Supporting Information

Organic Base-Catalyzed Cascade Reaction Of Electron-Deficient Cyclopentadienone With Prop-2-yn-1-ols: Formation of 3-Methylenetetrahydrofuran Ring Condensed With Cyclopentenone

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Reaction of 1a and 2a-k with DABCO (general procedure)

A solution of **1a** (0.50 g, 1.4 mmol), 2-propyn-1-ol (**2a**) (0.24 g, 4.3 mmol) and DABCO (20 mg, 0.18 mmol) in $CHCl_3$ (3 mL) was stirred at room temperature for 1 day. After evaporation of the solvent, the residue was chromatographed on silica gel using benzene–AcOEt eluent to give the bicyclic compound **4a** (488 mg, 84 %).

Compound 4a: colorless prisms; mp 84–85 °C (from EtOH); IR (KBr) cm^{-1}: 1742, 1710 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 3.11 (3H, s, C3a-CO_2CH_3), 3.86 (3H, s, C5-CO_2CH_3), 4.55 (1H, ddd, *J* = 13.2, 2.3, 2.3 Hz, 2-H_{endo}), 4.91 (1H, ddd, *J* = 13.2, 2.3, 2.3 Hz, 2-H_{exo}), 5.32 (1H, brs, =CH_2), 5.45 (1H, brs, =CH_2), 7.26–7.38 (8H, m, Ph), 7.42 (2H, d, *J* = 8.6 Hz, Ph); ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.1 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 71.5 (C2), 73.7 (C3a), 98.1 (C6a), 111.6 (=CH_2), 126.4, 128.2, 128.6, 128.7, 129.5, 131.3 (aromatic CH), 130.8, 134.4, 136.6 (sp^2 quaternary C), 143.3 (C3), 164.1 (C5-COO), 167.5 (C3a-COO), 168.3 (C6), 192.2 (C=O); MS (FAB, m/z): 405 (M^++1). Anal. Calcd. for $C_{24}H_{20}O_6$: C, 71.28; H, 4.98. Found: C, 71.13; H, 5.05.

With LDA

A solution of **1a** (0.50 g, 1.4 mmol), 3-methyl-1-butyn-3-ol (**2c**) (0.20 g, 2.4 mmol) and LDA (1.4 mmol) in THF (3 mL) was stirred at room temperature for 4 days. After evaporation of the solvent, the residue was chromatographed on silica gel using toluene–AcOEt eluents to give the bicyclic compound **4c** (85 mg, 14 %) and the tetracyclic compound **5c** (90 mg, 15 %).

Compound 4c: colorless prisms; mp 163–165 °C; IR (KBr) cm^{-1}: 1748, 1738, 1708 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.36 (3H, s, C2-CH_3 (*endo*)), 1.69 (3H, s, C2-CH_3 (*exo*)), 3.08 (3H, s, C3a-$COOCH_3$), 3.85 (3H, s, C5-CO_2CH_3), 5.18 (1H, s, =CH_2), 5.44 (1H, s, =CH_2), 7.24–7.34 (8H, m, Ph), 7.48 (2H, d, J = 7.5 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.7, 30.7 (C2-CH_3), 52.0 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 75.0 (C3a), 87.4 (C2), 95.5 (C6a), 111.0 (=CH_2), 126.5, 128.0, 128.4, 128.5, 129.8, 131.2 (aromatic CH), 131.3, 132.8, 137.6 (sp^2 quaternary C), 152.1 (C3), 164.4 (C5-COO), 167.8 (C3a-COO), 170.2 (C6), 193.0 (C=O) ppm; MS (FAB, m/z): 433 (M^++H). Anal. Calcd. for $C_{26}H_{24}O_6$: C, 72.21; H, 5.59. Found: C, 72.13; H, 5.63.

Compound 5c: yellow prisms; mp 175–177 °C; IR (KBr) cm^{-1}: 1731 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.63 (3H, s, C4-CH_3), 1.80 (3H, s, C4-CH_3), 3.28 (3H, s, C2a-CO_2CH_3), 3.86 (3H, s, C1-CO_2CH_3), 6.36 (1H, s, C5-H), 7.06 (1H, d, J = 7.5 Hz, aromatic H), 7.15–7.19 (4H, m, aromatic H), 7.25–7.29 (3H, m, aromatic H), 7.74 (1H, d, J = 7.5 Hz, aromatic H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.3, 29.5 (C4-CH_3), 51.9 (C2a-CO_2CH_3), 52.4 (C1-CO_2CH_3), 67.1 (C9c), 88.9 (C4), 89.4 (C2a), 120.3 (C5), 127.4, 127.8, 127.9, 128.2, 128.4, 129.1, 132.0 (aromatic CH), 127.2, 128.7, 133.5, 135.5, 153.2 (sp^2 quaternary C), 162.3 (C1-COO), 168.9 (C2a-COO), 181.1 (C9b), 196.5 (C=O) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{26}H_{22}O_6Na$ (M^++Na): 453.13141. Found: 453.13040.

With P4-*t*-Bu

A solution of **1a** (0.50 g, 1.4 mmol), 1-ethynylcyclopentanol (**2d**) (0.16 g, 1.4 mmol) and P4-*t*-Bu (0.35 mL of 1M hexane solution, 0.35 mmol) in dry toluene (3 mL) was stirred at room temperature for 3 day. After evaporation of the solvent, the residue was chromatographed on silica gel to give the bicyclic compound **4d** (514 mg, 80 %).

Compound 4d: Colorless prisms; mp 211–213 °C; IR (KBr) cm^{-1}: 1742, 1712 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62–1.89 (6H, m, -CH_2-), 2.01–2.08 (1H, m, -CH_2-), 2.38–2.41 (1H, m, -CH_2-), 3.07 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 5.22 (1H, s, =CH_2), 5.41 (1H, s, =CH_2), 7.23–7.36 (8H, m, Ph), 7.52 (2H, br d, J = 7.7 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.0, 25.1, 41.8, 42.8 (-CH_2-), 52.0 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 75.1 (C3a), 95.3 (C6a), 96.6 (C2), 110.5 (=CH_2), 126.6, 128.0, 128.4, 128.5, 129.8, 131.2 (aromatic CH), 131.4, 133.2, 137.6 (sp^2 quaternary C), 151.2 (C3), 164.6 (C6), 167.8 (C5-COO), 169.6 (C3a-COO), 193.3 (C=O) ppm; MS (FAB, m/z): 459 (M^++H). Anal. Calcd. for $C_{28}H_{26}O_6$: C, 73.35; H, 5.72. Found: C, 73.33; H, 5.76.

According to the general procedure, bicyclic compounds (**4**) were obtained from the corresponding prop-2-yn-1-ols (**2**) with **3** and/or **5**. The physical properties and spectral data of the products are as follows.

Compound 3a: colorless prisms; mp 152–155 °C (from EtOH); IR (KBr) cm^{-1}: 1706 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.55 (3H, s, CO_2CH_3), 5.34 (2H, s, 3-H), 6.96–7.02 (4H, m, Ph), 7.16–7.20 (6H, m, Ph), 7.81 (1H, s, 4-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.4 (CO_2CH_3), 67.9 (C3), 121.2 (C5), 127.1, 127.3, 127.5, 127.6, 129.6, 129.9 (aromatic CH), 124.8, 134.0, 137.4, 138.4, 142.0, 142.4, 145.8 (sp^2 quaternary C), 168.4, 168.7 (CO_2CH_3) ppm; MS (EI, m/z): 344 (M^+). Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.43; H, 4.74.

Compound 3b: colorless powder; mp 169–171 °C; IR (Nujol) cm^{-1}; 1736 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.72 (3H, d, J = 6.9 Hz, CH_3), 3.55 (3H, s, CO_2CH_3), 5.59 (1H, q, J = 6.9 Hz, C3-H), 6.95–7.02 (4H, m, Ph), 7.16–7.20 (6H, m, Ph), 7.75 (1H, s, C4-H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3), 52.4 (CO_2CH_3), 75.8 (C3), 120.8 (C4), 127.1, 127.3, 127.5, 127.6, 129.7 (aromatic CH), 124.9, 134.1, 137.5, 138.4, 142.0, 142.3, 150.5 (sp^2 quaternary C), 168.1, 168.5 (COO) ppm; MS (EI, m/z): 359 (M^++1). Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.15; H, 5.03.

Compound 3f: colorless prisms; mp 222–224 °C; IR (KBr) cm-1: 1772, 1737 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24 (3H, s, C-CO_2CH_3), 5.17 (2H, s, C3-H), 7.05–7.09 (4H, m, Ph), 7.15–7.16 (3H, m, Ph), 7.20–7.22 (3H, m, Ph), 7.40–7.48 (5H, m, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.9 (C-CO_2CH_3), 67.8 (C3), 127.3, 127.4, 127.5, 127.6, 128.2, 128.9, 130.0, 130.1 (aromatic CH), 133.3, 134.1, 135.1, 136.8, 140.9, 141.0, 145.3 (sp^2 quaternary C), 168.0, 169.1 (COO) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{28}H_{20}O_4Na$ (M^++Na): 443.12593. Found: 443.12439.

Compound 3h: yellow powder; mp 158–160 °C; IR (KBr) cm^{-1}: 1756 (COO). ^1H NMR (500 MHz, $CDCl_3$) δ 2.35 (3H, s, CH3), 3.49 (3H, s, CO_2CH_3), 5.26 (2H, s, C3-H), 6.98–7.08 (4H, m, Ph), 7.13–7.17 (6H, m, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0 (CH_3), 52.1 (CO_2CH_3), 67.5 (C3), 127.2, 127.3, 127.4, 129.9, 130.1 (aromatic CH), 123.1, 128.0, 134.1, 137.1, 139.3, 139.9, 140.6, 145.6 (sp^2 quaternary C), 168.6, 169.3 (COO) ppm. MS (EI, m/z): 358 (M^+). Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 76.96; H, 5.17.

Compound 3i: yellow powder; mp 130–135 °C; IR (Nujol) cm-1: 1758, 1724 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.30 (3H, t, J = 7.7 Hz, CH_3), 2.71 (2H, q, J = 7.7 Hz, -CH_2-), 3.48 (3H, s, CO_2CH_3), 5.33 (2H, s, C3-H), 6.99–7.03 (4H, m, Ph), 7.17–7.19 (6H, m, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.5 (CH_3), 23.7 (CH_2), 52.1 (CO_2CH_3), 67.2 (C3), 127.3, 127.4, 127.5, 130.0, 130.2 (aromatic CH), 123.5, 134.2, 137.2, 139.6, 142.5, 145.1 (sp^2 quaternary C), 168.7, 169.3 (COO) ppm. MS (EI, m/z): 372 (M^+). Anal. Calcd. for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.13; H, 5.42.

Compound 4b (*endo/exo* mixture): colorless prisms; mp 125–128 °C; IR (KBr) cm^{-1}: 1741, 1709 (C=O); ^1H NMR (500 MHz, $CDCl_3$) (*endo*) δ 1.41 (3H, d, J = 6.3 Hz, CH_3), 3.11 (3H, s, C3a-CO_2CH_3), 3.84 (3H, s, C5-CO_2CH_3), 5.22 (1H, s, =CH_2), 5.35 (1H, q, J = 6.3 Hz, CH), 5.51 (1H, s, =CH_2), 7.24 (10H, m, Ph); (*exo*) δ 1.58 (3H, d, J = 5.7 Hz, CH_3), 3.09 (3H, s, C3a-CO_2CH_3), 3.85 (3H, s, C5-CO_2CH_3), 4.64 (1H, q, J = 5.7 Hz, CH), 5.19 (1H, s, =CH_2), 5.41 (1H, s, =CH_2), 7.24 (10H, m, Ph) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{25}H_{22}O_6Na$ (M^++Na): 441.13141. Found: 441.13161.

Compound 4e: Colorless prisms; mp 222–224 °C; IR (KBr) cm-1: 1744, 1707 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.07–1.84 (9H, m, spiro methylenes), 2.30 (1H, d, J = 13.2, -CH_2-), 3.07 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 5.16 (1H, s, =CH_2), 5.44 (1H, s, =CH_2), 7.25–7.36 (8H, m, Ph), 7.45 (1H, d, J = 7.5 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.6, 22.6, 25.1, 38.6, 39.2 (-CH_2-), 52.0 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 76.8 (3a), 88.8 (C6a), 95.5 (C2), 110.9 (=CH2), 126.5, 128.1, 128.5, 130.2, 131.3 (aromatic CH), 131.0, 132.2, 138.1 (sp^2 quaternary C), 152.2 (C3), 164.6 (C5-COO), 168.0 (C3a-COO), 170.4 (C6), 193.1 (C=O) ppm; MS (FAB, m/z): 473 (M^++H). HRMS Calcd. for $C_{29}H_{29}O_6$ (M^++H): 473.1964. Found: 473.1978.

Compound *E*-4f: colorless prisms; mp 178–180 °C; IR (KBr) cm^{-1}: 1747, 1710 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 2.67 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 4.64 (1H, d, J = 12.0 Hz, C2-H), 4.86 (1H, d, J = 12.0 Hz, C2-H), 6.83 (1H, s, =CH), 7.47 (2H, d, J = 8.0, Ph), 7.78 (2H, d, J = 8.0 Hz, Ph), 7.20–7.35 (11H, m, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 51.5 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 72.2 (C3a), 73.7 (C2), 99.4 (C6a), 126.4, 131.0, 133.5, 134.7, 136.2, 136.4 (aromatic CH), 128.1, 128.2, 128.4, 128.7, 129.4, 131.2 (sp^2 quaternary C), 164.1 (C5-COO), 166.2 (C3a-COO), 167.2 (C6), 192.9 (C=O) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{30}H_{24}O_6Na$ (M^++Na): 503.14706. Found: 503.14562.

Compound 4g: colorless prisms; mp 197–199 °C; IR (KBr) cm^{-1}: 1740, 1707 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ (for *E*-form) 2.13 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 4.73 (1H, d, *J* = 12.6 Hz, C2-H), 5.00 (1H, d, *J* = 12.6 Hz, C2-H), 7.13–7.50 (13H, m, aromatic H), 7.37 (1H, s, =CH), 7.74 (1H, d, *J* = 8.0 Hz, aromatic H), 7.80 (1H, d, *J* = 8.0 Hz, aromatic H), 7.99 (1H, d, *J* = 8.6 Hz, aromatic H), 8.22 (1H, d, *J* = 6.9 Hz, aromatic H) ppm; δ (for *Z*-form) 3.21 (3H, s, C3a-CO_2CH_3), 3.90 (3H, s, C5-CO_2CH_3), 4.73 (1H, d, *J* = 13.5 Hz, C2-H), 5.02 (1H, d, *J* = 13.5 Hz, C2-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (for *E*-form) 50.8 (C3a-CO_2CH_3), 52.7 (C5-CO_2CH_3), 72.4 (C3a), 73.0 (C2), 98.7 (C6a), 124.5, 125.5, 125.9, 126.3, 127.1, 127.8, 128.3, 128.5, 129.3, 131.0 (aromatic CH), 131.2, 131.7, 133.0, 136.2, 136.4, 136.6 (sp^2 quaternary C), 164.2 (C5-COO), 166.0 (C3a-COO), 137.0 (C6), 193.0 (C=O) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{34}H_{26}O_6Na$ (M^++Na): 553.16271. Found: 553.16002.

Compound *E*-4j: yellow powder; mp 75–77 °C; IR (KBr) cm^{-1}: 3429 (OH), 1743 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 3.11 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 4.16 (1H, dd, *J* = 15.3, 5.2 Hz, CH_2OH), 4.30 (1H, dd, *J* = 5.7, 15.3 Hz, CH_2OH), 4.45 (1H, dd, *J* = 12.6, 2.3 Hz, C2-H), 4.82 (1H, d, *J* = 12.6 Hz, C2-H), 5.89 (1H, ddd, *J* = 5.7, 5.2, 2.3 Hz, =CH), 7.21–7.39 (8H, m, Ph), 7.43 (2H, d, *J* = 8.0 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.2 (C3a-CO_2CH_3), 52.8 (C5-CO_2CH_3), 60.3 (CH_2OH), 71.6 (C2), 72.4 (C3a), 99.0 (C6a), 127.0 (=CH-), 126.6, 130.5, 134.9, 136.1 (sp^2 quaternary C), 128.1, 128.6, 128.8, 129.6, 131.6 (aromatic CH), 163.9 (C3a-COO), 167.7 (C5-COO), 169.1 (C6), 194.0 (C=O) ppm. HRMS (ESI^+, m/z) Calcd. for $C_{25}H_{22}O_7Na$ (M^++Na): 457.12632. Found: 457.12077.

Compound *E*-4k: colorless prisms; mp 152–154 °C; IR (KBr) cm^{-1}: 3444 (OH), 1739, 1702 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.22 (3H, s, C2-CH_3), 1.32 (3H, s, C2-CH_3), 1.34 (3H, s, CH_3), 1.67 (3H, s, CH_3), 3.06 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 5.17 (1H, s, OH), 5.50 (1H, s, =CH-), 6.70 (1H, d, *J* = 7.5 Hz, Ph), 7.14 (1H, dd, *J* = 7.5 Hz, Ph), 7.20–7.36 (5H, m, Ph), 7.53 (2H, d, *J* = 8.6 Hz, Ph), 7.84 (1H, d, *J* = 8.6 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.5, 30.3 (CH_3), 30.8, 31.1 (C2-CH_3), 51.5 (C5-CO_2CH_3), 52.8 (C3a-CO_2CH_3), 71.0 (C-OH), 73.2 (C3a), 88.5 (C2), 97.0 (C6a), 126.5, 126.9, 128.1, 128.3, 128.5, 129.9, 131.4, 135.1 (aromatic CH), 131.4, 133.1, 137.5, 138.1 (sp^2 quaternary C), 164.4 (C5-COO), 167.3 (C3a-COO), 172.5 (C6), 198.5 (C=O) ppm. MS (EI, m/z): 490 (M^+). HRMS (ESI^+, m/z) Calcd. for $C_{29}H_{30}O_7Na$ (M^++Na): 513.18892. Found: 513.18789.

Compound 5d: yellow oil; IR (Nujol) cm^{-1}: 1738 (C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 1.75–1.82 (1H, m, -CH_2-), 1.89–1.97 (3H, m, -CH_2-), 2.06–2.10 (3H, m, -CH_2-), 2.70–2.77, (1H, m, -CH_2-), 3.22 (3H, s, C2a-CO_2CH_3), 3.87 (3H, s, C1-CO_2CH_3), 6.36 (1H, s, C5), 7.05 (1H, d, *J* = 7.5 Hz, aromatic H), 7.16–7.19 (4H, m, aromatic H), 7.23–7.29 (3H, m, aromatic H), 7.80 (1H, d, *J* = 7.5 Hz, aromatic H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.3, 24.7, 38.9, 40.2 (-CH_2-), 51.8 (C2a-CO_2CH_3), 52.4 (C1-CO_2CH_3), 67.2 (C9c), 99.1 (C4), 89.4 (C2a), 119.8 (C5), 127.4, 128.1, 128.4, 129.1, 132.0 (aromatic CH), 127.7, 128.9, 133.6, 136.1, 151.6 (sp^2 quaternary C), 162.3 (C1-COO), 168.9

(C2a-COO), 181.0 (C9b), 196.4 (C=O) ppm. HRMS (ESI$^+$, m/z) Calcd. for $C_{28}H_{24}O_6Na$ (M^++Na): 479.14706. Found: 479.14597.

Compound 5e: yellow oil; IR (Nujol) cm^{-1}: 1756, 1730 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32–1.37, (1H, m, -CH_2-), 1.57–1.81 (8H, m, -CH_2-), 2.48 (1H, d, *J* = 12.6 Hz, -CH_2-), 3.27 (3H, s, C2a-CO_2CH_3), 3.86 (3H, s, C1-CO_2CH_3), 6.35 (1H, s, C5), 7.06 (1H, d, *J* = 7.5 Hz, aromatic H), 7.12–7.18 (4H, m, aromatic H), 7.24–7.27 (3H, m, aromatic H), 7.73 (1H, d, *J* = 6.9 Hz, aromatic H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.0, 22.5, 25.2, 35.5, 38.2 (-CH_2-), 51.8 (C2a-CO_2CH_3), 52.4 (C1-CO_2CH_3), 67.1 (C9c), 89.9 (C4), 89.4 (C2a), 120.3 (C5), 127.5, 127.7, 128.1, 128.4, 129.2, 131.9 (aromatic CH), 127.1, 128.9, 131.9, 133.8, 135.8, 153.7 (sp^2 quaternary C), 162.3 (C1-COO), 169.0 (C2a-COO), 181.4 (C9b), 196.8 (C=O) ppm. HRMS (ESI$^+$, m/z) Calcd. for $C_{29}H_{26}O_6Na$ (M^++Na): 493.16271. Found: 493.16190.

Compound 5h: yellow prisms. mp 182–184 °C; IR (Nujol) cm^{-1}: 1756, 1714 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.06 (3H, s, C5-CH_3), 3.12 (3H, s, C2a-CO_2CH_3), 3.87 (3H, s, C1-CO_2CH_3), 5.06 (1H, d, *J* = 12.0 Hz, C4-H), 5.24 (1H, d, *J* = 12.0 Hz, C4-H), 7.10–7.19 (6H, m, aromatic H), 7.24–7.26 (1H, m, aromatic H), 7.34–7.37 (1H, m, aromatic H), 7.86 (1H, d, *J* = 8.0 Hz, aromatic H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.8 (C5-CH_3), 51.8 (C2a-CO_2CH_3), 52.4 (C1-CO_2CH_3), 74.5 (C4), 66.1 (C9c), 91.0 (C2a), 125.0, 127.8, 127.9, 128.8, 132.2 (aromatic CH), 127.2, 128.1, 129.1, 135.4, 137.0, 140.5 (sp^2 quaternary C), 162.2 (C1-COO), 168.5 (C2a-COO), 179.4 (C9b), 194.7 (C=O) ppm. HRMS (FAB, m/z) Calcd. for $C_{25}H_{21}O_6$ (M^++H): 417.1339. Found: 417.1357.

Compound 5i: pale yellow prisms; mp 166–168 °C; IR (KBr) cm^{-1}: 1738 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (3H, t, *J* = 7.5, C5-CH_2CH_3), 2.42 (1H, dt, *J* = 14.9, 7.5 Hz, C5-CH_2CH_3), 2.54 (1H, dt, *J* = 14.9, 7.5 Hz, C5-CH_2CH_3), 3.12 (3H, s, C2a-CO_2CH_3), 3.87 (3H, s, C1-CO_2CH_3), 5.04 (1H, d, *J* = 12.0 Hz, C4-H), 5.23 (1H, d, *J* = 12.0 Hz, C4-H), 7.11–7.26 (7H, m, aromatic H), 7.35 (1H, d, *J* = 7.7 Hz, aromatic H), 7.88 (1H, d, *J* = 7.5 Hz, aromatic H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7 (C5-CH_2CH_3), 23.9 (C5-CH_2CH_3), 51.8 (C2a-CO2CH3), 52.4 (C1-CO_2CH_3), 66.0 (C9c), 74.2 (C4), 90.9 (C2a), 124.8, 127.7, 127.9, 129.2, 132.1 (aromatic CH), 127.9, 129.6, 133.3, 134.1, 137.0, 140.1 (sp^2 quaternary C), 162.2 (C1-COO), 168.6 (C2a-COO), 179.6 (C9b), 196.8 (C=O) ppm. HRMS (FAB, m/z) Calcd. for $C_{26}H_{23}O_6$ (M^++H): 431.1495. Found: 431.1524.

Reaction of 1a and 2l

A solution of **1a** (0.50 g, 1.4 mmol), 4-(diethylamino)but-2-yn-1-ol (**2l**) (0.20 g, 1.6 mmol) in $CHCl_3$ (3 mL) was stirred at room temperature for 1 day. After evaporation of the solvent, the residue was chromatographed on silica gel using *n*-hexane–AcOEt eluent to give the bicyclic compounds **4l** (498 mg, 73 %) and **4l'** (82 mg, 14 %).

Compound 4l: Brown oil; IR (KBr) cm^{-1}: 1741, 1713 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (6H, t, *J* = 7.2 Hz, -CH_2CH_3), 2.40 (2H, dq, *J* = 20.1, 7.2 Hz, -CH_2CH_3), 2.56 (2H, dq, *J* = 20.1, 7.2 Hz, -CH_2CH_3), 3.08 (1H, br d, *J* =

16.0 Hz, -CH=CH_2-N-), 3.09 (3H, s, C3a-CO_2CH_3), 3.31 (1H, br d, *J* = 16.0 Hz, -CH=CH_2-N-), 3.84 (3H, s, C5-CO_2CH_3), 4.44 (1H, dd, *J* = 12.6, 2.9 Hz, C2-H), 4.79 (1H, d, *J* = 12.6 Hz, C2-H), 5.83 (1H, br s, =CH-), 7.24–7.38 (10H, m, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (-CH_2CH_3), 47.1 (-CH_2CH_3), 52.0 (C3a-CO_2CH_3), 52.2 (-CH=CH_2-N-), 52.7 (C5-CO_2CH_3), 71.4 (C2), 72.5 (C3a), 98.8 (C6a), 127.9, 128.1, 128.5, 128.7, 129.3, 131.3 (aromatic CH), 130.6, 134.8, 135.3, 136.2 (sp^2 quaternary C), 164.1 (C5-COO), 167.3 (C3a-COO), 167.5 (C6), 191.1 (C=O) ppm. HRMS (ESI$^+$, m/z) Calcd. for $C_{29}H_{32}NO_6$ (M^++H): 490.22296. Found: 490.22333.

Compound 4l': pale yelleow powder; mp 74–76 °C; IR (KBr) cm^{-1}: 1742 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.09 (3H, s, C3a-CO_2CH_3), 3.85 (3H, s, C5-CO_2CH_3), 4.55 (1H, dt, *J* = 12.0, 4.6 Hz, C2-H), 4.92 (1H, dt, *J* = 12.0, 3.4 Hz, C2-H), 5.14 (1H, ddd, *J* = 12.0, 4.6, 3.4 Hz, =CH_2), 5.22 (1H, ddd, *J* = 12.0, 4.6, 3.4 Hz, =CH_2), 7.24–7.36 (8H, m, Ph), 7.44 (2H, d, *J* = 8.0 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.0 (C3a-CO_2CH_3), 52.6 (C5-CO_2CH_3), 68.6 (C2), 72.5 (C3a), 82.7 (=CH_2), 97.8 (C6a), 100.1 (C3), 126.4, 127.2, 128.0, 128.3, 128.4, 128.5, 128.7, 128.8, 129.4, 131.3 (aromatic CH), 130.5, 134.7, 136.1 (sp^2 quaternary C), 164.0 (C5-COO), 166.9 (C3a-COO), 167.3 (C6), 191.8 (C=O), 201.5 (C=C=CH_2) ppm. HRMS (ESI$^+$, m/z) Calcd. for $C_{25}H_{20}O_6Na$ (M^++Na): 439.11576. Found: 439.11324.

Compound 4bl: yellow prisms; mp 159–161 °C; IR (KBr) cm^{-1}: 1762, 1728 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (6H, t, *J* = 6.9 Hz, -CH_2CH_3), 2.40 (2H, dq, *J* = 16.9, 6.9 Hz, -CH_2CH_3), 2.55 (2H, dt, *J* = 16.9, 6.9 Hz, -CH_2CH_3), 3.06 (1H, br d, *J* = 16.0 Hz, -CH=CH_2-N-), 3.17 (3H, s, C3a-CO_2CH_3), 3.30 (1H, br d, J = 16.0 Hz, -CH=CH_2-N-), 3.86 (3H, s, C5-CO_2CH_3), 4.44 (1H, dd, *J* = 12.6, 2.3 Hz, C2-H), 4.81 (1H, d, *J* = 12.6 Hz, C2-H), 5.84 (1H, br s, =CH-), 7.27 (4H, d, *J* = 8.6 Hz, Ph), 7.42 (4H, d, *J* = 8.6 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.9 (-CH_2CH_3), 47.1 (-CH_2CH_3), 52.2 (C3a-CO_2CH_3), 52.2 (-CH=CH_2-N-), 52.9 (C5-CO_2CH_3), 71.5 (C2), 72.1 (C3a), 98.2 (C6a), 129.3, 130.7, 132.0 (aromatic CH), 123.2, 126.4, 128.1, 128.3, 135.1, 135.6 (sp^2 quaternary C), 163.7 (C5-COO), 165.4 (C3a-COO), 167.0 (C6), 190.6 (C=O) ppm. HRMS (ESI$^+$, m/z) for $C_{29}H_{30}NO_6Br_2$ (M^++H): 648.04194. Found: 648.04270.

Compound 4bl': pale yellow prisms; mp 177–180 °C; IR (KBr) cm^{-1}: 1741, 1721 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.19 (3H, s, C3a-CO_2CH_3), 3.87 (3H, s, C5-CO_2CH_3), 4.56 (1H, ddd, *J* = 11.5, 5.2, 5.2 Hz, C2-H), 4.92 (1H, dd, *J* = 11.5, 2.9 Hz, C2-H), 5.16 (1H, dd, *J* = 11.5, 5.2 Hz, =CH_2), 5.25 (1H, dd, *J* = 11.5, 5.2 Hz, =CH_2), 7.33 (4H, d, *J* = 7.5 Hz, Ph), 7.43 (4H, d, *J* = 7.5 Hz, Ph) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 52.3 (C3a-CO_2CH_3), 52.9 (C5-CO_2CH_3), 68.8 (C2), 72.1 (C3a), 83.0 (=CH2), 97.3 (C6a), 99.8 (C3), 128.2, 129.3, 130.3, 130.8, 131.3, 131.8, 132.0, 135.1 (aromatic CH), 123.1, 126.4, 128.9, 135.1 (sp^2 quaternary C), 163.6 (C5-COO), 165.3 (C3a-COO), 166.7 (C6), 191.5 (C=O), 201.5 (C=C=CH_2) ppm. HRMS (ESI$^+$, m/z) Calcd. for $C_{25}H_{18}Br_2O_6Na$ (M^++Na): 596.93474. Found: 596.93365.

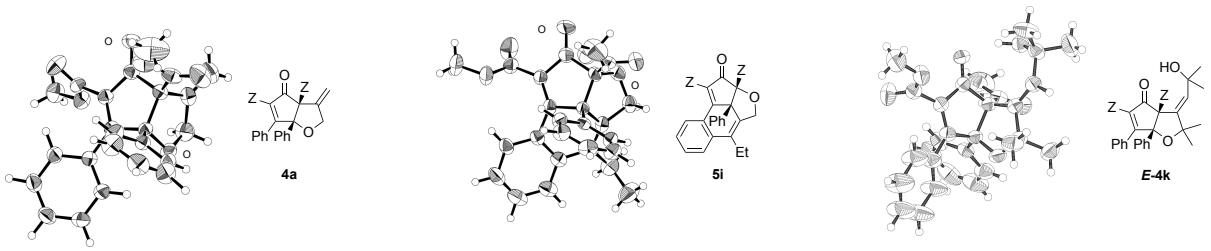
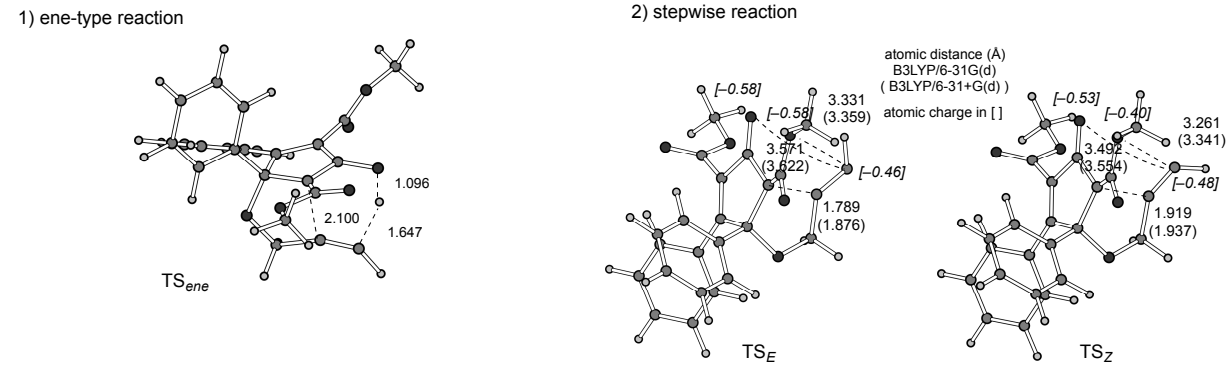


Figure S1. X-ray structures of **4a**, **5i** and ***E*-4k**

The data for **4a**, **5i**, ***E*-4k** have been deposited at CCDC.[12]



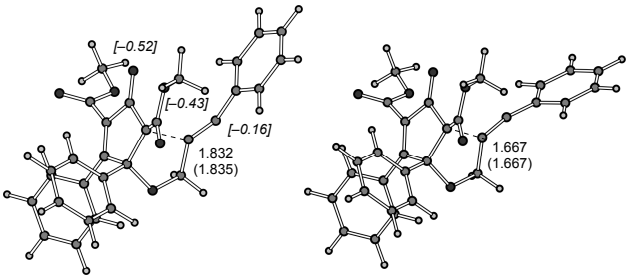
	GS	TS_{ene}	**4a**
B3LYP/6-31G(d)			
E [a)]	–1377.84051	–1377.78584	–1377.90456
(E_{ZPE} [a)])	(–1377.43127)	(–1377.38200)	(–1377.49429)
ΔE_{rel} [b,c)]	0	30.9	-39.5

[a] hartree. [b] Potential energy barriers relative to E_{ZPE} of GS. [c] kcal/mol

	GS	TS_E	TS_Z
B3LYP/6-31G(d)			
E [a)]	–1377.29269	–1377.26145	–1377.24884
(E_{ZPE} [a)])	(–1376.89807)	(–1376.86816)	(–1376.85581)
ΔE_{rel} [b,c)]	0	18.8	26.5
B3LYP/6-31+G(d)			
E [a)]	–1377.36101	–1377.33173	–1377.31766
(E_{ZPE} [a)])	(–1376.96752)	(–1376.93937)	(–1376.92572)
ΔE_{rel} [b,c)]	0	17.7	26.2

[a] hartree. [b] Potential energy barriers relative to E_{ZPE} of GS. [c] kcal/mol

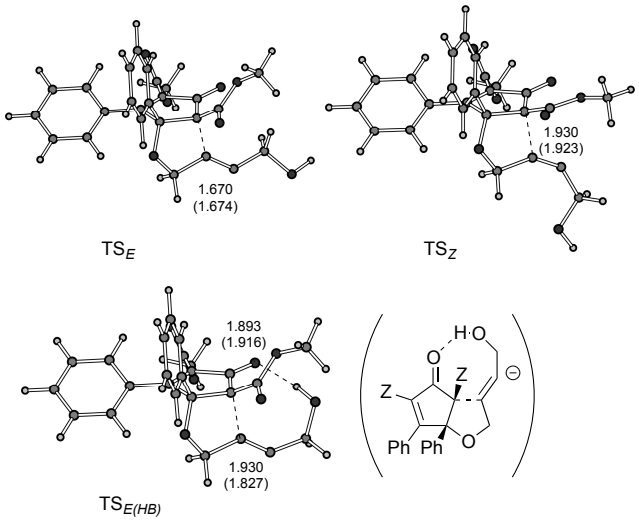
Figure S2. Calculated TS geometries and reaction barriers of the two possible reaction pathways of **1a** and **2a**



	GS	TS$_E$	TS$_Z$
B3LYP/6-31G(d)			
E [a)]	–1608.36058	–1608.33597	–1608.33445
(E_{ZPE} [a)])	(–1607.88042)	(–1607.85810)	(–1607.85660)
ΔE_{rel} [b,c)]	0	14.0	15.0
B3LYP/6-31+G(d)			
E [a)]	–1608.43351	–1608.40907	–1608.40728
(E_{ZPE} [a)])	(–1607.95474)	(–1607.93247)	(–1607.93070)
ΔE_{rel} [b,c)]	0	14.0	15.1

[a] hartree. [b] Potential energy barriers relative to E_{ZPE} of GS. [c] kcal/mol

Figure S3. Calculated TS geometries and reaction barriers leading to *E*, *Z*-isomers for the stepwise reaction pathway of **1a** and **2f**



	TS$_E$	TS$_Z$	TS$_{E(HB)}$
B3LYP/6-31G(d)			
E [a)]	–1491.78497	–1491.77763	–1491.80136
(E_{ZPE} [a)])	(–1491.35668)	(–1491.34938)	(–1491.37197)
ΔE_{rel} [b,c)]	0	4.6	–9.6
B3LYP/6-31+G(d)			
E [a)]	–1491.86420	–1491.85525	–1491.87571
(E_{ZPE} [a)])	(–1491.43697)	(–1491.42821)	(–1491.44751)
ΔE_{rel} [b,c)]	0	5.5	–6.6

[a] hartree. [b] Potential energy difference relative to E_{ZPE} of TS$_E$. [c] kcal/mol

Figure S4. Calculated TS energies and geometries for the stepwise reaction pathway of **1a** and **2j**