

## Supporting Information

### Preferential carbene insertion into Ge–H vs other heavier group 14 hydrides via samarium carbenoids

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## 1. Materials

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. THF and THP were distilled from benzophenone and sodium prior to use.

(3-Cyanophenyl)diphenylgermane,<sup>1</sup> and (4-aminophenyl)diphenylgermane were prepared according to palladium-catalyzed single arylation of diphenylgermane with aryl iodide. [(Dimethylsilyl)methyl]dimethylgermane was prepared according to the literature.<sup>2</sup> Material identity and purity was confirmed by <sup>1</sup>H & <sup>13</sup>C NMR, EI-MS and elemental analysis or HRMS.

**(4-Aminophenyl)diphenylgermane:** To a solution of Pd(P(*t*Bu)<sub>3</sub>)<sub>2</sub> (0.48 g, 0.93 mmol) in THF (20 mL) were added 4-iodoaniline (4.56 g, 20.8 mmol), diisopropylethylamine (5.0 mL, 28.3 mmol), and diphenylgermane (12.0 mL, 64.0 mmol). After stirring for 9 d at room temperature, the reaction mixture was quenched with water, extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure, and column chromatography produced (4-aminophenyl)diphenylgermane (2.73 g, 41%) as colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53-7.51 (m, 4H), 7.39-7.33 (m, 6H), 7.29 (d, 2H, *J* = 8.6 Hz), 6.69 (d, 2H, *J* = 8.3 Hz), 5.63 (s, 1H), 3.71 (brs, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 147.3 (C<sub>q</sub>), 136.3 (CH), 136.2 (C<sub>q</sub>), 135.1 (CH), 128.9 (CH), 128.2 (CH), 122.9 (C<sub>q</sub>), 115.1 (CH); EI-MS *m/z* 321 (M<sup>+</sup>). FAB-HRMS Calcd for C<sub>18</sub>H<sub>17</sub>GeN: 321.0576. Found: 321.0545 (M<sup>+</sup>).

## 2. Spectroscopic data for products

**Methyltriphenylgermane (2):**<sup>3</sup> Colorless solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.45 (m, 6H), 7.38-7.32 (m, 9H), 0.90 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.0 (C<sub>q</sub>), 134.5 (CH), 128.8 (CH), 128.2 (CH), -4.2 (CH<sub>3</sub>); EI-MS *m/z* 320 (M<sup>+</sup>).

**Dideuteriummethyltriphenylgermane (4):** Colorless needles. Mp: 69.2-69.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50-7.46 (m, 6H), 7.36-7.31 (m, 9H), 0.86 (quin, 1H, *J* = 1.7 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 137.9 (C<sub>q</sub>), 134.5 (CH), 128.9 (CH), 128.2 (CH), -4.7 (quin, CD<sub>2</sub>, *J* = 19 Hz); EI-MS *m/z* 322 (M<sup>+</sup>); FAB-HRMS Calcd for C<sub>19</sub>H<sub>16</sub>D<sub>2</sub>Ge: 322.0746. Found: 322.0739 (M<sup>+</sup>).

**Tributylmethylgermane (5):** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.28-1.22 (m, 12H), 0.84-0.79 (m, 9H), 0.64-0.59 (m, 6H), -0.04 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 27.5 (CH<sub>2</sub>), 26.5 (CH<sub>2</sub>), 13.9 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>), -6.2 (CH<sub>3</sub>); EI-MS *m/z* 260 (M<sup>+</sup>); FAB-HRMS Calcd for C<sub>13</sub>H<sub>30</sub>Ge: 260.1562. Found: 260.1539 (M<sup>+</sup>).

**Ethyltriphenylgermane (6):**<sup>4</sup> Colorless powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50-7.46 (m, 6H), 7.37-7.32 (m, 9H), 1.54 (q, 2H, *J* = 8.0 Hz), 1.19 (t, 3H, *J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 137.1 (C<sub>q</sub>), 135.0 (CH), 128.8 (CH), 128.1 (CH), 9.1 (CH<sub>3</sub>), 6.3 (CH<sub>2</sub>); EI-MS *m/z* 334 (M<sup>+</sup>).

**Triethyl(4-phenylbutyl)germane (7):** Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30-7.25 (m,

2H), 7.19-7.15 (m, 3H), 2.61 (t, 2H,  $J = 7.7$  Hz), 1.63 (quin, 2H,  $J = 7.7$  Hz), 1.45-1.37 (m, 2H), 1.00 (t, 9H,  $J = 7.7$  Hz), 0.77-0.67 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9 ( $\text{C}_q$ ), 128.3 (CH), 138.2 (CH), 125.5 (CH), 35.6 ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ), 24.9 ( $\text{CH}_2$ ), 11.2 ( $\text{CH}_2$ ), 9.0 ( $\text{CH}_3$ ), 3.9 ( $\text{CH}_2$ ); EI-MS  $m/z$  294 ( $\text{M}^+$ ); FAB-HRMS Calcd for  $\text{C}_{16}\text{H}_{28}\text{Ge}$ : 294.1406. Found: 294.1380 ( $\text{M}^+$ ).

**(2,2-Dimethylpropyl)triphenylgermane (8):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.52 (m, 6H), 7.36-7.32 (m, 9H), 1.79 (s, 2H), 0.94 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6 ( $\text{C}_q$ ), 135.1 (CH), 128.6 (CH), 128.0 (CH), 32.9 ( $\text{CH}_3$ ), 31.5 ( $\text{C}_q$ ), 31.1 ( $\text{CH}_2$ ); EI-MS  $m/z$  376 ( $\text{M}^+$ ); FAB-HRMS Calcd for  $\text{C}_{23}\text{H}_{26}\text{Ge}$ : 376.1251. Found: 376.1260 ( $\text{M}^+$ ).

**Methyl(4-aminophenyl)diphenylgermane (9):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.46 (m, 4H), 7.37-7.33 (m, 6H), 7.25 (d, 2H,  $J = 8.4$  Hz), 6.68 (d, 2H,  $J = 8.4$  Hz), 3.68 (s, 2H), 0.85 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.1 ( $\text{C}_q$ ), 138.7 ( $\text{C}_q$ ), 135.6 (CH), 134.5 (CH), 128.7 (CH), 128.0 (CH), 125.5 ( $\text{C}_q$ ), 115.0 (CH), -4.0 ( $\text{CH}_3$ ); EI-MS  $m/z$  335 ( $\text{M}^+$ ); FAB-HRMS Calcd for  $\text{C}_{18}\text{H}_{17}\text{GeN}$ : 335.0733. Found: 335.0765 ( $\text{M}^+$ ).

**Methyl(3-cyanophenyl)diphenylgermane (10):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (s, 1H), 7.67 (d, 1H,  $J = 7.6$  Hz), 7.64 (d, 1H,  $J = 7.6$  Hz), 7.47-7.36 (m, 11H), 0.94 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.6 ( $\text{C}_q$ ), 138.6 (CH), 137.8 (CH), 136.3 (CN), 134.3 (CH), 132.3 (CH), 129.4 (CH), 128.6 (CH), 128.4 (CH), 119.0 ( $\text{C}_q$ ), 112.4 ( $\text{C}_q$ ), -4.4 ( $\text{CH}_3$ ). EI-MS  $m/z$  345 ( $\text{M}^+$ ). FAB-HRMS Calcd for  $\text{C}_{20}\text{H}_{17}\text{GeN}$ : 345.0577. Found: 345.0598 ( $\text{M}^+$ ).

**Dimethyldiphenylgermane (11):**<sup>5</sup> Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49-7.45 (m, 4H), 7.34-7.30 (m, 6H), 0.63 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.2 ( $\text{C}_q$ ), 133.6 (CH), 128.6 (CH), 128.1 (CH), -3.1 ( $\text{CH}_3$ ); EI-MS  $m/z$  258 ( $\text{M}^+$ ).

**Butyltriethylgermane (12):**<sup>6</sup> Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.35-1.30 (m, 4H), 1.01 (t, 9H,  $J = 6.4$  Hz), 0.89 (t, 3H,  $J = 5.7$  Hz), 0.73-0.67 (m, 8H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  27.4 ( $\text{CH}_2$ ), 26.6 ( $\text{CH}_2$ ), 13.8 ( $\text{CH}_3$ ), 11.1 ( $\text{CH}_2$ ), 8.9 ( $\text{CH}_3$ ), 3.8 ( $\text{CH}_2$ ); EI-MS  $m/z$  218 ( $\text{M}^+$ ).

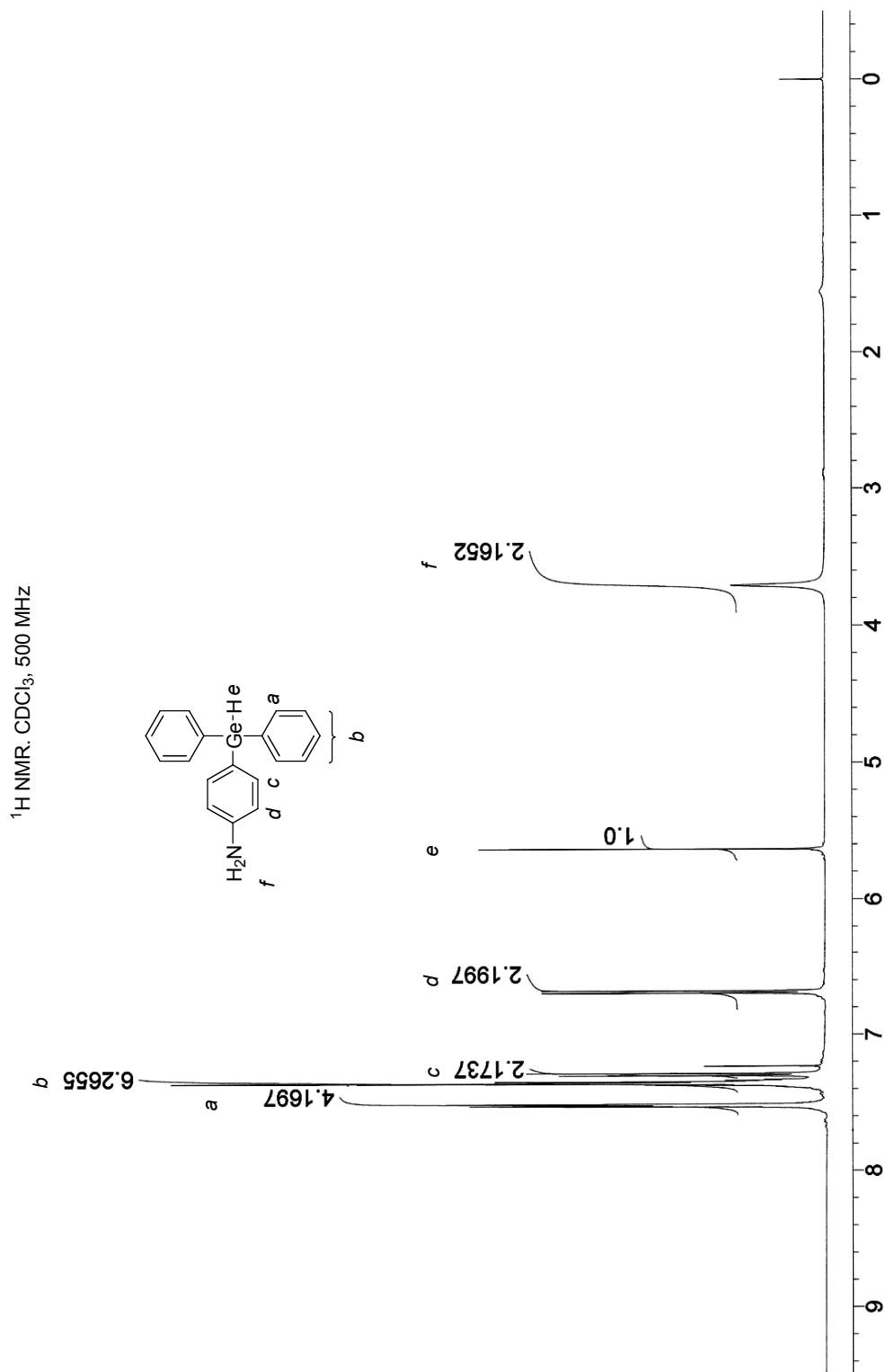
**Dimethyl(4-phenylbutyl)germyl dimethylsilyl methane (13):** Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 3.89 (septet, 1H,  $J = 3.6$  Hz), 2.61 (t, 2H,  $J = 8.0$  Hz), 1.63 (quin, 2H,  $J = 7.7$  Hz), 1.45-1.37 (m, 2H), 0.78-0.73 (m, 2H), 0.13 (s, 6H), 0.08 (d, 6H,  $J = 3.6$  Hz), -0.18 (d, 2H,  $J = 4.1$  Hz);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9 ( $\text{C}_q$ ), 128.4 (CH), 128.2 (CH), 125.5 (CH), 35.6 ( $\text{CH}_2$ ), 35.1 ( $\text{CH}_2$ ), 24.7 ( $\text{CH}_2$ ), 17.4 ( $\text{CH}_2$ ), -1.3 ( $\text{CH}_2$ ), -1.5 ( $\text{CH}_3$ ), -1.8 ( $\text{CH}_3$ ); EI-MS  $m/z$  310 ( $\text{M}^+$ ); FAB-HRMS Calcd for  $\text{C}_{15}\text{H}_{28}\text{GeSi}$ : 310.1175. Found: 310.1145 ( $\text{M}^+$ ).

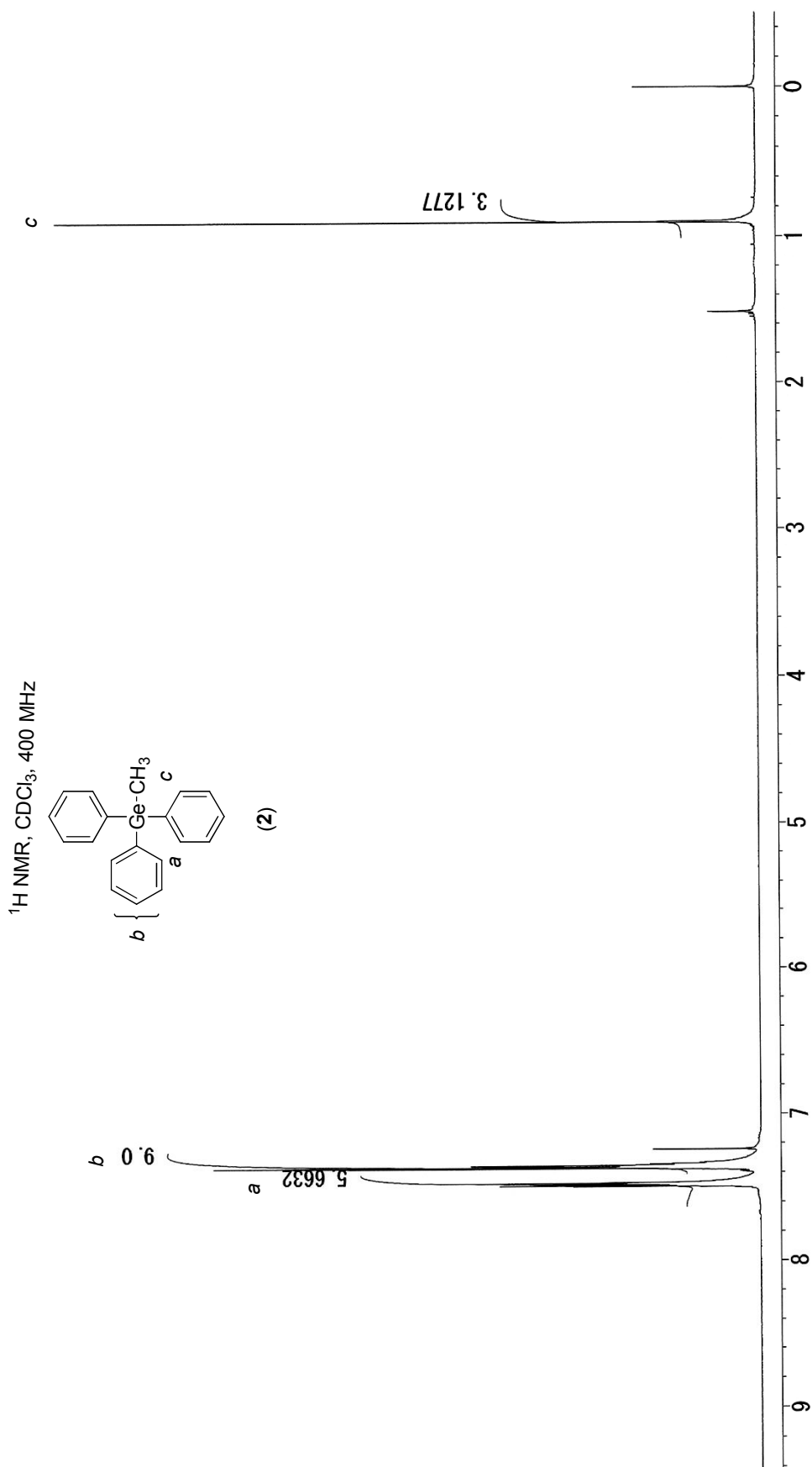
### 3. References

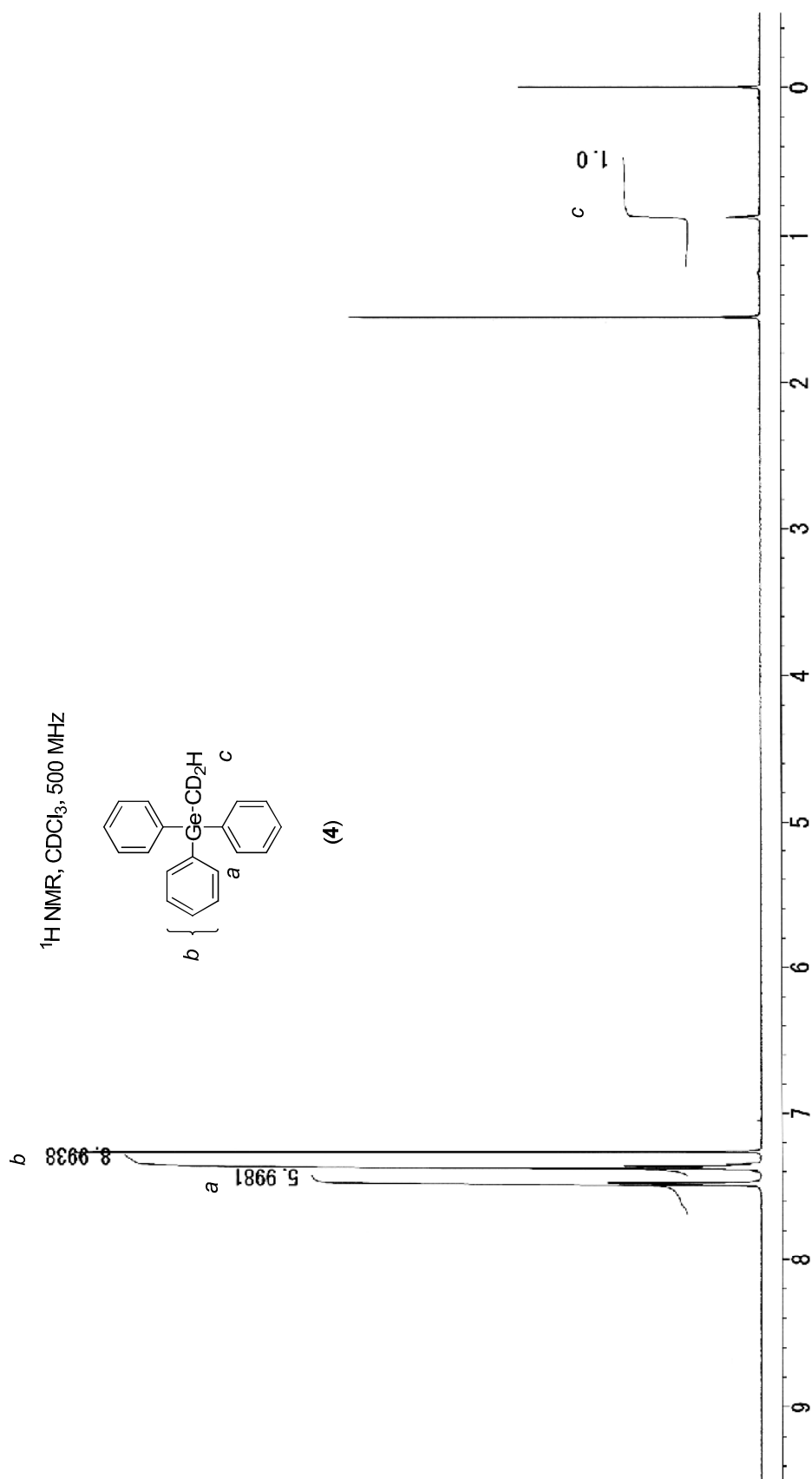
- (1) A. Lesbani, H. Kondo, Y. Yabusaki, M. Nakai, Y. Yamanoi, H. Nishihara, *Chem. Eur. J.*, 2010, **16**, 13519.
- (2) J. Barrau, N. B. Hamida, J. Satgé, *J. Organomet. Chem.*, 1990, **387**, 65.
- (3) A. G. Brook, G. J. D. Peddle, *J. Am. Chem. Soc.*, 1963, **85**, 1869.

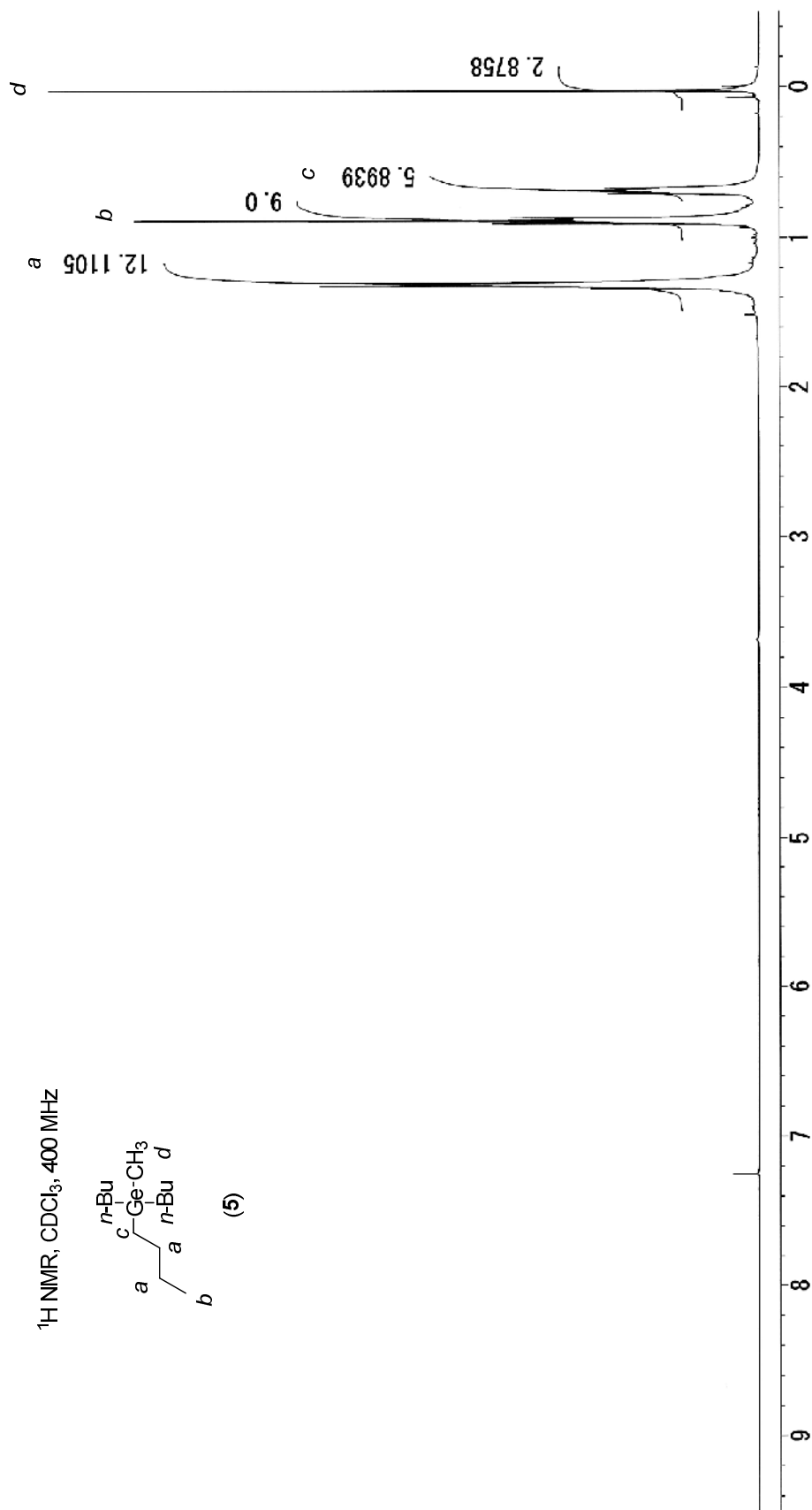
- (4) (a) R. J. P. Corriu, C. Guerin, *J. Organomet. Chem.*, 1980, **197**, C19. (b) Y. Ura, R. Hara, T. Takahashi, *J. Organomet. Chem.*, 2000, **611**, 299.
- (5) This compound is commercially available.
- (6) H. Gilman, M. B. Hughes, C. W. Gerow, *J. Org. Chem.*, 1959, **24**, 352.

#### 4. Copies of $^1\text{H}$ NMR spectra

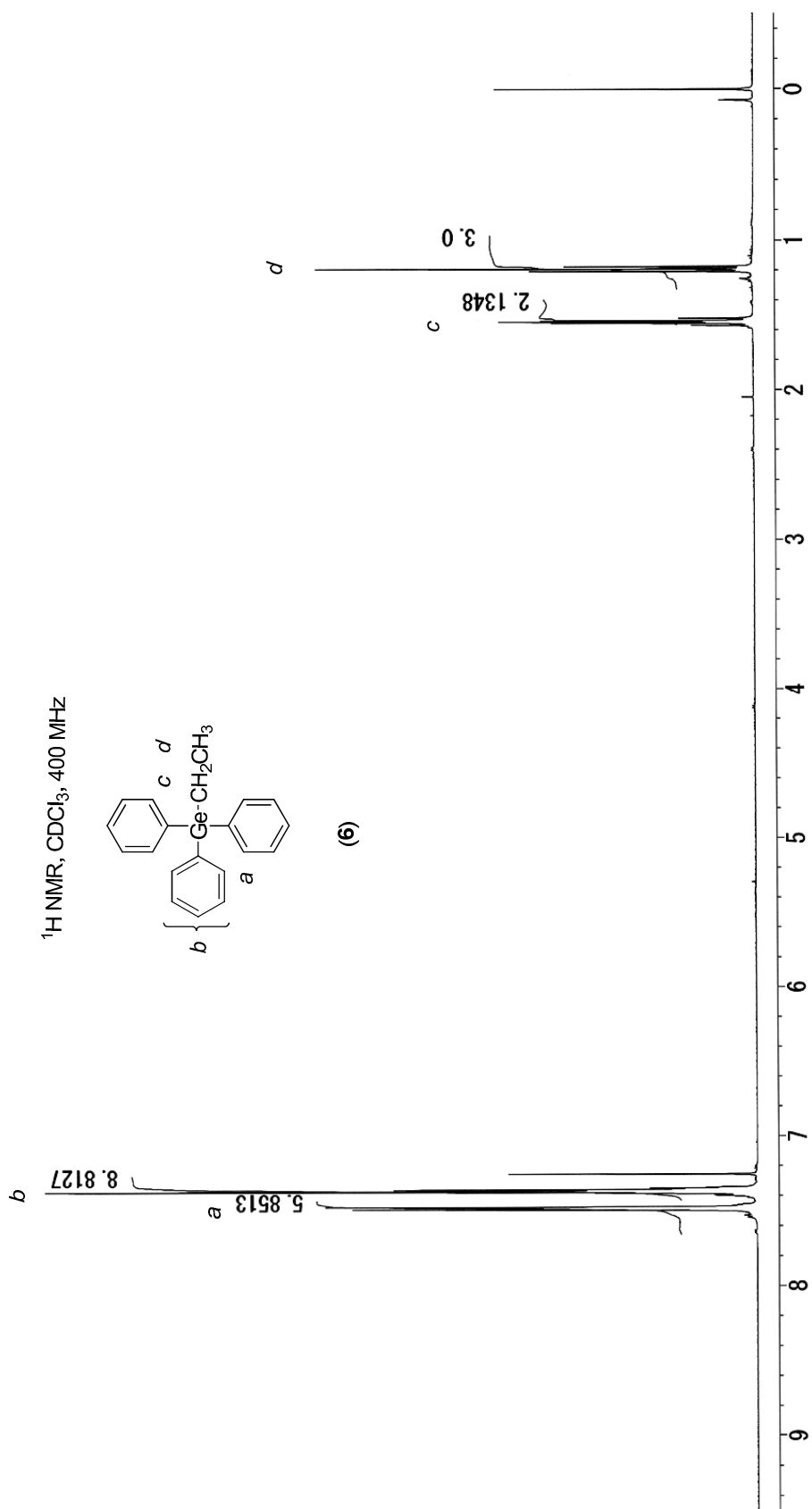


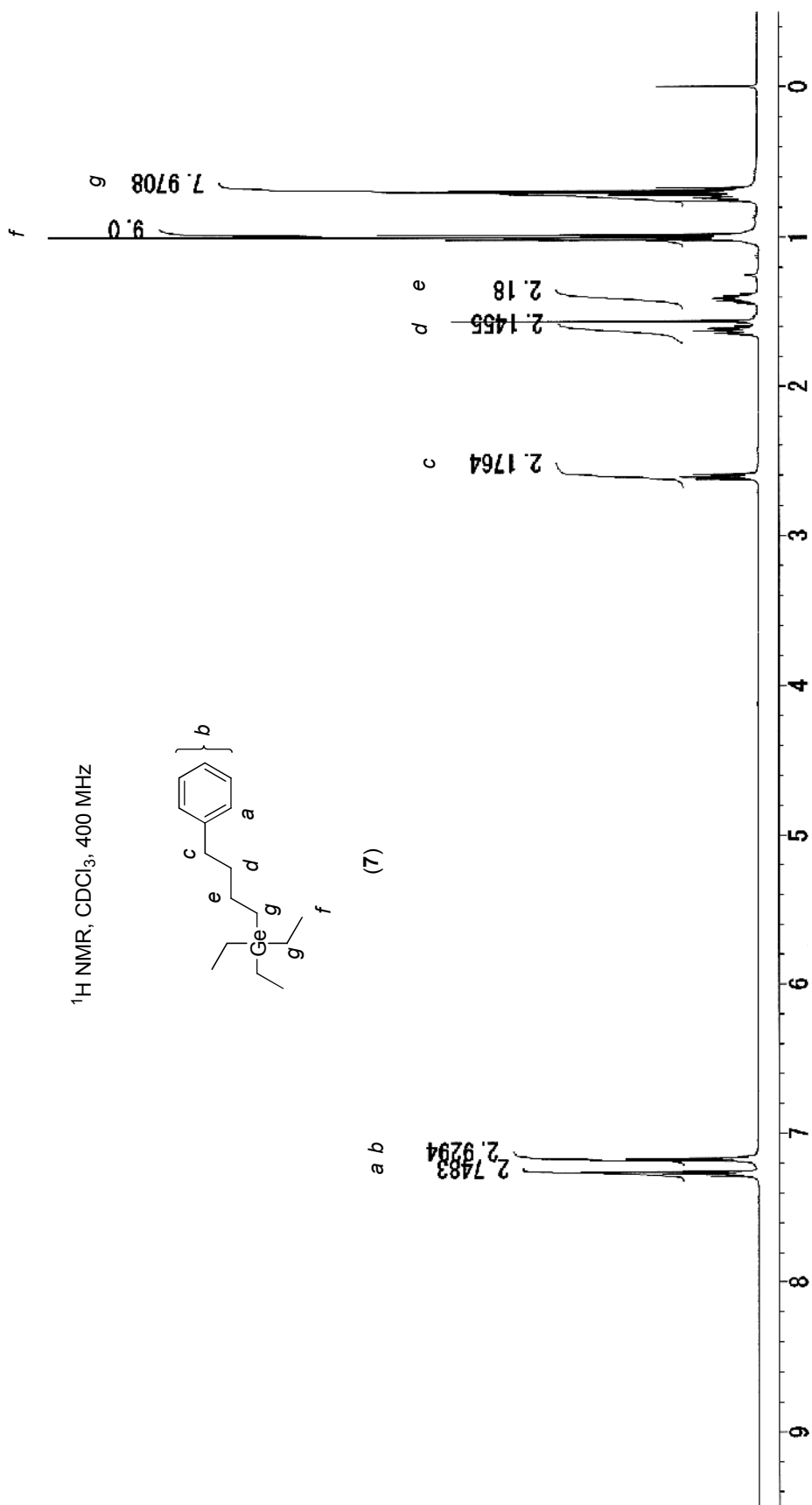


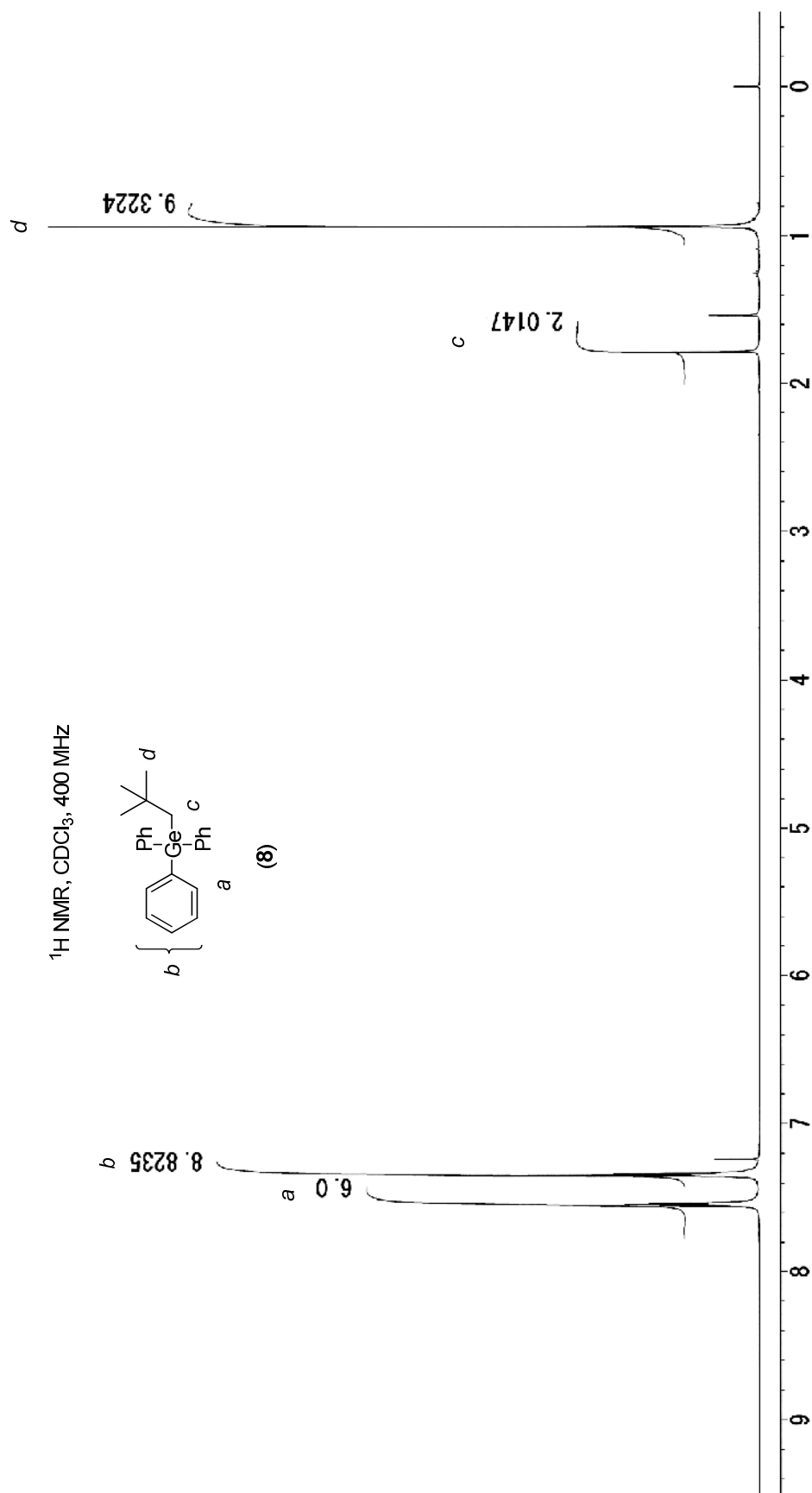


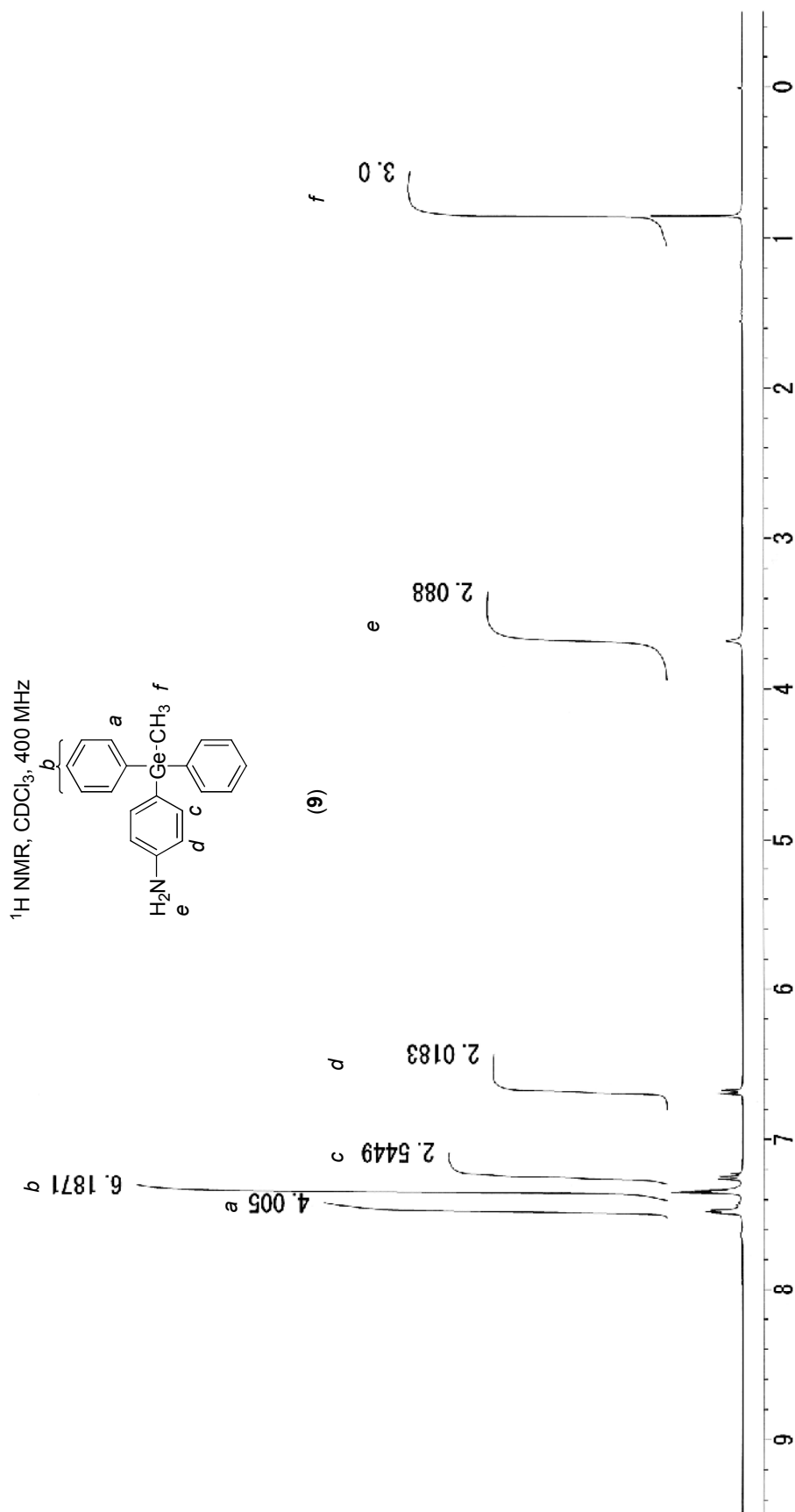


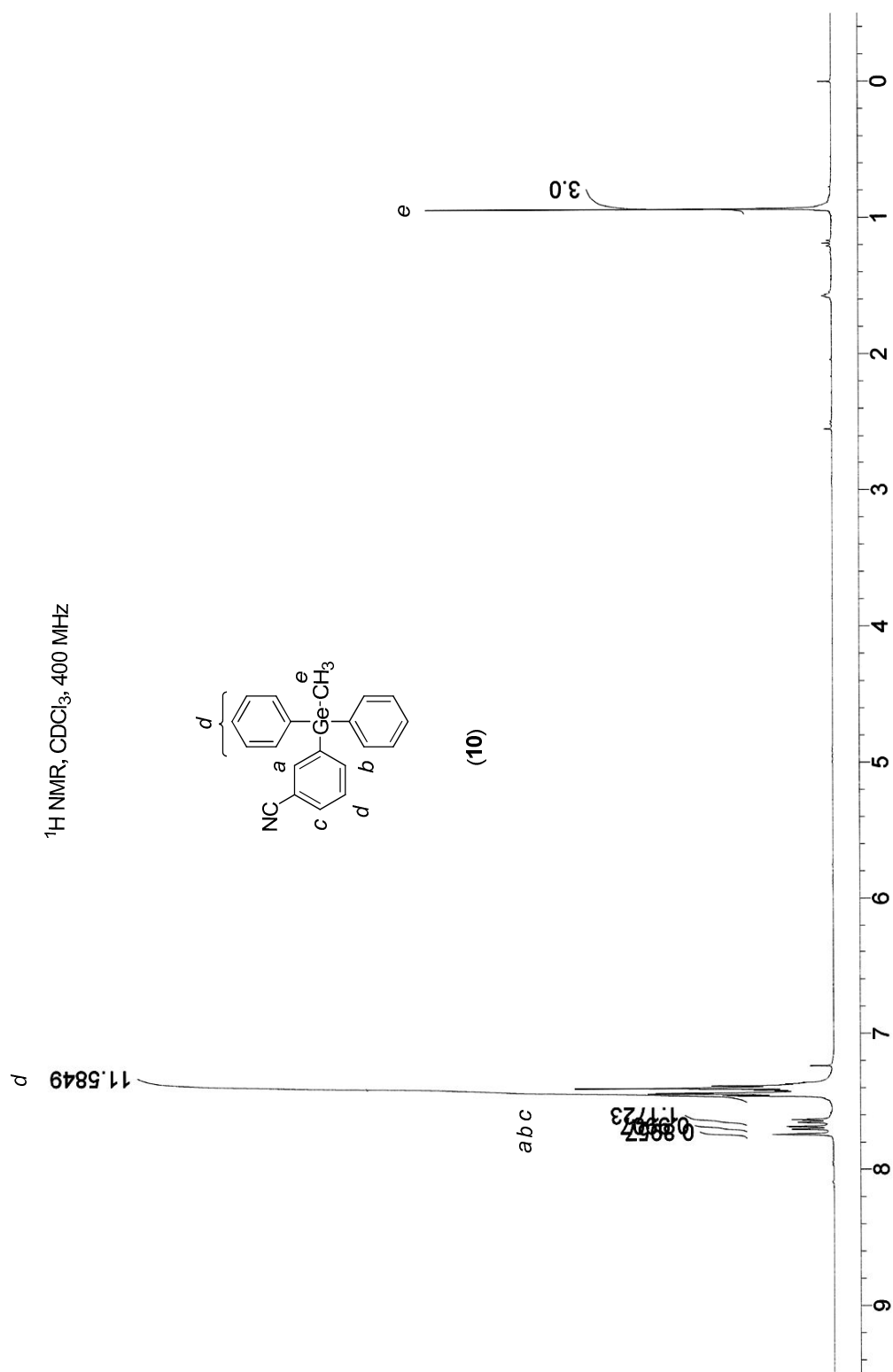


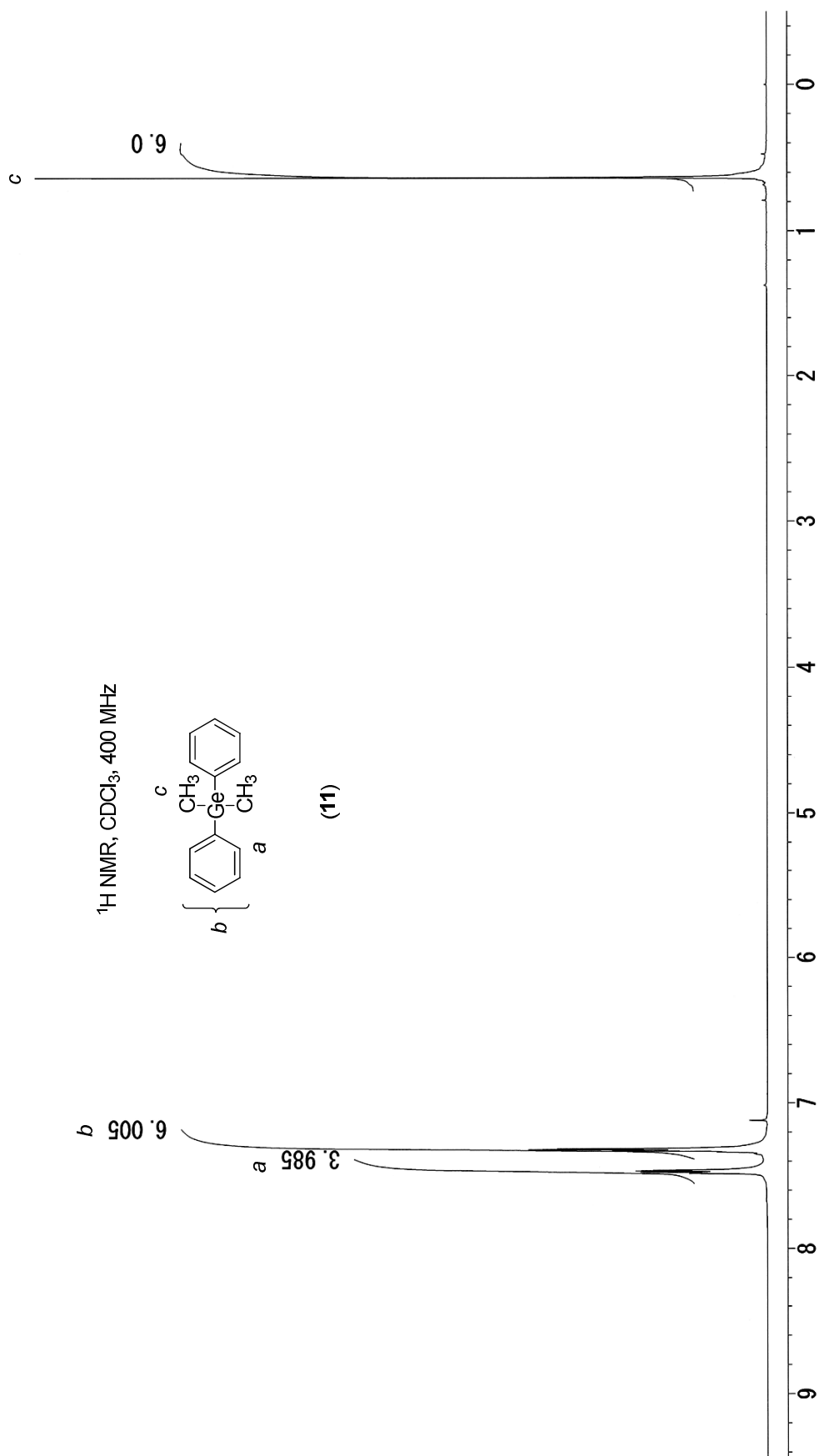


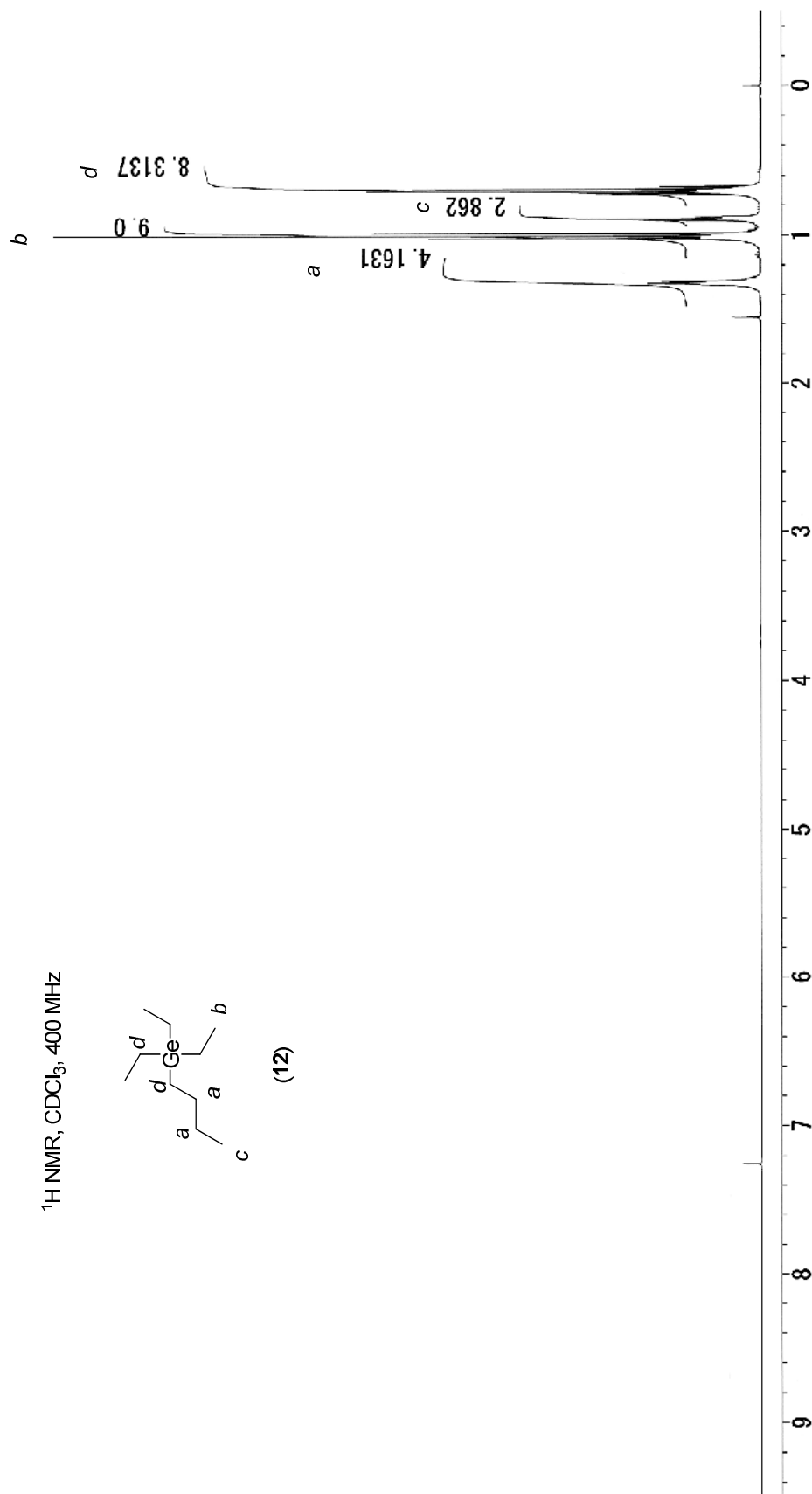




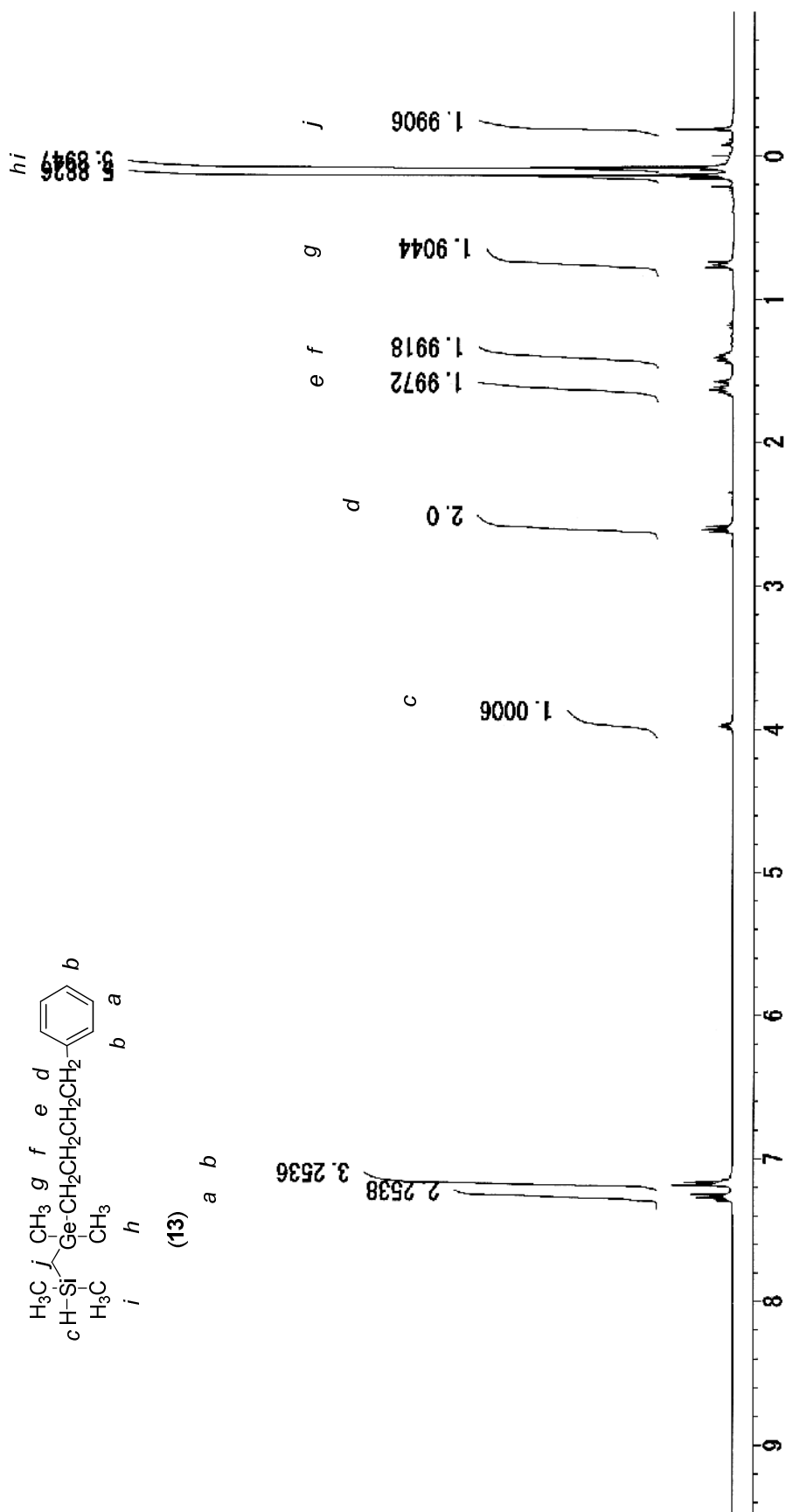
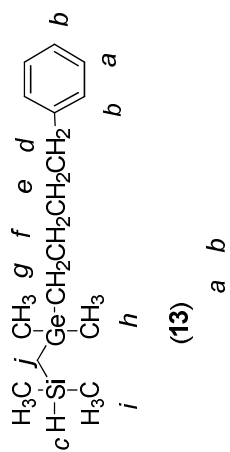






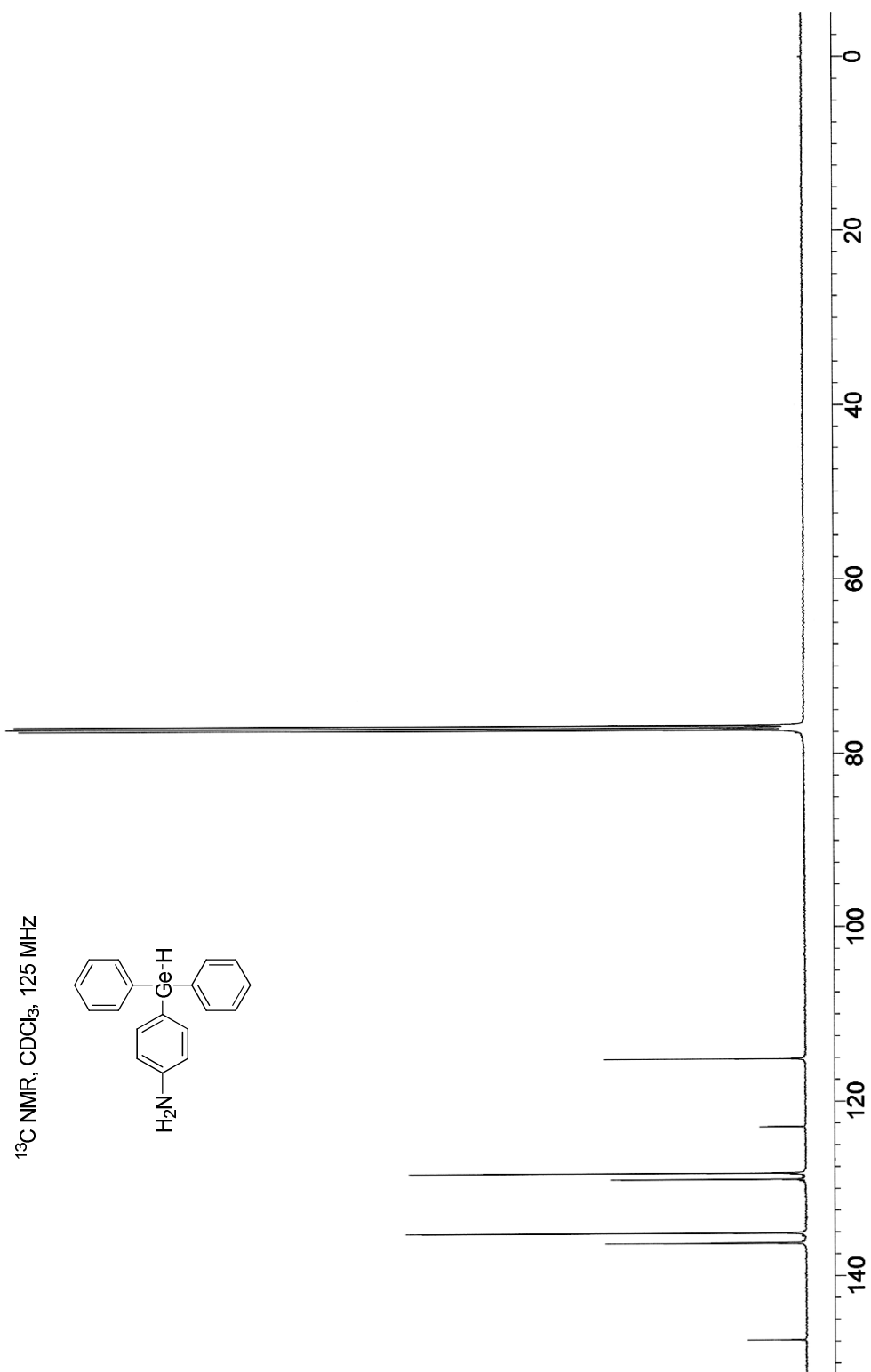


$^1\text{H}$  NMR,  $\text{CDCl}_3$ , 400 MHz

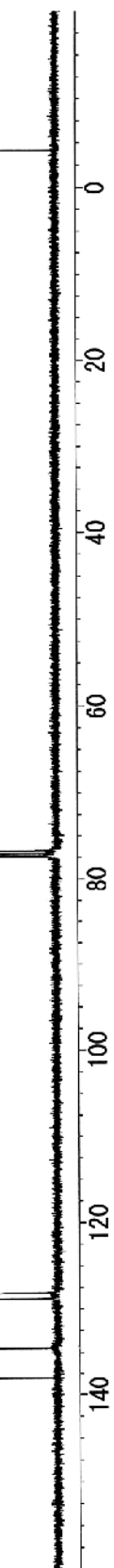
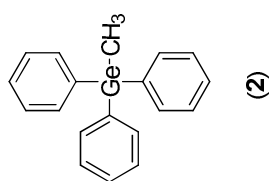




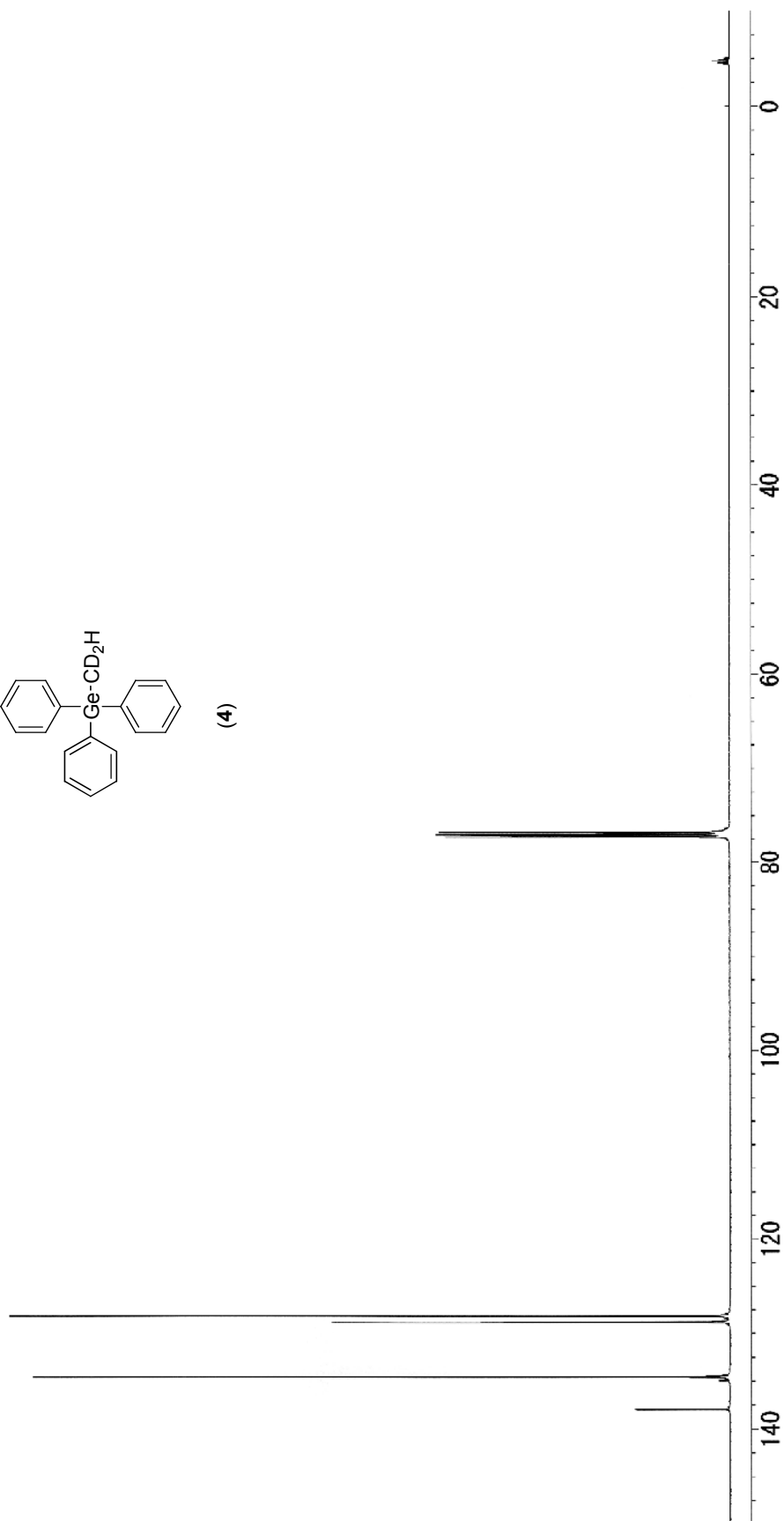
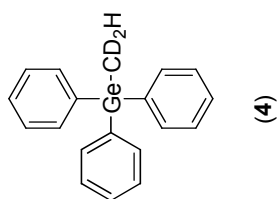
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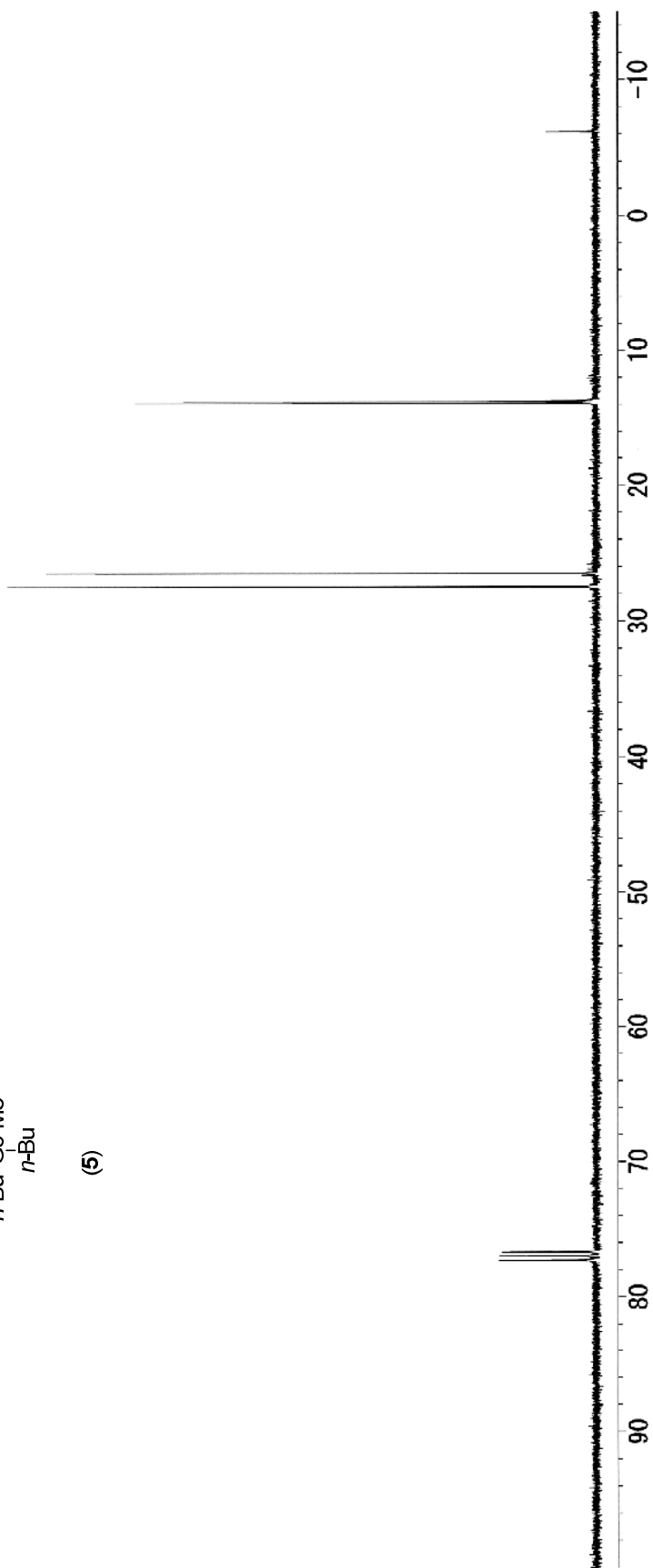
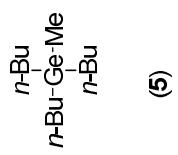
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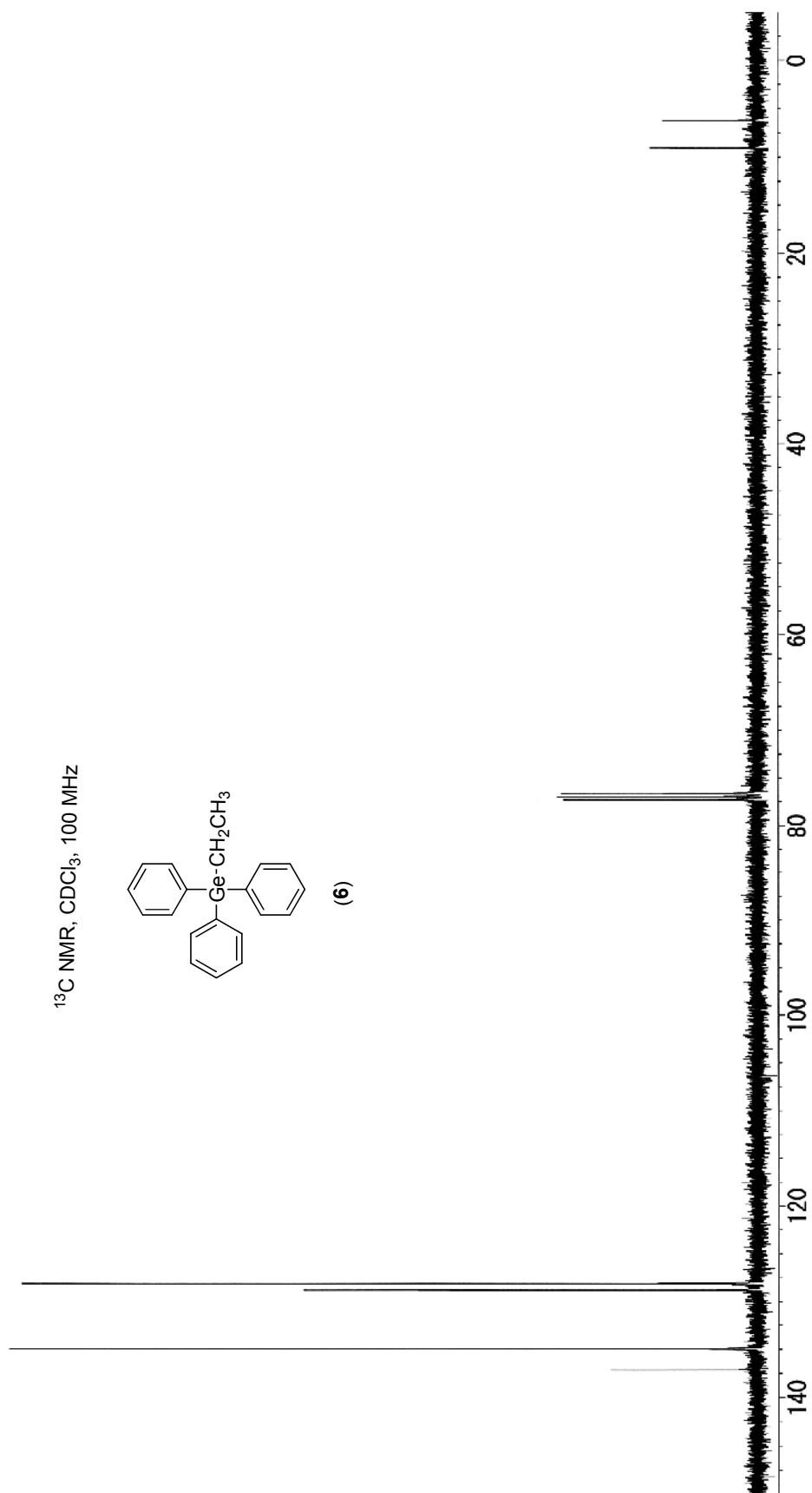


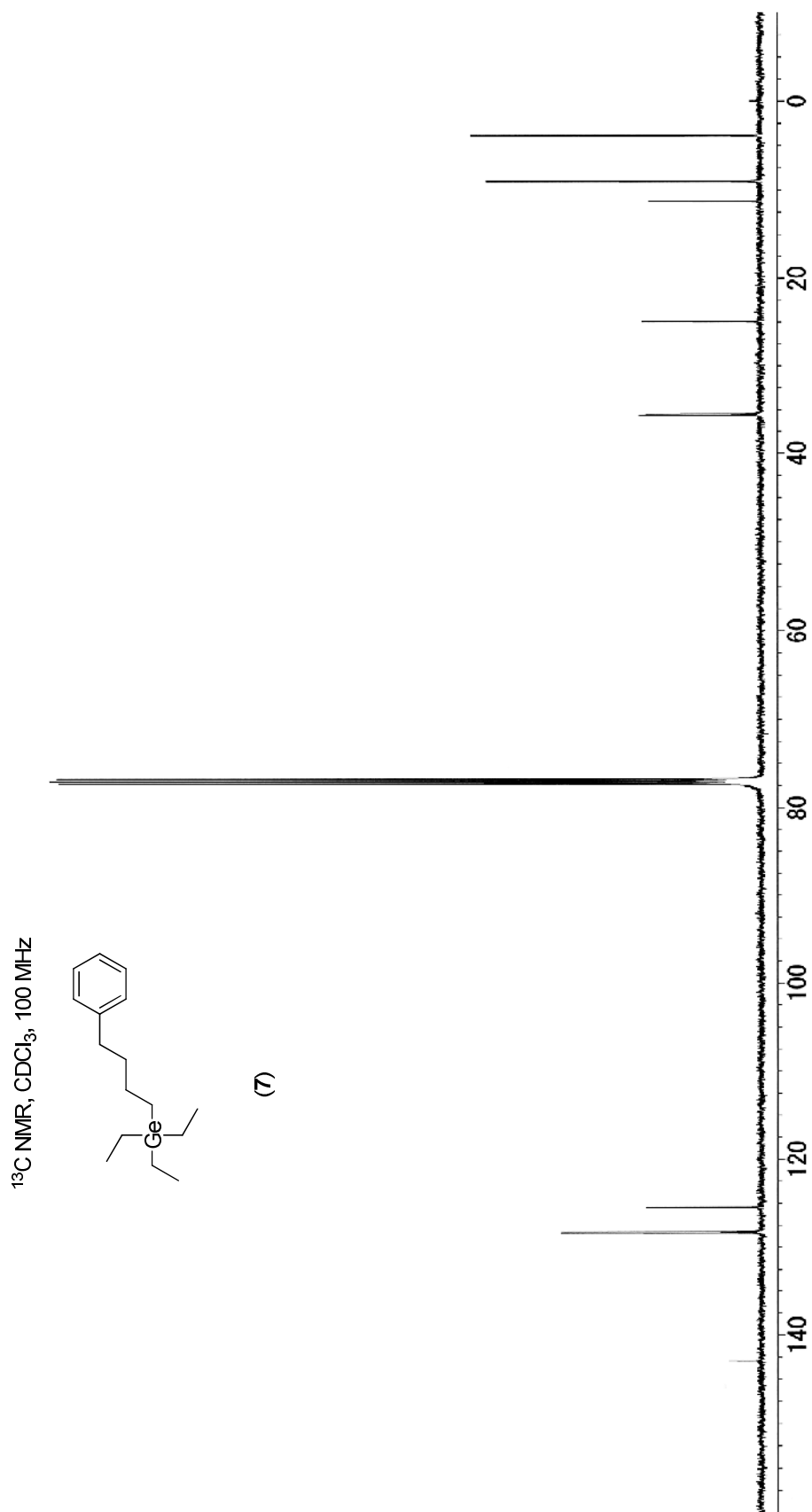
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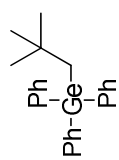
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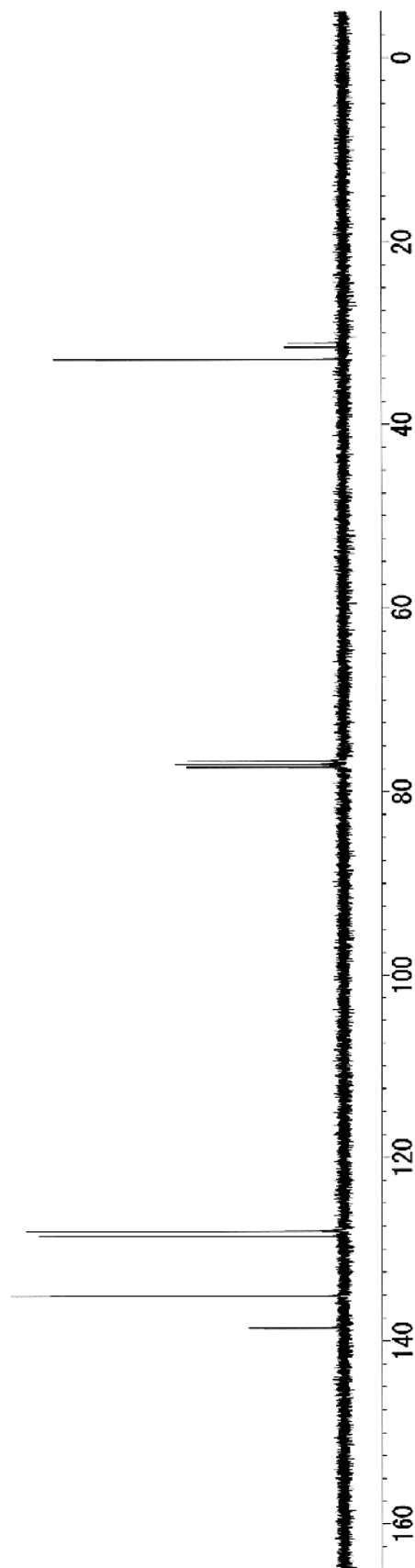




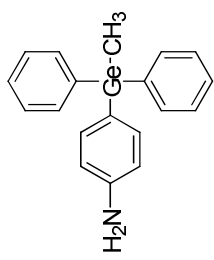
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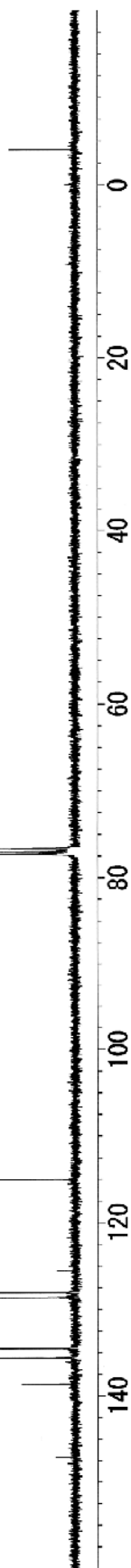


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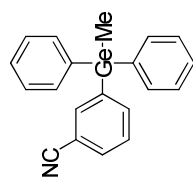
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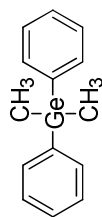
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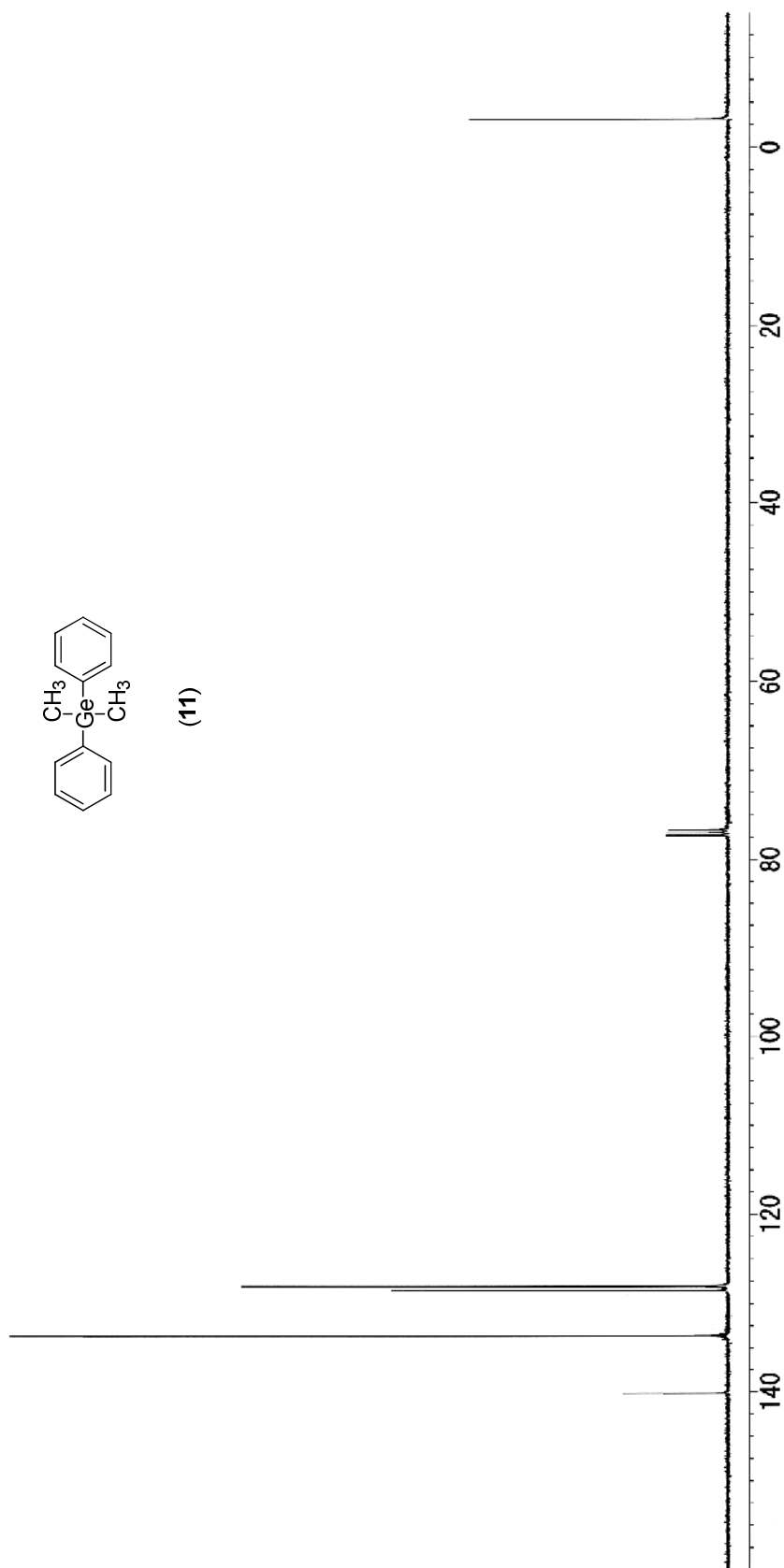
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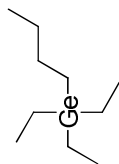
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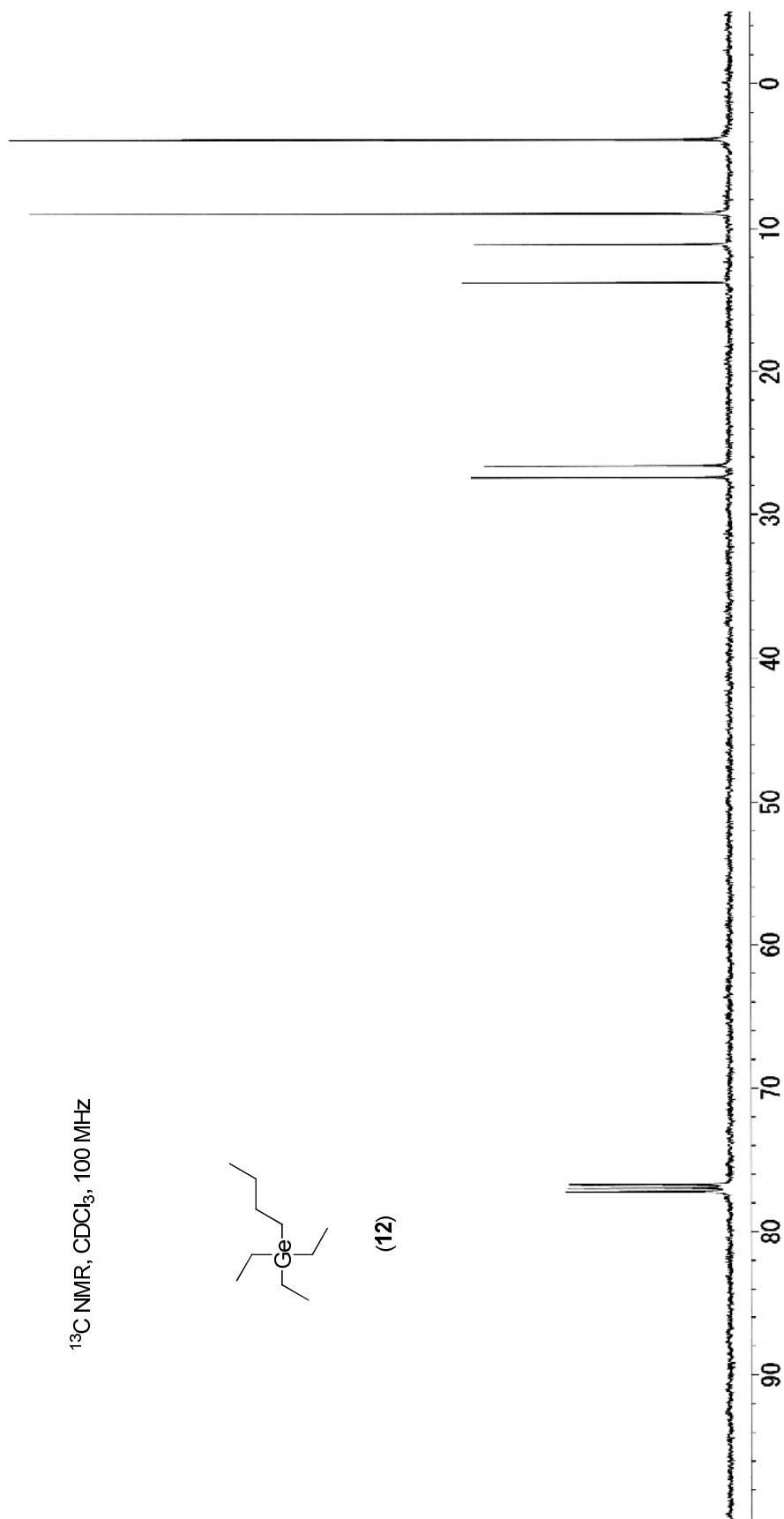
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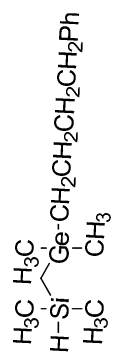
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(12)



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



(13)

