

## Supporting Information

### ***“Regioselective Cobalt-Catalyzed Alder-ene reaction towards towards Silicon- and Boron-Functionalized Building Blocks”***

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#### **Content:**

Preparation of alkenes and alkynes	S 2
General Procedures A and B	S 2
Analytical Data of the <i>Alder-ene</i> products	S 2 – S 9
Analytical Data of the follow-up products	S 9 – S 13
$^1\text{H}/^{13}\text{C}$ Spectra	S 14 – S 36

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## Preparation of alkynes and alkenes

Commercially unavailable allylsilanes were easily furnished by reacting allylmagnesium chloride with the corresponding chlorosilane.<sup>1</sup> The propargylsilane was received out of lithiation of 2-heptyne and quenching with the accordant chlorosilane.<sup>2</sup> A copper-mediated allylation of methyl propiolate with allylbromide gave the eneyneone in one step<sup>3</sup> while the alkynylphenone was produced in an alkylation-oxidation sequence commencing with benzaldehyde.<sup>4</sup>

### General procedure A for the cobalt-catalyzed *Alder-ene* reaction with electron-rich alkynes

Anhydrous zinc iodide (20 mol%), zinc dust (20 mol%) and CoBr<sub>2</sub>(dppp) (10 mol%) were suspended in 1.0 mL dichloromethane under argon atmosphere. Then the terminal alkene (1.0 eq.) and the alkyne (1.5 eq.) were added and the mixture was stirred at room temperature for 16 h or until complete conversion of the starting materials was monitored by GC. The reaction mixture was filtered over a short pad of silica gel and the solvent was removed under vacuum. The residue was then purified by flash column chromatography or bulb-to-bulb-distillation.

### General procedure B for the cobalt-catalyzed *Alder-ene* reaction with electron-poor alkynes

Anhydrous zinc iodide (40 mol%), zinc dust (40 mol%) and CoBr<sub>2</sub>(dppe) (20 mol%) were suspended in 1.0 mL dichloromethane under argon atmosphere. Then the terminal alkene (1.0 eq.) was added. The alkyne (3.0 eq.) was added to the reaction mixture over 7 h in seven portions. Then the mixture was stirred at room temperature for another 9 h or until complete conversion of the starting materials was monitored by GC. The reaction mixture was filtered over a short pad of silica gel and the solvent was removed under vacuum. The residue was then purified by flash column chromatography or bulb-to-bulb-distillation.

### ((*2E,5E*)-5-Benzylidenenon-2-enyl)trimethylsilane (**3a**)

According to the general procedure A the catalyst was prepared from zinc iodide (320 mg, 1.0 mmol), zinc dust (65 mg, 1.0 mmol) and CoBr<sub>2</sub>(dppp) (315 mg, 0.5 mmol) in 5.0 mL dichloromethane. Then but-3-enyltrimethylsilane (0.88 mL, 5.0 mmol) and hex-1-ynylbenzene (1.32 mL, 7.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane) the desired product **3a** was obtained as colorless oil (1.081 g, 3.77 mmol, 75%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 7.35-7.28 (m, 2H), 7.23-7.16 (m, 3H), 6.29-6.27 (s, 1H), 5.56-5.45 (m, 1H), 5.36-5.27 (m, 1H), 2.85 (d,  $J$  = 6.8 Hz, 2H), 2.26-2.20 (m, 2H), 1.55-1.44 (m, 4H), 1.38-1.28 (m, 2H), 0.90 (t,  $J$  = 7.4 Hz, 3H), 0.02 (s, 9H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 143.2, 138.7, 128.6, 128.4, 128.0, 126.4, 125.8, 125.2, 40.8, 30.6, 30.4, 22.9, 22.8, 14.0, -1.9.

IR (film, cm<sup>-1</sup>): 2955, 2927, 2872, 1656, 1599, 1493, 1466, 1444, 1383, 1248, 1155, 967, 852, 747, 698.

MS (EI):  $m/z$  = 286 (M<sup>+</sup>, 10), 271 (1), 229 (9), 212 (7), 184 (3), 169 (2), 161 (2), 155 (16), 141 (4), 135 (4), 129 (8), 115 (10), 104 (1), 91 (12), 73 (100).

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<sup>(2)</sup> Harmata, M.; Huang, C.; Rooshenas, P.; Schreiner, P. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 8696.

<sup>(3)</sup> Bieber, L. W.; da Silva, M. F. *Tetrahedron Lett.* **2007**, *48*, 7088.

<sup>(4)</sup> Herrero, M. T.; Tellitu, I.; Domínguez, E.; Hernández, S.; Moreno, I. *Tetrahedron* **2002**, *58*, 8581.

**HRMS (EI):** calculated for  $C_{19}H_{30}Si$ :  $m/z = 286.2117$ ; found  $m/z = 286.2104$ .

**Benzyl((1*E*,4*E*)-4-benzylideneoct-1-enyl)dimethylsilane (3b)**

According to the general procedure A the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and  $CoBr_2(dppp)$  (63 mg, 0.1 mmol) in 1.0 mL dichloromethane. Then allyl(benzyl)dimethylsilane (190 mg, 1.0 mmol) and hex-1-ynylbenzene (0.26 mL, 1.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane) the desired product **3b** was obtained as yellow oil (241 mg, 0.69 mmol, 69%).

**$^1H$  NMR ( $CDCl_3$ , 300 MHz):**  $\delta = 7.36$ -7.20 (m, 7H), 7.14-7.01 (m, 3H), 6.32 (s, 1H), 6.03-5.95 (m, 1H), 5.84-5.70 (m, 1H), 2.46-2.36 (m, 2H), 2.16 (s, 2H), 1.67-1.60 (m, 2H), 1.59-1.49 (m, 2H), 1.47-1.37 (m, 2H), 0.95 (t,  $J = 7.2$  Hz, 3H), 0.04 (s, 6H).

**$^{13}C$  NMR ( $CDCl_3$ , 75 MHz):**  $\delta = 141.1, 139.9, 138.3, 133.2, 128.7, 128.2, 128.1, 127.5, 126.1, 126.0, 124.1, 31.6, 27.3, 25.4, 23.1, 21.9, 14.0, -3.70$ .

**IR (film,  $cm^{-1}$ ):** 3058, 3022, 2955, 2927, 2871, 1599, 1493, 1452, 1248, 1207, 1155, 1031, 962, 834, 751, 698, 524, 474.

**MS (EI):**  $m/z = 348$  ( $M^+$ , 12), 257 (7), 149 (100), 135 (4), 121 (37), 105 (2), 91 (10), 77 (1), 59 (4).

**HRMS (EI):** calculated for  $C_{24}H_{32}Si$ :  $m/z = 348.2273$ ; found  $m/z = 348.2284$ .

**((1*E*,4*E*)-4-Benzylidenehex-1-enyl)diisopropylsilane (3c)**

According to the general procedure A the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and  $CoBr_2(dppp)$  (63 mg, 0.1 mmol) in 1.0 mL dichloromethane. Then allyldiisopropylsilane (156 mg, 1.0 mmol) and but-1-ynylbenzene (0.22 mL, 1.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane) the desired product **3c** was obtained as colorless oil (217 mg, 0.76 mmol, 76%).

**$^1H$  NMR ( $CDCl_3$ , 300 MHz):**  $\delta = 7.38$ -7.30 (m, 2H), 7.28-7.19 (m, 3H), 6.30 (s, 1H), 6.27 (td,  $J = 6.3, 18.4$  Hz, 1H), 5.70 (tdd,  $J = 1.5, 4.6, 18.5$  Hz, 1H), 3.65 (d,  $J = 4.5$  Hz, 1H), 3.05 (d,  $J = 6.4$  Hz, 2H), 2.29 (q,  $J = 7.6$  Hz, 2H), 1.11 (t,  $J = 7.6$  Hz, 3H), 1.05 (m, 14H).

**$^{13}C$  NMR ( $CDCl_3$ , 75 MHz):**  $\delta = 149.0, 142.9, 138.4, 128.5, 128.1, 126.0, 125.8, 124.3, 44.7, 23.9, 18.8, 18.5, 12.9, 10.6$ .

**IR (film,  $cm^{-1}$ ):** 3023, 2939, 2889, 2863, 2098, 1608, 1493, 1461, 1383, 1266, 1070, 996, 916, 881, 789, 760, 740, 697.

**MS (EI):**  $m/z = 286$  ( $M^+$ , 29), 243 (100), 230 (4), 215 (18), 201 (29), 187 (28), 173 (34), 159 (36), 145 (43), 135 (19), 121 (44), 111 (30), 91 (29), 73 (16), 59 (25).

**HRMS (EI):** calculated for  $C_{19}H_{30}Si$ :  $m/z = 286.2117$ ; found  $m/z = 286.2119$ .

**((5*E*)-3-Butylnona-2,5-dienyl)diisopropylsilane (3d)**

According to the general procedure A the catalyst was prepared from zinc iodide (32 mg, 0.10 mmol), zinc dust (7 mg, 0.10 mmol) and  $CoBr_2(dppp)$  (32 mg, 0.05 mmol) in 0.5 mL dichloromethane. Then hex-1-ene (0.065 mL, 0.50 mmol) and hept-2-ynyldiisopropylsilane

(158 mg, 0.75 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane) the desired product **3d** was obtained as colorless oil (136 mg, 0.46 mmol, 92%) containing the (2*E*)- and the (2*Z*)-isomer in a 50:50 ratio which was determined with the singlet at 3.54 and 3.42 ppm. The spectroscopic data are given for both isomers.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 5.48-5.32 (m, 2H), 5.21 (t, *J* = 9.0 Hz, 0.5H), 5.02 (t, *J* = 6.0 Hz, 0.5H), 3.54 (bs, 0.5H), 3.42 (bs, 0.5H), 2.71-2.63 (m, 2H), 2.05-1.96 (m, 4H), 1.57-1.50 (m, 2H), 1.44-1.25 (m, 6H), 1.04-1.02 (m, 12H), 0.94-0.86 (m, 5H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 136.6, 136.3, 135.8, 131.8, 130.4, 128.9, 128.8, 128.3, 123.2, 120.8, 120.6, 42.2, 40.4, 34.8, 34.7, 34.6, 32.2, 30.3, 29.8, 29.5, 29.2, 28.1, 23.0, 22.9, 22.8, 22.7, 22.5, 19.0, 18.9, 18.7, 14.1, 13.8, 13.7, 12.8, 11.0, 10.7, 10.0, 9.9.

**IR (film, cm<sup>-1</sup>):** 2956, 2932, 2891, 2864, 2100, 1653, 1463, 1379, 1366, 1243, 1159, 1070, 1003, 969, 918, 881, 850, 802, 707, 649, 431.

**MS (EI):** *m/z* = 294 (*M*<sup>+</sup>, 7), 251 (71), 223 (13), 209 (7), 195 (25), 181 (46), 167 (28), 153 (35), 141 (44), 125 (49), 111 (29), 99 (31), 87 (38), 73 (63), 59 (100).

**HRMS (EI):** calculated for C<sub>19</sub>H<sub>38</sub>Si: *m/z* = 294.2743; found *m/z* = 294.2743.

### ((2*E*)-5-((Diisopropylsilyl)methylene)non-2-enyl)trimethylsilane (**3e**)

According to the general procedure A the catalyst was prepared from zinc iodide (26 mg, 0.08 mmol), zinc dust (5 mg, 0.08 mmol) and CoBr<sub>2</sub>(dppp) (25 mg, 0.04 mmol) in 0.4 mL dichloromethane. Then but-3-enyltrimethylsilane (0.07 mL, 1.0 mmol) and hept-2-ynyl-diisopropylsilane (100 mg, 1.2 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane) the desired product **3e** was obtained as colorless oil (72 mg, 0.21 mmol, 53%) containing the (5*E*)- and the (5*Z*)-isomer in a 58:42 ratio which was determined with the singlet at 3.55 and 3.43 ppm. The spectroscopic data are given for both isomers.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 5.48-5.31 (m, 1H), 5.28-4.97 (m, 2H), 3.55 (bs, 0.4H), 3.43 (bs, 0.6H), 2.72-2.60 (m, 2H), 2.06-1.93 (m, 2H), 1.60-1.48 (m, 2H), 1.47-1.39 (m, 2H), 1.39-1.24 (m, 4H), 1.12-0.99 (m, 14H), 0.95-0.86 (m, 3H), -0.01 (s, 9H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 136.9, 136.1, 127.6, 127.4, 127.2, 127.1, 123.0, 120.6, 42.4, 40.6, 32.2, 30.2, 29.4, 28.1, 23.0, 22.7, 22.6, 22.5, 19.0, 18.9, 18.8, 14.1, 14.0, 12.8, 11.0, 10.7, 10.0, -1.9.

**IR (film, cm<sup>-1</sup>):** 3012, 2955, 2891, 2864, 2100, 1659, 1462, 1383, 1248, 1156, 1064, 1003, 966, 918, 880, 850, 802, 696.

**MS (EI):** *m/z* = 338 (*M*<sup>+</sup>, 5), 295 (10), 267 (4), 221 (7), 211 (7), 195 (30), 181 (14), 167 (4), 153 (9), 139 (5), 129 (5), 111 (4), 101 (8), 87 (11), 73 (100), 59 (35).

**HRMS (EI):** calculated for C<sub>20</sub>H<sub>42</sub>Si<sub>2</sub>: *m/z* = 338.2825; found *m/z* = 338.2832.

### 2-((4*E*)-4-Benzylideneoct-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)

According to the general procedure A the catalyst was prepared from zinc iodide (638 mg, 2.0 mmol), zinc dust (131 mg, 2.0 mmol) and CoBr<sub>2</sub>(dppp) (631 mg, 1.0 mmol) in 5.0 mL dichloromethane. Then 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.87 mL, 5.0 mmol) and hex-1-ynylbenzene (1.32 mL, 7.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by bulb-to-bulb-distillation

(0.5 mbar, 170 °C) the desired product **3f** was obtained as yellow oil (1.209 g, 3.70 mmol, 74%) containing the (1*Z*)- and the (1*E*)-isomer in a 89:11 ratio which was determined with the doublet at 3.30 and 3.01 ppm. The boron-functionalized carbon atom could not be detected in <sup>13</sup>C NMR.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 7.34-7.28 (m, 2H), 7.23-7.16 (m, 3H), 6.55-6.44 (m, 1H), 6.30 (s, 1H), 5.50-5.44 (m, 1H), 3.30 (d, *J* = 7.6 Hz, 2H), 2.25-1.19 (m, 2H), 1.58-1.46 (m, 2H), 1.36-1.22 (m, 14H), 0.89 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 152.6, 142.4, 141.0, 138.6, 128.6, 128.0, 126.8, 126.0, 125.9, 82.9, 40.3, 30.6, 30.3, 24.9, 24.8, 22.8, 14.0.

**<sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz):** δ = 29.54.

**IR (film, cm<sup>-1</sup>):** 2978, 2958, 2931, 2871, 1625, 1599, 1435, 1420, 1371, 1326, 1260, 1145, 1110, 1007, 968, 847, 748, 700.

**MS (EI):** *m/z* = 326 (*M*<sup>+</sup>, 100), 311 (7), 282 (11), 269 (15), 242 (18), 226 (76), 211 (9), 198 (47), 183 (73), 169 (81), 155 (79), 141 (44), 129 (71), 115 (60), 101 (69), 91 (88).

**HRMS (EI):** calculated for C<sub>21</sub>H<sub>31</sub>BO<sub>2</sub>: *m/z* = 326.2417; found *m/z* = 326.2412.

#### **4,4,5,5-Tetramethyl-2-((4*E*)-4-methyl-5-phenylpenta-1,4-dienyl)-1,3,2-dioxaborolane (3g)**

According to the general procedure A the catalyst was prepared from zinc iodide (638 mg, 2.0 mmol), zinc dust (131 mg, 2.0 mmol) and CoBr<sub>2</sub>(dppp) (631 mg, 1.0 mmol) in 5.0 mL dichloromethane. Then 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.87 mL, 5.0 mmol) and prop-1-ynylbenzene (1.26 mL, 10.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by bulb-to-bulb-distillation (0.5 mbar, 140 °C) the desired product **3g** was obtained as yellow oil (853 mg, 3.00 mmol, 60%) containing the (1*Z*)- and the (1*E*)-isomer in a 93:7 ratio which was determined with the doublet at 3.29 and 3.00 ppm. The boron-functionalized carbon atom could not be detected in <sup>13</sup>C NMR.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 7.35-7.28 (m, 2H), 7.27-7.22 (m, 2H), 7.21-7.15 (m, 1H), 6.56-6.45 (m, 1H), 6.33 (s, 1H), 5.48 (d, *J* = 13.6 Hz, 1H), 3.29 (d, *J* = 7.6 Hz, 2H), 1.86 (s, 3H), 1.29 (s, 12H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 151.9, 138.6, 137.7, 128.8, 128.0, 125.9, 125.7, 82.9, 43.3, 24.9, 24.8, 17.7.

**<sup>11</sup>B NMR (CDCl<sub>3</sub>, 128 MHz):** δ = 29.62.

**IR (film, cm<sup>-1</sup>):** 2979, 2934, 1625, 1419, 1371, 1326, 1260, 1215, 1145, 1110, 968, 879, 846, 766, 742, 700.

**MS (EI):** *m/z* = 284 (*M*<sup>+</sup>, 33), 269 (4), 240 (12), 227 (7), 211 (2), 193 (7), 184 (100), 169 (40), 156 (67), 143 (47), 128 (42), 115 (44), 101 (47), 91 (39), 80 (30).

**HRMS (EI):** calculated for C<sub>18</sub>H<sub>25</sub>BO<sub>2</sub>: *m/z* = 284.1948; found *m/z* = 284.1940.

#### **(2*E*, 5*Z*)-Ethyl 3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexa-2,5-dienoate (3h)**

According to the general procedure B the catalyst was prepared from zinc iodide (128 mg, 0.4 mmol), zinc dust (26 mg, 0.4 mmol) and CoBr<sub>2</sub>(dppe) (126 mg, 0.2 mmol) in 1.0 mL dichloromethane. Then 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.19 mL, 1.0 mmol)

and ethyl but-2-ynoate (0.35 mL, 3.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by bulb-to-bulb-distillation (0.5 mbar, 120°C) the desired product **3h** was obtained as yellow oil (185 mg, 0.66 mmol, 66%). The boron-functionalized carbon atom could not be detected in  $^{13}\text{C}$  NMR.

**$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  = 6.42-6.31 (m, 1H), 5.70-5.67 (m, 1H), 5.49 (dt,  $J$  = 1.2, 13.5 Hz, 1H), 4.12 (q,  $J$  = 6.9 Hz, 2H), 3.24 (d,  $J$  = 7.6 Hz, 2H), 2.15 (s, 3H), 1.25 (t,  $J$  = 8.6 Hz, 3H), 1.25 (s, 12H).

**$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  = 166.8, 158.3, 149.3, 116.3, 83.0, 59.4, 43.2, 24.8, 18.7, 14.3.

**$^{11}\text{B}$  NMR ( $\text{CDCl}_3$ , 128 MHz):**  $\delta$  = 29.52.

**IR (film,  $\text{cm}^{-1}$ ):** 2980, 2935, 1717, 1650, 1625, 1419, 1380, 1370, 1327, 1261, 1217, 1143, 1054, 968, 879, 846, 751, 677.

**MS (EI):**  $m/z$  = 280 ( $\text{M}^+$ , 2), 265 (2), 234 (7), 219 (4), 206 (6), 193 (2), 180 (45), 164 (16), 151 (66), 136 (48), 121 (6), 107 (100), 91 (16), 79 (54), 67 (13).

**HRMS (EI):** calculated for  $\text{C}_{15}\text{H}_{25}\text{BO}_4$ :  $m/z$  = 280.1846; found  $m/z$  = 280.1845.

#### **(2*E*,5*E*)-Ethyl 3-methyl-7-(trimethylsilyl)hepta-2,5-dienoate (3i)**

According to the general procedure B the catalyst was prepared from zinc iodide (640 mg, 2.0 mmol), zinc dust (130 mg, 2.0 mmol) and  $\text{CoBr}_2(\text{dppe})$  (617 mg, 1.0 mmol) in 5.0 mL dichloromethane. Then but-3-enyltrimethylsilane (0.88 mL, 5.0 mmol) and ethyl but-2-ynoate (1.74 mL, 15.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3i** was obtained as colorless oil (966 mg, 4.02 mmol, 80%).

**$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  = 5.69 (s, 1H), 5.63-5.53 (m, 1H), 5.32-5.23 (m, 1H), 4.14 (q,  $J$  = 7.2 Hz, 2H), 2.82 (d,  $J$  = 7.2 Hz, 2H), 2.16 (s, 3H), 1.48 (d,  $J$  = 8.7 Hz, 2H), 1.27 (t,  $J$  = 7.2 Hz, 3H), 0.00 (s, 9H).

**$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  = 166.9, 158.9, 128.8, 122.4, 115.6, 59.4, 38.1, 19.0, 18.6, 14.3, -1.8.

**IR (film,  $\text{cm}^{-1}$ ):** 3013, 2980, 2955, 1718, 1651, 1428, 1384, 1367, 1350, 1283, 1249, 1218, 1143, 1097, 1046, 944, 855, 724, 701.

**MS (EI):**  $m/z$  = 240 ( $\text{M}^+$ , 3), 225 (4), 195 (16), 181 (3), 151 (6), 122 (18), 117 (4), 107 (12), 94 (19), 79 (34), 73 (100).

**HRMS (EI):** calculated for  $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$ :  $m/z$  = 240.1546; found  $m/z$  = 240.1546.

#### **(2*E*,5*E*)-Ethyl 6-(benzyltrimethylsilyl)-3-methylhexa-2,5-dienoate (3j)**

According to the general procedure B the catalyst was prepared from zinc iodide (638 mg, 2.0 mmol), zinc dust (131 mg, 2.0 mmol) and  $\text{CoBr}_2(\text{dppe})$  (617 mg, 1.0 mmol) in 5.0 mL dichloromethane. Then allyl(benzyl)dimethylsilane (952 mg, 5.0 mmol) and ethyl but-2-ynoate (1.74 mL, 15.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3j** was obtained as colorless oil (1.205 g, 3.98 mmol, 80%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 7.21 (t,  $J$  = 7.4 Hz, 2H), 7.08 (t,  $J$  = 7.4 Hz, 1H), 7.01 (d,  $J$  = 6.8 Hz, 2H), 6.29 (ddd,  $J$  = 7.2, 7.4, 14.2 Hz, 1H), 5.69-5.63 (m, 2H), 4.15 (q,  $J$  = 7.2 Hz, 2H), 2.81 (d,  $J$  = 7.2 Hz, 2H), 2.17 (s, 2H), 2.12 (s, 3H), 1.28 (t,  $J$  = 7.0 Hz, 3H), 0.12 (s, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.7, 157.8, 144.6, 139.7, 130.5, 128.1, 124.1, 116.4, 59.6, 44.0, 26.6, 19.0, 14.3, -1.7.

**IR (film, cm<sup>-1</sup>):** 3060, 3024, 2959, 1718, 1651, 1601, 1494, 1451, 1383, 1282, 1250, 1218, 1145, 1053, 835, 795, 764, 699.

**MS (EI):**  $m/z$  = 302 ( $M^+$ , 1), 257 (7), 211 (15), 193 (6), 183 (3), 165 (100), 149 (17), 135 (6), 121 (15), 103 (50), 91 (28), 75 (43), 59 (11).

**HRMS (EI):** calculated for C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>Si:  $m/z$  = 302.1702; found  $m/z$  = 302.1714.

### **(2E)-Ethyl 6-(diisopropylsilyl)-3-methylhexa-2,5-dienoate (3l)**

According to the general procedure B the catalyst was prepared from zinc iodide (638 mg, 2.0 mmol), zinc dust (131 mg, 2.0 mmol) and CoBr<sub>2</sub>(dppe) (617 mg, 1.0 mmol) in 5.0 mL dichloromethane. Then allyldiisopropylsilane (782 mg, 5.0 mmol) and ethyl but-2-ynoate (1.74 mL, 15.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3l** was obtained as colorless oil (873 mg, 3.25 mmol, 65%) containing the (5E)- and the (5Z)-isomer in a 80:20 ratio which was determined with the dublet at 3.04 and 2.95 ppm.

Spectroscopic data for the major (5E)-isomer:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 6.45 (m, 1H), 5.70-5.66 (m, 2H), 4.14 (q,  $J$  = 7.2 Hz, 2H), 3.86 (d,  $J$  = 7.2 Hz, 1H), 3.04 (d, 7.2 Hz, 2H), 2.16 (s, 3H), 1.27 (t, 7.2 Hz, 3H), 1.02-1.00 (m, 14H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.8, 158.0, 146.3, 125.4, 116.3, 59.5, 44.0, 19.0, 18.8, 18.5, 14.3, 10.8.

**IR (film, cm<sup>-1</sup>):** 2941, 2891, 2864, 2103, 1719, 1651, 1601, 1462, 1383, 1218, 1145, 1051, 1001, 881, 803, 710, 693, 655.

**MS (EI):**  $m/z$  = 268 ( $M^+$ , 1), 225 (100), 197 (52), 179 (43), 167 (22), 151 (74), 137 (15), 123 (14), 109 (44), 89 (32), 77 (30), 61 (34).

**HRMS (EI):** calculated for C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>Si:  $m/z$  = 268.1859; found  $m/z$  = 268.1842.

### **(2E,5E)-Methyl 3-allyl-7-(trimethylsilyl)hepta-2,5-dienoate (3m)**

According to the general procedure B the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and CoBr<sub>2</sub>(dppe) (63 mg, 0.1 mmol) in 0.5 mL dichloromethane. Then but-3-enyltrimethylsilane (0.09 mL, 0.5 mmol) and methyl hex-5-en-2-ynoate (186 mg, 1.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 20:1) the desired product **3m** was obtained as colorless oil (76 mg, 0.30 mmol, 60%).

**<sup>1</sup>NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.89-5.75 (m, 1H), 5.73 (s, 1H), 5.65-5.54 (m, 1H), 5.31-5.21 (m, 1H), 5.14-5.02 (m, 2H), 3.68 (s, 3H), 3.39 (d,  $J$  = 6.8 Hz, 2H), 2.84 (d,  $J$  = 7.2 Hz, 2H), 1.46 (d,  $J$  = 8.7 Hz, 2H), 0.00 (s, 9H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.9, 160.2, 135.1, 129.1, 122.2, 116.4, 115.7, 50.9, 36.8, 35.1, 22.3, 18.5, 14.0, -1.8.

**IR (film, cm<sup>-1</sup>):** 3079, 3013, 2953, 2900, 1722, 1651, 1634, 1434, 1367, 1249, 1181, 1144, 1031, 959, 914, 856, 725, 701.

**MS (EI):**  $m/z$  = 252 (M<sup>+</sup>, 1), 237 (1), 221 (3), 211 (2), 179 (1), 163 (5), 148 (5), 133 (10), 120 (10), 107 (32), 91 (15), 73 (100), 59 (11).

**HRMS (EI):** calculated for C<sub>14</sub>H<sub>24</sub>O<sub>2</sub>Si:  $m/z$  = 252.1546; found  $m/z$  = 252.1550.

### **(2E,5E)-Methyl 3-allyl-6-(benzyltrimethylsilyl)hexa-2,5-dienoate (3n)**

According to the general procedure B the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and CoBr<sub>2</sub>(dppe) (63 mg, 0.1 mmol) in 0.5 mL dichloromethane. Then allyl(benzyl)dimethylsilane (95 mg, 0.5 mmol) and methyl hex-5-en-2-ynoate (186 mg, 1.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3n** was obtained as colorless oil (67 mg, 0.21 mmol, 43%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 7.24-7.18 (m, 2H), 7.12-7.05 (m, 1H), 7.03-6.97 (m, 2H), 6.34-6.24 (m, 1H), 5.83-5.73 (m, 1H), 5.71-5.65 (m, 2H), 5.12-5.03 (m, 2H), 3.70 (s, 3H), 3.36 (d,  $J$  = 6.8 Hz, 2H), 2.84 (d,  $J$  = 7.2 Hz, 2H), 2.16 (s, 2H), 0.10 (s, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.6, 159.2, 144.3, 139.7, 135.9, 134.7, 130.8, 128.2, 128.1, 124.1, 116.7, 116.3, 50.9, 41.0, 37.0, 26.6, -1.8.

**IR (film, cm<sup>-1</sup>):** 3080, 3024, 2951, 2897, 1720, 1650, 1633, 1602, 1493, 1434, 1372, 1250, 1195, 1143, 1030, 916, 834, 699.

**MS (EI):**  $m/z$  = 314 (M<sup>+</sup>, 1), 283 (1), 223 (9), 191 (36), 175 (4), 163 (14), 149 (21), 135 (7), 121 (28), 105 (8), 89 (100), 75 (33), 59 (39).

**HRMS (EI):** calculated for C<sub>19</sub>H<sub>26</sub>O<sub>2</sub>Si:  $m/z$  = 314.1702; found  $m/z$  = 314.1721.

### **(2E)-Methyl 3-allyl-6-(diisopropylsilyl)hexa-2,5-dienoate (3o)**

According to the general procedure B the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and CoBr<sub>2</sub>(dppe) (63 mg, 0.1 mmol) in 0.5 mL dichloromethane. Then allyldiisopropylsilane (78 mg, 0.5 mmol) and methyl hex-5-en-2-ynoate (186 mg, 1.5 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3o** was obtained as colorless oil (78 mg, 0.28 mmol, 56%) containing the (5E)- and the (5Z)-isomer in a 58:42 ratio which was determined with the doublet at 3.07 and 2.99 ppm. The spectroscopic data are given for both isomers.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 6.49-6.40 (m, 0.6H), 6.16-6.06 (m, 0.4H), 5.90-5.75 (m, 1H), 5.71 (s, 1H), 5.69-5.61 (m, 1H), 5.15-4.98 (m, 2H), 3.84 (d,  $J$  = 6.8 Hz, 0.4H), 3.69 (s, 3H), 3.60-3.57 (m, 0.6H), 3.40 (d,  $J$  = 6.8 Hz, 2H), 3.07 (d,  $J$  = 7.2 Hz, 1.2H), 2.99 (d,  $J$  = 6.4 Hz, 0.8H), 1.00 (m, 14H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.7, 159.5, 158.8, 146.2, 146.0, 136.1, 135.7, 134.8, 134.7, 130.9, 126.7, 125.6, 116.8, 116.7, 116.6, 116.4, 115.8, 115.7, 50.9, 45.3, 41.1, 36.8, 36.4, 32.0, 18.9, 18.8, 18.6, 18.5, 18.4, 16.6, 10.8, 10.6.



**IR (film, cm<sup>-1</sup>):** 3079, 2944, 2891, 2864, 2103, 1722, 1650, 1634, 1605, 1462, 1434, 1368, 1249, 1194, 1144, 999, 881, 803.

**MS (EI):**  $m/z$  = 280 ( $M^+$ , 1), 265 (1), 249 (1), 237 (19), 223 (1), 205 (18), 177 (28), 167 (86), 149 (33), 135 (33), 115 (24), 103 (19), 91 (100), 75 (78), 59 (60).

**HRMS (EI):** calculated for C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>Si:  $m/z$  = 280.1859; found  $m/z$  = 280.1851.

### **(5E)-3-Methyl-1-phenyl-7-(trimethylsilyl)hepta-2,5-dien-1-one (3p)**

According to the general procedure B the catalyst was prepared from zinc iodide (64 mg, 0.2 mmol), zinc dust (13 mg, 0.2 mmol) and CoBr<sub>2</sub>(dppe) (63 mg, 0.1 mmol) in 0.5 mL dichloromethane. Then but-3-enyltrimethylsilane (0.09 mL, 0.5 mmol) and 1-phenylbut-2-yn-1-one (144 mg, 2.0 mmol) were added to the reaction mixture which subsequently was stirred for 16 h. After work up and purification by flash column chromatography (silica gel, pentane/diethyl ether 10:1) the desired product **3p** was obtained as yellow oil (64 mg, 0.23 mmol, 47%) containing the (2E)- and the (2Z)-isomer in a 80:20 ratio which was determined with the singlet at 2.20 and 2.17 ppm.

Spectroscopic data for the major (2E)-isomer:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 7.95-7.90 (m, 2H), 7.55-7.41 (m, 3H), 6.78-6.76 (m, 1H), 5.71-5.60 (m, 1H), 5.42-5.33 (m, 1H), 2.95 (d,  $J$  = 7.2 Hz, 2H), 2.20 (s, 3H), 1.54 (d,  $J$  = 8.7 Hz, 2H), 0.03 (s, 9H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 191.8, 158.9, 139.3, 132.2, 129.0, 128.4, 128.2, 122.5, 120.6, 38.6, 20.1, 18.6, -1.7.

**IR (film, cm<sup>-1</sup>):** 3391, 3013, 2954, 1662, 1612, 1579, 1448, 1421, 1387, 1361, 1247, 1155, 1050, 1003, 857, 774, 701, 660.

**MS (EI):**  $m/z$  = 272 ( $M^+$ , 3), 257 (3), 231 (3), 217 (3), 181 (4), 167 (8), 152 (2), 141 (3), 128 (3), 115 (3), 105 (23), 91 (5), 73 (100).

**HRMS (EI):** calculated for C<sub>17</sub>H<sub>24</sub>OSi:  $m/z$  = 272.1596; found  $m/z$  = 272.1594.

### **(E)-Ethyl 4-(4-chloro-2,6-diethyltetrahydro-2H-pyran-3-yl)-3-methylbut-2-enoate (4)**

A solution of (2E,5E)-ethyl 3-methyl-7-(trimethylsilyl)hepta-2,5-dienoate (**3i**) (100 mg, 0.42 mmol) and propionaldehyde (0.062 mL, 0.84 mmol) in 1.0 mL dichloromethane is cooled to -78 °C. Then a solution of titanium tetrachloride (0.420 mL, 1 M in dichloromethane) is added slowly. The reaction mixture is then stirred for 16 h while warming up to room temperature. After complete conversion 2 mL water are added and the mixture is transferred in a 20/20 mL water-dichloromethane mixture. The aqueous phase is extracted twice with 20 mL dichloromethane and the organic phase is dried over magnesium sulfate. After filtration and evaporation the crude product is purified by flash column chromatography (silica gel, pentane/diethyl ether 20:1) to obtain **4** as yellow oil (78 mg, 0.26 mmol, 61%). Spectroscopic analysis reveals two diastereomers in a 50:50 ratio.

Spectroscopic data for both isomers:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.80-5.74 (m, 1H), 4.28-4.19 (m, 0.5H), 4.12 (qd,  $J$  = 3.6, 7.1 Hz, 2H), 3.82-3.72 (m, 0.5H), 3.26-3.18 (m, 1H), 3.18-3.11 (m, 0.5H), 2.99-2.91 (m, 0.5H), 2.65-2.57 (m, 0.5H), 2.40 (m,  $J$  = 4.9 Hz, 1H), 2.20 (s, 3H), 2.18-2.08 (m, 1H), 1.91-1.83 (m, 0.5H), 1.81-1.30 (m, 6H), 1.26 (td,  $J$  = 3.0, 7.2 Hz, 3H), 0.96-0.84 (m, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.7, 166.5, 159.8, 158.0, 117.6, 116.9, 82.4, 82.3, 78.8, 77.5, 62.9, 61.9, 59.5, 59.4, 47.3, 42.8, 42.1, 40.6, 37.5, 34.1, 28.7, 26.5, 19.4, 18.8, 14.3, 10.8, 10.1, 9.9, 9.8.

**IR (film, cm<sup>-1</sup>):** 2965, 2936, 2878, 2847, 1716, 1646, 1463, 1369, 1349, 1320, 1301, 1276, 1224, 1149, 1096, 1081, 1046, 883, 743.

**MS (EI):**  $m/z$  = 302 (M<sup>+</sup>, 6), 267 (10), 257 (23), 237 (5), 221 (6), 209 (41), 191 (9), 179 (14), 163 (26), 135 (100), 121 (29), 107 (30), 93 (68), 81 (46), 67 (21), 59 (40).

**HRMS (EI):** calculated for C<sub>16</sub>H<sub>27</sub>ClO<sub>3</sub>:  $m/z$  = 302.1649; found  $m/z$  = 302.1651.

### **(E)-Ethyl 6-hydroxy-3,7-dimethyl-5-vinyloct-2-enoate (5)**

To a solution of (2*E*,5*E*)-ethyl 3-methyl-7-(trimethylsilyl)hepta-2,5-dienoate (**3i**) (380 mg, 1.58 mmol) and isobutyraldehyde (0.10 mL, 1.05 mmol) in 2.5 mL dichloromethane is added dropwise a solution of titanium tetrachloride (1.58 mL, 1 M in dichloromethane) at room temperature. The reaction mixture is then stirred for 16 h. After complete conversion the mixture is transferred in a 20/20 mL water-dichloromethane mixture. The aqueous phase is extracted twice with 20 mL dichloromethane and the organic phase is dried over magnesium sulfate. After filtration and evaporation the crude product is purified by flash column chromatography (silica gel, pentane/diethyl ether 3:1) to obtain **5** as yellow oil (182 mg, 0.76 mmol, 72%) containing the *anti*- and the *syn*-alcohol in a 60:40 ratio which was determined by GCMS analysis. The isomers could be separated partially by column chromatography.

Spectroscopic data for the *anti*-alcohol:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.62 (s, 1H), 5.52 (td,  $J$  = 9.8, 17.1 Hz, 1H), 5.09-4.96 (m, 2H), 4.12 (q,  $J$  = 6.9 Hz, 2H), 3.25 (dd,  $J$  = 4.5, 6.8 Hz, 1H), 2.60 (dd,  $J$  = 3.4, 13.2 Hz, 1H), 2.47-2.33 (m, 1H), 2.12 (s, 3H), 2.06 (dd,  $J$  = 10.8, 13.4 Hz, 1H), 1.88-1.76 (m, 1H), 1.51 (bs, 1H), 1.26 (t,  $J$  = 7.2 Hz, 3H), 0.92 (dd,  $J$  = 6.8, 18.1 Hz, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.6, 158.5, 138.4, 117.2, 116.6, 79.0, 59.4, 46.0, 41.7, 30.3, 20.0, 18.9, 15.6, 14.3.

Spectroscopic data for the *syn*-alcohol:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.74-5.61 (m, 2H), 5.18-5.04 (m, 2H), 4.13 (q,  $J$  = 7.2 Hz, 2H), 3.12-3.05 (m, 1H), 2.55-2.44 (m, 1H), 2.41-2.32 (m, 1H), 2.23-2.15 (m, 1H), 2.13 (s, 3H), 1.68 (dq,  $J$  = 6.8, 13.6 Hz, 1H), 1.50 (bs, 1H), 1.26 (dq,  $J$  = 7.2 Hz, 3H), 0.93 (dd,  $J$  = 6.4, 12.1 Hz, 1H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 166.6, 157.5, 136.9, 117.8, 117.5, 77.9, 59.5, 44.6, 43.2, 31.2, 19.3, 18.7, 17.9, 14.3.

Spectroscopic data for both isomers:

**IR (film, cm<sup>-1</sup>):** 3499, 3074, 2968, 2875, 1708, 1645, 1460, 1380, 1286, 1227, 1152, 1048, 998, 919, 876, 834, 739, 686, 626.

**MS (EI):**  $m/z$  = 240 (M<sup>+</sup>, 1), 225 (1), 197 (4), 179 (4), 168 (20), 153 (12), 139 (32), 122 (28), 111 (25), 95 (100), 79 (36), 67 (11), 55 (27).

**HRMS (EI):** calculated for C<sub>14</sub>H<sub>24</sub>O<sub>3</sub>:  $m/z$  = 240.1725; found  $m/z$  = 240.1722.

### **Ethyl 2-(5-isopropyl-2-methyl-4-vinyltetrahydrofuran-2-yl)acetate (6)**

A solution containing (*E*)-ethyl 6-hydroxy-3,7-dimethyl-5-vinyloct-2-enoate (91 mg, 0.38 mmol) in 5.0 mL tetrahydrofuran is cooled to 0 °C. Then sodium hydride (8 mg, 0.19 mmol,

60% in paraffin oil) is added and the reaction is warmed to room temperature over 2 h. After full conversion the reaction mixture is quenched with 2 mL water and is transferred in a 10/20 mL water-diethyl ether mixture. The aqueous phase is extracted twice with 20 mL diethyl ether and the organic phase is dried over magnesium sulfate. After filtration and evaporation the crude product is purified by filtration through a short plug of silica gel (pentane/diethyl ether 10:1) to obtain the desired product **6** as pale yellow oil (80 mg, 0.33 mmol, 88%). The resulting 4 diastereomers could be resolved partially by cyclisation of the separated *syn*- and *anti*-alcohol.

Spectroscopic data for both cycloisomerization products of the *anti*-alcohol, the ratio (50:50) was determined with the singlet at 1.42 and 1.31 ppm:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.97-5.80 (m, 1H), 5.04-4.99 (m, 1H), 4.98 (s, 1H), 4.12 (q,  $J$  = 7.2 Hz, 2H), 3.44 (ddd,  $J$  = 5.1, 9.3, 17.8 Hz, 1H), 2.89-2.73 (m, 1H), 2.62-2.51 (m, 2H), 2.39-2.30 (m, 0.5H), 2.03-1.98 (m, 1H), 1.75-1.62 (m, 1.5H), 1.42 (s, 1.5H), 1.31 (s, 1.5H), 1.25 (t,  $J$  = 7.2 Hz, 3H), 0.95 (dd,  $J$  = 4.0, 6.6 Hz, 3H), 0.81 (dd,  $J$  = 4.0, 6.6 Hz, 3H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 171.1, 171.0, 138.4, 138.3, 115.0, 86.8, 85.7, 79.5, 79.2, 60.2, 60.1, 47.4, 46.9, 46.7, 46.1, 44.8, 44.2, 29.0, 28.9, 28.2, 26.5, 20.4, 20.2, 19.0, 18.6, 14.2.

Spectroscopic data for both cycloisomerization products of the *syn*-alcohol, the ratio (70:30) was determined with the singlet at 1.36 and 1.28 ppm:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  = 5.75-5.62 (m, 1H), 5.09-4.95 (m, 2H), 4.16-4.07 (m, 2H), 3.51-3.45 (m, 1H), 2.74-2.61 (m, 1H), 2.56-2.48 (m, 2H), 2.07-1.92 (m, 1.5H), 1.81-1.69 (m, 1.5H), 1.36 (s, 0.9H), 1.28 (s, 2.1H), 1.25 (t,  $J$  = 7.2 Hz, 3H), 0.94-0.86 (m, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  = 171.1, 170.9, 139.5, 139.3, 115.4, 115.3, 87.8, 87.4, 79.7, 79.5, 60.2, 60.1, 46.7, 46.6, 46.4, 44.9, 44.7, 31.4, 31.0, 27.8, 27.4, 19.4, 17.9, 17.6, 14.2, 14.1.

Spectroscopic data for all cycloisomerization products:

**IR (film, cm<sup>-1</sup>):** 3078, 2970, 2879, 1736, 1641, 1460, 1377, 1332, 1303, 1223, 1105, 1035, 956, 916, 848, 806.

**MS (EI):**  $m/z$  = 239 ( $M^+$ , 1), 225 (1), 197 (17), 168 (71), 153 (37), 122 (43), 109 (34), 95 (100), 79 (36), 67 (18), 55 (21).

**HRMS (EI):** calculated for C<sub>14</sub>H<sub>24</sub>O<sub>3</sub>:  $m/z$  = 240.1725; found  $m/z$  = 240.1720.

### (2*E*)-Ethyl 6-iodo-3-methylhexa-2,5-dienoate (**7**)

To a solution of (2*E*,5*E*)-ethyl 3-methyl-6-(trimethylsilyl)hexa-2,5-dienoate (**3k**) (100 mg, 0.44 mmol) in 4 mL acetonitrile is added *N*-iodosuccinimide (169 mg, 0.75 mmol) in one portion. The solution is then heated to 80 °C for 4 h and the reaction is carried out in the dark. After GCMS analysis indicates full conversion the reaction is quenched with 4 mL saturated sodium sulfite. The reaction mixture is transferred into a 20/20 mL water-diethyl ether mixture and the aqueous phase is extracted twice with 20 mL diethyl ether. The combined organic phases are washed with 30 mL brine and dried over magnesium sulfate. After filtration and evaporation the crude product is purified by flash column chromatography (silica gel, pentane/diethyl ether 10:1) to obtain the desired product **7** as colorless oil (100 mg, 0.36 mmol, 81%) containing the (5*E*)- and the (5*Z*)-isomer in a 76:24 ratio which was determined with the dublet at 2.99 and 2.84 ppm.

Spectroscopic data for the major (5*E*)-isomer:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 6.54-6.43 (m, 1H), 6.23-6.13 (m, 1H), 5.71-5.66 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.99 (d, *J* = 6.8 Hz, 2H), 2.18 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 166.5, 155.4, 136.8, 116.8, 85.8, 59.7, 45.4, 19.0, 14.3.

**IR (film, cm<sup>-1</sup>):** 3066, 2981, 2936, 1716, 1651, 1606, 1444, 1383, 1368, 1352, 1307, 1273, 1221, 1146, 1096, 1049, 954, 912, 867, 695, 623.

**MS (EI):** *m/z* = 280 (M<sup>+</sup>, 4), 235 (29), 207 (1), 167 (9), 153 (36), 141 (1), 125 (36), 117 (2), 107 (57), 97 (12), 79 (100), 67 (16), 53 (19).

**HRMS (EI):** calculated for C<sub>9</sub>H<sub>13</sub>IO<sub>2</sub>: *m/z* = 279.9960; found *m/z* = 279.9965.

#### **(2*E*,5*E*,10*E*)-Ethyl 3,10-dimethyl-11-phenylundeca-2,5,7,10-tetraenoate (8)**

To a degassed mixture of (2*E*)-ethyl 6-iodo-3-methylhexa-2,5-dienoate (**7**) (310 mg, 1.14 mmol), 4,4,5,5-tetramethyl-2-((4*Z*)-4-methyl-5-phenylpenta-1,4-dienyl)-1,3,2-dioxaborolane (**3g**) (260 mg, 0.92 mmol) in 12 mL tetrahydrofuran and 4 mL water is added thallium carbonate (1072 mg, 2.29 mmol) and tetrakis triphenylphosphinopalladium (53 mg, 0.05 mmol) in one portion. The reaction mixture is then stirred for 3 h at room temperature. After full conversion the mixture is filtered through a short pad containing silica gel and magnesium sulfate. The crude product is then purified by flash column chromatography (silica gel, pentane/diethyl ether 10:1) to obtain the desired product **8** as pale yellow oil (280 mg, 0.90 mmol, 99%) containing the (7*E*)- and the (7*Z*)-isomer in a 76:24 ratio corresponding to the deployed vinyl iodide **7**.

Spectroscopic data for the major (7*E*)-isomer:

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):** δ = 7.35-7.29 (m, 2H), 7.26-7.16 (m, 3H), 6.52-6.45 (m, 1H), 6.42-6.34 (m, 1H), 6.31 (s, 1H), 5.73-5.70 (m, 1H), 5.69-5.59 (m, 1H), 5.55-5.45 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 3.08-3.02 (m, 4H), 2.19-2.18 (m, 3H), 1.87 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ = 166.7, 157.8, 138.3, 137.1, 130.6, 128.8, 128.0, 127.1, 126.0, 125.9, 125.7, 124.4, 116.3, 59.5, 43.9, 38.5, 19.0, 18.0, 14.3.

**IR (film, cm<sup>-1</sup>):** 2982, 2937, 1716, 1650, 1494, 1447, 1382, 1351, 1222, 1151, 1097, 1042, 973, 921, 879, 858, 749, 702, 650, 514.

**MS (EI):** *m/z* = 310 (M<sup>+</sup>, 4), 264 (1), 249 (1), 237 (3), 219 (3), 207 (4), 195 (4), 183 (16), 167 (20), 155 (24), 143 (31), 129 (47), 115 (46), 105 (32), 91 (100), 77 (21), 65 (10), 55 (8).

**HRMS (EI):** calculated for C<sub>21</sub>H<sub>26</sub>O<sub>2</sub>: *m/z* = 310.1933; found *m/z* = 310.1935.

#### **(2*E*,4*E*,6*E*,8*E*,10*E*)-Ethyl 3,10-dimethyl-11-phenylundeca-2,4,6,8,10-pentaenoate (9)**

To a solution of (2*E*,5*E*,10*E*)-ethyl 3,10-dimethyl-11-phenylundeca-2,5,7,10-tetraenoate (**8**) (100 mg, 0.32 mmol) in 2.5 mL benzene is added DDQ (87 mg, 0.38 mmol). The reaction mixture is stirred for 2 h at room temperature. After full conversion the mixture is filtered through a short pad of silica gel (eluent: pentane/diethyl ether 10:1). The crude product is then purified by flash column chromatography (silica gel, pentane/diethyl ether 20:1) to obtain the desired product **9** as yellow solid (37 mg, 0.12 mmol, 37%).

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ = 7.31-7.24 (m, 4H), 7.21-7.15 (m, 1H), 6.64 (dd, *J* = 10.8, 15.2 Hz, 1H), 6.53 (s, 1H), 6.50-6.43 (m, 2H), 6.40-6.32 (m, 2H), 6.23 (d, *J* = 15.5 Hz, 1H), 5.72 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.27 (s, 3H), 2.00 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H).

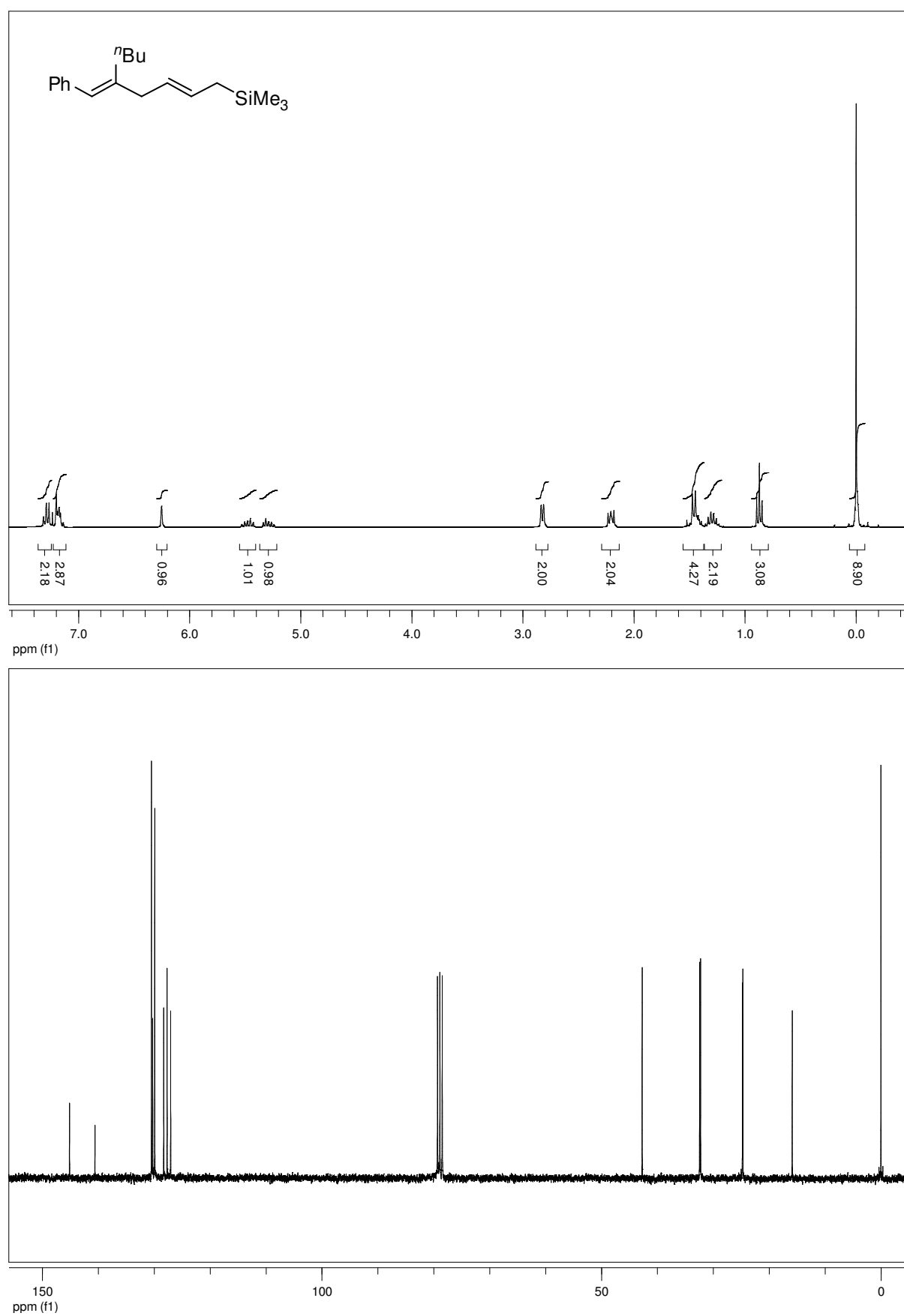
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ = 167.1, 152.2, 140.1, 137.7, 136.7, 135.9, 135.4, 134.8, 133.0, 132.2, 129.2, 128.4, 128.2, 126.8, 119.1, 59.7, 14.3, 13.9, 13.7.

**IR (film, cm<sup>-1</sup>):** 2980, 1704, 1596, 1567, 1444, 1385, 1365, 1351, 1237, 1145, 1040, 990, 921, 874, 834, 753, 703.

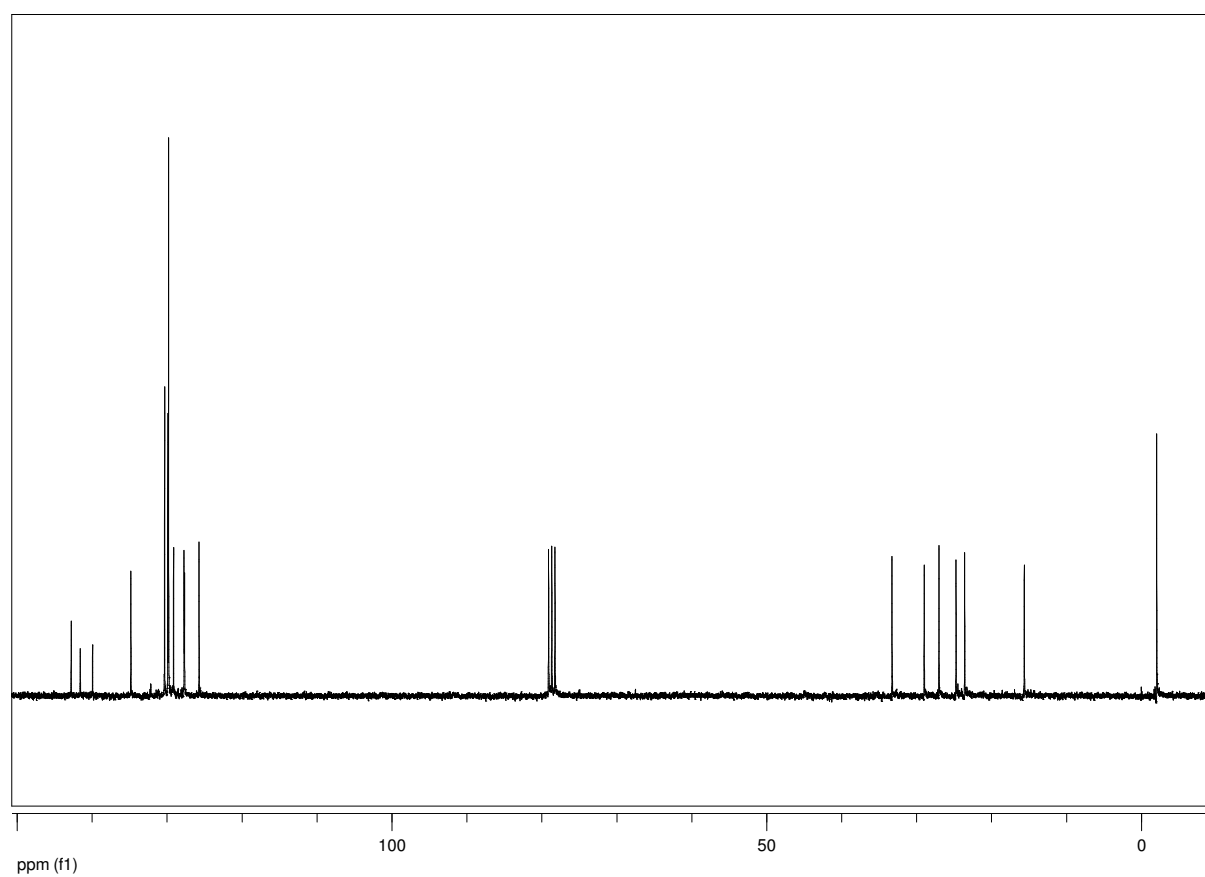
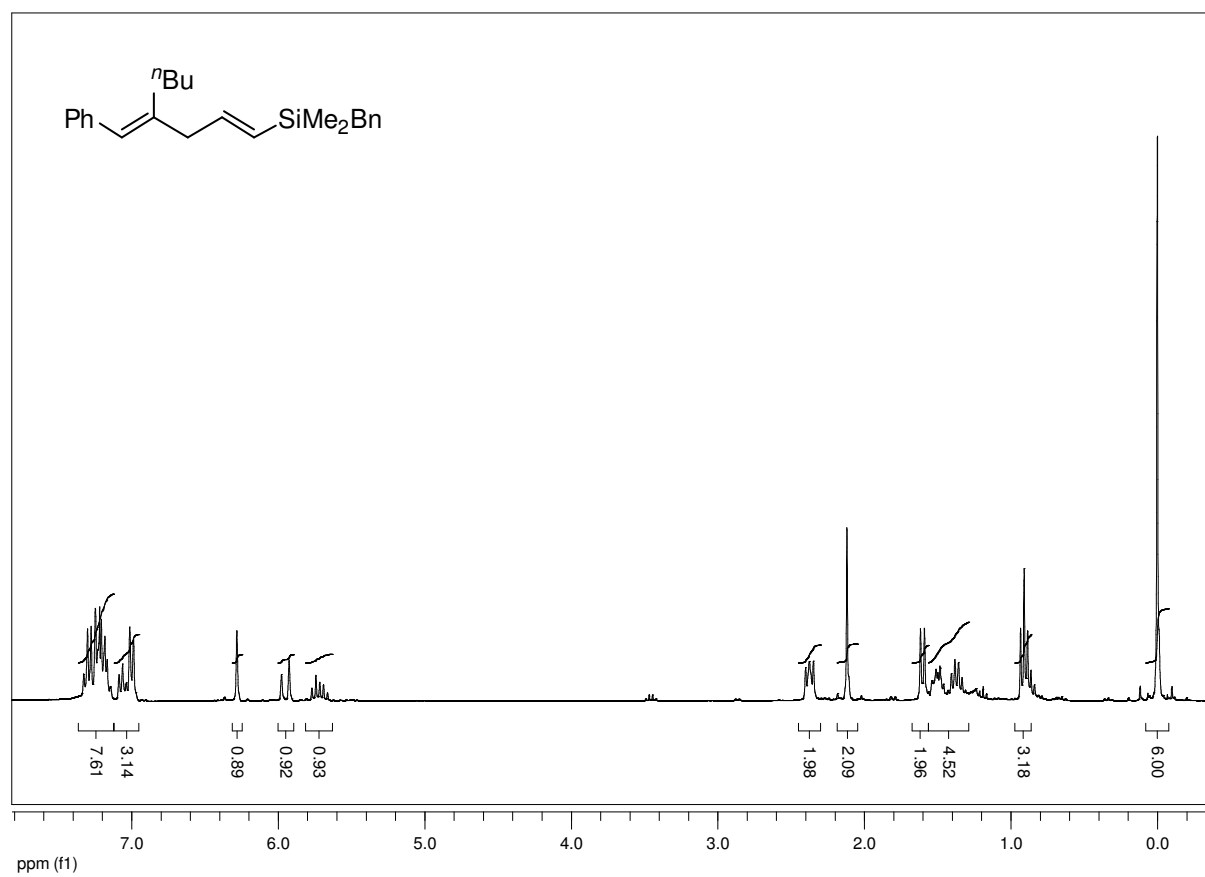
**MS (EI):** m/z = 308 (M<sup>+</sup>, 100), 293 (9), 279 (11), 262 (20), 247 (23), 235 (96), 219 (92), 205 (45), 193 (40), 179 (51), 165 (51), 143 (46), 128 (44), 115 (50), 105 (37), 91 (41).

**HRMS (EI):** calculated for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>: m/z = 308.1776; found m/z = 308.1764.

**3a**



3b

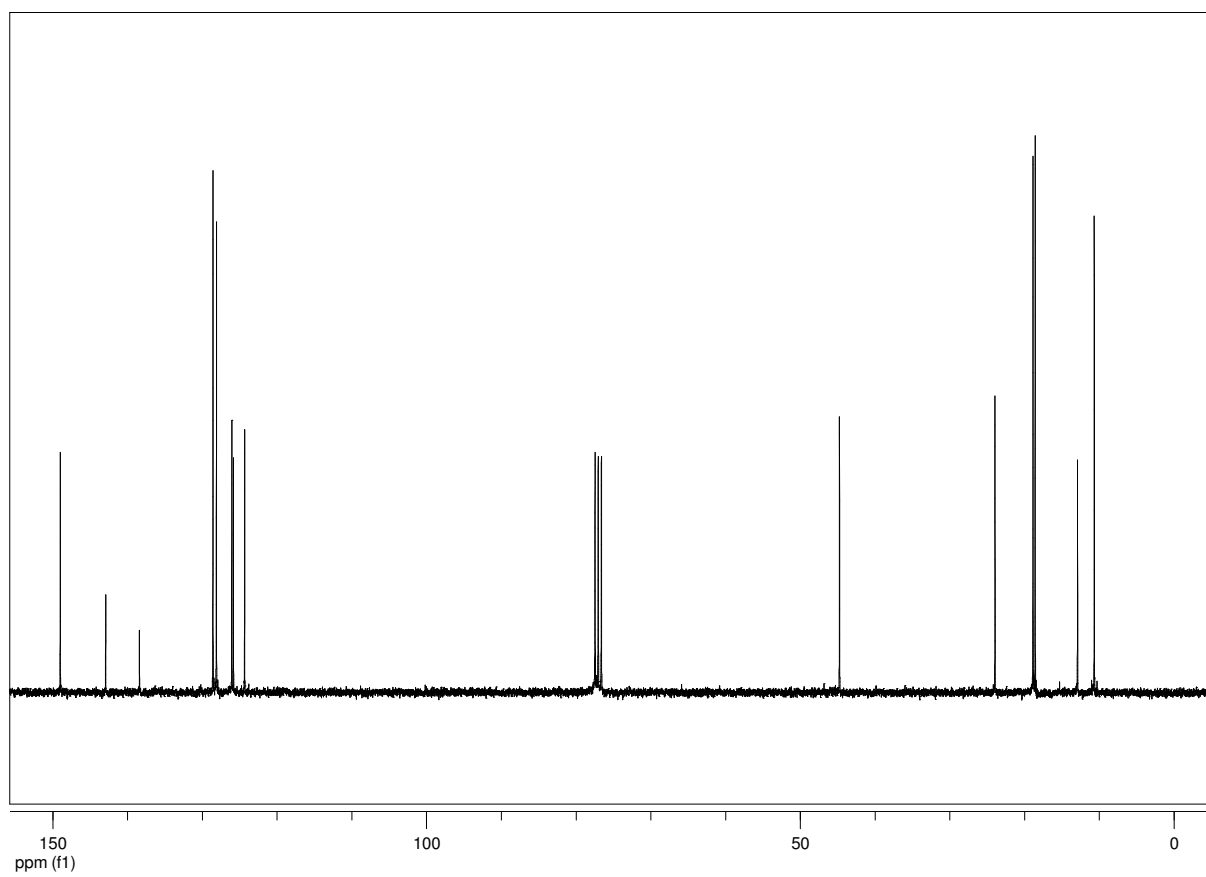


CC(C)=CC=C[Si](C)(C)C  

Chemical structure: CC(C)=CC=C[Si](C)(C)C

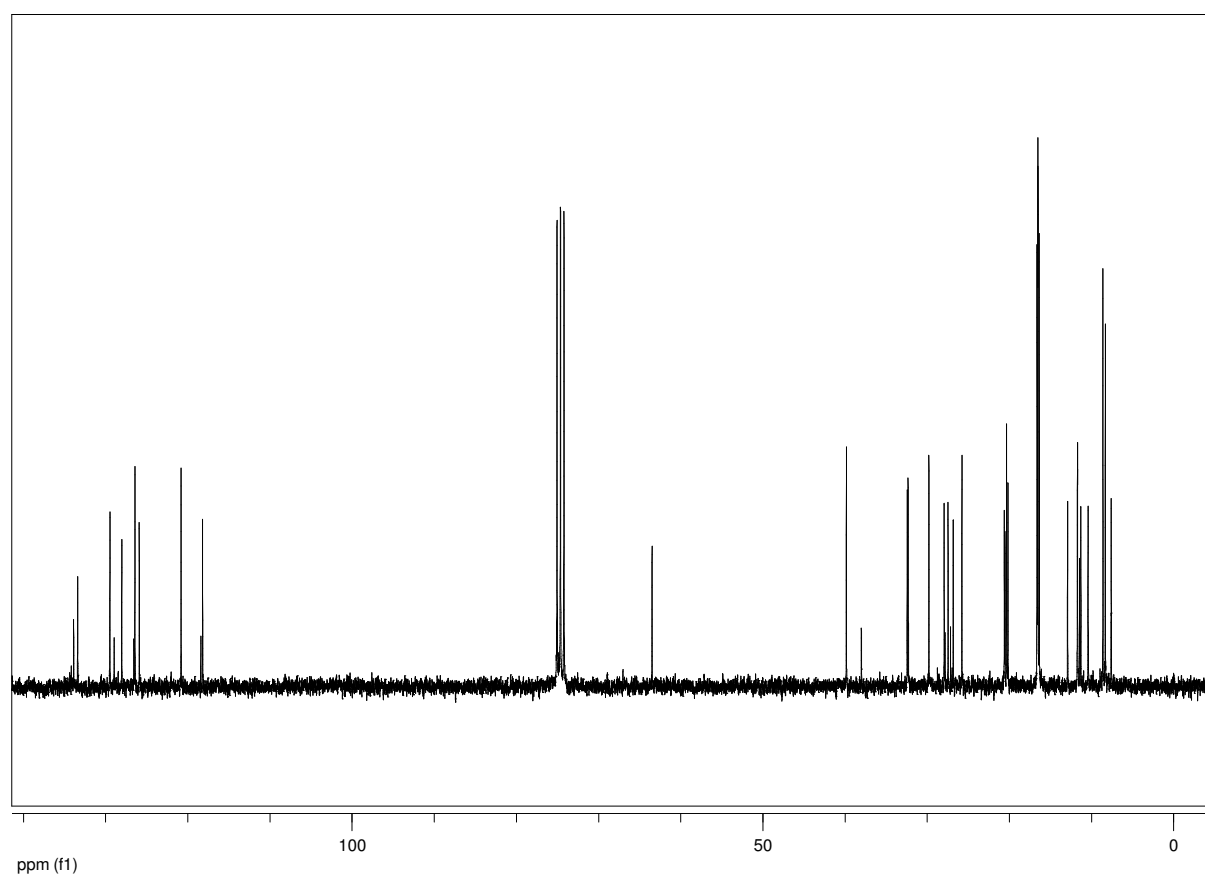
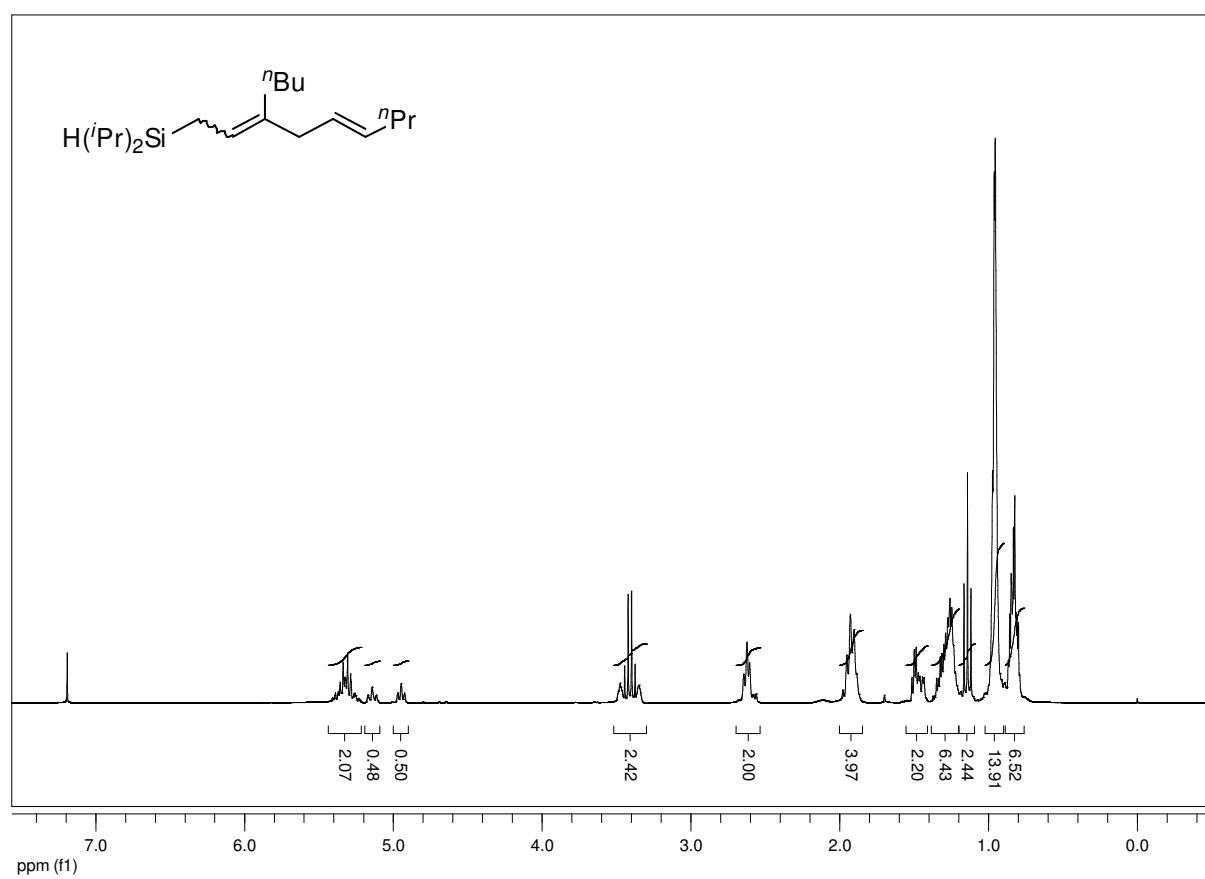
<sup>1</sup>H NMR spectrum (ppm):

- 7.29 (m, 2H, integration 2.07)
- 7.27 (m, 2H, integration 2.09)
- 6.09 (m, 1H, integration 1.88)
- 5.61 (m, 1H, integration 0.94)
- 4.91 (m, 1H, integration 0.91)
- 3.01 (m, 2H, integration 2.01)
- 2.00 (m, 2H, integration 2.00)
- 1.36 (m, 9H, integration 3.36)

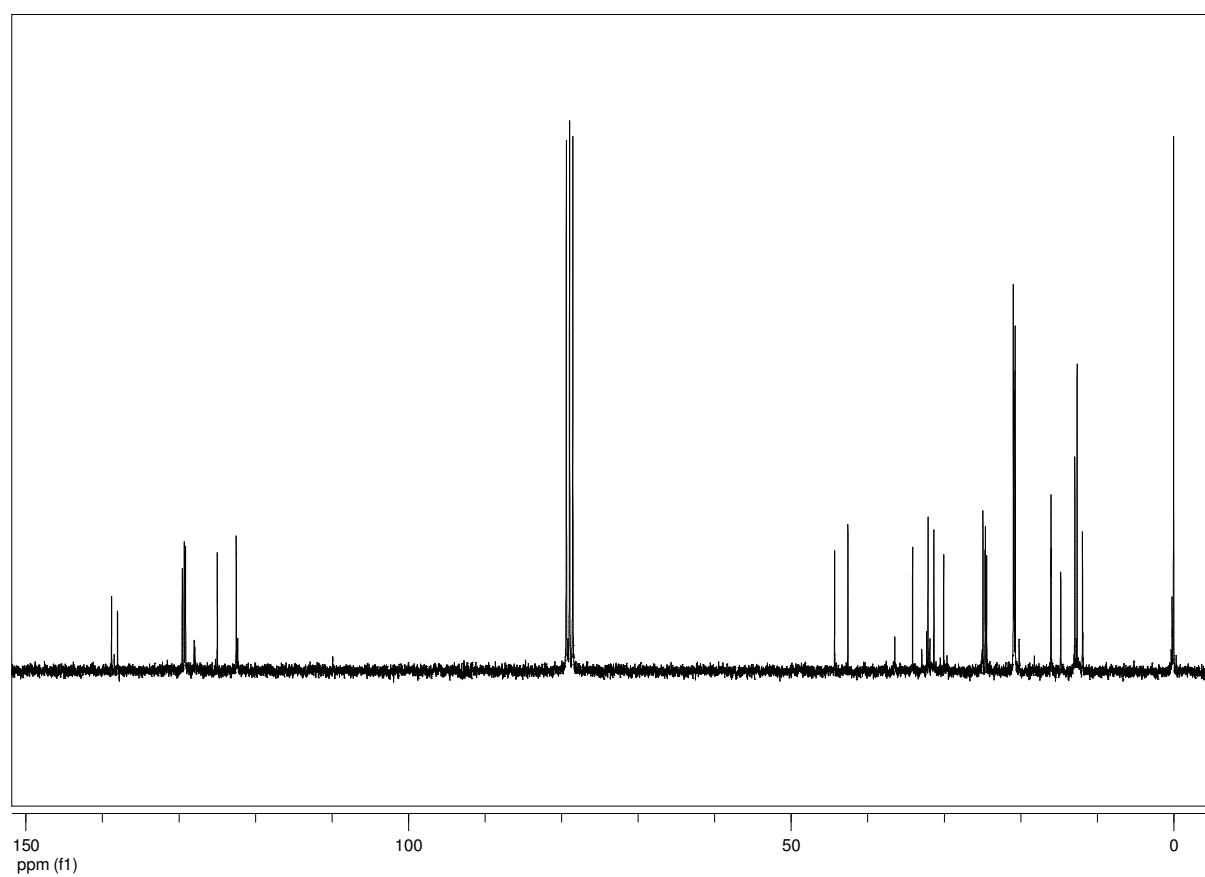
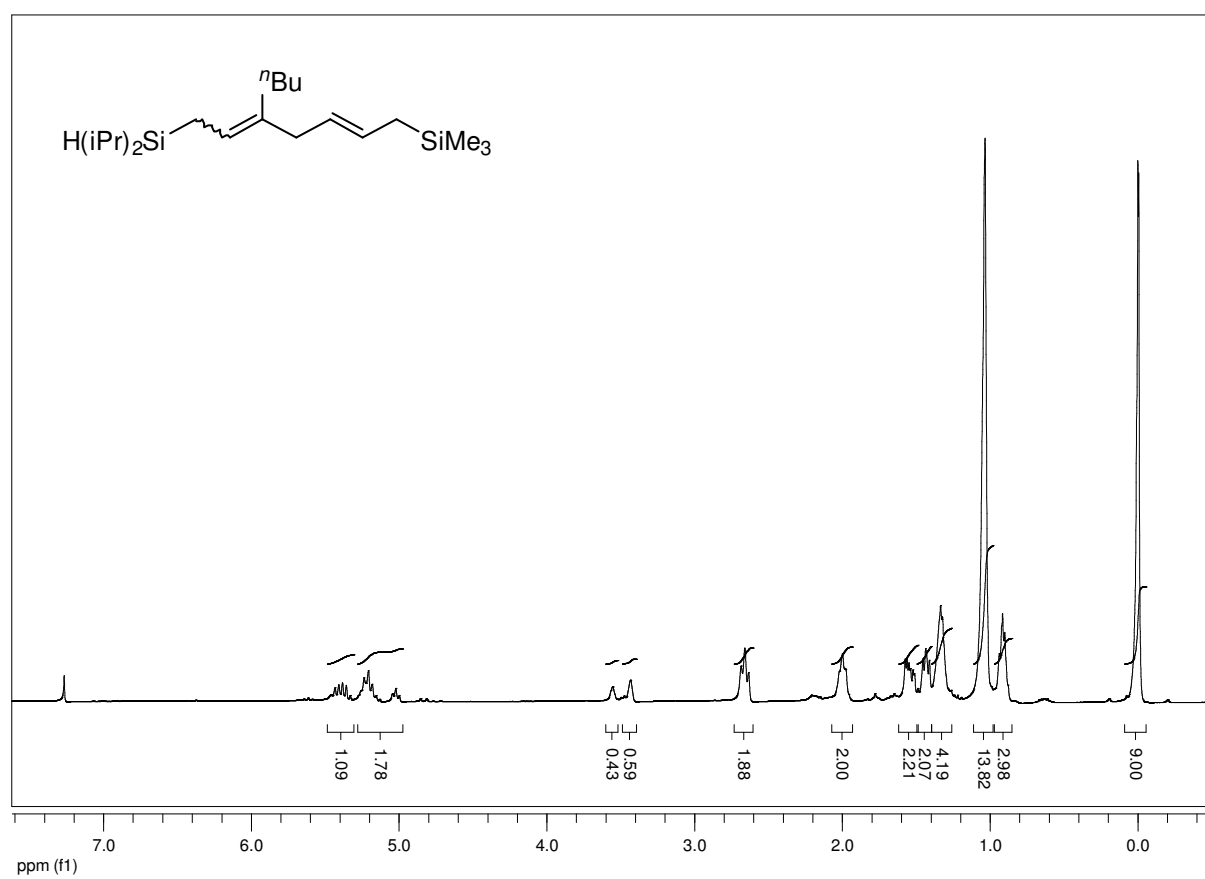




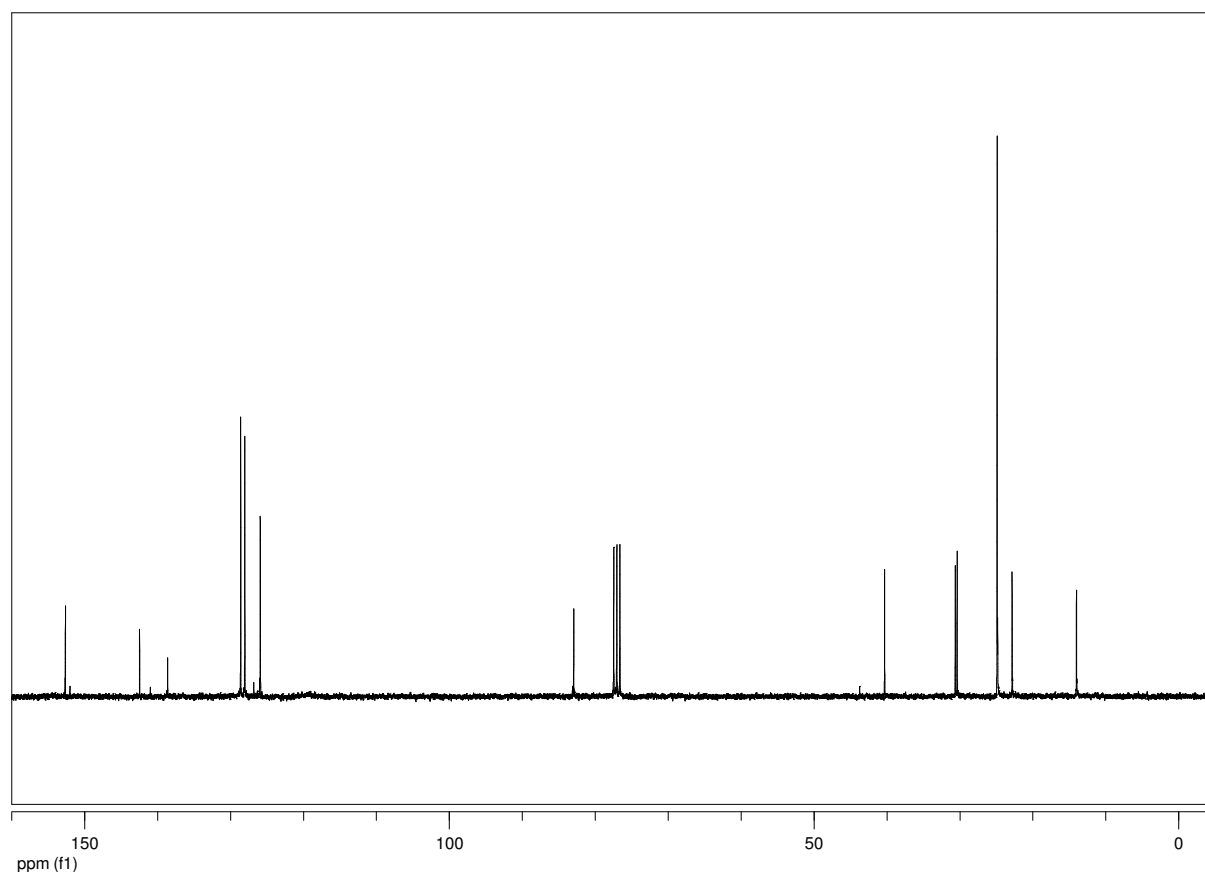
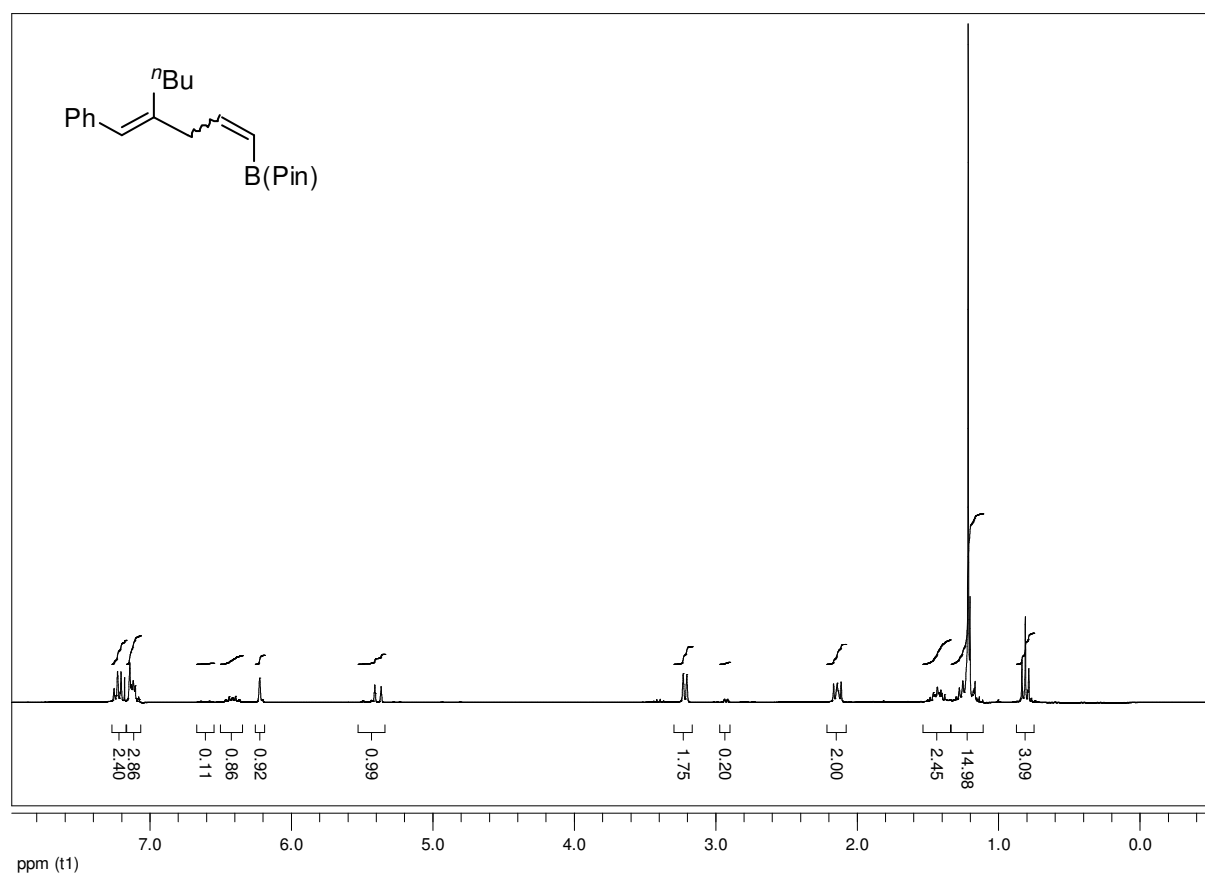
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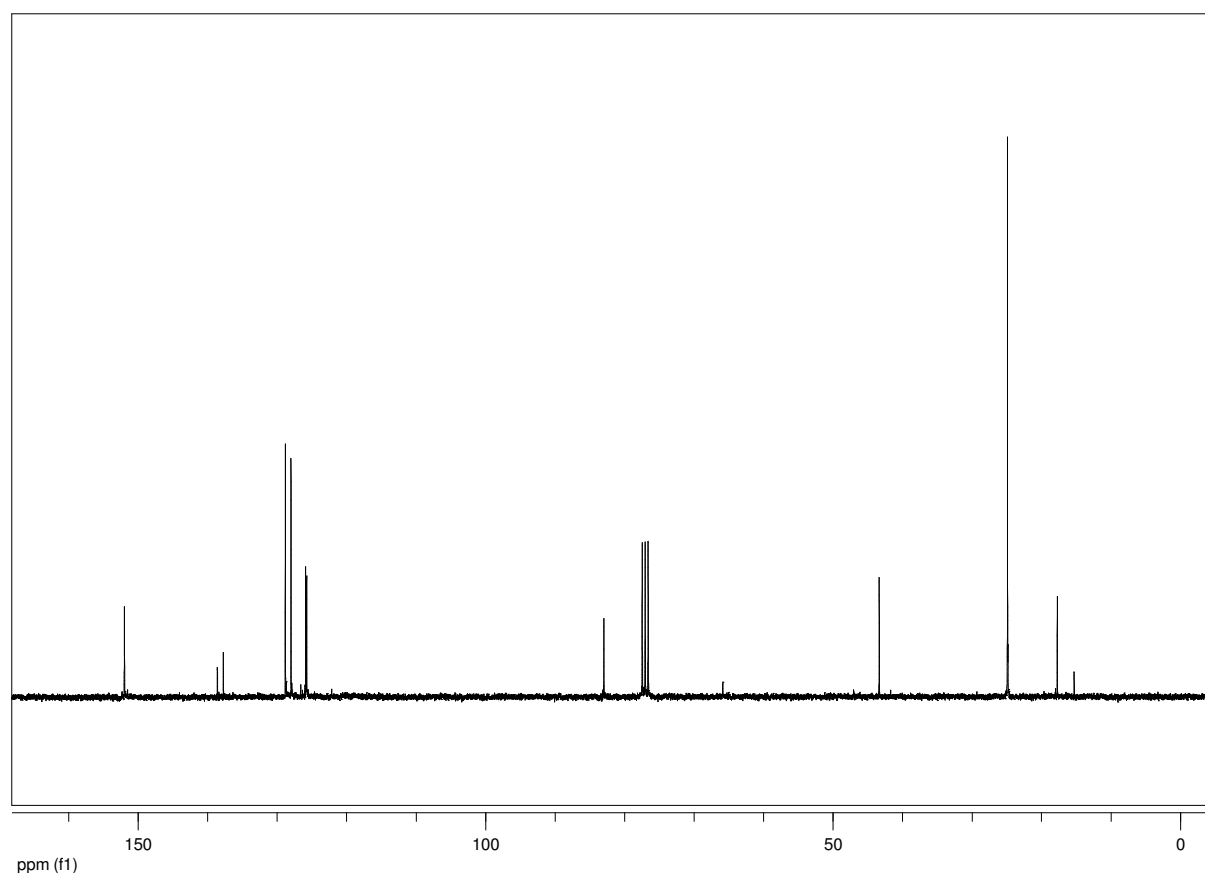
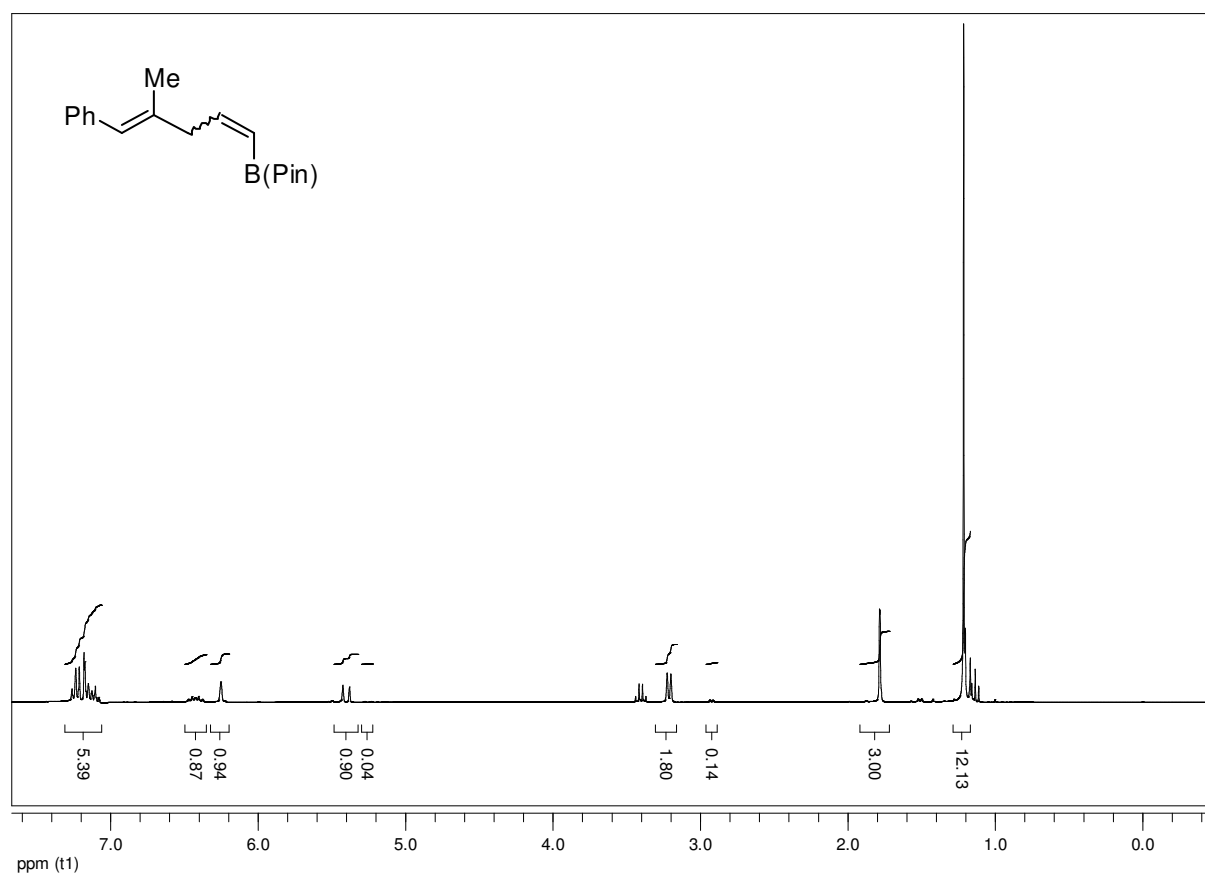
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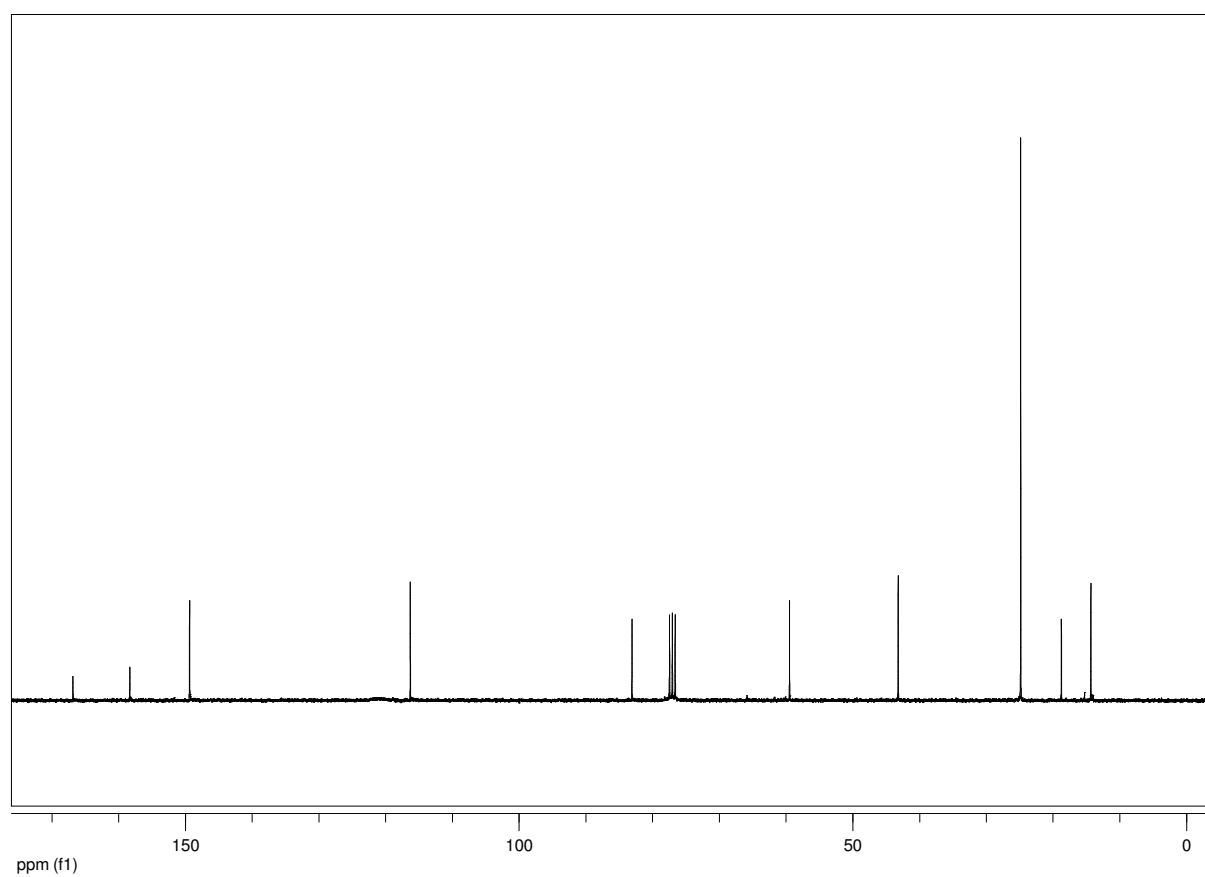
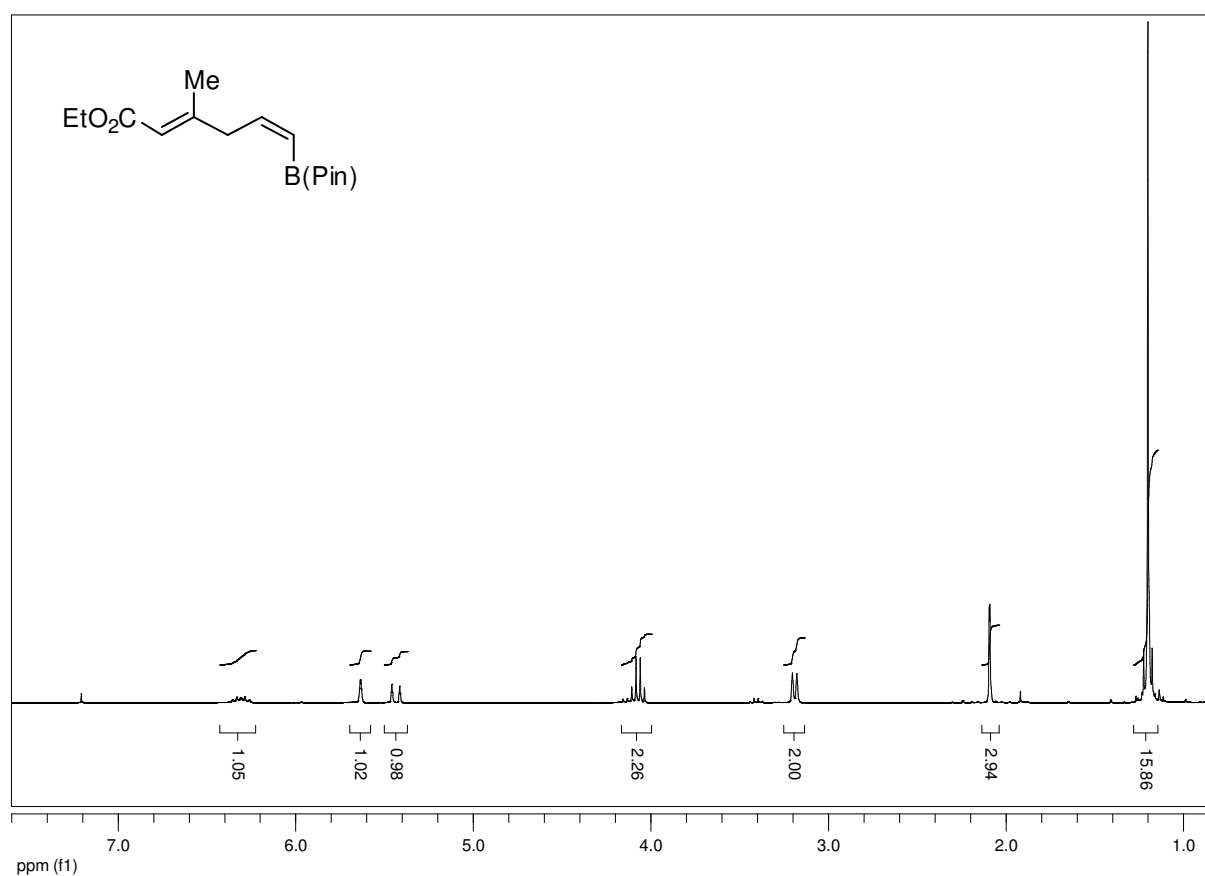
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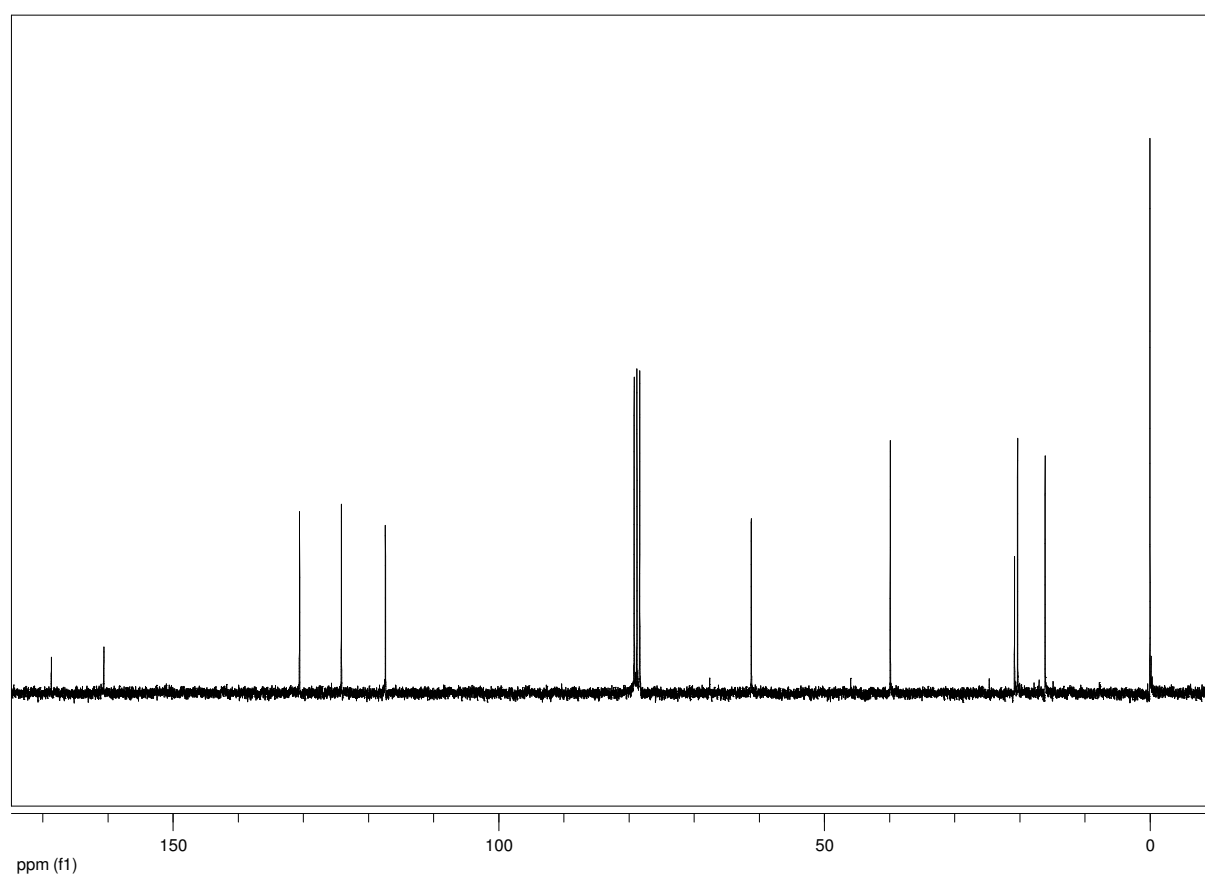
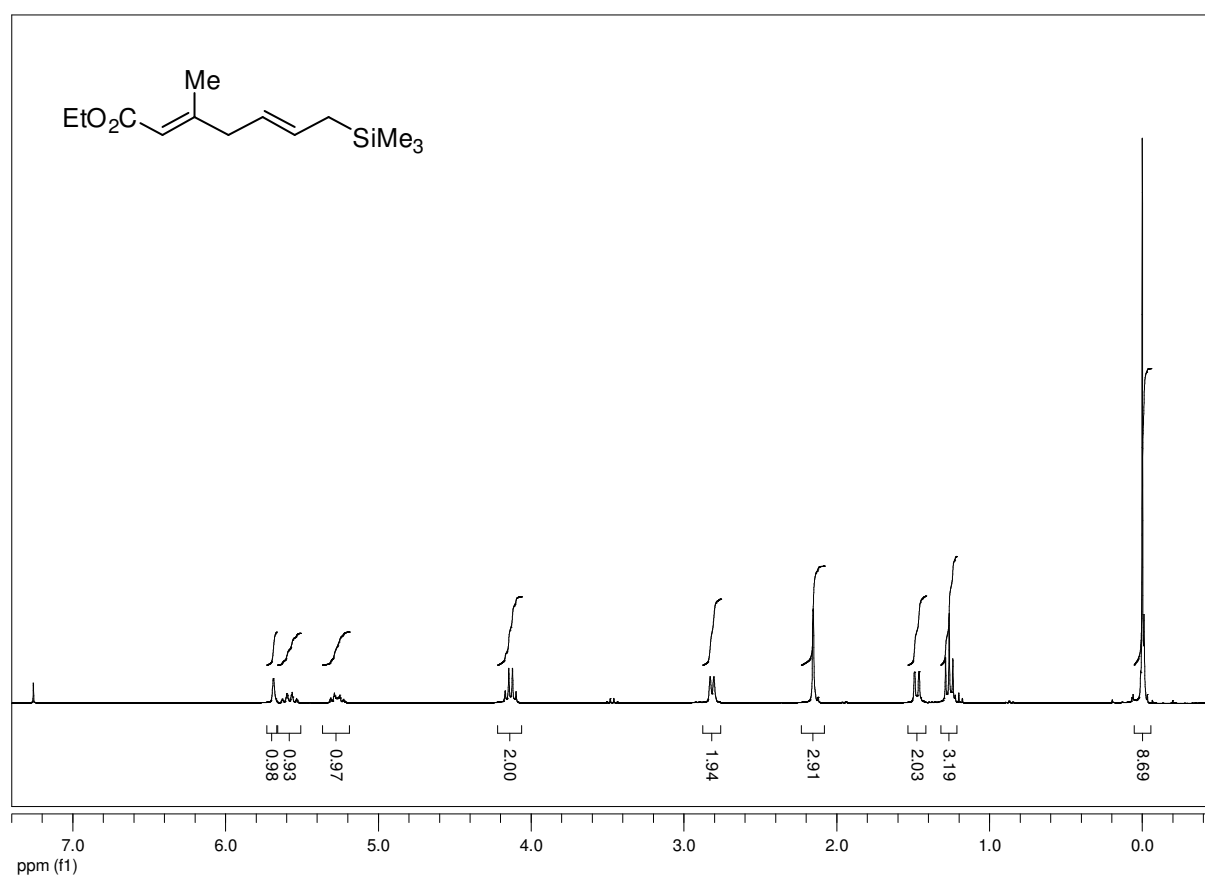
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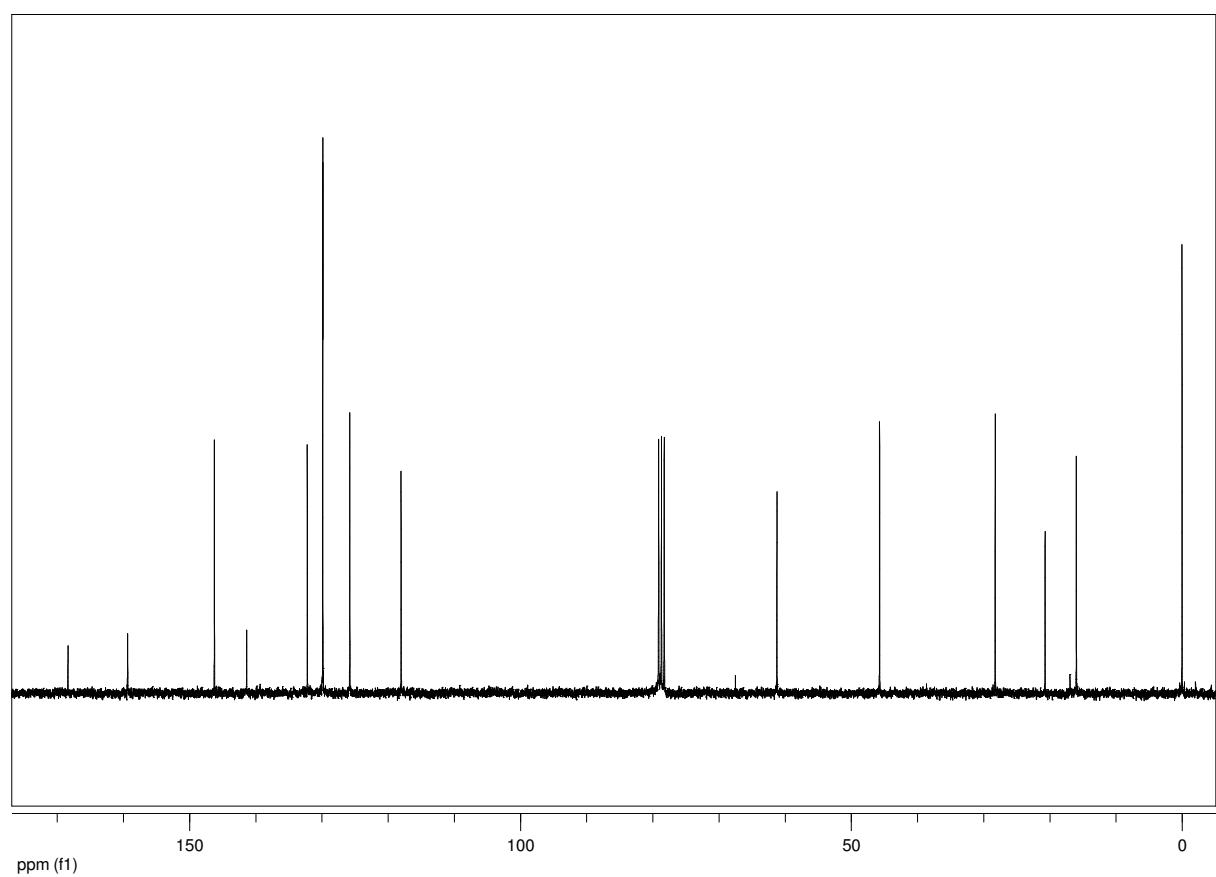
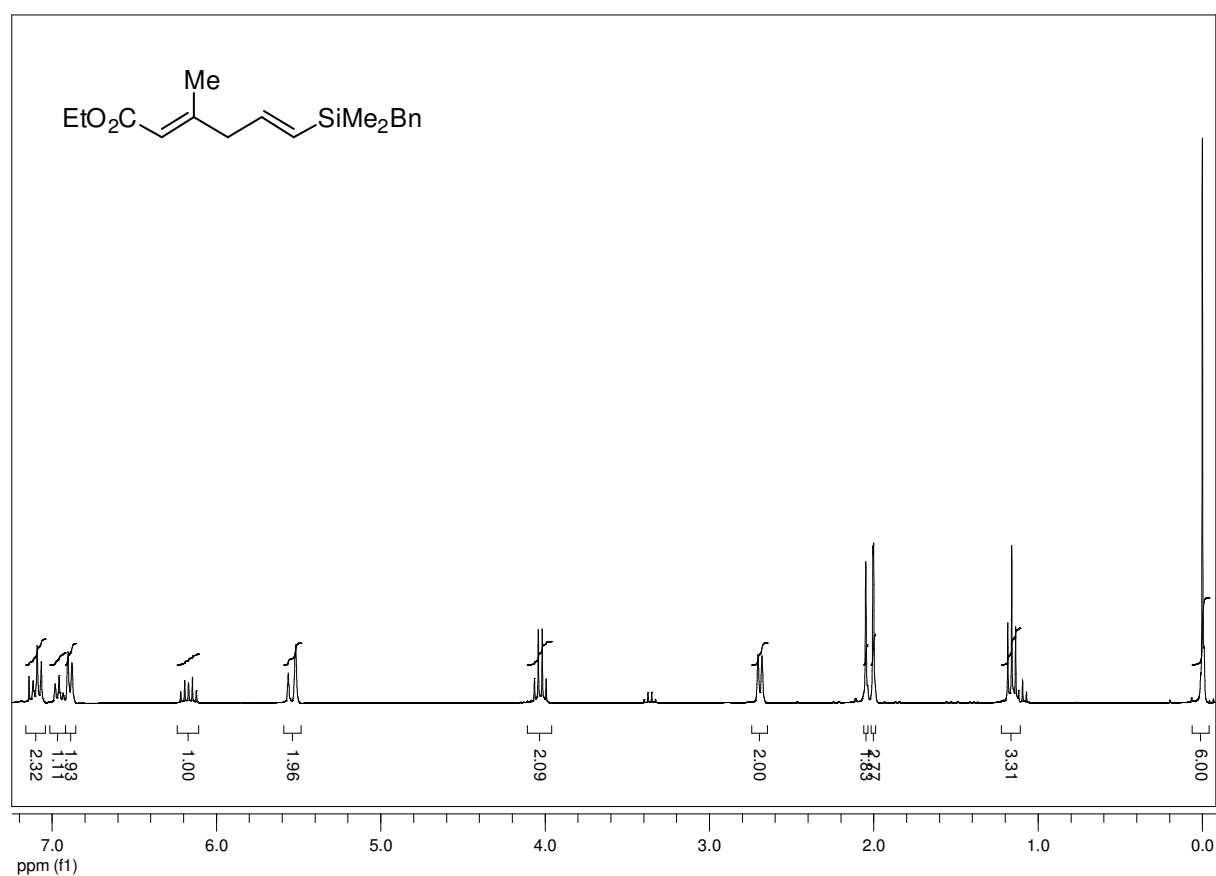
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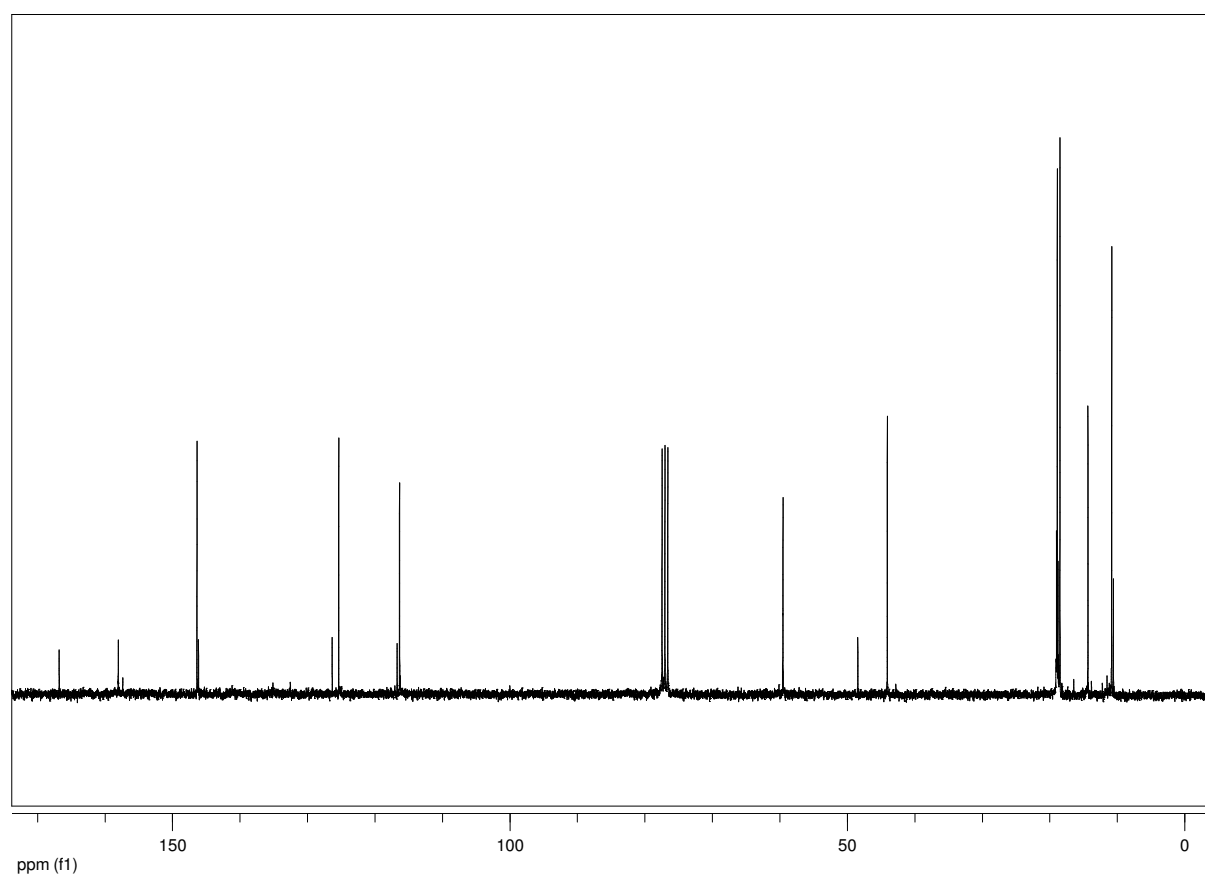
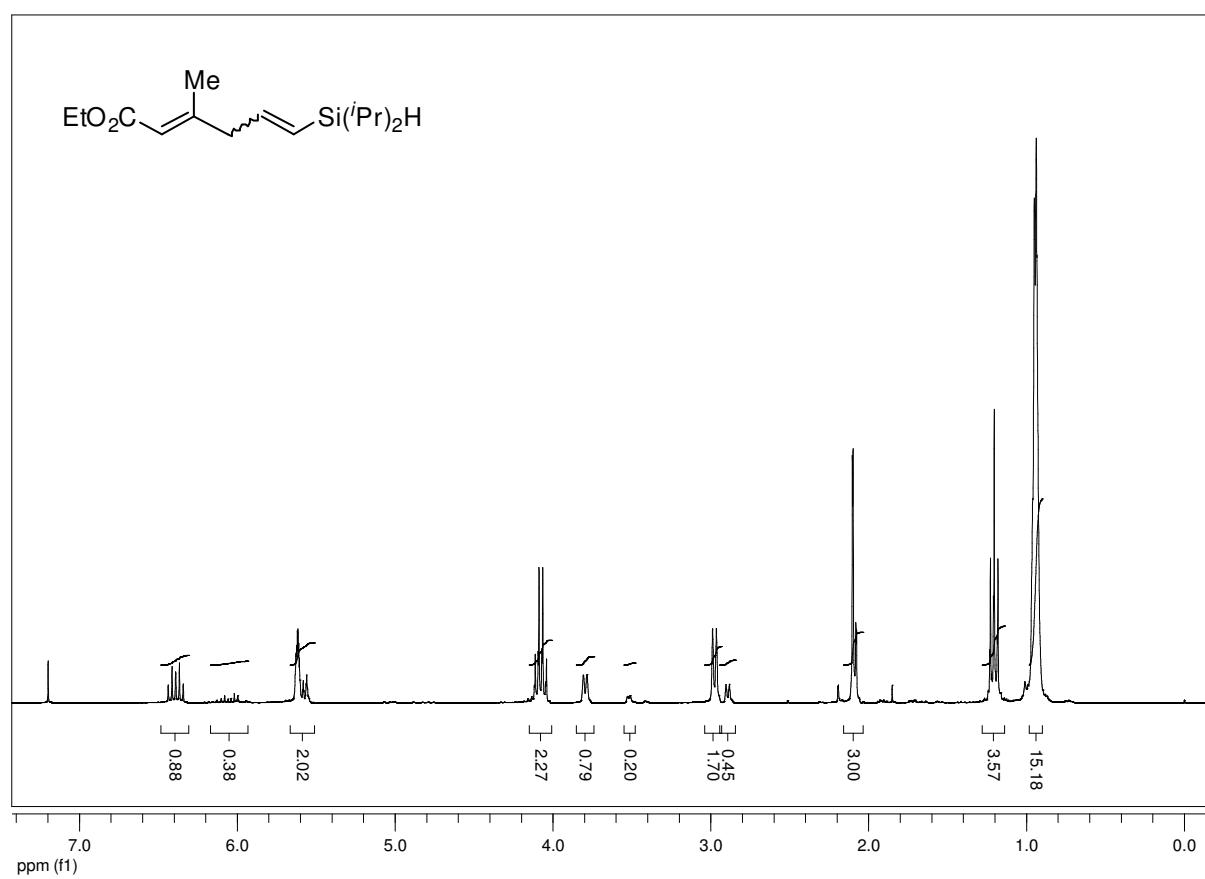
3i



3j

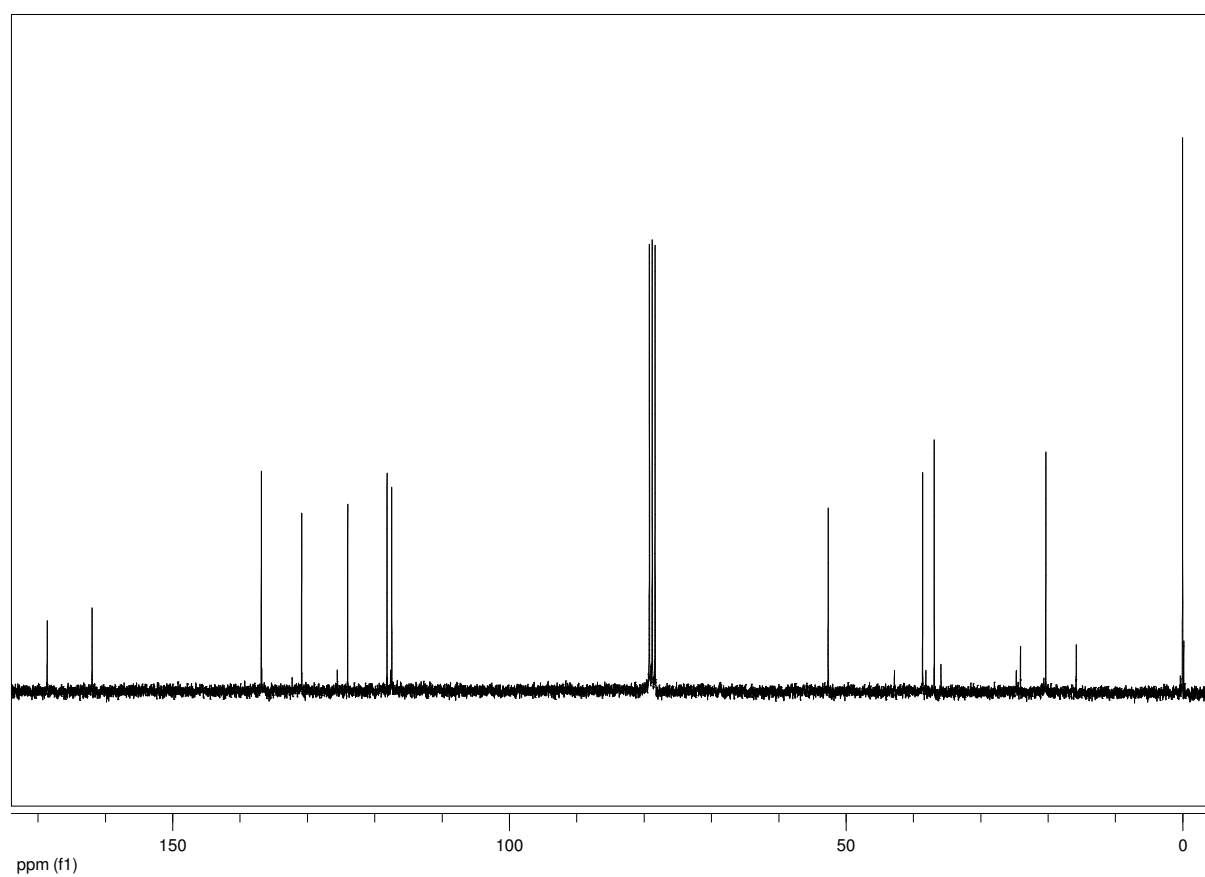
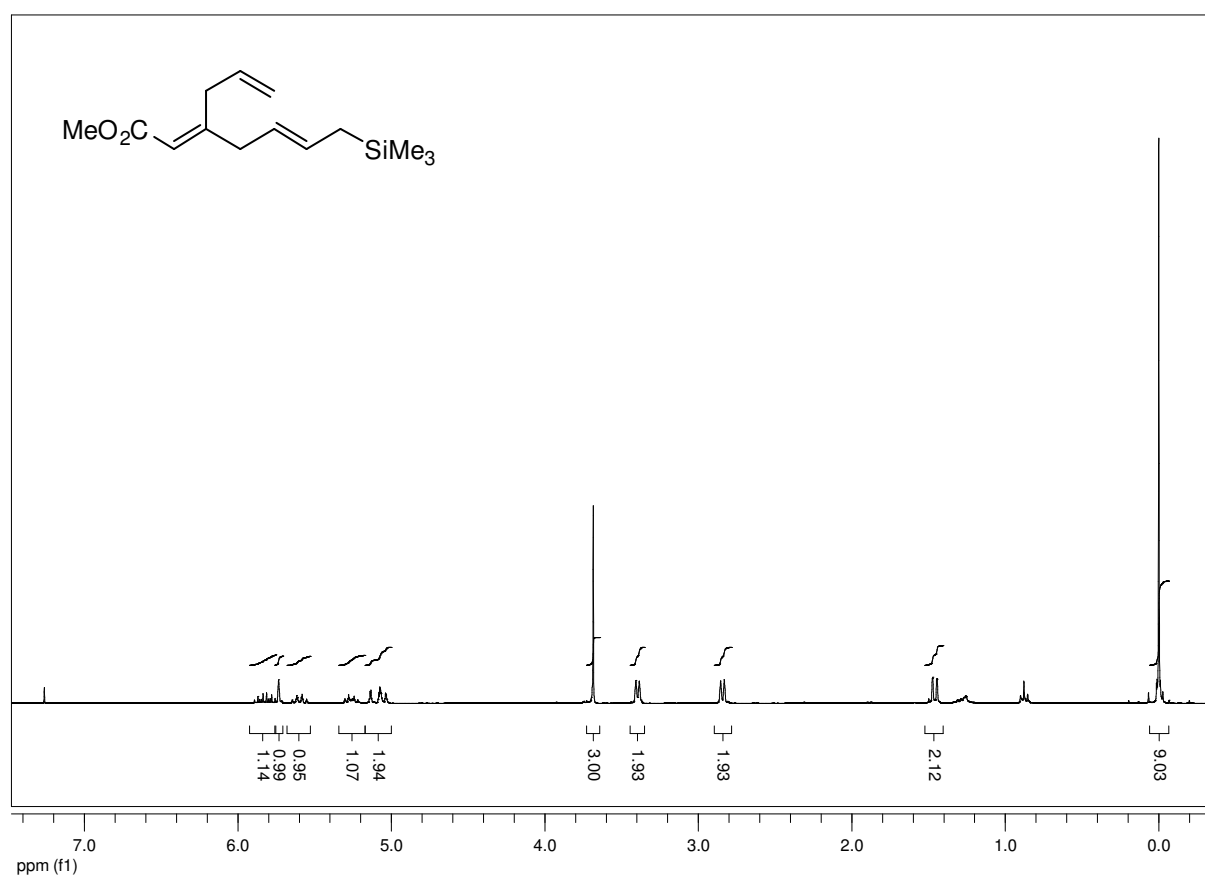


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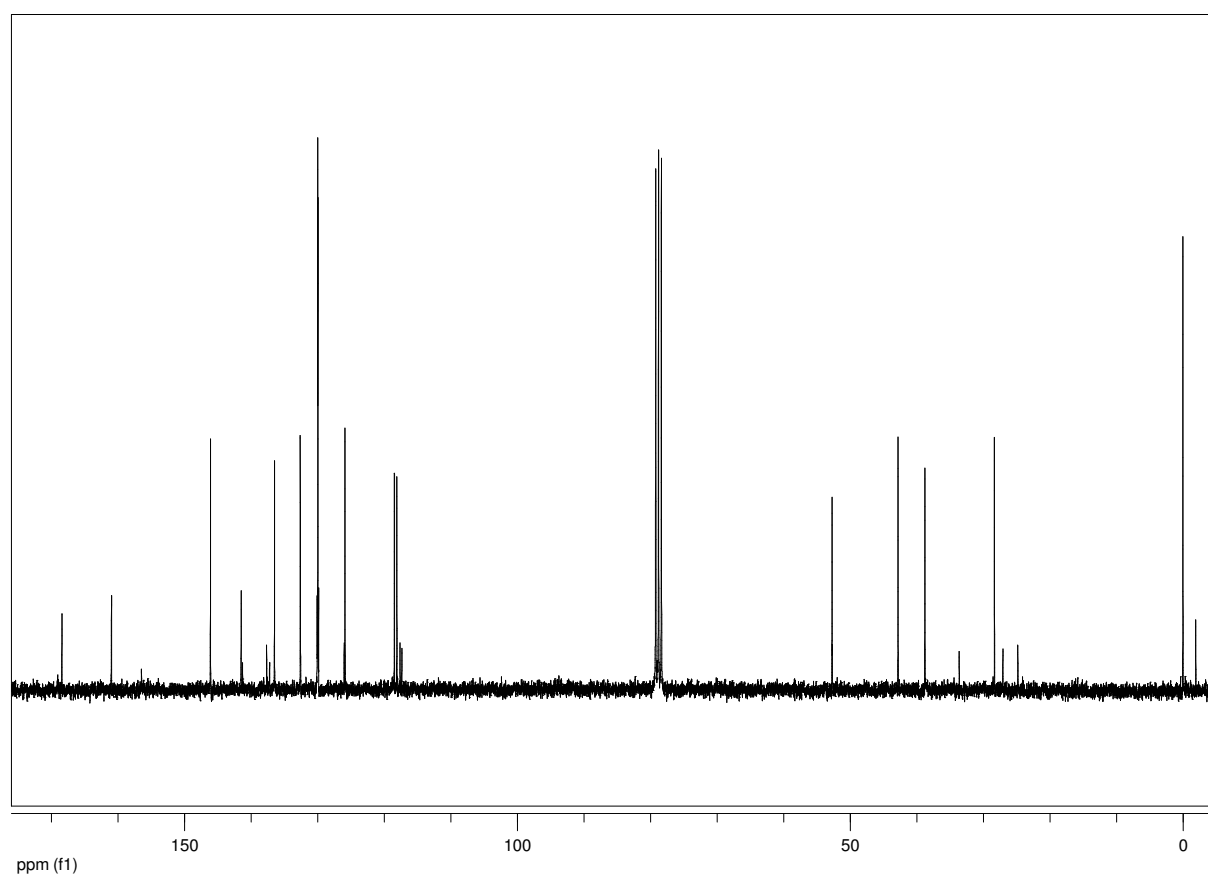
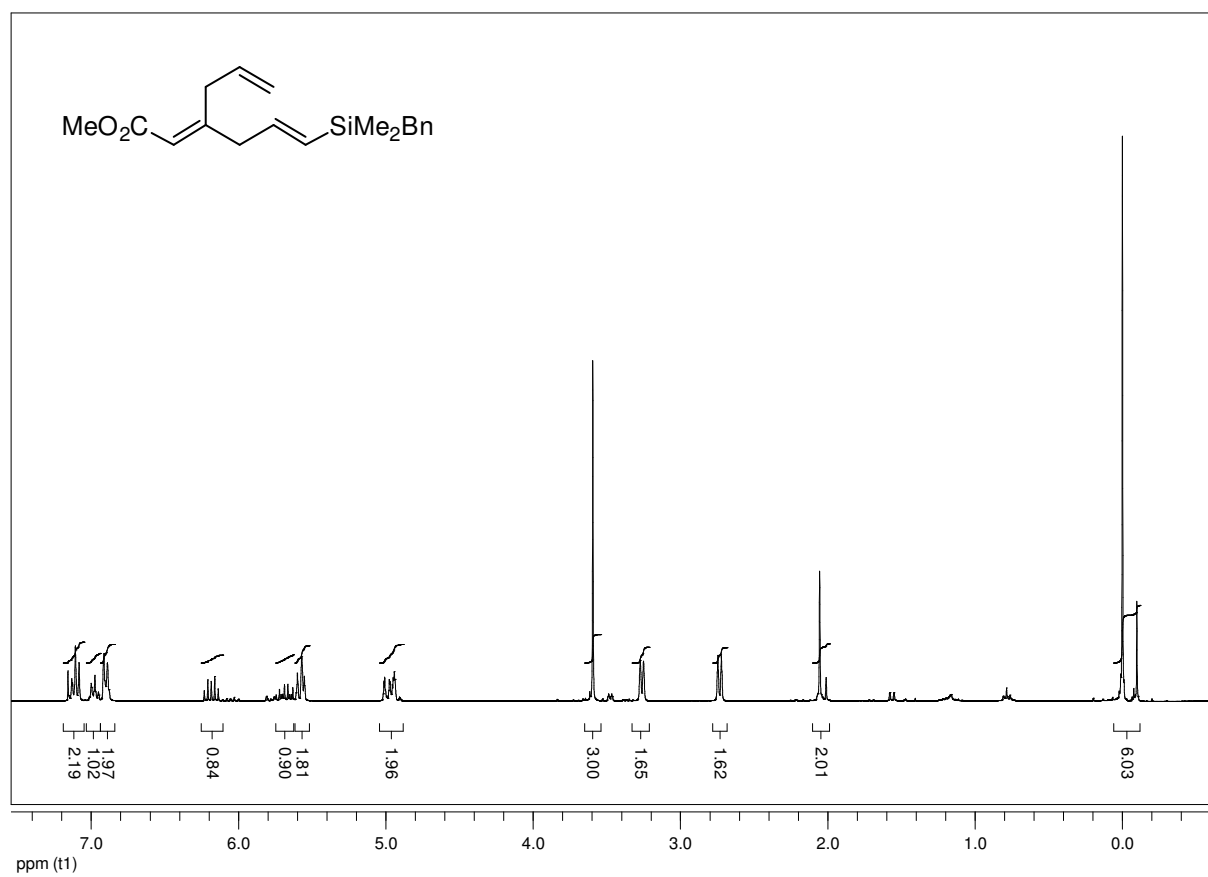




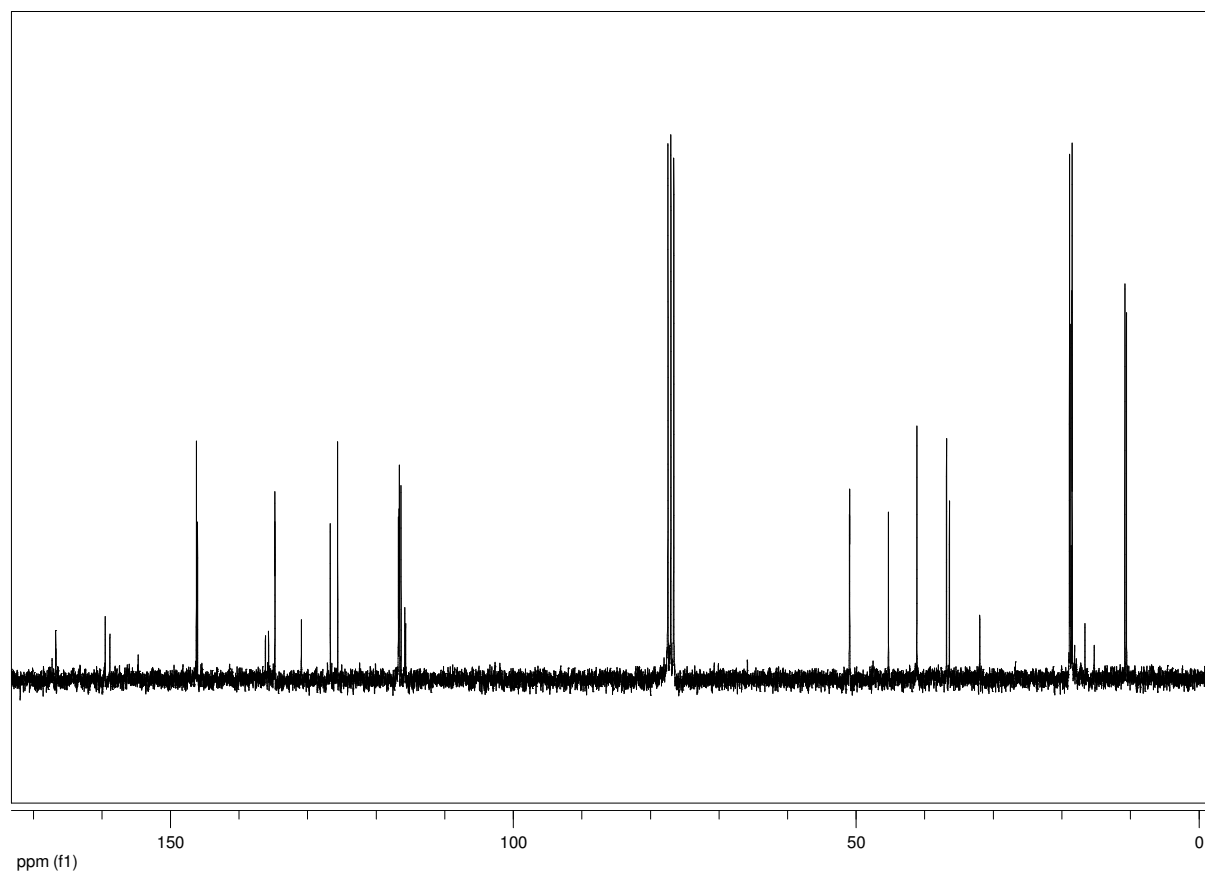
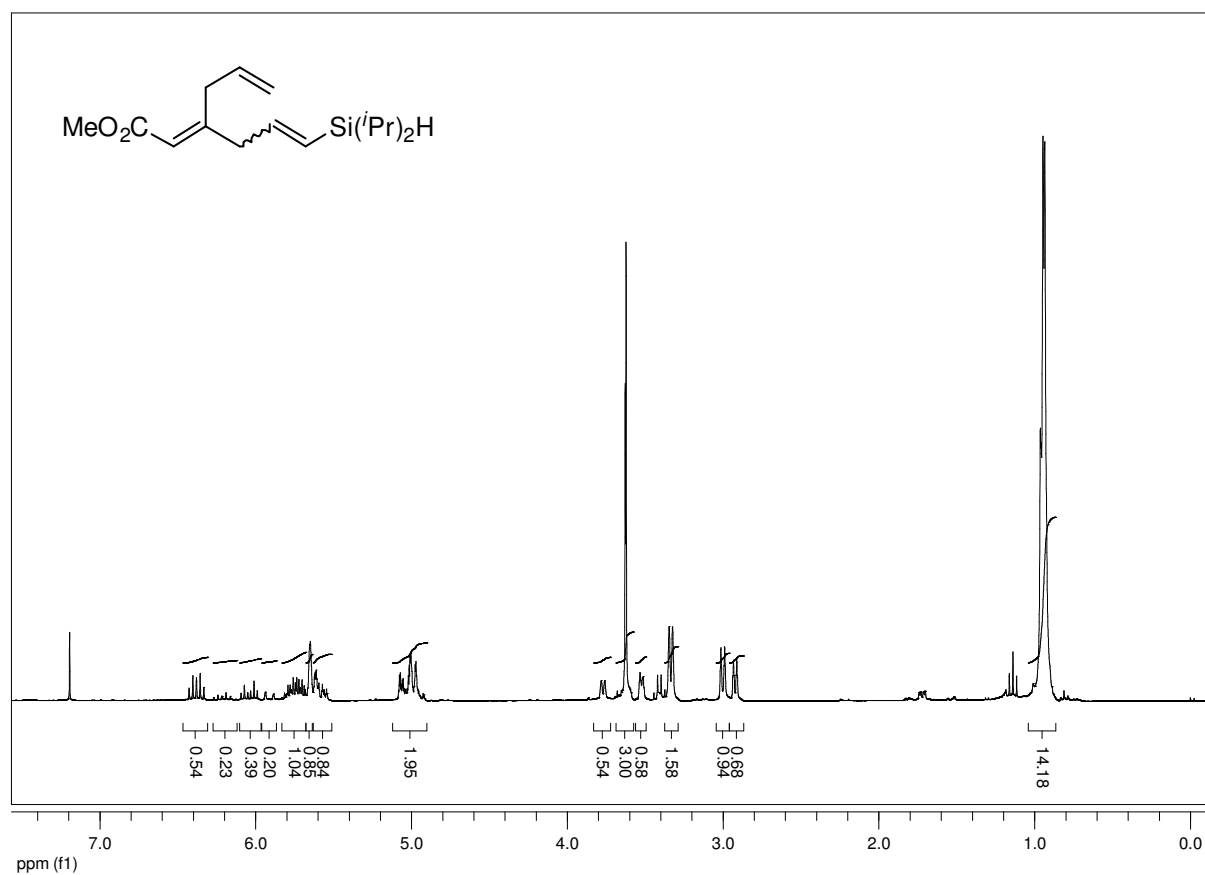
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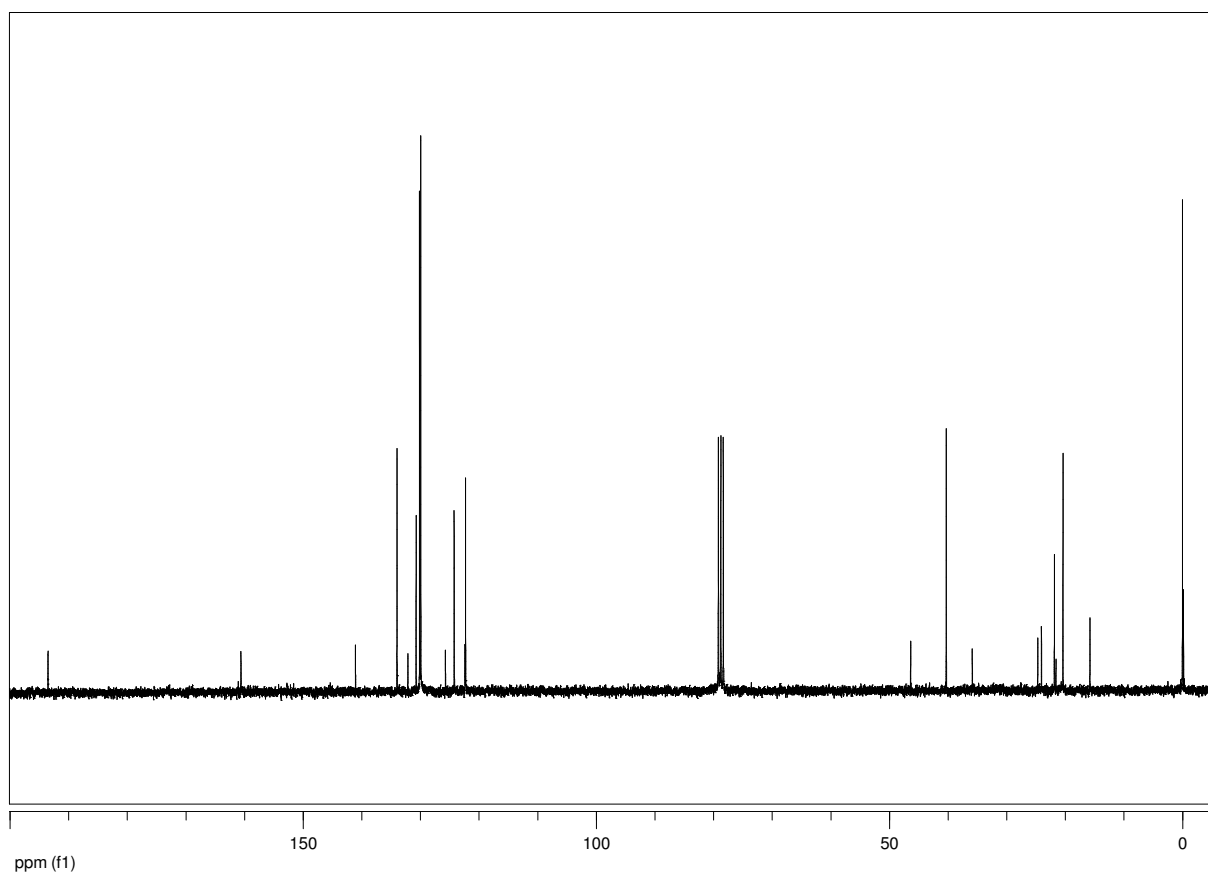
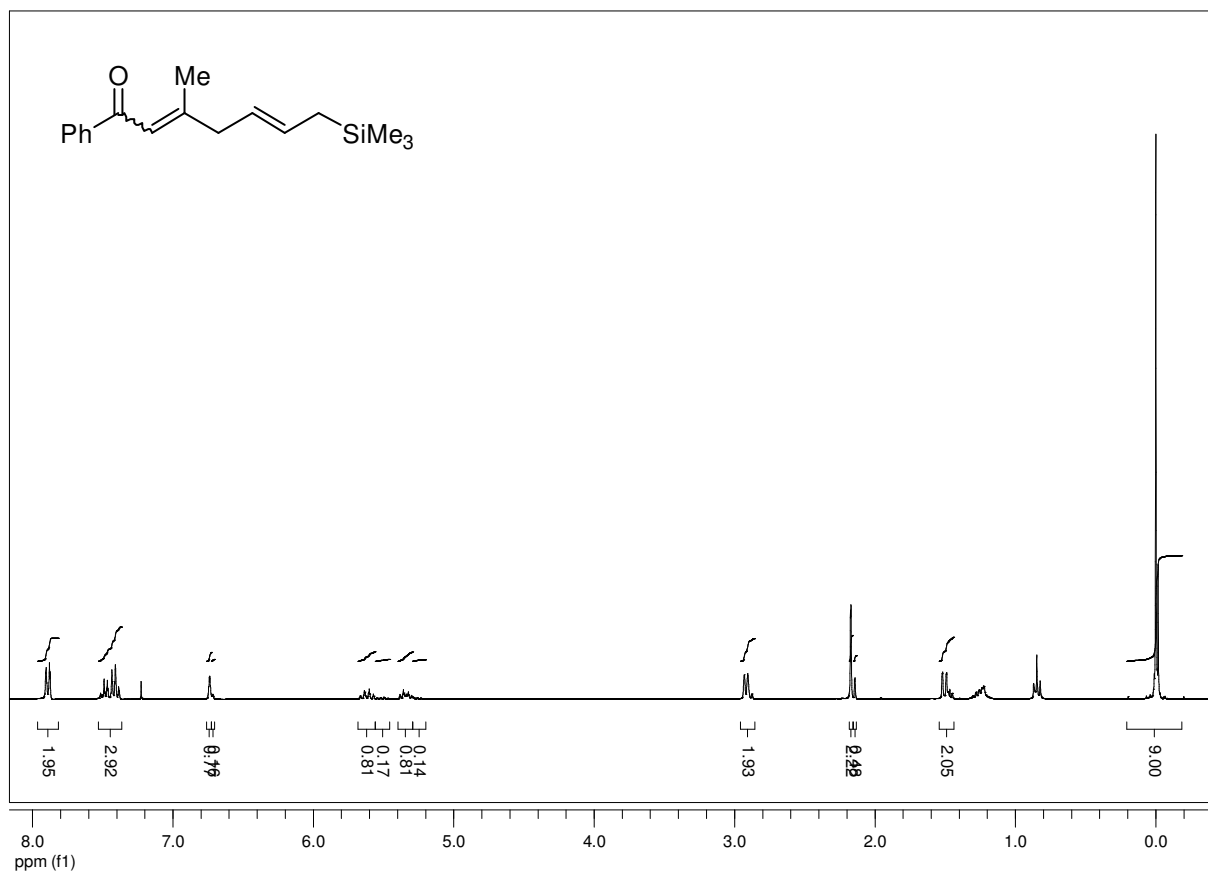
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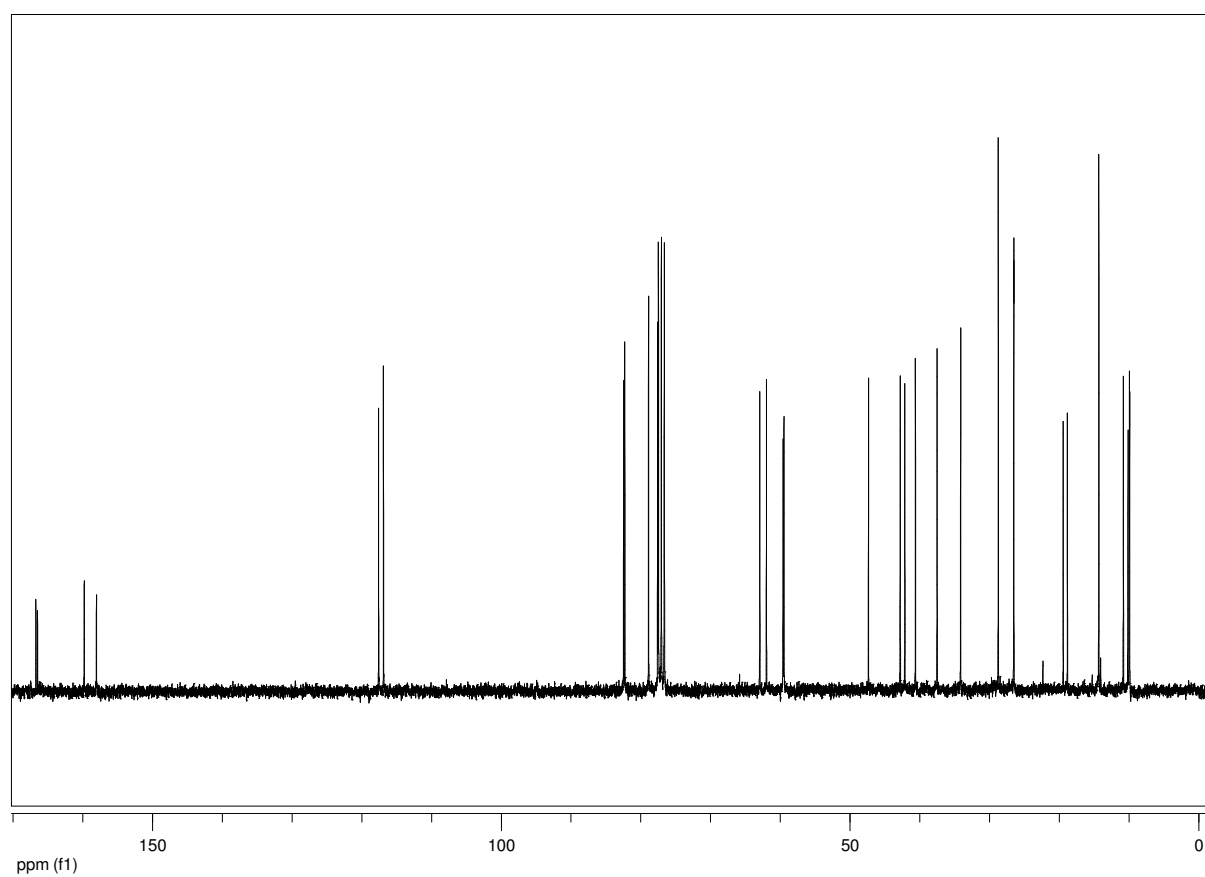
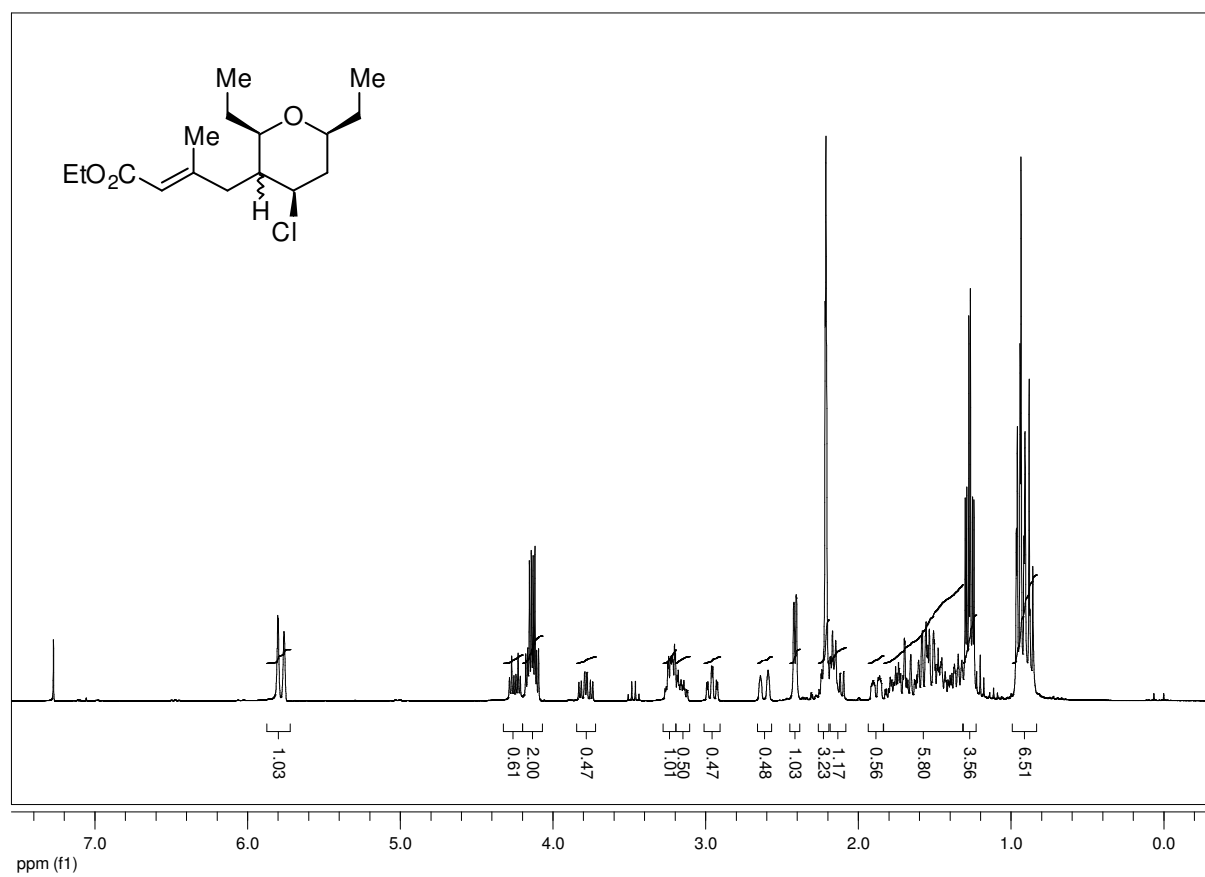
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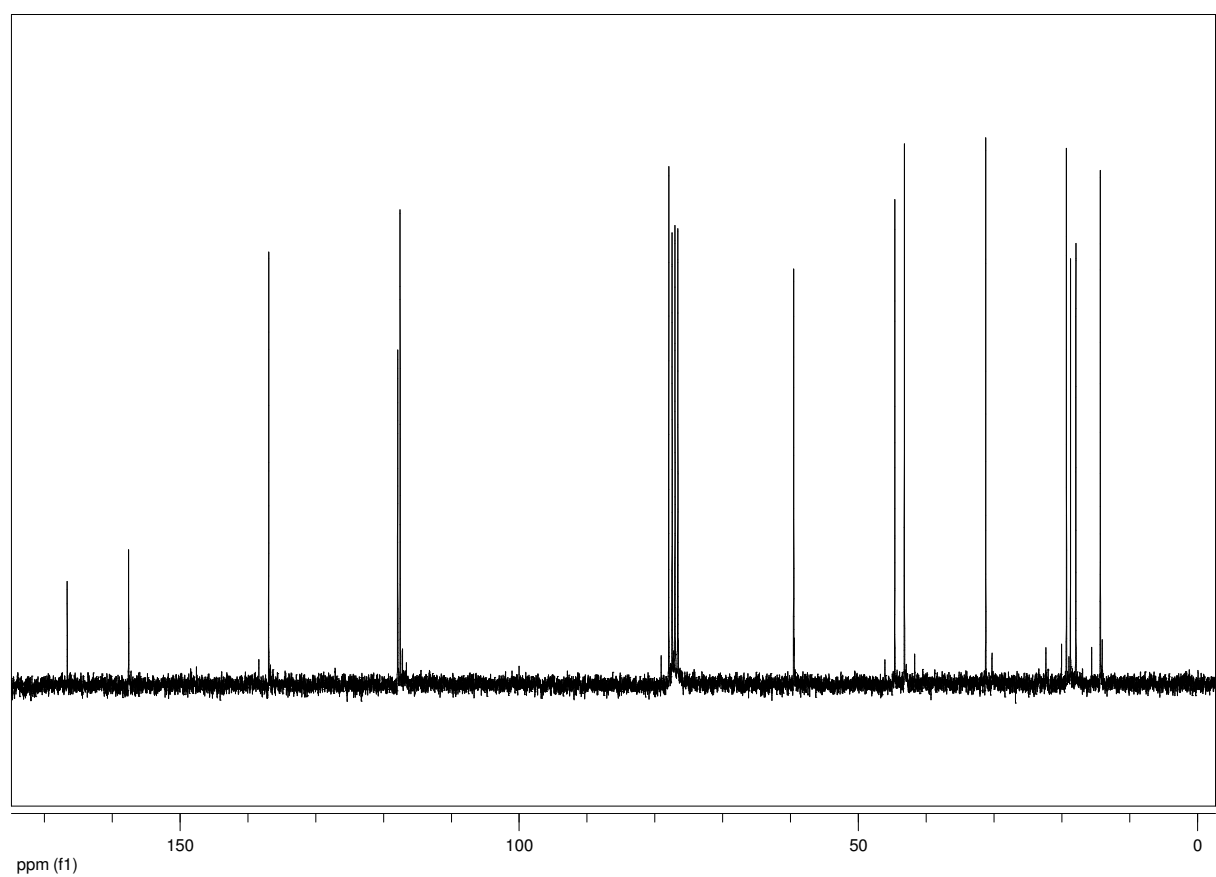
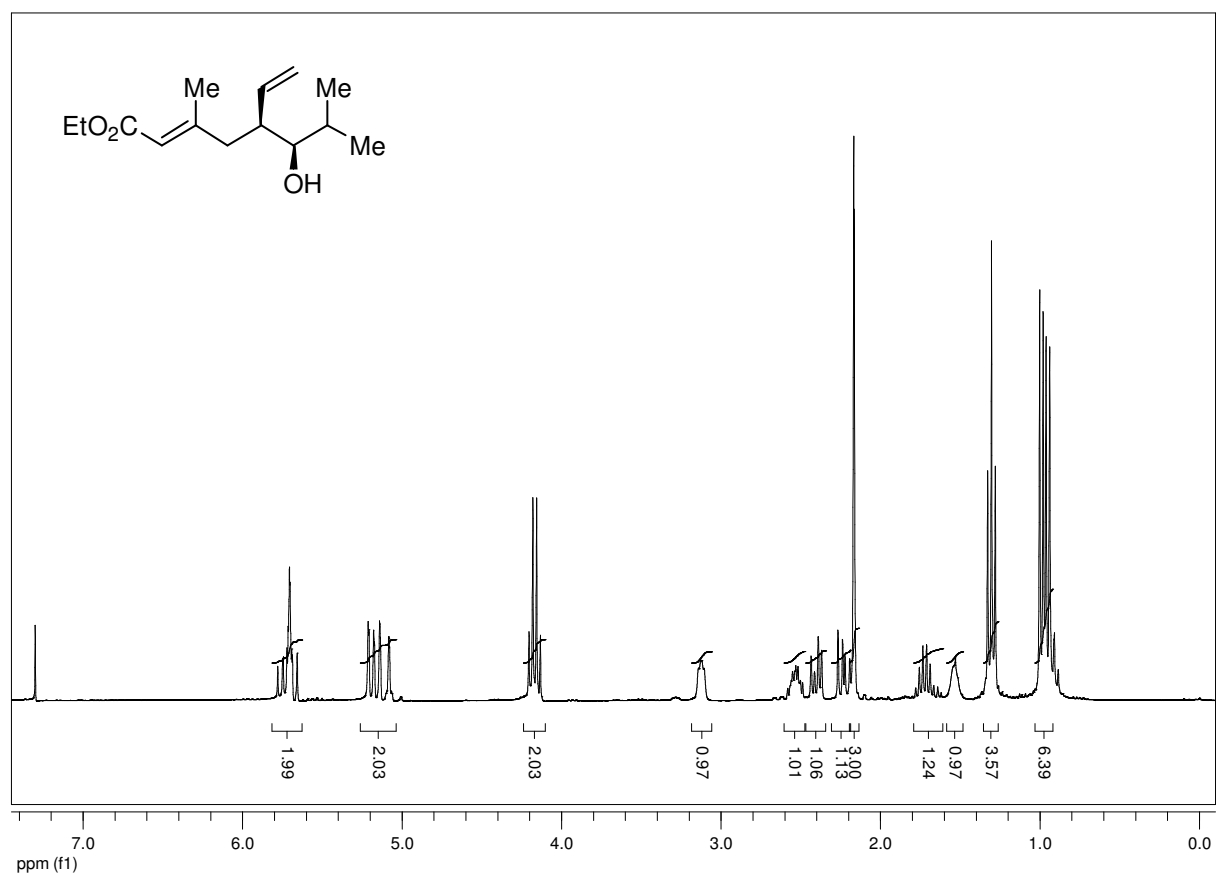
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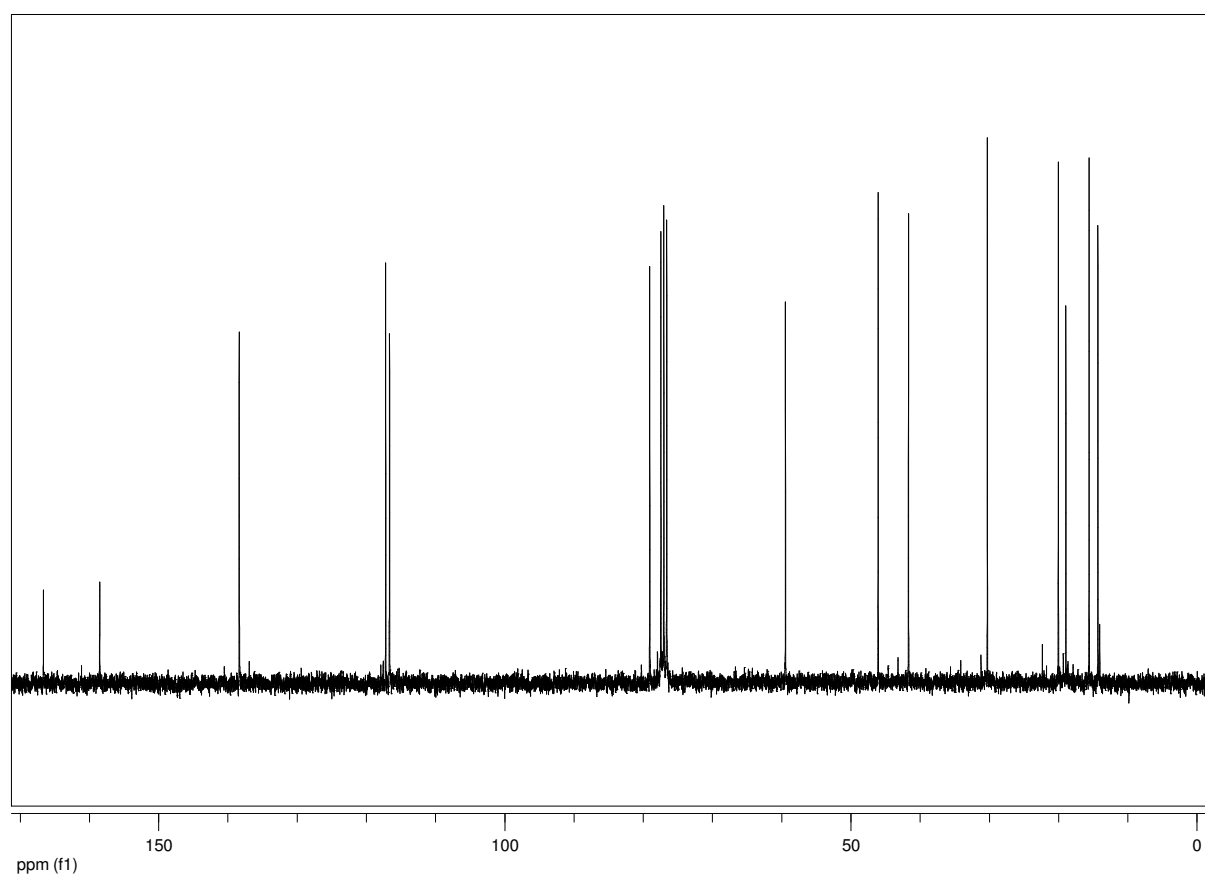
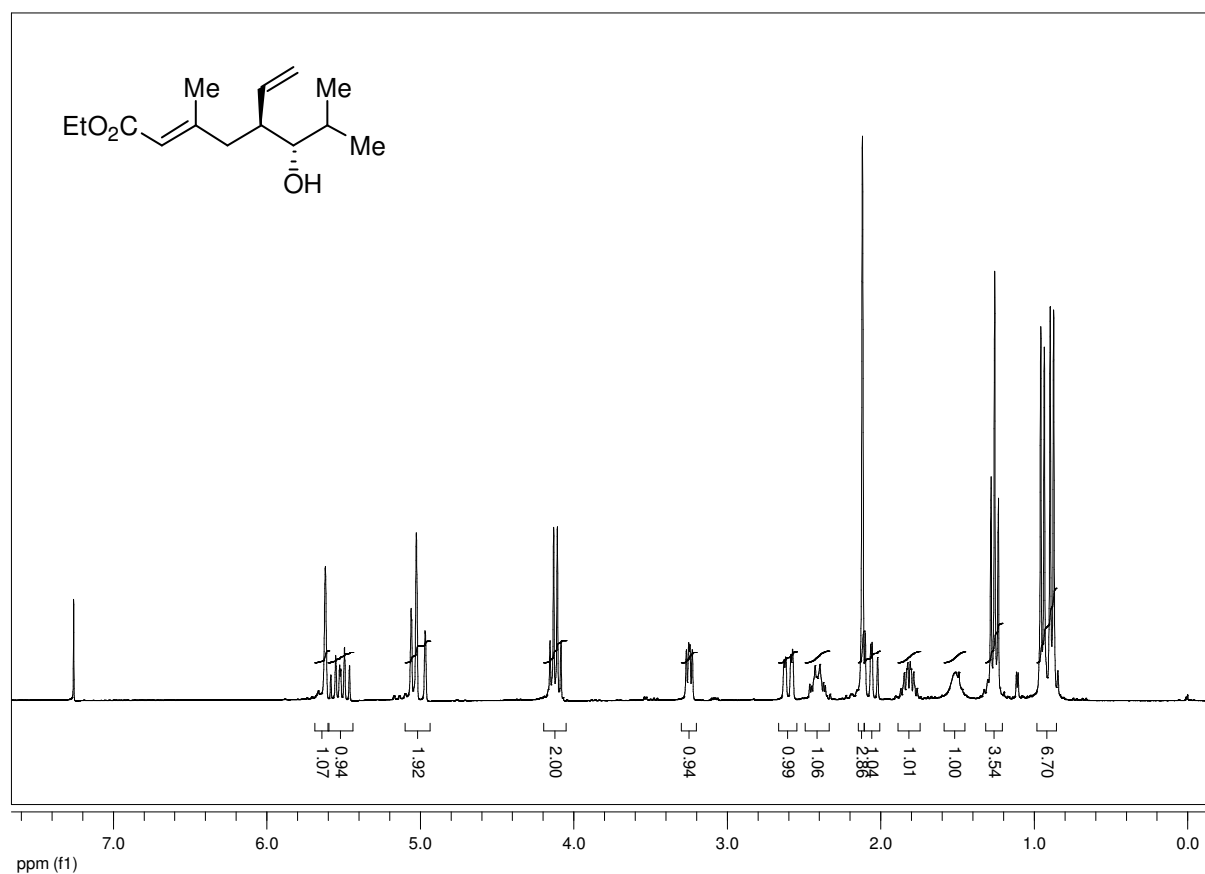
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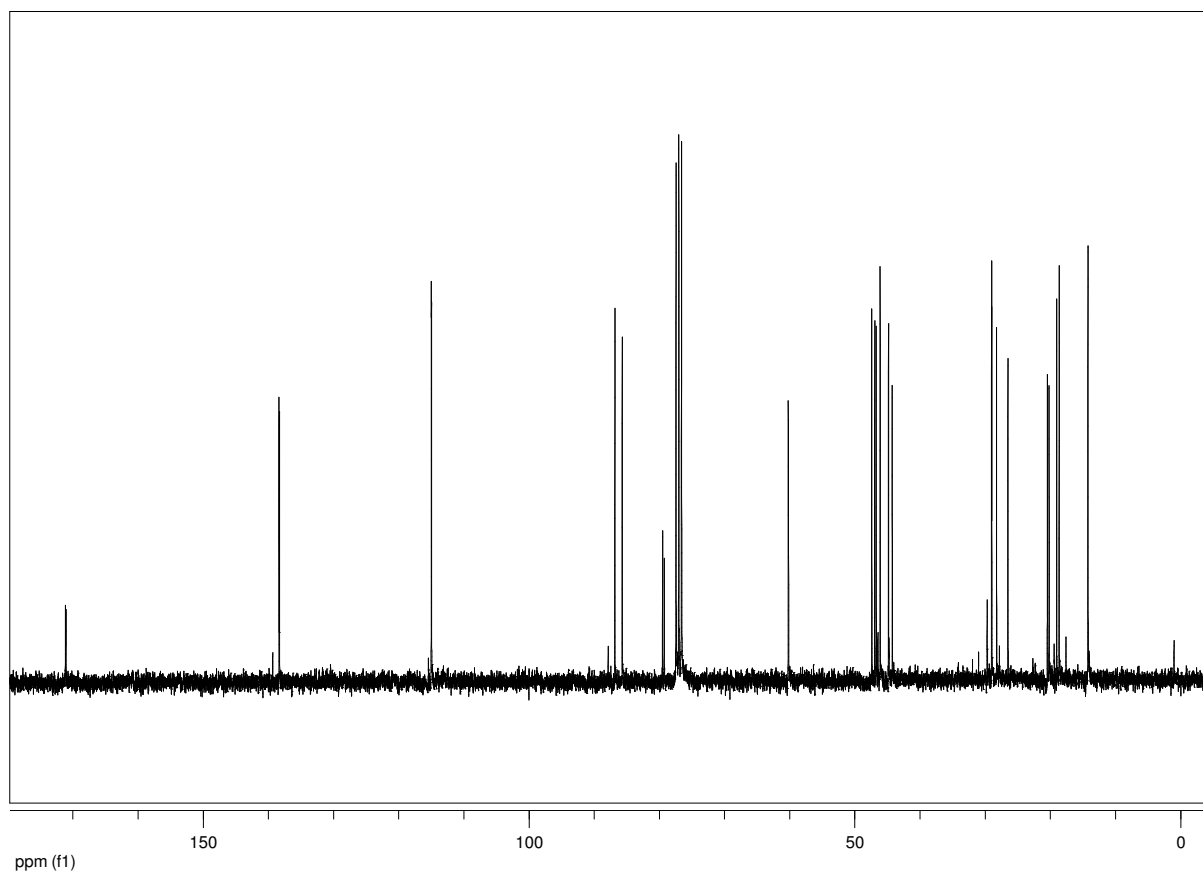
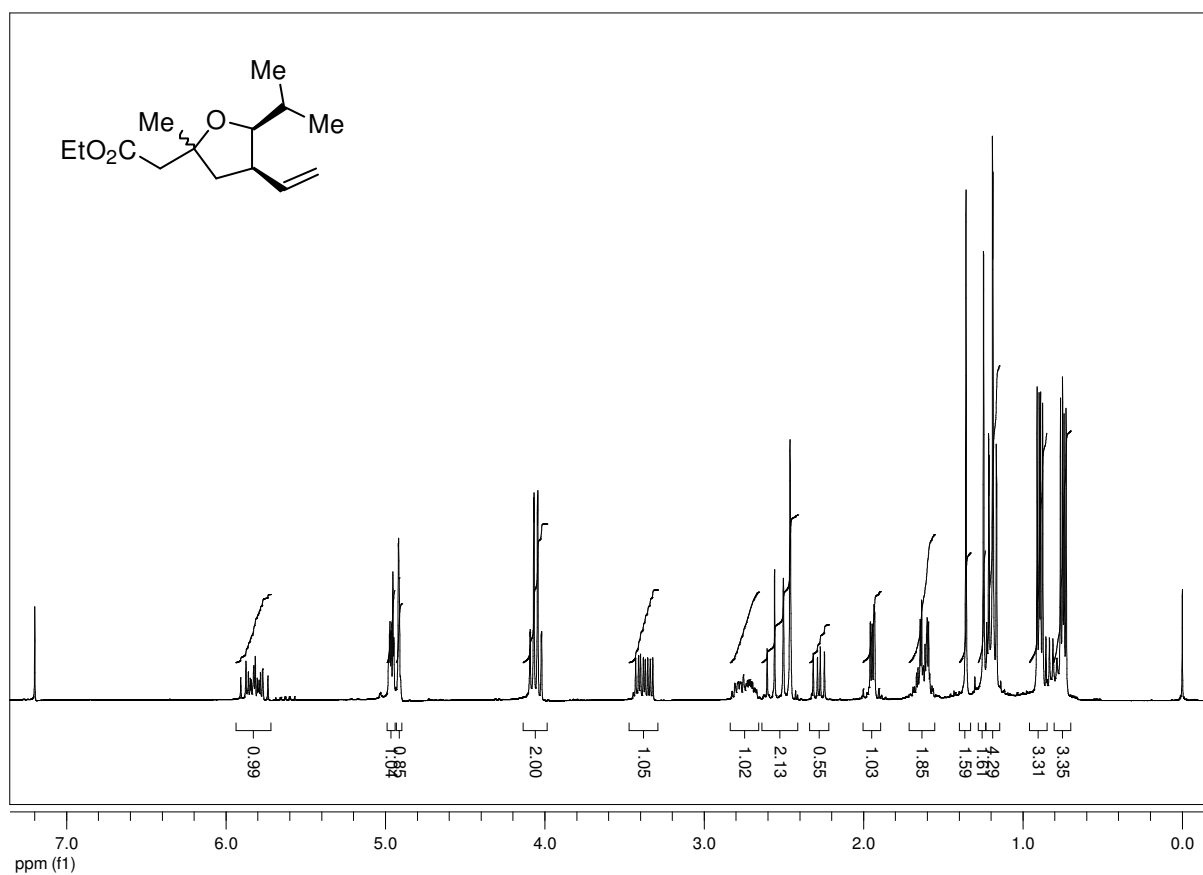
*syn-5*



***anti-5***

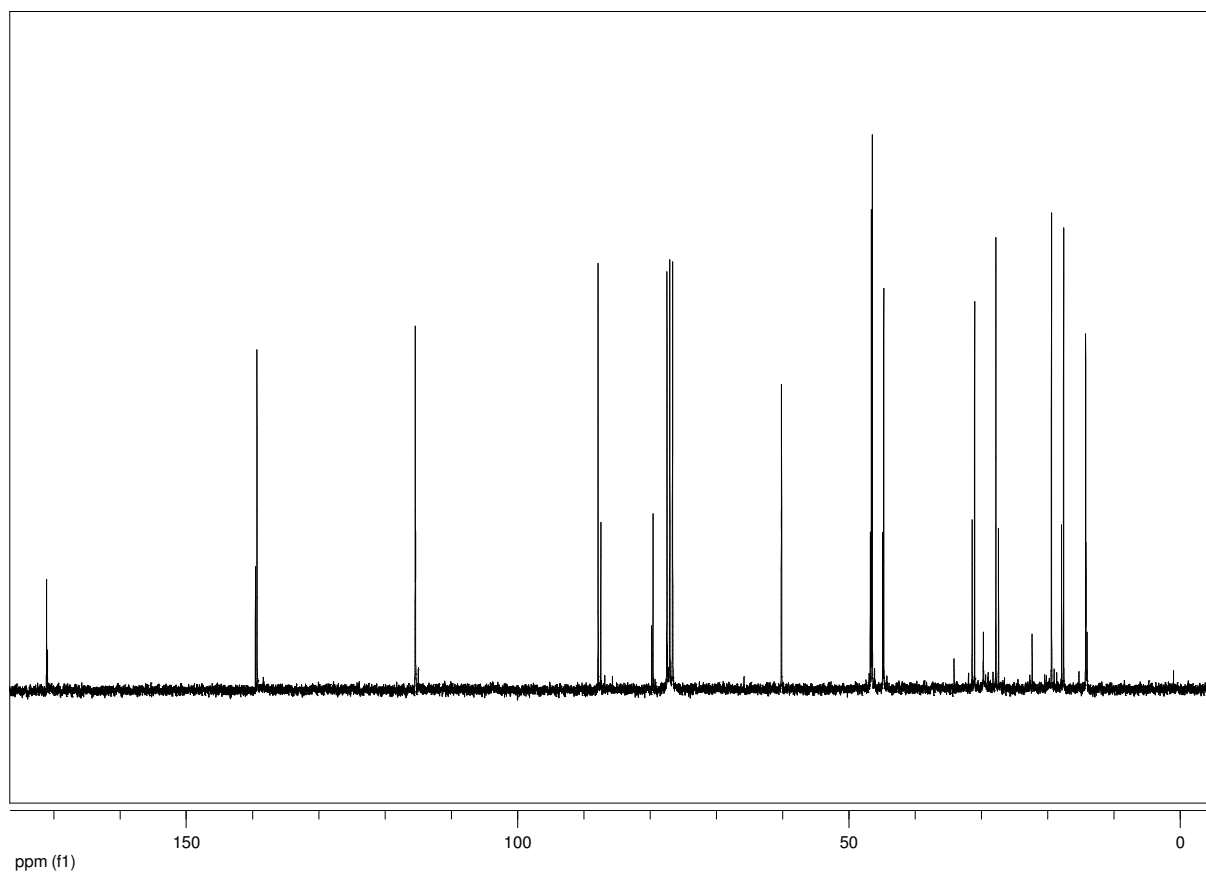
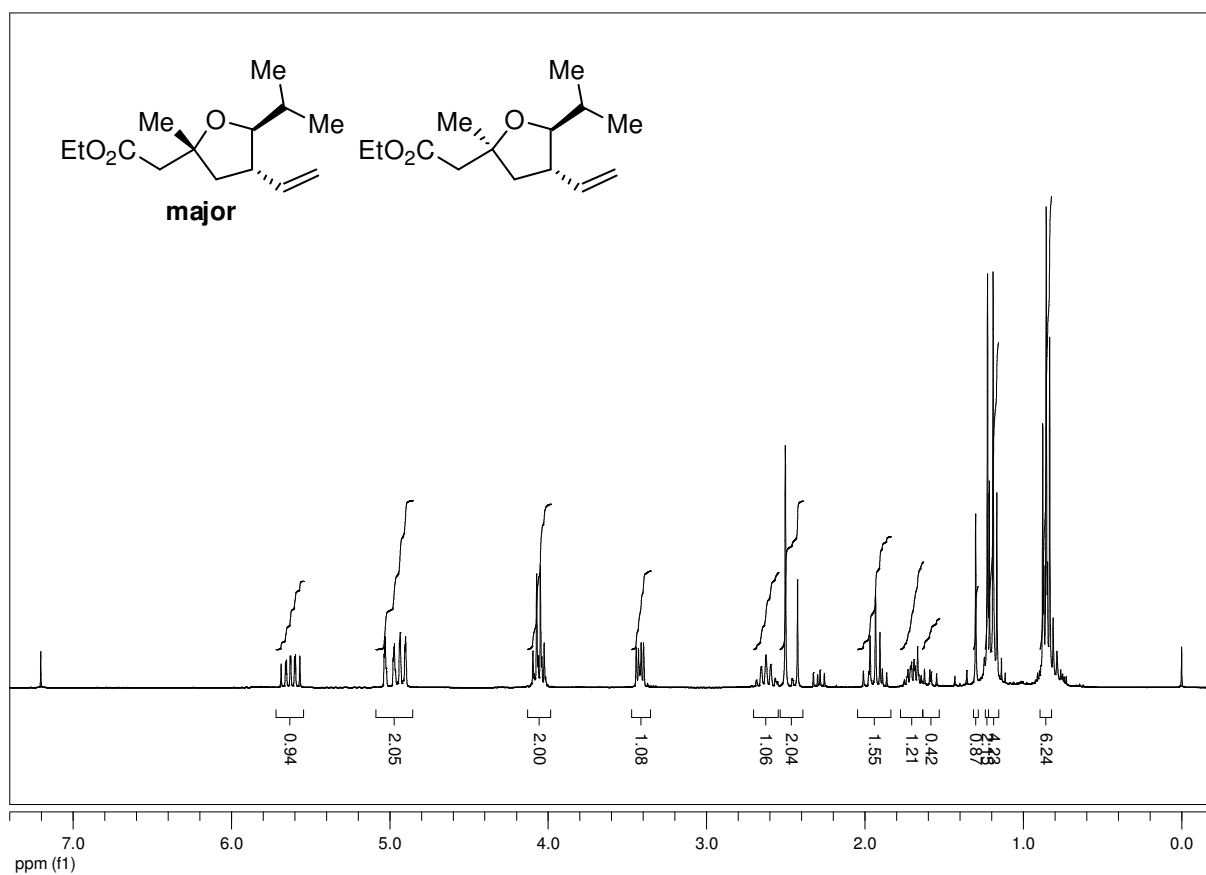


6

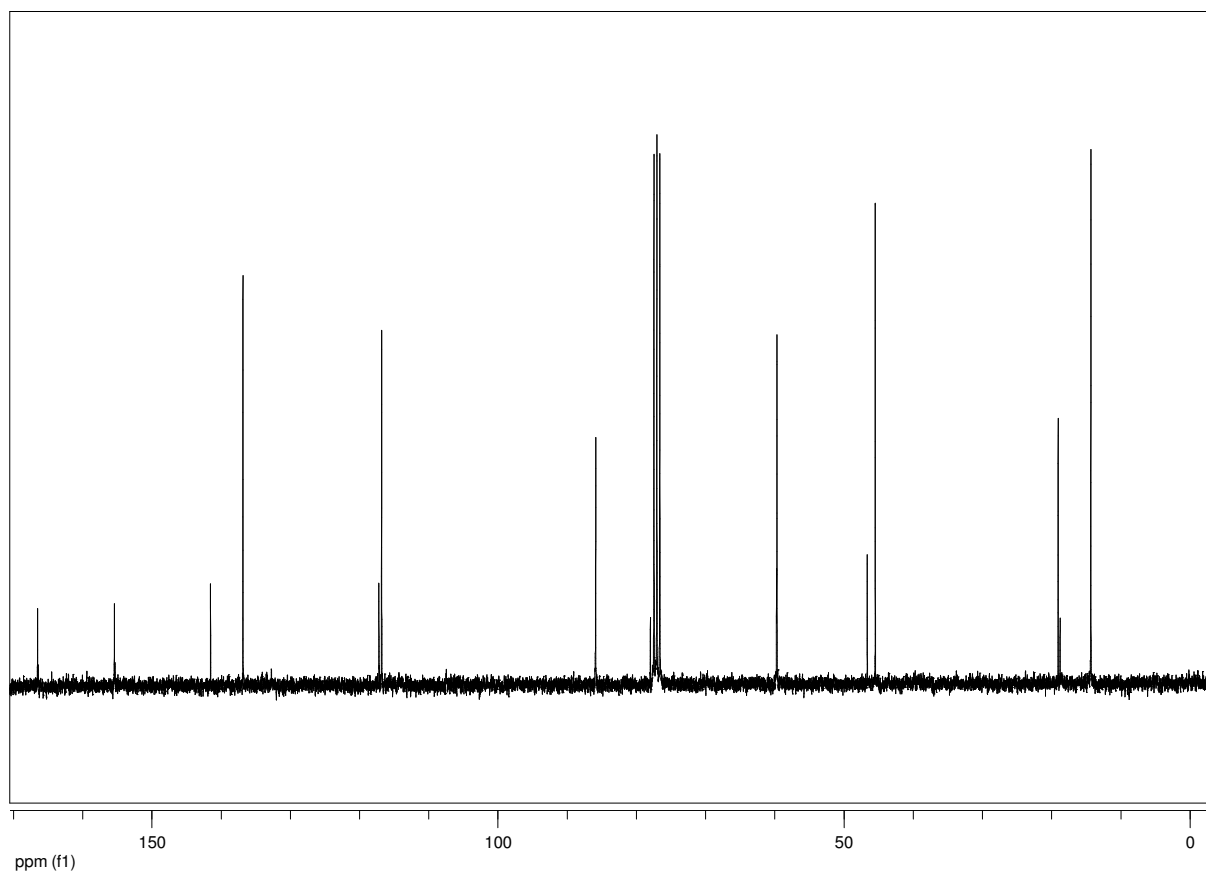
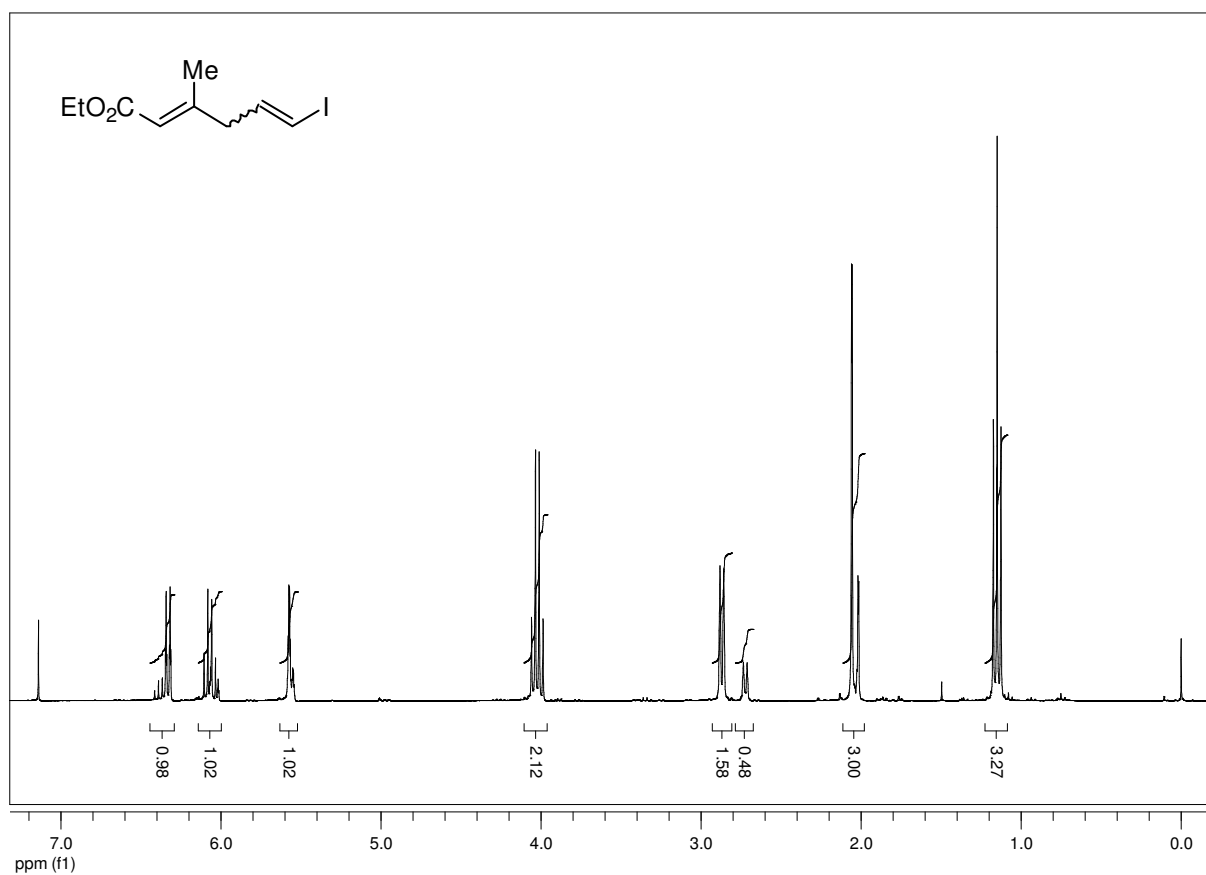




6



7



8

