

**Metal-free regioselective mono- and poly-halogenation of 2-substituted indazoles**

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<sup>#</sup> Contribute equally

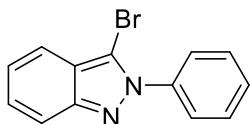
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### **3-bromo-2-phenyl-2*H*-indazole (2a)**



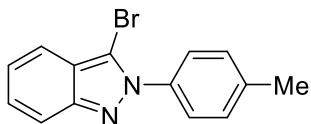
White solid, m.p. 72.4-72.9 °C, 98% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.8$  Hz, 1H), 7.68 (d,  $J = 7.3$  Hz, 2H), 7.63 – 7.50 (m, 6H), 7.38 (t, 1H), 7.19 (t, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.2, 139.2, 129.4, 129.2, 127.7, 126.3, 123.1, 122.9, 119.8, 118.2, 106.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_{10}\text{BrN}_2$  [M+H] $^+$  273.0022, found 273.0026.

### **3-bromo-2-(4-methoxyphenyl)-2*H*-indazole (2b)**



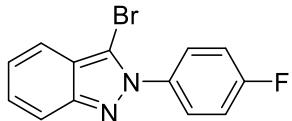
White solid, m.p. 125.4-126.7 °C, 99% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.8$  Hz, 1H), 7.58 (d,  $J = 8.9$  Hz, 3H), 7.40 – 7.32 (m, 1H), 7.20 – 7.13 (m, 1H), 7.08 – 7.00 (m, 2H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 149.1, 132.3, 127.6, 127.5, 122.9, 122.8, 119.7, 118.2, 114.3, 106.6, 55.7. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{O}$  [M+H] $^+$  303.0128, found 303.0132.

### **3-bromo-2-(p-tolyl)-2*H*-indazole (2c)**



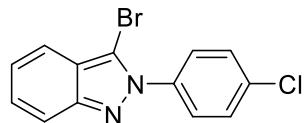
White solid, m.p. 97.5-98.3 °C, 95% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.7$  Hz, 1H), 7.61 – 7.52 (m, 3H), 7.36 (t,  $J = 8.7$  Hz, 3H), 7.23 – 7.13 (m, 1H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.15, 139.50, 136.87, 129.73, 127.60, 126.03, 122.98, 122.90, 119.76, 118.23, 106.34, 21.40. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2$  [M+H] $^+$  287.0178, found 287.0182.

### **3-bromo-2-(4-fluorophenyl)-2*H*-indazole (2d)**



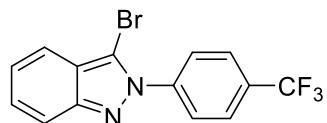
White solid, m.p. 105.0-105.7 °C, 96% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.70 – 7.61 (m, 2H), 7.58 (d,  $J = 8.5$  Hz, 1H), 7.43 – 7.33 (m, 1H), 7.27 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.8 (d,  $^1J = 248.4$  Hz), 149.3, 135.4 (d,  $^4J = 3.1$  Hz), 128.2 (d,  $^3J = 9.0$  Hz), 127.9, 123.3, 122.9, 119.8, 118.2, 116.2 (d,  $^2J = 23.0$  Hz), 106.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.19. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrFN}_2$  [M+H] $^+$  290.9928, found 290.9932.

**3-bromo-2-(4-chlorophenyl)-2*H*-indazole (2e)**



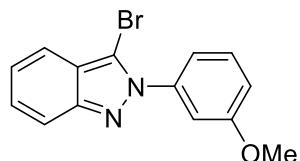
White solid, m.p. 146.4–147.7 °C, 96% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.64 (d,  $J = 8.7$  Hz, 2H), 7.57 (d,  $J = 8.5$  Hz, 1H), 7.53 (d,  $J = 8.7$  Hz, 2H), 7.40 – 7.34 (m, 1H), 7.22 – 7.15 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 137.8, 135.3, 129.4, 128.0, 127.5, 123.3, 123.1, 120.0, 118.3, 106.2. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrClN}_2$  [M+H] $^+$  306.9632, found 306.9636.

**3-bromo-2-(4-(trifluoromethyl)phenyl)-2*H*-indazole (2f)**



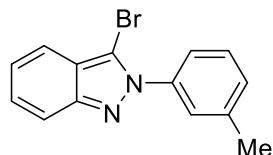
White solid, m.p. 111.7–112.4 °C, 96% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (q,  $J = 8.7$  Hz, 4H), 7.74 (d,  $J = 8.8$  Hz, 1H), 7.59 (d,  $J = 8.5$  Hz, 1H), 7.42 – 7.36 (m, 1H), 7.24 – 7.17 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 142.0, 131.2 (q,  $^2J = 32.8$  Hz), 128.3, 126.5, 126.4 (q,  $^3J = 3.7$  Hz), 123.7 (q,  $^1J = 270.8$  Hz), 123.6, 123.3, 119.9, 118.3, 106.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.53. HRMS (ESI+) calculated for  $\text{C}_{14}\text{H}_9\text{BrF}_3\text{N}_2$  [M+H] $^+$  340.9896, found 340.9900.

**3-bromo-2-(3-methoxyphenyl)-2*H*-indazole (2g)**



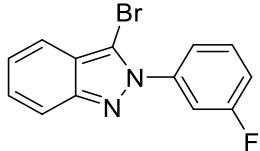
White solid, m.p. 87.1–89.2 °C, 87% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.8$  Hz, 1H), 7.59 (d,  $J = 8.5$  Hz, 1H), 7.46 (t,  $J = 8.1$  Hz, 1H), 7.39 – 7.34 (m, 1H), 7.28 – 7.25 (m, 1H), 7.22 (t,  $J = 2.2$  Hz, 1H), 7.21 – 7.16 (m, 1H), 7.09 – 7.03 (m, 1H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 149.2, 140.2, 129.8, 127.8, 123.1, 123.0, 119.8, 118.50, 118.2, 115.6, 111.8, 106.4, 55.7. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{O}$  [M+H] $^+$  303.0128, found 303.0130.

**3-bromo-2-(m-tolyl)-2*H*-indazole (2h)**



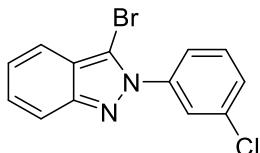
White solid, m.p. 55.6-56.8 °C, 93% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.8$  Hz, 1H), 7.59 (d,  $J = 8.5$  Hz, 1H), 7.51 – 7.31 (m, 5H), 7.22 – 7.15 (m, 1H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 139.4, 139.1, 130.1, 128.9, 127.7, 126.8, 123.3, 123.0, 122.9, 119.8, 118.2, 106.3, 21.5. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{BrN}_2$  [M+H] $^+$  287.0178, found 287.0182

### **3-bromo-2-(3-fluorophenyl)-2*H*-indazole (2i)**



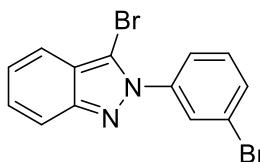
White solid, m.p. 92.2-93.5 °C, 95% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.58 (d,  $J = 8.5$  Hz, 1H), 7.56 – 7.50 (m, 2H), 7.50 – 7.43 (m, 1H), 7.41 – 7.34 (m, 1H), 7.26 – 7.14 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $^1J = 247.0$  Hz), 149.4, 140.5 (d,  $^3J = 10.0$  Hz), 130.4 (d,  $^3J = 8.9$  Hz), 128.1, 123.4, 123.2, 122.0 (d,  $^4J = 3.3$  Hz), 119.8, 118.3, 116.4 (d,  $^2J = 20.9$  Hz), 114.0 (d,  $^2J = 24.9$  Hz), 106.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.61. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrFN}_2$  [M+H] $^+$  290.9928, found 290.9932.

### **3-bromo-2-(3-chlorophenyl)-2*H*-indazole (2j)**



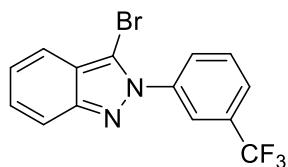
White solid, m.p. 105.0-105.4 °C, 91% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 – 7.70 (m, 2H), 7.64 – 7.56 (m, 2H), 7.53 – 7.46 (m, 2H), 7.40 – 7.35 (m, 1H), 7.22 – 7.14 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 140.2, 134.9, 130.2, 129.5, 128.1, 126.6, 124.4, 123.4, 123.2, 119.8, 118.3, 106.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrClN}_2$  [M+H] $^+$  306.9632, found 306.9633.

### **3-bromo-2-(3-bromophenyl)-2*H*-indazole (2k)**



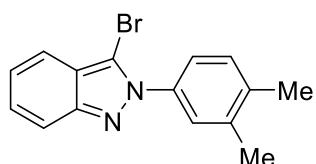
White solid, m.p. 109.7-110.6 °C, 88% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (t,  $J = 1.9$  Hz, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 7.68 – 7.62 (m, 2H), 7.57 (td,  $J = 8.5$  Hz, 1H), 7.42 (t,  $J = 8.1$  Hz, 1H), 7.40 – 7.34 (m, 1H), 7.22 – 7.16 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.4, 140.3, 132.4, 130.4, 129.4, 128.1, 124.9, 123.4, 123.1, 122.6, 119.8, 118.3, 106.3. HRMS (ESI): calculated for  $\text{C}_{13}\text{H}_9\text{Br}_2\text{N}_2$  [M+H] $^+$  350.9127, found 350.9131.

### **3-bromo-2-(3-(trifluoromethyl)phenyl)-2*H*-indazole (2l)**



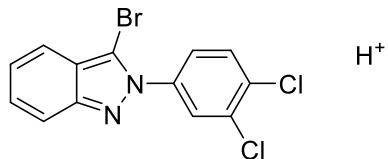
Yellow oil, 82% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1H), 7.92 (d,  $J = 8.0$  Hz, 1H), 7.81 – 7.64 (m, 3H), 7.58 (d,  $J = 8.5$  Hz, 1H), 7.42 – 7.34 (m, 1H), 7.23 – 7.14 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 139.7, 131.9 ( $^2J = 33.1$  Hz), 129.8, 129.4, 128.2, 126.0 ( $^3J = 3.6$  Hz), 123.5, 123.5 ( $^qJ = 270.9$  Hz), 123.4 ( $^qJ = 3.9$  Hz) 123.3, 119.8, 118.3, 106.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.66. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_9\text{BrF}_3\text{N}_2$  [M+H] $^+$  340.9896, found 340.9900.

### 3-bromo-2-(3,4-dimethylphenyl)-2H-indazole (2m)



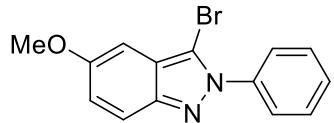
Yellow oil, 75% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.8$  Hz, 1H), 7.58 (d,  $J = 8.4$  Hz, 1H), 7.46 (s, 1H), 7.42 – 7.33 (m, 2H), 7.29 (d,  $J = 8.0$  Hz, 1H), 7.17 (t, 1H), 2.36 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.1, 138.1, 137.8, 137.0, 130.0, 127.5, 127.1, 123.4, 122.9, 122.8, 119.7, 118.2, 106.2, 19.9, 19.7. HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{14}\text{BrN}_2$  [M+H] $^+$  301.0335, found 301.0338.

### 3-bromo-2-(3,4-dichlorophenyl)-2H-indazole (2n)



White solid, m.p. 140.8–142.4 °C, 83% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 2.3$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.65 – 7.54 (m, 3H), 7.40 – 7.34 (m, 1H), 7.22 – 7.14 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 138.4, 133.7, 133.3, 130.8, 128.3, 128.1, 125.3, 123.6, 123.3, 119.8, 118.3, 106.2. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_8\text{BrCl}_2\text{N}_2$  [M+H] $^+$  340.9242, found 340.9242.

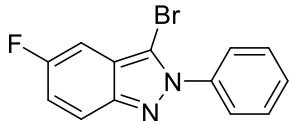
### 3-bromo-5-methoxy-2-phenyl-2H-indazole (2o)



White solid, m.p. 139.0–150.5 °C, 31% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.60 (m, 3H), 7.59 – 7.45 (m, 3H), 7.06 (d,  $J = 9.2$  Hz, 1H), 6.73 (s, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.2,

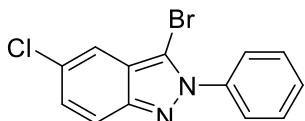
146.1, 139.4, 129.1, 126.1, 123.1, 123.0, 119.7, 104.6, 95.4, 55.6. HRMS (ESI) calculated for C<sub>14</sub>H<sub>12</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 303.0128, found 303.0129.

### **3-bromo-5-fluoro-2-phenyl-2*H*-indazole (2p)**



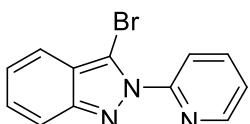
White solid, m.p. 123.1-123.5 °C, 91% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 – 7.70 (m, 1H), 7.69 – 7.64 (m, 2H), 7.60 – 7.51 (m, 3H), 7.21 – 7.12 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.1 (d, <sup>1</sup>J = 241.4 Hz), 146.6, 139.2, 129.5, 129.2, 126.2, 122.5 (d, <sup>3</sup>J = 11.9 Hz), 120.6 (d, <sup>3</sup>J = 9.6 Hz), 119.6 (d, <sup>2</sup>J = 28.9 Hz), 106.0 (d, <sup>4</sup>J = 8.9 Hz), 102.4 (d, <sup>2</sup>J = 25.1 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -117.57. HRMS (ESI) calculated for C<sub>13</sub>H<sub>9</sub>BrFN<sub>2</sub> [M+H]<sup>+</sup> 290.9928, found 290.9930.

### **3-bromo-5-chloro-2-phenyl-2*H*-indazole (2q)**



Yellow solid, m.p. 140.2-140.9 °C, 98% yield, <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.69 – 7.63 (m, 3H), 7.58 – 7.48 (m, 4H), 7.30 – 7.26 (m, 1H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 147.60, 139.07, 129.55, 129.22, 129.18, 128.81, 126.13, 123.41, 119.91, 118.51, 105.77. HRMS (ESI+) calculated for C<sub>13</sub>H<sub>9</sub>BrClN<sub>2</sub> [M+H]<sup>+</sup> 306.9632, found 306.9632.

### **3-bromo-2-(pyridin-2-yl)-2*H*-indazole (2r)**



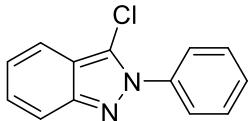
Orange oil, 81% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.63 (d, J = 4.1 Hz, 1H), 7.94 – 7.82 (m, 2H), 7.72 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.43 – 7.29 (m, 2H), 7.18 – 7.10 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.0, 149.4, 148.5, 138.6, 128.2, 123.9, 123.6, 123.3, 120.1, 119.8, 118.4, 105.5. HRMS (ESI+) calculated for C<sub>12</sub>H<sub>9</sub>BrN<sub>3</sub> [M+H]<sup>+</sup> 273.9974, found 273.9977.

### **3-bromo-2-(tert-butyl)-2*H*-indazole (2s)**



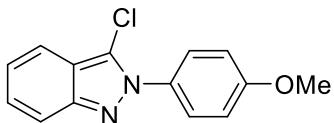
Yellow oil, 36% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 8.7$  Hz, 1H), 7.52 (d,  $J = 8.5$  Hz, 1H), 7.31 – 7.27 (m, 1H), 7.14 – 7.08 (m, 1H), 1.90 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.5, 126.6, 124.0, 122.4, 119.3, 118.1, 102.6, 63.6, 29.9. HRMS (ESI) calculated for  $\text{C}_{11}\text{H}_{14}\text{BrN}_2$  [M+H] $^+$  253.0335, found 253.0338.

### **3-chloro-2-phenyl-2*H*-indazole (5a)**



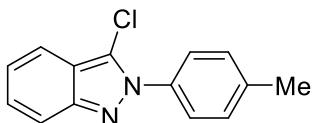
Yellow solid, m.p. 39.0–40.8 °C, 85% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77 – 7.68 (m, 3H), 7.63 (d,  $J = 8.5$  Hz, 1H), 7.59 – 7.49 (m, 3H), 7.36 (t, 1H), 7.17 (t, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.6, 138.6, 129.3, 127.7, 125.8, 122.9, 121.2, 120.0, 119.6, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_{10}\text{ClN}_2$  [M+H] $^+$  229.0527, found 229.0531.

### **3-chloro-2-(4-methoxyphenyl)-2*H*-indazole (5b)**



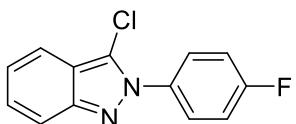
White solid, m.p. 89.5–91.1 °C, 82% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.8$  Hz, 1H), 7.60 (t,  $J = 7.4$  Hz, 3H), 7.35 (t,  $J = 7.7$  Hz, 1H), 7.15 (t,  $J = 7.5$  Hz, 1H), 7.05 (d,  $J = 8.8$  Hz, 2H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 148.4, 131.5, 127.5, 127.1, 122.7, 119.8, 119.9, 119.0, 118.2, 114.3, 55.7. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}$  [M+H] $^+$  259.0633, found 259.0635.

### **3-chloro-2-(p-tolyl)-2*H*-indazole (5c)**



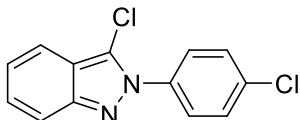
White solid, m.p. 87.2–88.3 °C, 88% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.8$  Hz, 1H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.60 – 7.54 (m, 2H), 7.39 – 7.32 (m, 3H), 7.19 – 7.13 (m, 1H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.52, 139.43, 136.13, 129.82, 127.60, 125.61, 122.79, 119.93, 119.64, 119.09, 118.26, 21.40. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{ClN}_2$  [M+H] $^+$  243.0684, found 243.0688.

### **3-chloro-2-(4-fluorophenyl)-2*H*-indazole (5d)**



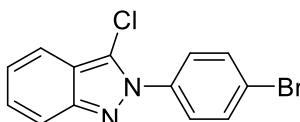
White solid, m.p. 103.6–105.1 °C, 45% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.73 – 7.63 (m, 3H), 7.61 (d,  $J$  = 8.5 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.28 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 162.8 (d,  $^1J$  = 248.4 Hz), 148.6, 134.6 (d,  $^4J$  = 3.1 Hz), 127.8, 127.7 (d,  $^3J$  = 8.8 Hz), 123.0, 119.9, 119.7, 119.0, 118.2, 116.2 (d,  $^2J$  = 23.0 Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) δ -111.37. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{ClFN}_2$  [M+H] $^+$  247.0433, found 247.0435.

### **3-chloro-2-(4-chlorophenyl)-2*H*-indazole (5e)**



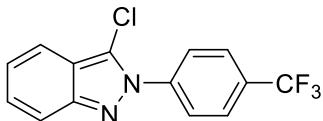
White solid, m.p. 138.7–140.0 °C, 86% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.71 (d,  $J$  = 8.8 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.61 (d,  $J$  = 8.5 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.39 – 7.33 (m, 1H), 7.20 – 7.14 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 148.8, 137.1, 135.2, 129.5, 128.0, 127.0, 123.1, 120.1, 119.6, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{Cl}_2\text{N}_2$  [M+H] $^+$  263.0137, found 263.0140.

### **3-chloro-2-(4-chlorophenyl)-2*H*-indazole (5f)**



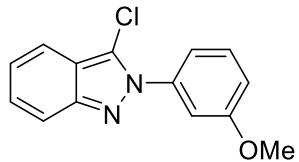
White solid, m.p. 144.3–146.5 °C, 63% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.76 – 7.63 (m, 3H), 7.63 – 7.52 (m, 3H), 7.39 – 7.32 (m, 1H), 7.20 – 7.13 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 148.8, 137.6, 132.5, 128.0, 127.2, 123.3, 123.1, 119.5, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrClN}_2$  [M+H] $^+$  306.9632, found 306.9636.

### **3-chloro-2-(4-(trifluoromethyl)phenyl)-2*H*-indazole (5g)**



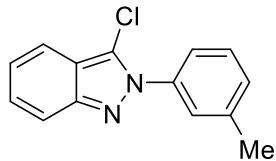
Yellow oil, 62% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ 7.90 (d,  $J$  = 8.5 Hz, 2H), 7.83 (d,  $J$  = 8.6 Hz, 2H), 7.72 (d,  $J$  = 8.8 Hz, 1H), 7.62 (d,  $J$  = 8.6 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.21 – 7.13 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) δ 149.0, 141.4, 131.1 (q,  $^2J$  = 32.8 Hz), 128.2, 126.5 (q,  $^3J$  = 3.7 Hz), 126.0, 123.8 (q,  $^1J$  = 270.8 Hz), 123.4, 120.3, 119.7, 119.1, 118.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) δ -62.60. HRMS (ESI+) calculated for  $\text{C}_{14}\text{H}_9\text{ClF}_3\text{N}_2$  [M+H] $^+$  297.0401, found 297.0405.

### **3-chloro-2-(3-methoxyphenyl)-2*H*-indazole (5h)**



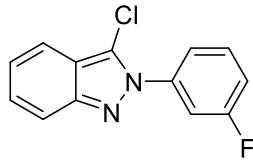
Yellow oil, 87% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.44 (t,  $J = 8.1$  Hz, 1H), 7.39 – 7.33 (m, 1H), 7.29 (d,  $J = 8.6$  Hz, 1H), 7.26 – 7.23 (m, 1H), 7.16 (t, 1H), 7.05 (dd,  $J = 8.3, 2.3$  Hz, 1H), 3.87 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.1, 148.5, 139.5, 129.9, 127.7, 122.9, 120.0, 119.6, 119.1, 118.2, 118.0, 115.4, 111.3, 55.7. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O} [\text{M}+\text{H}]^+$  259.0633, found 259.0635.

### **3-chloro-2-(3-methoxyphenyl)-2H-indazole (5i)**



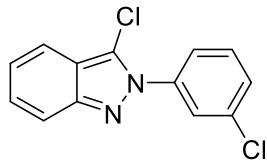
Yellow oil, 90% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.63 (d,  $J = 8.5$  Hz, 1H), 7.52 (s, 1H), 7.50 (d,  $J = 8.2$  Hz, 1H), 7.43 (t,  $J = 7.7$  Hz, 1H), 7.39 – 7.33 (m, 1H), 7.31 (d,  $J = 7.5$  Hz, 1H), 7.19 – 7.13 (m, 1H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5, 139.4, 138.4, 130.0, 128.9, 127.6, 126.4, 122.8, 122.7, 119.9, 119.5, 119.0, 118.2, 21.4. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{ClN}_2 [\text{M}+\text{H}]^+$  243.0684, found 243.0686.

### **3-chloro-2-(3-fluorophenyl)-2H-indazole (5j)**



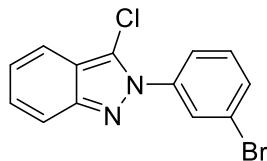
Yellow solid, m.p. 69.8–72.0 °C, 85% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.8$  Hz, 1H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.58 – 7.47 (m, 3H), 7.40 – 7.33 (m, 1H), 7.25 – 7.12 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3 (d,  $^1\text{J} = 246.9$  Hz), 148.8, 139.7 (d,  $^3\text{J} = 10.0$  Hz), 130.5 (d,  $^3\text{J} = 8.9$  Hz), 128.0, 123.2, 121.4 (d,  $^4\text{J} = 3.3$  Hz), 120.1, 119.6, 119.1, 118.3, 116.2 (d,  $^2\text{J} = 20.9$  Hz), 113.4 (d,  $^2\text{J} = 25.0$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.55. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{ClFN}_2 [\text{M}+\text{H}]^+$  247.0433, found 247.0437.

### **3-chloro-2-(3-chlorophenyl)-2H-indazole (5k)**



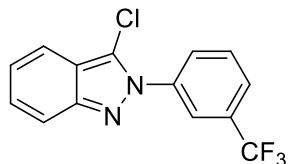
White solid, m.p. 67.7-70.0 °C, 85% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (s, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.65 – 7.58 (m, 2H), 7.48 (d,  $J = 5.0$  Hz, 2H), 7.40 – 7.32 (m, 1H), 7.20 – 7.12 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.78, 139.5, 134.9, 130.2, 129.3, 128.0, 126.2, 123.8, 123.2, 120.1, 119.6, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{Cl}_2\text{N}_2$  [M+H] $^+$  263.0137, found 263.0140.

### 2-(3-bromophenyl)-3-chloro-2H-indazole (5l)



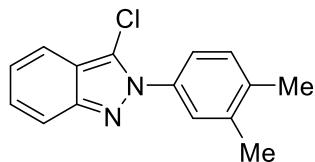
Yellow solid, m.p. 92.7-94.3 °C, 81% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (t,  $J = 1.9$  Hz, 1H), 7.73 – 7.55 (m, 4H), 7.41 (t,  $J = 8.1$  Hz, 1H), 7.38 – 7.32 (m, 1H), 7.19 – 7.12 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.8, 139.5, 132.2, 130.4, 128.8, 128.0, 124.2, 123.2, 122.7, 120.1, 119.6, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrClN}_2$  [M+H] $^+$  306.9632, found 306.9632.

### 3-chloro-2-(3-(trifluoromethyl)phenyl)-2H-indazole (5m)



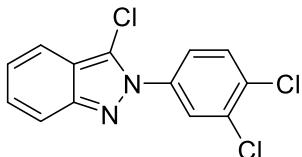
Yellow oil, 72% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (s, 1H), 7.94 (d,  $J = 8.0$  Hz, 1H), 7.77 (d,  $J = 7.8$  Hz, 1H), 7.74 – 7.66 (m, 2H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.40 – 7.34 (m, 1H), 7.20 – 7.14 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 139.0, 132.0 (q,  $^2J = 33.1$  Hz), 129.9, 128.8, 128.8, 128.2, 125.8 (q,  $^3J = 3.7$  Hz), 123.5 (q,  $^1J = 270.1$  Hz), 123.3, 122.8 (q,  $^3J = 3.9$  Hz), 120.2, 119.1, 118.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.68. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_9\text{ClF}_3\text{N}_2$  [M+H] $^+$  297.0401, found 297.0405.

### 3-chloro-2-(3,4-dimethylphenyl)-2H-indazole (5n)



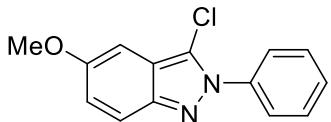
Yellow oil, 60% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.8$  Hz, 1H), 7.62 (d,  $J = 8.5$  Hz, 1H), 7.47 (s, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.38 – 7.32 (m, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.19 – 7.12 (m, 1H), 2.36 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.4, 138.1, 137.9, 136.3, 130.1, 127.5, 126.7, 122.9, 122.7, 119.9, 119.5, 119.0, 118.2, 19.95, 19.7. HRMS (ESI) calculated for  $\text{C}_{15}\text{H}_{14}\text{ClN}_2$  [M+H] $^+$  257.0840, found 257.0844.

### 3-chloro-2-(3,4-dichlorophenyl)-2*H*-indazole (**5o**)



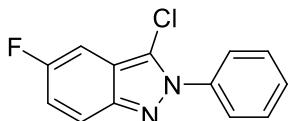
White solid, m.p. 137.4–141.5 °C, 72% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (s, 1H), 7.69 (d,  $J = 8.8$  Hz, 1H), 7.65 – 7.56 (m, 3H), 7.36 (t, 1H), 7.21 – 7.13 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.9, 137.7, 133.6, 133.4, 130.9, 128.2, 127.6, 124.7, 123.4, 120.2, 119.6, 119.1, 118.3. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_8\text{Cl}_3\text{N}_2$  [M+H] $^+$  296.9748, found 296.9752.

### 3-chloro-5-methoxy-2-phenyl-2*H*-indazole (**5p**)



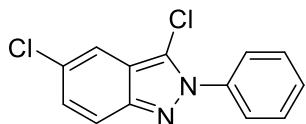
White solid, m.p. 148.4–148.5 °C, 26% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (d,  $J = 7.5$  Hz, 2H), 7.61 (d,  $J = 9.3$  Hz, 1H), 7.55 (t,  $J = 7.6$  Hz, 2H), 7.48 (t,  $J = 7.0$  Hz, 1H), 7.06 (dd,  $J = 9.3, 2.3$  Hz, 1H), 6.77 (d,  $J = 2.1$  Hz, 1H), 3.89 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 145.5, 138.7, 129.2, 129.0, 125.6, 123.1, 120.0, 119.8, 118.1, 94.7, 55.6. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}$  [M+H] $^+$  259.0633, found 259.0633.

### 3-chloro-5-fluoro-2-phenyl-2*H*-indazole (**5q**)



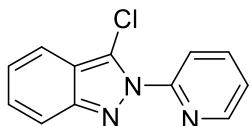
White solid, m.p. 102.6–104.9 °C, 85% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.66 (m, 3H), 7.59 – 7.50 (m, 3H), 7.23 – 7.09 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9 (d,  $^1J = 241.4$  Hz), 146.0, 138.5, 129.4, 129.3, 125.7, 120.7 (d,  $^3J = 9.6$  Hz), 119.6 (d,  $^4J = 9.0$  Hz), 119.6 (d,  $^2J = 29.0$  Hz), 119.4 (d,  $^3J = 11.9$  Hz), 101.6 (d,  $^2J = 25.1$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.71. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{ClFN}_2$  [M+H] $^+$  247.0433, found 247.0437.

### **3,5-dichloro-2-phenyl-2*H*-indazole (5r)**



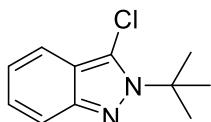
Yellow solid, m.p. 115.8–116.9 °C, 89% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.63 (m, 3H), 7.61 (s, 1H), 7.59 – 7.50 (m, 3H), 7.30 – 7.26 (m, 1H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 138.3, 129.5, 129.3, 129.2, 128.7, 125.7, 120.4, 119.9, 119.3, 117.8. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{Cl}_2\text{N}_2$  [M+H] $^+$  263.0137, found 263.0140.

### **3-chloro-2-(pyridin-2-yl)-2*H*-indazol (5s)**



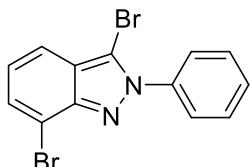
Blown oil, 81% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (d,  $J$  = 4.2 Hz, 1H), 7.92 (td,  $J$  = 7.8, 1.7 Hz, 1H), 7.87 (d,  $J$  = 8.0 Hz, 1H), 7.70 (d,  $J$  = 8.9 Hz, 1H), 7.63 (d,  $J$  = 8.5 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.37 – 7.31 (m, 1H), 7.14 (dd,  $J$  = 8.4, 6.7 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.6, 148.8, 148.7, 138.7, 128.2, 123.9, 123.2, 120.6, 119.9, 119.6, 119.4, 118.4. HRMS (ESI) calculated for  $\text{C}_{12}\text{H}_9\text{ClN}_3$  [M+H] $^+$  230.0480, found 230.0484.

### **2-(*tert*-butyl)-3-chloro-2*H*-indazole (5t)**



Yellow oil, 36% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  7.63 (d,  $J$  = 8.7 Hz, 1H), 7.54 (d,  $J$  = 8.4 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.15 – 7.08 (m, 1H), 1.77 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}$ )  $\delta$  145.2, 126.4, 122.3, 120.3, 118.2, 118.0, 116.5, 62.8, 29.0. HRMS (ESI) calculated for  $\text{C}_{11}\text{H}_{14}\text{ClN}_3$  [M+H] $^+$  209.0480, found 209.0484.

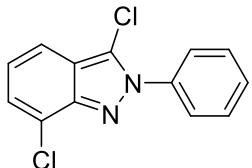
### **3,7-dibromo-2-phenyl-2*H*-indazole (3a)**



White solid, m.p. 204.3–205.1 °C, 67% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J$  = 7.3 Hz, 2H), 7.62 – 7.49 (m, 5H), 7.05 (t,  $J$  = 7.8 Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 139.1, 130.4, 129.7,

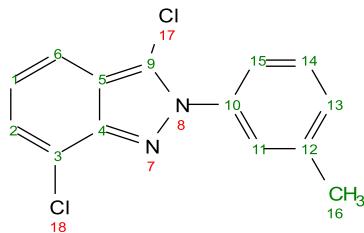
129.2, 126.6, 123.7, 123.6, 119.4, 111.7, 107.7. HRMS (ESI) calculated for  $C_{13}H_9Br_2N_2$  [M+H]<sup>+</sup> 350.9127, found 350.9131.

### 3,7-dichloro-2-phenyl-2*H*-indazole (3b)



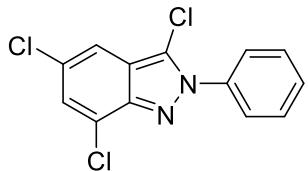
White solid, m.p. 172.3-173.5 °C, 64% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68 (m, 2H), 7.59 – 7.52 (m, 5H), 7.36 (d, *J* = 1.7 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.6, 138.0, 129.8, 129.4, 129.4, 128.1, 126.3, 125.9, 124.7, 120.9, 116.8. HRMS (ESI) calculated for  $C_{13}H_9Cl_2N_2$  [M+H]<sup>+</sup> 263.0137, found 263.0141.

### 3,7-dichloro-2-phenyl-2*H*-indazole (3c)



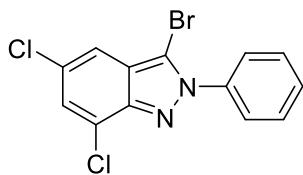
Blown oil, 70% yield, <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.57 (dd, *J* = 8.5, 0.9 Hz, 1H, 6), 7.54 (s, 1H, 11), 7.50 (d, *J* = 8.2 Hz, 1H, 15), 7.45 (t, *J* = 7.7 Hz, 1H, 14), 7.41 (dd, *J* = 7.1, 0.9 Hz, 1H, 2), 7.35 (d, *J* = 7.8 Hz, 1H, 13), 7.11 (dd, *J* = 8.5, 7.2 Hz, 1H, 1), 2.49 (s, 3H, 16). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 145.91 (4), 139.49 (12), 138.05 (10), 130.30 (13), 128.86 (14), 126.78 (2), 126.62 (11), 123.34 (3), 122.97 (15), 122.96 (1), 120.98 (5), 120.84 (9), 117.95 (6), 21.38 (16). HRMS (ESI) calculated for  $C_{13}H_{11}Cl_2N_2$  [M+H]<sup>+</sup> 277.0294, found 277.0294.

### 3,5,7-trichloro-2-phenyl-2*H*-indazole (3d)



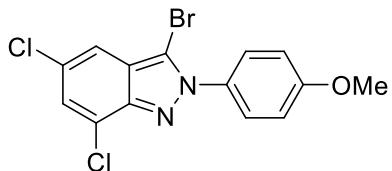
Blown solid, m.p. 177.5-178.8 °C, 66% yield, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.67 (m, 2H), 7.60 – 7.53 (m, 4H), 7.37 (d, *J* = 1.6 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.65, 137.98, 129.86, 129.39, 128.13, 125.96, 124.98, 124.71, 120.93, 120.67, 116.88. HRMS (ESI) calculated for  $C_{13}H_8Cl_3N_2$  [M+H]<sup>+</sup> 296.9748, found 296.9750.

### 3-bromo-5,7-dichloro-2-phenyl-2*H*-indazole (3e)



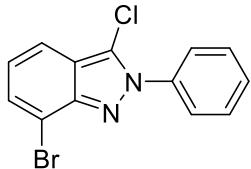
White solid, m.p. 188.2-190.8 °C, 56% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 – 7.64 (m, 2H), 7.60 – 7.52 (m, 5H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 146.0, 131.3, 131.1, 127.6, 127.3, 122.5, 117.4, 114.5, 114.5, 111.0, 55.8. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_8\text{BrCl}_2\text{N}_2$  [M+H] $^+$  340.9242, found 340.9346.

### **3-bromo-5,7-dichloro-2-(4-methoxyphenyl)-2H-indazole (3f)**



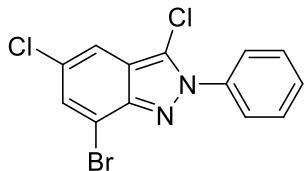
White solid, m.p. 174.5-178.2 °C, 44% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 – 7.29 (m, 4H), 7.04 (d,  $J = 6.8$  Hz, 2H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 146.0, 131.3, 131.1, 127.6, 127.23, 122.5, 117.4, 114.5, 114.5, 111.0, 55.8. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_2\text{N}_2\text{O}$  [M+H] $^+$  370.9348, found 370.9352.

### **7-bromo-3-chloro-2-phenyl-2H-indazole (3g)**



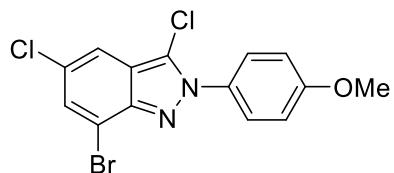
White solid, m.p. 174.5-178.2 °C, 65% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 – 7.64 (m, 3H), 7.61 – 7.49 (m, 5H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 138.0, 133.4, 129.8, 129.4, 126.1, 126.0, 120.8, 118.7, 115.6, 113.1. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_9\text{BrClN}_2$  [M+H] $^+$  306.9632, found 306.9634.

### **7-bromo-3,5-dichloro-2-phenyl-2H-indazole (3h)**



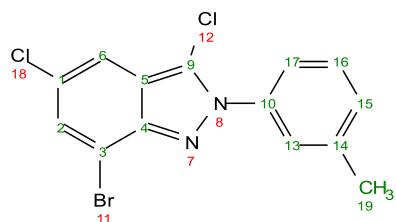
White solid, m.p. 182.8-184.7 °C, 68% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.66 (m, 2H), 7.58 – 7.52 (m, 5H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 138.0, 131.3, 129.8, 129.4, 128.4, 126.4, 126.0, 120.5, 117.4, 113.0. HRMS (ESI) calculated for  $\text{C}_{13}\text{H}_8\text{BrCl}_2\text{N}_2$  [M+H] $^+$  340.9242, found 340.9246.

### **7-bromo-3,5-dichloro-2-phenyl-2H-indazole (3i)**



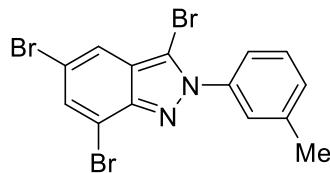
Purple solid, m.p. 178.1–179.9 °C, 69% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.51 (m, 4H), 7.05 (s, 1H), 7.03 (d,  $J$  = 2.0 Hz, 1H), 3.88 (s, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  160.5, 145.5, 131.1, 131.0, 128.2, 127.3, 120.8, 120.3, 117.4, 114.5, 112.8, 55.8. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_2\text{N}_2\text{O}$  [M+H] $^+$  370.9348, found 370.9352.

### 7-bromo-3,5-dichloro-2-phenyl-2H-indazole (3j)



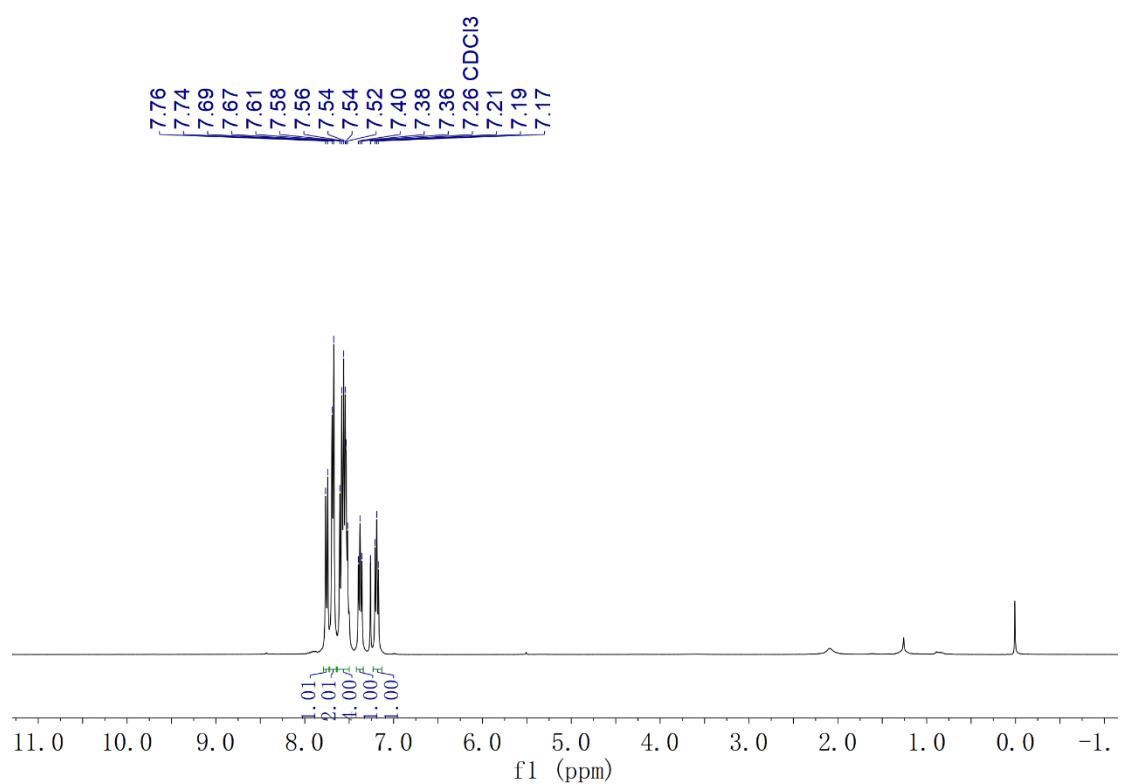
Purple solid, m.p. 163.0–163.8 °C, 74% yield,  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J$  = 1.6 Hz, 1H, 6), 7.71 (d,  $J$  = 1.6 Hz, 1H, 2), 7.51 – 7.48 (m, 1H, 11), 7.48 – 7.43 (m, 2H, 13, 15), 7.39 – 7.35 (m, 1H, 14), 2.49 (d,  $J$  = 0.8 Hz, 3H, 16).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  146.33 (4), 139.53 (12), 138.60 (10), 133.22 (2), 130.59 (14), 128.86 (13), 126.90 (11), 124.14 (9), 123.34 (15), 121.42 (6), 115.60 (5), 112.80 (3), 106.95 (1), 21.34 (16). HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{10}\text{BrCl}_2\text{N}_2$  [M+H] $^+$  354.9399, found 354.9403.

### 3,5,7-tribromo-2-phenyl-2H-indazole (4b)

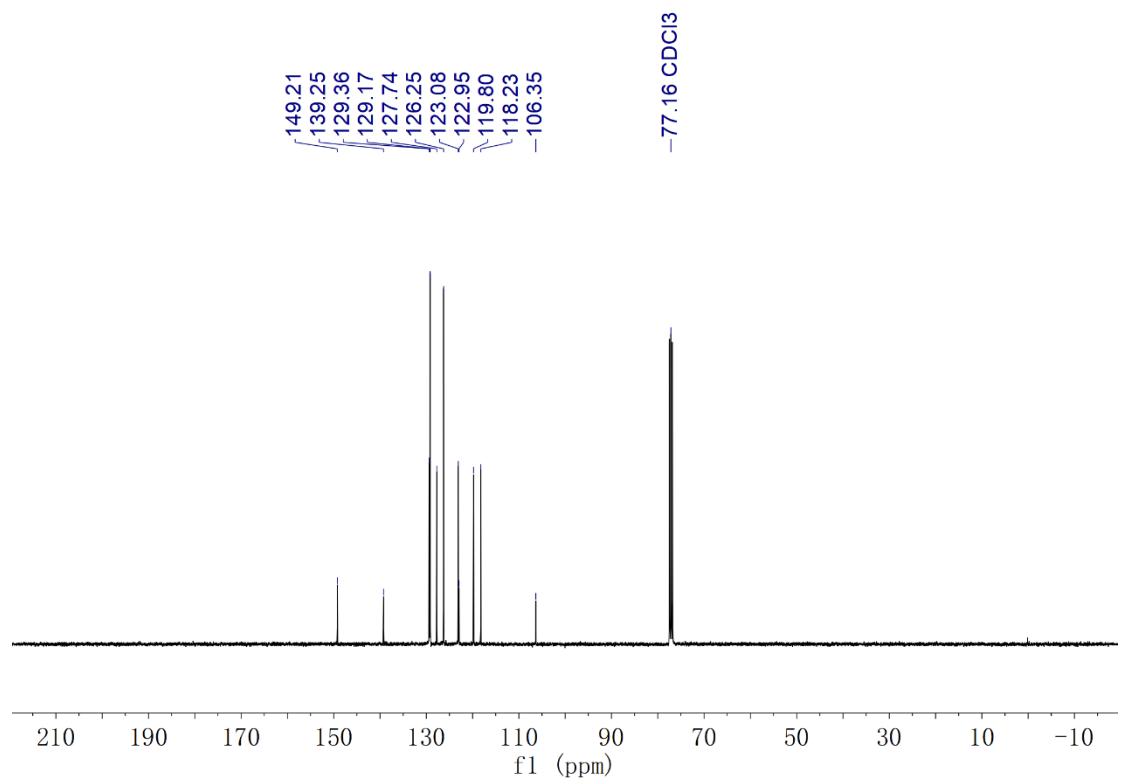


White solid, m.p. 205.1–205.3 °C, 72% yield,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (s, 1H), 7.66 (s, 1H), 7.46 (s, 1H), 7.44 – 7.38 (m, 2H), 7.36 – 7.30 (m, 1H), 2.45 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.3, 139.6, 138.6, 133.2, 130.6, 128.9, 126.9, 124.1, 123.4, 121.5, 115.6, 112.8, 107.1, 77.2, 21.5. HRMS (ESI) calculated for  $\text{C}_{14}\text{H}_{10}\text{Br}_3\text{N}_2$  [M+H] $^+$  442.8389, found 442.8393.

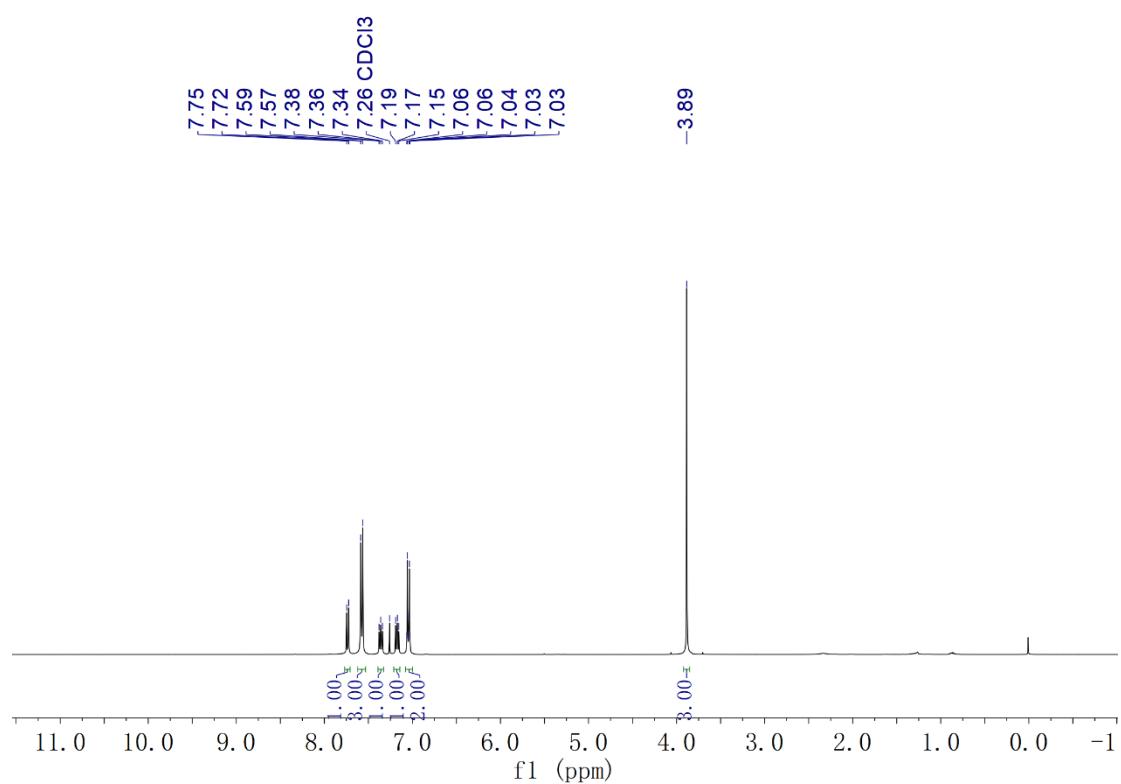
**2a  $^1\text{H-NMR}$**



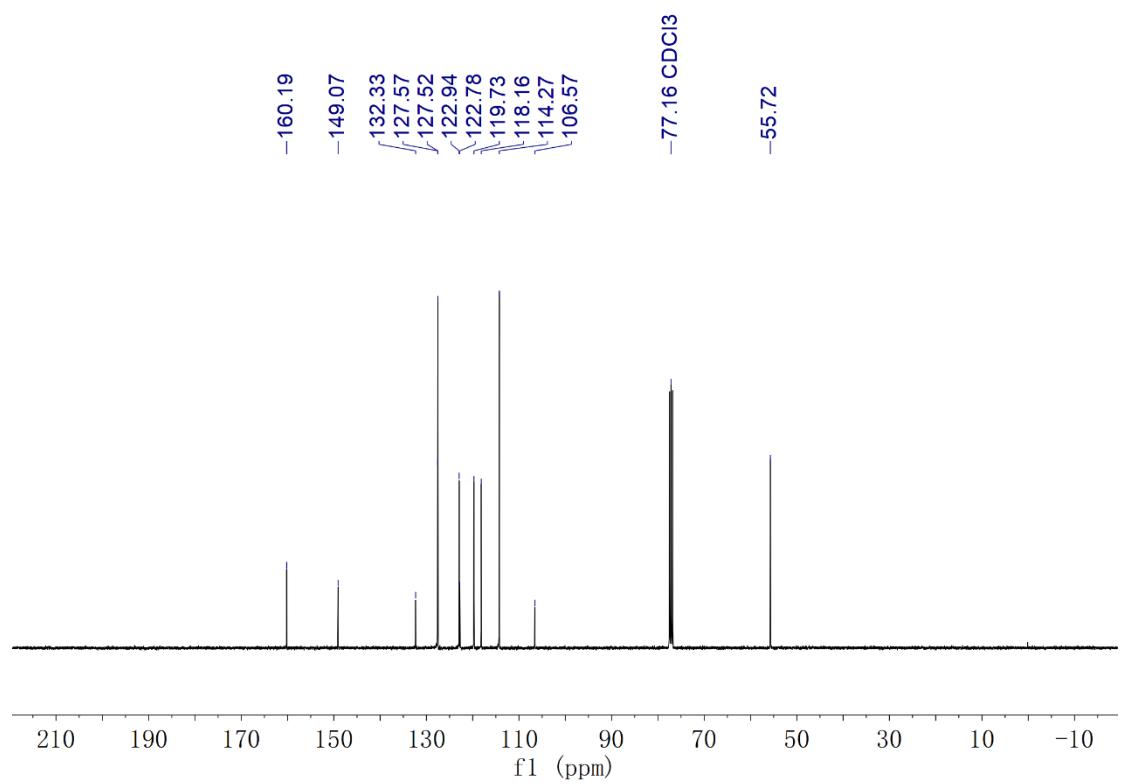
**2a  $^{13}\text{C-NMR}$**



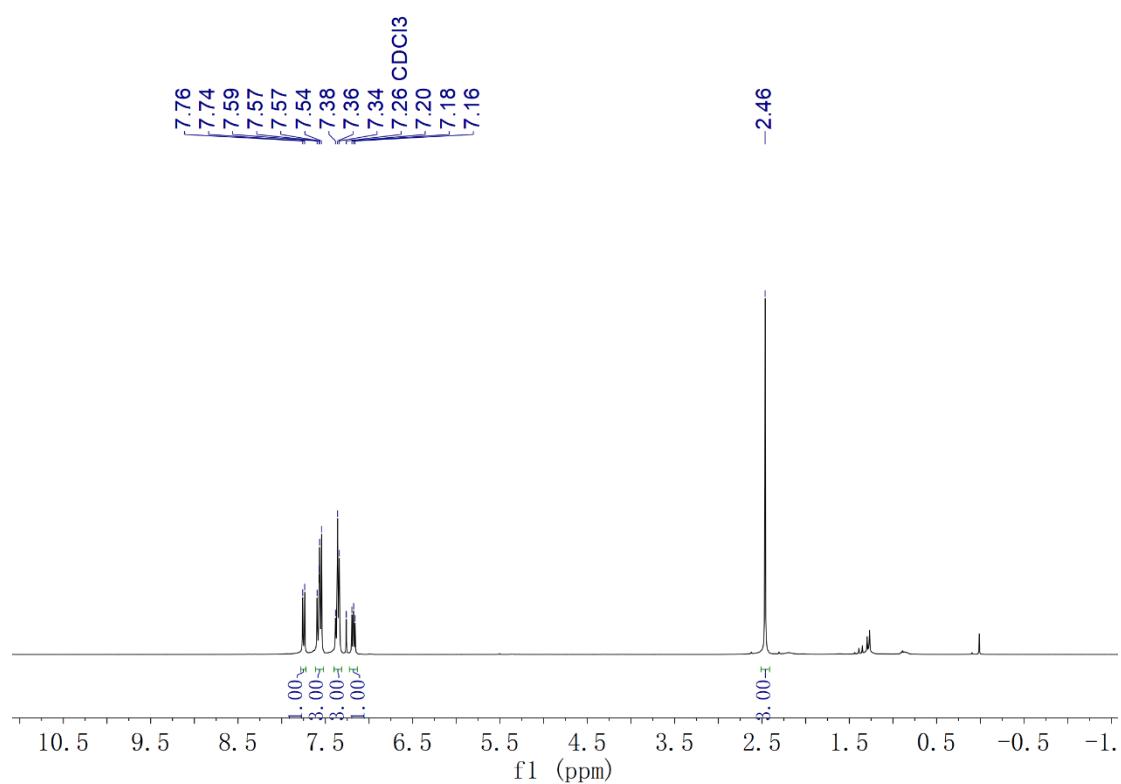
**2b  $^1\text{H-NMR}$**



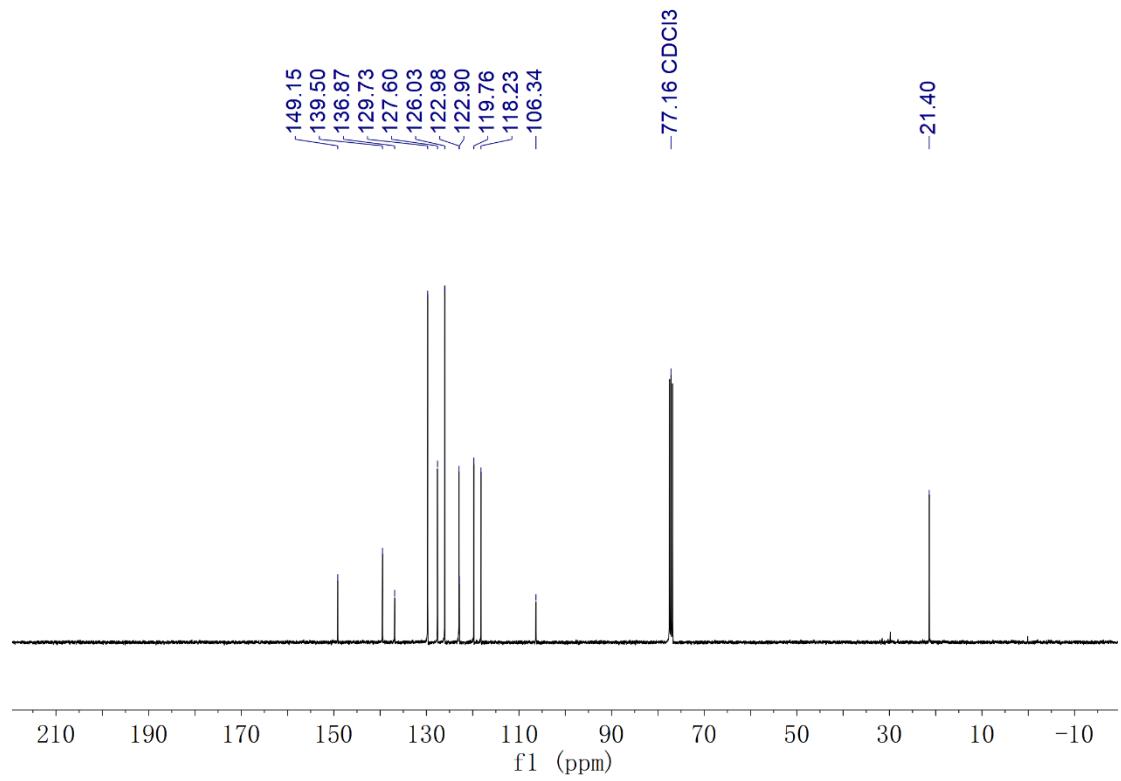
**2b  $^{13}\text{C-NMR}$**



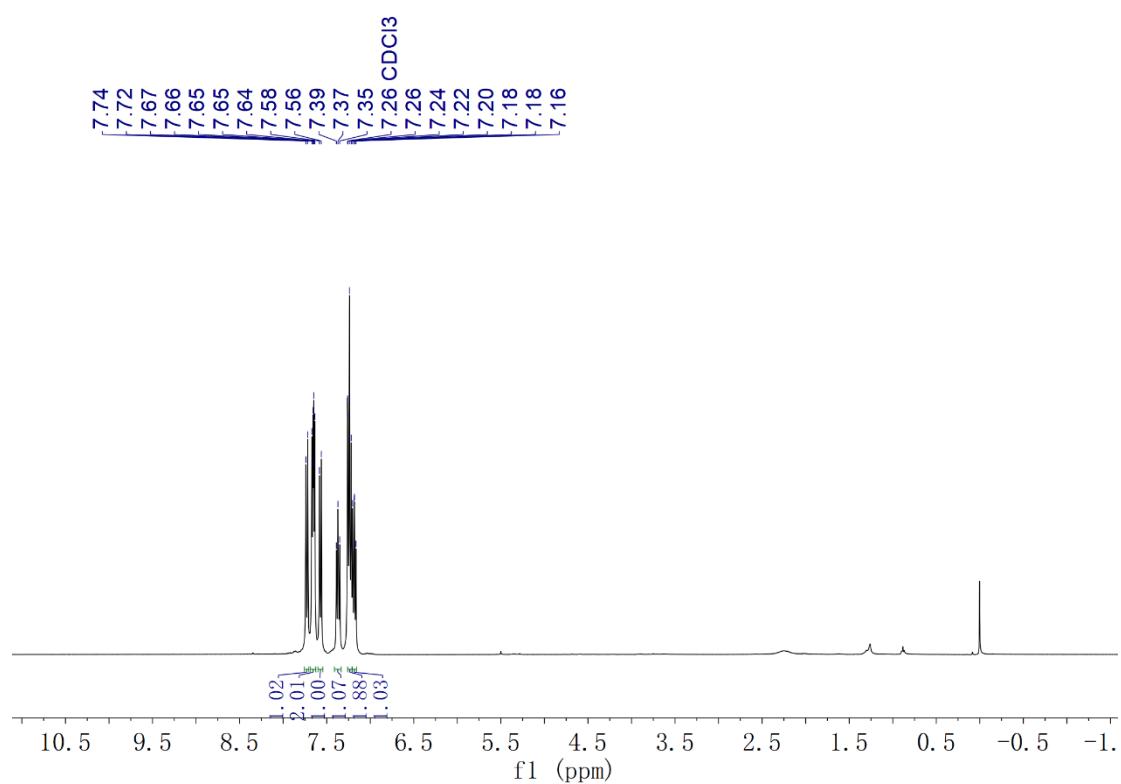
**2c  $^1\text{H-NMR}$**



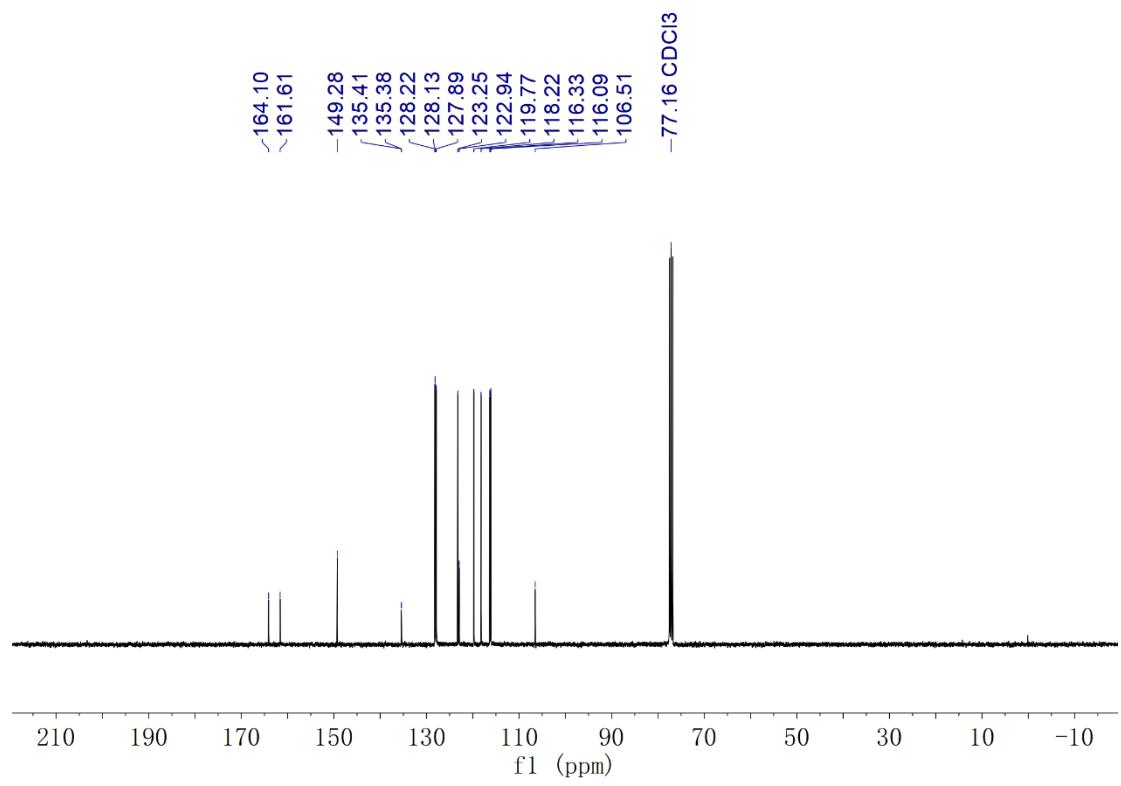
**2c  $^{13}\text{C-NMR}$**



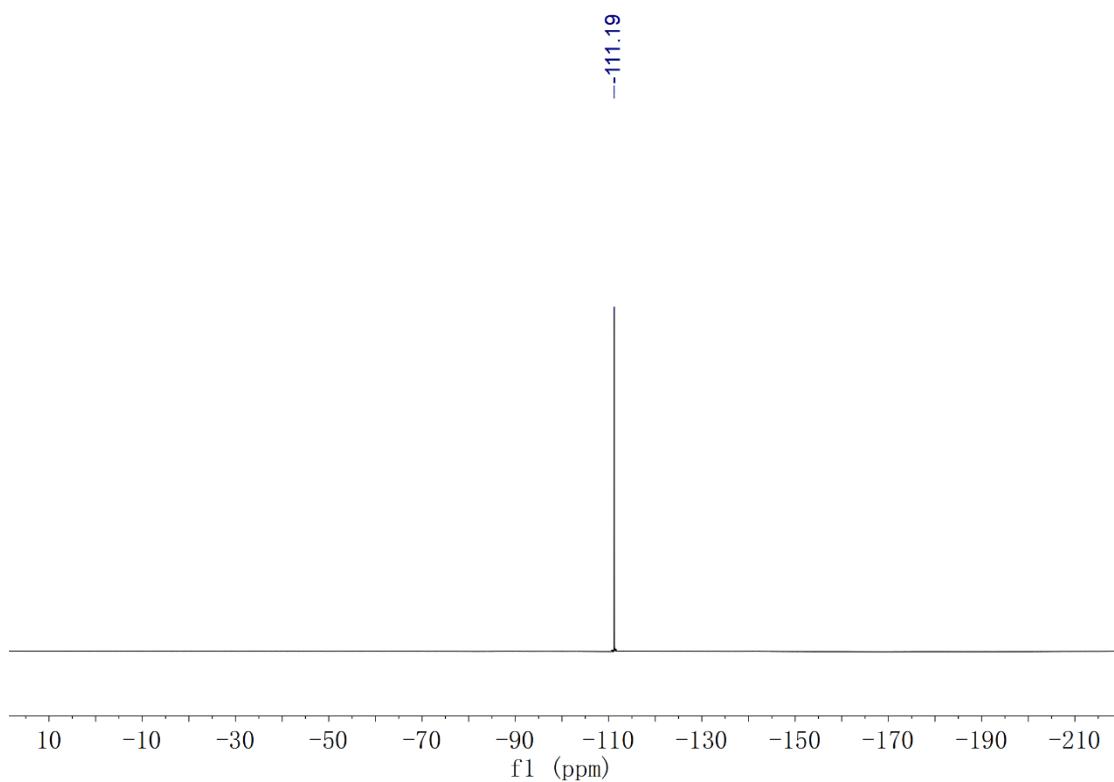
**2d  $^1\text{H-NMR}$**



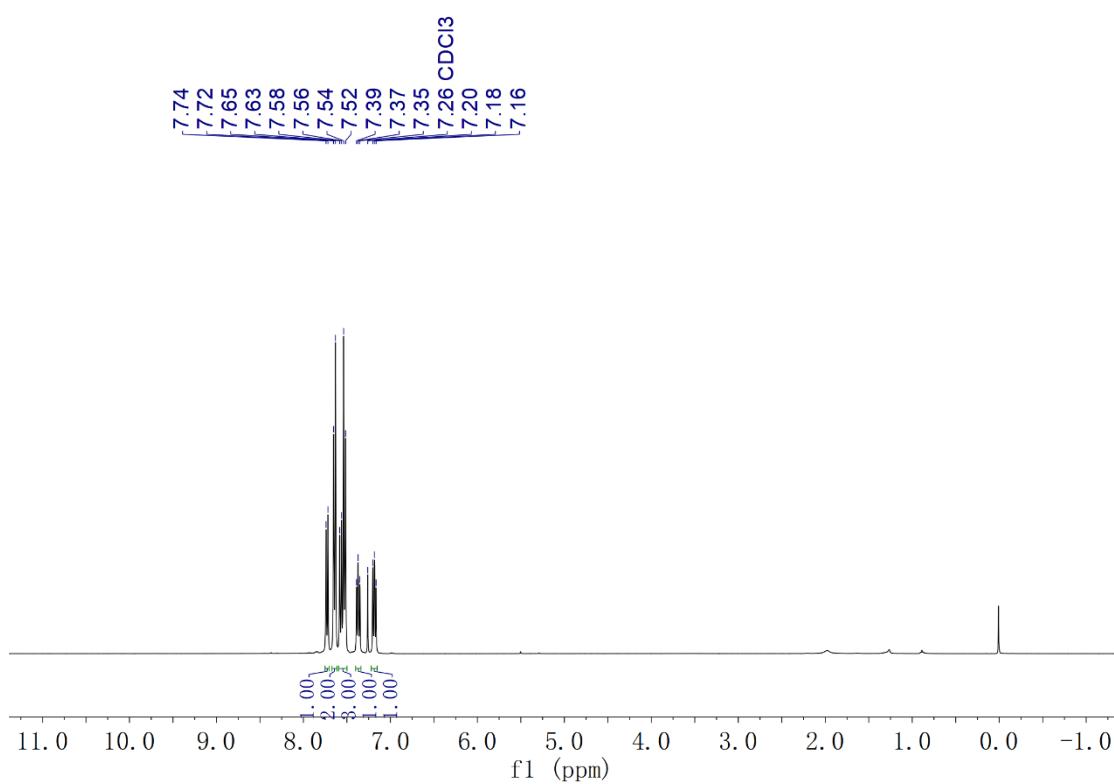
**2d  $^{13}\text{C-NMR}$**



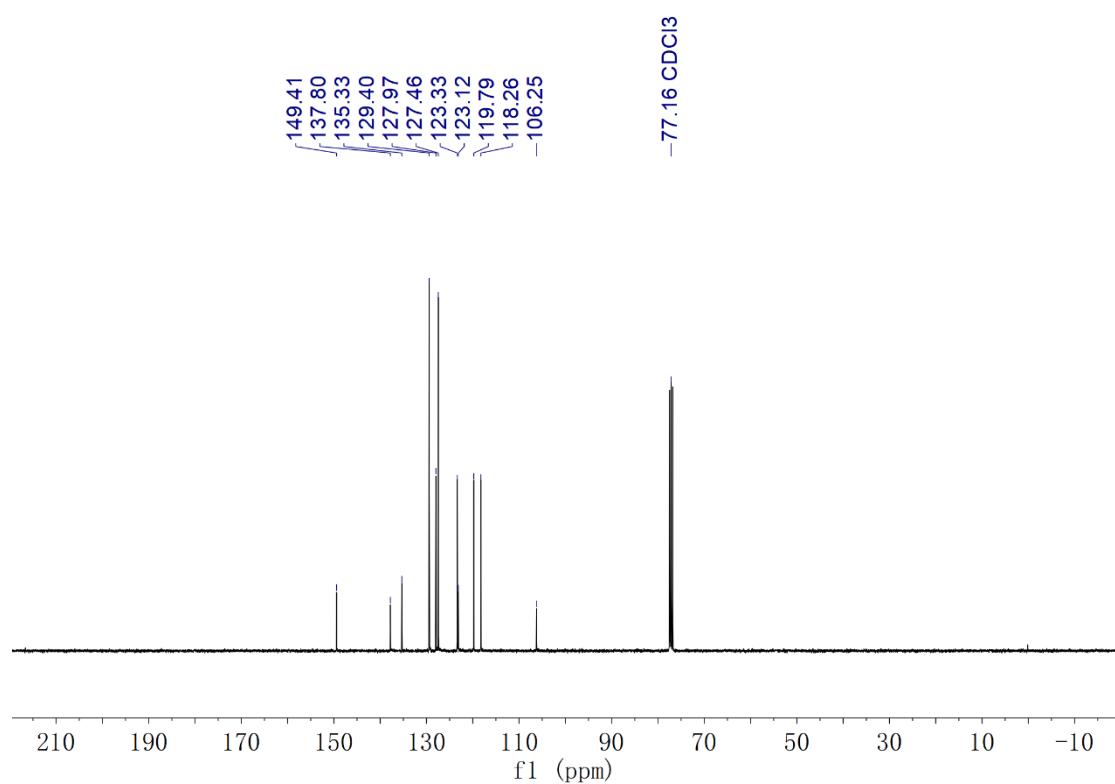
## 2d $^{19}\text{F}$ -NMR



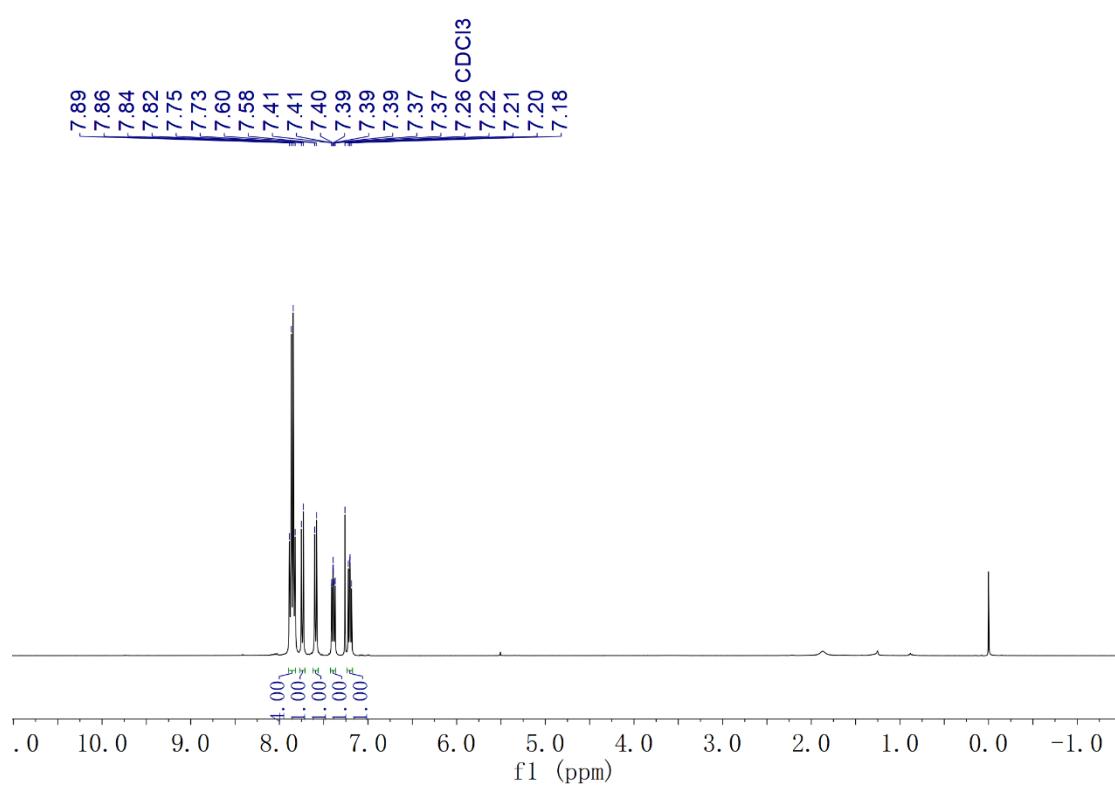
## 2e $^1\text{H-NMR}$



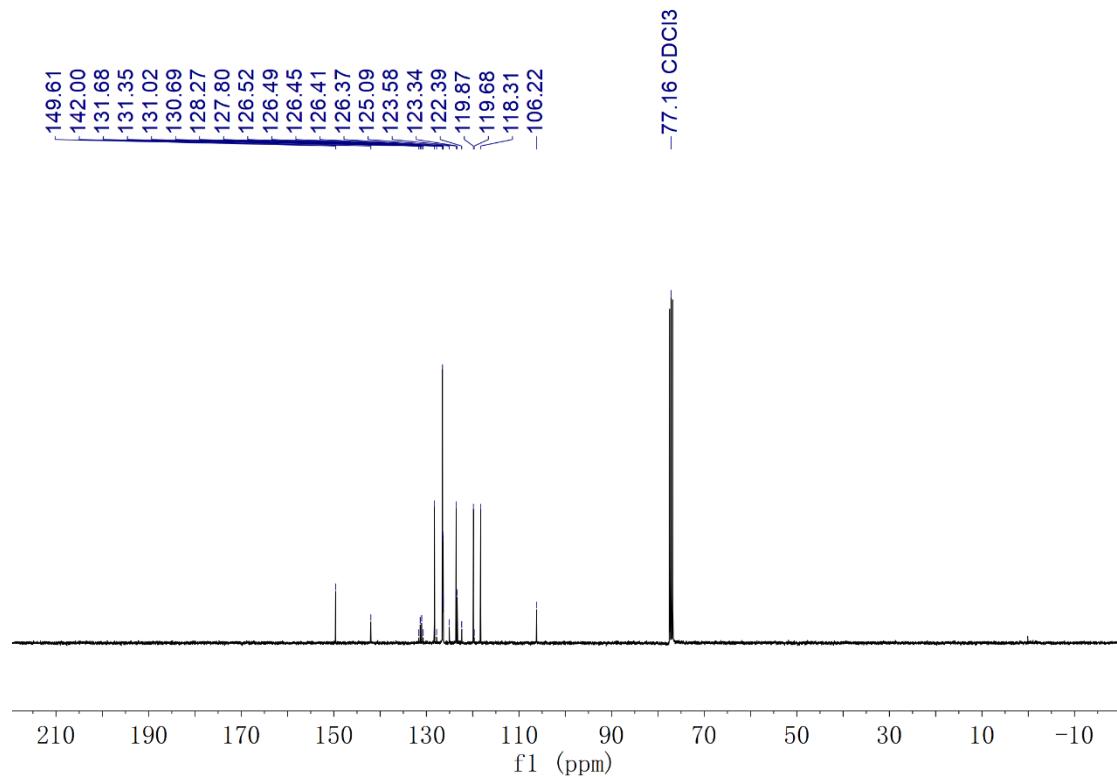
**2e  $^{13}\text{C}$ -NMR**



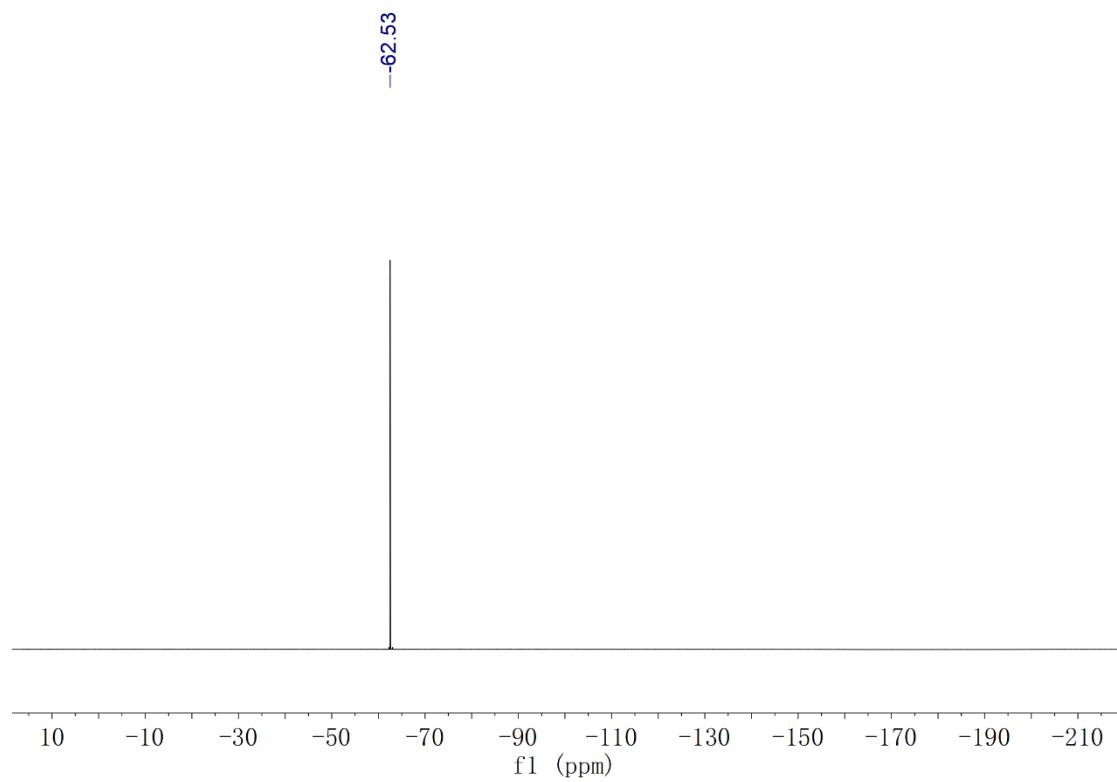
**2f  $^1\text{H}$ -NMR**



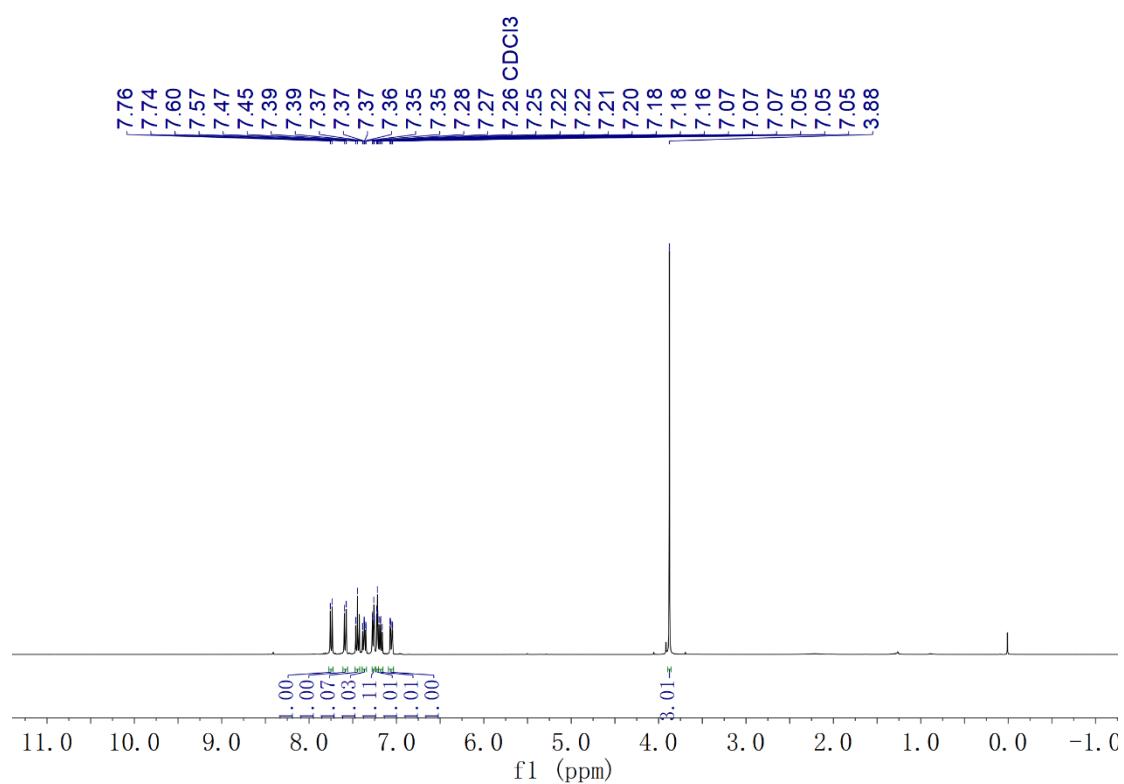
**2f  $^{13}\text{C}$ -NMR**



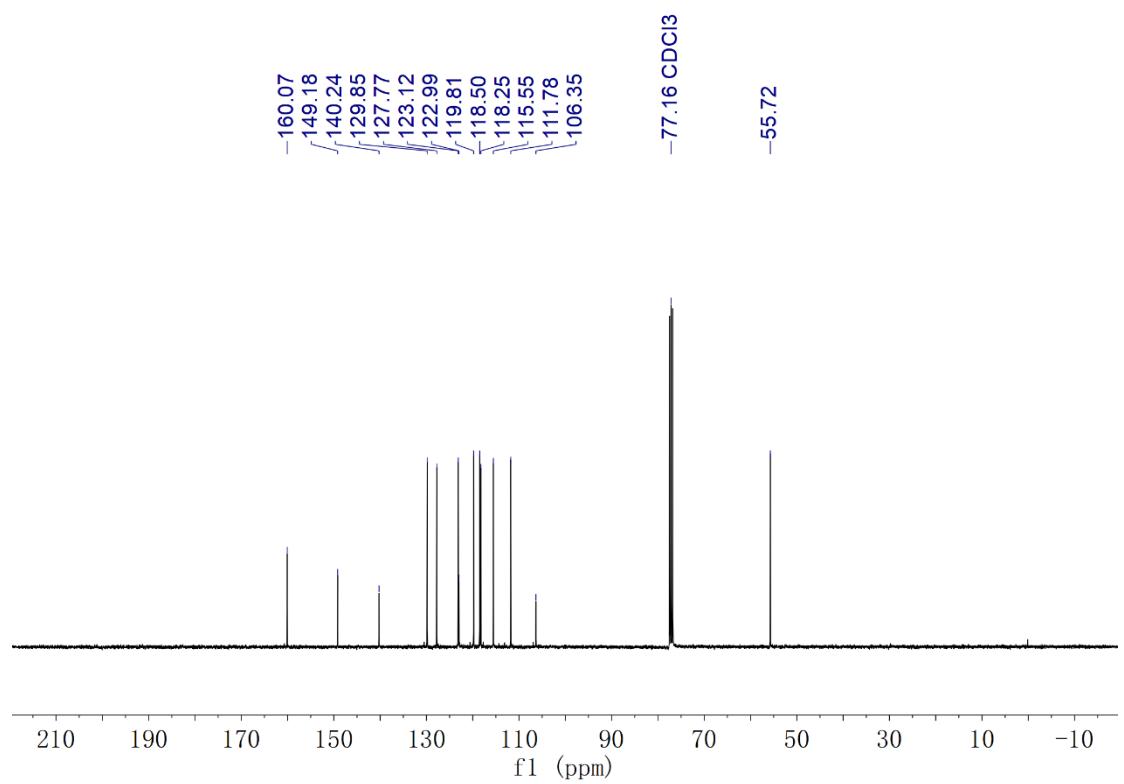
**2f  $^{19}\text{F}$ -NMR**



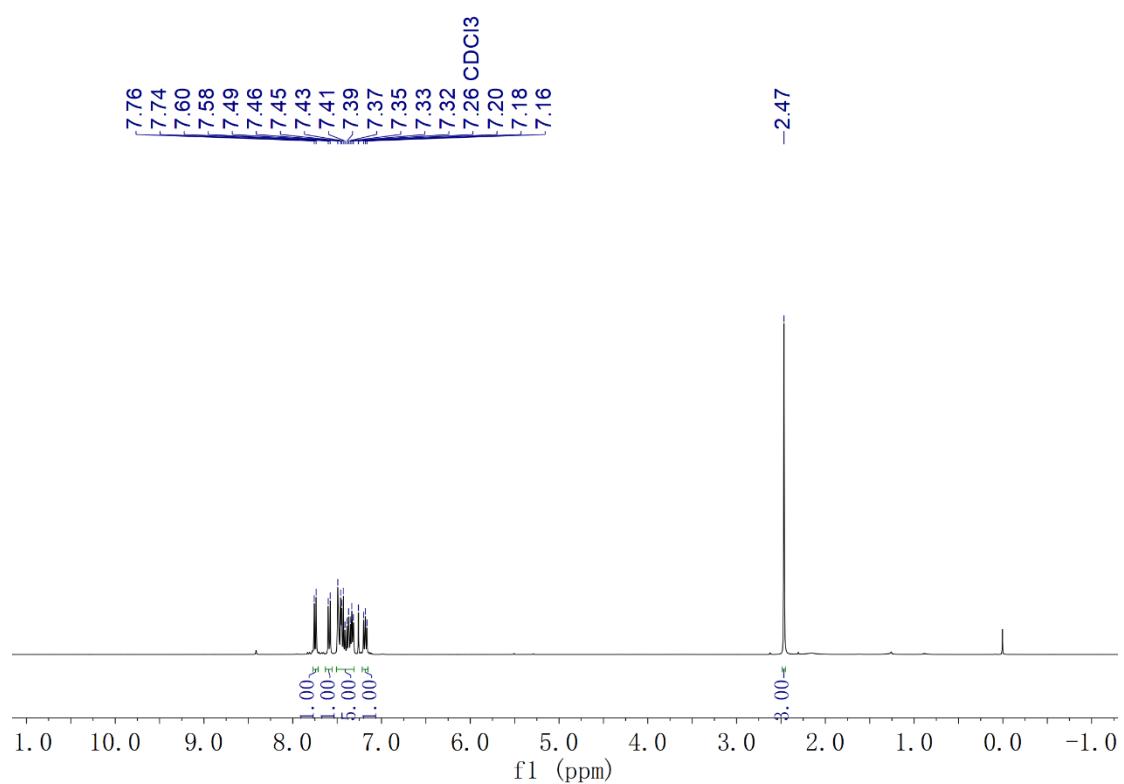
**2g  $^1\text{H-NMR}$**



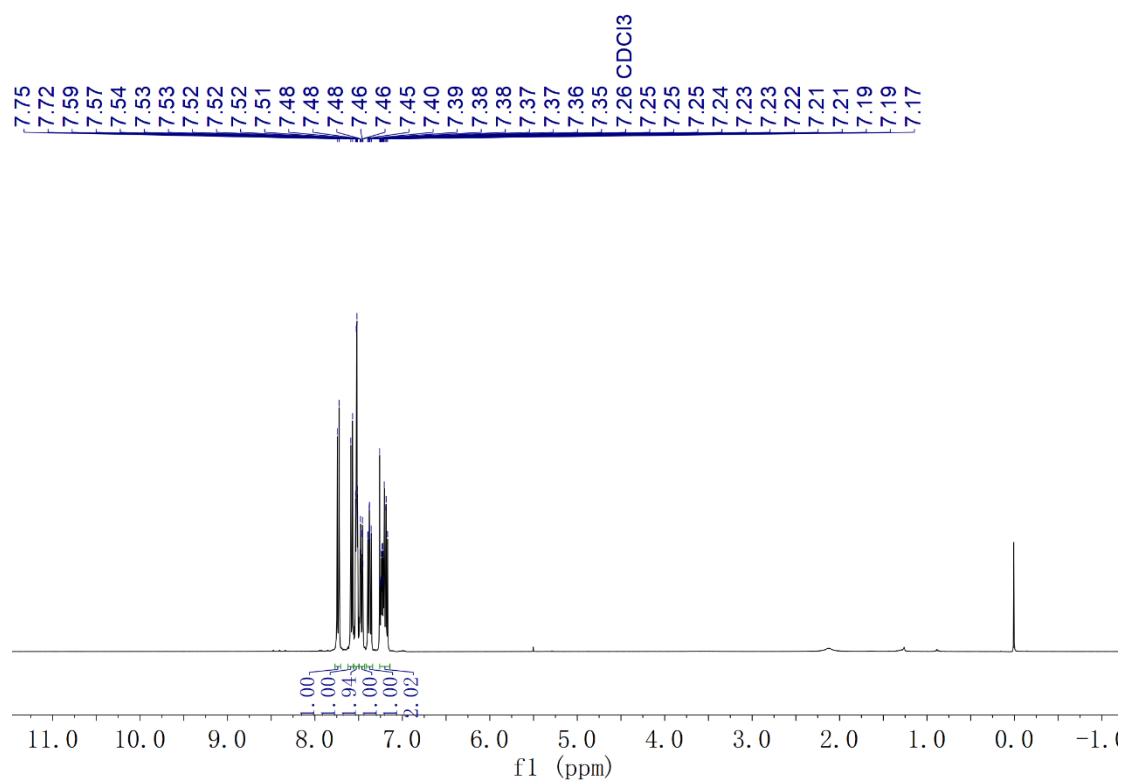
**2g  $^{13}\text{C-NMR}$**



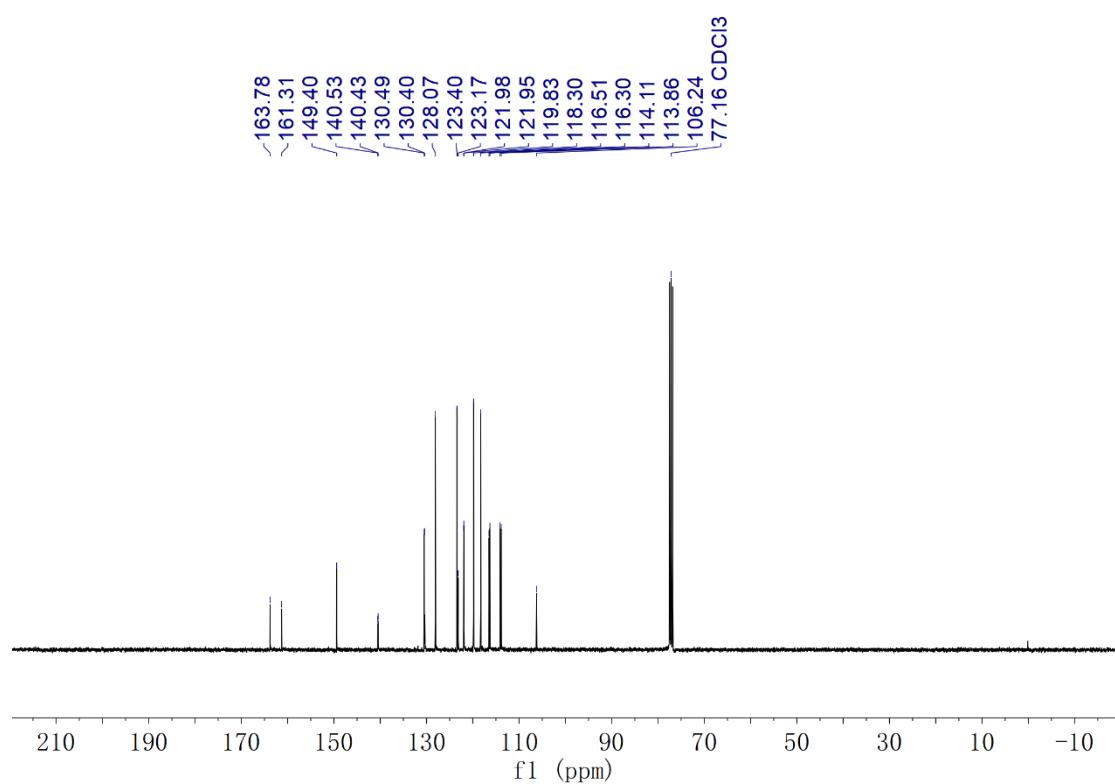
**2h  $^1\text{H-NMR}$**



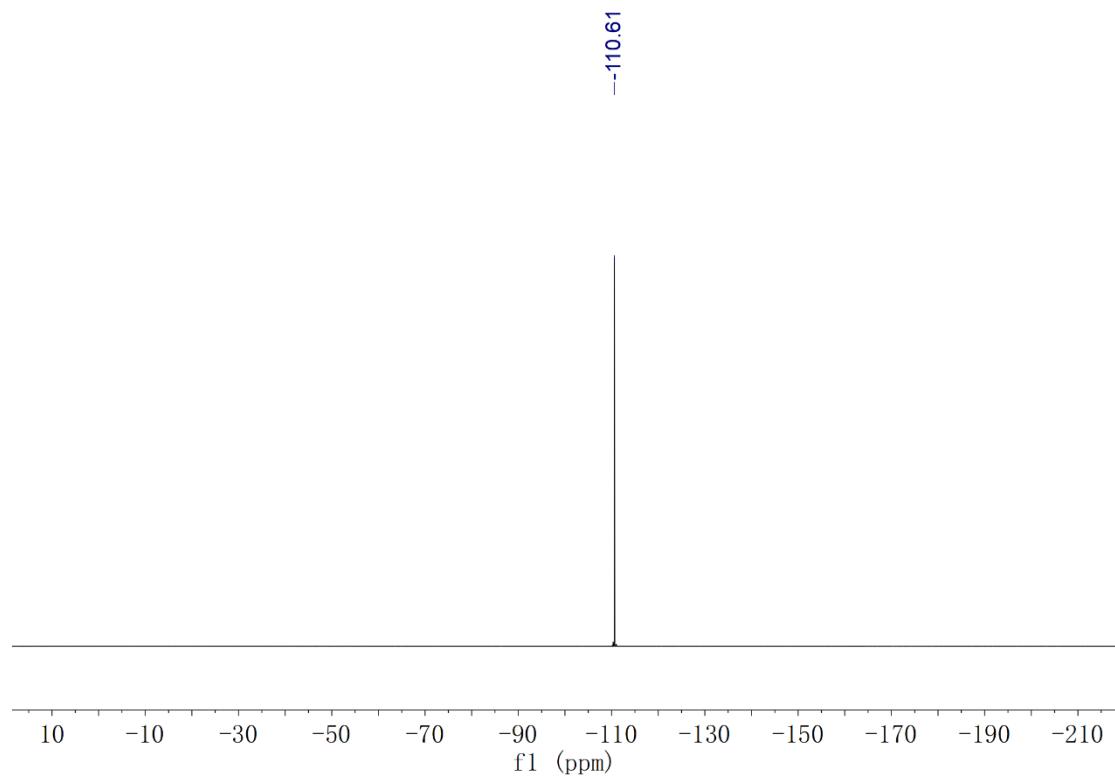
**2i  $^1\text{H-NMR}$**



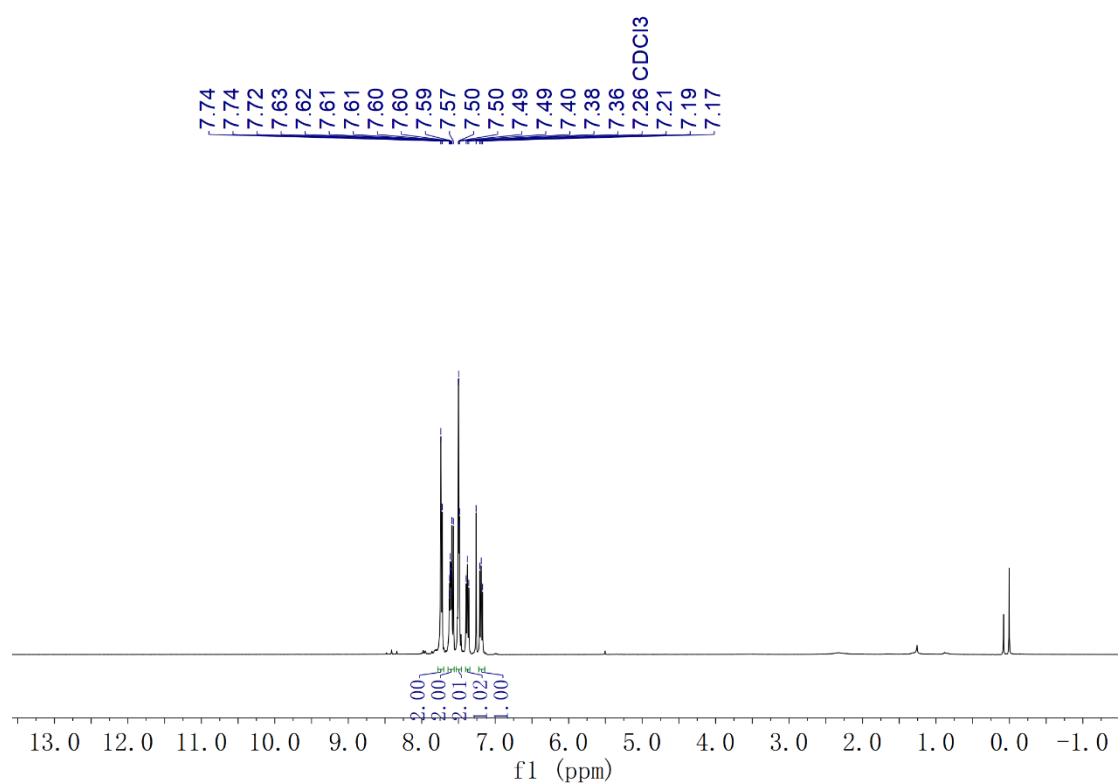
**2i  $^{13}\text{C}$ -NMR**



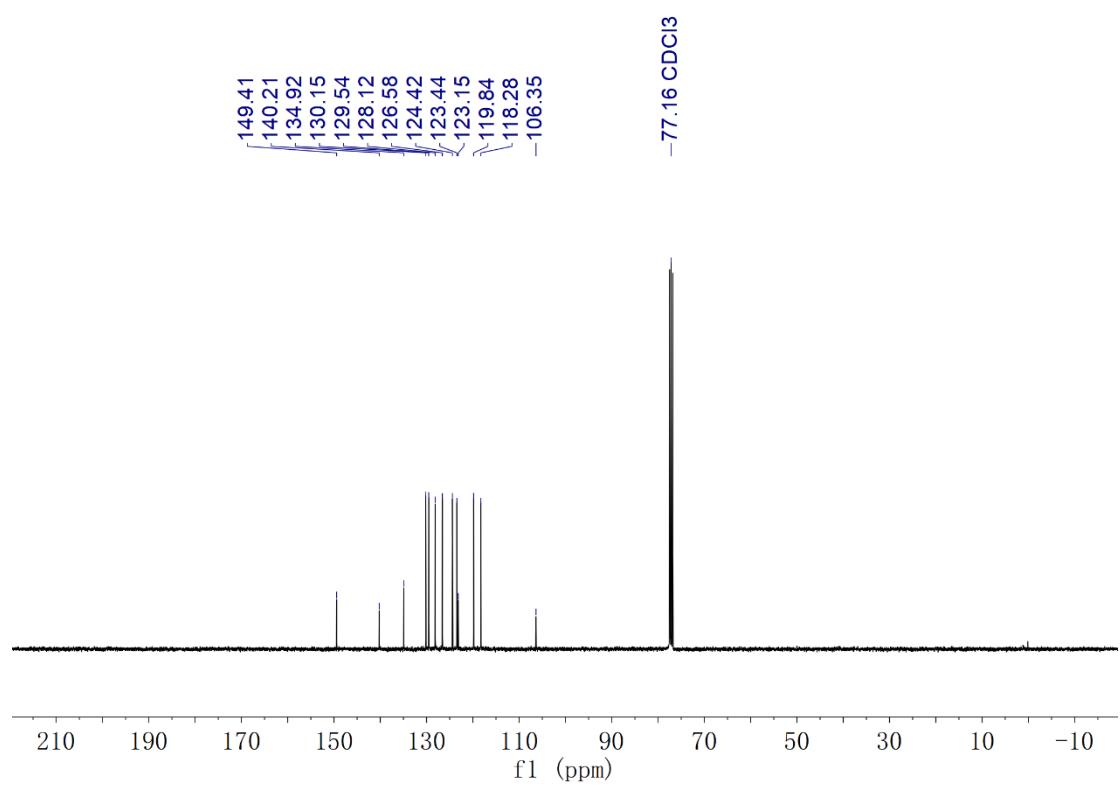
**2i  $^{19}\text{F}$ -NMR**



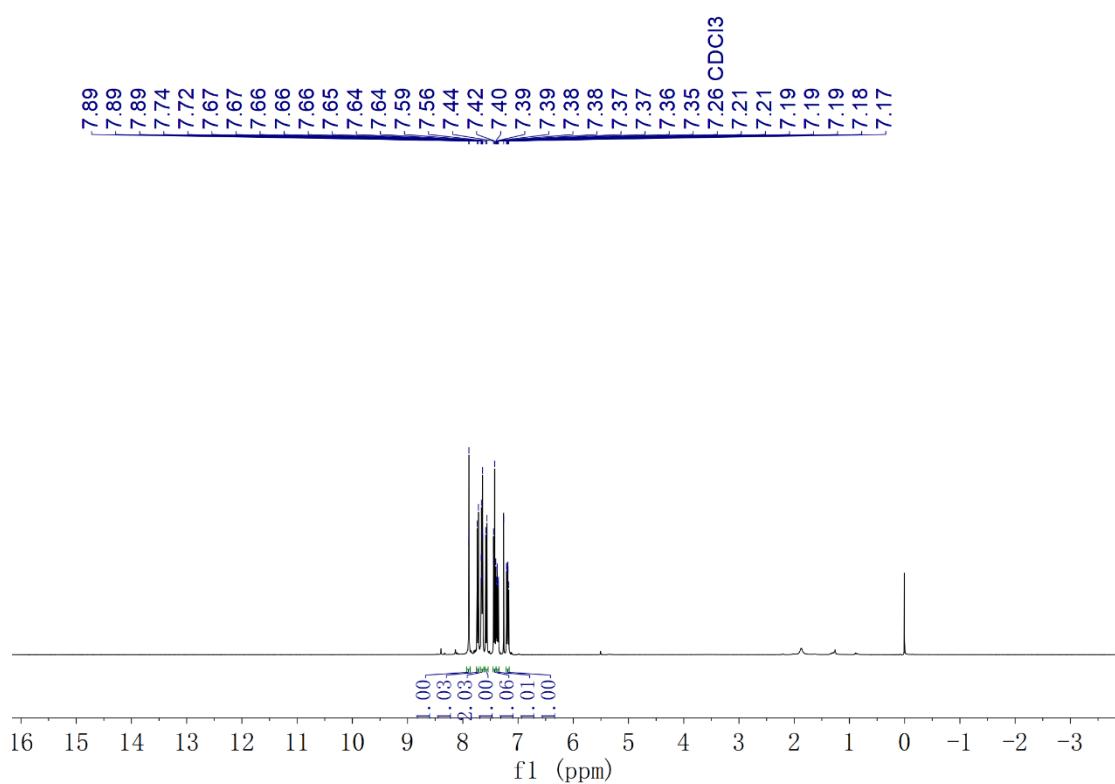
**2j  $^1\text{H-NMR}$**



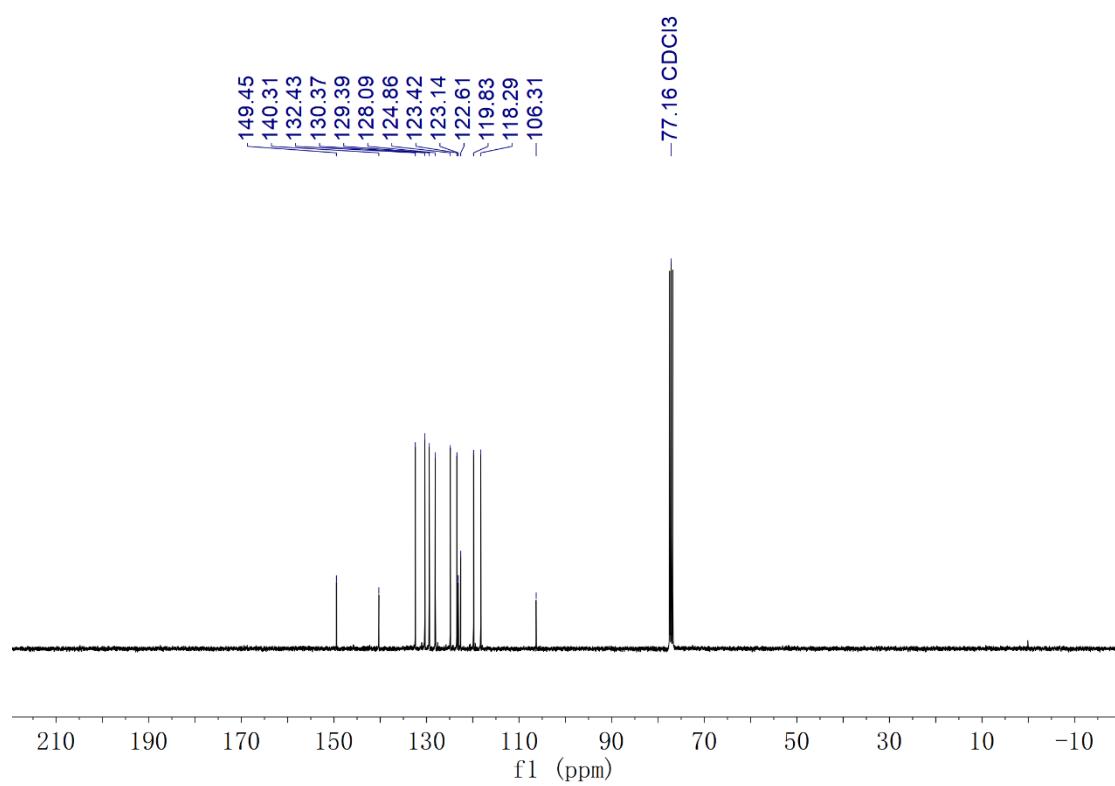
**2j  $^{13}\text{C-NMR}$**



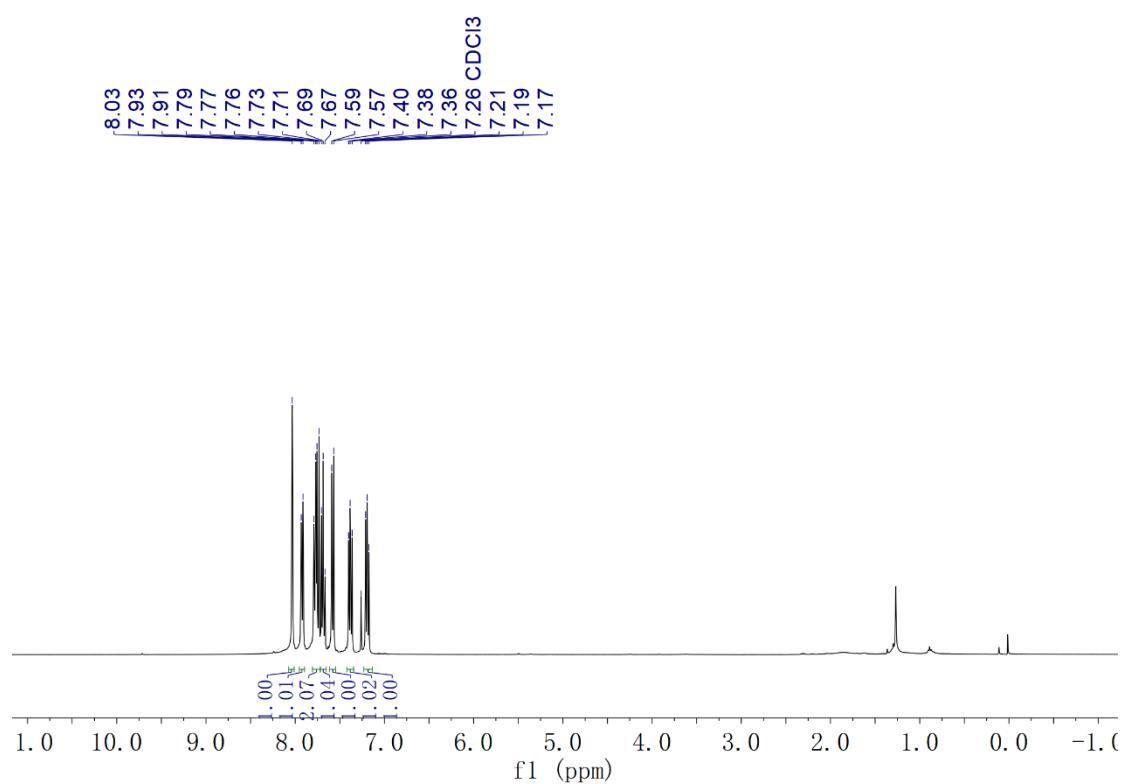
**2k  $^1\text{H}$ -NMR**



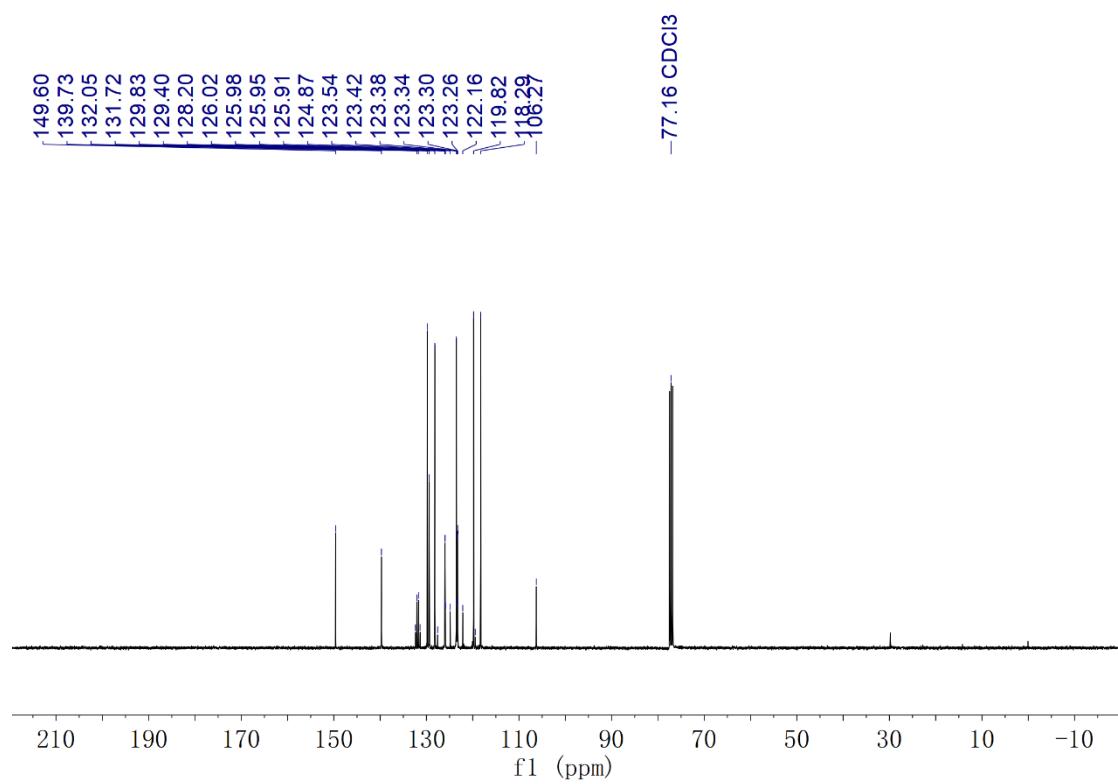
**2k  $^{13}\text{C}$ -NMR**



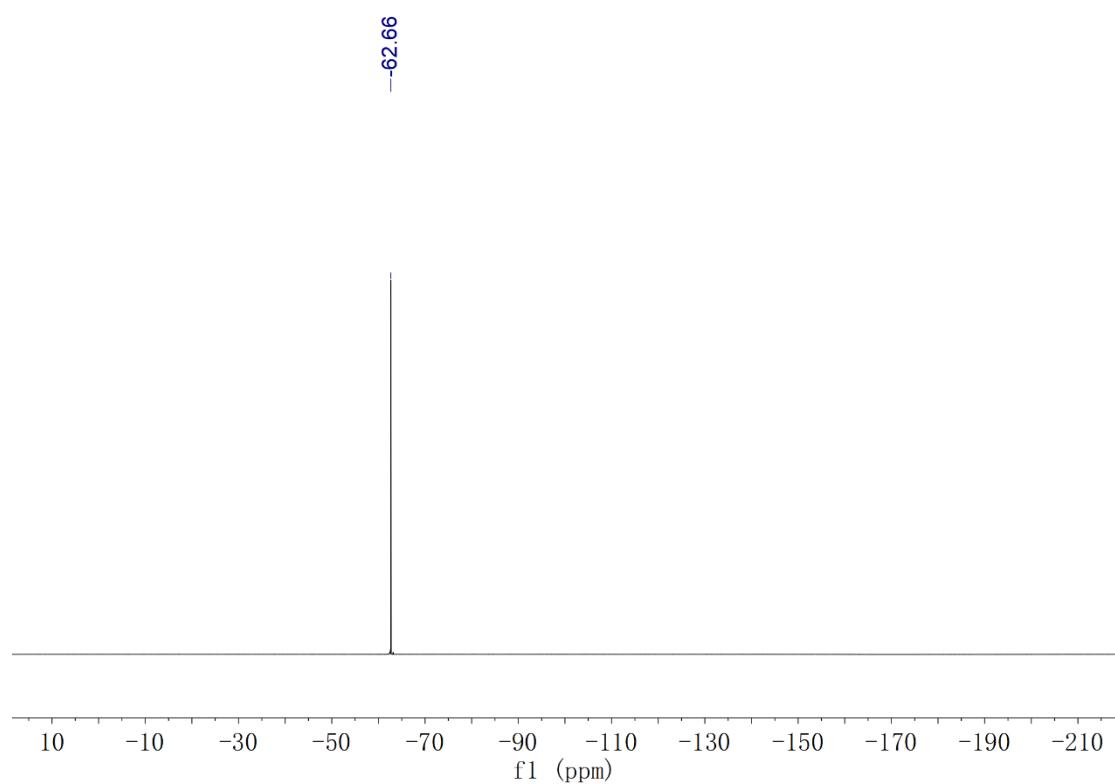
**2l  $^1\text{H}$ -NMR**



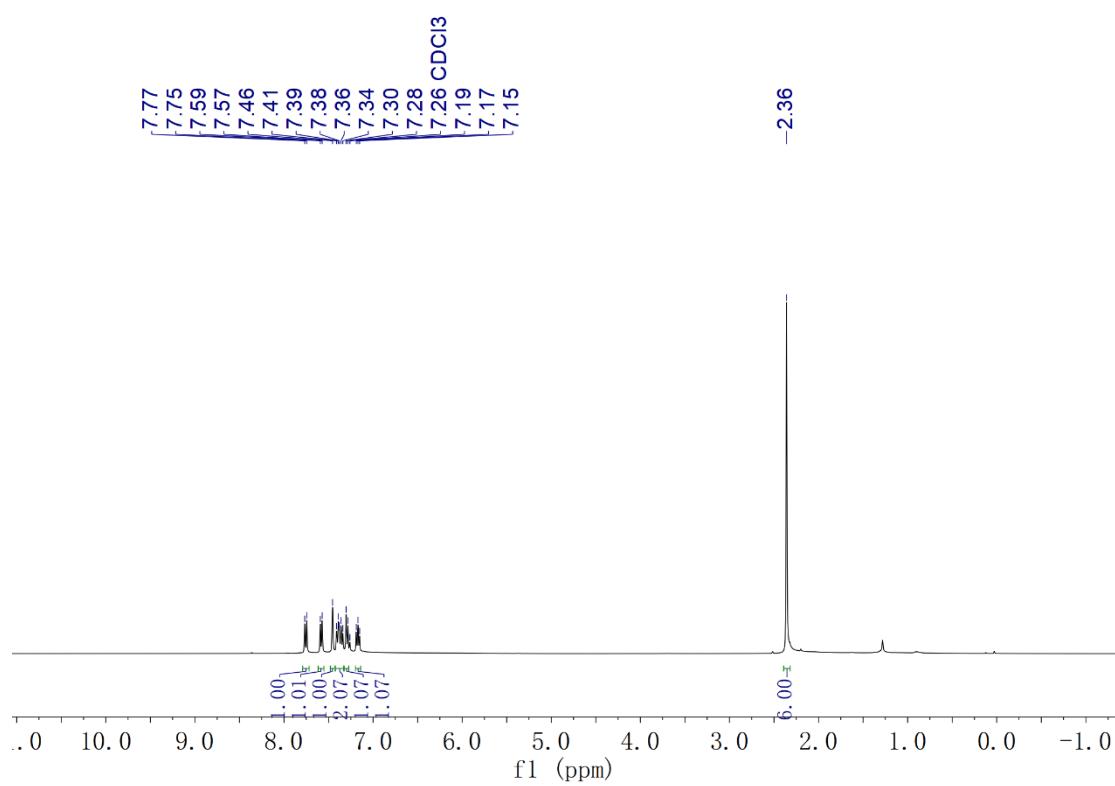
**2l  $^{13}\text{C}$ -NMR**



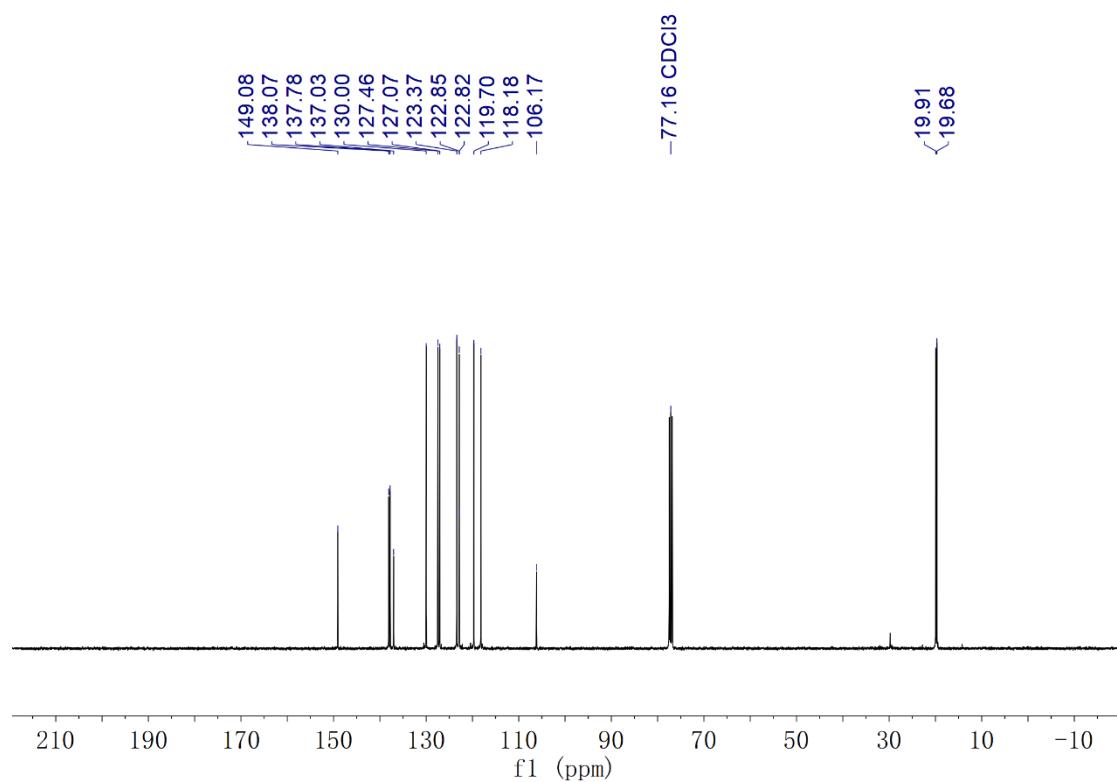
**2l  $^{19}\text{F-NMR}$**



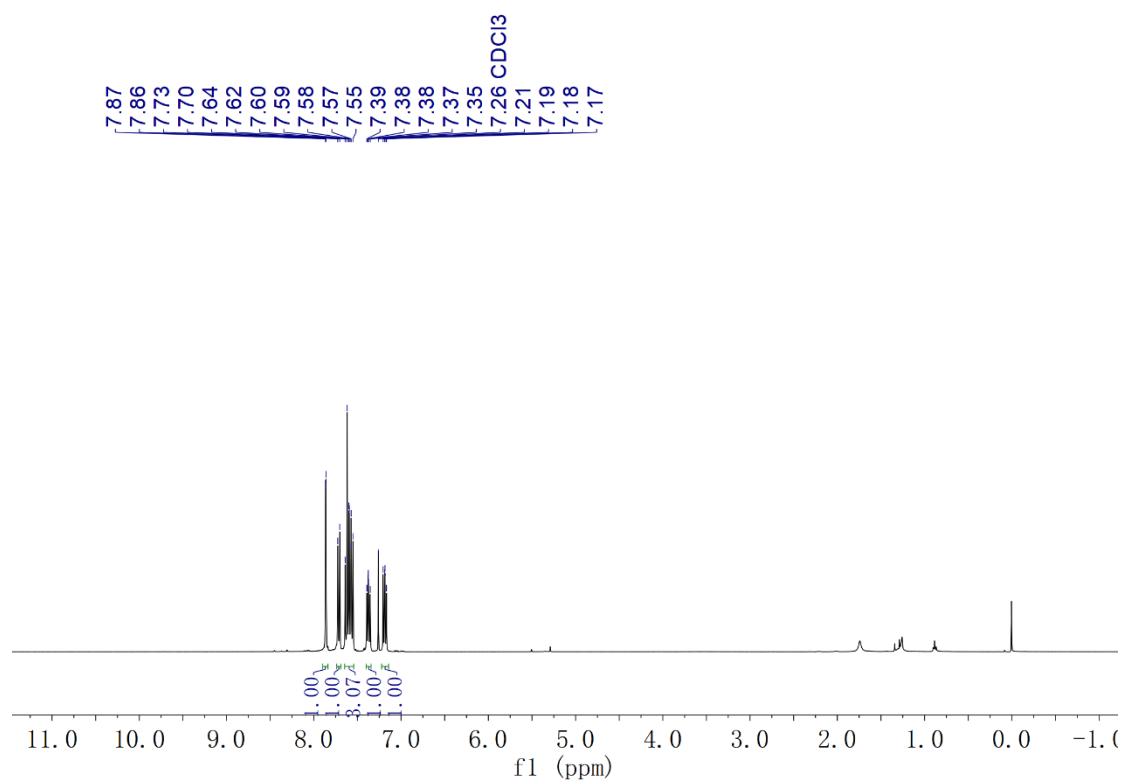
**2m  $^1\text{H-NMR}$**



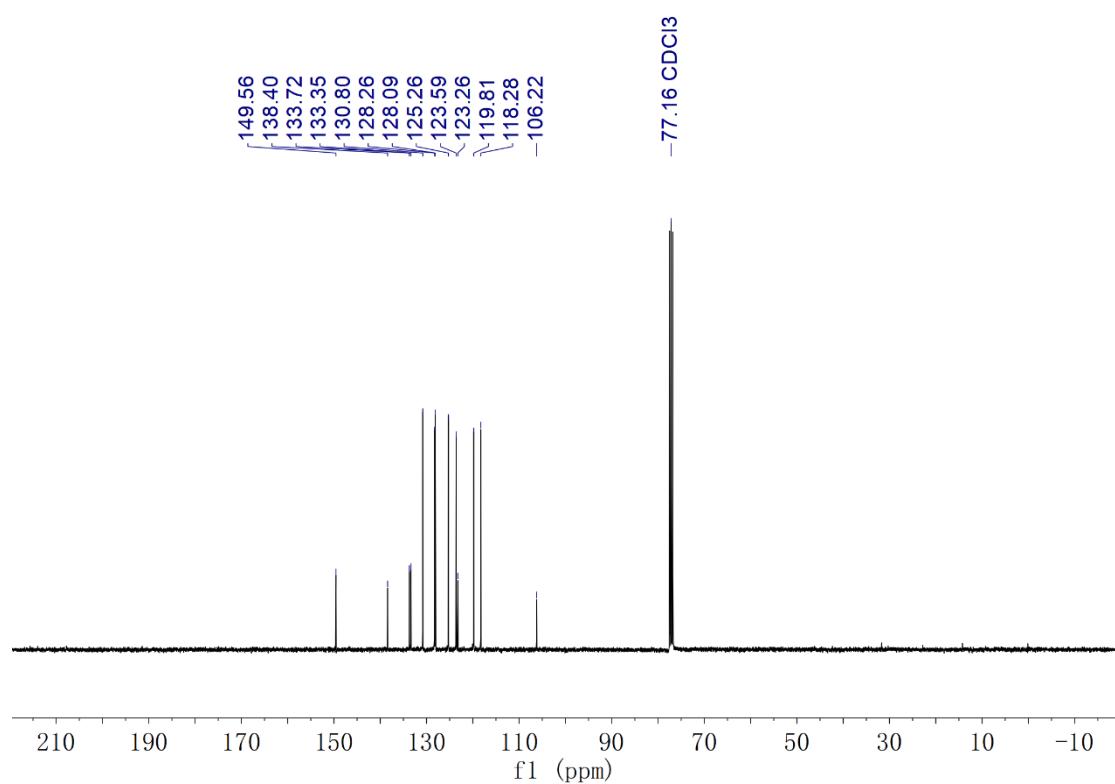
**2m  $^{13}\text{C-NMR}$**



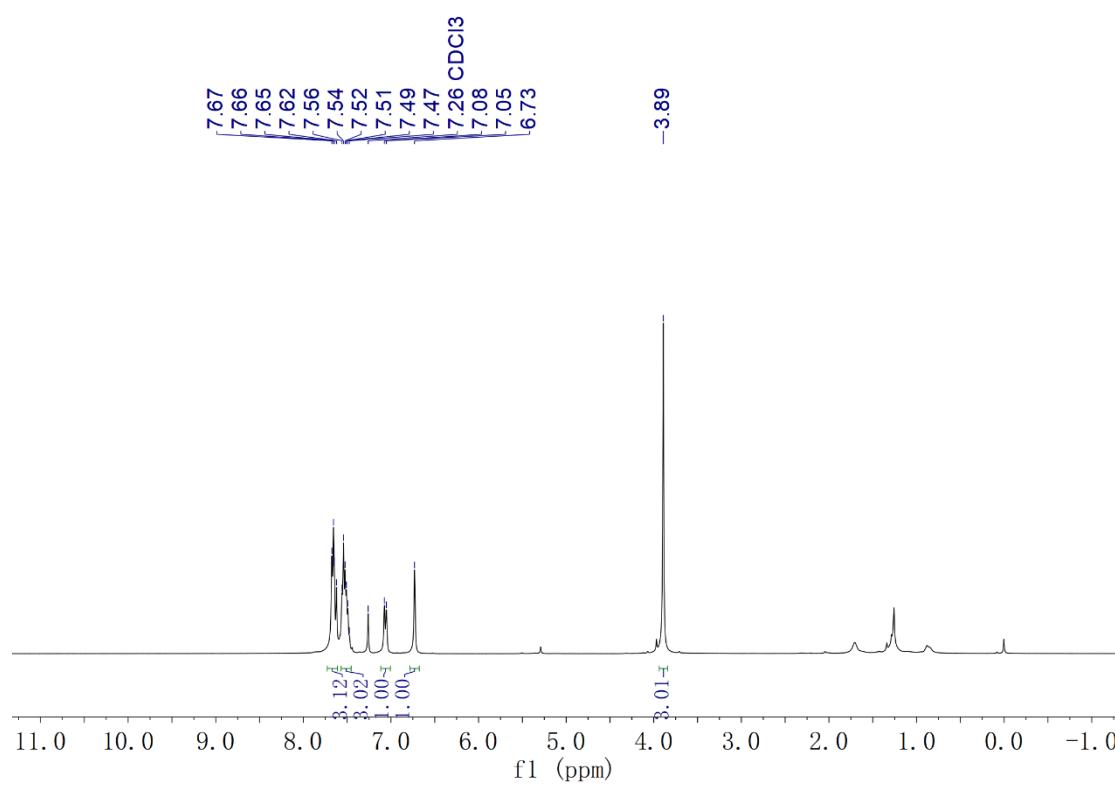
**2n  $^1\text{H-NMR}$**



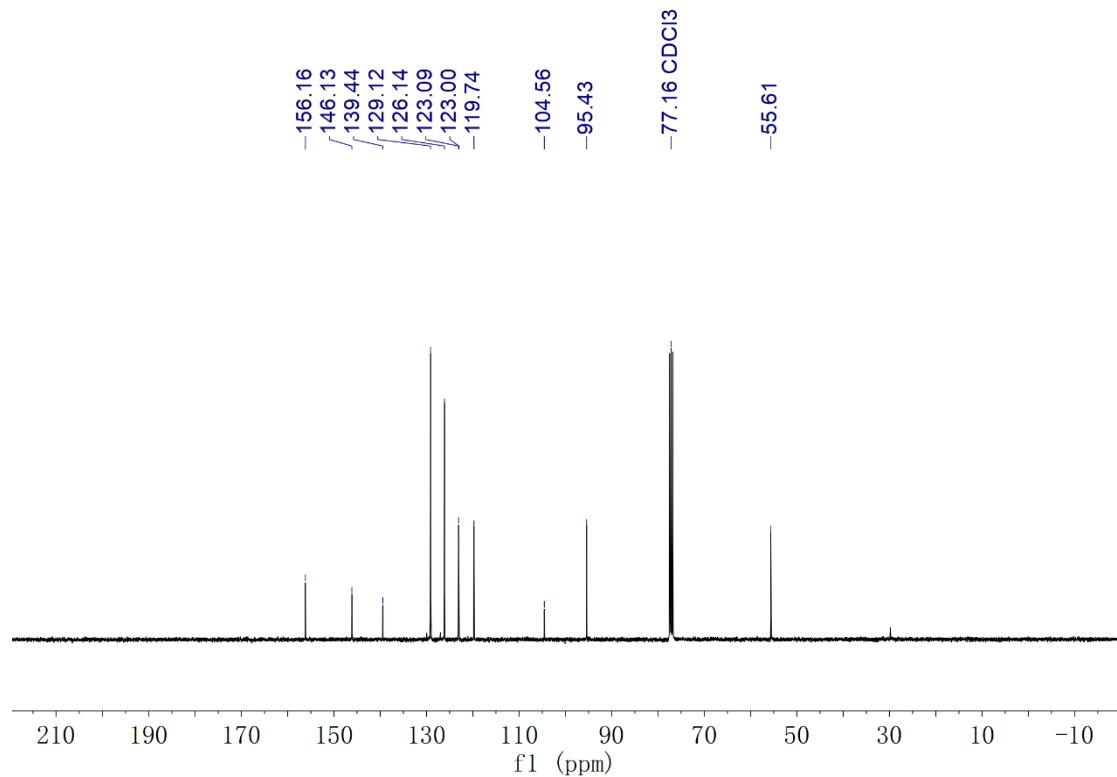
**2n  $^{13}\text{C}$ -NMR**



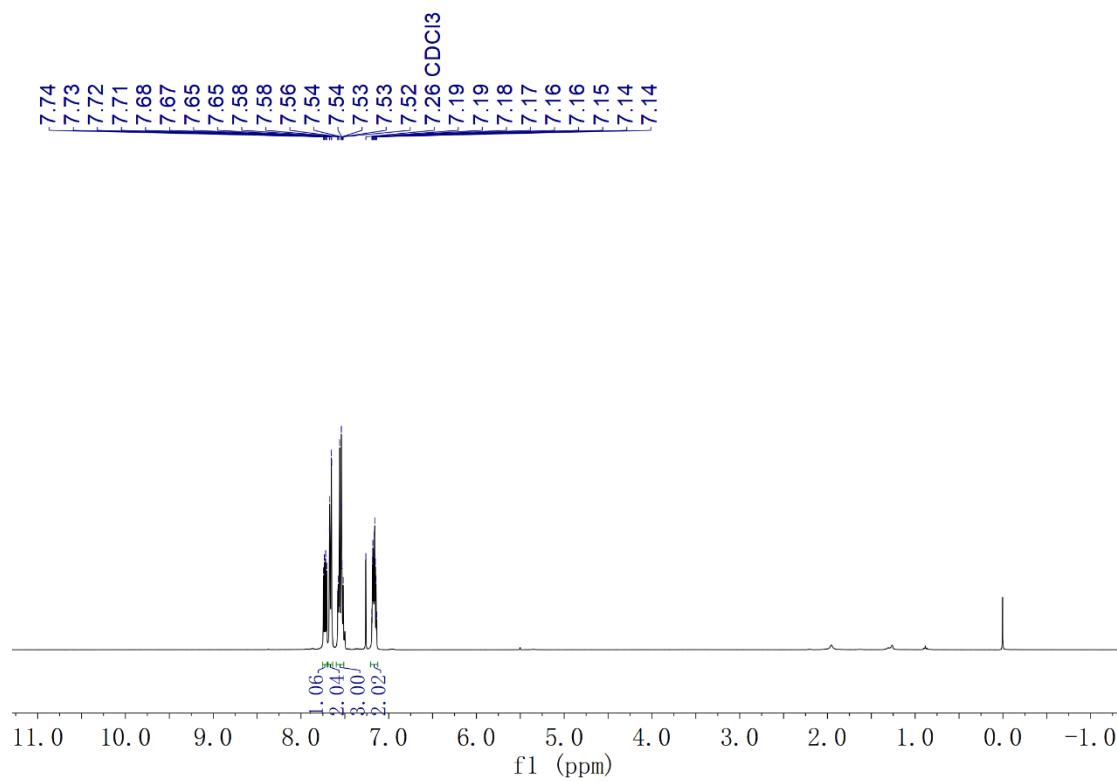
**2o  $^1\text{H}$ -NMR**



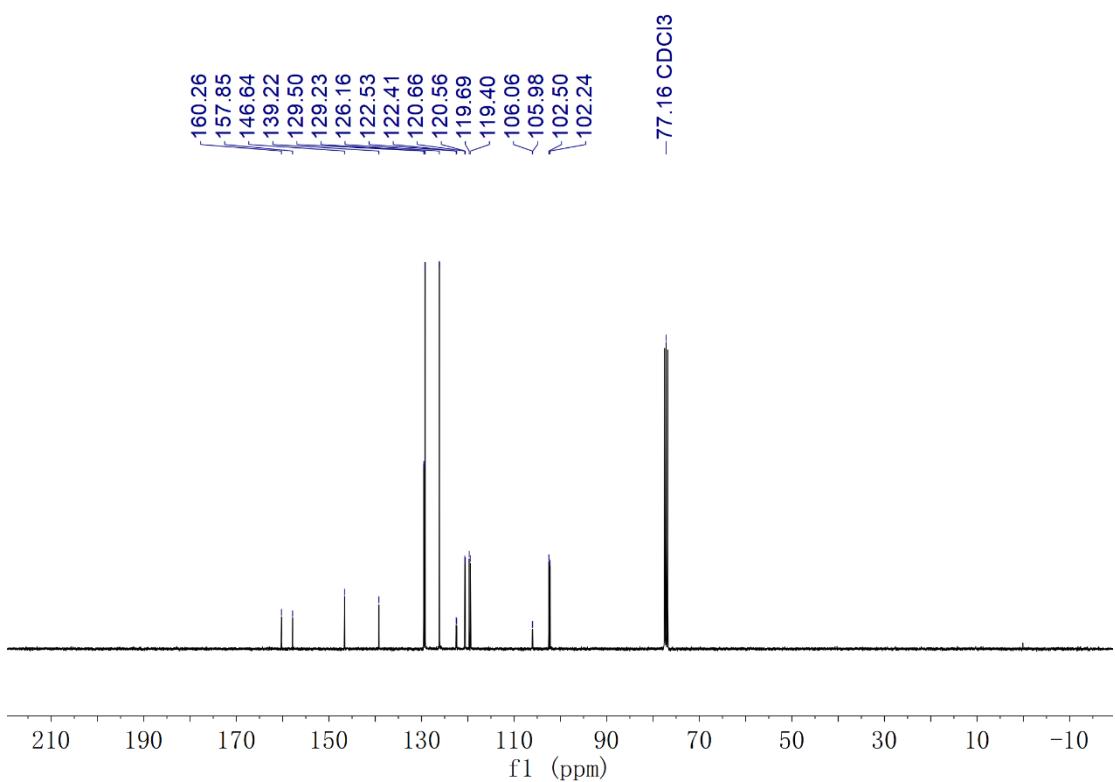
20 <sup>13</sup>C-NMR



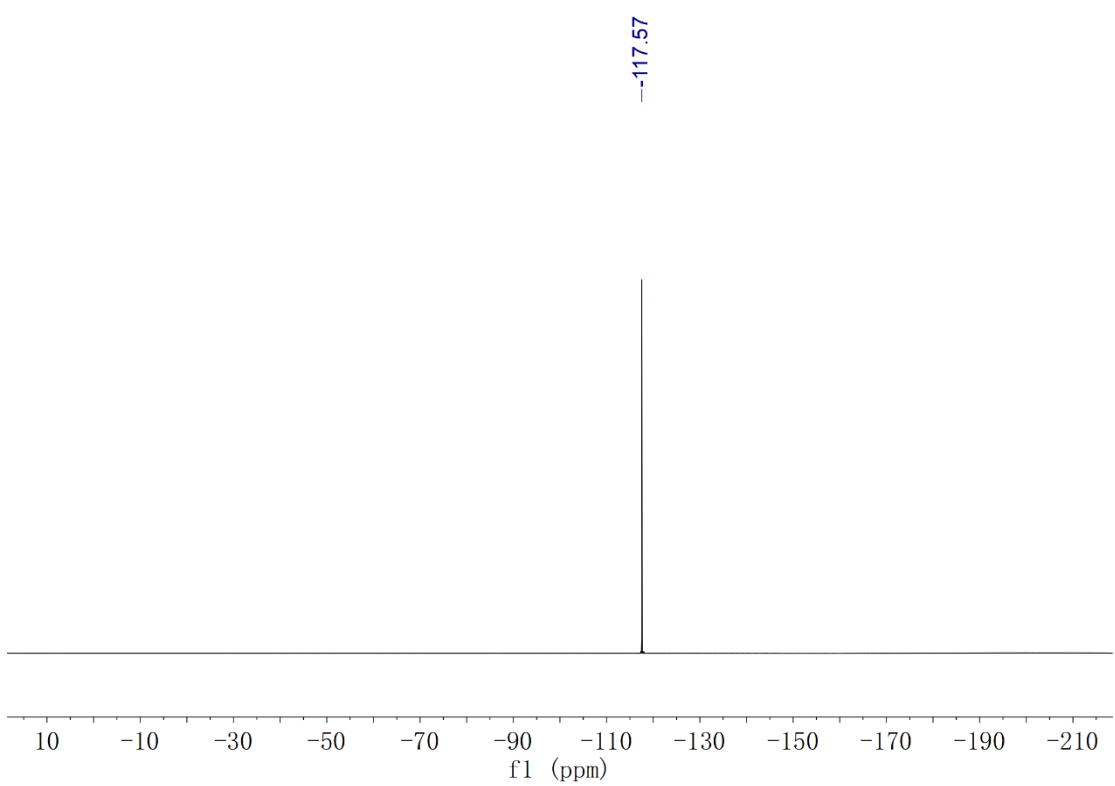
## 2p $^1$ H-NMR



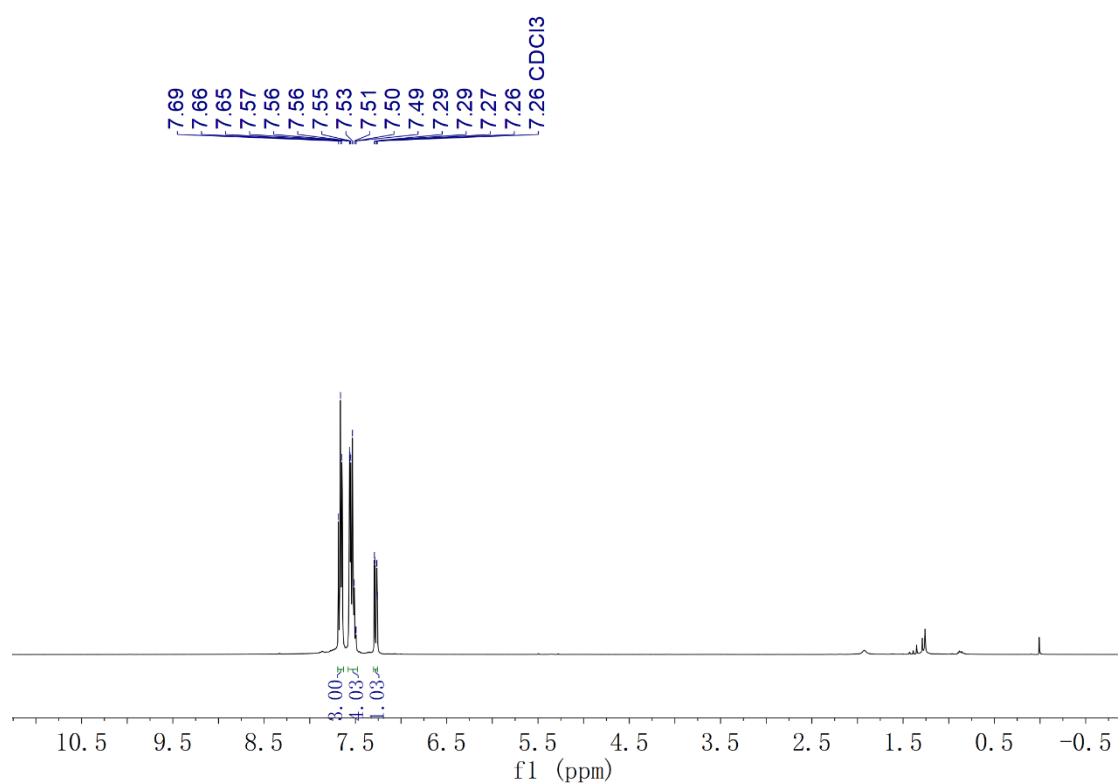
**2p  $^{13}\text{C}$ -NMR**



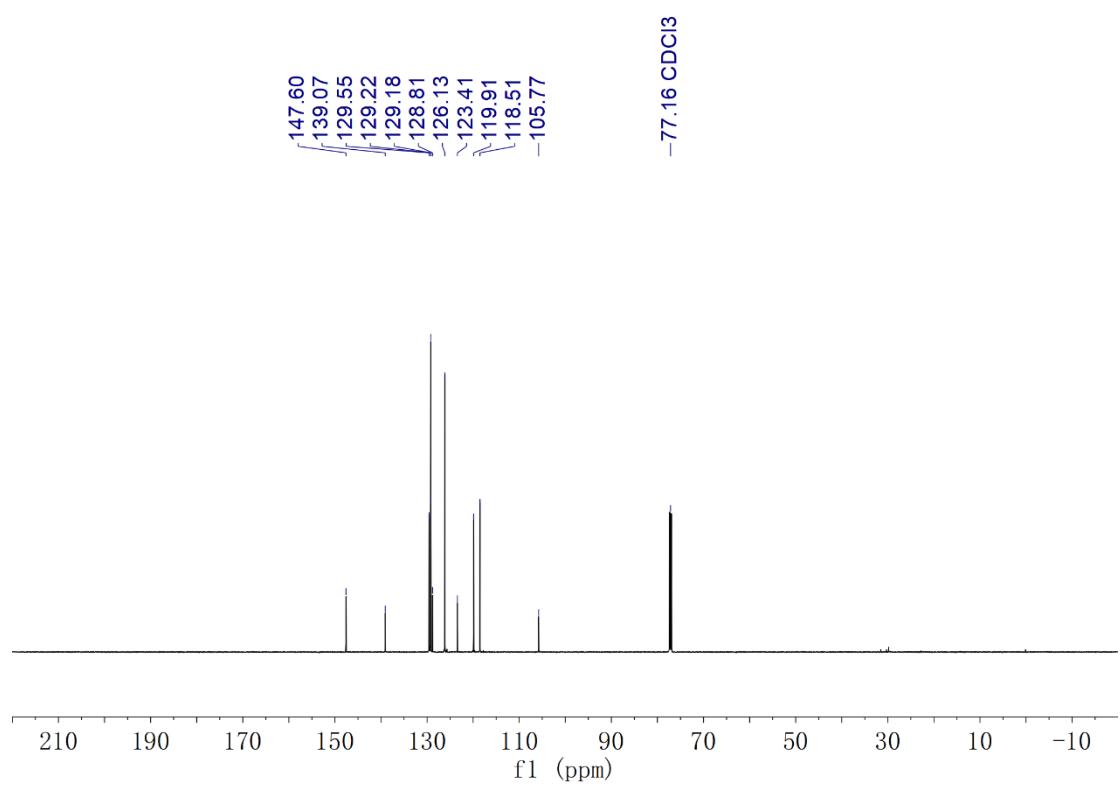
**2p  $^{19}\text{F}$ -NMR**



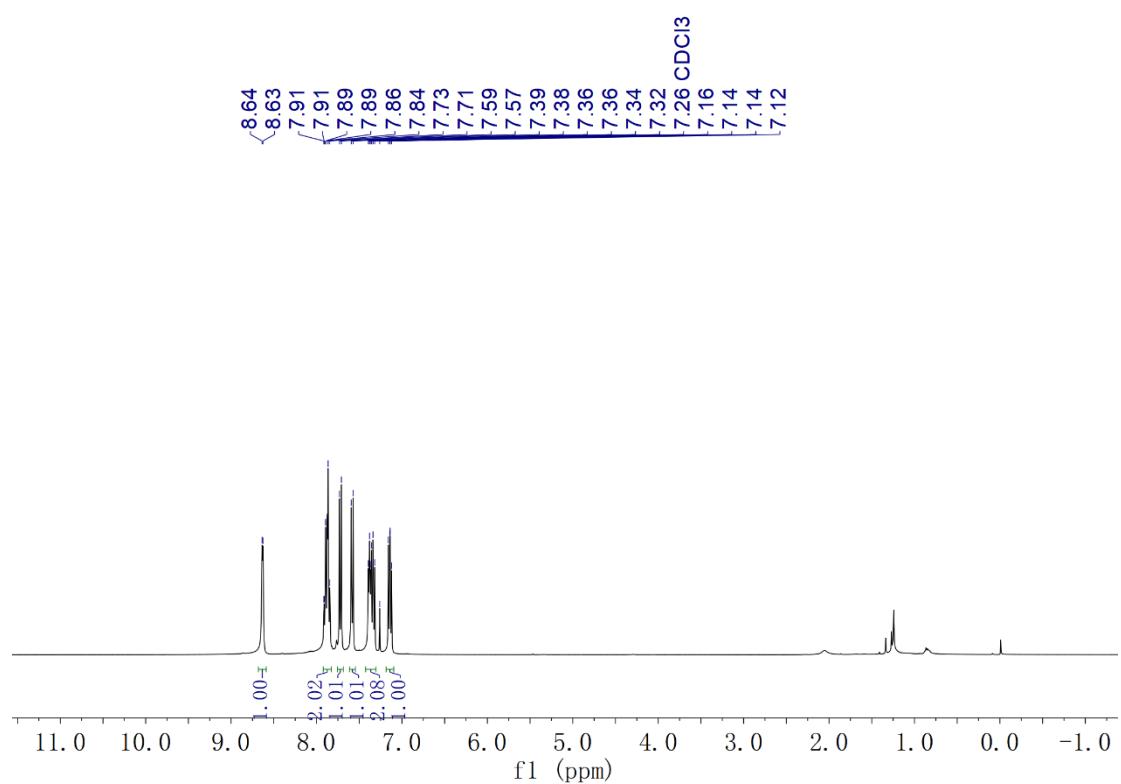
**2q  $^1\text{H-NMR}$**



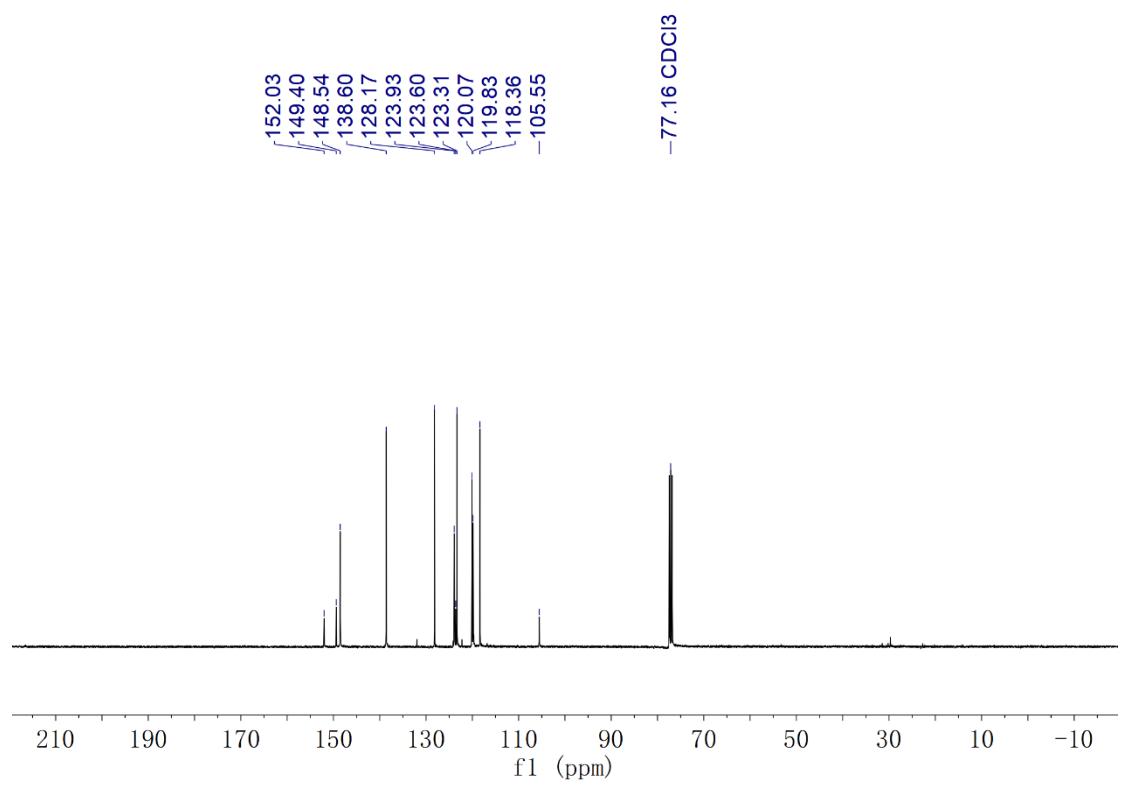
**2q  $^{13}\text{C-NMR}$**



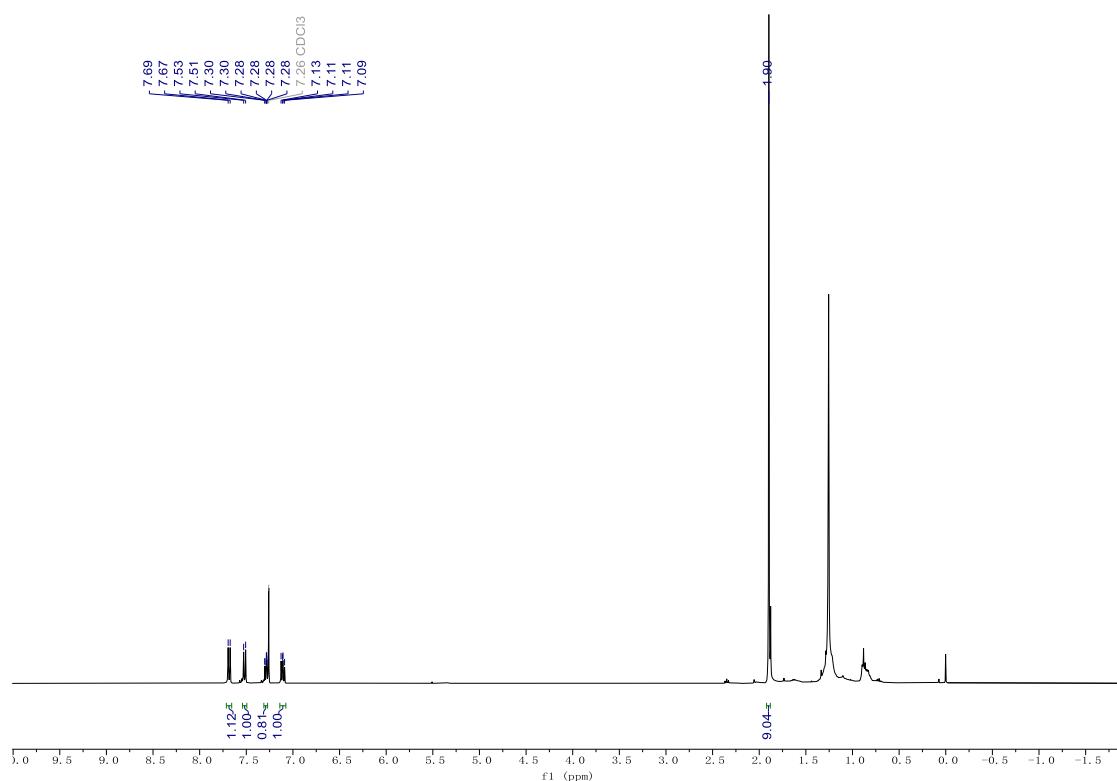
**2r  $^1\text{H}$ -NMR**



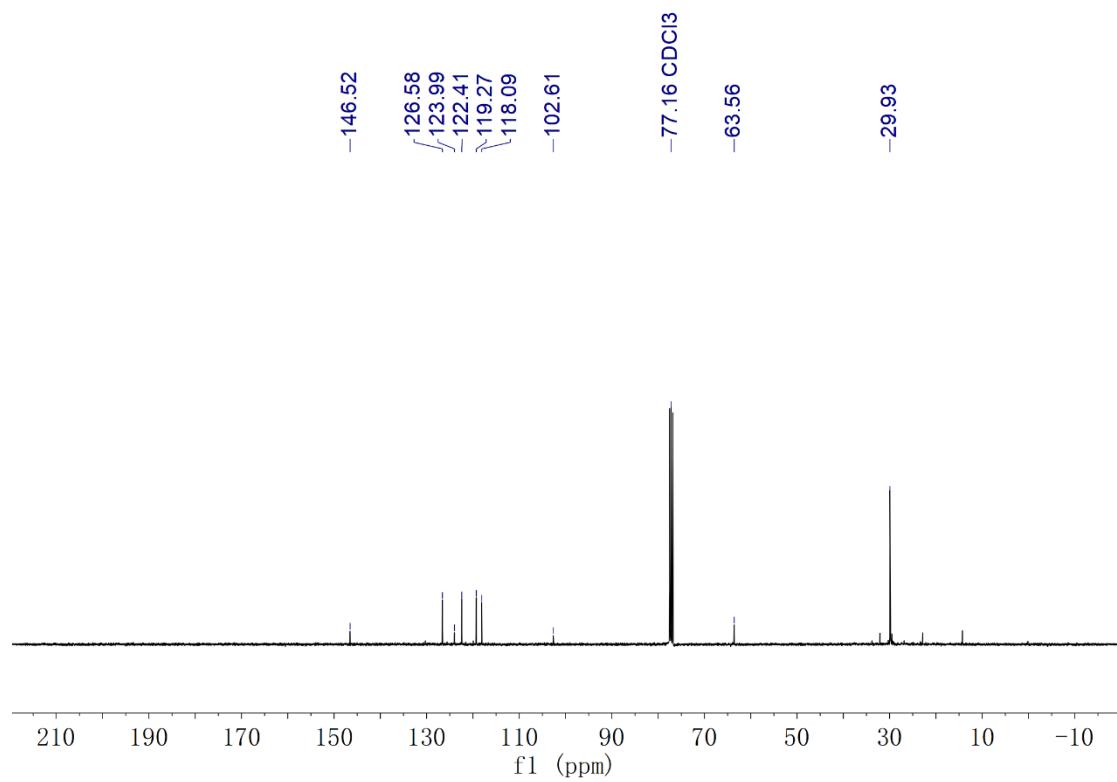
**2r  $^{13}\text{C}$ -NMR**



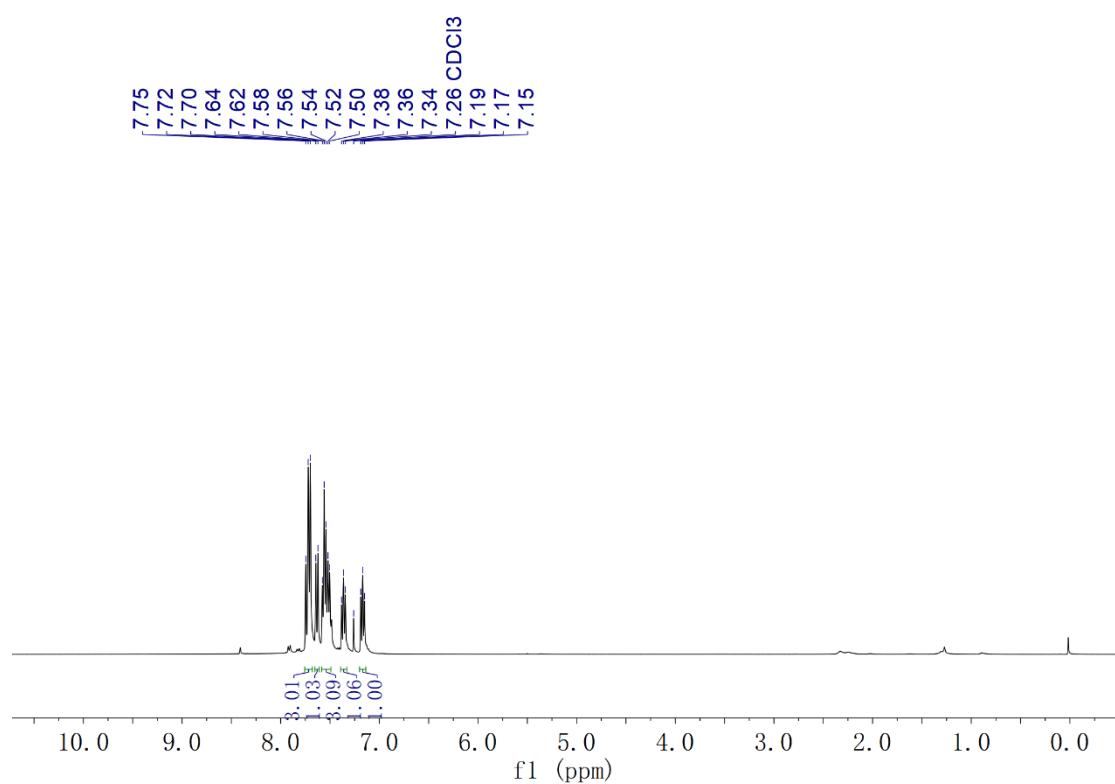
**2s  $^1\text{H-NMR}$**



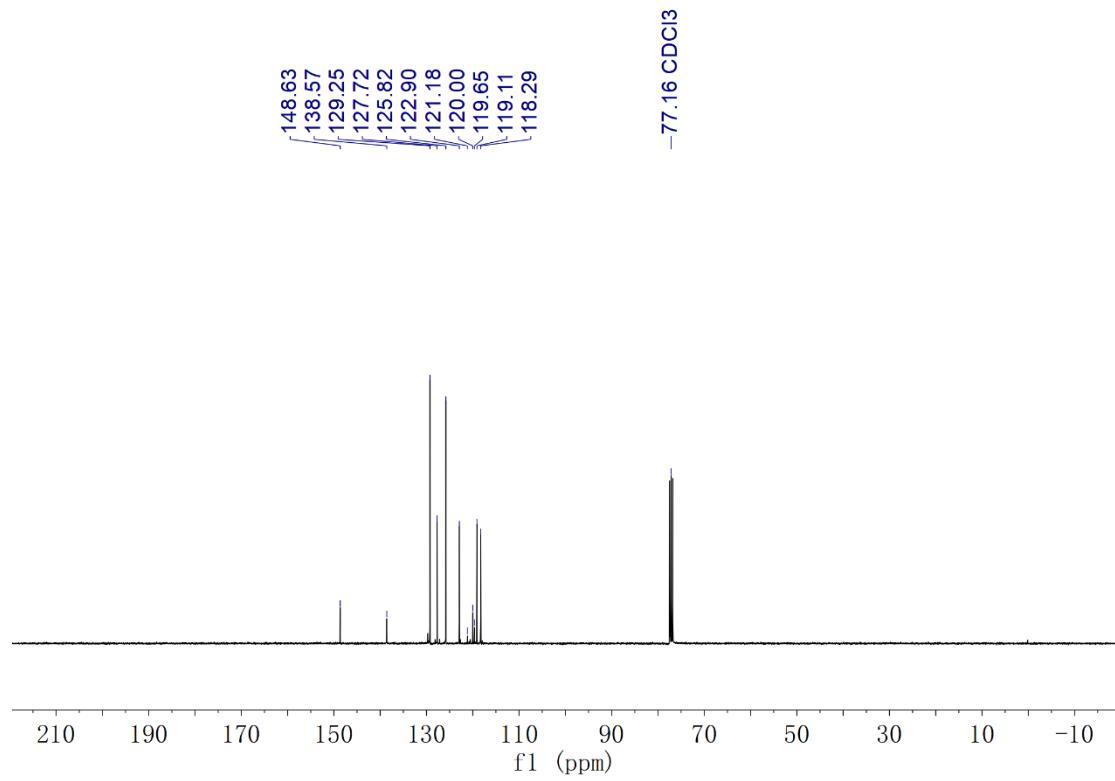
**2s  $^{13}\text{C-NMR}$**



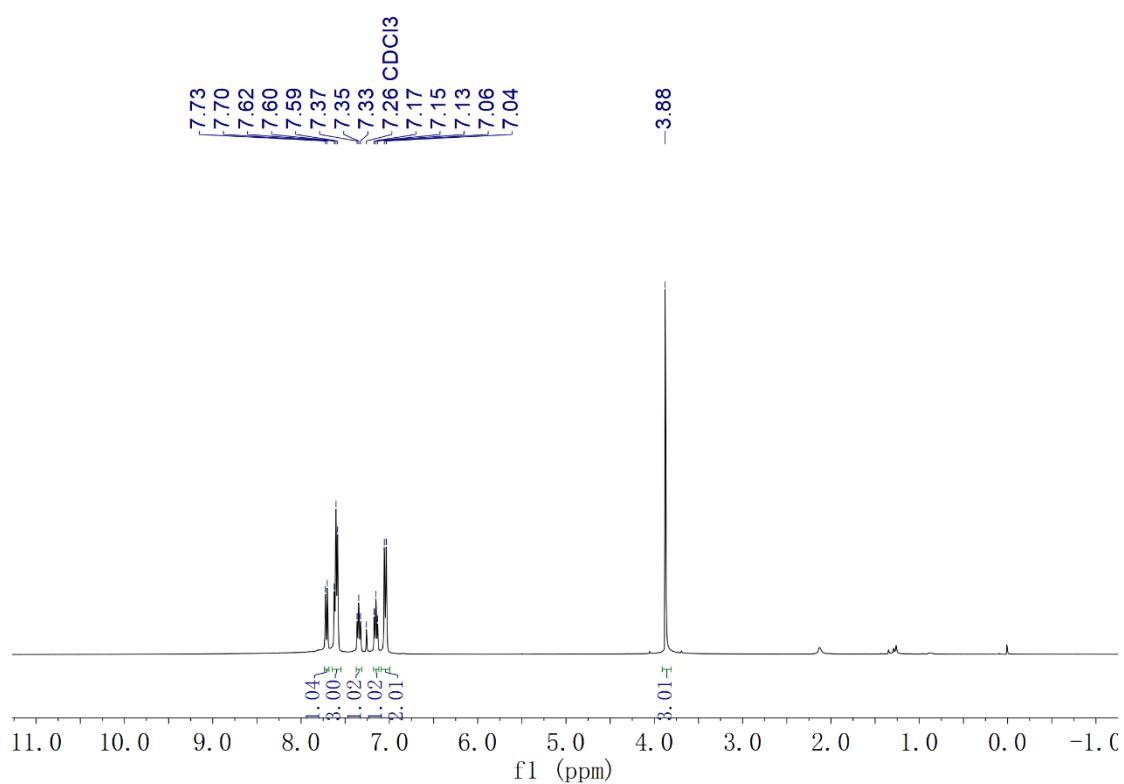
**5a  $^1\text{H-NMR}$**



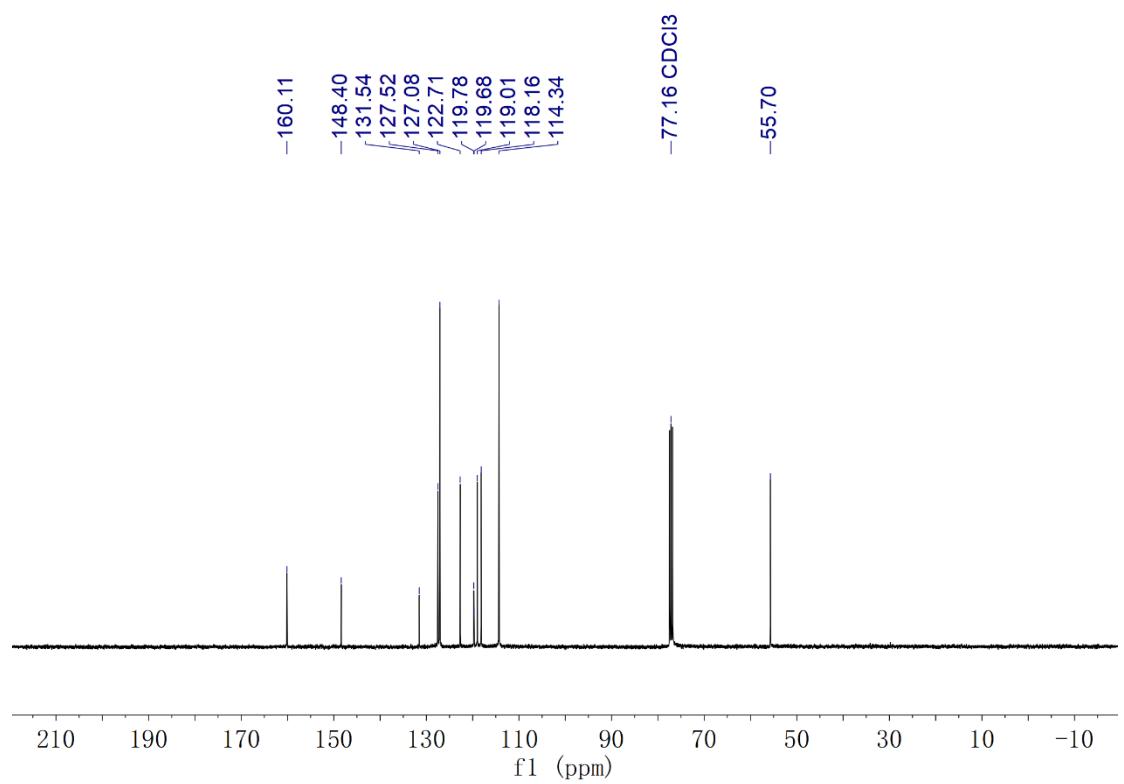
**5a  $^{13}\text{C-NMR}$**



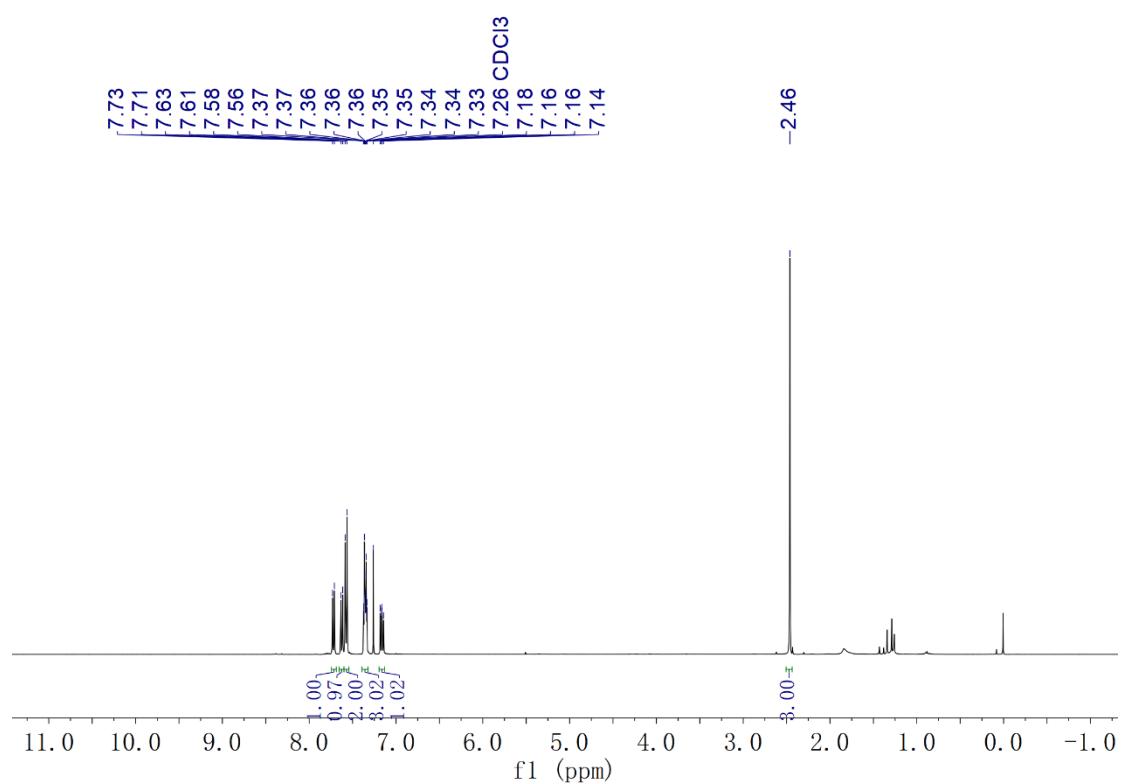
**5b**  $^1\text{H-NMR}$



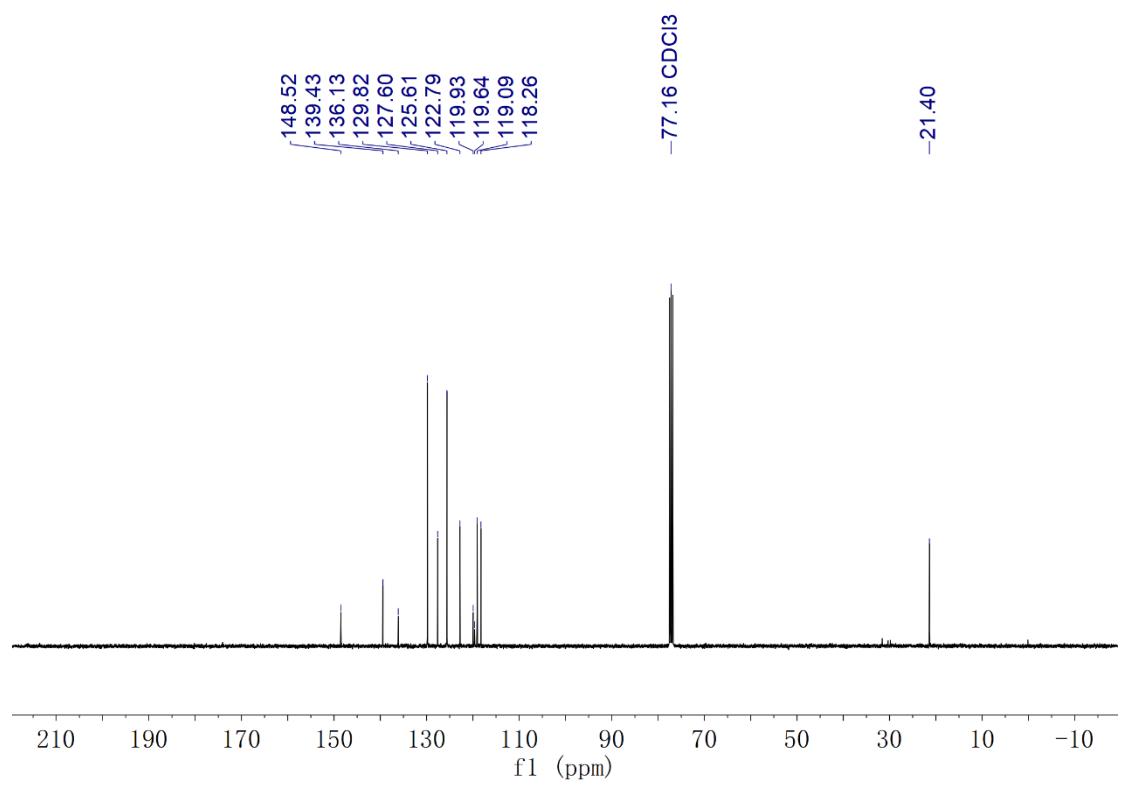
**5b**  $^{13}\text{C-NMR}$



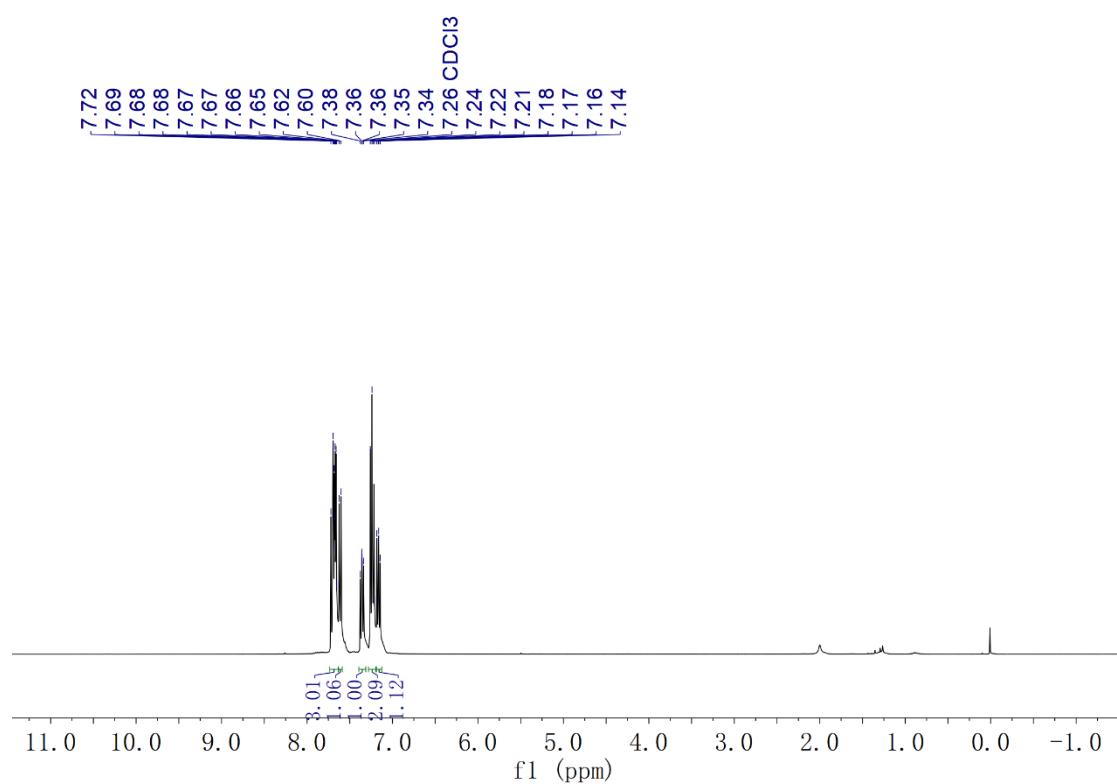
**5c  $^1\text{H-NMR}$**



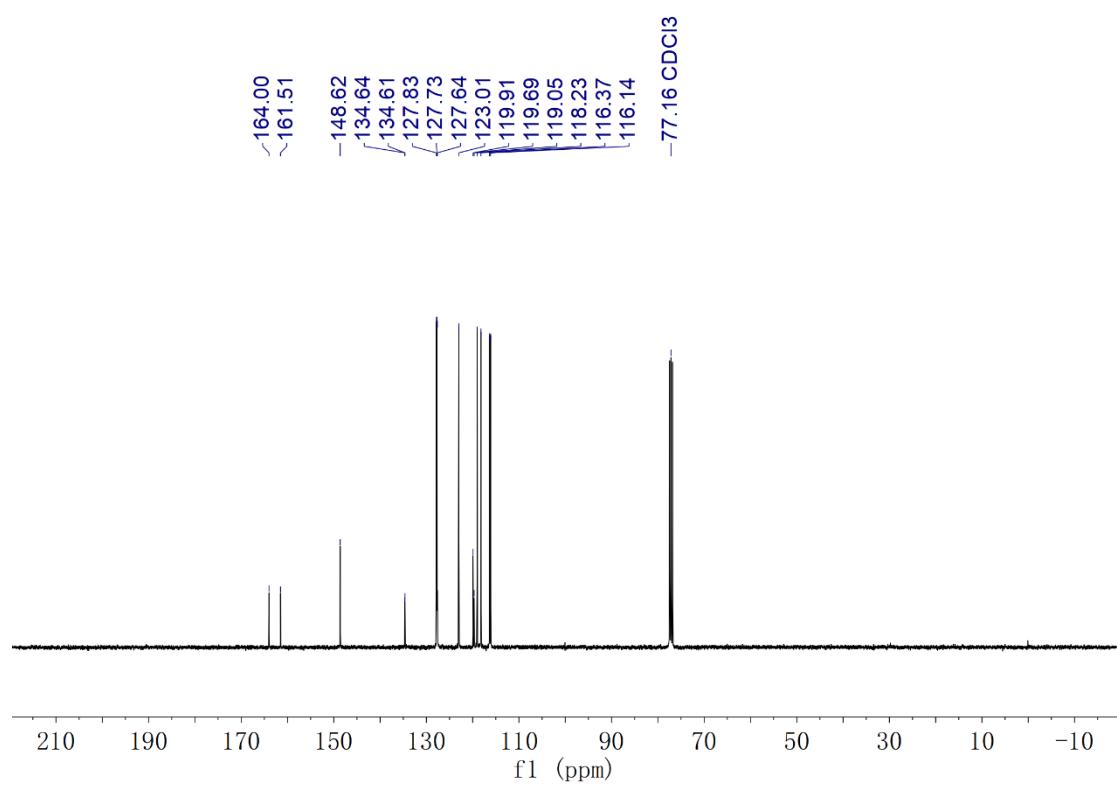
**5c  $^{13}\text{C-NMR}$**



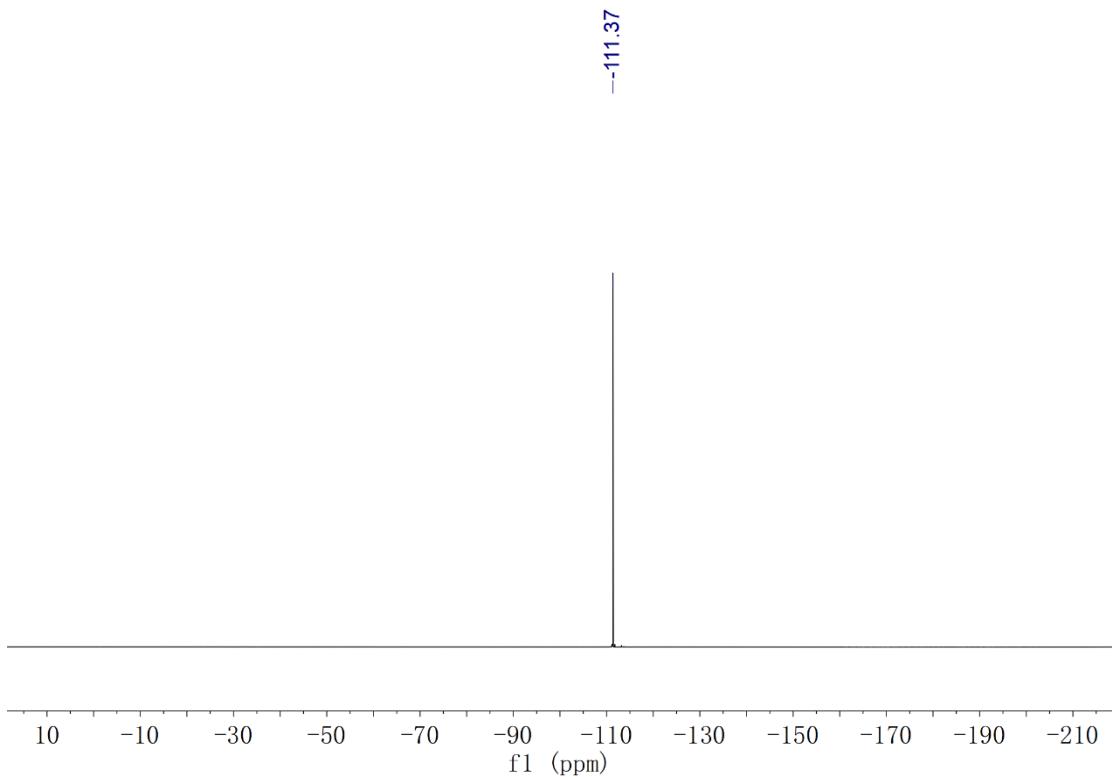
**5d  $^1\text{H-NMR}$**



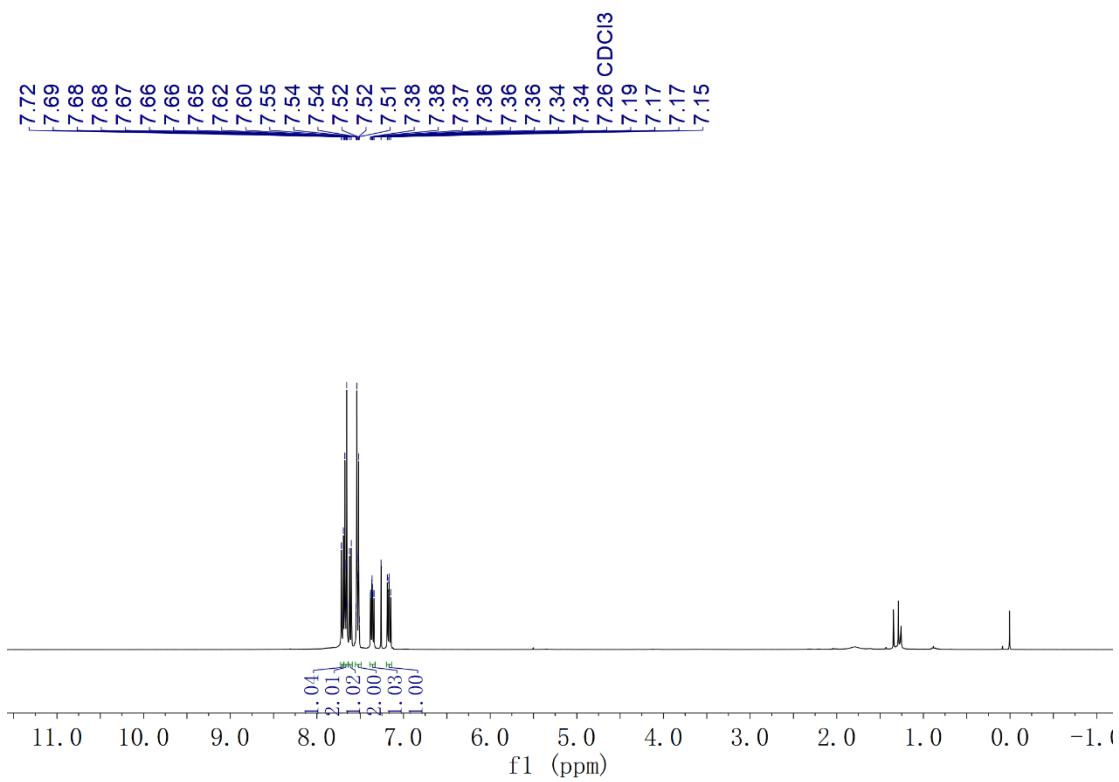
**5c  $^{13}\text{C-NMR}$**



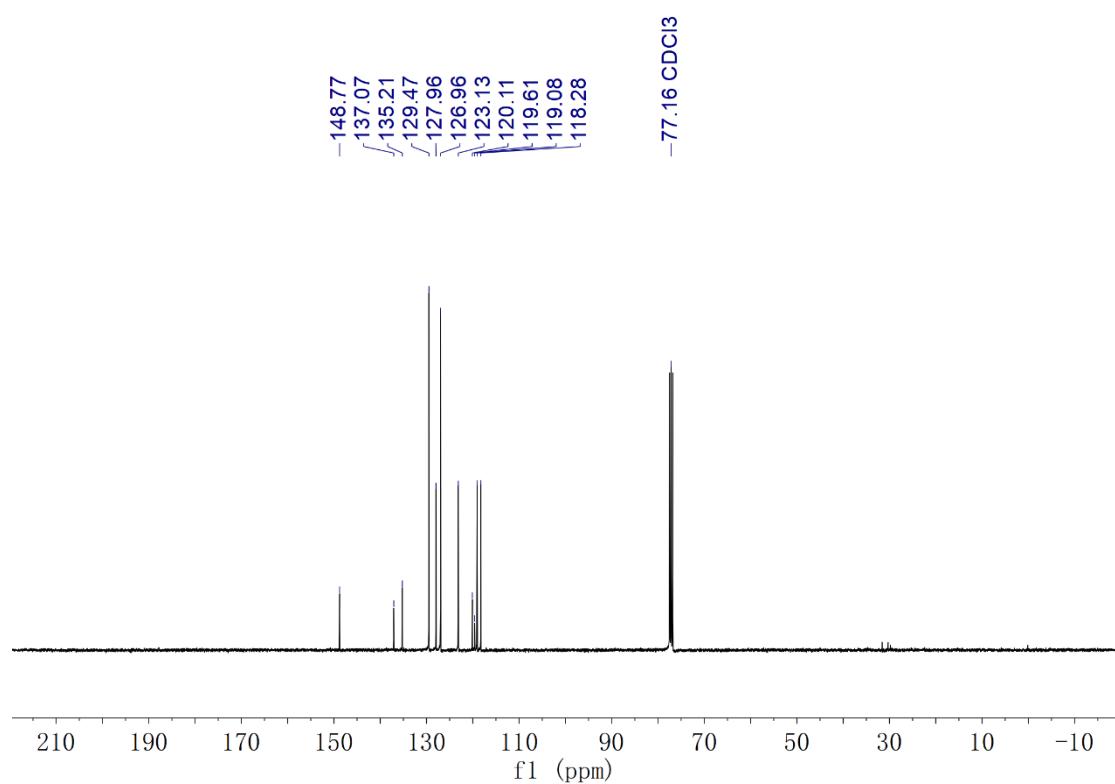
**5c  $^{19}\text{F-NMR}$**



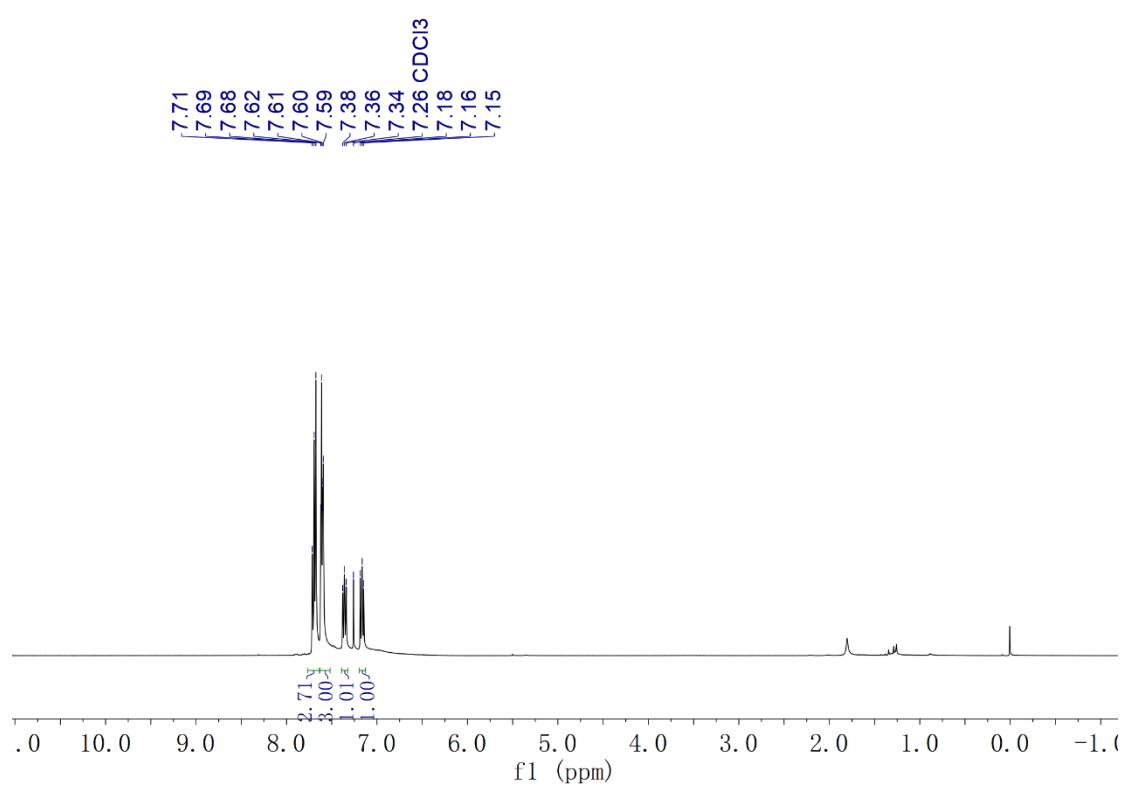
**5e  $^1\text{H-NMR}$**



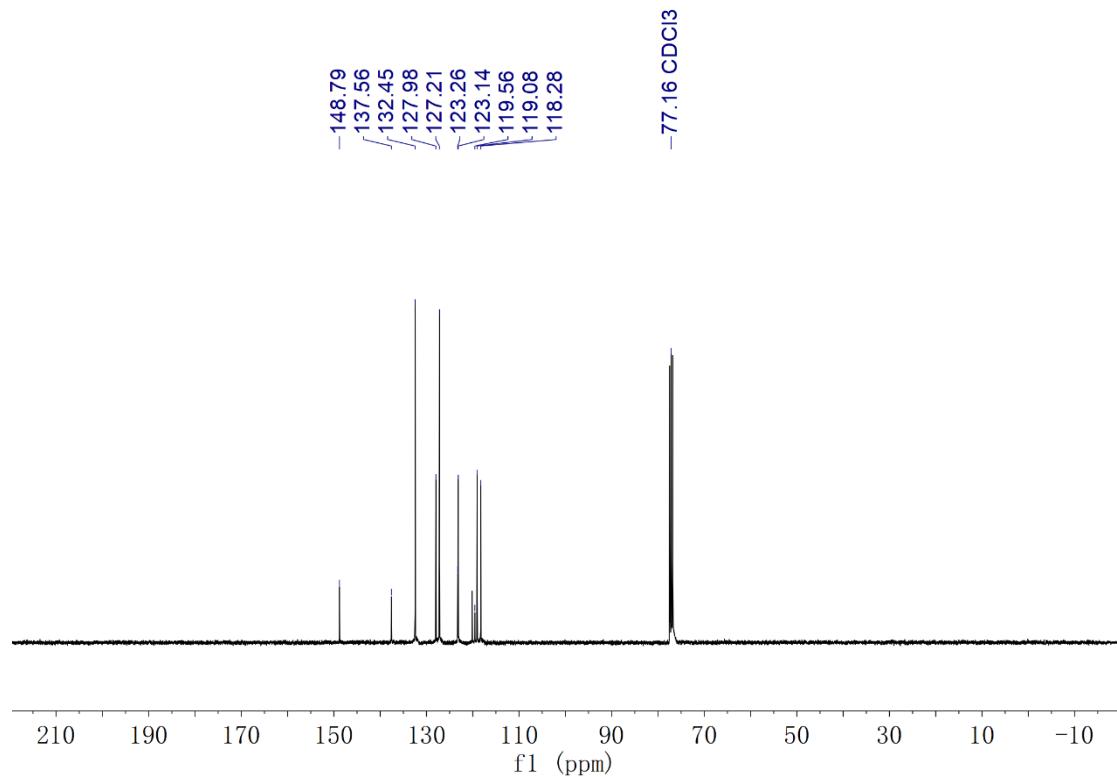
**5e  $^{13}\text{C}$ -NMR**



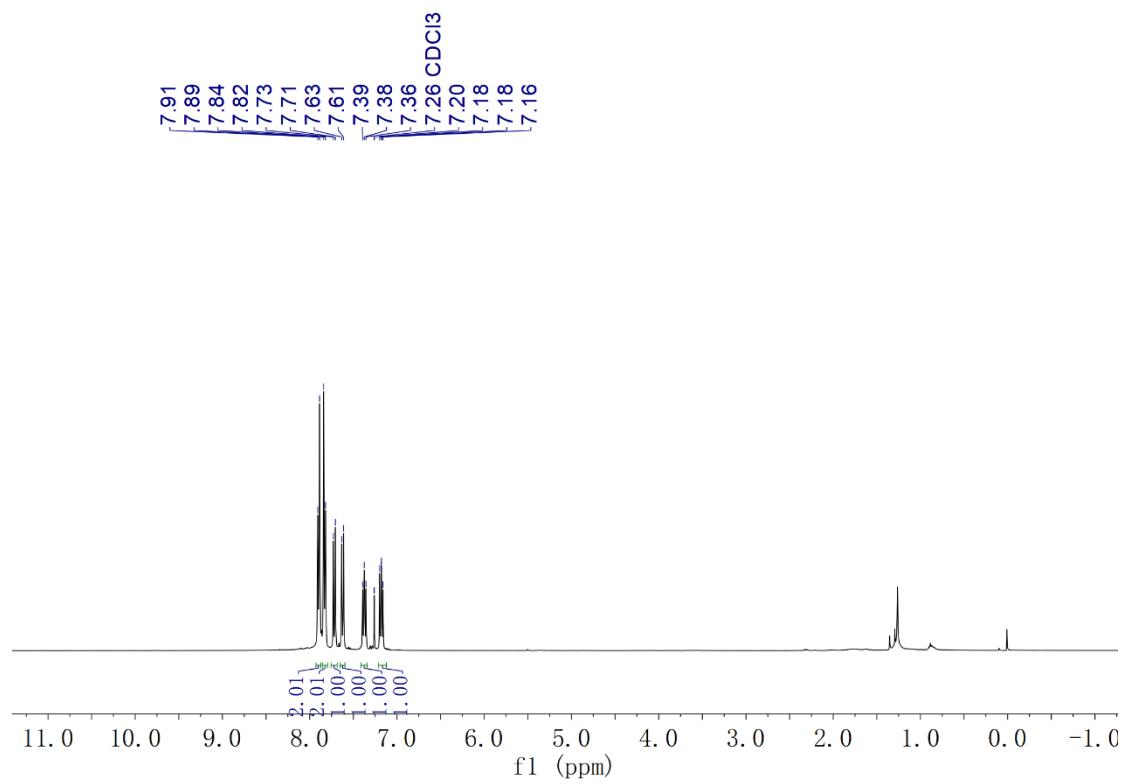
**5f  $^1\text{H}$ -NMR**



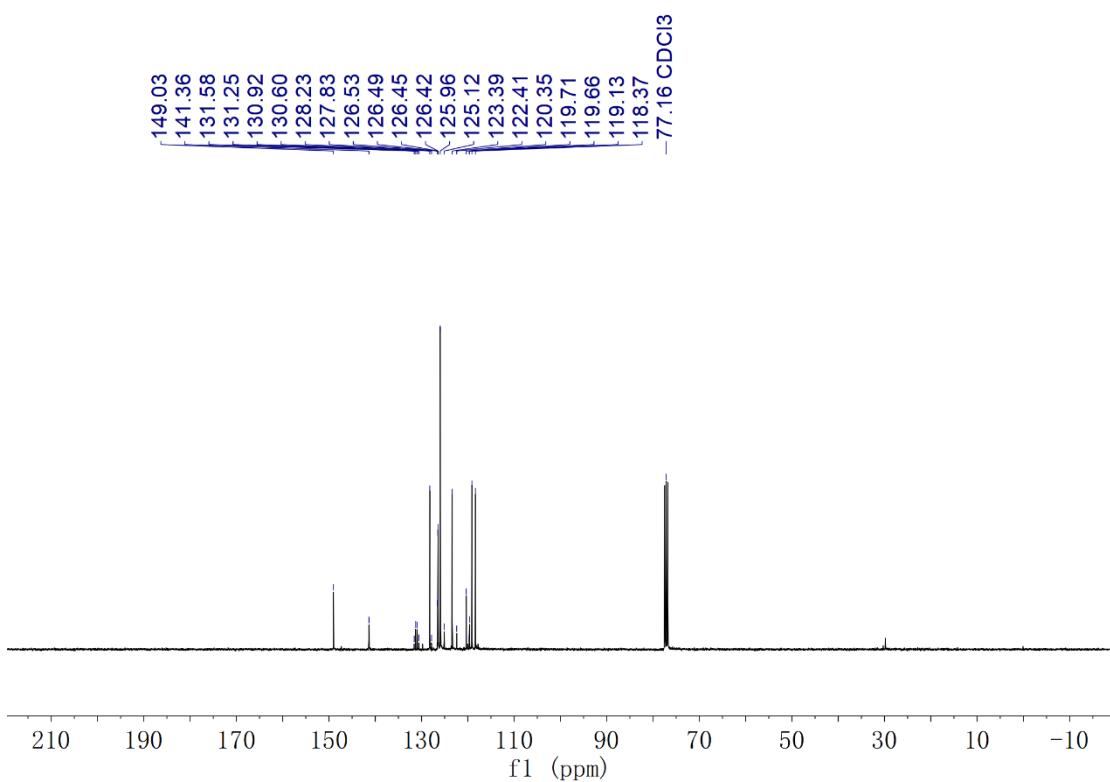
**5f  $^{13}\text{C}$ -NMR**



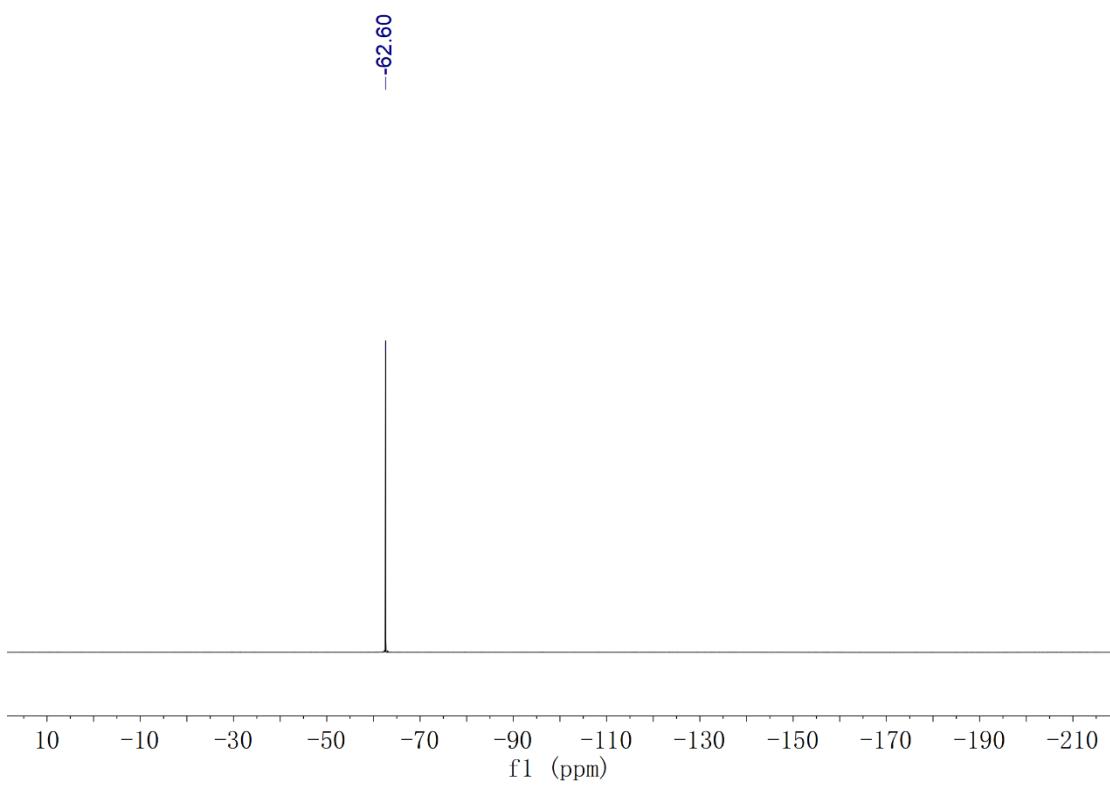
**5g  $^1\text{H}$ -NMR**



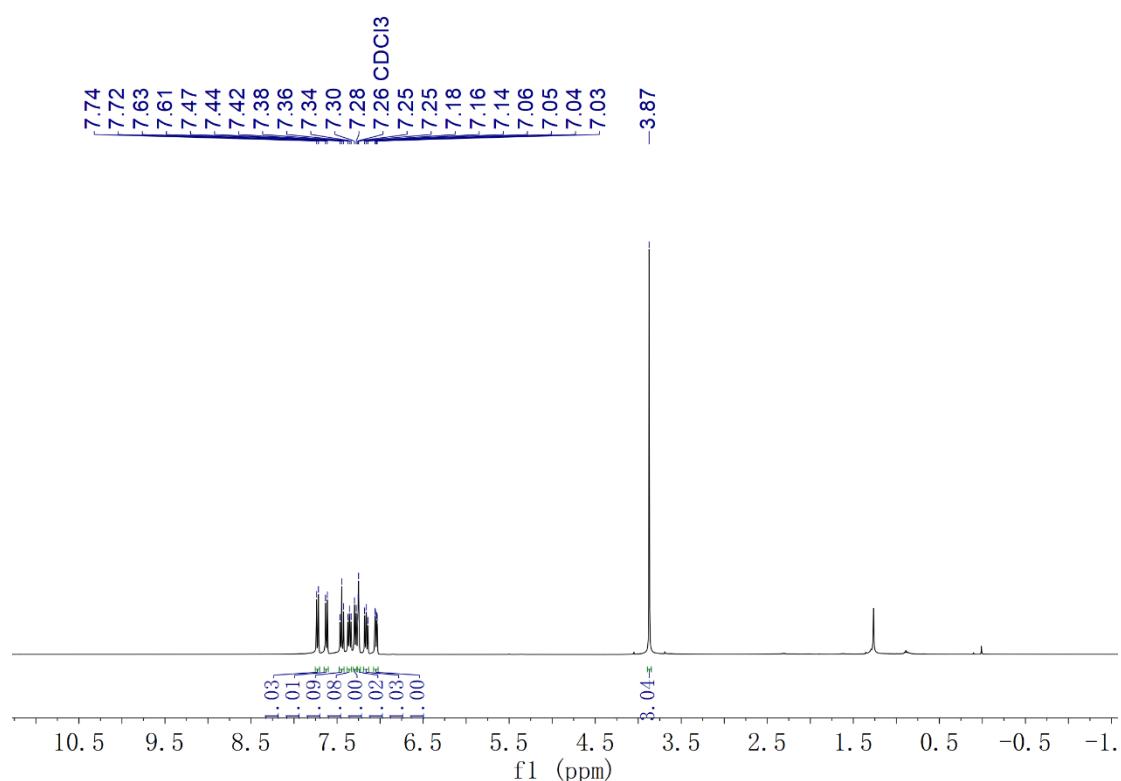
**5g  $^{13}\text{C}$ -NMR**



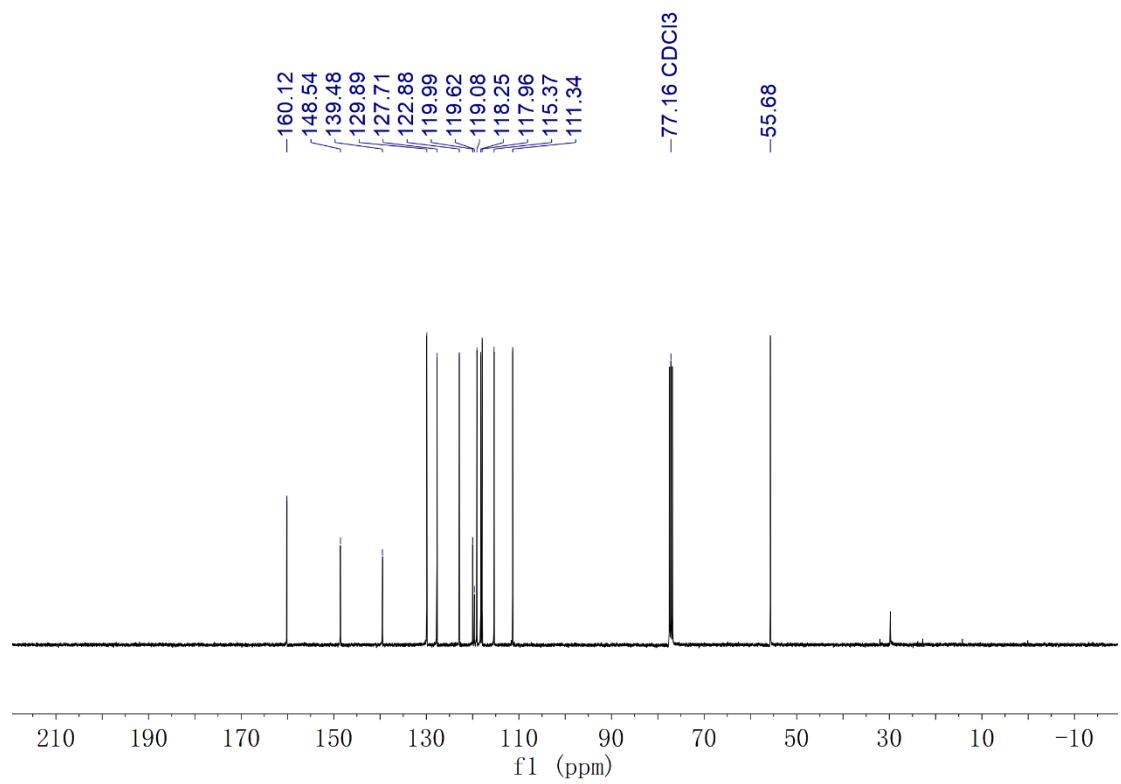
**5g  $^{19}\text{F}$ -NMR**



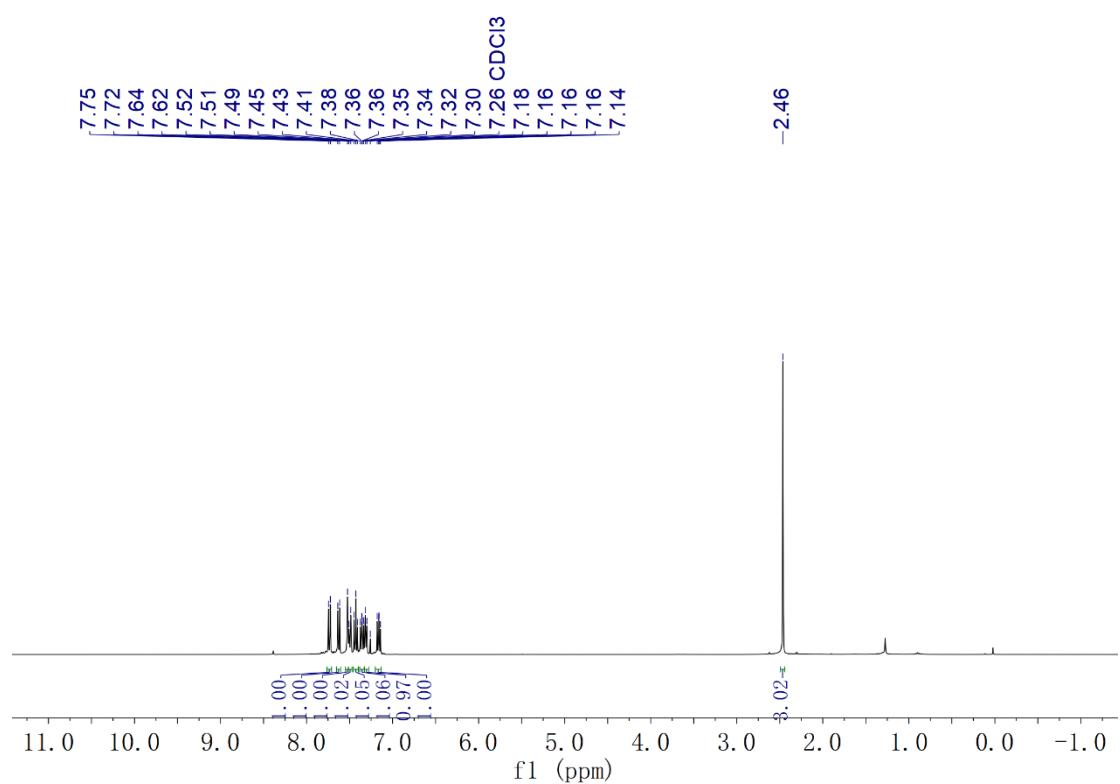
**5h  $^1\text{H}$ -NMR**



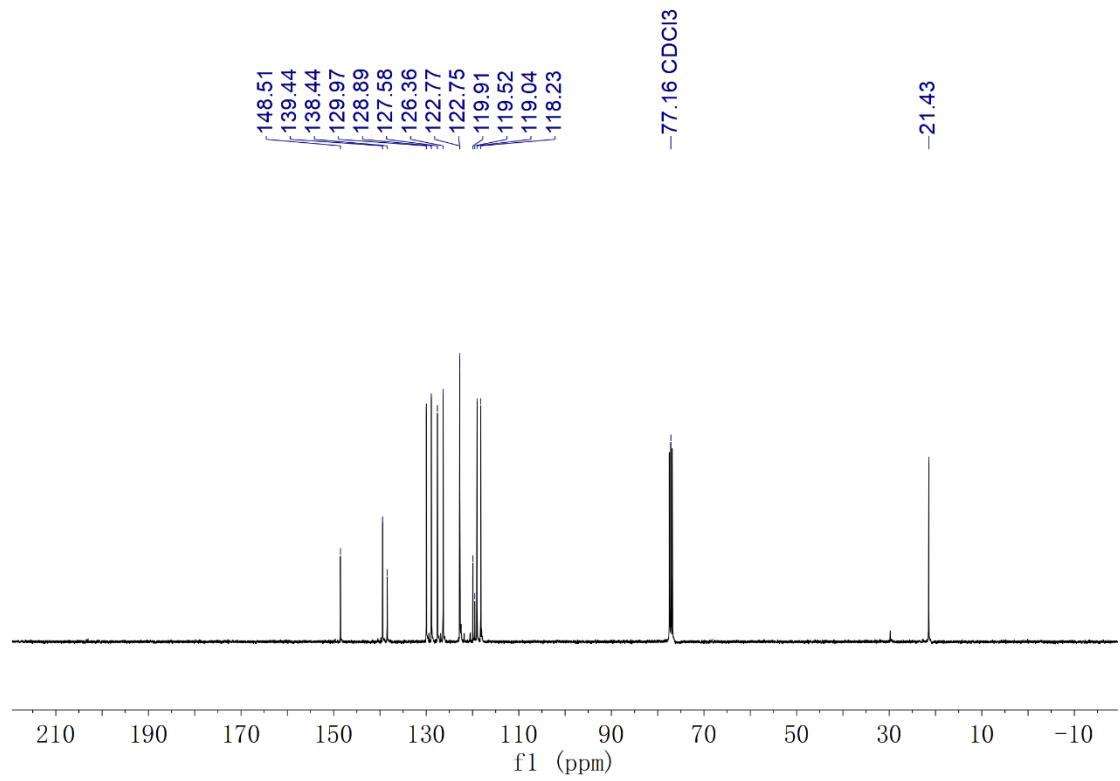
**5h  $^{13}\text{C}$ -NMR**



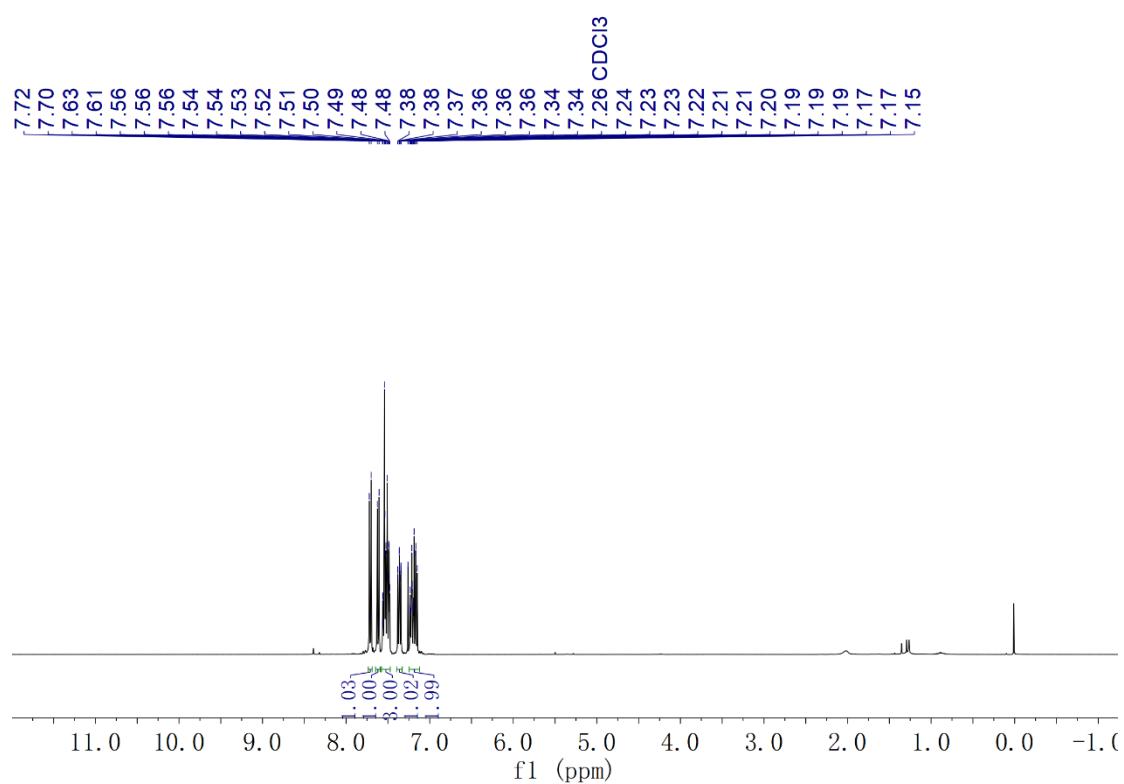
**5i  $^1\text{H}$ -NMR**



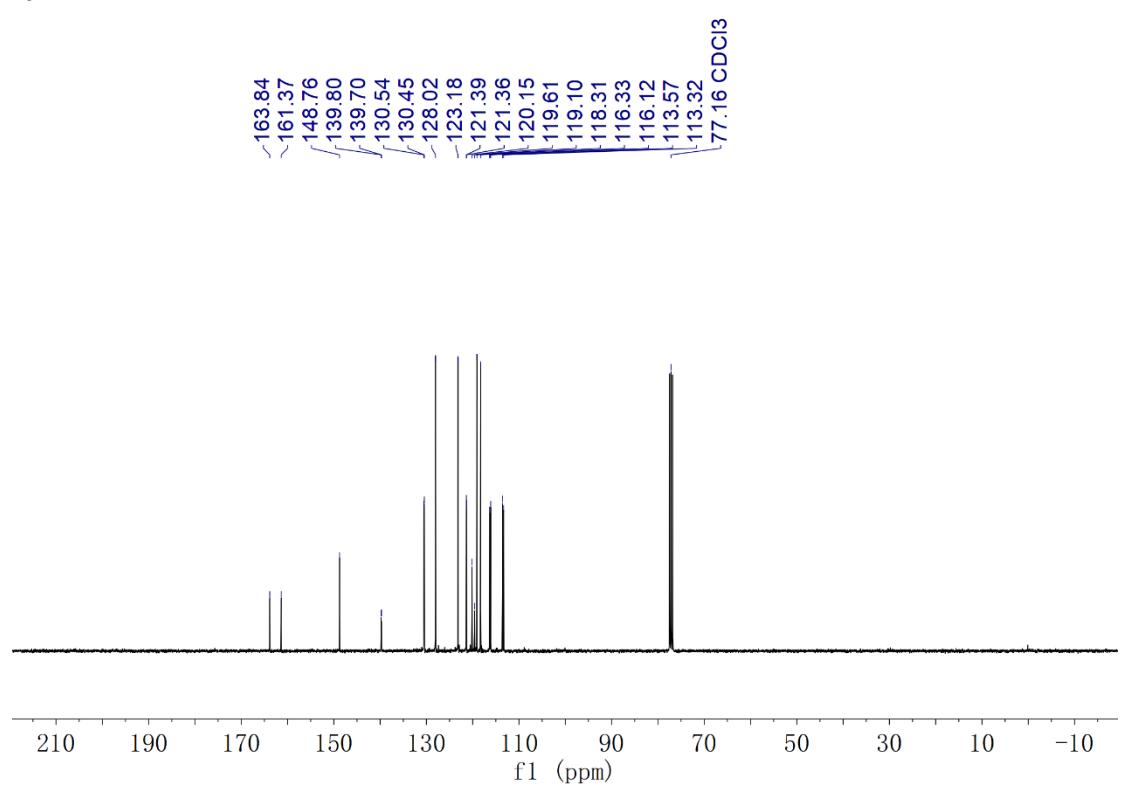
**5i  $^{13}\text{C}$ -NMR**



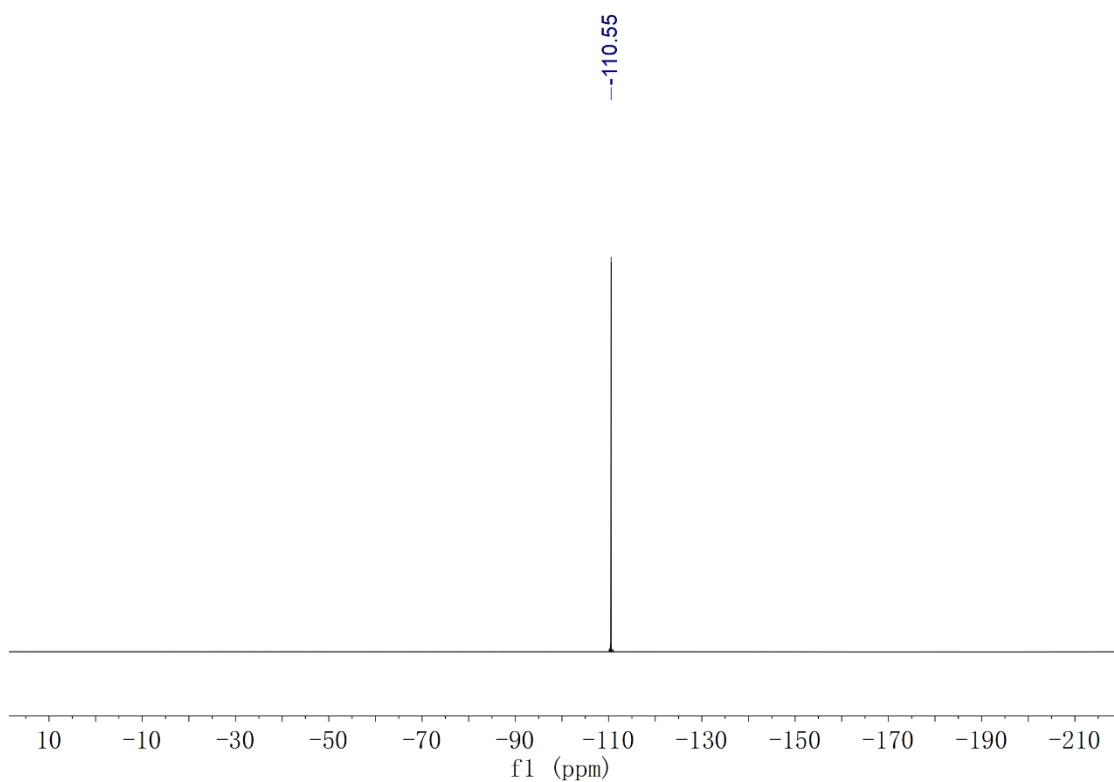
**5j  $^1\text{H}$ -NMR**



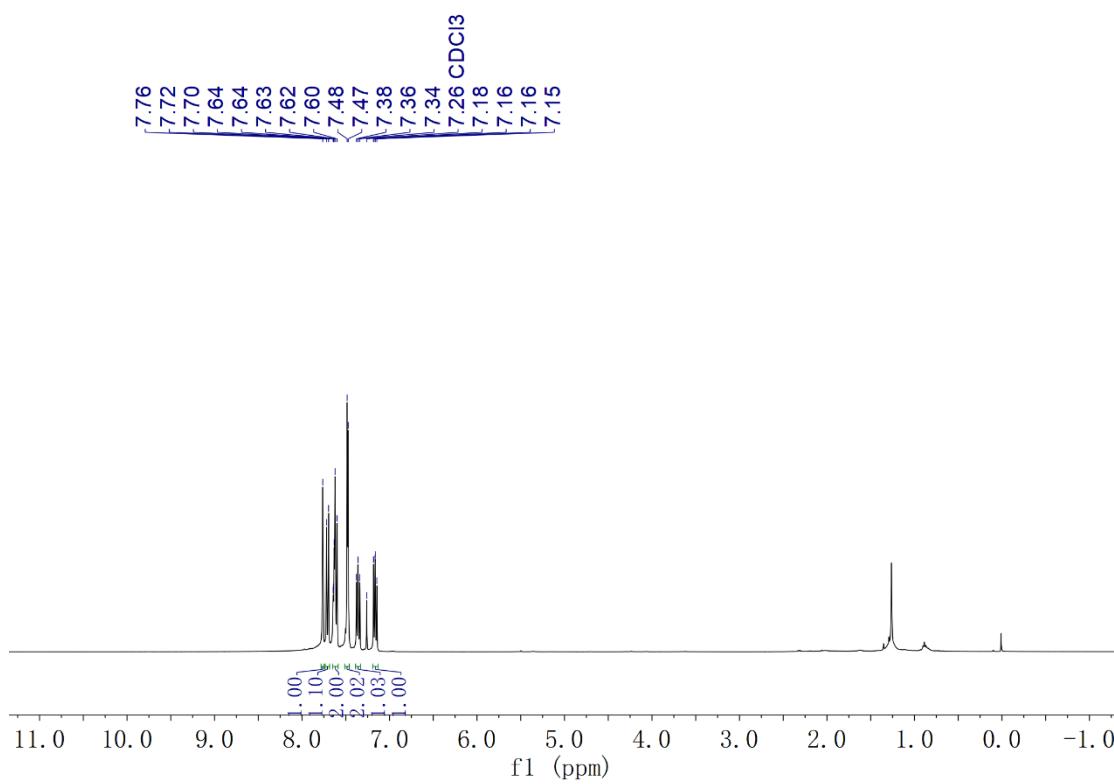
**5j  $^{13}\text{C}$ -NMR**



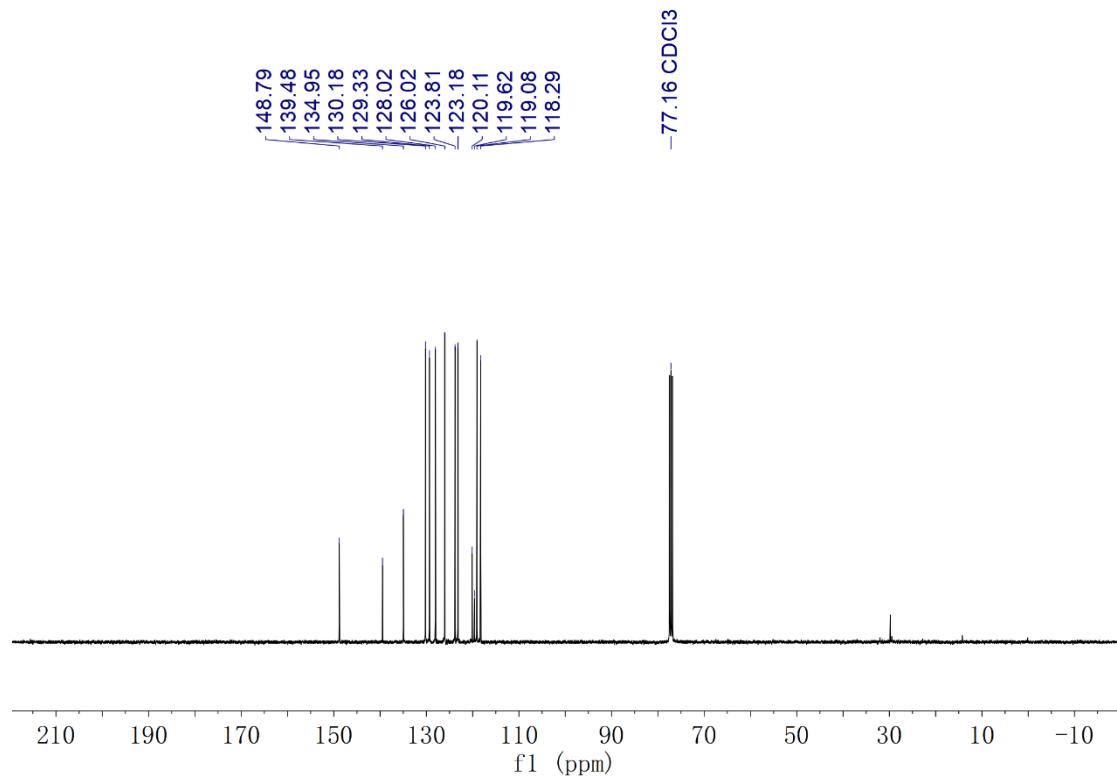
### 5j $^{19}\text{F}$ -NMR



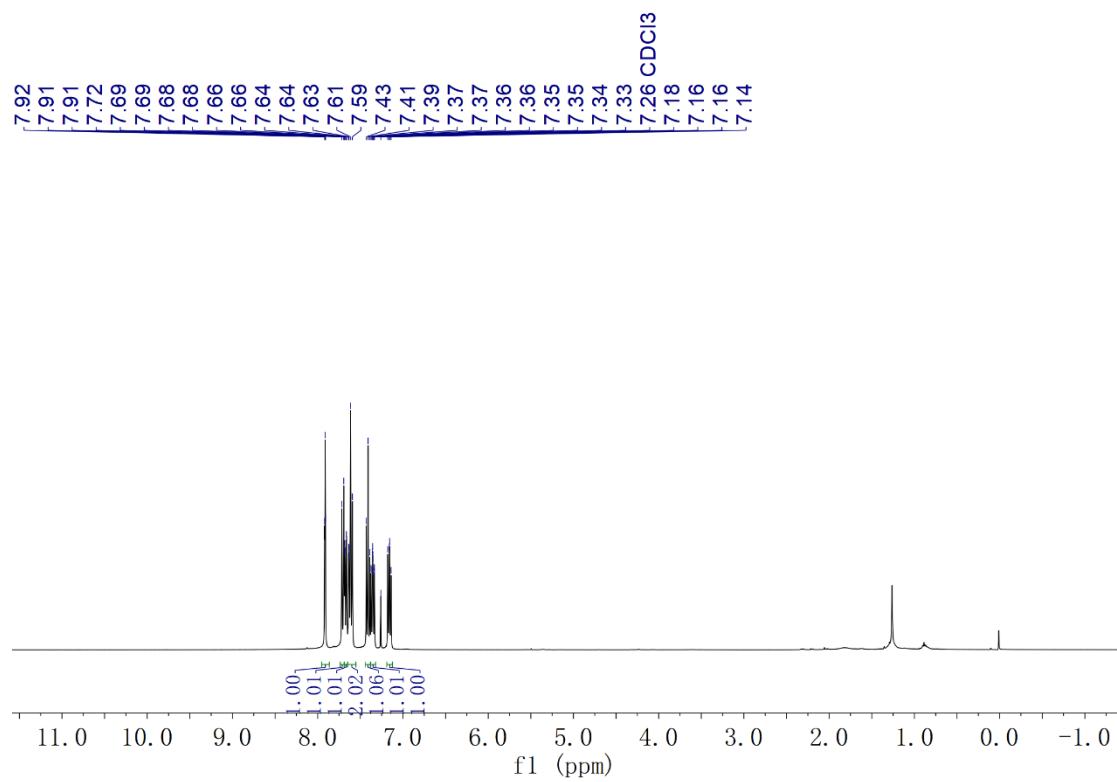
## 5k $^1\text{H-NMR}$



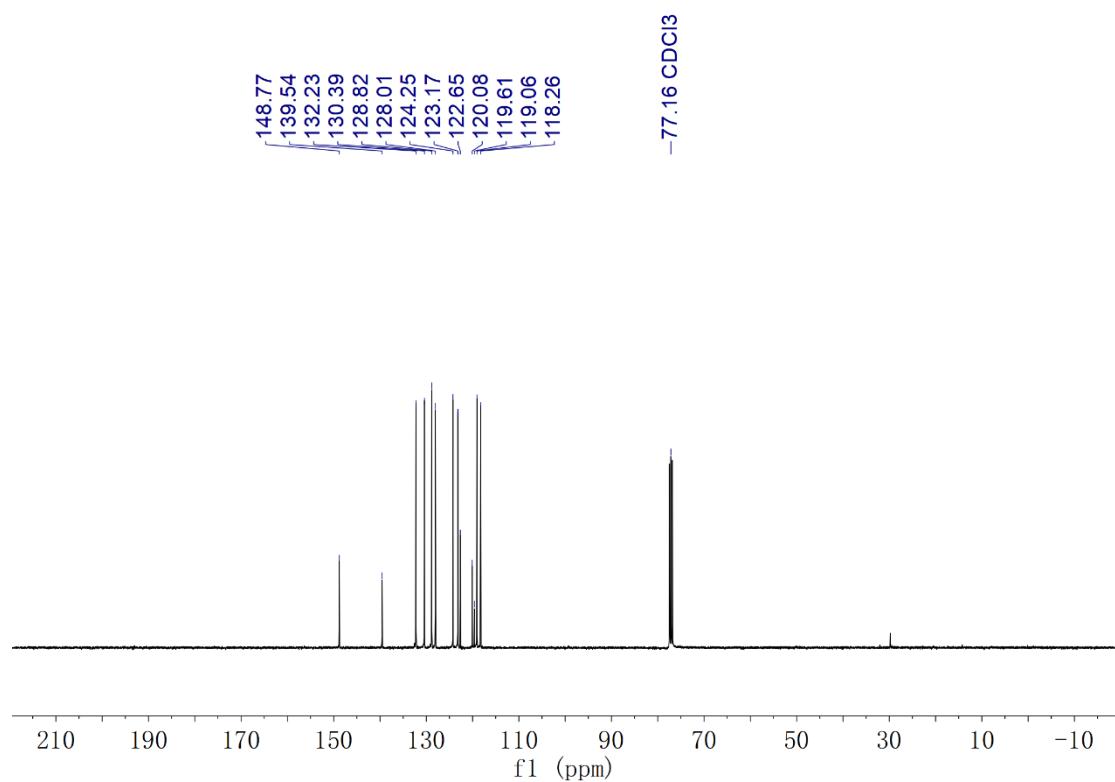
## 5k $^{13}\text{C}$ -NMR



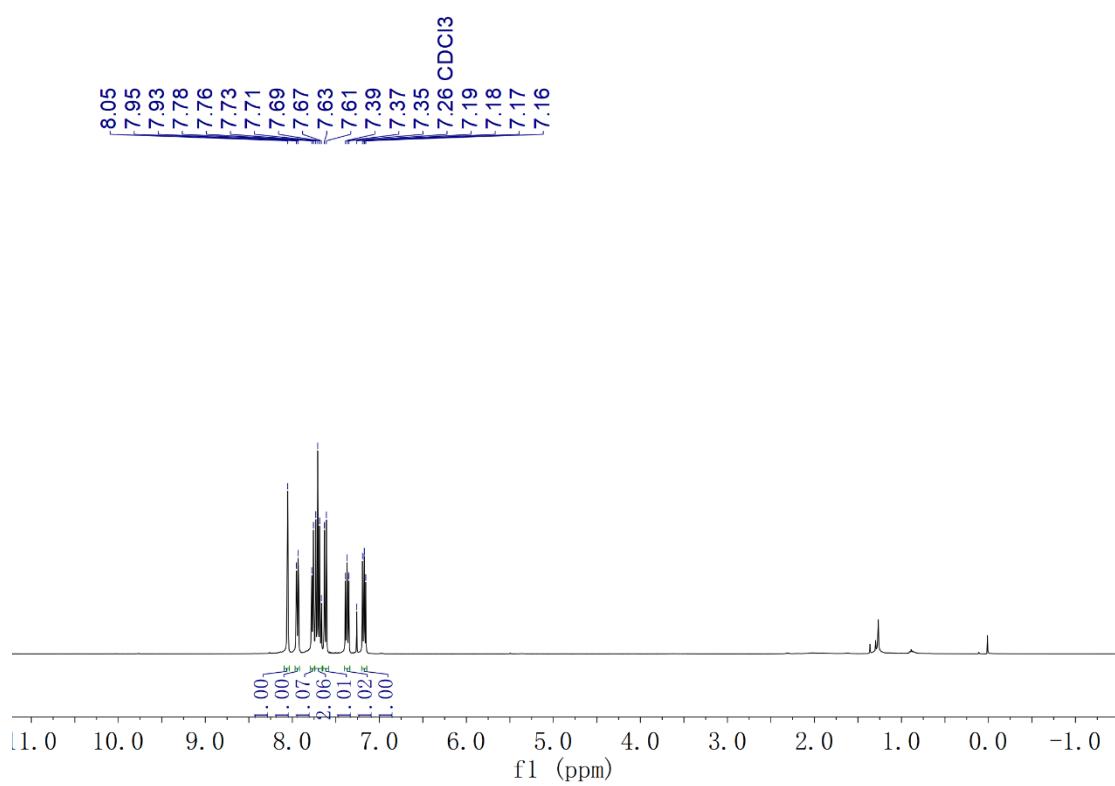
### 5l $^1\text{H-NMR}$



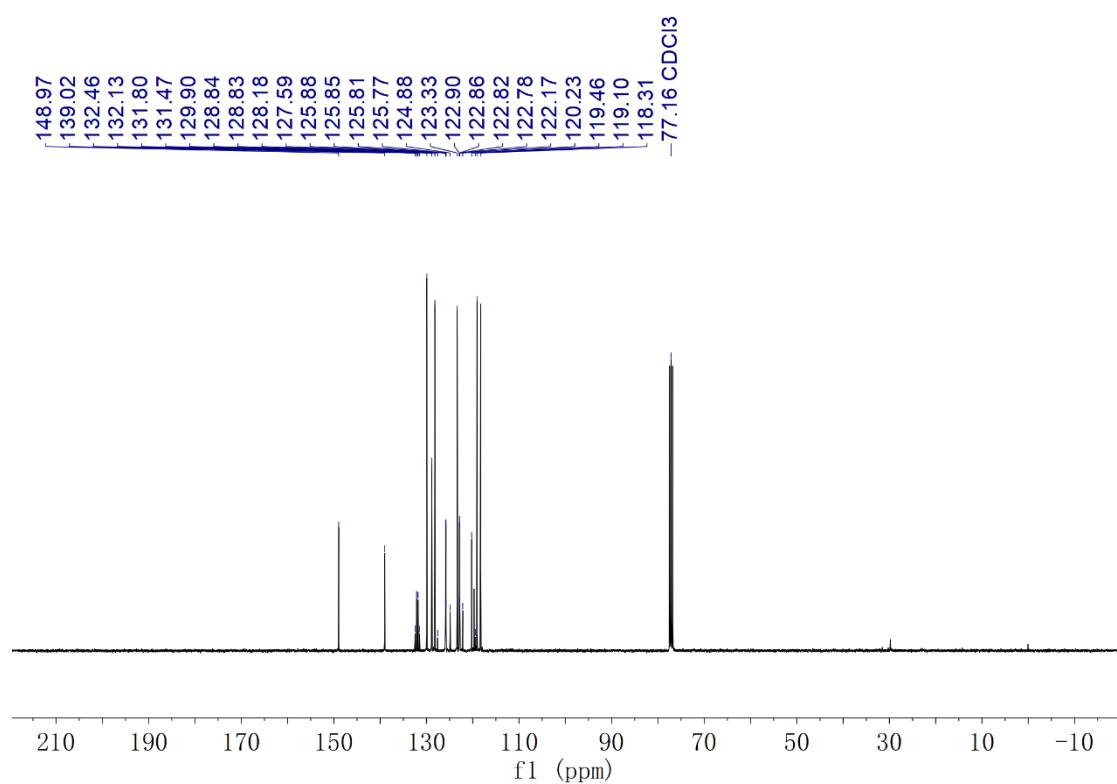
**5l  $^{13}\text{C-NMR}$**



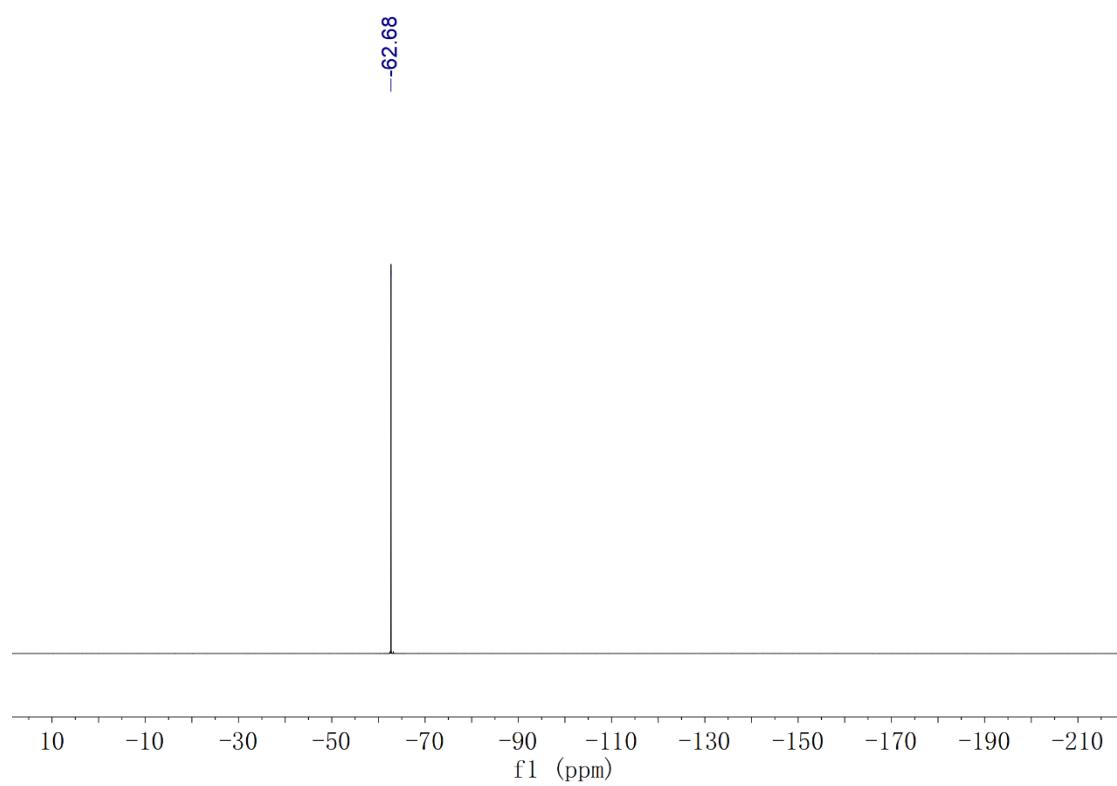
**5m  $^1\text{H-NMR}$**



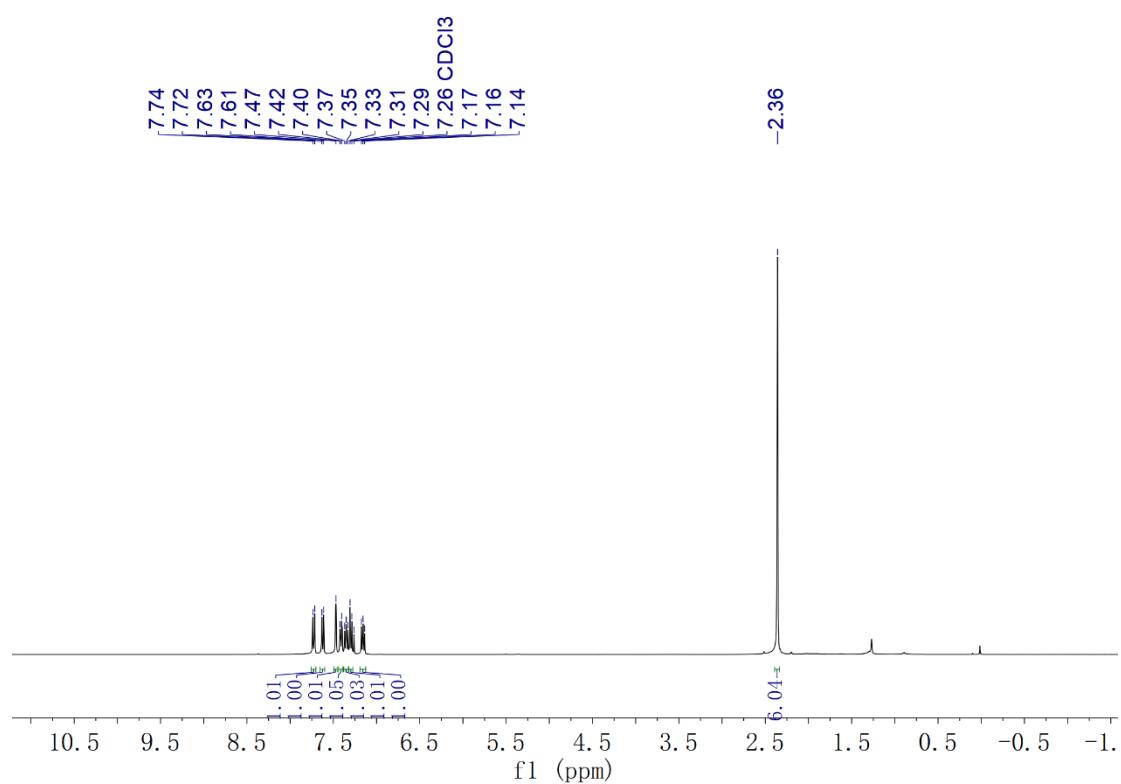
**5m  $^1\text{H-NMR}$**



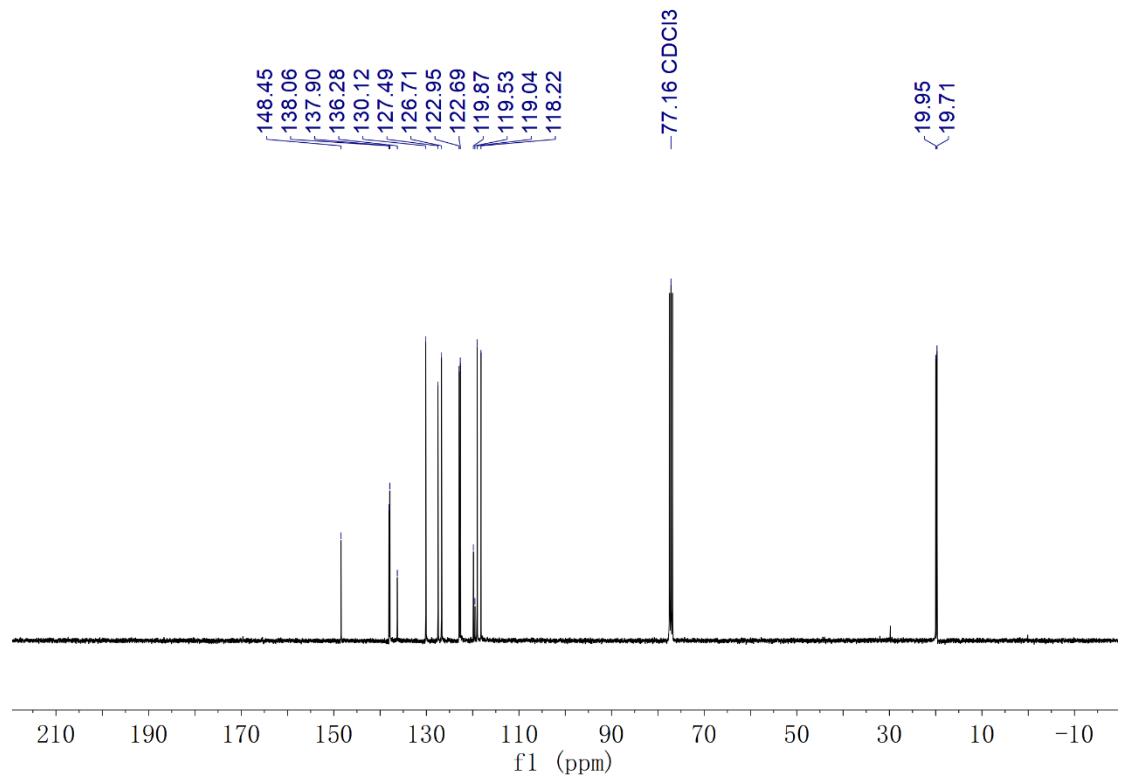
**5m  $^{19}\text{F-NMR}$**



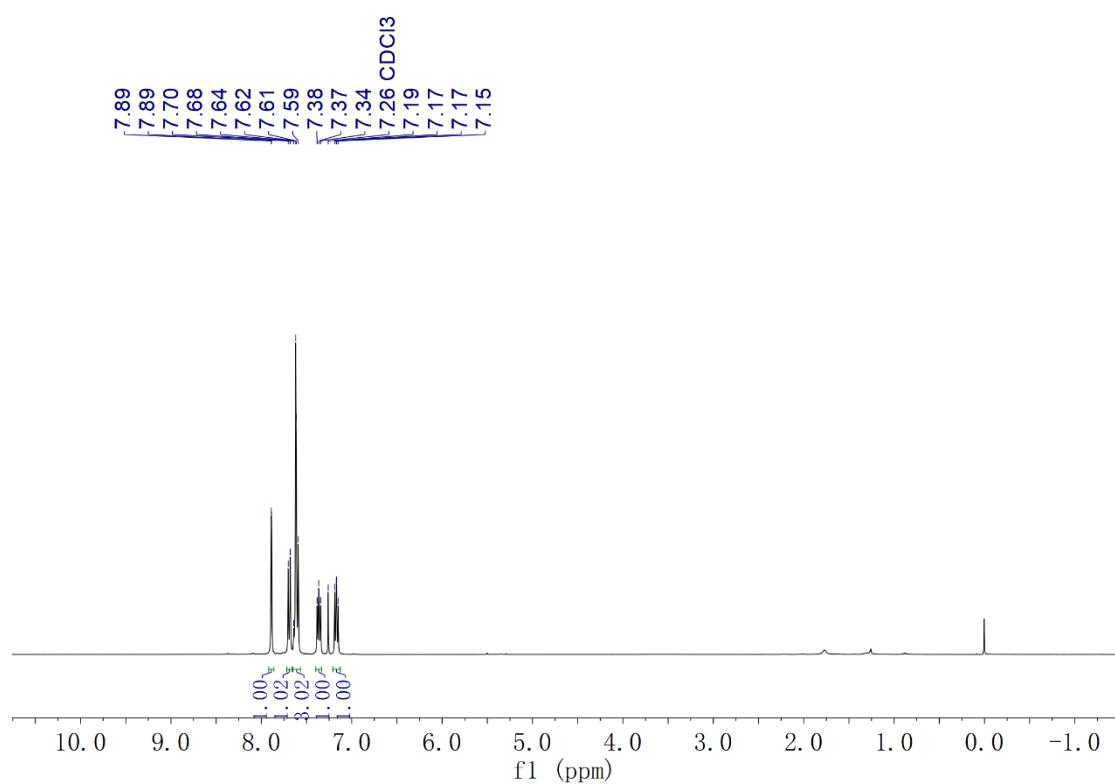
**5n  $^1\text{H-NMR}$**



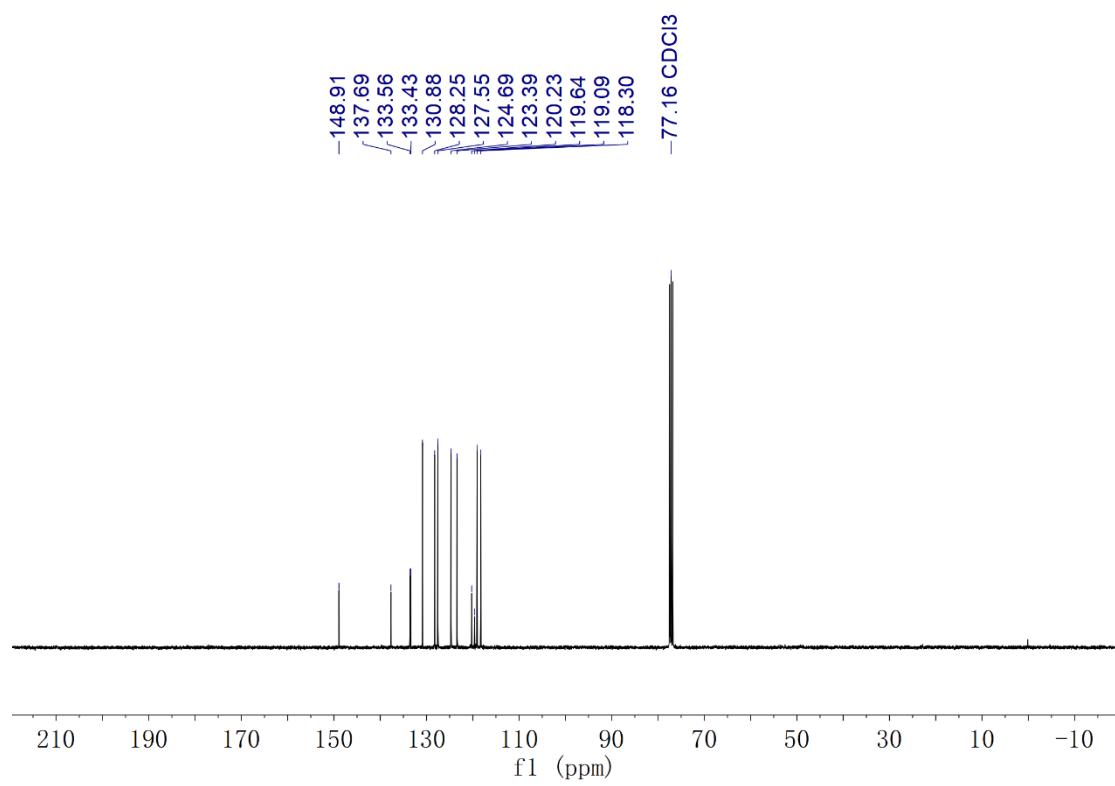
**5n  $^{13}\text{C-NMR}$**



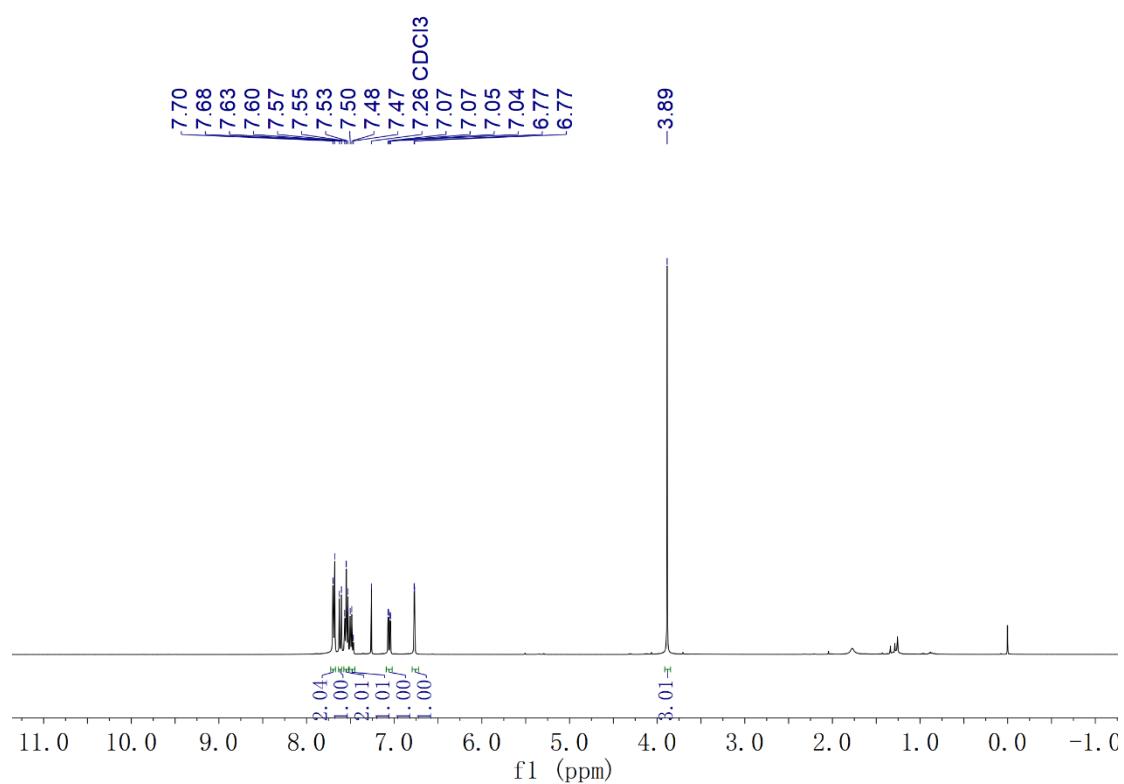
## 5o $^1\text{H-NMR}$



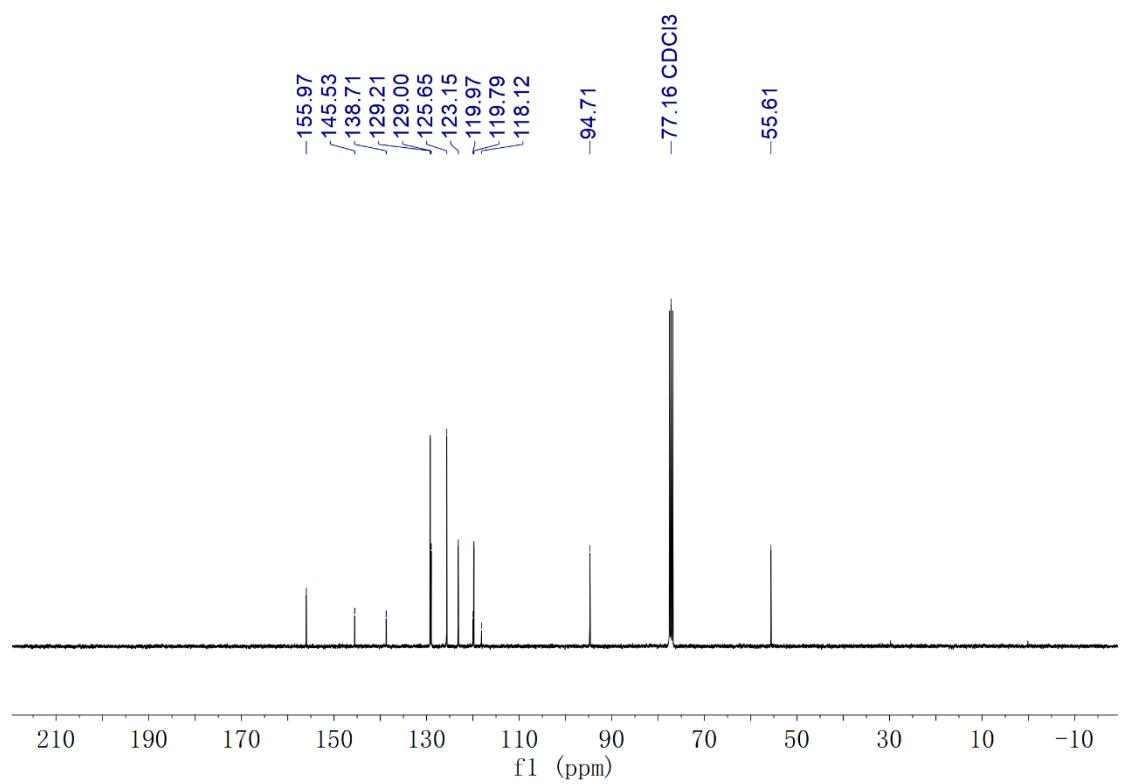
50  $^{13}\text{C}$ -NMR



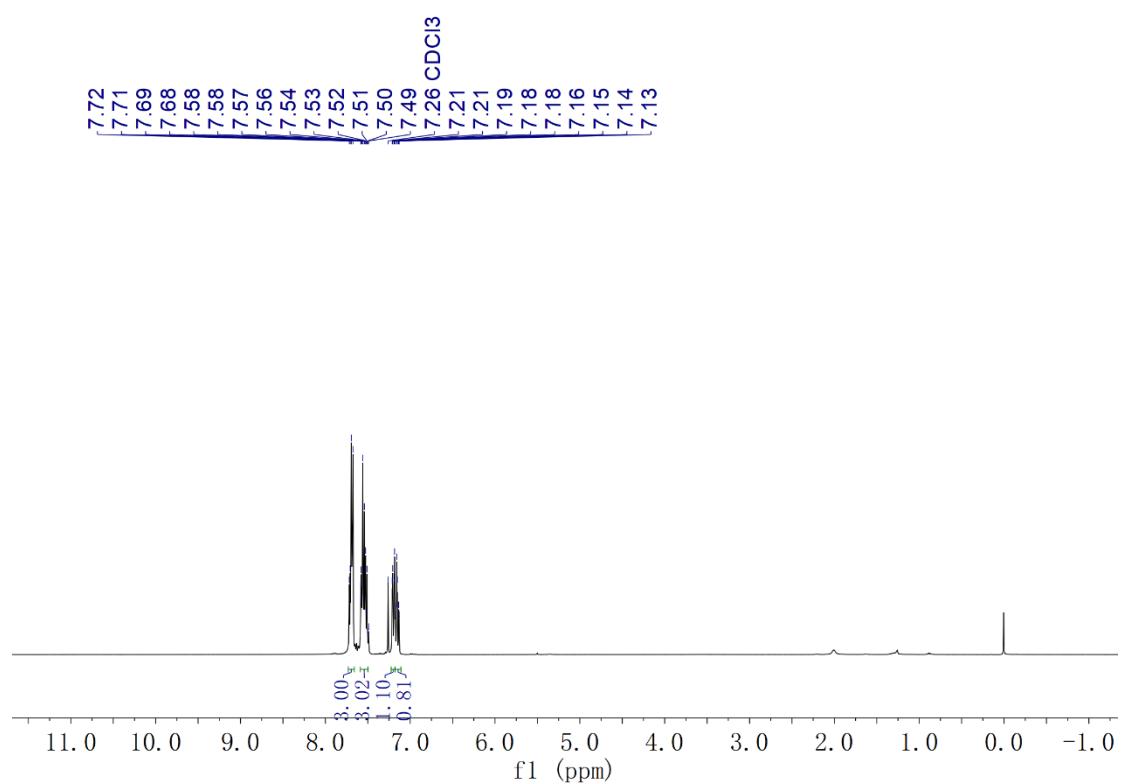
**5p  $^1\text{H-NMR}$**



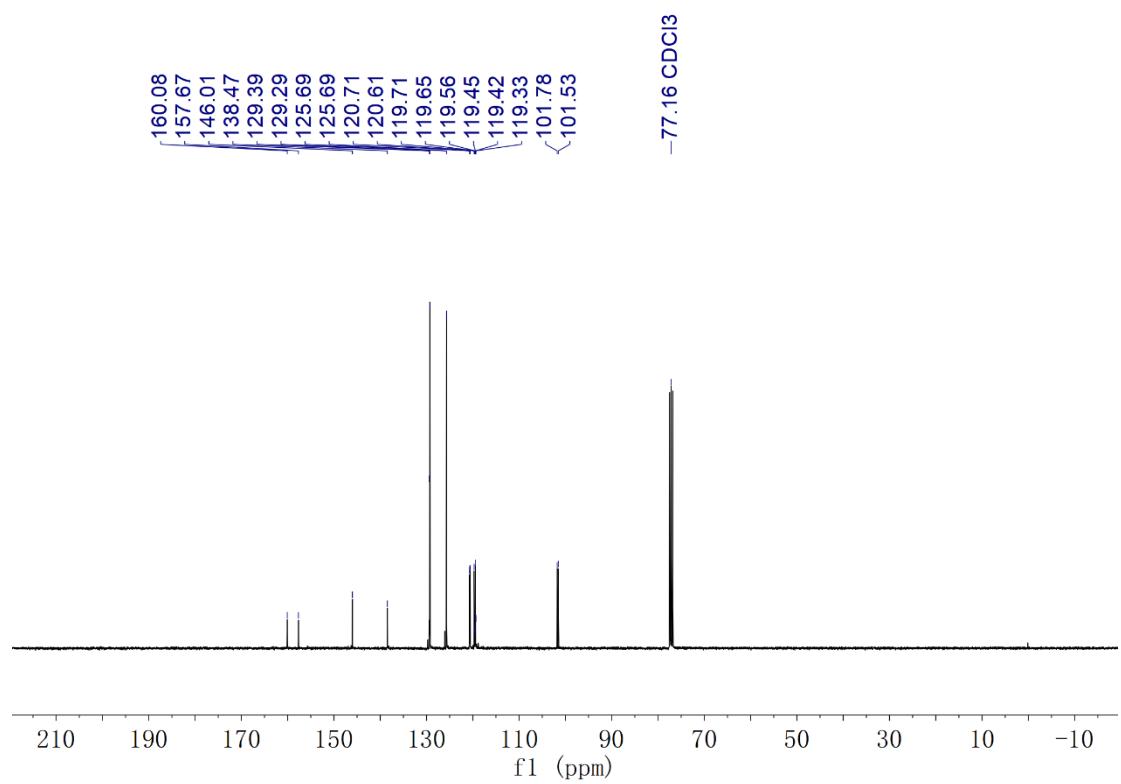
**5p  $^{13}\text{C-NMR}$**



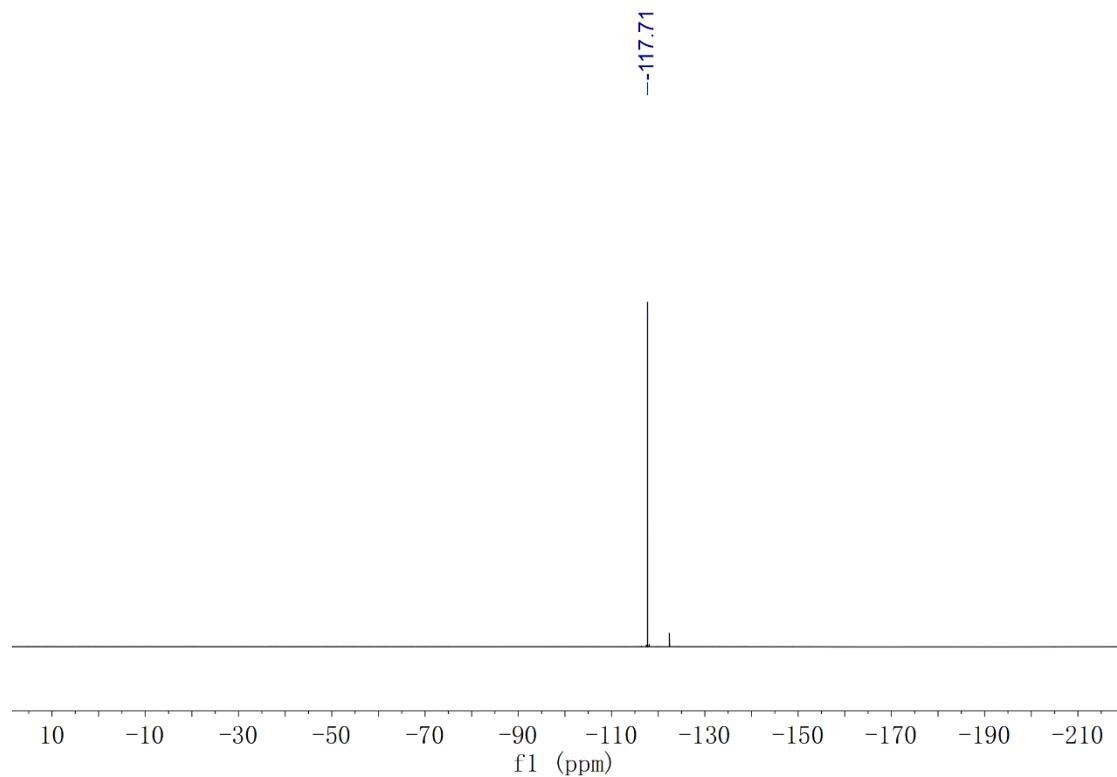
**5q  $^1\text{H-NMR}$**



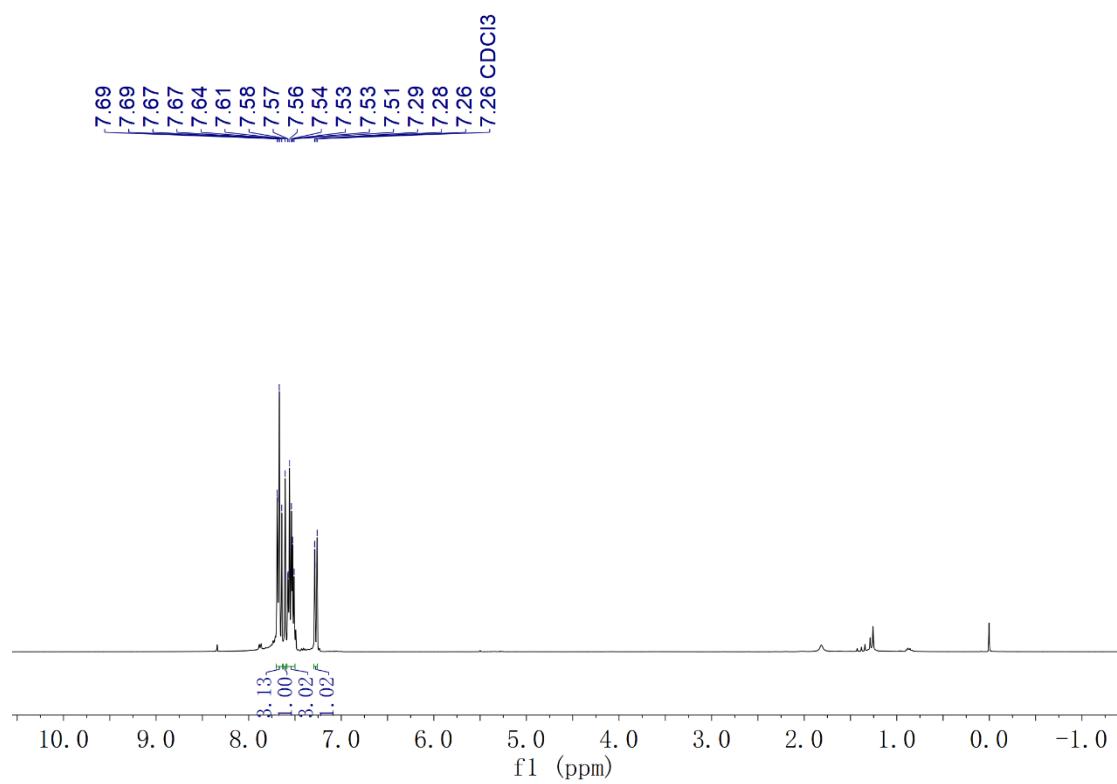
**5q  $^{13}\text{C-NMR}$**



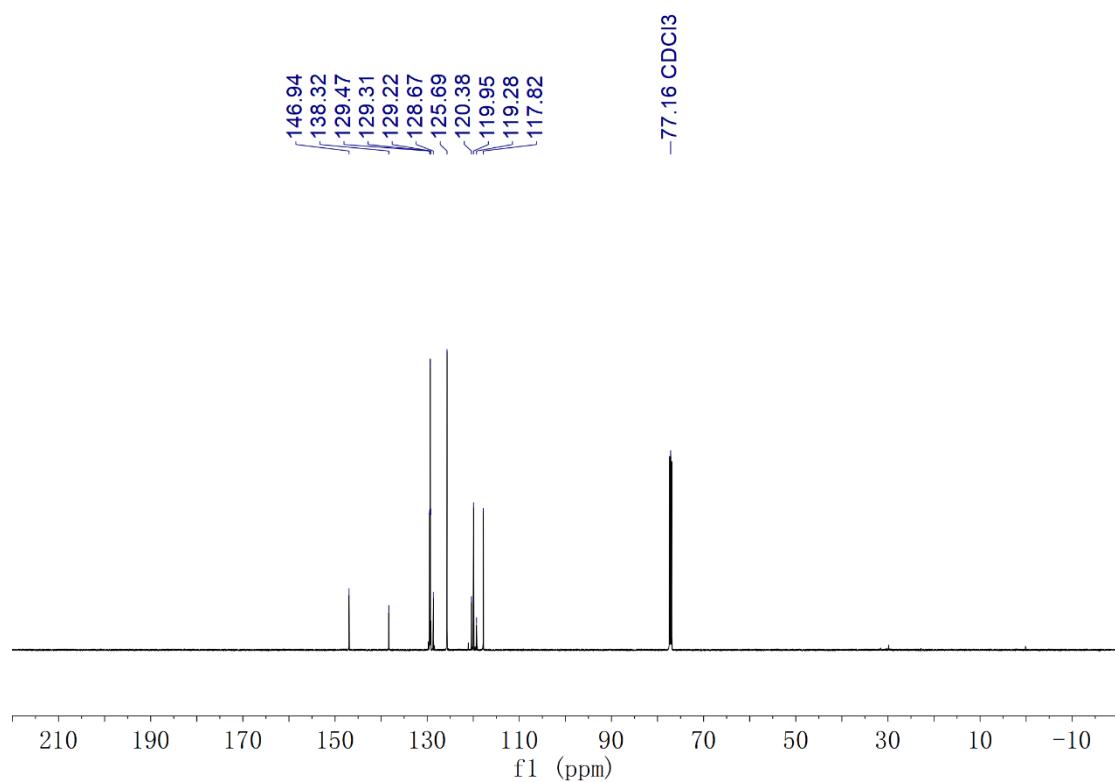
**5q  $^{19}\text{F}$ -NMR**



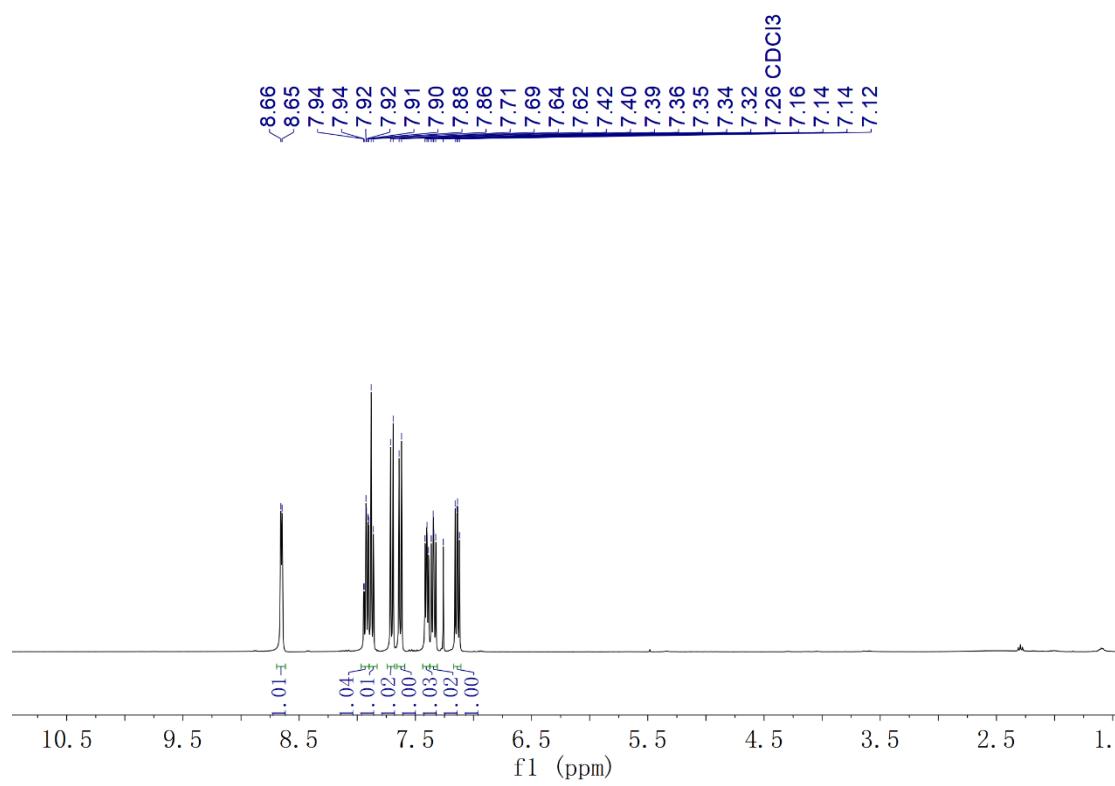
**5r  $^1\text{H}$ -NMR**



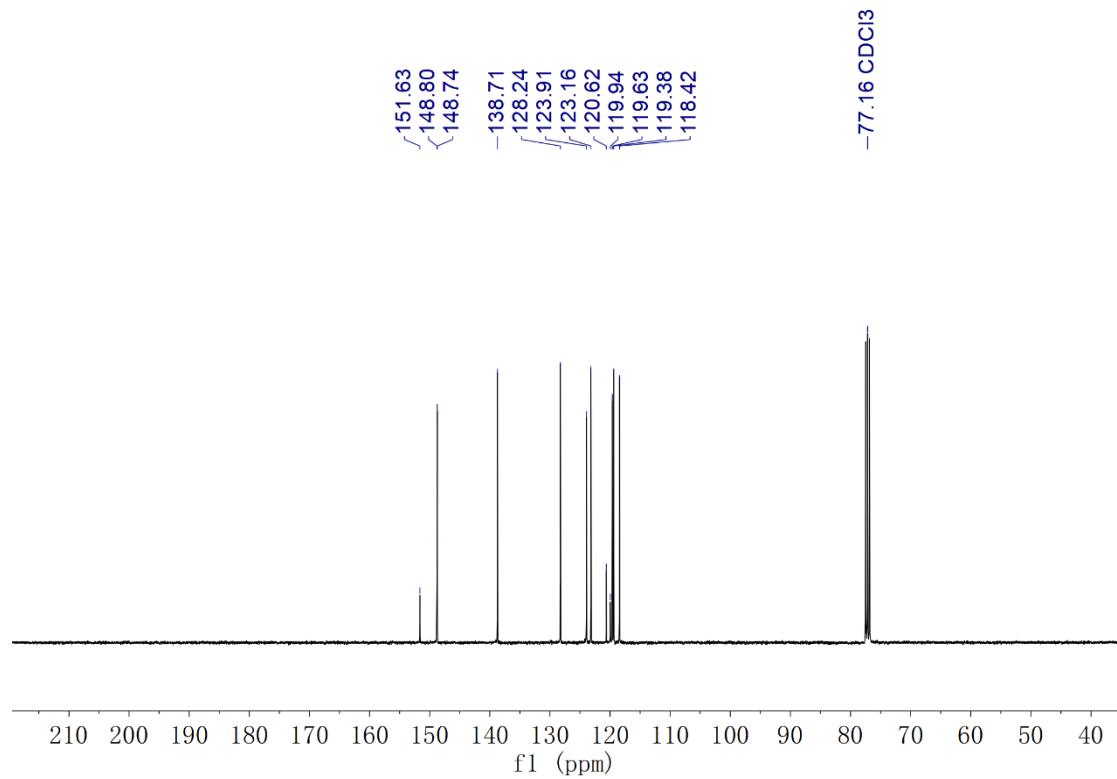
**5r  $^{13}\text{C}$ -NMR**



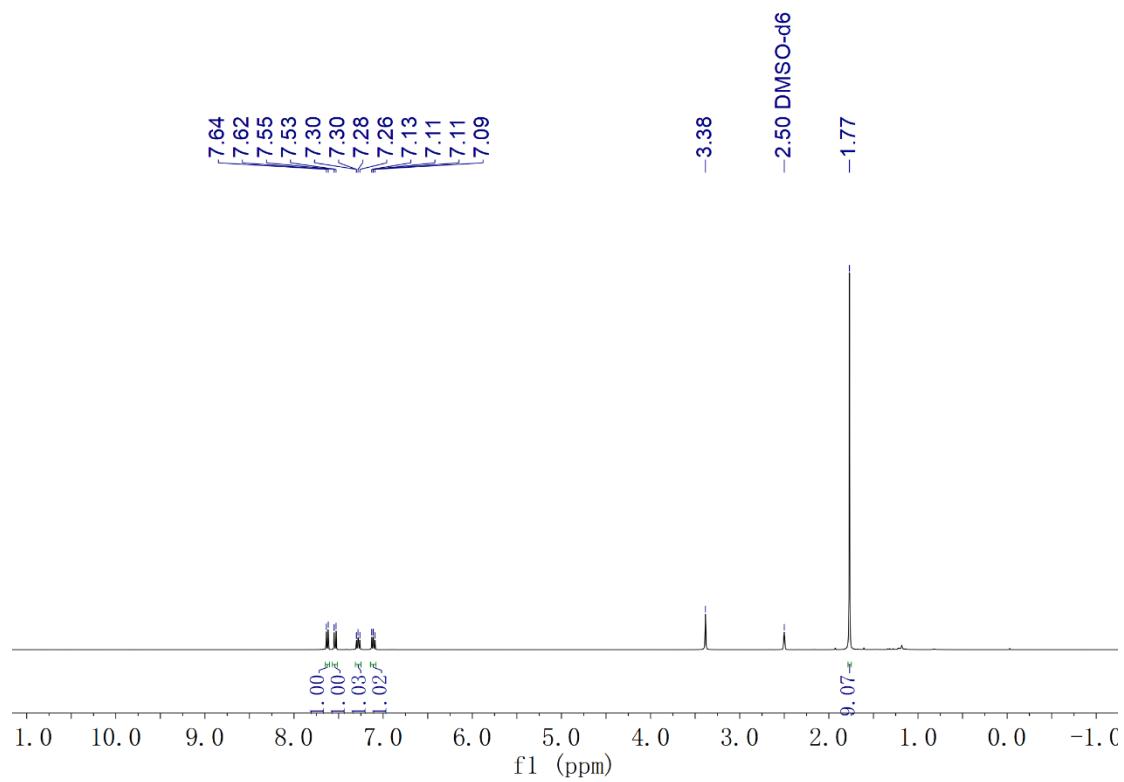
**5s  $^1\text{H}$ -NMR**



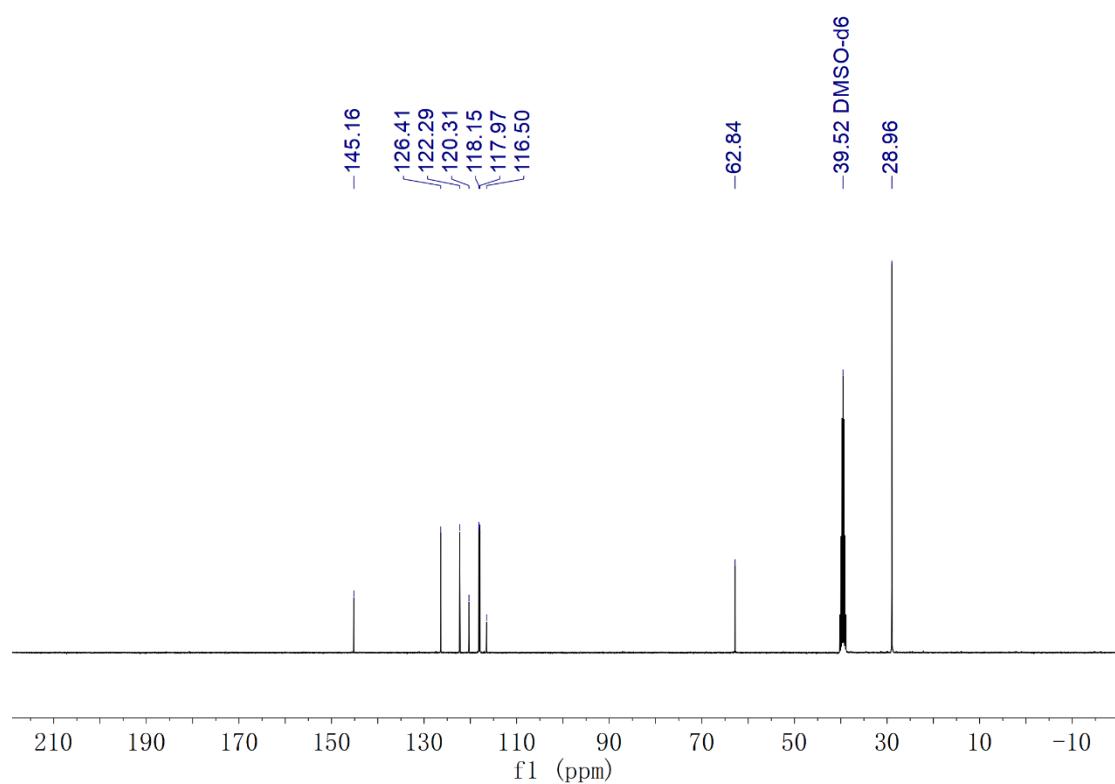
**5s  $^{13}\text{C}$ -NMR**



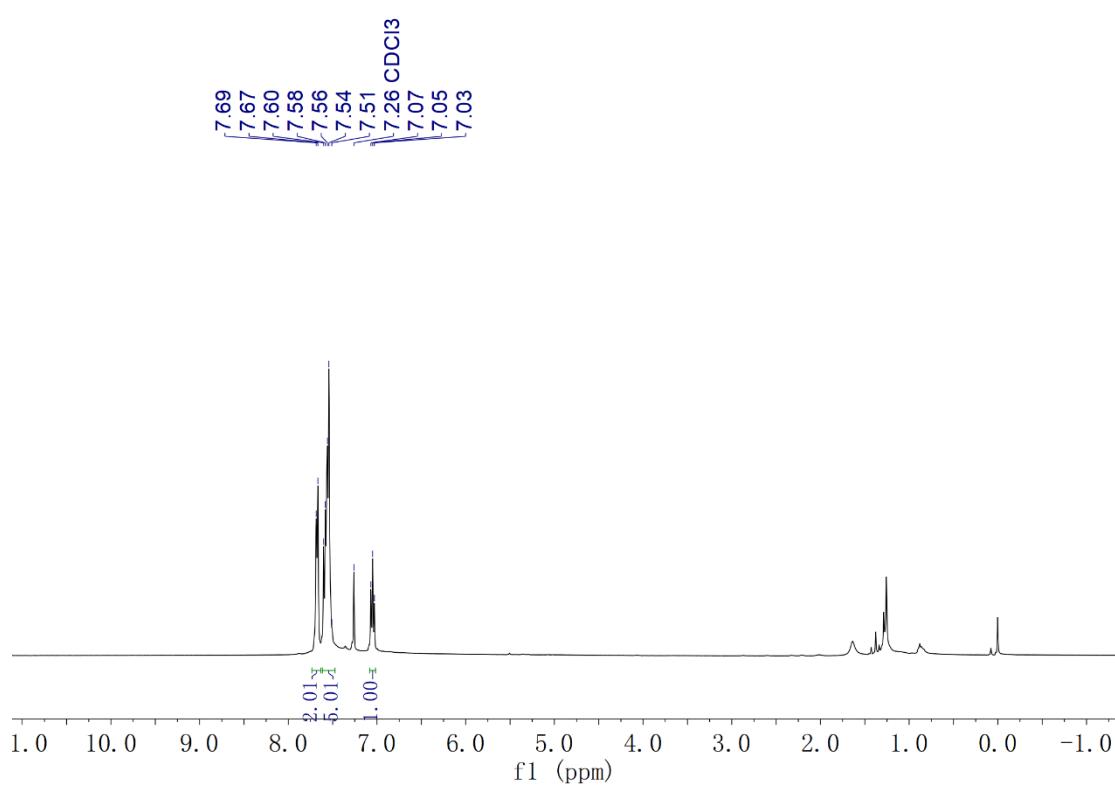
**5t  $^1\text{H}$ -NMR**



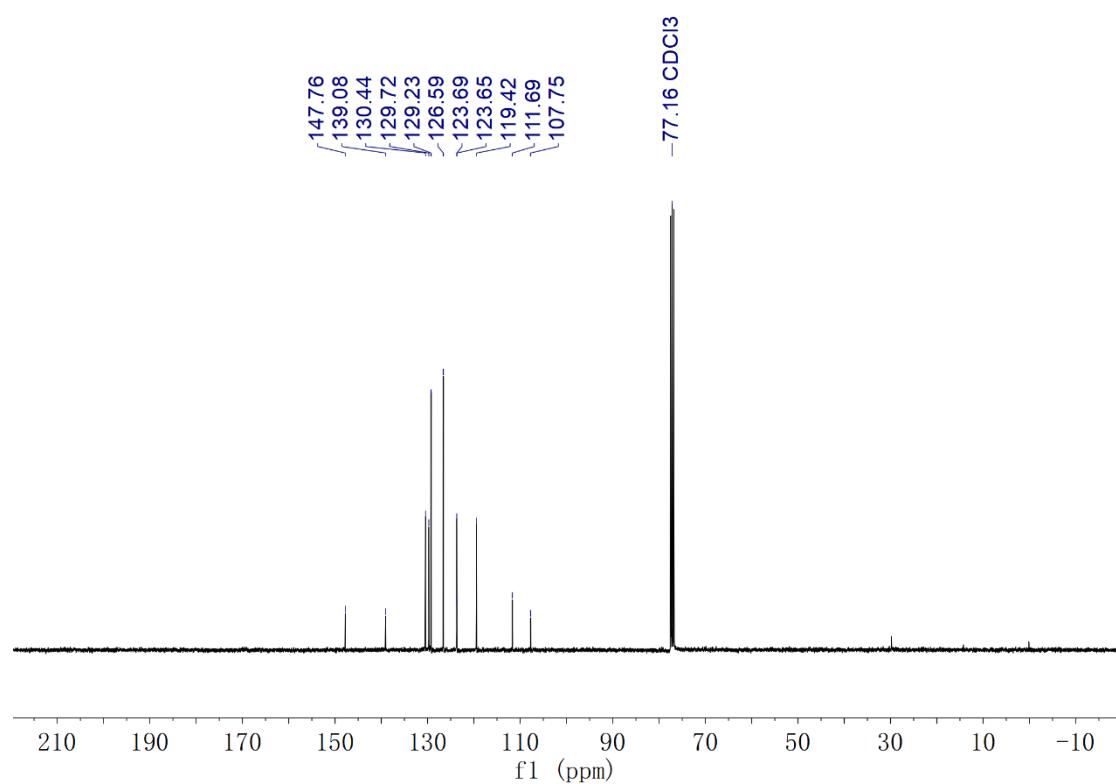
**5t  $^{13}\text{C}$ -NMR**



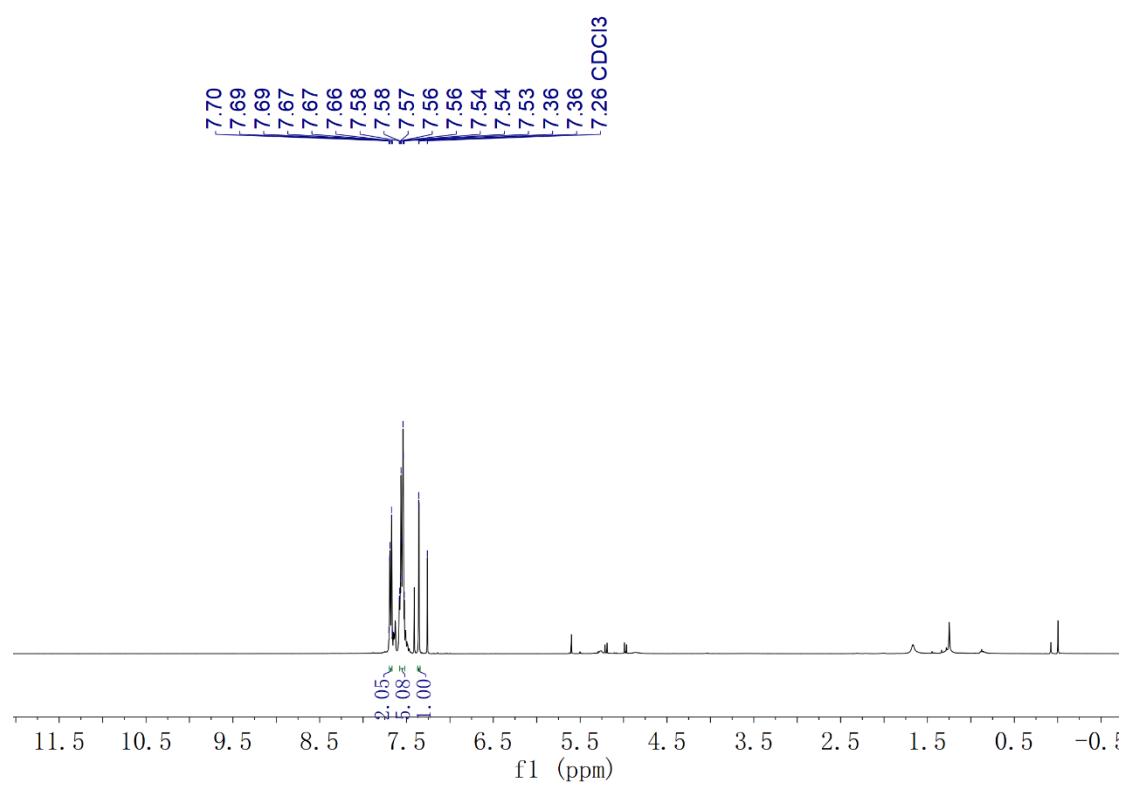
**3a  $^1\text{H}$ -NMR**



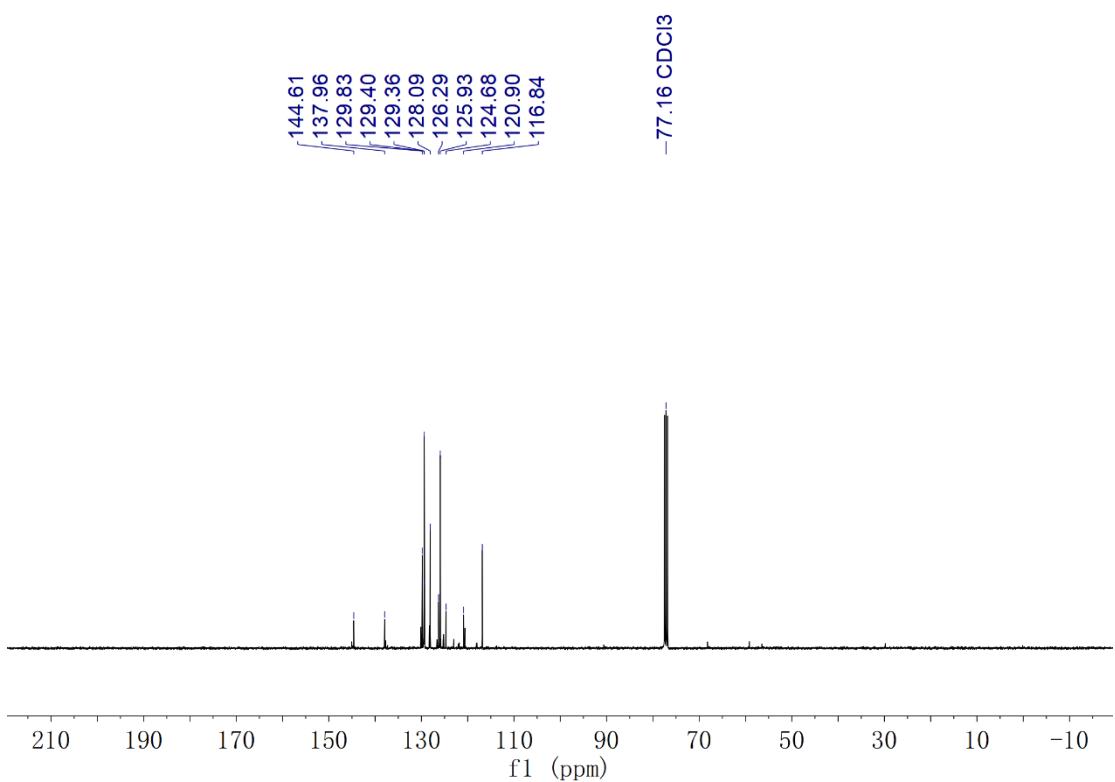
### 3a $^{13}\text{C}$ -NMR



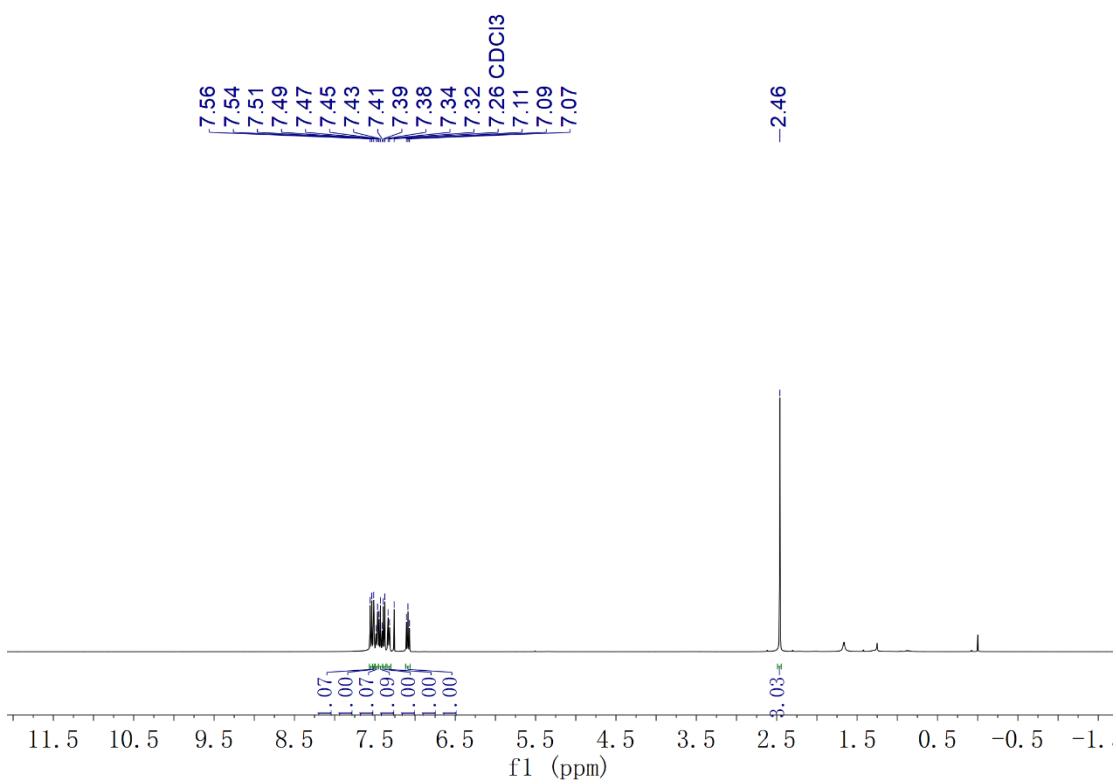
### 3b $^1\text{H-NMR}$



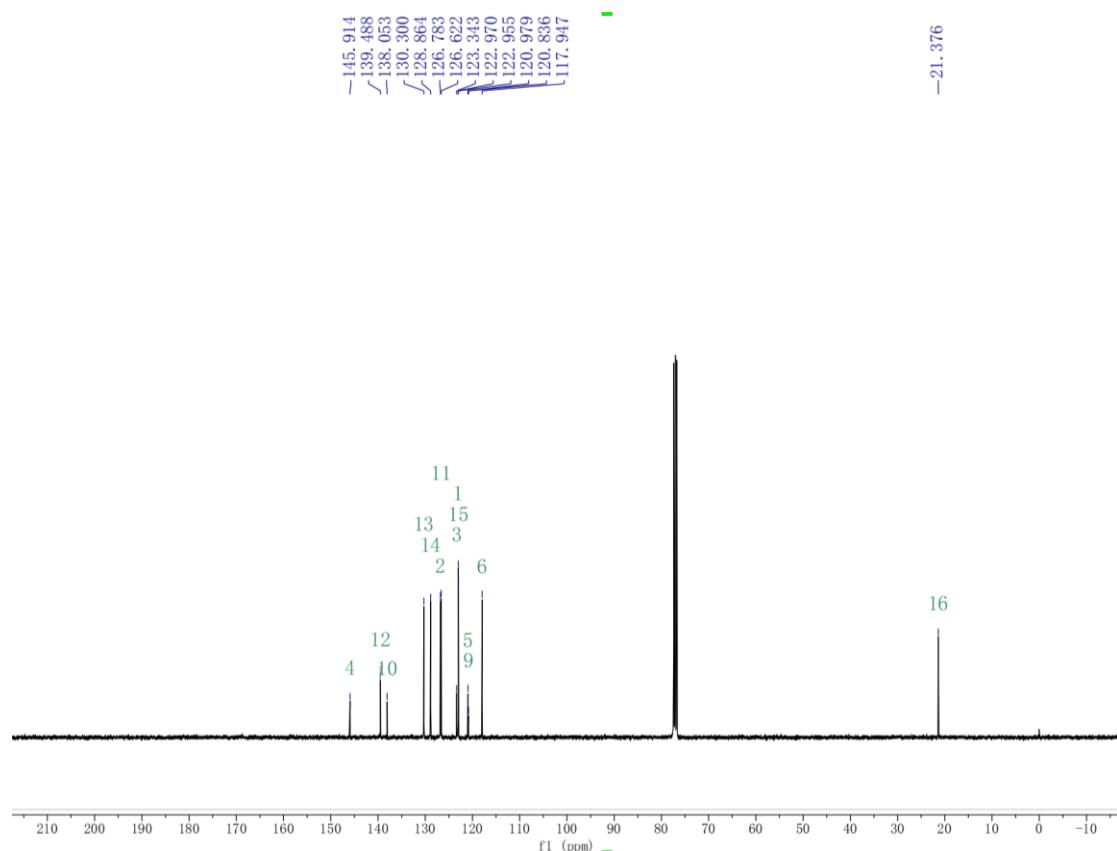
**3b  $^{13}\text{C}$ -NMR**



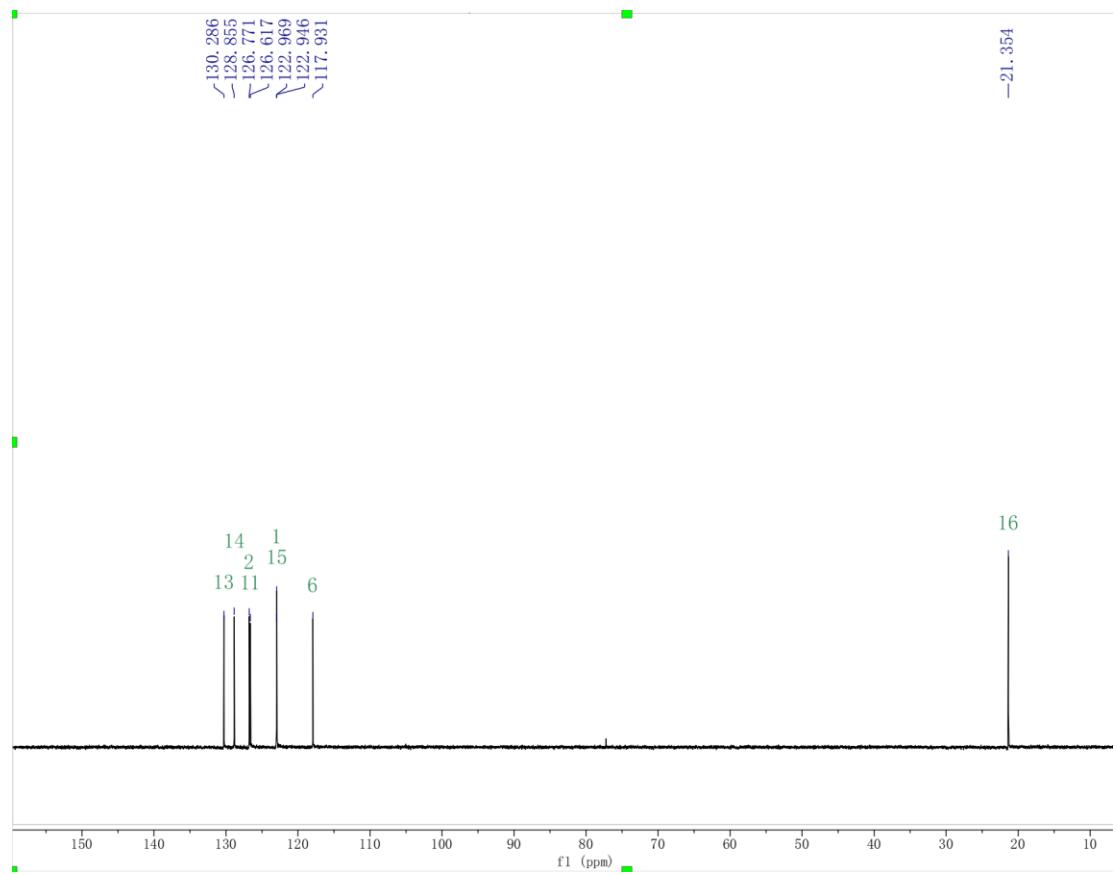
**3c  $^1\text{H}$ -NMR**



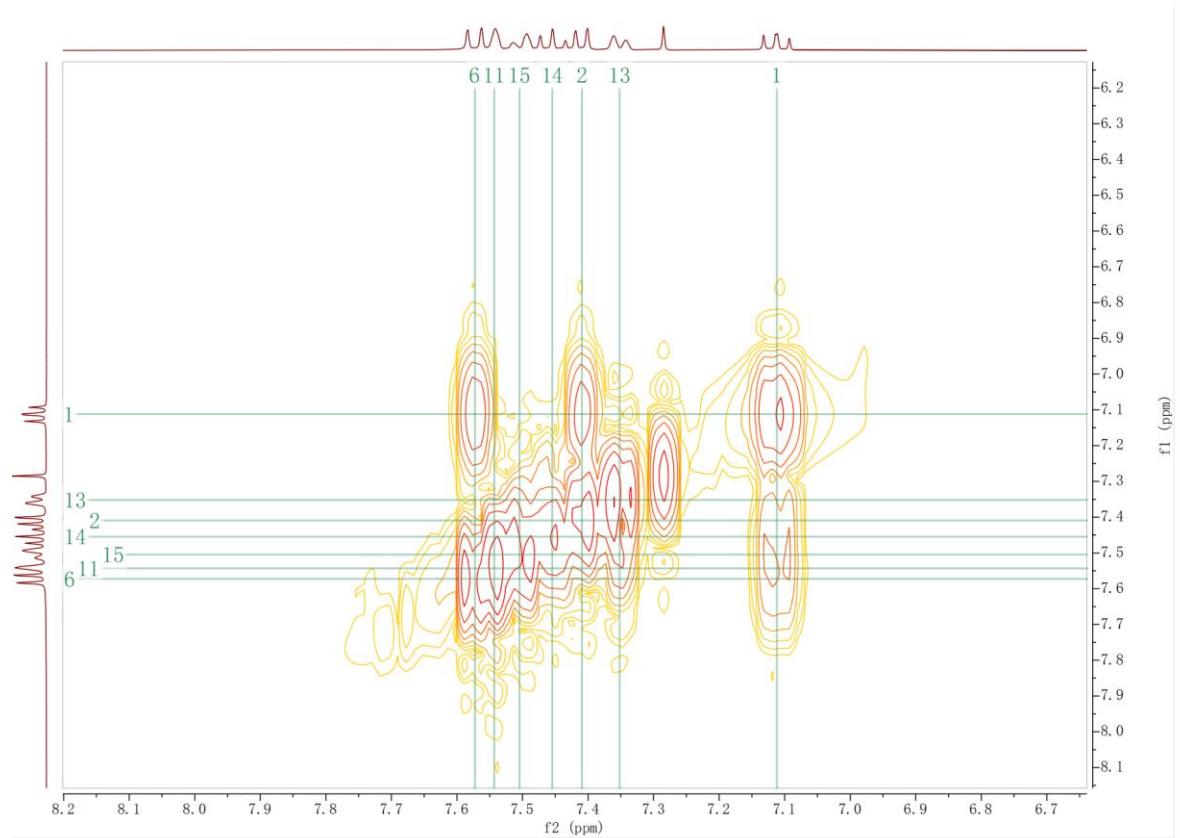
**3c**  $^{13}\text{C}$ -NMR



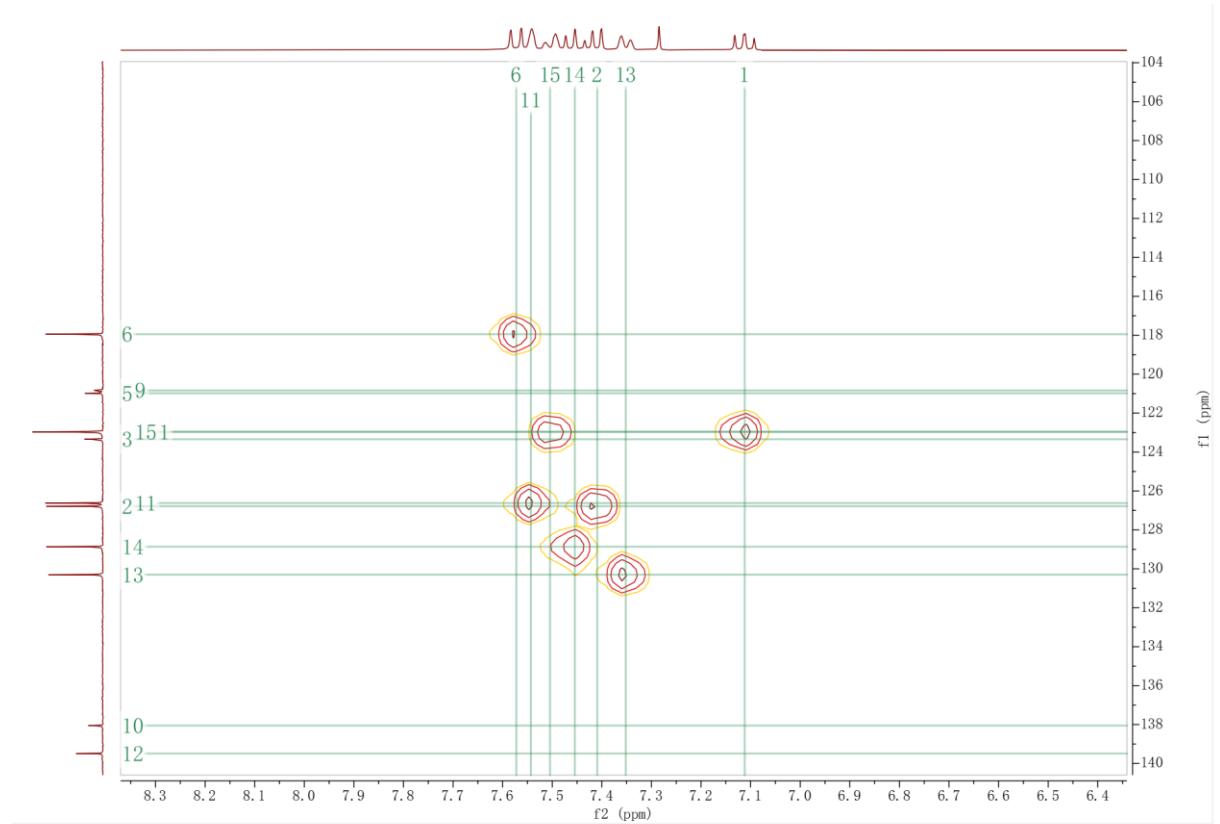
**3c DEPT135**



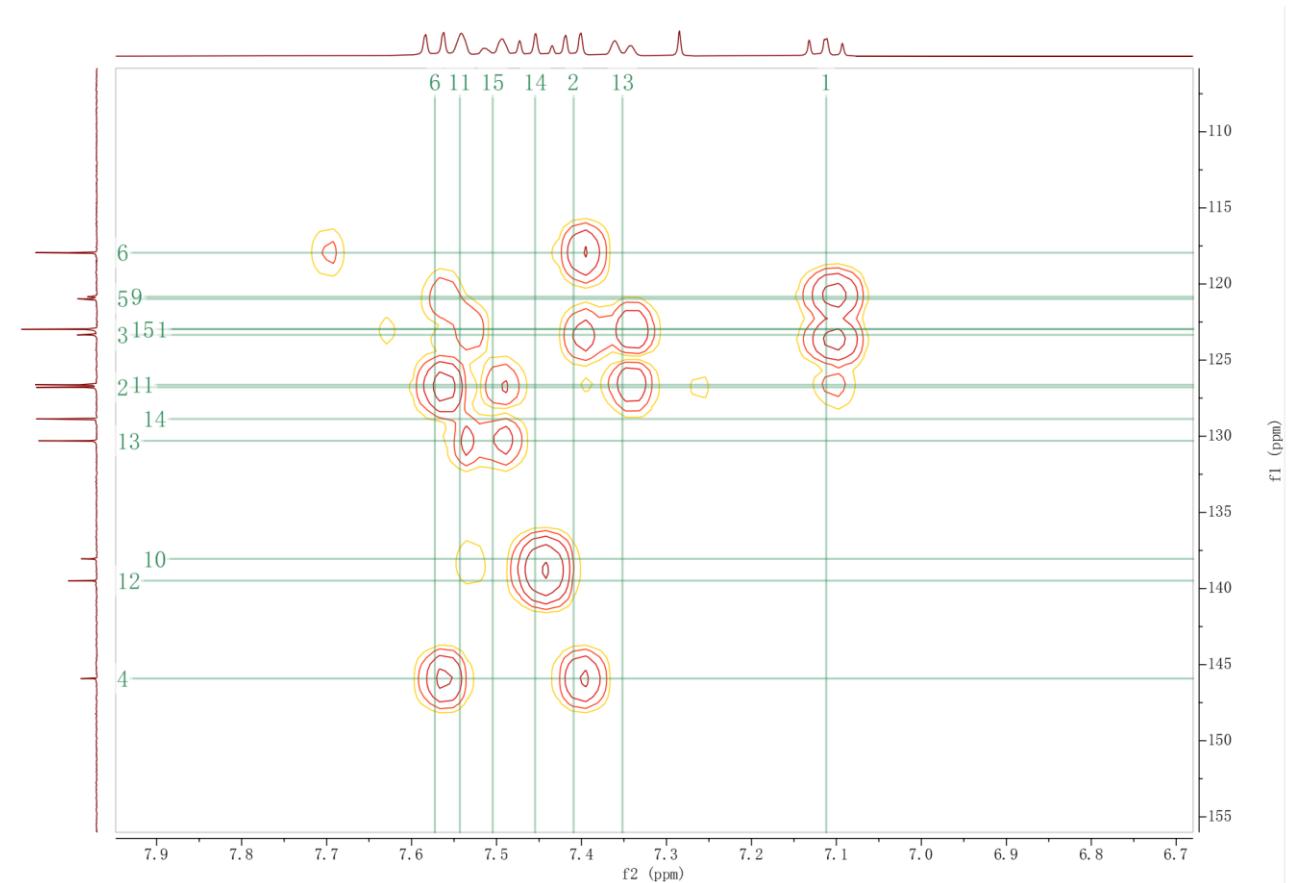
### 3c $^1\text{H}$ - $^1\text{H}$ COSY



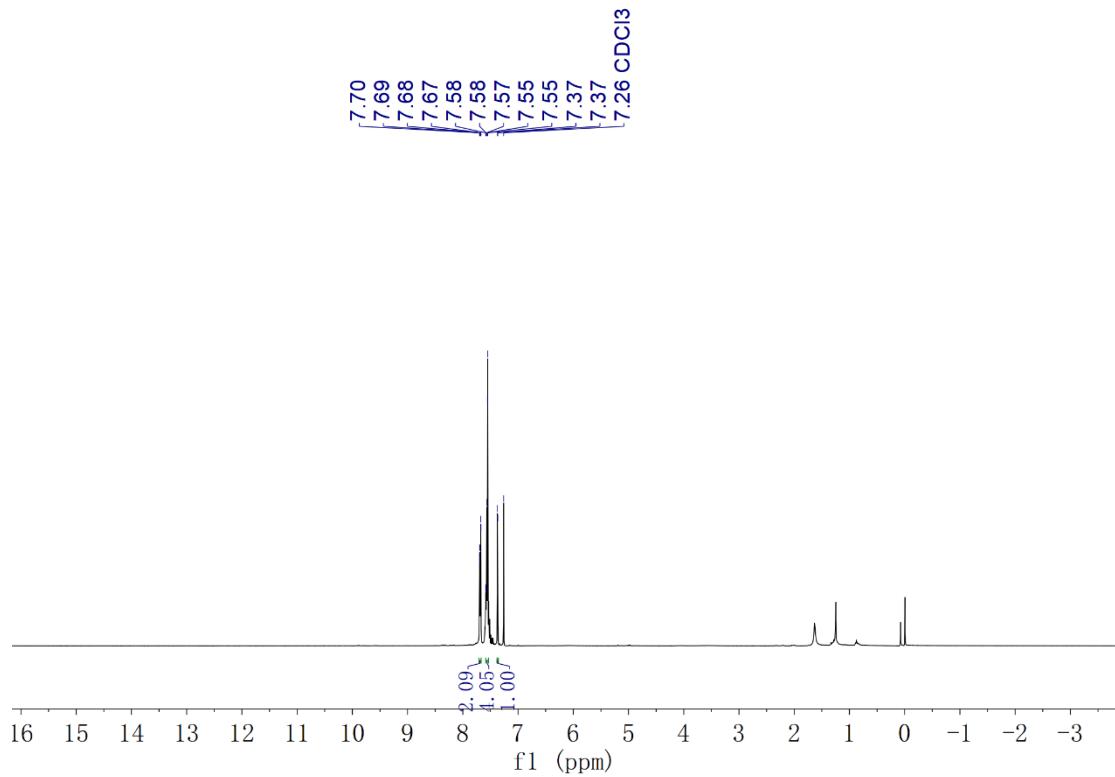
### 3c $^1\text{H}$ - $^{13}\text{C}$ HSQC



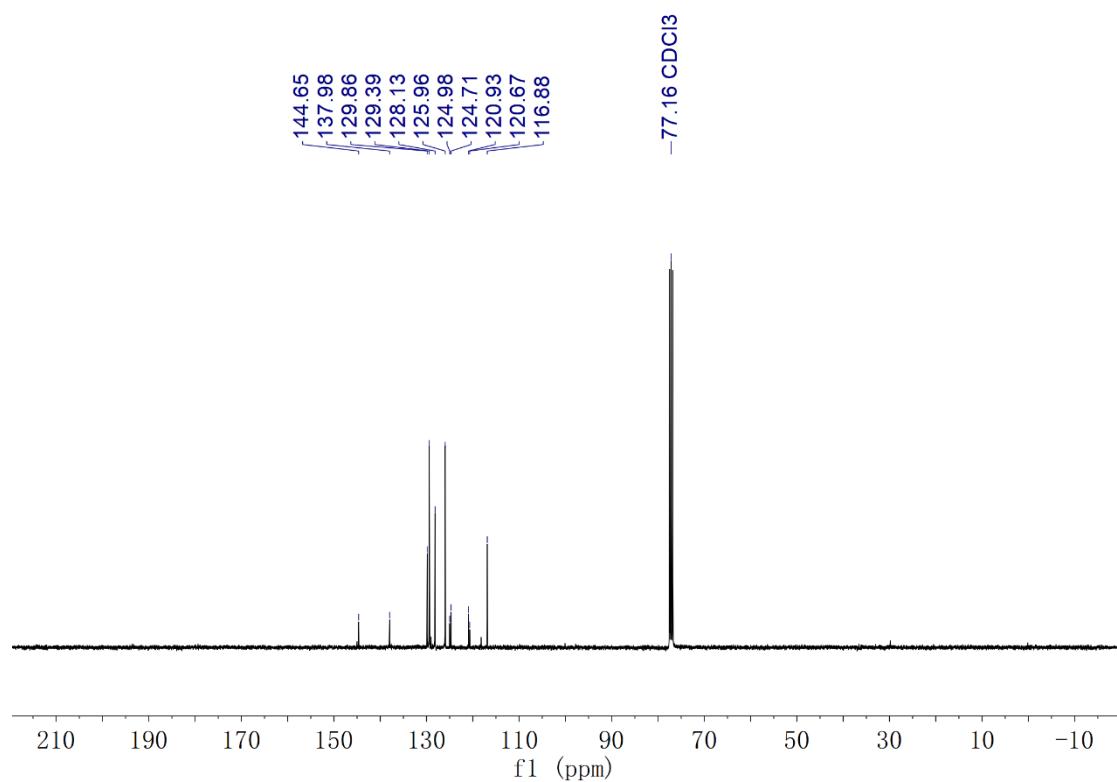
**3c  $^1\text{H}$ - $^{13}\text{C}$  HMBC**



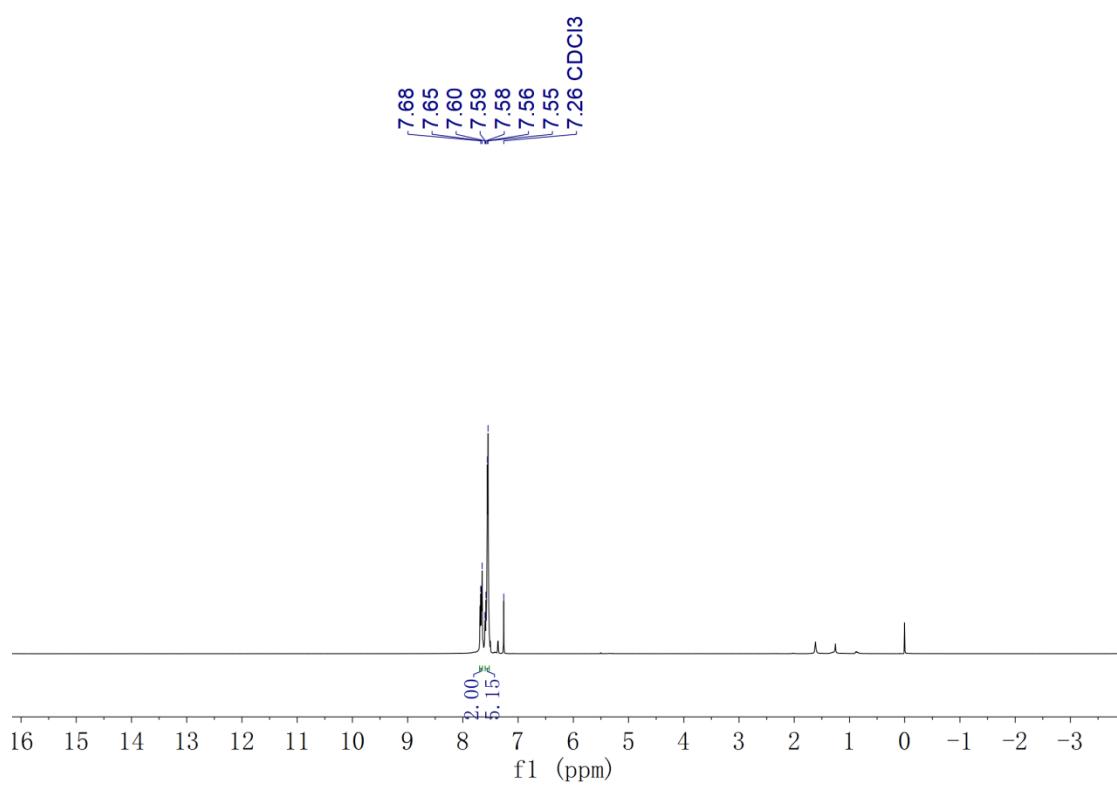
**3d  $^1\text{H}$ -NMR**



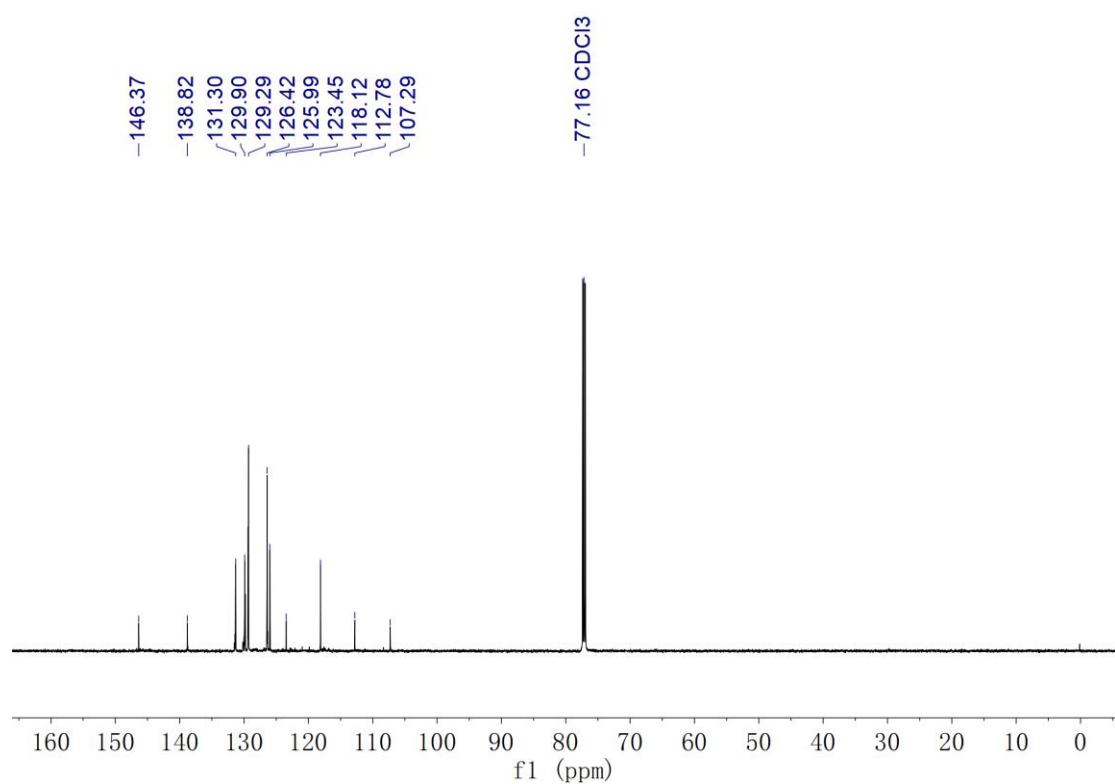
**3d  $^{13}\text{C}$ -NMR**



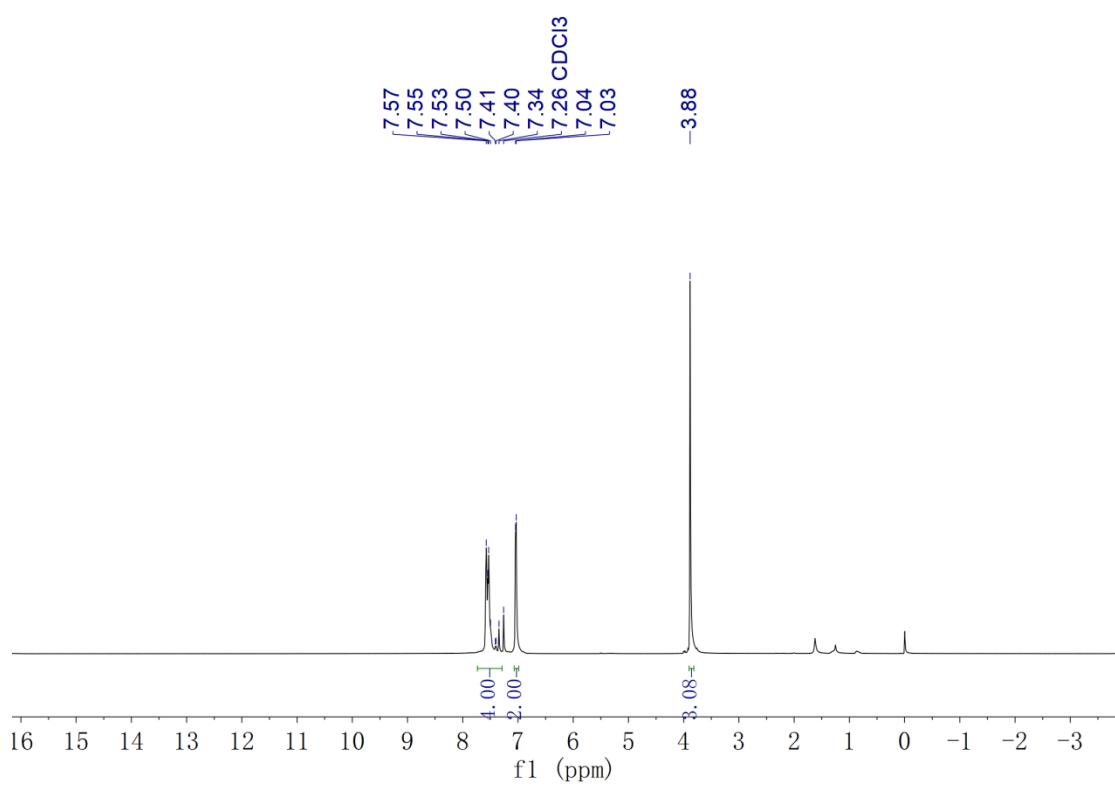
**3e  $^1\text{H}$ -NMR**



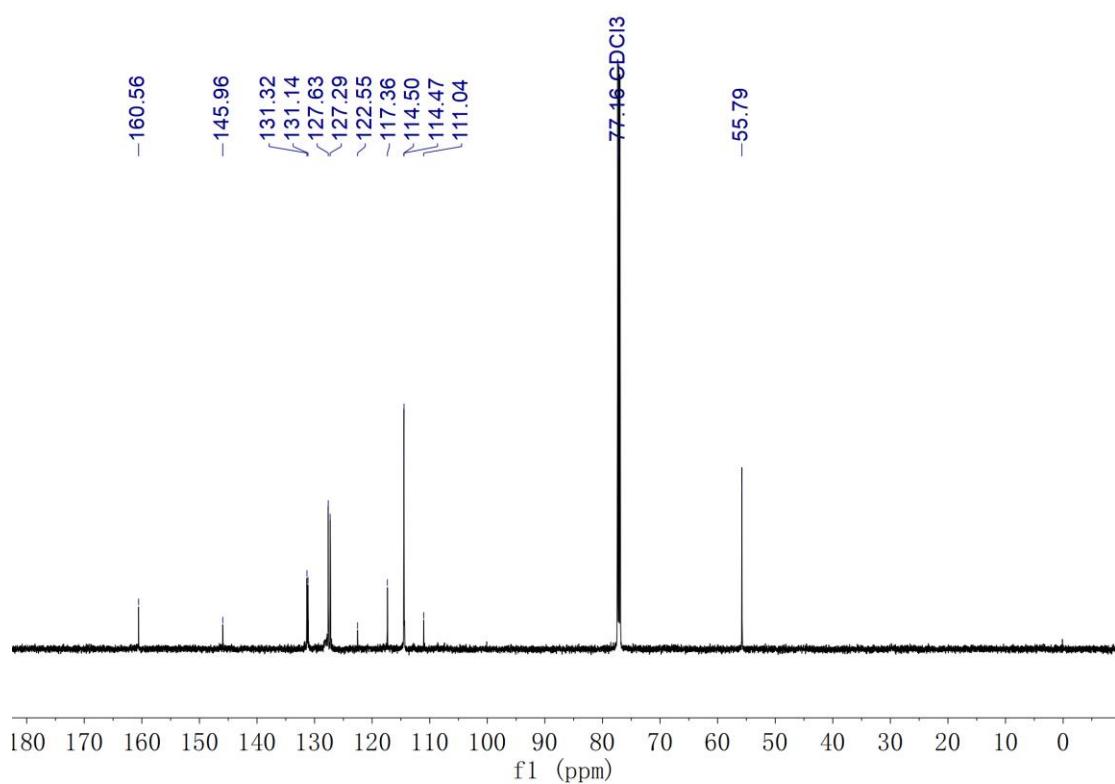
**3e  $^{13}\text{C}$ -NMR**



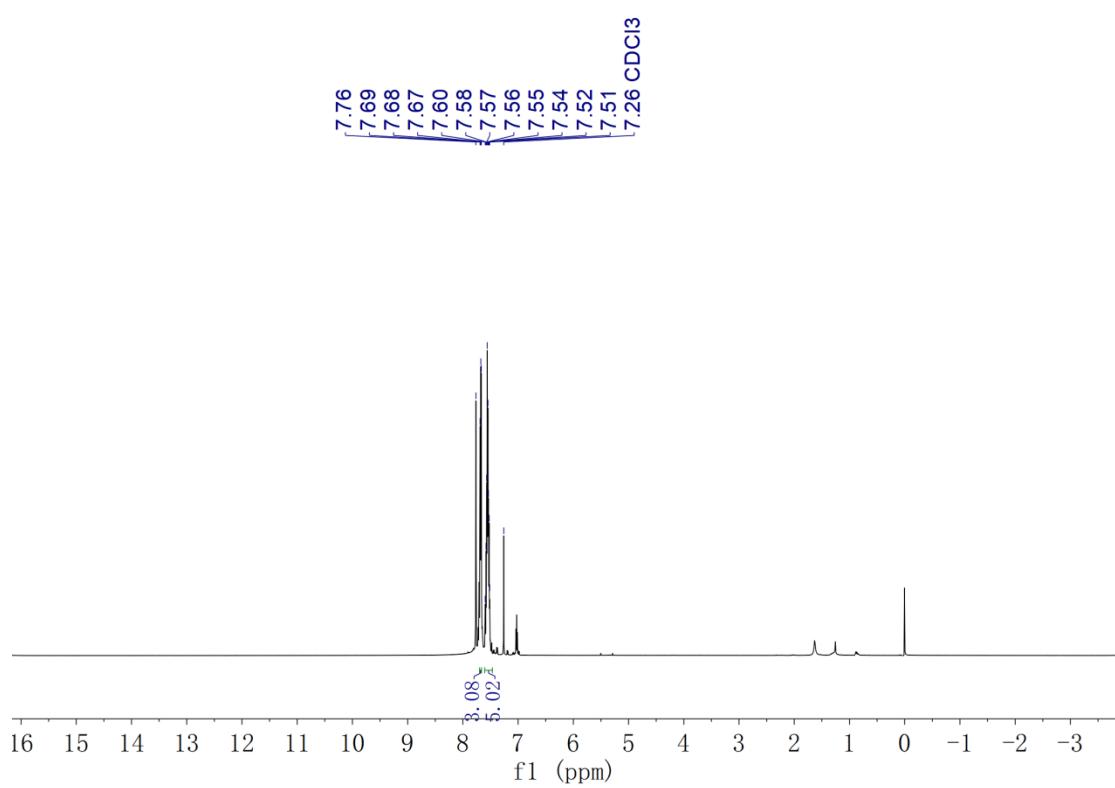
**3f  $^1\text{H}$ -NMR**



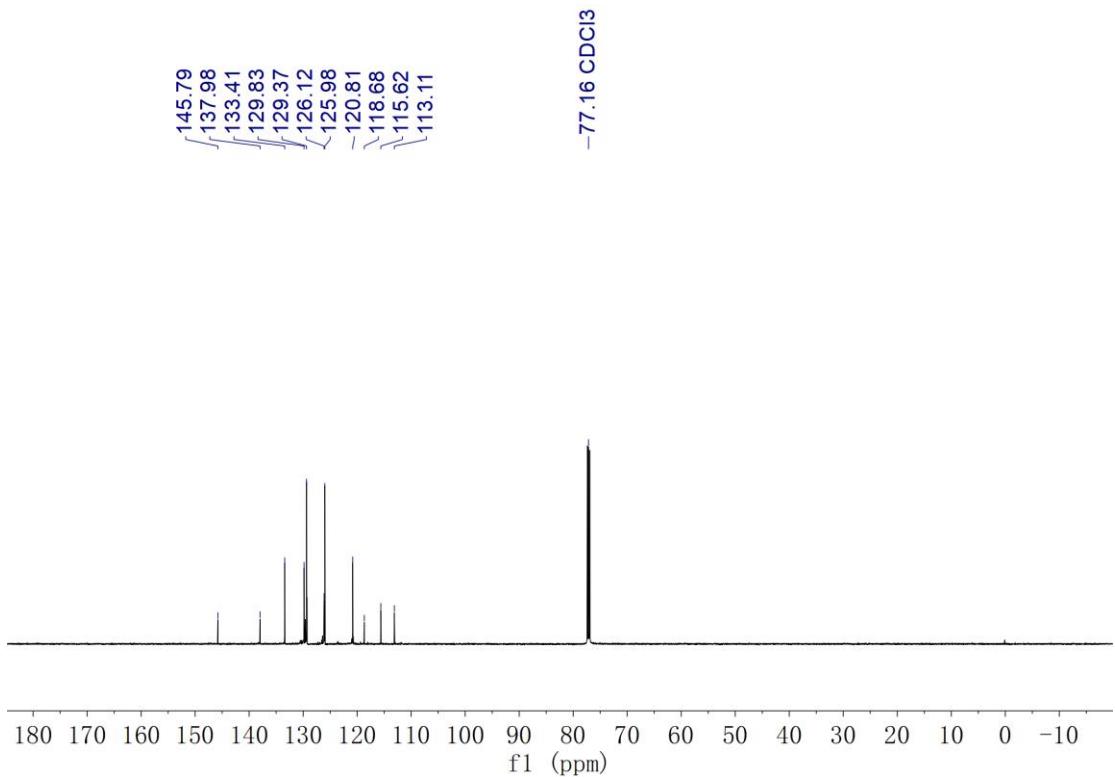
**3f  $^{13}\text{C}$ -NMR**



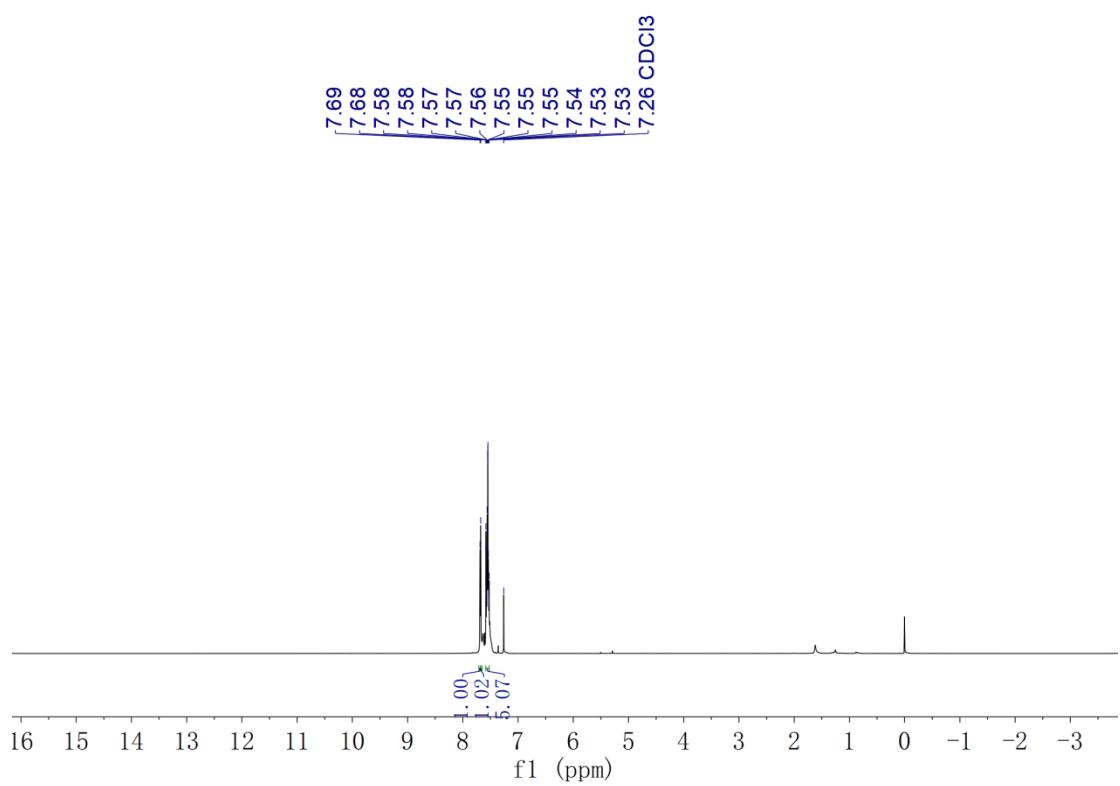
**3g  $^1\text{H}$ -NMR**



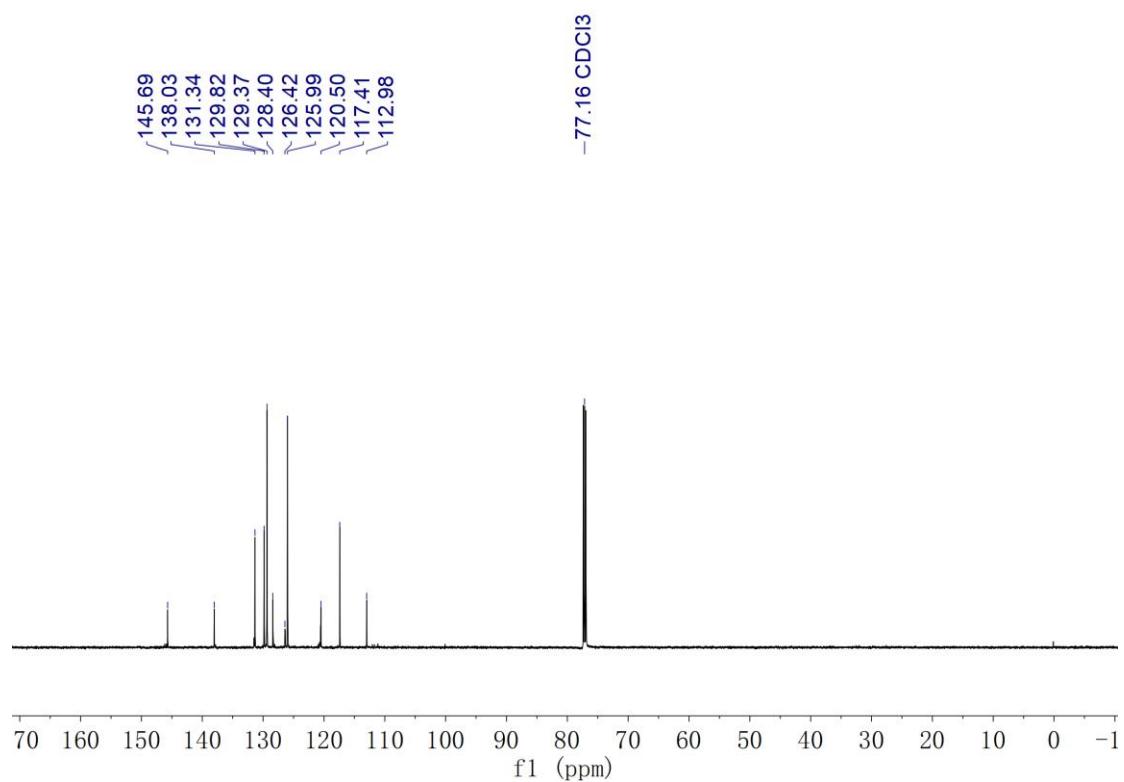
**3g  $^{13}\text{C}$ -NMR**



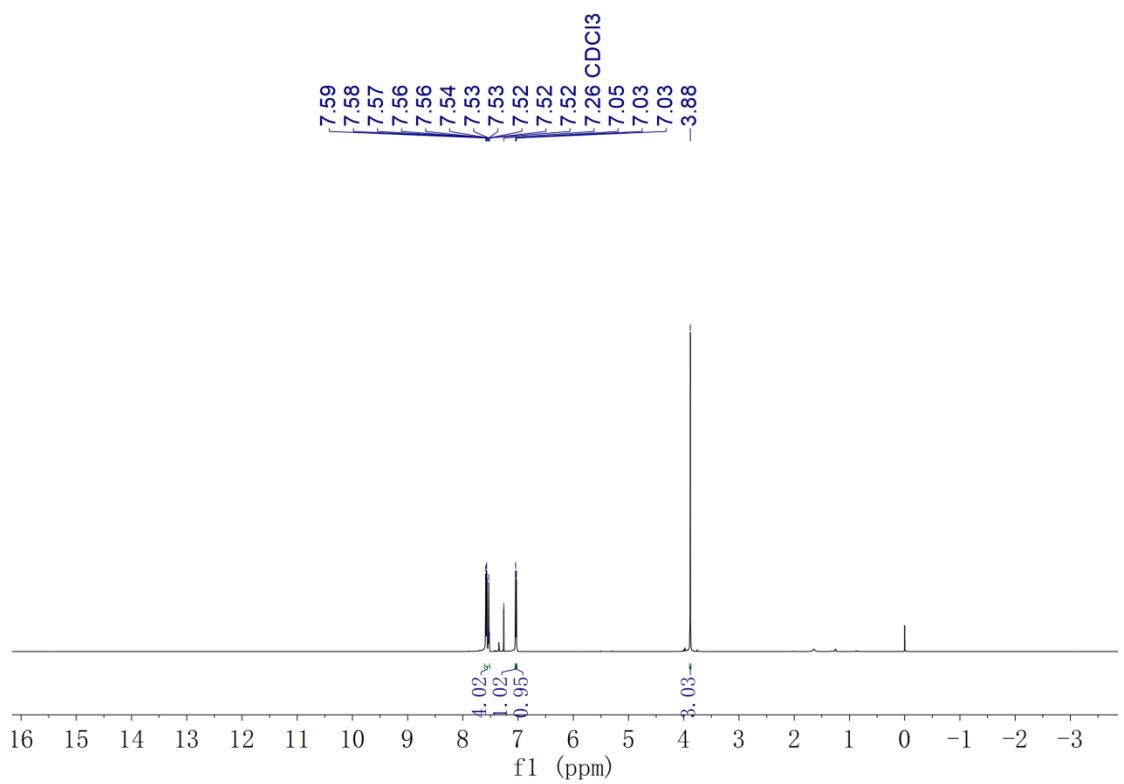
**3h  $^1\text{H}$ -NMR**



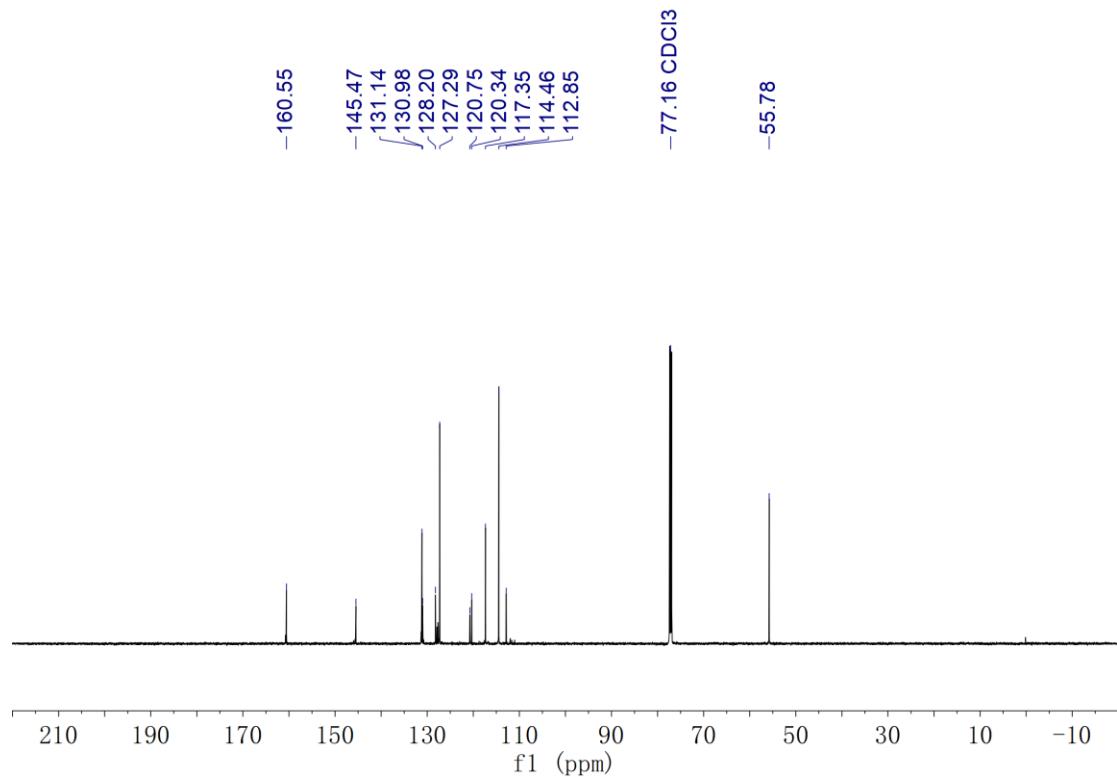
**3h  $^{13}\text{C}$ -NMR**



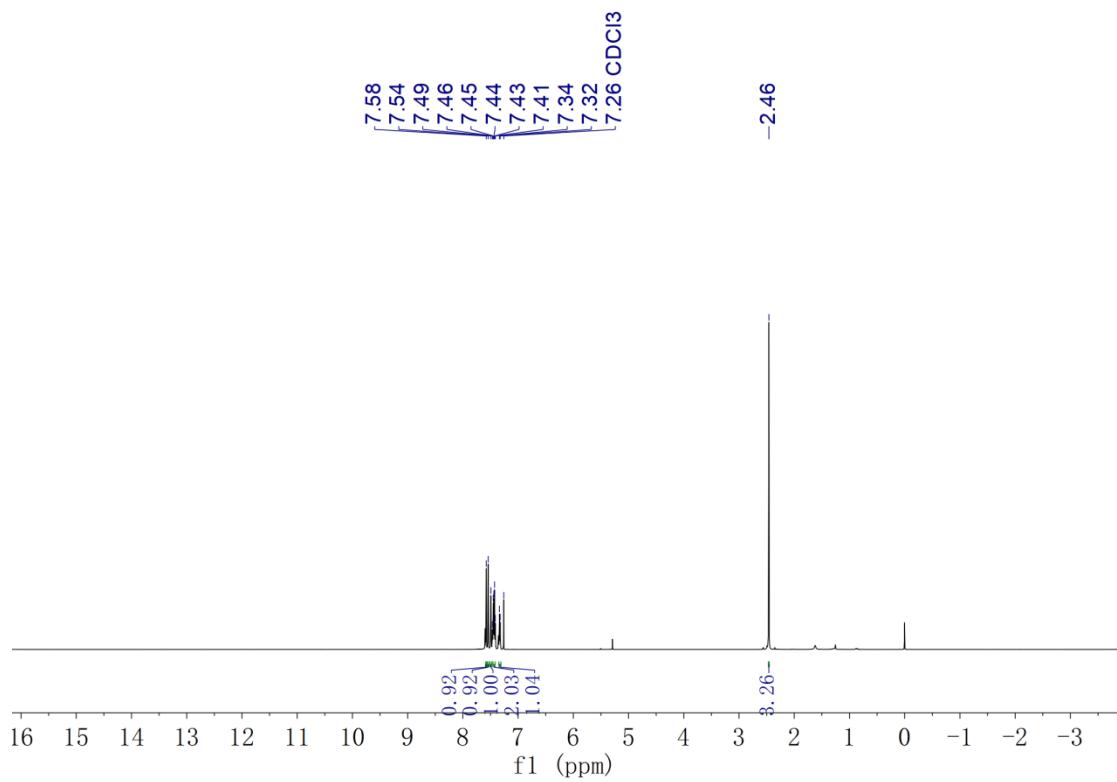
**3i  $^1\text{H}$ -NMR**



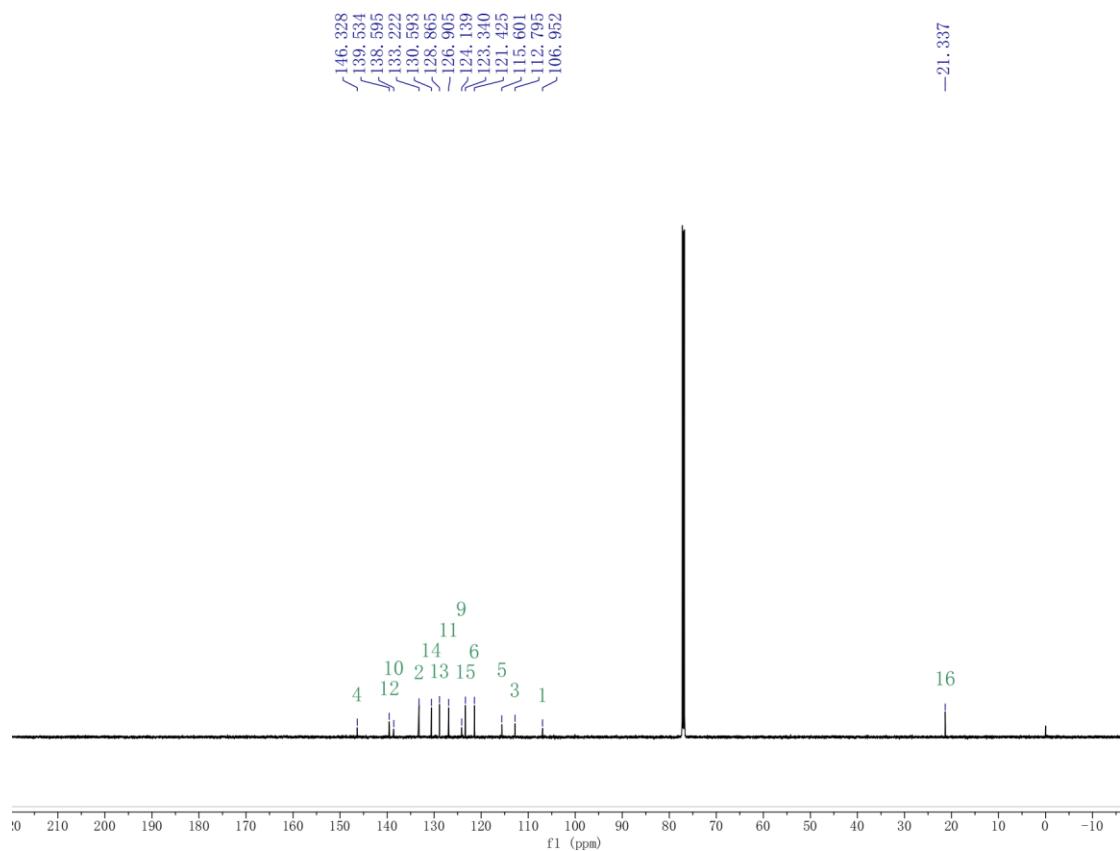
**3i  $^{13}\text{C}$ -NMR**

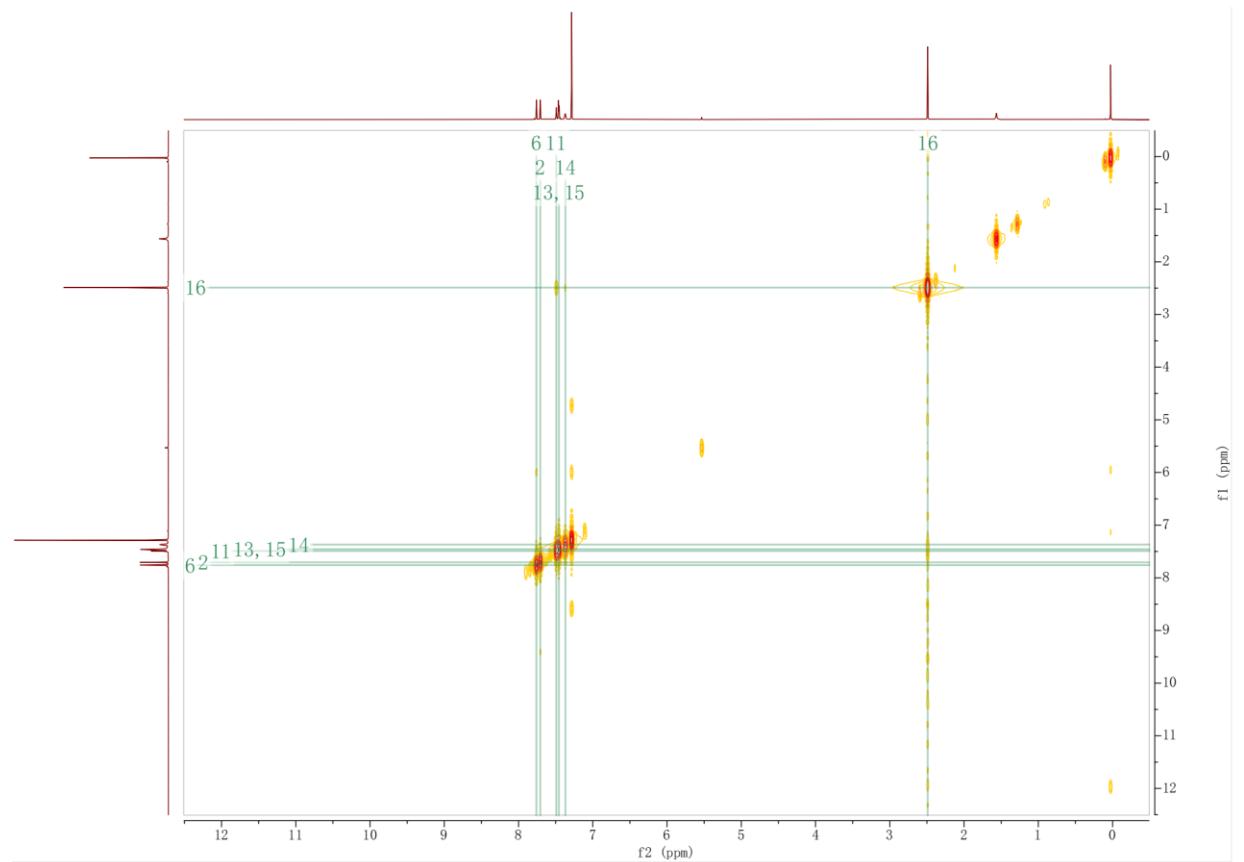
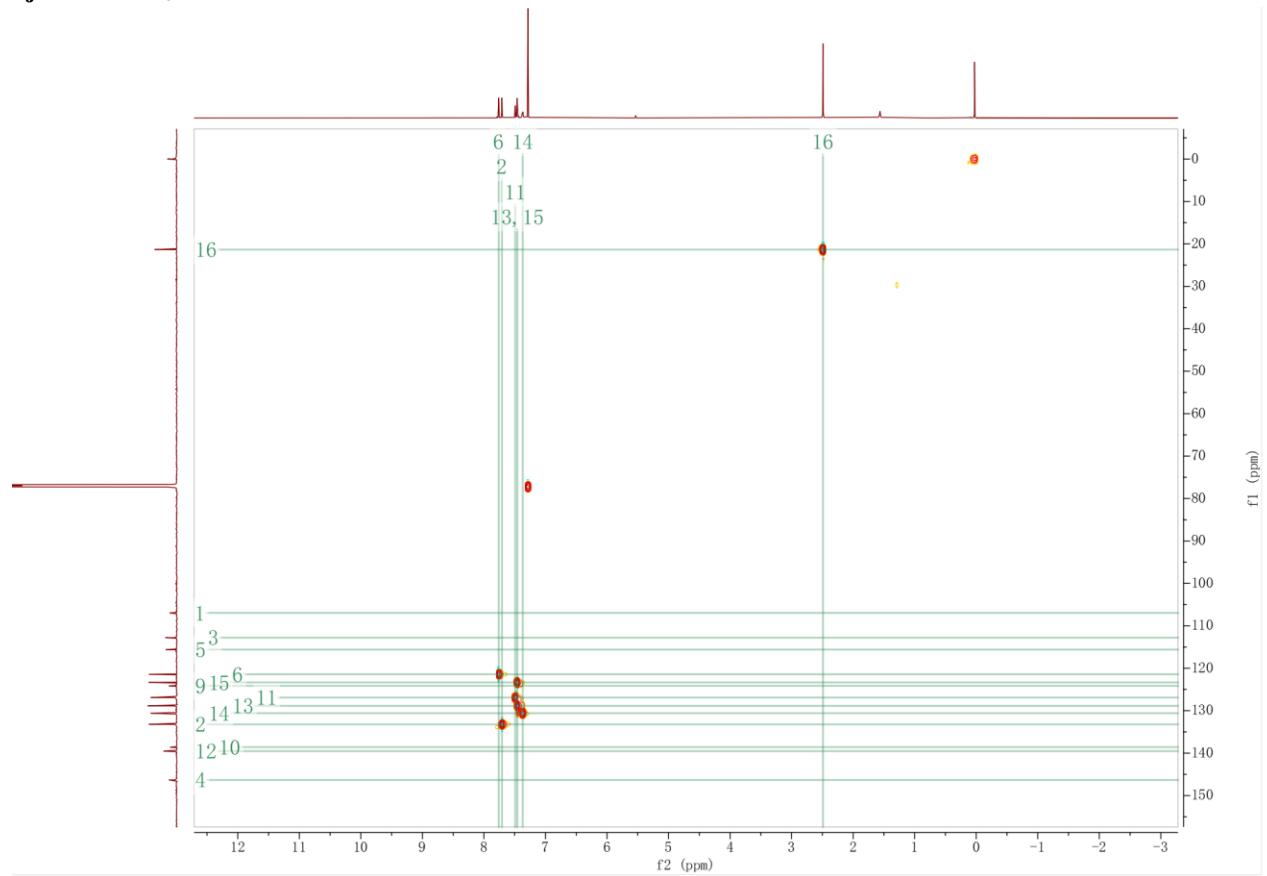


**3j  $^1\text{H}$ -NMR**

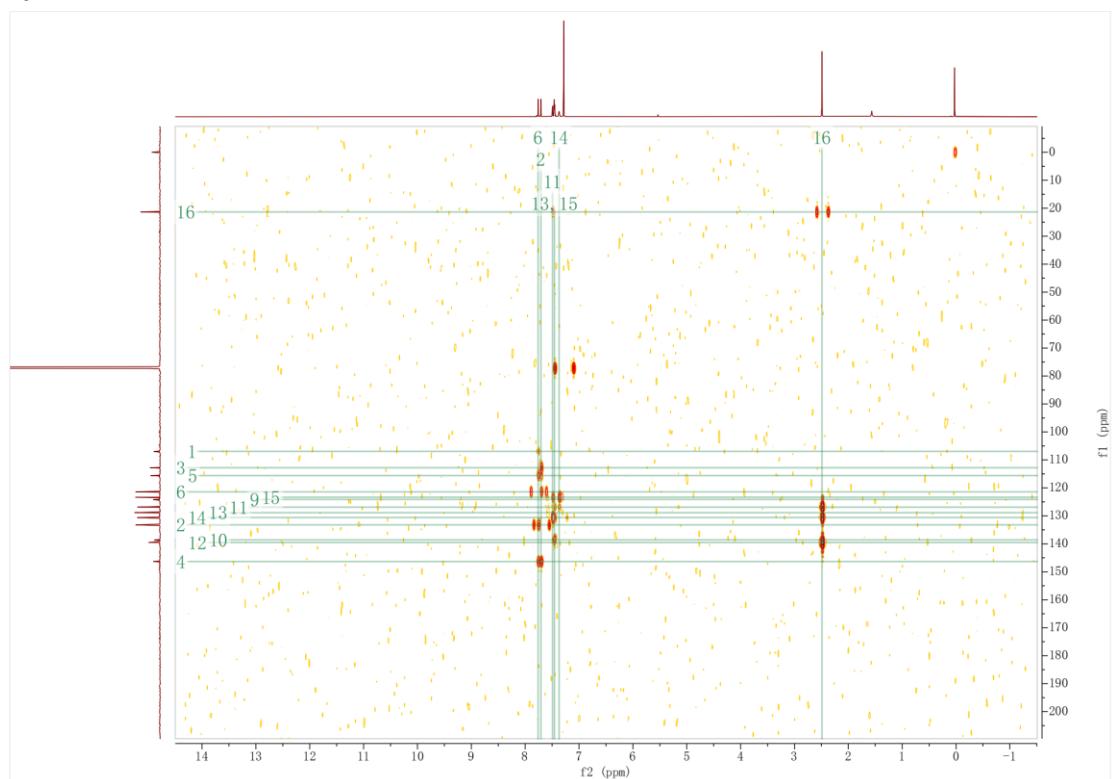


**3j**  $^{13}\text{C}$ -NMR

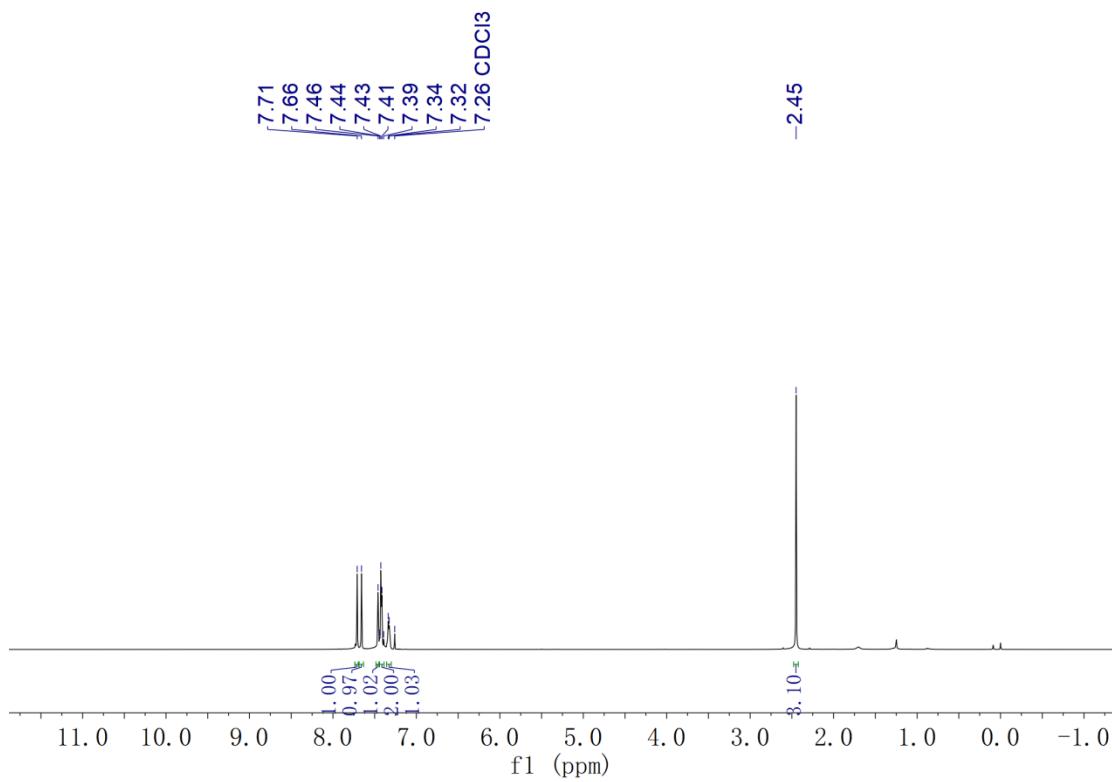


**3j  $^1\text{H}$ - $^1\text{H}$  COSY****3j  $^1\text{H}$ - $^{13}\text{C}$  HSQC**

**3j  $^1\text{H}$ - $^{13}\text{C}$  HMBC**



**4b  $^1\text{H}$ -NMR**



**4b**  $^{13}\text{C}$ -NMR

