

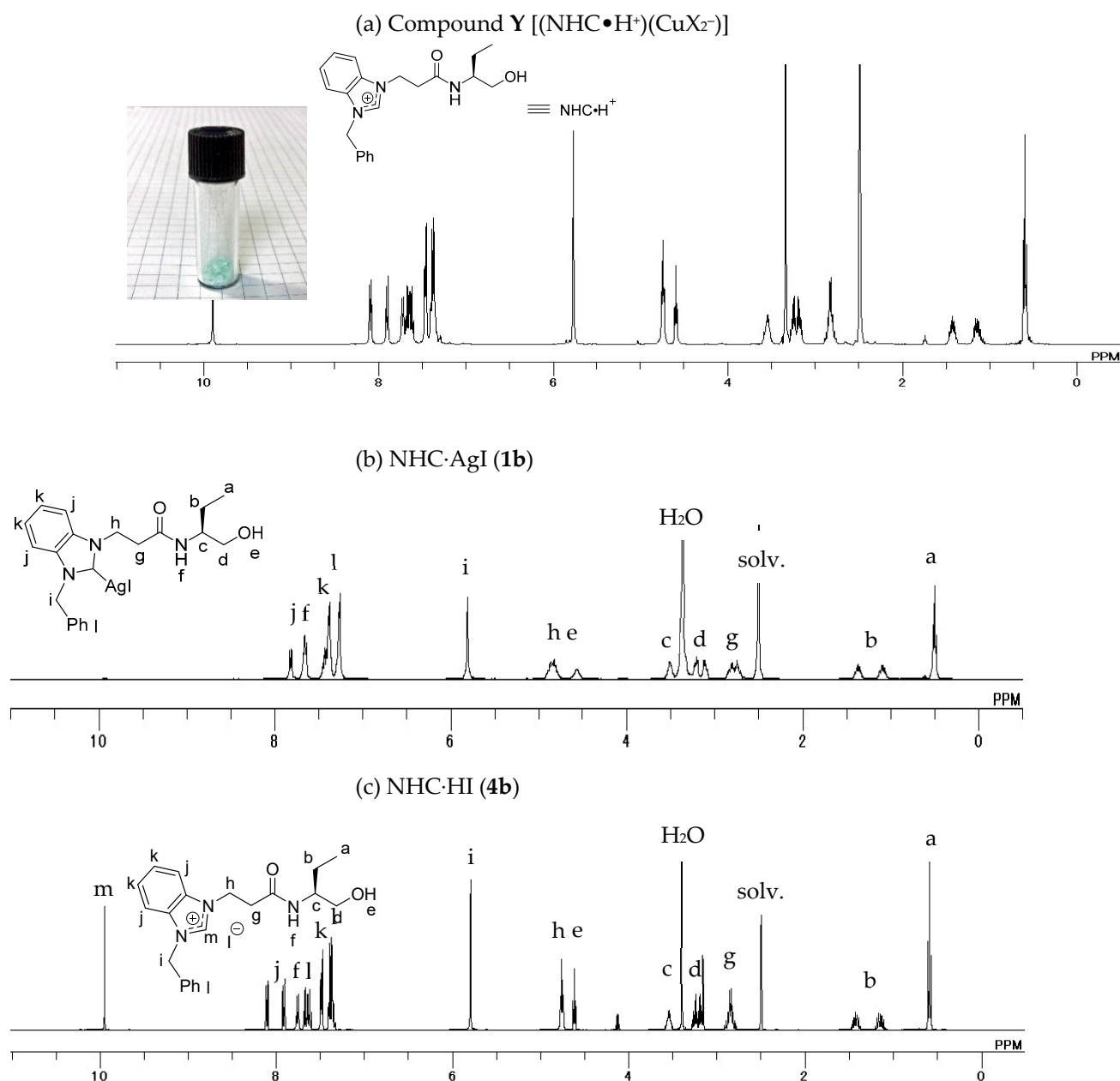
Supplementary Materials

# Reversal of Enantioselectivity in the Conjugate Addition Reaction of Cyclic Enones with the CuOTf/Azolium Catalytic System

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**Figure S1.** <sup>1</sup>H NMR spectra of (a) compound **Y**, (b) NHC•AgI (**1b**) and (c) NHC•HI (**4b**) in DMSO-*d*<sub>6</sub>.

## 2. Spectral data for azolium compounds

### 4a (R<sup>1</sup>=Me, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.48 (s, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.63-7.48 (m, 6H), 7.40-7.31 (m, 3H), 5.80 (d, *J* = 15.4 Hz, 1H), 5.71 (d, *J* = 15.4 Hz, 1H), 4.97-4.92 (m, 1H), 4.86-4.82 (m, 1H), 3.93-3.86 (m, 1H), 3.61-3.54 (m, 1H), 3.49-3.40 (m, 3H), 3.11-3.06 (m, 2H), 1.05 (d, *J* = 6.3 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 141.7, 132.1, 131.8, 130.9, 129.4, 128.3, 127.3, 113.6, 113.3, 65.3, 51.8, 48.2, 44.1, 35.4, 16.5.

### 4b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.51 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.62-7.57 (m, 1H), 7.52-7.44 (m, 5H), 7.40-7.33 (m, 3H), 5.80 (d, *J* = 15.1 Hz, 1H), 5.74 (d, *J* = 15.1 Hz, 1H), 4.99-4.93 (m, 1H), 4.88-4.81 (m, 1H), 3.77-3.69 (m, 1H), 3.51-3.44 (m, 3H), 3.31 (br, 1H), 3.17-3.09 (m, 1H), 1.47-1.34 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.2, 141.7, 132.1, 131.8, 130.9, 129.4, 129.4, 128.3, 127.4, 127.3, 113.6, 113.3, 63.7, 53.9, 51.8, 44.0, 35.3, 23.8, 10.5.

### Ent-4b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.52 (s, 1H), 7.89 (d, *J* = 8.7 Hz, 1H), 7.64-7.57 (m, 1H), 7.54-7.43 (m, 5H), 7.40-7.33 (m, 3H), 5.80 (d, *J* = 15.1 Hz, 1H), 5.75 (d, *J* = 15.1 Hz, 1H), 5.00-4.93 (m, 1H), 4.88-4.82 (m, 1H), 3.77-3.69 (m, 1H), 3.52-3.42 (m, 3H), 3.29 (br, 1H), 3.16-3.10 (m, 1H), 1.47-1.36 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.4, 141.9, 132.3, 131.8, 130.9, 129.4, 129.3, 128.3, 127.3, 127.2, 113.7, 113.4, 63.7, 53.8, 51.9, 44.1, 35.5, 23.8, 10.5.

### 4c (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.45 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.59-7.56 (m, 1H), 7.50-7.47 (m, 4H), 7.38-7.32 (m, 4H), 5.78 (d, *J* = 15.1 Hz, 1H), 5.73 (d, *J* = 15.1 Hz, 1H), 4.97-4.92 (m, 1H), 4.86-4.81 (m, 1H), 3.94-3.91 (m, 1H), 3.50-3.40 (m, 3H), 3.26-3.25 (br, 1H), 3.12-3.07 (m, 1H), 1.43-1.30 (m, 2H), 1.16-1.10 (m, 1H), 0.78 (d, *J* = 6.2 Hz, 3H), 0.74 (d, *J* = 6.2 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.2, 142.0, 132.3, 131.8, 130.9, 129.4, 129.3, 128.3, 127.3, 127.2, 113.7, 113.4, 64.6, 51.9, 50.4, 44.1, 39.7, 35.5, 24.7, 22.8, 22.1.

### 4d (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.55 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 1H), 7.61-7.57 (m, 1H), 7.52-7.49 (m, 4H), 7.40-7.34 (m, 4H), 5.80 (d, *J* = 15.0 Hz, 1H), 5.74 (d, *J* = 15.0 Hz, 1H), 5.00-4.95 (m, 1H), 4.88-4.85 (m, 1H), 3.71-3.66 (m, 1H), 3.62-3.51 (m, 2H), 3.45-3.42 (m, 1H), 3.23 (br, 1H), 3.15-3.08 (m, 1H), 1.57-1.55 (m, 1H), 1.35-1.31 (m, 1H), 1.02-0.95 (m, 1H), 0.79-0.74 (m, 6H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.2, 141.9, 132.2, 131.7, 130.8, 129.3, 129.2, 128.2, 127.2, 127.1, 113.6, 113.3, 61.8, 56.3, 51.8, 44.1, 35.4, 35.4, 25.6, 15.2, 11.1.

### 4e (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.54 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.63-7.59 (m, 1H), 7.54-7.47 (m, 4H), 7.40-7.36 (m, 3H), 7.21 (d, *J* = 9.4 Hz, 1H), 5.80 (d, *J* = 15.3 Hz, 1H), 5.70 (d, *J* = 15.3 Hz, 1H), 5.04-4.97 (m, 1H), 4.79-4.76 (m, 1H), 3.82-3.67 (m, 3H), 3.60-3.56 (m, 1H), 3.11-3.04 (m, 2H), 0.86 (s, 9H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.7, 141.8, 132.2, 131.8, 130.8, 129.3, 129.3, 128.2, 127.3, 127.2, 113.6, 113.3, 60.6, 60.1, 51.8, 43.9, 35.1, 33.5, 26.9.

### 5a (R<sup>1</sup>=Me, R<sup>2</sup>=Me)

<sup>1</sup>H-NMR (DMSO, 400 MHz): δ 9.66 (s, 1H), 8.09-8.05 (m, 1H), 8.03-8.00 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.82-7.66 (m, 2H), 4.71-4.68 (m, 2H), 4.63 (t, *J* = 5.5 Hz, 1H), 4.07 (s, 3H), 3.75-3.65 (m, 1H), 3.24-3.19 (m, 1H), 3.16-3.12 (m, 1H), 2.75 (t, *J* = 7.3 Hz, 2H), 0.89 (d, *J* = 7.3 Hz, 3H); <sup>13</sup>C-NMR (DMSO, 100 MHz): δ 168.3, 143.1, 131.6, 130.8, 126.4, 126.4, 113.6, 113.5, 64.1, 46.5, 43.2, 34.3, 33.2, 16.9.

### 5b (R<sup>1</sup>=Et, R<sup>2</sup>=Me)

<sup>1</sup>H-NMR (DMSO, 400 MHz): δ 9.67 (s, 1H), 8.10-8.07 (m, 1H), 8.02-7.99 (m, 1H), 7.73-7.68 (m, 3H), 4.72 (t, *J* = 6.4 Hz, 2H), 4.58 (t, *J* = 5.5 Hz, 1H), 4.08 (s, 3H), 3.59-3.51 (m, 1H), 3.26-3.15 (m, 2H), 2.86-2.74 (m, 2H), 1.49-1.38 (m, 1H), 1.22-1.10 (m, 1H), 0.64 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C-NMR (DMSO, 100 MHz): δ 168.7, 143.1, 131.6, 130.7, 126.5, 126.4, 113.6, 113.5, 62.6, 52.2, 43.3, 34.4, 33.2, 23.4, 10.1.

**5c** (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Me)

<sup>1</sup>H-NMR (DMSO, 400 MHz): δ 9.65 (s, 1H), 8.08-8.05 (m, 1H), 8.03-7.99 (m, 1H), 7.71-7.68 (m, 3H), 4.76-4.66 (m, 2H), 4.58 (br, 1H), 4.07 (s, 3H), 3.74-3.69 (m, 1H), 3.49-3.34 (m, 2H), 2.86-2.72 (m, 2H), 1.22-1.04 (m, 3H), 0.71 (d, *J* = 7.3 Hz, 3H), 0.67 (d, *J* = 7.3 Hz, 3H); <sup>13</sup>C-NMR (DMSO, 100 MHz): δ 168.3, 143.1, 131.6, 130.7, 126.5, 126.4, 113.6, 113.4, 63.6, 48.7, 43.4, 39.7, 34.4, 33.2, 24.0, 23.1, 21.6.

**5d** (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Me)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.29 (s, 1H), 7.95-7.89 (m, 1H), 7.74-7.68 (m, 1H), 7.68-7.60 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 5.00-4.93 (m, 1H), 4.89-4.83 (m, 1H), 4.20 (s, 3H), 3.72-3.66 (m, 1H), 3.62-3.55 (m, 1H), 3.48-3.41 (m, 2H), 3.31 (t, *J* = 5.6 Hz, 1H), 3.16-3.09 (m, 1H), 1.58-1.48 (m, 1H), 1.36-1.26 (m, 1H), 1.06-0.93 (m, 1H), 0.78-0.74 (m, 6H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.4, 142.1, 131.4, 131.1, 127.0, 126.9, 113.5, 112.5, 61.5, 55.9, 43.8, 35.5, 35.2, 34.2, 25.4, 15.0, 11.0.

**5e** (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Me)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.29 (s, 1H), 7.91-7.88 (m, 1H), 7.70-7.63 (m, 3H), 7.18 (d, *J* = 9.6 Hz, 1H), 5.03-4.96 (m, 1H), 4.80-4.74 (m, 1H), 4.19 (s, 3H), 3.82-3.77 (m, 1H), 3.70-3.59 (m, 3H), 3.21 (br, 1H), 3.10-3.04 (m, 1H), 0.87 (s, 9H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.9, 142.1, 131.7, 131.5, 127.4, 127.3, 113.5, 112.5, 60.6, 60.1, 43.8, 35.3, 34.1, 33.6, 26.9.

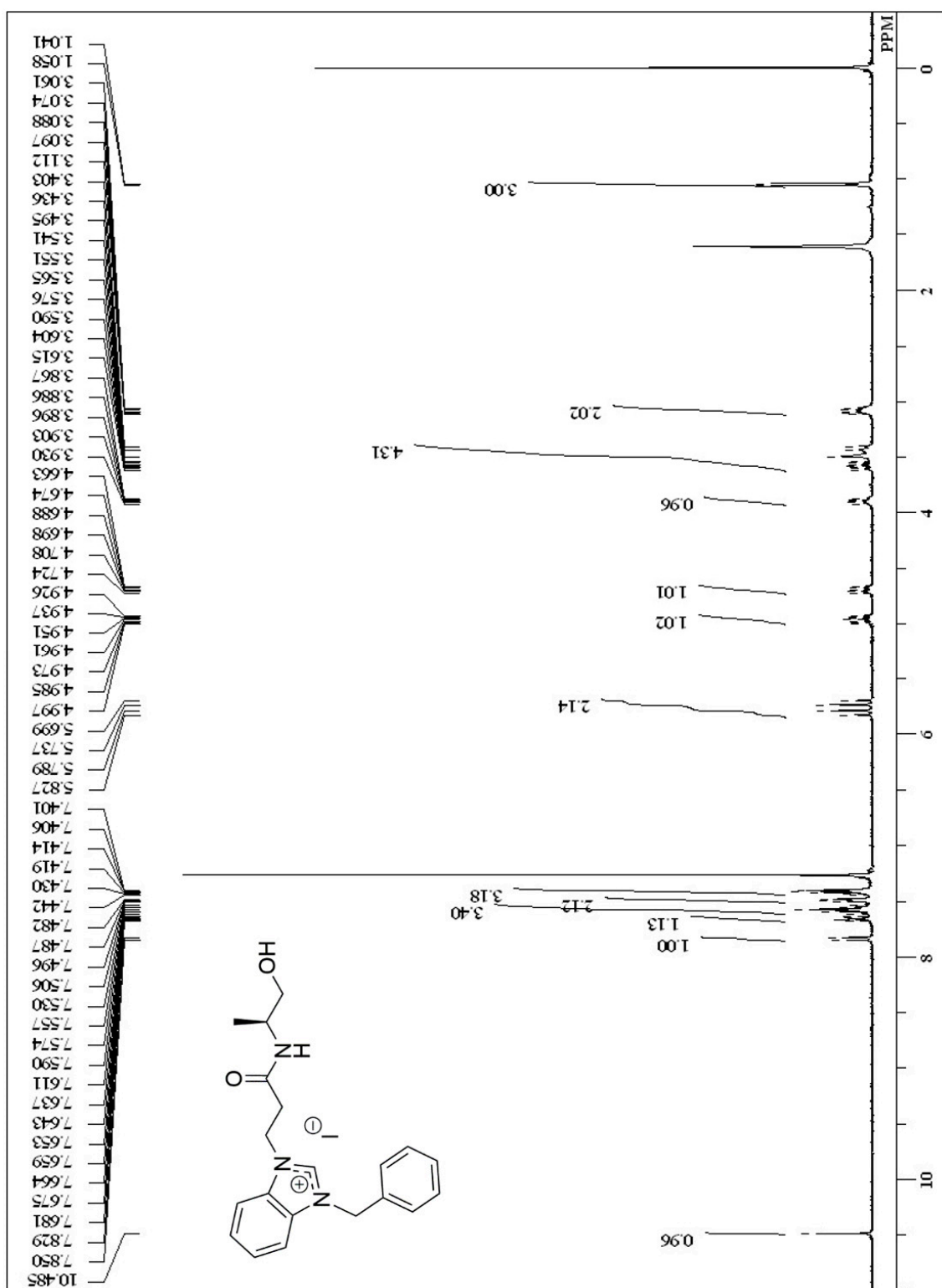
**10b** (R<sup>1</sup>=Et, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.77 (s, 1H), 7.92-7.86 (m, 2H), 7.60-7.56 (m, 1H), 7.54-7.47 (m, 4H), 7.38-7.32 (m, 3H), 5.82 (d, *J* = 15.3 Hz, 1H), 5.76 (d, *J* = 15.3 Hz, 1H), 4.99-4.92 (m, 1H), 4.88-4.82 (m, 1H), 3.91 (br, 1H), 3.66 (br, 1H), 3.50-3.38 (m, 3H), 3.14-3.07 (m, 1H), 1.43-1.36 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.1, 142.3, 132.4, 131.7, 130.7, 129.2, 129.1, 128.1, 127.0, 127.0, 113.5, 113.3, 63.4, 53.6, 51.5, 44.0, 35.3, 23.7, 10.3.

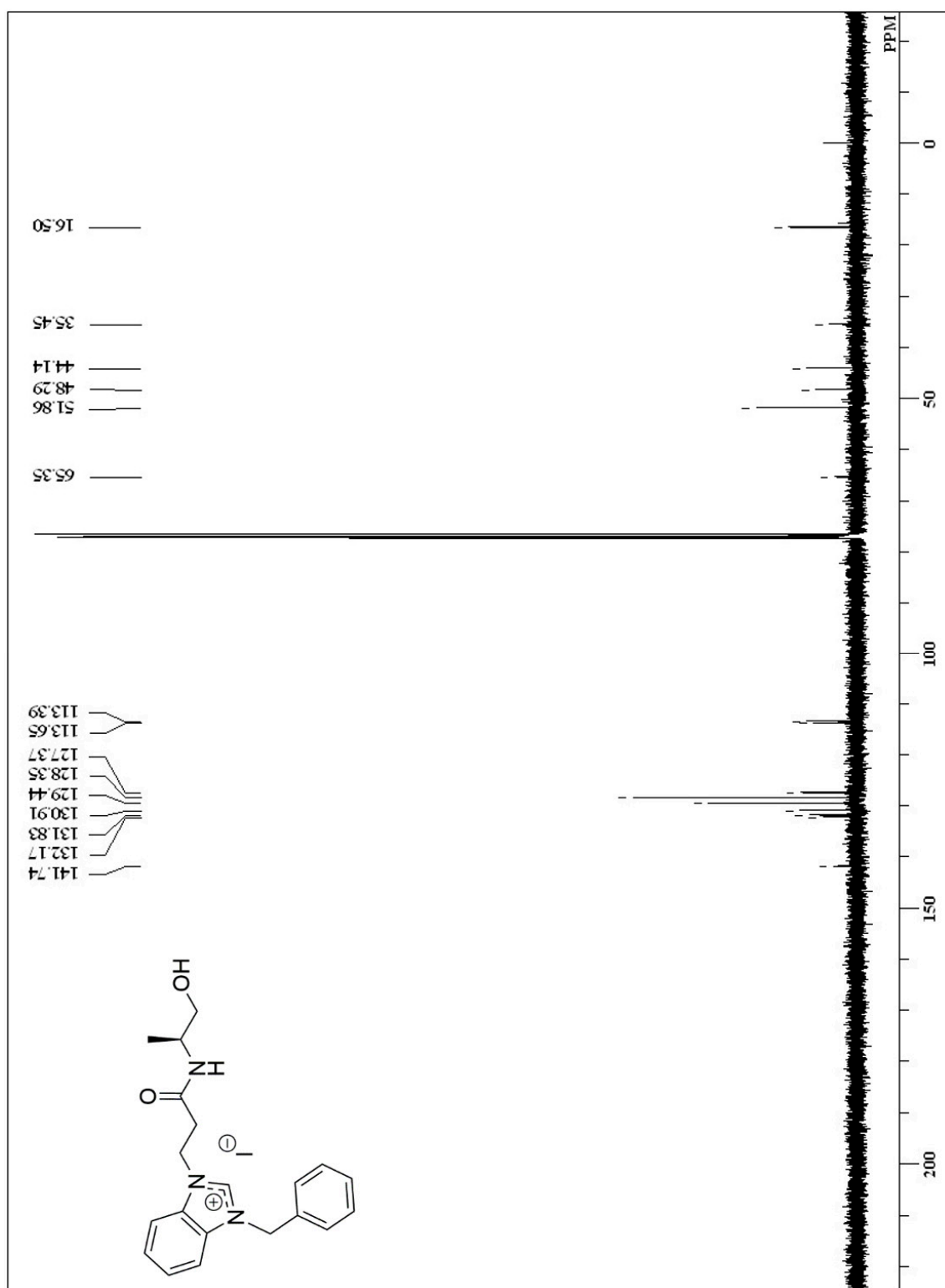
*Ent*-**10b** (R<sup>1</sup>=Et, R<sup>2</sup>=Bn)

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.77 (s, 1H), 7.90-7.86 (m, 2H), 7.60-7.54 (m, 1H), 7.52-7.47 (m, 4H), 7.37-7.30 (m, 3H), 5.82 (d, *J* = 15.1 Hz, 1H), 5.75 (d, *J* = 15.1 Hz, 1H), 4.98-4.92 (m, 1H), 4.87-4.81 (m, 1H), 3.88 (br, 1H), 3.68-3.62 (m, 1H), 3.50-3.37 (m, 3H), 3.13-3.06 (m, 1H), 1.45-1.34 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ 169.1, 142.3, 132.4, 131.7, 130.7, 129.2, 129.1, 128.1, 127.0, 127.0, 113.5, 113.3, 63.4, 53.6, 51.5, 44.0, 35.3, 23.7, 10.3.

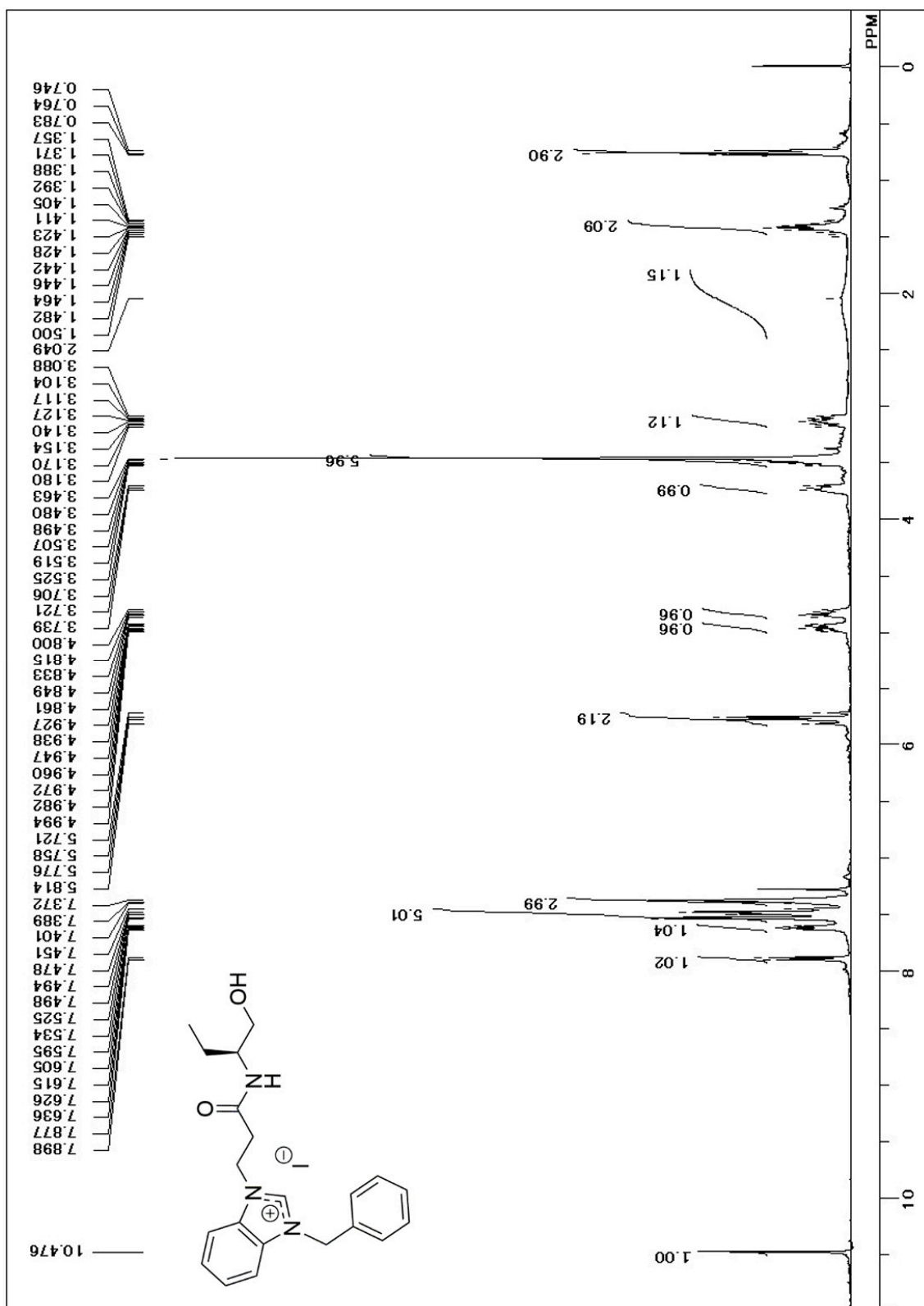
### 3. NMR chart



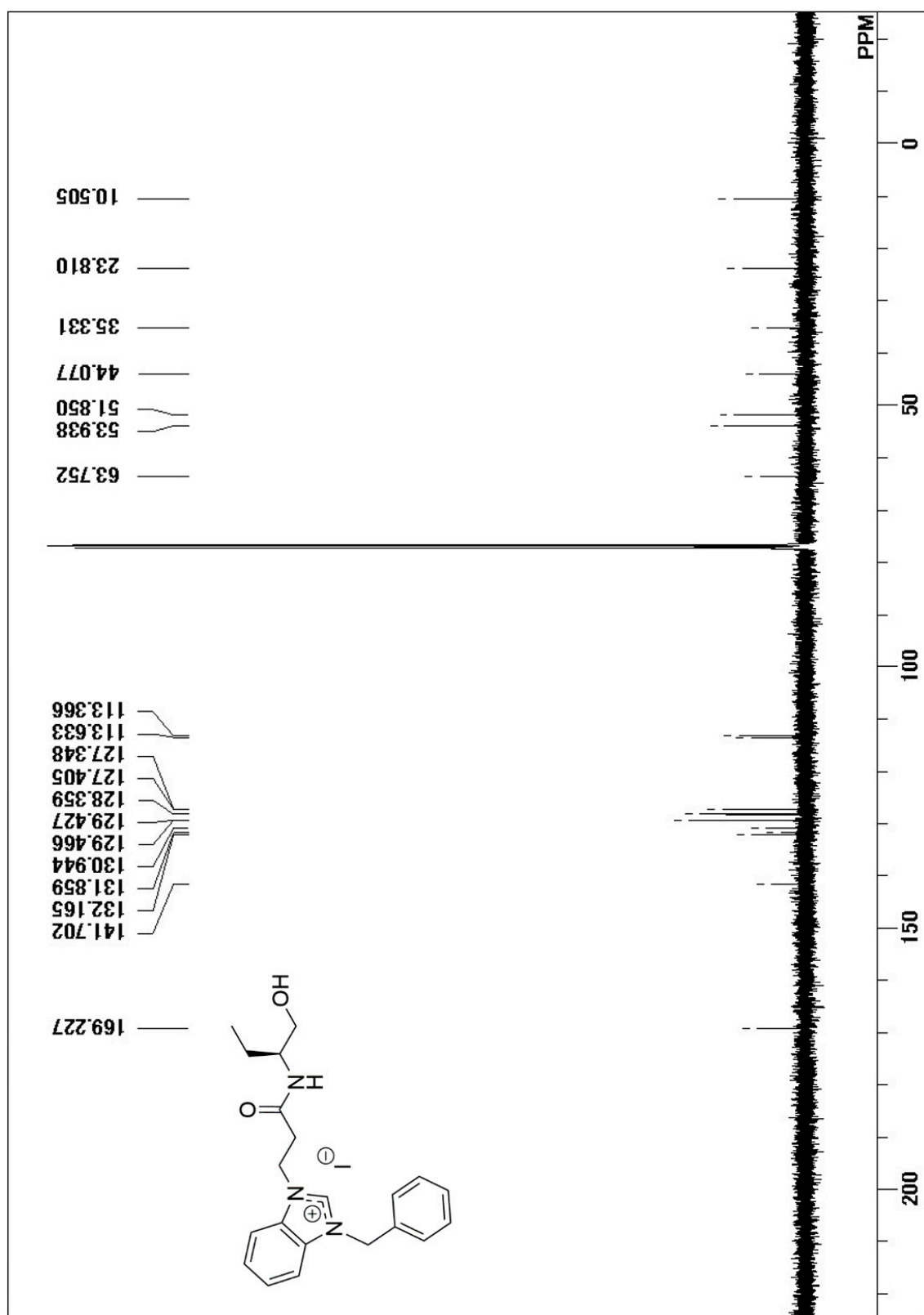
4a (R<sup>1</sup>=Me, R<sup>2</sup>=Bn).



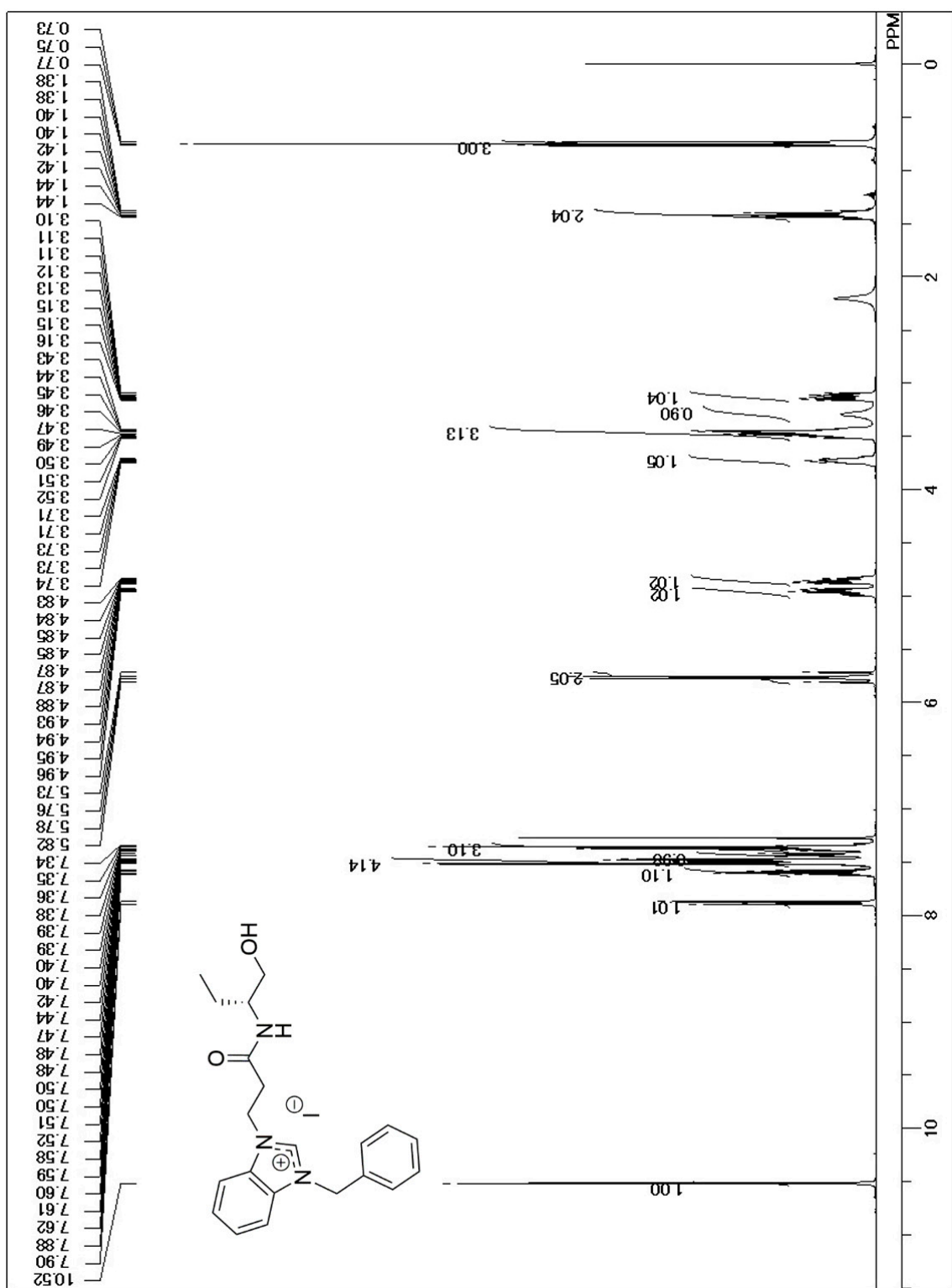
4a (R<sup>1</sup>=Me, R<sup>2</sup>=Bn).



4b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).

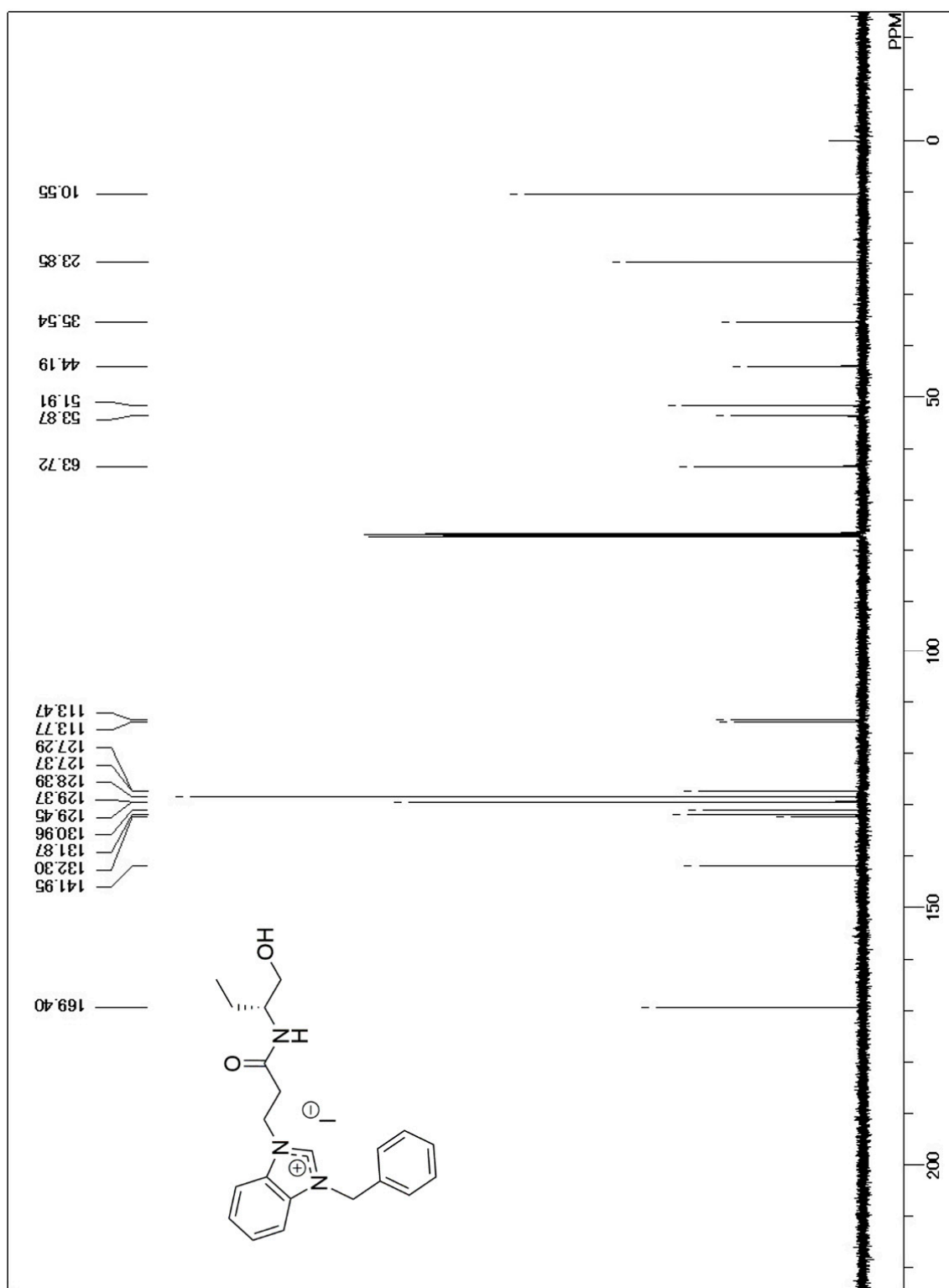


4b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).

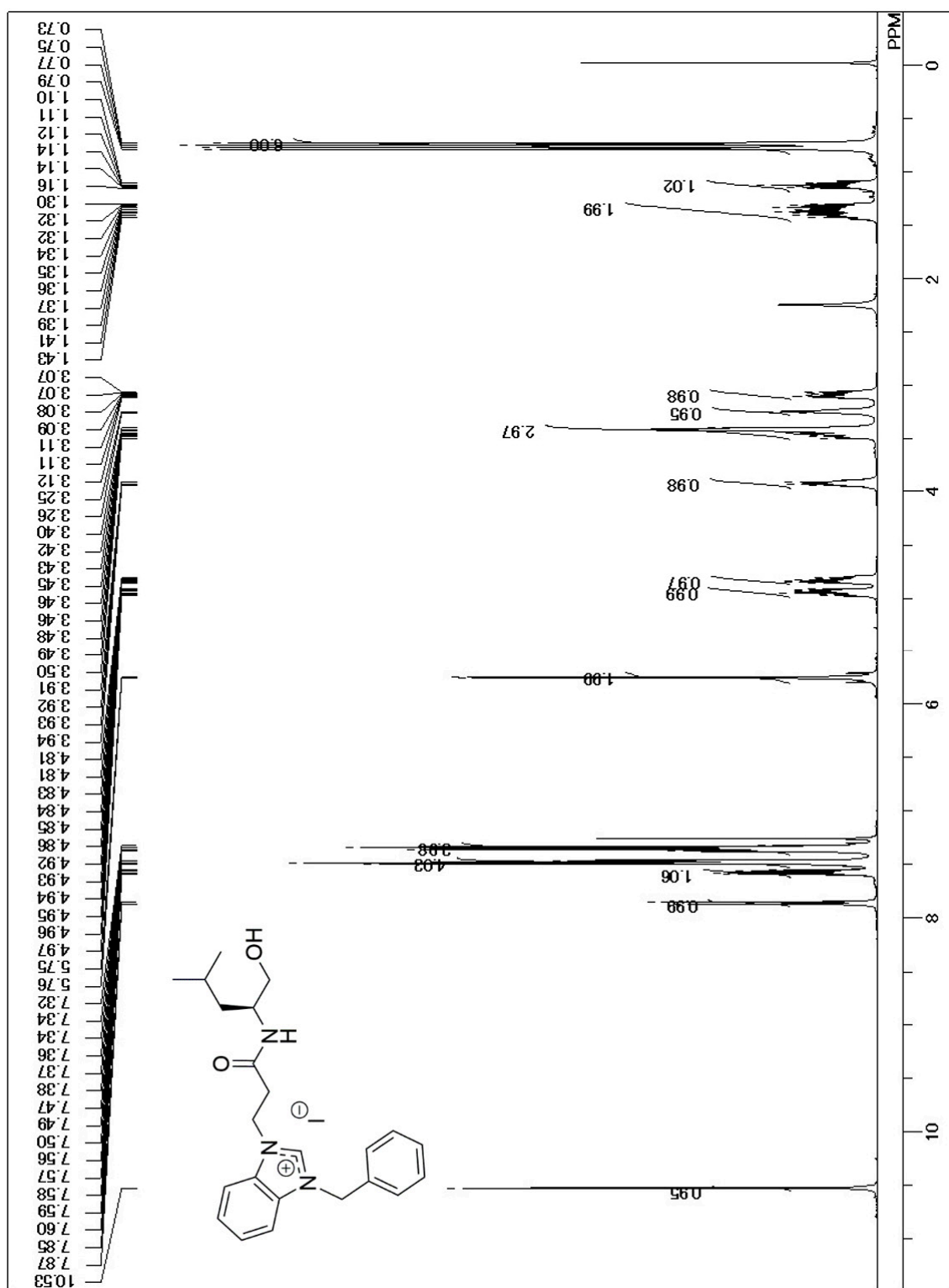


**Ent-4b** (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).

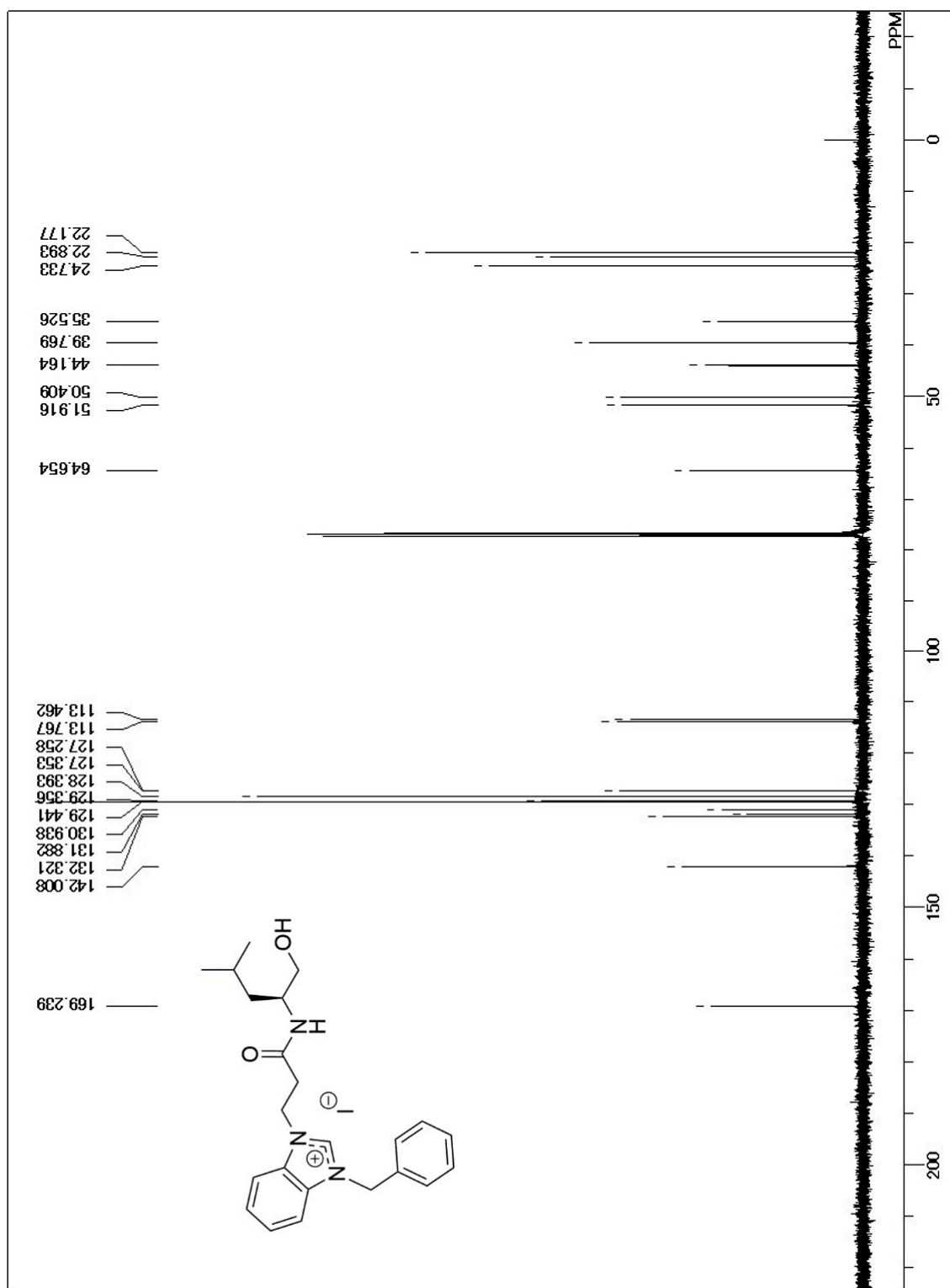




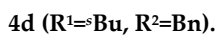
Ent-4b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).



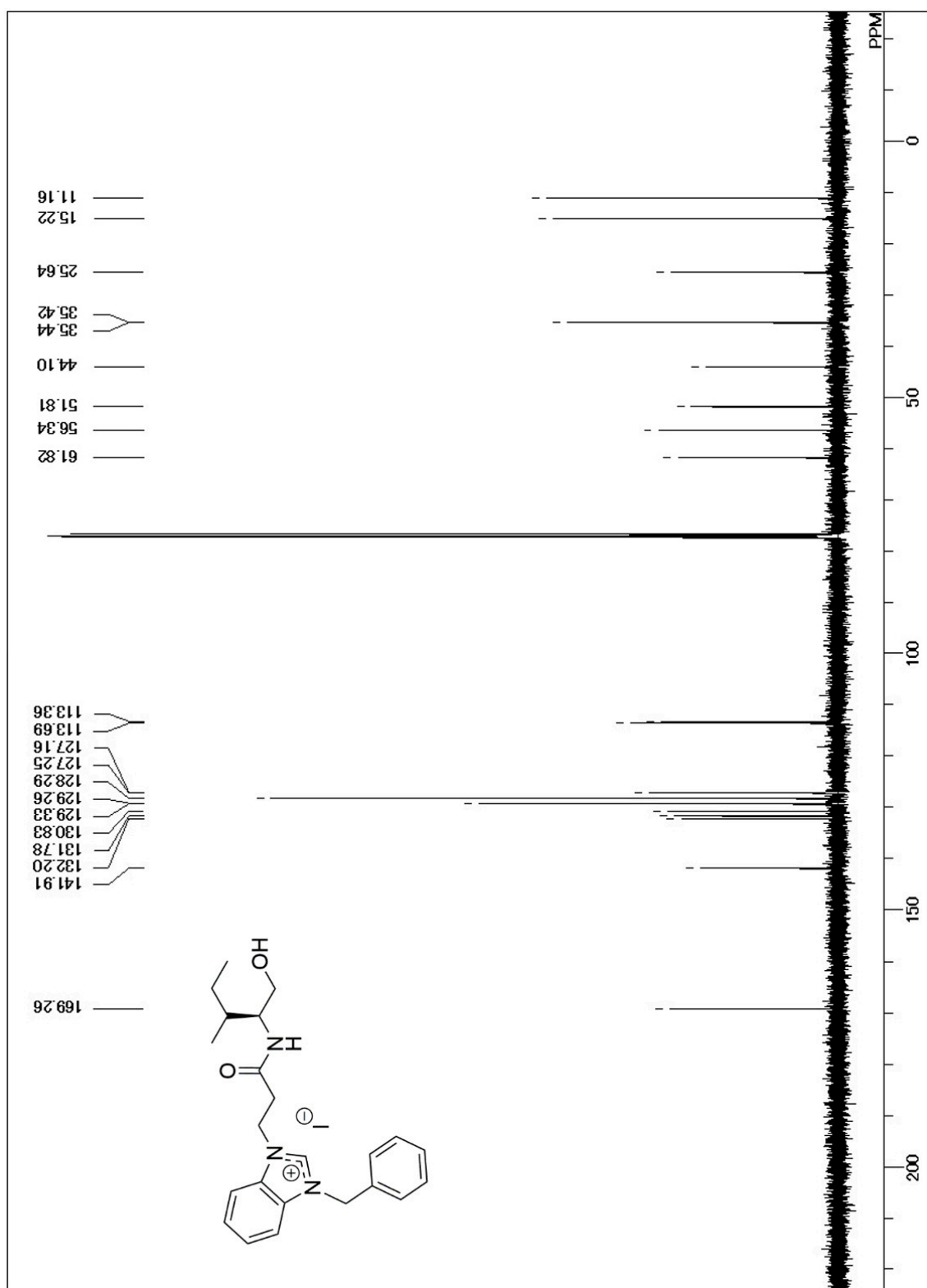
4c (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Bn).



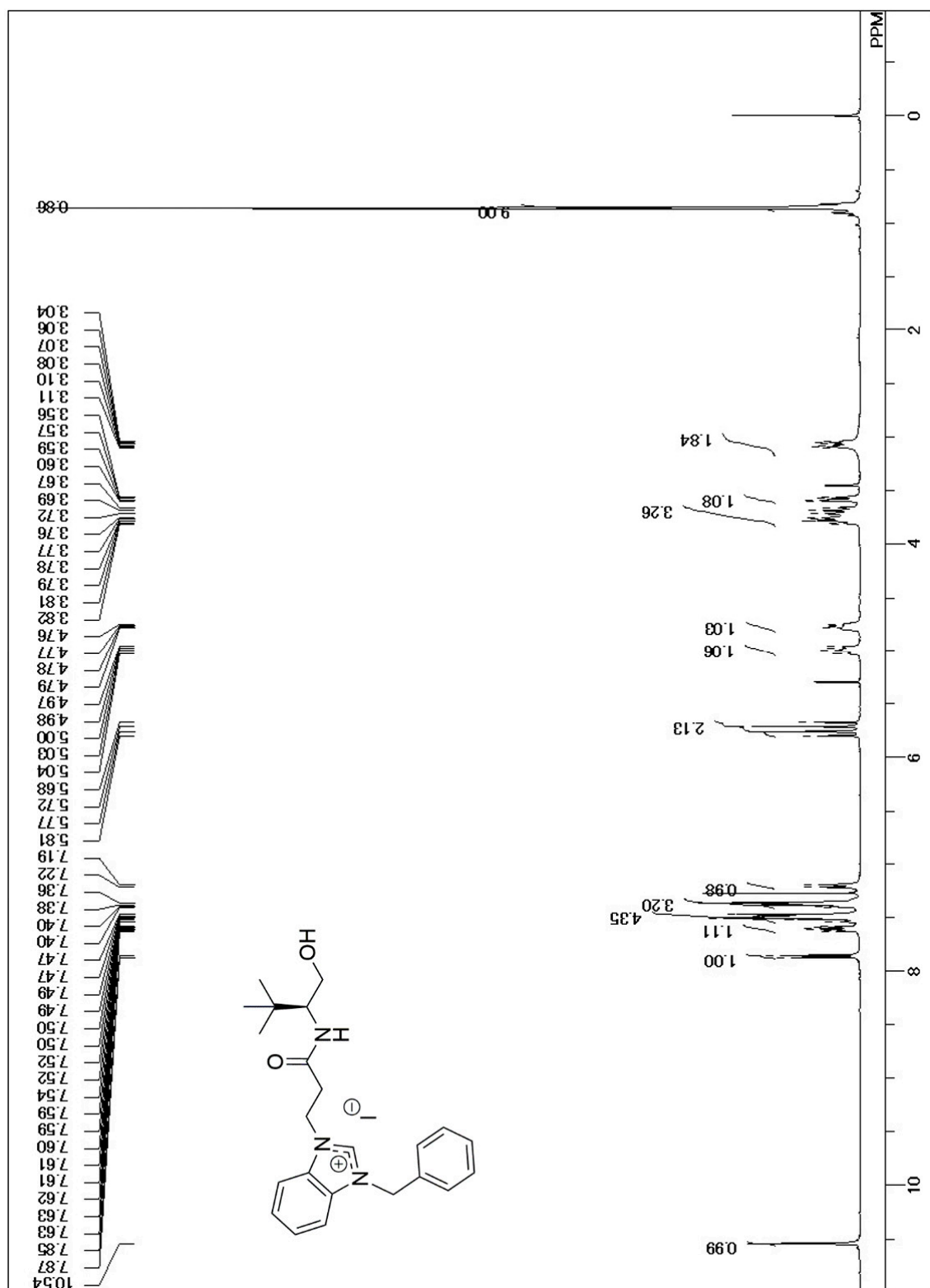
4c (R<sup>1</sup>=*i*Bu, R<sup>2</sup>=Bn).



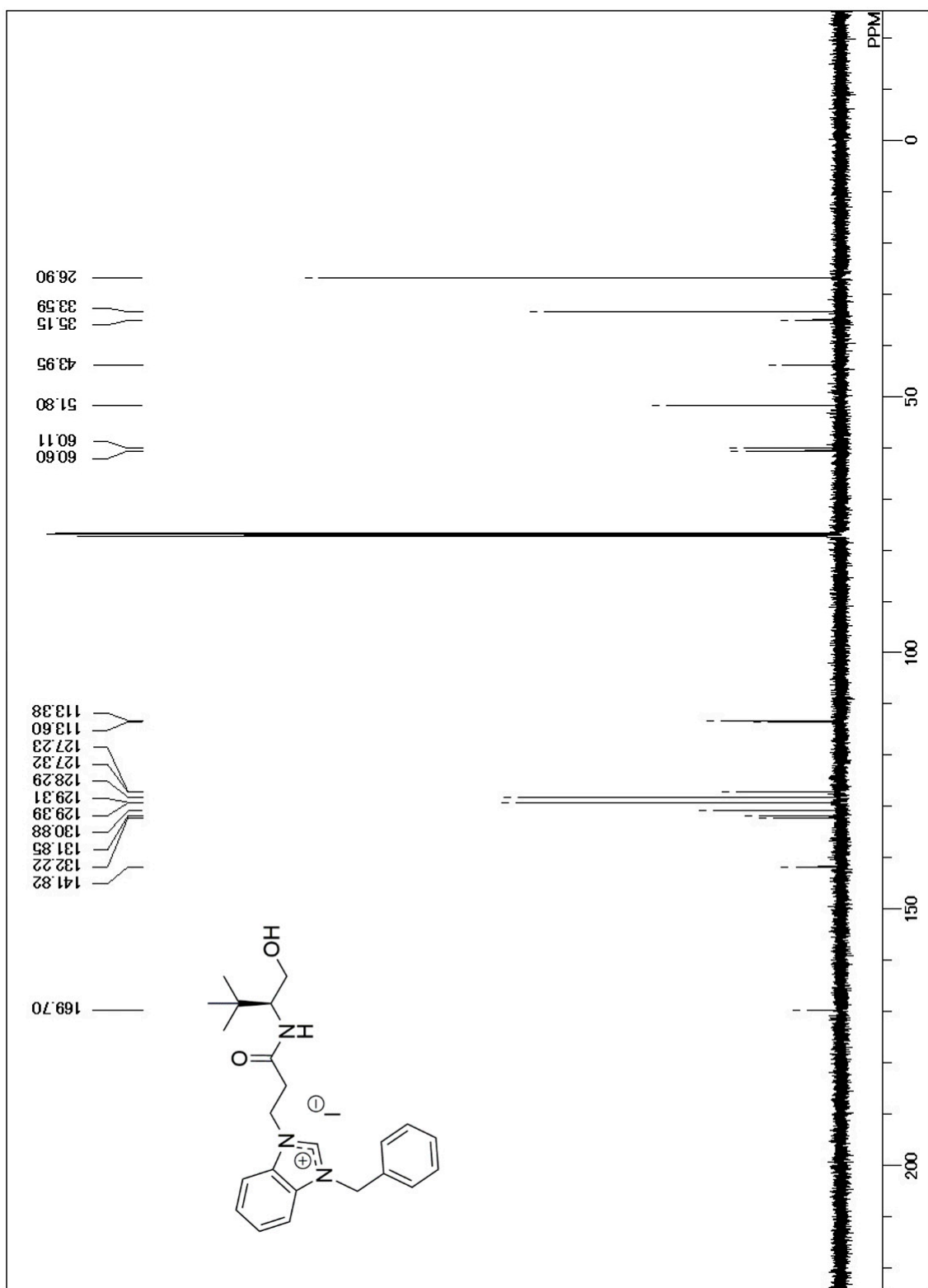
**4d (R<sup>1</sup>=*s*Bu, R<sup>2</sup>=Bn).**



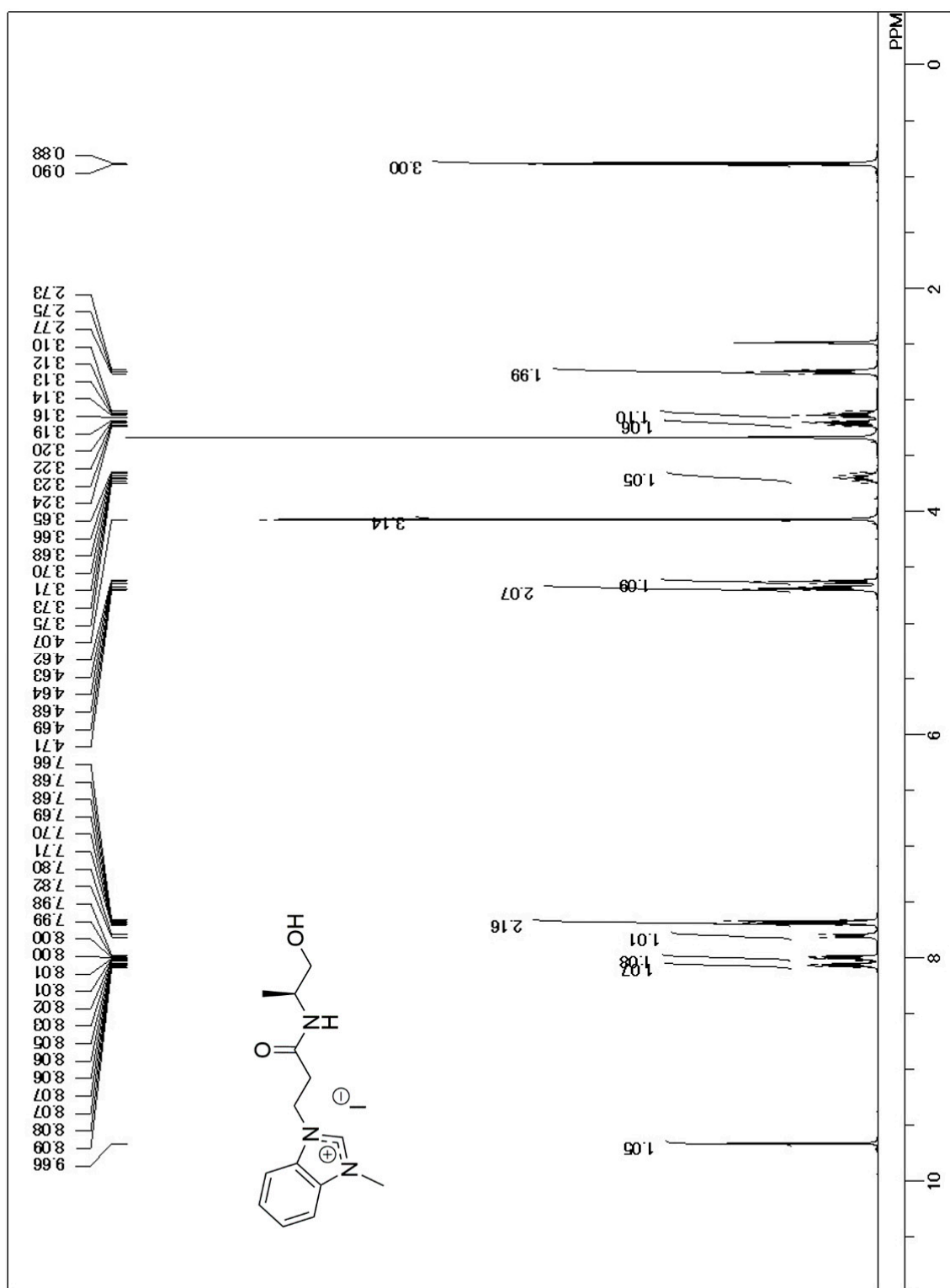
4d ( $R^1 = \text{secBu}$ ,  $R^2 = \text{Bn}$ ).



4e ( $R^1=iBu$ ,  $R^2=Bn$ ).

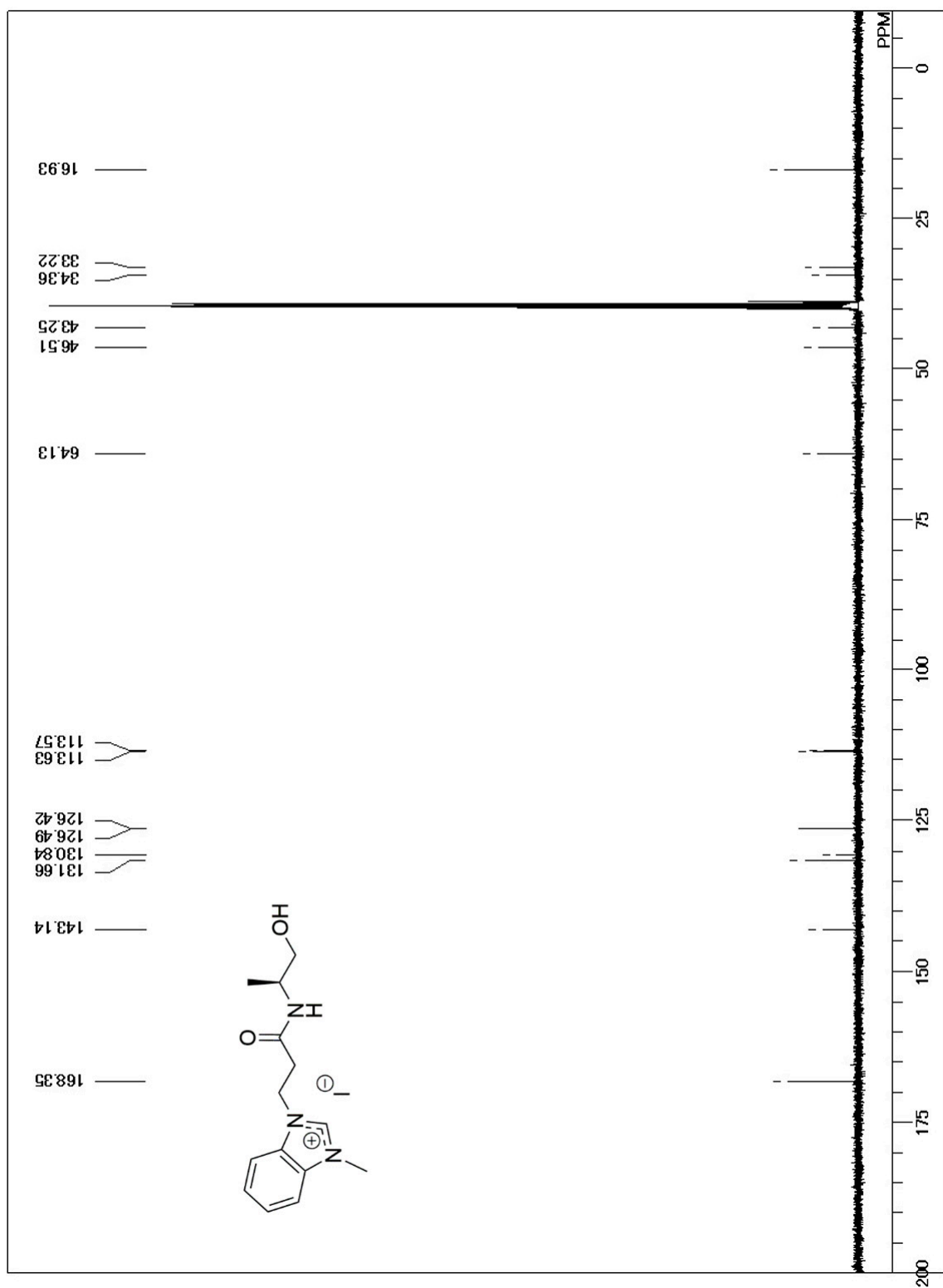


**4e** ( $\text{R}^1=\text{'Bu}$ ,  $\text{R}^2=\text{Bn}$ ).

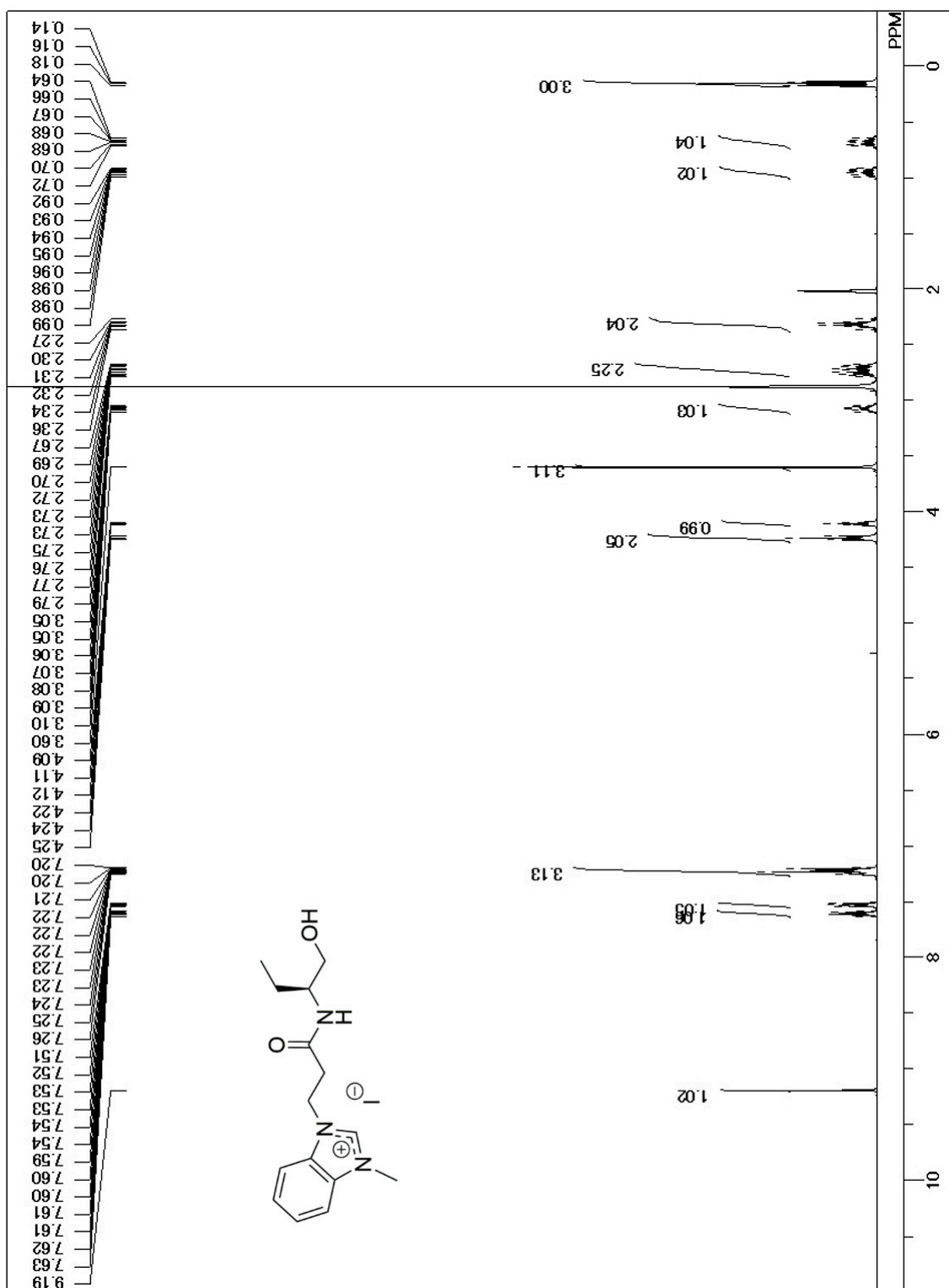


5a (R<sup>1</sup>=Me, R<sup>2</sup>=Me).

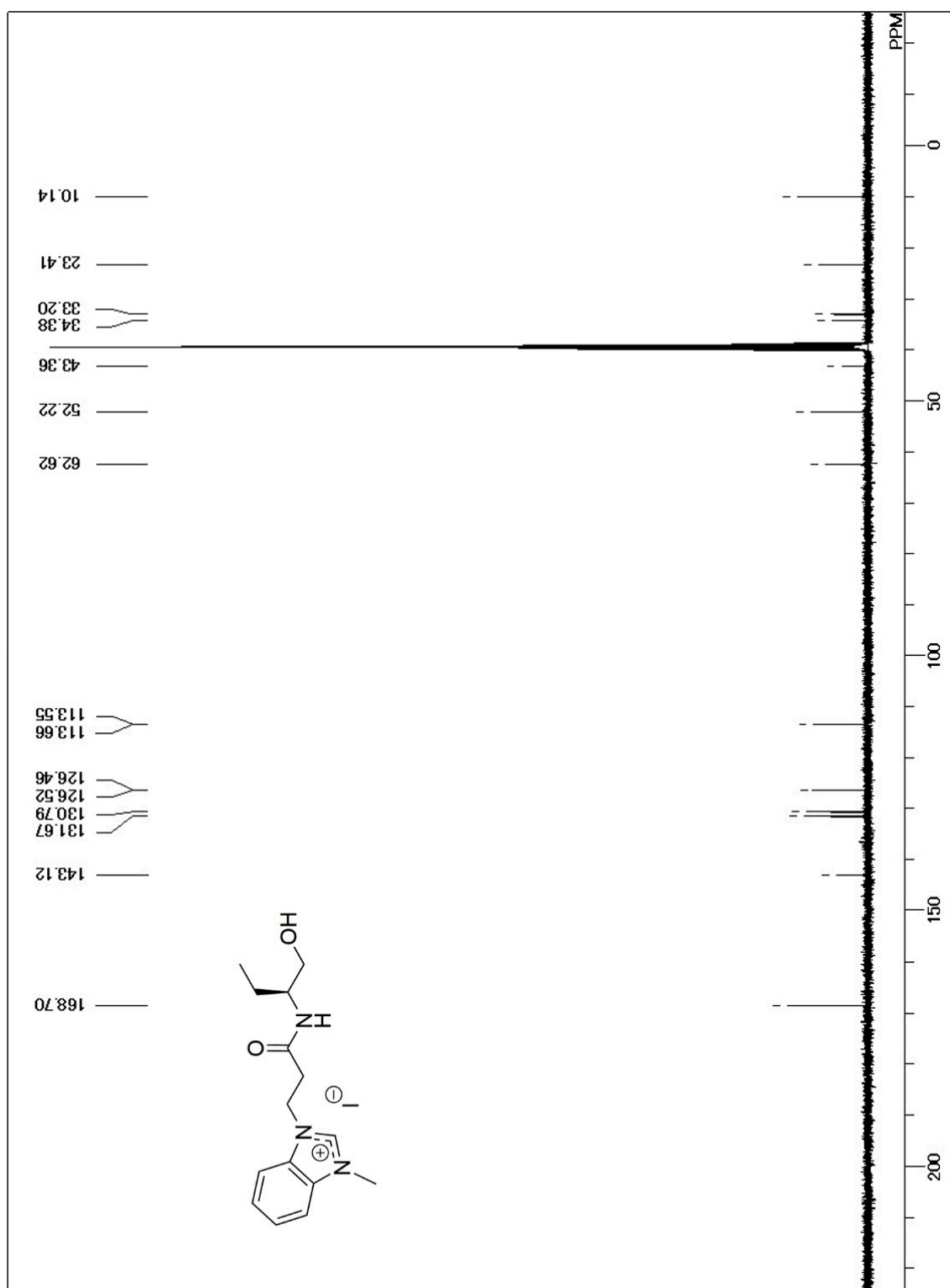




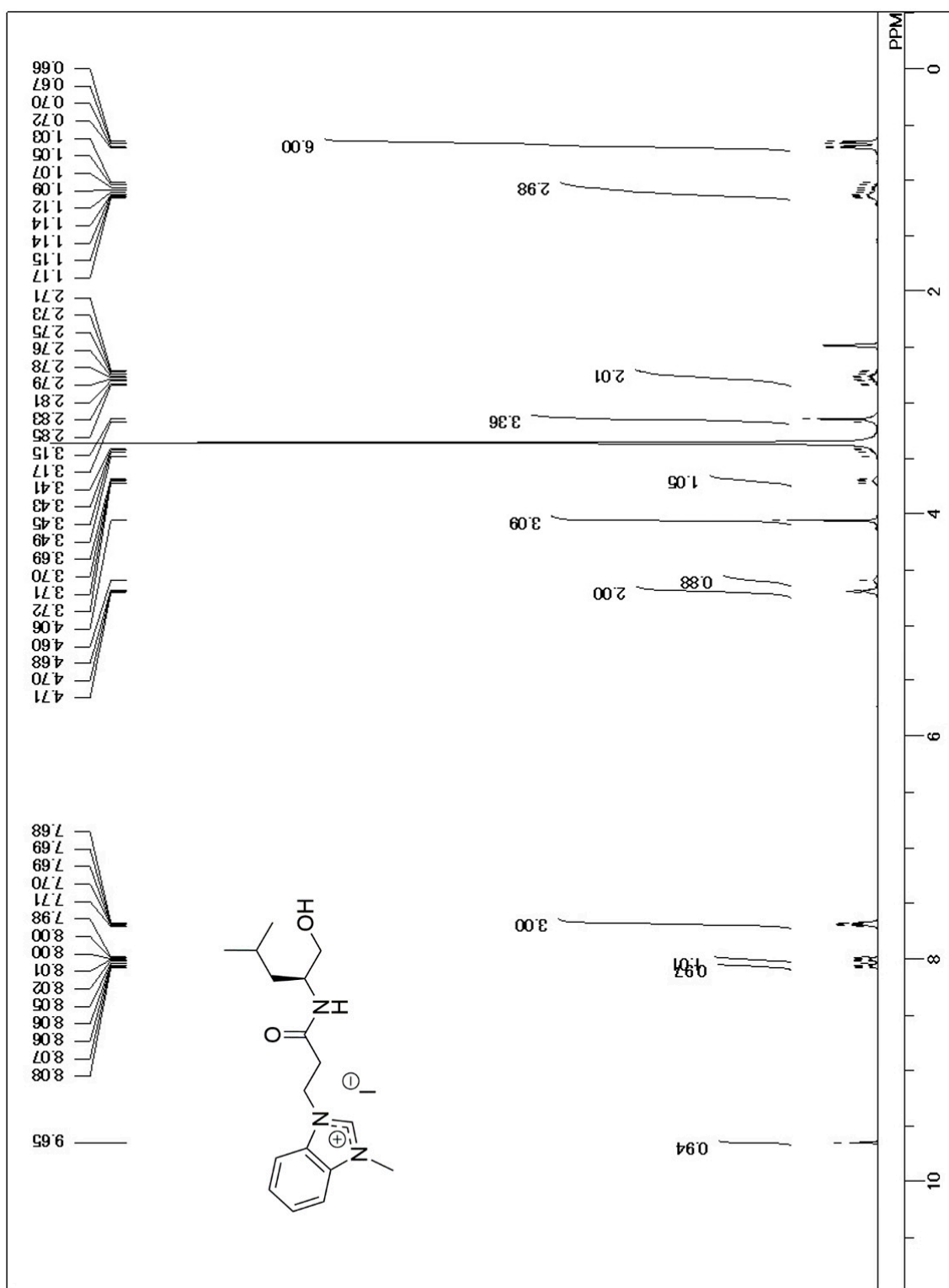
5a (R<sup>1</sup>=Me, R<sup>2</sup>=Me).



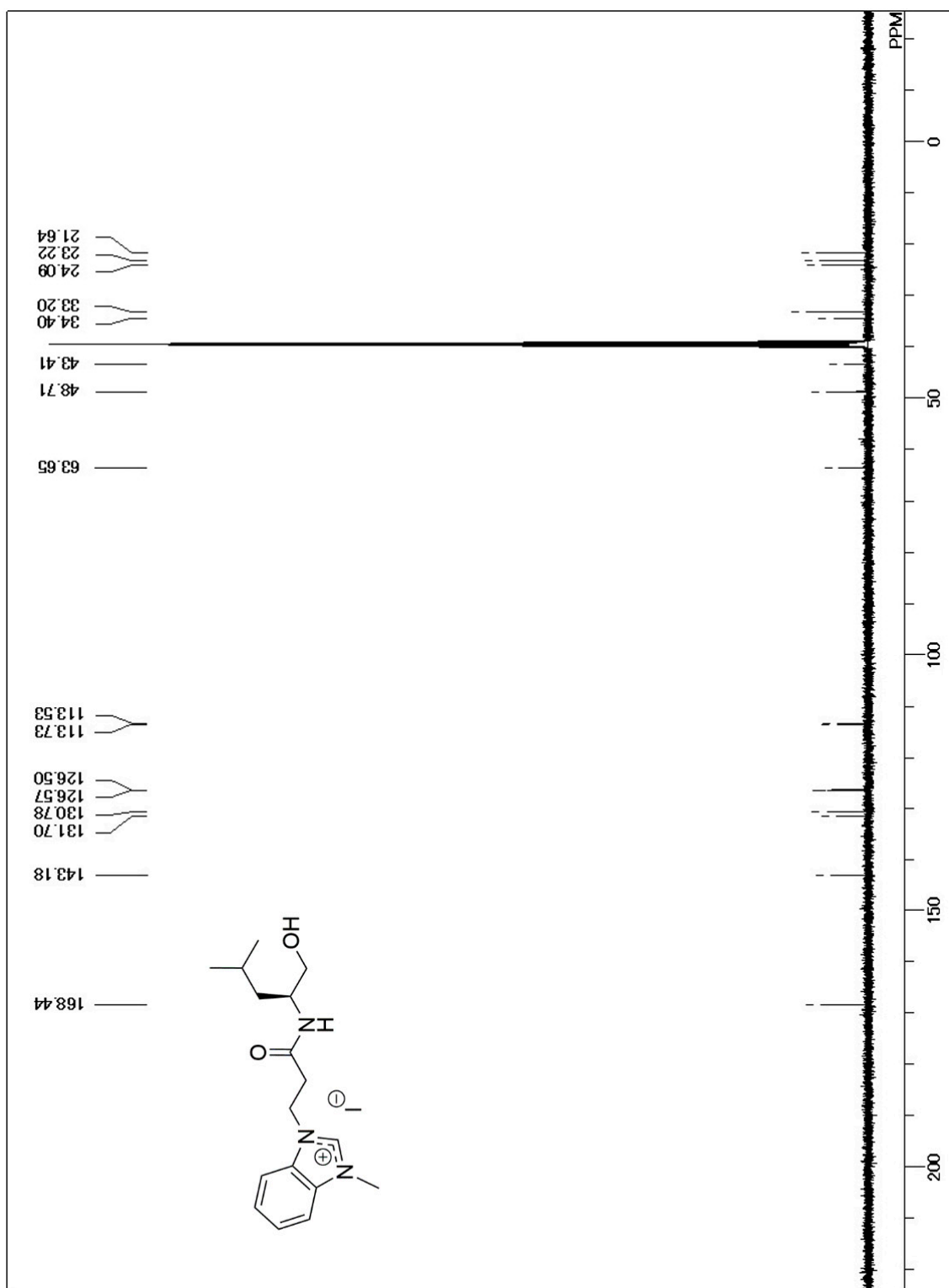
5b (R<sup>1</sup>=Et, R<sup>2</sup>=Me).



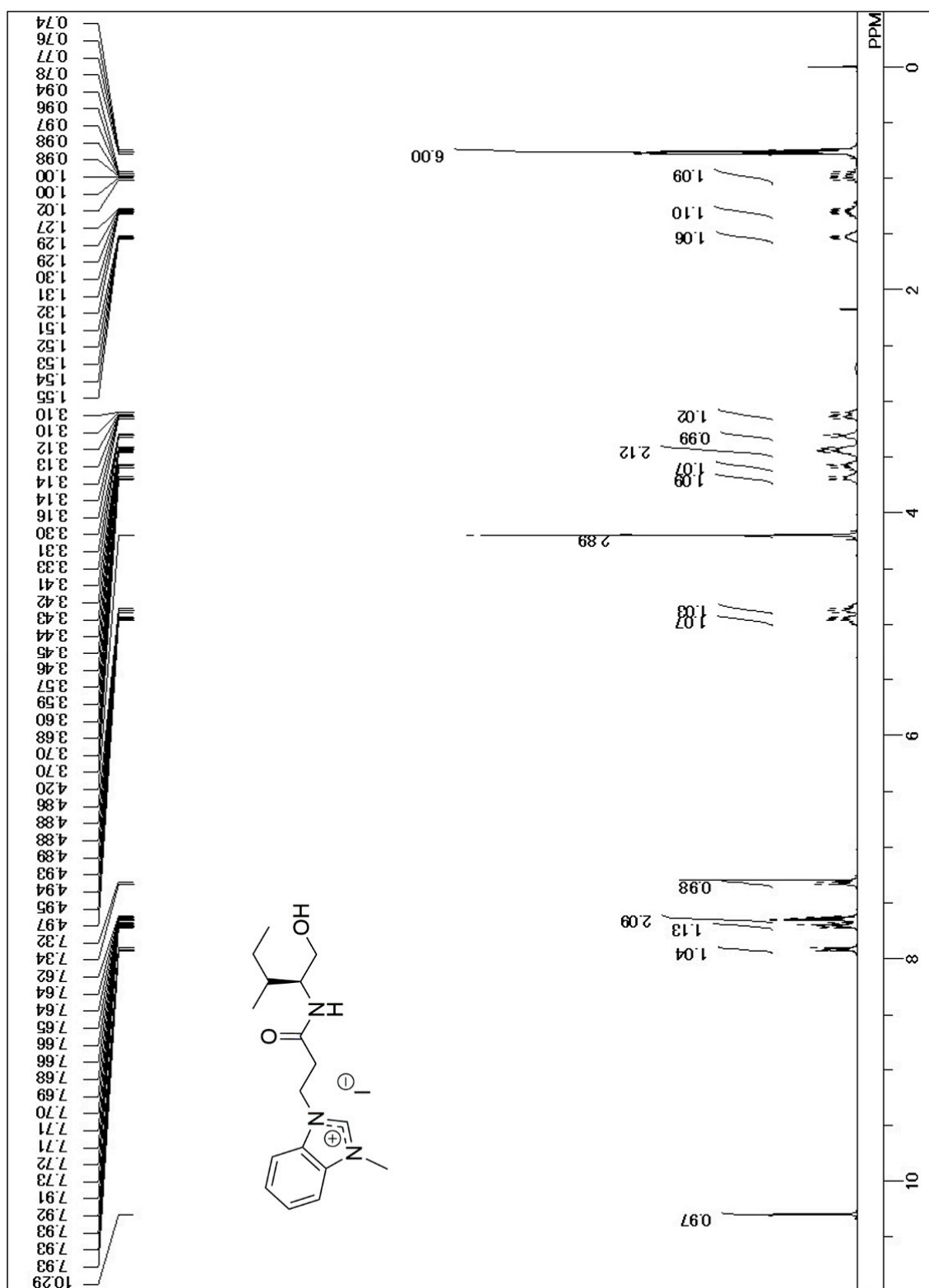
5b (R<sup>1</sup>=Et, R<sup>2</sup>=Me).



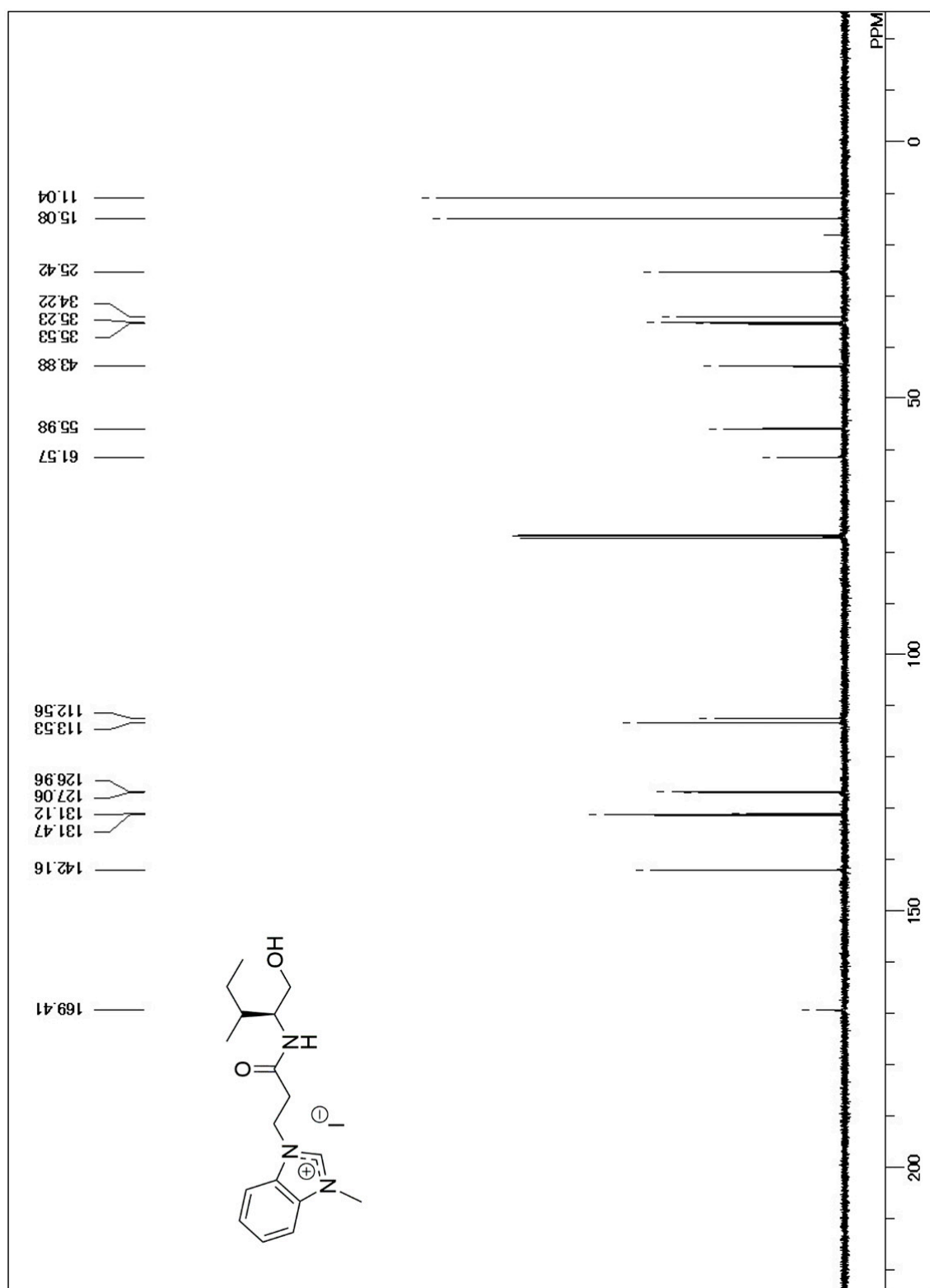
5c (R<sup>1</sup>=iBu, R<sup>2</sup>=Me).



5c (R<sup>1</sup>=Bu, R<sup>2</sup>=Me).



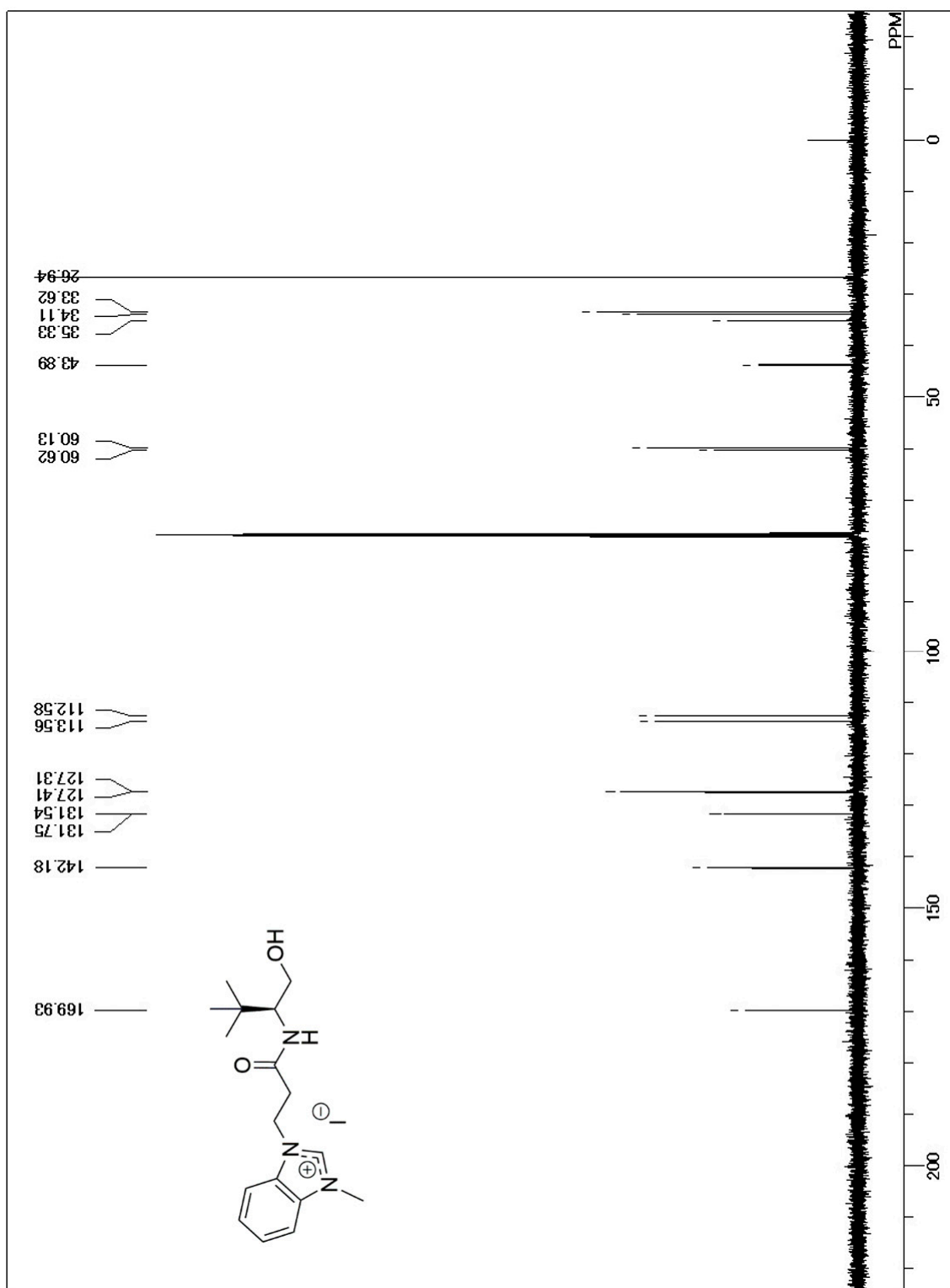
5d (R<sup>1</sup>=Bu, R<sup>2</sup>=Me).



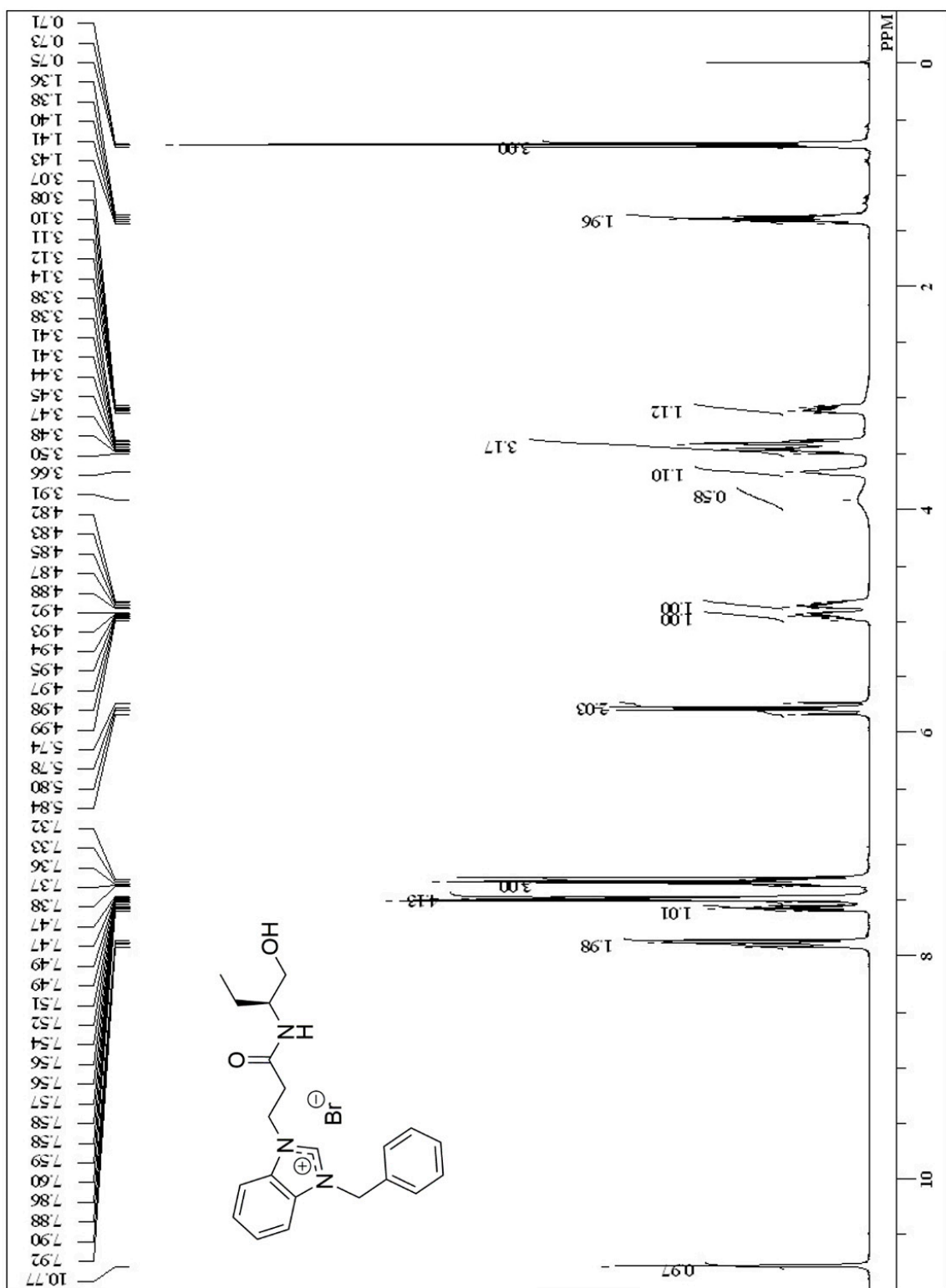
5d (R<sup>1</sup>=8Bu, R<sup>2</sup>=Me).



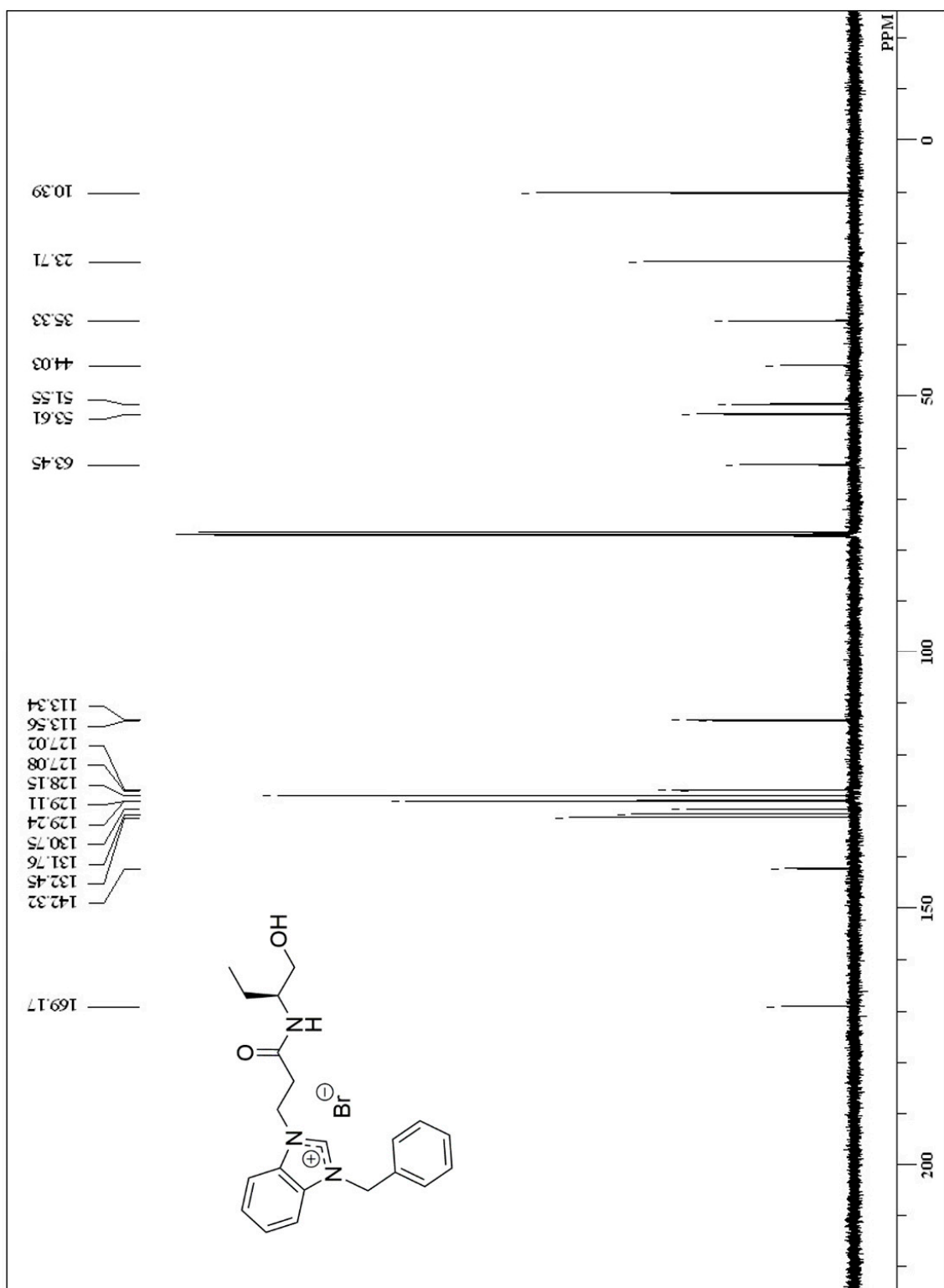




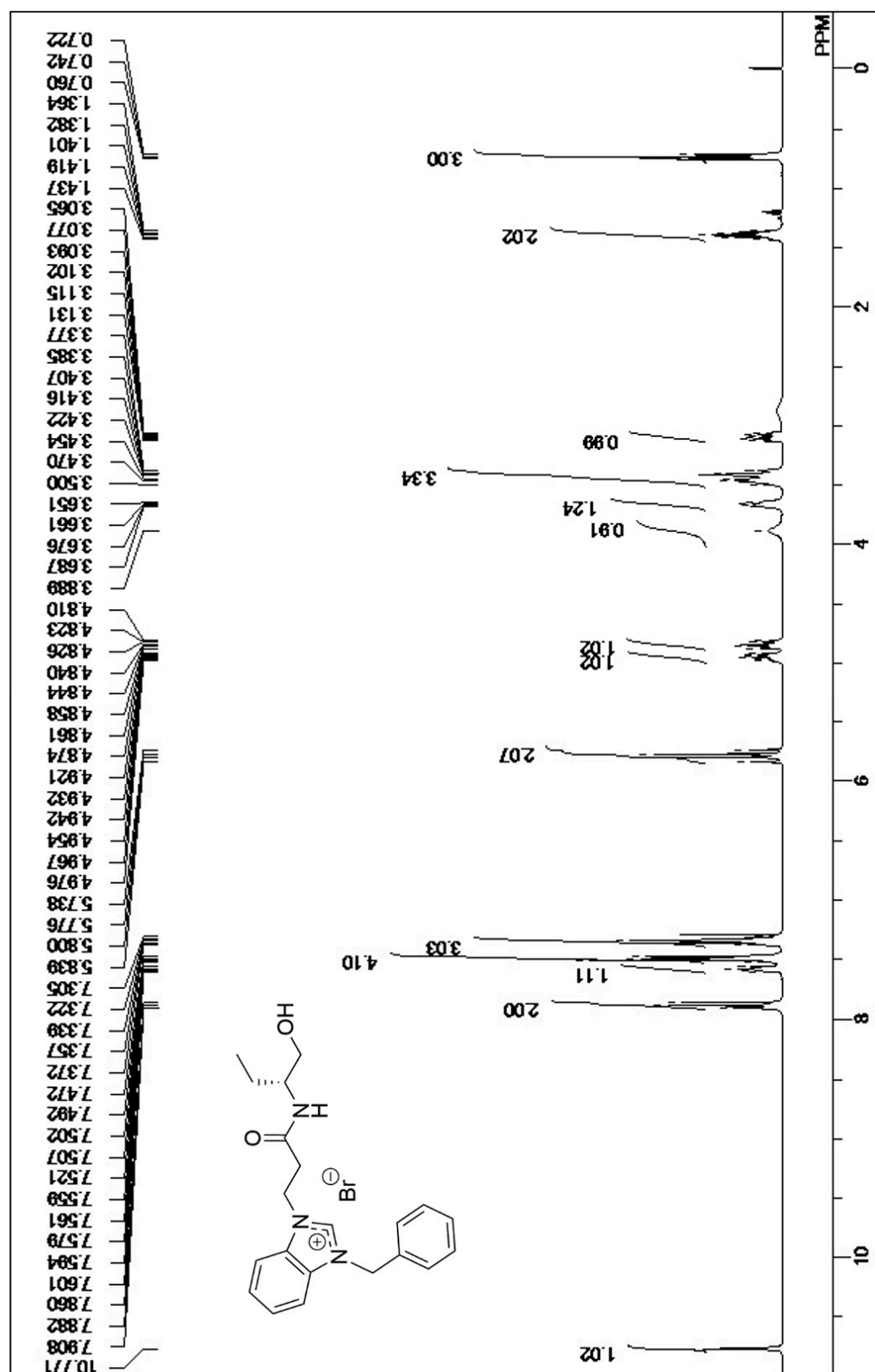
5e (R<sup>1</sup>=Bu, R<sup>2</sup>=Me).



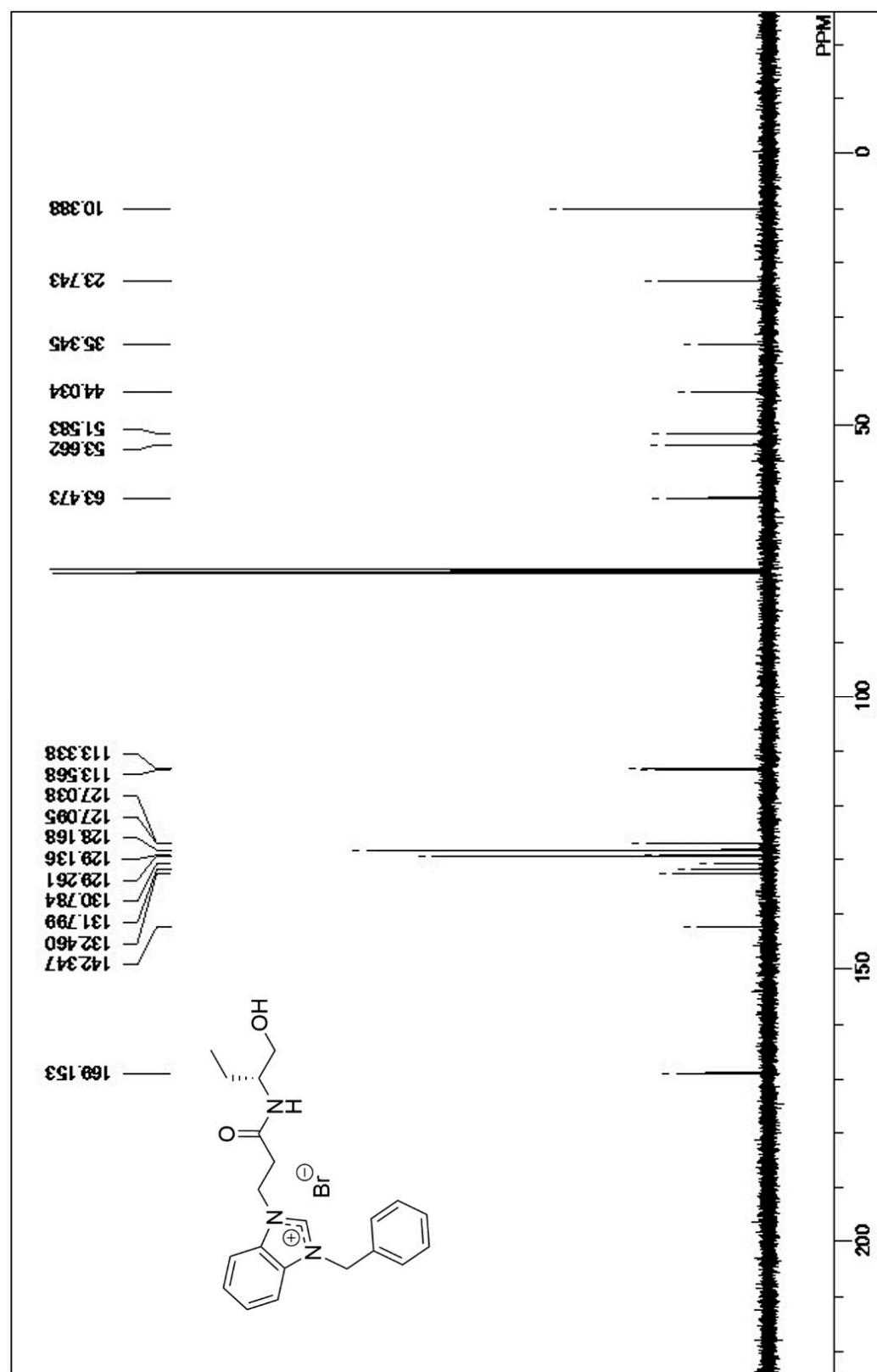
10b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).



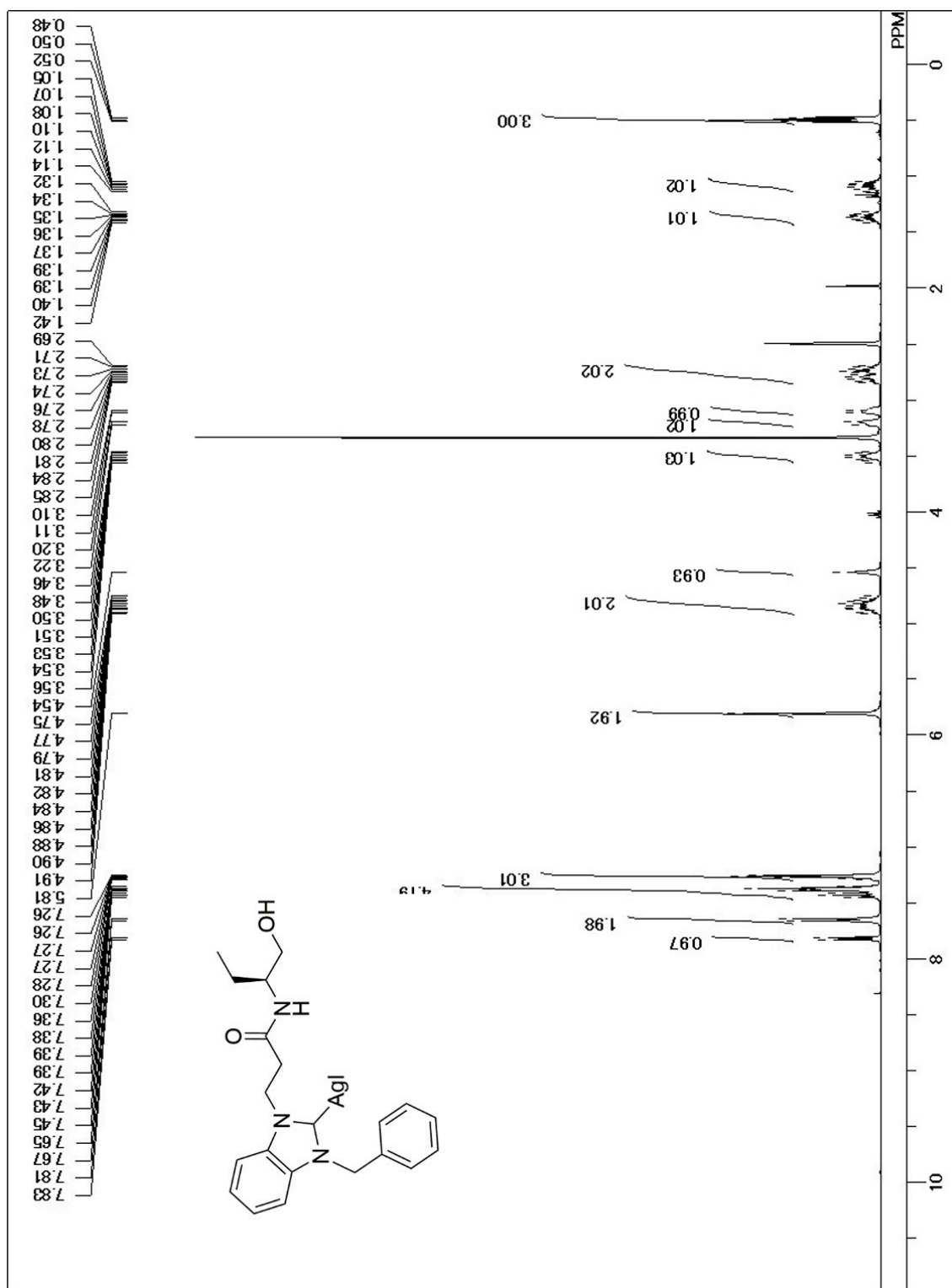
10b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).



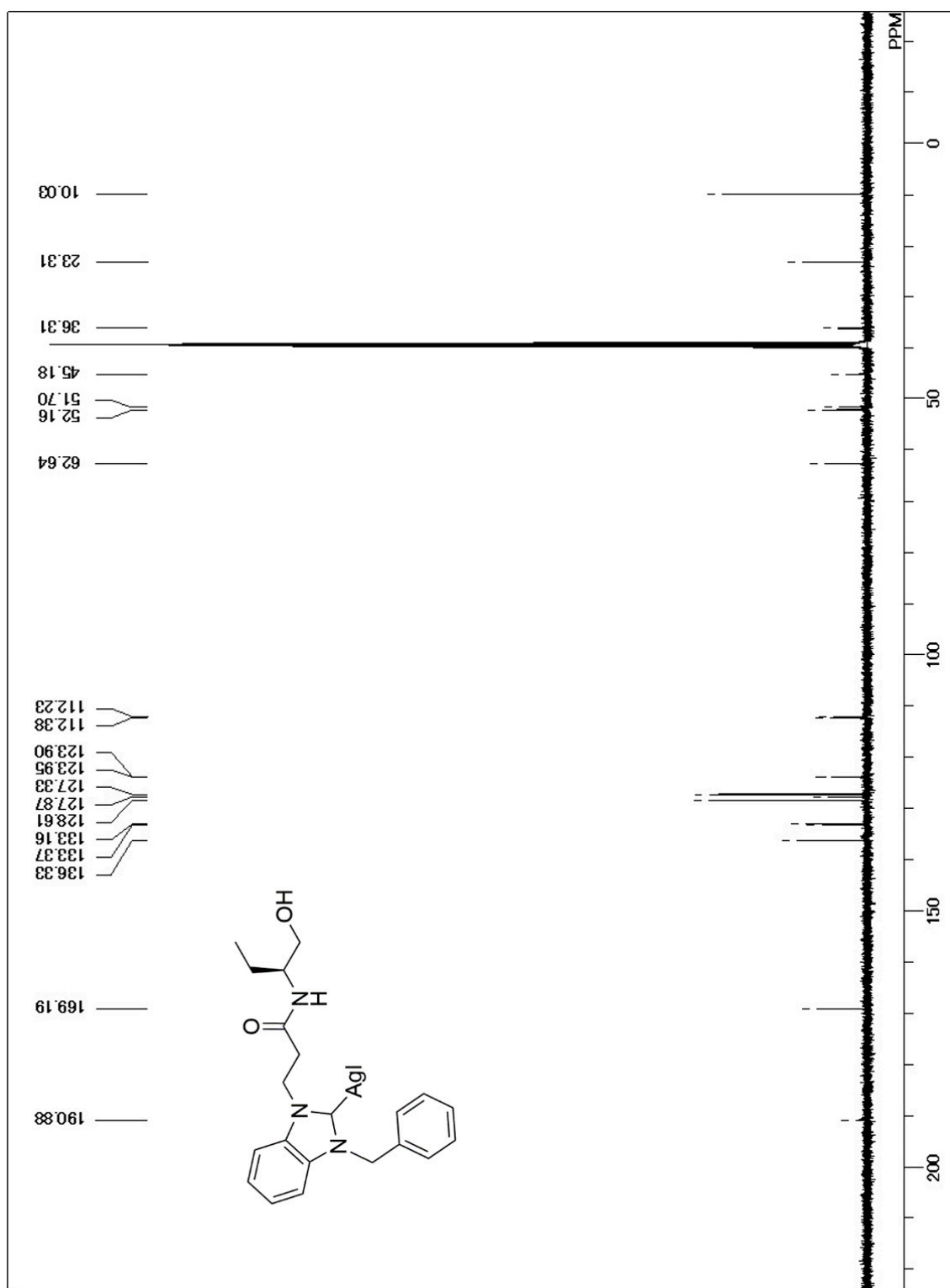
Ent-10b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).



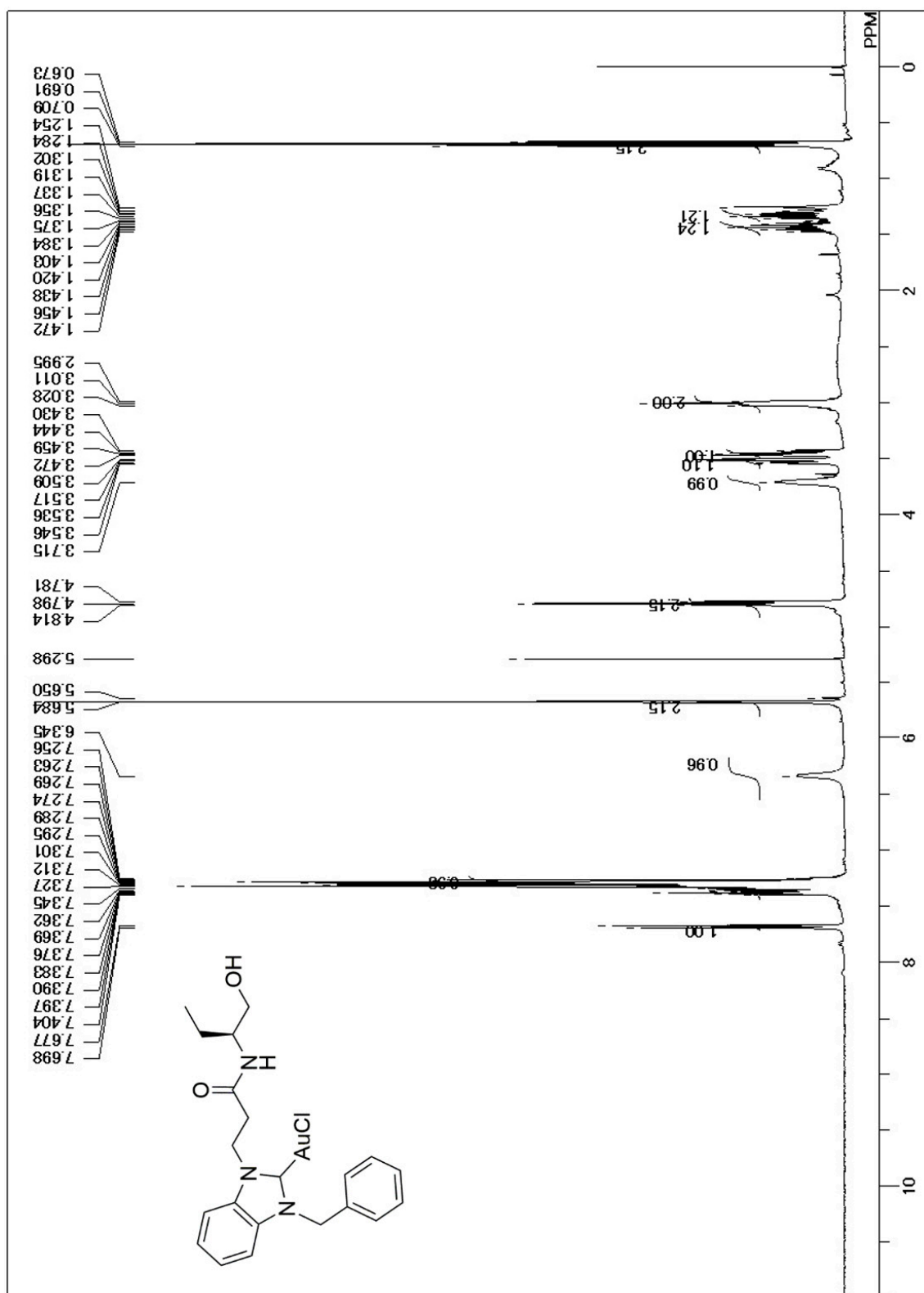
Ent-10b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).



NHC• AgI 1b (R¹=Et, R²=Bn).

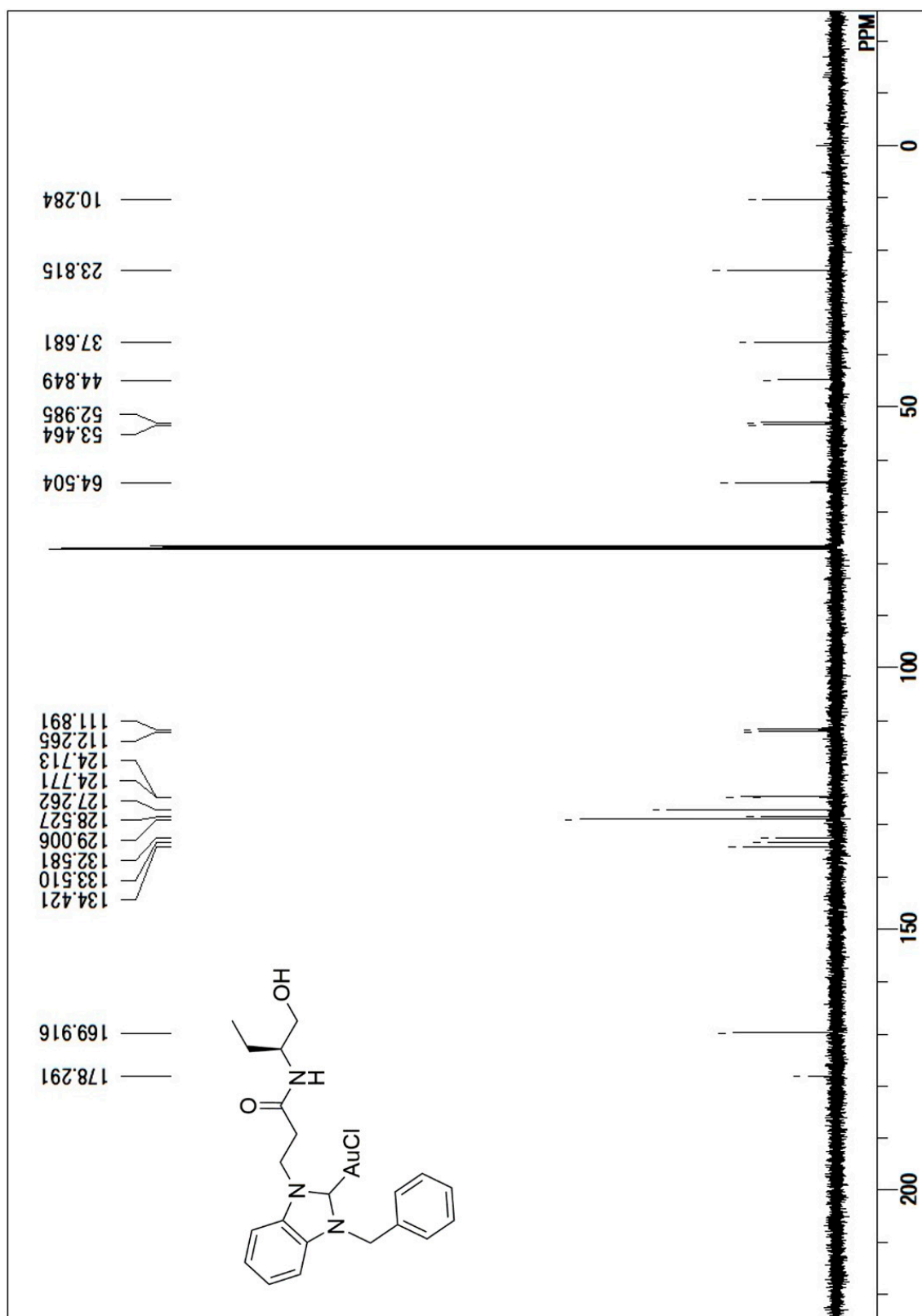


NHC• AgI 1b ( $R^1=Et$ ,  $R^2=Bn$ ).



NHC•AuCl 11b (R¹=Et, R²=Bn).





NHC•AuCl 11b (R<sup>1</sup>=Et, R<sup>2</sup>=Bn).

#### 4. Selected Chiral GC Traces in the ACA Reaction

The enantiomeric excess of 1,4-adducts in the ACA reaction was determined by chiral GLC according to the previously reported procedures..

<b>3-Ethylcyclohexanone (3):</b> pages 37-39	Supelco $\gamma$ -Dex225 70 °C, N <sub>2</sub> gas Linear velocity of 27.5 cm/s	Rt = 58 min ( <i>S</i> ) Rt = 60 min ( <i>R</i> )
<b>3-Ethyl-4,4-dimethylcyclohexanone (6):</b> page 40	Supelco $\gamma$ -Dex225, 85 °C, N <sub>2</sub> gas Linear velocity of 27.5 cm/s	Rt = 58 min ( <i>R</i> ) Rt = 59 min ( <i>S</i> )
<b>3-Ethylcycloheptanone (7):</b> page 41	Supelco $\beta$ -Dex225, 80 °C, N <sub>2</sub> gas Linear velocity of 27.5 cm/s	Rt = 57 min ( <i>S</i> ) Rt = 60 min ( <i>R</i> )
<b>3-Methylcyclohexanone (8):</b> page 42	Supelco $\gamma$ -Dex225 60 °C, N <sub>2</sub> gas Linear velocity of 27.5 cm/s	Rt = 53 min ( <i>S</i> ) Rt = 60 min ( <i>R</i> )
<b>3-Methylcycloheptanone (9):</b> page 42	Supelco $\beta$ -Dex225 70 °C, N <sub>2</sub> gas Linear velocity of 27.5 cm/s	Rt = 58 min ( <i>S</i> ) Rt = 72 min ( <i>R</i> )

#### 3-Ethylcyclohexanone (3)

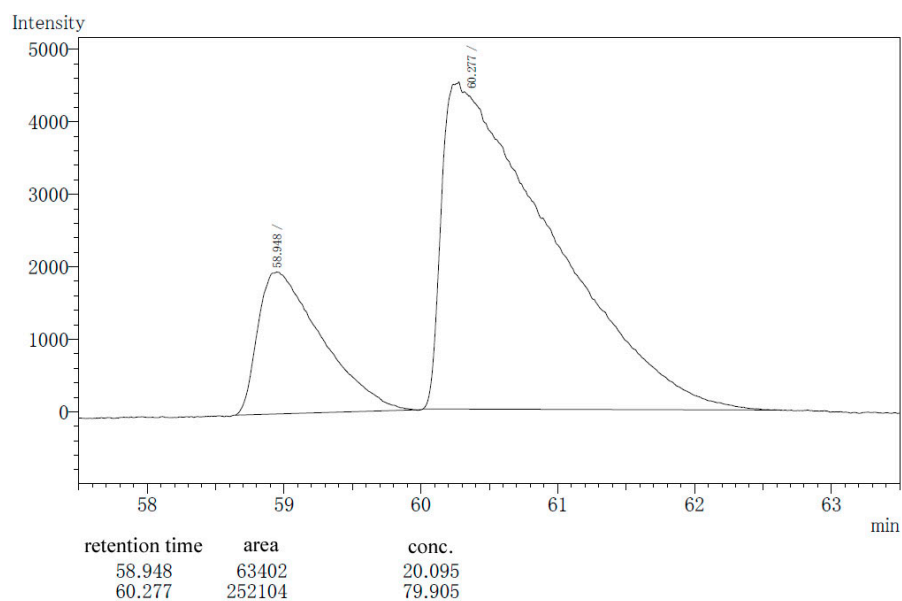


Table 1, entry 2, right: (*S*)-**3**; 80% *ee*

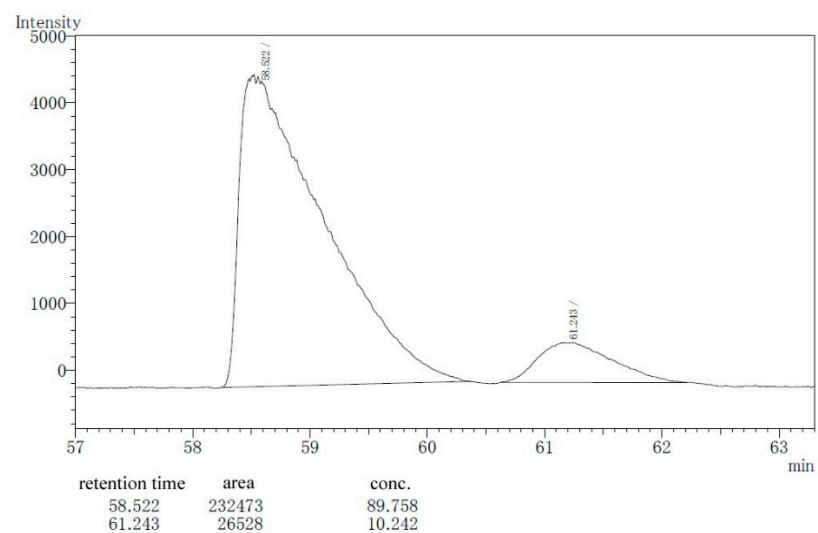


Table 2, entry 5, left: (R)-3; 75% ee

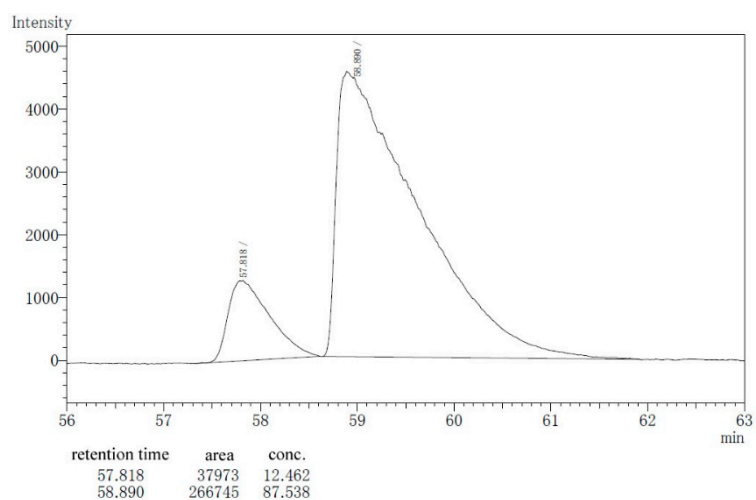


Table 2, entry 3, right: (S)-3; 87% ee

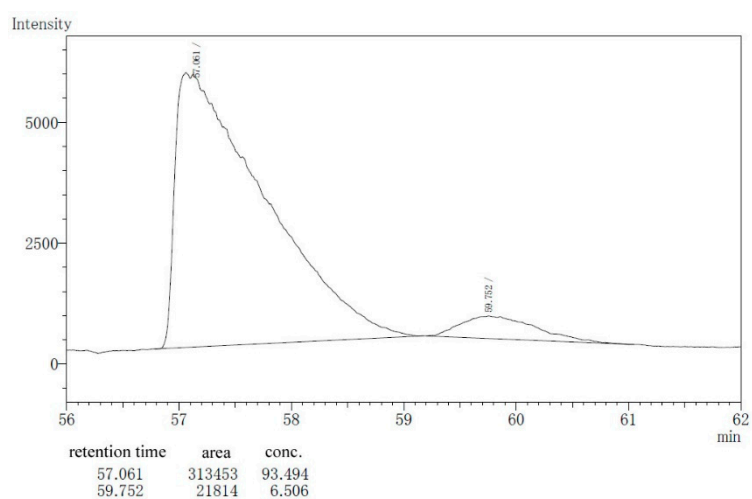


Table 2, entry 7, right: (S)-3; 89% ee

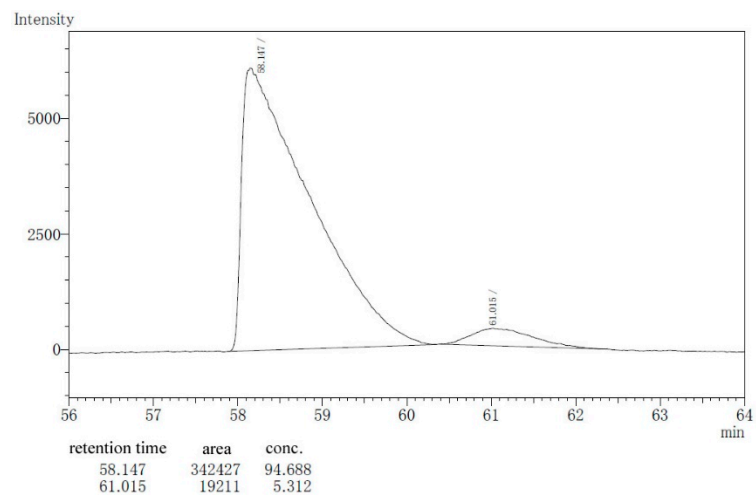


Table 3, entry 2, left: (S)-3; 69% *ee*

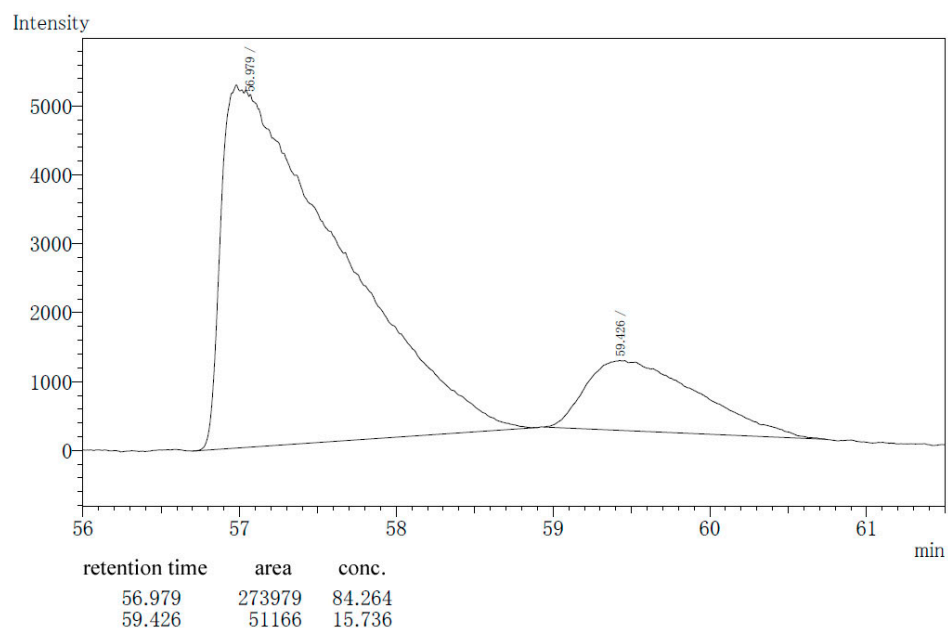
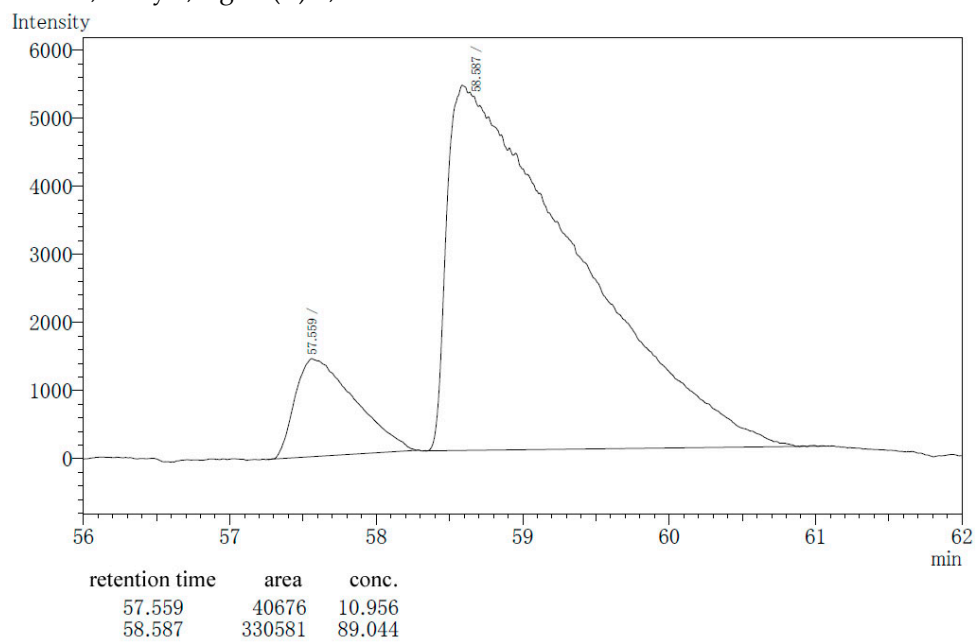


Table 3, entry 2, right: (R)-3; 78% *ee*



### 3-Ethyl-4,4-dimethylcyclohexanone (6)

Table 3, entry 3, left: (*S*)-6; 57% *ee*

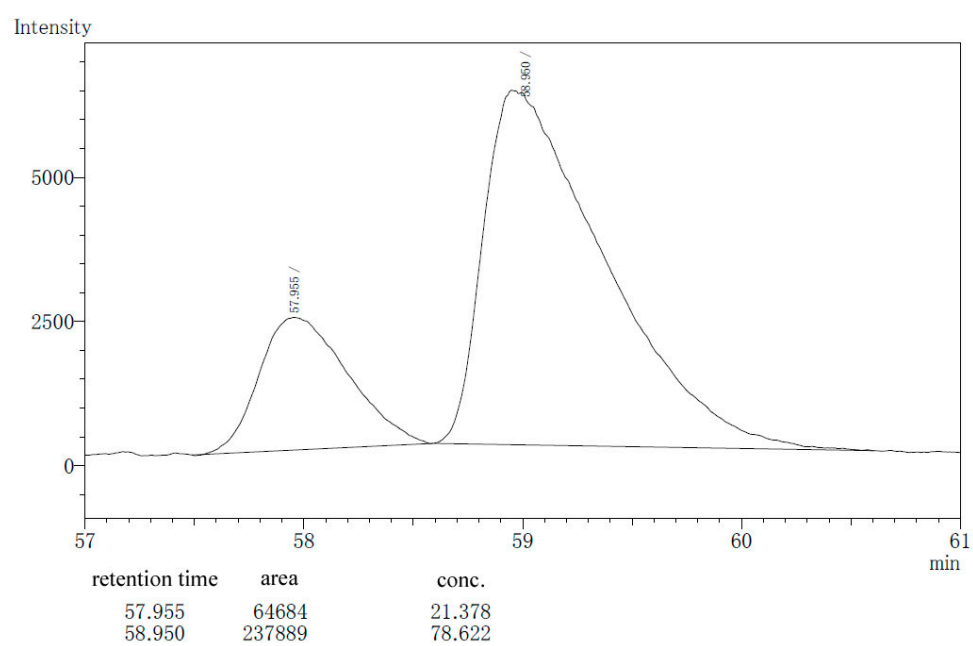
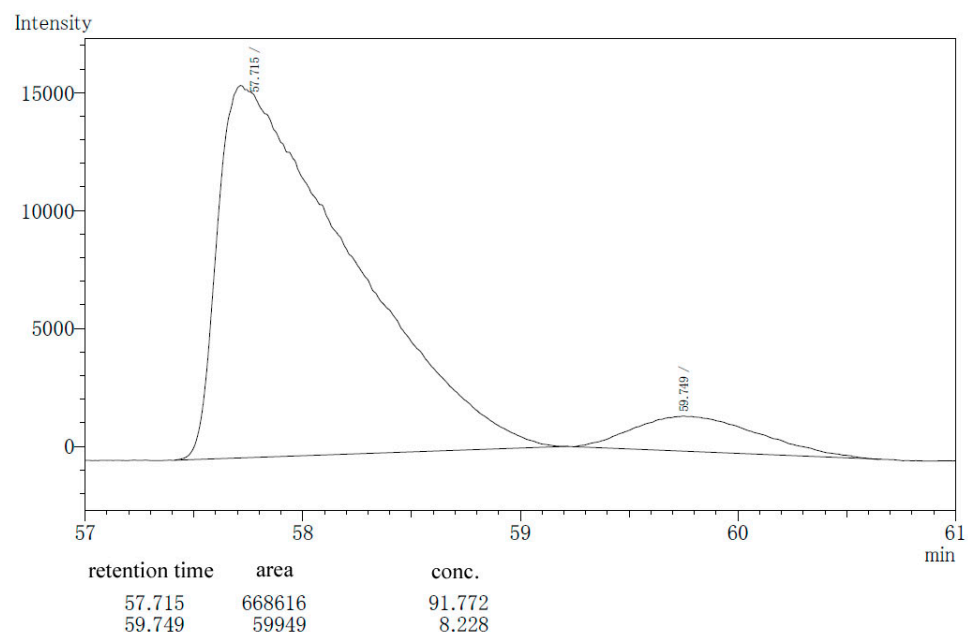


Table 3, entry 3, right: (*R*)-6; 84% *ee*



### 3-Ethylcycloheptanone (7)

Table 3, entry 4, left: (R)-7; 73% *ee*

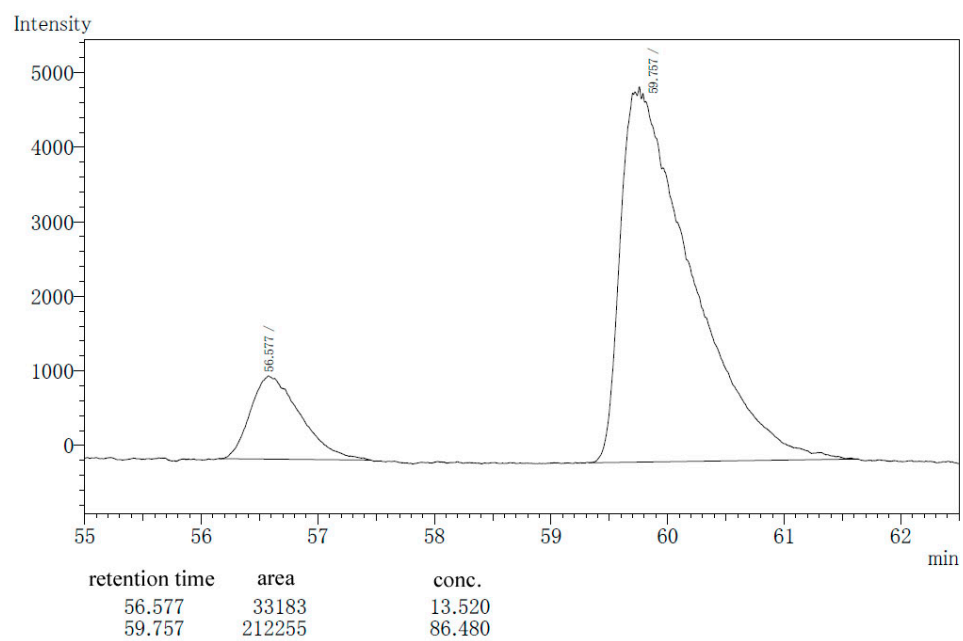
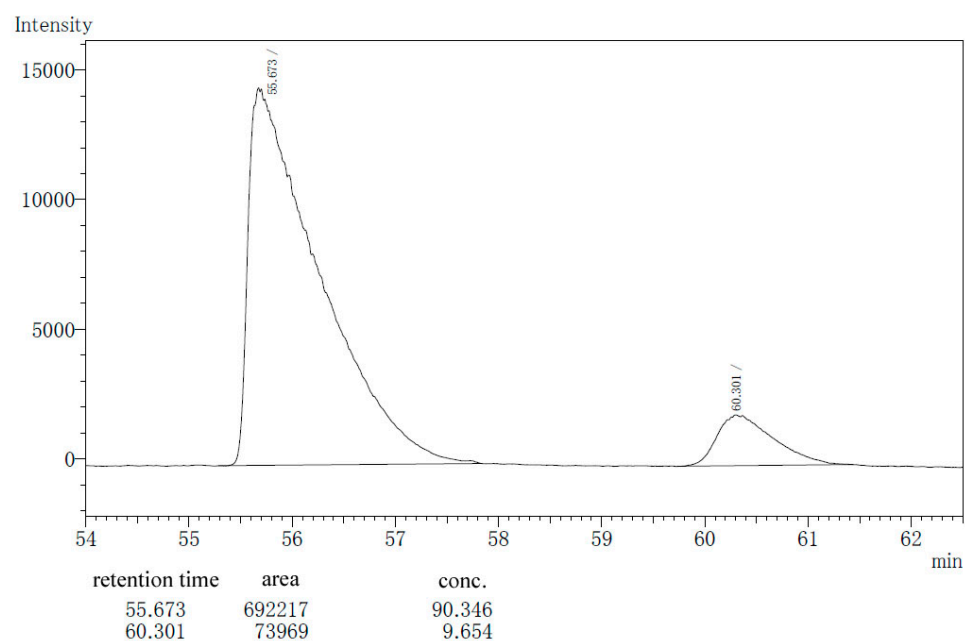
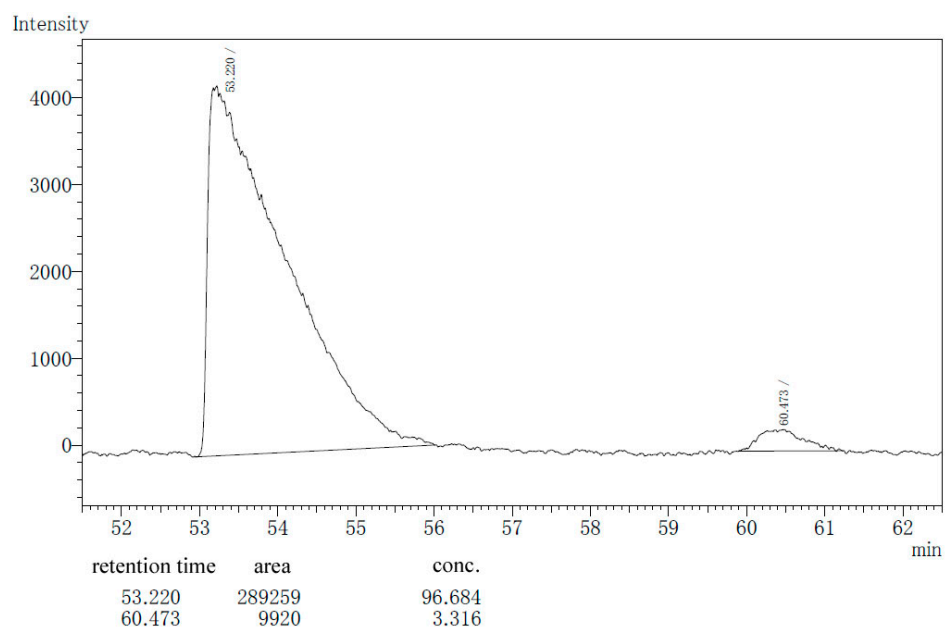


Table 3, entry 4, right: (S)-7; 81% *ee*



### 3-Methylcyclohexanone (8)

Table 3, entry 5, right: (S)-8; 93% *ee*



### 3-Methylcycloheptanone (9)

Table 3, entry 6, right: (S)-9; 93% *ee*

