Supporting Information

Phosphine-Catalyzed Cascade Michael Addition/[4+2] Cycloaddition Reaction of Allenoates and 2-Arylidene-1,3-Indanediones

Wangyu Shi,[†] Biming Mao,[†] Jiaqing Xu,[†] Qijun Wang,[†] Wei Wang,[‡] Yongjun Wu,[‡] Xuefeng Li,[†] and Hongchao Guo*,[†]

[†]Department of Chemistry, China Agricultural University, Beijing 100193, P. R. China.

[‡]College of Public Health, Zhengzhou University, Zhengzhou 450001, P. R. China

Email: hchguo@cau.edu.cn

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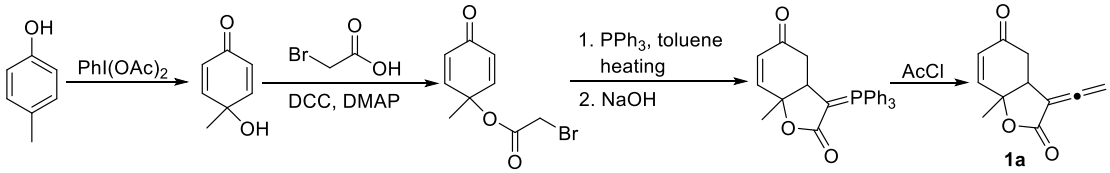
General Information

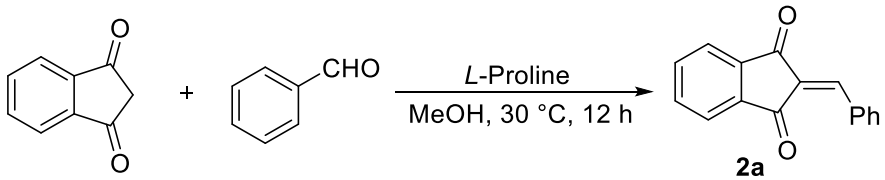
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. All heating options were performed in oil bath. Reactions were monitored through thin layer chromatography (TLC) on silica gel–precoated glass plates. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm. Flash column chromatography was performed using Qingdao Haiyang flash silica gel (200–300 mesh). Infrared spectra were recorded using a Bruker Optics TENSOR 27 instrument. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using 300 MHz NMR or 500 MHz instrument (referenced internally to Me_4Si). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet; d = doublet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), and integral. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Optical rotation was obtained on an Autopol VI automatic polarimeter. Accurate mass measurements were performed on an electrospray ionization (ESI): apparatus using time-of-flight (TOF) mass spectrometry. Melting points were determined on a Stuard SMP3 melting point apparatus. X-ray crystallographic data were collected using a MM007HF Saturn724^{+}. HPLC analysis was performed on Agilent 1100 series, UV detection monitored at 254 nm, using Chiralpak OD-H column with hexane and *i*-PrOH as the eluent.

General Procedure for Preparation of Tetrahydrobenzofuranone-Derived Allenoates[1]



The tetrahydrobenzofuranone-derived allenoates were prepared by the reported procedure.[1]

General Procedure for Preparation of 2-Arylidene-1,3-Indanedione[2]

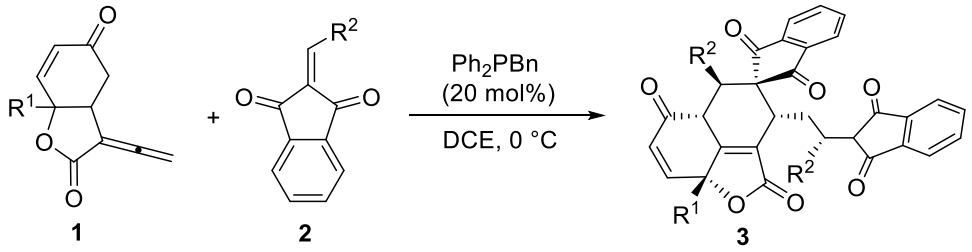


The 2-arylidene-1,3-indanediones were prepared according to the reported procedure.[2]

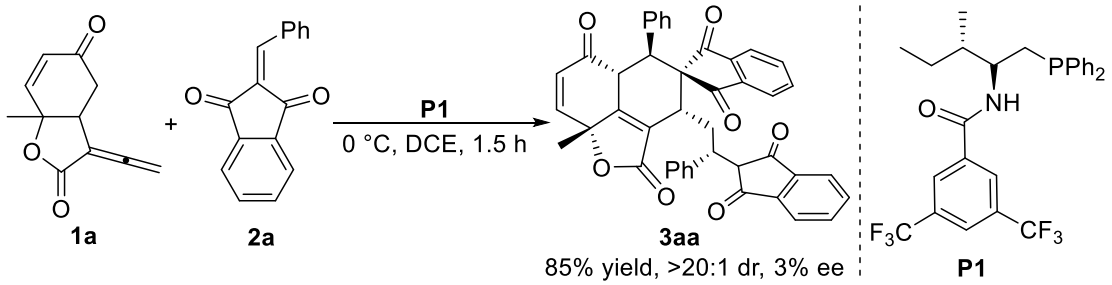
[1] Mao, B.; Shi, W.; Liao, J.; Liu, H.; Zhang, C.; Guo, H. *Org. Lett.* **2017**, *19*, 6340.
[2] Yang, S.-M.; Reddy, G. M.; Wang, T.-P.; Yeh Y.-S.; Wang, M.; Lin, W. *Chem. Commun.* **2017**, *53*, 7649.

General Procedure for Achiral Phosphine-Catalyzed Cascade Michael Addition/[4+2] Cycloaddition Reaction

Under an Ar atmosphere, tetrahydrobenzofuranone-derived allenoates **1** (0.1 mmol, 1.0 equiv), 2-arylidene-1,3-indanedione **2** (0.2 mmol, 2.0 equiv), Ph_2PBn (5.5 mg, 0.02 mmol, 20 mol %) and 1 mL of 1,2-dichloroethane were added in the flask. The reaction mixture was stirred at 0 ℃ until the reactant was completely consumed (determined by TLC). The mixture was directly purified by column chromatography on a silica gel (petroleum ether/EtOAc = 2:1 as the eluent) to furnish the corresponding product **3**.



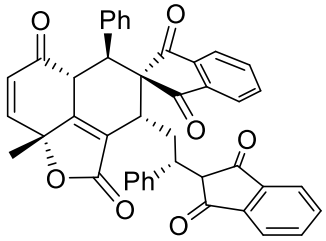
General Procedure for Chiral Phosphine-Catalyzed Cascade Michael Addition/[4+2] Cycloaddition Reaction



Under an Ar atmosphere, tetrahydrobenzofuranone-derived allenoates **1a** (9.5 mg, 0.05 mmol, 1.0 equiv), 2-arylidene-1,3-indanedione **2a** (23.4 mg, 0.1 mmol, 2.0 equiv), **P1** (5.3 mg, 0.01 mmol, 20 mol%) and 0.5 mL of 1,2-dichloroethane were added in the flask. The reaction mixture was stirred at 0 ℃ until the reactant was completely consumed (determined by TLC). The mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1 as the eluent) to furnish the product **3aa**.

Characterization Data for Achiral Phosphine-Catalyzed Cascade Michael Addition/[4+2] Cycloaddition Reaction products 3

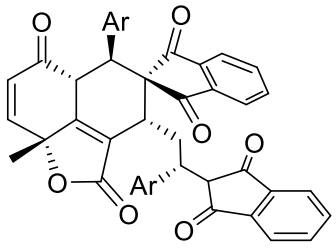
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-phenylethyl)-8a'-methyl-5'-phenyl-3',5',5a', 8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]1,2',3,6'-tetraone (3aa)



3aa

88% yield (58.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 189−192 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 1H), 7.88 (ddd, J = 13.3, 6.3, 2.6 Hz, 3H), 7.76 – 7.65 (m, 2H), 7.63 – 7.55 (m, 2H), 7.23 – 7.07 (m, 6H), 6.96 – 6.80 (m, 5H), 6.02 (d, *J* = 9.9 Hz, 1H), 4.02 (d, *J* = 5.8 Hz, 2H), 3.59 (s, 1H), 3.35 (d, *J* = 4.0 Hz, 1H), 2.87 (s, 1H), 2.67 – 2.55 (m, 1H), 2.53 – 2.38 (m, 1H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 199.5, 199.2, 193.5, 168.8, 163.5, 145.5, 142.5, 142.0, 141.2, 140.8, 138.5, 138.3, 135.83, 135.77, 134.81, 134.78, 128.9, 128.6, 128.2, 128.0, 127.6, 127.2, 126.6, 124.3, 123.5, 123.2, 122.4, 122.3, 80.7, 59.7, 56.1, 50.0, 43.9, 41.5, 34.3, 32.1, 24.3; IR (film) ν_{max} 3032, 1760, 1742, 1704, 1683, 1593, 1455, 1352, 1276, 1253, 1101, 1037, 764 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{30}O_7Na^+$ $[M+Na]^+$ 681.1884, found 681.1884.

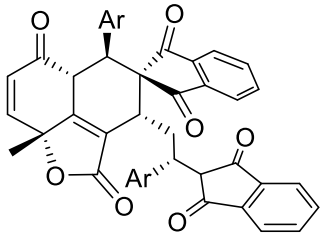
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(2-fluorophenyl)ethyl)-5'-(2-fluorophenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]1,2',3,6'-tetraone (3ab)



3ab (Ar = 2-FC_6H_4)

95% yield (66.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 166−169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.97 – 7.90 (m, 2H), 7.78 – 7.71 (m, 2H), 7.69 – 7.61 (m, 2H), 7.16 (d, *J* = 9.9 Hz, 1H), 7.12 – 6.86 (m, 6H), 6.81 – 6.63 (m, 2H), 6.10 (d, *J* = 9.9 Hz, 1H), 4.48 (d, *J* = 4.8 Hz, 1H), 3.99 (s, 1H), 3.89 (s, 1H), 3.31 (d, *J* = 3.6 Hz, 1H), 2.89 (s, 1H), 2.52 (s, 1H), 2.40 (s, 1H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 199.4, 198.5, 192.8, 168.4, 162.6, 161.6 (d, *J* = 39.4 Hz), 158.4 (d, *J* = 38.9 Hz), 145.4, 142.4, 141.9 141.2 140.9, 136. 135.9, 134.9 129.7 (d, *J* = 3.7 Hz), 129.1 (d, *J* = 8.7 Hz), 128.8, 28.1 (d, *J* = 8.4 Hz), 127.6 125.9 (d, *J* = 14.2 Hz), 124.6 124.2 (d, *J* = 2.9 Hz), 123.7, 123.4 (d, *J* = 3.5 Hz), 123.2, 122.5, 122.4 115.3 (d, *J* = 23.1 Hz), 114.8 (d, *J* = 23.3 Hz), 80.5, 58.7 54.9, 49.6, 36.3, 33.8, 30.5, 29.3, 24.3; IR (film) ν_{max} 3055, 1761, 1745, 1706, 1683, 1592, 1492, 1455, 1264, 1179, 1098, 1037, 733, 703, 407 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}F_2NO_7^+$ $[M+NH_4]^+$ 712.2141, found 712.2136.

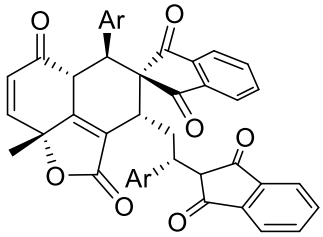
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(3-fluorophenyl)ethyl)-5'-(3-fluorophenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ac)



3ac (Ar = 3-FC_6H_4)

88% yield (61.1 mg), PE/EtOAc = 2:1, pale yellow solid, mp 194−196 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 4.7, 1.9 Hz, 1H), 7.95 – 7.83 (m, 3H), 7.78 – 7.60 (m, 4H), 7.16 (dd, *J* = 14.0, 8.8 Hz, 2H), 7.01 – 6.76 (m, 4H), 6.70 – 6.48 (m, 3H), 6.03 (d, *J* = 9.9 Hz, 1H), 3.99 (d, *J* = 6.2 Hz, 2H), 3.57 (s, 1H), 3.35 (d, *J* = 3.9 Hz, 1H), 2.82 (s, 1H), 2.47 (dd, *J* = 24.3, 17.2 Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.53, 199.38, 199.13, 198.69, 193.32, 168.70, 163.6 (d, *J* = 22.1 Hz), 160.4 (d, *J* = 21.6 Hz), 160.23, 145.67, 142.33, 141.91, 141.05, 140.97, 140.87, 140.62, 136.07, 136.02, 135.01, 129.7 (d, *J* = 8.3 Hz), 129.2 (d, *J* = 8.2 Hz), 128.84, 124.4 (d, *J* = 2.7 Hz), 124.06, 123.58, 123.39, 122.52, 122.48, 115.80, 115.51, 114.3 (d, *J* = 20.9 Hz), 113.7 (d, *J* = 20.9 Hz), 80.79, 59.51, 55.95, 49.83, 43.36, 41.13, 34.38, 32.06, 24.23; IR (film) ν_{max} 3064, 1760, 1742, 1702, 1682, 1614, 1589, 1488, 1450, 1257, 1102, 1041, 783, 765, 736, 692 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}F_2NO_7^+$ $[M+NH_4]^+$ 712.2141, found 712.2134.

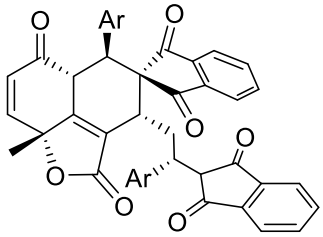
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-fluorophenyl)ethyl)-5'-(4-fluorophenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ad)



3ad (Ar = 4-FC_6H_4)

80% yield (55.6 mg), PE/EtOAc = 2:1, pale yellow solid, mp 187−190 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.97 (m, 1H), 7.94 – 7.84 (m, 3H), 7.79 – 7.60 (m, 4H), 7.19 – 7.08 (m, 3H), 6.94 – 6.77 (m, 4H), 6.59 (t, *J* = 8.7 Hz, 2H), 6.02 (d, *J* = 9.9 Hz, 1H), 4.00 (t, *J* = 6.0 Hz, 2H), 3.54 (s, 1H), 3.32 (d, *J* = 4.0 Hz, 1H), 2.77 (s, 1H), 2.53 (dt, *J* = 22.3, 11.7 Hz, 2H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 199.6, 199.4, 198.9, 193.5, 168.8, 163.5, 163.1 (d, *J* = 18.3 Hz), 159.8 (d, *J* = 17.0 Hz), 145.6, 142.2 (d, *J* = 31.4 Hz), 141.9 (d, *J* = 42.7 Hz), 136.0, 136.0, 135.0, 134.2 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 6.3 Hz), 130.3 (d, *J* = 8.0 Hz), 128.9, 124.1, 123.5, 123.3, 122.5, 122.4, 115.1 (d, *J* = 21.4 Hz), 114.5 (d, *J* = 21.1 Hz), 80.8, 59.7, 56.4, 49.9, 43.0, 40.7, 34.5, 32.3, 24.3; IR (film) ν_{max} 3065, 1760, 1742, 1703, 1683, 1603, 1509, 1253, 1226, 1163, 1041, 837, 765, 737 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}F_2NO_7^+$ $[M+NH_4]^+$ 712.2141, found 712.2133.

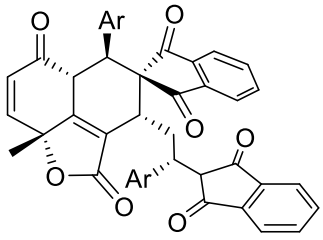
5'-(4-Chlorophenyl)-3'-(2-(4-chlorophenyl)-2-(1,3-dioxo-2,3-dihydro-1H-inden-2-yl)ethyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ae)



3ae (Ar = 4-ClC_6H_4)

84% yield (61.1 mg), PE/EtOAc = 2:1, pale yellow solid, mp 183−186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 1H), 7.89 (dd, *J* = 8.2, 5.8 Hz, 3H), 7.79 – 7.58 (m, 4H), 7.12 (q, *J* = 8.0 Hz, 5H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.01 (d, *J* = 9.9 Hz, 1H), 3.98 (t, *J* = 9.0 Hz, 2H), 3.54 (s, 1H), 3.33 (d, *J* = 3.9 Hz, 1H), 2.76 (s, 1H), 2.52 (d, *J* = 5.7 Hz, 2H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 199.5, 199.2, 198.7, 193.5, 168.8, 163.5, 145.6, 142.3, 141.9, 141.1, 140.5, 137.0, 136.7, 136.1, 136.0, 135.1, 133.1, 132.6, 130.3, 130.1, 128.9, 128.4, 128.0, 127.9, 124.0, 123.6, 123.4, 122.6, 122.5, 80.8, 59.6, 56.3, 49.8, 42.8, 40.8, 34.7, 32.2, 24.3; IR (film) ν_{max} 2929, 1760, 1742, 1703, 1684, 1593, 1493, 1274, 1250, 1095, 1040., 1015, 767 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}Cl_2NO_7^+$ $[M+NH_4]^+$ 744.1550, found 744.1547.

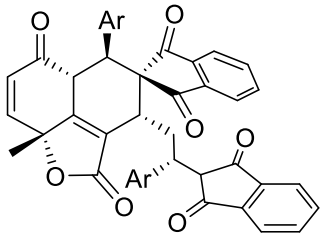
5'-(4-Bromophenyl)-3'-(2-(4-bromophenyl)-2-(1,3-dioxo-2,3-dihydro-1H-inden-2-yl)ethyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3af)



3af (Ar = 4-BrC_6H_4)

87% yield (71.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 183−185 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.87 (s, 3H), 7.79 – 7.61 (m, 5H), 7.29 (d, *J* = 8.2 Hz, 3H), 7.11 (d, *J* = 9.9 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 3H), 6.00 (d, *J* = 9.9 Hz, 1H), 3.97 (t, *J* = 11.2 Hz, 2H), 3.53 (s, 1H), 3.33 (d, *J* = 3.9 Hz, 1H), 2.76 (s, 1H), 2.52 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 199.4, 199.2, 198.6, 193.5, 168.8, 163.5, 145.6, 142.3, 141.9, 141.1, 140.5, 137.5, 137.2, 136.1, 136.0, 135.1, 131.4, 130.8, 130.7, 130.5, 128.9, 123.9, 123.6, 123.4, 122.6, 122.5, 121.4, 120.8, 80.8, 59.5, 56.3, 49.8, 42.8, 40.8, 34.7, 32.2, 24.3; IR (film) ν_{max} 2928, 1759, 1742, 1703, 1683, 1592, 1489, 1352, 1275, 1252, 1164, 1098, 1076, 1040, 1011, 766, 523 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{27}Br_2O_7^-$ $[M-H]^-$ 813.0129, found 813.0147.

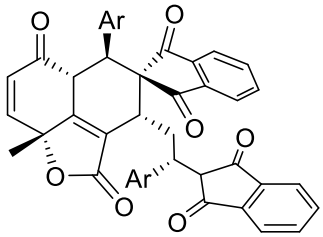
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-iodophenyl)ethyl)-5'-(4-iodophenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ag)



3ag (Ar = 4-IC_6H_4)

84% yield (76.5 mg), PE/EtOAc = 2:1, pale yellow solid, mp 196−199 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 1H), 7.92 – 7.83 (m, 3H), 7.79 – 7.63 (m, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.22 (s, 2H), 7.11 (d, *J* = 9.9 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.00 (d, *J* = 9.9 Hz, 1H), 3.95 (t, *J* = 13.6 Hz, 2H), 3.51 (s, 1H), 3.33 (d, *J* = 3.9 Hz, 1H), 2.75 (s, 1H), 2.51 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 199.4, 199.1, 198.6, 193.4, 168.8, 163.5, 145.6, 142.3, 141.9, 141.1, 140.5, 138.2, 137.9, 137.3, 136.8, 136.1, 136.0, 135.1, 130.9, 130.7, 128.9, 123.9, 123.6, 123.4, 122.6, 122.5, 93.1, 92.7, 80.8, 59.5, 56.3, 49.8, 42.9, 40.9, 34.8, 32.2, 24.3; IR (film) ν_{max} 2927, 1758, 1742, 1702, 1682, 1592, 1486, 1255, 1098, 1040, 1006, 778, 765, 734, 700, 427 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{32}I_2NO_7^+$ $[M+NH_4]^+$ 928.0263, found 928.0262.

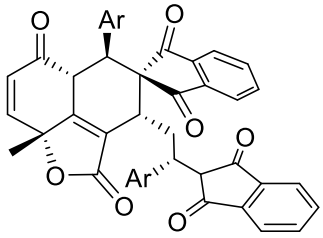
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-(trifluoromethyl)phenyl)ethyl)-8a'-methyl-5'-(4-(trifluoromethyl)phenyl)-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ah)



3ah (Ar = 4-$CF_3C_6H_4$)

83% yield (66.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 192−194 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 1H), 7.97 – 7.89 (m, 3H), 7.80 – 7.65 (m, 5H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 9.9 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.03 (d, *J* = 9.8 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.70 (s, 1H), 3.41 (d, *J* = 3.7 Hz, 1H), 2.84 (s, 1H), 2.61 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 199.2, 198.9, 198.4, 193.24, 168.7, 163.4, 145.7, 142.5, 142.2, 141.8, 141.0, 140.5, 136.2, 136.1, 135.2, 129.7, 129.4, 129.2, 129.1, 128.8, 128.7 125.2(q, *J* = 3.8Hz), 124.7(q, *J* = 3.8Hz), 123.9, 123.7, 123.4, 122.6, 122.5, 80.9, 59.5, 56.1, 49.8, 43.0, 41.1, 34.6, 32.1, 30.5, 29.3, 24.2; IR (film) ν_{max} 2917, 1760, 1743, 1705, 1683, 1325, 1255, 1166, 1116, 1070, 1041, 1018, 765, 737, 610 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{32}F_6NO_7^+$ $[M+NH_4]^+$ 812.2077, found 812.2065.

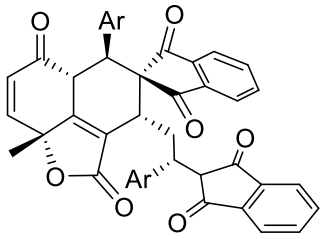
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-nitrophenyl)ethyl)-8a'-methyl-5'-(4-nitrophenyl)-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ai)



3ai (Ar = 4-$NO_2C_6H_4$)

72% yield (53.9 mg), PE/EtOAc = 2:1, pale yellow solid, mp 217−220 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 3H), 7.98 – 7.91 (m, 3H), 7.85 – 7.65 (m, 7H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 9.9 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.07 (d, *J* = 9.9 Hz, 1H), 4.21 – 4.03 (m, 2H), 3.71 (s, 1H), 3.42 (d, *J* = 3.8 Hz, 1H), 2.78 (s, 1H), 2.59 (d, *J* = 20.8 Hz, 2H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 198.9, 198.8, 198.1, 193.0, 168.6, 163.3, 146.9, 146.6, 145.8, 142.0, 141.7, 140.9, 140.4, 136.5, 135.5, 130.0, 129.7, 128.7, 123.8, 123.7, 123.6, 123.4, 122.9, 122.73, 122.65, 81.0, 59.3, 55.9, 49.5, 43.1, 41.2, 34.6, 31.8, 24.3; IR (film) ν_{max} 2930, 1758, 1742, 1702, 1683, 1596, 1519, 1345, 1319, 1252, 1109, 1040, 857, 779, 768, 756, 734, 696 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{29}N_2O_{11}^+$ $[M+H]^+$ 749.1766, found 749.1767.

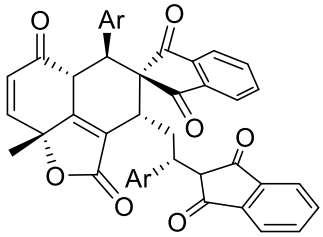
5'-(2,4-Dichlorophenyl)-3'-(2-(2,4-dichlorophenyl)-2-(1,3-dioxo-2,3-dihydro-1H-inden-2-yl) ethyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3aj)



3aj (Ar = 2,4-$Cl_2C_6H_3$)

59% yield (47.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 185−187 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 – 7.98 (m, 1H), 7.97 – 7.91 (m, 3H), 7.86 – 7.81 (m, 2H), 7.76 (dd, *J* = 5.6, 2.6 Hz, 2H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.05 – 6.97 (m, 3H), 6.08 (d, *J* = 9.9 Hz, 1H), 4.59 (d, *J* = 6.3 Hz, 1H), 3.91 (d, *J* = 27.4 Hz, 2H), 3.31 (d, *J* = 3.5 Hz, 1H), 2.73 (s, 1H), 2.47 (s, 2H), 1.82 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 199.1, 198.9, 197.8, 192.5, 168.3, 162.8, 145.5, 142.1, 142.0, 141.2, 136.13, 136.06, 135.3, 135.1, 134.3, 133.5, 132.9, 130.6, 129.6, 128.8, 127.8, 127.2, 126.9, 124.1, 123.9, 123.3, 122.8, 122.7, 80.5, 58.2, 55.8, 49.9, 38.4, 36.9, 33.8, 29.3, 24.5; IR (film) ν_{max} 2929, 1760, 1702, 1683, 1589, 1474, 1351, 1264, 1105, 1048, 947, 870, 824, 734, 702, 593 cm^{-1}; HRMS (ESI) calcd for $C_{43}H_{30}Cl_4NO_7^+$ $[M+NH_4]^+$ 812.0771, calcd for 812.0769.

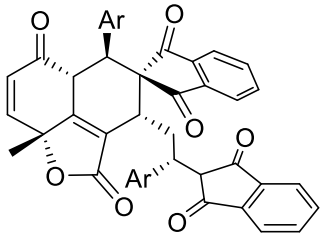
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(o-tolyl)ethyl)-8a'-methyl-5'-(o-tolyl)-3',5',5a', 8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ak)



3ak (Ar = 2-MeC_6H_4)

78% yield (53.6 mg), PE/EtOAc = 2:1, pale yellow solid, mp 183−186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 – 7.91 (m, 2H), 7.90 – 7.75 (m, 3H), 7.63 (dt, *J* = 6.7, 4.9 Hz, 3H), 7.15 (d, *J* = 9.9 Hz, 1H), 7.11 – 6.91 (m, 5H), 6.82 (dd, *J* = 11.3, 4.6 Hz, 3H), 6.03 (d, *J* = 9.9 Hz, 1H), 4.31 (d, *J* = 6.9 Hz, 1H), 4.03 (s, 1H), 3.82 (s, 1H), 3.44 (d, *J* = 3.9 Hz, 1H), 2.79 (d, *J* = 34.5 Hz, 2H), 2.41 (s, 3H), 2.33 – 2.24 (m, 1H), 1.91 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.4, 199.5, 199.0, 193.7, 168.9, 164.1, 145.6, 142.8, 142.1, 141.2, 141.1, 138.0, 137.7, 137.5, 135.8, 134.8, 130.6, 130.1, 129.0, 127.5, 126.9, 126.3, 125.9, 125.7, 125. 6, 124.2, 123.6, 123.1, 122.40, 122.36, 80.7, 59.3, 55.9, 51.1, 38.5, 36.3, 35.1, 33.3, 30.5, 24.4, 19.9, 18.9; IR (film) ν_{max} 3059, 1759, 1742, 1702, 1682, 1593, 1491, 1351, 1254, 1165, 1103, 1036, 948, 760, 731, 701 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{38}NO_7^+$ $[M+NH_4]^+$ 704.2643, found 704.2631.

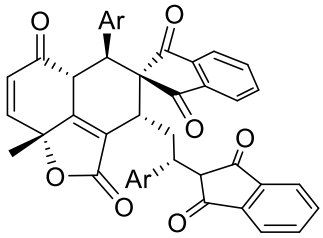
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(m-tolyl)ethyl)-8a'-methyl-5'-(m-tolyl)-3',5', 5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3al)



3al (Ar = 3-MeC_6H_4)

83% yield (57.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 184−186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.6, 1.9 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.76 – 7.56 (m, 5H), 7.11 (d, *J* = 9.9 Hz, 1H), 7.05 (d, *J* = 7.1 Hz, 1H), 6.99 – 6.89 (m, 3H), 6.77 (dd, *J* = 10.0, 5.6 Hz, 1H), 6.72 – 6.60 (m, 3H), 6.00 (d, *J* = 9.9 Hz, 1H), 4.06 (s, 1H), 3.97 (d, *J* = 6.7 Hz, 1H), 3.51 (s, 1H), 3.34 (d, *J* = 4.1 Hz, 1H), 2.80 (s, 1H), 2.67 – 2.38 (m, 2H), 2.22 (s, 3H), 2.01 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 199.8, 199.4, 199.1, 193.7, 168.8, 163.6, 145.6, 142.6, 142.1, 141.3, 140.8, 138.4, 138.0, 137.6, 137.1, 135.73, 135.65, 134.8, 130.0, 129.5, 129.0, 128.03, 127.96, 127.5, 127.4, 125.7, 124.2, 123.5, 123.1, 122.4, 122.3, 80.7, 59.8, 56.3, 49.9, 43.8, 41.4, 34.6, 32.3, 24.3, 21.1, 20.8; IR (film) ν_{max} 2923, 1760, 1742, 1702, 1682, 1592, 1351, 1276, 1254, 1165, 1102, 1040, 950, 782, 765 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{38}NO_7^+$ $[M+NH_4]^+$ 704.2643, found 704.2633.

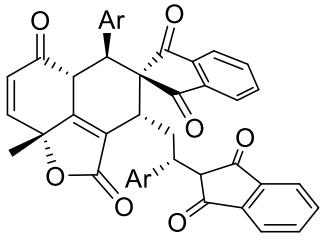
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(p-tolyl)ethyl)-8a'-methyl-5'-(p-tolyl)-3',5',5a', 8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3am)



3am (Ar = 4-MeC_6H_4)

78% yield (53.6 mg), PE/EtOAc = 2:1, pale yellow solid, mp 186−190 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 5.3, 2.4 Hz, 1H), 7.92 – 7.81 (m, 3H), 7.76 – 7.66 (m, 2H), 7.60 (dd, *J* = 6.2, 2.8 Hz, 2H), 7.11 (d, *J* = 9.9 Hz, 1H), 7.01 (dd, *J* = 16.6, 8.0 Hz, 4H), 6.76 – 6.66 (m, 4H), 6.00 (d, *J* = 9.9 Hz, 1H), 3.99 (t, *J* = 5.9 Hz, 2H), 3.54 (s, 1H), 3.34 (d, *J* = 4.0 Hz, 1H), 2.83 (s, 1H), 2.64 – 2.35 (m, 2H), 2.20 (s, 3H), 2.02 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 199.5, 199.2, 193.7, 168.8, 163.6, 145.5, 142.5, 142.1, 141.3, 140.8, 136. 8, 136.0, 135.74, 135.67, 135.5, 135.2, 134.8, 134.7, 128.9, 128.8, 128.5, 128.3, 124.2, 123.5, 123.2, 122.4, 122.3, 80.7, 59.8, 56.3, 50.1, 43.5, 41.1, 34.4, 32.4, 24.3, 20.6, 20.5; IR (film) ν_{max} 2923, 1759, 1742, 1702, 1683, 1593, 1515, 1350, 1254, 1099, 1040, 765, 736, 526 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{35}O_7^+$ $[M+H]^+$ 687.2377, found 687.2378.

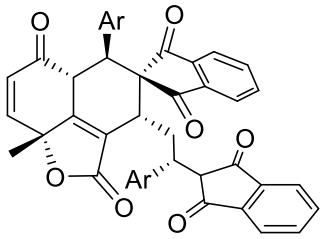
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-ethylphenyl)ethyl)-5'-(4-ethylphenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3an)



3an (Ar = 4-EtC_6H_4)

90% yield (64.3 mg), PE/EtOAc = 2:1, pale yellow solid, mp 178−181 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 1H), 7.87 (dd, *J* = 10.1, 6.2 Hz, 3H), 7.74 – 7.67 (m, 2H), 7.61 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.15 – 7.00 (m, 5H), 6.76 (q, *J* = 8.3 Hz, 4H), 6.02 (d, *J* = 9.9 Hz, 1H), 4.03 (s, 2H), 3.61 (s, 1H), 3.38 (d, *J* = 3.6 Hz, 1H), 2.91 (s, 1H), 2.67 – 2.24 (m, 7H), 1.86 (s, 3H), 1.14 (t, *J* = 7.6 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 199.5, 199.4, 193.6, 168.9, 163.6, 145.5, 143.0, 142.5, 142.3, 142.1, 141.2, 140.8, 135.7, 135.7, 134.70, 134.65, 128.9, 128.8, 128.5, 127.7, 127.1, 124.3, 123.5, 123.2, 122.4, 122.3, 80.7, 59.9, 56.2, 50.2, 43.5, 41.1, 34.4, 32.3, 29.3, 27.9, 27.8, 24.2, 14.72, 14.69; IR (film) ν_{max} 2930, 1759, 1742, 1702, 1682, 1593, 1350, 1264, 1164, 1099, 1039, 834, 764, 732, 703, 594, 530 cm^{-1}; HRMS (ESI) calcd for $C_{47}H_{39}O_7^+$ $[M+H]^+$ 715.2690, found 715.2693.

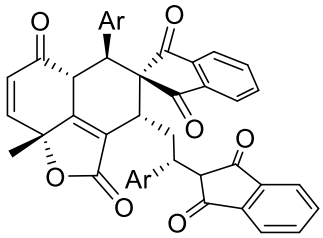
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(3-methoxyphenyl)ethyl)-5'-(3-methoxyphenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ao)



3ao (Ar = 3-OMeC$_6$H$_4$)

81% yield (58.2 mg), PE/EtOAc = 2:1, pale yellow solid, mp 160−162 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 5.6, 1.8 Hz, 1H), 7.85 (t, *J* = 5.7 Hz, 3H), 7.75 – 7.66 (m, 2H), 7.63 – 7.57 (m, 2H), 7.09 (dd, *J* = 13.7, 8.9 Hz, 2H), 6.71 (dt, *J* = 26.3, 8.1 Hz, 4H), 6.49 (s, 1H), 6.41 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.31 (d, *J* = 7.6 Hz, 1H), 6.00 (d, *J* = 9.9 Hz, 1H), 4.13 – 4.04 (m, 1H), 3.96 (d, *J* = 6.7 Hz, 1H), 3.69 (s, 3H), 3.57 (s, 3H), 3.33 (d, *J* = 4.0 Hz, 1H), 2.82 (s, 1H), 2.56 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.8, 199.3, 199.0, 193.6, 168.8, 163.6, 159.0, 158.7, 145.5, 142.6, 142.0, 141.2, 140.7, 140.0, 139.5, 135.8, 135.7, 135.4, 134.8, 134.8, 129.1, 129.0, 128.5, 124.1, 123.5, 123.2, 122.4, 122.3, 121.2, 115.0, 113.5, 113.2, 112.7, 80.7, 59.6, 56.4, 54.8, 54.6, 49.8, 44.0, 41.6, 34.6, 32.2, 24.3; IR (film) ν_{max} 2934, 1759, 1742, 1702, 1682, 1594, 1489, 1455, 1326, 1264, 1163, 1102, 1040, 733, 701 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{38}NO_9^+$ $[M+NH_4]^+$ 736.2541, found 736.2538.

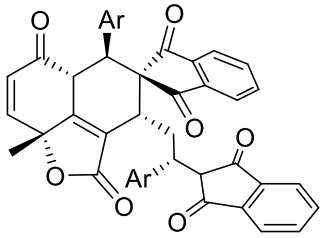
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(4-methoxyphenyl)ethyl)-5'-(4-methoxyphenyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ap)



3ap (Ar = 4-OMeC$_6$H$_4$)

48% yield (34.5 mg), PE/EtOAc = 2:1, pale yellow solid, mp 163−166 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.5 Hz, 1H), 7.86 (d, *J* = 5.5 Hz, 3H), 7.77 – 7.58 (m, 4H), 7.09 (dd, *J* = 14.1, 9.1 Hz, 3H), 6.73 (dd, *J* = 15.9, 8.5 Hz, 4H), 6.43 (d, *J* = 8.5 Hz, 2H), 6.01 (d, *J* = 9.9 Hz, 1H), 3.99 (t, *J* = 10.0 Hz, 2H), 3.69 (s, 3H), 3.54 (s, 4H), 3.32 (d, *J* = 3.4 Hz, 1H), 2.80 (s, 1H), 2.55 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 200.0, 199.7, 194.2, 169.3, 158.7, 158.3, 145.9, 142.9, 142.4, 141.6, 141.1, 136.2, 136.1, 135.2, 131.2, 130.8, 130.1, 129.4, 128.6, 128.5, 123.8, 123.6, 122.8, 122.7, 113.9, 113.3, 81.1, 60.2, 56.9, 55.1, 54.9, 50.4, 43.4, 41.0, 29.7, 24.7, 14.2; IR (film) ν_{max} 2986, 1760, 1705, 1683, 1593, 1475, 1438, 1351, 1264, 1177, 1098, 1037, 896, 733, 703, 596 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{38}NO_9^+$ $[M+NH_4]^+$ 736.2541, found 736.2524.

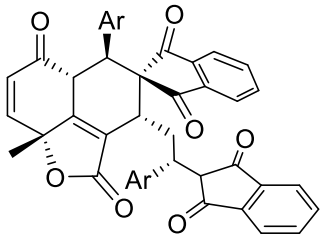
5'-(2,5-Dimethylphenyl)-3'-(2-(2,5-dimethylphenyl)-2-(1,3-dioxo-2,3-dihydro-1H-inden-2-yl) ethyl)-8a'-methyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3aq)



3aq (Ar = 2,5-$Me_2C_6H_3$)

56% yield (40.0 mg), PE/EtOAc = 2:1, pale yellow solid, mp 175−177 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.89 – 7.81 (m, 3H), 7.74 – 7.62 (m, 3H), 7.17 (d, *J* = 9.9 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.81 (t, *J* = 9.6 Hz, 3H), 6.68 (q, *J* = 7.4 Hz, 2H), 6.03 (d, *J* = 9.9 Hz, 1H), 4.26 (d, *J* = 8.0 Hz, 1H), 4.12 (s, 1H), 3.71 (s, 1H), 3.44 (d, *J* = 4.9 Hz, 1H), 2.73 (s, 2H), 2.51 – 2.34 (m, 4H), 2.03 (s, 6H), 1.88 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 200.5, 199.4, 198.9, 193.9, 168.9, 164.2, 145.7, 142.9, 142.2, 141.4, 141.1, 136.9, 136.7, 135.7, 135.0, 134.8, 132. 6, 130.5, 129.8, 129.1, 128.6, 127.6, 127.1, 126.4, 124.2, 123.5, 122.8, 122.4, 122.2, 80.5, 59.1, 56.5, 50.6, 38.6, 36.6, 35.3, 33.4, 29.4, 24.6, 20.6, 20.5, 19.4, 18.4; IR (film) ν_{max} 2918, 1760, 1742, 1704, 1682, 1593, 1504, 1352, 1265, 1222, 1106, 1037, 814, 735, 703 cm^{-1}; HRMS (ESI) calcd for $C_{47}H_{39}O_7$ $[M+H]^+$ 715.2690, found 715.2688.

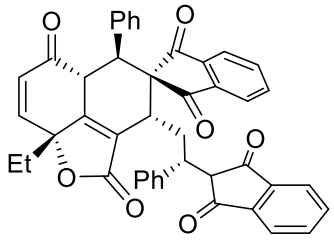
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-(naphthalen-1-yl)ethyl)-8a'-methyl-5'-(naphthaalen-1-yl)-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ar)



3ar (Ar = 1-naphthyl)

69% yield (52.4 mg), PE/EtOAc = 2:1, pale yellow solid, mp 202−205 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, *J* = 5.3 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.84 – 7.75 (m, 3H), 7.71 – 7.65 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.52 – 7.42 (m, 6H), 7.37 – 7.27 (m, 3H), 7.26 – 7.07 (m, 5H), 6.02 (d, *J* = 10.0 Hz, 1H), 5.05 (d, *J* = 5.3 Hz, 1H), 4.59 (s, 1H), 4.06 (s, 1H), 3.45 (s, 1H), 2.97 (s, 1H), 2.69 (d, *J* = 30.6 Hz, 2H), 1.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.5, 199. 9, 199.4, 193.6, 169.0, 145.9, 142.9, 142.2, 141.8, 141.3, 136.3, 136.18, 136.15, 135.1, 133.7, 133.6, 132.6, 131.6, 129.1, 128.9, 128.5, 128.3, 127.5, 126.3, 125.9, 125.6, 125.1, 125.0, 124.2, 124.1, 123.7, 122.8, 122.6, 81.0, 59.6, 56.3, 52.0, 37.5, 35.3, 31.0, 29.7, 24.7; IR (film) ν_{max} 3053, 1759, 1742, 1702, 1682, 1593, 1350, 1320, 1264, 1164, 1098, 1037, 799, 780, 765, 733, 702 cm^{-1}; HRMS (ESI) calcd for $C_{51}H_{38}NO_7^+$ $[M+NH_4]^+$ 776.2643, found 776.2637.

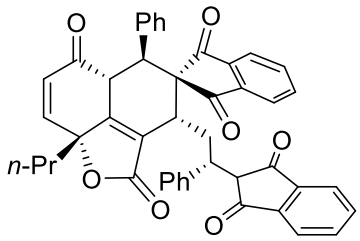
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-phenylethyl)-8a'-ethyl-5'-phenyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ba)



3ba

84% yield (56.5 mg), PE/EtOAc = 2:1, pale yellow solid, mp 190−193 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.5, 1.8 Hz, 1H), 7.87 (t, *J* = 5.6 Hz, 3H), 7.74 – 7.65 (m, 2H), 7.60 (dt, *J* = 5.4, 3.5 Hz, 2H), 7.21 – 7.09 (m, 6H), 6.85 (dt, *J* = 6.7, 4.4 Hz, 5H), 6.04 (d, *J* = 9.9 Hz, 1H), 3.98 (t, *J* = 6.9 Hz, 2H), 3.54 (s, 1H), 3.34 (d, *J* = 3.9 Hz, 1H), 2.84 (s, 1H), 2.66 – 2.44 (m, 2H), 2.26 (dq, *J* = 14.5, 7.2 Hz, 1H), 2.04 – 1.89 (m, 1H), 1.16 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 199.8, 199.6, 199.2, 193.9, 169.0, 161.8, 145.7, 142.5, 142.0, 141.2, 140.7, 138.5, 138.0, 135.9, 135.8, 134.9, 134.8, 129.1, 129.0, 128.8, 128.2, 128.0, 127.8, 127.6, 127.2, 126.7, 125.5, 123.5, 123.3, 122.4, 83.5, 59.7, 56.4, 49.7, 44.1, 41.8, 34.7, 32.3, 30.8, 7.3; IR (film) ν_{max} 3032, 1760, 1742, 1704, 1683, 1593, 1455, 1352, 1276, 1253, 1101, 1037, 764 cm^{-1}; HRMS (ESI) calcd for $C_{44}H_{33}O_7^+$ $[M+H]^+$ 673.2221, found 673.2221.

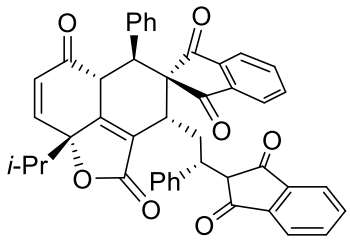
3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-phenylethyl)-5'-phenyl-8a'-propyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3ca)



3ca

59% yield (40.5 mg), PE/EtOAc = 2:1, pale yellow solid, mp 164−167 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 5.5, 1.9 Hz, 1H), 7.94 – 7.86 (m, 3H), 7.77 – 7.68 (m, 2H), 7.67 – 7.61 (m, 2H), 7.19 (dd, *J* = 11.0, 8.0 Hz, 6H), 6.91 (d, *J* = 5.1 Hz, 3H), 6.88 – 6.83 (m, 2H), 6.06 (d, *J* = 9.9 Hz, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 3.56 (s, 1H), 3.36 (d, *J* = 4.0 Hz, 1H), 2.86 (s, 1H), 2.70 – 2.47 (m, 2H), 2.27 – 2.13 (m, 1H), 1.98 – 1.84 (m, 1H), 1.72 (d, *J* = 12.2 Hz, 1H), 1.64 – 1.46 (m, 1H), 1.06 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 199.8, 199.6, 199.2, 193.9, 169.0, 162.1, 145.7, 142.5, 142.0, 141.2, 140.8, 138.5, 135.81, 135.75, 134.81, 134.77, 129.0, 128.7, 128.2, 127.8, 127.6, 127.2, 126.7, 125.2, 123.5, 123.3, 122.38, 122.35, 83.3, 59.7, 56.4, 49.7, 44.2, 41.9, 39.8, 34.6, 32.2, 16.4, 13.8; IR (film) ν_{max} 3032, 1760, 1742, 1704, 1683, 1593, 1455, 1352, 1276, 1253, 1101, 1037, 764 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{34}O_7Na^+$ $[M+Na]^+$ 709.2197, found 709.2197.

3'-(2-(1,3-Dioxo-2,3-dihydro-1H-inden-2-yl)-2-phenylethyl)-8a'-isopropyl-5'-phenyl-3',5',5a', 8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (3da)

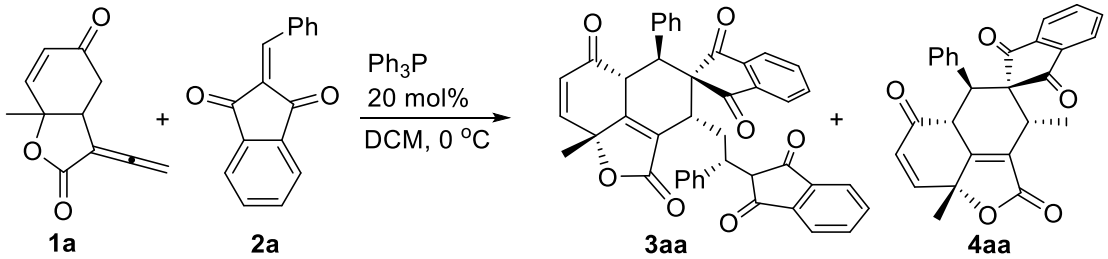


3da

89% yield (61.1 mg), PE/EtOAc = 2:1, pale yellow solid, mp 166−169 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.5 Hz, 1H), 7.90 – 7.82 (m, 3H), 7.76 – 7.55 (m, 5H), 7.23 (d, *J* = 10.0 Hz, 1H), 7.18 – 7.09 (m, 4H), 6.94 – 6.86 (m, 3H), 6.84 – 6.78 (m, 2H), 6.08 (d, *J* = 10.0 Hz, 1H), 4.06 (s, 1H), 3.90 (d, *J* = 7.0 Hz, 1H), 3.47 (s, 1H), 3.33 (d, *J* = 3.9 Hz, 1H), 2.79 (s, 1H), 2.59 (s, 2H), 2.27 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 199.81, 199.75, 199.1, 194.1, 169.2, 161.9, 146.2, 142.5, 142.0, 141.3, 140.7, 138.5, 137.7, 135.9, 135.8, 134.9, 134.8, 129.4, 129.0, 128.9, 128.6, 128.1, 128.0, 127.8, 127.6, 127.1, 126.7, 125.5, 123.4, 123.3, 122.4, 85.6, 59.6, 56.7, 49.5, 44.3, 42.2, 36.6, 35.1, 32.4, 16.63, 16.59; IR (film) ν_{max} 3032, 1760, 1742, 1704, 1683, 1593, 1455, 1352, 1276, 1253, 1101, 1037, 764 cm^{-1}; HRMS (ESI) calcd for $C_{45}H_{34}O_7Na^+$ $[M+Na]^+$ 709.2197, found 709.2197.

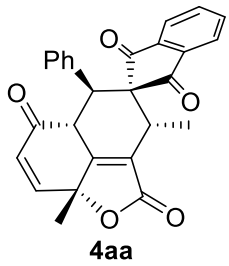
Preparation of [4 + 2] annulation product 4aa

Under an Ar atmosphere, tetrahydrobenzofuranone-derived allenoates **1a** (19 mg, 0.1 mmol, 1.0 equiv), 2-arylidene-1,3-indanedione **2a** (46.8 mg, 0.2 mmol, 2.0 equiv), Ph_3P (5.2 mg, 0.02 mmol, 20 mol %) and 1 mL of dichloromethane were added in the flask. The reaction mixture was stirred at 0 °C until the reactant was completely consumed (determined by TLC). The mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1-2:1 as the eluent) to furnish the corresponding product **4aa** (9.3 mg, 22% yield, >20:1 dr) and **3aa** (40.8 mg, 62% yield, 8:1 dr).



1a **2a** **3aa** **4aa**

3',8a'-Dimethyl-5'-phenyl-3',5',5a',8a'-tetrahydro-2'H,6'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-1,2',3,6'-tetraone (4aa)



4aa

22% yield (9.3 mg), PE/EtOAc = 4:1-2:1, White solid, mp 191−193 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.82 (dd, *J* = 9.5, 4.3 Hz, 3H), 7.22 – 7.10 (m, 6H), 6.07 (d, *J* = 9.9 Hz, 1H), 4.06 (s, 1H), 3.97 (d, *J* = 6.2 Hz, 1H), 2.97 (d, *J* = 6.4 Hz, 1H), 1.90 (s, 3H), 1.24 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 199.1, 193.6, 169.0, 162.8, 145.4, 141.0, 138.4, 135.6, 129.0, 128.7, 128.2, 127.2, 125.0, 123.2, 123.0, 80.8, 59.6, 49.9, 41.1, 30.6, 24.3, 13.8; IR (film) ν_{max} 3032, 1760, 1742, 1704, 1683, 1593, 1455, 1352, 1276, 1253, 1101, 1037, 764 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{21}O_5^+$ $[M+H]^+$ 425.1384, found 425.1374

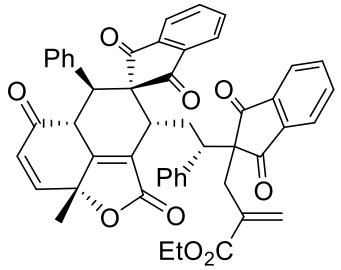
Preparation of the Product 3aa on Gram Scale.

Under an Ar atmosphere, tetrahydrobenzofuranone-derived allenoates **1a** (0.19 g, 1 mmol, 1.0 equiv), 2-arylidene-1,3-indanedione **2a** (0.47 g, 2 mmol, 2.0 equiv), Ph_2PBn (55.3 mg, 0.2 mmol, 20 mol %) and 10 mL of 1,2-dichloroethane were added in the flask. The reaction mixture was stirred at 0 ℃ until the reactant was completely consumed (determined by TLC). The solvent was distilled under reduced pressure and the residue was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1 as the eluent) to obtain the desired product **3aa** (0.55 g, 83% yield, 15:1 dr).

Transformation of the Product 3aa

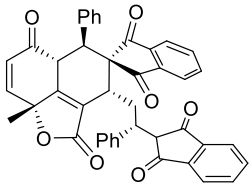
Under an Ar atmosphere, the cascade reaction product **3aa** (65.9 mg, 0.1 mmol), ethyl 2-(acetoxymethyl)acrylate (34.4 mg, 0.2 mmol, 2.0 equiv), Ph_2PBn (5.5 mg, 0.02 mmol, 20 mol %) and 1.0 mL of 1,2-dichloroethane were added in the flask. The reaction mixture was stirred at room temperature until the reactant was completely consumed (determined by TLC). The mixture was directly purified by column chromatography on silica gel (petroleum ether/EtOAc = 2:1 as the eluent) to afford the product **5** (50.9 mg, 66% yield, 15:1 dr).

Ethyl 2-((2-((S)-2-((3'S,5'S,5a'R,8a'R)-8a'-methyl-1,2',3,6'-tetraoxo-5'-phenyl-1,3,5',5a',6',8a'-hexahydro-2'H,3'H-spiro[indene-2,4'-naphtho[1,8-bc]furan]-3'-yl)-1-phenylethyl)-1,3-dioxo-2,3-dihydro-1H-inden-2-yl)methyl)acrylate (5)



5

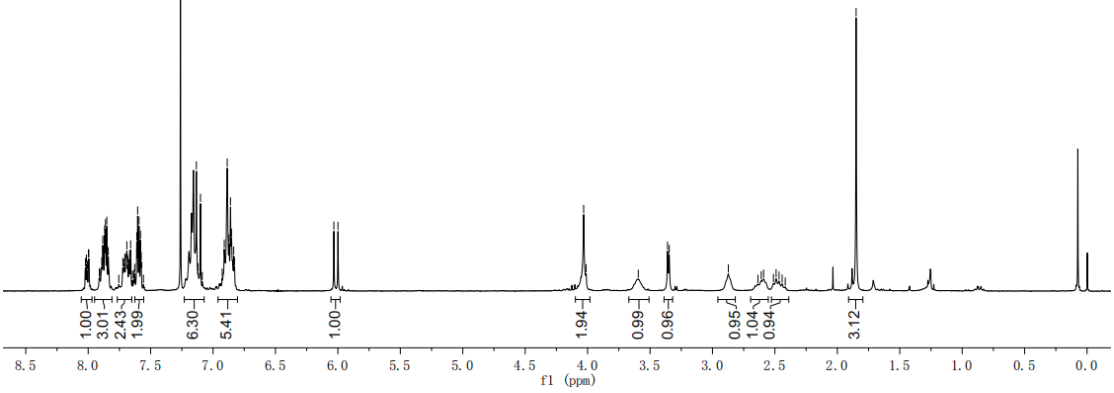
66% yield (50.9 mg), PE/EtOAc = 2:1, pale yellow solid, mp 151−154 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.4 Hz, 1H), 7.91 – 7.71 (m, 5H), 7.65 – 7.57 (m, 1H), 7.53 – 7.41 (m, 2H), 7.25 – 7.08 (m, 7H), 6.89 (dt, *J* = 7.7, 6.2 Hz, 1H), 6.74 (s, 3H), 5.98 (dd, *J* = 5.5, 4.2 Hz, 2H), 5.53 (s, 1H), 4.22 (dd, *J* = 8.8, 1.9 Hz, 1H), 4.00 – 3.93 (m, 3H), 3.33 (d, *J* = 13.6 Hz, 1H), 3.19 – 3.01 (m, 2H), 2.79 (t, *J* = 13.1 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.40 (d, *J* = 8.8 Hz, 1H), 1.81 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 201.6, 200.1, 199.4, 194.1, 168.6, 166.1, 163.7, 145.7, 142.6, 141.9, 141.3, 140.5, 138.2, 135.8, 135.7, 134.8, 134.7, 129.4, 129.2, 129.0, 128.0, 127.6, 127.2, 127.0, 126.8, 123.8, 123.2, 123.1, 122.0, 80.3, 61.6, 60.4, 59.4, 49.7, 49.0, 41.5, 35.0, 34.0, 27.9, 24.5, 13.6; IR (film) ν_{max} 2981, 1759, 1741, 1702, 1682, 1594, 1495, 1455, 1331, 1249, 1163, 1103, 1033, 954, 764, 735, 701, 591, 523 cm^{-1}; HRMS (ESI) calcd for $C_{49}H_{42}NO_9^+$ $[M+NH_4]^+$ 788.2854, found 788.2838.

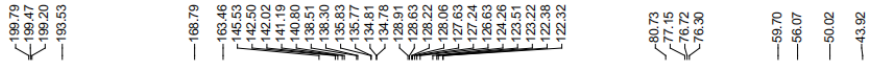


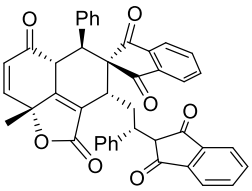
3aa

^{1}H NMR of **3aa**

$CDCl_3$, 300 MHz



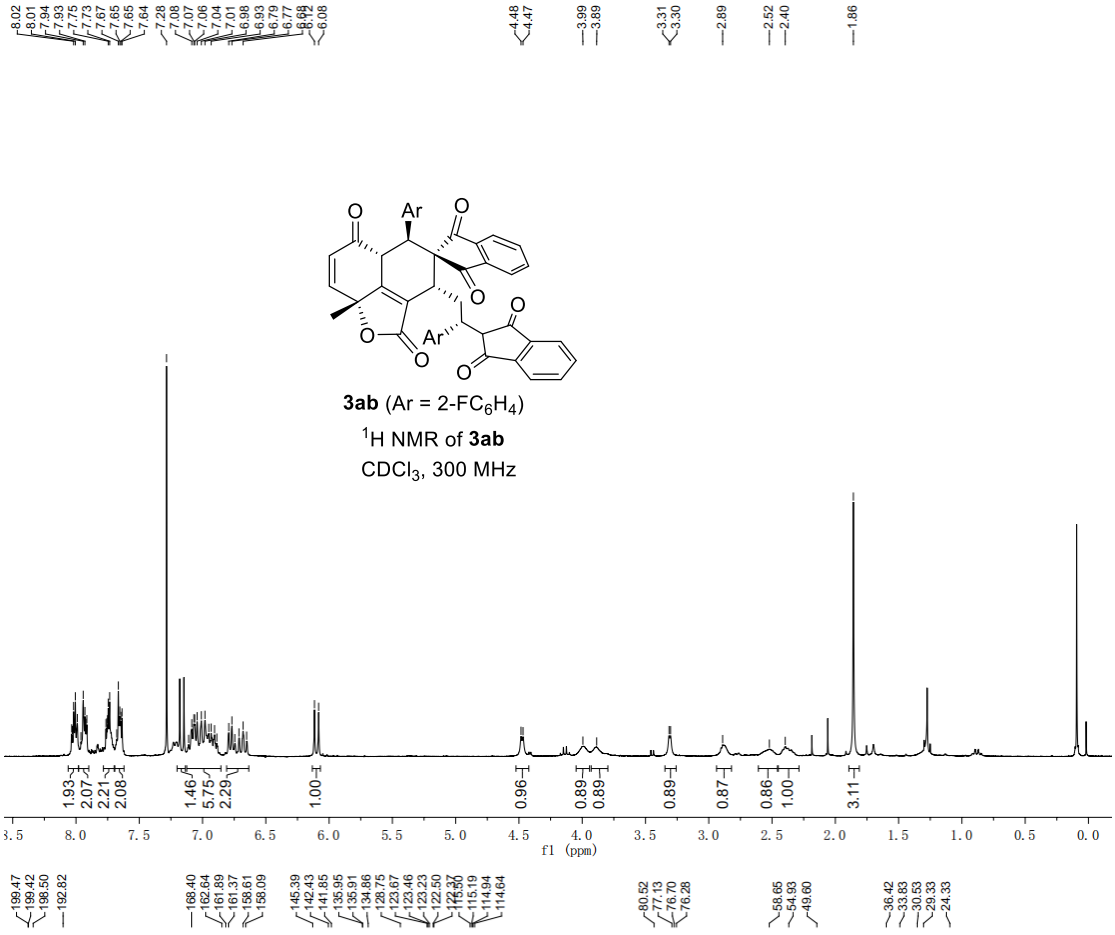




3aa

^{13}C NMR of **3aa**

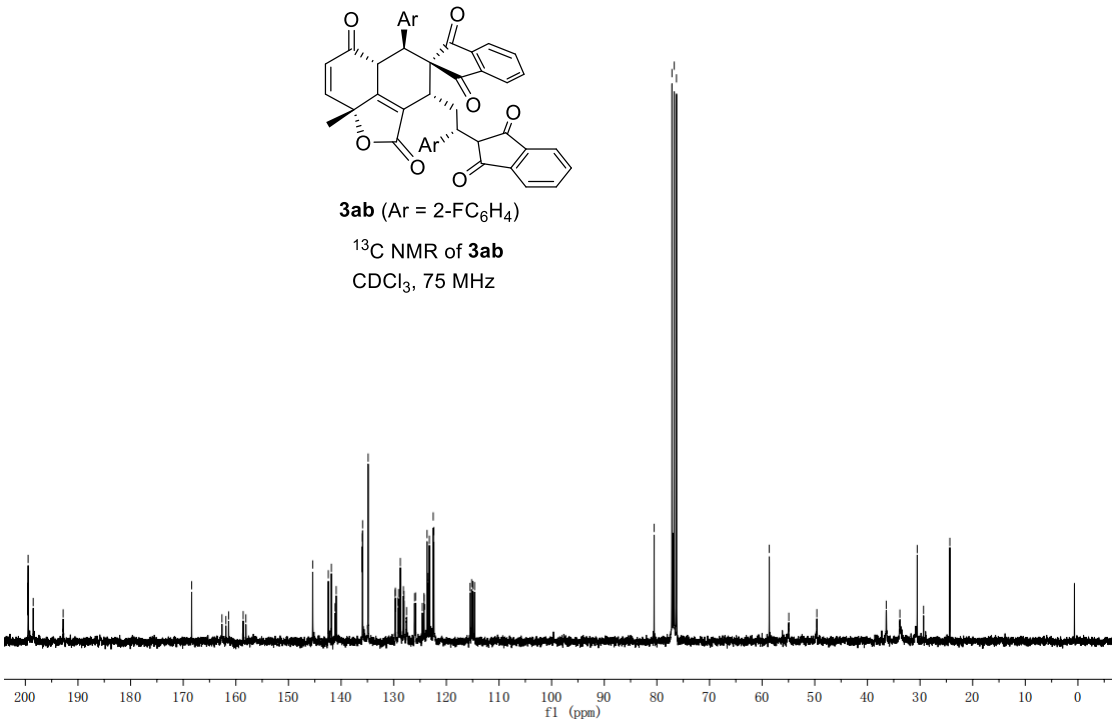
$CDCl_3$, 75 MHz



3ab (Ar = 2-FC_6H_4)

^{1}H NMR of **3ab**

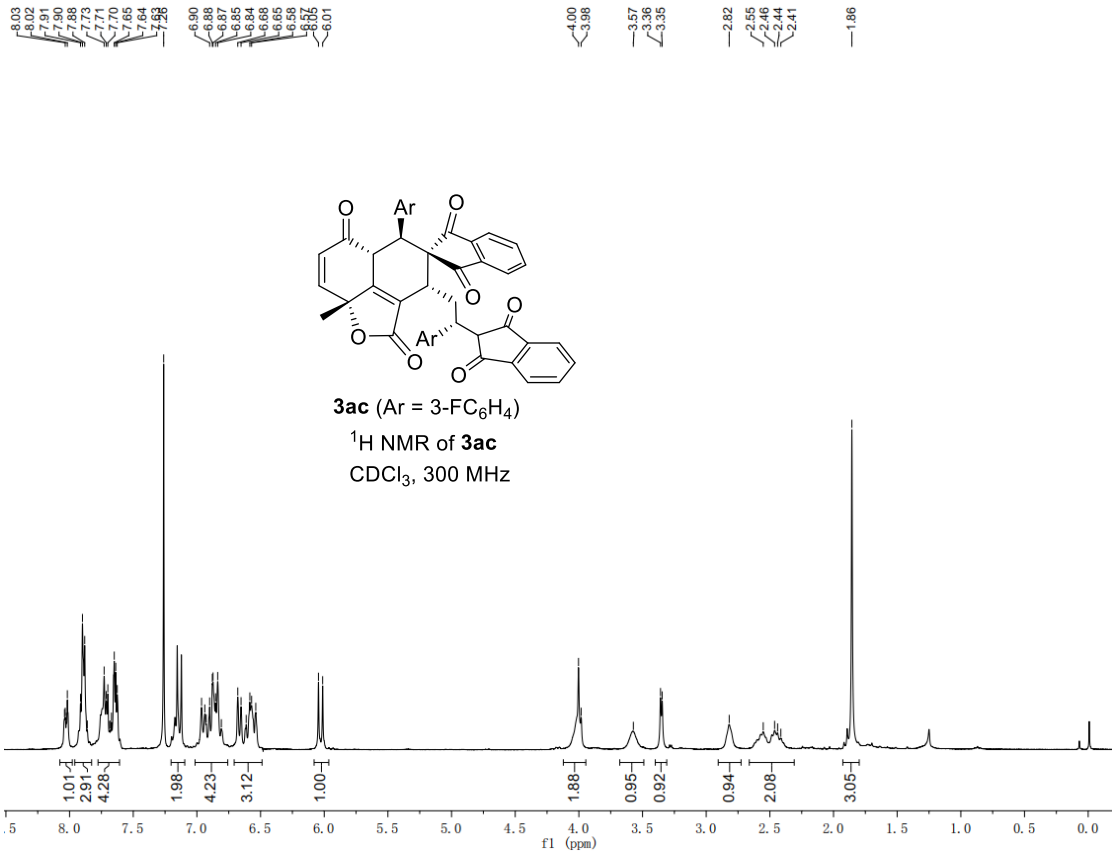
$CDCl_3$, 300 MHz



3ab (Ar = 2-FC_6H_4)

^{13}C NMR of **3ab**

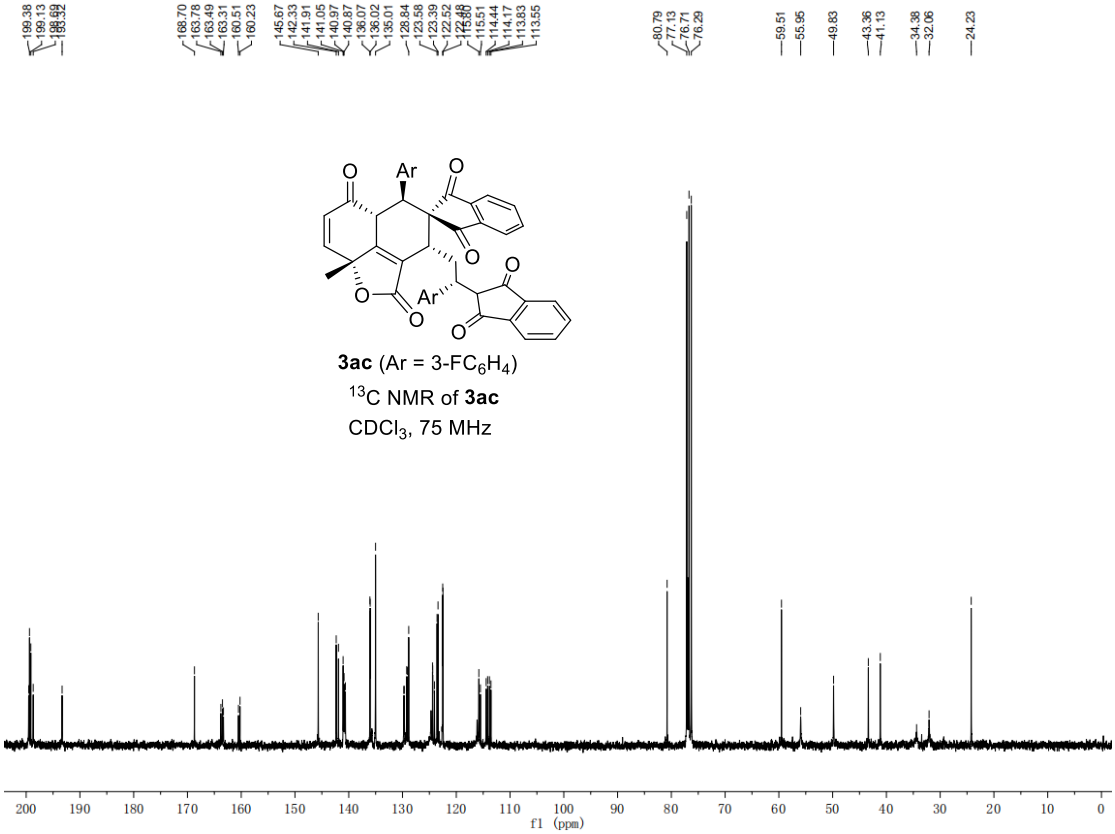
$CDCl_3$, 75 MHz



3ac (Ar = 3-FC_6H_4)

^{1}H NMR of **3ac**

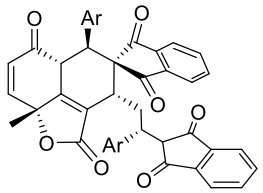
$CDCl_3$, 300 MHz



3ac (Ar = 3-FC_6H_4)

^{13}C NMR of **3ac**

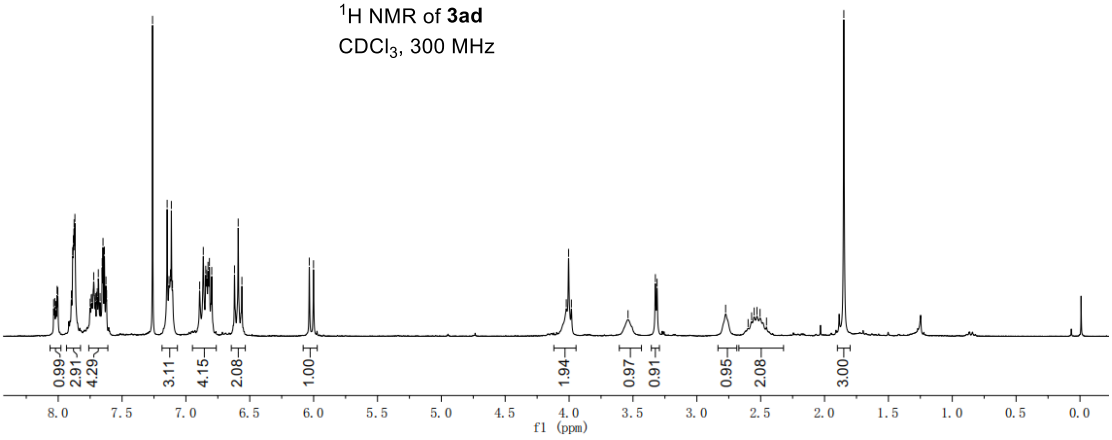
$CDCl_3$, 75 MHz

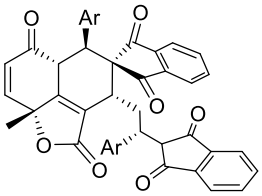


3ad (Ar = 4-FC_6H_4)

^{1}H NMR of **3ad**

$CDCl_3$, 300 MHz

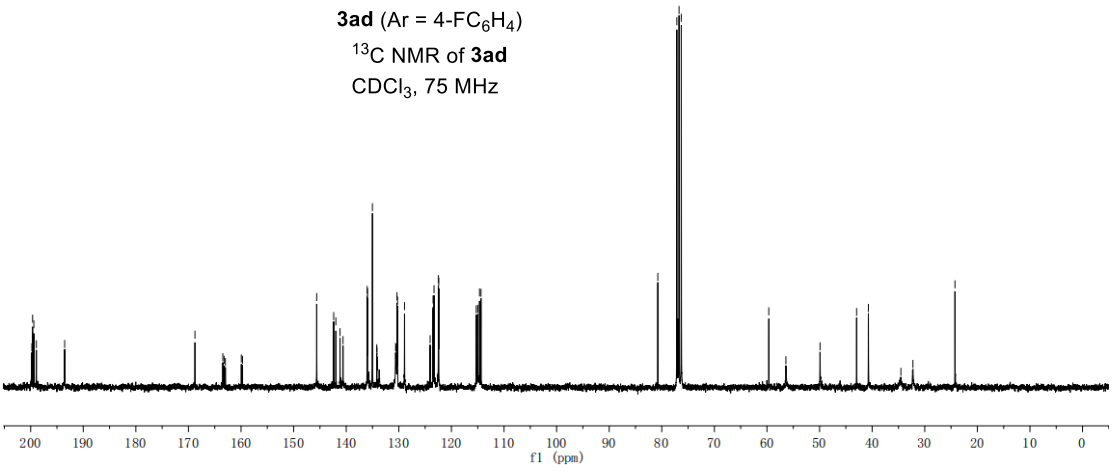


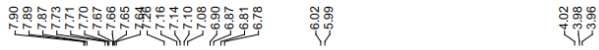


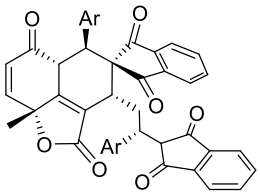
3ad (Ar = 4-FC_6H_4)

^{13}C NMR of **3ad**

$CDCl_3$, 75 MHz



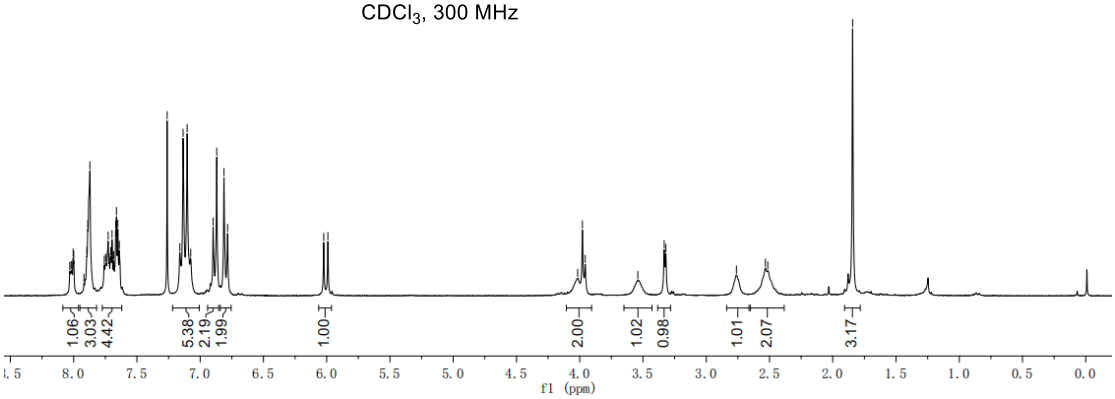


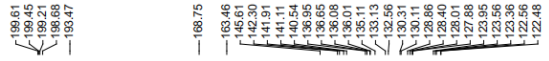


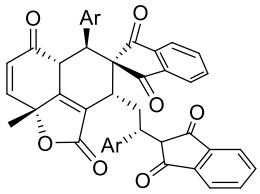
3ae (Ar = 4-ClC$_6$H$_4$)

^{1}H NMR of **3ae**

CDCl$_3$, 300 MHz



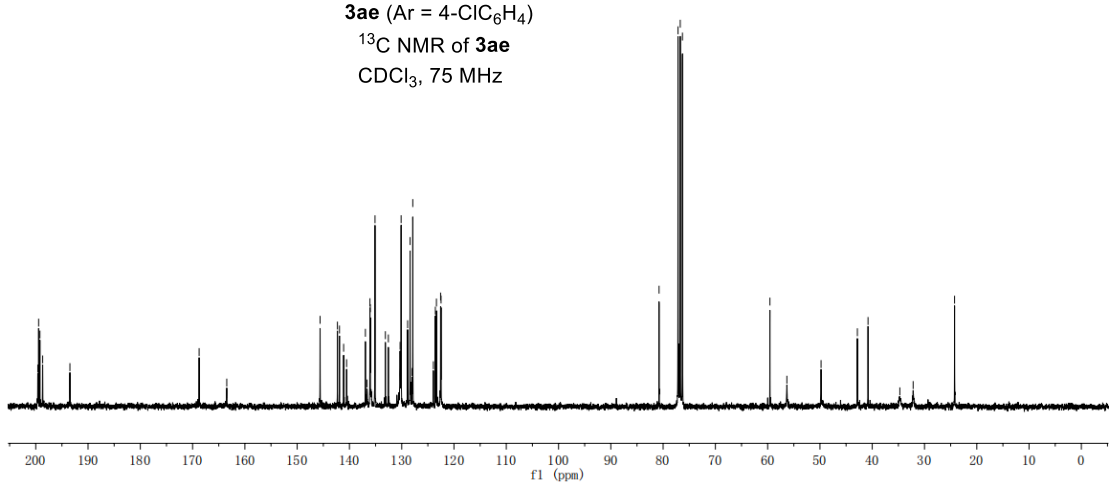


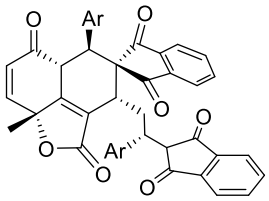


3ae (Ar = 4-ClC$_6$H$_4$)

^{13}C NMR of **3ae**

CDCl$_3$, 75 MHz

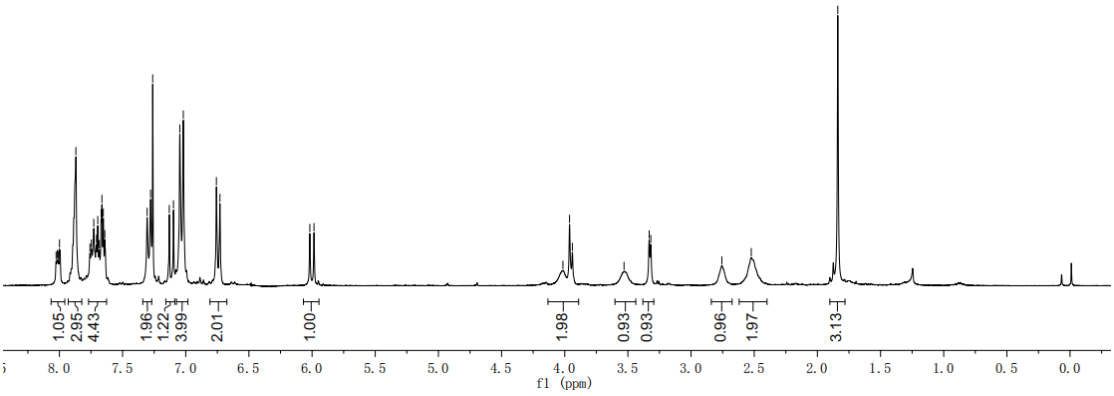


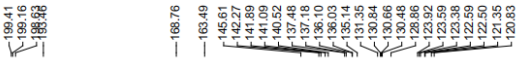


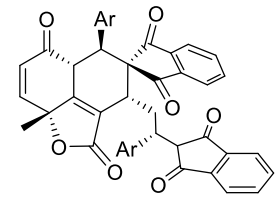
3af (Ar = 4-BrC_6H_4)

^{1}H NMR of **3af**

$CDCl_3$, 300 MHz



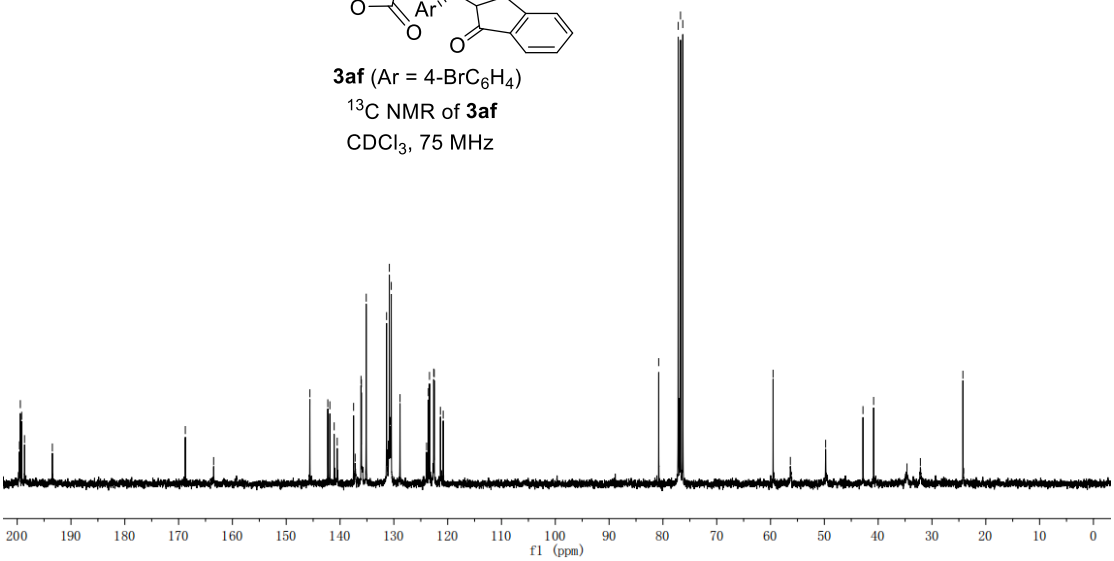


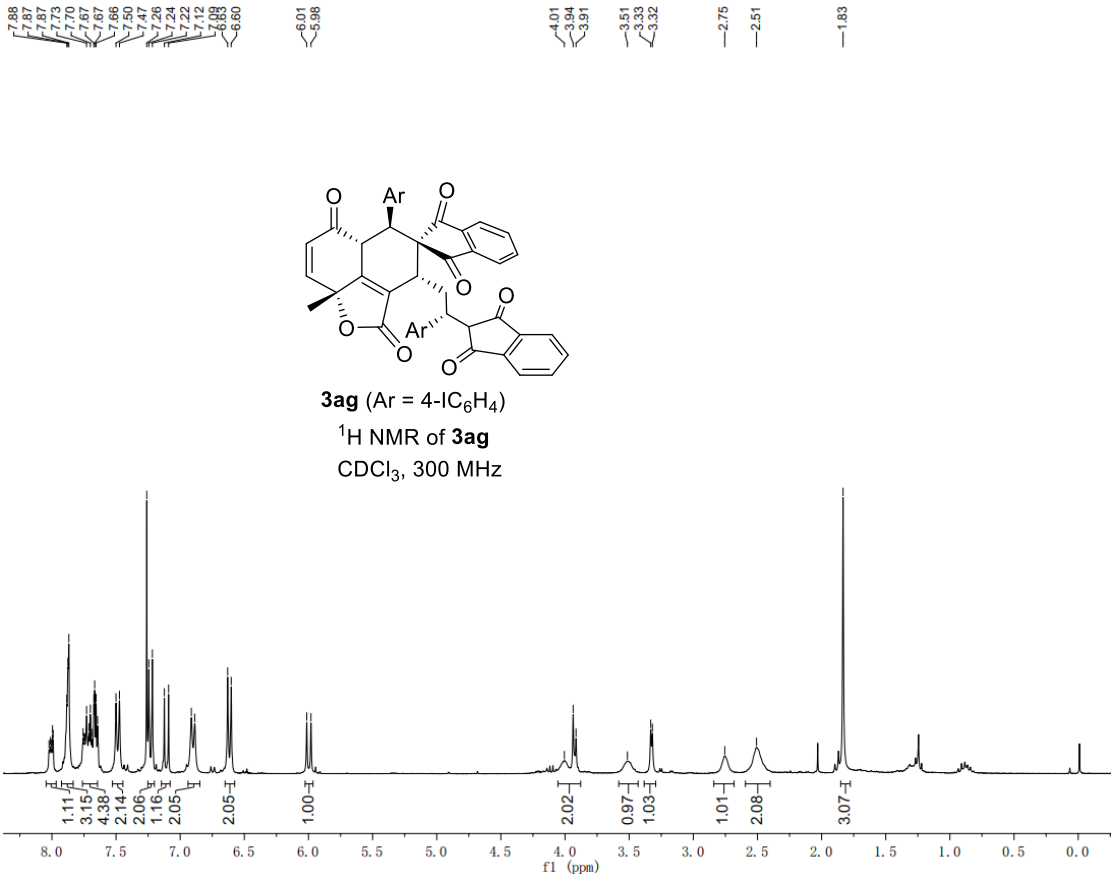


3af (Ar = 4-BrC_6H_4)

^{13}C NMR of **3af**

$CDCl_3$, 75 MHz

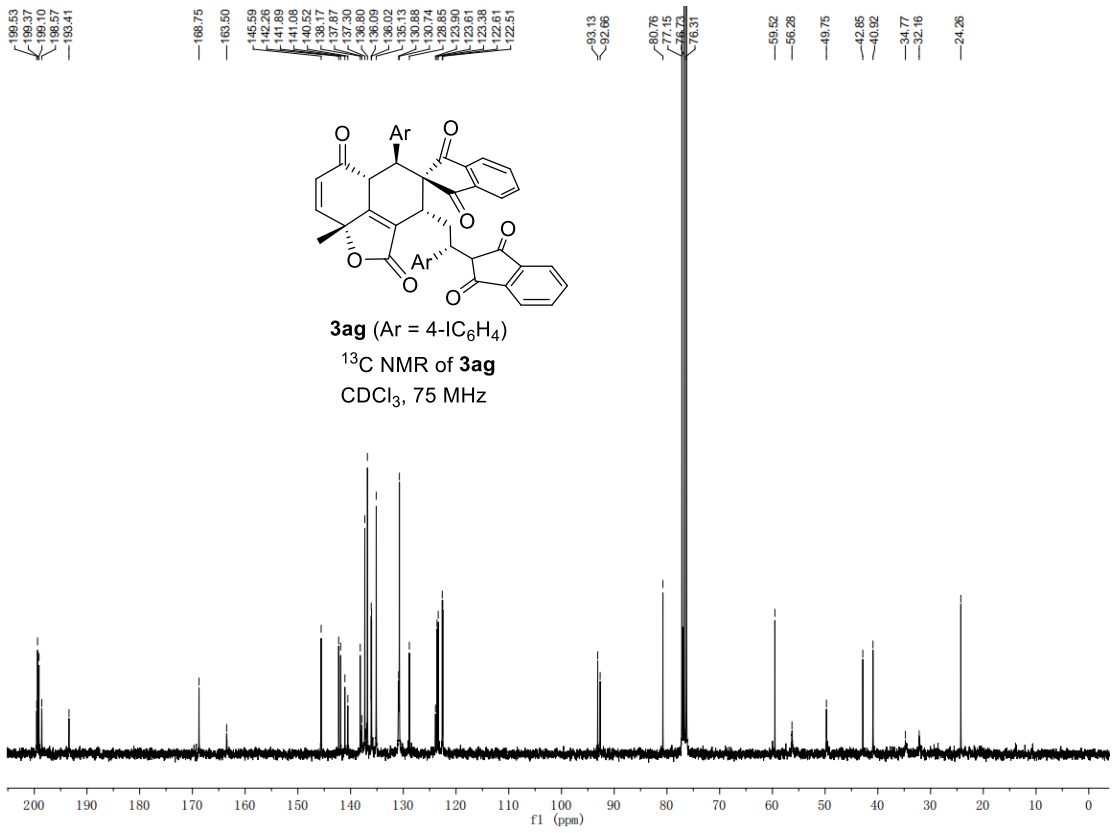




3ag (Ar = 4-IC_6H_4)

^{1}H NMR of **3ag**

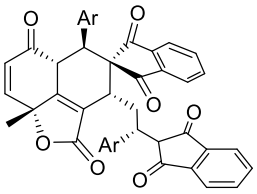
$CDCl_3$, 300 MHz



3ag (Ar = 4-IC_6H_4)

^{13}C NMR of **3ag**

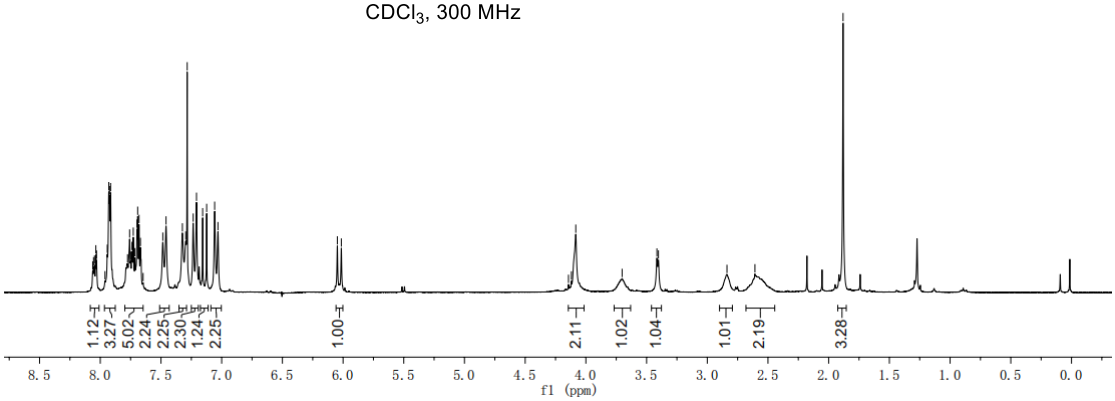
$CDCl_3$, 75 MHz

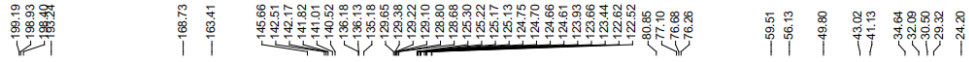


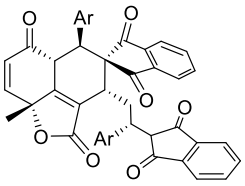
3ah (Ar = 4-$CF_3C_6H_4$)

^{1}H NMR of **3ah**

$CDCl_3$, 300 MHz



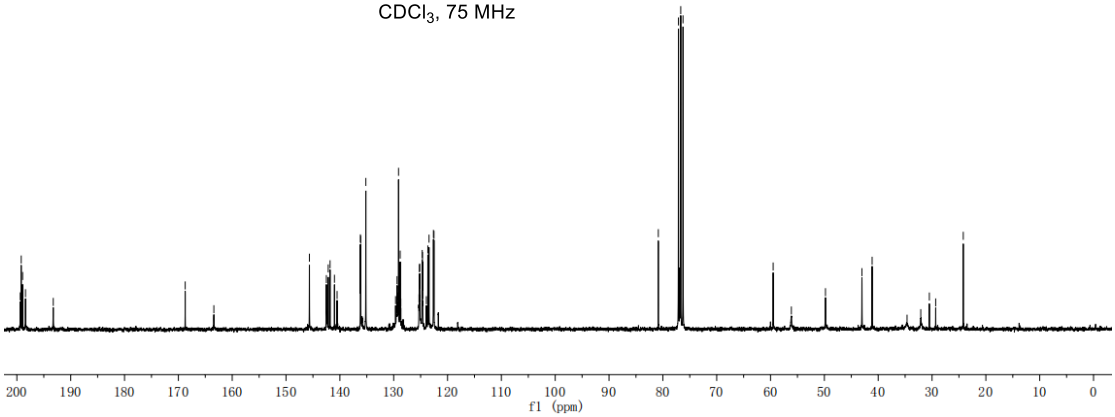


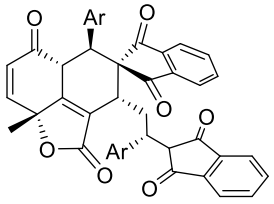


3ah (Ar = 4-$CF_3C_6H_4$)

^{13}C NMR of **3ah**

$CDCl_3$, 75 MHz

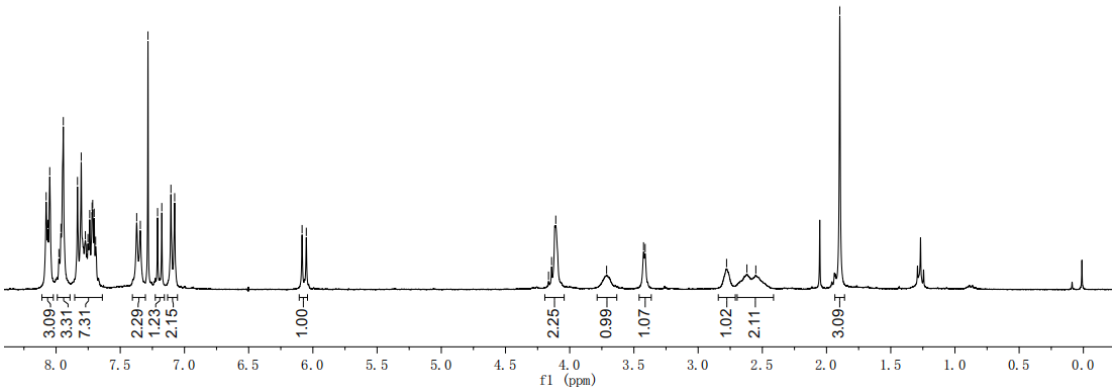


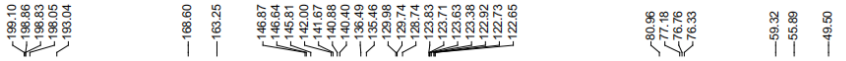


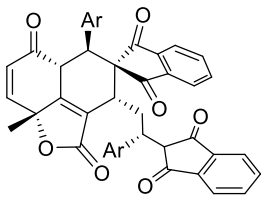
3ai (Ar = 4-$NO_2C_6H_4$)

^{1}H NMR of **3ai**

$CDCl_3$, 300 MHz



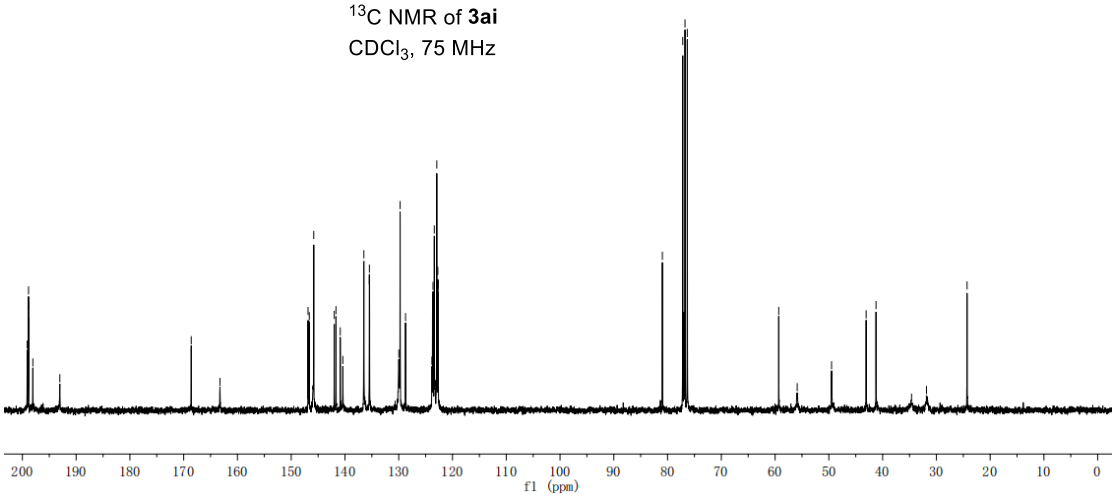


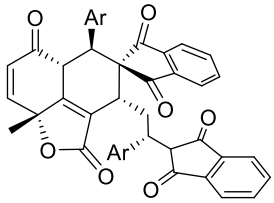


3ai (Ar = 4-$NO_2C_6H_4$)

^{13}C NMR of **3ai**

$CDCl_3$, 75 MHz

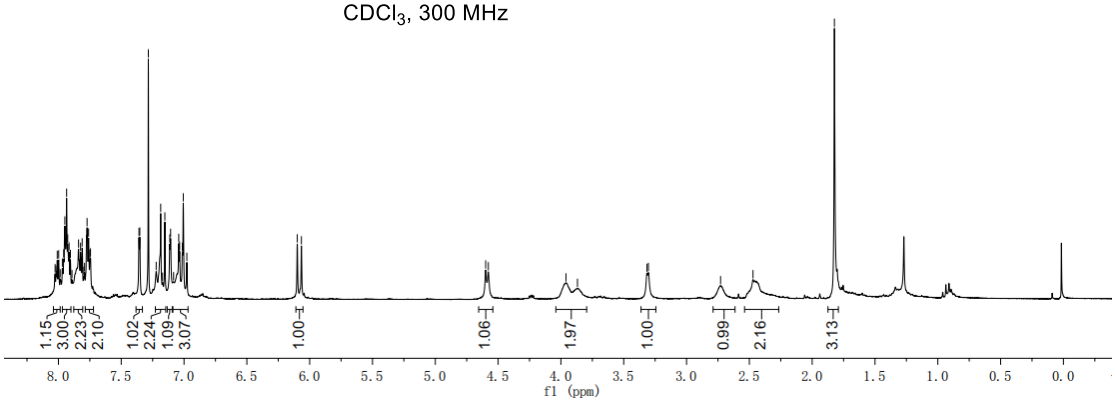


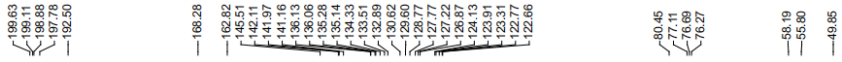


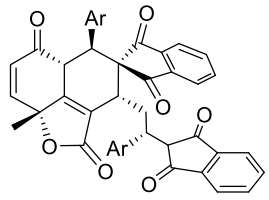
3aj (Ar = 2,4-$Cl_2C_6H_3$)

^{1}H NMR of **3aj**

$CDCl_3$, 300 MHz



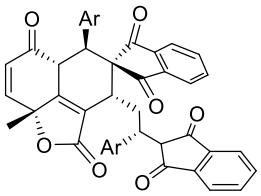




3aj (Ar = 2,4-$Cl_2C_6H_3$)

^{13}C NMR of **3aj**

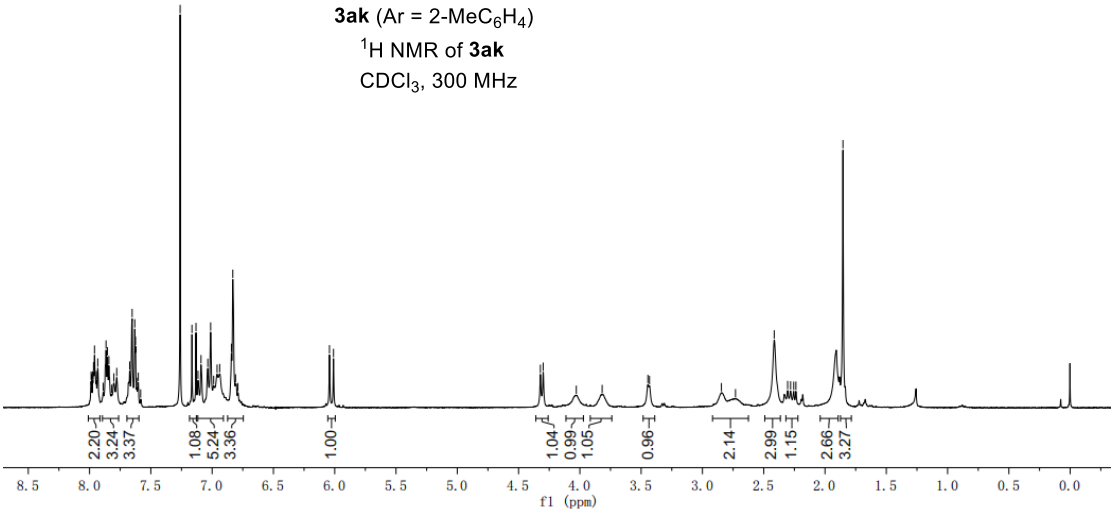
$CDCl_3$, 75 MHz

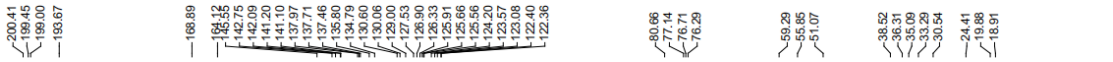


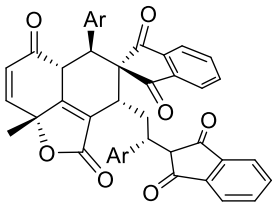
3ak (Ar = 2-MeC_6H_4)

^{1}H NMR of **3ak**

$CDCl_3$, 300 MHz



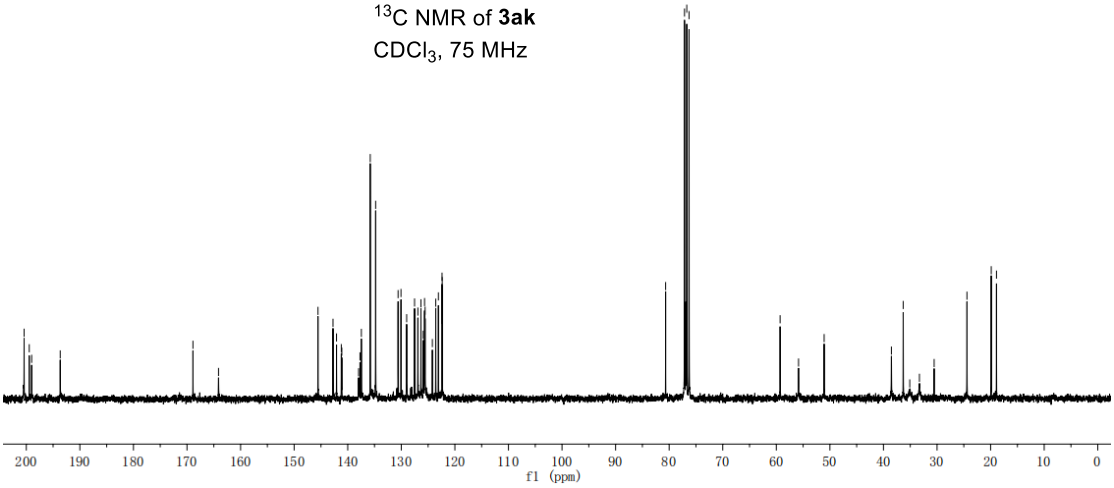


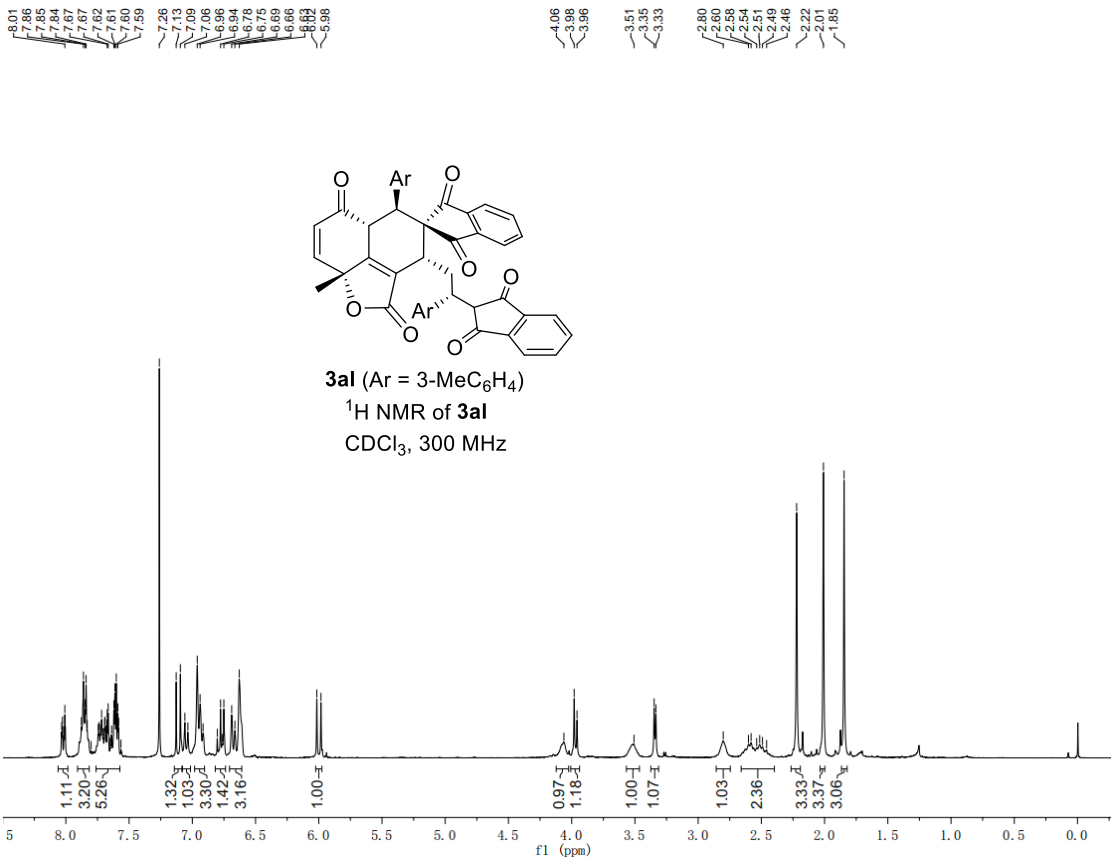


3ak (Ar = 2-MeC_6H_4)

^{13}C NMR of **3ak**

$CDCl_3$, 75 MHz

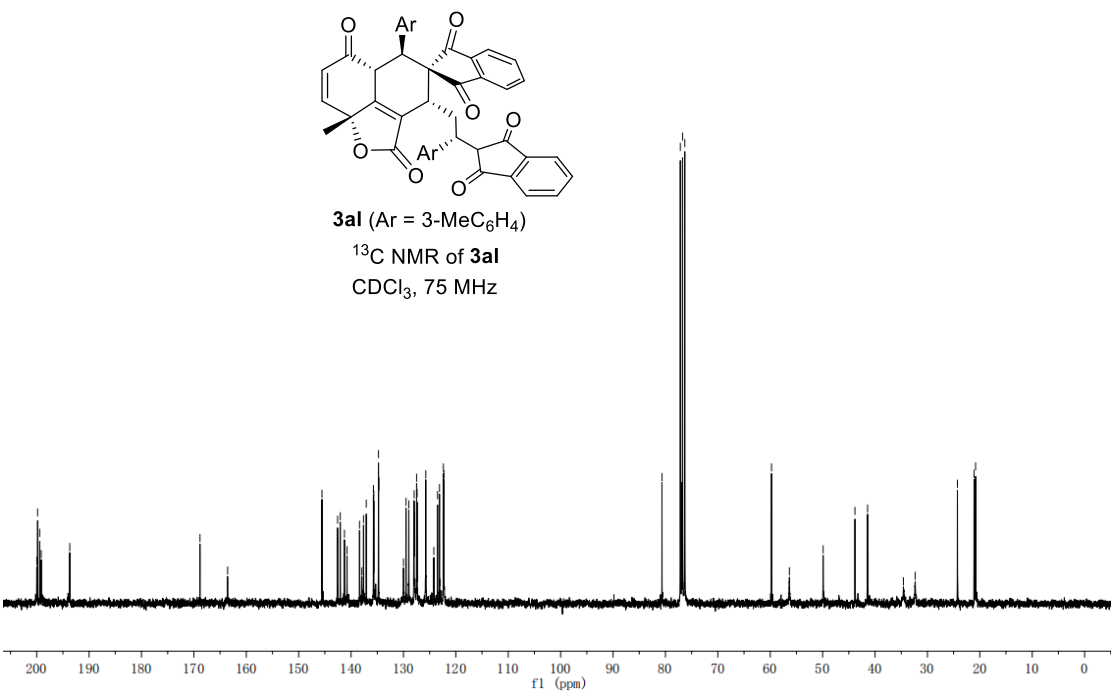




3al (Ar = 3-MeC_6H_4)

^{1}H NMR of **3al**

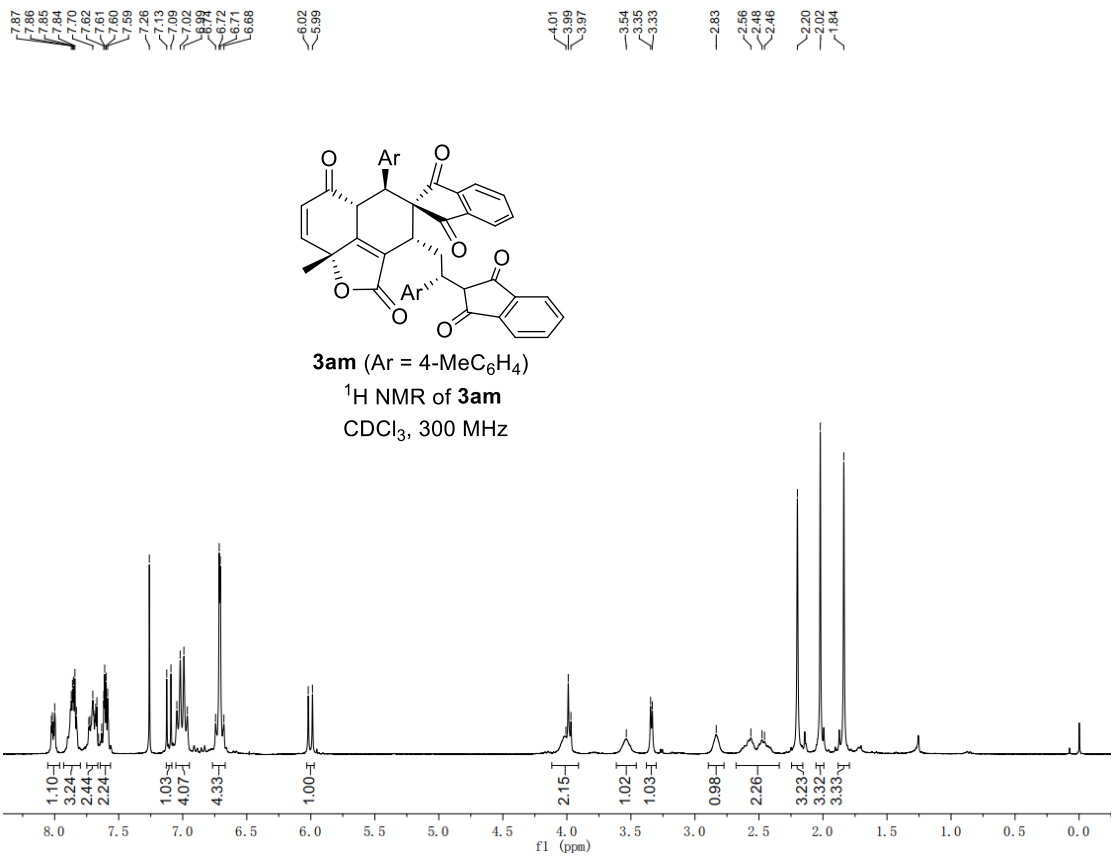
$CDCl_3$, 300 MHz



3al (Ar = 3-MeC_6H_4)

^{13}C NMR of **3al**

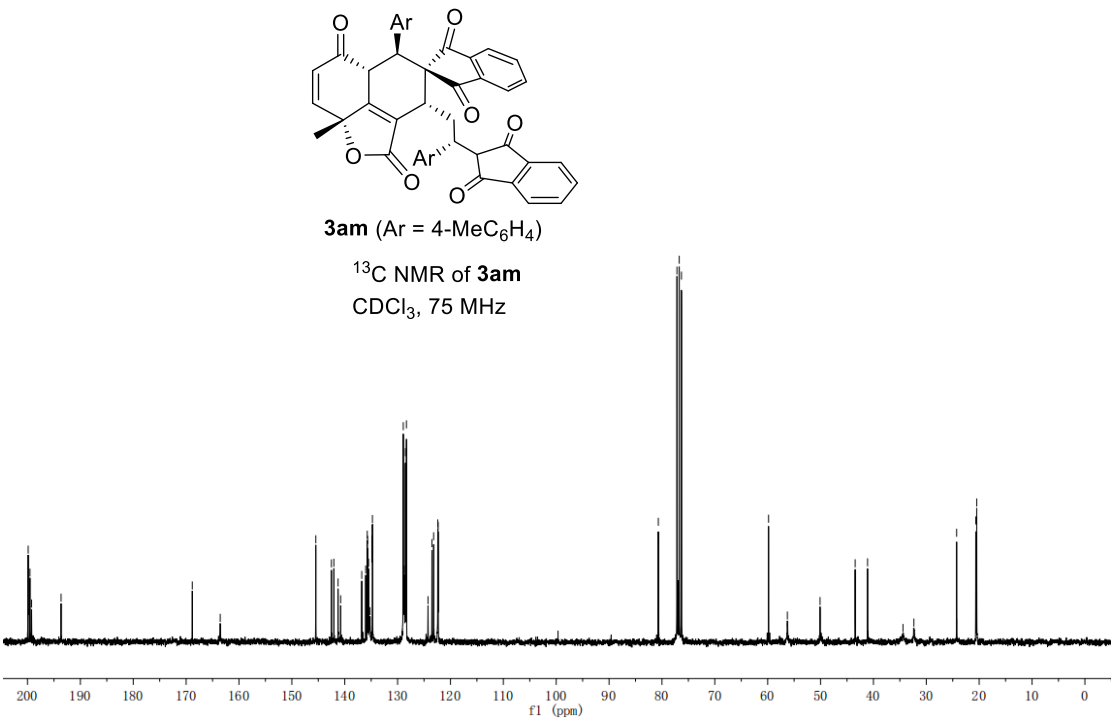
$CDCl_3$, 75 MHz



3am (Ar = 4-MeC_6H_4)

^{1}H NMR of **3am**

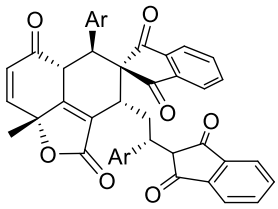
$CDCl_3$, 300 MHz



3am (Ar = 4-MeC_6H_4)

^{13}C NMR of **3am**

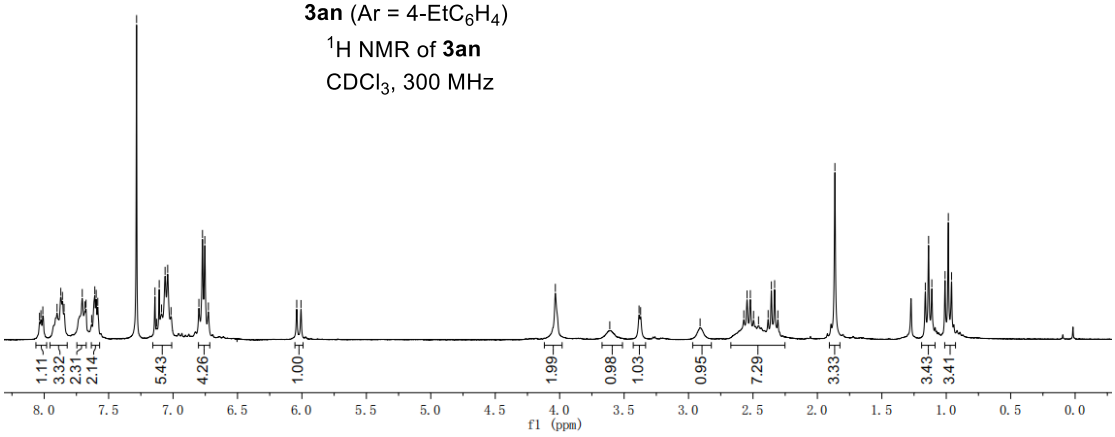
$CDCl_3$, 75 MHz

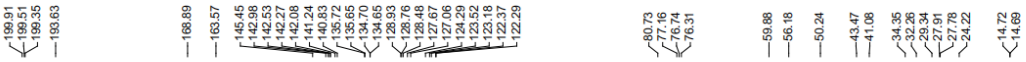


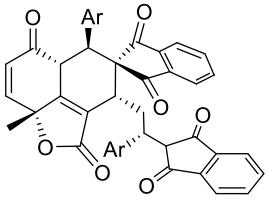
3an (Ar = 4-EtC_6H_4)

^{1}H NMR of **3an**

$CDCl_3$, 300 MHz



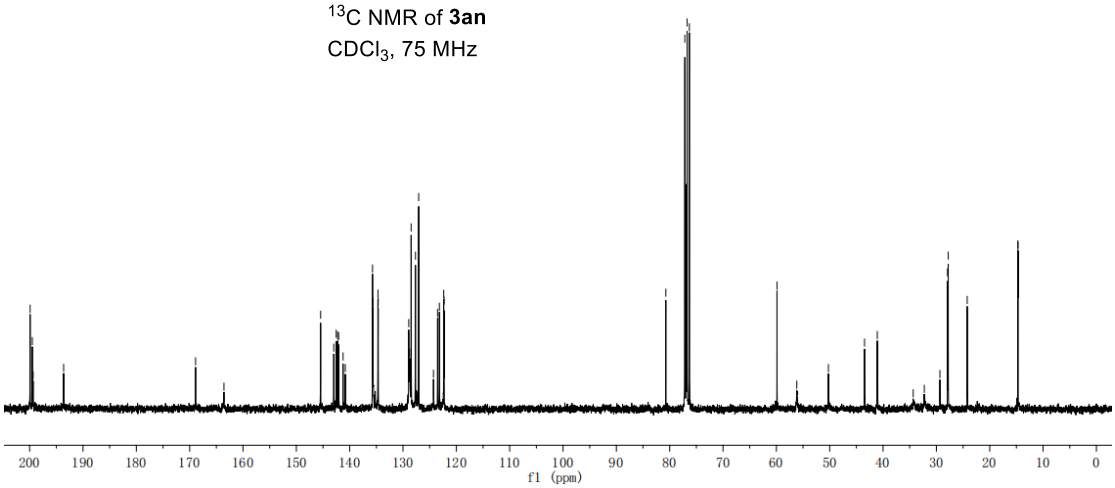


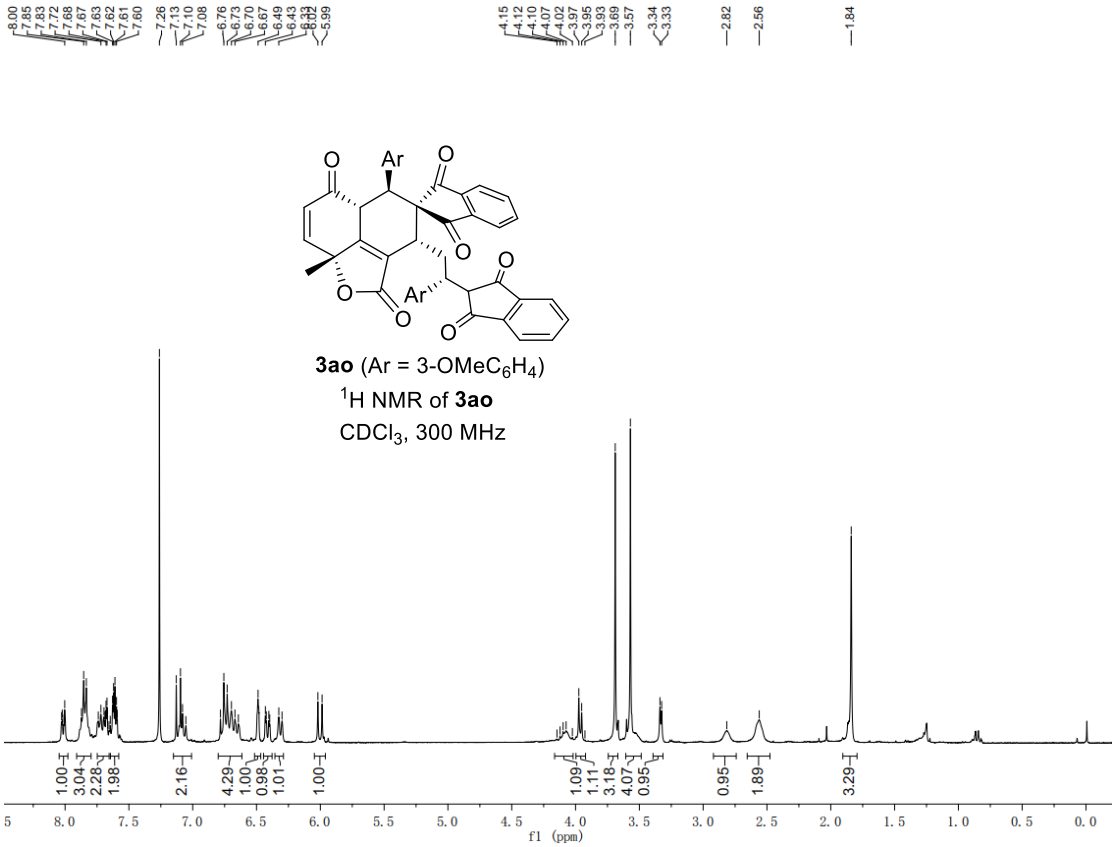


3an (Ar = 4-EtC_6H_4)

^{13}C NMR of **3an**

$CDCl_3$, 75 MHz

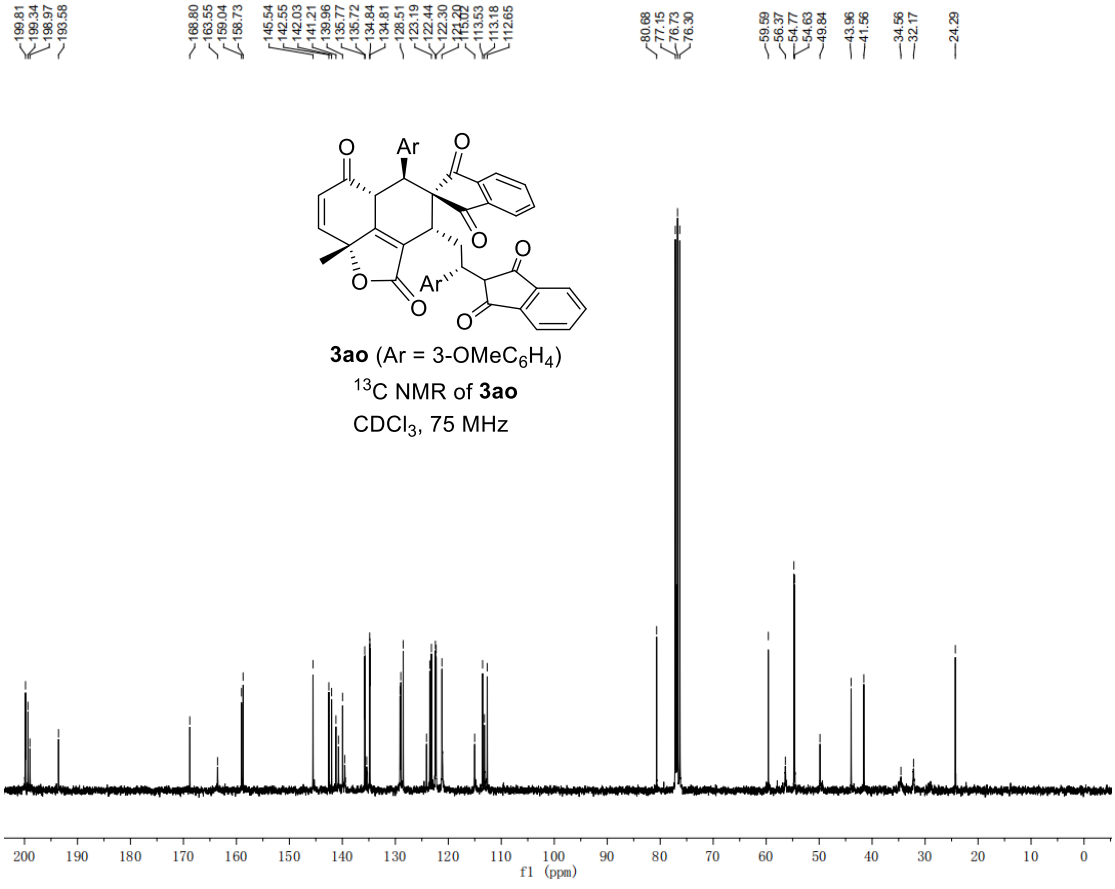




3ao (Ar = 3-OMeC$_6$H$_4$)

^{1}H NMR of **3ao**

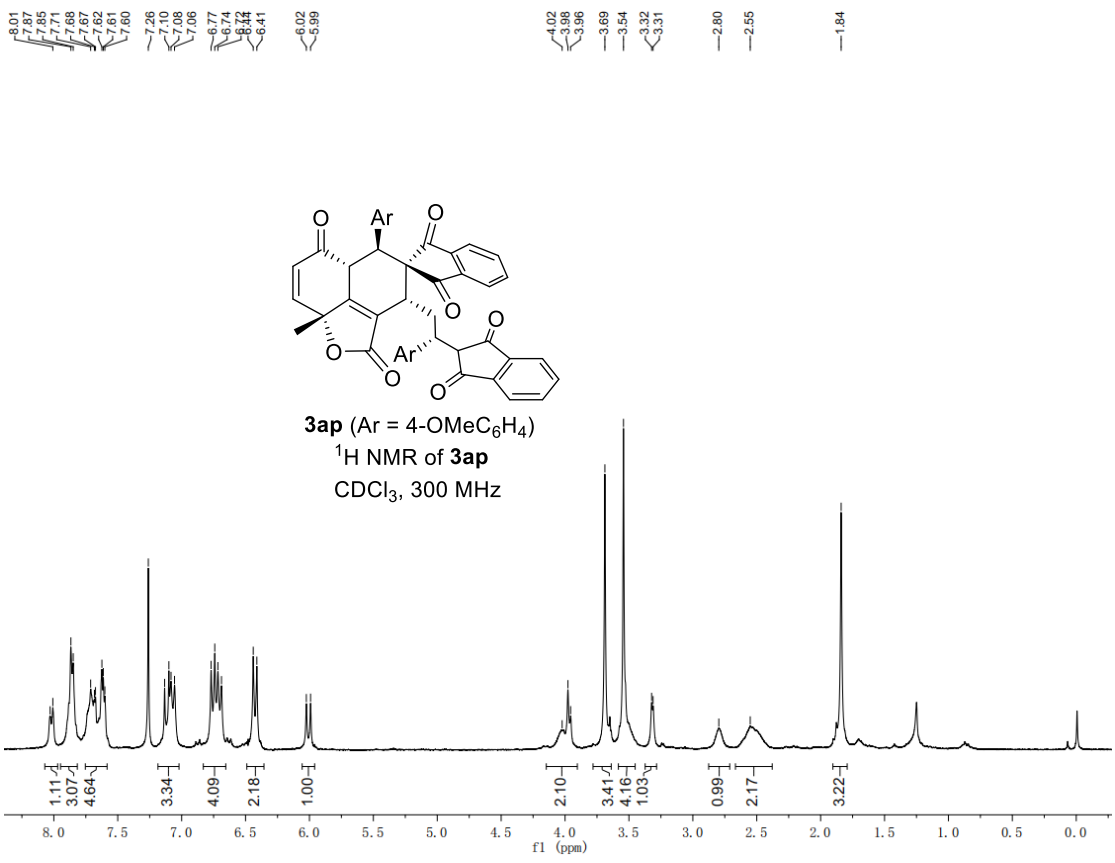
CDCl$_3$, 300 MHz



3ao (Ar = 3-OMeC$_6$H$_4$)

^{13}C NMR of **3ao**

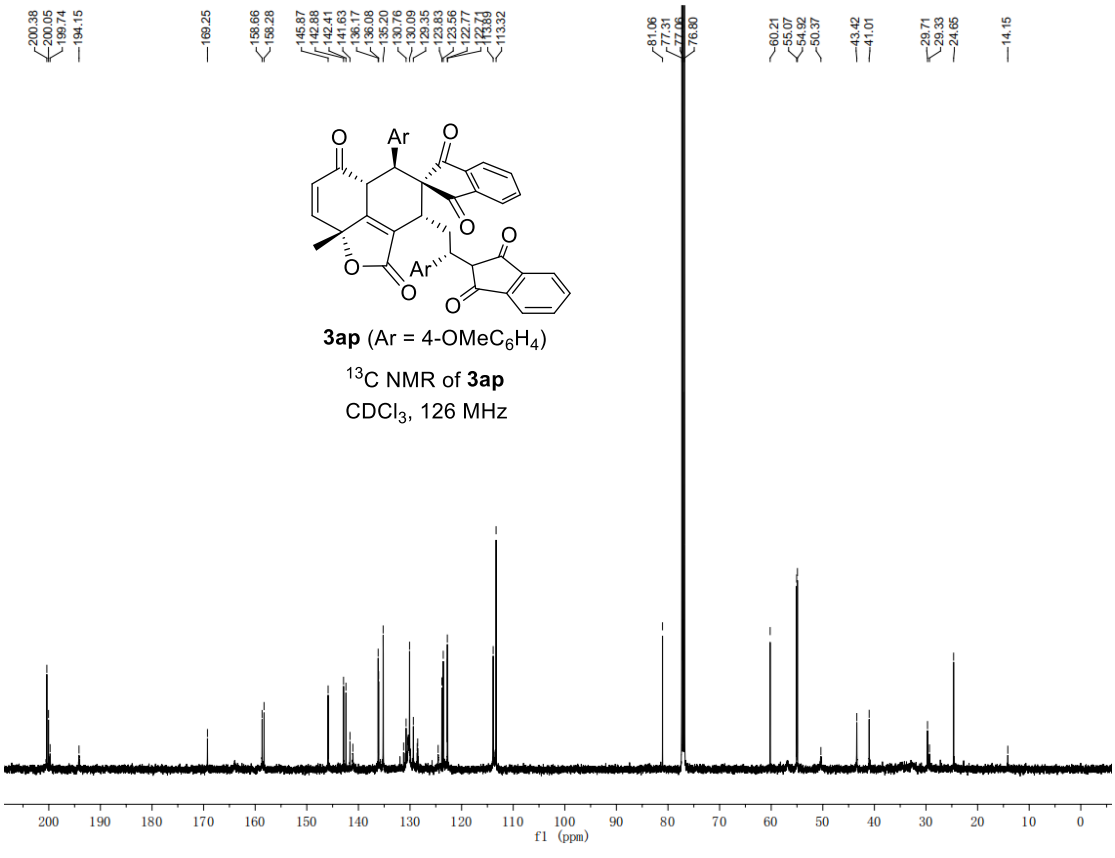
CDCl$_3$, 75 MHz



3ap (Ar = 4-OMeC$_6$H$_4$)

^{1}H NMR of **3ap**

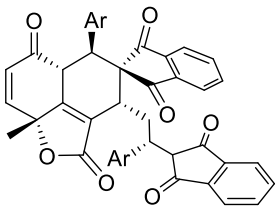
CDCl$_3$, 300 MHz



3ap (Ar = 4-OMeC$_6$H$_4$)

^{13}C NMR of **3ap**

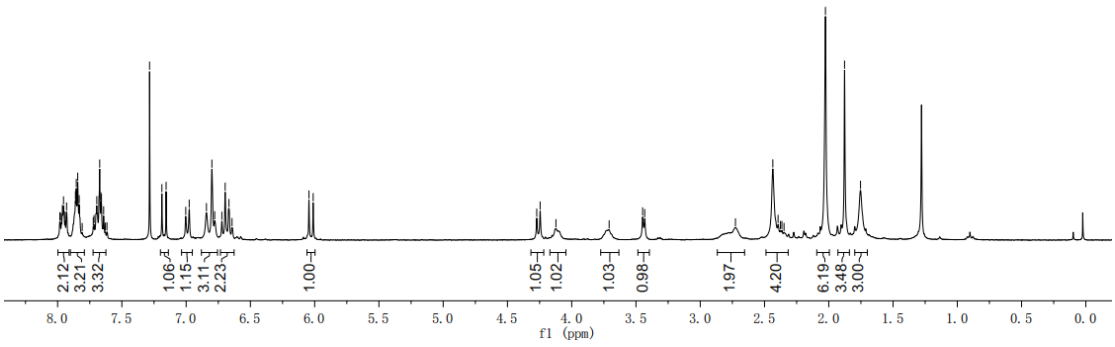
CDCl$_3$, 126 MHz

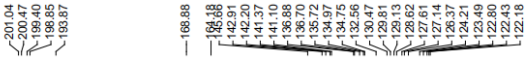


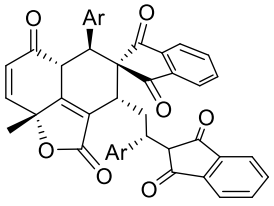
3aq (Ar = 2,5-$Me_2C_6H_3$)

^{1}H NMR of **3aq**

$CDCl_3$, 300 MHz



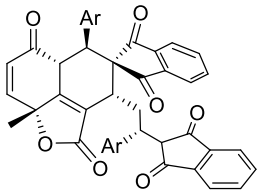




3aq (Ar = 2,5-$Me_2C_6H_3$)

^{13}C NMR of **3aq**

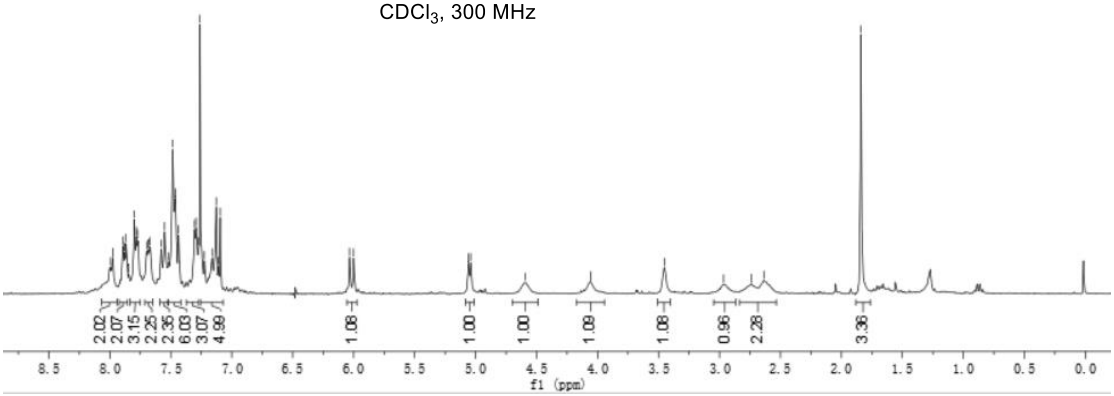
$CDCl_3$, 75 MHz

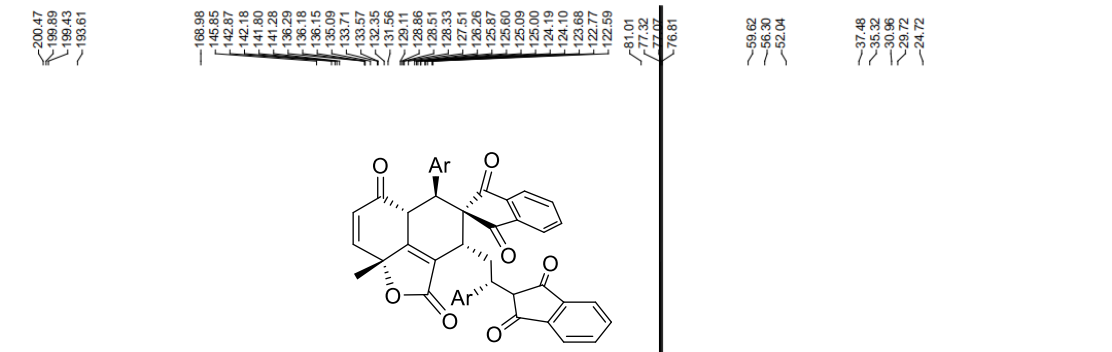


3ar (Ar = 1-naphthyl)

^{1}H NMR of **3ar**

$CDCl_3$, 300 MHz

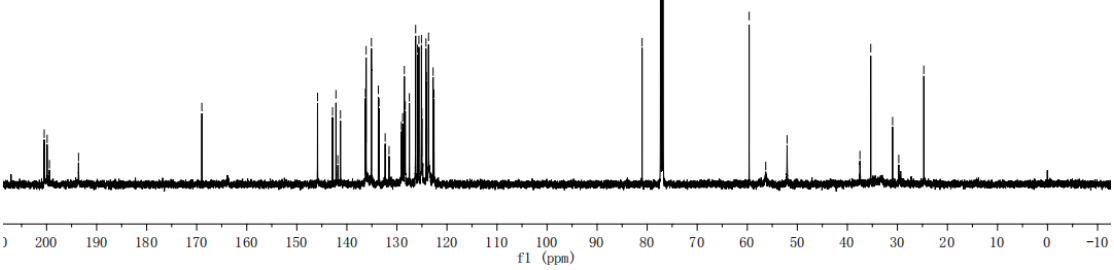


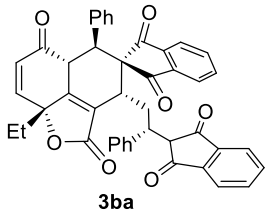


3ar (Ar = 1-naphthyl)

^{13}C NMR of **3ar**

$CDCl_3$, 126 MHz

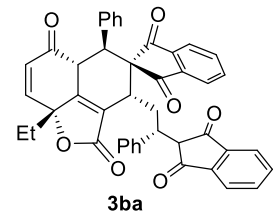




3ba

^{1}H NMR of **3ba**

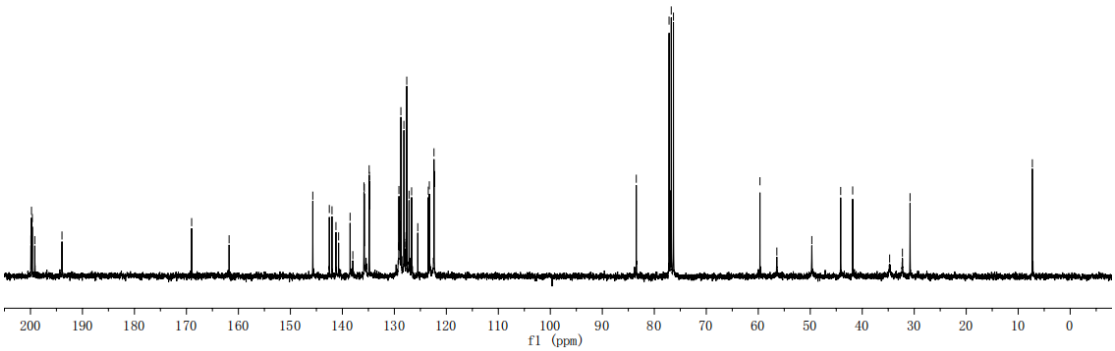
$CDCl_3$, 300 MHz

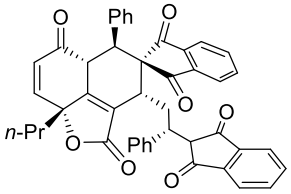


3ba

^{13}C NMR of **3ba**

$CDCl_3$, 75 MHz

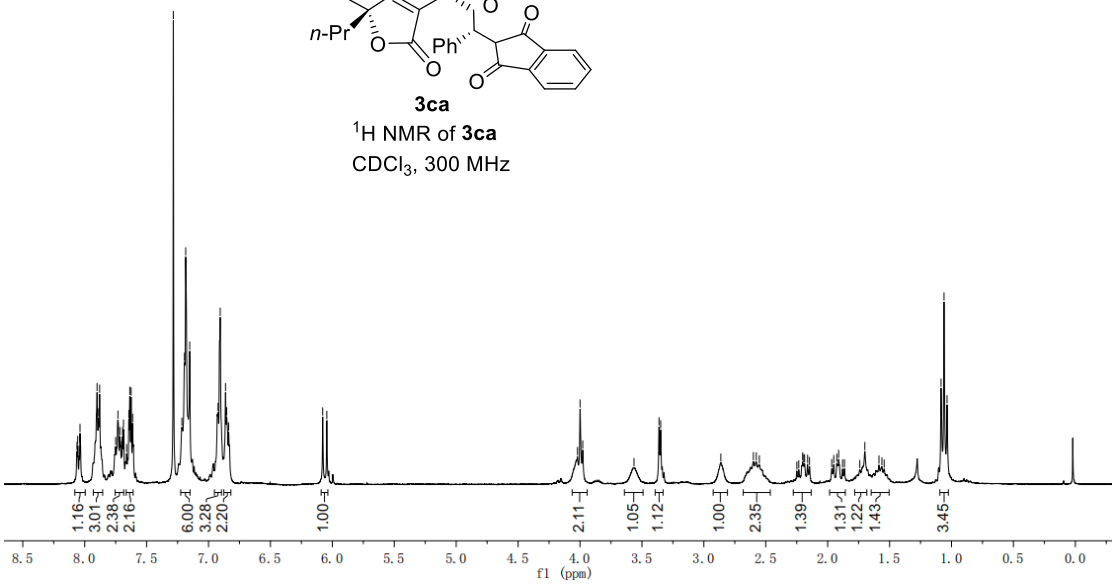


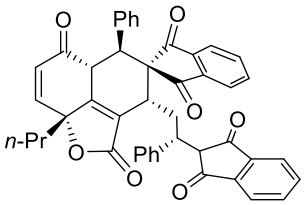


3ca

^{1}H NMR of **3ca**

$CDCl_3$, 300 MHz

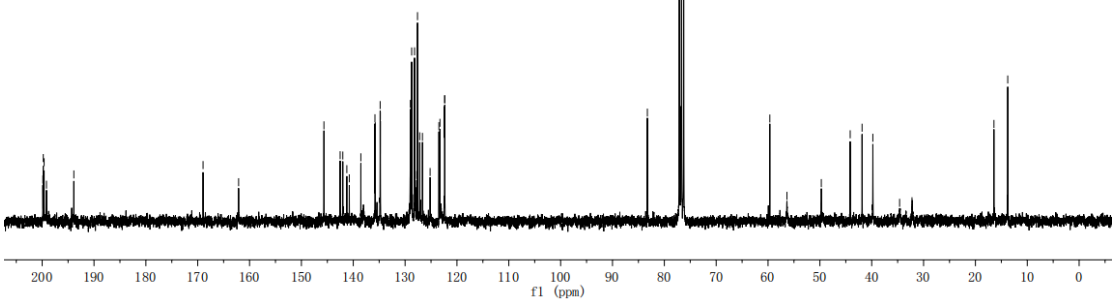


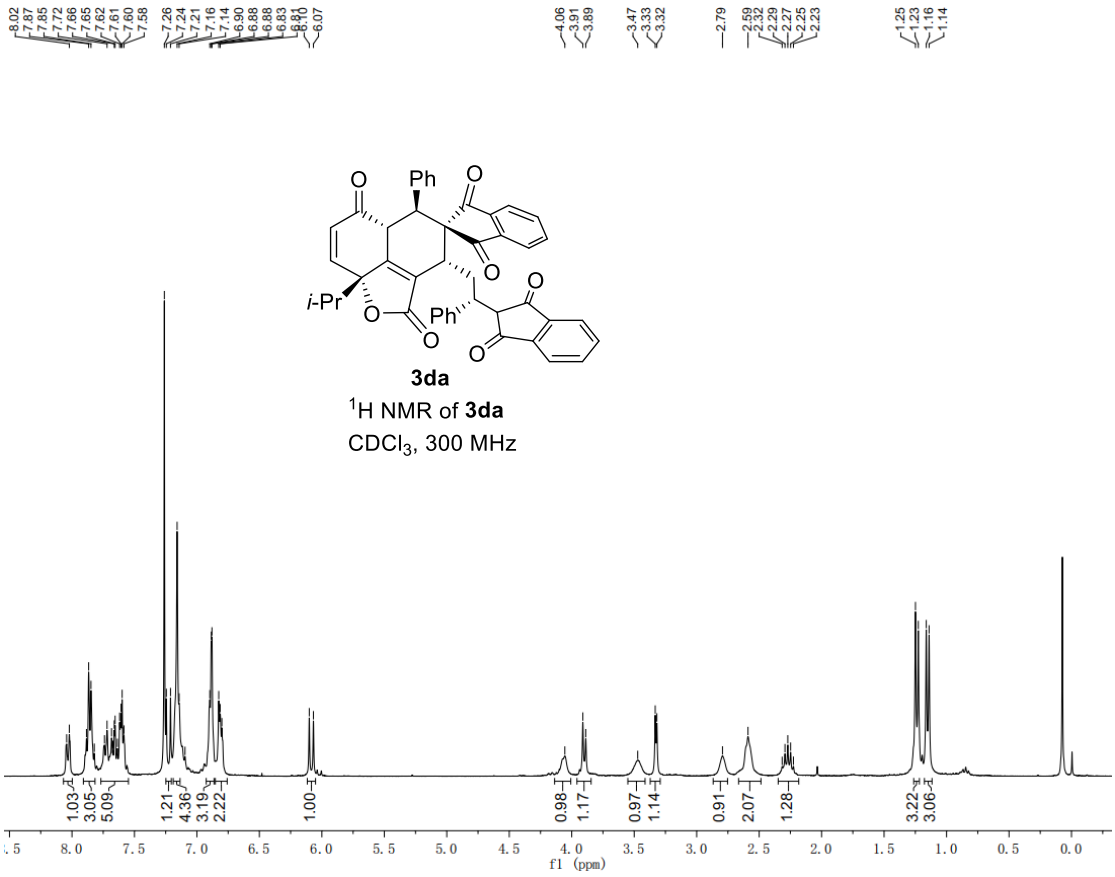


3ca

^{13}C NMR of **3ca**

$CDCl_3$, 75 MHz

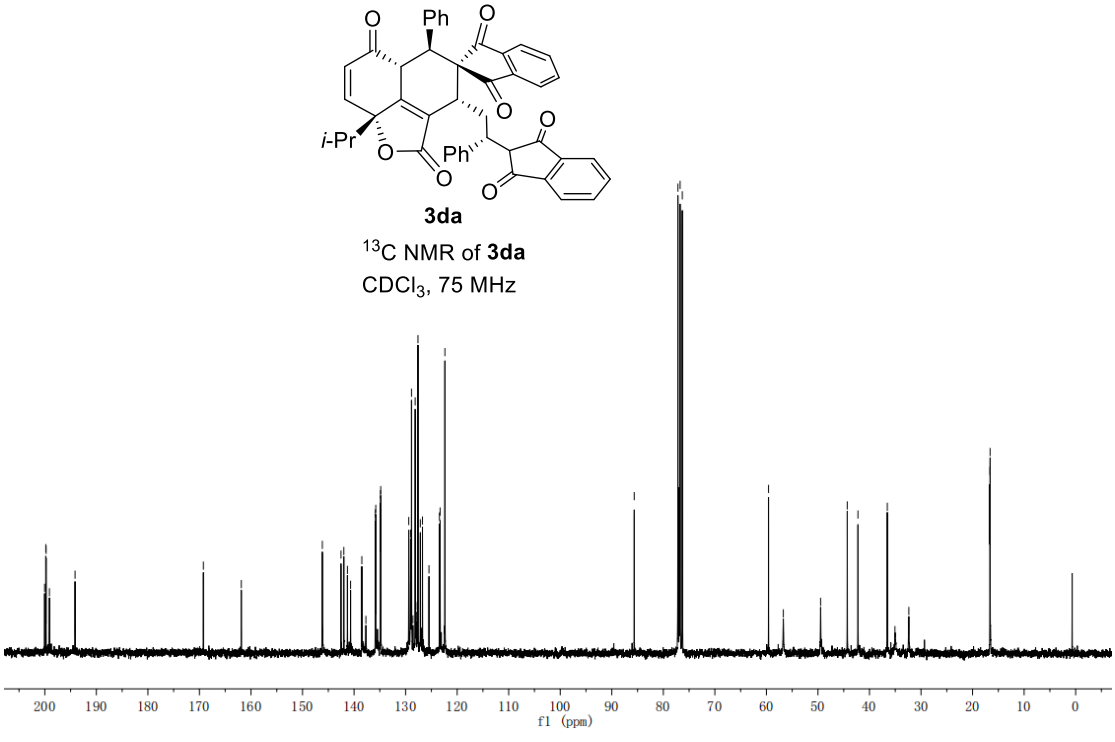




3da

^{1}H NMR of **3da**

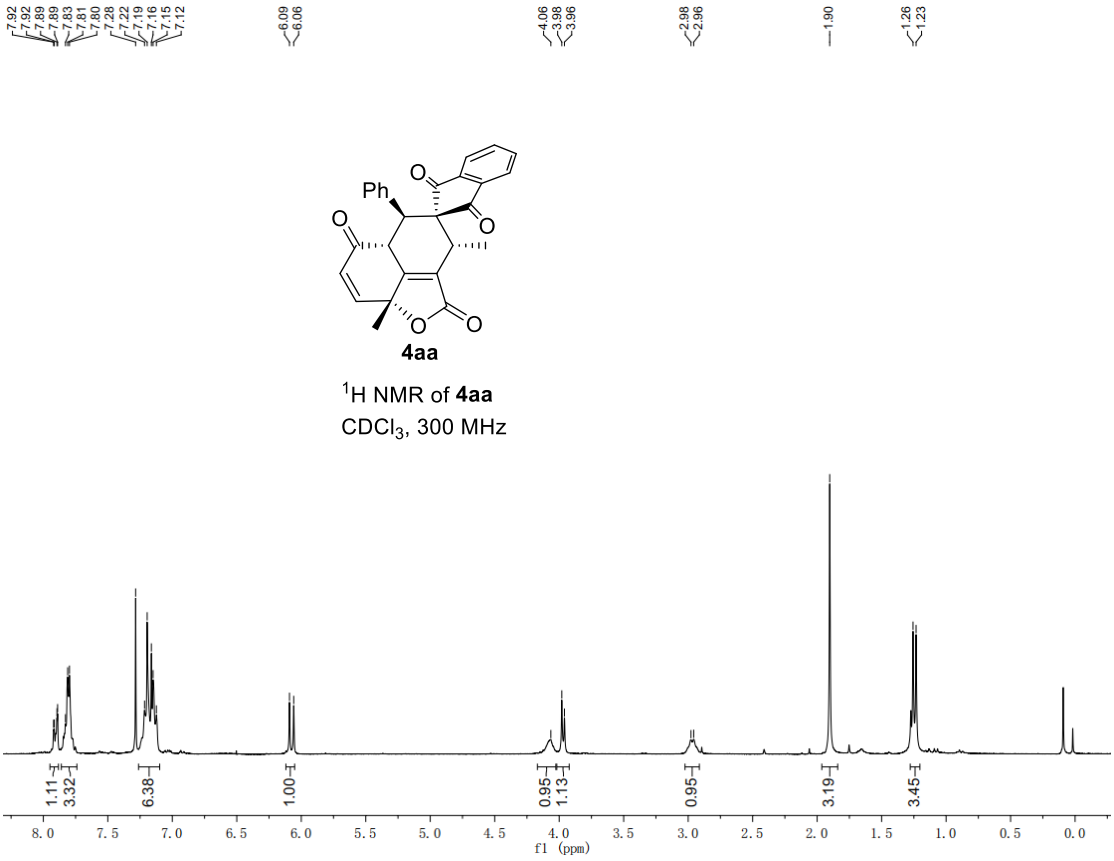
$CDCl_3$, 300 MHz

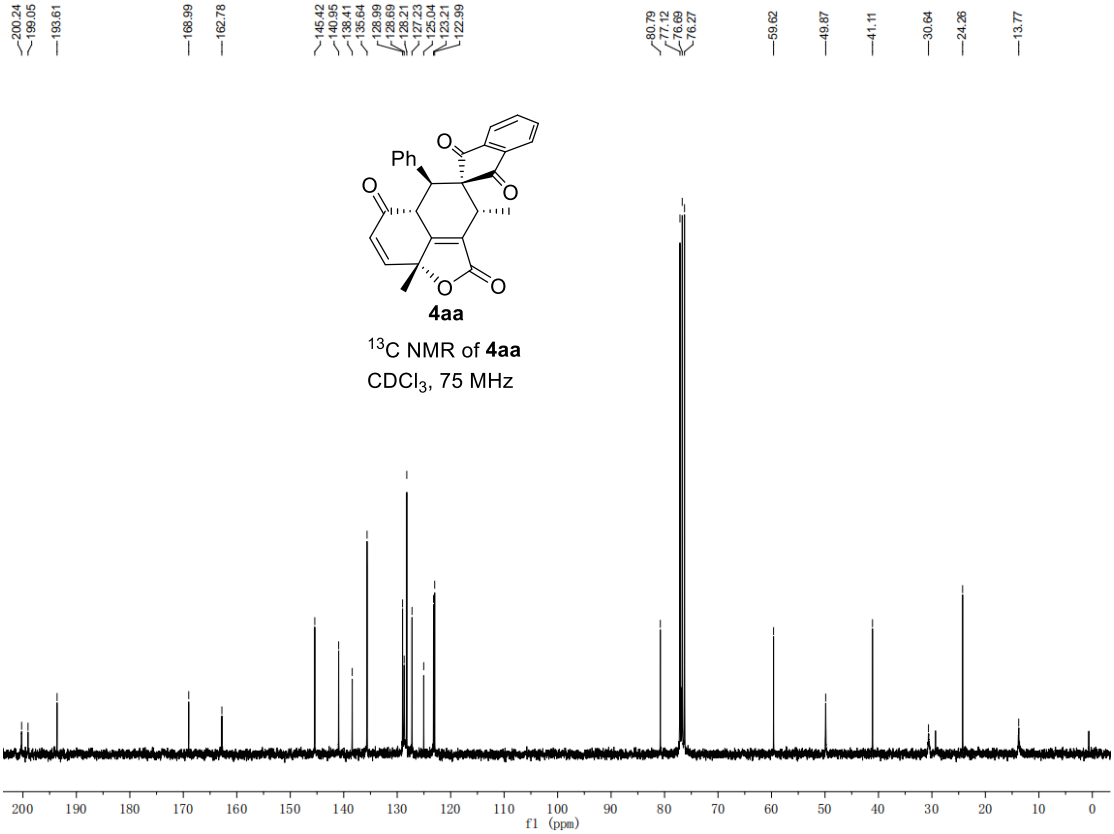


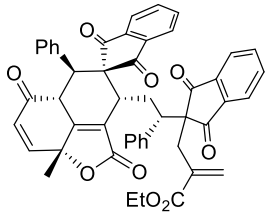
3da

^{13}C NMR of **3da**

$CDCl_3$, 75 MHz


7.92
7.92
7.89
7.89
7.83
7.81
7.80
7.28
7.22
7.19
7.16
7.15
7.12
6.09
6.06
4.06
3.98
3.96
2.98
2.96
1.90
1.26
1.23
Ph
O
O
O
O
O
4aa
1H NMR of 4aa
CDCl3, 300 MHz
1.11
3.32
6.38
1.00
0.95
1.13
0.95
3.19
3.45
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

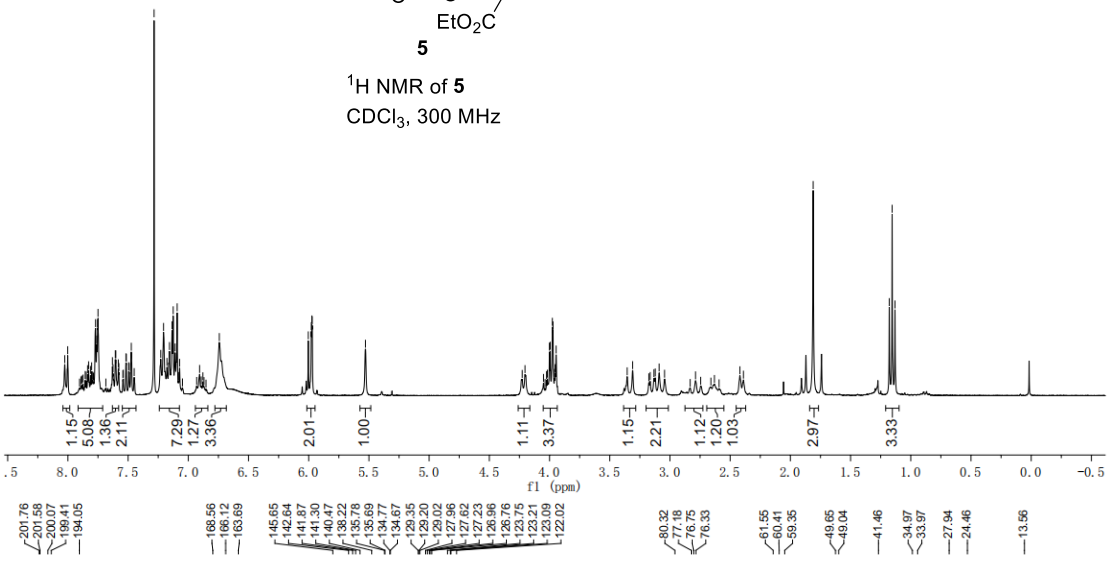

200.24
199.05
193.61
168.99
162.78
145.42
140.95
138.41
135.64
128.99
128.69
128.21
127.23
125.04
123.21
122.99
80.79
77.12
76.69
76.27
59.62
49.87
41.11
30.64
24.26
13.77
Ph
O
O
O
O
O
4aa
13C NMR of 4aa
CDCl3, 75 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

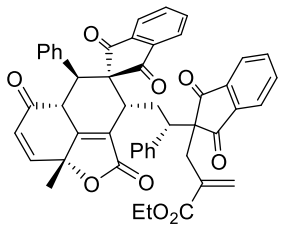


5

^{1}H NMR of **5**

$CDCl_3$, 300 MHz

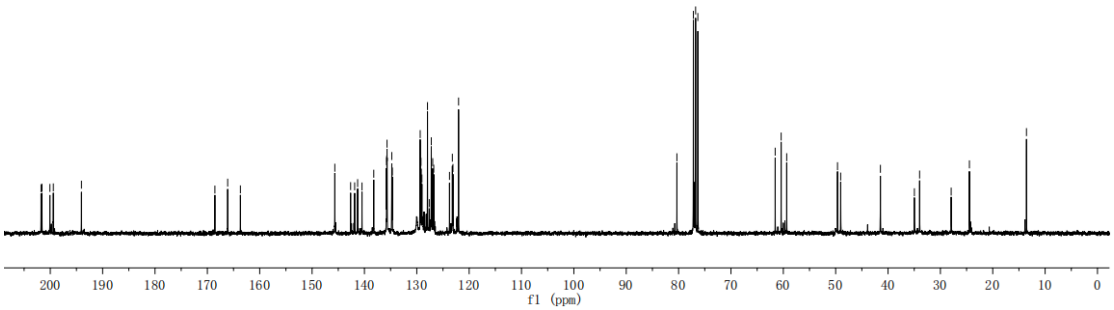




5

^{13}C NMR of **5**

$CDCl_3$, 75 MHz



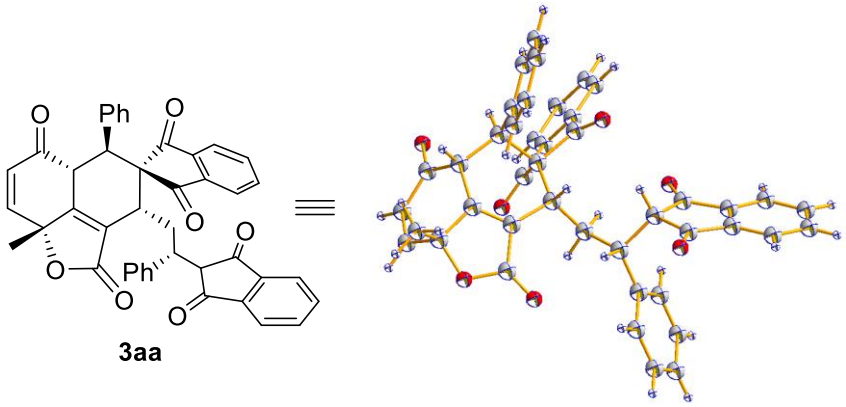
X-ray diffraction analysis of compound 3aa and 4aa.

Crystallization procedure of 3aa: To a 50 mL flat bottom of flask loaded with 100 mg of the pale yellow solid **3aa**, small amount of $CHCl_3$ was slowly added, which was just enough to dissolve the solid. Small amount of CH_3OH was then added to make a turbid mixture. Subsequently, $CHCl_3$ was slowly added until the mixture became a clear solution. Then the flask was sealed and left standing set them at room temperature. Bulky yellow crystals suitable for X-ray analysis were collected after 2 days.

Crystallization procedure of 4aa: 30 mg of **4aa** was added in a vial and dissolved by 1 mL of ethyl acetate, and then 0.5 mL of petroleum ether was added. The bottle was then sealed and left standing at room temperature overnight, giving small amount of colorless stick-liked crystals suitable for X-ray analysis.

X-Ray Crystallography Data Crystallographic data for **3aa** and **4aa** has been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 1898871 and 1921150. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

X-Ray Crystallography Data Crystallographic data for **3aa**. The ellipsoid contour percent probability level of **3aa** is 30%.



3aa

Table S1. Crystal data and structure refinement for **3aa.**

Identification code	**3aa**
Empirical formula	$C_{44.25}H_{32}Cl_3O_{7.25}$
Formula weight	786.05
Temperature/K	153.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	19.442(4)
b/Å	9.779(2)
c/Å	20.905(4)

α/°	90
β/°	106.26(3)
γ/°	90
Volume/Å^3	3815.5(14)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.293
F(000)	1626.0
Crystal size/mm^3	0.12 × 0.1 × 0.04
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.182 to 54.918
Index ranges	-25 ≤ h ≤ 25, -12 ≤ k ≤ 12, -27 ≤ l ≤ 25
Reflections collected	27391
Independent reflections	8637 [R_{int} = 0.0426, R_{sigma} = 0.0436]
Data/restraints/parameters	8637/18/506
Goodness-of-fit on F^2	1.170
Final R indexes [I>=2σ (I)]	R_1 = 0.1067, wR_2 = 0.2582
Final R indexes [all data]	R_1 = 0.1173, wR_2 = 0.2666
Largest diff. peak/hole / e Å^{-3}	0.61/-0.87

X-Ray Crystallography Data Crystallographic data for **4aa**. The ellipsoid contour percent probability level of **4aa** is 30%.

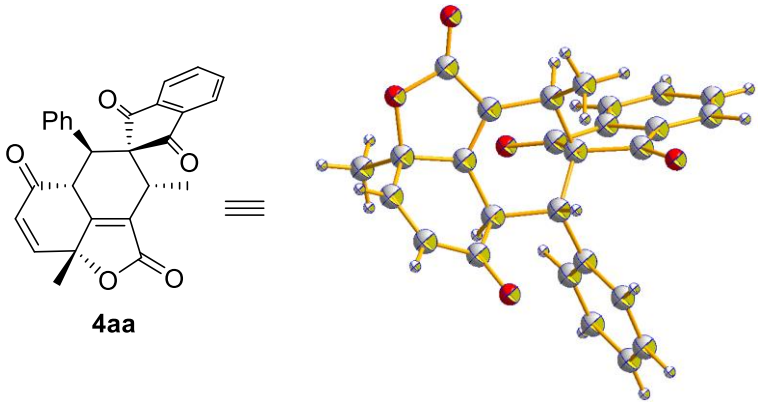


Table S2. Crystal data and structure refinement for **4aa**.

Identification code	**4aa**
Empirical formula	$C_{55}H_{42}Cl_2O_{10}$
Formula weight	933.78
Temperature/K	153.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.867(2)
b/Å	13.765(3)
c/Å	59.046(12)
α/°	90

β/°	90
γ/°	90
Volume/Å^3	8833(3)
Z	8
ρ_{calc}g/cm^3	1.404
μ/mm^{-1}	0.212
F(000)	3888.0
Crystal size/mm^3	0.12 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.138 to 55.04
Index ranges	-14 ≤ h ≤ 12, -17 ≤ k ≤ 17, -73 ≤ l ≤ 76
Reflections collected	40856
Independent reflections	10003 [R_{int} = 0.0815, R_{sigma} = 0.0787]
Data/restraints/parameters	10003/54/636
Goodness-of-fit on F^2	1.317
Final R indexes [I>=2σ (I)]	R_1 = 0.1275, wR_2 = 0.2182
Final R indexes [all data]	R_1 = 0.1482, wR_2 = 0.2284
Largest diff. peak/hole / e Å^{-3}	1.00/-0.33