

Supplementary information

Oxidative Cyclization of 2-Allenyl-1,1'-biphenyls with α -Carbonyl Alkyl Bromides: Facile Access to Functionalized Phenanthrenes

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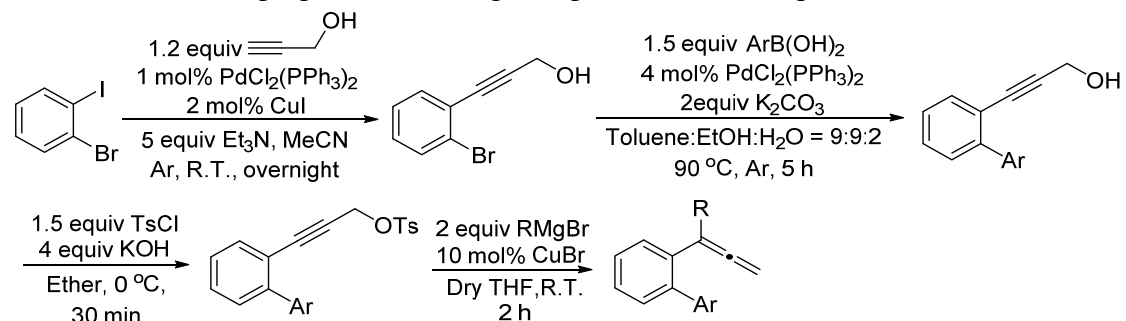
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(A) Typical Experimental Procedure

(a) Materials

All allenes were prepared according to reported literatures procedures^{1,2,3}:

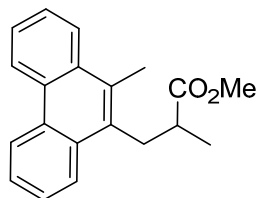


(b) Typical Experimental Procedure for the Cyclization of 2-Allenyl-1,1'-biphenyls with α -Carbonyl Alkyl Bromides

To a Schlenk tube were added **1** (0.2 mmol), **2** (0.6 mmol), CuCl (5 mol%), Ag₂CO₃ (2 equiv) and Dioxane (1 mL). Then the tube was charged with argon, and was stirred at 120 °C for 16 h until complete consumption of the starting material (TLC monitoring). When the reaction had finished, the mixture was washed with brine. The aqueous phase was re-extracted with diethyl ether. The combined organic extracts were dried over Na₂SO₄ and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product **3**.

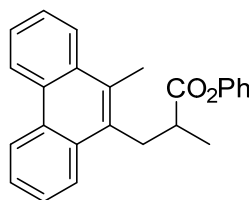
(B) Analytical data

Methyl 2-methyl-3-(10-methylphenanthren-9-yl)propanoate (3aa)



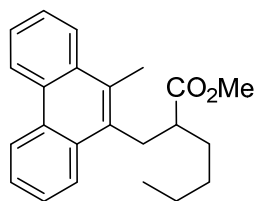
White solid, mp 100.2-100.6 °C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.72 (d, *J* = 7.6 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.63-7.59 (m, 4H), 3.69-3.66 (m, 1H), 3.63 (s, 3H), 3.40-3.34 (m, 1H), 2.99-2.90 (s, 1H), 2.74 (s, 3H), 1.19 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 176.8, 132.0, 131.2, 130.8, 130.7, 129.8, 129.6, 127.7(2C), 125.9, 125.5, 124.9, 124.5, 123.0, 122.7, 51.7, 40.3, 32.6, 16.4(2C); LRMS (EI 70 ev) *m/z* (%): 292 (M⁺, 27), 205 (100), 190 (12) 165 (8); HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₀H₂₁O₂: 293.1536, found: 293.1545.

Phenyl 2-methyl-3-(10-methylphenanthren-9-yl)propanoate (3ab)



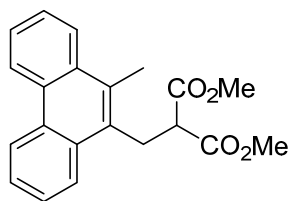
White solid, mp: 89.2-90.7 °C (uncorrected); ¹H NMR (400 MHz, CDCl₃) δ: 8.77-8.73 (m, 2H), 8.20-8.14 (m, 2H), 7.66-7.63 (m, 4H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.87-3.82 (m, 1H), 3.55-3.49 (m, 1H), 3.26-3.17 (m, 1H), 2.80 (s, 3H), 1.35 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 174.9, 150.7, 131.9, 131.3, 131.0, 130.6, 130.0, 129.9, 129.3(2C), 126.9, 126.8, 126.0, 125.7, 125.0, 124.6, 123.1, 122.8, 121.5, 40.6, 32.7, 16.6, 16.5; LRMS (EI 70 ev) *m/z* (%): 354 (M⁺, 13), 261 (26), 233 (100), 179 (54); HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₅H₂₃O₂: 355.1692, found: 355.1702.

Methyl 2-((10-methylphenanthren-9-yl)methyl)hexanoate (3ac)



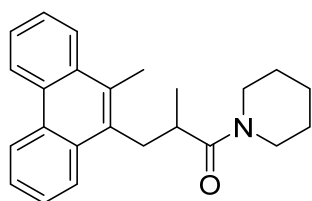
White solid, mp: 93.2-94.8 °C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.73-8.70 (m, 2H), 8.11-8.08 (m, 2H), 7.63-7.62 (m, 4H), 3.62-3.57 (m, 1H), 3.54 (s, 3H), 3.43-3.37 (m, 1H), 2.86-2.80 (m, 1H), 2.74 (s, 3H), 1.88-1.81 (m, 1H), 1.30-1.20 (m, 5H), 0.83 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 176.5, 132.0, 131.3, 130.9, 130.6, 129.8, 129.7, 126.7, 126.6, 125.9, 125.5, 124.9, 124.5, 123.0, 122.7, 51.5, 46.6, 32.1, 31.9, 29.9, 22.6, 16.3, 13.9; LRMS (EI 70 ev) *m/z* (%): 334 (M⁺, 25), 205 (100), 190 (11), 165 (5); HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₃H₂₇O₂: 335.2006, found: 335.2014.

Dimethyl 2-((10-methylphenanthren-9-yl)methyl)malonate (3ad)



Light yellow solid, mp: 106.3-106.9 °C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.73-8.69 (m, 2H), 8.13-8.05 (m, 2H), 7.63-7.62 (m, 4H), 3.94-3.93 (m, 2H), 3.85-3.81 (m, 1H), 3.65 (s, 6H), 2.74 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 169.6, 131.9, 131.2, 130.7, 129.9, 129.8, 129.2, 126.9, 126.7, 126.2, 125.7, 125.0, 124.0, 123.2, 122.7, 52.6, 52.0, 28.2, 16.0; LRMS (EI 70 ev) *m/z* (%): 336 (M⁺, 39), 318 (14), 217 (16), 205 (100), 189 (19), 165 (12); HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₁H₂₁O₄: 337.1434, found: 337.1439.

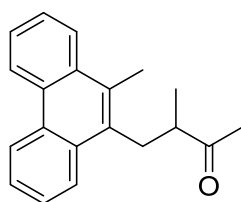
2-Methyl-3-(10-methylphenanthren-9-yl)-1-(piperidin-1-yl)propan-1-one (3ae)



Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ: 8.72-8.69 (m, 2H), 8.11-8.07 (m, 2H), 7.64-7.61 (m, 4H), 3.63-3.58 (m, 1H), 3.52-3.47 (m, 1H), 3.41-3.32 (m, 2H), 3.29-3.22 (m, 1H), 2.95-2.90 (m, 1H), 2.74 (s, 3H), 1.73-1.67 (m, 1H), 1.41-1.31 (m, 2H), 1.28 (d, *J*

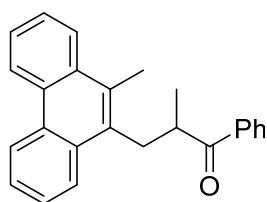
= 6.4 Hz, 3H), 1.18-1.14 (m, 2H), 1.05-1.01 (m, 1H), 0.63-0.51 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 174.4, 132.0, 131.6, 131.5, 130.8, 129.7, 129.5, 126.7(2C), 125.8, 125.5, 124.9, 124.6, 123.0, 122.7, 46.5, 42.8, 35.5, 33.7, 26.0, 25.4, 24.3, 18.4, 16.3; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{28}\text{NO}$: 346.2165, found: 346.2172.

3-Methyl-4-(10-methylphenanthren-9-yl)butan-2-one (3af)



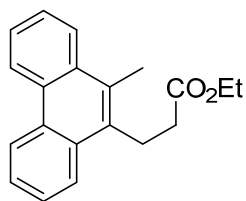
White solid, mp: 83.1-84.9 °C (uncorrect); ^1H NMR (400 MHz, CDCl_3) δ : 8.75-8.71 (m, 2H), 8.14-8.12 (m, 1H), 8.07-8.04 (m, 1H), 7.63-7.61 (m, 4H), 3.64-3.58 (m, 1H), 3.33-3.27 (m, 1H), 3.09-3.04 (m, 1H), 2.74 (s, 3H), 2.08 (s, 3H), 1.43 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 212.5, 132.0, 131.7, 131.2(2C), 129.9, 129.6, 126.8(2C), 126.0, 125.6, 125.0, 124.5, 123.1, 122.8, 47.6, 31.6, 29.4, 16.5, 16.2; LRMS (EI 70 ev) m/z (%): 276 (M^+ , 22), 243 (11), 205 (100), 190 (16), 165 (11); HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{21}\text{O}$: 277.1587, found: 277.1593.

2-Methyl-3-(10-methylphenanthren-9-yl)-1-phenylpropan-1-one (3ag)



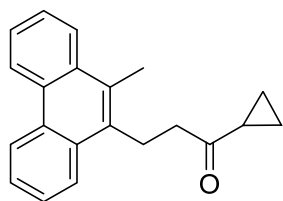
Light yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.73-8.68 (m, 2H), 8.11-8.07 (m, 2H), 7.78 (d, $J = 7.6$ Hz, 2H), 7.65-7.58 (m, 4H), 7.46-7.42 (m, 1H), 7.32-7.27 (m, 2H), 3.99-3.94 (m, 1H), 3.69-3.64 (m, 1H), 3.56-3.50 (m, 1H), 2.74 (s, 3H), 1.26 (d, $J = 5.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 205.6, 136.6, 132.8, 131.0, 131.4, 131.3, 130.8, 129.9, 129.6, 128.4, 128.1, 126.7, 126.6, 125.8, 125.5, 124.9, 124.6, 123.1, 122.7, 41.5, 32.1, 17.7, 16.5; LRMS (EI 70 ev) m/z (%): 338 (M^+ , 21), 320 (28), 205 (100), 190 (17), 165 (11); HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{23}\text{O}$: 339.1743, found: 339.1747.

Ethyl 3-(10-methylphenanthren-9-yl)propanoate (3ah)



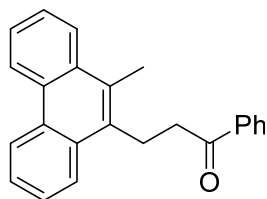
White solid, mp 69.8-70.7 °C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.72 (d, *J* = 7.2 Hz, 2H), 8.11 (d, *J* = 7.2 Hz, 2H), 7.63-7.59 (m, 4H), 4.23-4.18(m, 2H), 3.56 (t, *J* = 8.4 Hz, 2H), 2.75 (s, 3 H), 2.70-2.63(m, 2H), 1.29 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 173.1, 132.0, 131.8, 130.8, 129.8(2C), 129.6, 126.9, 126.7, 125.9, 125.6, 124.7, 124.0, 123.1, 122.8, 60.6, 34.5, 24.8, 15.6, 14.2; LRMS (EI 70 ev) *m/z* (%): 292 (M⁺, 68), 205 (100), 191 (33), 165 (13); HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₀H₂₁O₂: 293.1536, found: 293.1541.

1-Cyclopropyl-3-(10-methylphenanthren-9-yl)propan-1-one (3ai)



White solid, mp: 108.4-110.3°C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.74-8.70 (m, 2H), 8.13-8.11 (m, 1H), 8.07-8.05 (m, 1H), 7.64-7.62 (m, 4H), 3.52 (t, *J* = 8.0 Hz, 2H), 2.94 (t, *J* = 8.0 Hz, 2H), 2.74 (s, 3H), 1.93-1.90 (m, 1H), 1.13-1.07 (m, 2H), 0.91-0.88 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ: 210.3, 132.4, 132.0, 130.9, 129.8, 129.6, 129.5, 126.9, 126.7, 125.8, 125.6, 124.7, 124.1, 123.1, 122.8, 43.4, 23.4, 20.6, 15.6, 11.0; LRMS (EI 70 ev) *m/z* (%): 288 (M⁺, 44), 270 (15), 241 (44), 204 (100), 189 (25), 165 (16); HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₁H₂₁O: 289.1587, found: 289.1595.

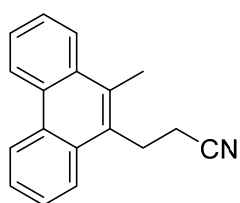
3-(10-Methylphenanthren-9-yl)-1-phenylpropan-1-one (3aj)



White solid, mp: 100.2–101.7 °C (uncorrect); ¹H NMR (400 MHz, CDCl₃) δ: 8.76-8.72 (m, 2H), 8.12-8.09 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.65-7.60 (m, 4H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44

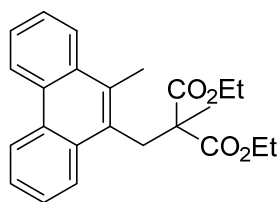
(t, $J = 7.6$ Hz, 2H), 3.69-3.65 (m, 2H), 3.37-3.33 (m, 2 H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 199.5, 136.8, 133.2, 132.5, 132.0, 130.9, 129.9, 129.7, 129.6, 128.6, 128.1, 127.0, 126.7, 125.8, 125.6, 124.7, 124.1, 123.2, 122.8, 38.8, 23.6, 15.6; LRMS (EI 70 eV) m/z (%): 324 (M^+ , 37), 306 (47), 204 (100), 190 (16), 165 (13); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{24}\text{H}_{21}\text{O}$: 325.1587, found: 325.1595.

3-(10-Methylphenanthren-9-yl)propanenitrile (3ak)



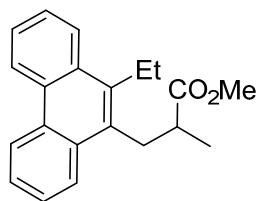
White solid, mp 149.2-151.4 °C (uncorrect); ^1H NMR (400 MHz, CDCl_3) δ : 8.75-8.70 (m, 2H), 8.13 (t, $J = 4.8$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.65-7.63 (m, 4H), 3.62 (t, $J = 8.0$ Hz, 2H), 2.78 (s, 3 H), 2.69 (t, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ : 131.7, 130.9, 130.1, 130.0, 129.8, 129.30, 127.2, 126.9, 126.4, 125.9, 125.0, 123.4, 123.3, 122.8, 119.2, 25.2, 17.4, 15.9; LRMS (EI 70 eV) m/z (%): 245 (M^+ , 35), 205 (100), 190 (14), 165 (10); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{18}\text{H}_{16}\text{N}$: 246.1277, found: 246.1284.

Diethyl 2-methyl-2-((10-methylphenanthren-9-yl)methyl)malonate (3al)



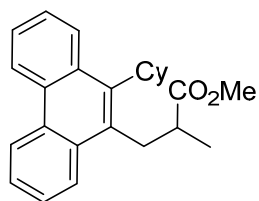
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.69 (d, $J = 6.4$ Hz, 2H), 8.15-8.10 (m, 2H), 7.64-7.62 (m, 2H), 7.57-7.53 (m, 2H), 4.22-4.04 (m, 6H), 2.71 (s, 3H), 1.22 (s, 3H), 1.22-1.14 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 172.7, 132.4, 132.3, 131.9, 129.8, 129.6, 129.0, 126.6, 126.3, 126.1, 125.5, 125.2, 125.1, 122.9, 122.7, 61.5, 54.4, 32.2, 19.9, 17.2, 13.9; LRMS (EI 70 eV) m/z (%): 378 (M^+ , 14), 360 (17), 205 (100), 190 (12), 165 (6); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{24}\text{H}_{27}\text{O}_4$: 379.1904, found: 379.1910.

Methyl 3-(10-ethylphenanthren-9-yl)-2-methylpropanoate (3ba)



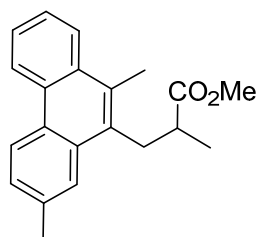
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.72 (d, $J = 7.6$ Hz, 2H), 8.15-8.10 (m, 2H), 7.61-7.59 (m, 4H), 3.70-3.55 (m, 4H), 3.37-3.20 (m, 3H), 3.05-2.98 (m, 1H), 1.31 (d, $J = 7.6$ Hz, 3H), 1.21 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.9, 137.0, 131.2, 130.7, 130.2, 130.0, 129.9, 126.7, 125.8, 125.6, 124.9, 124.7, 123.0(2C), 51.7, 40.3, 32.1, 22.3, 16.5, 15.0; LRMS (EI 70 eV) m/z (%): 306 (M^+ , 47), 219 (100), 205 (31), 191 (23); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{O}_2$: 307.1693, found: 307.1697.

Methyl 3-(10-cyclohexylphenanthren-9-yl)-2-methylpropanoate (3ca)



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ : 8.71 (t, $J = 9.2$ Hz, 2H), 8.58 (d, $J = 5.6$ Hz, 1H), 8.14 (d, $J = 5.6$ Hz, 1H), 7.62-7.54 (m, 4H), 3.65 (s, 3H), 3.63-3.55 (m, 1H), 3.44-3.38 (m, 1H), 2.98-2.92 (m, 1H), 2.55-2.40 (m, 2H), 1.98-1.96 (m, 2H), 1.89-1.80 (m, 3H), 1.55-1.45 (m, 3H), 1.28-1.21 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.9, 139.7, 131.6, 130.9, 130.8, 130.7, 129.9, 127.3, 126.7, 125.6, 125.5, 125.3, 125.2, 123.1, 122.9, 51.7, 42.2, 40.6, 32.5, 31.7, 31.4, 27.8, 27.7, 26.3, 16.5; LRMS (EI 70 eV) m/z (%): 360 (M^+ , 32), 259 (22), 215 (24), 205 (31), 191 (100); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{25}\text{H}_{29}\text{O}_2$: 361.2162, found: 361.2167.

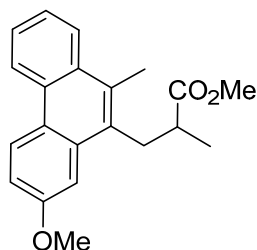
Methyl 3-(7,10-dimethylphenanthren-9-yl)-2-methylpropanoate (3da)



White solid, mp: 107.4-108.5 $^\circ\text{C}$ (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.67-8.65 (m, 1H), 8.60 (d, $J = 8.4$ Hz, 1H), 8.11-8.09 (m, 1H), 7.88 (s, 1H), 7.60-7.58 (m, 2H), 7.42 (t, $J = 8.42$

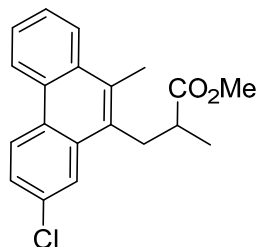
Hz, 1H), 3.67-3.62 (m, 4H), 3.39-3.33 (m, 1H), 2.97-2.92 (m, 1H), 2.73 (s, 3H), 2.58 (s, 3H), 1.19 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.9, 136.3, 131.6, 131.4, 130.7, 130.6, 129.7, 127.6, 127.2, 126.2, 125.8, 124.9, 124.3, 122.9, 122.5, 51.7, 40.3, 32.6, 22.0, 16.4, 16.3; LRMS (EI 70 ev) m/z (%): 306 (M^+ , 35), 219 (100), 203 (19), 189 (6); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{O}_2$: 307.1693, found: 307.1703.

Methyl 3-(7-methoxy-10-methylphenanthren-9-yl)-2-methylpropanoate (3ea)



White solid, mp: 128.6-130.0 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.62-8.58 (m, 2H), 8.08 (d, $J = 8.8$ Hz, 1H), 7.60-7.51 (m, 3H), 7.24-7.21 (m, 1H), 3.98 (s, 3H), 3.64 (s, 3H), 3.62-3.58 (m, 1H), 3.35-3.29 (m, 1H), 2.99-2.90 (m, 1H), 2.73 (s, 3H), 1.20 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.9, 158.4, 132.6, 131.3, 130.9, 130.4, 129.7, 126.0, 125.7, 124.9, 124.6, 124.1, 122.2, 115.3, 105.9, 55.3, 51.7, 40.2, 33.1, 16.4(2C); LRMS (EI 70 ev) m/z (%): 322 (M^+ , 34), 235 (100), 222 (23), 207 (17), 191 (19); HRMS (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{O}_3$: 323.1642, found: 323.1654.

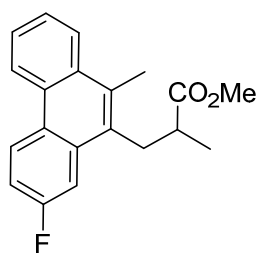
Methyl 3-(7-chloro-10-methylphenanthren-9-yl)-2-methylpropanoate (3fa)



White solid, mp: 120.6-122.0 °C (uncorrected); ^1H NMR (400 MHz, CDCl_3) δ : 8.62 (d, $J = 8.4$ Hz, 2H), 8.13-8.11 (m, 1H), 8.06 (s, 1H), 7.65-7.63 (m, 2H), 7.54 (d, $J = 8.8$ Hz, 1H), 3.65 (s, 3H), 3.62-3.57 (m, 1H), 3.34-3.29 (m, 1H), 2.93-2.88 (m, 1H), 2.74 (s, 3H), 1.21 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 176.5, 132.8, 132.5,

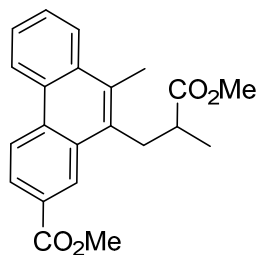
132.2, 131.8, 130.0, 129.2, 128.2, 127.0, 126.3, 125.9, 125.1, 124.7, 124.0, 122.7, 51.8, 40.3, 32.6, 16.6, 16.4; LRMS (EI 70 ev) m/z (%): 328 (M^{+2} , 9), 326 (M^{+} , 22), 239 (100), 203 (37), 189 (14); HRMS (ESI): m/z [$M + H$] $^{+}$ calcd for $C_{20}H_{20}^{35}ClO_2$: 327.1146, found: 327.1151.

Methyl 3-(7-fluoro-10-methylphenanthren-9-yl)-2-methylpropanoate (3ga)



White solid, mp: 113.7-115.9 °C (uncorrected); 1H NMR (400 MHz, $CDCl_3$) δ : 8.70-8.66 (m, 1H), 8.62-8.60 (m, 1H), 8.12-8.10 (m, 1H), 7.75-7.71 (m, 1H), 7.65-7.60 (s, 2H), 7.36-7.31 (m, 1H), 3.65 (s, 3H), 3.61-3.55 (m, 1H), 3.33-3.27 (m, 1H), 2.94-2.88 (m, 1H), 2.74 (s, 3H), 1.20 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 176.5, 161.7 (d, $J_{C-F} = 243.3$ Hz), 133.0 (d, $J_{C-F} = 7.9$ Hz), 132.2, 131.5, 130.3 (d, $J_{C-F} = 3.7$ Hz), 129.4, 126.5, 126.4, 126.3, 125.3 (d, $J_{C-F} = 8.8$ Hz), 125.1, 122.6, 114.3 (d, $J_{C-F} = 23.4$ Hz), 109.4 (d, $J_{C-F} = 22.0$ Hz), 51.7, 40.2, 32.8, 16.5, 16.4; ^{19}F NMR (375 MHz, $CDCl_3$) δ : -114.1; LRMS (EI 70 ev) m/z (%): 310 (M^{+} , 29), 223 (100), 207 (8), 183 (8); HRMS (ESI): m/z [$M+H$] $^{+}$ calcd for $C_{20}H_{20}FO_2$: 311.1442, found: 311.1450.

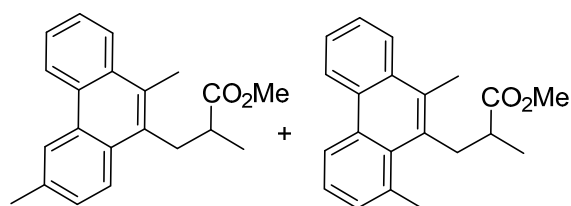
Methyl 10-(3-methoxy-2-methyl-3-oxopropyl)-9-methylphenanthrene-2-carboxylate (3ha)



White solid, mp: 119.4-121.3 °C (uncorrected); 1H NMR (400 MHz, $CDCl_3$) δ : 8.87 (s, 1H), 8.74 (d, $J = 9.2$ Hz, 2H), 8.21-8.14 (m, 2H), 7.69-7.66 (m, 2H), 4.02 (s, 3H), 3.75-3.70 (m, 1H), 3.65 (s, 1H), 3.45-3.39 (m, 1H), 2.97-2.92 (m, 1H), 2.76 (s, 3H), 1.24 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 176.5, 167.4, 133.0, 132.9, 131.7,

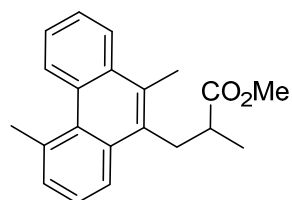
131.4, 130.8, 129.0, 128.0, 127.8, 127.0, 126.3, 125.5, 125.1, 123.4, 123.3, 52.3, 51.7, 40.6, 32.7, 16.6, 16.4; LRMS (EI 70 ev) m/z (%): 350 (M^+ , 22), 318 (100), 263 (100), 203 (19); HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{22}H_{23}O_4$: 351.1591, found: 351.1597.

Methyl 3-(6,10-dimethylphenanthren-9-yl)-2-methylpropanoate (3ia) and Methyl 3-(8,10-dimethylphenanthren-9-yl)-2-methylpropanoate (2:1) (3ia')



Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 8.71-8.69 (m, 0.67H), 8.66-8.64 (m, 0.36H), 8.58 (d, $J = 8.0$ Hz, 0.34H), 8.51 (s, 0.62H), 8.12-8.07 (m, 1H), 8.00 (d, $J = 8.8$ Hz, 0.64 H), 7.62-7.57 (m, 2H), 7.46-7.42 (m, 1H), 7.38 (d, $J = 7.2$ Hz, 0.42H), 3.92-3.87 (m, 0.35H), 3.67-3.62 (m, 2.73H), 3.55-3.49 (m, 0.42H), 3.43 (s, 0.92H), 3.39-3.33 (m, 0.80H), 2.97-2.91 (m, 0.81H), 2.86 (s, 0.94H), 2.76 (s, 0.96H), 2.73 (s, 1.81H), 2.60 (s, 1.98H), 2.54-2.49 (m, 0.39H), 1.18 (d, $J = 6.8$ Hz, 2H), 0.81 (d, $J = 6.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 176.9, 176.8, 135.1, 134.1, 132.2, 132.0, 131.6, 131.4, 131.0, 130.8, 130.1, 129.9, 129.7, 129.5, 129.2, 128.4, 126.5, 125.8, 125.7, 125.0, 124.9, 124.7, 124.5, 123.1, 122.8, 122.7, 121.2, 51.7, 51.4, 40.8, 40.4, 34.9, 32.6, 26.3, 21.8, 16.7, 16.4, 16.2, 15.9.

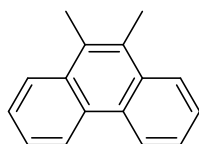
Methyl 3-(5,10-dimethylphenanthren-9-yl)-2-methylpropanoate (3ja)



Colorless oil; 1H NMR (400 MHz, $CDCl_3$) δ : 8.74 (d, $J = 8.0$ Hz, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.63-7.54 (m, 2H), 7.53-7.45 (m, 2H), 3.68-3.64 (m, 4H), 3.40-3.34 (m, 1H), 3.10 (s, 3H), 2.97-2.92 (m, 1H), 2.74 (s, 3H), 1.17 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 176.9, 135.3, 133.1, 132.7, 131.2, 130.6(2C), 130.3,

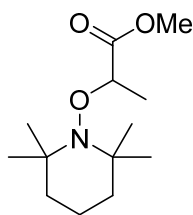
130.2, 127.8, 126.0, 125.8, 124.5, 124.3, 122.5, 51.7, 40.3, 33.0, 27.3, 16.6, 16.4;
LRMS (EI 70 ev) m/z (%): 306 (M^+ , 39), 219 (100), 204 (21), 189 (9); HRMS (ESI):
 m/z [$M+H$]⁺ calcd for $C_{21}H_{23}O_2$: 307.1693, found: 307.1701.

9,10-Dimethylphenanthrene (4aa)⁴



White solid; ¹H NMR (400 MHz, $CDCl_3$) δ : 8.72-8.70 (m, 2H), 8.13-8.11 (m, 2H), 7.62-7.60 (m, 4H), 2.74 (s, 6H); ¹³C NMR (100 MHz, $CDCl_3$) δ : 132.2, 129.3(2C), 126.5, 125.4, 124.6, 122.7, 15.9; LRMS (EI 70 ev) m/z (%): 206 (M^+ , 49), 191 (100), 165 (19).

Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (5)⁵



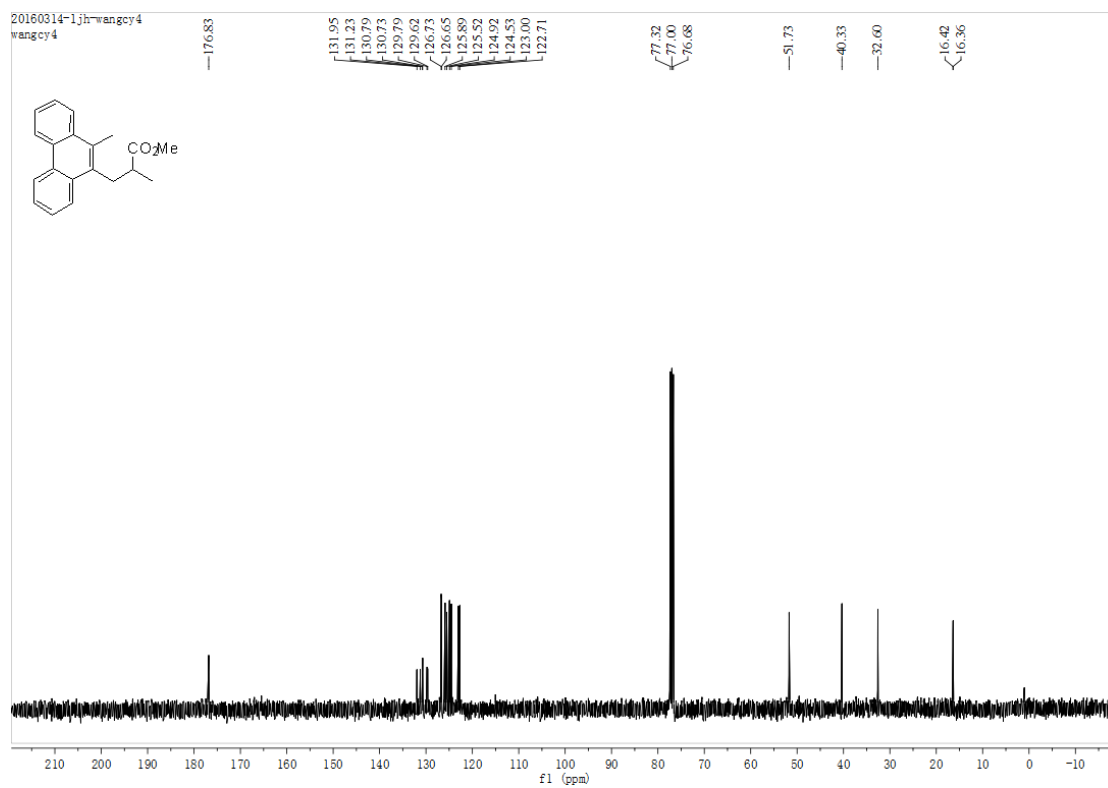
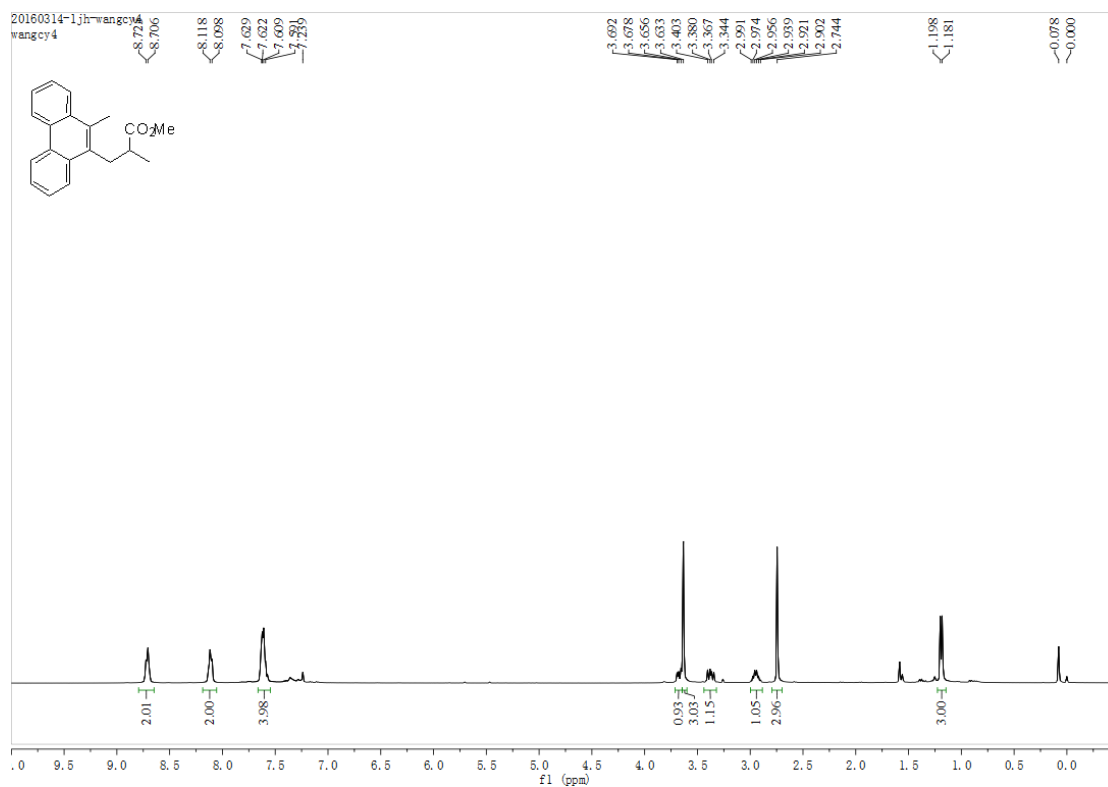
Colorless liquid; ¹H NMR (400 MHz, $CDCl_3$) δ : 4.36-4.31 (m, 1H), 3.71 (s, 3H), 1.57-1.50 (m, 1H), 1.48-1.42 (m, 4H), 1.40 (d, $J = 6.8$ Hz, 3H), 1.35-1.25 (m, 1H), 1.18 (s, 3H), 1.12 (s, 6H), 1.02 (s, 3H); ¹³C NMR (100 MHz, $CDCl_3$) δ : 174.5, 81.6, 60.0, 59.4, 51.4, 40.2, 40.1, 33.6, 32.8, 20.1, 20.0, 18.1, 17.1.

(C) References

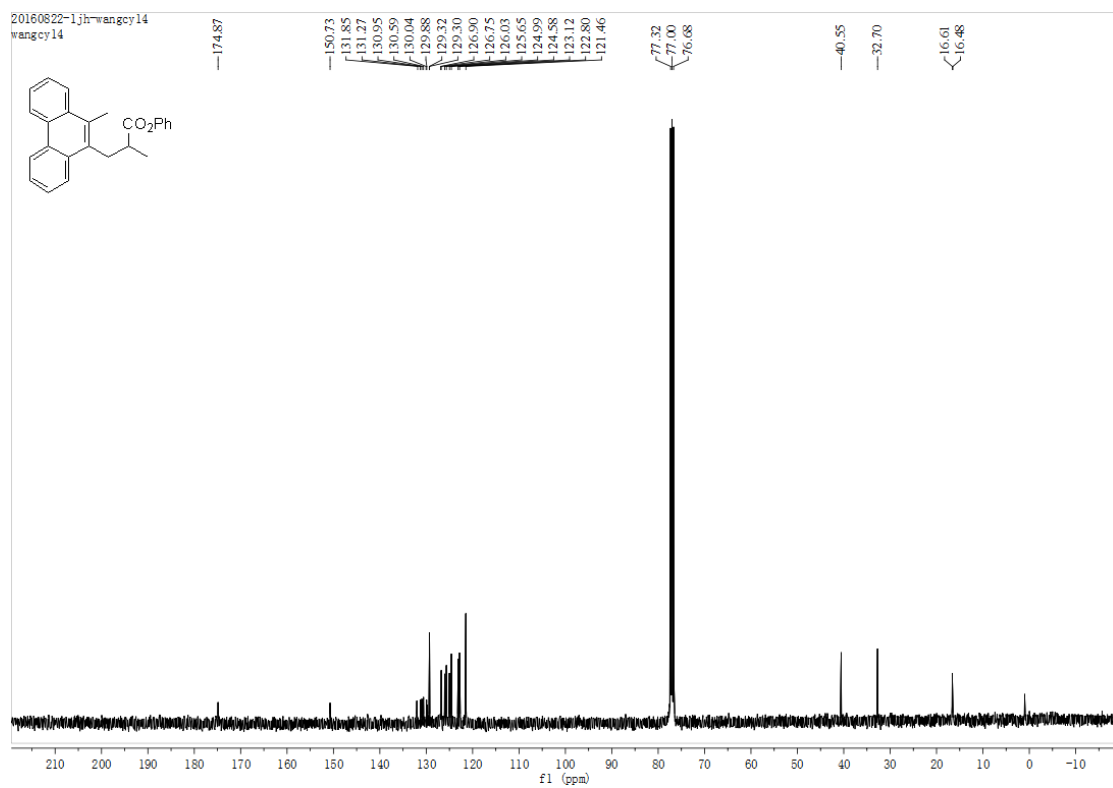
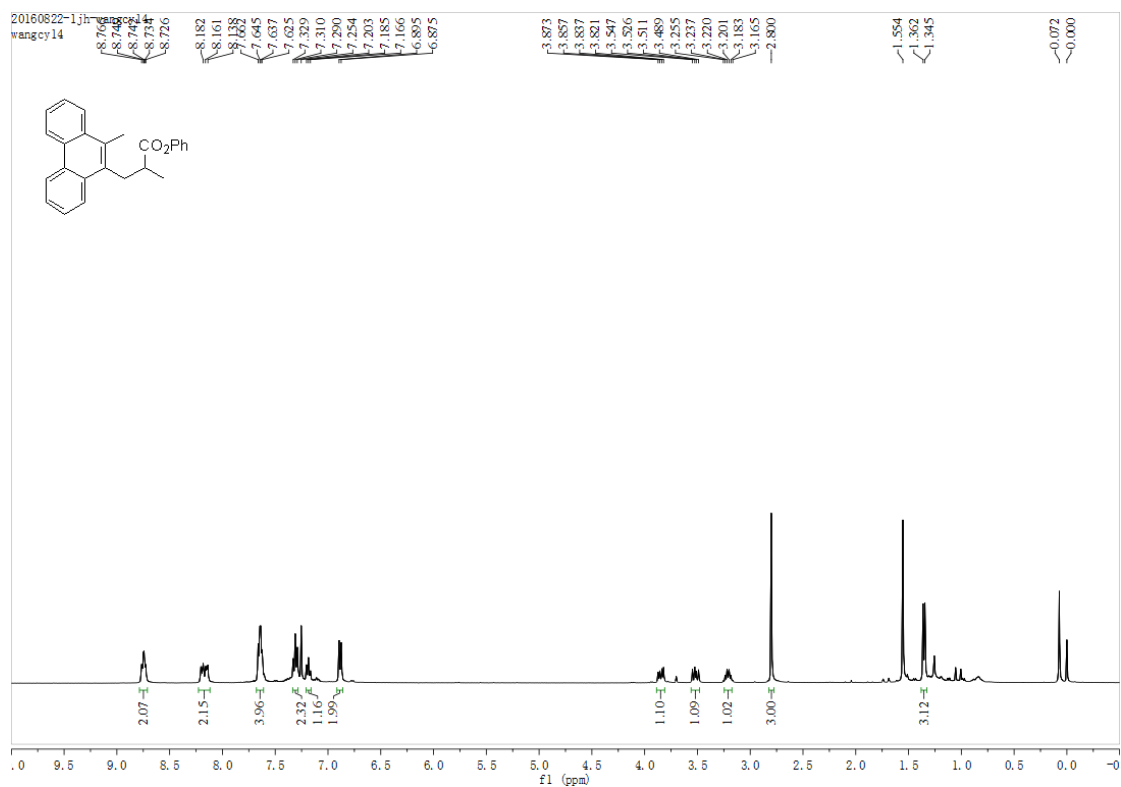
- (1) J. Tummatorn, G. B. Dudley, *Org. Lett.*, 2011, **13**, 1572.
- (2) M. Šámal, S. Chercheja, J. Rybáček, J. V. Chocholoušová, J. Vacek, L. Bednárová, D. Šaman, I. G. Stará, I. Starý, *J. Am. Chem. Soc.*, 2015, **137**, 8469.
- (3) T. Kippo, T. Fukuyama, I. Ryu, *Org. Lett.*, 2011, **13**, 3864.
- (4) C. Zhu, L. Qiu, G. Xu, J. Li, J. Sun, *Chem. Eur. J.*, 2015, **21**, 12871.
- (5) J.-H. Fan, W.-T. Wei, M.-B. Zhou, R.-J. Song, J.-H. Li, *Angew. Chem. Int. Ed.*, 2014, **53**, 6650.

(D) Spectra

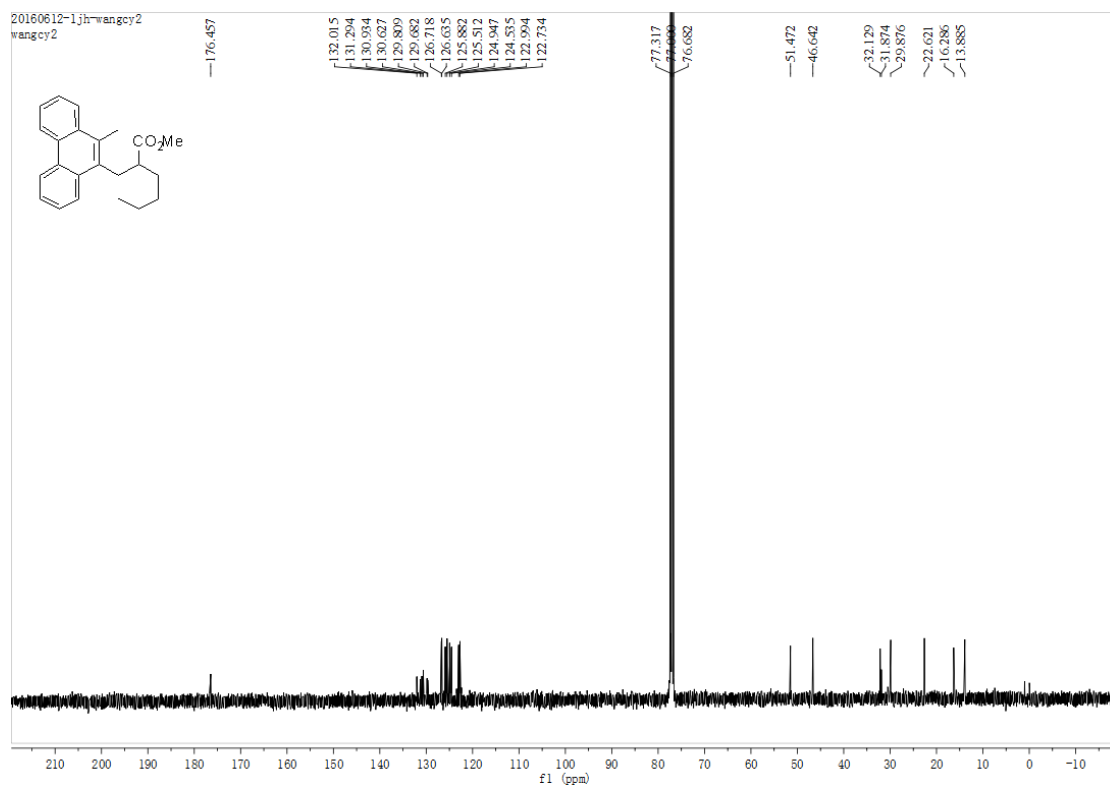
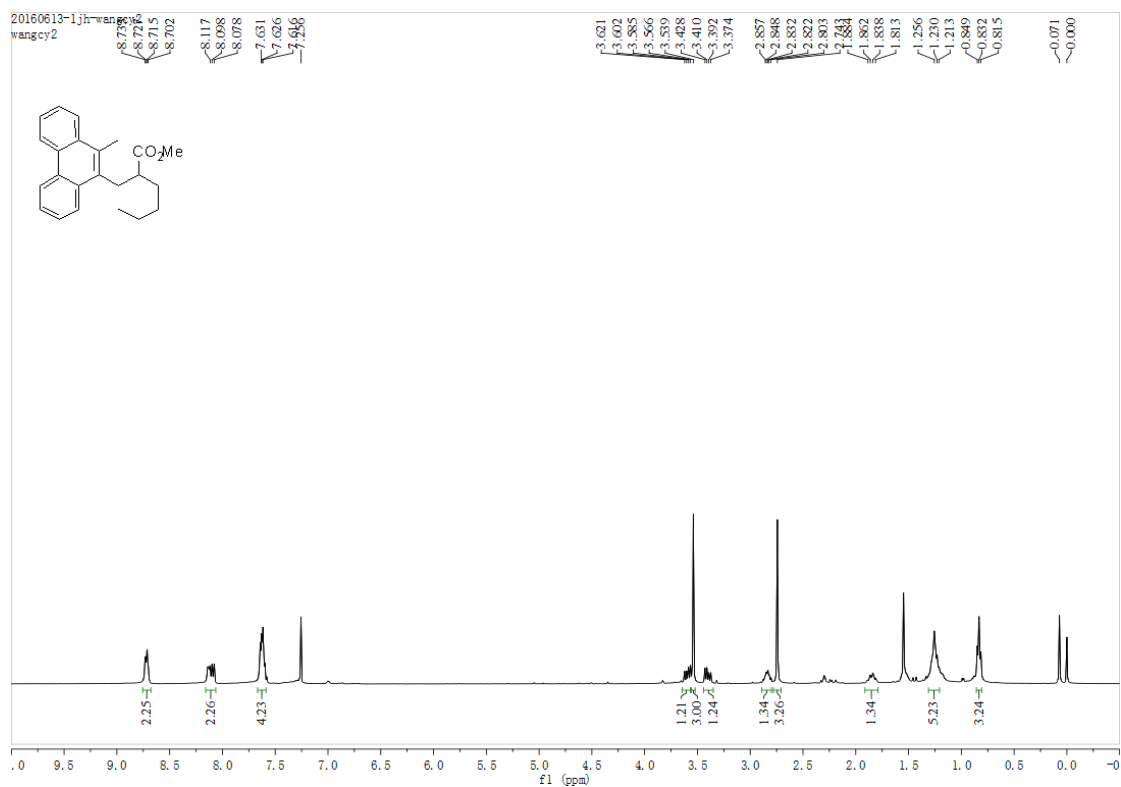
Methyl 2-methyl-3-(10-methylphenanthren-9-yl)propanoate (3aa)



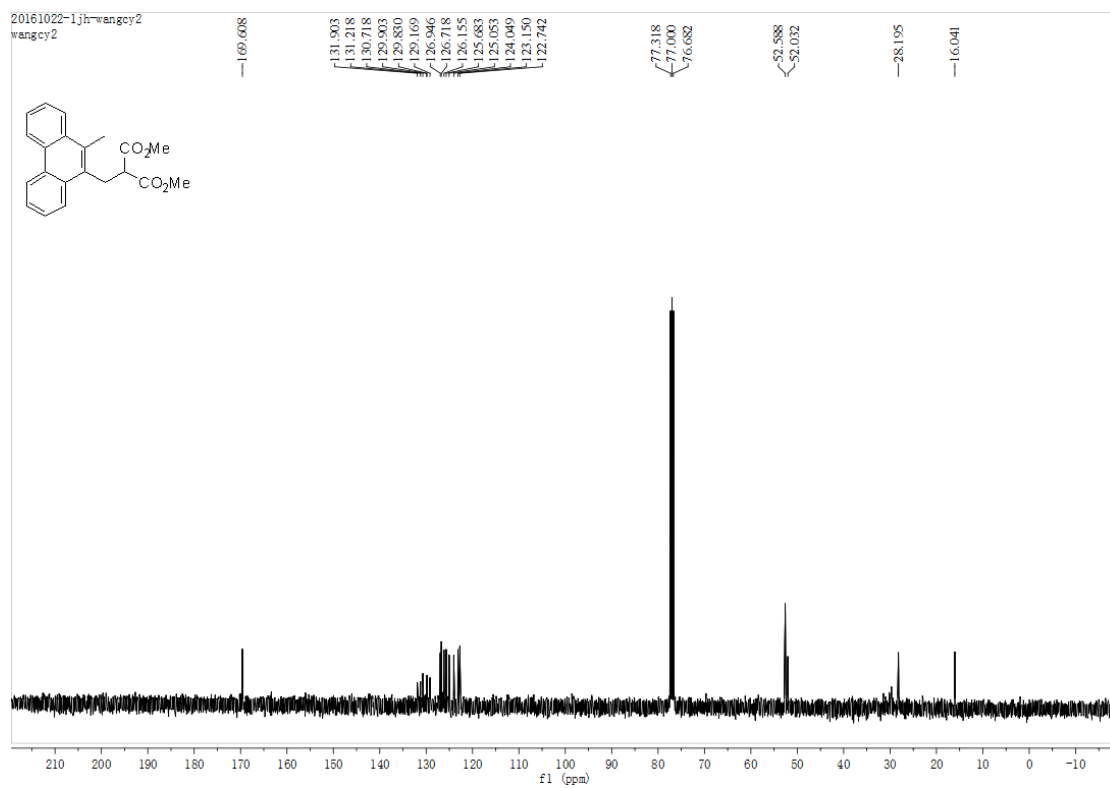
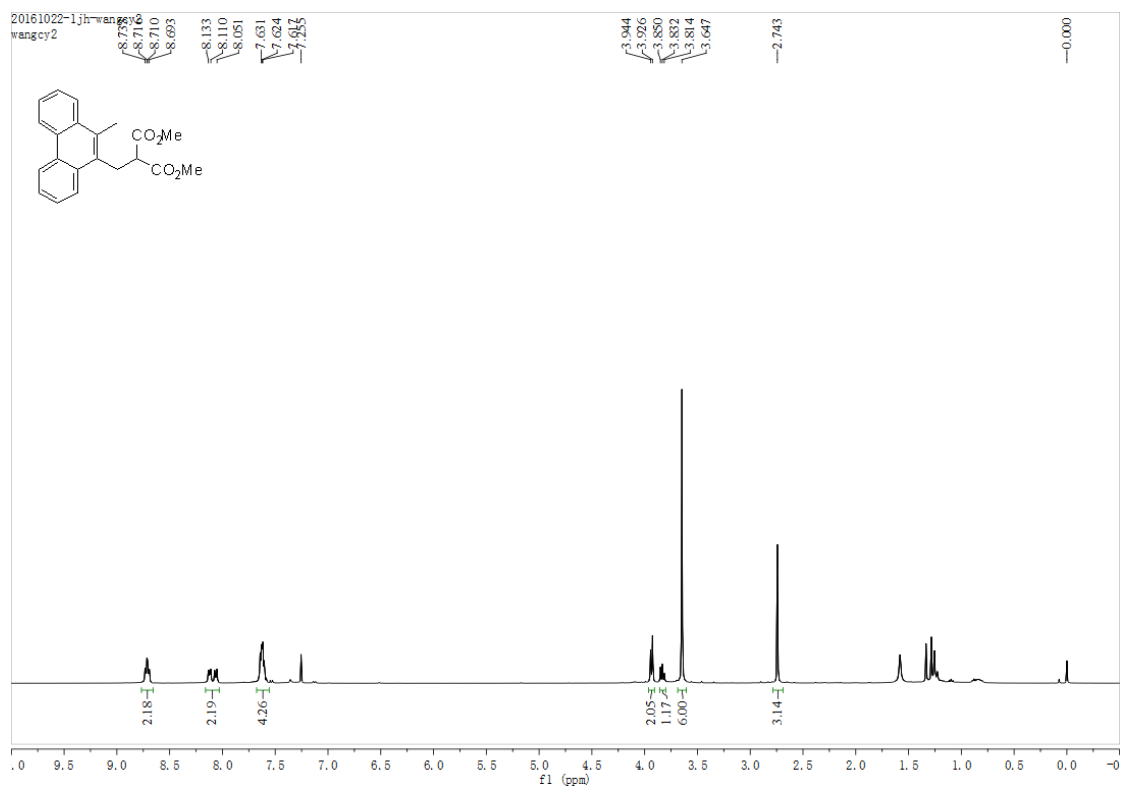
Phenyl 2-methyl-3-(10-methylphenanthren-9-yl)propanoate (3ab)



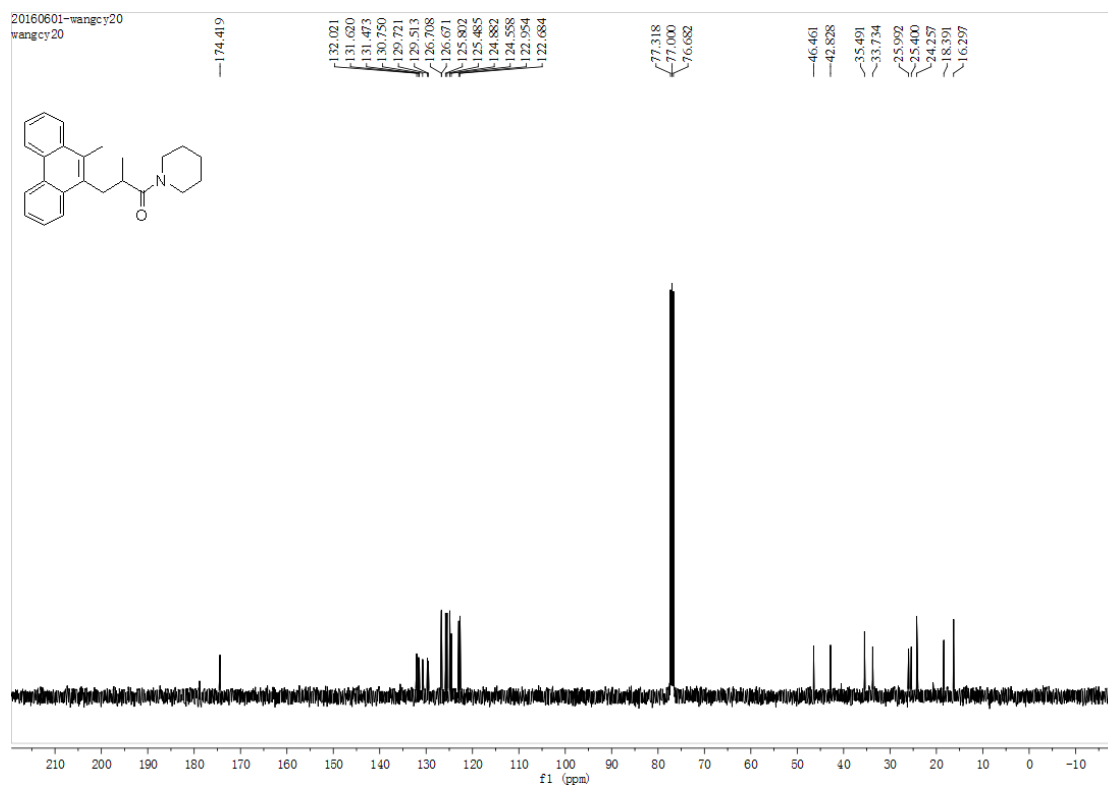
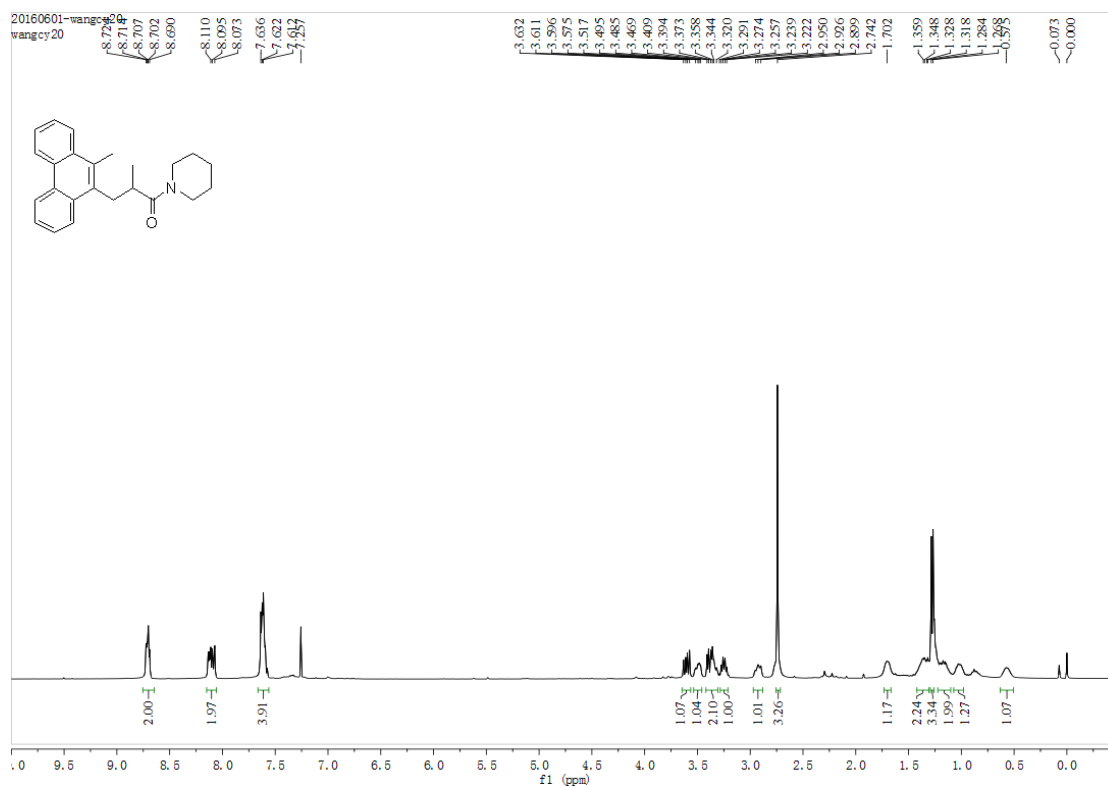
Methyl 2-((10-methylphenanthren-9-yl)methyl)hexanoate (3ac)



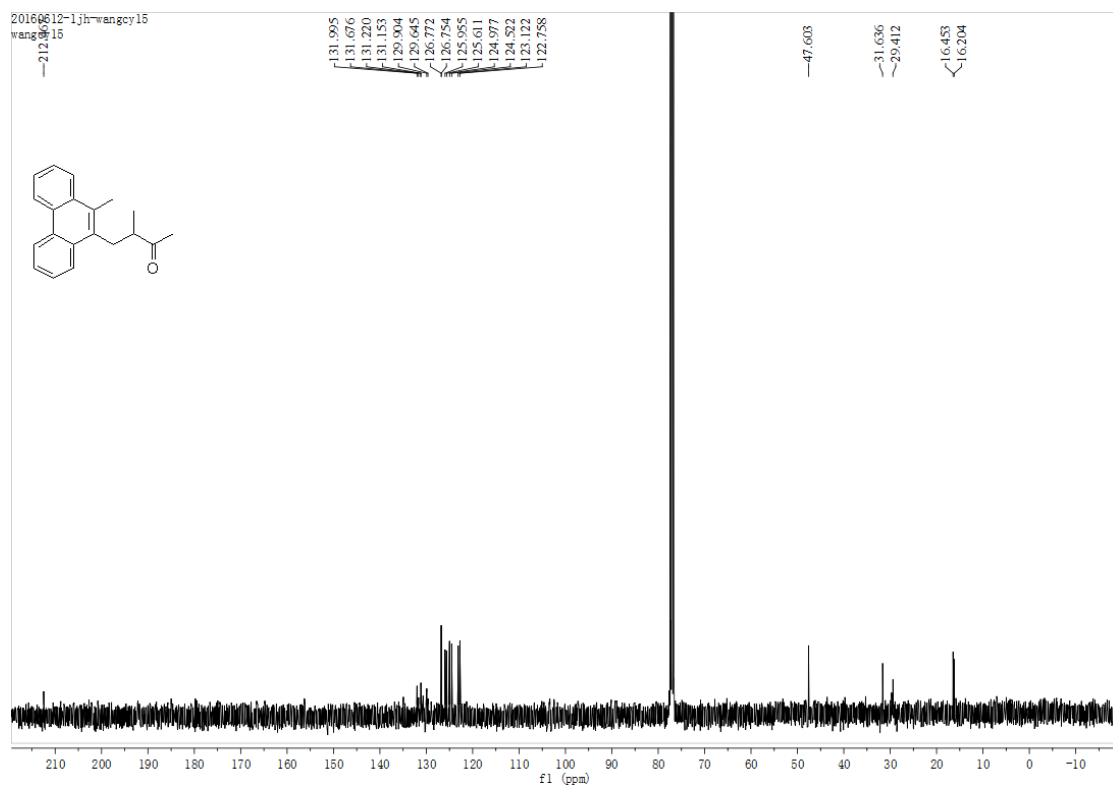
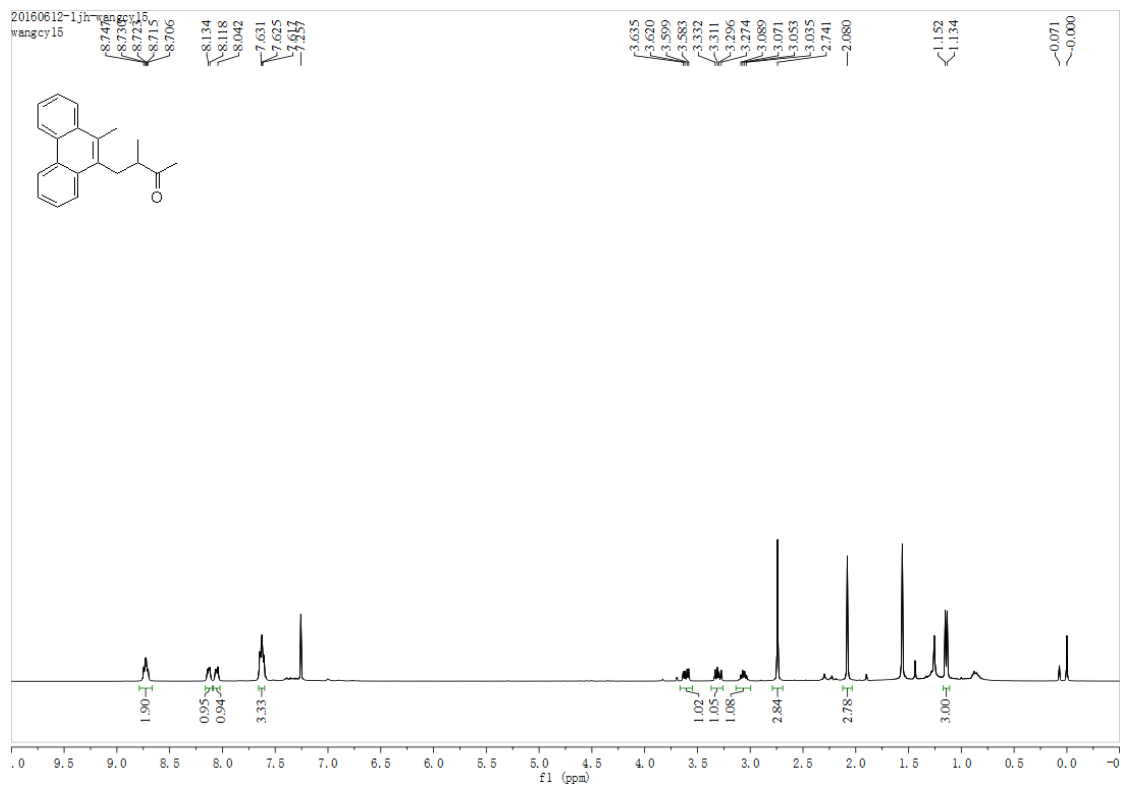
Dimethyl 2-((10-methylphenanthren-9-yl)methyl)malonate (3ad)



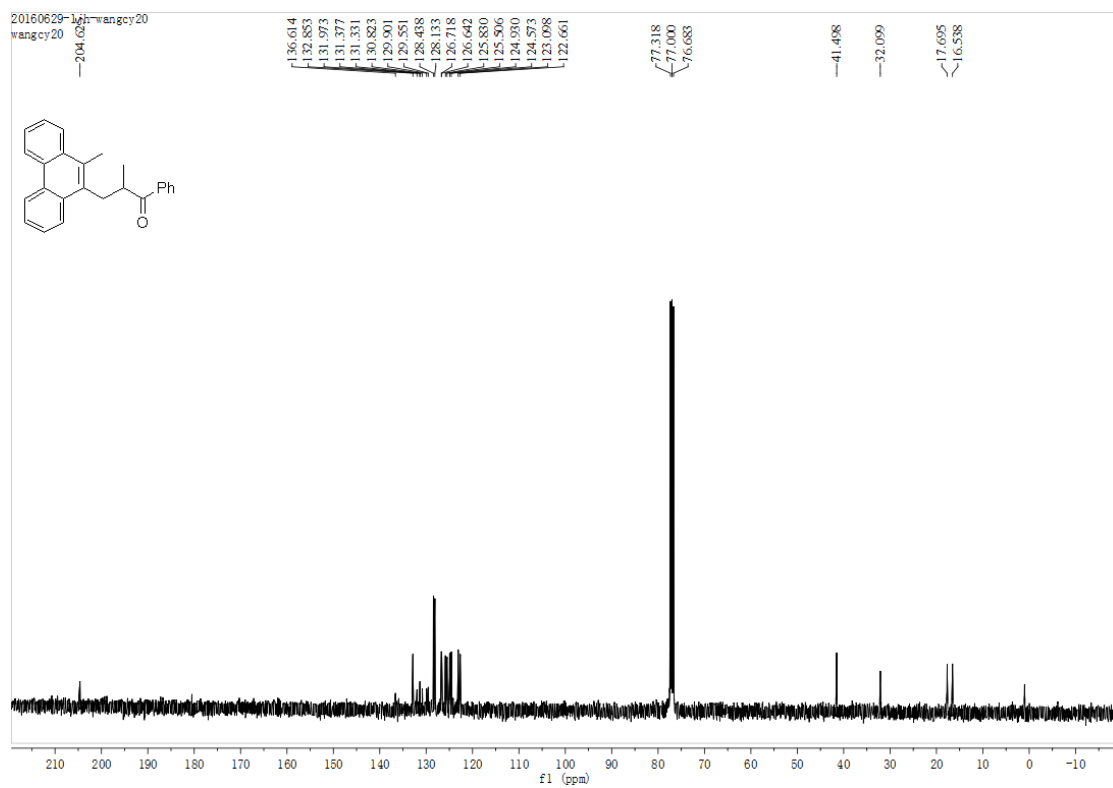
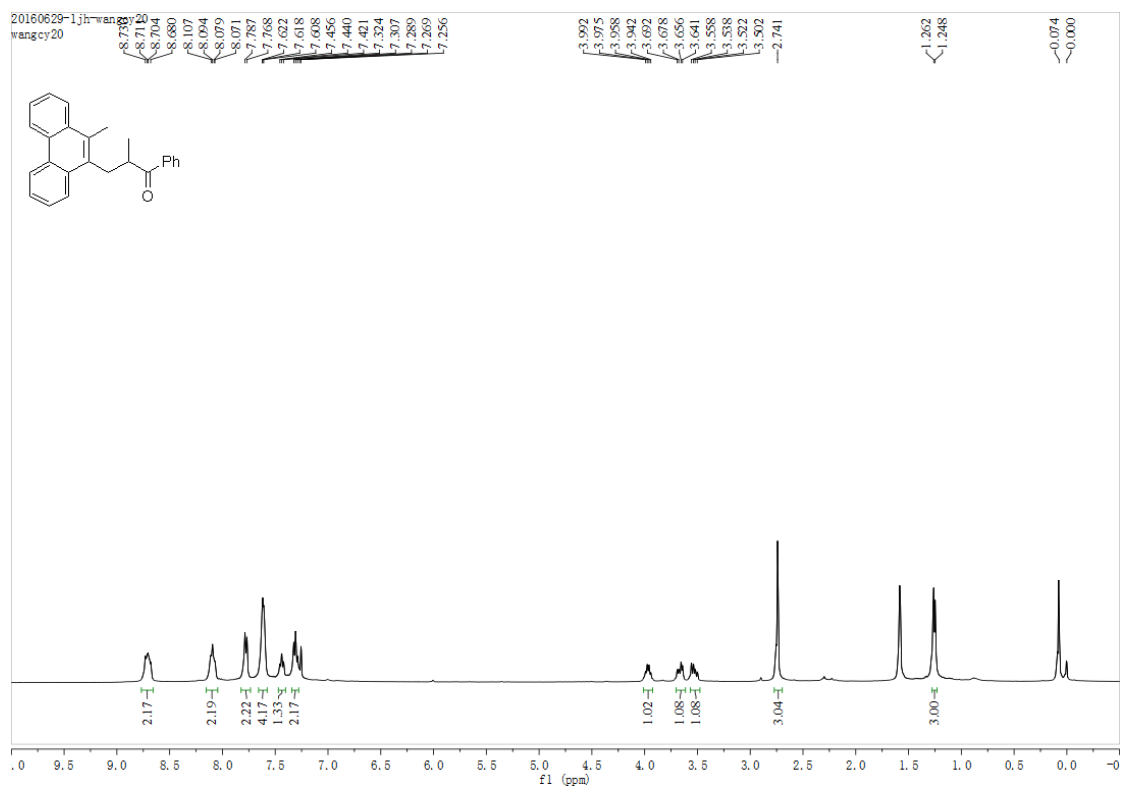
2-Methyl-3-(10-methylphenanthren-9-yl)-1-(piperidin-1-yl)propan-1-one (3ae)



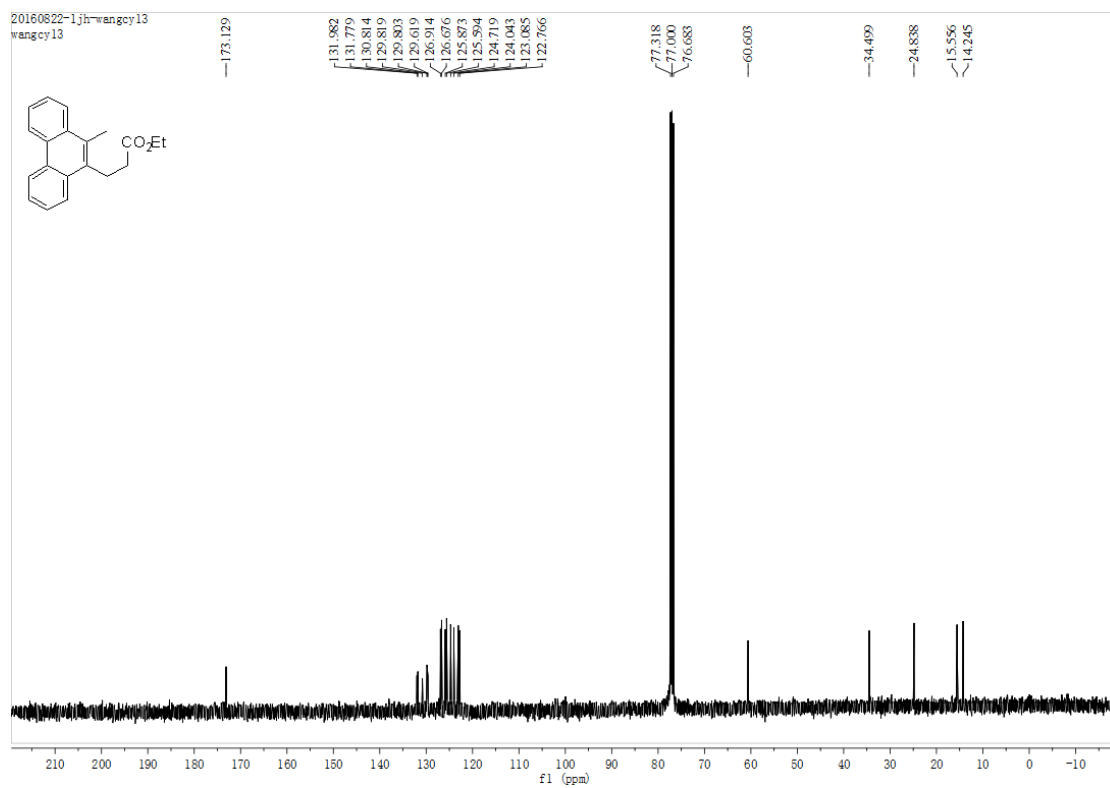
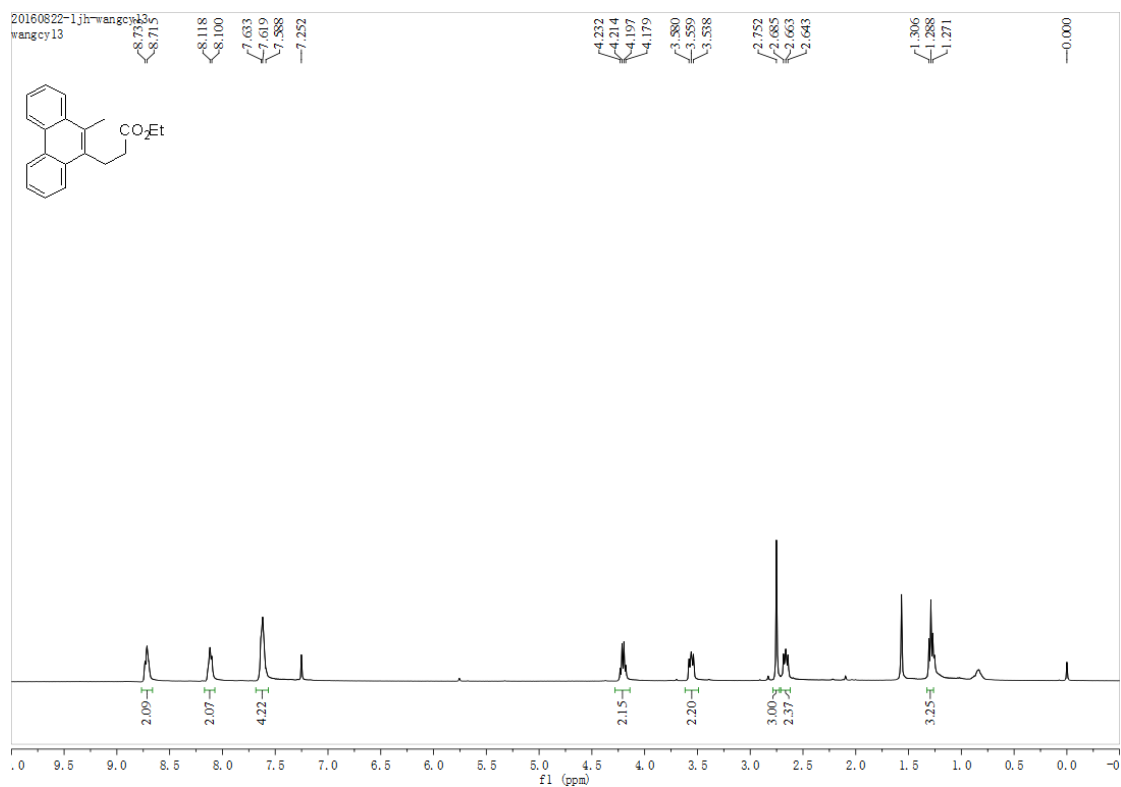
3-Methyl-4-(10-methylphenanthren-9-yl)butan-2-one (3af)



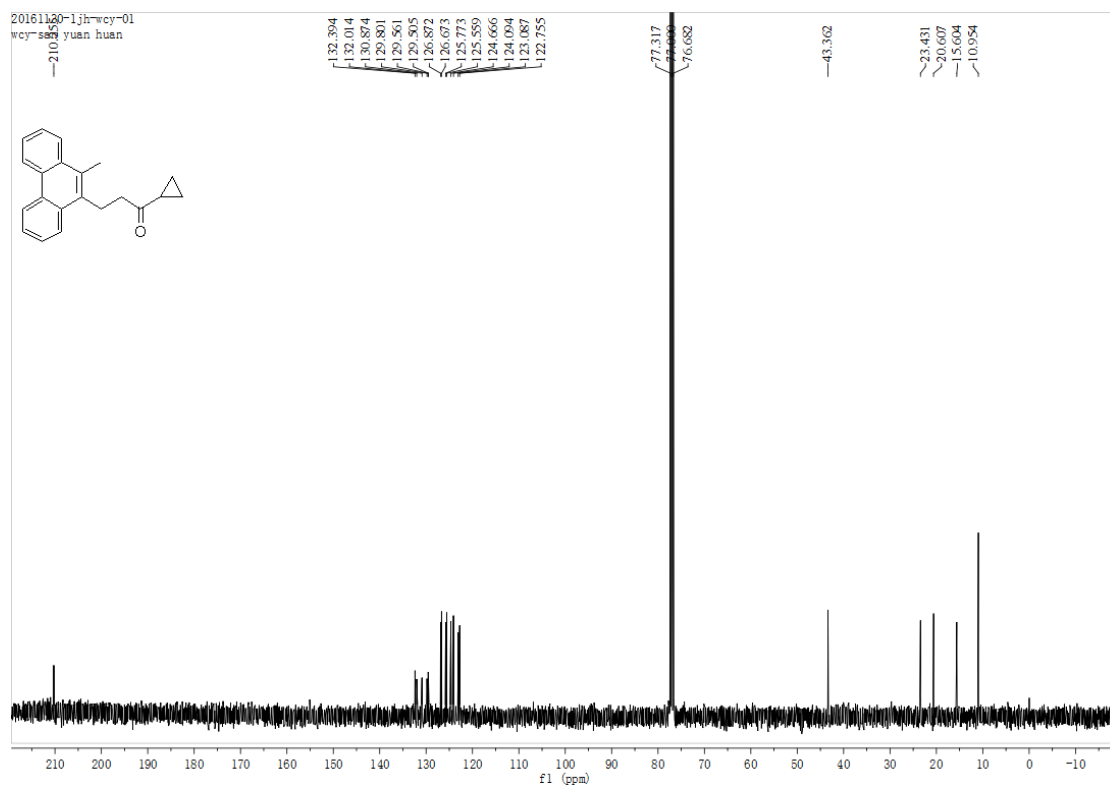
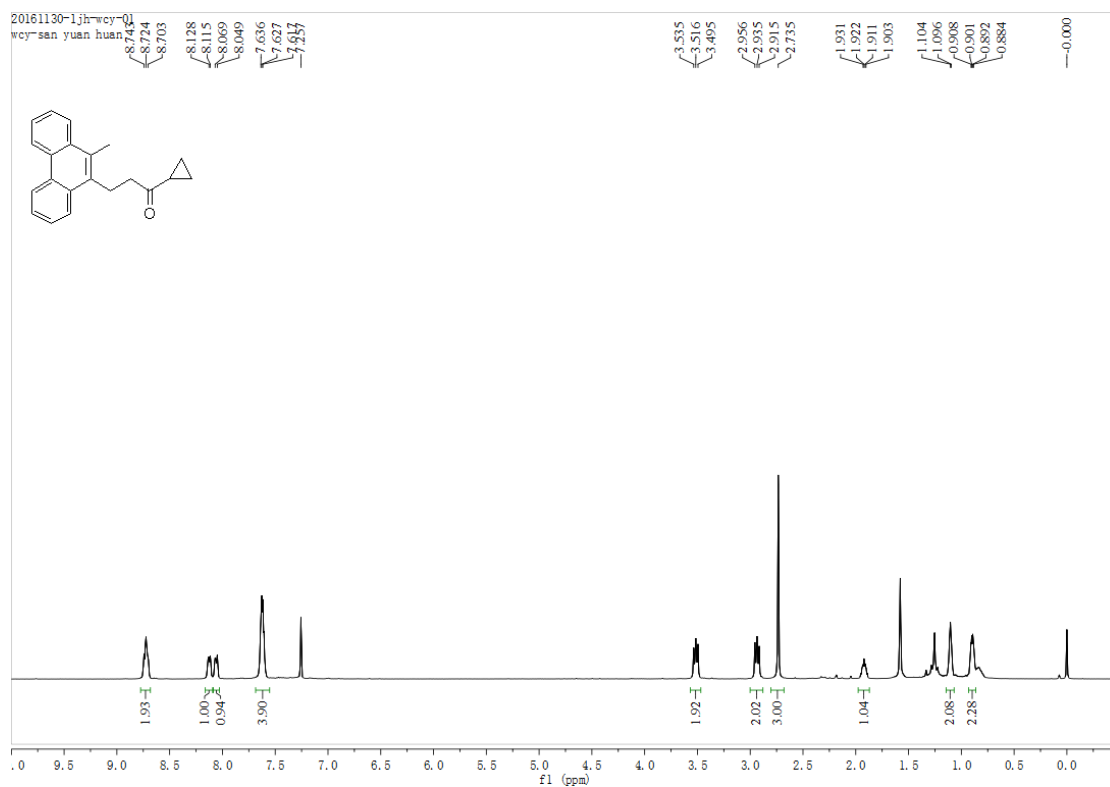
2-Methyl-3-(10-methylphenanthren-9-yl)-1-phenylpropan-1-one (3ag)



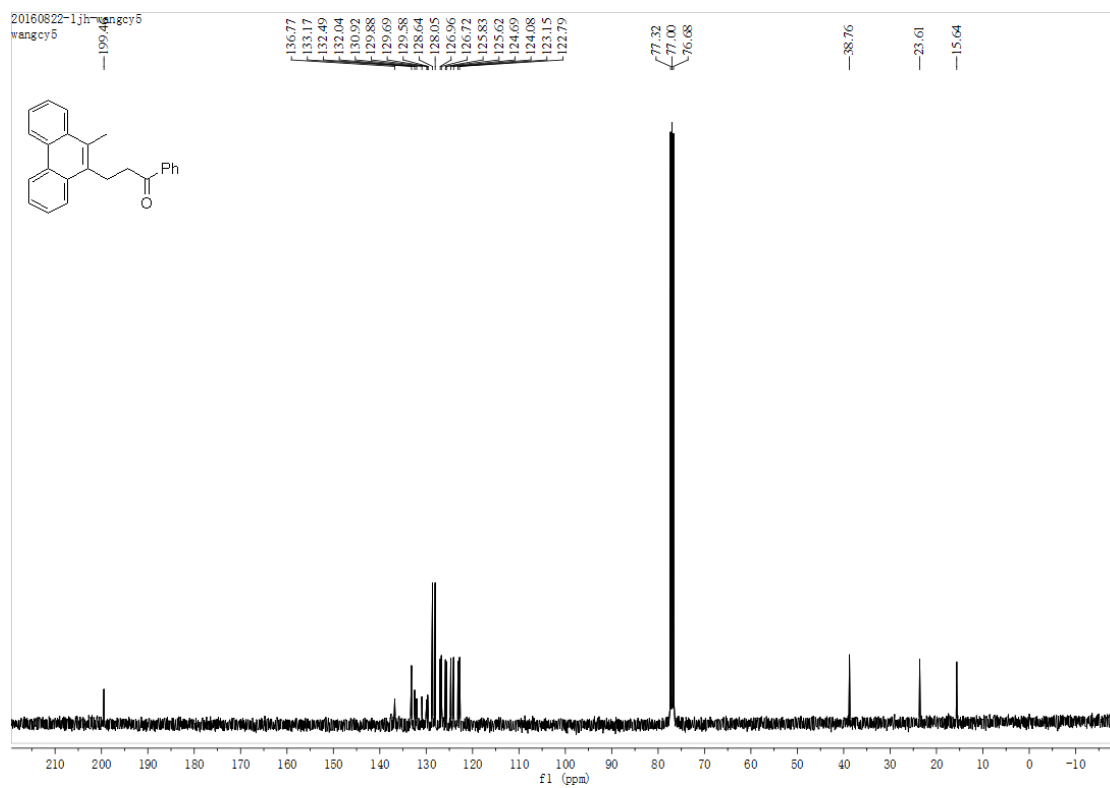
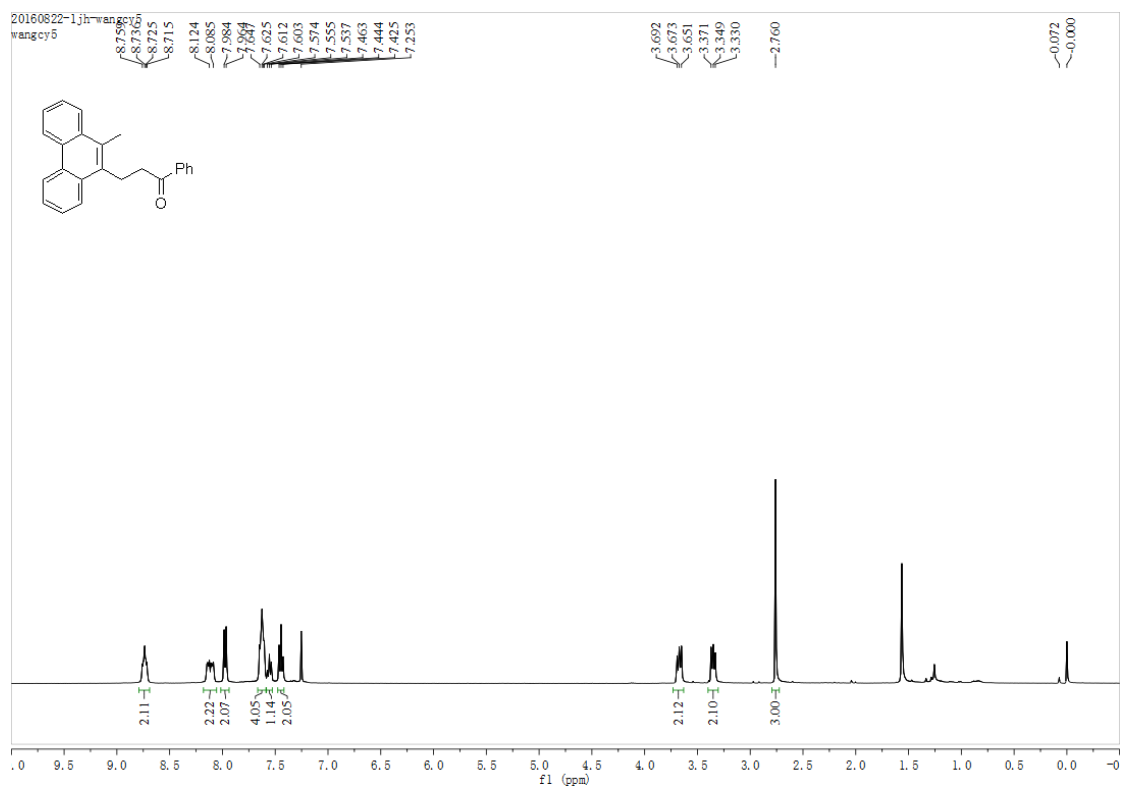
Ethyl 3-(10-methylphenanthren-9-yl)propanoate (3ah)



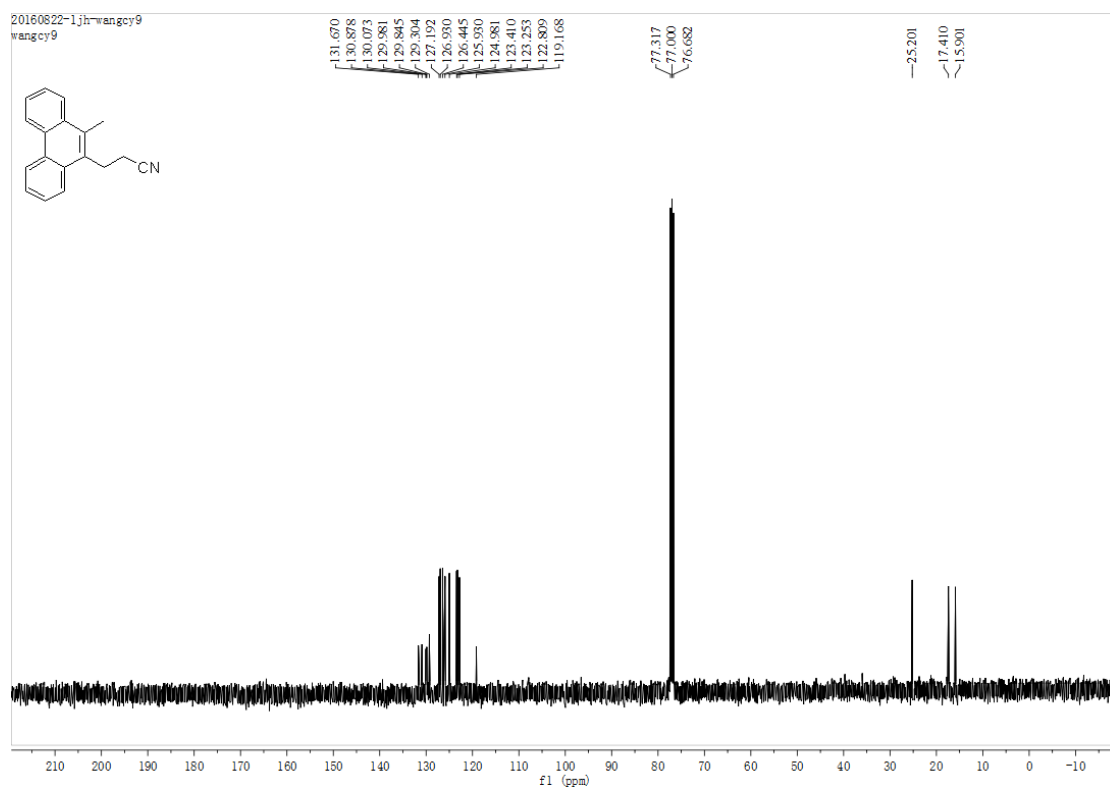
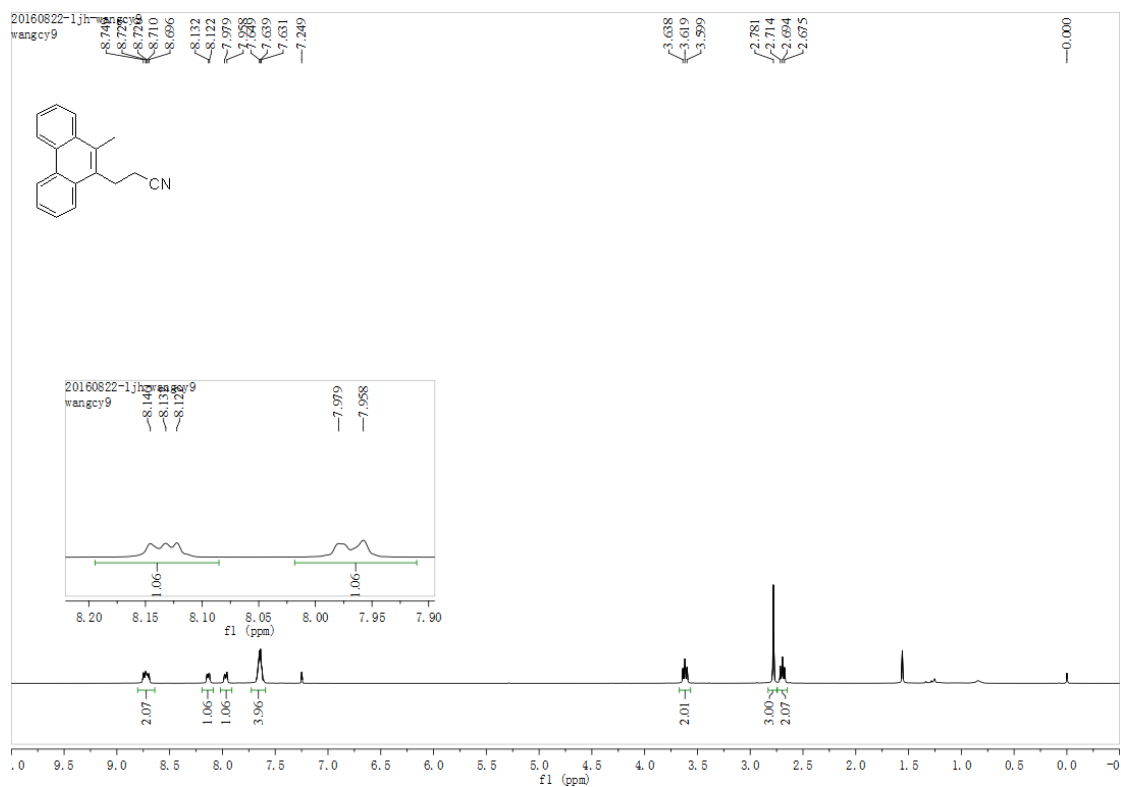
1-Cyclopropyl-3-(10-methylphenanthren-9-yl)propan-1-one (3ai)



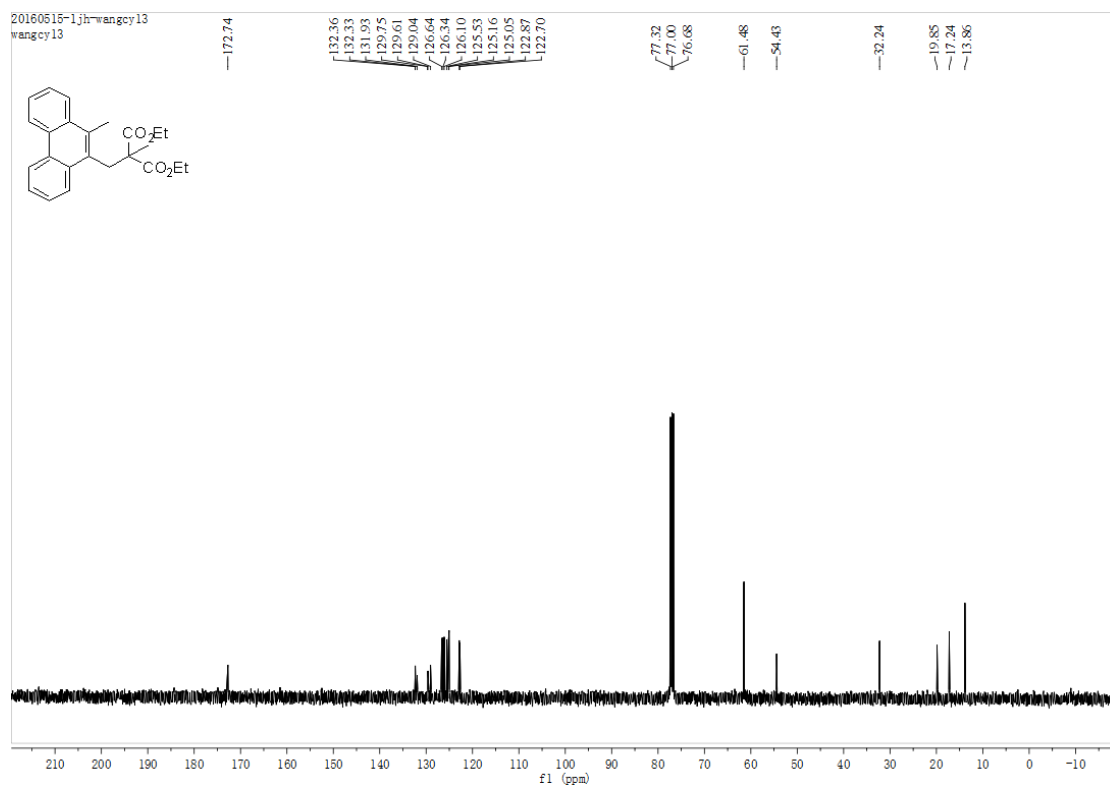
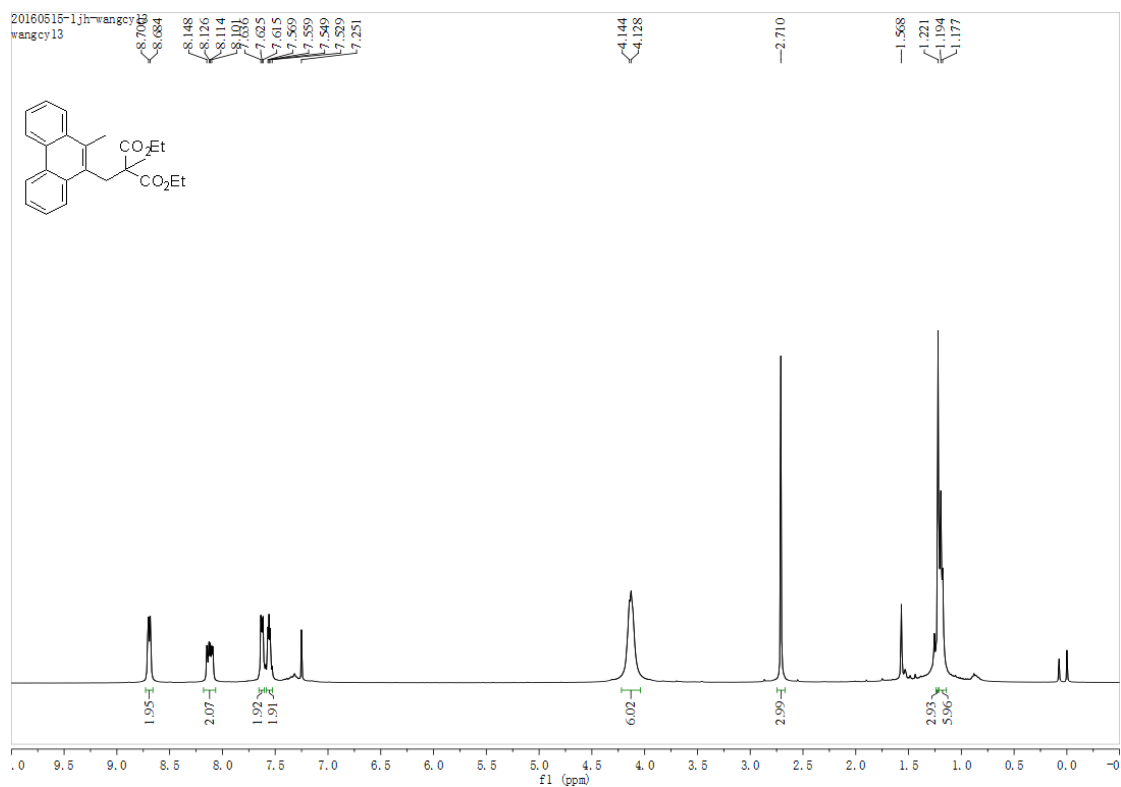
3-(10-Methylphenanthren-9-yl)-1-phenylpropan-1-one (3aj)



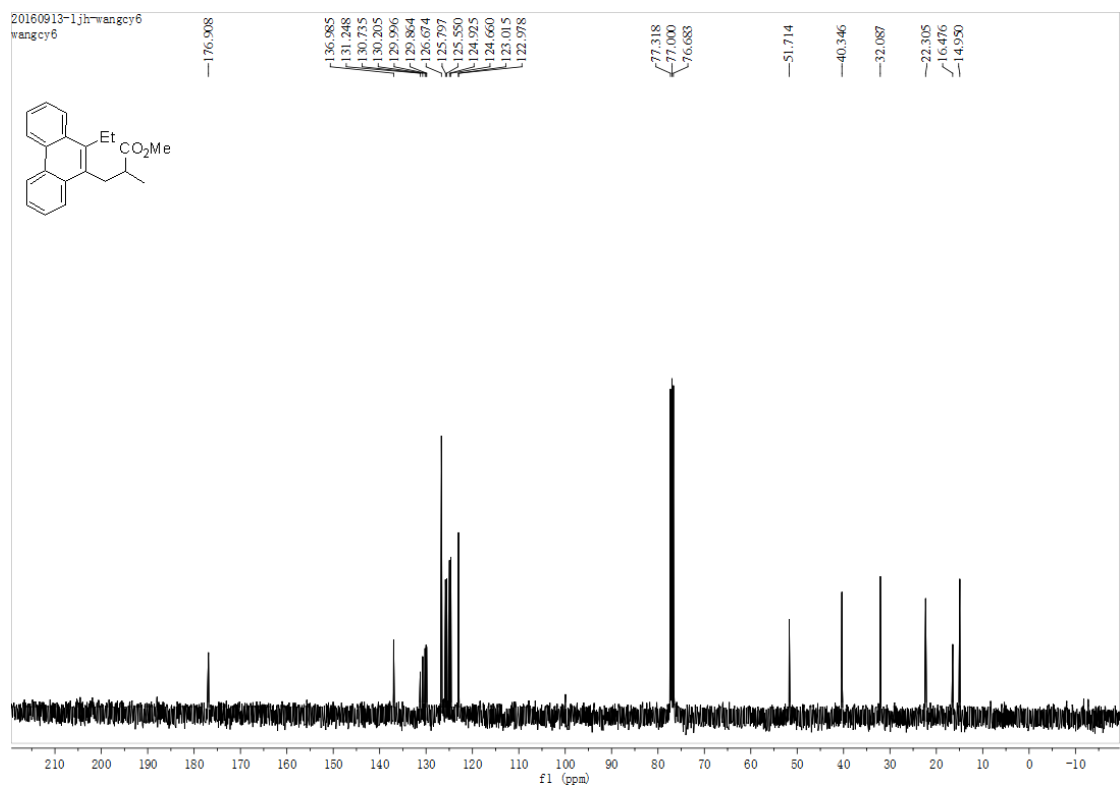
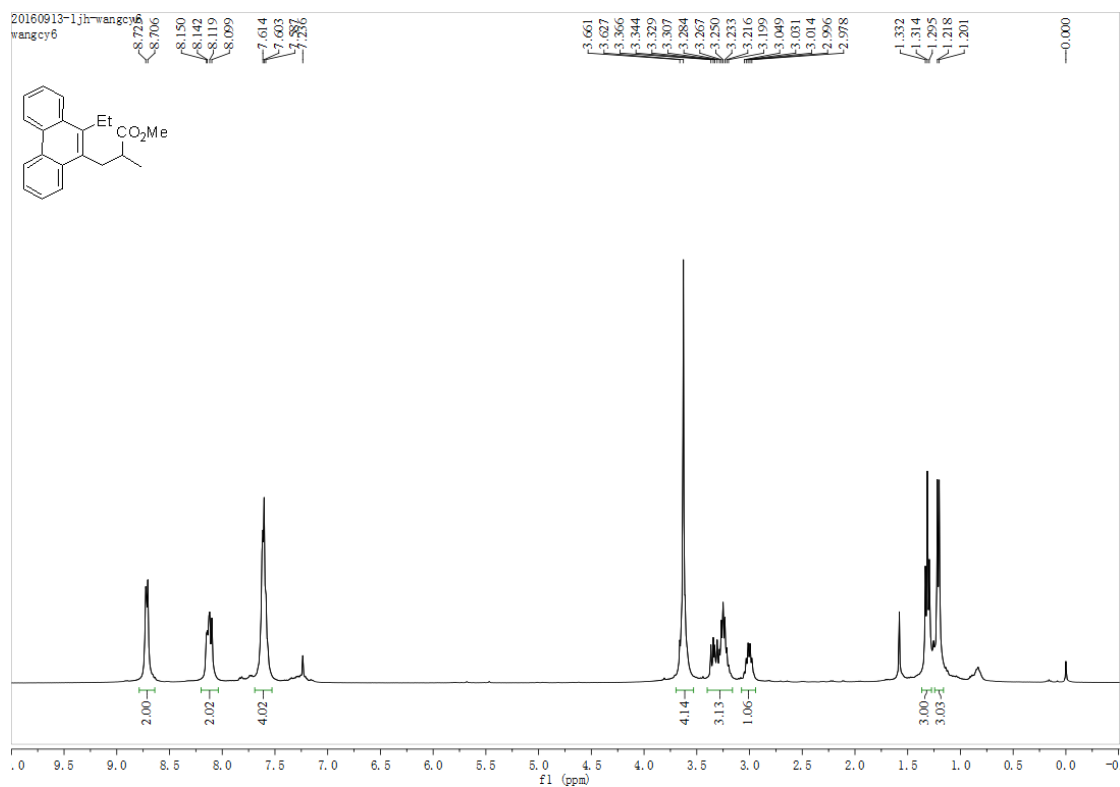
3-(10-Methylphenanthren-9-yl)propanenitrile (3ak)



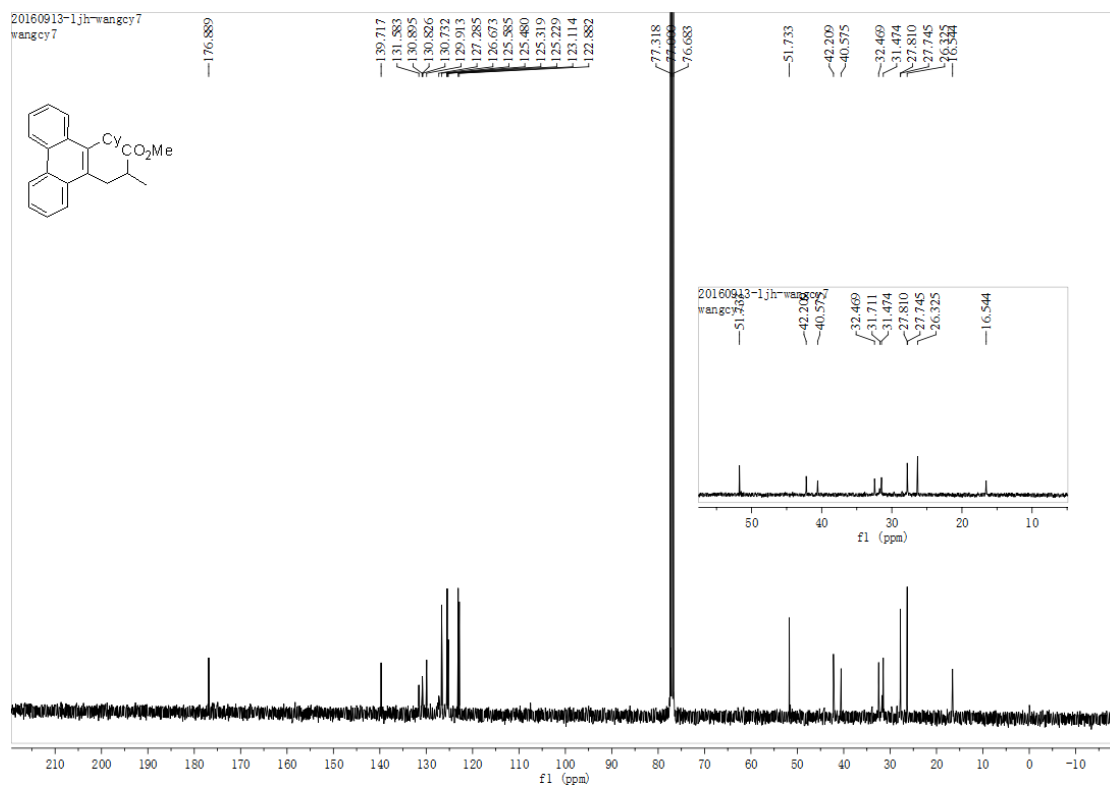
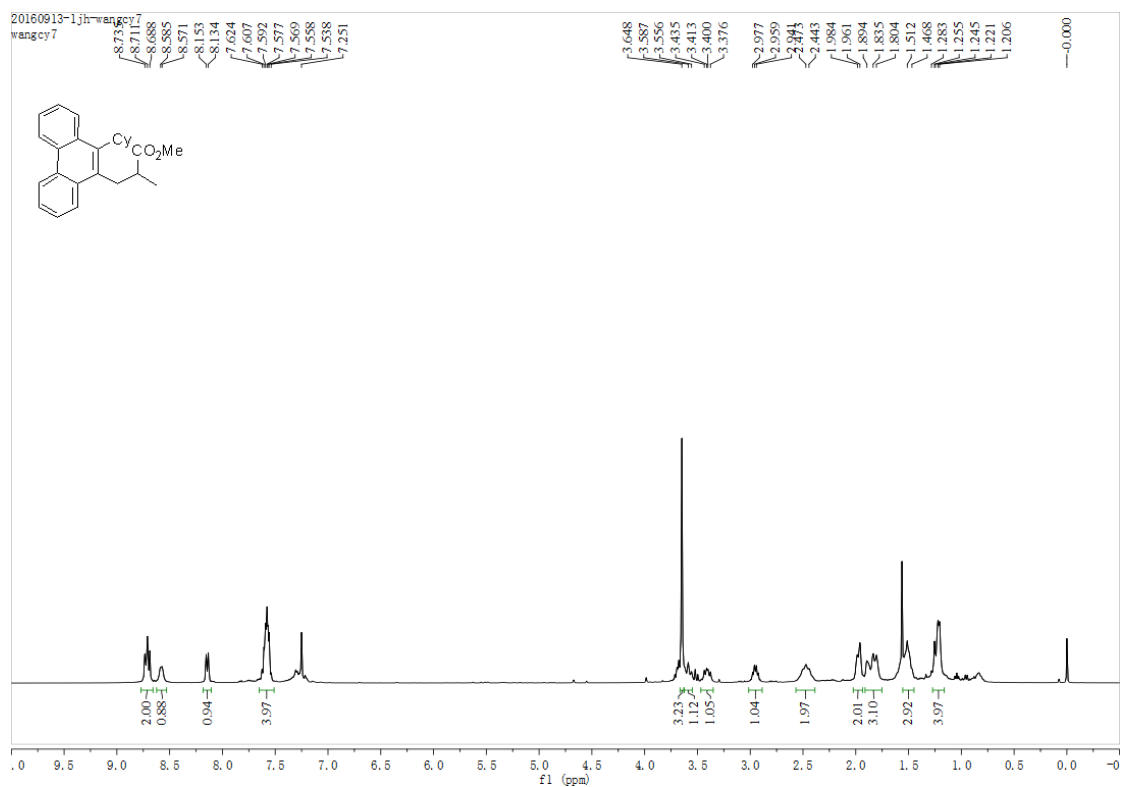
Diethyl 2-methyl-2-((10-methylphenanthren-9-yl)methyl)malonate (3aI)



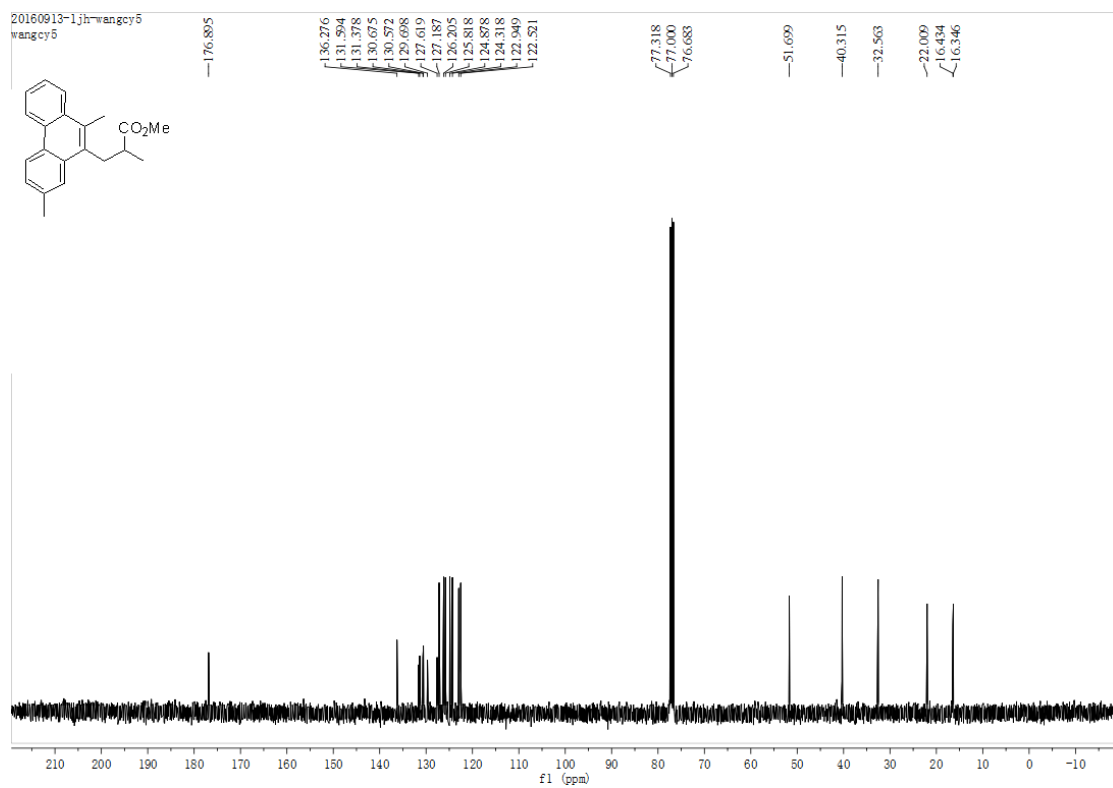
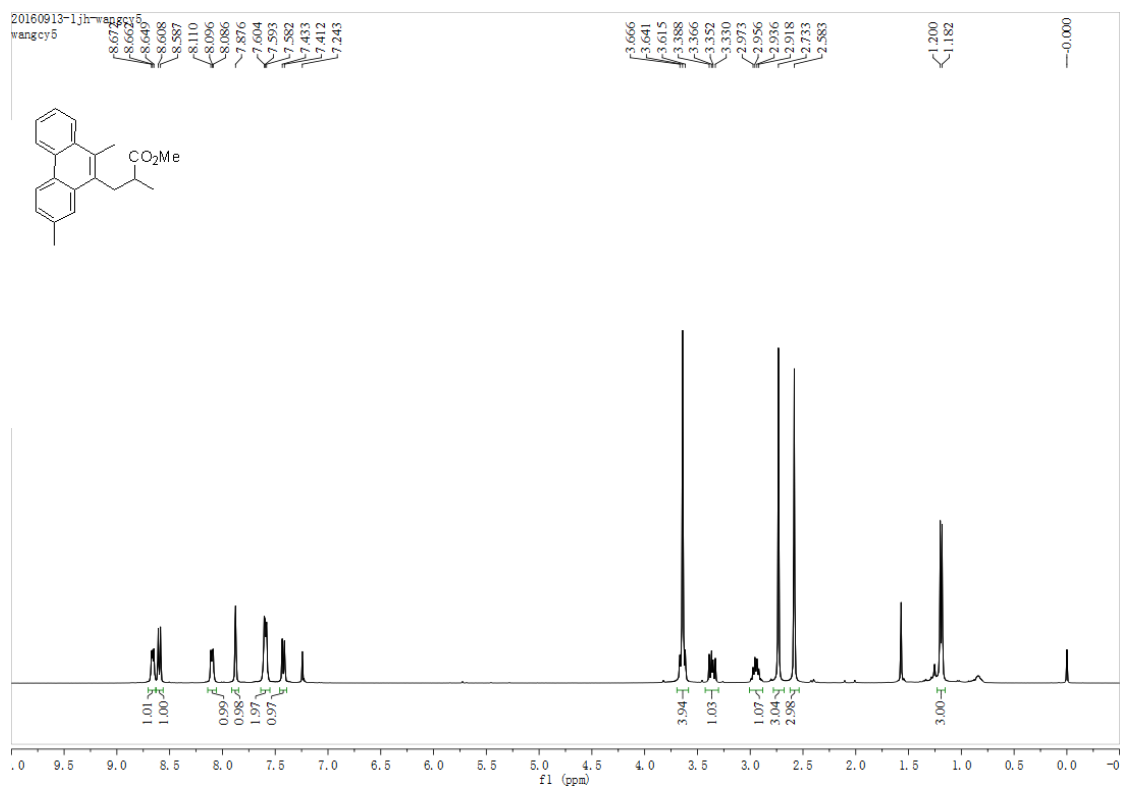
Methyl 3-(10-ethylphenanthren-9-yl)-2-methylpropanoate (3ba)



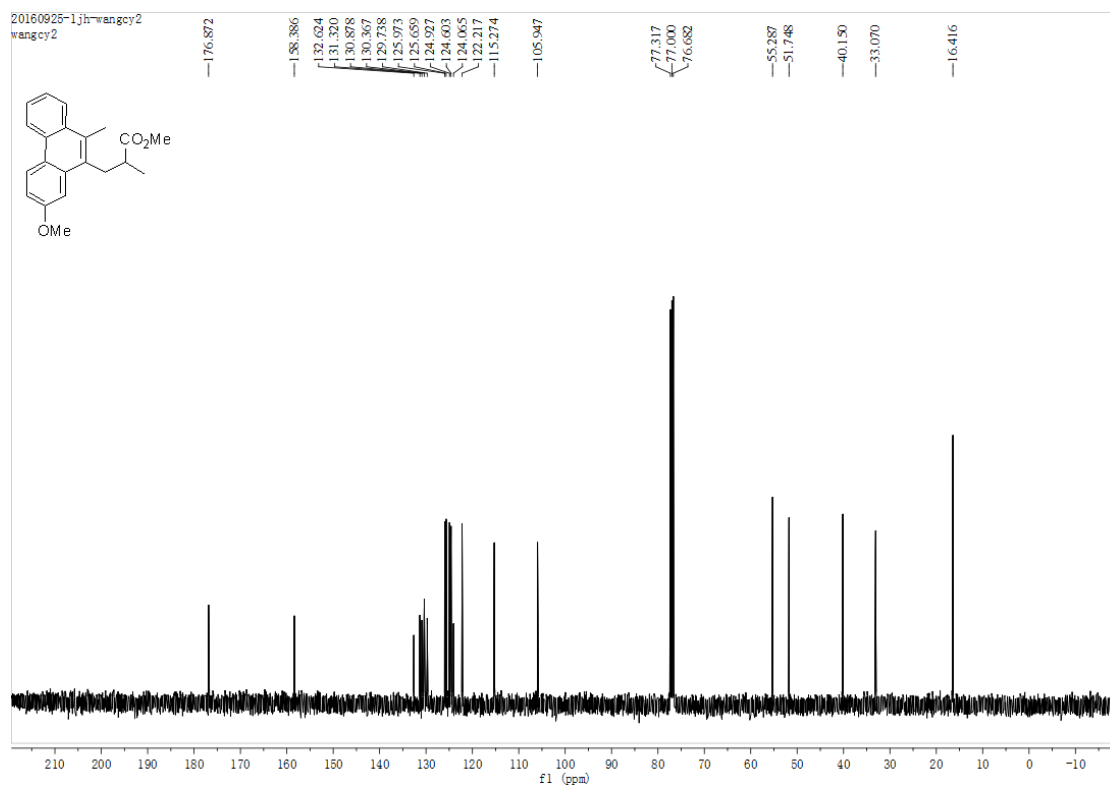
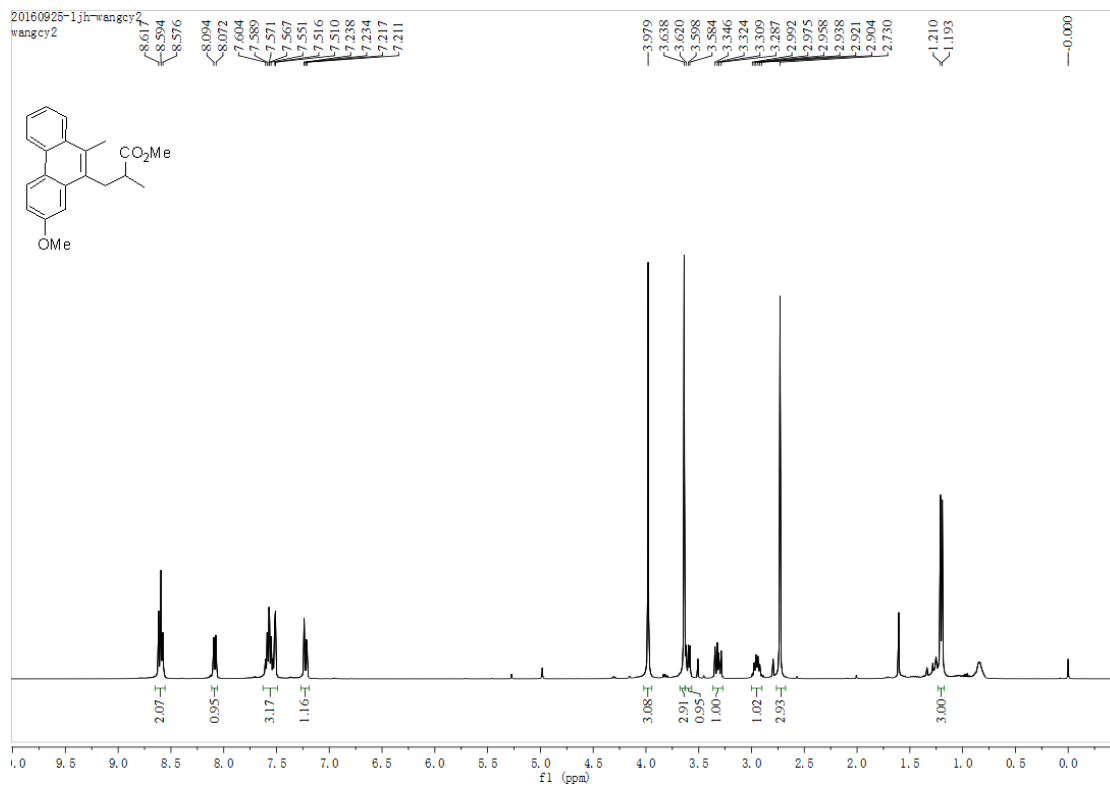
Methyl 3-(10-cyclohexylphenanthren-9-yl)-2-methylpropanoate (3ca)



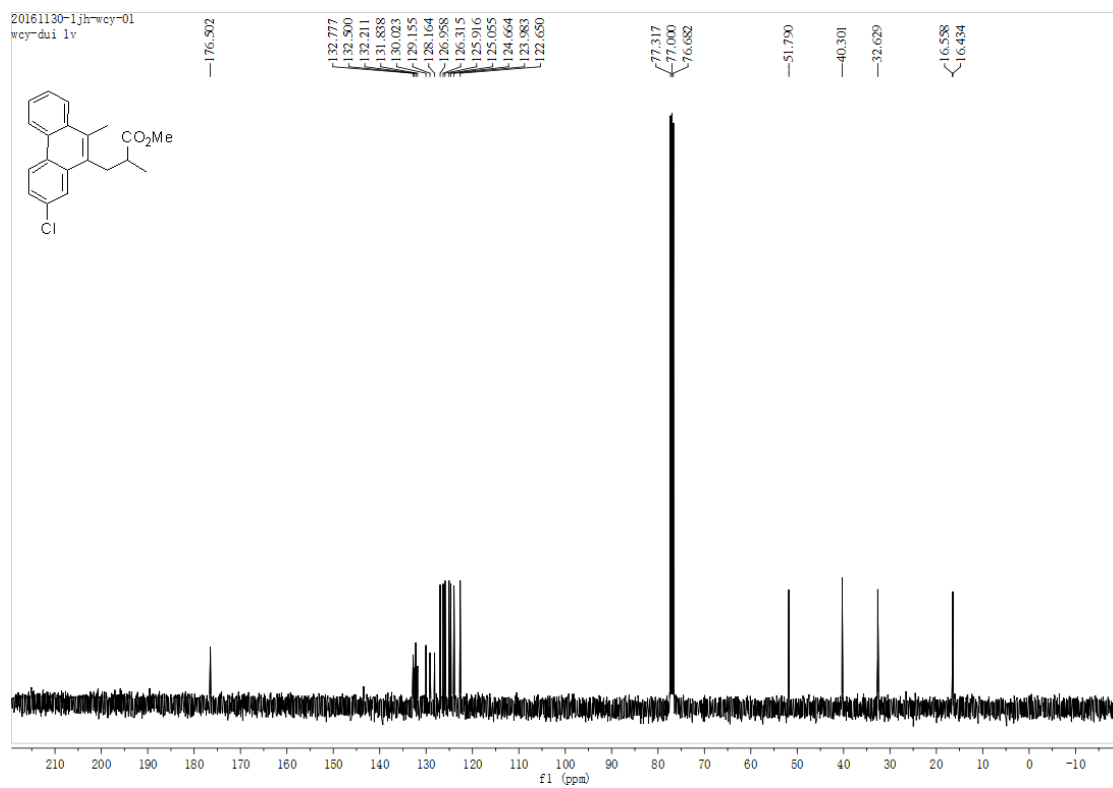
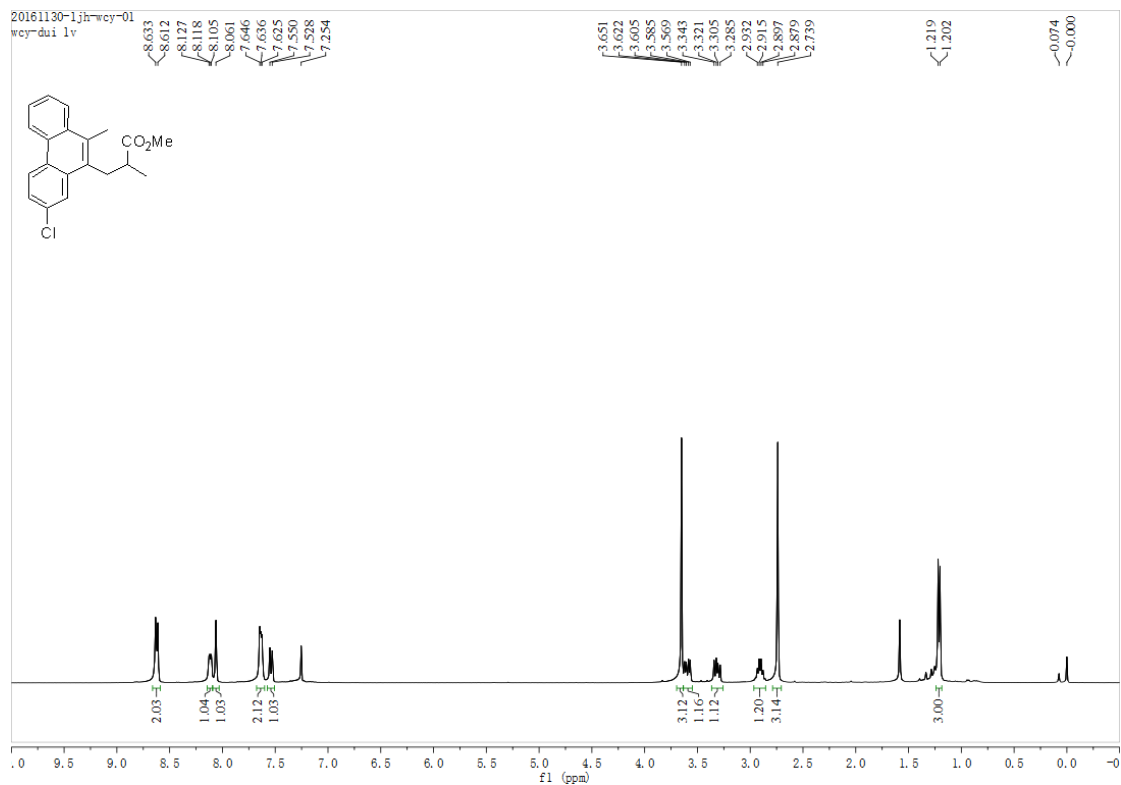
Methyl 3-(7,10-dimethylphenanthren-9-yl)-2-methylpropanoate (3da)



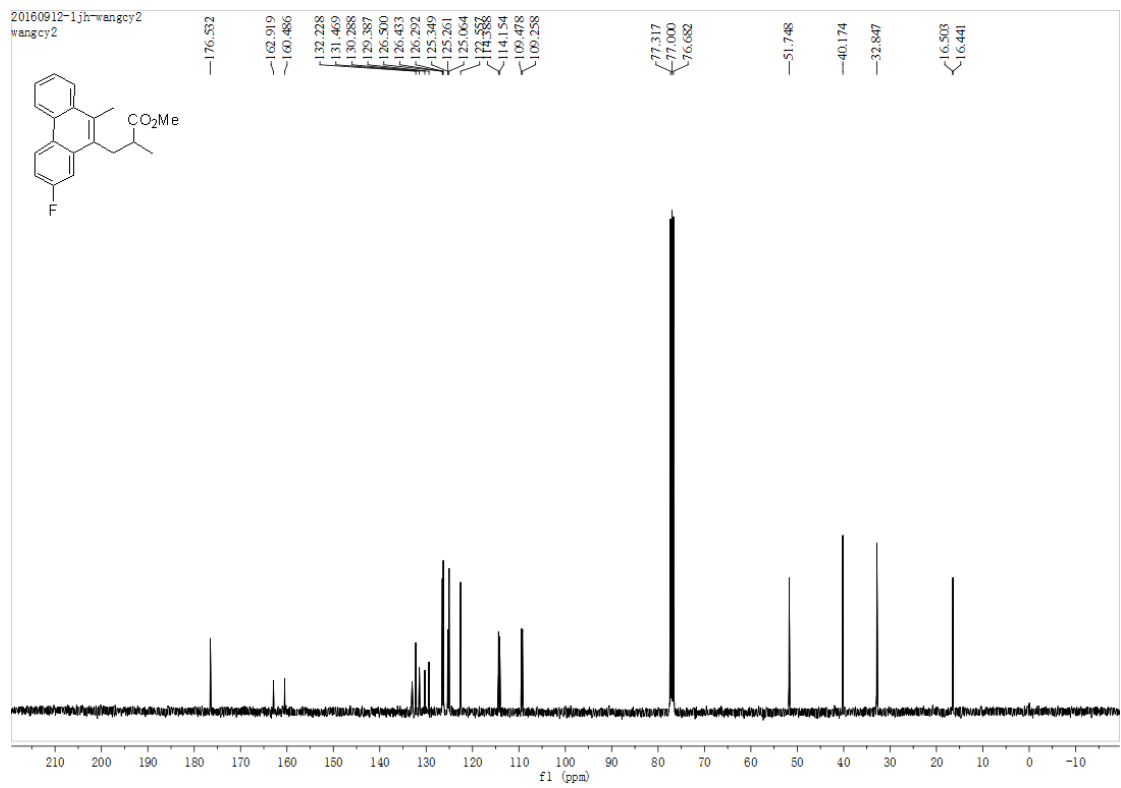
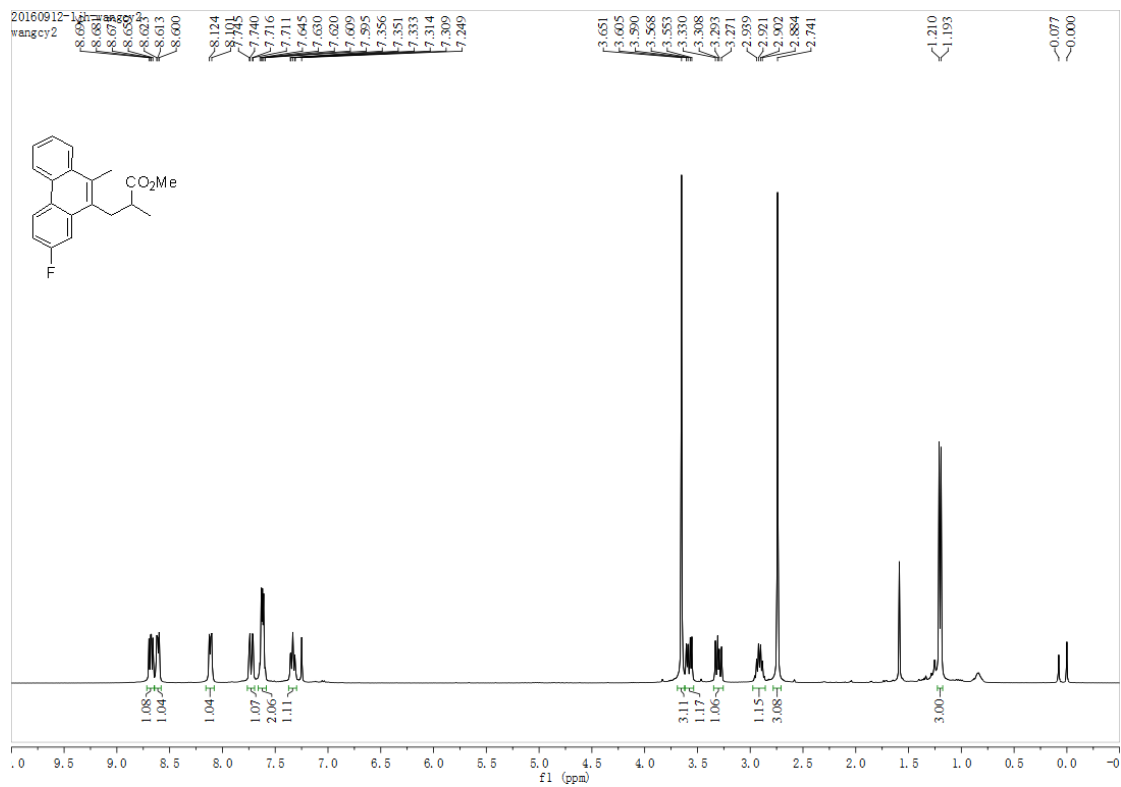
Methyl 3-(7-methoxy-10-methylphenanthren-9-yl)-2-methylpropanoate (3ea)



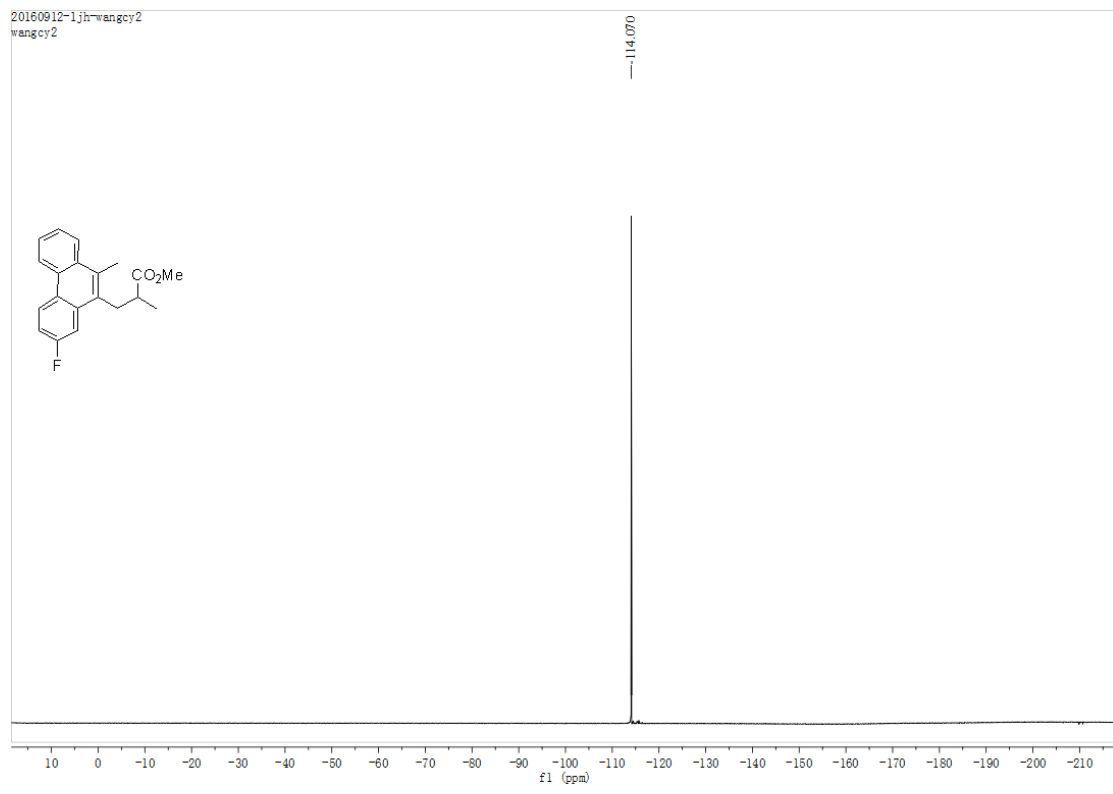
Methyl 3-(7-chloro-10-methylphenanthren-9-yl)-2-methylpropanoate (3fa)



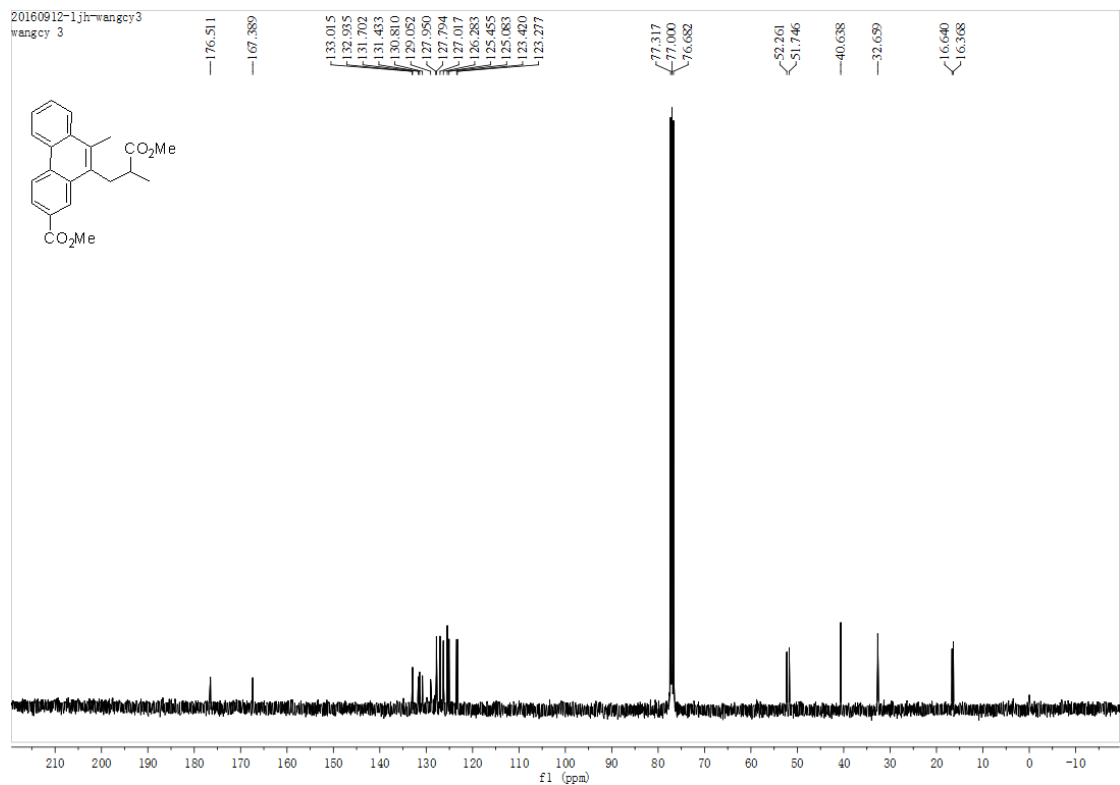
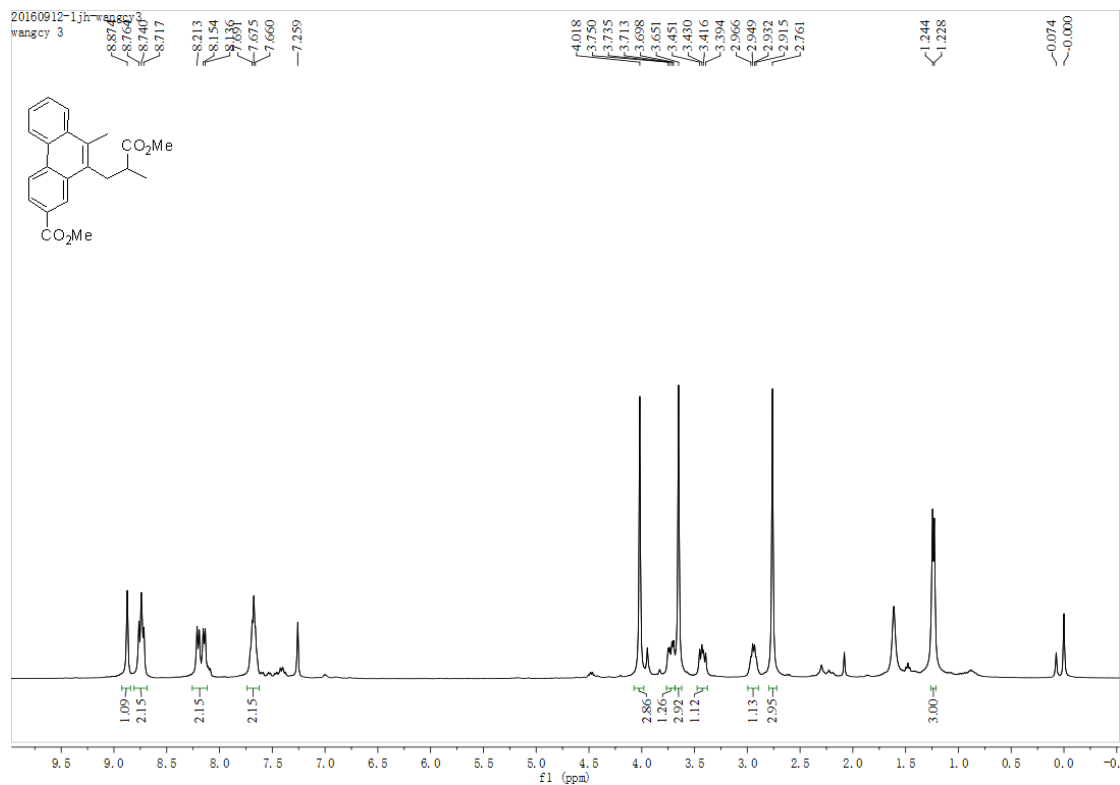
Methyl 3-(7-fluoro-10-methylphenanthren-9-yl)-2-methylpropanoate (3ga)



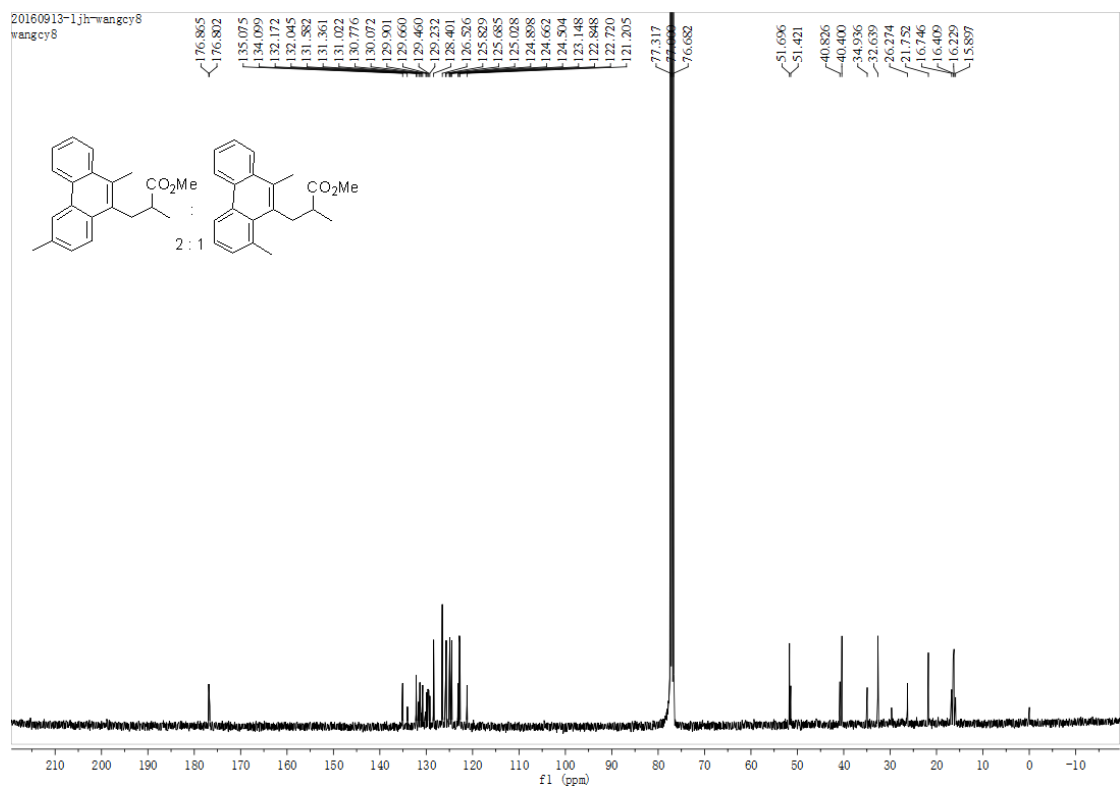
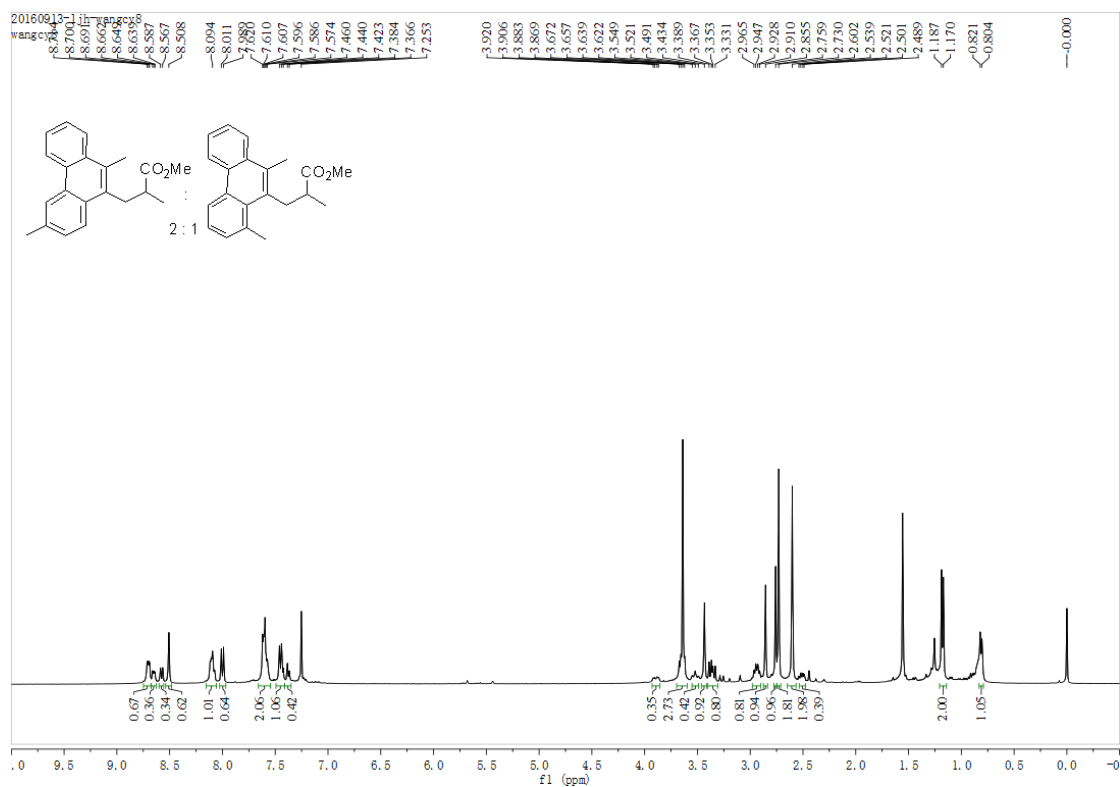
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wangcy2



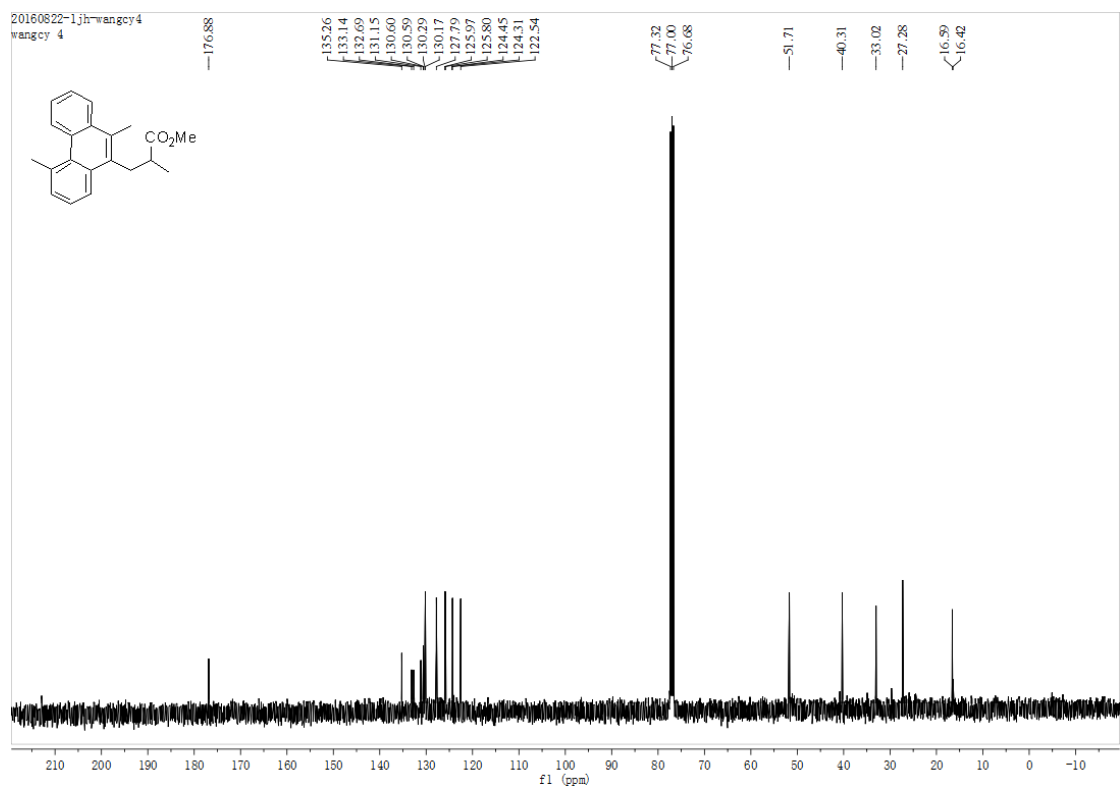
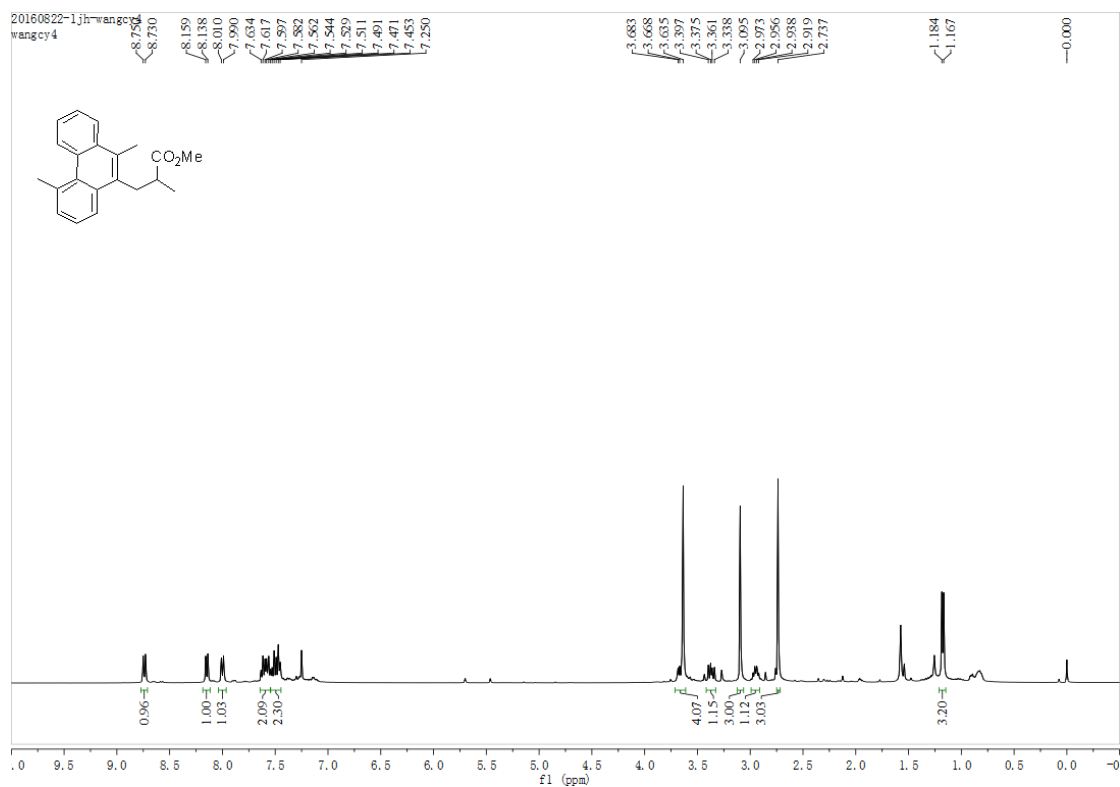
Methyl 10-(3-methoxy-2-methyl-3-oxopropyl)-9-methylphenanthrene-2-carboxylate (3ha)



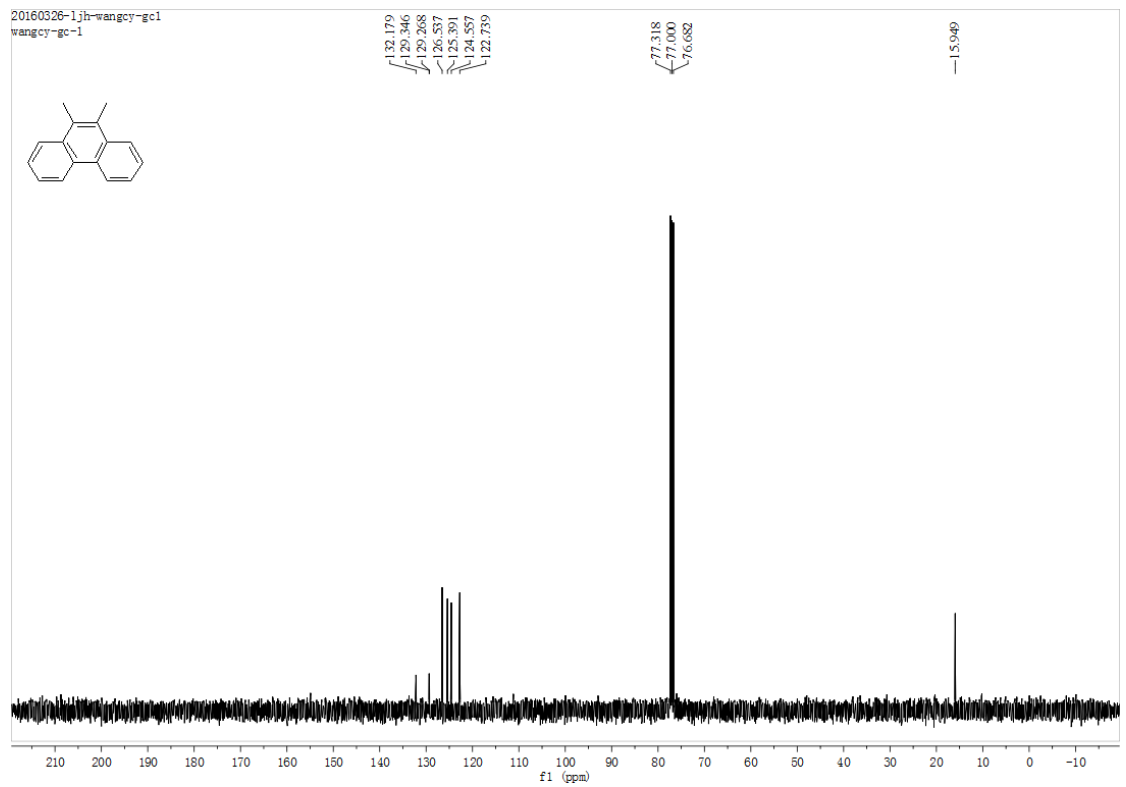
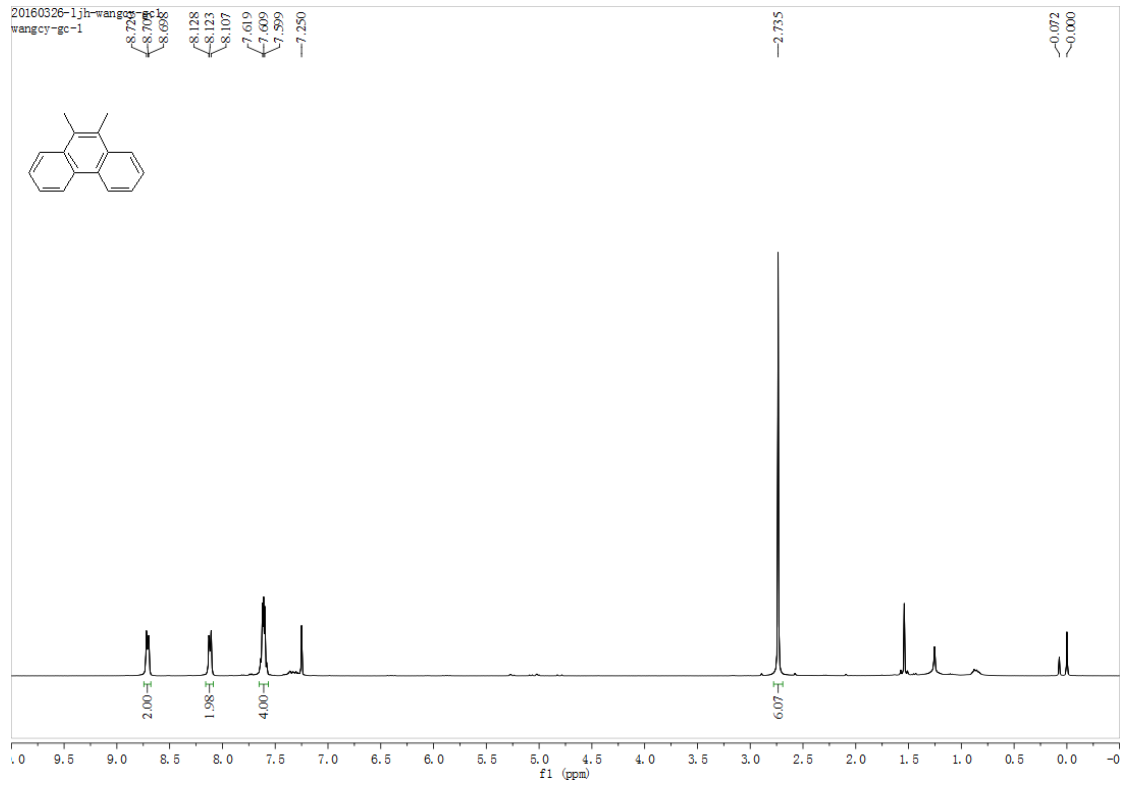
Methyl 3-(6,10-dimethylphenanthren-9-yl)-2-methylpropanoate and Methyl 3-(8,10-dimethylphenanthren-9-yl)-2-methylpropanoate (2:1)(3ia)



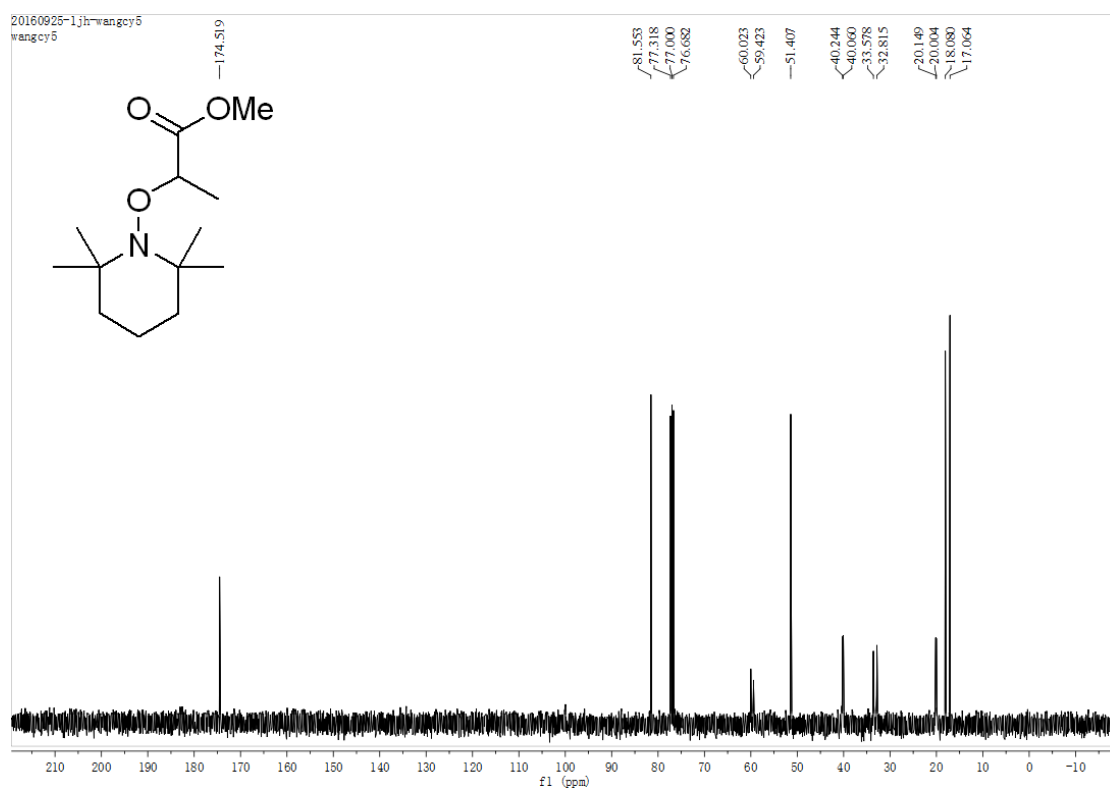
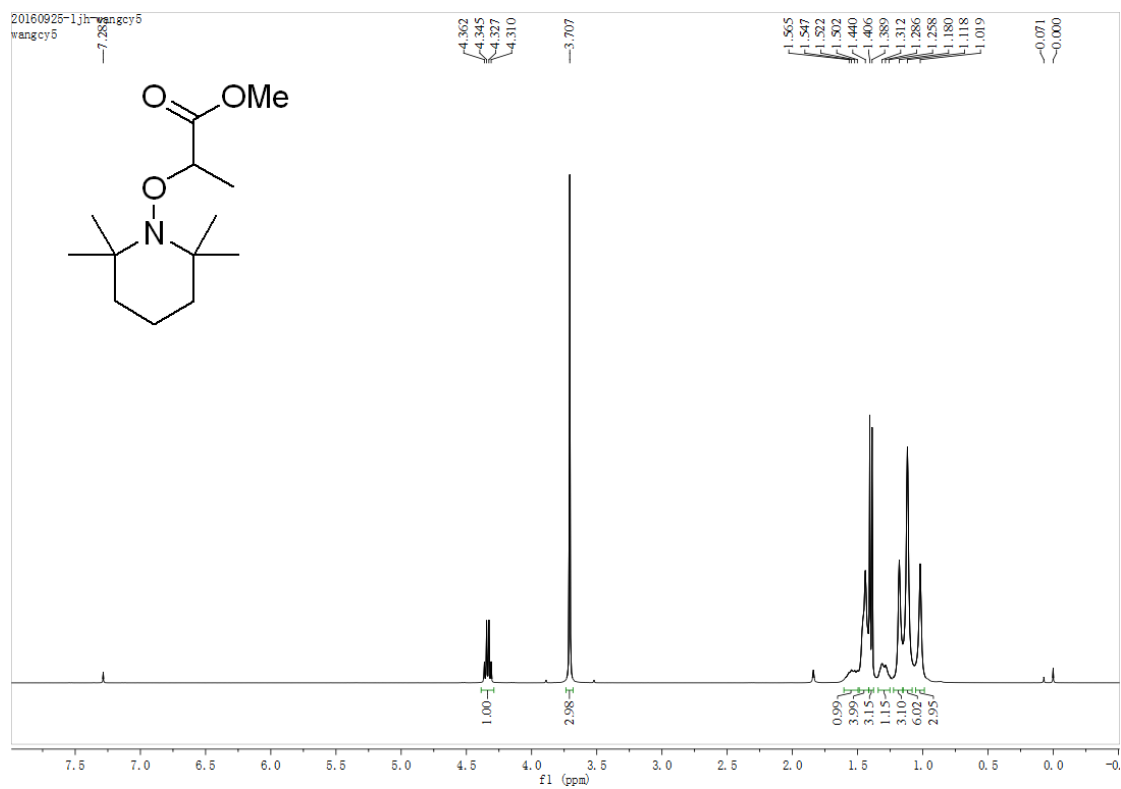
Methyl 3-(5,10-dimethylphenanthren-9-yl)-2-methylpropanoate (3ja)



9,10-Dimethylphenanthrene (4aa)



Methyl 2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (5)



(E) The X-ray single-crystal diffraction analysis of 3ea

