Synthesis of Cyclic Compounds Having *exo*-Methylene Groups through the Diels-Alder Reactions of Vinyl Allenes Obtained from Propargyl Bromide and Indium

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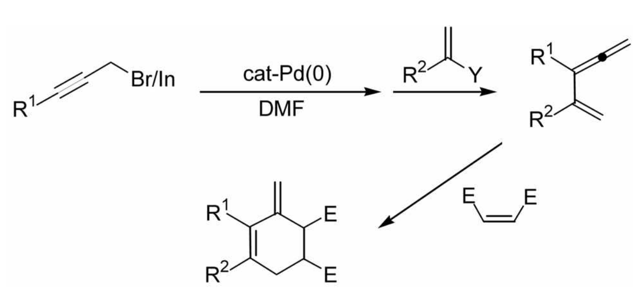
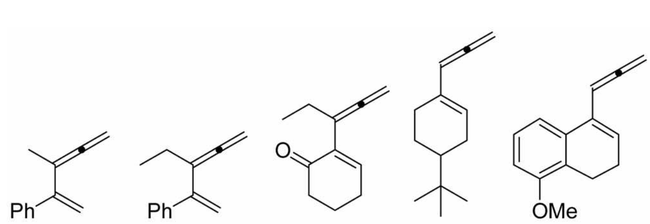
Because allene is a very interesting compound having a hybrid character of C-C double and triple bond, vinyl allenes have been recognized as versatile building blocks in organic synthesis.[1] In particular, vinyl allenes take part in not only the Diels-Alder reaction[2] as the 1,3-diene moiety but also transition metal-catalyzed organic reactions,[3] affording efficient synthetic methods for complex ring compounds. However, because it is not easy to effectively prepare a variety of vinyl allenes, its application to organic reactions has been limited despite the potential of vinyl allenes in organic synthesis. Although vinyl allenes were used in the Diels-Alder reactions, development of synthetic method of cyclic compounds having *exo*-methylene group is still required due to its utility in synthesis of natural products with biological activities.[4] Recently, we have demonstrated that allenylindiums generated in situ from indium and propargyl bromides are effective cross-coupling partners in palladium-catalyzed cross-coupling reactions to produce substituted allenes in excellent yields.[5] In continuation of our studies directed toward preparative method of vinyl allenes with allenyindium, we describe herein the Diels-Alder reaction of vinyl allenes possessing 3,4- and 4,5-disubstituents and ketone group with a variety of dienophiles to give cyclic compounds having *exo*-methylene group (Scheme 1).

First, 3-methyl-4-phenyl-1,2,4-pentatriene (**1a**) as vinyl allene was prepared from the reaction of α-bromostyrene with allenylindium obtained from indium and 1-bromo-2-butyne and then, the Diels-Alder reactions with dienophiles were examined to obtain cyclic compounds having *exo*-methylene group. The results are summarized in Table 1. Reaction of **1a** with maleic anhydride (**2a**) produced the Diels-Alder adduct **3a** in 96% yield in toluene at 100 °C for 3 h (entry 1). Also, 3-ethyl-4-phenyl-1,2,4-pentatriene (**1b**) reacted with a variety of dienophiles such as **2a**, *N*-phenyl maleimide (**2b**), dimethyl maleate (**2c**), and 1,4-naphthoquinone (**2d**), producing the desired products (**3b**, **3c**, **3d**, and **3e**) in good to excellent yields in toluene (entries 2-5). Stimulated by these results, tandem cross-coupling reaction of α-bromostyrene with 1-bromo-2-pentyne and indium (1 equiv.) in the presence of $Pd(PPh_3)_4$ (4 mol%) in DMF followed by Diels-Alder reaction with **2a** was attempted to obtain **3b** in one-pot procedure. However, the desired product **3b** was produced in 7% yield in DMF. Although the cross-coupling product **1b** was produced smoothly, the following Diels-Alder reaction did not proceed effectively. Treatment of **1b** with **2a** did not proceed in THF and DMF. In addition, hetero Diels-Alder reactions were tested. Subjecting **1b** to ethyl glyoxylate (**2e**) provided exclusively 3,6-dihydro-2*H*-pyran (**3f**) having *exo*-methylene group in 80% yield (entry 6). No constitutional isomeric product is formed in this reaction, indicating that the electron-rich central carbon of vinyl allene preferentially adds to the more electron-deficient carbon of dienophile. Although compound **1b** reacted with ethyl acrylate (**2f**) to afford mixture of



Scheme 1. Synthesis of cyclic compounds having *exo*-methylene group from vinyl allenes and dienophiles.



1a **1b** **1c** **1d** **1e**

Figure 1. Vinyl allenes.

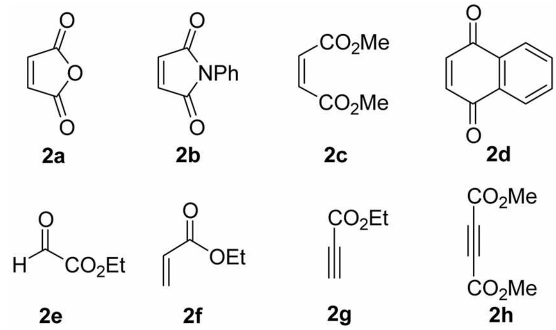
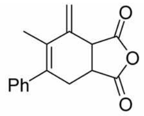
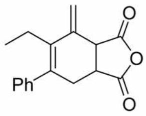
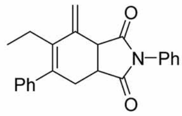
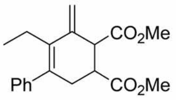
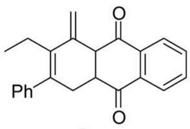
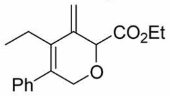
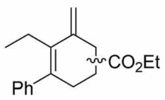
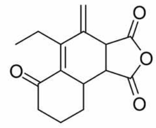
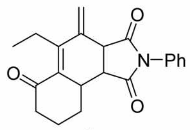
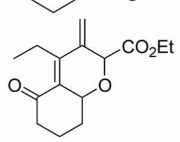
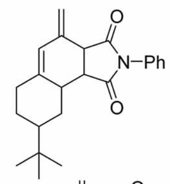
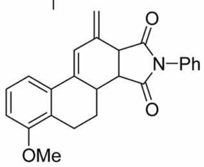
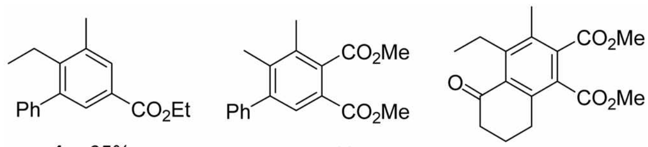


Figure 2. Dienophiles.

Table 1. [4+2] Cycloaddition reaction of vinyl allenes with dienophiles[a]

Entry	Reactants	Time (h)	Products		Yield (%)[b]
1	**1a / 2a**	3		**3a**	96
2	**1b / 2a**	3		**3b**	80
3	**1b / 2b**	4		**3c**	85
4	**1b / 2c**	18		**3d**	30 70[c]
5	**1b / 2d**	5		**3e**	43 87[c]
6	**1b / 2e**	20		**3f**	80[d]
7	**1b / 2f**	20		**3g**	76[e](1:2)[f]
8	**1c / 2a**	13		**3h**	20[g] 77
9	**1c / 2b**	13		**3i**	40[g] 83
10	**1c / 2e**	16		**3j**	30[h] 87[i]
11	**1d / 2b**	12		**3k**	92(1:1.5)[c,j]
12	**1e / 2b**	16		**3l**	74

[a]Reactions were carried out with vinyl allene (1 equiv.) and dienophile (1 equiv.) unless otherwise noted. Reaction conditions: Toluene (100 °C) for entries 1-7 and 11-12. CH_2Cl_2 (25 °C) for entries 8 and 9. CH_2Cl_2 (65 °C) for entry 10. [b]Isolated yields. [c]Dienophile (3 equiv.) was used. [d]Dienophile (30 equiv.) was used. [e]Dienophile (5 equiv.) was used. [f]Regioisomeric ratio. Ethyl 4-ethyl-5-methylene-3-phenylcyclohex-3-enecarboxylate was produced in major. [g]Toluene (25 °C) was used. [h]CH_2Cl_2 (25 °C) was used. [i]Dienophile (2 equiv.) was used. [j]Diastereomeric ratio.



4a 65% **4b** 82% **4c** 95%

Figure 3. Benzene derivatives from Diels-Alder reaction and aromatization.

regioisomeric products in 76% yield, ethyl 4-ethyl-5-methylene-3-phenylcyclohex-3-enecarboxylate was produced in major (entry 7). Although exposure of vinyl allene **1c** to **2a** gave *exo*-methylenecyclohexene derivative **3h** in 20% yield in toluene, adduct **3h** was produced in 77% yield in CH_2Cl_2 at room temperature for 13 h (entry 8). In the case of **2b**, [4+2] cycloaddition adduct **3i** was obtained in 83% yield in CH_2Cl_2 at room temperature for 13 h (entry 9). Reaction of **1c** with **2e** furnished pyran **3j** having *exo*-methylene group in 87% yield with complete regioselectivity (entry 10). Vinyl allenes (**1d** and **1e**) obtained from vinyl triflates and allenylindium were treated with **2b** to produce the desired products (**3k** and **3l**) in 92% (dr = 1:1.5) and 74% yields, respectively (entries 11 and 12). Dienophiles having triple bond such as ethyl propiolate (**2g**) and DMAD (**2h**) were used to Diels-Alder reaction to give rise to multi-substituted benzene derivatives. Reaction of **1b** with **2g** produced selectively ethyl 4-ethyl-3-methyl-5-phenyl benzoate (**4a**) in 65% yield in toluene at 100 °C for 20 h. Compound **1a** and **1c** were treated with DMAD to afford **4b** and **4c** in 82% (toluene, 100 °C, 4 h) and 95% (CH_2Cl_2, 65 °C, 15 h) yields, respectively, through Diels-Alder reaction followed by aromatization.

In summary, we have shown that cyclic compounds having *exo*-methylene group were selectively produced through the Diels-Alder reaction of vinyl allenes obtained from propargyl bromide and indium with a variety of symmetric and unsymmetric dienophiles in good to excellent yields. Also, dienophiles having triple bond gave multi-substituted benzene derivatives through Diels-Alder reaction followed by aromatization.

Experimental Section

5-Methyl-4-methylene-6-phenyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (3a): A mixture of 3-methyl-4-phenyl-1,2,4-pentatriene (**1a**) (46.8 mg, 0.3 mmol) and maleic anhydride (29.4 mg, 0.3 mmol) in toluene (1.0 mL) was heated at 100 °C for 4 h. The reaction mixture was cooling to room temperature and then quenched with $NaHCO_3$ (sat. aq.). The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3) and the combined organics were washed with brine, dried with $MgSO_4$ and concentrated. Recrystallization using methylene chloride and *n*-hexane gave **3a** (74.0 mg, 96%) as a white solid. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 7.40-7.28 (m, 3H), 7.18-7.15 (m, 2H), 5.52 (s, 1H), 5.47(s, 1H), 4.06 (d, J = 9.34 Hz, 1H), 3.56 (ddd, J = 9.58, 6.66, 3.19 Hz, 1H), 2.94 (dd, J = 16.92, 2.80 Hz, 1H), 2.78-2.66 (m, 1H), 1.82 (d, J = 1.54 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 171.3, 141.4, 135.5, 135.4, 129.6, 128.4, 128.1, 127.4, 116.2, 46.2, 40.0, 29.4, 17.0; IR (film) 2951, 1731, 1434, 1241, 1060, 912, 818, 759 cm^{-1}; m.p. 108-109 °C; HRMS (EI) calcd for $C_{16}H_{14}O_3$ M$^+$ 254.0943, found 254.0945.

5-Ethyl-4-methylene-6-phenyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (3b): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.38-7.34 (m, 2H), 7.31-7.28 (m, 1H), 7.14-7.11 (m, 1H), 5.50 (d, J = 0.7 Hz, 1H), 5.45 (s, 1H), 4.04 (d, J = 9.51 Hz, 1H), 3.56 (ddd, J = 9.39, 6.56, 2.70 Hz, 1H), 2.87 (dd, J = 16.24, 2.81 Hz, 1H), 2.67 (ddd, J = 16.25, 6.56, 2.23 Hz, 1H), 2.40-2.31 (m, 1H), 2.23-2.14 (m, 1H), 0.88 (t, J = 7.40 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 171.3, 141.3, 137.0, 135.0, 134.4, 128.5, 127.6, 127.3, 116.0, 47.7, 40.3, 29.8, 22.9, 13.3; IR (film) 1844, 1781, 1700, 904 cm^{-1}; m.p. 135-136 °C; MS (EI) m/z 268 (M$^+$).

5-Ethyl-4-methylene-2,6-diphenyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione (3c): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.48-7.45 (m, 2H), 7.40-7.32 (m, 3H), 7.27-7.24 (m, 3H), 7.17-7.14 (m, 2H), 5.50 (s, 1H), 5.40 (s, 1H), 3.93 (d, J = 8.87 Hz, 1H), 3.45-3.41 (m, 1H), 3.00 (dd, J = 15.73, 2.27 Hz, 1H), 2.67 (ddd, J = 15.70, 6.39, 2.37 Hz, 1H), 2.48-2.39 (m, 1H), 2.26-2.17 (m, 1H), 0.85 (t, J = 7.25 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5, 176.3, 141.7, 137.2, 137.1, 134.7, 132.1, 129.2, 128.6, 128.3, 127.9, 127.0, 126.3, 115.1, 48.4, 39.9, 30.4, 23.0, 13.6; IR (film) 1781, 1715, 1381, 1175 cm^{-1}; m.p. 141-142 °C; MS (EI) m/z 343 (M$^+$).

Dimethyl 4-ethyl-3-methylene-5-phenyl-cyclohex-4-ene-1,2-dicarboxlate (3d): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.36-7.31 (m, 2H), 7.28-7.24 (m, 1H), 7.15-7.12 (m, 2H), 5.30 (s, 1H), 5.23 (s, 1H), 3.93 (d, J = 3.56 Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 3.05-2.94 (m, 2H), 2.69-2.58 (m, 1H), 2.21-2.05 (m, 2H), 0.91 (t, J = 7.43 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 172.1, 142.9, 139.5, 137.2, 133.0, 128.3, 128.2, 127.7, 126.7, 113.9, 52.0, 48.6, 41.1, 32.3, 22.1, 13.7; IR (film) 2952, 1739, 1205 cm^{-1}; MS (EI) m/z 314 (M$^+$).

2-Ethyl-1-methylene-3-phenyl-1,4,4a,9a-tetrahydroanthraquinone (3e): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 8.10-8.07 (m, 1H), 8.05-8.03 (m, 1H), 7.78-7.72 (m, 2H), 7.38-7.33 (m, 2H), 7.29-7.25 (m, 3H), 5.31 (s, 1H), 4.88 (s, 1H), 4.11 (dt, J = 3.61, 1.41 Hz, 1H), 3.58 (q, J = 5.56 Hz, 1H), 2.95 (dd, J = 18.08, 5.97 Hz, 1H) 2.61 (dd, J = 18.06, 5.45 Hz, 1H), 2.17-2.11 (m, 2H), 0.92 (t, J = 7.45 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 196.9, 142.9, 137.1, 136.4, 135.1, 134.4, 134.3, 134.1, 133.8, 128.3, 127.7, 126.9, 126.8, 127.7, 113.7, 54.8, 47.8, 32.8, 22.1, 14.0; IR (film) 3060, 1695, 1594, 703 cm^{-1}; m.p. 101-102 °C; MS (EI) m/z 328 (M$^+$).

Ethyl 4-ethyl-3-methylene-5-phenyl-3,6-dihydro-2*H*-pyran-2-carboxylate (3f): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.38-7.28 (m, 3H), 7.18-7.15 (m, 2H), 5.32 (s, 1H), 5.15 (s, 1H), 4.88 (s, 1H), 4.71 (d, J = 17.13 Hz, 1H), 4.37 (d, J = 17.13 Hz, 1H), 4.28 (q, J = 7.11 Hz, 2H), 2.19 (q, J = 7.29 Hz, 2H) , 1.32 (t, J = 7.17 Hz, 3H), 0.97 (t, J = 7.47 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 138.1, 136.0, 135.6, 131.3, 128.4, 128.3, 127.5, 111.1, 68.0, 61.2, 21.2, 14.3, 13.8; IR (film) 2975, 1739, 1609, 1465, 1130 cm^{-1}; MS (EI) m/z 199 (M$^+$-CO_2Et).

Ethyl 4-ethyl-5-methylene-3-phenylcyclohex-3-enecarboxylate (3g, major compound): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.35 (m, 2H), 7.27 (m, 1H), 7.16 (d, J = 6.83 Hz, 2H), 5.09 (s, 1H), 4.97 (s, 1H), 4.14 (q, J = 7.11 Hz, 2H), 2.83-2.77 (m, 1H), 2.71 (dd, J = 14.1, 3.46 Hz, 1H), 2.65-2.54 (m, 3H), 2.18-2.07 (m, 2H), 1.25 (t, J = 7.16 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 143.4, 141.0, 136.6, 134.6, 128.2, 127.7, 126.6, 110.1, 60.4, 40.2, 35.8, 35.1, 21.9, 14.3, 14.2; IR (film) 2932, 1732, 1442, 1178, 1038, 884, 761, 701 cm^{-1}; MS (EI) m/z 270 (M$^+$).

Ethyl 3-ethyl-2-methylene-4-phenylcyclohex-3-enecarboxylate (3g, minor compound): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.33 (t, J = 7.38 Hz, 2H), 7.24 (m, 1H), 7.12 (m, 2H), 5.22 (s, 1H), 4.98 (s, 1H), 4.19 (m, 2H), 3.40 (t, J = 5.18 Hz, 1H), 2.49 (m, 1H), 2.33 (dt, J = 18.4, 5.20 Hz, 1H), 2.25-2.12 (m, 3H), 1.98 (m, 1H), 1.28 (t, J = 7.10 Hz, 3H), 0.95 (t, J = 7.44 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 143.8, 140.5, 137.9, 133.7, 128.1, 127.6, 126.4, 111.1, 60.4, 47.5, 31.1, 25.7, 22.2, 14.3, 13.9; IR (film) 2931, 1732, 1605, 1443, 1373, 1308, 1258, 1155, 1040, 759 cm^{-1}; MS (EI) m/z 270 (M$^+$).

5-Ethyl-4-methylene-3a,7,8,9,9a,9b-hexahydro-4*H*-naphtho[1,2-*c*]furan-1,3,6-trione (3h): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 5.67 (s, 1H), 5.63 (s, 1H), 4.02 (d, J = 9.52 Hz, 1H), 3.46 (dd, J = 9.50, 5.15 Hz, 1H), 3.15 (octet, J = 7.27, 12.02, 14.68 Hz, 1H), 2.68-2.62 (m, 1H), 2.57-2.48 (m, 1H), 2.46-2.35 (m, 1H), 2.33-2.03 (m, 2H), 2.09-1.97 (m, 2H), 1.76-1.63 (m, 1H), 1.00 (t, J = 7.39 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 171.0, 170.4, 153.3, 137.6, 131.2, 121.0, 49.7, 44.7, 40.0, 37.2, 25.8, 25.3, 21.2, 13.1; IR (film) 1885, 1780, 1662, 1549, 1200 cm^{-1}; m.p. 156 °C; MS (EI) m/z 260 (M$^+$).

5-Ethyl-4-methylene-2-phenyl-3a,7,8,9,9a,9b-hexahydro-4*H*-benzo[*e*]isoindole-1,3,6-trione (3i): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.65-7.32 (m, 3H), 7.15-7.13 (m, 2H), 5.63 (s, 1H), 5.62 (s, 1H), 3.90 (d, J = 9.04 Hz, 1H), 3.46 (dd, J = 4.92, 8.87 Hz, 1H), 3.19 (octet, J = 7.29, 11.72, 14.63 Hz, 1H), 2.72-2.67 (m, 1H), 2.54-2.33 (m, 3H), 2.28-2.17 (m, 1H), 2.08-1.99 (m, 2H), 1.76-1.62 (m, 1H), 1.00 (t, J = 7.33 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 176.4, 175.0, 153.5, 139.7, 131.7, 131.1, 129.2, 128.7, 126.4, 120.0, 49.9, 43.7, 40.0, 38.2, 25.8, 25.5, 21.4, 13.4; IR (film) 1713, 1668, 1498 cm^{-1}; m.p. 160-161 °C; MS (EI) m/z 335 (M$^+$).

Ethyl 4-ethyl-3-methylene-5-oxo-3,5,6,7,8,8a-hexahydro-2*H*-chromene-2-carboxylate (3j): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 5.56 (s, 1H), 5.27 (s, 1H), 4.74 (t, J = 1.53 Hz, 1H), 4.42-4.30 (m, 3H), 2.59-2.28 (m, 5H), 2.07-2.00 (m, 1H), 1.92-1.82 (m, 1H), 1.75-1.63 (m, 1H), 1.35 (t, J = 7.10 Hz, 3H), 1.13 (t, J = 7.45 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 169.2, 142.6, 137.3, 135.4, 114.1, 76.8, 61.5, 42.7, 31.5, 21.8, 19.2, 14.4, 14.2; IR (film) 2940, 1735, 1685, 1457, 1192 cm^{-1}; MS (EI) *m/z* 264 (M^+).

8-*tert*-Butyl-4-methylene-2-phenyl-3a,4,6,7,8,9,9a,9b-octahydrobenzo[e]isoindole-1,3-dione (3k, major compound): ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.44 (t, J = 7.70 Hz, 2H), 7.36 (t, J = 7.47 Hz, 1H), 7.23 (d, J = 7.56 Hz, 2H), 6.04 (s, 1H), 5.30 (s, 1H), 5.17 (s, 1H), 3.80 (d, J = 8.30 Hz, 1H), 3.36 (dd, J = 8.01, 6.86 Hz, 1H), 2.77 (m, 1H), 2.37 (m, 1H), 2.25 (m, 1H), 2.02 (td, J = 12.65, 8.87 Hz, 1H), 1.73 (m, 2H), 1.52 (m, 1H), 1.32 (qd, J = 12.48, 5.41 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 175.0, 142.1, 133.0, 130.9, 128.0, 127.4, 125.3, 121.1, 113.5, 43.5, 42.2, 41.4, 32.3, 31.1, 30.1, 26.0, 24.8, 21.5; IR (film) 3463, 2959, 2867, 2249, 1775, 1709 cm^{-1}; MS (EI) *m/z* 349 (M^+).

4-Methoxy-12-methylene-16-phenyl-6,7,8,12,13,14-hexahydro-16-aza-cyclopenta[a]phenanthrene-15,17-dione (3l): ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.41 (m, 2H), 7.33 (m, 1H), 7.23 (m, 3H), 7.14 (t, J = 8.05 Hz, 1H), 6.85 (d, J = 2.25 Hz, 1H), 6.75 (d, J = 8.02 Hz, 1H), 5.52 (s, 1H), 5.35 (s, 1H), 3.92 (d, J = 8.09 Hz, 1H), 3.83 (s, 3H), 3.50 (dd, J = 8.07, 5.44 Hz, 1H), 3.27 (td, J = 16.33, 3.32 Hz, 1H), 2.88 (m, 1H), 2.55 (qd, J = 13.06, 3.81 Hz, 1H), 2.33 (m, 1H), 2.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 174.8, 155.8, 135.6, 134.8, 133.0, 130.9, 127.9, 127.3, 126.4, 125.5, 125.3, 121.1, 116.1, 114.7, 108.1, 54.5, 45.0, 43.3, 34.3, 23.0, 21.8, IR (film) 2834, 1710, 1572, 1499, 1387, 1261 cm^{-1}; m.p. 189-190 °C; MS (EI) *m/z* 371 (M^+).

Ethyl 4-ethyl-5-methyl-3-phenyl benzoate (4a): ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 7.84 (d, J = 1.33 Hz, 1H), 7.70 (d, J = 1.69 Hz, 1H), 7.46-7.37 (m, 3H), 7.30-7.27 (m, 2H), 4.35 (q, J = 7.09 Hz, 2H), 2.60 (q, J = 7.52 Hz, 2H), 2.44 (s, 3H), 1.36 (t, J = 7.18 Hz, 3H), 0.99 (t, J = 7.51 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.6, 142.4, 141.8, 136.6, 130.5, 129.2, 129.0, 128.0, 127.3, 127.0, 60.8, 23.3, 19.7, 14.4, 14.1; IR (film) 2971, 2930, 1717, 1223 cm^{-1}; MS (EI) *m/z* 268 (M^+).

Dimethyl 3,4-dimethyl-5-phenylphthalate (4b): A mixture of 3-methyl-4-phenyl-1,2,4-pentatriene (**1a**) (46.86 mg, 0.3 mmol) and DMAD (42.63 mg, 0.3 mmol) was heated in toluene (1.0 mL) at 100 °C for 4 h. The reaction mixture was quenched with $NaHCO_3$ (sat. aq.). The aqueous layer was extracted with CH_2Cl_2 (20 mL × 3) and the combined organics were washed with water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. It was purified by recrystallization (CH_2Cl_2:Hex) to give **4b** (73.0 mg, 82%). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 7.78 (s, 1H), 7.47-7.36 (m, 3H), 7.28-7.25 (m, 2H), 3.99 (s, 3H), 3.86 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 166.1, 143.1, 141.0, 140.4, 134.6, 134.4, 129.2, 129.1, 128.2, 127.3, 124.3, 52.6, 52.3, 17.8, 17.1; IR (film) 1730, 1432, 1323 cm^{-1}; m.p. 107-108 °C; MS (EI) *m/z* 298 (M^+).

Dimethyl 4-ethyl-3-methyl-5-oxo-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (4c): ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS) δ 3.90 (s, 3H), 3.87 (s, 3H), 2.99 (q, J = 7.34 Hz, 2H), 2.96 (t, J = 6.26 Hz, 2H), 2.67 (t, J = 6.75 Hz, 2H), 2.33 (s, 3H), 2.04 (quintet, J = 6.50 Hz, 2H), 1.20 (t, J = 7.33 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 169.0, 168.1, 148.4, 141.1, 136.4, 133.7, 133.4, 128.5, 52.6, 52.5, 40.7, 28.1, 23.9, 22.3, 15.6, 14.1; IR (film) 2953, 2359, 1739, 1690, 1436 cm^{-1}; MS (EI) *m/z* 304 (M^+).

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