL *t*-BuOH, 1 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 150:1) to give **47** as colorless oil. Yield = 50%, electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.28 (m, 5H), 5.63 (ddd, *J* = 48.1, 9.0, 4.2 Hz, 1H), 3.61 – 3.39 (m, 2H), 2.26 – 1.92 (m, 2H), 1.20 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 140.46 (d, *J* = 19.5 Hz), 128.53, 128.34 (d, *J* = 2.0 Hz), 125.78 (d, *J* = 6.8 Hz), 91.90 (d, *J* = 168.9 Hz), 73.01, 57.34 (d, *J* = 4.8 Hz), 38.34 (d, *J* = 23.6 Hz), 27.65. ¹⁹F NMR (377 MHz, CDCl₃) δ -177.41. HRMS (ESI) m/z calculated for C₁₃H₁₉FONa (M+Na)⁺: 233.13121, found: 233.13113.



An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped platinum plate (15 mm × 15 mm × 0.3 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode and then charged with argon gas by glove box. Cyclopropylbenzene (0.5 mmol), Et₃N·3HF (1.2 mL) and ether (4.8 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. The reaction was diluted with water. The organic layer was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

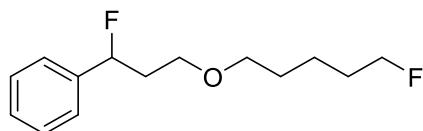


(1-fluoro-3-(4-fluorobutoxy)propyl)benzene (48). 0.5 mmol scale, 4 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50:1) to give **48** as colorless oil. Yield = 43%, electricity = 2.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 5H), 5.60 (ddd, *J* = 47.9, 8.8, 4.4 Hz, 1H), 4.46 (dt, *J* = 47.2, 5.9 Hz, 2H), 3.64 – 3.42 (m, 4H), 2.28 – 1.96 (m, 2H), 1.84 – 1.65 (m, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 140.22 (d, *J* = 19.6 Hz), 128.55, 128.38 (d, *J* = 1.9 Hz), 125.63 (d, *J* = 6.7 Hz), 91.79 (d, *J* = 169.6 Hz), 84.00 (d, *J* = 164.4 Hz), 70.49, 66.44 (d, *J* = 4.9 Hz), 37.58 (d, *J* = 23.9 Hz), 27.41 (d, *J* = 19.8 Hz), 25.62 (d, *J* = 5.2 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -177.31, -218.13. HRMS (ESI) m/z calcd for C₁₃H₁₈F₂ONa (M+Na)⁺: 251.12179, found: 251.12178.



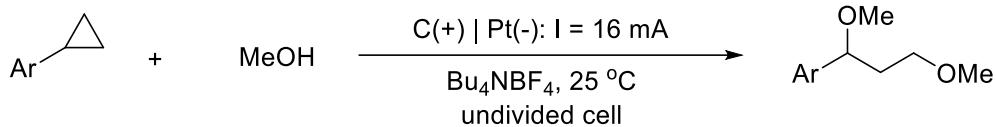
(1-fluoro-3-(2-methoxyethoxy)propyl)benzene (49). 0.5 mmol scale, 4 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl

acetate = 10:1) to give **49** as colorless oil. Yield = 44%, electricity = 2.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.30 (m, 5H), 5.64 (ddd, *J* = 47.9, 8.9, 4.3 Hz, 1H), 3.71 – 3.50 (m, 6H), 3.40 (s, 3H), 2.31 – 2.00 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.18 (d, *J* = 19.5 Hz), 128.56, 128.39 (d, *J* = 1.9 Hz), 125.66 (d, *J* = 6.7 Hz), 91.73 (d, *J* = 169.5 Hz), 71.97, 70.43, 67.06 (d, *J* = 4.9 Hz), 59.21, 37.44 (d, *J* = 23.8 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -177.53. HRMS (ESI) m/z calcd for C₁₂H₁₇FO₂Na (M+Na)⁺: 235.11048, found : 235.11037.

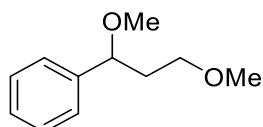


(1-Fluoro-3-((5-fluoropentyl)oxy)propyl)benzene (50). 0.5 mmol scale, add 1 mL DCE, 4 h. After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 50:1) to give **50** as colorless oil. Yield = 36%, electricity = 2.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.26 (m, 5H), 5.61 (ddd, *J* = 47.9, 8.8, 4.4 Hz, 1H), 4.44 (dt, *J* = 47.3, 6.1 Hz, 2H), 3.63 – 3.41 (m, 4H), 2.28 – 1.96 (m, 2H), 1.79 – 1.57 (m, 4H), 1.53 – 1.43 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.21 (d, *J* = 19.5 Hz), 128.53, 128.37 (d, *J* = 2.0 Hz), 125.64 (d, *J* = 6.7 Hz), 91.80 (d, *J* = 169.5 Hz), 84.08 (d, *J* = 164.3 Hz), 70.91, 66.44 (d, *J* = 5.0 Hz), 37.58 (d, *J* = 23.9 Hz), 30.30 (d, *J* = 19.5 Hz), 29.37, 22.04 (d, *J* = 5.5 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -177.27, -218.23. HRMS (ESI) m/z calcd for C₁₄H₂₀F₂ONa (M+Na)⁺: 265.13744, found : 265.13684.

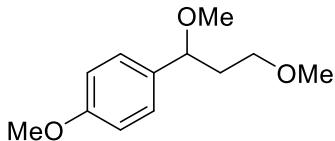
6) Procedures and analytical data of 1,3-dioxygenation compounds



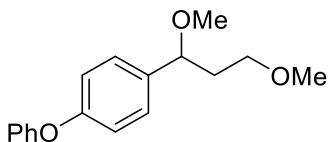
An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped carbon cloth (15 mm×15 mm) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode and then charged with argon gas by glove box. Arylcyclopropane (0.25 mmol), Bu₄NBF₄ (0.25 mmol) and MeOH (6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 16 mA for 1 h under room temperature. The reaction mixture was concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.



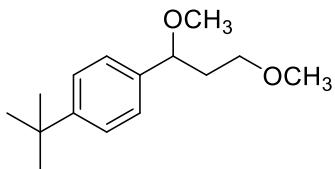
(1,3-Dimethoxypropyl)benzene (5). GC yield = 95%, Electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.19 (m, 5H), 4.28 (dd, *J* = 8.1, 5.7 Hz, 1H), 3.53 – 3.42 (m, 1H), 3.37 – 3.26 (m, 4H), 3.20 (s, 3H), 2.11 – 1.80 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 142.07, 128.48, 127.63, 126.71, 80.73, 69.21, 58.64, 56.69, 38.23. HRMS (ESI) m/z calculated for C₁₁H₁₇O₂ (M+H)⁺: 181.12231, found: 181.12160.



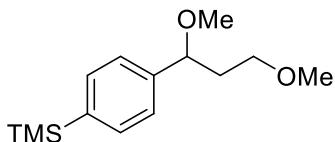
1-(1,3-Dimethoxypropyl)-4-methoxybenzene (51). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) to give **51** as colorless oil. Isolated yield = 74%, Electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.17 (m, 2H), 6.91 – 6.84 (m, 2H), 4.21 (dd, *J* = 7.9, 6.0 Hz, 1H), 3.79 (s, 3H), 3.47 – 3.42 (m, 1H), 3.33 – 3.24 (m, 4H), 3.17 (s, 3H), 2.14 – 1.74 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.21, 134.03, 128.00, 113.91, 80.33, 69.39, 58.74, 56.51, 55.35, 38.16. HRMS (ESI) m/z calculated for C₁₂H₁₉O₃ (M+H)⁺ : 211.13287, found: 211.13254.



1-(1,3-Dimethoxypropyl)-4-phenoxybenzene (52). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) to give **52** as colorless oil. Isolated yield = 93%, reaction time 50 min, Electricity = 2 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.30 (m, 2H), 7.28 – 7.21 (m, 2H), 7.13 – 7.06 (m, 1H), 7.04 – 6.95 (m, 4H), 4.26 (dd, *J* = 8.0, 5.8 Hz, 1H), 3.52 – 3.45 (m, 1H), 3.38 – 3.27 (m, 4H), 3.21 (s, 3H), 2.14 – 1.78 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.24, 156.84, 136.80, 129.84, 128.14, 123.40, 119.06, 118.76, 80.27, 69.26, 58.73, 56.68, 38.19. HRMS (ESI) m/z calculated for C₁₇H₂₀O₃Na (M+Na)⁺ : 295.13047, found: 295.13041.

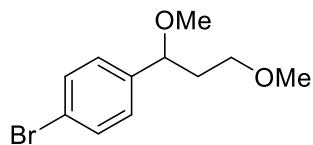


1-(Tert-butyl)-4-(1,3-dimethoxypropyl)benzene (53). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **53** as colorless oil. Isolated yield = 85%, Electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.25 (dd, *J* = 8.1, 5.6 Hz, 1H), 3.56 – 3.46 (m, 1H), 3.36 – 3.28 (m, 4H), 3.20 (s, 3H), 2.14 – 1.70 (m, 2H), 1.31 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.52, 138.96, 126.42, 125.39, 80.51, 69.40, 58.73, 56.77, 38.19, 34.62, 31.51. HRMS (ESI) m/z calculated for C₁₅H₂₄O₂Na (M+Na)⁺ : 259.16685, found: 259.16656.

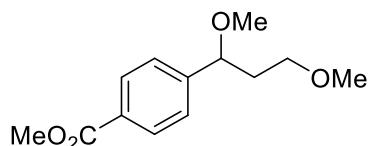


(4-(1,3-Dimethoxypropyl)phenyl)trimethylsilane (54). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **54** as colorless oil. Isolated yield = 85%, Electricity = 2.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.46 (m, 2H), 7.31 – 7.25 (m, 2H), 4.27 (dd, *J* = 8.2, 5.5 Hz, 1H), 3.55 – 3.45 (m, 1H), 3.40 – 3.28

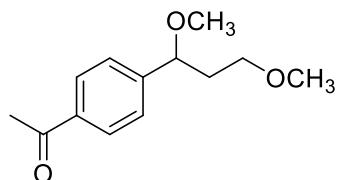
(m, 4H), 3.21 (s, 3H), 2.12 – 1.79 (m, 2H), 0.26 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.71, 139.74, 133.58, 126.11, 80.75, 69.31, 58.74, 56.89, 38.28, -0.96. HRMS (ESI) m/z calculated for $\text{C}_{14}\text{H}_{24}\text{O}_2\text{SiNa} (\text{M}+\text{Na})^+$: 275.14378, found: 275.14359.



1-Bromo-4-(1,3-dimethoxypropyl)benzene (55). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) to give **55** as colorless oil. Isolated yield = 95%, Electricity = 2.4 F mol⁻¹. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.16 (dd, *J* = 8.2, 1.5 Hz, 2H), 4.24 (dd, *J* = 7.8, 6.1 Hz, 1H), 3.50 – 3.41 (m, 1H), 3.38 – 3.21 (m, 4H), 3.18 (s, 3H), 2.08 – 1.72 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.21, 131.67, 128.47, 121.42, 80.15, 69.00, 58.73, 56.83, 38.16. HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{26}\text{BrO}_2 (\text{M}+\text{H})^+$: 259.03282, found: 259.03278.

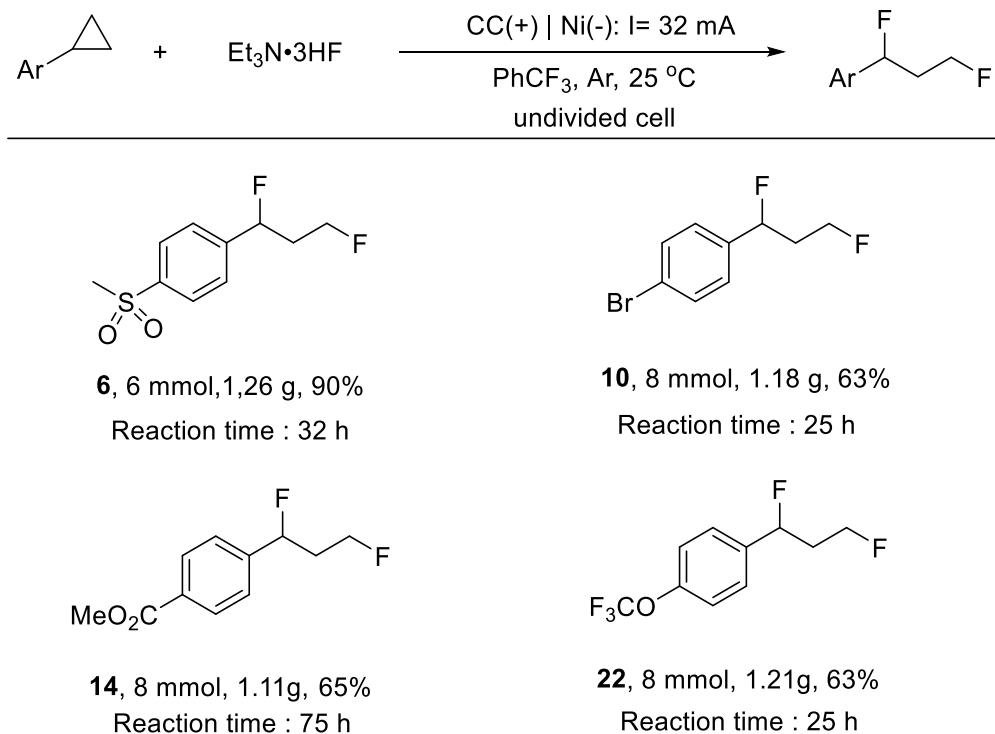


Methyl 4-(1,3-dimethoxypropyl)benzoate (56). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) to give **56** as colorless oil. Isolated yield = 85%, Electricity = 2.4 F mol⁻¹. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 4.28 (dd, *J* = 8.1, 5.6 Hz, 1H), 3.84 (s, 3H), 3.45 – 3.39 (m, 1H), 3.26 – 3.17 (m, 4H), 3.15 (s, 3H), 2.11 – 1.67 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.05, 147.60, 129.91, 129.58, 126.67, 80.38, 68.94, 58.74, 57.02, 52.17, 38.15. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{18}\text{O}_4\text{Na} (\text{M}+\text{Na})^+$: 261.10973, found: 261.10965.



1-(4-(1,3-Dimethoxypropyl)phenyl)ethan-1-one (57). The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) to give **57** as colorless oil. Isolated yield = 84%, Electricity = 2.4 F mol⁻¹. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 2H), 7.39 – 7.36 (m, 2H), 4.33 (dd, *J* = 8.2, 5.5 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.34 – 3.23 (m, 4H), 3.19 (s, 3H), 2.57 (s, 3H), 2.08 – 1.94 (m, 1H), 1.84 – 1.76 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.92, 147.85, 136.65, 128.70, 126.84, 80.33, 68.92, 58.74, 57.05, 38.14, 26.72. HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{19}\text{O}_3 (\text{M}+\text{H})^+$: 223.13287, found: 223.13293.

7) General procedure for gram scale reaction



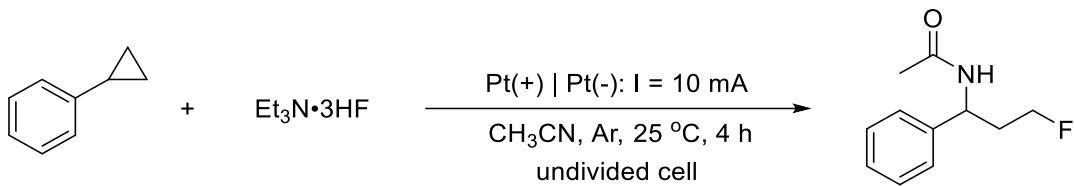
An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped carbon cloth (20 mm×25mm) as the anode and nickel foam (20 mm×25 mm) as the cathode and then charged with argon gas by glove box. Arylcyclopropane (6 or 8 mmol), Et₃N·3HF (14.5 mmol, 2.4 mL) and PhCF₃ (9.6 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 32 mA under room temperature. Then, the reaction was diluted with water. The organic layer was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

8) Mechanistic study

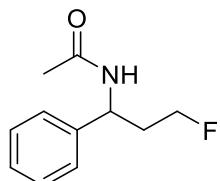
Cyclic voltammetry studies:

Cyclic voltammetry was performed in a three-electrode cell. The working electrode was a Pt electrode, the counter electrode a graphite rod. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. CH₃CN (10 mL) containing 0.5 mmol ⁷Bu₄NBF₄ was tested as blank background. The cyclic voltammogram of cyclopropanes (10 mM) were recorded at room temperature in an electrolyte of ⁷Bu₄NBF₄ (50 mM) in MeCN. The scan rate is 100 mV/s.

Trap of benzyl carbonium intermediate:



An oven-dried undivided three-necked bottle equipped with a stir bar. The bottle was equipped platinum plate (15 mm \times 15 mm \times 0.3 mm) as the anode and platinum plate (15 mm \times 15 mm \times 0.3 mm) as the cathode and then charged with argon gas by glove box. Phenylcyclopropane (0.5 mmol), Et₃N•3HF (1.2 mL) and CH₃CN (4.8 mL) were added. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature for 4 h. The reaction was diluted with water. The organic layer was extracted with CH₂Cl₂, dried with anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained by flash column chromatography on silica gel.

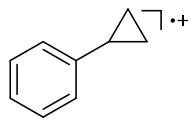


N-(3-fluoro-1-phenylpropyl)acetamide (58). After work-up, the crude residue was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate: Et₃N = 50:100:0.15) to give product as yellow solid. Yield = 43%, electricity = 2.9 F mol⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.22 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.14 (td, *J* = 7.6, 7.2 Hz, 1H), 4.54 – 4.26 (m, 2H), 2.19 – 2.05 (m, 2H), 1.92 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 169.84, 141.47, 128.70, 127.47, 126.49, 81.35 (d, *J* = 164.3 Hz), 50.40 (d, *J* = 4.5 Hz), 36.62 (d, *J* = 19.4 Hz), 23.20. ¹⁹F NMR (377 MHz, CDCl₃) δ -219.44. HRMS (ESI) *m/z* calculated for C₁₁H₁₅FNO (M+H)⁺: 196.11322, found: 196.11252.

9) General Computational Calculation Details

DFT calculations were performed using the M06-2x method¹² with the Gaussian09 program¹³. The 6-311G(d,p) basis set was used for all the elements and PhCF₃ was employed as the solvent during the geometry optimization by using SMD model¹⁴. For the integration grid in the calculations, the parameter int = ultrafine was used. Frequency calculations at the same level of theory have been performed to identify all of the stationary points as minima (zero imaginary frequencies). Grimme's dispersion correction¹⁵ was used during the calculations.

The electrostatic potential surface was generated using Multiwfn¹⁶ and VMD¹⁷.



Thermal correction to Gibbs Free Energy= 0.129230

Sum of electronic and thermal Free Energies= -348.535613

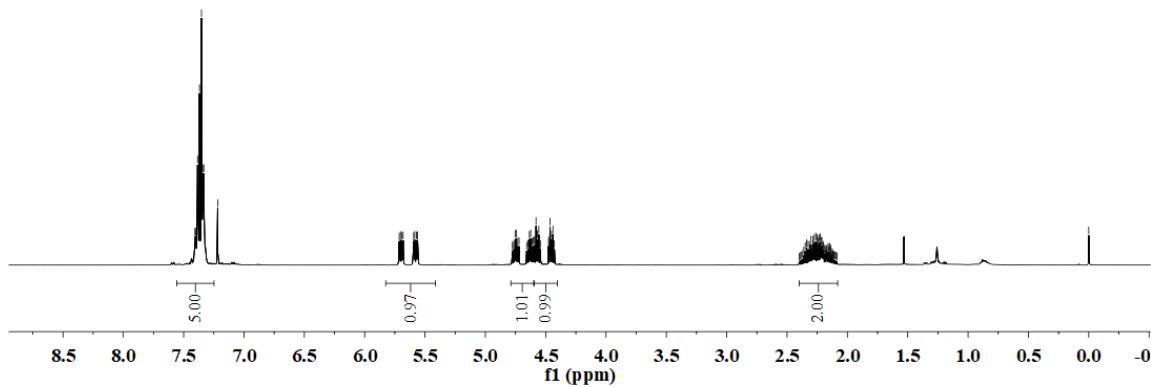
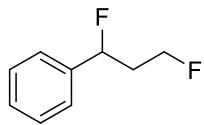
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C	2.18095900	-1.01290300	-0.00017700
C	2.57627800	0.33858700	-0.00038100
H	1.94814200	2.40616400	0.00000100
H	-0.44652700	1.87386500	0.00085100
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H	-3.30264600	-0.38216900	-1.25518300
H	-2.17456500	1.07478500	-1.25773400

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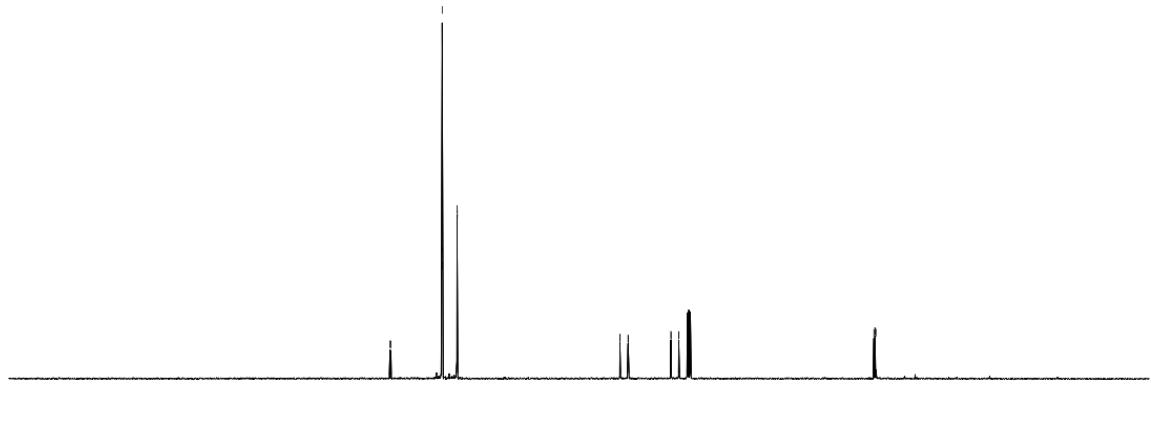
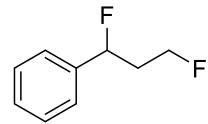
NMR Spectra of Products

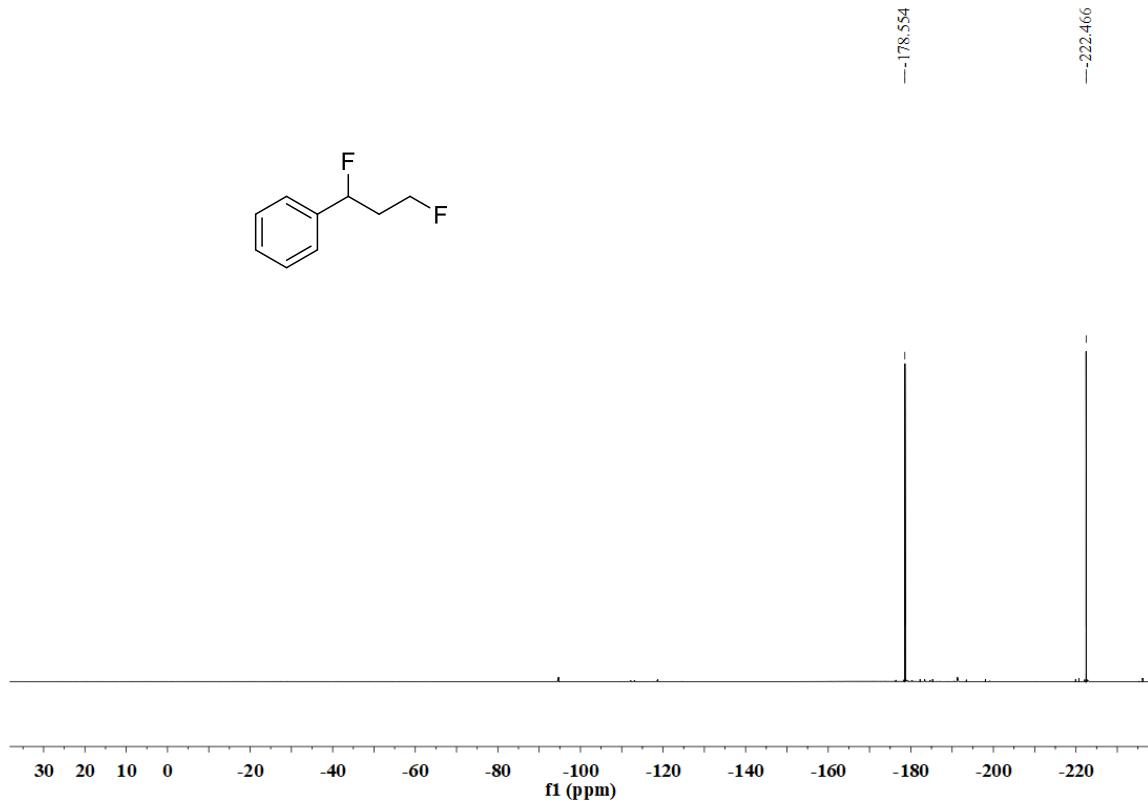
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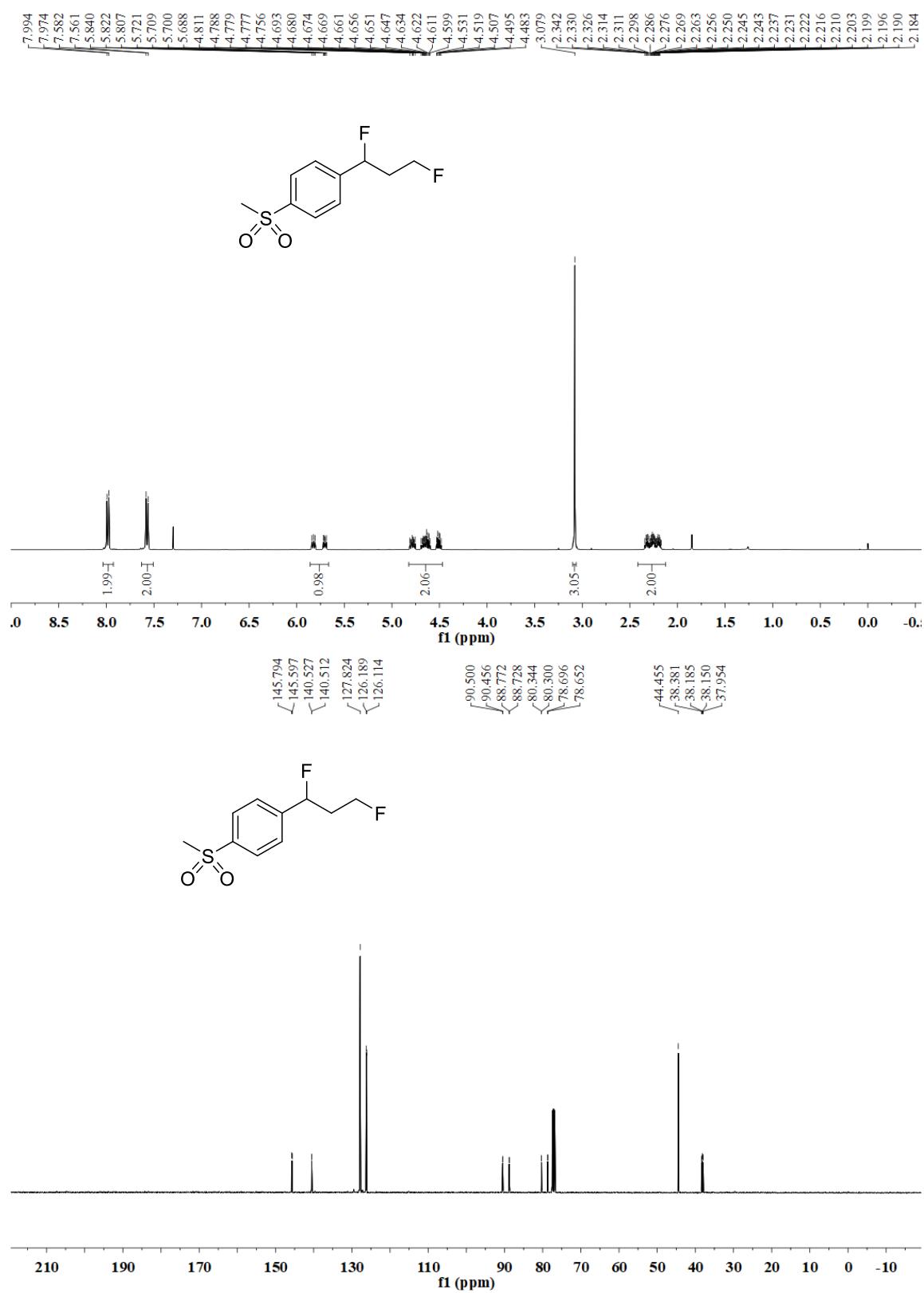
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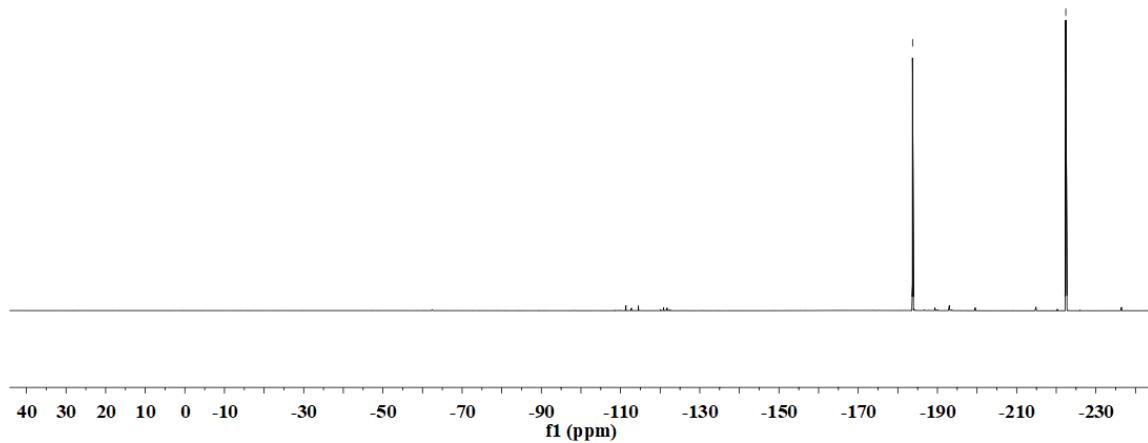
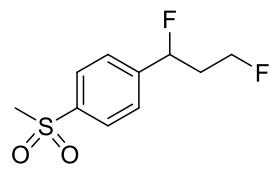
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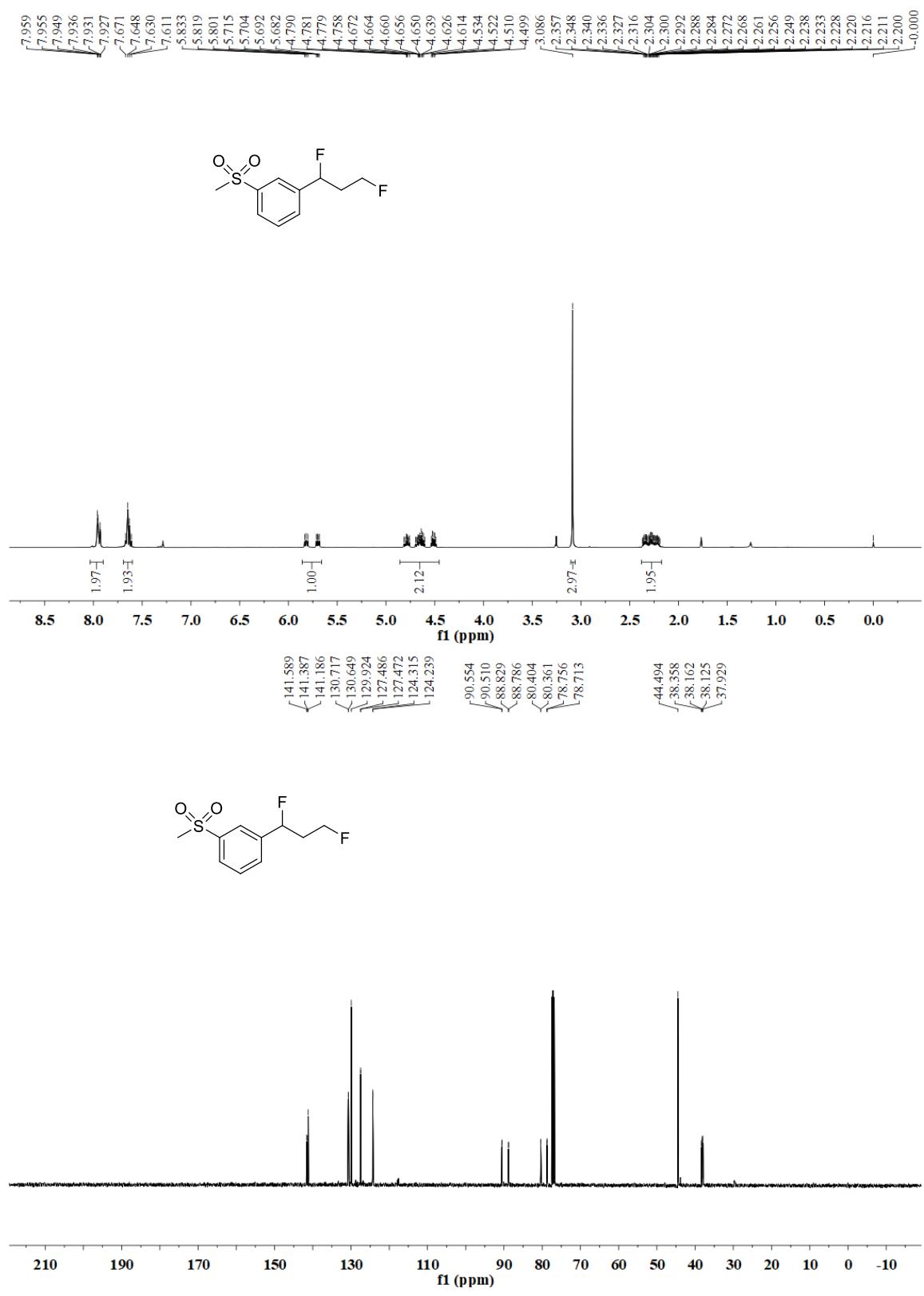


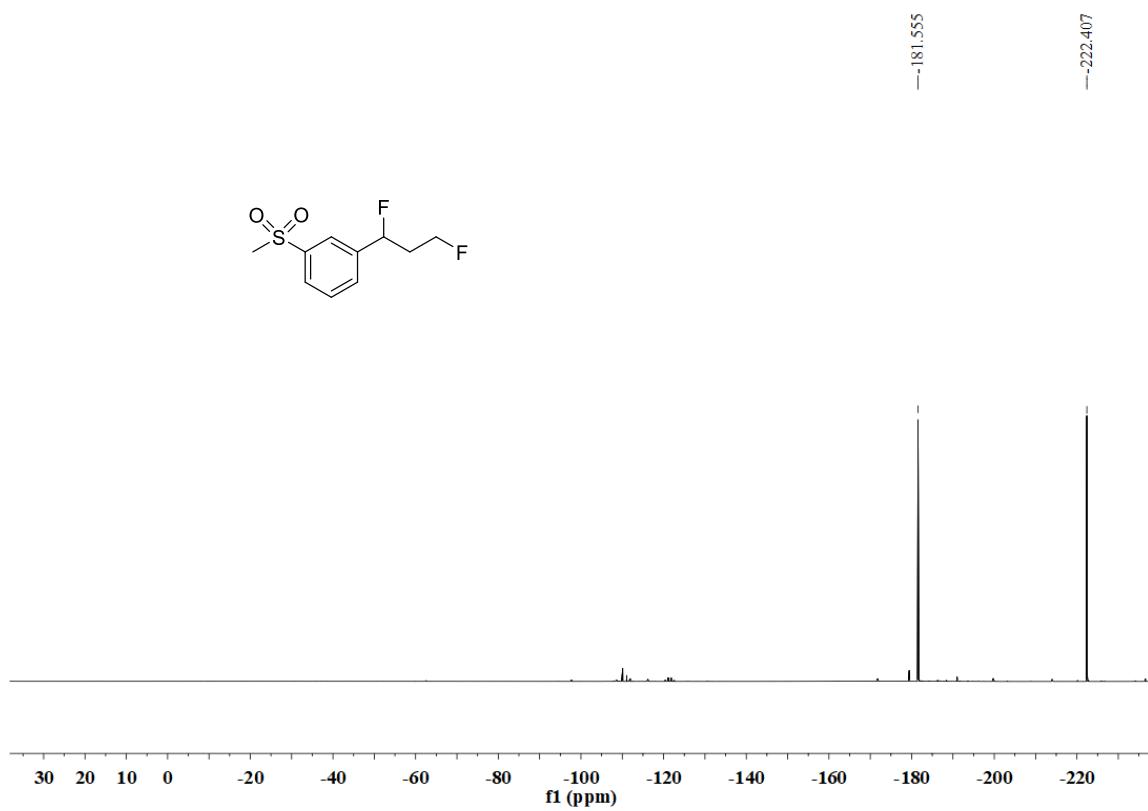


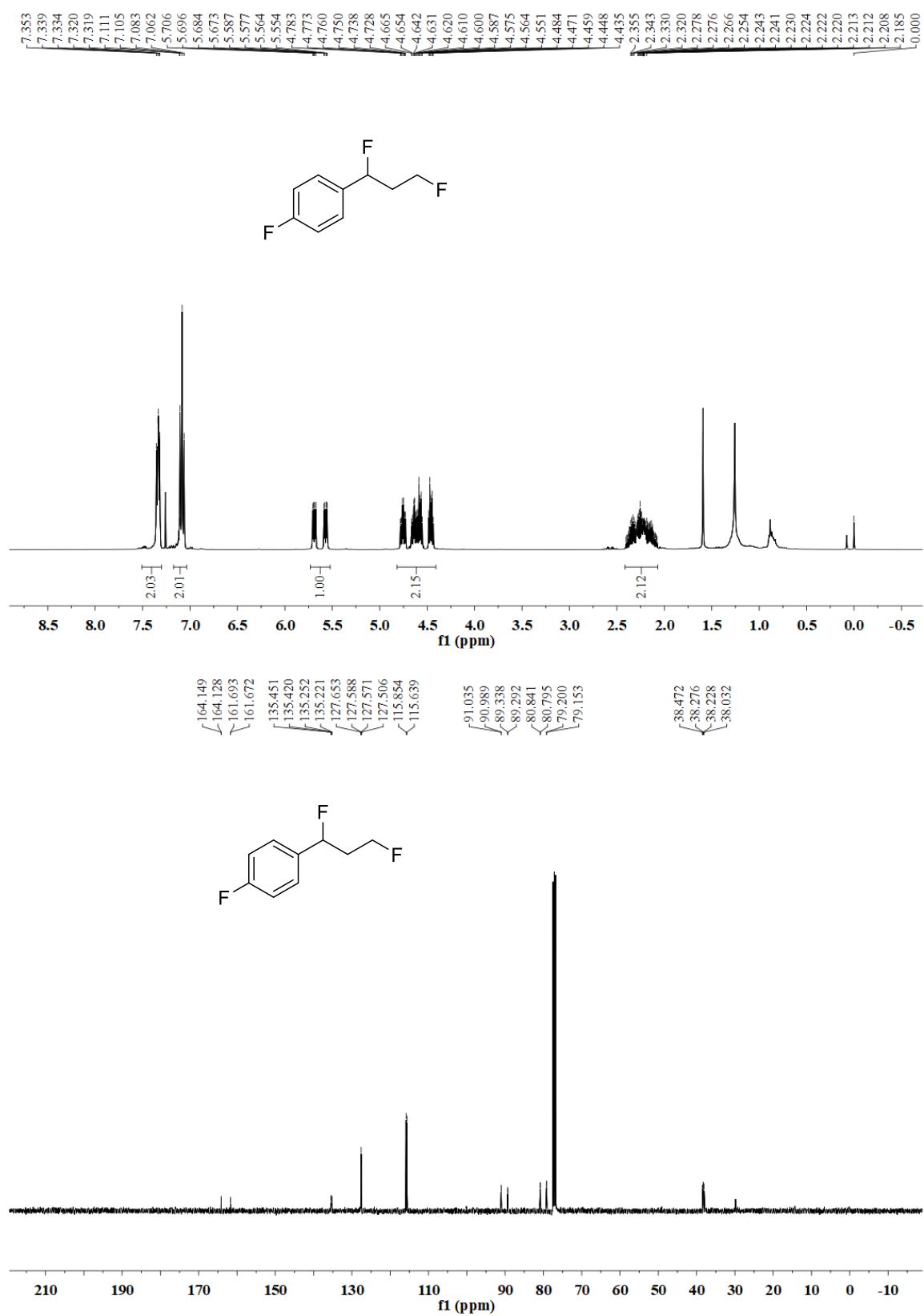
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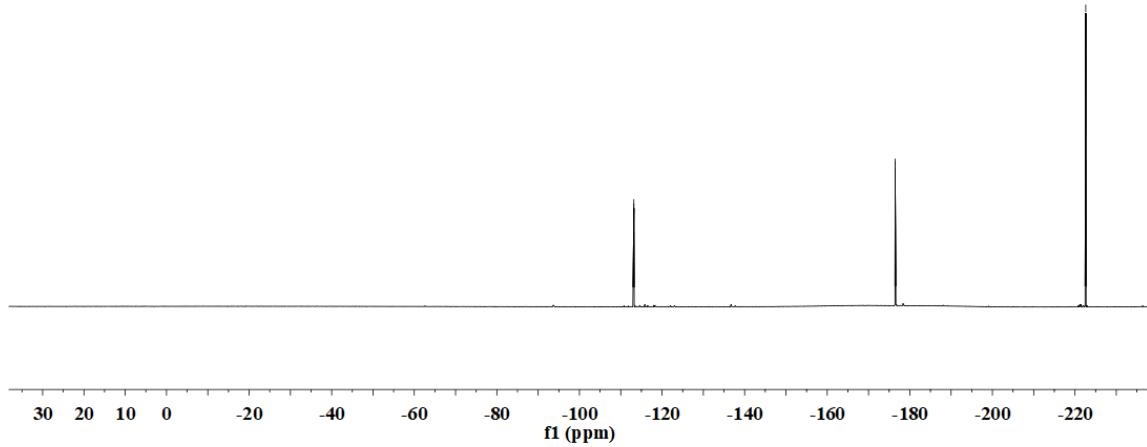
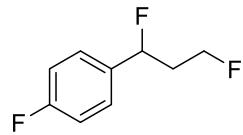


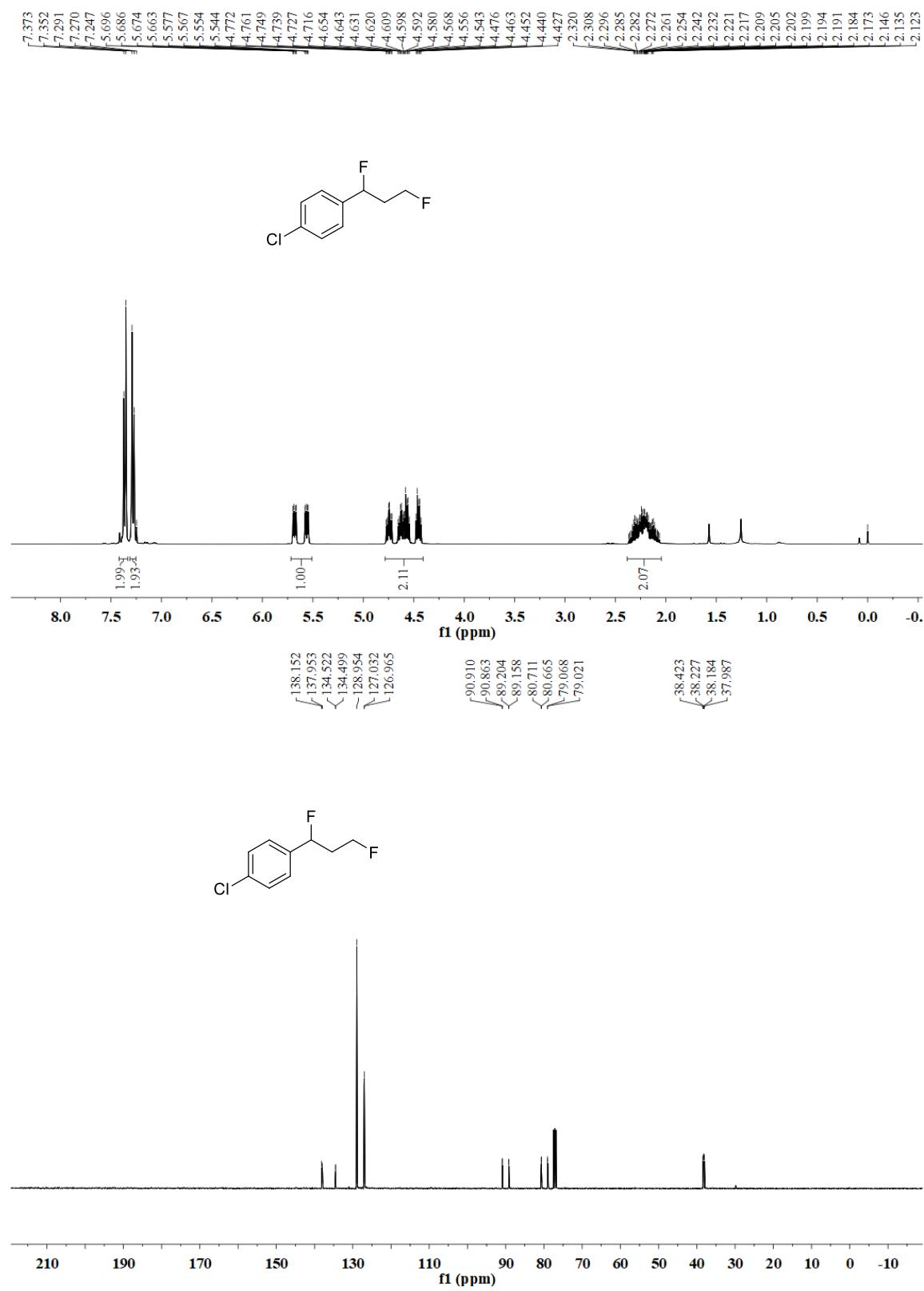


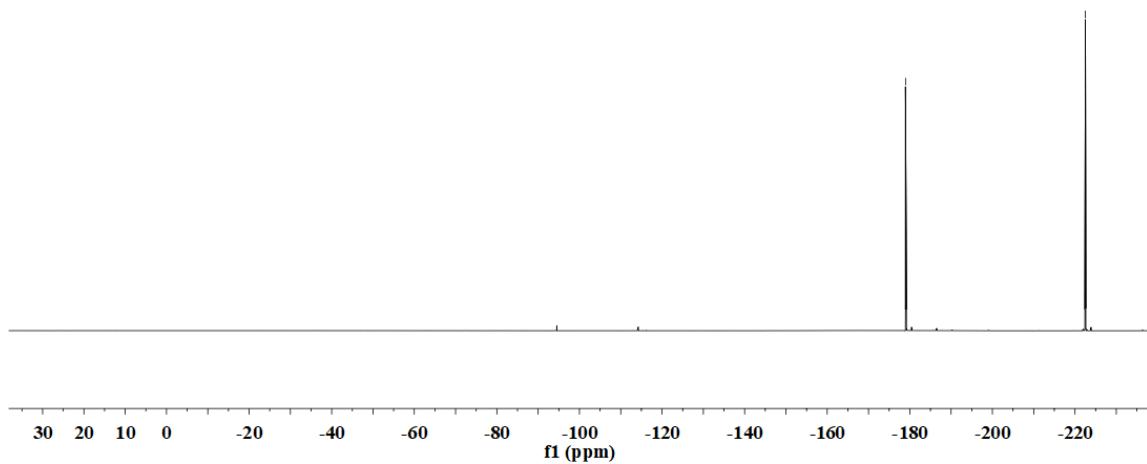
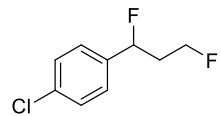
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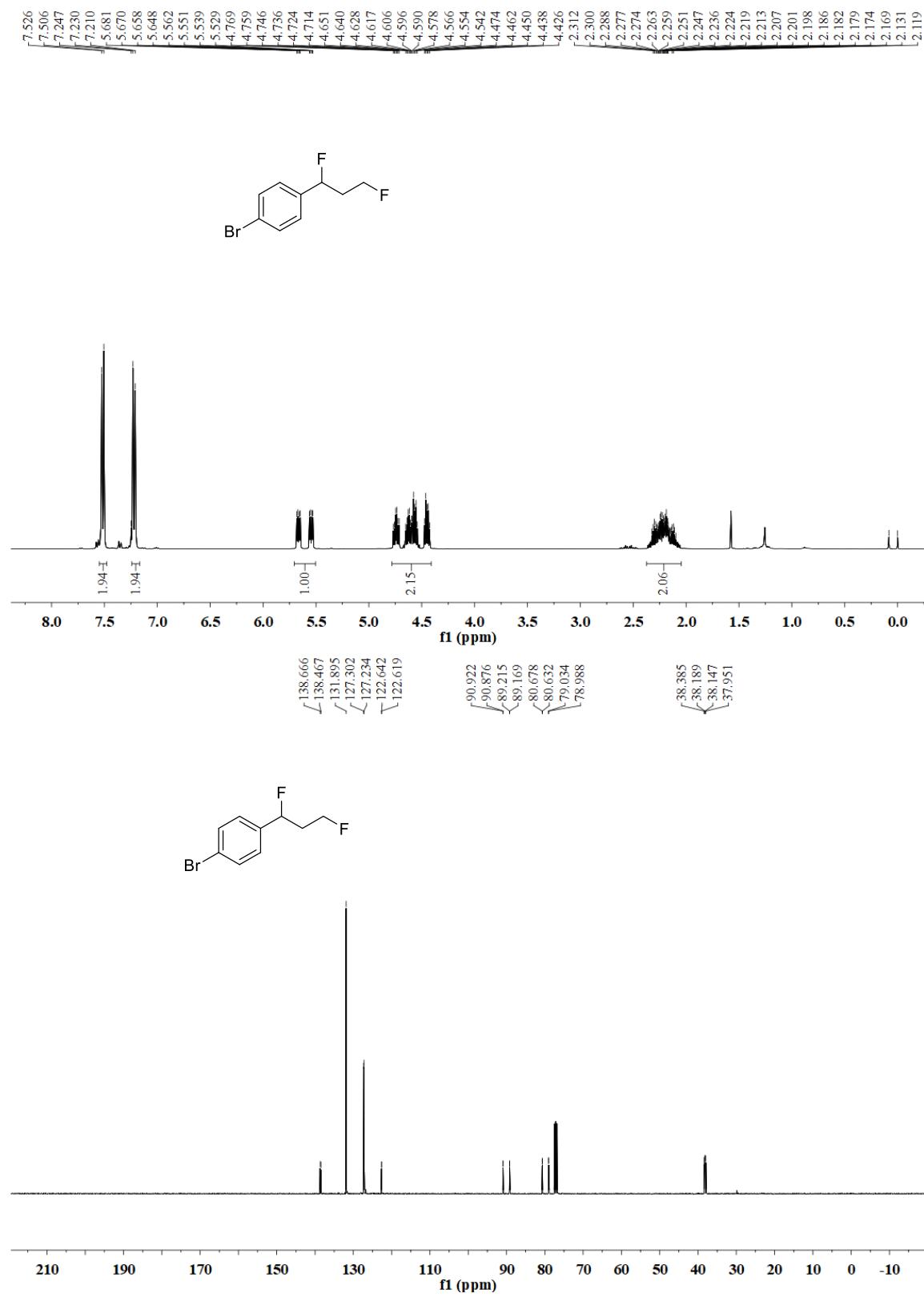
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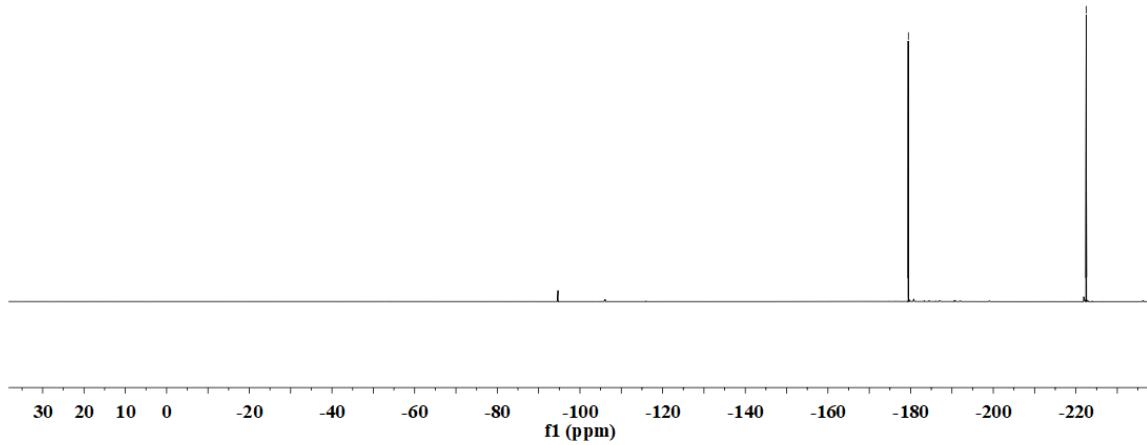


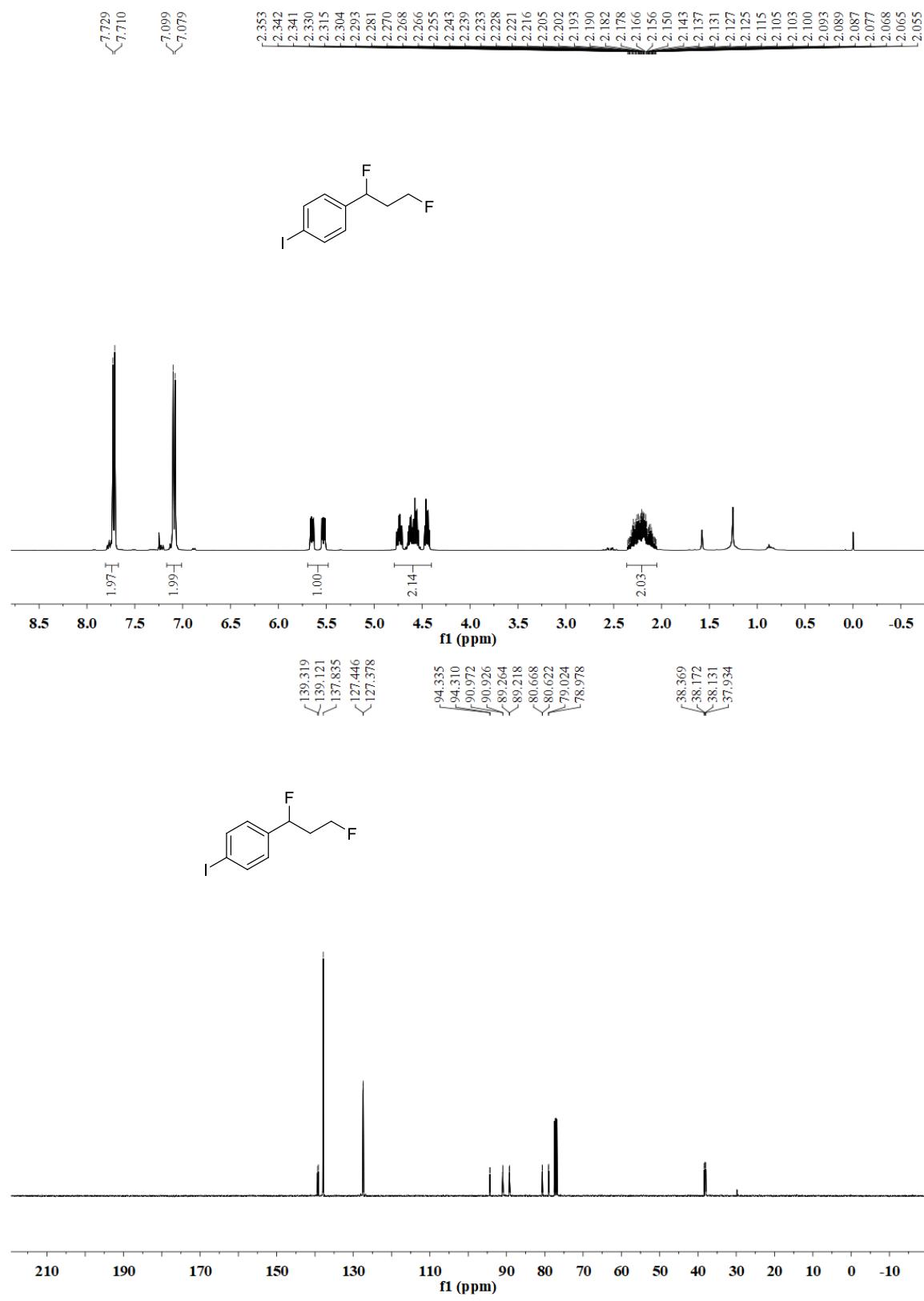


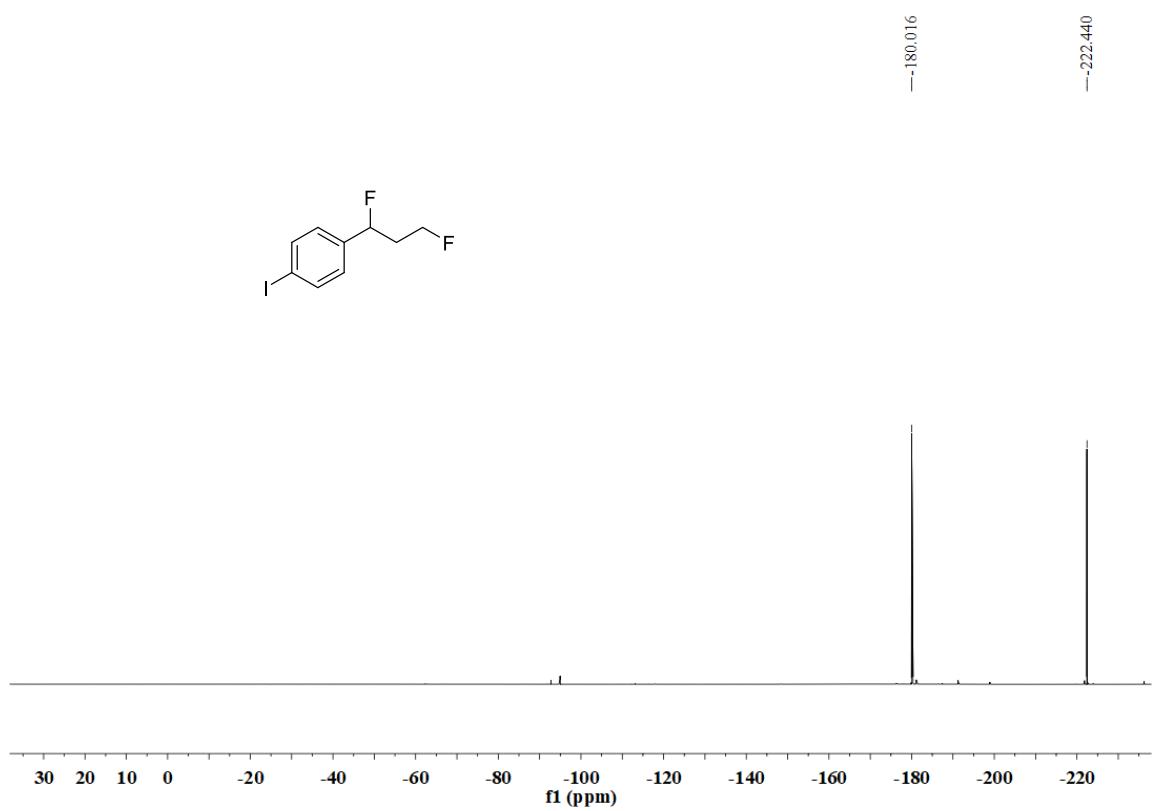


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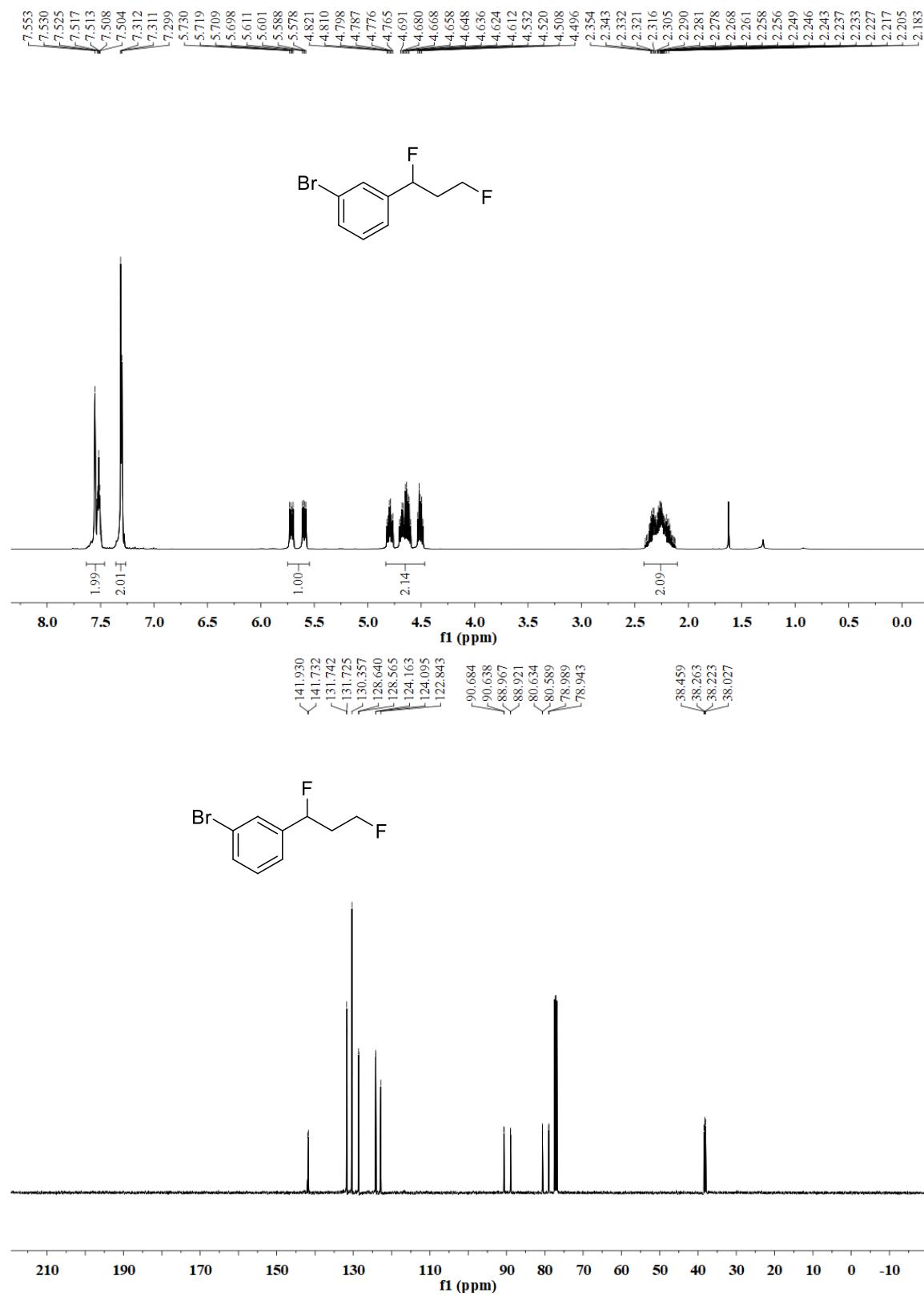


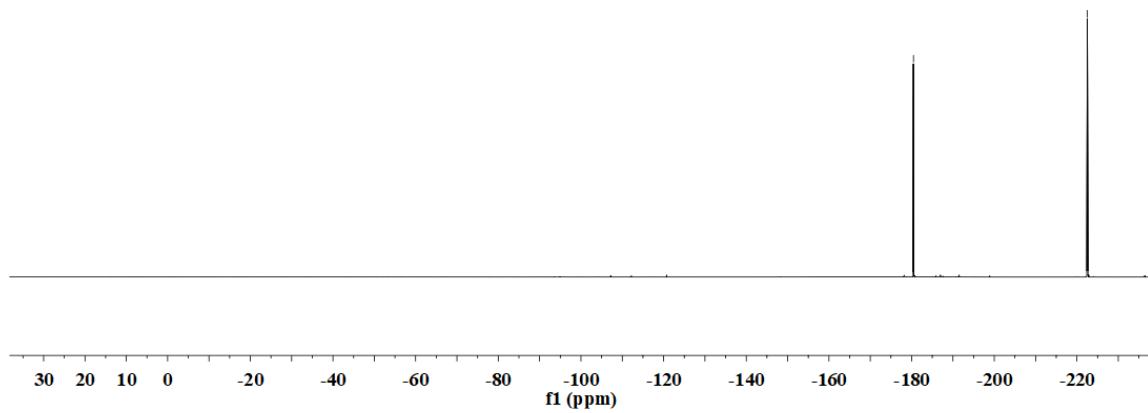
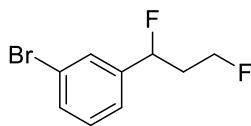




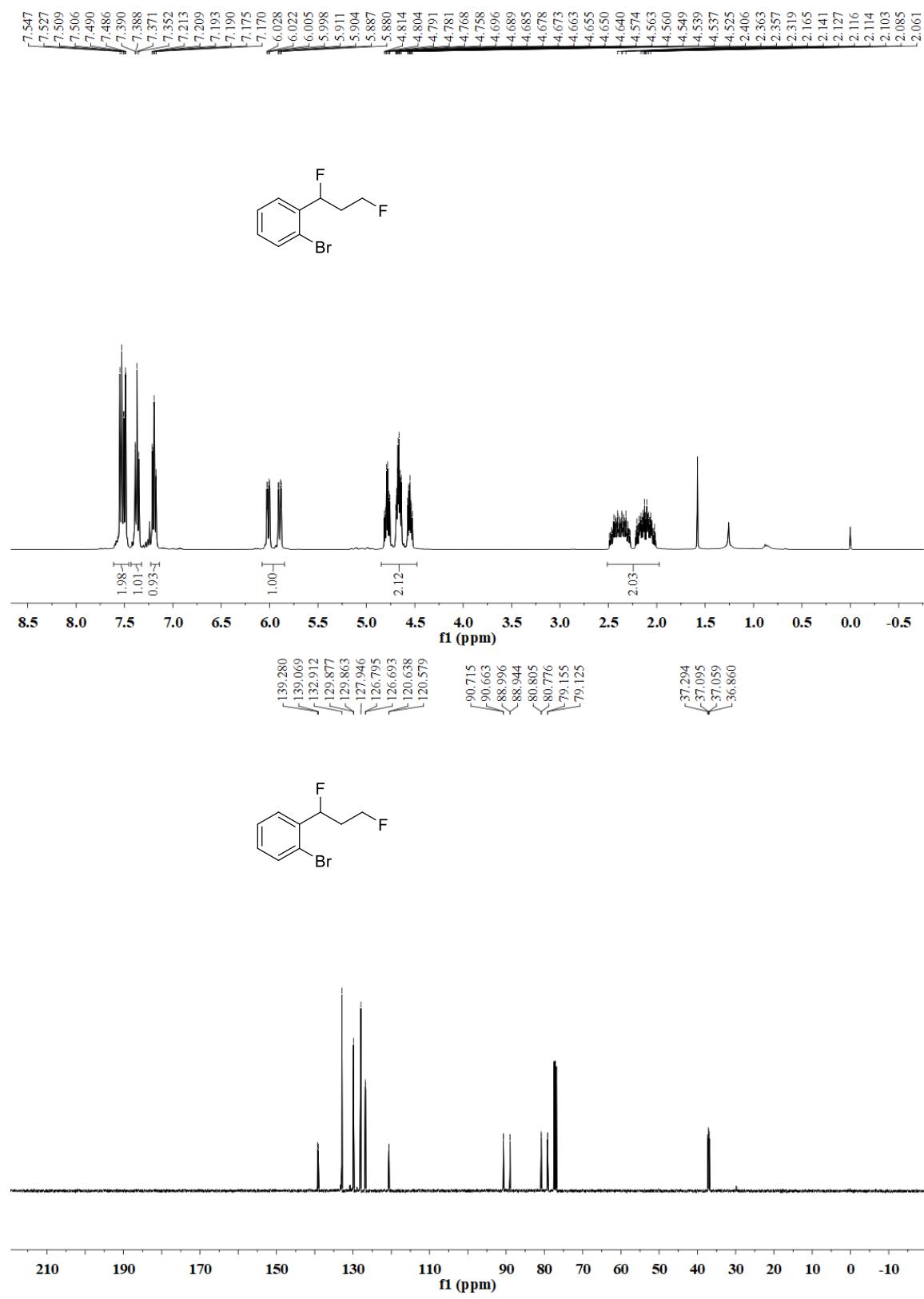


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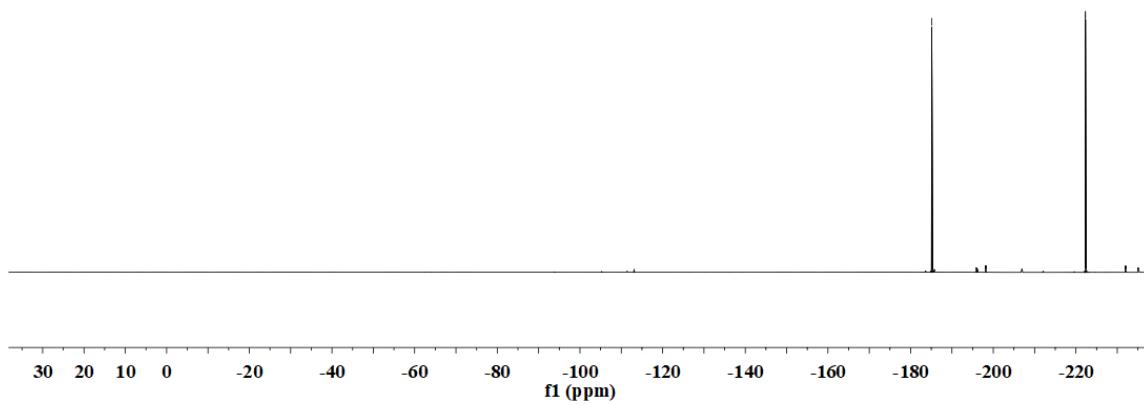
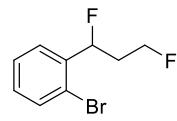


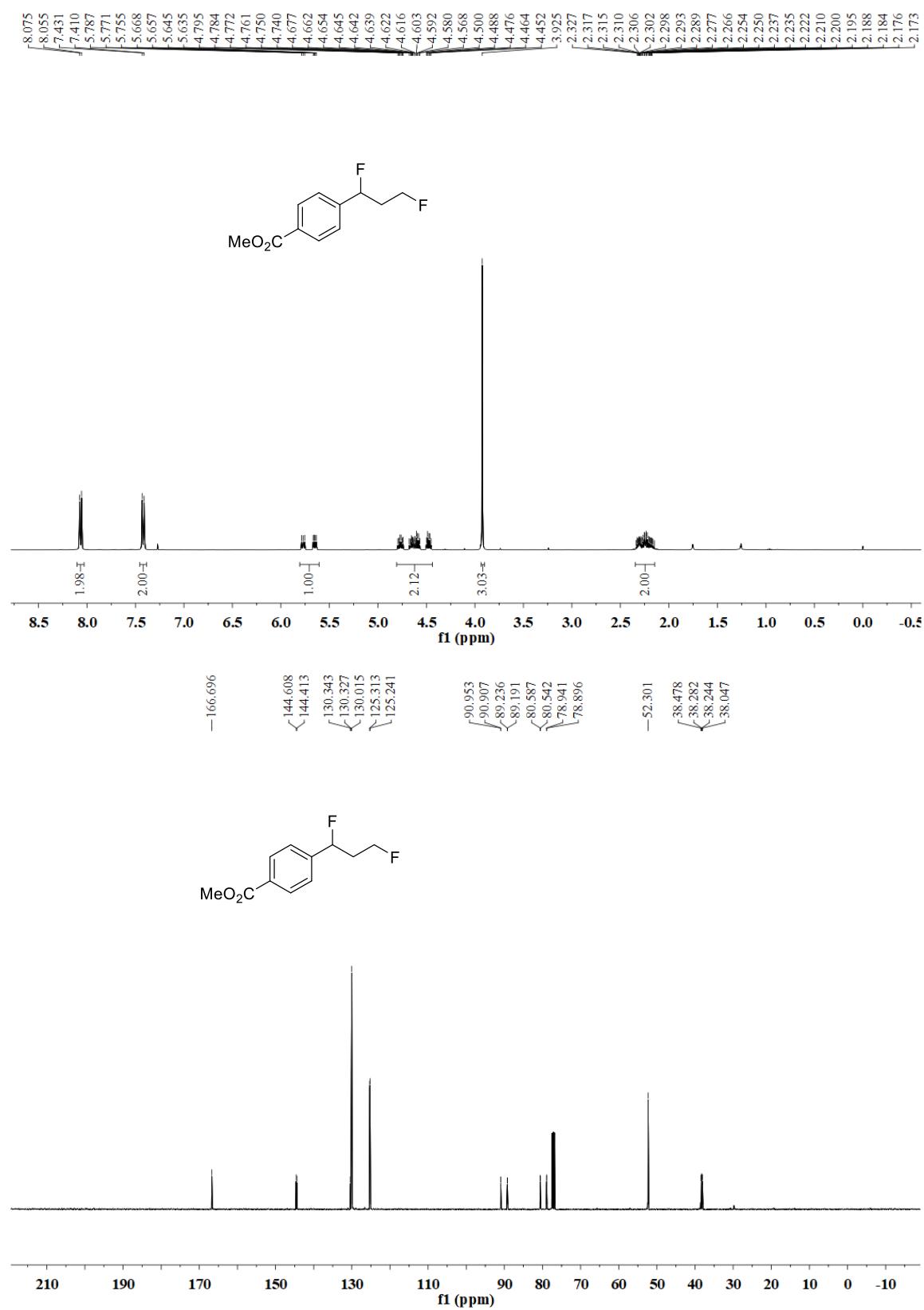


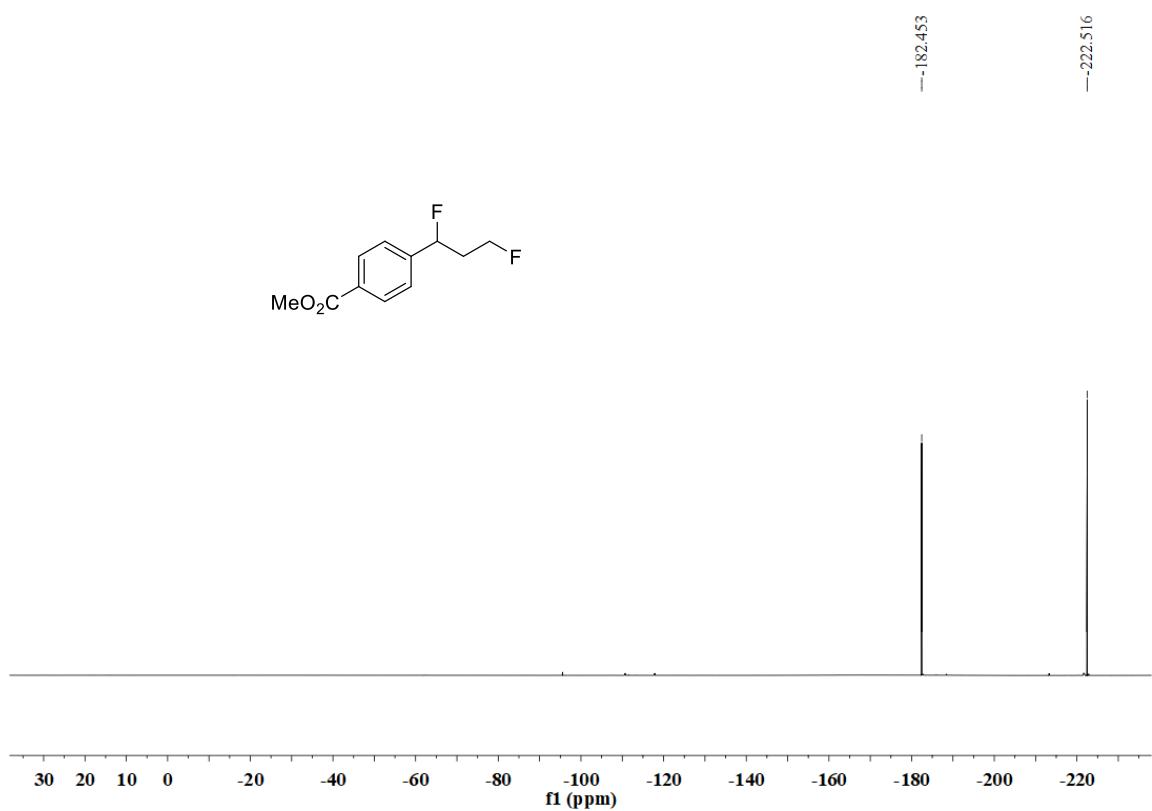
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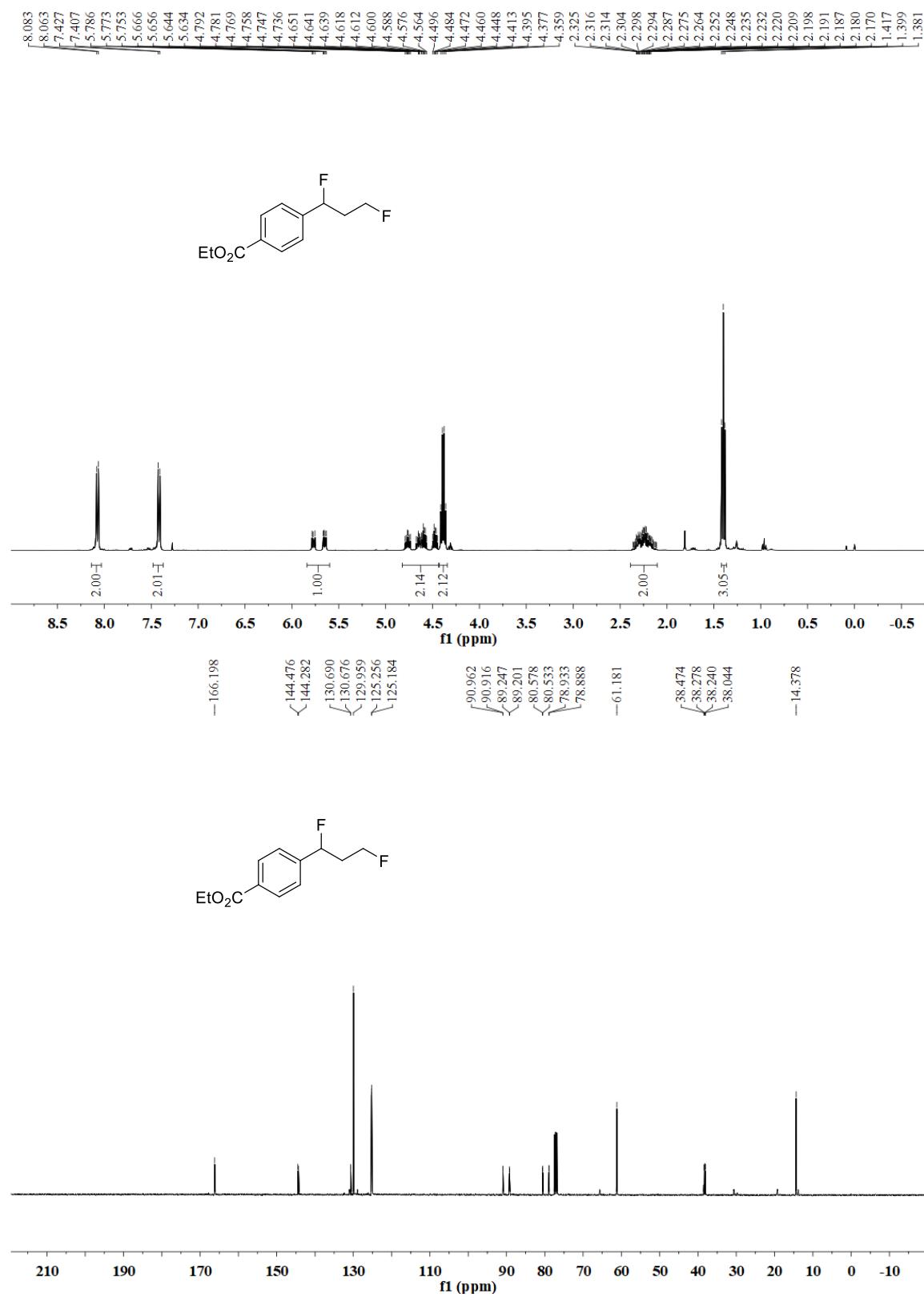
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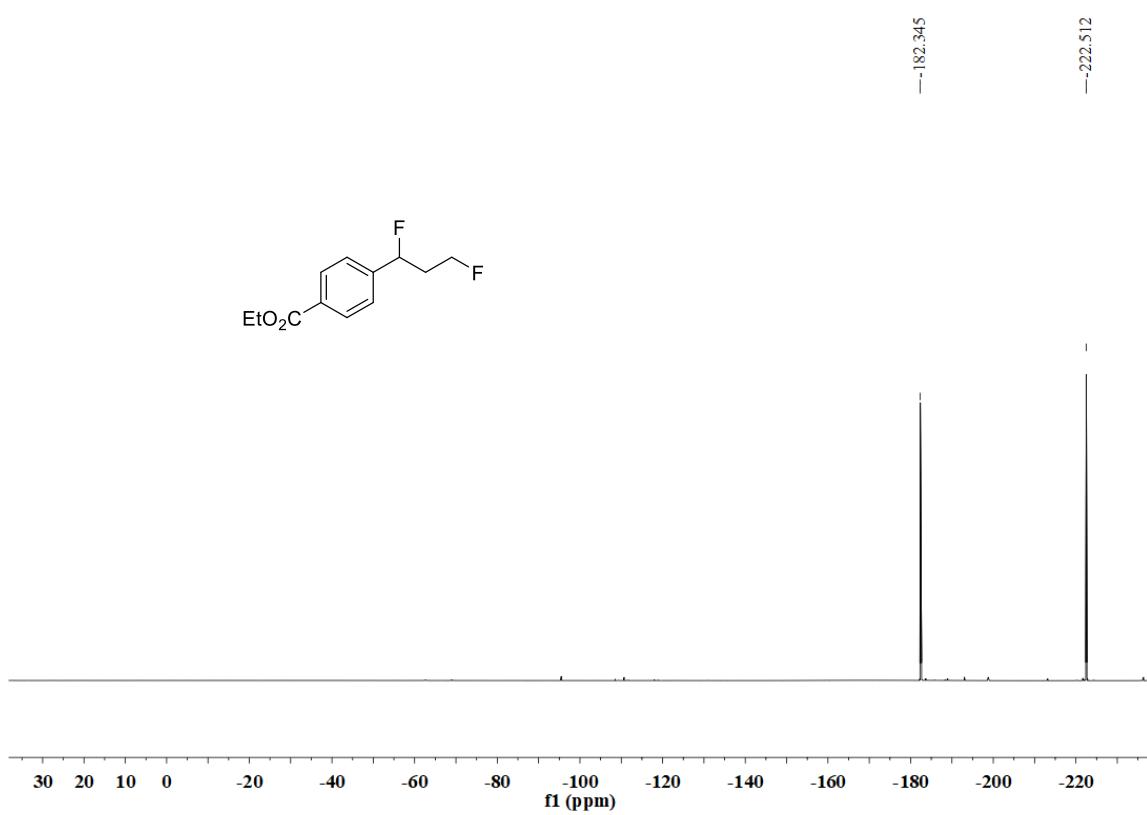
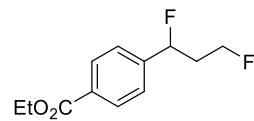






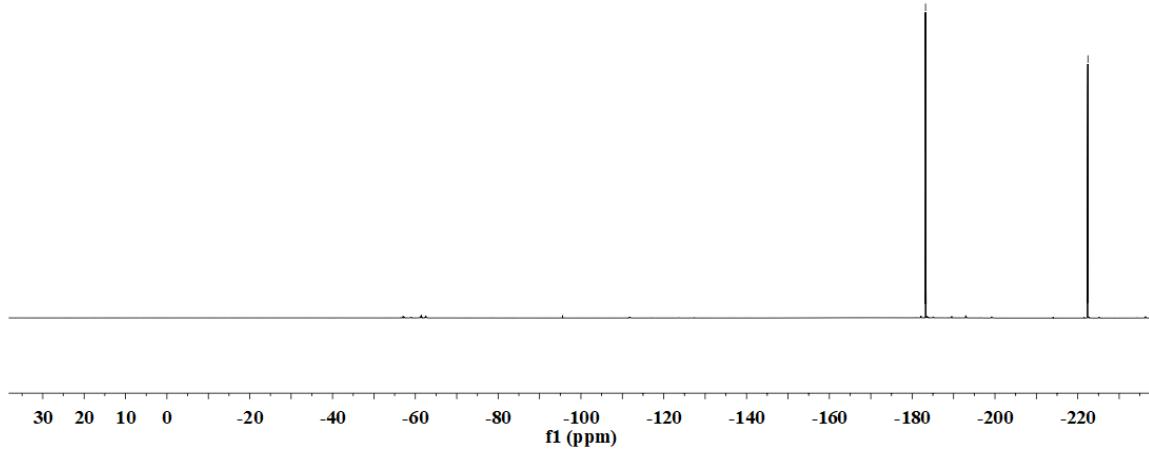
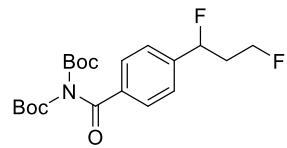
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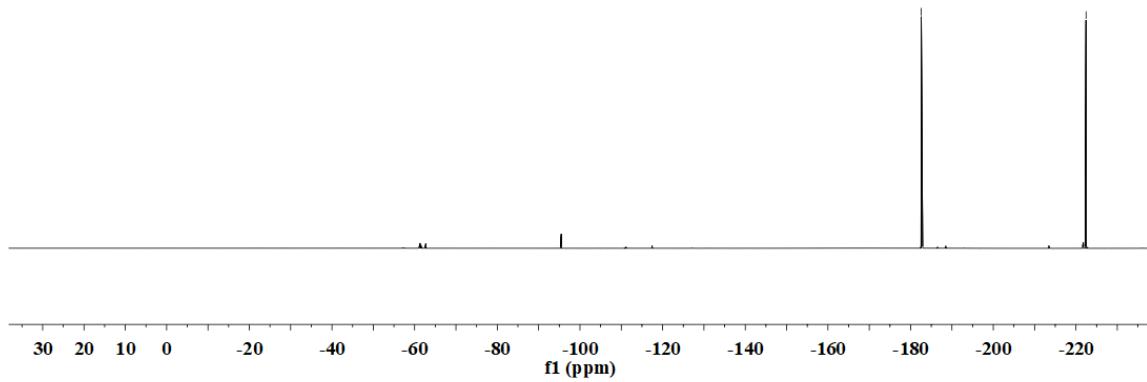
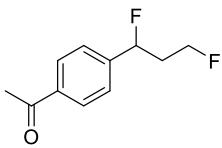
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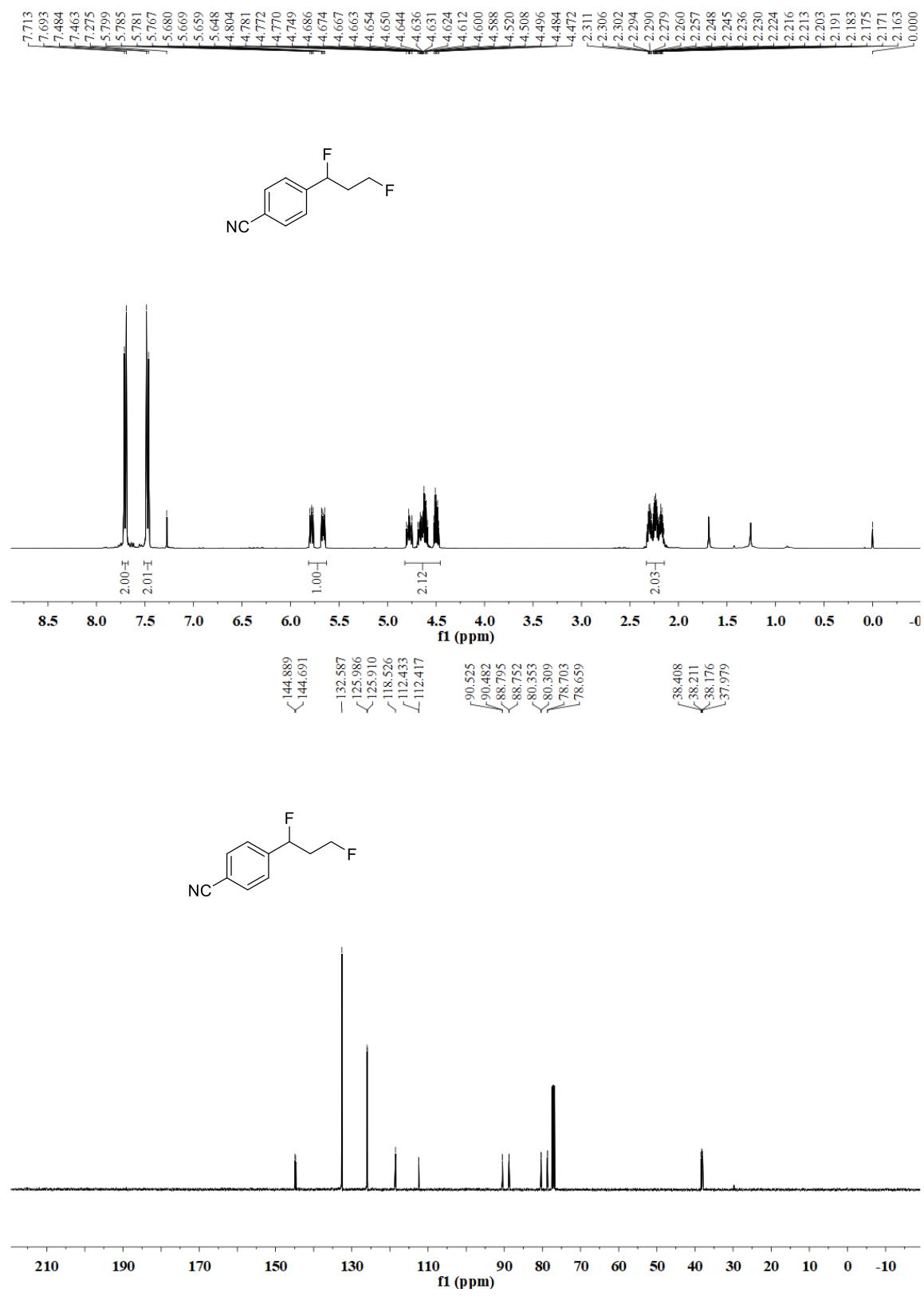


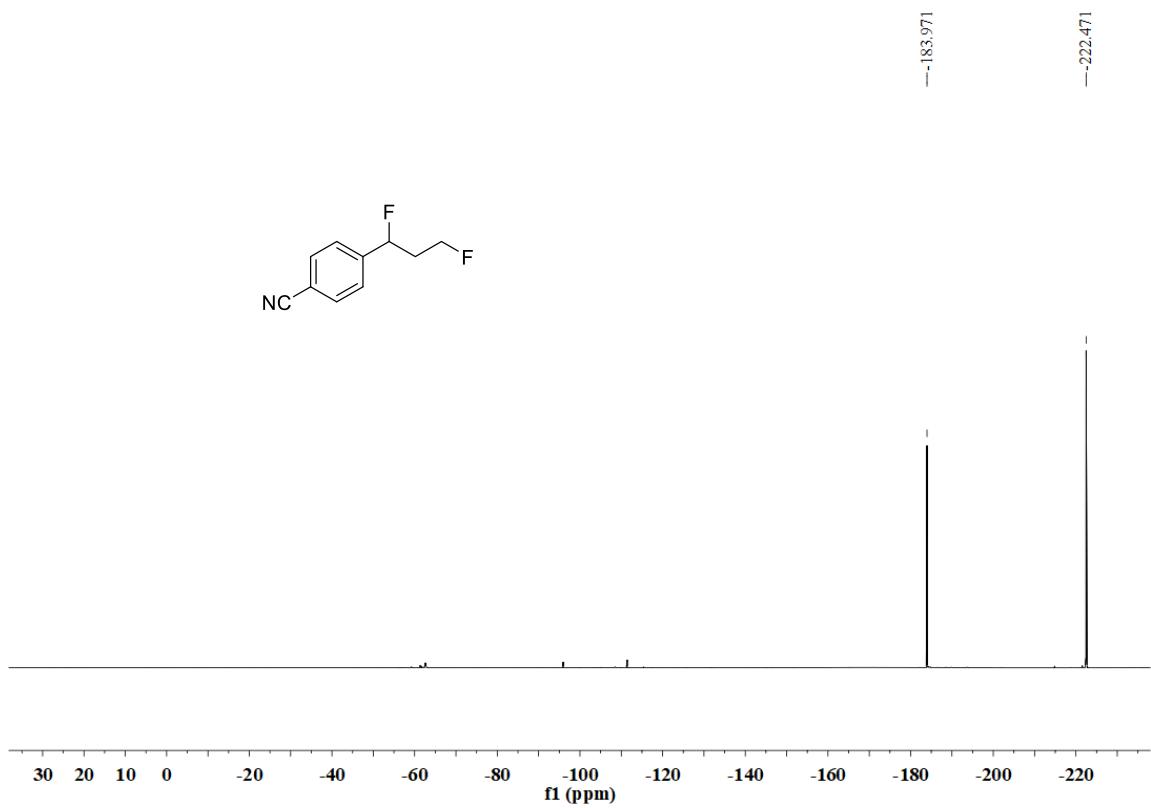
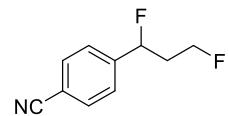
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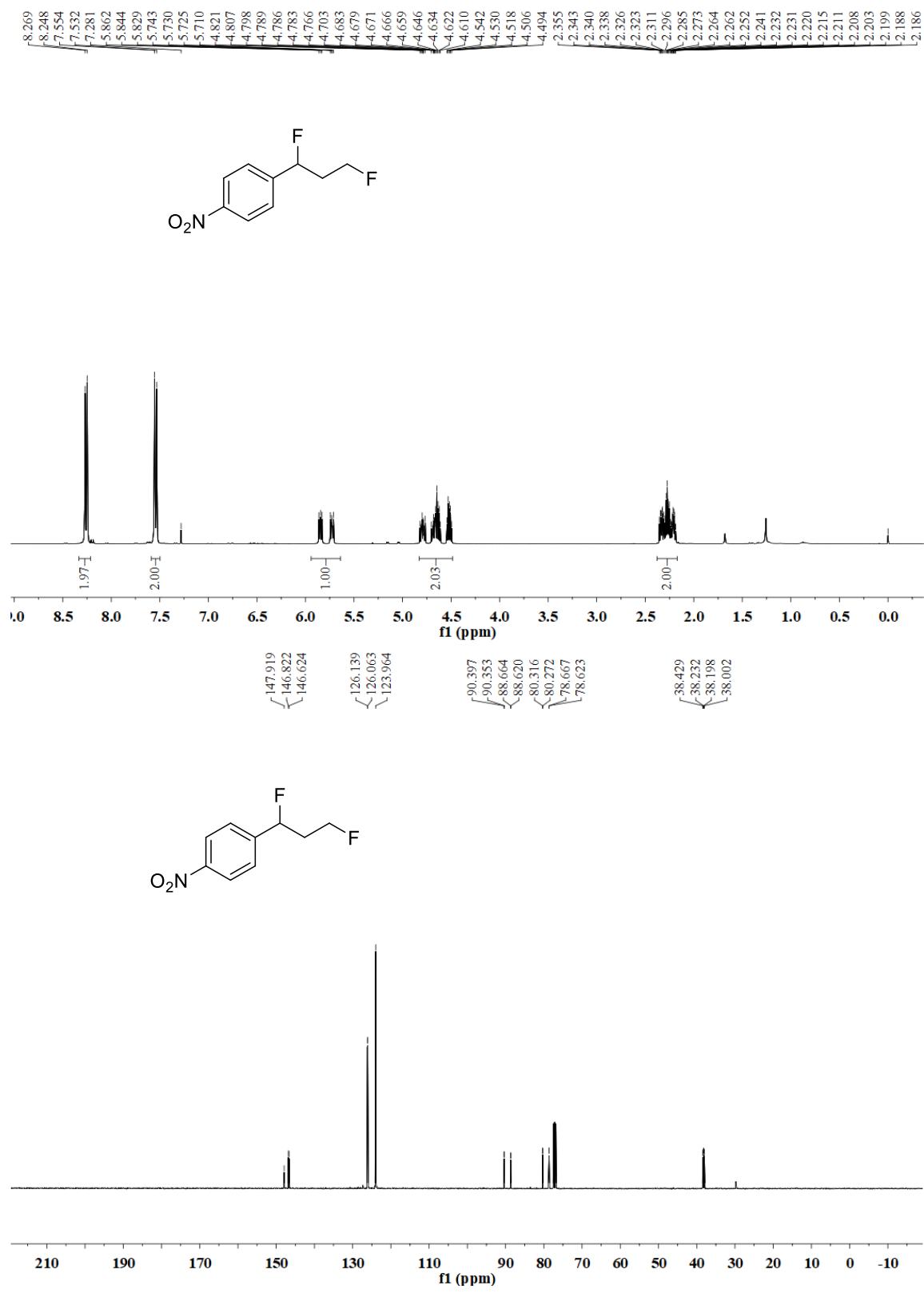


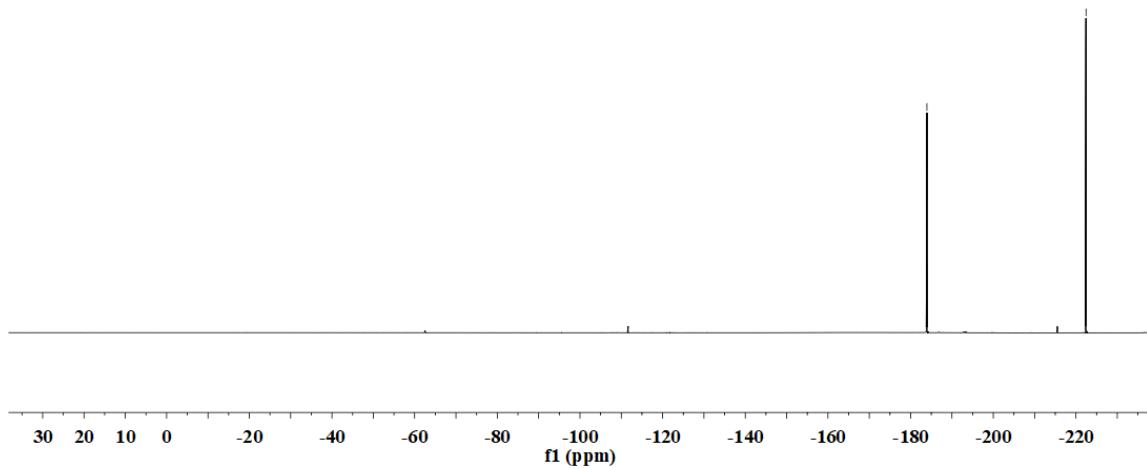
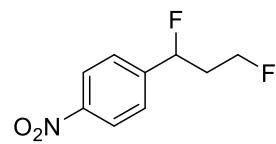
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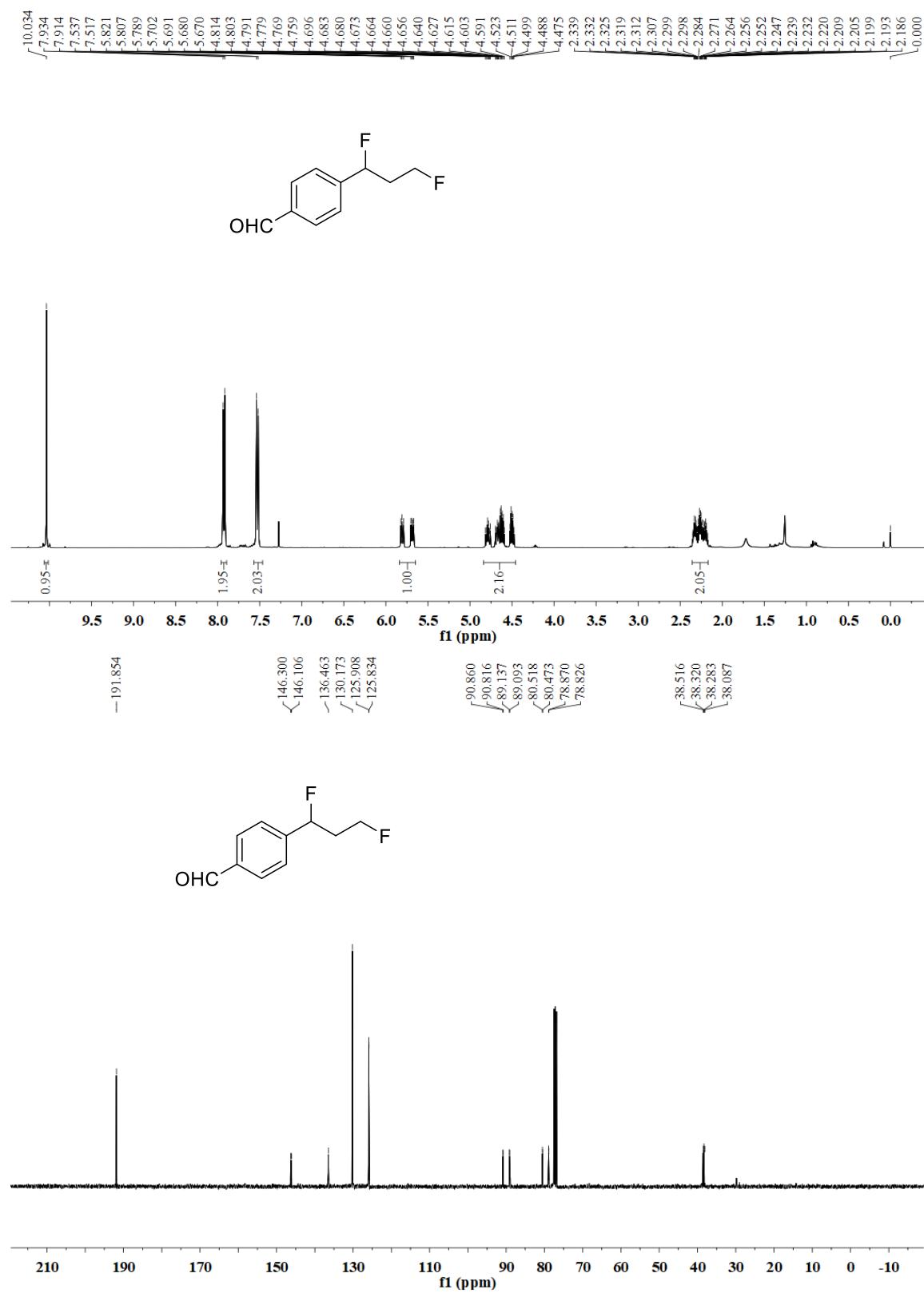


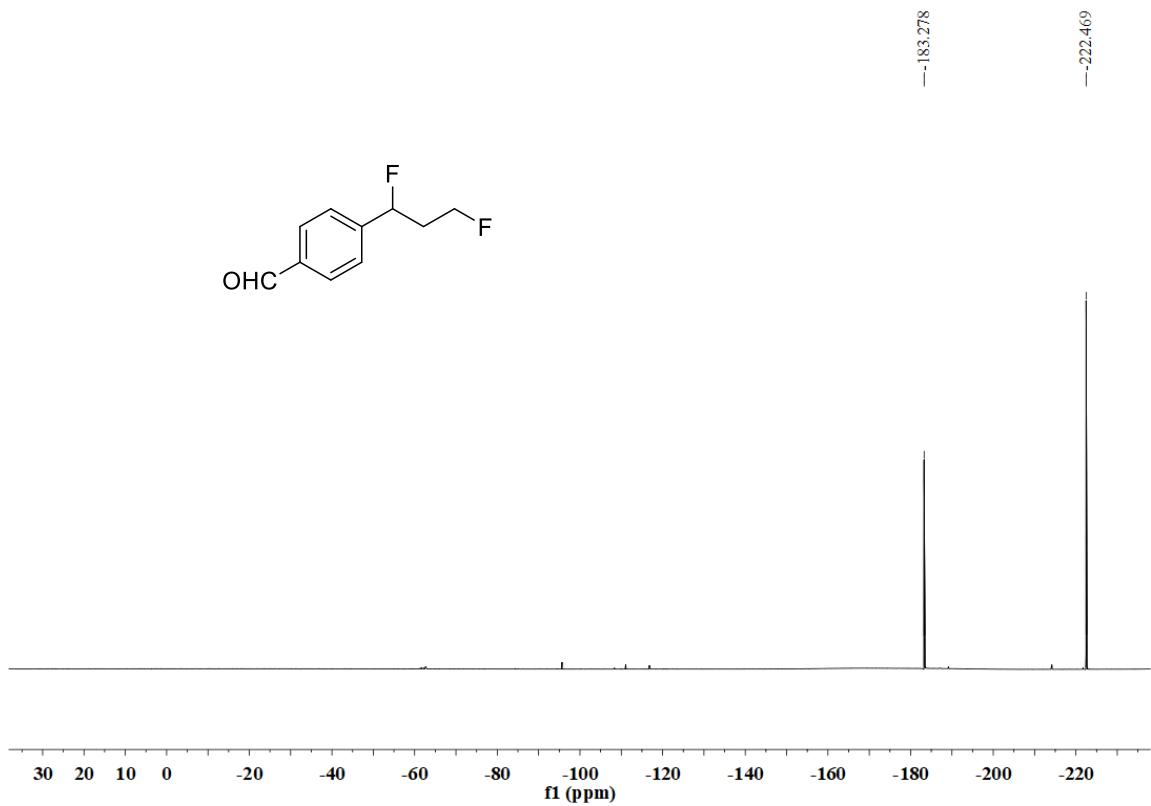
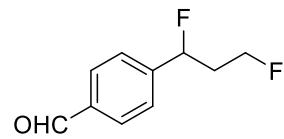
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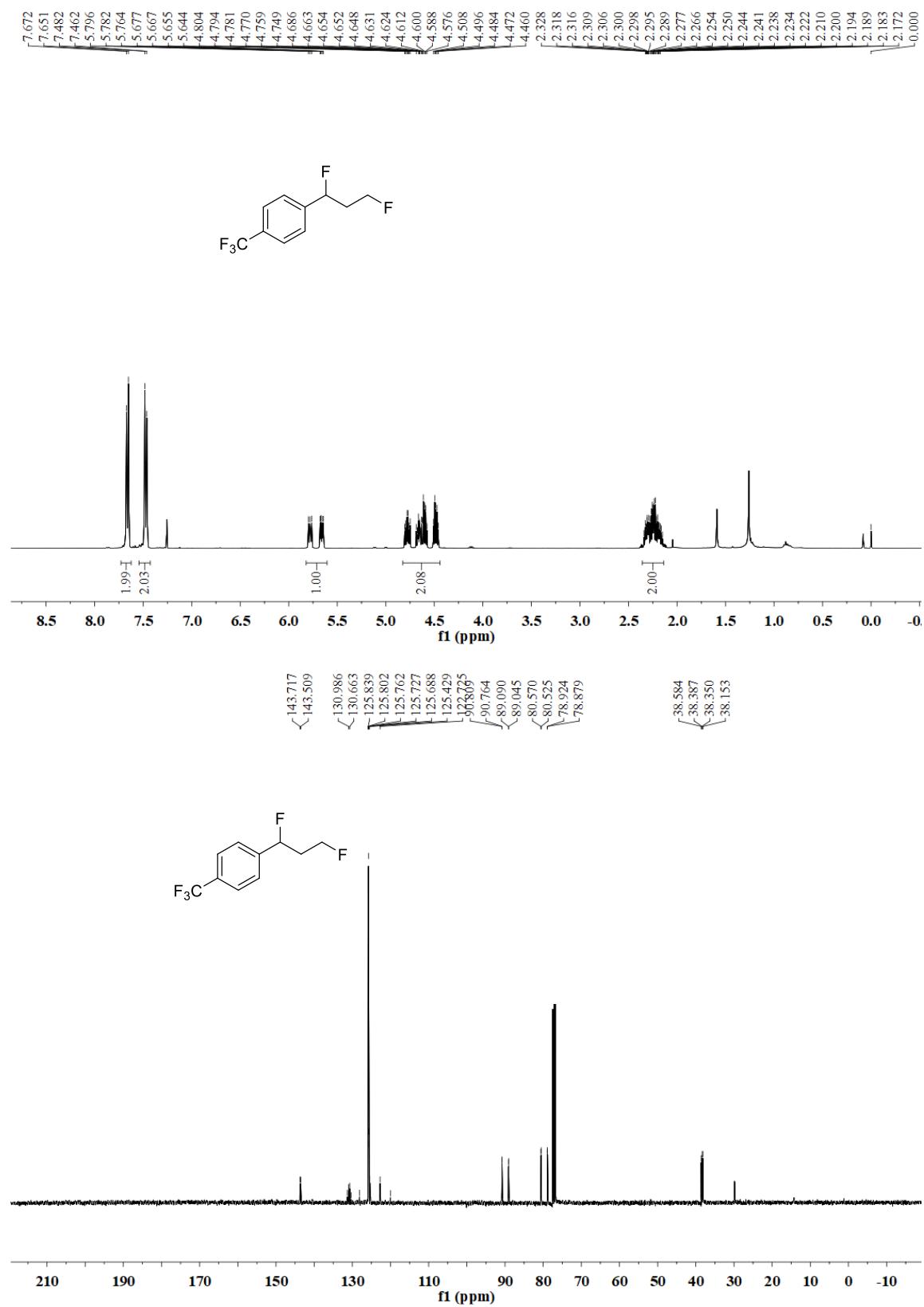


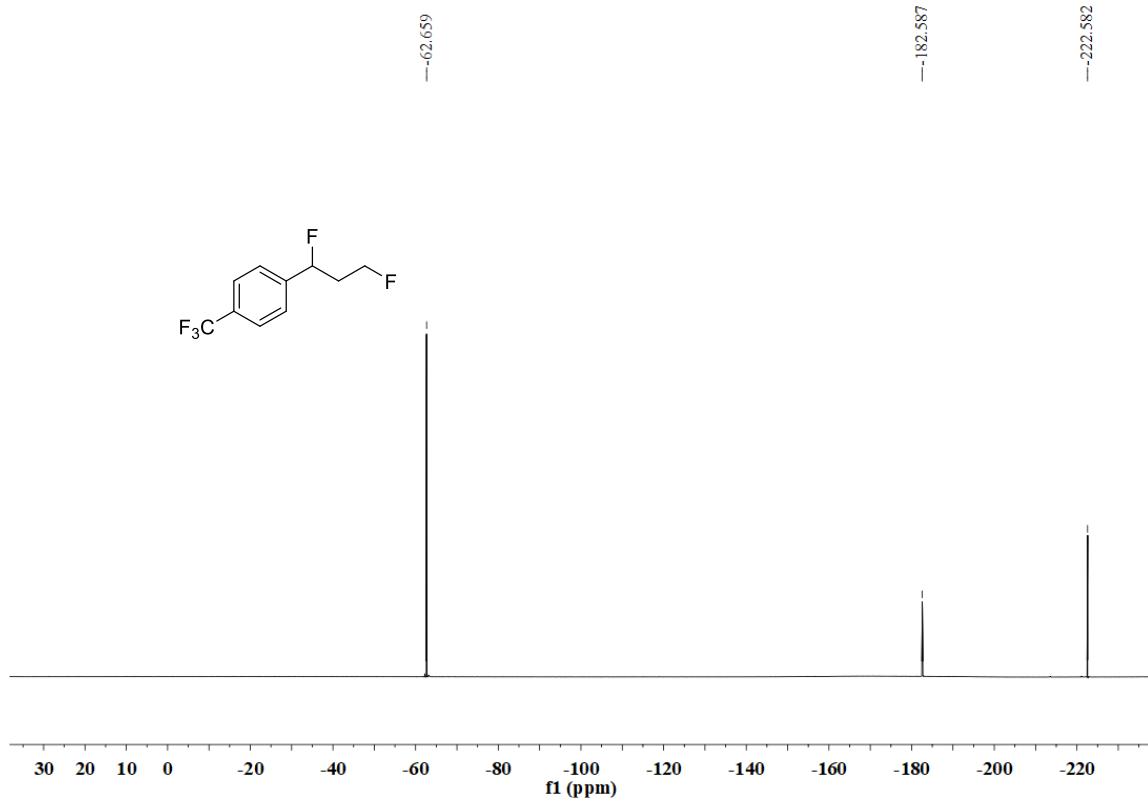
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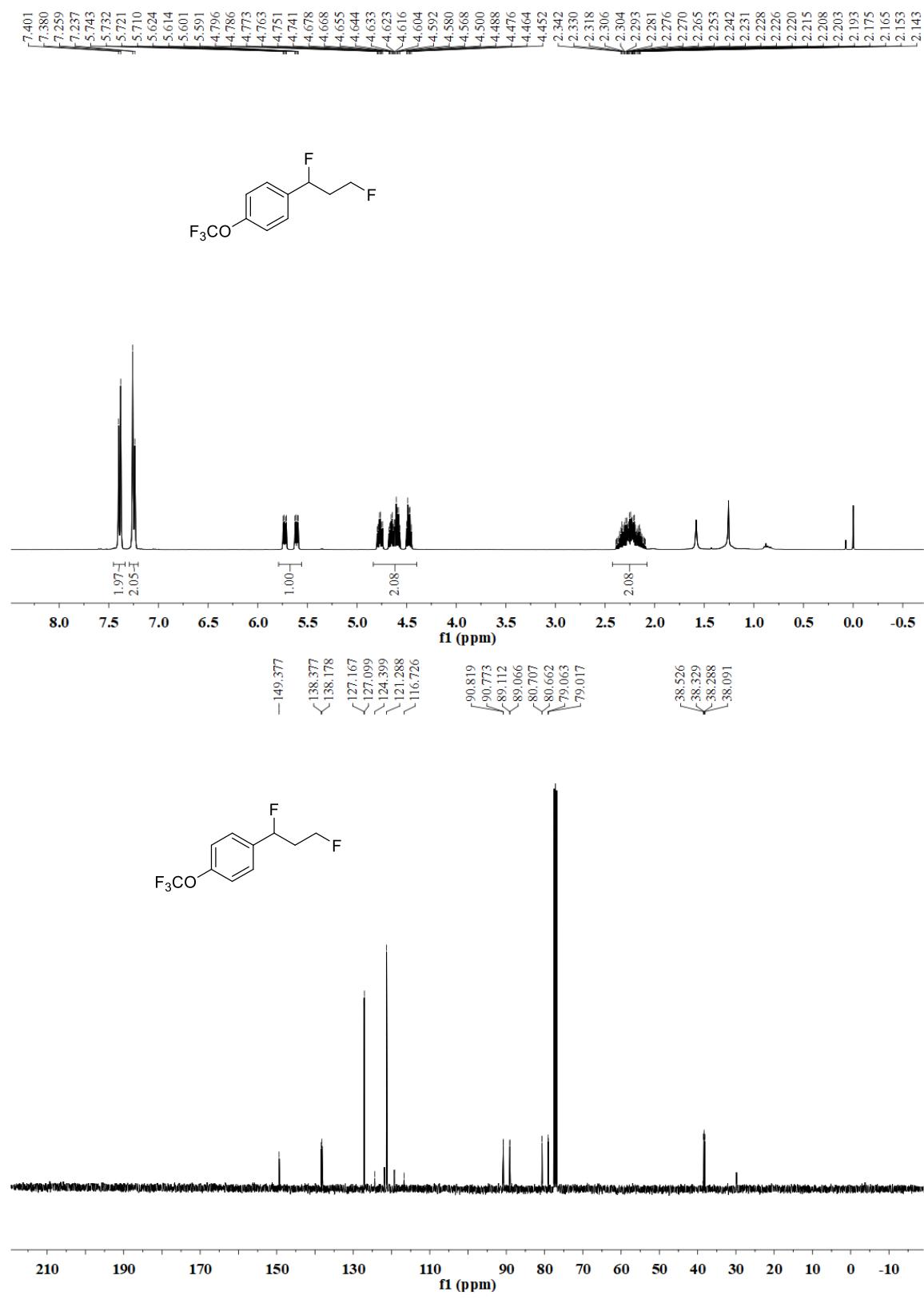


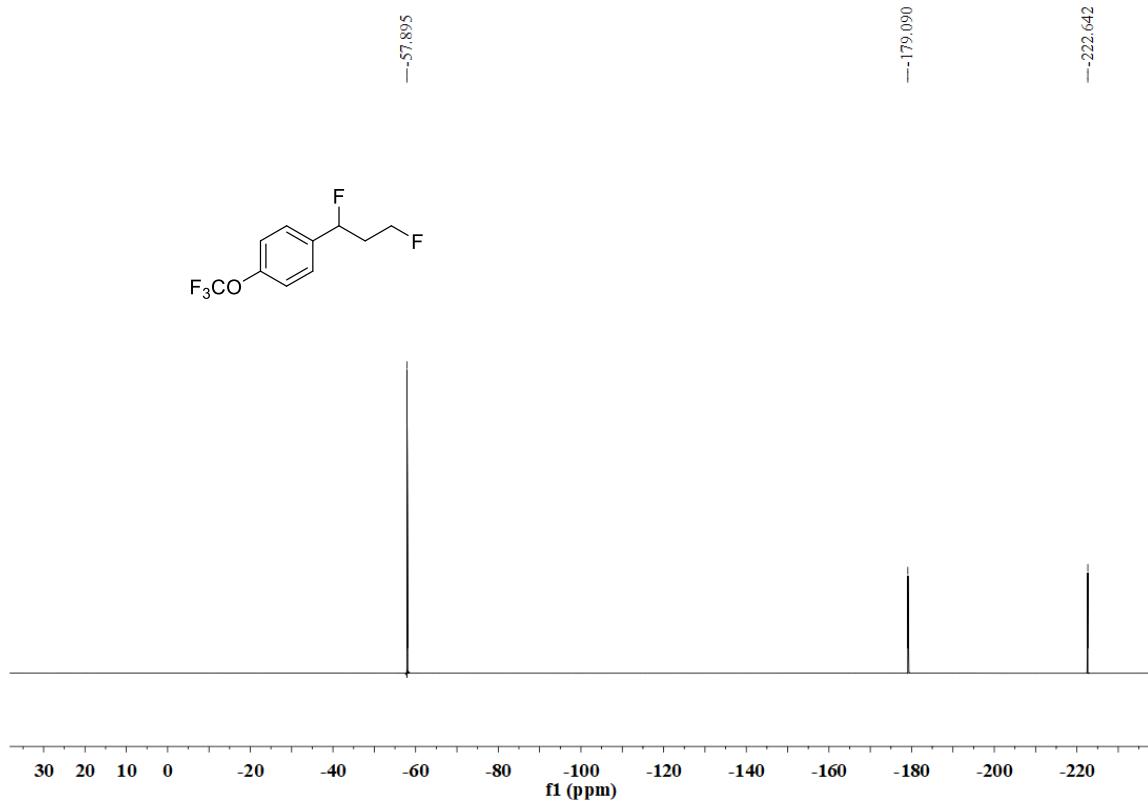


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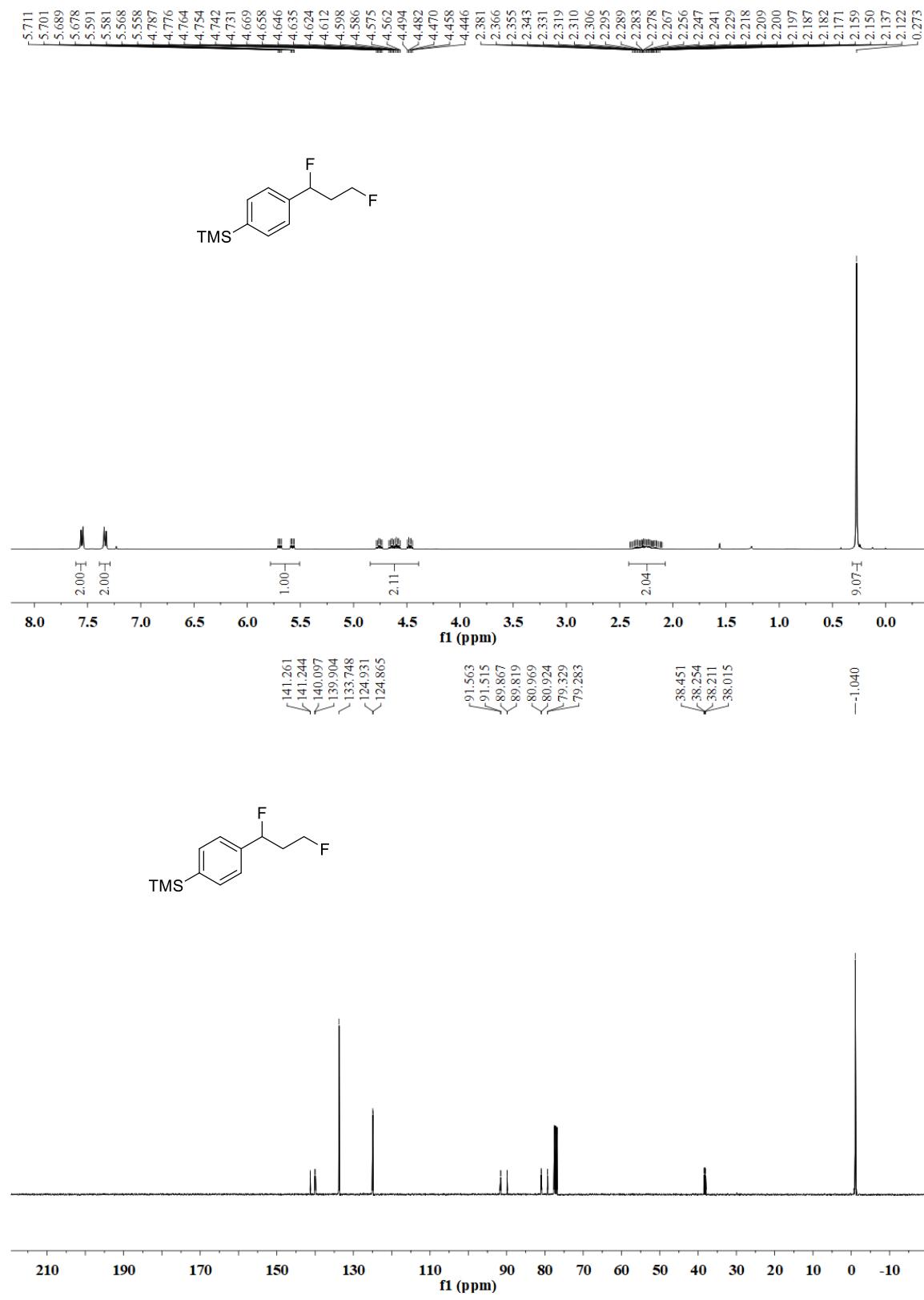


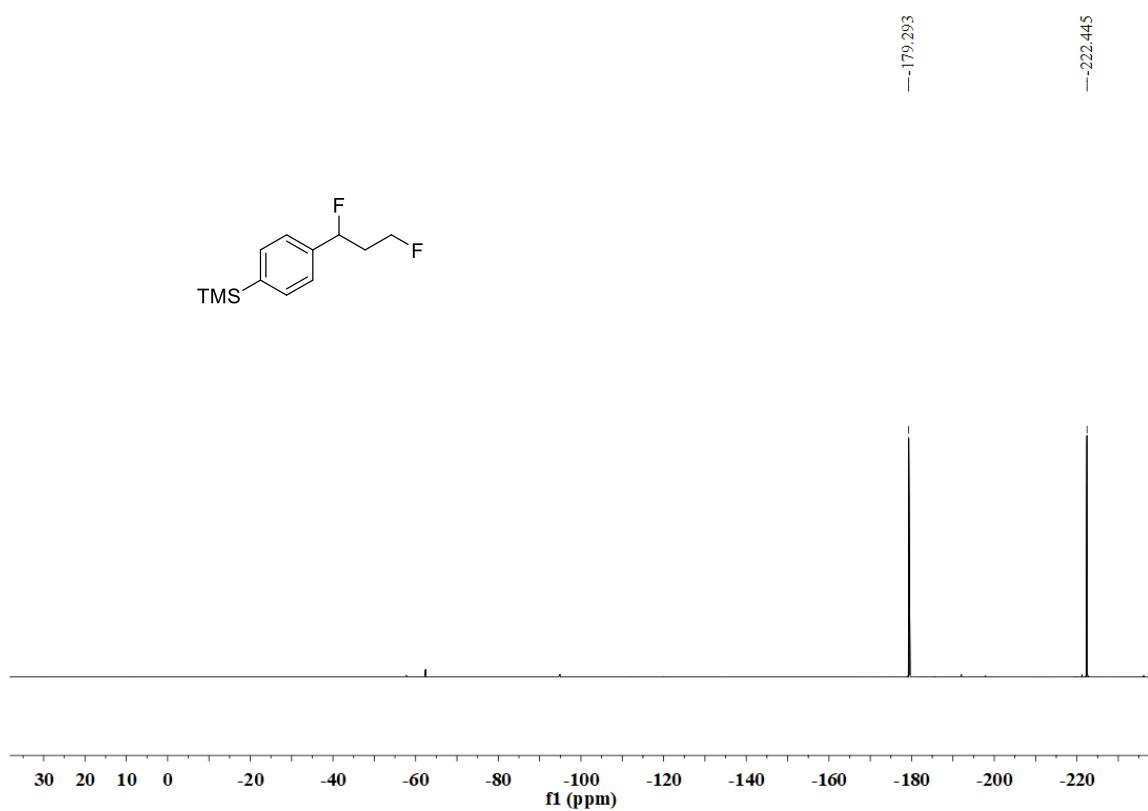


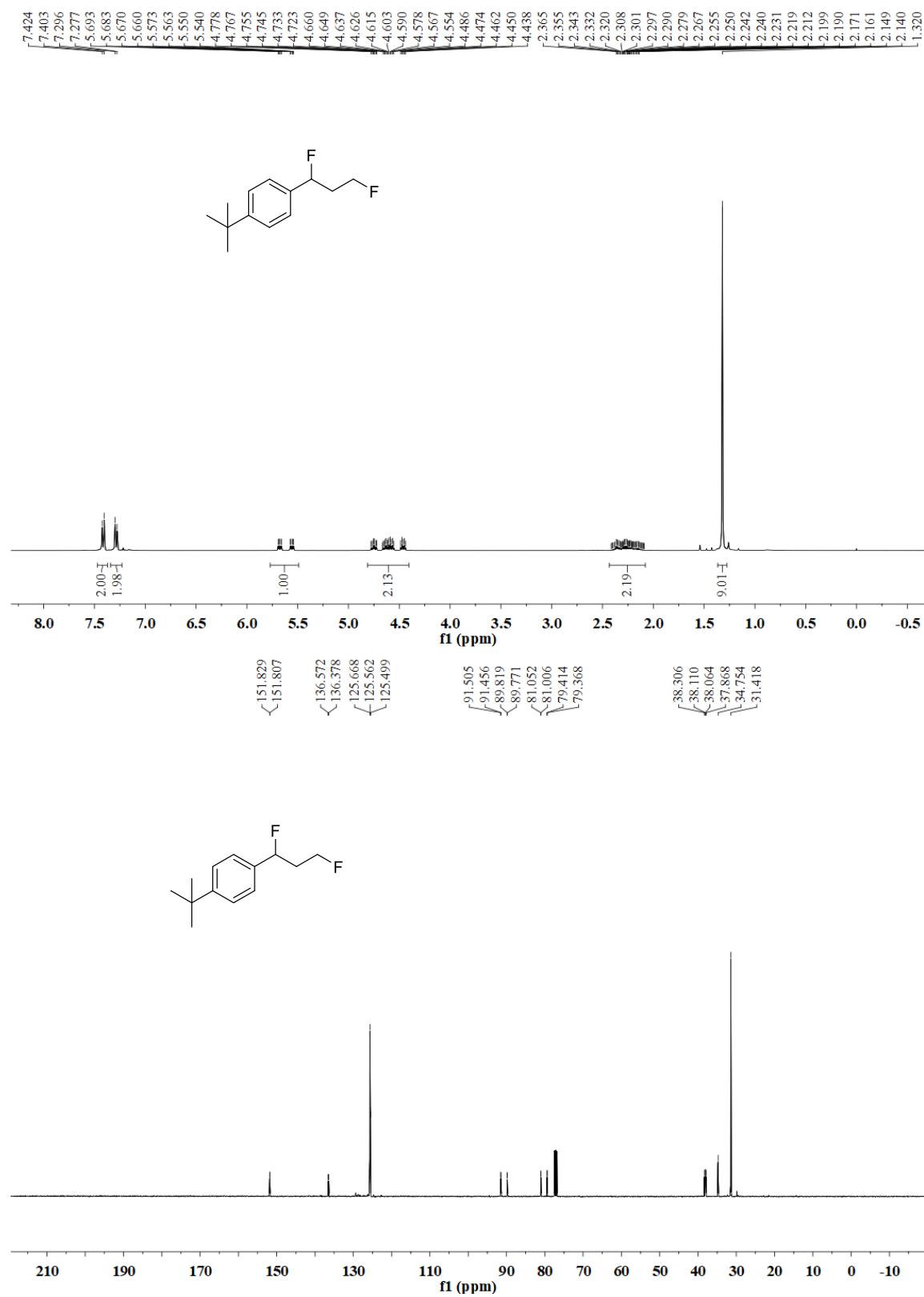


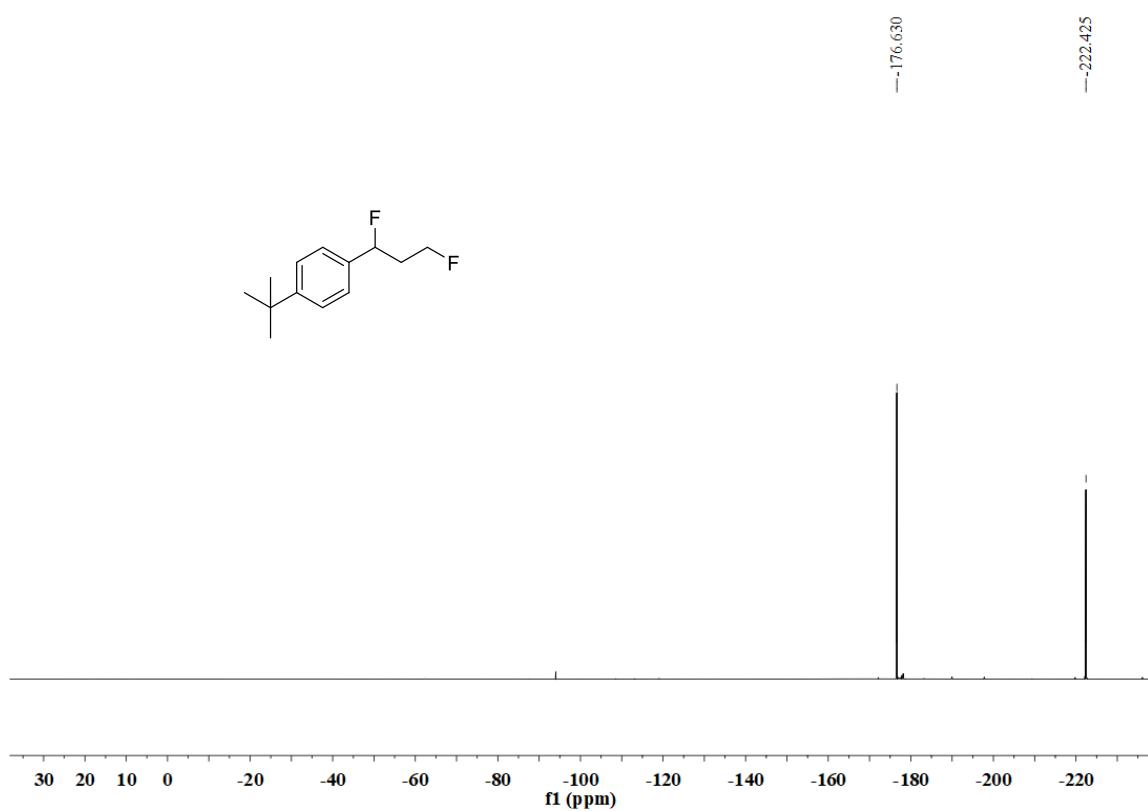


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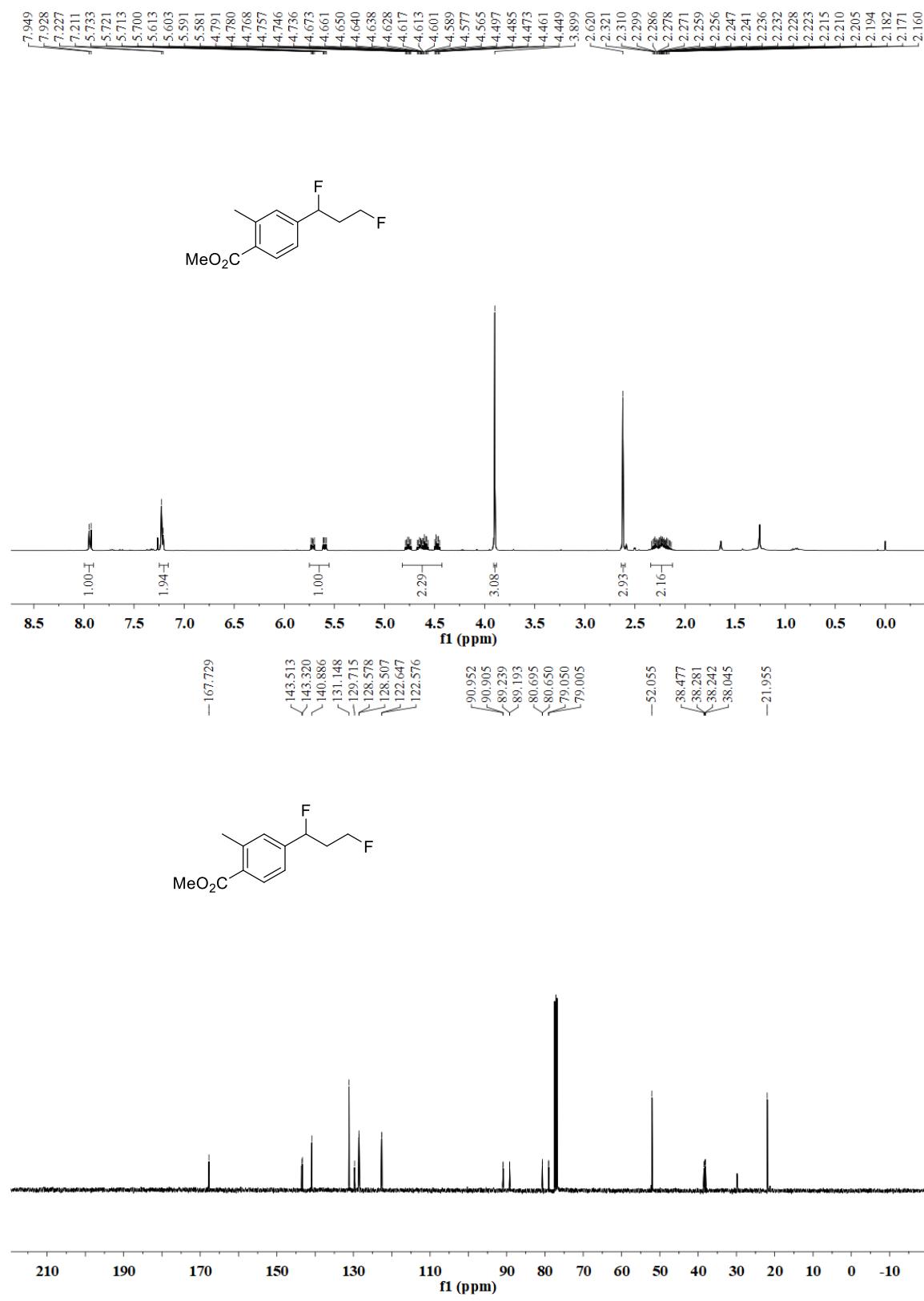


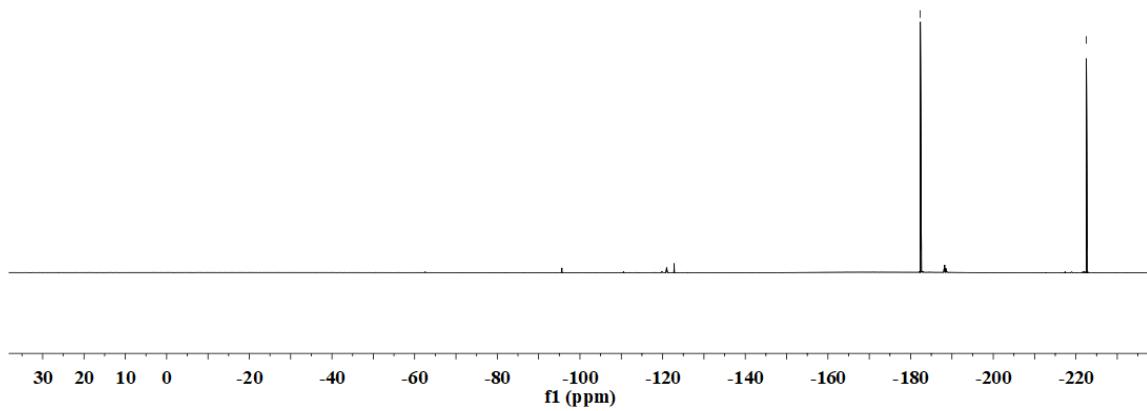
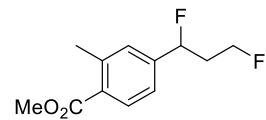




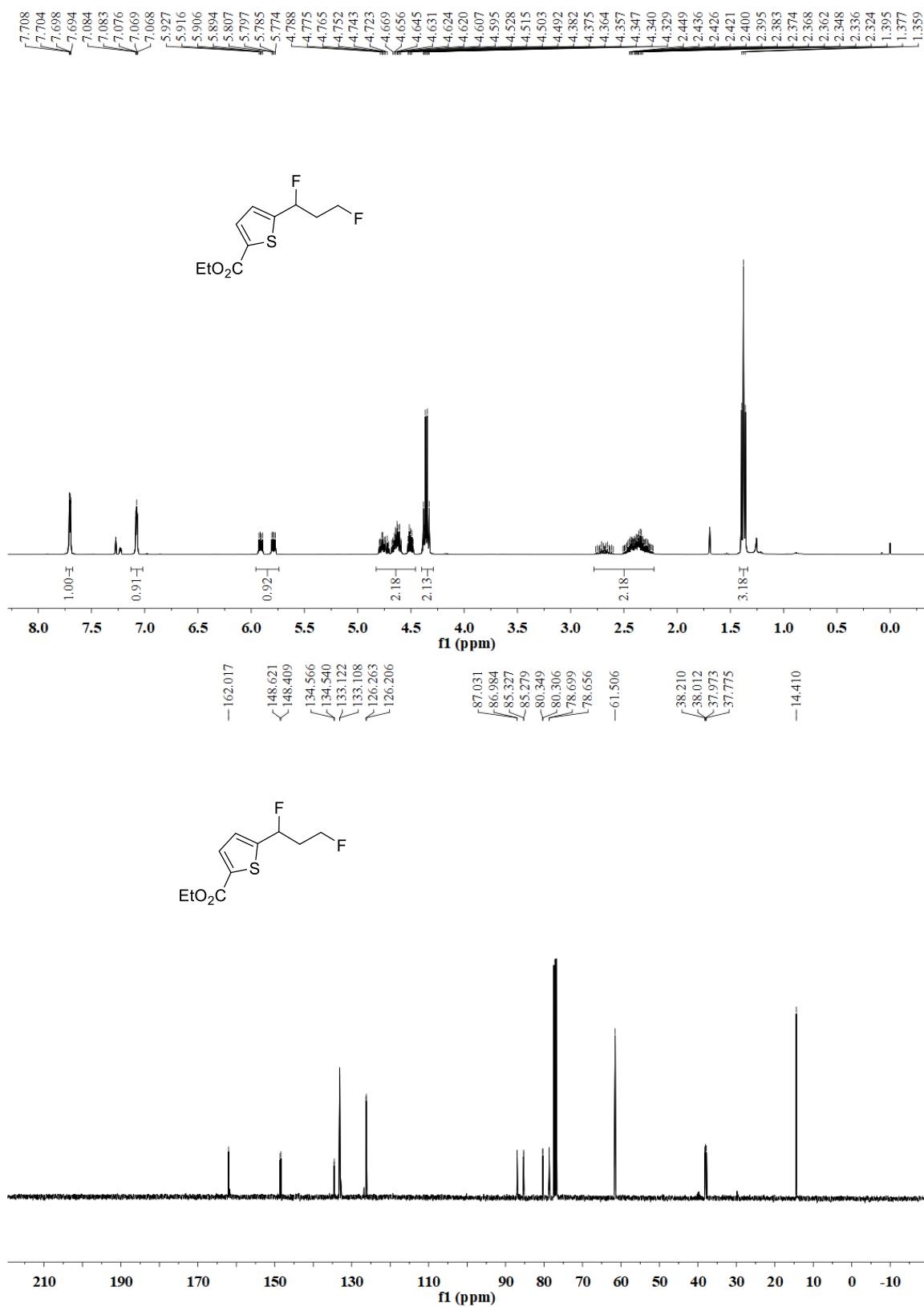


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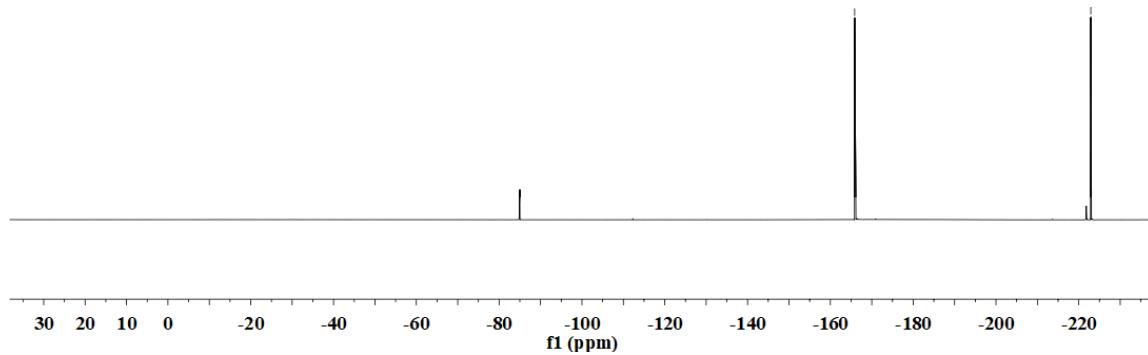
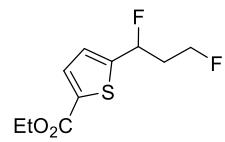


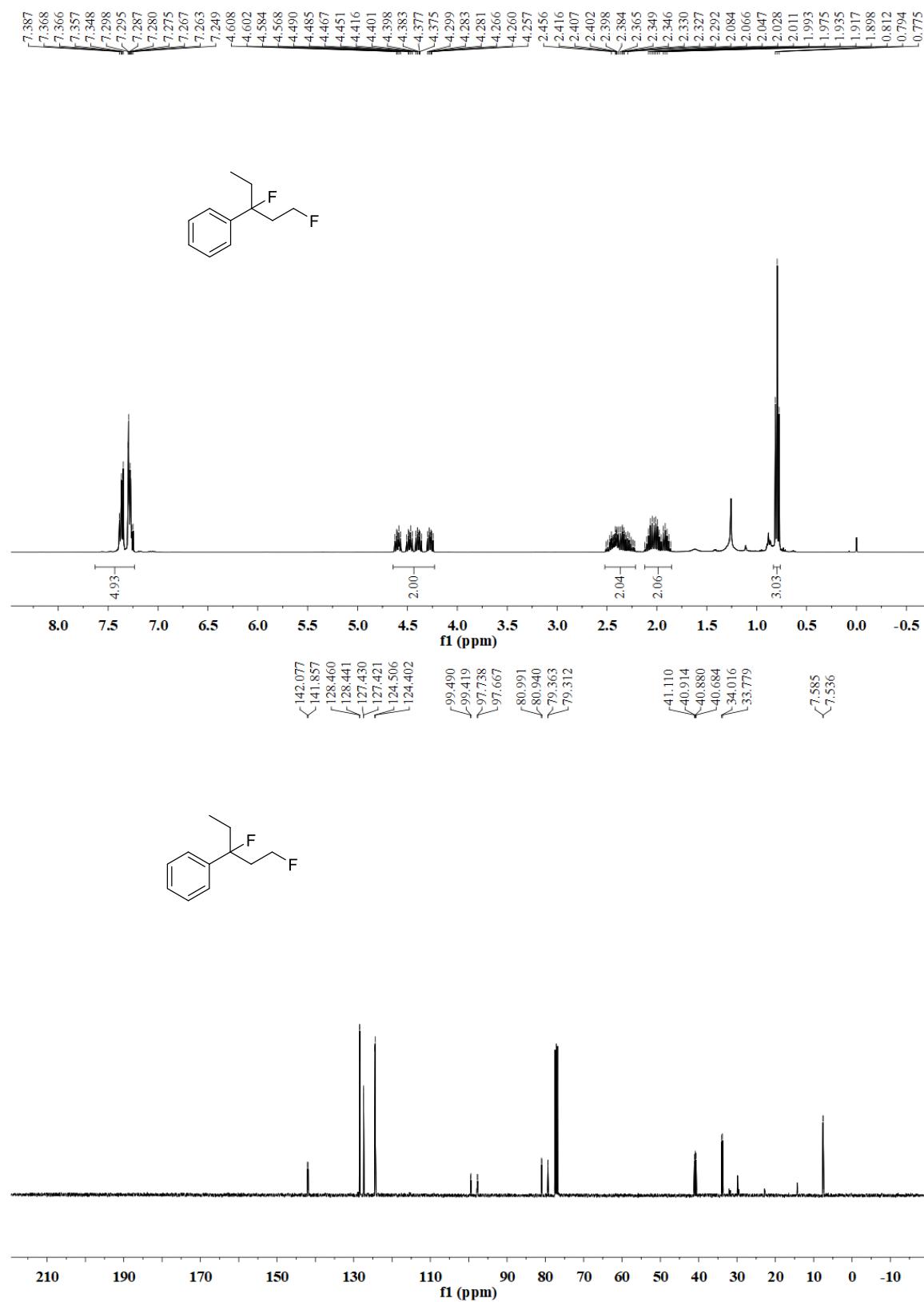


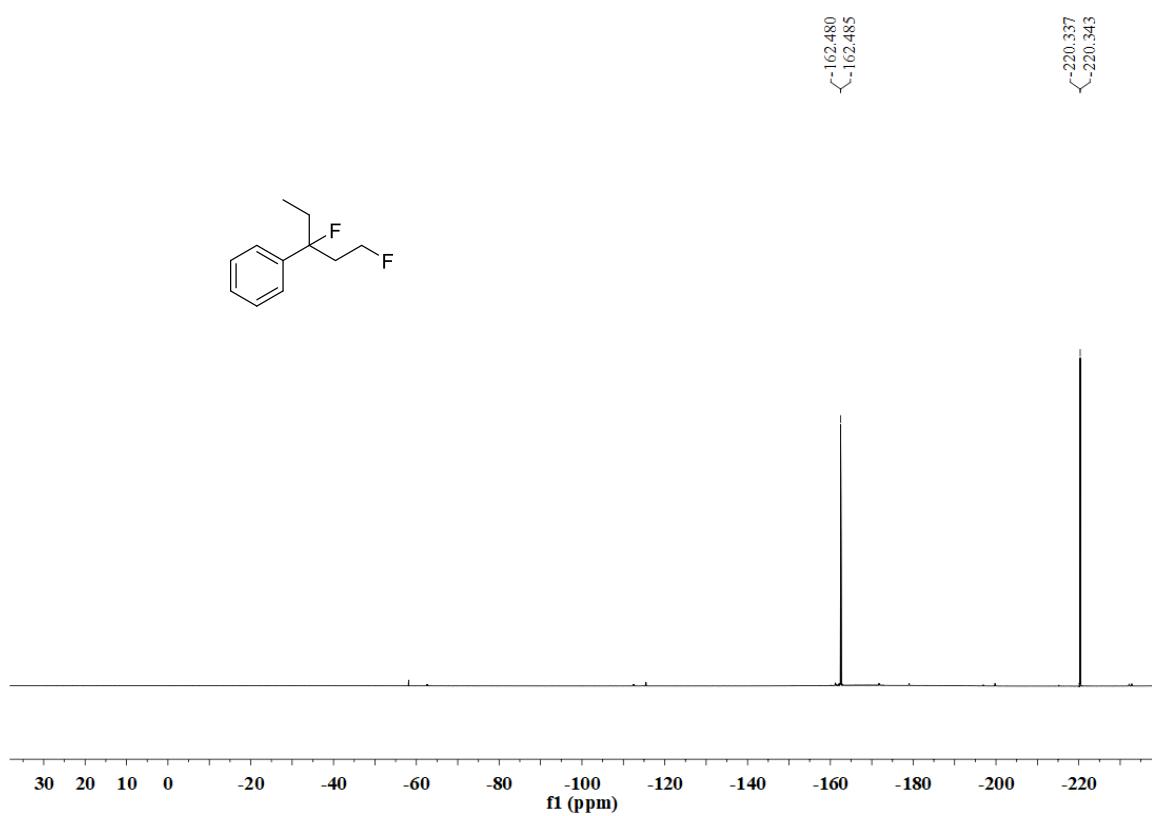
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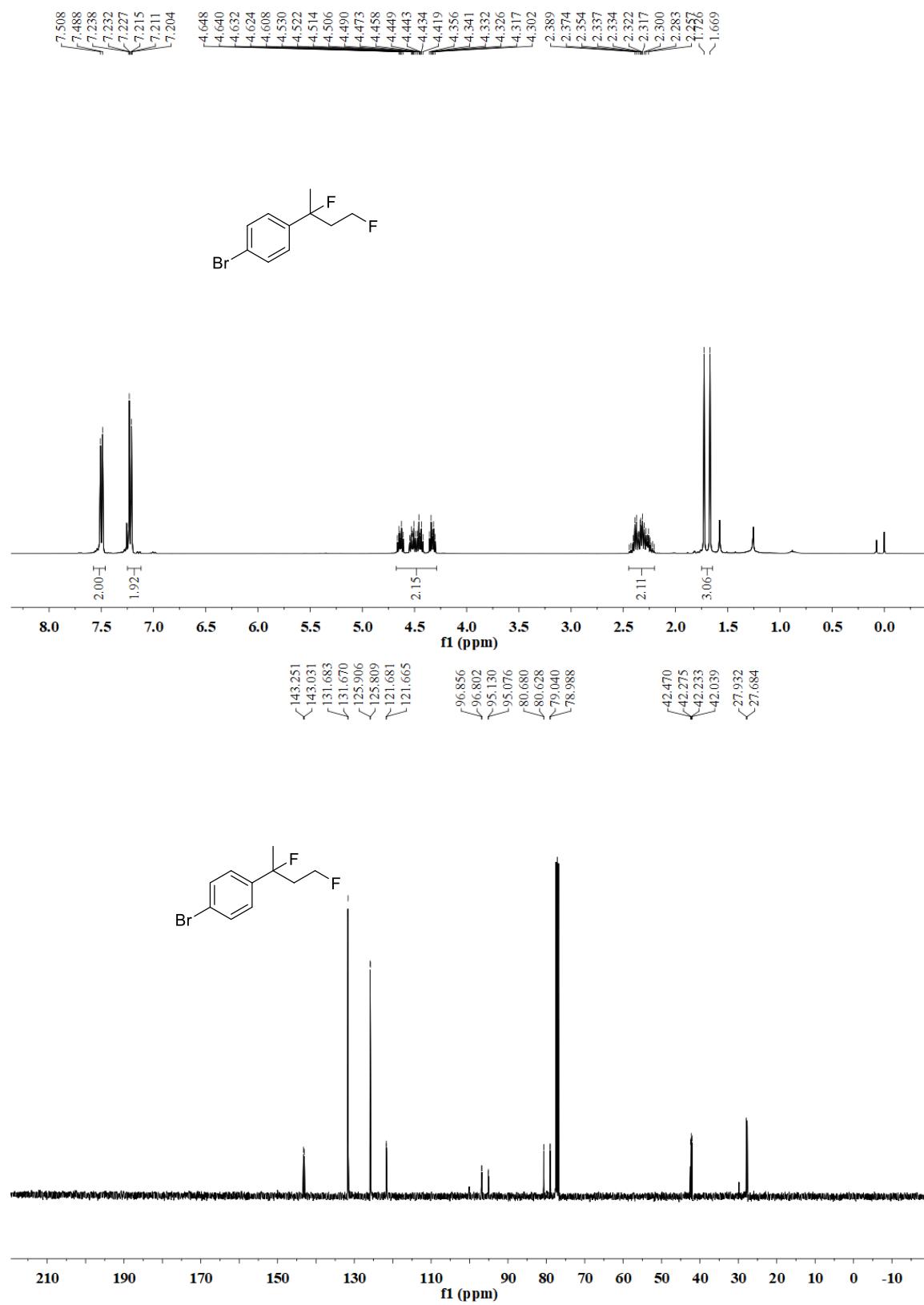


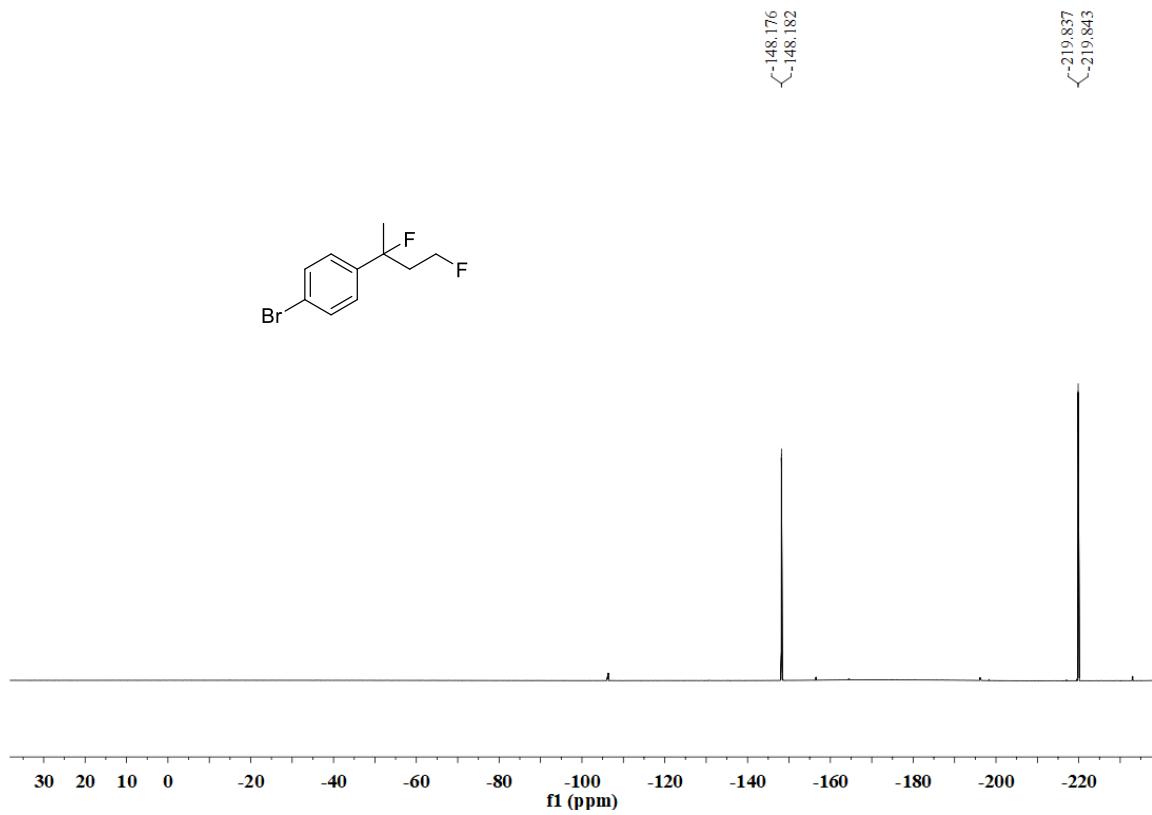
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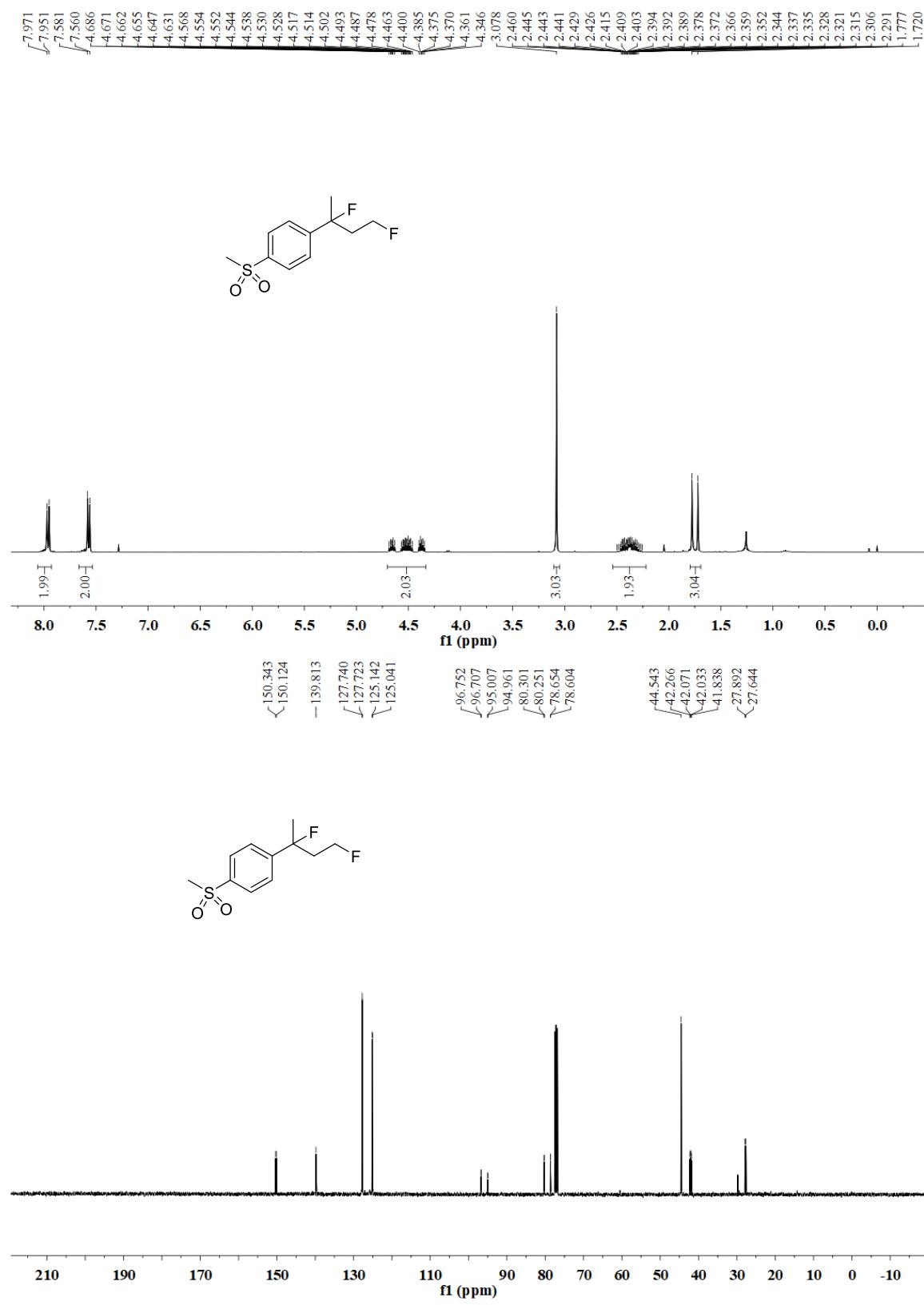


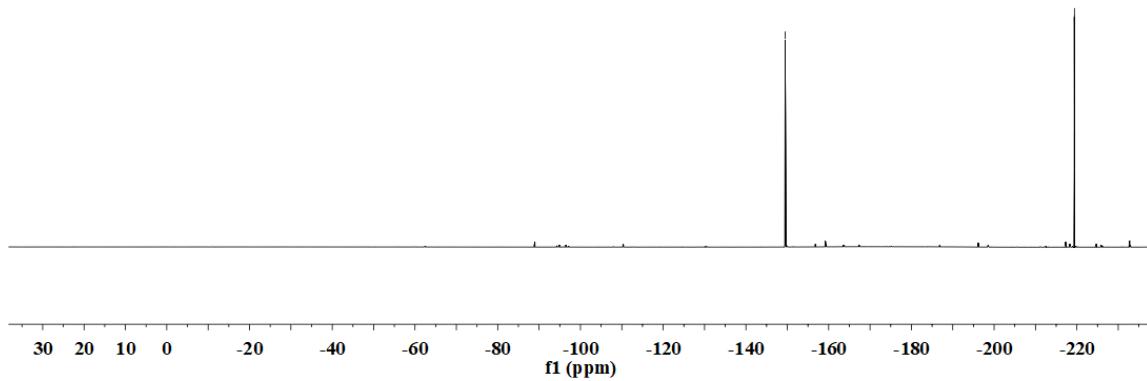




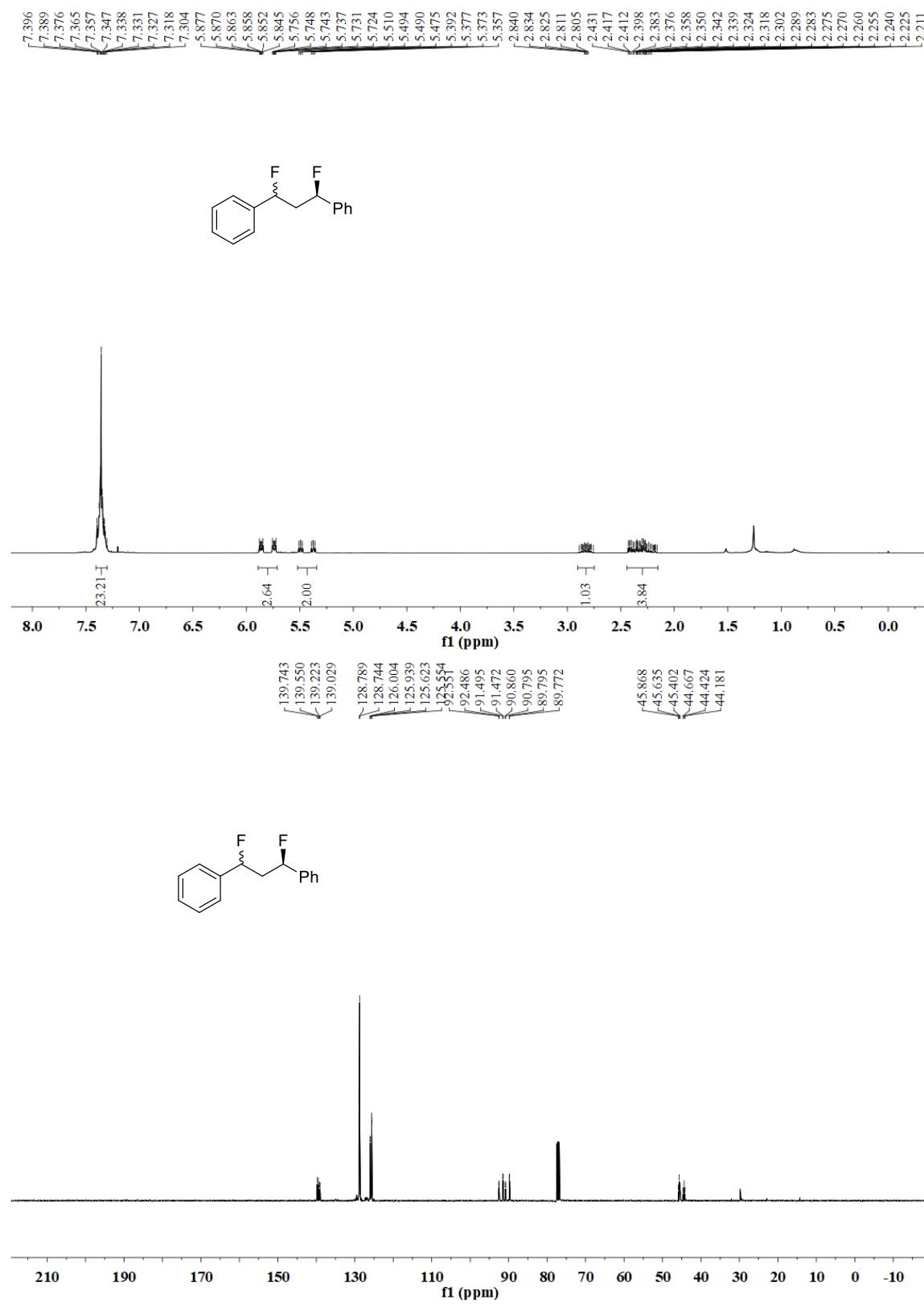


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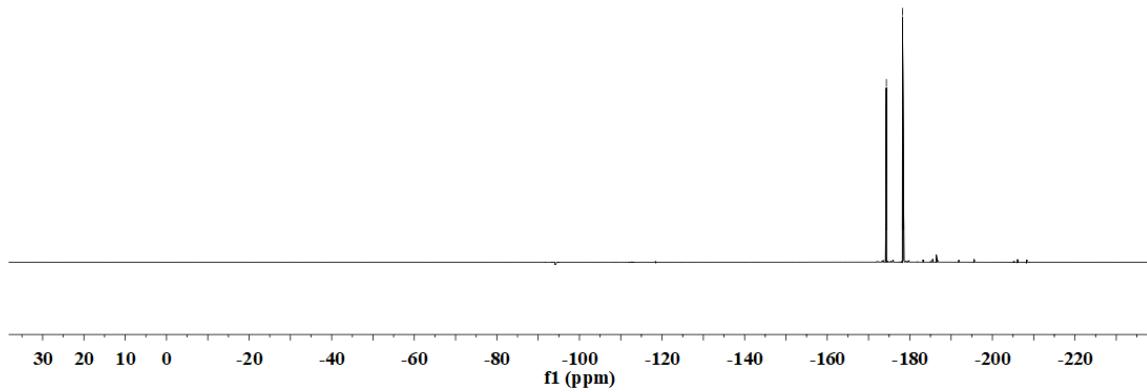
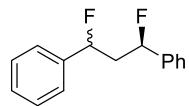




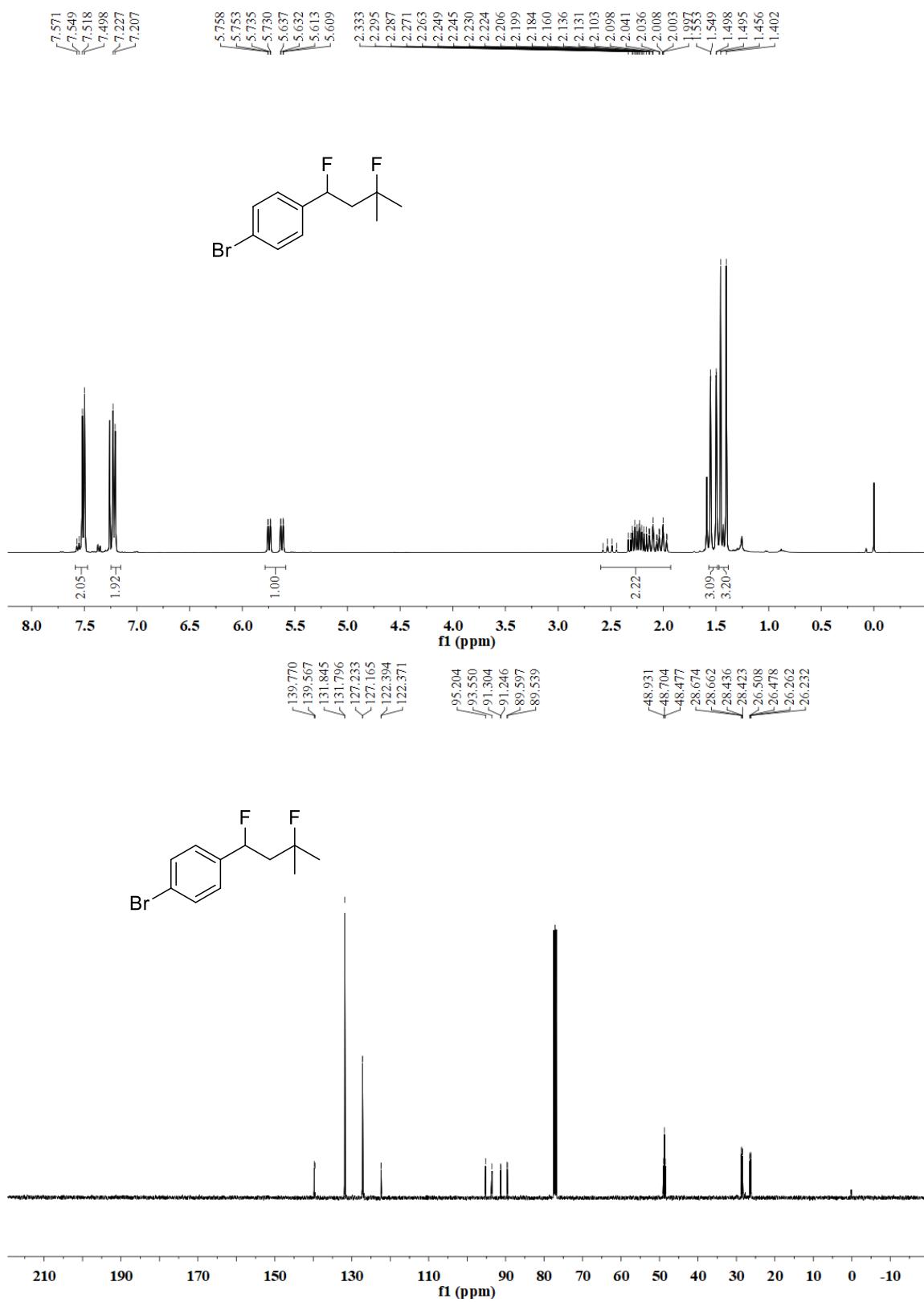
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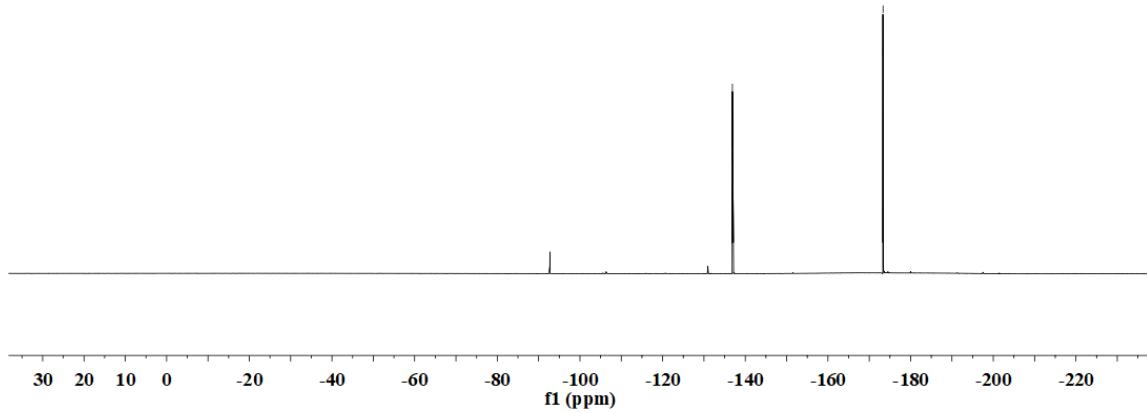
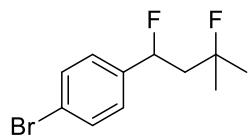


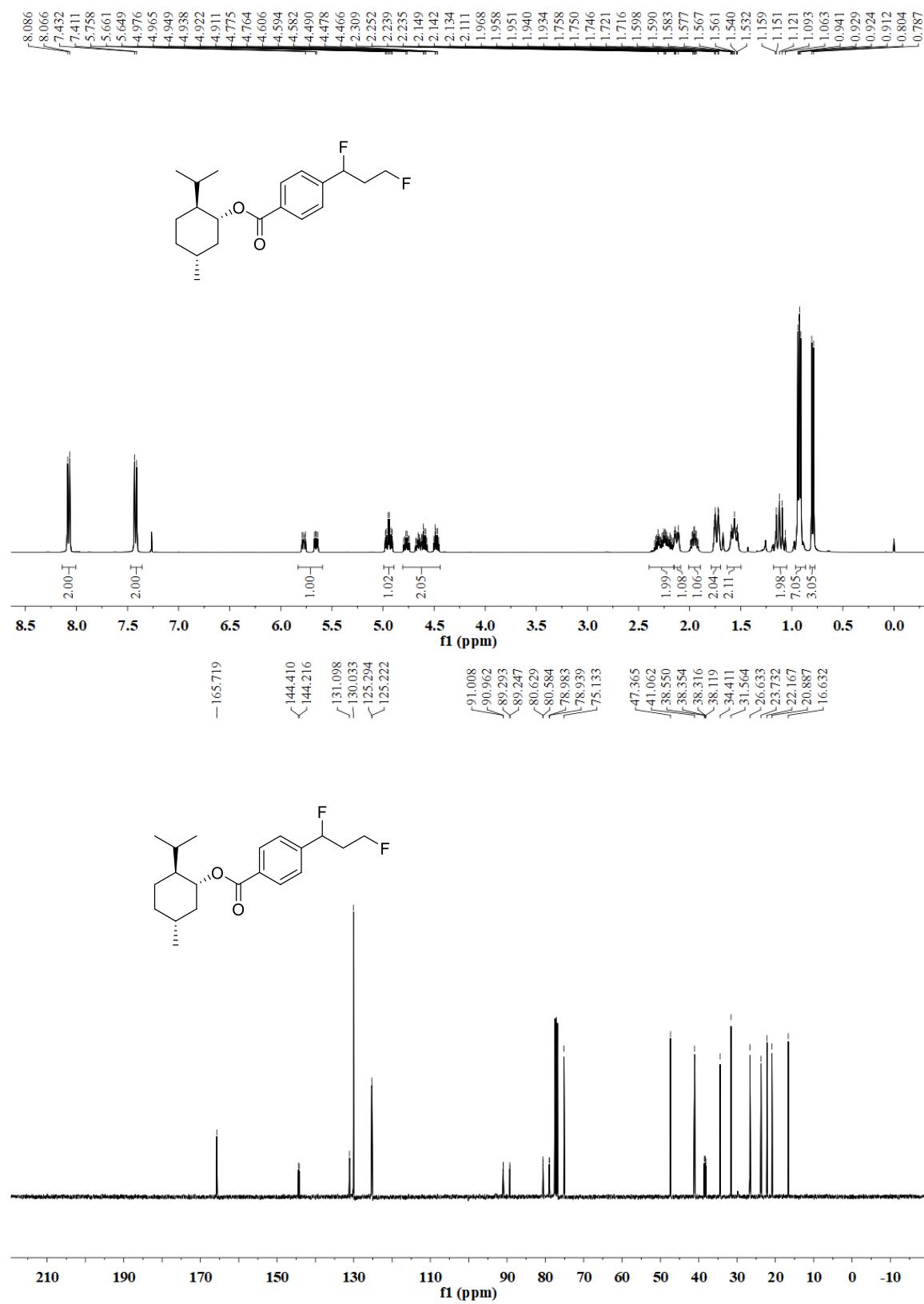
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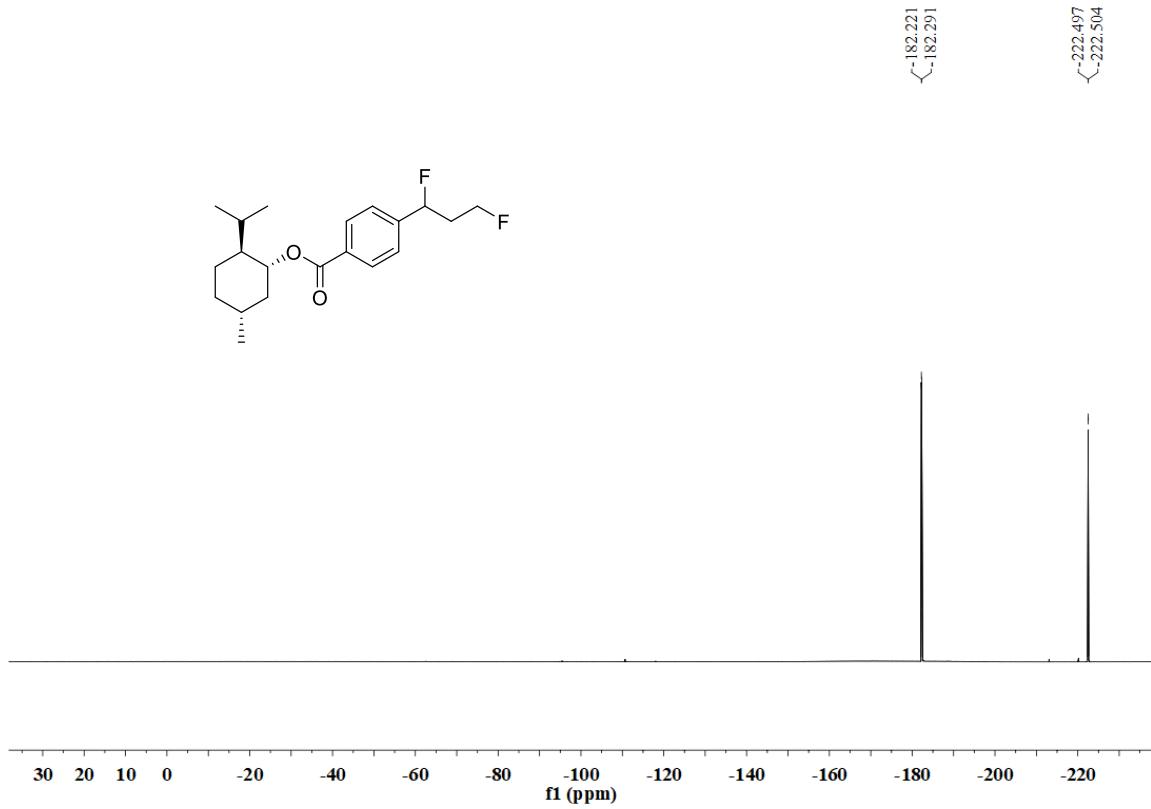


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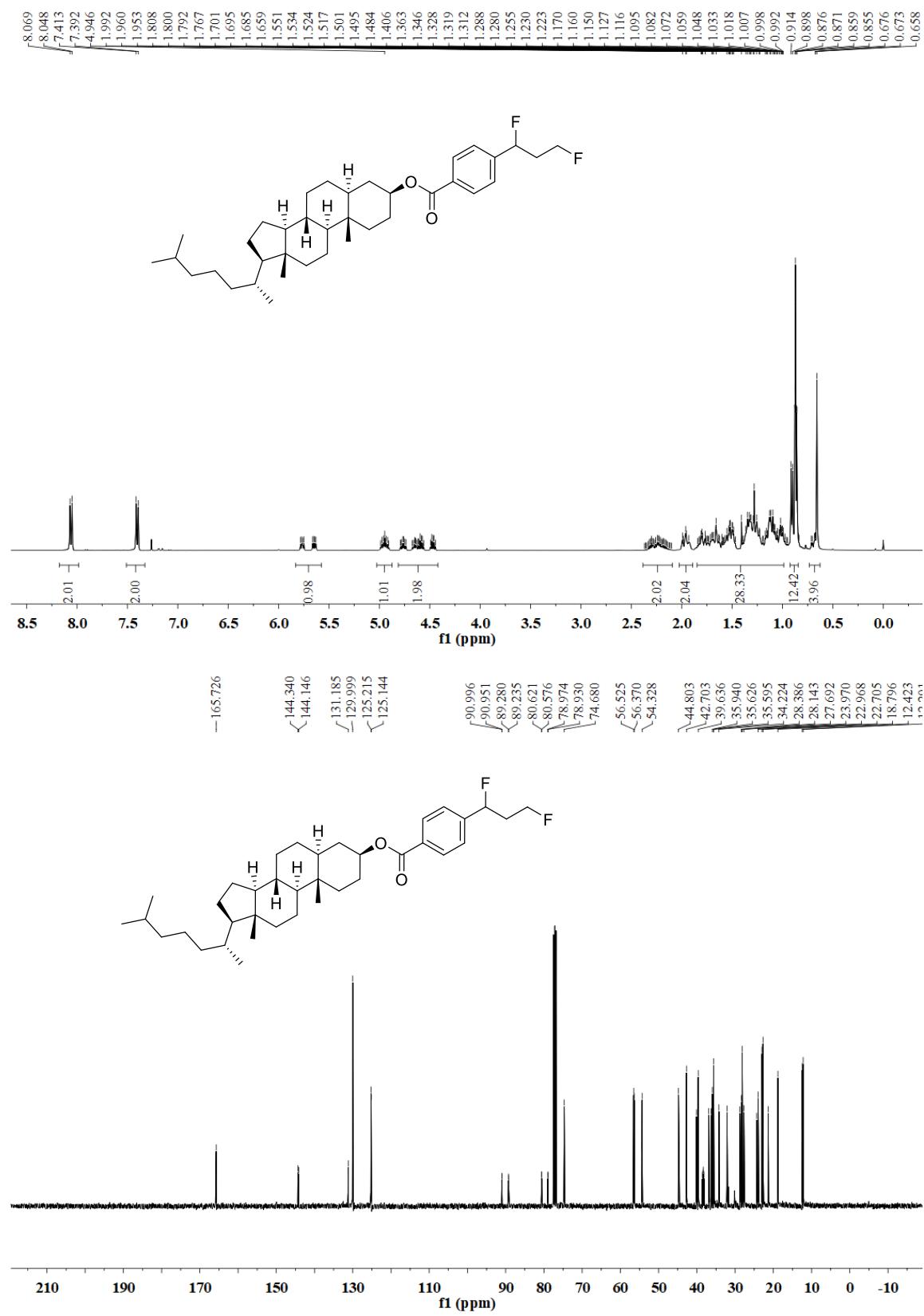


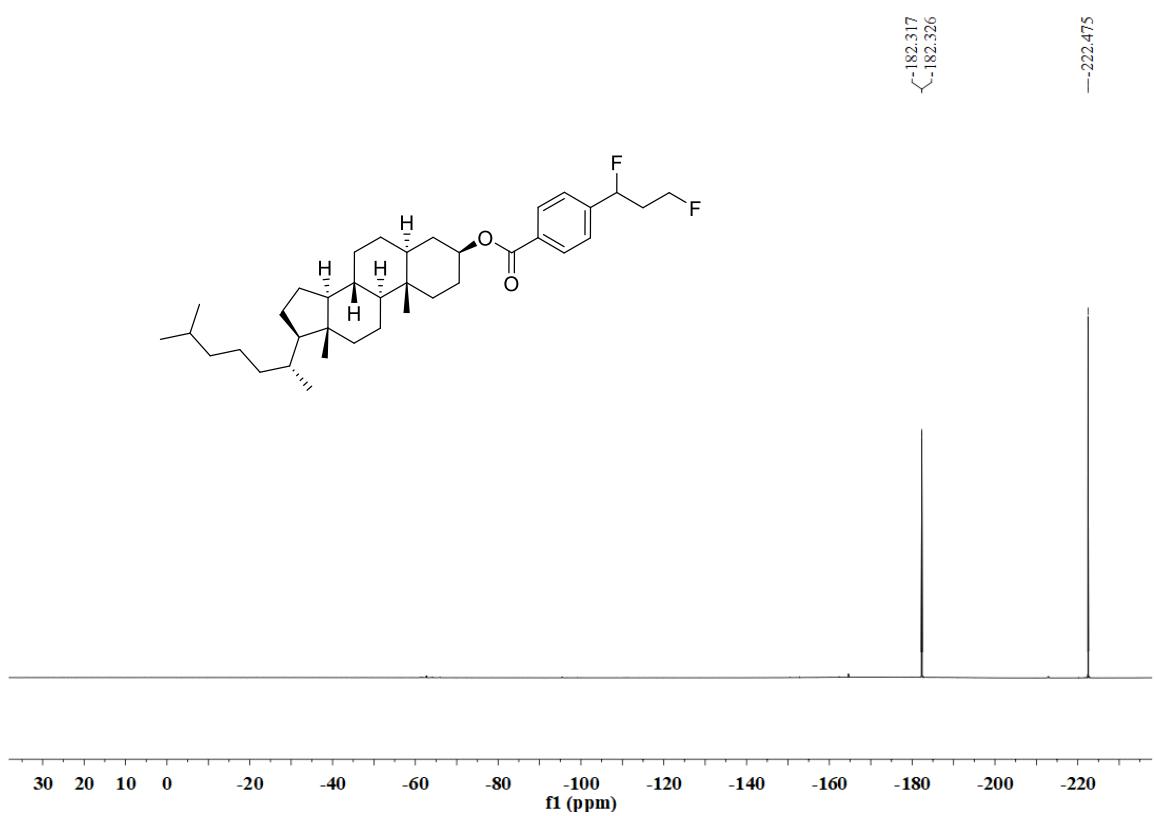


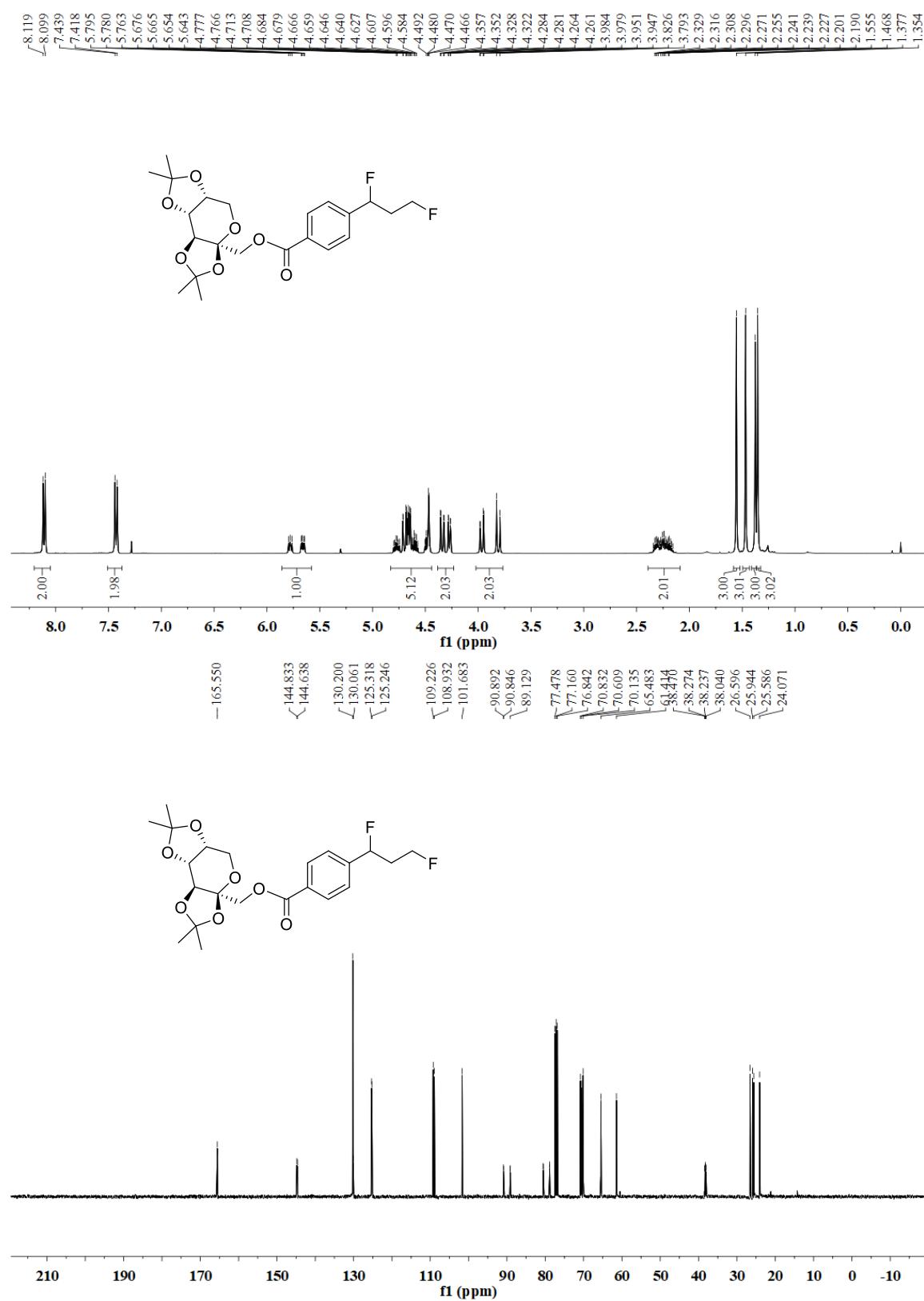


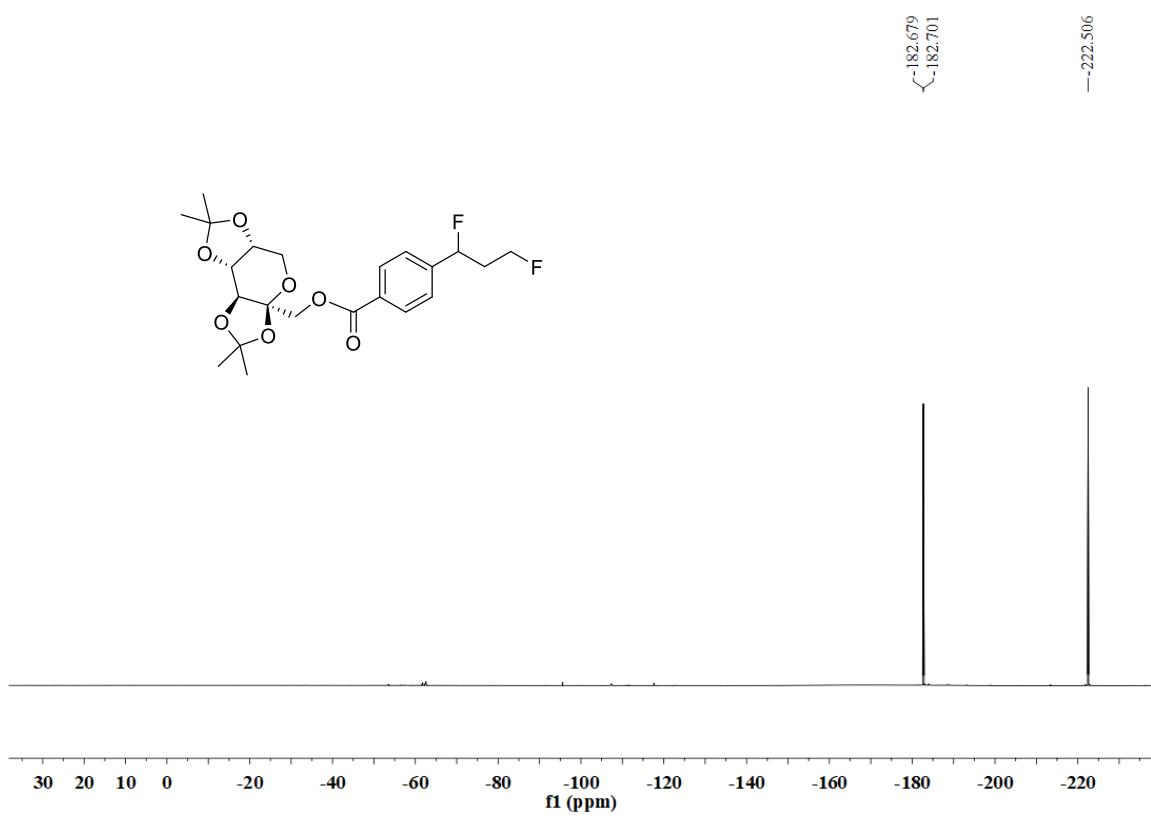


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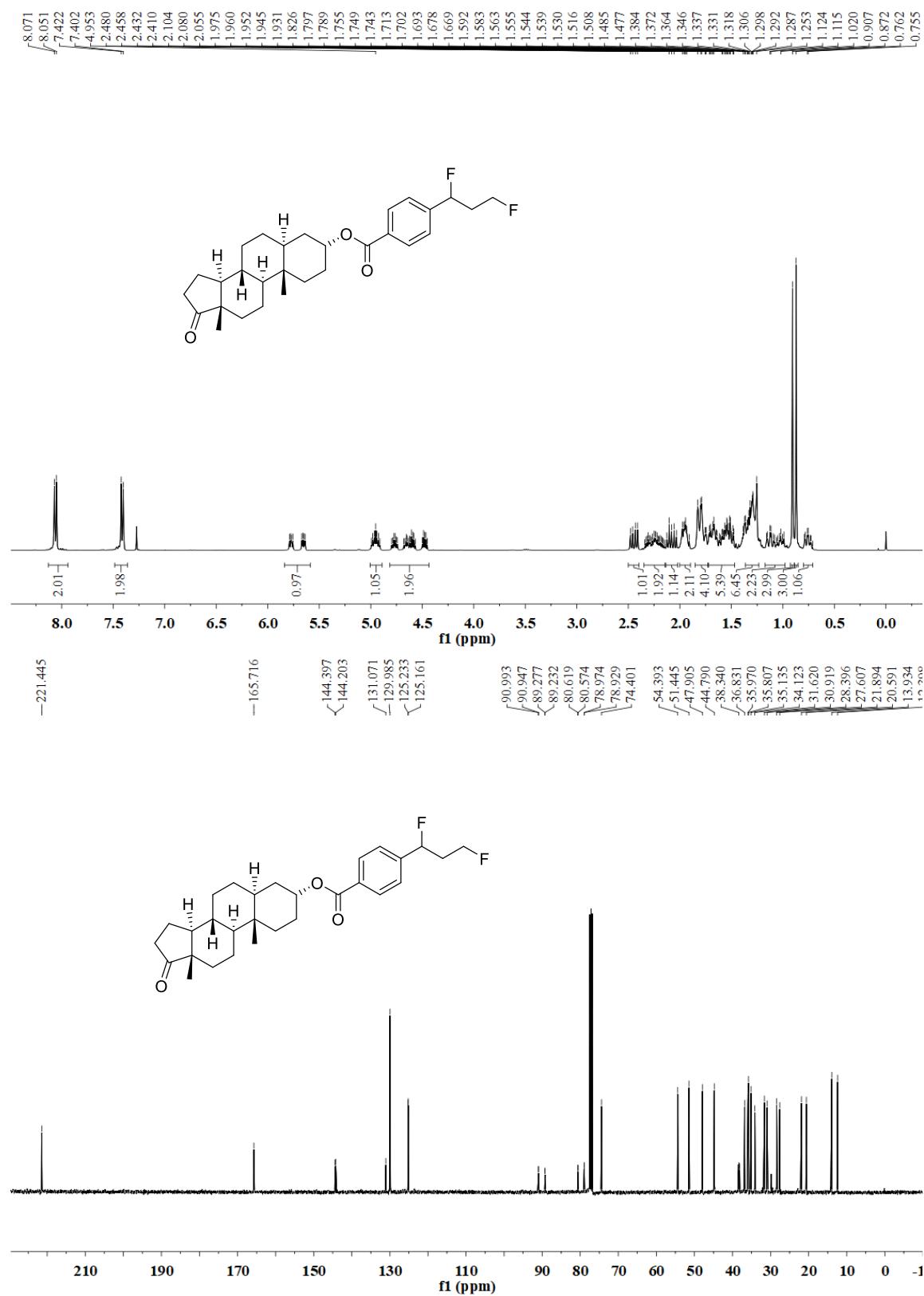


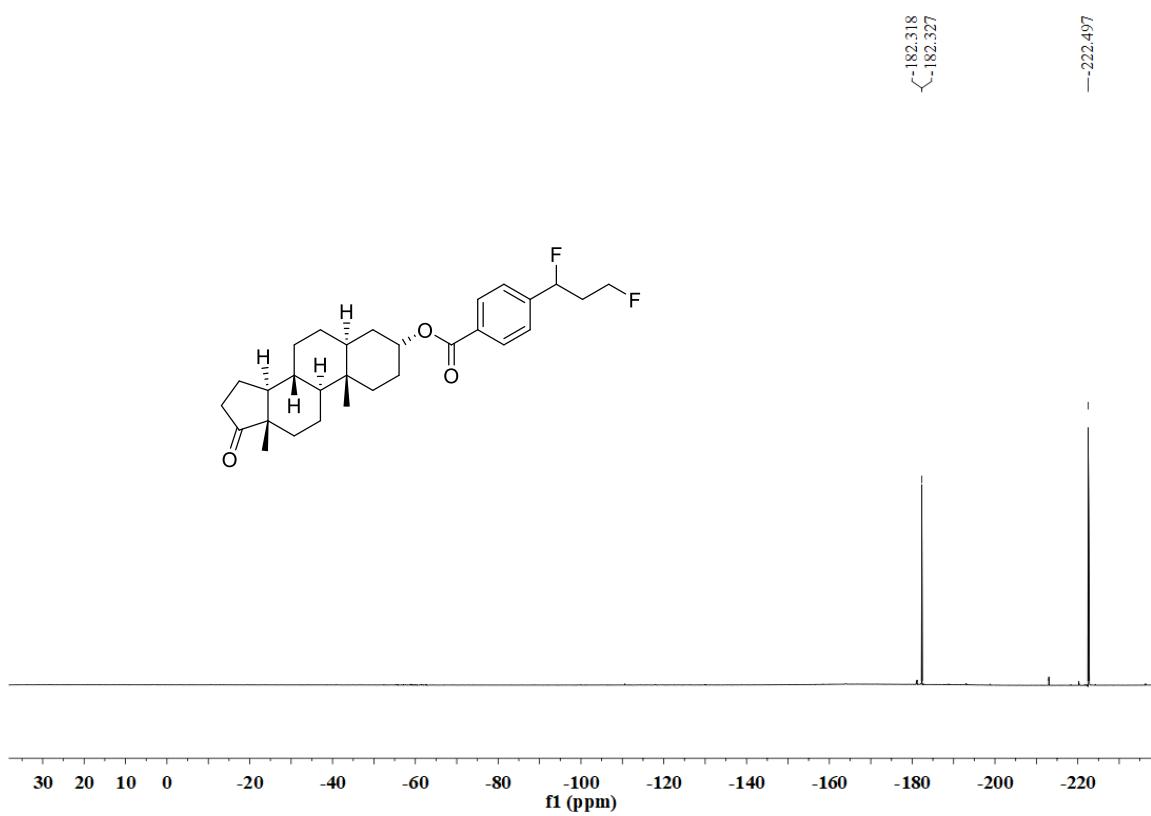




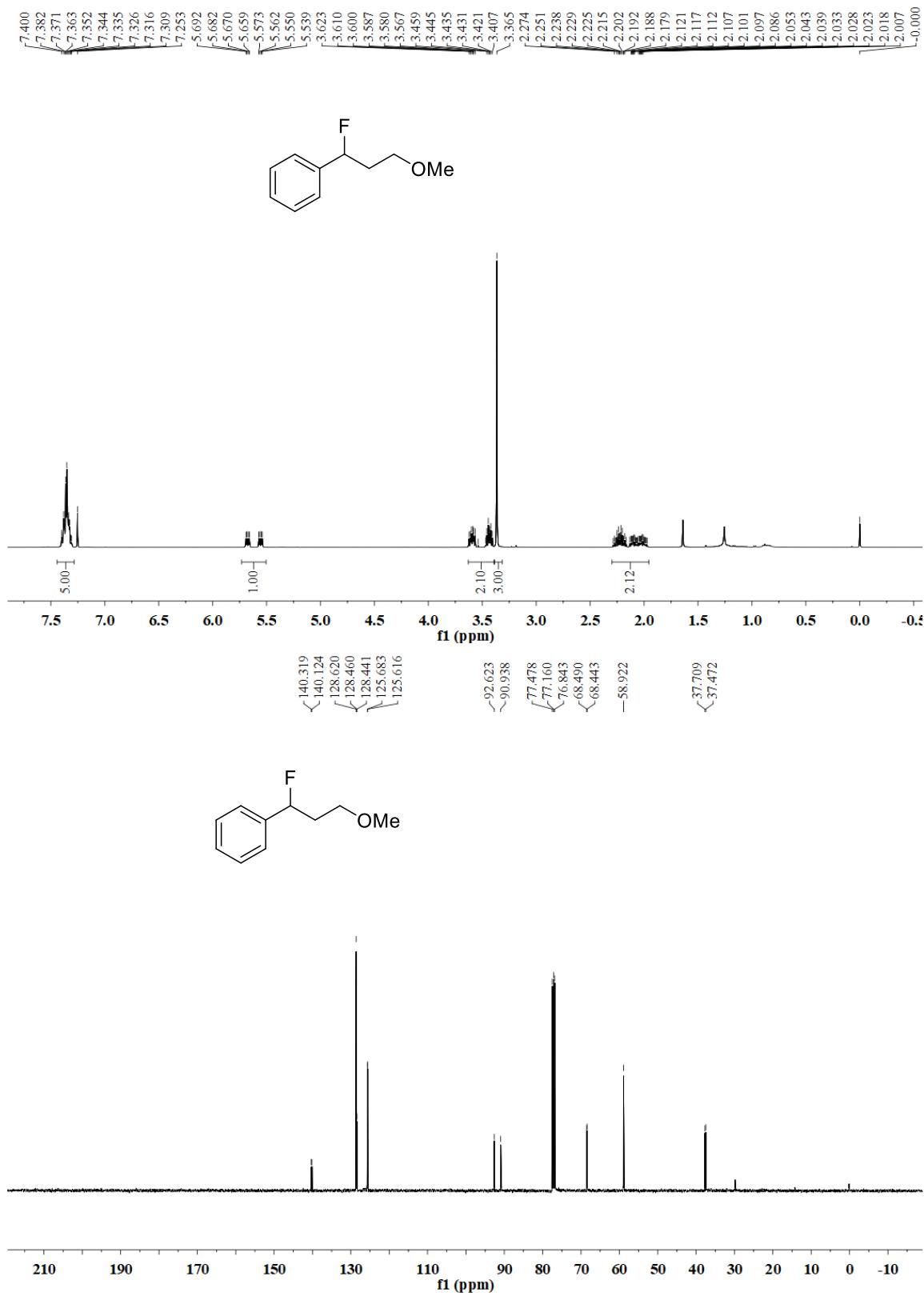


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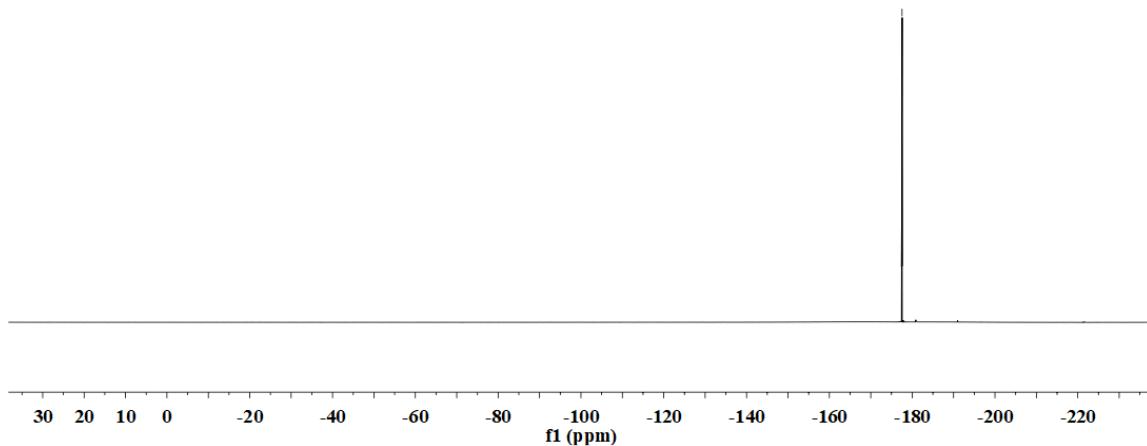
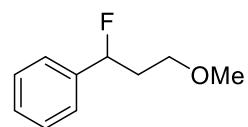




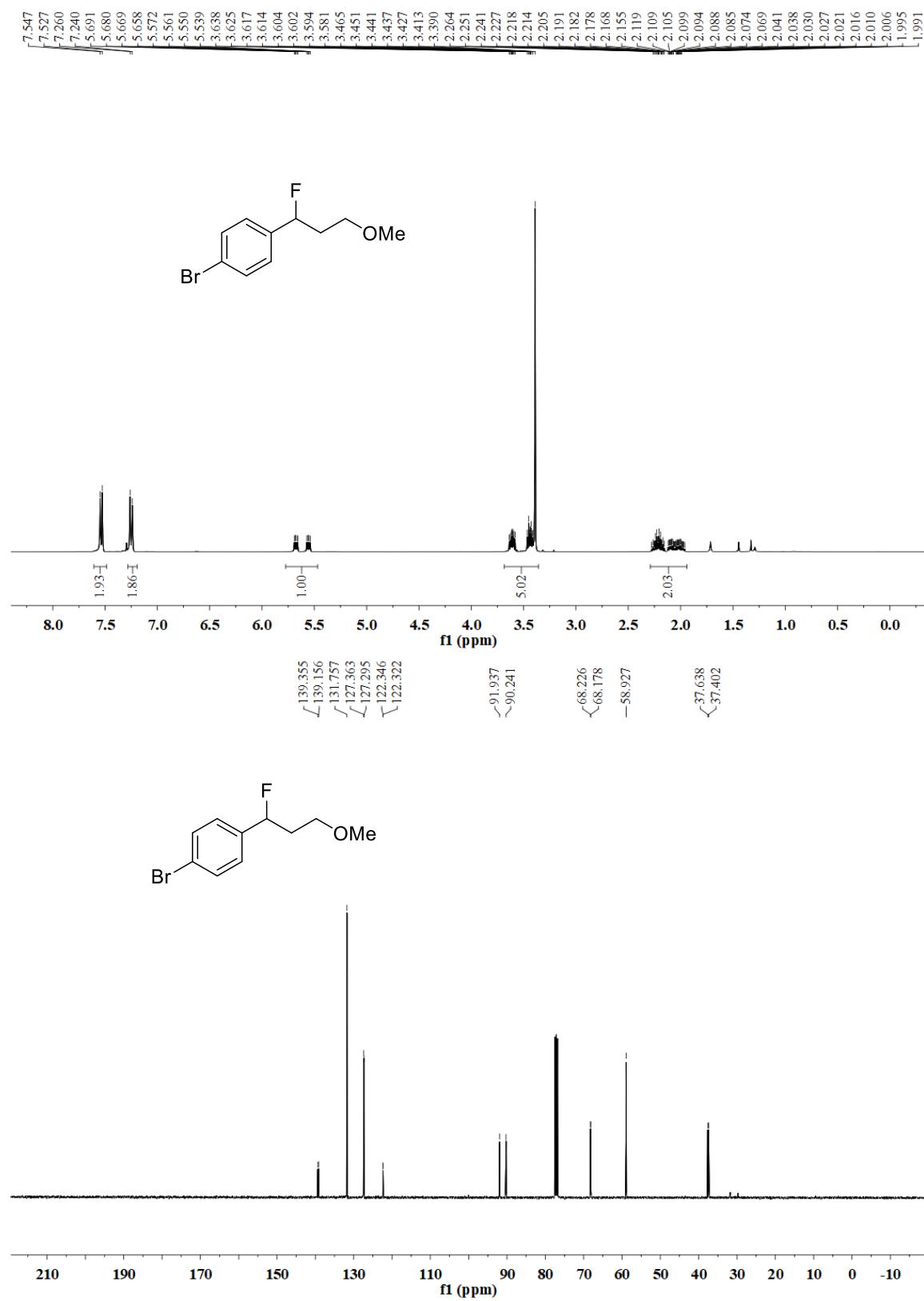
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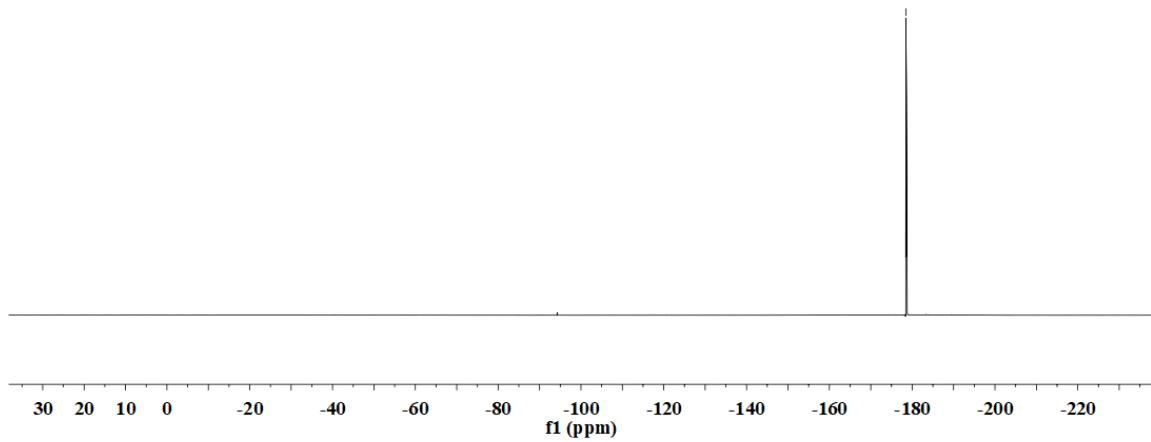
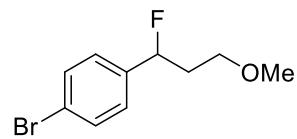
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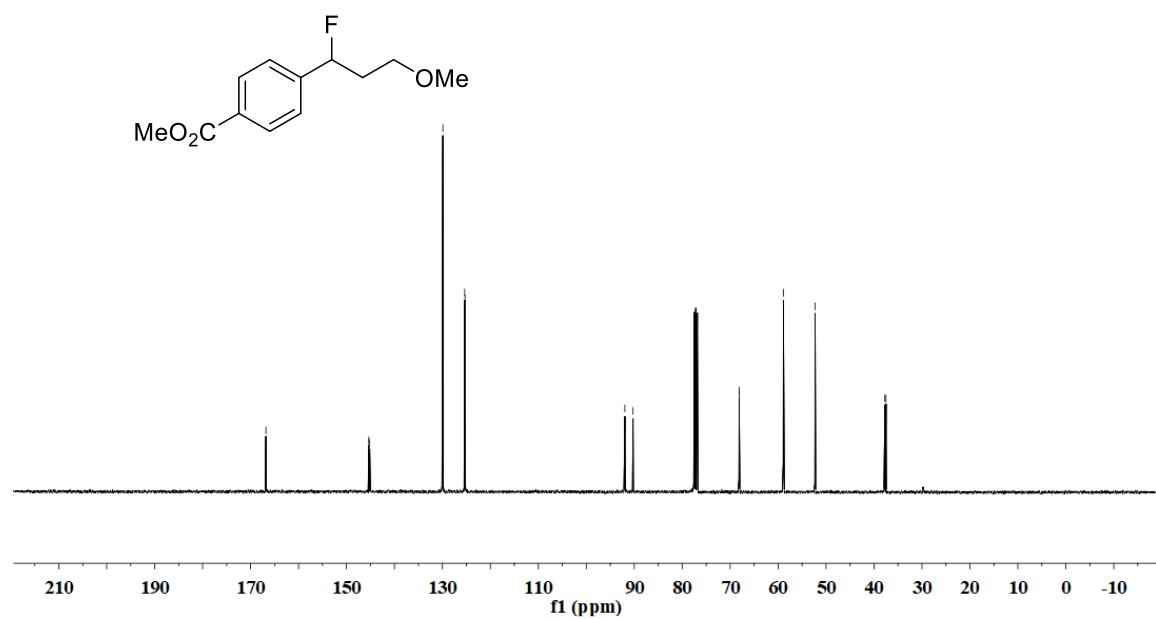
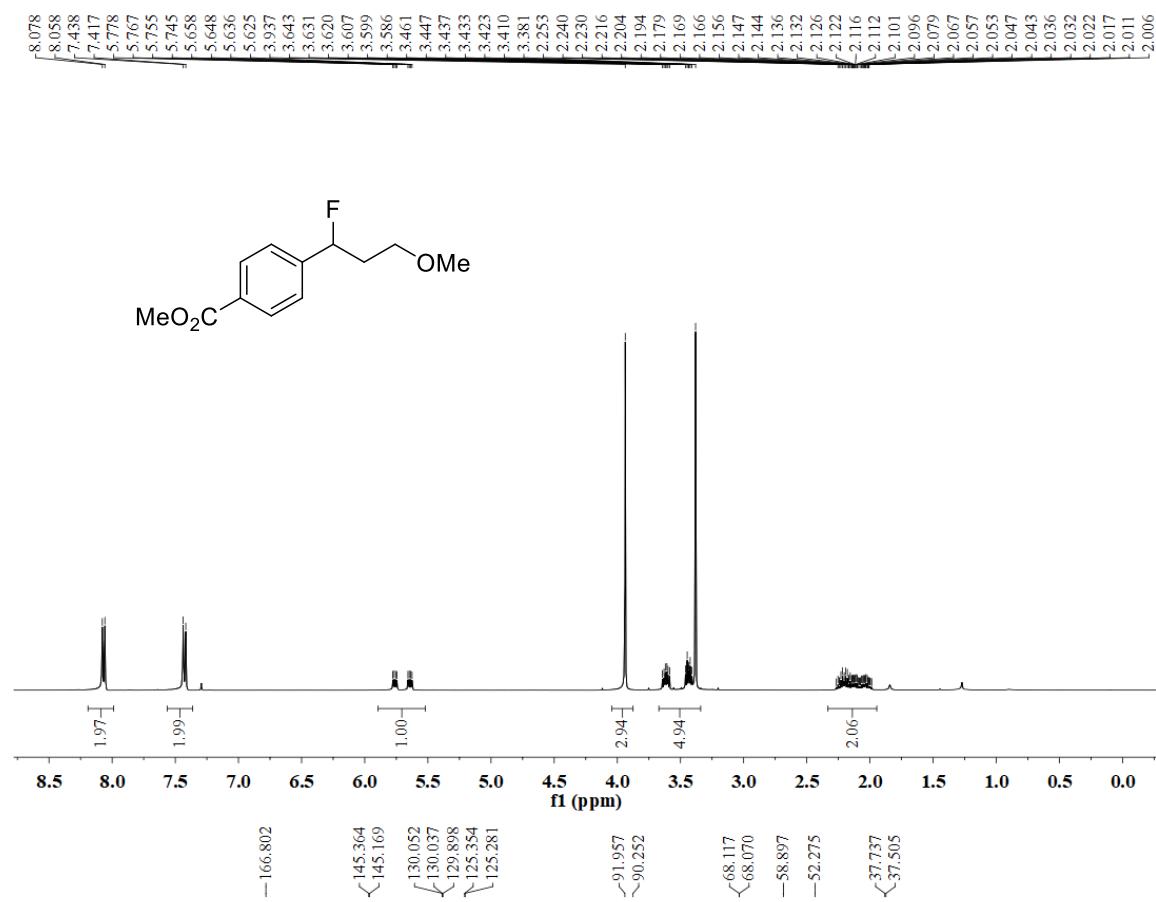


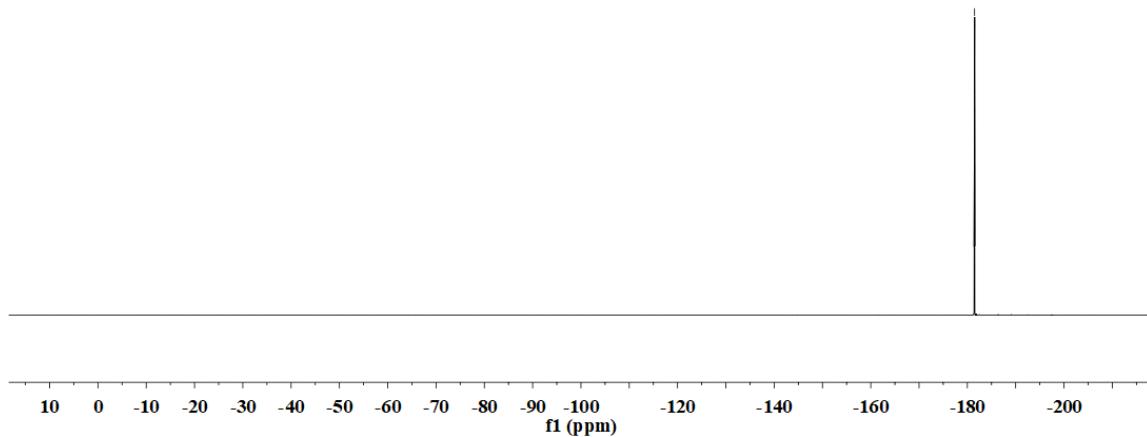
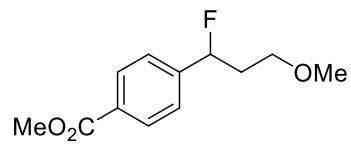
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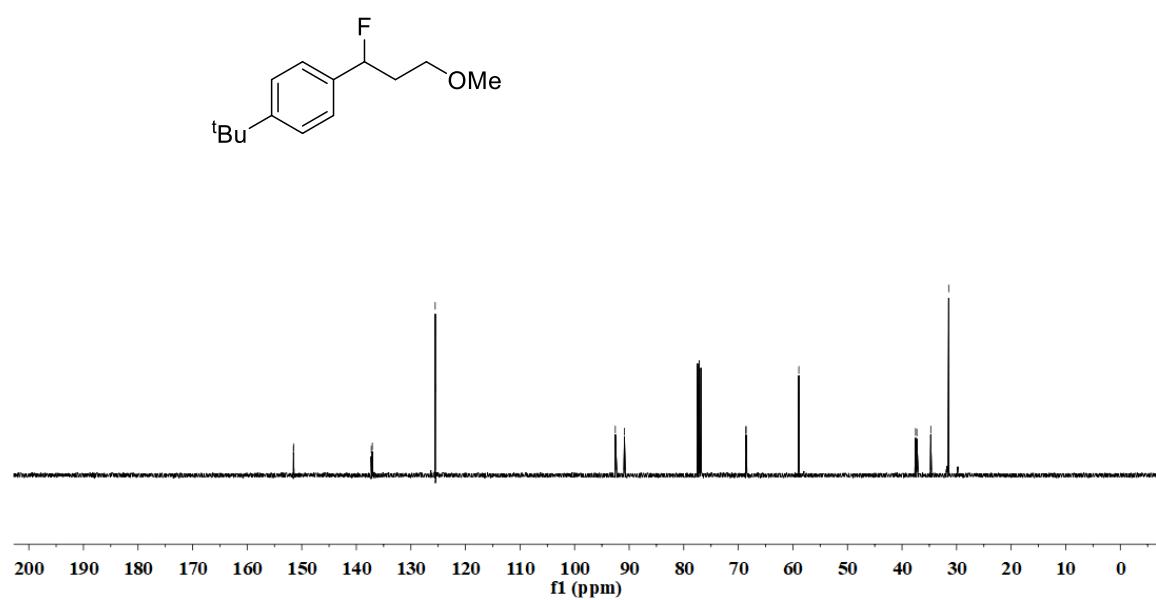
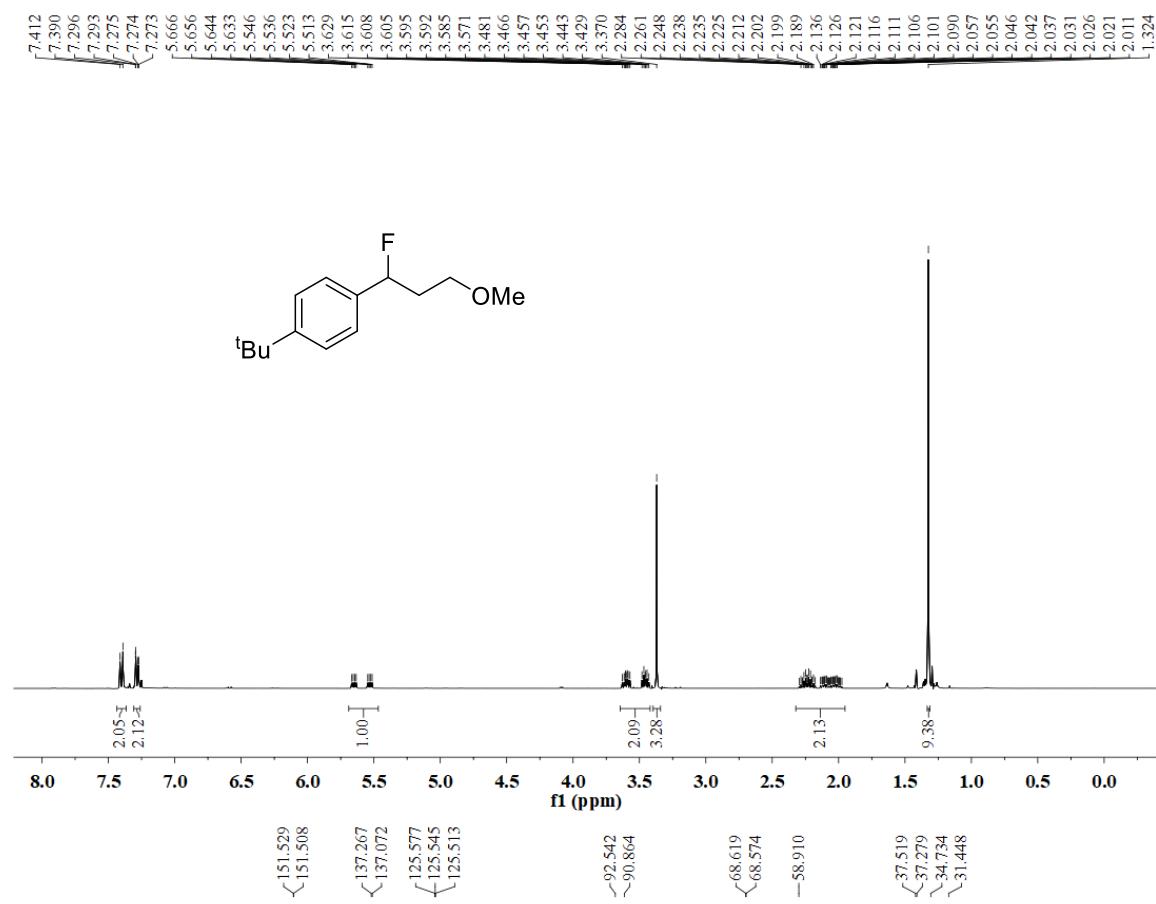
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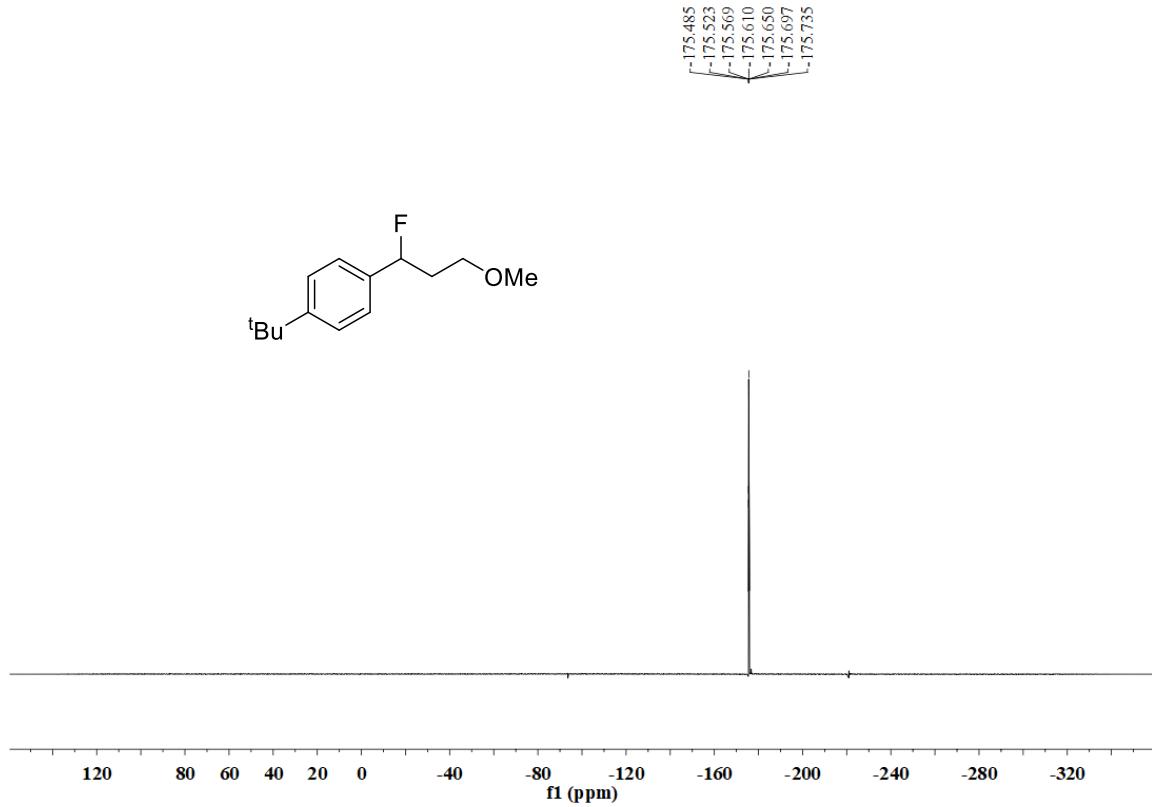




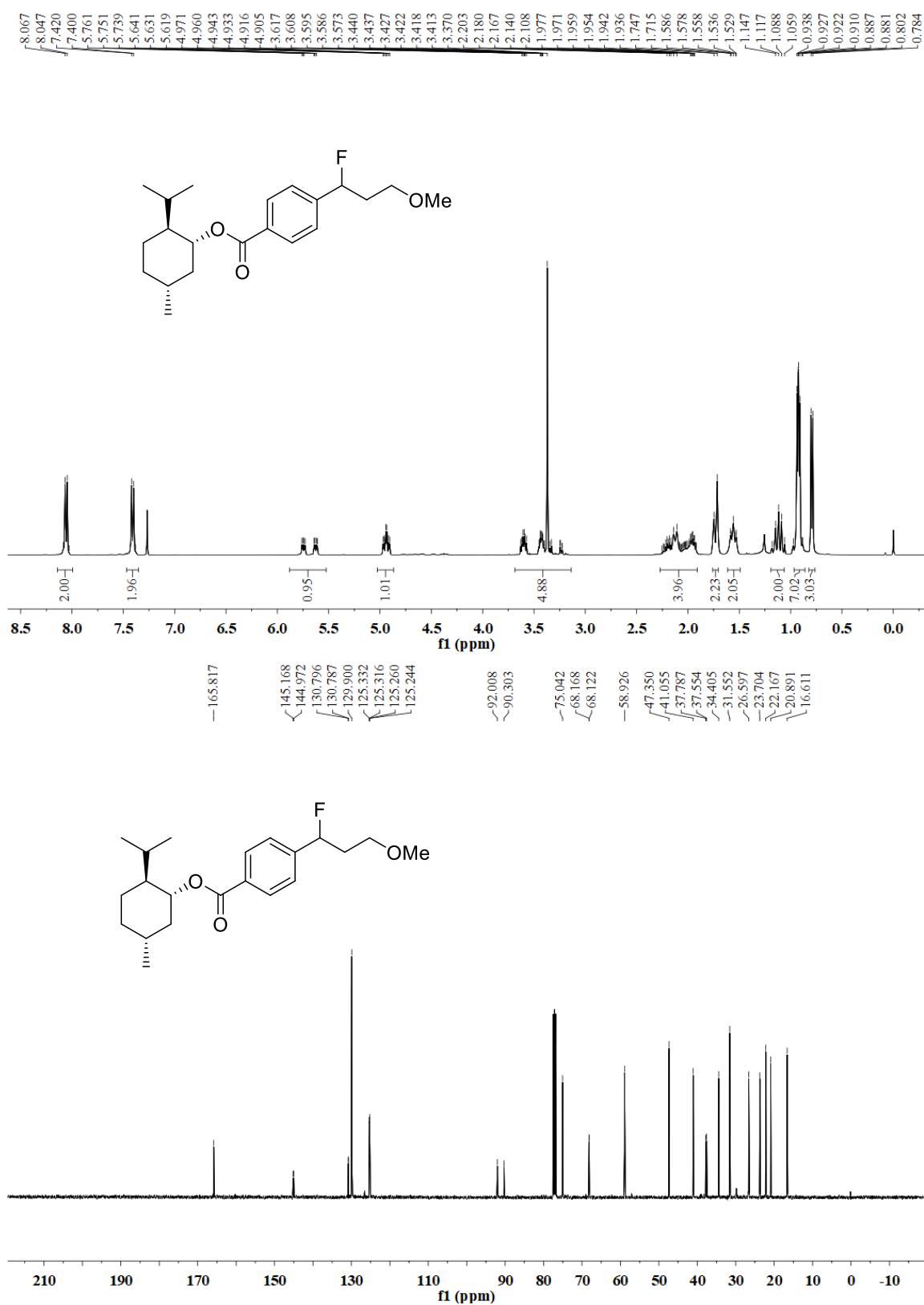


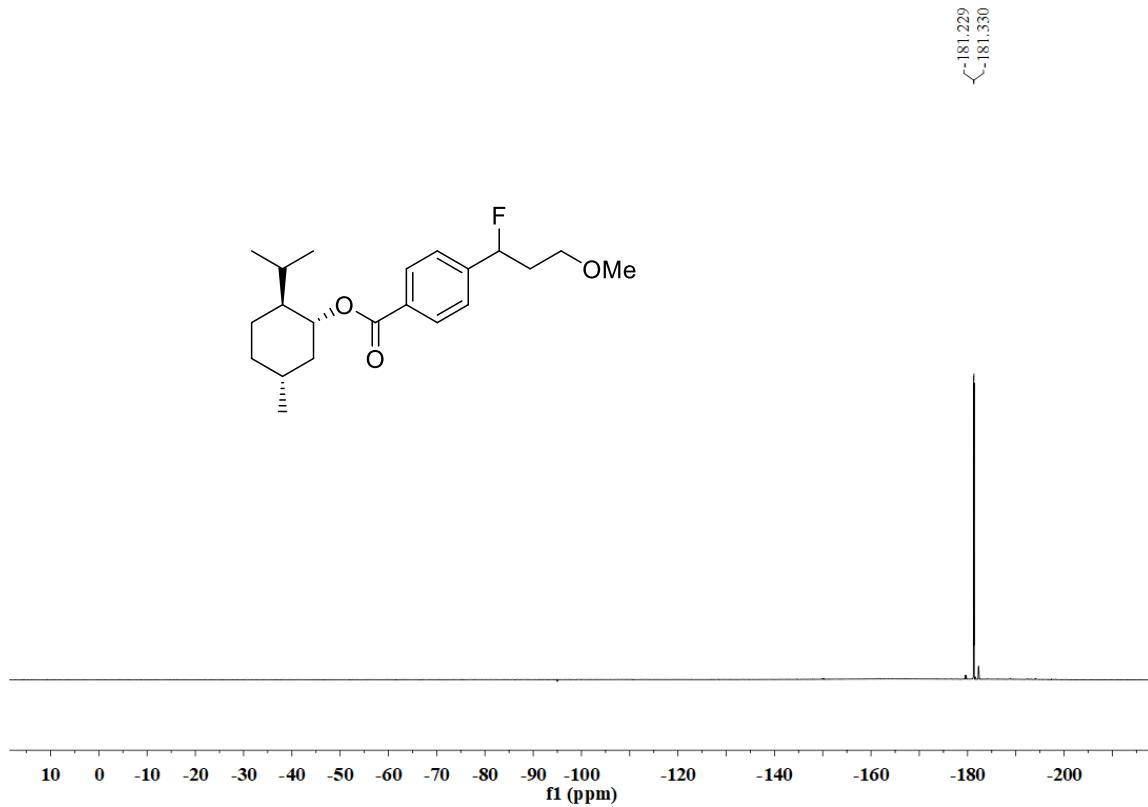
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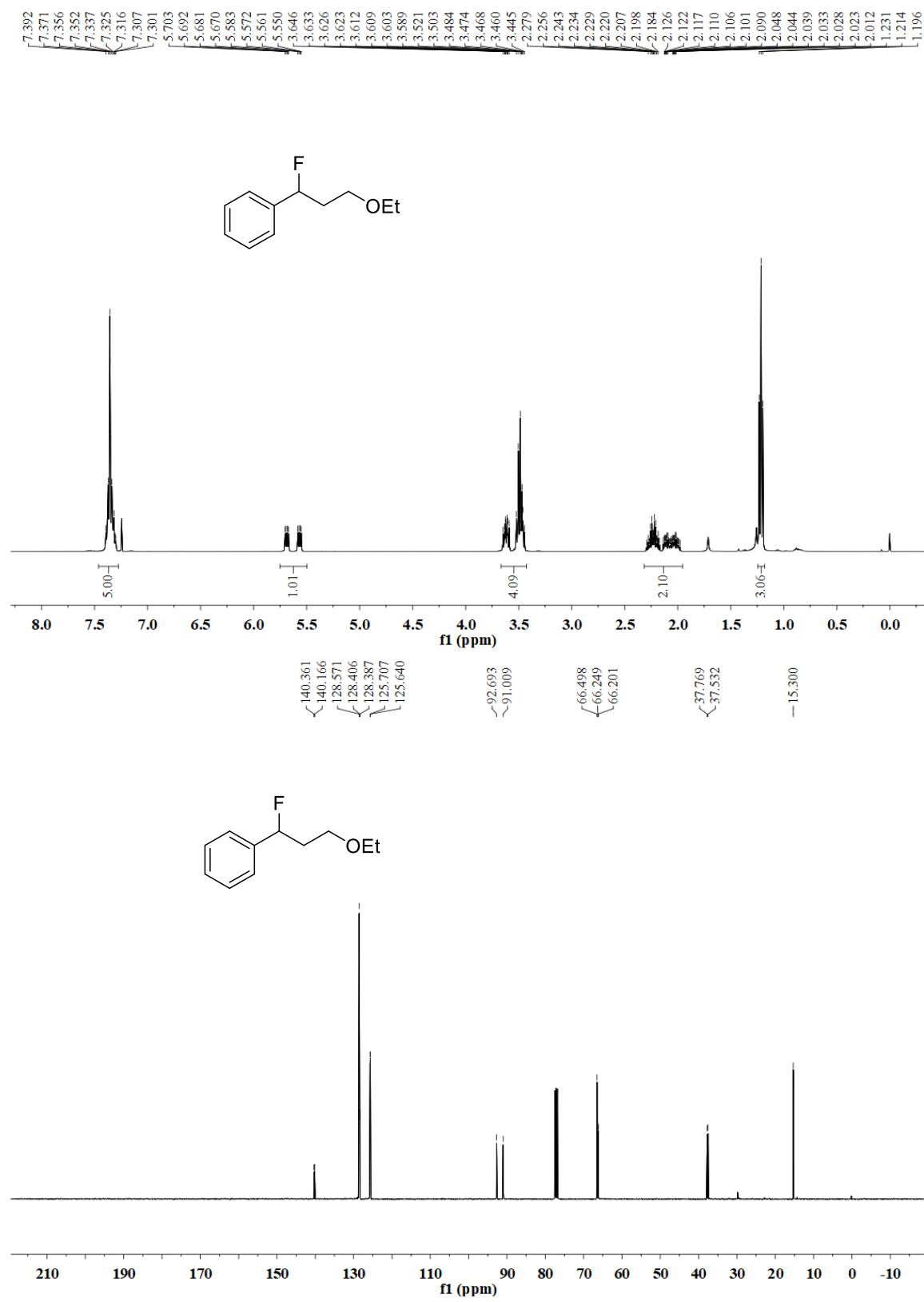


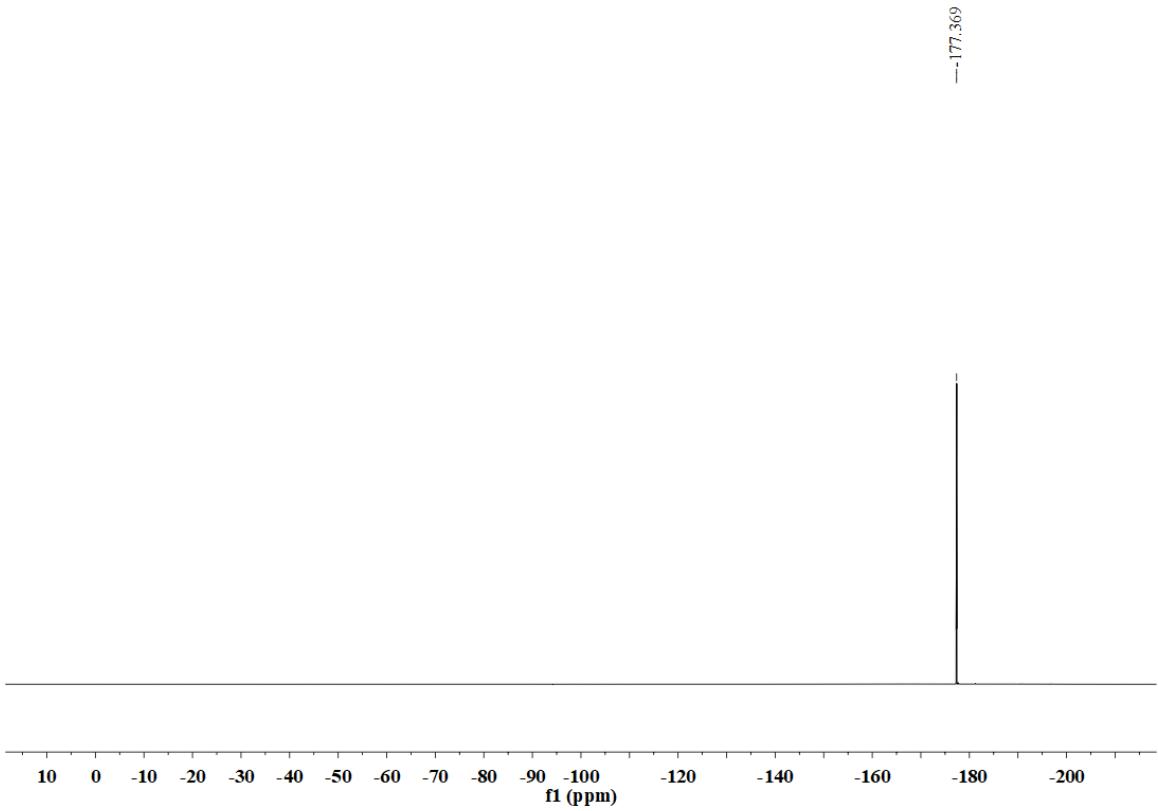


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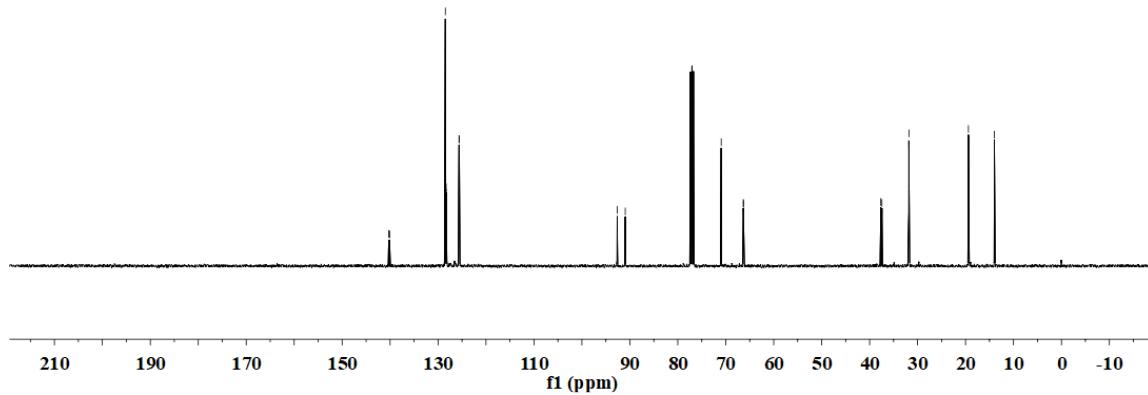
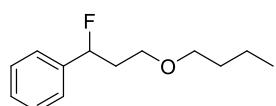
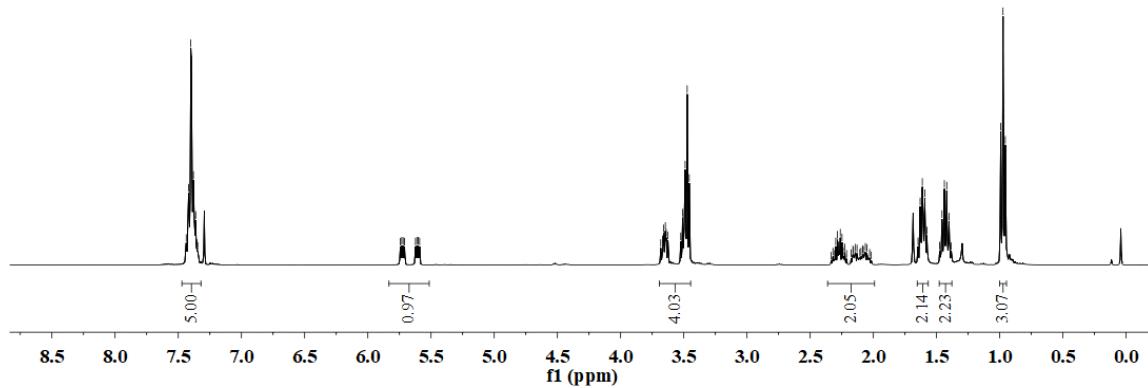
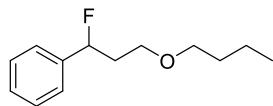




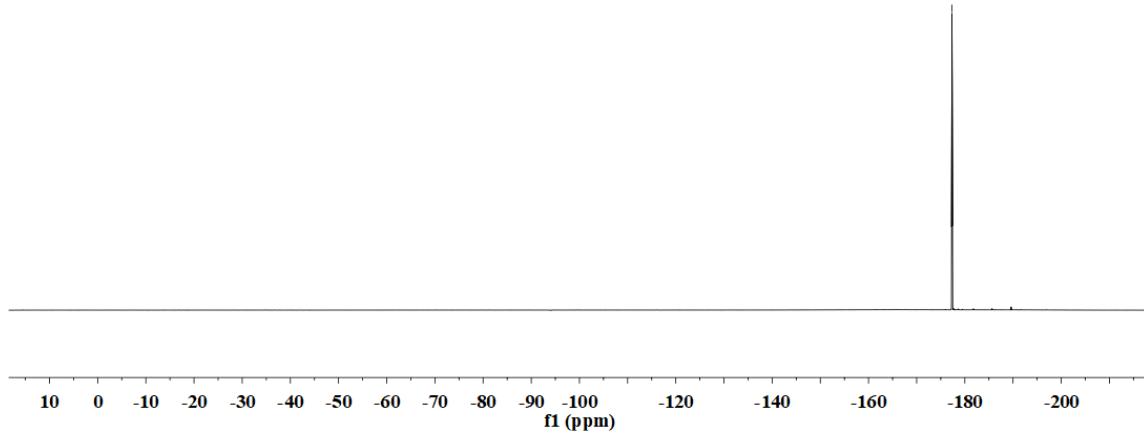
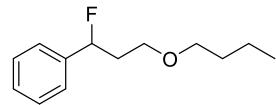


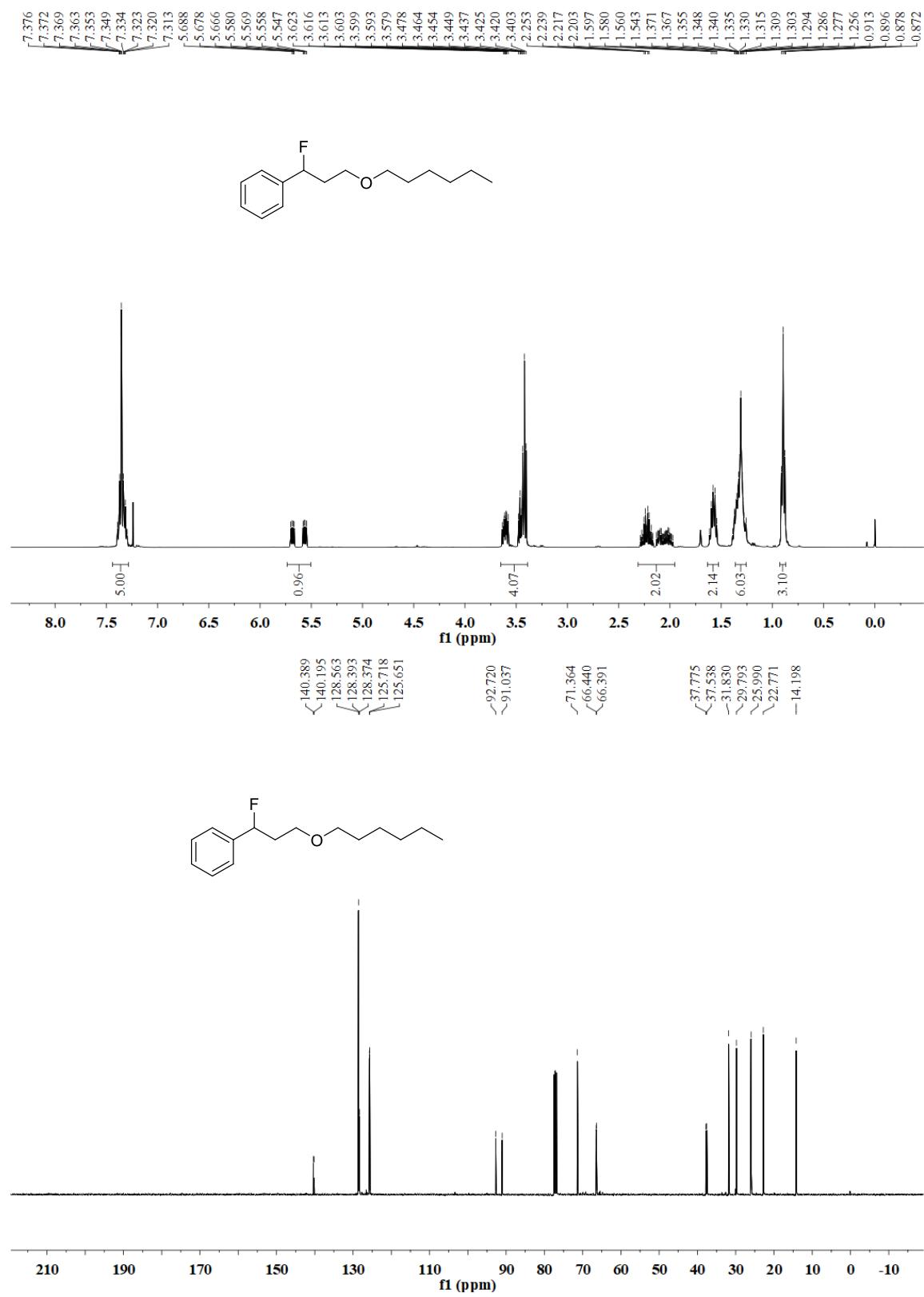


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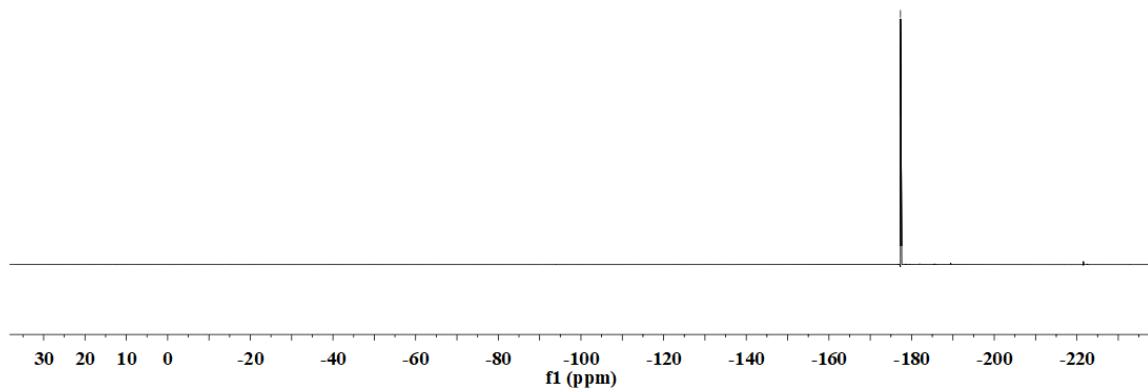
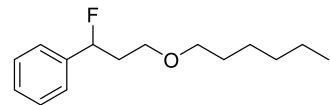


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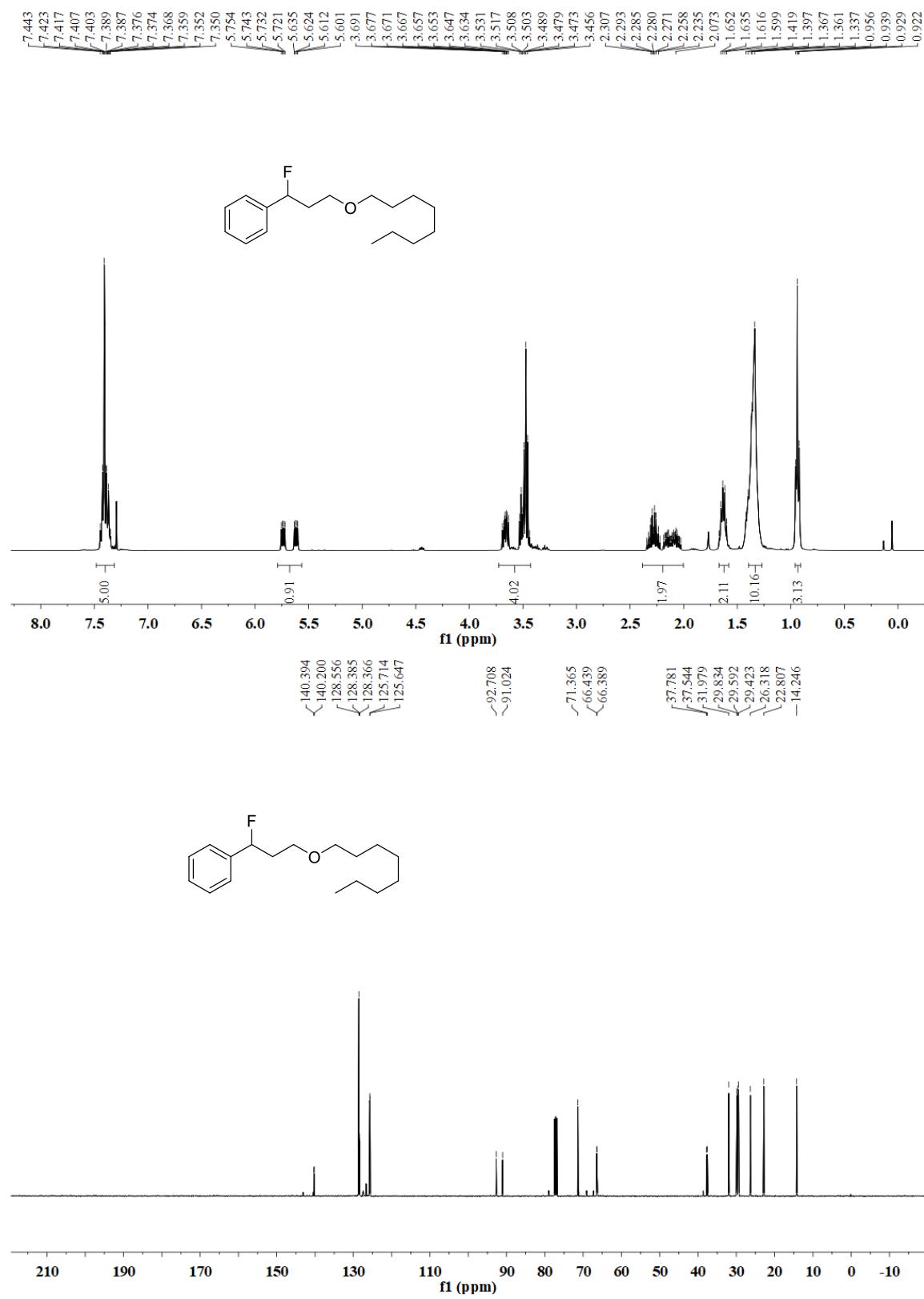




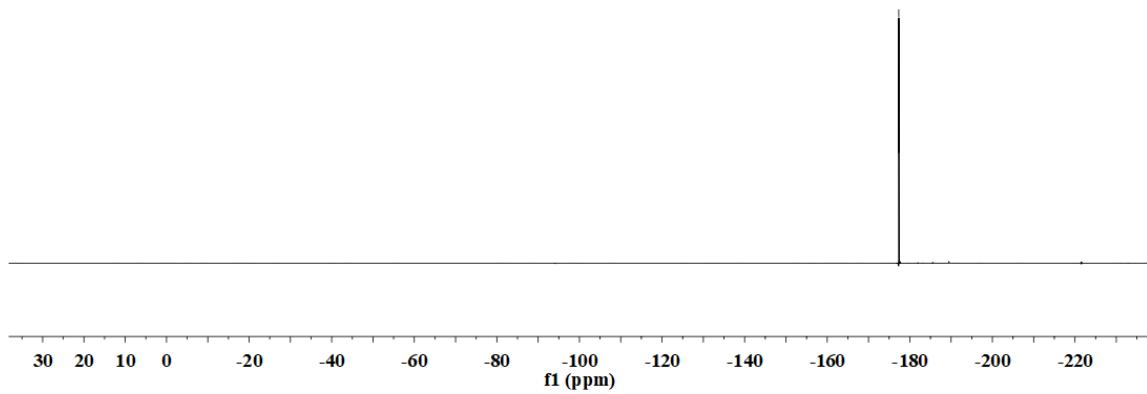
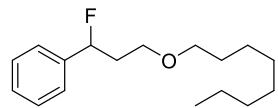
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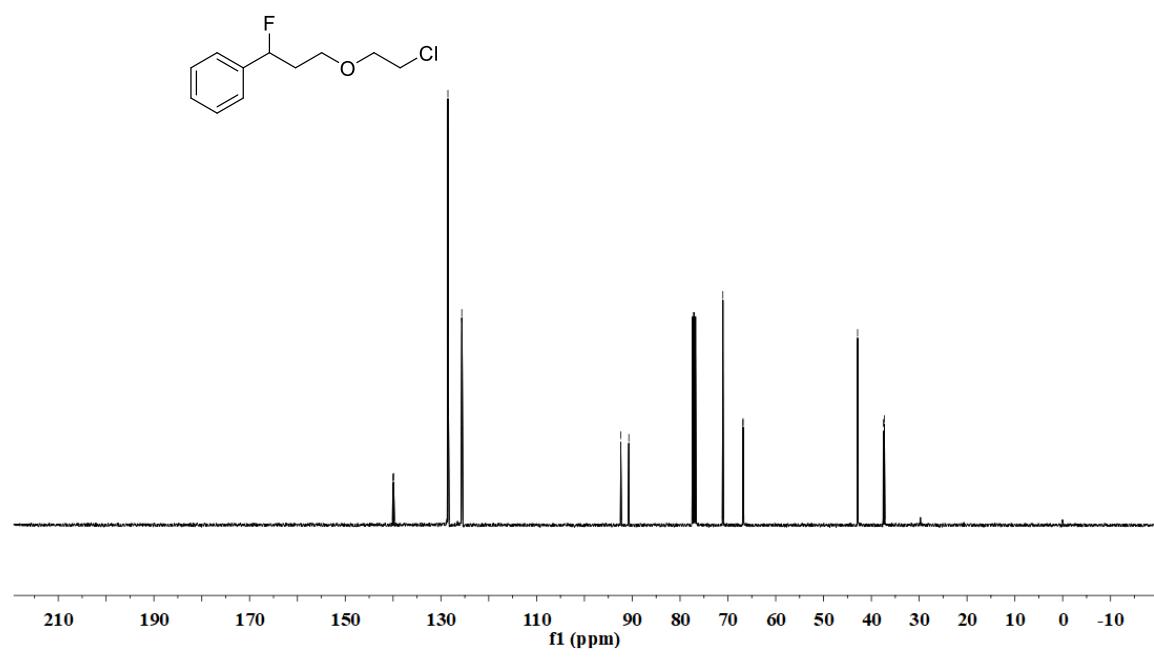
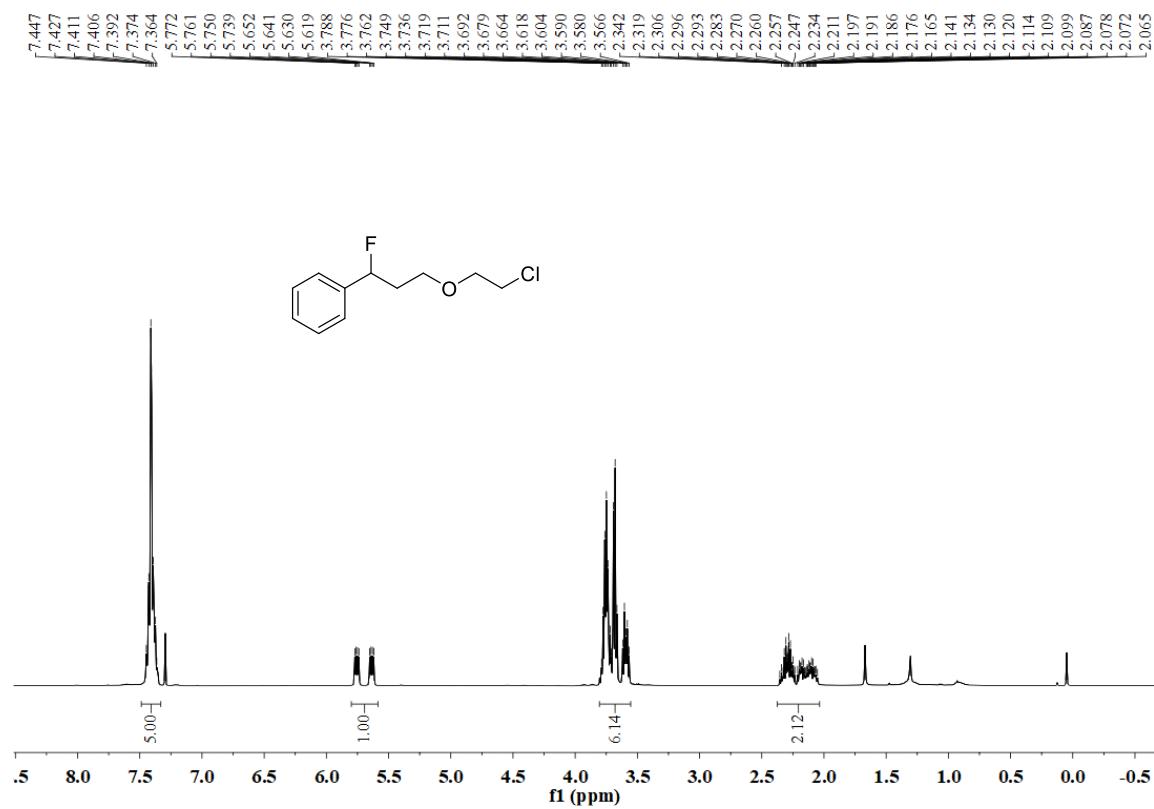


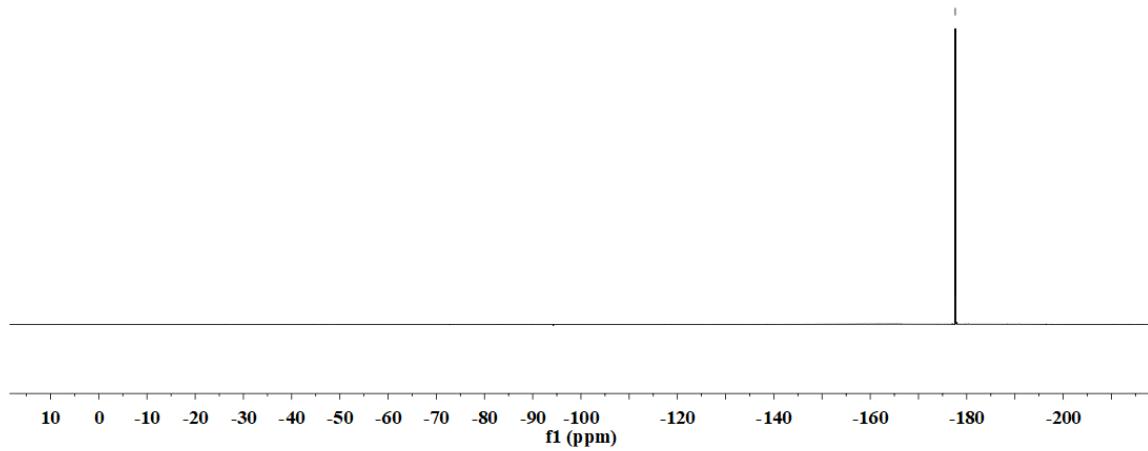
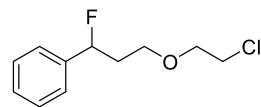
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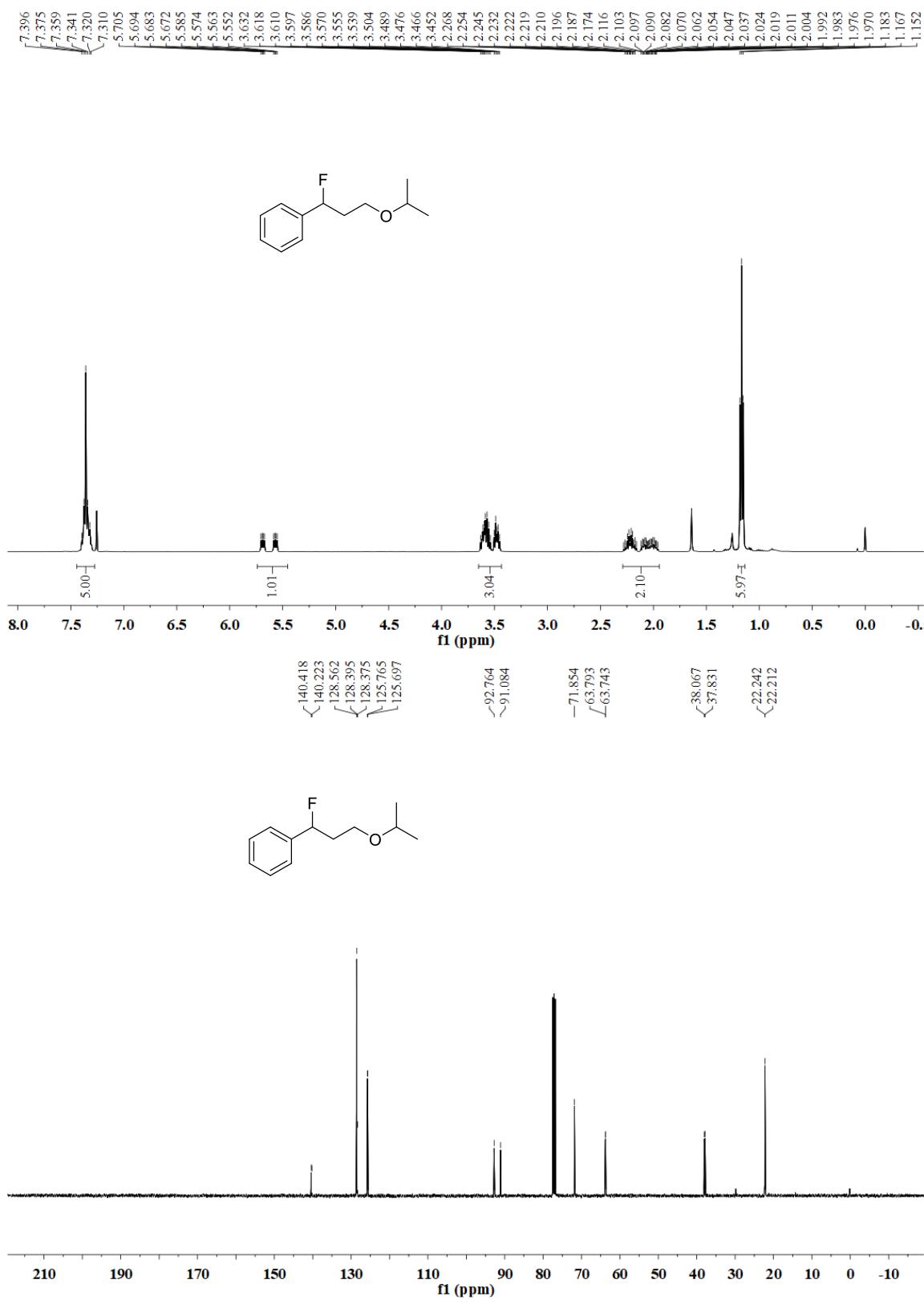
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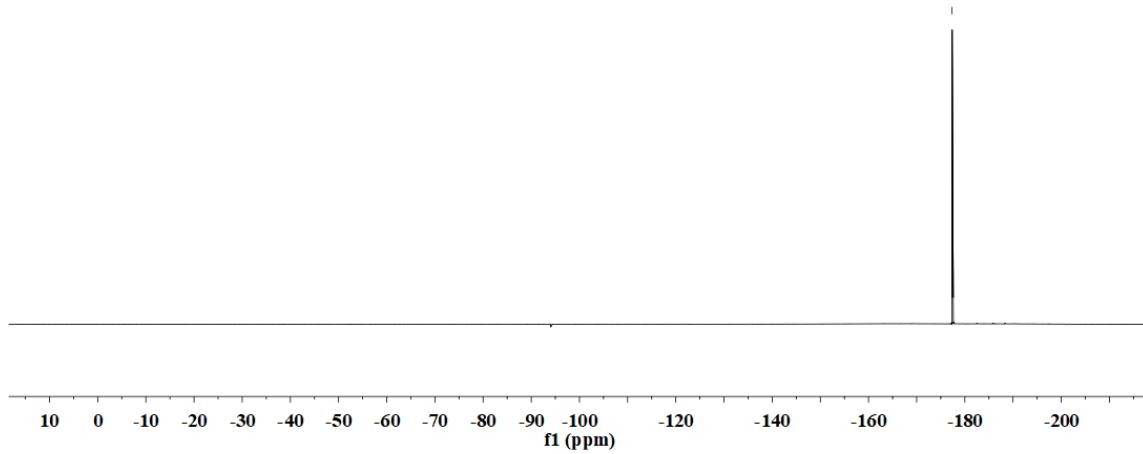
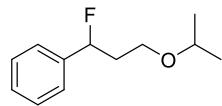




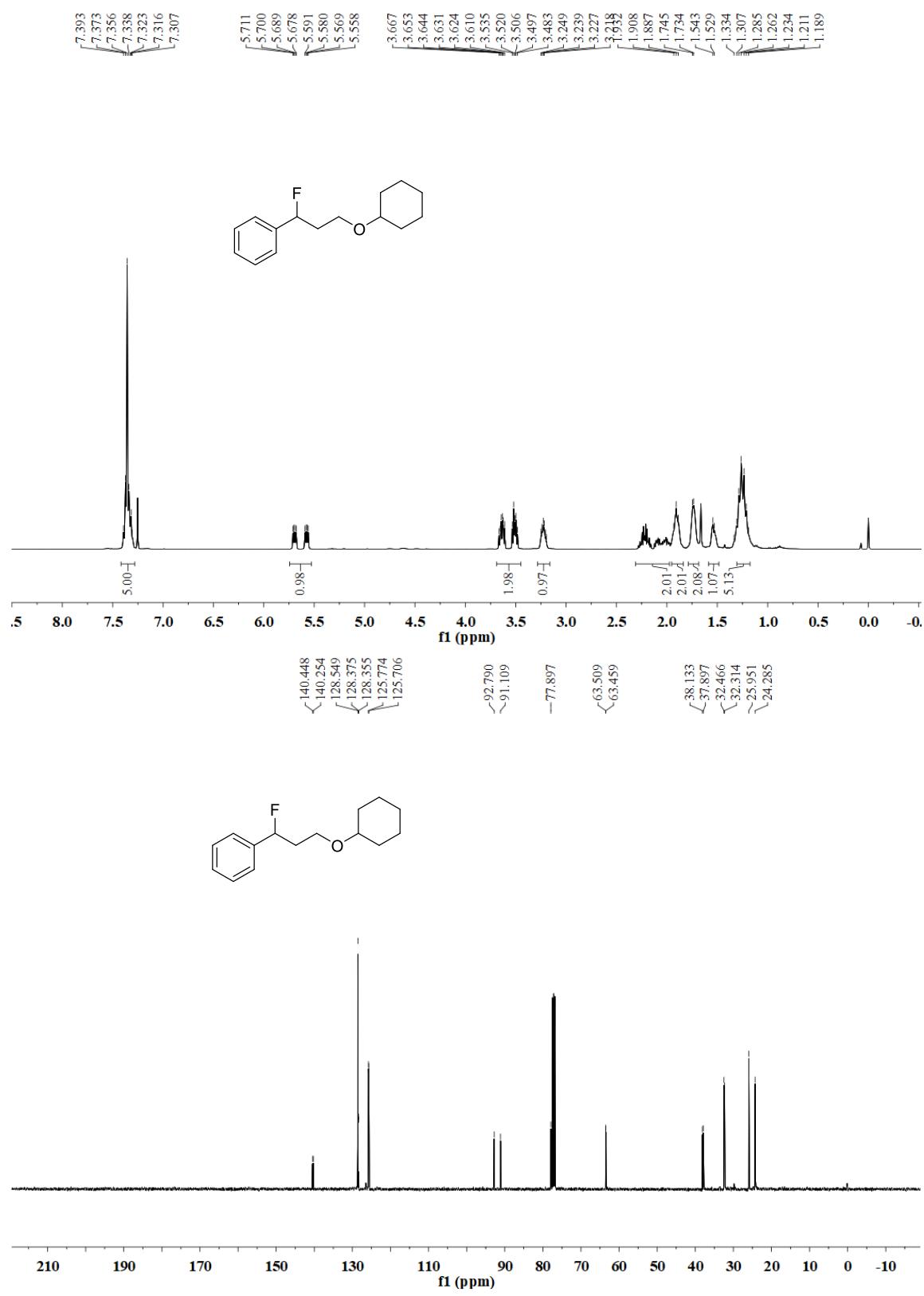
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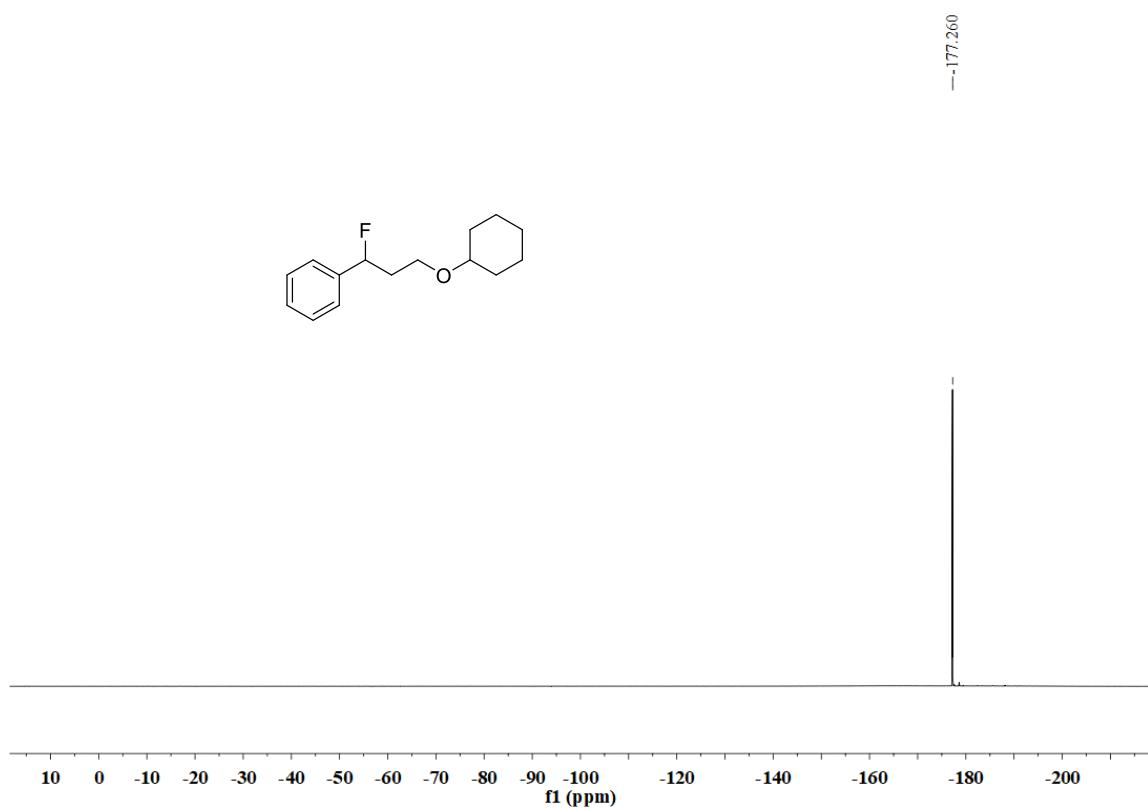


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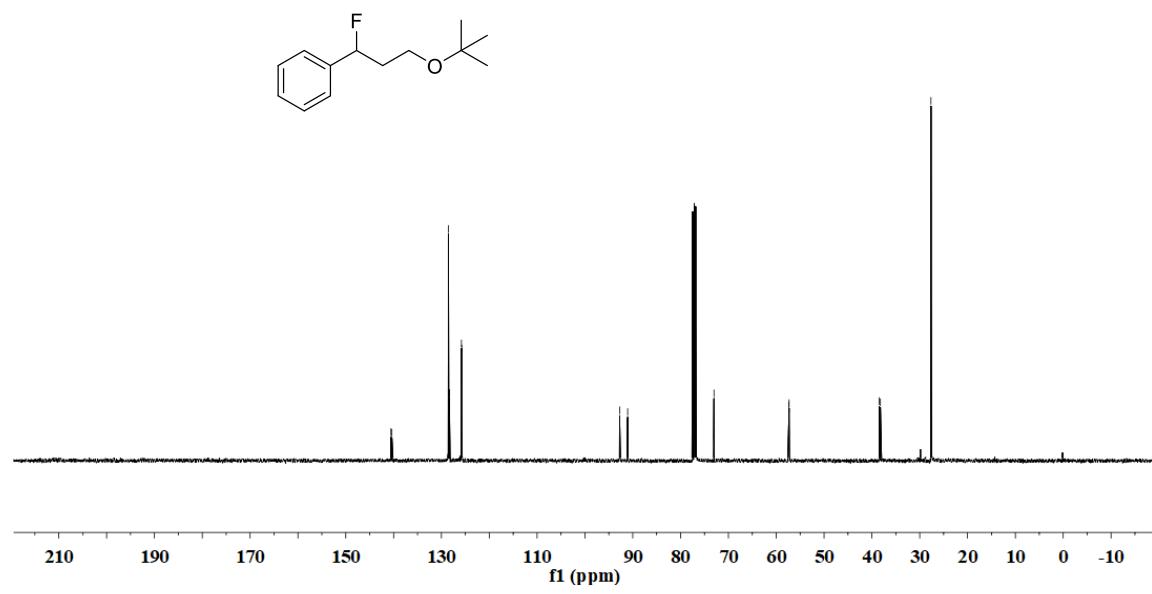
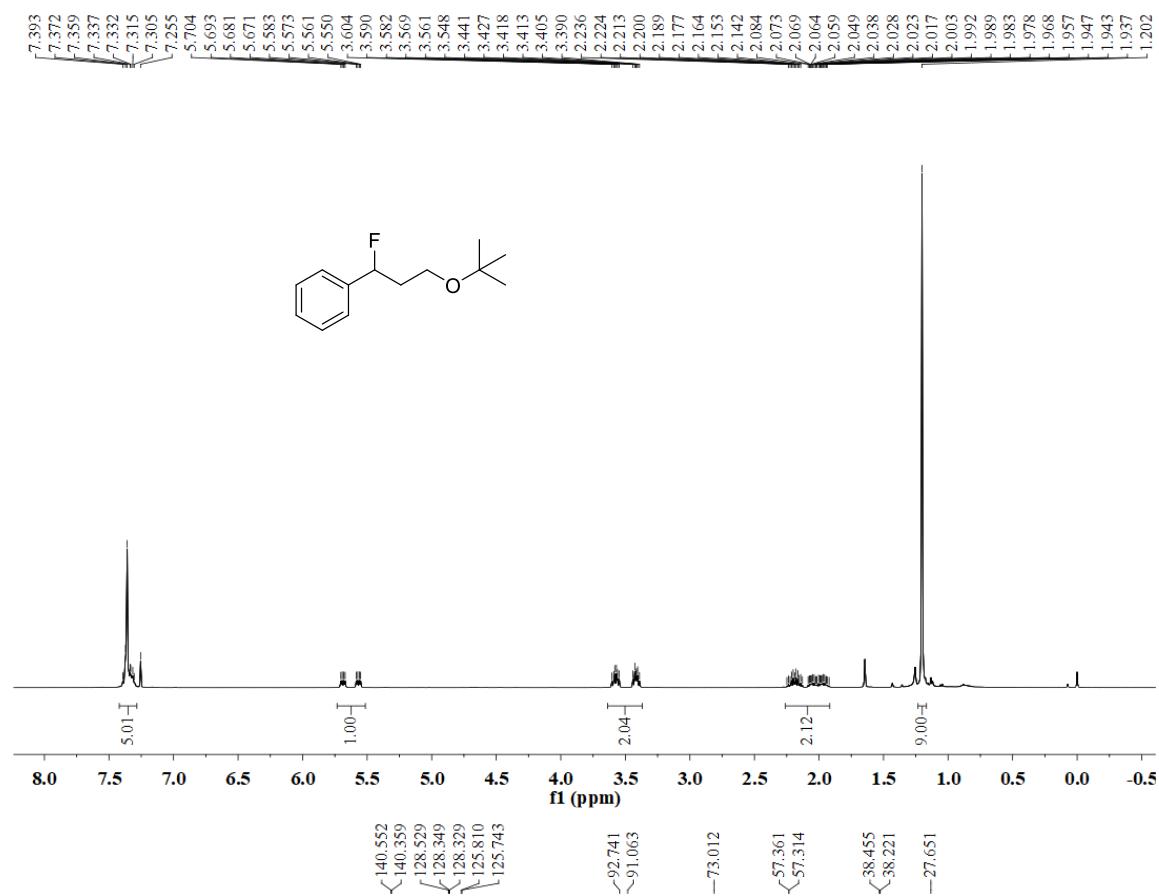


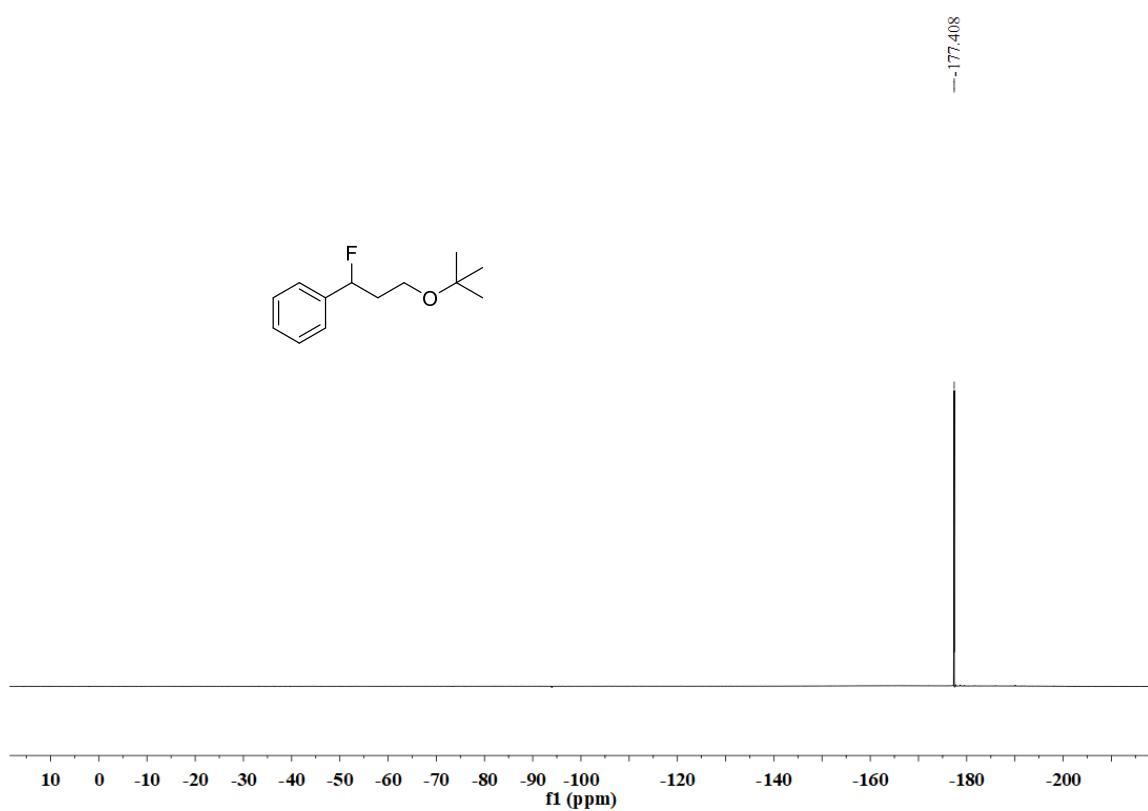
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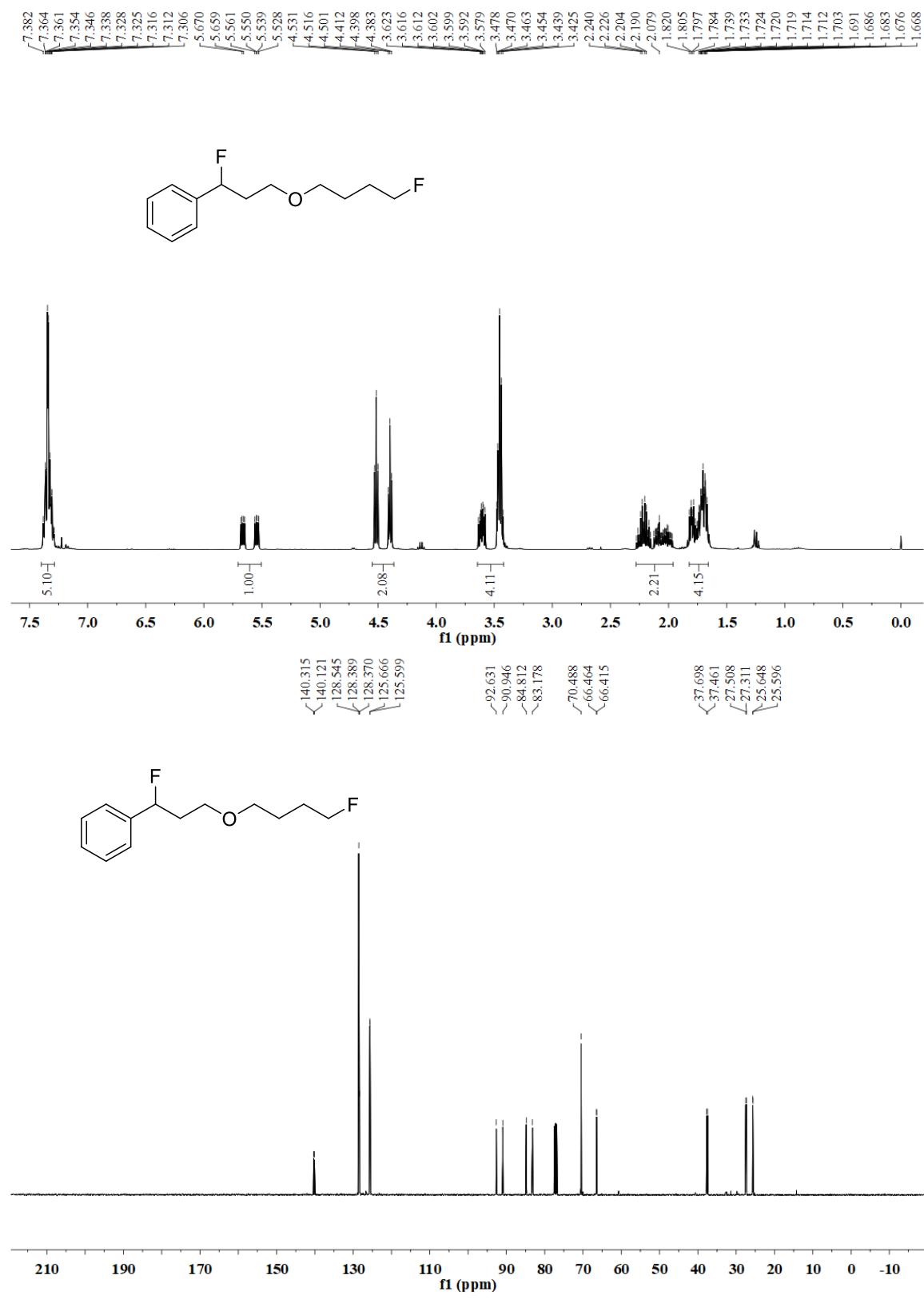


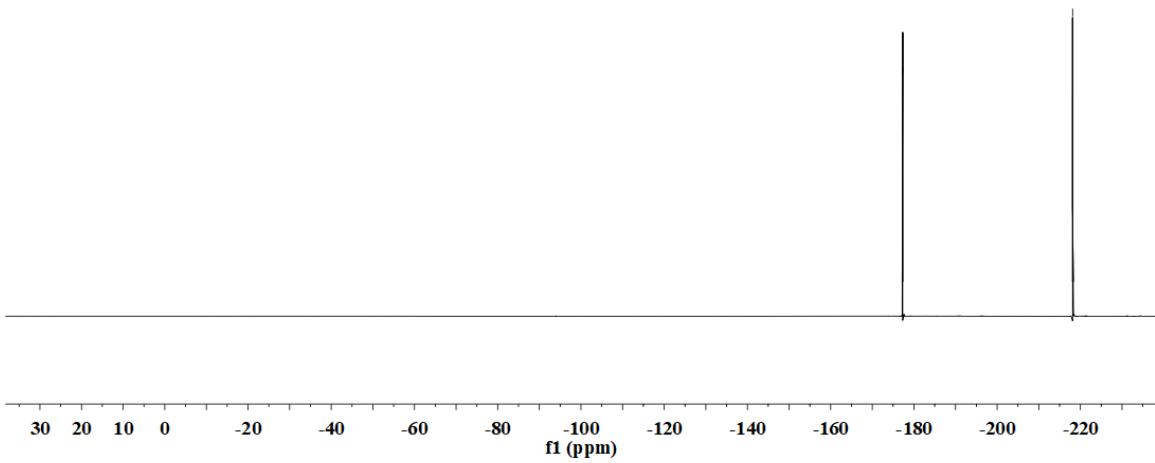
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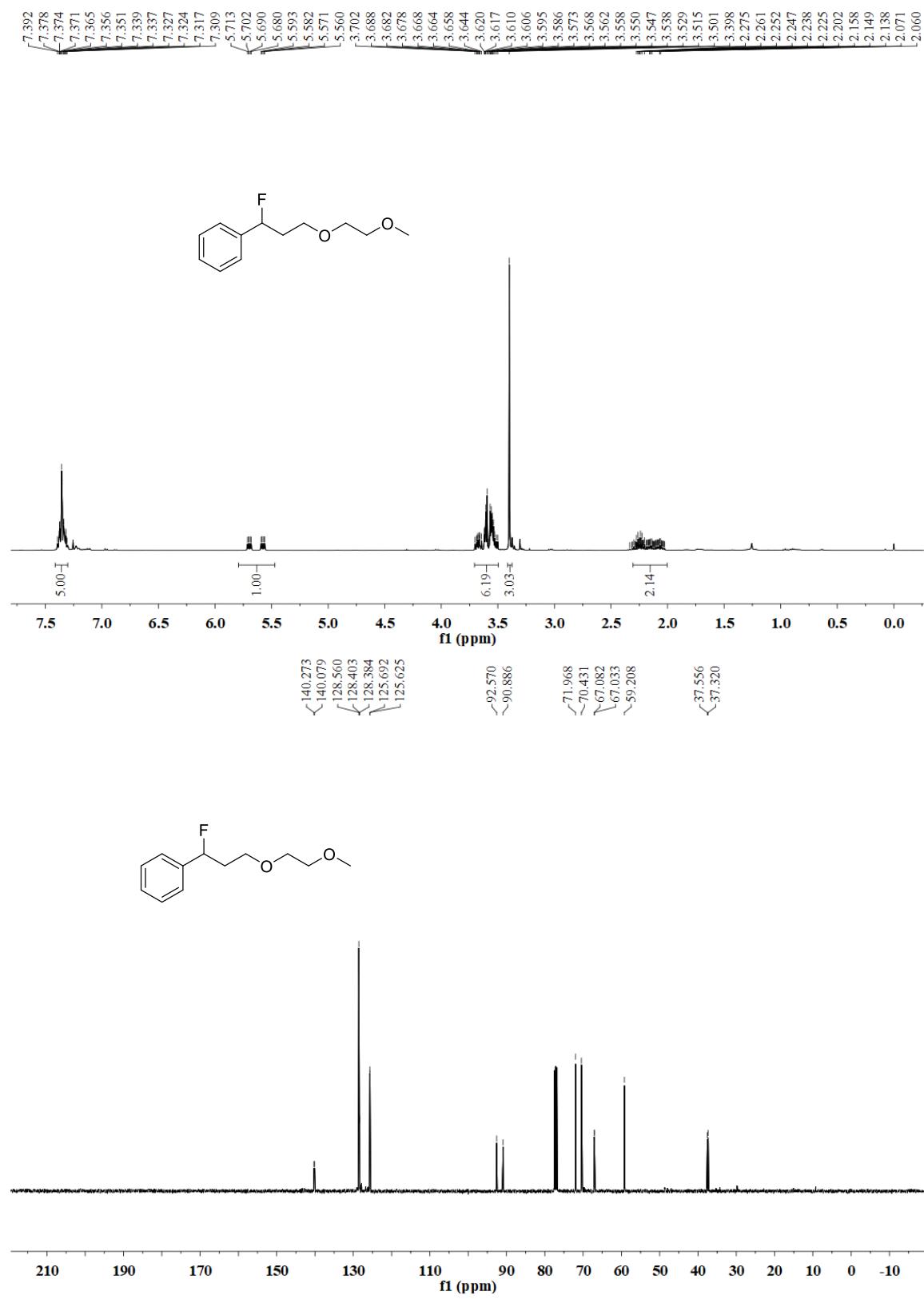
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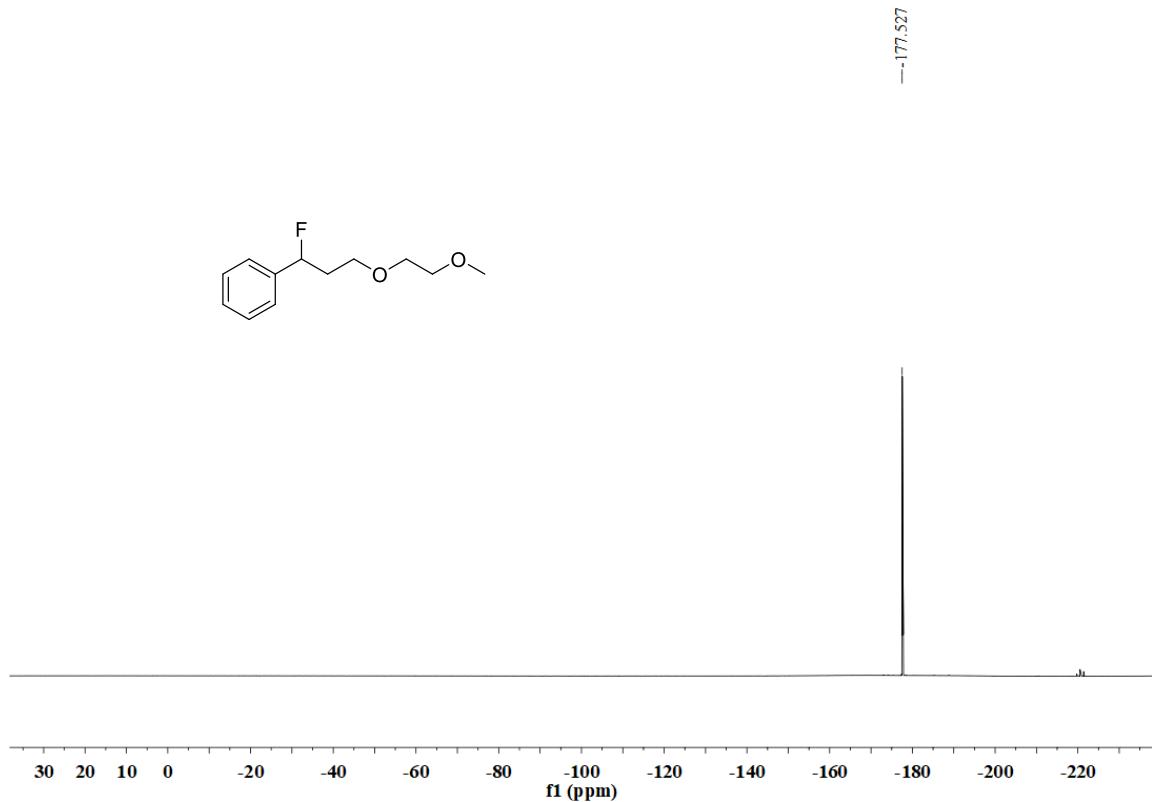




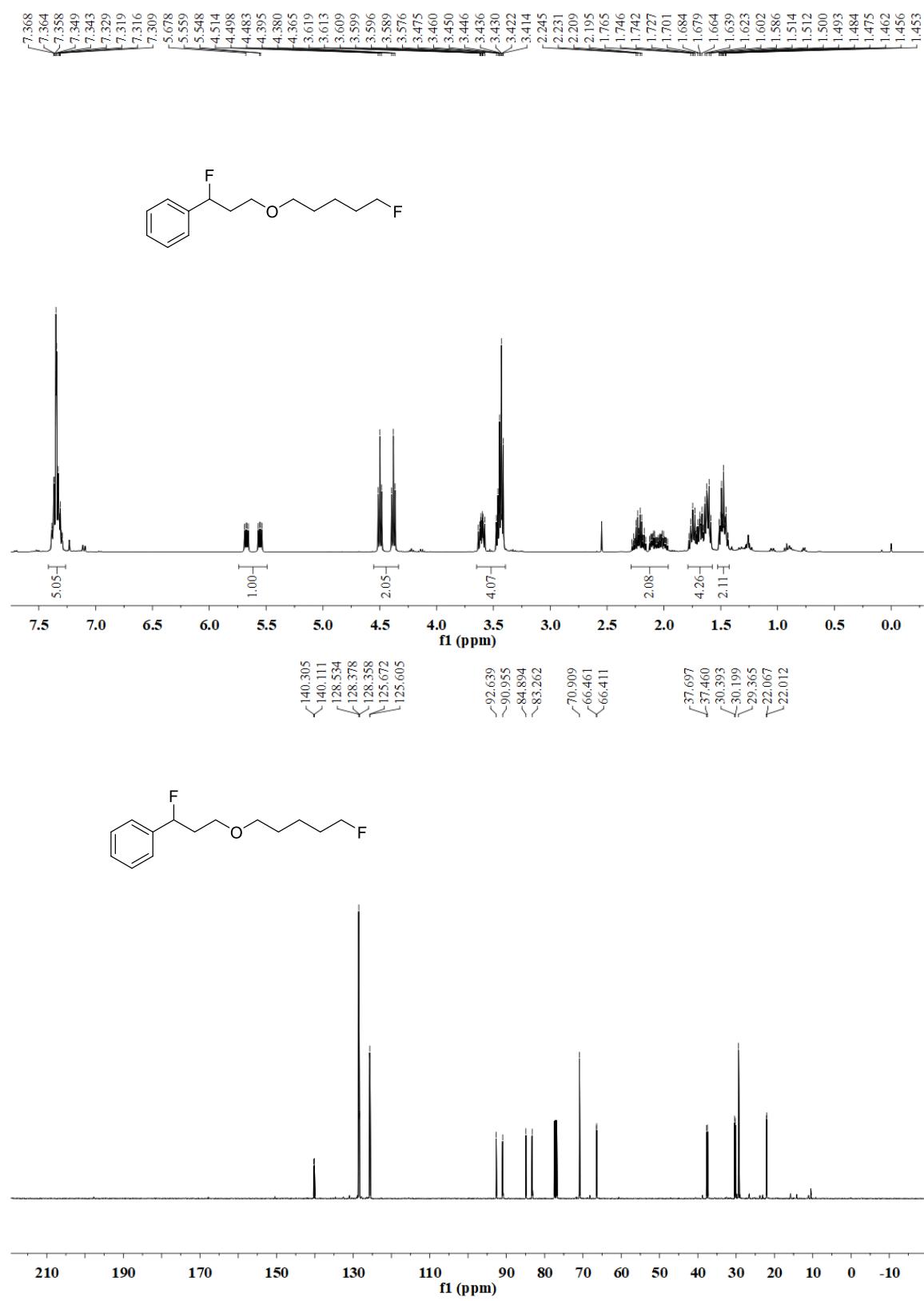
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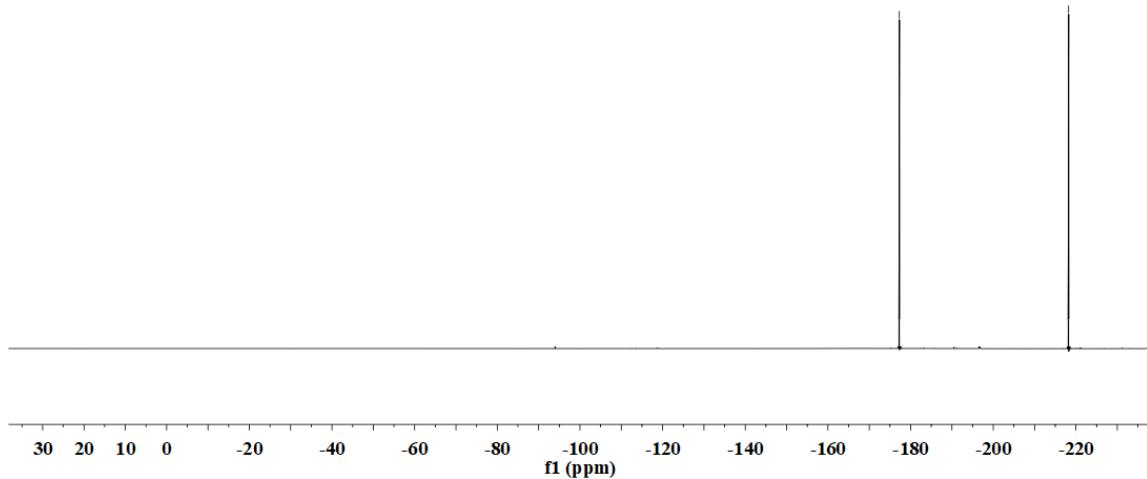
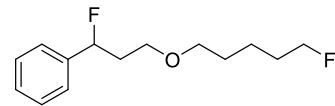
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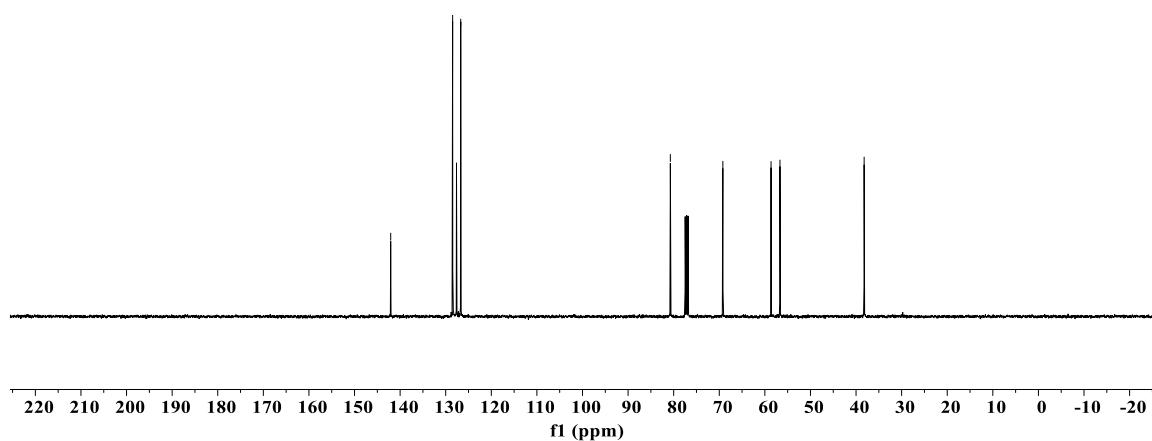
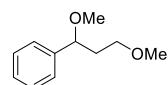
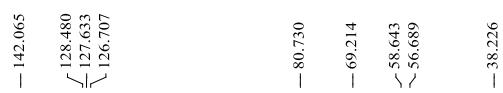
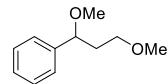
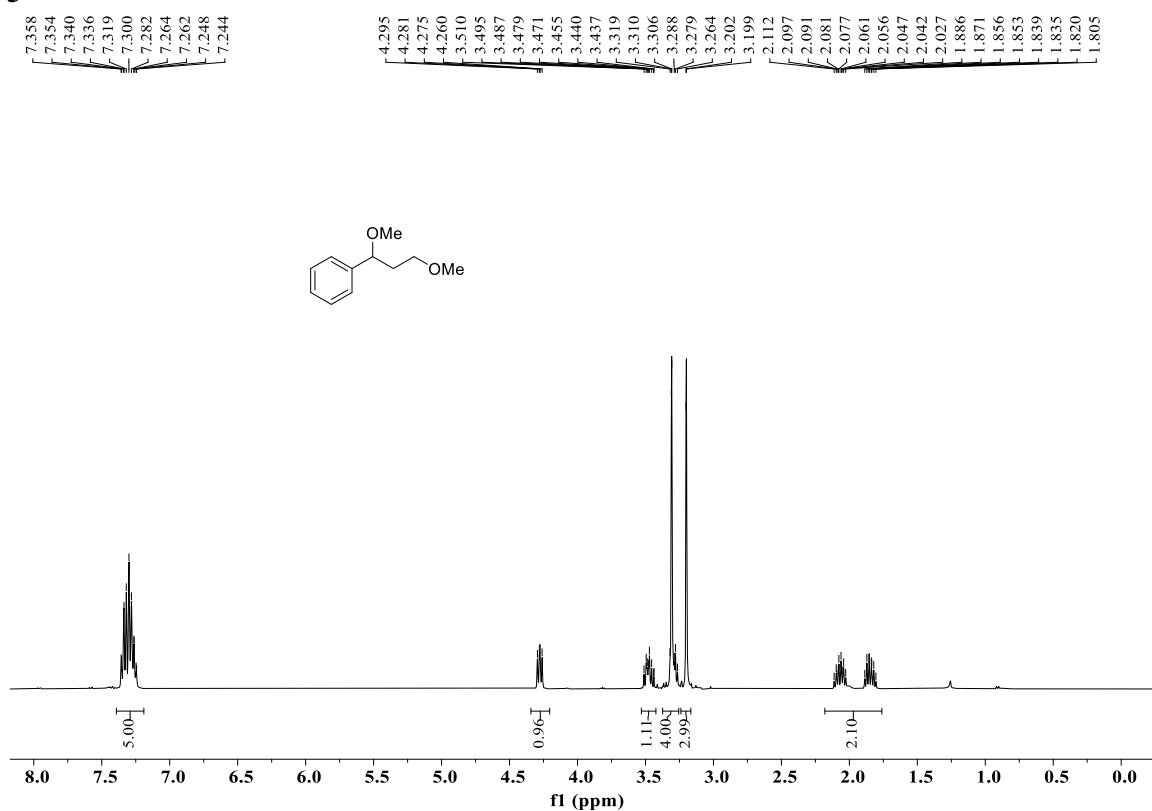


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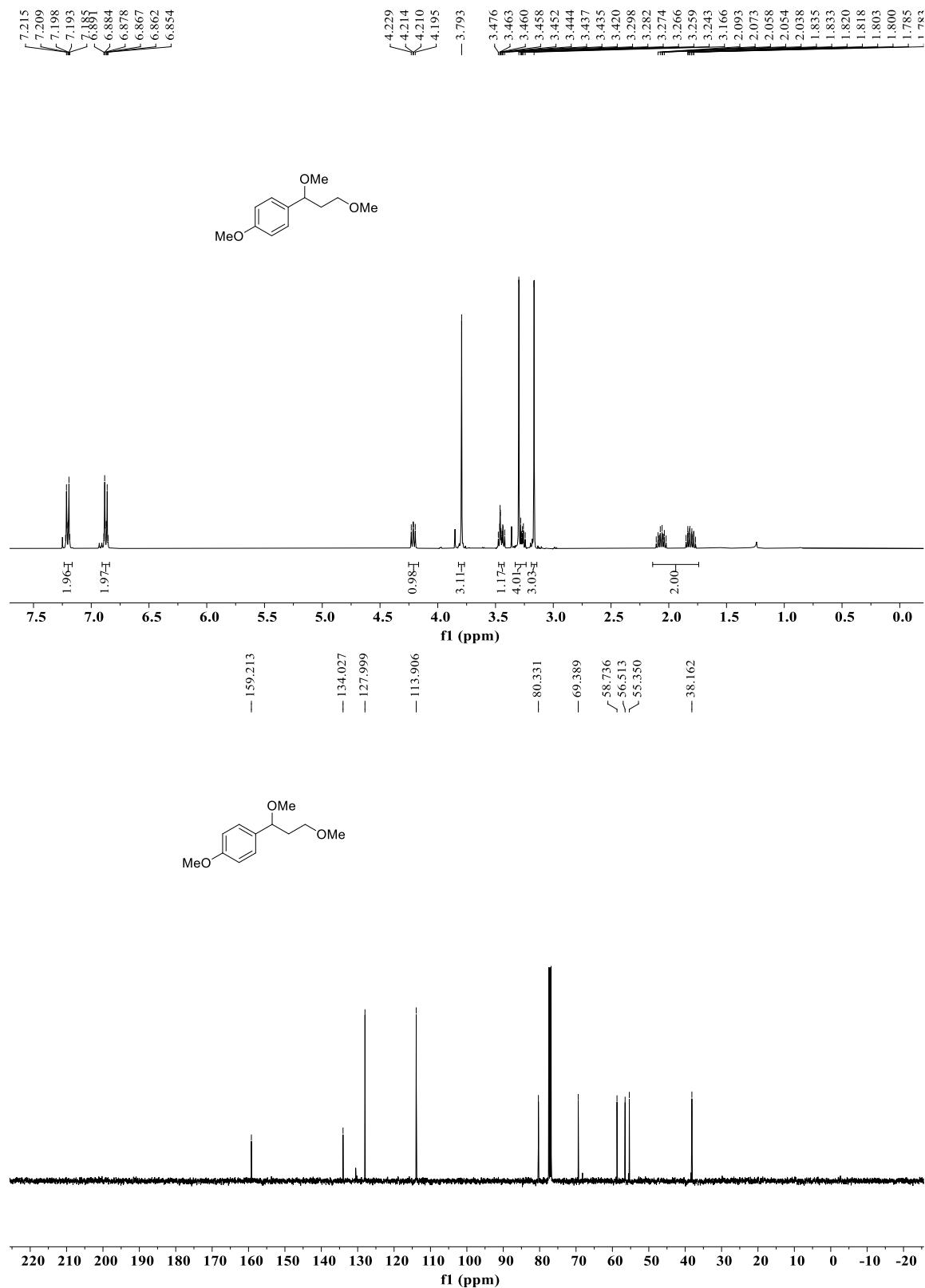




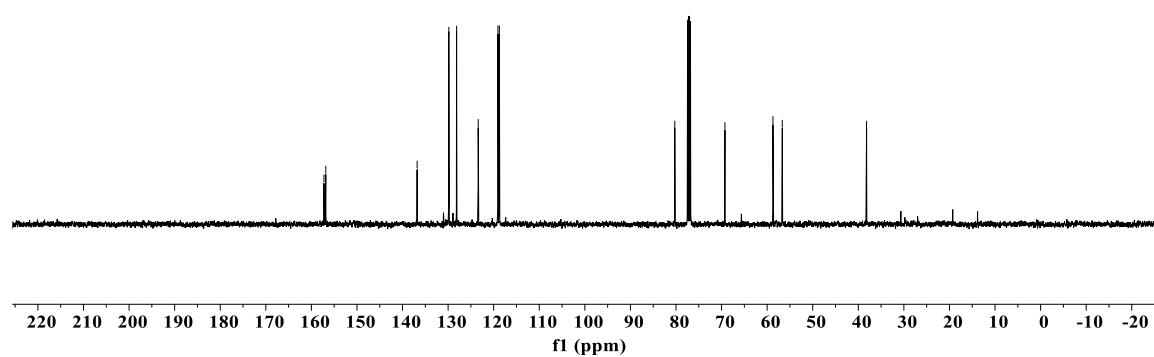
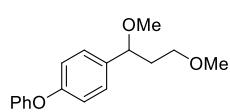
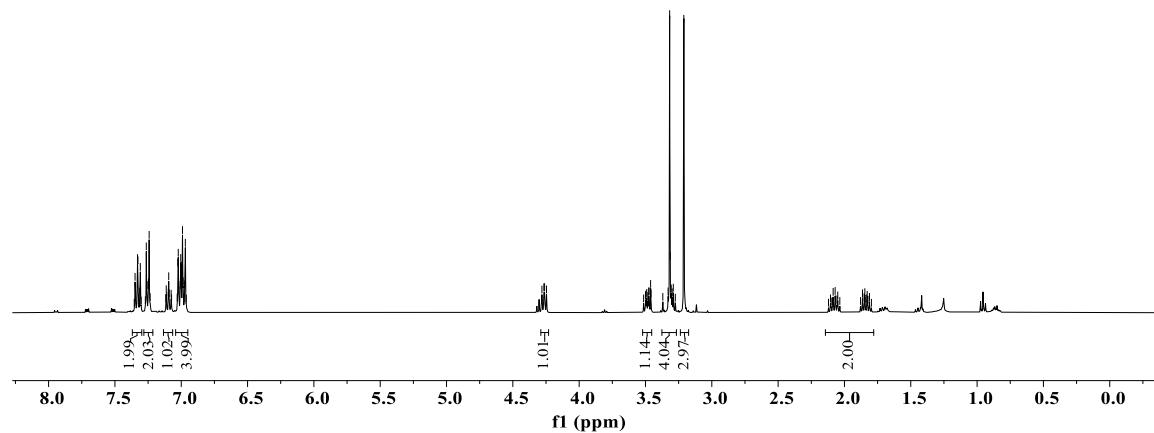
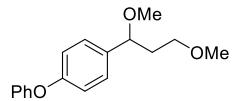
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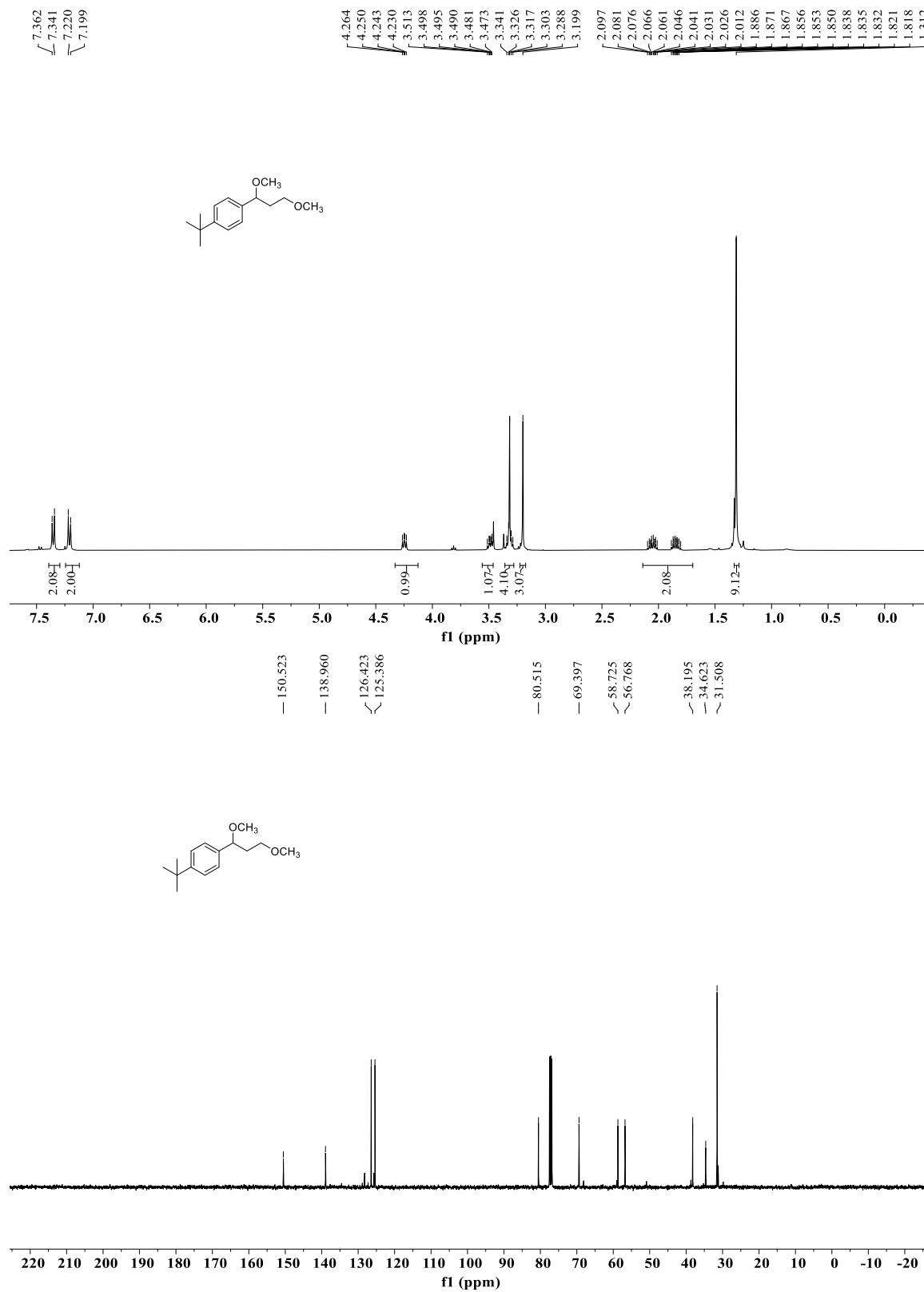


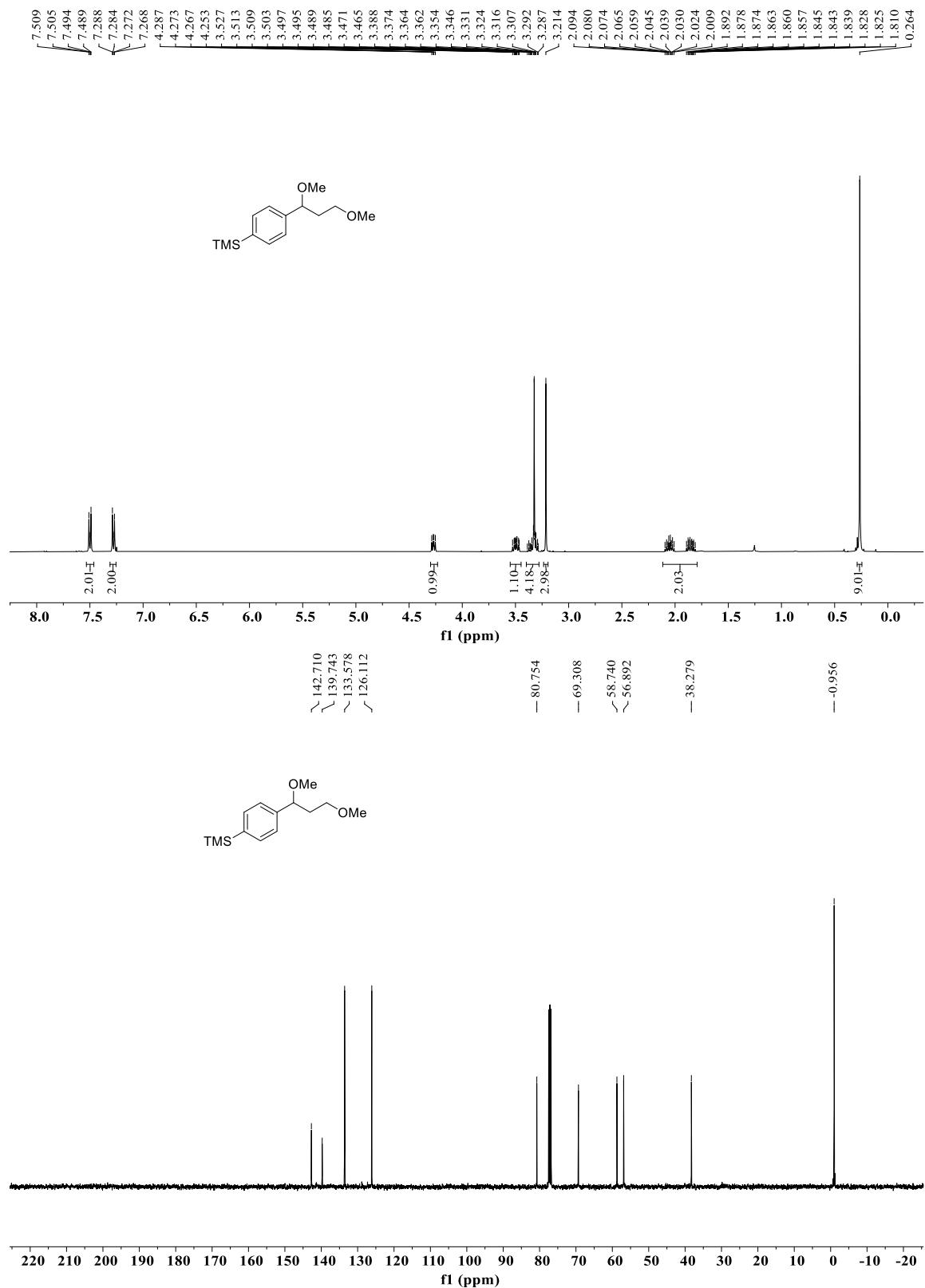
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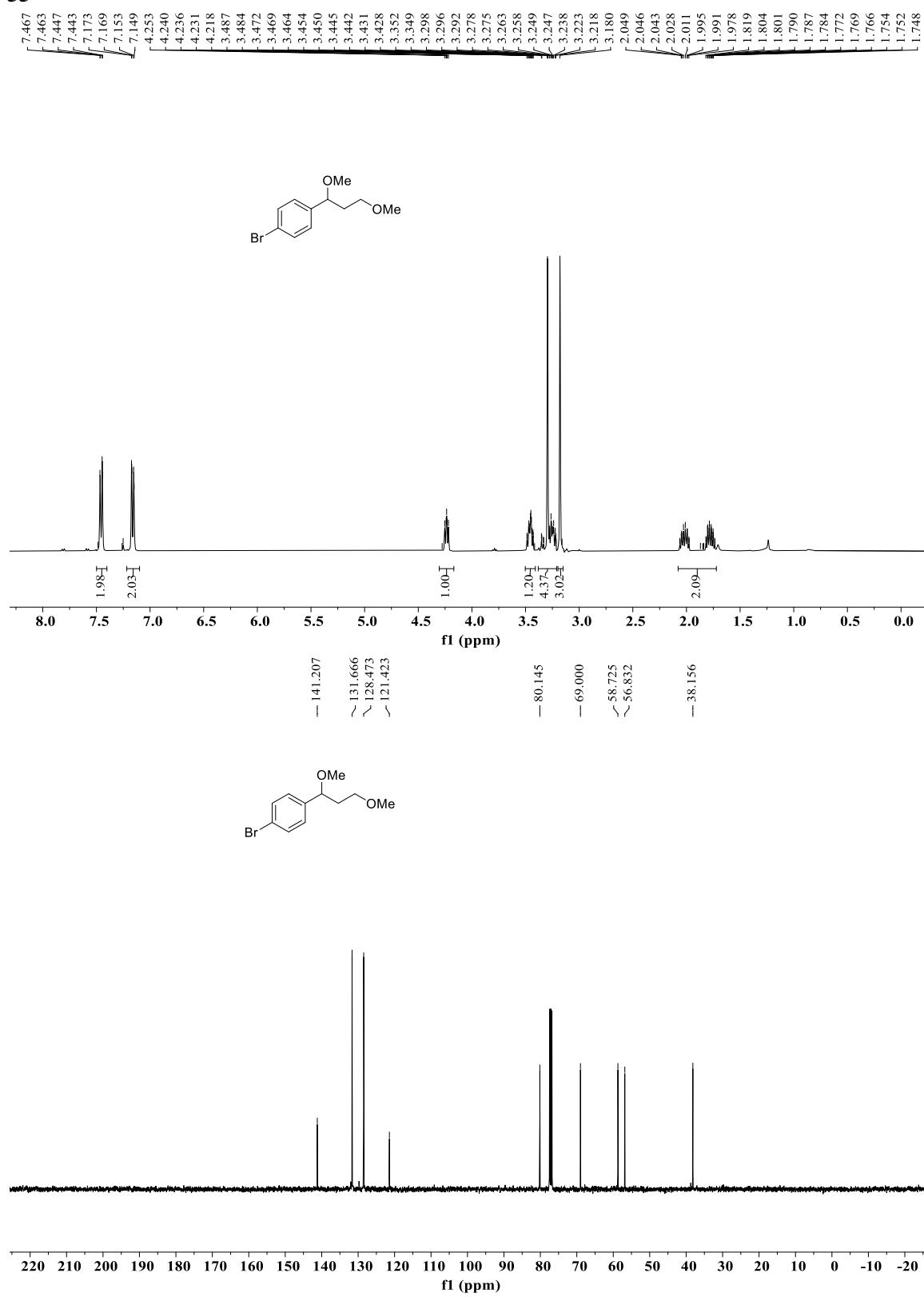
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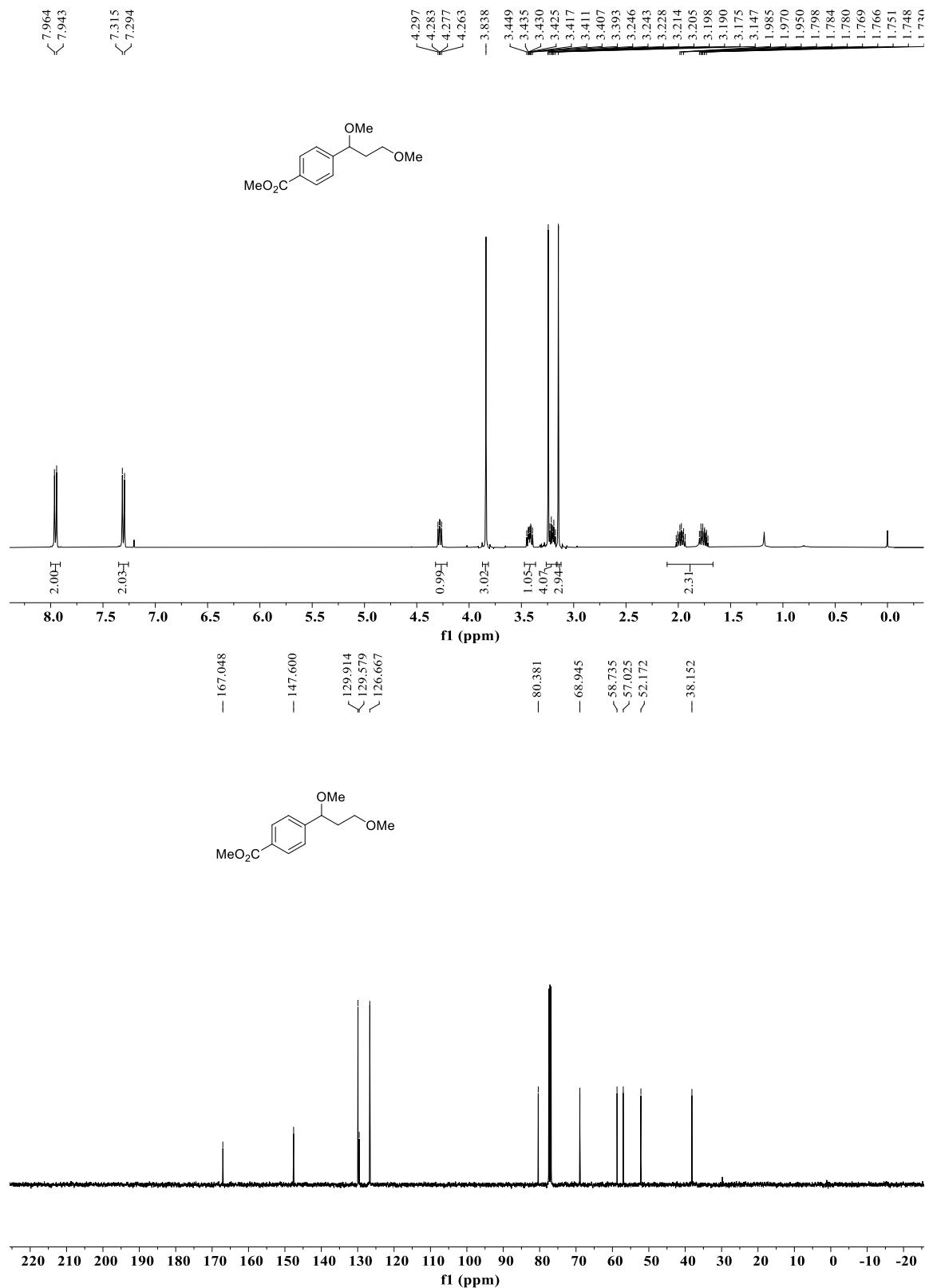


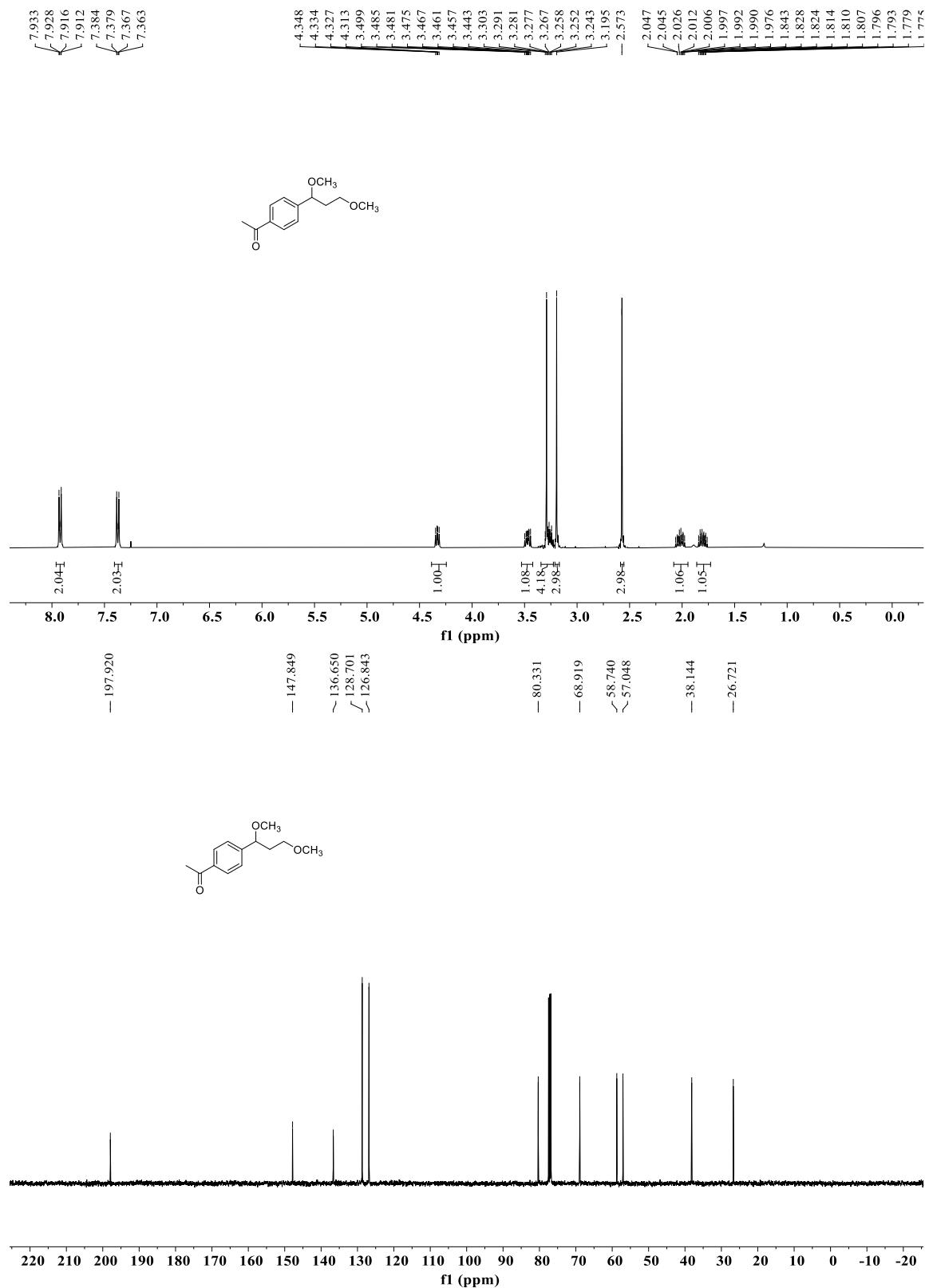


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