SUPPORTING INFORMATION

Organocatalyzed benzannulation for the construction of diverse anthraquinones and tetracenediones

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TABLE OF CONTENTS

1. Experimental Section………………………………………………………………………………S2
2. General Procedure for Synthesis of Compounds 3, 4 and 9……………………………………S2
3. $^1$H NMR and $^{13}$C NMR Data of Synthesized Compounds 3, 4 and 9………………………S2
4. $^1$H NMR and $^{13}$C NMR Spectra of Synthesized Compounds 3, 4 and 9………………..S12
5. Theoretical Investigation of azadiene 5a and dienophiles 1a & 1c…………………………S41
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 ($\delta$) relative to TMS (0 ppm) as internal standard or relative to the resonance of the residual protonated solvent ($^1$H : CDCl$_3$, $\delta$ = 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$_3$, $\delta$ = 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 $^\circ$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 $^\circ$C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 183.2, 182.7, 145.1, 134.8, 133.9, 133.8, 133.4, 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$_3$) $\delta$ 8.32-8.29 (4H, m), 7.80-7.77 (4H, m); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 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$_8$O$_2$: 208.0524. Found: 208.0526.

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

Yield 67% (149 mg) as a yellow solid: mp 171-173 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-Ethylantracene-9,10-dione (3d)

Yield 60% (142 mg) as a yellow solid: mp 96-98 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_8$O$_3$: 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\(_3\)) \( \delta \) 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\(_3\)) \( \delta \) 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, 977, 704 cm\(^{-1}\); HRMS \( m/z \) (M\(^+\)) calcd for C\(_{15}\)H\(_{10}\)O\(_3\): 238.0630. Found: 238.0631.

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

Yield 94% (239 mg) as an orange color solid: mp 176-178 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 12.77 (1H, s), 12.77 (1H, s), 8.10 (1H, d, \( J = 8.1 \) Hz), 8.00 (1H, s); IR (KBr) 3428, 1636, 1587, 1450, 1343, 1220, 1148, 1020, 779, 577 cm\(^{-1}\); HRMS \( m/z \) (M\(^+\)) calcd for C\(_{14}\)H\(_8\)O\(_4\): 240.0421. Found: 240.0421.
Yield 90% (229 mg) as an orange color solid: mp 234-236 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 189.0, 186.8, 157.3, 157.0, 148.7, 137.3, 134.8, 133.7, 130.2, 129.3, 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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-methylantracene-9,10-dione (3m)

![Structure of 1,4-Dimethoxy-5-methylantracene-9,10-dione](image)

Yield 91% (257 mg) as a yellow solid: mp 105-107 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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-methylantracene-9,10-dione (3n)

![Structure of 2-Bromo-3-methylantracene-9,10-dione](image)

Yield 47% (142 mg) as a yellow solid: mp 223-225 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 182.7, 182.0, 145.1, 134.2, 133.3, 133.2, 132.3, 132.1, 132.0, 131.2, 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$_9$BrO$_2$: 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')

![Structure of 2-(4-Methylpent-3-enyl)anthracene-9,10-dione and 2-Methyl-1-(3-methylbut-2-en-1-yl)anthracene-9,10-dione](image)

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$_3$) $\delta$ 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$_3$) $\delta$ 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, 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.

3\(\alpha\)': 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 (3\(p\)) and 5,8-Dihydroxy-2-methyl-1-(3-methylbut-2-en-1-yl)anthracene-9,10-dione (3\(p'\))

\(3p\) 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\(_3\)) \(\delta\) 12.82 (1H, s), 12.79 (1H, s), 8.12 (1H, d, \(J = 7.2\) Hz), 8.02 (1H, d, \(J = 7.2\) Hz), 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\(_3\)) \(\delta\) 187.0, 186.6, 157.6, 157.5, 150.1, 134.7, 133.2, 133.1, 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.

3\(p'\): \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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 (3\(q\)) and 1-Hydroxy-7-methylanthracene-9,10-dione (3\(q'\))

\(3q\) and \(3q'\) were obtained as an inseparable 77:23 mixture in 77% (183 mg) yield (2\(a\) was used) and as an inseparable 15:85 mixture in 66% yield (2\(f\) was used). \(3q\) (2\(a\) was used): A yellow solid: mp 128-130 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 188.3 & 182.4 (3\(q\), C=O), 188.7 & 182.0 (3\(q'\), C=O), 162.4, 162.3, 145.9, 145.3, 136.5, 136.4, 135.3, 134.8, 133.5, 133.4, 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 \((3q, \text{CH}_3\), 21.8 \((3q', \text{CH}_3\); IR (KBr) 3428, 1672, 1633, 1597, 1454, 1354, 1295, 1261, 1151, 1035, 772, 711 cm\(^{-1}\); HRMS \(m/z\) (M\(^+\)) calcd for \(C_{13}H_{10}O_3\): 238.0630. Found: 238.0626.

3q' (2f was used): A yellow solid: mp 156-158 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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')

\[\begin{array}{c}
\text{OMe} \\
3r \\
\text{O} \\
\end{array} + \begin{array}{c}
\text{OMe} \\
3r' \\
\text{O} \\
\end{array}\]

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; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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')

\[\begin{array}{c}
\text{OMe} \\
3s \\
\text{O} \\
\end{array} + \begin{array}{c}
\text{OMe} \\
3s' \\
\text{O} \\
\end{array}\]

3s and 3s' were obtained as an inseparable 05:95 mixture in 85% (214 mg) yield. 3s': A yellow solid: mp 170-172 °C; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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, 732, cm$^{-1}$; HRMS m/z (M$^+$) calcd for C$_{16}$H$_{12}$O$_3$: 252.0786. Found: 252.0784.

3s: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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°C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$: 236.0837. Found: 236.0839.

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

Yield 86% (234 mg) as an orange color solid: mp 238-240°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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$_3$) $\delta$ 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°C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 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-$d_6$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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$_3$) $\delta$ 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, 129.1, 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$_3$) $\delta$ 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$_3$) $\delta$ 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; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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, 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; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 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\(_3\)) \(\delta\) 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\(_8\)O\(_2\): 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 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$_3$
$\text{C NMR of 3d}$
$75 \text{ MHz, CDCl}_3$

$\text{H NMR of 3d}$
$300 \text{ MHz, CDCl}_3$
$^1$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-$d_6$
$^1$H NMR of 3i
600 MHz, CDCl$_3$

$^{13}$C NMR of 3i
150 MHz, CDCl$_3$
$^1$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$_3$
$^{1}$H NMR of 3I
600 MHz, CDCl$_3$

$^{13}$C NMR of 3I
150 MHz, CDCl$_3$
$^{1}H$ NMR of 3m
600 MHz, CDCl$_3$

$^{13}C$ NMR of 3m
150 MHz, CDCl$_3$
$^{1}H$ 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$_3$
$^1$H NMR of $3p$
600 MHz, CDCl$_3$

$^{13}$C NMR of $3p$
150 MHz, CDCl$_3$
\[ \text{O} \quad \text{C} \quad \text{H} \quad \text{Cl} \quad \text{O} \quad \text{OH} \]

\[ \text{C} \quad \text{NMR of 3q} \]

\[ 150 \text{ MHz, CDCl}_3 \]

L-proline (20 mol%) / Benzoic acid (10 mol%)

\[ \text{H} \quad \text{NMR of 3q} \]

\[ 600 \text{ MHz, CDCl}_3 \]

L-proline (20 mol%) / Benzoic acid (10 mol%)

\[ \text{CH}_2\text{Cl}_2 \]

\[ \text{O} \quad \text{O} \quad \text{OH} \]

\[ \text{C} \quad \text{NMR of 3q} \]

\[ 150 \text{ MHz, CDCl}_3 \]

L-proline (20 mol%) / Benzoic acid (10 mol%)
$^1$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%)
$\text{H NMR of 3s'}$
600 MHz, CDCl$_3$

$\text{C NMR of 3s'}$
150 MHz, CDCl$_3$
$\text{H NMR (600 MHz, CDCl}_3\text{)}$

$\text{C NMR (150 MHz, CDCl}_3\text{)}$
$^1$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$_6$
S36

$^{13}$C NMR of 4c
150 MHz, CDCl$_3$

$^1$H NMR of 4c
600 MHz, CDCl$_3$

O
O
C
O$^{13}$

O
O
H
N$^{13}$

O
O

S36
$^{13}$C NMR of 4d
150 MHz, CDCl$_3$

$^1$H NMR of 4d
600 MHz, CDCl$_3$
$\text{^1H NMR of 4e}
600 MHz, CDCl$_3$
$^1$H NMR of 9a
300 MHz, CDCl$_3$

$^1$C NMR of 9a
75 MHz, CDCl$_3$

$^1$H NMR of 9b
300 MHz, CDCl$_3$

$^1$C NMR of 9b
600 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 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

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Number of imaginary frequencies = 0

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

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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

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
Reference: