

Supporting Information

Palladium-Catalyzed NHC Ligand-Controlled Regiodivergent Allyl-Fluoroallyl Cross-Couplings

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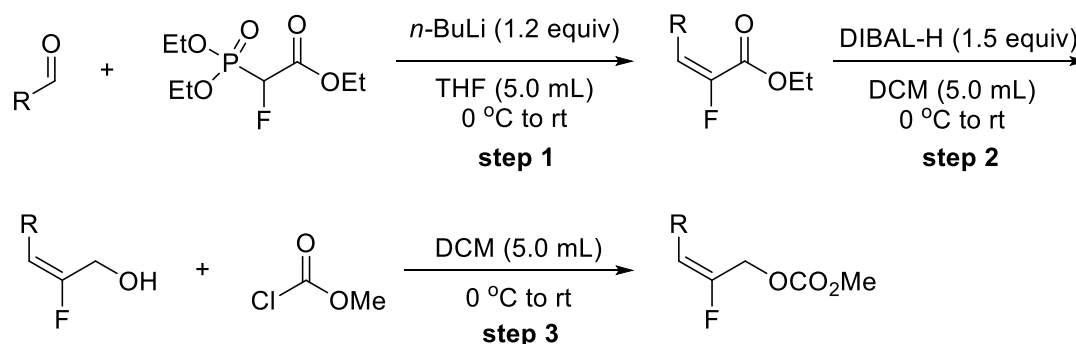
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1. General information

^1H NMR spectra were recorded on Bruker 400 MHz or 600 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for CDCl_3 . The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at Bruker 100 MHz or 150 MHz and referenced to the internal solvent signals (central peak is 77.0 ppm in CDCl_3), ^{19}F NMR spectra were obtained at Bruker 376 MHz or 564 MHz. CDCl_3 was used as the NMR solvent. CDCl_3 was used as the NMR solvent. APEX II (Bruker Inc.) was used for ESI-MS and EI-MS. Tetrahydrofuran (THF), *n*-butyllithium (*n*-BuLi), ethyl acetate (EtOAc), diisobutylaluminium hydride (DIBAL-H), dichloromethane (DCM), sodium sulfate (Na_2SO_4). Absorption spectra and fluorescence spectra were tested on Shimadzu UV-3600 UV-VIS-NIR spectrophotometer and HITACHI F-4600 fluorescence spectrophotometer, respectively. Flash column chromatography was performed over silica gel 200-300. All reagents were weighed and handled in air at room temperature. All chemical reagents were purchased from Alfa, Acros, Aldrich, TCI, Energy, and J&K and used without further purification.

2. Synthesis of (*E*)-2-fluoroallyl carbonate 1

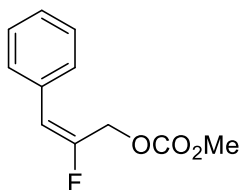


The (*E*)-2-fluoroallyl carbonates were prepared according to the known procedure.¹

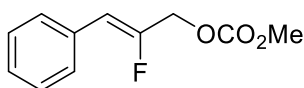
Step 1: Ethyl 2-(diethoxyphosphoryl)-2-fluoroacetate (1.2 equiv) was dissolved in dry THF under N_2 . The solution was cooled to $0\text{ }^\circ\text{C}$ and *n*-BuLi (2.5 M, 1.2 equiv) was added. The solution was stirred for 1 h at $0\text{ }^\circ\text{C}$. Aldehyde (1.0 equiv) was added and the solution was left overnight at room temperature. The reaction was quenched with water and extracted with EtOAc, dried over Na_2SO_4 and evaporated. The product was separated by column chromatography (petroleum ether/ethyl acetate).

Step 2: (*E*)-Ethyl 2-fluoro-3-phenylacrylate (1.0 equiv) was dissolved in dry DCM (5.0 mL) in dry glassware. DIBAL-H (1.0 M, 1.5 equiv) was added at 0 °C. The solution was stirred at room temperature overnight, quenched with water under vigorous stirring, extracted with DCM (3 × 50 mL), washed with water (2 × 50 mL), dried over Na₂SO₄ and evaporated. Product was separated by column chromatography (petroleum ether: ethyl acetate).

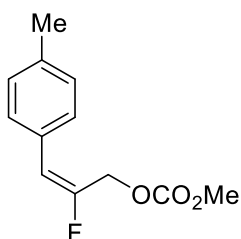
Step 3: (*E*)-2-Fluoro-3-phenylprop-2-en-1-ol (1.0 equiv) and pyridine (2.0 equiv) was dissolved in DCM (5.0 mL) at 0 °C. Methyl chloroformate (2.0 equiv) was added slowly at 0 °C. The solution was stirred at room temperature for 12 h and quenched with HCl (0.5 M). It was then diluted with water, extracted with DCM, dried over Na₂SO₄ and evaporated. Product was separated by column chromatography (petroleum ether/ethyl acetate).



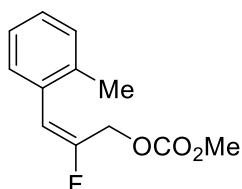
(*E*)-2-Fluoro-3-phenylallyl methyl carbonate (1a) (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ¹H NMR (600 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.24-7.23 (m, 2H), 6.55 (d, *J* = 19.0 Hz, 1H), 4.87 (d, *J* = 21.4 Hz, 2H), 3.83 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 155.4, 154.7 (d, *J*_{C-F} = 254.2 Hz), 132.3 (d, *J*_{C-F} = 11.0 Hz), 128.7, 128.6 (d, *J*_{C-F} = 2.2 Hz), 127.9, 114.6 (d, *J*_{C-F} = 24.6 Hz), 62.7 (d, *J*_{C-F} = 29.0 Hz), 55.2; ¹⁹F NMR (565 MHz, CDCl₃) δ -107.8. The characterization data were consistent with the literature.^{1a}



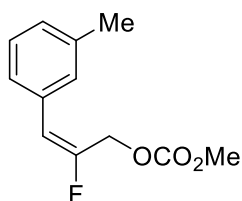
(*Z*)-2-fluoro-3-phenylallyl methyl carbonate (1a') (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ¹H NMR (600 MHz, CDCl₃) δ 7.51 (d, *J* = 6.0 Hz, 2H), 7.23-7.35 (m, 3H), 5.86 (d, *J* = 29.8 Hz, 1H), 4.77 (d, *J* = 14.2 Hz, 2H), 3.80 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 155.3, 152.9 (d, *J*_{C-F} = 266.2 Hz), 132.0 (d, *J*_{C-F} = 3.6 Hz), 128.9 (d, *J*_{C-F} = 7.2 Hz), 128.4, 128.0, 111.4 (d, *J*_{C-F} = 6.6 Hz), 66.1 (d, *J*_{C-F} = 31.2 Hz), 55.0; ¹⁹F NMR (565 MHz, CDCl₃) δ -107.4. **1a'** was synthesized according to the literature and the characterization data were consistent.^{1a}



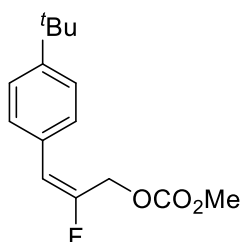
(E)-2-Fluoro-3-(*p*-tolyl)allyl methyl carbonate (1b) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.16 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 6.52 (d, $J = 19.1$ Hz, 1H), 4.86 (d, $J = 21.4$ Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.4, 154.4 (d, $J_{\text{C-F}} = 253.4$ Hz), 137.8, 129.4, 128.5 (d, $J_{\text{C-F}} = 2.8$ Hz), 114.6 (d, $J_{\text{C-F}} = 25.2$ Hz), 62.8 (d, $J_{\text{C-F}} = 29.0$ Hz), 55.1, 21.1; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -108.6. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 247.0741; found: 247.0737.



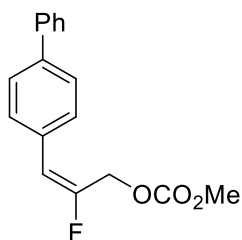
(E)-2-Fluoro-3-(*o*-tolyl)allyl methyl carbonate (1c) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.22-7.20 (m, 1H), 7.18-7.16 (m, 2H), 7.14-7.12 (m, 1H), 6.52 (d, $J = 18.6$ Hz, 1H), 4.76 (d, $J = 20.4$ Hz, 2H), 3.79 (s, 3H), 2.26 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.3, 154.6 (d, $J_{\text{C-F}} = 255.2$ Hz), 136.9 (d, $J_{\text{C-F}} = 3.2$ Hz), 131.3 (d, $J_{\text{C-F}} = 10.8$ Hz), 129.9, 129.0, 128.2, 126.0, 113.1 (d, $J_{\text{C-F}} = 23.2$ Hz), 62.3 (d, $J_{\text{C-F}} = 28.6$ Hz), 55.0, 19.9; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -109.2. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 247.0741; found: 247.0738.



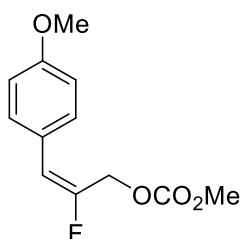
(E)-2-Fluoro-3-(*m*-tolyl)allyl methyl carbonate (1d) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.25-7.23 (m, 1H), 7.11 (d, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 7.6$ Hz, 1H), 7.02 (s, 1H), 6.52 (d, $J = 19.1$ Hz, 1H), 4.87 (d, $J = 21.2$ Hz, 2H), 3.83 (s, 3H), 2.35 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.4, 154.6 (d, $J_{\text{C-F}} = 253.6$ Hz), 138.4, 132.2 (d, $J_{\text{C-F}} = 11.6$ Hz), 129.3 (d, $J_{\text{C-F}} = 2.2$ Hz), 128.6 (d, $J_{\text{C-F}} = 5.2$ Hz), 125.6 (d, $J_{\text{C-F}} = 2.8$ Hz), 114.6 (d, $J_{\text{C-F}} = 24.4$ Hz), 62.7 (d, $J_{\text{C-F}} = 28.6$ Hz), 55.1, 21.3; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -108.2. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 247.0741; found: 247.0737.



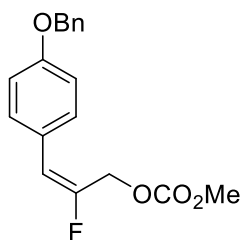
(E)-3-(4-(*tert*-Butyl)phenyl)-2-fluoroallyl methyl carbonate (1e) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.38 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 6.52 (d, $J = 19.2$ Hz, 1H), 4.88 (d, $J = 21.5$ Hz, 2H), 3.83 (s, 3H), 1.32 (s, 9H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.4, 154.4 (d, $J_{\text{C-F}} = 253.2$ Hz), 151.0, 129.3 (d, $J_{\text{C-F}} = 11.6$ Hz), 128.3 (d, $J_{\text{C-F}} = 2.2$ Hz), 125.7, 114.5 (d, $J_{\text{C-F}} = 24.6$ Hz), 62.8 (d, $J_{\text{C-F}} = 29.2$ Hz), 55.1, 34.6, 31.2; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -108.4. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 289.1210; found: 289.1211.



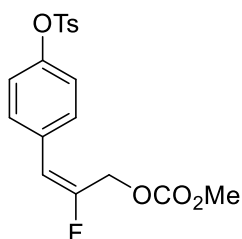
(E)-3-([1,1'-Biphenyl]-4-yl)-2-fluoroallyl methyl carbonate (1f) (petroleum ether: ethyl acetate = 10:1, $R_f = 0.5$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59-7.58 (m, 4H), 7.46-7.43 (m, 2H), 7.37-7.34 (m, 1H), 7.31 (d, $J = 8.2$ Hz, 2H), 6.58 (d, $J = 19.0$ Hz, 1H), 4.92 (d, $J = 21.4$ Hz, 2H), 3.84 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 155.4, 154.8 (d, $J_{\text{C-F}} = 254.6$ Hz), 140.7, 140.3, 131.2 (d, $J_{\text{C-F}} = 11.2$ Hz), 129.0 (d, $J_{\text{C-F}} = 2.2$ Hz), 128.8, 127.5, 127.4, 127.0, 114.3 (d, $J_{\text{C-F}} = 25.2$ Hz), 62.8 (d, $J_{\text{C-F}} = 29.2$ Hz), 55.2; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -107.1. HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{15}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 309.0897; found: 309.0895.



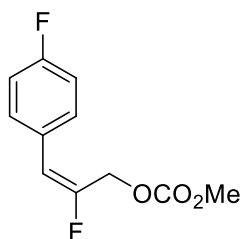
(E)-2-Fluoro-3-(4-methoxyphenyl)allyl methyl carbonate (1g) (petroleum ether: ethyl acetate = 10:1, $R_f = 0.4$); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.16 (d, $J = 8.4$ Hz, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 6.49 (d, $J = 19.2$ Hz, 1H), 4.86 (d, $J = 21.6$ Hz, 2H), 3.83 (s, 3H), 3.81 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 159.3, 155.4, 153.9 (d, $J_{\text{C-F}} = 252.2$ Hz), 129.8, 124.5 (d, $J_{\text{C-F}} = 11.8$ Hz), 114.3 (d, $J_{\text{C-F}} = 25.4$ Hz), 62.8 (d, $J_{\text{C-F}} = 29.4$ Hz), 55.2, 55.1; $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -109.3. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{13}\text{FNaO}_4$ [$\text{M} + \text{Na}^+$], 263.0690; found: 263.0687.



(E)-3-(4-(Benzyloxy)phenyl)-2-fluoroallyl methyl carbonate (1h) (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^1H NMR (600 MHz, CDCl_3) δ 7.43-7.42 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.32 (m, 1H), 7.16 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 6.49 (d, J = 19.2 Hz, 1H), 5.07 (s, 2H), 4.86 (d, J = 21.6 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.5, 155.4, 154.0 (d, $J_{\text{C-F}}$ = 252.0 Hz), 136.7, 129.8 (d, $J_{\text{C-F}}$ = 2.4 Hz), 128.6, 128.0, 127.4, 124.8 (d, $J_{\text{C-F}}$ = 11.0 Hz), 115.1, 114.3 (d, $J_{\text{C-F}}$ = 25.4 Hz), 70.0, 62.8 (d, $J_{\text{C-F}}$ = 29.8 Hz), 55.2; ^{19}F NMR (565 MHz, CDCl_3) δ -109.1. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{FNaO}_4$ [$\text{M} + \text{Na}^+$], 339.1003; found: 339.1006.

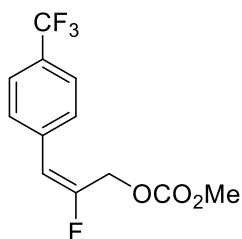


(E)-4-(2-Fluoro-3-((methoxycarbonyloxy)prop-1-en-1-yl)phenyl) 4-methylbenzenesulfonate (1i) (petroleum ether: ethyl acetate = 5:1, R_f = 0.4); ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 6.47 (d, J = 18.7 Hz, 1H), 4.80 (d, J = 21.2 Hz, 2H), 3.83 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.3, 155.2 (d, $J_{\text{C-F}}$ = 255.4 Hz), 149.1, 145.5, 132.3, 131.3 (d, $J_{\text{C-F}}$ = 11.8 Hz), 129.9, 129.8, 128.5, 122.8, 113.4 (d, $J_{\text{C-F}}$ = 26.2 Hz), 62.4 (d, $J_{\text{C-F}}$ = 29.4 Hz), 55.3, 21.7; ^{19}F NMR (565 MHz, CDCl_3) δ -105.9. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{FNaO}_6\text{S}$ [$\text{M} + \text{Na}^+$], 403.0622; found: 403.0624.

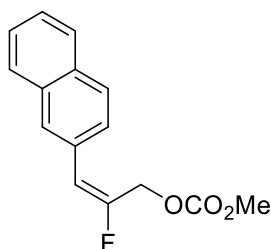


(E)-2-Fluoro-3-(4-fluorophenyl)allyl methyl carbonate (1j) (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^1H NMR (600 MHz, CDCl_3) δ 7.23-7.20 (m, 2H), 7.07-7.04 (m, 2H), 6.51 (d, J = 18.6 Hz, 1H), 4.83 (d, J = 21.2 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 162.4 (d, $J_{\text{C-F}}$ = 248.0 Hz), 155.4, 154.8 (d, $J_{\text{C-F}}$ = 255.3 Hz), 131.3 (d, $J_{\text{C-F}}$ = 2.2 Hz), 130.2 (d, $J_{\text{C-F}}$ = 2.8 Hz), 128.3 (d, $J_{\text{C-F}}$ = 3.2 Hz), 128.2 (d, $J_{\text{C-F}}$ = 3.4 Hz), 115.8 (d, $J_{\text{C-F}}$ = 21.4 Hz),

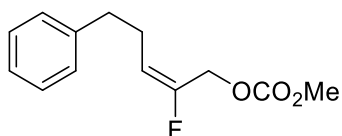
113.6 (d, $J_{C-F} = 25.6$ Hz), 62.5 (d, $J_{C-F} = 29.6$ Hz), 55.2; ^{19}F NMR (565 MHz, CDCl_3) δ -107.6, -113.6. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{10}\text{F}_2\text{NaO}_3$ [$\text{M} + \text{Na}^+$], 251.0490; found: 251.0489.



(E)-2-Fluoro-3-(4-(trifluoromethyl)phenyl)allyl methyl carbonate (1k) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); ^1H NMR (600 MHz, CDCl_3) δ 7.62 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 6.56 (d, $J = 18.4$ Hz, 1H), 4.84 (d, $J = 21.0$ Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 156.0 (d, $J_{C-F} = 258.2$ Hz), 155.3, 136.0 (d, $J_{C-F} = 11.8$ Hz), 130.0 (q, $J_{C-F} = 32.8$ Hz), 128.9 (d, $J_{C-F} = 3.0$ Hz), 125.7 (q, $J_{C-F} = 3.4$ Hz), 123.9 (q, $J_{C-F} = 271.8$ Hz), 113.4 (d, $J_{C-F} = 26.2$ Hz), 62.3 (d, $J_{C-F} = 29.4$ Hz), 55.3; ^{19}F NMR (565 MHz, CDCl_3) δ -62.7, -104.5. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{10}\text{F}_4\text{NaO}_3$ [$\text{M} + \text{Na}^+$], 301.0458; found: 301.0462.



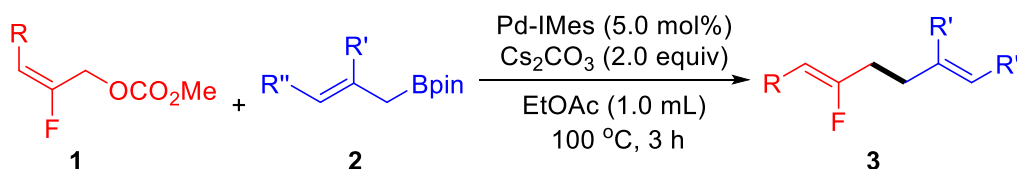
(E)-2-Fluoro-3-(naphthalen-2-yl)allyl methyl carbonate (1l) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); ^1H NMR (600 MHz, CDCl_3) δ 7.83-7.81 (m, 3H), 7.69 (s, 1H), 7.50-7.46 (m, 2H), 7.34 (dd, $J = 8.4, 1.4$ Hz, 1H), 6.69 (d, $J = 19.0$ Hz, 1H), 4.94 (d, $J = 21.2$ Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.4, 155.0 (d, $J_{C-F} = 255.0$ Hz), 133.2, 132.6, 129.7 (d, $J_{C-F} = 11.2$ Hz), 128.4, 128.0, 127.7, 127.6, 126.5, 126.4, 126.3 (d, $J_{C-F} = 2.0$ Hz), 114.7 (d, $J_{C-F} = 25.2$ Hz), 62.8 (d, $J_{C-F} = 29.3$ Hz), 55.2; ^{19}F NMR (565 MHz, CDCl_3) δ -107.2. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{13}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 283.0741; found: 283.0739.



(E)-2-Fluoro-5-phenylpent-2-en-1-yl methyl carbonate (1m) (petroleum ether: ethyl acetate = 20:1, $R_f = 0.5$); ^1H NMR (600 MHz, CDCl_3) δ 7.30-7.27 (m, 2H), 7.21-7.18 (m, 1H), 7.17-7.15 (m, 2H), 5.38 (dt, $J = 16.8, 8.2$ Hz, 1H),

4.57 (d, $J = 20.9$ Hz, 2H), 3.78 (s, 3H), 2.69 (t, $J = 7.5$ Hz, 2H), 2.40-2.36 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 155.4, 153.7 (d, $J_{\text{C-F}} = 248.4$ Hz), 140.6, 128.5, 128.4, 126.1, 111.7 (d, $J_{\text{C-F}} = 19.5$ Hz), 61.2 (d, $J_{\text{C-F}} = 30.4$ Hz), 55.0, 35.8 (d, $J_{\text{C-F}} = 2.2$ Hz), 27.3 (d, $J_{\text{C-F}} = 7.2$ Hz); ^{19}F NMR (565 MHz, CDCl_3) δ -111.4. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{15}\text{FNaO}_3$ [$\text{M} + \text{Na}^+$], 261.0897; found: 261.0896.

3. General procedure and characterization data for product 3



A flame-dried reaction tube (10.0 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IMes (3.0 mg, 5.0 mol%). The reaction tube was transferred to the glovebox and charged with **1** (0.1 mmol), allylboronate **2** (0.2 mmol), Cs_2CO_3 (65.0 mg) and EtOAc (1.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 3 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (3.0 mL). The solvent was evaporated *in vacuo* to give the crude product. The residue was purified by column chromatography on silica gel to give the pure product **3**. Product **3** is known compounds as the yellow oil, and the characterization data were consistent with the reported literature.²

1-(2-Fluorohexa-1,5-dien-1-yl)-3-methylbenzene (3a) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 15.3 mg (87%). ^1H NMR (600 MHz, CDCl_3) δ 7.45 (d, $J = 7.7$ Hz, 2H), 7.31 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 1H), 5.89-5.87 (m, 1H), 5.46 (d, $J_{\text{C-F}} = 39.5$ Hz, 1H), 5.09 (dd, $J = 17.2, 1.5$ Hz, 1H), 5.02 (dd, $J = 10.2, 1.0$ Hz, 1H), 2.43-2.38 (m, 2H), 2.37-2.33 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.2 (d, $J_{\text{C-F}} = 266.5$ Hz), 136.8, 133.7, 128.4, 128.3 (d, $J_{\text{C-F}} = 6.7$ Hz), 126.7, 126.6, 115.6, 106.1 (d, $J_{\text{C-F}} = 8.8$ Hz), 32.7 (d, $J_{\text{C-F}} = 26.4$ Hz), 30.5. ^{19}F NMR (565 MHz, CDCl_3) δ -101.3.

1-(2-Fluorohexa-1,5-dien-1-yl)-4-methylbenzene (3b) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.9 mg (89%). ^1H NMR (600 MHz, CDCl_3) δ 7.33 (d, $J = 8.8$ Hz, 2H), 6.77 (d, $J = 8.8$ Hz, 2H), 5.81-5.75 (m, 1H), 5.34 (d, $J_{\text{C-F}} = 39.5$ Hz, 1H), 5.02 (dd, $J = 17.2, 1.5$ Hz, 1H), 4.95 (dd, $J = 10.2, 1.0$ Hz, 1H), 3.72 (s, 3H), 2.35-2.30 (m, 2H), 2.29-2.25 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.9 (d, $J_{\text{C-F}} = 263.4$ Hz), 158.3, 158.2, 137.0, 129.5 (d, $J_{\text{C-F}} = 6.7$ Hz), 126.5, 126.4, 115.5, 113.8, 105.5 (d, $J_{\text{C-F}} = 8.9$ Hz), 55.2, 32.6 (d, $J_{\text{C-F}} = 26.4$ Hz), 30.5. ^{19}F NMR (565 MHz, CDCl_3) δ -104.3.

1-(2-Fluorohexa-1,5-dien-1-yl)-2-methylbenzene (3c) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 12.9 mg (68%). ^1H NMR (600 MHz, CDCl_3) δ 7.59 (d, $J = 7.6$ Hz, 1H), 7.18-7.11 (m, 3H), 5.90-5.84 (m, 1H), 5.60 (d, $J_{C-F} = 38.6$ Hz, 1H), 5.11 (dd, $J = 17.2, 1.4$ Hz, 1H), 5.05 (dd, $J = 10.2, 1.0$ Hz, 1H), 2.48-2.42 (m, 2H), 2.39-2.36 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8 (d, $J_{C-F} = 264.9$ Hz), 136.9, 135.4, 132.2, 129.9, 129.1 (d, $J_{C-F} = 9.9$ Hz), 126.8, 125.8, 115.7, 103.6 (d, $J_{C-F} = 9.9$ Hz), 32.6 (d, $J_{C-F} = 27.5$ Hz), 30.6, 20.2. ^{19}F NMR (565 MHz, CDCl_3) δ -103.8.

1-(2-Fluorohexa-1,5-dien-1-yl)-3-methylbenzene (3d) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.7 mg (88%). ^1H NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 11.2$ Hz, 2H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 5.89-5.82 (m, 1H), 5.44 (d, $J_{C-F} = 39.6$ Hz, 1H), 5.10 (dd, $J = 17.2, 1.4$ Hz, 1H), 5.03 (dd, $J = 10.2, 1.0$ Hz, 1H), 2.44-2.39 (m, 2H), 2.37-2.35 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.1 (d, $J_{C-F} = 266.2$ Hz), 137.9, 136.9, 133.6, 133.5, 129.0 (d, $J_{C-F} = 7.8$ Hz), 128.3, 127.5, 125.4, 125.3, 115.6, 106.2 (d, $J_{C-F} = 8.8$ Hz), 32.6 (d, $J_{C-F} = 26.6$ Hz), 30.5, 21.4. ^{19}F NMR (565 MHz, CDCl_3) δ -101.4.

1-(*Tert*-butyl)-4-(2-fluorohexa-1,5-dien-1-yl)benzene (3e) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 19.5 mg (84%). ^1H NMR (600 MHz, CDCl_3) δ 7.41 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 5.89-5.82 (m, 1H), 5.46 (d, $J_{C-F} = 39.8$ Hz, 1H), 5.09 (dd, $J = 17.1, 1.6$ Hz, 1H), 5.02 (dd, $J = 10.3, 1.3$ Hz, 1H), 2.44-2.39 (m, 2H), 2.37-2.33 (m, 2H), 1.31 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.8 (d, $J_{C-F} = 266.2$ Hz), 149.7, 136.9, 130.9, 130.8, 128.0 (d, $J_{C-F} = 7.7$ Hz), 125.3, 115.6, 105.8 (d, $J_{C-F} = 8.7$ Hz), 34.5, 32.6 (d, $J_{C-F} = 27.5$ Hz), 31.3, 30.6. ^{19}F NMR (565 MHz, CDCl_3) δ -102.4.

4-(2-Fluorohexa-1,5-dien-1-yl)-1,1'-biphenyl (3f) Isolated by column chromatography (petroleum ether : ethyl acetate = 100:1, $R_f = 0.4$); yield: 18.4 mg (73%). ^1H NMR (600 MHz, CDCl_3) δ 7.60 (d, $J = 7.5$ Hz, 2H), 7.56-7.53 (m, 4H), 7.43 (d, $J = 7.8$ Hz, 2H), 7.33 (d, $J = 7.3$ Hz, 1H), 5.90-5.83 (m, 1H), 5.52 (d, $J_{C-F} = 39.5$ Hz, 1H), 5.11 (dd, $J = 17.1, 1.4$ Hz, 1H), 5.04 (dd, $J = 10.2, 1.0$ Hz, 1H), 2.47-2.42 (m, 2H), 2.40-2.36 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.5 (d, $J_{C-F} = 267.2$ Hz), 140.7, 139.4, 139.3, 136.8, 132.8, 132.7, 128.7, 128.6 (d, $J_{C-F} = 7.7$ Hz), 115.7, 105.8 (d, $J_{C-F} = 8.7$ Hz), 32.7 (d, $J_{C-F} = 26.3$ Hz), 30.5. ^{19}F NMR (565 MHz, CDCl_3) δ -101.3.

1-(2-Fluorohexa-1,5-dien-1-yl)-4-methoxybenzene (3g) Isolated by column chromatography (petroleum ether : ethyl acetate = 50:1, $R_f = 0.5$); yield: 19.4 mg (94%). ^1H NMR (600 MHz, CDCl_3) δ 7.40 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.89-5.82 (m, 1H), 5.41 (d, $J_{C-F} = 39.5$ Hz, 1H), 5.09 (dd, $J = 17.1, 1.4$ Hz, 1H), 5.02 (dd, $J = 17.1, 1.4$ Hz, 1H), 3.80 (s, 3H), 2.43-2.37 (m, 2H), 2.36-2.33 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 158.8 (d, J_{C-F}

= 262.9 Hz), 158.3, 158.2, 137.0, 129.4 (d, J_{C-F} = 6.7 Hz), 126.5, 126.4, 115.5, 113.8, 105.5 (d, J_{C-F} = 8.8 Hz), 55.2, 32.6 (d, J_{C-F} = 26.2 Hz), 30.6. ^{19}F NMR (565 MHz, CDCl_3) δ -101.3.

1-(Benzyloxy)-4-(2-fluorohexa-1,5-dien-1-yl)benzene (3h) Isolated by column chromatography (petroleum ether : ethyl acetate = 20:1, R_f = 0.5); yield: 27.1 mg (96%). ^1H NMR (600 MHz, CDCl_3) δ 7.35-7.28 (m, 6H), 7.24 (d, J = 6.9 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.80-5.74 (m, 1H), 5.33 (d, J_{C-F} = 38.7 Hz, 1H), 5.01 (dd, J = 17.1, 1.4 Hz, 1H), 4.98 (s, 2H), 4.94 (dd, J = 10.2, 1.0 Hz, 1H), 2.34-2.30 (m, 2H), 2.29-2.26 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.0 (d, J_{C-F} = 263.9 Hz), 158.0, 157.5, 137.0, 136.9, 129.5 (d, J_{C-F} = 7.7 Hz), 129.2, 128.6, 128.5, 128.0, 127.9, 127.4, 126.7, 115.6, 114.9, 114.8, 105.5 (d, J_{C-F} = 7.8 Hz), 70.0, 69.9, 32.6 (d, J_{C-F} = 26.4 Hz), 30.6. ^{19}F NMR (565 MHz, CDCl_3) δ -104.1.

4-(2-Fluorohexa-1,5-dien-1-yl)phenyl 4-methylbenzenesulfonate (3i) Isolated by column chromatography (petroleum ether : ethyl acetate = 20:1, R_f = 0.4); yield: 22.8 mg (66%). ^1H NMR (600 MHz, CDCl_3) δ 7.36 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 5.86-5.80 (m, 1H), 5.43 (d, J_{C-F} = 38.9 Hz, 1H), 5.09 (dd, J = 17.1, 1.4 Hz, 1H), 5.03 (dd, J = 10.2, 1.0 Hz, 1H), 2.44 (s, 3H), 2.43-2.38 (m, 2H), 2.35-2.32 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 160.9 (d, J_{C-F} = 267.5 Hz), 147.9, 147.8, 145.3, 136.7, 132.7, 132.4, 129.7, 129.3 (d, J_{C-F} = 7.7 Hz), 128.5, 122.3, 115.8, 105.0 (d, J_{C-F} = 8.0 Hz), 32.5 (d, J_{C-F} = 26.5 Hz), 30.3, 21.7. ^{19}F NMR (565 MHz, CDCl_3) δ -100.5.

1-Fluoro-4-(2-fluorohexa-1,5-dien-1-yl)benzene (3j) Isolated by column chromatography (petroleum ether, R_f = 0.5); yield: 15.1 mg (78%). ^1H NMR (600 MHz, CDCl_3) δ 7.44-7.42 (m, 2H), 7.01-6.98 (m, 2H), 5.89-5.82 (m, 1H), 5.45 (d, J_{C-F} = 39.2 Hz, 1H), 5.10 (dd, J = 17.2, 1.4 Hz, 1H), 5.04 (dd, J = 10.2, 1.0 Hz, 1H), 2.44-2.39 (m, 2H), 2.37-2.34 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 161.5 (d, J_{C-F} = 245.7 Hz), 159.9 (d, J_{C-F} = 266.2 Hz), 136.8, 129.9 (d, J_{C-F} = 7.8 Hz), 129.8 (d, J_{C-F} = 7.8 Hz), 115.7, 115.3, 115.2, 105.1 (d, J_{C-F} = 8.8 Hz), 32.5 (d, J_{C-F} = 26.3 Hz), 30.5. ^{19}F NMR (565 MHz, CDCl_3) δ -102.6, -115.1.

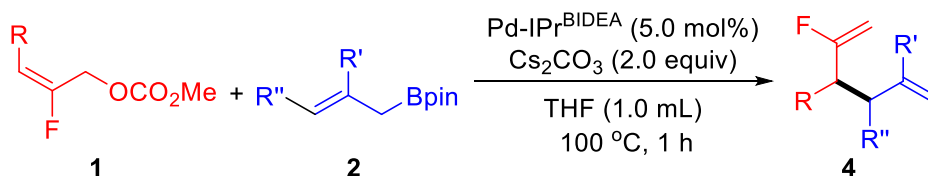
1-(2-Fluorohexa-1,5-dien-1-yl)-4-(trifluoromethyl)benzene (3k) Isolated by column chromatography (petroleum ether, R_f = 0.5); yield: 15.4 mg (63%). ^1H NMR (600 MHz, CDCl_3) δ 7.55 (s, 4H), 5.88-5.82 (m, 1H), 5.53 (d, J_{C-F} = 38.7 Hz, 1H), 5.11 (dd, J = 17.1, 1.4 Hz, 1H), 5.05 (dd, J = 10.2, 1.0 Hz, 1H), 2.48-2.42 (m, 2H), 2.39-2.36 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 162.1 (d, J_{C-F} = 269.7 Hz), 137.2, 136.5, 128.4 (d, J_{C-F} = 7.7 Hz), 125.3 (q, J_{C-F} = 3.4 Hz), 124.2 (q, J_{C-F} = 271.7 Hz), 115.9, 105.3 (d, J_{C-F} = 7.8 Hz), 48.5, 48.3, 32.6 (d, J_{C-F} = 26.4 Hz), 30.3. ^{19}F NMR (565 MHz, CDCl_3) δ -62.5 (3F), -97.9.

2-(2-Fluorohexa-1,5-dien-1-yl)naphthalene (3l) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 17.6 mg (78%). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.87 (s, 1H), 7.78-7.75 (m, 3H), 7.63 (d, $J = 8.6$ Hz, 1H), 7.44-7.39 (m, 2H), 5.90-5.84 (m, 1H), 5.61 (d, $J_{C-F} = 39.4$ Hz, 1H), 5.11 (d, $J = 17.3$ Hz, 1H), 5.04 (d, $J = 10.4$ Hz, 1H), 2.48-2.43 (m, 2H), 2.40-2.37 (m, 2H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 160.6 (d, $J_{C-F} = 267.4$ Hz), 136.8, 133.5, 132.2, 131.3, 131.2, 127.9, 127.8, 127.5, 127.1, 127.0, 126.5 (d, $J_{C-F} = 7.7$ Hz), 126.0, 125.7, 115.7, 106.3 (d, $J_{C-F} = 7.7$ Hz), 32.7 (d, $J_{C-F} = 26.5$ Hz), 30.5. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -100.7.

(Z)-(2-Fluorohexa-1,5-diene-1,5-diyl)dibenzene (3o) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 23.2 mg (92%). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.45-7.43 (m, 2H), 7.42-7.40 (m, 2H), 7.35-7.33 (m, 2H), 7.31-7.27 (m, 3H), 7.21-7.18 (m, 1H), 5.41 (d, $J_{C-F} = 39.4$ Hz, 1H), 5.32 (s, 1H), 5.13 (s, 1H), 2.83-2.80 (m, 2H), 2.49-2.44 (m, 2H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 160.1 (d, $J_{C-F} = 266.8$ Hz), 146.9, 140.6, 133.7 (d, $J_{C-F} = 2.0$ Hz), 128.4, 128.3 (d, $J_{C-F} = 7.6$ Hz), 127.6, 126.7 (d, $J_{C-F} = 1.8$ Hz), 126.1, 113.3, 106.2 (d, $J_{C-F} = 8.2$ Hz), 32.3 (d, $J_{C-F} = 26.6$ Hz), 32.2. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -101.8.

(Z)-(2-Fluoro-5-methylhexa-1,5-dien-1-yl)benzene (3p) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 10 mg (53%). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39-7.38 (m, 2H), 7.24-7.22 (m, 2H), 7.13-7.11 (m, 1H), 5.41 (d, $J_{C-F} = 39.4$ Hz, 1H), 4.71 (s, 1H), 4.68 (s, 1H), 2.42-2.37 (m, 2H), 2.26-2.23 (m, 2H), 1.70 (s, 3H). $^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 160.5 (d, $J_{C-F} = 266.6$ Hz), 144.2, 133.8 (d, $J_{C-F} = 2.0$ Hz), 128.4, 128.3 (d, $J_{C-F} = 7.6$ Hz), 126.7, 110.8, 105.9 (d, $J_{C-F} = 8.8$ Hz), 34.4, 31.6 (d, $J_{C-F} = 26.6$ Hz), 22.4. $^{19}\text{F NMR}$ (565 MHz, CDCl_3) δ -101.1.

4. General procedure and characterization data for product 4



A flame-dried reaction tube (10.0 cm³) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IPr^{BIDEA} (4.3 mg, 5.0 mol%). The reaction tube was transferred to the glovebox and charged with **1** (0.1 mmol), allylboronate **2** (0.2 mmol), Cs₂CO₃ (65.0 mg) and THF (1.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 1 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (3.0 mL). The solvent was evaporated *in vacuo* to give the crude product. The residue was purified by column chromatography on silica gel to give the pure product **4**.

Products **4** is known compounds as the yellow oil, and the characterization data were consistent with the reported literature.²

(2-Fluorohexa-1,5-dien-3-yl)benzene (4a) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.0 mg (91%). ¹H NMR (600 MHz, CDCl₃) δ 7.33-7.30 (d, $J = 7.6$ Hz, 2H), 7.27-7.24 (m, 3H), 5.75-5.58 (m, 1H), 5.06 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.62 (dd, $J_{C-F} = 17.8, J = 2.8$ Hz, 1H), 4.36 (dd, $J_{C-F} = 49.9, J = 2.8$ Hz, 1H), 3.48 (dt, $J = 16.7, 7.6$ Hz, 1H), 2.70-2.65 (m, 1H), 2.53-2.48 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 167.2 (d, $J_{C-F} = 260.4$ Hz), 140.1, 135.5, 128.5, 127.9, 127.0, 116.8, 90.7 (d, $J_{C-F} = 19.9$ Hz), 48.5 (d, $J_{C-F} = 25.3$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz). ¹⁹F NMR (565 MHz, CDCl₃) δ -99.1.

1-(2-Fluorohexa-1,5-dien-3-yl)-4-methylbenzene (4b) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.7 mg (88%). ¹H NMR (600 MHz, CDCl₃) δ 7.16-7.12 (m, 4H), 5.75-5.68 (m, 1H), 5.06 (dd, $J = 17.1, 1.3$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.60 (dd, $J_{C-F} = 17.7, J = 2.8$ Hz, 1H), 4.41 (dd, $J_{C-F} = 50.0, J = 2.8$ Hz, 1H), 3.44 (dt, $J = 16.7, 7.6$ Hz, 1H), 2.68-2.63 (m, 1H), 2.51-2.46 (m, 1H), 2.32 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 167.5 (d, $J_{C-F} = 260.5$ Hz), 137.1, 136.6, 135.7, 129.2, 127.7, 116.8, 90.5 (d, $J_{C-F} = 19.9$ Hz), 48.1 (d, $J_{C-F} = 26.1$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz), 21.0. ¹⁹F NMR (565 MHz, CDCl₃) δ -99.2.

1-(2-Fluorohexa-1,5-dien-3-yl)-2-methylbenzene (4c) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 13.7 mg (72%). ¹H NMR (600 MHz, CDCl₃) δ 7.30 (d, $J = 7.8$ Hz, 1H), 7.21-7.15 (m, 3H), 5.76-5.69 (m, 1H), 5.07 (dd, $J = 17.1, 1.5$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.63 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.30 (dd, $J_{C-F} = 50.2, J = 3.0$ Hz, 1H), 3.75 (dt, $J = 17.5, 7.7$ Hz, 1H), 2.71-2.66 (m, 1H), 2.52-2.47 (m, 1H), 2.34 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 167.2 (d, $J_{C-F} = 260.0$ Hz), 138.1, 136.2, 135.6, 130.5, 126.8, 126.7, 126.2, 116.8, 90.7 (d, $J_{C-F} = 20.8$ Hz), 43.7 (d, $J_{C-F} = 25.4$ Hz), 36.7 (d, $J_{C-F} = 3.3$ Hz), 19.6. ¹⁹F NMR (565 MHz, CDCl₃) δ -97.9.

1-(2-Fluorohexa-1,5-dien-3-yl)-3-methylbenzene (4d) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.5 mg (87%). ¹H NMR (600 MHz, CDCl₃) δ 7.21 (t, $J = 7.6$ Hz, 1H), 7.07 (d, $J = 9.2$ Hz, 3H), 5.75-5.69 (m, 1H), 5.07 (dd, $J = 17.1, 1.5$ Hz, 1H), 5.01 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.62 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.37 (dd, $J_{C-F} = 50.2, J = 3.0$ Hz, 1H), 3.44 (dt, $J = 17.5, 7.7$ Hz, 1H), 2.68-2.64 (m, 1H), 2.52-2.47 (m, 1H), 2.34 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 167.3 (d, $J_{C-F} = 260.9$ Hz), 140.1, 138.1, 135.6, 128.6, 128.4, 127.8, 124.8, 116.8, 90.6 (d, $J_{C-F} = 20.0$ Hz), 48.5 (d, $J_{C-F} = 25.4$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz), 21.4. ¹⁹F NMR (565 MHz, CDCl₃) δ -99.1.

1-(tert-Butyl)-4-(2-fluorohexa-1,5-dien-3-yl)benzene (4e) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 20.6 mg (89%). ¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.2$ Hz, 2H), 5.77-

5.71 (m, 1H), 5.08 (dd, $J = 17.7, 2.8$ Hz, 1H), 5.01 (d, $J = 10.0$ Hz, 1H), 4.61 (dd, $J_{C-F} = 17.7, J = 2.8$ Hz, 1H), 4.35 (dd, $J_{C-F} = 49.9, J = 2.8$ Hz, 1H), 3.45 (dt, $J = 18.5, 7.6$ Hz, 1H), 2.68-2.64 (m, 1H), 2.53-2.48 (m, 1H), 1.31 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.3 (d, $J_{C-F} = 260.0$ Hz), 149.8, 137.1, 135.8, 127.4, 125.4, 116.7, 90.6 (d, $J_{C-F} = 20.8$ Hz), 48.1 (d, $J_{C-F} = 25.4$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz), 34.4, 31.3. ^{19}F NMR (565 MHz, CDCl_3) δ -99.6.

4-(2-Fluorohexa-1,5-dien-3-yl)-1,1'-biphenyl (4f) Isolated by column chromatography (petroleum ether : ethyl acetate = 100:1, $R_f = 0.4$); yield: 21.2 mg (84%). ^1H NMR (600 MHz, CDCl_3) δ 7.58 (d, $J = 7.5$ Hz, 2H), 7.55 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 3H), 5.79-5.72 (m, 1H), 5.09 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.03 (d, $J = 10.2$ Hz, 1H), 4.66 (dd, $J_{C-F} = 17.8, J = 2.8$ Hz, 1H), 4.40 (dd, $J_{C-F} = 49.9, J = 2.8$ Hz, 1H), 3.53 (dt, $J = 17.7, 7.6$ Hz, 1H), 2.73-2.69 (m, 1H), 2.57-2.52 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.1 (d, $J_{C-F} = 260.0$ Hz), 140.8, 140.0, 139.2, 135.5, 128.7, 128.3, 127.3, 127.2, 127.0, 117.0, 90.8 (d, $J_{C-F} = 20.8$ Hz), 48.2 (d, $J_{C-F} = 25.4$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -99.2.

1-(2-Fluorohexa-1,5-dien-3-yl)-4-methoxybenzene (4g) Isolated by column chromatography (petroleum ether : ethyl acetate = 100:1, $R_f = 0.5$); yield: 19.4 mg (94%). ^1H NMR (600 MHz, CDCl_3) δ 7.19 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 5.74-5.68 (m, 1H), 5.05 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.60 (dd, $J_{C-F} = 17.8, J = 2.8$ Hz, 1H), 4.33 (dd, $J_{C-F} = 49.9, J = 2.8$ Hz, 1H), 3.80 (s, 3H), 3.43 (dt, $J = 17.7, 7.6$ Hz, 1H), 2.68-2.63 (m, 1H), 2.50-2.45 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.6 (d, $J_{C-F} = 260.7$ Hz), 158.6, 135.7, 132.2, 128.8, 116.8, 113.9, 90.4 (d, $J_{C-F} = 20.8$ Hz), 55.2, 47.7 (d, $J_{C-F} = 25.1$ Hz), 37.0 (d, $J_{C-F} = 3.3$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -99.4.

1-(Benzyloxy)-4-(2-fluorohexa-1,5-dien-3-yl)benzene (4h) Isolated by column chromatography (petroleum ether : ethyl acetate = 50:1, $R_f = 0.5$); yield: 26.8 mg (95%). ^1H NMR (600 MHz, CDCl_3) δ 7.34 (d, $J = 8.6$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.10 (d, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 6.9$ Hz, 2H), 5.66-5.59 (m, 1H), 4.97 (dd, $J = 17.1, 1.4$ Hz, 1H), 4.93 (s, 2H), 4.92 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.52 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.24 (dd, $J_{C-F} = 50.0, J = 3.0$ Hz, 1H), 3.37-3.31 (m, 1H), 2.57-2.54 (m, 1H), 2.41-2.37 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.5 (d, $J_{C-F} = 259.8$ Hz), 157.8, 137.0, 135.6, 132.4, 128.9, 128.5, 127.9, 127.5, 116.8, 114.8, 90.4 (d, $J_{C-F} = 19.8$ Hz), 70.0, 47.7 (d, $J_{C-F} = 25.3$ Hz), 37.0 (d, $J_{C-F} = 3.3$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -99.3.

4-(2-Fluorohexa-1,5-dien-3-yl)phenyl 4-methylbenzenesulfonate (4i) Isolated by column chromatography (petroleum ether : ethyl acetate = 10:1, $R_f = 0.4$); yield: 31.1 mg (90%). ^1H NMR (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 6.94 (d, $J = 8.7$ Hz, 2H), 5.69-5.63 (m, 1H), 5.02 (dd,

$J = 17.1, 1.4$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.63 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.34 (dd, $J_{C-F} = 50.0, J = 3.0$ Hz, 1H), 3.44 (dt, $J = 17.0, 7.6$ Hz, 1H), 2.65-2.60 (m, 1H), 2.45 (s, 3H), 2.44-2.40 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.5 (d, $J_{C-F} = 259.9$ Hz), 148.5, 145.3, 139.1, 135.0, 132.4, 129.7, 129.0, 128.5, 122.3, 117.2, 91.1 (d, $J_{C-F} = 19.8$ Hz), 47.9 (d, $J_{C-F} = 25.6$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz), 21.6. ^{19}F NMR (565 MHz, CDCl_3) δ -99.5.

1-Fluoro-4-(2-fluorohexa-1,5-dien-3-yl)benzene (4j) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 15.9 mg (82%). ^1H NMR (600 MHz, CDCl_3) δ 7.24-7.22 (m, 2H), 7.01 (t, $J = 8.6$ Hz, 2H), 5.72-5.65 (m, 1H), 5.05 (dd, $J = 17.0, 1.3$ Hz, 1H), 5.01 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.63 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.35 (dd, $J_{C-F} = 50.0, J = 3.0$ Hz, 1H), 3.47 (dt, $J = 17.3, 7.9$ Hz, 1H), 2.68-2.64 (m, 1H), 2.49-2.44 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.1 (d, $J_{C-F} = 259.8$ Hz), 161.9 (d, $J_{C-F} = 245.0$ Hz), 135.8 (d, $J_{C-F} = 3.3$ Hz), 135.2, 129.4, 129.3, 117.1, 115.4, 115.3, 90.8 (d, $J_{C-F} = 20.9$ Hz), 47.8 (d, $J_{C-F} = 25.1$ Hz), 37.0 (d, $J_{C-F} = 3.3$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -99.4, -115.9.

1-(2-Fluorohexa-1,5-dien-3-yl)-4-(trifluoromethyl)benzene (4k) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 17.3 mg (71%). ^1H NMR (600 MHz, CDCl_3) δ 7.59 (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 5.72-5.65 (m, 1H), 5.06 (d, $J = 17.0$ Hz, 1H), 5.03 (d, $J = 10.2$ Hz, 1H), 4.68 (dd, $J_{C-F} = 17.6, J = 2.8$ Hz, 1H), 4.41 (dd, $J_{C-F} = 49.8, J = 2.8$ Hz, 1H), 3.58-3.52 (m, 1H), 2.72-2.67 (m, 1H), 2.53-2.48 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 166.3 (d, $J_{C-F} = 260.6$ Hz), 144.1, 134.8, 129.4 (q, $J_{C-F} = 32.2$ Hz), 128.3, 125.5 (q, $J_{C-F} = 3.4$ Hz), 124.1 (q, $J_{C-F} = 271.8$ Hz), 117.5, 91.4 (d, $J_{C-F} = 19.8$ Hz), 48.4 (d, $J_{C-F} = 25.9$ Hz), 36.8 (d, $J_{C-F} = 3.6$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -62.5, -99.3.

2-(2-Fluorohexa-1,5-dien-3-yl)naphthalene (4l) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 19.4 mg (86%). ^1H NMR (600 MHz, CDCl_3) δ 7.80 (d, $J = 8.2$ Hz, 3H), 7.70 (s, 1H), 7.47-7.42 (m, 2H), 7.40 (d, $J = 8.6$ Hz, 1H), 5.77-5.70 (m, 1H), 5.07 (dd, $J = 17.3, 1.3$ Hz, 1H), 5.00 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.67 (dd, $J_{C-F} = 17.8, J = 2.8$ Hz, 1H), 4.41 (dd, $J_{C-F} = 49.9, J = 2.8$ Hz, 1H), 3.65 (dt, $J = 16.7, 7.6$ Hz, 1H), 2.78-2.74 (m, 1H), 2.63-2.58 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.2 (d, $J_{C-F} = 260.0$ Hz), 137.5, 135.4, 133.4, 133.0, 128.2, 127.8, 127.6, 126.7, 126.1, 126.0, 125.7, 117.0, 90.9 (d, $J_{C-F} = 19.6$ Hz), 48.6 (d, $J_{C-F} = 25.4$ Hz), 36.9 (d, $J_{C-F} = 3.3$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -98.5.

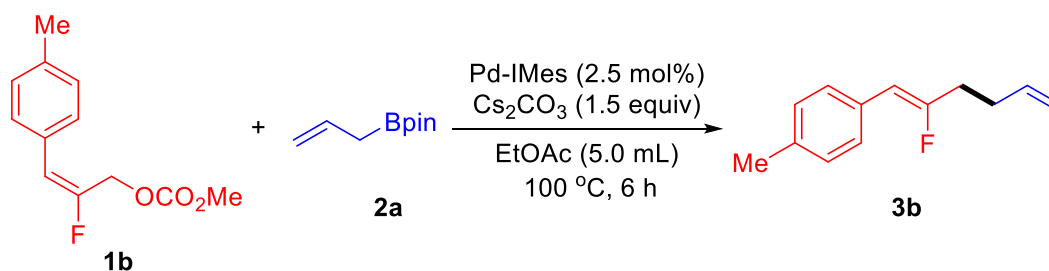
(3-(1-Fluorovinyl)hex-5-en-1-yl)benzene (4n) Isolated by column chromatography (petroleum ether, $R_f = 0.4$); yield: 15.9 mg (78%). ^1H NMR (600 MHz, CDCl_3) δ 7.28 (t, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 8.2$ Hz, 3H), 5.78-5.71 (m, 1H), 5.05 (dd, $J = 17.1, 1.4$ Hz, 1H), 5.03 (dd, $J = 10.2, 1.0$ Hz, 1H), 4.62 (dd, $J_{C-F} = 17.7, J = 3.0$ Hz, 1H), 4.25 (dd, J_{C-F}

= 50.0, $J = 3.0$ Hz, 1H), 2.73-2.69 (m, 1H), 2.60-2.55 (m, 1H), 2.31-2.18 (m, 2H), 1.83-1.70 (m, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.3 (d, $J_{\text{C-F}} = 260.7$ Hz), 142.0, 135.7, 128.4, 128.3, 125.9, 116.6, 90.9 (d, $J_{\text{C-F}} = 20.9$ Hz), 42.1 (d, $J_{\text{C-F}} = 25.5$ Hz), 33.2, 32.9 (d, $J_{\text{C-F}} = 3.3$ Hz), 29.7. ^{19}F NMR (565 MHz, CDCl_3) δ -105.6.

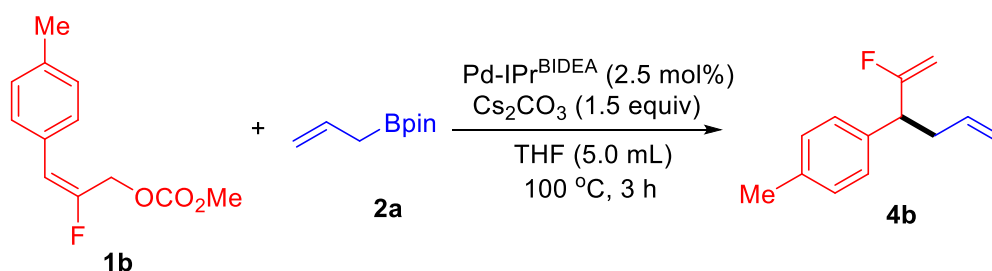
(5-Fluorohexa-1,5-diene-2,4-diyl)dibenzene (4o) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 22.7 mg (90%, $B/L = 7:1$). ^1H NMR (600 MHz, CDCl_3) δ 7.34-7.33 (m, 4H), 7.30-7.28 (m, 3H), 7.23-7.18 (m, 3H), 5.22 (s, 1H), 4.98 (s, 1H), 4.59 (dd, $J_{\text{C-F}} = 17.6$, $J = 2.8$ Hz, 1H), 4.28 (dd, $J_{\text{C-F}} = 50.0$, $J = 2.8$ Hz, 1H), 3.52 (dt, $J = 18.8$, 7.6 Hz, 1H), 3.17 (dd, $J = 14.4$, 7.6 Hz, 1H), 2.91 (dd, $J = 14.4$, 7.6 Hz, 1H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.0 (d, $J_{\text{C-F}} = 260.6$ Hz), 145.4, 140.3 (d, $J_{\text{C-F}} = 56.4$ Hz), 128.43, 128.41, 127.9, 127.6, 127.0, 126.4, 126.1, 115.3, 90.9 (d, $J_{\text{C-F}} = 20.6$ Hz), 47.0 (d, $J_{\text{C-F}} = 25.6$ Hz), 38.7 (d, $J_{\text{C-F}} = 3.0$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -100.1.

(2-Fluoro-5-methylhexa-1,5-dien-3-yl)benzene (4p) Isolated by column chromatography (petroleum ether, $R_f = 0.5$); yield: 16.7 mg (88%, $B/L = 20:1$). ^1H NMR (600 MHz, CDCl_3) δ 7.33-7.29 (m, 2H), 7.28-7.26 (m, 2H), 7.25-7.24 (m, 1H), 4.75 (s, 1H), 4.67 (s, 1H), 4.60 (dd, $J_{\text{C-F}} = 17.6$, $J = 2.8$ Hz, 1H), 4.35 (dd, $J_{\text{C-F}} = 50.0$, $J = 2.8$ Hz, 1H), 3.64 (dt, $J = 18.8$, 7.6 Hz, 1H), 2.66 (dd, $J = 14.4$, 7.6 Hz, 1H), 2.46 (dd, $J = 14.4$, 7.6 Hz, 1H), 1.70 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 167.5 (d, $J_{\text{C-F}} = 260.6$ Hz), 142.3, 140.4, 128.5, 127.8, 127.0, 112.9, 90.6 (d, $J_{\text{C-F}} = 20.6$ Hz), 46.9 (d, $J_{\text{C-F}} = 25.4$ Hz), 40.8 (d, $J_{\text{C-F}} = 3.0$ Hz). ^{19}F NMR (565 MHz, CDCl_3) δ -99.2.

5. Scale-up synthesis of product 3b and 4b



A flame-dried reaction tube (50 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IMes (16.0 mg, 2.5 mol%). The reaction tube was transferred to the glovebox and charged with **1b** (1.0 mmol), allylboronate **2a** (1.5 mmol), Cs_2CO_3 (488.0 mg) and EtOAc (5.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 6 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (10.0 mL). The solvent was evaporated *in vacuo* to give the crude product. L/B ratio was determined by ^1H NMR analysis. The residue was purified by column chromatography on silica gel to give the pure product **3b** (165 mg, 87% yield, $L/B > 50:1$).

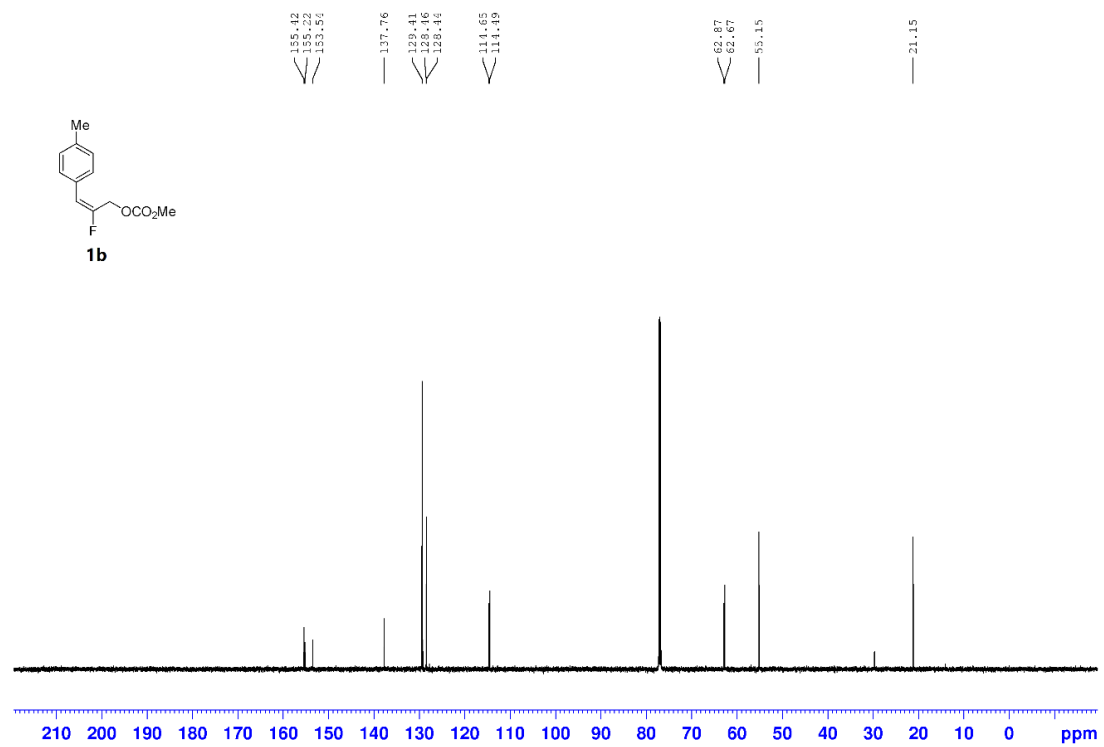
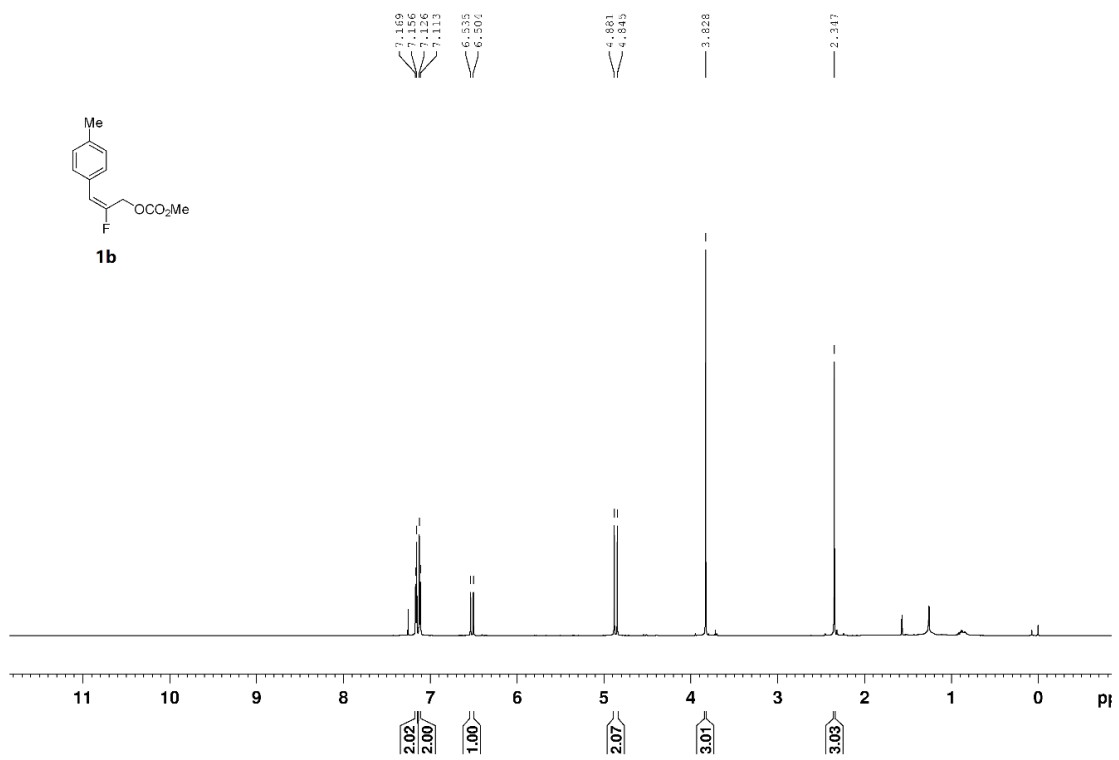


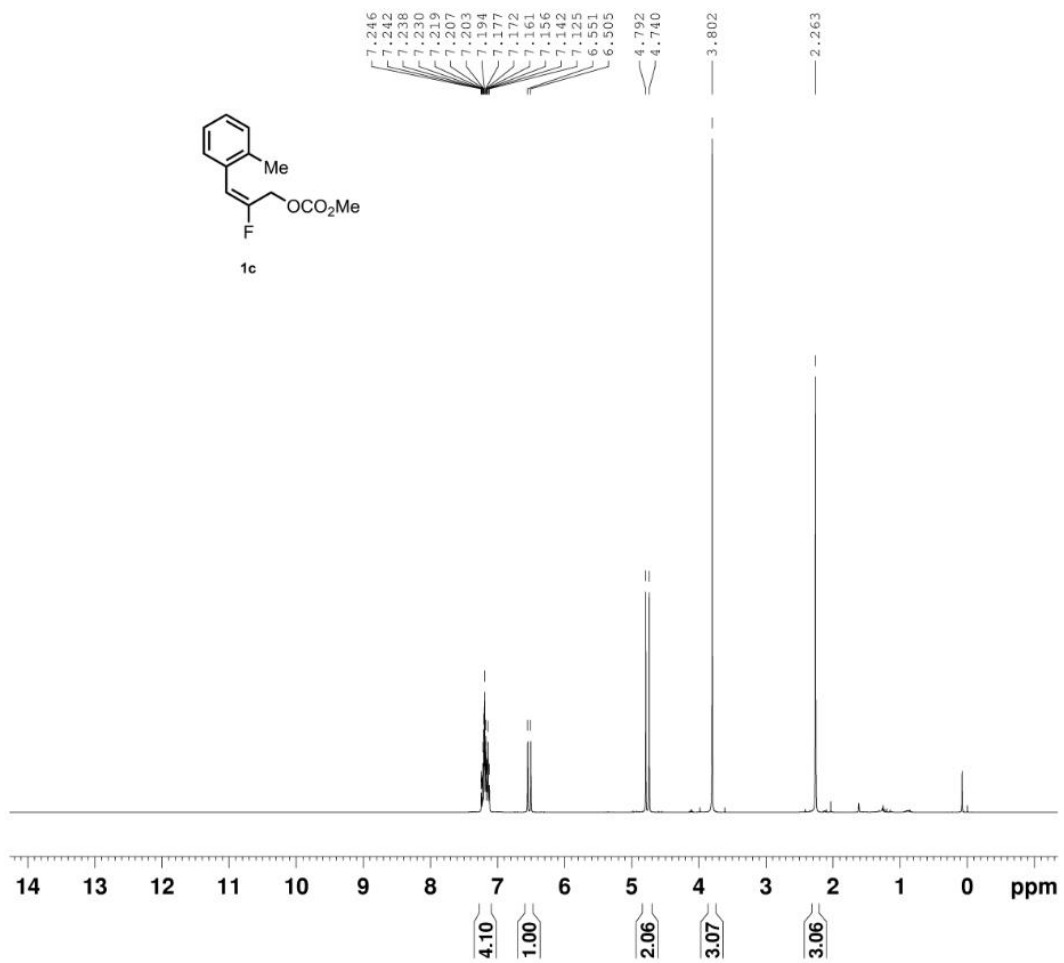
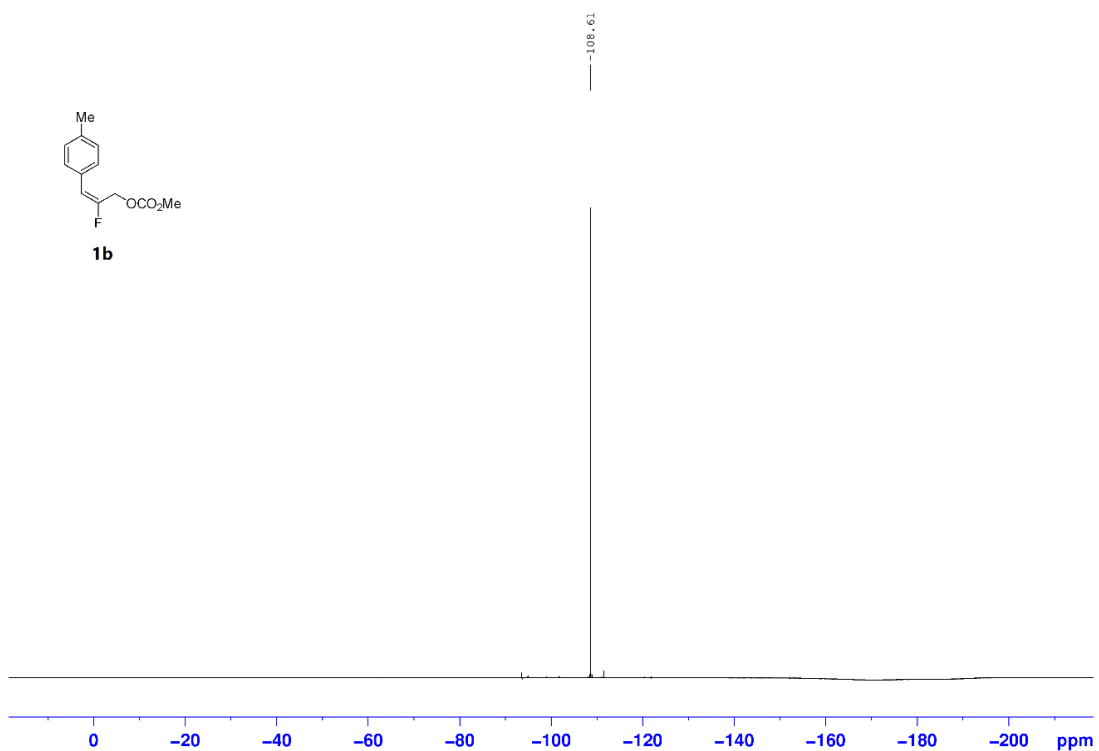
A flame-dried reaction tube (50 cm³) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IPr^{BIDEA} (21.4 mg, 2.5 mol%). The reaction tube was transferred to the glovebox and charged with **1b** (1.0 mmol), allylboronate **2a** (1.5 mmol), Cs₂CO₃ (488.0 mg) and THF (5.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 3 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (10.0 mL). The solvent was evaporated *in vacuo* to give the crude product. **B/L** ratio was determined by ¹H NMR analysis. The residue was purified by column chromatography on silica gel to give the pure product **4b** (158 mg, 83% yield, **B/L** > 80:1).

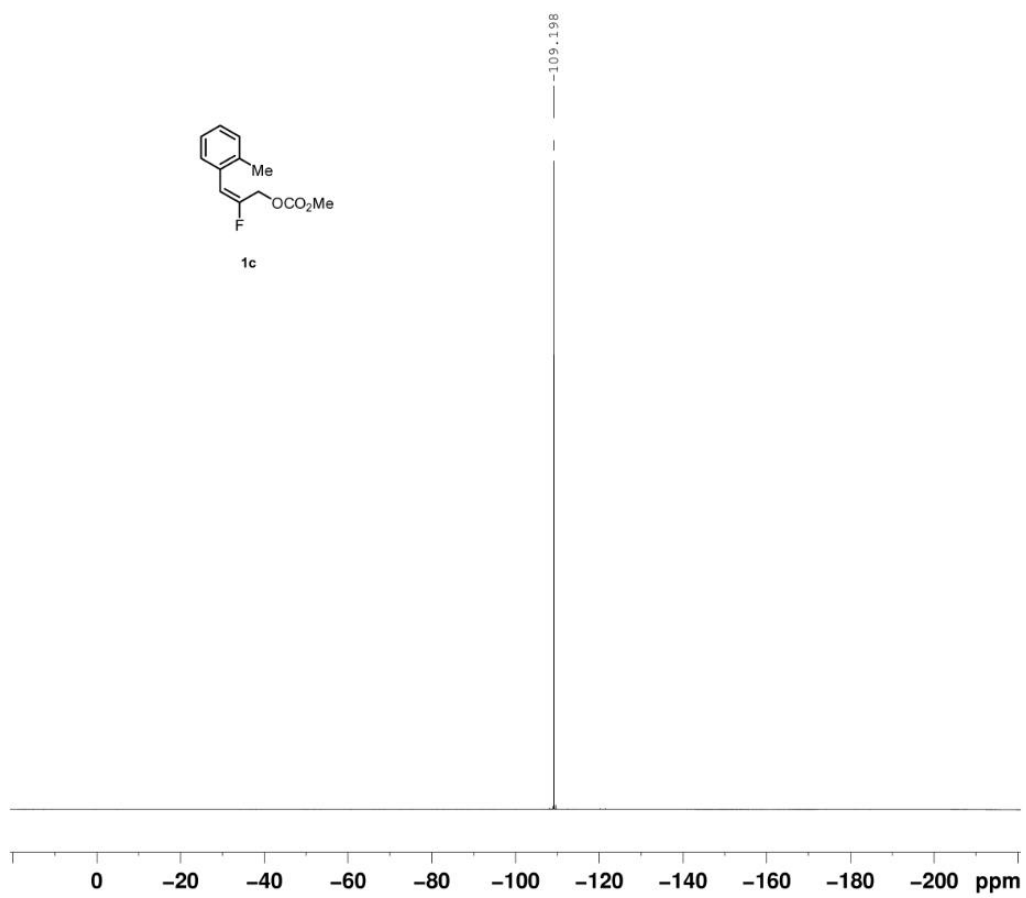
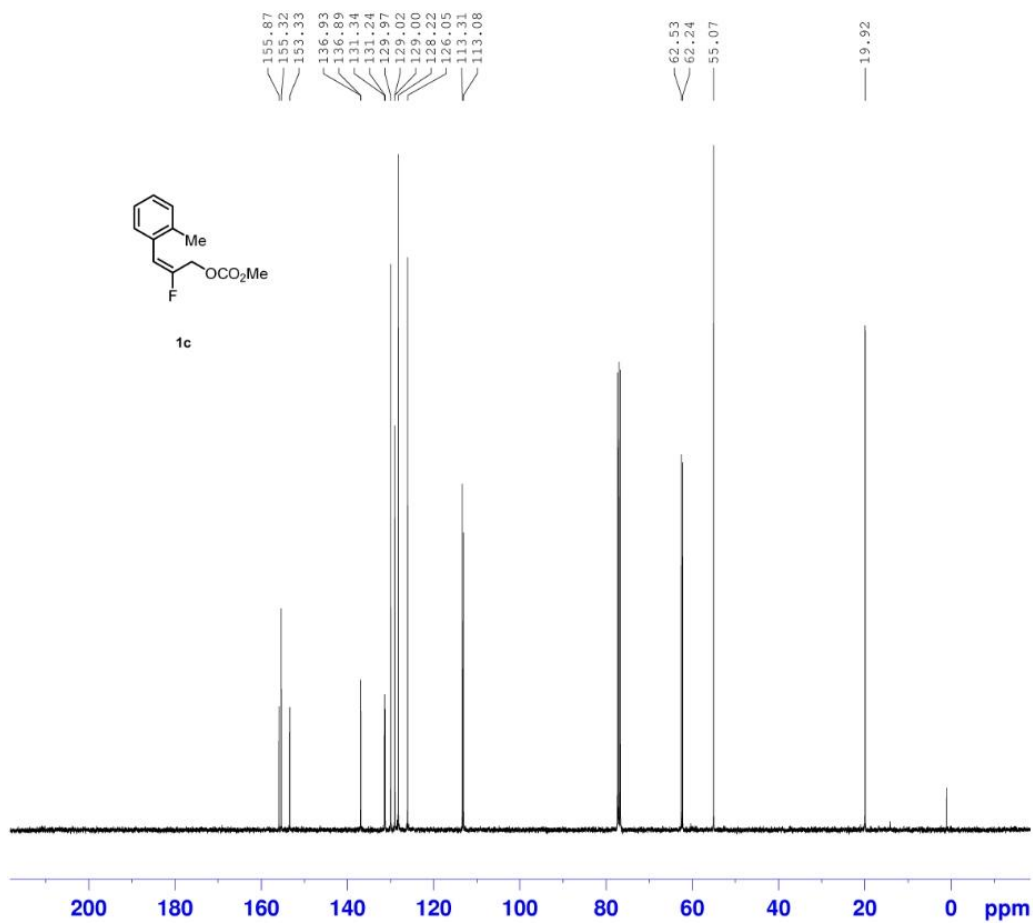
6. References

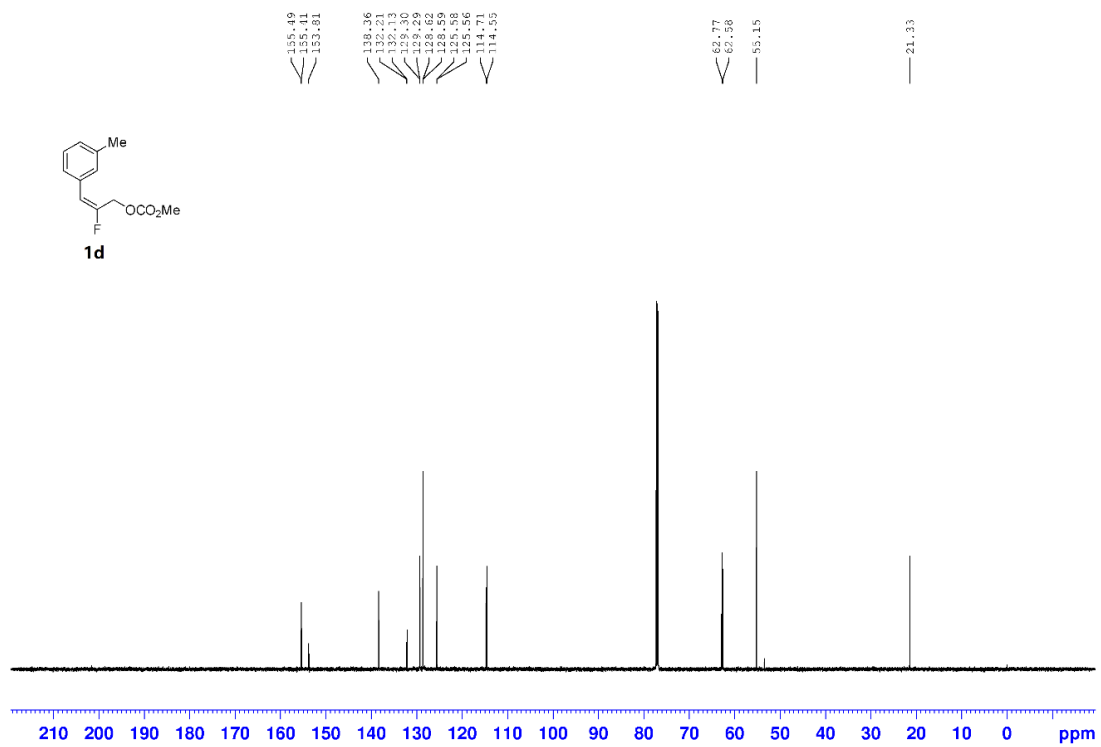
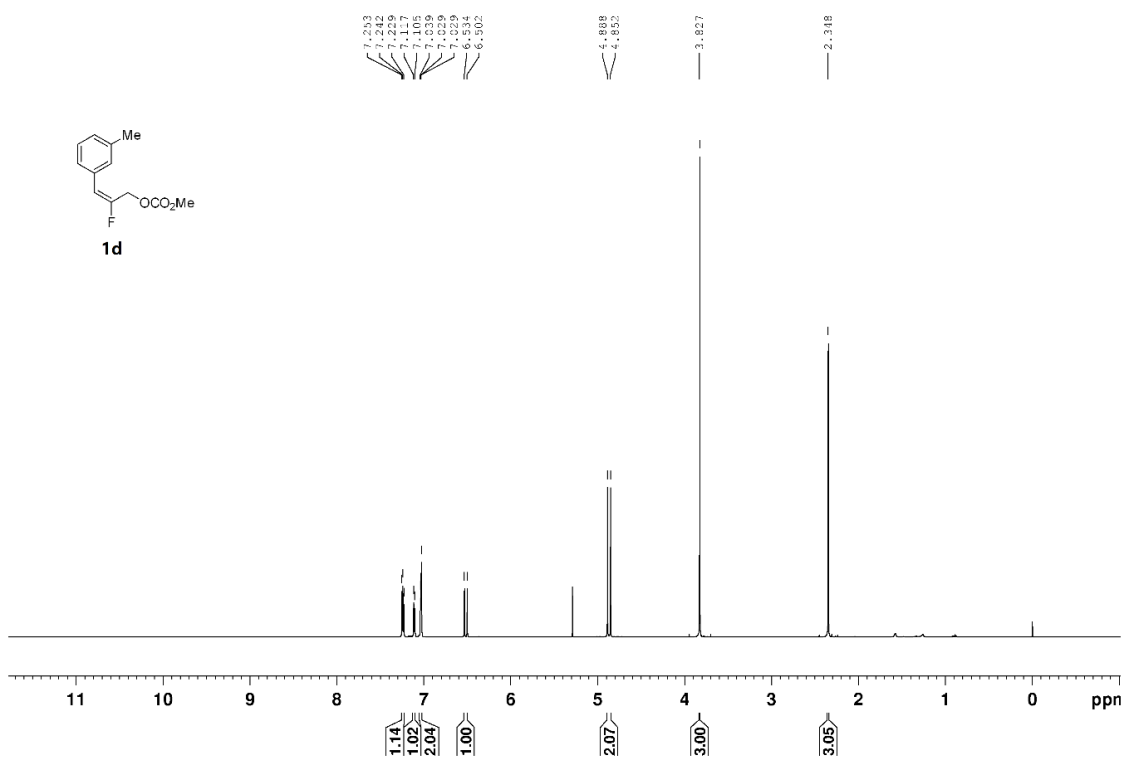
- [1] (a) M. Engman, J. S. Diesen, A. Paptchikhine, P. G. Andersson, *J. Am. Chem. Soc.* **2007**, *129*, 4536. (b) M. Yamamoto, S. Hayashi, K. Isa, M. Kawatsura, *Org. Lett.* **2014**, *16*, 700.
- [2] (a) Lv, L.; Qian, H.; Crowell, A. B.; Chen, S.; Li, Z. *ACS Catal.* **2022**, *12*, 6495. (b) Wu, L.; Wang, M.; Liang, Y.; Shi, Z. *Chin. J. Chem.* **2022**, *40*, 2345.

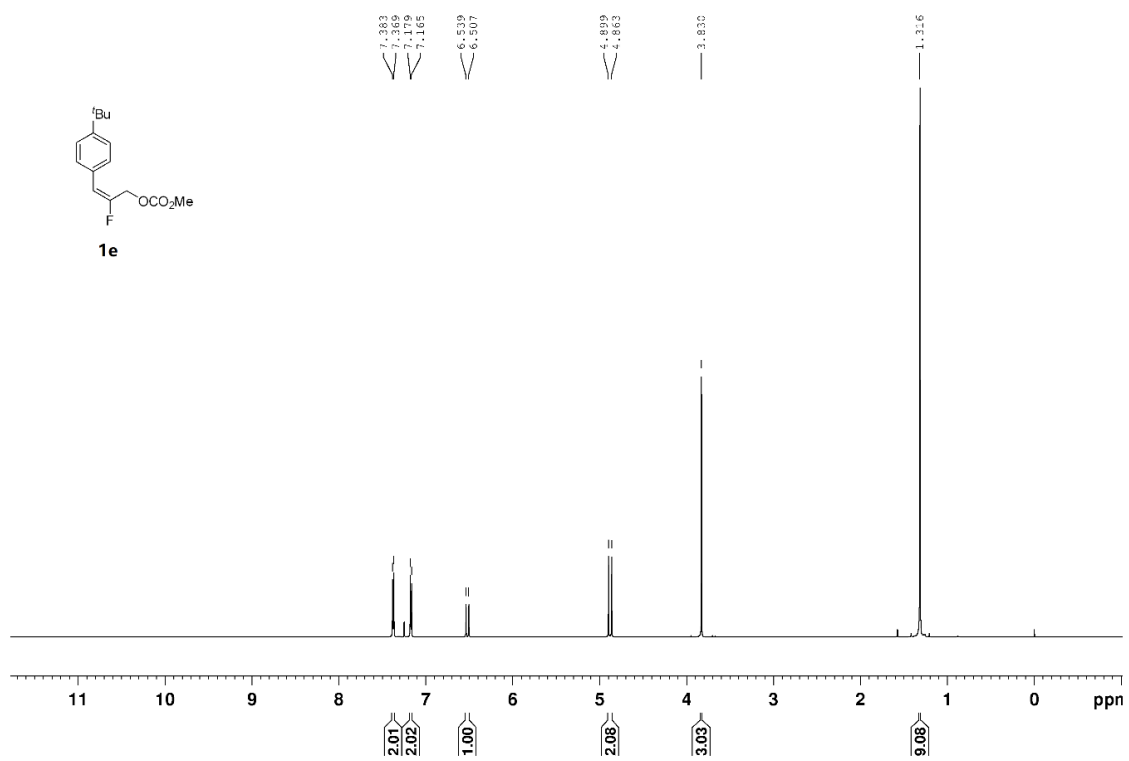
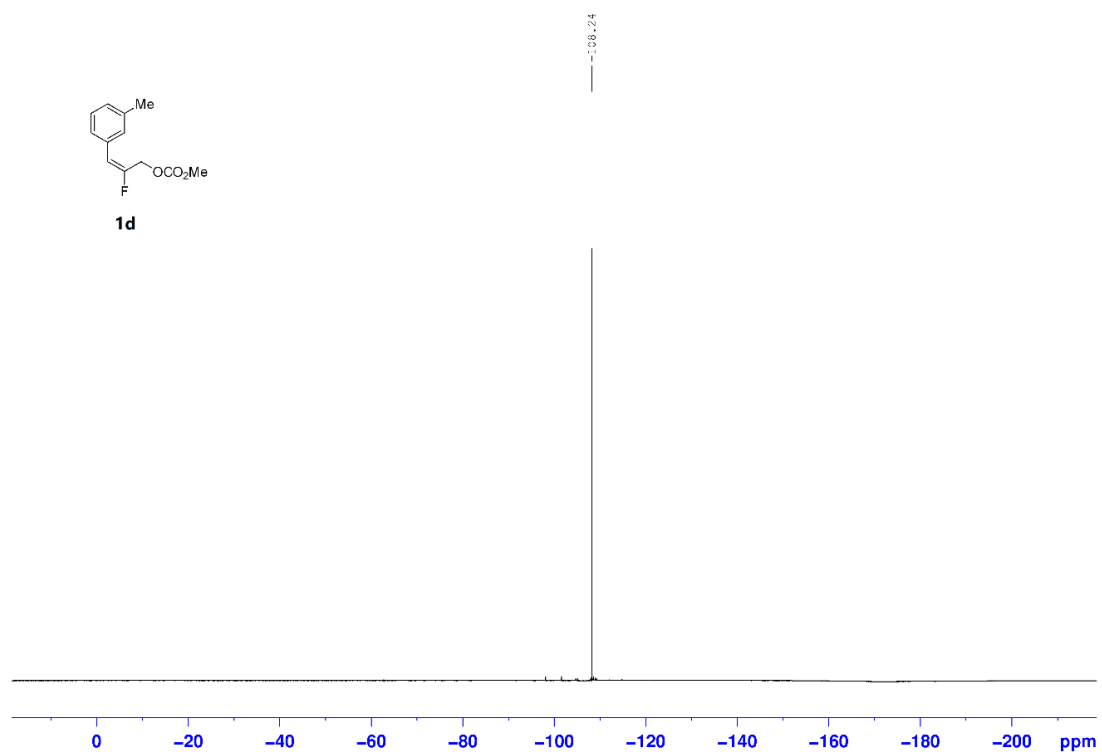
7. Copies of ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra for all new compounds and products

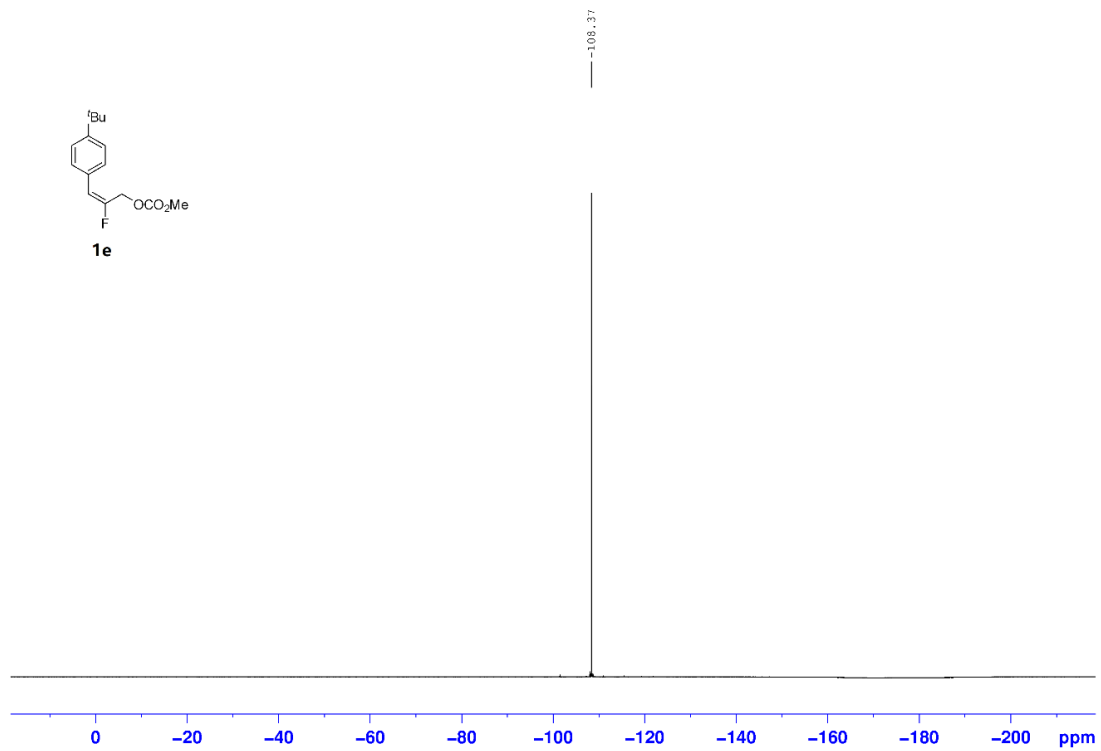
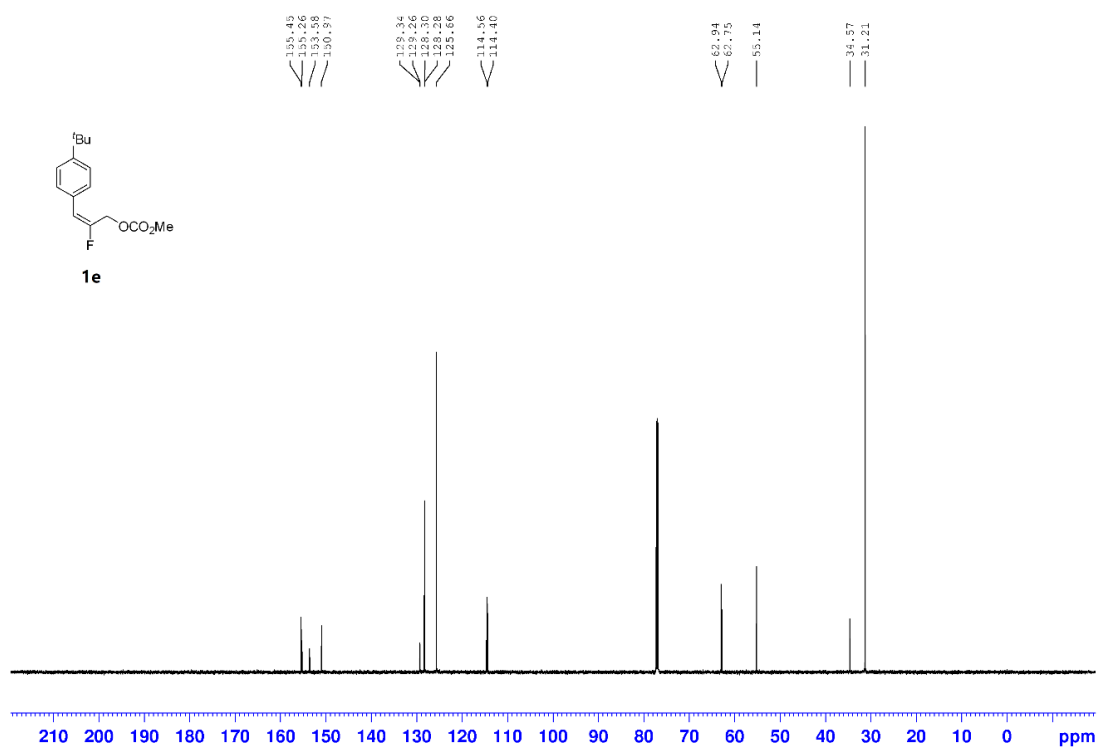


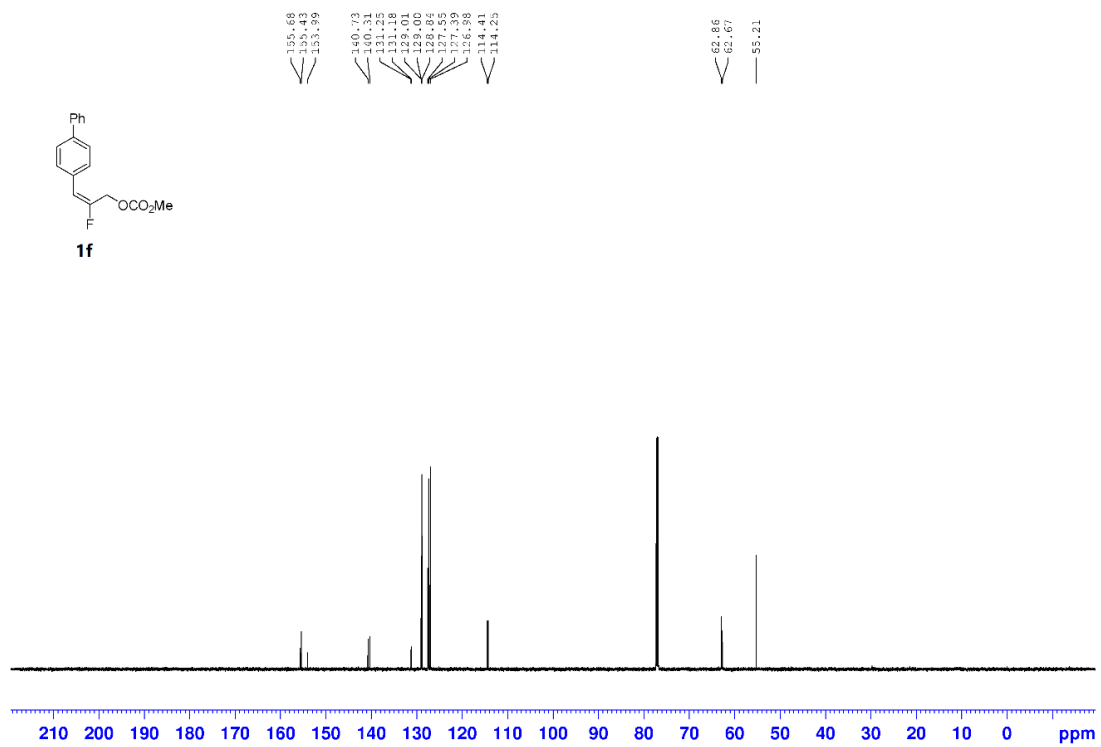
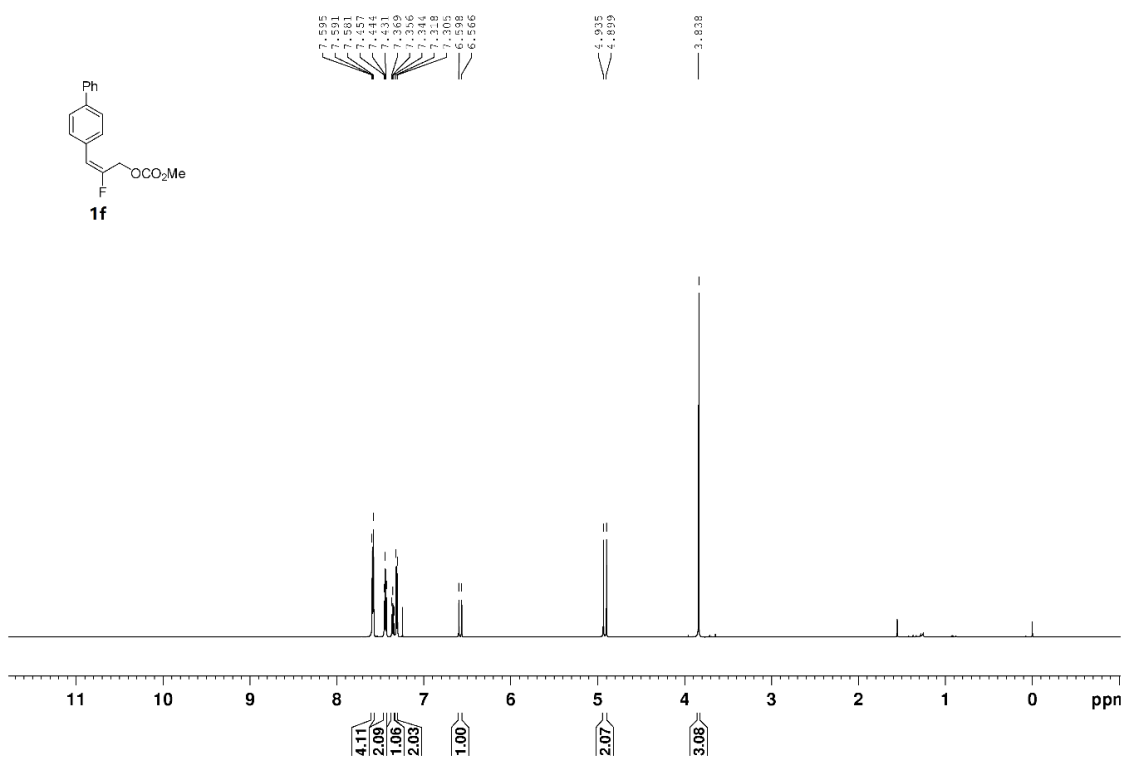


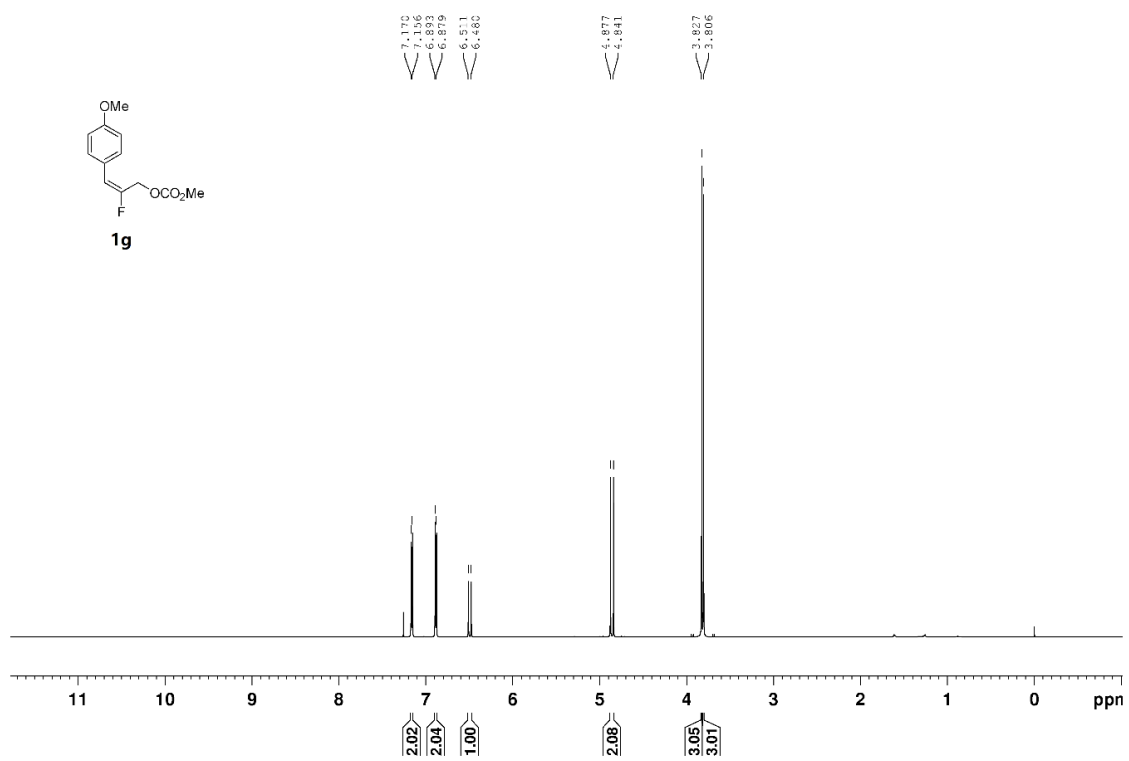
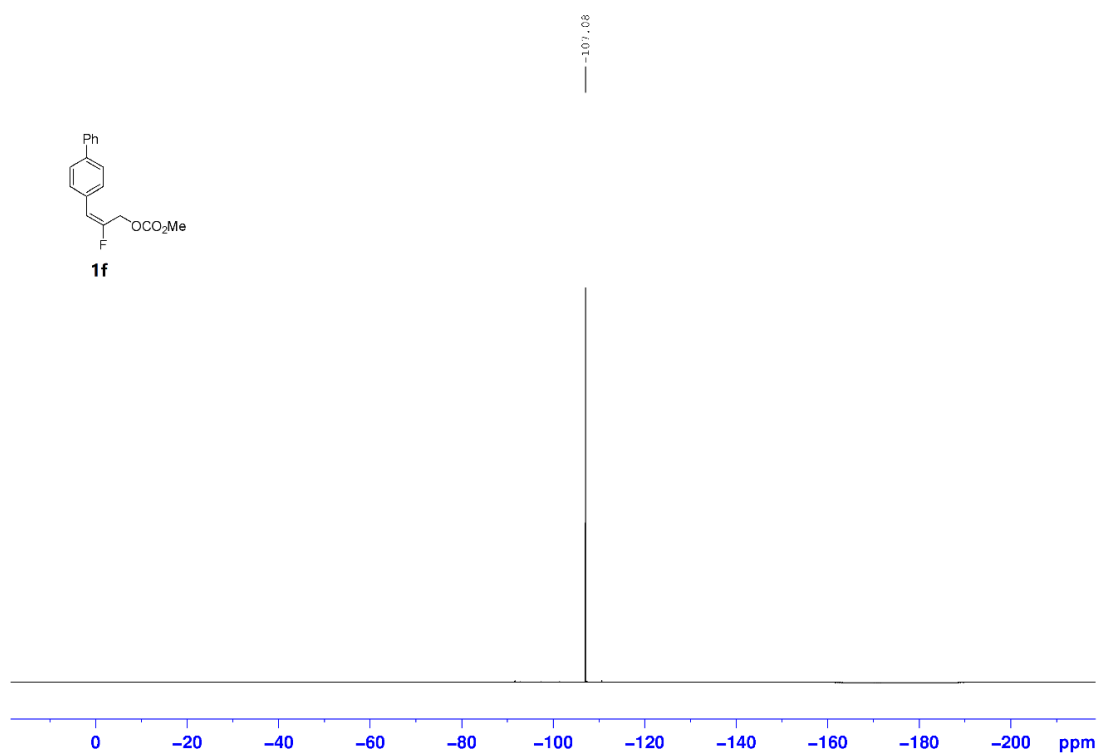


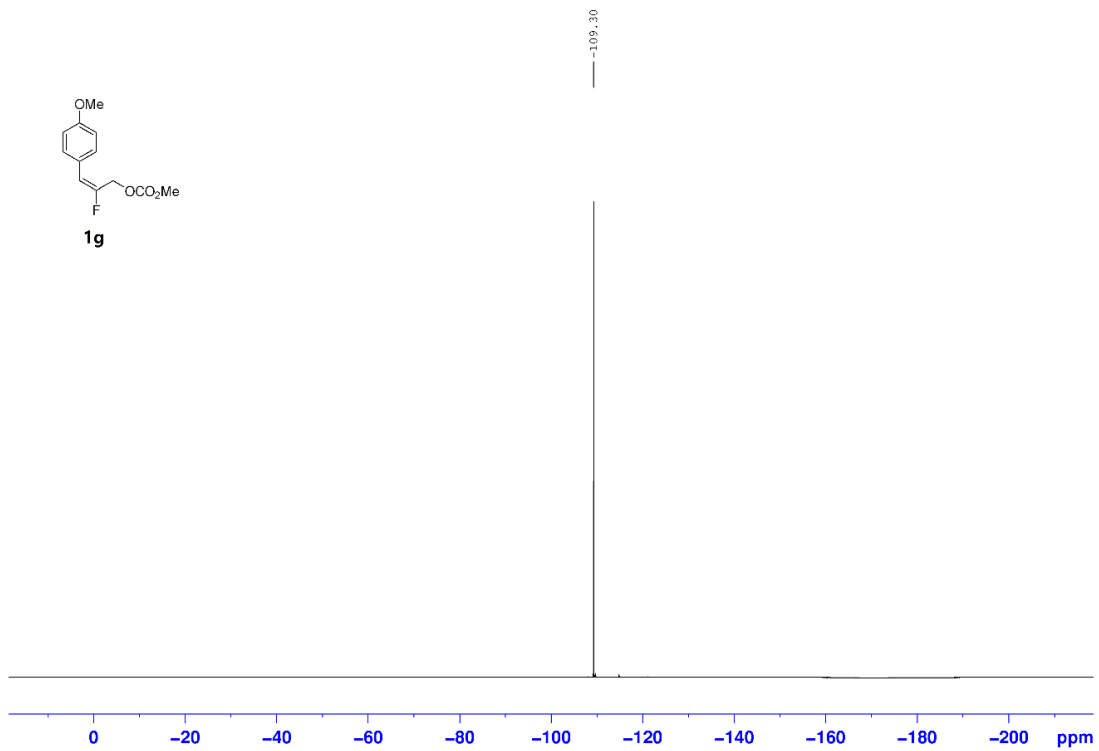
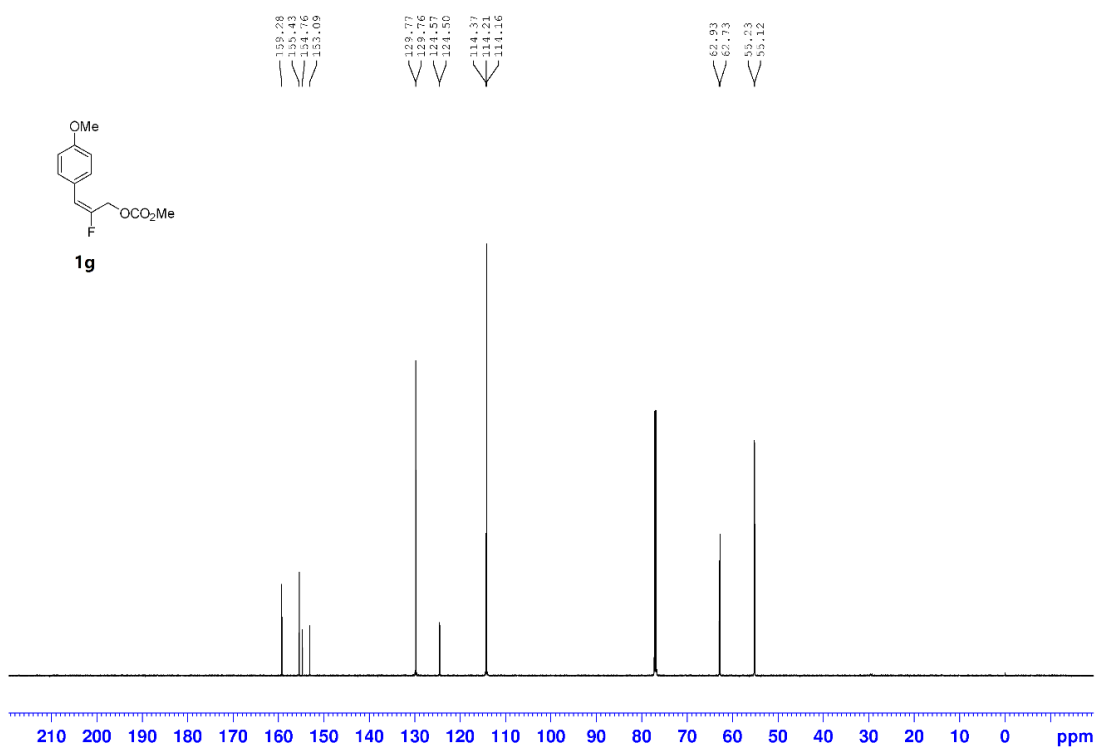


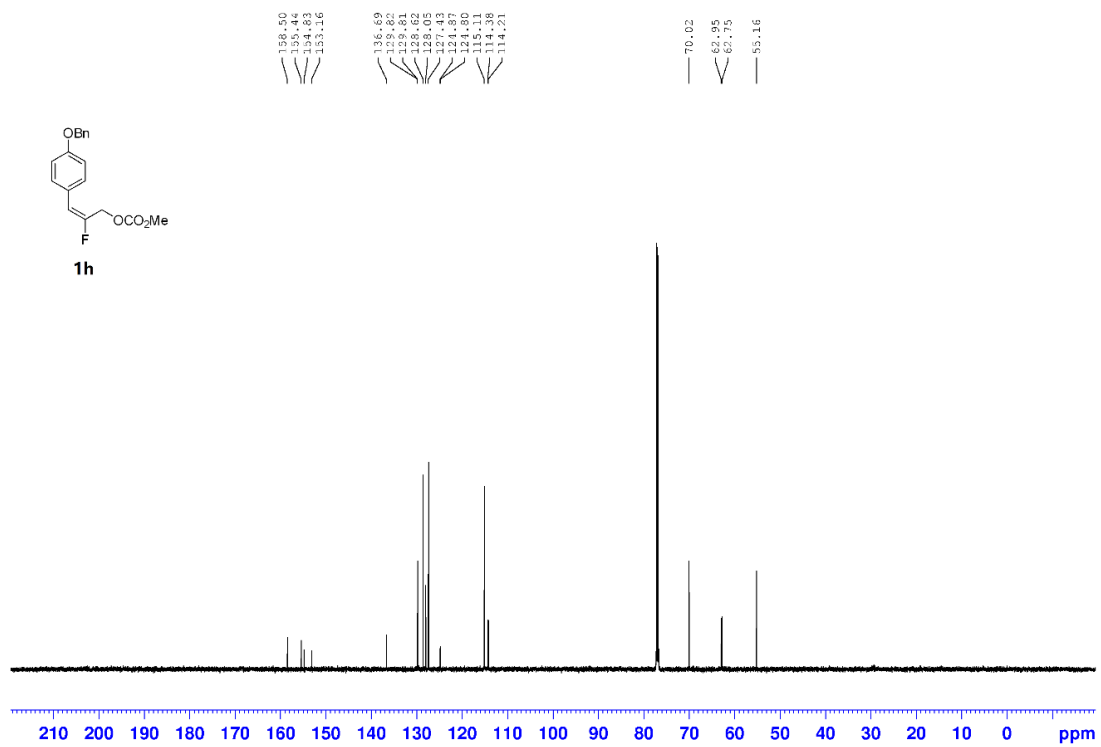
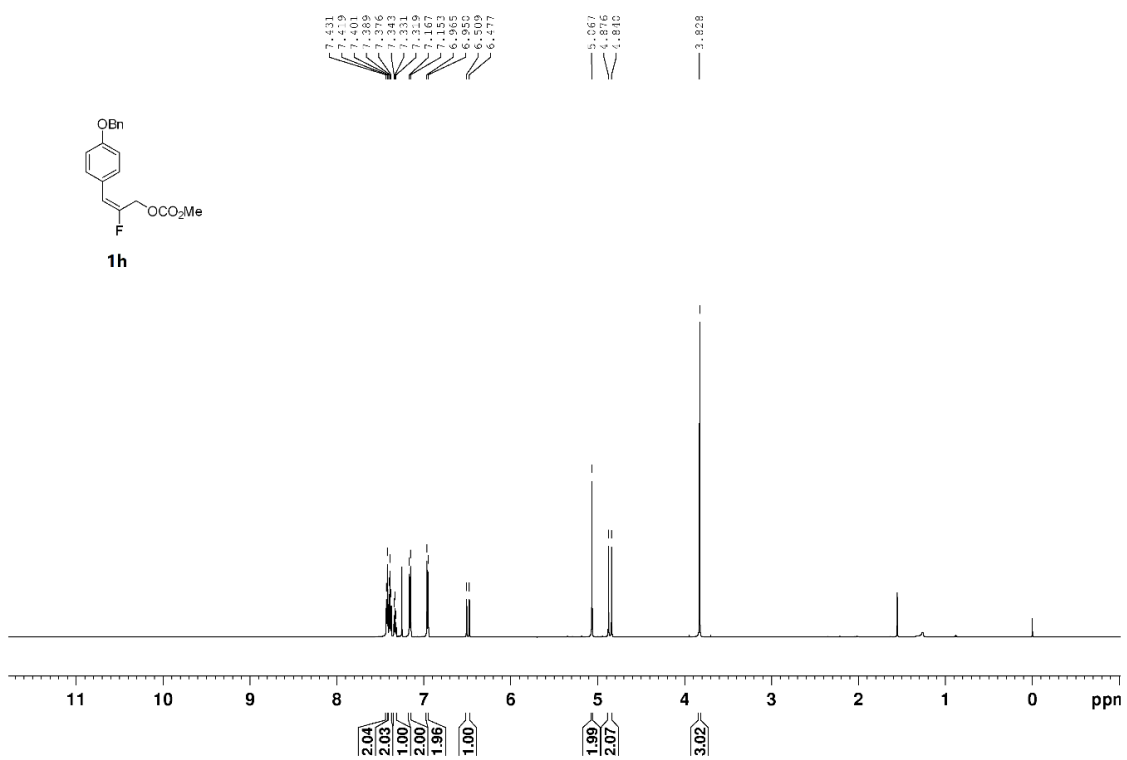


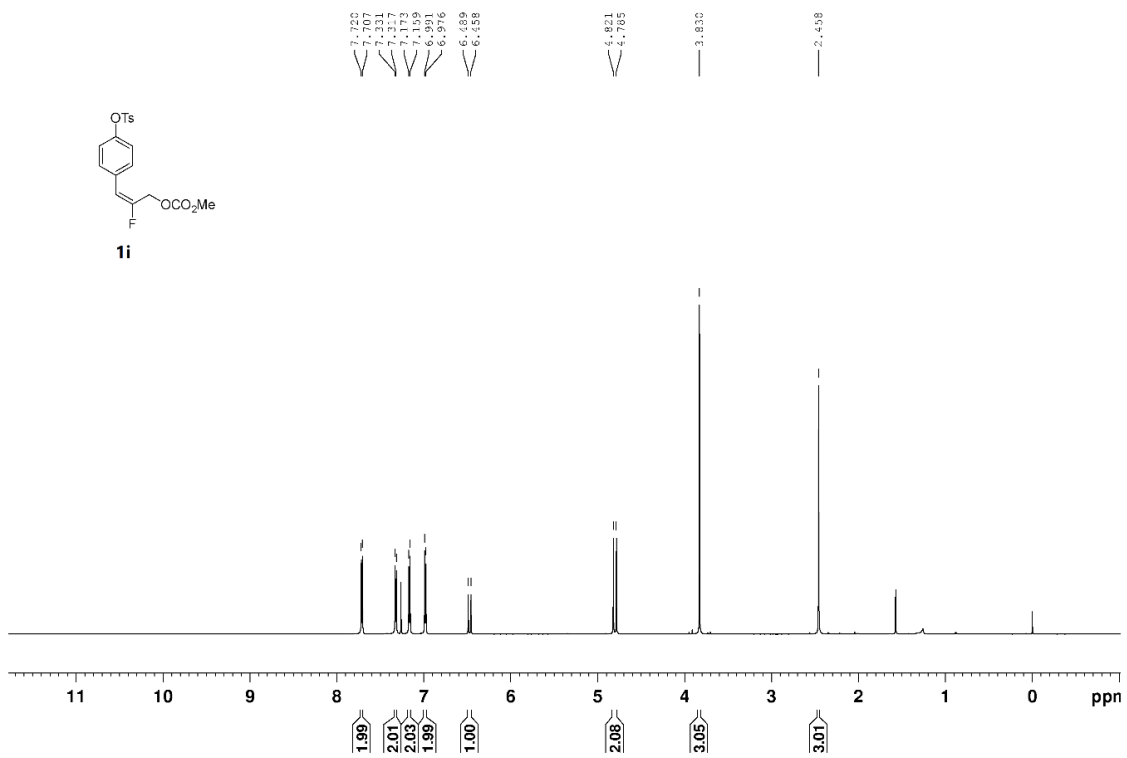
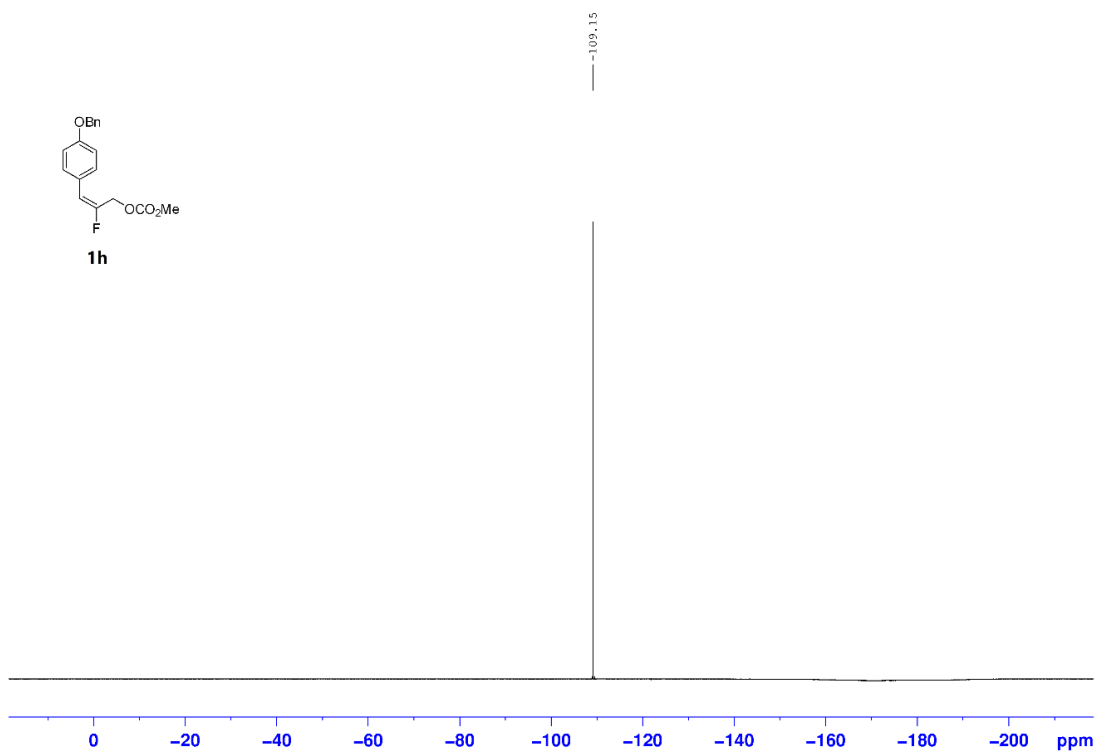


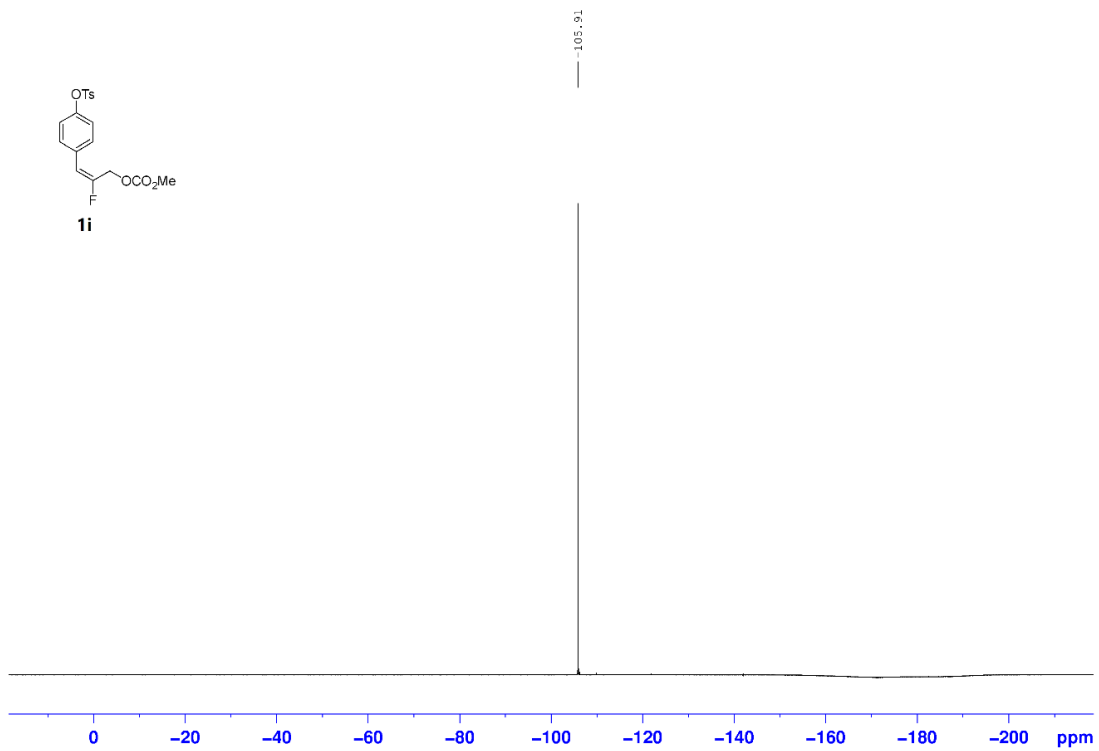
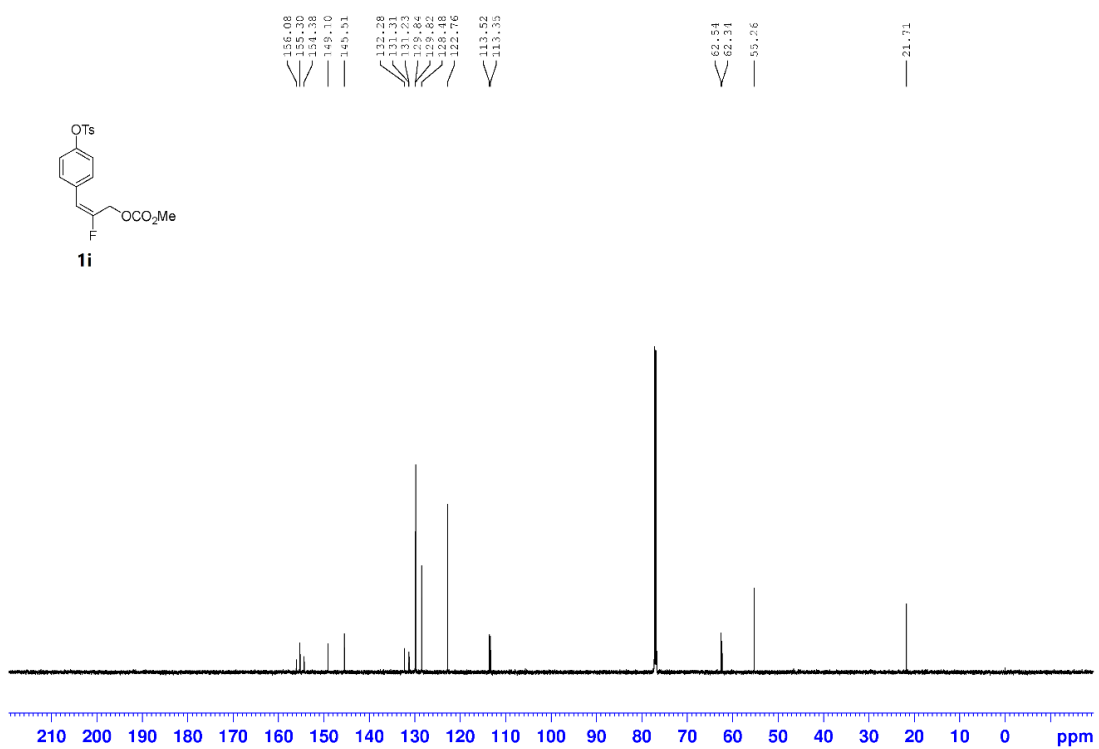


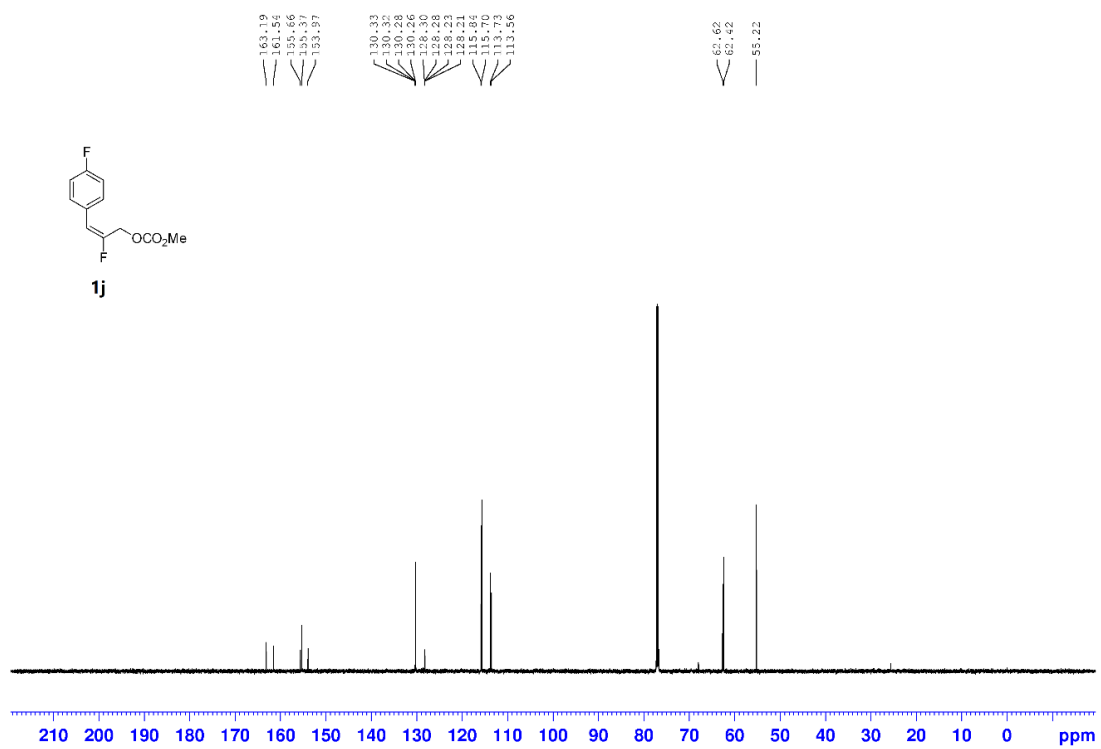
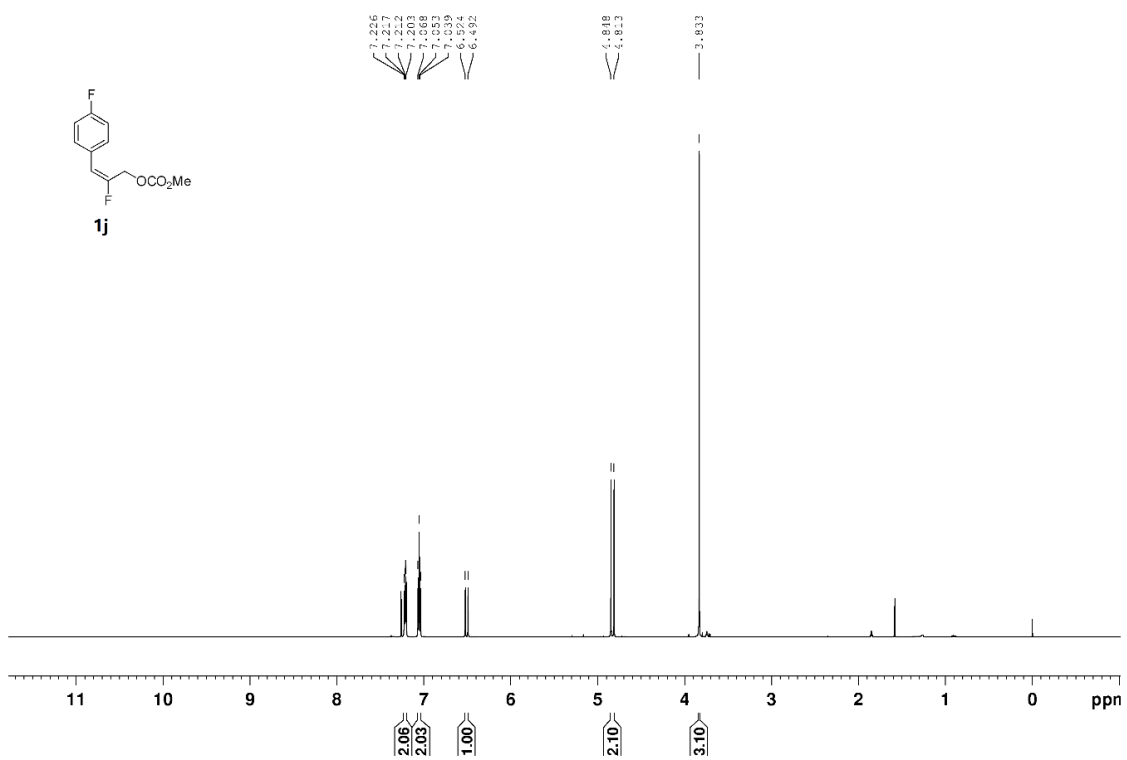


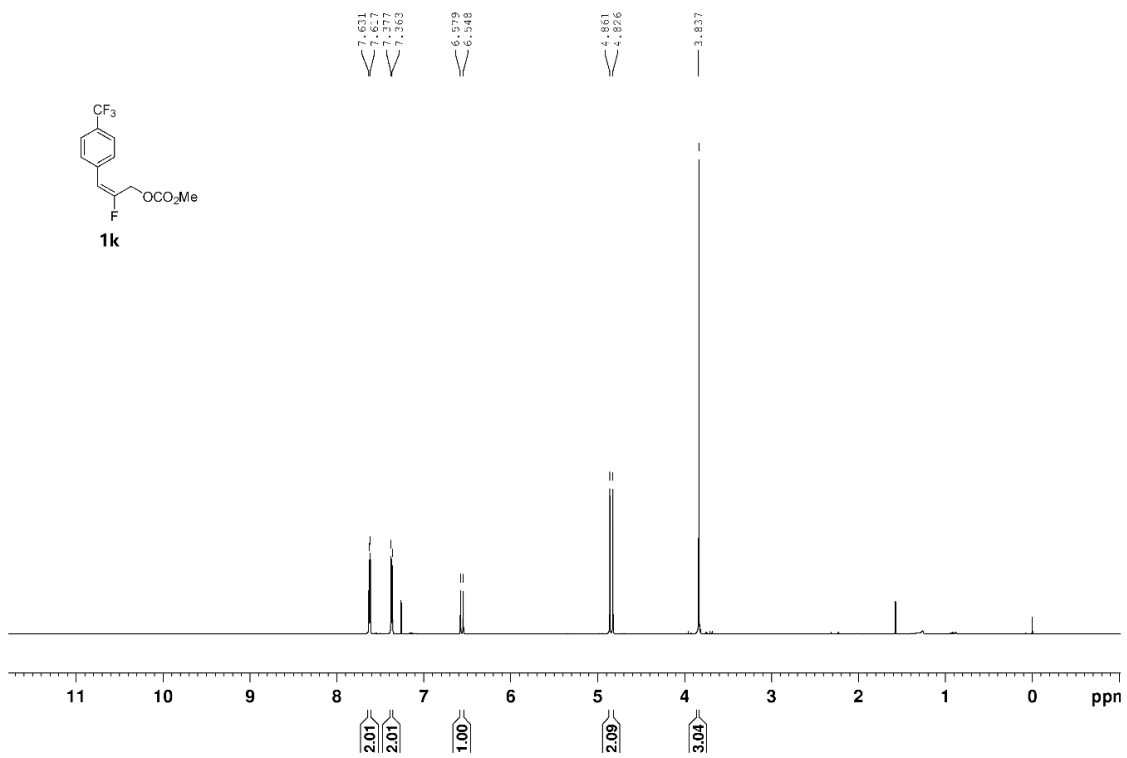
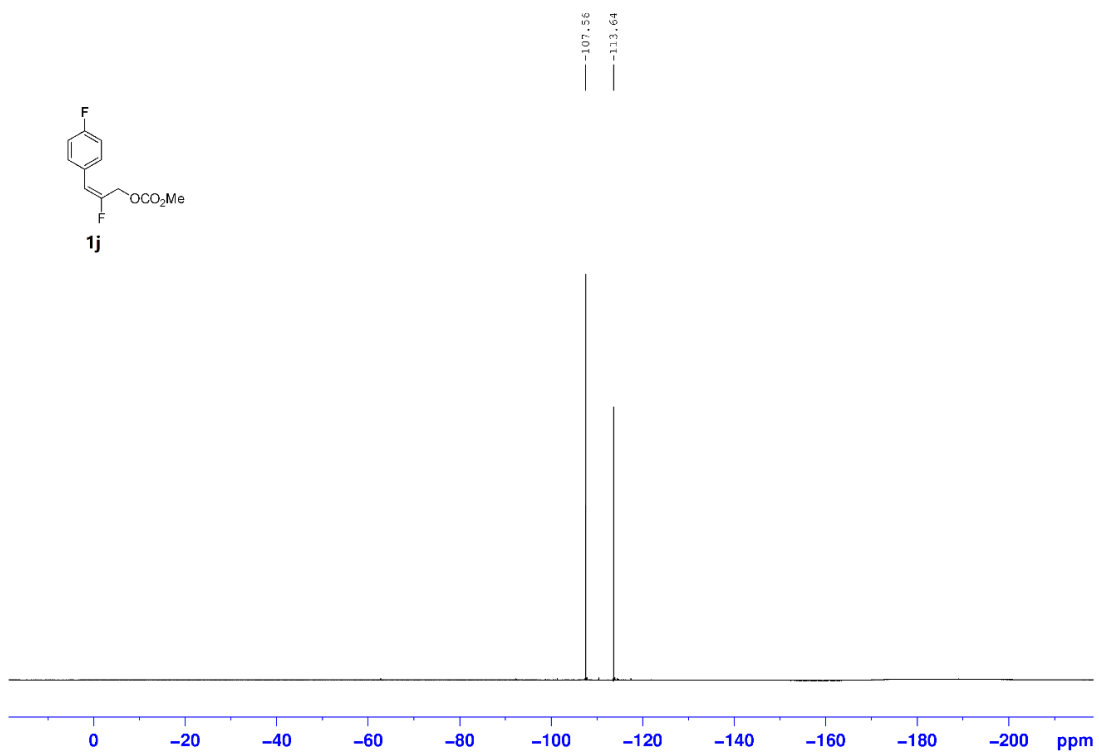


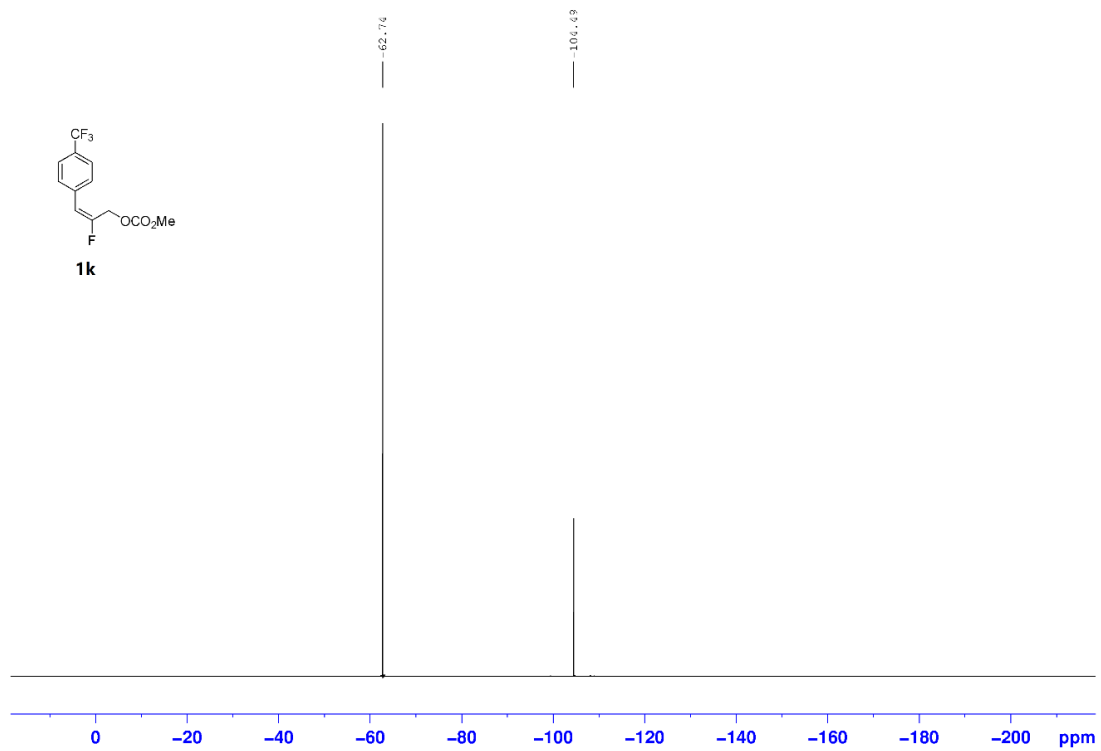
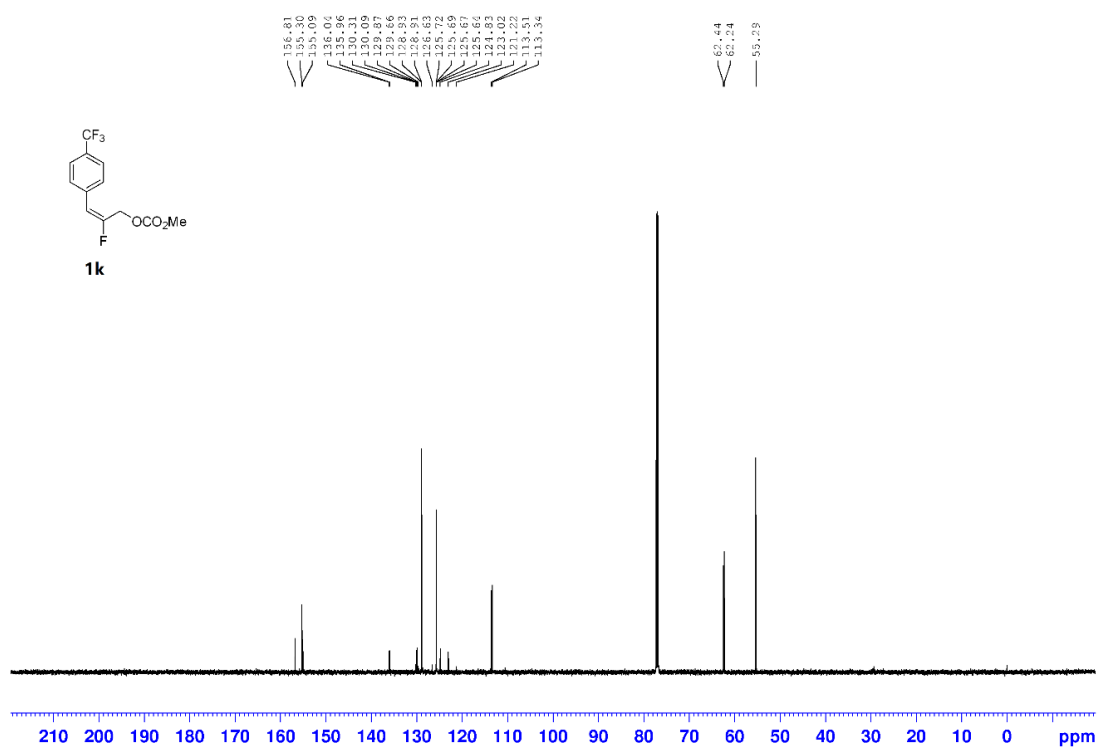


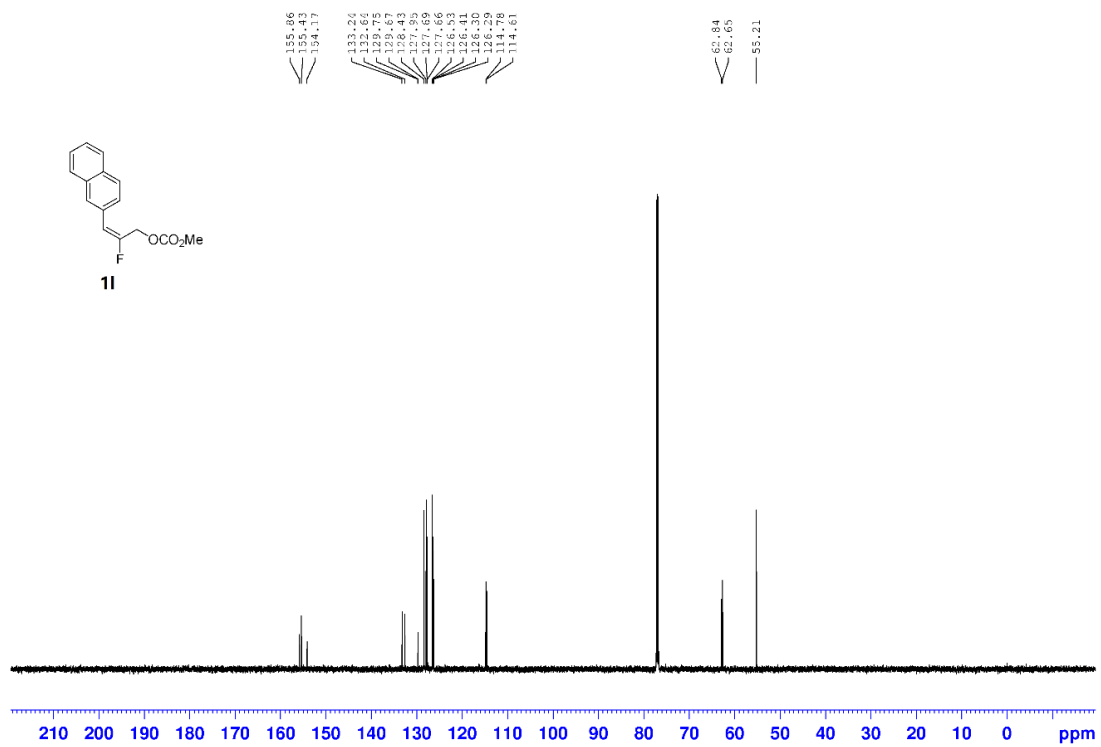
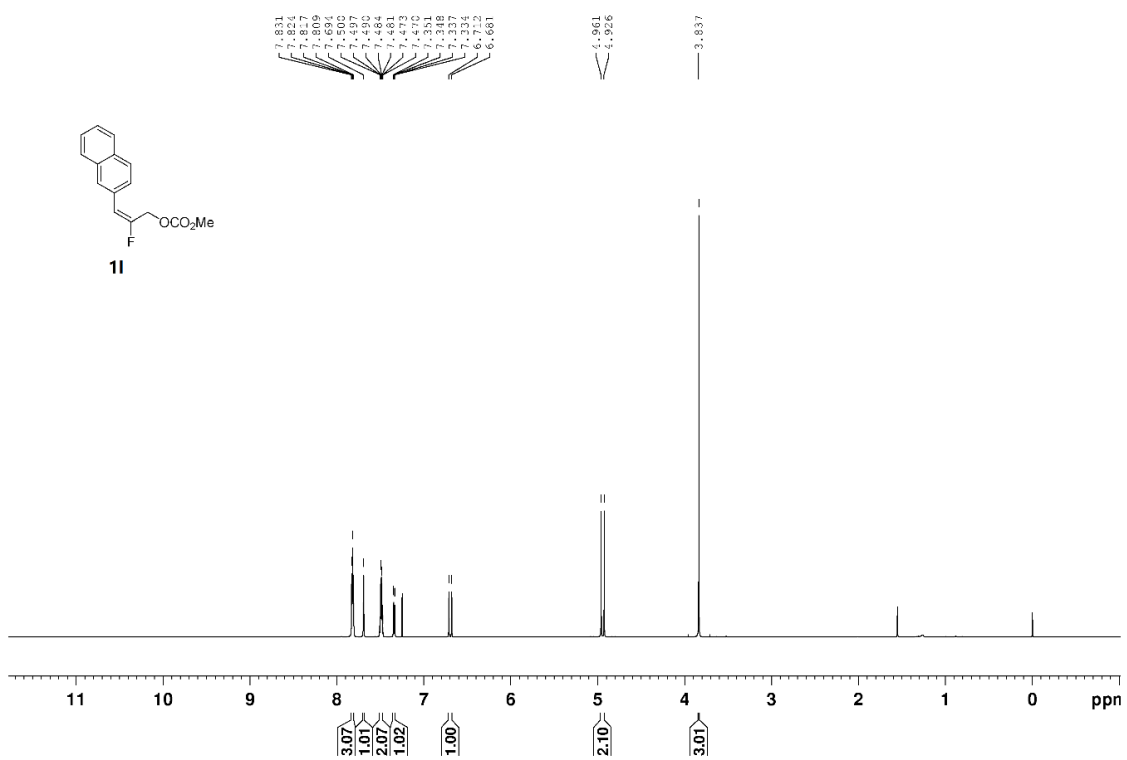


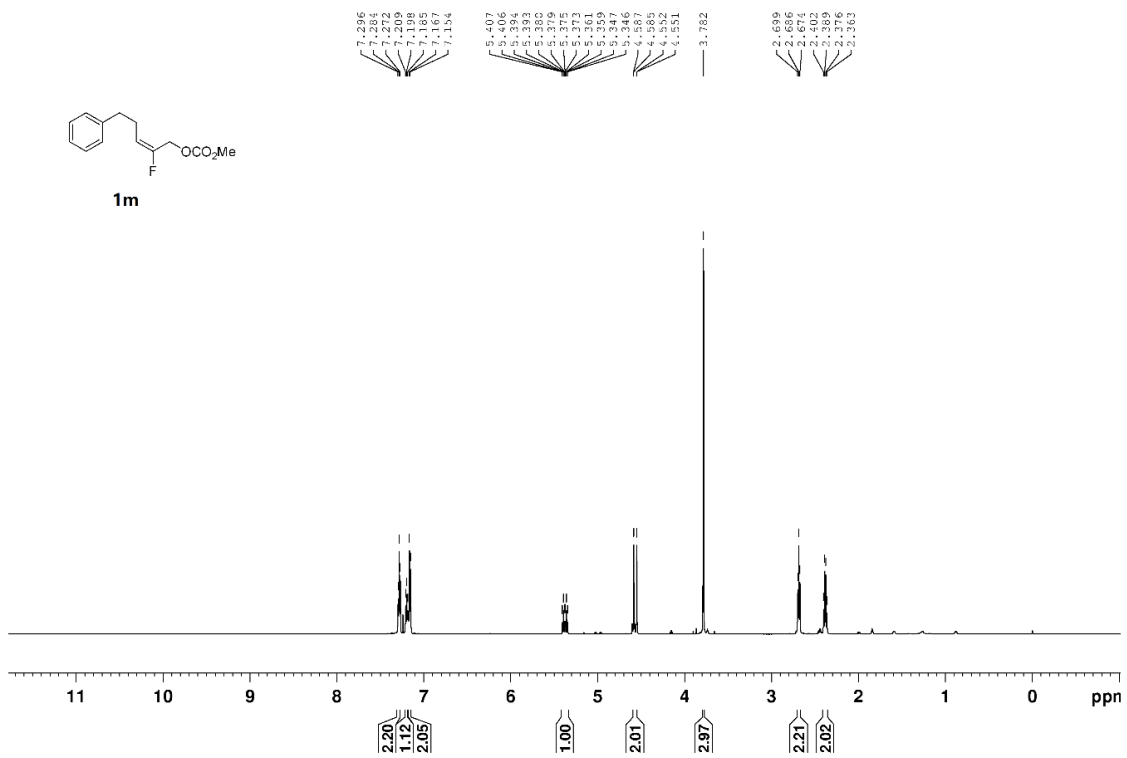
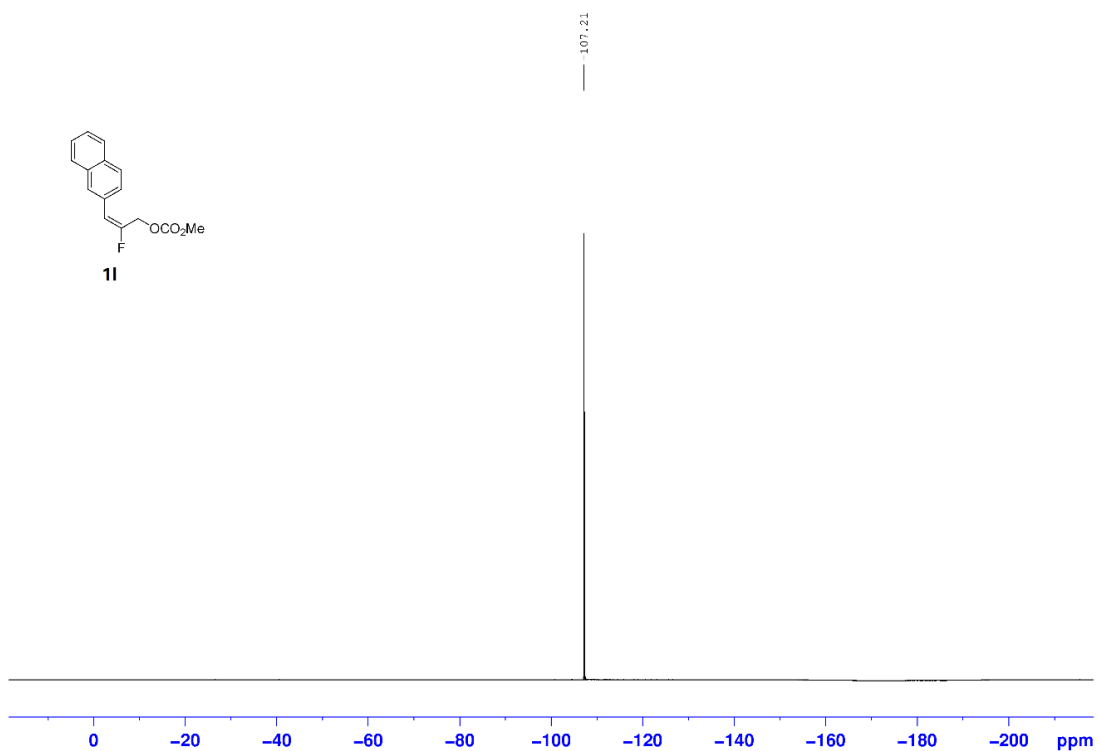


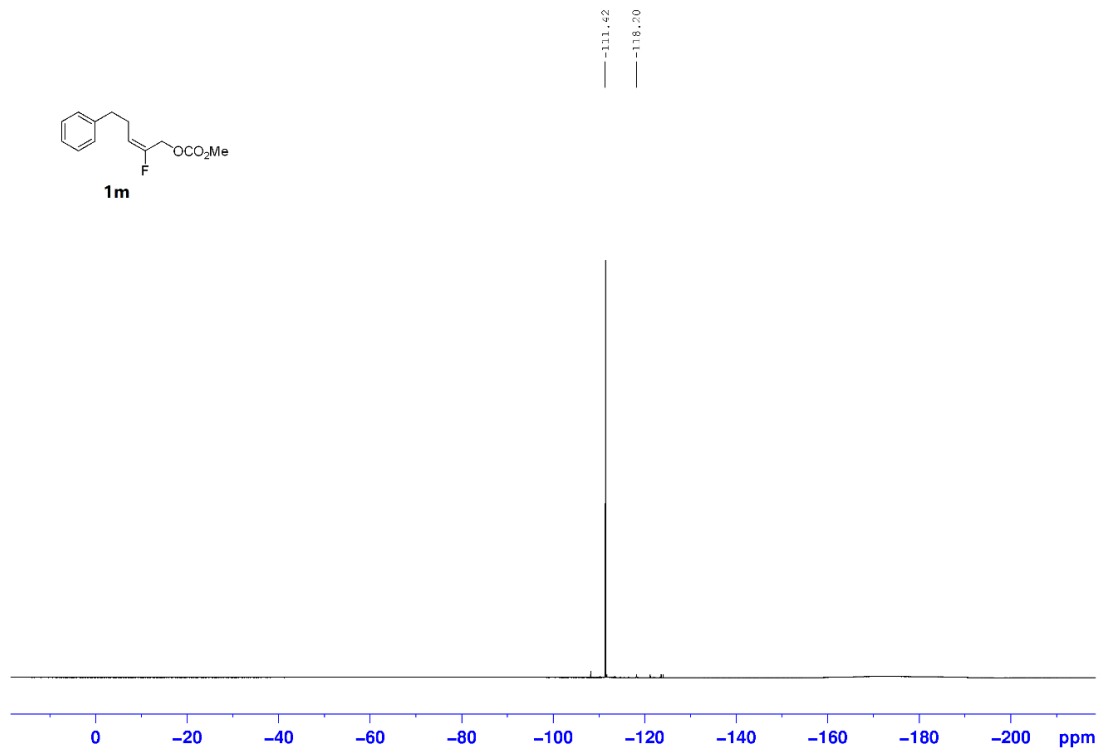
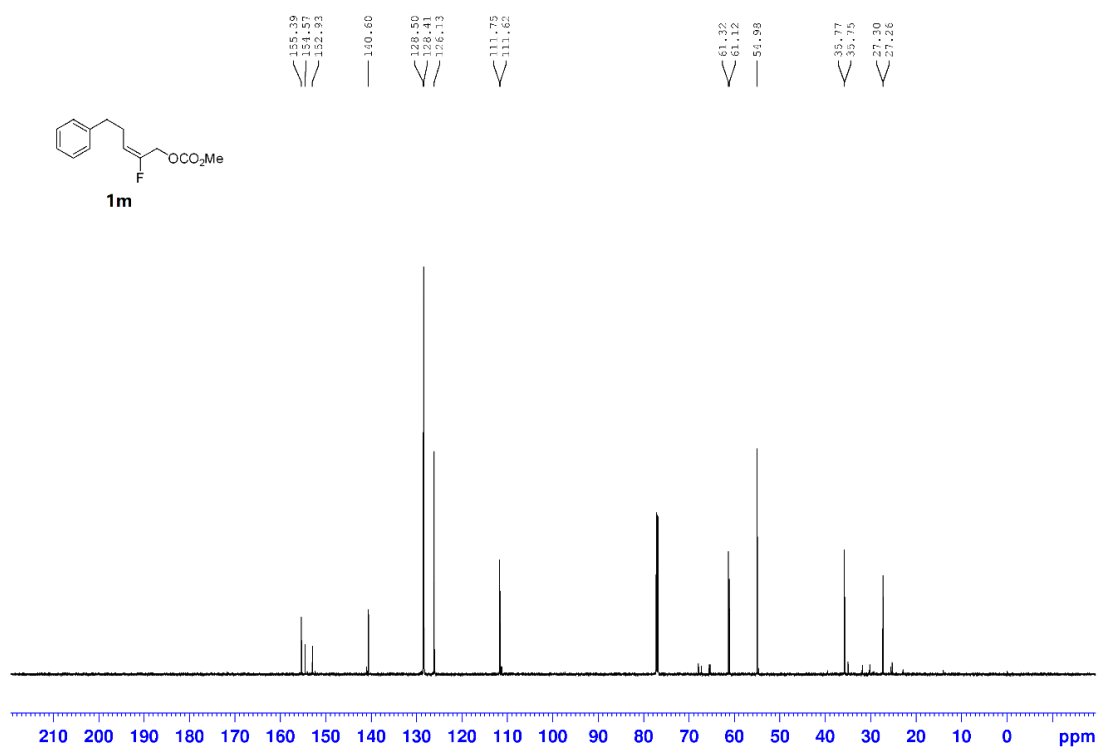


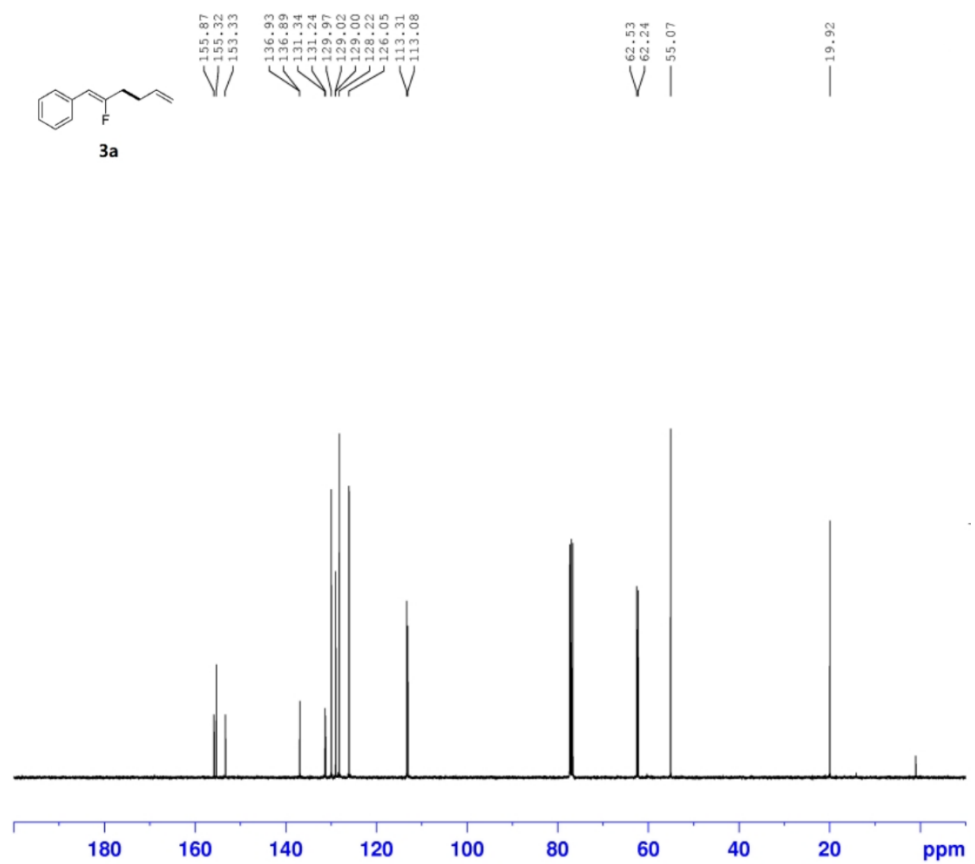
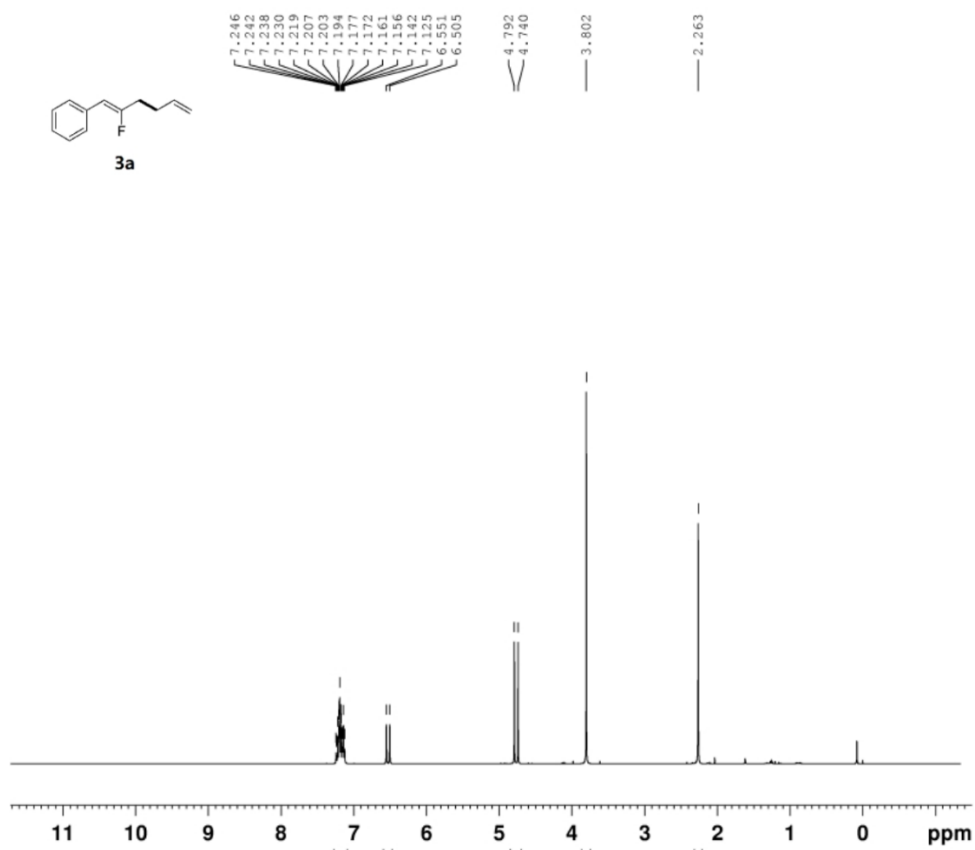


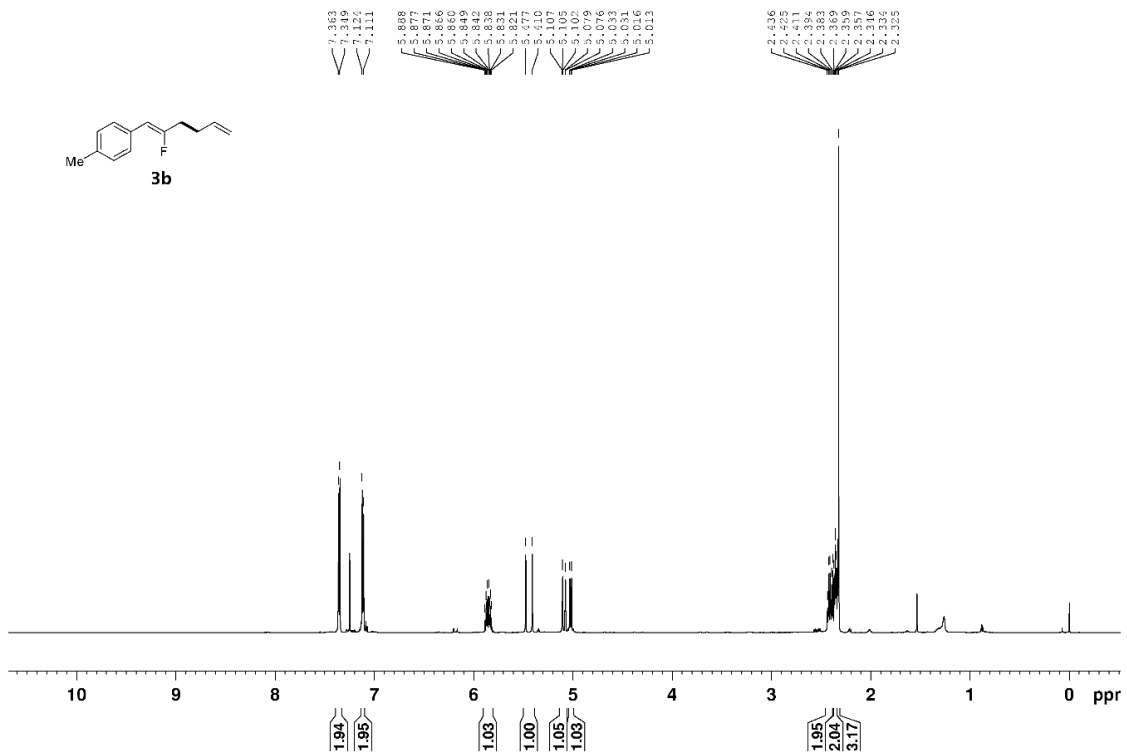
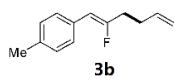
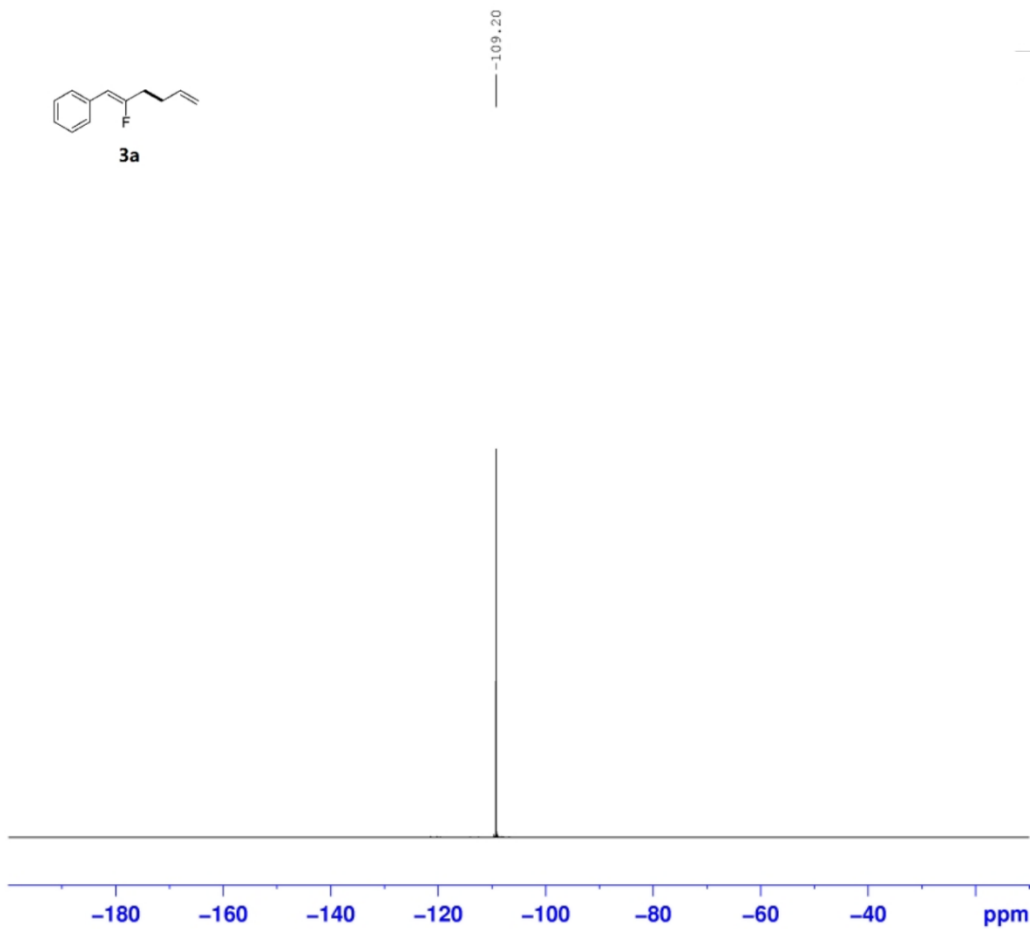
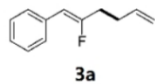


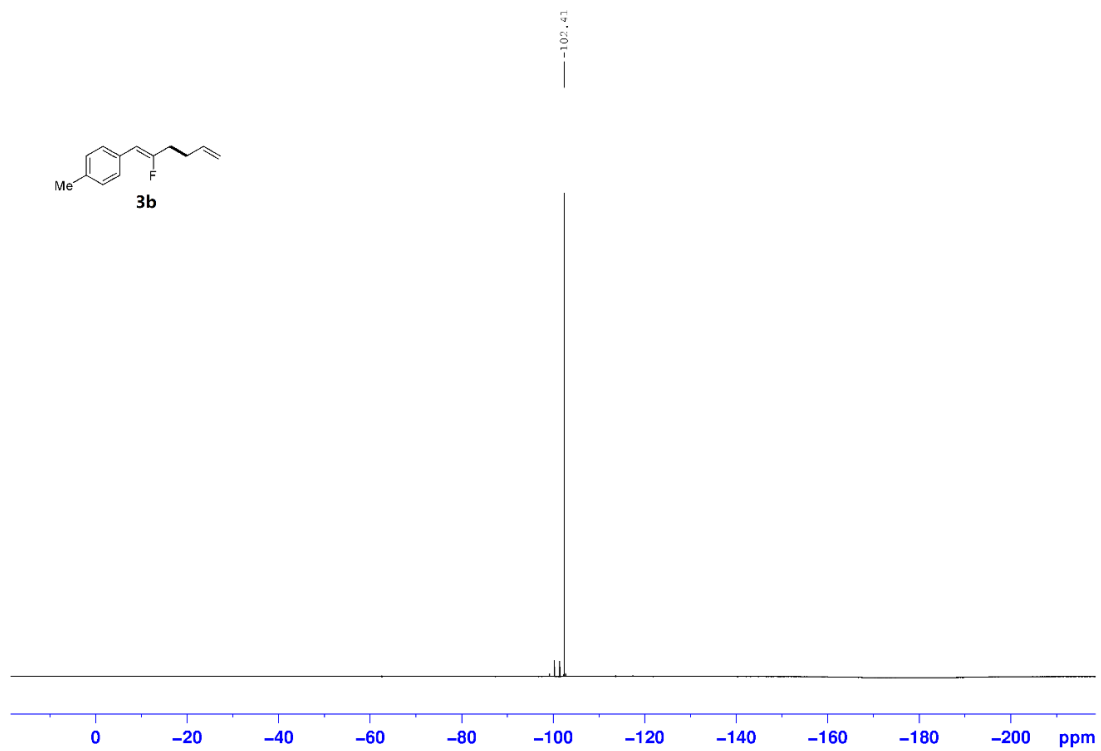
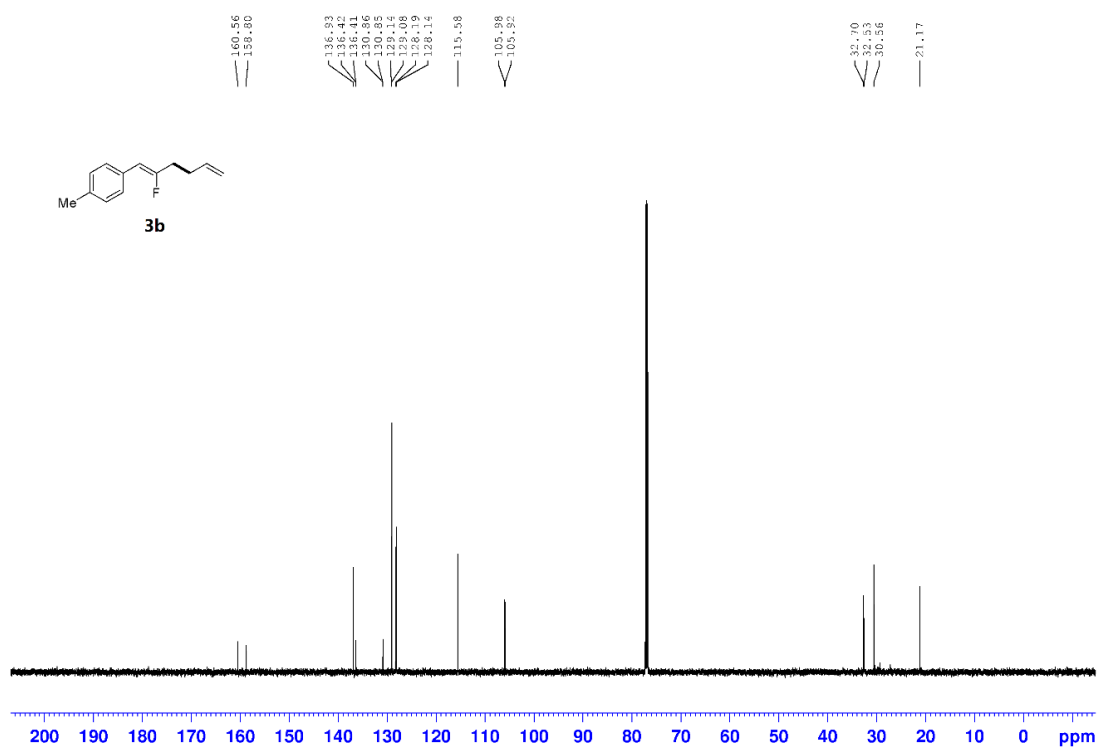


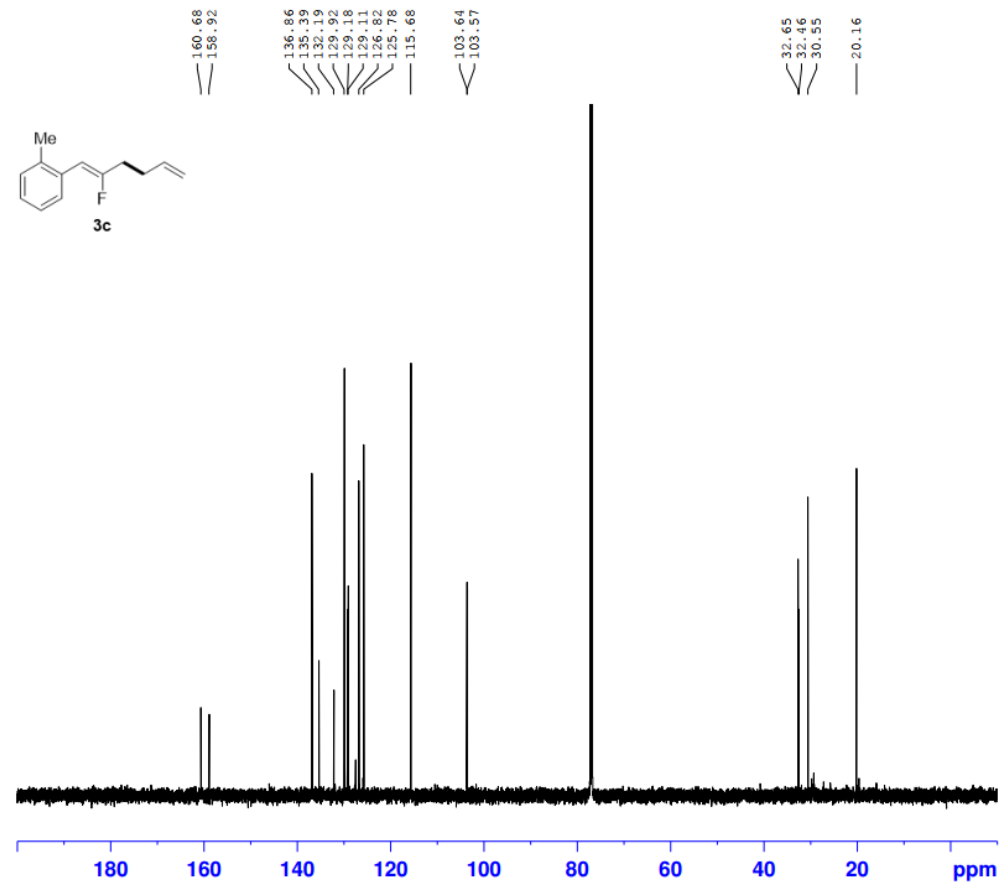
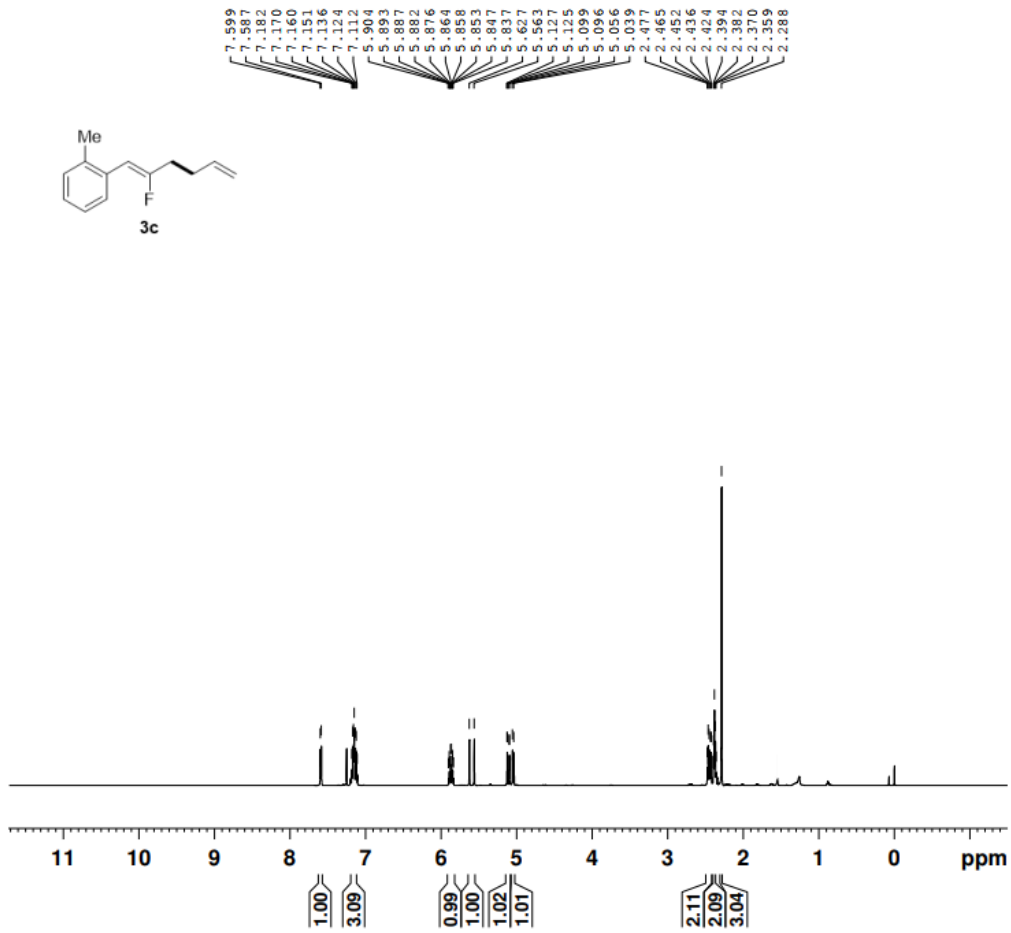


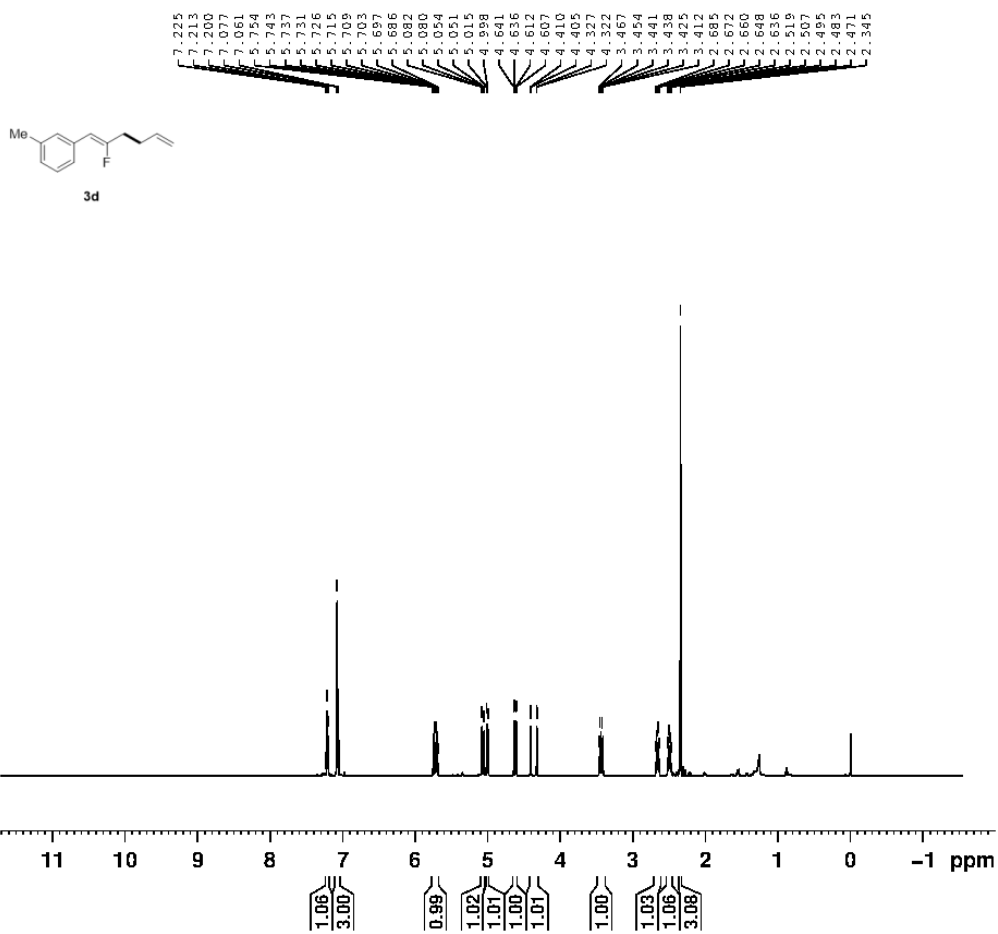
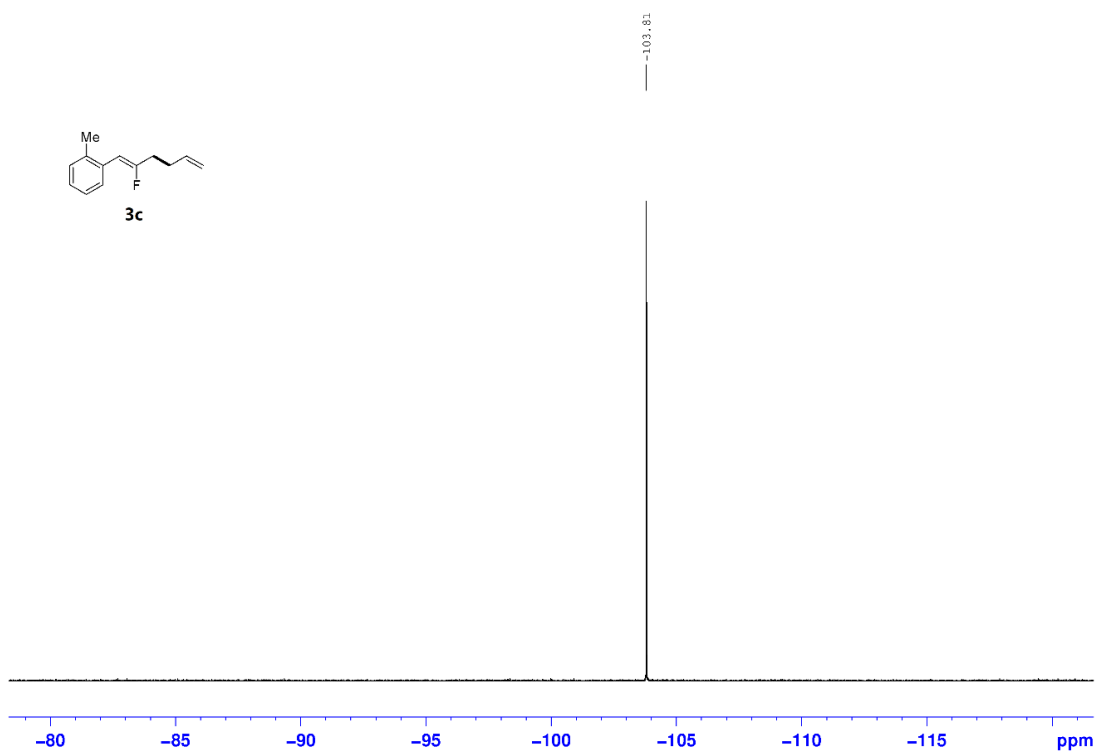


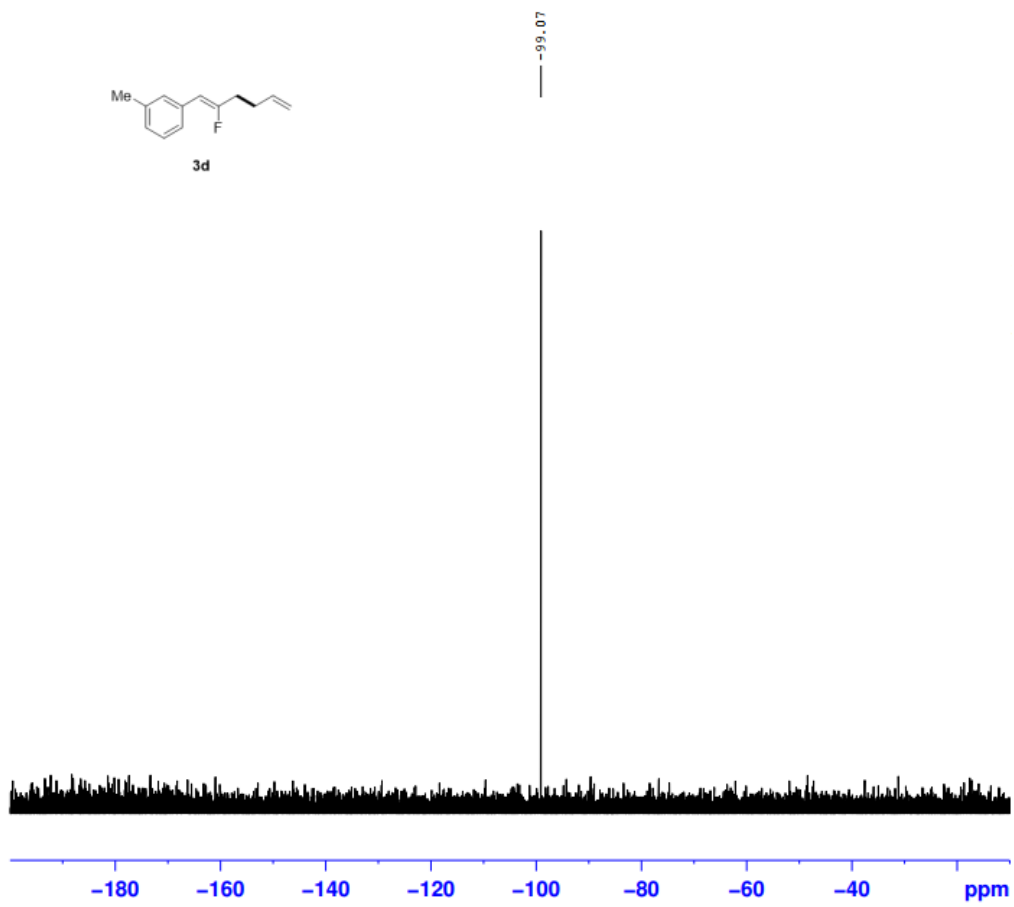
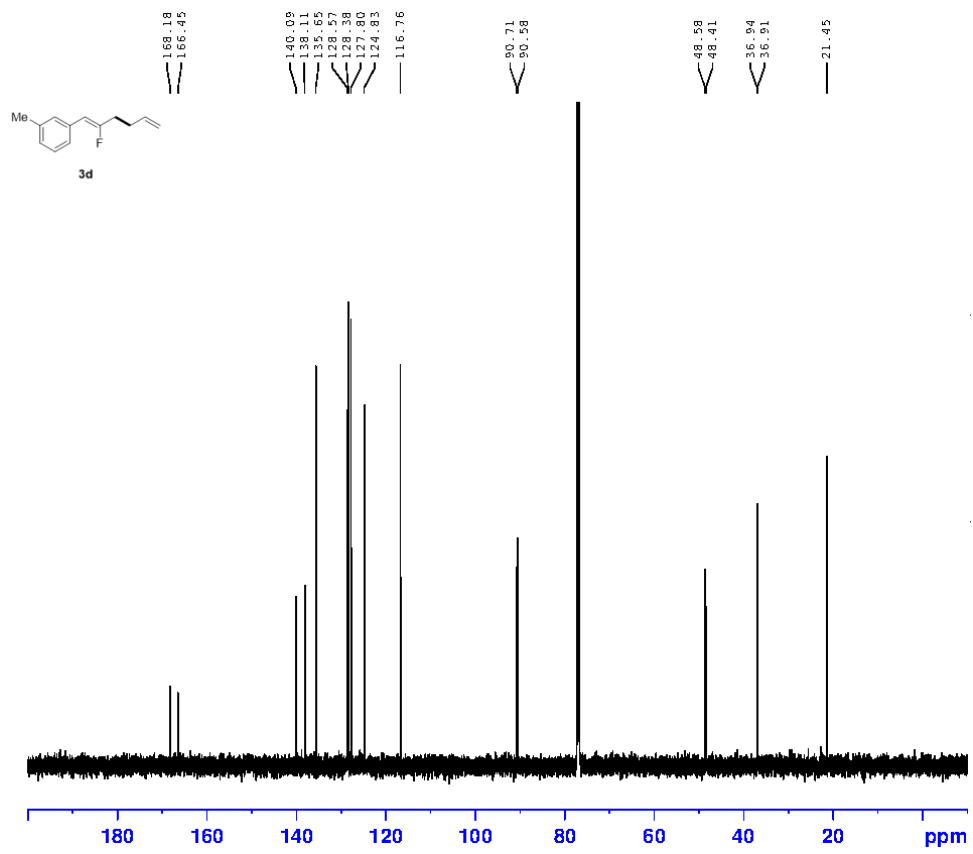


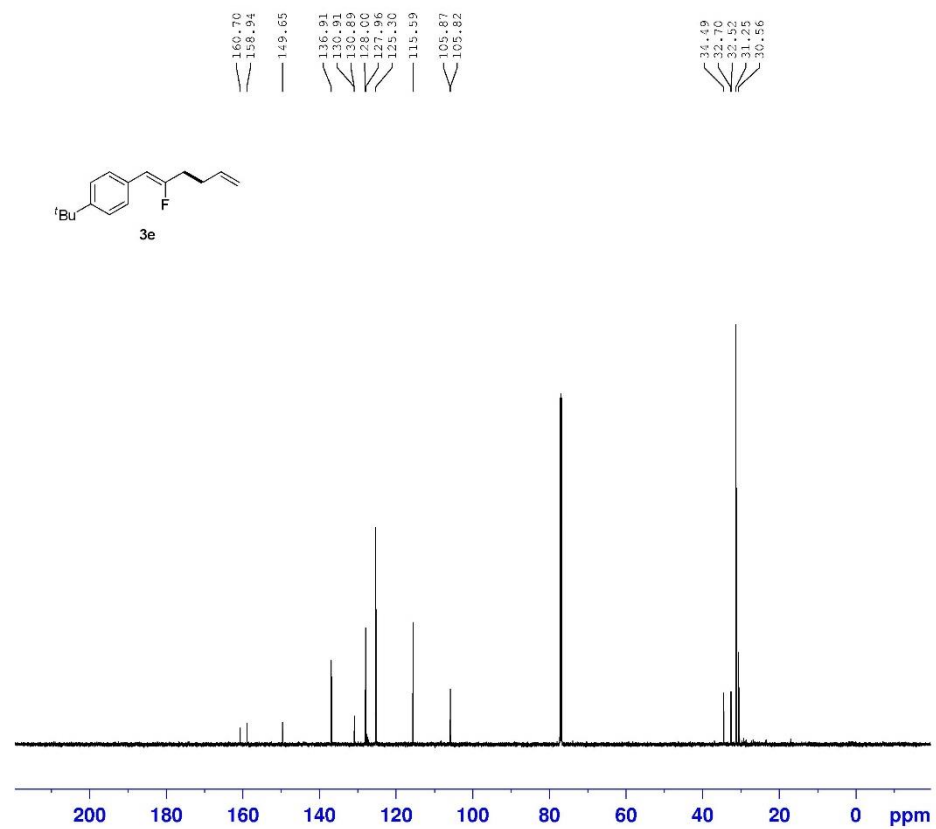
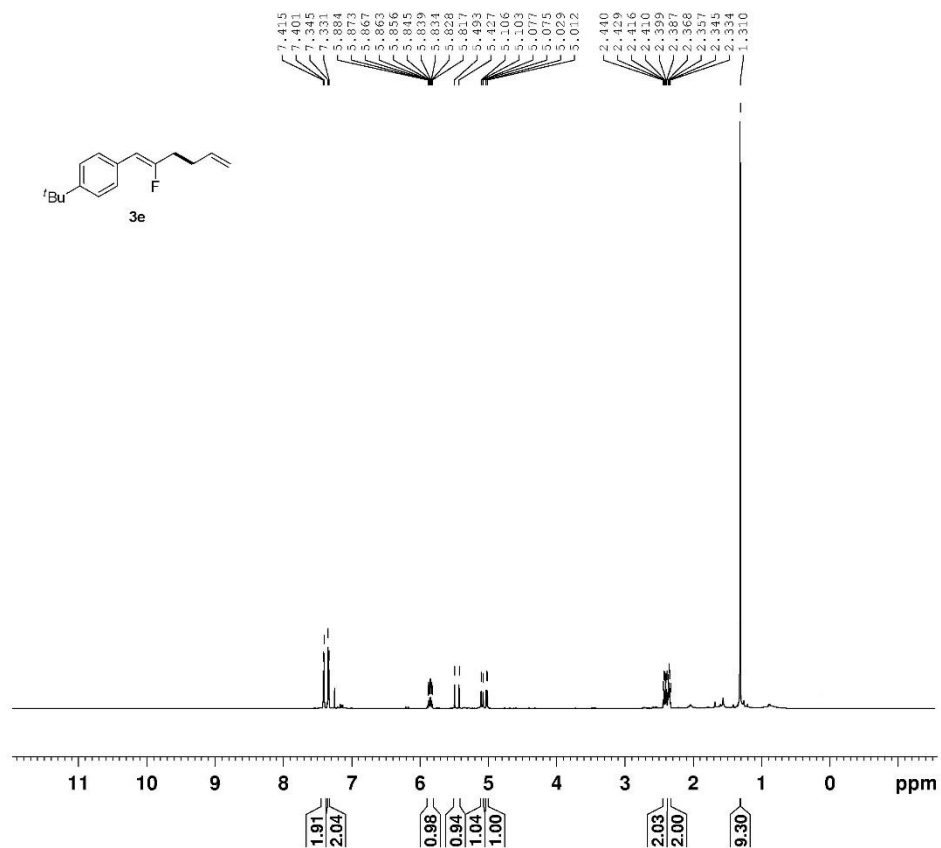


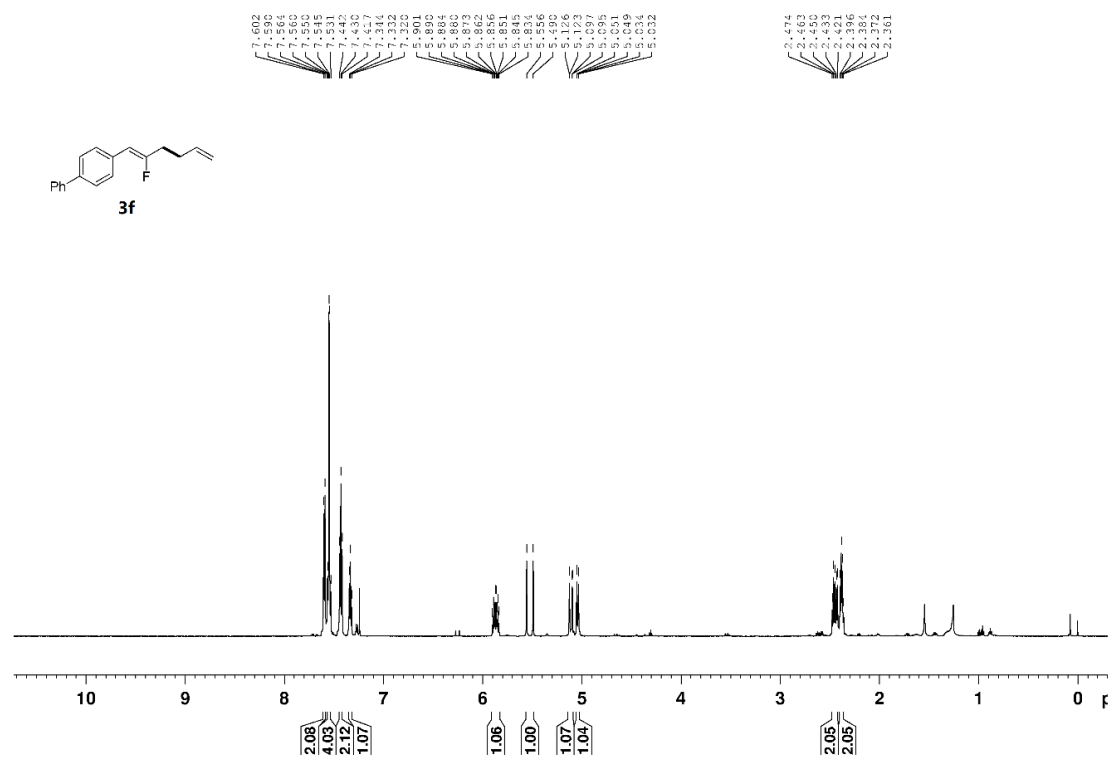
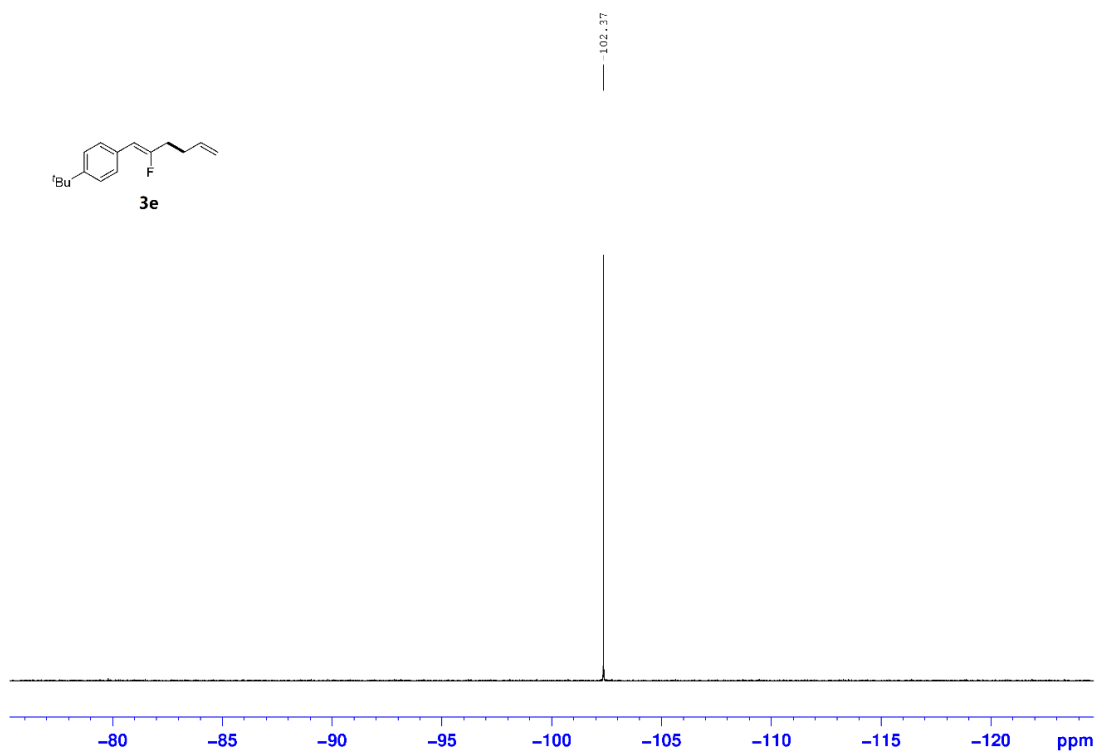


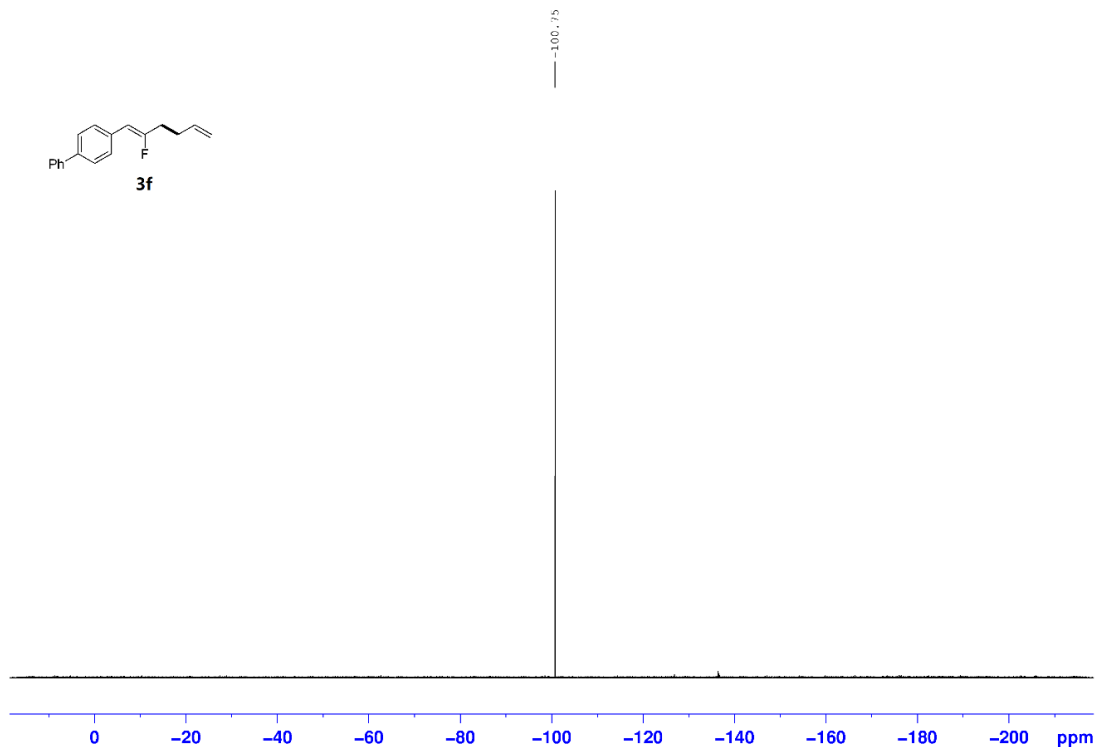
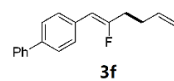
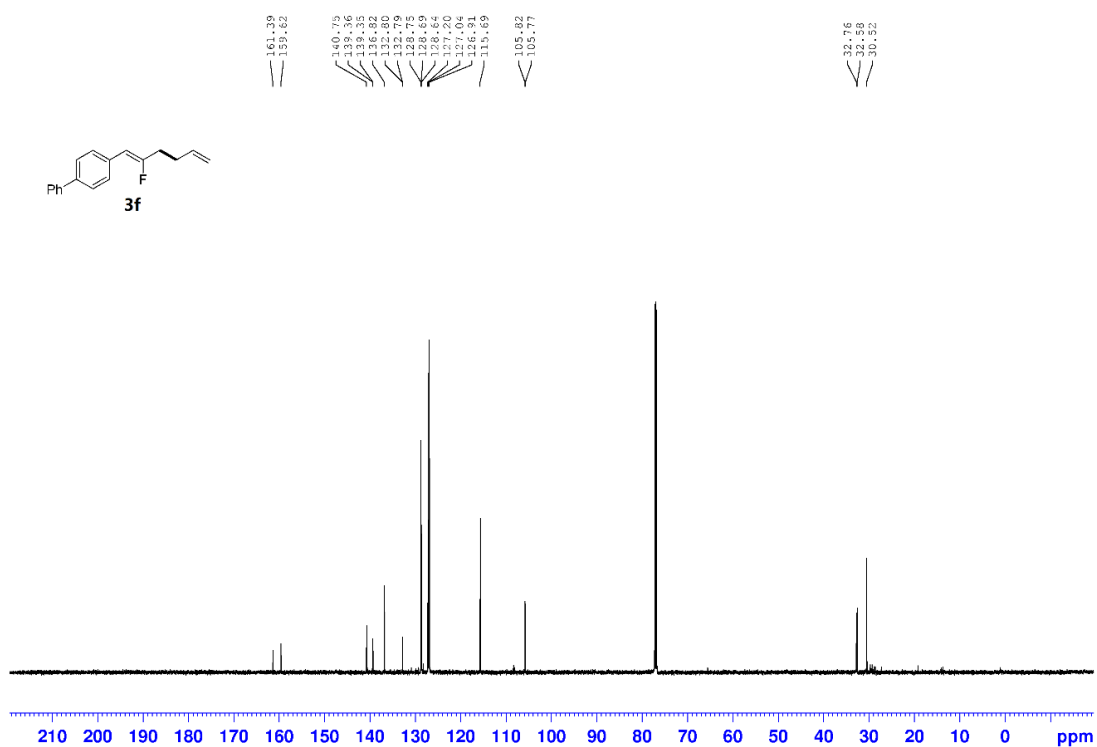
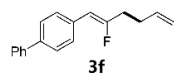


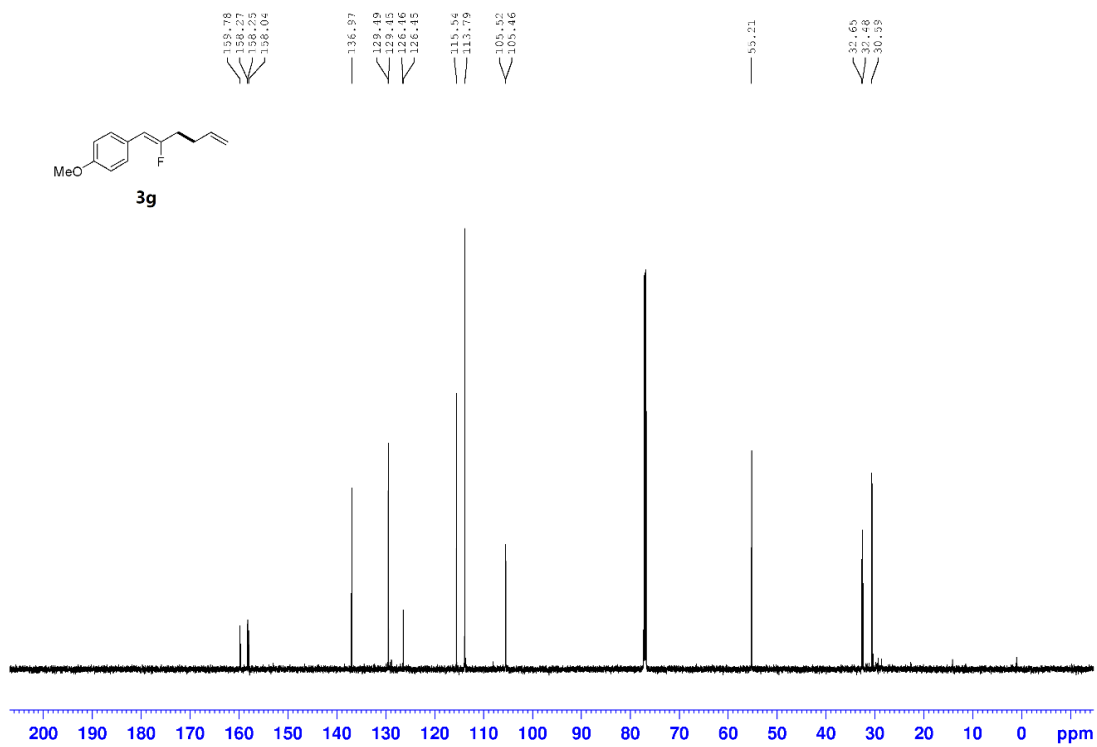
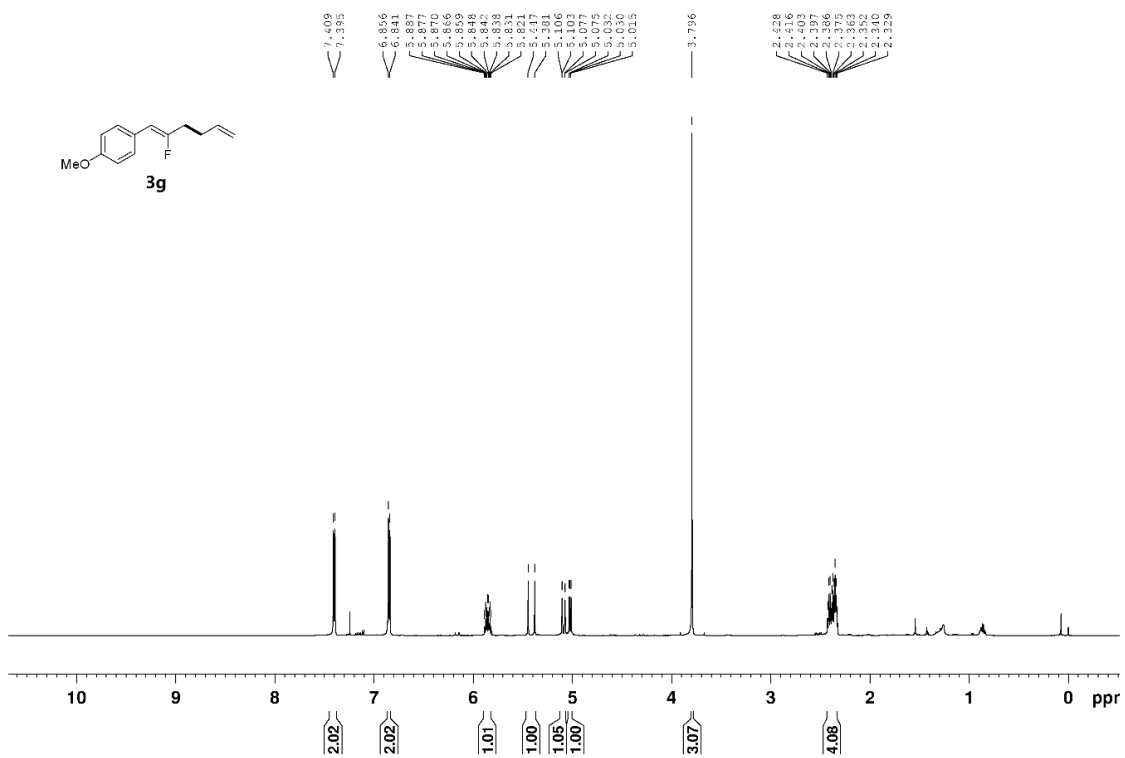


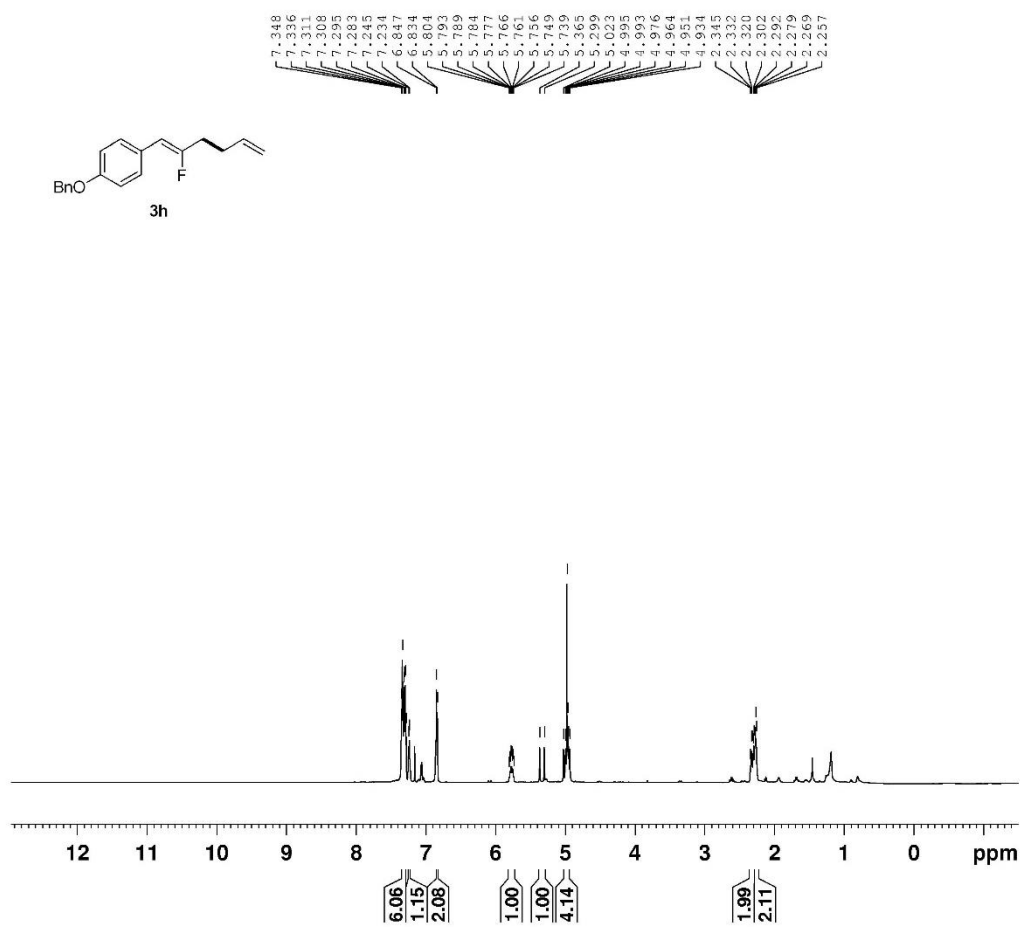
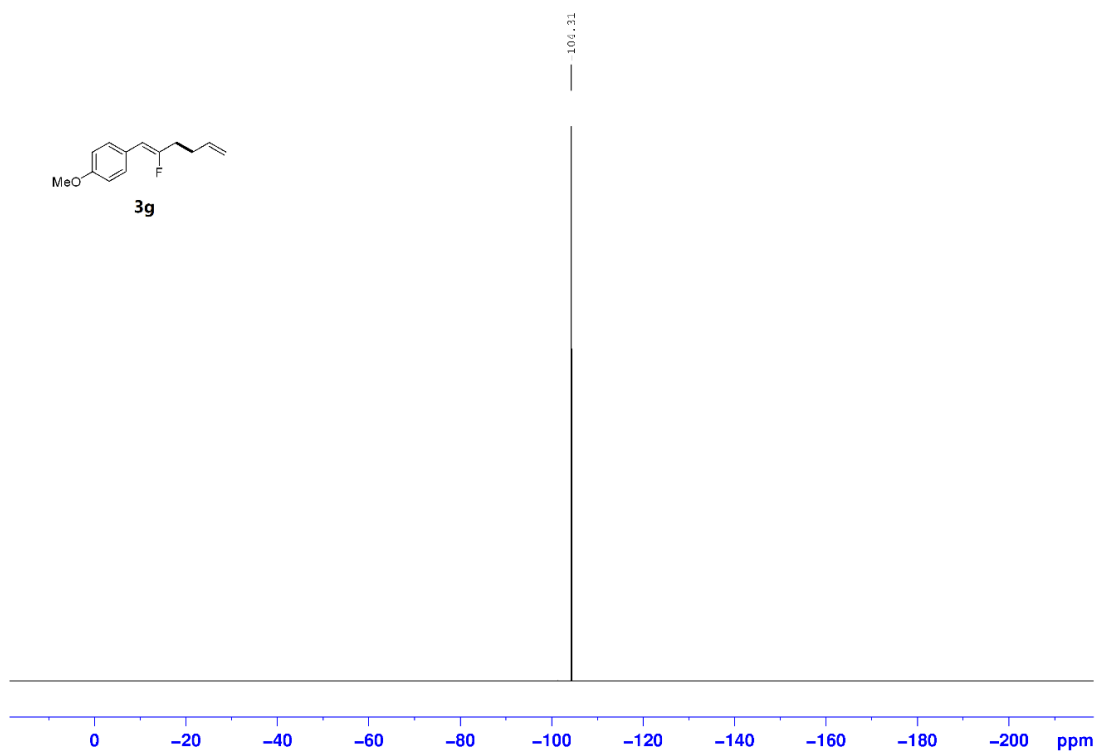


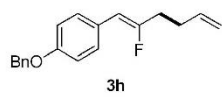








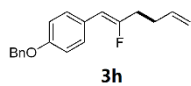
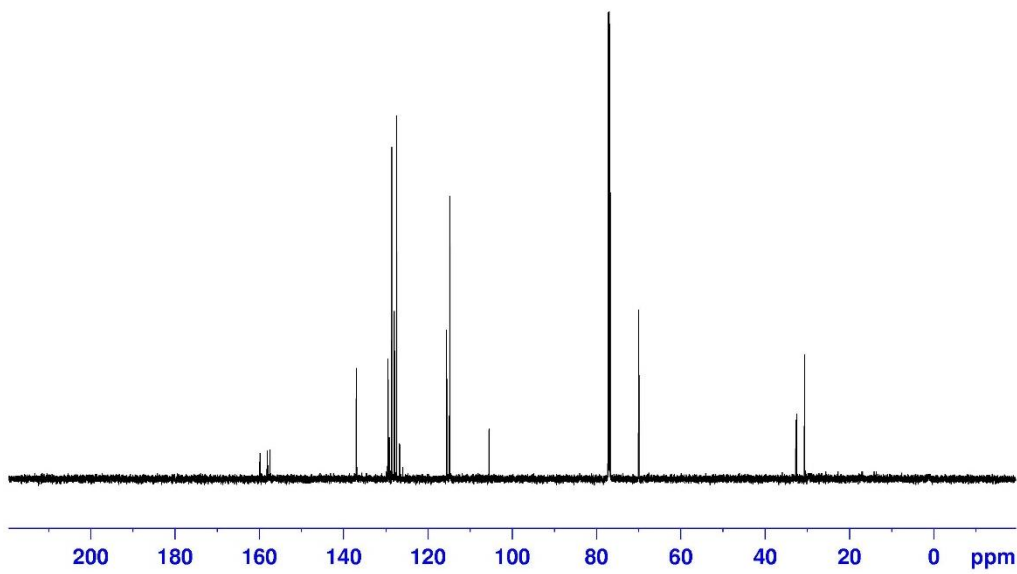




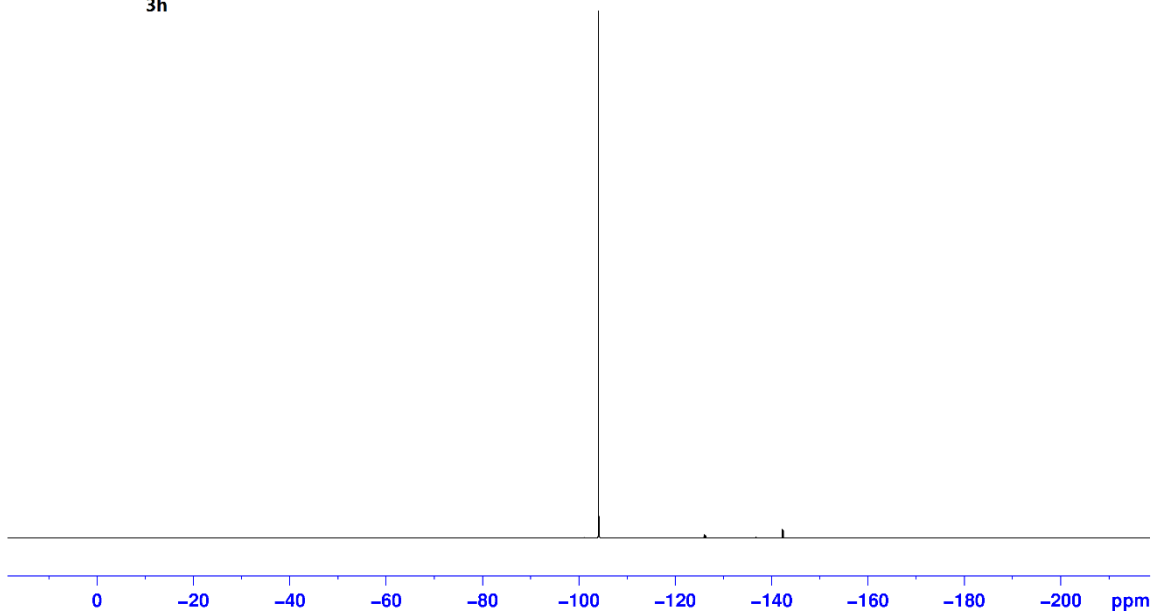
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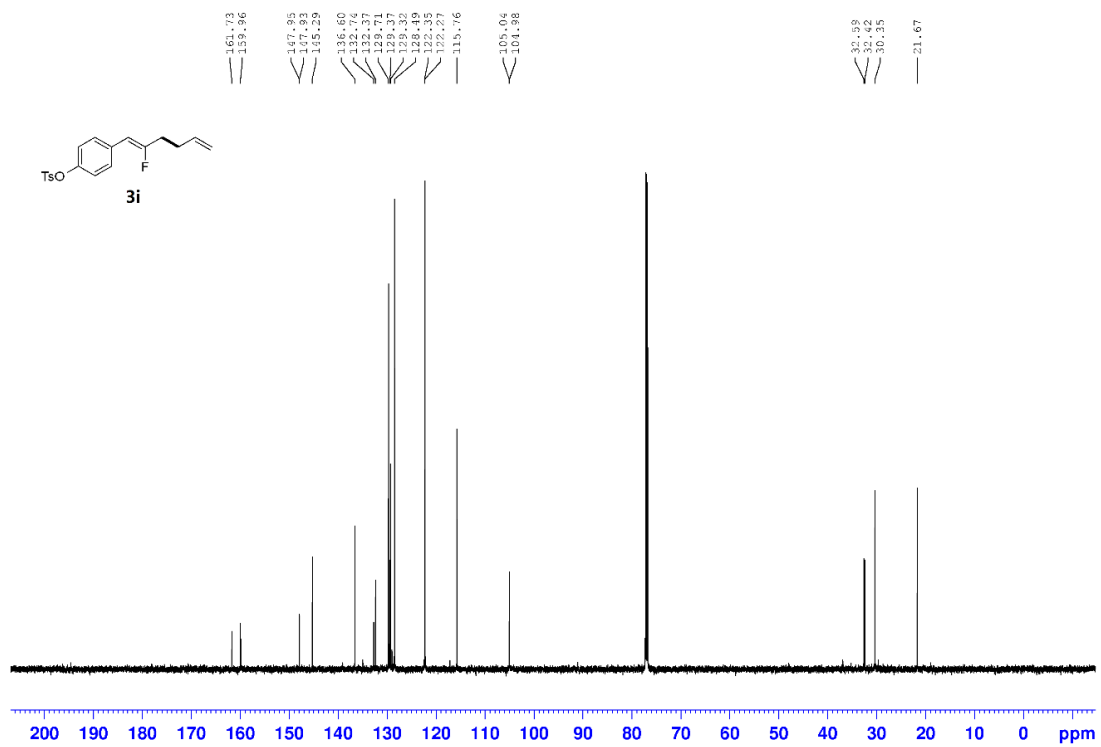
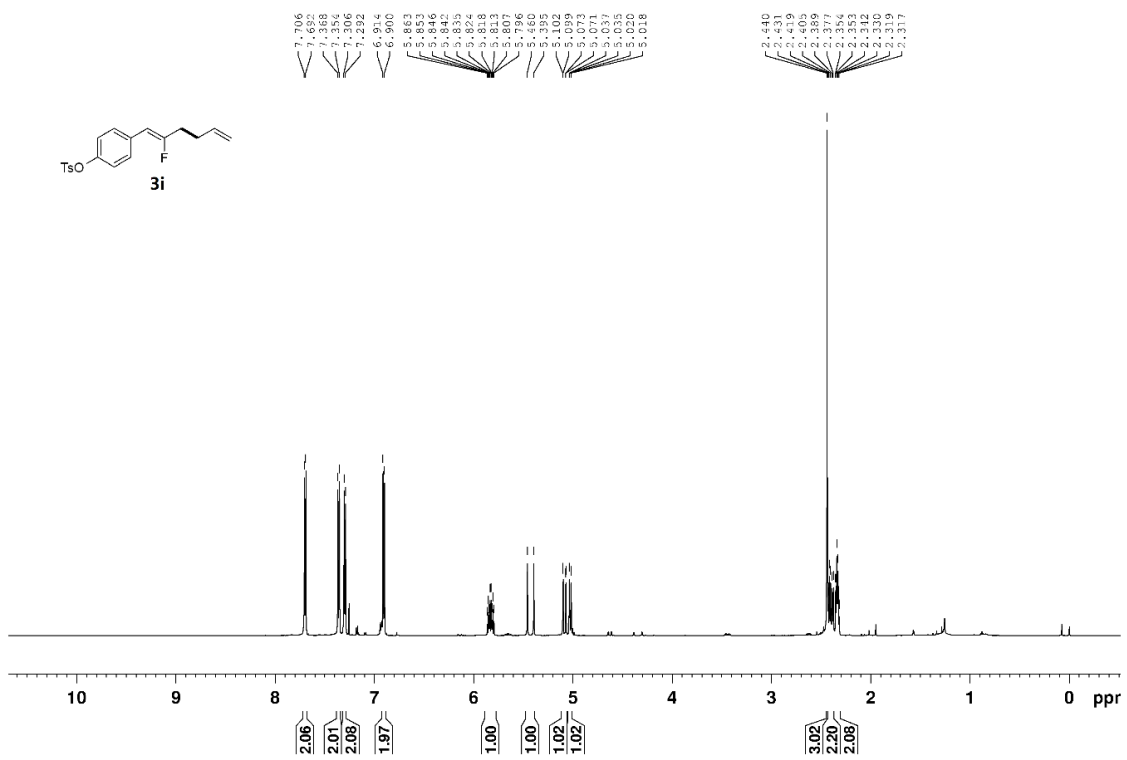
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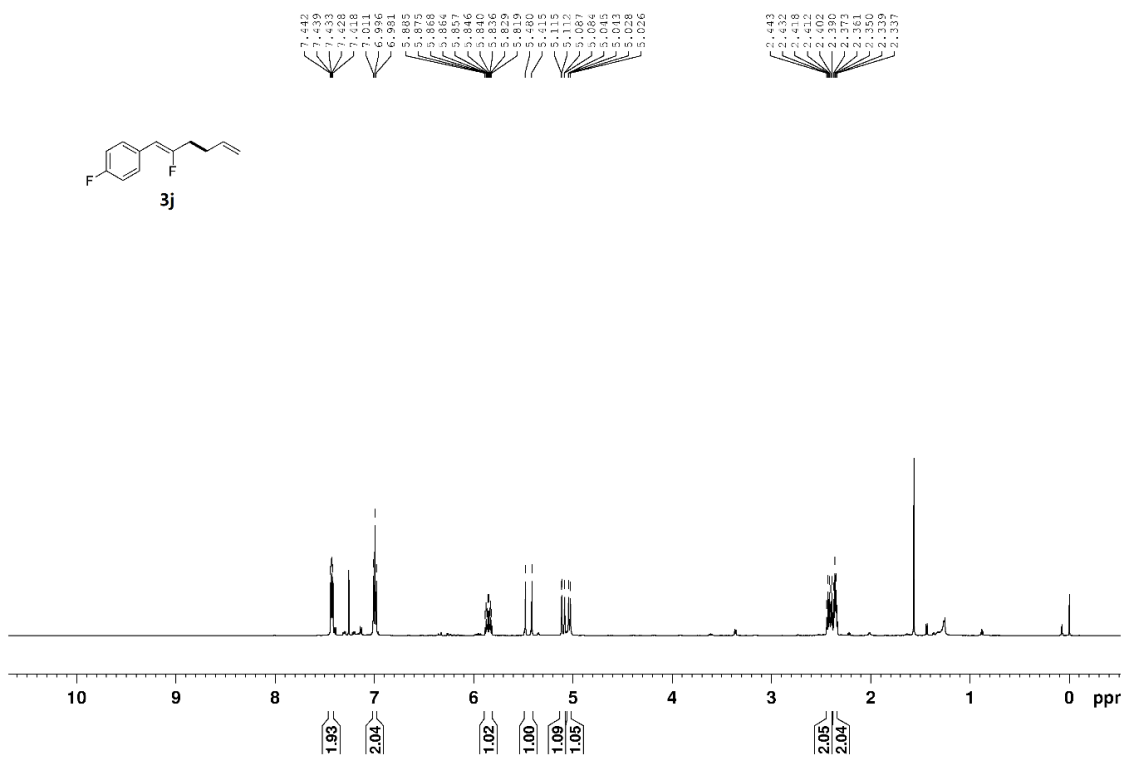
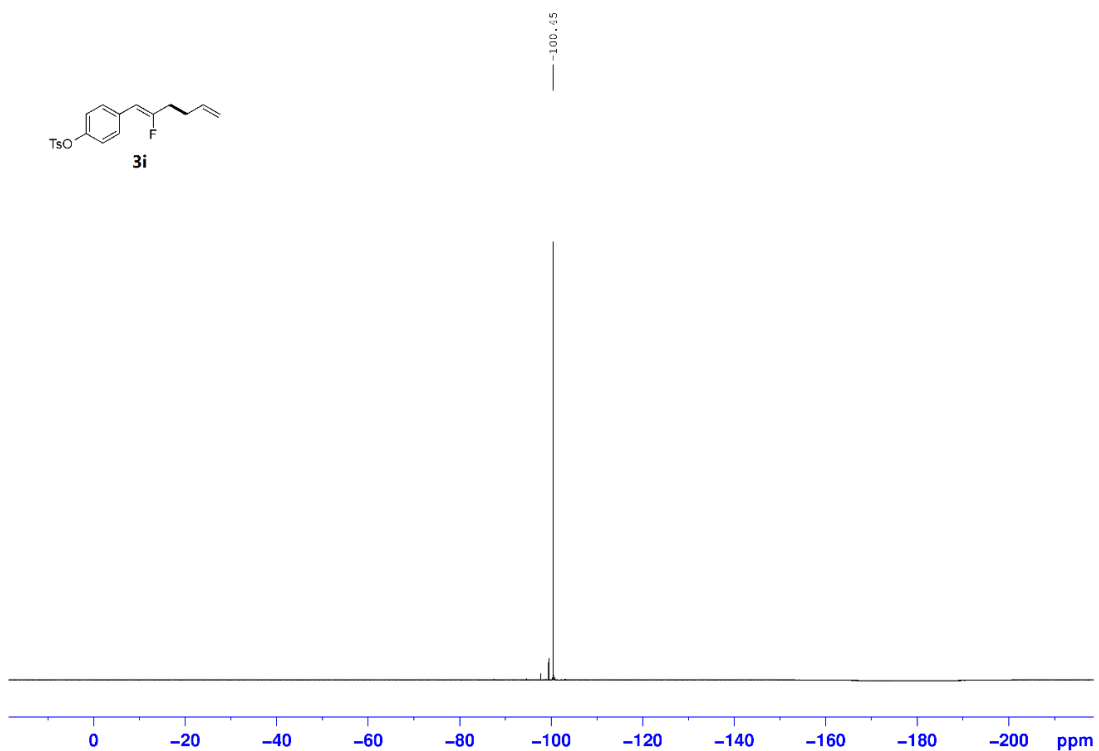
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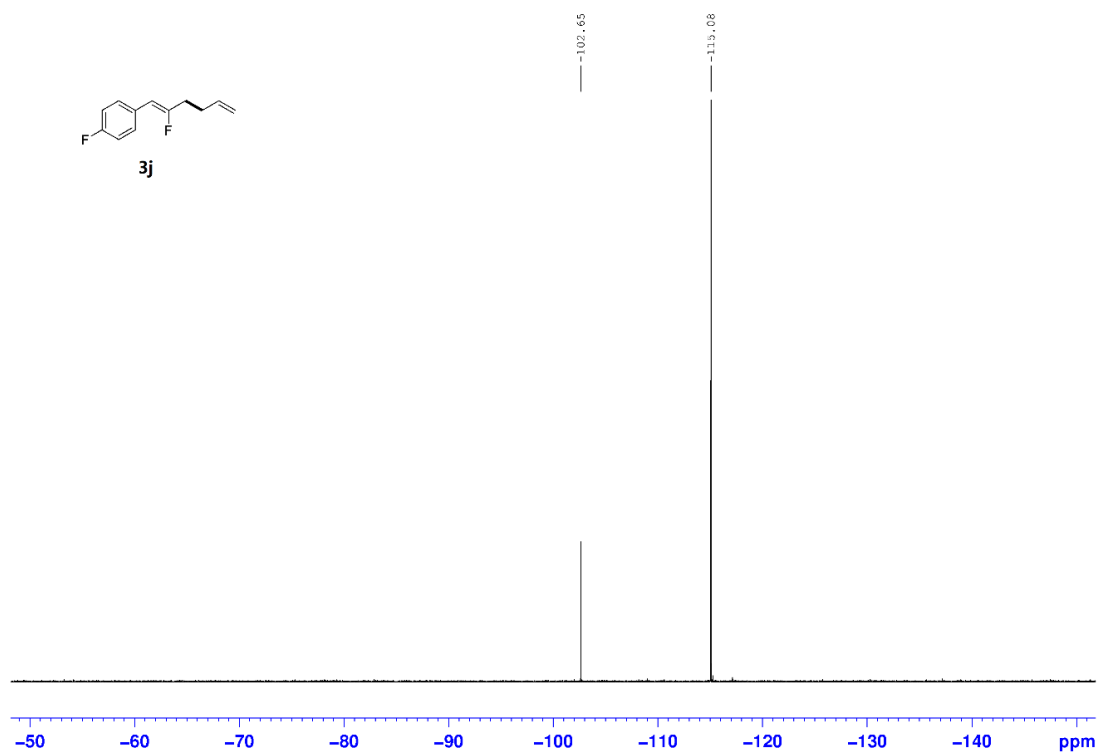
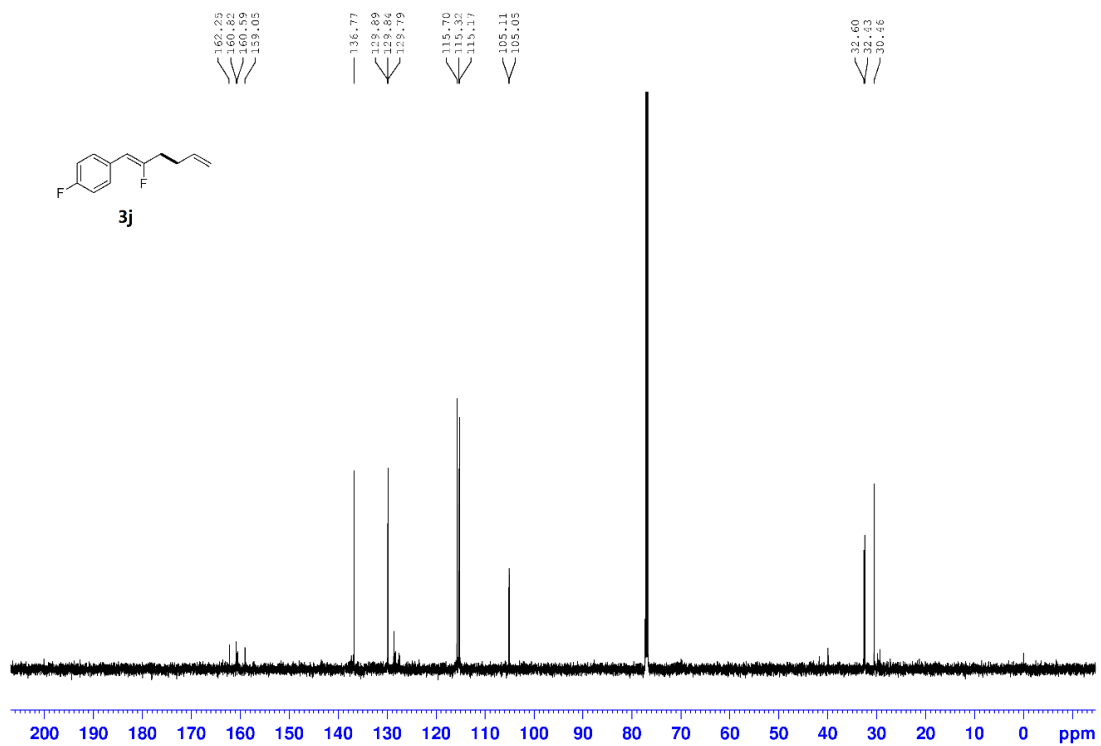


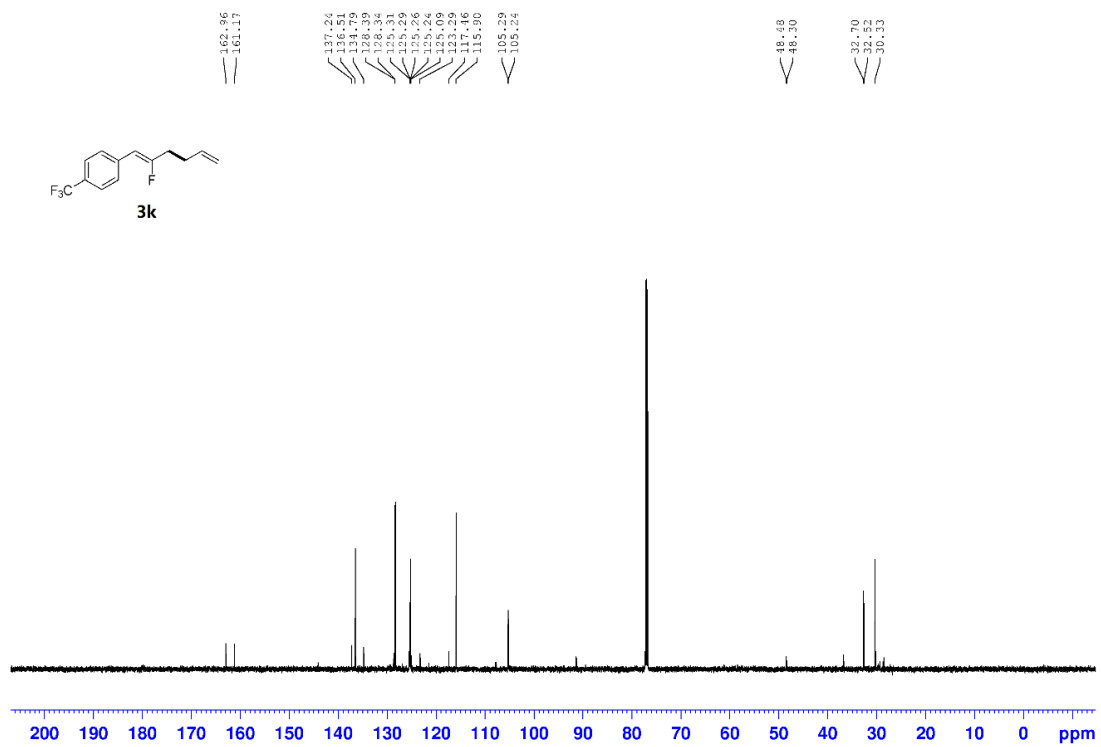
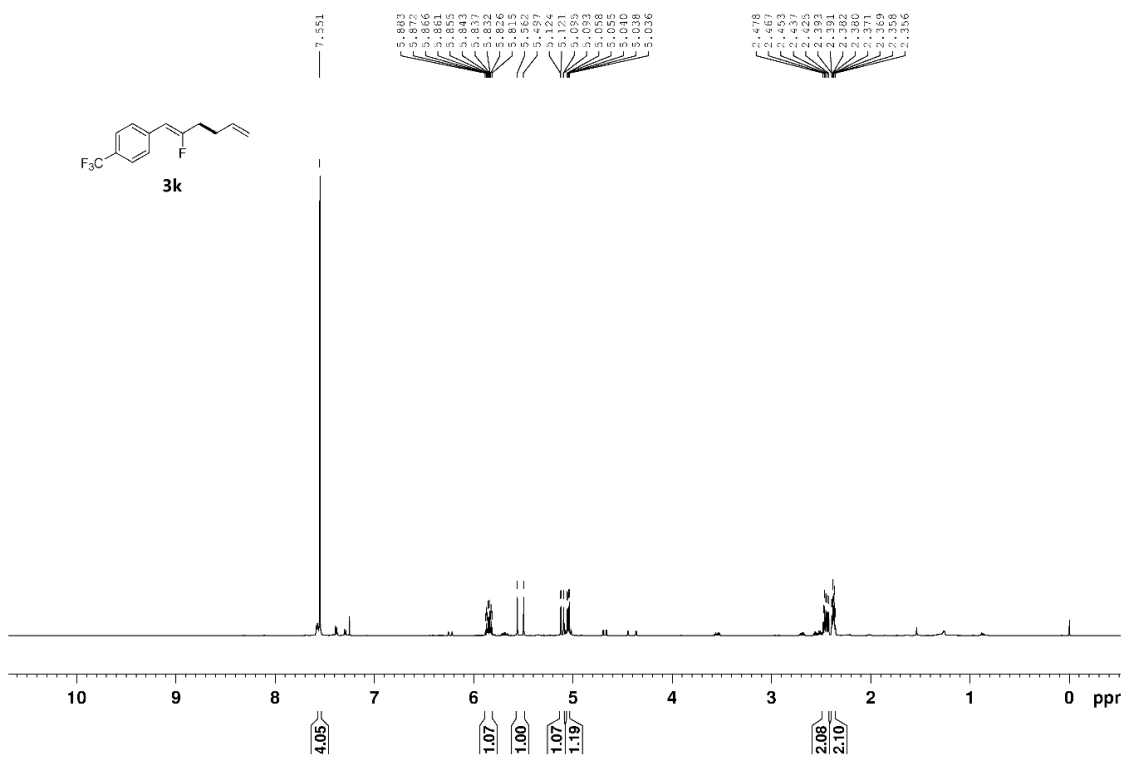
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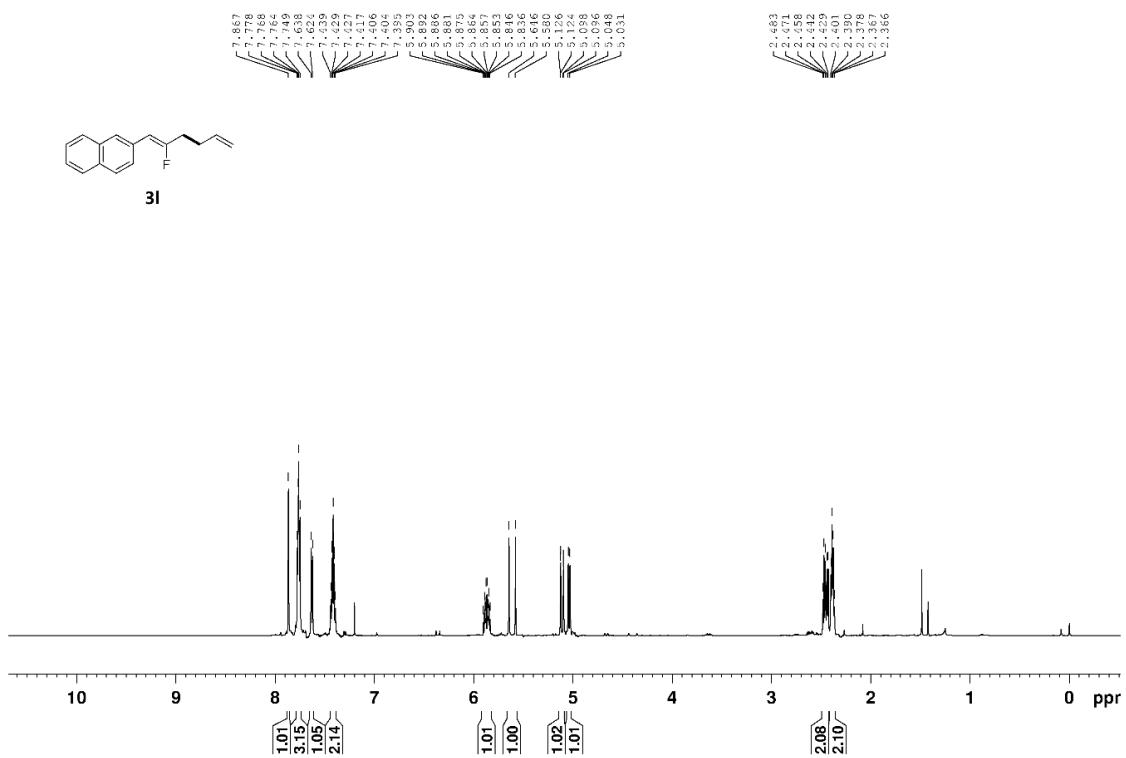
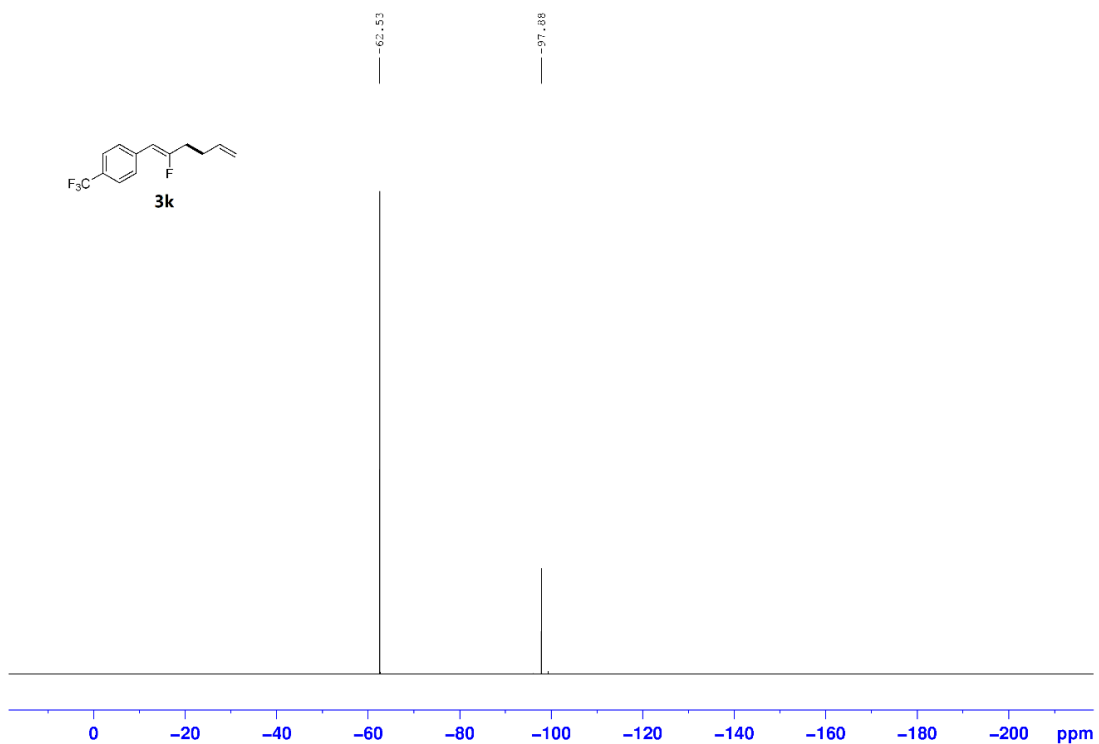


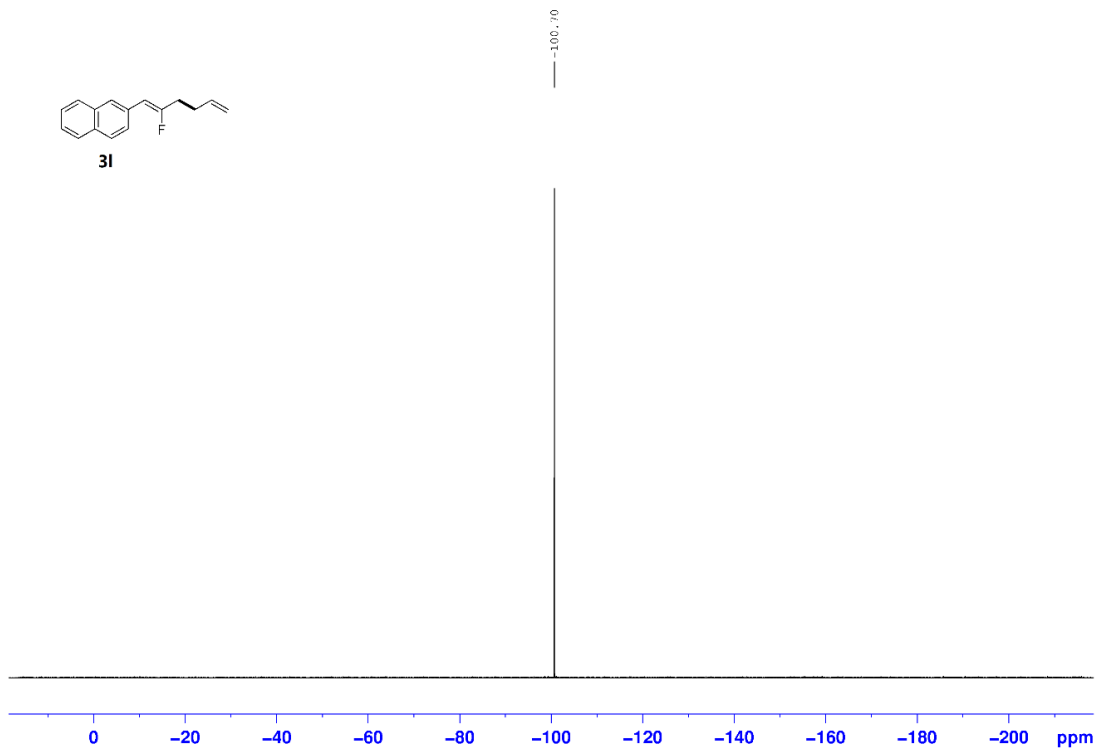
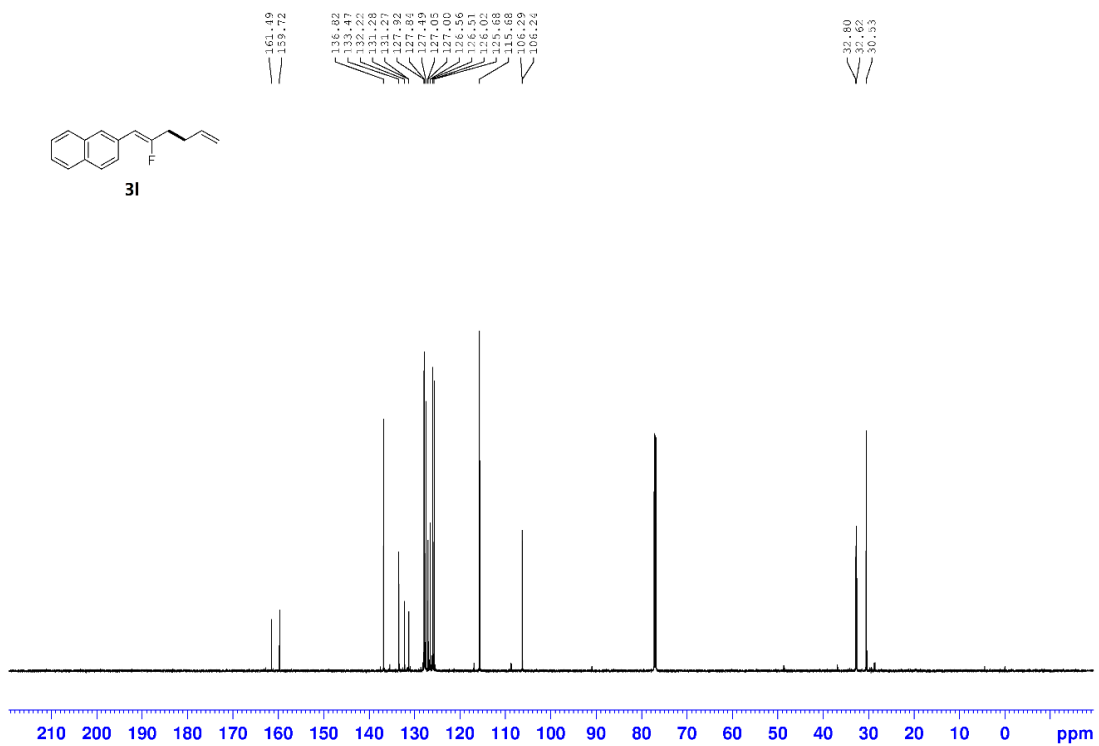


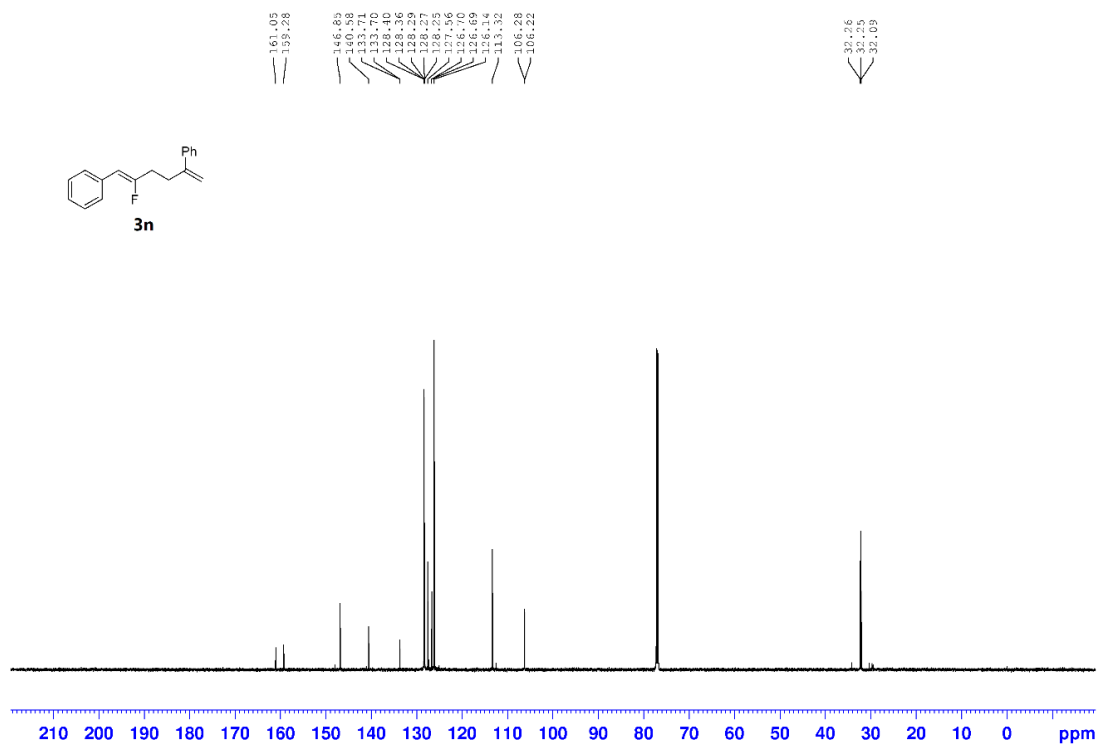
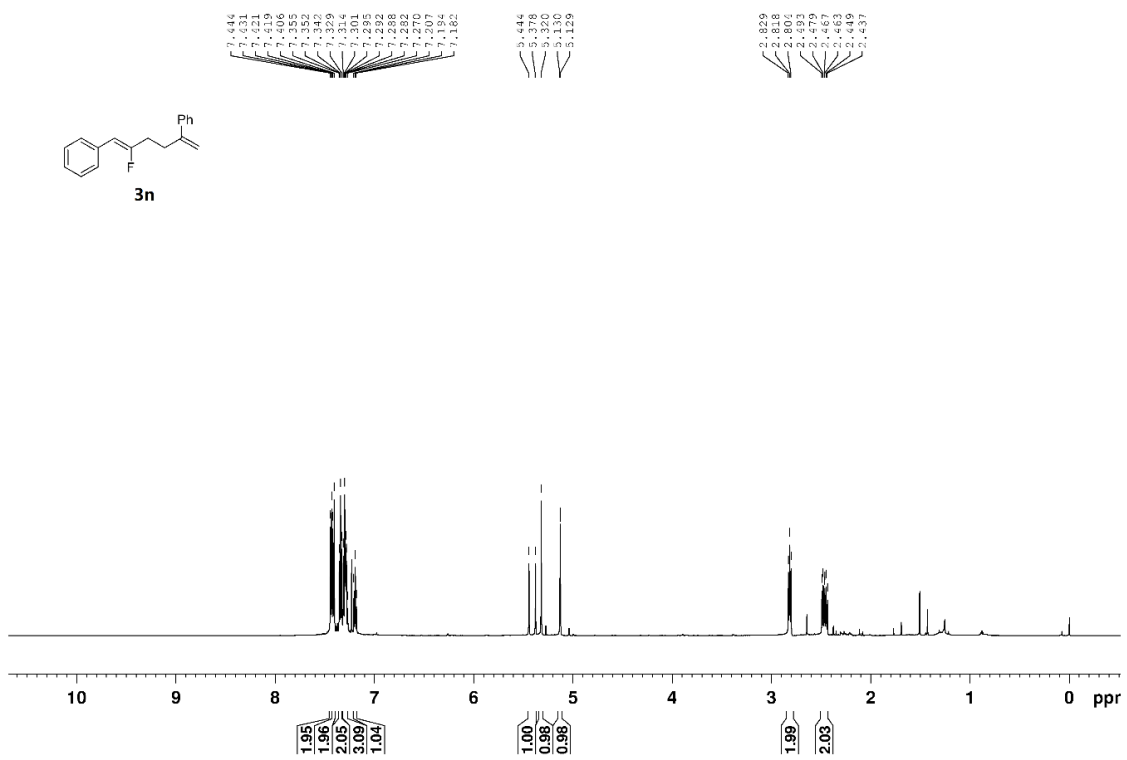


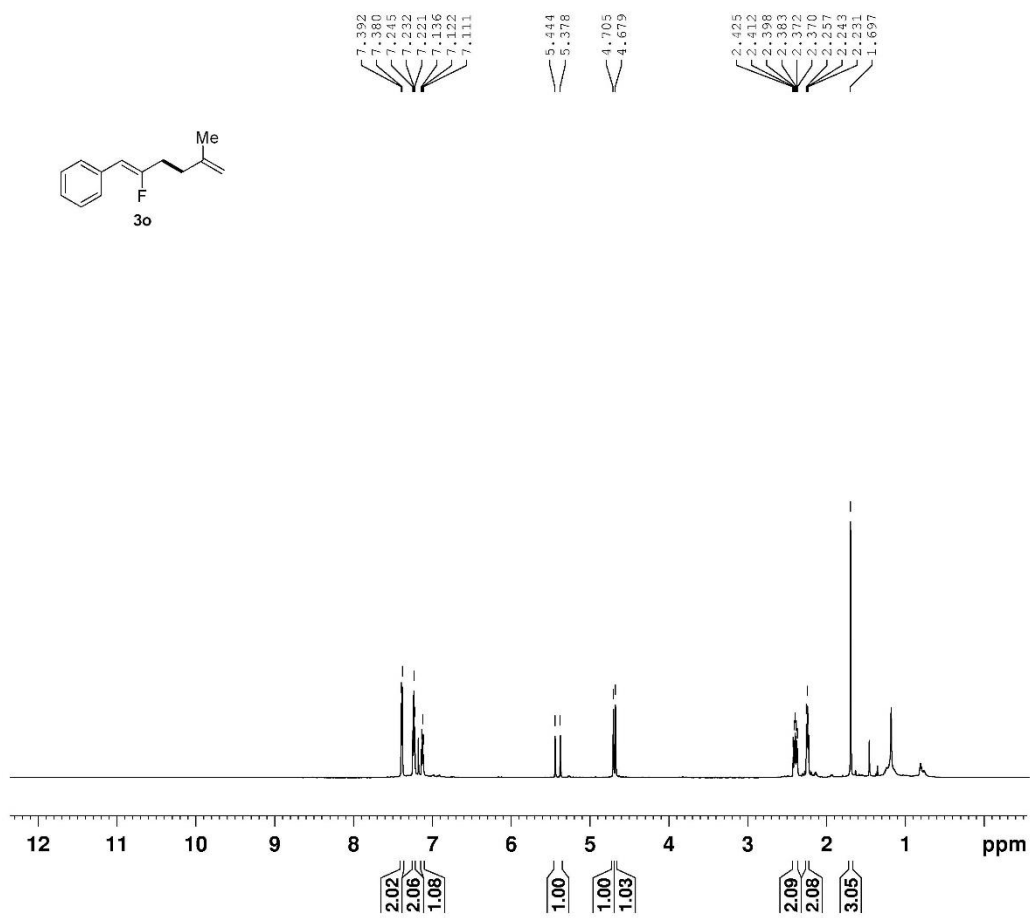
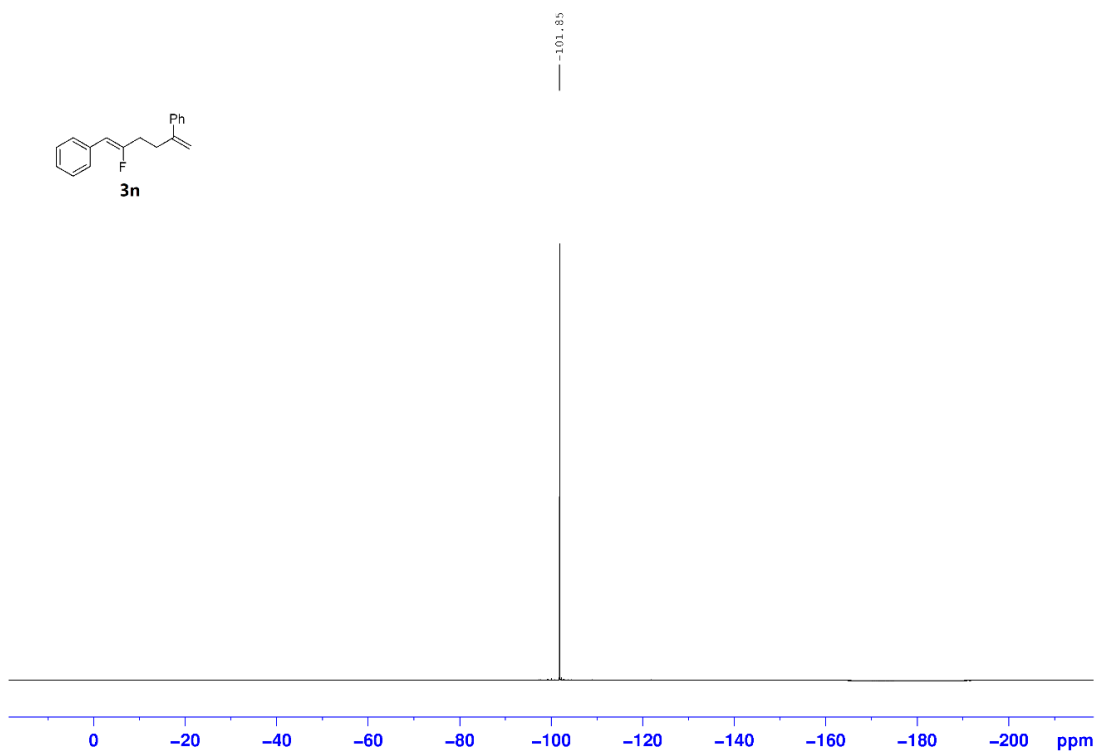


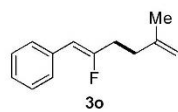






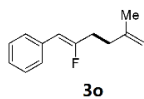
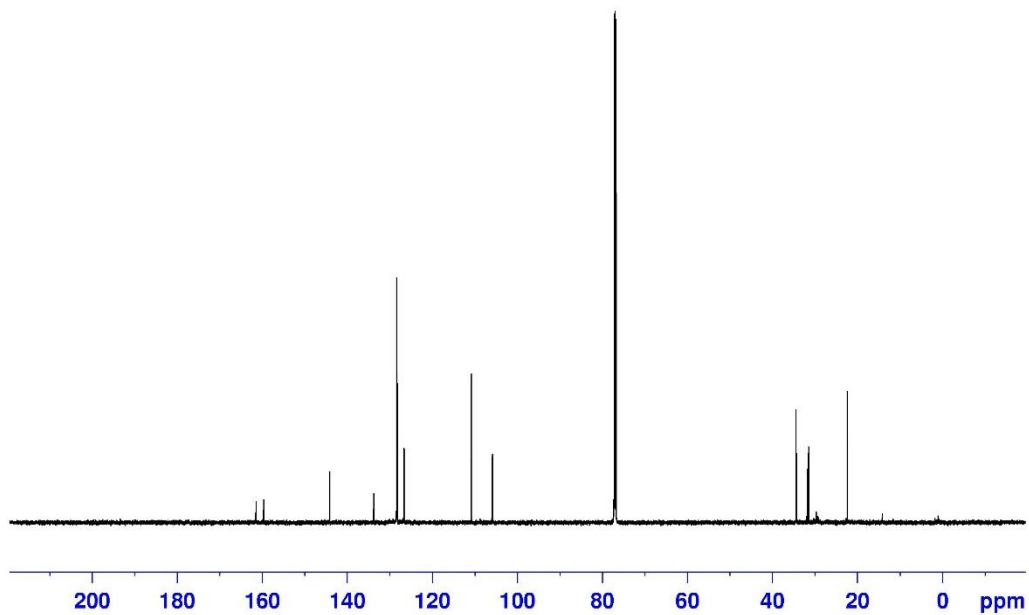




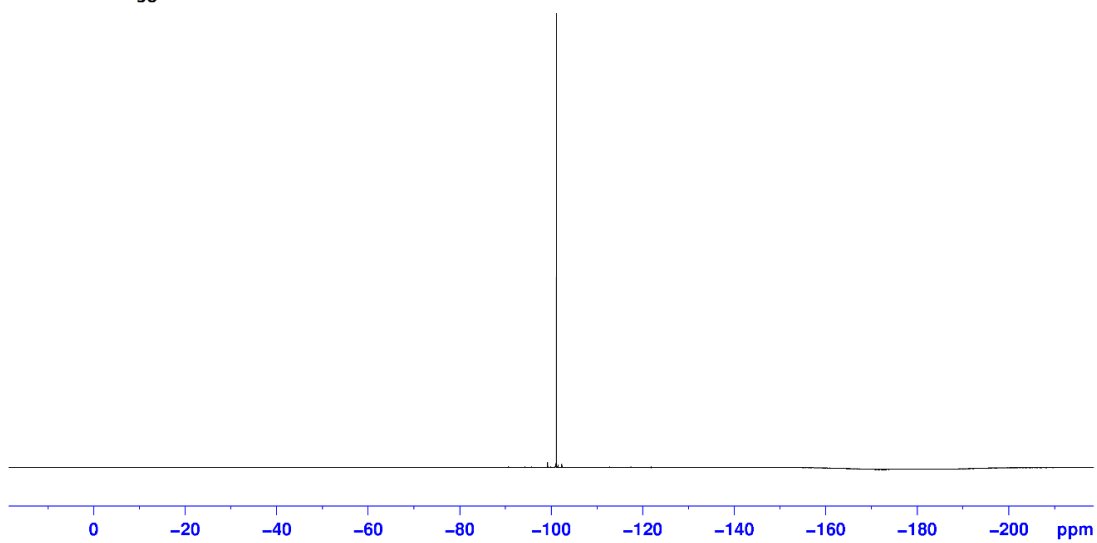


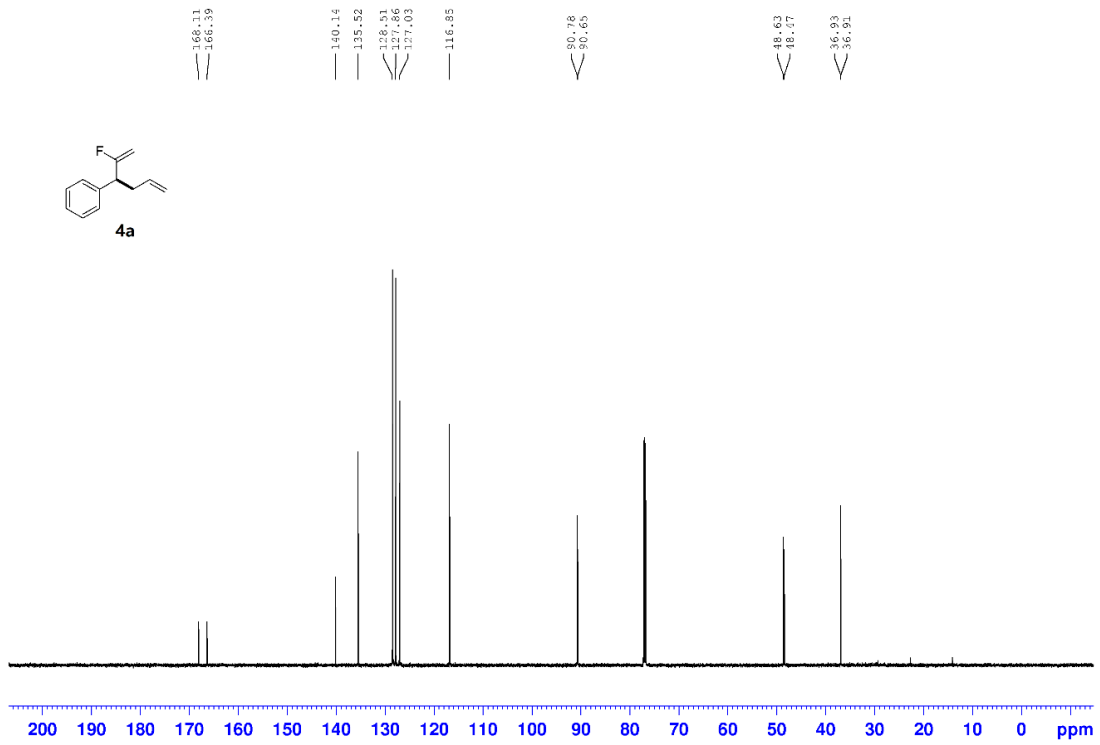
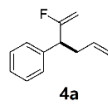
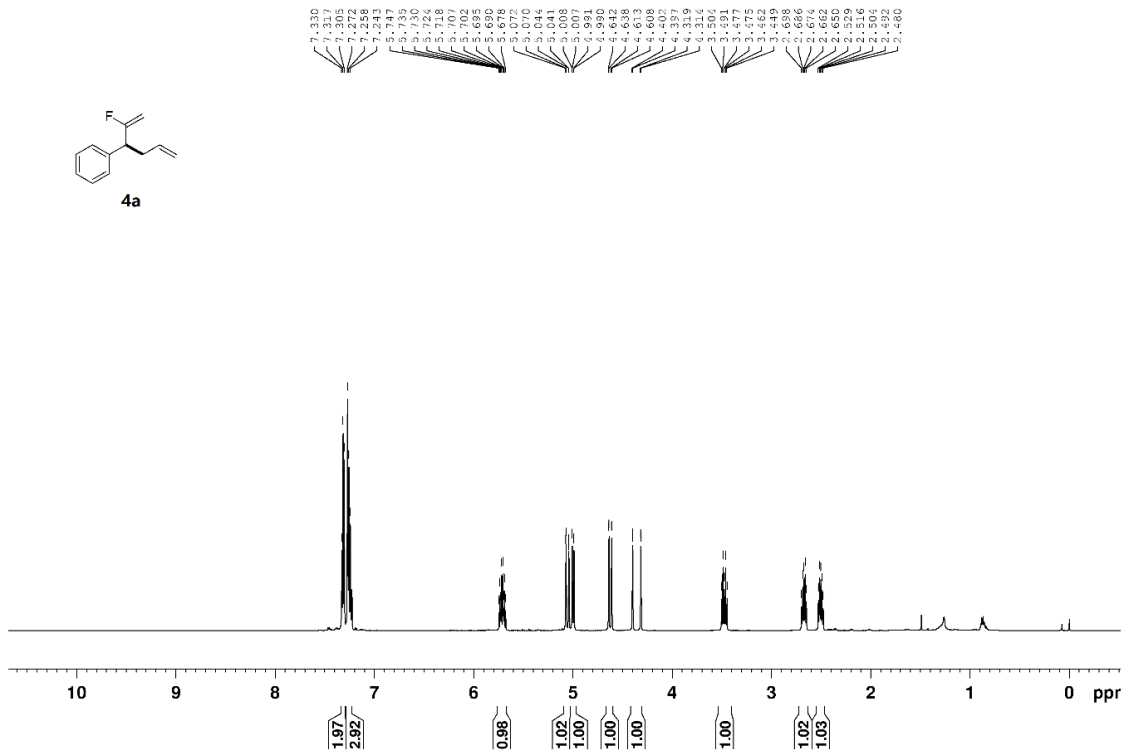
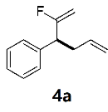
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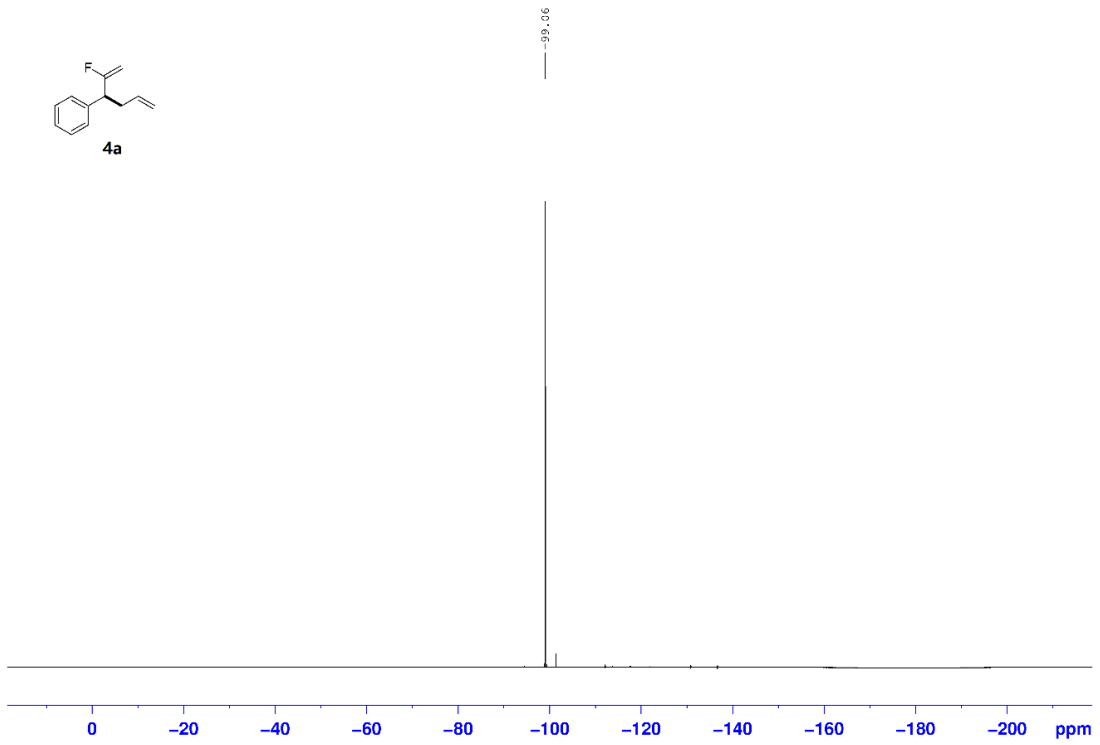
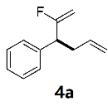
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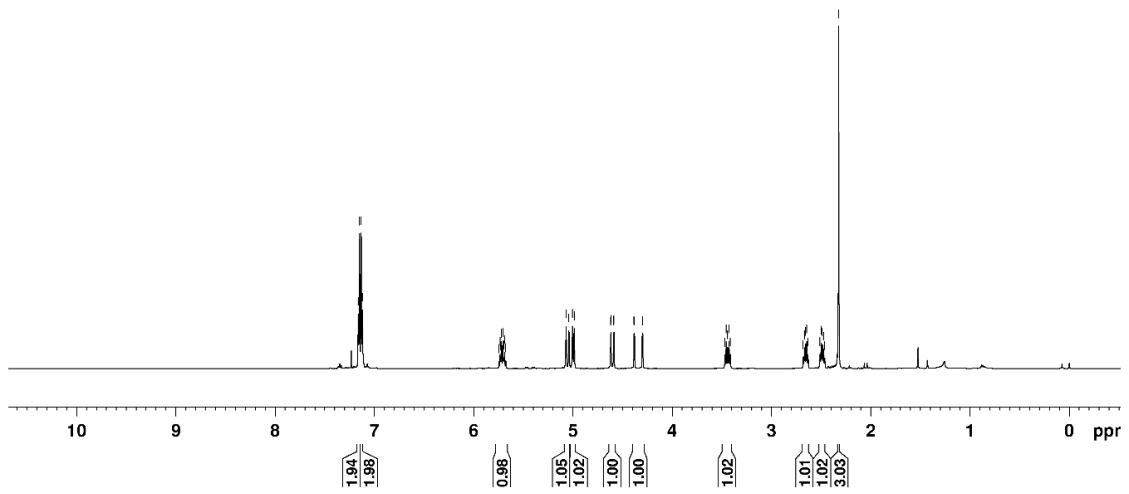
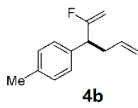
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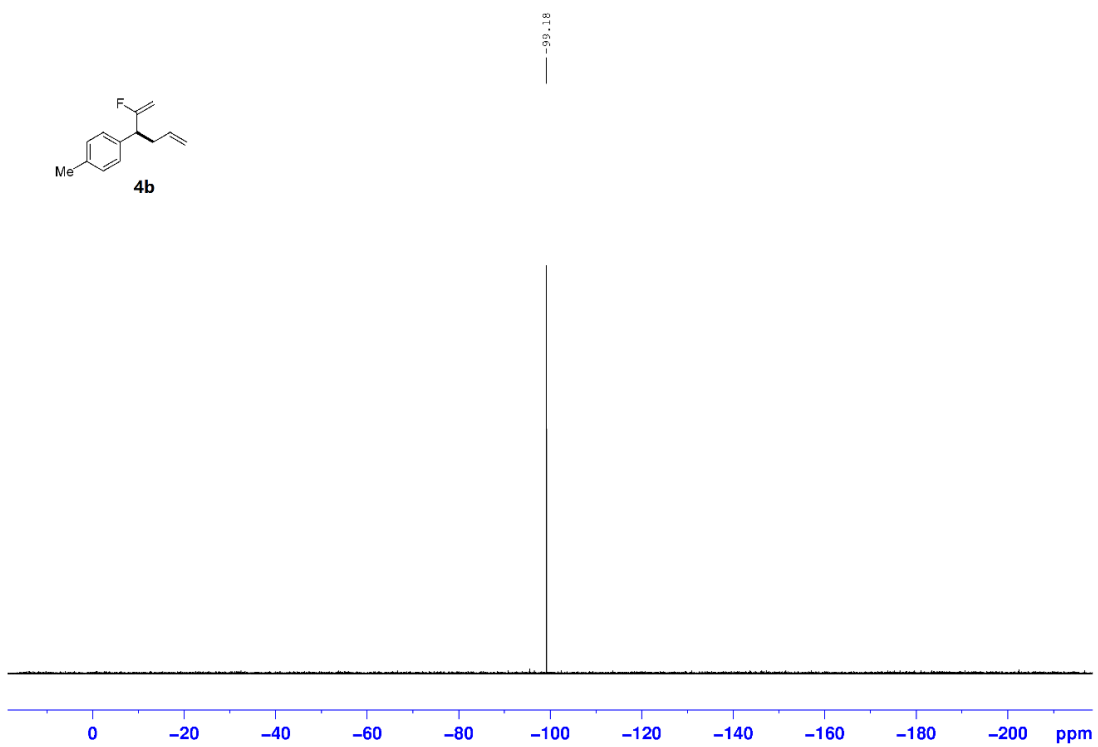
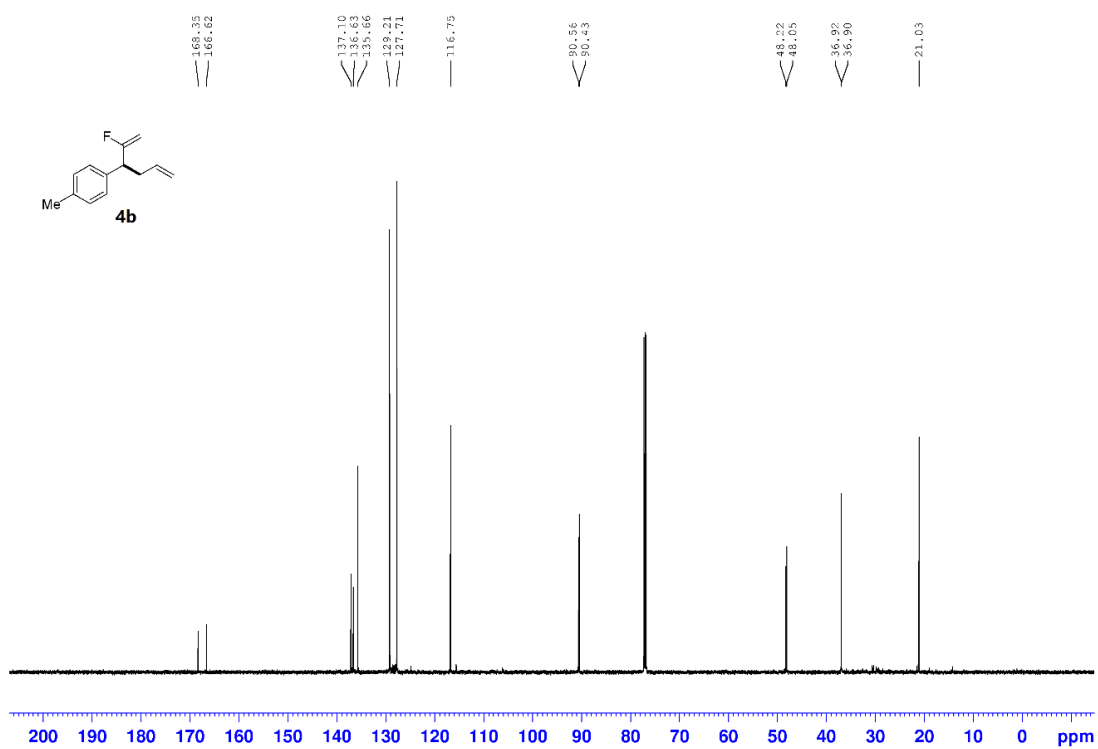


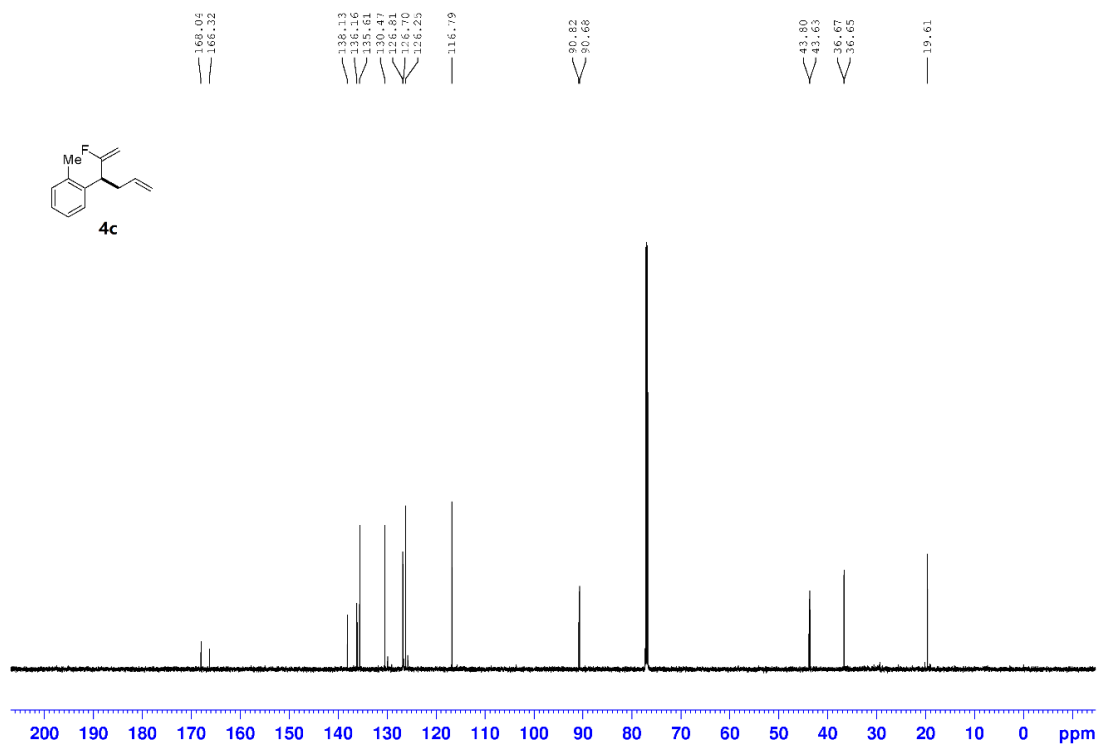
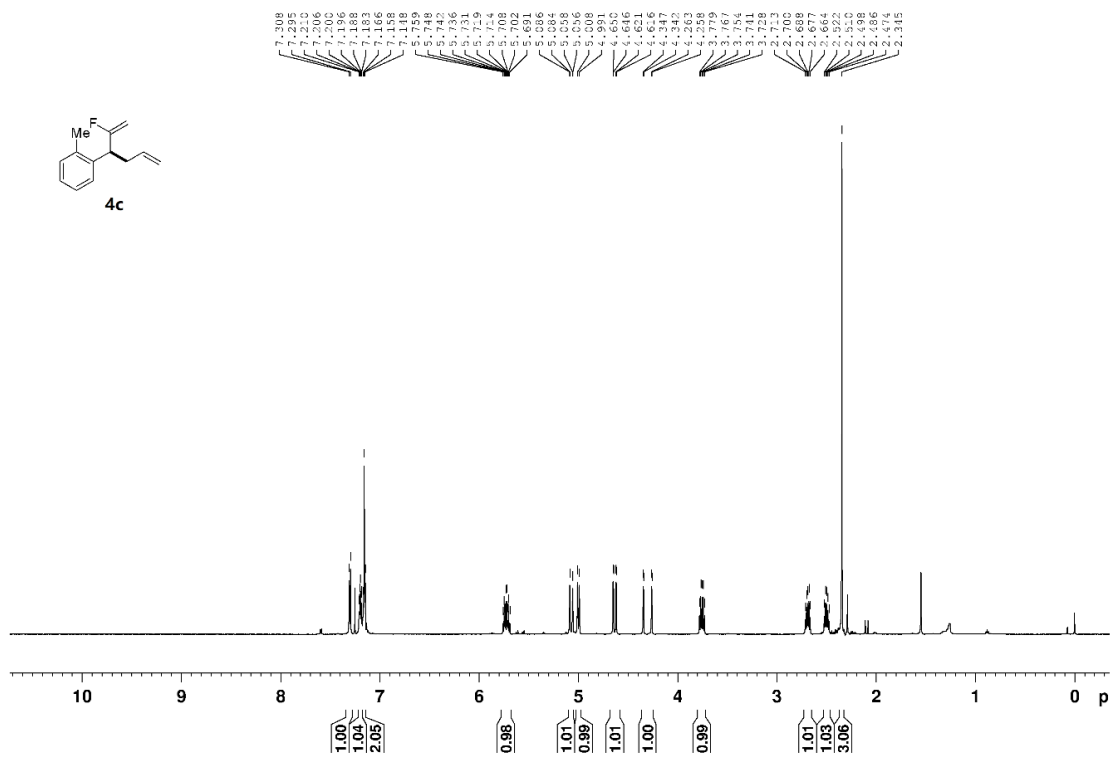


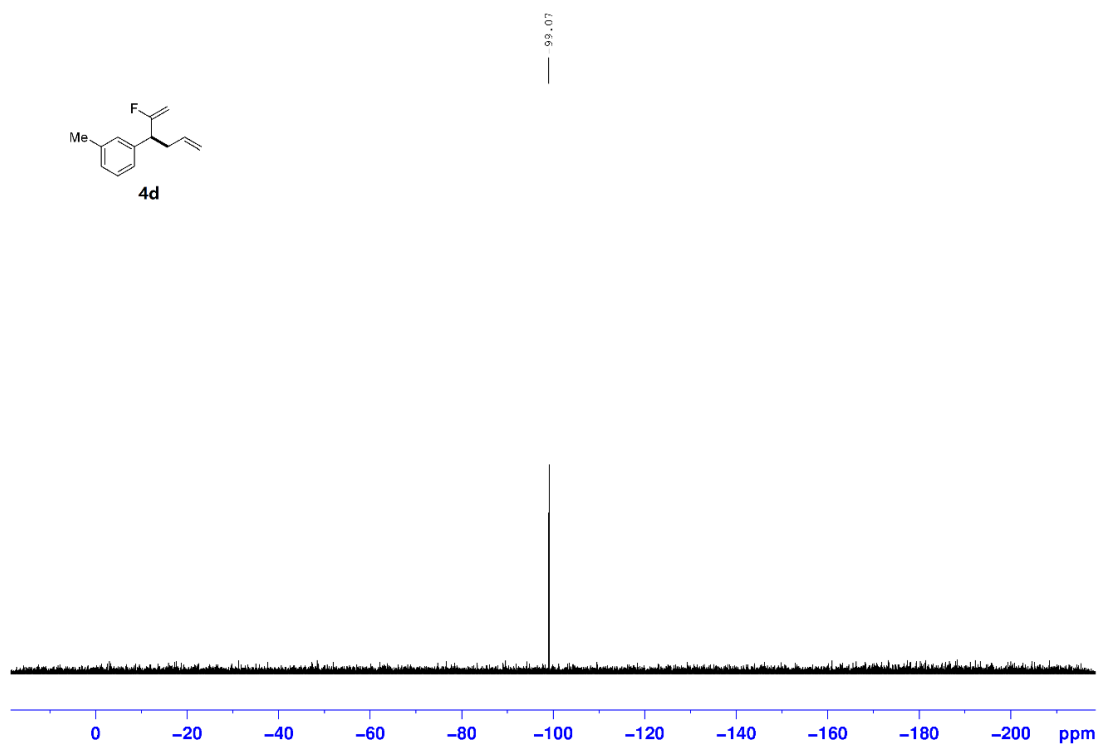
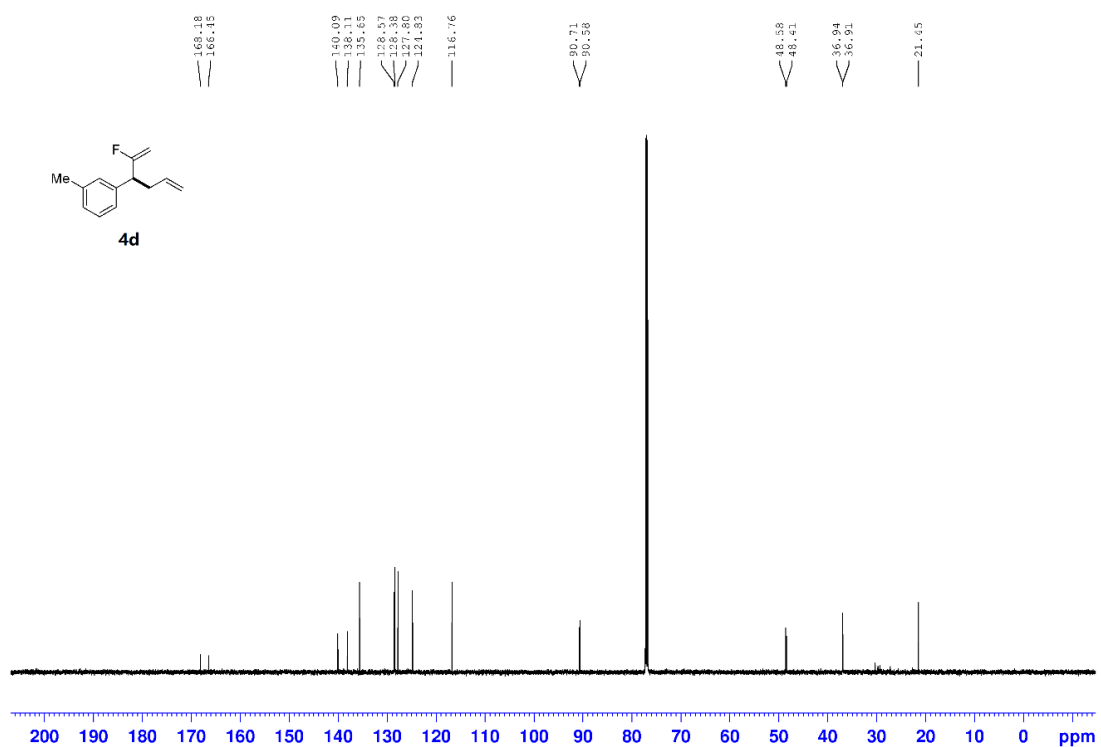


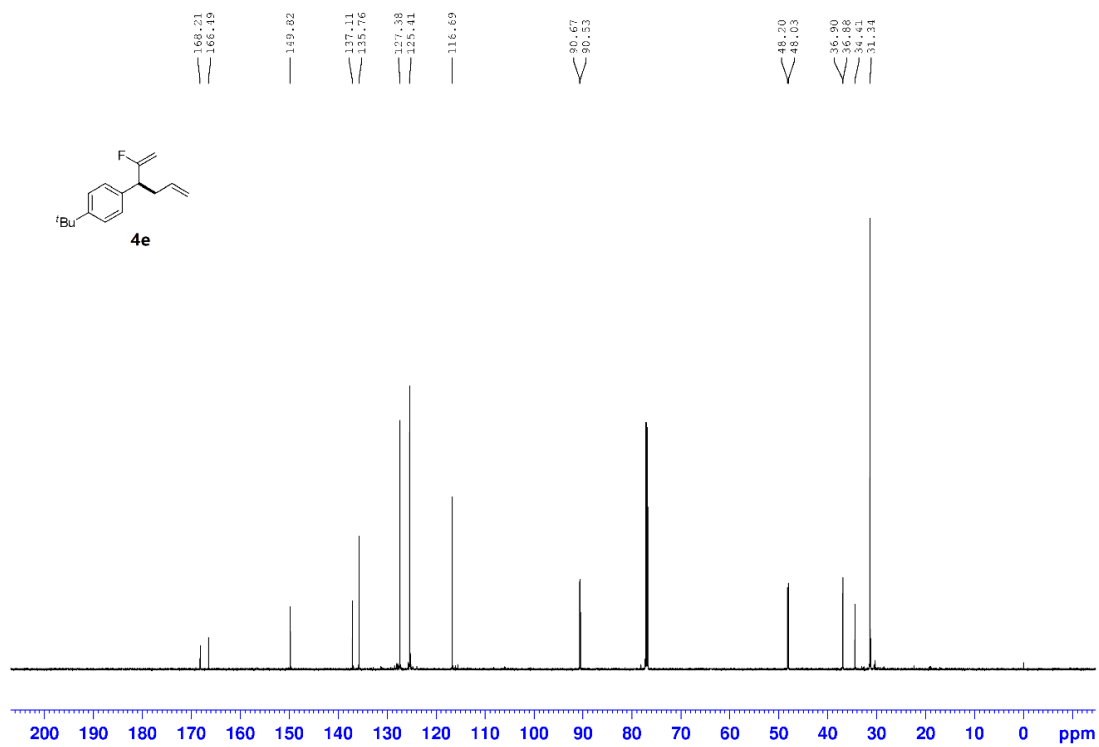
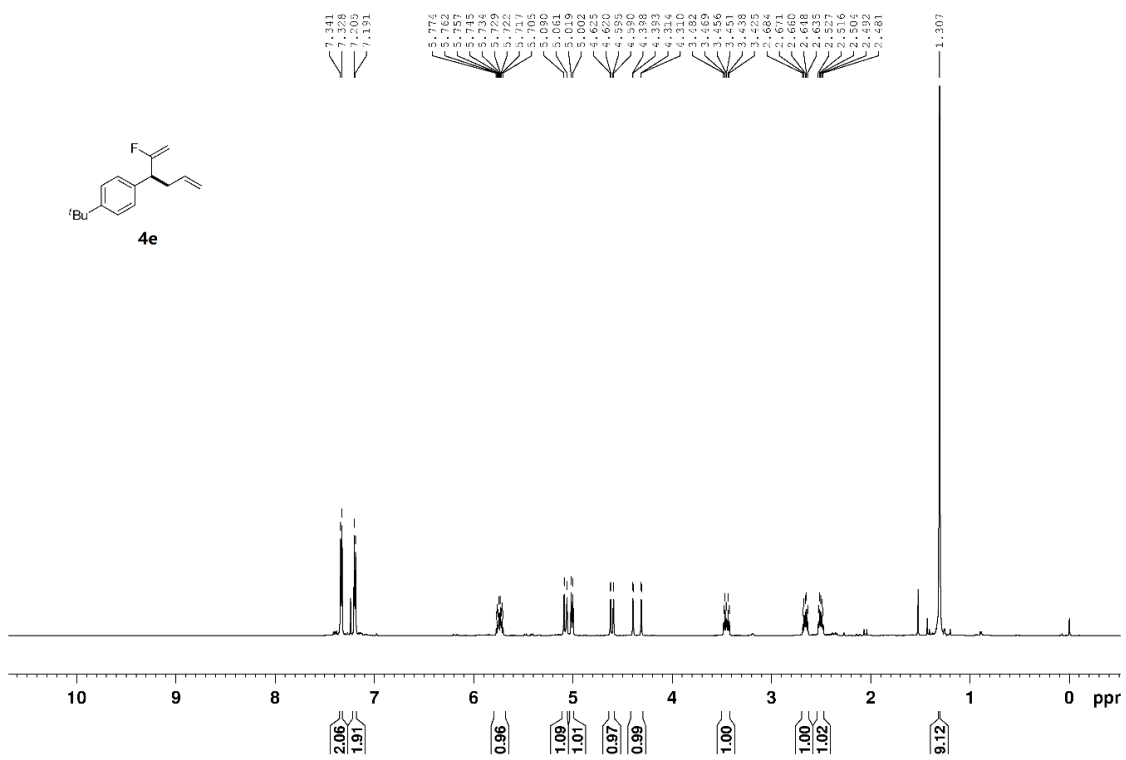
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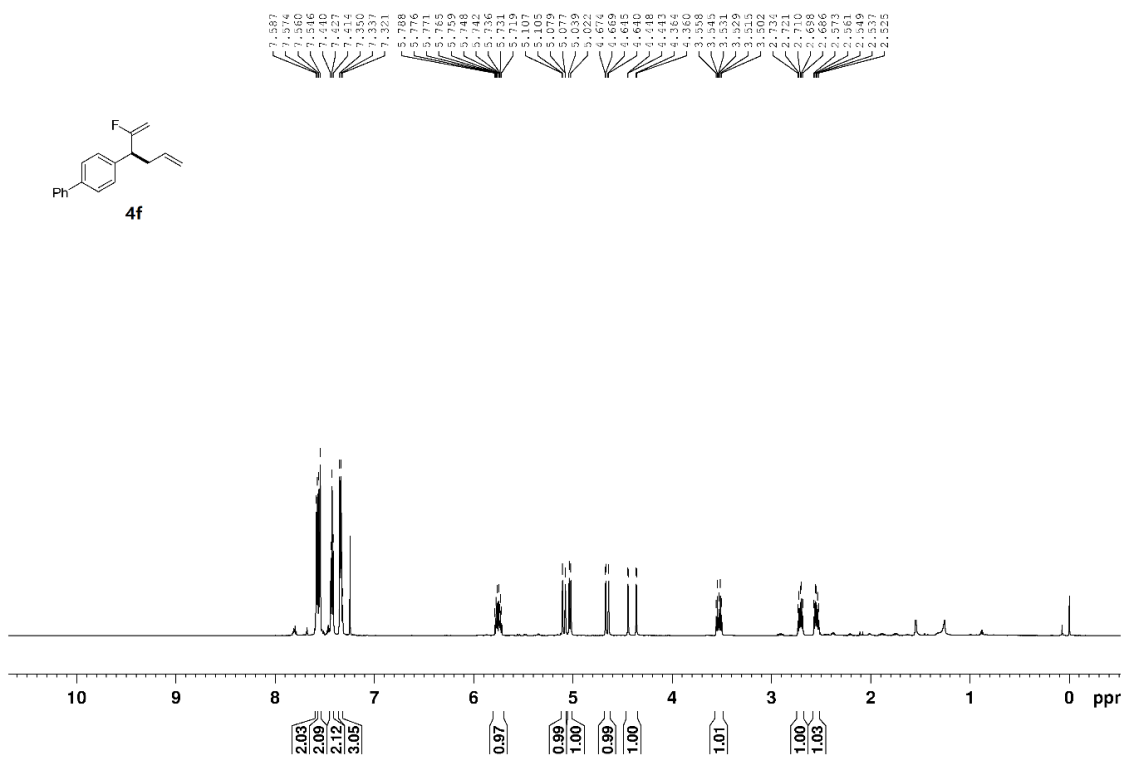
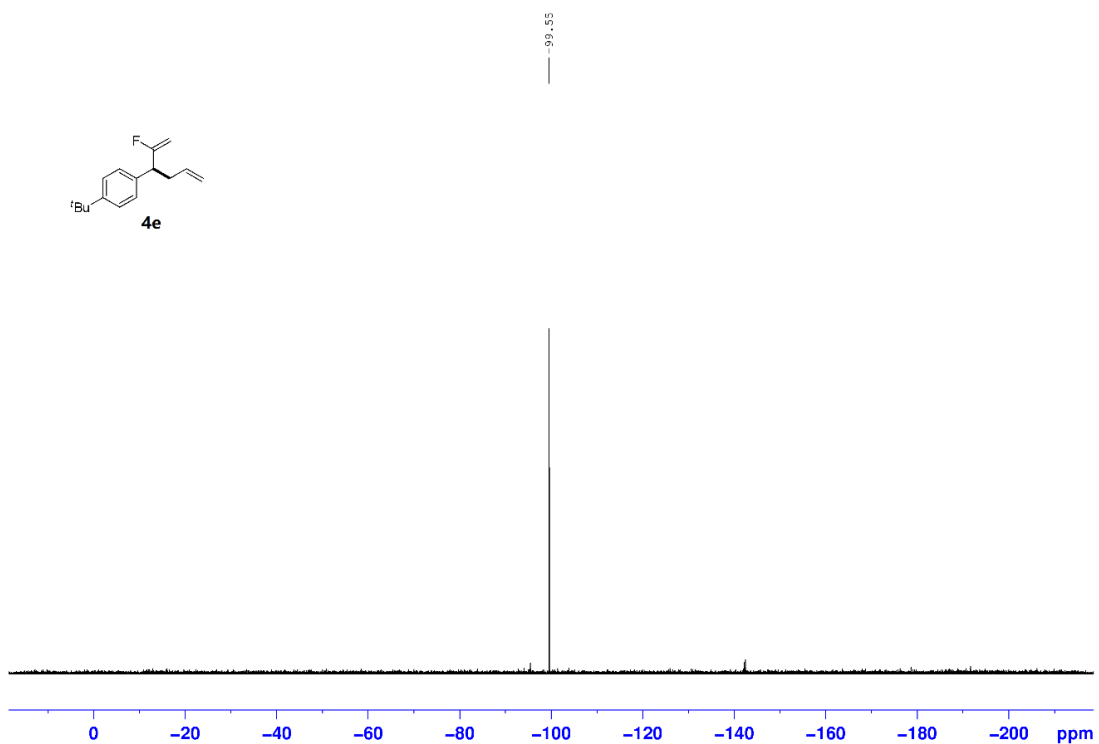


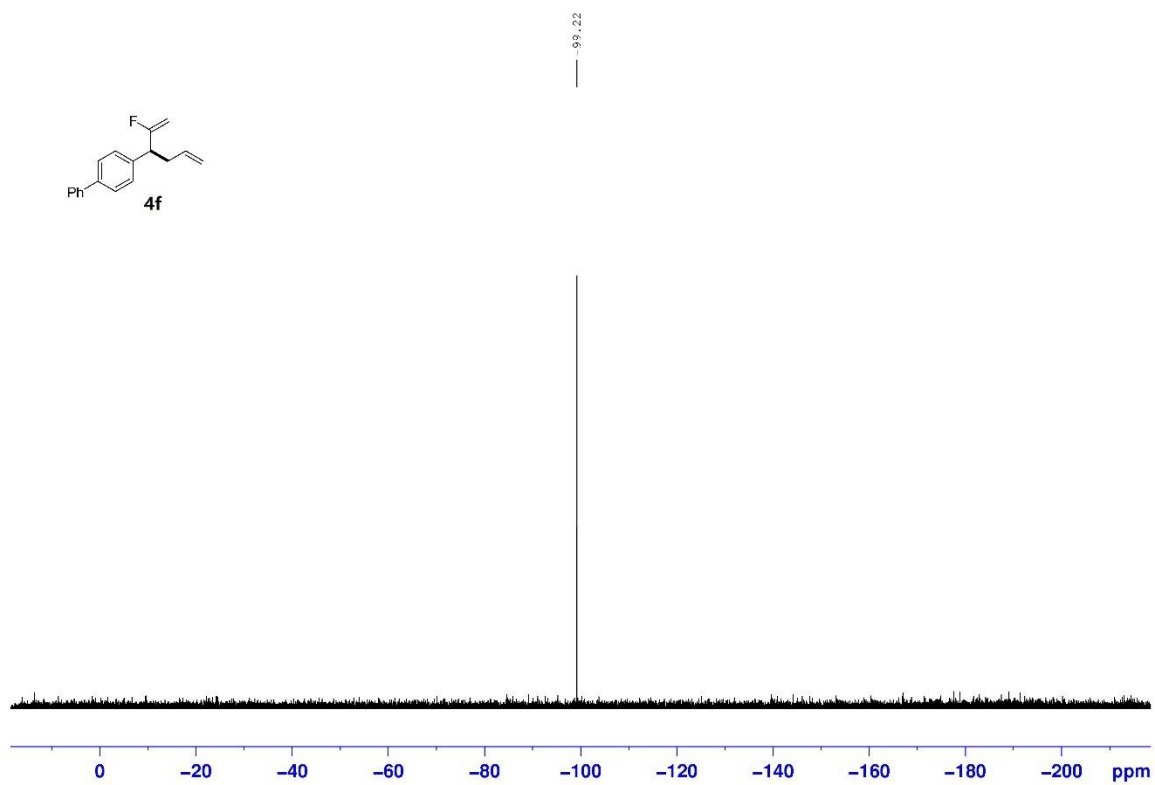
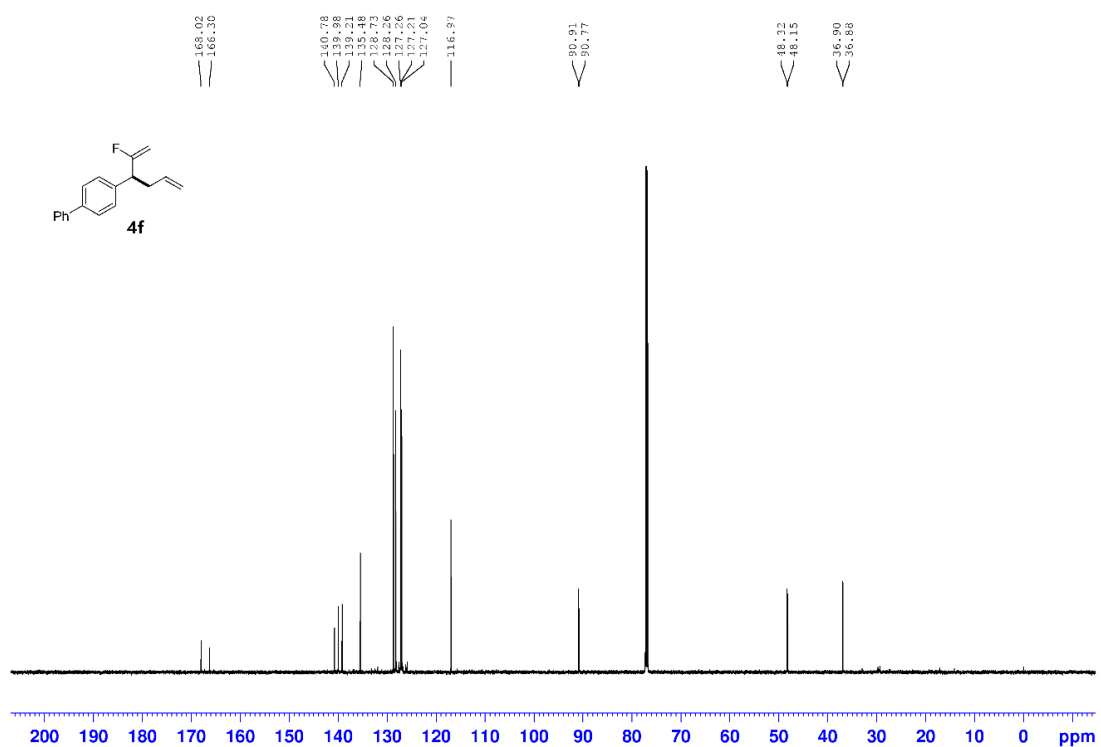


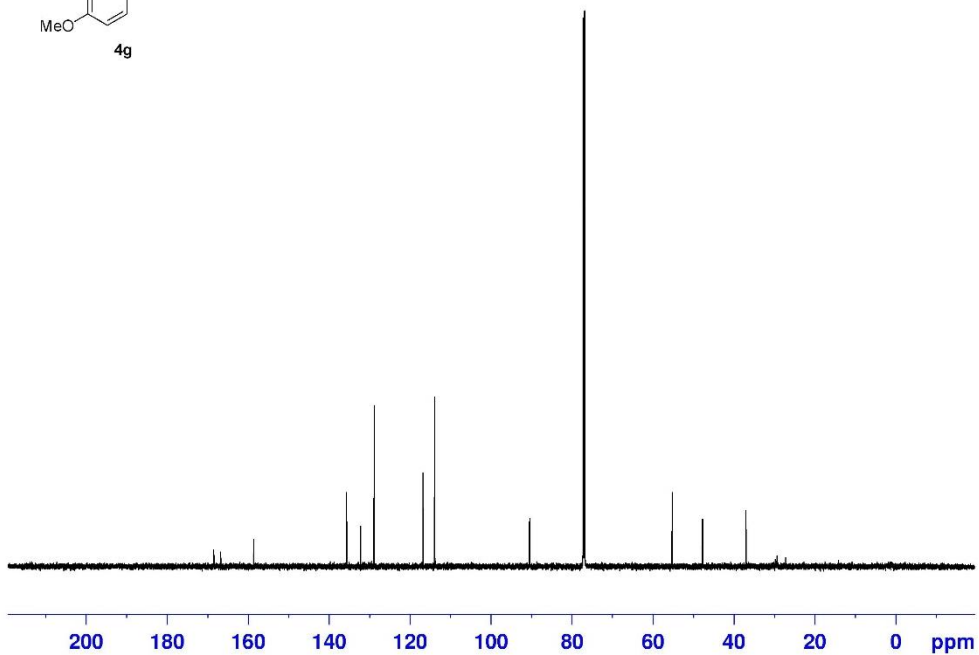
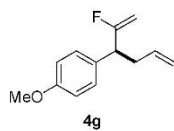
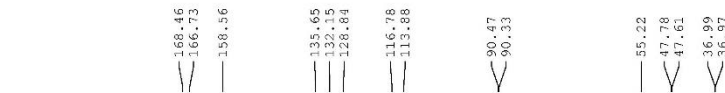
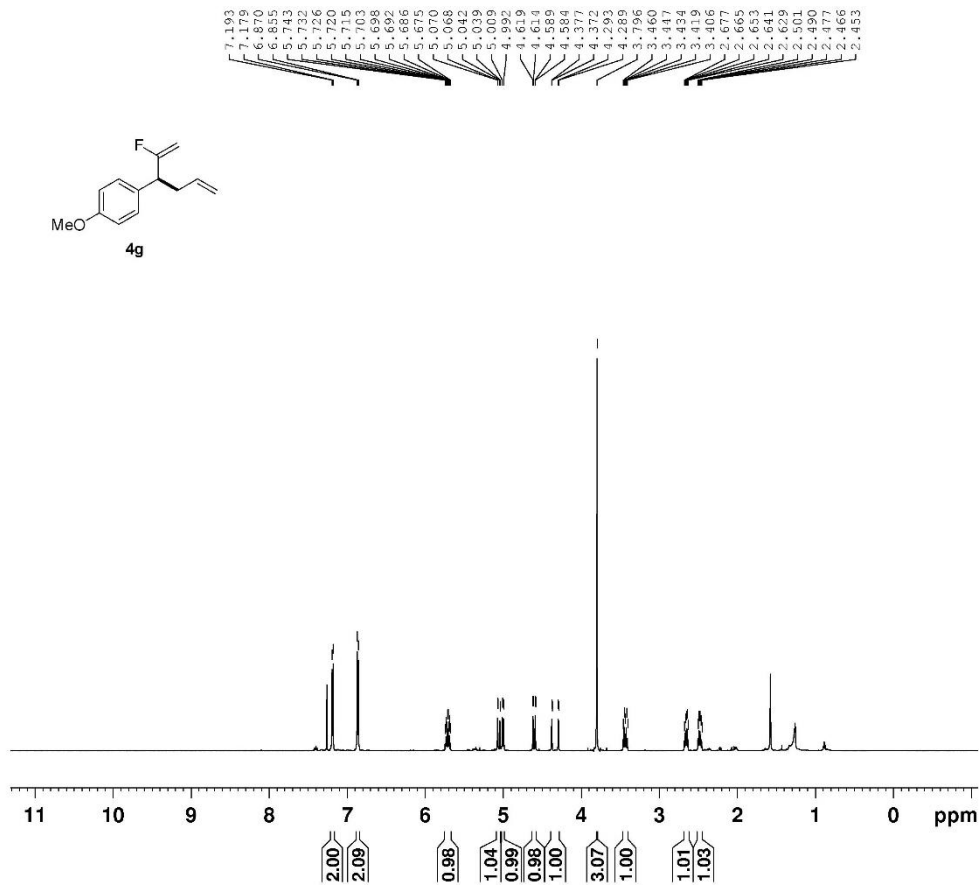
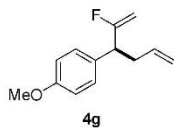


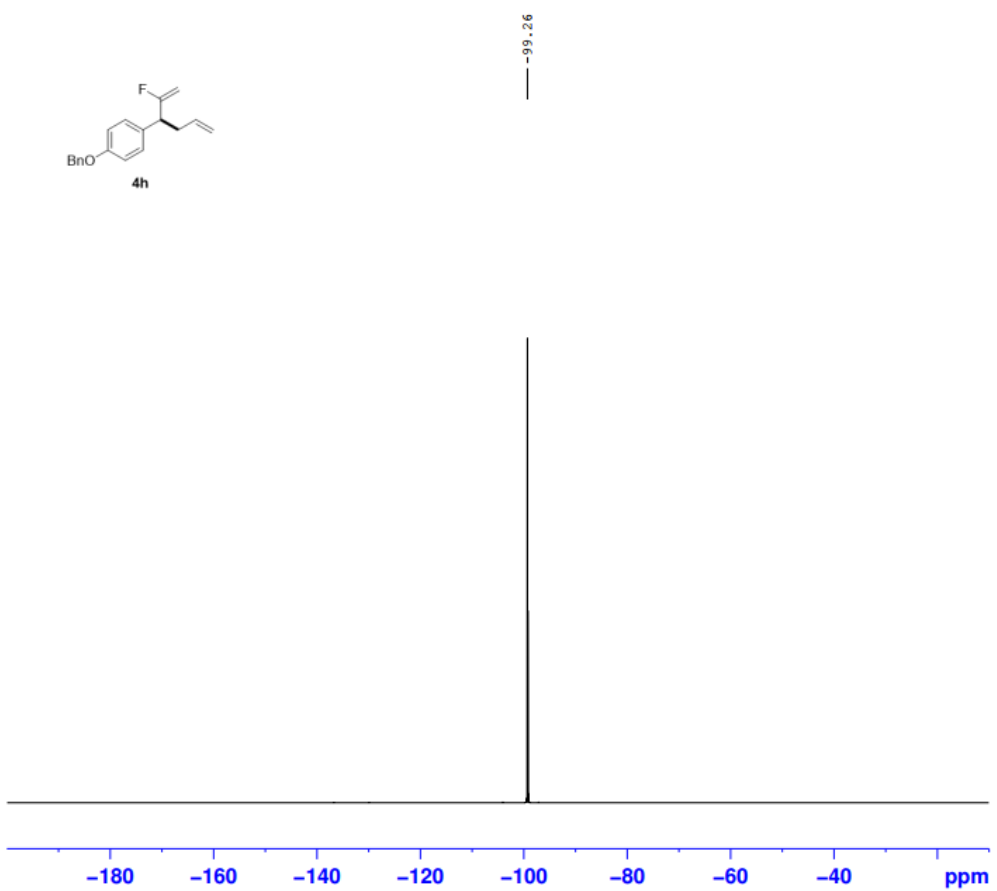
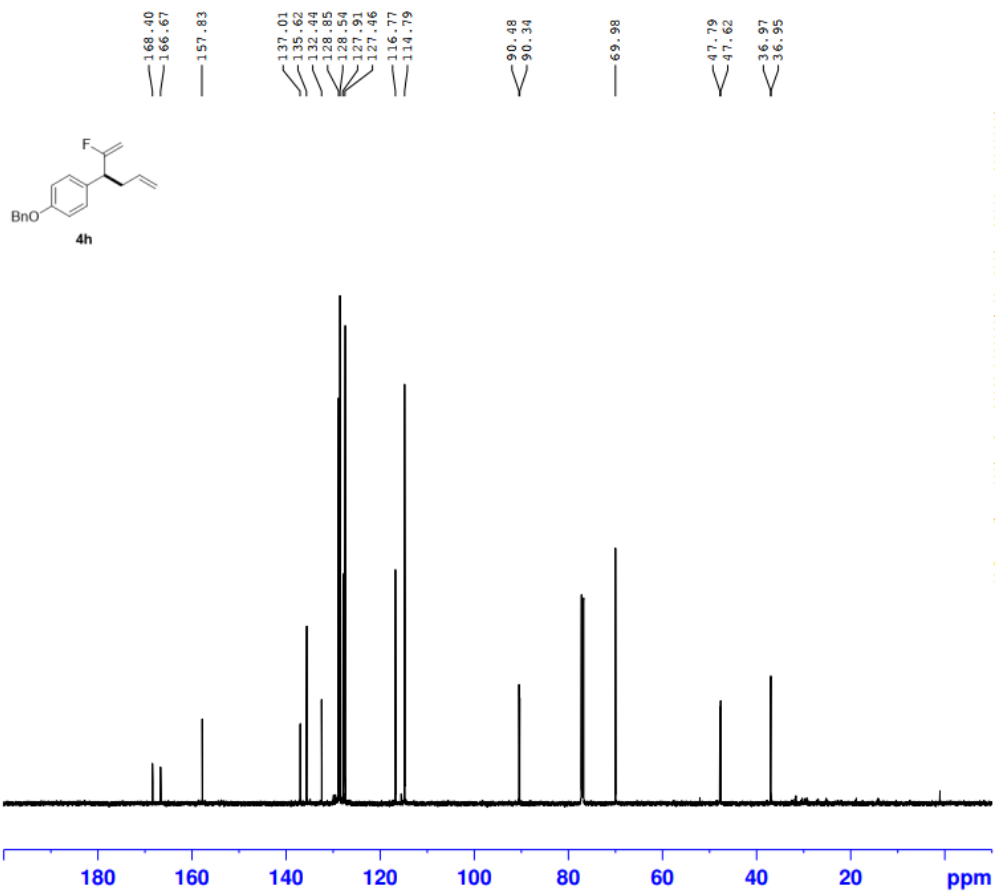


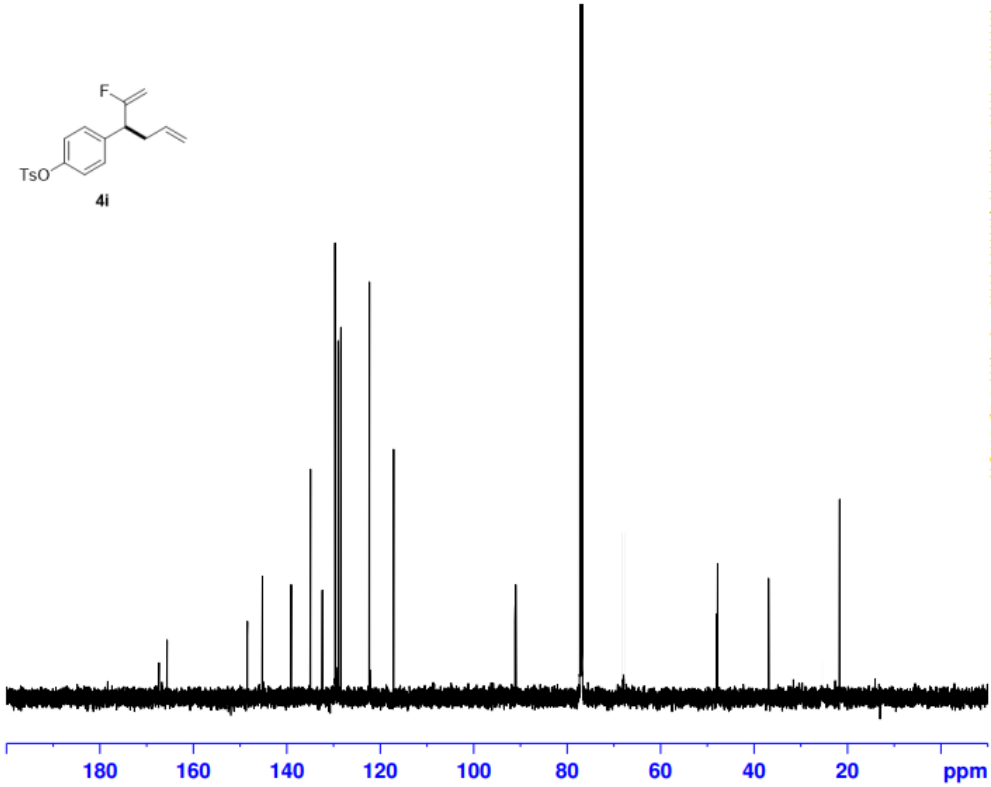
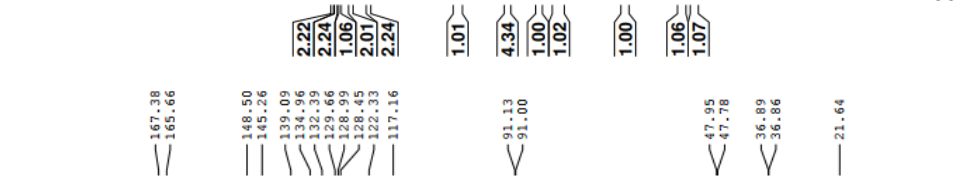
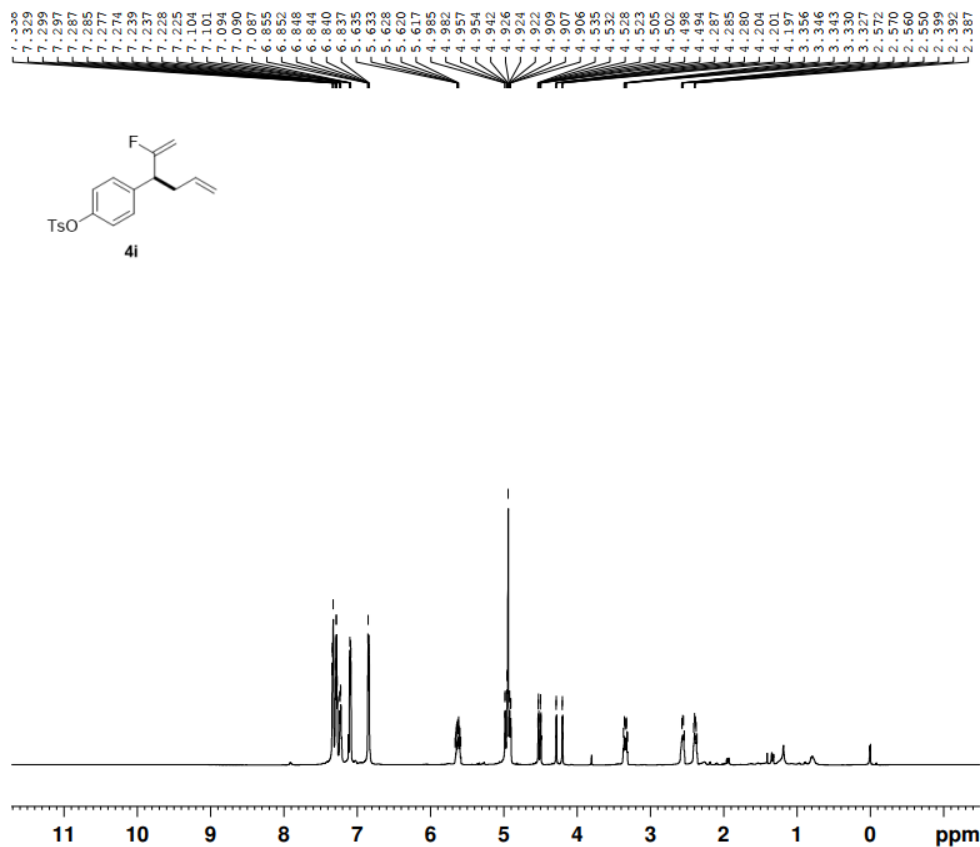


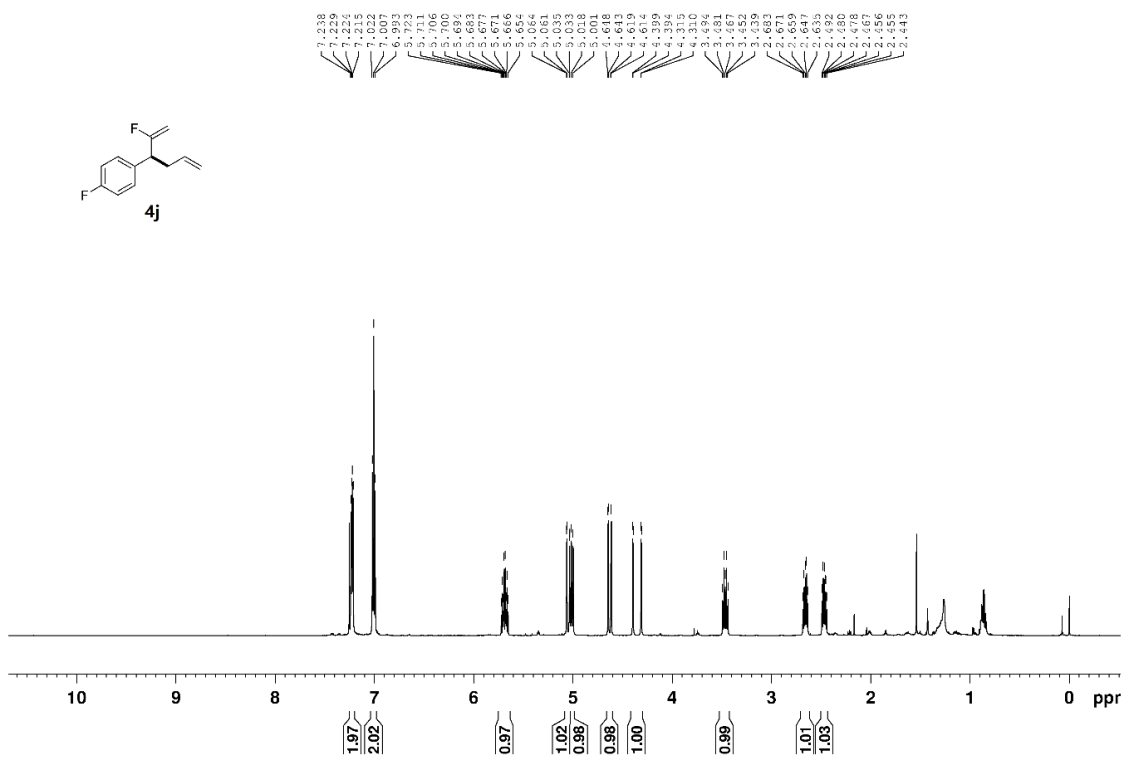
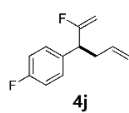
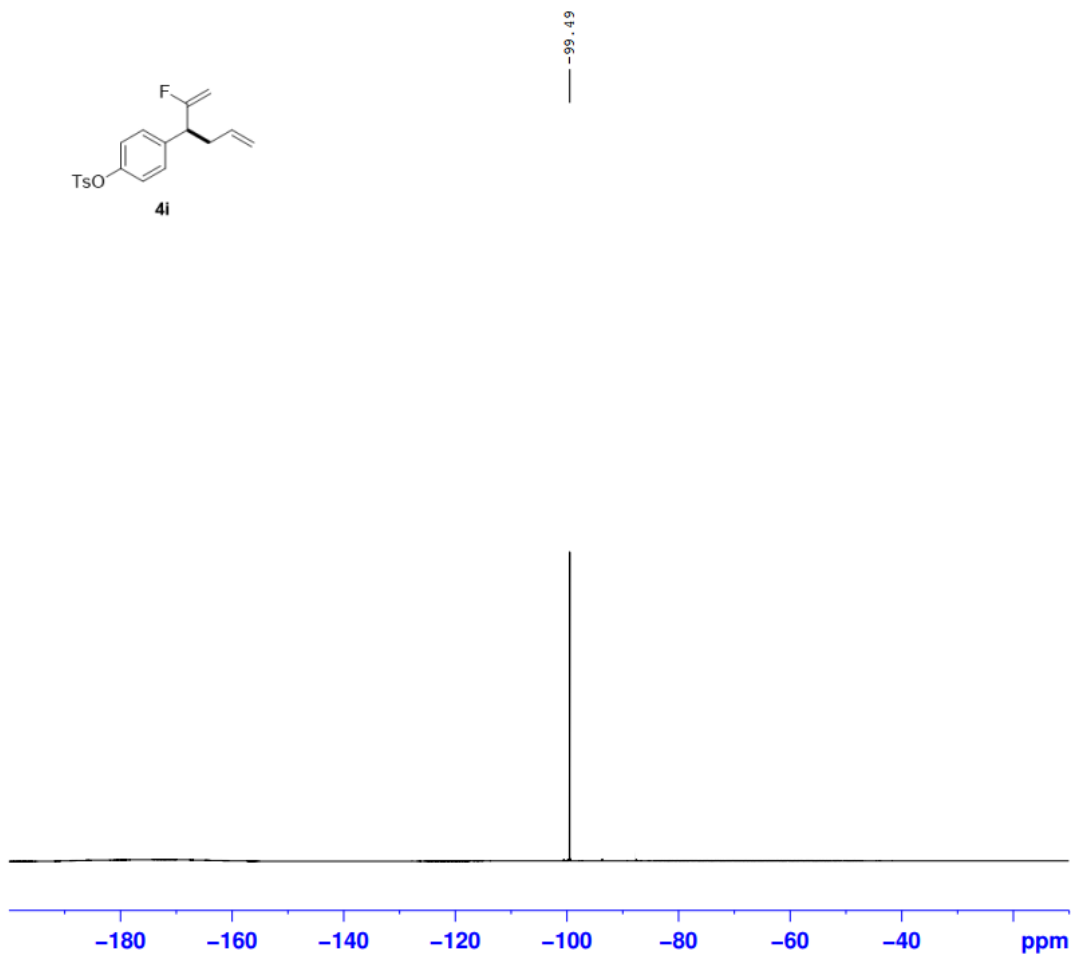
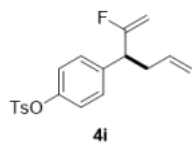


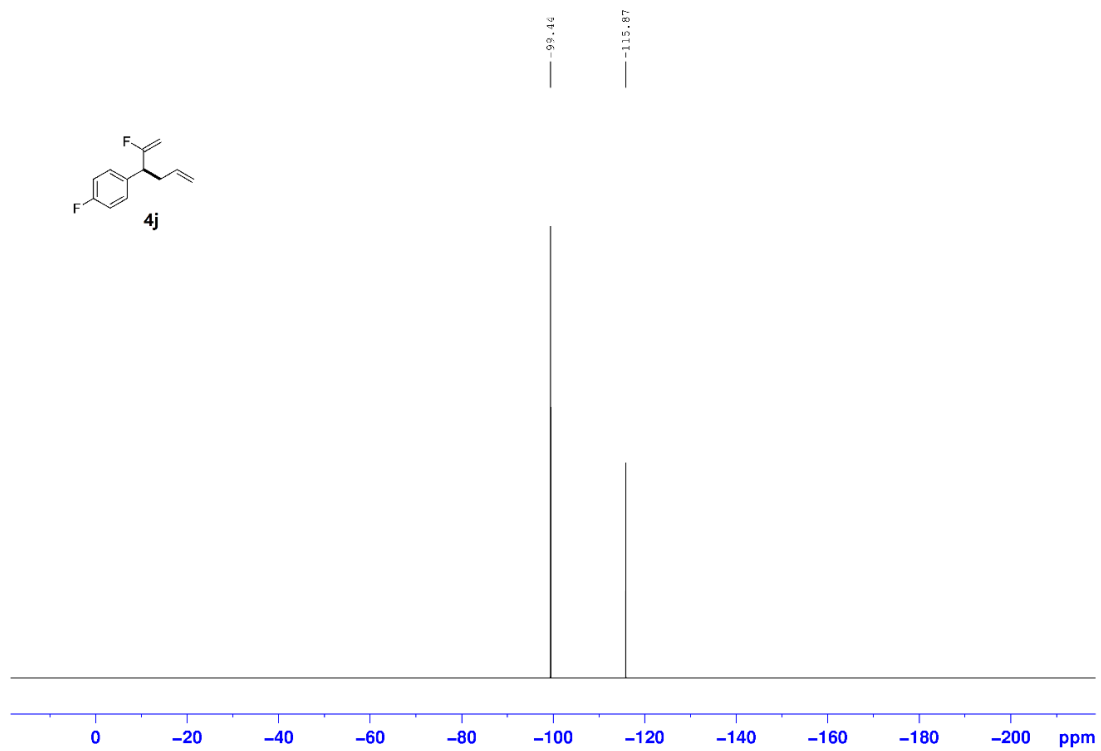
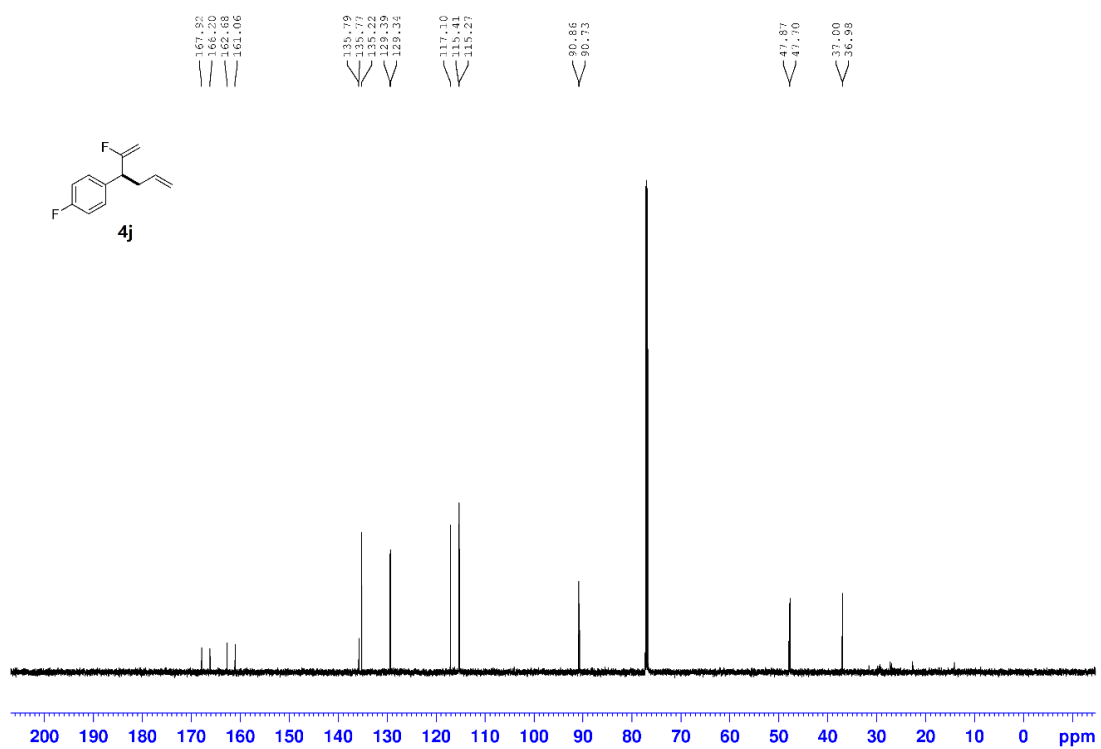


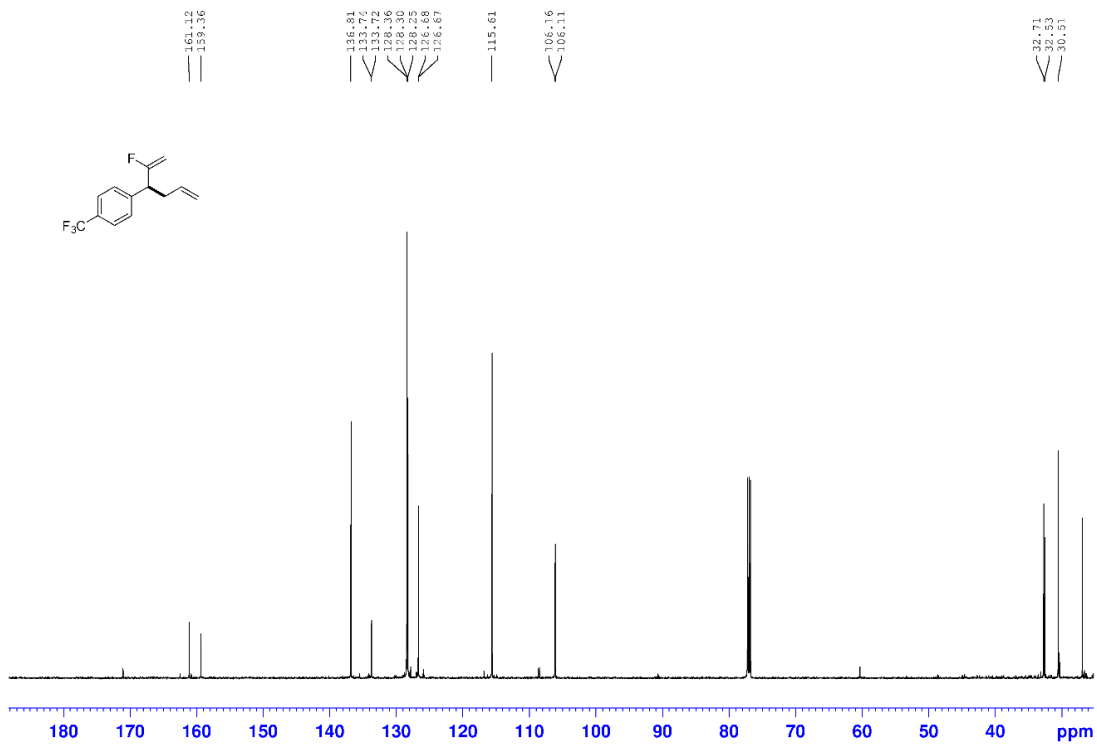
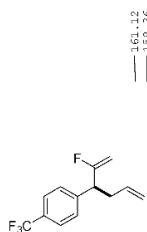
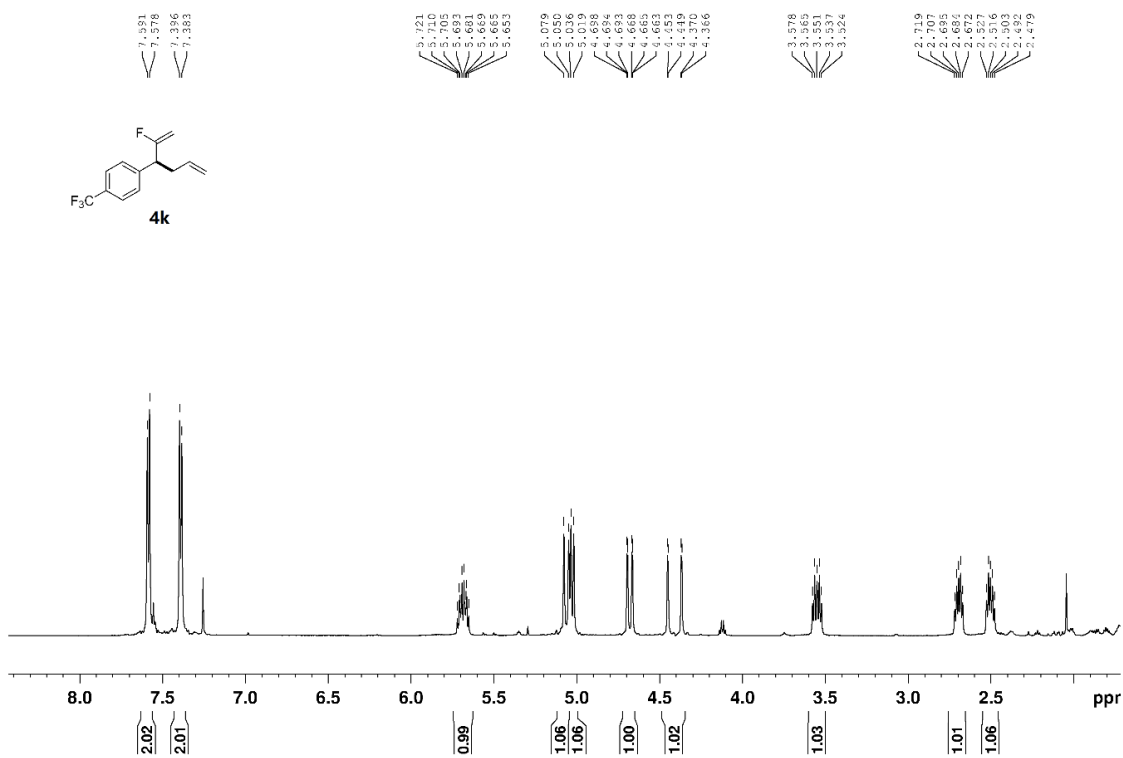
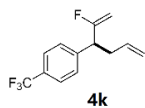


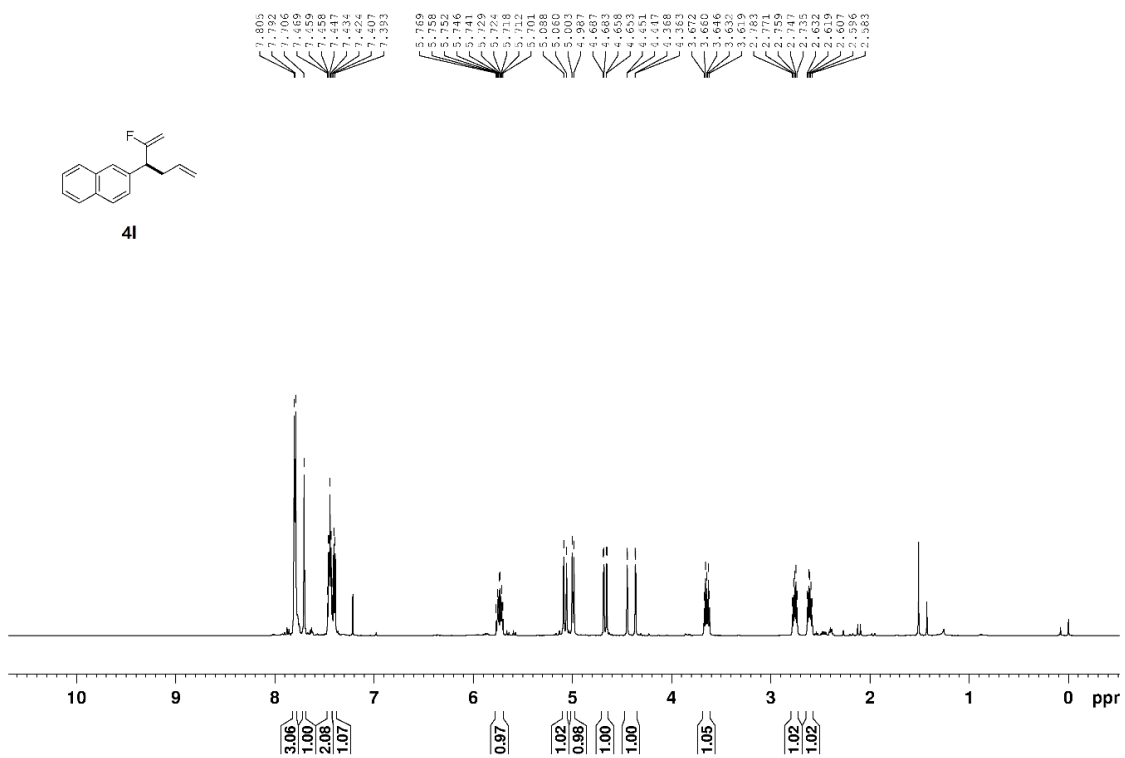
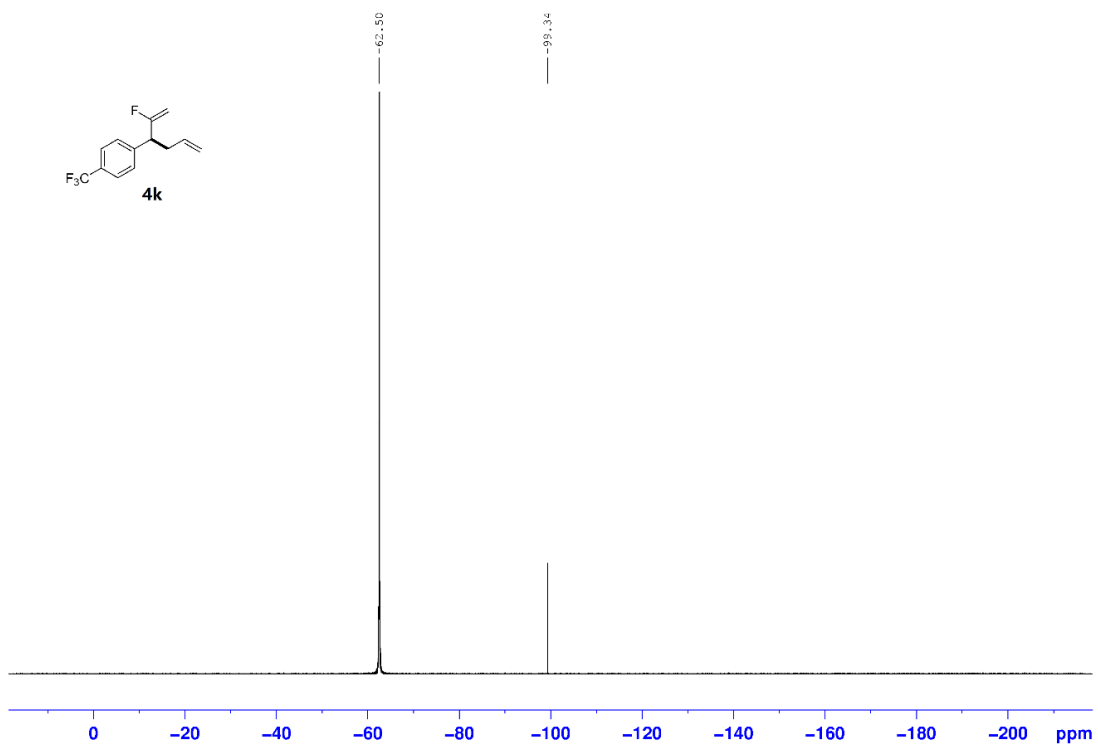


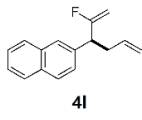




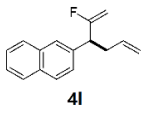
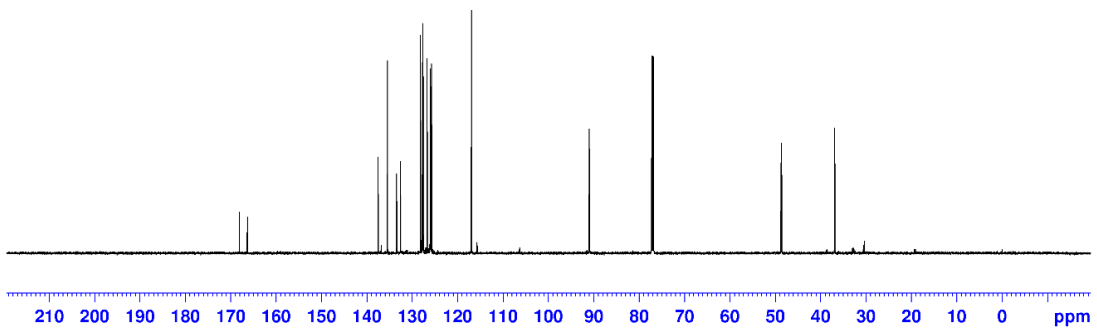








- 168.09
- 166.37
- 137.52
- 135.16
- 132.59
- 128.21
- 127.76
- 126.87
- 126.70
- 125.07
- 124.96
- 124.73
- 116.96
- 91.03
- 90.88
- 48.73
- 48.58
- 36.87
- 36.85



-98.59

