

Supporting Information for

Tandem Pauson-Khand reaction and Diels-Alder reaction for access to polycycles in a one-pot
reaction

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General. IR spectra were obtained in CH₂Cl₂ solution with a Shimadzu IR-470. ¹H NMR and ¹³C NMR spectra were obtained with a Bruker 300 spectrometer. Elemental analyses were done at National Center for Inter-University Research Facilities, Seoul National University. High Resolution Mass spectra were obtained at Korea Basic Science Institute (Dae Gu).

Compound **1a**. Yield: 48%; ¹H NMR (CDCl₃): δ 3.95 (m, 1 H), 3.67 (s, 3 H), 3.59 (s, 3 H), 3.37 (dd, *J* = 2.4, 4.4 Hz, 1 H), 2.78 (s, 1 H), 2.68 (m, 1 H), 2.53 (s, 1 H), 2.26 (d, *J* = 8.7 Hz, 1 H), 2.09 ~ 2.00 (m, 3 H), 1.77 (m, 1 H), 1.67 (m, 3 H), 1.47 ~ 1.39 (m, 3 H), 1.19 ~ 1.09 (m, 4 H), 0.99 (s, 2 H); ¹³C NMR (CDCl₃): δ 209.6, 174.0, 172.7, 149.8, 130.1, 57.9, 52.6, 51.6, 49.0, 44.6, 43.4, 43.1, 41.1, 41.0, 39.2, 35.6, 34.6, 28.5, 28.3, 28.1, 26.6, 26.5; IR ν(C=O) 1691 cm⁻¹; HRMS for C₂₂H₂₈O₅: calcd. 372.1937, obsd. 372.1936.

Compound **1b**. Yield: 42%; ^1H NMR (CDCl_3): δ 3.78 (s, 3 H), 3.71 (s, 3 H), 3.13 (dd, $J = 6.4$, 11.8 Hz, 1 H), 2.69 (m, 1 H), 2.63 (s, 1 H), 2.56 (t, $J = 11.3$ Hz, 1 H), 2.26 ~ 2.19 (m, 2 H), 2.12 (m, 1 H), 1.95 (s, 1 H), 1.83 ~ 1.76 (m, 3 H), 1.60 ~ 1.48 (m, 4 H), 1.30 ~ 1.24 (m, 2 H), 1.24 ~ 1.18 (m, 3 H), 1.08 (s, 2 H); ^{13}C NMR (CDCl_3): δ 209.0, 175.2, 173.4, 151.0, 130.8, 57.0, 52.2, 52.1, 47.2, 46.1, 45.6, 44.5, 42.6, 41.3, 40.4, 34.7, 32.2, 29.3, 28.9, 28.8, 27.8, 26.3; IR $\nu(\text{C}=\text{O})$ 1698 cm^{-1} ; HRMS for $\text{C}_{22}\text{H}_{28}\text{O}_5$: calcd. 372.1937, obsd. 372.1931.

Compound **2a**. Yield: 48%; ^1H NMR (CDCl_3): δ 6.13 (m, 1 H), 6.09 (m, 1 H), 3.97 (m, 1 H), 3.68 (s, 3 H), 3.58 (s, 3 H), 3.39 (dd, $J = 2.3$, 4.3 Hz, 1 H), 3.09 (s, 1 H), 2.80 (t, $J = 1.8$ Hz, 1 H), 2.69 (m, 1 H), 2.62 (s, 1 H), 2.37 (d, $J = 8.0$ Hz, 1 H), 2.13 (s, 1 H), 2.11 (m, 1 H), 1.79 (m, 1 H), 1.72 ~ 1.63 (m, 3 H), 1.44 (m, 1 H), 1.31 (dt, $J = 1.6$, 9.2 Hz, 1 H), 1.19 ~ 1.11 (m, 3 H); ^{13}C NMR (CDCl_3): δ 207.0, 174.0, 172.6, 150.5, 138.2, 137.7, 133.2, 56.3, 52.7, 51.7, 49.0, 48.4, 46.8, 44.2, 43.6, 43.4, 40.8, 39.1, 35.7, 28.1, 26.6, 26.4; IR $\nu(\text{C}=\text{O})$ 1690 cm^{-1} ; HRMS for $\text{C}_{22}\text{H}_{26}\text{O}_5$: calcd. 370.1780, obsd. 370.1779.

Compound **2b**. Yield: 36%; ^1H NMR (CDCl_3): δ 6.13 (m, 1 H), 6.08 (m, 1 H), 3.74 (m, 1 H), 3.73 (s, 3 H), 3.64 (s, 3 H), 3.10 (s, 1 H), 3.06 (dd, $J = 6.4$, 11.9 Hz, 1 H), 2.65 (m, 1 H), 2.52 (t, $J = 11.3$ Hz, 1 H), 2.45 (s, 1 H), 2.25 ~ 2.10 (m, 3 H), 1.75 ~ 1.69 (m, 3 H), 1.48 (m, 2 H), 1.33 (dt, $J = 1.5$, 9.2 Hz, 1 H), 1.25 ~ 1.09 (m, 3 H); ^{13}C NMR (CDCl_3): δ 206.4, 175.1, 173.3

151.2, 138.4, 137.8, 133.9, 55.5, 52.1, 52.0, 47.9, 47.1, 46.3, 46.0, 44.5, 43.6, 41.1, 40.9, 32.1, 29.2, 28.7, 26.3; IR $\nu(\text{C}=\text{O})$ 1697 cm^{-1} ; HRMS for $\text{C}_{22}\text{H}_{26}\text{O}_5$: calcd. 370.1780, obsd. 370.1780.

Compound **3**. Yield: 47%; ^1H NMR (d_6 -DMSO): δ 6.39 (m, 1 H), 6.34 (m, 1 H), 3.92 (dd, $J = 6.8, 8.9$ Hz, 1 H), 3.64 (t, $J = 8.1$ Hz, 1 H), 3.26 (m, 1 H), 3.05 (s, 1 H), 2.94 (s, 1 H), 2.84 (d, $J = 7.9$ Hz, 1 H), 2.59 (m, 1 H), 2.48 (m, 1 H), 2.35 (d, $J = 8.3$ Hz, 1 H), 2.05 (m, 1 H), 1.97 (m, 1 H), 1.86 ~ 1.80 (m, 2 H), 1.63 ~ 1.57 (m, 2 H), 1.47 (m, 1 H), 1.37 (d, $J = 9.0$ Hz, 1 H), 1.26 (d, $J = 9.0$ Hz, 1 H); IR $\nu(\text{C}=\text{O})$ 1690 cm^{-1} ; HRMS for $\text{C}_{20}\text{H}_{20}\text{O}_4$: calcd. 324.1362, obsd. 324.1358; Anal. Calcd.: C, 74.06, H, 6.21. Found: C, 73.93; H, 6.25.

Compound **4**. Yield: 53%; ^1H NMR (CDCl_3): δ 7.93 (br, 1 H), 6.29 ~ 6.17 (m, 2 H), 3.38 ~ 3.32 (m, 2 H), 3.17 ~ 3.06 (m, 3 H), 2.76 (s, 1 H), 2.47 (d, $J = 7.8$ Hz, 2 H), 2.41 ~ 2.21 (m, 3 H), 2.00 ~ 1.78 (m, 2 H), 1.69 ~ 1.53 (m, 2 H), 1.41 ~ 1.26 (m, 3 H); ^{13}C NMR (CDCl_3): δ 206.2, 177.4, 177.0, 156.5, 138.5, 138.1, 136.2, 57.7, 49.3, 47.9, 45.5, 45.3, 43.7, 43.6, 40.6, 40.3, 25.3, 23.4, 21.6, 20.2; IR $\nu(\text{C}=\text{O})$ 1686 cm^{-1} ; HRMS for $\text{C}_{20}\text{H}_{21}\text{O}_3\text{N}_1$: calcd. 323.1521, obsd. 323.1518.

Compound **5**. Yield: 75%; ^1H NMR (CDCl_3): δ 6.26 (m, 1 H), 6.24 (m, 1 H), 3.38 ~ 3.30 (m, 2 H), 3.16 ~ 3.09 (m, 3 H), 2.83 (s, 3 H), 2.79 (s, 1 H), 2.43 (d, $J = 8.1$ Hz, 2 H), 2.37 (m, 1 H), 1.98 ~ 1.78 (m, 2 H), 1.69 ~ 1.53 (m, 2 H), 1.51 ~ 1.43 (m, 2 H), 1.43 ~ 1.26 (m, 3 H); ^{13}C

NMR (CDCl₃): δ 206.0, 177.4, 177.0, 156.0, 138.3, 137.4, 135.5, 57.5, 49.0, 47.6, 46.4, 44.5, 43.9, 43.5, 40.3, 40.1, 24.9, 23.2, 21.4, 20.0, 14.1; IR $\nu(\text{C}=\text{O})$ 1695 cm⁻¹; HRMS for C₂₁H₂₃O₃N₁: calcd. 337.1678, obsd. 337.1676.

Compound **7a**. Yield: 37%; ¹H NMR (CDCl₃): δ 7.38 ~ 7.34 (m, 2 H), 7.25 ~ 7.21 (m, 2 H), 5.67 (s, 1 H), 5.25 (s, 1 H), 4.12 (m, 1 H), 3.86 (s, 3 H), 3.69 (s, 3 H), 3.00 (s, 1 H), 2.91 (m, 1 H), 2.78 (s, 1 H), 2.79 ~ 2.71 (m, 2 H), 2.60 (dd, $J = 5.3, 8.3$ Hz, 1 H), 1.95 (m, 1 H), 1.92 ~ 1.78 (m, 3 H), 1.63 (m, 1 H), 1.36 ~ 1.25 (m, 2 H); ¹³C NMR (CDCl₃): δ 204.3, 173.6, 172.5, 151.3, 145.5, 145.0, 131.6, 127.1, 127.0, 119.7, 119.5, 85.3, 83.2, 57.6, 52.9, 51.8, 49.0, 45.1, 43.3, 40.6, 39.3, 35.8, 28.3, 26.6, 26.5; IR $\nu(\text{C}=\text{O})$ 1697 cm⁻¹; HRMS for C₂₅H₂₆O₆: calcd. 422.1729, obsd. 422.1730.

Compound **7c**. Yield: 30%; ¹H NMR (CDCl₃): δ 7.44 (m, 1 H), 7.32 (m, 1 H), 7.32, 7.29 ~ 7.18 (m, 5 H), 7.15 (m, 1 H), 5.59 (s, 1 H), 5.43 (s, 1 H), 5.31 (s, 1 H), 5.19 (s, 1H), 3.14 (m, 1 H), 2.87 ~ 2.71 (m, 2 H), 2.69 (d, $J = 7.9$ Hz, 1 H), 2.41 (dd, $J = 3.5, 7.9$ Hz, 1 H), 2.31 ~ 2.20 (m, 2 H), 1.83 (t, $J = 9.4$ Hz, 1 H), 1.80 ~ 1.67 (m, 2 H), 1.60 (m, 1 H), 1.58 ~ 1.41 (m, 3 H); ¹³C NMR (CDCl₃): δ 203.9, 158.8, 146.2 145.7, 145.5, 145.4, 135.7, 127.5, 127.3, 127.2, 126.3, 119.9, 119.8, 119.4, 119.2, 86.7, 83.8, 83.5, 83.3, 58.6, 52.3, 50.8, 48.5, 45.6, 41.2, 28.8, 26.3, 21.9, 21.7; IR $\nu(\text{C}=\text{O})$ 1684 cm⁻¹; HRMS for C₂₉H₂₆O₃: calcd. 422.1882,

obsd. 422.1885.

Compound **8**. Two isomers were not separable. Yield: 95%; ^1H NMR (CDCl_3): **8a** δ 3.77 (s, 3 H), 3.70 (s, 3 H), 3.51 (dd, $J = 3.2, 5.2$ Hz, 1 H), 2.62 (m, 1 H), 2.51 (br, 1 H), 2.43 ~ 2.37 (m, 1 H), 2.36 ~ 2.27 (m, 1 H), 2.21 (s, 1 H), 2.14 (s, 1 H), 2.09 (m, 1 H), 2.05 (s, 3 H), 2.01 (br, 1 H), 1.54 (m, 2 H), 1.21 (m, 2 H), 1.08 (br, 2 H); **8b** δ 3.74 (s, 3 H), 3.67 (s, 3 H), 3.12 (dt, $J = 4.1, 7.4$ Hz, 1 H), 3.01 (m, 1 H), 2.70 (m, 1 H), 2.50 (br, 1 H), 2.47 ~ 2.43 (m, 1 H), 2.36 ~ 2.27 (m, 2 H), 2.19 ~ 2.17 (m, 2 H), 2.10 (s, 3 H), 1.54 (m, 2 H), 1.21 (m, 2 H), 1.08 (br, 2 H); ^{13}C NMR (CDCl_3): δ 208.5, 208.0, 174.6, 174.0, 173.7, 172.5, 144.4, 143.0, 132.9, 131.7, 57.2, 56.7, 52.4, 52.1, 51.9, 51.8, 47.9, 45.7, 45.1, 44.2, 43.9, 42.9, 42.6, 42.4, 41.1, 41.0, 40.9, 40.4, 35.4, 34.5, 34.4, 32.3, 28.8, 28.5, 28.1, 27.6, 18.5, 18.2; IR $\nu(\text{C}=\text{O})$ 1697 cm^{-1} ; HRMS for $\text{C}_{19}\text{H}_{24}\text{O}_5$: calcd. 332.1624, obsd. 332.1625.

Compound **9**. Two isomers were not separable. Yield: 77%; ^1H NMR (CDCl_3): **9a** δ 6.26 ~ 6.22 (m, 1 H), 6.16 ~ 6.13 (m, 1 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 3.52 (dd, $J = 3.0, 4.9$ Hz, 1 H), 3.17 ~ 3.12 (m, 1 H), 2.72 (m, 1 H), 2.60 (br, 1 H), 2.44 (d, $J = 7.4$ Hz, 1 H), 2.37 ~ 2.32 (m, 2 H), 2.30 ~ 2.25 (m, 1 H), 2.16 (m, 1 H), 2.07 (s, 3 H), 1.44 ~ 1.38 (m, 1 H), 1.25 ~ 1.21 (m, 1 H); **9b** δ 6.22 ~ 6.18 (m, 1 H), 6.13 ~ 6.10 (m, 1 H), 3.75 (s, 3 H), 3.65 (s, 3 H), 3.17 ~ 3.12 (m, 2 H), 3.03 (m, 1 H), 2.74 (br, 1 H), 2.64 (br, 1 H), 2.51 (t, $J = 11.0$ Hz, 1 H), 2.37 ~ 2.32

(m, 1 H), 2.30 ~ 2.25 (m, 2 H), 2.14 (s, 3 H), 1.44 ~ 1.38 (m, 1 H), 1.25 ~ 1.21 (m, 1 H); ^{13}C NMR (CDCl_3): δ 205.9, 205.3, 174.4, 173.8, 173.7, 172.4, 145.1, 143.3, 138.2, 138.1, 138.0, 137.7, 136.0, 134.8, 55.6, 55.2, 52.4, 52.1, 51.9, 51.8, 48.3, 47.9, 47.8, 46.6, 46.0, 45.1, 44.2, 44.1, 44.0, 43.8, 42.9, 42.3, 41.1, 40.8, 35.1, 32.2, 18.5, 18.1; IR $\nu(\text{C}=\text{O})$ 1697 cm^{-1} ; HRMS for $\text{C}_{19}\text{H}_{22}\text{O}_5$: calcd. 330.1467, obsd. 330.1464.

Compound **10**. Yield: 92%; ^1H NMR (CDCl_3): δ 6.26 (m, 1 H), 6.23 (m, 1 H), 3.36 (d, $J = 7.7$ Hz, 1 H), 3.31 (d, $J = 9.9$ Hz, 1 H), 3.22 (d, $J = 7.7$ Hz, 1 H), 3.16 (d, $J = 9.9$ Hz, 1 H), 3.11 (s, 1 H), 2.87 (s, 3 H), 2.81 (s, 1 H), 2.79 (d, $J = 7.2$ Hz, 2 H), 2.42 (m, 1 H), 2.23 (s, 3 H), 1.38 (d, $J = 9.1$ Hz, 1 H), 1.24 (d, $J = 9.1$ Hz, 1H); ^{13}C NMR (CDCl_3): δ 206.0, 178.6, 177.6, 149.4, 138.3, 137.8, 134.4, 57.2, 49.0, 47.8, 45.9, 44.7, 43.4, 43.1, 39.7, 34.2, 24.9, 19.5; IR $\nu(\text{C}=\text{O})$ 1696 cm^{-1} ; HRMS for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}_1$: calcd. 297.1365, obsd. 297.1367.