

Supporting Information

for

A novel and efficient synthesis of phenanthrene derivatives via palladium/norbornadiene-catalyzed domino one-pot reaction

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Spectral data of products, and ¹H NMR and ¹³C NMR spectra for the products

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1. Spectral data of products

1-Methylphenanthrene (y-1)

Following the general procedure on a 0.30 mmol scale, compound **y-1** (56.5 mg, 98 %) was obtained as white solid. ${}^{1}\mathbf{H}$ **NMR** (500 MHz, CDCl₃) δ 8.71 (d, J = 8.2 Hz, 1H), 8.59 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.79 (d, J = 9.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.61 – 7.57 (m, 1H), 7.57 – 7.52 (m, 1H), 7.45 (d, J = 7.1 Hz, 1H), 2.76 (s, 3H). ${}^{13}\mathbf{C}$ **NMR** (126 MHz, CDCl₃) δ 134.91, 131.70, 130.85, 130.71, 130.39, 128.51, 127.80, 126.72, 126.58, 126.45, 126.18, 122.99, 122.90, 120.90, 19.99. HRMS (ESI) calcd. for $\mathbf{C}_{15}\mathbf{H}_{12}\left[\mathbf{M}+\mathbf{H}\right]^{+}$:193.1017, found 193.1014; $\left[\mathbf{M}+\mathbf{Na}\right]^{+}$: 215.0837, found 215.0835.

Chrysene (y-2)

Following the general procedure on a 0.30 mmol scale, compound **y-2** (43.8 mg, 64 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.82 (d, J = 8.4 Hz, 2H), 8.76 (d, J = 9.0 Hz, 2H), 8.04 (t, J = 8.2 Hz, 4H), 7.74 (m, J = 8.3, 7.0, 1.3 Hz, 2H), 7.71 – 7.64 (m, 2H). ¹³C **NMR** (126 MHz, CDCl₃) δ 132.18, 130.56, 128.57, 128.22, 127.35, 126.68, 126.38, 123.16, 121.22. HRMS (ESI) calcd. for C₁₈H₁₂ [M+H]⁺:229.1017, found 229.1012; [M+Na]⁺: 251.0837, found 251.0834.

1-Methoxyphenanthrene (y-3)

Following the general procedure on a 0.30 mmol scale, compound **y-3** (58.1 mg, 93 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.70 (d, J = 8.2 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 9.1 Hz, 1H), 7.92 (dd, J = 7.9, 1.1 Hz, 1H), 7.78 (d, J = 9.1 Hz, 1H), 7.68 – 7.58 (m, 3H), 7.04 (d, J = 7.8 Hz, 1H), 4.07 (s, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 154.99, 131.27, 130.54, 129.09, 127.56, 125.69, 125.62, 125.43, 125.08, 122.22, 119.39, 114.04, 104.86, 54.76. HRMS (ESI) calcd. for $C_{15}H_{12}O$ [M+H] $^{+}$:209.0966, found 209.0970; [M+Na] $^{+}$: 231.0786, found 231.0789.

1-Phenylphenanthrene (y-4)

Following the general procedure on a 0.30 mmol scale, compound **y-4** (67.14 mg, 88 %) was obtained as colorless oil. 1 **H NMR** (500 MHz, CDCl₃) δ 8.78 (dd, J = 8.3, 4.6 Hz, 2H), 7.91 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.75 – 7.69 (m, 3H), 7.66 – 7.62 (m, 1H), 7.58 (dd, J = 7.2, 1.0 Hz, 1H), 7.54 (d, J = 4.3 Hz, 4H), 7.51 – 7.46 (m, 1H). 13 **C NMR** (126 MHz, CDCl₃) δ 141.14, 141.04, 131.76, 130.71, 130.44, 130.25, 129.95, 128.49, 128.30, 127.92, 127.27, 126.89, 126.72, 126.68, 125.98, 124.63, 122.99, 122.17. HRMS (ESI) calcd. for $C_{20}H_{14}$ [M+H] $^{+}$:255.1174, found 255.1178; [M+Na] $^{+}$: 277.0993, found 277.0995.

1-Ethylphenanthrene (y-5)

Following the general procedure on a 0.30 mmol scale, compound **y-5** (56.3 mg, 91 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.74 (d, J = 7.8 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.93 (dd, J = 7.8, 1.3 Hz, 1H), 7.81 (d, J = 9.2 Hz, 1H), 7.75 – 7.56 (m, 3H), 7.51 (d, J = 7.1 Hz, 1H), 3.21 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.6 Hz, 3H). 13 C **NMR** (126 MHz, CDCl₃) δ 141.05, 131.67, 130.91, 130.68, 130.08, 128.46, 126.73, 126.56, 126.46, 126.36, 126.22, 123.01, 122.58, 120.91, 15.54. HRMS (ESI) calcd. for $C_{16}H_{14}$ [M+H] $^{+}$:207.1174, found 207.1179; [M+Na] $^{+}$: 229.0993, found 277.0999.

1-Isopropylphenanthrene (y-6)

Following the general procedure on a 0.30 mmol scale, compound **y-6** (59.5 mg, 90 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.76 (d, J = 8.2 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 8.14 (d, J = 9.3 Hz, 1H), 7.94 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 9.3 Hz, 1H), 7.71 – 7.60 (m, 4H), 3.88 (m, 1H), 1.49 (d, J = 6.8 Hz, 6H). 13 **C NMR** (126 MHz, CDCl₃) δ 145.27, 131.49, 130.94, 130.64, 129.58, 128.33, 126.64, 126.51, 126.42, 126.34, 123.01, 122.73, 122.08, 120.65, 28.84, 23.75. HRMS (ESI) calcd. for $C_{17}H_{16}$ [M+H] $^{+}$:221.1330, found 221.1327; [M+Na] $^{+}$: 243.1150, found 243.1148.

1,2-Dimethylphenanthrene (y-7)

Following the general procedure on a 0.30 mmol scale, compound **y-7** (53.8 mg, 87 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.71 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 8.5 Hz, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.80 (d, J = 9.2 Hz, 1H), 7.67 (m, 1H), 7.62 – 7.58 (m, 1H), 7.51 (d, J = 8.5 Hz, 1H), 2.70 (s, 3H), 2.57 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 134.39, 132.31, 131.14, 130.94, 130.78, 129.08, 128.73, 128.31, 126.64, 126.44, 126.06, 122.88, 122.69, 120.19, 20.91, 15.04. HRMS (ESI) calcd. for $C_{16}H_{14}[M+H]^{+}$:207.1174, found 207.1171; $[M+Na]^{+}$: 229.0993, found 229.0989.

1-Methyl-4-nitrophenanthrene (y-8)

Following the general procedure on a 0.30 mmol scale, compound **y-8** (60.5 mg, 85 %) was obtained as light yellow solid. 1 **H NMR** (500 MHz, CDCl₃) δ 9.48 (s, 1H), 8.76 (d, J = 8.3 Hz, 1H), 8.25 (s, 1H), 8.00 – 7.96 (m, 3H), 7.81 – 7.76 (m, 1H), 7.74 – 7.70 (m, 1H), 2.85 (s, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 145.33, 137.02, 134.61, 131.90, 130.85, 130.80, 130.00, 128.89, 127.87, 127.81, 123.15, 122.05, 121.00, 117.23, 20.17. HRMS (ESI) calcd. for $C_{15}H_{11}NO_{2}$ [M+H] $^{+}$:238.0868, found 238.0872; [M+Na] $^{+}$: 260.0687, found 260.0683.

1-Nitrophenanthrene (y-9)

$$O_2N$$

Following the general procedure on a 0.30 mmol scale, compound **y-9** (50.2 mg, 75 %) was obtained as light yellow solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.99 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 9.3 Hz, 1H), 8.21 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 9.1 Hz, 2H), 7.79 – 7.70 (m, 3H). 13 C **NMR** (126 MHz, CDCl₃) δ 147.87, 131.77, 131.59, 130.63, 129.24, 128.82, 127.96, 127.93, 127.78, 125.12, 124.18, 123.24, 122.92, 120.12. HRMS (ESI) calcd. for $C_{14}H_9NO_2$ [M+H] $^+$:224.0712, found 224.0716; [M+Na] $^+$: 246.0531, found 246.0537.

1-(Trifluoromethyl)phenanthrene (y-10)

Following the general procedure on a 0.30 mmol scale, compound **y-10** (70.2 mg, 95 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.92 (d, J = 8.4 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 8.14 (dd, J = 9.3, 1.9 Hz, 1H), 8.00 (d, J = 7.4 Hz, 1H), 7.96 (d, J = 9.0 Hz, 1H), 7.91 (d, J = 9.3 Hz, 1H), 7.76 – 7.67 (m, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 130.49, 130.21, 128.88, 127.84, 127.61, 127.29, 126.33, 126.21, 125.84, 125.56, 125.20, 124.05, 123.79, 121.75, 121.04. HRMS (ESI) calcd. for $C_{15}H_9F_3$ [M+H] $^{+}$:247.0735, found 247.0739; [M+Na] $^{+}$: 269.0554, found 269.0558.

1-Fluorophenanthrene (y-11)

Following the general procedure on a 0.30 mmol scale, compound **y-11** (51.2 mg, 87 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.69 (d, J = 8.2 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 7.95 (d, J = 7.6 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.68 – 7.65 (m, 1H), 7.61 (m, 1H), 7.32 (dd, J = 9.8, 7.6 Hz, 1H). ¹³**C NMR** (126 MHz, CDCl₃) δ 160.23, 158.24, 132.12,

132.08, 132.02, 129.59, 129.57, 128.73, 127.34, 127.32, 127.06, 126.95, 126.46, 126.39, 122.96, 121.57, 121.45, 118.49, 118.43, 118.36, 118.33, 111.04, 110.88. HRMS (ESI) calcd. for $C_{14}H_9F$ [M+H] $^+$:197.0767, found 197.0773; [M+Na] $^+$: 219.0586, found 219.0589.

1-Chlorophenanthrene (y-12)

Following the general procedure on a 0.30 mmol scale, compound **y-12** (54.9 mg, 86 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.71 (d, J = 8.2 Hz, 1H), 8.66 (d, J = 8.4 Hz, 1H), 8.27 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 9.2 Hz, 1H), 7.72 (m, 2H), 7.69 – 7.65 (m, 1H), 7.61 – 7.57 (m, 1H). 13 **C NMR** (126 MHz, CDCl₃) δ 132.70, 131.89, 131.88, 129.93, 129.32, 128.70, 128.21, 127.18, 127.07, 127.06, 126.43, 122.95, 122.50, 121.62. HRMS (ESI) calcd. for $C_{14}H_9Cl$ [M+H] $^{+}$:213.0471, found 213.0475; [M+Na] $^{+}$: 235.0290, found 235.0297.

1-Phenanthrenecarboxylic acid, methyl ester (y-13)

Following the general procedure on a 0.30 mmol scale, compound **y-13** (66.6 mg, 94 %) was obtained as light yellow oil. ${}^{1}\mathbf{H}$ **NMR** (500 MHz, CDCl₃) δ 8.93 (d, J = 8.4 Hz, 1H), 8.81 (d, J = 9.3 Hz, 1H), 8.71 (d, J = 8.2 Hz, 1H), 8.24 (dd, J = 7.4, 1.0 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.90 (d, J = 9.3 Hz, 1H), 7.73 – 7.64 (m, 3H), 4.06 (s, 3H). ${}^{13}\mathbf{C}$ **NMR** (126 MHz, CDCl₃) δ 168.42, 131.61, 130.93, 130.63, 130.03, 129.81, 128.76, 128.53, 128.22, 127.10, 127.07, 126.90, 125.28, 123.74, 122.78, 52.30. HRMS (ESI) calcd. for $\mathbf{C}_{16}\mathbf{H}_{12}\mathbf{O}_{2}$ [M+H] ${}^{+}$:237.0916, found 237.0912; [M+Na] ${}^{+}$: 259.0735, found 259.0731.

1,3-Dimethylphenanthrene (v-14)

Following the general procedure on a 0.30 mmol scale, compound **y-14** (58.8 mg, 95 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.74 (d, J = 8.2 Hz, 1H), 8.43 (s, 1H), 7.94 (dd, J = 15.2, 8.0 Hz, 2H), 7.77 (d, J = 9.1 Hz, 1H), 7.68 (m, 1H), 7.65 – 7.60 (m, 1H), 7.34 (s, 1H), 2.77 (s, 3H), 2.63 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 135.73, 134.66, 131.84, 130.48, 130.38, 129.62, 128.75, 128.43, 126.30, 126.27, 125.72, 122.93, 122.77, 120.56, 22.06, 19.84. HRMS (ESI) calcd. for C₁₆H₁₄ [M+H]⁺:207.1174, found 207.1179; [M+Na]⁺: 229.0993, found 229.0997.

3-Fluoro-1-methylphenanthrene (y-15)

Following the general procedure on a 0.30 mmol scale, compound **y-15** (60.6 mg, 95 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.58 (d, J = 8.1 Hz, 1H), 8.21 (dd, J = 11.0, 2.2 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.76 (d, J = 9.1 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.25 (d, J = 9.1 Hz, 1H), 2.78 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 161.26, 158.83, 136.89, 136.80, 131.01, 130.94, 129.15, 129.10, 127.51, 126.54, 125.97, 125.55, 124.82, 124.79, 122.10, 121.39, 115.78, 115.54, 104.72, 104.51, 18.93. HRMS (ESI) calcd. for $C_{15}H_{11}F[M+H]^+$:211.0923, found 211.0918; $[M+Na]^+$: 233.0742, found 233.0739.

7-Methoxy-1-methylphenanthrene (z-1)

Following the general procedure on a 0.30 mmol scale, compound **z-1** (62.7 mg, 94 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.63 (d, J = 8.9 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 9.1 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.42 (d, J = 7.1 Hz, 1H), 7.31 (m, 2H), 4.00 (s, 3H), 2.78 (s, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 158.20, 134.88, 133.07, 130.52, 129.82, 126.81, 126.25, 126.22, 125.07, 124.61, 123.49, 120.41, 117.20, 108.34, 55.41, 19.92. HRMS (ESI) calcd. for C₁₆H₁₄O [M+H] $^{+}$:223.1123, found 223.1128; [M+Na] $^{+}$: 245.0942, found 245.0948.

1,7-Dimethylphenanthrene (z-2)

Following the general procedure on a 0.30 mmol scale, compound **z-2** (56.3 mg, 91 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.62 (d, J = 8.5 Hz, 1H), 8.58 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 9.1 Hz, 1H), 7.75 (d, J = 9.1 Hz, 1H), 7.71 (s, 1H), 7.58 – 7.54 (m, 1H), 7.51 (dd, J = 8.5, 1.7 Hz, 1H), 7.45 (d, J = 7.0 Hz, 1H), 2.79 (s, 3H), 2.60 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 136.12, 134.81, 131.80, 130.45, 130.36, 128.51, 128.35, 127.98, 127.31, 126.42, 126.05, 122.85, 120.66, 21.45, 19.95. HRMS (ESI) calcd. for $C_{16}H_{14}[M+H]^+$:207.1174, found 207.1179; $[M+Na]^+$: 229.0993, found 229.0999.

1-Methyl-7-(trifluoromethyl)phenanthrene (z-3)

Following the general procedure on a 0.30 mmol scale, compound **z-3** (64.0 mg, 82 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.82 (d, J = 8.7 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.21 (s,

1H), 8.09 (d, J = 9.1 Hz, 1H), 7.86 (dd, J = 9.0, 2.9 Hz, 2H), 7.66 – 7.60 (m, 1H), 7.55 (d, J = 7.1 Hz, 1H), 2.81 (s, 3H). ¹³C **NMR** (126 MHz, CDCl₃) δ 135.22, 132.67, 131.51, 130.92, 129.69, 128.86, 126.76, 126.45, 125.82, 125.78, 124.37, 123.90, 122.36, 122.33, 121.23, 19.94. HRMS (ESI) calcd. for $C_{16}H_{11}F_{3}[M+H]^{+}$:261.0891, found 261.0886; $[M+Na]^{+}$: 283.0711, found 283.0708.

7-Fluoro-1-methylphenanthrene (z-4)

Following the general procedure on a 0.30 mmol scale, compound **z-4** (53.6 mg, 85 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.69 (dd, J = 9.1, 5.4 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 9.1 Hz, 1H), 7.74 (d, J = 9.1 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.48 (d, J = 7.1 Hz, 1H), 7.42 (m, 1H), 2.79 (s, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 162.21, 160.25, 135.08, 133.05, 132.98, 130.30, 130.29 , 130.18, 127.61, 127.29, 127.27, 126.58, 125.91, 125.88, 125.38, 125.31, 124.20, 120.67, 115.61, 115.42, 112.43, 112.27, 19.95. HRMS (ESI) calcd. for $C_{15}H_{11}F$ [M+H]*:211.0923, found 211.0928; [M+Na]*: 233.0742, found 233.0749.

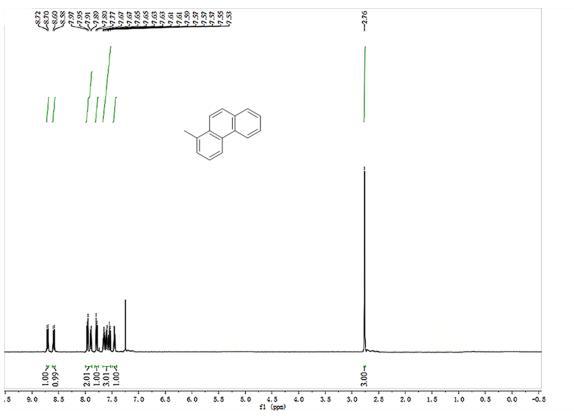
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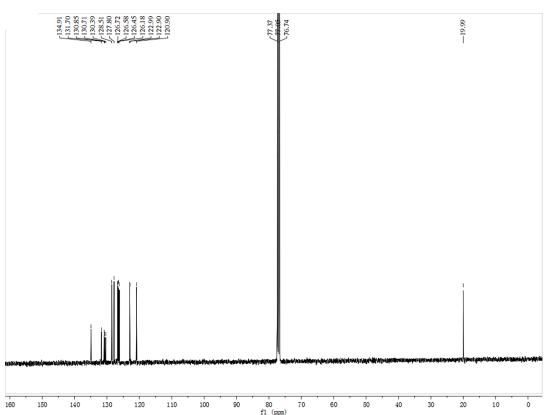
Following the general procedure on a 0.30 mmol scale, compound **z-5** (59.2 mg, 87 %) was obtained as white solid. 1 **H NMR** (500 MHz, CDCl₃) δ 8.63 (d, J = 8.9 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 9.1 Hz, 1H), 7.89 (d, J = 2.2 Hz, 1H), 7.72 – 7.69 (m, 1H), 7.63 – 7.57 (m, 2H), 7.49 (d, J = 7.1 Hz, 1H), 2.78 (s, 3H). 13 **C NMR** (126 MHz, CDCl₃) δ 135.10, 132.68, 132.20, 130.67, 129.97, 128.99, 128.05, 127.34, 126.99, 126.60, 125.59, 124.67, 124.19, 120.76, 19.93. HRMS (ESI) calcd. for $C_{15}H_{11}Cl$ [M+H] ${}^{+}$:227.0628, found 227.0623; [M+Na] ${}^{+}$: 249.0447, found 249.0443.

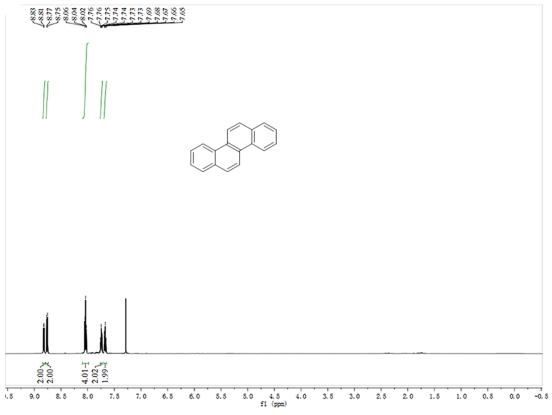
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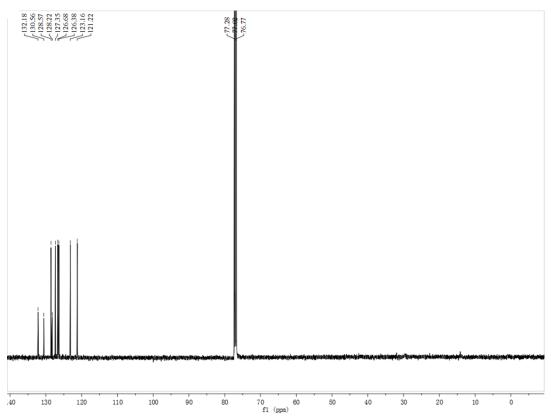
Following the general procedure on a 0.30 mmol scale, compound **z-6** (71.9 mg, 95 %) was obtained as white solid. ¹**H NMR** (500 MHz, CDCl₃) δ 8.44 (d, J = 8.4 Hz, 1H), 8.03 (s, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.70 (d, J = 9.0 Hz, 1H), 7.58 – 7.48 (m, 1H), 7.40 (d, J = 7.0 Hz, 1H), 7.25 (s, 1H), 4.12 (s, 3H), 4.06 (s, 3H), 2.76 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ 149.32, 149.25, 134.96, 130.14, 129.74, 126.83, 126.74, 125.76, 125.73, 125.26, 121.19, 120.41, 108.09, 103.63, 55.99, 55.91, 20.01. HRMS (ESI) calcd. for $C_{17}H_{16}O_{2}$ [M+H]⁺:253.1229, found 253.1224; [M+Na]⁺: 275.1048, found 275.1043.

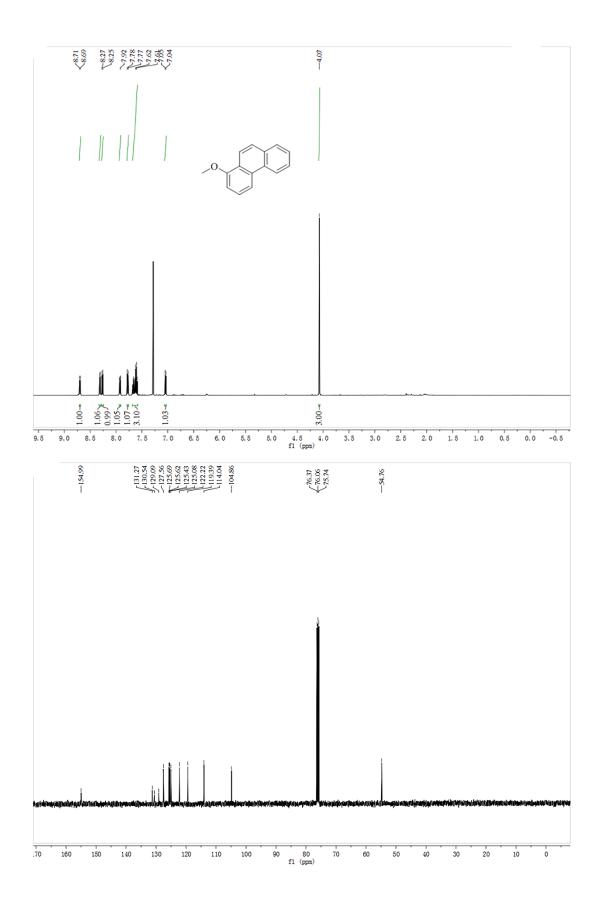
2. ¹H NMR and ¹³C NMR spectra for the products

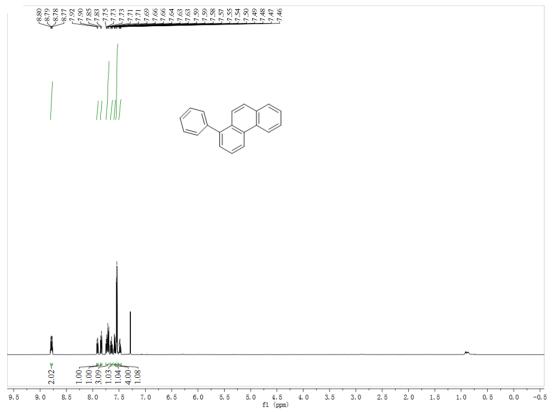


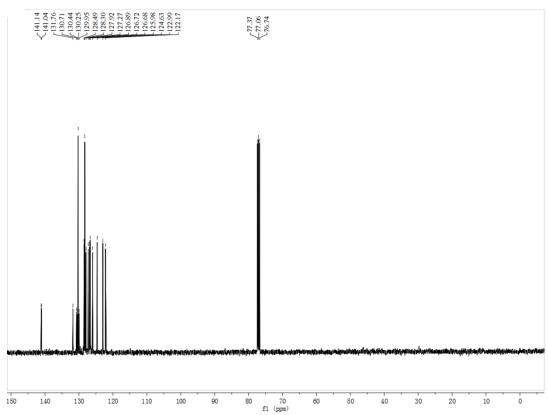


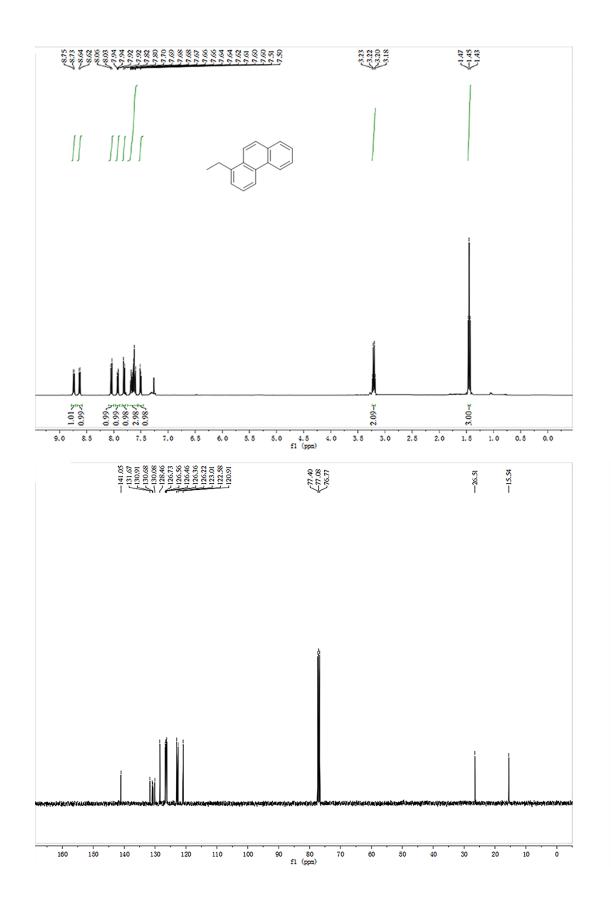


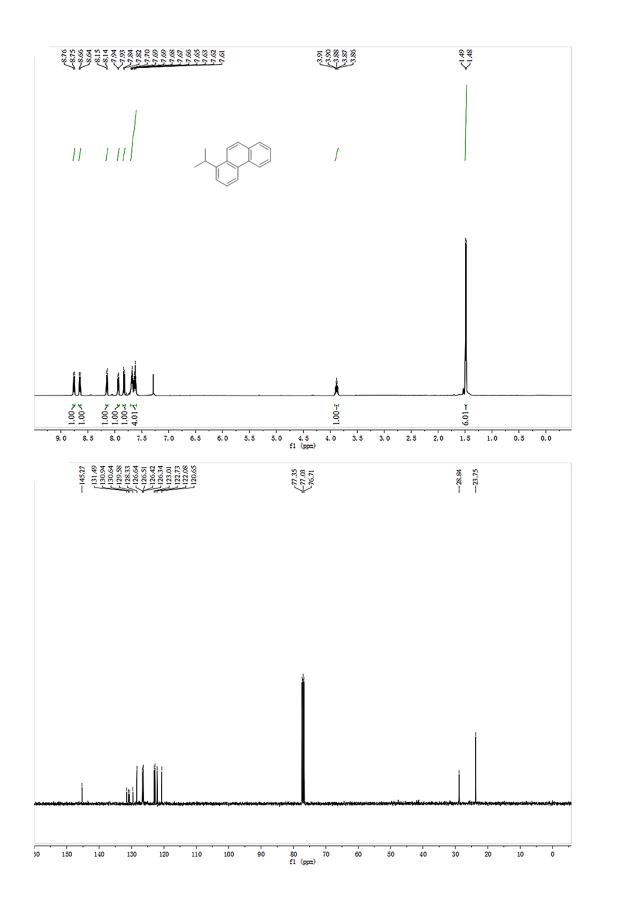


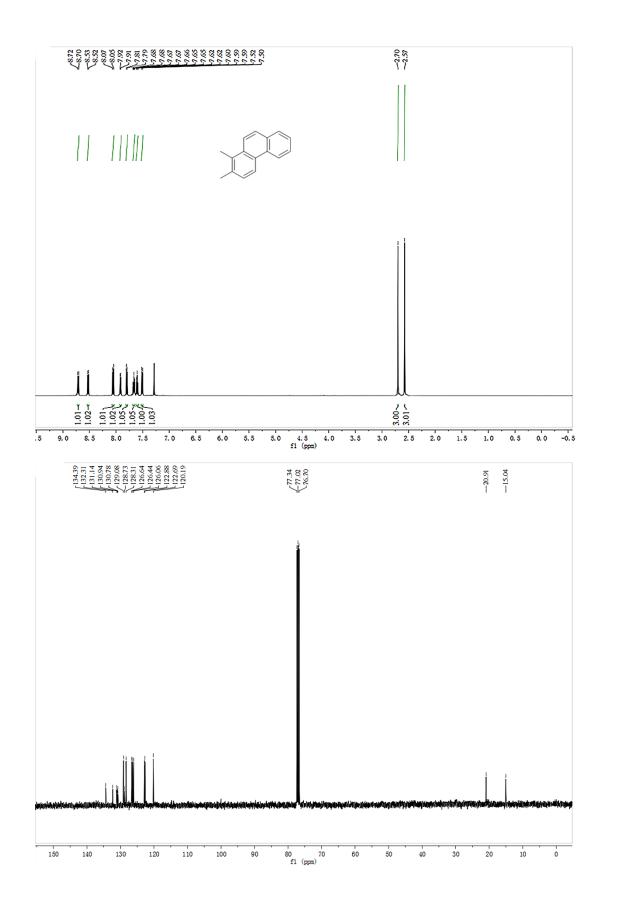


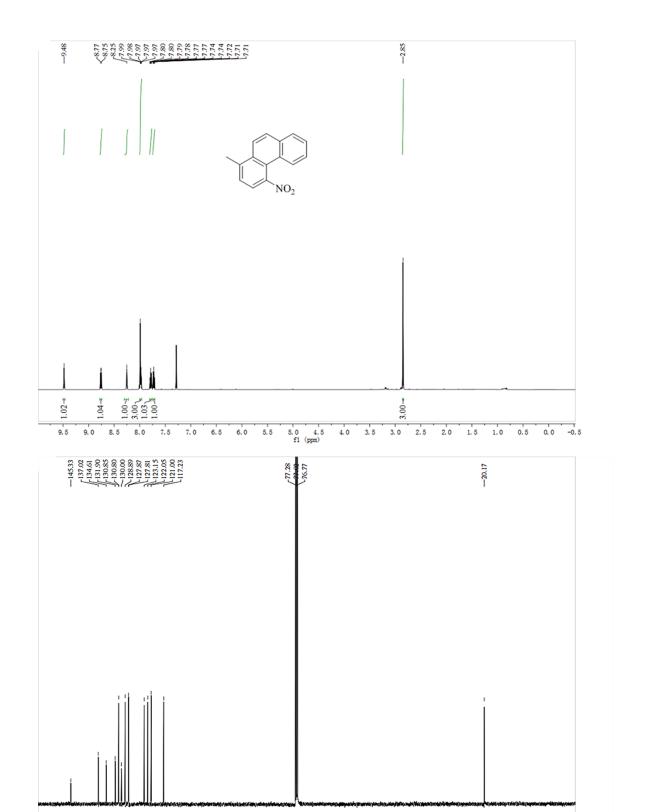




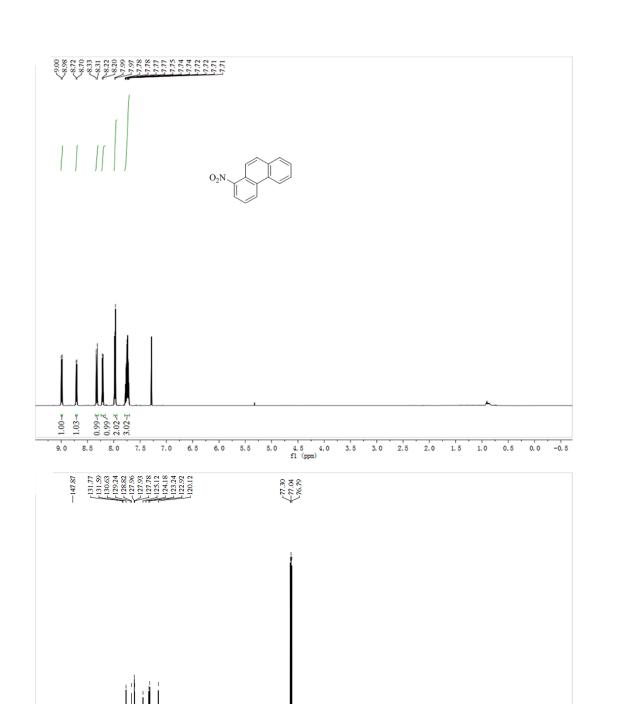






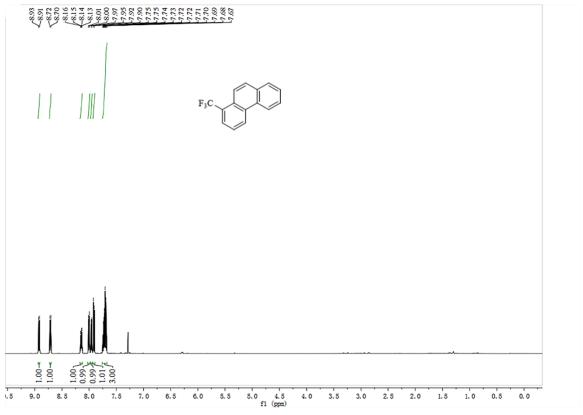


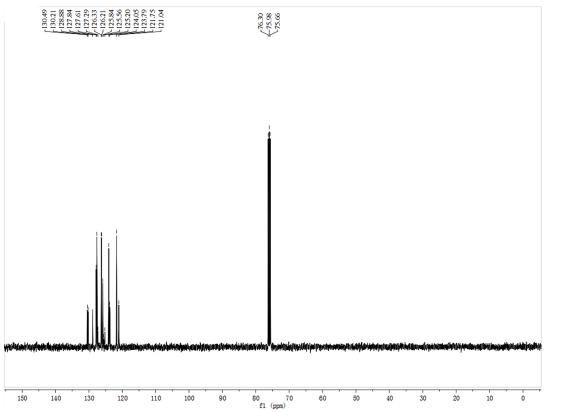
80 70 fl (ppm)

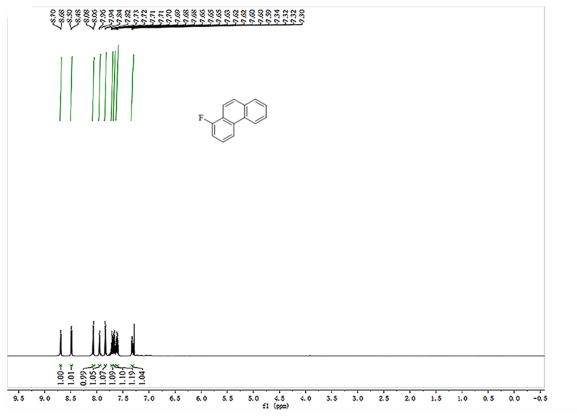


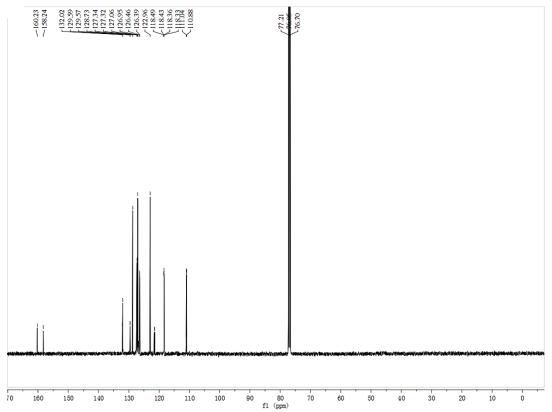
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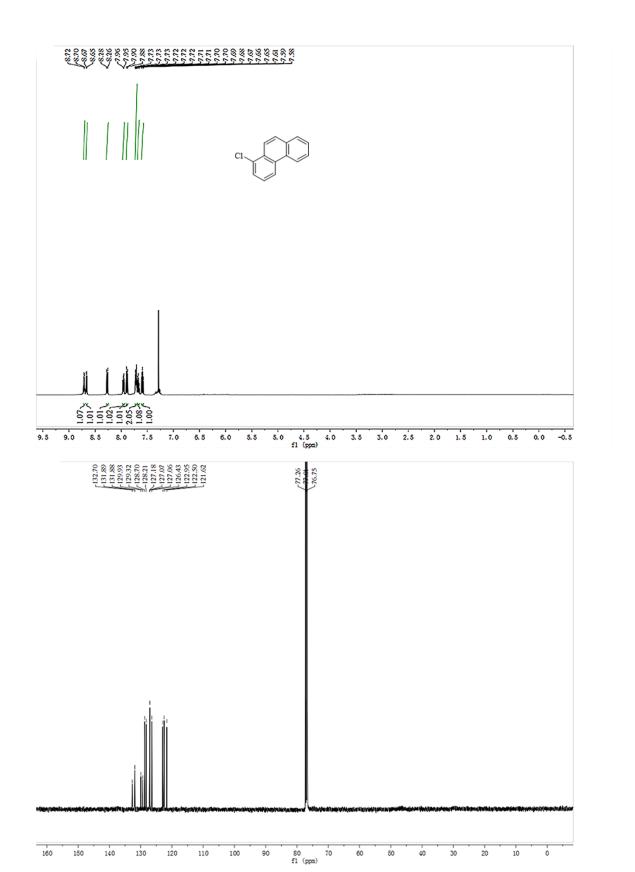
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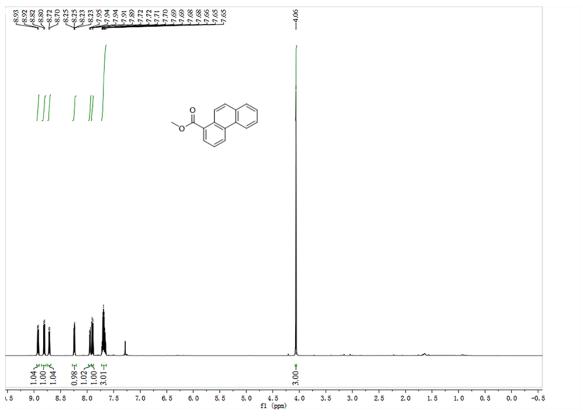


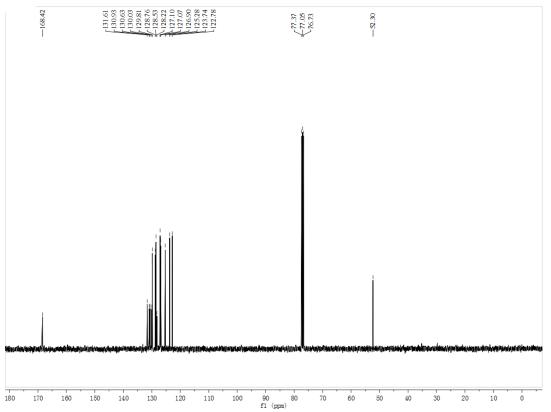


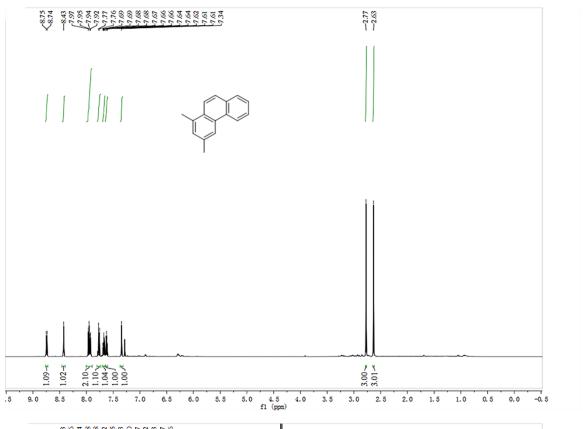


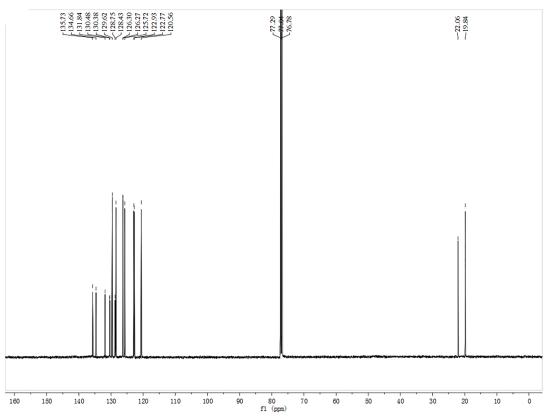


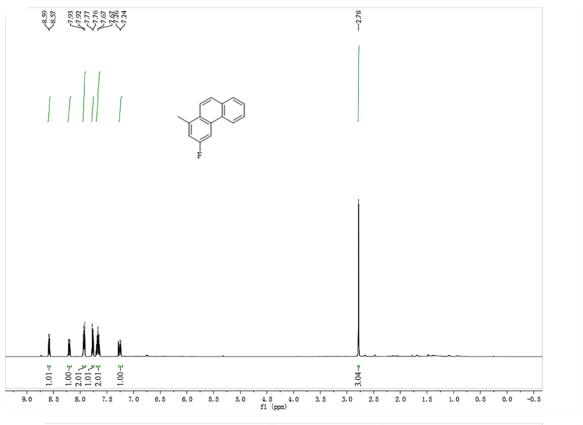


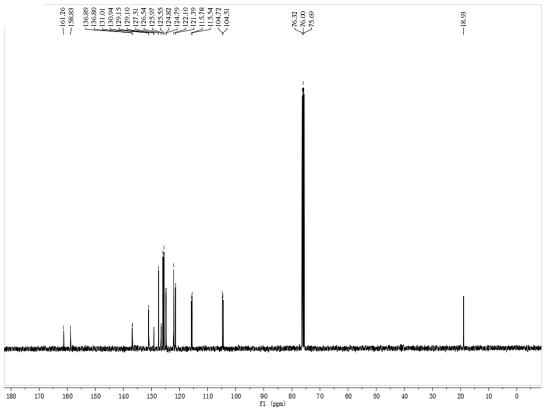


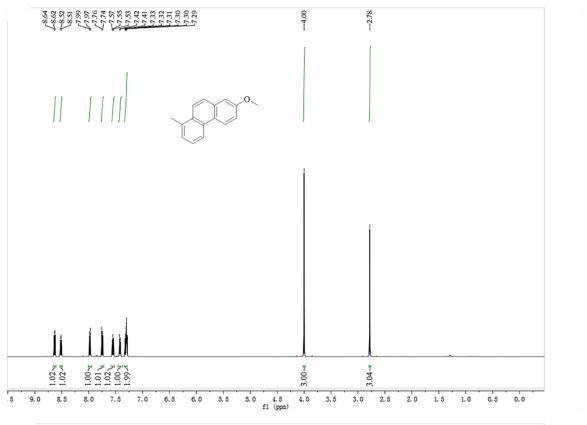


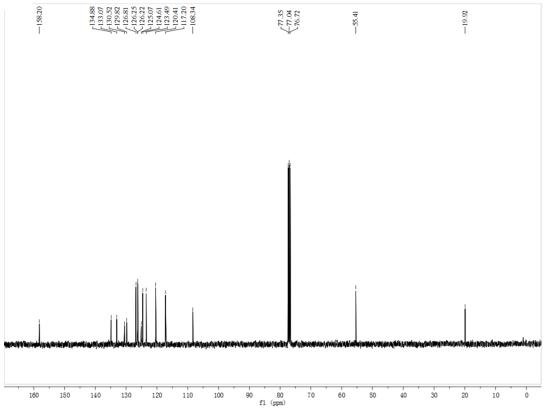


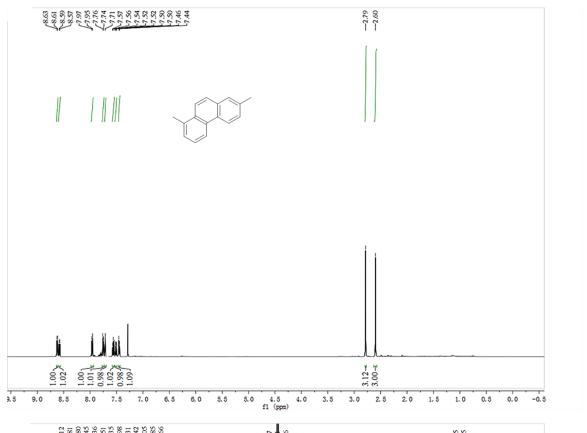


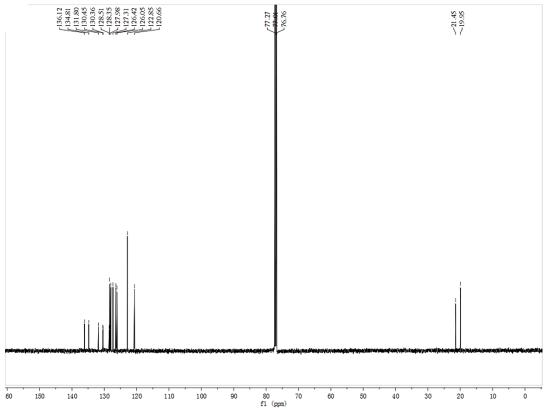


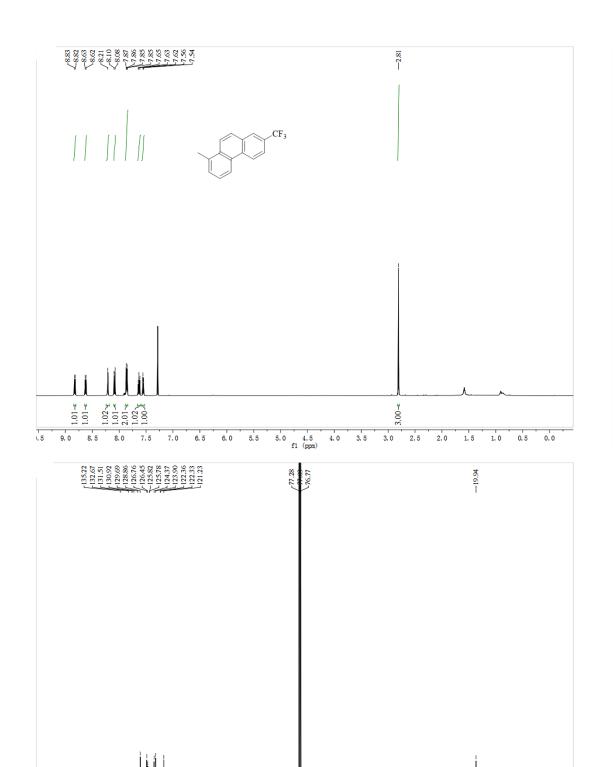












80 70 fl (ppm)

