

Supporting Information

Silver-Catalyzed Decarboxylative Alkylfluorination of Alkenes

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1. General Information

Materials

All reagents were used as received from commercial sources unless specified otherwise, or prepared as described in the literature. CH₃CN, CH₂Cl₂, DCM, DMF, THF, DMSO, 1,4-Dioxane and MeOH were purchased from Sigma-Aldrich and used without any purification.

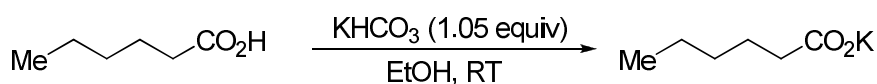
Analytic Methods

¹H NMR, ¹³C NMR, ¹⁹F NMR spectra were recorded on a Bruker Advance 600 spectrometer at the ambient temperature in CDCl₃, *d*₆-DMSO or D₂O. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C NMR are reported in terms of chemical shift (δ ppm). Data for ¹⁹F NMR are reported in terms of chemical shift (δ ppm). Gas Chromatography-Mass Spectrometer (GC-MS) analyses were performed on a Thermo Trace 1300 ISQ Series GC-MS System. GC-MS method: initial temp.: 50 °C (hold for 1 min), rate: 40 °C/min, final temp.: 250 °C (hold for 12 min). Room-temperature Electron Spin Resonance (ESR) spectra were obtained using a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band). Microwave power employed was 5 mW; sweep width ranged from 2000 to 4000 G. Modulation frequency and modulation amplitude were 100 kHz and 3.5 G, respectively. Column chromatography was performed using 50-500 mesh silica gel. High-resolution mass spectra (HRMS) were recorded on an ACQUITY UPLC LCT Premier XE spectrometer with ESI mode. Organic solutions were concentrated under reduced pressure on a BUCHI rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. General Procedure

AgNO₃ (20 mol%, 0.04 mmol, 6.8 mg), potassium carboxylate (3 equiv, 0.6 mmol) were placed in a Schlenk tube equipped with a stirring bar. The solvent 1,4-dioxane/H₂O (v/v = 1:1, 2 mL) and alkene (0.2 mmol) were added under Ar atmosphere. The reaction mixture was stirred at room temperature for 12 h. Then, the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo, purified by flash column chromatography with a mixture of ethyl acetate/petroleum ether as eluent on silica gel to afford alkylfluorination product.

3. Preparation of Potassium Carboxylate



To a solution of *n*-hexanoic acid (1.16 g, 10 mmol) in EtOH (5 mL) was added dropwise KHCO₃ (1.05 g, 10.5 mmol, dissolved in 5 mL of EtOH). The reaction mixture was stirred at room temperature for 3 h. Then, the reaction solution was dried over with anhydrous MgSO₄. After filtration, anhydrous Et₂O was added dropwise, and dropping was stopped when a small amount of crystals precipitated, followed by cooled the solution at a 0 °C. Filtration and collected the white crystals, dried in vacuum to obtain potassium hexanoate (92% yield, 1.41 g).

4. Optimization of Reaction Conditions

Table S1. Optimization Experiments for the Catalysts.

Entry	Catalyst	Yield (%)
1	AgNO ₃	15
2	Ag ₂ CO ₃	12
3	AgOTf	11
4	Ag ₂ SO ₄	14
5	AgSbF ₆	10
6	AgOAc	13
7	AgBF ₄	11
8	AgPF ₆	9
9	AgSO ₃ CF ₃	10
10	--	0

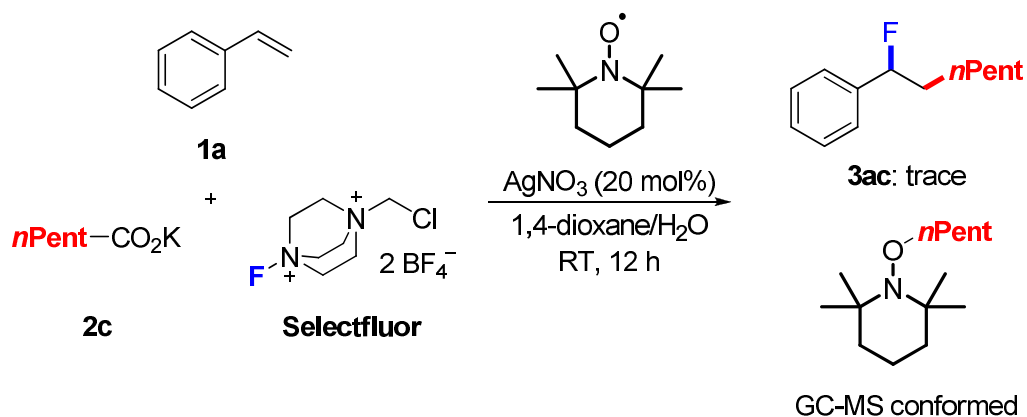
^aReaction conditions: **1b** (0.2 mmol), **2b** (0.6 mmol), Selectfluor (0.6 mmol), AgNO₃ (0.04 mmol), KHCO₃ (0.5 mmol), MeCN/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolated yield.

Table S2. Optimization Experiments for Other Conditions.

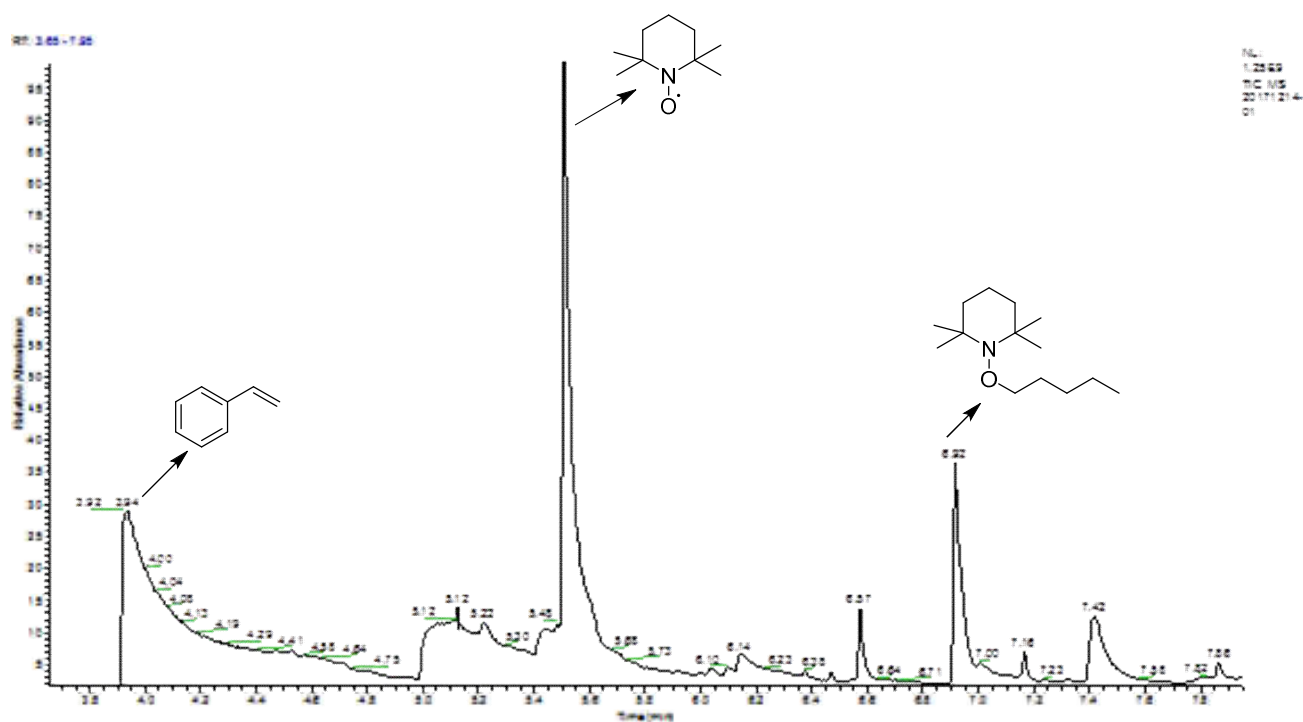
Entry	Me-CO ₂ X	Temp (°C)	time (h)	Yield (%)
1	KOAc (3 equiv)	RT	12	78
2	NaOAc (3 equiv)	RT	12	56
3	KOAc (4 equiv)	RT	12	79
4	KOAc (2 equiv)	RT	12	54
5	KOAc (3 equiv)	50	12	48
6	KOAc (3 equiv)	0	12	59
7	KOAc (3 equiv)	RT	16	80
8	KOAc (3 equiv)	RT	8	64

^aReaction conditions: **1b** (0.2 mmol), Me-CO₂X (0.6 mmol), Selectfluor (0.6 mmol), AgNO₃ (0.04 mmol), KHCO₃, 1,4-dioxane/H₂O (v/v = 1/1, 2 mL). Isolated yield.

5. Radical Trapping Experiment



When one equivalent of TEMPO (2,2,6,6-tetramethyl-1-oxylpiperidine), the radical trapper, was added in the reaction, the desired alkylfluorination product was reduced in a trace yield, with the adduct of alkyl radical with TEMPO be detected by GC-MS.



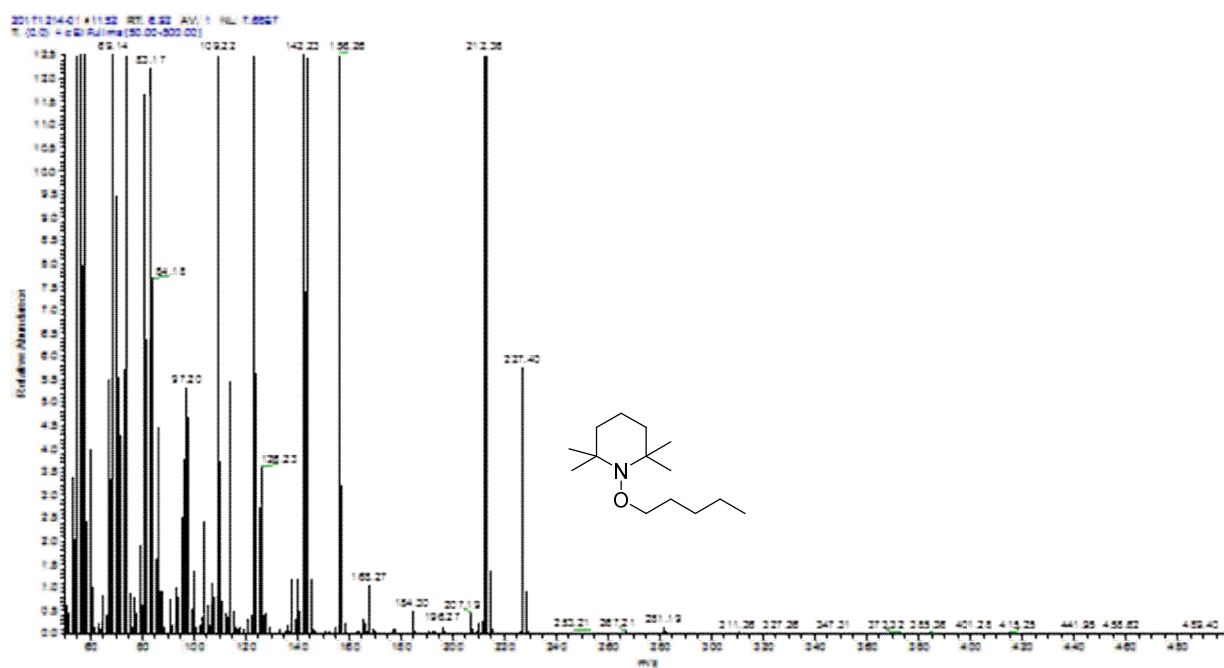
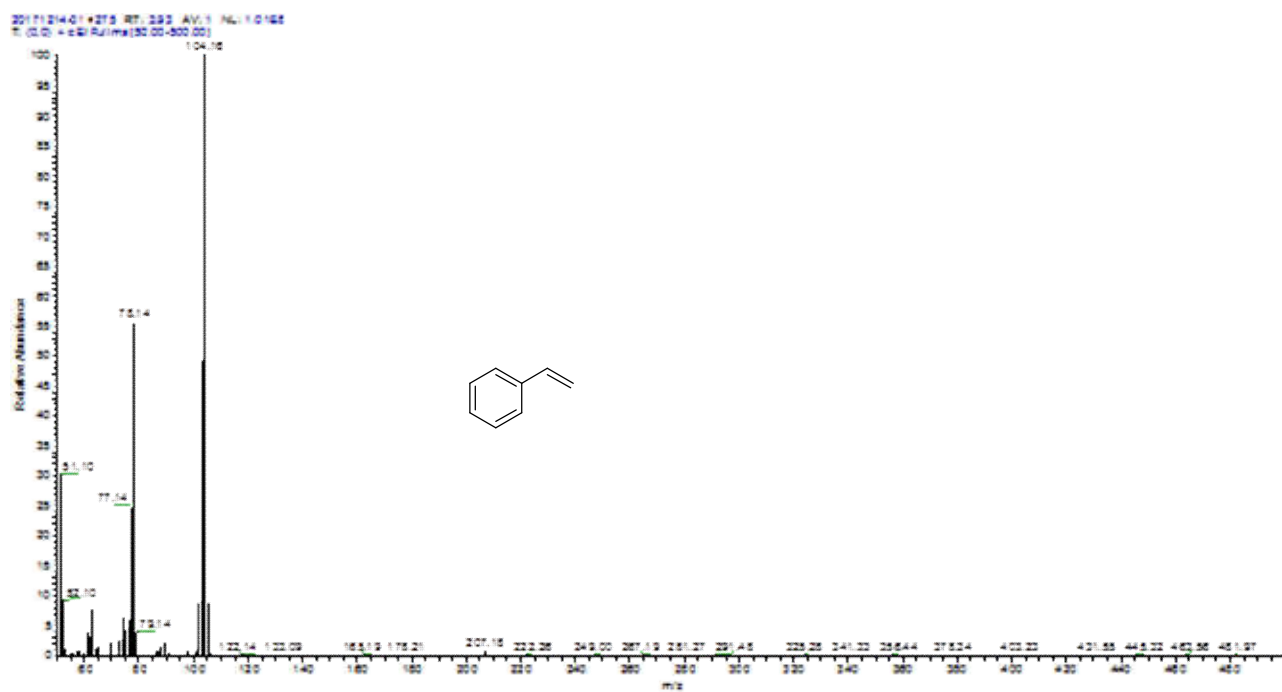
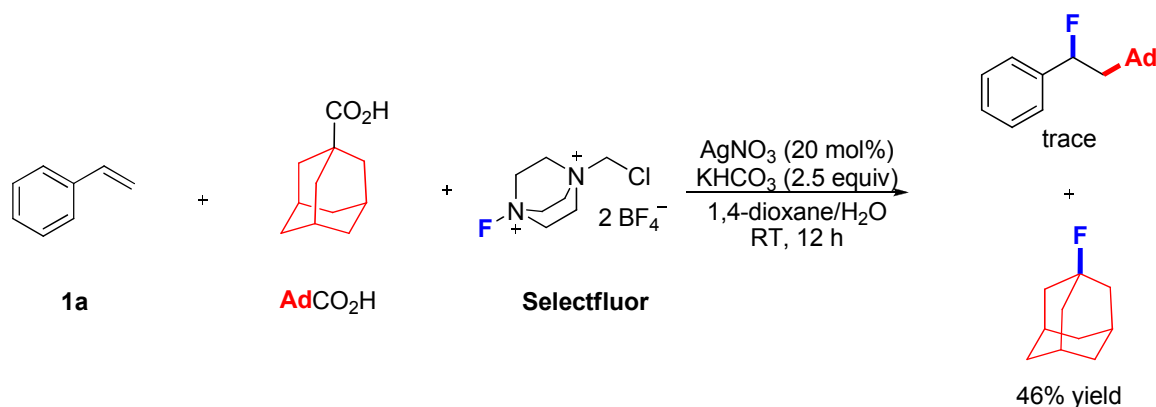


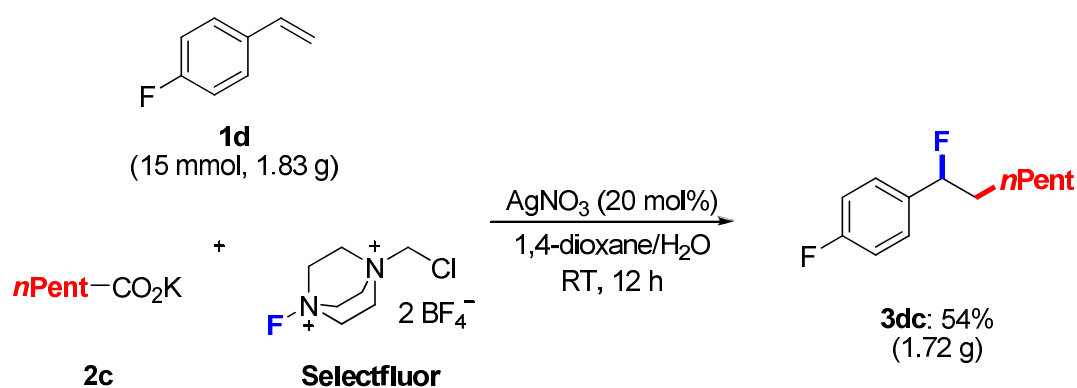
Fig S1. GC-MS Analysis of the Radical Trapping Reaction Mixture

6. Reaction of Tertiary Aliphatic Carboxylic Acid



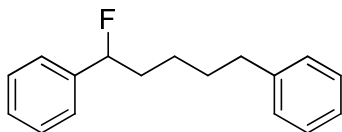
The reaction with tertiary aliphatic carboxylic acid, such as 1-adamantanecarboxylic acid, delivered the desired alkylfluorination product in trace amount. The competitive undesired decarboxylative fluorination of tertiary aliphatic carboxylic acid occurred, affording the fluorination byproduct in moderate yield.

7. Gram-Scale Synthesis

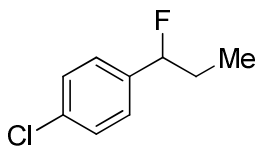


Potassium hexanoate **2c** (45 mmol, 6.93 g), Selectfluor (45 mmol, 15.93 g), AgNO₃ (3.0 mmol, 510 mg) were placed in a 250 mL flask equipped with a stirring bar. The solvent 1,4-dioxane/H₂O (v/v = 1:1, 150 mL) and 4-fluorostyrene **1d** (15 mmol, 1.83 g) were added under Ar atmosphere. The reaction mixture was stirred at room temperature for 12 h. Then, the mixture was quenched with water and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and concentrated under vacuo, purified by flash column chromatography with ethyl acetate/petroleum ether (v/v = 1:100) as eluent on silica gel to afford 1.72 g (54%) of **3dc** as a colorless oil.

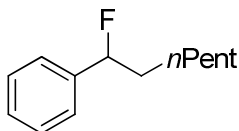
8. Characterization of product



(1-Fluoropentane-1,5-diyl)dibenzene (3aa). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), potassium 4-phenylbutanoate **2a** (122 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 36.8 mg (76%) of **3aa** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.24 – 7.19 (m, 3H), 5.44 (ddd, J = 47.9, 7.9, 4.9 Hz, 1H), 2.66 – 2.62 (m, 2H), 2.03 – 1.96 (m, 1H), 1.94 – 1.80 (m, 1H), 1.76 – 1.64 (m, 2H), 1.62 – 1.51 (m, 1H), 1.48 – 1.45 (m, 1H). ¹³C NMR (151 MHz, CDCl₃) δ 142.36, 140.48 (d, J = 19.9 Hz), 128.39, 128.35, 128.27, 128.15 (d, J = 1.8 Hz), 125.69, 125.49 (d, J = 6.8 Hz), 94.55 (d, J = 170.4 Hz), 37.09 (d, J = 23.6 Hz), 35.77, 31.22, 24.82 (d, J = 4.2 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -174.32 – -174.55 (m). HRMS (EI⁺) calcd for [C₁₇H₁₉F]⁺ ([M]⁺): 242.1471, found: 242.1468. The spectrum data matches previously reported values.¹

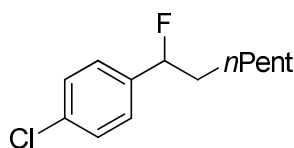


1-Chloro-4-(1-fluoropropyl)benzene (3bb). The representative procedure was followed using 1-chloro-4-vinylbenzene **1b** (28 mg, 0.2 mmol), potassium acetate **2b** (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 26.1 mg (76%) of **3bb** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.34 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.34 (ddd, J = 47.5, 7.4, 5.3 Hz, 1H), 2.04 – 1.73 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.90 (d, J = 20.4 Hz), 134.00 (d, J = 2.6 Hz), 128.66, 127.04 (d, J = 7.1 Hz), 95.08 (d, J = 171.5 Hz), 30.20 (d, J = 24.1 Hz), 9.30 (d, J = 5.8 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -175.83 – -175.99 (m). HRMS (EI⁺) calcd for [C₉H₁₀ClF]⁺ ([M]⁺): 172.0455, found: 172.0450.

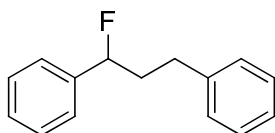


(1-Fluorobutyl) benzene (3ac). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 31.0 mg (80%) of **3ac** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, J = 7.5 Hz, 2H), 7.37 – 7.33 (m, 3H), 5.44 (ddd, J = 47.9, 7.8, 5.1 Hz, 1H), 2.05 – 1.92 (m, 1H), 1.90 – 1.74 (m, 1H), 1.43 – 1.24 (m, 8H), 0.91 (t, J = 6.7 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.65 (d, J = 19.8 Hz), 128.36, 128.10 (d, J = 2.0 Hz), 125.53 (d, J = 6.8 Hz), 94.68 (d, J = 170.1 Hz), 37.24 (d, J = 24.0 Hz), 31.68, 29.03, 25.08,

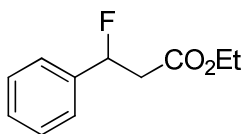
22.56, 14.04. ^{19}F NMR (564 MHz, CDCl_3) δ -174.12 – -174.33 (m). HRMS (EI+) calcd for $[\text{C}_{13}\text{H}_{19}\text{F}]^+$ ($[\text{M}]^+$): 194.1471, found: 194.1465. The spectrum data matches previously reported values.¹



1-Chloro-4-(1-fluoroheptyl)benzene (3bc). The representative procedure was followed using 1-chloro-4-vinylbenzene **1b** (28 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO_3 (6.8 mg, 0.04 mmol), in 1,4-dioxane/ H_2O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 29.6 mg (65%) of **3bc** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.43 – 7.30 (m, 4H), 5.45 (ddd, J = 47.9, 8.0, 5.0 Hz, 1H), 2.05 – 1.78 (m, 2H), 1.56 – 1.24 (m, 8H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 140.65 (d, J = 19.9 Hz), 128.35, 128.09 (d, J = 2.0 Hz), 125.52 (d, J = 6.9 Hz), 94.67 (d, J = 170.1 Hz), 37.24 (d, J = 23.5 Hz), 31.68, 29.03, 25.06 (d, J = 4.4 Hz), 22.56, 14.03. ^{19}F NMR (564 MHz, CDCl_3) δ -174.48 – -174.71 (m). HRMS (EI+) calcd for $[\text{C}_{13}\text{H}_{18}\text{ClF}]^+$ ($[\text{M}]^+$): 228.1081, found: 228.1089.

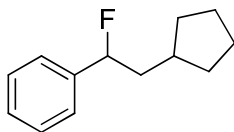


(1-Fluoropropane-1,3-diyl)dibenzene (3ad). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), potassium 2-phenylacetate **2d** (105 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO_3 (6.8 mg, 0.04 mmol), in 1,4-dioxane/ H_2O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 25.7 mg (60%) of **3ad** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.40 – 7.34 (m, 2H), 7.34 – 7.26 (m, 5H), 7.22 – 7.17 (m, 3H), 5.43 (ddd, J = 47.8, 8.5, 4.3 Hz, 1H), 2.86 – 2.68 (m, 2H), 2.37 – 2.23 (m, 1H), 2.18 – 2.00 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.10, 140.20, 140.08, 140.07, 128.45, 128.44, 128.28, 128.27, 93.64 (d, J = 171.0 Hz), 38.81 (d, J = 22.5 Hz), 31.31 (d, J = 4.3 Hz). ^{19}F NMR (564 MHz, CDCl_3) δ -175.55 – -176.19 (m). HRMS (EI+) calcd for $[\text{C}_{15}\text{H}_{15}\text{F}]^+$ ($[\text{M}]^+$): 214.1158, found: 214.1152.

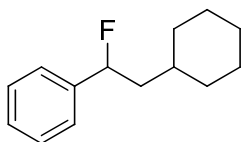


Ethyl 3-fluoro-3-phenylpropanoate (3ae). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), potassium 2-ethoxy-2-oxoacetate **2e** (94 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO_3 (6.8 mg, 0.04 mmol), in 1,4-dioxane/ H_2O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 20.0 mg (51%) of **3ae** as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 7.48 – 7.29 (m, 5H), 5.98 – 5.86 (m, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.05 – 3.00 (m, 1H), 2.83 – 2.74 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.29 (d, J = 5.1 Hz), 141.34 (d, J = 19.6 Hz), 131.46 (d, J = 1.9 Hz), 131.29, 128.26 (d, J = 6.5 Hz), 93.30 (d, J = 171.0 Hz), 63.62, 45.16 (d, J = 27.0 Hz), 16.78. ^{19}F NMR (564 MHz, CDCl_3) δ -172.50 – -172.84 (m). HRMS (EI+) calcd for $[\text{C}_{11}\text{H}_{13}\text{FO}_2]^+$ ($[\text{M}]^+$): 196.0900,

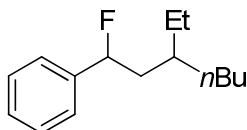
found: 196.0894.



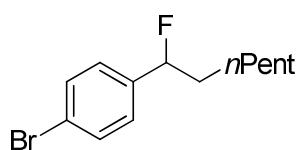
(2-Cyclopentyl-1-fluoroethyl)benzene (3af). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), potassium cyclopentanecarboxylate **2f** (92 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in CH₃CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 21.9 mg (57%) of **3af** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.40 – 7.30 (m, 5H), 5.45 (ddd, *J* = 48.0, 8.5, 4.9 Hz, 1H), 2.06 (dd, *J* = 14.1, 6.7 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.87 – 1.72 (m, 3H), 1.63 (d, *J* = 6.9 Hz, 2H), 1.53 (dd, *J* = 7.4, 4.0 Hz, 2H), 1.23 – 1.11 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 143.41 (d, *J* = 19.8 Hz), 131.06, 130.83 (d, *J* = 2.0 Hz), 128.27 (d, *J* = 6.6 Hz), 97.08 (d, *J* = 169.6 Hz), 46.20 (d, *J* = 23.0 Hz), 39.03 (d, *J* = 3.8 Hz), 35.59, 35.22, 27.74, 27.58. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.06 – -173.50 (m). HRMS (EI+) calcd for [C₁₃H₁₇F]⁺ ([M]⁺): 192.1314, found: 192.1306.



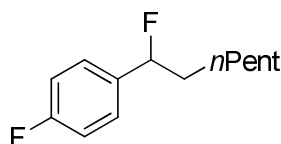
(2-Cyclohexyl-1-fluoroethyl)benzene (3ag). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), cyclohexanecarboxylic acid **2g** (77 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (50 mg, 0.5 mmol), in CH₃CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 26.8 mg (65%) of **3ag** as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.18 (m, 5H), 5.54 (ddd, *J* = 12.5, 9.4, 3.8 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.69 – 1.49 (m, 5H), 1.22 – 1.00 (m, 4H), 0.97 – 0.85 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 128.44, 128.17, 125.59, 125.53, 92.80 (d, *J* = 182.0 Hz), 45.24, 33.87, 32.81, 26.49, 26.25, 26.10. ¹⁹F NMR (376 MHz, CDCl₃) δ -173.78 (s). HRMS (EI+) calcd for [C₁₄H₁₉F]⁺ ([M]⁺): 206.1471, found: 206.1465.



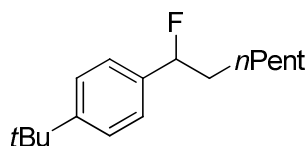
(3-Ethyl-1-fluoroheptyl)benzene (3ah). The representative procedure was followed using styrene **1a** (21 mg, 0.2 mmol), 2-ethylhexanoic acid **2h** (87 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), KHCO₃ (50 mg, 0.5 mmol), in CH₃CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 22.6 mg (51%) of **3ah** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 3H), 5.51 (ddd, *J* = 48.3, 9.2, 4.0 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.69 – 1.63 (m, 1H), 1.53 – 1.23 (m, 9H), 0.94 – 0.85 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 141.03 (d, *J* = 19.8 Hz), 128.40, 128.11, 125.52 (d, *J* = 6.5 Hz), 93.29 (d, *J* = 169.7 Hz), 41.41 (d, *J* = 23.2 Hz), 35.23 (d, *J* = 26.6 Hz), 32.72 (d, *J* = 77.5 Hz), 28.61 (d, *J* = 14.6 Hz), 25.84 (d, *J* = 114.0 Hz), 23.03 (d, *J* = 5.6 Hz), 14.11, 10.51 (d, *J* = 29.5 Hz). ¹⁹F NMR (564 MHz, CDCl₃) δ -172.97 – -175.35 (m). HRMS (EI+) calcd for [C₁₅H₂₃F]⁺ ([M]⁺): 222.1784, found: 222.1778.



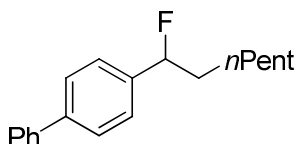
1-Bromo-4-(1-fluoroheptyl)benzene (3cc). The representative procedure was followed using 1-bromo-4-vinylbenzene **1c** (37 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 37.0 mg (68%) of **3cc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.45 – 5.31 (m, 1H), 1.99 – 1.71 (m, 2H), 1.51 – 1.41 (m, 1H), 1.40 – 1.21 (m, 7H), 0.88 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.61 (d, *J* = 20.3 Hz), 131.50, 127.20 (d, *J* = 6.9 Hz), 121.97 (d, *J* = 2.4 Hz), 93.94 (d, *J* = 171.2 Hz), 37.13 (d, *J* = 23.3 Hz), 31.64, 28.97, 24.88 (d, *J* = 4.3 Hz), 22.53, 14.04. ¹⁹F NMR (564 MHz, CDCl₃) δ -175.02 – -175.26 (m). HRMS (EI+) calcd for [C₁₃H₁₈⁷⁹BrF]⁺ ([M]⁺): 272.0576, found: 272.0570.



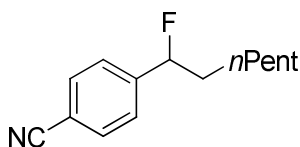
1-Fluoro-4-(1-fluoroheptyl)benzene (3dc). The representative procedure was followed using 1-fluoro-4-vinylbenzene **1d** (25 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 25.0 mg (59%) of **3dc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.30 (m, 4H), 5.45 (ddd, *J* = 47.9, 8.0, 5.0 Hz, 1H), 2.05 – 1.78 (m, 2H), 1.56 – 1.24 (m, 8H), 0.92 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.65 (d, *J* = 19.9 Hz), 128.35, 128.09 (d, *J* = 2.0 Hz), 125.52 (d, *J* = 6.9 Hz), 94.67 (d, *J* = 170.1 Hz), 37.24 (d, *J* = 23.5 Hz), 31.68, 29.03, 25.06 (d, *J* = 4.4 Hz), 22.56, 14.03. ¹⁹F NMR (564 MHz, CDCl₃) δ -174.48 – -174.71 (m). HRMS (EI+) calcd for [C₁₃H₁₈F₂]⁺ ([M]⁺): 212.1377, found: 212.1371.



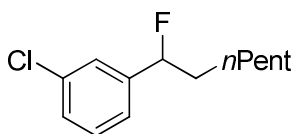
1-(*Tert*-butyl)-4-(1-fluoroheptyl)benzene (3ec). The representative procedure was followed using 1-*tert*-butyl-4-vinylbenzene **1e** (32 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in CH₃CN/H₂O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 40.0 mg (80%) of **3ec** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 2H), 5.40 (ddd, *J* = 48.0, 8.1, 4.9 Hz, 1H), 2.03 – 1.75 (m, 2H), 1.54 – 1.44 (m, 1H), 1.40 – 1.25 (m, 15H), 0.89 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 151.17, 137.55 (d, *J* = 19.9 Hz), 125.41 (d, *J* = 6.4 Hz), 125.29, 94.70 (d, *J* = 169.0 Hz), 37.06 (d, *J* = 23.7 Hz), 34.57, 31.69, 31.32, 29.05, 25.18 (d, *J* = 4.1 Hz), 22.57, 14.06. ¹⁹F NMR (564 MHz, CDCl₃) δ -172.13 – -172.38 (m). HRMS (EI+) calcd for [C₁₇H₂₇F]⁺ ([M]⁺): 250.2097, found: 250.2091.



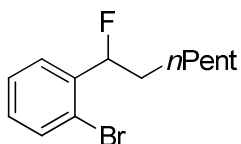
4-(1-Fluoroheptyl)-1,1'-biphenyl (3fc). The representative procedure was followed using 4-vinylbiphenyl **1f** (36 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 43.7 mg (81%) of **3fc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.63 – 7.61 (m, 4H), 7.48 – 7.36 (m, 5H), 5.49 (ddd, *J* = 47.9, 7.8, 5.1 Hz, 1H), 2.12 – 1.77 (m, 2H), 1.58 – 1.49 (m, 1H), 1.46 – 1.27 (m, 7H), 0.91 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 144.93, 143.64, 142.87, 131.42, 130.20, 129.72, 129.66, 80.70 (d, *J* = 171.0 Hz), 41.23, 34.46, 31.88, 28.55, 25.32, 16.79. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.62 – -173.87 (m). HRMS (EI⁺) calcd for [C₁₉H₂₃F]⁺ ([M]⁺): 270.1784, found: 270.1778.



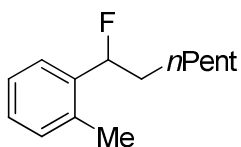
4-(1-Fluoroheptyl)benzonitrile (3gc). The representative procedure was followed using 4-vinylbenzonitrile **1g** (26 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 18.8 mg (43%) of **3gc** as a colorless oil. ¹H NMR (600 MHz, acetone-d₆) δ 7.58 – 7.19 (m, 4H), 5.40 (ddd, *J* = 47.9, 8.0, 5.0 Hz, 1H), 2.21 – 1.87 (m, 1H), 1.84 – 1.73 (m, 1H), 1.58 – 1.38 (m, 1H), 1.39 – 1.16 (m, 7H), 0.87 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (151 MHz, acetone-d₆) δ 148.80 (d, *J* = 20.2 Hz), 134.92, 128.93 (d, *J* = 7.5 Hz), 120.89, 114.40, 96.05 (d, *J* = 171.5 Hz), 39.51 (d, *J* = 22.8 Hz), 34.14, 31.40, 27.32 (d, *J* = 4.0 Hz), 24.95, 16.04. ¹⁹F NMR (564 MHz, acetone-d₆) δ -180.14 – 180.31 (m). HRMS (EI⁺) calcd for [C₁₄H₁₈FN]⁺ ([M]⁺): 219.1423, found: 219.1418.



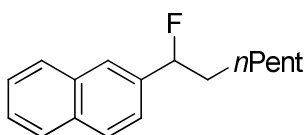
1-Chloro-3-(1-fluoroheptyl)benzene (3hc). The representative procedure was followed using 1-chloro-3-vinylbenzene **1h** (28 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 32.4 mg (71%) of **3hc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.32 (s, 1H), 7.30 – 7.29 (m, 2H), 7.21 – 7.17 (m, 1H), 5.39 (ddd, *J* = 47.7, 8.0, 4.8 Hz, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.73 (m, 1H), 1.50 – 1.41 (m, 1H), 1.36 – 1.25 (m, 7H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 142.68 (d, *J* = 20.4 Hz), 134.34, 129.69, 128.18 (d, *J* = 1.5 Hz), 125.63 (d, *J* = 7.5 Hz), 123.56 (d, *J* = 7.0 Hz), 93.80 (d, *J* = 172.0 Hz), 37.18 (d, *J* = 23.2 Hz), 31.63, 28.97, 24.89 (d, *J* = 4.1 Hz), 22.54, 14.04. ¹⁹F NMR (564 MHz, CDCl₃) δ -176.12 – -176.35 (m). HRMS (EI⁺) calcd for [C₁₃H₁₈ClF]⁺ ([M]⁺): 228.1081, found: 228.1076.



1-Bromo-2-(1-fluoroheptyl)benzene (3ic). The representative procedure was followed using 1-bromo-2-vinylbenzene **1i** (37 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 33.2 mg (61%) of **3ic** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.53 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.18 – 7.14 (m, 1H), 5.75 (ddd, *J* = 47.3, 8.4, 3.6 Hz, 1H), 2.01 – 1.69 (m, 2H), 1.57 – 1.44 (m, 2H), 1.41 – 1.24 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 140.35 (d, *J* = 21.6 Hz), 132.66, 129.37 (d, *J* = 2.1 Hz), 127.70, 126.91 (d, *J* = 10.1 Hz), 120.81 (d, *J* = 6.3 Hz), 93.47 (d, *J* = 172.0 Hz), 36.33 (d, *J* = 23.7 Hz), 31.77, 28.98, 25.15 (d, *J* = 3.1 Hz), 22.66, 14.15. ¹⁹F NMR (564 MHz, CDCl₃) δ -181.53 – -181.70 (m). HRMS (EI+) calcd for [C₁₃H₁₈⁷⁹BrF]⁺ ([M]⁺): 272.0576, found: 272.0570.

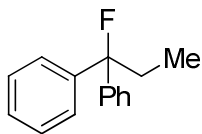


1-(1-Fluoroheptyl)-2-methylbenzene (3jc). The representative procedure was followed using 1-methyl-2-vinylbenzene **1j** (24 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 31.2 mg (75%) of **3jc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.43 – 7.42 (m, 1H), 7.26 – 7.17 (m, 3H), 5.67 (ddd, *J* = 47.5, 8.6, 4.1 Hz, 1H), 2.35 (s, 3H), 1.98 – 1.77 (m, 2H), 1.59 – 1.56 (m, 1H), 1.34 – 1.12 (m, 7H), 0.92 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 138.83 (d, *J* = 18.9 Hz), 134.18 (d, *J* = 5.2 Hz), 130.34, 127.84 (d, *J* = 1.9 Hz), 126.07, 125.17 (d, *J* = 8.6 Hz), 91.91 (d, *J* = 168.8 Hz), 36.34 (d, *J* = 24.0 Hz), 31.71, 29.04, 25.37 (d, *J* = 3.4 Hz), 22.58, 18.92, 14.07. ¹⁹F NMR (564 MHz, CDCl₃) δ -177.27 – -177.73 (m). HRMS (EI+) calcd for [C₁₄H₂₁F]⁺ ([M]⁺): 208.1627, found: 208.1622.

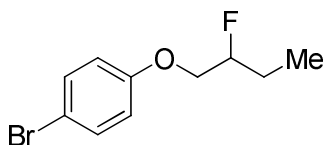


2-(1-Fluoroheptyl)naphthalene (3kc). The representative procedure was followed using 2-vinylnaphthalene **1k** (31 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), AgNO₃ (6.8 mg, 0.04 mmol), in 1,4-dioxane/H₂O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 27.3 mg (56%) of **3kc** as a colorless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.87 – 7.79 (m, 3H), 7.78 (s, 1H), 7.52 – 7.47 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 1H), 5.59 (ddd, *J* = 47.7, 7.8, 5.2 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.95 – 1.84 (m, 1H), 1.54 – 1.43 (m, 1H), 1.41 – 1.23 (m, 7H), 0.88 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 137.94 (d, *J* = 19.7 Hz), 133.15, 133.03, 128.26, 128.04, 127.69, 126.25, 126.12, 124.68 (d, *J* = 8.1 Hz), 123.31 (d, *J* = 5.7 Hz), 94.88 (d, *J* = 170.3 Hz), 37.16 (d, *J* = 23.5 Hz), 31.68, 29.05, 25.07 (d, *J* = 4.3 Hz), 22.56, 14.05. ¹⁹F NMR (564 MHz, CDCl₃) δ -173.76 – -173.98 (m). HRMS

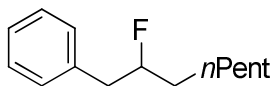
(EI+) calcd for $[C_{17}H_{21}F]^+$ ($[M]^+$): 244.1627, found: 244.1622.



(1-Fluoropropane-1,1-diyl)dibenzene (3lb). The representative procedure was followed using ethene-1,1-diyl dibenzene **1l** (36 mg, 0.2 mmol), potassium acetate **2b** (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), in 1,4-dioxane/ H_2O (v/v = 1/1, 2 mL), at room temperature for 12 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 18.4 mg (43%) of **3lb** as a colorless oil. 1H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 4H), 7.33 – 7.31 (m, 4H), 7.24 – 7.22 (m, 2H), 2.33 (q, J = 7.3 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.54, 130.78, 129.42, 128.76, 81.12, 37.09, 10.84. ^{19}F NMR (564 MHz, $CDCl_3$) δ -152.29 (t, J = 24.5 Hz). HRMS (EI+) calcd for $[C_{15}H_{15}F]^+$ ($[M]^+$): 214.1158, found: 214.1152.



1-Bromo-4-(2-fluorobutoxy)benzene (3mb). The representative procedure was followed using 1-(allyloxy)-4-bromobenzene **1m** (43 mg, 0.2 mmol), potassium acetate **2b** (59 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $KHCO_3$ (20 mg, 0.2 mmol), in CH_3CN/H_2O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 20.7 mg (42%) of **3mb** as a colorless oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 9.0 Hz, 2H), 6.80 (d, J = 9.0 Hz, 2H), 4.84 – 4.66 (m, 1H), 4.10 – 3.98 (m, 2H), 1.84 – 1.74 (m, 2H), 1.05 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.70, 132.33, 116.46, 113.40, 92.91 (d, J = 172.5 Hz), 69.69 (d, J = 23.6 Hz), 24.68 (d, J = 21.1 Hz), 9.21 (d, J = 5.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -187.41 – -187.85 (m). HRMS (EI+) calcd for $[C_{10}H_{12}^{79}BrFO]^+$ ($[M]^+$): 246.0056, found: 246.0050.

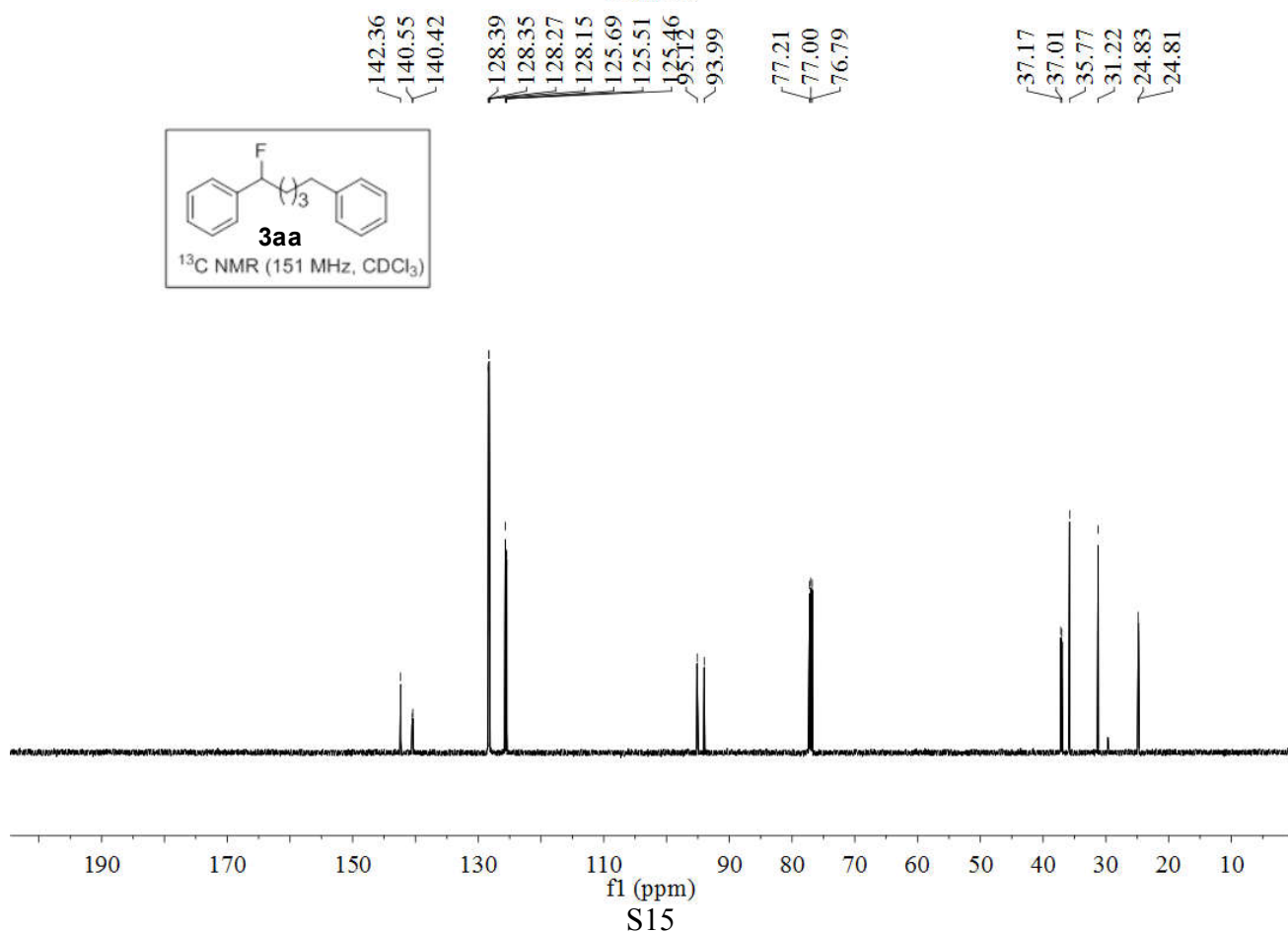
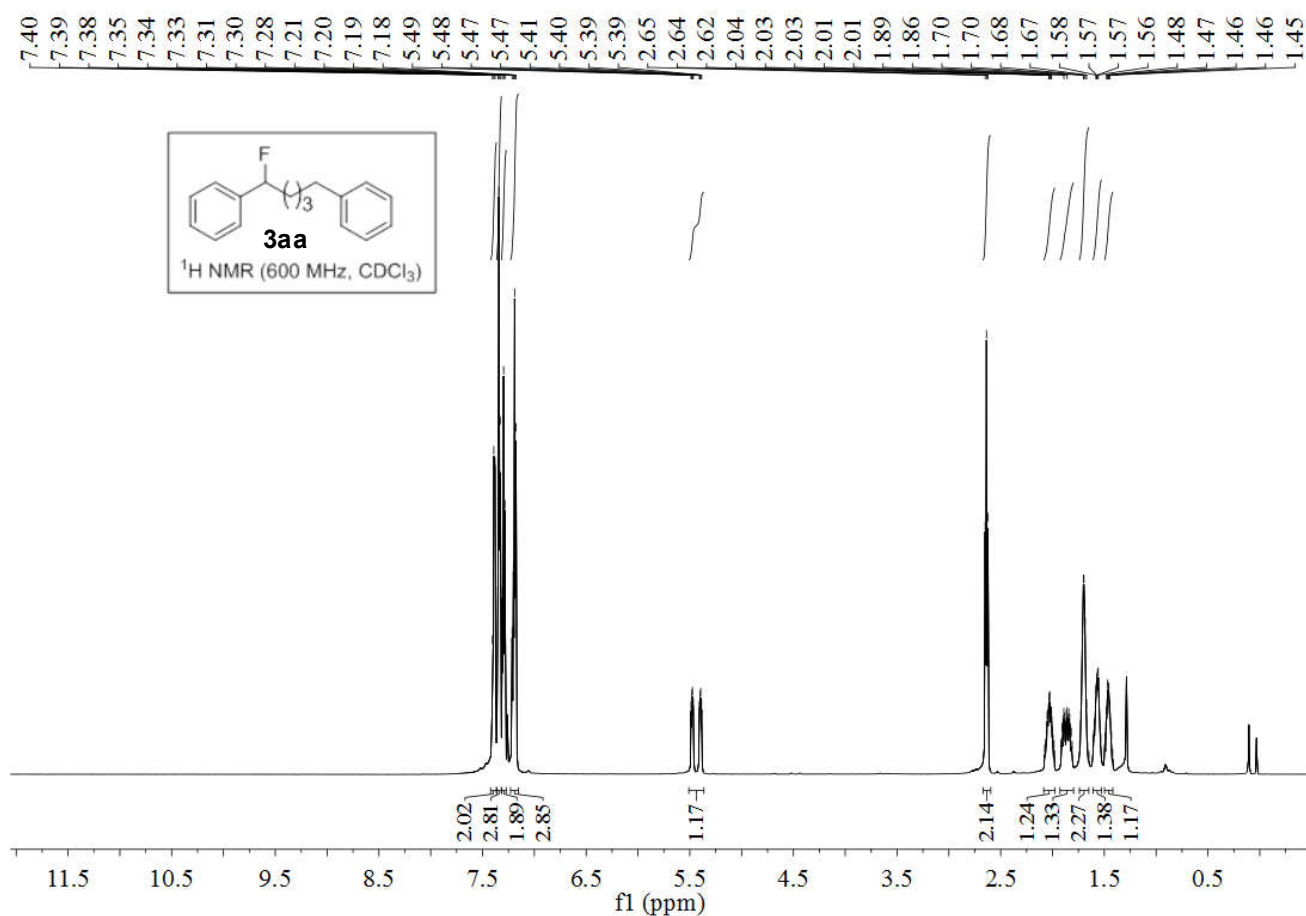


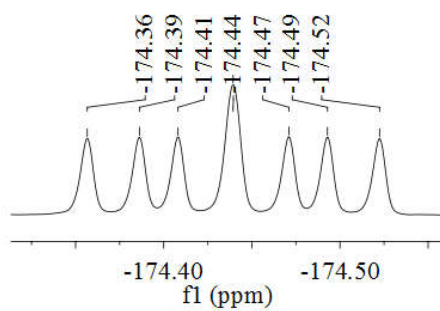
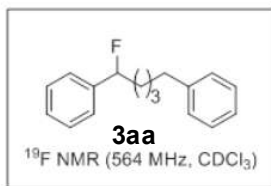
(2-Fluorooctyl)benzene (3nc). The representative procedure was followed using allylbenzene **1n** (23 mg, 0.2 mmol), potassium hexanoate **2c** (93 mg, 0.6 mmol), Selectfluor (213 mg, 0.6 mmol), $AgNO_3$ (6.8 mg, 0.04 mmol), $KHCO_3$ (20 mg, 0.2 mmol), in CH_3CN/H_2O (v/v = 1/1, 2 mL), at room temperature for 24 h. Isolation by column chromatography (petroleum ether/EtOAc: 100/1) yielded 19.6 mg (47%) of **3nc** as a colorless oil. 1H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.30 (m, 2H), 7.25 – 7.22 (m, 3H), 4.74 – 4.58 (m, 1H), 3.04 – 2.78 (m, 2H), 1.69 – 1.47 (m, 4H), 1.33 – 1.23 (m, 6H), 0.88 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.49 (d, J = 4.5 Hz), 129.35, 128.37, 126.46, 94.62 (d, J = 170.7 Hz), 41.66 (d, J = 21.7 Hz), 34.63, 31.71, 29.08, 25.06 (d, J = 4.3 Hz), 22.55, 14.04. ^{19}F NMR (564 MHz, $CDCl_3$) δ -167.58 – -179.99 (m). HRMS (EI+) calcd for $[C_{14}H_{21}F]^+$ ($[M]^+$): 208.1627, found: 208.1622.

9. Reference

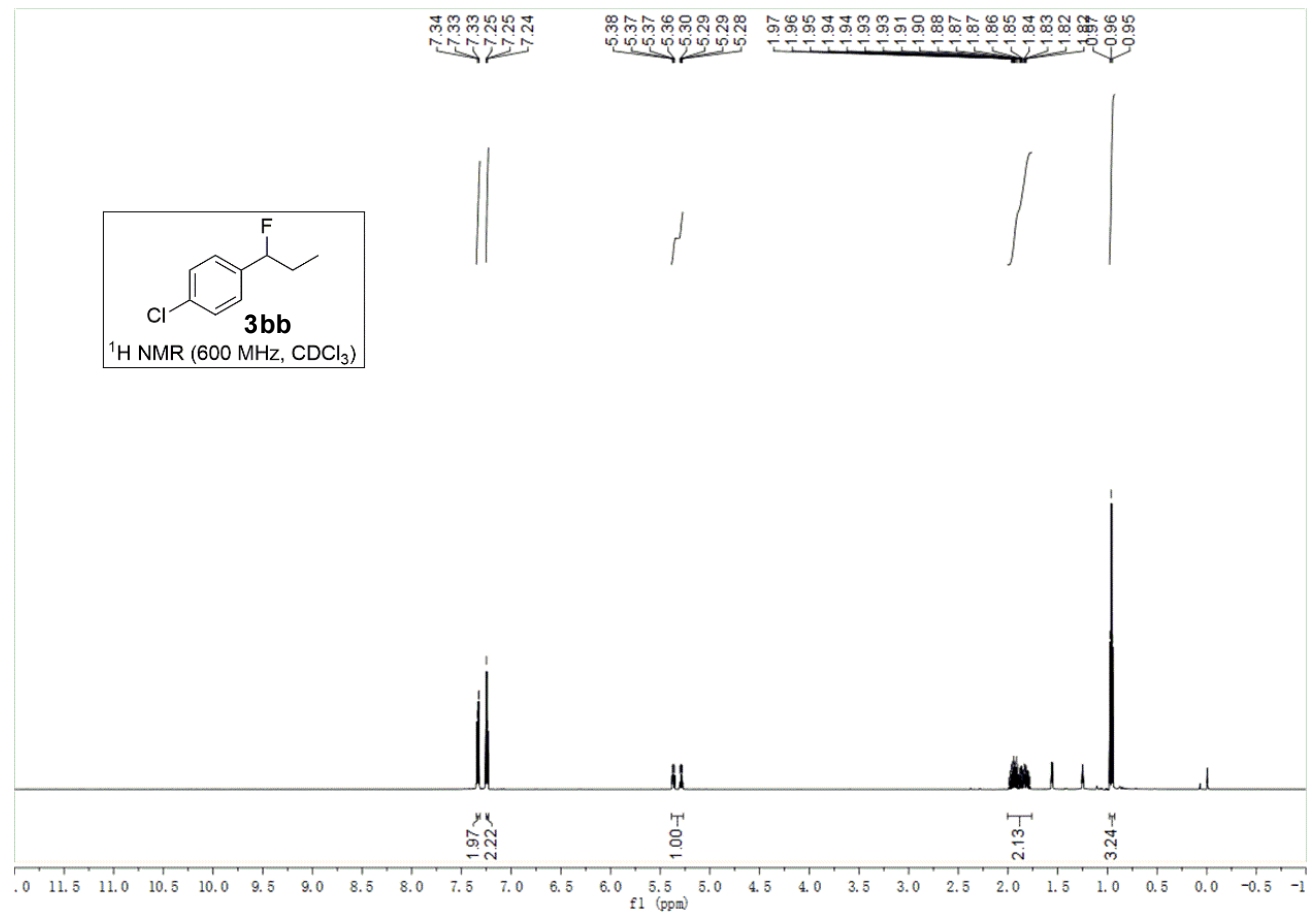
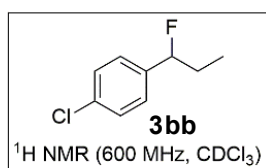
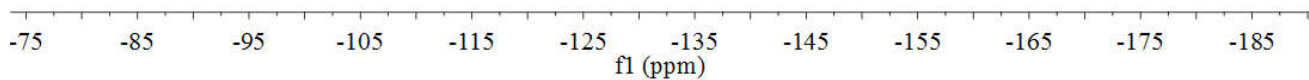
- (1) Deng, W.; Feng, W.; Li, Y.; Bao, H. *Org. Lett.* **2018**, *20*, 4245.

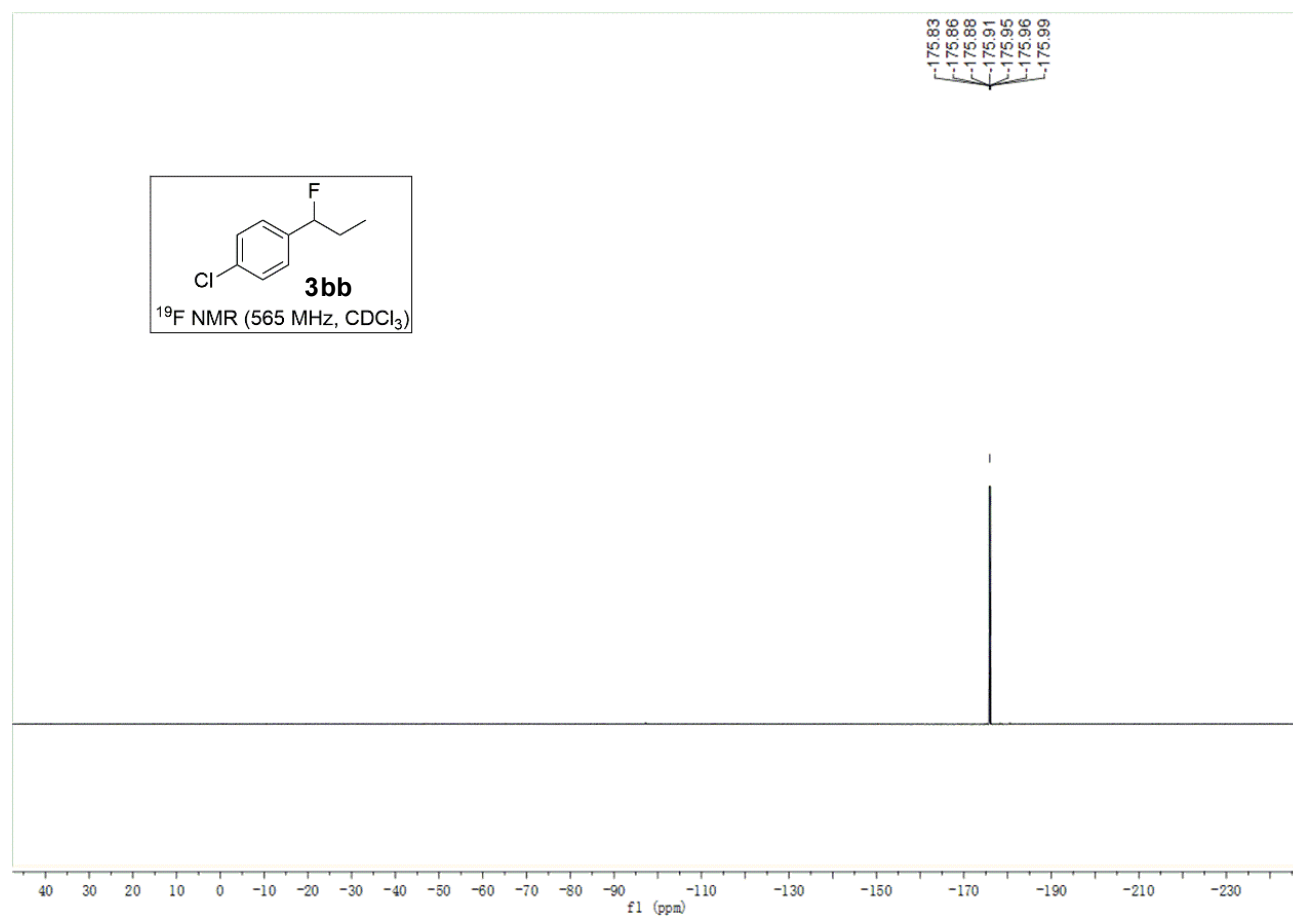
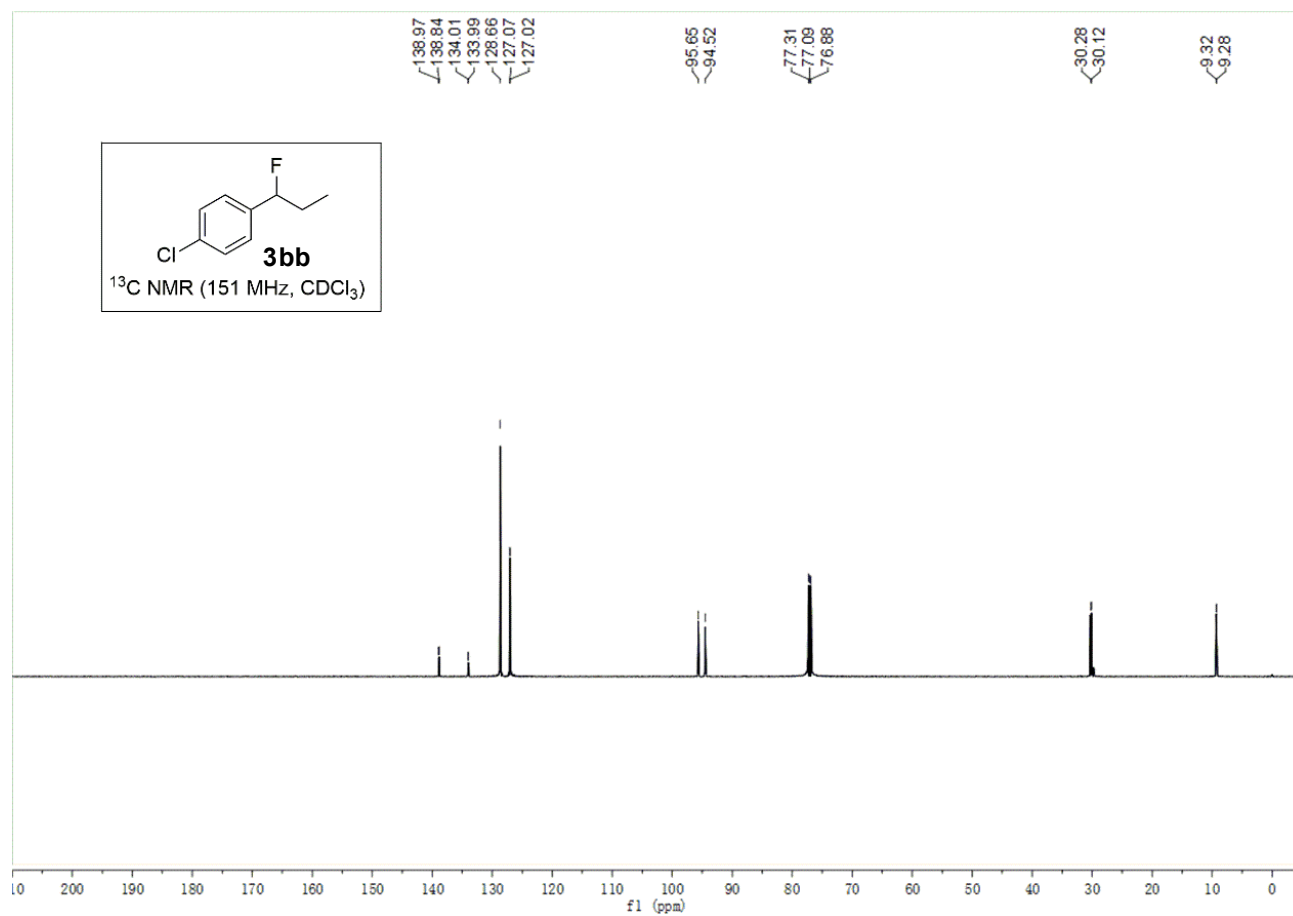
10. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR Spectra

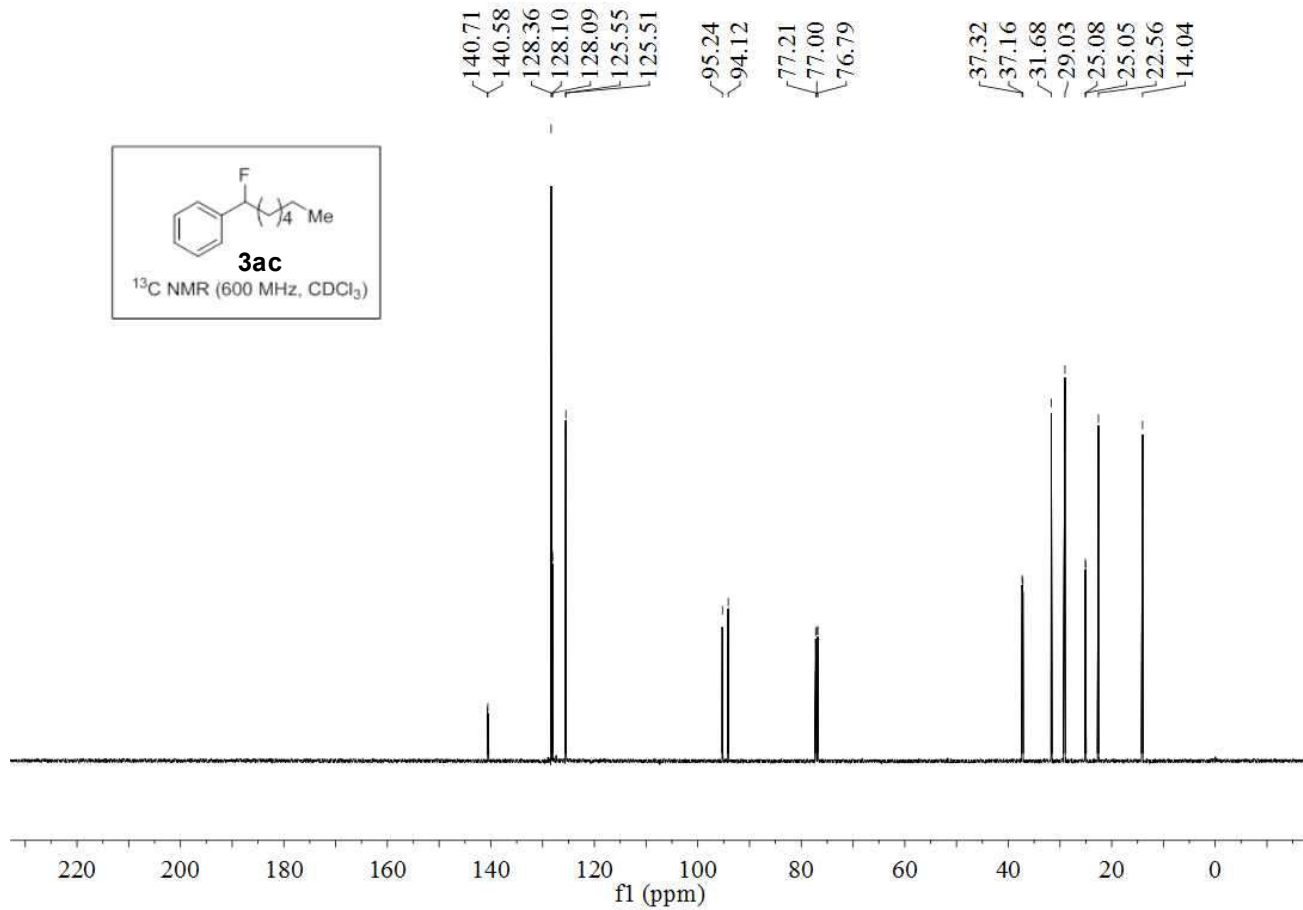
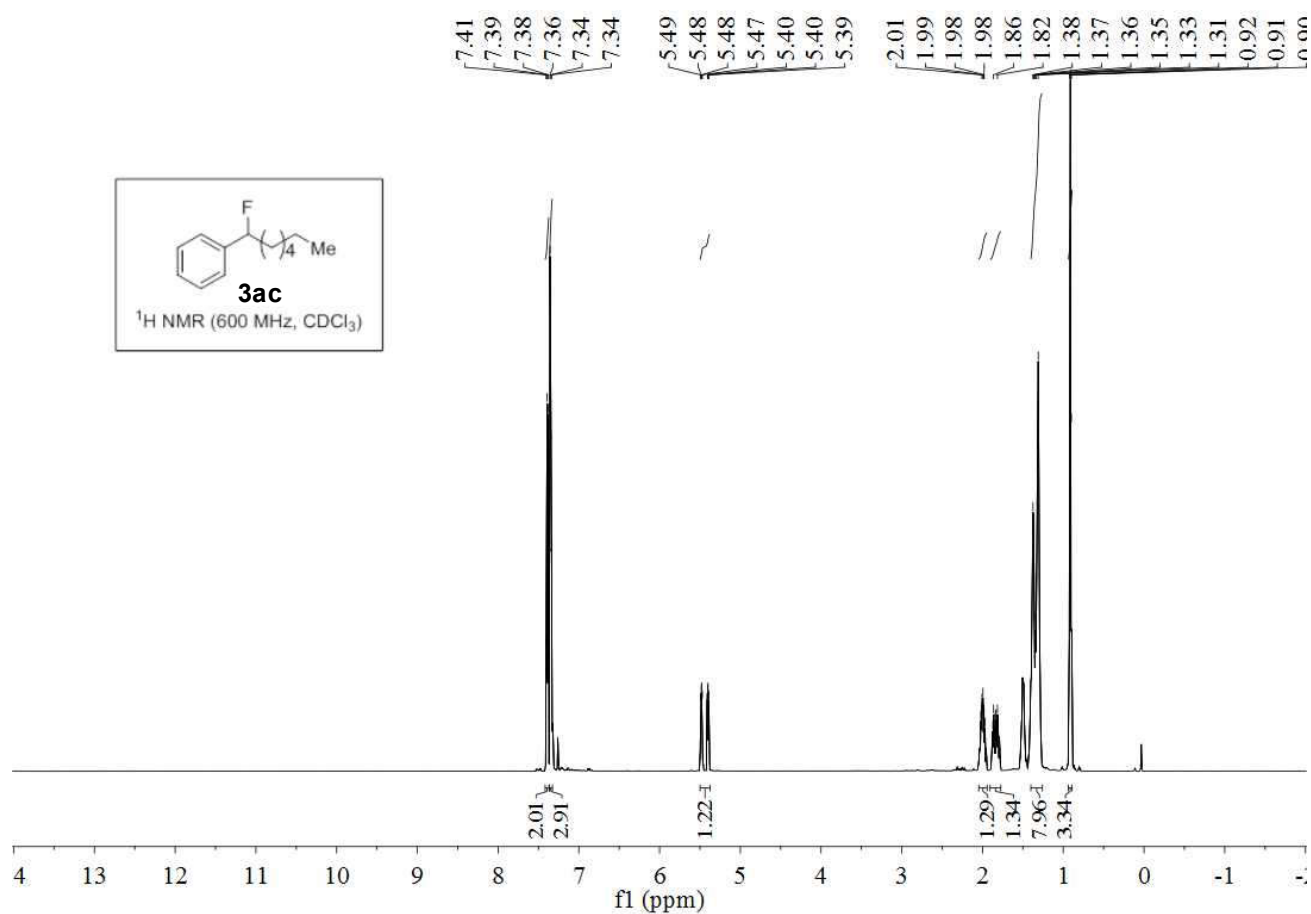


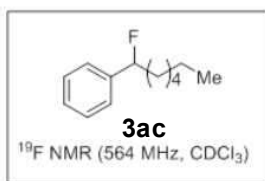


-174.36
 -174.39
 -174.41
 -174.44
 -174.47
 -174.49
 -174.52

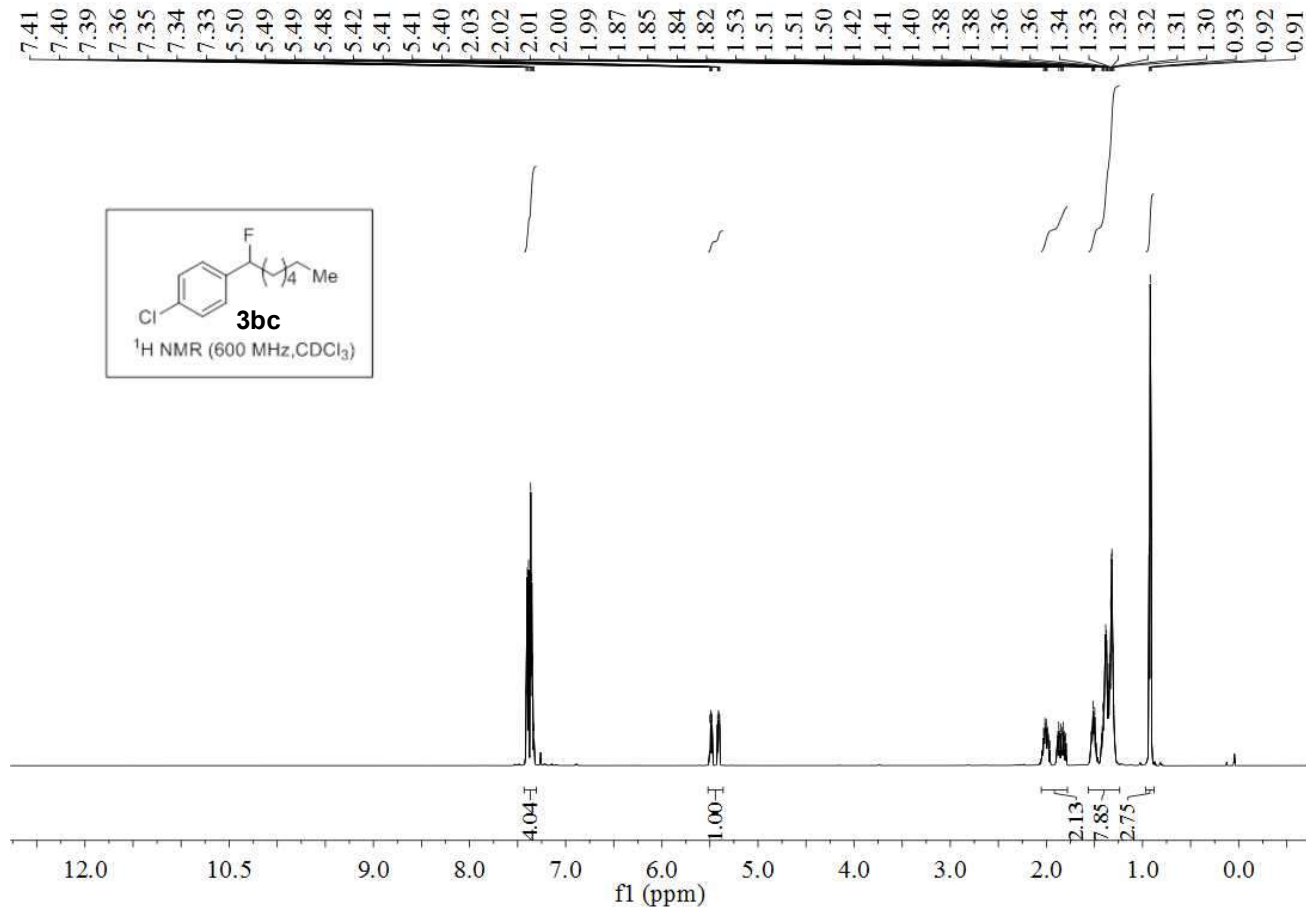
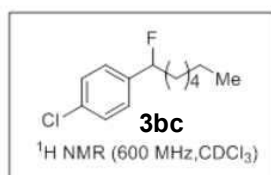
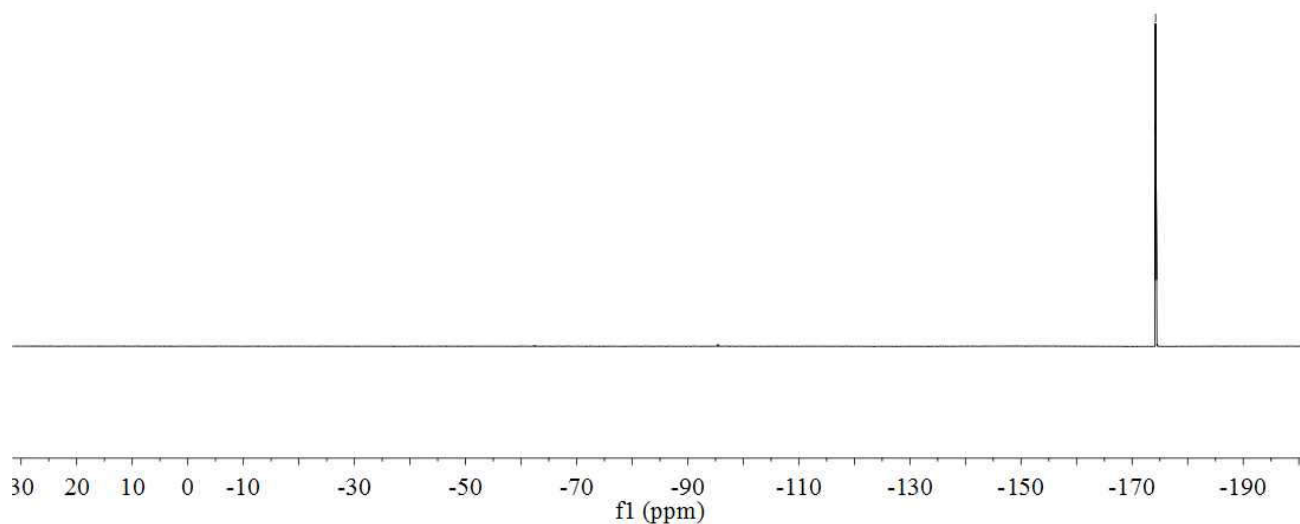


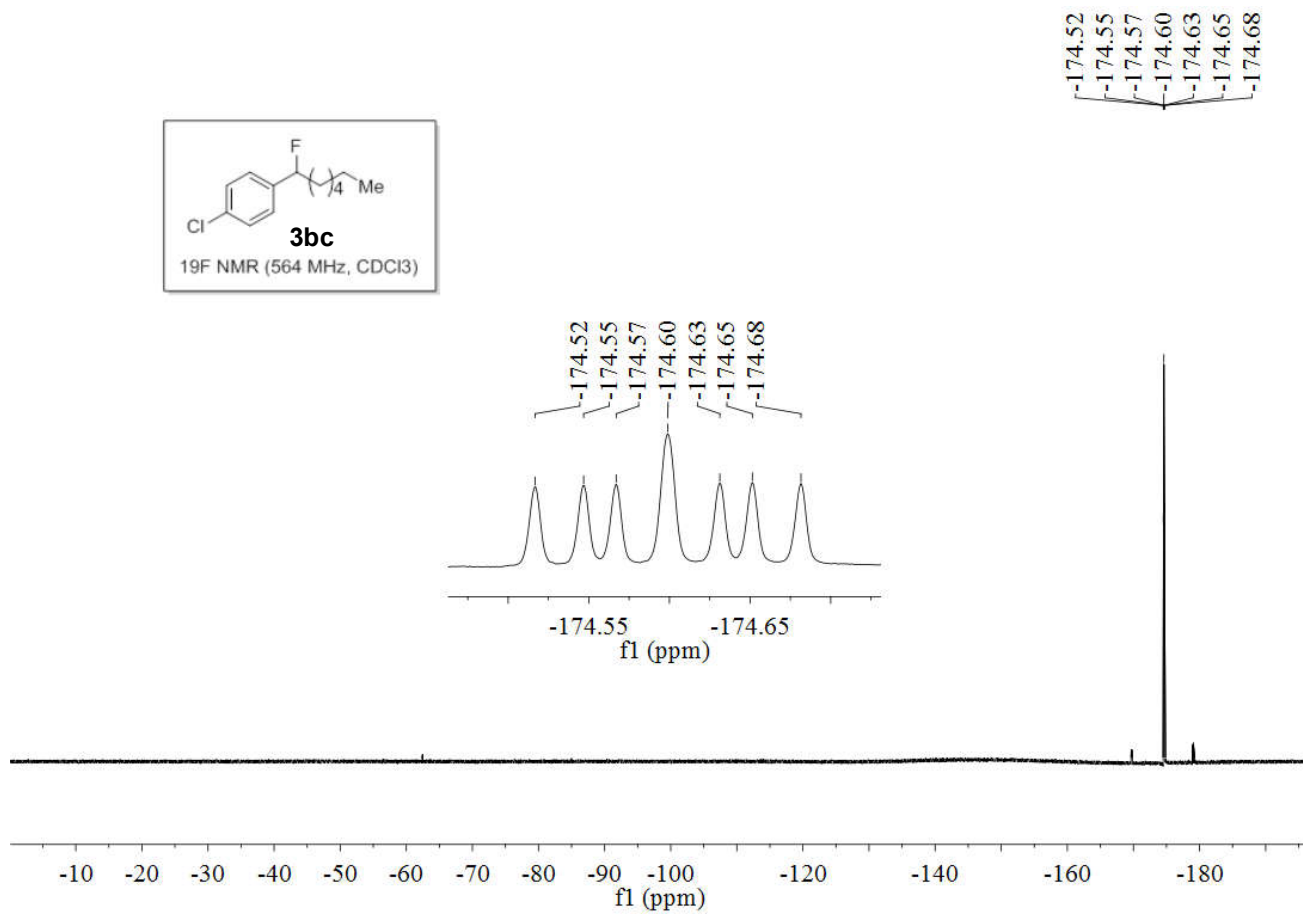
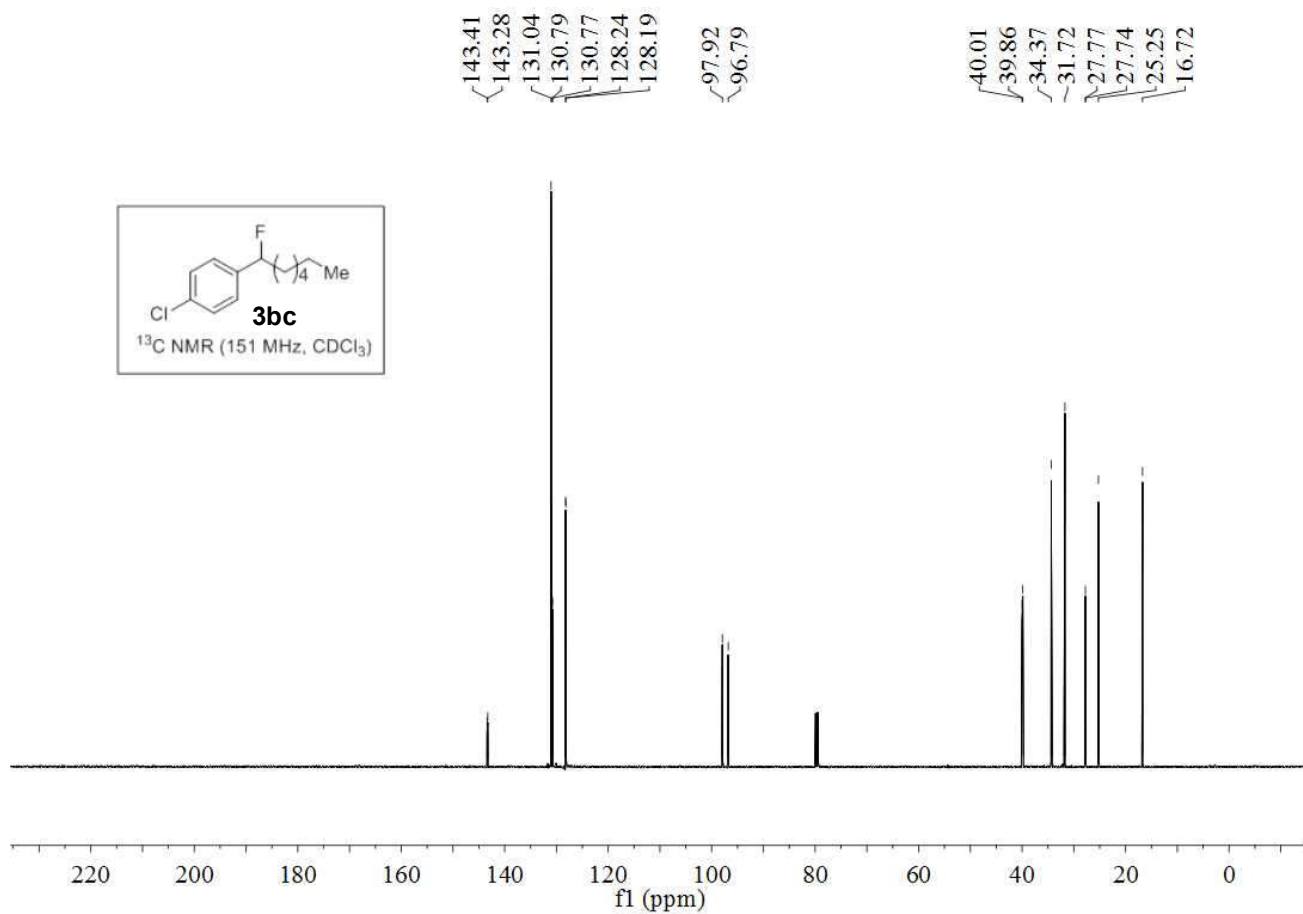


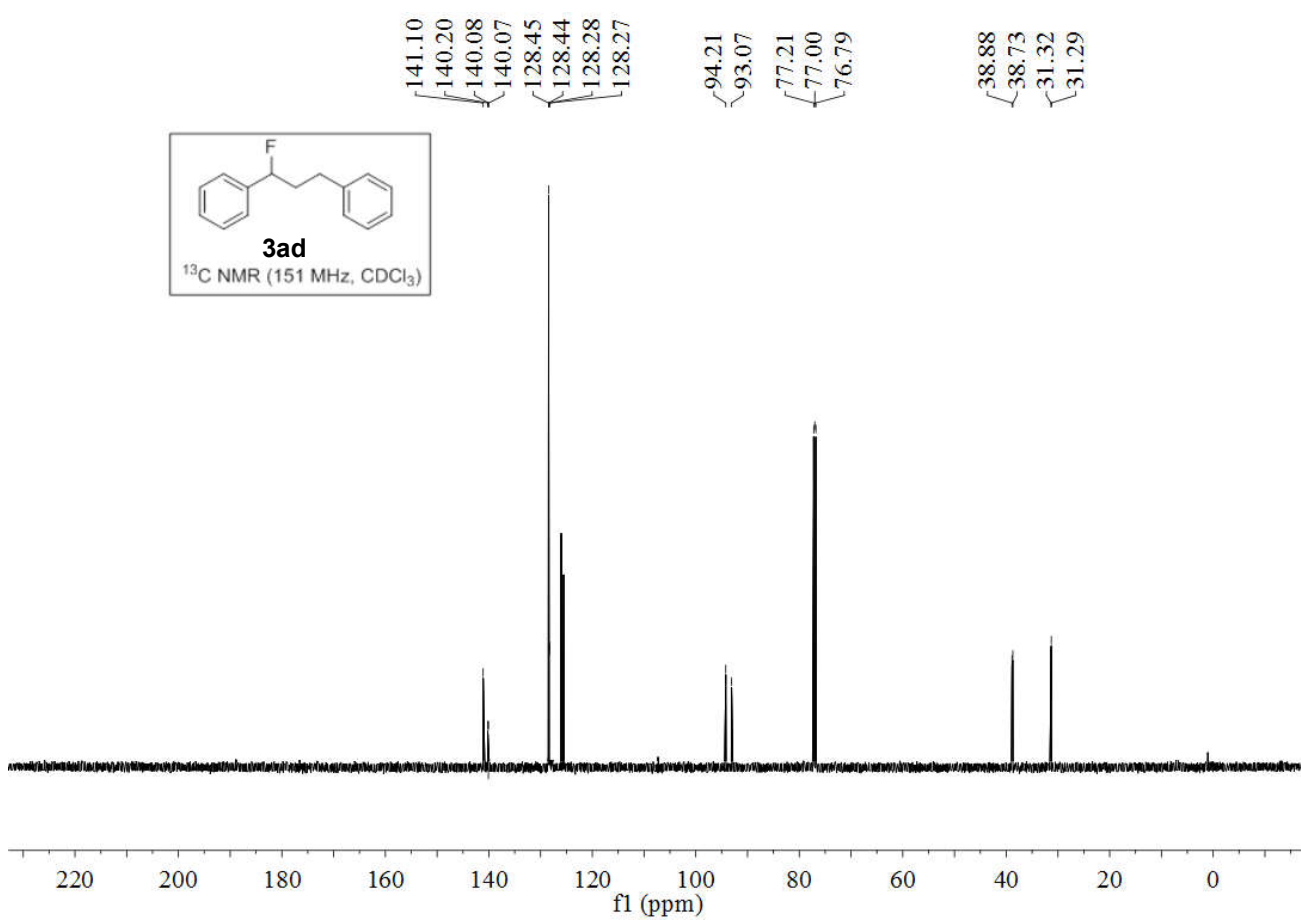
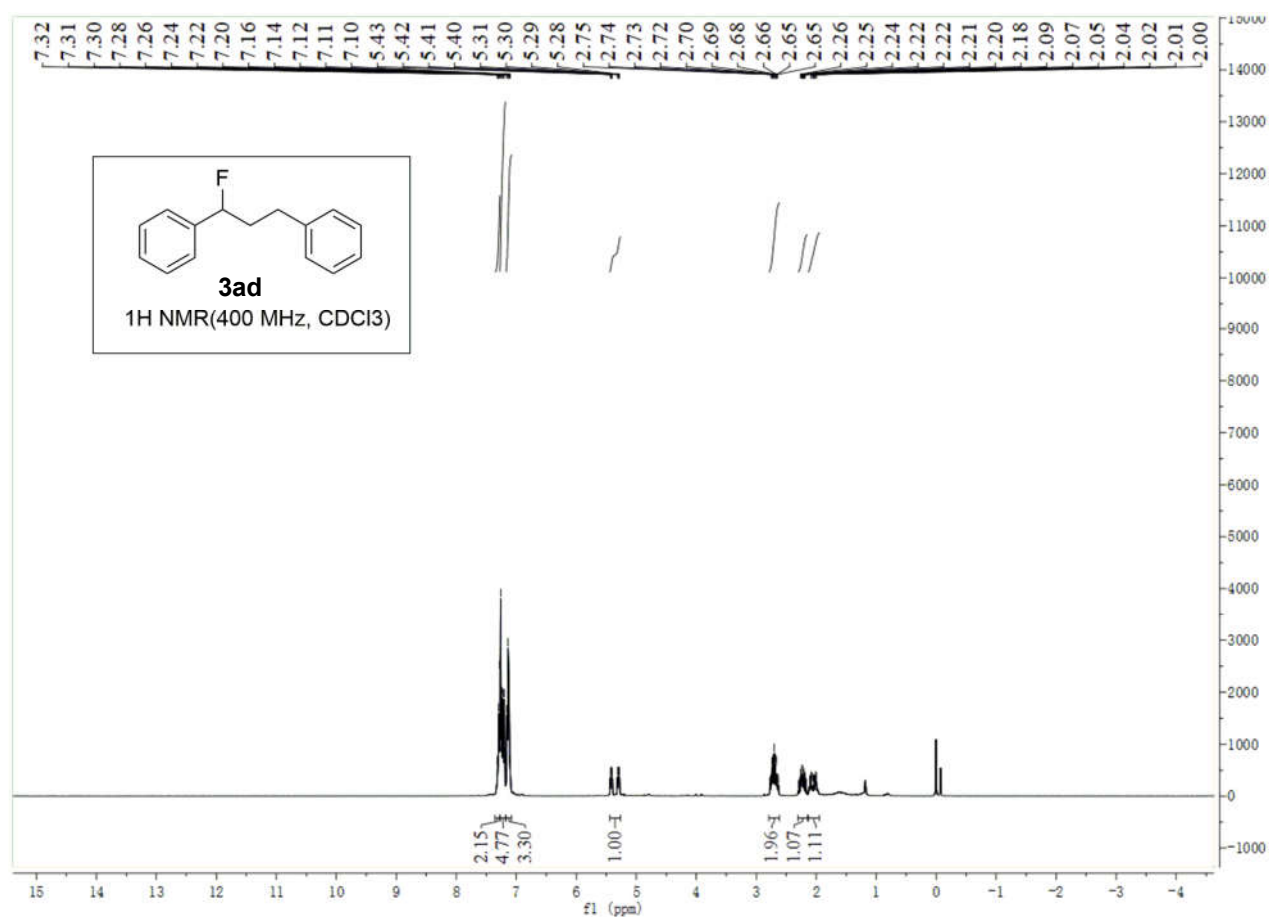


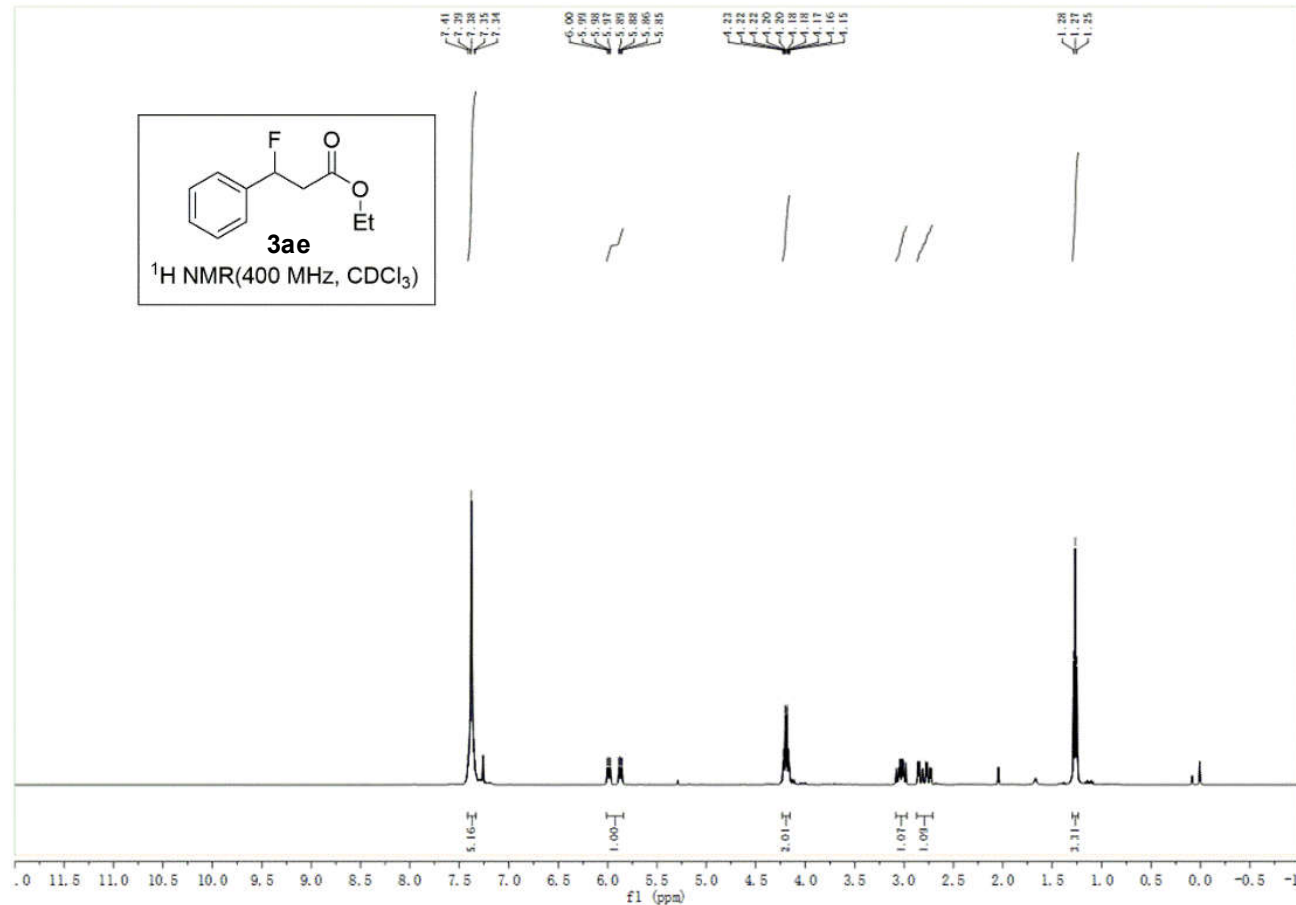
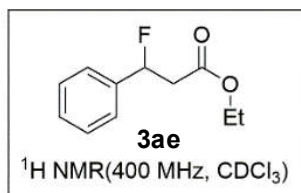
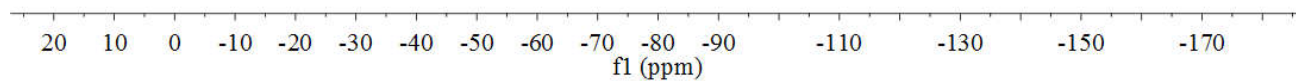
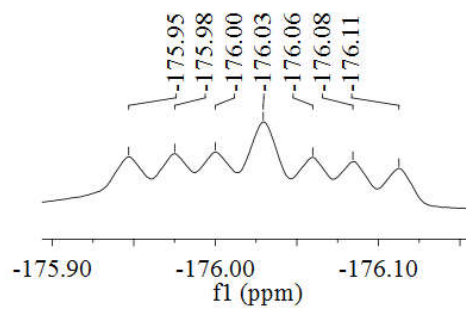


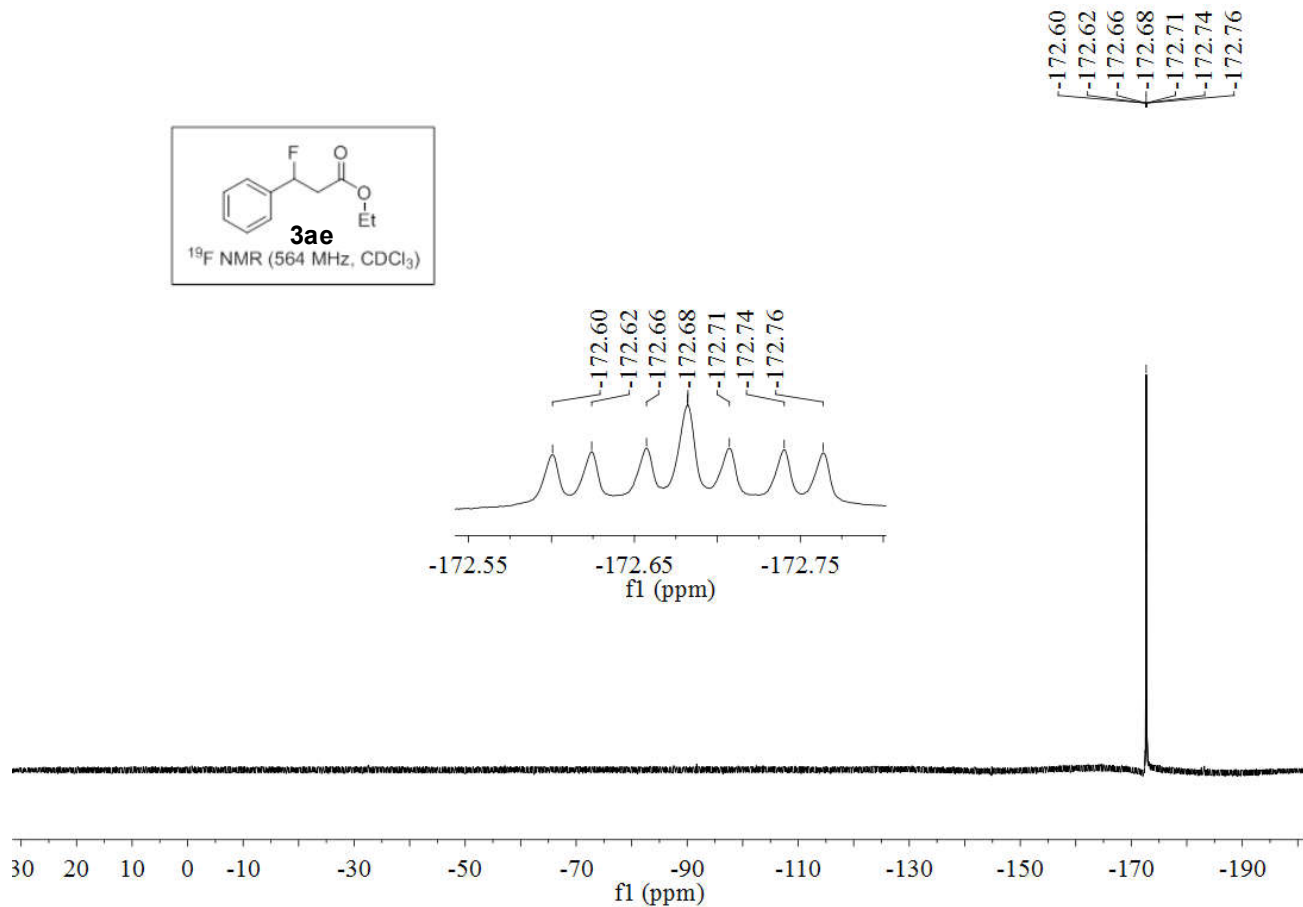
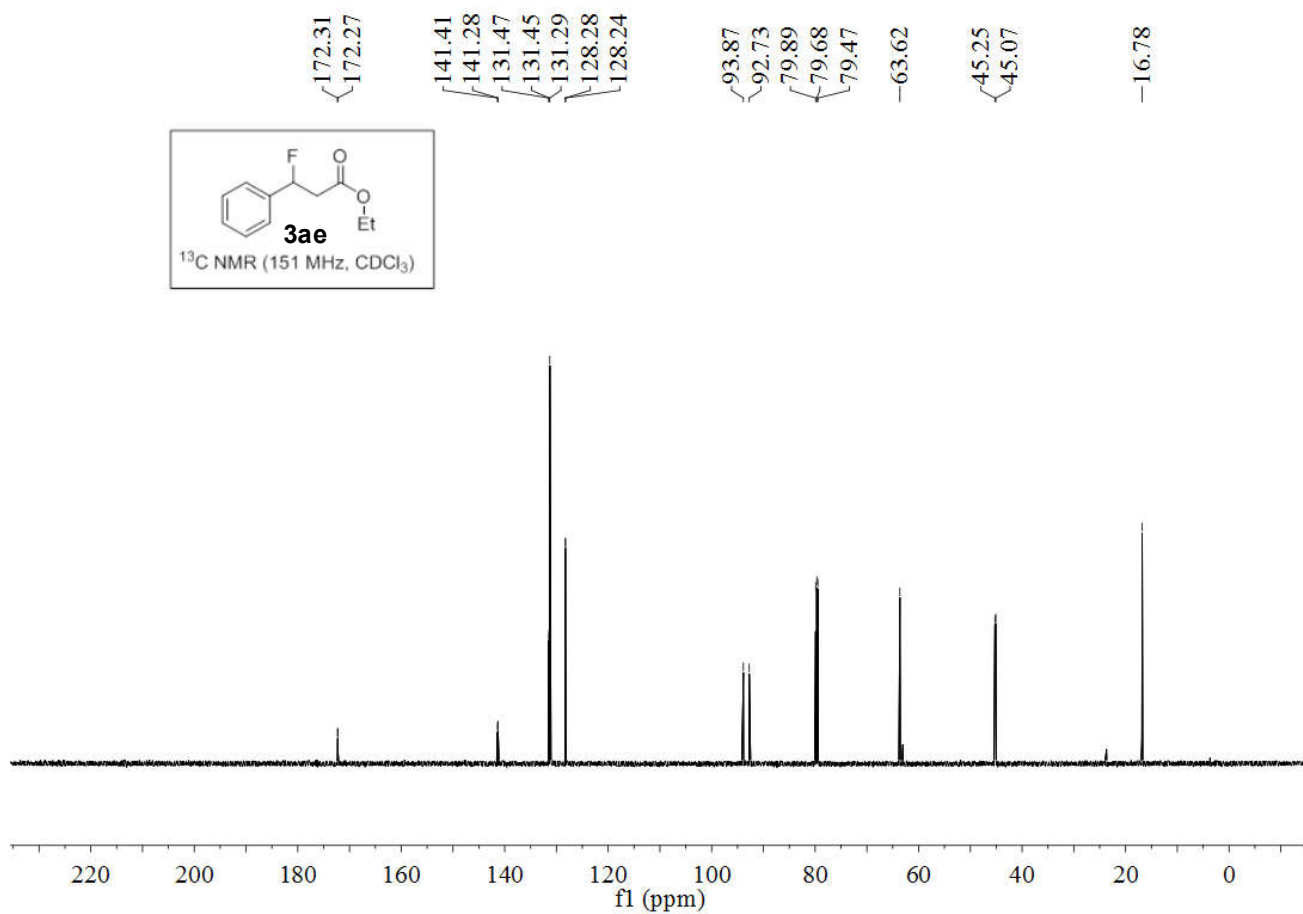
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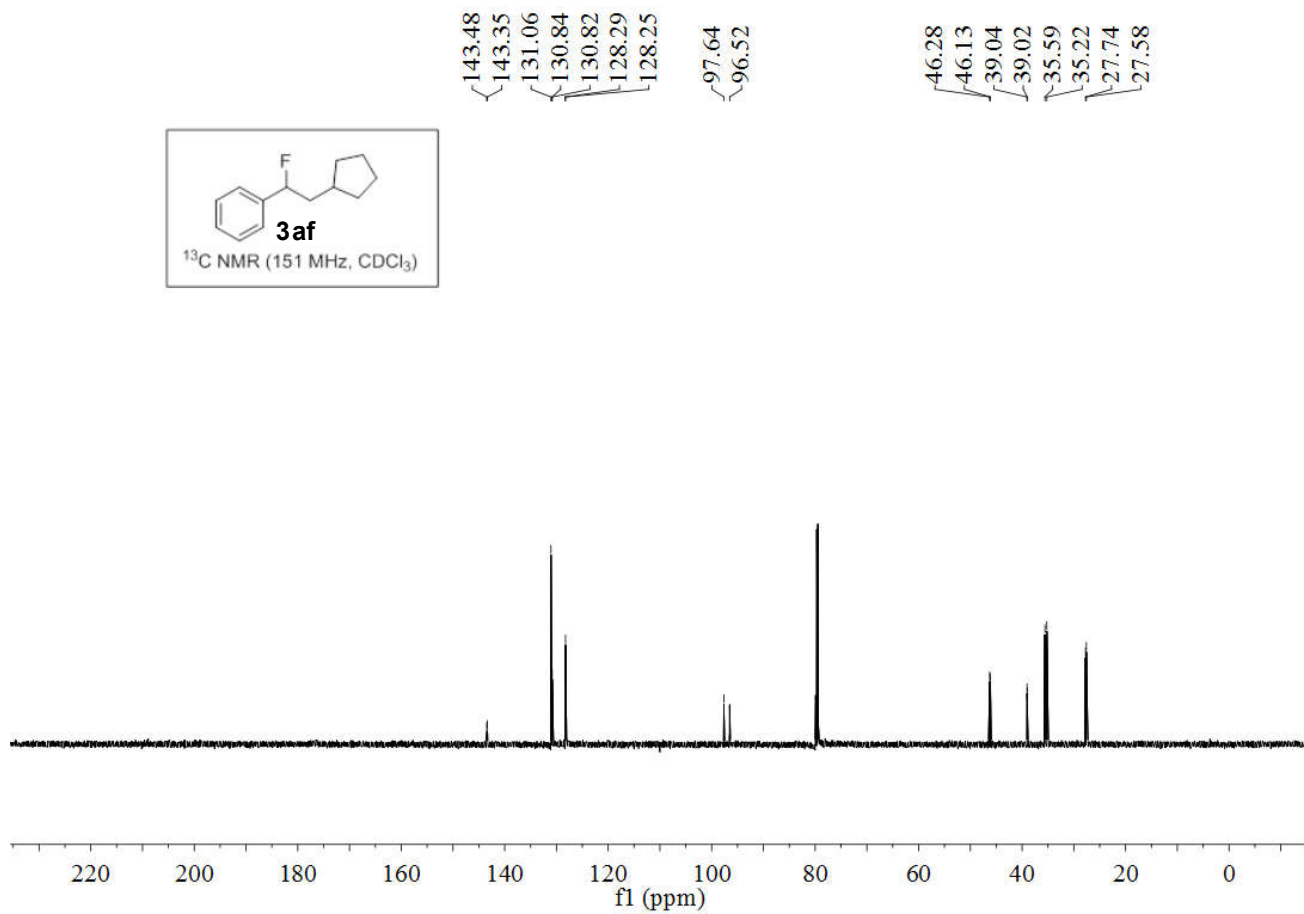
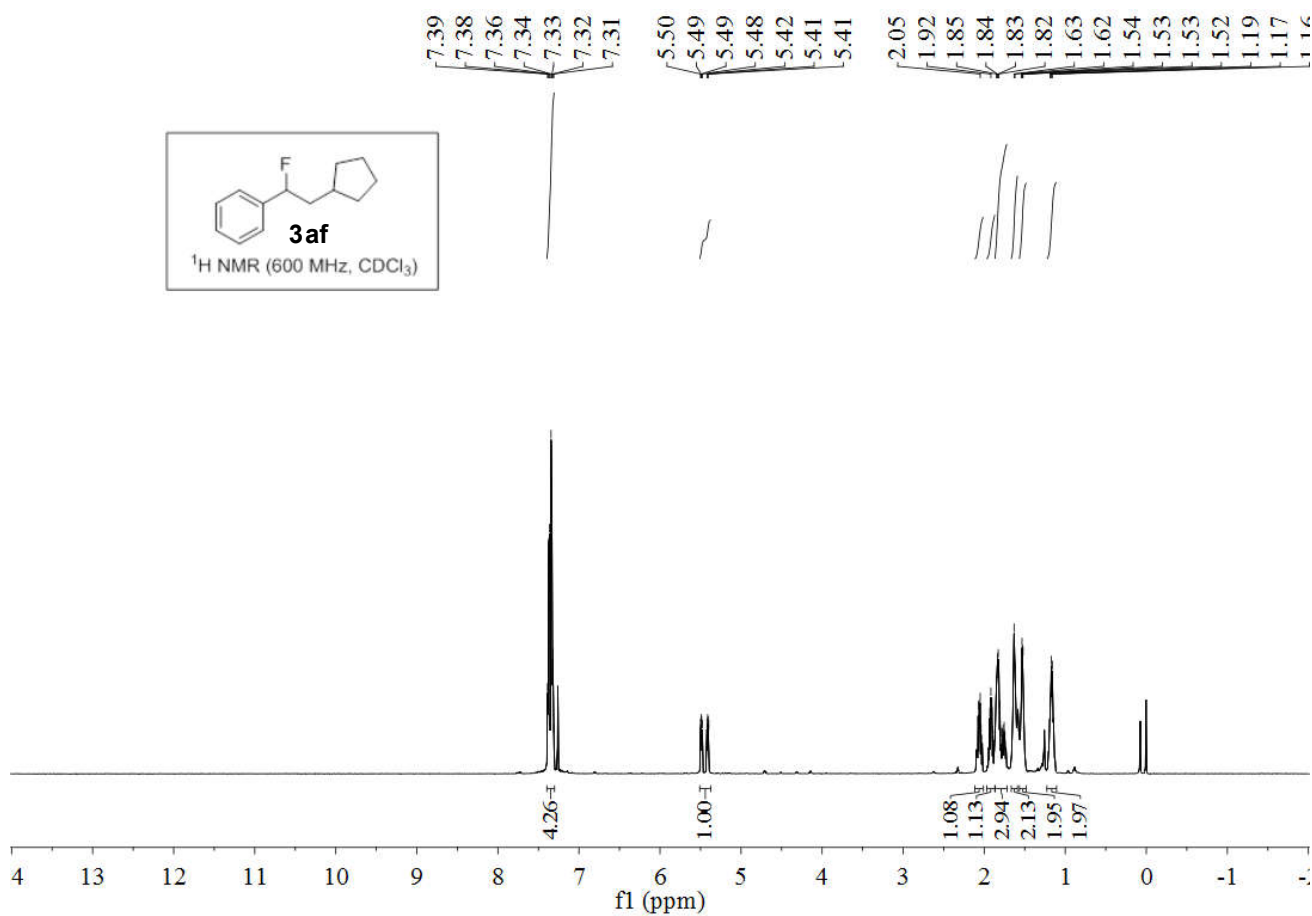


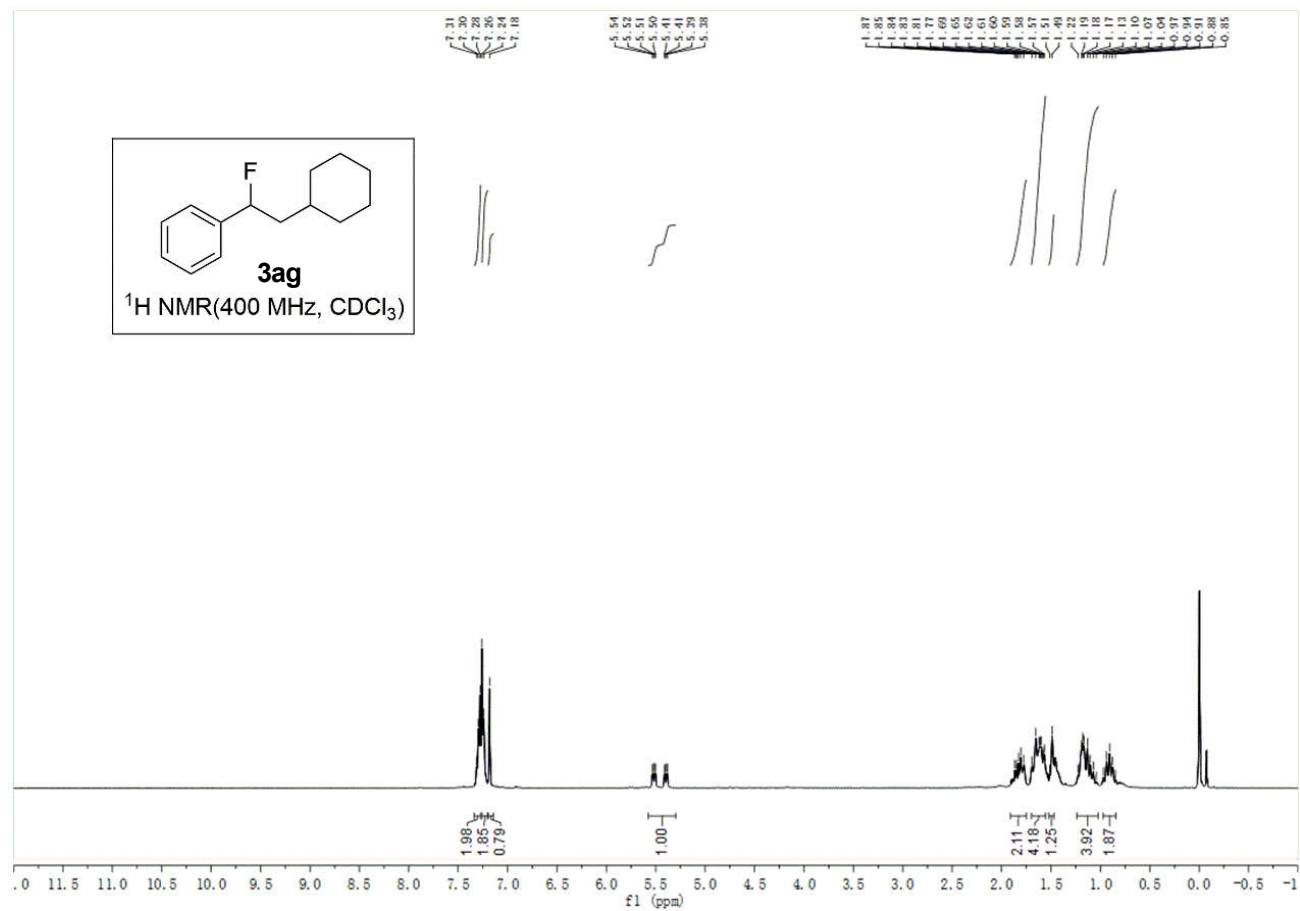
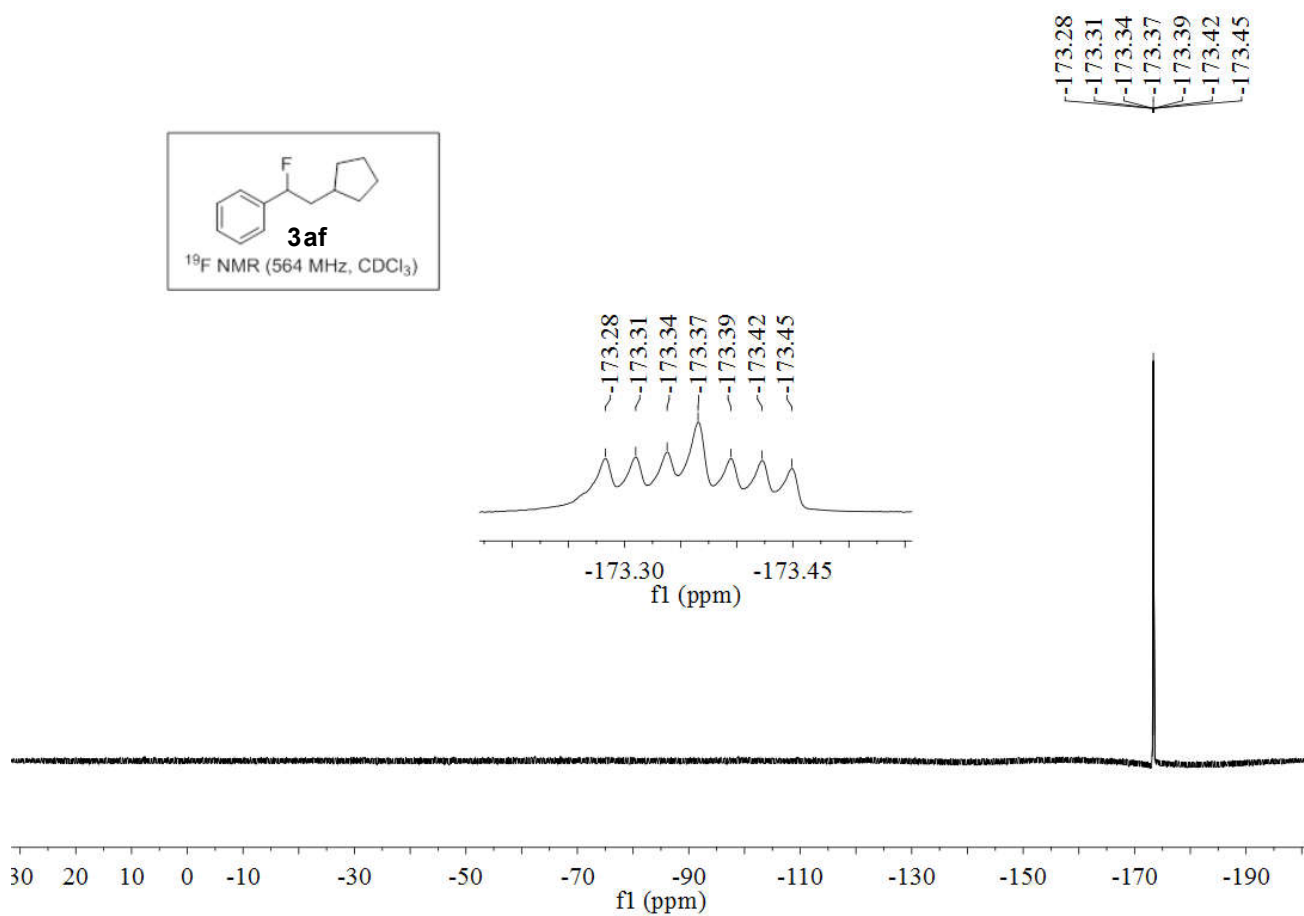


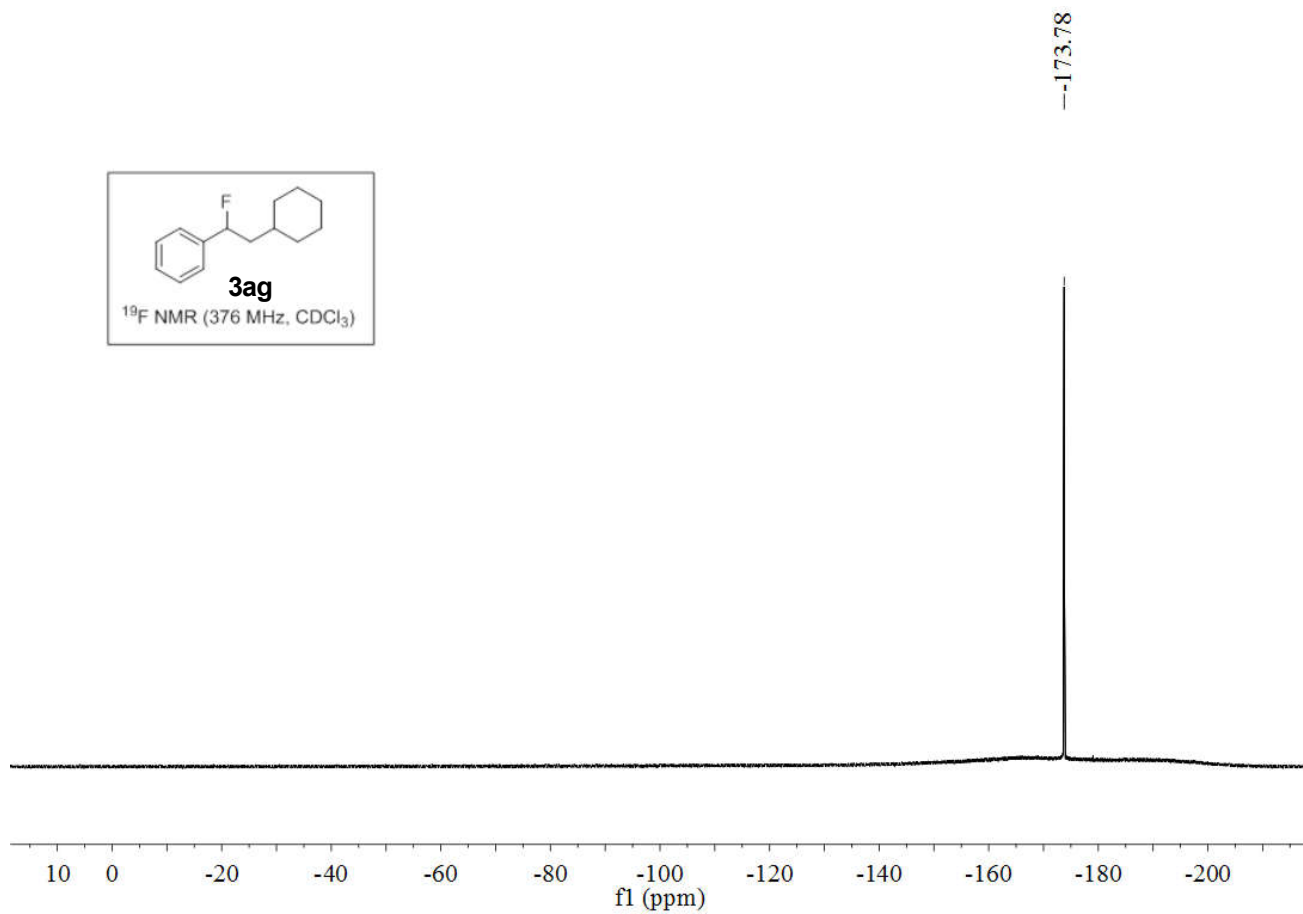
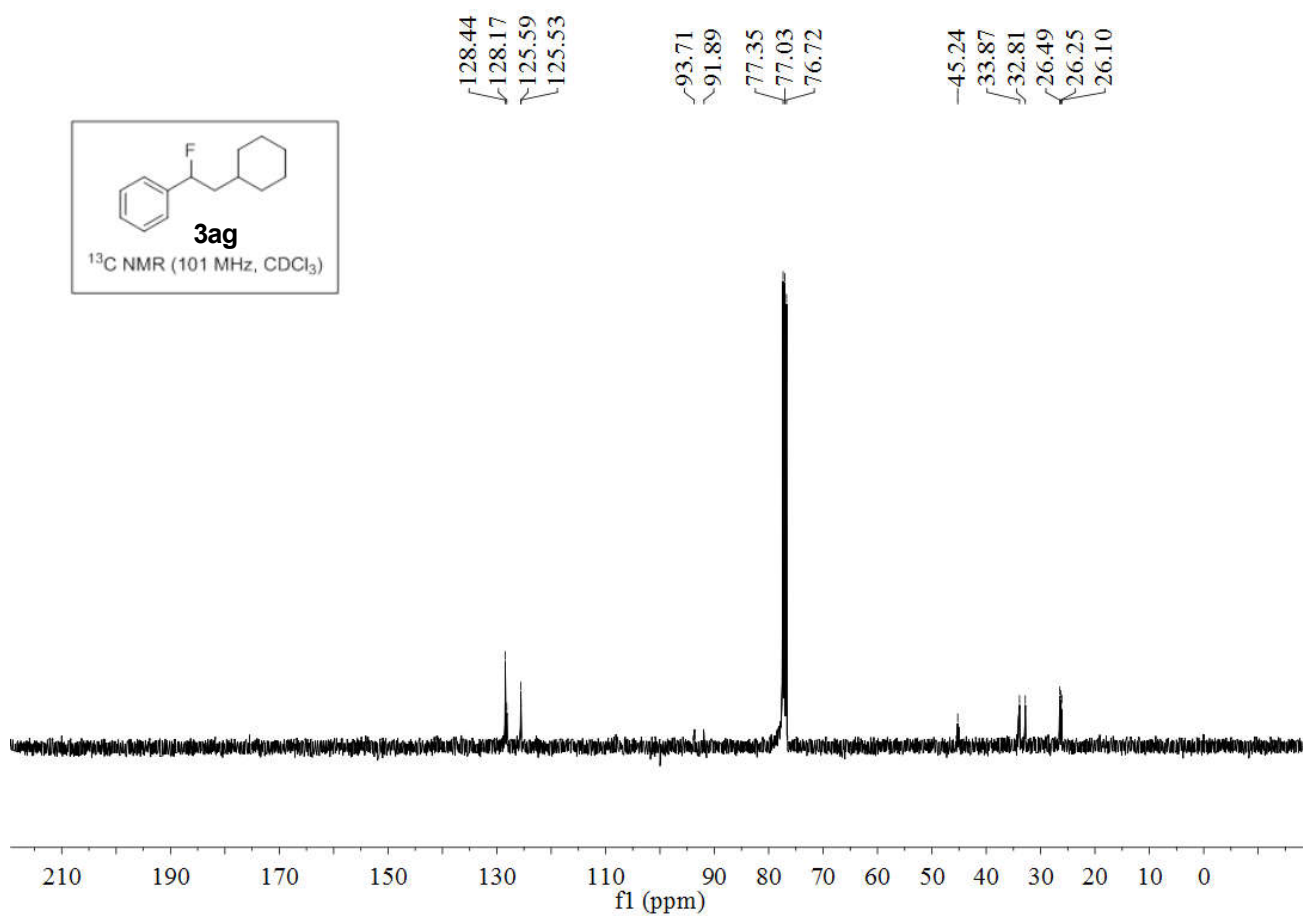


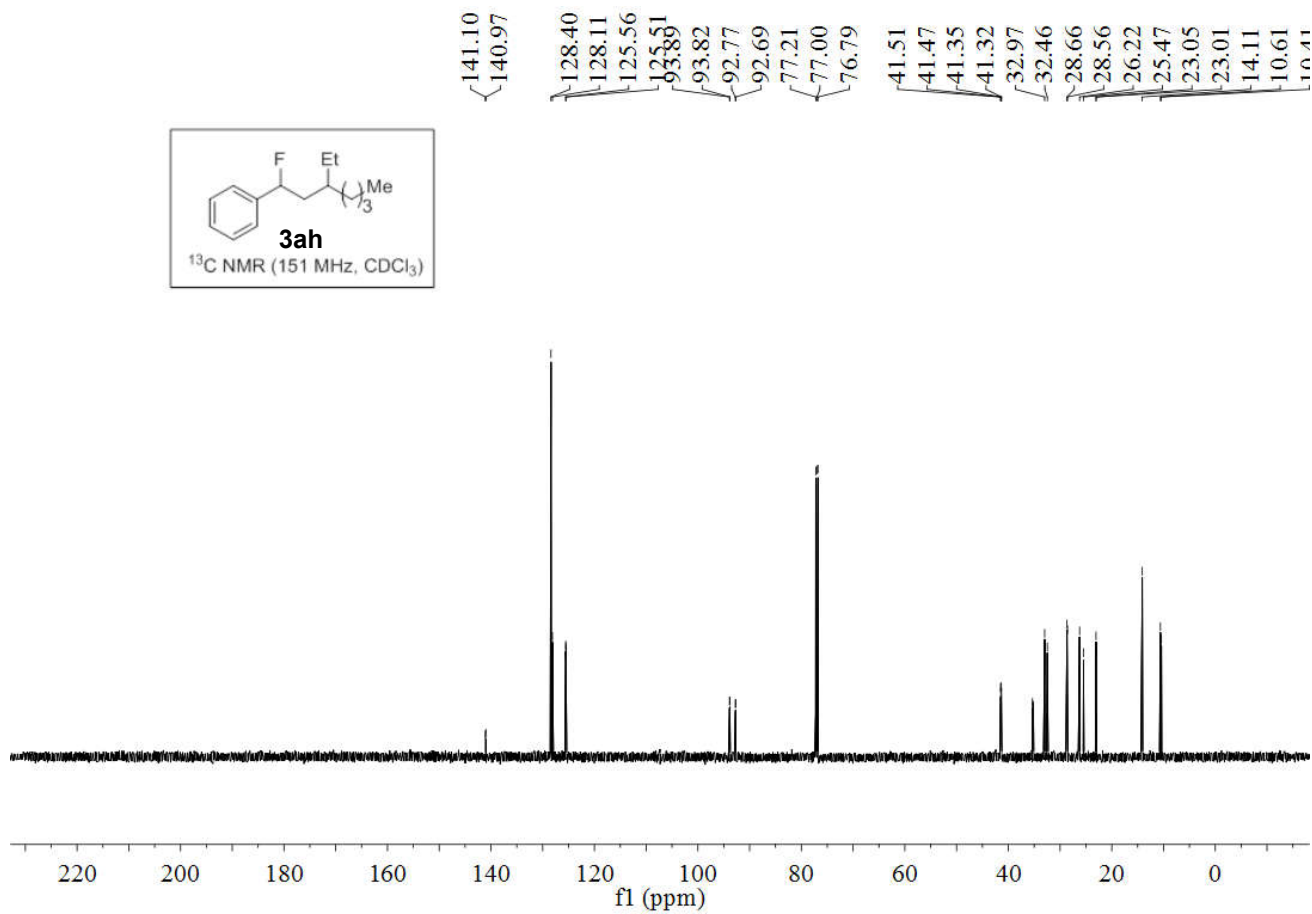
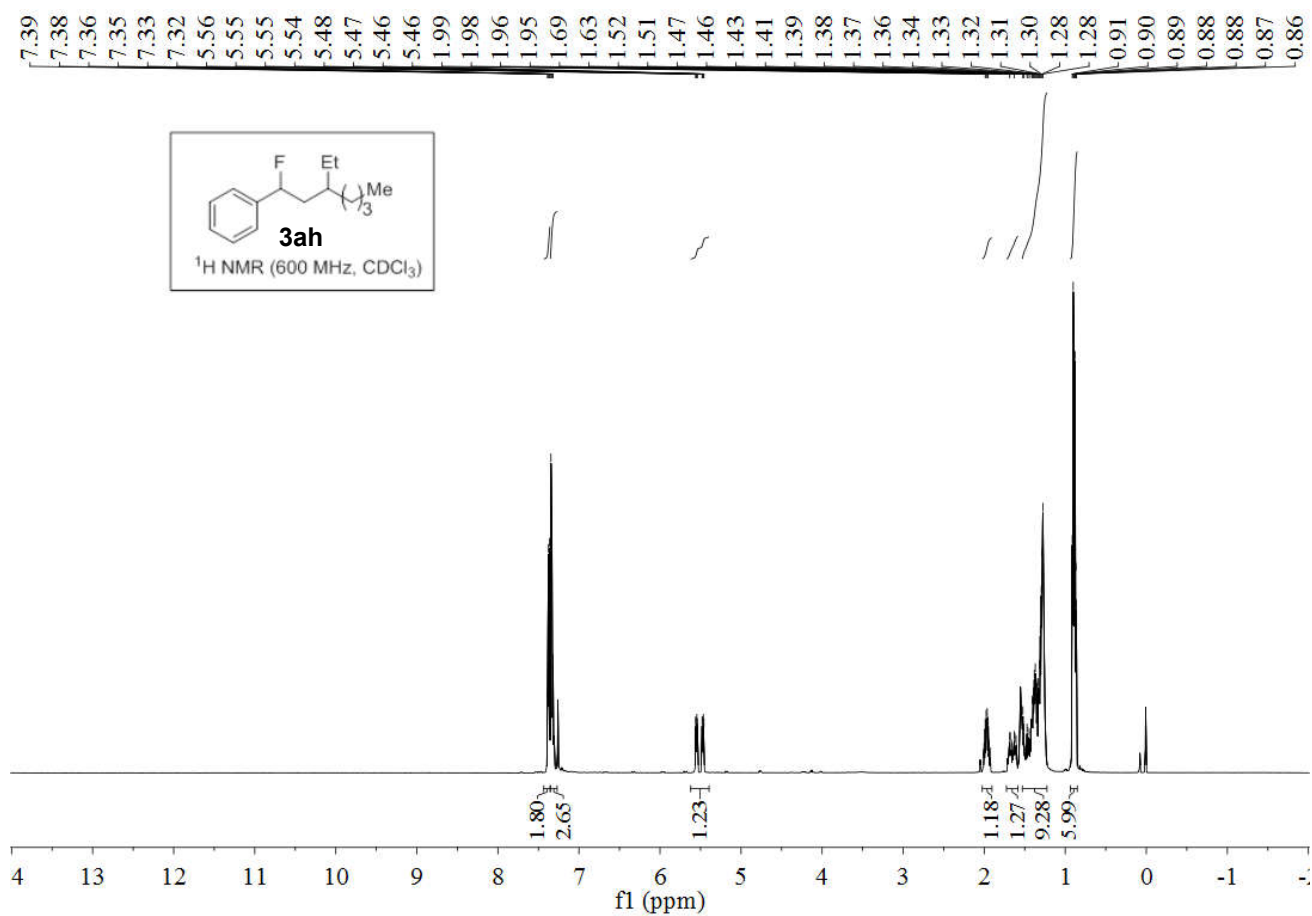


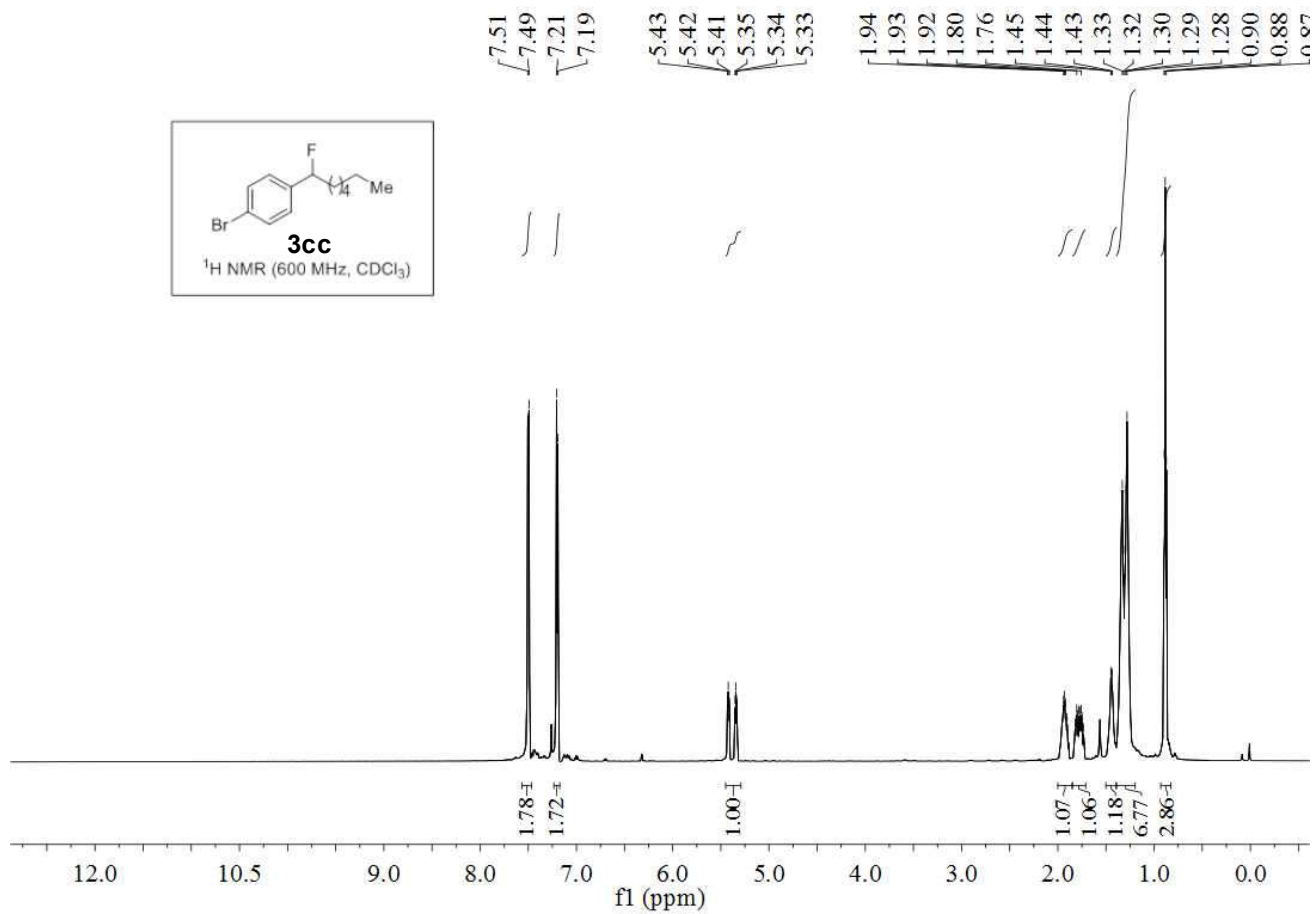
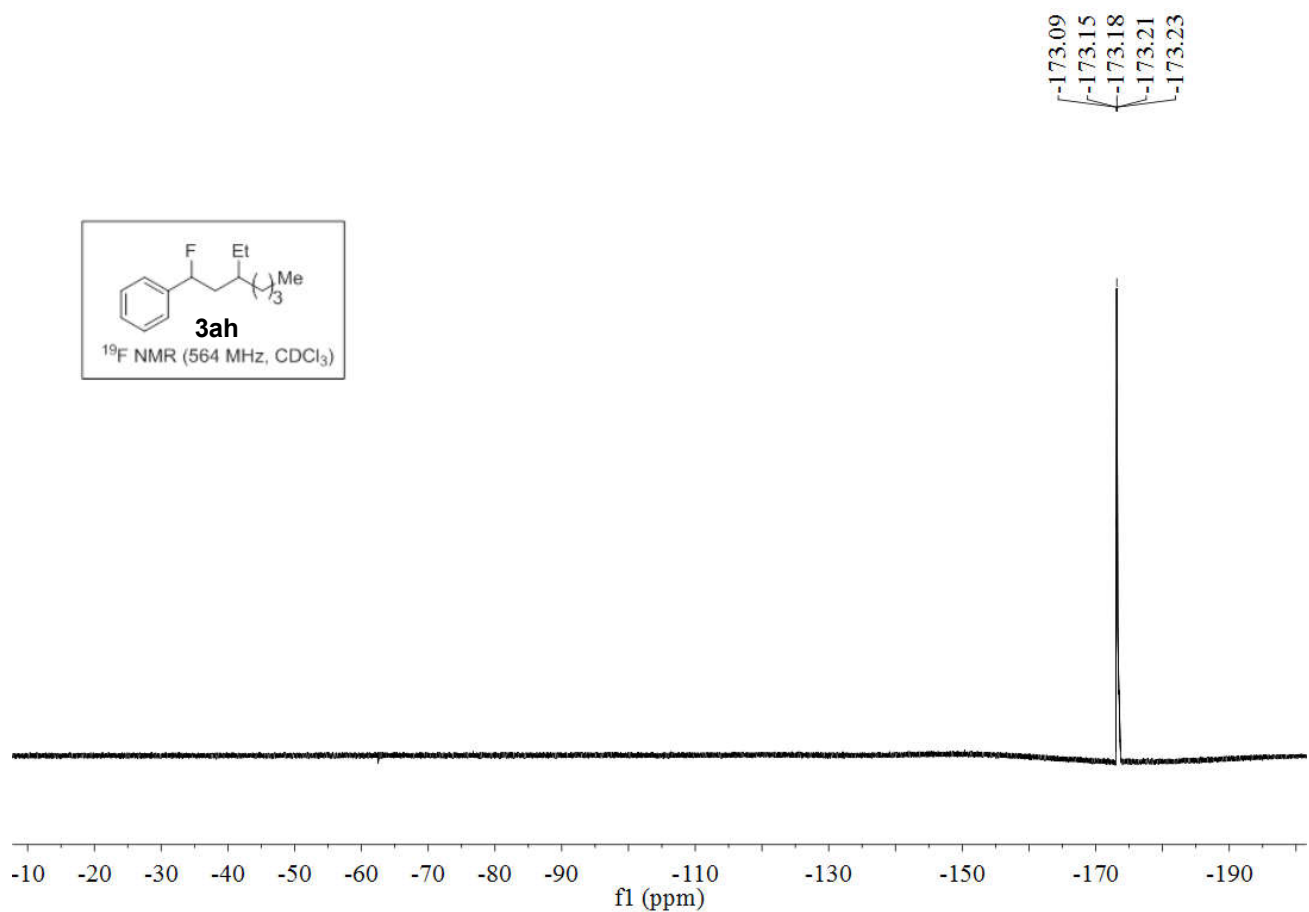


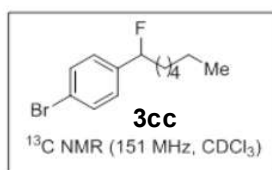




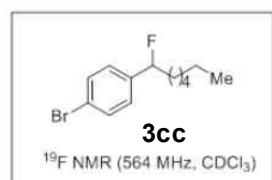
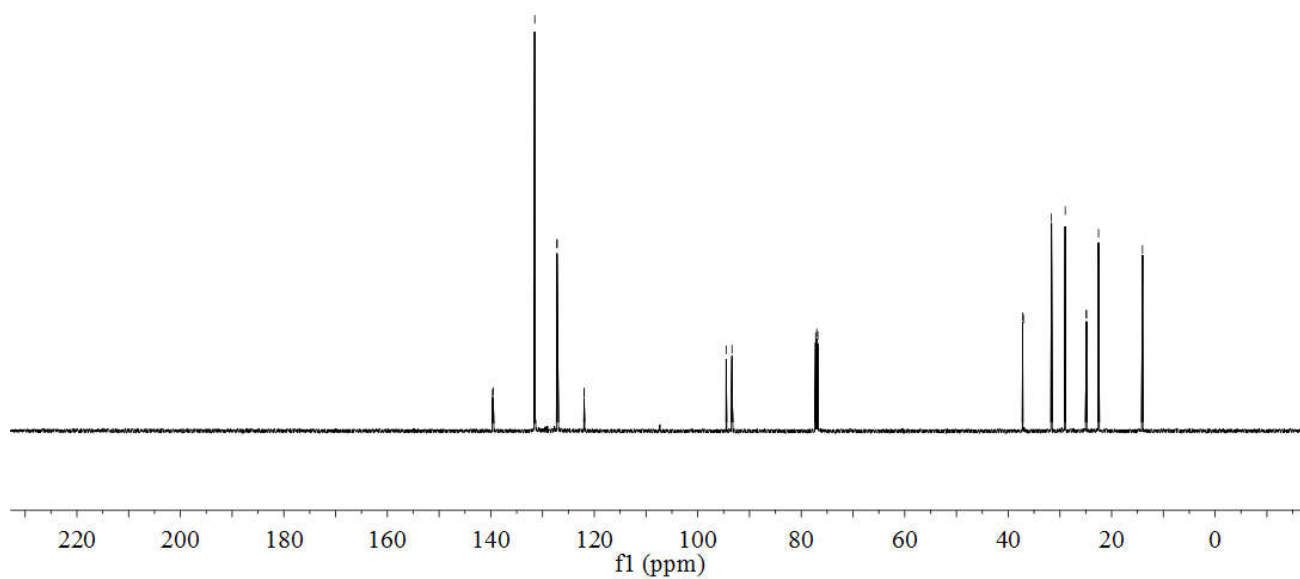








139.68, 139.54, 131.50, 127.22, 127.18, 121.98, 121.96, 94.51, 93.37, 77.21, 77.00, 76.79, 37.20, 37.05, 31.64, 28.97, 24.90, 24.87, 22.53, 14.04



-175.06, -175.09, -175.11, -175.14, -175.17, -175.19, -175.22

