Supporting Information

Reversal of Chemoselectivity in Diels-Alder Reaction with α,β-Unsaturated Aldehydes and Ketones Catalyzed by Brønsted Acid or Lewis Acid

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General.

Infrared (IR) spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance 500 (500 MHz $^1$H, 125 MHz $^{13}$C). Tetramethylsilane was used as internal standard for $^1$H NMR (δ 0.0 ppm) and CDCl$_3$ for $^{13}$C NMR (δ 77.0). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). All experiments were carried out in dried glassware with magnetic stirring under an atmosphere of dry argon. Analytical thin layer chromatography (TLC) was performed on Whatman pre-coated silica gel flexible plates (0.25 mm) with F$_{254}$ indicator. Visualization was accomplished by UV light and phosphomolybdic acid solution in ethanol by heating. Flash column chromatography was performed on silica gel 60 (E. Merck 230-400 mesh). Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane (anhydrous, 99.9 %, 18 L in Pure-Pac™) purchased from Aldrich was purified by M. BRAUN solvent purification system (A2 Alumina). Acrolein, methacrolein and crotonaldehyde were distilled from calcium hydride. Ethyl vinyl ketone, 3-methyl-3-buten-2-one and 2-hexen-4-one were distilled from anhydrous magnesium sulfate. 1,3-Cyclopentadiene was cracked at 170 °C and redistilled. 1,3-Cyclohexadiene, 2,3-dimethyl-1,3-butadiene and isoprene were distilled. Triflylimide and pentafluorophenylbistriflylmethane were purchased and 0.1 M solutions in dichloromethane were prepared without further purification under an atmosphere of dry argon.
**General Procedure for the Chemoselective Diels-Alder Reaction:** To a solution of catalyst (0.05 mmol) in dichloromethane (1.5 mL) was cooled at -78 °C and added α,β-unsaturated ketone (1 mmol) and aldehyde (1 mmol). Then a solution of freshly prepared 1,3-cyclopentadiene (83 µL, 1 mmol) in dichloromethane (0.5 mL) was added dropwise along the wall of the flask over 5 min period. After the solution was stirred for 1 h at -78 °C, the reaction was quenched with triethylamine (200 µL) and saturated aqueous NaHCO₃. The mixture was extracted with ether, dried over anhydrous MgSO₄, filtered, and concentrated at 0 °C. The crude product was purified by column chromatography on silica gel (eluent, pentane-ether) to give the mixture of the corresponding Diels-Alder products. The ratio of the product was determined by 500 MHz ¹H NMR.

**Physical Data of the Diels-Alder Products**

*endo-Bicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (1):*¹ ¹H NMR (500 MHz, CDCl₃) δ 9.42 (d, J = 2.8 Hz, 1 H), 6.22 (dd, J = 5.6, 3.1 Hz, 1 H), 6.00 (dd, J = 5.6, 2.8 Hz, 1 H), 3.25 (br, 1H), 2.99 (br, 1H), 2.90 (m, 1H), 1.91 (ddd, J = 12.2, 9.1, 3.7 Hz, 1H), 1.55–1.15 (m, 3H). The endo/exo ratio was determined by ¹H NMR analysis of Diels-Alder adducts; ¹H NMR (500 MHz, CDCl₃) δ 9.79 (d, J = 2.3 Hz, 1H, CHO (exo)), 9.42 (d, J = 2.8 Hz, 1H, CHO (endo)).

*endo-1-[Bicyclo[2,2,1]hept-5-en-2-yl]-propan-1-one (2):*² ¹H NMR (500 MHz, CDCl₃) δ 6.15 (dd, J = 7.0, 3.8 Hz, 1H), 5.82 (dd, J = 7.0, 3.5 Hz, 1H), 3.22 (br, 1H), 3.02 (dt, J = 11.2, 5.6 Hz, 1H), 2.90 (br, 1H), 2.44 (m, 2H), 1.80-1.70 (m, 1H), 1.55 – 1.20 (m, 3H), 1.03 (t, J = 9.2 Hz, 3H). Only endo adduct was obtained.

*exo-Bicyclo[2,2,1]hept-5-ene-2-methyl-2-carboxaldehyde (3):*³ ¹H NMR (500 MHz, CDCl₃) δ 9.69 (s, 1H), 6.29 (m,1H), 6.10 (m, 1H), 2.89 (br, 1H), 2.82 (br, 1H), 2.25 (dd, J = 12.0, 4.0 Hz, 1H), 1.40–1.20 (m, 2H), 1.01 (s, 3H), 0.76 (d, J = 12.0 Hz, 1H). The endo/exo ratio was determined by ¹H NMR...
analysis of Diels-Alder adducts; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.69 (s, 1H, CHO (exo)), 9.40 (s, 1H, CHO (endo)).

2-Acetyl-2-Methylbicyclo[2,2,1]hept-5-ene (4): $^4$ endo-adduct; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.11 (m, 1H), 6.00 (m, 1H), 2.83 (br, 1H), 2.78 (br, 1H), 2.10 (s, 3H), 1.99 (dd, $J = 12.0$, 2.5 Hz, 1H), 1.70–1.20 (m, 2H), 1.36 (s, 3H). exo-adduct; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.25 (m, 1H), 6.11 (m, 1H), 2.98 (br, 1H), 2.80 (br, 1H), 2.40 (dd, $J = 12.0$, 4.0 Hz, 1H), 2.22 (s, 3H), 1.70–1.20 (m, 2H), 1.08 (s, 3H).

3-Methylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde (5): $^1,5$ endo-adduct; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.37 (d, $J = 3.5$ Hz, 1H), 6.29 (dd, $J = 5.5$, 3.0 Hz, 1H), 6.05 (dd, $J = 5.5$, 2.5 Hz, 1H), 3.13 (br, 1H), 2.56 (br, 1H), 2.32 (m, 1H), 1.82 (m, 1H), 1.60–1.40 (m, 2H), 1.17 (d, $J = 7.0$ Hz, 3H). exo-adduct; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.78 (d, $J = 3.0$ Hz, 1H), 6.24 (dd, $J = 5.5$, 3.0 Hz, 1H), 6.16 (dd, $J = 5.5$, 2.5 Hz, 1H), 3.01 (br, 1H), 2.79 (br, 1H), 2.50–2.40 (m, 1H), 1.80–1.75 (m, 1H), 1.50–1.40 (m, 2H), 0.90 (d, $J = 6.5$ Hz, 3H).

endol-[3-Methylbicyclo[2,2,1]hept-5-en-2-yl]-propan-1-one(6): $^6$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.22 (m, 1H), 5.89 (m, 1H), 3.13 (br, 1H), 2.55–2.39 (m, 4H), 1.90 (m, 1H), 1.59 (d, $J = 8.5$ Hz, 1H), 1.44 (dd, $J = 8.5$, 1.5 Hz, 1H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.01 (t, $J = 7.5$ Hz, 3 H). The endo/exo ratio was determined by $^1$H NMR analysis of Diels-Alder adducts: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.40 (m, 1H (exo)), 6.22 (m, 1H (endo)), 6.10 (m, 1H (exo)), 5.89 (m, 1H (endo)).

endol-[Bicyclo[2,2,2]oct-5ene-2-yl]-propan-1-one (Table 4, entry 1): IR (neat) 3044, 2939, 2866, 1713, 1458, 1374, 1414, 1128, 706 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.29 (t, $J = 7.0$ Hz, 1H), 6.10 (t, $J = 8.0$ Hz, 1H), 2.88–2.86 (m, 1H), 2.70–2.65 (m, 1H), 2.65–2.55 (m, 1H), 2.55–2.35 (m, 2H), 1.70–1.20 (m, 6H), 1.02 (t, $J = 7.5$ Hz, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 212.5, 135.0, 131.1, 50.5, 33.9, 32.1, 29.5, 28.8, 25.9, 24.4, 8.0; MS (Cl) Exact Mass Calcd for C$_{11}$H$_{16}$O (M+H)$^+$: 165.1. Found: 165.1. Only endo-adduct was obtained.
endo-Bicyclo[2,2,2]oct-5ene-2-carboxaldehyde (Table 4, entry 2):$^6 \text{H} NMR (500 MHz, CDCl$_3$) $\delta$
9.46 (d, $J = 1.3$ Hz, 1H), 6.34 (t, $J = 7.7$ Hz, 1H), 6.12 (t, $J = 7.5$ Hz, 1H), 2.96 (m, 1H), 2.66 (m, 1H),
2.57 (m, 1H), 1.80–1.20 (m, 6H). Only endo-adduct was obtained.

1-(3,4-Dimethylcyclohex-3-en-1-yl)-propan-1-one (Table 4, entry 3):$^7 \text{H} NMR (500 MHz, CDCl$_3$) $\delta$
2.70–2.40 (m, 3H), 2.20 (m, 1H), 2.10–1.90 (m, 3H), 1.85 (m, 1H), 1.63 (s, 3H), 1.61 (s, 3H),
1.54 (m, 1H), 1.05 (t, $J = 7.3$ Hz, 3H).

3,4-Dimethylcyclohex-3-ene-1-carboxaldehyde (Table 4, entry 4):$^{1,6} \text{H} NMR (500 MHz, CDCl$_3$) $\delta$
9.68 (s, 1H), 2.48 (m, 1H), 2.30–1.90 (m, 6H), 1.65 (s, 3H), 1.61 (s, 3H).

1-(4-Methylcyclohex-3-en-1-yl)-propan-1-one (Table 4, entry 5):$^8 \text{H} NMR (500 MHz, CDCl$_3$) $\delta$
5.40 (br, 1H), 2.60–2.40 (m, 3H), 2.14 (m, 1H), 2.00 (m, 1H), 1.91 (m, 1H), 1.65 (s, 3H), 1.65 (m, 1H),
1.05 (t, $J = 7.3$ Hz, 3H).

4-Methylcyclohex-3-ene-1-carboxaldehyde (Table 4, entry 6):$^{1,1} \text{H} NMR (500 MHz, CDCl$_3$) $\delta$
9.70 (s, 1H), 5.41 (br, 1H), 2.44 (m, 1H), 2.21 (br, 2H), 2.00 (br, 2H), 1.97 (m, 1H), 1.69 (m, 1H), 1.65 (s, 3H).

Reference
