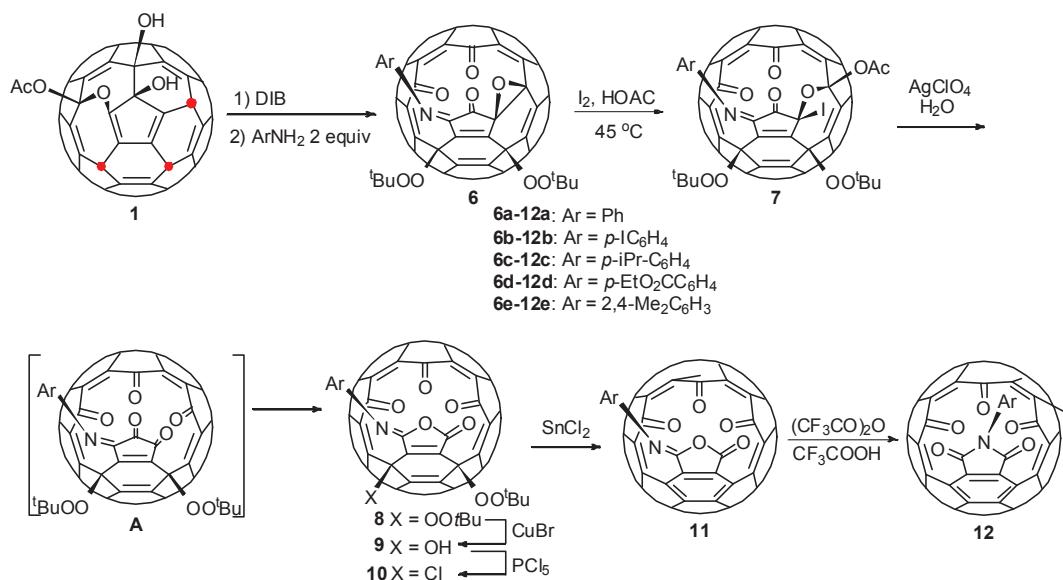


# Molecular containers with a dynamic orifice: open-cage fullerenes capable of encapsulating either H<sub>2</sub>O or H<sub>2</sub> under mild conditions

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## Experimental Section

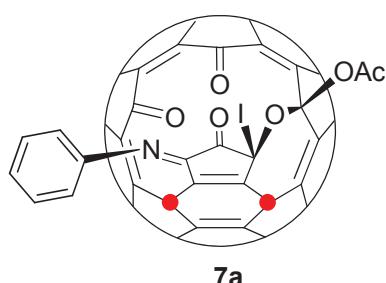
All the reagents were used as received. Dichloromethane was distilled over phosphorus pentoxide. Benzene and toluene were distilled over sodium. Other solvents were used as received. Compound **1** was prepared according to reported procedure<sup>10e</sup>. The reactions were carried out under atmosphere condition. NMR spectra were recorded at room temperature (298 K). Chemical shifts are given in ppm relative to TMS or CDCl<sub>3</sub> (for <sup>13</sup>C NMR). ESI-HRMS spectra were recorded with CHCl<sub>3</sub>/CH<sub>3</sub>OH or CDCl<sub>3</sub>/CH<sub>3</sub>OH as the solvent; positive-mode spectra were recorded, unless otherwise noted. FTIR spectra were recorded in the microscope mode. Chromatographic purifications were carried out with silica gel of mesh 200–300. **Caution:** Peroxides are potentially explosive compounds; care must be taken to avoid possible explosion.

## General Procedure for Preparation of Compounds **7a-7e**

Iodobenzene diacetate (0.119 mmol) was added to the solution of compound **1** (0.070 mmol) in benzene (25 mL) at 30 °C. Progress of the reaction was monitored by TLC. After compound **1** was completely consumed about 60 minutes, aniline (0.140 mmol) dissolved in benzene (5 mL) was slowly dropped into the reaction mixture. Progress of the reaction was monitored by TLC. After the desired product **6** reached its maximum yield (about 20 min), the temperature was raised to 45 °C and 1.0 g iodine was added into the reaction mixture. After compound **7** reached its maximum yield as indicated by TLC (less than 10 min), the reaction mixture was directly chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (v/v) = 100 : 1. The second red band was collected and evaporated to give **7**.

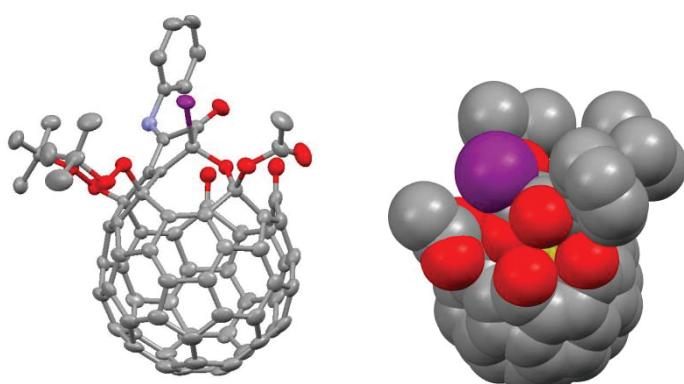
| Entry | <b>1</b> (mg) | Product   | Ar  | mg, (yield %) |
|-------|---------------|-----------|---|---------------|
| 1     | 706           | <b>7a</b> | Ph  | 386 (48%)     |
| 2     | 344           | <b>7b</b> | <i>p</i> -IC <sub>6</sub> H <sub>4</sub>                  | 150 (35%)     |
| 3     | 700           | <b>7c</b> | <i>p</i> - <sup>i</sup> Pr-C <sub>6</sub> H <sub>4</sub>  | 362 (44%)     |
| 4     | 700           | <b>7d</b> | <i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 305 (36%)     |
| 5     | 350           | <b>7e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>                 | 189 (47%)     |

**Table 1.** Yields of compounds **7a**–**7e**



**7a**

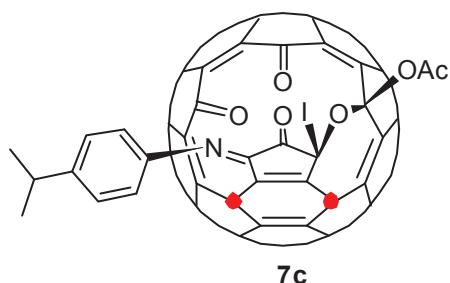
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.56 – 7.54 (2H), 7.50 - 7.46 (2H), 7.30 – 7.28 (1H), 2.32 (s, 3H), 1.33 (s, 9H), 1.29 (s, 9H).. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): All signals represent 1C except noted. δ: 186.84, 183.87, 179.45, 166.93, 150.91, 149.99, 149.81, 149.74, 149.58, 149.49, 149.45, 149.19, 149.12(2C), 149.11(2C), 148.64, 148.50, 148.14, 148.11, 148.08, 147.95, 147.82, 147.58, 147.48, 147.16, 146.29, 146.14, 146.04, 145.47, 145.18, 145.14, 144.65, 144.64, 144.59, 144.30, 143.50, 143.47, 143.45, 143.35, 142.69, 142.65, 142.43, 141.82, 141.76, 141.51, 141.30, 141.22, 140.89, 140.64, 140.39, 139.99, 138.09, 137.36, 136.09, 133.40, 133.20, 131.57, 128.45(2C), 125.87, 120.86(2C), 108.24, 87.12, 82.34, 82.05, 82.02, 59.15, 26.95(3C), 26.69(3C), 22.00 . FT-IR (microscope): 3324, 2928, 1779, 1749, 1580, 1497, 1364, 1191, 1126, 1007, 980, 936, 731 cm<sup>-1</sup>. ESI-HRMS: C<sub>76</sub>H<sub>27</sub>NIO<sub>10</sub> (M + H<sup>+</sup>) calcd 1240.06742 , found 1240.06552 .



**Figure 1** Single-crystal X ray structure of **7a**. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen; purple, iodine

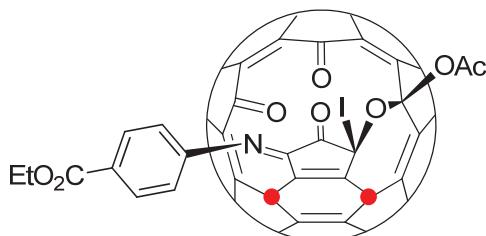
Crystal of **7a** suitable for X-ray diffraction was obtained by slow evaporation in

toluene. Crystal data: triclinic, space group P1. Unit cell dimensions:  $a = 11.5690$  (13) Å,  $\alpha = 97.570$  (11)°,  $b = 12.6230$  (15) Å,  $\beta = 102.490$  (12)°,  $c = 20.413$  (3) Å,  $\gamma = 113.570$  (8)°, volume = 2587.1 (5) Å<sup>3</sup>. Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0900$ ,  $wR_2 = 0.1444$ . Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-905498.



7c

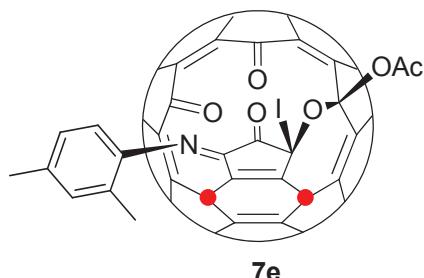
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$ : 7.57 (d,  $J = 8.0$  Hz, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H), 3.03 – 2.97 (m, 1H), 2.32 (s, 3H), 1.35 (s, 3H), 1.32 (s, 12H), 1.29 (s, 9H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 125 MHz): All signals represent 1C except noted.  $\delta$ : 186.59, 183.61, 179.34, 166.69, 150.05, 149.80, 149.63, 149.56, 149.42, 149.27(2C), 148.99, 148.91(3C), 148.32, 147.94(2C), 147.88, 147.77, 147.63, 147.60, 147.38, 147.29, 147.10, 146.96, 146.12, 145.93, 145.86, 145.26, 145.24, 145.17, 144.98, 144.46, 144.41, 144.37, 144.02, 143.30(2C), 143.21, 143.16, 142.51, 142.49, 142.25, 141.64, 141.58, 141.35, 141.08, 141.05, 140.66, 140.38, 140.17, 139.66, 138.01, 137.23, 135.99, 133.26, 133.05, 131.46, 126.25(2C), 121.87(2C), 108.05, 87.03, 82.15, 81.83, 81.77, 59.38, 33.77, 26.83(3C), 26.60(3C), 24.03, 23.98, 21.92. FT-IR (microscope): 2973, 2926, 1784, 1496, 1457, 1364, 1192, 1152, 1121, 984, 730 cm<sup>-1</sup>. ESI-HRMS: C<sub>79</sub>H<sub>33</sub>NIO<sub>10</sub> (M + H<sup>+</sup>) calcd 1282.11437, found 1282.11301.



7d

<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$ : 8.17 (d,  $J = 8.3$  Hz, 2H), 7.48 (d,  $J = 8.3$  Hz, 2H), 4.43 (q,  $J = 7.1$  Hz, 2H), 2.31 (s, 3H), 1.44 (t,  $J = 7.1$  Hz, 3H), 1.34 (s, 9H), 1.28 (s, 9H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 125 MHz): All signals represent 1C except noted.  $\delta$ : 186.86, 183.66, 179.27, 166.73, 166.47, 153.26, 151.45, 149.88, 149.68, 149.59, 149.43(2C), 149.32, 149.12, 149.05, 149.03(2C), 148.39, 148.04, 147.99, 147.97, 147.80, 147.73(2C), 147.48(2C), 147.38, 147.06, 146.08, 145.91, 145.34, 145.05, 144.55, 144.47, 144.40(2C), 144.34, 143.48, 143.38, 143.31, 143.26, 142.50(2C), 142.36, 141.78, 141.67, 141.41, 141.20, 141.04, 140.86, 140.71, 140.29, 140.07, 137.71, 137.21, 135.78, 133.18, 133.02, 131.33, 130.28(2C), 126.78, 119.17(2C), 108.12,

86.84, 82.25, 82.06, 81.99, 60.60, 58.44, 26.89(3C), 26.61(3C), 21.92, 14.40.  
 ESI-HRMS: C<sub>79</sub>H<sub>31</sub>NIO<sub>12</sub> (M + H<sup>+</sup>) calcd 1312.08854, found 1312.08210.



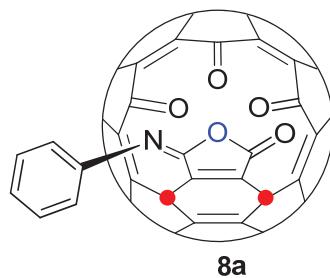
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.49 (d, *J* = 7.7 Hz, 1H), 7.11-7.09(m, 2H) 2.42 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.33 (s, 9H), 1.26 (s, 9H). ESI-HRMS: C<sub>78</sub>H<sub>31</sub>NIO<sub>10</sub> (M + H<sup>+</sup>) calcd 1268.09549, found 1268.09872.

### General Procedure for Preparation of Compounds 8a-8e

Compound **7** (0.1mmol) was dissolved in toluene (30 mL) and stirred vigorously. Then AgClO<sub>4</sub> (2 equiv of **7**) was added to the solution. Progress of the reaction was monitored by TLC. After **7** was completely consumed (within 30 minutes), the reaction mixture was directly chromatographed on a silica gel column eluting with toluene/ethyl acetate (v/v) = 100 : 1. The desired yellow band was collected and evaporated to give **8**

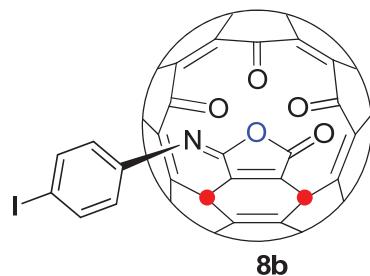
| Entry | <b>7</b> (mg) | Product   | Ar  | mg, (yield %) |
|-------|---------------|-----------|---|---------------|
| 1     | 183           | <b>8a</b> | Ph  | 90.8 (48%)    |
| 2     | 94.5          | <b>8b</b> | <i>p</i> -IC <sub>6</sub> H <sub>4</sub>                  | 38.9 (46%)    |
| 3     | 362           | <b>8c</b> | <i>p</i> - <sup>i</sup> Pr-C <sub>6</sub> H <sub>4</sub>  | 163.2 (52%)   |
| 4     | 248           | <b>8d</b> | <i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 106 (49%)     |
| 5     | 189           | <b>8e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>                 | 73.9 (57%)    |

**Table 2.** Yields of compounds **8a – 8e**

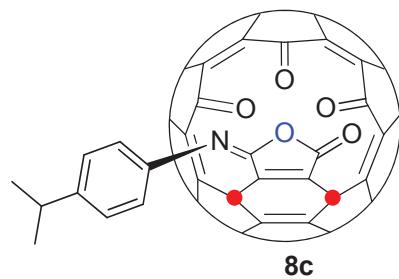


<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.71 – 7.69 (m, 2H), 7.54 - 7.50 (2H), 7.31 – 7.27 (1H), 1.29 (s, 9H), 1.24 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): All signals represent 1C except noted. δ: 183.53, 183.14, 182.94, 161.61, 149.65, 149.56, 149.50(2C), 149.46, 149.39(2C), 149.36(3C), 148.07, 148.05(3C), 148.03, 147.98, 147.98, 147.98, 147.31, 147.29, 147.26, 146.91, 146.75, 146.56, 145.40, 145.38, 145.29(2C), 145.22,

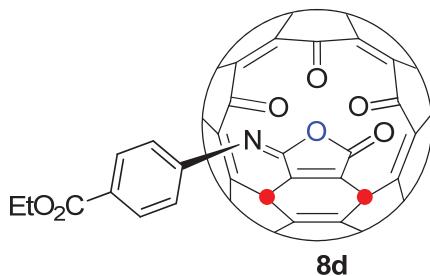
145.15(2C), 145.02, 144.47, 144.45, 144.42, 144.33, 144.28, 143.48(3C), 143.40, 142.09, 141.85, 141.29, 141.10, 138.72, 138.37, 137.87, 137.49, 136.25, 135.63, 134.73, 128.85, 128.80(2C), 128.65, 126.05, 124.18(2C), 84.39, 83.65, 82.06, 81.89, 26.98(3C), 26.75(3C). FT-IR (microscope): 2979, 2925, 2853, 1812, 1785, 1748, 1697, 1593, 1572, 1494, 1489, 1364, 1191, 1118, 1089, 956, 866, 739, 693 cm<sup>-1</sup>. HRMS (ESI) for C<sub>73</sub>H<sub>24</sub>NO<sub>9</sub> [M+H<sup>+</sup>]: calculated 1058.14456, found 1058.14744.



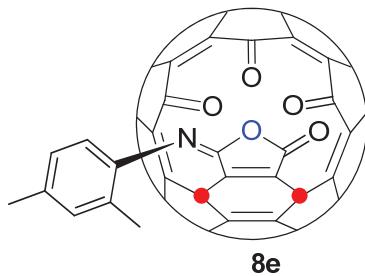
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.82 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 1.27 (s, 9H), 1.24 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 183.54, 183.19, 183.04, 161.21, 149.65, 149.51, 149.45(3C), 149.40, 149.39, 149.36, 149.35, 149.33, 148.05, 148.03(3C), 147.99, 147.96, 147.94, 147.92, 147.30, 147.28, 147.12, 147.10, 146.89, 146.70, 145.37, 145.30, 145.27, 145.19, 145.08(2C), 144.88, 144.85, 144.40(2C), 144.37, 144.27, 144.22, 143.50, 143.49, 143.47, 143.39, 142.10, 141.87, 141.28, 141.09, 138.48, 138.20, 137.92(2C), 137.84, 137.47, 136.56, 135.51, 134.62, 128.79, 128.58, 126.18(2C), 90.85, 84.31, 83.60, 82.10, 81.90, 26.96(3C), 26.74(3C). ESI-HRMS: C<sub>73</sub>H<sub>23</sub>NIO<sub>9</sub> (M + H<sup>+</sup>) calcd 1184.04120, found 1184.04397 .



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.69 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 3.12 – 2.79 (m, 1H), 1.33 (d, *J* = 6.4 Hz, 6H), 1.28 (s, 9H), 1.23 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 183.50, 183.13, 182.88, 161.86, 149.67, 149.59, 149.52(2C), 149.47, 149.42, 149.40(2C), 149.37(2C), 148.07(4C), 148.03, 148.01(2C), 147.97, 147.40, 147.33, 147.30, 147.21, 146.92, 146.76, 145.97, 145.47, 145.39, 145.32, 145.27, 145.25, 145.21, 145.08, 144.48, 144.46(2C), 144.32(2C), 143.52, 143.48(2C), 143.42, 142.74, 142.10, 141.82, 141.30, 141.09, 138.85, 138.41, 137.87, 137.43, 135.70, 135.67, 134.76, 128.91, 128.72, 126.88(2C), 125.05(2C), 84.41, 83.69, 82.01, 81.83, 33.96, 27.03(3C), 26.80(3C), 24.20, 24.11. FT-IR (microscope): 2973, 2927, 1181, 1749, 1589, 1495, 1456, 1387, 1364, 1218, 1191, 1117, 1089, 1000, 956, 932, 739 cm<sup>-1</sup>. ESI-HRMS: C<sub>76</sub>H<sub>30</sub>NO<sub>9</sub>(M + H<sup>+</sup>) calcd 1100.19151, found 1100.18922.



<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ : 8.21 (d,  $J = 8.4$  Hz, 2H), 7.66 (d,  $J = 8.4$  Hz, 2H), 4.44 (q,  $J = 7.1$  Hz, 2H), 1.46 (t,  $J = 7.1$  Hz, 3H), 1.29 (s, 9H), 1.24 (s, 9H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 125 MHz): All signals represent 1C except noted.  $\delta$ : 183.53, 183.19, 183.07, 166.50, 161.01, 149.65, 149.50(2C), 149.46, 149.44(2C), 149.40(2C), 149.36, 149.35, 149.33, 148.06, 148.04, 148.03(2C), 148.00, 147.96, 147.93(2C), 147.57, 147.31, 147.29, 146.92(2C), 146.72, 145.38, 145.32, 145.23, 145.17, 145.06, 145.04, 144.85, 144.41(2C), 144.36, 144.29, 144.21, 143.51(2C), 143.48, 143.40, 142.12, 141.91, 141.29, 141.12, 138.38, 138.18, 137.88, 137.55, 137.12, 135.45, 134.59, 130.46(2C), 128.78, 128.56, 127.44, 123.07(2C), 84.32, 83.59, 82.15, 81.98, 60.83, 26.97(3C), 26.74(3C), 14.4. ESI-HRMS:  $\text{C}_{76}\text{H}_{28}\text{NO}_{11}$  ( $M + \text{H}^+$ ) calcd 1130.16569, found 1130.16237.



<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ : 7.74 (d,  $J = 8.0$  Hz, 1H), 7.19 (d,  $J = 8.0$  Hz, 1H), 7.10 (s, 1H), 2.48 (s, 3H), 2.40 (s, 3H), 1.24 (s, 9H), 1.22 (s, 9H). ESI-HRMS:  $\text{C}_{75}\text{H}_{28}\text{NO}_9$  ( $M + \text{H}^+$ ) calcd 1086.17586, found 1086.17351.

### General Procedure for Preparation of Compounds 9a-9f

$\text{CuBr}$  (0.5 mmol) and  $\text{H}_2\text{O}$  (0.5 mmol) was added to a solution of **8** (0.1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) at 30 °C. The mixture was stirred in dark and progress of the reaction was monitored by TLC. When the desired product **9** reached its maximum yield (about 5 hours), the reaction mixture was directly chromatographed on a silica gel column and eluted with toluene/ethyl acetate. The first yellow band was collected and evaporated to give **9**,

| Entry | <b>8</b> (mg) | Product   | Ar  | mg, (yield %) |
|-------|---------------|-----------|---|---------------|
| 1     | 93.1          | <b>9a</b> | Ph  | 57.8 (66%)    |
| 2     | 21.9          | <b>9b</b> | <i>p</i> -IC <sub>6</sub> H <sub>4</sub>                  | 12.8 (62%)    |
| 3     | 69.2          | <b>9c</b> | <i>p</i> -iPr-C <sub>6</sub> H <sub>4</sub>               | 42.2 (65%)    |
| 4     | 101.0         | <b>9d</b> | <i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 24.2 (26%)    |
| 5     | 73.9          | <b>9e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>                 | 58.1 (84%)    |

**Table 3** Yields of compounds **9a – 9f**

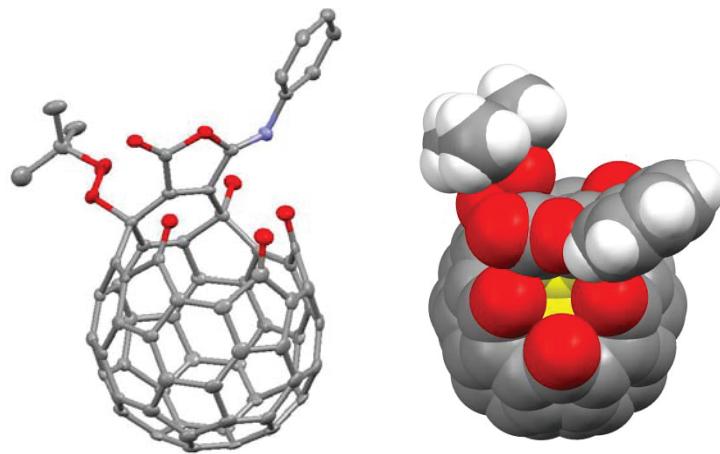
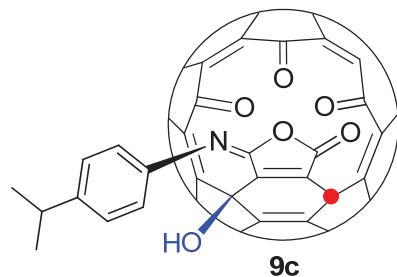
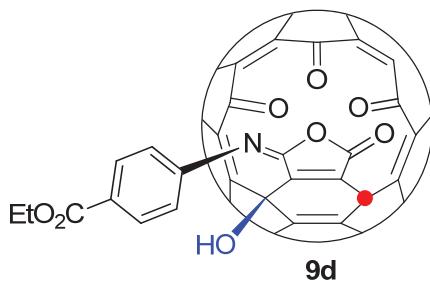


Figure 2 Single-crystal X ray structure of 9a. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen

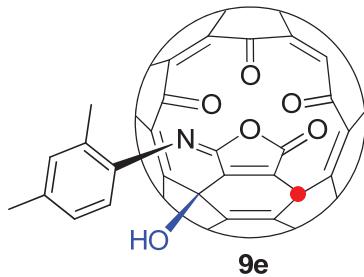
Crystal of **9a** suitable for X–ray diffraction was obtained by slow evaporation in chloroform-d. Crystal data: triclinic, space group P1. Unit cell dimensions:  $a = 14.3061(15)$  Å,  $\alpha = 76.592$  (15)°,  $b = 14.457$  (2) Å,  $\beta = 66.580$  (13)°,  $c = 15.4664$  (19) Å,  $\gamma = 61.681$ (10) (8)°, volume = 2580.2 (6) Å<sup>3</sup>. Final *R* indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0506$ ,  $wR_2 = 0.1379$ . Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-905499.



<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ : 7.78 (s, 2H), 7.40 (s, 2H), 7.00 (s, 1H), 3.02 (s, 1H), 1.33 (s, 6H), 1.23 (s, 9H). <sup>13</sup>C NMR ( $\text{CDCl}_3$ , 125 MHz): All signals represent 1C except noted.  $\delta$ : 183.81, 183.56, 183.41, 160.88, 149.67, 149.45(2C), 149.38, 149.36(3C), 149.31, 149.27(2C), 149.09, 149.05, 148.95, 148.22, 148.12, 148.06, 148.01, 147.96, 147.91(2C), 147.74, 147.35, 147.01, 146.69, 146.63, 145.60, 145.58, 145.35, 145.02, 144.76, 144.75, 144.55, 144.47(2C), 144.35, 144.15, 144.07, 143.42, 143.40, 143.37(3C), 142.61, 142.32, 141.40, 140.75, 140.27, 137.51, 137.41, 137.09, 135.42, 134.77, 132.09, 129.52, 127.23(2C), 126.57, 126.32(2C), 83.88, 82.26, 76.37, 33.99, 26.51(3C), 23.98(2C). FT–IR (microscope): 3358, 2959, 2925, 1822, 1747, 1570, 1495, 1457, 1364, 1189, 1115, 1089, 1014, 904, 835, 755 cm<sup>-1</sup>. ESI-HRMS:  $\text{C}_{72}\text{H}_{22}\text{NO}_8(\text{M} + \text{H}^+)$  calcd 1028.13399, found 1028.13194.



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ: 8.22 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 6.68 (s, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.24 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 184.03, 183.60, 183.50, 166.14, 160.23, 150.86, 149.73, 149.51, 149.45, 149.39(5C), 149.34, 149.29, 148.69, 148.25, 148.13, 148.09, 148.05, 148.01, 147.96(2C), 147.77, 147.40, 147.07, 146.75(2C), 146.66, 145.61, 145.47, 145.33, 145.07, 144.73, 144.53, 144.50, 144.45, 144.39, 144.37, 144.12, 143.92, 143.47(2C), 143.42, 143.19, 142.70, 142.41, 141.48, 140.86, 137.61, 137.29, 137.24, 135.28, 134.68, 133.58, 130.65(2C), 129.45, 128.93, 126.66, 124.91(2C), 83.85, 82.46, 76.33, 61.10, 26.53(3C), 14.39. ESI-HRMS: C<sub>72</sub>H<sub>20</sub>NO<sub>10</sub> (M + H<sup>+</sup>) calcd 1058.10817, found 1058.10678.



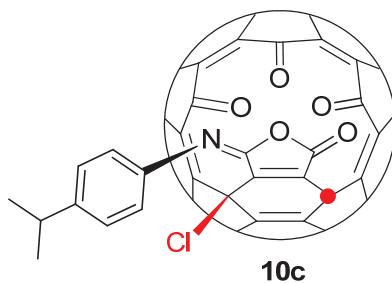
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.90 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.03 (s, 1H), 2.41 (s, 6H), 1.23 (s, 9H). ESI-HRMS: C<sub>71</sub>H<sub>20</sub>NO<sub>8</sub> (M + H<sup>+</sup>) calcd 1014.11715, found 1014.11715.

### General Procedure for Preparation of Compounds 10a-10f

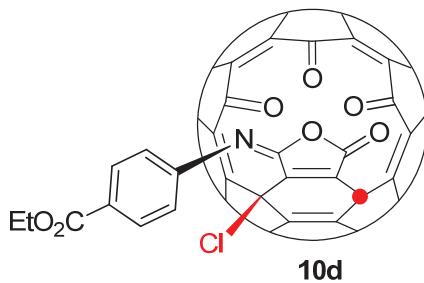
Compound **9** (0.1 mmol) was dissolved in dichloromethane (10 mL) and stirred vigorously in dark. Then PCl<sub>5</sub> (5 equiv of **9**) was added to the solution. Progress of the reaction was monitored by TLC. After **9** was completely consumed (within 2 h), water (10 mL) was added to the reaction mixture and then continue stirred for 10 minutes. The mixture was extracted with dichloromethane and dried with Na<sub>2</sub>SO<sub>4</sub>, then chromatographed on a silica gel column eluting with toluene/ethyl acetate (v/v) = 100 : 1. The desired red band was collected and evaporated to give **10**

| Entry | <b>9</b> (mg) | Product    | Ar  | mg, (yield %) |
|-------|---------------|------------|---|---------------|
| 1     | 27.6          | <b>10a</b> | Ph  | 24.3 (86%)    |
| 2     | 47.0          | <b>10b</b> | <i>p</i> -IC <sub>6</sub> H <sub>4</sub>                  | 42.2 (88%)    |
| 3     | 42.2          | <b>10c</b> | <i>p</i> - <sup>i</sup> Pr-C <sub>6</sub> H <sub>4</sub>  | 34.5 (85%)    |
| 4     | 24.2          | <b>10d</b> | <i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 21.1 (86%)    |
| 5     | 58.1          | <b>10e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>                 | 52.8 (89%)    |

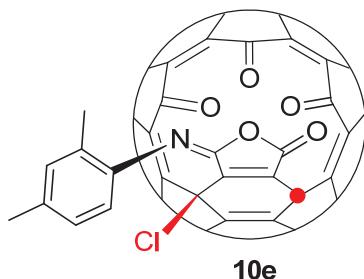
**Table 4** Yields of compounds **10a –10f**



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.76 (d, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 6.9 Hz, 2H), 3.14 – 2.82 (m, 1H), 1.34 (d, *J* = 5.6 Hz, 6H), 1.24 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 183.28, 183.20, 182.74, 161.07, 149.62, 149.52, 149.46(2C), 149.44, 149.39, 149.37, 149.32, 149.28(2C), 148.12, 148.08, 148.07, 148.05, 148.02, 148.00, 147.96, 147.94, 147.84, 147.34, 147.19, 146.83, 146.66, 146.61, 145.51, 145.18, 145.01, 144.77(2C), 144.51, 144.37, 144.32, 144.28, 143.94, 143.52, 143.44, 143.37(2C), 142.97, 142.75, 142.44, 142.31, 141.71, 141.69, 141.47, 141.06, 140.87, 138.23, 137.71, 137.16, 135.69, 134.64, 134.45, 129.76, 127.83, 127.00(2C), 125.69(2C), 83.43, 82.38, 61.51, 33.99, 26.52(3C), 24.09, 24.04. FT-IR (microscope): 2959, 2926, 1812, 1748, 1570, 1497, 1458, 1218, 1189, 1119, 1088, 953, 934, 834, 756, 740 cm<sup>-1</sup>. ESI-HRMS: C<sub>72</sub>H<sub>21</sub>ClNO<sub>7</sub> (M + H<sup>+</sup>) calcd 1046.10011, found 1046.10171.



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ: 8.22 (t, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 183.36, 183.32, 183.01, 166.44, 160.31, 149.69, 149.60, 149.54, 149.46(2C), 149.43, 149.41, 149.39, 149.34, 149.29, 148.48, 148.18, 148.11, 148.10, 148.08, 147.98(2C), 147.87, 147.40, 147.26, 146.90, 146.70, 146.66, 146.13, 145.47, 145.25, 145.09, 144.76, 144.41(2C), 144.35, 144.30, 143.76, 143.59, 143.51, 143.48, 143.43, 142.88, 142.63, 142.56, 142.42, 141.56, 141.45, 141.01, 140.98, 138.10, 137.83, 137.37, 136.00, 135.50, 134.53, 130.53(2C), 129.68, 128.04, 127.77, 125.24, 123.71(2C), 83.40, 82.62, 82.55, 60.94, 26.53(3C), 14.42. ESI-HRMS: C<sub>72</sub>H<sub>19</sub>ClNO<sub>9</sub> (M + H<sup>+</sup>) calcd 1076.07429, found 1076.07347.



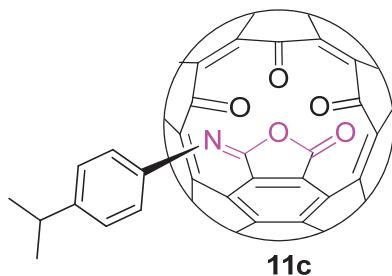
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.88 (d, *J* = 8.0, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 2.45 (s, 3H), 2.41 (s, 3H), 1.24 (s, 9H). ESI-HRMS: C<sub>71</sub>H<sub>19</sub>ClNO<sub>7</sub> (*M* + H<sup>+</sup>) calcd 1032.08446, found 1032.08175.

### General Procedure for Preparation of Compounds 11a-11f

Compound **10** (0.1 mmol) was dissolved in chloroform (25 mL) and stirred vigorously in dark. Then SnCl<sub>2</sub> (3 equiv of **10**) was added to the solution. Progress of the reaction was monitored by TLC. After **10** was completely consumed (within 15 minutes), water (10 mL) was added to the reaction mixture and then continue stirred for 10 minutes. The mixture was extracted with dichloromethane and dried with Na<sub>2</sub>SO<sub>4</sub>, then chromatographed on a silica gel column eluting with toluene/ethyl acetate (v/v) = 100 : 1. The desired band was collected and evaporated to give **11**

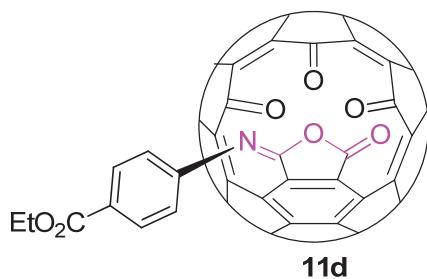
| Entry | <b>10</b> (mg) | Product    | Ar  | mg, (yield %) |
|-------|----------------|------------|---|---------------|
| 1     | 24.3           | <b>11a</b> | Ph  | 16.8 (76%)    |
| 2     | 42.2           | <b>11b</b> | <i>p</i> -IC <sub>6</sub> H <sub>4</sub>                  | 28.6 (75%)    |
| 3     | 34.5           | <b>11c</b> | <i>p</i> -iPr-C <sub>6</sub> H <sub>4</sub>               | 26.0 (85%)    |
| 4     | 21.1           | <b>11d</b> | <i>p</i> -EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 13.9 (74%)    |
| 5     | 52.8           | <b>11e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>                 | 34.0 (73%)    |

Table 5 Yields of compounds **11a –11f**



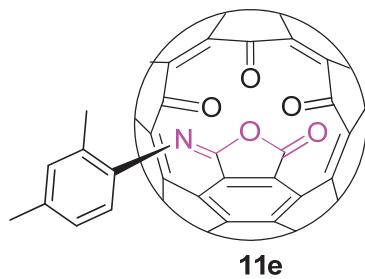
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.72 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 2H), 3.05 – 2.98 (m, 1H), 1.34 (d, *J* = 6.6 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 1C except noted. δ: 185.76(2C), 183.73, 162.68, 150.47, 150.40, 150.02, 149.70, 149.62, 149.58, 149.55(2C), 149.39, 148.89, 147.72, 146.86, 146.81(3C), 146.76, 146.73, 146.69, 146.38, 146.34, 146.29, 146.27, 146.19, 145.99(2C), 145.73, 145.58, 145.42, 143.70, 143.68, 143.60, 143.58, 143.43, 143.42, 143.27, 143.07, 142.91, 142.90, 142.87, 142.74, 142.42, 141.72, 141.68, 138.06, 137.80, 137.41, 137.25, 137.07, 136.37, 135.74, 135.36, 133.49, 132.73, 132.04,

128.36, 127.66, 127.27, 127.04(2C), 125.10(2C), 33.96, 24.08, 24.05. FT-IR (microscope): 2957, 2924, 1799, 1743, 1561, 1495, 1200, 1133, 1053, 1029, 927, 801, 743 cm<sup>-1</sup>. ESI-HRMS: C<sub>68</sub>H<sub>12</sub>NO<sub>5</sub> (M + H<sup>+</sup>) calcd 922.07100, found 922.07133.



**11d**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 8.23 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 4.45 (dd, J = 15.2, 7.2 Hz, 2H), 1.50 – 1.42 (t, 7.1 Hz 3H). ESI-HRMS: C<sub>68</sub>H<sub>10</sub>NO<sub>7</sub> (M + H<sup>+</sup>) calcd 952.04518, found 952.04407.



**11e**

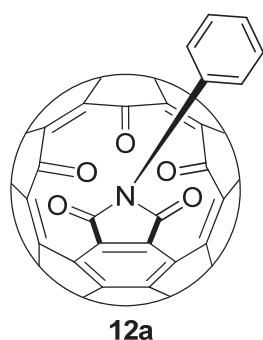
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.87 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.11 (s, 1H), 2.41 (s, 6H). ESI-HRMS: C<sub>67</sub>H<sub>10</sub>NO<sub>5</sub> (M + H<sup>+</sup>) calcd 908.05535, found 908.05394.

### General Procedure for Preparation of Compounds 12a-12f

Compound **11** (0.1 mmol) was dissolved in toluene (30 mL) and stirred vigorously. Then CF<sub>3</sub>CO<sub>2</sub>H (15 equiv of **11**) and (CF<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>O (15 equiv equiv of **11**) was added to the solution at 100 °C. Progress of the reaction was monitored by TLC. After **11** was completely consumed (about 2 days), the solution was then chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (v/v) = 100 : 1. The desired red band was collected and evaporated to give **12**.

| Entry | <b>11</b> (mg) | Product    | Ar  | mg, (yield %) |
|-------|----------------|------------|---|---------------|
| 1     | 7.7            | <b>12a</b> | Ph  | 4.0 (52%)     |
| 2     | 13.3           | <b>12b</b> | p-IC <sub>6</sub> H <sub>4</sub>                  | 6.8 (51%)     |
| 3     | 12.2           | <b>12c</b> | p- <sup>i</sup> Pr-C <sub>6</sub> H <sub>4</sub>  | 6.4 (52%)     |
| 4     | 11.9           | <b>12d</b> | p-EtO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> | 4.5 (38%)     |
| 5     | 9.2            | <b>12e</b> | 2,4-dimethylC <sub>6</sub> H <sub>4</sub>         | 5.0 (54%)     |

**Table 6** Yields of compounds **12a** – **12f**



$^1\text{H}$  NMR(400 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 8.02(d, 2H,  $J=7.2$ ), 7.78 (t, 2H,  $J=8.0$ ), 7.62 (t, 1H,  $J=7.2$ ). ESI-HRMS:  $\text{C}_{65}\text{H}_5\text{NO}_5$  ( $\text{M} + \text{H}^+$ ) calcd 880.02405, found 880.02237.

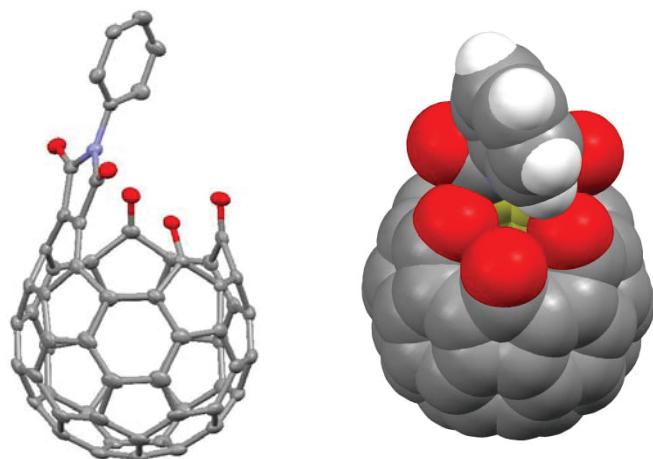
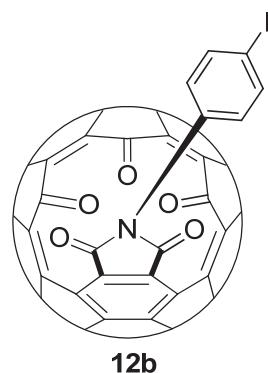


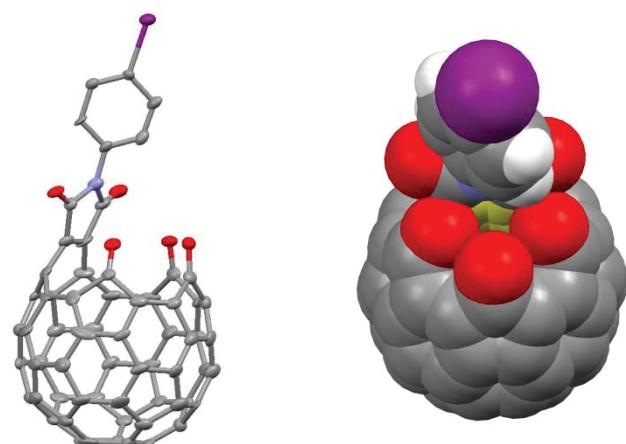
Figure 5 Single-crystal X ray structure of 12a. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen

Crystal of **12a** suitable for X-ray diffraction was obtained by slow evaporation in toluene. Crystal data: Monoclinic, space group P2/c. Unit cell dimensions:  $a = 18.742$  (4) Å,  $\alpha = 90^\circ$ ,  $b = 13.442$  (3) Å,  $\beta = 114.400$  (3)°,  $c = 18.553$  (4) Å,  $\gamma = 90^\circ$ , volume = 4256.6(16) Å<sup>3</sup>. Final  $R$  indices [ $I > 2\sigma (I)$ ]:  $R_1 = 0.0621$ ,  $wR_2 = 0.1519$ . Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-905500.



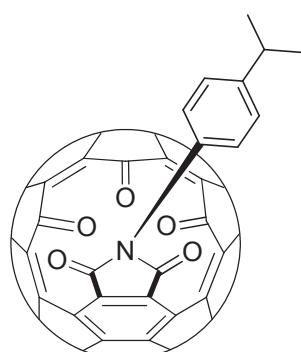
**12b**

<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$ : 8.08 (d,  $J$  = 8.5 Hz, 2H), 7.85 (d,  $J$  = 8.5 Hz, 2H). FT-IR (microscope): 2926, 2854, 1774, 1736, 1486, 1374, 1135, 1109, 1033, 827, 756, 741  $\text{cm}^{-1}$ . ESI-HRMS:  $\text{C}_{65}\text{H}_8\text{IN}_2\text{O}_5$  ( $\text{M} + \text{NH}_4^+$ ) calcd 1022.94724, found 1022.94595.



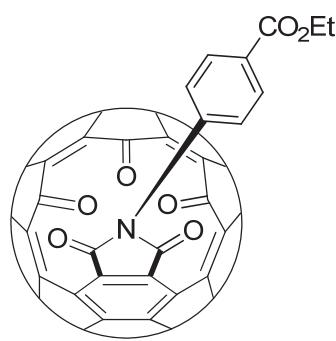
**Figure 6** Single-crystal X ray structure of **12b**. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen; purple, iodine

Crystal of **12b** suitable for X-ray diffraction was obtained by slow evaporation in chloroform. Crystal data: triclinic, space group P1. Unit cell dimensions:  $a = 12.754$  (3) Å,  $\alpha = 78.32(3)^\circ$ ,  $b = 12.843$  (3) Å,  $\beta = 82.27$  (3)°,  $c = 14.630$  (3) Å,  $\gamma = 68.22$  (3)°, volume = 2174.59 Å<sup>3</sup>. Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.0707$ ,  $wR_2 = 0.1392$ . Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-905501.



**12c**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 7.99 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 3.11 (m, 1H), 1.42 (s, 3H), 1.40 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): All signals represent 2C except noted. δ: 185.56, 183.75(1C), 165.12(1C), 150.38, 150.05(1C), 149.65, 149.55, 149.37, 149.15, 147.01, 146.91, 146.70, 146.66, 146.34, 146.17, 146.06, 145.75, 143.82, 143.72, 143.65, 143.54, 143.12, 142.96, 141.89, 138.03, 137.77, 137.55, 133.56, 131.92, 130.88, 130.04, 128.22, 127.57, 127.31, 34.19(1C), 24.11. FT-IR (microscope): 2956, 2924, 2854, 1797, 1774, 1739, 1514, 1494, 1459, 1375, 1132, 1107, 831, 741 cm<sup>-1</sup>. ESI-HRMS: C<sub>68</sub>H<sub>12</sub>NO<sub>5</sub> (M + H<sup>+</sup>) calcd 922.07100, found 922.07325.



**12d**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ: 8.43 (d, *J* = 8.5 Hz, 2H), 8.20 (d, *J* = 8.5 Hz, 2H), 4.50 (dd, *J* = 14.3, 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). ESI-HRMS: C<sub>68</sub>H<sub>10</sub>NO<sub>7</sub> (M + H<sup>+</sup>) calcd 952.04518, found 952.04674.

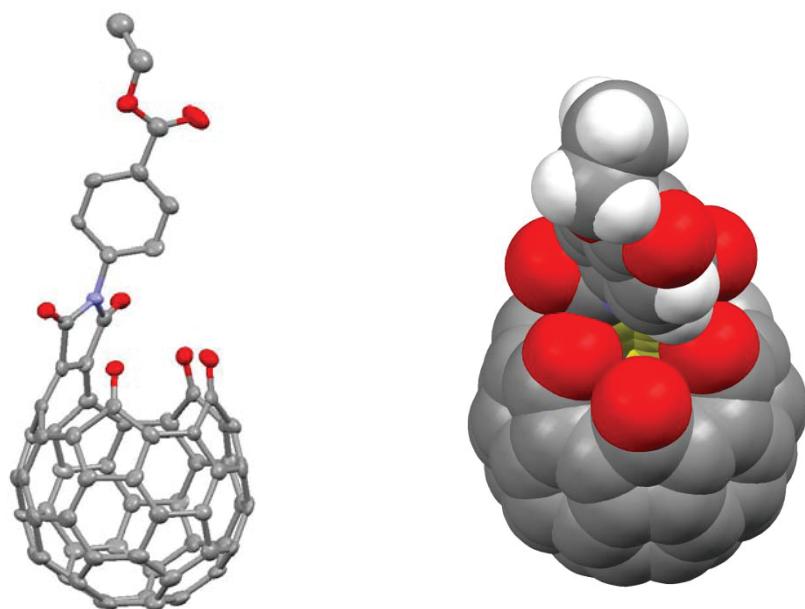
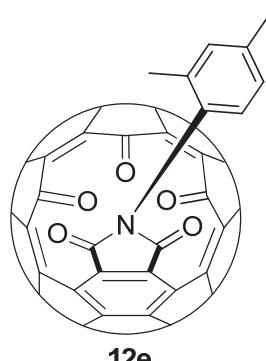


Figure 4 Single-crystal X ray structure of 12d. Ellipsoids were drawn at the 50% level; for clarity hydrogen atoms were not shown. Color key: gray, carbon; red, oxygen; blue, nitrogen

Crystal of 12d suitable for X-ray diffraction was obtained by slow evaporation in toluene. Crystal data: Monoclinic, space group P2/c. Unit cell dimensions:  $a = 19.163(6)$  Å,  $\alpha = 90^\circ$ ,  $b = 13.468(4)$  Å,  $\beta = 114.320(4)^\circ$ ,  $c = 18.553(7)$  Å,  $\gamma = 90^\circ$ , volume =  $4363(3)$  Å<sup>3</sup>. Final  $R$  indices [ $I > 2\sigma(I)$ ]:  $R_1 = 0.1190$ ,  $wR_2 = 0.2952$ . Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition number CCDC-905502.



12e

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): Conformer A: 8.12 (d,  $J = 7.9$  Hz, 1H), 7.49 (d,  $J = 7.4$  Hz, 1H), 7.25 (s, 1H), 3.24 (s, 3H), 2.43 (s, 3H). Conformer B: 7.43 (s, 1H), 7.13 (d,  $J = 8.3$  Hz, 1H), 6.99 (d,  $J = 7.9$  Hz, 1H), 2.47 (s, 3H), 2.09 (s, 3H). ESI-HRMS: C<sub>67</sub>H<sub>10</sub>NO<sub>5</sub> (M + H<sup>+</sup>) calcd 908.05535, found 908.05692

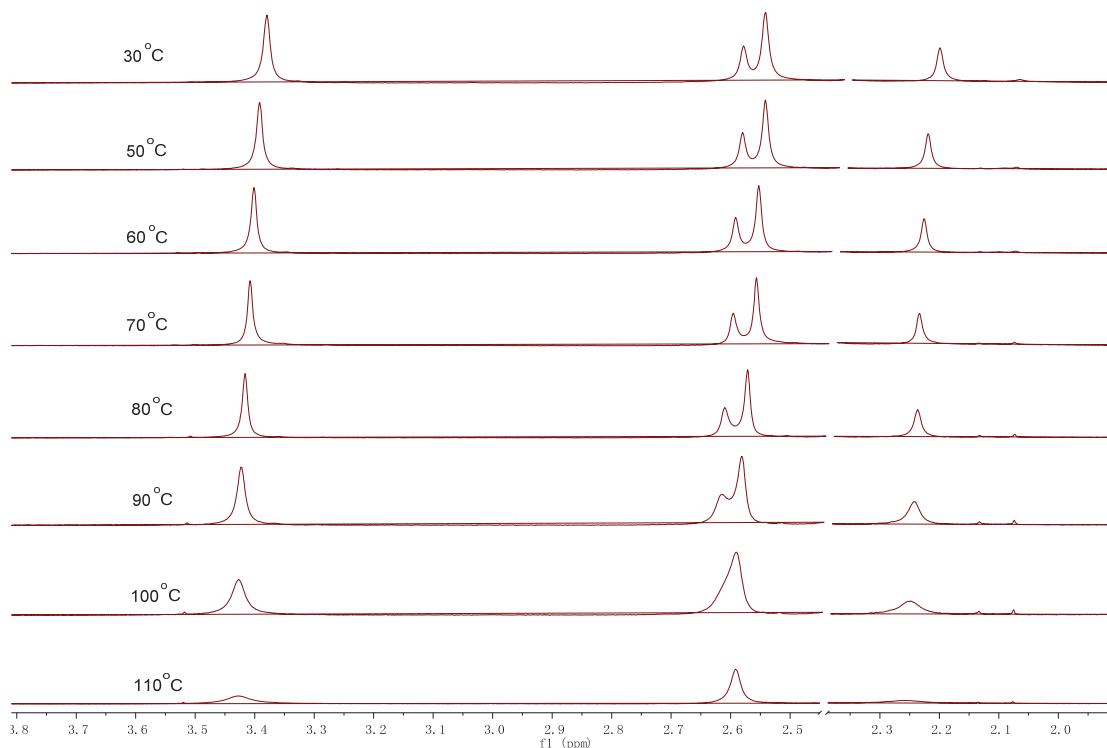
## Variable Temperature $^1\text{H}$ NMR

### Thermodynamic study

A sample was dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  or  $\text{ODCB}-d_4$  with a small amount of tetramethylsilane, and the solution was placed in a standard 5 mm NMR sample tube. The samples were loaded into the NMR spectrometer and the probe was heated, allowing  $\sim 10$  min equilibration time at each temperature before the spectrum was collected. Fourier transforms were performed using Topspin 3.0 data processing software. At all temperatures, the standard peak width was determined by measuring the peak width at half-height of the tetramethylsilane internal standard. Line-shape analysis of each spectrum was also accomplished with Topspin 3.0.

### References

- (1) K. Damodaran, S. D. Nielsen, S. J. Geib, W. Zhang, Y. Lu and D. P. Curran, *J. Org. Chem.* 2009, **74**, 5481
- (2) W. R. Carroll, P. Pellechia, and K. D. Shimizu, *Org. Lett.*, 2008, **10**, 3547.



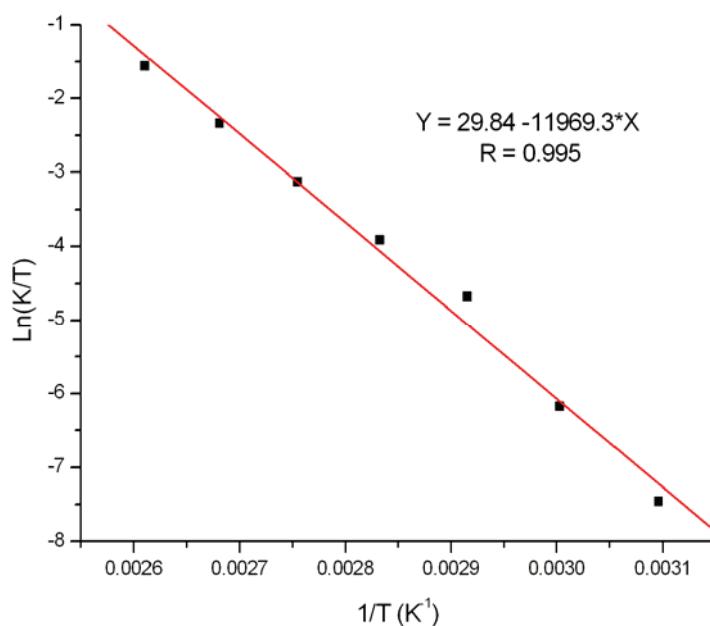
**Figure 1** Expanded region of the variable temperature spectra of **12e** in  $\text{TCE}-d_2$ .

The  $^1\text{H}$  NMR as a function of temperature can give information about the barrier to interconversion. This rate of interconversion can be obtained using the change in linewidth using the following equation:

$k = \pi(\text{width at half-height} - 2.56)$ , 2.56 is the width at half-height at  $30^\circ\text{C}$  for the methyl signal at 3.4 ppm.

| T   | width at half-height | k    | Ink/T | 1/T    |
|-----|----------------------|------|-------|--------|
| 303 | 2.56                 |      |       | 0.0033 |
| 323 | 2.62                 | 0.2  | -7.46 | 0.0031 |
| 333 | 2.78                 | 0.5  | -6.18 | 0.0030 |
| 343 | 3.86                 | 3.4  | -4.43 | 0.0029 |
| 353 | 4.81                 | 3.0  | -3.91 | 0.0028 |
| 363 | 7.64                 | 8.9  | -3.13 | 0.0028 |
| 373 | 14.07                | 20.2 | -2.33 | 0.0027 |
| 383 | 28.32                | 44.8 | -1.55 | 0.0026 |

**Table 1** Values for the rate of spin at each temperature for **12e** in TCE-d<sub>2</sub>



**Figure 2** Erying plot of the VT NMR data for **12e** recorded in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> from 50 to 110 °C

### Eyring Plot Equation

$$\ln(K/T) = -(\Delta H^\ddagger/R)(1/T) + \Delta S^\ddagger/R + \ln(k_B/h)$$

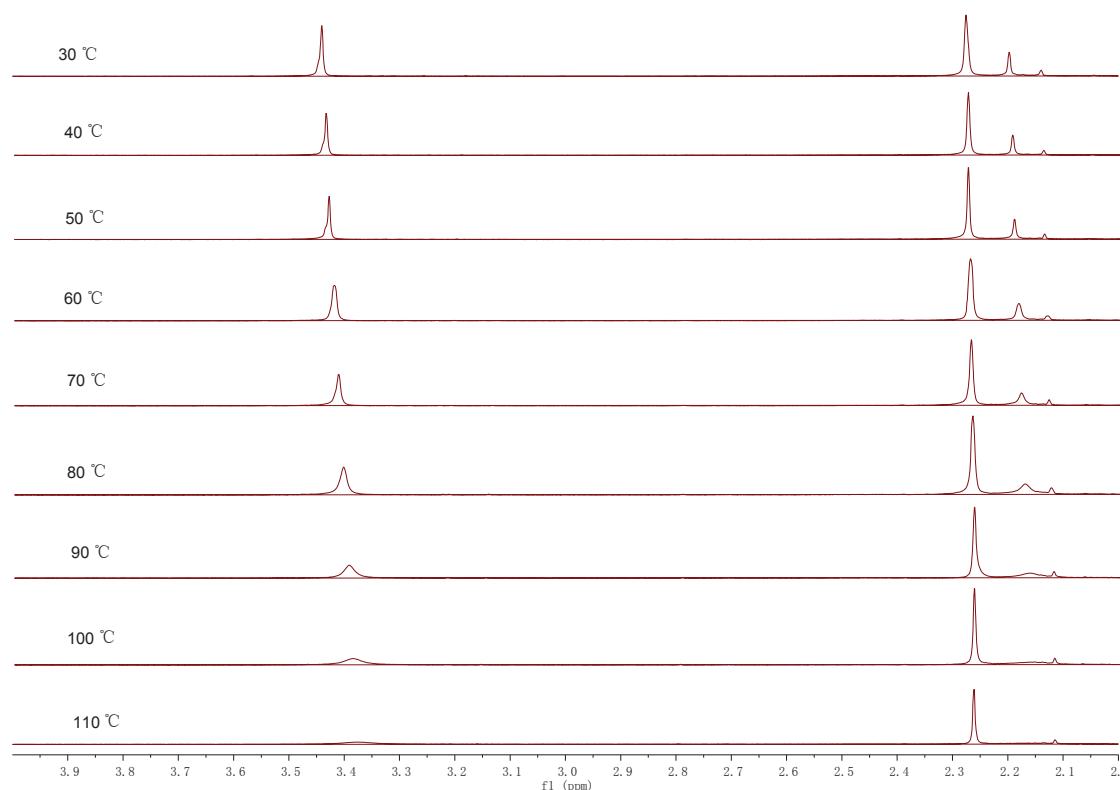
T = absolute temperature in degrees Kelvin [ K ]

R = Universal Gas Constant [ 8.3144 J · mol<sup>-1</sup> · K<sup>-1</sup> ]

k<sub>B</sub> = Boltzmann's constant [ 1.381 · 10<sup>-23</sup> J · K<sup>-1</sup> ]

h = Plank constant [ 6.626 · 10<sup>-34</sup> J · s ]

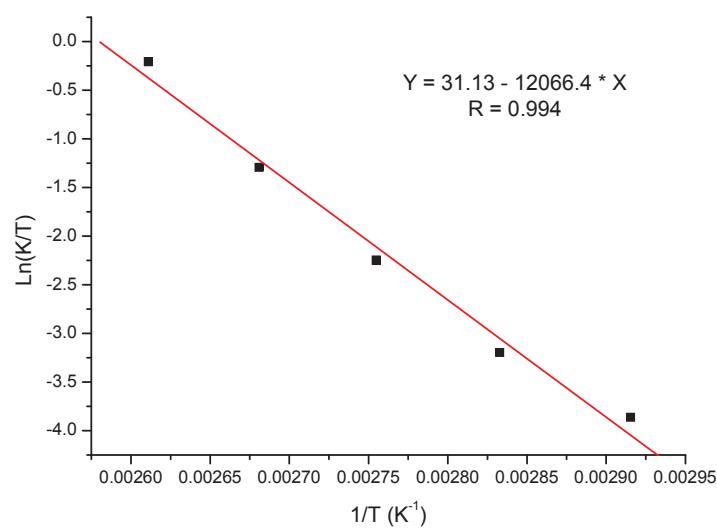
The slope is  $-R \cdot \Delta H^\ddagger$ . The intercept is  $\Delta S^\ddagger/R + \ln(k_B/h)$ .  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ .  $E_a = \Delta H^\ddagger + RT$ . This gives a  $\Delta H^\ddagger$  of 23.8 kcal/mol, a  $T\Delta S^\ddagger$  of 3.6 kcal/mol at 298 K, a  $\Delta G^\ddagger$  of 20.2 kcal/mol and  $E_a$  of 24.4 kcal/mol.



**Figure 3** Expanded region of the variable temperature spectra of **12e** in ODCB-*d*2

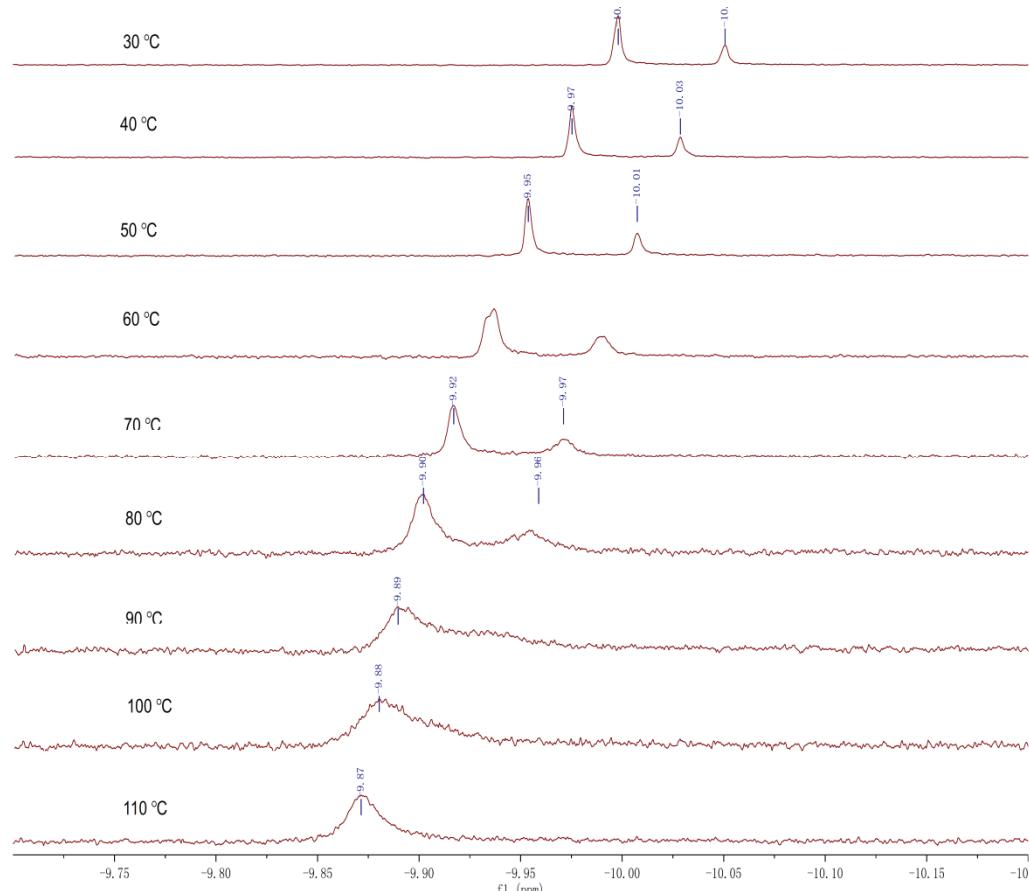
| T   | width at half-height | k      | Ink/T | 1/T    |
|-----|----------------------|--------|-------|--------|
|     | 2.8                  |        |       |        |
| 343 | 5.10                 | 7.21   | -3.86 | 0.0029 |
| 353 | 7.39                 | 14.41  | -3.20 | 0.0028 |
| 363 | 15.00                | 38.31  | -2.25 | 0.0028 |
| 373 | 35.38                | 102.30 | -1.29 | 0.0027 |
| 383 | 101.92               | 311.25 | -0.21 | 0.0026 |

**Table 2** Values for the rate of spin at each temperature for **12e** in ODCB-*d*2.  
Therefore  $k = \pi(\text{width at half-height} - 2.8)$ , 2.8 is the average width at half-height at 30–50 °C for the methyl signal at 3.4 ppm.



**Figure 4** Eyring plot of the VT NMR data for **12e** recorded in ODCB-*d*2 from 70 to 110 °C

The slope is  $-R^* \Delta H^\ddagger$ . The y intercept is  $\Delta S^\ddagger / R + \ln(k/h)$ .  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ .  $E_a = \Delta H^\ddagger + RT$ . This gives a  $\Delta H^\ddagger$  of 24.0 kcal/mol, a  $T\Delta S^\ddagger$  of 4.3 kcal/mol at 298 K, a  $\Delta G^\ddagger$  of 19.6 kcal/mol and  $E_a$  of 24.6 kcal/mol.

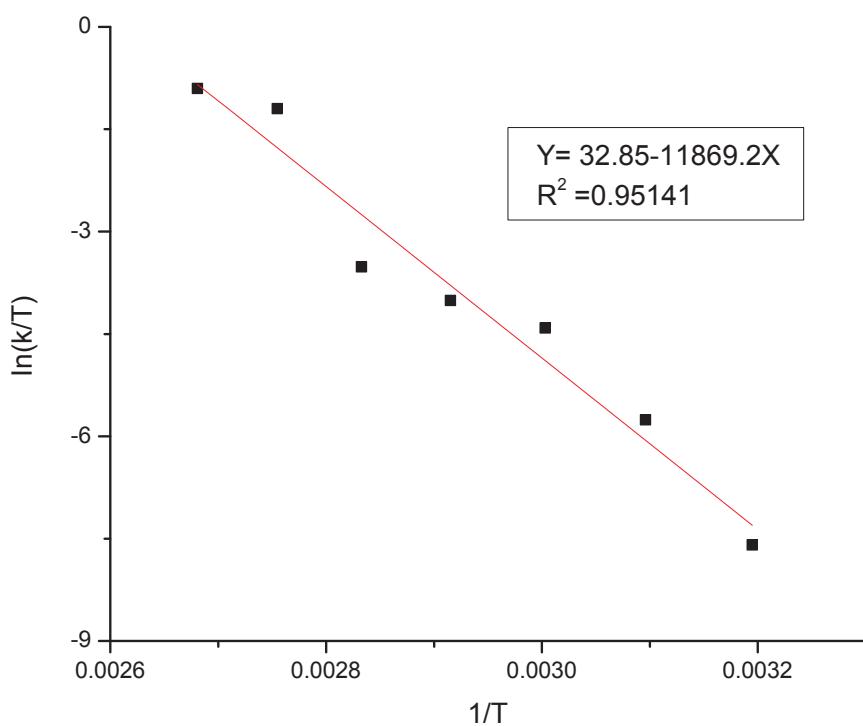


**Figure 5** Expanded region of the variable temperature spectra of **12e** in ODCB-*d*2

| T   | width at half-height | k      | Ink/T | 1/T    |
|-----|----------------------|--------|-------|--------|
| 303 | 1.24                 |        |       | 0.0033 |
| 313 | 1.29                 | 0.16   | -7.60 | 0.0032 |
| 323 | 1.56                 | 1.02   | -5.76 | 0.0031 |
| 333 | 2.52                 | 4.03   | -4.41 | 0.0031 |
| 343 | 3.21                 | 6.205  | -4.01 | 0.0029 |
| 353 | 4.57                 | 10.46  | -3.52 | 0.0028 |
| 363 | 36.02                | 109.20 | -1.20 | 0.0028 |
| 373 | 49.21                | 150.62 | -0.91 | 0.0027 |

**Table 3** Values for the rate of spin at each temperature for **12e** in ODCB-*d*2.

Therefore  $k = \pi(\text{width at half-height} - 1.24)$ , 1.24 is the half-height at 30°C for the water signal at -10.0 ppm..



**Figure 6** Erying plot of the VT NMR data for **12e** recorded in ODCB-*d*2 from 30 to 100 °C

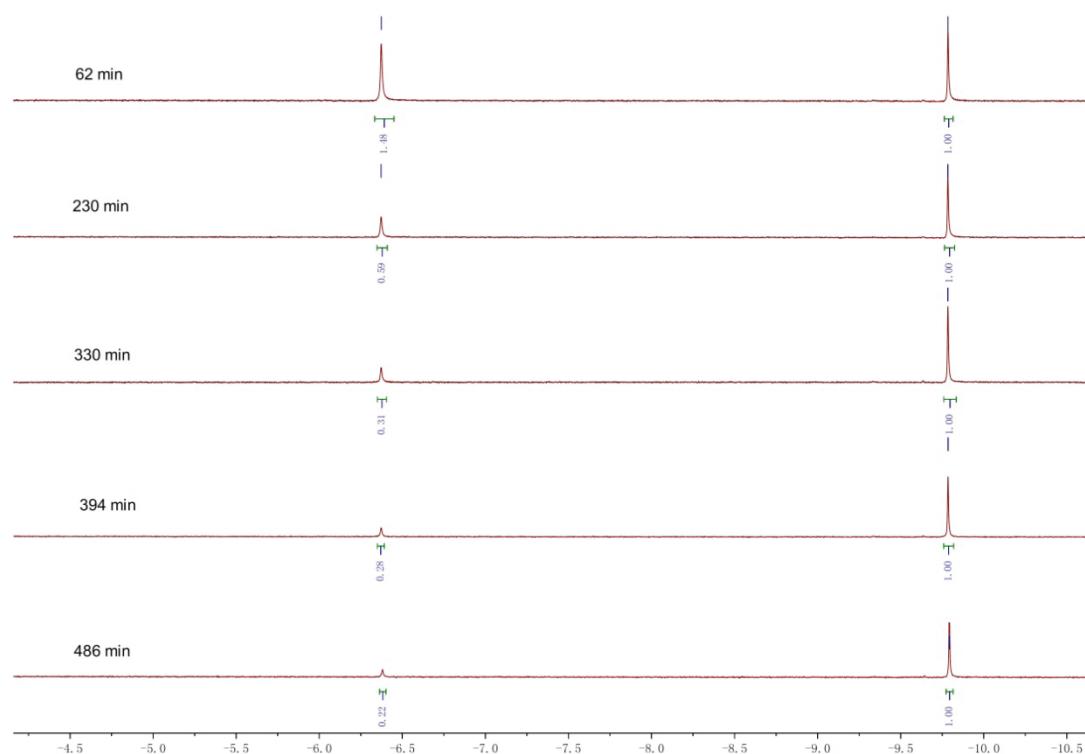
The slope is  $-R * \Delta H^\ddagger$ . The y intercept is  $\Delta S^\ddagger / R + \ln(k/h)$ .  $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ .  $E_a = \Delta H^\ddagger + RT$ . This gives a  $\Delta H^\ddagger$  of 23.6 kcal/mol, a  $T\Delta S^\ddagger$  of 5.4 kcal/mol at 298 K, a  $\Delta G^\ddagger$  of 18.2 kcal/mol and  $E_a$  of 24.2 kcal/mol.

Note: the above results obtained from the line shape analysis of the encapsulated water signal correspond to the rotation process for the water encapsulated complex

$\text{H}_2\text{O}@\mathbf{12e}$ . The results obtained from Figure 3, Table 2 and Figure 4 with the line shape analysis of the methyl group at 3.4 ppm are for the mixture of  $\text{H}_2\text{O}@\mathbf{12e}$  and empty **12e**. As expected, they are the same within experimental error since the trapped water molecule has little effect on the rotation of the Ar-N bond. The present data are less accurate than those from the methyl group because the encapsulated water signals are not as intense as the methyl signal.

### Half-life of trapped hydrogen in **12c** and **12e**

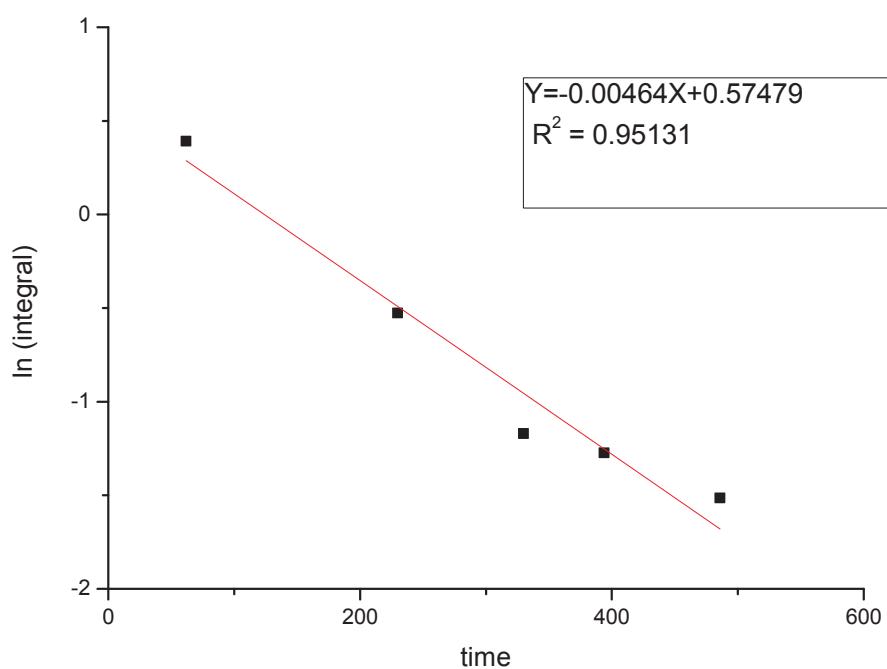
A sample was dissolved in  $\text{C}_2\text{D}_2\text{Cl}_4$  and loaded into a stainless-steel autoclave. The reaction vessel was charged with  $\text{H}_2$  (the pressure reached 120 MPa). The mixture was allowed to warm and heated at 50 °C for 16 h. The solution was directly placed into a standard 5 mm NMR sample tube and  $^1\text{H}$ -NMR spectroscopy was measured at different time intervals.



**Figure 7** Expanded region of  $^1\text{H}$  NMR spectra of  $\text{H}_2@\mathbf{12c}$  in  $\text{TCE-d}_2$  recorded after the sample was kept for different time intervals at r.t.

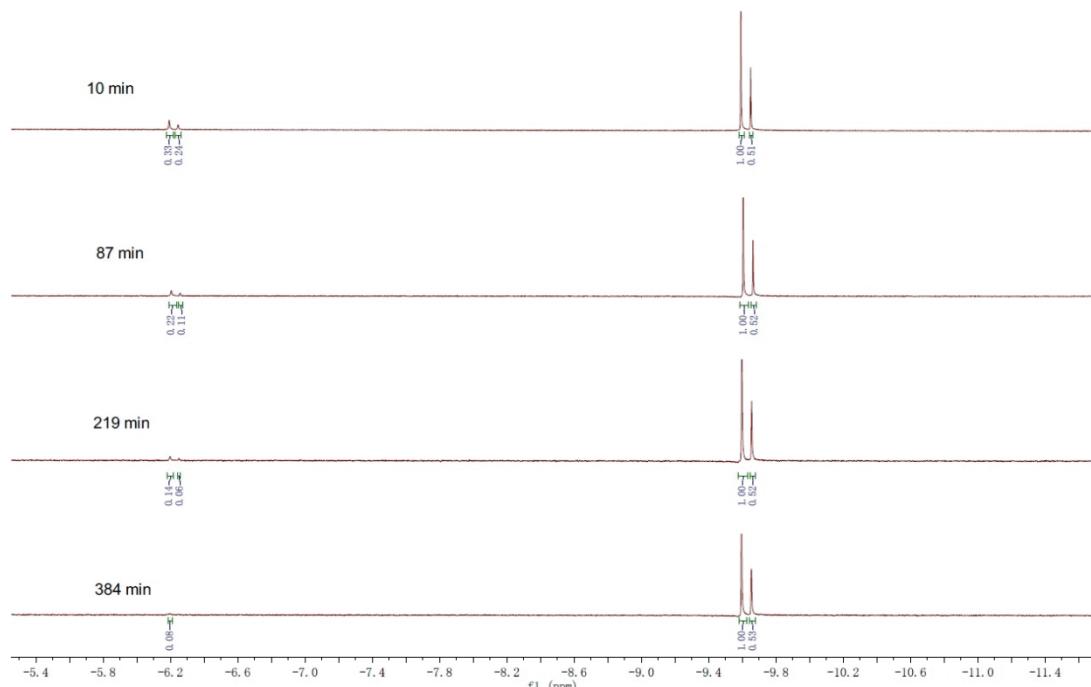
| Time(min) | ln(integral) |
|-----------|--------------|
| 62        | 0.39         |
| 230       | -0.53        |
| 330       | -1.17        |
| 394       | -1.27        |
| 486       | -1.51        |

**Table 4** Values for the integral of trapped hydrogen at each time for **12c**



**Figure 8** Erying plot of the integral data for **12c**

The slope is  $k = 0.00464$ .  $t_{1/2} = \ln 2/k$ . This gives a half-life of  $t_{1/2} = 149$  min.

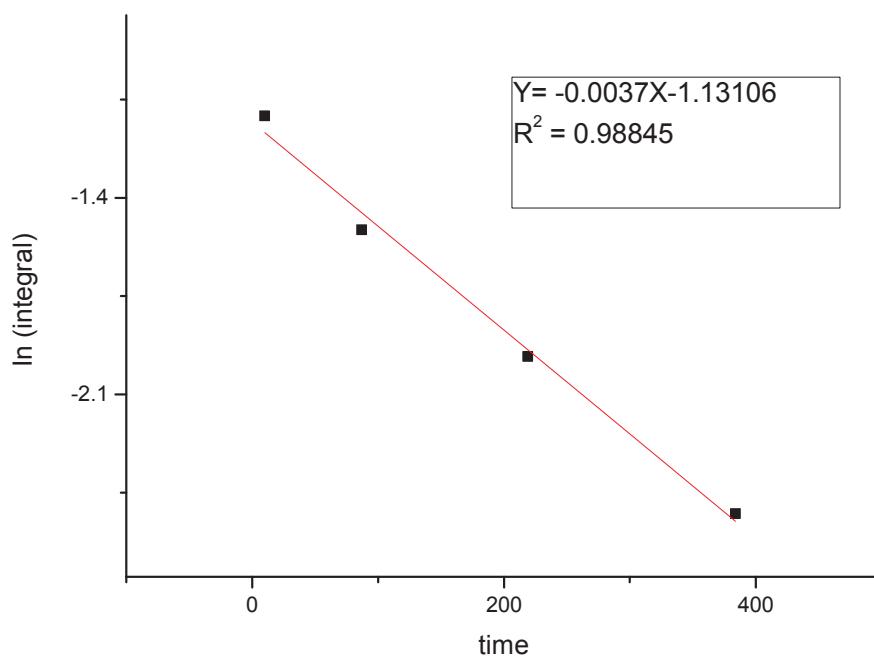


**Figure 9** Expanded region of <sup>1</sup>H NMR spectra of H<sub>2</sub>@**12e** in TCE-d<sub>2</sub> recorded after the

sample was kept for different time intervals at r.t.

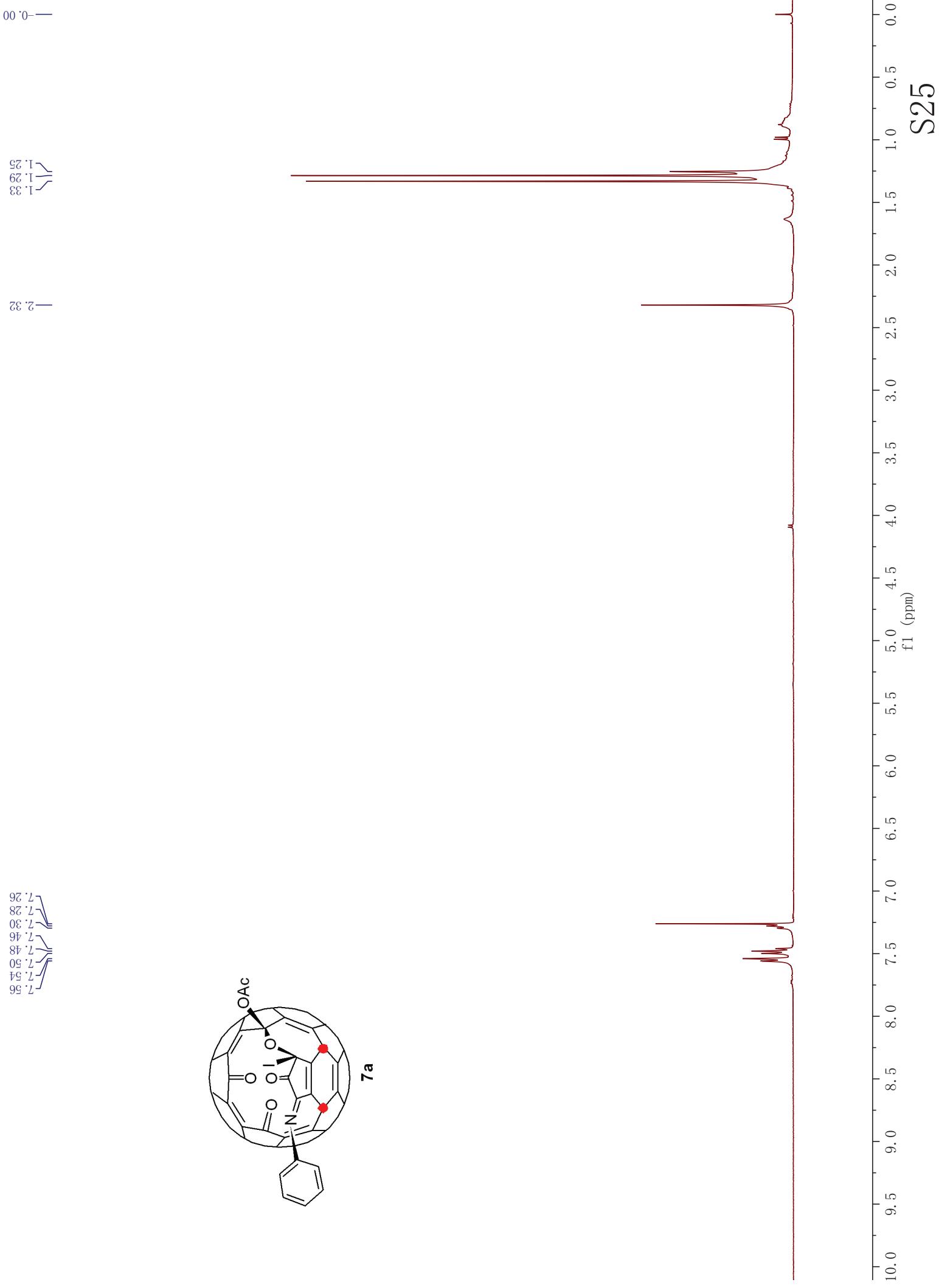
| Time(min) | ln(integral) |
|-----------|--------------|
| 10        | -1.10866     |
| 87        | -1.51413     |
| 219       | -1.96611     |
| 384       | -2.52573     |

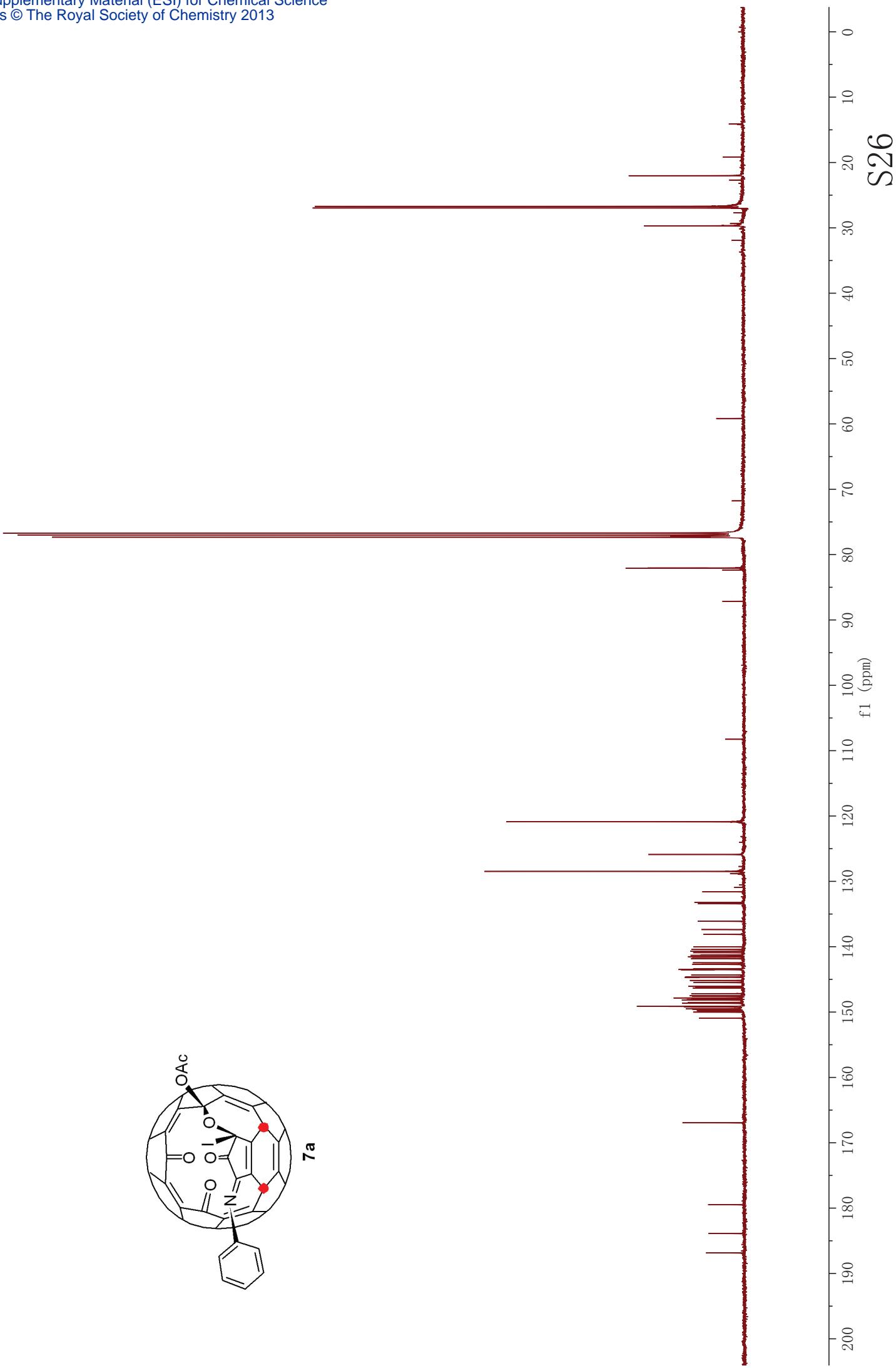
**Table 5** Values for the integral of trapped hydrogen at each time for **12e**



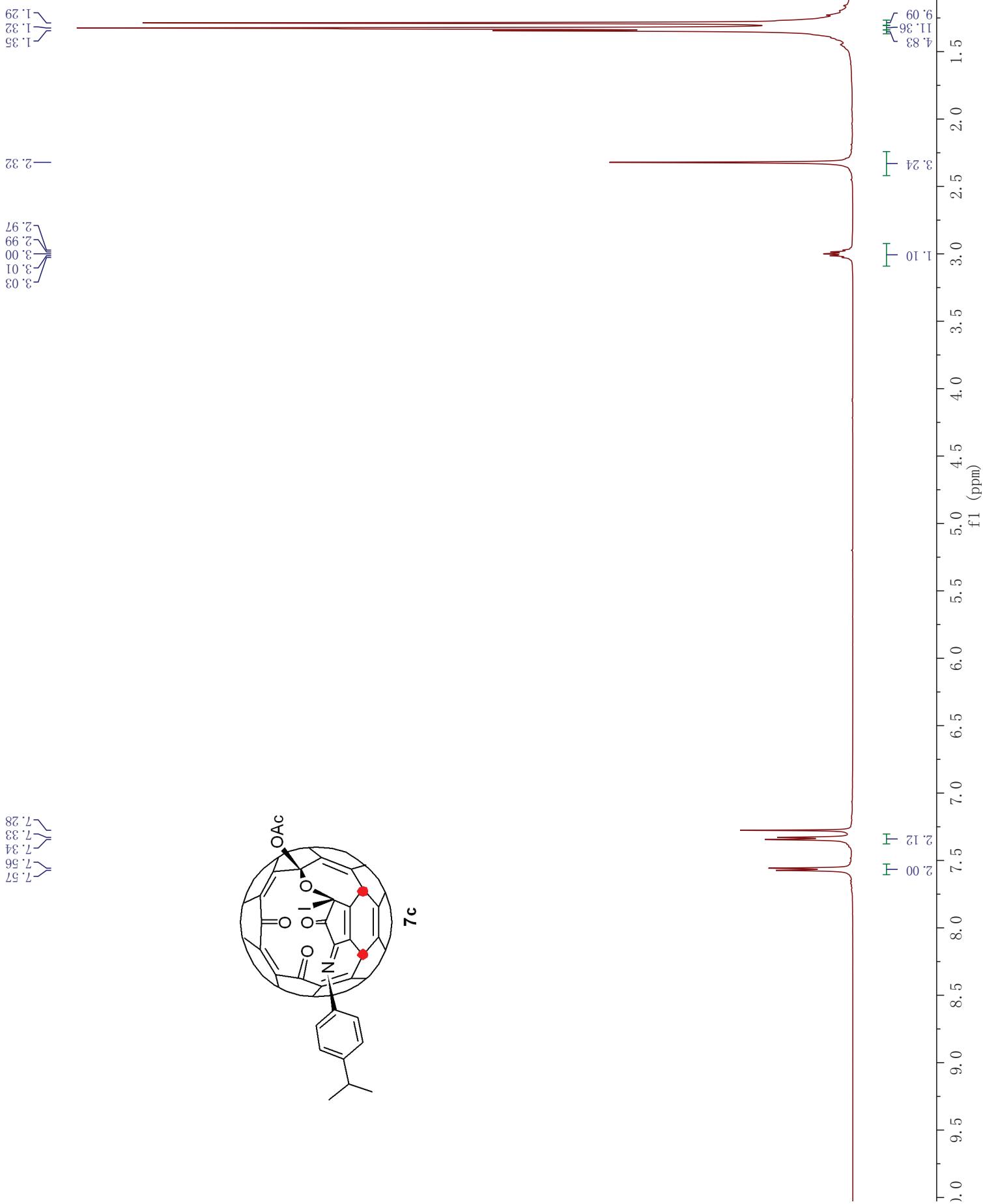
**Figure 10** Eyring plot of the integral data for **12e**

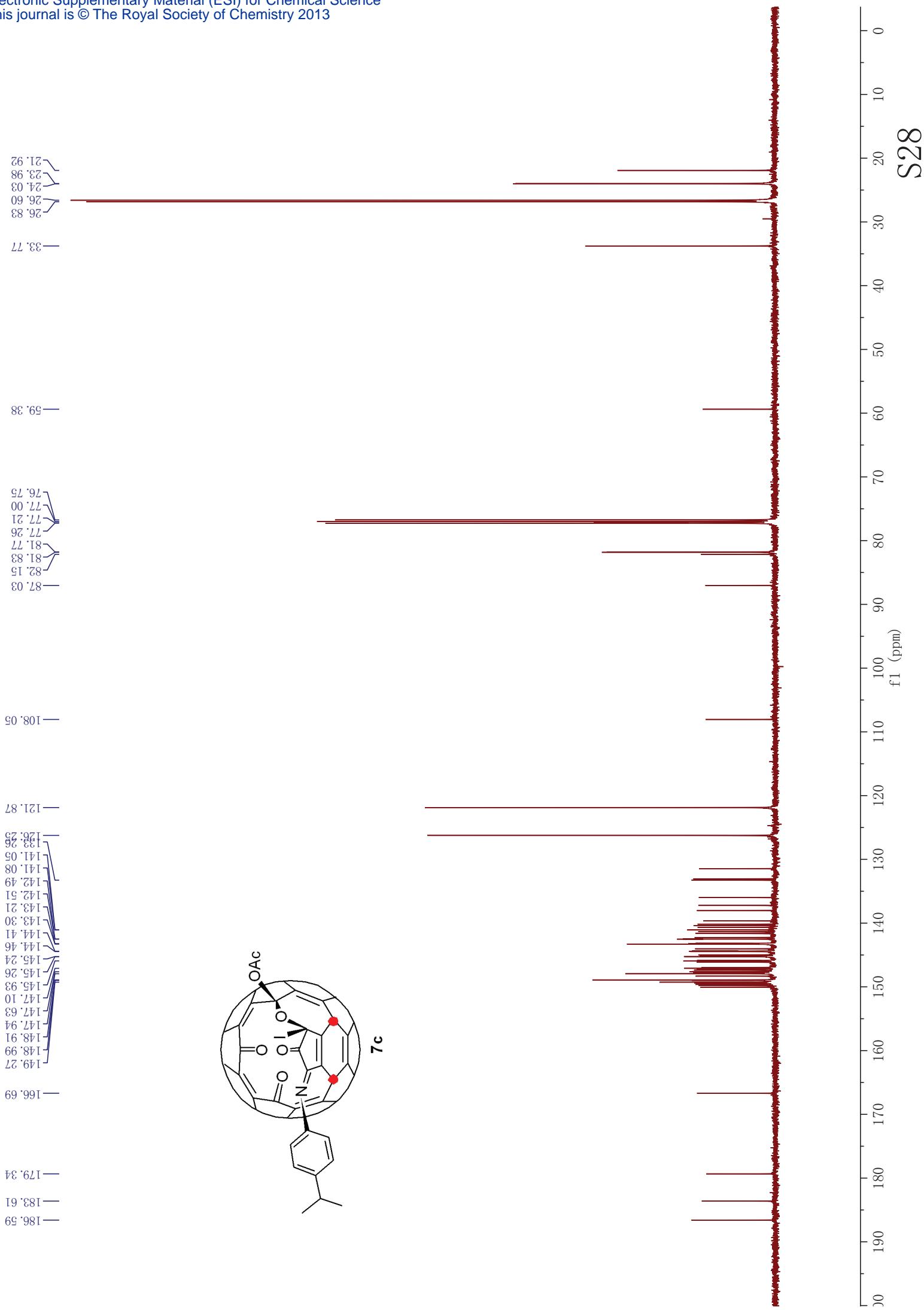
The slope is  $k = 0.0037$ .  $t_{1/2} = \ln 2/k$ . This gives a half-life of  $t_{1/2} = 187$  min.





S27





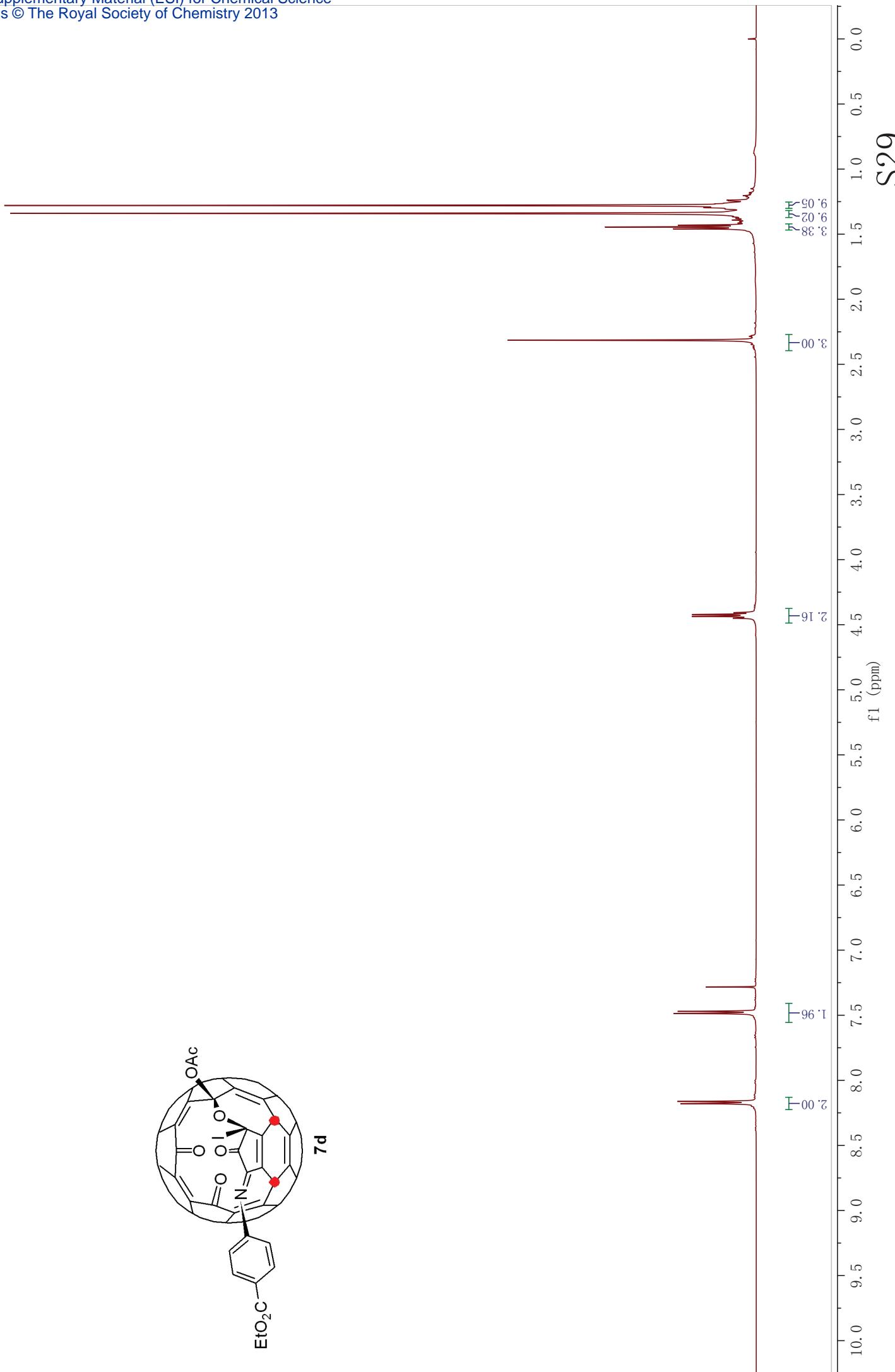
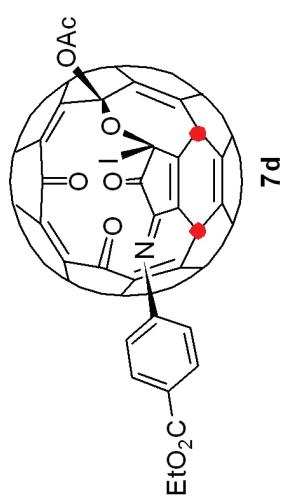
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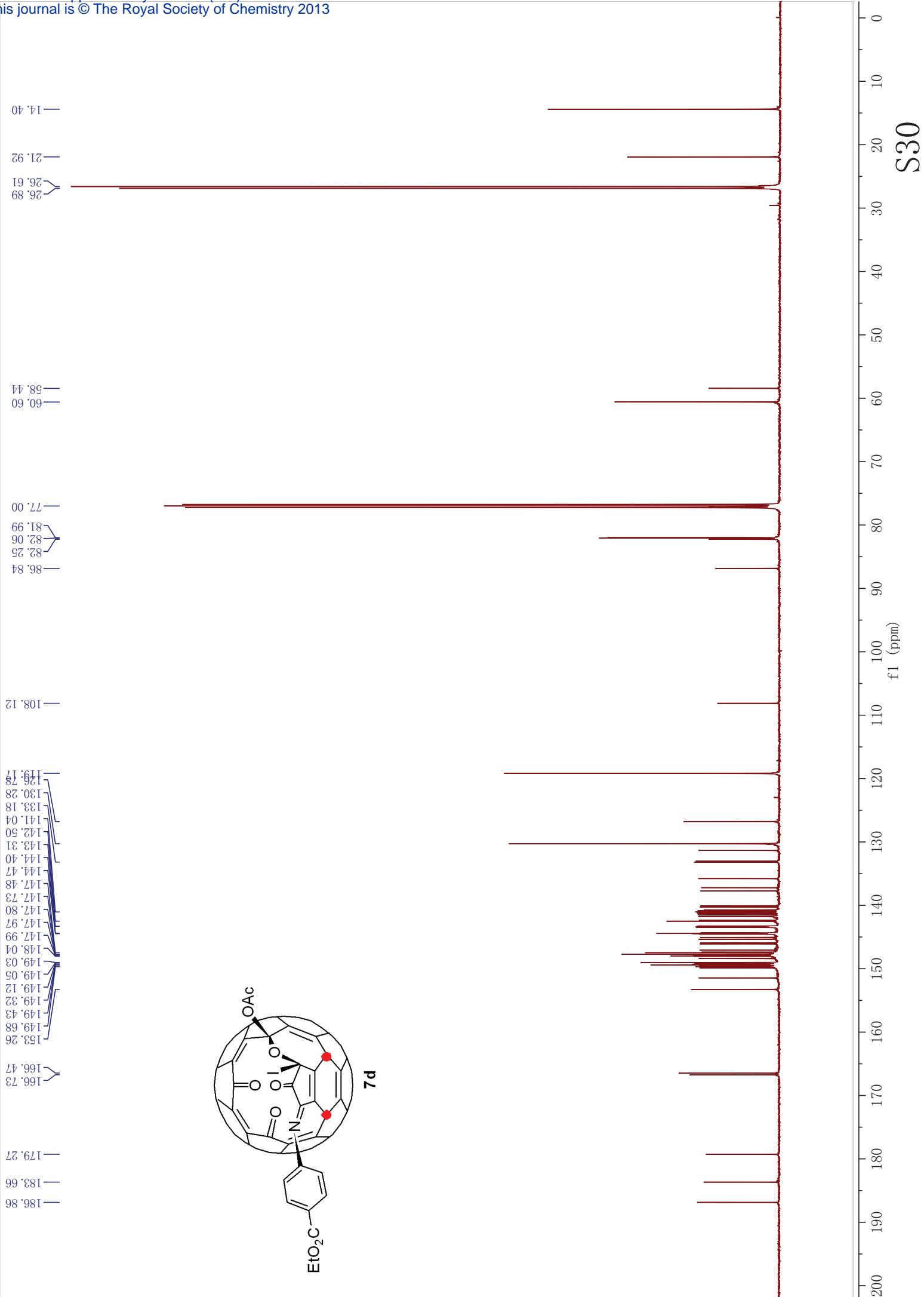
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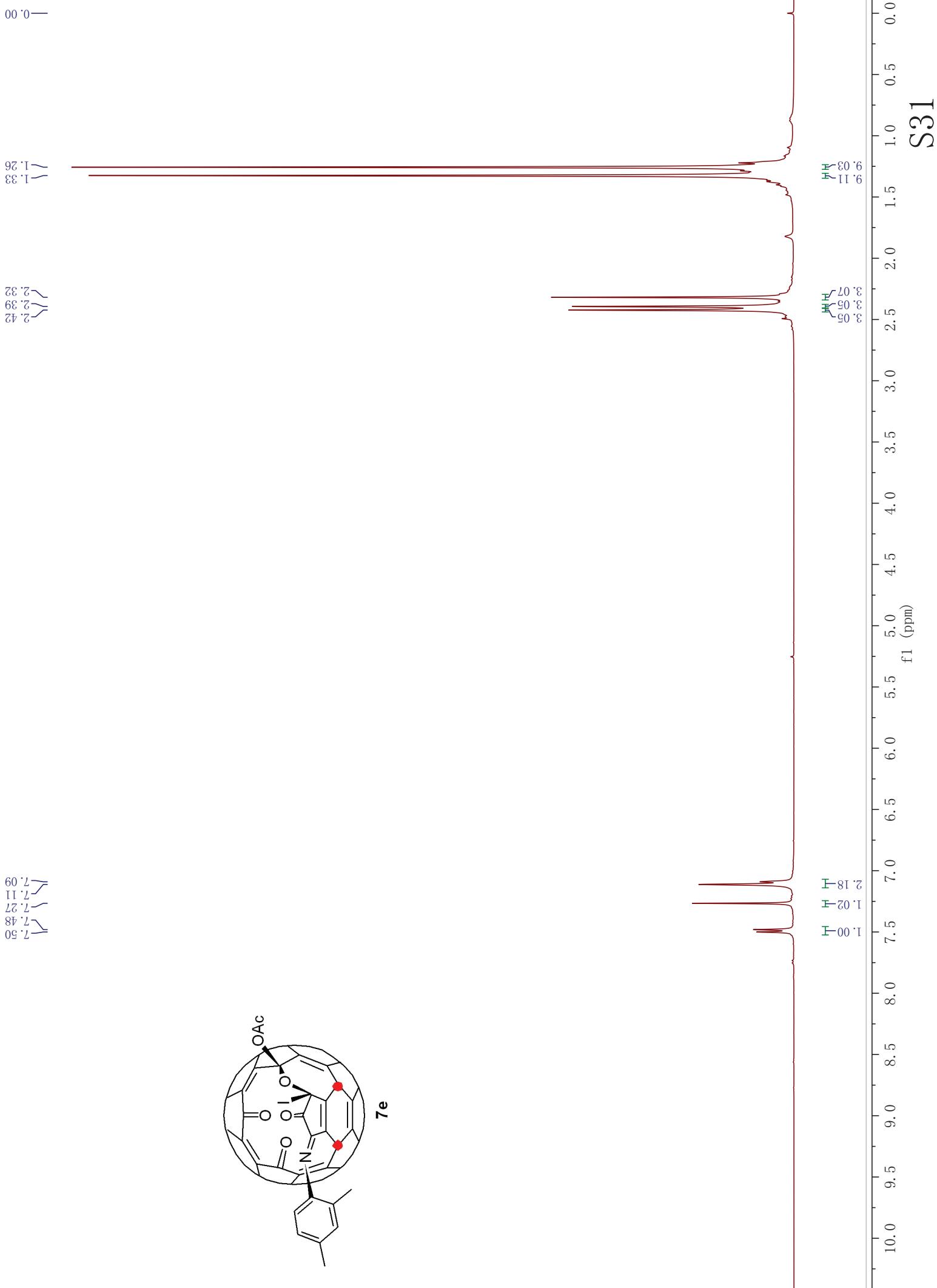
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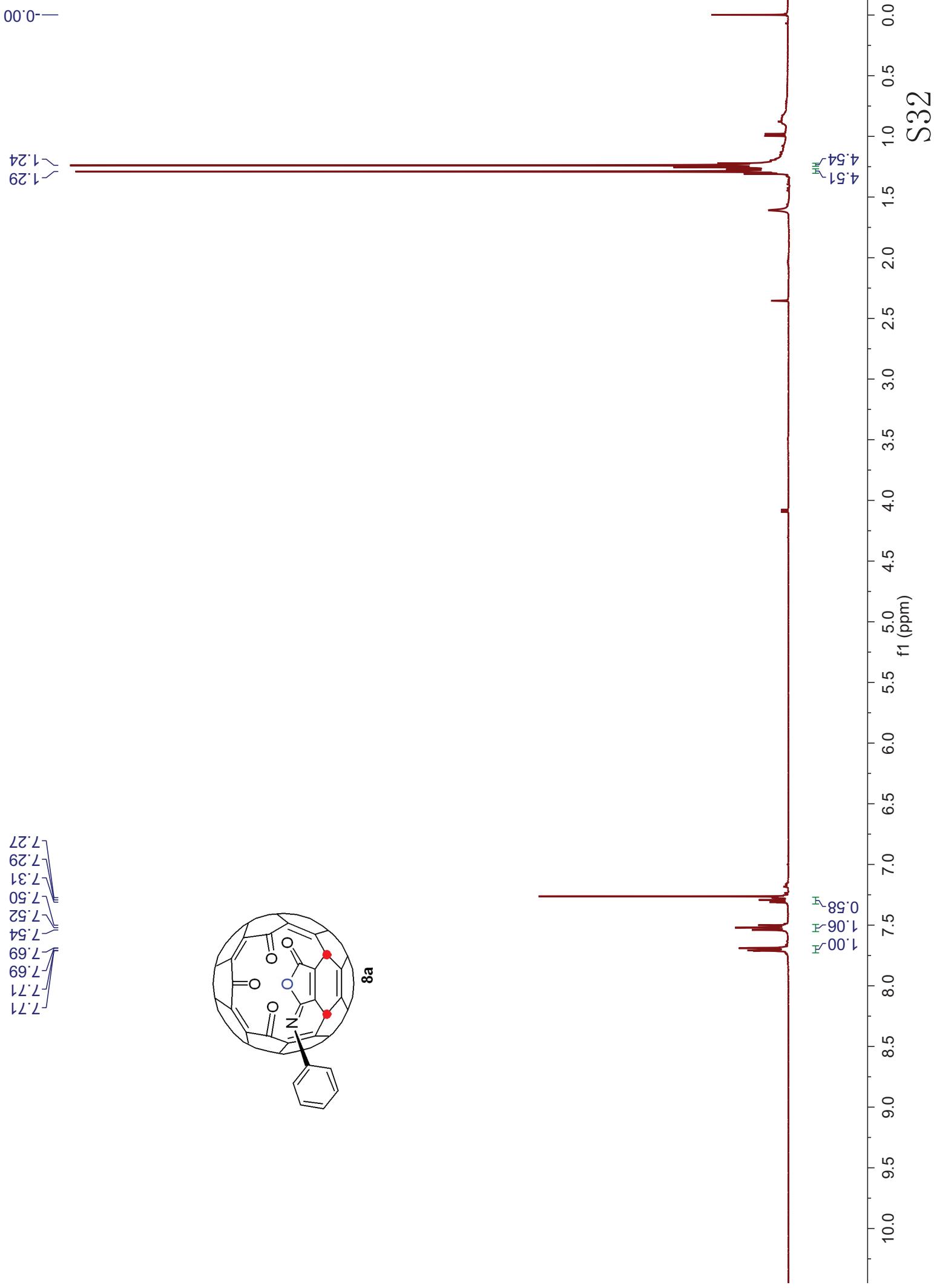
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8.18  
8.16







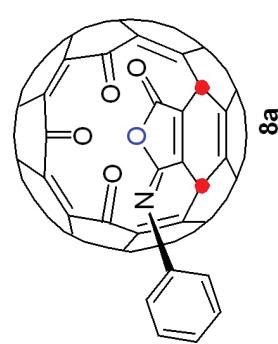


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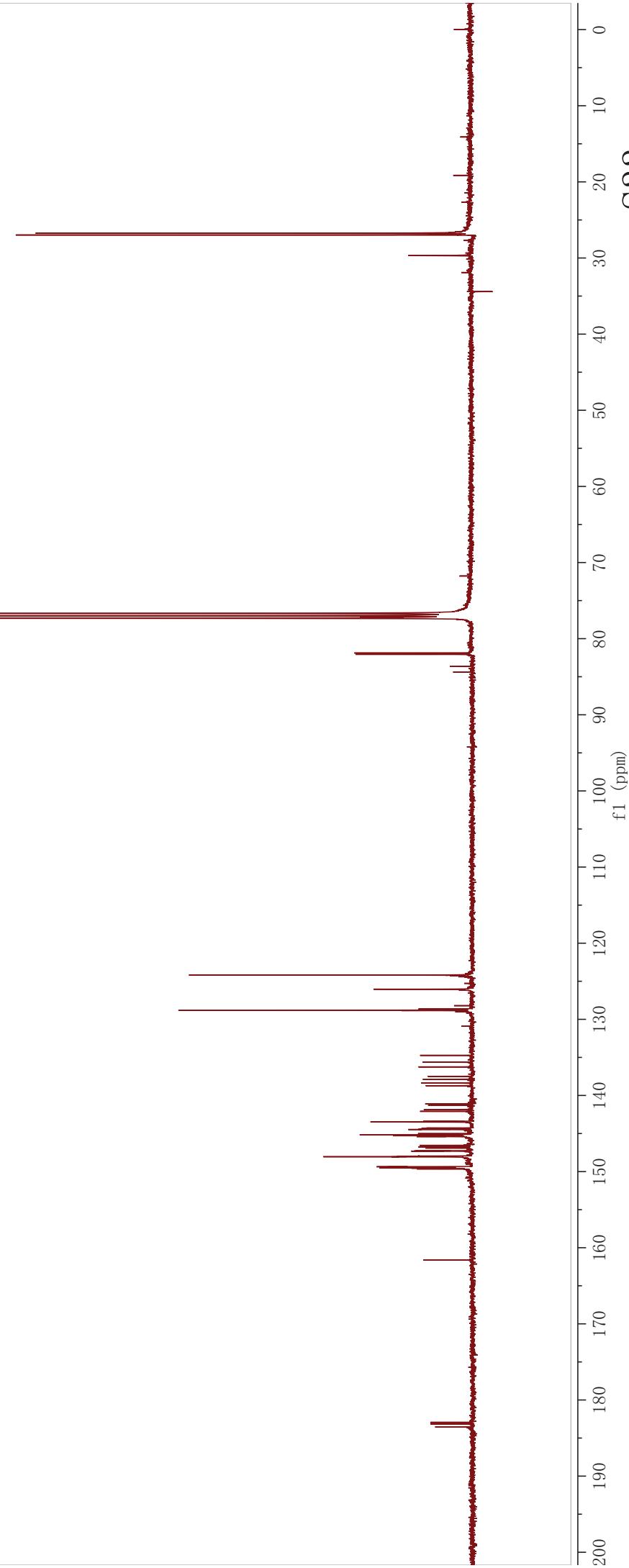
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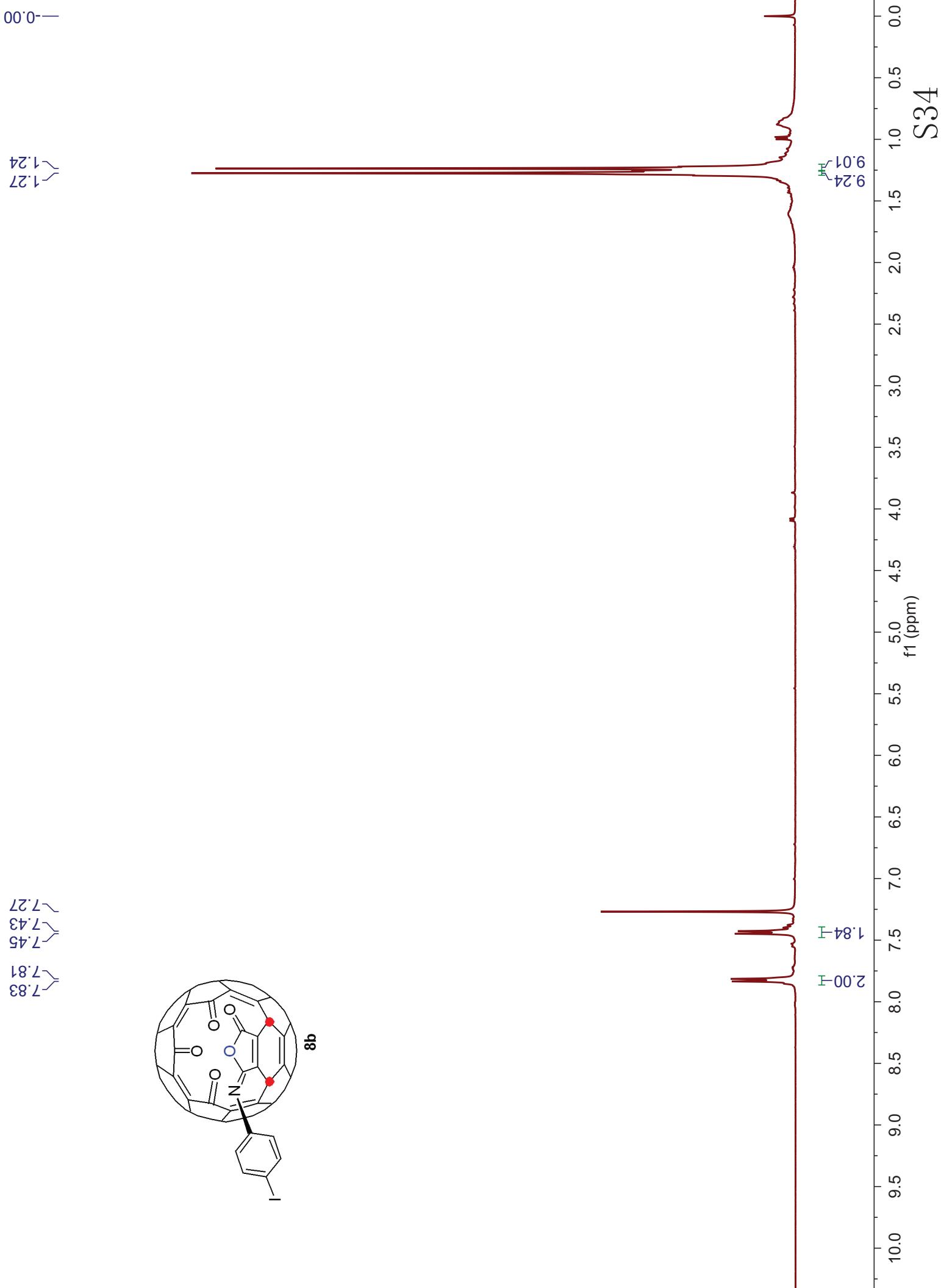
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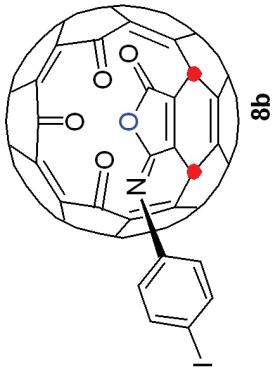
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183.53



**a8**





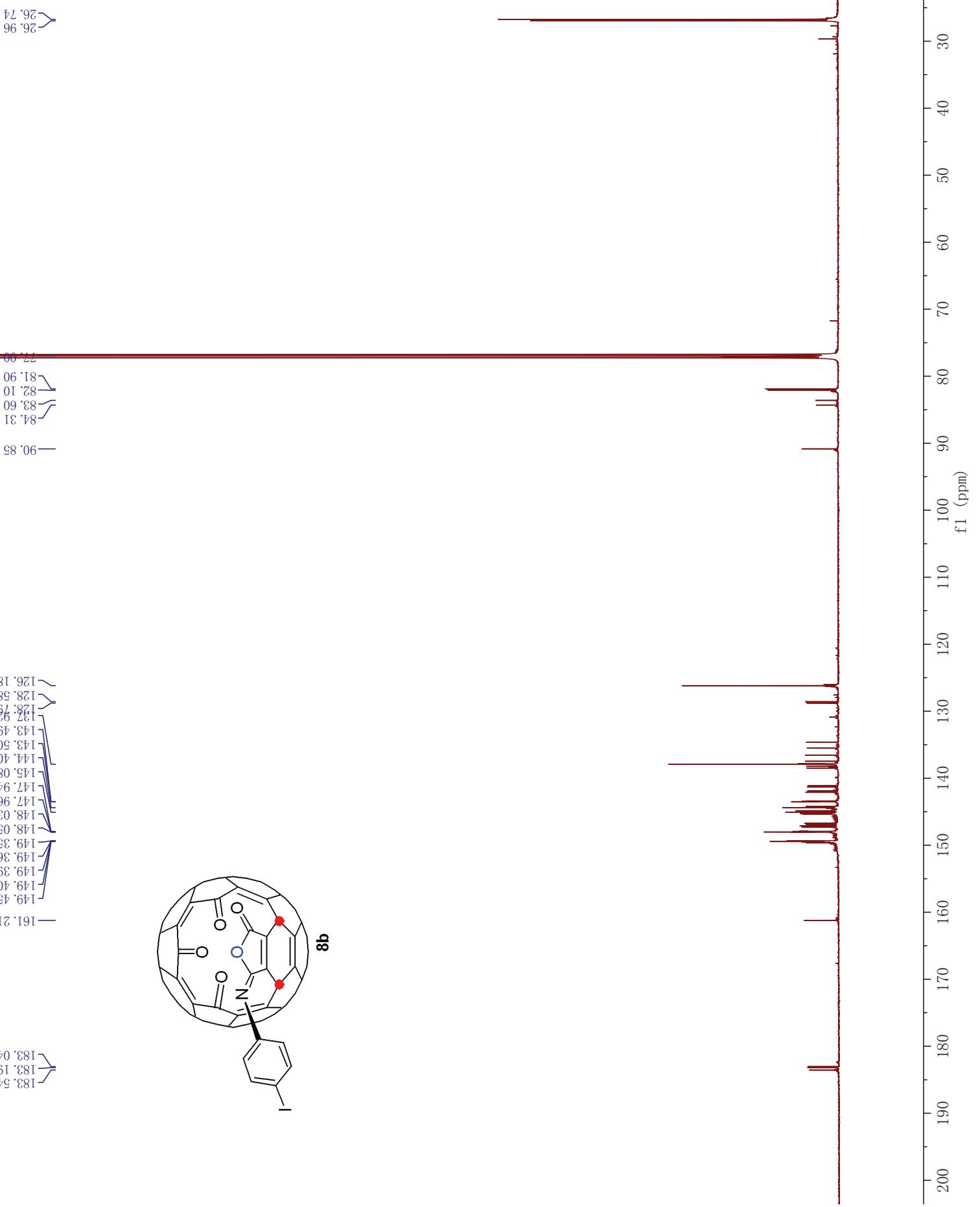


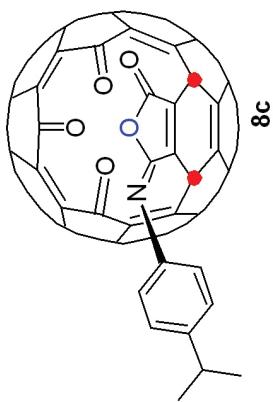
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— 77.00  
— 84.31  
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— 161.21  
— 149.45  
— 149.40  
— 149.36  
— 149.35  
— 149.39  
— 149.40  
— 148.03  
— 148.05  
— 147.96  
— 147.94  
— 147.90  
— 143.49  
— 143.50  
— 144.40  
— 144.49  
— 128.58  
— 128.79  
— 128.92  
— 126.18

— 183.54  
— 183.19  
— 183.04





1.34  
1.32  
1.28  
1.23

3.02  
3.00  
2.99

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7.36  
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6.36  
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6.07

1.12

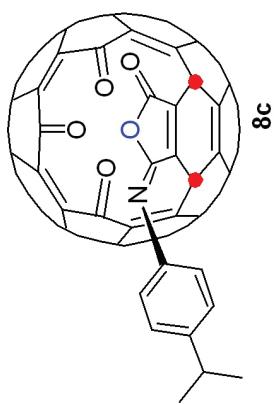
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S36

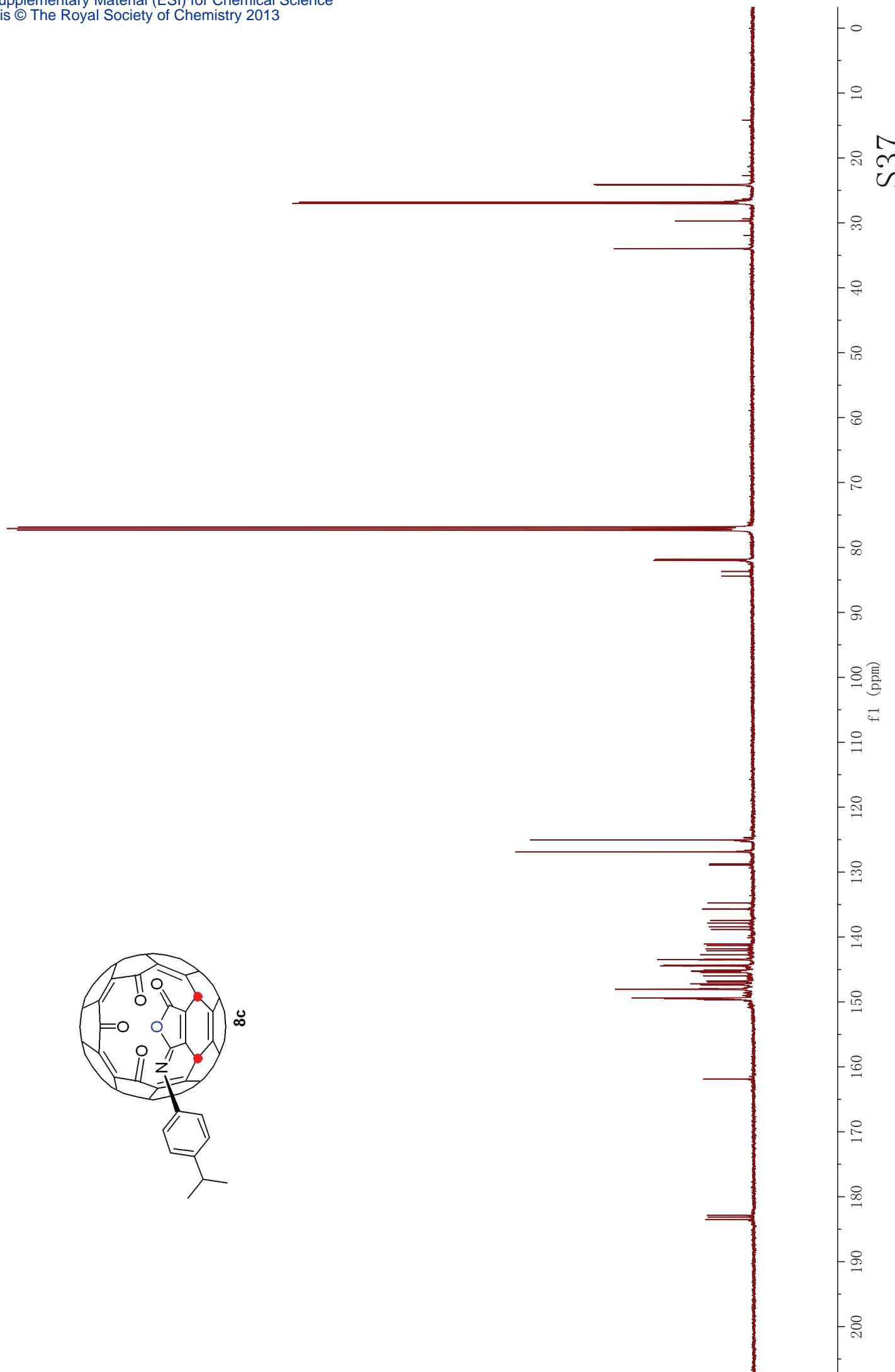
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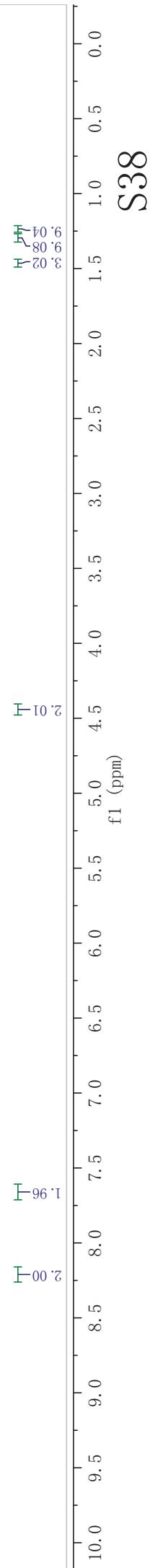
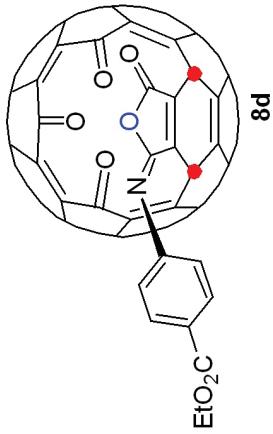
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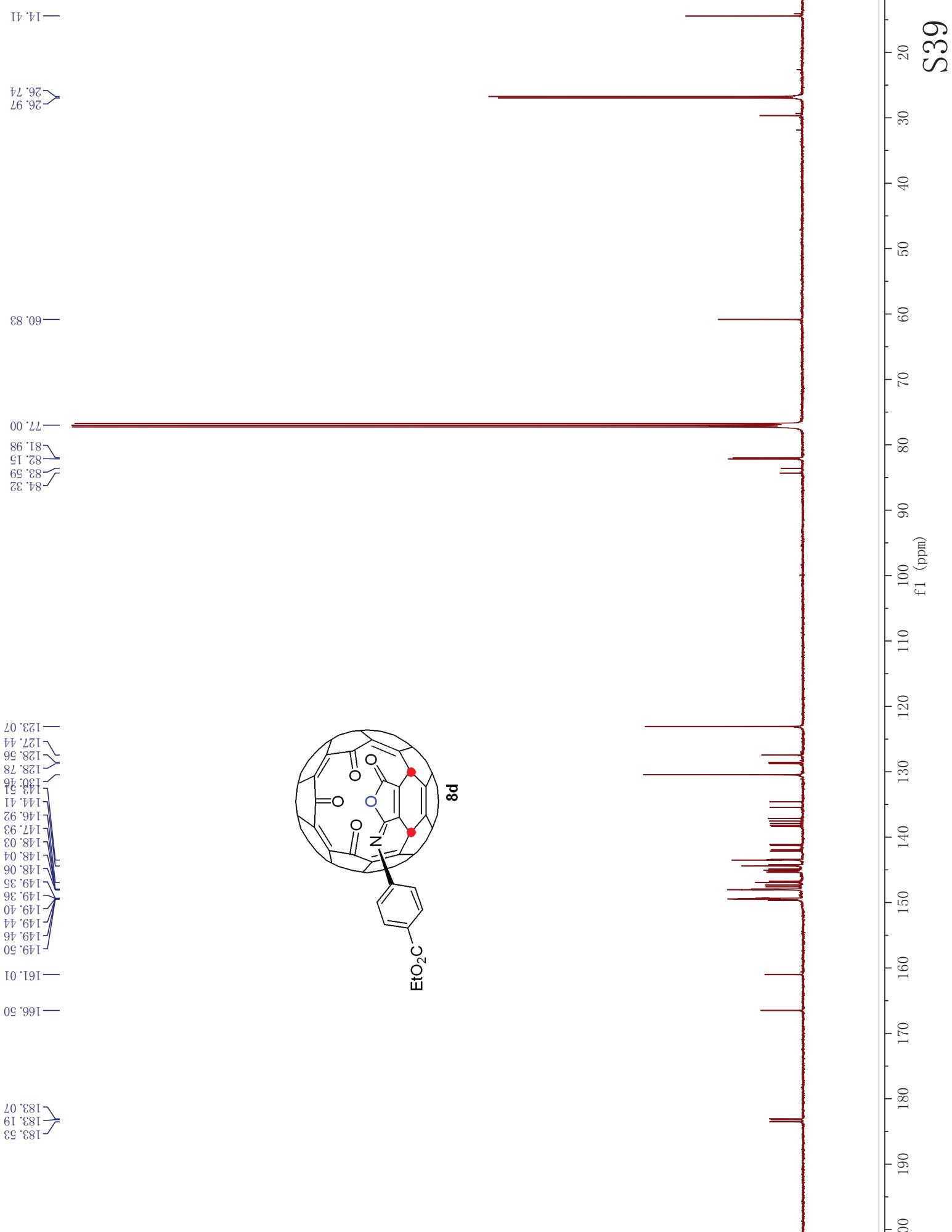
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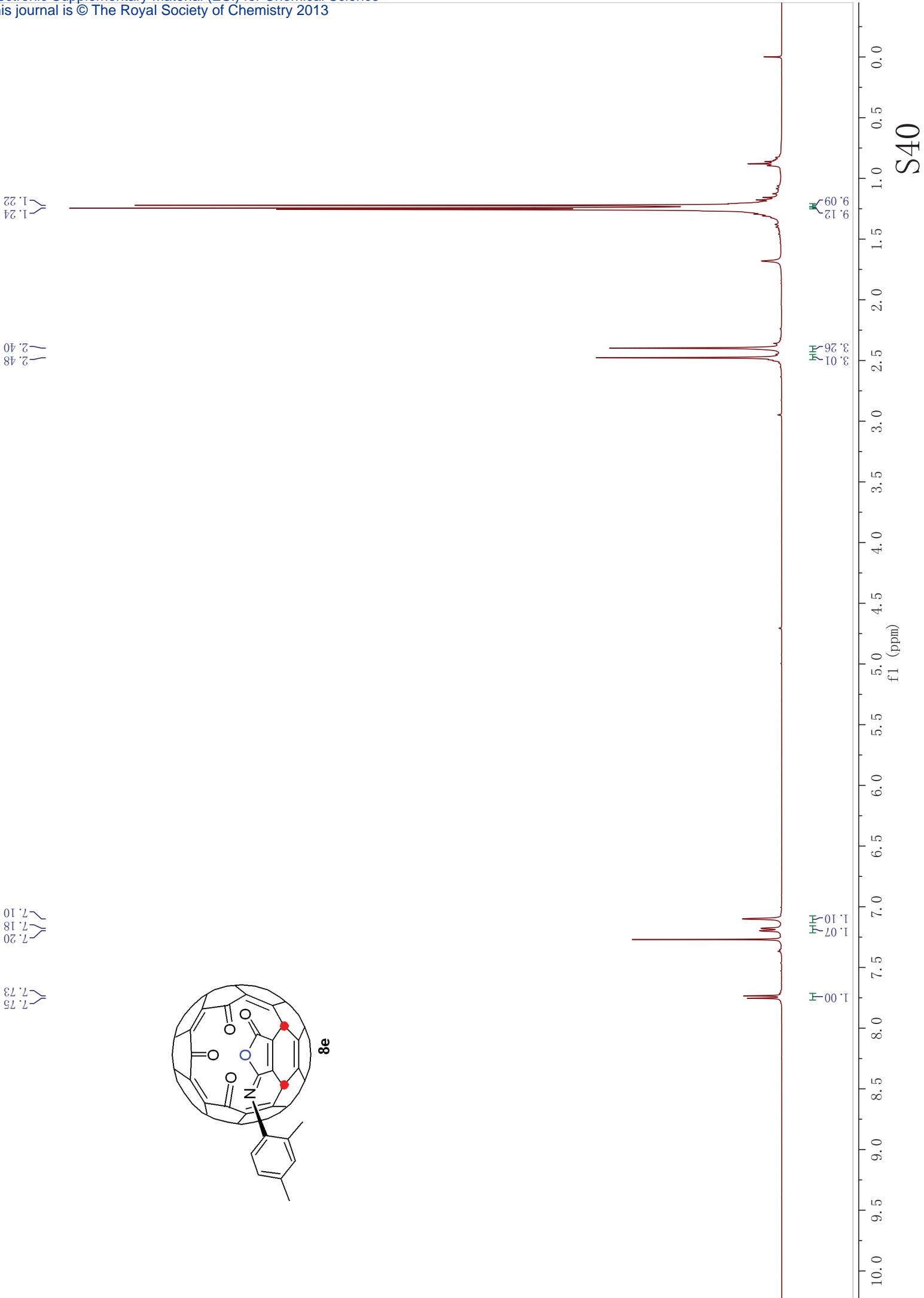


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—1.23

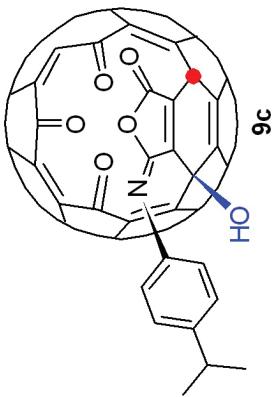
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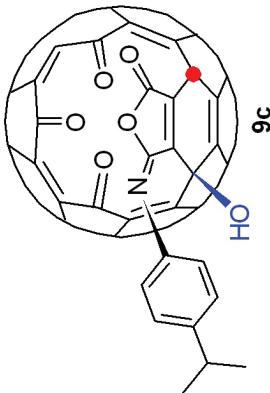
S41

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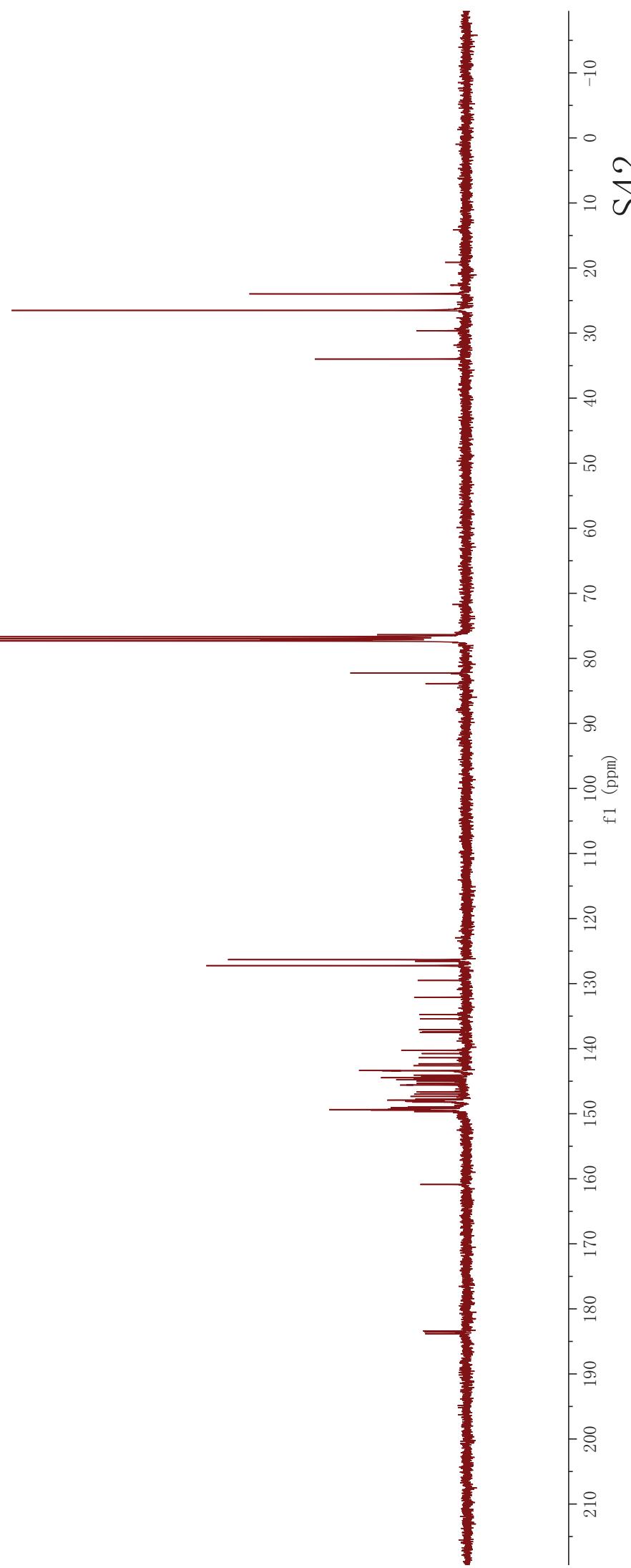
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f1 (ppm)



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83.88  
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126.32  
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127.23  
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140.27  
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142.61  
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143.37  
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143.40  
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143.42  
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144.07  
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144.47  
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183.81  
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183.56  
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183.41



S42

-0.00

1.48  
1.47  
1.46  
1.45  
1.43

4.47  
4.46  
4.45  
4.43

6.68

7.27

7.78

8.00

8.21

8.23

S43

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5.0

5.5

6.0

6.5

7.0

7.5

8.0

8.5

9.0

9.5

10.0

0.0

0.5

1.0

1.5

2.0

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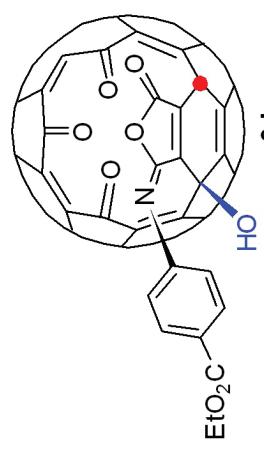
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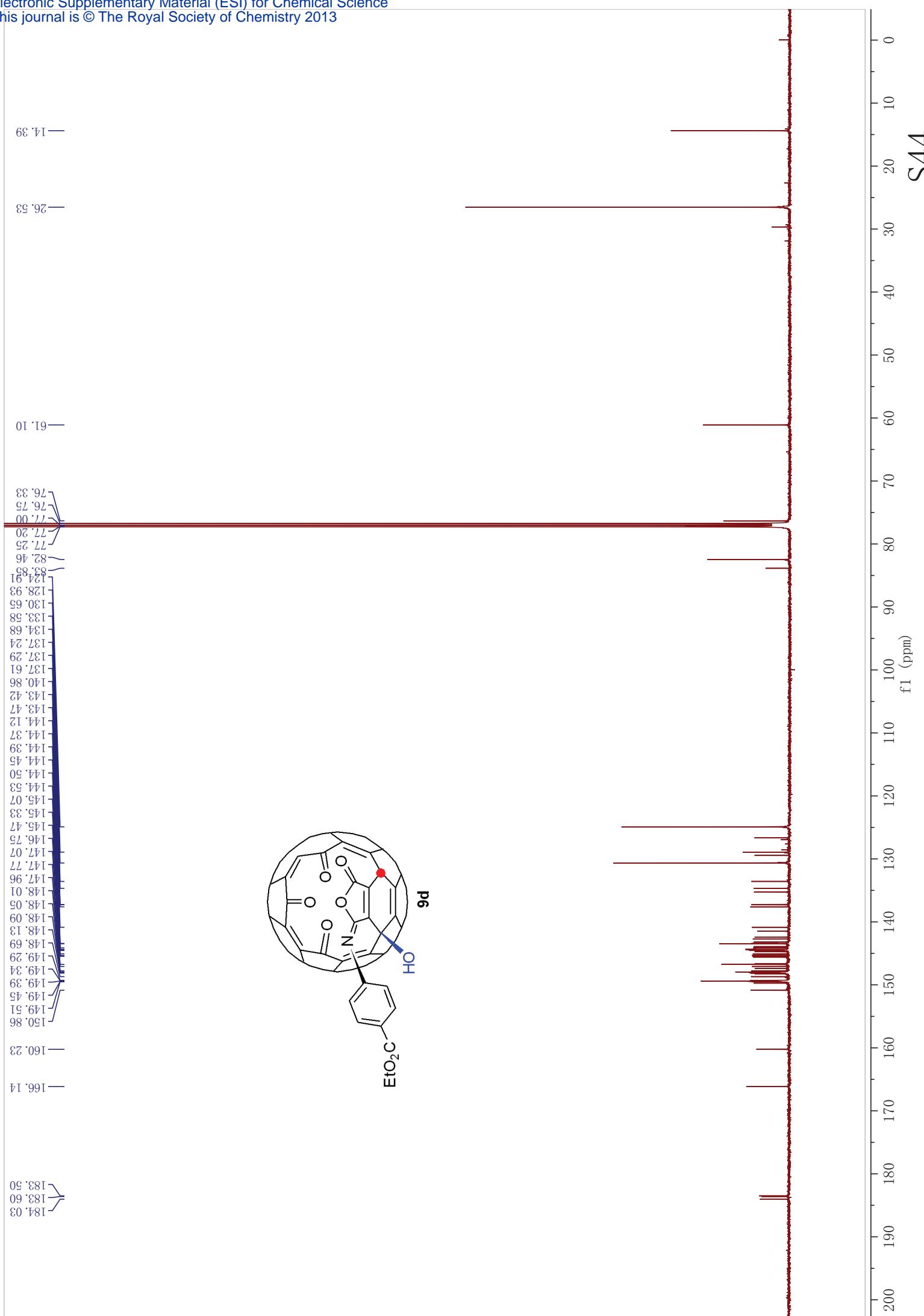
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p6





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— 7.24

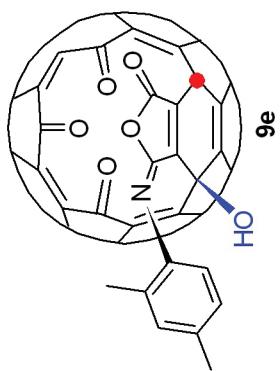
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— 7.91



S45

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7.5

7.0

6.5

6.0

5.5

5.0

4.5

4.0

3.5

3.0

2.5

2.0

1.5

1.0

0.5

0.0

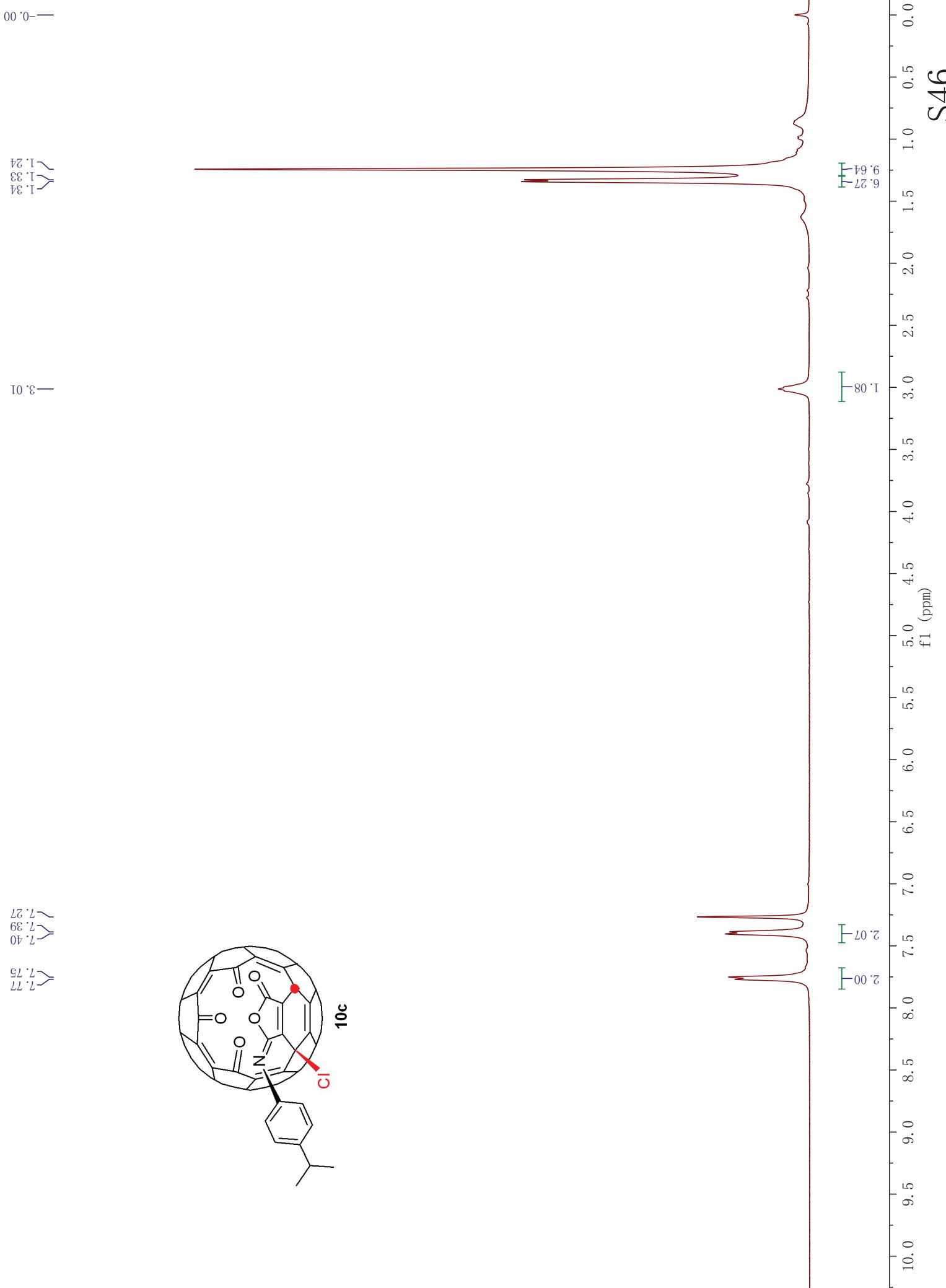
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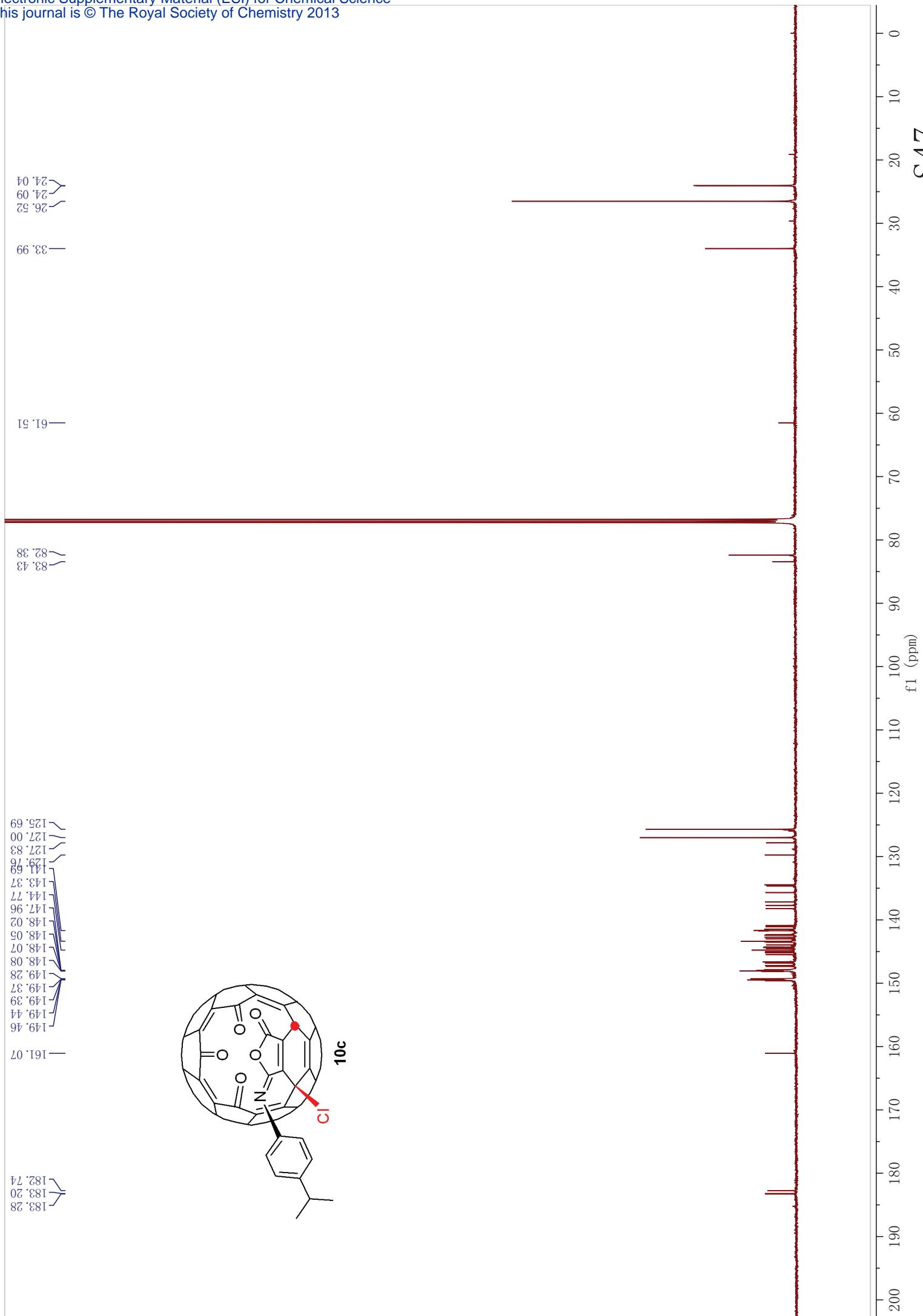
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0.99 H

1.03 H

1.00 H





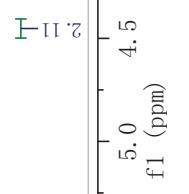
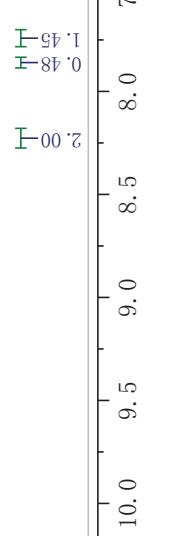
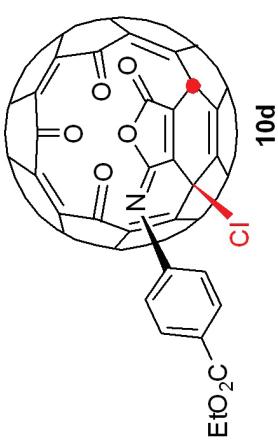
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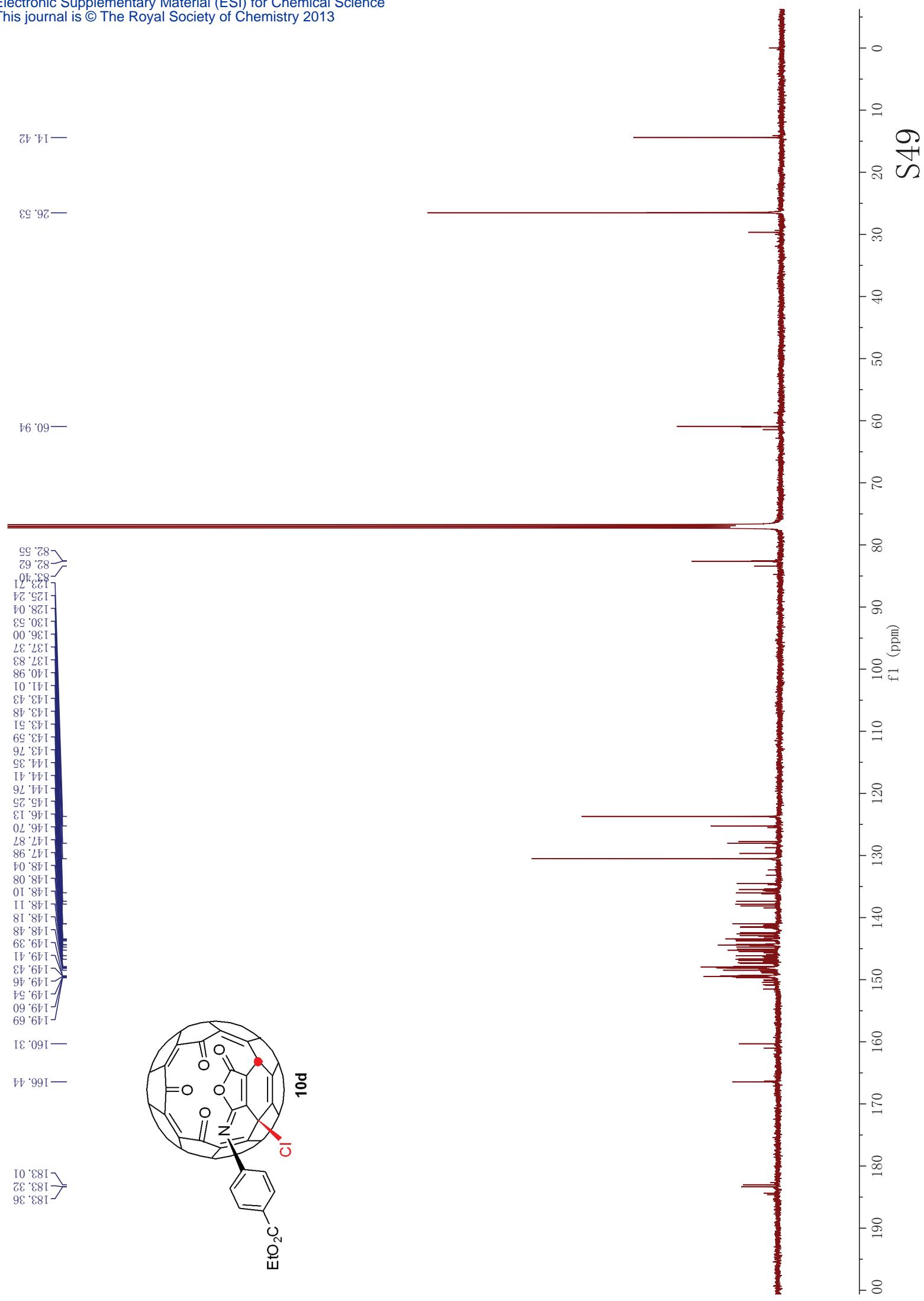
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1.45  
1.44  
1.26  
1.20

4.46  
4.45  
4.43  
4.42

—7.26

8.23  
8.22  
8.21  
7.87  
7.85  
7.75  
7.73





—0.00

—1.24

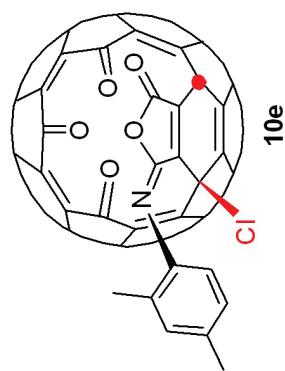
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—7.87

—7.89

—7.87



S50

f1 (ppm)

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9.0

8.5

8.0

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2.0

1.5

1.0

0.5

0.0

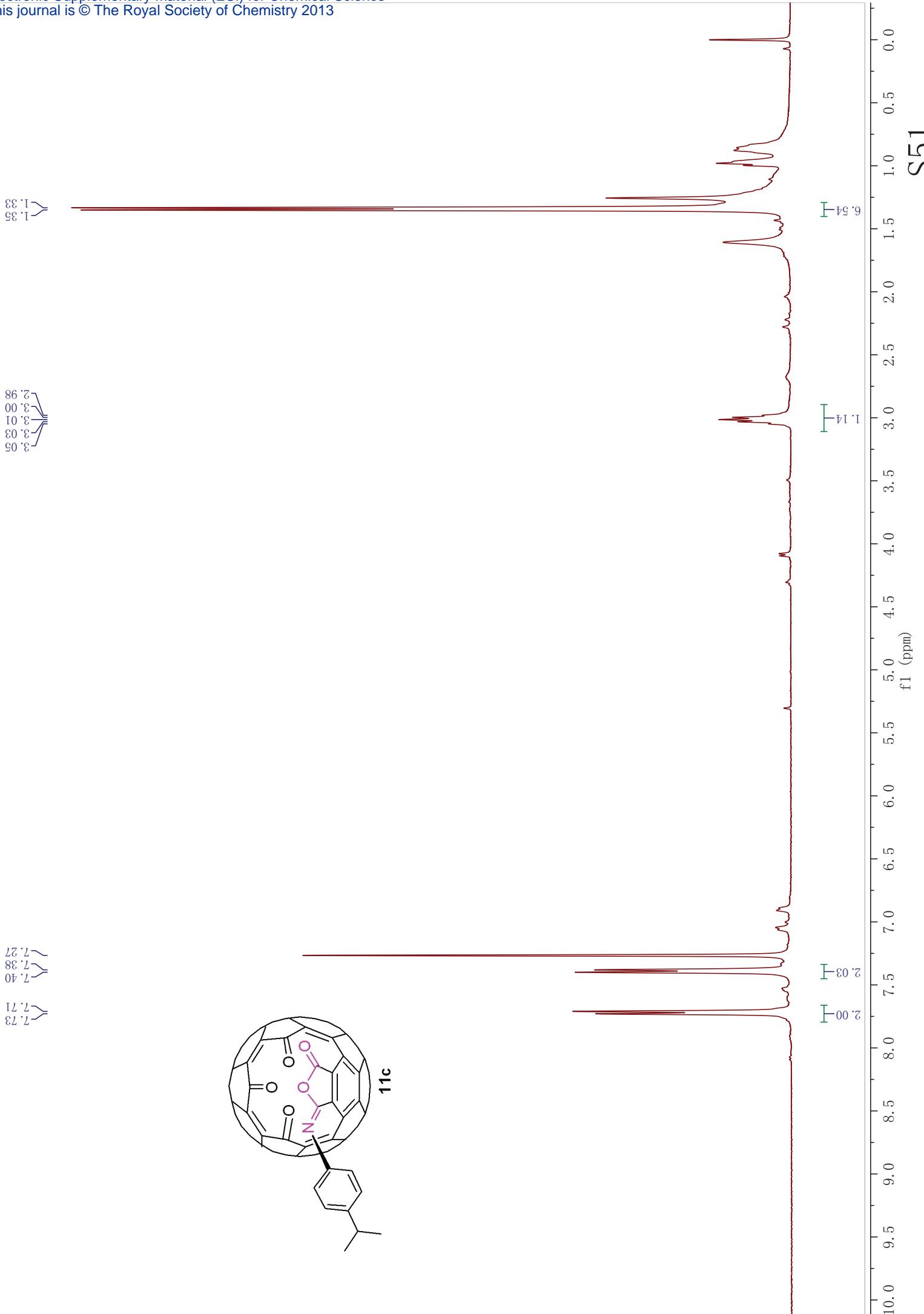
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3.04

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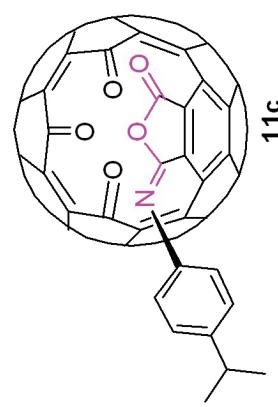
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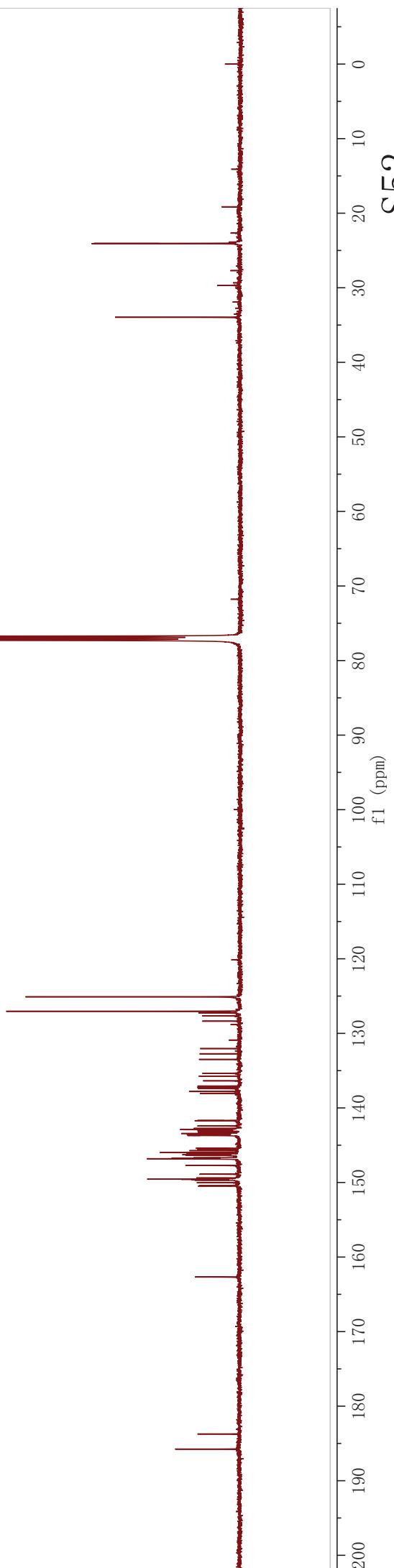
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33.96

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133.56  
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145.42  
145.58  
145.99  
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146.27  
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146.38  
146.69  
146.73  
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147.72  
148.89  
149.39  
149.55  
149.58  
149.62  
149.70  
150.40  
150.68  
183.73  
185.76



11c



-0.00

1.48

1.47

1.45

4.48

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4.11

4.10

4.09

4.08

4.07

4.06

4.05

4.04

4.03

4.02

4.01

4.00

3.99

3.98

3.97

3.96

3.95

3.94

3.93

3.92

3.91

3.90

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3.86

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3.84

3.83

3.82

3.81

3.80

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3.76

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3.70

3.69

3.68

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2.79

2.78

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2.04

2.03

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2.01

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1.96

1.95

1.94

1.93

1.92

1.91

1.90

1.89

1.88

1.87

1.86

1.85

1.84

1.83

1.82

1.81

1.80

1.79

1.78

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1.54

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1.52

1.51

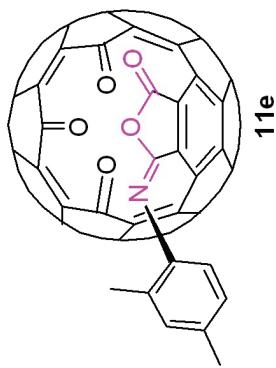
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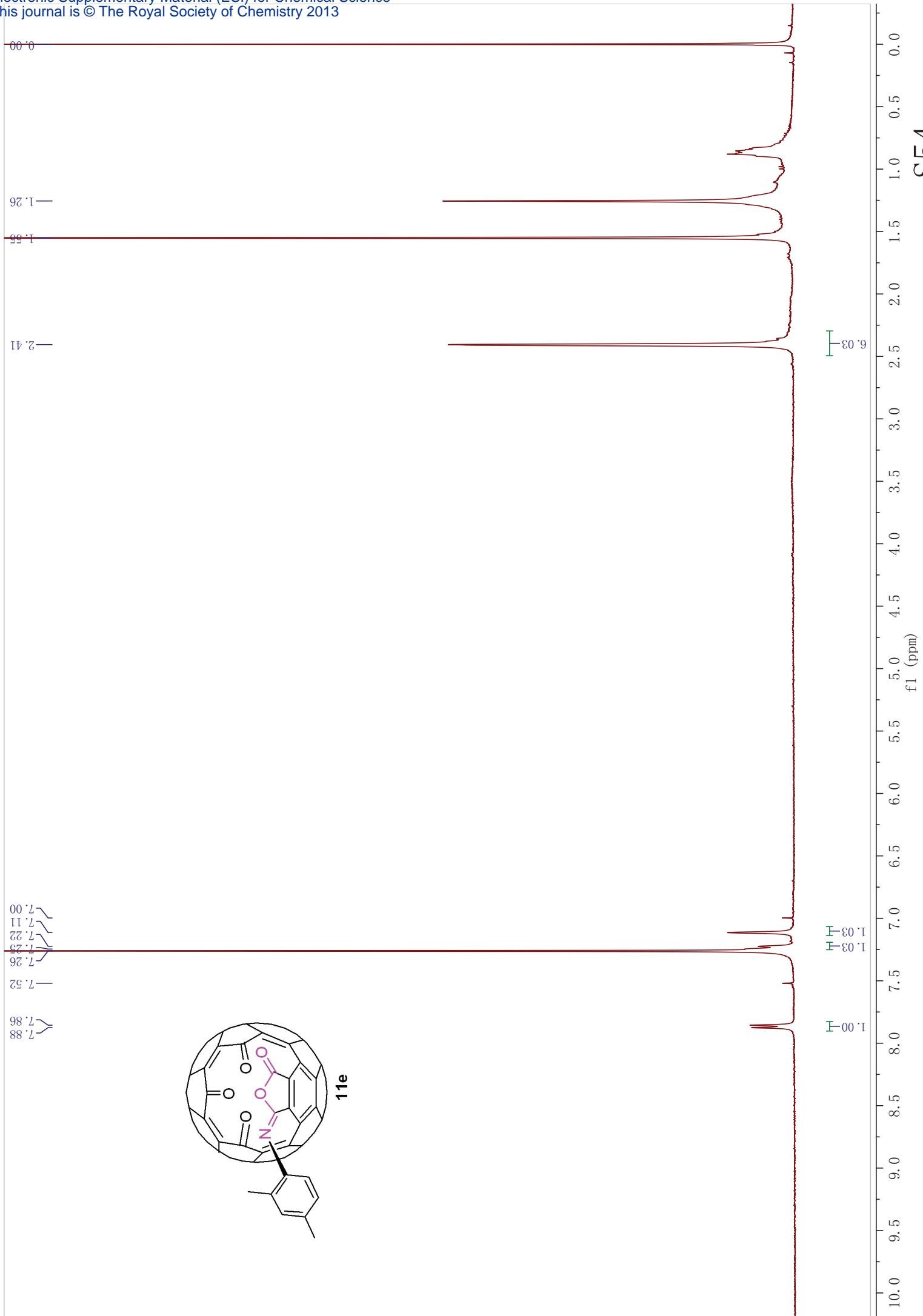
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1.47

1.46



**11e**



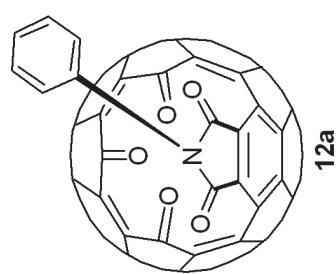
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1.18

1.45

6.24

7.91  
7.92  
7.90  
7.72  
7.71  
7.69  
7.58  
7.56  
7.54



2.00 H  
1.09 H

S55

0.0

0.5

1.0

1.5

2.0

2.5

3.0

3.5

4.0

4.5

5.0

5.5

6.0

6.5

7.0

7.5

8.0

8.5

9.0

9.5

10.0

S55

0.0

0.5

1.0

1.5

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3.5

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5.5

6.0

6.5

7.0

7.5

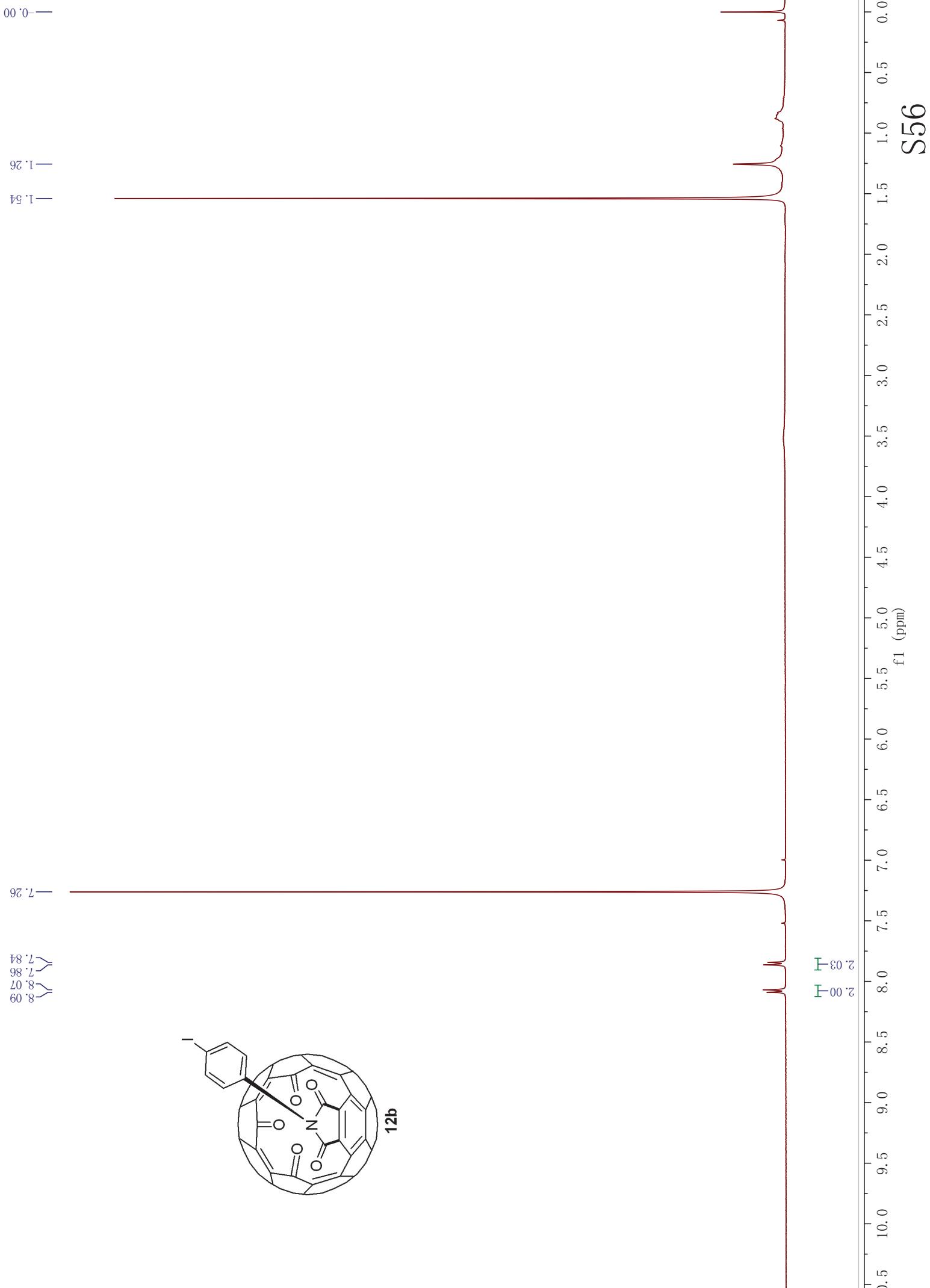
8.0

8.5

9.0

9.5

10.0



—0.00

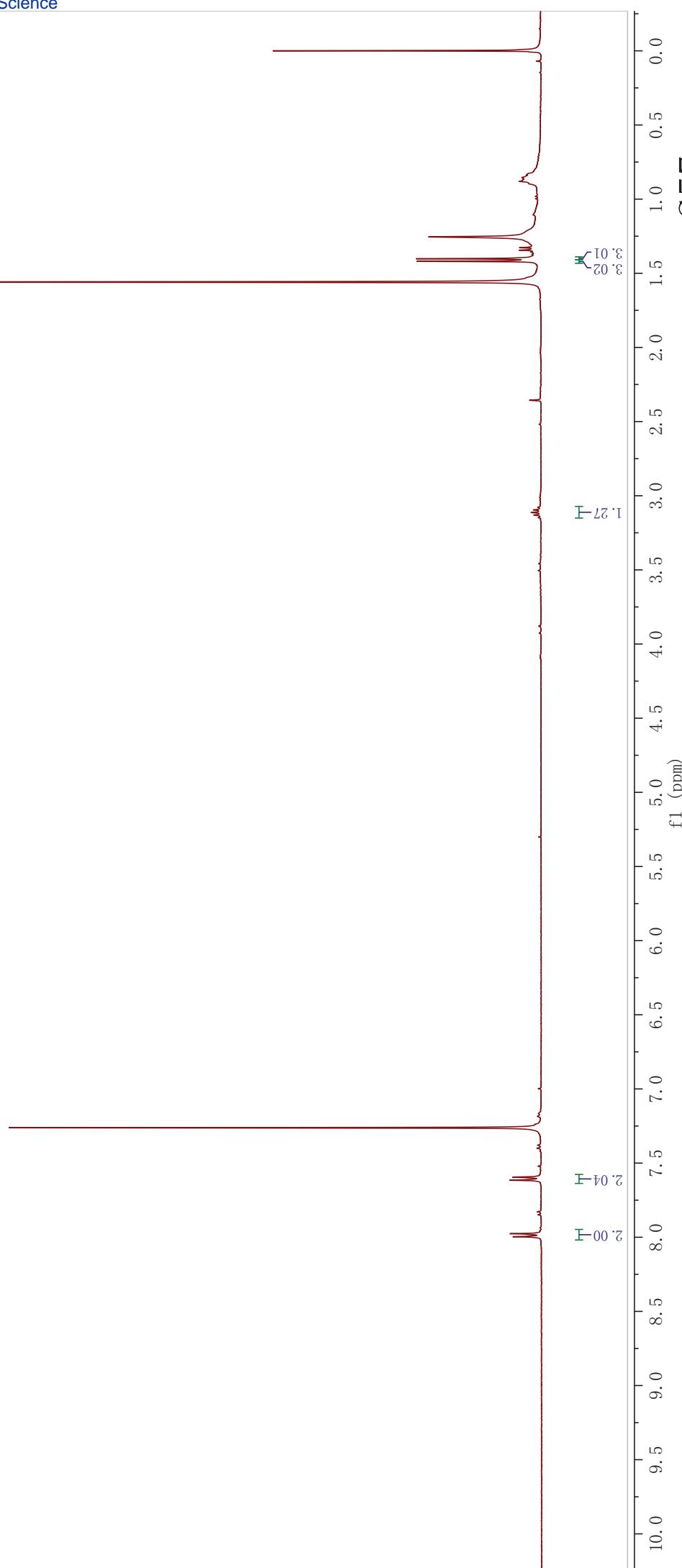
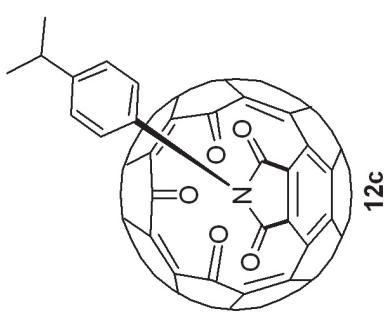
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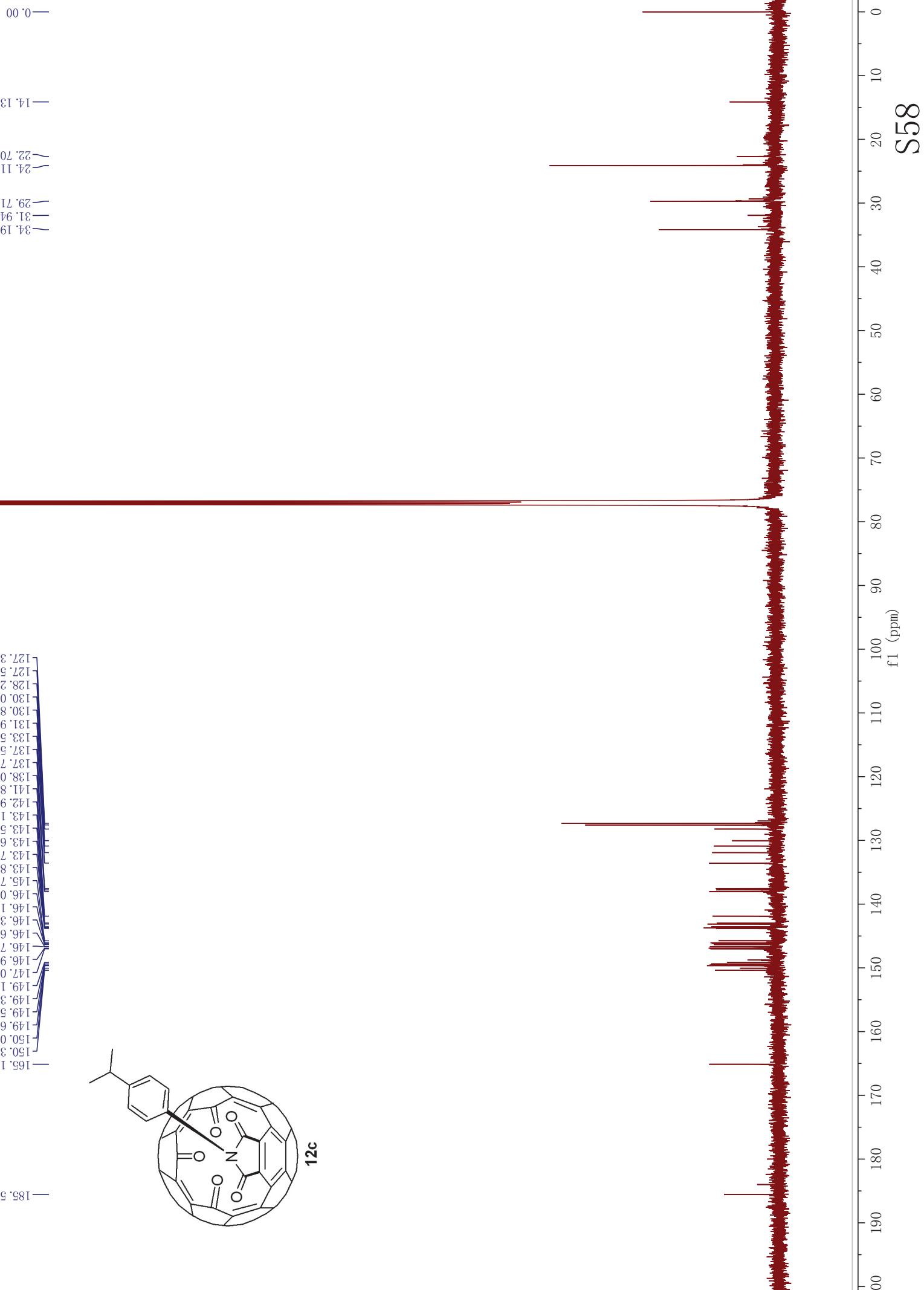
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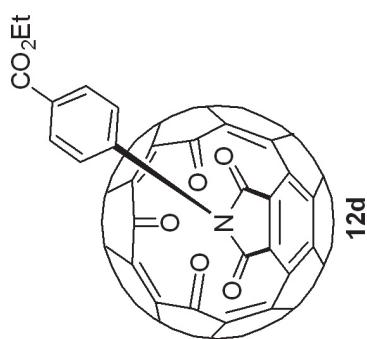
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—8.00  
—7.98







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4.53  
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4.49  
4.47

7.26

8.44  
8.42  
8.21  
8.19

1.48  
1.49

