Supporting Information for

Oxazaborolidinone-Catalyzed Enantioselective Diels–Alder Reaction of Acyclic α,β-Unsaturated Ketones

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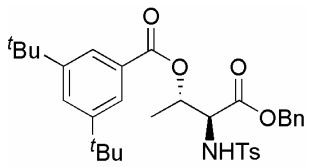
1. General. All reactions were performed under an inert atmosphere of dry Ar or N_2. Dichloromethane (CaH_2), Et_2O, and toluene (Na-benzophenone) were freshly distilled from the indicated drying agents. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on 500 MHz, ^{1}H (126 MHz, ^{13}C) spectrometers. Spectra are referenced to residual chloroform (δ 7.26 ppm, ^{1}H; δ 77.0 ppm, ^{13}C).

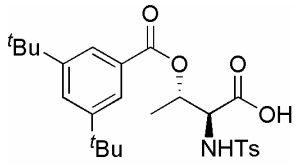
The following ligands were prepared by a literature method:[1] *O*-*p*-biphenoyl-*N*-tosyl-(L)- *allo*-threonine, *O*-2-naphthoyl-*N*-tosyl-(L)-*allo*-threonine, *O*-benzoyl-*N*-tosyl-(L)-*allo*-threonine, and *O*-*p*-anisoyl-*N*-tosyl-(L)-*allo*-threonine.

2. Preparation of OXB Ligand.



11

***O*-(3,5-Di-*t*-butylbenzoyl)-*N*-tosyl-(L)-*allo*-threonine Benzyl Ester (11)**: Prepared by esterification of *N*-tosyl-(L)-*allo*-threonine benzyl ester with 3,5-di-*t*-butylbenzoyl chloride in 87% yield accoriding to the procedure reported previously;[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (18H, s), 1.36 (3H, d, *J* = 6.5 Hz), 2.41 (3H, s), 4.28 (1H, dd, *J* = 4.5 and 9.6 Hz), 4.95 (2H, m), 5.28 (1H, dq, *J* = 4.5 and 6.5 Hz), 5.41 (1H, br d, *J* = 9.6 Hz), 7.13 (2H, m), 7.18 (2H, d, *J* = 8.1 Hz), 7.25–7.32 (3H, m), 7.63 (1H, t, *J* = 1.9 Hz), 7.69 (2H, d, *J* = 8.1 Hz), 7.86 (2H, d, *J* = 1.9 Hz).



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***O*-(3,5-Di-*t*-butylbenzoyl)-*N*-tosyl-(L)-*allo*-threonine (12)**: Prepared by hydrogenolysis (10% Pd/C) of the benzyl ester in 100% yield; mp 73–79 ºC (recrystallized from benzene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (18H, s), 1.41 (3H, d, *J* = 6.5 Hz), 2.36 (3H, s), 4.32 (1H, dd, *J* = 4.0 and 9.4 Hz), 5.28 (1H, dq, *J* = 4.0 and 6.5 Hz), 5.42 (1H, br d, *J* = 9.4 Hz), 7.22 (2H, d, *J* = 8.1 Hz), 7.64 (1H, t, *J* = 1.9 Hz), 7.71 (2H, d, *J* = 8.3 Hz), 7.86 (2H, d, *J* = 1.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 15.8, 21.4, 31.3, 34.9, 58.8, 70.9, 124.0, 127.0, 127.6, 128.7, 129.7, 136.5, 143.9, 151.1, 166.4. Anal. Calcd for $C_{26}H_{35}NO_6S$: C, 63.78; H, 7.21. Found: C, 63.64; H, 7.74.

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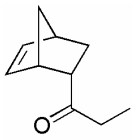
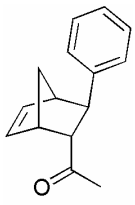
[1] X. Wang, S. Adachi, H. Iwai, H. Takatsuki, K. Fujita, M. Kubo, A. Oku, T. Harada, *J. Org. Chem*. **2003**, *68*, 10046.

3. Diels–Alder Adducts 7a–x.



***endo*-7a**

1-[(1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-en-2-yl]propan-1-one (7a)[2]: *Typical Procedure for Asymmetric Diels-Alder Reaction.* To a solution of *O*-(*p*-biphenoyl)-*N*-tosyl-(L)-*allo*-threonine[1] (140 mg, 0.309 mmol) in CH_2Cl_2 (2.5 mL) under argon atmosphere at room temperature was added dichlorophenylborane (40 μL, 0.31 mmol). After being stirred for 30 min, the mixture was concentrated in *vacuo*. To a solution of the resulting OXB **3a** in CH_2Cl_2 (1.7 mL) at –78 °C were added 2,6-di-*tert*-butylpyridine (17 μL, 0.77 mmol), ethyl vinyl ketone (260 mg, 3.09 mmol), and 1,3-cyclopentadiene (1.04 mL, 15.5 mmol). The resulting solution was stirred at –78 ºC for 24 h. The mixture was quenched by the addition of saturated aqueous $NaHCO_3$ and filtered. The filtrate was extracted three times with ether, dried (Na_2SO_4), and concentrated in *vacuo*. The residue was purified by flash chromatography (SiO_2, gradient elution with 1–2% ethyl acetate in hexane) to give 408 mg (2.72 mmol, 88%) of the adduct **7a**: $[\alpha]_D^{23}$ –104 (*c* 1.1, $CHCl_3$) (92% *ee*). Lit.[2] for the (1*R*,2*R*,4*R*)-enantiomer; $[\alpha]_D^{23}$ +111 (*c* 0.76, $CHCl_3$) (97 % *ee*). *Endo-exo* ratio was determined by GC analysis using a OV-1 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 10 ºC/min ramp to 320 ºC); retention times: 6.5 min (*endo*), 6.2 min (*exo*). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 26.9 min (major), 26.7 min (minor).



***endo*-7b**

1-[(1*S*,2*S*,3*R*,4*S*)-3-Phenylbicyclo[2.2.1]hept-5-en-2-yl]ethanone (7b).[3] Purified by flash column chromatography (SiO_2, gradient elution with 4–5% ethyl acetate in hexane); mp 81–81.5 ºC (recrystallized from ethyl acetate and hexane); $[\alpha]_D^{23}$ –95.4 (*c* 1.0, $CHCl_3$) (91 % *ee*);[4] ^{1}H NMR (500

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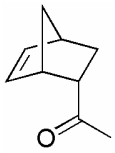
[2] Ryu, D. H.; Lee, T. W.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 9992.

[3] Asao, N.; Asano, T.; Yamamoto, Y. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3206.

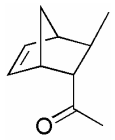
[4] Table 2, entry 3.

MHz, $CDCl_3$) δ 1.61 (1H, qd, *J* = 1.7 and 8.6 Hz), 1.86 (1H, br d, *J* = 8.6 Hz), 2.15 (3H, s), 3.01 (1H, br s), 3.07 (1H, dd, *J* = 3.6 and 4.9 Hz), 3.18 (1H, dd, *J* = 1.3 and 4.9 Hz), 3.29 (1H, br), 6.02 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.40 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.18 (1H, m), 7.24–7.33 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.1, 45.3, 45.5, 47.5, 48.5, 61.3, 126.0, 127.5, 128.5, 133.1, 139.4, 144.4, 208.1. Anal. Calcd for $C_{15}H_{16}O$: C, 84.86; H, 7.60. Found: C, 85.11; H, 7.92. The *endo* adduct was obtained as a single diastereomer as determined by GC and ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (9% *i*-PrOH in hexane, 1 mL/min); retention times: 6.1 min (major), 7.5 min (minor). The absolute stereochemistry was assumed by analogy.



***endo*-7c**

1-[(1*S*,2*S*,4*S*)-Bicyclo[2.2.1]hept-5-en-2-yl]ethanone [5] **(7c).** Purified by flash column chromatography (SiO_2, gradient elution with 1–2% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (1H, d, *J* = 8.0 Hz), 1.45-1.63 (2H, m), 1.77 (1H, ddd, *J* = 3.8, 9.0, and 11.5 Hz), 2.15 (3H, s), 2.92 (1H, br s), 3.03 (1H, td, *J* = 3.7 and 8.9 Hz), 3.26 (1H, br s), 5.87 (1H, m), 6.17 (1H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 27.4, 29.2, 42.6, 45.8, 49.9, 52.3, 131.2, 137.8, 209.0; $[\alpha]_D^{23}$ –71.9 (*c* 0.55, ethanol) (85% *ee*). Lit.[2] $[\alpha]_D^{23}$ –93.6 (*c* 1.23, ethanol). Lit.[6] for the (1*R*,2*R*,4*R*)-enantiomer, $[\alpha]_D^{23}$ +65.6 (*c* 4.36, ethanol) (81% *ee*). The *endo* adduct was obtained as a single diastereomer as determined by GC and ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 21.6 min (major), 21.3 min (minor).



***endo*-7d**

1-[(1*S*, 2*S*, 3*R*, 4*S*)-3-Methylbicyclo[2.2.1]hept-5-en-2-yl]ethanone (7d).[7] Purified by flash column chromatography (SiO_2, gradient elution with 3–5% ethyl acetate in hexane); $[\alpha]_D^{23}$ –106 (*c* 1.07, $CHCl_3$) (87 % *ee*). Lit.[6] for the (1*R*,2*R*,3*S*,4*R*)-enantiomer; +70.4 (*c* = 1.0, $CHCl_3$) (61 % ee). *Endo-exo* ratio

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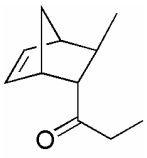
[5] Nakazaki, M; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1976**, *41*, 1229.

[6] Hawkins, J. M.; Nambu, M.; Loren, S. *Org. Lett.* **2003**, *5*, 4293.

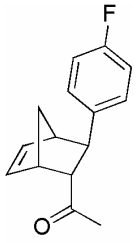
[7] Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 2458.

was determined by GC analysis using a OV-1 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 10 ºC/min ramp to 320 ºC); retention times: 5.9 min (*endo*), 5.6 min (*exo*). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 23.3 min (major), 24.4 min (minor).



***endo*-7e**

1-[(1*S*,2*S*,3*R*,4*S*)-3-Methylbicyclo[2.2.1]hept-5-en-2-yl]propan-1-one (7e).[6] Purified by flash column chromatography (SiO_2, gradient elution with 3-5% ethyl acetate in hexane); $[\alpha]_D^{23}$ –111 (*c* 1.0, $CHCl_3$) (94 % *ee*). Lit.[6] for the (1*R*,2*R*,3*R*,4*R*)-enantiomer; $[\alpha]_D^{23}$ +101.7 (*c* 1.0, $CHCl_3$) (90 % *ee*). *Endo*-*exo* ratio was determined by GC analysis using a OV-1 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 10 ºC/min ramp to 320 ºC); retention times: 7.2 min (*endo*), 7.0 min (*exo*). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 27.7 min (major), 28.9 min (minor).

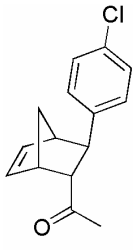


***endo*-7f**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(4-Fluorophenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7f). Purified by flash column chromatography (SiO_2, gradient elution with 4–10% ethyl acetate in hexane); mp. 66.5–67 ºC (recrystallized from hexane and ethyl acetate); $[\alpha]_D^{23}$ –73.3 (*c* 1.0, $CHCl_3$) (89 % *ee*);[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (1H, br d, *J* = 8.6 Hz), 1.81 (1H, br d, *J* = 8.6 Hz), 2.15 (3H, s), 2.96–2.99 (2H, m), 3.16 (1H, br d, *J* = 4.7 Hz), 3.33 (1H, br s), 6.01 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.38 (1H, dd, *J* = 3.3 and 5.6 Hz), 6.94–6.98 (2H, m), 7.18–7.22 (2H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.0, 44.4, 46.5, 47.5, 48.4, 61.4, 115.1 (d, *J* = 21.0 Hz), 128.7, 128.8, 139.4, 140.1 (d, *J* = 3.4 Hz), 161.2 (d, *J* = 244 Hz), 207.8. Anal. Calcd for $C_{15}H_{15}OF$: C, 78.23; H, 6.57. Found: C, 77.82; H, 6.78. The *endo* adduct was obtained as a single diastereomer as ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by

[8] Specific rotation was measured for the product of the reaction with OXB **3d** (10 mol %) at –60 ºC for 72 h in CH_2Cl_2 (76% yield, *endo*:*exo* >98:2, 89% ee).

HPLC analysis using a Chiralcel OJ column (hexane, 1 mL/min); retention times: 63.8 min (major), 54.9 min (minor). The absolute stereochemistry was assumed by analogy.

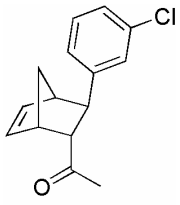


***endo*-7g**

1-**[(1*S*,2*S*,3*R*,4*S*)-3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7g).** Purified by flash column chromatography (SiO_2, gradient elution with 4–8% ethyl acetate in hexane); mp 91.5–92.5 ºC (recrystallized from ether); $[\alpha]_D^{23}$ –73.4 (*c* 1.0, $CHCl_3$) (90 % *ee*);[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (1H, qd, *J* = 1.7 and 8.6 Hz), 1.80 (1H, br d, *J* = 8.6 Hz), 2.16 (3H, s), 2.96–3.00 (2H, m), 3.17 (1H, dd, *J* = 1.2 and 4.8 Hz), 3.34 (1H, br), 6.02 (1H, dd, *J* = 2.7 and 5.7 Hz), 6.39 (1H, dd, *J* = 3.2 and 5.7 Hz), 7.18 (2H, d, *J* = 8.7 Hz), 7.25 (2H, d, *J* = 8.7 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.0, 44.5, 46.5, 47.6, 48.3, 61.3, 128.5, 128.8, 131.6, 133.1, 139.4, 143.0, 207.7. Anal. Calcd for $C_{15}H_{15}OCl$: C, 73.02; H, 6.13. Found: C, 73.24; H, 6.33. The *endo* adduct was obtained as a single diastereomer as ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OJ column (0.3% *i*-PrOH in hexane, 1 mL/min); retention times: 36.9 min (major), 29.9 min (minor).

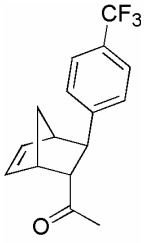
The absolute stereochemistry was determined by X-ray crystallographic analysis. Single crystals suitable for X-ray analysis were obtained by recrystallization from ether as colorless needles. Crystal data: $C_{15}H_{15}OCl$, M = 246.74, orthorhombic, space group $P2_12_12_1$, a = 8.0660(9) Å, b = 28.263(2) Å, c = 5.5141(7) Å, V = 1257.0(2) Å^3, Z = 4. Of the 2412 reflections that were collected, 1617 were unique. The structure was solved by direct methods and expanded using Fourier techniques. The anisotropic and isotropic temperature factors were applied to the non-hydrogen atoms and the hydrogen atoms, respectively. The final cycle of full-matrix least-squares refinement was based on 1617 observed reflections ($I > 2.00\ \sigma(I)$) and converged with unweighted and weighted agreement factors of R = 0.040 and R_w = 0.102, respectively, for solution using the 1*S*,2*S*,3*R*,4*S* enantiomer model, Flack parameter = –0.007(19).

[9] Specific rotation was measured for the product of the reaction with OXB **3d** (10 mol %) at –60 ºC for 72 h in CH_2Cl_2 (97% yield, *endo*:*exo* >98:2, 90% ee).



***endo*-7h**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(3-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7h). Purified by flash column chromatography (SiO_2, gradient elution with 3–6% ethyl acetate in hexane); $[\alpha]_D^{23}$ –45.7 (*c* 1.02, $CHCl_3$) (91 % ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.63 (1H, qd, *J* = 1.6 and 8.7 Hz), 1.82 (1H, d, *J* = 8.7 Hz), 2.17 (3H, s), 2.99-3.02 (2H, m), 3.17 (1H, br d, *J* = 4.7 Hz), 3.35 (1H, br), 6.02 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.39 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.12–7.28 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.1, 44.7, 46.6, 47.6, 48.2, 61.2, 125.8, 126.1, 127.5, 129.7, 133.1, 134.3, 139.3, 146.6, 207.6; MS (EI) *m/z* (relative intensity) 246 (M^+, 2), 215 (89), 181 (100); HRMS calcd for $C_{15}H_{15}OCl$, 246.0811, found: 246.0801. The *endo* adduct was obtained as a single diastereomer by the ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (0.3% *i*-PrOH in hexane, 1 mL/min); retention times: 15.5 min (major), 25.6 min (minor). The absolute stereochemistry was assumed by analogy.

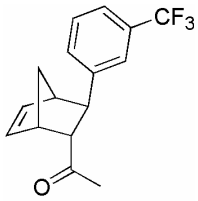


***endo*-7i**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(4-Trifuloromethylphenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7i). Purified by flash column chromatography (SiO_2, gradient elution with 4–8% ethyl acetate in hexane); mp 63–64 ºC (recrystallized from ether); $[\alpha]_D^{23}$ –62.1 (*c* 1.0, $CHCl_3$) (88 % *ee*);[10] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66 (1H, qd, *J* = 1.6 and 8.6 Hz), 1.82 (1H, d, *J* = 8.6 Hz), 2.17 (3H, s), 3.01 (1H, dd, *J* = 3.8 and 4.7 Hz), 3.05 (1H, br s), 3.27 (1H, br d, *J* = 4.7 Hz), 3.38 (1H, br), 6.03 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.41 (1H, dd, *J* = 3.3 and 5.6 Hz), 7.36 (2H, d, *J* = 8.1 Hz), 7.53 (2H, d, *J* = 8.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.1, 44.8, 46.6, 47.6, 47.9, 61.2, 124.2 (q, *J* = 272 Hz), 125.3 (q, *J* = 3.8 Hz), 127.7, 128.1 (q, *J* = 32 Hz), 133.1 139.3, 148.7, 207.6. Anal. Calcd for $C_{16}H_{15}OF_3$: C, 68.56; H, 5.39. Found: C, 68.66; H, 5.51. The *endo* adduct was obtained as a single diastereomer as ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OJ column (0.3% *i*-PrOH in

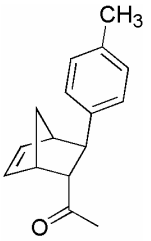
[10] Specific rotation was measured for the product of the reaction with OXB **3d** (10 mol %) at –60 ºC for 72 h in CH_2Cl_2 (98% yield, *endo*:*exo* >98:2, 88% ee).

hexane, 1 mL/min); retention times: 35.8 min (major), 30.3 min (minor). The absolute stereochemistry was assumed by analogy.



***endo*-7j**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(3-Trifluoromethylphenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7j). Purified by flash column chromatography (SiO_2, 5% ethyl acetate in hexane); $[\alpha]_D^{23}$ –70.0 (*c* 1.00, $CHCl_3$) (93 % ee); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66 (1H, qd, *J* = 1.6 and 8.7 Hz), 1.83 (1H, d, *J* = 8.7 Hz), 2.18 (3H, s), 3.01–3.06 (2H, m), 3.27 (1H, d, *J* = 3.8 Hz), 3.38 (1H, br), 6.04 (1H, dd, *J* = 2.7 and 5.7 Hz), 6.41 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.35–7.49 (4H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.0, 44.8, 46.6, 47.6, 48.2, 61.2, 122.8 (q, *J* = 3.8 Hz), 122.8 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272 Hz), 128.9, 130.8 (q, *J* = 32 Hz), 131.3, 133.1, 139.3, 145.5, 207.4; MS (EI) *m/z* (relative intensity) 261 (M^+, 2), 261 (8), 215 (100); HRMS calcd for $C_{16}H_{15}OF_3$, 280.1075, found: 280.1094. The *endo* adduct was obtained as a single diastereomer by the ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, temperature at 140 ºC); retention times: 30.4 min (major), 32.1 min (minor). The absolute stereochemistry was assumed by analogy.

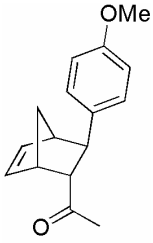


***endo*-7k**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(4-Methylphenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7k). Purified by flash column chromatography (SiO_2, gradient elution with 4–8% ethyl acetate in hexane); mp 33–34 ºC (recrystallized from ether); $[\alpha]_D^{23}$ –93.0 (*c* 1.0, $CHCl_3$) (88 % *ee*);[11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (1H, qd, *J* = 1.7 and 8.5 Hz), 1.86 (1H, br d, *J* = 8.5 Hz), 2.15 (3H, s), 2.33 (3H, s), 2.98 (1H, br s), 3.06 (1H, dd, *J* = 3.5 and 4.7 Hz), 3.15 (1H, br d, *J* = 4.5 Hz), 3.33 (1H, br s), 6.03 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.40 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.12 (2H, d, *J* = 8.1 Hz), 7.17 (2H, d, *J* = 8.1 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 20.9, 29.2, 45.0, 46.4, 47.5, 48.8, 61.1, 127.4, 129.2, 133.1, 135.5, 139.4, 141.3,

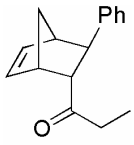
[11] Specific rotation was measured for the product of the reaction with OXB **3d** (10 mol %) at –60 ºC for 72 h in CH_2Cl_2 (62% yield, *endo*:*exo* >98:2, 88% ee).

208.2. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.86; H, 8.13. The *endo* adduct was obtained as a single diastereomer as ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OJ column (0.3% *i*-PrOH in hexane, 1 mL/min); retention times: 45.2 min (major), 32.4 min (minor). The absolute stereochemistry was assumed by analogy.



***endo*-7l**

1-[(1*S*,2*S*,3*R*,4*S*)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl]ethanone (7l). Purified by flash column chromatography (SiO_2, 4% ethyl acetate in hexane); mp 125–126 ºC (recrystallized from ether); $[\alpha]_D^{23}$ –95.5 (*c* 1.0, $CHCl_3$) (91 % *ee*);[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60 (1H, qd, *J* = 1.7 and 8.6 Hz), 1.84 (1H, br d, *J* = 8.6 Hz), 2.14 (3H, s), 2.94 (1H, br s), 3.02 (1H, dd, *J* = 3.6 and 4.8 Hz), 3.12 (1H, d, *J* = 4.7 Hz), 3.31 (1H, br s), 3.78 (3H, s), 6.02 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.38 (1H, dd, *J* = 3.2 and 5.6 Hz), 6.85 (2H, d, *J* = 8.6 Hz), 7.19 (2H, d, *J* = 8.6 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 29.1, 44.6, 46.4, 47.5, 48.8, 55.2, 61.2, 113.9, 128.4, 133.1, 136.4, 139.4, 157.8, 208.2. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.38; H, 7.58. The *endo* adduct was obtained as a single diastereomer as ^{1}H NMR analysis (>98:2). Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (9% *i*-PrOH in hexane, 1 mL/min); retention times: 13.0 min (major), 15.3 min (minor). The absolute stereochemistry was assumed by analogy.



***endo*-7m**

1-[(1*S*,2*S*,3*R*,4*S*)-3-Phenylbicyclo[2.2.1]hept-5-en-2-yl]propan-1-one (7m). Purified by flash column chromatography (SiO_2, gradient elution with 4–5% ethyl acetate in hexane); mp 55–55.5 ºC (recrystallized from ether); $[\alpha]_D^{23}$ –92.7 (*c* 1.0, $CHCl_3$) (90 % *ee*);[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 0. 95 (3H, t, *J* = 7.3 Hz), 1.52 (1H, qd, *J* = 1.7 and 8.6 Hz), 1.77 (1H, br d, *J* = 8.6 Hz), 2.30–2.44 (2H, m), 2.92 (1H, br s), 2.98 (1H, dd, *J* = 3.5 and 5.0 Hz), 3.12 (1H, dd, *J* = 1.4 and 5.0 Hz), 3.23 (1H, br s), 5.92 (1H, dd, *J* = 2.8 and 5.6 Hz), 6.31 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.10 (1H, m), 7.17–7.23 (4H, m),

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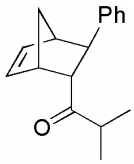
[12] Specific rotation was measured for the product of the reaction with OXB **3d** (10 mol %) at –60 ºC for 72 h in CH_2Cl_2 (8% yield, *endo*:*exo* >98:2, 88% ee).

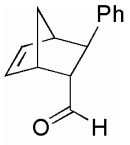
[13] Specific rotation was measured for the product of the reaction with OXB **3a** (20 mol %) at –60 ºC for 72 h in CH_2Cl_2 (59% yield, *endo*:*exo* >98:2, 90% ee).

minor *exo* isomer resonated at 5.87 and 6.28; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.8, 34.8, 45.4, 45.5, 47.5, 48.5, 60.0, 152.9, 127.4, 128.4, 133.2, 139.2, 144.5, 210.6; FTIR (neat film) 1697, 1134, 1107, 1028, 743, 729, 698 cm^{-1}; MS (EI) *m/z* (relative intensity) 226 (M^+, 2), 161 (100), 131 (63); HRMS calcd for $C_{16}H_{18}O$ 226.1358, found: 226.1351. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.90; H, 8.07. *Endo-exo* ratio was determined by ^{1}H NMR analysis. Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (7% *i*-PrOH in hexane, 1 mL/min); retention times: 5.5 min (major), 5.1 min (minor). The absolute stereochemistry was assumed by analogy.



***endo*-7n**

2-Methyl-1-[(1*S*,2*S*,3*R*,4*S*)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl]propan-1-one (7n). Purified by flash column chromatography (SiO_2, gradient elution with 4–5% ethyl acetate in hexane); $[\alpha]_D^{23}$ –64.7 (*c* 1.0, $CHCl_3$) (61 % *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (3H, d, *J* = 6.7 Hz), 1.06 (3H, d, *J* = 7.0 Hz), 1.60 (1H, qd, *J* = 1.6 and 8.6 Hz), 1.86 (1H, br d, *J* = 8.6 Hz), 2.74 (1H, septet, *J* = 6.8 Hz), 3.02 (1H, br s), 3.18 (1H, br d, *J* = *ca.* 5 Hz), 3.21 (1H, dd, *J* = 3.3 and 5.0 Hz), 3.29 (1H, br s), 5.95 (1H, dd, *J* = 2.7 and 5.6 Hz), 6.39 (1H, dd, *J* = 3.2 and 5.6 Hz), 7.17 (1H, m), 7.21–7.32 (4H, m), minor *exo* isomer resonated at 6.03 and 6.37; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 18.9, 19.1, 39.4, 45.5, 46.8, 47.7, 48.4, 58.4, 125.8, 127.3, 128.4, 133.2, 139.0, 144.6, 214.1; IR (neat film) 1700, 1025, 745, 720, 695 cm^{-1}; MS (EI) *m/z* (relative intensity) 226 (M^+, 2), 175 (96), 131 (100); HRMS calcd for $C_{17}H_{20}O$ 240.1514, found: 240.1504. *Endo-exo* ratio was determined by ^{1}H NMR analysis. Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (2% *i*-PrOH in hexane, 1 mL/min); retention times: 4.9 min (major), 5.3 min (minor). The absolute stereochemistry was assumed by analogy.

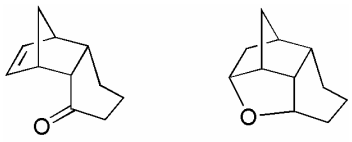


***endo*-7o**

***endo*-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (7o):** [14] Purified by flash column chromatography (SiO_2, 5% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (1H, m), 1.81 (1H, br d, *J* = 8.7 Hz), 2.98 (1H, m), 3.07 (1H, br d, *J* = 4.7 Hz), 3.13 (1H, br s), 3.38 (1H, br s), 6.18 (1H, dd, *J* = 2.8 and 5.6 Hz), 6.42 (1H, dd, *J* = 3.3 and 5.6 Hz), 7.17–7.35 (5H, m), 9.60 (1H, d, *J* = 2.2

[14] Ishihara, K.; Kurihara, H.; Matsumoto, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 6920.

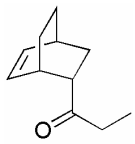
Hz); [minor *exo* isomer resonated at δ 6.07 (1H, dd, *J* = 3.3 and 5.6 Hz), 6.34 (1H, dd, *J* = 3.0 and 5.6 Hz), 9.93 (1H,d, *J* = 2.0 Hz)]. *Endo-exo* ratio was determined by ^{1}H NMR analysis. Enantioselectivity was determined by acetalization with (–)-(2*R*, 4*R*)-pentanediol and ^{1}H NMR analysis [4.40 (1H for minor *endo* ennatiomer, d, *J* = 8.0 Hz), 4.47 (1H for major *endo* enantiomer, d, *J* = 8.2 Hz), 4.84 (1H for major *exo* enantiomer, d, *J* = 6.5 Hz), and 4.86 (1H for minor *exo* enantiomer, d, *J* = 5.4 Hz)].[7] The absolute stereochemistry was not established.



***endo*-7p** **13**

(1*S*,2*S*,7*S*,8*R*)-Tricyclo[6.2.1.0^{2,7}]undec-9-en-3-one (7p).[2,6] Purified by flash column chromatography (SiO_2, gradient elution with 3–4% ethyl acetate in hexane); $[\alpha]_D^{23}$ –45.1 (*c* 0.43, $CHCl_3$) (44 % *ee*). Lit.[2] for the (1*R*,2*R*,3*R*,4*S*)-enantiomer; $[\alpha]_D^{23}$ +233 (*c* 0.99, $CHCl_3$) (95 % *ee*). Lit.[6] for the (1*R*,2*R*,3*R*,4*S*)-enantiomer; $[\alpha]_D^{23}$ +120.6 (*c* 1.00, $CHCl_3$) (63 % *ee*). The *endo* adduct was obtained as a single diastereomer as determined by ^{1}H NMR analysis (>98:2).

Reduction of the adduct with $LiAlH_4$ and purification of the crude alcohol by silica gel column chromatography afforded the tetracyclic ether **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (1H, d, *J* = 10.0 Hz), 1.21–1.45 (4H, m), 1.52–1.73 (4H, m), 1.78 (1H, m), 1.88 (2H, br s), 2.03 (1H, m), 2.70 (1H, t, *J* = 4.9 Hz), 4.11 (1H, br s), 4.28 (1H, dd, *J* = 5.4 and 7.4 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 16.8, 24.9, 27.7, 36.0, 36.5, 37.3, 38.8, 40.4, 49.5, 76.2, 79.8. Enantioselectivity of ether **13** was determined by using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 75 ºC, 1 ºC/min ramp to 200 ºC); retention times: 35.0 min (major), 45.5 min (minor).

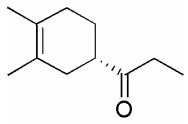


***endo*-7q**

1-[(1*S*,2*S*,4*S*)-Bicyclo[2.2.2]oct-5-en-2-yl]propan-1-one (7q). [15] Purified by flash column chromatography (SiO_2, gradient elution with 1–2% ethyl acetate in hexane); $[\alpha]_D^{23}$ –15.7 (*c* 1.0, $CHCl_3$) (88 % *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (3H, t, *J* = 7.3 Hz), 1.21–1.34 (2H, m), 1.50 (1H, m), 1.59 (1H, m), 1.65 (1H, br s), 1.66 (1H, br s), 2.35–2.50 (2H, m), 2.60 (1H, m), 2.68 (1H, dt, *J* = 1.9 and 7.8 Hz), 2.87 (1H, m), 6.10 (1H, t, *J* = 7.7 Hz), 6.27 (1H, t, *J* = 7.7 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 8.0, 24.4, 25.8, 28.8, 29.5, 32.0, 33.8, 50.4, 131.1, 134.9, 212.3; IR (neat film) 1705, 1125, 700 cm^{-1}; MS (EI) *m/z* (relative intensity) 164 (M^+, 33), 107 (32), 79 (100); HRMS calcd for $C_{11}H_{16}O$ 164.1201,

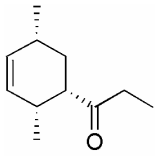
[15] Hollis, T. K.; Robinson, N. P.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 5464.

found: 164.1203. *Endo-exo* ratio was determined by GC analysis using a OV-1 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 10 ºC/min ramp to 320 ºC); retention times: 8.5 min (*endo*), 8.3 min (*exo*). Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 35.6 min (major), 35.3 min (minor). The absolute stereochemistry was assumed by analogy.



7r

1-[(*S*)-3,4-Dimethylcyclohex-3-enyl]propan-1-one (7r). [16, 17] Purified by flash column chromatography (SiO_2, gradient elution with 2–3% ethyl acetate in hexane); $[\alpha]_D^{23}$ –25.5 (*c* 1.15, $CHCl_3$) (81 % *ee*). Lit.[9] for the (*S*)-enantiomer; $[\alpha]_D^{23}$ –77 (*c* 1.0, CH_2Cl_2) (67 % *ee*). Enantioselectivity as well as the absolute stereochemistry was determined by reduction with $LiAlH_4$ to the corresponding alcohol (*ca.* 1:1 diastereomer mixture) and conversion to the (*R*)-MTPA ester derivative [0.72 (3H for minor enantiomer, t, *J* = 7.5 Hz) and 0.74 (3H for major enantiomer, t, *J* = 7.5 Hz)].[10]



7s

1-[(1*S*,2*R*,5*R*)-2,5-Dimethylcyclohex-3-enyl]propan-1-one (7s). Purified by flash column chromatography (gradient elution with 2–3% ethyl acetate in hexane); $[\alpha]_D^{23}$ –19.1 (*c* 1.1, $CHCl_3$) (80 % *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (3H, d, *J* = 7.0 Hz), 0.94 (3H, d, *J* = 6.9 Hz), 0.99 (3H, t, *J* = 7.2 Hz), 1.24 (1H, dt, *J* = 11.1 and 13.1 Hz), 1.68 (1H, m), 2.08 (1H, m), 2.32 (1H, m), 2.46 (1H, m), 2.58 (1H, br), 2.70 (1H, ddd, *J* = 2.4, 5.4, and 12.8 Hz), 5.40 (1H, br d, *J* = *ca.* 10 Hz), 5.55 (1H, ddd, *J* = 2.5, 4.9, and 9.8 Hz), minor diastereomer resonated at 5.31 and 5.49; ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.7, 16.4, 21.6, 27.2, 31.1, 31.2, 34.1, 50.4, 131.0, 132.8, 213.5; IR (neat film) 1710, 1110, 755 cm^{-1}; MS (EI) *m/z* (relative intensity) 165 (M^+– H, 28), 123 (100), 107 (94); HRMS calcd for $C_{11}H_{17}O$ (M^+ – H) 165.1279, found: 165.1284. Diastereomer ratio was determined by ^{1}H NMR analysis. Enantioselectivity was determined by GC analysis using a Chrompack Cp-Cyclodextrin-β-236-M-19 column (30 m, 1.8 kg/cm^2, initial temperature 50 ºC, 2 ºC/min ramp to 200 ºC); retention times: 27.1 min (major), 27.6 min (minor). The absolute stereochemistry was assumed by analogy.

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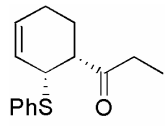
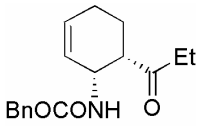
[16] Rickerby, J.; Vallet, M.; Bernardinelli, G.; Viton, F.; Kündig, E. P. *Chem. Eur. J.* **2007**, *13*, 3354.

[17] Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2003**, *125*, 6388.



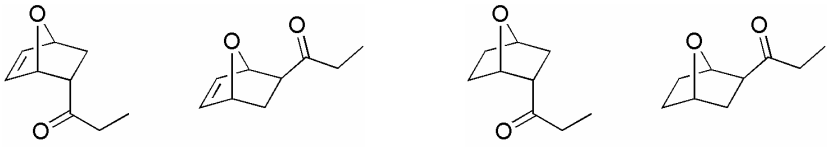
7t

1-[(1*S*,2*R*)-2-(Phenylsulfanyl)cyclohex-3-en-1-yl]propan-1-one (7t). Purified by flash column chromatography (2% ethyl acetate in toluene); $[\alpha]_D^{23}$ –280 (*c* 0.500, $CHCl_3$) (76% *ee*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 7.2 Hz), 1.84–1.88 (2H, m), 2.03 (1H, m), 2.06 (1H, br d, *J* = 18.0 Hz), 2.34 (2H, q, *J* = 7.2 Hz), 2.89 (1H, td, 4.5 and 10.4 Hz), 4.10 (1H, m), 5.78 (1H, m), 5.92 (1H, m), 7.20–7.29 (3H, m), 7.40–7.42 (2H, m); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.4, 19.4, 24.8, 34.2, 47.0, 50.9, 127.3, 127.4, 128.8, 128.9, 132.9, 134.9, 210.6; MS (EI) *m/z* (relative intensity) 246 (M^+, 37), 137 (100), 109 (66); HRMS (EI) calcd for $C_{15}H_{18}OS$ 246.1078, found: 246.1079. Enantioselectivity was determined by HPLC analysis using a Chiralcel OD column (0.2% *i*-PrOH in hexane, 1 mL/min); retention times: 23.8 min (major), 27.7 min (minor). The absolute stereochemistry was assumed by analogy.



7u

Benzyl (1*S*,2*R*)-6-propionylcyclohex-2-en-1-ylcarbamate (7u):[6] Purified by flash column chromatography (gradient elution with 5–15% ethyl acetate in hexane); $[\alpha]_D^{23}$ –111 (*c* 0.500, $CHCl_3$) (86% ee). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (3H, t, *J* = 7.2 Hz), 1.70 (1H, m), 1.82 (1H, m), 1.92–2.08 (2H, m), 2.42 (1H, qd, *J* = 7.2 and 17.9 Hz), 2.68 (1H, qd, *J* = 7.3 and 17.9 Hz), 2.86 (1H, m), 4.63 (1H, br s), 4.97–5.07 (3H, m), 5.70 (1H, m), 5.82 (1H, m), 7.26–7.39 (5H, m). Enantioselectivity was determined by HPLC analysis using a Chiralcel AD-H column (3% *i*-PrOH in hexane, 1 mL/min); retention times: 31.9 min (major), 23.8 min (minor). The absolute stereochemistry was assumed by analogy.

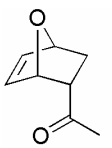


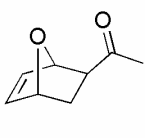
endo-**7v** *exo*-**7v** *endo*-**14** *exo*-**14**

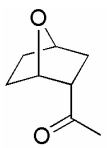
(1*S*,2*S*,4*S*)- and (1*R*,2*S*,4*R*)-1-(7-Oxabicyclo[2.2.1]hept-5-en-2-yl)propan-1-one (*endo*- and *exo*-7v): *Typical Procedure for Asymmetric Diels-Alder Reaction with Furan.* To a solution of *O*-(benzoyl)-*N*-tosyl-(L)-*allo*-threonine[1] (75.5 mg, 0.200 mmol) in CH_2Cl_2 (2 mL) under argon atmosphere at room temperature was added dichlorophenylborane (28.5 μL, 0.22 mmol). After being stirred for 30 min, the mixture was concentrated in *vacuo*. To a mixture of the resulting OXB **3c** in toluene (6.4 mL) at –78 °C were added ethyl vinyl ketone (168 mg, 2.00 mmol), and furan (0.73 mL, 10 mmol). The resulting

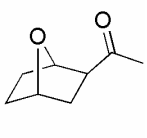
solution was stirred at –78 ºC for 20 min. The mixture was quenched by the addition of saturated aqueous $NaHCO_3$ and filtered. The filtrate was extracted three times with ether, dried ($MgSO_4$), and concentrated in *vacuo*. The toluene solution of the crude product was subjected to a flash chromatography (SiO_2, gradient elution with 0–25% Et_2O in hexane) to obtain 269 mg (1.77 mmol, 88%) of a 93:7 mixture of *endo*-**7v** and *exo*-**7v**. The *endo* and *exo* adducts were isolated by flash chromatography. *endo*-**7v** (98% ee): R_f 0.33 (SiO_2, 30% ethyl acetate in hexane); $[\alpha]_D^{23}$ –75.2 (*c* 1.00, $CHCl_3$) (96% *ee*);[18] ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (3H, t, *J* = 7.2 Hz), 1.59 (1H, dd, *J* = 4.0 and 11.2 Hz), 2.00 (1H, ddd, *J* = 4.8, 9.1, and 11.3 Hz), 2.33-2.50 (2H, m), 3.20 (1H, td, *J* = 4.3 and 9.0 Hz), 5.01 (1H, dd, *J* = 1.1 and 4.7 Hz), 5.17 (1H, br d, *J* = 4.7 Hz), 6.15 (1H, dd, *J* = 1.5 and 5.9 Hz), 6.40 (1H, dd, *J* = 1.7 and 5.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.6, 27.4, 35.8, 50.8, 78.9, 79.2, 134.8, 136.8, 208.9; HRMS (EI) calcd for $C_9H_{12}O_2$ 152.0837, found: 152.0838. *exo*-**7v** (36% ee):[19] R_f 0.27 (SiO_2, 30% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (3H, t, *J* = 7.3 Hz), 1.51 (1H, dd, *J* = 8.5 and 11.4 Hz), 1.62 (1H, br s), 2.03 (1H, td, *J* = 4.4 and 11.4 Hz), 2.47–2.61 (2H, m), 5.07 (1H, br d, *J* = 4.4 Hz), 5.09 (1H, d, *J* = 1.0 Hz), 6.36 (1H, dd, *J* = 1.6 and 5.8 Hz), 6.38 (1H, dd, *J* = 1.6 and 5.8 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.9. 28.4, 34.5, 49.8, 78.0, 79.9, 134.9, 136.8, 210.9; HRMS (EI) calcd for $C_9H_{12}O_2$ 152.0837, found: 152.0832.

Endo-exo ratio was determined by 500 MHz ^{1}H NMR analysis. The absolute stereochemistry was assumed by analogy. A 93:7 mixture of the *endo* and *exo* adduct was hydrogenated in the presence of Pd/C (10 %) in hexane to give a mixture of *endo*-**14** and *exo*-**14**. Enantioselectivity was determined by GC analysis using a BETA DEX^{TM} 225 (m) column (30 m, 1.8 kg/cm^2, initial temperature 90 ºC, 1 ºC/min ramp to 170 ºC); retention times: 26.3 min (major *endo* enantiomer), 28.2 min (minor *endo* enantiomer), 37.9 min (major *exo* enantiomer), 36.9 min (minor *exo* enantiomer). (1*S*,2*S*,4*S*)-1-(7-Oxabicyclo[2.2.1]hept-2-yl)propan-1-one (*endo*-**14**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (3H, t, *J* = 7.4 Hz), 1.38 (1H, m), 1.50 (1H, m), 1.58 (1H, m), 1.63–1.77 (2H, m), 1.98 (1H, dd, *J* = 4.7 and 11.8 Hz), 2.33–2.48 (2H, m), 3.18 (1H, m), 4.59 (1H, t, *J* = 5.3 Hz), 4.76 (1H, t, *J* = 5.2 Hz), a minor *exo*-isomer resonates at 4.64 (1H, t, *J* = 5.0 Hz) and 4.72 (1H, d, *J* = 4.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 7.6, 20.1, 29.9, 31.6, 36.6, 55.7, 77.4, 78.1, 209.2.


endo-**7w**


exo-**7w**


endo-**15**

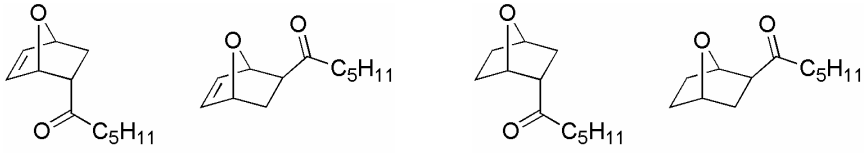

exo-**15**

[18] Specific rotation was measured for the product of the reaction with OXB **3c** (5 mol %) at –78 ºC for 0.3 h in toluene (34% yield, *endo*:*exo* = 86:14, *endo;* 96% ee, *exo;* 23% ee).

[19] Bloch, R.; Gilbert, L. *Tetrahedron* **1988**, *44*, 2523.

(1*S*,2*S*,4*S*)-1-(7-Oxabicyclo[2.2.1]hept-5-en-2-yl)ethanone (*endo*- and *exo*-7w).[20] *endo*-**7w**: R_f 0.27 (SiO_2, 30% ethyl acetate in hexane); $[\alpha]_D^{23}$ –88.8 (*c* 0.750, $CHCl_3$) (93% *ee*); ^{1}H NMR(500 MHz, $CDCl_3$) δ 1.59 (1H, dd, *J* = 4.0 and 11.3 Hz), 2.01 (1H, ddd, *J* = 4.8, 9.0, and 11.3 Hz), 2.14 (3H, s), 3.19 (1H, td, *J* = 4.3 and 9.0 Hz), 5.01 (1H, dd, *J* = 1.5 and 4.7 Hz), 5.18 (1H, dd, *J* = 0.6 and 4.7 Hz), 6.19 (1H, dd, *J* = 1.5 and 5.9 Hz), 6.40 (1H, dd, *J* = 1.7 and 5.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 27.3, 29.8, 52.0, 78.8, 79.2, 131.7, 137.0, 206.1. *exo*-**7w**: R_f 0.20 (SiO_2, 30% ethyl acetate in hexane); δ 1.52 (1H, dd, *J* = 8.6 and 11.5 Hz), 2.01 (1H, td, *J* = 4.2 and 11.5 Hz), 2.23 (3H, s), 2.47 (1H, td, *J* = 4.1 and 8.6 Hz), 5.07 (1H, d, *J* = 4.4 Hz), 5.10 (1H, d, *J* = 1.2 Hz), 6.35 (1H, dd, *J* = 1.7 and 5.8 Hz), 6.38 (1H, dd, *J* = 1.6 and 5.8 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 28.40, 28.44, 50.82, 78.0, 79.8, 134.8, 136.8, 208.6.

Endo-exo ratio was determined by 500 MHz ^{1}H NMR analysis. The absolute stereochemistry was assumed by analogy. A 77:23 mixture of the *endo* and *exo* adduct was hydrogenated in the presence of Pd/C (10 %) in hexane to give a mixture of *endo*-**15**[21] and *exo*-**16**. Enantioselectivity was determined by GC analysis using a BETA DEX™ 225 (m) column (30 m, 1.8 kg/cm^2, initial temperature 90 ºC, 1 ºC/min ramp to 170 ºC); retention times: 20.3 min (major *endo* enantiomer), 22.0 min (minor *endo* enantiomer), 32.5 min (major *exo* enantiomer), 31.4 min (minor *exo* enantiomer). (1*S*,2*S*,4*S*)-1-(7-Oxabicyclo[2.2.1]hept-2-yl)ethanone (*endo*-**15**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (1H, m), 1.50 (1H, m), 1.63 (1H, m), 1.65–1.77 (2H, m), 1.96 (1H, dd, *J* = 4.6 and 11.8 Hz), 2.16 (3H, s), 3.19 (1H, m), 4.60 (1H, t, *J* = 5.3 Hz), 4.76 (1H, t, *J* = 5.2 Hz). (1*R*,2*S*,4*R*)-1-(7-Oxabicyclo[2.2.1]hept-2-yl)ethanone (*exo*-**15**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44–1.57 (2H, m), 1.66 (1H, dd, *J* = 9.0 and 12.1 Hz), 1.69–1.83 (2H, m), 2.18 (3H, s), 2.65 (1H, dd, *J* = 5.0 and 9.0 Hz), 4.65 (1H, t, *J* = 5.0 Hz), 4.74 (1H, d, *J* = 4.9 Hz).



endo-**7x** *exo*-**7x** *endo*-**16** *exo*-**16**

(1*S*,2*S*,4*S*)-1-(7-Oxabicyclo[2.2.1]hept-5-en-2-yl)hexan-1-one (*endo*- and *exo*-7x). *endo*-**7x**: R_f 0.50 (SiO_2, 30% ethyl acetate in hexane); mp 45–46.5 ºC (recrystallized from pentane); $[\alpha]_D^{25}$ –78.4 (*c* 0.75, $CHCl_3$) (98% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.3 Hz), 1.21–1.33 (4H, m), 1.52–1.61 (3H, m), 2.00 (1H, ddd, *J* = 4.8 and 9.0 and 11.2 Hz), 2.33–2.47 (2H, m), 3.20 (1H, td, *J* = 4.3 and 9.0 Hz), 5.01 (1H, dd, *J* = 1.5 and 4.7 Hz), 5.18 (1H, dd, *J* = 1.6 and 5.9 Hz), 6.16 (1H, dd, *J* = 1.4

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[20] Adams, J. M.; Dyer, S.; Martin, K.; Matear, W. A.; McCabe, R. W. *J. Chem. Soc., Perkin Trans. 1* **1994**, 761.

[21] Lambert, J. B.; Larson, E. G. *J. Am. Chem. Soc.* **1985**, *107*, 7546.

and 5.8 Hz), 6.40 (1H, dd, J = 1.6 and 5.8 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.9, 22.4, 23.2, 27.4, 31.3, 42.7, 51.1, 79.0, 79.2, 131.8, 136.8, 208.6. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.13; H, 9.34. Found: C, 73.71; H, 9.20. *exo*-**7x**: R_f 0.65 (SiO_2, 30% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.2 Hz), 1.23–1.34 (5H, m), 1.50 (1H, dd, J = 8.5 and 11.4 Hz), 1.57–1.63 (2H, m), 2.03 (1H, dt, J = 4.4 and 11.4 Hz), 2.46–2.56 (2H, m), 5.07 (1H, br d, J = 4.4 Hz), 5.09 (1H, br s), 6.35 (1H, dd, J = 1.5 and 5.8 Hz), 6.38 (1H, dd, J = 1.4 and 5.8 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.9, 22.5, 23.5, 28.3, 31.4, 41.4, 50.1, 78.0, 79.8, 134.9, 136.8, 210.5.

Endo-exo ratio was determined by 500 MHz ^{1}H NMR analysis. The absolute stereochemistry was assumed by analogy. A 86:14 mixture of the *endo* and *exo* adduct was hydrogenated in the presence of Pd/C (10 %) in hexane to give a mixture of *endo*-**16** and *exo*-**16**. Enantioselectivity was determined by GC analysis using a BETA DEX^{TM} 225 (m) column (30 m, 1.8 kg/cm^2, initial temperature 90 ºC, 1 ºC/min ramp to 170 ºC); retention times: 55.8 min (major *endo* enantiomer), 56.6 min (minor *endo* enantiomer), 64.6 min (major *exo* enantiomer), 65.6 min (*exo* minor). (1*S*,2*S*,4*S*)-1-(7-Oxabicyclo[2.2.1]hept-2-yl)hexan-1-one (*endo*-**16**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.2 Hz), 1,22–1.34 (4H, m), 1.39 (1H, m), 1.50 (1H, m) 1.54–1.63 (3H, m), 1.64–1.76 (2H, m), 1.96 (1H, dd, J = 4.6 and 11.7 Hz), 2.31–2.46 (2H, m), 3.18 (1H, m), 4.58 (1H, t, J = 5.3 Hz), 4.76 (1H, t, J = 5.3 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.9, 22.4, 23.2, 26.1, 29.9, 31.4, 31.6, 43.4, 56.0, 77.4, 78.2, 208.9. (1*R*,2*S*,4*R*)-1-(7-Oxabicyclo[2.2.1]hept-2-yl)propan-1-one: (*exo*-**16**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 7.2 Hz), 1,21–1.35 (4H, m), 1.43–1.66 (5H, m), 1.67–1.81 (2H, m), 2.06 (1H, m), 2.37–2.51 (2H, m), 2.65 (1H, dd, J = 5.1 and 9.0 Hz), 4.64 (1H, t, J = 5.0 Hz), 4.72 (1H, d, J = 4.9 Hz); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 13.9, 22.4, 23.5, 29.5, 30.0, 31.4, 33.4, 40.7, 55.5, 76.3, 77.8, 209.7.