

## Iron(III) chloride promoted Ritter amidation of saturated cyclopropane-containing polycyclic hydrocarbons

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### Experimental Section

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker Avance-III Ascend instrument (500.17 MHz for  $^1\text{H}$  and 125.78 MHz for  $^{13}\text{C}$  in  $\text{CDCl}_3$ ) or (400.13 MHz for  $^1\text{H}$  and 100.25 MHz for  $^{13}\text{C}$  in  $\text{CDCl}_3$ ). The structures of compounds were confirmed by one-dimensional ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and two-dimensional (COSY, NOESY, HSQC, HMBC). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m  $\times$  0.25 mm, helium as the carrier gas, temperature programming from 40 to 300°C at 8 °C  $\text{min}^{-1}$ , evaporation temperature of 280°C, ion source temperature of 200°C, and ionization energy of 70 eV). IR spectra were measured on a Bruker Vertex-70v instrument. The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m  $\times$  3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270°C at 8 °C  $\text{min}^{-1}$ , helium as the carrier gas (47 ml  $\text{min}^{-1}$ )].

**Amidation of hydrocarbons (general procedure).** A 10 ml glass tube was charged with hydrocarbon (0.1 g each, *i.e.* **1** 0.92 mmol, **3** 0.83 mmol, **5** 0.76 mmol, and **8-11** 0.54 mmol),  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.027-0.046 mmol) (for **1**: 0.048 mmol; for **3**: 0.046 mmol; for **5**: 0.038 mmol; for **8-11**: 0.027 mmol), RCN (5.4-9 mmol), and water (0.01 g, 0.55 mmol). The tube was sealed, placed into a steel microautoclave, and heated at 145°C for 6-12 hours. After completion of the reaction, the vessel was cooled down to room temperature, the reaction mixture was filtered through a layer of  $\text{Al}_2\text{O}_3$  (elution with  $\text{CHCl}_3$ ), the solvent was evaporated, and the residue was recrystallized from EtOAc.

**2-*exo*-Acetamidobicyclo[3.2.1]octane *exo*-2a and 2-*endo*-acetamidobicyclo[3.2.1]octane *endo*-2a**, a mixture. Yield 0.14 g (90%), white crystals.  $^1\text{H}$  NMR (500.17 MHz,  $\text{CDCl}_3$ ): 1.01-1.09 (m, 4H), 1.10-1.13 (m, 2H), 1.23-1.39 (m, 3H), 1.43-1.52 (m, 7H), 1.59-1.78 (m, 5H), 1.96 (s, 3H,  $\text{CH}_3$ , *exo*-2), 1.97 (s, 3H,  $\text{CH}_3$ , *endo*-2), 2.09-2.29 (m, 3H), 3.80-3.82 (m, 1H,  $\text{CHNHCOCH}_3$ , *endo*-2), 3.96-3.98 (m, 1H,  $\text{CHNHCOCH}_3$ , *exo*-2), 5.65 (s, 1H, NH, *endo*-2),

5.77 (s, 1H, NH, *exo*-2). <sup>13</sup>C NMR (125.78 MHz, CDCl<sub>3</sub>), *exo*-2: 23.79 (C10), 23.83 (C7), 24.50 (C6), 27.02 (C4), 28.85 (C3), 28.93 (C5), 33.48 (C8), 38.93 (C1), 47.32 (C2), 169.32 (C9). *endo*-2: 19.90 (C7), 23.68 (C10), 24.57 (C5), 24.65 (C6), 25.69 (C4), 27.96 (C3), 35.40 (C8), 38.93 (C1), 49.98 (C2), 169.63 (C9). MS (EI, 70eV), *m/z*, 167(49) [M]<sup>+</sup>, 168(6), 152(7), 138(10), 124(28), 108(74), 96(21), 56(29), 43(10).

**6-*exo*-Acetamidotricyclo[3.2.1.0<sup>2,4</sup>]octane *exo*-4a and 6-*endo*-acetamidotricyclo[3.2.1.0<sup>2,4</sup>]octane *endo*-4a**, a mixture. Yield 0.11 g (77%), white crystals, <sup>1</sup>H NMR (500.17 MHz, CDCl<sub>3</sub>): 0.28-0.38 (m, 4H), 0.87-0.98 (m, 5H), 1.07-1.10 (m, 2H), 1.13-1.17 (m, 1H), 1.28-1.30 (m, 1H), 1.47-1.50 (m, 3H), 1.59-1.68 (m, 3H), 1.91 (s, 3H, CH<sub>3</sub>, *endo*-4a), 1.96 (s, 3H, CH<sub>3</sub>, *exo*-4a), 2.04-2.16 (m, 5H), 3.85 (s, 1H, CHNH, *endo*-4a), 3.99 (s, 1H, CHNH, *exo*-4a), 5.70 (br.s, 1H, NH, *endo*-4a), 5.90 (br.s, 1H, NH, *exo*-4a). <sup>13</sup>C NMR (125.78 MHz, CDCl<sub>3</sub>): *exo*-4a: 5.47 (C3), 16.03 (C4), 16.94 (C2), 23.60 (C11), 24.48 (C9), 25.11 (C8), 28.03 (C7), 32.62 (C1), 38.68 (C5), 49.21 (C6), 169.27 (C10); *endo*-4a: 4.07 (C3), 13.12 (C4), 16.68 (C2), 23.60(C11), 26.15 (C9), 29.46 (C8), 30.54 (C7), 33.19 (C1), 39.16 (C5), 51.26 (C6), 169.94 (C10). MS (EI, 70eV), *m/z*, 179(16) [M]<sup>+</sup>, 164(2), 136(15), 120(100), 91(66), 79(53), 60(44), 56(71), 43 (75), 40(2).

**6-*exo*-Propioamidotricyclo[3.2.1.0<sup>2,4</sup>]octane *exo*-4b and 6-*endo*-propioamidotricyclo[3.2.1.0<sup>2,4</sup>]octane *endo*-4b**, a mixture. Yield 0.11 g (71%), white crystals. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 0.26-0.34 (m, 4H), 0.91-1.02 (m, 6H), 1.06 (br.s, 3H, CH<sub>3</sub>, *endo*-4b), 1.08 (br.s, 3H, CH<sub>3</sub>, *exo*-4b), 1.22-1.26 (m, 4H), 1.45-1.66 (m, 7H), 1.98-2.18 (m, 7H), 3.86 (s, 1H, CHNH, *endo*-4b), 3.95 (s, 1H, CHNH, *exo*-4b), 5.91 (s, 1H, NH, *endo*-4b), 6.01 (s, 1H, NH, *exo*-4b). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): *exo*-4b: 5.45 (C3), 10.06 (C12), 16.03 (C4), 18.36 (C2), 24.48 (C11), 25.01 (C9), 27.99 (C7), 29.86 (C8), 33.62 (C1), 38.68 (C5), 48.99 (C6), 173.10 (C10). *endo*-4b: 4.06 (C3), 13.10 (C12), 15.86 (C4), 16.68 (C2), 23.40 (C11), 26.05 (C9), 27.62 (C7), 29.61 (C8), 33.44 (C1), 37.80 (C5), 51.04 (C6), 173.15 (C10). MS (EI, 70eV), *m/z*, 193(16) [M]<sup>+</sup>, 178(1), 164(7), 136(17), 120(100), 105(37), 91 (65), 74(68), 57(75), 56(87), 41(26).

**9-Acetamidotetracyclo[6.1.1.0<sup>3,8</sup>.0<sup>5,7</sup>]decane 6a**. Yield 0.10 g (71%), white crystals, m.p. 117-118°C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 0.22-0.23 (m, 2H), 0.93-0.96 (m, 2H), 1.06-1.28 (m, 4H), 1.43-1.55 (m, 1H), 1.86 (s, 3H), 1.98-2.03 (m, 3H), 3.33 (d, 1H, *J* 6.4 Hz), 6.28 (s, NH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): 9.72 (C3), 21.45 (C12), 22.98 (C4), 23.11 (C2), 34.05 (C10), 35.70 (C8), 38.75 (C7), 38.93 (C6), 40.72 (C5), 50.71 (C1), 60.01 (C9), 169.40 (C11). MS (EI, 70eV), *m/z*, 191(15) [M]<sup>+</sup>, 176(1), 148(13), 133(11), 132(100), 58(5), 43(55). IR (Nujol):  $\nu_{\max}$  3262, 1633, 1556 cm<sup>-1</sup>. Found (%): C 75.43; H 8.92; N 7.34. C<sub>12</sub>H<sub>17</sub>NO. Calculated (%): C 75.35; H 8.96; N 7.32

**9-Propioamidotetracyclo[6.1.1.0<sup>3,8</sup>.0<sup>5,7</sup>]decane 6b**. Yield 0.09g (60%), white crystals, m.p. 129-131°C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 0.26-0.32 (m, 1H), 1.00-1.03 (m, 3H),

1.08-1.12 (m, 3H), 1.27-1.62 (m, 4H), 1.82-2.19 (m, 6H), 3.41 (d, 1H, *J* 8 Hz), 5.68 (s, 1H, NH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): 9.86 (C3), 10.00 (C13), 21.59 (C4), 23.15 (C2), 29.77 (C12), 34.27 (C10), 35.87 (C8), 38.89 (C7), 39.11 (C6), 40.90 (C5), 51.36 (C1), 60.00 (C9), 173.01 (C11). MS (EI, 70eV), *m/z*, 205(25) [M]<sup>+</sup>, 190(1), 176 (5), 164(4), 149(15), 132(100), 70(45), 57(54). IR (Nujol):  $\nu_{\max}$  3296, 1636, 1540 cm<sup>-1</sup>. Found (%): C 74.52; H 9.89; N 7.30. C<sub>12</sub>H<sub>19</sub>NO. Calculated (%): C 74.57; H 9.91; N 7.28

**Tetracyclo[6.1.1.0<sup>3,8</sup>.0<sup>5,7</sup>]decan-9-ol 7.** Yield 0.04 g (40%), white crystals, m.p. 118-120 °C. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>): 0.84-0.87 (m, 2H), 1.04-1.07 (m, 2H), 1.19-1.26 (m, 2H), 1.54-1.74 (m, 2H), 1.88-1.92 (m, 2H), 2.01-2.06 (m, 2H), 2.34-2.38 (m, 1H, OH), 3.43 (s, 1H, CHOH). <sup>13</sup>C NMR (100.62 MHz, CDCl<sub>3</sub>): 9.46 (C3), 20.21 (C4), 23.19 (C2), 33.41 (C10), 34.22 (C7), 38.43 (C8), 38.72 (C6), 43.00 (C5), 52.59 (C1), 81.38 (C9). MS (EI, 70eV), *m/z*, 150(11) [M]<sup>+</sup>, 132(24), 117(80), 91 (100), 79(77), 66(20), 54(40), 41(27). IR (Nujol):  $\nu_{\max}$  3350, 1343, 1110 cm<sup>-1</sup>. Found (%): C 79.93; H 9.42. C<sub>10</sub>H<sub>14</sub>O. Calculated (%): C 79.96; H 9.39.

**4-*exo*-Acetamidopentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 12.** Yield 0.1 g (80%), white crystals, m.p. 164-166°C. <sup>1</sup>H NMR (500.17 MHz, CDCl<sub>3</sub>): 0.84-0.87 (m, 2H), 0.97-1.09 (m, 2H), 1.32-1.34 (m, 3H), 1.48-1.50 (m, 2H), 1.58-1.59 (m, 1H), 1.74-1.79 (m, 2H), 1.86-1.88 (m, 2H), 1.92 (s, 3H), 1.98-2.06 (m, 3H), 2.47 (s, 1H), 3.33 (d, 1H, *J* 10.0 Hz), 5.71 (s, 1H, NH). <sup>13</sup>C NMR (125.78 MHz, CDCl<sub>3</sub>): 23.57 (C16), 29.29 (C11, 12), 34.95 (C14), 37.13 (C6), 38.47(C13), 40.37 (C5), 41.90 (C8), 41.94 (C10), 43.77 (C1), 47.25 (C9), 55.52 (C2), 56.21 (C7), 57.78 (C3), 63.32 (C4), 169.07 (C15). MS (EI, 70eV), *m/z*, 245(86) [M]<sup>+</sup>, 246(15), 230(64), 202(44), 186(65), 91(66), 56(56), 43(100). IR (Nujol):  $\nu_{\max}$  3251, 1630, 1558 cm<sup>-1</sup>. Found (%): C 78.35; H 9.47; N 5.73. C<sub>16</sub>H<sub>23</sub>NO. Calculated (%): C 78.38; H 9.45; N 5.71.

**4-*exo*-Acetamidopentacyclo[8.2.1.1<sup>5,8</sup>.0<sup>2,9</sup>.0<sup>3,7</sup>]tetradecane 13.** Yield 0.12 g (94%), white crystals, m.p. 142-144°C. <sup>1</sup>H NMR (500.17 MHz, CDCl<sub>3</sub>): 0.85-0.87 (m, 2H), 1.25-1.46 (m, 6H), 1.59 (d, 1H, *J* 10.0 Hz), 1.65 (d, 1H, *J* 5.0 Hz), 1.78-1.83 (m, 2H), 1.93 (s, 3H), 1.95-1.96 (m, 1H), 1.99-2.00 (m, 1H), 2.14 (d, 2H, *J* 5.0 Hz), 2.20 (s, 1H), 2.43-2.47 (m, 1H), 3.26 (d, 1H, *J* 5.0 Hz), 5.62-5.63 (m, 1H, NH). <sup>13</sup>C NMR (125.78 MHz, CDCl<sub>3</sub>): 23.59 (C16), 24.09 (C12), 24.11 (C11), 37.75 (C14), 38.57 (C6), 39.11(C5), 41.39 (C1), 41.93 (C8), 41.99 (C10), 42.41 (C13), 47.24 (C9), 51.66 (C2), 52.33 (C7), 54.53 (C3), 63.24 (C4), 169.05 (C15). MS (EI, 70eV), *m/z*, 245(42) [M]<sup>+</sup>, 246(15), 230(57), 217(50), 202 (32), 186 (49), 91 (52), 56(57), 43 (100). IR (Nujol):  $\nu_{\max}$  3244, 1623, 1552 cm<sup>-1</sup>. Found (%): C 78.40; H 9.46; N 5.69. C<sub>16</sub>H<sub>23</sub>NO. Calculated (%): C 78.38; H 9.45; N 5.71.

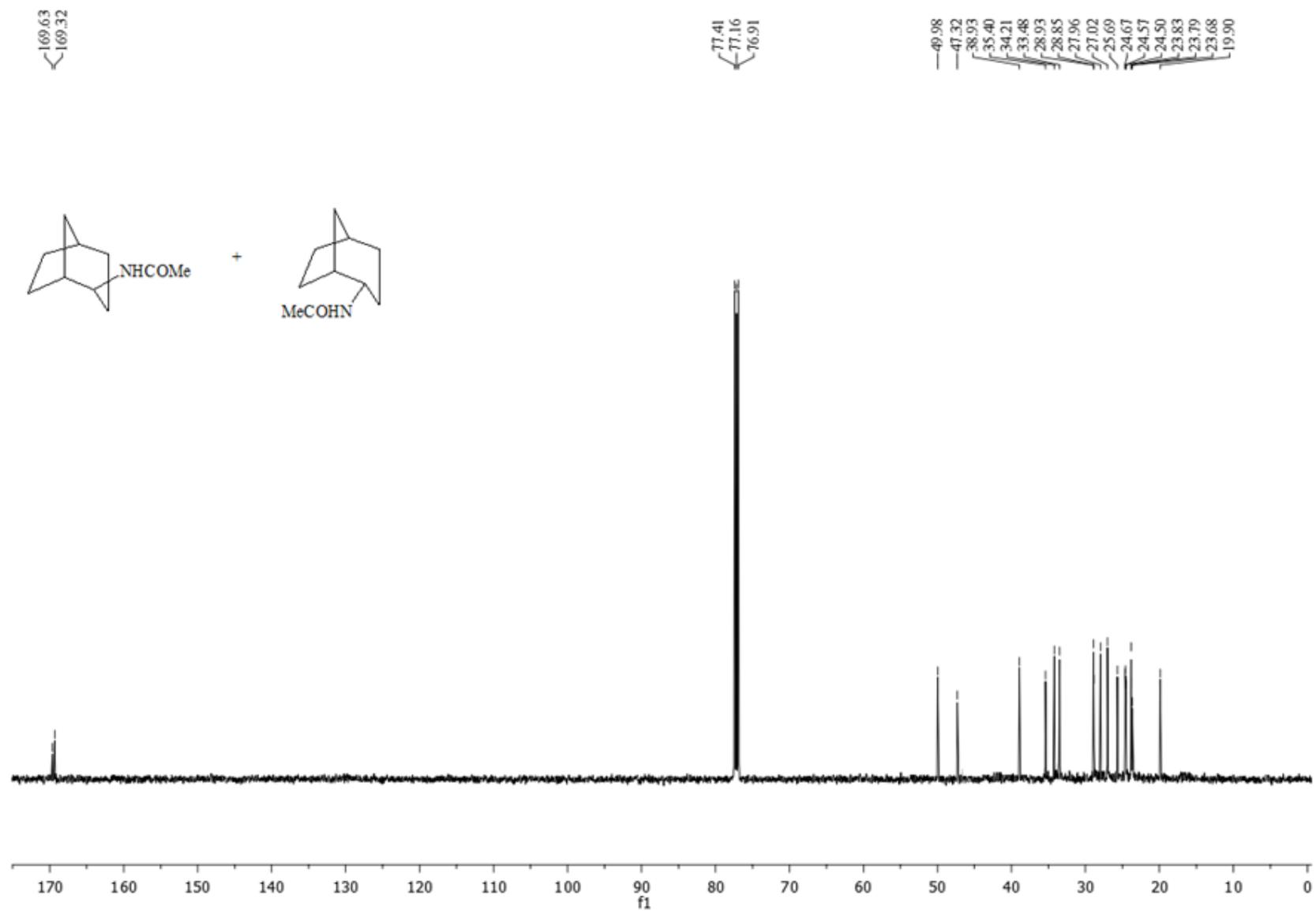
## X-ray crystal structure analysis for compound 12

**Table S1** Bond lengths for 12

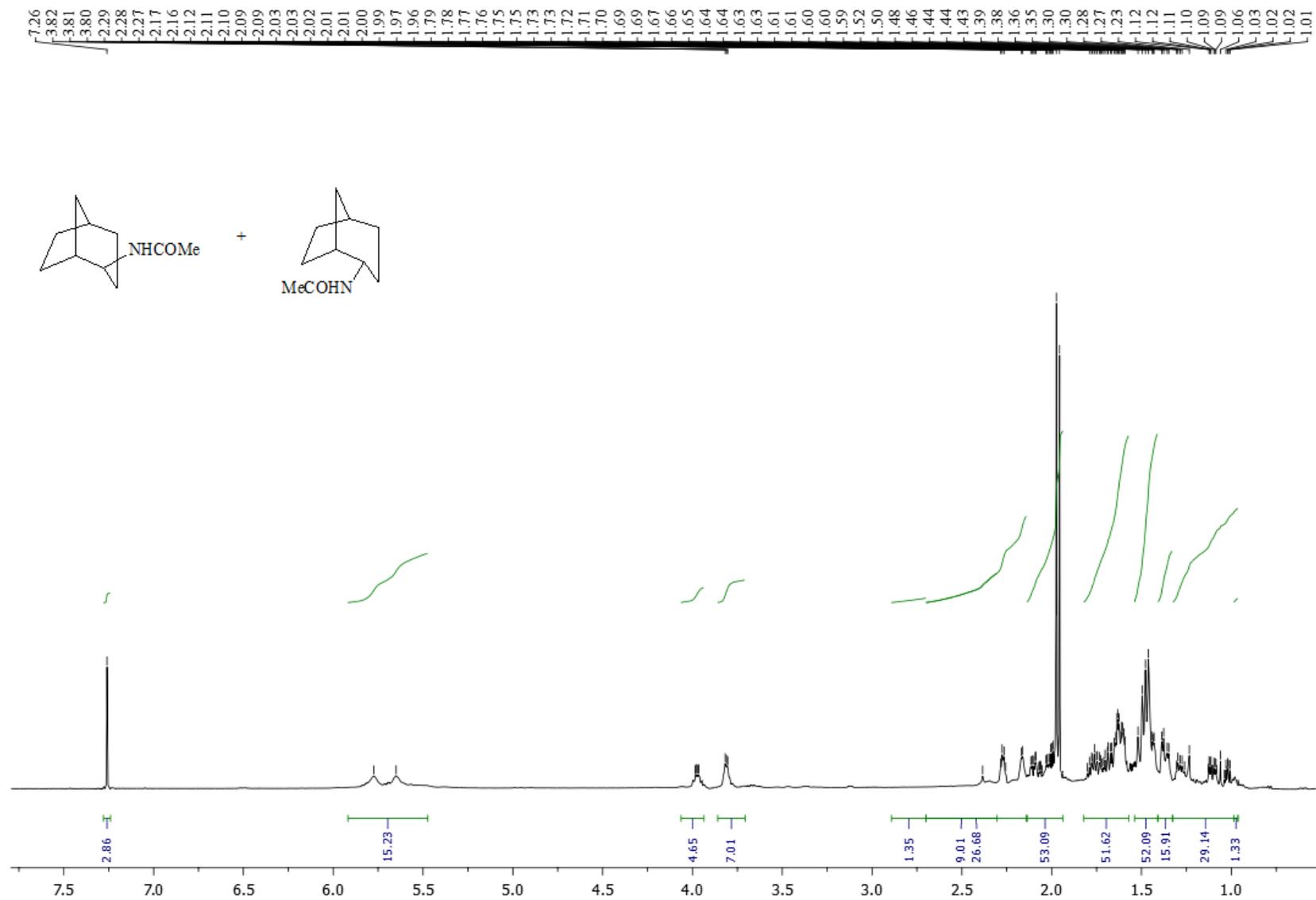
<b>Bond</b>	<b>Length (Å)</b>	<b>Bond</b>	<b>Length (Å)</b>
C <sup>1</sup> -C <sup>12</sup>	1.513(5)	C <sup>1'</sup> -C <sup>12'</sup>	1.550(5)
C <sup>1</sup> -C <sup>13</sup>	1.513(4)	C <sup>1'</sup> -C <sup>13'</sup>	1.514(5)
C <sup>2</sup> -C <sup>1</sup>	1.524(4)	C <sup>2'</sup> -C <sup>1'</sup>	1.507(5)
C <sup>2</sup> -C <sup>9</sup>	1.562(3)	C <sup>2'</sup> -C <sup>9'</sup>	1.573(5)
C <sup>3</sup> -C <sup>2</sup>	1.521(4)	C <sup>3'</sup> -C <sup>2'</sup>	1.541(4)
C <sup>3</sup> -C <sup>7</sup>	1.528(4)	C <sup>3'</sup> -C <sup>7'</sup>	1.541(4)
C <sup>3</sup> -C <sup>4</sup>	1.555(4)	C <sup>3'</sup> -C <sup>4'</sup>	1.543(4)
C <sup>4</sup> -C <sup>5</sup>	1.546(4)	C <sup>4'</sup> -C <sup>5'</sup>	1.548(5)
C <sup>5</sup> -C <sup>6</sup>	1.503(5)	C <sup>5'</sup> -C <sup>6'</sup>	1.515(6)
C <sup>5</sup> -C <sup>14</sup>	1.505(5)	C <sup>5'</sup> -C <sup>14'</sup>	1.487(5)
C <sup>7</sup> -C <sup>6</sup>	1.531(5)	C <sup>7'</sup> -C <sup>6'</sup>	1.517(5)
C <sup>8</sup> -C <sup>7</sup>	1.533(4)	C <sup>7'</sup> -C <sup>8'</sup>	1.533(5)
C <sup>8</sup> -C <sup>9</sup>	1.546(4)	C <sup>9'</sup> -C <sup>8'</sup>	1.522(5)
C <sup>8</sup> -C <sup>14</sup>	1.551(5)	C <sup>8'</sup> -C <sup>14'</sup>	1.544(6)
C <sup>9</sup> -C <sup>10</sup>	1.520(4)	C <sup>9'</sup> -C <sup>10'</sup>	1.518(5)
C <sup>10</sup> -C <sup>11</sup>	1.529(5)	C <sup>10'</sup> -C <sup>11'</sup>	1.504(5)
C <sup>12</sup> -C <sup>11</sup>	1.538(5)	C <sup>12'</sup> -C <sup>11'</sup>	1.514(6)
C <sup>13</sup> -C <sup>10</sup>	1.522(5)	C <sup>10'</sup> -C <sup>13'</sup>	1.498(5)
C <sup>15</sup> -C <sup>16</sup>	1.483(4)	C <sup>15'</sup> -C <sup>16'</sup>	1.489(4)
N <sup>1</sup> -C <sup>4</sup>	1.446(4)	N <sup>1'</sup> -C <sup>4'</sup>	1.447(4)
N <sup>1</sup> -C <sup>15</sup>	1.326(3)	N <sup>1'</sup> -C <sup>15'</sup>	1.321(4)
O <sup>1</sup> -C <sup>15</sup>	1.234(3)	O <sup>1'</sup> -C <sup>15'</sup>	1.234(3)

**Table S2** Bond angles for **12**

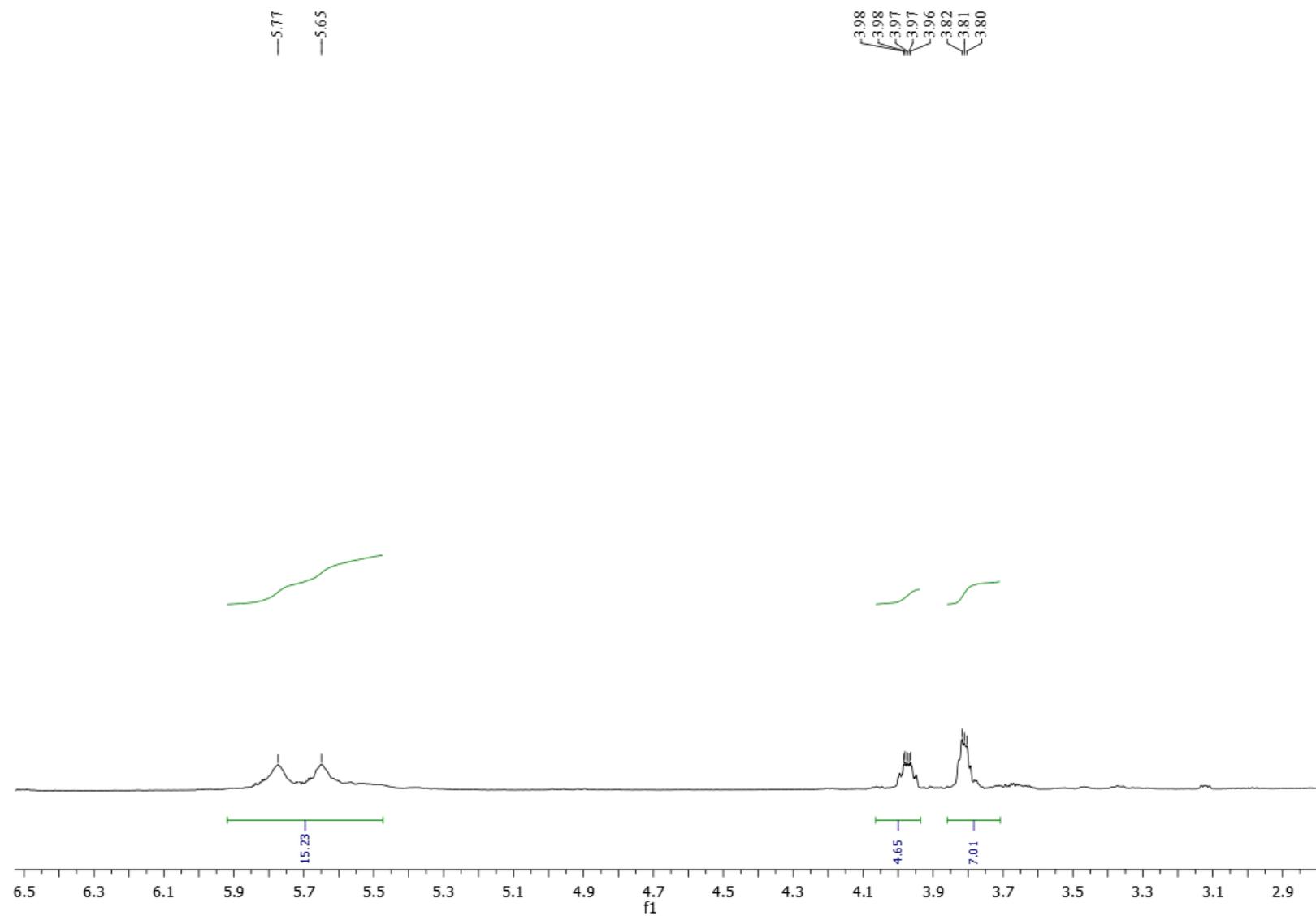
Angle (°)	Angle (°)	Angle (°)	Angle (°)
C <sup>15</sup> -N <sup>1</sup> -C <sup>4</sup>	122.0(3)	C <sup>15'</sup> -N <sup>1'</sup> -C <sup>4'</sup>	122.9(2)
C <sup>2</sup> -C <sup>3</sup> -C <sup>4</sup>	113.4(2)	N <sup>1'</sup> -C <sup>15'</sup> -C <sup>16'</sup>	116.3(2)
C <sup>2</sup> -C <sup>3</sup> -C <sup>7</sup>	107.0(2)	O <sup>1'</sup> -C <sup>15'</sup> -N <sup>1'</sup>	121.8(3)
C <sup>7</sup> -C <sup>3</sup> -C <sup>4</sup>	102.5(2)	O <sup>1'</sup> -C <sup>15'</sup> -C <sup>16'</sup>	121.9(3)
N <sup>1</sup> -C <sup>4</sup> -C <sup>3</sup>	113.9(2)	C <sup>2'</sup> -C <sup>3'</sup> -C <sup>4'</sup>	111.6(2)
N <sup>1</sup> -C <sup>4</sup> -C <sup>5</sup>	109.7(2)	C <sup>7'</sup> -C <sup>3'</sup> -C <sup>4'</sup>	102.4(3)
C <sup>5</sup> -C <sup>4</sup> -C <sup>3</sup>	103.1(2)	C <sup>7'</sup> -C <sup>3'</sup> -C <sup>2'</sup>	107.1(3)
C <sup>3</sup> -C <sup>2</sup> -C <sup>9</sup>	104.7(2)	N <sup>1'</sup> -C <sup>4'</sup> -C <sup>3'</sup>	113.0(2)
C <sup>3</sup> -C <sup>2</sup> -C <sup>1</sup>	118.7(2)	N <sup>1'</sup> -C <sup>4'</sup> -C <sup>5'</sup>	110.0(2)
C <sup>1</sup> -C <sup>2</sup> -C <sup>9</sup>	102.6(2)	C <sup>3'</sup> -C <sup>4'</sup> -C <sup>5'</sup>	102.8(3)
C <sup>9</sup> -C <sup>8</sup> -C <sup>14</sup>	111.9(3)	C <sup>3'</sup> -C <sup>2'</sup> -C <sup>9'</sup>	104.9(2)
C <sup>7</sup> -C <sup>8</sup> -C <sup>9</sup>	106.8(2)	C <sup>1'</sup> -C <sup>2'</sup> -C <sup>3'</sup>	116.1(3)
C <sup>7</sup> -C <sup>8</sup> -C <sup>14</sup>	101.3(3)	C <sup>1'</sup> -C <sup>2'</sup> -C <sup>9'</sup>	102.4(3)
C <sup>8</sup> -C <sup>9</sup> -C <sup>2</sup>	104.7(2)	C <sup>10'</sup> -C <sup>9'</sup> -C <sup>2'</sup>	102.3(3)
C <sup>10</sup> -C <sup>9</sup> -C <sup>2</sup>	102.5(2)	C <sup>10'</sup> -C <sup>9'</sup> -C <sup>8'</sup>	118.2(3)
C <sup>10</sup> -C <sup>9</sup> -C <sup>8</sup>	117.0(3)	C <sup>8'</sup> -C <sup>9'</sup> -C <sup>2'</sup>	104.5(2)
N <sup>1</sup> -C <sup>15</sup> -C <sup>16</sup>	116.5(3)	C <sup>6'</sup> -C <sup>5'</sup> -C <sup>4'</sup>	99.3(3)
O <sup>1</sup> -C <sup>13</sup> -N <sup>1</sup>	121.2(3)	C <sup>14'</sup> -C <sup>5'</sup> -C <sup>4'</sup>	107.9(3)
O <sup>1</sup> -C <sup>15</sup> -C <sup>16</sup>	122.3(2)	C <sup>14'</sup> -C <sup>5'</sup> -C <sup>6'</sup>	103.2(4)
C <sup>3</sup> -C <sup>7</sup> -C <sup>8</sup>	99.8(2)	C <sup>6'</sup> -C <sup>7'</sup> -C <sup>3'</sup>	103.6(3)
C <sup>3</sup> -C <sup>7</sup> -C <sup>6</sup>	103.0(2)	C <sup>6'</sup> -C <sup>7'</sup> -C <sup>8'</sup>	104.7(3)
C <sup>6</sup> -C <sup>7</sup> -C <sup>8</sup>	105.1(3)	C <sup>8'</sup> -C <sup>7'</sup> -C <sup>3'</sup>	100.0(2)
C <sup>13</sup> -C <sup>1</sup> -C <sup>2</sup>	103.8(2)	C <sup>5'</sup> -C <sup>6'</sup> -C <sup>7'</sup>	99.4(3)
C <sup>13</sup> -C <sup>1</sup> -C <sup>12</sup>	100.5(3)	C <sup>2'</sup> -C <sup>1'</sup> -C <sup>13'</sup>	103.4(3)
C <sup>12</sup> -C <sup>1</sup> -C <sup>2</sup>	107.7(3)	C <sup>2'</sup> -C <sup>1'</sup> -C <sup>12'</sup>	108.0(3)
C <sup>1</sup> -C <sup>13</sup> -C <sup>10</sup>	94.3(3)	C <sup>13'</sup> -C <sup>1'</sup> -C <sup>12'</sup>	99.0(3)
C <sup>9</sup> -C <sup>10</sup> -C <sup>13</sup>	103.3(2)	C <sup>13'</sup> -C <sup>10'</sup> -C <sup>9'</sup>	104.5(3)
C <sup>9</sup> -C <sup>10</sup> -C <sup>11</sup>	107.7(3)	C <sup>13'</sup> -C <sup>10'</sup> -C <sup>11'</sup>	99.07(3)
C <sup>13</sup> -C <sup>10</sup> -C <sup>11</sup>	100.7(3)	C <sup>11'</sup> -C <sup>10'</sup> -C <sup>9'</sup>	107.8(3)
C <sup>6</sup> -C <sup>5</sup> -C <sup>4</sup>	100.1(2)	C <sup>9'</sup> -C <sup>8'</sup> -C <sup>7'</sup>	107.1(3)
C <sup>6</sup> -C <sup>5</sup> -C <sup>14</sup>	102.4(3)	C <sup>9'</sup> -C <sup>8'</sup> -C <sup>14'</sup>	111.2(3)
C <sup>14</sup> -C <sup>5</sup> -C <sup>4</sup>	107.5(3)	C <sup>7'</sup> -C <sup>8'</sup> -C <sup>14'</sup>	101.1(3)
C <sup>5</sup> -C <sup>6</sup> -C <sup>7</sup>	95.2(3)	C <sup>10'</sup> -C <sup>13'</sup> -C <sup>1'</sup>	95.1(3)
C <sup>1</sup> -C <sup>12</sup> -C <sup>11</sup>	103.3(3)	C <sup>5'</sup> -C <sup>14'</sup> -C <sup>8'</sup>	105.2(3)
C <sup>10</sup> -C <sup>11</sup> -C <sup>12</sup>	102.7(3)	C <sup>11'</sup> -C <sup>12'</sup> -C <sup>1'</sup>	102.9(3)
C <sup>5</sup> -C <sup>14</sup> -C <sup>8</sup>	104.7(3)	C <sup>10'</sup> -C <sup>11'</sup> -C <sup>12'</sup>	103.9(3)



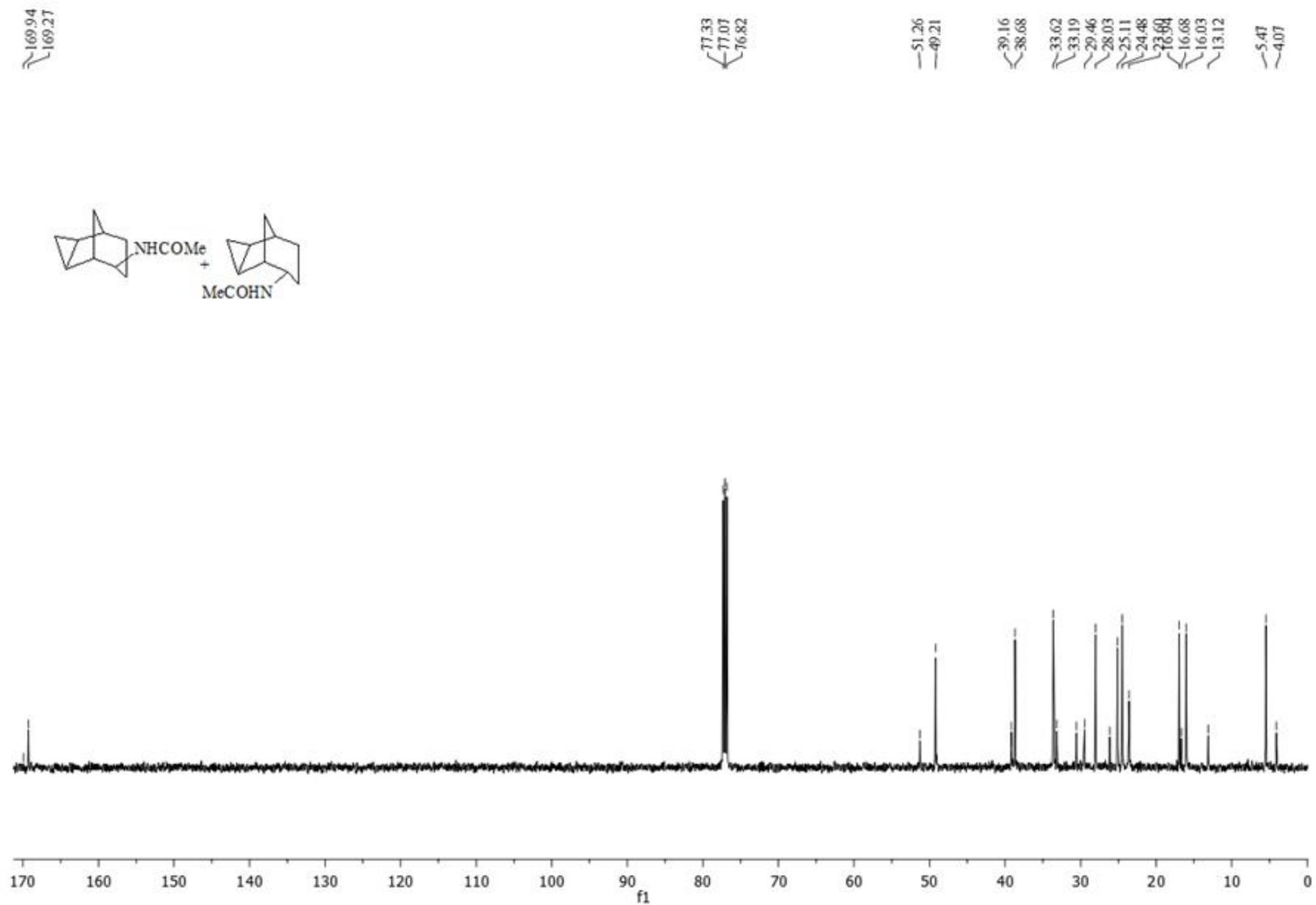
**Figure S1**  $^{13}\text{C}$  NMR spectrum for compounds *exo-2* and *endo-2* in  $\text{CDCl}_3$



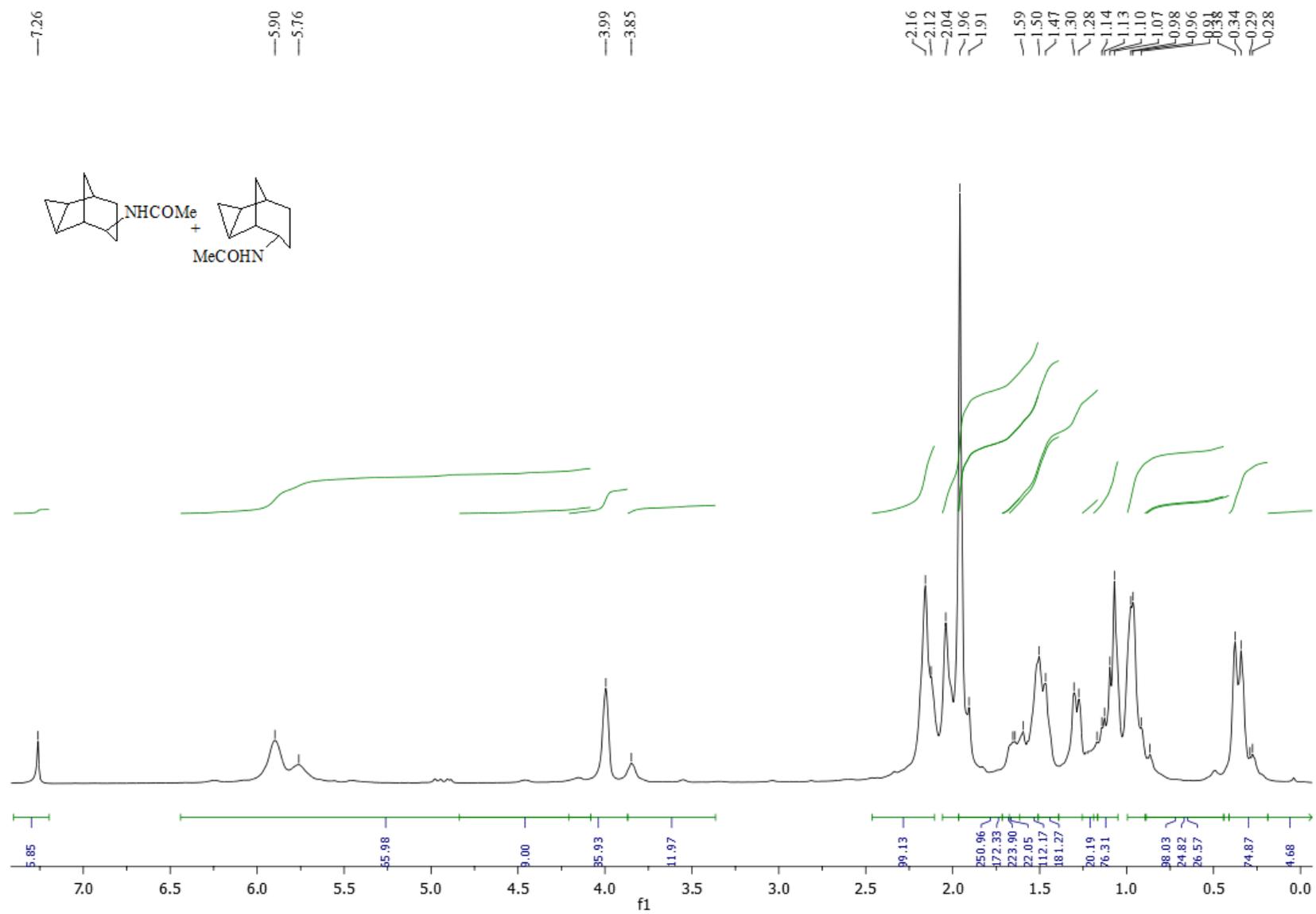
**Figure S2** <sup>1</sup>H NMR spectrum for compounds *exo-2* and *endo-2* in CDCl<sub>3</sub>



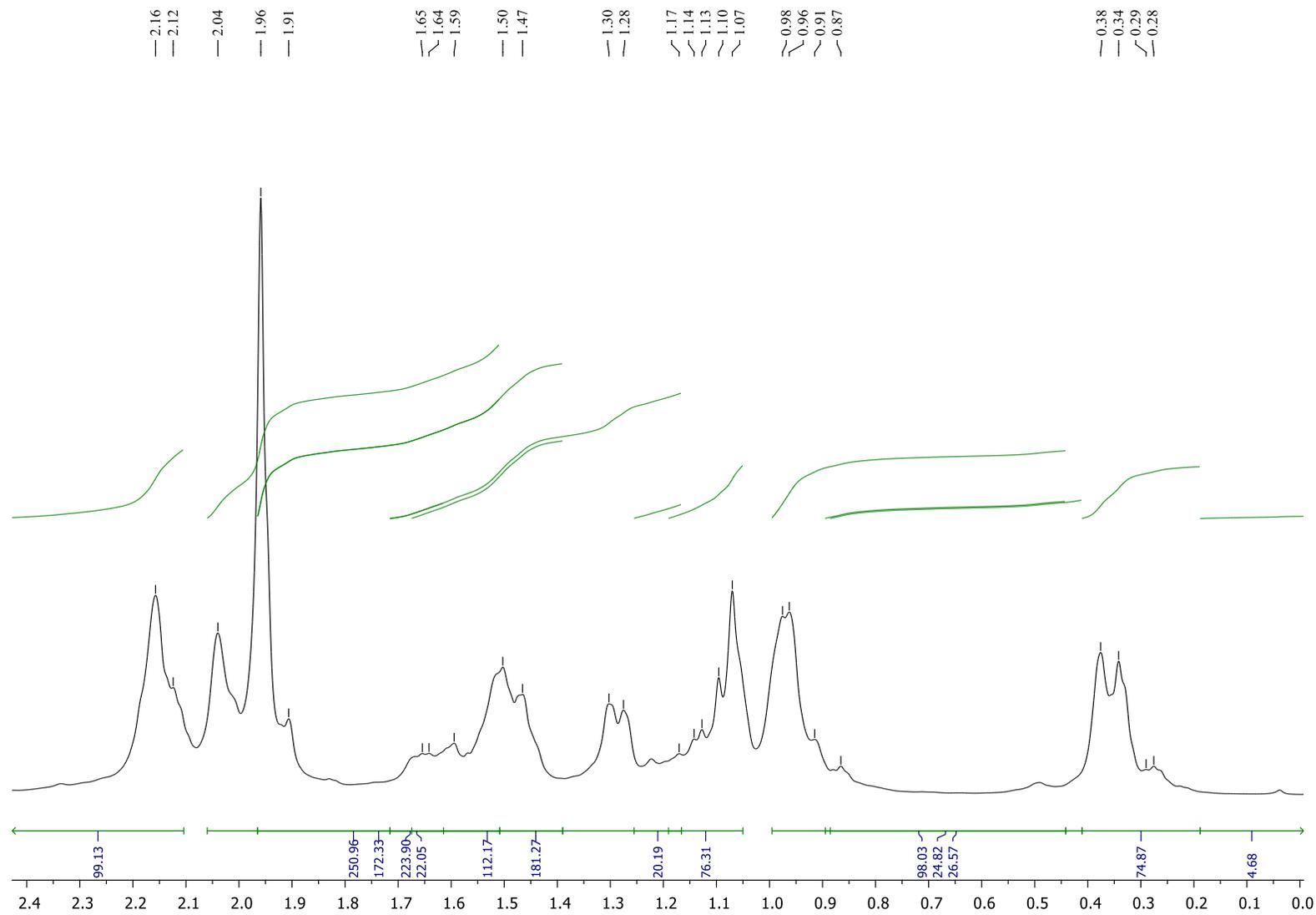
**Figure S3**  $^1\text{H}$  NMR spectrum (fragment) for compounds *exo-2* and *endo-2* in  $\text{CDCl}_3$



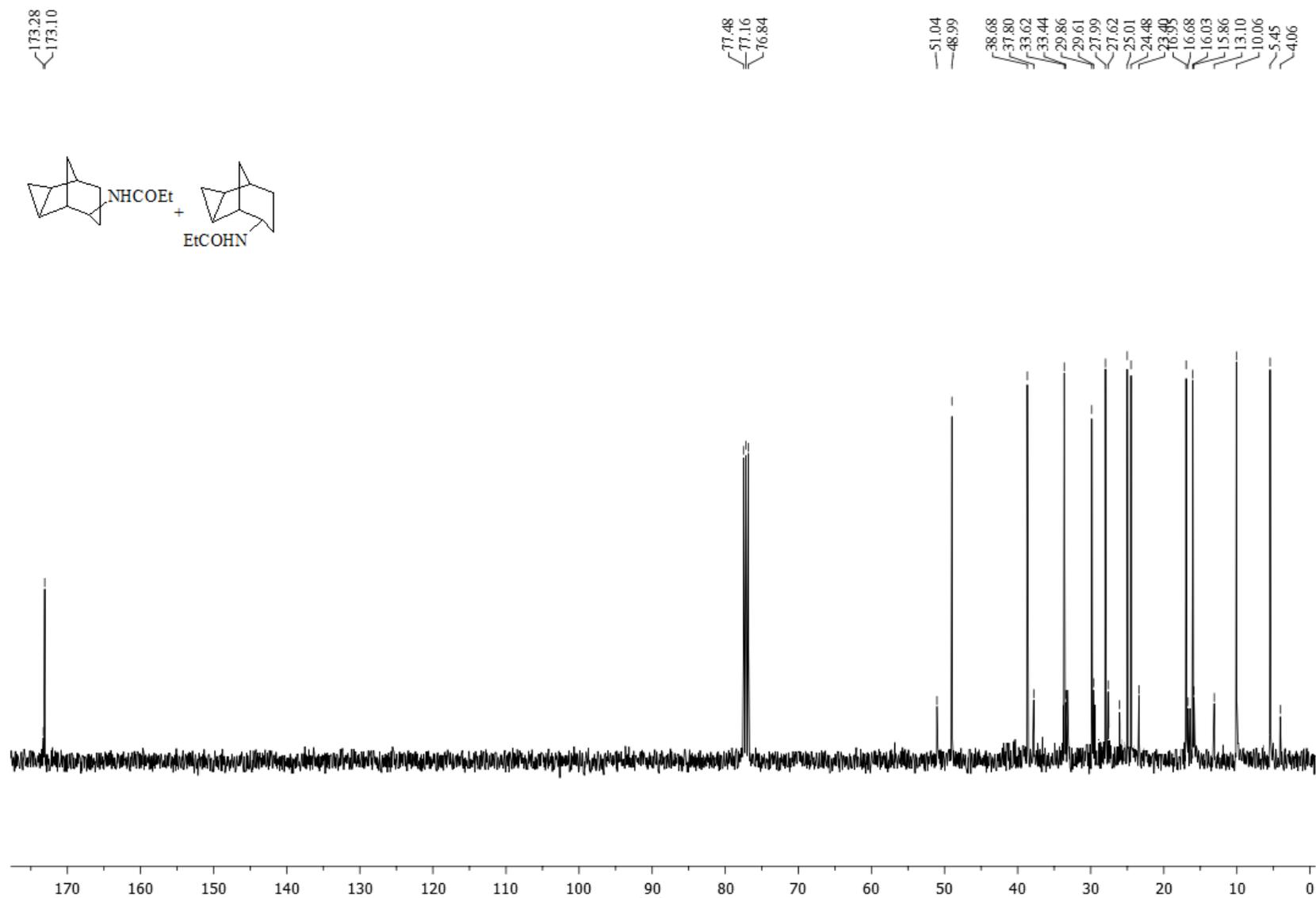
**Figure S4**  $^{13}\text{C}$  NMR spectrum for compounds *exo*-**4a** and *endo*-**4a** in  $\text{CDCl}_3$



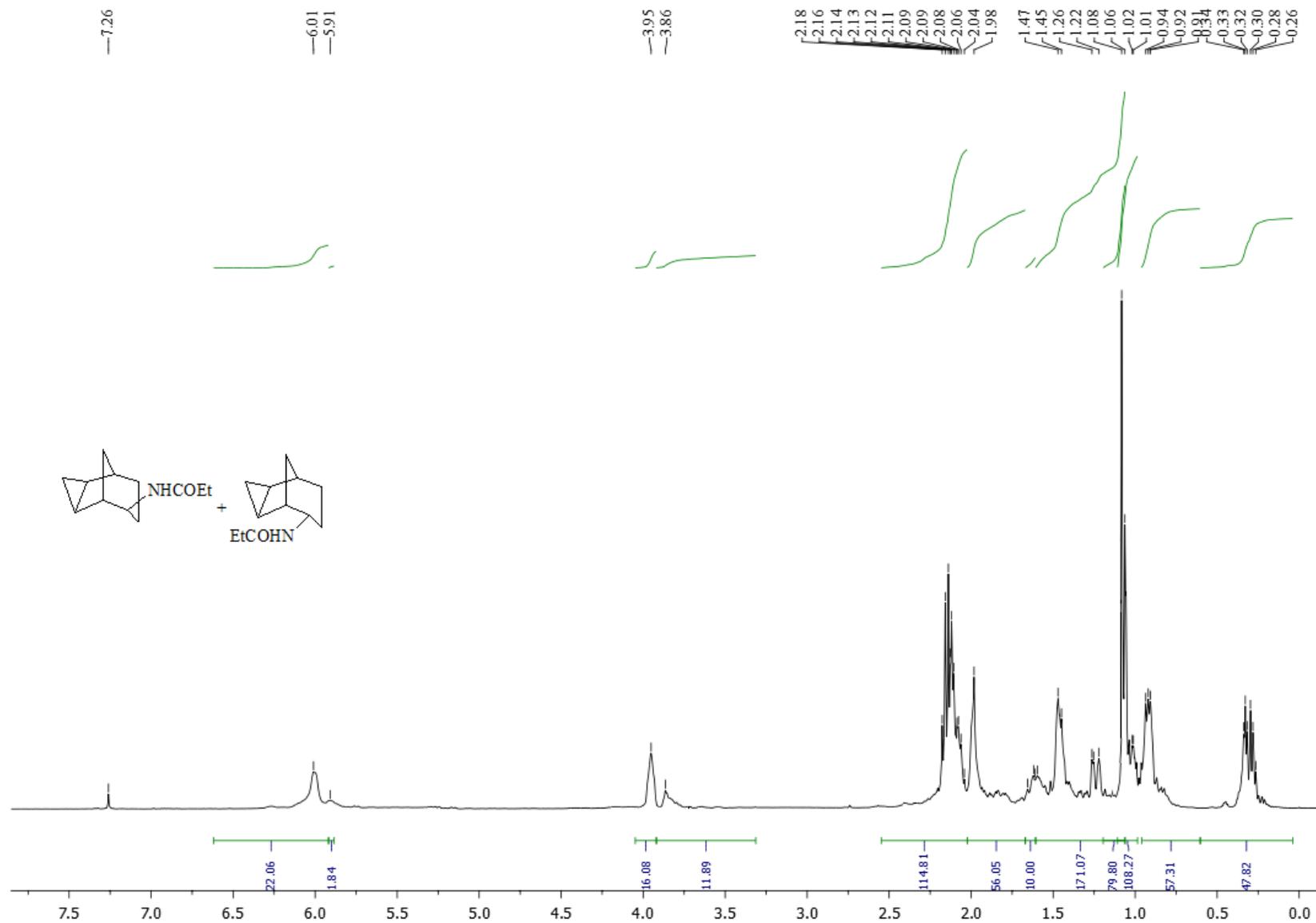
**Figure S5** <sup>1</sup>H NMR spectrum for compounds *exo-4a* and *endo-4a* in CDCl<sub>3</sub>



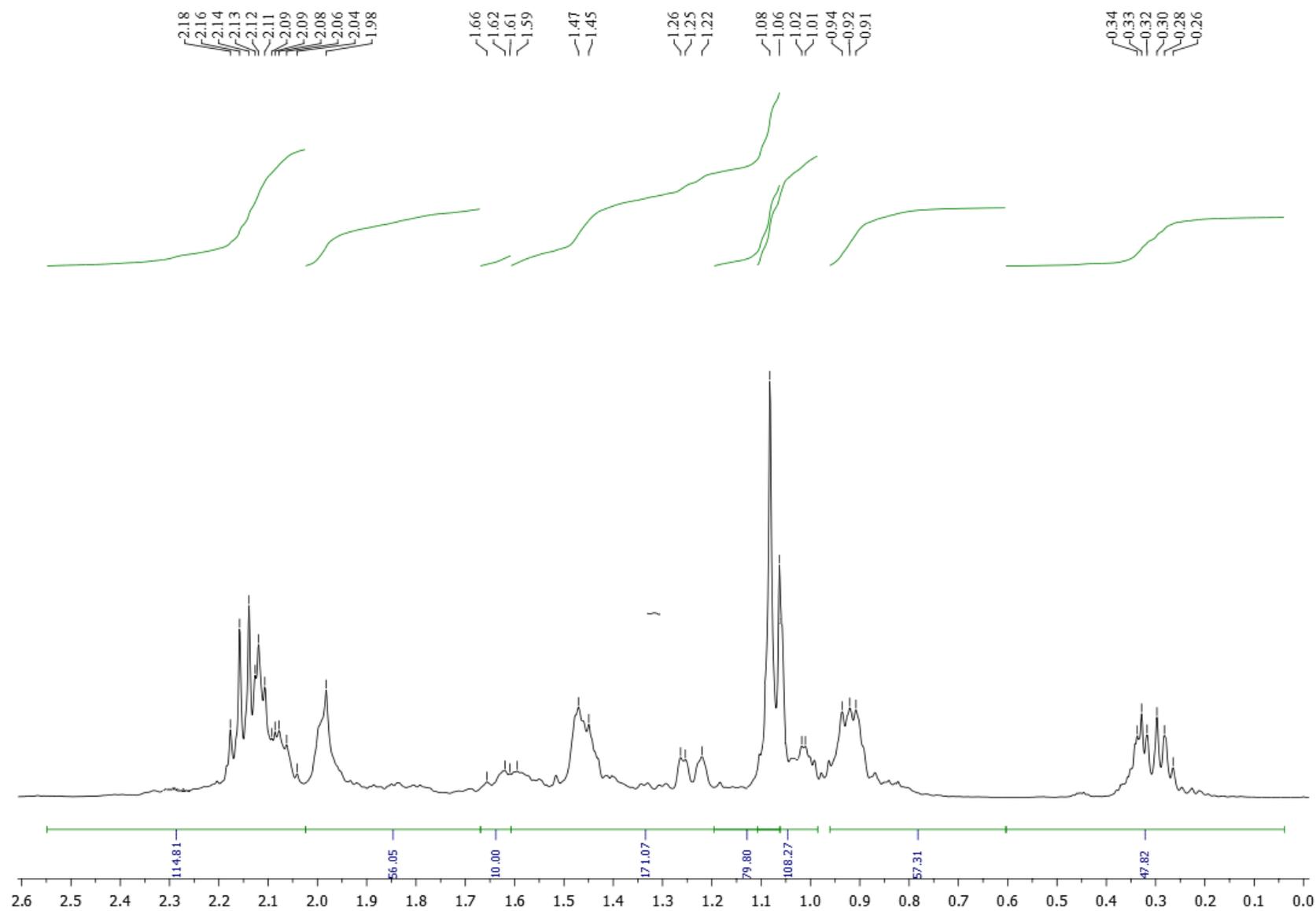
**Figure S6**  $^1\text{H}$  NMR spectrum (fragment) for compounds *exo-4a* and *endo-4a* in  $\text{CDCl}_3$



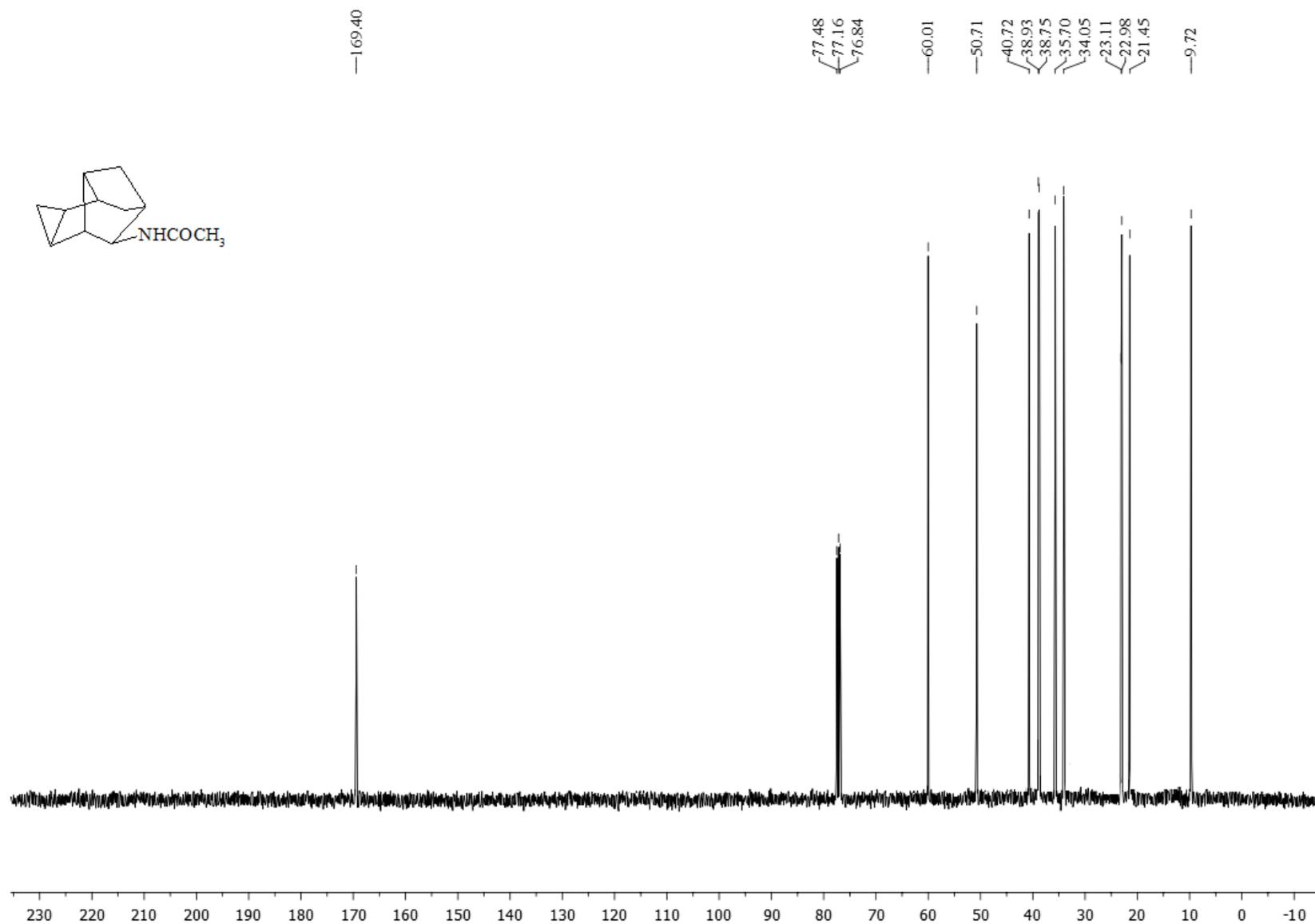
**Figure S7**  $^{13}\text{C}$  NMR spectrum for compounds *exo-4b* and *endo-4b* in  $\text{CDCl}_3$



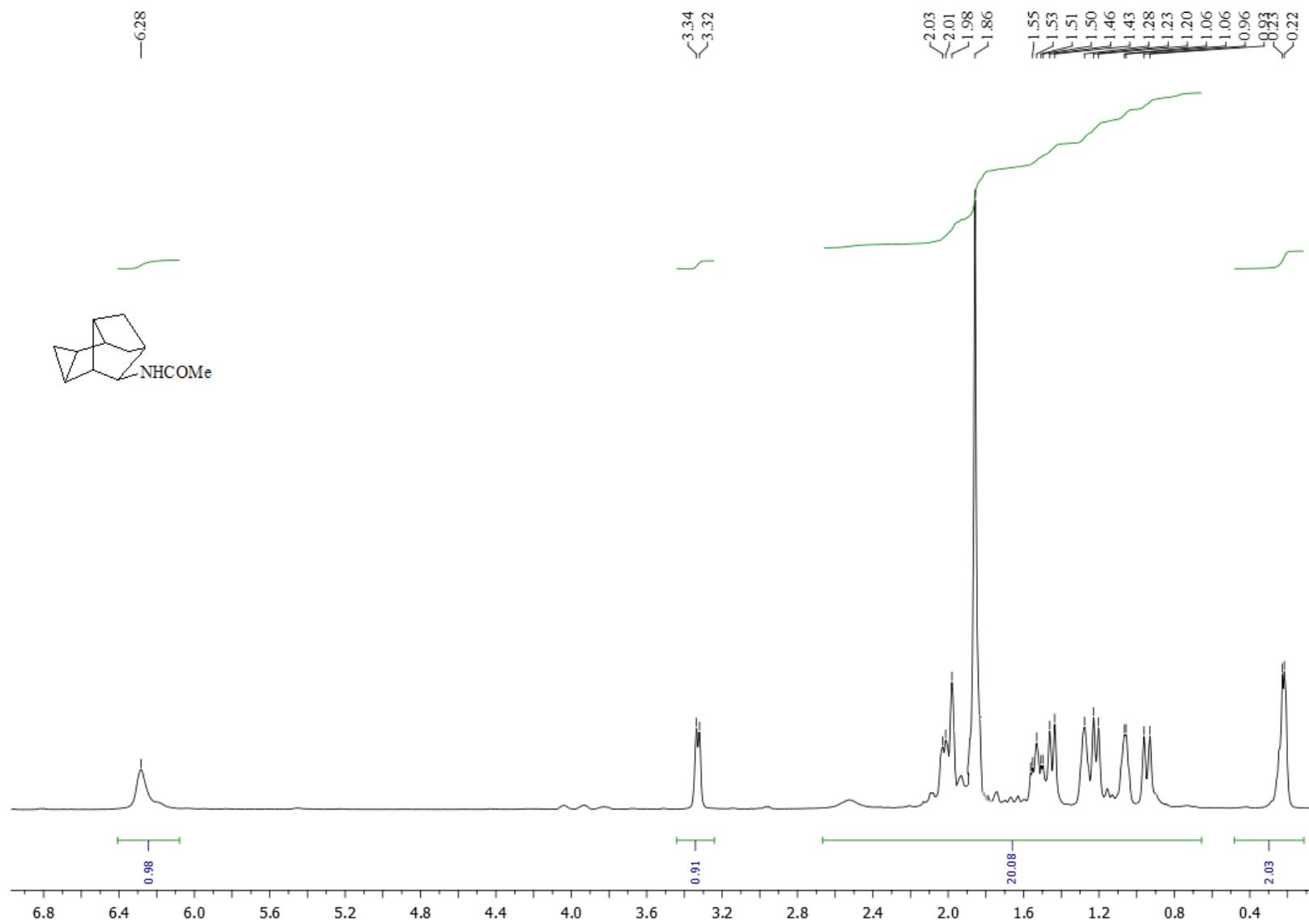
**Figure S8**  $^1\text{H}$  NMR spectrum for compounds *exo-4b* and *endo-4b* in  $\text{CDCl}_3$



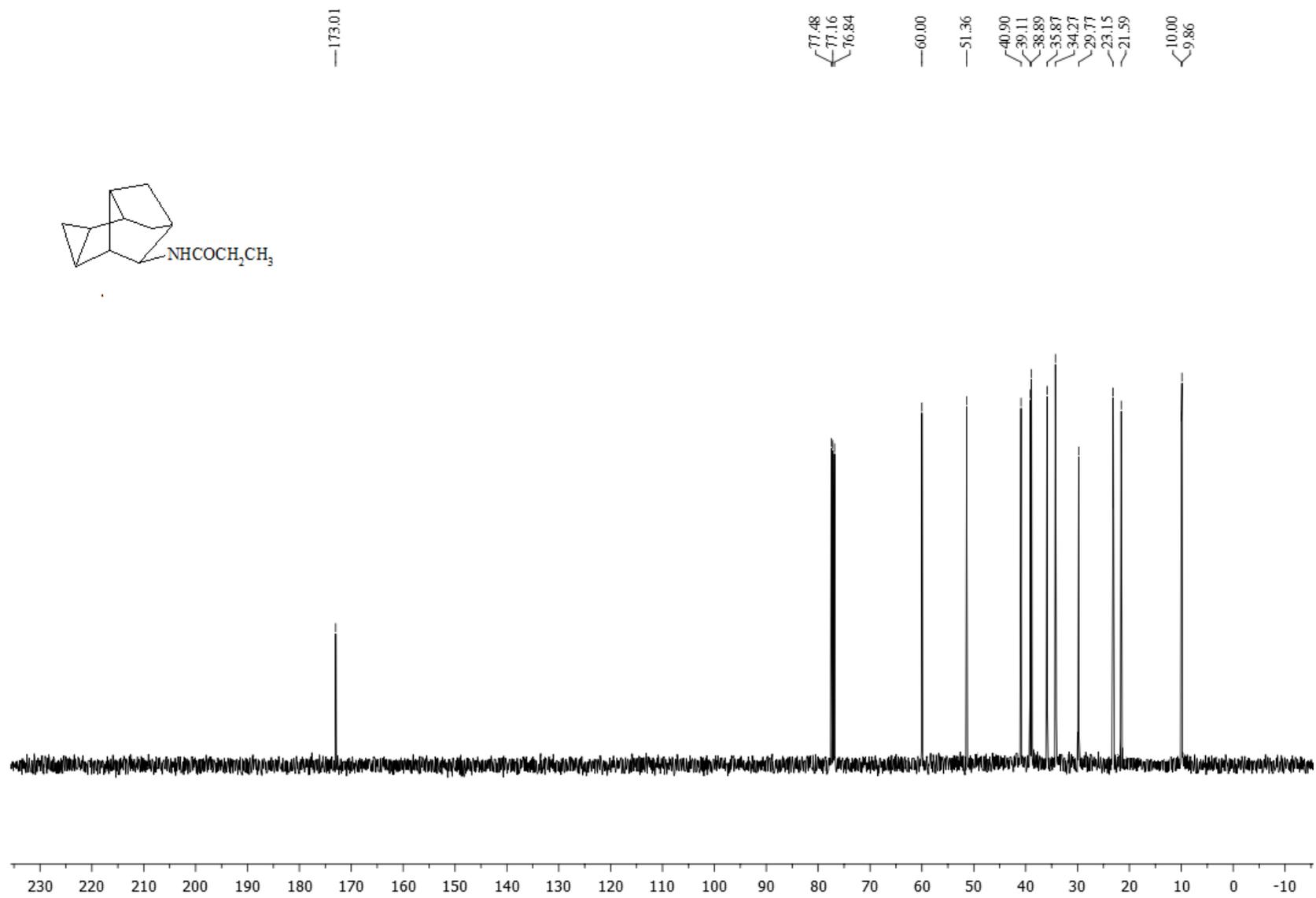
**Figure S9**  $^1\text{H}$  NMR spectrum (fragment) for compounds *exo-4b* and *endo-4b* in  $\text{CDCl}_3$



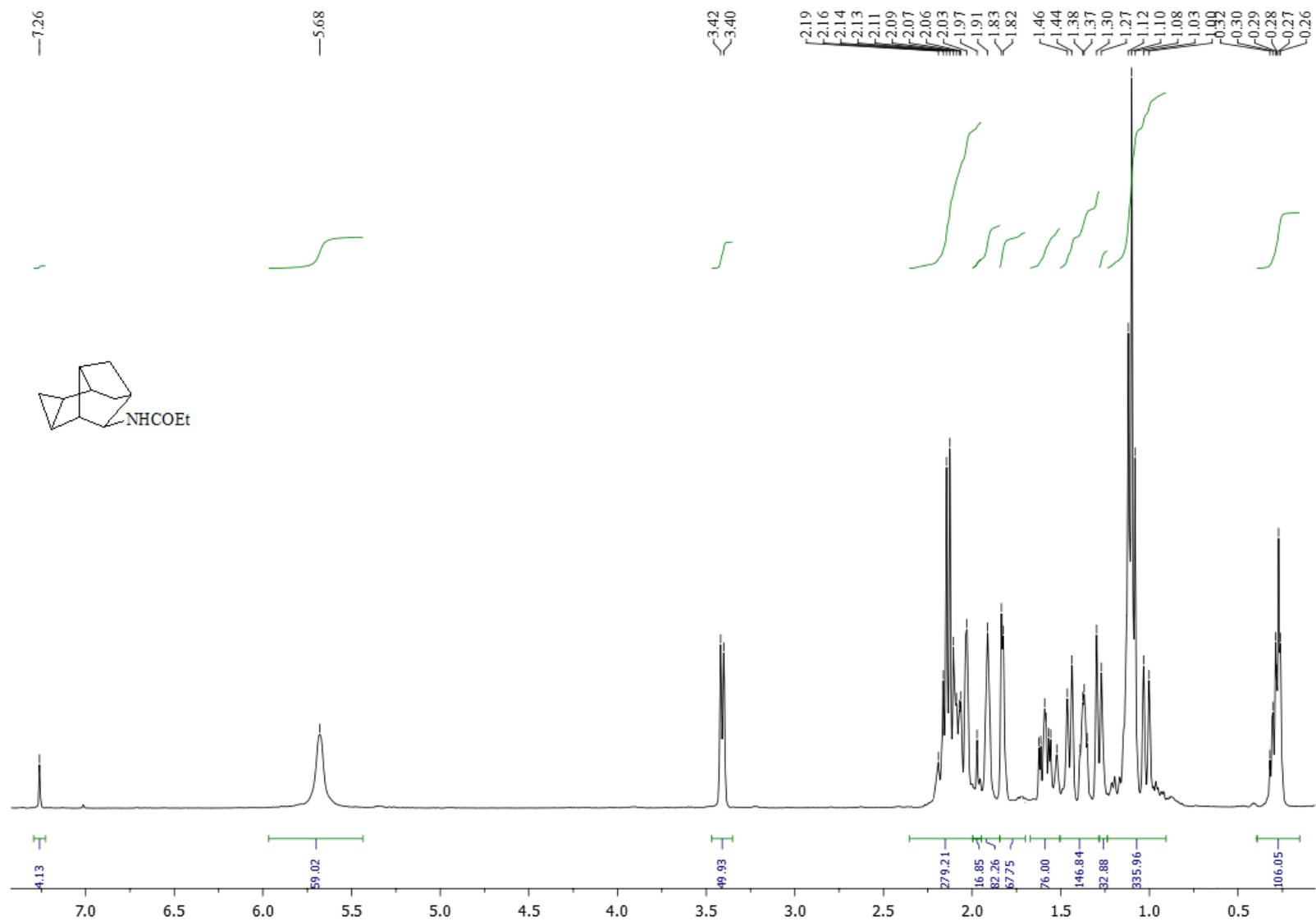
**Figure S10**  $^{13}\text{C}$  NMR spectrum for compound 6a in CDCl<sub>3</sub>



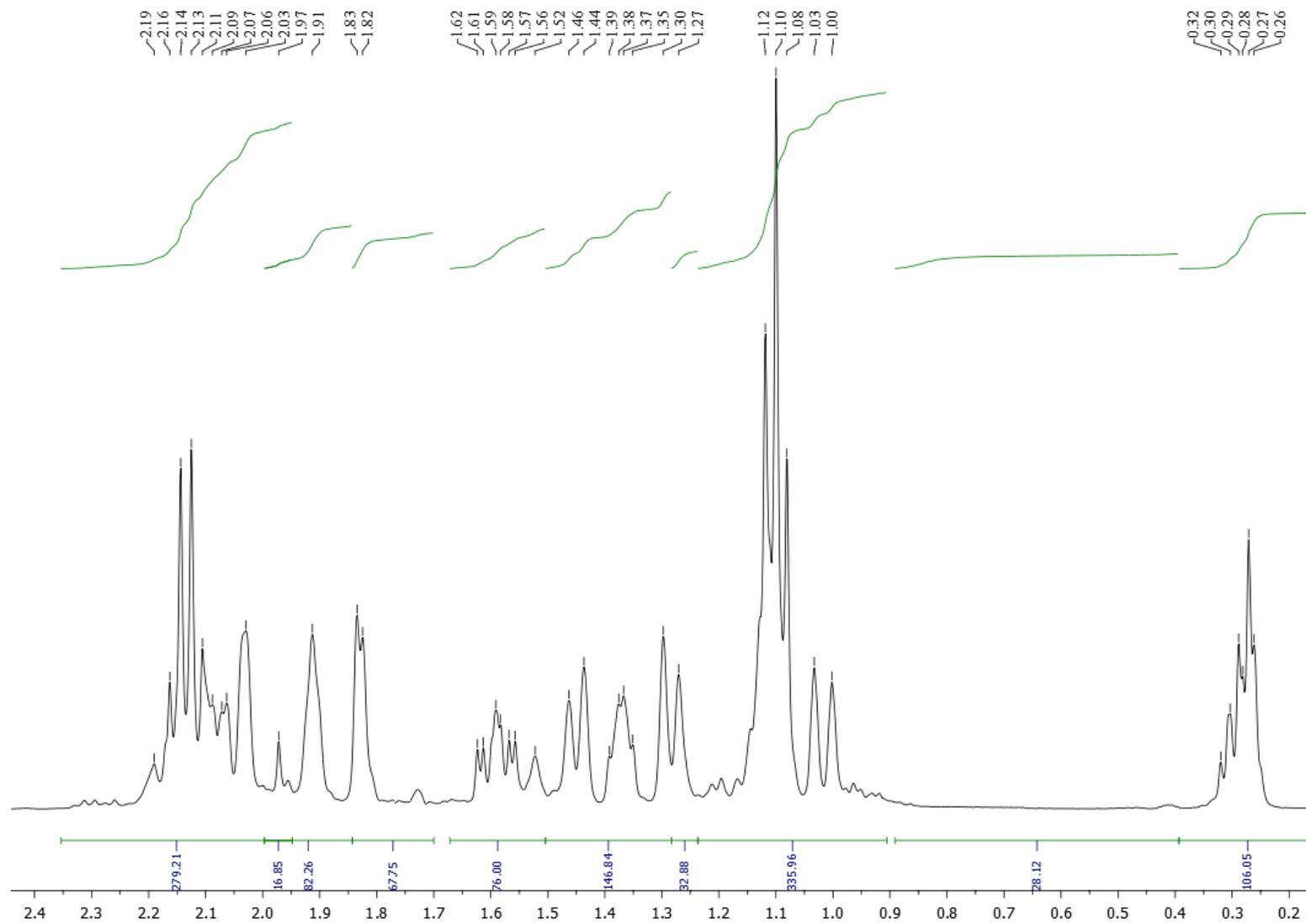
**Figure S11**  $^1\text{H}$  NMR spectrum for compound **6a** in CDCl<sub>3</sub>



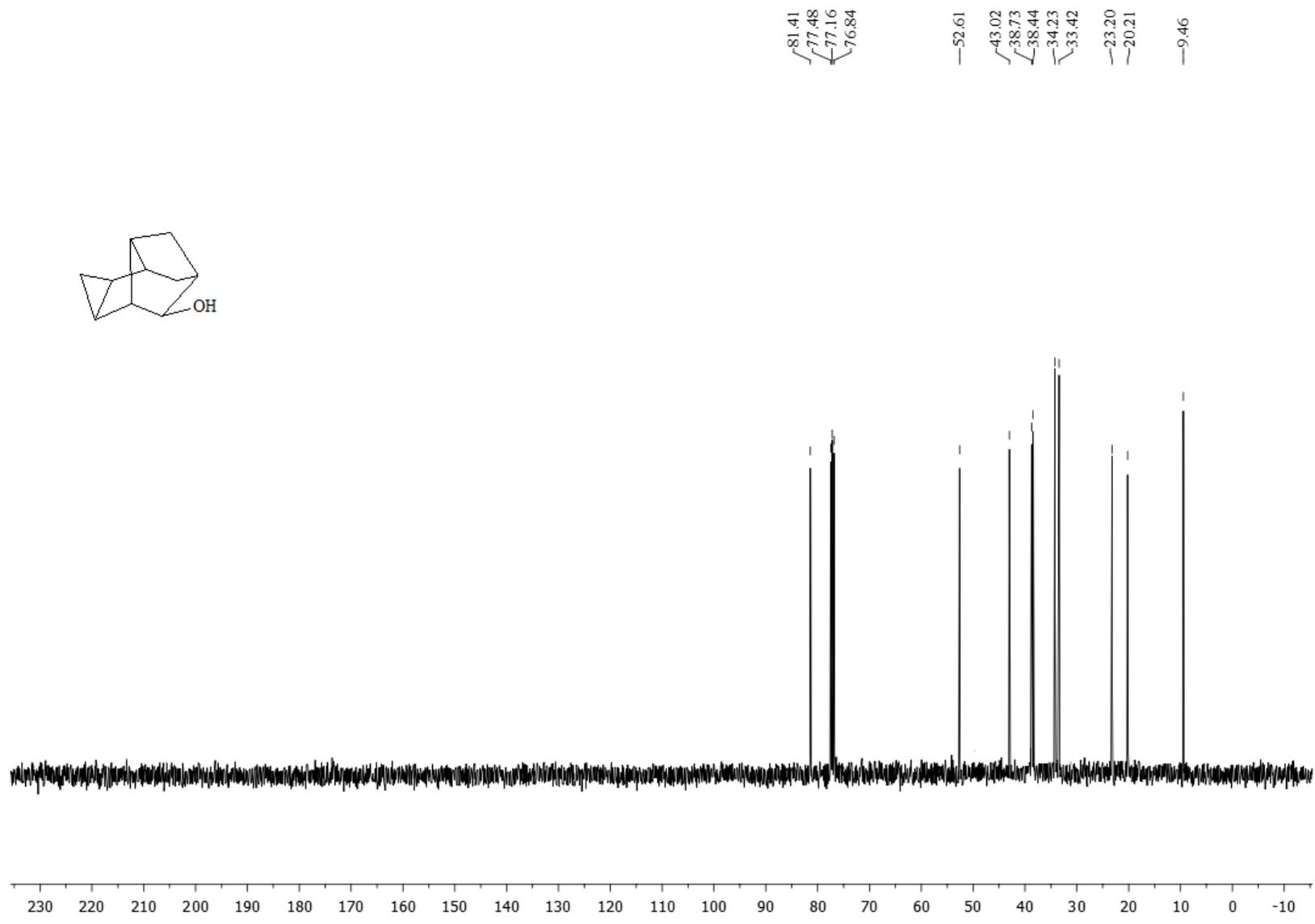
**Figure S12**  $^{13}\text{C}$  NMR spectrum for compound **6b** in CDCl<sub>3</sub>



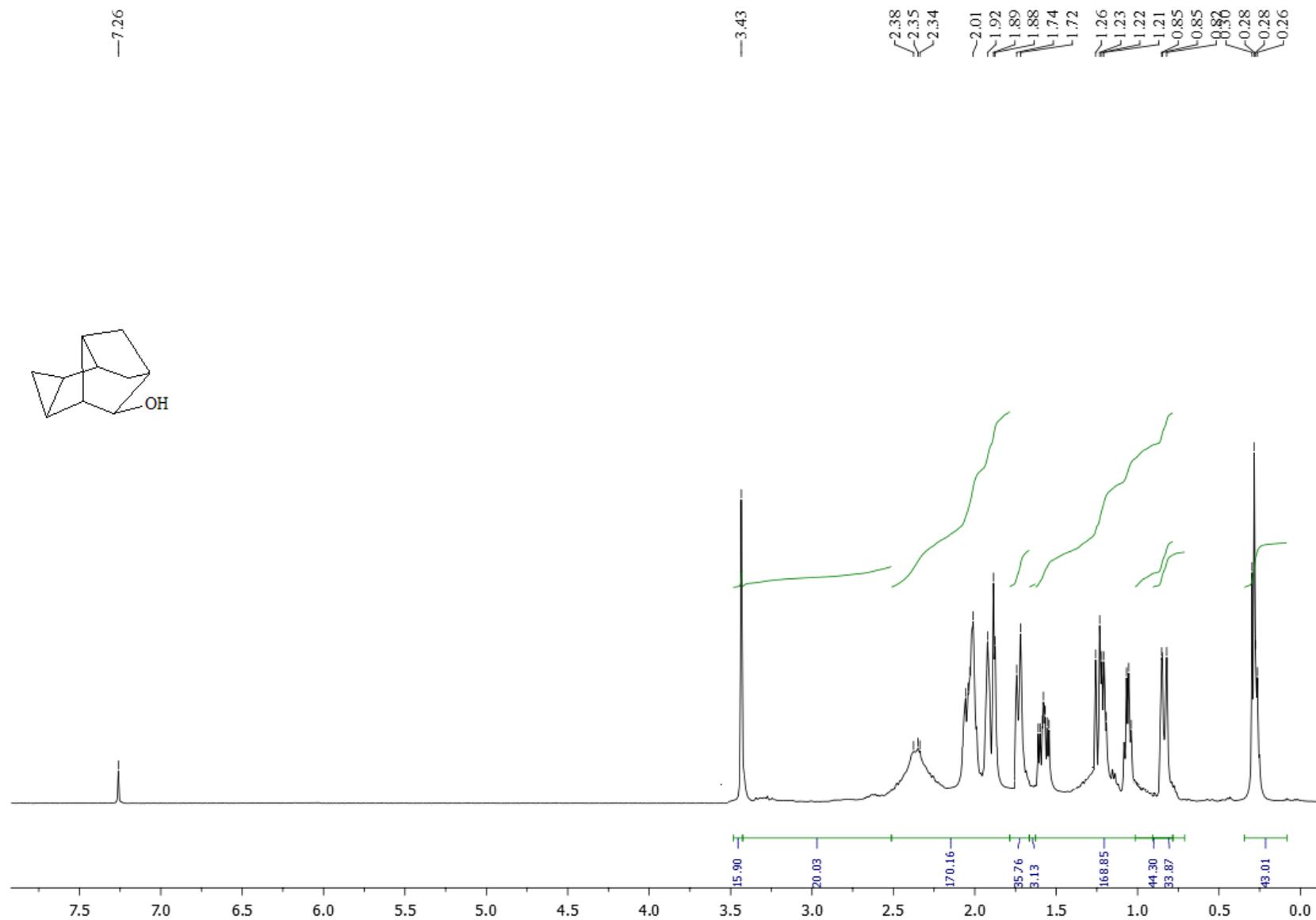
**Figure S13** <sup>1</sup>H NMR spectrum for compound **6b** in CDCl<sub>3</sub>



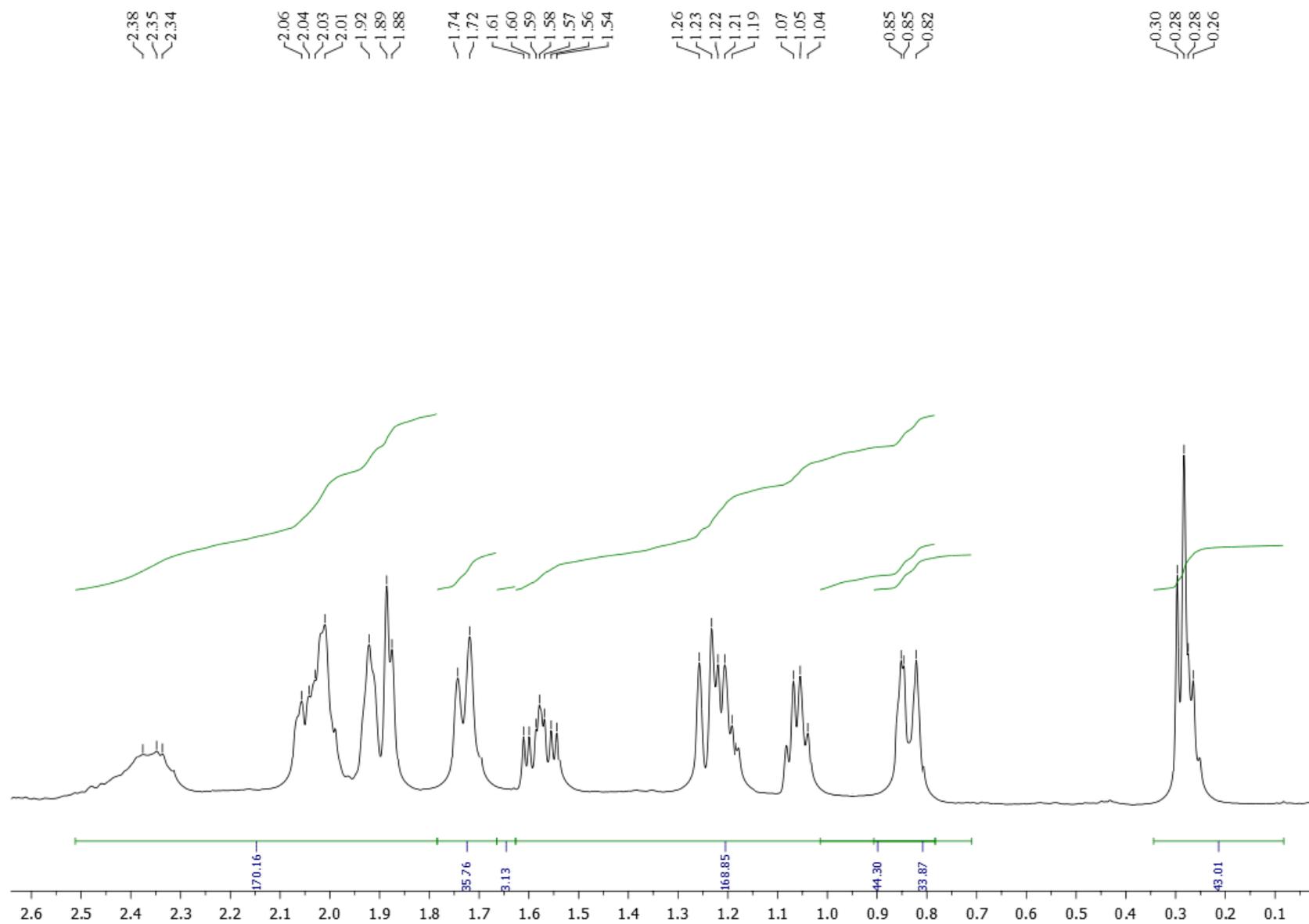
**Figure S14**  $^1\text{H}$  NMR spectrum (fragment) for compound **6b** in  $\text{CDCl}_3$



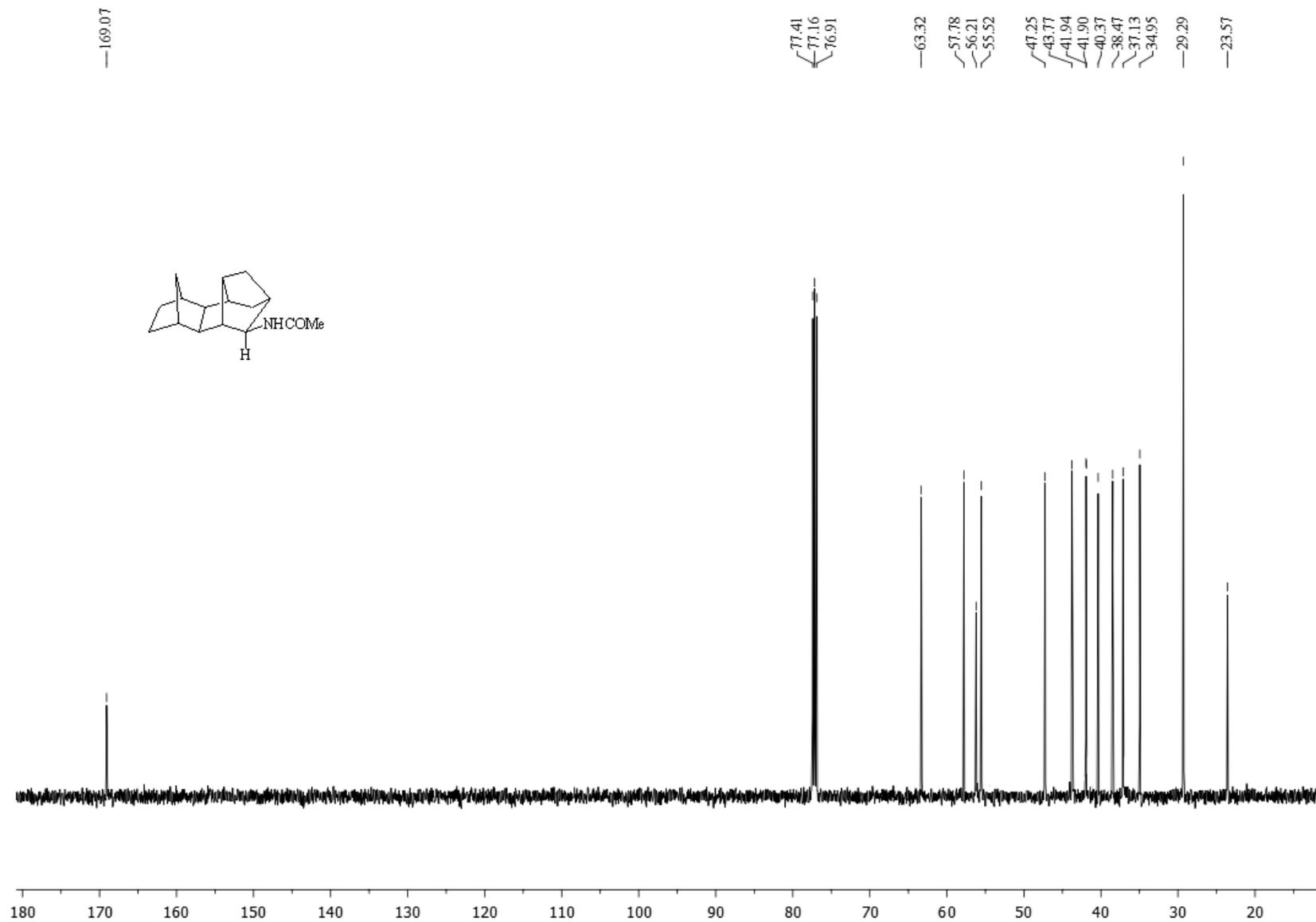
**Figure S15** <sup>13</sup>C NMR spectrum for compound 7 in CDCl<sub>3</sub>



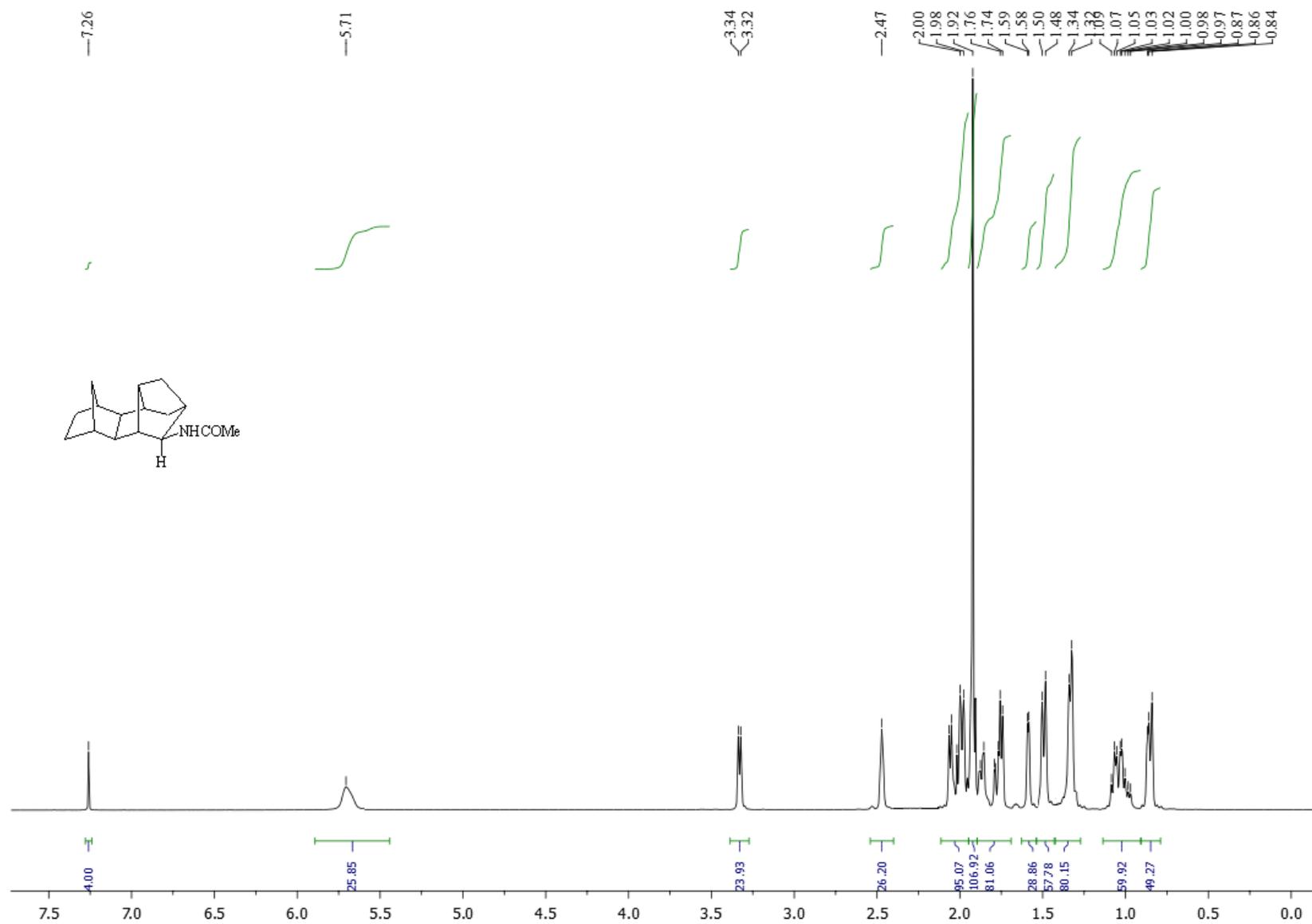
**Figure S16** <sup>1</sup>H NMR spectrum for compound **7** in CDCl<sub>3</sub>



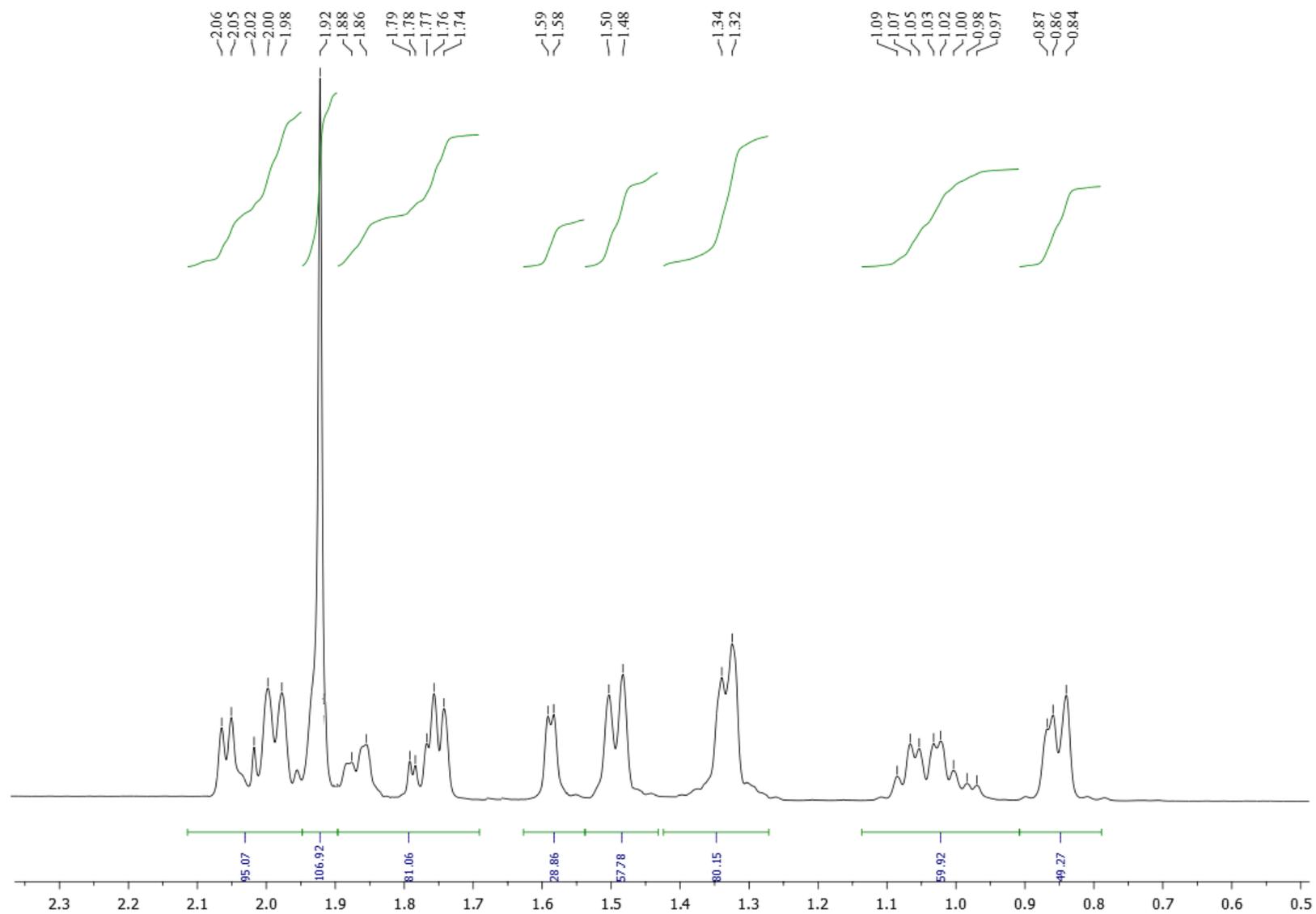
**Figure S17**  $^1\text{H}$  NMR spectrum (fragment) for compound **7** in  $\text{CDCl}_3$



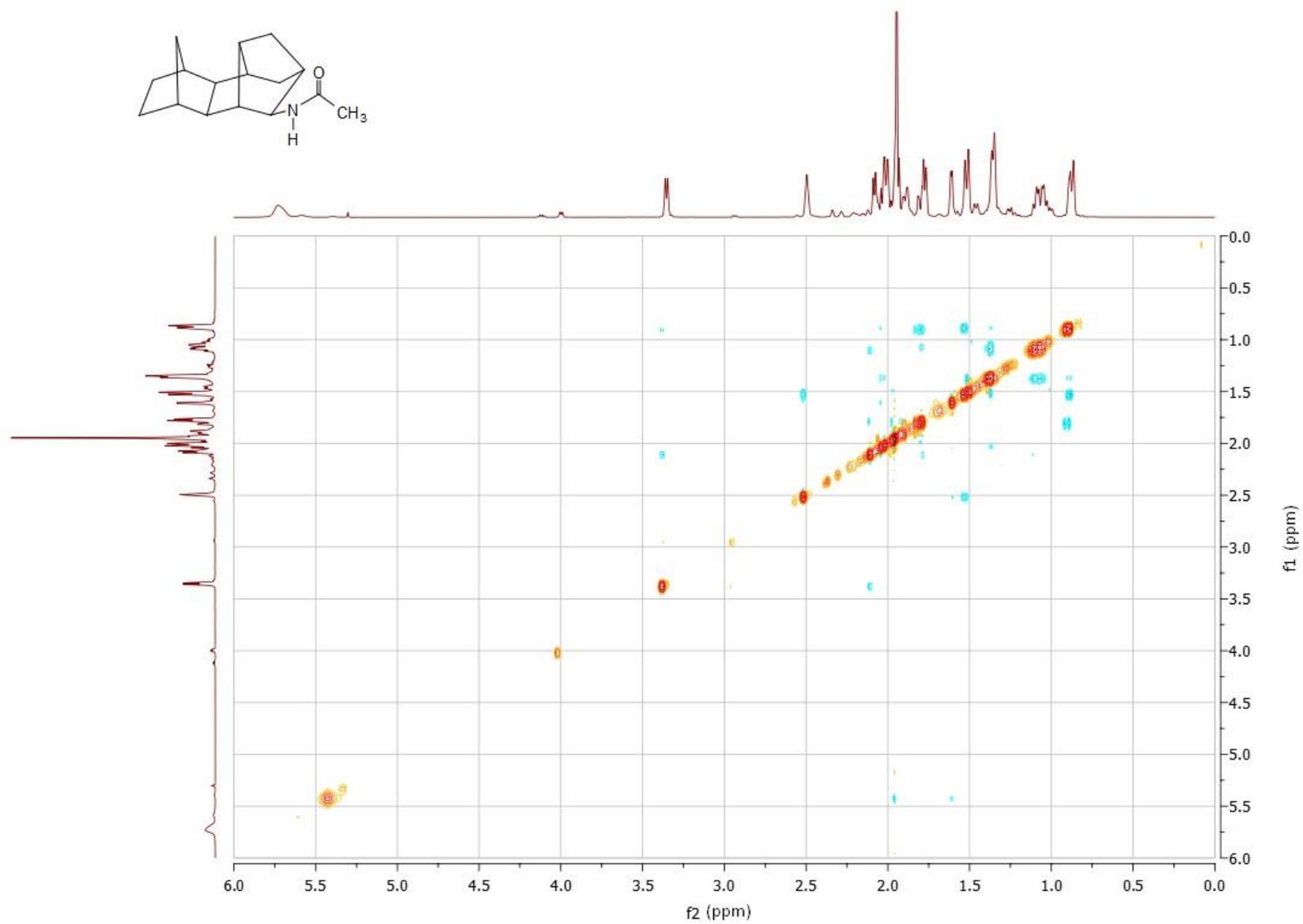
**Figure S18**  $^{13}\text{C}$  NMR spectrum for compound **12** in  $\text{CDCl}_3$



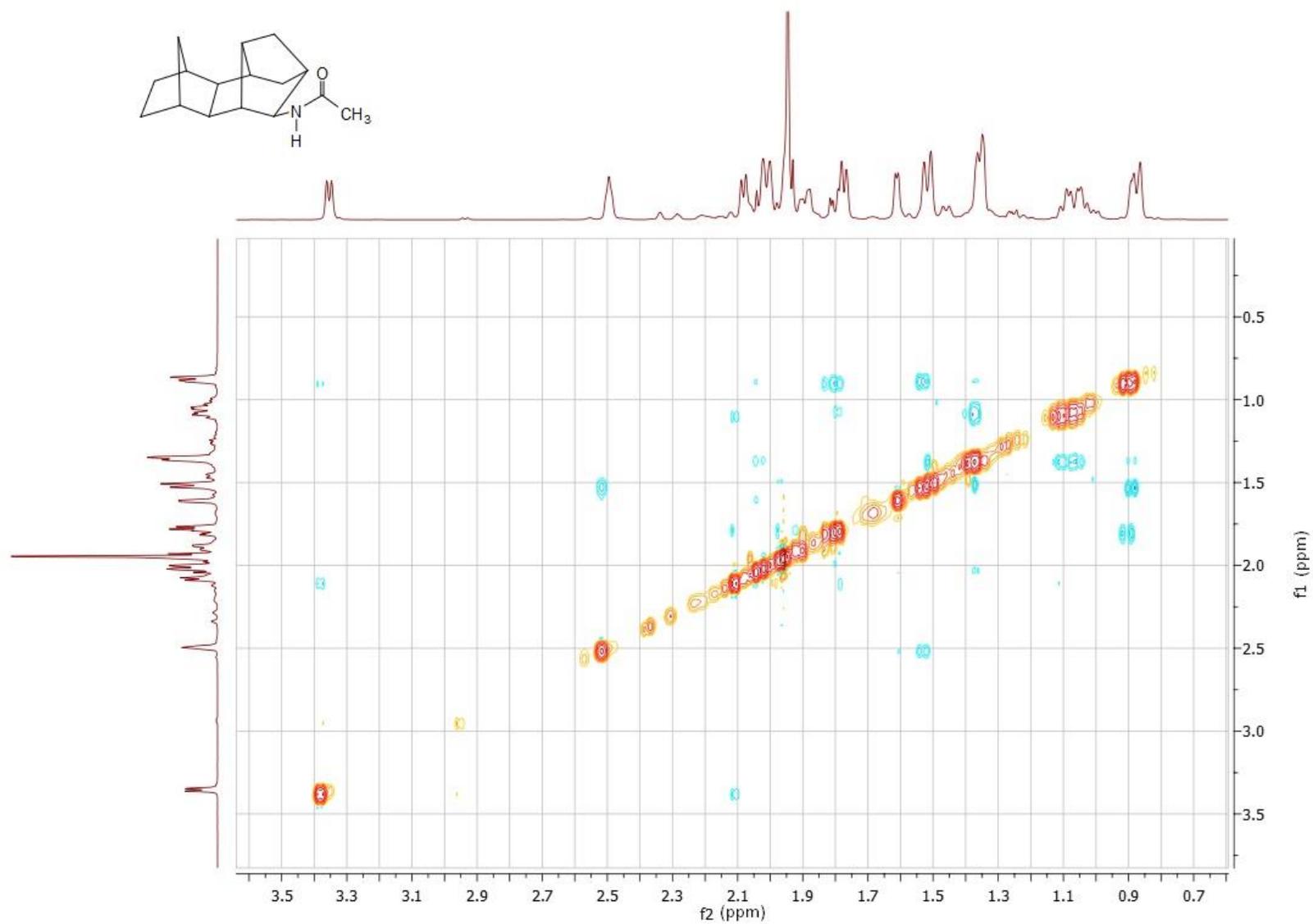
**Figure S19**  $^1\text{H}$  NMR spectrum for compound **12** in CDCl<sub>3</sub>



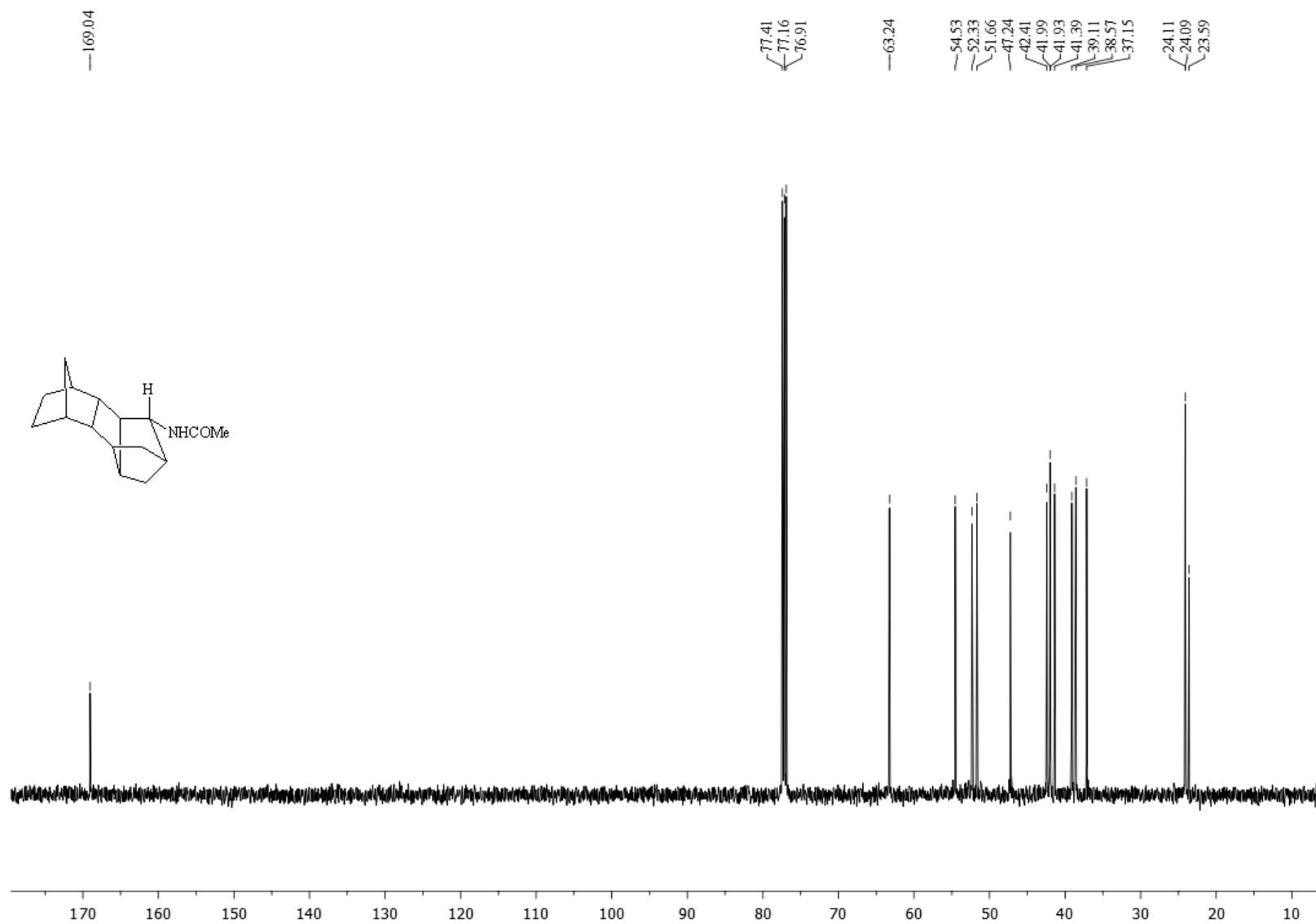
**Figure S20**  $^1\text{H}$  NMR spectrum (fragment) for compound **12** in  $\text{CDCl}_3$



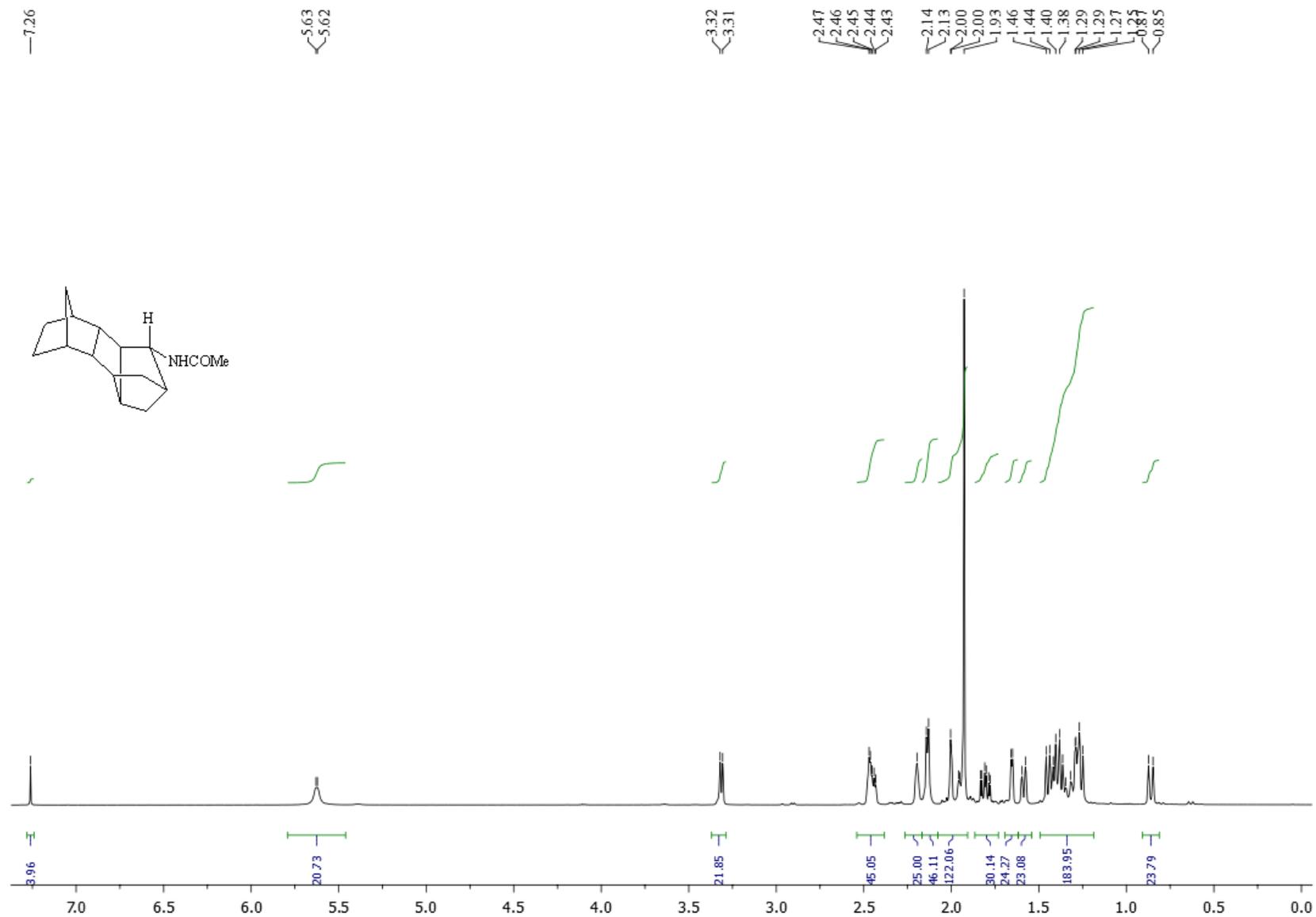
**Figure S21** COSY spectrum for compound **12** in  $\text{CDCl}_3$



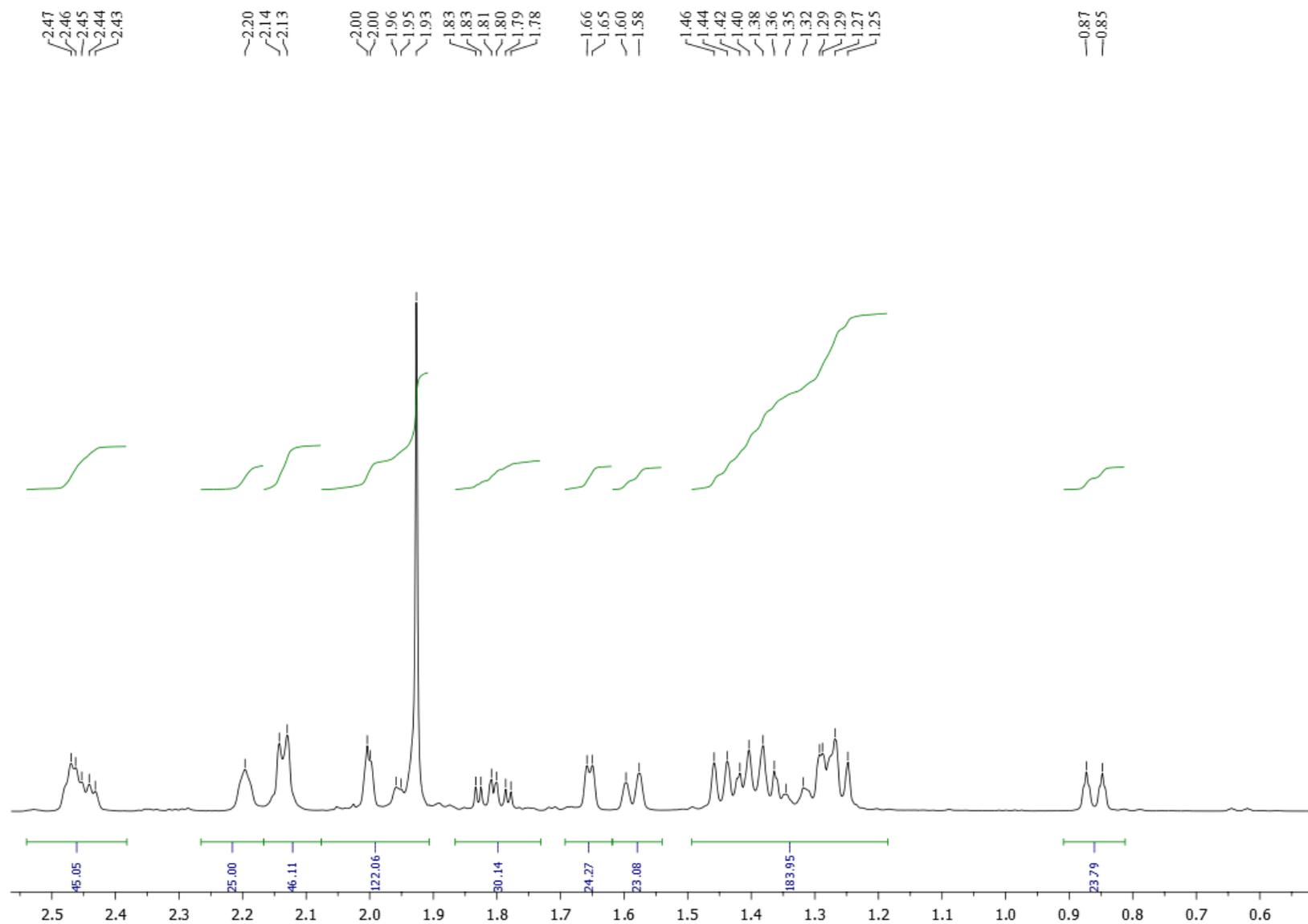
**Figure S22** COSY spectrum (fragment) for compound **12** in CDCl<sub>3</sub>



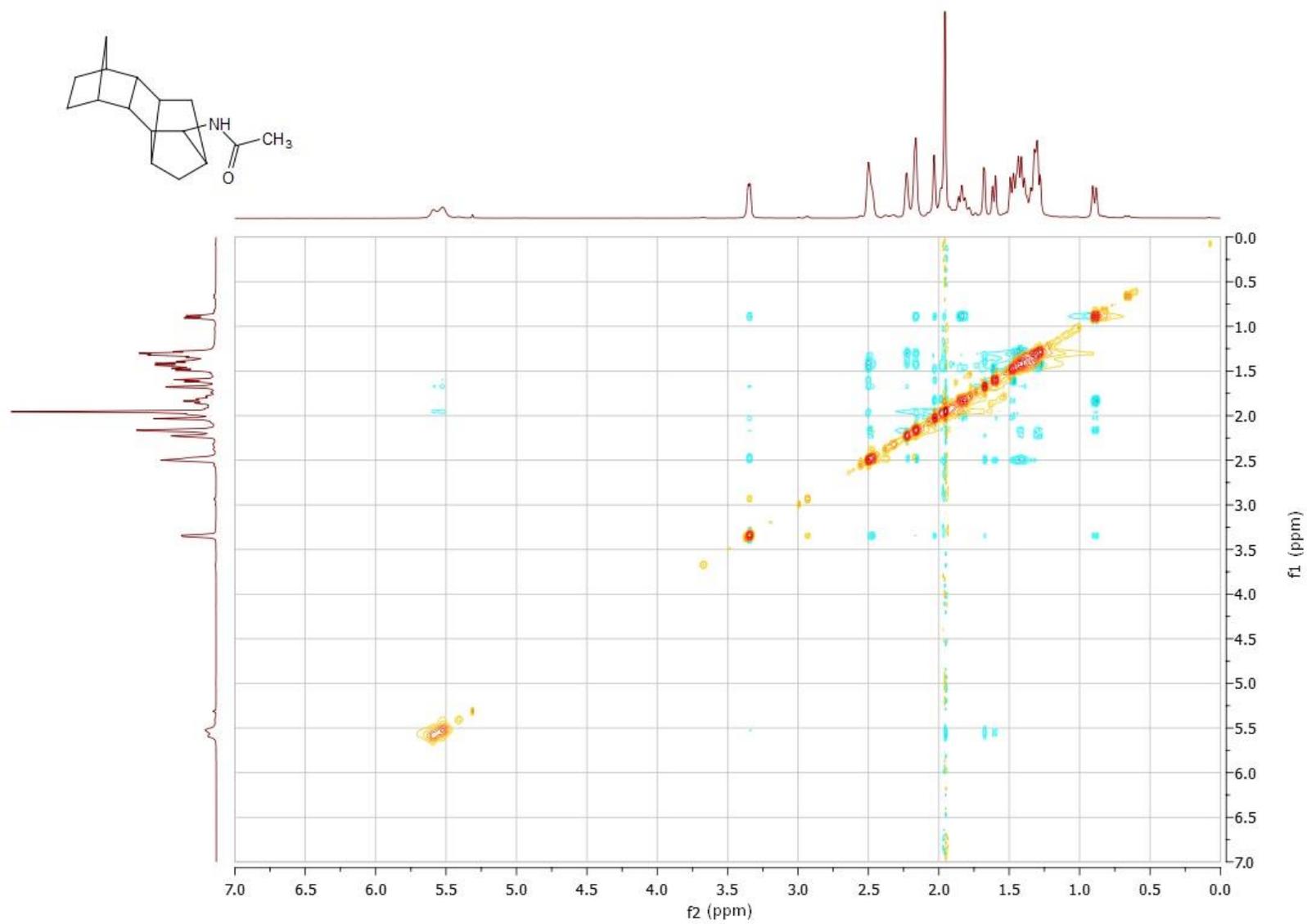
**Figure S23**  $^{13}\text{C}$  NMR spectrum for compound **13** in  $\text{CDCl}_3$



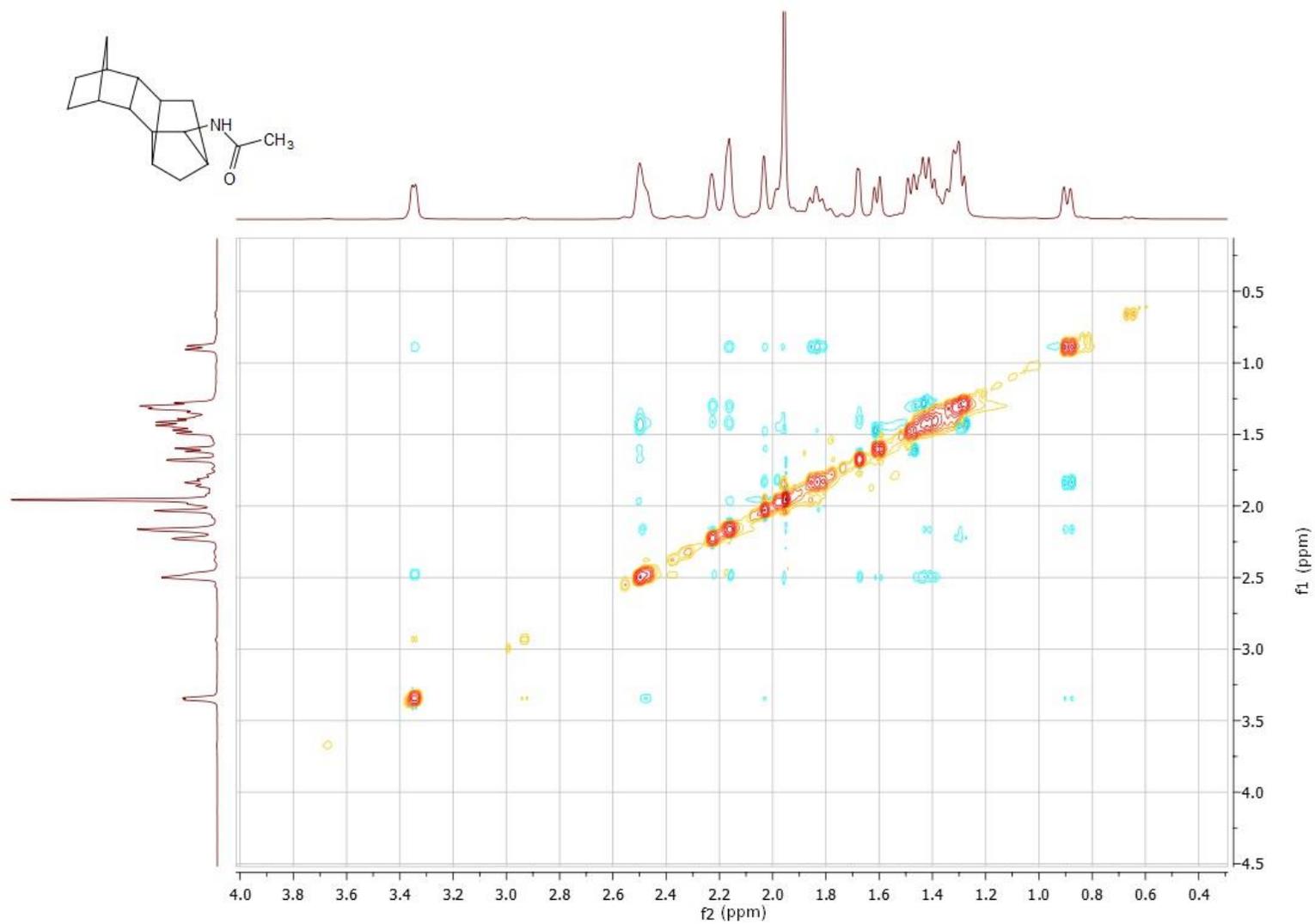
**Figure S24** <sup>1</sup>H NMR spectrum for compound **13** in CDCl<sub>3</sub>



**Figure S25**  $^1\text{H}$  NMR spectrum (fragment) for compound **13** in  $\text{CDCl}_3$



**Figure S26** COSY spectrum for compound **13** in  $\text{CDCl}_3$



**Figure S27** COSY spectrum (fragment) for compound **13** in  $\text{CDCl}_3$