A Chiral Acrylate Equivalent for Metal-Free Diels-Alder Reactions: *Endo*-2-Acryloylisoborneol.

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Supporting Information

General.

All reactions were carried out under an atmosphere of nitrogen in oven or flame-dried glassware with magnetic stirring. Solvents were distilled prior to use. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium metal/benzophenone ketyl. Dichloromethane (CH₂Cl₂) was distilled from calcium hydride. Cyclopentadiene was distilled by cracking dicyclopentadiene prior to use. Other dienes were used without purification. Purification of reaction products was carried out by flash chromatography using silicagel 60 (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and p-anisaldehyde solution followed by heating. Melting points were measured with a Mettler FP 80 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Gemini-200 spectrometer and are reported in ppm from CHCl₃. Combustion analyses were performed on a Carlo Erba CHNS-O EA1108 elemental analyzer. Optical rotations were measured at 25 ± 0.2 °C in methylene chloride unless otherwise stated. Analytical high performance liquid chromatography (HPLC) was performed on a Waters chromatograph equipped with a diode array UV detector, using the columns specified to the end of this report.

(1R)-2-endo-propenoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 3

Methoxyallene¹ (2.94 g, 42 mmol) was added to a solution of nBuLi (2.5 M in hexanes, 16 mL, 40 mmol) cooled to -30 °C under a nitrogen atmosphere. After stirring for 30 minutes at the same temperature, TMDA (6.1 mL, 40 mmol) and a solution of (1R)-(+)-camphor

¹ (a) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Elsevier: New York, 1981. (b) Tius, M. A. In *Encyclopedia of Reagent for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995, Vol. 5, pp.3316-3320. (c) Zimmer, R.; Khan, F. A. *J. prak.Chem.* **1996**, 338, 92-94. (d) Pulz, R. *Synlett* **2000**, 1697.

(3.04 g, 20 mmol) in THF (2.6 mL) were added dropwise. The resulting mixture was allowed to stir for 2 hours at $-30\text{ }^{\circ}\text{C}$ and then was quenched with a saturated aqueous solution of NH_4Cl (20 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organics were dried over MgSO_4 , and the solvent was removed under reduced pressure. The product **2** was purified by distillation (about 10% of starting camphor was separated) and collected as a colorless liquid. Yield of (1R)-2-*endo*-1-methoxy-1,2-propanodienyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**2**): 3.33 g (75%); b.p. $70\text{--}72^{\circ}\text{C}/0.1\text{ torr}$; $[\alpha]_{\text{D}}^{25} +38.0$ (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 3585, 2950, 2924, 2868, 1951, 1066, 876; ^1H NMR (CDCl_3) δ 5.55 (d, 1H, $\text{HC}=\text{C}$, $J=7.7\text{ Hz}$), 5.47 (d, 1H, $\text{HC}=\text{C}$, $J=7.7\text{ Hz}$), 3.44 (s, 3H, OCH_3), 2.80 (s, 1H, OH), 2.06-1.95 (m, 1H, HCH), 1.80-1.73 (d, 1H, HCH, $J=13\text{ Hz}$) 1.69-1.57 (m, 1H, HCH), 1.48-1.29 (m, 2H, HCH), 1.12 (s, 3H, CH_3), 1.08-0.88 (m, 2H, HCH), 1.00 (s, 3H, CH_3), 0.80 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 197.5, 138.9, 92.1, 82.0, 56.4, 52.9, 49.8, 44.8, 42.5, 31.5, 26.6, 21.1, 20.9, 11.3. The distillate product was dissolved in CH_2Cl_2 (30 mL) and washed twice with 1 M HCl (15 mL). The organic layer was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure to give the vinyl ketone **3** as a white solid. Purification was effected by flash silica gel column chromatography using a 1:30 ethyl acetate/hexane mixture as the eluant. Yield of (1R)-2-*endo*-propenoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**3**): 3.12 g (100% from **2**); m.p. $72.5\text{--}73.0\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} -34.5$ (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 3488 (OH), 1685 (CO); ^1H NMR (CDCl_3) δ 6.88 (dd, 1H, $\text{HC}=\text{C}$, $J=10.6\text{ Hz}$, $J'=17.2\text{ Hz}$), 6.34 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{ Hz}$, $J'=16.9\text{ Hz}$), 5.67 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{ Hz}$, $J'=10.3\text{ Hz}$), 2.88 (s, 1H, OH), 2.34-2.25 (m, 1H, HCH), 1.88-1.64 (m, 2H, HCH), 1.44-0.80 (m, 4H, HCH), 1.10 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.82 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 201.6, 131.8, 128.7, 86.9, 52.6, 50.6, 45.2, 41.3, 30.2, 26.5, 20.9, 20.4, 10.6; Anal. calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2$ (208.33) C, 74.94; H, 9.70. Found: C, 74.85; H, 10.01.

(1R)-2-*endo*-propenoyl-2-*exo*-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane. 4

Methyl iodide (0.51 mL, 8 mmol) was added to a solution of NaH (0.20 g, 8 mmol) in dry DMF (12 mL) cooled to $-50\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. Then a solution of allene **2** reported above (0.889 g, 4 mmol) in DMF (4 mL) was added at the same temperature and the mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 1 hour. The reaction was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and then was extracted twice with Et_2O (15 mL), and the combined organic layers were washed with water (2 x 10 mL). The organic layer was dried over MgSO_4 , and the solvent was removed under reduced pressure. The residue thus obtained was dissolved in Et_2O (8 mL) and a 5% aqueous solution of H_2SO_4 (8 mL) was added at $0\text{ }^{\circ}\text{C}$ and the mixture was stirred at the same temperature for 16 hours. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organics were dried over MgSO_4 , and the solvent was removed under reduced pressure. Purification of the product **4** was effected by flash silica gel column chromatography using a 1:30 ethyl acetate/hexane mixture as the eluant. Yield of (1R)-2-*endo*-propenoyl-2-*exo*-methoxy-1,7,7-trimethylbicyclo[2.2.1]heptane (**4**): 0.534 g (60% from **2**); oil; $[\alpha]_{\text{D}}^{25} +27.0$ (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 1691 (CO); ^1H NMR (CDCl_3) δ 6.98 (dd, 1H, $\text{HC}=\text{C}$, $J=10.3\text{ Hz}$, $J'=17.2\text{ Hz}$), 6.33 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{ Hz}$, $J'=17.6\text{ Hz}$), 5.64 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{ Hz}$, $J'=10.3\text{ Hz}$), 3.00 (s, 3H, CH_3), 2.16 (d, 1H, HCH, $J=12.8$), 1.92-1.55 (m, 3H, HCH), 1.35-1.10 (m, 2H, HCH), 1.00 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 0.87-0.75 (m, 1H, HCH), 0.81 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 201.6, 132.5, 127.9, 93.5, 52.1, 51.1, 50.6, 45.2, 33.3, 30.6, 26.0, 20.6, 20.6, 11.3.

(1R)-2-endo-propenoyl-2-exo-trimethylsilyloxy-1,7,7-trimethylbicyclo[2.2.1]-heptane. 5

To a mixture of the α' -hydroxy vinyl ketone **3** (2.08 g, 10 mmol) and 3-trimethylsilyl-2-oxazolidinone TMSO (2.32 mL, 15 mmol) under a nitrogen atmosphere was added one drop of trifluoromethanesulfonic acid. The reaction mixture was stirred at room temperature for 1 hour. Then CH_2Cl_2 (25 mL) was

added and the resulting solution was washed with a saturated aqueous solution of NaHCO_3 (2 x 15 mL). The organic layer was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. Hexane (15 mL) was added to the oily residue and the resulting white solid was filtered and washed with additional hexane (15 mL). The solvent was evaporated and the crude product was purified by column chromatography (eluant: ethyl acetate/hexane 1:30). Yield (1R)-2-endo-propenoyl-2-exo-trimethylsilyloxy-1,7,7-trimethylbicyclo[2.2.1]-heptane (**5**): 2.78 g (99%); oil; $[\alpha]_{\text{D}}^{25}$ -15.0 (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 1696 (CO); ^1H NMR (CDCl_3) δ 6.92 (dd, 1H, $\text{HC}=\text{C}$, $J=10.3\text{Hz}$, $J'=17.2\text{Hz}$), 6.35 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{Hz}$, $J'=17.2\text{Hz}$), 5.68 (dd, 1H, $\text{HCH}=\text{C}$, $J=2.2\text{Hz}$, $J'=10.3\text{Hz}$), 2.57 (d, 1H, HCH , $J=12.5$), 1.90-1.74 (m, 1H, HCH), 1.67-1.40 (m, 1H, HCH), 1.37-0.68 (m, 4H, HCH), 1.09 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 0.85 (s, 3H, CH_3), 0.08 (s, 9H, 3 CH_3); ^{13}C NMR (CDCl_3) δ 199.8, 133.2, 127.6, 90.0, 51.8, 50.9, 45.5, 40.0, 30.0, 25.8, 21.0, 20.4, 1.7.

(1R)-2-endo-2'-butenoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 6²

To a solution of **2** (0.222 g, 1mmol) in THF (4 mL) at -78°C , $n\text{BuLi}$ (2.5 M in hexanes, 1.2 mL, 3 mmol) was added and the reaction was stirred at -25°C for 4 h. Then, MeI (0.21 mL, 3.5 mmol) was added and the mixture was stirred for 2 h at the same temperature. The reaction was quenched with 1N HCl (5 mL) and extracted with CH_2Cl_2 (2 x 15 mL). The organic layer was dried over MgSO_4 , filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (eluant: ethyl acetate/hexane 1:60) to afford the corresponding enone. 0.150 g (67%); m.p. 82°C ; $[\alpha]_{\text{D}}^{25}$ -54.0 (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 3427 (OH), 1680 (CO); ^1H NMR (CDCl_3) δ 7.01-6.90 (dq, 1H, $\text{HC}=\text{C}$, $J=7.0\text{Hz}$, $J'=14.7\text{Hz}$), 6.61 (dq, 1H, $\text{HC}=\text{C}$, $J=2.0\text{Hz}$, $J'=15.0\text{Hz}$), 3.13 (s, 1H, OH), 2.24 (d, 1H, HCH , $J=12.8\text{Hz}$), 1.87 (d, 3H, CH_3 , 7.0Hz), 1.80-1.61 (m, 2H, HCH), 1.40-1.14 (m, 3H, HCH), 1.08 (s, 3H, CH_3), 1.06-0.72 (m, 1H, HCH), 0.85 (s, 3H, CH_3), 0.80 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 201.5, 143.5, 127.0, 86.6, 52.6, 50.5, 45.2, 41.1, 30.2, 26.6, 20.9, 20.4, 18.5, 10.6; Anal. calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$ (222.36) C, 75.62; H, 9.99. Found: C, 75.33; H, 10.07.

General procedure for the Heck reaction

A mixture of $\text{Pd}_2(\text{dba})_3$ (0.0022 g, 2.4 μmol), PPh_3 (0.0052 g, 20 μmol) and Et_3N (0.28 mL, 2 mmol) in CH_3CN (4 mL) was stirred for 30 minutes at room temperature. Then a solution of ketone **3** (0.208 g, 1 mmol) and the corresponding iodobenzene (3 mmol) was added and the mixture was stirred at 80°C for 1.5 h. After this time, the reaction was allowed to warm to room temperature and then 1N HCl (5 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 15 mL). The combined organic extracts were dried over MgSO_4 , filtered, and the solvent evaporated. The crude

² For alkylations of 1-alkoxyallenes, see: Hausherr, A.; Orschel, B.; Scherer, S.; Reissig, H.-U. *Synthesis* **2001**, 1377-1385.

product was purified by column chromatography (eluant: ethyl acetate/hexane 1:60) to afford the corresponding enone.

(1R)-2-endo-cinnamoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 7

The title compound was prepared according to general procedure from iodobenzene (0.34 mL, 3 mmol) in 86% yield (0.245 g). m.p. 133 °C; $[\alpha]_D^{25}$ -28.3 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3462 (OH), 1649 (CO); ¹H NMR (CDCl₃) δ 7.73-7.05 (m, 5H, arom.), 7.69 (d, 1H, HC=C, *J*=15.7Hz), 7.28 (d, 1H, HC=C, *J*=15.7 Hz), 3.06 (s, 1H, OH), 2.41 (d, 1H, HCH, *J*=12.5Hz), 1.98-1.11 (m, 6H, 3 CH₂), 1.19 (s, 3H, CH₃), 0.97 (s, 3H, CH₃), 0.88 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 219.0, 134.9, 130.6, 129.0, 128.6, 87.3, 53.2, 50.8, 47.7, 43.6, 41.7, 30.6, 27.0, 21.1, 20.6, 19.6, 10.8; Anal. calcd for C₁₉H₂₄O₂ (284.43) C, 80.23; H, 8.52. Found: C, 80.36; H, 8.66.

(1R)-2-endo-p-methylcinnamoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 8

The title compound was prepared according to general procedure from 4-iodotoluene (0.65 g, 3 mmol) in 98% yield (0.292 g). m.p. 105-106 °C; $[\alpha]_D^{25}$ -18.9 (*c* 0.52, Cl₂CH₂); IR (neat, cm⁻¹) 3467 (OH), 1675 (CO); ¹H NMR (CDCl₃) δ 7.41 (d, 1H, HC=C, *J*=15.8Hz), 7.21 (d, 2H, arom., *J*=8.1Hz), 6.98 (d, 1H, HC=C, *J*=15.0Hz), 6.92 (d, 2H, arom., *J*=8.0Hz), 2.88 (s, 1H, OH), 2.14 (d, 1H, HCH, *J*=12.0Hz), 2.12 (s, 3H, CH₃), 1.74-1.44 (m, 3H, HCH), 1.23-0.58 (m, 3H, HCH), 0.91 (s, 3H, CH₃), 0.69 (s, 3H, CH₃), 0.61 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 201.5, 143.0, 140.5, 131.9, 129.3, 128.3, 121.0, 87.0, 52.4, 50.6, 45.3, 41.3, 30.3, 26.5, 21.4, 20.9, 20.4, 10.7; Anal. calcd for C₂₀H₂₆O₂ (298.46) C, 80.48; H, 8.80. Found: C, 80.54; H, 8.79.

(1R)-2-endo-p-methoxycinnamoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 9

The title compound was prepared according to general procedure from 4-iodoanisole (0.70 g, 3 mmol) in 85% yield (0.267 g). m.p. 122-123 °C; $[\alpha]_D^{25}$ -16.6 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3467 (OH), 1664 (CO); ¹H NMR (CDCl₃) δ 7.66 (d, 1H, HC=C, *J*=15.8Hz), 7.53 (d, 2H, arom., *J*=8.8Hz), 7.15 (d, 1H, HC=C, *J*=15.4Hz), 6.90 (d, 2H, arom., *J*=8.8Hz), 3.84 (s, 3H, CH₃), 3.17 (s, 1H, OH), 2.38 (d, 1H, HCH, *J*=12.8Hz), 2.00-1.72 (m, 4H, HCH), 1.49-1.24 (m, 4H, HCH), 1.17 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 0.87 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 201.8, 161.5, 143.1, 130.2, 127.5, 119.3, 114.3, 87.1, 55.4, 53.0, 50.6, 45.4, 41.5, 30.4, 26.9, 21.0, 20.4, 10.7; Anal. calcd for C₂₀H₂₆O₃ (314.46) C, 76.39; H, 8.35. Found: C, 76.45; H, 8.29.

(1R)-2-endo-p-chlorocinnamoyl-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. 10

The title compound was prepared according to general procedure from 1-chloro-4-iodobenzene (0.72 g, 3 mmol) in 92% yield (0.293 g). m.p. 126-127 °C; $[\alpha]_D^{25}$ -19.6 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3457 (OH), 1680 (CO); ¹H NMR (CDCl₃) δ 7.58 (d, 1H, HC=C, *J*=15.8Hz), 7.46 (d, 2H, arom., *J*=8.4Hz), 7.32 (d, 2H, arom., *J*=8.4Hz), 7.22 (d, 1H, HC=C, *J*=15.9Hz), 2.95 (s, 1H, OH), 2.39 (d, 1H, HCH, *J*=12.8Hz), 1.96-1.67 (m, 2H, HCH), 1.46-1.03 (m, 4H, HCH), 1.15 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 0.85 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 201.4, 141.6, 136.2, 133.2, 129.5, 129.1, 122.2, 87.2, 52.8, 50.7, 45.4, 41.6, 30.4, 26.7, 20.9, 20.5, 10.8; Anal. calcd for C₁₉H₂₃O₂Cl (318.87) C, 71.56; H, 7.28. Found: C, 70.97; H, 7.19.

Diels-Alder reactions with enone **3**

General procedure A

To a solution of α' -hydroxy vinyl ketone **3** (0.208 g, 1 mmol) in CH_2Cl_2 (4 mL) cooled to $-25\text{ }^\circ\text{C}$ under a nitrogen atmosphere, the corresponding diene (5 mmol) and trifluoroacetic acid (0.06 mL, 0.3 mmol) were added dropwise. The mixture was stirred at $-25\text{ }^\circ\text{C}$ for 20 hours

and then was quenched with a saturated aqueous solution of NaHCO_3 (10 mL). The resulting mixture was allowed to warm to room temperature, after which the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organics were dried over MgSO_4 , and the solvent was removed under reduced pressure. Purification of the crude product **12** was effected by flash silica gel column chromatography using a 1:30 ethyl acetate/hexane mixture as the eluant.

General procedure B

To a solution of α' -hydroxy vinyl ketone **3** (0.208 g, 1 mmol) in CH_2Cl_2 (4 mL) cooled to $-78\text{ }^\circ\text{C}$ under a nitrogen atmosphere, the corresponding diene (5 mmol) and triflic acid (0.01 mL, 0.1 mmol) were added dropwise. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 hour and then was quenched with a saturated aqueous solution of NaHCO_3 (10 mL). The resulting mixture was allowed to warm to room temperature, after which the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The combined organics were dried over MgSO_4 , and the solvent was removed under reduced pressure. Purification of the crude product **12** was effected by flash silica gel column chromatography using a 1:30 ethyl acetate/hexane mixture as the eluant.

(1R)-2-endo-[(1R)-4-methylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (12a). The title compound was prepared according to general procedure A from isoprene (0.50 mL, 5 mmol). 0.252 g (91%); oil; $[\alpha]_{\text{D}}^{25} -13.0$ (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 1696 (CO); ^1H NMR (CDCl_3) δ 5.36 (m, 1H, $\text{HC}=\text{C}$), 3.00-2.95 (m, 1H, CH), 2.82 (s, 1H, OH), 2.24 (d, 1H, HCH, $J=13.2\text{Hz}$), 2.04-1.68 (m, 6H, HCH), 1.63 (s, 3H, CH_3), 1.46-0.93 (m, 6H, HCH), 1.08 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.81 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 218.0, 133.5, 119.3, 87.8, 52.6, 50.2, 45.0, 42.7, 40.7, 30.2, 29.6, 29.2, 26.7, 26.2, 23.4, 20.8, 20.3, 10.6.

(1R)-2-endo-[(1R)-3,4-dimethylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (12b). The title compound was prepared according to general procedure A or B from 2,3-dimethyl-1,3-butadiene (0.56 mL, 5 mmol). 0.218 g (75%) (procedure A), 0.285 g (98%) (procedure B); m.p. $59\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{25} -3.0$ (c 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 1696 (CO); ^1H NMR (CDCl_3) δ 3.32-2.95 (m, 1H, CH), 2.85 (s, 1H, OH), 2.25 (d, 1H, HCH, $J=13.2\text{Hz}$), 2.15-1.64 (m, 8H, HCH), 1.59 (s, 6H, 2 CH_3), 1.47-0.57 (m, 4H, CH), 1.09 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.82 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 218.0, 125.2, 124.0, 87.7, 52.7, 50.2, 45.0, 43.8, 40.7, 35.2, 31.3, 30.2, 26.8, 26.4, 20.8, 20.3, 19.0, 18.9, 10.6; Anal. calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2$ (290.49) C, 78.55; H, 10.43. Found: C, 79.01; H, 10.25.

(1R)-2-endo-[(1R, 2R, 4R)-bicyclo[2.2.1]hept-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (12c). The title compound was prepared according to general procedure B from

cyclopentadiene (0.40 mL, 5 mmol) in 1 h. 0.269 g (98%); m.p. 102-103 °C; $[\alpha]_D^{25} +71.0$ (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 1701 (CO); ¹H NMR (CDCl₃) δ 6.23 (dd, 1H, HC=C, J=2.9Hz, J'=5.5Hz), 5.69 (dd, 1H, HC=C, J=2.9Hz, J'=5.5Hz), 3.45 (m, 1H, CH), 3.14 (m, 1H, CH), 3.10 (s, 1H, OH), 2.92 (m, 1H, CH), 2.32 (d, 1H, HCH, J=13.6Hz), 2.07-1.97 (m, 1H, HCH), 1.88-1.70 (m, 3H, HCH), 1.46-1.09 (m, 5H, HCH), 1.07 (s, 3H, CH₃), 1.03-0.80 (m, 1H, HCH), 0.82 (s, 3H, CH₃), 0.81 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 216.6, 137.6, 130.8, 86.0, 53.3, 50.5, 49.7, 47.6, 46.8, 45.1, 43.3, 40.2, 30.6, 29.9, 27.2, 20.7, 20.1, 9.9; Anal. calcd for C₁₈H₂₆O₂ (274.44) C, 78.77; H, 9.57. Found: C, 78.59; H, 9.56.

(1R)-2-endo-[(1R, 2R, 4R)-bicyclo[2.2.1]oct-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (12d). The title compound was prepared according to general procedure B from 1,3-cyclohexadiene (0.48 mL, 5 mmol). 0.245 g (85%); m.p. 83-84 °C; $[\alpha]_D^{25} -10.0$ (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 1685 (CO); ¹H NMR (CDCl₃) δ 6.35 (t, 1H, HC=C, J=8.0Hz), 6.04 (t, 1H, HC=C, J=7.0Hz), 3.13 (m, 1H, CH), 3.10 (s, 1H, OH), 2.68-2.64 (m, 2H, CH), 2.15 (d, 1H, HCH, J=13.6Hz), 2.05-1.95 (m, 1H, HCH), 1.87-1.42 (m, 6H, HCH), 1.38-1.12 (m, 4H, HCH), 1.08 (s, 3H, CH₃), 1.00-0.80 (m, 1H, HCH), 0.81 (s, 6H, 2 CH₃); ¹³C NMR (CDCl₃) δ 216.6, 134.9, 130.3, 86.1, 53.3, 49.8, 45.5, 45.1, 40.5, 32.2, 31.2, 29.8, 29.5, 27.2, 26.6, 23.5, 20.7, 20.1, 10.0; Anal. calcd for C₁₉H₂₈O₂ (288.47) C, 79.10; H, 9.80. Found: C, 79.18; H, 9.76.

Diels-Alder reactions with enone 6-10

To a solution of the corresponding α'-hydroxy vinyl ketone (1 mmol) in CH₂Cl₂ (4 mL) cooled to -78 °C under a nitrogen atmosphere, the corresponding diene (5 mmol) and triflic acid (0.01 mL, 0.1 mmol) or (0.03 mL, 0.3 mmol) were added dropwise. The mixture was stirred at -78 °C for 0.5 to 3 hours and then was quenched with a saturated aqueous solution of NaHCO₃ (10 mL). The resulting mixture was allowed to warm to room temperature, after which the layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL). The combined organics were dried over MgSO₄, and the solvent was removed under reduced pressure. Purification of the crude product was effected by flash silica gel column chromatography using a 1:30 ethyl acetate/hexane mixture as the eluant.

(1R)-2-endo-[(1S, 6S)-4,6-dimethylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (13)

The title compound was prepared according to general procedure from **6** (0.222 g, 1 mmol), isoprene (0.50 mL, 5 mmol) and TfOH (0.1 mmol) in 0.5 h. 0.270 g (93%); oil; $[\alpha]_D^{25} +49.0$ (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3534 (OH), 1691 (CO); ¹H NMR (CDCl₃) δ 5.31 (m, 1H, HC=C), 2.93-2.80 (m, 1H, CH), 2.34-2.19 (m, 1H, CH), 2.32 (s, 1H, OH), 2.13-1.82 (m, 3H, HCH), 1.80-1.65 (m, 4H, HCH), 1.60 (s, 3H, CH₃), 1.41-0.88 (m, 4H, HCH), 1.09 (s, 3H, CH₃), 0.93 (s, 3H, CH₃), 0.85 (s, 3H, CH₃), 0.80 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 217.4, 133.6, 119.1, 87.8, 52.3, 50.7, 48.0, 44.8, 41.1, 38.9, 32.3, 30.8, 29.9, 26.4, 23.1, 20.9, 20.5, 20.2, 10.8.

(1R)-2-endo-[(1S, 6S)-3,4,6-trimethylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (14)

The title compound was prepared according to general procedure from **6** (0.222 g, 1 mmol), 2,3-dimethyl-1,3-butadiene (0.56 mL, 5 mmol) and TfOH (0.1 mmol) in 1 h. 0.289 g (95%); oil; $[\alpha]_D^{25} +54.0$ (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3519 (OH), 1611 (CO); ¹H NMR (CDCl₃) δ 2.97-2.84 (m, 1H, CH), 2.40 (s, 1H, OH), 2.29 (d, 1H, HCH, J=12.5Hz), 2.00-1.59 (m, 8H, CH), 1.55 (s, 6H, 2 CH₃), 1.39-0.88 (m, 4H, CH), 1.08 (s, 3H, CH₃), 0.92 (s, 3H, CH₃), 0.82 (d, 3H, CH₃, J=5.9Hz),

0.80 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 217.4, 125.2, 123.8, 87.7, 52.3, 50.6, 50.0, 44.9, 41.0, 40.6, 37.0, 32.6, 29.9, 26.5, 20.8, 20.5, 20.0, 18.7, 18.7, 10.9.

(1R)-2-endo-[(1R, 2R, 3S, 4S)-3-methylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (15)

The title compound was prepared according to general procedure from **6** (0.222 g, 1mmol), cyclopentadiene (0.40 mL, 5 mmol) and TFA (0.3 mmol) at -25 °C for 1 h. 0.274 g (95%); m.p. 63-64 °C; [α]_D²⁵ +101.0 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3508, (OH), 1685 (CO); ¹H NMR (CDCl₃) δ 6.32 (dd, 1H, HC=C, *J*=3.3Hz, *J'*=5.9Hz), 5.69 (dd, 1H, HC=C, *J*=2.9Hz, *J'*=5.9Hz), 3.10 (m, 1H, CH), 2.98 (m, 1H, CH), 2.95 (s, 1H, OH), 2.49 (m, 1H, CH), 2.33 (d, 1H, HCH, *J*=13.9Hz), 2.06-1.95 (m, 1H, HCH), 1.88-1.70 (m, 3H, HCH), 1.70-1.19 (m, 4H, HCH), 1.10 (d, 3H, CH₃, *J*=8.1Hz), 1.08 (s, 3H, CH₃), 1.04-0.83 (m, 1H, HCH), 0.89 (s, 3H, CH₃), 0.81 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 216.0, 138.3, 131.2, 85.9, 55.7, 53.4, 50.1, 49.8, 48.2, 46.8, 47.1, 45.0, 40.0, 38.0, 29.8, 27.0, 20.7, 20.6, 20.1, 10.0; Anal. calcd for C₁₉H₂₈O₂ (288.47) C, 79.10; H, 9.80. Found: C, 79.23; H, 9.59.

(1R)-2-endo-[(1R, 2R, 3S, 4S)-3-methylbicyclo[2.2.1]oct-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (16)

The title compound was prepared according to general procedure from **6** (0.222 g, 1 mmol), 1,3-cyclohexadiene (0.48 mL, 5 mmol) and TfOH (0.1 mmol) in 1.5 h. 0.272 g (90%); oil; [α]_D²⁵ +12.0 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 1685 (CO); ¹H NMR (CDCl₃) δ 6.46 (t, 1H, HC=C, *J*=8.1Hz), 5.87 (t, 1H, HC=C, *J*=7.7Hz), 2.95 (s, 1H, OH), 2.63 (m, 3H, HCH), 2.30-2.26 (m, 1H, HCH), 2.17 (d, 1H, HCH, *J*=13.9Hz), 2.10-1.63 (m, 4H, HCH), 1.57-0.80 (m, 6H, HCH), 1.07 (s, 3H, CH₃), 1.00 (d, 3H, CH₃, *J*=7.0Hz), 0.86 (s, 3H, CH₃), 0.80 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 216.1, 137.0, 129.0, 85.8, 54.5, 53.5, 49.9, 45.0, 40.4, 36.2, 34.2, 33.2, 29.9, 27.1, 26.7, 20.6, 20.1, 19.3, 17.7, 10.0.

(1R)-2-endo-[(1S, 6S)-4-methyl-6-phenylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (17)

The title compound was prepared according to general procedure from **7** (0.284 g, 1mmol), isoprene (0.50 mL, 5 mmol) and TfOH (0.3 mmol) in 2 h. 0.300 g (85%); oil; [α]_D²⁵ +12.6 (*c* 2.6, Cl₂CH₂); IR (neat, cm⁻¹) 3550 (OH), 1696 (CO); ¹H NMR (CDCl₃) δ 7.25-7.04 (m, 5H, arom.), 5.40 (m, 1H, HC=C), 3.52-3.41 (m, 1H, HCPH), 3.06-2.92 (m, 2H, HCCO), 2.60-2.20 (m, 2H, HCH), 1.90 (d, 1H, HCH, *J*=13.9Hz), 1.70 (s, 3H, CH₃), 1.76-1.36 (m, 3H, HCH), 1.19-0.52 (m, 5H, HCH), 0.88 (s, 3H, CH₃), 0.81 (s, 3H, CH₃), 0.67 (s, 3H, CH₃), 0.49 (s, 1H, OH); ¹³C NMR (CDCl₃) δ 216.4, 143.5, 133.2, 128.3, 128.3, 126.9, 119.3, 87.8, 51.9, 51.0, 47.8, 44.8, 44.2, 41.8, 36.2, 30.4, 30.2, 26.0, 23.3, 20.9, 20.6, 11.2.

(1R)-2-endo-[(1R, 2S, 3S, 4S)-3-phenylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (18)

The title compound was prepared according to general procedure from **7** (0.284 g, 1 mmol), cyclopentadiene (0.40 mL, 5 mmol) and TfOH (0.3 mmol) in 3 h. 0.305 g (87%); oil; [α]_D²⁵ +129.0 (*c* 1.0, Cl₂CH₂); IR (neat, cm⁻¹) 3514 (OH), 1680 (CO); ¹H NMR (CDCl₃) δ 7.31-7.16 (m, 5H, arom.), 6.48 (dd, 1H, HC=C, *J*=3.3Hz, *J'*=5.5Hz), 5.87 (dd, 1H, HC=C, *J*=2.9Hz, *J'*=5.5Hz), 3.65 (dd, 1H, HCPH, *J*=3.3Hz, *J'*=5.5Hz), 3.28 (m, 1H, CH), 3.02 (dd, 1H, HCCO, *J*=1.5Hz, *J'*=5.5Hz), 2.89 (m, 1H, CH), 2.85 (s, 1H, OH), 2.33 (d, 1H, HCH, *J*=13.9Hz), 2.06-1.68 (m, 3H, HCH), 1.66-1.54 (m, 2H, HCH), 1.25-0.63 (m, 3H, HCH), 1.06 (s, 3H, CH₃), 0.85 (s, 3H, CH₃), 0.75 (s, 3H,

CH₃); ¹³C NMR (CDCl₃) δ 215.1, 143.6, 138.7, 132.5, 128.3, 127.2, 126.1, 86.1, 53.9, 53.3, 51.0, 49.9, 48.8, 47.9, 44.9, 40.3, 29.4, 27.0, 20.6, 20.0, 10.1.

(1R)-2-endo-[(1S, 6S)-3,4 –dimethyl-6-p-methylphenylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (19)

The title compound was prepared according to general procedure from **8** (0.298 g, 1 mmol), 2,3-dimethyl-1,3-butadiene (0.56 mL, 5 mmol) and TfOH (0.3 mmol) in 1.5 h. 0.342 g (90%); oil; [α]_D²⁵ + 32.1 (*c* 1.45, Cl₂CH₂); IR (neat, cm⁻¹) 3549 (OH), 1701 (CO); ¹H NMR (CDCl₃) δ 7.18-7.01 (m, 4H, arom.), 3.49 (m, 1H, HCAr), 2.90 (m, 1H, HCCO), 2.50-1.91 (m, 3H, HCH), 2.22 (s, 3H, CH₃C₆H₄), 1.60 (s, 6H, 2 CH₃), 1.55-1.40 (m, 3H, HCH), 1.38-0.68 (m, 5H, HCH), 0.89 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.68 (s, 3H, CH₃), 0.56 (s, 1H, OH); ¹³C NMR (CDCl₃) δ 216.4, 140.4, 136.4, 128.9, 128.3, 128.1, 124.9, 124.0, 87.8, 51.9, 51.0, 48.8, 44.9, 44.2, 41.8, 37.9, 36.6, 30.3, 26.0, 21.0, 21.0, 20.6, 18.8, 18.7, 11.3.

(1R)-2-endo-[(1R, 2S, 3S, 4S)-3-p-methoxyphenylbicyclo[2.2.1]hept-5-en-2-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (20)

The title compound was prepared according to general procedure from **9** (0.314 g, 1 mmol), cyclopentadiene (0.40 mL, 5 mmol) and TfOH (0.3 mmol) in 1 h. 0.320 g (84%); oil; [α]_D²⁵ +123.5 (*c* 0.9, Cl₂CH₂); IR (neat, cm⁻¹) 3503 (OH), 1685 (CO); ¹H NMR (CDCl₃) δ 7.12 (d, 2H, J=8.8Hz, arom.), 6.80 (d, 2H, J=8.8Hz, arom.), 6.44 (dd, 1H, HC=C, J=2.2Hz, J'=6.6Hz), 5.82 (dd, 1H, HC=C, J=3.3Hz, J'=5.9Hz), 3.71 (s, 3H, CH₃O), 3.54 (dd, 1H, HCAr, J=2.9Hz, J'=5.5Hz), 3.22 (m, 1H, CH), 2.93 (m, 1H, HCCO), 2.81 (s, 1H, OH), 2.76 (m, 1H, CH), 2.26 (d, 1H, HCH, J=13.9Hz), 2.12-1.84 (m, 3H, HCH), 1.79-1.47 (m, 3H, HCH), 1.20-1.04 (m, 1H, HCH), 1.00 (s, 3H, CH₃), 0.85-0.59 (m, 1H, HCH), 0.78 (s, 3H, CH₃), 0.69 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 215.1, 157.9, 138.9, 132.5, 128.2, 113.8, 86.2, 55.2, 54.3, 53.5, 51.3, 50.0, 48.3, 48.0, 45.0, 40.3, 29.5, 27.1, 20.7, 20.1, 10.1.

(1R)-2-endo-[(1S, 6S)-3,4 –dimethyl-6-p-chlorophenylcyclohex-3-en-1-ylcarbonyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol. (21)

The title compound was prepared according to general procedure from **10** (0.319 g, 1mmol), 2,3-dimethyl-1,3-butadiene (0.56 mL, 5 mmol) and TfOH (0.1 mmol) in 1 h. 0.381 g (95%); oil; [α]_D²⁵ +28.4 (*c* 2.6, Cl₂CH₂); IR (neat, cm⁻¹) 3565 (OH), 1691 (CO); ¹H NMR (CDCl₃) δ 7.25-7.04 (m, 4H, arom.), 3.47 (m, 1H, HCAr, J=5.5Hz, J'=11.0Hz), 3.05 (m, 1H, HCCO, J=5.1Hz, J'=11.4Hz), 2.43-1.97 (m, 4H, HCH), 1.89 (d, 1H, HCH, J= 13.2Hz), 1.59 (s, 6H, 2 CH₃), 1.55-1.40 (m, 3H, HCH), 1.35-0.60 (m, 4H, HCH), 0.91 (s, 3H, CH₃), 0.82 (s, 3H, CH₃), 0.69 (s, 3H, CH₃); ¹³C NMR (CDCl₃) δ 215.8, 142.2, 132.3, 129.7, 128.2, 124.8, 124.0, 87.5, 52.0, 50.9, 48.5, 44.8, 43.7, 41.6, 38.2, 36.8, 30.0, 26.1, 20.9, 20.5, 18.8, 18.7, 11.1.

Detachment of the Auxiliary and Stereochemical Assignments

General procedure for the oxidation of Diels-Alder adducts

To a solution of the corresponding α' -hydroxy ketone **12** (1 mmol) in acetonitrile (12 mL) at 0 °C was added dropwise a solution of cerium ammonium nitrate (CAN) (1.64 g, 3 mmol) in water (6 mL) and the mixture was stirred at the same temperature for 10 minutes. Then

water (3 mL) was added and the mixture was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with a saturated aqueous solution of NaHCO_3 (2 x 10 mL), dried over MgSO_4 , filtered, and the solvent evaporated to afford the starting (R)-(+)-camphor in 90% yield. The basic aqueous layer was acidified by adding concentrate HCl and then extracted with CH_2Cl_2 (2 x 20 mL). The combined extracts were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The crude product was purified by column chromatography (eluant: ethyl acetate/hexane 1:30) to afford the corresponding carboxylic acid.

(1R)-4-methylcyclohex-3-enecarboxylic acid³. **22**

The title compound was prepared according to general procedure from **12a** (0.276 g, 1 mmol). 0.126 g (90%); m.p. 80 °C; $[\alpha]_{\text{D}}^{25} +71.2$ (*c* 2.22, Cl_2CH_2); IR (neat, cm^{-1}) 2986 (OH), 1706 (CO); ^1H NMR (CDCl_3) δ 11.78 (sb, 1H, OH), 5.35 (sb, 1H, $\text{HC}=\text{C}$), 2.58-2.44 (m, 1H, HCCO), 2.31-2.16 (m, 2H, HCH), 2.07-1.95 (m, 3H, HCH), 1.80-1.58 (m, 1H, HCH), 1.63 (s, 3H, CH_3); ^{13}C NMR (CDCl_3) δ 182.7, 133.7, 118.9, 39.1, 29.1, 27.4, 25.2, 23.5; Anal. calcd for $\text{C}_8\text{H}_{12}\text{O}_2$ (140.2) C, 68.53; H, 8.64. Found: C, 68.76; H, 8.53.

(1R, 2R, 4R)-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid⁴. **23**

The title compound was prepared according to general procedure from **12c** (0.274 g, 1 mmol). 0.124 g (90%); m.p. 34-35 °C; $[\alpha]_{\text{D}}^{25} +140.0$ (*c* 1.0, EtOH); IR (neat, cm^{-1}) 2986 (OH), 1706 (CO); ^1H NMR (CDCl_3) δ 6.19 (dd, 1H, $\text{HC}=\text{C}$, $J=2.9\text{Hz}$, $J'=5.7\text{Hz}$), 5.97 (dd, 1H, $\text{HC}=\text{C}$, $J=2.9\text{Hz}$, $J'=5.5\text{Hz}$), 3.21 (m, 1H, HCC), 3.02-2.89 (m, 1H, HCCO), 2.90 (m, 1H, HCC), 1.96-1.83 (m, 1H, HCH), 1.47-1.24 (m, 3H, HCH); ^{13}C NMR (CDCl_3) δ 181.0, 137.8, 132.3, 49.7, 45.7, 43.3, 42.6, 29.1; Anal. calcd for $\text{C}_8\text{H}_{10}\text{O}_2$ (138.18) C, 69.53; H, 7.31. Found: C, 69.49; H, 7.25.

(1R, 2S, 3S, 4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid. **24**

The title compound was prepared according to general procedure from **18** (0.350 g, 1 mmol). 0.188 g (88%); m.p. 41 °C; $[\alpha]_{\text{D}}^{25} +126.0$ (*c* 1.0, Cl_2CH_2); IR (neat, cm^{-1}) 2975 (OH), 1700 (CO); ^1H NMR (CDCl_3) δ 7.35-7.17 (m, 5H, arom.), 6.43 (dd, 1H, $\text{HC}=\text{C}$, $J=3.3\text{Hz}$, $J'=5.9\text{Hz}$), 6.18 (dd, 1H, $\text{HC}=\text{C}$, $J=2.6\text{Hz}$, $J'=5.5\text{Hz}$), 3.32 (m, 1H, HCC), 3.10-3.04 (m, 3H, HCCO , HCC, HCPH), 1.79 (d, 1H, HCC, $J=9.3\text{Hz}$), 1.60 (dd, 1H, HCH, $J=1.8\text{Hz}$, $J'=8.8\text{Hz}$); ^{13}C NMR (CDCl_3) δ 181.1, 143.8, 139.1, 134.5, 128.4, 127.3, 126.0, 52.5, 48.2, 47.3, 47.2, 46.2; Anal. calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$ (381.58) C,

³ $[\alpha]_{\text{D}}^{20} = +69.2$ (*c*=0.48, CHCl_3) Burke M. J.; Allan M. M.; Parvez M.; Keay B. A. *Tetrahedron Asymmetry* **2000**, 2733-2739.

⁴ Compound (-)-**23**: $[\alpha]_{\text{D}}^{20} = -139.0$ (*c*=1.38, EtOH) Choy W.; Reed L.A.; Masamune S. *J. Org. Chem.* **1983**, 48, 1137-1139.

78.47; H, 6.60. Found: C, 78.59; H, 6.65. Optical rotation for the corresponding benzyl ester: $[\alpha]_D^{25} +119.2$ (c 1.2, CH_2Cl_2)⁵.

General procedure for ketone synthesis

nBuLi (2.5 M in hexanes, 1.2 mL, 3 mmol) or MeLi (1.4 M in Et₂O, 2.14 mL, 3 mmol) was added to a solution of the corresponding α'-hydroxy ketone **12a** (0.276 g, 1 mmol) in THF (3 mL) at -78 °C and the solution was stirred at 0 °C for 1.5 h. The reaction mixture was quenched with a saturated aqueous solution of NH₄Cl (5 ml) and the resulting mixture was allowed to warm to room temperature, after which the layers were separated and the aqueous layer was extracted twice with CH₂Cl₂ (15 mL). The combined organic layers were dried over MgSO₄ and the solvent removed under reduced pressure. The residue thus obtained was subjected to oxidative scission by treatment with CAN, under the same conditions reported above. The resulting crude product **25** or **26** was purified by column chromatography (eluant: ethyl acetate/hexane 1:30).

Methyl-[(1R)-4-methylcyclohex-3-enyl]ketone. **25**

The title compound was prepared according to general procedure from **12a** and MeLi. 0.102 g (74%); b.p. 90 °C/15 mmHg; $[\alpha]_D^{25} +26.0$ (c 0.36, CH_2Cl_2); IR (neat, cm^{-1}) 1711 (CO); ¹H NMR (CDCl_3) δ 5.37 (m, 1H, HC=C), 2.53-2.43 (m, 1H, HCC), 2.19-1.83 (m, 4H, CH₂), 2.15 (s, 3H, CH₃CO), 1.67-1.48 (m, 2H, CH₂), 1.63 (s, 3H, CH₃); ¹³C NMR (CDCl_3) δ 211.7, 133.7, 119.2, 47.2, 29.5, 28.0, 27.1, 24.9, 23.4.

Butyl-[(1R)-4-methylcyclohex-3-enyl]ketone. **26**

The title compound was prepared according to general procedure from **12a** and nBuLi. 0.135 g (75%); b.p. 95 °C/18 mmHg; $[\alpha]_D^{25} +89.0$ (c 1.0, CH_2Cl_2); IR (neat, cm^{-1}) 1706 (CO); ¹H NMR (CDCl_3) δ 5.37-5.36 (t, 1H, HC=C, $J=2.2\text{Hz}$), 2.58-2.35 (m, 1H, HCCO), 2.25-1.84 (m, 6H, HCH), 1.62 (s, 3H, CH₃), 1.59-1.37 (m, 4H, HCH), 1.34-1.18 (m, 2H, HCH), 0.88 (t, 3H, CH₃, $J=7.3\text{Hz}$); ¹³C NMR (CDCl_3) δ 214.0, 133.6, 119.3, 46.5, 40.5, 29.6, 27.2, 25.9, 25.1, 23.5, 22.5, 14.0.

Determination of isomeric ratios

Diastereomeric and *endo:exo* ratios of the Diels-Alder adducts were determined by ¹³C NMR and/or by HPLC, using a Merck LiChrospher 100 RP-18 column (eluent acetonitrile/water 70:30, flow rate 1 mL/min).

The enantiomeric purity of carboxylic acids **22** and **23** was determined by HPLC analysis of their methyl esters using a Chiralcel OD-H and OB-H columns, respectively, and hexane as the eluant (flow 0.5 mL/min), and it was confirmed by comparison of the chromatograms with those corresponding to racemic products. The enantiomeric purity of ketone **25** was determined by HPLC

⁵ $[\alpha]_D^{20} = +121$ ($c=1.33$, CHCl_3) Evans D. A.; Chapman K. T.; Bisaha J. *J. Am. Chem. Soc.* **1988**, *110*, 1238-1256.

analysis, using a Chiralcel OB-H column and a mixture isopropanol/hexane 2:98 as the eluant (flow 0.5 mL/min), and it was confirmed by comparison of the chromatogram with that of the racemic ketone. The enantiomeric purity of ketone **26** was determined by HPLC analysis using a Chiralcel OD-R column and a mixture methanol/water 0.32/0.18 as the eluant (flow 0.5 mL/min) and it was confirmed by comparison of the chromatogram with that of the racemic ketone.

The mixture of regioisomers from the reaction of α' -hydroxy vinyl ketone **3** with isoprene was determined by ^{13}C NMR analysis of the crude product, and it was confirmed by ^{13}C NMR analysis of the isomeric carboxylic acids formed from the oxidative cleavage of the adducts with cerium ammonium nitrate (CAN).

6

6

12a

12a

Exo

Exo

13

13

14

14

18

18

21

21

24

24

	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Codes
1		6.184	7909	0.21	895	bb			Unknown	
2		6.874	3722540	98.14	317797	bb			Unknown	
3		8.033	62741	1.65	5087	bb			Unknown

	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Codes
1		7.803	62259	0.61	6023	bb			Unknown	
2		8.422	10169522	99.39	727853	bb			Unknown

	Area	Retention Time	% Area	Height	Int Type	Amount	Units	Peak Type	Codes
1	39971631	18.626	99.00	1006922	bb			Unknown	
2	405176	20.828	1.00	15894	bb			Unknown

	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Codes
1		9.841	29414	0.96	2801	bb			Unknown	
2		10.350	3031942	99.04	251997	bb			Unknown

	Name	Retention Time	Area	% Area	Height	Int Type	Amount	Units	Peak Type	Codes
1		70.573	603511	0.88	6427	bb			Unknown	I08
2		73.705	67741325	99.12	407341	bb			Unknown	