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SUPPORTING INFORMATION

Organocatalyzed benzannulation for the construction of diverse anthraquinones and tetracenediones

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1. Experimental Section

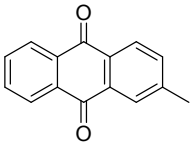
All experiments were carried out in a nitrogen atmosphere. Merck, pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H NMR spectra were recorded on Varian 300 or 600 MHz spectrometers and the chemical shifts were described in parts per million (δ) relative to TMS (0 ppm) as internal standard or relative to the resonance of the residual protonated solvent (^{1}H : $CDCl_3$, δ = 7.24 ppm). ^{13}C NMR spectra were obtained at 75 MHz or 150 MHz spectrometers and referenced to the internal solvent signals (^{13}C: $CDCl_3$, δ = 77.0 ppm). IR spectra were recorded on a Jasco FTIR 5300 spectrophotometer. Melting points were measured with a Fisher-Johns melting point apparatus and uncorrected. The high-resolution mass spectra (HRMS) were measured using a JEOL JMS-600 mass spectrometer (positive ion EI mode) at the Korean Basic Science Institute.

2. General Procedure for Synthesis of Compounds 3, 4 and 9

Mixture of 1,4-naphthoquinones (**1a-e**) or 1,4-anthracenedione (**1f**) or 1,2-naphthoquinone (**8**) or 1,4 benzoquinone (**10**) (1.0 mmol), aldehydes (**2**, 1.6 mmol), L-Proline (20 mol %) and benzoic acid (10 mol %) in Toluene (5 mL) was stirred at 50 ^{o}C for 5 h. After completion of reaction as indicated by TLC, the reaction mixture was evaporated in rotary evaporator and the residue was purified on a silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired product.

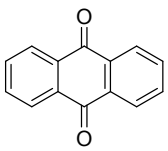
3. ^{1}H NMR and ^{13}C NMR Data of Synthesized Compounds 3, 4 and 9

2-Methylanthracene-9,10-dione (3a)



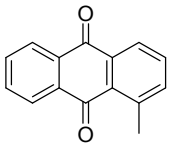
Yield 78% (173 mg) as an orange color solid: mp 170-172 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23-8.17 (2H, m), 8.09 (1H, d, J = 7.8), 7.98 (1H, s), 7.72-7.68 (2H, m), 7.49 (1H, dd, J = 0.6, 8.1 Hz), 2.45 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.2, 182.7, 145.1, 134.8, 133.9, 133.8, 133.4, 133.3, 133.2, 131.0, 127.3, 127.2, 127.0, 126.9, 21.8; IR (KBr) 2924, 2856, 1673, 1593, 1462, 1328, 1294, 710 cm^{-1}; HRMS *m/z* (M^{+}) calcd for $C_{15}H_{10}O_2$: 222.0681. Found: 222.0681.

Anthracene-9,10-dione (3b)



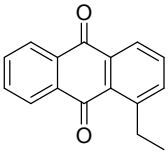
Yield 75% (156 mg) as a yellow solid: mp 283-285 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32-8.29 (4H, m), 7.80-7.77 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.1, 134.1, 133.5, 127.2; IR (KBr) 2923, 1675, 1584, 1284, 1165, 1027, 937, 810, 694 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_8O_2$: 208.0524. Found: 208.0526.

1-Methylanthracene-9,10-dione (3c)



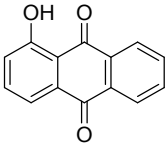
Yield 67% (149 mg) as a yellow solid: mp 171-173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23-8.18 (3H, m), 7.77-7.68 (2H, m), 7.62-7.51 (2H, m), 2.81 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.9, 183.5, 141.9, 138.1, 134.8, 134.6, 134.0, 133.4, 133.0, 132.7, 131.1, 127.1, 126.6, 126.0, 23.4; IR (KBr) 2925, 1673, 1584, 1324, 1270, 1161, 969, 809, 703 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{10}O_2$: 222.0681. Found: 222.0683.

1-Ethylanthracene-9,10-dione (3d)



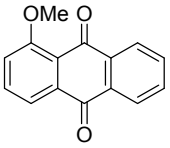
Yield 60% (142 mg) as a yellow solid: mp 96-98 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24-8.21 (3H, m), 7.78-7.72 (2H, m), 7.67-7.57 (2H, m), 3.27 (2H, q, J = 7.2 Hz), 1.30 (3H, t, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.8, 183.6, 148.1, 136.9, 135.4, 134.9, 134.1, 133.4, 133.3, 132.6, 130.7, 127.2, 126.5, 126.0, 28.7, 15.1; IR (KBr) 2965, 1671, 1582, 1264, 1095, 1024, 803, 702 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_2$: 236.0837. Found: 236.0835.

1-Hydroxyanthracene-9,10-dione (3e)



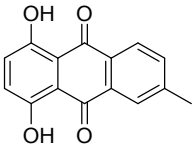
Yield 80% (179 mg) as a yellow solid: mp 194-196 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.52 (1H, s), 8.23 (2H, br s), 7.74 (3H, br s), 7.60 (1H, t, J = 8.1 Hz), 7.24-7.18 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8, 182.5, 162.7, 136.9, 134.8, 134.3, 133.8, 133.6, 133.3, 127.6, 127.0, 124.5, 119.7, 116.3; IR (KBr) 3459, 1637, 1588, 1457, 1359, 1289, 775, 706 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_8O_3$: 224.0473. Found: 224.0473.

1-Methoxyanthracene-9,10-dione (3f)



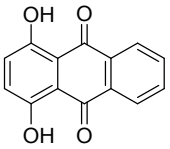
Yield 83% (198 mg) as a yellow solid: mp 168-170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19-8.12 (2H, m), 7.87 (1H, d, J = 7.5 Hz), 7.72-7.59 (3H, m), 7.26 (1H, d, J = 8.4 Hz), 3.97 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.6, 182.6, 160.6, 135.9, 135.1, 135.2, 134.4, 133.4, 132.6, 127.4, 126.7, 121.7, 119.9, 118.1, 56.7; IR (KBr) 2927, 1671, 1582, 1445, 1320, 1267, 965, 777, 704 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}O_3$: 238.0630. Found: 238.0631.

1,4-Dihydroxy-6-methylanthracene-9,10-dione (3g)



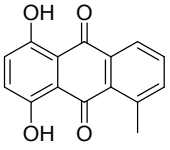
Yield 94% (239 mg) as an orange color solid: mp 176-178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.82 (1H, s), 12.77 (1H, s), 8.10 (1H, d, J = 8.1 Hz), 8.00 (1H, s), 7.53 (1H, d, J = 7.2 Hz), 7.20 (2H, s), 2.49 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.9, 186.6, 157.6, 157.5, 145.8, 135.2, 133.2, 131.0, 129.2, 128.9, 127.1, 127.0, 112.7, 112.6, 21.9; IR (KBr) 3428, 1630, 1586, 1448, 1335, 1261, 1212, 970, 787, 578 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}O_4$: 254.0579. Found: 254.0580.

1,4-Dihydroxyanthracene-9,10-dione (3h)



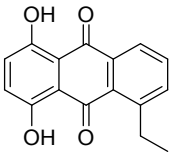
Yield 82% (197 mg) as an orange color solid: mp 196-198 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.73 (2H, s), 8.20-8.17 (2H, m), 7.73-7.70 (2H, m), 7.16 (2H, s); ^{13}C NMR (150 MHz, $CDCl_3$ + DMSO-d_6) δ 186.5, 157.5, 134.2, 133.1, 129.1, 126.7, 112.4; IR (KBr) 3422, 1636, 1587, 1450, 1343, 1220, 1148, 1020, 779, 577 cm^{-1}; HRMS m/z (M^+) calcd for $C_{14}H_8O_4$: 240.0423. Found: 240.0421.

1,4-Dihydroxy-5-methylanthracene-9,10-dione (3i)



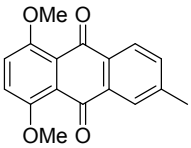
Yield 90% (229 mg) as an orange color solid: mp 234-236 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.01 (1H, s), 12.77 (1H, s), 8.18 (1H, d, J = 7.8 Hz), 7.57 (1H, t, J = 7.8 Hz), 7.50 (1H, d, J = 7.8 Hz), 7.20-7.16 (2H, m), 2.78 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.3, 187.0, 157.4, 157.1, 142.7, 138.7, 134.7, 133.5, 130.9, 129.4, 128.2, 125.8, 113.5, 112.5, 23.9; IR (KBr) 3452, 1688, 1617, 1578, 1450, 1382, 1224, 1068, 784, 587 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{10}O_4$: 254.0579. Found: 254.0580.

5-Ethyl-1,4-dihydroxyanthracene-9,10-dione (3j)



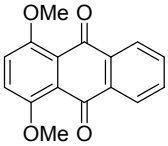
Yield 93% (250 mg) as an orange color solid: mp 98-100 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.02 (1H, s), 12.75 (1H, s), 8.15 (1H, dd, J = 1.2, 7.8 Hz), 7.60 (1H, t, J = 7.8 Hz), 7.53 (1H, dd, J = 1.2, 7.2 Hz), 7.19-7.14 (2H, m), 3.22 (2H, q, J = 7.8 Hz), 1.25 (3H, t, J = 7.8 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.0, 186.8, 157.3, 157.0, 148.7, 137.3, 134.8, 133.7, 130.2, 129.3, 128.1, 125.7, 113.5, 112.3, 29.0, 14.9; IR (KBr) 3465, 1615, 1578, 1451, 1371, 1223, 1067, 784, 578 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_4$: 268.0736. Found: 268.0732.

1,4-Dimethoxy-6-methylanthracene-9,10-dione (3k)



Yield 93% (262 mg) as a yellow solid: mp 178-180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (1H, d, J = 7.8 Hz), 7.92 (1H, s), 7.48 (1H, d, J = 8.4 Hz), 7.30 (2H, s), 3.97 (6H, s), 2.46 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.7, 183.3, 154.1, 144.2, 134.2, 134.1, 132.0, 126.6, 126.5, 123.2, 123.1, 120.2, 120.0, 57.0, 21.8; IR (KBr) 2941, 1661, 1576, 1460, 1408, 1325, 1259, 1195, 1061, 992, 819 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{17}H_{14}O_4$: 282.0892. Found: 282.0891.

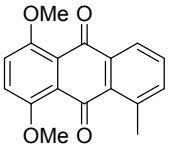
1,4-Dimethoxyanthracene-9,10-dione (3l)



Yield 88% (236 mg) as a yellow solid: mp 170-172 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14-8.11 (2H, m), 7.68-7.66 (2H, m), 7.31 (2H, s), 3.96 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.3, 154.1, 134.2, 133.2, 126.3,

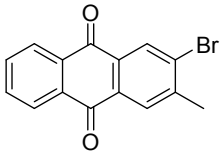
123.1, 120.3, 57.0; IR (KBr) 2947, 1670, 1577, 1467, 1410, 1255, 1179, 1052, 973, 818, 726, 576 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_4$: 268.0736. Found: 268.0733.

1,4-Dimethoxy-5-methylanthracene-9,10-dione (3m)



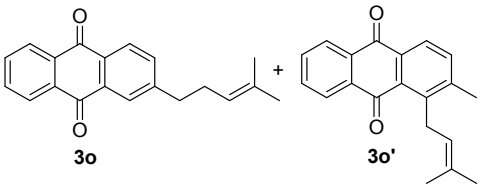
Yield 91% (257 mg) as a yellow solid: mp 105-107 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (1H, d, J = 7.8 Hz), 7.46 (1H, t, J = 7.8 Hz), 7.40 (1H, d, J = 7.8 Hz), 7.22-7.18 (2H, m), 3.91 (3H, s), 3.90 (3H, s), 2.69 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.8, 184.1, 153.2, 153.0, 139.5, 136.6, 135.7, 132.8, 132.1, 125.3, 124.8, 122.7, 120.0, 118.6, 57.0, 56.8, 22.0; IR (KBr) 2931, 1669, 1577, 1463, 1412, 1259, 1192, 1049, 985, 804, 728 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{17}H_{14}O_4$: 282.0892. Found: 282.0888.

2-Bromo-3-methylanthracene-9,10-dione (3n)



Yield 47% (142 mg) as a yellow solid: mp 223-225 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (1H, s), 8.26-8.25 (2H, m), 8.09 (1H, s), 7.78-7.76 (2H, m), 2.54 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 182.7, 182.0, 145.1, 134.2, 133.3, 133.2, 132.3, 132.1, 132.0, 131.2, 129.2, 127.3, 127.2, 23.5; IR (KBr) 3068, 1673, 1585, 1325, 1311, 1283, 1208, 988, 950, 710, 654, 599 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_9BrO_2$: 299.9786. Found: 299.9788.

2-(4-Methylpent-3-enyl)anthracene-9,10-dione (3o) and 2-Methyl-1-(3-methylbut-2-en-1-yl)anthracene-9,10-dione (3o')

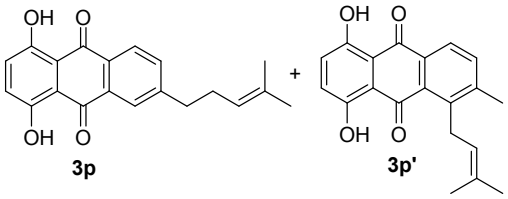


3o and **3o'** were obtained as an inseparable 95:05 mixture in 67% (195 mg) yield. **3o:** An orange color solid: mp 80-82 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29-8.27 (2H, m), 8.19 (1H, d, J = 7.8 Hz), 8.10 (1H, d, J = 1.2 Hz), 7.78-7.75 (2H, m), 7.58 (1H, dd, J = 1.2, 7.8 Hz), 5.13 (1H, t, J = 7.2 Hz), 2.79 (2H, t, J = 7.8 Hz), 2.36 (2H, q, J = 7.8 Hz), 1.66 (3H, s), 1.52 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.3, 182.9, 149.6, 134.4, 133.9,

133.8, 133.7, 133.6, 133.4, 133.0, 131.5, 127.3, 127.1, 127.0, 126.9, 122.6, 36.2, 29.3, 25.6, 17.6; IR (KBr) 2918, 1673, 1591, 1326, 1295, 930, 710 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1309.

3o': 4.93 (1H, t, *J* = 5.4 Hz), 3.94 (2H, d, *J* = 5.4 Hz), 2.42 (3H, s), 1.82 (3H, s), 1.76 (3H, s).

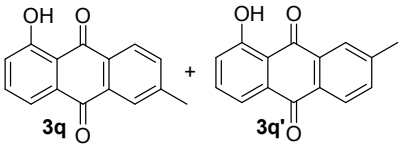
1,4-Dihydroxy-6-(4-methylpent-3-en-1-yl)anthracene-9,10-dione (3p) and 5,8-Dihydroxy-2-methyl-1-(3-methylbut-2-en-1-yl)anthracene-9,10-dione (3p')



3p and **3p'** were obtained as an inseparable 87:13 mixture in 85% (274 mg) yield. **3p:** An orange color solid: mp 68-70 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.82 (1H, s), 12.79 (1H, s), 8.12 (1H, d, *J* = 7.2 Hz), 8.02 (1H, s), 7.54 (1H, dd, *J* = 1.2, 7.8 Hz), 7.19 (2H, s), 5.12 (1H, t, *J* = 7.2 Hz), 2.76 (2H, t, *J* = 7.8 Hz), 2.34 (2H, q, *J* = 7.8 Hz), 1.66 (3H, s), 1.52 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.0, 186.6, 157.6, 157.5, 150.1, 134.7, 133.2, 133.1, 131.1, 129.1, 128.9, 127.0, 126.6, 122.5, 112.7, 112.6, 36.2, 29.2, 25.6, 17.6; IR (KBr) 3460, 2929, 1586, 1447, 1336, 1232, 1154, 787, 573 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{20}H_{18}O_4$: 322.1205. Found: 322.1206.

3p': ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.93 (1H, s), 12.78 (1H, s), 8.06 (1H, d, *J* = 7.8 Hz), 7.47 (1H, d, *J* = 8.4 Hz), 7.19 (2H, s), 5.00 (1H, t, *J* = 6.0 Hz), 3.91 (2H, d, *J* = 6.0 Hz), 2.39 (3H, s), 1.81 (3H, s), 1.70 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.5, 186.7, 157.2, 156.8, 146.3, 144.3, 135.8, 133.0, 132.8, 130.5, 128.0, 125.5, 121.0, 117.9, 113.8, 112.4, 29.8, 25.7, 20.9, 18.1.

1-Hydroxy-6-methylanthracene-9,10-dione (3q) and 1-Hydroxy-7-methylanthracene-9,10-dione (3q')

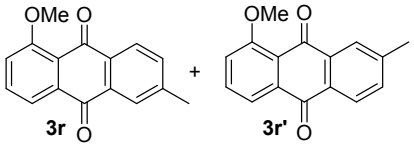


3q and **3q'** were obtained as an inseparable 77:23 mixture in 77% (183 mg) yield (**2a** was used) and as an inseparable 15:85 mixture in 66% yield (**2f** was used). **3q** (**2a** was used)**:** A yellow solid: mp 128-130 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.56 (1H, s), 8.08 (1H, d, *J* = 7.8 Hz), 7.97 (1H, s), 7.73-7.71 (1H, m), 7.60-7.57 (1H, m), 7.50 (1H, d, *J* = 7.8 Hz), 7.21 (1H, dd, *J* = 1.2, 7.8 Hz), 2.47 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 188.3 & 182.4 (**3q**, C=O), 188.7 & 182.0 (**3q'**, C=O), 162.4, 162.3, 145.9, 145.3, 136.5, 136.4, 135.3, 134.8, 133.5, 133.4, 133.3, 132.9, 131.2, 130.7, 127.6, 127.5, 127.0, 126.9, 124.1, 124.0, 119.33, 119.31, 116.1, 116.0,

21.9 (**3q**, CH_3), 21.8 (**3q',** CH_3); IR (KBr) 3428, 1672, 1633, 1597, 1454, 1354, 1295, 1261, 1227, 1151, 1035, 772, 711 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{10}O_3$: 238.0630. Found: 238.0626.

3q' (**2f** was used)**:** A yellow solid: mp 156-158 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 12.51 (1H, s), 8.07 (1H, d, J = 7.8 Hz), 7.98 (1H, s), 7.73-7.71 (1H, m), 7.60-7.57 (1H, m), 7.50 (1H, d, J = 7.8 Hz), 7.21 (1H, dd, J = 1.2, 7.8 Hz), 2.47 (3H, s); IR (KBr) 3428, 1670, 1639, 1595, 1351, 1290, 1155, 1032, 901, 770, 710, 663 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_{10}O_3$: 238.0630. Found: 238.0627.

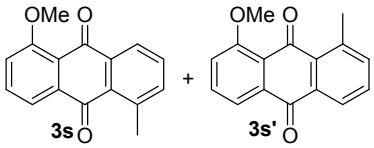
1-Methoxy-6-methylanthracene-9,10-dione (3r) and 1-Methoxy-7-methylanthracene-9,10-dione (3r')



3r and **3r'** were obtained as an inseparable 20:80 mixture in 91% (230 mg) yield (**2a** was used) and as an inseparable 74:26 mixture in 77% yield (**2f** was used). **3r'**(**2a** was used)**:** A yellow solid: mp 148-150 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.97 (1H, d, J = 7.2 Hz), 7.90 (1H, s), 7.80 (1H, d, J = 7.2 Hz), 7.58-7.56 (1H, m), 7.39 (1H, d, J = 7.2 Hz), 7.21-7.20 (1H, m), 3.92 (3H, s), 2.39 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.4 & 182.2 (**3r**, C=O), 182.9 & 182.5 (**3r'**, C=O), 160.1, 145.2, 144.0, 140.7, 136.0, 135.6, 134.9, 134.8, 134.7, 134.6, 133.9, 132.6, 132.1, 130.0, 127.3, 127.2, 126.6, 126.5, 121.4, 121.3, 119.6, 119.5, 117.7, 117.6, 56.3 (**3r'**, OCH_3), 56.2 (**3r**, OCH_3), 21.8 (**3r'**, CH_3), 21.5 (**3r**, CH_3); IR (KBr) 2946, 1669, 1583, 1443, 1325, 1274, 1192, 1064, 974, 848, 744 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0785.

3r (**2f** was used)**:** A yellow solid: mp 112-114 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.02 (1H, d, J = 7.2 Hz), 7.86 (1H, s), 7.80 (1H, d, J = 7.2 Hz), 7.58-7.56 (1H, m), 7.44 (1H, d, J = 7.2 Hz), 7.21-7.20 (1H, m), 3.88 (3H, s), 2.38 (3H, s); IR (KBr) 2942, 1672, 1580, 1444, 1325, 1274, 1063, 976, 842, 786, 742 cm^{-1}; HRMS m/z (M^+) calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0788.

1-Methoxy-5-methylanthracene-9,10-dione (3s) and 1-Methoxy-8-methylanthracene-9,10-dione (3s')

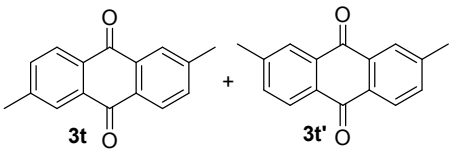


3s and **3s'** were obtained as an inseparable 05:95 mixture in 85% (214 mg) yield. **3s':** A yellow solid: mp 170-172 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.08 (1H, dd, J = 1.8, 7.2 Hz), 7.83 (1H, d, J = 7.8 Hz), 7.61 (1H, t, J = 7.8 Hz), 7.52-7.48 (2H, m), 7.27 (1H, d, J = 8.4 Hz), 3.99 (3H, s), 2.77 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 185.1, 184.0, 159.7, 140.9, 138.1, 135.0, 134.2, 133.8, 133.2, 132.1, 125.2, 123.3, 119.0, 117.9, 56.5, 22.9; IR

(KBr) 2924, 1671, 1583, 1446, 1324, 1248, 981, 796, 732, cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_3$: 252.0786. Found: 252.0784.

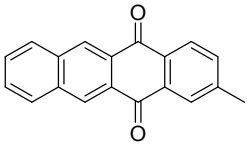
3s: ^1H NMR (600 MHz, $CDCl_3$) δ 8.12 (1H, d, J = 7.8 Hz), 7.88 (1H, d, J = 7.8 Hz), 7.61 (1H, t, J = 7.8 Hz), 7.52-7.48 (2H, m), 7.32 (1H, d, J = 9.0 Hz), 4.01 (3H, s), 2.77 (3H, s).

2,6-Dimethylanthracene-9,10-dione (3t) and 2,7-Dimethylanthracene-9,10-dione (3t')



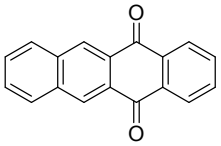
3t and **3t'** were obtained as an inseparable 50:50 mixture in 62% (146 mg) yield. A yellow solid: mp 237-239 ^oC; ^1H NMR (600 MHz, $CDCl_3$) δ 8.12 (2H, dd, J = 1.8, 7.8 Hz), 8.02 (2H, s), 7.52 (2H, d, J = 7.8 Hz), 2.47 (6H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.1 (**3t**, C=O), [183.5, 182.7 (**3t'**, C=O)], 154.0, 144.9, 134.7, 134.6, 133.5, 133.4, 131.35, 131.32, 127.37, 127.35, 127.32, 127.2, 21.82, 21.80; IR (KBr) 1667, 1592, 1391, 1304, 1148, 976, 852, 725 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{16}H_{12}O_2$: 236.0837. Found: 236.0839.

2-Methyltetracene-5,12-dione (4a)



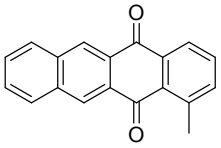
Yield 86% (234 mg) as an orange color solid: mp 238-240 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (2H, s), 8.20 (1H, d, J = 7.8 Hz), 8.09 (1H, s), 8.02-7.99 (2H, m), 7.63-7.60 (2H, m), 7.54 (1H, d, J = 7.8 Hz), 2.49 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 182.6, 145.2, 135.1, 135.0, 134.9, 134.2, 132.1, 130.0, 129.8, 129.7, 129.4, 129.3, 129.2, 127.6, 21.8; IR (KBr) 1667, 1589, 1450, 1394, 1287, 1176, 972, 749, 551 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{12}O_2$: 272.0837. Found: 272.0836.

Tetracene-5,12-dione (4b)



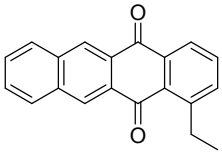
Yield 60% (155 mg) as an orange color solid: mp 184-186 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 8.82 (2H, s), 8.38-8.35 (2H, m), 8.08-8.05 (2H, m), 7.68-7.65 (2H, m); ^{13}C NMR (75 MHz, DMSO-d_6) δ 182.2, 134.5, 134.0, 130.1, 129.7, 129.4, 128.9, 126.9, 126.6; IR (KBr) 1672, 1580, 1451, 1394, 1280, 957, 754, 711 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{18}H_{10}O_2$: 258.0681. Found: 258.0681.

1-Methyltetracene-5,12-dione (4c)



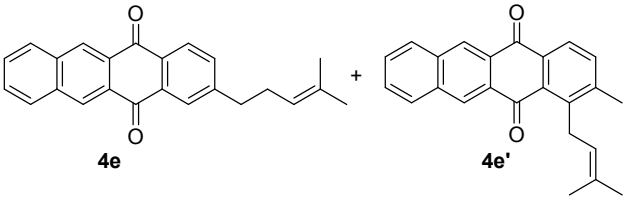
Yield 75% (204 mg) as an orange color solid: mp 230-232 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (2H, d, J = 9.0 Hz), 8.26 (1H, dd, J = 1.2, 7.8 Hz), 8.02-8.00 (2H, m), 7.63-7.59 (3H, m), 7.54 (1H, d, J = 7.8 Hz), 2.85 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.8, 183.4, 142.2, 138.1, 135.9, 135.2, 134.8, 133.0, 132.1, 130.9, 130.0, 129.9, 129.3, 29.2, 129.0, 128.7, 126.9, 126.2, 23.6; IR (KBr) 1666, 1577, 1448, 1405, 1271, 1161, 977, 753 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{19}H_{12}O_2$: 272.0837. Found: 272.0835.

1-Ethyltetracene-5,12-dione (4d)



Yield 78% (223 mg) as a yellow solid: mp 142-144 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (2H, d, J = 6.0 Hz), 8.28 (1H, d, J = 7.8 Hz), 8.02-8.01 (2H, m), 7.65-7.57 (4H, m), 3.30 (2H, q, J = 7.2 Hz), 1.32 (3H, t, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.7, 183.4, 148.3, 136.9, 136.1, 135.2, 134.7, 133.3, 131.7, 131.0, 129.9, 129.3, 129.2, 129.2, 129.1, 129.1, 128.7, 126.2, 28.8, 15.2; IR (KBr) 1667, 1579, 1451, 1394, 1277, 1206, 963, 756 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{20}H_{14}O_2$: 286.0994. Found: 286.0993.

2-(4-Methylpent-3-en-1-yl)tetracene-5,12-dione (4e) and 2-Methyl-1-(3-methylbut-2-en-1-yl)tetracene-5,12-dione (4e')

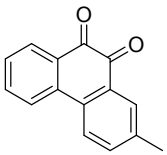


4e and **4e'** were obtained as an inseparable 96:04 mixture in 74% (252 mg) yield. **4e:** An orange color solid: mp 133-135 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (2H, d, J = 3.6 Hz), 8.26 (1H, d, J = 7.8 Hz), 8.16 (1H, s), 8.06-8.04 (2H, m), 7.66-7.64 (2H, m), 7.59 (1H, dd, J = 1.8, 7.8 Hz), 5.14 (1H, t, J = 7.2 Hz), 2.80 (2H, t, J = 7.8 Hz), 2.39-2.35 (2H, m), 1.66 (3H, s), 1.53 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 183.0, 182.6, 149.5, 135.0, 134.9, 134.4, 134.3, 133.0, 132.4, 130.0, 129.9, 129.8, 129.4, 129.3, 129.2, 127.5, 127.1, 122.7, 36.2,

29.3, 25.6, 17.6; IR (KBr) 1667, 1590, 1448, 1391, 1287, 1174, 938, 751 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{24}H_{20}O_2$: 340.1463. Found: 340.1465.

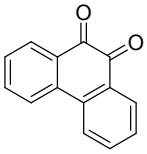
4e': 4.93 (1H, t, *J* = 6.6 Hz), 3.97 (2H, d, *J* = 6.6 Hz), 2.43 (3H, s), 1.84 (3H, s), 1.72 (3H, s).

2-Methylphenanthrene-9,10-dione (9a)



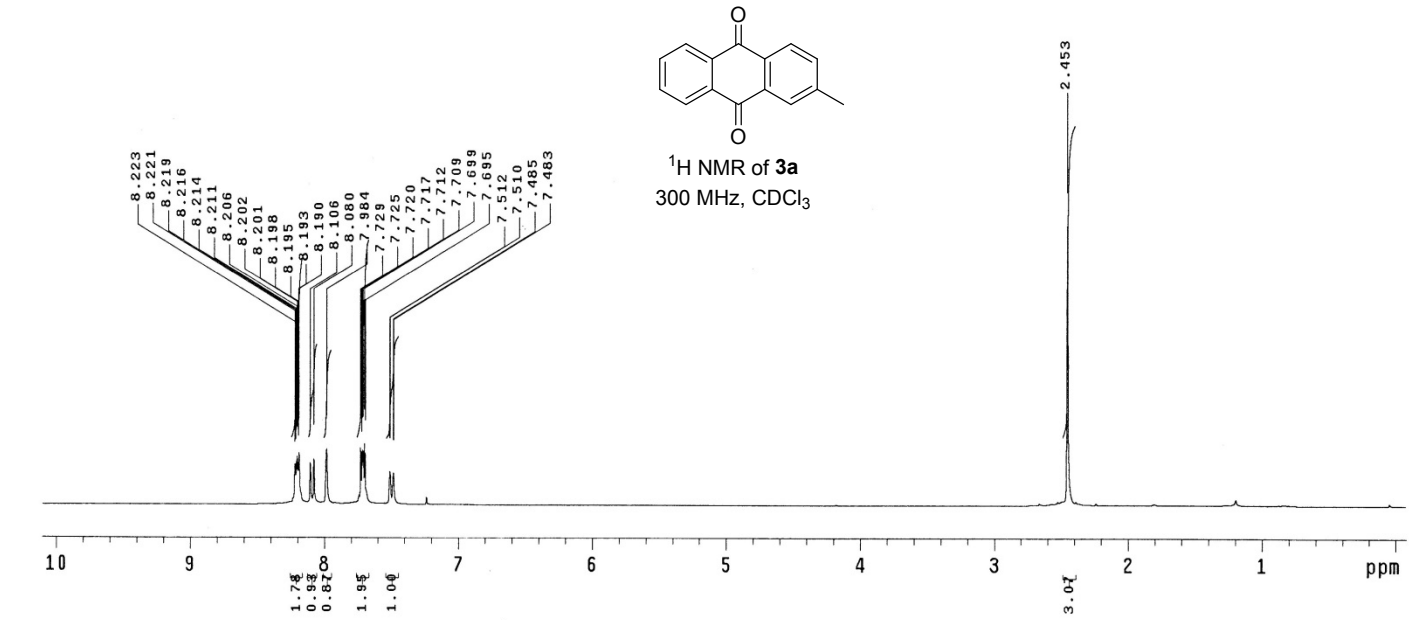
Yield 53% (118 mg) as a yellow solid: mp 180-182 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.07 (1H, d, *J* = 7.8 Hz), 7.97 (1H, d, *J* = 7.8 Hz), 7.89 (1H, d, *J* = 8.1 Hz), 7.71(1H, s), 7.60 (1H, t, *J* = 7.2 Hz), 7.36 (1H, t, *J* = 7.2 Hz), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.6, 179.8, 147.3, 135.9, 135.8, 135.7, 131.1, 130.7, 130.5, 130.4, 129.4, 128.8, 124.5, 123.8, 22.3; IR (KBr) 2926, 1672, 1593, 1443, 1290, 925, 773, 534 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{10}O_2$: 222.0681. Found: 222.0682.

Phenanthrene-9,10-dione (9b)

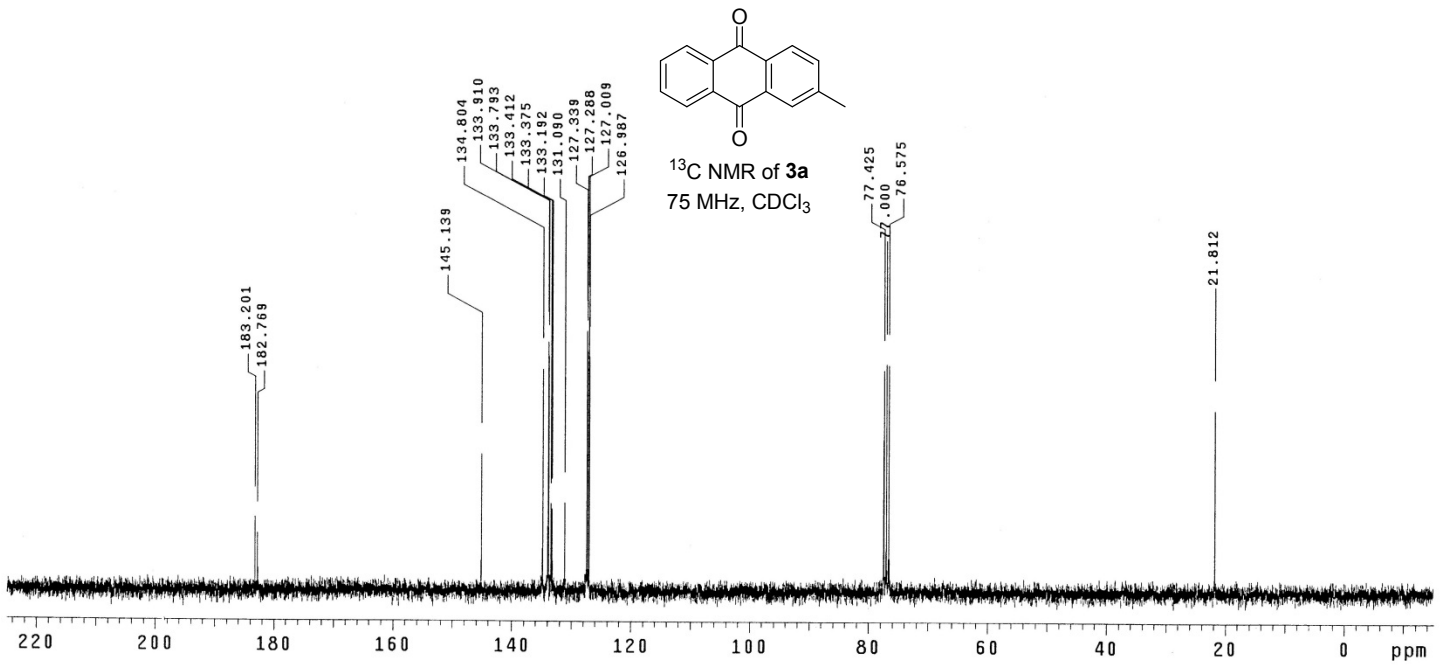


Yield 57% (119 mg) as a yellow solid: mp 205-207 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 8.17 (2H, d, *J* = 7.8 Hz), 8.00 (2H, d, *J* = 7.8 Hz), 7.69 (2H, t, *J* = 7.2 Hz), 7.45 (2H, t, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 180.3, 135.9, 135.8, 131.0, 130.4, 129.5, 123.9; IR (KBr) 2926, 1674, 1590, 1448, 1283, 923, 763 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_8O_2$: 208.0524. Found: 208.0523.

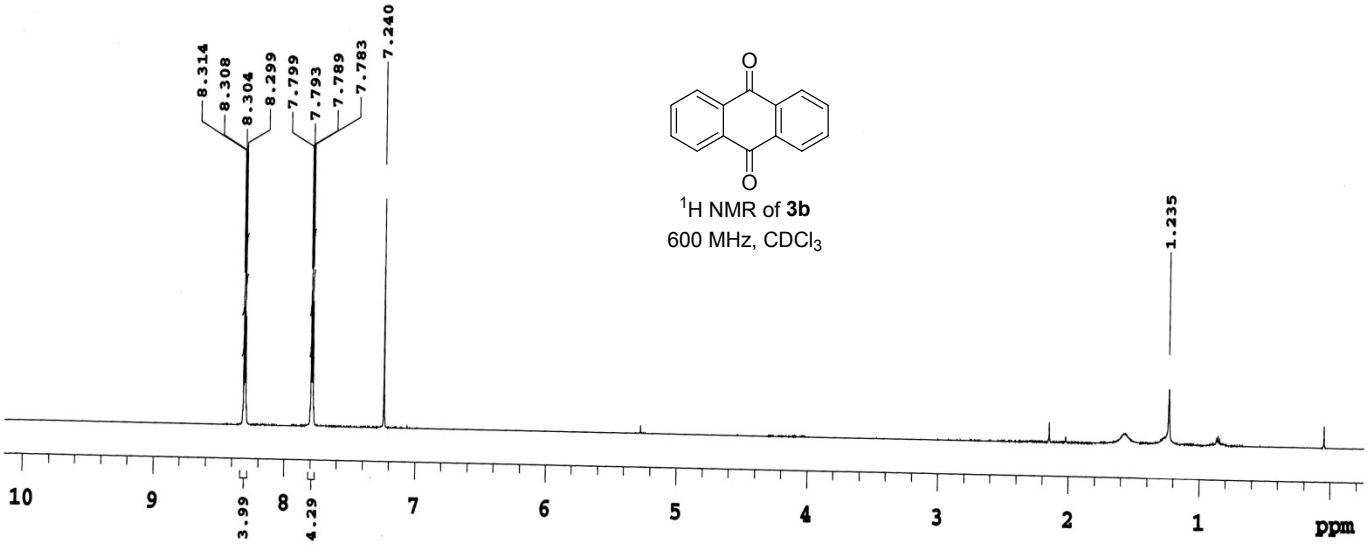
4. ^{1}H NMR and ^{13}C NMR Spectra of Synthesized Compounds 3, 4 and 9



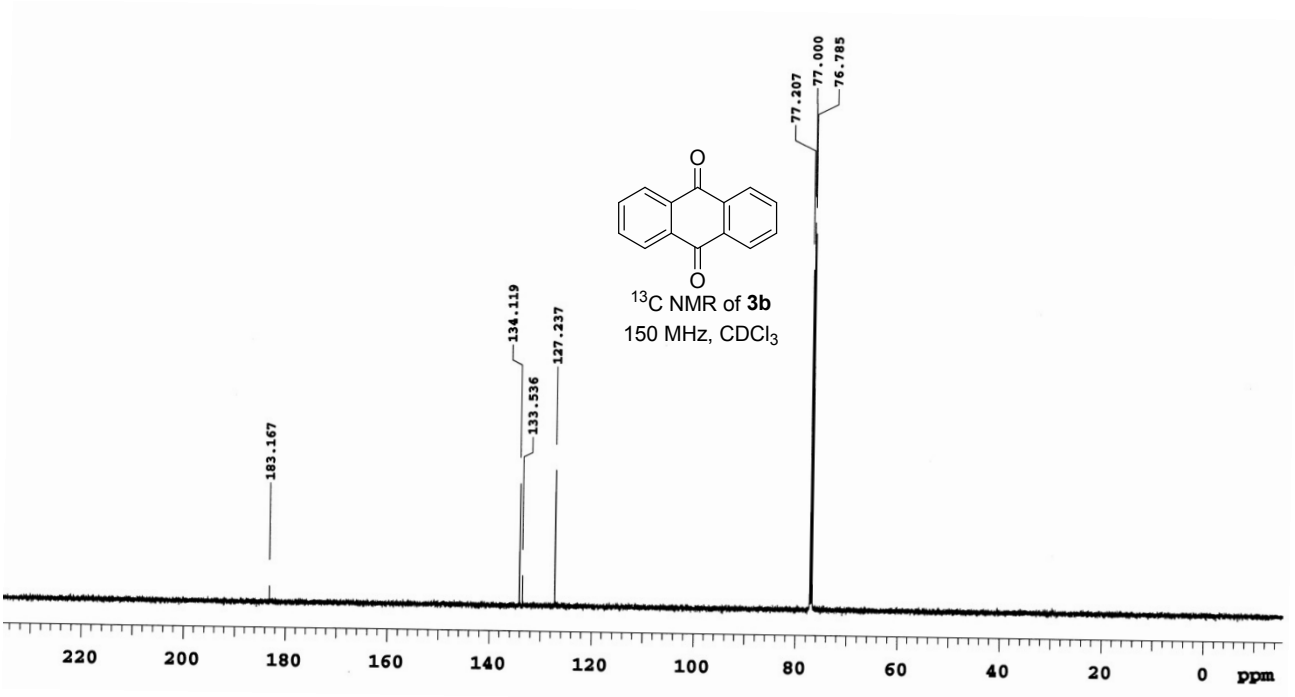
^{1}H NMR of **3a**
300 MHz, $CDCl_3$



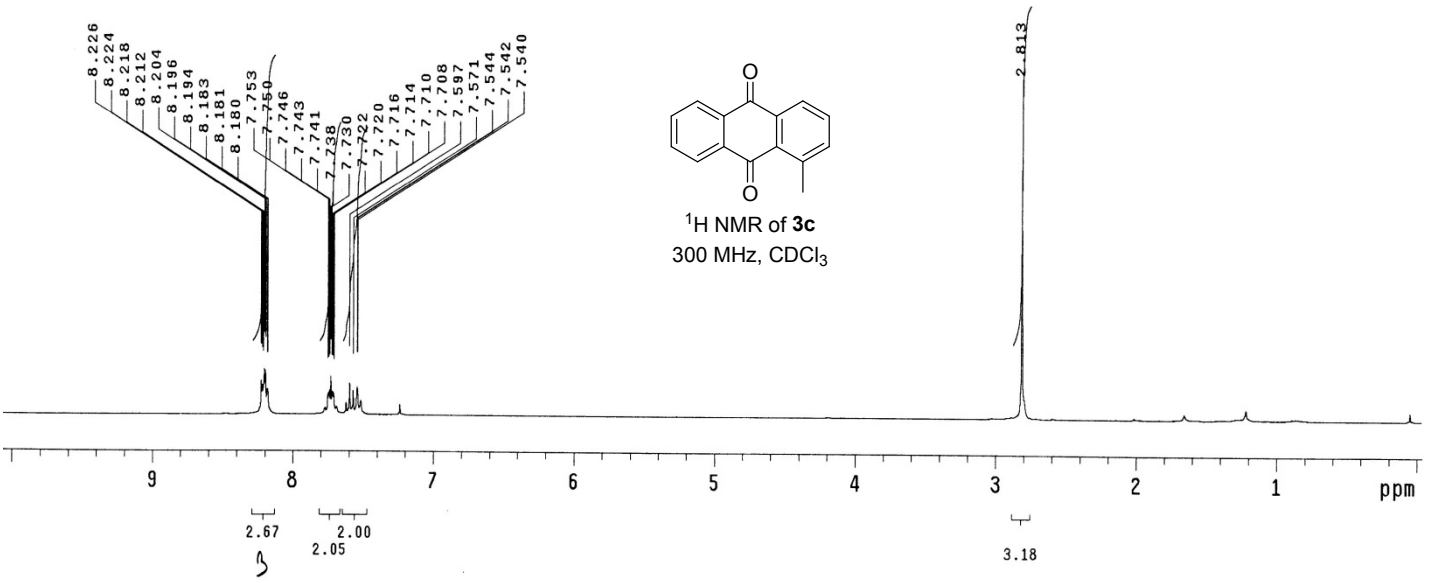
^{13}C NMR of **3a**
75 MHz, $CDCl_3$



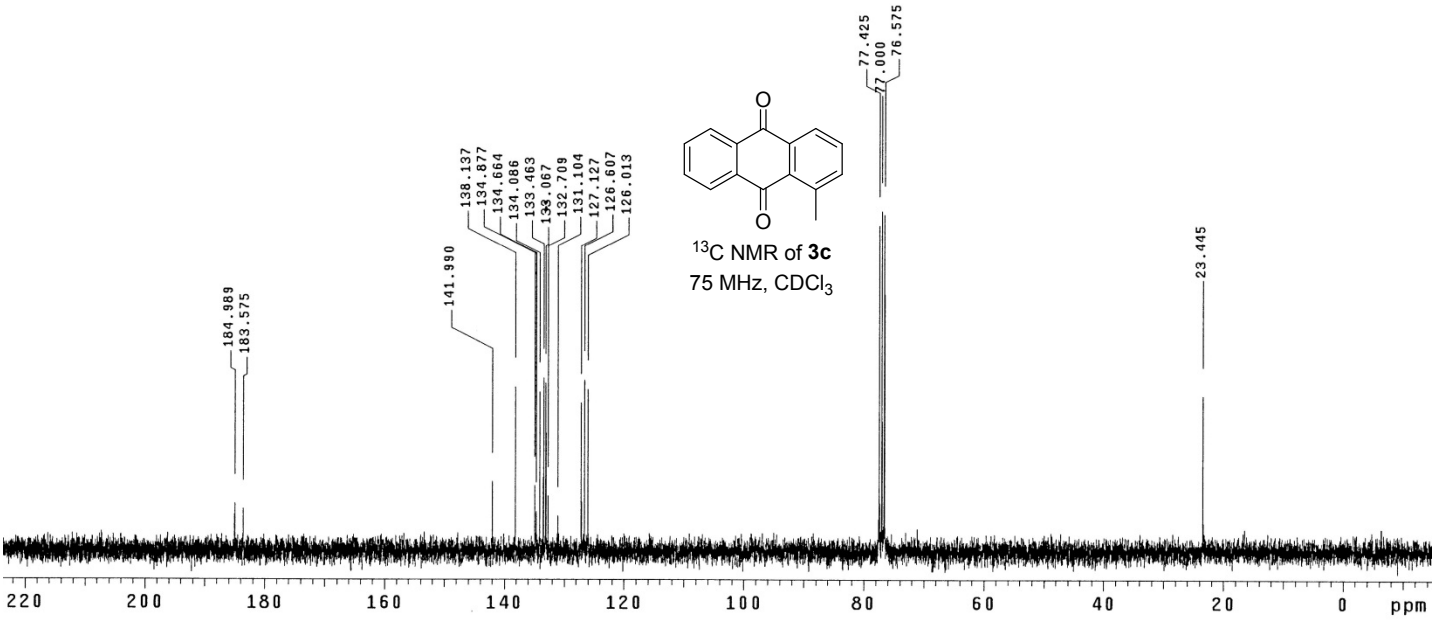
^{1}H NMR of **3b**
600 MHz, $CDCl_3$



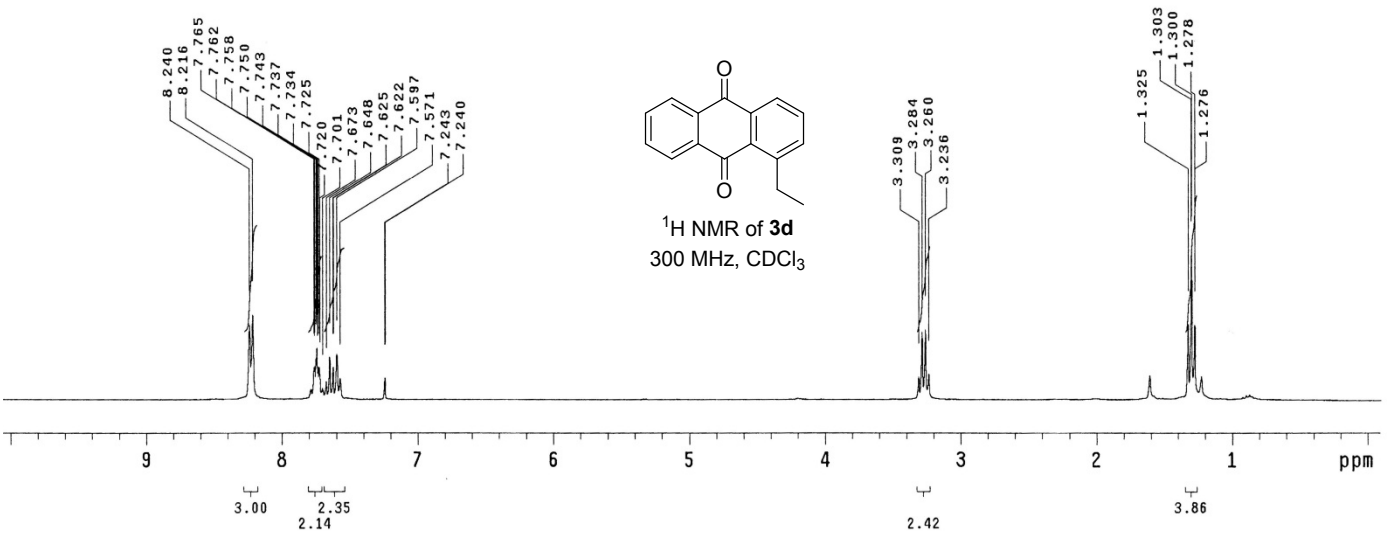
^{13}C NMR of **3b**
150 MHz, $CDCl_3$



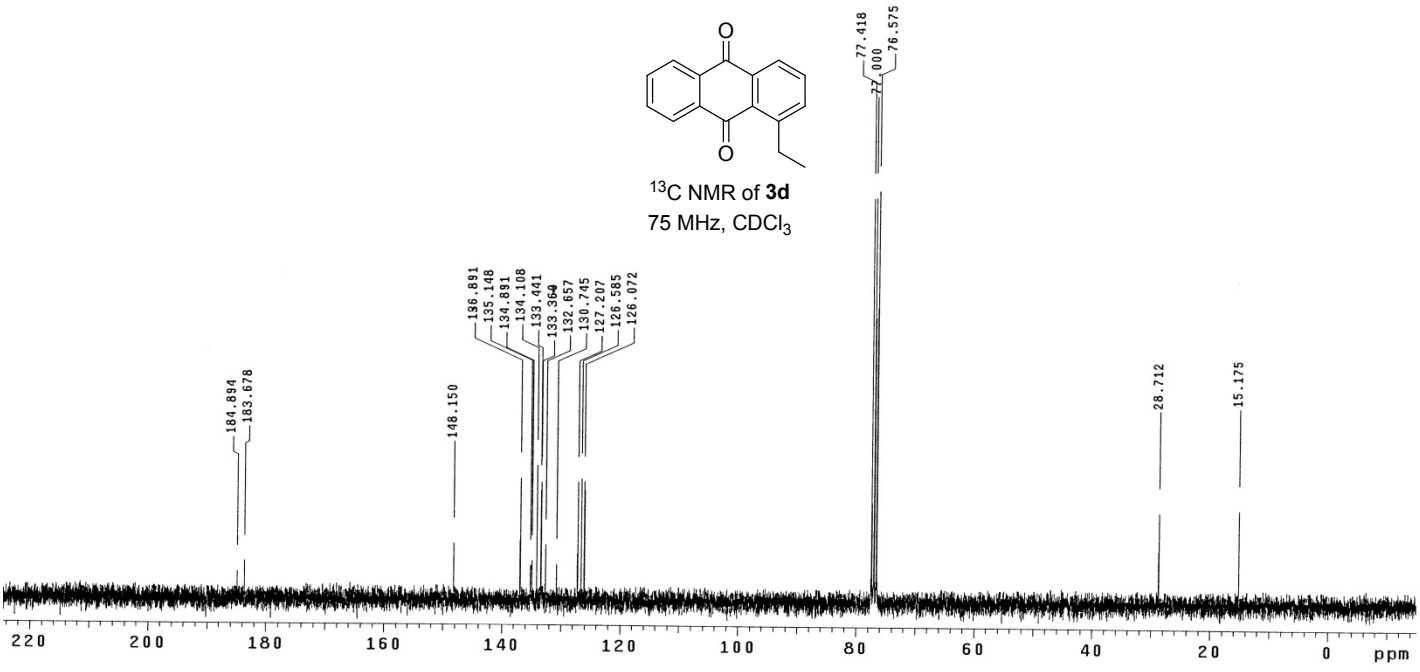
^{1}H NMR of **3c**
300 MHz, $CDCl_3$



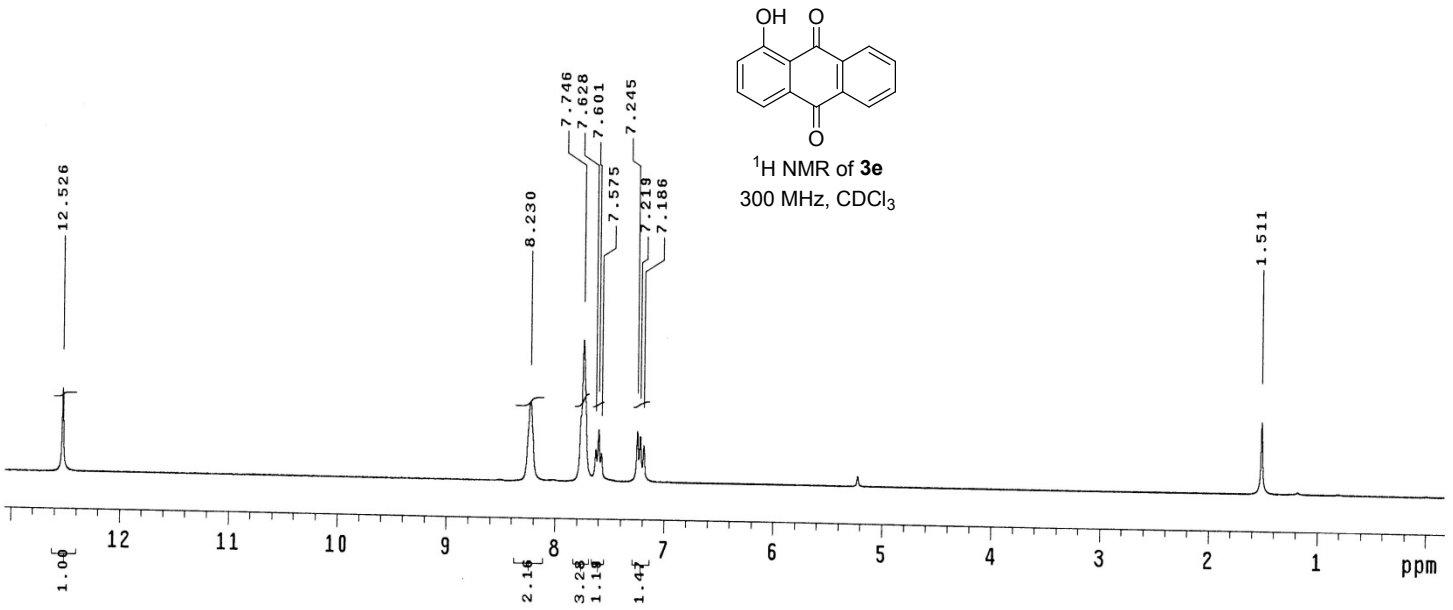
^{13}C NMR of **3c**
75 MHz, $CDCl_3$



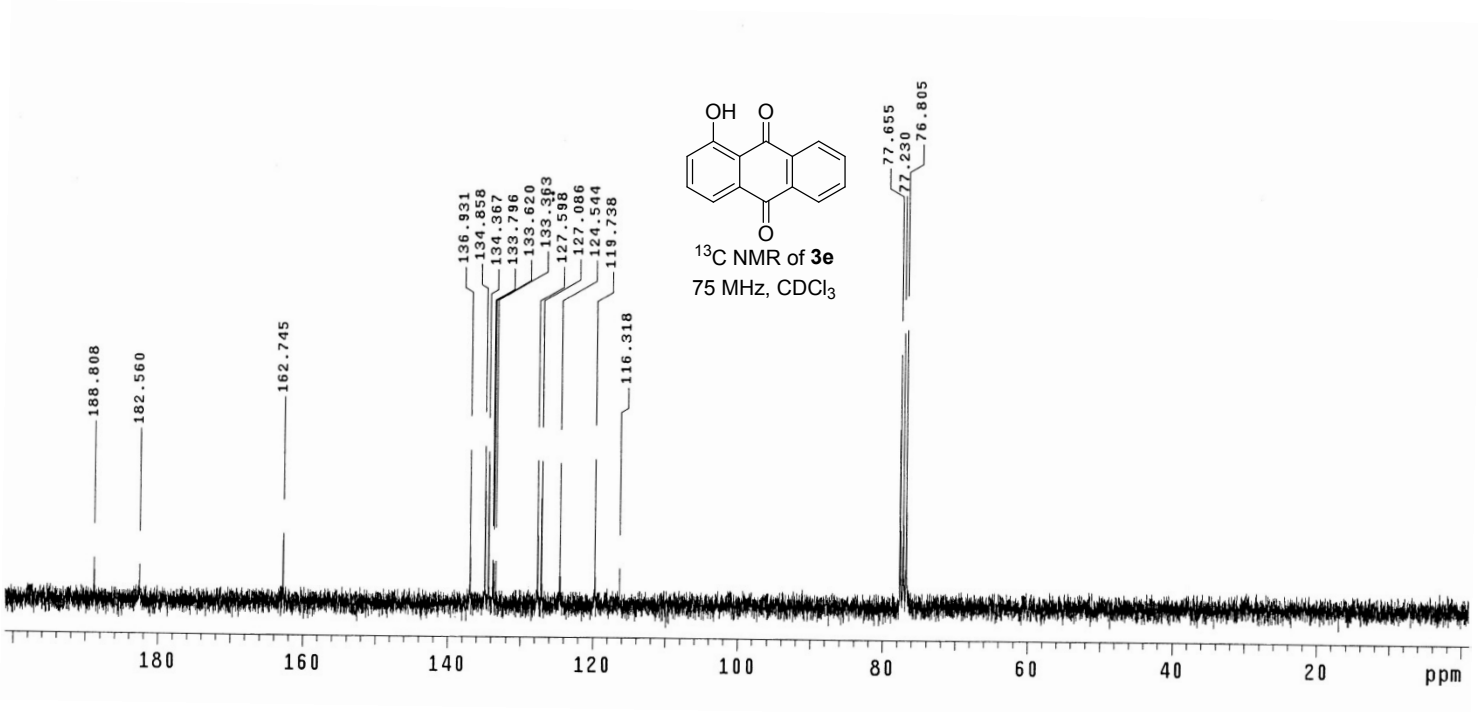
^{1}H NMR of **3d**
300 MHz, $CDCl_3$



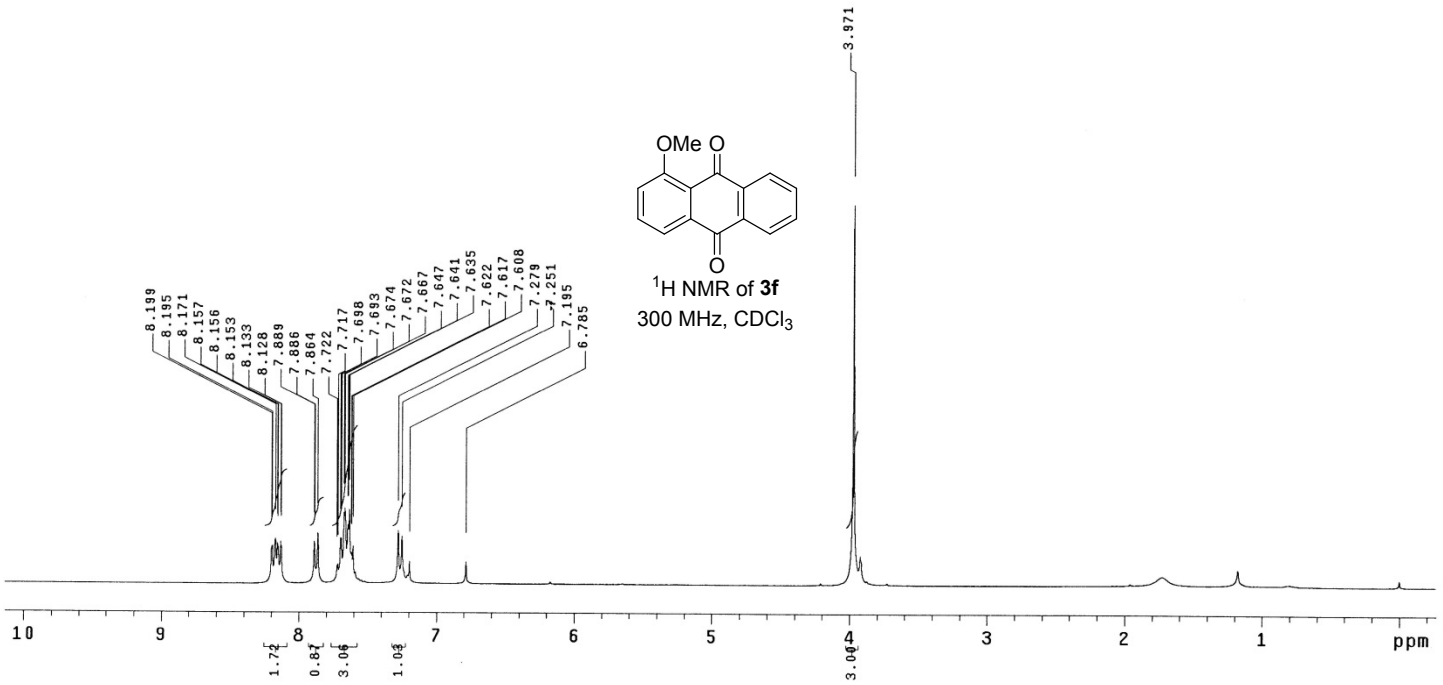
^{13}C NMR of **3d**
75 MHz, $CDCl_3$



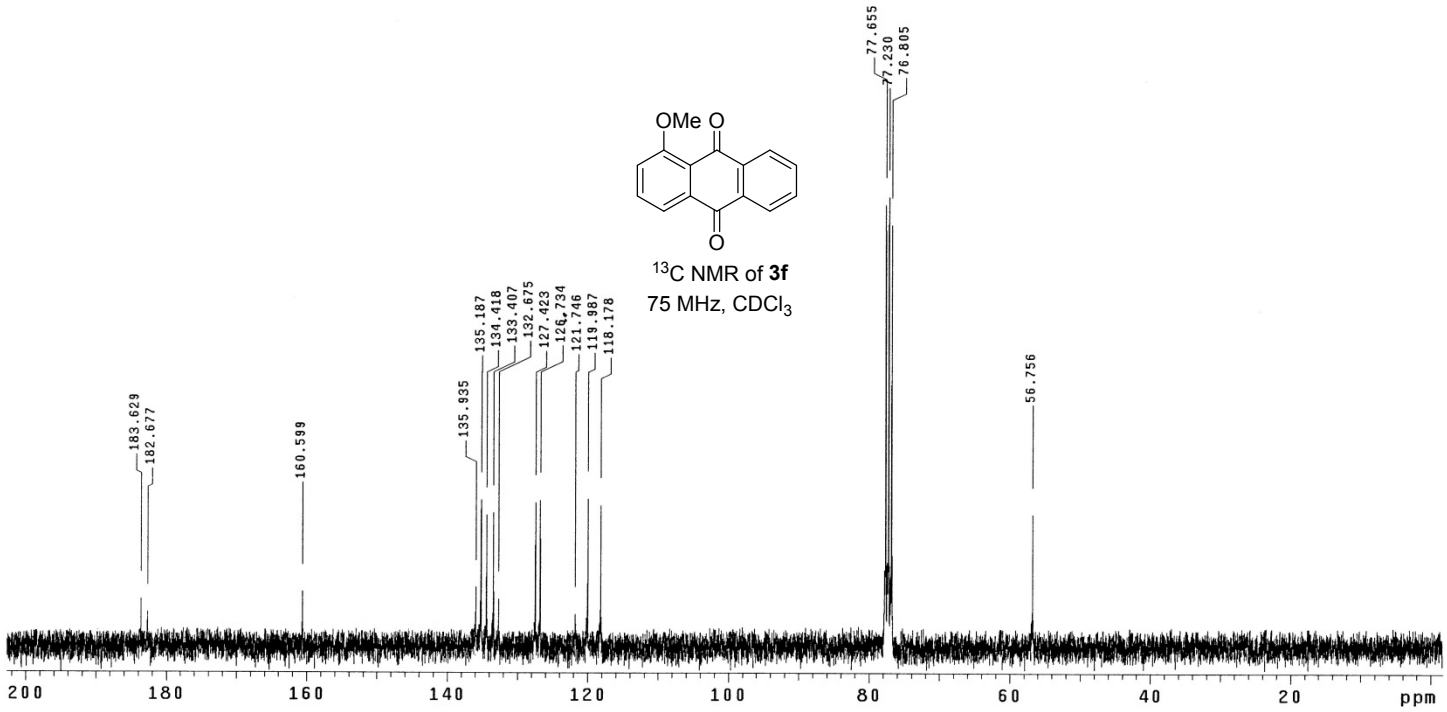
^{1}H NMR of **3e**
300 MHz, $CDCl_3$



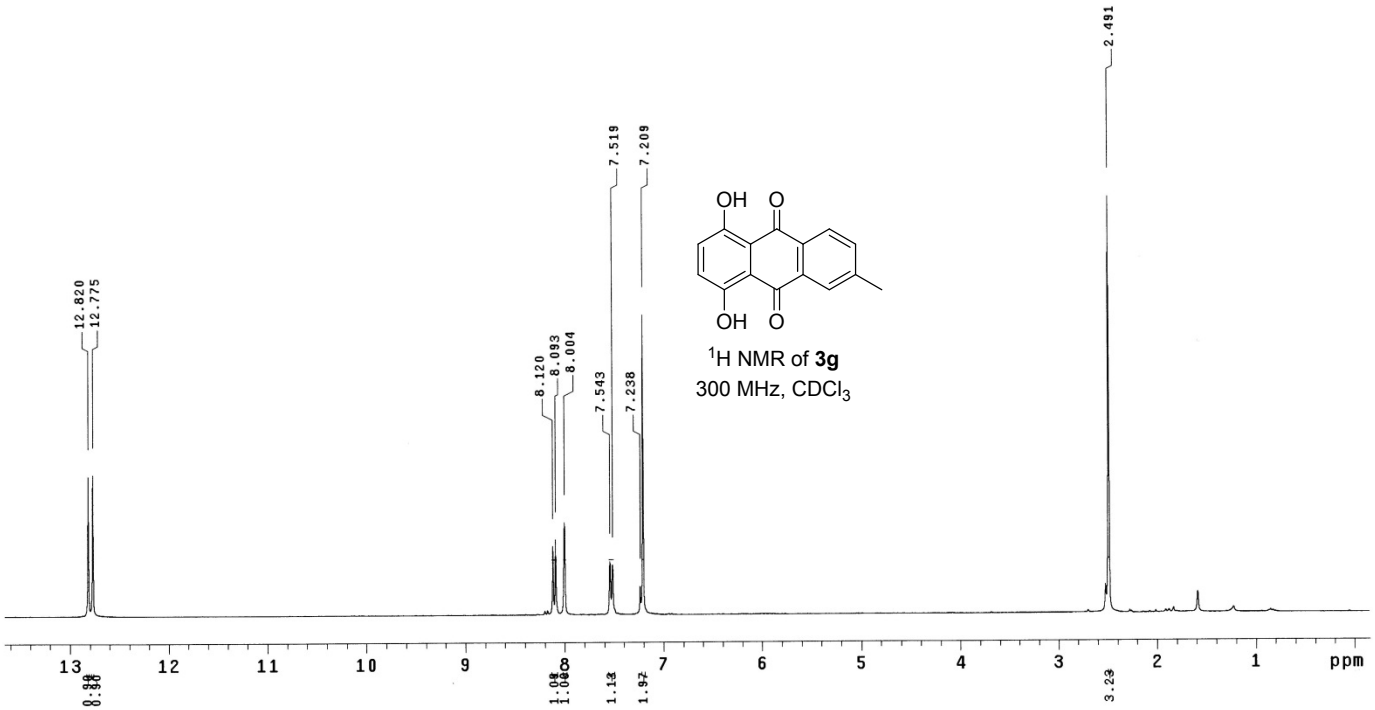
^{13}C NMR of **3e**
75 MHz, $CDCl_3$



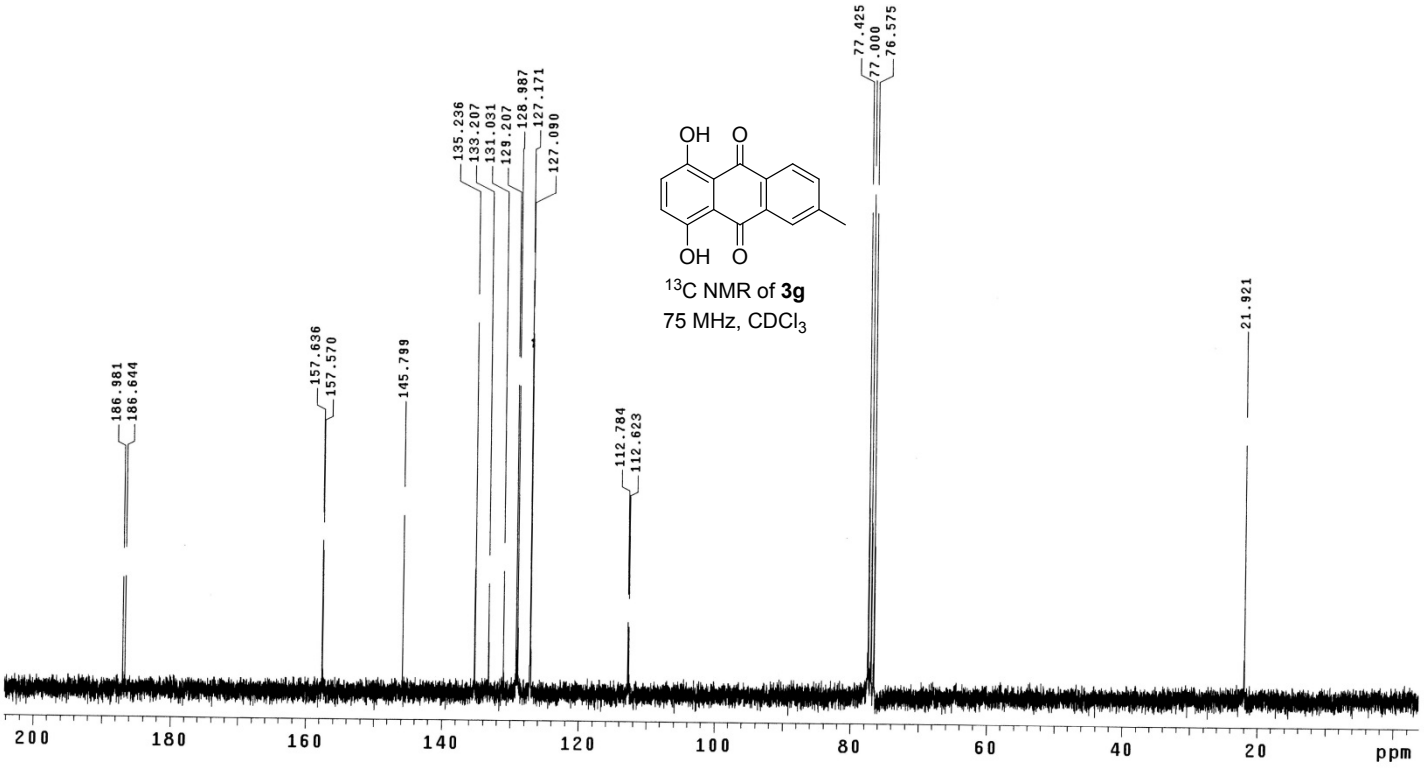
^{1}H NMR of **3f**
300 MHz, $CDCl_3$



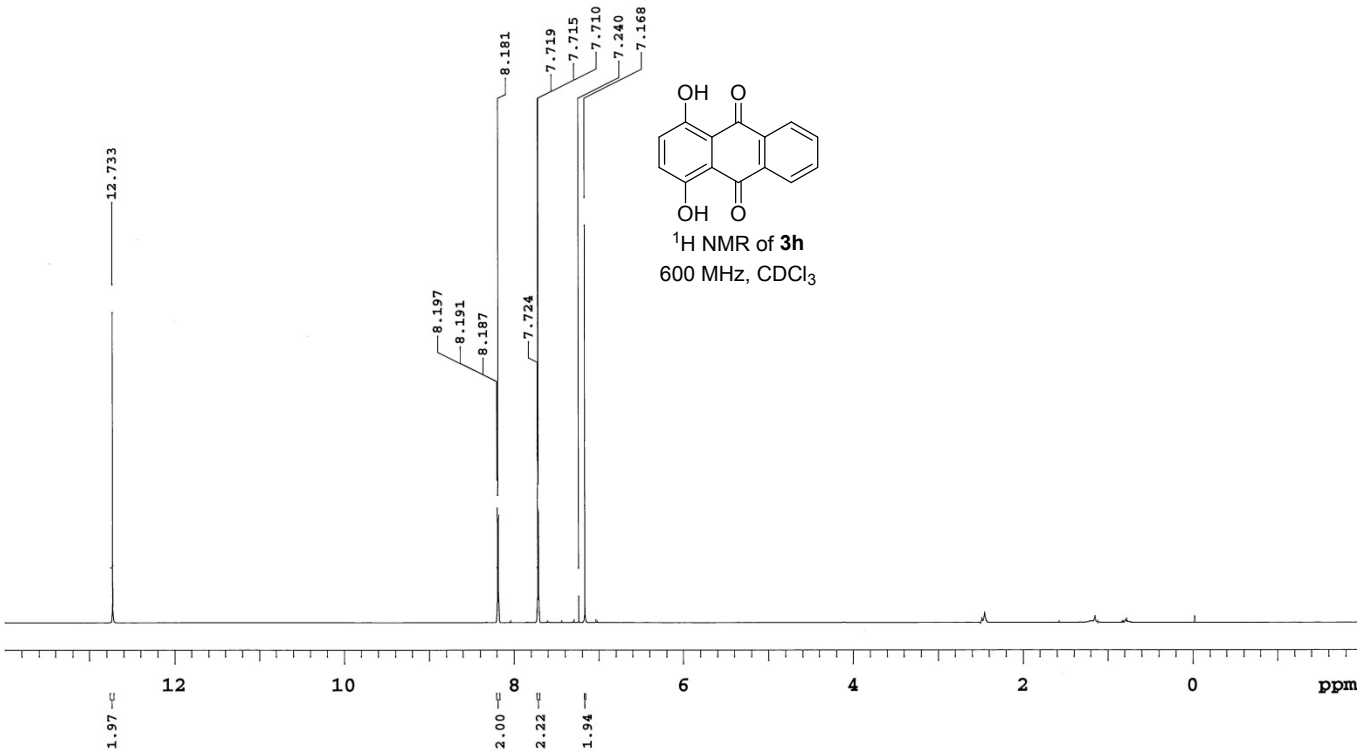
^{13}C NMR of **3f**
75 MHz, $CDCl_3$



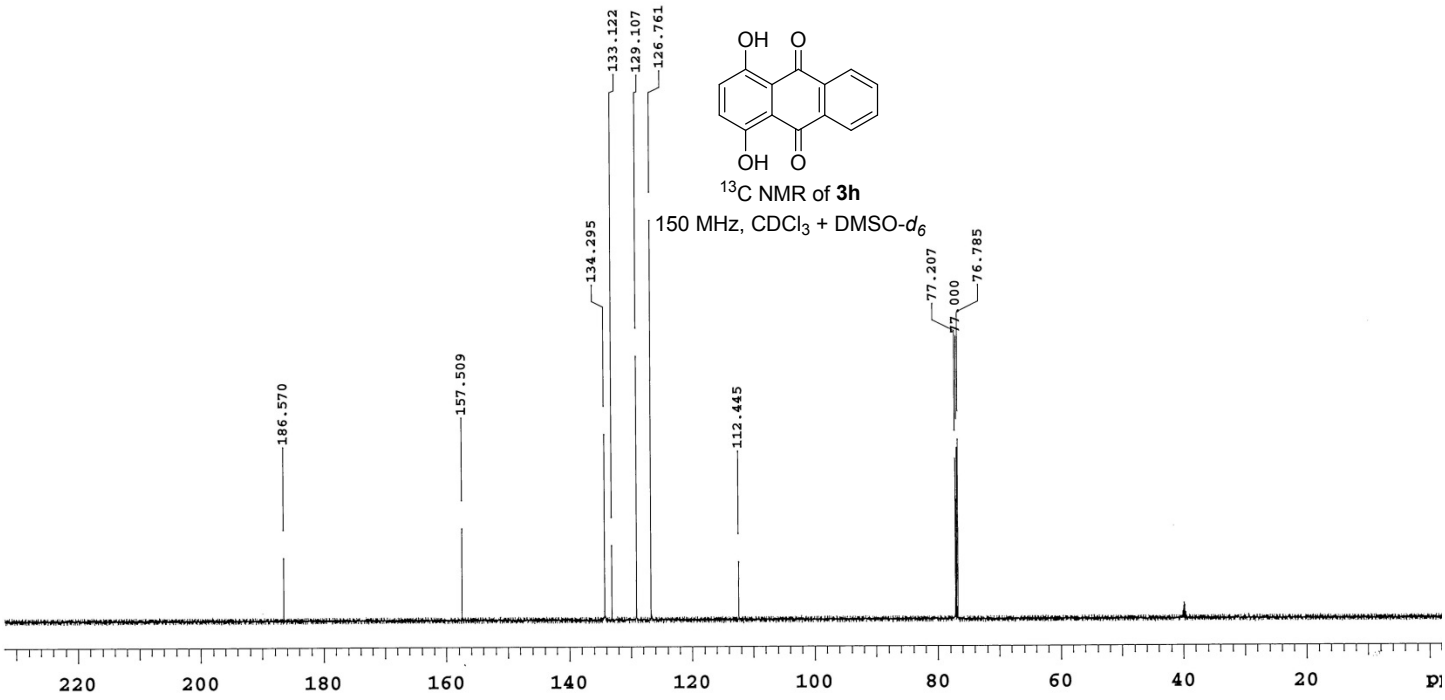
^{1}H NMR of **3g**
300 MHz, $CDCl_3$



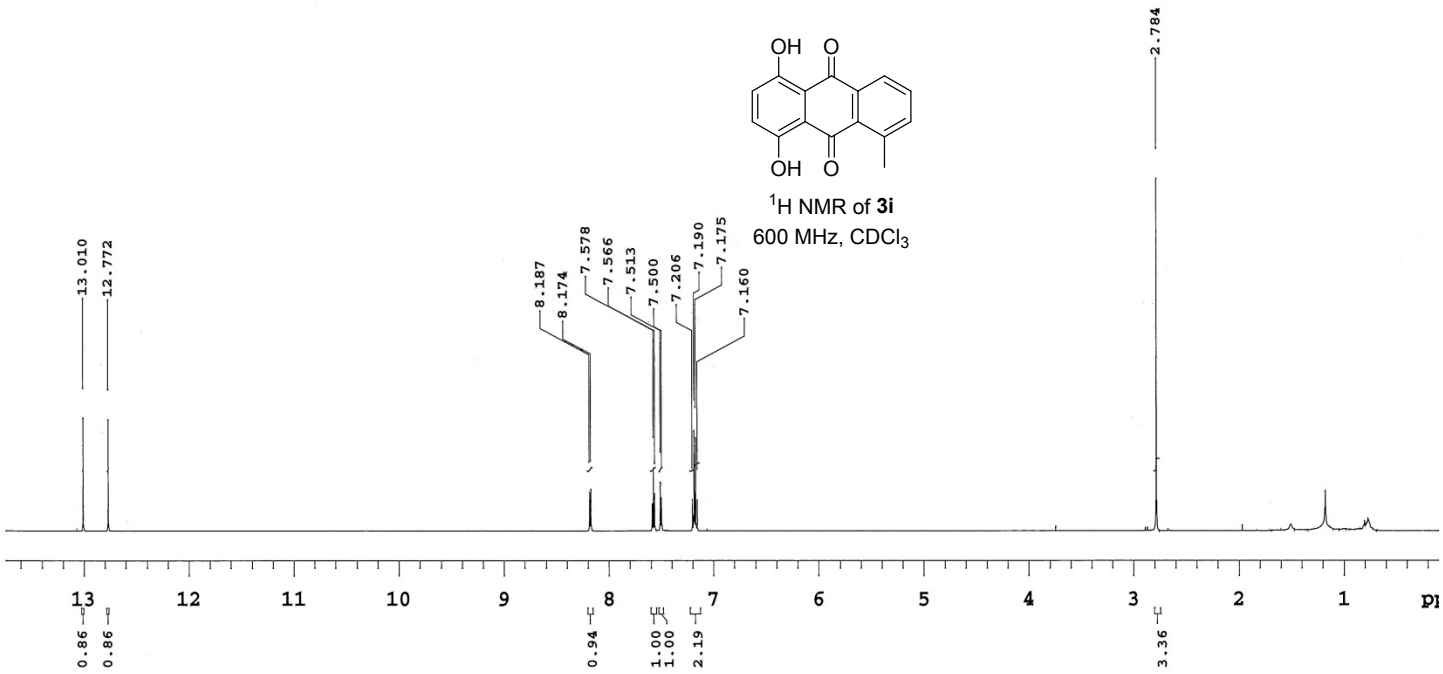
^{13}C NMR of **3g**
75 MHz, $CDCl_3$

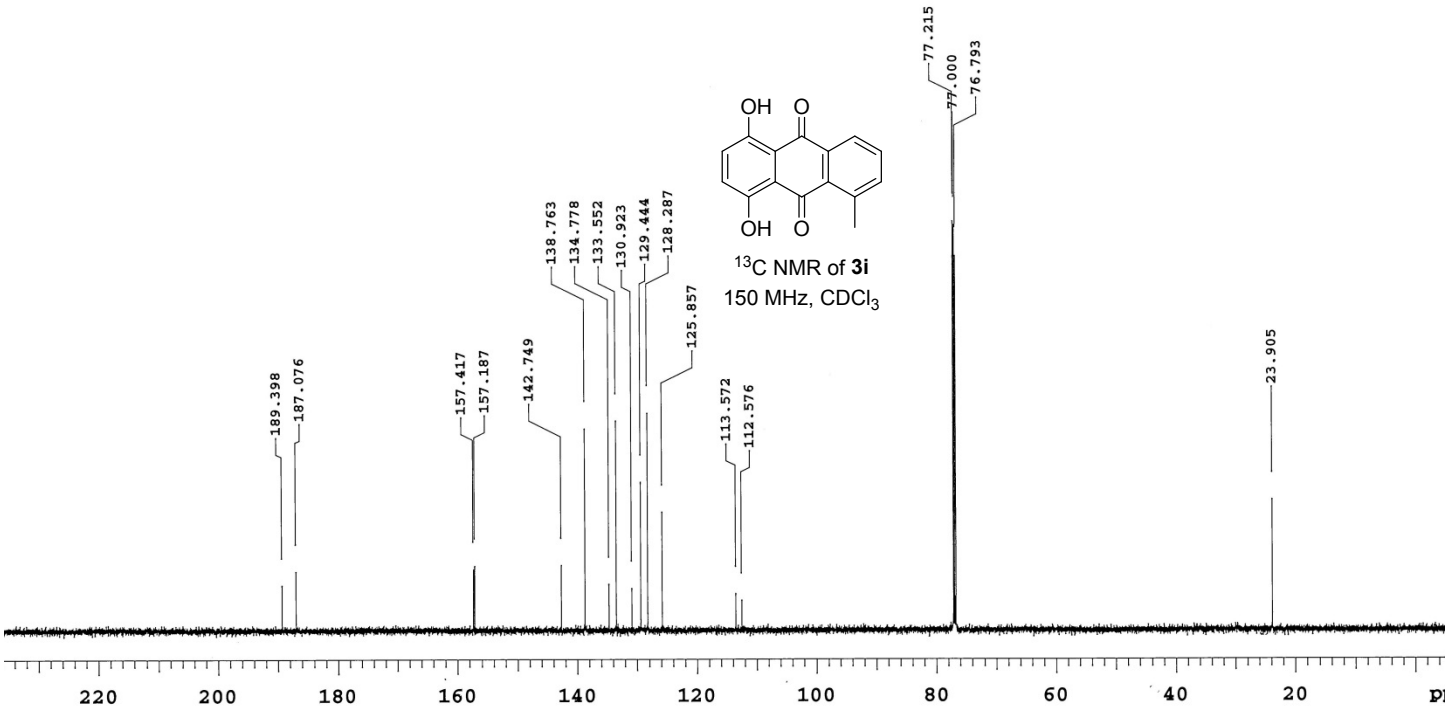


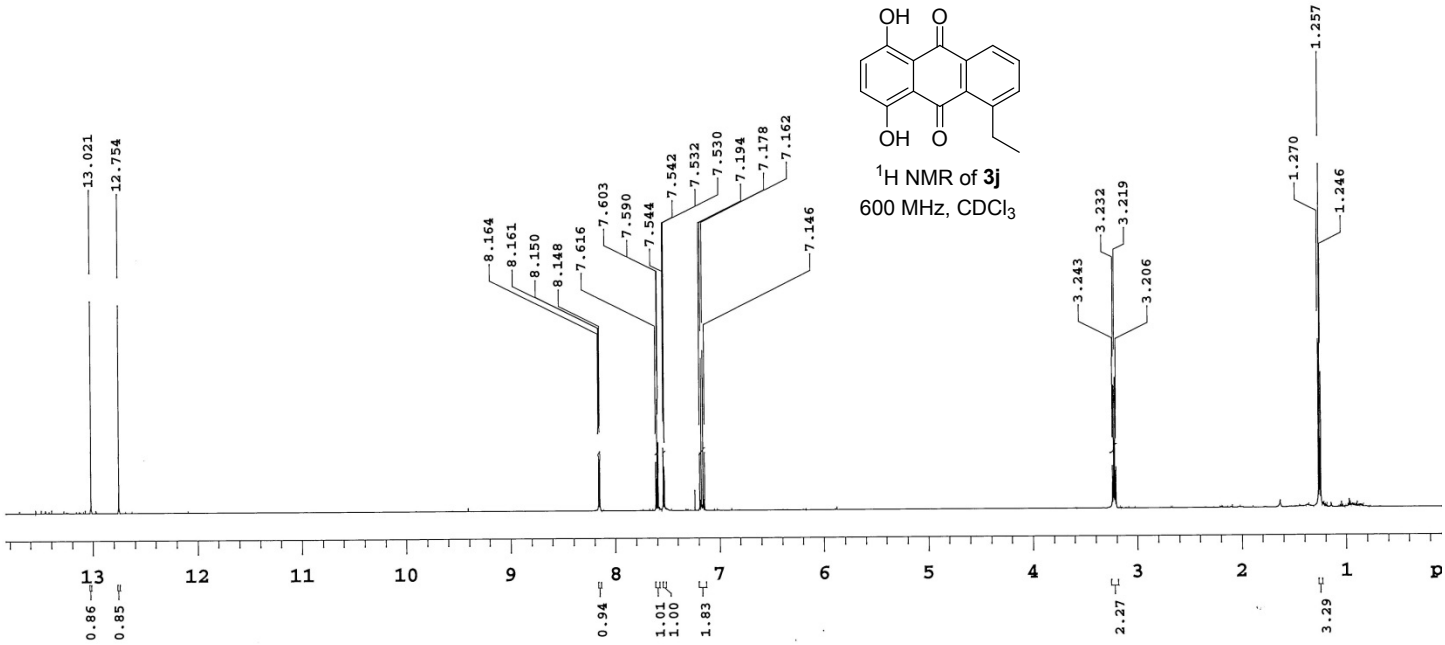
^{1}H NMR of **3h**
600 MHz, $CDCl_3$



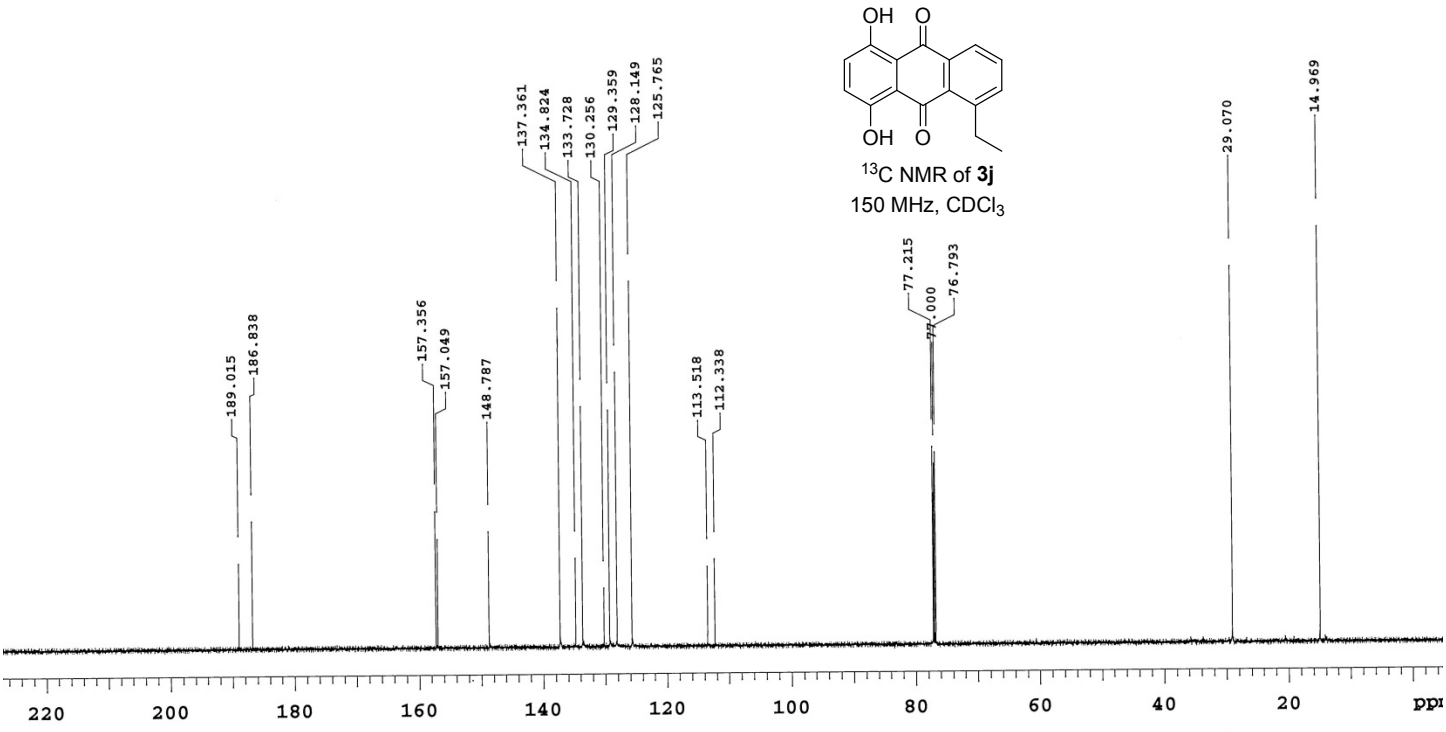
^{13}C NMR of **3h**
150 MHz, $CDCl_3$ + DMSO-d_6


OH O
OH O
^{1}H NMR of **3i**
600 MHz, $CDCl_3$
13.010
12.772
8.187
8.174
7.578
7.566
7.513
7.500
7.206
7.190
7.175
7.160
2.784
0.86
0.86
0.94
1.00
1.00
2.19
3.36

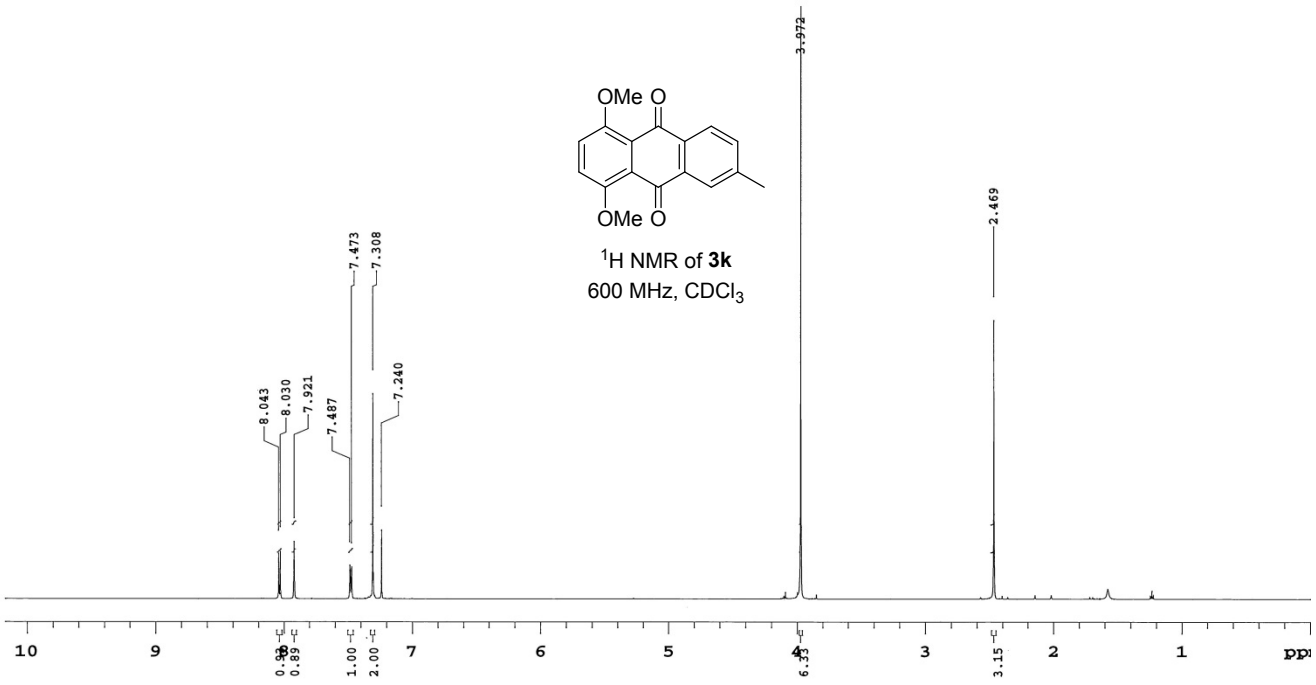

OH O
OH O
^{13}C NMR of **3i**
150 MHz, $CDCl_3$
189.398
187.076
157.417
157.187
142.749
138.763
134.778
133.552
130.923
129.444
128.287
125.857
113.572
112.576
77.215
77.000
76.793
23.905



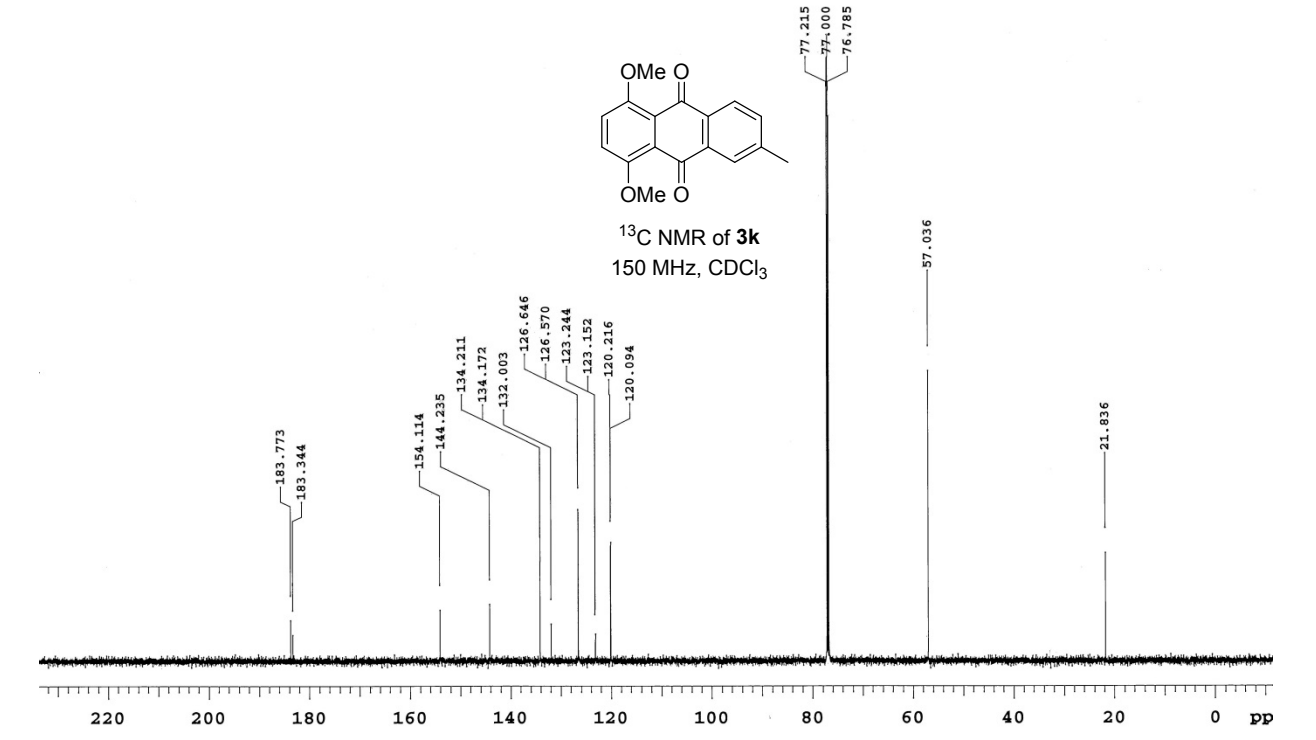
^{1}H NMR of **3j**
600 MHz, $CDCl_3$



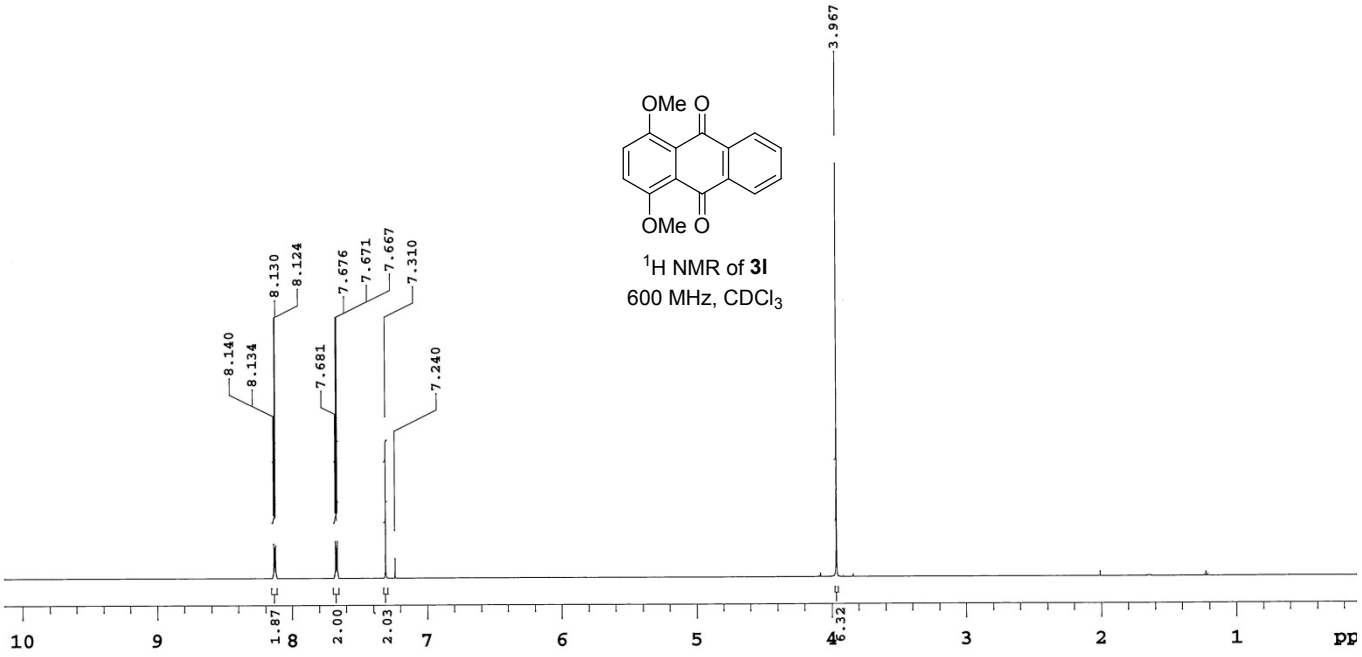
^{13}C NMR of **3j**
150 MHz, $CDCl_3$

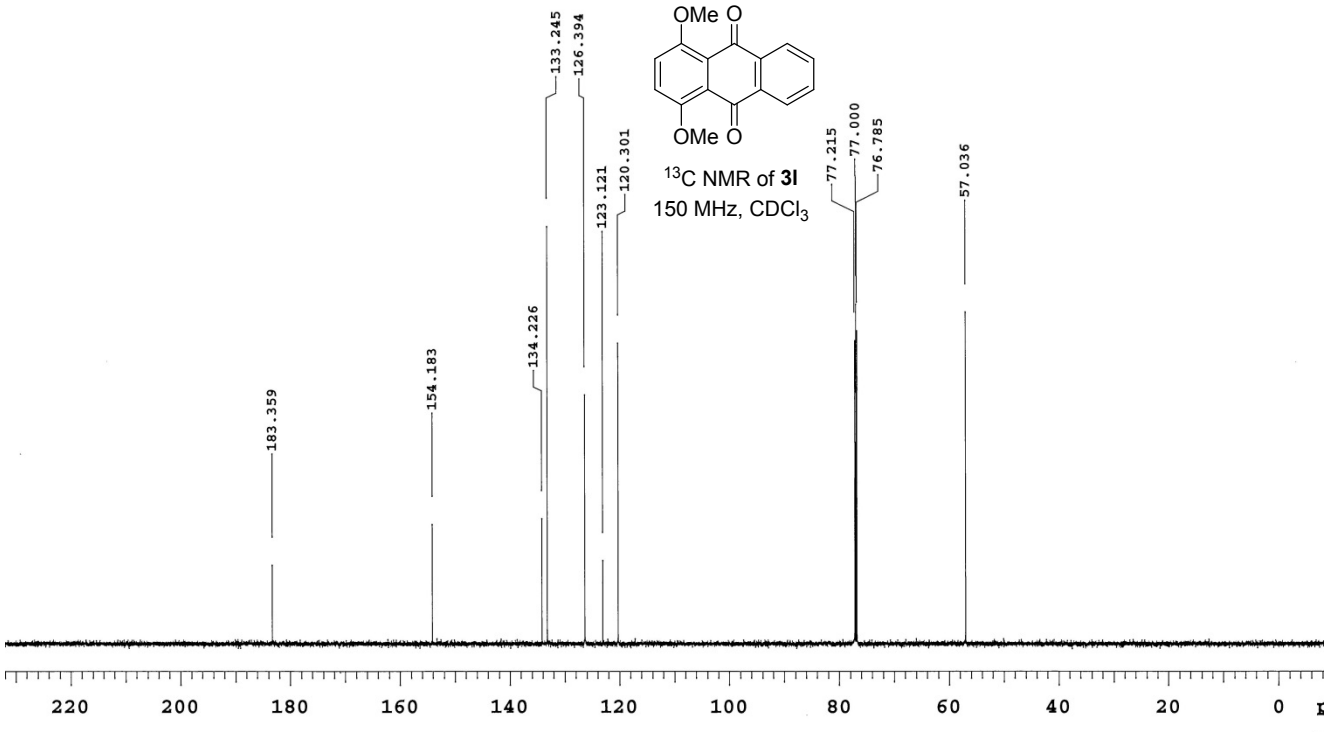


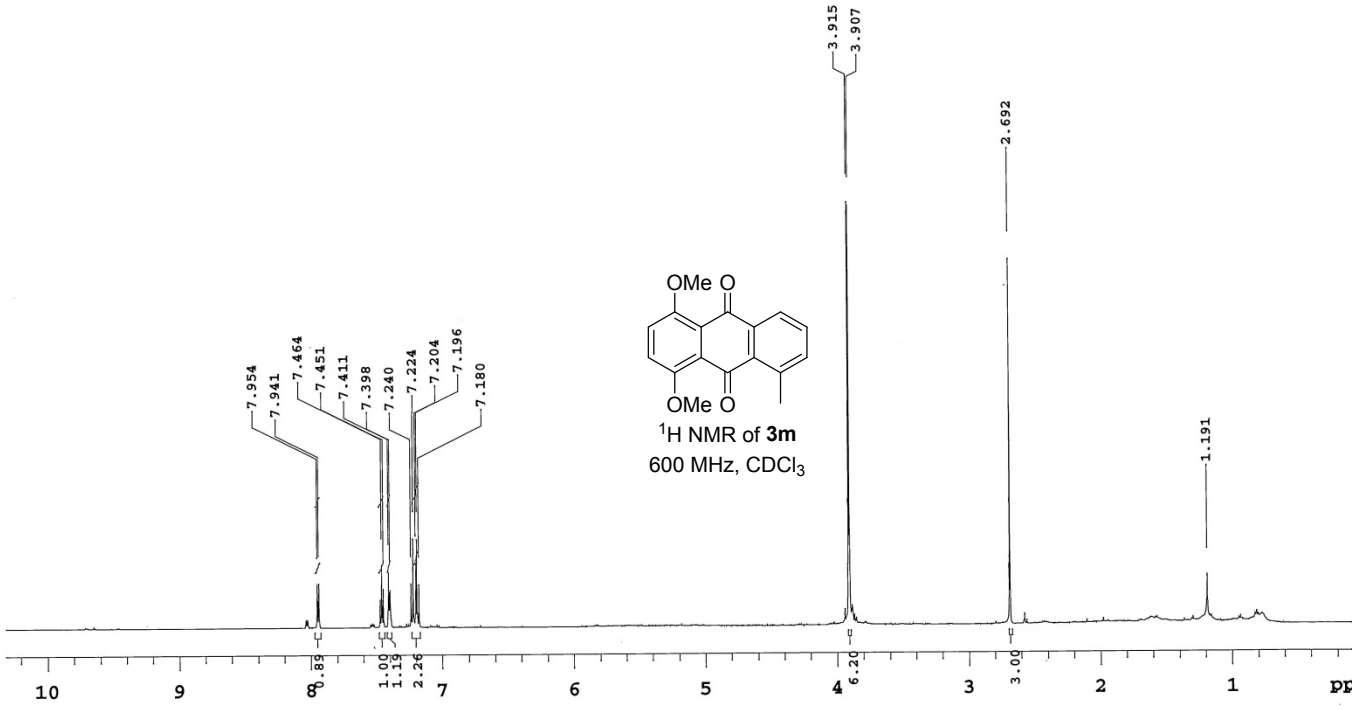
^{1}H NMR of **3k**
600 MHz, $CDCl_3$

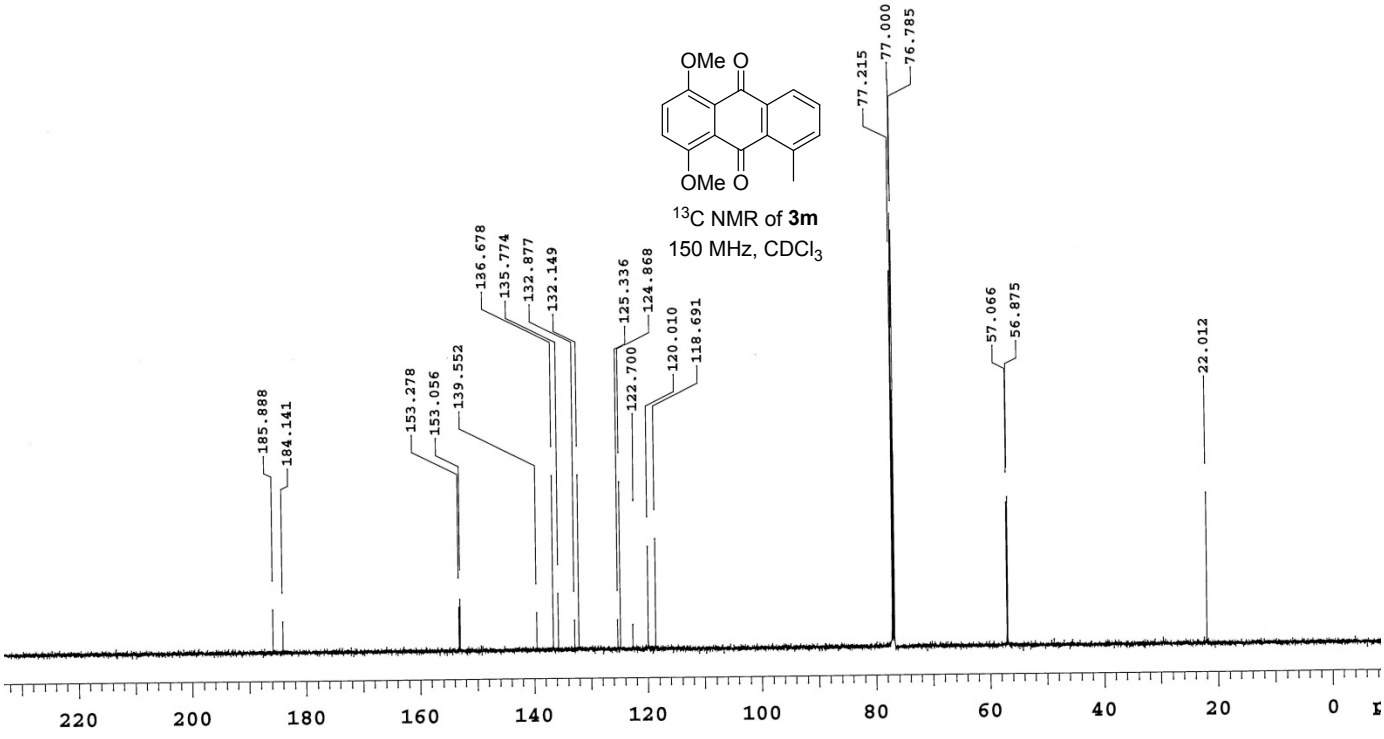


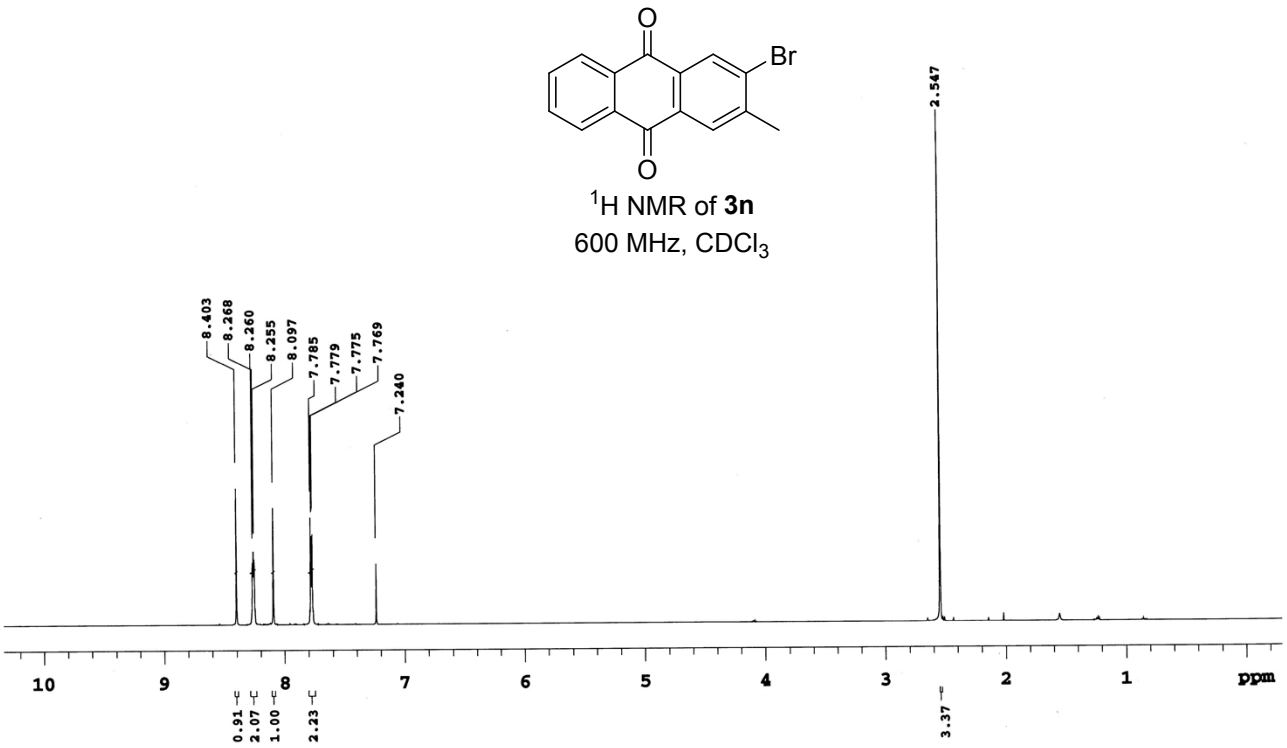
^{13}C NMR of **3k**
150 MHz, $CDCl_3$


OMe O
OMe O
^{1}H NMR of **3l**
600 MHz, $CDCl_3$
3.967
8.140
8.134
8.130
8.124
7.681
7.676
7.671
7.667
7.310
7.240
1.87
2.00
2.03
4.32
10
9
8
7
6
5
4
3
2
1
ppm

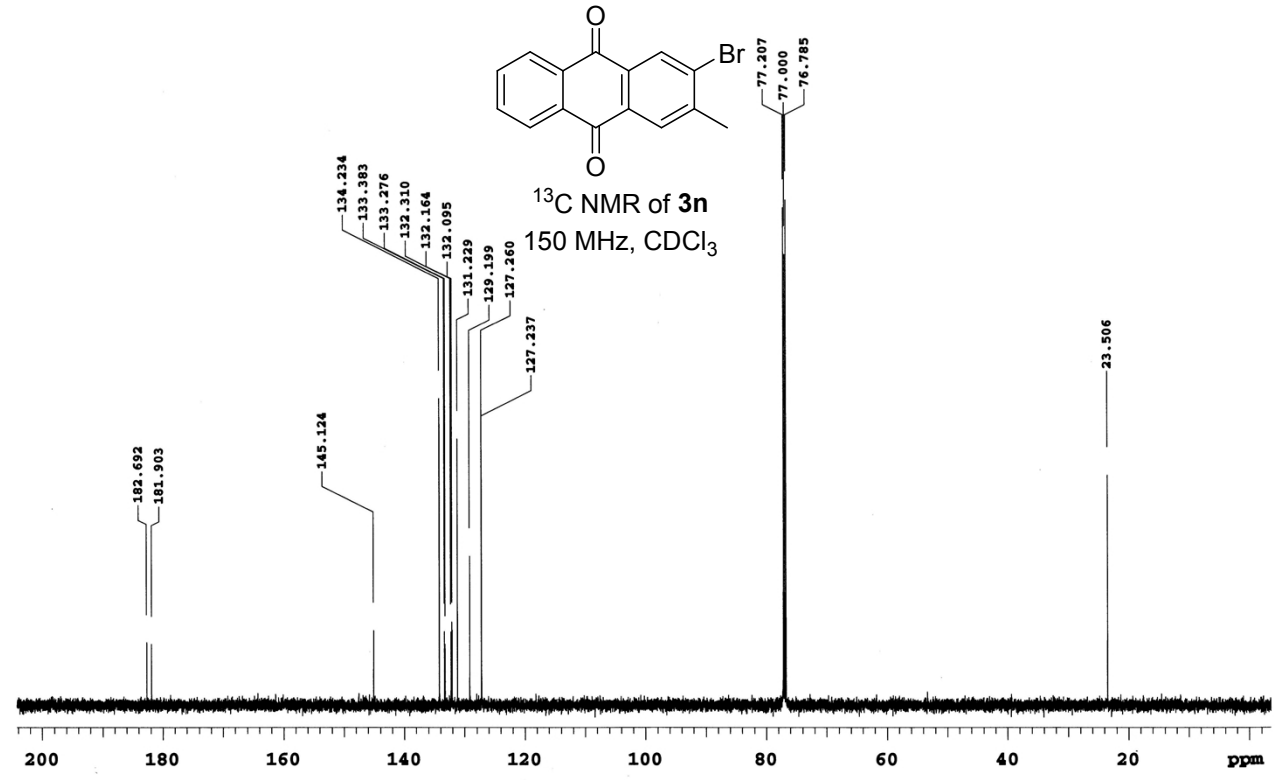

OMe O
OMe O
^{13}C NMR of **3l**
150 MHz, $CDCl_3$
183.359
154.183
134.226
133.245
126.394
123.121
120.301
77.215
77.000
76.785
57.036
220
200
180
160
140
120
100
80
60
40
20
0


OMe O
OMe O
^{1}H NMR of **3m**
600 MHz, $CDCl_3$
7.954
7.941
7.464
7.451
7.411
7.398
7.240
7.224
7.204
7.196
7.180
3.915
3.907
2.692
1.191

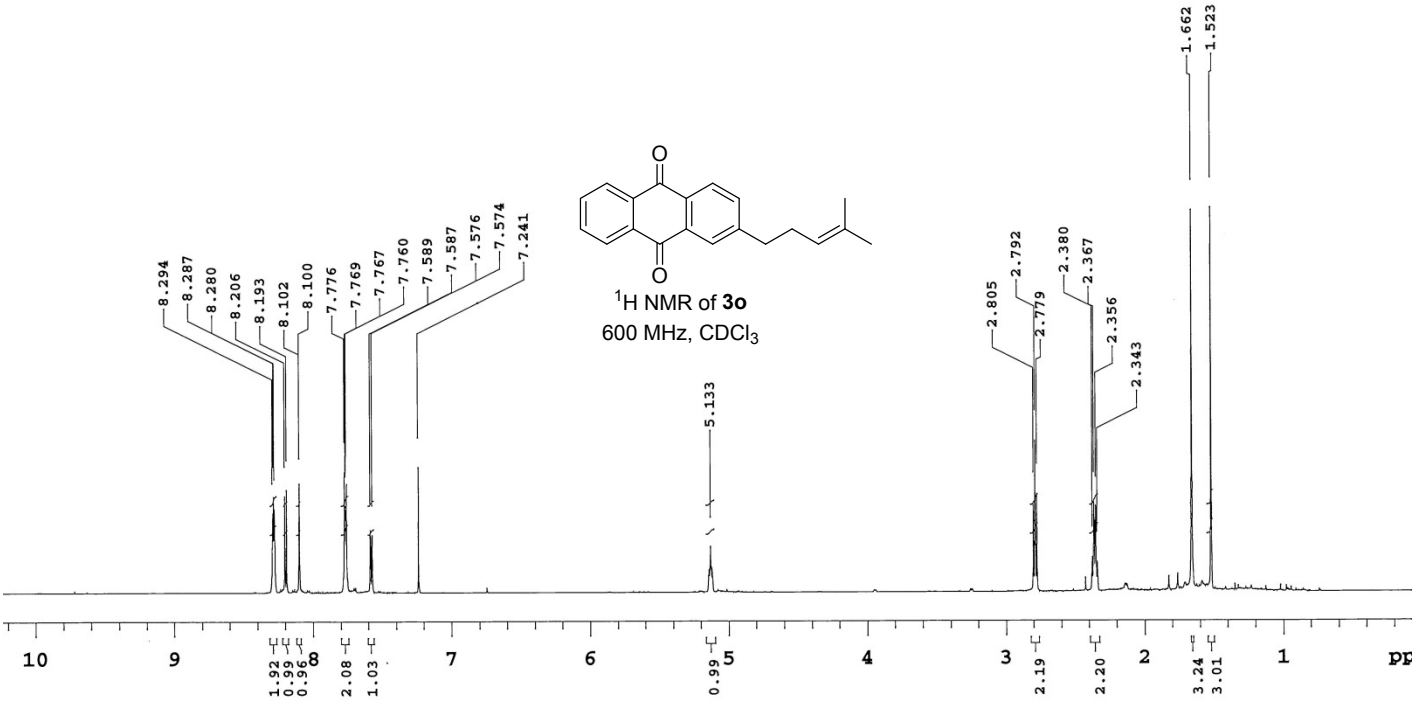

OMe O
OMe O
^{13}C NMR of **3m**
150 MHz, $CDCl_3$
185.888
184.141
153.278
153.056
139.552
136.678
135.774
132.877
132.149
125.336
124.868
122.700
120.010
118.691
77.215
77.000
76.785
57.066
56.875
22.012



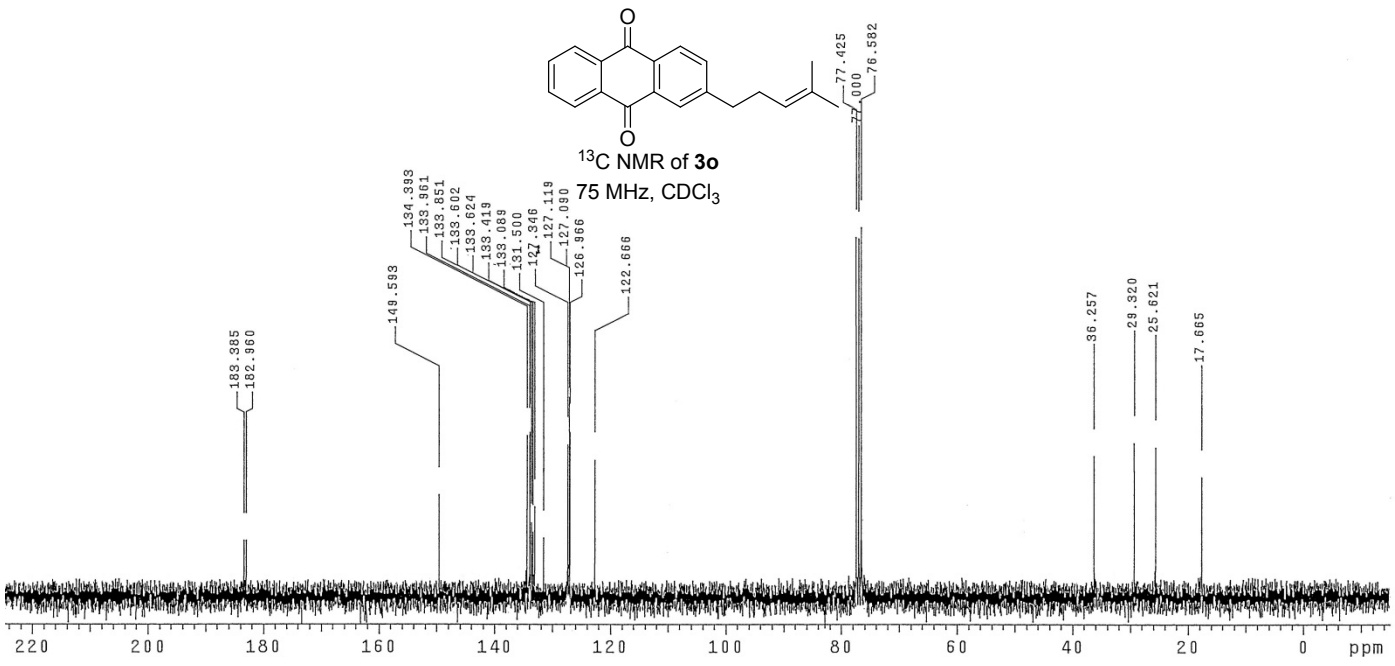
^{1}H NMR of **3n**
600 MHz, $CDCl_3$



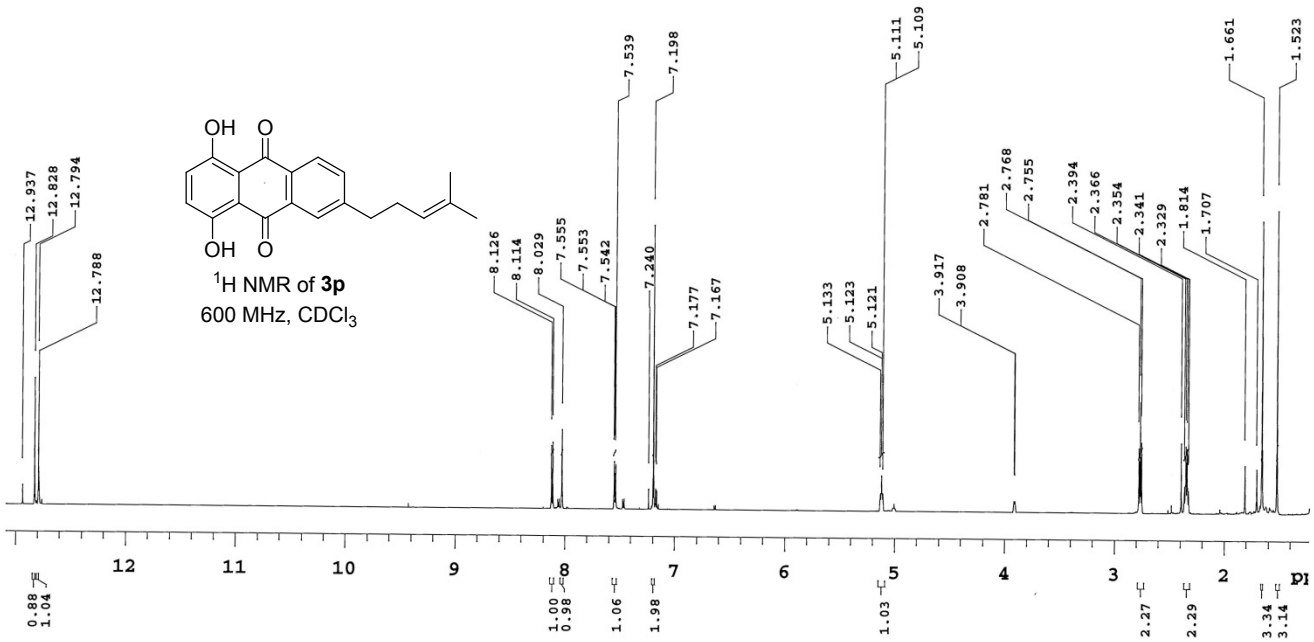
^{13}C NMR of **3n**
150 MHz, $CDCl_3$

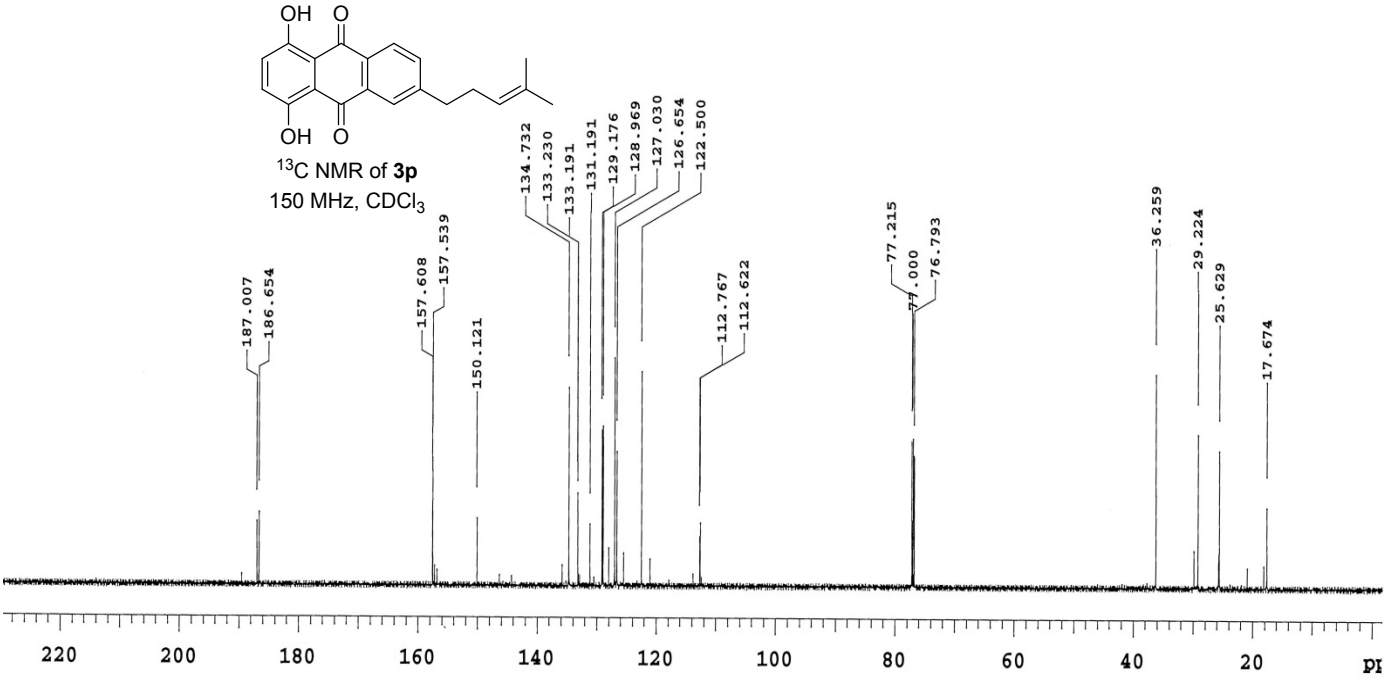


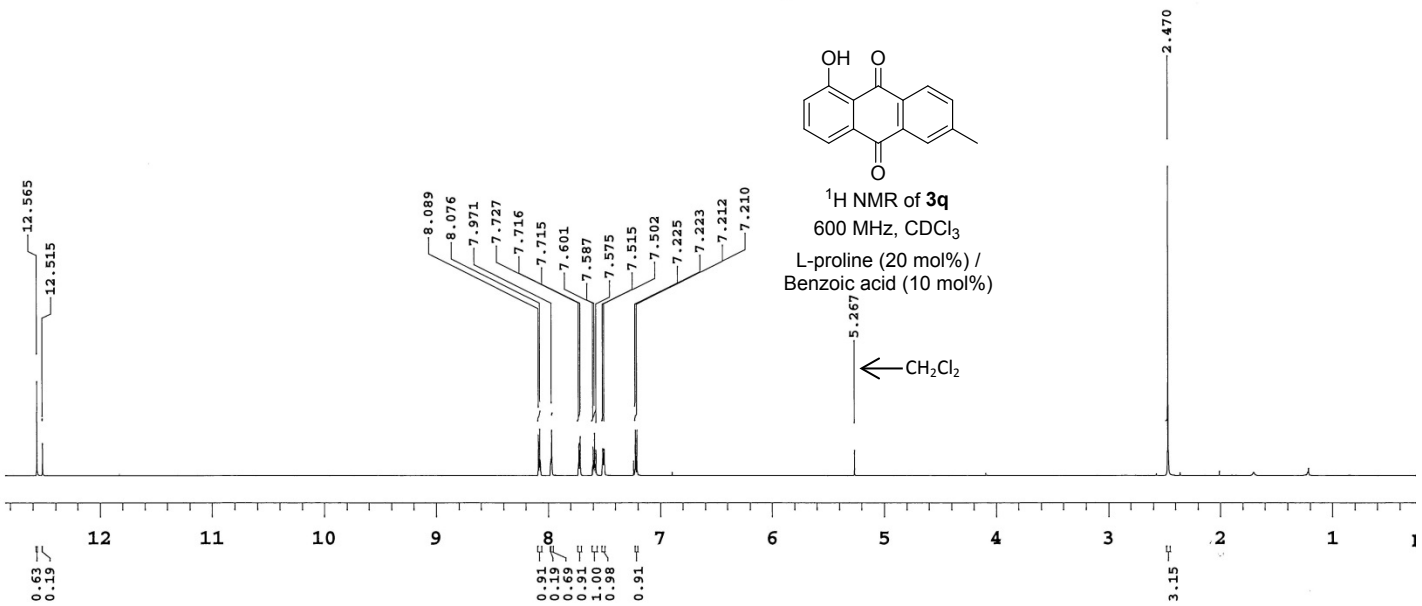
^{1}H NMR of **3o**
600 MHz, $CDCl_3$

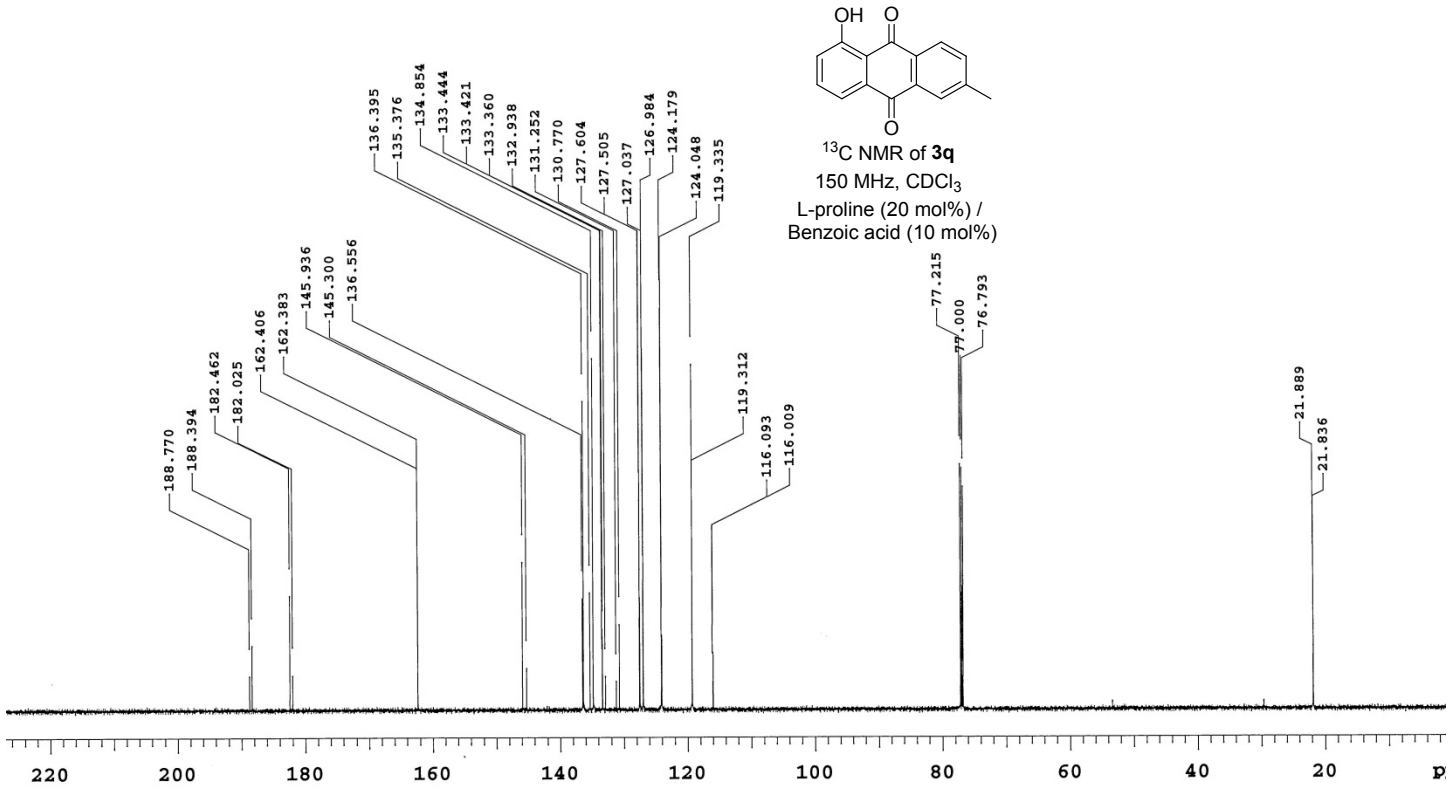


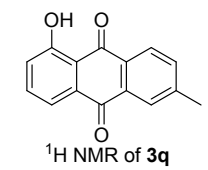
^{13}C NMR of **3o**
75 MHz, $CDCl_3$


OH O
OH O
^{1}H NMR of **3p**
600 MHz, $CDCl_3$
12.937
12.828
12.794
12.788
8.126
8.114
8.029
7.555
7.553
7.542
7.539
7.240
7.198
7.177
7.167
5.133
5.123
5.121
5.111
5.109
3.917
3.908
2.781
2.768
2.755
2.394
2.366
2.354
2.341
2.329
1.814
1.707
1.661
1.523
0.88
1.04
1.00
0.98
1.06
1.98
1.03
2.27
2.29
3.34
3.14
pI


OH O
OH O
^{13}C NMR of **3p**
150 MHz, $CDCl_3$
187.007
186.654
157.608
157.539
150.121
134.732
133.230
133.191
131.191
129.176
128.969
127.030
126.654
122.500
112.767
112.622
77.215
77.000
76.793
36.259
29.224
25.629
17.674
pI


OH
O
O
^{1}H NMR of **3q**
600 MHz, $CDCl_3$
L-proline (20 mol%) /
Benzoic acid (10 mol%)
CH_2Cl_2
12.565
12.515
8.089
8.076
7.971
7.727
7.716
7.715
7.601
7.587
7.575
7.515
7.502
7.225
7.223
7.212
7.210
5.267
2.470
0.63
0.19
0.91
0.19
0.69
0.91
1.00
0.98
0.91
3.15


OH
O
O
^{13}C NMR of **3q**
150 MHz, $CDCl_3$
L-proline (20 mol%) /
Benzoic acid (10 mol%)
136.395
135.376
134.854
133.444
133.421
133.360
132.938
131.252
130.770
127.604
127.505
127.037
126.984
124.179
124.048
119.335
119.312
116.093
116.009
188.770
188.394
182.462
182.025
162.406
162.383
145.936
145.300
136.556
77.215
77.000
76.793
21.889
21.836

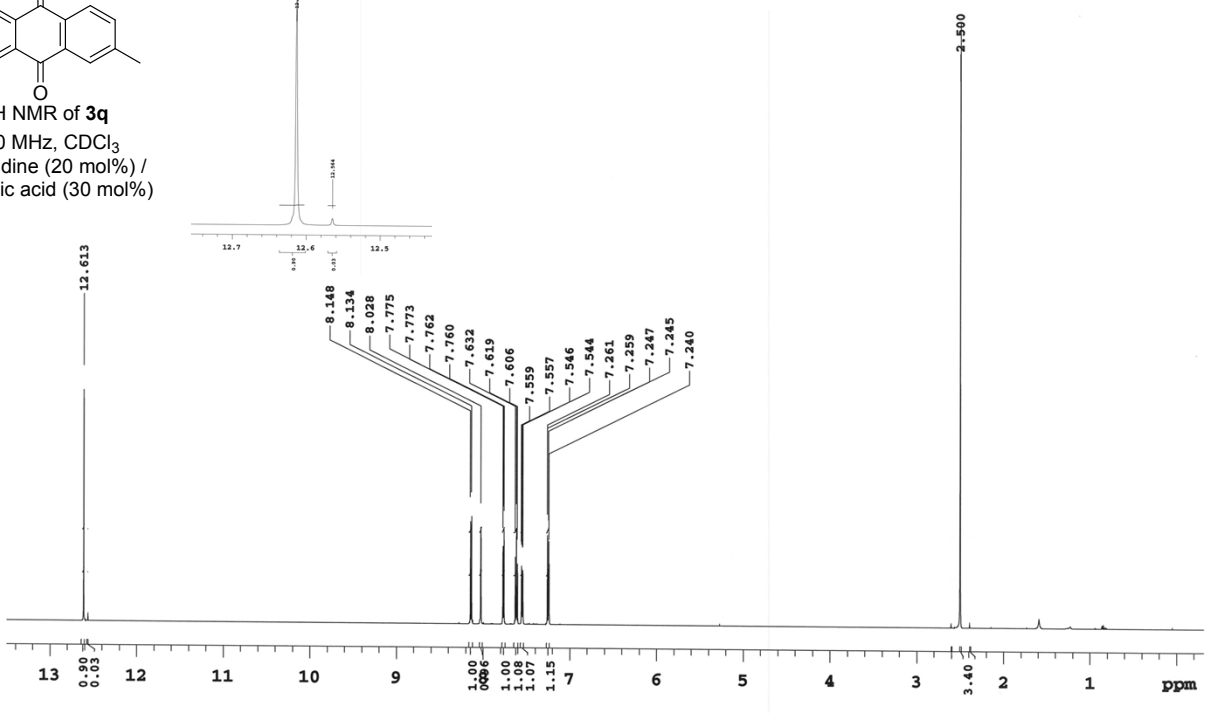


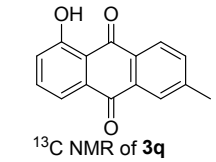
^{1}H NMR of **3q**

600 MHz, $CDCl_3$

Pyrrolidine (20 mol%) /

Benzoic acid (30 mol%)



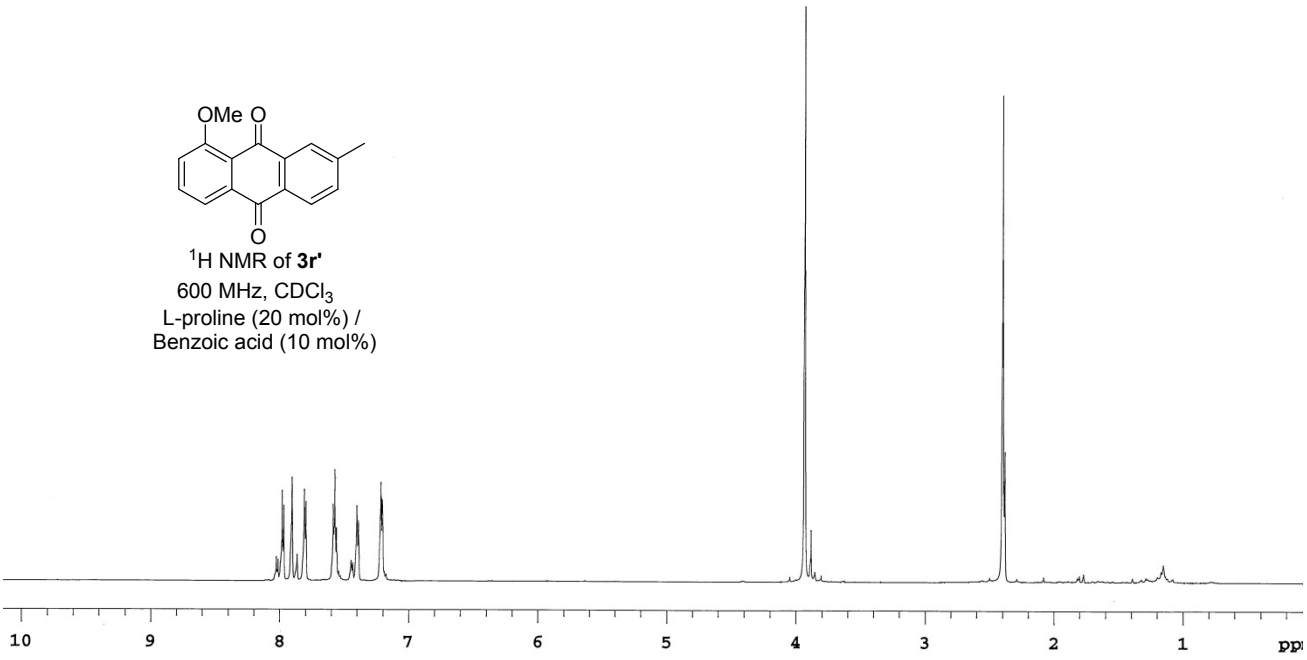


^{13}C NMR of **3q**

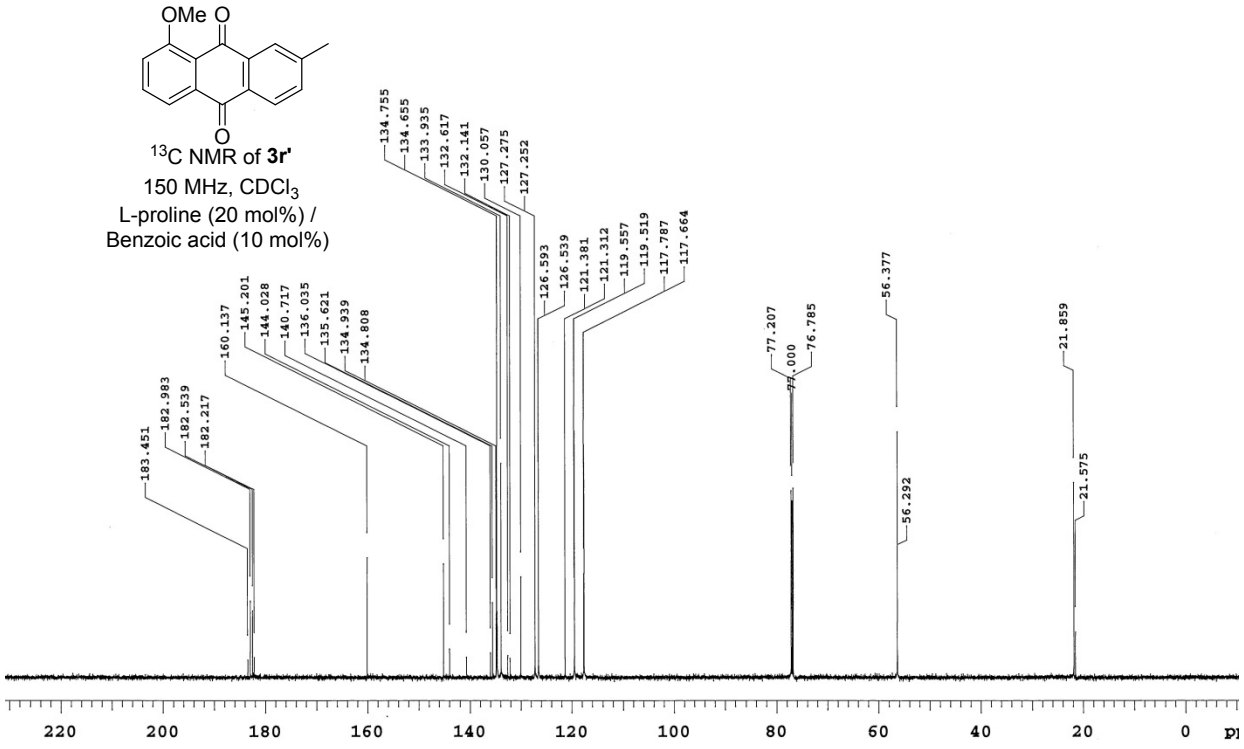
150 MHz, $CDCl_3$

Pyrrolidine (20 mol%) /

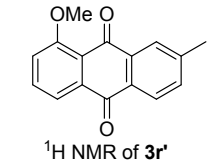
Benzoic acid (30 mol%)



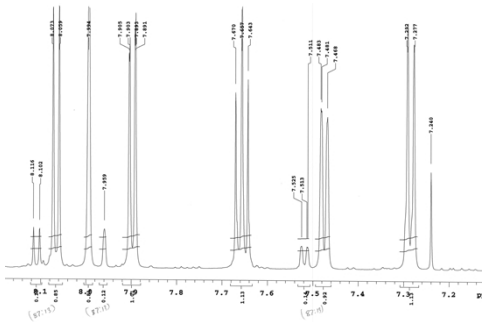
^{1}H NMR of **3r'**
600 MHz, $CDCl_3$
L-proline (20 mol%) /
Benzoic acid (10 mol%)

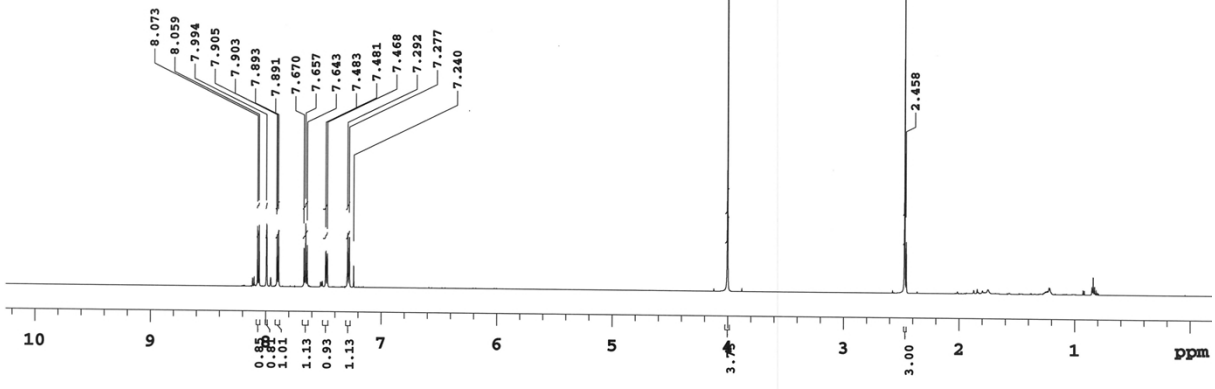


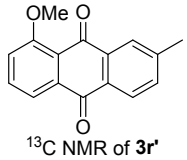
^{13}C NMR of **3r'**
150 MHz, $CDCl_3$
L-proline (20 mol%) /
Benzoic acid (10 mol%)



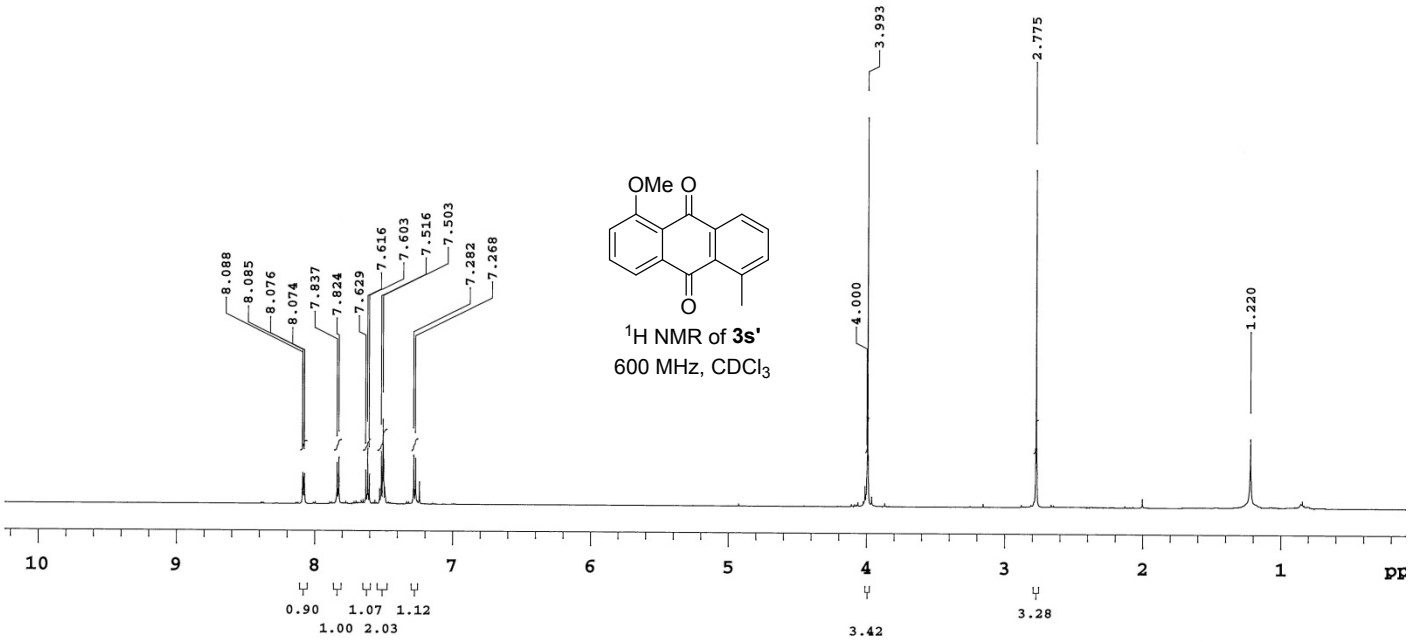
^{1}H NMR of **3r'**
600 MHz, $CDCl_3$
Pyrrolidine (20 mol%) /
Benzoic acid (30 mol%)



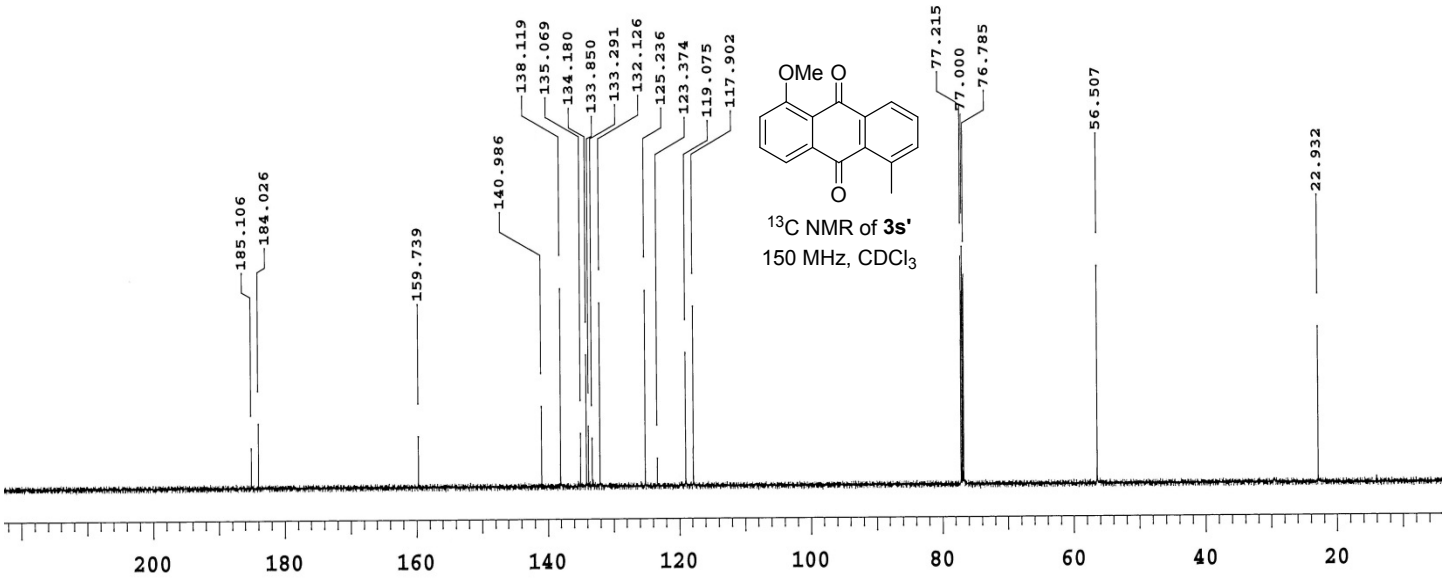




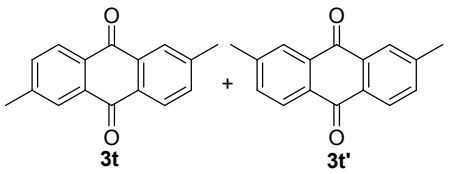
^{13}C NMR of **3r'**
150 MHz, $CDCl_3$
Pyrrolidine (20 mol%) /
Benzoic acid (30 mol%)



^{1}H NMR of **3s'**
600 MHz, $CDCl_3$

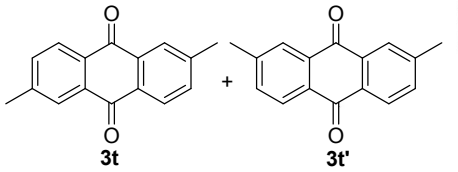


^{13}C NMR of **3s'**
150 MHz, $CDCl_3$



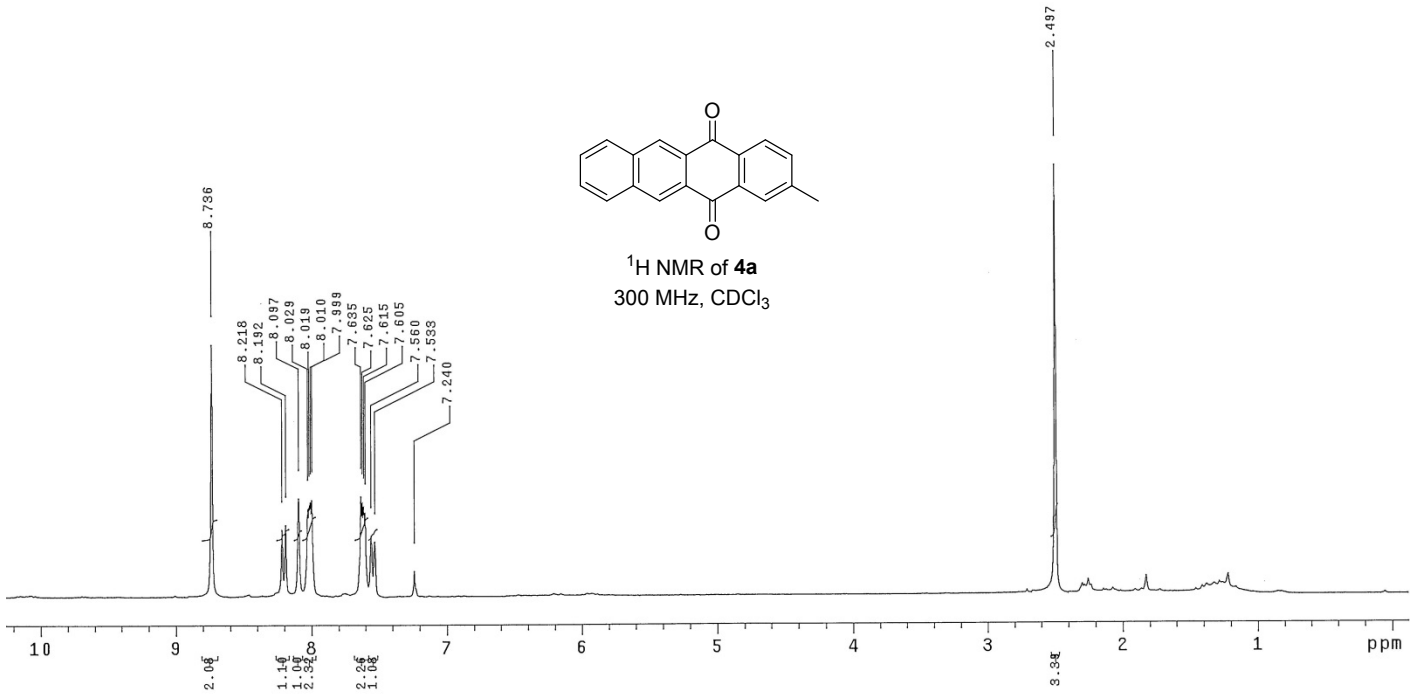
3t **3t'**

^{1}H NMR (600 MHz, $CDCl_3$)

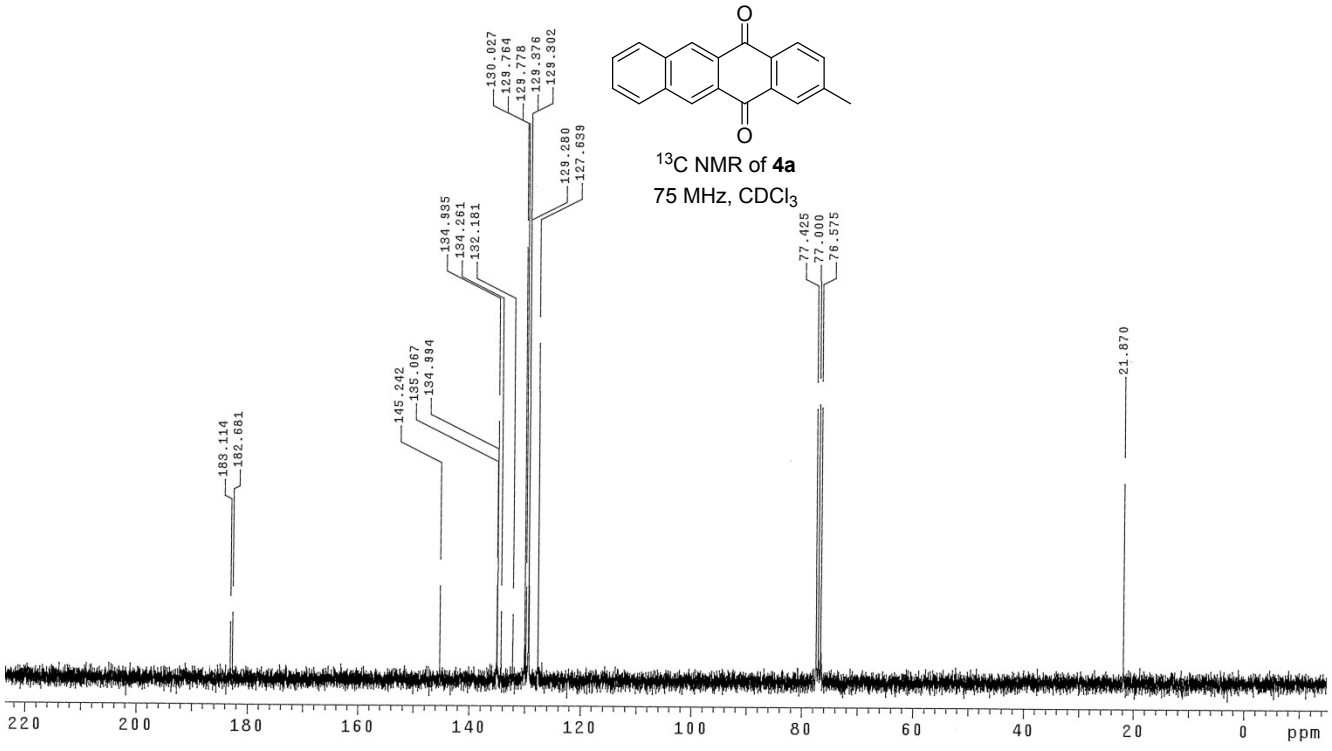


3t **3t'**

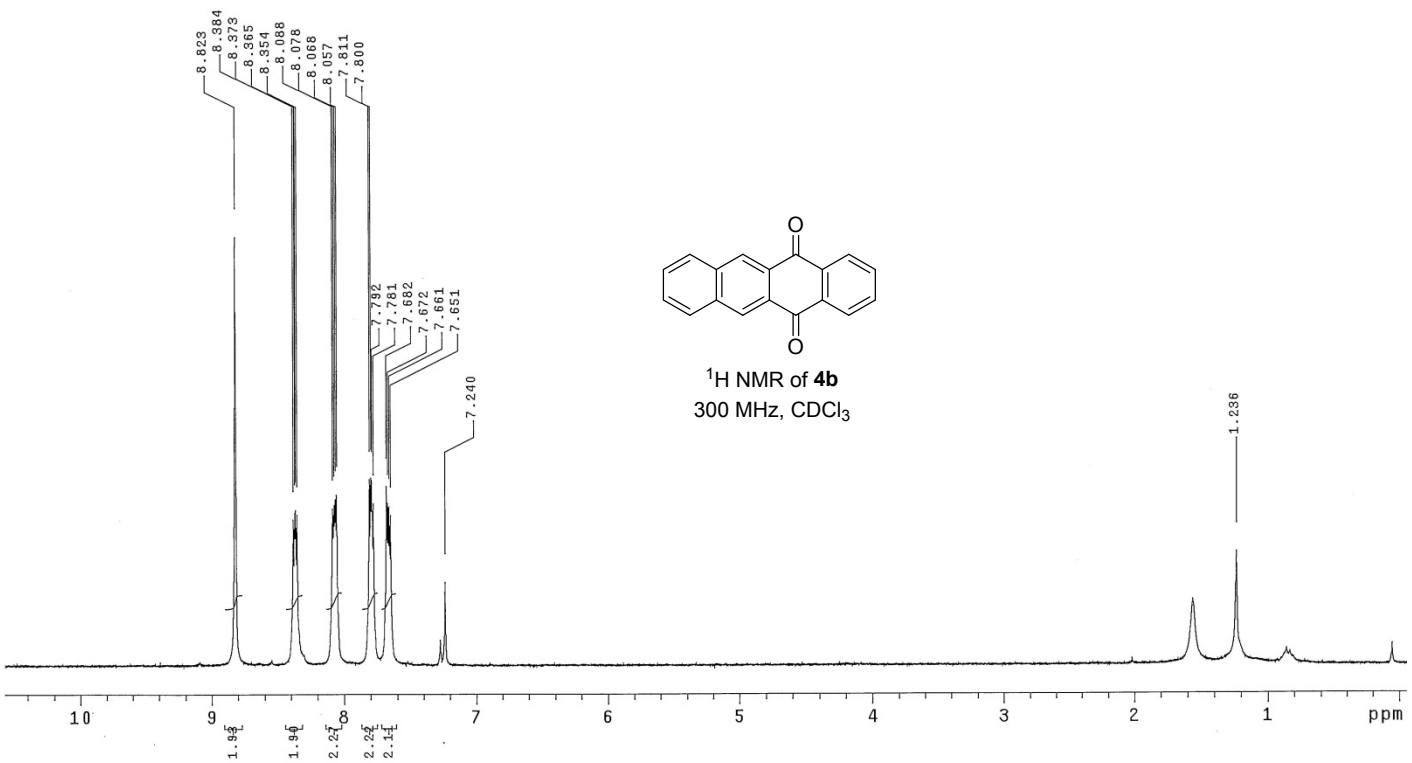
^{13}C NMR (150 MHz, $CDCl_3$)



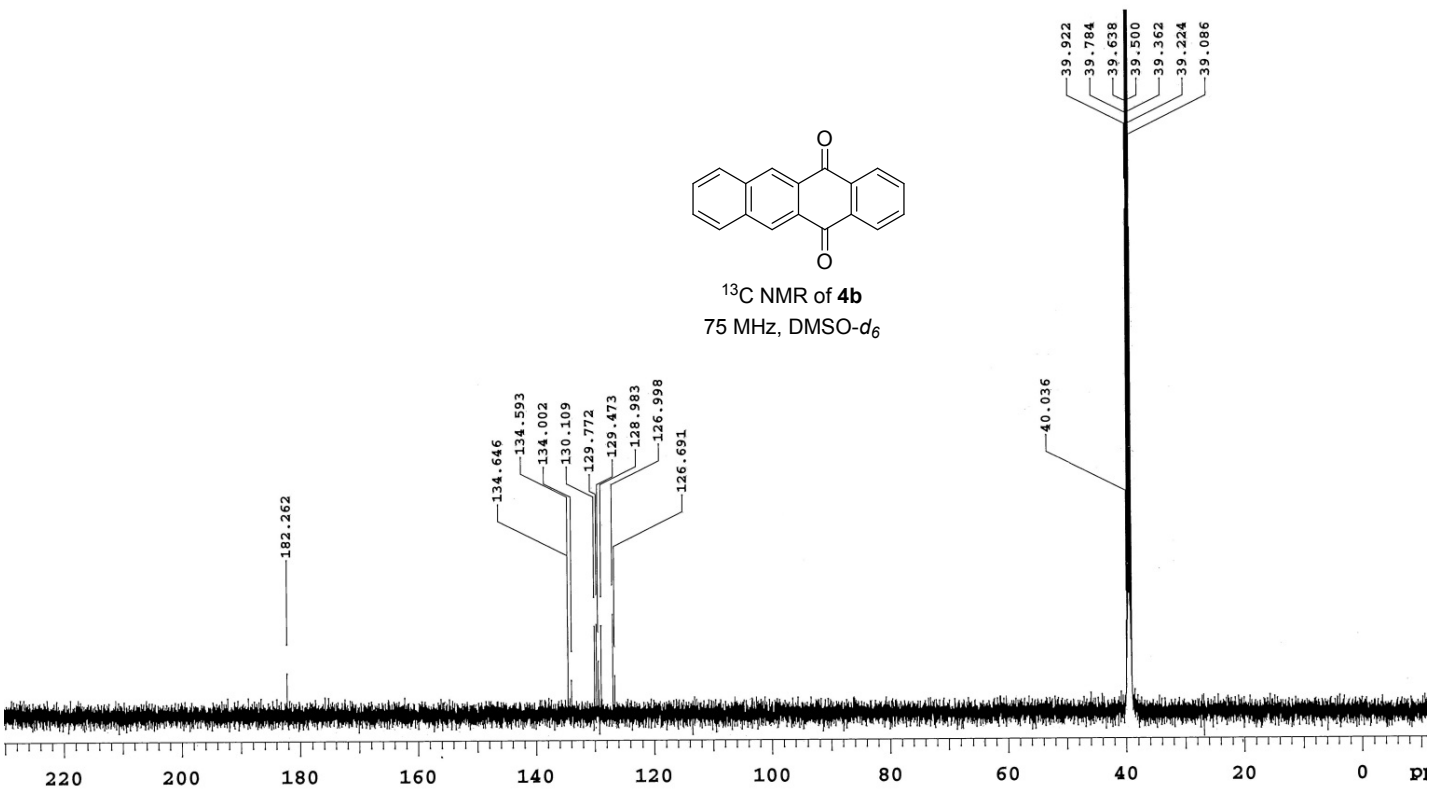
^{1}H NMR of **4a**
300 MHz, $CDCl_3$



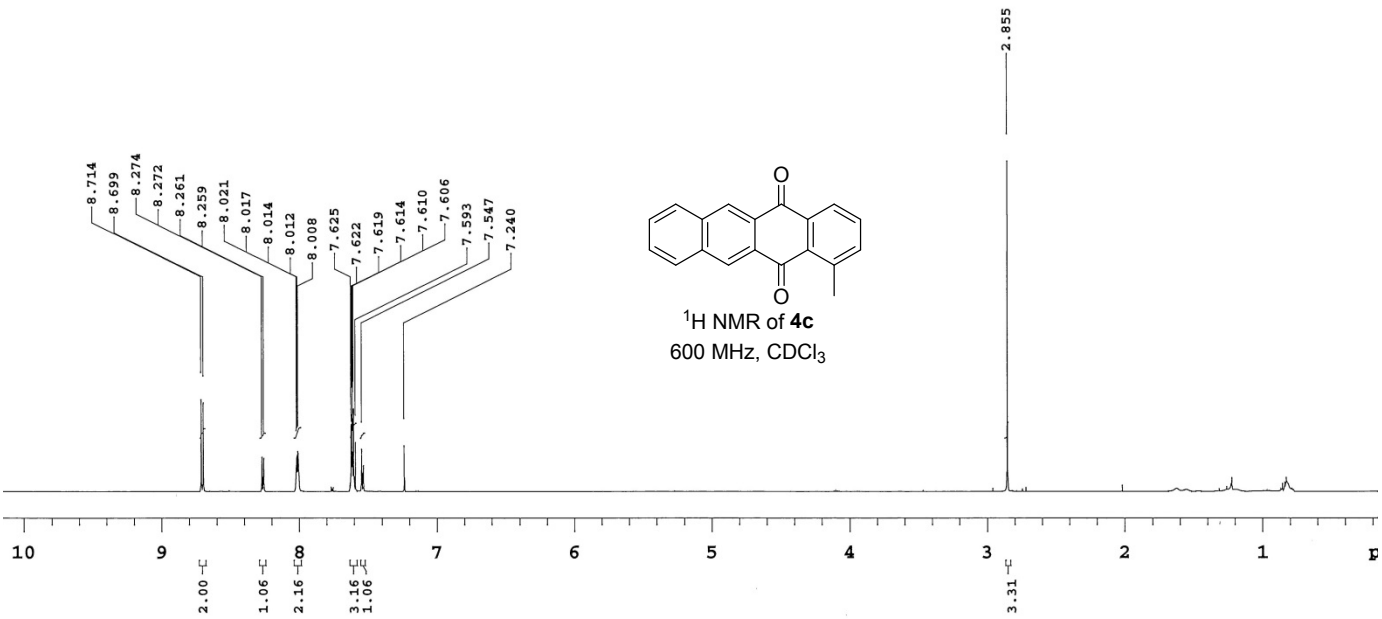
^{13}C NMR of **4a**
75 MHz, $CDCl_3$



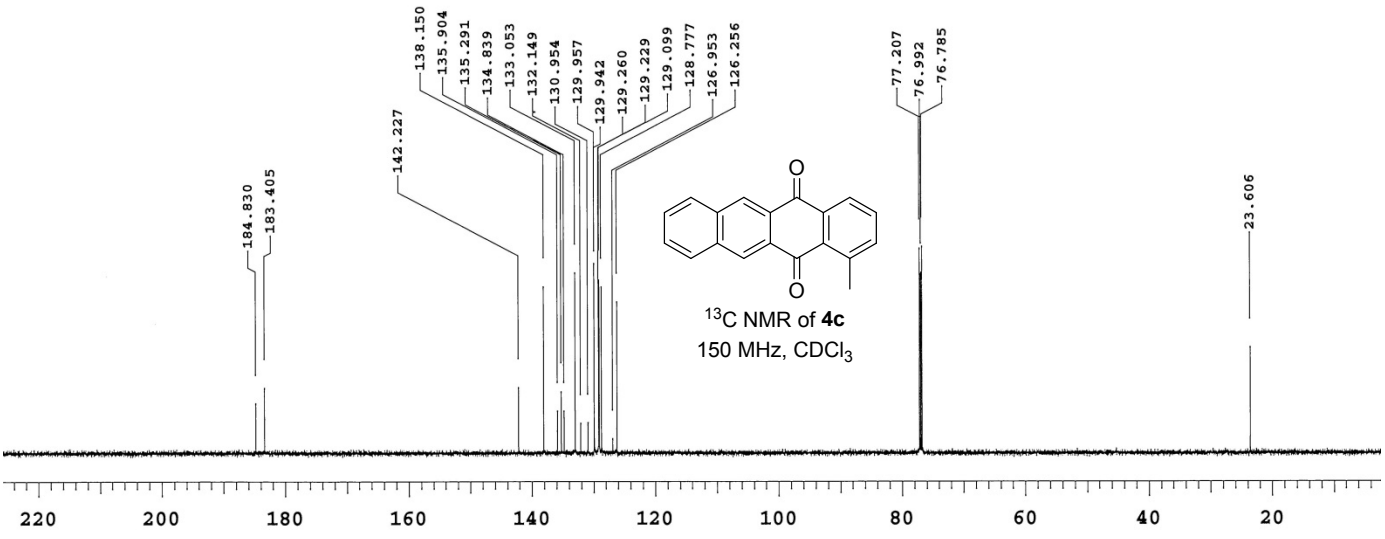
^{1}H NMR of **4b**
300 MHz, $CDCl_3$



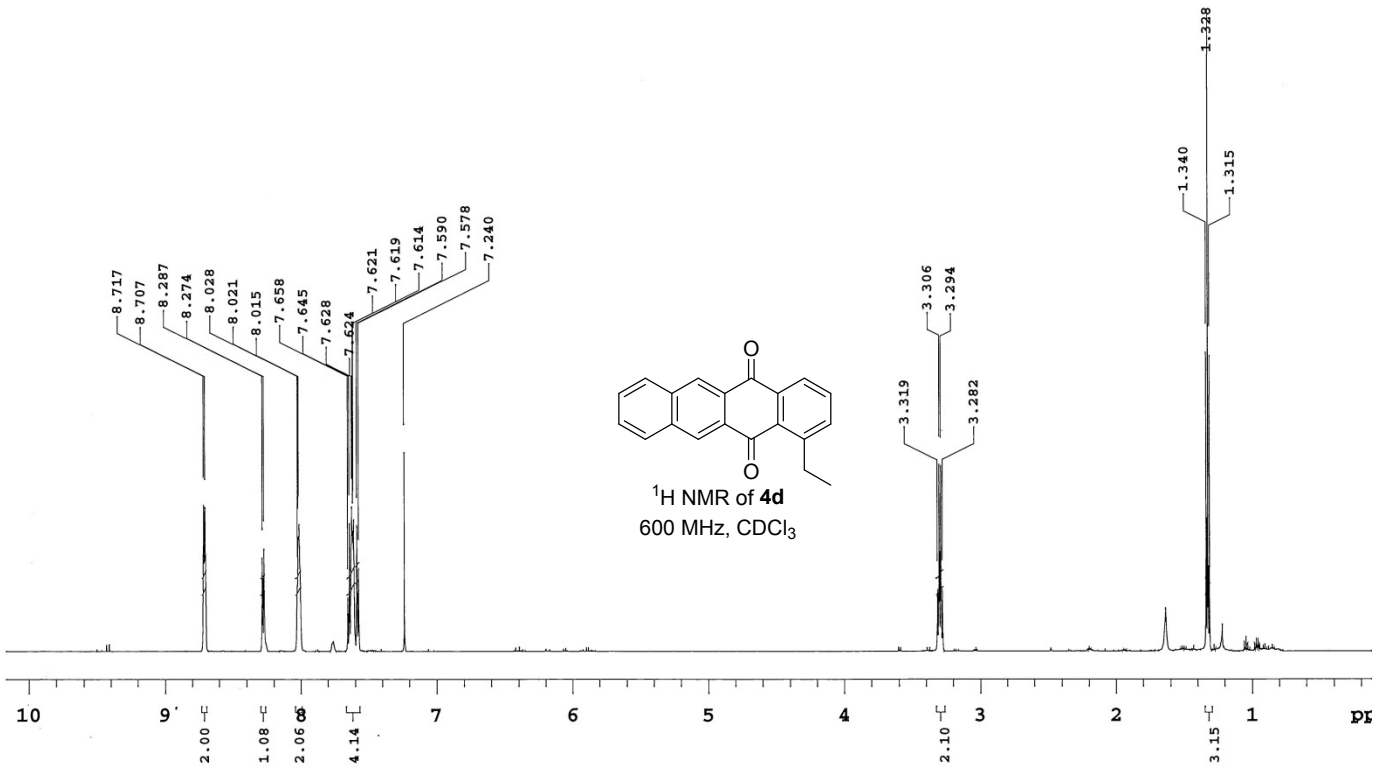
^{13}C NMR of **4b**
75 MHz, DMSO-d_6



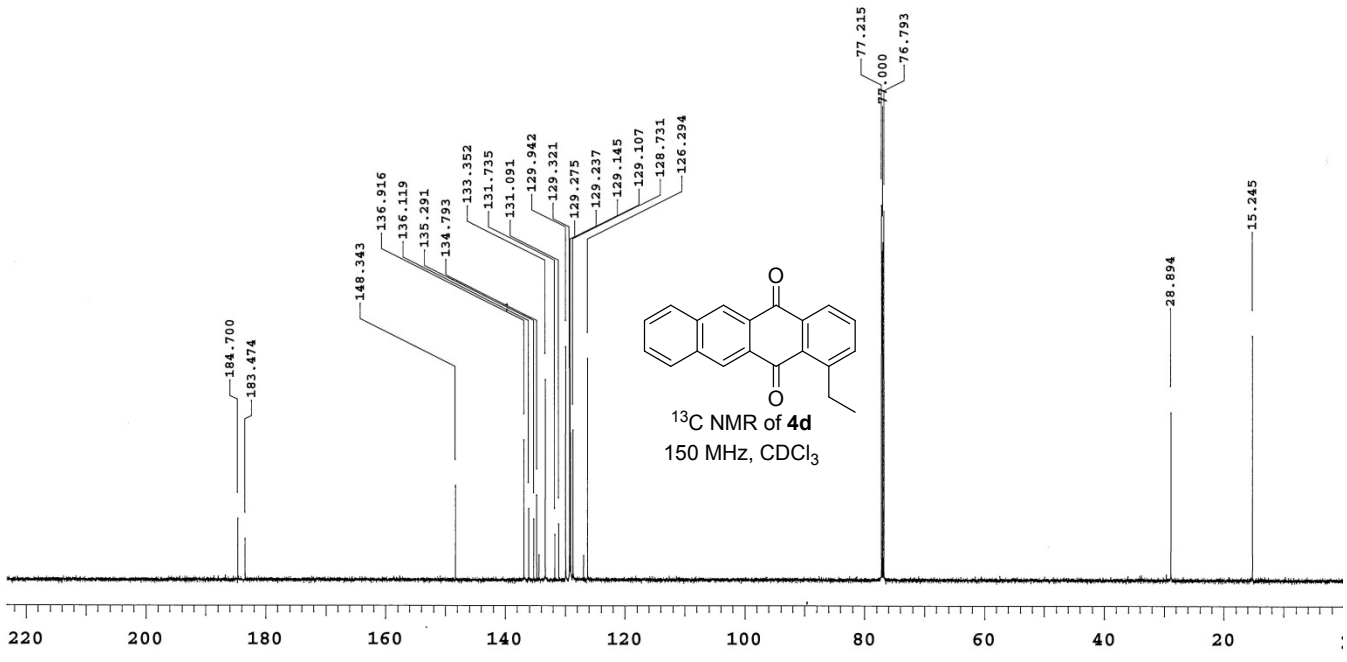
^{1}H NMR of **4c**
600 MHz, $CDCl_3$



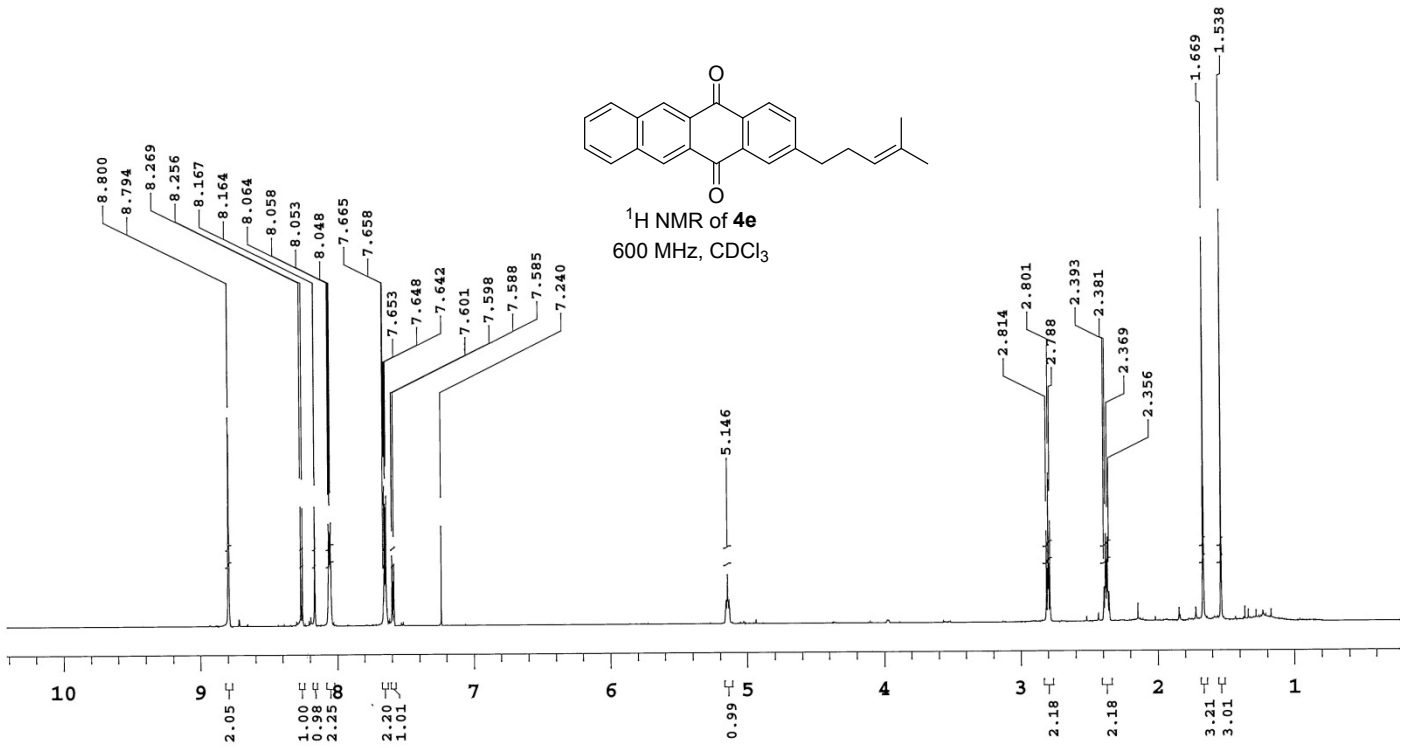
^{13}C NMR of **4c**
150 MHz, $CDCl_3$



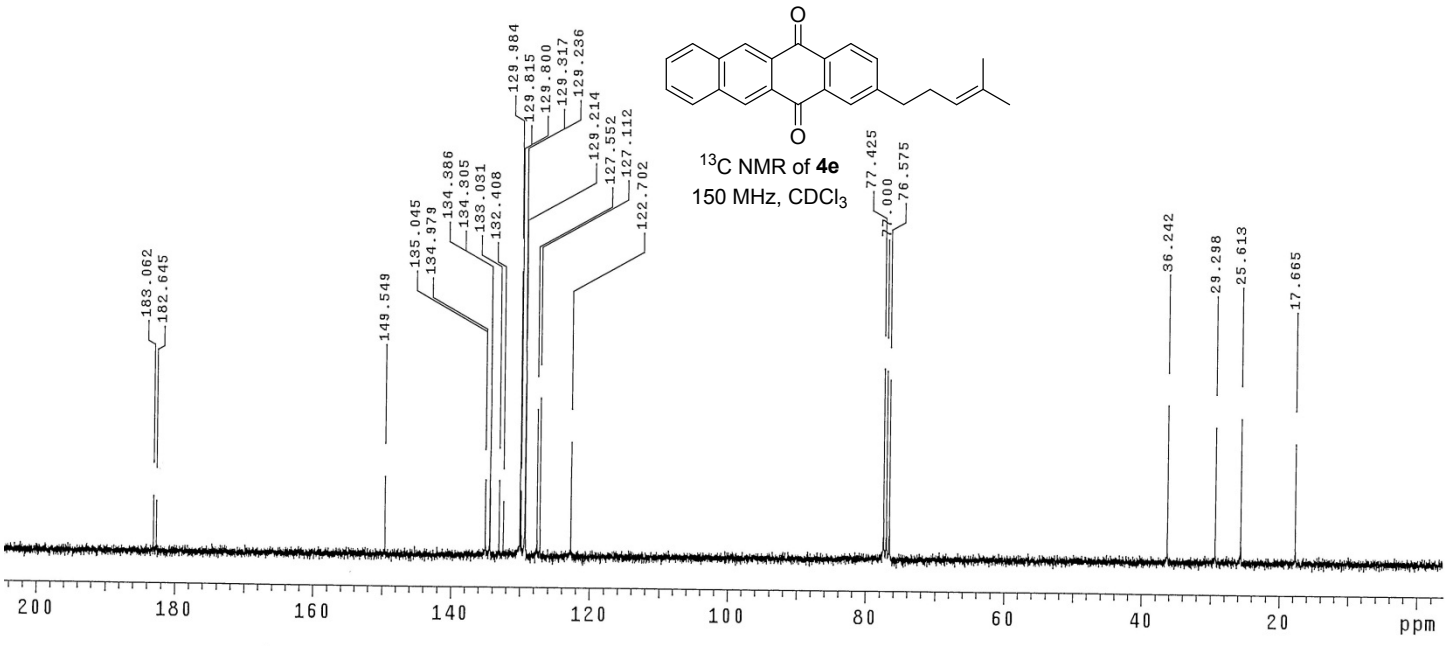
^{1}H NMR of **4d**
600 MHz, $CDCl_3$



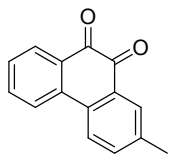
^{13}C NMR of **4d**
150 MHz, $CDCl_3$



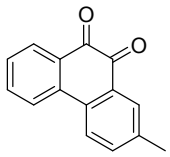
^{1}H NMR of **4e**
600 MHz, $CDCl_3$



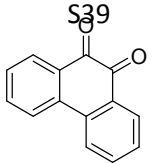
^{13}C NMR of **4e**
150 MHz, $CDCl_3$

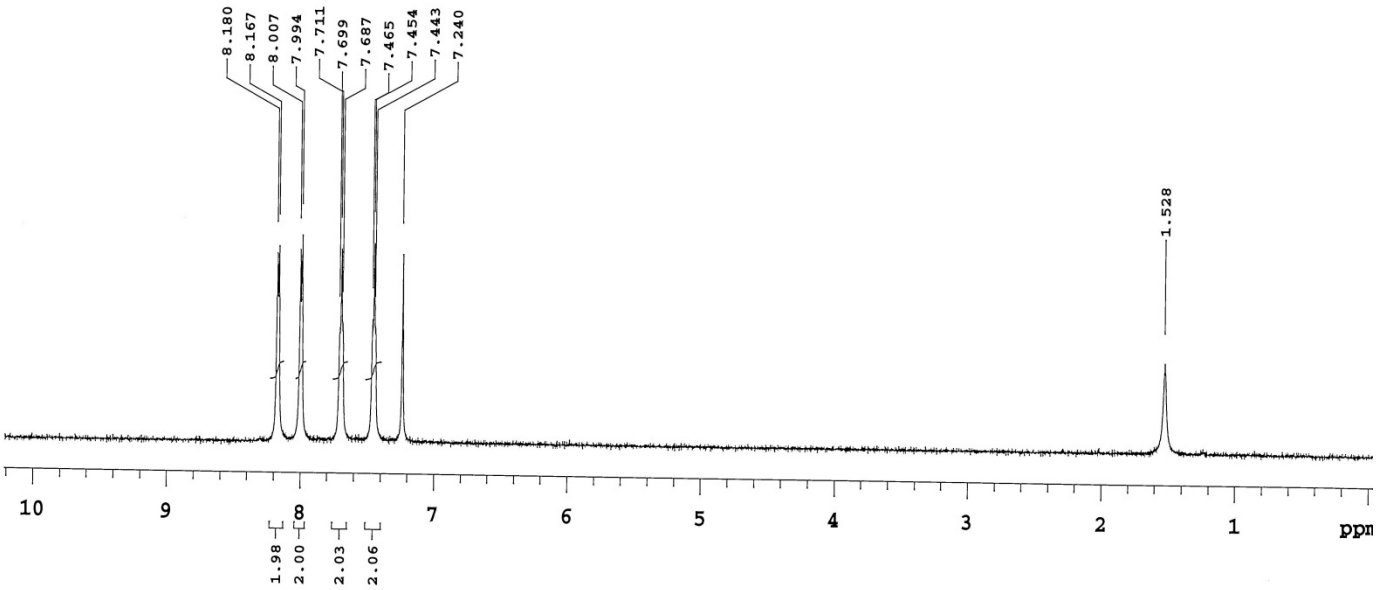


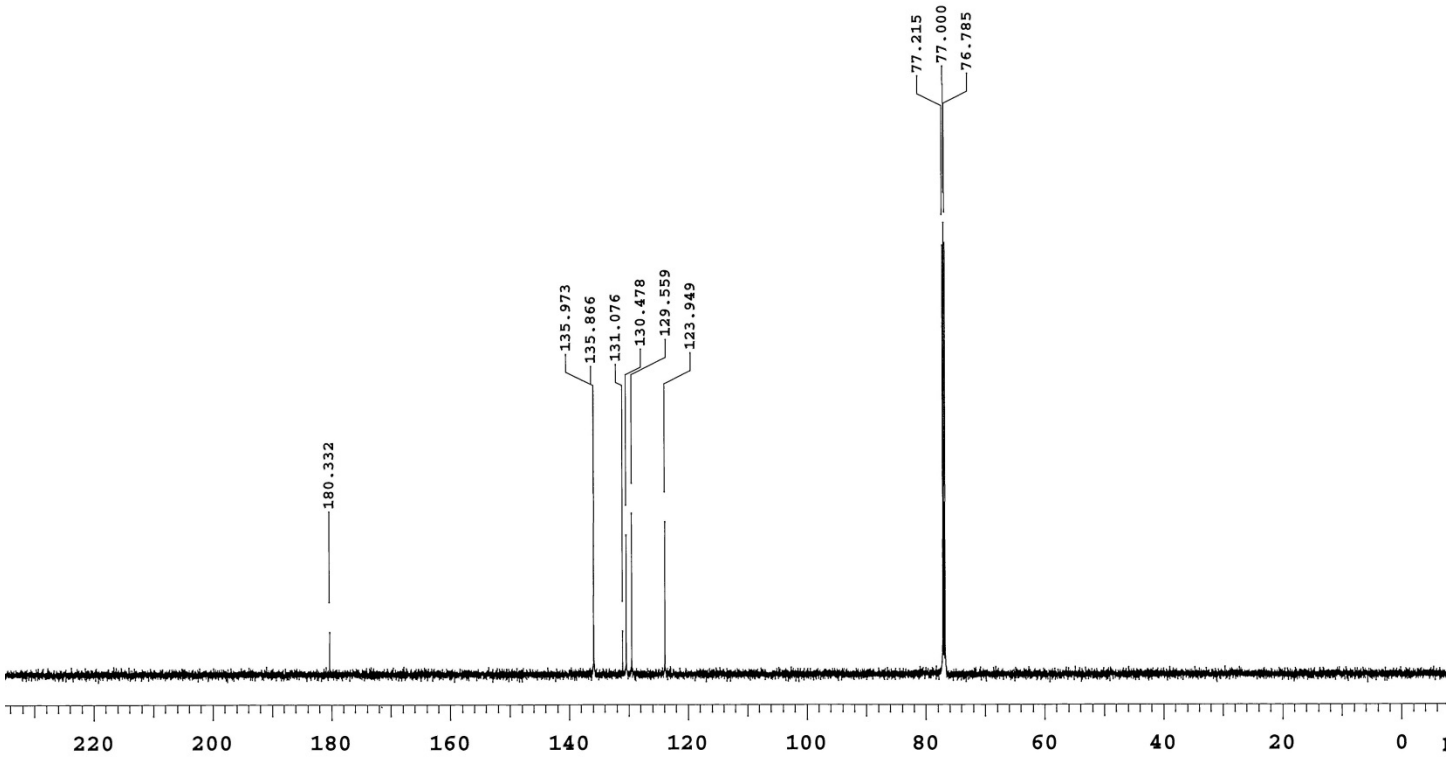
^{1}H NMR of **9a**
300 MHz, $CDCl_3$



^{13}C NMR of **9a**
75 MHz, $CDCl_3$







5. Theoretical Investigation of Selected Dienophiles 1a and 1c

Computational methods

Conformational searches for the dienophiles were run to locate the global minima at the B3LYP/6-31G++* level of theory. Selected structures were successively optimized at the RHF/AM1, RHF/3-21G and B3LYP/6-31G++* levels of theory. Geometries for all structures were fully optimized and normal mode analysis was used to confirm the nature of the stationary points and to evaluate the thermochemical properties. Reported thermochemical properties include zero-point energies (ZPEs) without scaling and were calculated at 1 atm and 298.15 K. The molecular orbitals of the reactants were calculated to analyze the frontier orbital interactions. Free energies in solution were computed on the structures optimized in the gas phase at the B3LYP/6-31G++* level of theory with the polarizable continuum model (PCM) using toluene as solvents. All the calculations were run with Gaussian 09 [s1] at the Supercomputing Center of Korea Institute of Science and Technology.

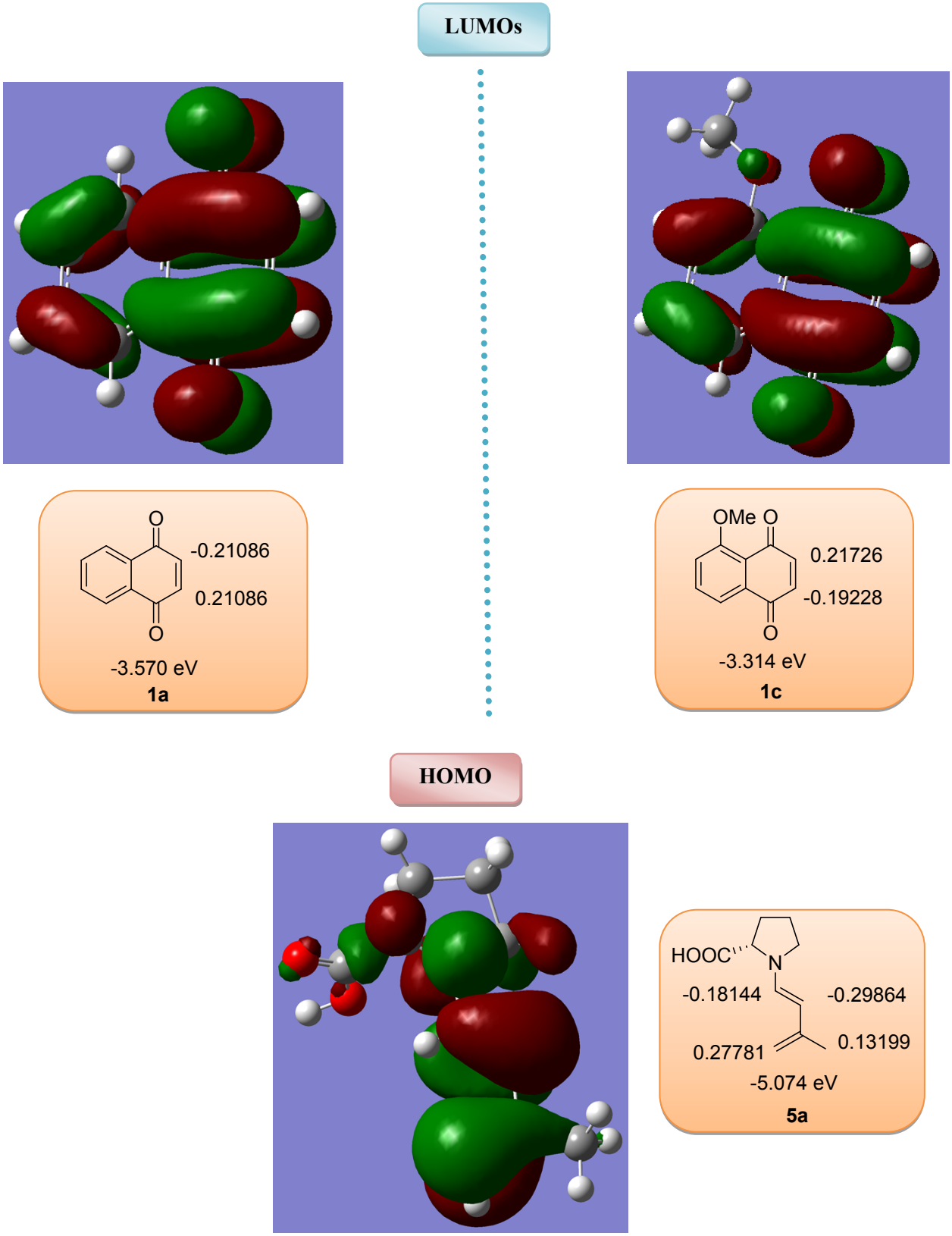


Figure S1. FMO shapes, energies and coefficients of azadiene **5a** and dienophiles **1a & 1c**.

Calculations in the gas phase

Dienophiles

Naphthalene-1,4-dione (**1a**)

B3LYP/6-31G++* Geometry

C	-2.68255	0.70014	-0.00011
C	-1.47552	1.40131	-0.00021
C	-0.26069	0.70603	-0.00008
C	-0.26069	-0.70603	-0.00001
C	-1.47552	-1.40131	0.00021
C	-2.68255	-0.70014	0.00019
H	-3.62447	1.2446	-0.00021
H	-1.46107	2.48799	-0.00037
C	1.02607	1.45943	0.00008
C	1.02607	-1.45943	-0.00027
H	-3.62447	-1.2446	0.00037
C	2.28373	-0.67254	-0.0001
C	2.28373	0.67254	0.00015
H	3.20538	-1.25195	-0.00011
H	3.20538	1.25195	0.00031
O	1.06674	-2.68909	-0.00028
O	1.06674	2.68909	0.00035
H	-1.46107	-2.48799	0.00037

B3LYP/6-31G++* Energy + ZPE = -535.004702

B3LYP/6-31G++* Free energy = -535.038804

B3LYP/6-31G++* Free energy in Tol = -535.043482

Number of imaginary frequencies = 0

5-Methoxynaphthalene-1,4-dione (**1c**)

B3LYP/6-31G++* Geometry

C	-0.69592	2.52929	-0.0001
C	0.63615	2.12194	-0.00016
C	0.93789	0.7587	-0.00013
C	-0.08328	-0.22378	-0.00002
C	-1.43667	0.21212	0.00004
C	-1.72415	1.58942	-0.00001
H	-0.94259	3.58789	-0.00014
H	1.45077	2.83801	-0.00025
C	2.38657	0.37122	-0.00025
C	0.29083	-1.66756	0.00006
H	-2.75282	1.93002	0.00002
C	1.74398	-1.99898	0.00008
C	2.71206	-1.06906	-0.00003
H	1.96139	-3.06413	0.00017
H	3.76941	-1.32119	0.00000
O	-0.51528	-2.59342	-0.00009
O	3.28076	1.21334	-0.00022
O	-2.40179	-0.73035	0.00012
C	-3.77078	-0.33903	0.00051
H	-4.33439	-1.27292	0.00082
H	-4.02041	0.24017	0.89854
H	-4.02099	0.23992	-0.89753

B3LYP/6-31G++* Energy + ZPE = -649.490746

B3LYP/6-31G++* Free energy = -649.528479

B3LYP/6-31G++* Free energy in Tol = -649.535647

Number of imaginary frequencies = 0

(*E*)-(3-methylbuta-1,3-dien-1-yl)-*L*-proline (**5a**)

B3LYP/6-31G++* Geometry

C	-3.24776	-0.24993	-0.00145
C	-1.97398	0.468	0.15575
C	-0.76636	-0.0312	-0.20905
H	-2.0352	1.47365	0.56837
N	0.4561	0.57723	-0.06744
C	2.02593	2.33472	-0.05941
H	2.51448	3.06141	0.59716
H	1.95705	2.77796	-1.06015
C	0.62702	1.93793	0.43472
H	0.54967	1.96323	1.53315
H	-0.15515	2.59366	0.03122
C	2.77986	0.99672	-0.12268
H	3.14173	0.71957	0.87405
H	3.63266	1.00313	-0.80673
C	1.68851	-0.00453	-0.58039
H	1.67639	-0.08792	-1.67691
C	2.0026	-1.40801	-0.0681
O	1.6715	-1.5887	1.23152
H	1.94034	-2.49542	1.47263
O	2.53714	-2.26622	-0.73884
C	-4.46298	0.63331	-0.19665
H	-5.38403	0.0457	-0.26531
H	-4.57171	1.33583	0.64167
H	-4.36988	1.23985	-1.10778
H	-0.71581	-1.01569	-0.67061
C	-3.37065	-1.59263	0.03127
H	-2.52679	-2.24639	0.23669
H	-4.32881	-2.07606	-0.14077

B3LYP/6-31G++* Energy + ZPE = -595.055309

B3LYP/6-31G++* Free energy = -595.097376

B3LYP/6-31G++* Free energy in Tol = -595.102704

Number of imaginary frequencies = 0

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S1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,

O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, 2009.