

## Electronic Supporting Information

### Formation of Titanacyclobutenes with a Spiro-bonded Cyclopropane

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#### General

THF was distilled from sodium and benzophenone. Preparative thin layer chromatography (PTLC) was carried out using Wakogel B-5F. Column chromatography was performed on Merck Aluminiumoxid 90. <sup>1</sup>H and <sup>13</sup>C NMR spectra (300 and 75 MHz, respectively) were recorded in CDCl<sub>3</sub> and chemical shift (δ) are quoted in parts per million from tetramethylsilane for <sup>1</sup>H NMR and from CDCl<sub>3</sub> for <sup>13</sup>C NMR spectroscopy. IR absorptions are reported in cm<sup>-1</sup>. All reactions were carried out in an argon atmosphere.

#### Typical Procedure for the Hydrolysis of 4:

A mixture of a THF (1 cm<sup>3</sup>) solution of **4a** (90 mg, 0.2 mmol) and 1 M NaOH (1 cm<sup>3</sup>) was refluxed for 3 h. After being cooled to room temperature, the reaction mixture was diluted with ether (5 cm<sup>3</sup>) and 1 M NaOH (5 cm<sup>3</sup>). The insoluble materials were filtered off through Celite and washed with ether (40 cm<sup>3</sup>). The layers were separated and the aqueous layer was extracted with ether (2 x 20 cm<sup>3</sup>). The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the residue was purified by PTLC (hexane) to give the alkenylcyclopropane **Z-6a** (49 mg, 68%).

#### Characterization Data

##### Formation of Titanacyclobutenes 4

**1',1'-Bis(η<sup>5</sup>-cyclopentadienyl)-2',3'-diphenylspiro[bicyclo[4.1.0]heptane-7,4'-(1'-titanacyclobut-2'-ene)] (4a)**: m.p. 196-198 °C (dec); <sup>1</sup>H NMR 0.85-0.99 (m, 2H), 1.10-1.31 (m, 4H), 1.73-2.06 (m, 4H), 6.11 (s, 10H), 6.58 (d, *J* = 7.2 Hz, 2H), 6.74 (d, *J* = 6.8 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 7.05 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.5, 7.5 Hz, 2H); <sup>13</sup>C NMR 22.2, 23.4, 24.7, 85.7, 105.0, 110.9, 124.9, 125.6, 127.6, 127.7, 127.8, 129.8, 137.5, 143.2, 205.0; IR

(KBr) 3072, 3057, 2975, 2925, 2853, 1591, 1540, 1487, 1476, 1458, 1440, 1382, 1171, 1155, 1066, 1016, 957, 838, 804, 778, 762; Anal. Calcd for C<sub>31</sub>H<sub>30</sub>Ti: C, 82.66; H, 6.71. Found: C, 82.73; H, 6.84.

**1',1'-Bis( $\eta^5$ -cyclopentadienyl)-2',3'-diphenylspiro[bicyclo[4.1.0]-2-oxaheptane-7,4'-(1'-titanacyclobut-2'-ene)] (4b):** m.p. 180-183 °C (dec); <sup>1</sup>H NMR 1.03-1.28 (m, 2H), 1.28-1.46 (m, 1H), 1.68-1.92 (m, 1H), 2.00-2.20 (m, 1H), 3.13-3.36 (m, 2H), 3.69 (d, *J* = 10.4 Hz, 1H), 6.12 (s, 5H), 6.32 (s, 5H), 6.57 (d, *J* = 7.3 Hz, 2H), 6.72 (d, *J* = 7.0 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 7.4, 7.4 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.4, 7.4 Hz, 2H); <sup>13</sup>C NMR 22.0, 22.8, 23.2, 61.1, 64.6, 78.7, 104.4, 111.3, 112.1, 124.9, 125.6, 127.5, 127.7, 128.2, 129.3, 137.0, 143.4, 204.4; IR (KBr) 3068, 2968, 2944, 2923, 2855, 1591, 1487, 1439, 1224, 1124, 1100, 1054, 1042, 1019, 806, 780, 766; Anal. Calcd for C<sub>30</sub>H<sub>28</sub>OTi: C, 79.64; H, 6.24. Found: C, 79.38; H, 6.37.

**1',1'-Bis( $\eta^5$ -cyclopentadienyl)-2',3'-bis(3-phenylpropyl)[bicyclo[4.1.0]heptane-7,4'-(1'-titanacyclobut-2'-ene)] (4c):** m.p. 119-123 °C (dec); <sup>1</sup>H NMR 0.92-1.03 (m, 2H), 1.15-1.36 (m, 6H), 1.36-1.47 (m, 2H), 1.74-1.98 (m, 6H), 2.43-2.60 (m, 4H), 2.66 (t, *J* = 7.5 Hz, 2H), 5.78 (s, 10H), 7.10-7.37 (m, 10H); <sup>13</sup>C NMR 21.7, 22.3, 23.5, 25.0, 30.7, 32.6, 36.6, 36.8, 37.6, 84.3, 95.0, 109.2, 125.71, 125.74, 128.3, 128.35, 128.40, 128.44, 142.4, 142.6, 218.2; IR (KBr) 3023, 2963, 2925, 2850, 1601, 1495, 1451, 1074, 1018, 834, 811, 793, 743; Anal. Calcd for C<sub>37</sub>H<sub>42</sub>Ti: C, 83.13; H, 7.92. Found: C, 83.30; H, 8.10.

#### Hydrolysis of Titanacyclobutenes 4

**meso-(1R\*,6S\*,7R\*)-7-[(Z)-1,2-Diphenylethenyl]bicyclo[4.1.0]heptane (Z-6a):** <sup>1</sup>H NMR 1.08-1.34 (m, 6H), 1.40 (t, *J* = 5.0 Hz, 1H), 1.64-1.82 (m, 2H), 1.82-2.00 (m, 2H), 6.30 (s, 1H), 6.78-6.92 (m, 2H), 6.96-7.09 (m, 3H), 7.13-7.20 (m, 2H), 7.20-7.38 (m, 3H); <sup>13</sup>C NMR 18.8, 21.4, 23.3, 32.8, 122.9, 125.7, 126.9, 127.8, 128.3, 128.8, 128.9, 137.7, 140.8, 144.8; IR (neat) 3078, 3054, 3020, 2925, 2852, 1598, 1494, 1445, 1019, 778, 756; Anal. Calcd for C<sub>21</sub>H<sub>22</sub>: C, 91.92; H, 8.08. Found: C, 91.88; H, 8.43.

**(1R\*,6R\*,7S\*)-7-[(Z)-1,2-Diphenylethenyl]bicyclo[4.1.0]-2-oxaheptane (Z-6b):** m.p. 70-73 °C; <sup>1</sup>H NMR 1.29-1.42 (m, 1H), 1.42-1.57 (m, 2H), 1.79 (dd, *J* = 2.0, 6.6 Hz, 1H), 1.83-2.12 (m, 2H), 3.20-3.40 (m, 1H), 3.49-3.68 (m, 2H), 6.24 (s, 1H), 6.79-6.92 (m, 2H), 6.96-7.11 (m, 3H), 7.12-7.34 (m, 5H); <sup>13</sup>C NMR 18.5, 19.3, 22.2, 32.8, 58.9, 64.4, 124.0, 126.0, 127.0, 127.8, 128.5, 128.7, 128.9, 137.2, 140.5, 141.6; IR (KBr) 3075, 3056, 3021, 2980, 2940, 2926, 2853, 1598, 1493, 1443, 1231, 1217, 1204, 1139, 1112, 1062, 1040, 1027, 1012, 922, 786, 765; Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O: C, 86.92; H, 7.29. Found: C, 86.71; H, 7.53.

**7-[(E)-5-Phenyl-1-(3-phenylpropyl)-1-pentenyl]bicyclo[4.1.0]heptane (E-6c):** <sup>1</sup>H NMR 0.91 (s, 3H), 1.06-1.33 (m, 4H), 1.53-1.69 (m, 4H), 1.69-1.79 (m, 2H), 1.80-1.92 (m, 2H), 1.97 (dt, *J* = 7.4, 7.4 Hz, 2H), 2.04 (t, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 2.57 (t, *J* = 7.8 Hz, 2H), 4.98 (t, *J* = 7.1 Hz, 1H), 7.08-7.33 (m, 10H); <sup>13</sup>C NMR 18.2, 21.5, 23.6, 27.2, 29.6, 30.5, 31.0, 31.9, 35.5, 35.9, 120.7, 125.56, 125.61, 128.19, 128.23, 128.3, 128.4, 140.8, 142.6, 142.7; IR (neat) 3084, 3061, 3025, 2926, 2854, 1604, 1496, 1452, 1077, 1030, 745; Anal. Calcd for C<sub>27</sub>H<sub>34</sub>: C, 90.44; H, 9.56. Found: C, 90.25; H, 9.54.

#### Formation of Alkenylcyclopropanes 6

**meso-(1R\*,6S\*,7S\*)-7-[(E)-1,2-Diphenylethenyl]bicyclo[4.1.0]heptane (E-6a):** m.p. 96-97 °C; <sup>1</sup>H NMR 0.65-1.01 (m, 6H), 1.23-1.45 (m, 4H), 2.02-2.18 (m, 1H), 6.91 (d, *J* = 2.6 Hz, 1H), 7.19-7.28 (m, 2H), 7.30-7.39 (m, 4H), 7.58-7.70 (m, 4H); <sup>13</sup>C NMR 14.9, 20.0, 20.6, 21.7, 126.4, 126.46, 126.54, 127.8, 127.9, 129.3, 131.8, 138.1, 138.2, 144.9; IR (KBr) 3049, 3018, 2991, 2918, 2856, 1492, 1460, 1447, 1077, 766, 693; Anal. Calcd for C<sub>21</sub>H<sub>22</sub>: C, 91.92; H, 8.08. Found: C, 92.15; H, 8.31.

**(1R\*,6R\*,7R\*)-7-[(E)-1,2-Diphenylethenyl]bicyclo[4.1.0]-2-oxaheptane (E-6b):** m.p. 98-99 °C; <sup>1</sup>H NMR 0.93-1.22 (m, 3H), 1.22-1.57 (m, 2H), 2.08 (ddd, *J* = 3.0, 6.1, 9.4 Hz, 1H), 2.94-3.12 (m, 1H), 3.17-3.30 (m, 1H), 3.79 (dd, *J* = 6.4, 6.4 Hz, 1H), 6.97 (d, *J* = 2.6 Hz, 1H), 7.24 (t, *J* = 7.3 Hz, 2H), 7.35 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.36 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 4H); <sup>13</sup>C NMR 15.1, 17.1, 21.9, 22.8, 53.8, 63.9, 126.1, 126.5, 126.7, 127.9, 128.0, 128.9, 132.5, 136.4, 138.2, 144.6; IR (KBr) 3003, 2927, 2852, 1607, 1511, 1447, 1294, 1250, 1175, 1037, 1005, 958, 828; Anal. Calcd for C<sub>20</sub>H<sub>20</sub>O: C, 86.92; H, 7.29. Found: C, 86.93; H, 7.55.

**A Mixture of 7-[(E)-5-Phenyl-1-(3-phenylpropyl)-1-pentenyl]bicyclo[4.1.0]heptane (E-6c) and 7-[5-Phenyl-1-(3-phenylpropyl)pentylidene]bicyclo[4.1.0]heptane (7a) (E-6c:7a = 94:6):** <sup>1</sup>H NMR 0.91 (s, 2.82H), 1.06-1.40 (m, 4H), 1.40-2.09 (m, 12H), 2.16 (t, *J* = 7.3 Hz, 0.24H), 2.46-2.67 (m, 4H), 4.98 (t, *J* = 7.1 Hz, 0.94H), 7.08-7.32 (m, 10H); <sup>13</sup>C NMR (major product) 18.2, 21.5, 23.6, 27.2, 29.6, 30.5, 31.0, 31.8, 35.5, 35.9, 120.7, 125.55, 125.60, 128.18, 128.22, 128.3, 128.4, 140.8, 142.63, 142.64; IR (neat) 3084, 3061, 3025, 2926, 2854, 1604, 1496, 1452, 1077, 1030, 745; Anal. Calcd for C<sub>27</sub>H<sub>34</sub>: C, 90.44; H, 9.56. Found: C, 90.46; H, 9.87.

**(1R\*,6R\*,7S\*)-7-[(E)-5-Phenyl-1-(3-phenylpropyl)-1-pentenyl]bicyclo[4.1.0]-2-oxaheptane (E-6d):** <sup>1</sup>H NMR 1.10 (q, *J* = 6.2 Hz, 1H), 1.34 (d, *J* = 6.2 Hz, 1H), 1.38-1.52 (m, 2H), 1.59 (tt, *J* = 7.6, 7.6 Hz, 2H), 1.76 (tt, *J* = 7.8, 7.8 Hz, 2H), 1.84-2.02 (m, 4H), 2.02-2.17 (m, 2H), 2.44-2.65 (m,

4H), 3.22-3.39 (m, 2H), 3.58 (dt,  $J = 10.8, 3.0$  Hz, 1H), 4.92 (t,  $J = 7.1$  Hz, 1H), 7.06-7.34 (m, 10H);  $^{13}\text{C}$  NMR 17.7, 19.4, 22.4, 27.1, 29.8, 30.3, 31.2, 31.7, 35.5, 35.9, 58.5, 64.3, 122.2, 125.58, 125.62, 128.20, 128.22, 128.4, 138.0, 142.5; IR (neat) 3084, 3061, 3025, 2930, 2855, 1496, 1454, 1231, 1211, 1134, 1112, 1045, 747; Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{O}$ : C, 86.62; H, 8.95. Found: C, 86.55; H, 9.18.

**A Mixture of 1-Butyl-2-[(*E*)-5-phenyl-1-(3-phenylpropyl)-1-pentenyl]cyclopropane (*E*-6e) and 1-Butyl-2-[5-phenyl-1-(3-phenylpropyl)pentylidene]cyclopropane (7b) (*E*-6e:7b = 94:6):**  $^1\text{H}$  NMR (major product) 0.38-0.41 (m, 1H), 0.55-0.76 (m, 2H), 0.82-0.98 (m, 3H), 0.98-1.07 (m, 1H), 1.19-1.48 (m, 6H), 1.54-1.90 (m, 4H), 1.92-2.13 (m, 4H), 2.52-2.72 (m, 4H), 5.04 (t,  $J = 7.1$  Hz, 1H), 7.15-7.37 (m, 10H);  $^{13}\text{C}$  NMR (major product) 12.2, 14.1, 20.2, 22.6, 24.6, 27.2, 30.7, 30.8, 31.75, 31.82, 34.1, 35.6, 36.0, 122.0, 125.58, 125.63, 128.21, 128.23, 128.36, 128.39, 140.3, 142.59, 142.61; IR (neat) 3084, 3062, 3026, 2998, 2926, 2856, 1496, 1454, 1030, 745; Anal. Calcd for  $\text{C}_{27}\text{H}_{36}$ : C, 89.94; H, 10.06. Found: C, 90.11; H, 10.42.

***trans*-1-(1-Naphthylmethyloxymethyl)-2-[(*E*)-1-propyl-1-pentenyl]cyclopropane (*trans*-*E*-6f):**  $^1\text{H}$  NMR 0.52 (ddd,  $J = 5.0, 5.0, 8.4$  Hz, 1H), 0.70 (ddd,  $J = 5.1, 5.1, 8.2$  Hz, 1H), 0.87 (t,  $J = 7.3$  Hz, 3H), 0.88 (t,  $J = 7.3$  Hz, 3H), 1.06-1.23 (m, 2H), 1.32 (tq,  $J = 7.4, 7.4$  Hz, 2H), 1.45 (tq,  $J = 7.5, 7.5$  Hz, 2H), 1.89-2.05 (m, 4H), 3.40 (dd,  $J = 6.7, 10.2$  Hz, 1H), 3.50 (dd,  $J = 6.3, 10.4$  Hz, 1H), 4.98 (s, 2H), 5.08 (t,  $J = 7.2$  Hz, 1H), 7.34-7.57 (m, 4H), 7.72-7.90 (m, 2H), 8.14 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR 10.4, 13.9, 14.2, 19.2, 22.0, 23.1, 23.2, 29.7, 33.0, 70.9, 74.2, 123.2, 124.1, 125.1, 125.7, 126.1, 126.2, 128.42, 128.45, 131.8, 133.7, 134.1, 138.9; IR (neat) 3045, 2957, 2869, 1511, 1456, 1376, 1168, 1094, 1073, 793, 775; Anal. Calcd for  $\text{C}_{23}\text{H}_{30}\text{O}$ : C, 85.66; H, 9.38. Found: C, 85.57; H, 9.52.

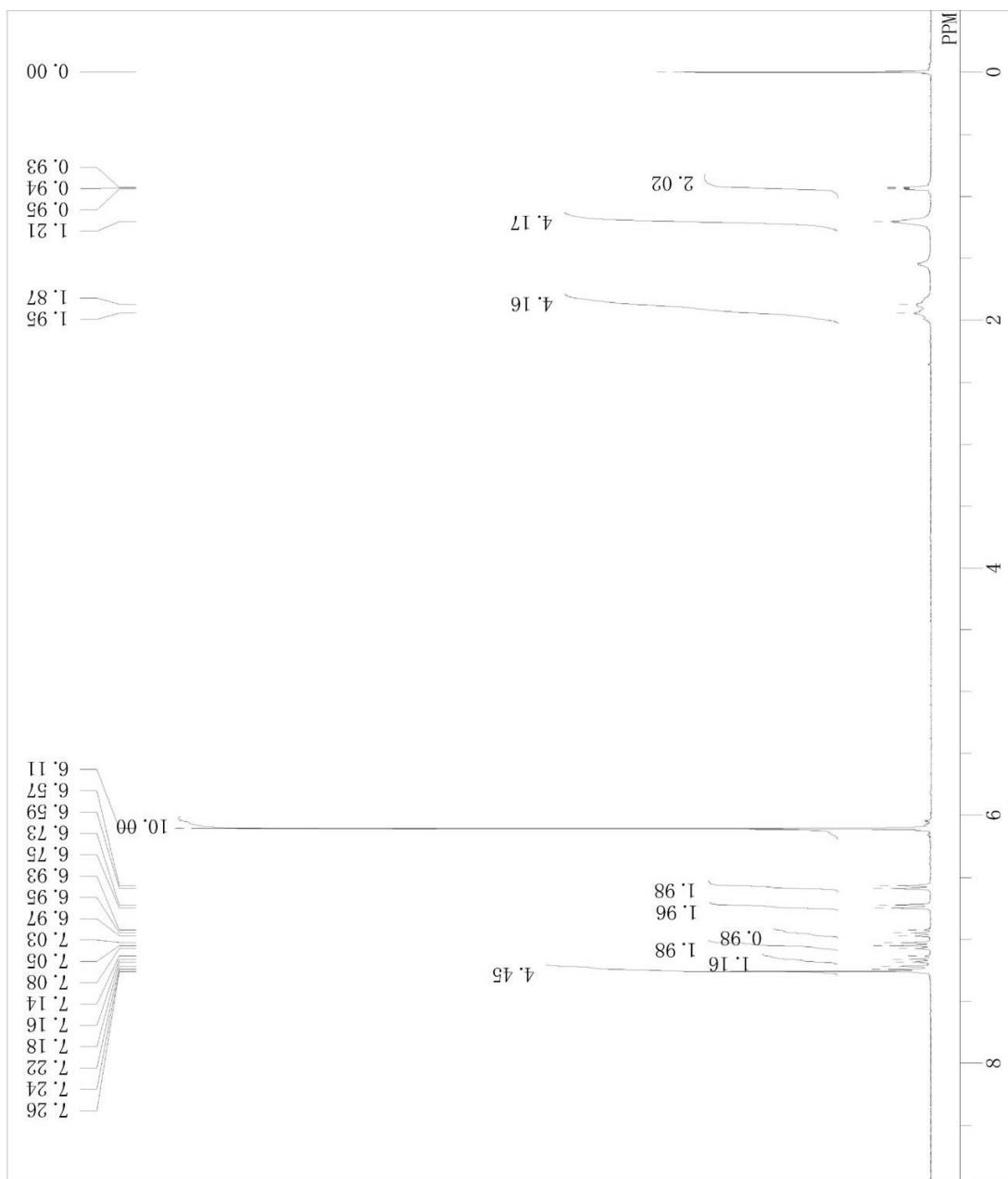
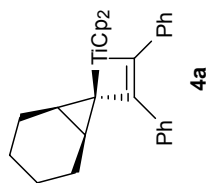
***cis*-1-(1-Naphthylmethyloxymethyl)-2-[(*E*)-1-propyl-1-pentenyl]cyclopropane (*cis*-*E*-6f):**  $^1\text{H}$  NMR 0.51 (ddd,  $J = 5.4, 5.4, 5.9$  Hz, 1H), 0.74 (ddd,  $J = 5.0, 8.2, 8.2$  Hz, 1H), 0.84 (t,  $J = 7.3$  Hz, 3H), 0.88 (t,  $J = 7.4$  Hz, 3H), 1.12-1.51 (m, 5H), 1.51-1.65 (m, 1H), 1.80-2.00 (m, 3H), 2.02-2.17 (m, 1H), 3.32 (dd,  $J = 6.8, 9.9$  Hz, 1H), 3.39 (dd,  $J = 7.7, 9.9$  Hz, 1H), 4.87 (d,  $J = 11.7$  Hz, 1H), 4.93 (d,  $J = 11.9$  Hz, 1H), 5.02 (t,  $J = 7.2$  Hz, 1H), 7.37-7.58 (m, 4H), 7.74-7.89 (m, 2H), 8.11 (d,  $J = 7.3$  Hz, 1H); IR (neat) 3067, 3005, 2956, 2929, 2869, 1464, 1090, 1073, 793, 775.

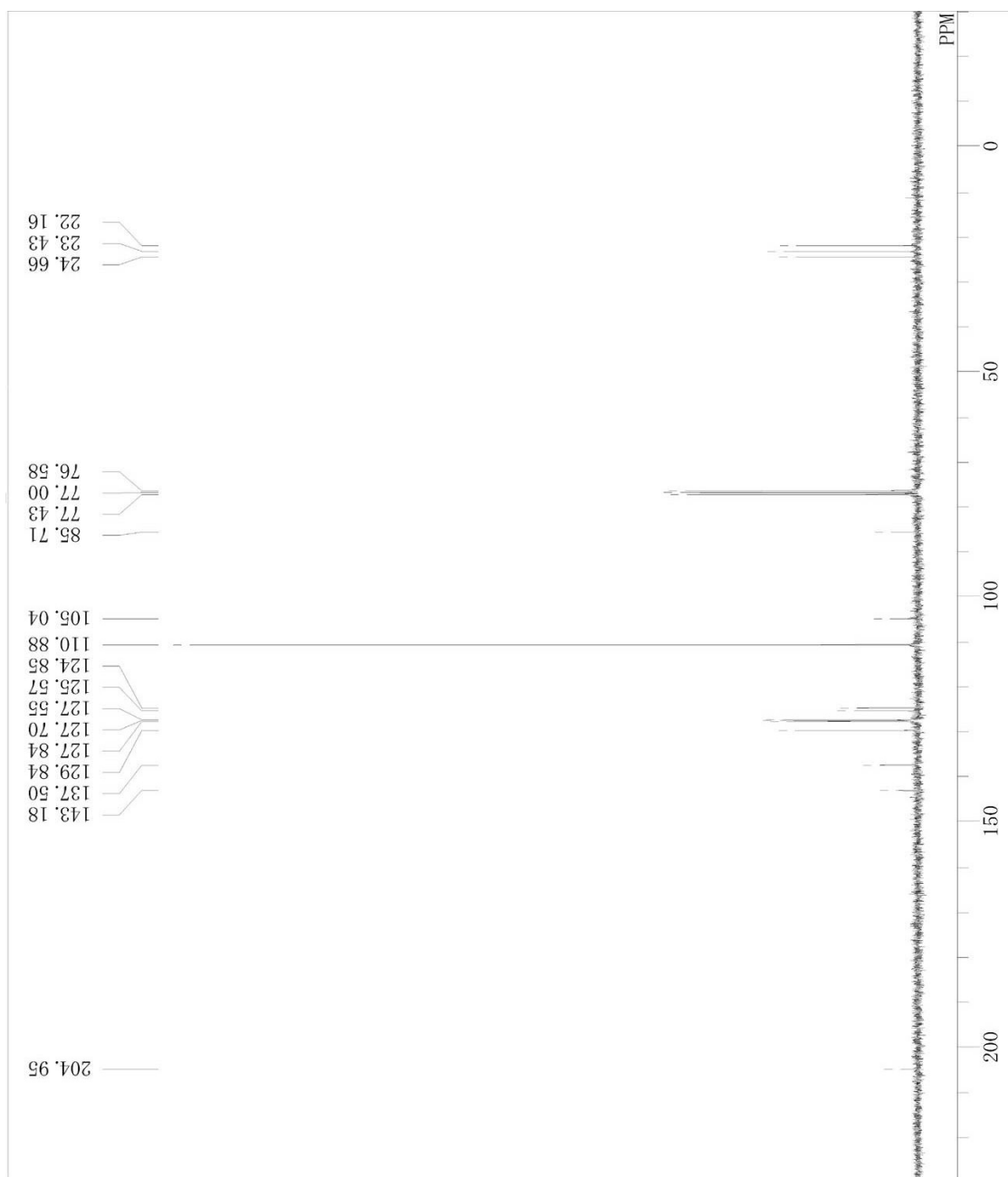
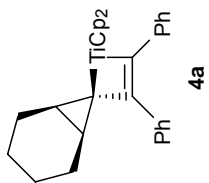
**A *cis/trans* Mixture of 7-[(*E*)-2-(*p*-Methoxyphenyl)ethenyl]bicyclo[4.1.0]heptane (6g) (ratio of stereoisomers = 67:33):**  $^1\text{H}$  NMR 0.96-1.45 (m, 7H), 1.49-1.63 (m, 1H), 1.63-1.78 (m, 1H), 1.79-2.01 (m, 2H), 3.78 (s, 2.01H), 3.79 (s, 0.99H), 5.62 (dd,  $J = 8.8, 15.8$  Hz, 0.67H), 6.01 (dd,  $J = 9.2, 15.8$  Hz, 0.33H), 6.32 (d,  $J = 15.8$  Hz, 0.67H), 6.51 (d,  $J = 15.6$  Hz, 0.33H), 6.80 (d,  $J = 8.8$  Hz, 1.34H), 6.83 (d,  $J = 9.0$  Hz, 0.66H), 7.21 (d,  $J = 8.8$  Hz, 1.34H), 7.28 (d,  $J = 8.8$  Hz, 0.66H);  $^{13}\text{C}$

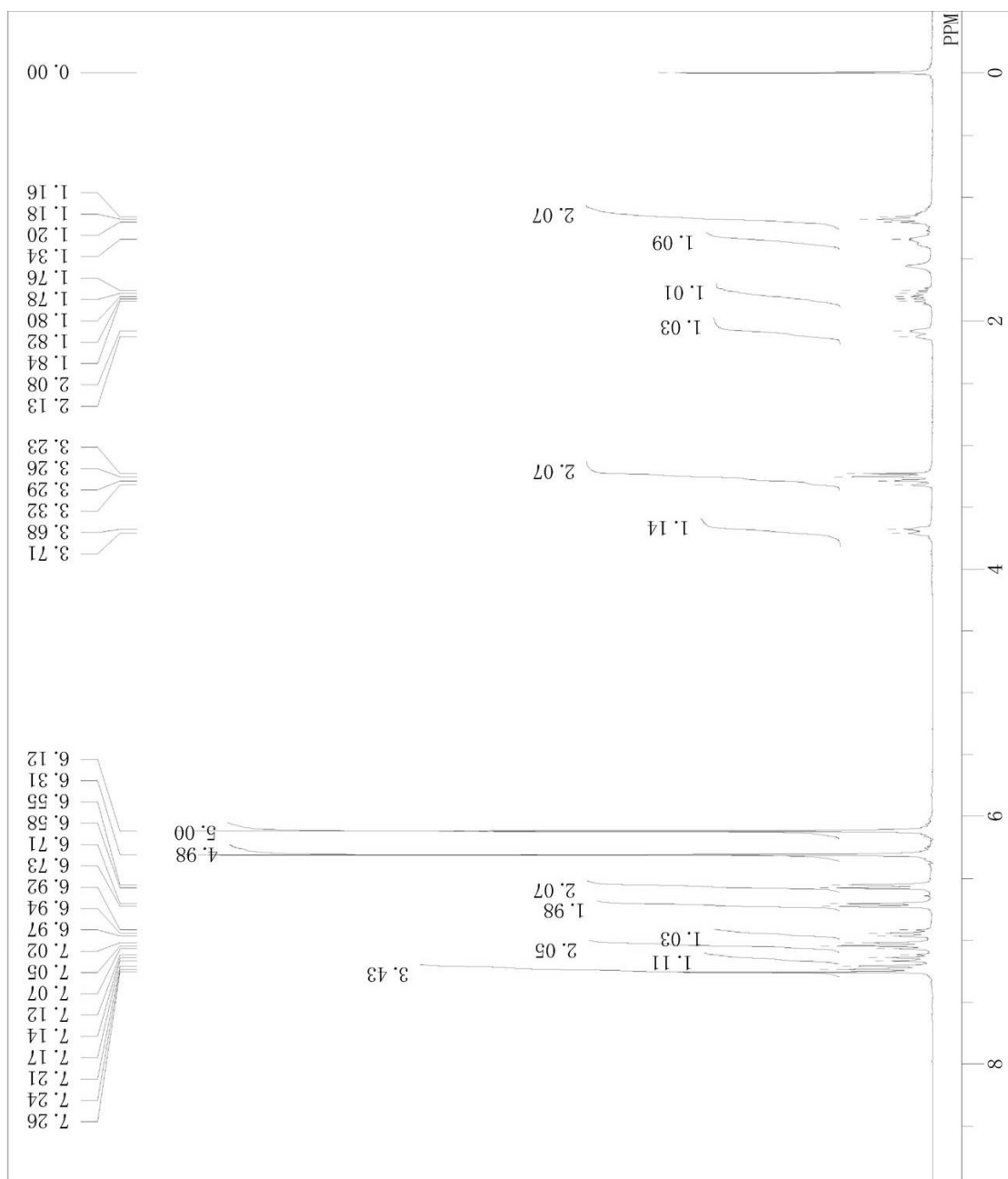
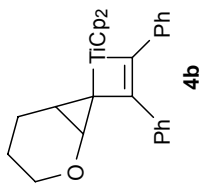
NMR 14.8, 19.4, 20.1, 21.4, 22.6, 22.9, 23.2, 27.7, 55.2, 55.3, 113.8, 113.9, 125.5, 126.0, 126.5, 126.6, 130.6, 130.9, 131.2, 133.1, 158.2; IR (neat) 3003, 2927, 2852, 1607, 1511, 1463, 1447, 1294, 1250, 1175, 1106, 1037, 1005, 958, 828, 802, 751; Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O: C, 84.16; H, 8.83. Found: C, 84.46; H, 8.94.

**7-[1-(*p*-Methoxyphenyl)ethenyl]bicyclo[4.1.0]heptane (6g')**: <sup>1</sup>H NMR 0.77-0.98 (m, 1H), 0.98-1.35 (m, 5H), 1.35-1.48 (m, 2H), 1.64-1.86 (m, 3H), 3.82 (s, 3H), 5.16 (dd, *J* = 1.9, 1.9 Hz, 1H), 5.60 (dd, *J* = 1.8, 1.9 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H); IR (neat) 3000, 2930, 2855, 1606, 1509, 1297, 1247, 1177, 1037, 835.

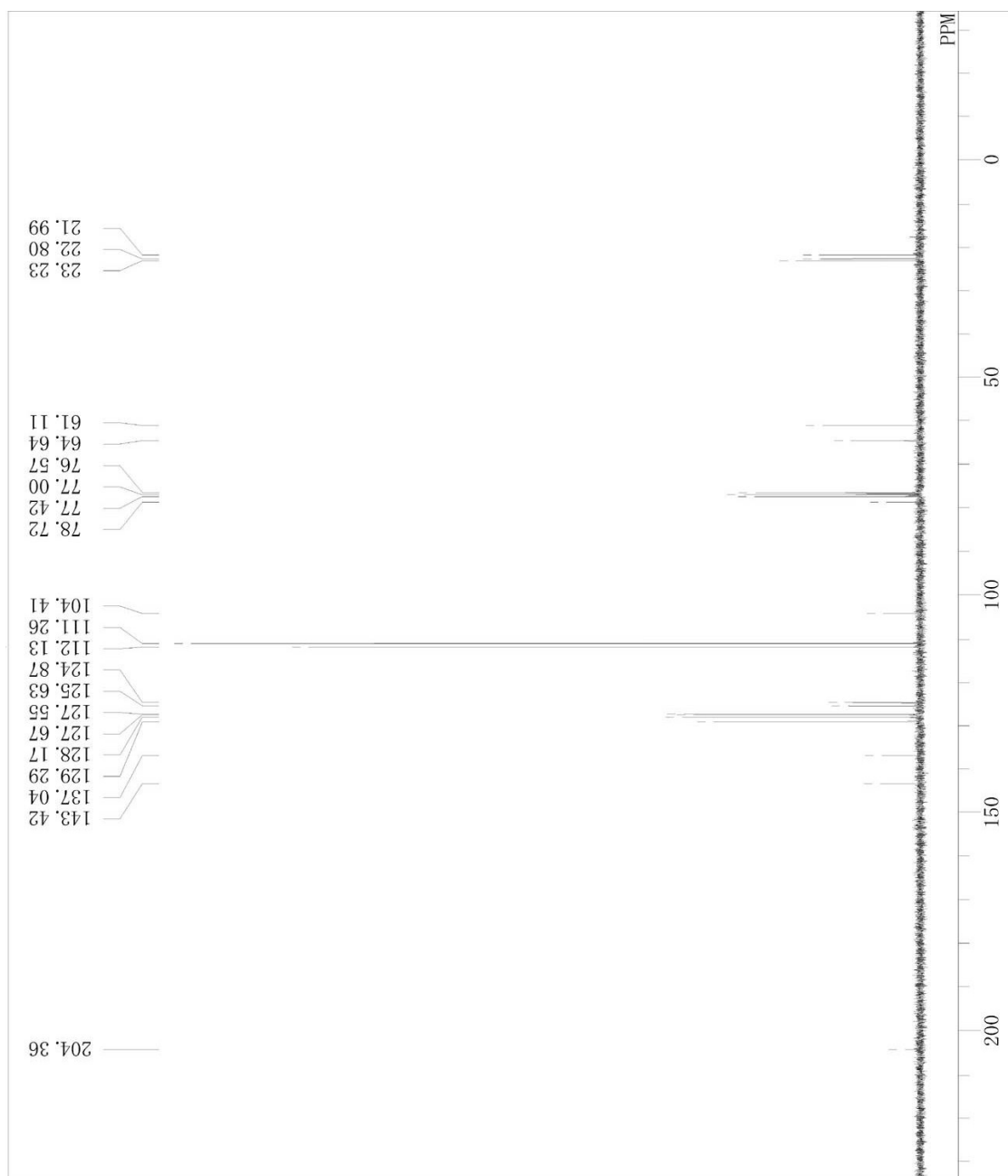
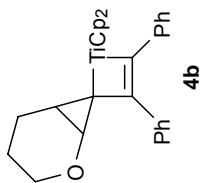
**Unexpected Conformation of Cyclohexane Ring in 4a shown by X-ray crystallographic analysis:** The cyclohexane ring (C4-C5-C6-C7-C8-C9) adopts a nearly ideal half-chair conformation, as shown by the Cremer and Pople ring puckering parameters of  $Q = 0.519(4) \text{ \AA}$ ,  $\theta = 128.9(4)^\circ$  and  $\phi = 27.6(5)^\circ$ .

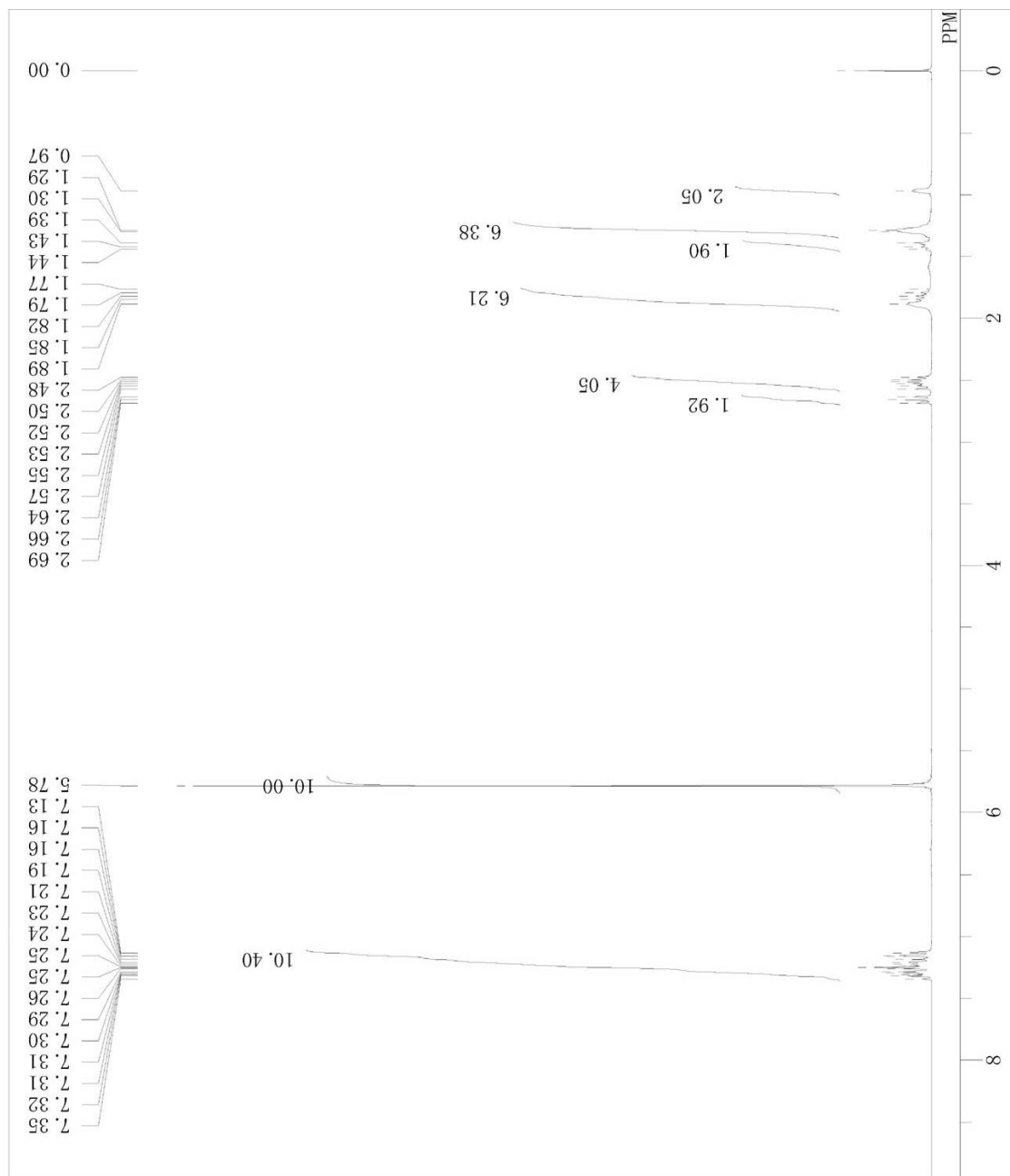
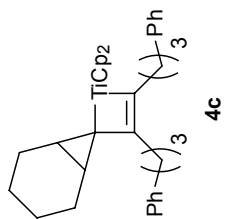


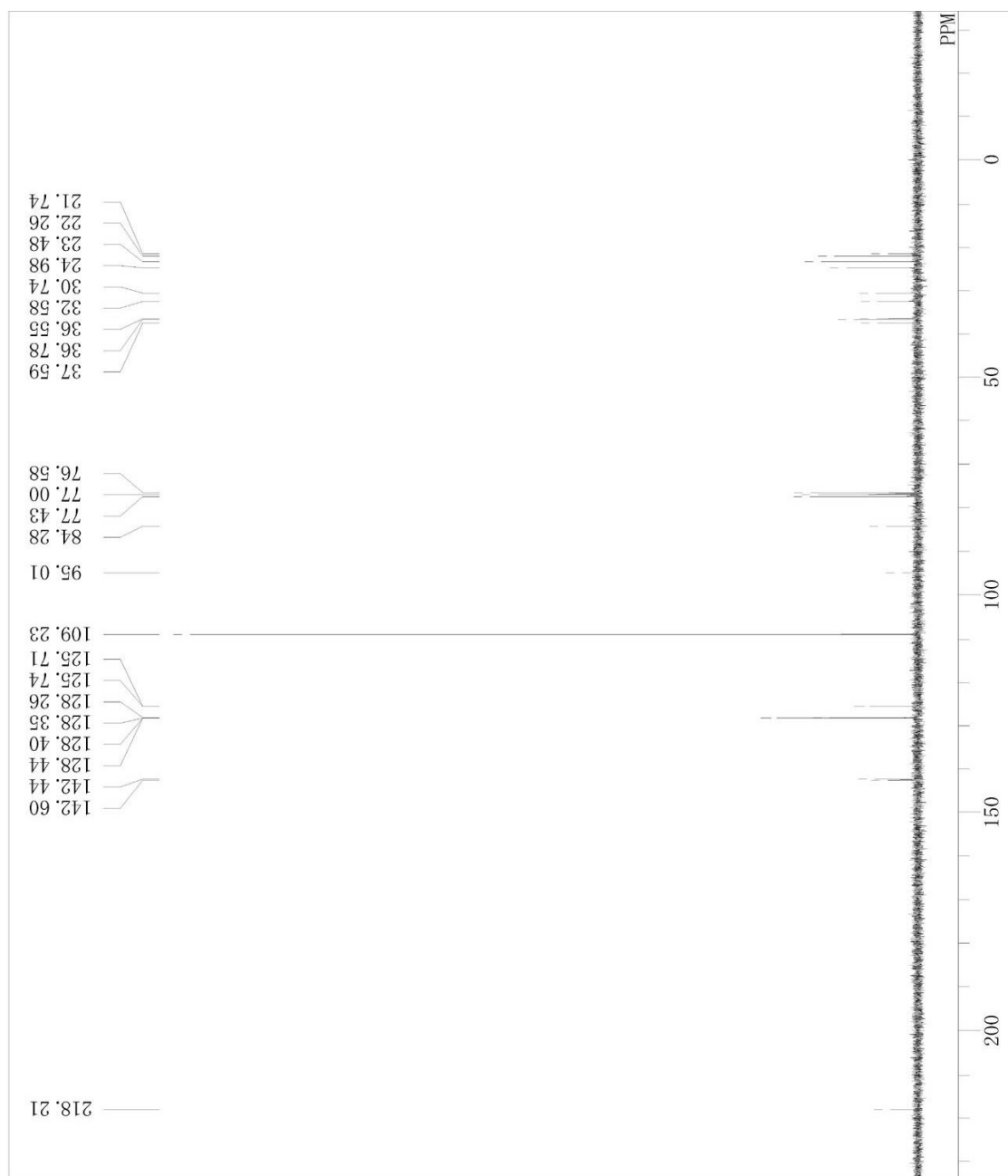
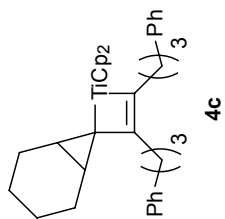


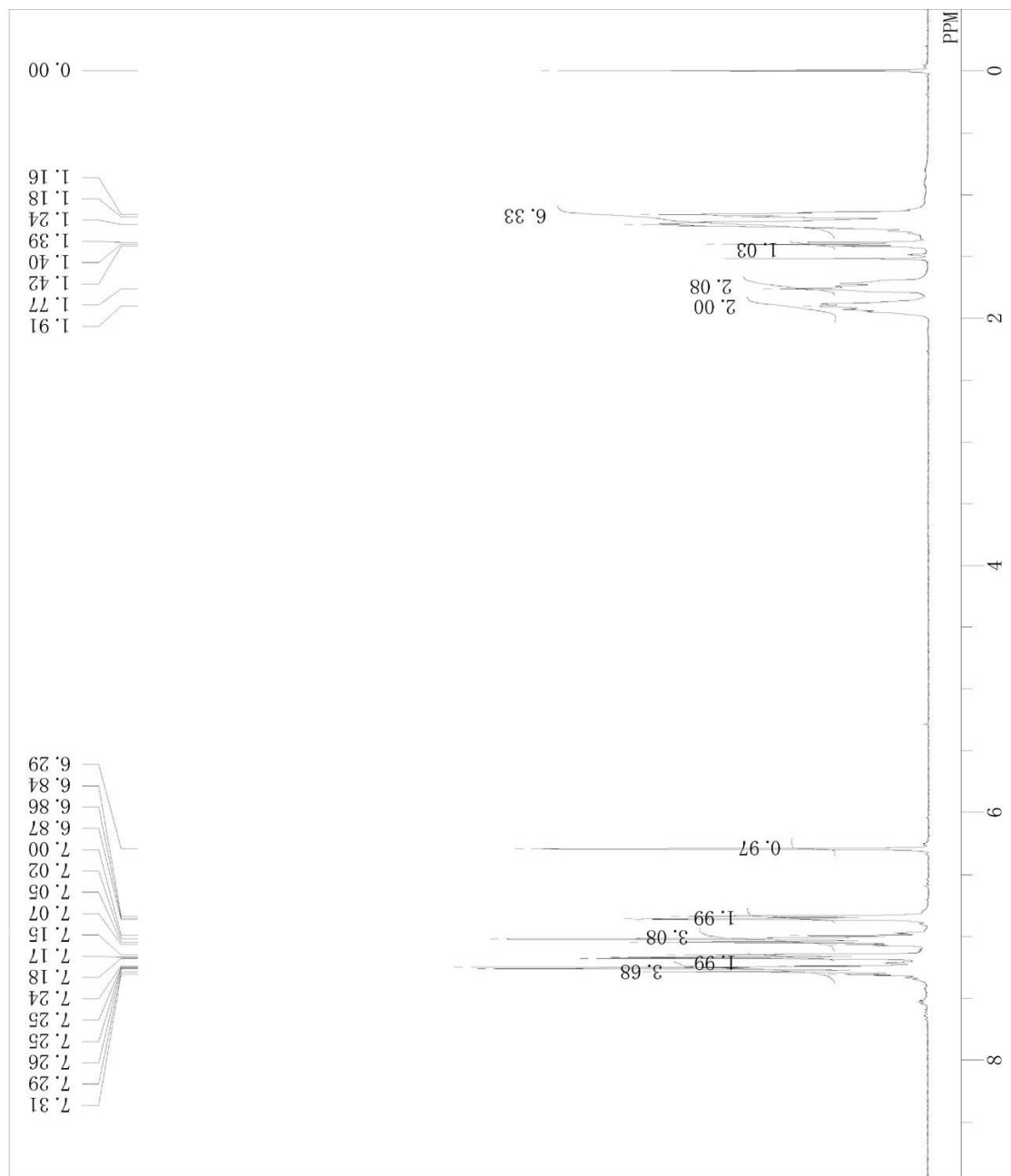
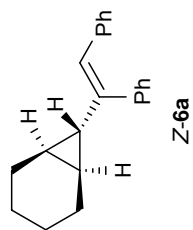


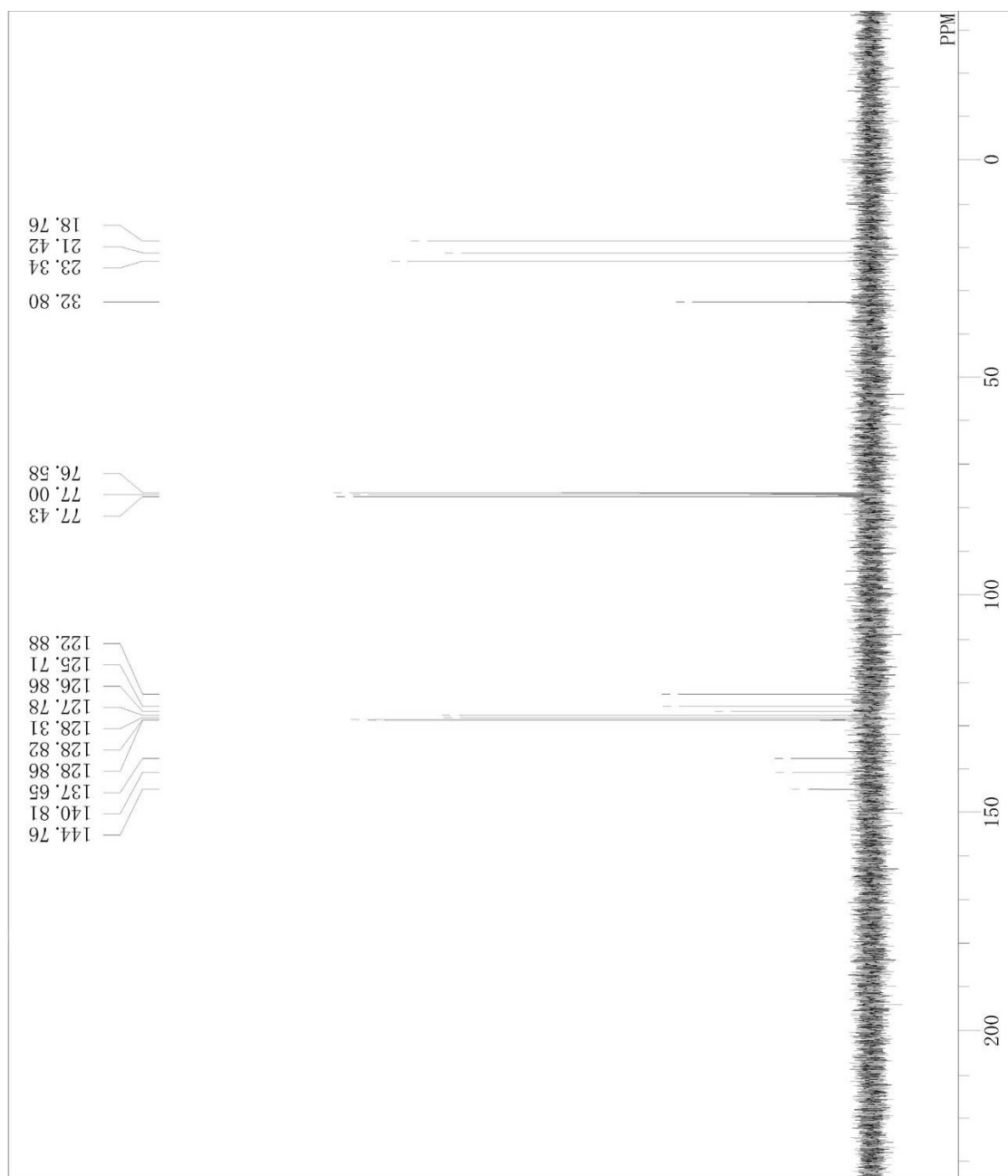
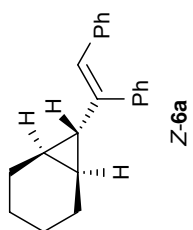


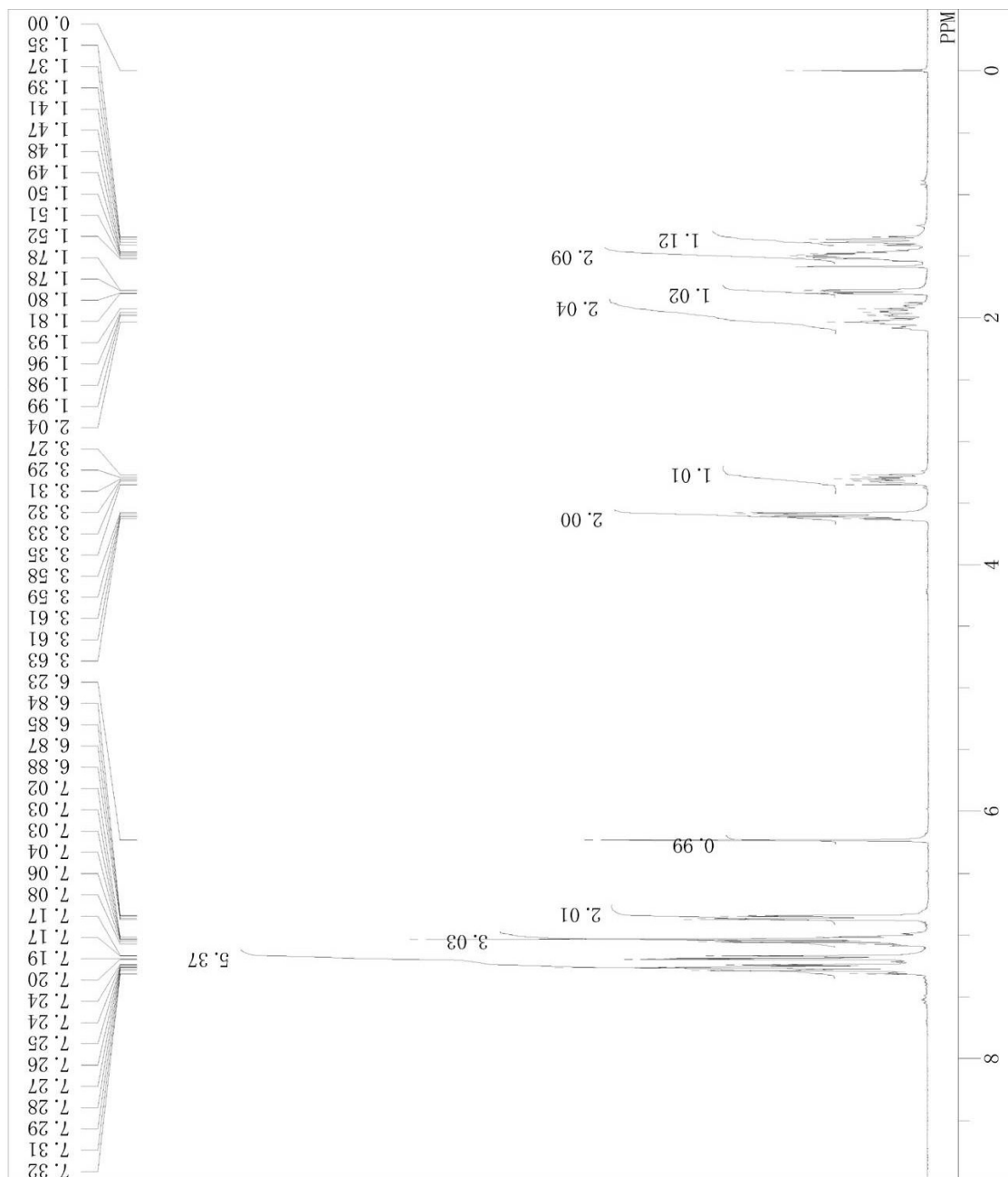
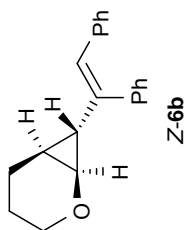


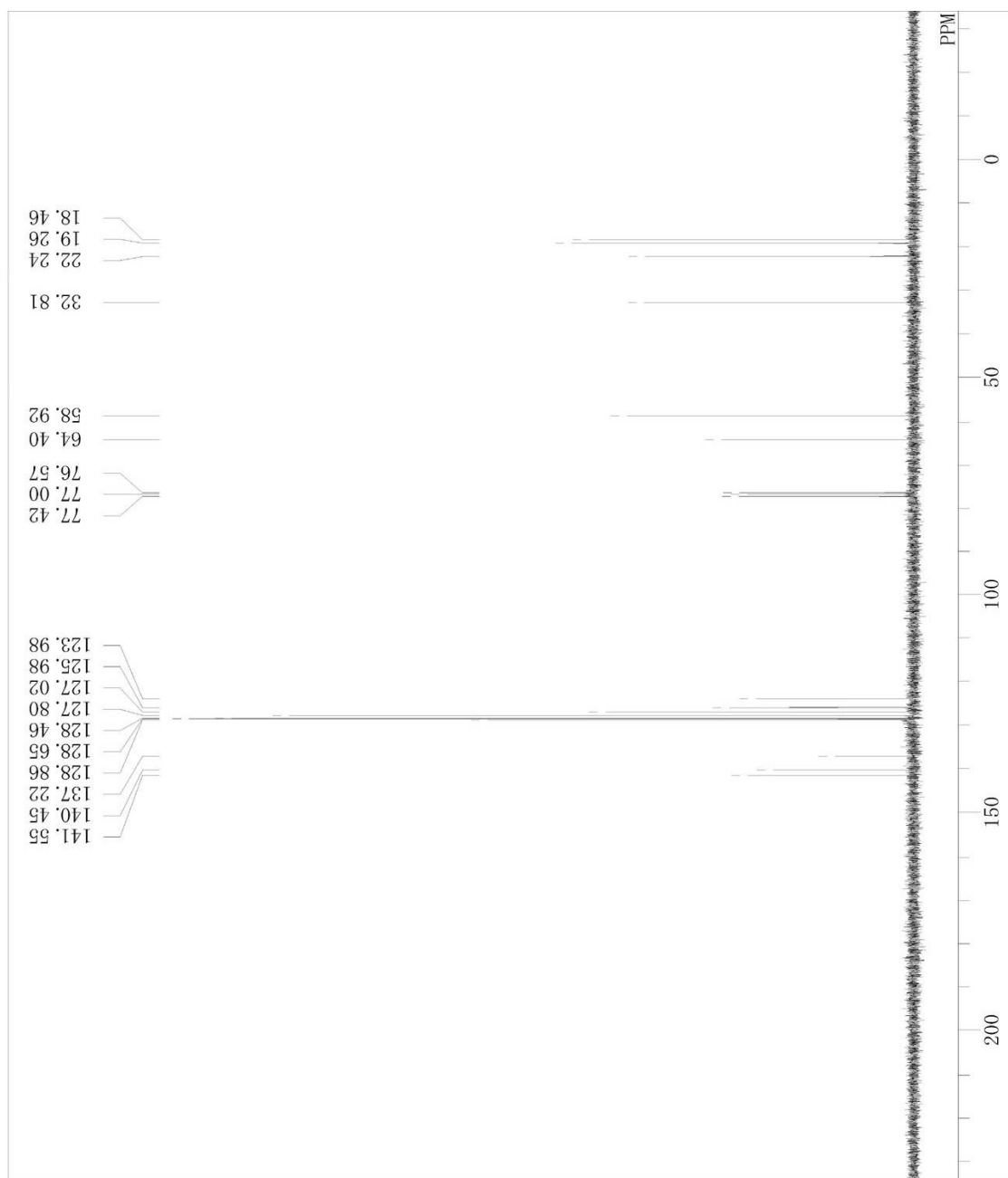
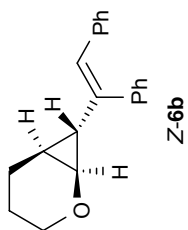


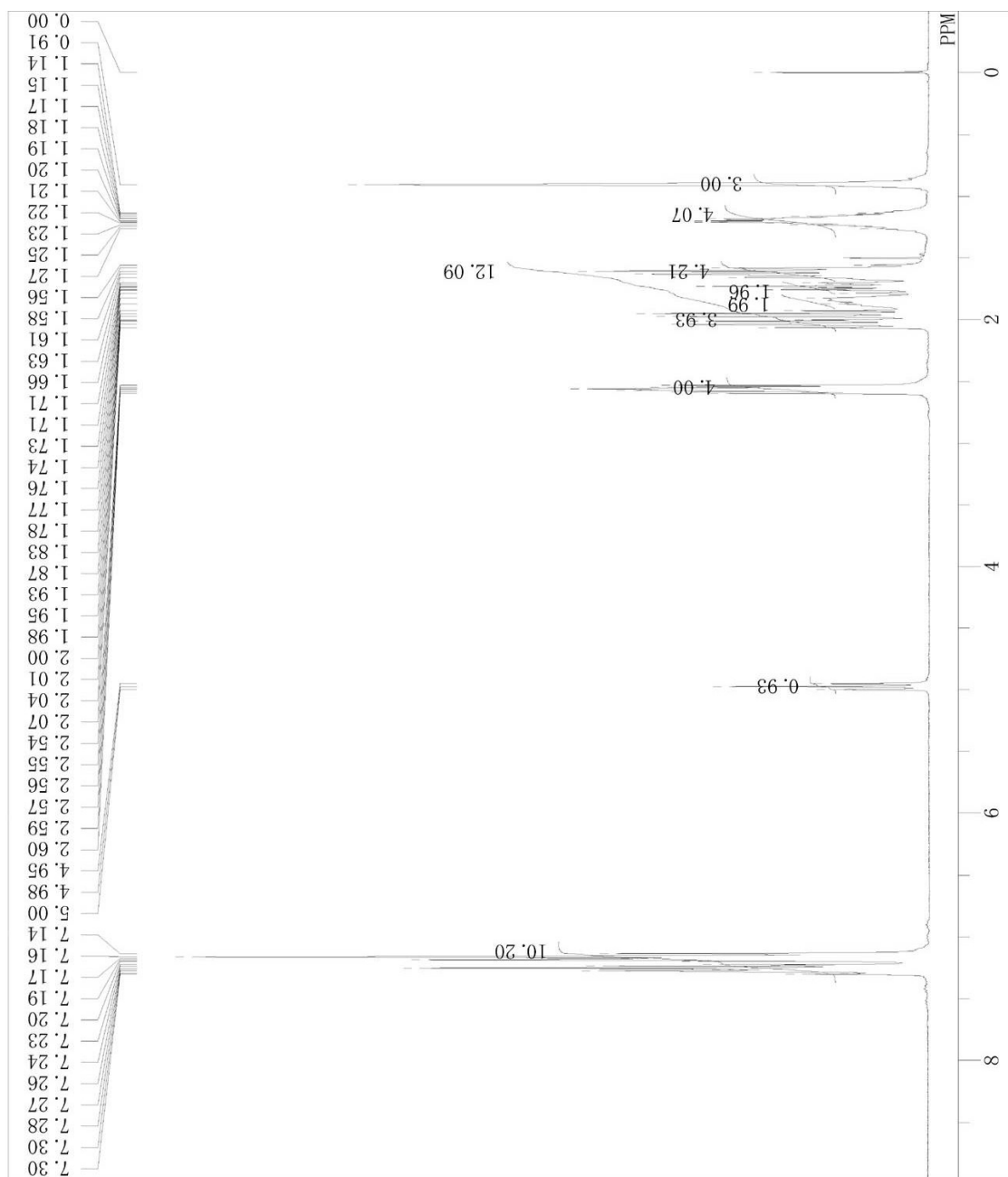
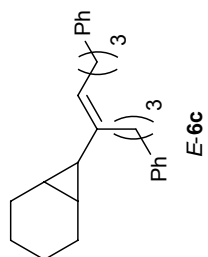




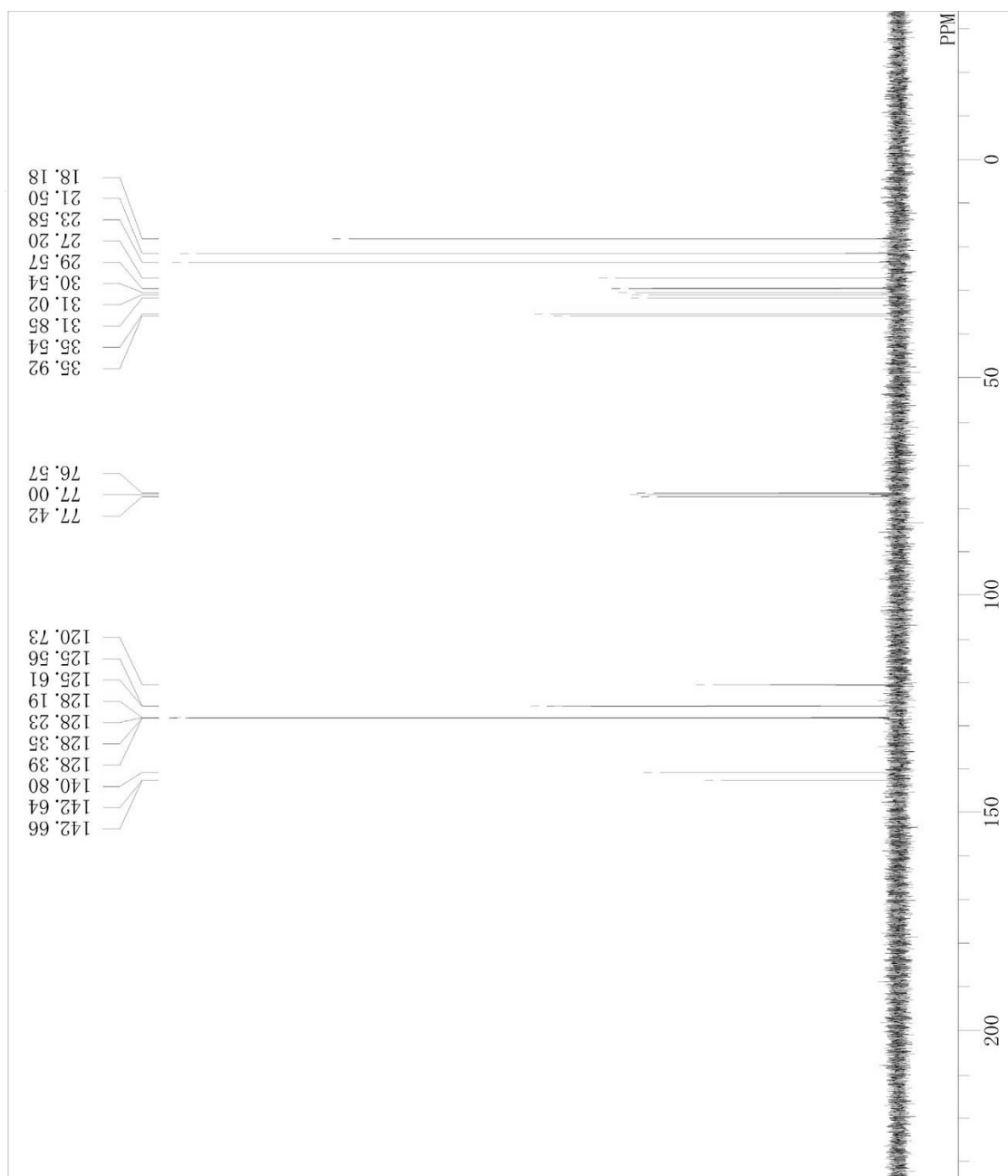
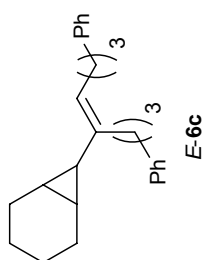


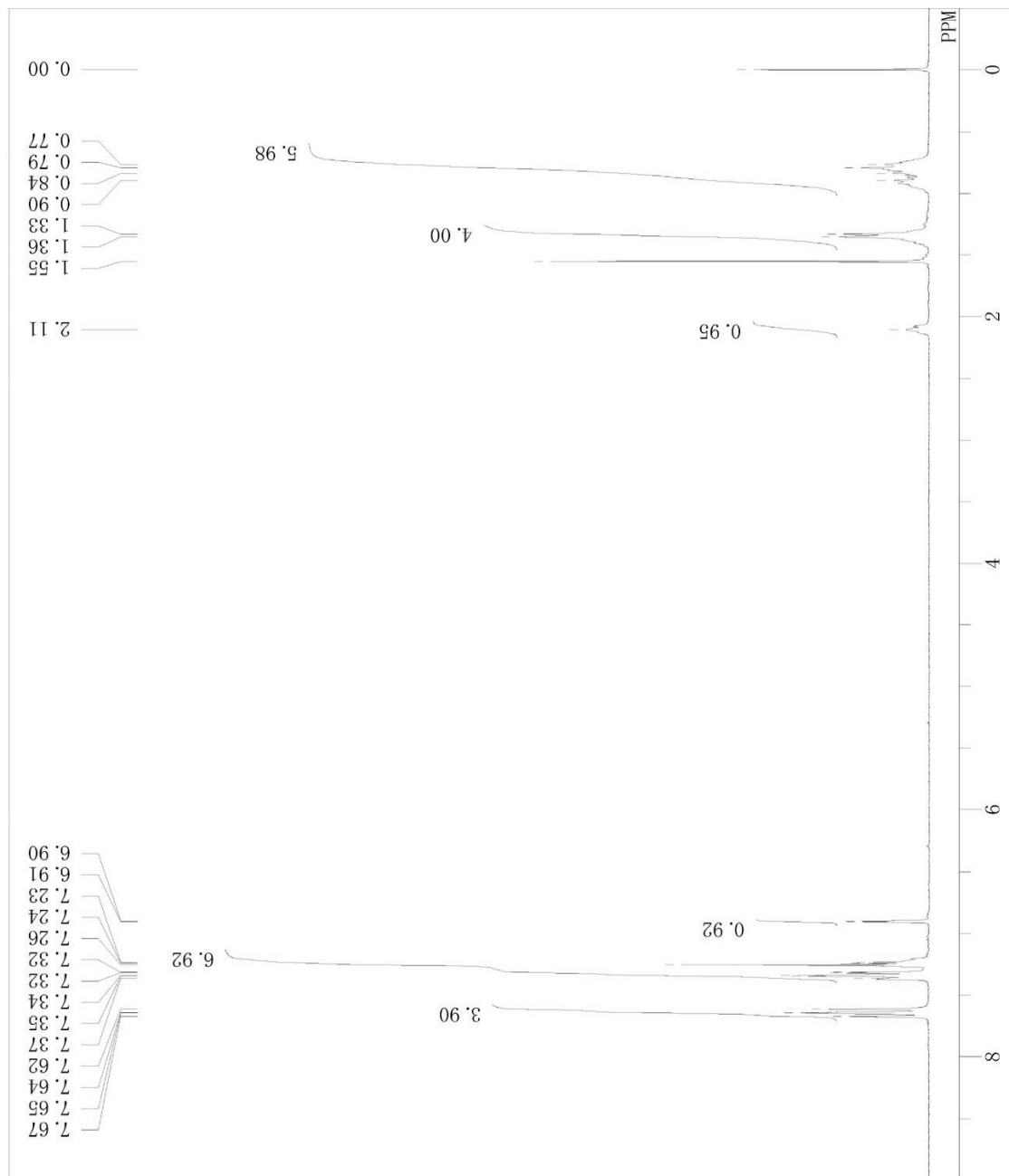
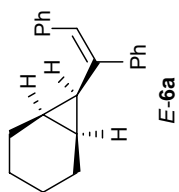


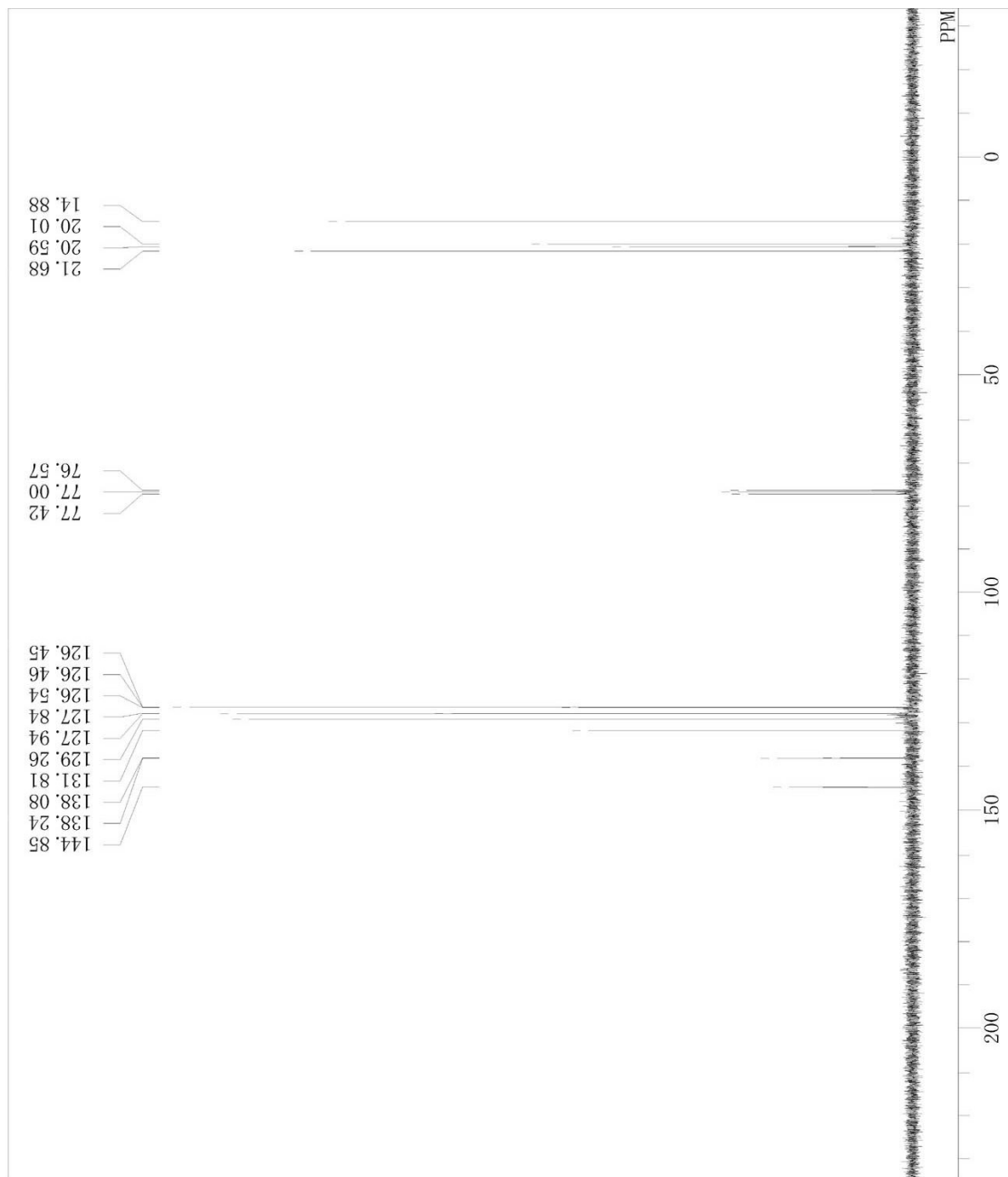
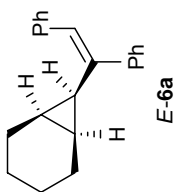


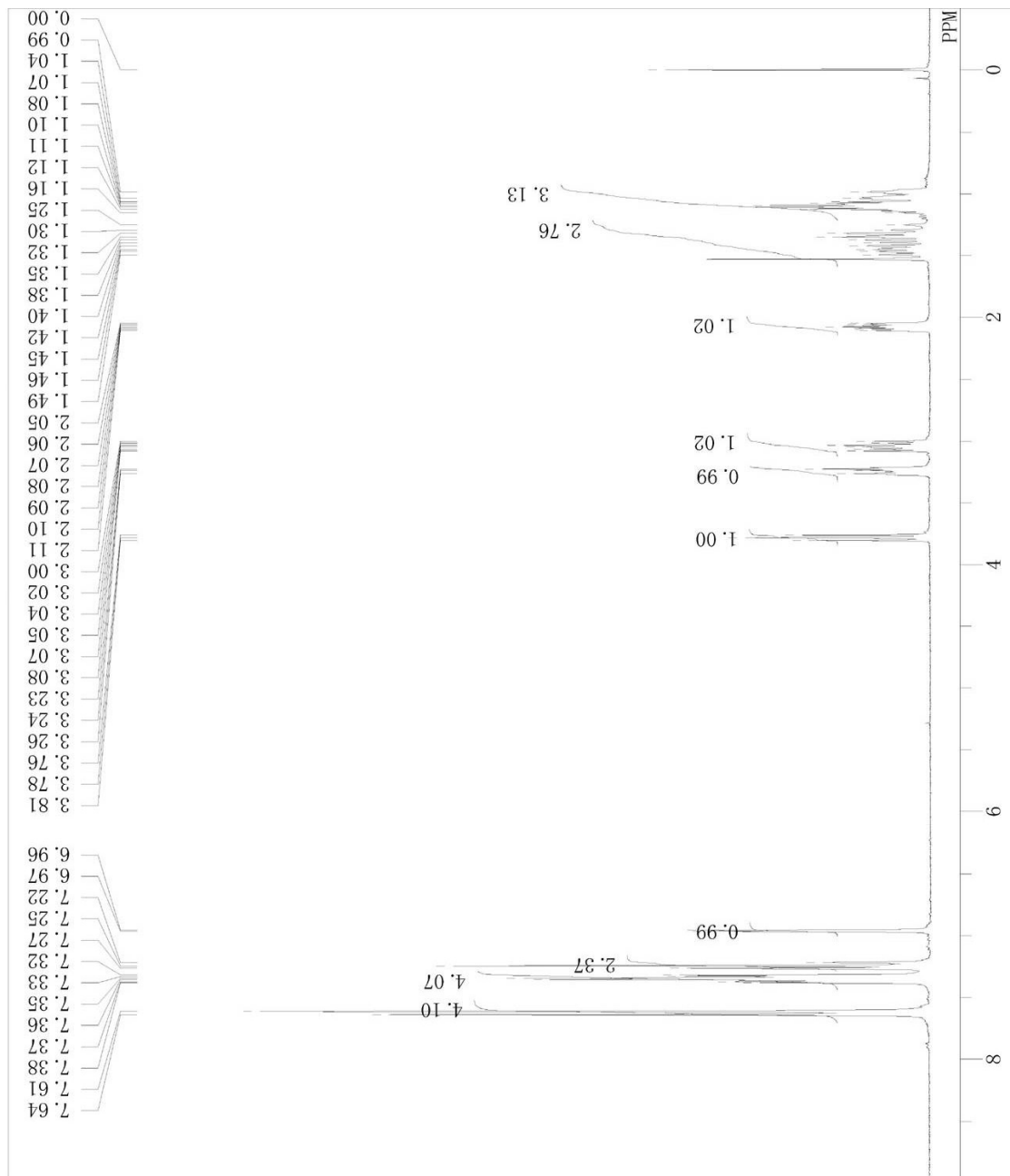
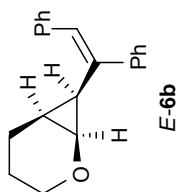


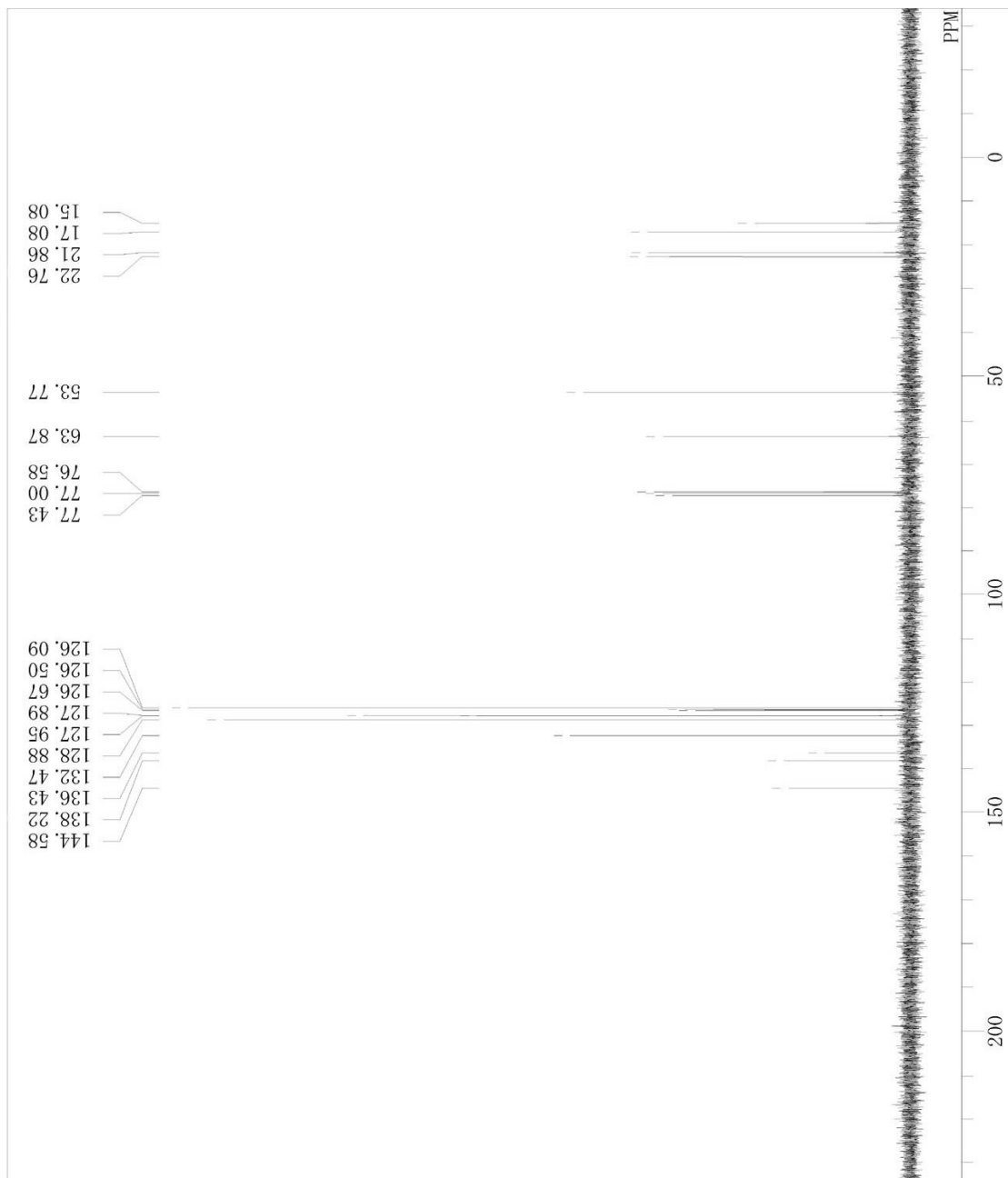
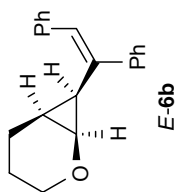


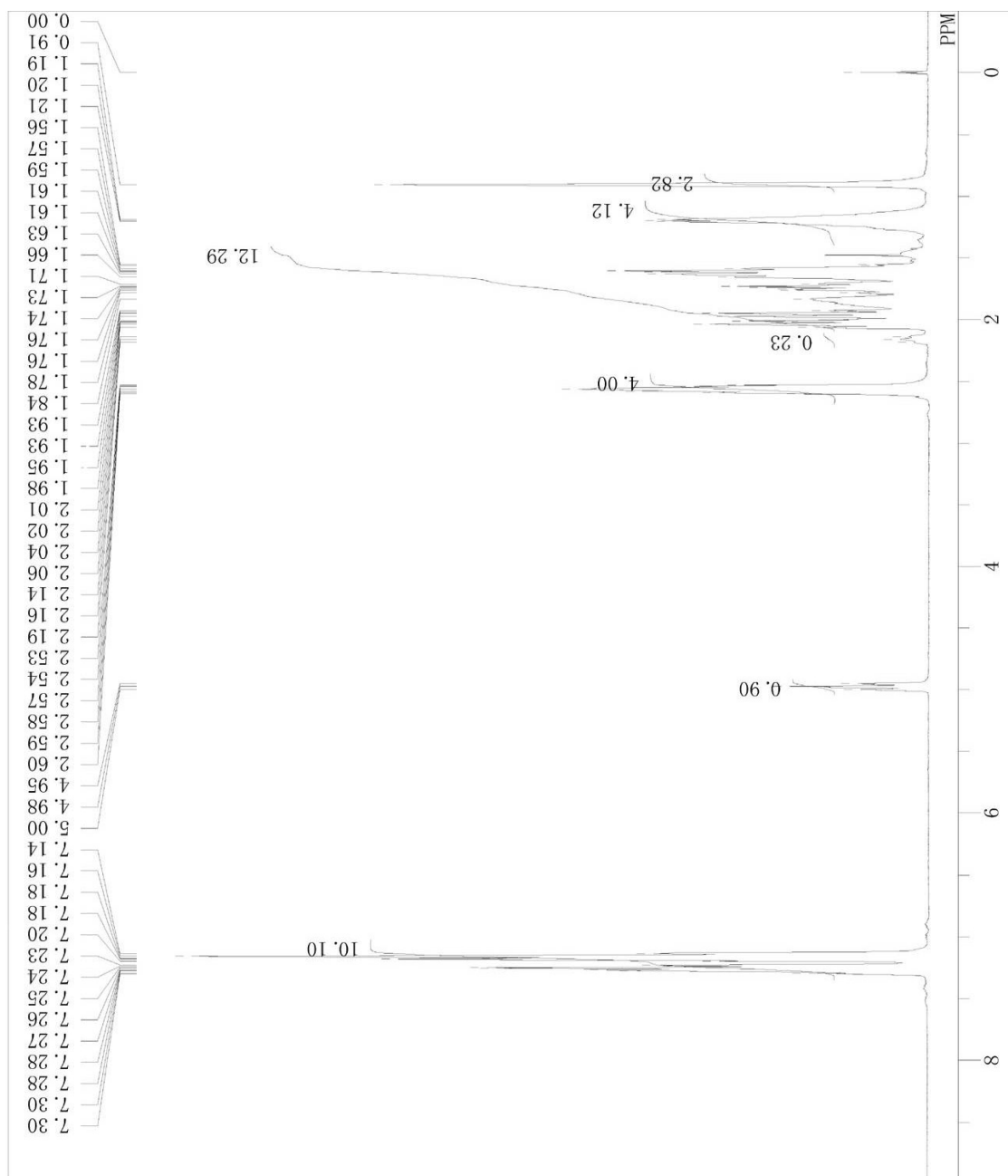
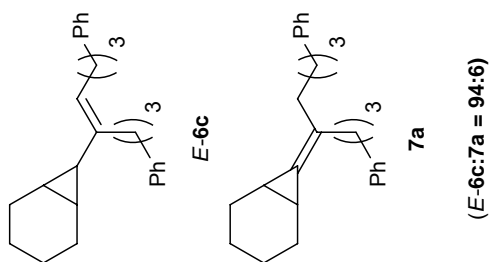


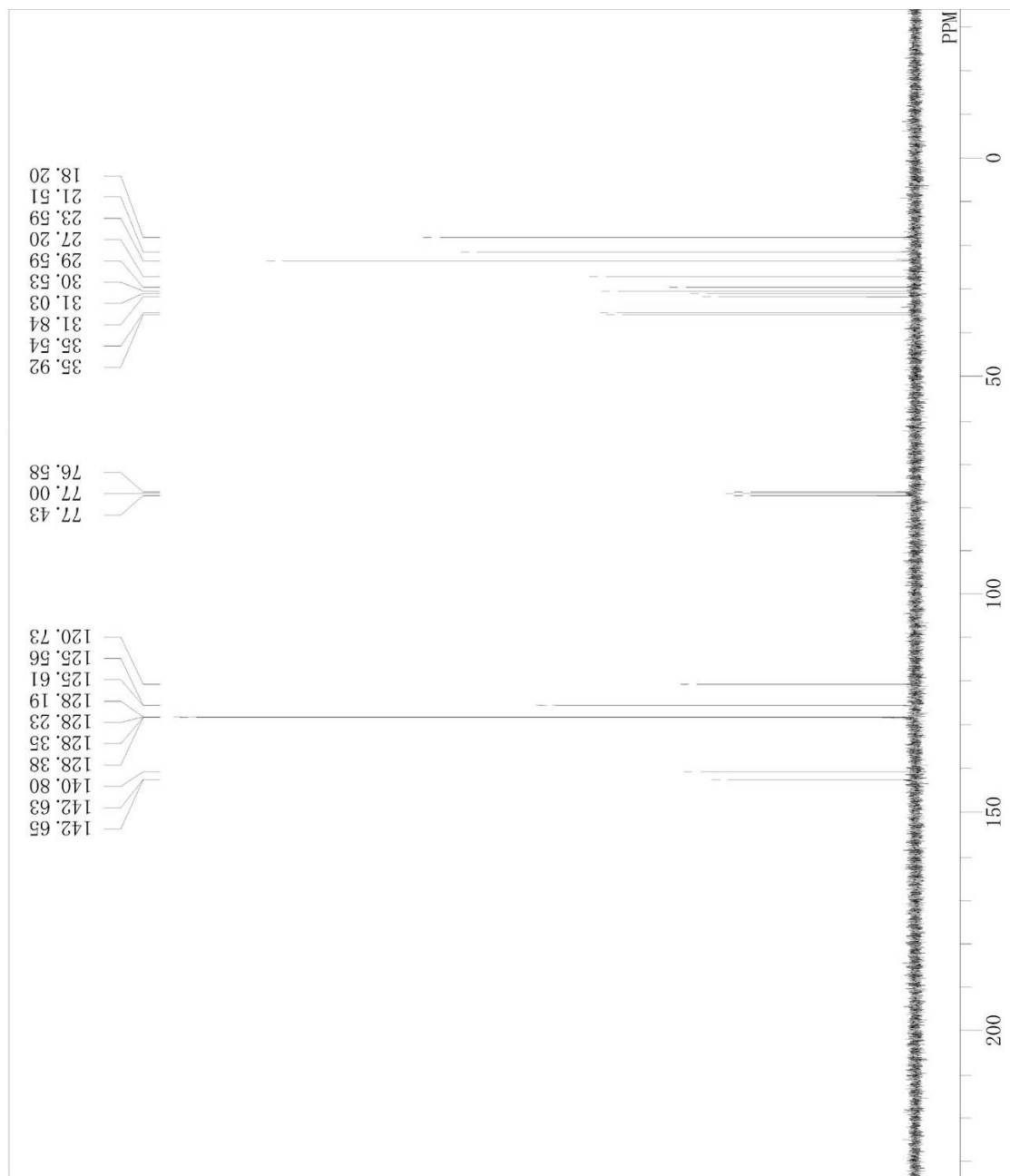
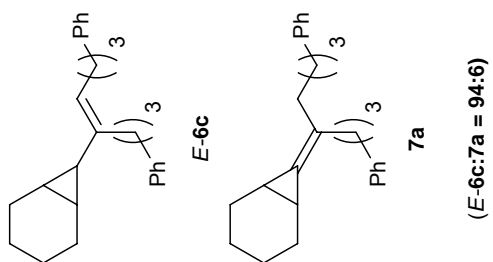


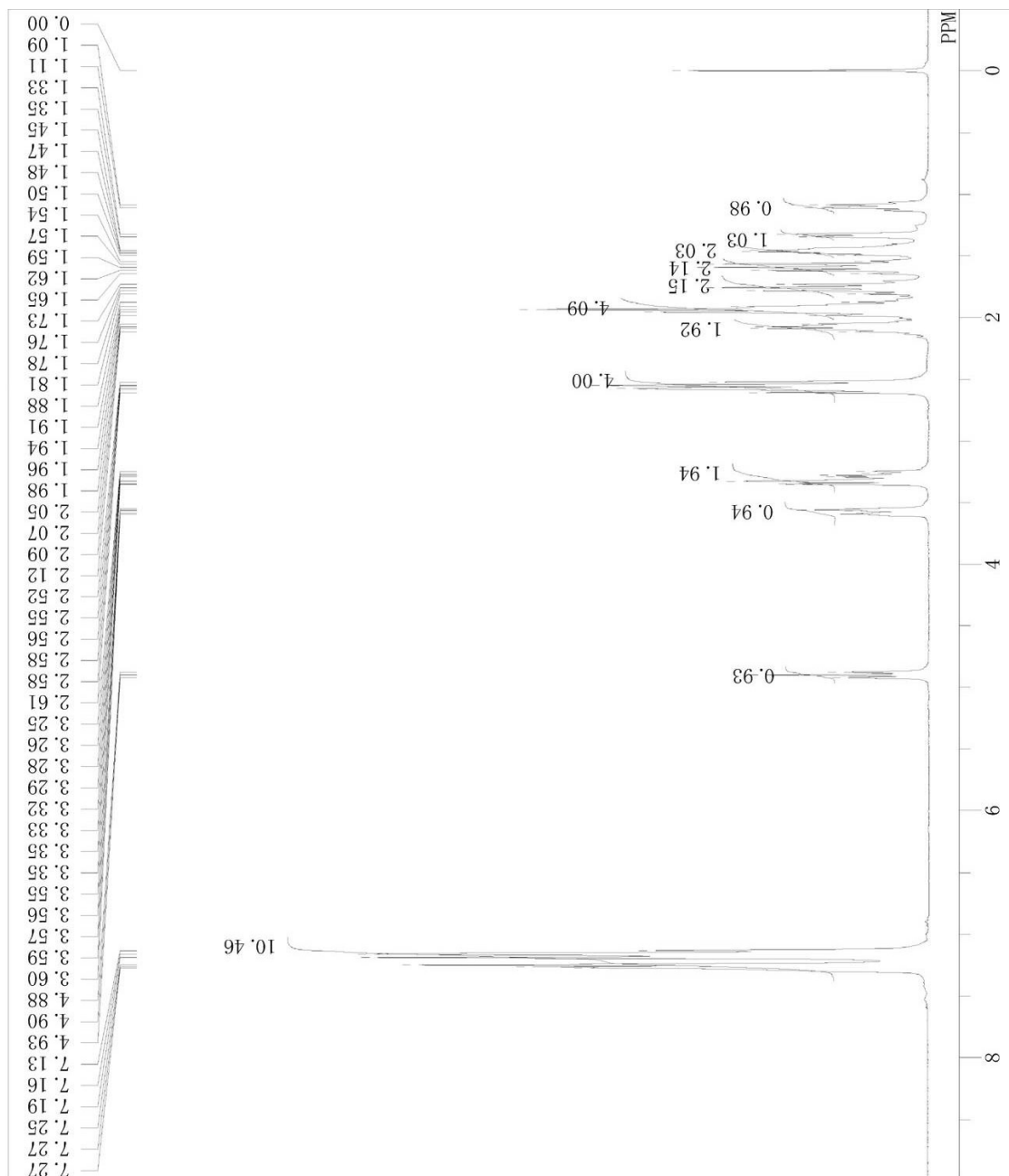
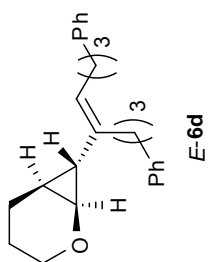




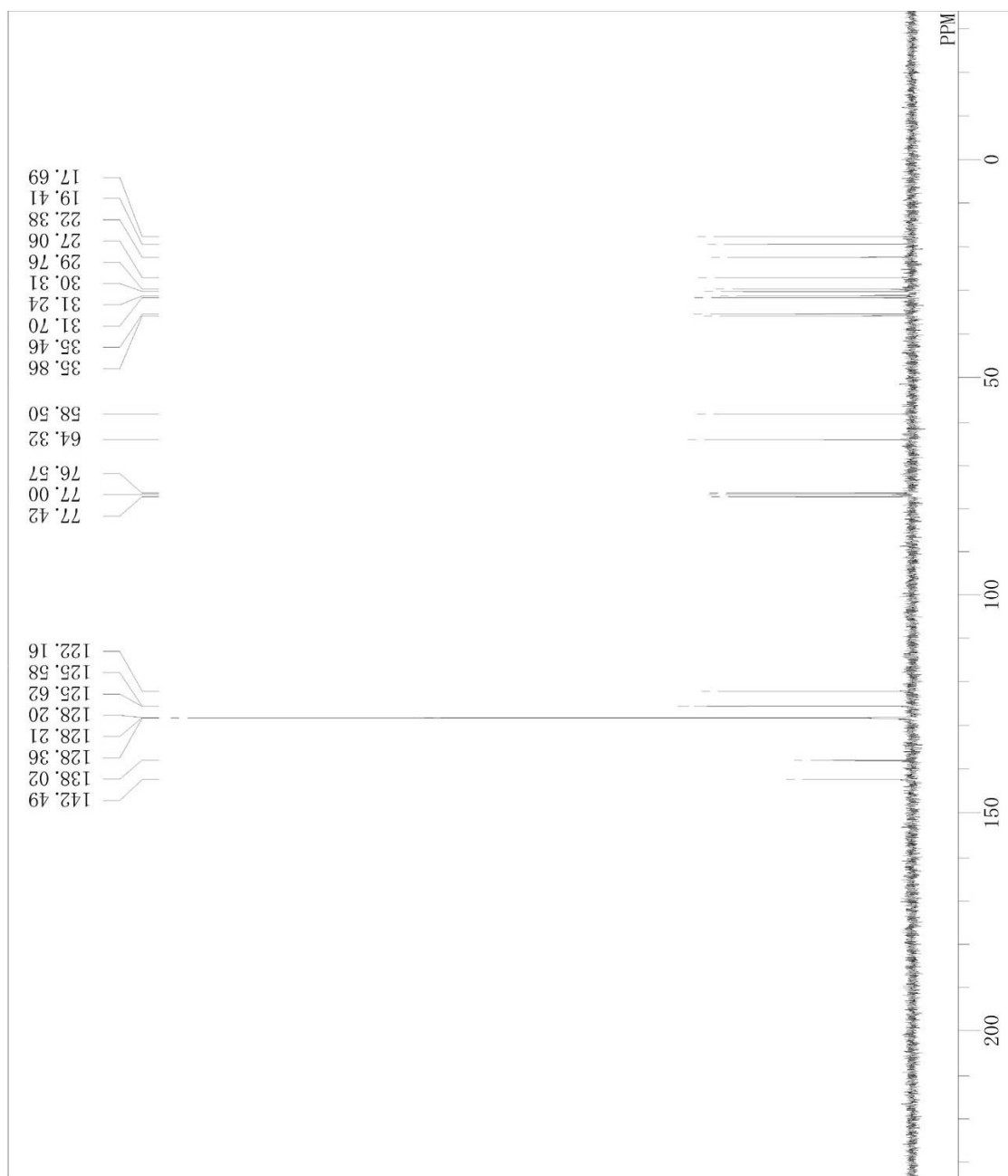
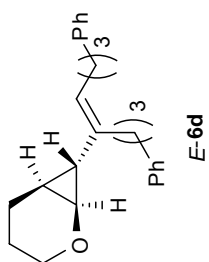


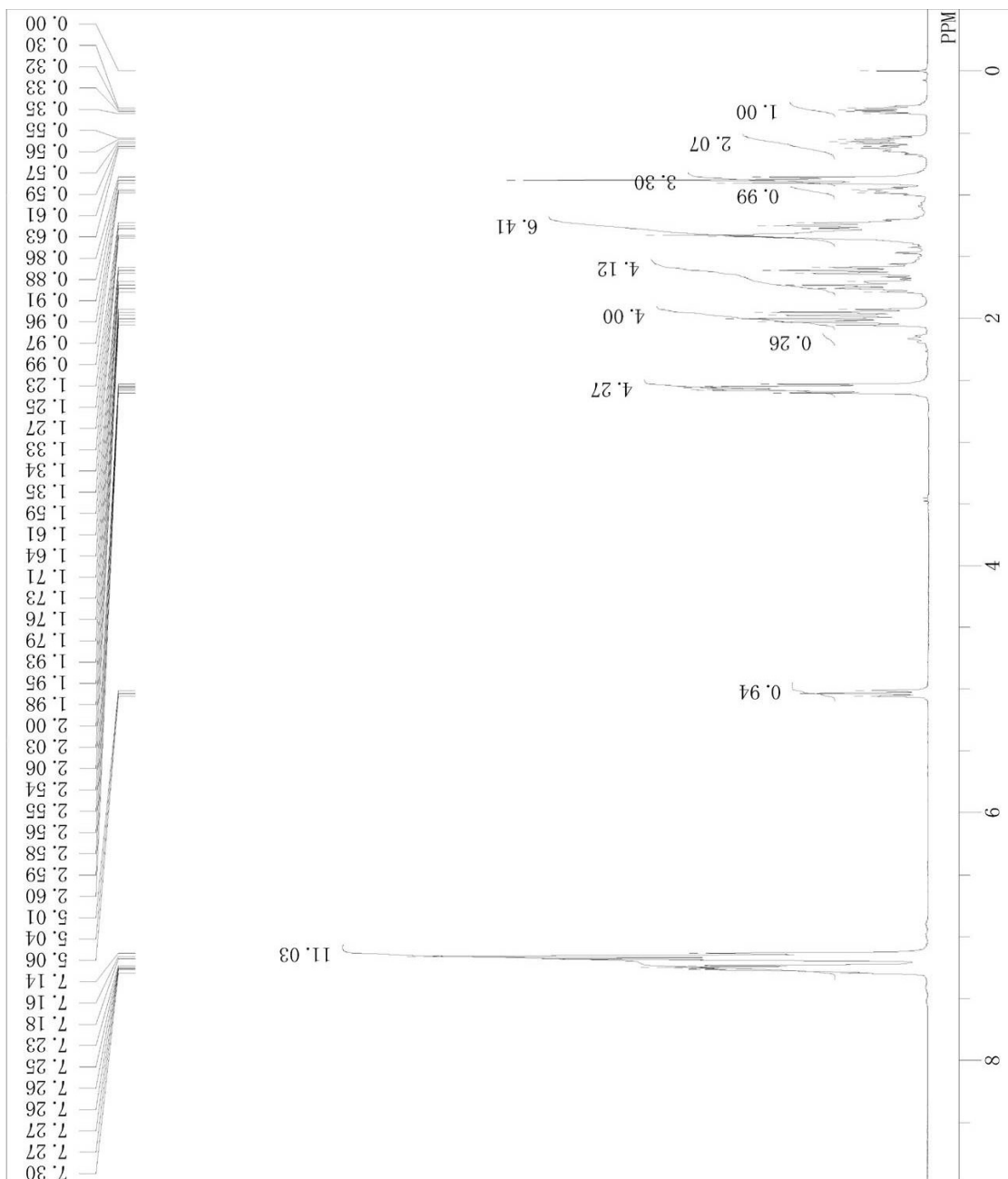
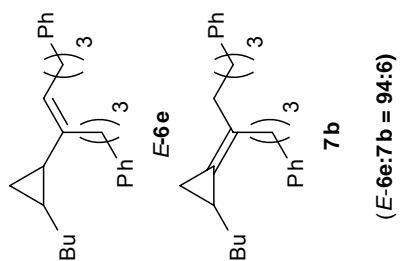


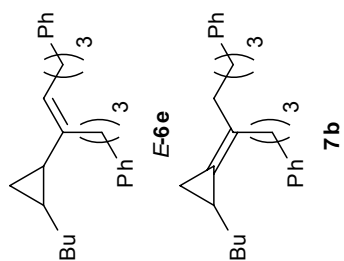




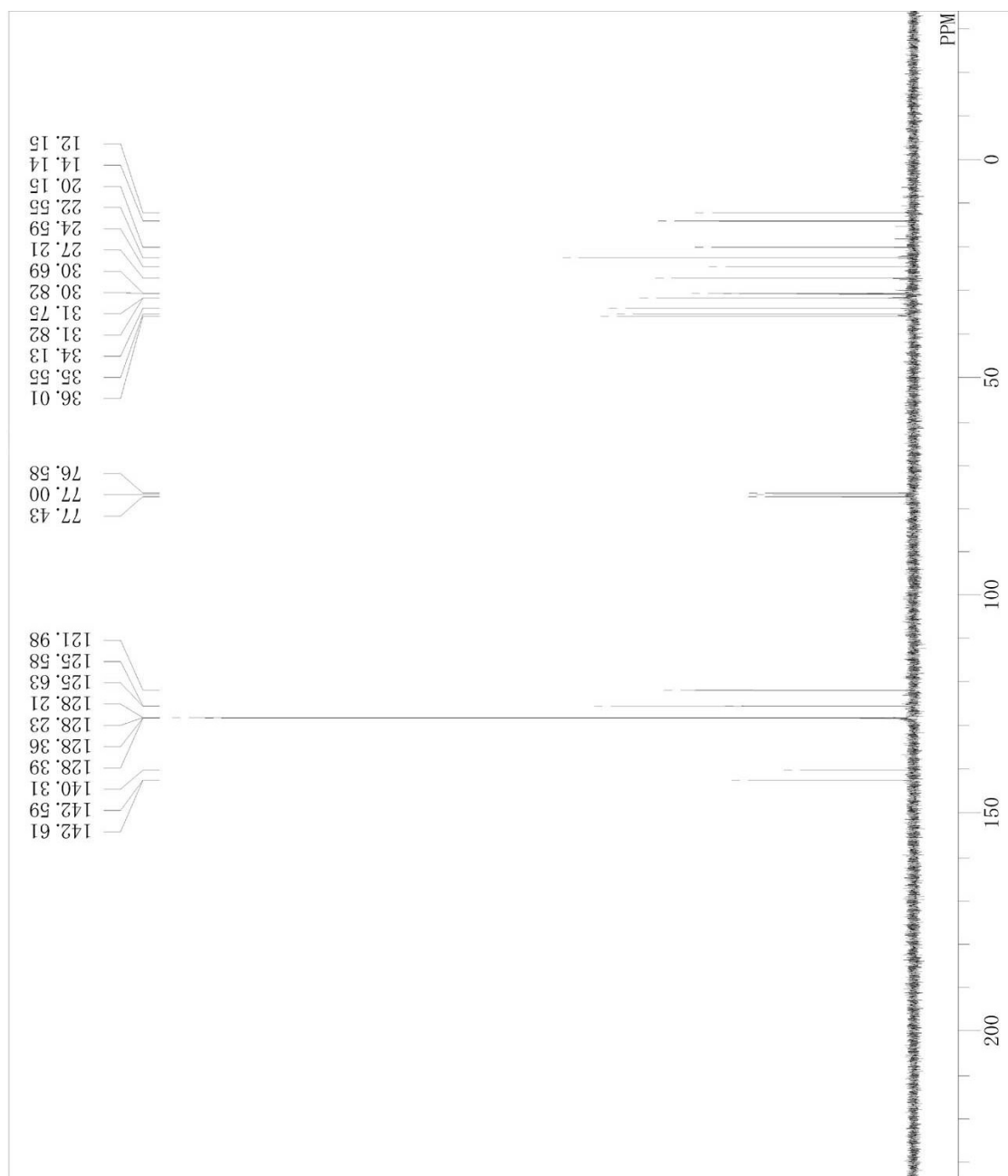


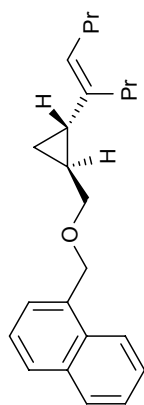






(*E*-6e:7b = 94:6)





*trans-E-6f*

