

# **Efficient Allyl to Propenyl Isomerization in Functionally Diverse Compounds with a Thermally Modified Grubbs 2<sup>nd</sup> Generation Catalyst**

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## **-Supporting Information-**

### **Contents:**

1. Generalities (S2)
2. Characterization data (S2-S12)
3. Copies of selected <sup>1</sup>H and <sup>13</sup>C NMR spectra (S13-S28)
4. HRMS spectra for deuteration experiment (S29)

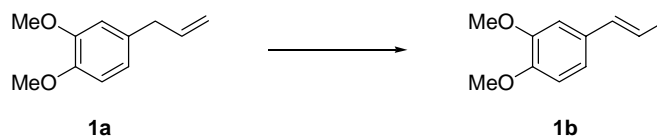
### Generalities:

All commercially available starting materials (**1a-4a**, **11a**, **16a** and **22a**) were used without further purification. All isomerization reaction were performed under normal atmosphere and with undistilled/undegased MeOH. All other reactions were performed under nitrogen atmosphere. NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ) spectra were recorded on a Bruker AV-400 spectrometer. Low- and high-resolution mass spectra were recorded on VG Micromass, AEI-MS 902 or Kratos MS-50 spectrometers using fast atom bombardement (FAB) or electrospray techniques. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter in a 1 dm cell at ambient temperature. Analytical thin-layer chromatography was performed on Merck 60F254 pre-coated silica gel plates. Visualization was performed by ultraviolet light and/or by staining with ceric ammonium molybdate or potassium permanganate. Flash column chromatography was performed using (40-60  $\mu\text{m}$ ) silica gel at increased pressure.

### General procedure for isomerization of terminal olefins.

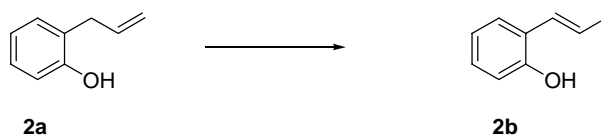
To a solution of the olefin (1 equiv.) in MeOH (0.075M) was added **I** (from Aldrich) (10 mol %) at room temperature. The suspension was then heated at 60 °C. After a few minutes, the insoluble catalyst (purple) dissolved completely and the resulting orange-brown solution was stirred at 60 °C until completion (typically, 3h for substrates in Table 1 and 12h for substrates in Table 2 and 3) after which time the solution was evaporated. The residue was purified by flash chromatography the give the isomerized olefin.

### 1,2-Dimethoxy-4-propenyl-benzene (**1b**)



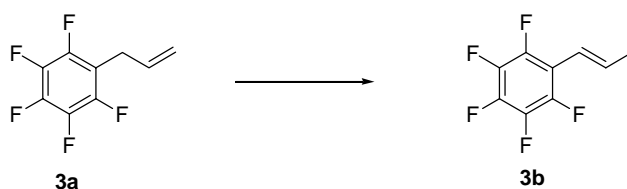
Following the general procedure with **1a**, **1b** was isolated in 80% yield (*E/Z*, 14:1). Spectral data identical to those of the literature.<sup>1</sup>

### 2-Propenyl-phenol (**2b**)



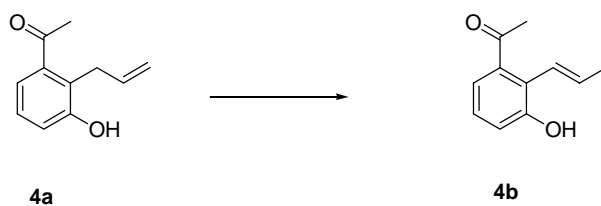
Following the general procedure with **2a**, **2b** was isolated in 92% yield (*E/Z*, 11:1). Spectral data identical to those of the literature.<sup>2</sup>

### 1,2,3,4,5-Pentafluoro-6-propenyl-benzene (**3b**)



Following the general procedure with **3a**, **3b** was isolated in 80% yield (*E/Z*, >20:1). Spectral data identical to those of the literature.<sup>3</sup>

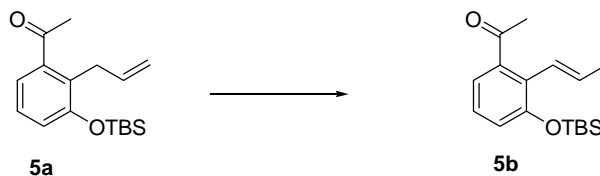
### 1-(3-Hydroxy-2-propenyl-phenyl)-ethanone (**4b**)



Following the general procedure with **4a**, **4b** was isolated in 89% yield (*E/Z*, 11:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 8.02 (s, 1H), 7.85 (m, 1H), 7.45 (dd, 1H, *J* = 1.9 and 8.4 Hz), 6.95 (d, 1H, *J* = 8.4 Hz), 6.67 (d, 1H, *J* = 16 Hz), 6.34 (m, 1H), 2.61 (s, 3H), 1.93 (d, 11/12 3H, *J* = 5.4 Hz), 1.77 (d, 1/12 3H, *J* = 5.5 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 198.3, 157.6, 129.2, 128.6, 128.4, 127.9, 125.0, 124.3, 122.9(min), 115.3, 25.9, 20.7(min), 18.5, 13.7(min); IR (film, cm<sup>-1</sup>) 3293, 1654, 1586, 1359, 1278, 1256.

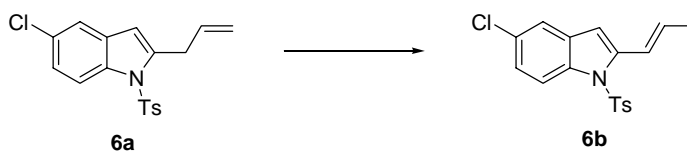
### 1-[3-(*tert*-Butyl-dimethyl-silanyloxy)-2-propenyl-phenyl]-ethanone (**5b**)



Following the general procedure **5a**<sup>4</sup>, **5b** was isolated in 90% yield (*E/Z*, >15:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 8.06 (d, 1H, *J* = 2.2 Hz), 7.72 (dd, 1H, *J* = 2.3 and 8.5 Hz), 6.82 (d, 1H, *J* = 8.5 Hz), 6.70 (d, 1H, *J* = 16.0 Hz), 6.27 (m, 1H), 2.57 (s, 3H), 1.92 (d, 3H<sub>Me, major</sub>, *J* = 6.5 Hz), 1.86 (d, 3H<sub>Me, minor</sub>, *J* = 7.1 Hz), 1.04 (s, 9H), 0.25 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 196.8, 156.3, 130.4, 129.2, 127.9, 126.8, 126.6, 125.0, 118.7, 26.0, 25.3, 18.4, 17.9, -4.5; IR (film, cm<sup>-1</sup>) 2931, 2859, 1681, 1595, 1490, 1356, 1260; HRMS calcd. for C<sub>17</sub>H<sub>27</sub>O<sub>2</sub>Si (M + H<sup>+</sup>) 291.1774, found: 291.1784.

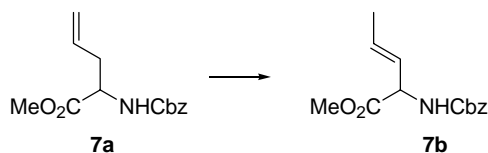
### 1-Benzenesulfonyl-2-propenyl-1*H*-indole (**6b**)



Following the general procedure with **6a**<sup>5</sup>, **6b** was isolated in 87% yield (*E/Z*, 2.7:1).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.15 (d, *J* = 8.9 Hz, 1H, *Z*-isomer), 8.10 (d, *J* = 8.9 Hz, 1H, *E*-isomer), 7.61-7.58 (m, 2H), 7.41 (d, *J* = 1.8 Hz, 1H, *Z*), 7.37 (d, *J* = 1.9 Hz, 1H, *E*), 7.26-7.15 (m, 3H), 7.02 (dq, *J* = 20.0 Hz, 0.9 Hz, 1H, *E*), 6.88 (dq, *J* = 11.1 Hz, 0.8 Hz, 1H, *Z*), 6.52 (s, 1H; *E*), 6.43 (s, 1H, *Z*), 6.19 (dq, *J* = 15.6 Hz, 6.8 Hz, 1H, *E*), 6.05 (dq, *J* = 11.7 Hz, 7.1 Hz, 1H, *Z*), 2.33 (s, 3H), 1.96 (dd, *J* = 6.8 Hz, 1.8 Hz, 3H, *E*), 1.79 (dd, *J* = 7.1 Hz, 1.9 Hz, 3H, *Z*); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 144.9, 141.3, 137.8 (min), 135.3, 135.2, 131.6, 131.3 (min), 131.2 (min), 130.7, 129.7 (min), 129.6, 129.6, 129.4 (min), 126.6, 124.8 (min), 124.6 (min), 124.3, 121.3, 120.6 (min), 120.2 (min), 120.0 (min), 119.8, 116.1 (min), 116.1, 111.1 (min), 107.9 (min), 106.8, 21.6, 18.8, 14.9 (min); IR (film, cm<sup>-1</sup>) 3080, 2956, 2923, 2851, 1597, 1445, 1372, 1170, 1090, 1047, 920, 874, 810, 716, 667; HRMS calcd for C<sub>18</sub>H<sub>16</sub>ClNO<sub>2</sub>SAg (M + Ag) 451.9635, found 451.9655.

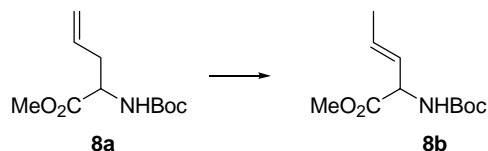
### 2-Benzyloxycarbonylamino-pent-3-enoic acid methyl ester (**7b**)



Following the general procedure with **7a**<sup>6</sup>, **7b** was isolated in 76 % yield (*E/Z*, 4:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 7.36 (m, 5H), 5.81 (m, 1H), 5.52 (m, 1H), 5.13 (s, 2H + 1H), 4.86 (t, 1H, *J* = 6.9 Hz), 3.76 (s, 3H), 1.84 (d, 1/5 3H, *J* = 6.5 Hz, minor *Z*), 1.73 (d, 4/5 3H, *J* = 6.5 Hz, major *E*); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 171.5(min), 171.1, 155.1, 135.8, 129.6, 128.2, 128.1, 127.9, 128.8, 127.8, 124.7, 69.3(min), 66.6, 55.3(min), 52.2, 17.3, 13.1(min); IR (film, cm<sup>-1</sup>) 3344, 3034, 2954, 1723, 1521, 1455, 1337, 1214, 1050; HRMS calcd. for C<sub>14</sub>H<sub>17</sub>NO<sub>4</sub>Na (*M* + Na<sup>+</sup>) 286.1049, found: 286.1049.

#### 2-*tert*-Butoxycarbonylamino-pent-3-enoic acid methyl ester (**8b**)

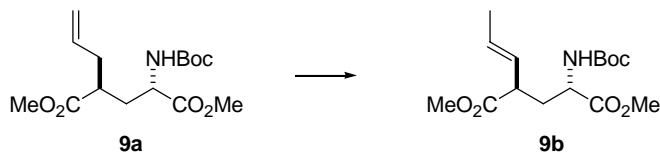


Following the general procedure with **8a**<sup>7</sup>, **8b** was isolated in 74 % yield (*E/Z*, 4:1).

Spectral data identical to those of the literature.<sup>8</sup>

HRMS calcd. for C<sub>11</sub>H<sub>19</sub>NO<sub>4</sub>Na (*M* + Na<sup>+</sup>) 252.1206, found: 252.1194.

#### (2*S*, 4*R*)-2-*tert*-Butoxycarbonylamino-4-propenyl-pentanedioic acid dimethyl ester (**9b**)

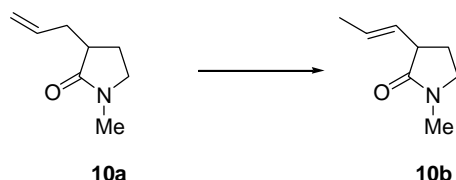


Following the general procedure with **9a**<sup>9</sup>, **9b** was isolated in 96% yield (*E/Z*, 4:1).

[α]<sub>D</sub> -23.0 (*c* 0.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 5.67 (m, 1H), 5.38 (m, 1H), 4.93 (d, 1H, *J* = 8.5 Hz), 4.30 (m, 1H), 3.72 (s, 3H), 3.67 (s, 3H), 3.10 (q, 1H, *J* =

7.5 Hz), 2.03 (m, 2H), 1.70 (dd, 4/5 of 3H,  $J = 1.3$  and 6.4 Hz (major *E*) with dd, 1/5 of 3H,  $J = 5.4$  Hz and 6.9 Hz (minor *Z*)) 1.44 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 173.9, 172.6, 154.9, 129.7, 126.5, 126.0 (min), 79.57, 60.0, 51.9, 51.6, 51.2, 45.3, 39.8, 34.2, 34.0 (min), 27.8, 20.6 (min), 17.6, 13.8 (min) 213.5, 128.7, 127.4, 59.6, 34.5(2), 17.8, 17.5; IR (film,  $\text{cm}^{-1}$ ) 3368, 2978, 1737, 1717, 1521, 1438, 1367, 1163; LRMS (ES+) 316.8 ( $\text{M} + \text{H}^+$ , 25), 216.5 ( $\text{M} - \text{Boc}$ , 100); HRMS calcd. for  $\text{C}_{15}\text{H}_{25}\text{NO}_6\text{Na}$  ( $\text{M} + \text{Na}^+$ ) 338.1574, found: 338.1572.

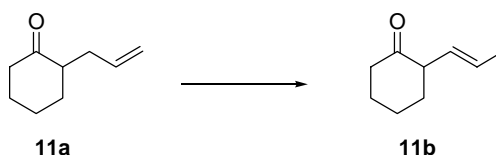
### 1-Methyl-3-propenyl-pyrrolidin-2-one (10b)



Following the general procedure with **10a**<sup>10</sup>, **10b** was isolated in 80% yield (*E/Z*, 4:1).

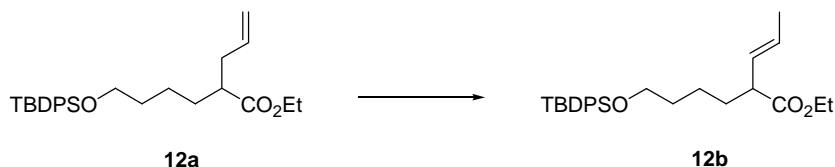
$^1\text{H}$  NMR (400 MHz,  $\text{CHCl}_3$ )  $\delta$  (ppm) 5.60 (m, 1H), 5.48 (m, 1H), 3.30 (m, 2H), 3.02 (q, 1H,  $J = 8.2$  Hz), 2.83 (s, 3H), 2.28 (m, 1H), 1.86 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 174.9, 127.9, 127.7, 127.6(min), 127.4(min), 47.3(min), 47.1, 44.8, 40.0(min), 29.6(min), 29.5, 25.7(min), 25.0, 17.6, 12.9(min); IR (film,  $\text{cm}^{-1}$ ) 2941, 2881, 1678, 1500, 1438, 1404, 1300; HRMS calcd. for  $\text{C}_8\text{H}_{14}\text{NO}$  ( $\text{M} + \text{H}^+$ ) 140.1069, found: 140.1073.

### 2-Propenyl-cyclohexanone (11b)



Following the general procedure with **11a**, **11b** was isolated in 90% yield (*E/Z*, 5:1). Spectral data identical to those of the literature.<sup>11</sup>

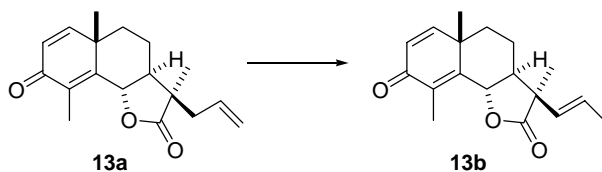
### 6-(*tert*-Butyl-diphenyl-silanyloxy)-2-propenyl-hexanoic acid ethyl ester (12b)



Following the general procedure with **12a**<sup>12</sup>, **12b** was isolated in 95% yield (*E/Z*, 4:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 7.71 (m, 4H), 7.43 (m, 6H), 5.62 (m, 1H), 5.45 (m, 1H), 4.16 (q, 2H, *J* = 7.1 Hz), 3.69 (t, 2H, *J* = 6.3 Hz), 3.35 (m, 1/5H), 2.96 (q, 4/5H, *J* = 7.6 Hz), 1.71 (d, 3H from Me, *J* = 6.3 Hz + 1H), 1.65-1.33 (m, 5H), 1.28 (t, 3H, *J* = 7.1 Hz), 1.09 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 174.3, 174.2(min), 135.2, 133.6, 129.1, 128.5, 128.1, 127.5, 127.2, 126.2, 63.3, 59.9, 49.0, 43.4(min), 32.1(min), 31.9(2), 26.4, 23.0, 18.8, 17.5, 13.9, 12.8(min); IR (film, cm<sup>-1</sup>) 2933, 2859, 1734, 1428, 1111; HRMS calcd. for C<sub>27</sub>H<sub>39</sub>O<sub>3</sub>Si (M + H<sup>+</sup>) 439.2663, found: 439.2672.

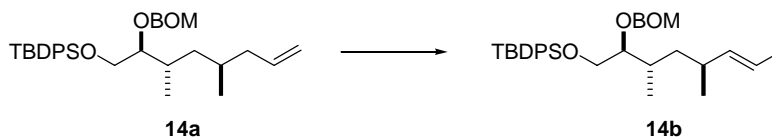
### Propenyl-santonin (**13b**)



Following the general procedure *in the absence of light* with **13a**<sup>13</sup>, **13b** was isolated in 90% yield (*E/Z*, >20:1).

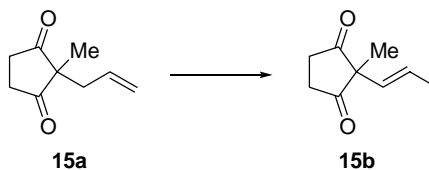
[α]<sub>D</sub> - 208.0 (*c* 0.1, CHCl<sub>3</sub>); m.p. 119-120 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) 6.35 (d, 1H, *J* = 9.8 Hz), 6.09 (d, 1H, *J* = 9.8 Hz), 5.62 (qd, 1H, *J* = 6.5 and 15.8 Hz), 5.12 (dd, 1H, *J* = 1.5 and 15.8 Hz), 4.57 (dd, 1H, *J* = 1.1 and 11.6 Hz), 2.61 (s, 3H), 1.57 (d, 3H, *J* = 6.4 Hz), 1.49 (m, 1H), 1.23 (s, 3H), 1.15 (m, 2H), 0.98 (m, 2H), 0.74 (s, 3H); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ (ppm) 184.7, 176.4, 153.4, 150.4, 128.5, 128.0, 125.9, 125.5, 78.2, 55.8, 48.2, 40.2, 36.7, 24.0, 21.0, 18.2, 17.4, 10.8; IR (film, cm<sup>-1</sup>) 2968, 2934, 1782, 1663, 1636, 1615, 1038; HRMS calcd. for C<sub>18</sub>H<sub>23</sub>O<sub>3</sub> (M + H<sup>+</sup>) 287.1641, found: 287.1634.

### (2*S*, 3*S*, 5*S*)-(2-Benzoyloxymethoxy-3,5-dimethyl-oct-6-enyloxy)-*tert*-butyl-diphenyl-silane (**14b**)



Following the general procedure with **14a**<sup>14</sup>, **14b** was isolated in 90 % yield (*E/Z*, 5:1).  $[\alpha]_{\text{D}} - 19.7$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>)  $\delta$  (ppm) 7.74 (m, 4H), 7.36 (m, 11H), 5.39 (m, 2H), 4.97 (d, 1H, *J* = 6.9 Hz), 4.87 (d, 1H, *J* = 6.9 Hz), 4.72 (d, 1H, *J* = 11.7 Hz), 4.62 (d, 1H, *J* = 11.7 Hz), 3.76 (m, 3H), 2.09 (m, 1H), 1.98 (m, 1H), 1.66 (d, 3H, *J* = 6.5 Hz with minor *Z*), 1.32 (m, 1H), 1.10 (s, 9H + 1H), 0.93 (m 8H with d of 6H *J* = 6.7 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 137.7, 137.5, 137.1(min), 136.4(min), 135.3, 135.2, 133.1, 129.3, 129.2, 128.0, 127.4, 127.3, 127.2, 127.1, 123.1(min), 122.2, 121.5(min), 94.5(min), 94.3, 82.4(min), 81.6, 69.2(min), 69.1, 63.8, 39.4(min), 39.2, 33.8, 32.2(min), 32.0, 31.8(min), 28.5(min), 26.4, 20.0(min), 19.8, 18.8, 17.6, 15.4(min), 15.3, 15.0(min); IR (film, cm<sup>-1</sup>) 3071, 2959, 1455, 1428, 1379, 1112, 1041; LRMS (ES+) 531.3 (*M* + H<sup>+</sup>, 25); HRMS calcd. for C<sub>34</sub>H<sub>46</sub>O<sub>3</sub>SiNa (*M* + Na<sup>+</sup>) 553.3108, found: 553.3113.

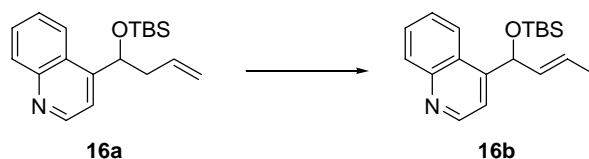
### 2-Methyl-2-propenyl-cyclopentane-1,3-dione (15b)



Following the general procedure with **15a**, **15b** was isolated in 92% yield (*E/Z*, >20:1). <sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 5.54 (m, 1H), 5.32 (dd, 1H, *J* = 1.5 and 15.6 Hz), 3.00-2.58 (m, 4H), 1.67 (dd, 3H, *J* = 1.5 and 6.5 Hz), 1.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 213.5, 128.7, 127.4, 59.6, 34.5(2), 17.8, 17.5; IR (film, cm<sup>-1</sup>) 2933, 1767, 1725, 1450, 1421, 1256, 1031; HRMS calcd. for C<sub>9</sub>H<sub>13</sub>O<sub>2</sub> (M + H<sup>+</sup>) 153.0910, found: 153.0911.

#### 4-[1-(*tert*-Butyl-dimethyl-silanyloxy)-but-2-enyl]-quinoline (16b)

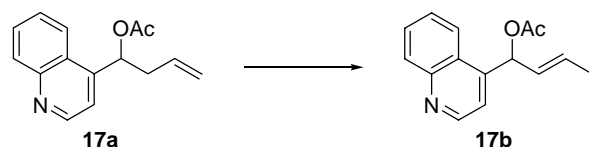




Following the general procedure with **16a**<sup>15</sup>, **16b** was isolated in 74% yield (*E/Z*, 10:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 8.92 (d, 1H, *J* = 4.5 Hz), 8.13 (d, 1H, *J* = 8.1 Hz), 8.10 (d, 1H, *J* = 8.5 Hz), 7.71 (t, 1H, *J* = 8.3 Hz), 7.60 (d, 1H, *J* = 4.5 Hz), 7.55 (d, 1H, *J* = 7.0 Hz), 5.80-5.60 (m, 3H), 1.95 (d, 1/11 3H<sub>minor,Me</sub>, *J* = 5.4 Hz), 1.66 (d, 9/11 3H<sub>major,Me</sub>, *J* = 6.2 Hz), 0.94 (s, 9H), 0.12 (s, 3H), 0.02 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 150.1, 149.2, 147.9, 132.5, 129.8, 128.4, 126.6, 125.7, 125.0, 123.4, 117.5, 71.9, 25.4, 17.9, 17.3, -4.9, -5.2; IR (film, cm<sup>-1</sup>) 2955, 2929, 1591, 1508, 1471, 1253, 1092; HRMS calcd. for C<sub>19</sub>H<sub>28</sub>NOSi (M + H<sup>+</sup>) 314.1934, found: 314.1940.

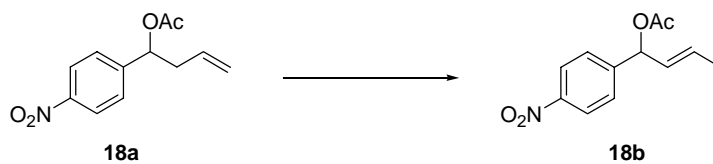
#### Acetic acid 1-quinolin-4-yl-but-2-enyl ester (**17b**)



Following the general procedure with **17a**<sup>15</sup>, **17b** was isolated in 61% yield (*E/Z*, 5:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 8.92 (d, 1H, *J* = 4.3 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 8.08 (d, 1H, *J* = 8.4 Hz), 7.73 (t, 1H, *J* = 7.0 Hz), 7.58 (m, 1H), 7.52-7.44 (m, 1H), 7.22 (d, 1/6H, *J* = 8.9 Hz), 6.90 (d, 5/6H, *J* = 5.4 Hz), 5.82 (m, 2H), 2.17 (s, 3H), 1.94 (d, 1/6 of 3H, *J* = 6.9 Hz), 1.71 (d, 5/6 of 3H, *J* = 5.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.4, 149.8, 148.0, 144.4, 131.2, 129.9, 128.8, 127.6, 126.3, 125.0, 123.2, 118.0, 72.0, 20.8, 17.4. IR (film, cm<sup>-1</sup>) 2935, 1743, 1593, 1508, 1231, 1036; HRMS calcd. for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub> (M + H<sup>+</sup>) 242.1175, found: 242.1176

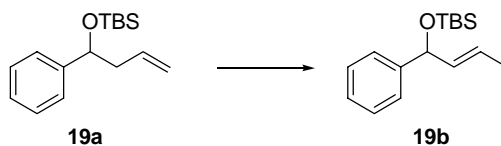
#### Acetic acid 1-(4-nitro-phenyl)-but-2-enyl ester (**18b**)



Following the general procedure with **18a**<sup>16</sup>, **18b** was isolated in 93 % yield (*E/Z*, 7:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 8.21 (d, 1H, *J* = 8.8 Hz), 7.50 (d, 1H, *J* = 8.6 Hz), 6.65 (d, 1/8H, *J* = 9.1 Hz), 6.26 (d, 7/8H, *J* = 7.2 Hz), 5.80 (m, 1H), 5.60 (m, 1H), 2.14 (s, 3H), 1.85 (d, 1/8 of 3H, *J* = 7.0 Hz), 1.74 (d, 7/8 of 3H, *J* = 6.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.4, 146.6, 130.9, 127.9, 127.0, 123.4, 74.9, 20.8, 17.4; IR (film, cm<sup>-1</sup>) 2944, 1736, 1606, 1521, 1348, 1228; HRMS calcd. for C<sub>12</sub>H<sub>13</sub>O<sub>4</sub>Na (M + Na<sup>+</sup>) 258.0736, found: 258.0782.

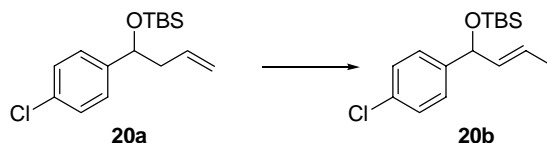
***tert*-Butyl-dimethyl-(1-phenyl-but-2-enyloxy)-silane (19b)**



Following the general procedure with **19a**<sup>17</sup>, **19b** was isolated in 92% yield (*E/Z*, 9:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 7.35 (m, 5H), 5.65 (m, 1H), 5.60 (m, 1H), 5.15 (d, 1H, *J* = 6.4 Hz), 1.83 (d, 1/10 of 3H, *J* = 5.4 Hz), 1.71 (d, 9/10 of 3H, *J* = 6.1 Hz), 0.94 (s, 9H), 0.09 (s, 3H), 0.03 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 144.1, 134.6, 127.7, 126.4, 125.4, 125.1, 124.7, 75.2, 69.4(min), 25.5, 17.9, 17.2, -4.8, -5.1; IR (film, cm<sup>-1</sup>) 2930, 2857, 1692, 1451, 1230, 1112; LRMS (ES+) 249.1 (M - Me<sub>TBS</sub>, 20), 233.1 (M - 2Me<sub>TBS</sub>, 85).

***tert*-Butyl-[1-(4-chloro-phenyl)-but-2-enyloxy]-dimethyl-silane (20b)**

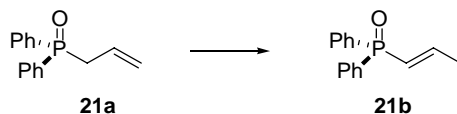


Following the general procedure with **20a**<sup>17</sup>, **20b** was isolated in 85% yield (*E/Z*, 9:1).

<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 7.30 (m, 4H), 5.69 (m, 1H), 5.55 (dd, 1H, *J* = 6.5 and 14.4 Hz), 5.13 (d, 1H, *J* = 6.5 Hz), 1.82 (d, 1/10 of 3H, *J* = 5.4 Hz), 1.72 (d, 9/10 of 3H, *J* = 6.4 Hz), 0.95 (s, 9H), 0.10 (s, 3H), 0.05 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 142.7, 134.3, 134.0(min), 132.0, 127.8, 126.9, 126.5 (min), 125.1, 123.1(min),

116.8(min), 74.6, 68.9(min), 25.5, 25.4(min), 17.9, 17.1, -4.8, -5.1; IR (film,  $\text{cm}^{-1}$ ) 2956, 2929, 2857, 1488, 1253, 1087; HRMS calcd. for  $\text{C}_{16}\text{H}_{25}\text{OSiClAg}$  ( $\text{M} + \text{Ag}$ ) 403.0435, found: 403.0420.

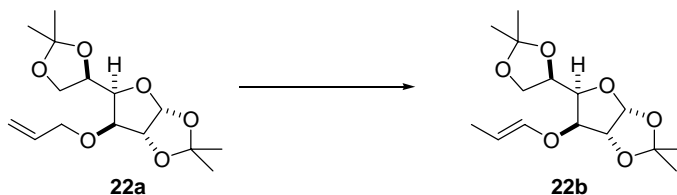
### 1-Propenyldiphenylphosphine oxide (21b)



Following the general procedure with **21a**, **21b** was isolated in 85% yield ( $E/Z$ , >20:1). Spectral data identical to those of the literature.<sup>18</sup>

HRMS calcd. for  $\text{C}_{15}\text{H}_{15}\text{OPNa}$  ( $\text{M} + \text{Na}^+$ ) 265.0752, found: 265.0760.

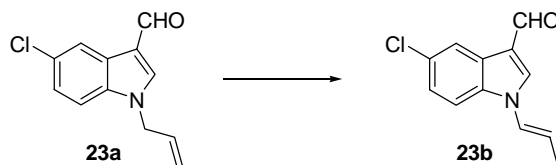
### (1R, 2R, 3S, 4R, 5R)-5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-6-propenyloxy-tetrahydro-furo[2,3-d][1,3]dioxole (22b)



Following the general procedure with **22a**<sup>29</sup>, **22b** was isolated in 75% yield ( $E/Z$ , 2:1).

$[\alpha]_{\text{D}} -9.8$  ( $c$  0.26,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CHCl}_3$ )  $\delta$  (ppm) 6.16 (dd, 1/3 H,  $J = 1.6$  and 12.5 Hz), 6.04 (dd, 2/3 H,  $J = 1.6$  and 6.1 Hz), 5.92 (d, 2/3 H,  $J = 3.7$  Hz), 5.87 (d, 1/3 H,  $J = 3.7$  Hz), 4.95 (sx, 1/3 H,  $J = 3.8$  Hz), 4.57-4.48 (m, 1H + 2/3H), 4.32 (qu, 1H,  $J = 7.2$  Hz), 4.23 (d, 1/3 H,  $J = 2.9$  Hz), 4.19-4.15 (m, 1H + 2/3H), 4.12-4.00 (m, 2H), 1.56 (m, 3H), 1.51 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.31 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 144.2, 143.5, 111.6, 111.4, 108.7, 108.6, 104.7(2), 102.9, 101.3, 82.6, 82.4, 81.7, 80.5, 80.3, 80.0, 71.9, 71.7, 66.6(2), 26.4(2), 26.3, 25.8, 24.9, 12.0, 8.8; IR (film,  $\text{cm}^{-1}$ ) 2928, 2936, 1670, 1373, 1255, 1216, 1165, 1131, 1076; HRMS calcd. for  $\text{C}_{15}\text{H}_{25}\text{O}_6$  ( $\text{M} + \text{H}^+$ ) 301.1645, found: 301.1647.

### 5-Chloro-1-propenyl-1H-indole-3-carbaldehyde (23b)

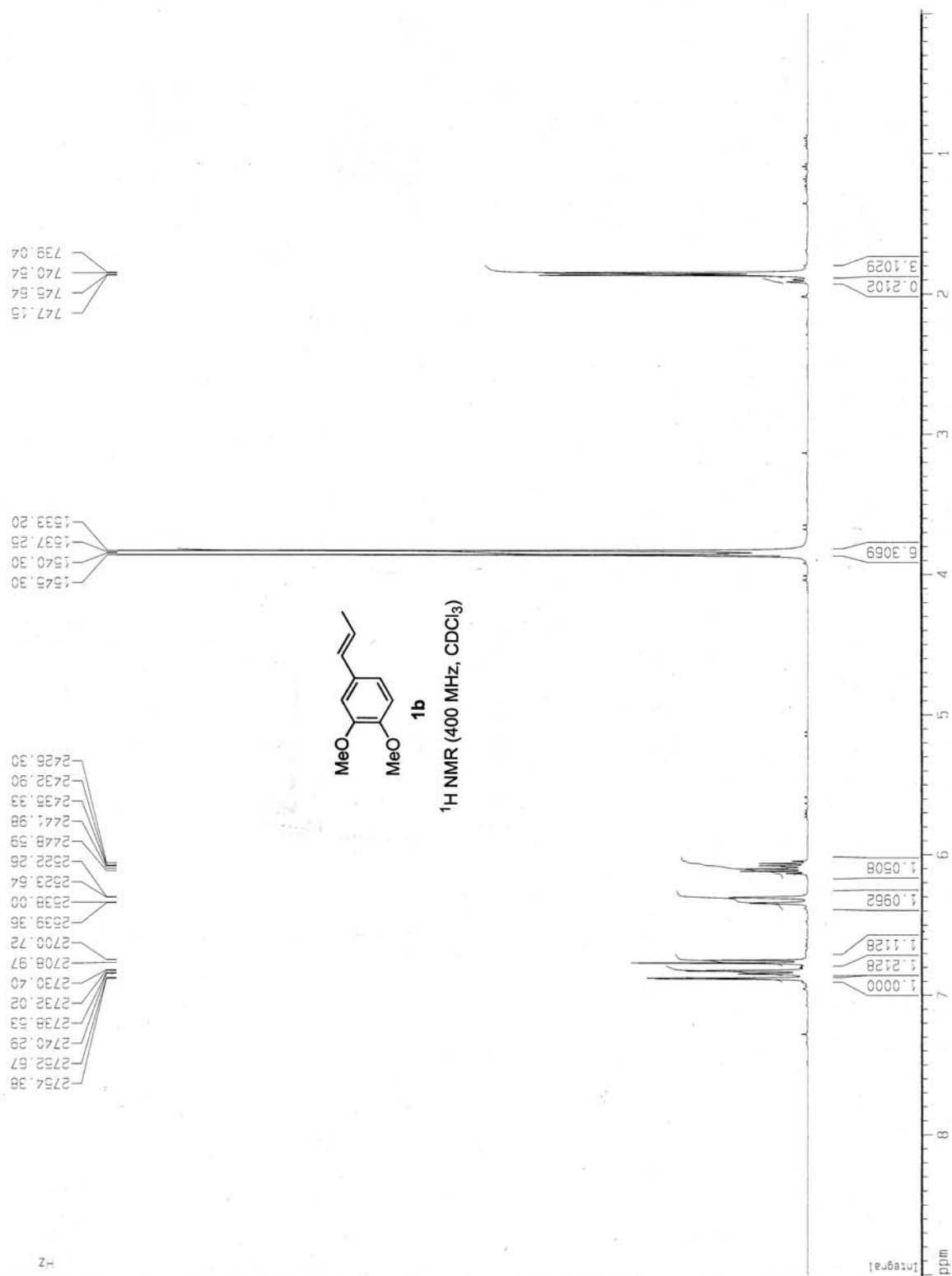


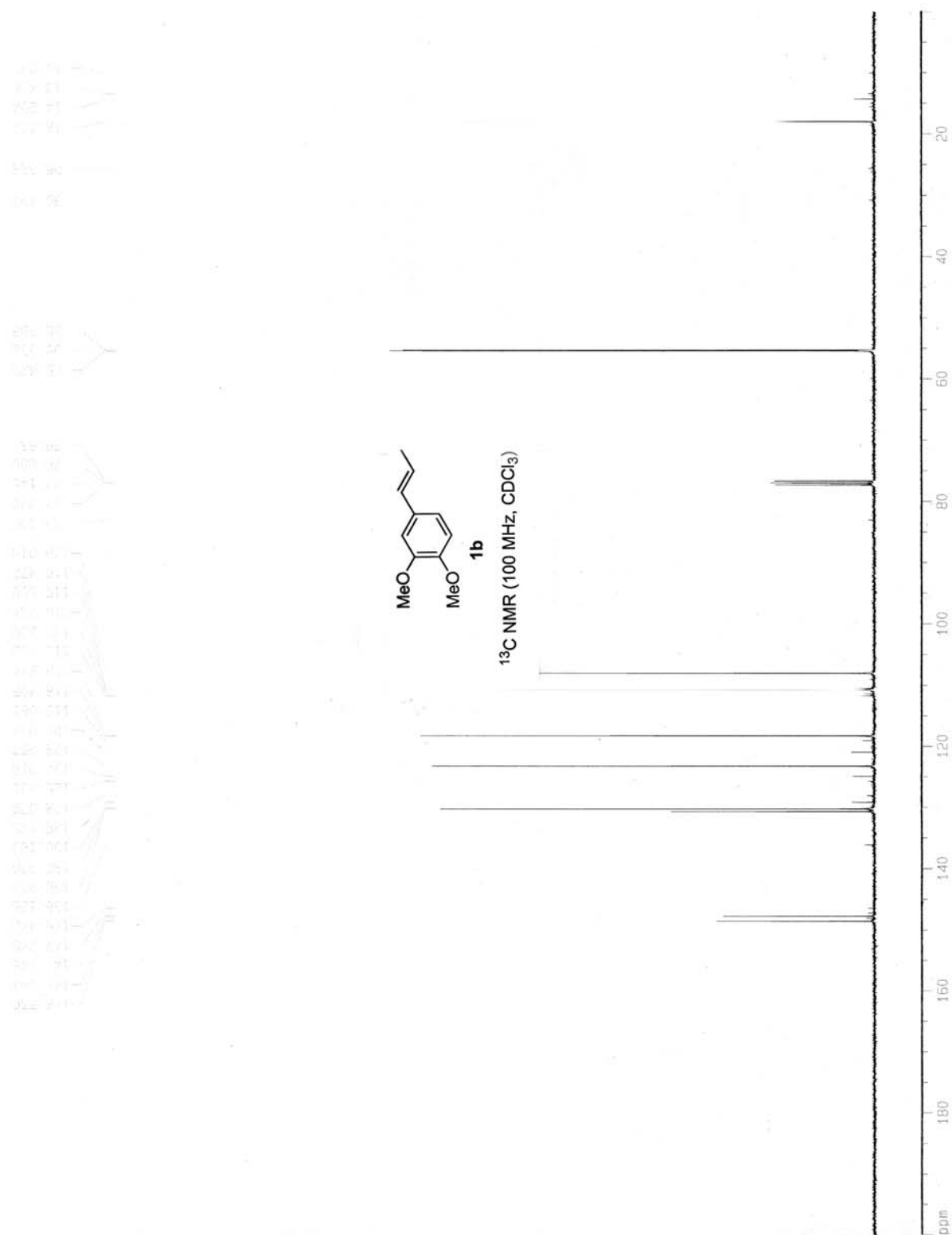
Following the general procedure with **23a**<sup>20</sup>, **23b** was isolated in 69% yield (*E/Z*, 4:1).

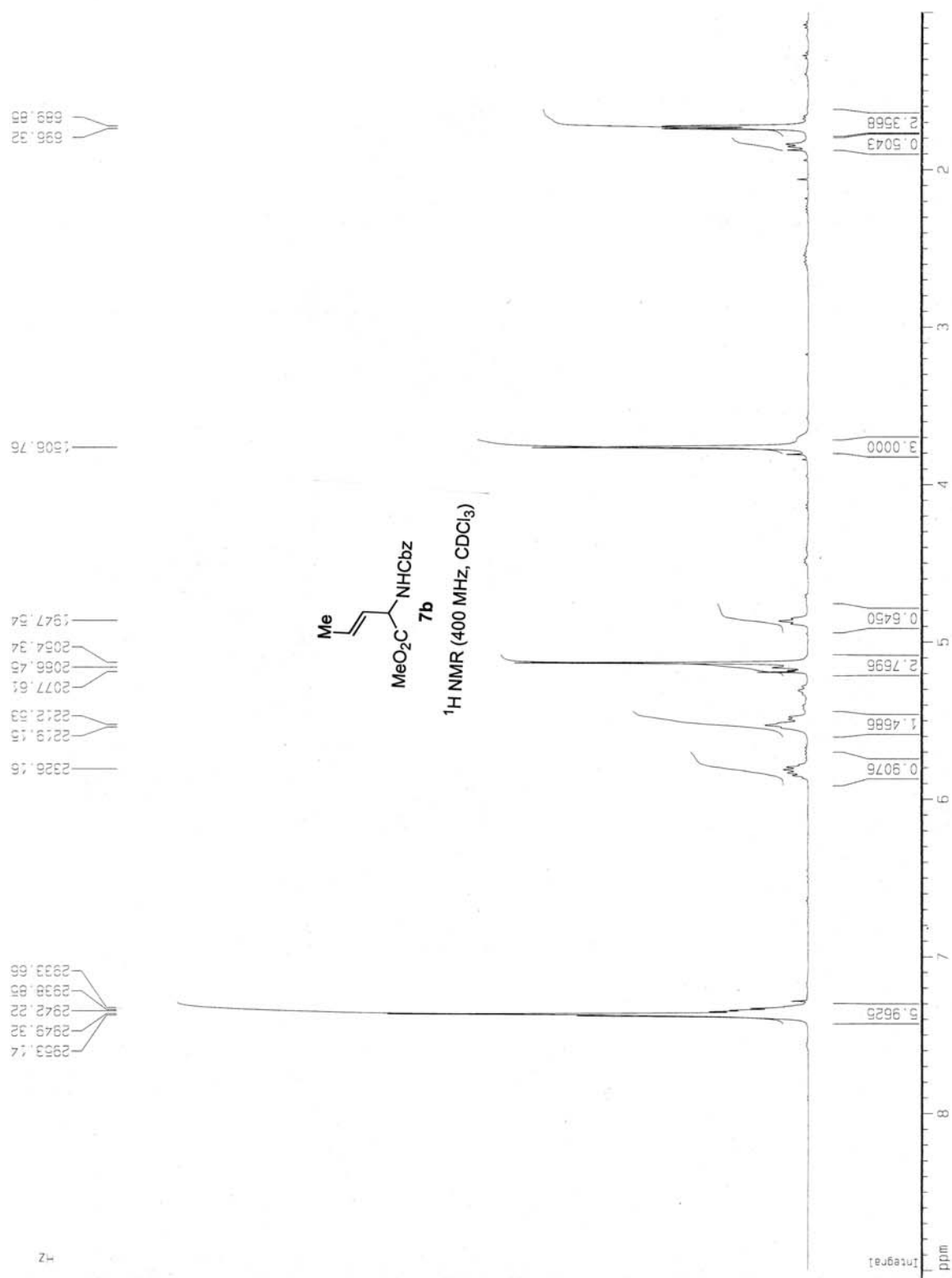
<sup>1</sup>H NMR (400 MHz, CHCl<sub>3</sub>) δ (ppm) 10.03 (s, 1/5H), 9.97 (s, 4/5H), 7.85 (s, 4/5H), 7.76 (s, 1/5H), 7.34-7.20 (m, 2H), 6.87 (d, 4/5H, *J* = 13.9 Hz), 6.76 (d, 1/5H, *J* = 8.3 Hz), 6.02 (dq, 4/5H, *J* = 6.8 Hz and 13.8 Hz); 5.89 (m, 1/5H), 1.95 (m, 4/5H), 1.95 (d, 4/5 of 3H, *J* = 6.8 Hz), 1.80 (d, 1.5 of 3H, *J* = 7.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 184.1, 138.2(min), 135.2, 134.4, 128.8, 125.6, 124.3, 124.2(min), 123.3, 122.9, 121.3, 121.2(min), 118.2(min), 117.9, 111.4(min), 110.8, 14.9, 12.5(min); IR (film, cm<sup>-1</sup>) 3110, 2791, 1663, 1530, 1455, 1404, 1180; HRMS calcd. for C<sub>12</sub>H<sub>11</sub>ClNO (*M* + *H*<sup>+</sup>) 220.0523, found: 220.0525.

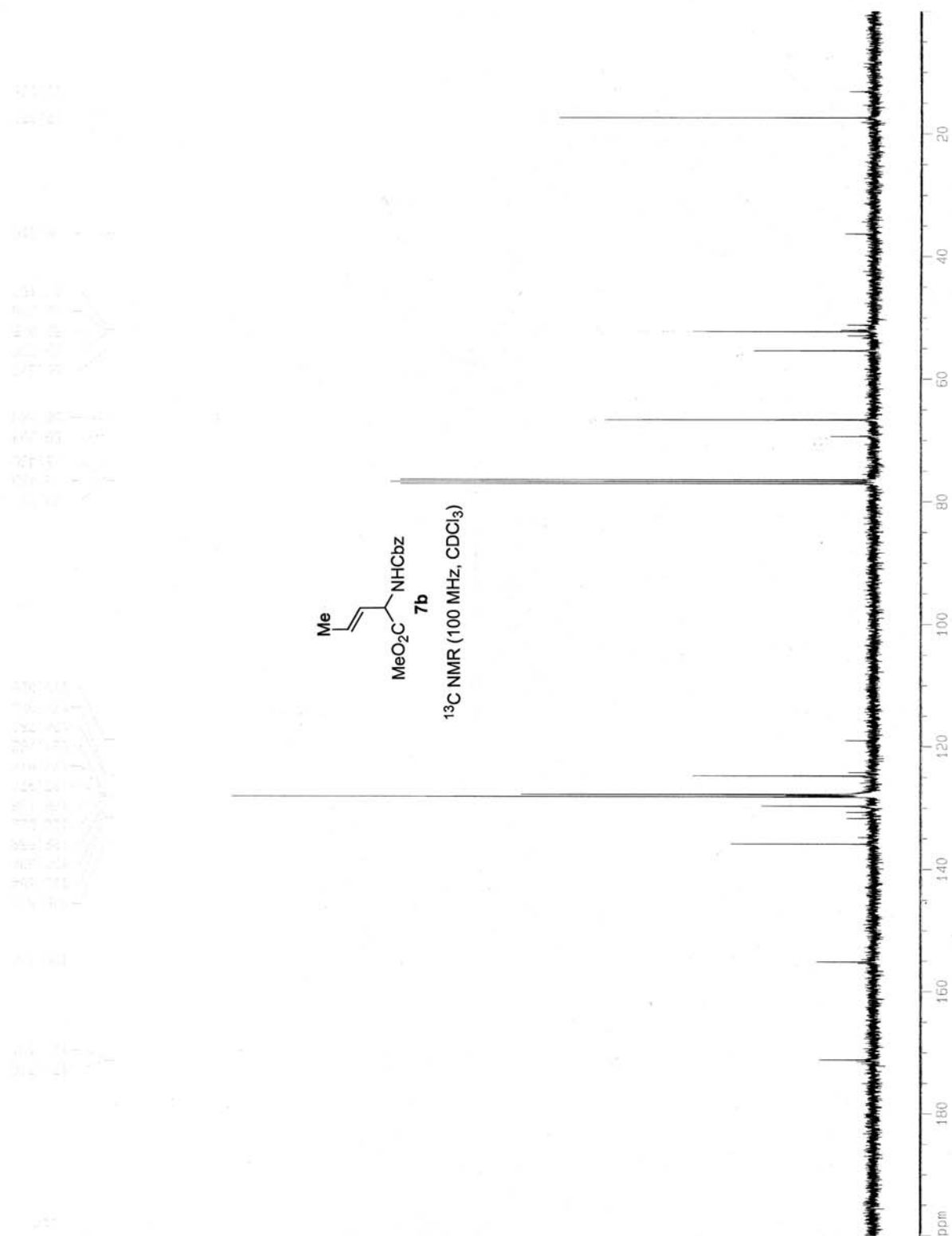
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- 5) **6a** was prepared *via* 3 steps (1. TsCl, NaOH, TBAHSO<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub> 2. *t*-BuLi, I<sub>2</sub>, Et<sub>2</sub>O, -78 °C, 3. *i*PrMgBr, CuCN·2LiCl, allylBr, THF, -30 °C) from commercially available 5-chloroindole.
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- 17) **19a** and **20a** were prepared by silylation (TBSCl, NEt<sub>3</sub>) of commercially available 4-Phenyl-1-butenol and 1-(4-Chlorophenyl)-3-buten-1-ol respectively.
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- 20) **23a** was prepared *via* allylation (allylBr, K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN) of commercially available 5-chloroindole-3-carboxaldehyde.

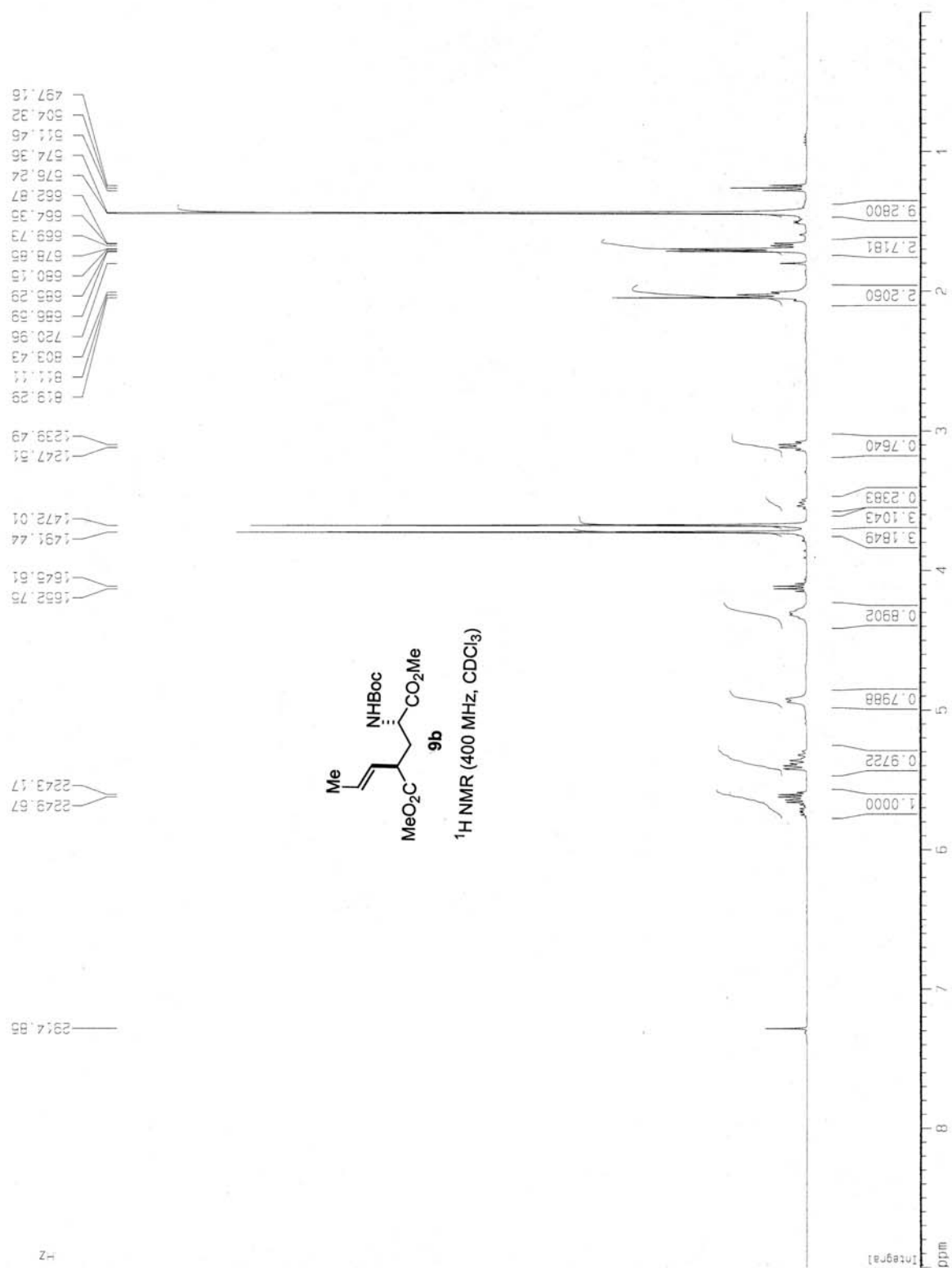


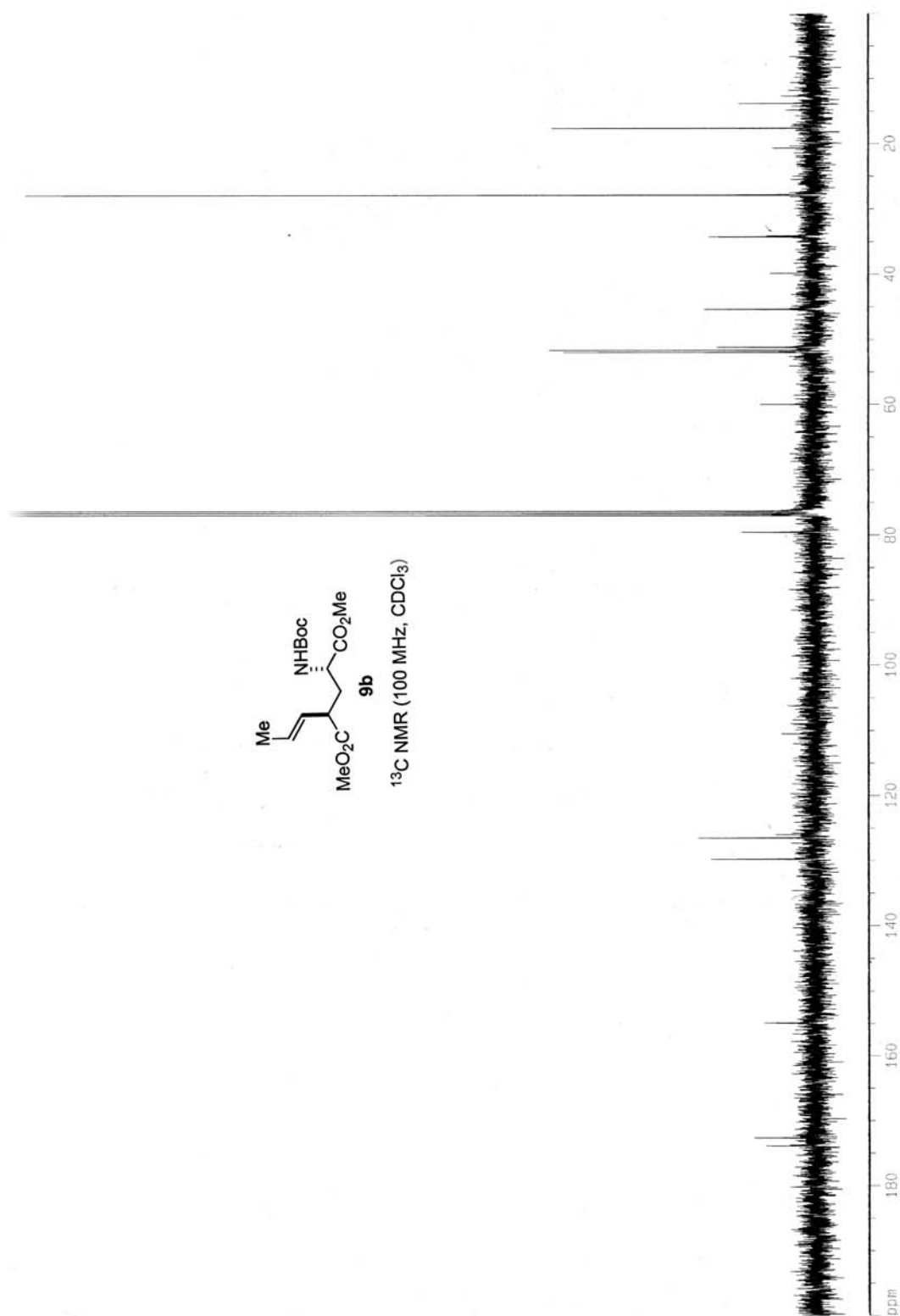


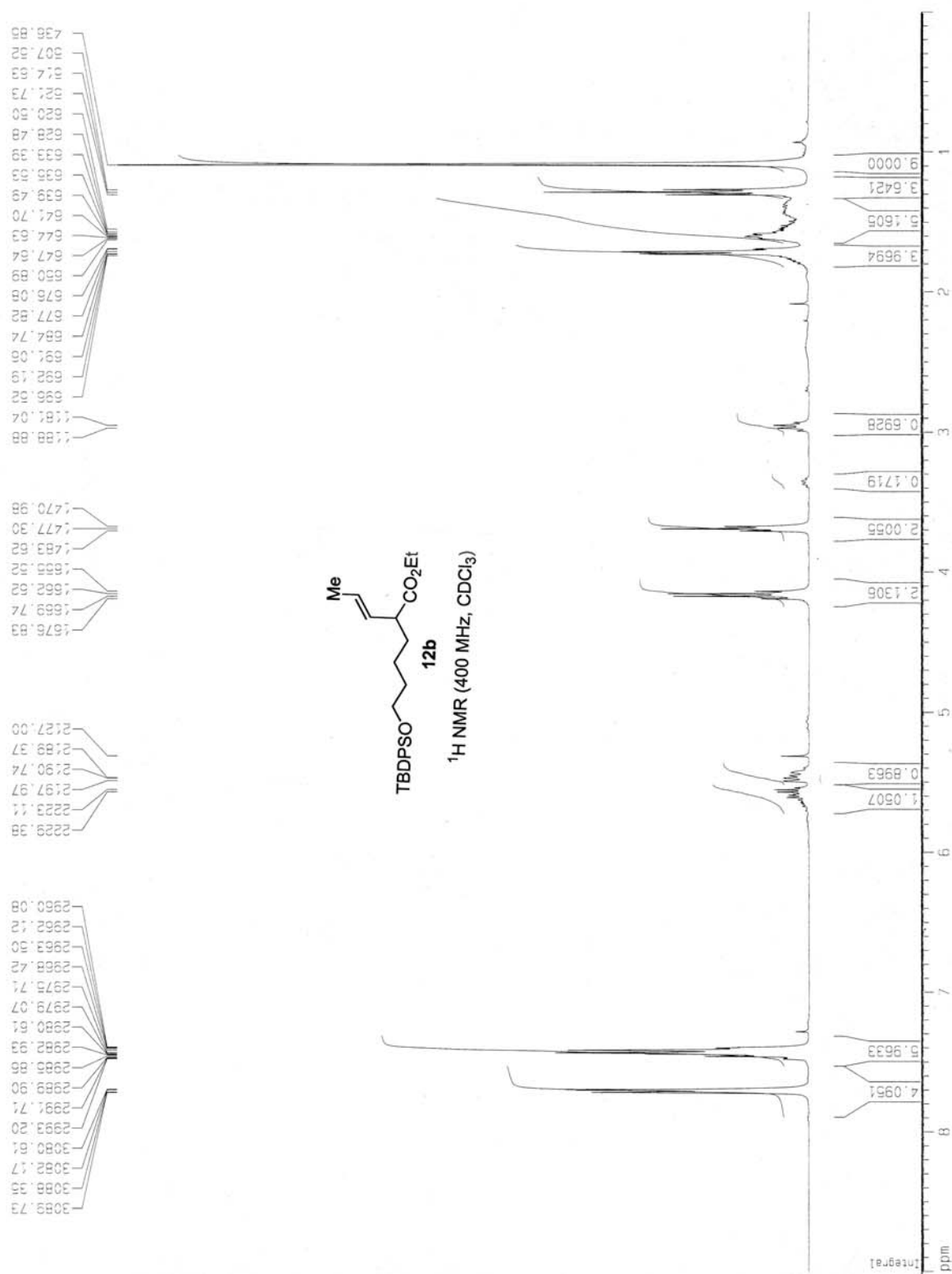


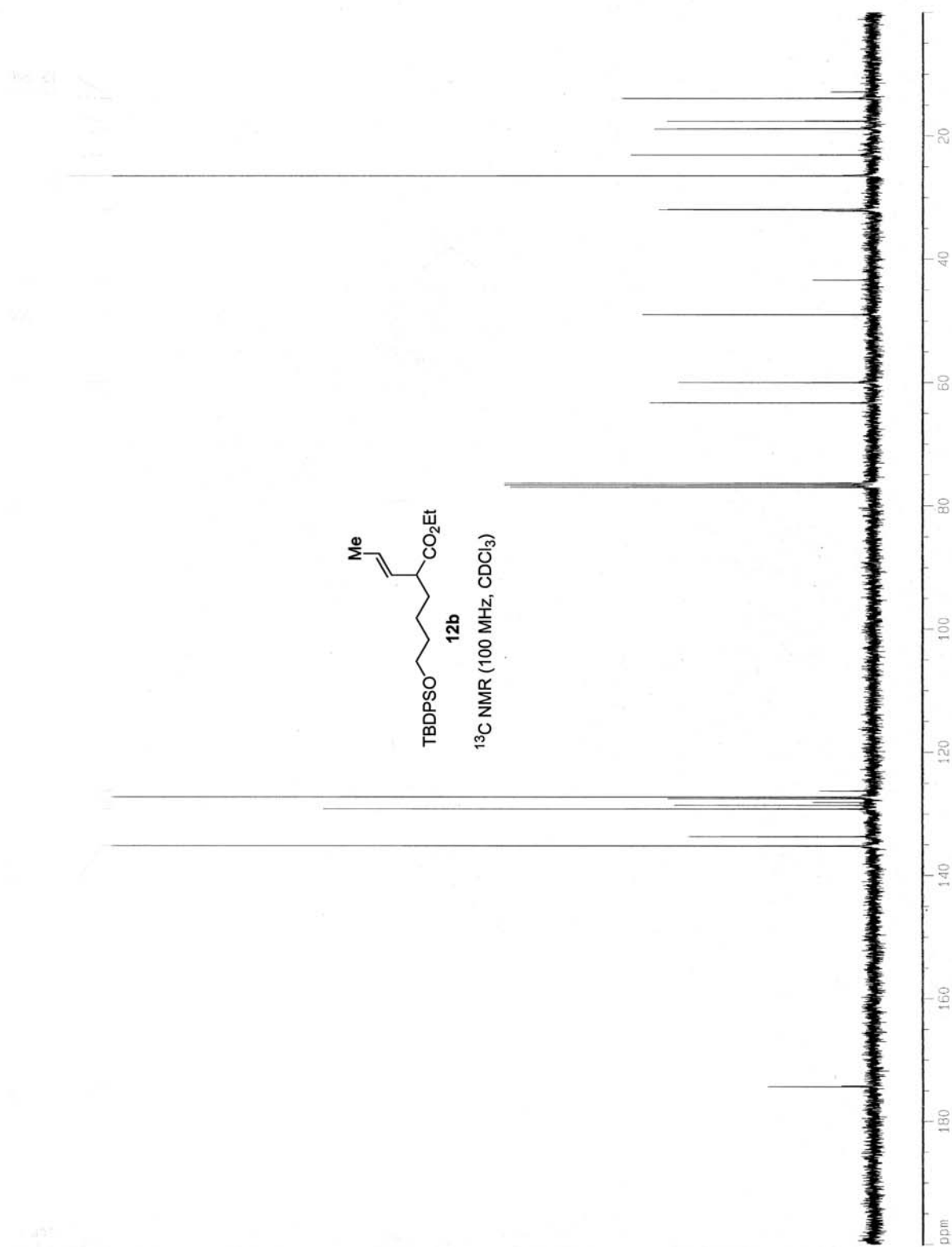


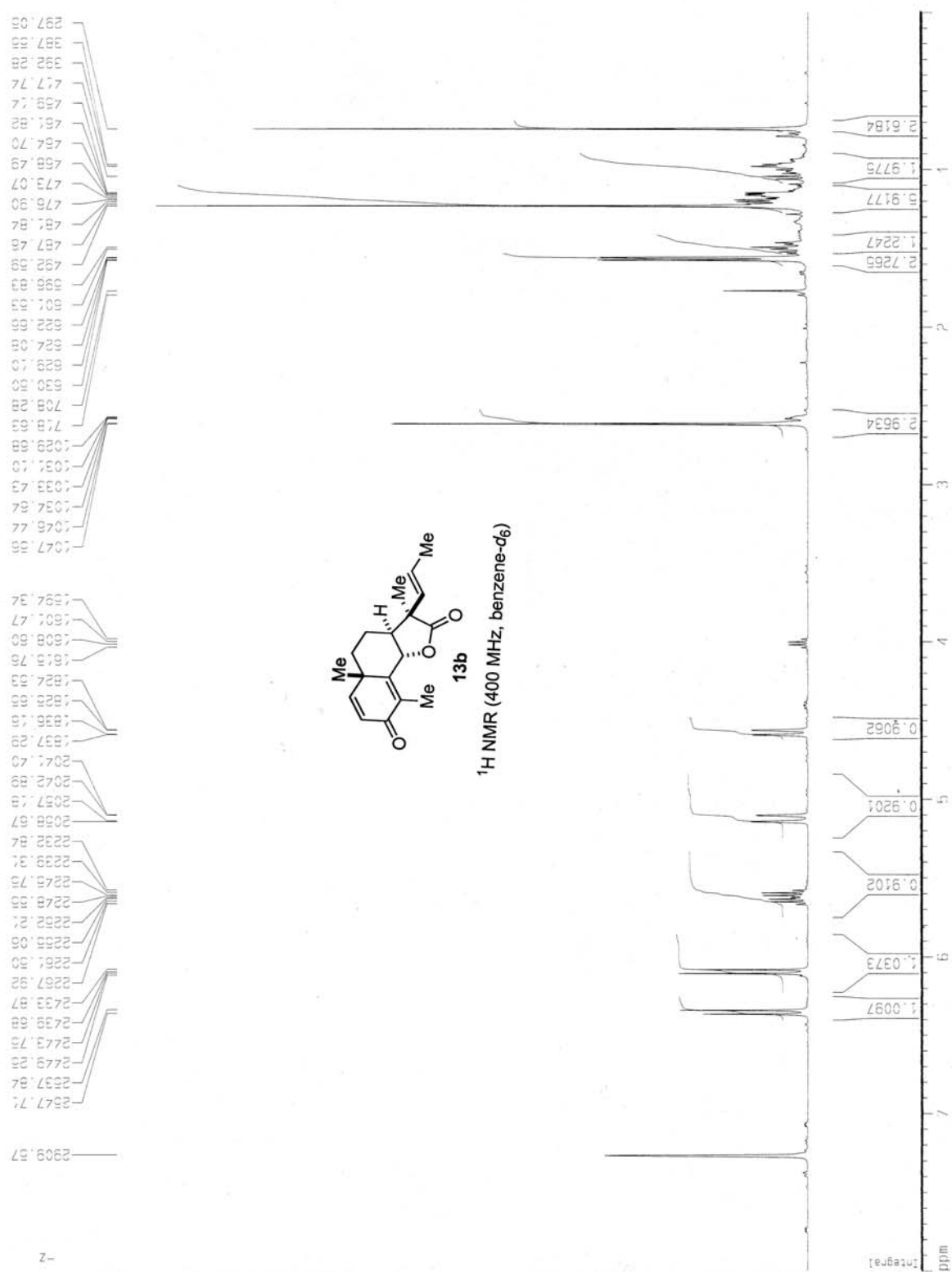


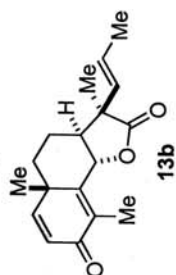




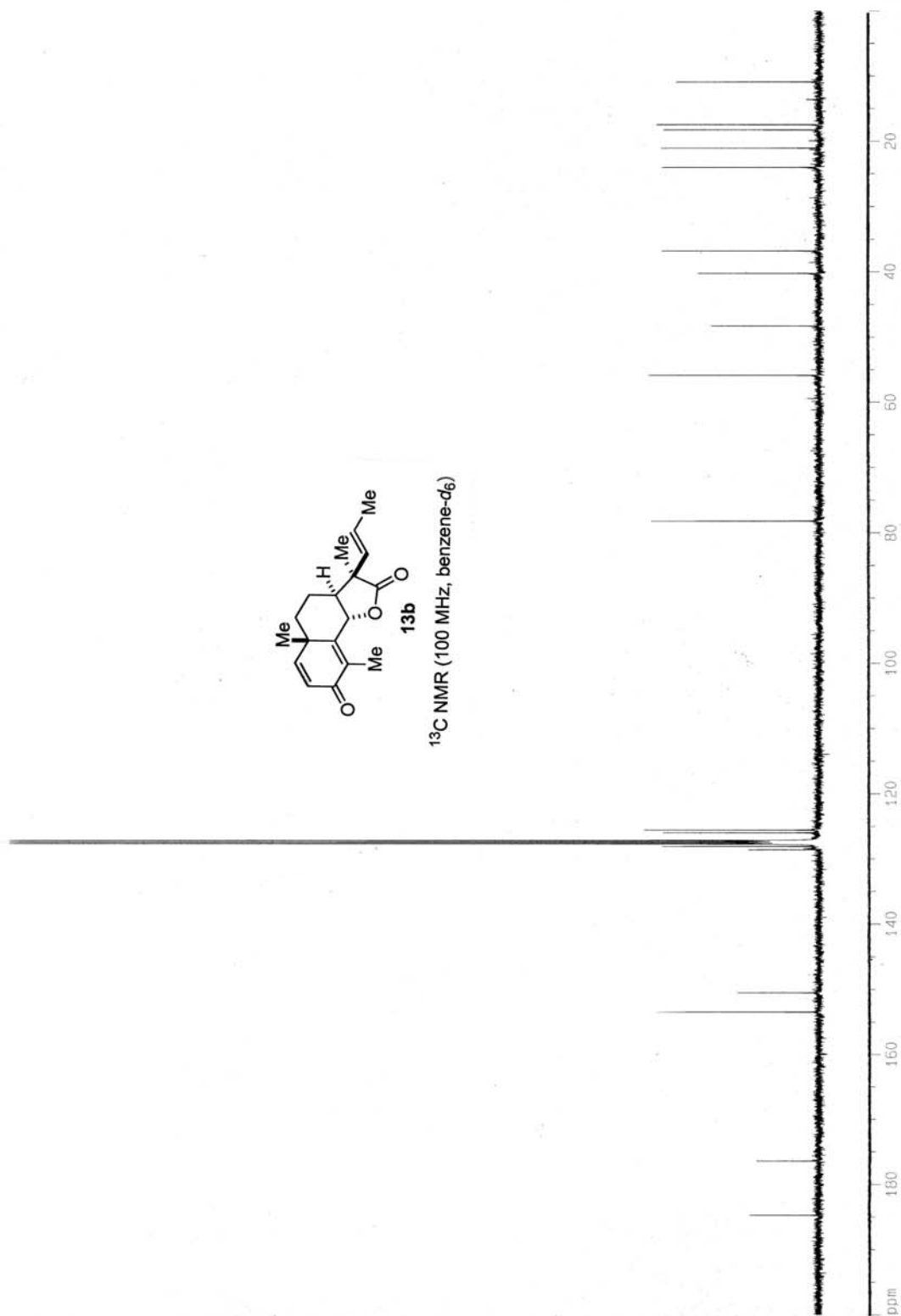




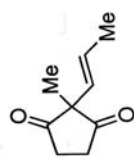




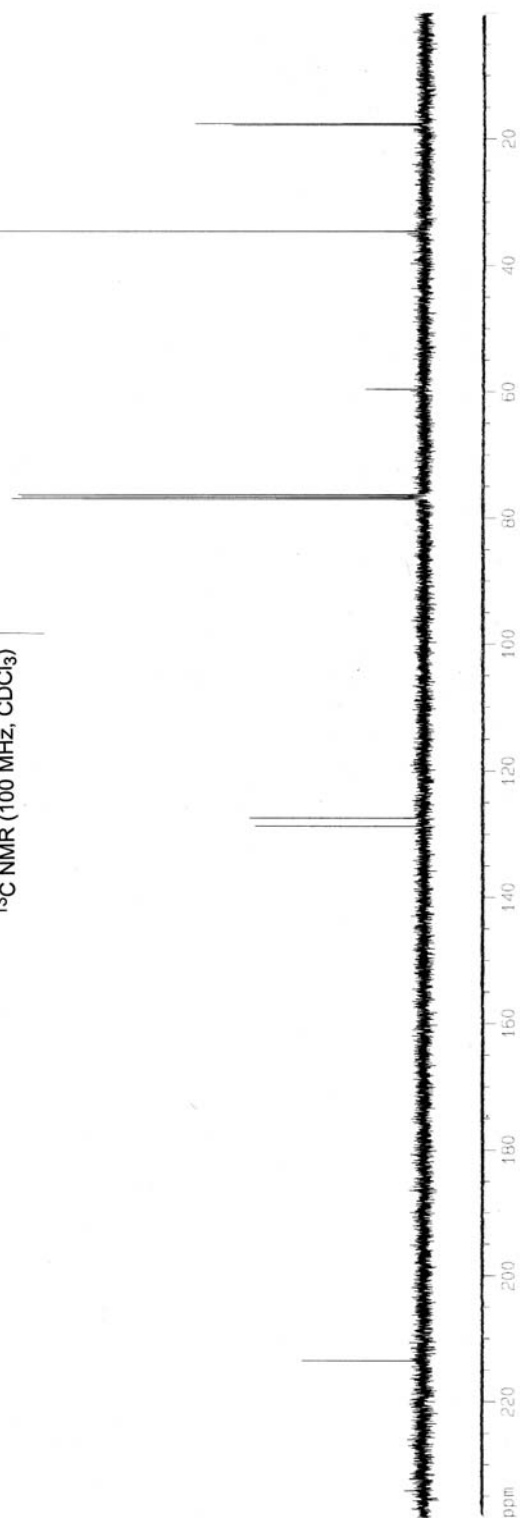
<sup>13</sup>C NMR (100 MHz, benzene-d<sub>6</sub>)



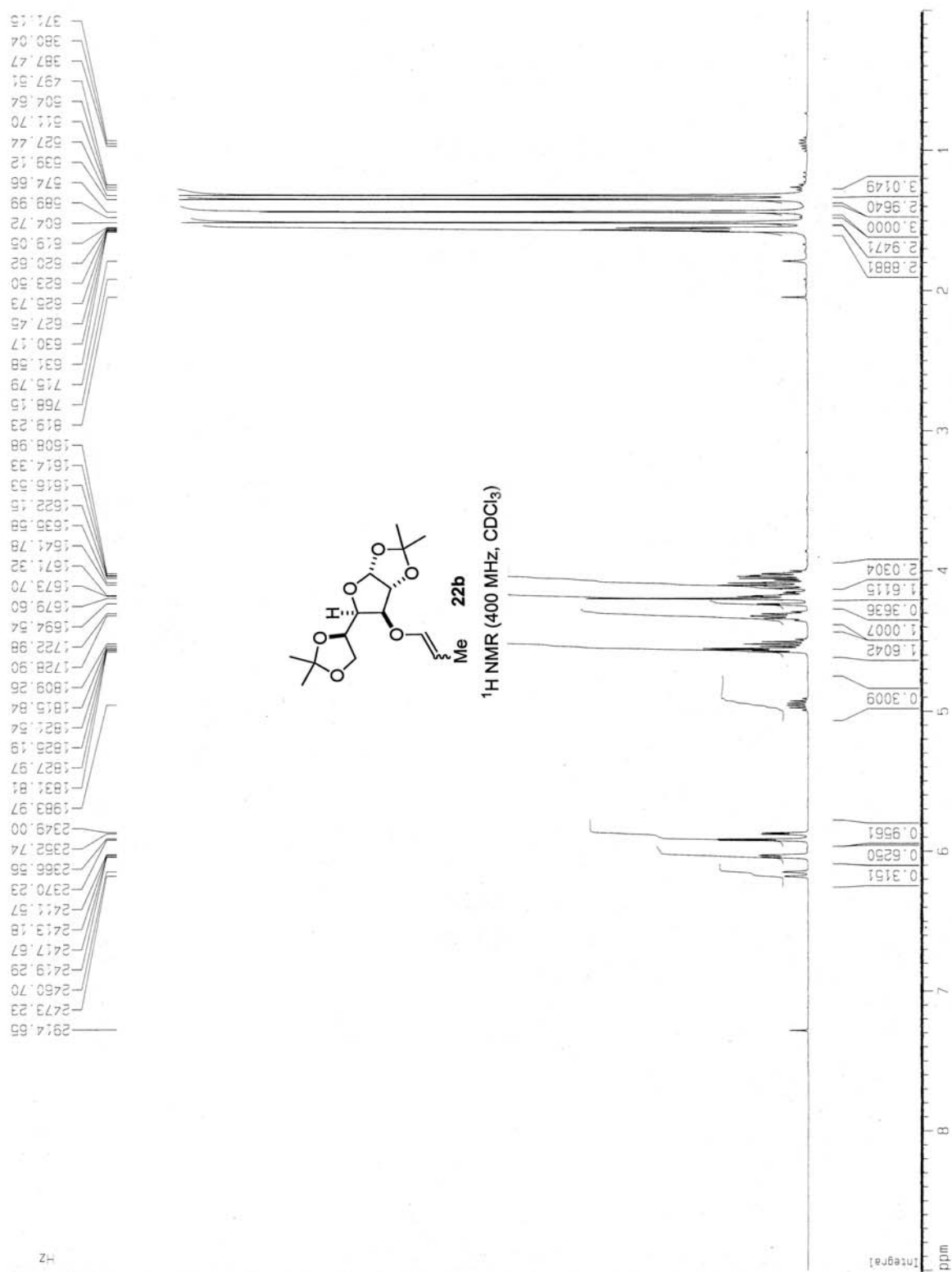


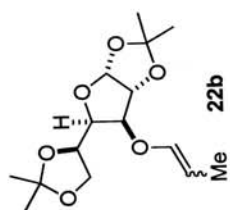
**15b**

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )

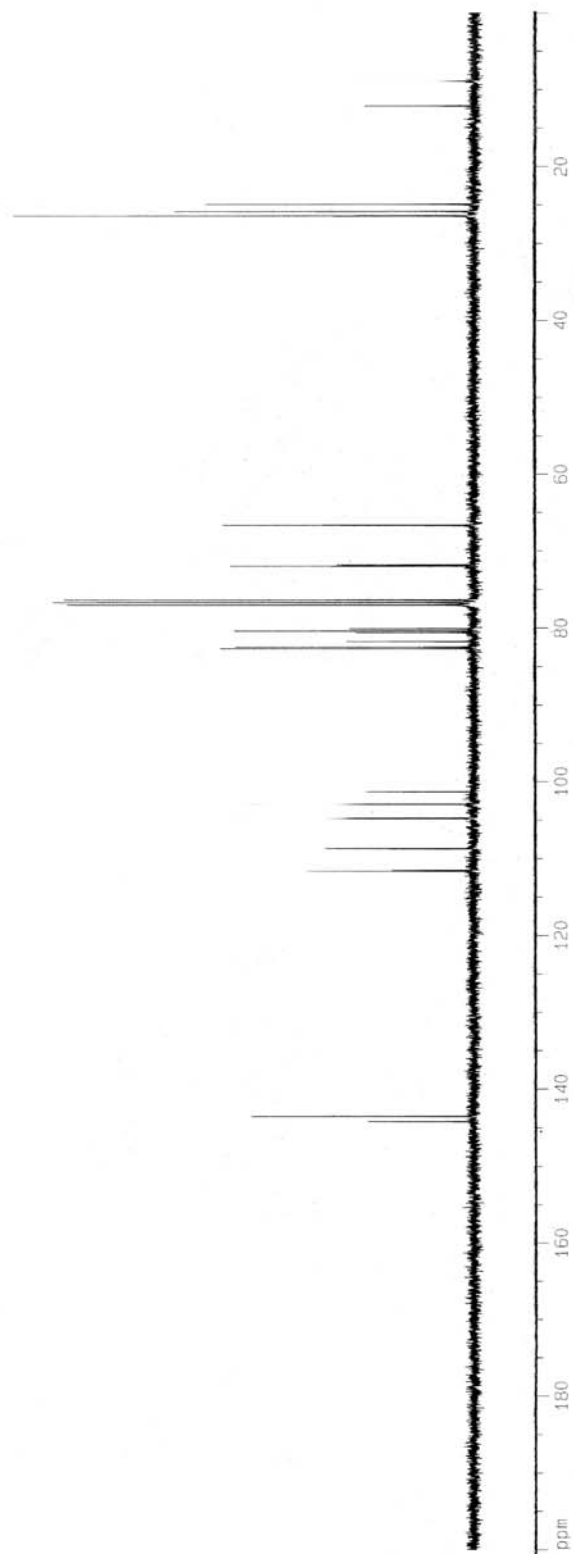


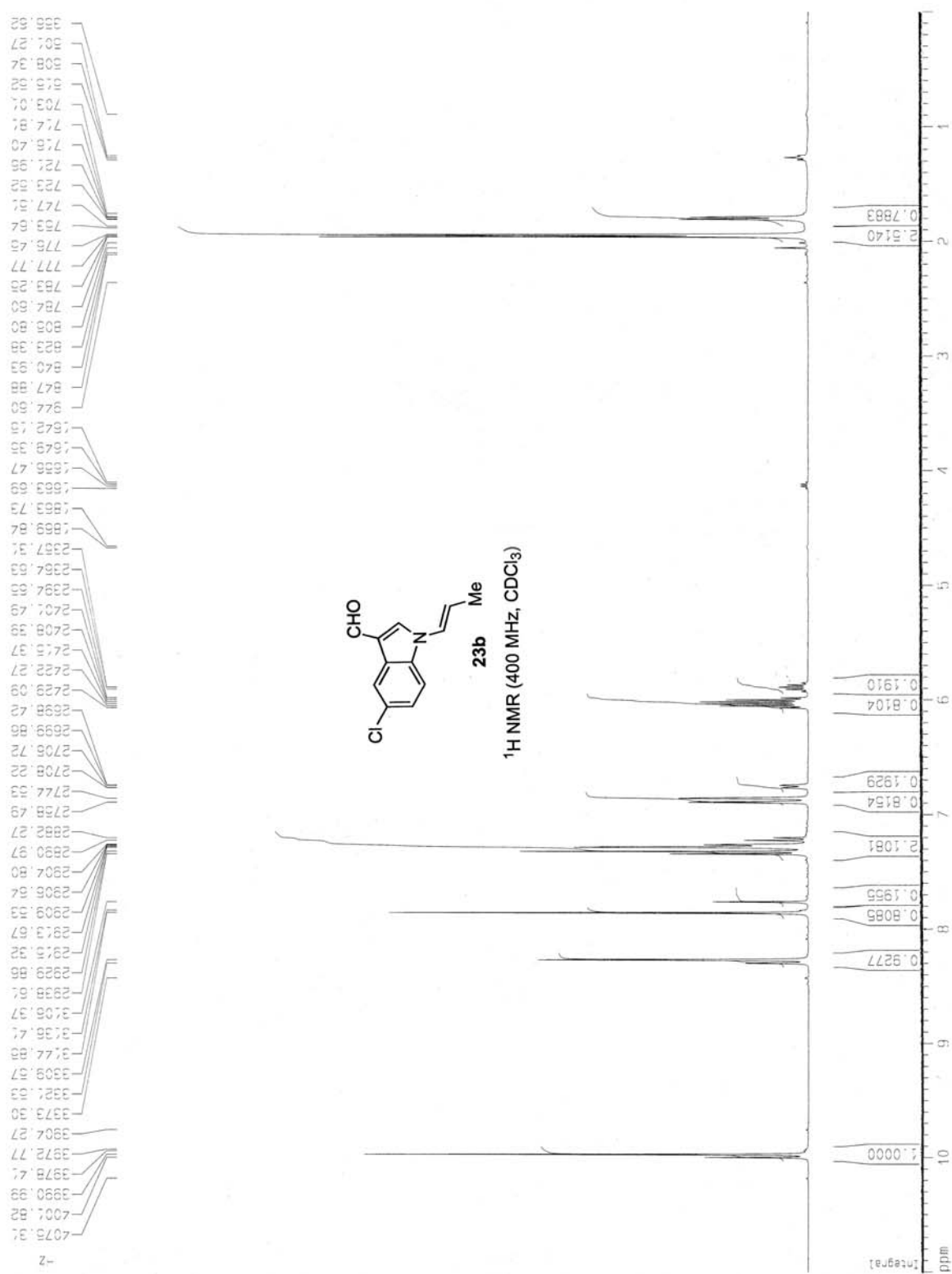


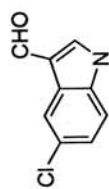




<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)





**23b** Me $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )