Electronic Supplementary Material (ESI) for Organic .

Supporting Information

Gold-Catalyzed Tandem Diels-Alder Reactions of Enynals/ Enynones with Alkenes: Generation and Trapping of Cyclic o-QDMs

Shifa Zhu,* Lang Hu, Huanfeng Jiang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

zhusf@scut.edu.cn

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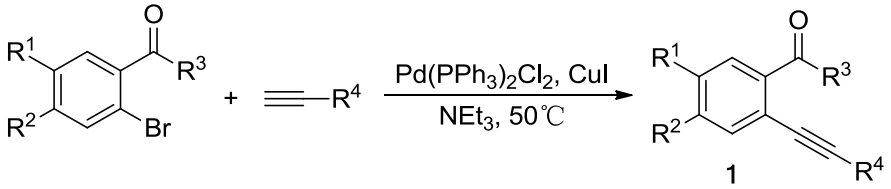
1. General Information

Unless specified, all reactions were carried out under an inert atmosphere of nitrogen in Schlenk tubes with dry solvents, using anhydrous conditions unless otherwise stated. 1,2-Dichloroethane (DCE) was distilled over calcium hydride under nitrogen prior to use. Acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), toluene, and triethylamine (NEt_3), were distilled under nitrogen prior to use by standard methods respectively. NHC-Au catalysts were prepared as described in the literature.[1] Unless otherwise stated, other reagents were used as received from commercial sources.

Melting points were recorded on a BUCHI Melting Point B-545 apparatus and were uncorrected. NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer in deuterated chloroform ($CDCl_3$) solutions, with residual chloroform (δ 7.26 ppm for ^{1}H NMR and δ 77.00 ppm for ^{13}C NMR) taken as the internal standard, and were reported in parts per million (ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer.

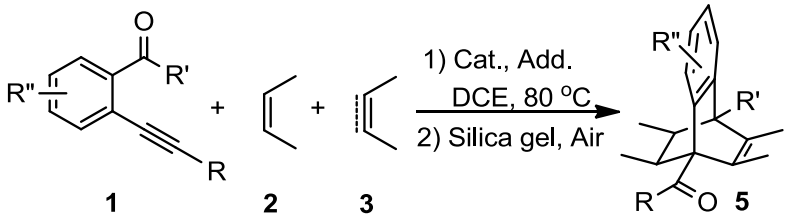
2. Experimental Procedures and Characterization

2.1 General procedure for the synthesis of enynals and enynones



To a solution of the corresponding 2-bromobenzaldehyde (1.0 eq.), $Pd(PPh_3)_2Cl_2$ (2.0 mol%), and CuI (1.0 mol%) in NEt_3 (0.25 M) was added the appropriate acetylene (1.2 eq.). The resulting mixture was stirred under nitrogen atmosphere at 50 ℃ overnight. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford the desired product **1**.[2]

2.2.1 General procedure for Gold-catalyzed tandem reaction of enynals/enynones with norbornene (NB) and benzoquinone

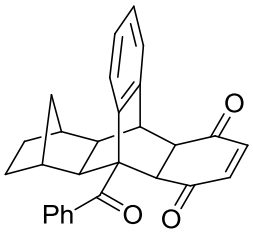


To a solution of the catalyst combination of SIMes-AuCl (2.70 mg, 0.005 mmol) and

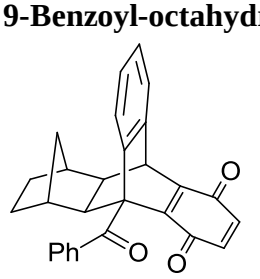
Selectfluor® (5.30 mg, 0.015 mmol) in DCE (1 mL, 0.1 M) was added the corresponding enynals/enynones (0.1 mmol) with norbornene (NB, 47.10 mg, 0.5 mmol) and benzoquinone (21.60 mg, 0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere at 80 ℃ for 24 hours. After the reaction was finished, the mixture was filtered by short silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (1: 10 to 1: 4, ethyl acetate: petroleum ether) to afford the desired product **5**.

2.2.2 Characterization

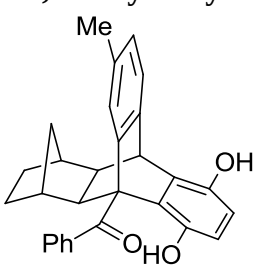
9-Benzoyl-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4a): Yellow solid; **mp** 162 ℃; yield: 99.0 %; **IR** (KBr): 3688, 3062, 2949, 2880, 2360, 1647, 1470, 1271, 1093, 767, 699, 645, 520, 438; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 1H), 7.74 – 7.60 (m, 1H), 7.47 – 7.33 (m, 2H), 7.17 (td, J = 7.7, 1.3 Hz, 1H), 7.10 (dt, J = 7.4, 6.0 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 6.32 (d, J = 10.3 Hz, 1H), 6.24 (d, J = 10.3 Hz, 1H), 4.07 (d, J = 9.8 Hz, 1H), 3.60 (s, 1H), 3.24 (dd, J = 9.8, 1.4 Hz, 1H), 2.35 (d, J = 9.0 Hz, 1H), 2.19 – 2.05 (m, 1H), 1.96 (s, 1H), 1.38 (d, J = 12.7 Hz, 1H), 1.30 (d, J = 6.7 Hz, 1H), 1.15 (d, J = 10.7 Hz, 1H), 0.42 (d, J = 10.1 Hz, 1H), 0.39 (d, J = 10.7 Hz, 1H), -0.01 (d, J = 10.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.7, 197.5, 196.9, 141.24, 141.1, 140.8, 137.2, 137.2, 130.1, 128.1, 127.8, 127.3, 127.2, 127.0, 125.5, 57.0, 52.2, 50.9, 49.1, 48.6, 44.6, 41.2, 38.8, 33.5, 31.1, 30.2; **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{24}O_3Na^+$ [M+Na^+] = 431.1618; found = 431.1622.



9-Benzoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5a): Yellow solid; **mp** 221 ℃; yield: 99.0 %; **IR** (KBr): 3681, 2944, 2879, 1688, 1656, 1583, 1463, 1305, 1241, 833, 767, 734, 693, 473; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.49 (s, 1H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 3H), 6.68 (d, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 10.1 Hz, 1H), 6.41 (d, *J* = 10.1 Hz, 1H), 4.66 (d, *J* = 2.3 Hz, 1H), 2.35 (s, 1H), 2.22 (d, *J* = 8.5 Hz, 1H), 1.88 (s, 1H), 1.66 (d, *J* = 6.8 Hz, 1H), 1.39 – 1.30 (m, 2H), 1.14 (d, *J* = 6.4 Hz, 1H), 0.95 (d, *J* = 7.4 Hz, 1H), 0.15 (d, *J* = 10.8 Hz, 1H), -1.23 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 183.3, 183.2, 148.9, 148.9, 139.3, 137.8, 137.0, 136.4, 135.1, 132.3, 127.2, 126.4, 126.3, 124.8, 77.3, 77.0, 76.7, 59.1, 51.0, 49.6, 42.2, 39.5, 38.5, 32.3, 31.1, 30.7, 29.7. **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{22}O_3Na^+$ [M+Na^+] = 429.1461; found = 429.1472.

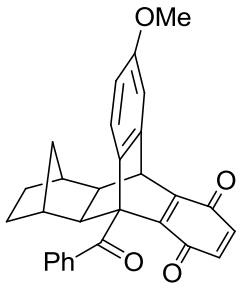


1,4-Dihydroxy-7-methyl-octahydro-9,10-[2]bicycloanthracen-9-yl)(phenyl)metha none (5b): Yellow solid; **mp** 164.8 ℃; yield: 83.5 %; **IR** (KBr): 3873, 2949, 2875, 2359, 1744, 1662, 1492, 1252, 1081, 1031, 869, 807, 694, 575, 478; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 10.7 Hz, 2H), 7.08 (d, J = 7.5 Hz, 1H), 6.84 (t, J = 6.8 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 6.34 (s,



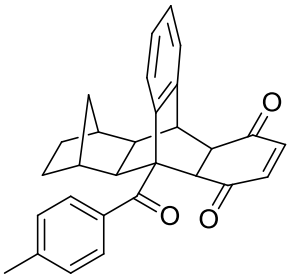
1H), 6.24 (d, J = 8.5 Hz, 1H), 5.14 (s, 1H), 4.59 (dd, J = 11.7, 2.4 Hz, 1H), 2.29 (d, J = 8.5 Hz, 1H), 2.10 (s, 1H), 1.94 (s, 1H), 1.81 (s, 1H), 1.66 – 1.57 (m, 1H), 1.26 (dd, J = 11.7, 8.6 Hz, 1H), 1.10 (d, J = 10.7 Hz, 1H), 0.90 (t, J = 7.8 Hz, 1H), 0.11 (d, J = 10.6 Hz, 1H), -1.07 (d, J = 10.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.31, 143.27, 142.47, 139.24, 138.35, 136.72, 133.72, 131.30, 130.82, 130.26, 127.96, 127.32, 126.58, 125.86, 123.26, 115.18, 113.61, 113.53, 59.50, 58.29, 50.10, 48.81, 40.87, 38.77, 37.50, 31.59, 30.17, 20.34, 20.00, 13.16. **HRMS** (MALDI-FTMS): calcd for $C_{29}H_{26}O_3Na^+$ [M+Na^+] = 445.1774; found = 445.1786

9-Benzoyl-6-methoxy-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5c): Yellow



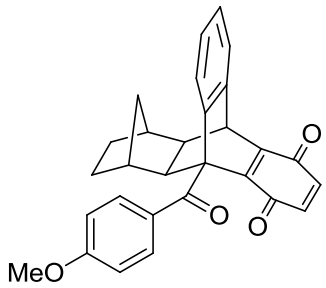
solid; mp 200.8 ℃; yield: 76.0 %; **IR** (KBr): 2880, 2359, 1734, 1689, 1655, 1585, 1488, 1303, 1249, 1144, 1037, 832, 695; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.45 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 2H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.60 (d, *J* = 10.1 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 6.47 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.41 (d, *J* = 10.1 Hz, 1H), 4.65 (s, 1H), 4.59 (d, *J* = 2.4 Hz, 1H), 3.70 (s, 3H), 2.35 (s, 1H), 2.19 (d, *J* = 8.5 Hz, 1H), 1.89 (s, 1H), 1.65 (d, *J* = 8.3 Hz, 1H), 1.35 (d, *J* = 3.2 Hz, 1H), 1.14 (d, *J* = 6.1 Hz, 1H), 0.93 (t, *J* = 8.5 Hz, 1H), 0.20 (d, *J* = 10.9 Hz, 1H), -1.05 (d, *J* = 10.9 Hz, 1H); ^{13}C **NMR** (101 MHz, $CDCl_3$) δ 197.40, 183.41, 183.29, 159.00, 149.48, 148.68, 139.33, 136.96, 136.41, 135.07, 132.27, 131.40, 127.14, 111.38, 110.87, 58.59, 55.40, 51.06, 49.65, 42.42, 39.45, 38.49, 32.56, 30.99, 30.69, 29.70. **HRMS** (MALDI-FTMS): calcd for $C_{29}H_{24}O4Na^+$ [M+Na^+] = 459.1569; found = 459.1576.

9-(4-Methylbenzoyl)-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4d): Brown



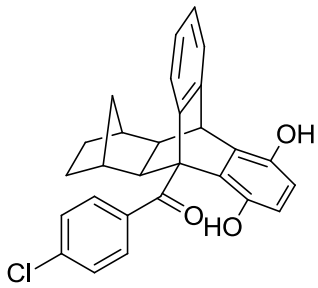
solid; **mp** 189 ℃; yield: 96.0 %; **IR** (KBr): 3683, 3620, 2949, 2877, 2358, 1658, 1601, 1464, 1303, 1246, 1183, 1036, 836, 734, 480; **1H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.7 Hz, 1H), 7.06 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.28 (d, J = 10.3 Hz, 1H), 6.20 (d, J = 10.3 Hz, 1H), 4.12 (d, J = 9.8 Hz, 1H), 3.58 (s, 1H), 3.23 (d, J = 9.8 Hz, 1H), 2.35 (s, 1H), 2.34 (s, 3H), 2.13 (d, J = 8.9 Hz, 1H), 2.07 (s, 1H), 1.94 (s, 1H), 1.33 (t, J = 10.7 Hz, 2H), 1.11 (t, J = 8.8 Hz, 1H), 0.96 (t, J = 9.5 Hz, 1H), 0.38 (d, J = 10.6 Hz, 1H), -0.01 (d, J = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.25, 197.63, 196.89, 141.28, 140.73, 140.53, 138.23, 137.42, 137.25, 128.73, 128.04, 127.23, 126.97, 125.47, 57.03, 52.34, 50.98, 49.06, 48.82, 44.57, 41.20, 38.80, 33.55, 31.13, 30.24, 21.42; HRMS (MALDI-FTMS): calcd for $C_{29}H_{27}O_3$ [M+H^+] = 423.1966; found = 423.1955.

9-(4-Methoxybenzoyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5e):

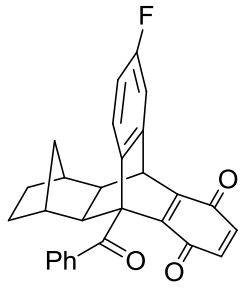


Yellow solid; **mp** 201.8 ℃; yield: 63.7 %; **IR** (KBr): 3336, 3064, 2944, 2878, 2359, 1662, 1598, 1498, 1457, 1304, 1252, 1174, 1032, 819, 737, 609; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.4 Hz, 1H), 7.25 (d, J = 7.3 Hz, 1H), 7.15 (t, J = 7.3 Hz, 1H), 6.97 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 7.2 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 6.60 (d, J = 10.0 Hz, 1H), 6.43 (t, J = 10.3 Hz, 2H), 4.65 (s, 1H), 3.74 (s, 3H), 2.34 (s, 1H), 2.21 (d, J = 8.5 Hz, 1H), 1.87 (s, 1H), 1.65 (d, J = 8.5 Hz, 1H), 1.33 (t, J = 9.1 Hz, 2H), 1.17 (d, J = 6.3 Hz, 1H), 1.13 (d, J = 6.8 Hz, 1H), 0.93 (t, J = 8.9 Hz, 1H), 0.13 (d, J = 10.8 Hz, 1H), -1.24 (d, J = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.97, 183.41, 183.31, 162.59, 148.91, 148.86, 139.45, 137.89, 136.50, 134.98, 131.91, 130.61, 130.24, 127.16, 126.48, 126.37, 124.80, 59.03, 55.36, 50.97, 49.60, 42.18, 39.45, 38.57, 32.35, 31.08, 30.68; HRMS (MALDI-FTMS): calcd for $C_{29}H_{25}O_4$ $[M+H^+]$ = 437.1752; found = 437.1747.

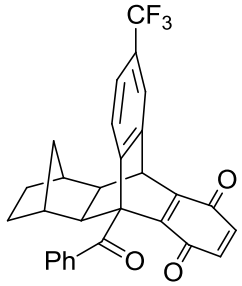
(4-Chlorophenyl)(1,4-dihydroxy-octahydro-9,10-[2]bicycloanthracen-9-yl)metha none (5f): Brown solid; **mp** 219.3-221 ℃; yield: 58.3 %; IR (KBr): 3856, 2932, 2878, 2360, 1690, 1656, 1584, 1475, 1304, 1240, 1095, 1013, 827, 738, 482; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.45 (s, 1H), 7.26 (d, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.63 (dd, *J* = 13.3, 8.9 Hz, 2H), 6.43 (d, *J* = 10.1 Hz, 1H), 4.67 (s, 1H), 2.33 (s, 1H), 2.21 (d, *J* = 8.4 Hz, 1H), 1.88 (s, 1H), 1.67 (s, 2H), 1.35 (s, 2H), 0.95 (d, *J* = 6.2 Hz, 1H), 0.15 (d, *J* = 10.9 Hz, 1H), -1.24 (d, *J* = 10.6 Hz, 1H; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.07, 183.18, 149.19, 148.47, 138.97, 138.55, 137.89, 136.38, 135.50, 135.20, 127.37, 126.46, 126.26, 124.98, 59.09, 51.05, 49.59, 42.24, 39.45, 38.50, 32.31, 31.04, 30.65, 29.68. **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{23}O_3ClNa^+$ $[M+Na^+]$ = 465.1228; found = 465.1245.



9-Benzoyl-6-fluoro-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5g): Yellow solid; **mp** 220.8 ℃; yield: 63.7 %; **IR** (KBr): 3660, 2937, 2878, 2358, 1687,1586, 1485, 1385, 1241, 1144, 1118, 868, 828, 741, 650; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.50 (s, 1H), 7.39 (d, J = 7.0 Hz, 1H), 7.00 (d, J = 7.9 Hz, 2H), 6.92 (s, 1H), 6.70 – 6.58 (m, 3H), 6.44 (d, J = 9.5 Hz, 1H), 4.64 (s, 1H), 2.35 (s, 1H), 2.21 (d, J = 8.2 Hz, 1H), 1.91 (s, 1H), 1.68 (d, J = 8.4 Hz, 1H), 1.36 (s, 2H), 0.93 (d, J = 11.4 Hz, 1H), 0.22 (d, J = 10.6 Hz, 1H), -1.13 (d, J = 10.5 Hz, 1H) ; **^{13}C NMR** (101 MHz, CDCl3) δ 196.81, 183.16, 183.14, 148.96, 148.22, 136.77, 136.44, 135.12, 135.01, 132.44, 127.64, 127.56, 113.18, 112.96, 112.42, 112.20, 58.68, 50.96, 49.60, 42.19, 39.40, 38.51, 32.52, 30.98, 30.66; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.82. **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{21}O_3F^+$ $[M+H^+]$ = 425.1548; found = 425.1556.

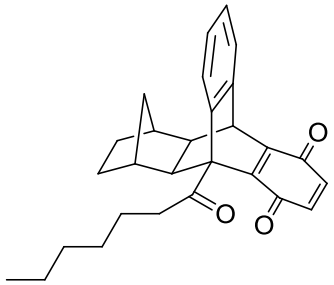


9-Benzoyl-6-(trifluoromethyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione



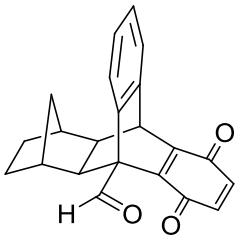
(5h): Yellow solid; **mp** 130.3-131.4 ℃; yield: 32.3 %; **IR** (KBr): 3328, 2934, 2879, 2358, 1666, 1588, 1500, 1445, 1325, 1245, 1127, 1077, 827, 743, 696; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.52 (s, 2H), 7.40 (t, J = 7.0 Hz, 1H), 7.23 (d, J = 7.9 Hz, 1H), 7.00 (s, 1H), 6.82 (t, J = 15.1 Hz, 2H), 6.64 (d, J = 10.0 Hz, 1H), 6.45 (d, J = 10.2 Hz, 1H), 4.75 (s, 1H), 2.38 – 2.25 (m, 2H), 1.94 (s, 1H), 1.72 (d, J = 8.4 Hz, 1H), 1.37 (s, 2H), 1.16 (s, 1H), 0.95 (d, J = 10.8 Hz, 1H), 0.19 (d, J = 11.0 Hz, 1H), -1.25 (d, J = 10.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.30, 181.98, 181.94, 147.12, 147.06, 142.18, 137.93, 135.55, 135.45, 134.14, 131.60, 125.61, 122.31, 122.28, 120.51, 120.48, 58.03, 49.90, 48.43, 41.12, 38.36, 37.48, 31.48, 30.04, 29.57; **^{19}F NMR** (376 MHz, CDCl3) δ -62.08 (s), -62.16. **HRMS** (ESI-MS): calcd for $C_{29}H_{21}O_3F_3Na^+$ [M+Na^+] = 497.1335; found = 497.1352.

9-Hexanoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5i): Brown solid; **mp** 134.1 ℃; yield: 41.7 %; **IR** (KBr): 3328, 2945, 2867, 2357, 1705, 1656, 1462, 1383, 1303, 1025, 830, 763, 664, 470; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.26 – 7.07 (m, 4H), 6.58 (d, *J* = 10.1 Hz, 1H), 6.52 (d, *J* = 10.1 Hz, 1H), 4.52 (d, *J* = 2.3 Hz, 1H), 2.92 – 2.72 (m, 1H), 2.63 – 2.48 (m, 1H), 2.22 (s, 1H), 1.97 (s, 1H), 1.91 (s, 3H), 1.80 (s, 1H), 1.54 (d, *J* = 6.4 Hz, 2H), 1.05 (t, *J* = 8.3 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 1H), 0.85 (t, *J* = 6.7 Hz, 3H), 0.21 (d, *J* = 10.4 Hz, 1H), -0.98 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 208.38, 183.49, 183.28, 151.41, 139.18, 138.15, 136.57, 134.89, 126.90, 126.71, 125.10, 50.51, 50.43, 41.89, 39.50, 38.83, 32.63, 31.83, 30.94, 30.65, 29.70, 29.13, 24.14, 22.62, 14.12. **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{30}O_3H^+$ [M+H^+] = 415.2268; found = 415.2286.

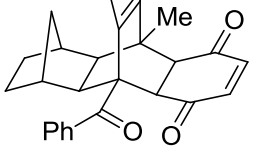


9-(Cyclopropanecarbonyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5j): Yellow solid; **mp** 164.8-166 ℃; yield: 85.8 %; **IR** (KBr): 3692, 2950, 2358, 1702, 1657, 1577, 1467, 1377, 1304, 1034, 987, 830, 740, 473; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 5.2, 3.4 Hz, 1H), 7.30 – 7.14 (m, 4H), 6.59 (q, *J* = 10.1 Hz, 2H), 4.57 (d, *J* = 2.5 Hz, 1H), 2.12 (s, 2H), 1.96 (s, 1H), 1.87 (s, 1H), 1.71 (d, *J* = 8.1 Hz, 1H), 1.57 (s, 1H), 1.34 (d, *J* = 6.6 Hz, 2H), 1.29 (dd, *J* = 8.7, 3.0 Hz, 2H), 1.13 – 0.96 (m, 4H), 0.91 (t, *J* = 8.7 Hz, 1H), 0.14 (d, *J* = 10.8 Hz, 1H), -1.08 (d, *J* = 9.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 207.84, 183.30, 183.05, 151.14, 139.43, 138.23, 136.56, 134.97, 127.11, 126.69, 125.22, 125.07, 50.27, 50.11, 42.08, 39.49, 38.34, 32.34, 30.90, 30.60, 29.71, 14.01. **HRMS** (MALDI-FTMS): calcd for $C_{25}H_{22}O_3H^+$ [M+H^+] = 371.1642; found = 371.1653.

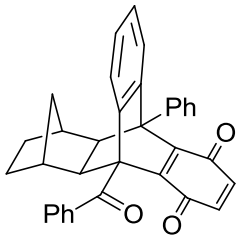
9-Carbaldehyde-decahydro-9,10-[2]bicycloanthracene-1,4-dione (5k): Yellow solid; **mp** 167.1 ℃; yield: 62.0 %; **IR** (KBr): 3432, 2928, 2877, 2358, 1714, 1653, 1587, 1465, 1385, 1308, 833, 760, 556, 511, 471; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.59 – 7.35 (m, 2H), 7.29 – 7.07 (m, 5H), 6.72 (s, 1H), 6.59 (q, *J* = 10.1 Hz, 2H), 4.57 (d, *J* = 2.5 Hz, 1H), 2.16 (d, *J* = 8.7 Hz, 1H), 2.04 (s, 1H), 1.93 (s, 1H), 1.83 – 1.76 (m, 2H), 1.33 (d, *J* = 7.0 Hz, 2H), 1.18 (s, 2H), 1.05 (t, *J* = 8.3 Hz, 1H), 1.00 – 0.92 (m, 1H), 0.23 (d, *J* = 10.8 Hz, 1H), -0.83 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.44, 183.57, 183.23, 151.40, 149.14, 139.51, 137.75, 136.56, 135.79, 135.43, 127.24, 126.89, 125.52, 123.53, 58.78, 48.71, 48.68, 41.93, 39.51, 37.88, 32.52, 30.79, 30.62. **HRMS** (ESI-MS): calcd for $C_{22}H_{18}O_3Na^+$ [M+Na^+] = 353.1148; found = 353.1160.



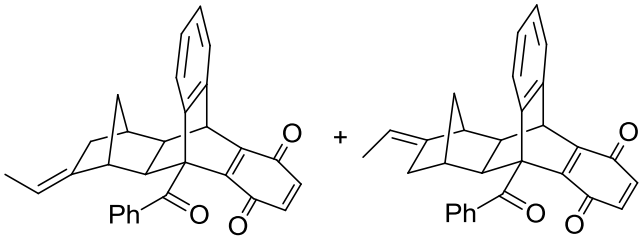
9-Benzoyl-10-methyl--decahydro--9,10-[2]bicycloanthracene-1,4-dione (4l): Yellow solid; **mp** 140-141 ℃; yield: 80.0 %; **IR** (KBr): 3659, 2959, 2878, 2358, 1673, 1458, 1382, 1259, 1097, 863, 766, 700, 657; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.78 – 7.65 (m, 2H), 7.43 (d, *J* = 7.2 Hz, 3H), 7.22 (dd, *J* = 6.6, 3.9 Hz, 3H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.24 (d, *J* = 10.3 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 3.08 (d, *J* = 8.8 Hz, 1H), 2.43 (d, *J* = 8.9 Hz, 1H), 2.14 (s, 1H), 2.07 (s, 1H), 1.88 (d, *J* = 8.9 Hz, 1H), 1.47 (s, 3H), 1.41 (dd, *J* = 10.6, 7.2 Hz, 2H), 1.10 (d, *J* = 10.8 Hz, 1H), 1.04 (d, *J* = 10.4 Hz, 1H), 0.40 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.42, 197.61, 197.61, 141.54, 141.27, 140.61, 139.33, 136.97, 129.92, 128.17, 127.73, 127.12, 127.06, 127.01, 123.24, 57.38, 57.11, 56.89, 52.41, 47.99, 41.63, 39.42, 38.32, 33.80, 31.41 , 19.45. **HRMS** (MALDI-FTMS): calcd for $C_{29}H_{26}O_3H^+$ [M+H^+] = 423.1955; found = 423.1957.



9-Benzoyl-10-phenyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5m): Colorless solid; **mp** 204.7 ℃; yield: 68.1 %; **IR** (KBr): 3683, 3291, 3065, 2931, 2338, 1692, 1658, 1554, 1296, 1050, 838, 767, 695, 474; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.52 (s, 3H), 7.40 (d, *J* = 6.5 Hz, 4H), 7.21 (d, *J* = 7.8 Hz, 3H), 7.11 (t, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 10.0 Hz, 1H), 6.29 (d, *J* = 10.0 Hz, 1H), 2.60 (s, 1H), 2.37 (s, 2H), 2.17 (s, 1H), 1.44 – 1.34 (m, 2H), 1.19 (s, 1H), 0.05 (d, *J* = 10.9 Hz, 1H), -1.58 (d, *J* = 11.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.27, 183.67, 183.19, 151.06, 147.85, 139.68, 139.09, 138.10, 137.34, 137.06, 134.05, 132.11, 127.04, 126.79, 126.63, 126.39, 125.83, 58.22, 56.27, 54.21, 51.98, 38.63, 38.16, 32.02, 31.02, 30.87. **HRMS** (MALDI-FTMS): calcd for $C_{34}H_{27}O_3Na^+$ [M+H^++Na^+] = 506.1852; found = 506.1866.

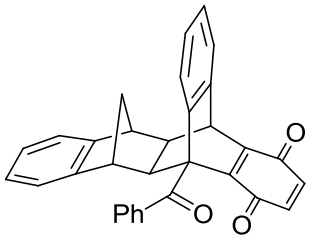


9-Benzoyl-16-ethylidene-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5n):



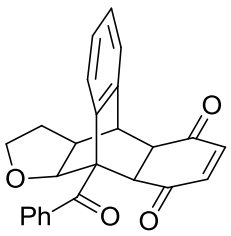
Yellow solid; **mp** 115-116 ℃; yield: 85.3 %; **IR** (KBr): 3131, 2925, 2359, 1732, 1689, 1655, 1560, 1305, 1240, 1025, 834, 688, 474, 452; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.47 (s, 1H), 7.36 (s, 1H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.16 (dd, *J* = 13.9, 6.3 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.74 – 6.63 (m, 1H), 6.59 (d, *J* = 10.0 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 5.46 (d, *J* = 6.4 Hz, 1H), 4.69 (s, 1H), 2.84 (s, 1H), 2.32 (dd, *J* = 15.2, 6.6 Hz, 1H), 2.02 (s, 1H), 1.92 – 1.82 (m, 1H), 1.77 (d, *J* = 7.4 Hz, 1H), 1.58 (d, *J* = 15.6 Hz, 1H), 1.37 (t, *J* = 6.5 Hz, 3H), 0.29 (d, *J* = 10.7 Hz, 1H), -1.15 (d, *J* = 9.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.02, 183.33, 183.13, 149.05, 148.86, 145.06, 139.34, 137.76, 136.94, 136.40, 135.07, 132.31, 127.32, 126.51, 126.45, 124.89, 113.09, 59.08, 50.50, 49.06, 46.82, 42.15, 39.69, 36.88, 32.76, 13.81; **HRMS** (MALDI-FTMS): calcd for $C_{30}H_{25}O_3^+$ [M+H$^+$] = 433.1789; found = 433.1810.

5-Benzoyl-tetrahydro-5,12-[1,2]benzeno-6,11-methanotetracene-15,18-dione (5o):



Yellow solid; **mp** 175.8-176 ℃; yield: 79 %; **IR** (KBr): 3308, 30668, 2933, 2357, 1608, 1589, 1386, 1241, 1081, 977, 843, 761, 694, 480; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.12 (s, 1H), 7.05 – 7.00 (m, 2H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 4.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 10.0 Hz, 1H), 6.37 (d, *J* = 10.1 Hz, 1H), 4.72 (s, 1H), 3.43 (s, 1H), 2.86 (s, 1H), 2.50 (d, *J* = 8.3 Hz, 1H), 2.01 (d, *J* = 8.5 Hz, 1H), 0.91 (d, *J* = 10.3 Hz, 1H), -0.67 (d, *J* = 10.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.95, 183.34, 183.07, 150.77, 150.34, 150.21, 139.67, 138.09, 136.84, 136.37, 135.03, 132.45, 128.99, 128.41, 128.12, 127.63, 127.30, 127.12, 127.02, 126.80, 125.79, 125.49, 125.36, 125.22, 124.17, 121.18, 120.54, 120.28, 58.83, 51.93, 50.21, 46.30, 45.38, 41.69, 41.26; **HRMS** (MALDI-FTMS): calcd for $C_{32}H_{23}O_3^+$ [M+H$^+$] = 455.1642; found = 455.1640.

9-Benzoyl-hexahydro-9,10-[2,3]furanoanthracene-1,4-dione (4p): Green solid; **mp**



235-236 ℃; yield: 45.6 %; **IR** (KBr): 3308, 30668, 2933, 2357, 1608, 1589, 1386, 1241, 1081, 977, 843, 761, 694, 480; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.50 (s, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 14.8 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 2H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.66 (d, *J* = 10.1 Hz, 1H), 6.48 (d, *J* = 10.1 Hz, 1H), 5.04 (d, *J* = 7.7 Hz, 1H), 4.62 (d, *J* = 2.6 Hz, 1H), 3.44 (td, *J* = 8.4, 4.4 Hz, 1H), 2.67 – 2.57 (m, 1H), 2.05 – 1.99 (m, 1H), 1.92 – 1.84 (m, 1H), 1.54 (d, *J* = 6.8 Hz, 1H), 1.31 – 1.22 (m, 2H); **^{13}C NMR** (101

MHz, $CDCl_3$) δ 195.50, 183.14, 183.01, 150.39, 146.67, 138.11, 136.80, 136.66, 136.35, 135.17, 132.48, 128.33, 127.16, 126.74, 125.25, 83.61, 70.40, 61.82, 45.15, 42.46, 29.70, 29.42. **HRMS** (ESI-MS): calcd for $C_{25}H_{20}O_4Na^+$ [M+Na^+] = 407.1254; found = 407.1241.

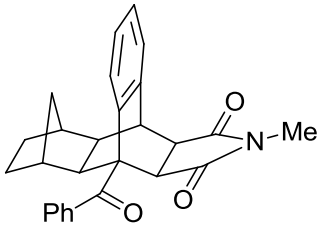
5-Benzoyl-hexahydro-5,12-[2]bicyclotetracene-6,11-dione (5q): Yellow solid; **mp** 272.6 ℃; yield: 86.6 %; **IR** (KBr): 3068, 2934, 2358, 1732, 1667, 1590, 1462, 1291, 1241, 960, 691, 702, 623, 568; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 11.8 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.16 (dd, *J* = 15.7, 8.4 Hz, 2H), 6.94 (t, *J* = 7.4 Hz, 2H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.87 (d, *J* = 2.1 Hz, 1H), 2.40 (s, 1H), 2.33 (d, *J* = 8.4 Hz, 1H), 1.92 (s, 1H), 1.75 (s, 1H), 1.35 (s, 2H), 1.13 (d, *J* = 14.3 Hz, 1H), 0.94 (t, *J* = 9.2 Hz, 1H), 0.17 (d, *J* = 10.8 Hz, 1H), -1.18 (d, *J* = 10.9 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.43, 181.40, 181.32, 151.37, 151.02, 139.33, 138.01, 137.24, 133.85, 133.56, 132.52, 132.13, 131.78, 127.16, 126.72, 126.50, 126.30, 126.27, 124.86, 59.44, 51.05, 49.58, 42.58, 39.55, 38.64, 32.40, 31.12, 30.71, 29.70. **HRMS** (MALDI-FTMS): calcd for $C_{32}H_{24}O_3H^+$ [M+H^+] = 457.1798; found = 457.1811.

10-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11-carbonitrile (5r): Yellow solid; **mp** 77-79 ℃; yield: 35.8 %; **IR** (KBr): 2964, 2880, 2358, 1729, 1678, 1587, 1475, 1251, 939, 910, 762, 702, 604, 424; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 6.6 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 1H), 3.28 (dd, *J* = 11.2, 4.9 Hz, 1H), 3.07 (s, 1H), 2.64 (d, *J* = 8.6 Hz, 1H), 2.29 (s, 1H), 2.06 (d, *J* = 2.6 Hz, 1H), 2.02 (s, 1H), 1.99 (d, *J* = 9.3 Hz, 1H), 1.79 (s, 1H), 1.31 (s, 2H), 1.12 (s, 1H), 0.16 (d, *J* = 10.7 Hz, 1H), -0.95 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.83, 141.62, 136.90, 132.68, 129.88, 129.57, 128.46, 128.22, 126.73, 126.29, 125.38, 120.95, 56.22, 47.99, 47.25, 40.78, 39.31, 38.60, 33.46, 32.46, 32.40, 31.34, 30.53. **HRMS** (ESI-MS): calcd for $C_{29}H_{24}O_3Na^+$ [M+Na^+] = 443.1774; found = 443.1784.

9-Benzoyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5s): Colorless solid; **mp** 126-128 ℃; yield: 89.3 %; **IR** (KBr): 3181, 2949, 2426, 1774, 1712, 1470, 1347, 1235, 1177, 975, 765, 706, 642, 480; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 6.8 Hz, 2H), 7.64 (s, 1H), 7.49 – 7.37 (m, 3H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.0 Hz, 1H), 3.81 (d, *J* = 8.6 Hz, 1H), 3.49 (s, 1H), 3.04 (dd, *J* = 8.6, 2.5 Hz, 1H), 2.22 (d, *J* = 8.8 Hz, 1H), 2.11 (s, 1H), 1.99 (d, *J* = 7.7 Hz, 2H), 1.50 – 1.33 (m, 2H), 1.14 (t, *J* = 9.8 Hz, 1H), 1.10 – 0.99 (m,

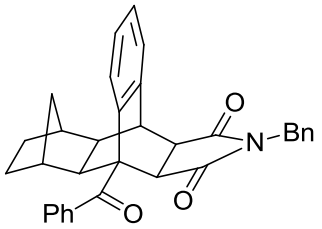
1H), 0.45 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.55, 177.21, 176.92, 140.74, 136.17, 134.71, 130.06, 128.19, 127.75, 127.69, 127.53, 126.96, 125.94, 55.28, 49.18, 47.80, 47.73, 46.98, 41.41, 41.13, 38.53, 33.64, 30.92, 30.27. **HRMS** (MALDI-FTMS): calcd for $C_{26}H_{23}NO_3H^+$ [M+H^+] = 398.1751; found = 398.1754.

9-Benzoyl-13-methyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,



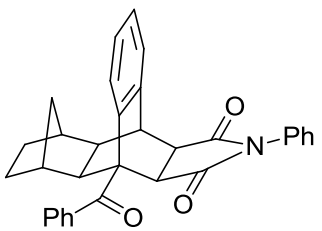
14-dione (5t): Colorless solid; **mp** 262.4 ℃; yield: 80.1 %; **IR** (KBr): 3068, 2749, 2358, 1772, 1698, 1540, 1439, 1381, 1269, 1234, 973, 762, 653, 462; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.17 (td, *J* = 7.6, 1.5 Hz, 1H), 7.11 (td, *J* = 7.4, 1.2 Hz, 1H), 6.96 (dd, *J* = 7.3, 1.1 Hz, 1H), 3.73 (d, *J* = 8.4 Hz, 1H), 3.46 (t, *J* = 2.5 Hz, 1H), 2.99 (dd, *J* = 8.4, 2.7 Hz, 1H), 2.33 (s, 3H), 2.21 (d, *J* = 8.9 Hz, 1H), 2.06 (d, *J* = 3.5 Hz, 1H), 1.98 (dd, *J* = 11.4, 2.5 Hz, 2H), 1.37 (dtdd, *J* = 27.2, 11.6, 7.8, 3.9 Hz, 2H), 1.10 (t, *J* = 9.9 Hz, 1H), 1.04 – 0.96 (m, 1H), 0.40 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.62, 177.26, 177.01, 140.90, 136.17, 134.68, 130.05, 128.17, 127.63, 127.57, 126.79, 125.71, 55.57, 49.29, 47.77, 46.68, 45.83, 41.69, 41.19, 38.56, 33.71, 30.93, 30.30, 24.13. **HRMS** (MALDI-FTMS): calcd for C27H25NO3H+ [M+H+] = 412.1907; found = 412.1910.

9-Benzoyl-13-benzyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,



14-dione (5u): red solid; **mp** 140.1-143.4 °C; yield: 80 %; **IR** (KBr): 3063, 2948, 2357, 1772, 1700, 1577, 1399, 1346, 1234, 1171, 1068, 930, 743, 702, 469. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 6.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 3H), 7.12 – 6.95 (m, 5H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.2 Hz, 2H), 4.11 (d, *J* = 5.0 Hz, 2H), 3.74 (d, *J* = 8.6 Hz, 1H), 3.46 (s, 1H), 2.99 (dd, *J* = 8.6, 2.4 Hz, 1H), 2.21 (d, *J* = 8.9 Hz, 1H), 2.04 (d, *J* = 3.0 Hz, 1H), 1.95 (d, *J* = 11.6 Hz, 2H), 1.42 – 1.30 (m, 2H), 1.09 (t, *J* = 9.9 Hz, 1H), 1.05 – 0.95 (m, 1H), 0.37 (d, *J* = 10.6 Hz, 1H), -0.14 (d, *J* = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.71, 176.91, 176.63, 140.91, 136.02, 134.77, 134.57, 129.99, 128.34, 128.18, 127.80, 127.74, 127.70, 127.55, 127.29, 126.79, 125.75, 55.31, 49.35, 47.98, 46.56, 45.66, 42.04, 41.50, 41.13, 38.53, 33.64, 30.93, 30.29. **HRMS** (MALDI-FTMS): calcd for $C_{33}H_{29}NO_3H^+$ [M+H^+] = 488.2220; found = 488.2229.

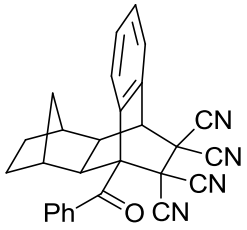
9-Benzoyl-13-phenyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,



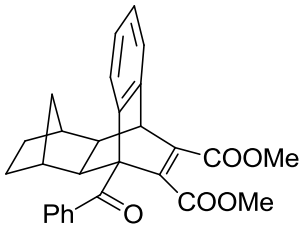
14-dione (5v): White solid; **mp** 167.1 ℃; yield: 60.3 %; **IR** (KBr): 3064, 2950, 2357, 1776, 1708, 1495, 1386, 1231, 1185, 1025, 913, 863, 747, 649, 471; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J*

= 7.3 Hz, 1H), 7.06 (d, *J* = 4.7 Hz, 1H), 7.05 – 6.99 (m, 3H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.27 – 6.13 (m, 2H), 3.79 (d, *J* = 8.5 Hz, 1H), 3.45 (s, 1H), 3.04 (dd, *J* = 8.5, 2.6 Hz, 1H), 2.19 (d, *J* = 8.9 Hz, 1H), 2.00 (d, *J* = 3.1 Hz, 1H), 1.97 – 1.86 (m, 2H), 1.34 – 1.22 (m, 2H), 1.01 (d, *J* = 11.6 Hz, 1H), 0.94 (d, *J* = 10.3 Hz, 1H), 0.33 (d, *J* = 10.7 Hz, 1H), -0.01 (d, *J* = 10.6 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.47, 176.48, 176.29, 140.88, 136.52, 135.08, 131.21, 130.10, 129.02, 128.72, 128.20, 127.77, 127.72, 127.64, 127.11, 126.39, 125.96, 55.94, 49.24, 47.68, 46.86, 45.95, 42.08, 41.29, 38.66, 33.87, 30.98, 30.34. **HRMS** (MALDI-FTMS): calcd for $C_{32}H_{27}NO_3H^+$ [M+H^+] = 474.2064; found = 474.2066.

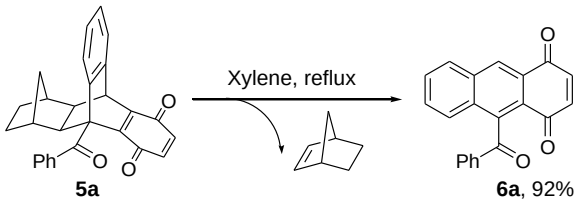
9-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11,11,12,12-tetracarbonitrile (5w): Red solid; **mp** 194.2 ℃; yield: 80.4 %; **IR** (KBr): 3720, 3665, 3070, 2956, 2924, 2359, 1716, 1664, 1551, 1456, 1247, 968, 672, 474; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48 – 7.32 (m, 5H), 3.91 (s, 1H), 2.58 (dd, *J* = 21.6, 9.0 Hz, 2H), 2.26 (d, *J* = 18.3 Hz, 2H), 1.37 (dd, *J* = 19.5, 8.9 Hz, 3H), 1.06 (d, *J* = 10.7 Hz, 1H), 0.75 (d, *J* = 10.8 Hz, 1H), 0.59 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 194.86, 135.89, 134.68, 133.45, 131.78, 131.24, 131.12, 129.88, 129.74, 128.27, 128.01, 111.75, 111.59, 110.92, 110.70, 65.87, 48.71, 48.53, 47.40, 46.41, 41.78, 41.18, 40.83, 33.73, 30.74, 29.99; **HRMS** (ESI-MS): calcd for $C_{28}H_{20}N_4ONa^+$ [M+Na^+] = 451.1529; found = 451.1528.



Dimethyl-9-benzoyl-octahydro-9,10-etheno-1,4-methanoanthracene-11,12-dicarboxylate (5x): Yellow solid; **mp** 175.7-177.3 ℃; yield: 51.2 %; **IR** (KBr): 3825, 3807, 3069, 2956, 2358, 2234, 1717, 1667, 1527, 1389, 1203, 950, 673, 612, 461; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.24 (dd, *J* = 11.0, 8.6 Hz, 3H), 7.16 (dd, *J* = 13.3, 5.9 Hz, 1H), 7.01 – 6.96 (m, 1H), 6.75 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* = 2.5 Hz, 1H), 3.73 (s, 3H), 3.08 (s, 3H), 2.42 (s, 1H), 2.35 (d, *J* = 8.5 Hz, 1H), 2.23 (d, *J* = 3.5 Hz, 1H), 2.19 (s, 1H), 1.86 – 1.78 (m, 2H), 1.33 (s, 1H), 0.98 (t, *J* = 9.2 Hz, 1H), 0.13 (d, *J* = 10.8 Hz, 1H), -1.22 (d, *J* = 10.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.74, 166.18, 165.48, 143.32, 142.30, 139.40, 138.60, 135.58, 132.96, 129.95, 128.02, 127.19, 126.29, 125.46, 124.41, 62.12, 52.50, 51.56, 50.86, 49.57, 47.02, 39.21, 38.72, 32.20, 31.04, 30.64. **HRMS** (MALDI-FTMS): calcd for $C_{28}H_{26}O_5Na^+$ [M+Na^+] = 465.1673; found = 465.1684.

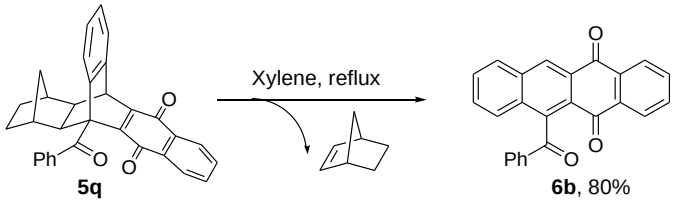


2.3.1 General procedure for derivatization reaction of 5a



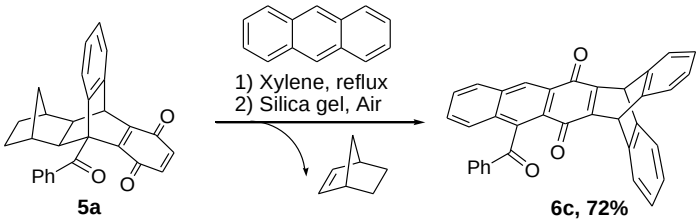
5a **6a**, 92%

To a solution of xylene (0.5 mL, 0.088 M) was added **5a** (18.0 mg, 0.044 mmol) . The reaction was stirred under nitrogen atmosphere at 170 ℃ for 6 hours.the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (1: 10 to 1: 4, ethyl acetate: petroleum ether) to afford the desired product **6a** (12.7 mg, 92 %).



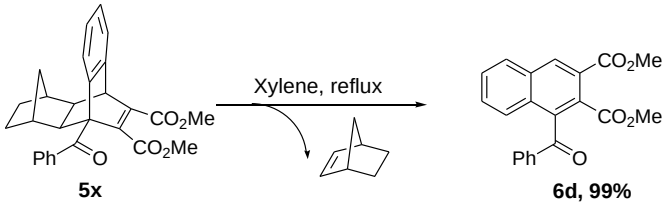
5q **6b**, 80%

To a solution of xylene (0.5 mL, 0.078 M) was added **5q** (18.0 mg, 0.039 mmol) . The reaction was stirred under nitrogen atmosphere at 170 ℃ for 6 hours.the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (1: 10 to 1: 4, ethyl acetate: petroleum ether) to afford the desired product **6b** (11.3 mg, 80 %) .



5a **6c, 72%**

To a solution of the **5a** (18.0 mg, 0.044 mmol) in xylene(0.5 mL, 0.088 M) was added the added anthracene (9.0 mg, 0.047 mmol) . The reaction mixture was stirred under nitrogen atmosphere at 170 ℃ for 6 hours. After the reaction was finished, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (1: 10 to 1: 4, ethyl acetate: petroleum ether) to afford the desired product **6c** (15.5 mg, 72 %).

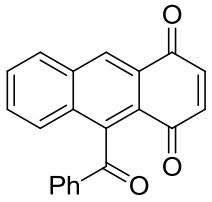


5x **6d, 99%**

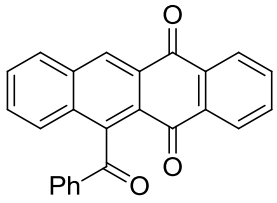
To a solution of xylene (0.5 mL, 0.064 M) was added **5x** (14.0 mg, 0.032 mmol) . The reaction was stirred under nitrogen atmosphere at 170 ℃ for 6 hours.the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel (1: 4, ethyl acetate: petroleum ether) to afford the desired product **6d** (11.2 mg, 99 %) .

2.3.2 Characterization

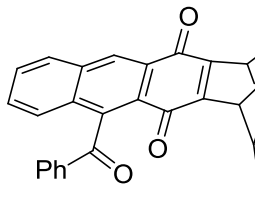
9-Benzoylanthracene-1,4-dione (6a): Yellow solid; **mp** 268.9-269.2 ^{o}C; Isolated yield: 92.0 %; **IR** (KBr): 2921, 2852, 2393, 2287, 1667, 1602, 1419, 1230, 1076, 911, 786, 701, 479; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.08 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 5.2 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 10.3 Hz, 1H), 6.88 (d, *J* = 10.3 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.53, 184.15, 184.08, 141.23, 140.04, 139.73, 137.13, 134.71, 133.58, 132.61, 130.68, 130.51, 130.17, 130.01, 128.82, 128.71, 128.12, 127.62, 125.74; **HRMS** (MALDI-FTMS): calcd for $C_{21}H_{14}O_3^+$ [M^+] = 314.0938; found = 314.0942.



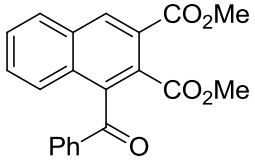
6-Benzoyltetracene-5,12-dione (6b): Yellow solid; **mp** 256.0-256.1^{o}C; Isolated yield: 80.0%; **IR** (KBr): 3056, 2972, 2392, 2286, 1661, 1312, 1459, 1296, 70, 722; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.32 (d, *J* = 7.6 Hz, 1H), 8.15 – 8.07 (m, 2H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.74 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.82, 182.59, 182.55, 141.85, 137.36, 135.03, 134.50, 134.39, 133.96, 133.42, 132.91, 130.88, 130.59, 130.38, 129.86, 129.58, 128.85, 128.71, 127.93, 127.53, 127.50; **HRMS** (MALDI-FTMS): calcd for $C_{25}H_{16}O_3^+$ [M^+] = 364.1094; found = 364.1099.



7-Benzoyl-5,14-[1,2]benzenopentacene-6,13-dione (6c): Yellow solid; **mp** 302.7 ^{o}C; Isolated yield: 72%; **IR**: 3304, 2920, 2851, 2393, 2286, 1731, 1672, 1579, 1424, 1284, 1162, 985, 791, 718; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 1H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.02 – 6.89 (m, 4H), 6.00 (s, 1H), 5.83 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.73, 180.40, 180.31, 155.55, 155.38, 143.62, 143.55, 143.38, 143.30, 141.26, 137.11, 134.59, 133.57, 132.53, 130.60, 130.24, 129.96, 129.78, 128.91, 128.79, 128.59, 127.60, 125.73, 125.70, 125.64, 125.60, 124.66, 124.60, 124.48, 47.96, 47.89; **HRMS** (MALDI-FTMS): calcd for $C_{35}H_{22}O_3^+$ [M^+] = 490.1564; found = 490.1568.



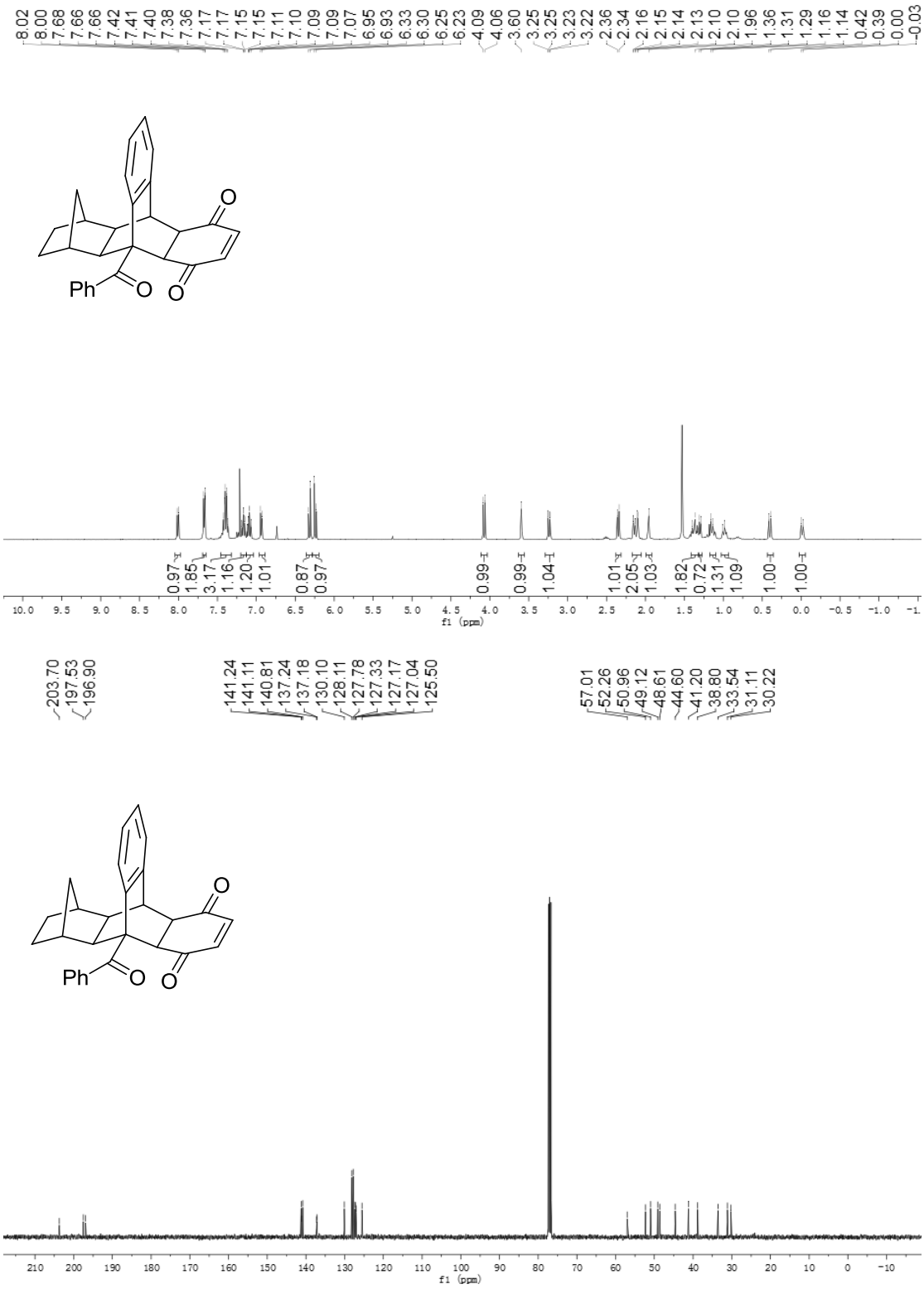
Dimethyl-1-benzoylnaphthalene-2,3-dicarboxylate (6d): White solid; **mp** 124.8 ^{o}C; Isolated yield: 98%; **IR**: 3053, 2980, 1727, 1668, 1581, 1445, 1297, 1164, 1070, 944, 782, 640; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55 (dd, *J* = 12.9, 5.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 3.88 (s, 3H), 3.54 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.67, 167.41, 166.90, 138.59, 137.27, 133.91, 132.89,



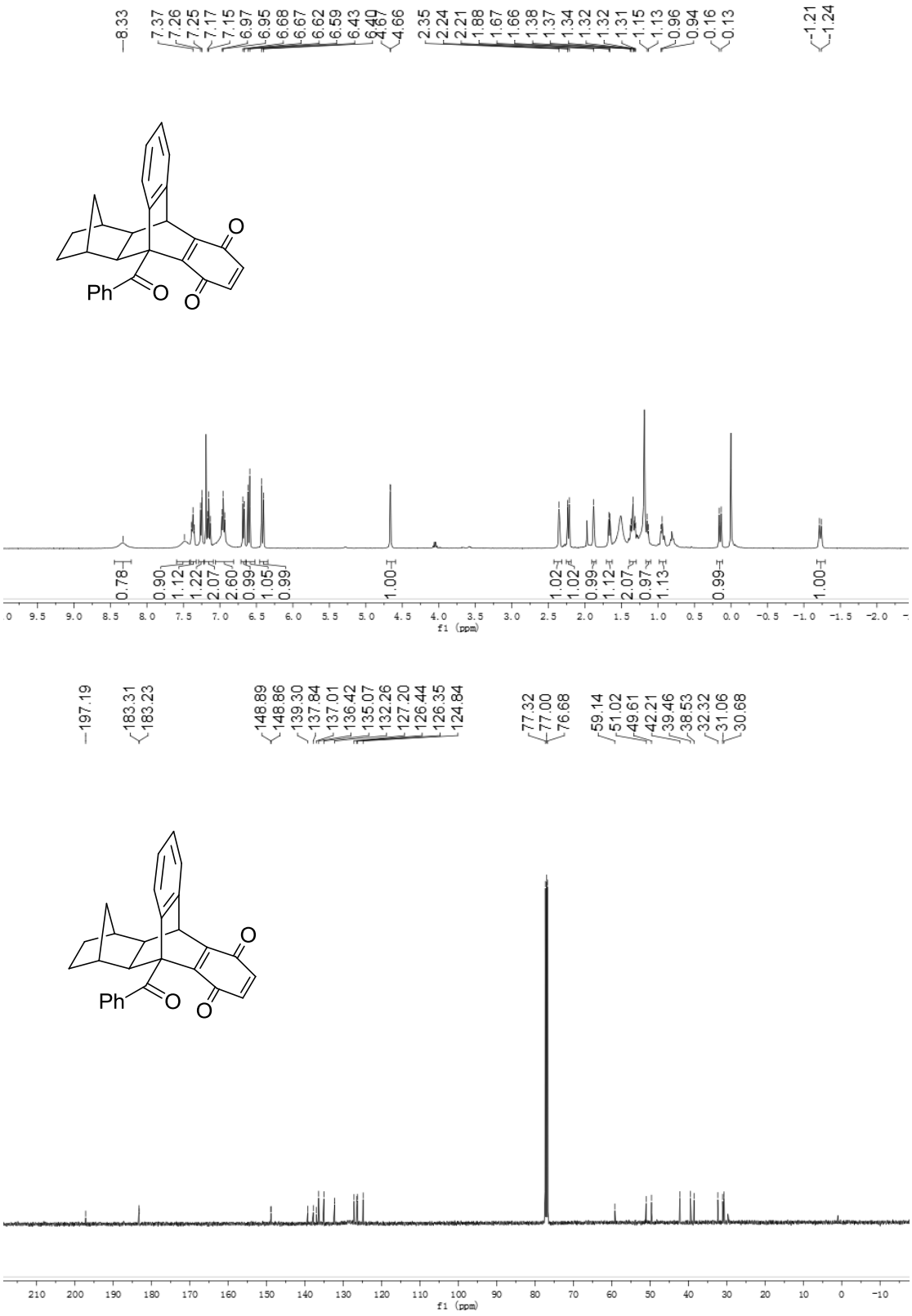
132.20, 131.31, 129.72, 129.57, 129.38, 128.71, 128.57, 128.16, 126.98, 126.30, 52.80, 52.55.

3. ^{1}H, ^{19}F , ^{13}C NMR and NOE Spectra

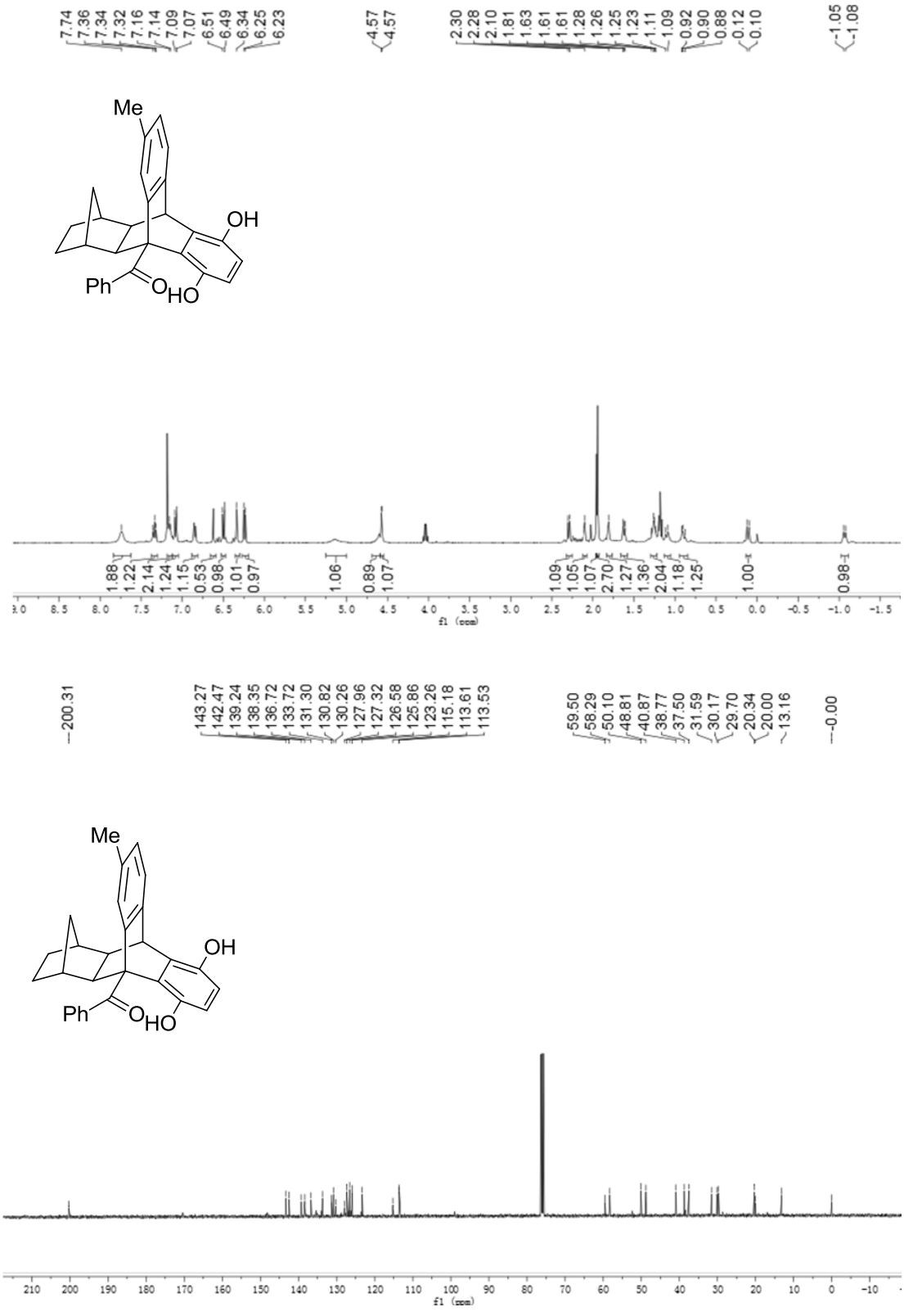
9-Benzoyl-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4a)



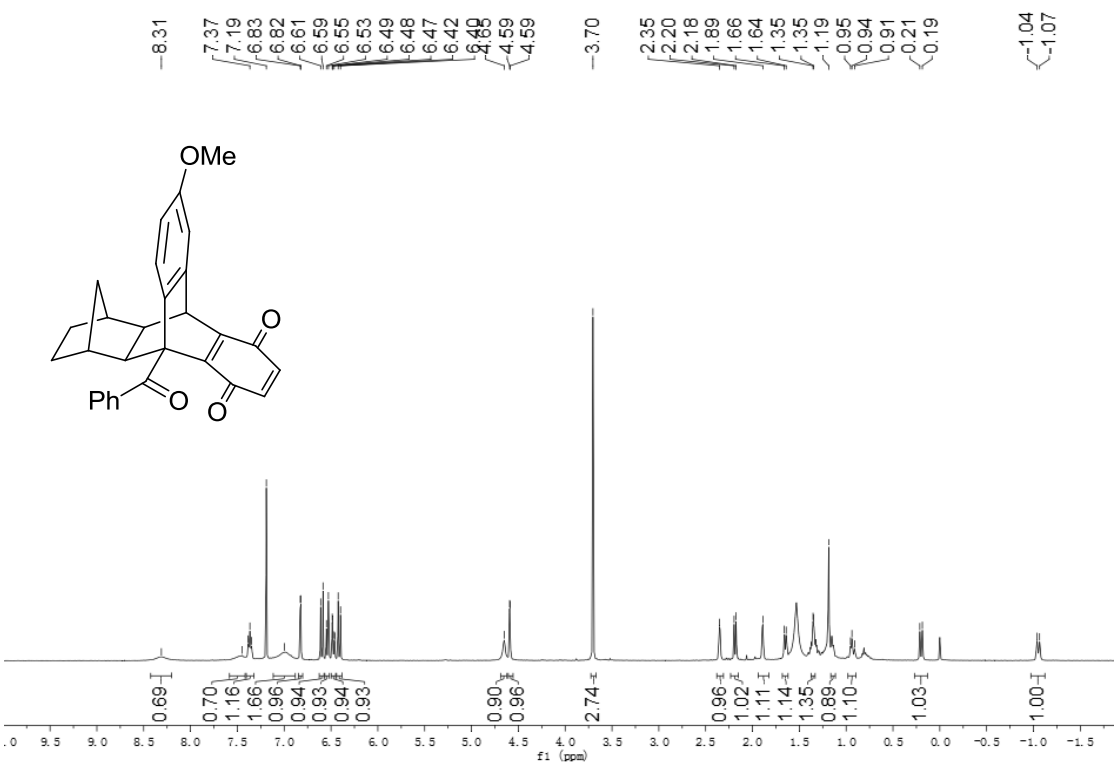
9-Benzoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5a)

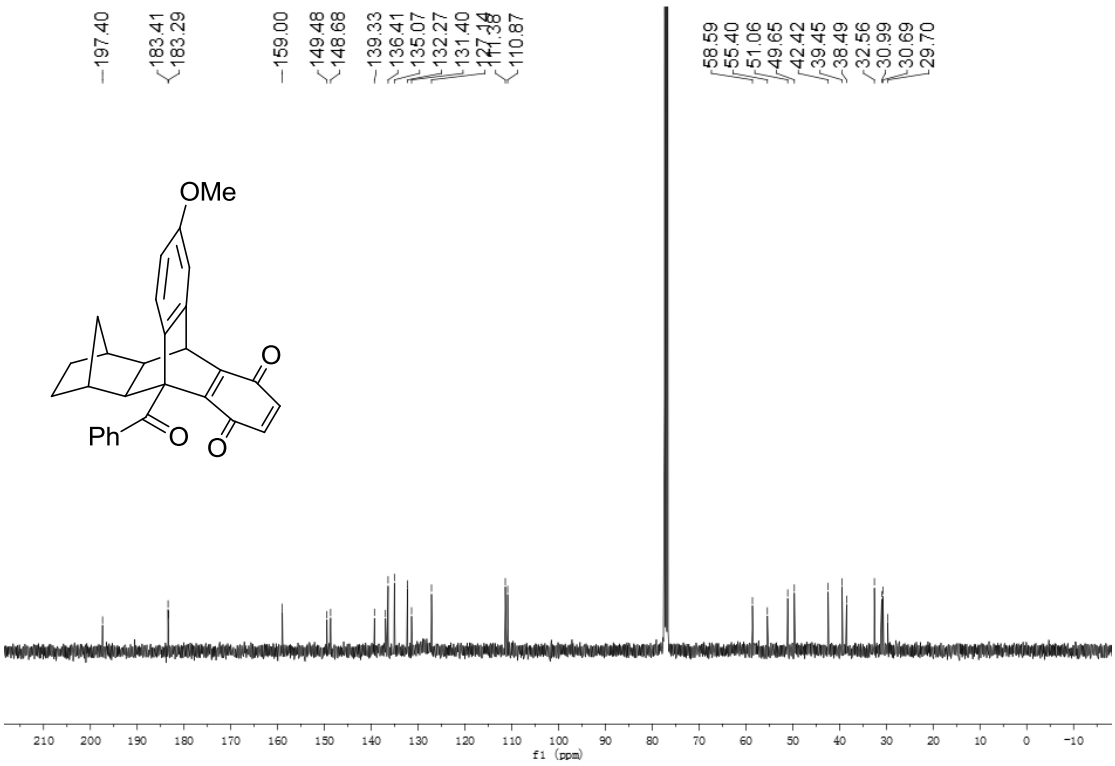


1,4-Dihydroxy-7-methyl-octahydro-9,10-[2]bicycloanthracen-9-yl)(phenyl)metha none (5b)

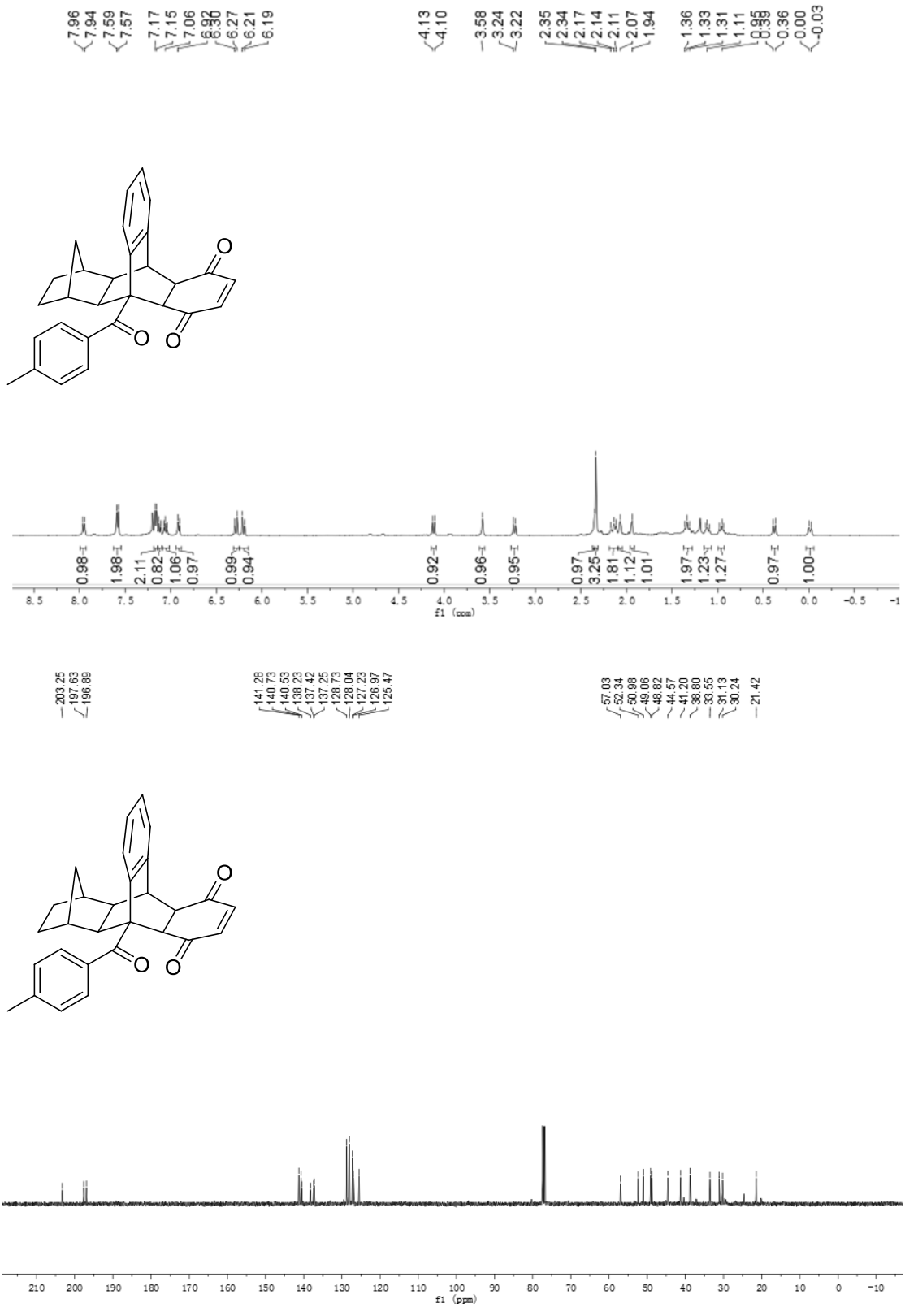


9-Benzoyl-6-methoxy-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5c)

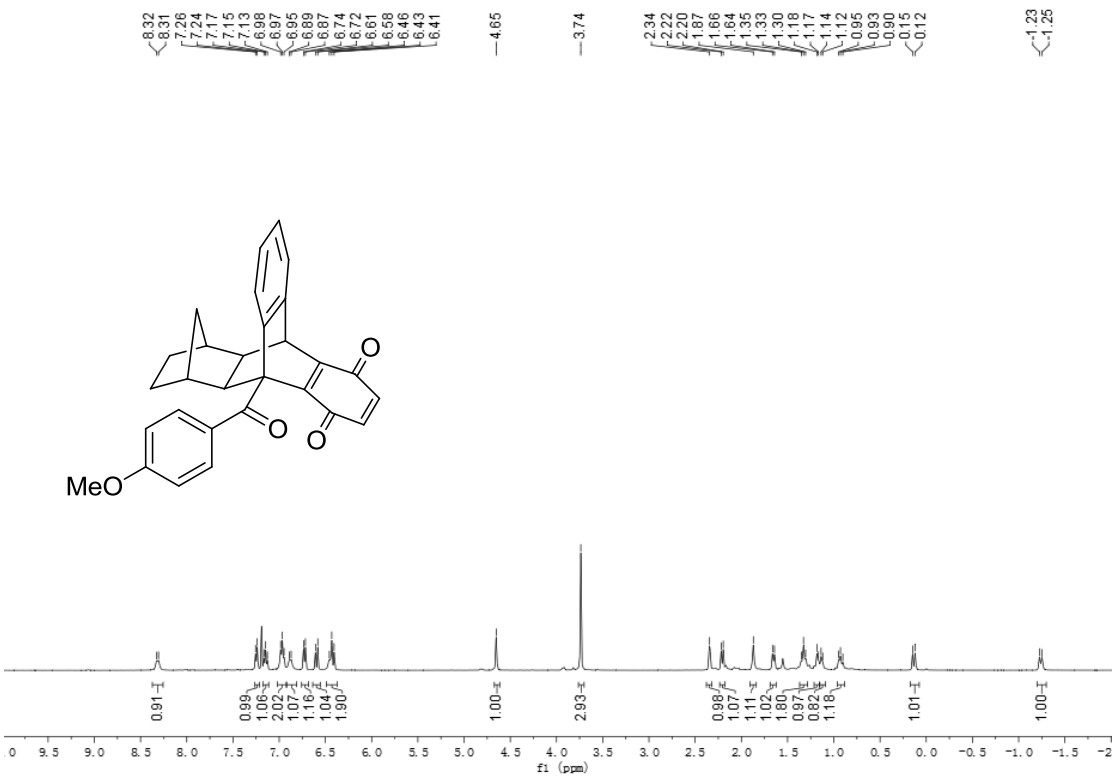


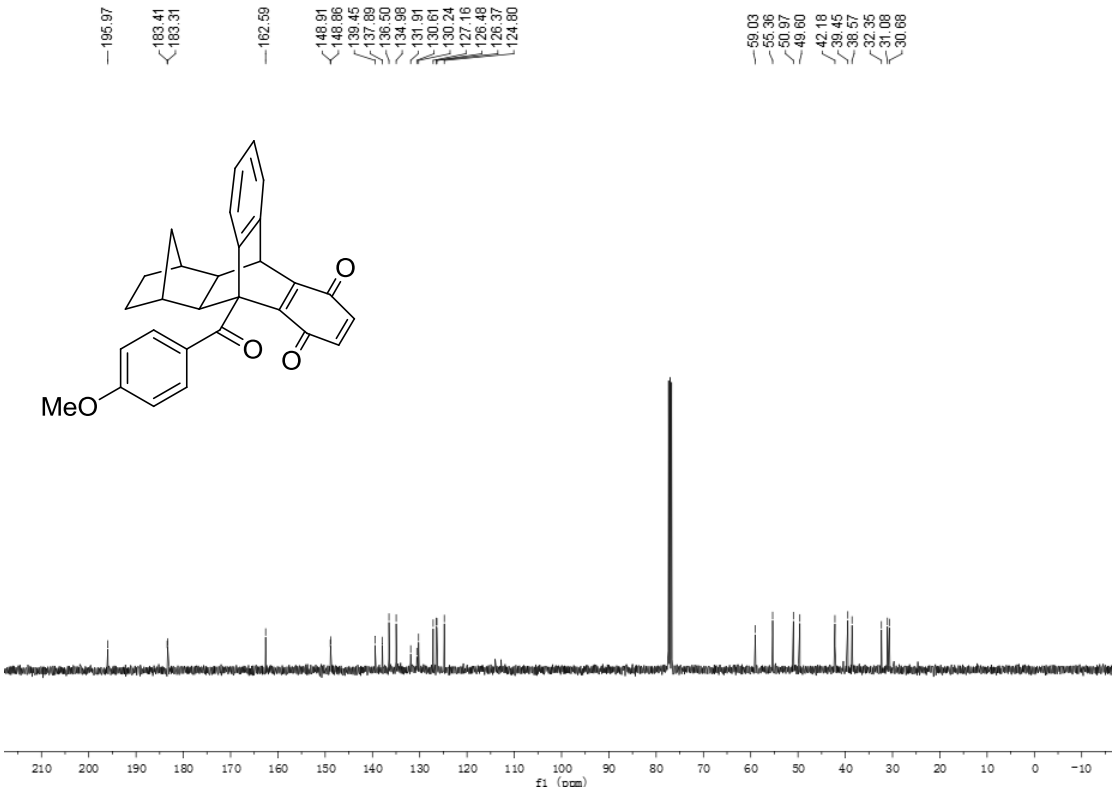


9-(4-Methylbenzoyl)-decahydro-9,10-[2]bicycloanthracene-1,4-dione (4d)

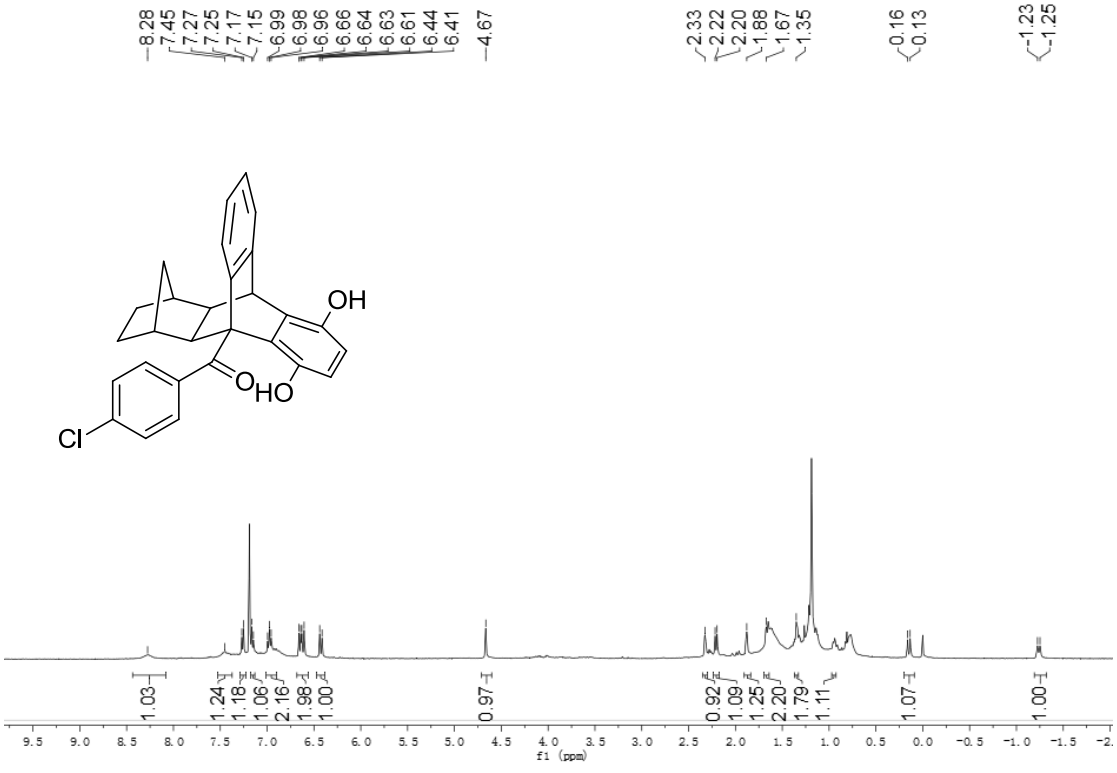


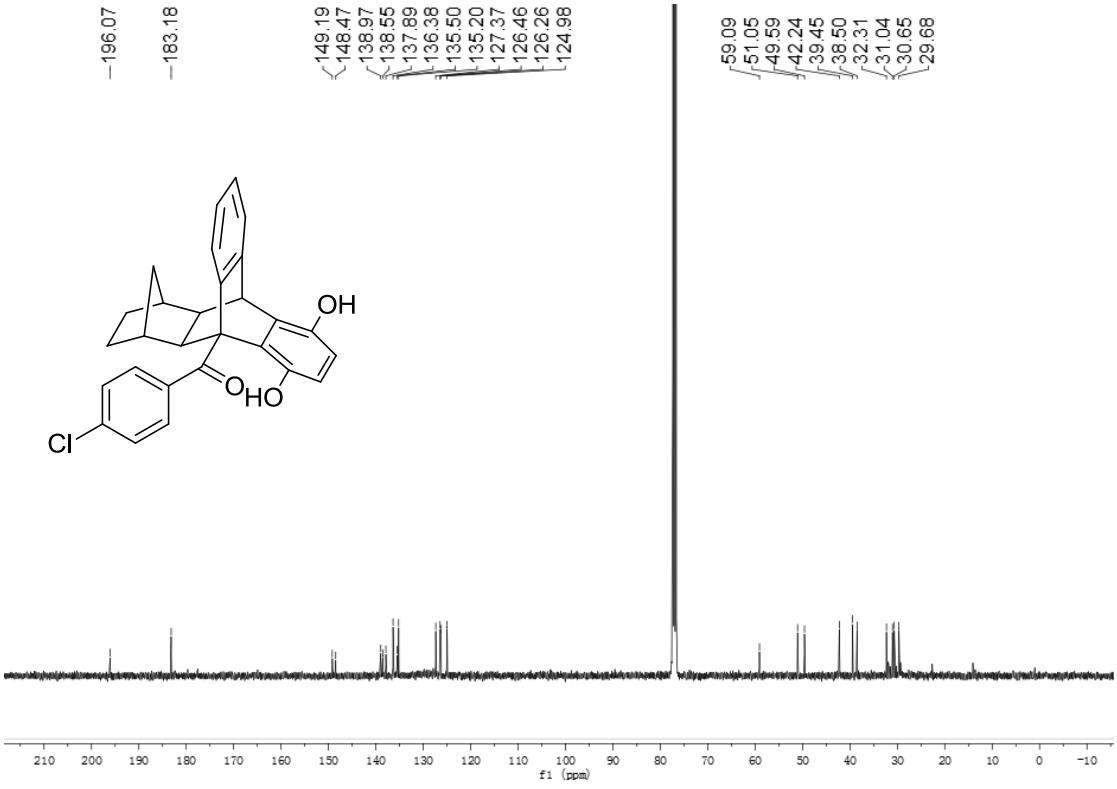
9-(4-Methoxybenzoyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5e)



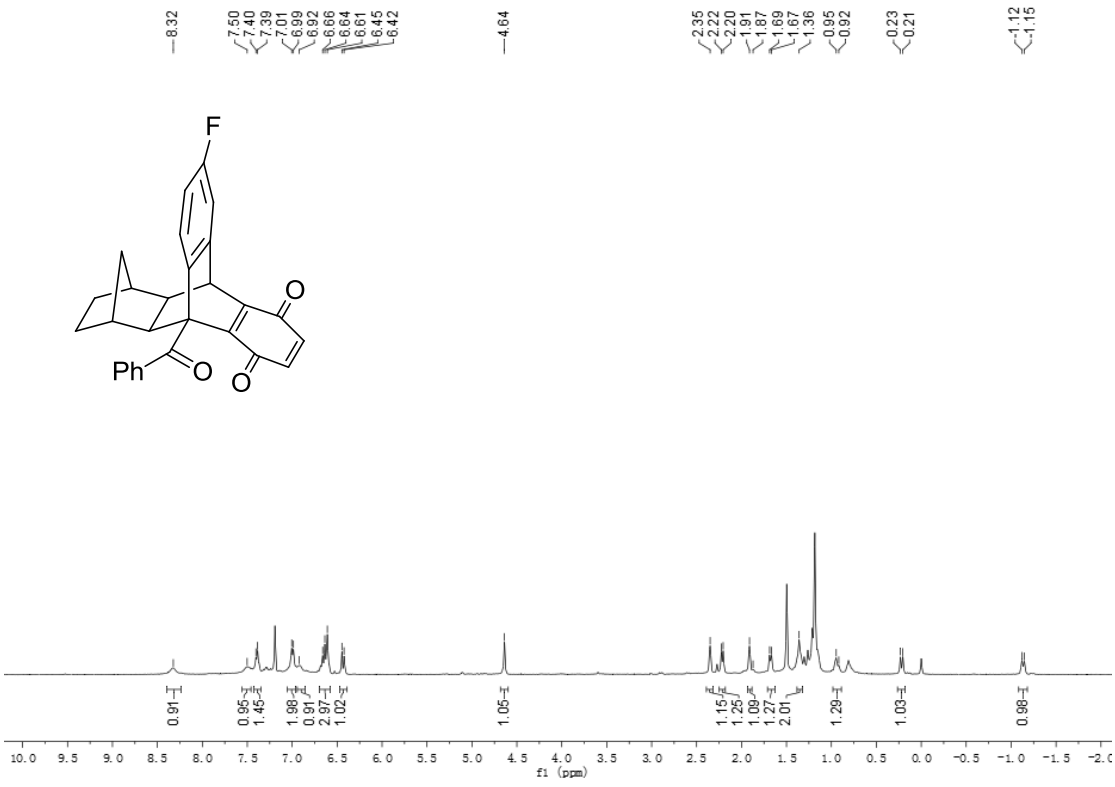


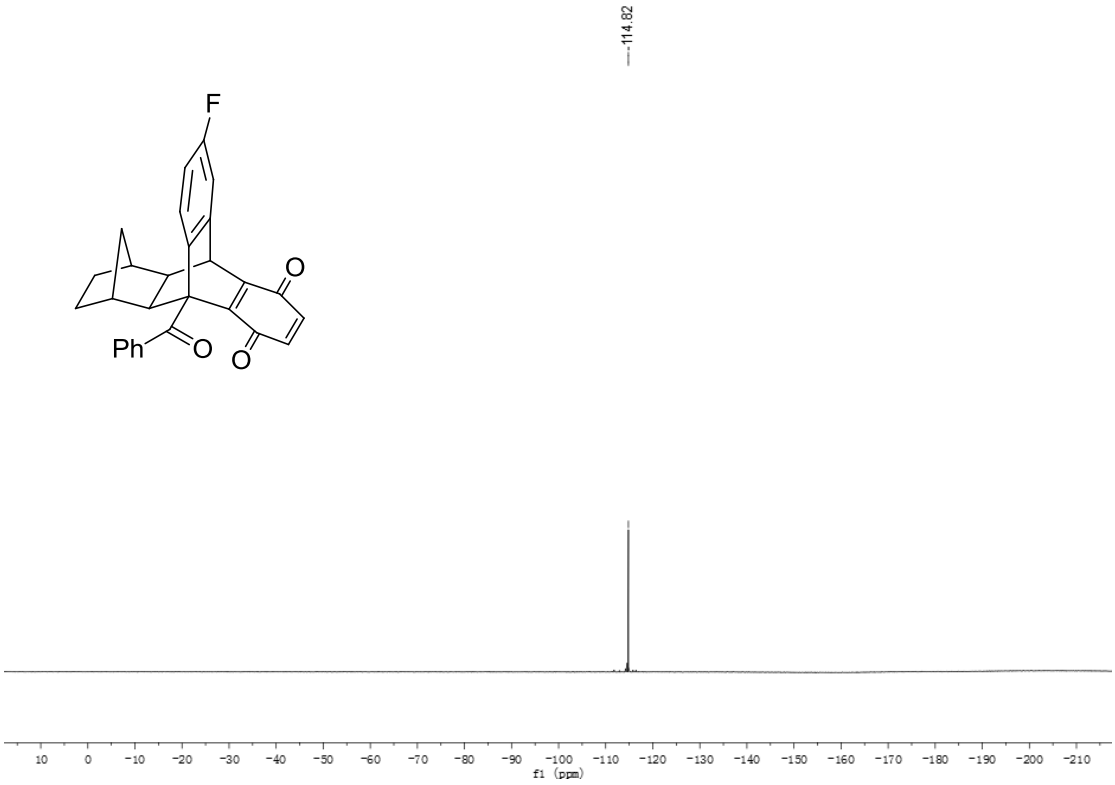
(4-Chlorophenyl)(1,4-dihydroxy-octahydro-9,10-[2]bicycloanthracen-9-yl)metha none (5f)

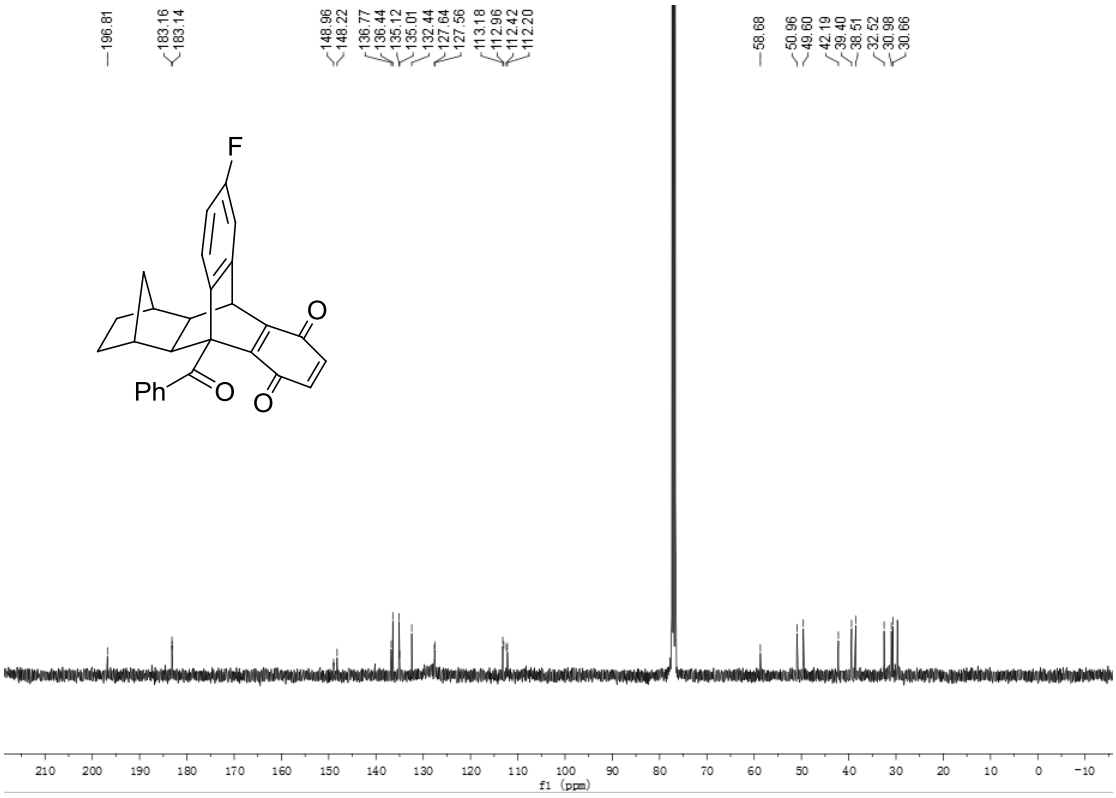




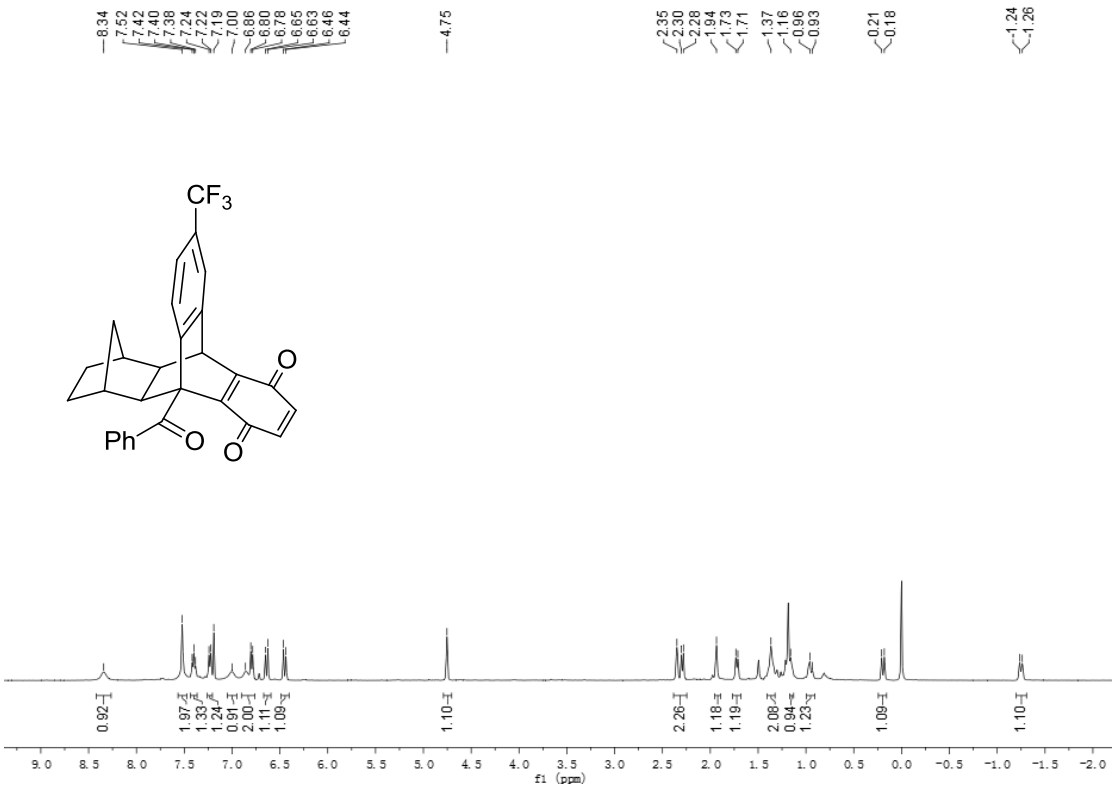
9-Benzoyl-6-fluoro-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5g)

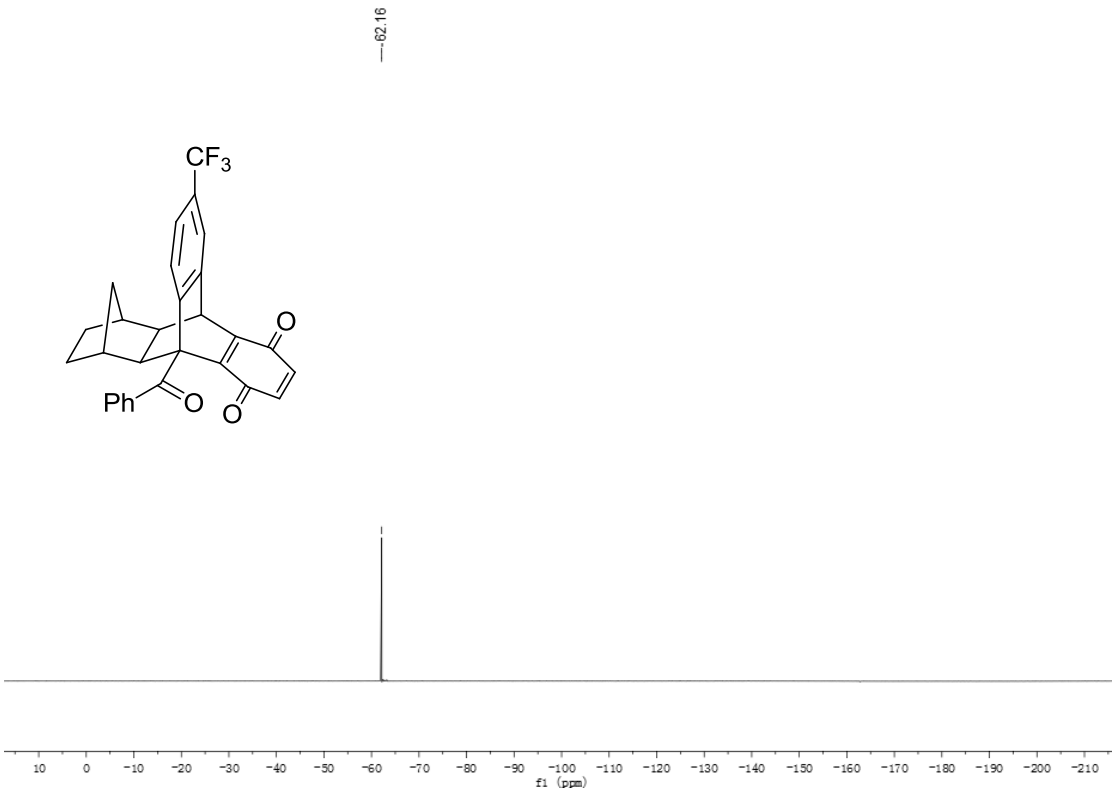


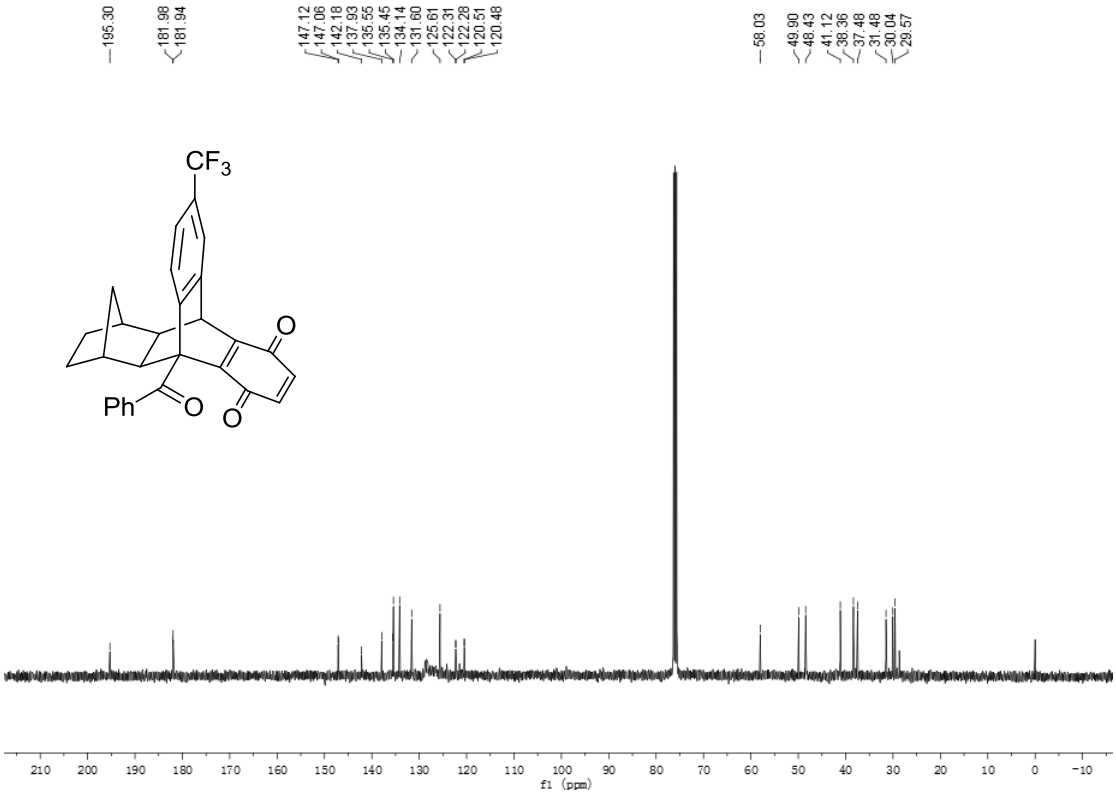



196.81
183.16
183.14
148.96
148.22
136.77
136.44
135.12
135.01
132.44
127.64
127.56
113.18
112.96
112.42
112.20
58.68
50.96
49.60
42.19
39.40
38.51
32.52
30.98
30.66
F
O
Ph
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

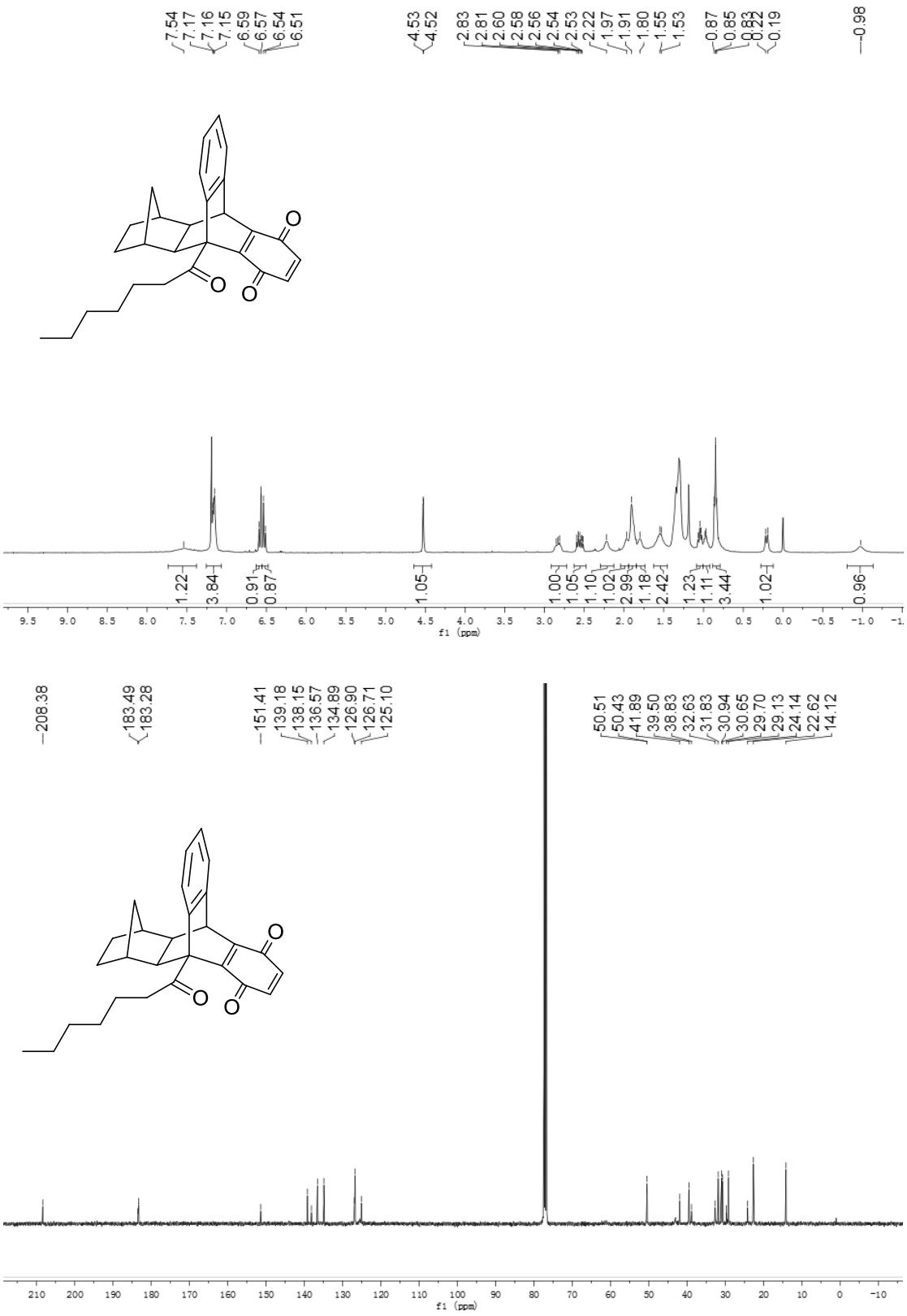
9-Benzoyl-6-(trifluoromethyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5h)



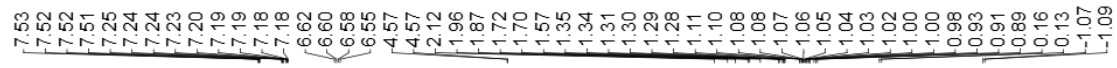


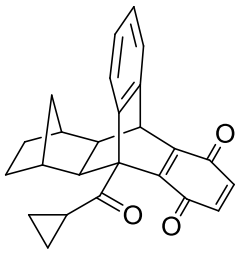

195.30
181.98
181.94
147.12
147.06
142.18
137.93
135.55
135.45
134.14
131.60
125.61
122.31
122.28
120.51
120.48
58.03
49.90
48.43
41.12
38.36
37.48
31.48
30.04
29.57
CF3
O
Ph
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

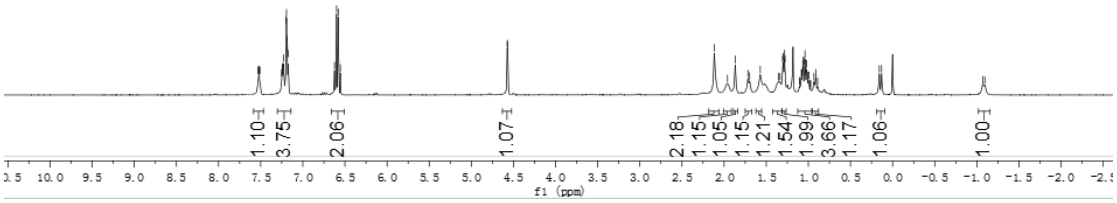
9-Hexanoyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5i)

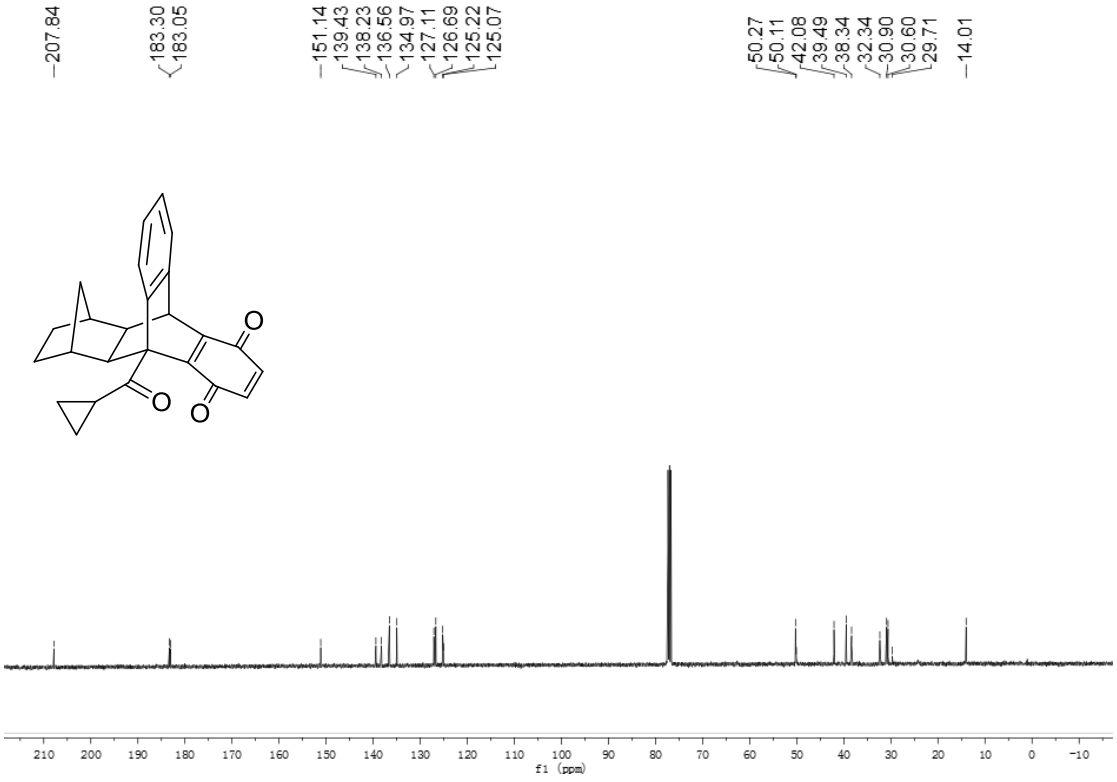


9-(Cyclopropanecarbonyl)-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5j)

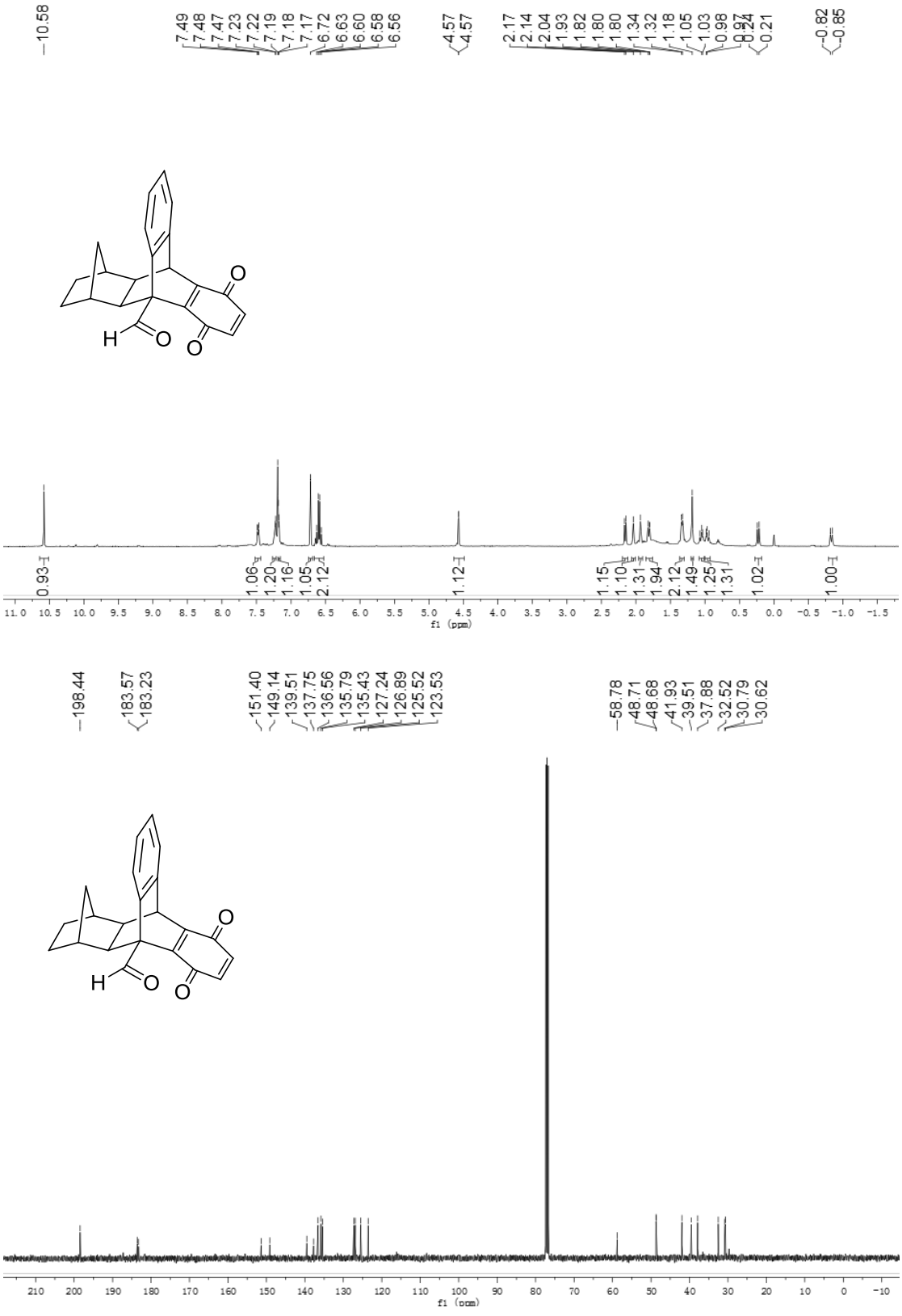




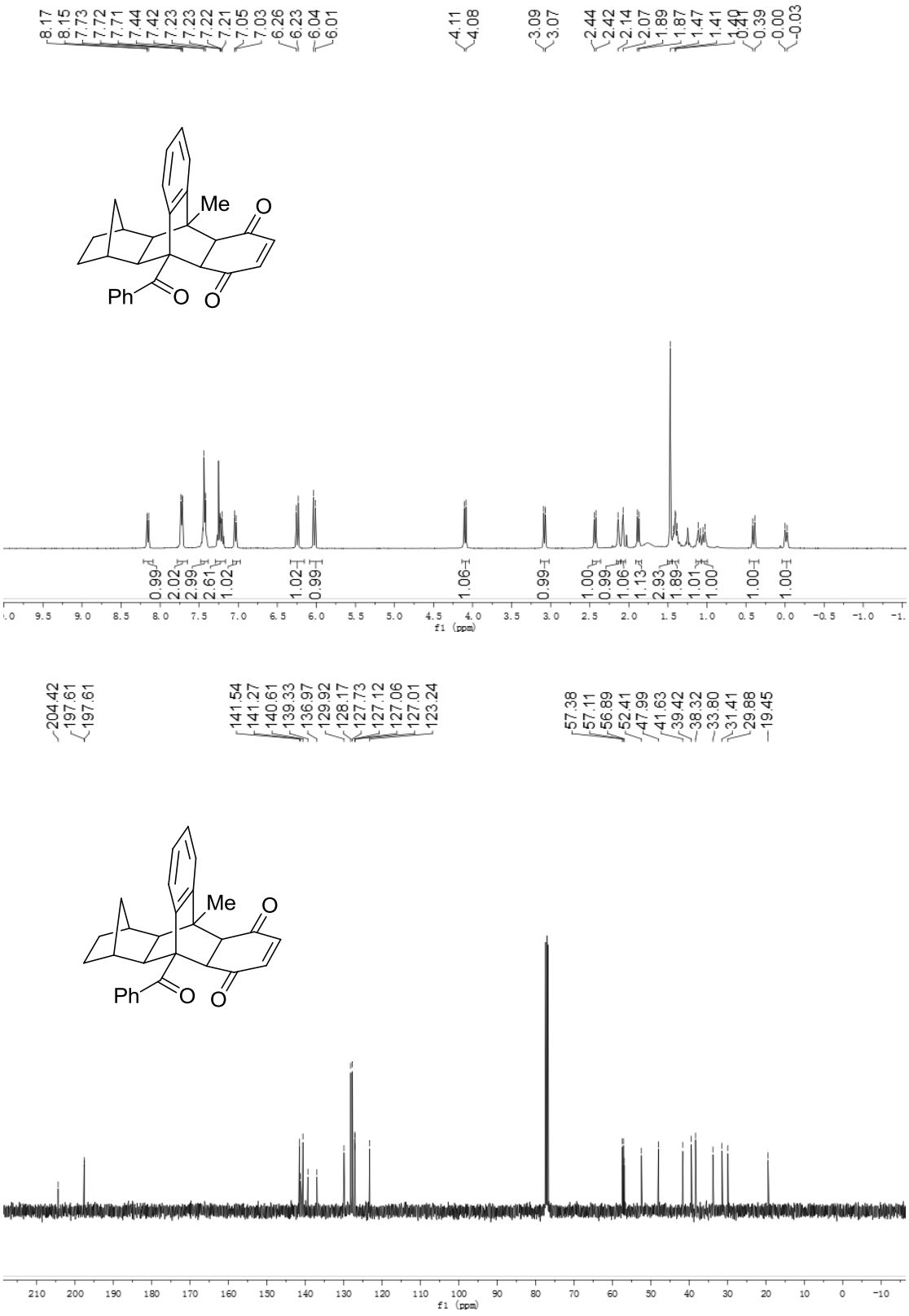




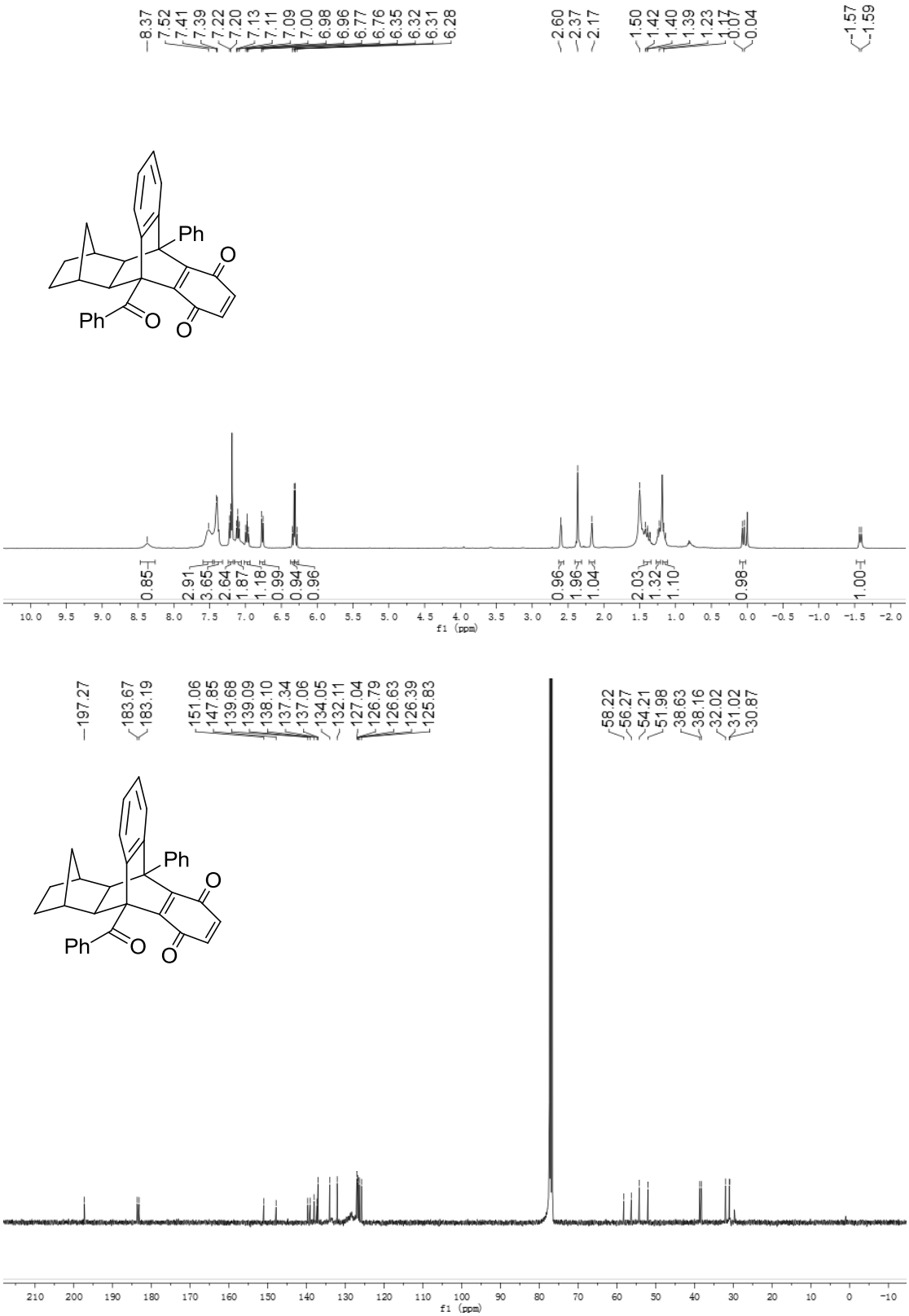
9-Carbaldehyde-decahydro-9,10-[2]bicycloanthracene- 1,4-dione (5k)



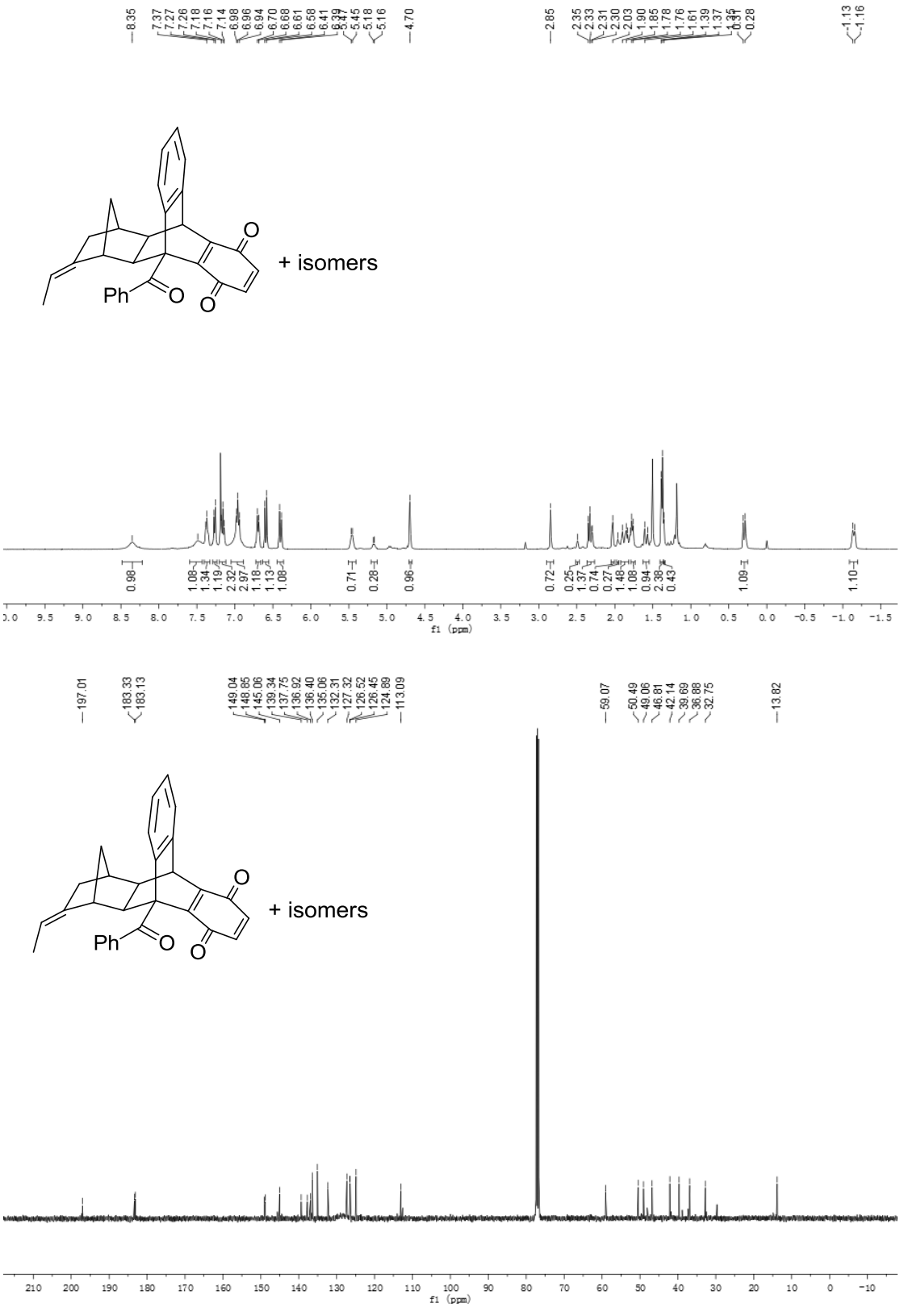
9-Benzoyl-10-methyl--decahydro--9,10-[2]bicycloanthracene-1,4-dione (4l)



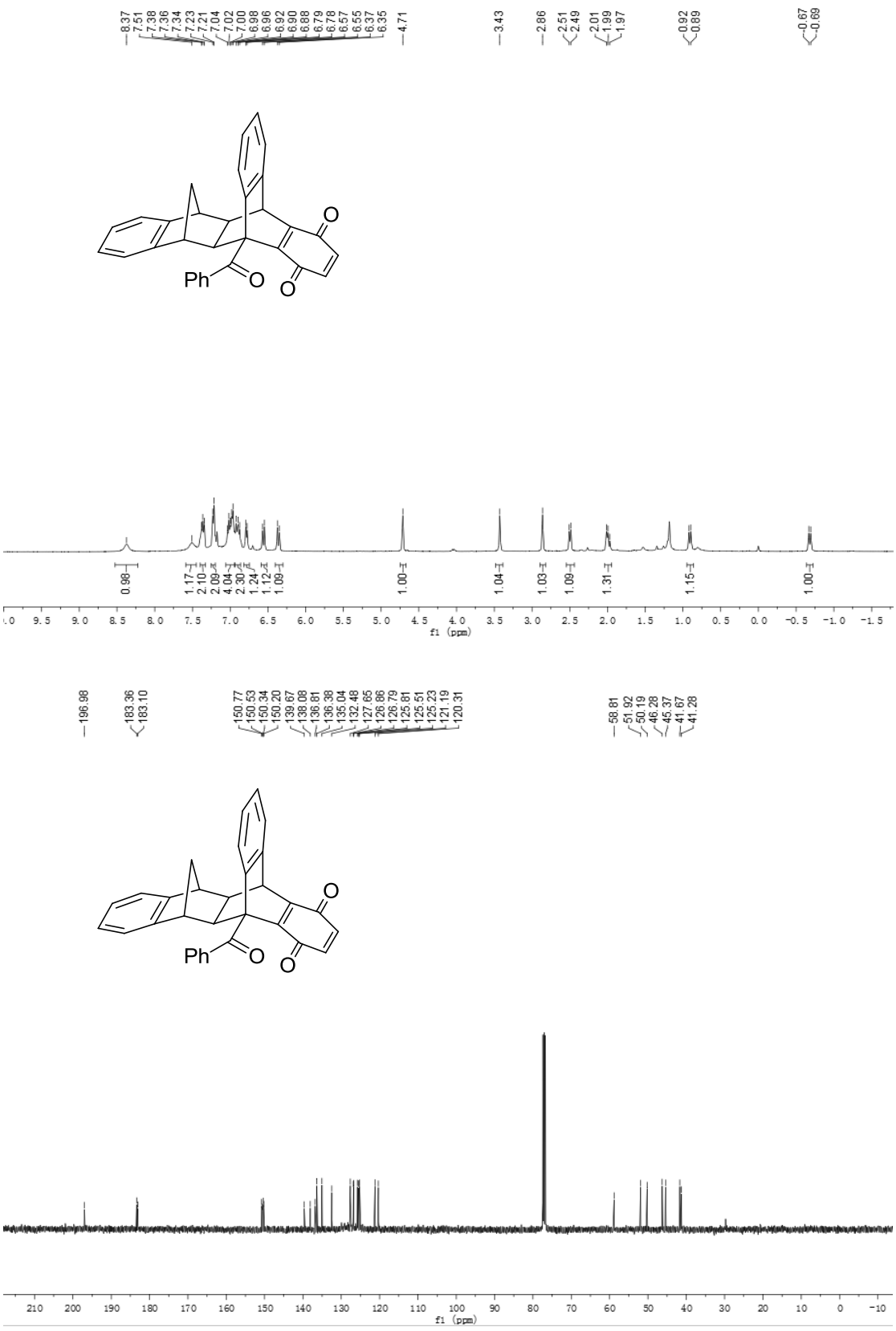
9-Benzoyl-10-phenyl-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5m)



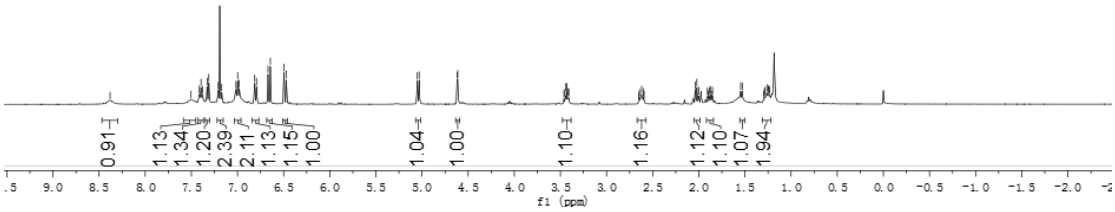
9-Benzoyl-16-ethylidene-octahydro-9,10-[2]bicycloanthracene-1,4-dione (5n)

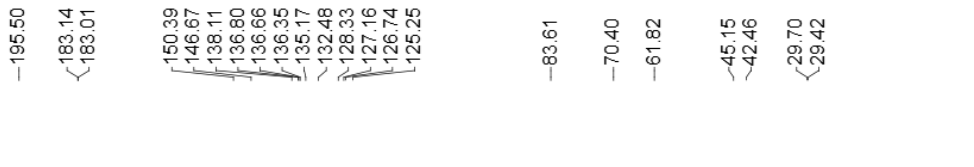


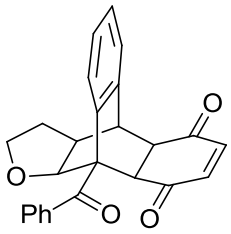
5-Benzoyl-tetrahydro-5,12-[1,2]benzeno-6,11-methanotetracene-15,18-dione (5o)



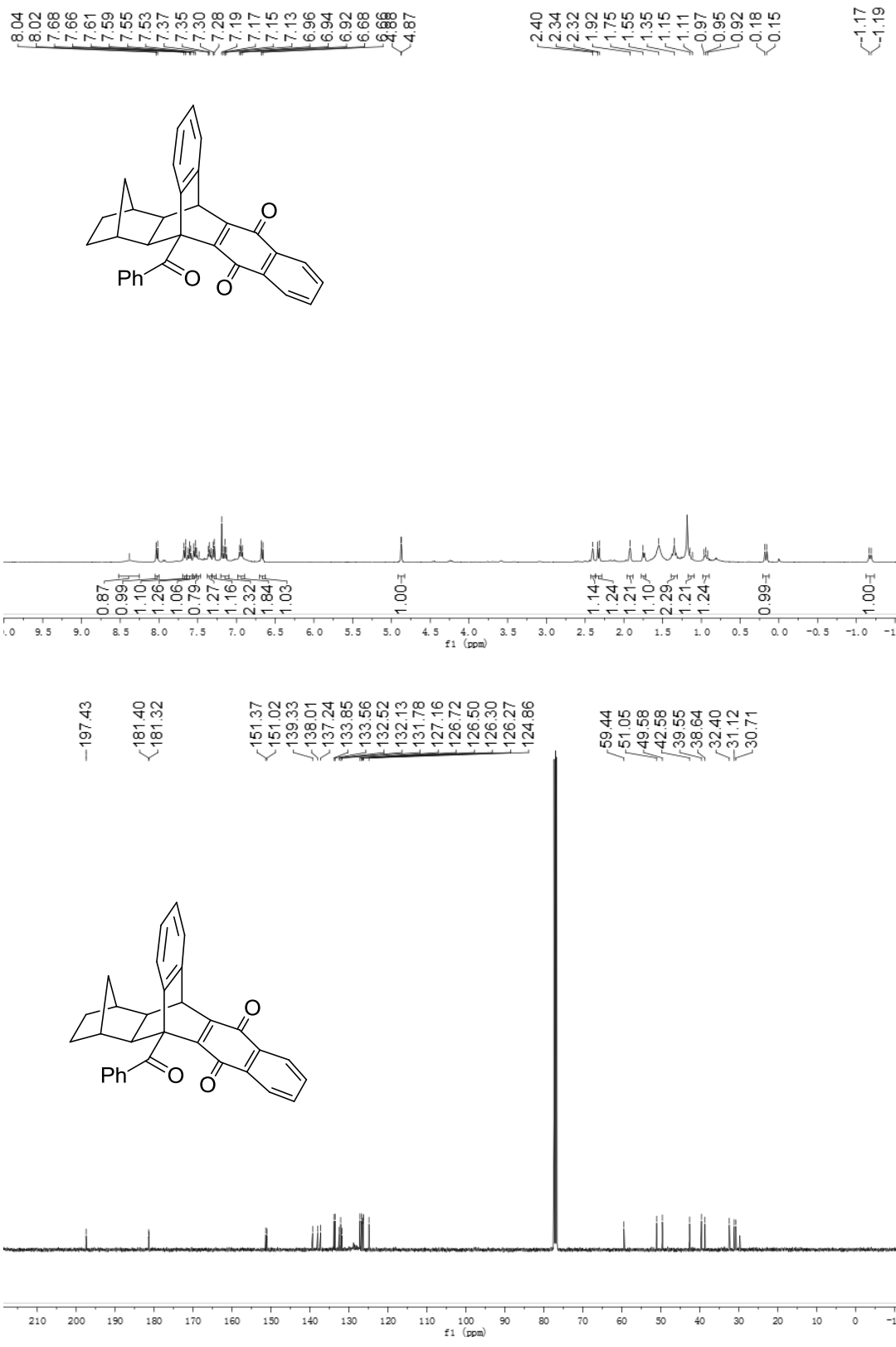
9-Benzoyl-hexahydro-9,10-[2,3]furanoanthracene-1,4-dione (4p)



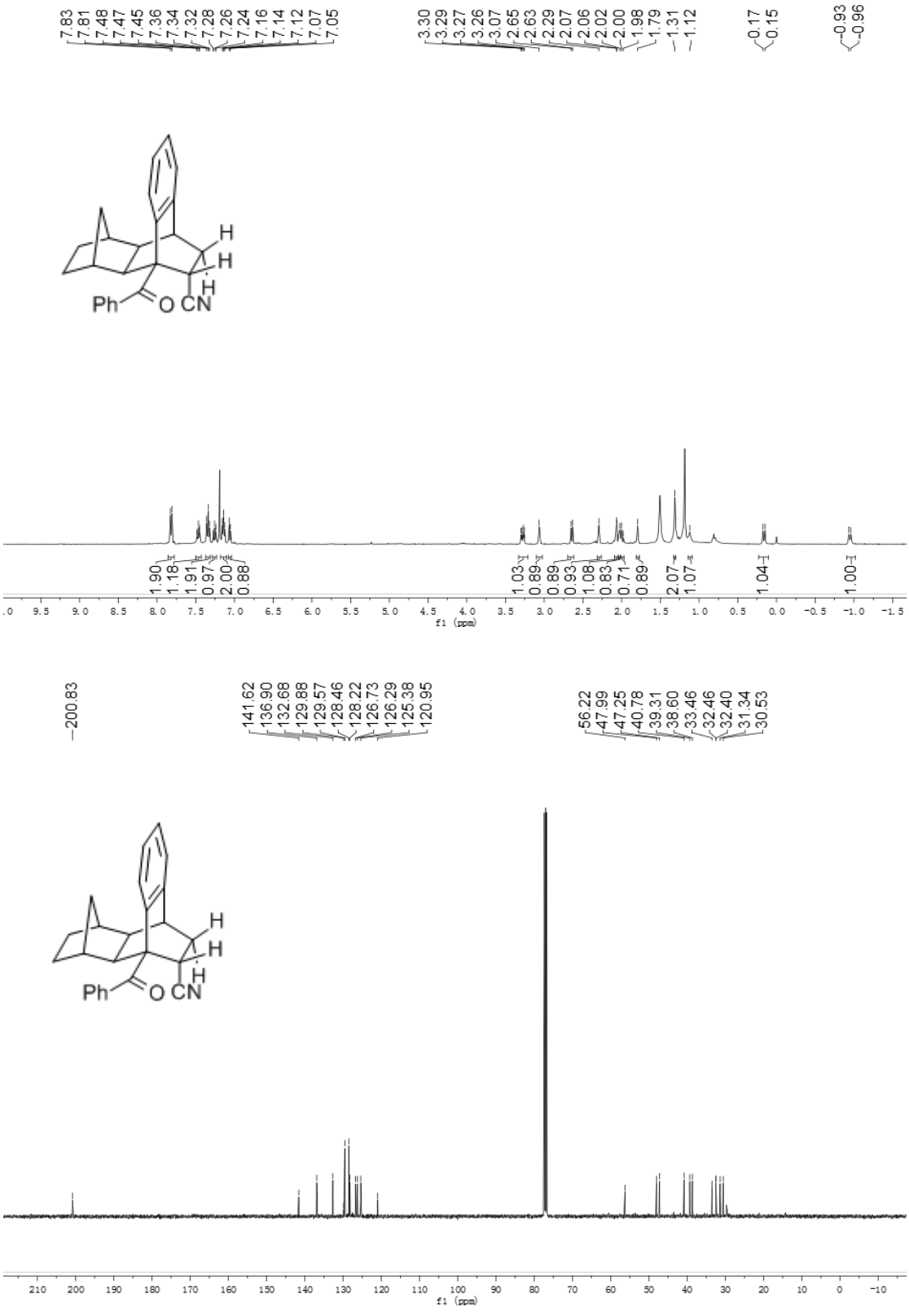




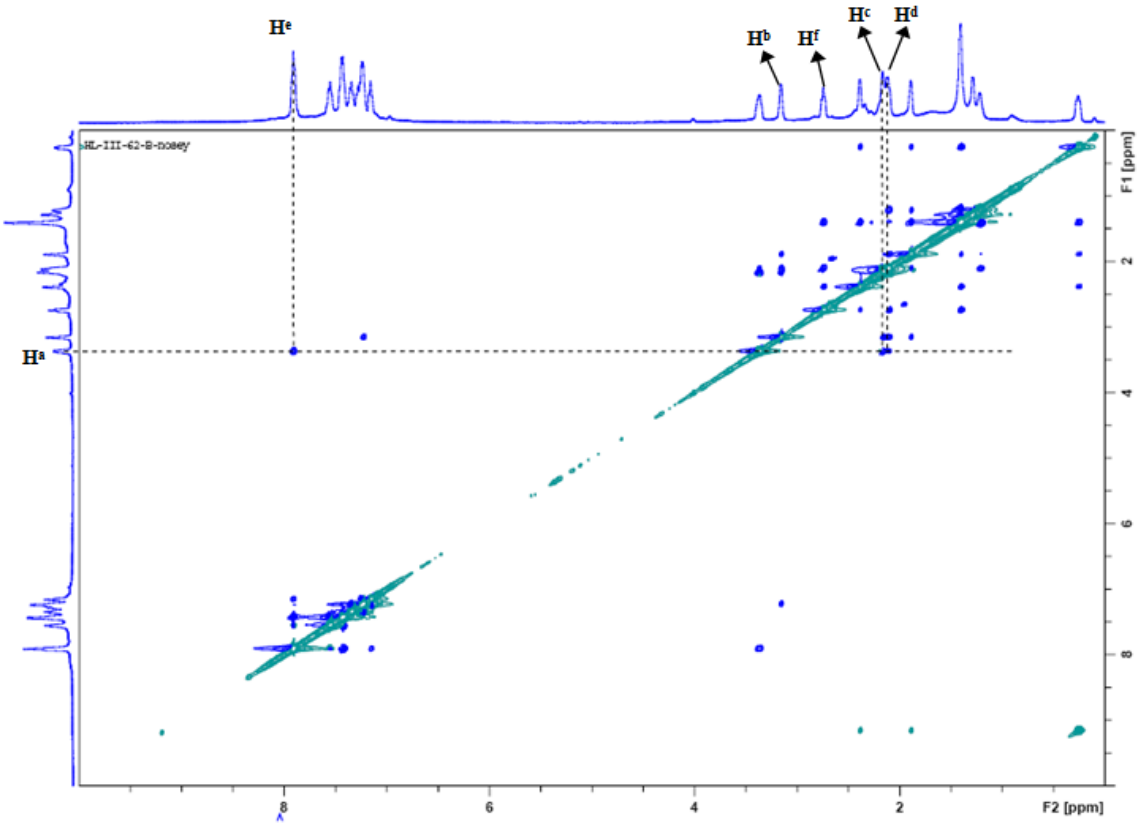
5-Benzoyl-hexahydro-5,12-[2]bicyclotetracene-6,11-dione (5q)

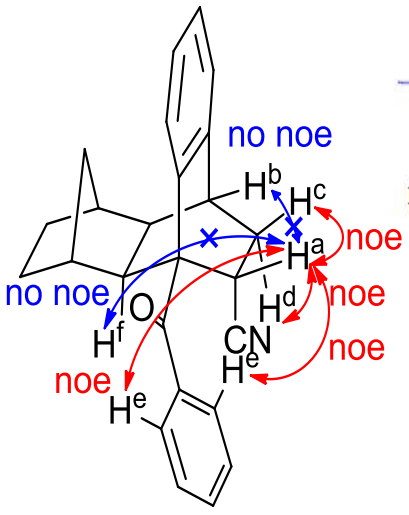


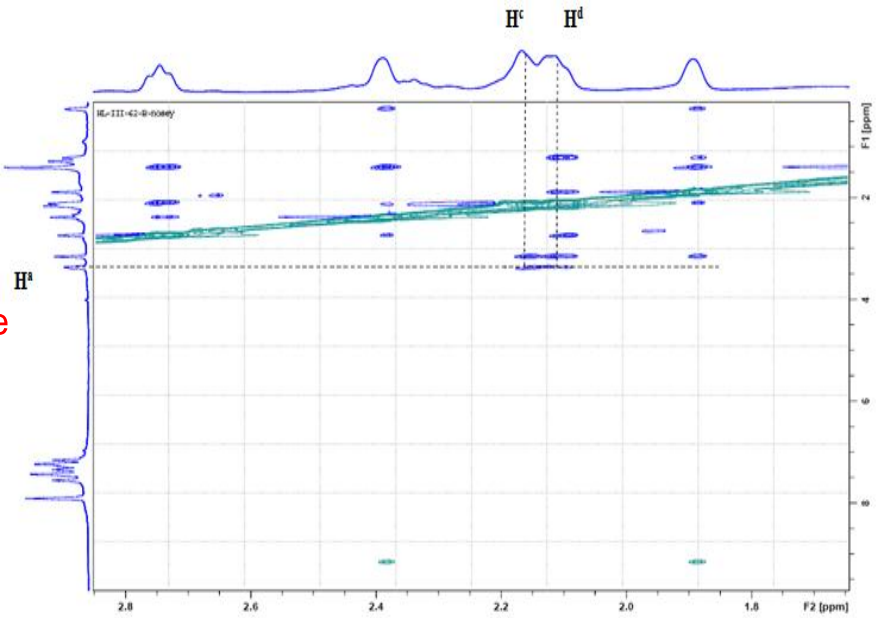
9-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11-carbonitrile (5r)



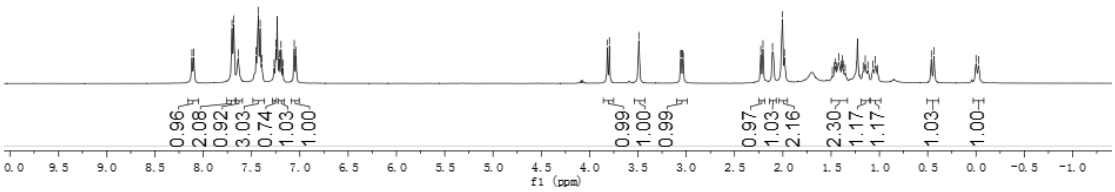
NOE spectrum of **5r**

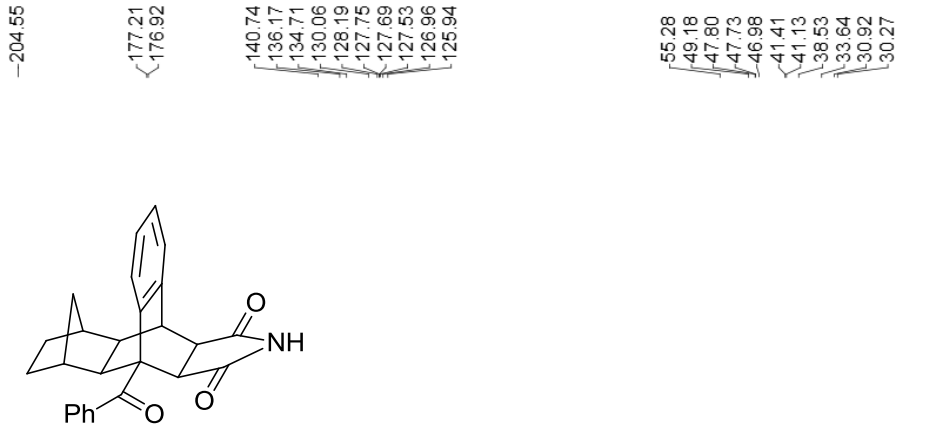




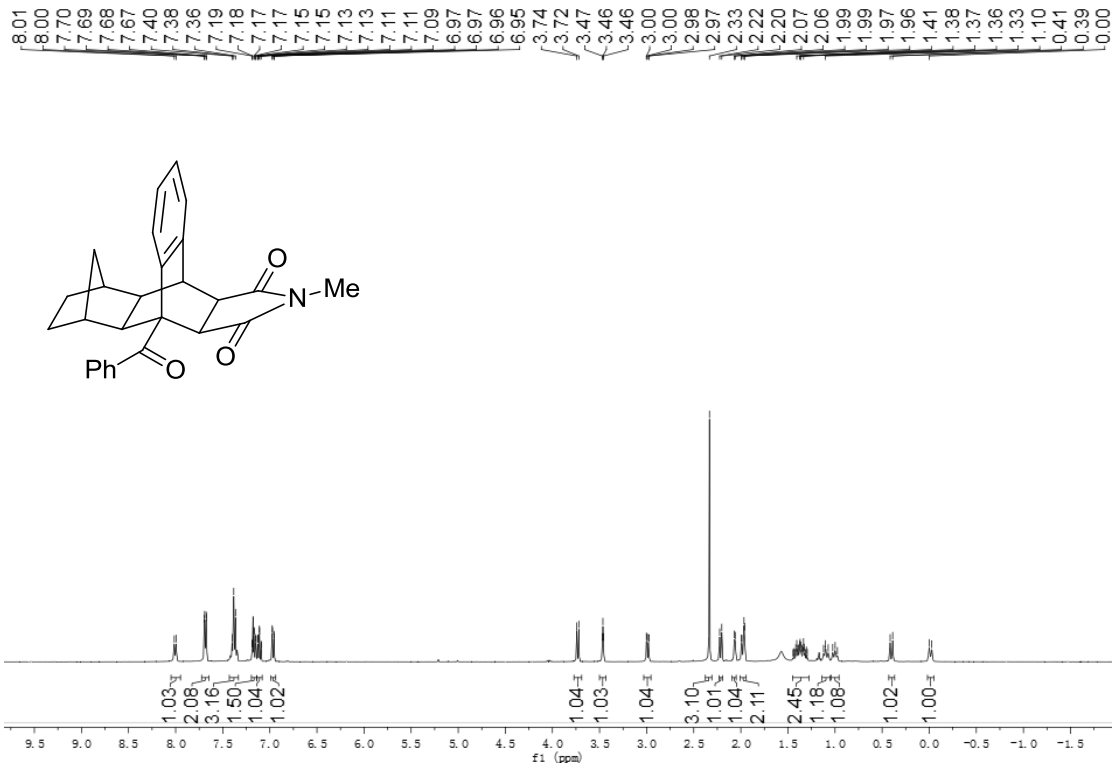


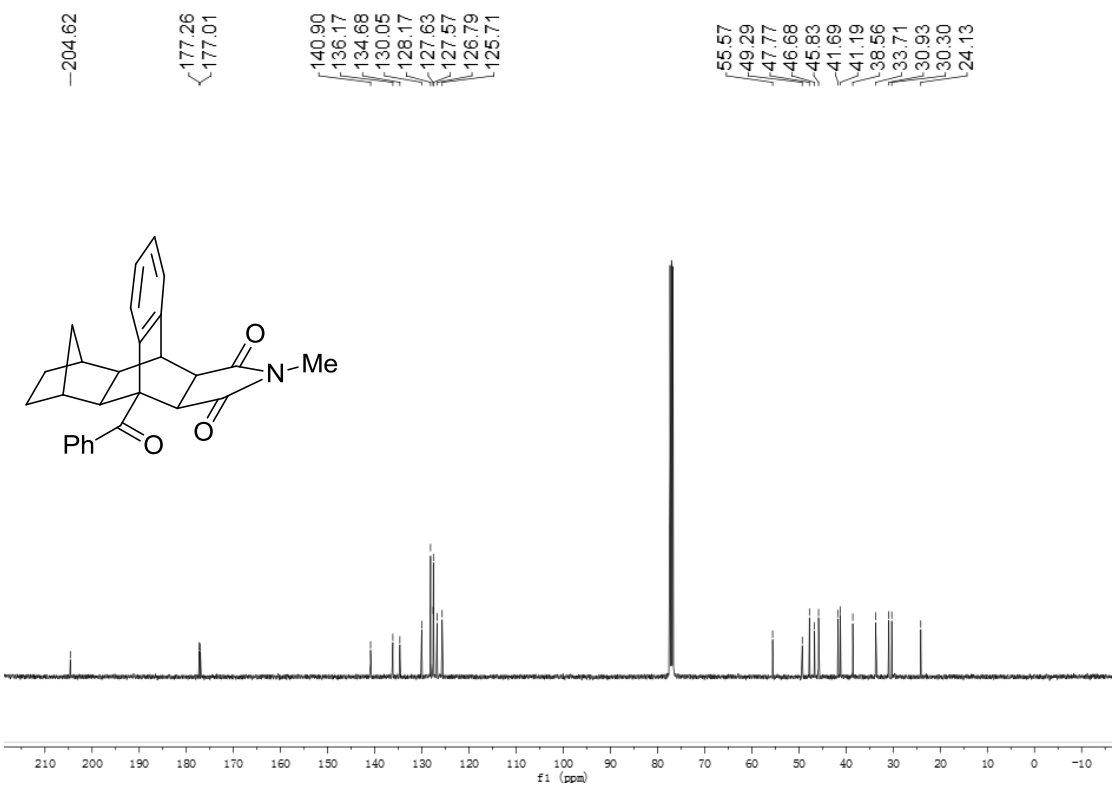
9-Benzoyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12,14-dione (5s)



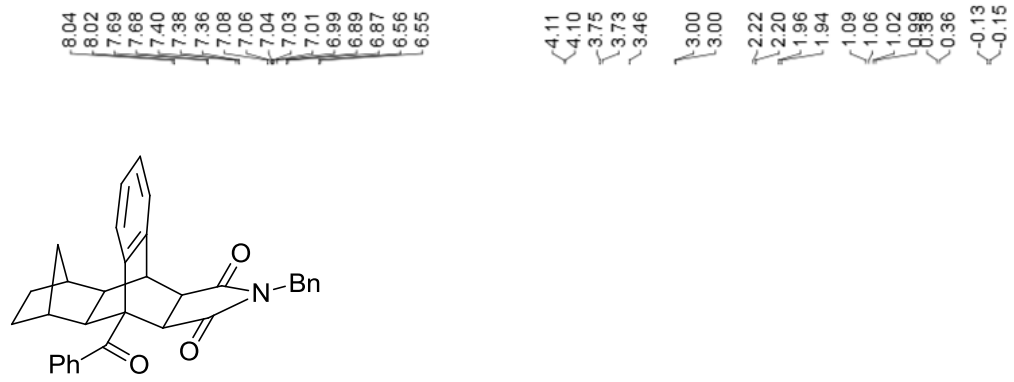


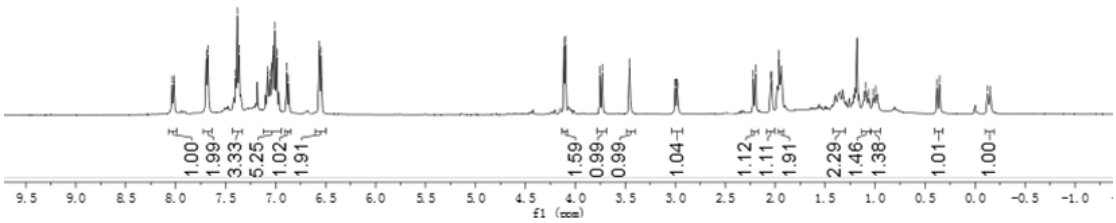
9-Benzoyl-13-methyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12, 14-dione (5t)

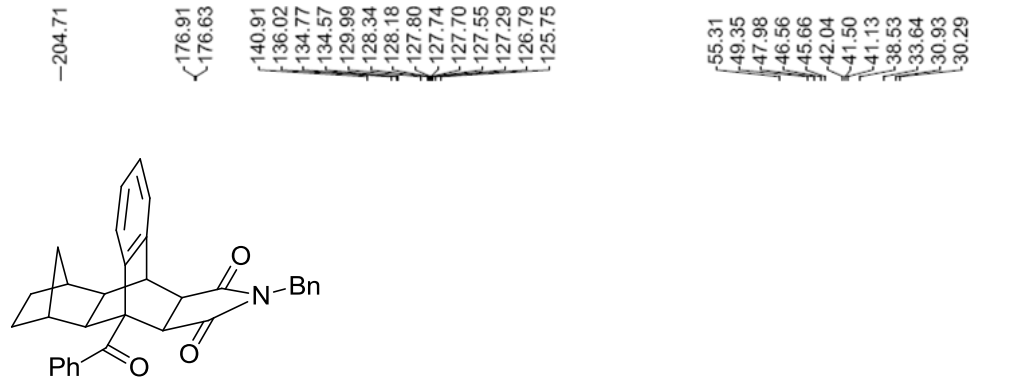


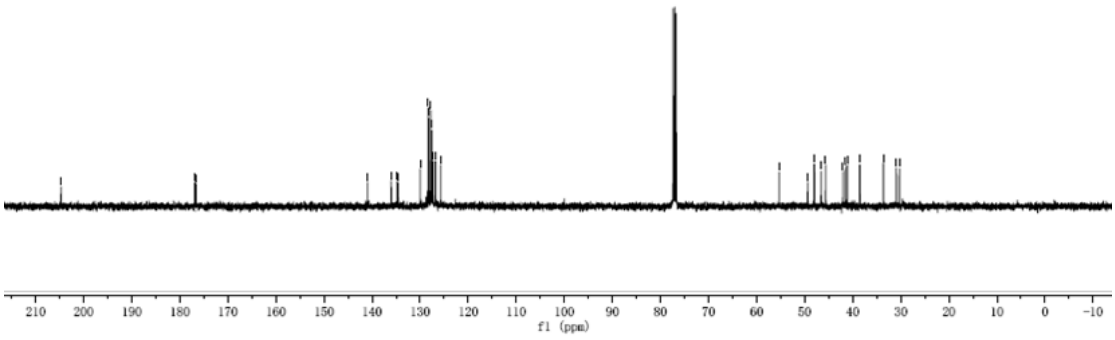


9-Benzoyl-13-benzyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12, 14-dione (5u)

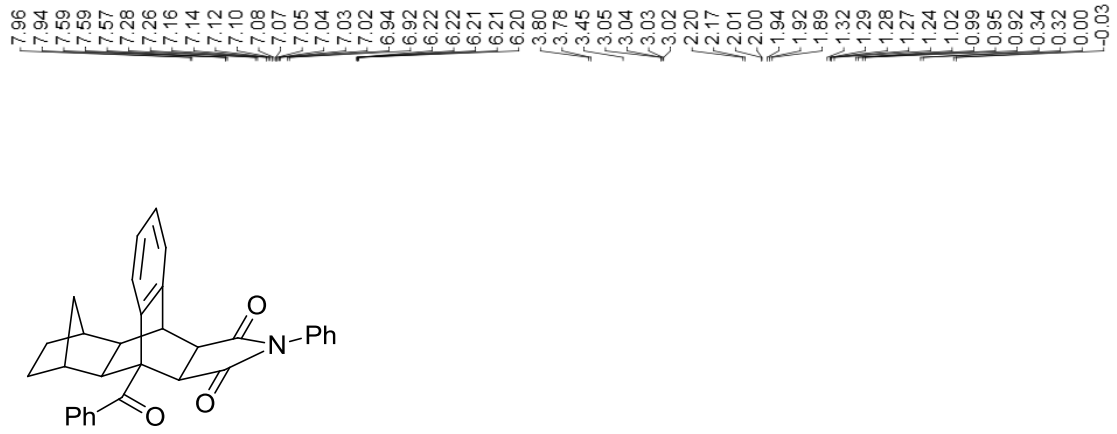


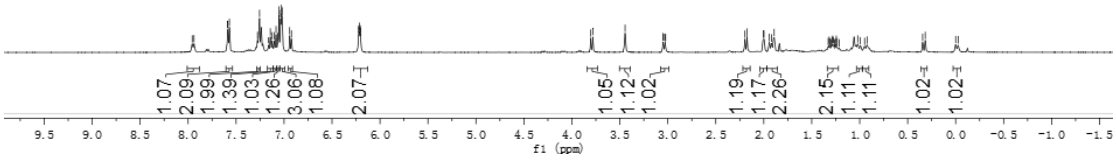


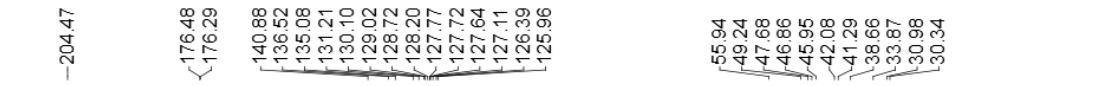


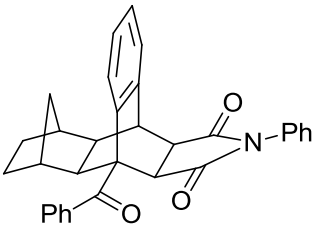


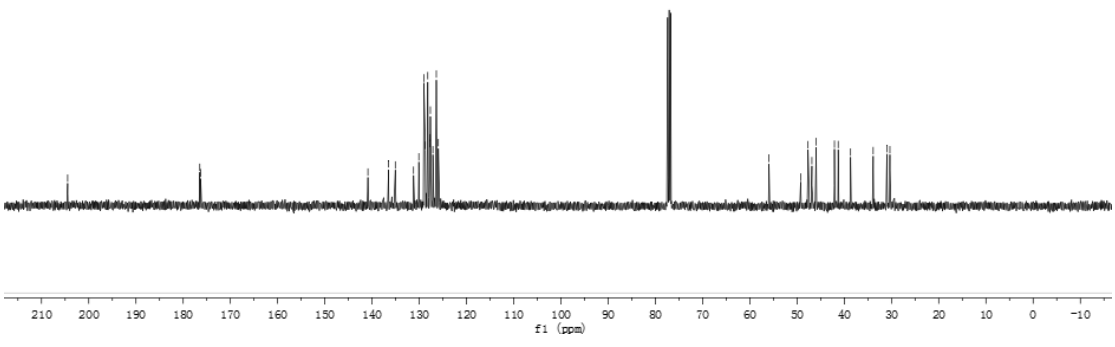
9-Benzoyl-13-phenyl-octahydro-9,10-[3,4]epipyrrolo-1,4-methanoanthracene-12, 14-dione (5v)



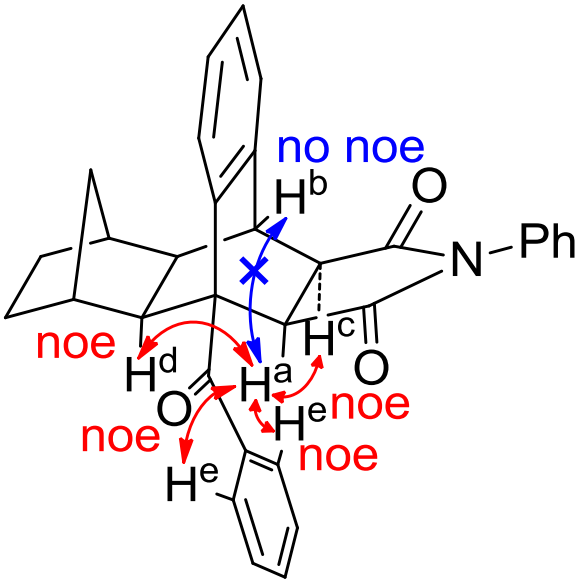


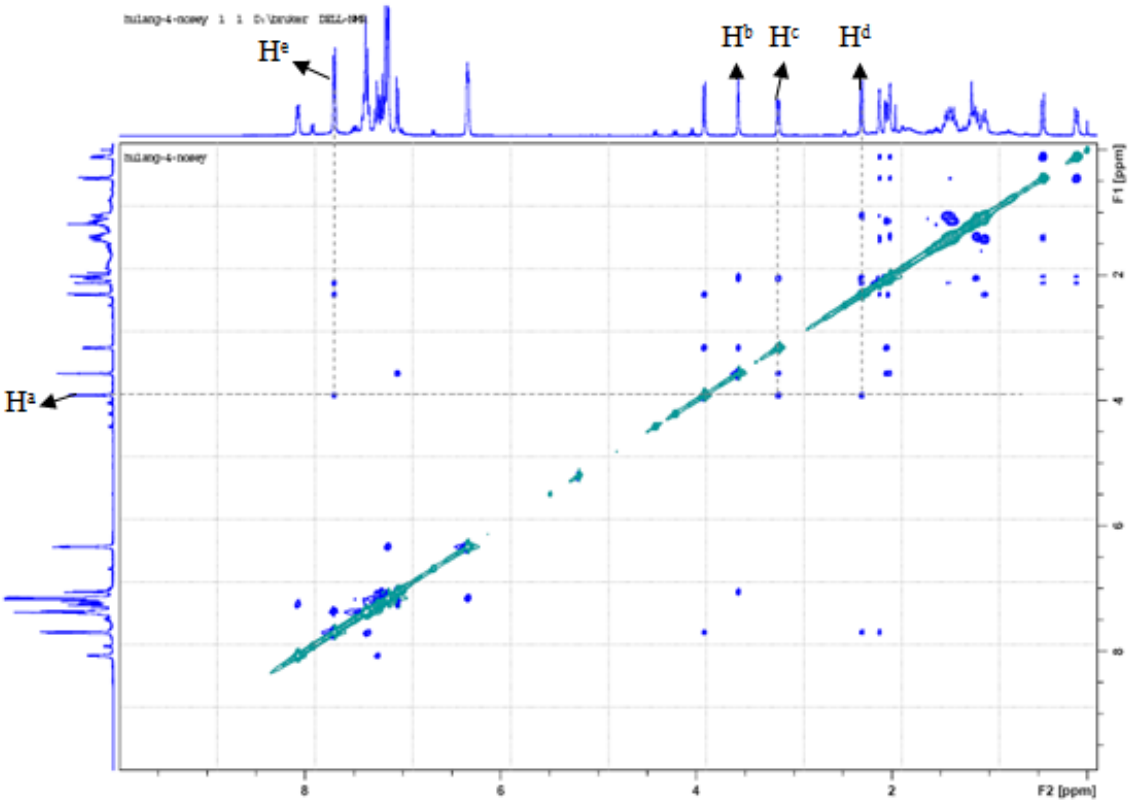




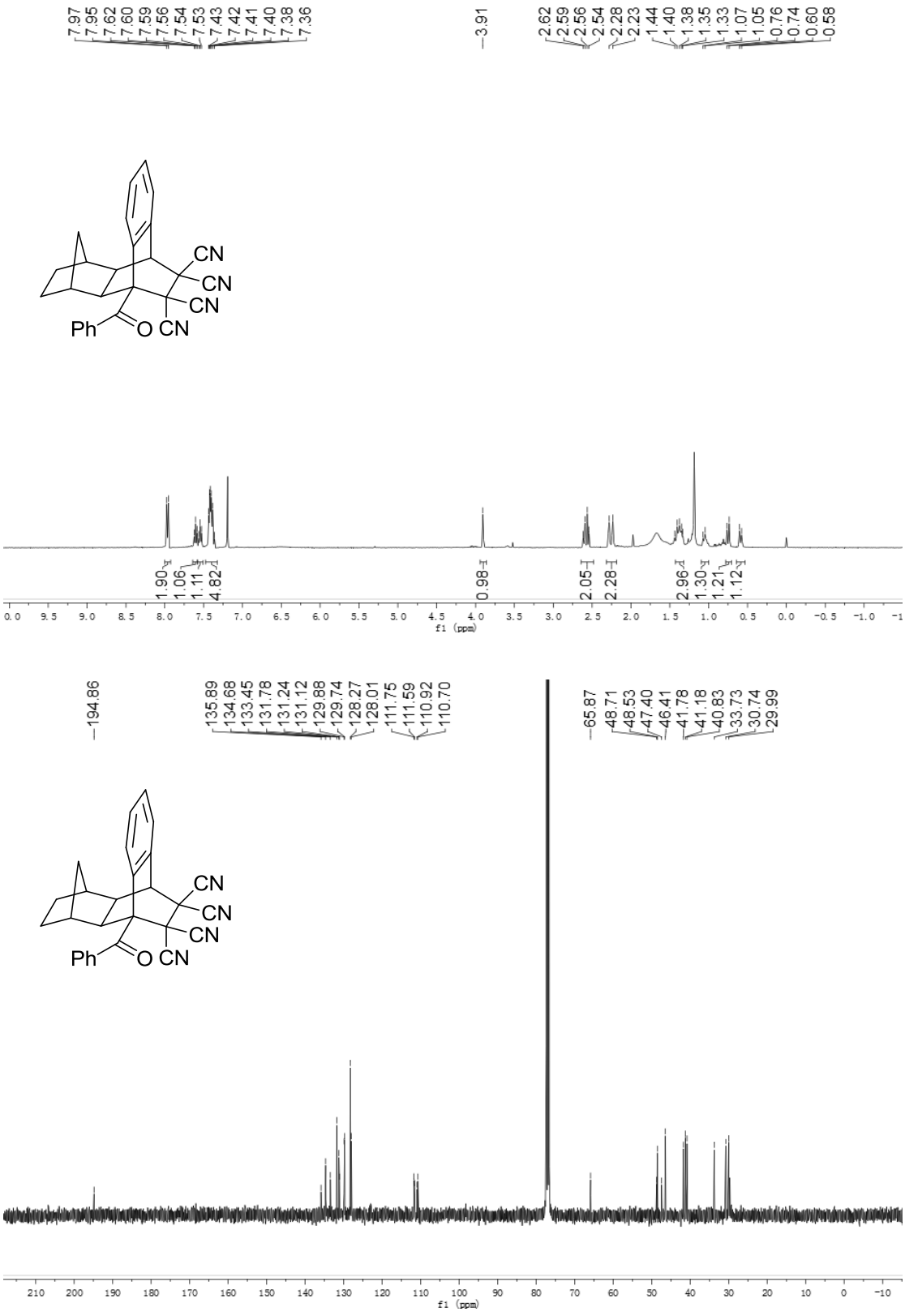


NOE spectrum of **5v**

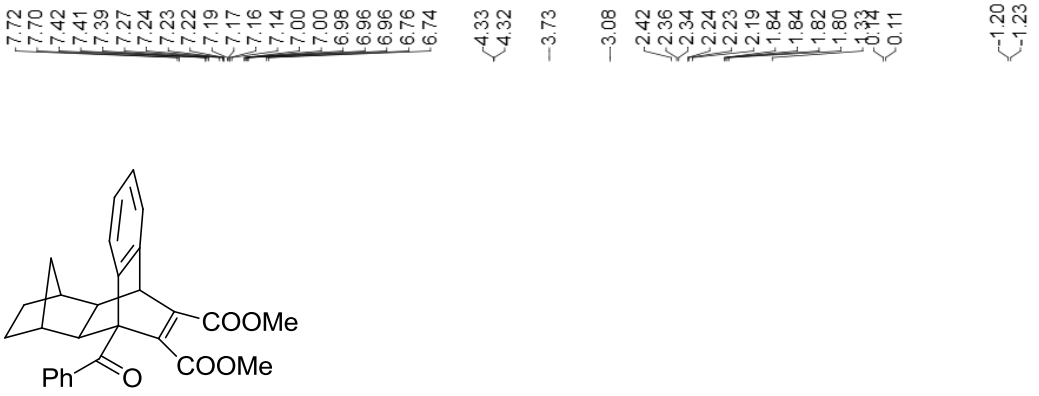


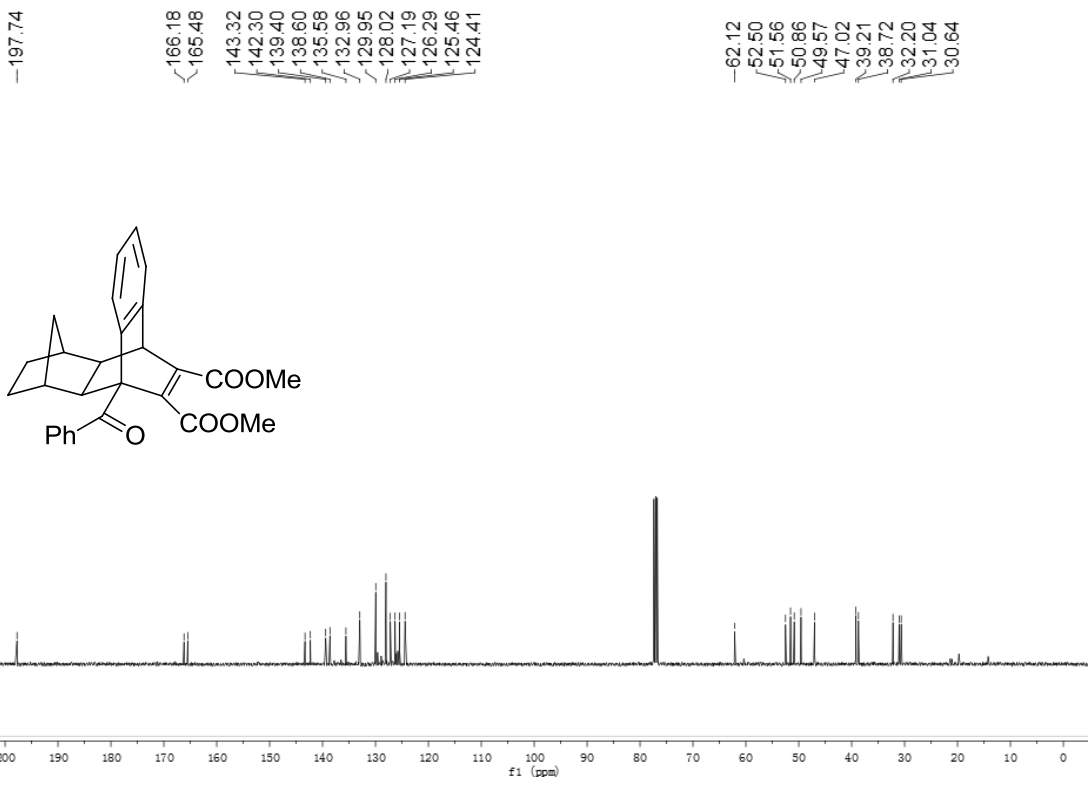


9-Benzoyl-octahydro-9,10-ethano-1,4-methanoanthracene-11,11,12,12-tetracarbonitrile (5w)

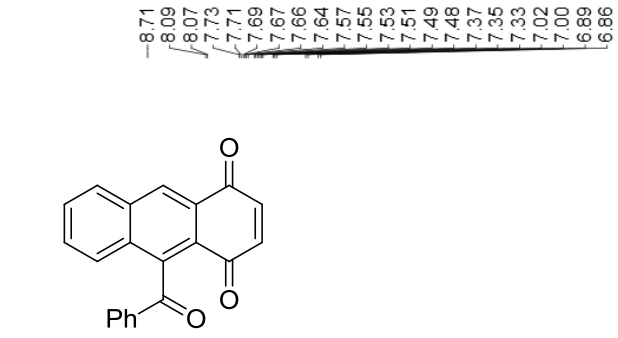


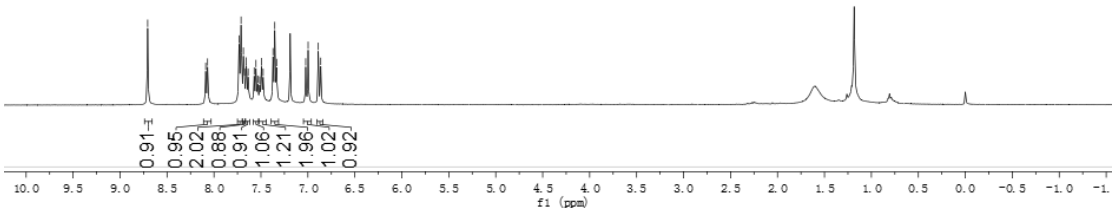
Dimethyl-9-benzoyl-octahydro-9,10-etheno-1,4-methanoanthracene-11,12-dicarboxylate (5x)

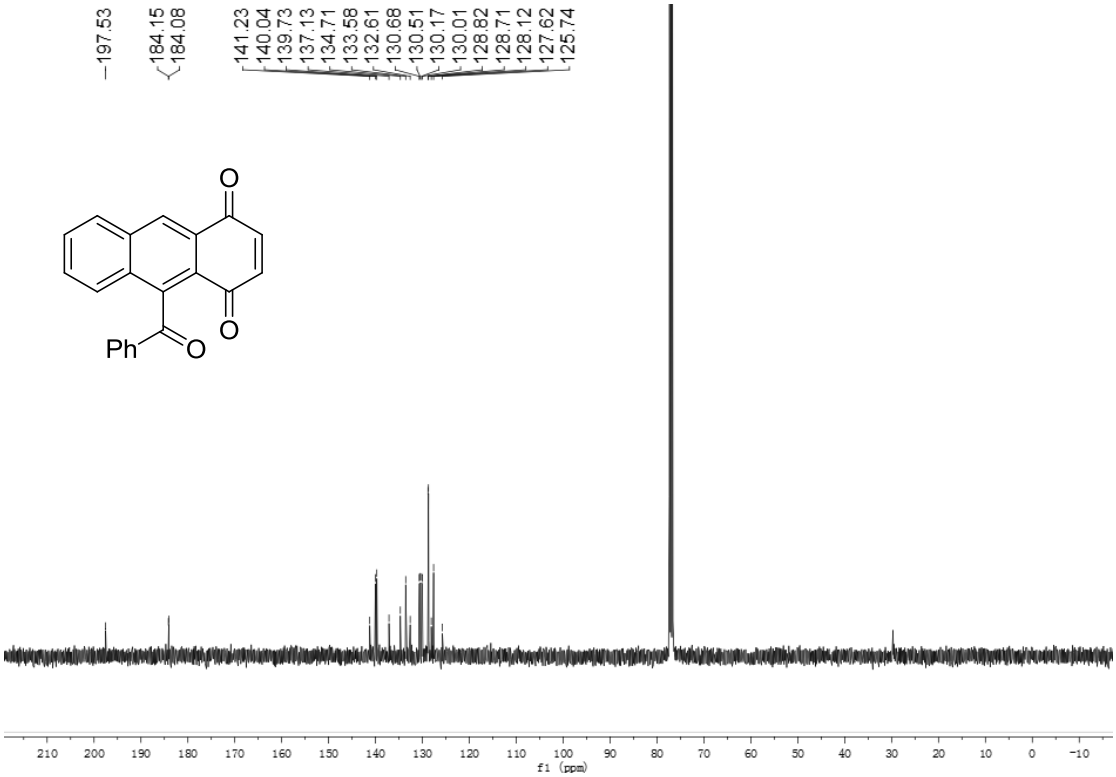




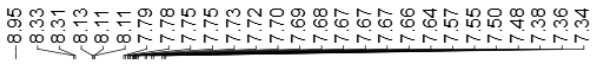
9-Benzoylanthracene-1,4-dione (6a)

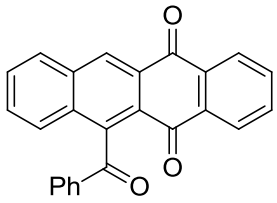


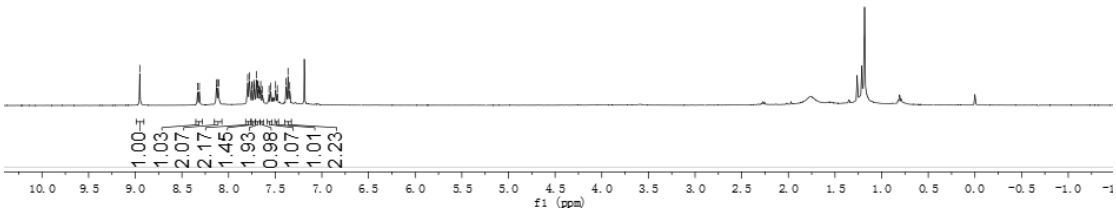


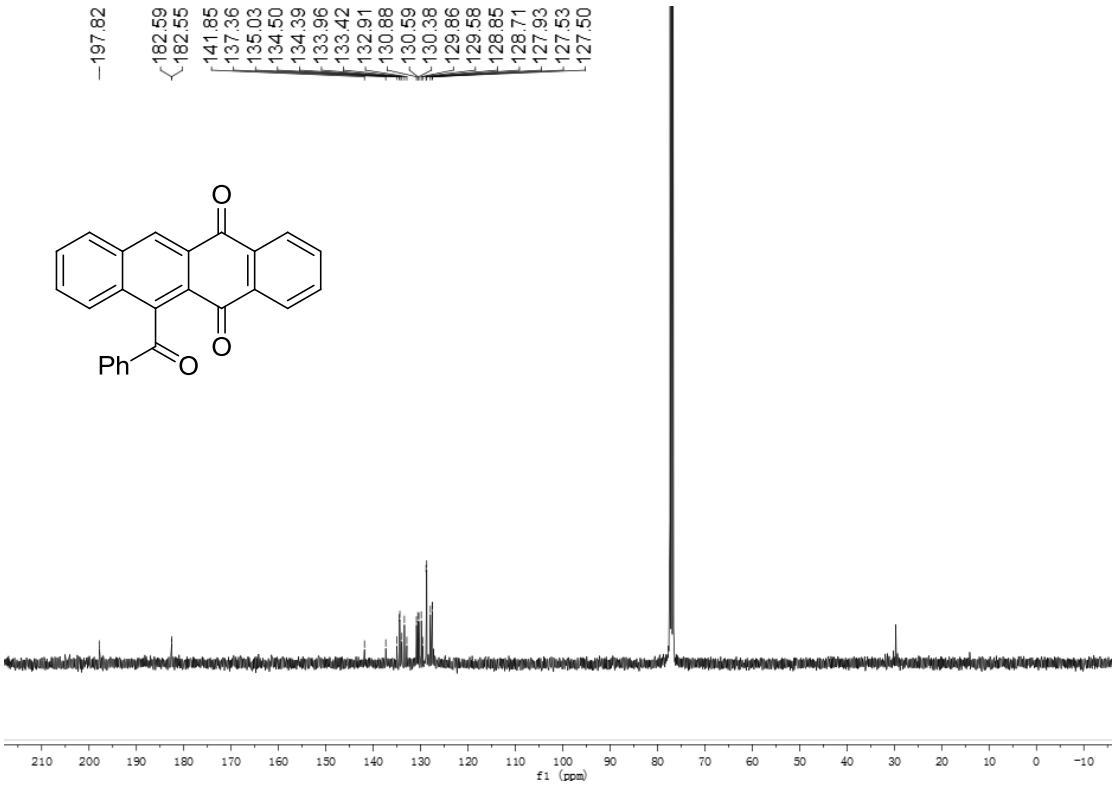


6-Benzoyltetracene-5,12-dione (6b)

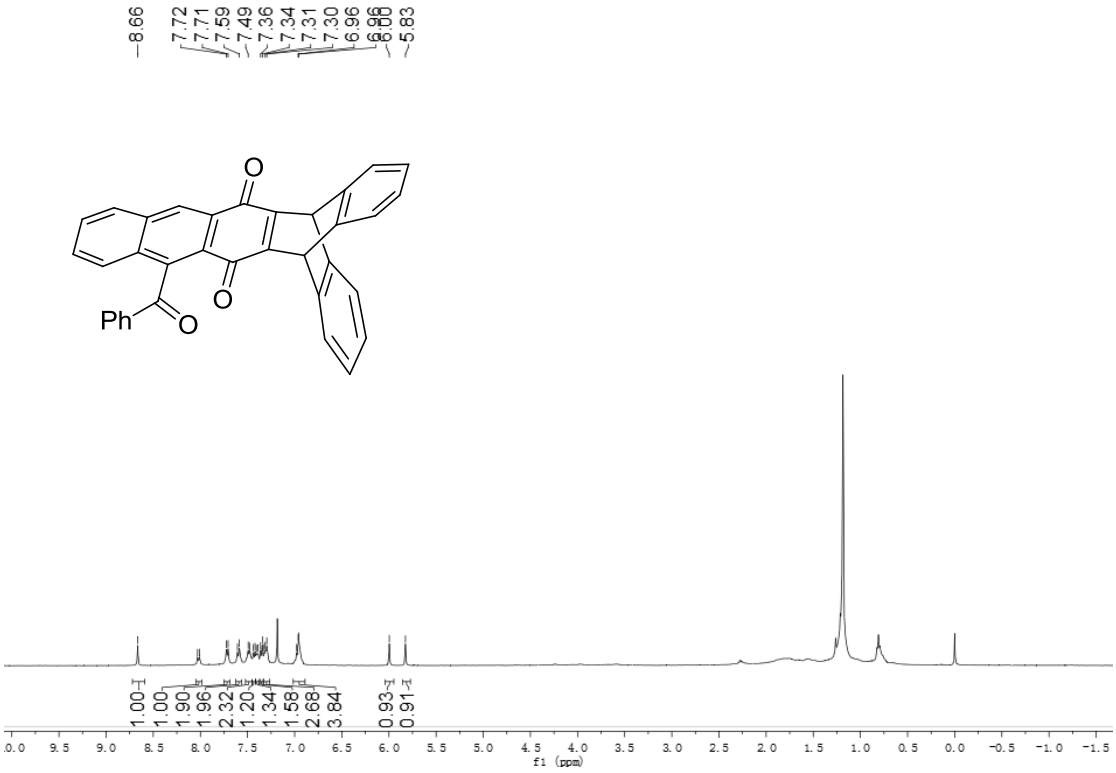


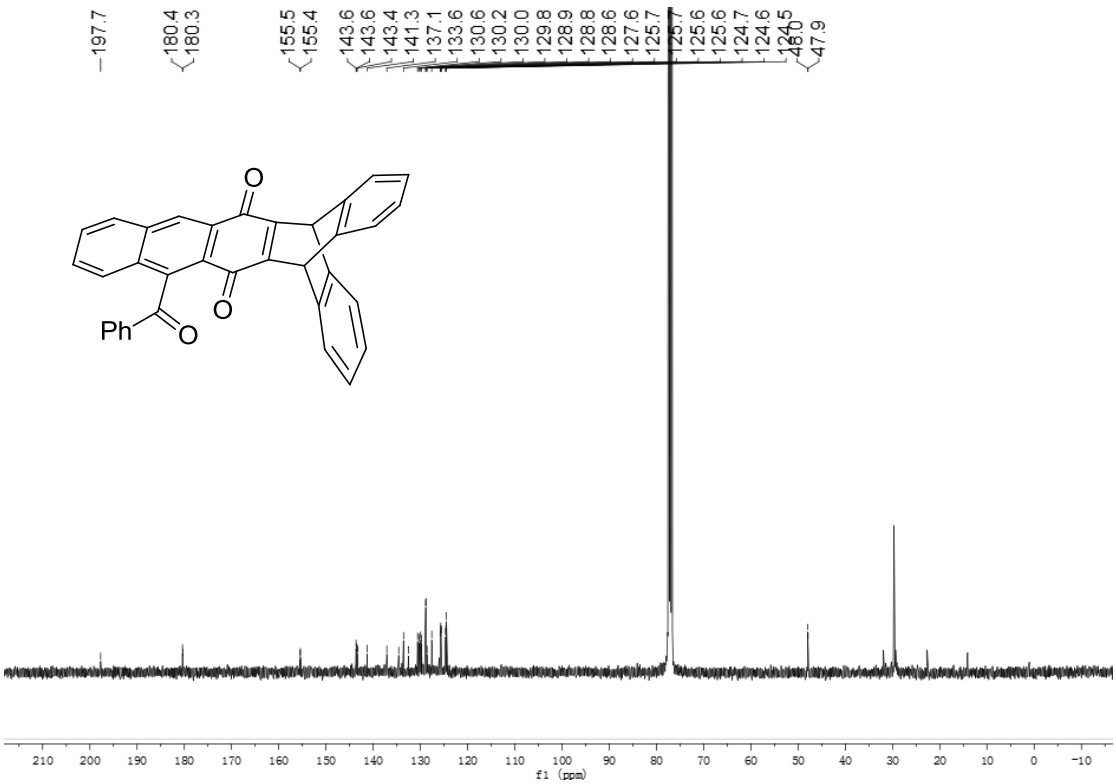




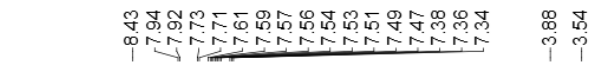


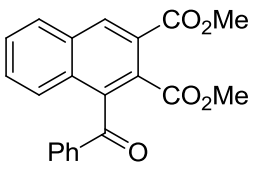
7-Benzoyl-5,14-[1,2]benzenopentacene-6,13-dione (6c)

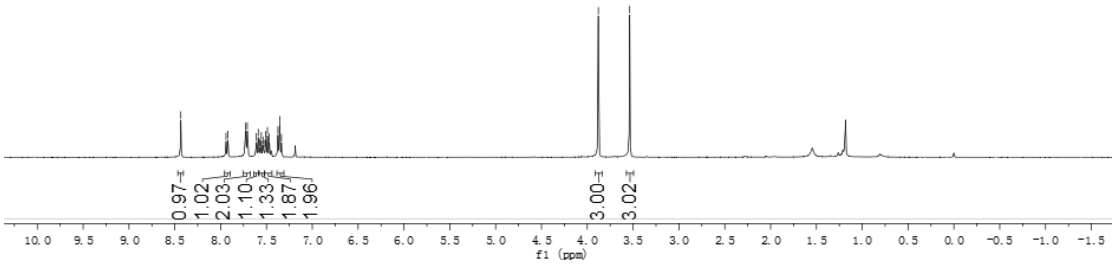


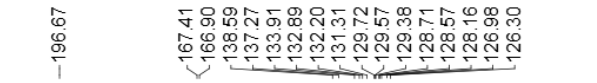


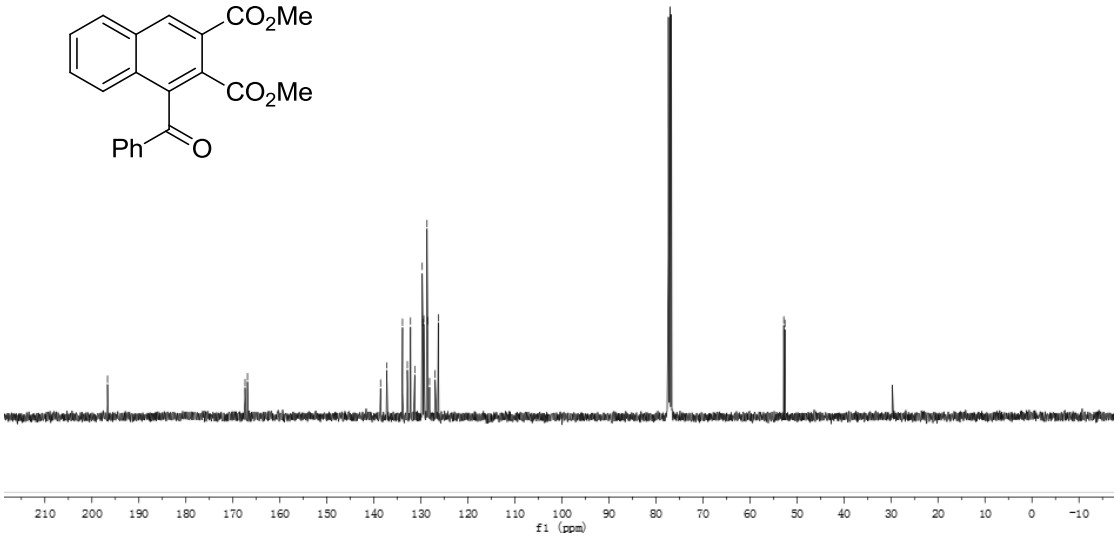
Dimethyl-1-benzoylnaphthalene-2,3-dicarboxylate (6d)











4. X-Ray Crystallography Data for Compound 4a and 5a

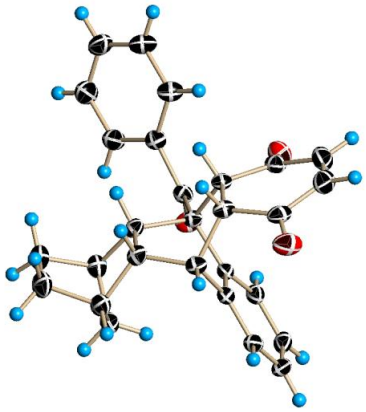


Table S1. Crystal data and structure refinement for **4a**.

ccdc number	983251
Identification code	shelxl
Empirical formula	$C_{28}\ H_{24}\ O_3$
Formula weight	408.47
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system, space group	?, P 21/c
Unit cell dimensions	a = 10.1157(3) A alpha = 90 deg. b = 21.1608(4) A beta = 116.050(3) deg. c = 10.7272(3) A gamma = 90 deg.
Volume	2062.95(9) A^3
Z, Calculated density	4, 1.315 Mg/m^3
Absorption coefficient	0.668 mm^{-1}
F(000)	864
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	4.18 to 66.85 deg.
Limiting indices	-11<=h<=12, -23<=k<=25, -12<=l<=12
Reflections collected / unique	12180 / 3647 [R(int) = 0.0281]
Completeness to theta = 66.85	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3647 / 0 / 280
Goodness-of-fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0374, wR2 = 0.1216
R indices (all data)	R1 = 0.0440, wR2 = 0.1317
Largest diff. peak and hole	0.245 and -0.195 $e.A^{-3}$

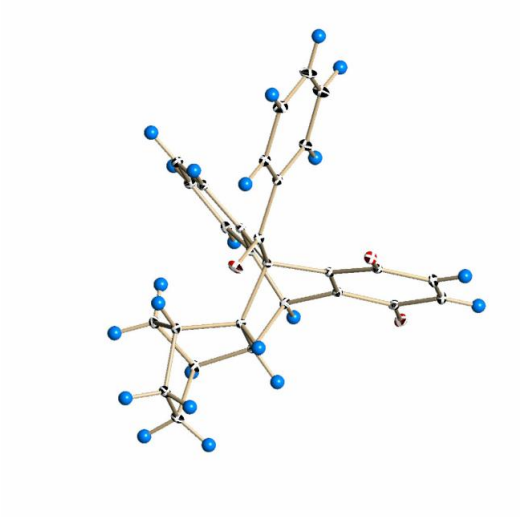


Table S2. Crystal data and structure refinement for **5a**.

ccdc number	983252
Identification code	shelxl
Empirical formula	$C_{28}H_{22}O_3$
Formula weight	406.46
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 12.1109(16) A alpha = 90 deg.
	b = 12.2037(16) A beta = 91.302(2) deg.
	c = 13.4259(18) A gamma = 90 deg.
Volume	1983.8(5) A^3
Z, Calculated density	4, 1.361 Mg/m^3
Absorption coefficient	0.087 mm^-
F(000)	856
Crystal size	0.20 x 0.10 x 0.10 mm
Theta range for data collection	2.24 to 27.06 deg.
Limiting indices	-15<=h<=11, -15<=k<=15, -17<=l<=15
Reflections collected / unique	9891 / 4294 [R(int) = 0.0206]
Absorption correction	Semi-empirical from equivalents
Completeness to theta = 27.06	98.8 %
Max. and min. transmission	0.9913 and 0.9827
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4294 / 0 / 280
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1055
R indices (all data)	R1 = 0.0589, wR2 = 0.1173
Largest diff. peak and hole	0.315 and -0.206 $e.A^{-3}$

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