

**Metal-free thermal organocatalytic pinacol coupling of arylaldehydes  
by an isonicotinate catalyst with bis(pinacolato)diboron**

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## 1. General Information

Reagents and solvents for syntheses were commercially purchased and used as received. Air and/or moisture sensitive reactions were carried out by using dry solvents under an argon atmosphere using an argon balloon. TLC analysis was performed using Merck TLC Silica gel 60 F<sub>254</sub>. Flash silica gel column chromatography was performed on Wako Wakosil<sup>®</sup> C-300 or Biotage<sup>®</sup> Rening Cartridge. Alumina column chromatography was performed on Merck Aluminium oxide 90 active neutral. IR spectra were recorded on a Jasco FT/IR-4700 spectrometer with ATR PRO ONE in ATR mode using diamond prism. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker spectrometer at 500 and 126 MHz. CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as a solvent and the residual solvent peaks were used as an internal standard (CDCl<sub>3</sub>: <sup>1</sup>H NMR: 7.26 ppm; <sup>13</sup>C NMR: 77.0 ppm; DMSO-*d*<sub>6</sub>: <sup>1</sup>H NMR: 2.50 ppm; <sup>13</sup>C NMR: 39.52 ppm). High resolution (HR) mass spectra (MS) were measured on JEOL JMS-T100LP using electrospray ionization (ESI). The reactions at high temperature were performed with Organic Synthesizer, EYELA ChemiStation, using aluminum heating block with cooling circulator. Ozonizer (HAMANETSU, SO-03UN-OX) was used for ozonolysis.

## 2. Synthesis of 1,1'-Biphenyl-2,2'-dicarbaldehydes

### 1,1'-Biphenyl-2,2'-dicarbaldehyde (4a)

1,1'-Biphenyl-2,2'-dicarbaldehyde (**4a**) was prepared according to a literature procedure.<sup>1</sup> A suspension of phenanthrene (1.00 g, 5.61 mmol) in methanol (25 mL) was cooled to -78 °C and ozone was bubbled into the solution until phenanthrene was consumed completely, which was judged by TLC analysis. After completion of the reaction, nitrogen gas was bubbled into the mixture for 30 minutes. Then, potassium iodide (2.80 g, 16.9 mmol) and acetic acid (5 mL) were added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated *aq.* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added until the brown color of iodine disappeared. Methanol was evaporated *in vacuo*. Saturated *aq.* NaHCO<sub>3</sub> (50 mL) was added to the mixture, and the mixture was extracted with EtOAc (50 mL). The organic extract was washed by saturated *aq.* NaHCO<sub>3</sub> (50 mL), water (50 mL), and brine (50 mL). The resulting organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered through Celite. The filtrate was concentrated *in vacuo* and the residue was purified by SiO<sub>2</sub> column chromatography (13-17% EtOAc/hexane) to afford **4a** (1.04 g, 88% yield) as a yellow solid. The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>2</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 9.84 (s, 2H), 8.04 (dd, *J* = 7.6, 0.9 Hz, 2H), 7.78 (ddd, *J* = 7.6, 7.6, 1.2 Hz, 2H), 7.69 (m, 2H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 2H) ppm.

### 3,3'-Difluoro-1,1'-biphenyl-2,2'-dicarbaldehyde (4b)

Dicarbaldehyde **4b** was prepared according to a literature procedure.<sup>3</sup> In a glove box, a test tube equipped with a magnetic stir bar was charged with 2-bromo-6-fluorobenzaldehyde (406 mg, 2.0 mmol), 2,2'-bipyridyl (171 mg, 1.1 mmol), Ni(COD)<sub>2</sub> (303 mg, 1.1 mmol), and 1,5-cyclooctadiene (123 μL, 1.0 mmol). To this test tube was added DMF (2.0 mL). The test tube was capped with a rubber septum, and the test tube was taken out from the glove box and placed in a preheated aluminum heating block at 60 °C. The mixture was stirred under argon atmosphere at 60 °C for 12 h. After cooling to room temperature, the

mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered through a small pad of silica gel. After evaporation of solvent, the crude product was purified by SiO<sub>2</sub> column chromatography (0-10% EtOAc/hexane) to give **4b** (209.9 mg, 85%) as a colorless solid. The NMR spectra were identical to those in the literature.<sup>4</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.22 (s, 2H), 7.61 - 7.57 (m, 2H), 7.24 - 7.22 (m, 2H), 6.97 (d, *J* = 7.6 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 187.3 (d, *J* = 8.3 Hz), 164.7 (d, *J* = 259.6 Hz), 141.9, 134.9 (d, *J* = 10.2 Hz), 126.3 (d, *J* = 3.5 Hz), 122.5 (d, *J* = 7.3 Hz), 116.2 (d, *J* = 21.6 Hz) ppm.

### **3,3'-Dichloro-1,1'-biphenyl-2,2'-dicarbaldehyde (4c)**

Dicarbaldehyde **4c** was prepared by the procedure similar to that of **4b** with 2-bromo-6-chlorobenzaldehyde (439 mg, 2.0 mmol). Purification by SiO<sub>2</sub> column chromatography (0-10% EtOAc/hexane) gave **4c** (71.9 mg, 26%) as a colorless solid.

IR (ATR): ν 1691, 1555, 1181, 786, 742 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.36 (s, 2H), 7.52 - 7.48 (m, 4H), 7.05 (dd, *J* = 6.3, 2.2 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 190.3, 142.6, 137.9, 133.3, 130.7, 130.2, 129.1 ppm. HRMS(ESI)(*m/z*) for C<sub>14</sub>H<sub>8</sub>Cl<sub>2</sub>NaO<sub>2</sub> (MNa<sup>+</sup>): Calculated 300.9799, found 300.9783.

### **3,3'-Dimethoxy-1,1'-biphenyl-2,2'-dicarbaldehyde (4e)**

Dicarbaldehyde **4e** was prepared by the procedure similar to that of **4b** with 2-chloro-6-methoxybenzaldehyde (341 mg, 2.0 mmol). Purification by SiO<sub>2</sub> column chromatography (0-10% EtOAc/hexane) gave **4e** (198.1 mg, 73%) as a colorless solid.

IR (ATR): ν 2364, 1681, 1574, 1465, 1402, 1256, 1186, 1023, 784, 658 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 10.29 (s, 2H), 7.50 (dd, *J* = 8.5, 7.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 7.5, 2H), 3.96 (s, 6H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 190.4, 161.6, 143.4, 134.1, 123.0, 122.6, 110.8, 55.9 ppm. HRMS(ESI)(*m/z*) for C<sub>16</sub>H<sub>14</sub>NaO<sub>4</sub> (MNa<sup>+</sup>): Calculated 293.0790, found 293.0773.

### **3,3'-Dibromo-1,1'-biphenyl-2,2'-dicarbaldehyde (4d)**

3,3'-Dibromo-1,1'-biphenyl-2,2'-dicarbaldehyde (**4d**) was synthesized by following the method for 1,1'-biphenyl-2,2'-dicarbaldehyde.<sup>5</sup> In a glove box, a test tube equipped with a magnetic stir bar was charged with 2,6-dibromobenzaldehyde (1.32 g, 5.0 mmol), bis(pinacolato)diboron (660 mg, 2.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.5 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (180 mg, 0.15 mmol). To this test tube was added 1,4-dioxane (12 mL). The test tube was capped with a rubber septum, and the test tube was taken out from the glove box. To this test tube was added water (2 mL). The mixture was stirred under argon atmosphere at 100 °C for 12 h with an aluminum heating block. After cooling to room temperature, water (10 mL) was added. The mixture was extracted with EtOAc (15 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered through Celite. The filtrate was evaporated *in vacuo* and the residue was purified by SiO<sub>2</sub> column chromatography (5% EtOAc/hexane) to afford **4d** (205.6 mg, 22% yield) as a colorless solid.

IR (ATR):  $\nu$  1740, 1216, 757, 727  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  10.24 (s, 2H), 7.71 (d,  $J = 7.8$  Hz, 2H), 7.41 (dd,  $J = 7.8, 7.8$  Hz, 2H), 7.09 (d,  $J = 7.8$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  192.2, 142.8, 133.5, 133.4, 131.7, 129.8, 126.9 ppm. HRMS(ESI)( $m/z$ ) for  $\text{C}_{14}\text{H}_8\text{Br}_2\text{NaO}_2$  ( $\text{MNa}^+$ ): Calculated 388.8789, found 388.8798.

### 3. Isonicotinate-catalyzed Pinacol Coupling

#### 3.1 Screening of pyridine catalysts and solvents (Table 1)

In a glove box, a test tube equipped with a magnetic stir bar was charged with **1a** (1.0 mmol), catalyst **2** (0.10 mmol) and bis(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) (152 mg, 0.60 mmol). To this test tube was added a solvent (1.0 mL). The test tube was capped with a rubber septum, and the test tube was taken out from the glove box and placed in a preheated aluminum heating block. The mixture was stirred under argon atmosphere at the reflux temperature. After 6 h, the reaction mixture was cooled to room temperature. This mixture was transferred to another test tube with  $\text{CH}_2\text{Cl}_2$  (3 mL) and stirred with 4.5 M *aq.*  $\text{KHF}_2$  (2 mL) at room temperature under air. After 3 h, the mixture was poured into water (20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered through Celite. The filtrate was evaporated *in vacuo* to give a crude product of **3a** as the diastereomeric mixture. The yield of **3a** as the diastereomeric mixture was determined by the  $^1\text{H}$  NMR analysis of the crude product using  $\text{CH}_3\text{NO}_2$  (0.500 mmol) as an internal standard in  $\text{CDCl}_3$ . The diastereomeric ratio was about 1:1.

#### 3.2 Intermolecular Coupling of Arylaldehydes of (Table 2)

In a glove box, a test tube equipped with a magnetic stir bar was charged with benzaldehyde **1** (1.0 mmol), catalyst **2d** (17.9 mg, 0.10 mmol) and bis(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) (178 mg, 0.70 mmol). To this test tube was added cyclopentyl methyl ether (CPME) (1.0 mL), and the test tube was capped with a rubber septum. The test tube was taken out from the glove box and placed in a preheated aluminum heating block. The mixture was stirred under argon atmosphere at the reflux temperature. After 6 h, the reaction mixture was cooled to room temperature. This mixture was transferred to another test tube with  $\text{CH}_2\text{Cl}_2$  (3 mL) and stirred with 4.5 M *aq.*  $\text{KHF}_2$  (2 mL) at room temperature under air. After 3 h, the mixture was poured into water (20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered through Celite, and the filtrate was evaporated *in vacuo*. The residue was dissolved in 50% *aq.* MeOH and evaporated again.<sup>6</sup> The residue was purified by  $\text{SiO}_2$  column chromatography or crystallization (EtOAc/hexane) to give diol **3** as a diastereomeric mixture.

#### 1,2-Bis(3-bromophenyl)ethane-1,2-diol (**3a**)

The reaction was carried out with 3-bromobenzaldehyde (185 mg, 1.0 mmol). Purification by  $\text{SiO}_2$  column chromatography (10-30% EtOAc/hexane) gave **3a** (144.5 mg, 77% yield,  $dr=1:1$ ). The  $^1\text{H}$  NMR

spectrum was identical to that in the literature.<sup>7,8</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.43 - 7.36 (m, 8H), 7.16 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.12 - 7.08 (m, 4H), 6.96 (d, *J* = 7.7 Hz, 2H), 4.78 (s, 2H), 4.63 (s, 2H), 2.87 (s, 2H), 2.31 (s, 2H) ppm.

### **1,2-Bis(2-bromophenyl)ethane-1,2-diol (3b)**

The reaction was carried out with 2-bromobenzaldehyde (185 mg, 1.0 mmol) for 8 h. Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3a** (148.6 mg, 80% yield, *dr*=1:1.5). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>9</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): *meso*-**3b** : δ 7.39 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.25 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.21 - 7.18 (m, 2H), 7.11 - 7.07 (m, 2H), 5.55 (s, 2H), 2.79 (s, 2H) ppm; *dl*-**3b** : δ 7.69 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.45 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.35 - 7.32 (m, 2H), 7.15 - 7.12 (m, 2H), 5.31 (s, 2H), 2.96 (s, 2H) ppm.

### **1,2-Bis(4-bromophenyl)ethane-1,2-diol (3c)**

The reaction was carried out with 4-bromobenzaldehyde (185 mg, 1.0 mmol) for 12 h. Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3c** (112.2 mg, 60% yield, *dr*=1:1). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>7</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.43 - 7.40 (m, 4H), 7.38 - 7.36 (m, 4H), 7.06 - 7.04 (m, 4H), 6.98 - 6.96 (m, 4H), 4.81 (s, 2H), 4.60 (s, 2H), 2.87 (s, 2H), 2.31 (s, 2H) ppm.

### **1,2-Bis(3,5-dibromophenyl)ethane-1,2-diol (3d)**

The reaction was carried out with 3,5-dibromobenzaldehyde (132 mg, 0.50 mmol), catalyst **2d** (9.0 mg, 0.050 mmol) and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (88.9 mg, 0.35 mmol) in CPME (0.5 mL). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3d** (125.2 mg, 94% yield, *dr*=1:1).

IR (ATR): ν 3397, 2358, 1585, 1557, 1421, 1276, 1260, 1194, 858, 765, 749, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.62 - 7.60 (m, 4H), 7.30 (d, *J* = 1.8 Hz, 4H), 7.23 (d, *J* = 1.7 Hz, 4H), 4.71 (s, 2H), 4.58 (s, 2H), 2.89 (s, 2H), 2.39 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.2, 143.2, 133.9, 133.9, 128.9, 128.6, 122.9, 122.8, 77.3, 76.5 ppm. HRMS(ESI)(*m/z*) for C<sub>14</sub>H<sub>10</sub>Br<sub>4</sub>NaO<sub>2</sub> (MNa<sup>+</sup>): Calculated 548.7312, found 548.7301.

### **1,2-Bis(3-fluorophenyl)ethane-1,2-diol (3e)**

The reaction was carried out with 3-fluorobenzaldehyde (124 mg, 1.0 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3e** (108.9 mg, 87% yield, *dr*=1:1).

IR (ATR): ν 3446, 2938, 2357, 1597, 1458, 1429, 1276, 1260, 1203, 1152, 1060, 837, 750, 698 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.27 - 7.22 (m, 2H), 7.21 - 7.17 (m, 2H), 6.99 - 6.89 (m, 10H), 6.83 (d, *J* = 7.7 Hz, 2H), 4.84 (s, 2H), 4.66 (s, 2H), 2.94 (s, 2H), 2.40 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 162.7 (d, *J* = 246.2 Hz), 162.6 (d, *J* = 246.2 Hz), 142.1 (d, *J* = 7.2 Hz), 142.0 (d, *J* = 6.7 Hz), 129.7 - 129.6 (m, 4C), 122.6 - 122.6

(m, 4C), 115.0 (d,  $J = 20.9$  Hz), 115.0 (d,  $J = 21.0$  Hz), 113.9 (d,  $J = 21.9$  Hz), 113.8 (d,  $J = 22.4$  Hz), 78.4, 77.2 ppm. HRMS(ESI)( $m/z$ ) for  $C_{14}H_{12}F_2NaO_2$  ( $MNa^+$ ): Calculated 273.0703, found 273.0690.

### **1,2-Bis(3-chlorophenyl)ethane-1,2-diol (3f)**

The reaction was carried out with 3-chlorobenzaldehyde (141 mg, 1.0 mmol). Purification by  $SiO_2$  column chromatography (10-30% EtOAc/hexane) gave **3f** (125.3 mg, 89% yield,  $dr=1:1$ ). The  $^1H$  NMR spectrum was identical to that in the literature.<sup>10</sup>

$^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.28 - 7.19 (m, 10H), 7.16 (dd,  $J = 7.8, 7.8$  Hz, 2H), 7.04 (ddd,  $J = 7.6, 1.3, 1.3$  Hz, 2H), 6.91 (ddd,  $J = 7.6, 1.2, 1.2$  Hz, 2H), 4.79 (s, 2H), 4.62 (s, 2H), 2.96 (s, 2H), 2.40 (s, 2H) ppm.

### **1,2-Bis(3-iodophenyl)ethane-1,2-diol (3g)**

The reaction was carried out with 3-iodobenzaldehyde (116 mg, 0.50 mmol), catalyst **2d** (9.0 mg, 0.050 mmol) and bis(pinacolato)diboron ( $B_2pin_2$ ) (88.9 mg, 0.35 mmol) in CPME (0.5 mL). Purification by  $SiO_2$  column chromatography (10-30% EtOAc/hexane) gave **3g** (83.8 mg, 72% yield,  $dr=1:1$ ).

IR (ATR):  $\nu$  3367, 2894, 1590, 1565, 1470, 1420, 1191, 1097, 1065, 995, 785, 737, 695, 663  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.63 - 7.61 (m, 2H), 7.59 (ddd,  $J = 7.2, 1.7, 1.7$  Hz, 2H), 7.56 (dd,  $J = 1.6, 1.6$  Hz, 2H), 7.52 (dd,  $J = 1.6, 1.6$  Hz, 2H), 7.13 - 7.11 (m, 2H), 7.04 - 6.95 (m, 6H), 4.71 (s, 2H), 4.56 (s, 2H), 2.96 (s, 2H), 2.39 (s, 2H) ppm.  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  141.8, 141.7, 137.2, 137.1, 136.0, 135.7, 129.8 (overlapped, 2C), 126.3, 126.2, 94.1 (overlapped, 2C), 78.0, 77.0 ppm. HRMS(ESI)( $m/z$ ) for  $C_{14}H_{12}I_2NaO_2$  ( $MNa^+$ ): Calculated 488.8824, found 488.8817.

### **1,2-Diphenylethane-1,2-diol (3h)**

The reaction was carried out with benzaldehyde (106 mg, 1.0 mmol) for 12 h. Purification by  $SiO_2$  column chromatography (10-30% EtOAc/hexane) gave **3h** (80.6 mg, 75% yield,  $dr=1:1$ ). The  $^1H$  NMR spectrum was identical to that in the literature.<sup>7,9,11</sup>

$^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.34 - 7.29 (m, 8H), 7.27 - 7.22 (m, 8H), 7.15 - 7.13 (m, 4H), 4.84 (s, 2H), 4.72 (s, 2H), 2.82 (s, 2H), 2.19 (s, 2H) ppm.

### **1,2-Bis(3-(trifluoromethyl)phenyl)ethane-1,2-diol (3i)**

The reaction was carried out with 3-(trifluoromethyl)benzaldehyde (174 mg, 1.0 mmol). Purification by  $SiO_2$  column chromatography (10-30% EtOAc/hexane) gave **3i** (129.0 mg, 74% yield,  $dr=1:1$ ). The  $^1H$  NMR spectrum was identical to that in the literature.<sup>11</sup>

$^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.54 - 7.51 (m, 4H), 7.41 - 7.31 (m, 10H), 7.25 (d,  $J = 7.8$  Hz, 2H), 4.96 (s, 2H), 4.73 (s, 2H), 3.00 (s, 2H), 2.52 (s, 2H) ppm.

### Dimethyl 3,3'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate (3j)

The reaction was carried out with methyl 3-formylbenzoate (164 mg, 1.0 mmol) for 12 h. Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3j** (115.6 mg, 70% yield, *dr*=1:1).

IR (ATR):  $\nu$  3446, 2358, 1716, 1434, 1278, 1200, 1109, 751, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.94 - 7.86 (m, 8H), 7.32 - 7.31 (m, 4H), 7.28 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.23 (ddd, *J* = 7.7, 1.5, 1.5 Hz, 2H), 4.94 (s, 2H), 4.77 (s, 2H), 3.88 (s, 6H), 3.87 (s, 6H), 3.15 (s, 2H), 2.62 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  166.9, 166.8, 140.1, 139.9, 131.6, 131.6, 130.1, 130.0, 129.2 (overlapped, 2C), 128.2, 128.2, 128.1, 127.9, 78.5, 77.4, 52.1 (overlapped) ppm. HRMS(ESI)(*m/z*) for C<sub>18</sub>H<sub>18</sub>NaO<sub>6</sub> (MNa<sup>+</sup>): Calculated 353.1001, found 353.0981.

### 3,3'-(1,2-Dihydroxyethane-1,2-diyl)dibenzonitrile (3k)

The reaction was carried out with methyl 3-formylbenzocyanide (131 mg, 1.0 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3k** (97.1 mg, 73% yield, *dr*=1:1). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>12</sup>

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.69 (ddd, *J* = 7.6, 1.3, 1.3 Hz, 2H), 7.67 - 7.65 (m, 4H), 7.56 - 7.55 (m, 4H), 7.50 - 7.42 (m, 6H), 5.68 (m, 2H), 5.63 (m, 2H), 4.80 (m, 2H), 4.65 (m, 2H) ppm.

### 1,1'-((1,2-Dihydroxyethane-1,2-diyl)bis(3,1-phenylene))bis(ethan-1-one) (3l)

The reaction was carried out with methyl 3-acetylbenzaldehyde (148 mg, 1.0 mmol). Purification by crystallization (EtOAc/hexane) gave **3l** (93.7 mg, 63% yield, *dr*=1:1). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>12</sup>

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  7.82 - 7.81 (m, 4H), 7.75 (d, *J* = 7.6, 2H), 7.67 (s, 2H), 7.51 (d, *J* = 7.6, 2H), 7.43 - 7.34 (m, 6H), 5.56 - 5.56 (m, 2H), 5.46 - 5.45 (m, 2H), 4.77 - 4.77 (m, 2H), 4.66 - 4.66 (m, 2H), 2.53 (s, 6H), 2.46 (s, 6H) ppm.

### 1,2-Di-*o*-tolylethane-1,2-diol (3m)

The reaction was carried out with methyl 2-methylbenzaldehyde (120 mg, 1.0 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3m** (89.7 mg, 74% yield, *dr*=1:1.3). The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>11</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): *meso*-**3m**:  $\delta$  7.34 - 7.32 (m, 2H), 7.22 - 7.17 (m, 4H), 7.09 - 7.08 (m, 2H), 5.19 (s, 2H), 2.22 (s, 2H), 2.18 (s, 6H) ppm; *dl*-**3m**:  $\delta$  7.62 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.22 - 7.17 (m, 2H), 7.12 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 2H), 4.97 (s, 2H), 2.97 (s, 2H), 1.67 (s, 6H) ppm.

### 1,2-Bis(2-ethylphenyl)ethane-1,2-diol (3n)

The reaction was carried out with methyl 2-ethylbenzaldehyde (134 mg, 1.0 mmol) for 24 h. Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **3n** (110.1 mg, 81% yield, *dr*=1:1.2).

IR (ATR):  $\nu$  3399, 2965, 2357, 2160, 2044, 2009, 1994, 1456, 1276, 1033, 751, 684, 670, 655, 640, 622, 607, 579, 559, 548, 524, 505  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): *meso*-**3n**:  $\delta$  7.44 (dd,  $J = 7.4, 1.8$  Hz, 2H), 7.27 - 7.16 (m, 6H), 5.20 (s, 2H), 2.78 - 2.70 (m, 2H), 2.60 - 2.52 (m, 2H), 2.03 - 1.95 (m, 2H), 1.22 (t,  $J = 7.6$  Hz, 6H) ppm; *dl*-**3n**:  $\delta$  7.61 (dd,  $J = 7.6, 1.5$  Hz, 2H), 7.27 - 7.16 (m, 4H), 7.00 (dd,  $J = 7.5, 1.2$  Hz, 2H), 5.07 (s, 2H), 2.89 (s, 2H), 2.30 - 2.22 (m, 2H), 2.03 - 1.95 (m, 2H), 0.91 (t,  $J = 7.6$  Hz, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  142.5, 141.9, 137.8, 137.3, 128.5, 128.3, 128.1, 127.9, 127.1, 126.6, 126.2, 125.9, 74.1, 73.3, 25.3, 24.5, 15.5, 15.1 ppm. HRMS(ESI)( $m/z$ ) for  $\text{C}_{18}\text{H}_{22}\text{NaO}_2$  ( $\text{MNa}^+$ ): Calculated 293.1518, found 239.1491.

### **1,2-Bis(2-methoxyphenyl)ethane-1,2-diol (3o)**

The reaction was carried out with methyl 2-methoxybenzaldehyde (136 mg, 1.0 mmol). Purification by  $\text{SiO}_2$  column chromatography (10-50% EtOAc/hexane) gave **3o** (106.5 mg, 78% yield,  $dr=1:1.5$ ). The  $^1\text{H}$  NMR spectrum was identical to that in the literature.<sup>13</sup>

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): *meso*-**3o**:  $\delta$  7.23 - 7.15 (m, 4H), 6.89 (ddd,  $J = 7.5, 7.5, 1.0$  Hz, 2H), 6.81 (dd,  $J = 8.2, 1.0$  Hz, 2H), 5.25 - 5.24 (m, 2H), 3.69 (s, 6H), 3.10 - 3.09 (m, 2H) ppm; *dl*-**3o**:  $\delta$  7.23 - 7.15 (m, 4H), 6.84 (ddd,  $J = 7.5, 7.5, 1.0$  Hz, 2H), 6.75 (dd,  $J = 8.1, 1.0$  Hz, 2H), 5.04 - 5.03 (m, 2H), 3.65 (s, 6H), 3.45 - 3.44 (m, 2H) ppm

### **1,2-Bis(3-methoxyphenyl)ethane-1,2-diol (3p)**

The reaction was carried out with methyl 3-methoxybenzaldehyde (136 mg, 1.0 mmol), catalyst **2d** (17.9 mg, 0.1 mmol) and bis(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) (178 mg, 0.7 mmol) in CPME (1.0 mL) for 24 h. Purification by  $\text{SiO}_2$  column chromatography (10-50% EtOAc/hexane) gave **3p** (94.9 mg, 69% yield,  $dr=1:1$ ). The  $^1\text{H}$  NMR spectrum was identical to that in the literature.<sup>13</sup>

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.23 (dd,  $J = 7.9, 7.9$  Hz, 2H), 7.15 (dd,  $J = 7.9, 7.9$  Hz, 2H), 6.86 - 6.82 (m, 4H), 6.79 - 6.76 (m, 4H), 6.72 - 6.69 (m, 4H), 4.77 (s, 2H), 4.65 (s, 2H), 3.73 (s, 6H), 3.71 (s, 6H), 2.95 (s, 2H), 2.33 (s, 2H) ppm.

### **1,2-Bis(4-methoxyphenyl)ethane-1,2-diol (3q)**

The reaction was carried out with methyl 4-methoxybenzaldehyde (136 mg, 1.0 mmol), catalyst **2d** (35.8 mg, 0.2 mmol) and bis(pinacolato)diboron ( $\text{B}_2\text{pin}_2$ ) (254 mg, 1.0 mmol) in CPME (1.0 mL) for 16 h. Purification by  $\text{SiO}_2$  column chromatography (10-50% EtOAc/hexane) gave **3q** (78.1 mg, 57% yield,  $dr=1:1$ ). The  $^1\text{H}$  NMR spectrum was identical to that in the literature.<sup>9,13</sup>

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.20 (d,  $J = 8.6$  Hz, 4H), 7.04 (d,  $J = 8.6$  Hz, 4H), 6.85 (d,  $J = 8.6$  Hz, 4H), 6.76 (d,  $J = 8.6$  Hz, 4H), 4.73 (s, 2H), 4.63 (s, 2H), 3.80 (s, 6H), 3.76 (s, 6H), 2.78 (s, 2H), 2.08 (s, 2H) ppm.

### **1,2-Bis(3,5-dimethoxyphenyl)ethane-1,2-diol (3r)**



The reaction was carried out with methyl 3,5-dimethoxybenzaldehyde (166 mg, 1.0 mmol). Purification by SiO<sub>2</sub> column chromatography (10-50% EtOAc/hexane) gave **3r** (103.2 mg, 62% yield, *dr*=1:1).

IR (ATR):  $\nu$  3446, 2938, 2357, 1597, 1458, 1429, 1276, 1260, 1203, 1152, 1060, 837, 750, 698 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.46 (d, *J* = 2.3 Hz, 4H), 6.39 (t, *J* = 2.3 Hz, 2H), 6.34 (s, 6H), 4.70 (s, 2H), 4.62 (s, 2H), 3.75 (s, 12H), 3.70 (s, 12H), 2.81 (s, 2H), 2.21 (s, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  160.7, 160.6, 142.4, 142.3, 105.0, 104.7, 100.4, 100.2, 78.8, 78.1, 55.4, 55.3 ppm. HRMS(ESI)(*m/z*) for C<sub>18</sub>H<sub>22</sub>NaO<sub>6</sub> (MNa<sup>+</sup>): Calculated 357.1314, found 357.1293.

### 3.3 Intramolecular Coupling of 1,1'-Biphenyl-2,2'-dicarbaldehydes (Table 3)

In a glove box, a test tube equipped with a magnetic stir bar was charged with 1,1'-biphenyl-2,2'-dicarbaldehyde **4** (0.20 mmol), catalyst **2d** (0.040 mmol) and bis(pinacolato)diboron (B<sub>2</sub>pin<sub>2</sub>) (0.28 mmol). To this test tube was added CPME (1.0 mL), and the test tube was capped with a rubber septum. The test tube was taken out from the glove box and placed in a preheated aluminum heating block. The mixture was stirred under argon atmosphere at the reflux temperature. After 24 h, the reaction mixture was cooled to room temperature. This mixture was transferred to another test tube with CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and stirred with 4.5 M *aq.* KHF<sub>2</sub> (2 mL) at room temperature under air. After 3 h, the mixture was poured into water (20 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL  $\times$  3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered through Celite, and the filtrate was evaporated *in vacuo*. The residue was dissolved in 50% *aq.* MeOH and evaporated again.<sup>6</sup> The residue was purified by SiO<sub>2</sub> column chromatography (EtOAc/hexane) to give diol **5**.

### 9,10-Dihydrophenanthrene-9,10-diol (**5a**)

The reaction was carried out with 1,1'-biphenyl-2,2'-dicarbaldehyde (**4a**)(42.0 mg, 0.20 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave *trans*-diol **5a** (12.3 mg, 29% yield, *trans* : *cis* = 10:1) as a pale yellow solid. The <sup>1</sup>H NMR spectrum was identical to that in the literature.<sup>14</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): *trans*-**5a**:  $\delta$  7.77 - 7.75 (m, 2H), 7.68 - 7.66 (m, 2H), 7.45 - 7.36 (m, 4H), 4.76 (s, 2H), 2.54 (s, 2H) ppm; *cis*-**5a**:  $\delta$  7.81 - 7.79 (m, 2H), 7.61 (d, *J* = 7.5, 1.2 Hz, 2H), 7.45 - 7.36 (m, 4H), 4.84 - 4.83 (m, 2H), 2.23 (s, 2H) ppm.

### 1,8-Difluoro-9,10-dihydrophenanthrene-9,10-diol (**5b**)

The reaction was carried out with 3,3'-difluoro-1,1'-biphenyl-2,2'-dicarbaldehyde (**4b**)(49.2 mg, 0.20 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave **5b** (26.3 mg, 53% yield, *trans* : *cis* = 10:1).

IR (ATR):  $\nu$  3370, 2925, 1698, 1620, 1574, 1481, 1458, 1303, 1233, 1012, 952, 785, 748 cm<sup>-1</sup>. <sup>1</sup>H NMR

(CDCl<sub>3</sub>): *trans*-**5b**:  $\delta$  7.65 (d,  $J$  = 7.8 Hz, 2H), 7.44 - 7.40 (m, 2H), 7.12 - 7.08 (m, 2H), 5.30 (d,  $J$  = 1.7 Hz, 2H), 1.81 (s, 2H) ppm; *cis*-**5b**:  $\delta$  7.58 (d,  $J$  = 7.8 Hz, 2H), 7.40 - 7.36 (m, 2H), 7.10 - 7.16 (m, 2H), 5.18 (s, 2H), 3.19 - 3.18 (m, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>): *trans*-**5b**:  $\delta$  162.0 (d,  $J$  = 247.8 Hz), 133.5, 130.7 (d,  $J$  = 9.0 Hz), 121.7 (d,  $J$  = 16.9 Hz), 120.1 (d,  $J$  = 3.0 Hz), 115.8 (d,  $J$  = 22.0 Hz), 63.5 (d,  $J$  = 4.5 Hz) ppm. HRMS(ESI)( $m/z$ ) for C<sub>14</sub>H<sub>10</sub>F<sub>2</sub>NaO<sub>2</sub> (MNa<sup>+</sup>): Calculated 271.0547, found 271.0529.

#### **1,8-Dichloro-9,10-dihydrophenanthrene-9,10-diol (5c)**

The reaction was carried out with 3,3'-dichloro-1,1'-biphenyl-2,2'-dicarbaldehyde (**4c**) (55.8 mg, 0.20 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave *trans*-diol **5c** (44.4 mg, 79% yield) as a pale yellow solid.

IR (ATR):  $\nu$  3379, 2929, 1557, 1444, 1186, 1134, 1015, 670, 634 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.76 (dd,  $J$  = 7.6, 1.3 Hz, 2H), 7.43 - 7.37 (m, 4H), 5.43 (d,  $J$  = 4.8 Hz, 2H), 1.88 (d,  $J$  = 4.8 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  136.2, 134.0, 132.1, 130.3, 129.8, 123.2, 67.6 ppm. HRMS(ESI)( $m/z$ ) for C<sub>14</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub> (MNa<sup>+</sup>): Calculated 302.9956, found 302.9938.

#### **1,8-Dibromo-9,10-dihydrophenanthrene-9,10-diol (5d)**

The reaction was carried out with 3,3'-dibromo-1,1'-biphenyl-2,2'-dicarbaldehyde (**4d**) (73.6 mg, 0.2 mmol). Purification by SiO<sub>2</sub> column chromatography (10-30% EtOAc/hexane) gave *trans*-diol **5d** (57.3 mg, 77% yield) as a pale yellow solid.

IR (ATR):  $\nu$  3566, 3396, 2359, 1698, 1542, 1457, 1442, 1007, 733, 658, 590 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.77 (dd,  $J$  = 7.9, 1.0 Hz, 2H), 7.59 (dd,  $J$  = 7.9, 1.0 Hz, 2H), 7.30 (d,  $J$  = 7.9, 7.9 Hz, 2H), 5.35 (d,  $J$  = 3.6 Hz, 2H), 2.01 (d,  $J$  = 3.6 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  134.3, 133.8, 133.1, 130.6, 126.8, 123.9, 70.3 ppm. HRMS(ESI)( $m/z$ ) for C<sub>14</sub>H<sub>10</sub>Br<sub>2</sub>NaO<sub>2</sub> (MNa<sup>+</sup>): Calculated 390.8945, found 390.8934.

#### **1,8-Dimethoxy-9,10-dihydrophenanthrene-9,10-diol (5e)**

The reaction was carried out with 3,3'-dimethoxy-1,1'-biphenyl-2,2'-dicarbaldehyde (**4e**) (54.1 mg, 0.2 mmol). Purification by SiO<sub>2</sub> column chromatography (10-50% EtOAc/hexane) gave *trans*-diol **5e** (35.2 mg, 65% yield) as a colorless solid.

IR (ATR):  $\nu$  3239, 2367, 2161, 1977, 1574, 1485, 1262, 1143, 1006, 820, 777, 739, 701, 669, 631, 601, 503 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.47 (d,  $J$  = 8.1 Hz, 2H), 7.38 (dd,  $J$  = 8.1, 8.1 Hz, 2H), 6.90 (d,  $J$  = 8.1 Hz, 2H), 5.38 (d,  $J$  = 4.6 Hz, 2H), 3.90 (s, 6H), 1.78 (d,  $J$  = 4.6 Hz, 2H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  = 158.5, 133.4, 130.0, 122.8, 116.8, 110.4, 64.3, 55.6 ppm. HRMS(ESI)( $m/z$ ) for C<sub>16</sub>H<sub>16</sub>NaO<sub>4</sub> (MNa<sup>+</sup>): Calculated 295.0946, found 295.0935.

### **4. Derivatization of 1,8-Dibromo-9,10-dihydrophenanthrene-9,10-diol (5d)**

#### **1,8-Dibromophenanthrene-9,10-dione (6d)**

The mixture of 1,8-dibromo-9,10-dihydrophenanthrene-9,10-diol (**5d**) (37.0 mg, 0.10 mmol), pyridinium chlorochromate (64.7 mg, 0.30 mmol), and silica gel (370 mg) in 1,2-dichloroethane (2.0 mL) in a test tube was stirred under argon atmosphere at the reflux temperature using aluminum heating block. After 12 h, the reaction mixture was cooled to room temperature. The mixture was filtered through a short neutral alumina column. The column was eluted with EtOAc and the solvent was evaporated *in vacuo*. The residue was washed with EtOH to afford 1,8-dibromophenanthrene-9,10-dione (**6d**) (19.2 mg, 53% yield) as a red solid.

IR (ATR):  $\nu$  2359, 2159, 1681, 1577, 1432, 1229, 781  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  = 8.32 (dd,  $J$  = 8.0, 0.7 Hz, 2H), 7.83 (dd,  $J$  = 8.0, 0.7 Hz, 2H), 7.66 (dd,  $J$  = 8.0, 8.0 Hz, 2H) ppm.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ):  $\delta$  180.4, 138.2, 136.2, 135.5, 128.3, 125.6, 122.9 ppm. HRMS (ESI) ( $m/z$ ) for  $\text{C}_{14}\text{H}_6\text{Br}_2\text{NaO}_2$  ( $\text{MNa}^+$ ): Calculated 386.8632, found 386.8625.

#### 1,8-Dibromo-9,10-dimethoxyphenanthrene (**7d**)

1,8-Dibromo-9,10-dimethoxyphenanthrene (**7d**) was synthesized by following the method for 9,10-dimethoxyphenanthrene.<sup>15</sup> The mixture of 1,8-dibromophenanthrene-9,10-dione (**6d**) (36.6 mg, 0.10 mmol), tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ) (12.9 mg, 0.04 mmol), and sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) (52.2 mg, 0.3 mmol) in water (250  $\mu\text{L}$ ) and tetrahydrofuran (THF) (250  $\mu\text{L}$ ) was stirred under argon atmosphere at room temperature. After 15 min, dimethyl sulfate (47.4  $\mu\text{L}$ , 0.5 mmol), 12 M *aq.* NaOH (2 mL), and ice (1 g) were added and the mixture was stirred at room temperature. After 30 min, EtOAc (2 mL) was added. The aqueous layer was separated and extracted with EtOAc (2 mL  $\times$  2). The combined organic layer was washed with water (3 mL  $\times$  2), 2.5% *aq.*  $\text{NH}_3$  (3 mL  $\times$  2), water (3 mL  $\times$  2), and finally brine (3 mL). The resulting organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered through Celite. The filtrate was evaporated *in vacuo* and the residue was purified by neutral alumina column chromatography ( $\text{CH}_2\text{Cl}_2$ ) to give 1,8-dibromo-9,10-dimethoxyphenanthrene (**7d**) (23.8 mg, 60% yield) as a pale brown solid.

IR (ATR):  $\nu$  2369, 1575, 1295, 1121, 1053, 976, 811, 764, 734, 692, 506  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.61 (dd,  $J$  = 8.4, 0.8 Hz, 2H), 7.94 (dd,  $J$  = 7.7, 0.8 Hz, 2H), 7.38 (dd,  $J$  = 8.4, 7.7 Hz, 2H), 4.01 (s, 6H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.0, 135.1, 130.9, 126.9, 126.4, 123.0, 116.3, 61.1 ppm. HRMS(ESI)( $m/z$ ) for  $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{O}_2$  ( $\text{MH}^+$ ): Calculated 394.9282, found 394.9272.

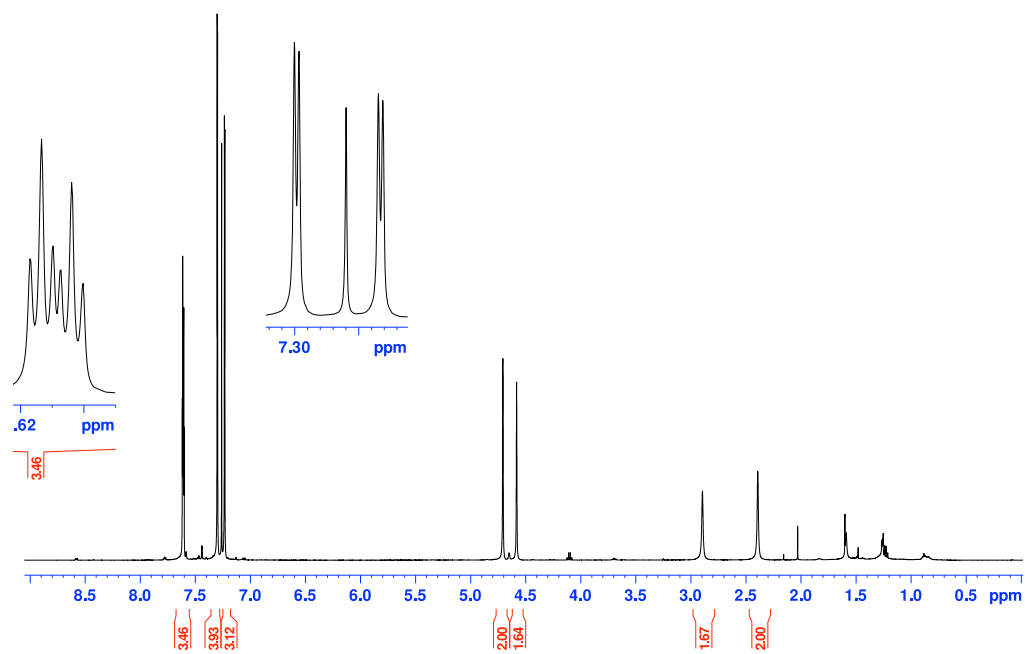
#### 4,11-Dibromo-2-phenyl-1H-phenanthro[9,10-d]imidazole (**8d**)

4,11-Dibromo-2-phenyl-1H-phenanthro[9,10-d]imidazole (**8d**) was synthesized by following the method for 2-phenyl-1H-phenanthro[9,10-d]imidazole.<sup>16</sup> The mixture of 1,8-dibromophenanthrene-9,10-dione (**6d**) (36.6 mg, 0.10 mmol), benzaldehyde (10.2  $\mu\text{L}$ , 0.10 mmol), ammonium acetate (38.5 mg, 0.50 mmol), and sulfamic acid (1.0 mg, 0.010 mmol) in ethanol (1.0 mL) in a test tube was stirred under argon atmosphere at the reflux temperature using aluminum heating block. After 12 h, the reaction mixture was

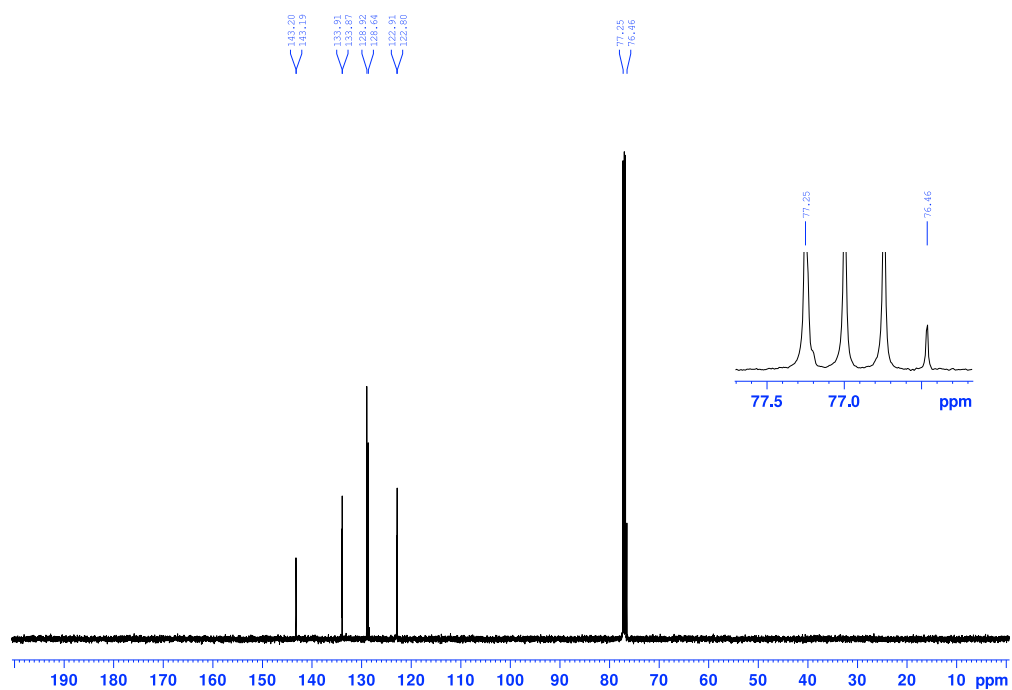
cooled to room temperature. The mixture was poured onto crushed ice and the resulting solid was filtered. The solid was then recrystallized from ethanol to afford **8d** (34.8 mg, 77% yield) as a pale yellow solid. IR (ATR):  $\nu$  3648, 3440 (NH), 2361, 1698, 1558, 1541, 1507, 1473, 1456, 1339, 1313, 759, 727, 711, 682, 545  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.60 (s, 1H), 8.71 (d,  $J = 8.0$  Hz, 1H), 8.65 (d,  $J = 8.0$  Hz, 1H), 8.18 - 8.16 (m, 2H), 8.04 (dd,  $J = 8.0, 0.9$  Hz, 1H), 7.89 (dd,  $J = 8.0, 0.9$  Hz, 1H), 7.57 - 7.54 (m, 2H), 7.50 - 7.47 (m, 1H), 7.44 - 7.40 (m, 2H) ppm.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  147.1, 138.4, 134.7, 132.6, 131.0, 130.3, 129.8, 129.7, 129.1, 127.1, 126.0, 125.9, 125.6, 125.6, 124.1, 123.1, 121.4, 118.2, 116.7 ppm. HRMS(ESI)( $m/z$ ) for  $\text{C}_{21}\text{H}_{13}\text{Br}_2\text{N}_2$  ( $\text{MH}^+$ ): Calculated 450.9446, found 450.9429.

## 5. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra

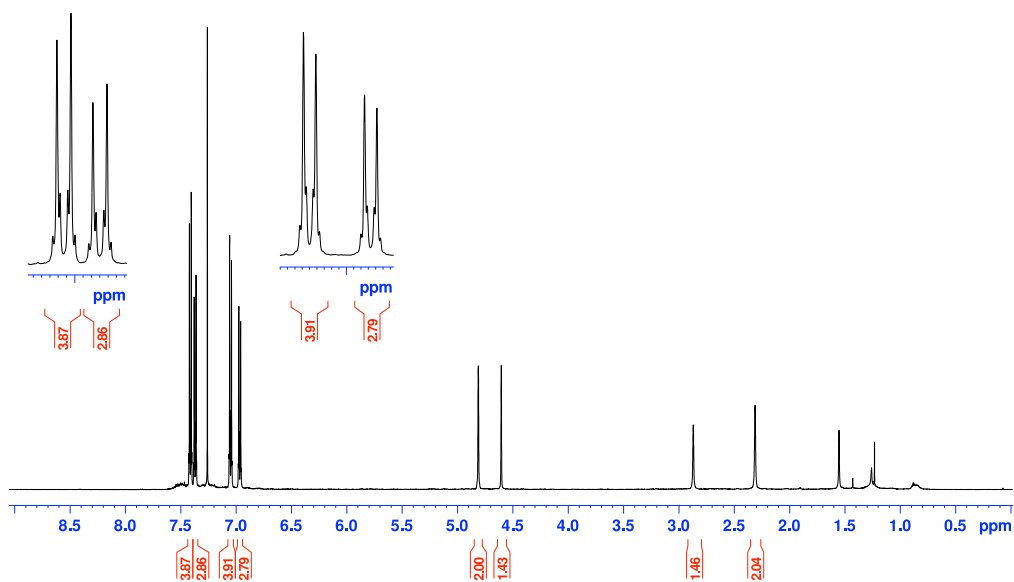
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3d**



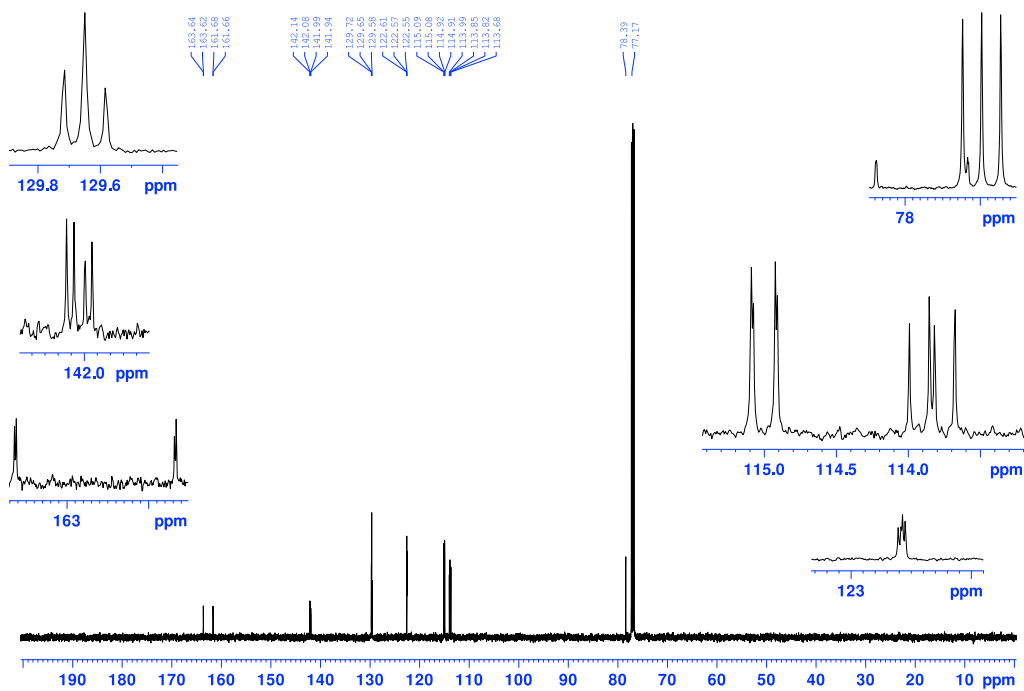
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3d**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3e**

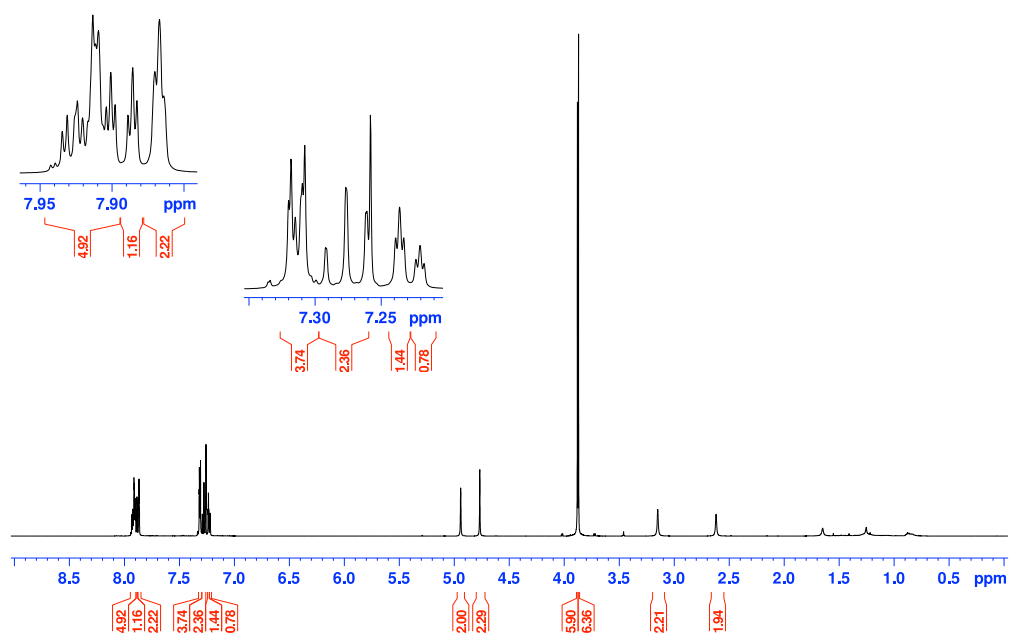


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3e**

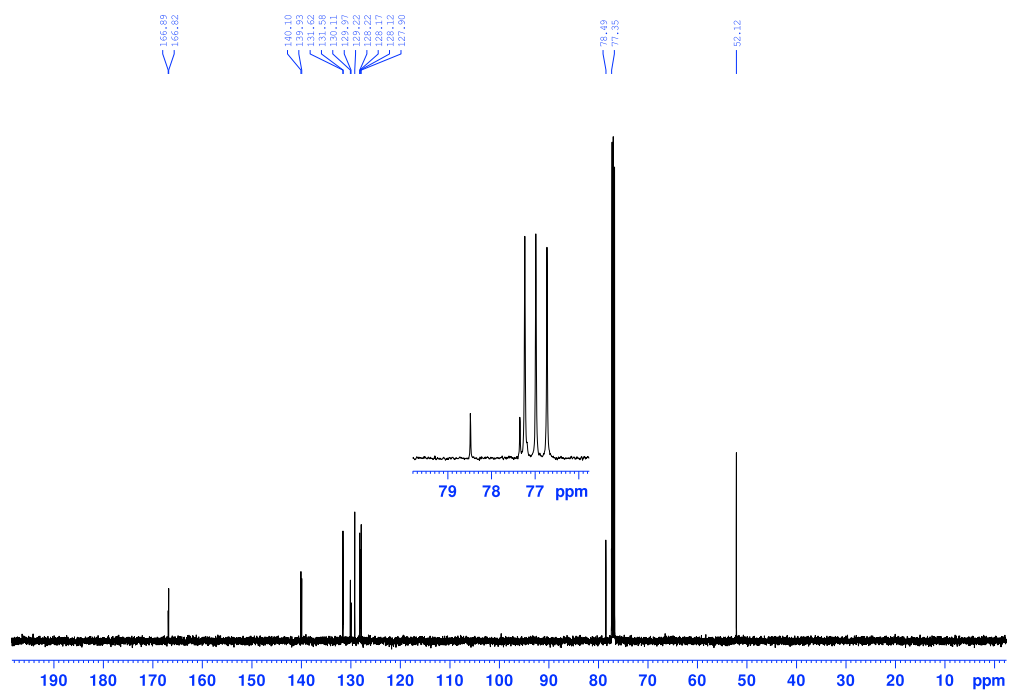




$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3j**

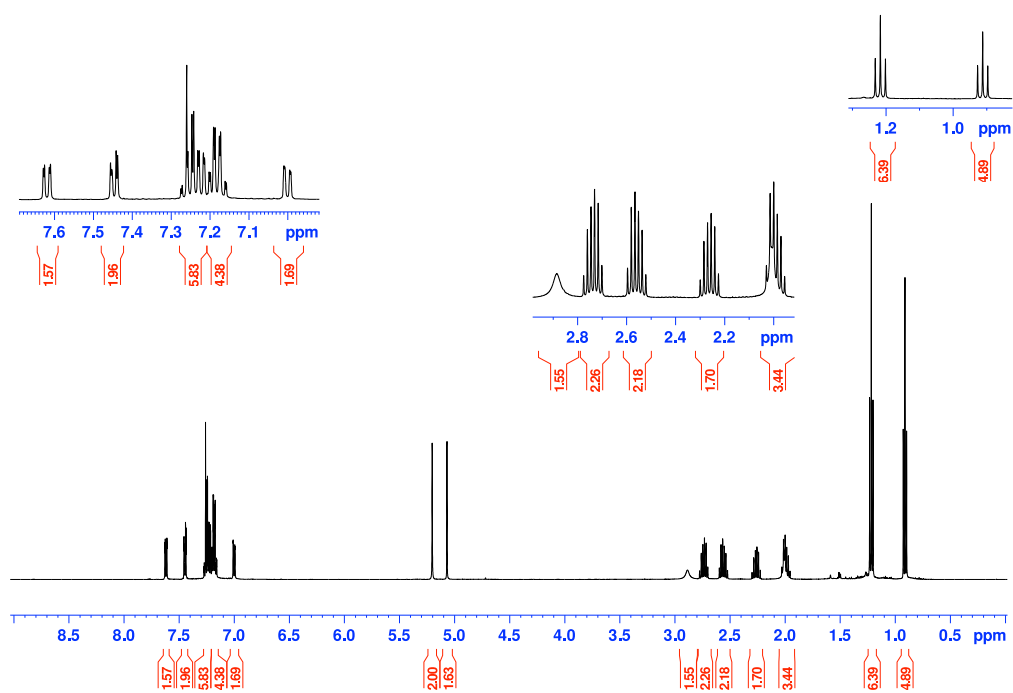


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3j**

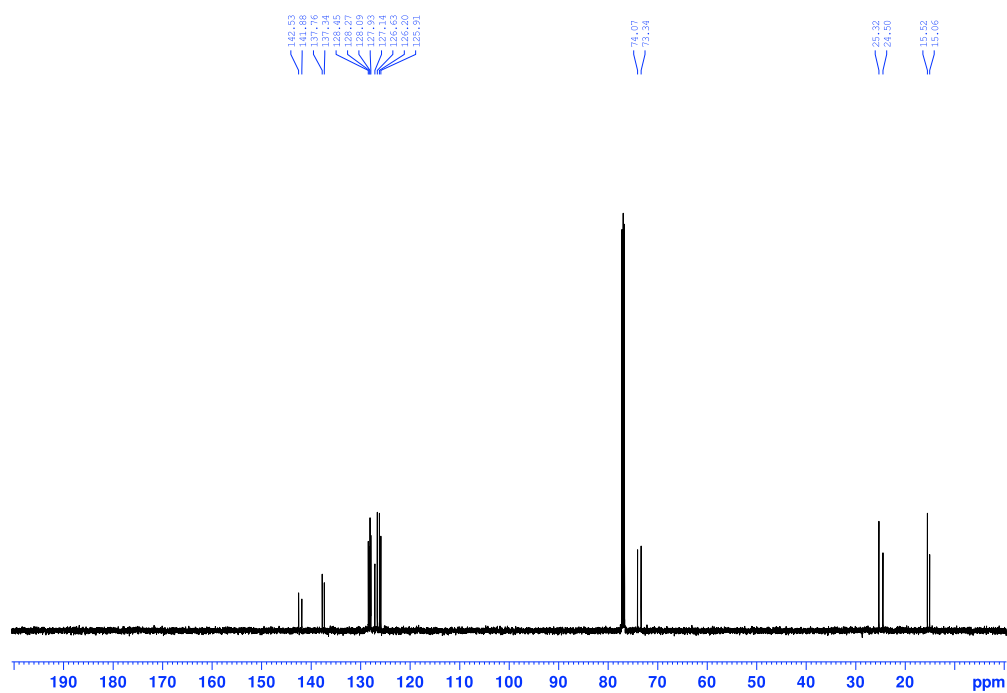




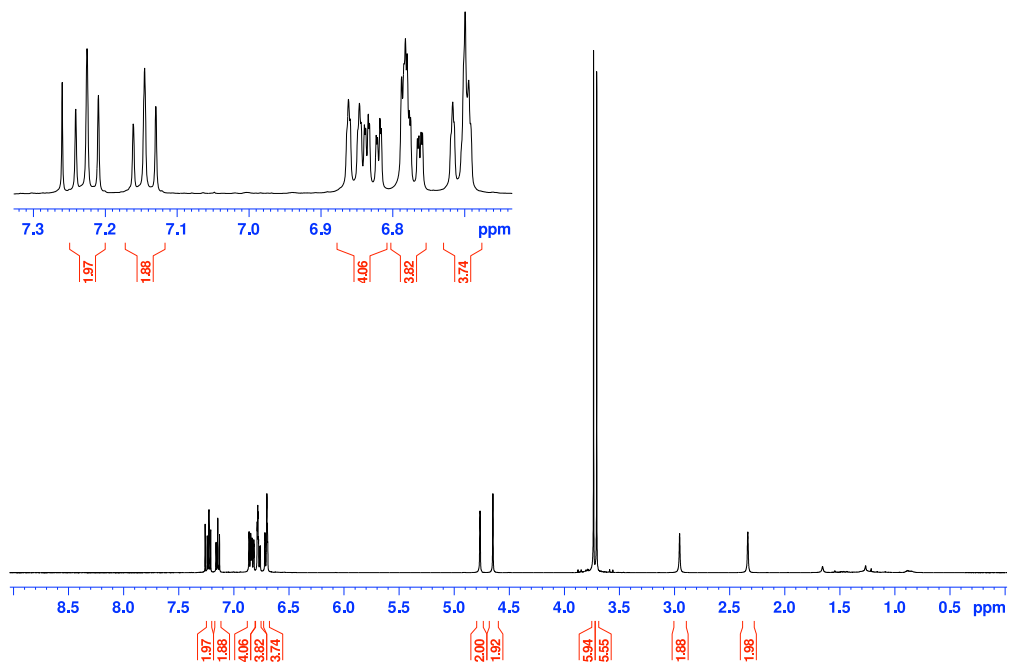
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3n**



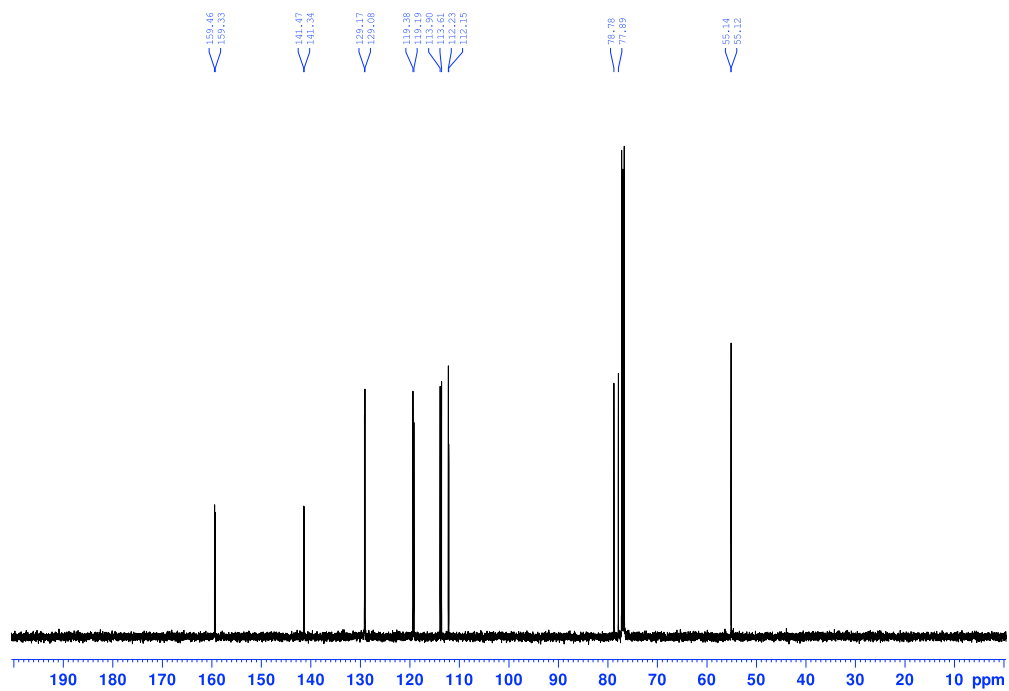
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3n**



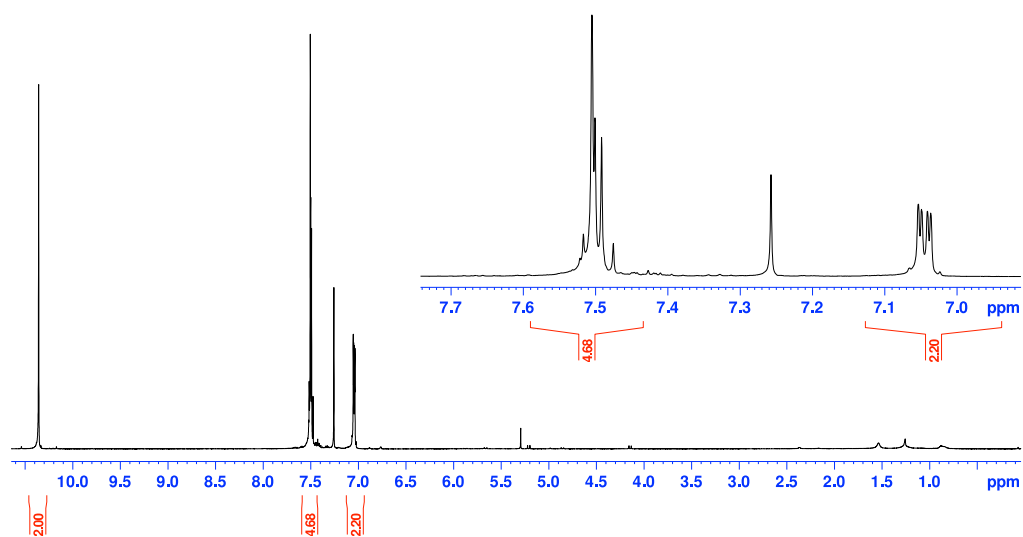
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3r**



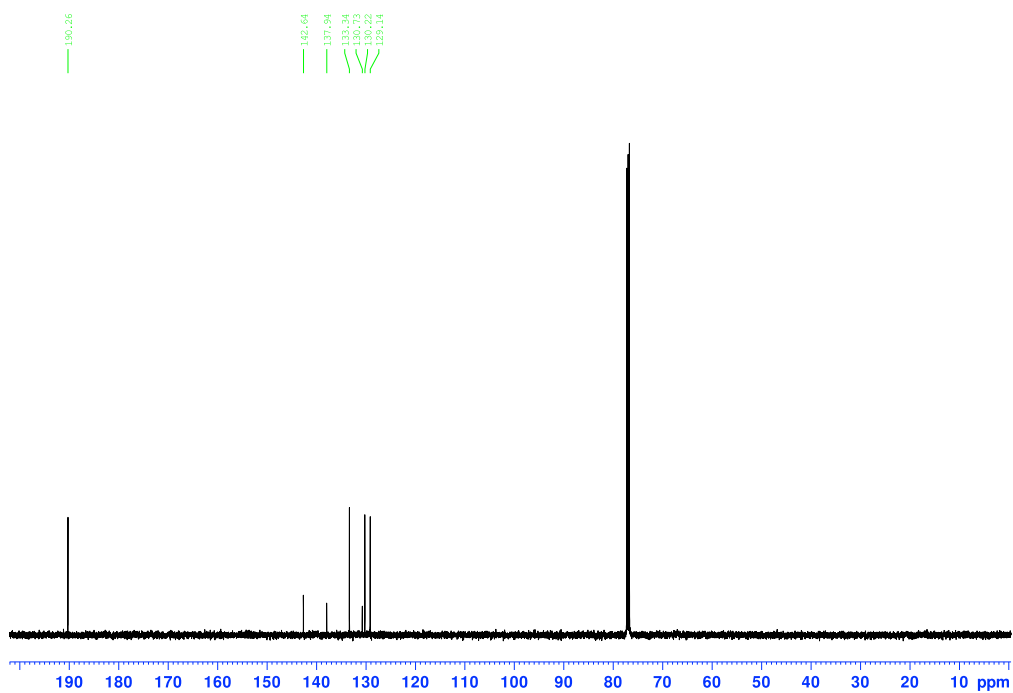
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **3r**



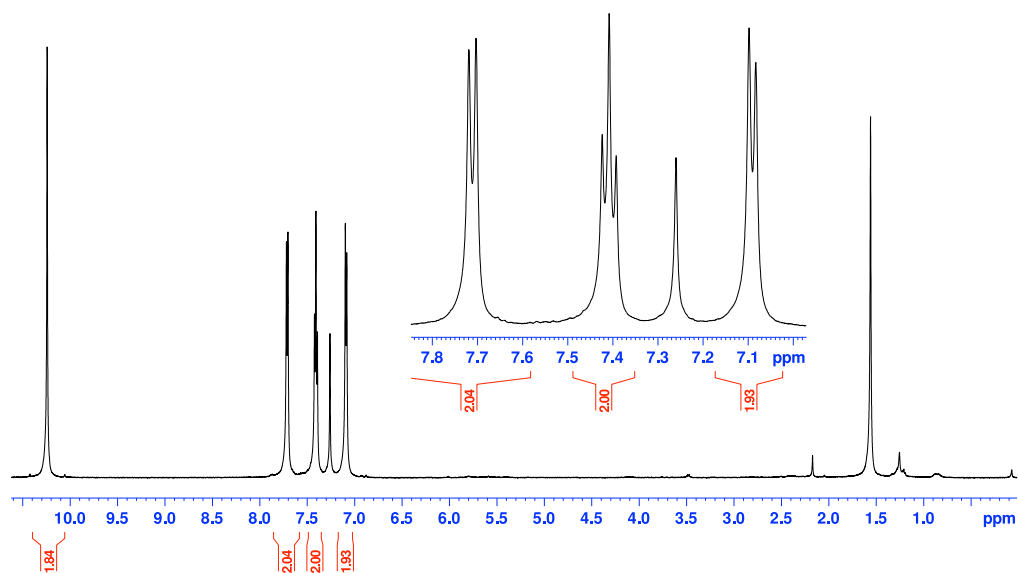
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4c**



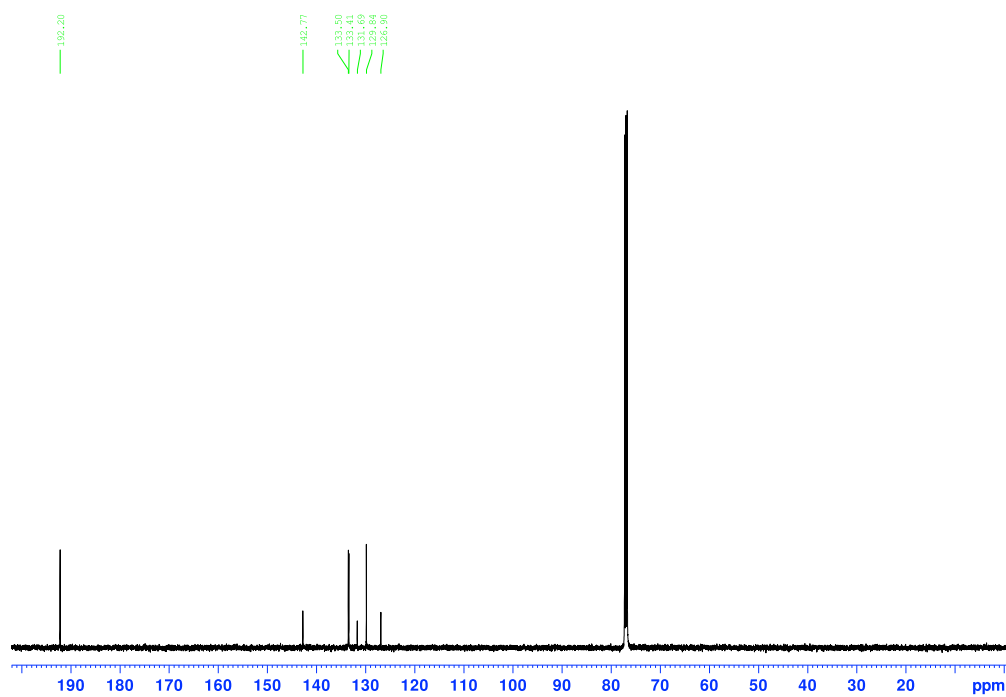
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4c**



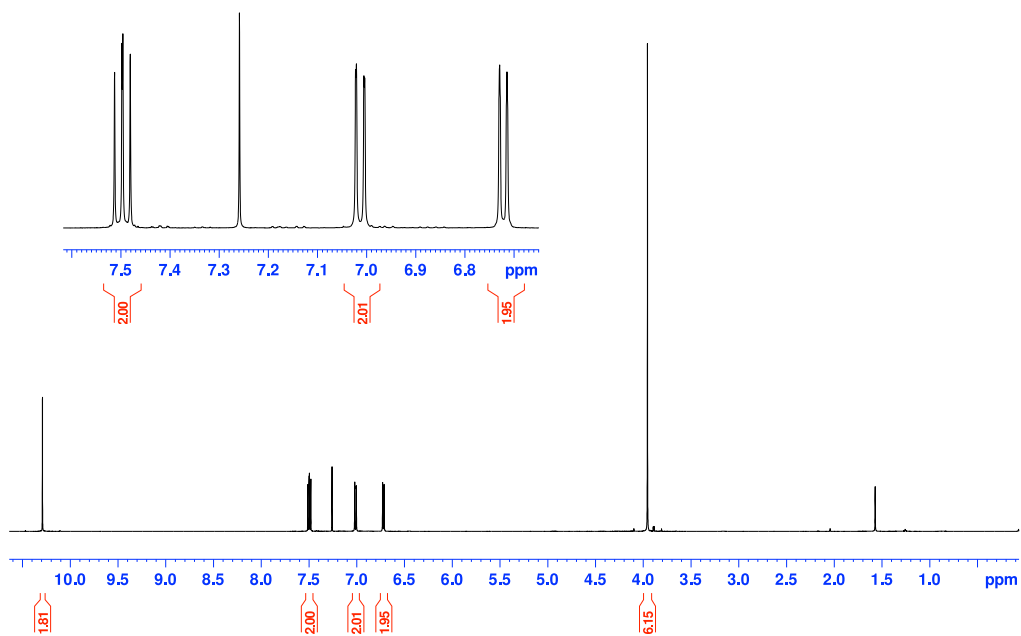
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4d**



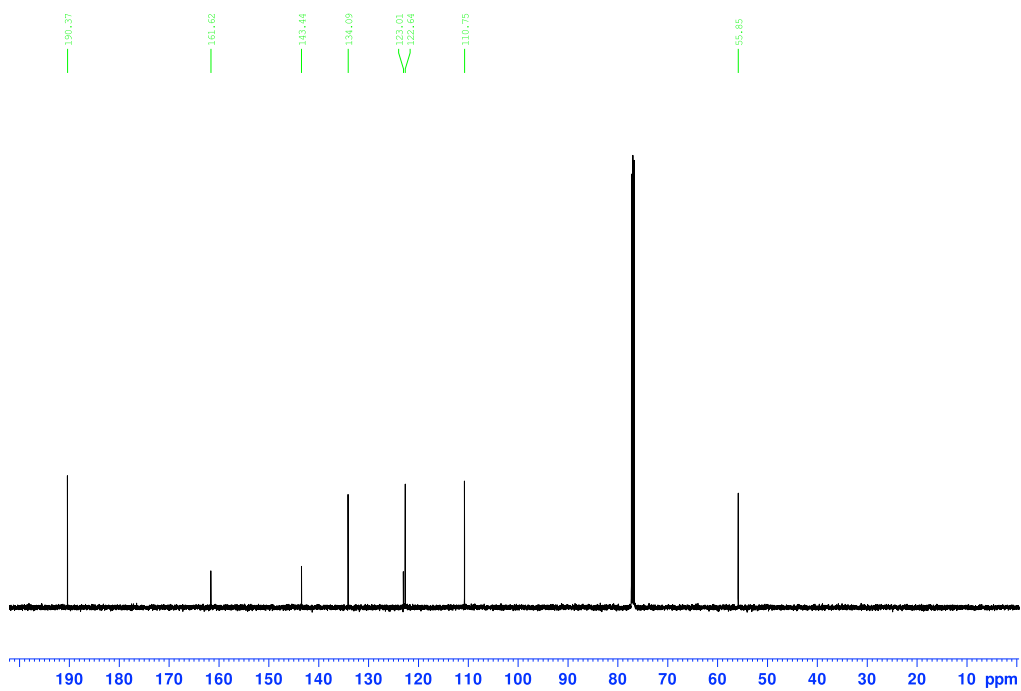
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4d**



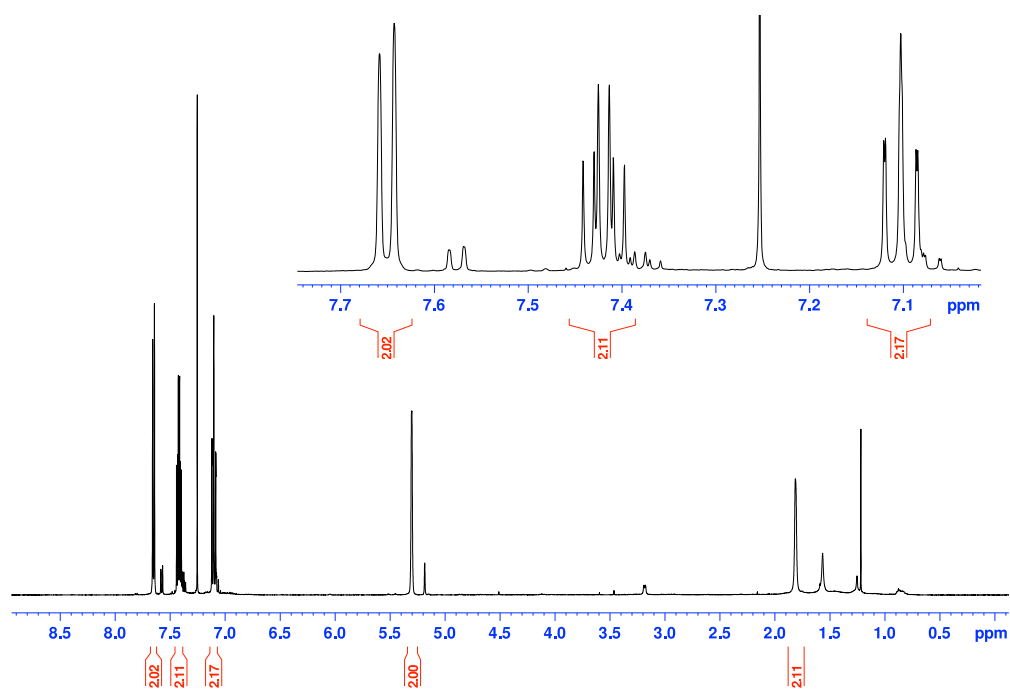
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4e**



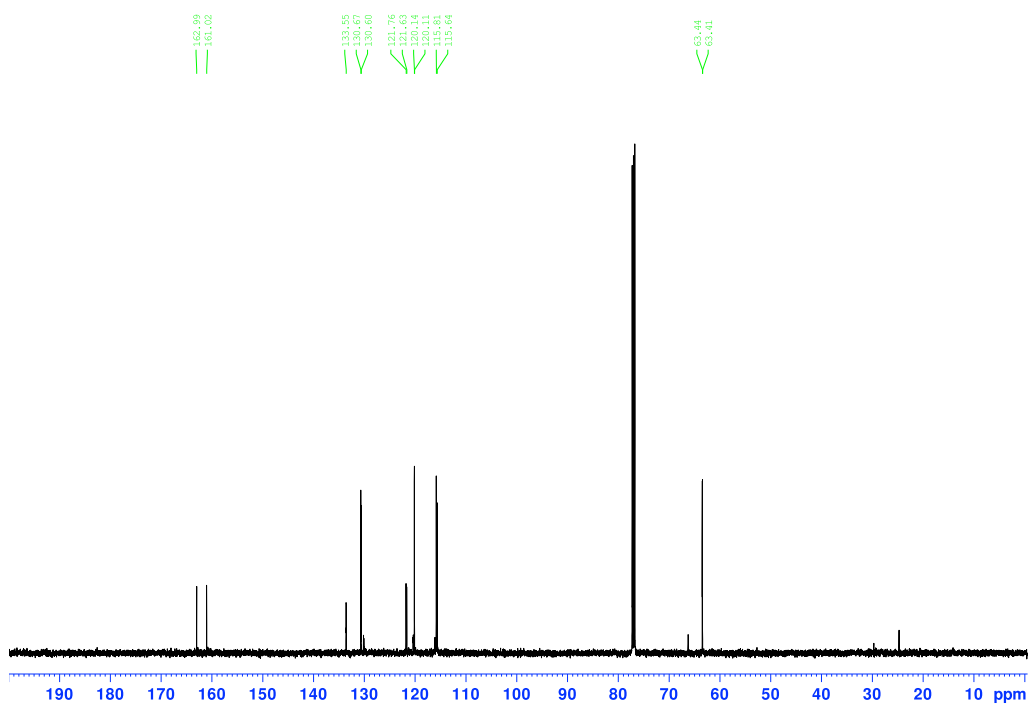
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **4e**



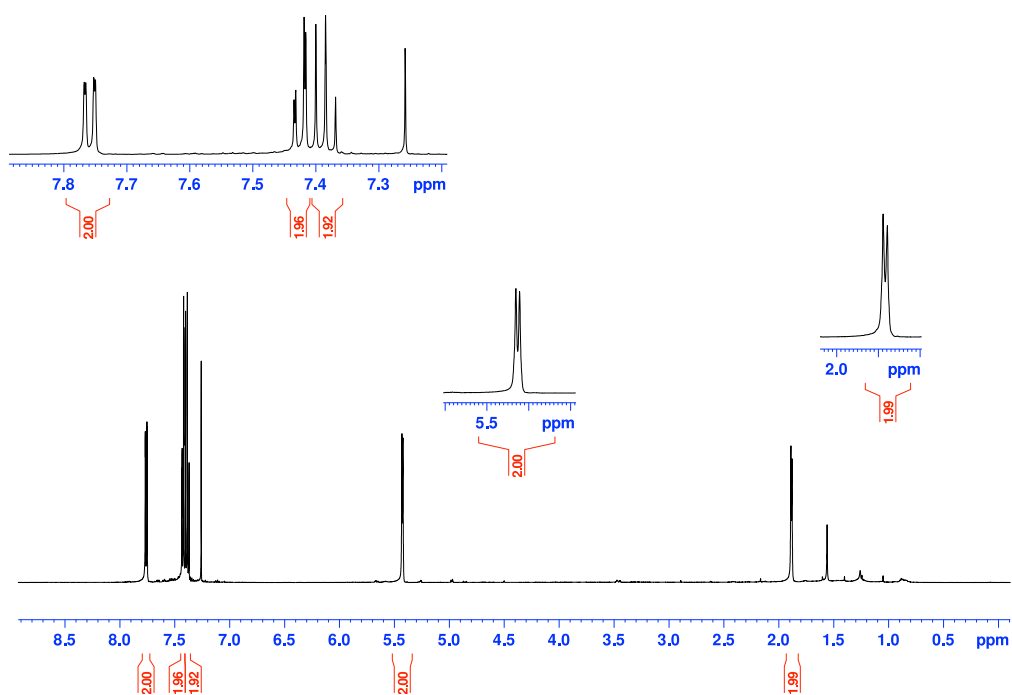
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5b**



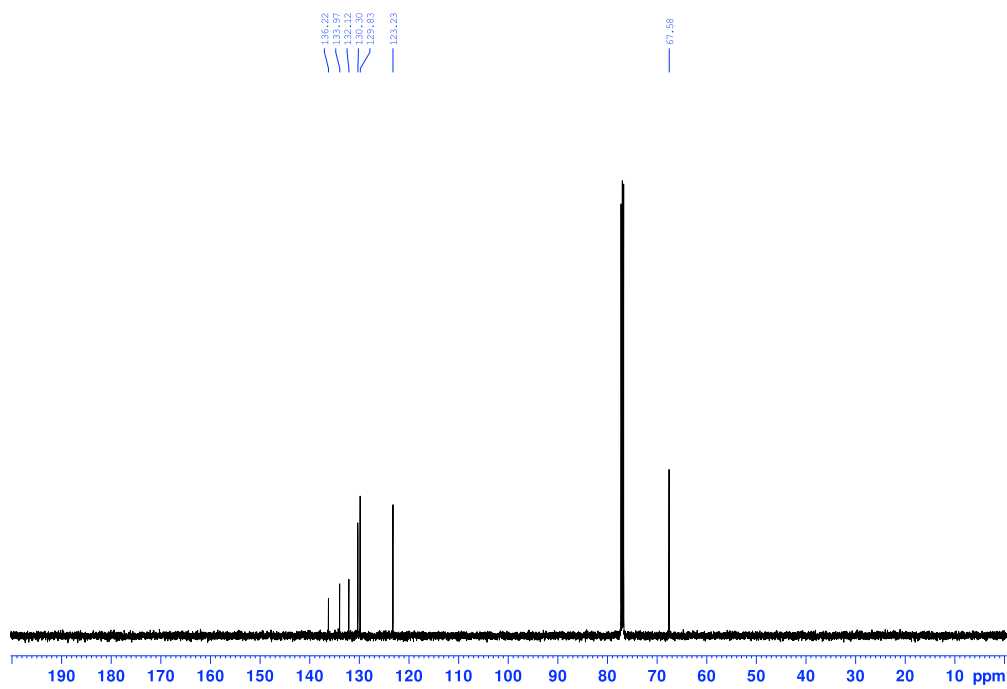
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5b**



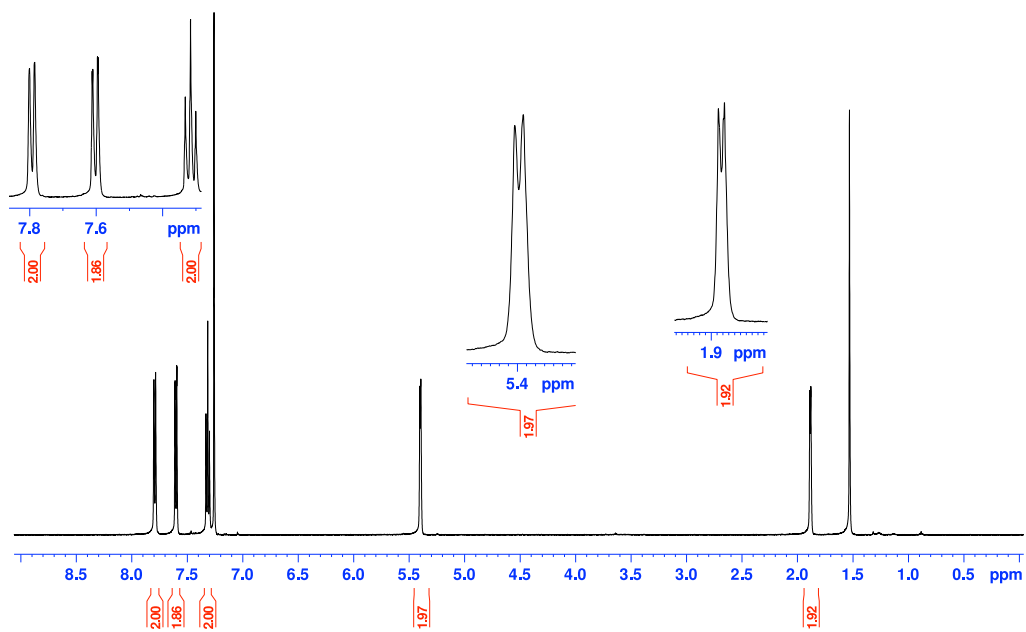
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5c**



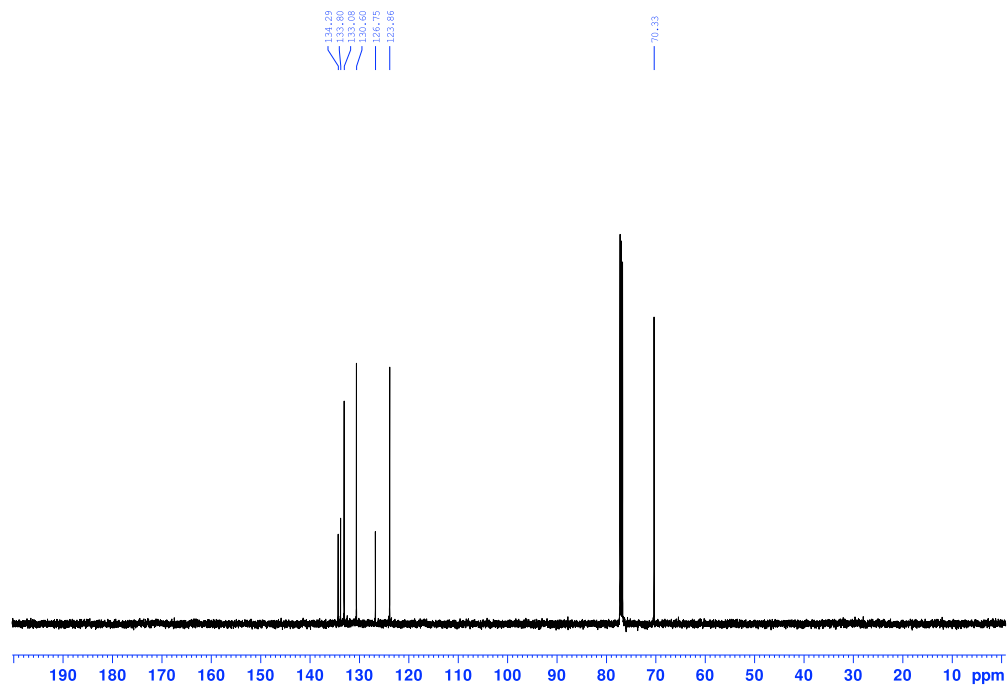
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5c**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5d**

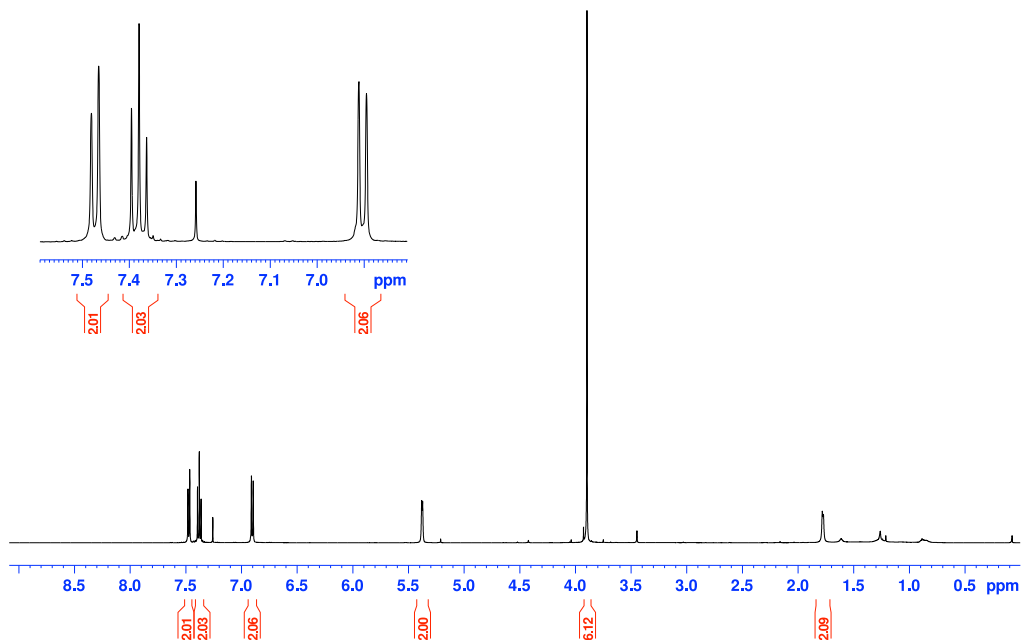


$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5d**

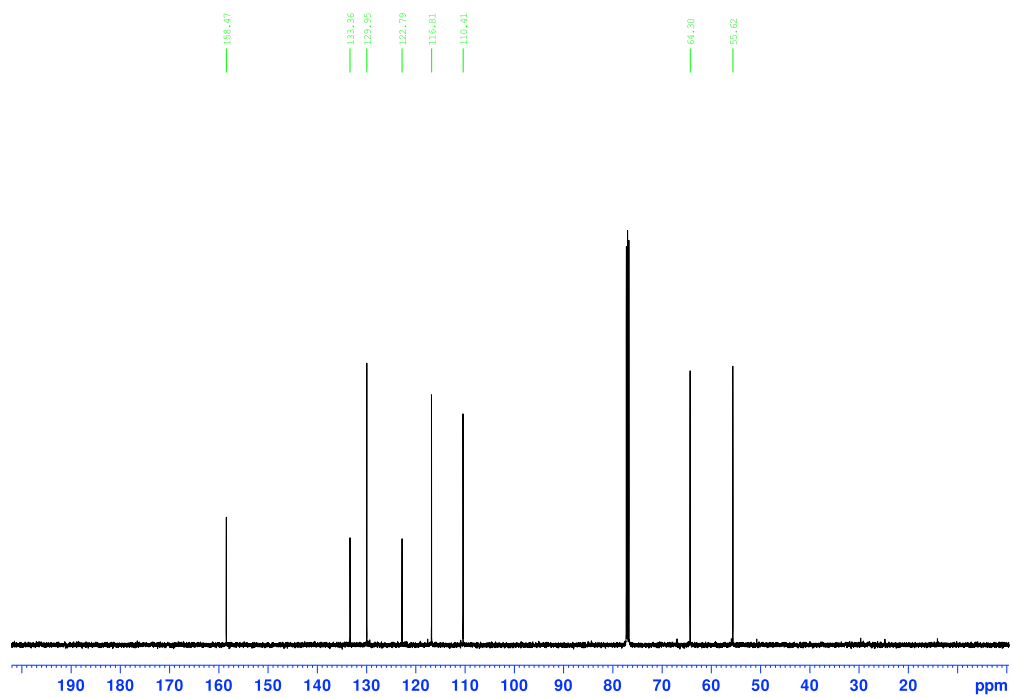




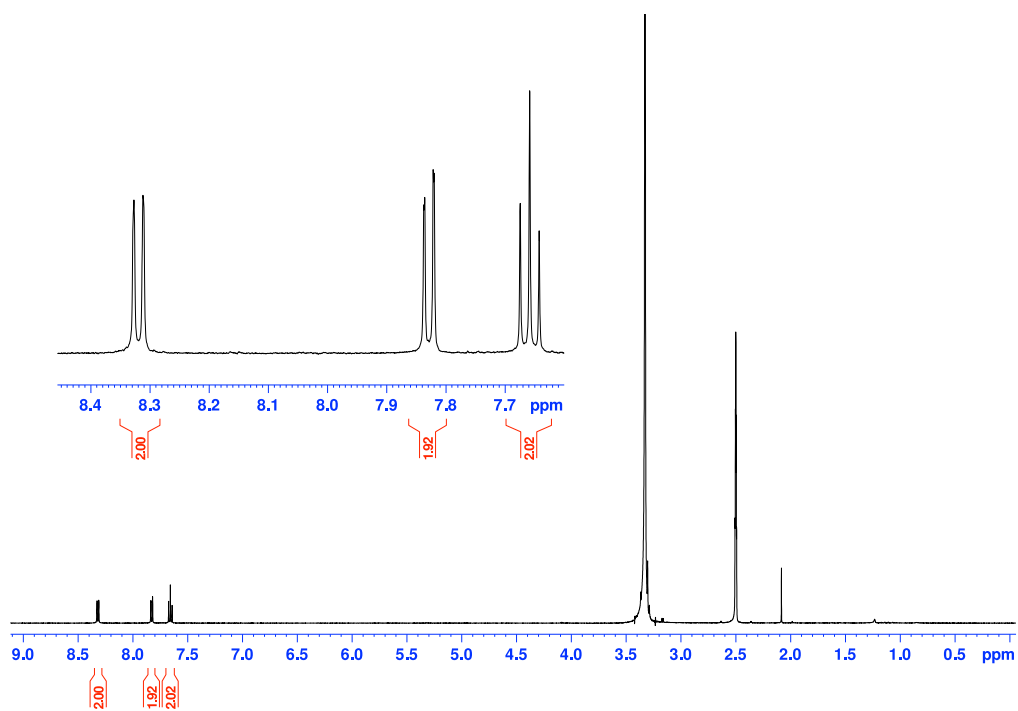
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5e**



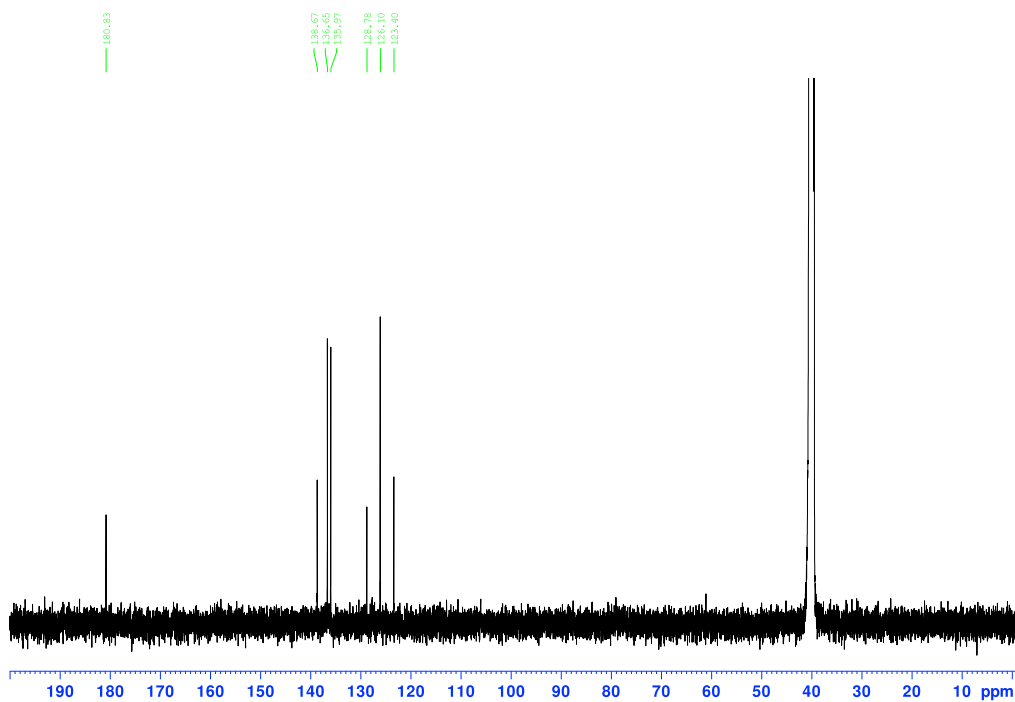
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **5e**



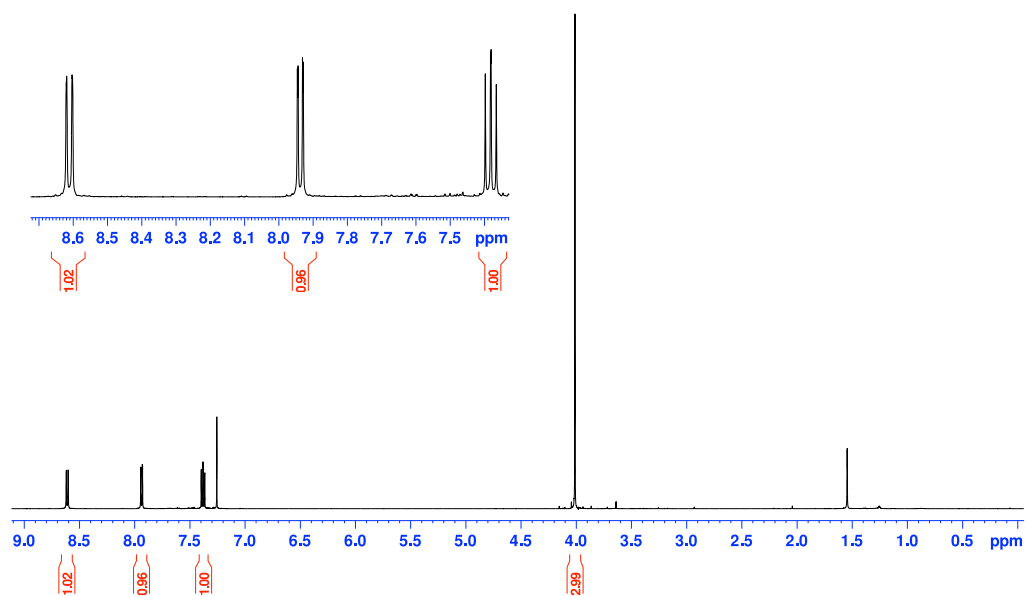
$^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **6d**



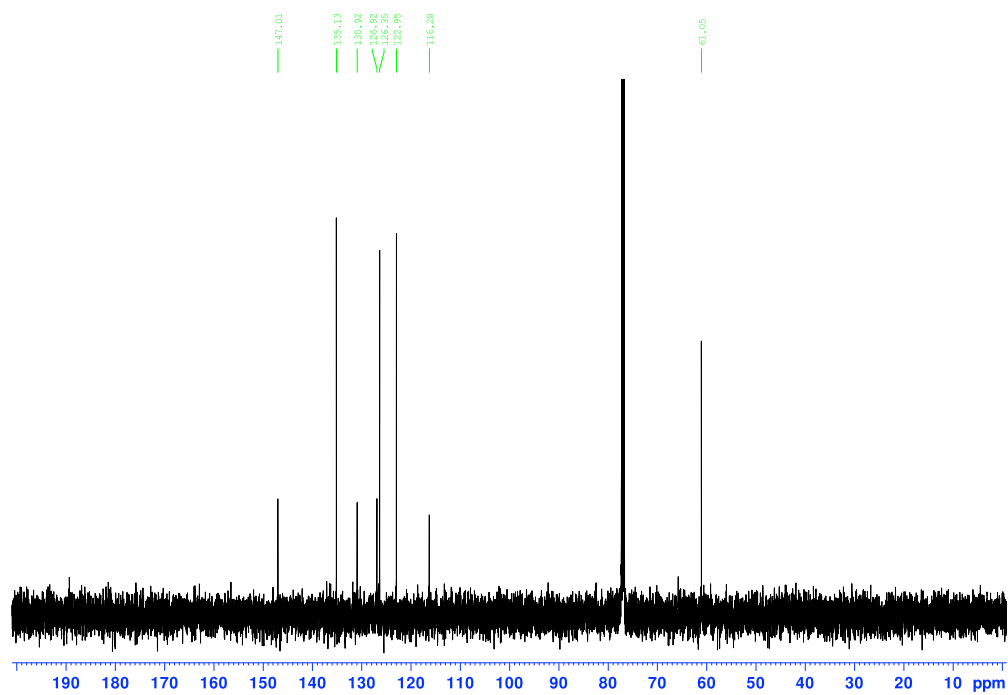
$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO-}d_6$ ) spectrum of compound **6d**



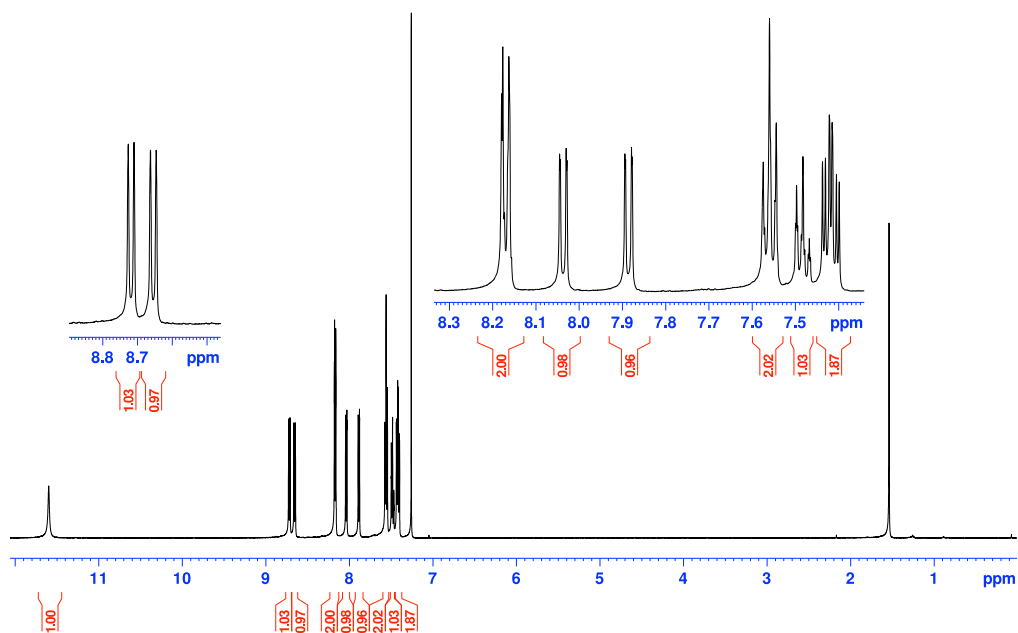
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **7d**



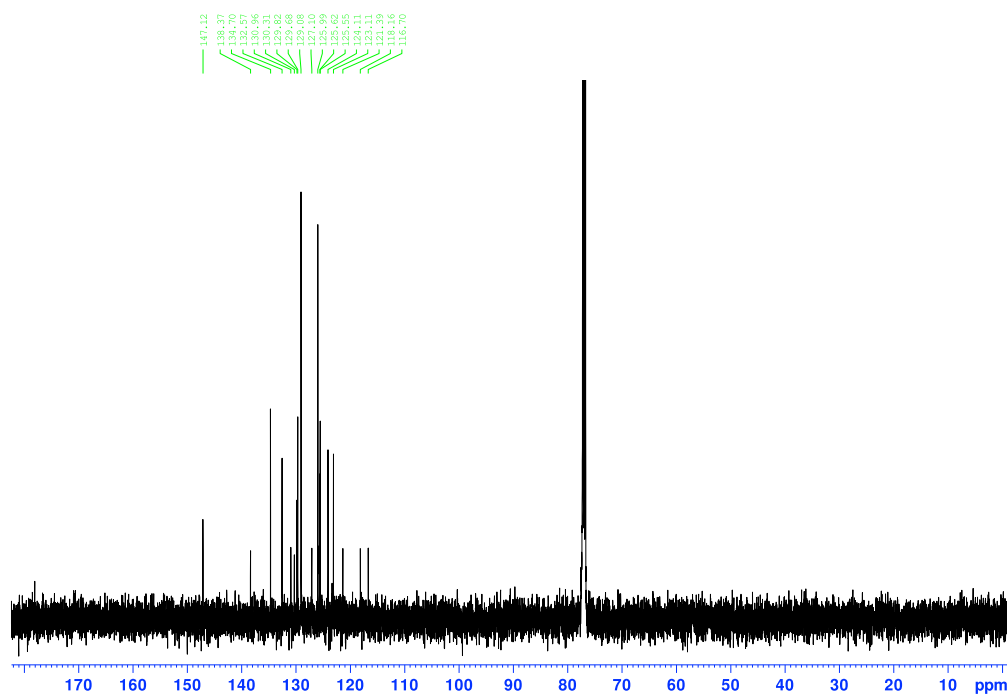
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **7d**



$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8d**



$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) spectrum of compound **8d**



## 6. References

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