

# $\alpha$ -Silicon Effect Assisted Curtin-Hammett Allylation Using Allylcopper Reagents Derived from 1,3-Dienylsilanes

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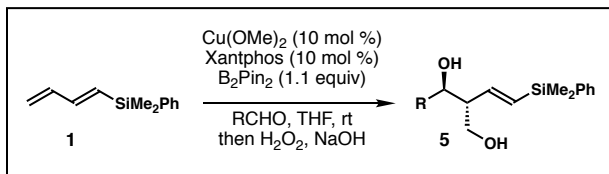
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data,  $^1\text{H}$  and

$^{13}\text{C}$  Spectra of New Compounds

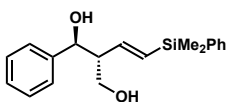
**General Experimental Details.** All reaction solvents were purified before use. Tetrahydrofuran, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of argon using flame-dried or oven-dried (120 °C) glassware. The term “concentrated under reduced pressure” refers to the removal of solvents and other volatile materials using a rotary evaporator with the water bath temperature below 30 °C, followed by the removal of residual solvents at high vacuum (< 0.2 mbar).

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were acquired on commercial instruments (400 and 600 MHz) at Auburn University NMR facility. Carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR) spectra were acquired at 101 and 151 MHz. The proton signal for the residual non-deuterated solvent ( $\delta$  7.26 for CHCl<sub>3</sub>) was used as an internal reference for <sup>1</sup>H NMR spectra. For <sup>13</sup>C NMR spectra, chemical shifts are reported relative to the  $\delta$  77.36 resonance of CHCl<sub>3</sub>. Coupling constants are reported in Hz. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry and Biochemistry, Auburn University.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or KMnO<sub>4</sub>. Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel, typically using a 50-100:1 weight ratio of silica gel to crude product.

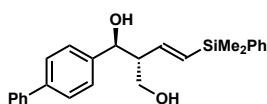


**General procedure for hydroxyalkylation of 1,3-dienylsilane 1:** In an Ar-filled glove box,  $\text{Cu(OMe)}_2$  (1.3 mg, 0.01 mmol), Xantphos (5.8 mg, 0.01 mmol), THF (0.5 mL), and a Teflon-coated magnetic stirring bar were sequentially added into a reaction vial. The resulting mixture was stirred at ambient temperature for 15 min.  $\text{B}_2\text{Pin}_2$  (28 mg, 0.11 mmol, 1.1 equiv) was added and the mixture was stirred for 5 min. Then dienylsilane **1** (19 mg, 0.10 mmol) and aldehyde (0.11 mmol) were added sequentially. The reaction mixture was stirred at ambient temperature inside the glove box and the reaction progress was monitored by  $^1\text{H}$  NMR analysis. After complete consumption of dienylsilane **1** (typically 12 to 48 h), 3 N NaOH (1.0 mL) was added followed by slow addition of 30%  $\text{H}_2\text{O}_2$  (0.5 mL) to the reaction mixture. The resulting mixture was stirred vigorously for 3 h. Brine (1 mL) and  $\text{Et}_2\text{O}$  (0.5 mL) were added, and the mixture was stirred for 5 min. The organic layer was separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 1 mL). The combined organic extracts were concentrated under reduced pressure. The crude reaction product was dissolved in  $\text{Et}_2\text{O}$  (1.0 mL), followed by addition of  $\text{NaIO}_4$  (107 mg, 0.5 mmol) and water (1.0 mL). The resulting mixture was stirred at ambient temperature for 2 h. Brine (1 mL) and  $\text{Et}_2\text{O}$  (0.5 mL) were added; the organic layer was separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography to give diol **5**.



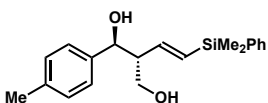
**(1S,2R)-2-((E)-2-(Dimethyl(phenyl)silyl)vinyl)-1-phenylpropane-1,3-diol (5a)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title

compound as colorless oil in 87% yield (27 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (app. d,  $J = 7.4$  Hz, 2H), 7.31 – 7.39 (m, 5H), 7.27 – 7.30 (m, 3H), 6.08 (dd,  $J = 18.8, 8.2$  Hz, 1H), 5.87 (d,  $J = 18.8$  Hz, 1H), 4.87 – 4.94 (m, 1H), 3.62 – 3.75 (m, 2H), 2.64 – 2.69 (m, 1H), 2.60 (d,  $J = 2.4$  Hz, 1H), 1.91 (t,  $J = 5.0$  Hz, 1H), 0.32 (s, 3H), 0.31 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  144.7, 142.3, 138.7, 134.4, 134.1, 129.3, 128.6, 128.1, 127.9, 126.7, 75.6, 64.1, 56.2, -2.26, -2.31. HRMS (ESI):  $m/z$  for  $\text{C}_{19}\text{H}_{24}\text{O}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$  calcd. 335.1443, found: 335.1418.



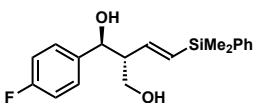
**(1*S*,2*R*)-1-([1,1'-biphenyl]-4-yl)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)propane-1,3-diol (5b)**

Prepared according to the general procedure, the crude mixture was purified by flash column chromatography to give the title compound as colorless oil in 92% yield (36 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.48 (m, 4H), 7.37 (app. dd, *J* = 7.7, 3.5 Hz, 3H), 7.29 – 7.35 (m, 3H), 6.12 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.91 (d, *J* = 18.8 Hz, 1H), 4.93 – 4.99 (m, 1H), 3.76 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.72 (dd, *J* = 10.6, 5.2 Hz, 1H), 2.69 – 2.73 (m, 1H), 2.56 (d, *J* = 2.5 Hz, 1H), 1.84 (t, *J* = 5.3 Hz, 1H), 0.332 (s, 3H), 0.325 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.7, 141.4, 141.1, 140.8, 138.7, 134.6, 134.1, 129.4, 129.1, 128.1, 127.6, 127.4, 127.3, 127.2, 75.4, 64.1, 56.2, -2.25, -2.28. HRMS (ESI): *m/z* for C<sub>25</sub>H<sub>28</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup> calcd. 411.1756, found: 411.1760.



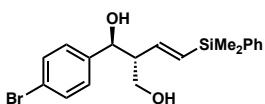
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(*p*-tolyl)propane-1,3-diol (5c)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 86% yield (28 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.44 (d, *J* = 6.0 Hz, 2H), 7.30 – 7.40 (m, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.7 Hz, 2H), 6.08 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.90 (d, *J* = 18.8 Hz, 1H), 4.85 (d, *J* = 4.8 Hz, 1H), 3.59 – 3.74 (m, 2H), 2.60 – 2.72 (m, 1H), 2.41 (br, 1H), 2.34 (s, 3H), 1.79 (br, 1H), 0.324 (s, 3H), 0.320 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.9, 139.2, 138.7, 137.7, 134.3, 134.1, 129.4, 129.3, 128.1, 126.7, 75.5, 64.0, 56.2, 21.5, -2.27, -2.29. HRMS (ESI): *m/z* for C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup> calcd. 349.1600, found: 349.1614.



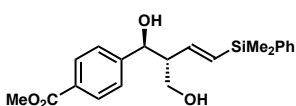
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(4-fluorophenyl)propane-1,3-diol (5d)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 79% yield (26 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.39 – 7.46 (m, 2H), 7.32 – 7.39 (m, 3H), 7.25 (dd, *J* = 7.6, 4.8 Hz, 2H), 7.00 (app. t, *J* = 8.6 Hz, 2H), 6.06 (dd, *J* = 18.8, 8.3 Hz, 1H), 5.84 (d, *J* = 18.8 Hz, 1H), 4.92 (d, *J* = 2.5 Hz, 1H), 3.70 (app. br, 2H), 2.72 (s, 1H), 2.59 – 2.63 (m, 1H), 1.91 (s, 1H), 0.32 (s, 3H), 0.31 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 162.2 (d, *J* = 245.7 Hz), 144.2, 138.6, 138.1 (d, *J* = 3.0 Hz), 134.7, 134.1, 129.4, 128.3 (d, *J* = 7.9 Hz), 128.1, 115.4 (d, *J* = 21.2 Hz), 74.9, 64.1, 56.1, -2.3 (2C). HRMS (ESI): *m/z* for C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>FSiNa [M+Na]<sup>+</sup> calcd. 353.1349, found: 353.1367.



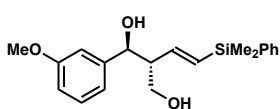
**(1*S*,2*R*)-1-(4-bromophenyl)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)propane-1,3-diol (5e)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 86% yield (33 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.39 (m, 5H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.06 (dd, *J* = 18.8, 8.3 Hz, 1H), 5.82 (d, *J* = 18.8 Hz, 1H), 4.92 (s, 1H), 3.63 – 3.86 (m, 2H), 2.71 (d, *J* = 2.5 Hz, 1H), 2.60 (dd, *J* = 7.5, 5.1 Hz, 1H), 1.84 (t, *J* = 5.0 Hz, 1H), 0.312 (s, 3H), 0.306 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 143.9, 141.4, 138.6, 134.8, 134.1, 131.6, 129.4, 128.4, 128.2, 121.6, 75.0, 64.2, 55.9, -2.3 (2C). HRMS (ESI): *m/z* for C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>BrSiNa [M+Na]<sup>+</sup> calcd. 413.0548, found: 413.0588.



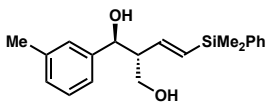
**Methyl 4-((1*S*,2*R*,*E*)-4-(dimethyl(phenyl)silyl)-1-hydroxy-2-(hydroxymethyl)but-3-en-1-yl)benzoate (5f)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 92% yield (34 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.45 (m, 7H), 6.06 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.79 (d, *J* = 18.8 Hz, 1H), 5.04 (d, *J* = 4.5 Hz, 1H), 3.92 (s, 3H), 3.73 – 3.81 (m, 2H), 2.63 – 2.67 (m, 1H), 1.61 (br, 2H), 0.30 (s, 3H), 0.29 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.3, 147.7, 143.7, 138.6, 134.8, 134.1, 129.8, 129.5, 129.4, 128.1, 126.6, 75.2, 64.3, 55.8, 52.5, -2.3 (2C). HRMS (ESI): *m/z* for C<sub>21</sub>H<sub>26</sub>O<sub>4</sub>SiNa [M+Na]<sup>+</sup> calcd. 393.1498, found: 393.1519.



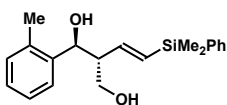
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(3-methoxyphenyl)propane-1,3-diol (5g)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 62% yield (21 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.31 – 7.38 (m, 3H), 7.21 – 7.27 (m, 1H), 6.87 (d, *J* = 7.2 Hz, 2H), 6.85 – 6.79 (m, 1H), 6.10 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.89 (d, *J* = 18.8 Hz, 1H), 4.88 (d, *J* = 5.4 Hz, 1H), 3.78 (s, 3H), 3.72 (dd, *J* = 10.7, 5.9 Hz, 1H), 3.67 (dd, *J* = 10.7, 5.8 Hz, 1H), 2.64 – 2.68 (m, 1H), 1.93 (br, 2H), 0.32 (s, 3H), 0.31 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 159.9, 144.8, 144.1, 138.7, 134.4, 134.1, 129.6, 129.4, 128.1, 119.0, 113.4, 112.0, 75.4, 64.1, 56.2, 55.5, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>20</sub>H<sub>26</sub>O<sub>3</sub>SiNa [M+Na]<sup>+</sup> calcd. 365.1549, found: 365.1555.



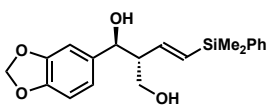
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(*m*-tolyl)propane-1,3-diol (5h)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the

title compound as colorless oil in 84% yield (27 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.30 – 7.38 (m, 3H), 7.22 (app. t, *J* = 7.5 Hz, 1H), 7.12 (s, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.09 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.90 (d, *J* = 18.8 Hz, 1H), 4.85 (d, *J* = 5.5 Hz, 1H), 3.70 (dd, *J* = 10.7, 5.9 Hz, 1H), 3.66 (dd, *J* = 10.7, 5.9 Hz, 1H), 2.63 – 2.70 (m, 1H), 2.34 (s, 3H), 1.61 (br, 2H), 0.33 (s, 3H), 0.32 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.9, 142.3, 138.7, 138.3, 134.3, 134.1, 129.4, 128.8, 128.5, 128.1, 127.4, 123.8, 75.6, 64.1, 56.3, 21.9, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup> calcd. 349.1600, found: 349.1635.



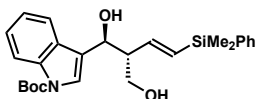
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(*o*-tolyl)propane-1,3-diol (5i)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the

title compound as colorless oil in 88% yield (28 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.44 (m, 2H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.30 – 7.37 (m, 3H), 7.14 – 7.22 (m, 2H), 7.13 (d, *J* = 6.9 Hz, 1H), 6.17 (dd, *J* = 18.8, 8.3 Hz, 1H), 5.81 (d, *J* = 18.8 Hz, 1H), 5.19 (d, *J* = 4.7 Hz, 1H), 3.79 (dd, *J* = 10.7, 5.7 Hz, 1H), 3.75 (dd, *J* = 10.6, 5.9 Hz, 1H), 2.60 – 2.64 (m, 1H), 2.32 (s, 3H), 0.32 (s, 3H), 0.31 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.5, 140.7, 138.8, 134.6, 134.5, 134.1, 130.7, 129.3, 128.1, 127.6, 126.7, 126.3, 71.3, 64.4, 54.9, 19.6, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>20</sub>H<sub>26</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup> calcd. 349.1600, found: 349.1588.



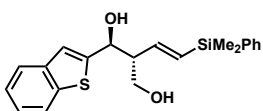
**(1*S*,2*R*)-1-(benzo[d][1,3]dioxol-5-yl)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)propane-1,3-diol (5j)** Prepared according to the general procedure, the crude mixture was purified by column

chromatography to give the title compound as colorless oil in 76% yield (27 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.48 (m, 2H), 7.33 – 7.36 (m, 3H), 6.83 (s, 1H), 6.70 – 6.80 (m, 2H), 6.08 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.95 (s, 2H), 5.91 (d, *J* = 18.8 Hz, 1H), 4.79 (d, *J* = 5.7 Hz, 1H), 3.68 (dd, *J* = 10.7, 5.7 Hz, 1H), 3.64 (dd, *J* = 10.7, 5.8 Hz, 1H), 2.58 – 2.62 (m, 1H), 2.45 (br, 1H), 1.74 (br, 1H), 0.335 (s, 3H), 0.329 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 148.0, 147.3, 144.9, 138.7, 136.3, 134.6, 134.1, 129.4, 128.1, 120.1, 108.3, 107.2, 101.4, 75.3, 64.0, 56.5, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>20</sub>H<sub>24</sub>O<sub>4</sub>SiNa [M+Na]<sup>+</sup> calcd. 379.1342, found: 379.1319.



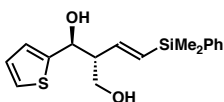
**Tert-butyl-3-((1*S*,2*R*,*E*)-4-(dimethyl(phenyl)silyl)-1-hydroxy-2-(hydroxymethyl)but-3-en-1-yl)-1*H*-indole-1-carboxylate (5k)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 70% yield (32 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.17 (br, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.39 (d, *J* = 6.1 Hz, 2H), 7.31 – 7.34 (m, 4H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.16 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.93 (d, *J* = 18.8 Hz, 1H), 5.24 (d, *J* = 4.6 Hz, 1H), 3.85 (dd, *J* = 10.4, 5.8 Hz, 1H), 3.77 (dd, *J* = 10.4, 5.5 Hz, 1H), 2.81 – 2.95 (m, 1H), 1.62 – 1.80 (br, 2H), 1.65 (s, 9H), 0.302 (s, 3H), 0.295 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 149.9, 144.7, 138.6, 136.0, 134.3, 134.0, 129.3, 128.8, 128.1, 124.9, 123.6, 122.9, 122.2, 120.1, 115.7, 84.1, 69.5, 64.3, 54.6, 28.5, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>26</sub>H<sub>33</sub>NO<sub>4</sub>SiNa [M+Na]<sup>+</sup> calcd. 474.2077, found: 474.2090.



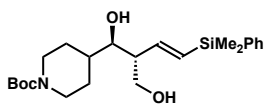
**(1*S*,2*R*)-1-(benzo[*b*]thiophen-2-yl)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)propane-1,3-diol (5l)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 80% yield (29 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.35 (m, 5H), 7.13 – 7.28 (m, 3H), 6.18 (dd, *J* = 18.8, 7.9 Hz, 1H), 6.00 (d, *J* = 18.8 Hz, 1H), 5.26 (app. s, 1H), 3.82 – 3.89 (m, 1H), 3.72 – 3.82 (m, 1H), 2.94 (d, *J* = 3.2 Hz, 1H), 2.76 – 2.89 (m, 1H), 1.79 (s, 1H), 0.33 (s, 3H), 0.32 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 147.0, 143.9, 139.7, 139.6, 138.6, 135.0, 134.1, 129.4, 128.1, 124.6, 124.4, 123.8, 122.7, 121.1, 72.3, 64.1, 55.6, -2.3, -2.4. HRMS (ESI): *m/z* for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>SSiNa [M+Na]<sup>+</sup> calcd. 391.1164, found: 391.1134.



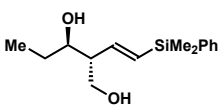
**(1*S*,2*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)-1-(thiophen-2-yl)propane-1,3-diol (5m)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 88% yield (28 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.40 – 7.52 (m, 2H), 7.35 (d, *J* = 6.9 Hz, 3H), 7.26 (s, 1H), 6.90 – 7.04 (m, 2H), 6.14 (dd, *J* = 18.8, 8.0 Hz, 1H), 6.00 (d, *J* = 18.8 Hz, 1H), 5.17 (app. s, 1H), 3.60 – 3.72 (m, 1H), 3.77 – 3.83 (m, 1H), 2.74 (app. s, 2H), 1.76 (br, 1H), 0.344 (s, 3H), 0.335 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 146.2, 144.3, 138.6, 134.9, 134.1, 129.4, 128.1, 126.9, 125.1, 124.7, 71.9, 64.0, 56.2, -2.30, -2.34. HRMS (ESI): *m/z* for C<sub>17</sub>H<sub>22</sub>O<sub>2</sub>SiSNa [M+Na]<sup>+</sup> calcd. 341.1008, found: 341.0982.



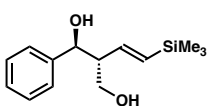
**Tert-butyl-4-((1*R*,2*R*,*E*)-4-(dimethyl(phenyl)silyl)-1-hydroxy-2-(hydroxymethyl)but-3-en-1-yl)piperidine-1-carboxylate (5n)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 75% yield (31 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 (dd, *J* = 6.2, 2.7 Hz, 2H), 7.31 – 7.41 (m, 3H), 6.24 (dd, *J* = 18.8, 8.6 Hz, 1H), 5.99 (d, *J* = 18.9 Hz, 1H), 4.11 (app. t, *J* = 15.0 Hz, 2H), 3.73 – 3.89 (m, 2H), 3.54 (dd, *J* = 8.3, 2.7 Hz, 1H), 2.55 (m, 3H), 1.73 – 2.01 (m, 4H), 1.49 – 1.64 (m, 2H), 1.36 – 1.50 (m, 9H), 1.01 – 1.23 (m, 2H), 0.36 (s, 3H), 0.35 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.2, 144.2, 139.0, 134.2, 134.0, 129.4, 128.2, 79.7, 77.6, 76.5, 65.6, 51.0, 44.1, 43.9, 40.2, 28.8, 28.2, -2.2, -2.3. HRMS (ESI): *m/z* for C<sub>23</sub>H<sub>37</sub>NO<sub>4</sub>SiNa [M+Na]<sup>+</sup> calcd. 442.2390, found: 442.2428.



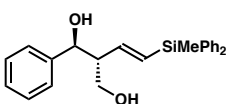
**(2*R*,3*R*)-2-((*E*)-2-(dimethyl(phenyl)silyl)vinyl)pentane-1,3-diol (5o)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 86% yield (23 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.52 (m, 2H), 7.34 – 7.36 (m, 3H), 6.17 (dd, *J* = 18.8, 8.2 Hz, 1H), 5.98 (d, *J* = 18.8 Hz, 1H), 3.65 – 3.94 (m, 3H), 2.32 – 2.49 (m, 1H), 1.96 (br, 1H), 1.90 (br, 1H), 1.41 – 1.56 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.35 (s, 3H), 0.34 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.6, 139.0, 134.1, 133.8, 129.4, 128.1, 74.8, 65.1, 53.4, 28.1, 10.6, -2.18, -2.23. HRMS (EI<sup>+</sup>): *m/z* for C<sub>15</sub>H<sub>21</sub>OSi [M-H<sub>2</sub>O]<sup>+</sup> calcd. 245.1362, found: 245.1358.



***rac*-(1*S*,2*R*)-1-Phenyl-2-((*E*)-2-(trimethylsilyl)vinyl)propane-1,3-diol (5p)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title compound as colorless oil in 68% yield (17 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.36 (m, 5H), 5.98 (dd, *J* = 18.8, 8.1 Hz, 1H), 5.80 (d, *J* = 18.8 Hz, 1H), 4.84 (d, *J* = 5.6 Hz, 1H), 3.65 (dd, *J* = 10.7, 5.6 Hz, 1H), 3.62 (dd, *J* = 10.7, 5.9 Hz, 1H), 2.59 – 2.63 (m, 1H), 1.81 (br, 2H), 0.05 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 142.9, 142.2, 137.1, 128.6, 128.1, 126.8, 75.5, 63.8, 56.3, -0.9. HRMS (ESI): *m/z* for C<sub>14</sub>H<sub>22</sub>O<sub>2</sub>SiNa [M+Na]<sup>+</sup> calcd. 273.1287, found: 273.1278.

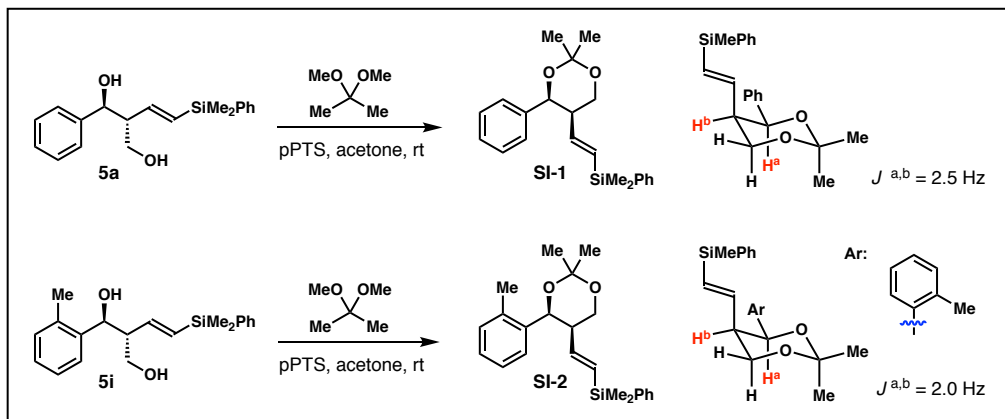


***rac*-(1*S*,2*R*)-2-((*E*)-2-(Methyldiphenylsilyl)vinyl)-1-phenylpropane-1,3-diol (5q)**

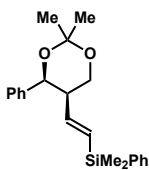
Prepared according to the general procedure, the crude mixture was purified by column chromatography to give the title



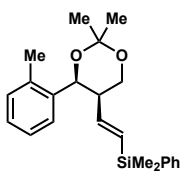
compound as colorless oil in 86% yield (32 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.44 (m, 15H), 6.13 (dd,  $J = 18.8, 8.1$  Hz, 1H), 6.03 (d,  $J = 18.8$  Hz, 1H), 4.94 – 4.95 (m, 1H), 3.70 – 3.77 (m, 2H), 2.72 – 2.76 (m, 1H), 2.55 (d,  $J = 1.7$  Hz, 1H), 1.87 (t,  $J = 6.3$  Hz, 1H), 0.59 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  146.7, 142.3, 136.53, 136.49, 135.09, 135.06, 132.0, 129.65, 129.63, 128.6, 128.2, 128.1, 127.9, 126.6, 75.5, 64.2, 56.3, –3.5. HRMS (ESI):  $m/z$  for  $\text{C}_{24}\text{H}_{26}\text{O}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$  calcd. 397.1600, found: 397.1602.



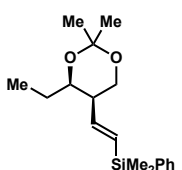
**General procedure for the synthesis of acetonides SI-1, SI-2, and 11:** To a solution of diol **5** in 2, 2-dimethoxypropane (1 mL) was added pPTS (2 mg) and acetone (0.2 mL). The reaction mixture was stirred at ambient temperature and the progress was monitored by TLC analysis. After complete consumption of diol **5**, the reaction mixture was filtered through a short pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and ethyl acetate) to afford acetonide as a colorless oil.



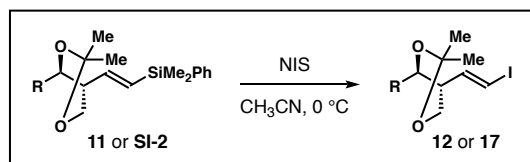
**(*E*)-2-((4*S*,5*R*)-2,2-dimethyl-4-phenyl-1,3-dioxan-5-yl)vinyl)dimethyl(phenyl)silane (SI-1)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give compound **SI-1** as colorless oil in 86% yield (18 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (app. t,  $J = 7.7$  Hz, 3H), 7.24 (m, 5H), 7.18 (d,  $J = 7.5$  Hz, 2H), 6.37 (dd,  $J = 18.8, 8.8$  Hz, 1H), 5.44 (d,  $J = 18.8$  Hz, 1H), 5.22 (d,  $J = 2.4$  Hz, 1H), 4.36 (dd,  $J = 11.5, 2.6$  Hz, 1H), 3.90 (d,  $J = 11.4$  Hz, 1H), 2.34 (d,  $J = 8.7$  Hz, 1H), 1.58 (s, 3H), 1.54 (s, 3H), 0.21 (s, 3H), 0.15 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 140.9, 139.2, 134.1, 131.2, 129.0, 128.3, 127.9, 127.2, 126.2, 99.6, 73.6, 65.4, 48.2, 30.0, 19.4, –2.3, –2.5. HRMS (ESI):  $m/z$  for  $\text{C}_{22}\text{H}_{28}\text{O}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$  calcd. 375.1756, found: 375.1736.



**((E)-2-((4S,5R)-2,2-dimethyl-4-(o-tolyl)-1,3-dioxan-5-yl)vinyl)dimethyl(phenyl)silane (SI-2)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give compound **SI-2** as colorless oil in 95% yield (17 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 6.7$  Hz, 1H), 7.30 (t,  $J = 7.2$  Hz, 1H), 7.25 (app. d,  $J = 8.5$  Hz, 2H), 7.19 (d,  $J = 6.7$  Hz, 2H), 7.15 (app. dd,  $J = 11.7, 6.6$  Hz, 2H), 7.10 (d,  $J = 6.4$  Hz, 1H), 6.37 (dd,  $J = 18.7, 8.8$  Hz, 1H), 5.39 (d,  $J = 18.7$  Hz, 1H), 5.34 (d,  $J = 2.0$  Hz, 1H), 4.33 (dd,  $J = 11.5, 2.6$  Hz, 1H), 3.88 (d,  $J = 11.4$  Hz, 1H), 2.39 (d,  $J = 7.0$  Hz, 1H), 2.29 (s, 3H), 1.60 (s, 3H), 1.54 (s, 3H), 0.20 (s, 3H), 0.14 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 139.2, 138.6, 134.1, 133.4, 130.9, 130.2, 129.0, 127.9, 127.09, 127.06, 126.0, 99.7, 70.8, 65.0, 45.7, 29.8, 19.54, 19.50, -2.3, -2.5. HRMS ( $\text{EI}^+$ ):  $m/z$  for  $\text{C}_{22}\text{H}_{28}\text{O}_2\text{Si}$   $[\text{M}-\text{CH}_3]^+$  calcd. 351.1775, found: 351.1798.

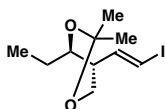


**((E)-2-((4R,5R)-4-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)vinyl)dimethyl(phenyl)silane (11)** Prepared according to the general procedure, the crude mixture was purified by column chromatography to give compound **11** as colorless oil in 82% yield (39 mg).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.53 (m, 2H), 7.35 – 7.37 (m, 3H), 6.56 (dd,  $J = 18.8, 9.2$  Hz, 1H), 5.85 (d,  $J = 18.8$  Hz, 1H), 4.16 (dd,  $J = 11.5, 2.6$  Hz, 1H), 3.85 (dd,  $J = 6.4, 4.4$  Hz, 1H), 3.77 (d,  $J = 10.7$  Hz, 1H), 2.07 (d,  $J = 8.2$  Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.33 – 1.46 (m, 2H), 0.87 (t,  $J = 7.4$  Hz, 3H), 0.351 (s, 3H), 0.348 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 139.5, 134.1, 130.9, 129.2, 128.0, 99.0, 72.9, 65.9, 46.0, 29.9, 26.7, 19.4, 9.7, -2.1, -2.3. HRMS (ESI):  $m/z$  for  $\text{C}_{18}\text{H}_{28}\text{O}_2\text{SiNa}$   $[\text{M}+\text{Na}]^+$  calcd. 327.1756, found: 327.1782.



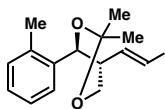
**General procedure for the synthesis of vinyl iodides 12 and 17:** To a solution of vinylsilane (**11** or **SI-2**, 1.0 equiv) in acetonitrile (0.5 mL) was added NIS (2.0 equiv). The reaction mixture was stirred at ambient temperature and the progress was monitored by TLC analysis. After complete consumption of the starting vinylsilane, saturated  $\text{Na}_2\text{S}_2\text{O}_3$  (2 mL) was added and the resulting mixture was stirred vigorously until it became colorless. The reaction mixture was diluted with  $\text{Et}_2\text{O}$  (5 mL). The organic layer

was separated and the aqueous layer was extracted with Et<sub>2</sub>O (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude reaction product was performed by flash chromatography to give vinyl iodide (**12** or **17**).



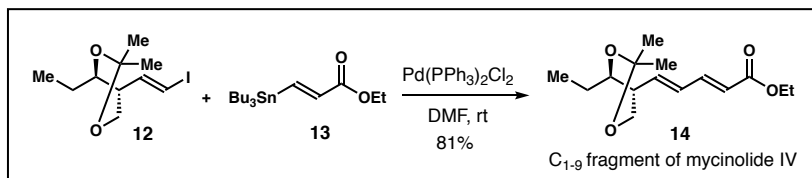
**(4*R*,5*R*)-4-ethyl-5-((*E*)-2-iodovinyl)-2,2-dimethyl-1,3-dioxane (12)**

Prepared according to the general procedure, the crude mixture was purified by column chromatography to give compound **12** as colorless oil in 80% yield (34 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 6.95 (dd, *J* = 14.3, 10.4 Hz, 1H), 6.14 (d, *J* = 14.6 Hz, 1H), 3.99 – 4.19 (m, 1H), 3.79 (s, 1H), 3.73 (d, *J* = 11.6 Hz, 1H), 2.05 (d, *J* = 9.6 Hz, 1H), 1.46 (s, 3H), 1.44 – 1.48 (m, 1H), 1.42 (s, 3H), 1.30 – 1.35 (m, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.0, 99.2, 77.1, 72.5, 65.0, 45.1, 30.0, 26.7, 19.2, 9.7. HRMS (EI<sup>+</sup>): *m/z* for C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>I [M-CH<sub>3</sub>]<sup>+</sup> calcd. 281.0033, found: 281.0035.



**(4*S*,5*R*)-5-((*E*)-2-iodovinyl)-2,2-dimethyl-4-(*o*-tolyl)-1,3-dioxane (17)**

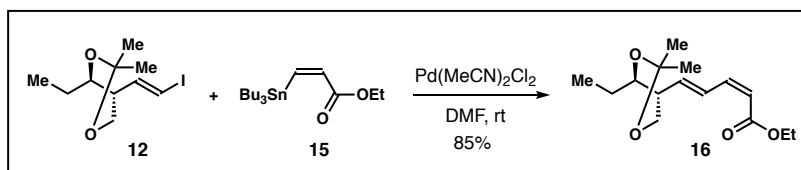
Prepared according to the general procedure, the crude mixture was purified by column chromatography to give compound **17** as colorless oil in 75% yield (27 mg). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.77 (dd, *J* = 14.6, 9.4 Hz, 1H), 5.74 (d, *J* = 14.6 Hz, 1H), 5.29 (s, 1H), 4.30 (d, *J* = 11.7 Hz, 1H), 3.87 (d, *J* = 11.5 Hz, 1H), 2.30 – 2.34 (m, 1H), 2.29 (s, 3H), 1.58 (s, 3H), 1.55 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 143.4, 137.9, 133.3, 130.4, 127.5, 127.1, 126.3, 99.9, 77.8, 70.5, 64.6, 45.1, 30.0, 19.5, 19.2. HRMS (EI<sup>+</sup>): *m/z* for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>I [M-CH<sub>3</sub>]<sup>+</sup> calcd. 343.0189, found: 343.0180.



**Ethyl-(2*E*,4*E*)-5-((4*R*,5*R*)-4-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)penta-2,4-dienoate 14:**

In an Ar-filled glove box, bis(triphenylphosphine)palladium(II) dichloride (3 mg, 5 mol %), vinyl iodide **12** (0.08 mmol, 1.0 equiv) and a Teflon-coated magnetic stirring bar

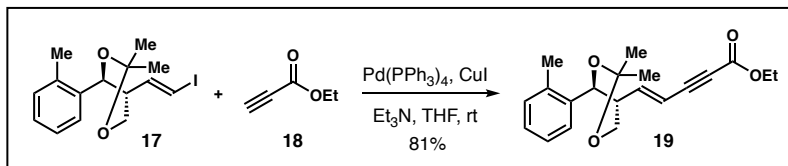
were sequentially added into a reaction tube. The tube was capped with a rubber septum and removed from glove box. *E*-vinylstannane **13** (0.12 mmol, 1.5 equiv) in DMF (0.2 mL) was added to the reaction mixture. The reaction was protected from light and stirred at ambient temperature for 18 h. After complete consumption of vinyl iodide **12**, the reaction mixture was diluted with EtOAc (2 mL) and washed with water (3 x 5 mL). The combined aqueous layers were extracted with EtOAc (5 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification of the crude reaction product was performed by flash chromatography to give diene **14** in 81% yield (17 mg) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.31 (dd, *J* = 15.2, 11.2 Hz, 1H), 6.54 (dd, *J* = 15.4, 9.9 Hz, 1H), 6.25 (dd, *J* = 15.3, 11.1 Hz, 1H), 5.81 (d, *J* = 15.5 Hz, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 4.17 – 4.19 (m, 1H), 3.87 (t, *J* = 5.7 Hz, 1H), 3.72 (d, *J* = 11.5 Hz, 1H), 2.11 (d, *J* = 9.6 Hz, 1H), 1.48 (s, 3H), 1.43 (s, 3H), 1.40 – 1.44 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.28 – 1.33 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 167.5, 145.1, 141.6, 130.4, 120.5, 99.2, 73.1, 65.6, 60.6, 42.0, 30.0, 26.9, 19.3, 14.6, 9.7. HRMS (ESI): *m/z* for C<sub>15</sub>H<sub>24</sub>O<sub>4</sub>Na [M+Na]<sup>+</sup> calcd. 291.1572, found: 291.1573.



**Ethyl(2*Z*,4*E*)-5-((4*R*,5*R*)-4-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)penta-2,4-dienoate (16)**

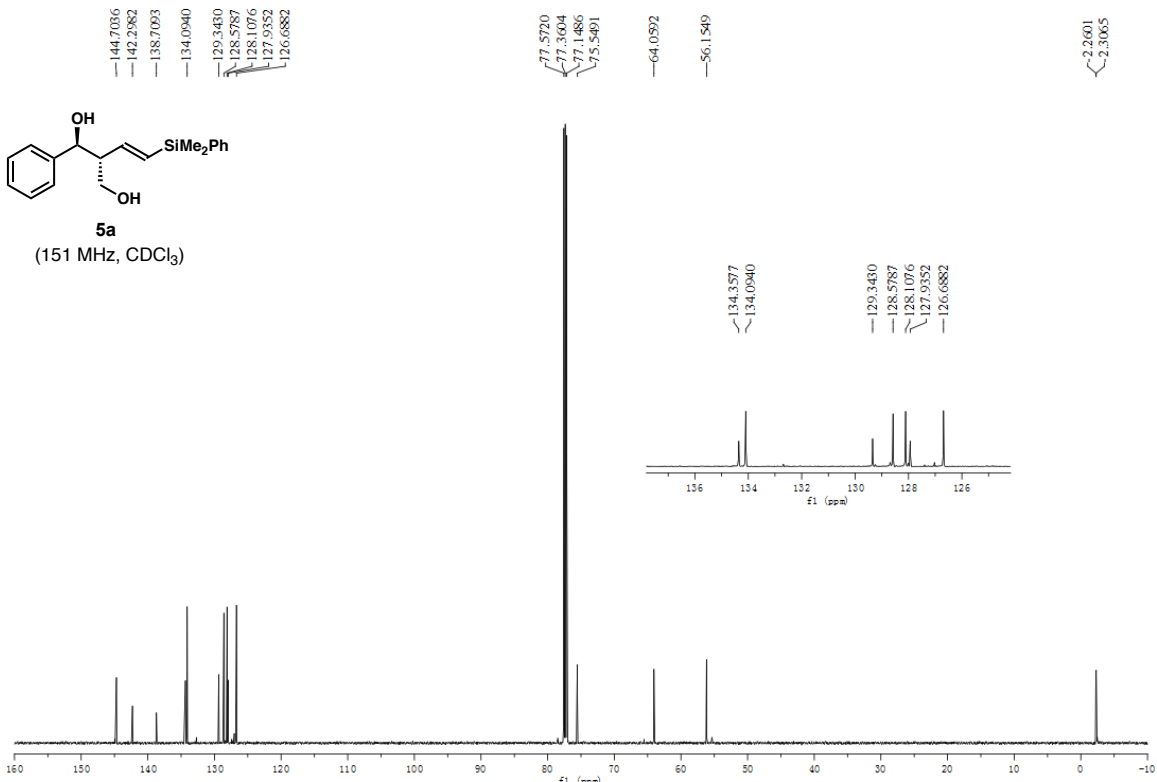
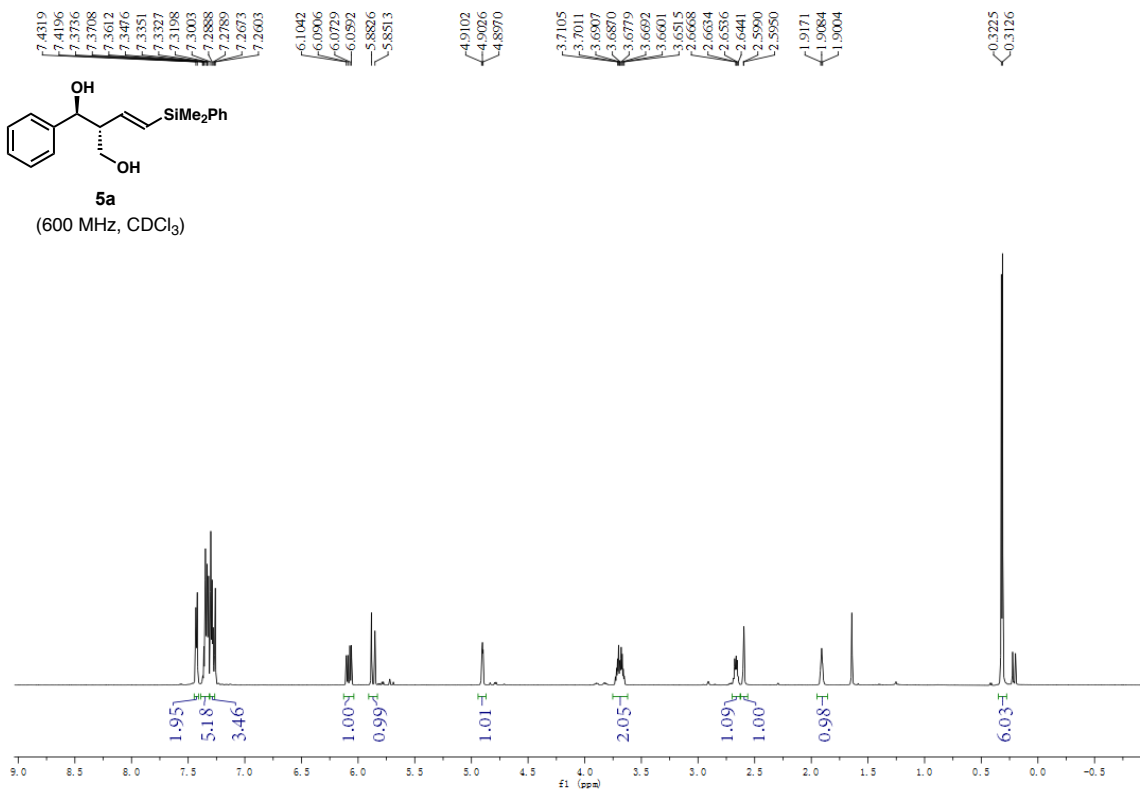
In an Ar-filled glove box, bis(acetonitrile)dichloropalladium(II) (1 mg, 5 mol %), vinyl iodide **12** (0.08 mmol, 1.0 equiv) and a Teflon-coated magnetic stirring bar were sequentially added into a reaction tube. The tube was capped with a rubber septum and removed from glove box. *Z*-vinylstannane **15** (0.12 mmol, 1.5 equiv) in DMF (0.2 mL) was added to the reaction mixture. The reaction was protected from light and stirred at ambient temperature for 18 h. After complete consumption of vinyl iodide **12**, the reaction mixture was diluted with EtOAc (2 mL) and washed with water (3 x 5 mL). The combined aqueous layers were extracted with EtOAc (5 mL). The combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Purification of the crude reaction product was performed by flash chromatography to give diene **16** in 85% yield (18 mg) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.44 (dd, *J* = 15.3, 11.6 Hz, 1H), 6.62 (app. t, *J* = 11.3 Hz, 1H), 6.50 (dd,

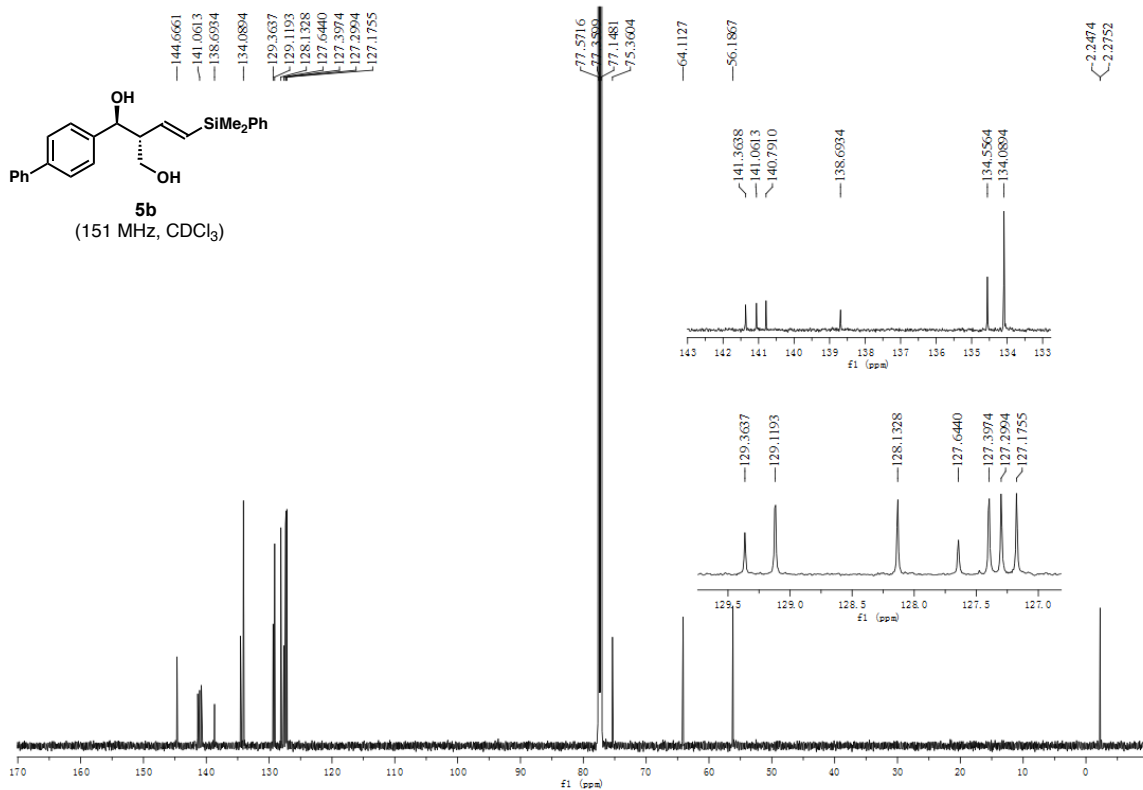
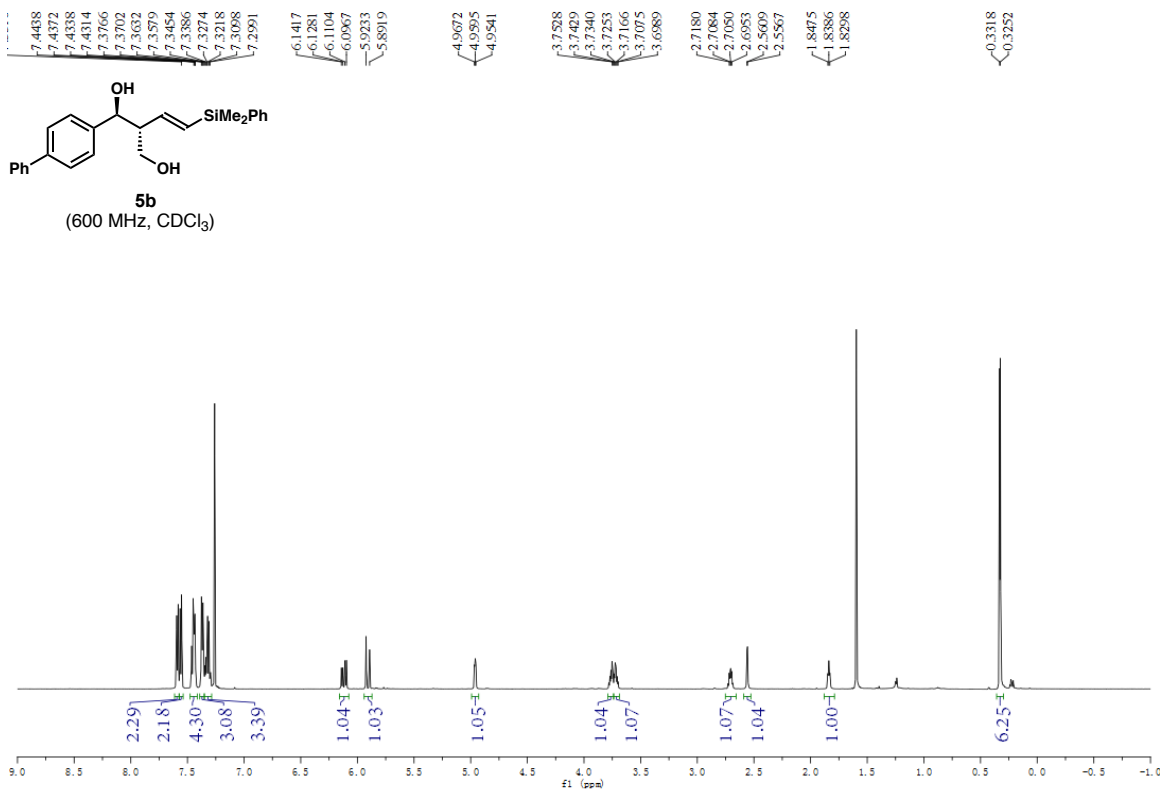
$J = 15.5, 10.1$  Hz, 1H), 5.62 (d,  $J = 11.3$  Hz, 1H), 4.10 – 4.23 (m, 3H), 3.88 (t,  $J = 5.8$  Hz, 1H), 3.73 (d,  $J = 11.4$  Hz, 1H), 2.18 (d,  $J = 9.7$  Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H), 1.39 – 1.46 (m, 1H), 1.29 (t,  $J = 7.1$  Hz, 3H), 1.30 – 1.36 (m, 1H), 0.86 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 145.5, 142.5, 128.8, 116.6, 99.2, 73.2, 65.9, 60.3, 42.2, 30.0, 27.0, 19.3, 14.6, 9.7. HRMS (ESI):  $m/z$  for  $\text{C}_{15}\text{H}_{24}\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$  calcd. 291.1572, found: 291.1568.

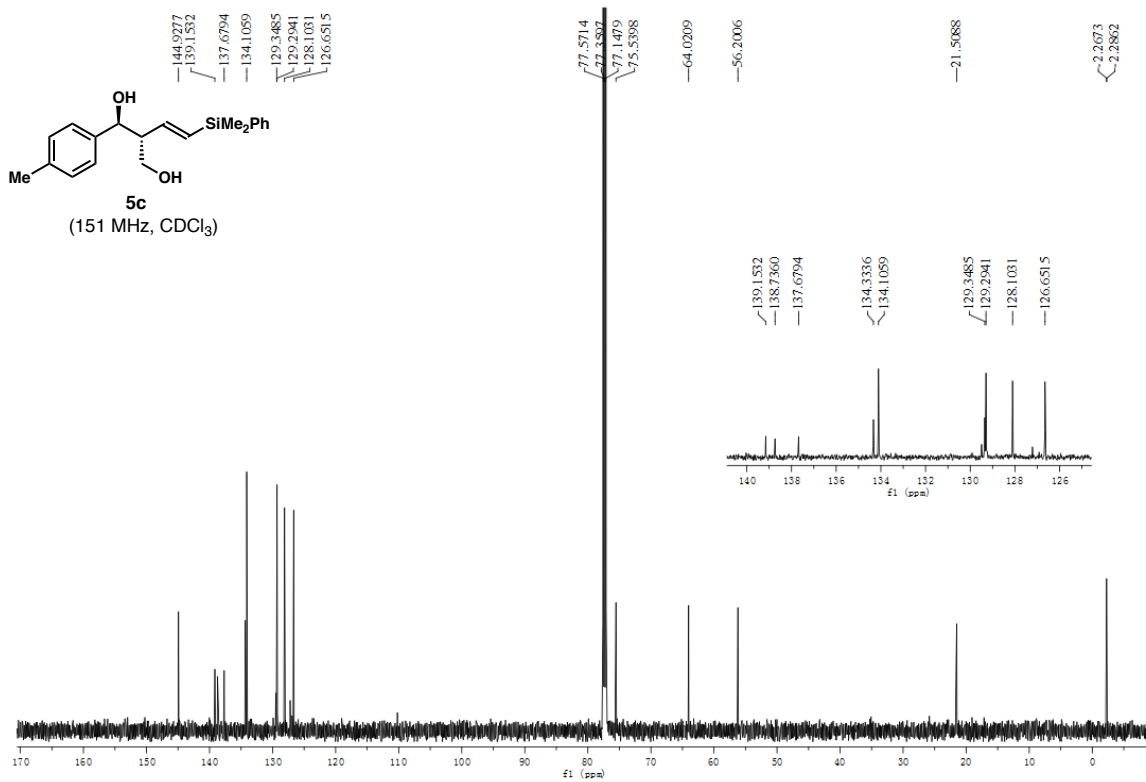
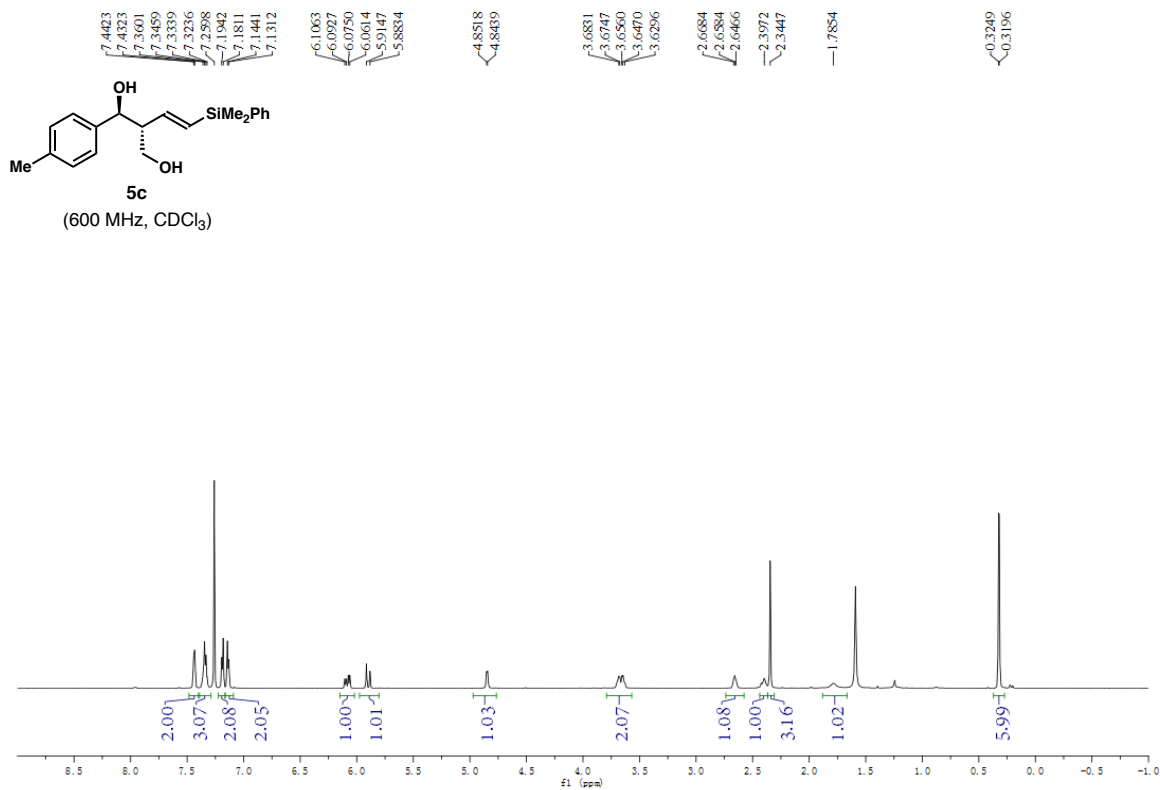


**Ethyl (*E*)-5-((4*S*,5*R*)-2,2-dimethyl-4-(*o*-tolyl)-1,3-dioxan-5-yl)pent-4-en-2-ynoate (**19**):**

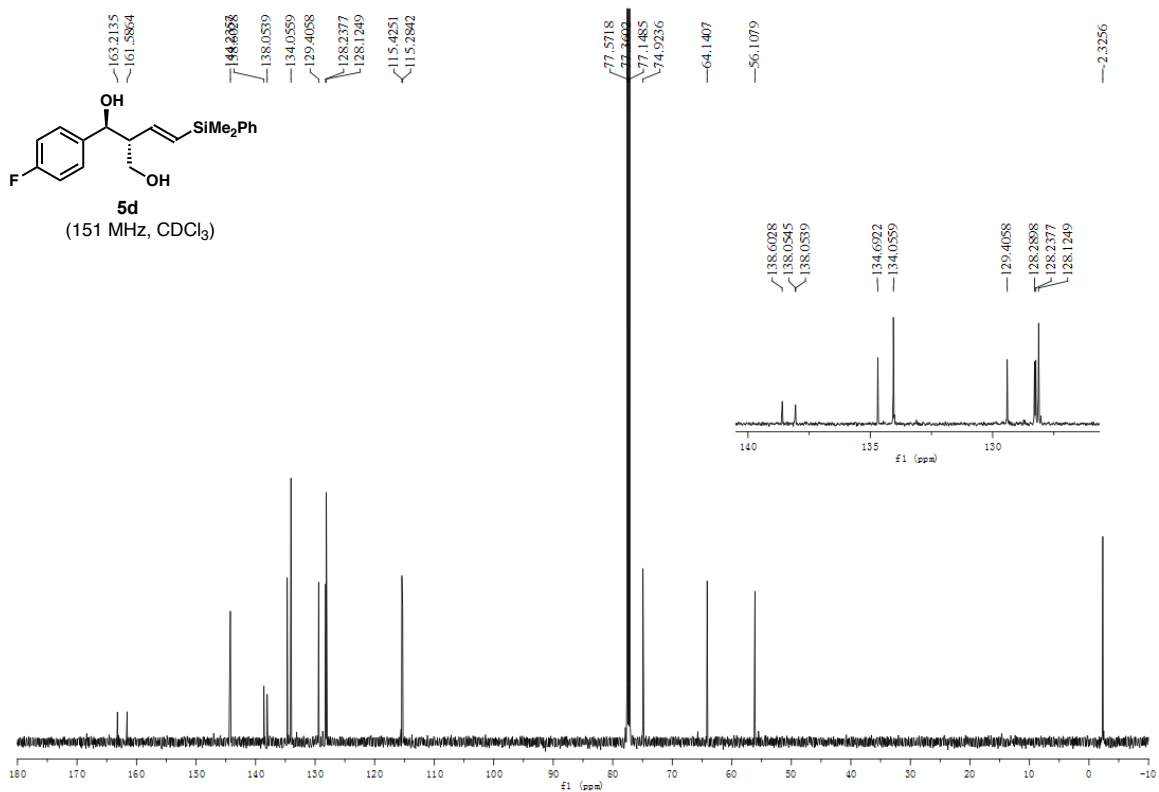
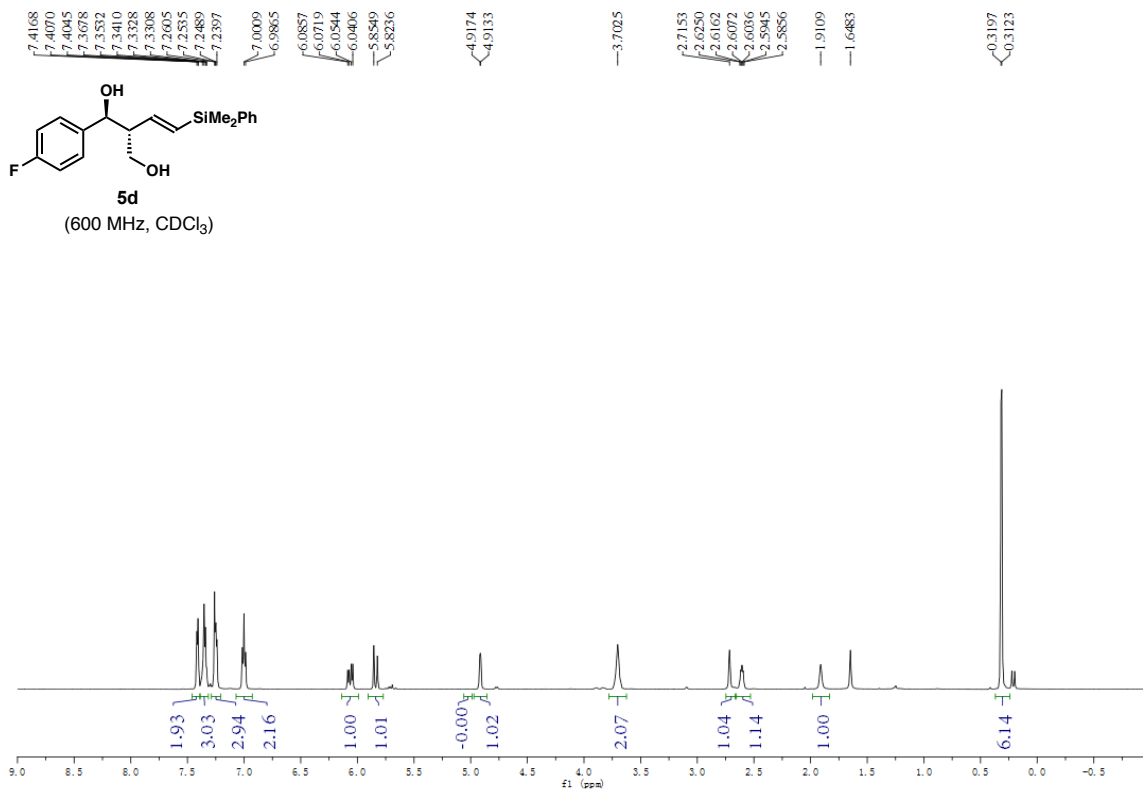
In an Ar-filled glove box, tetrakis(triphenylphosphane)palladium (9.3 mg, 0.008 mmol, 10 mol%), CuI (3.0 mg, 0.015 mmol, 20 mol%) and a Teflon-coated magnetic stirring bar were sequentially added into a reaction tube. The tube was capped with a rubber septum and removed from glove box. A solution of vinyl iodide **17** (27 mg, 0.075 mmol, 1.0 equiv) in  $\text{NEt}_3$  (0.1 mL) was added and the mixture was stirred for 30 min. Then a solution of ethyl propiolate **18** (15 mg, 0.15 mmol, 2 equiv) in THF (0.1 mL) was added and the resulting reaction mixture was stirred at ambient temperature. After complete consumption of vinyl iodide **17**, the reaction mixture was filtered through a short pad of silica gel and the solution was concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography to afford compound **19** (20 mg, 81%) as a colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 7.6$  Hz, 1H), 7.21 (t,  $J = 7.4$  Hz, 1H), 7.15 (t,  $J = 7.0$  Hz, 1H), 7.10 (d,  $J = 7.3$  Hz, 1H), 6.75 (dd,  $J = 16.2, 9.2$  Hz, 1H), 5.28 – 5.36 (m, 2H), 4.38 (dd,  $J = 11.4, 1.6$  Hz, 1H), 4.21 (q,  $J = 7.1$  Hz, 2H), 3.84 (d,  $J = 11.3$  Hz, 1H), 2.41 (d,  $J = 8.8$  Hz, 1H), 2.29 (s, 3H), 1.59 (s, 3H), 1.55 (s, 3H), 1.30 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  154.4, 149.4, 137.6, 133.2, 130.4, 127.6, 126.8, 126.4, 109.6, 100.0, 85.3, 80.1, 70.6, 64.8, 62.3, 42.4, 29.9, 19.5, 19.2, 14.4. HRMS ( $\text{EI}^+$ ):  $m/z$  for  $\text{C}_{19}\text{H}_{21}\text{O}_4$   $[\text{M}-\text{CH}_3]^+$  calcd. 313.1434, found: 313.1455.

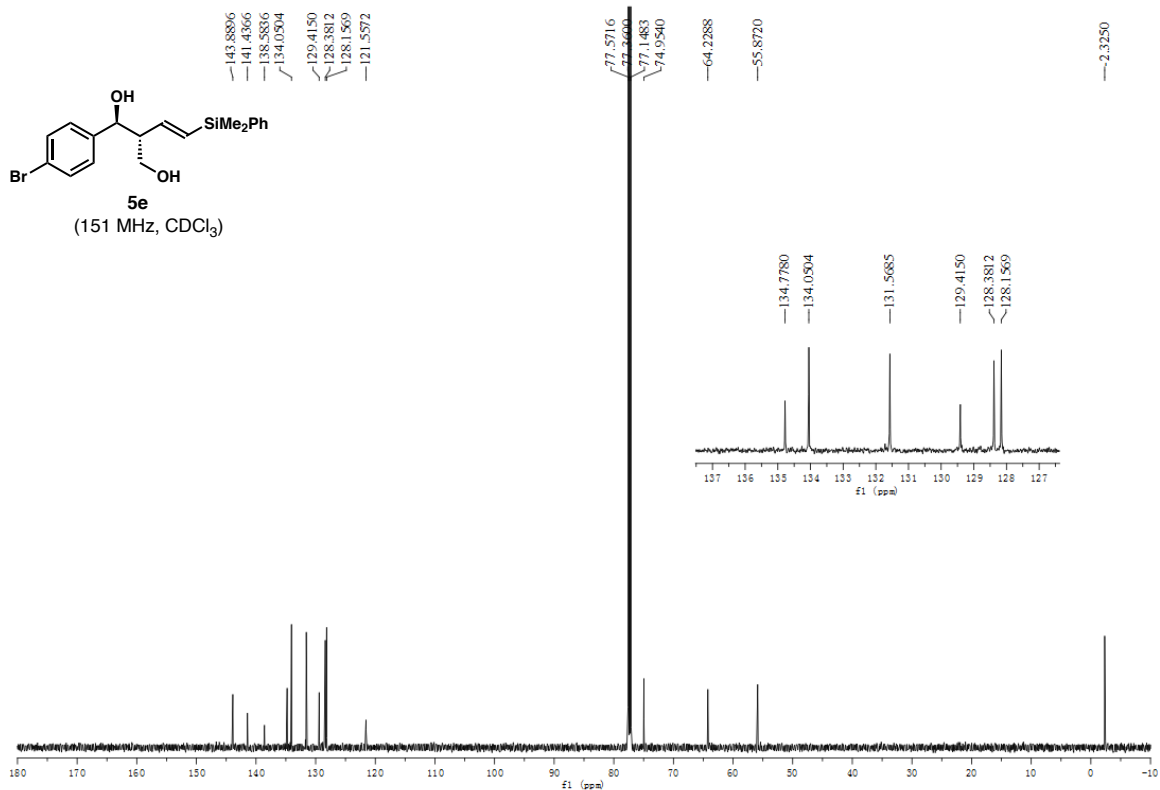
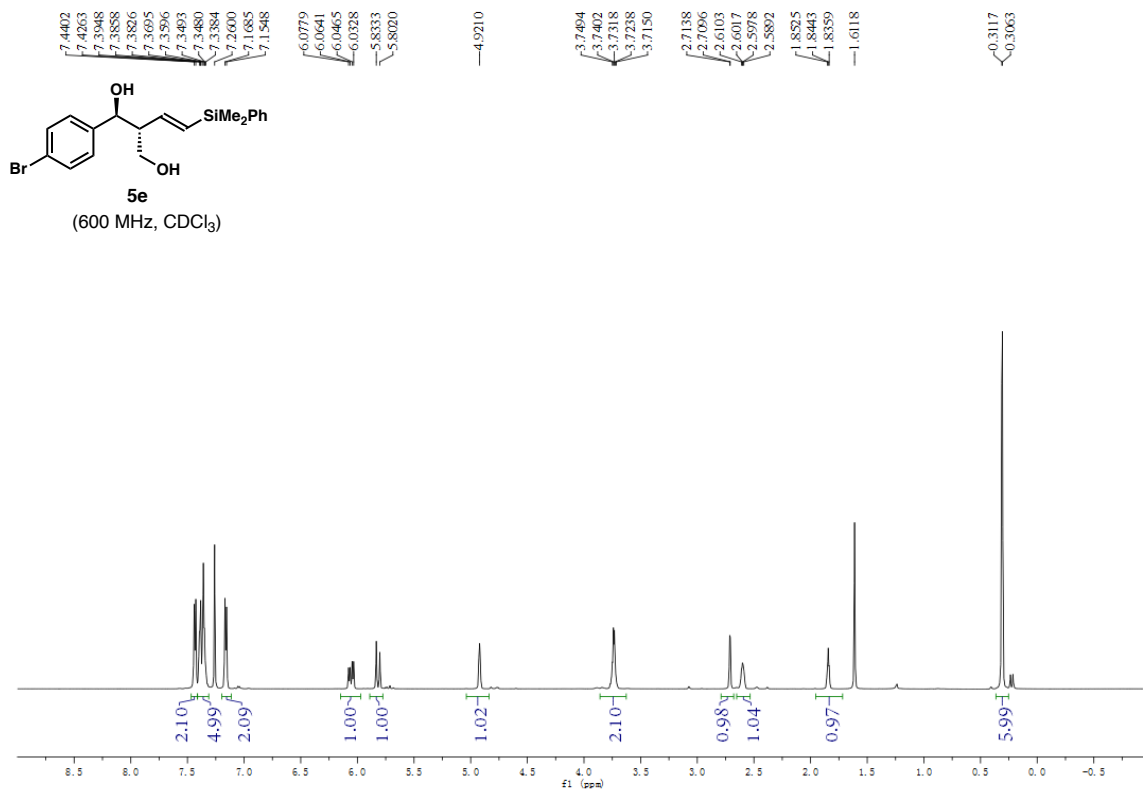


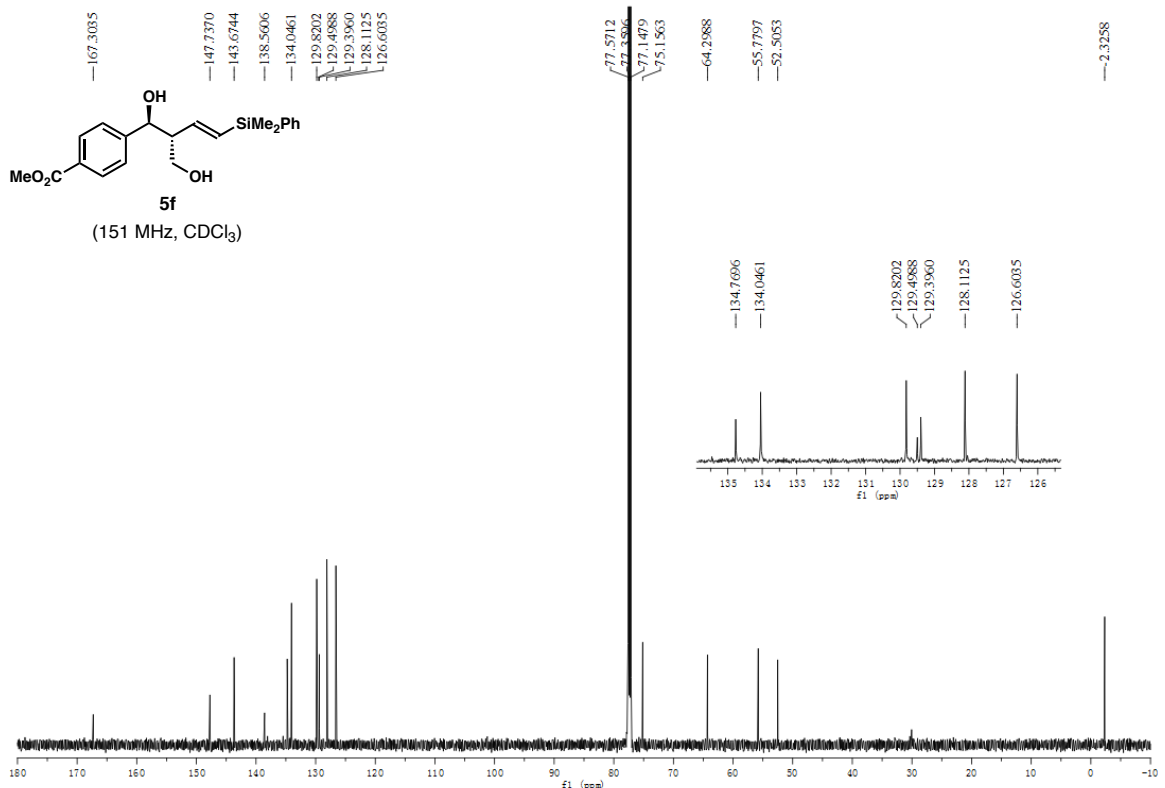
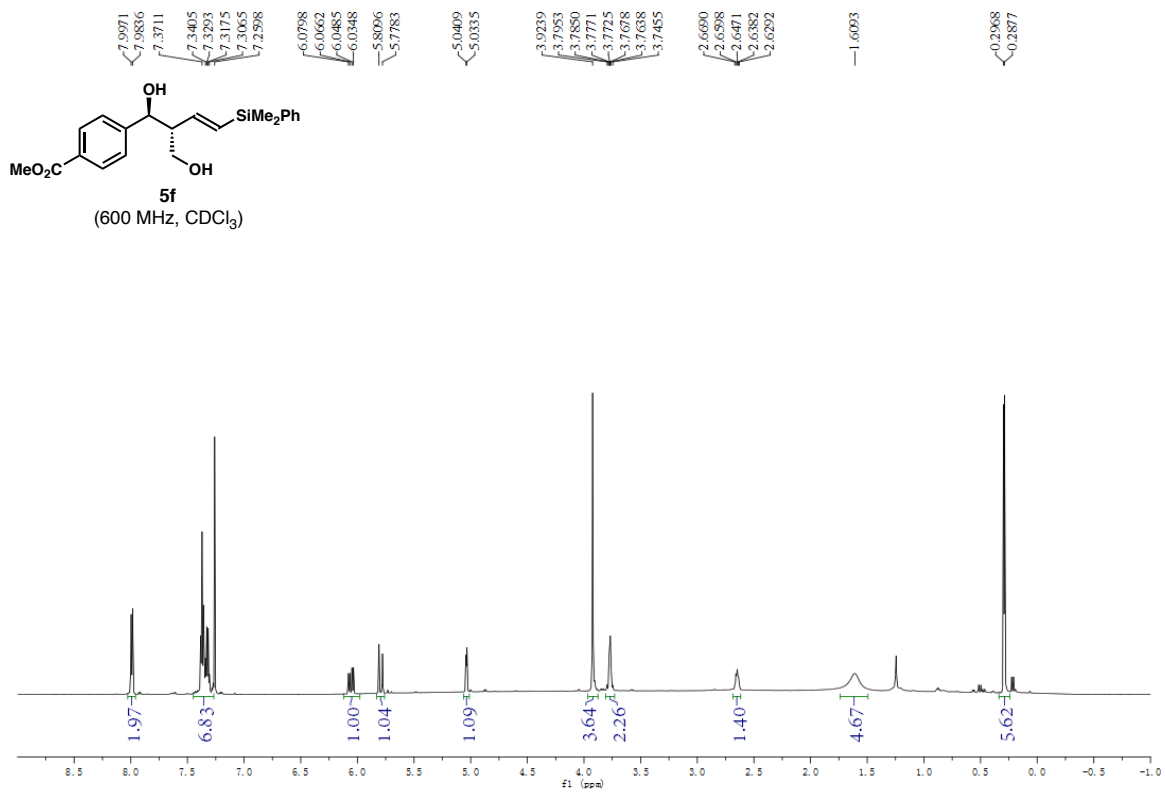


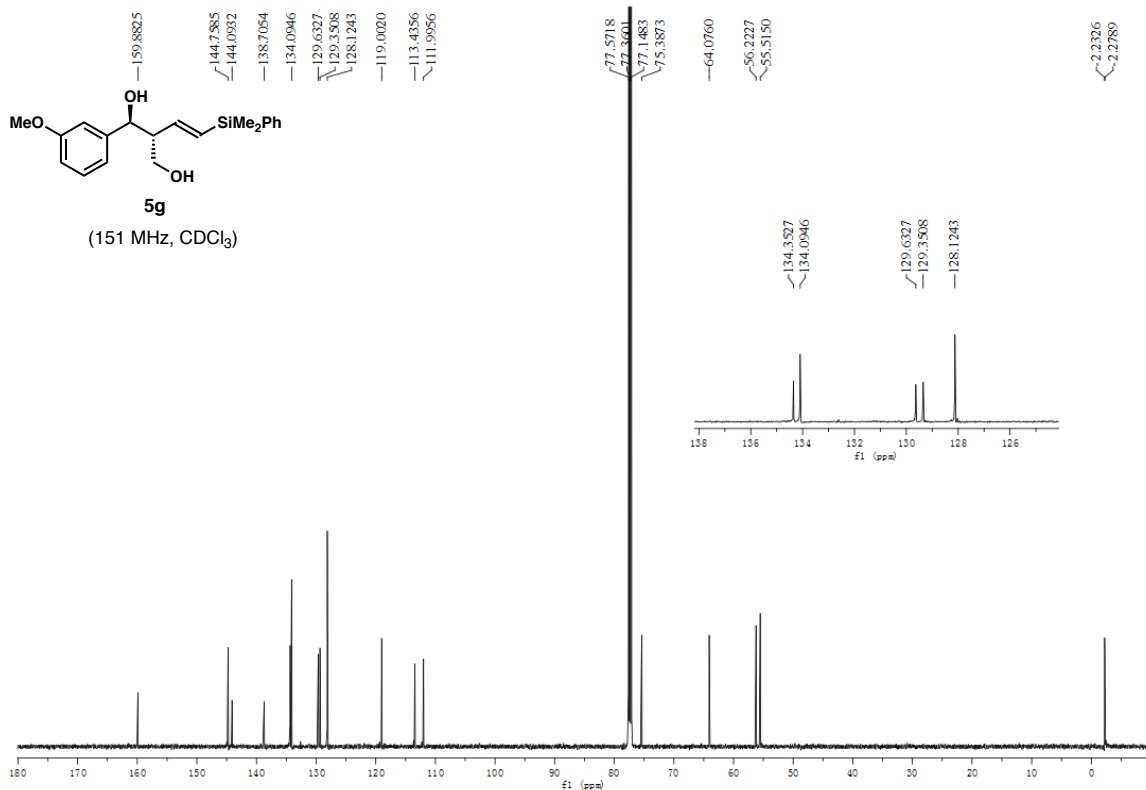
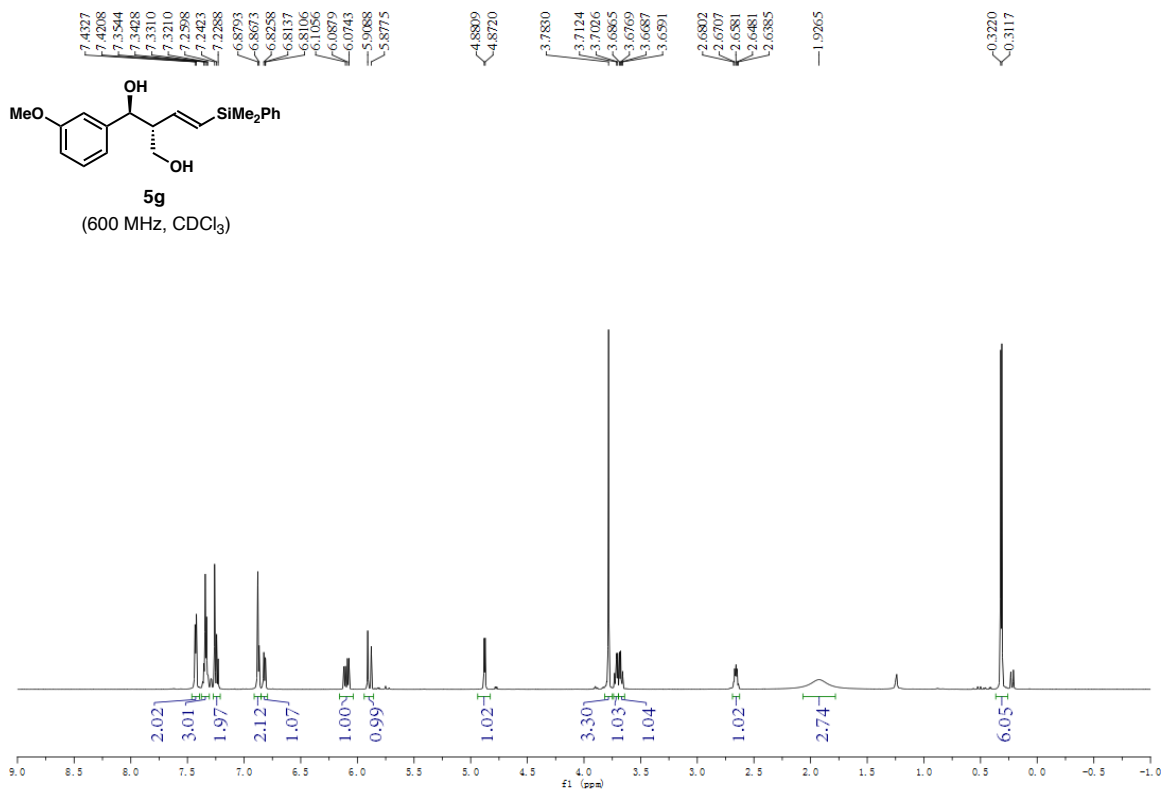


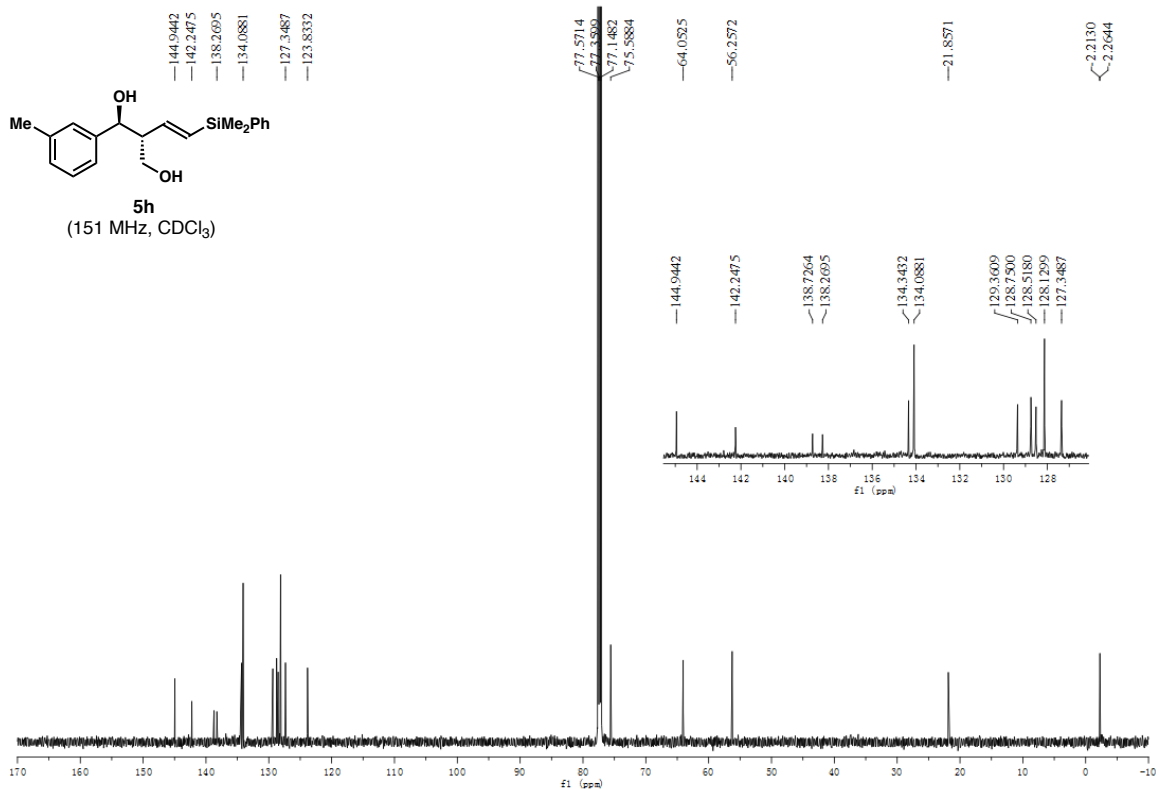
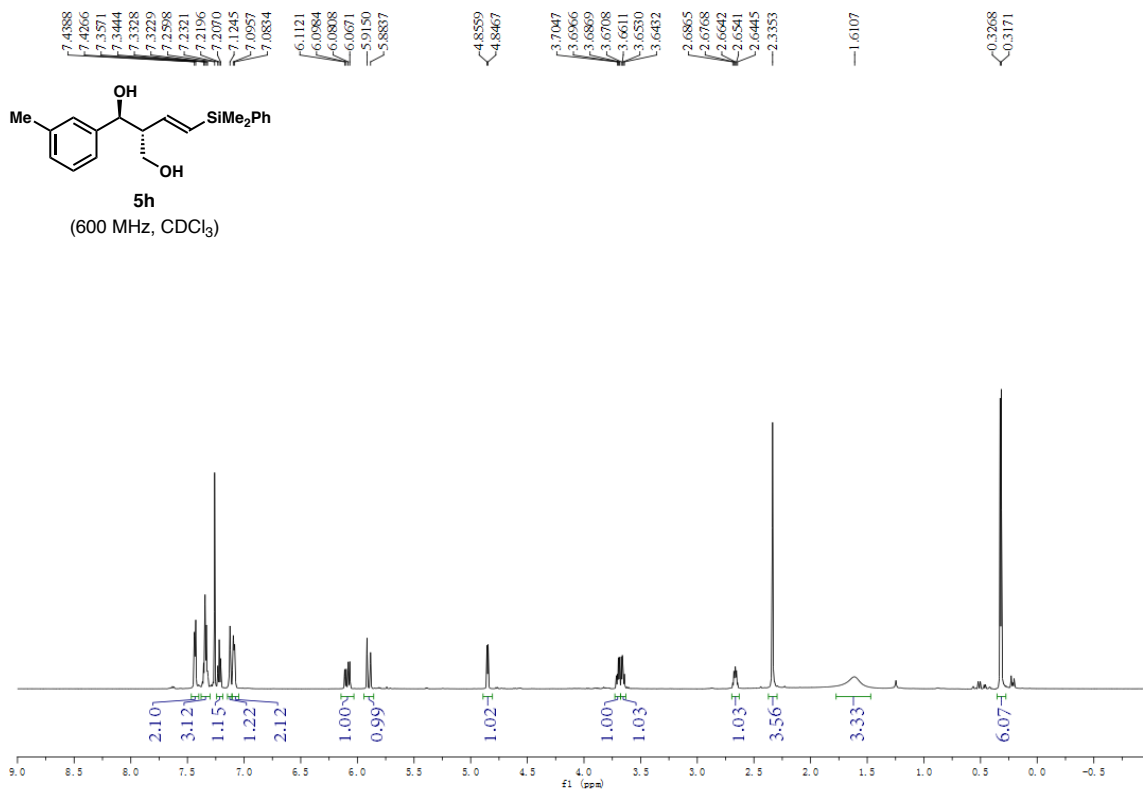


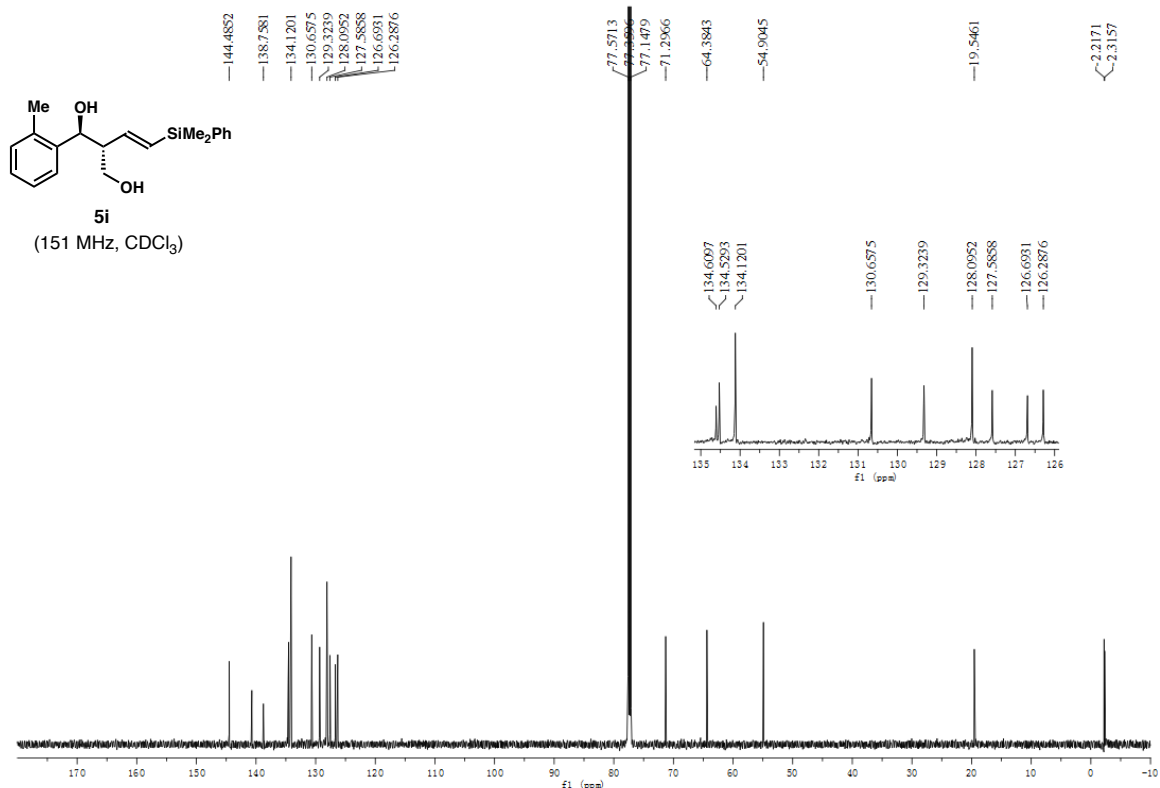
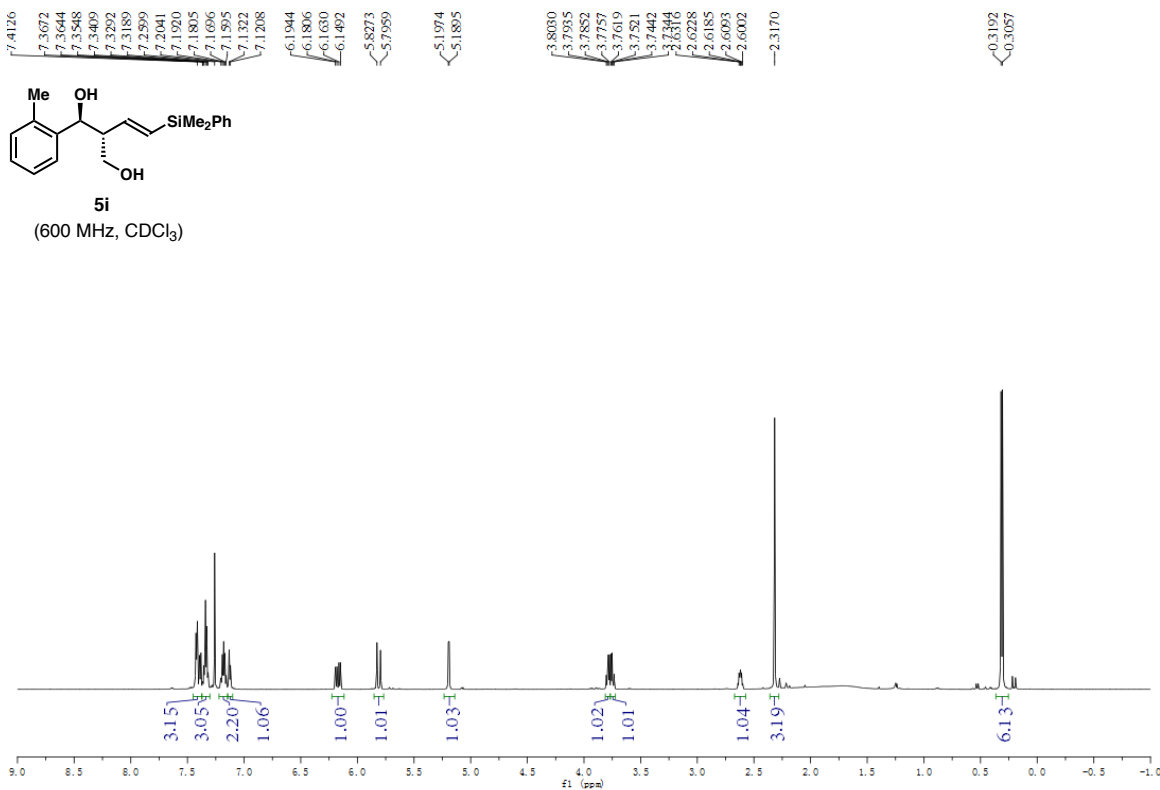


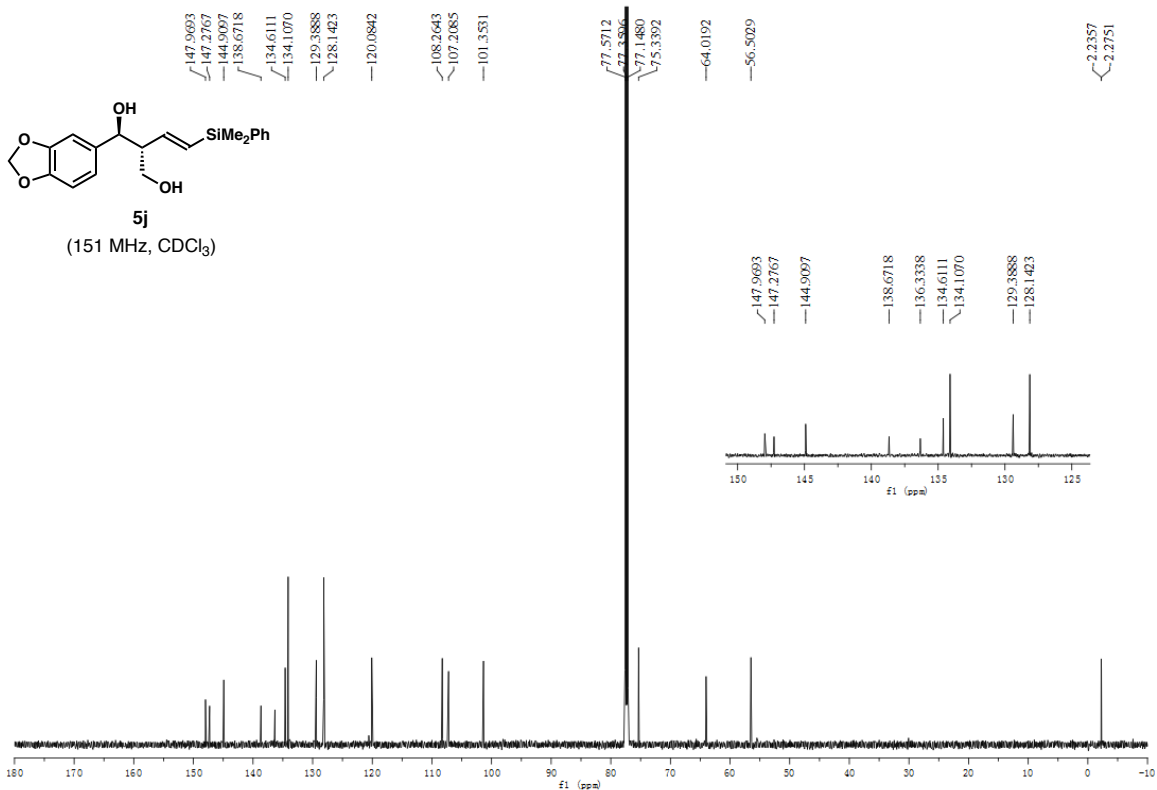
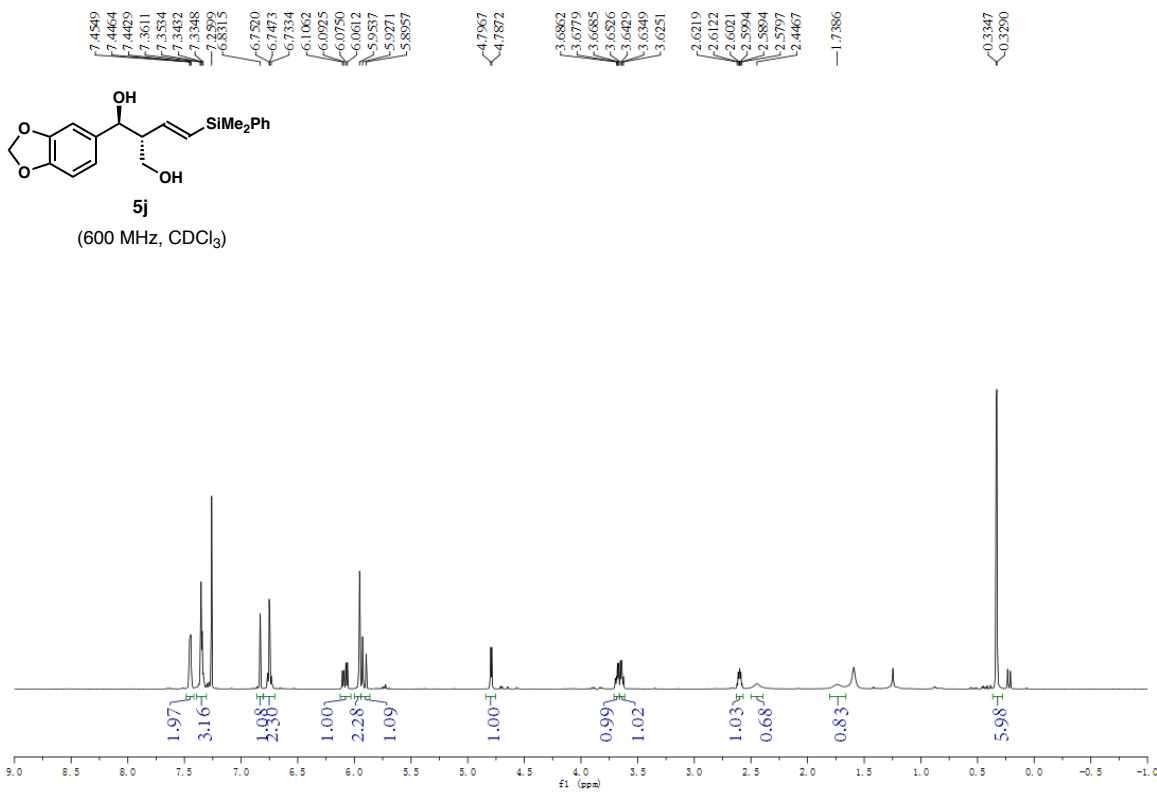


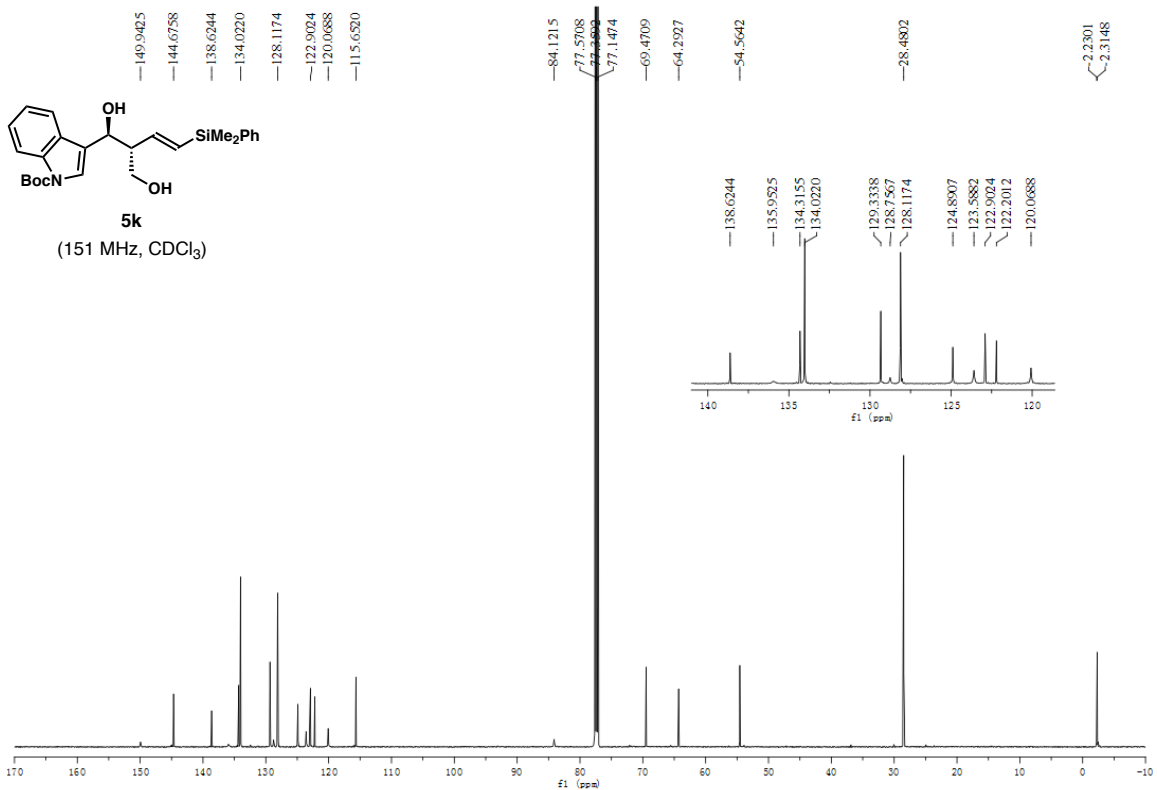
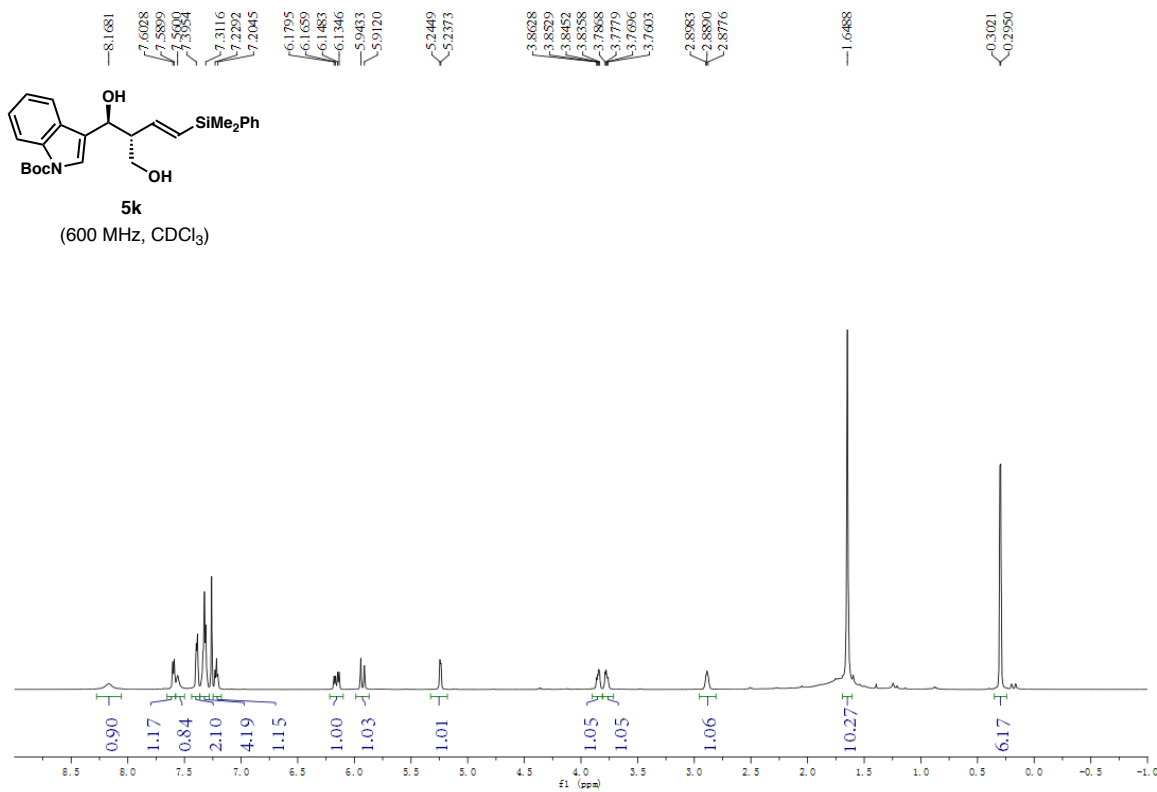




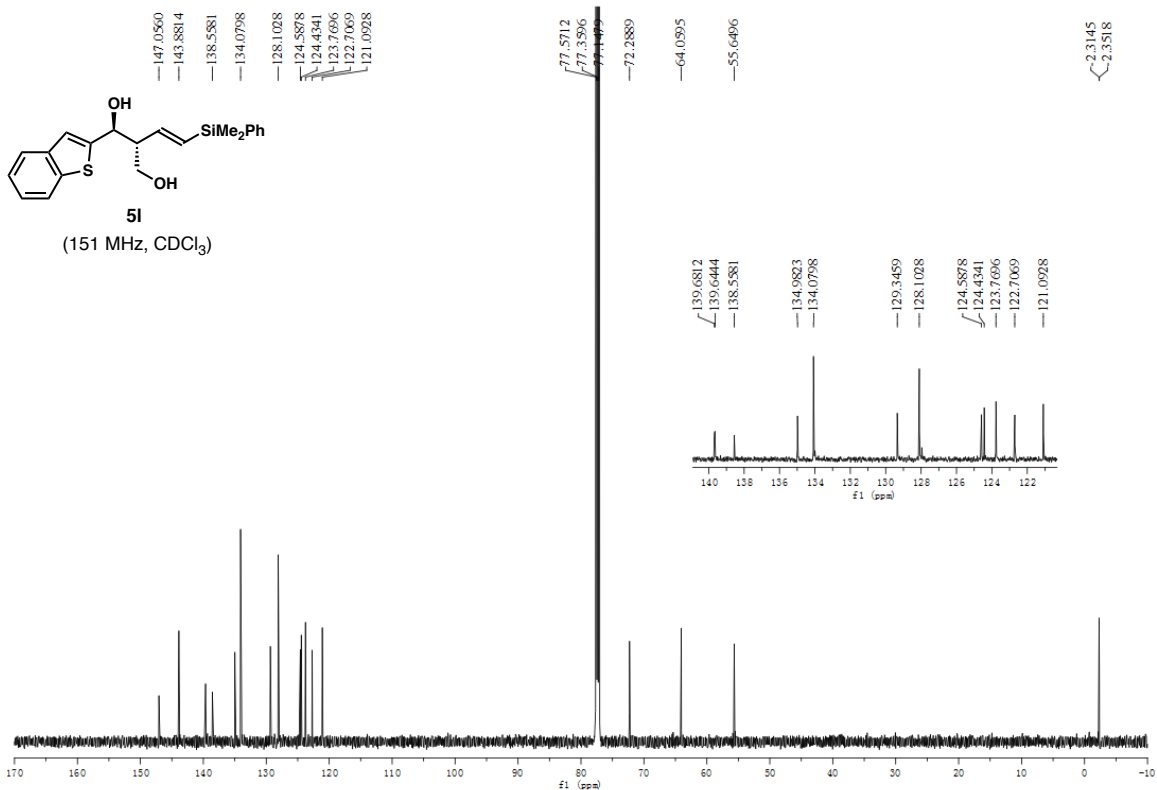
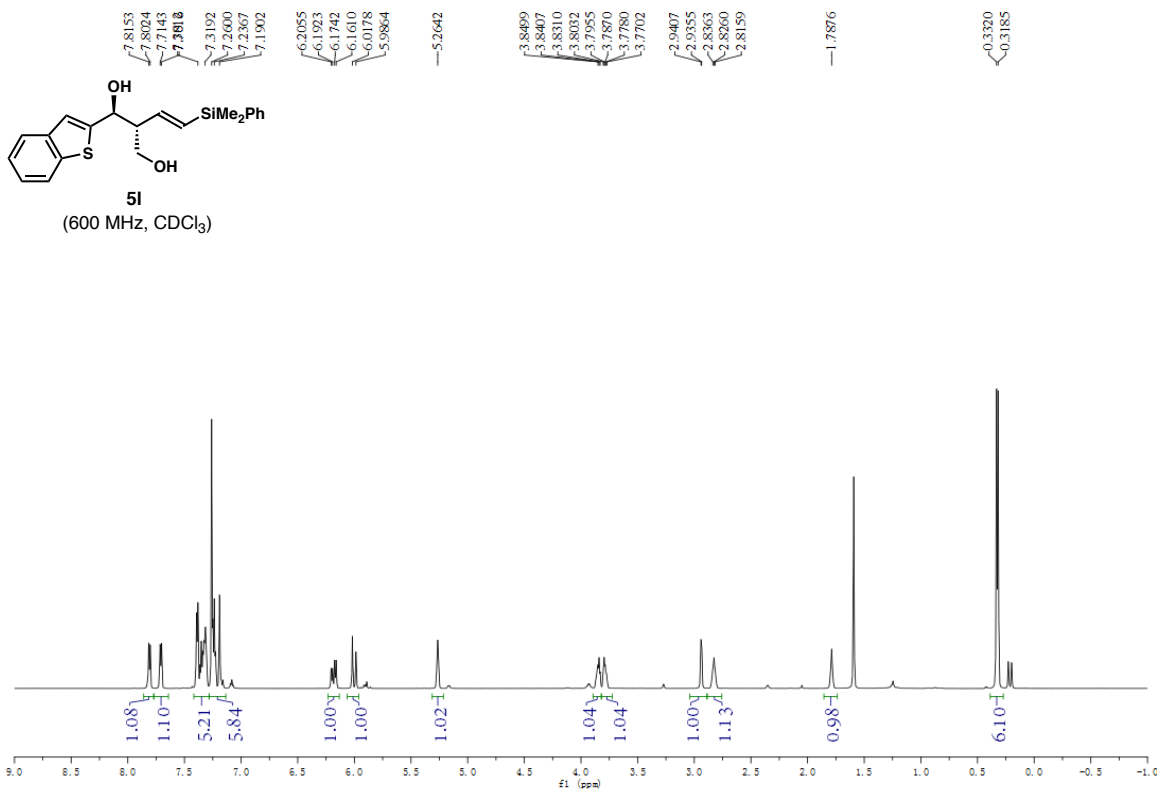


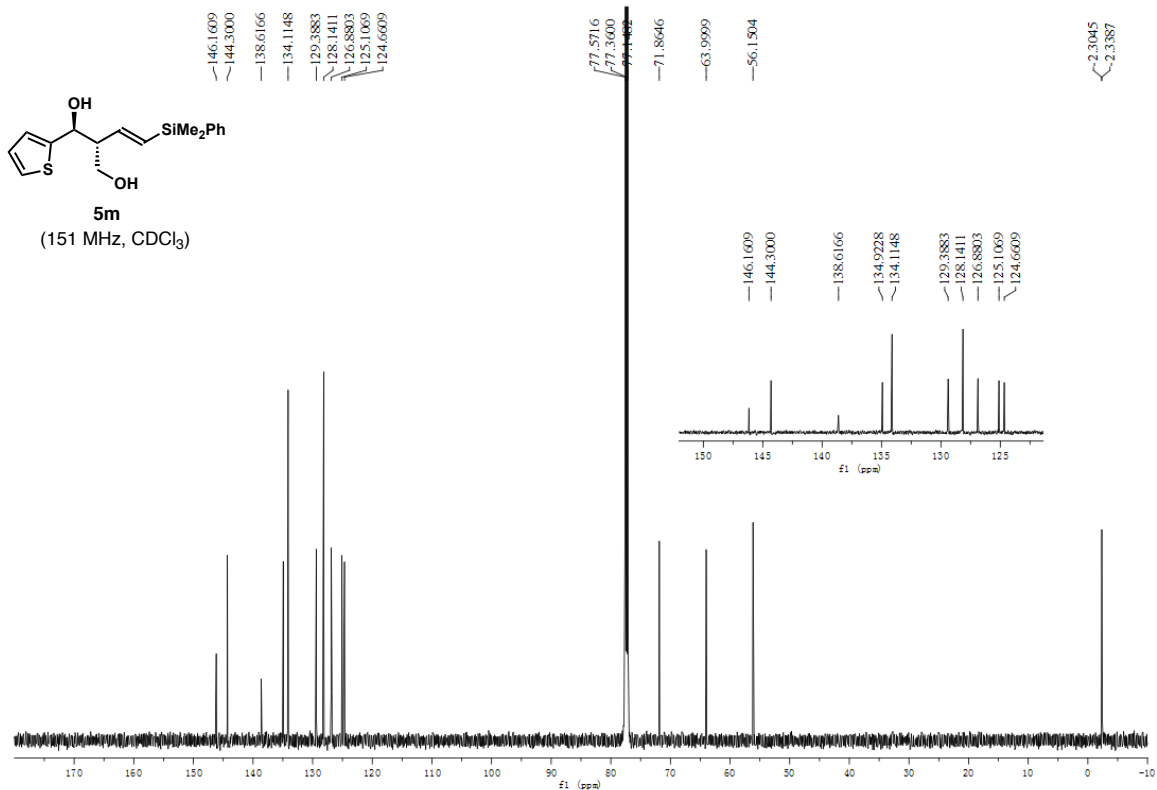
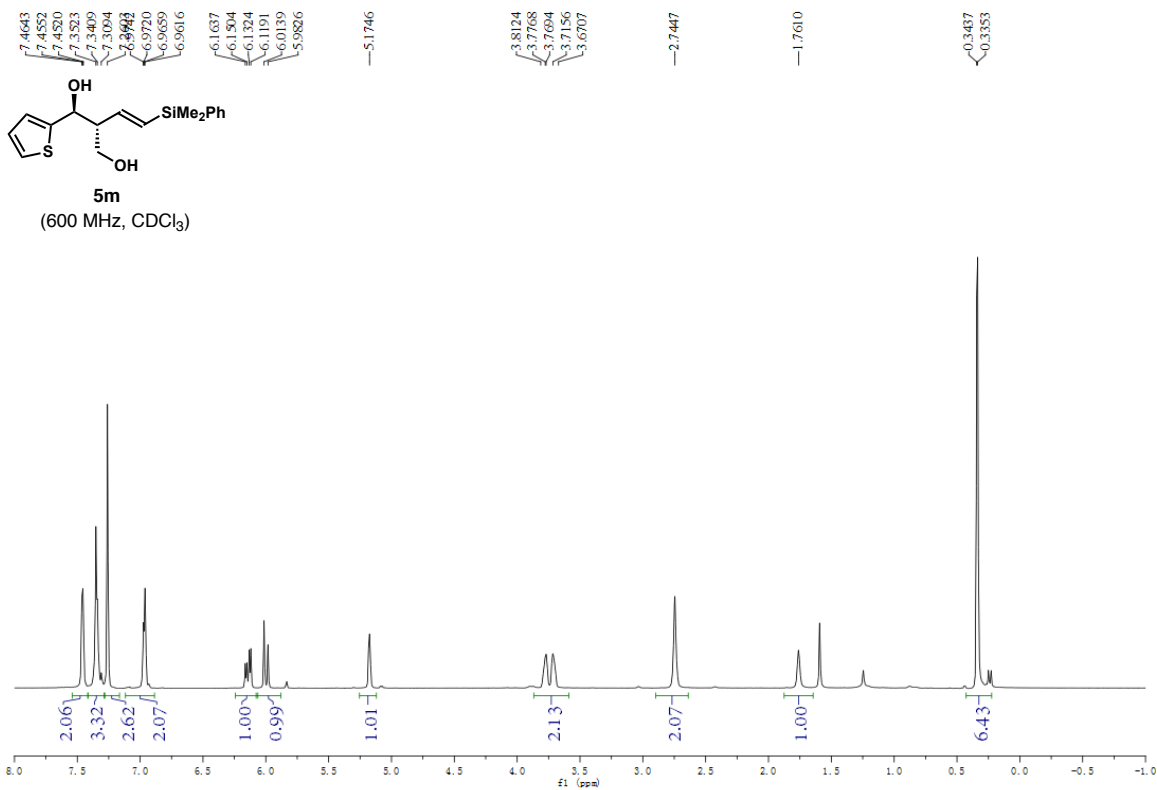


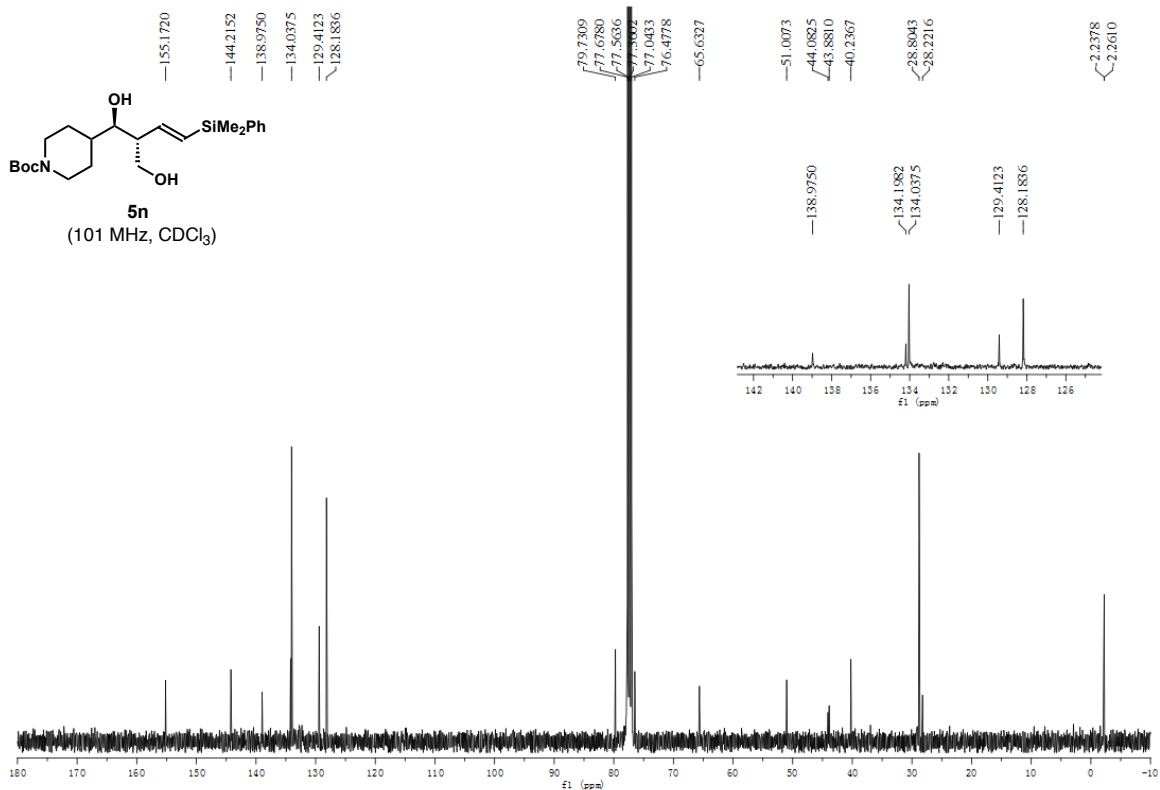
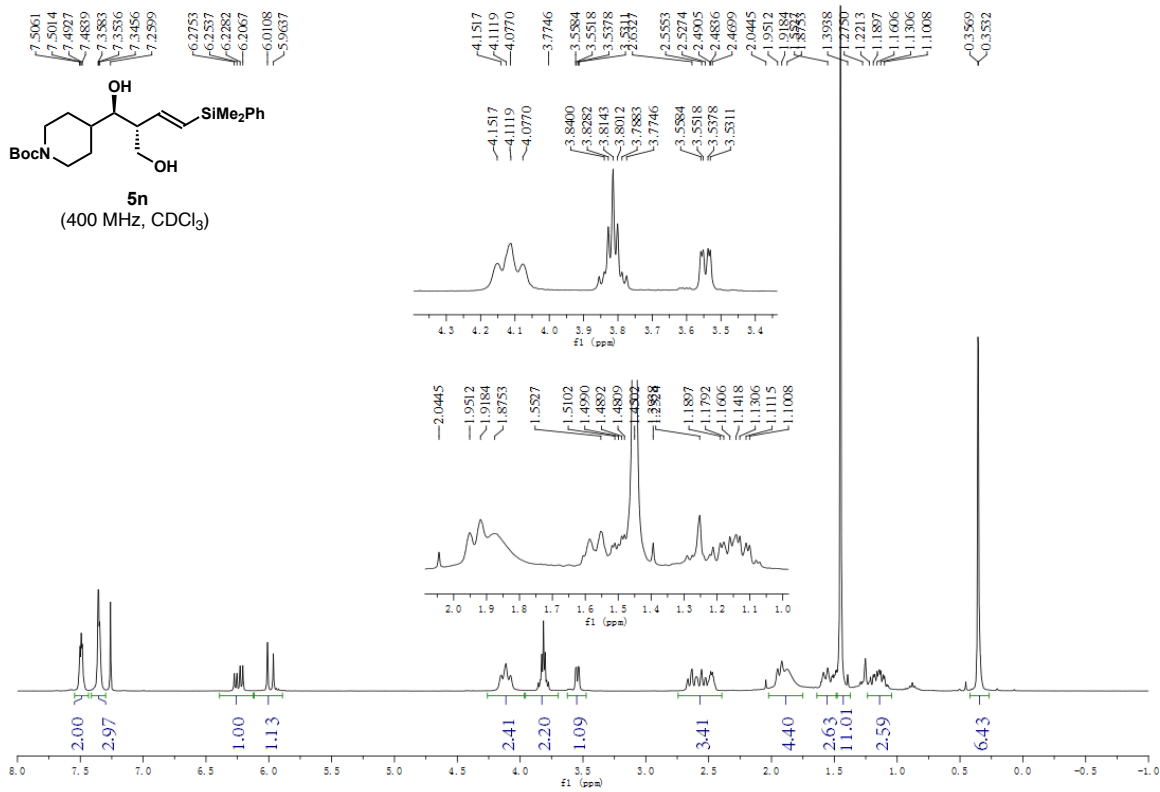


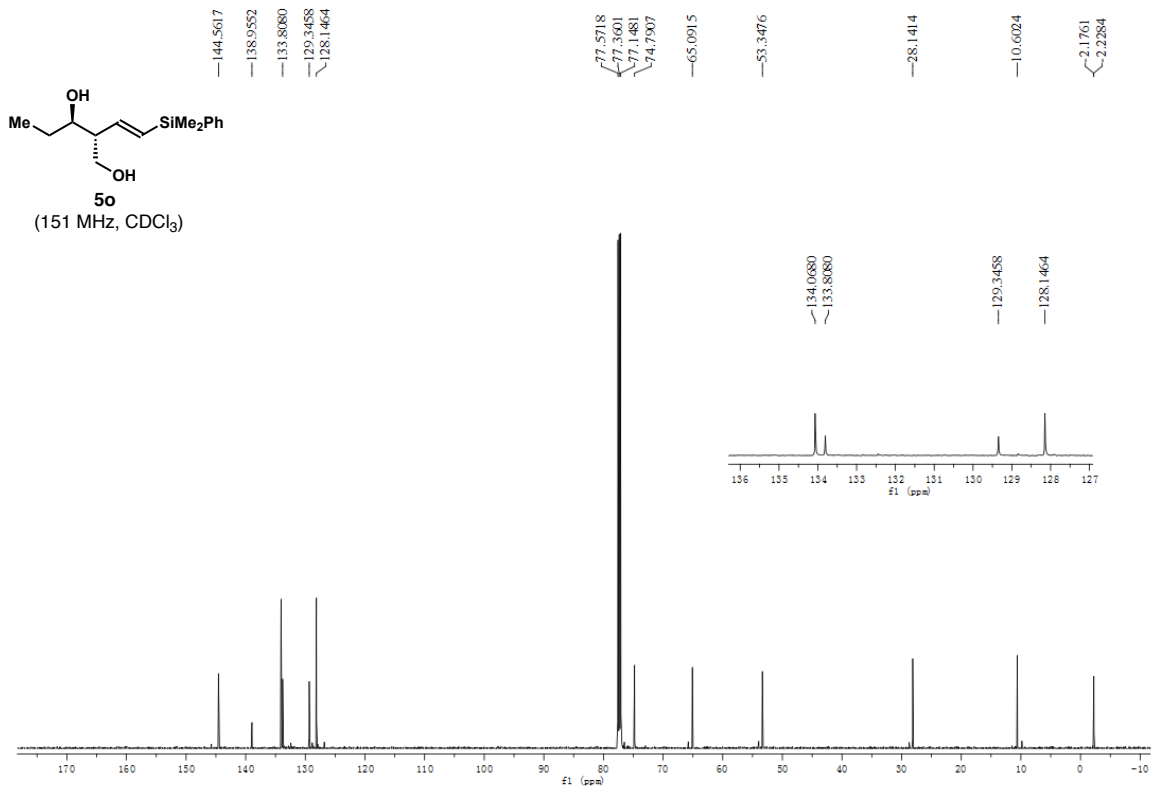
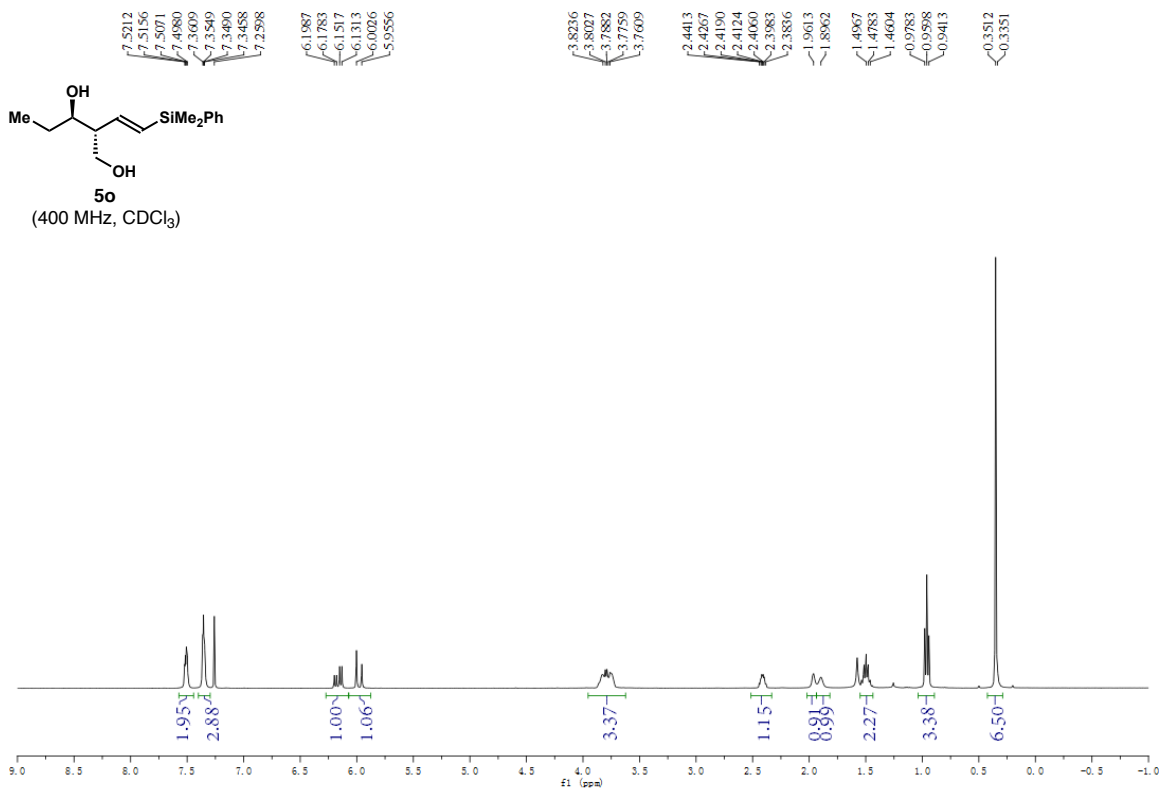


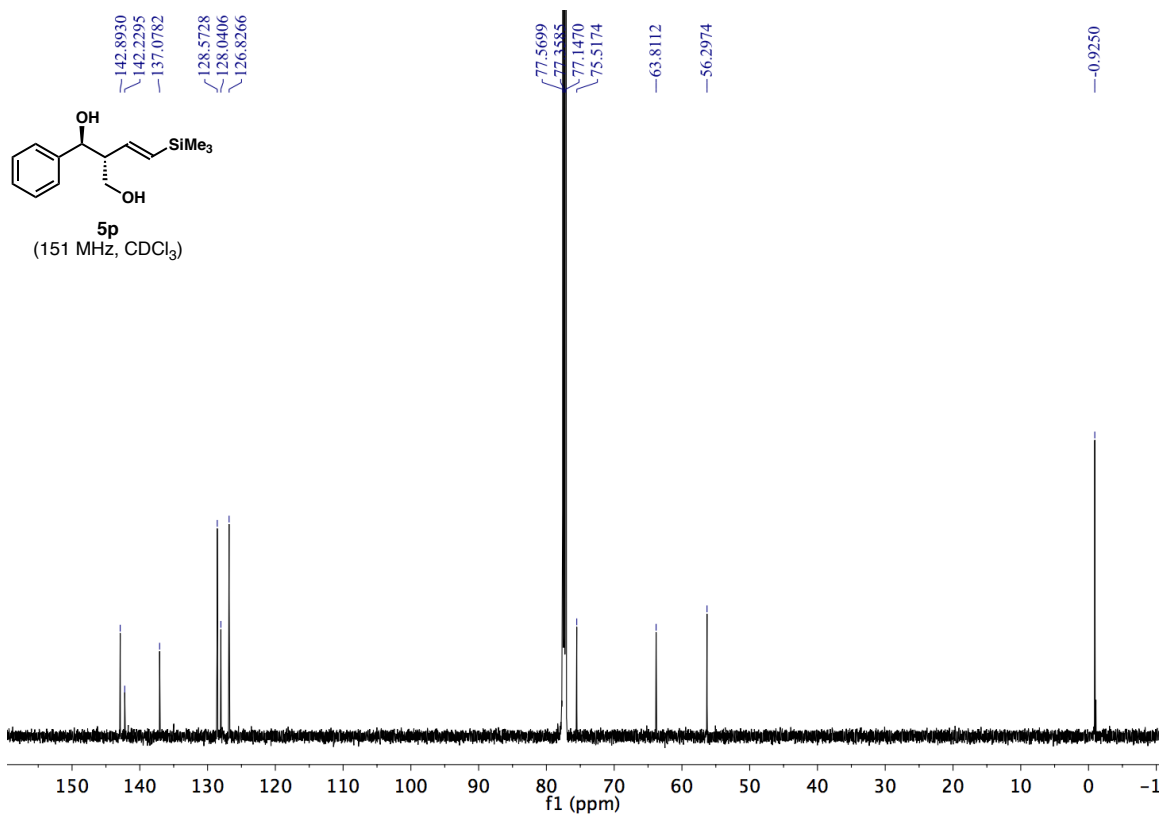
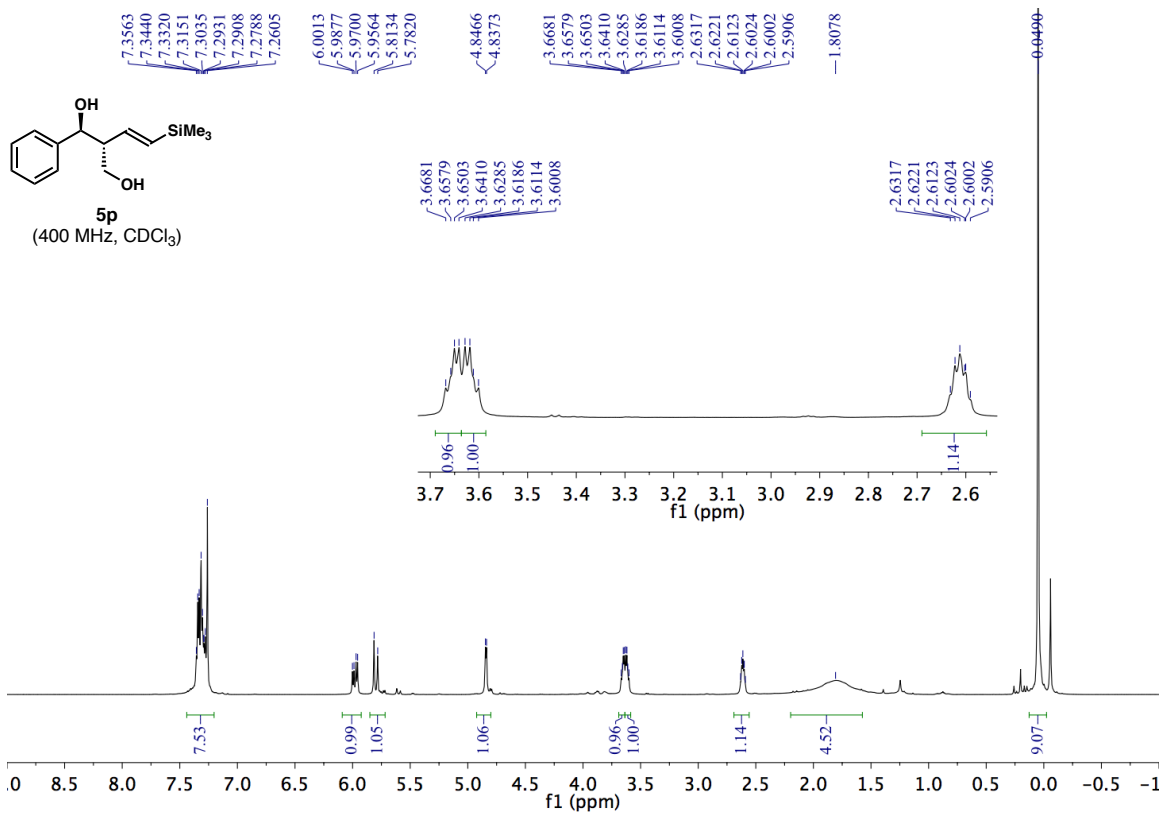


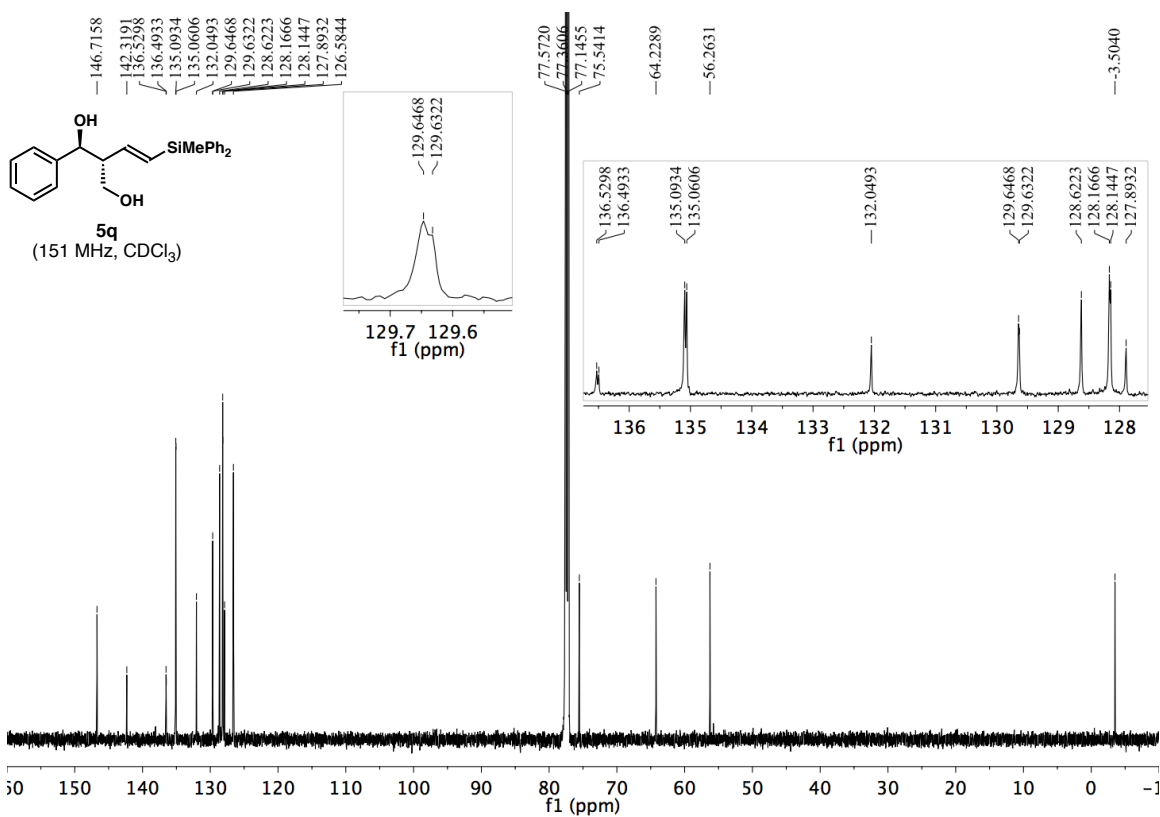
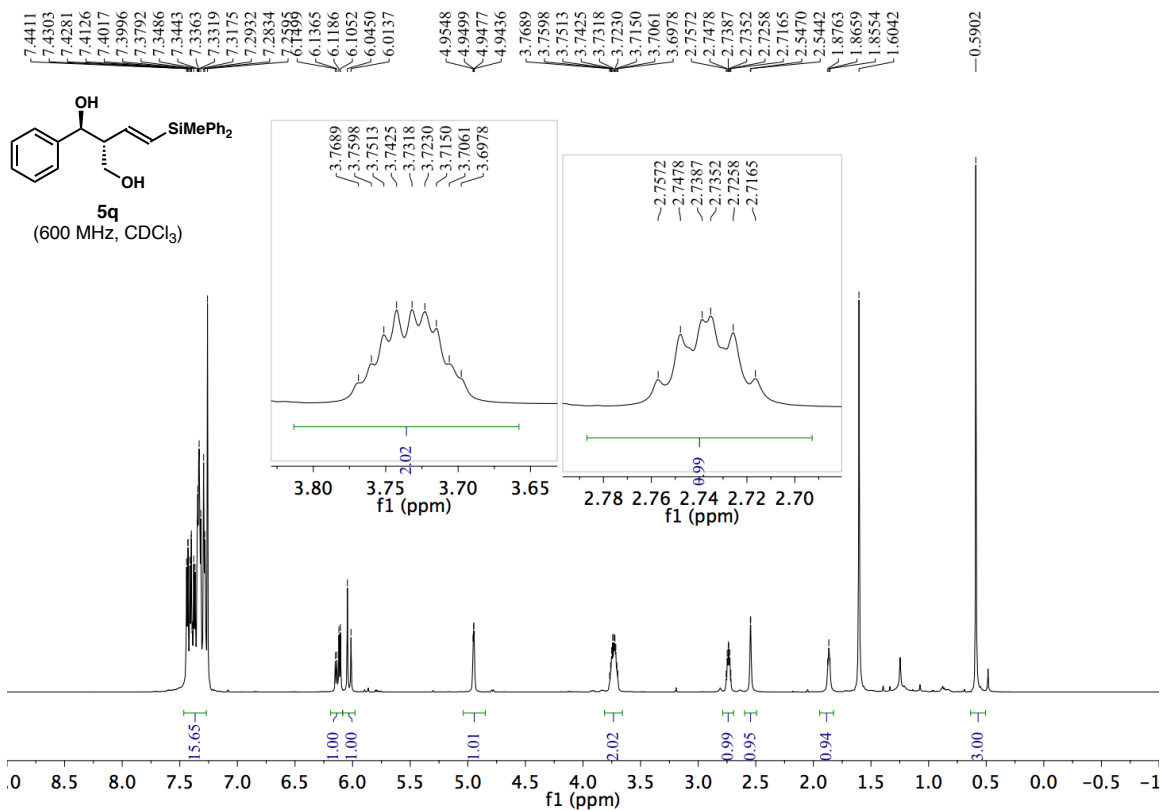


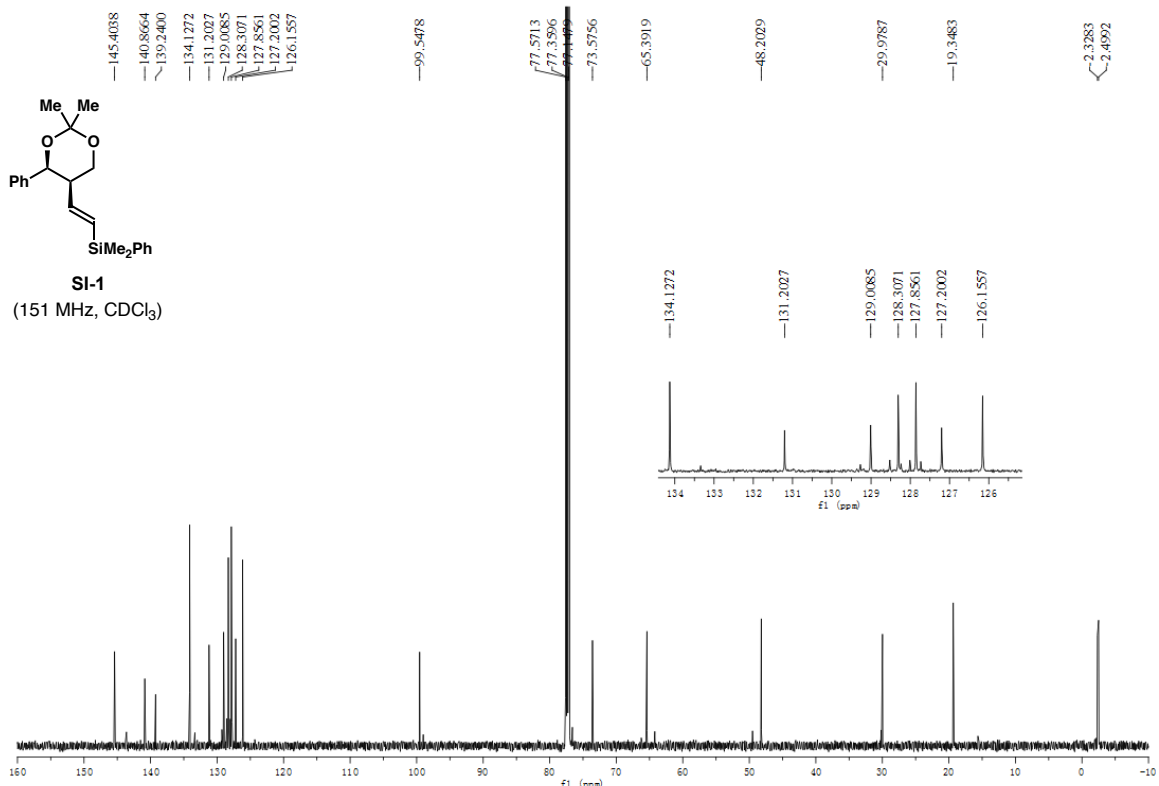
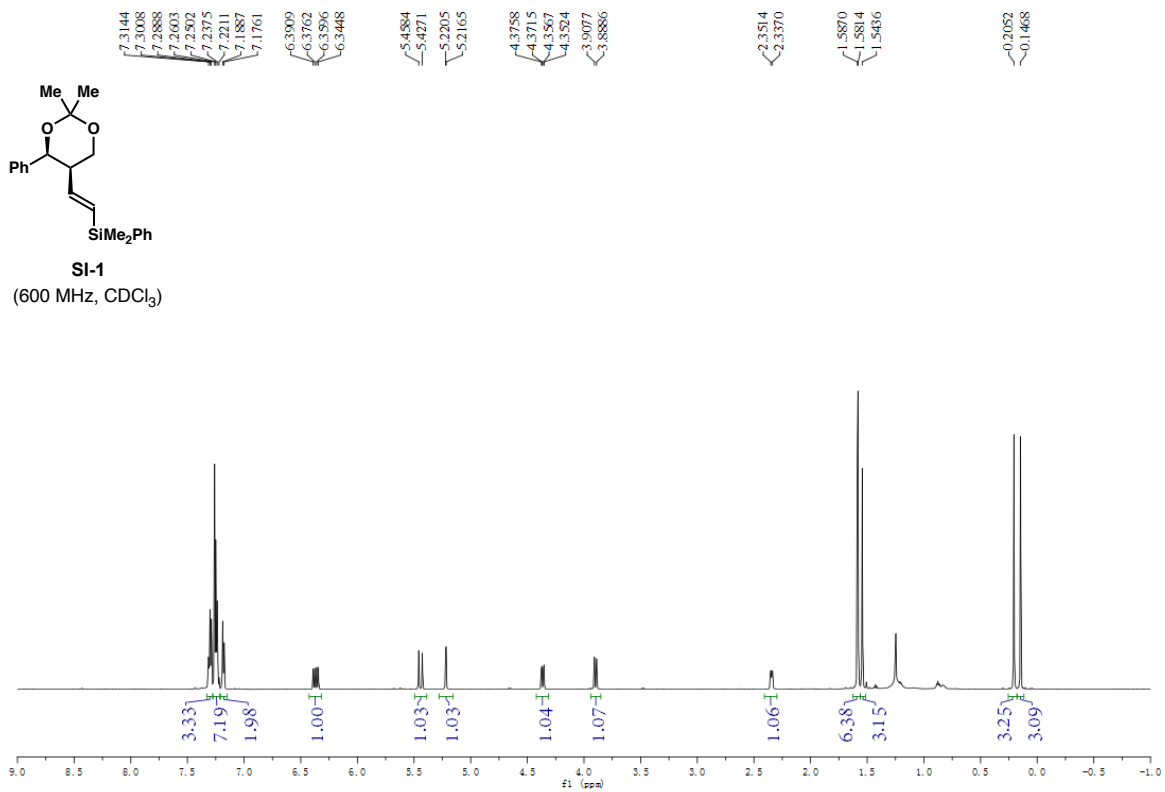


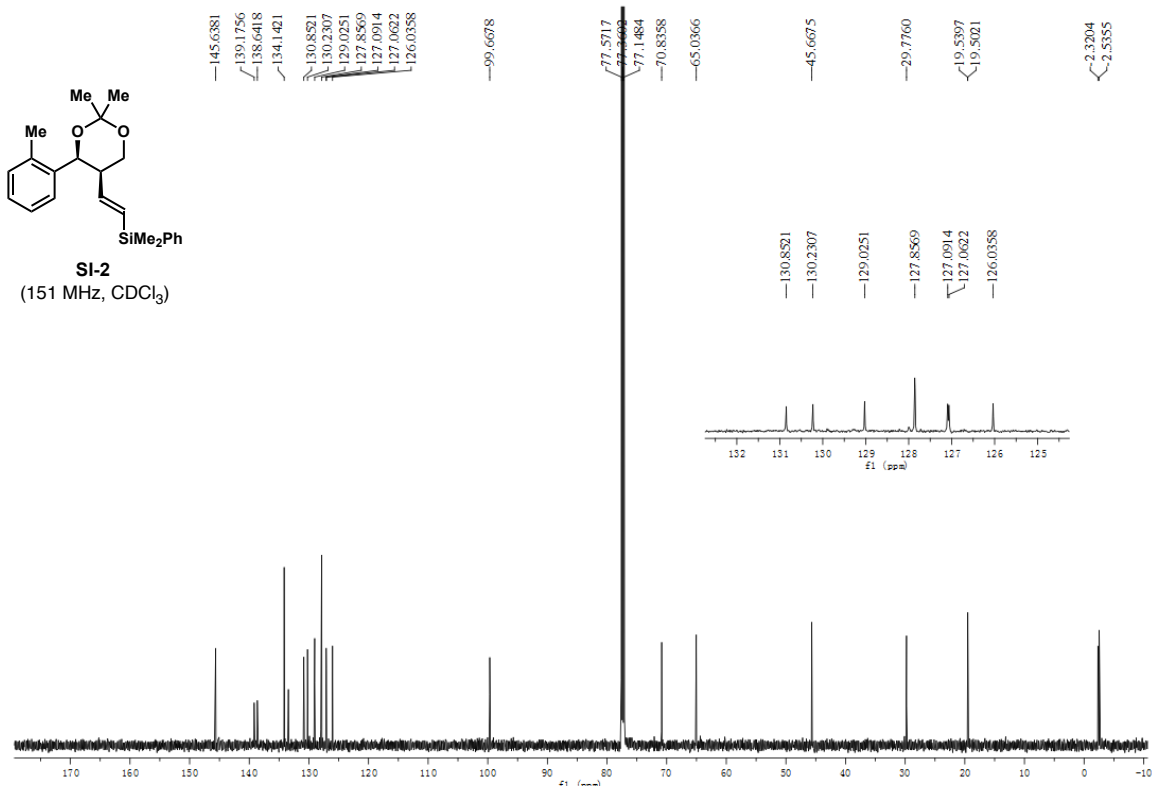
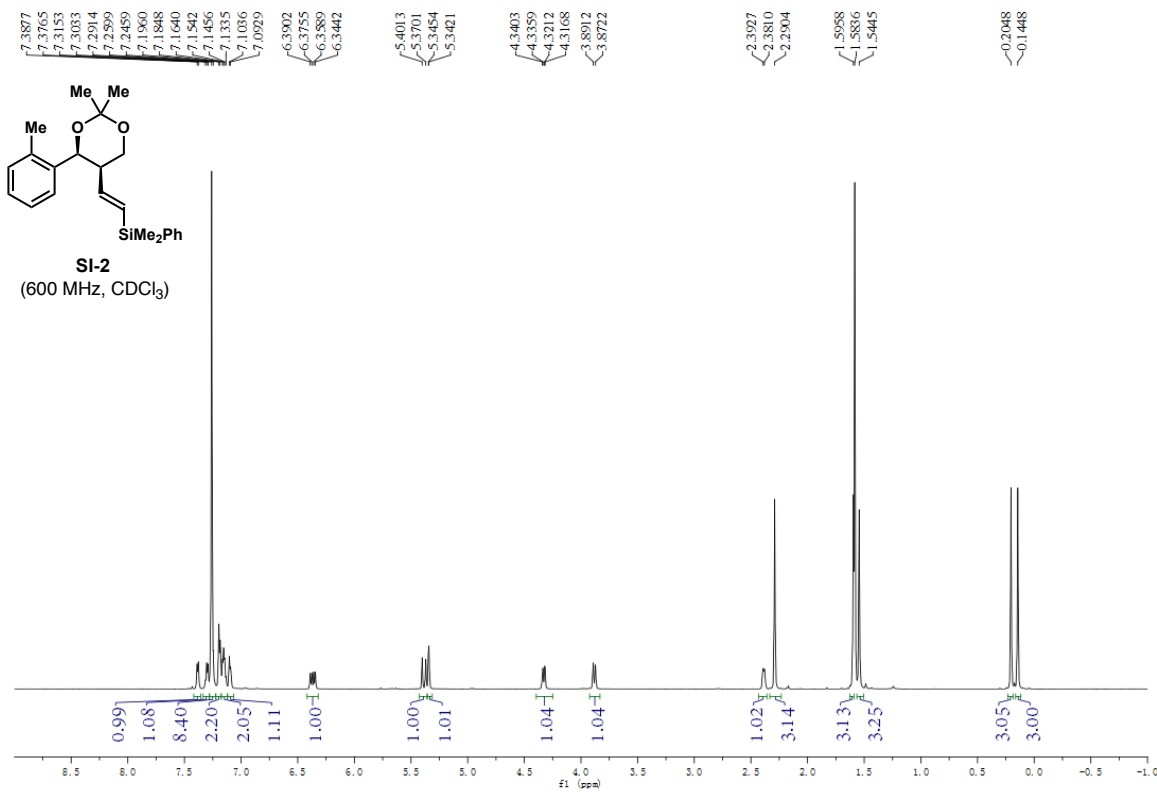




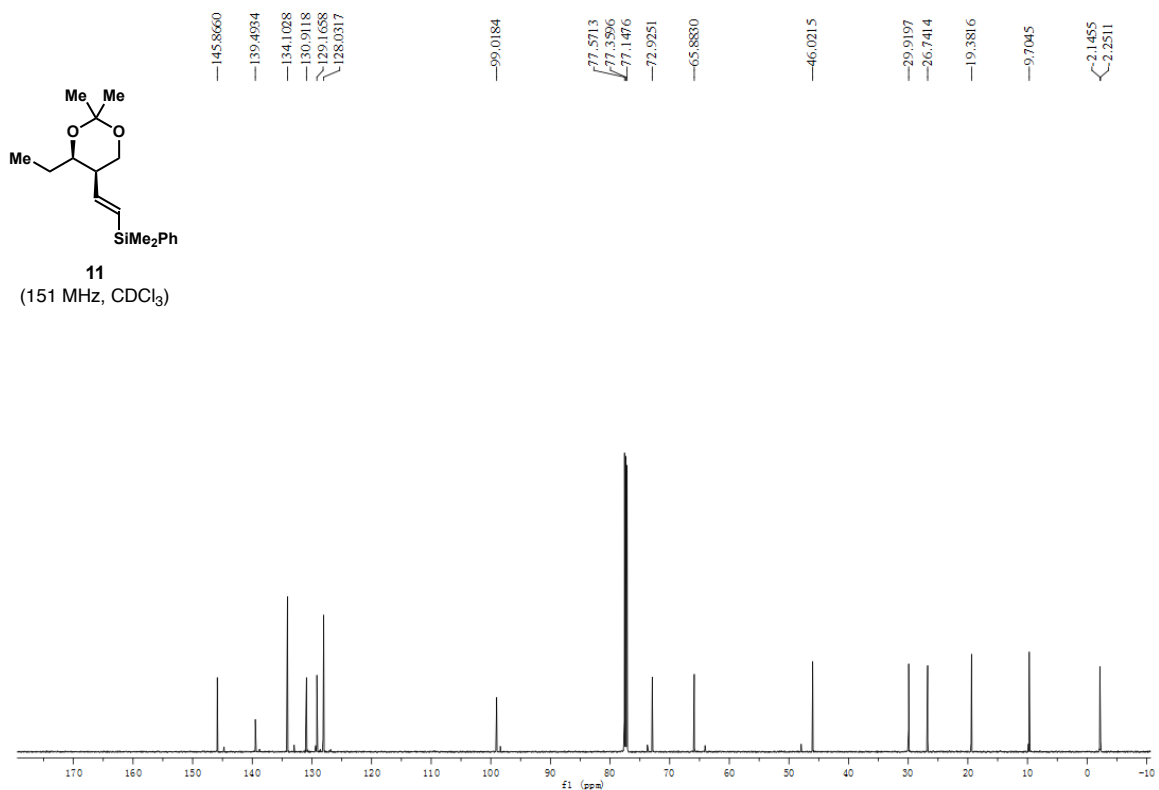
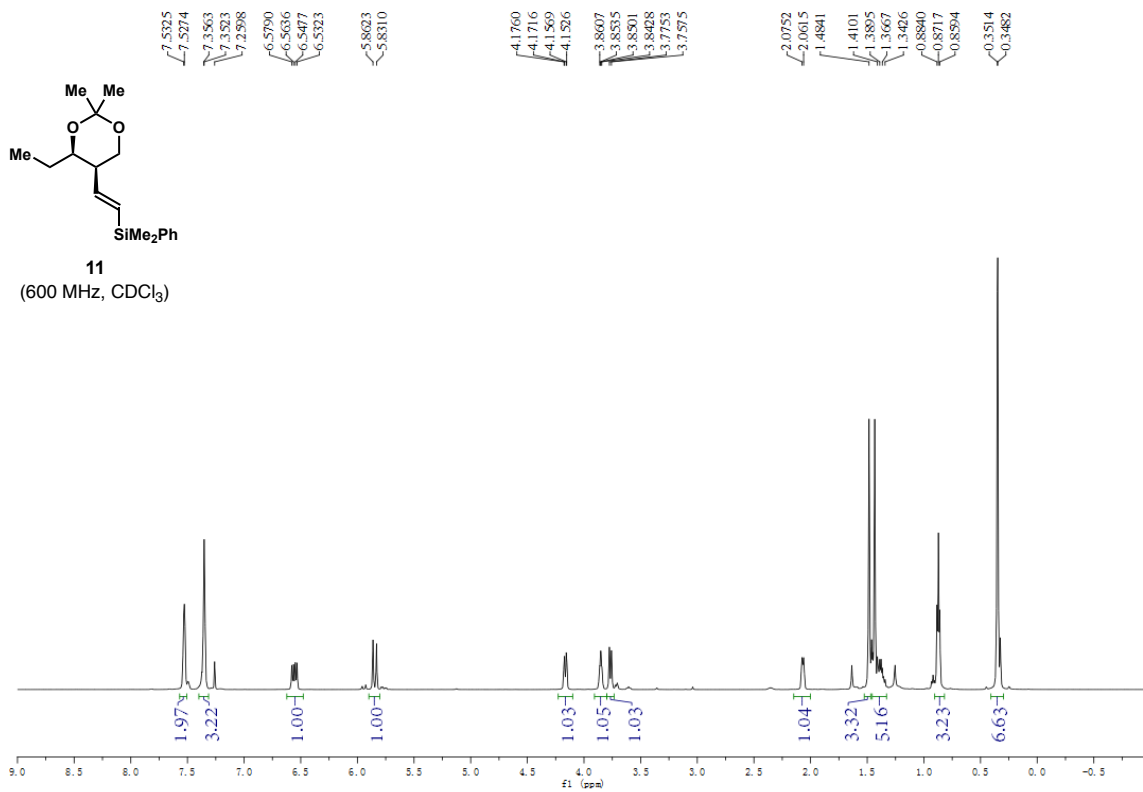


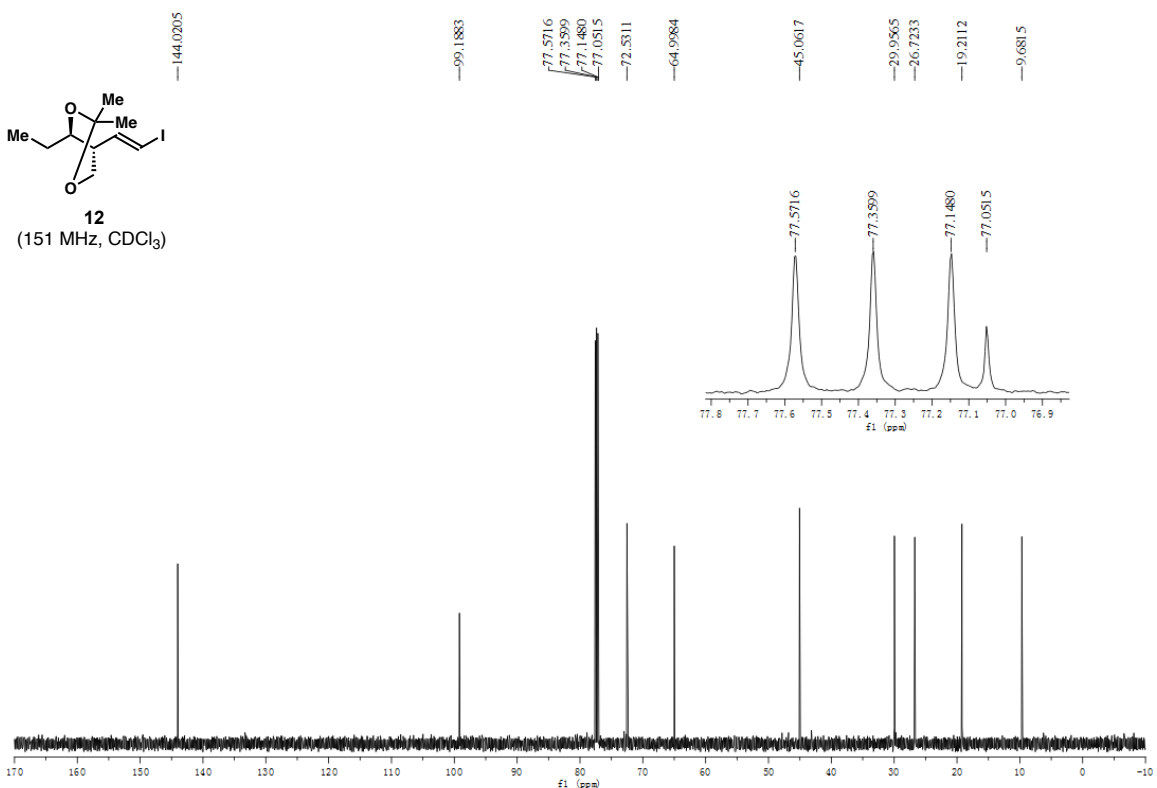
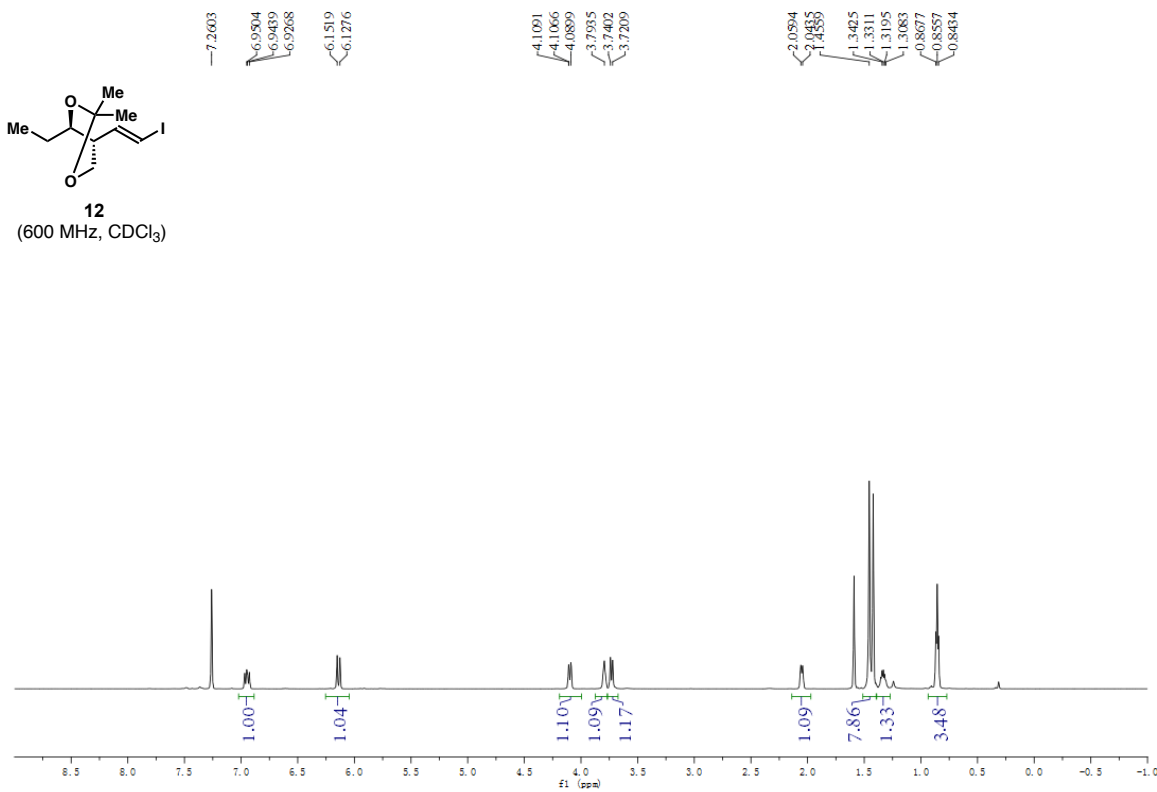


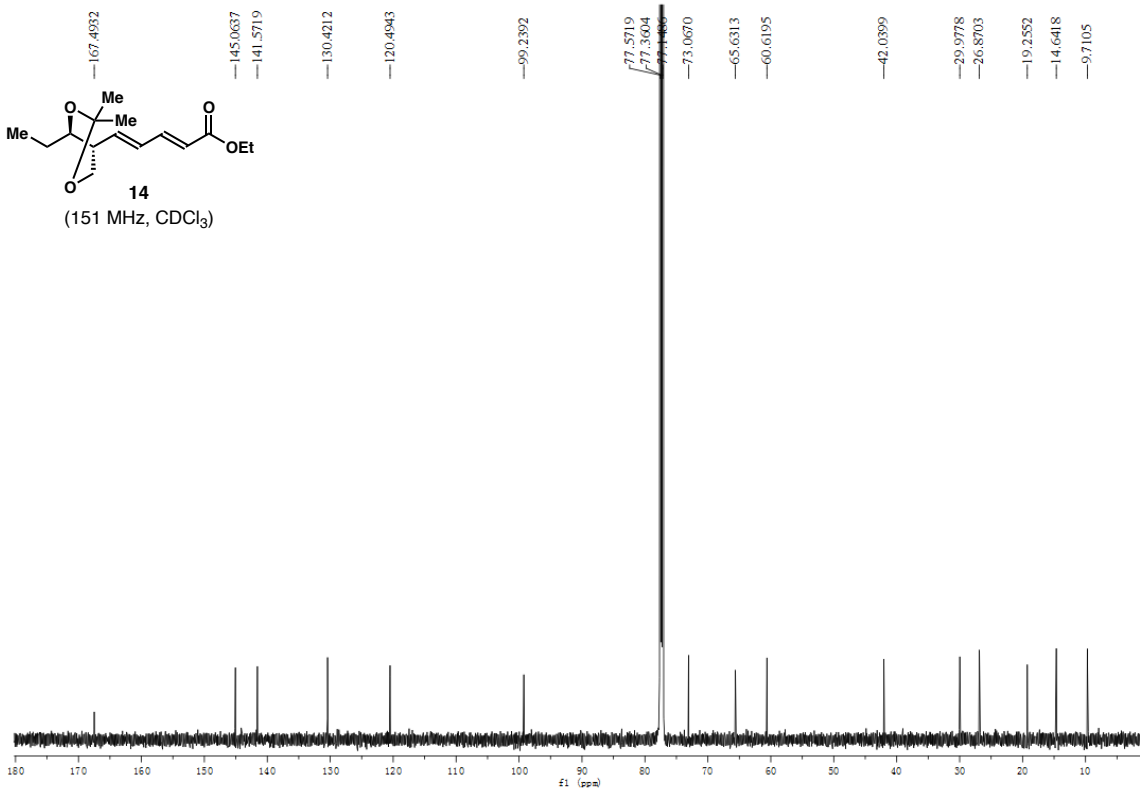
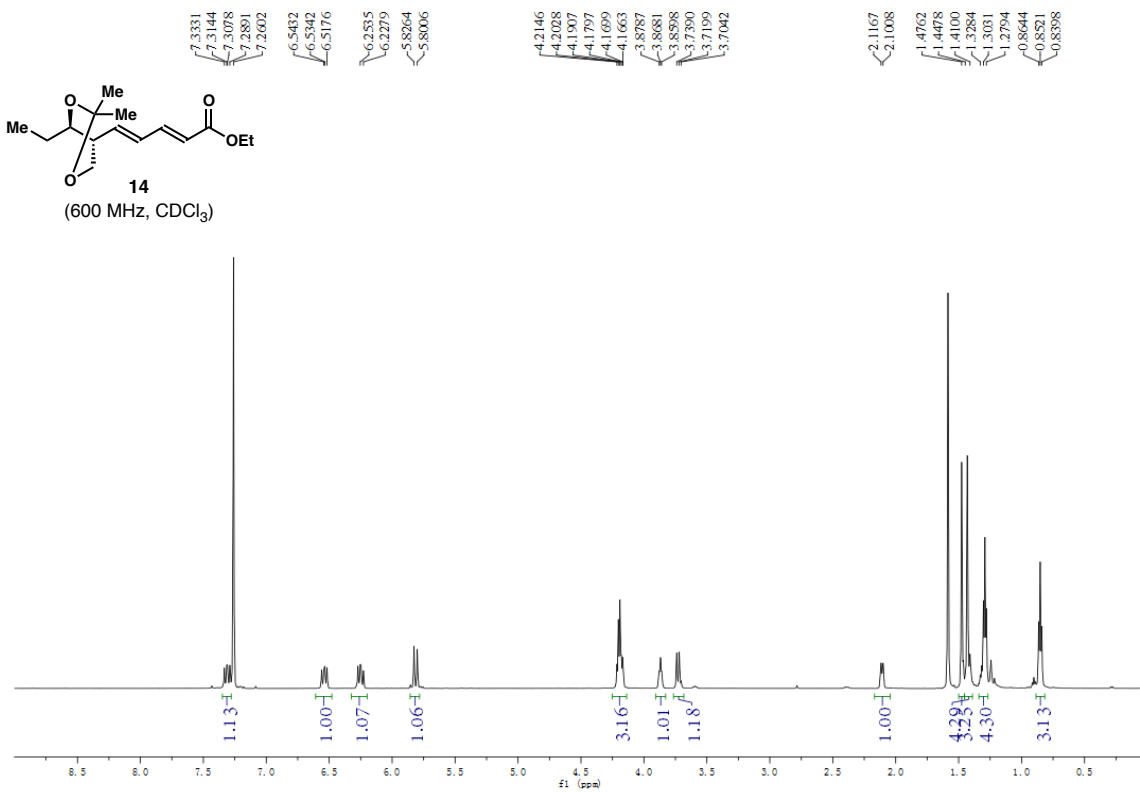


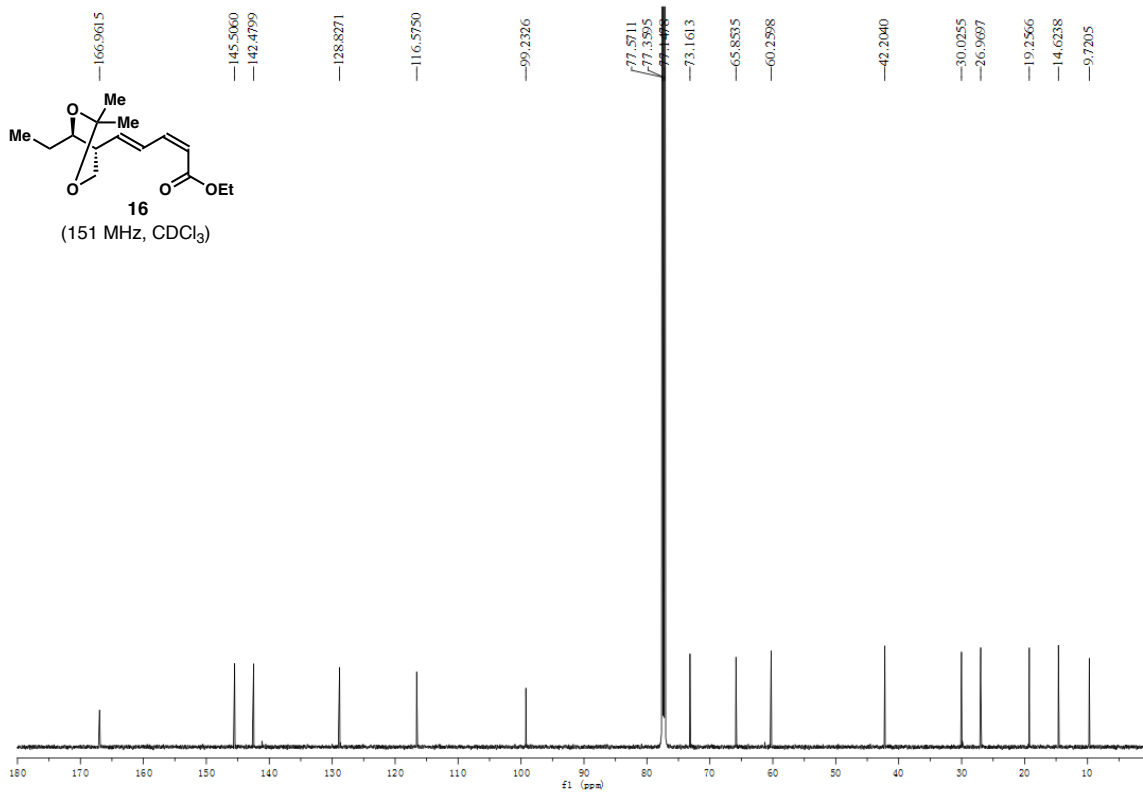
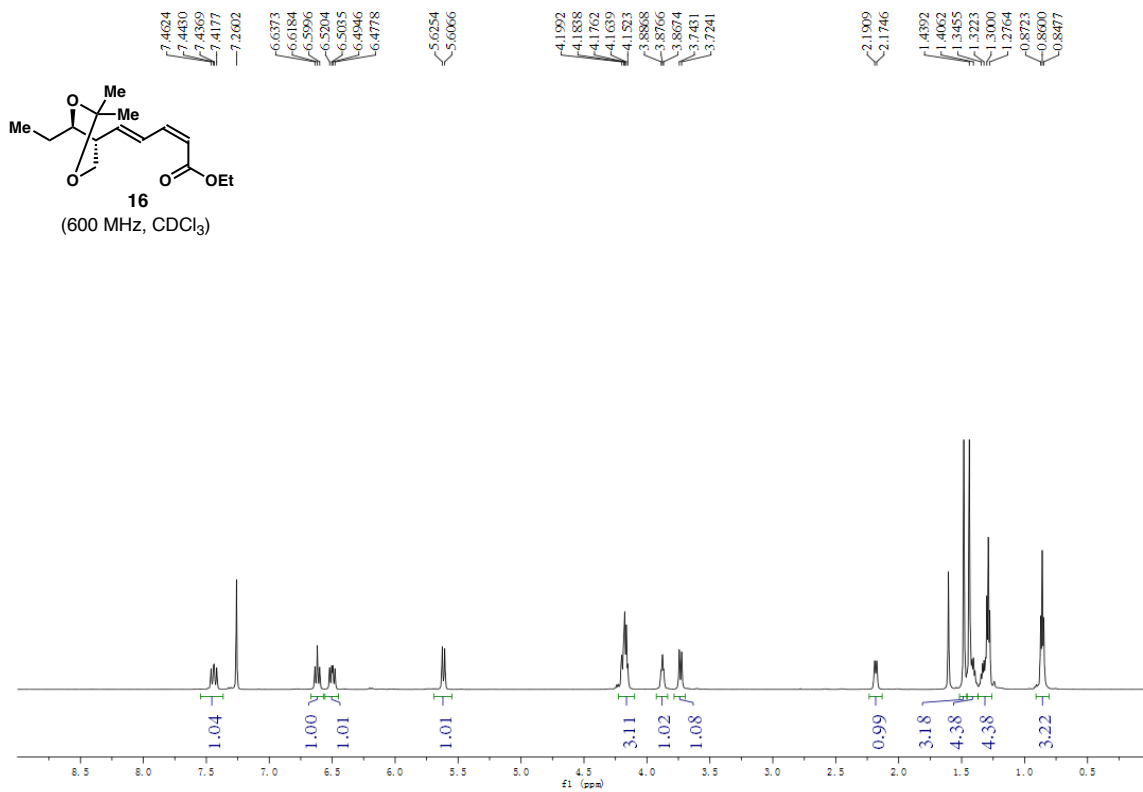




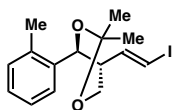




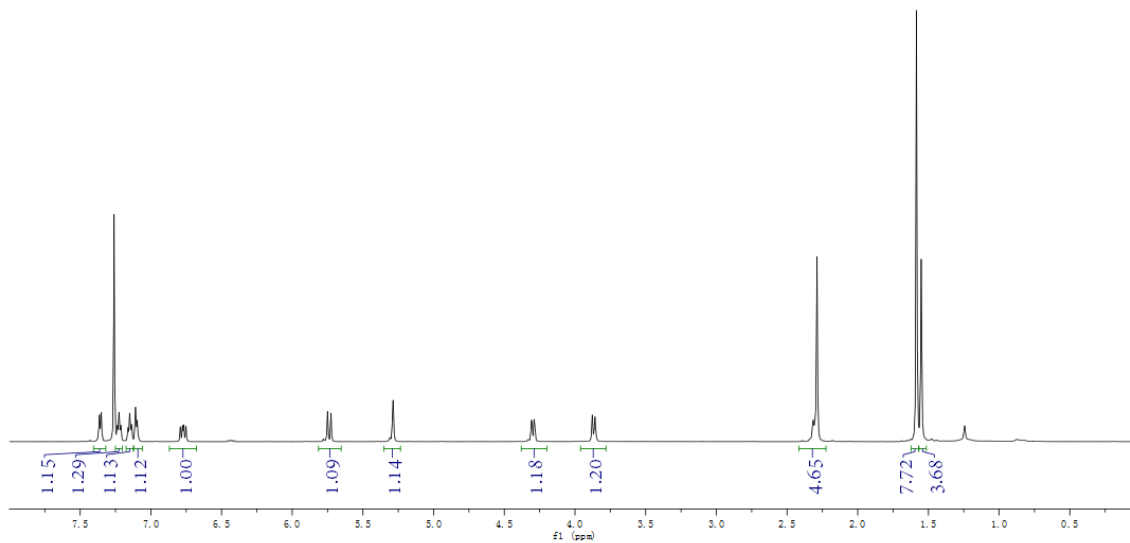




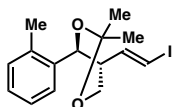
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6.7789  
6.7672  
6.7516



**17**  
(600 MHz, CDCl<sub>3</sub>)



143.4345  
137.8714  
133.2774  
130.5524  
127.5324  
127.0653  
126.2347



**17**  
(151 MHz, CDCl<sub>3</sub>)

