The First General Enantioselective Catalytic Diels-Alder Reaction with α,β-Unsaturated Ketones

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Supporting Information

General Information. Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Non-aqueous reagents were transferred under nitrogen via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 according to the method of Still.[2] Thin-layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by $KMnO_4$ stain.

^1H and ^{13}C NMR spectra were recorded on a Mercury 300 (300 MHz and 75 MHz) as noted, and are internally referenced to residual protio solvent signals. Data for ^1H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported in terms of chemical shift. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in terms of frequency of absorption (cm^{-1}). Mass spectra were obtained from the UC Irvine Mass Spectral facility. Gas liquid chromatography (GLC) was performed on Hewlett-Packard 6850 and 6890 Series gas chromatographs equipped with a split-mode capillary injection system and flame ionization detectors using a Bodman Chiraldex β-DM

[1]Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals;* 3rd ed., Pregamon Press, Oxford, 1988.
[2]Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978,** *43,* 2923.

(30 m x 0.25 mm) column. High performance liquid chromatography (HPLC) was performed on Hewlett-Packard 1100 Series chromatographs using either a Chiralcel OD-H column (25 cm) and OD guard (5 cm) or a Chiralcel AD column (25 cm) and AD guard (5 cm) as noted.

The α,β-unstaurated ketones: 3-penten-2-one,[3] 4-octen-3-one,[4] 6-methylhept-4-en-3-one,[5] 2-methylhex-4-en-3-one,[6] 6-methylhept-2-en-4-one;[7] dienes: buta-1,3-dienyl-carbamic acid benzyl ester,[8] 1-(methyleneallyl)-benzene;[9] and (*5S*)-*5*-benzyl-3-methyl-imidazolidin-4-one[10] were prepared as described in the literature.

(2*R*, 5*R*)-3-Methyl-2,5-diphenyl-imidazolidin-4-one (catalyst 3). A solution of (*R*)-phenylglycine methyl amide[11] (2.0 g, 12.2 mmol), benzaldehyde (990 μL, 9.7 mmol), and *p*-toluenesulfonic acid monohydrate (232 mg, 1.2 mmol) dissolved in 20 mL of methanol was heated to reflux for 16 hours. Concentration of the reaction mixture followed by silica gel chromatography (30-40% ethyl acetate in hexanes, linear gradient) afforded the title compound in 31% yield (750 mg, 3.0 mmol) and the more quickly eluting (2*S*, 5*R*) isomer in 58% yield (1.43g, 5.7 mmol). IR (film) 3478, 3324, 3086, 3063, 3031, 2958, 2917, 2863, 1959, 1890, 1814, 1698, 1603, 1477, 1456, 1428, 1400, 1343, 1281, 1204, 1107, 1069, 1027, 985.9, 935.2, 916.7, 868.6, 834.7, 732.9, 698.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 10H, ArH), 5.33 (s, 1H, NCHN), 4.66 (s, 1H, CHCO), 2.65 (s, 3H, CH_3), 2.46 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 139.0, 138.6, 129.8, 129.3, 128.9, 128.3, 128.0, 127.7, 77.3, 63.7, 28.0; HRMS

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[3] Chiu, P.; Wong, S. T. *Synth. Commun*. **1998**, *28*, 4513 - 4516.
[4] Chamberlin; Le Goff *Synth. Commun.* **1978**, *8*, 579-581.
[5] Piers,E.; Phillips-Johnson,W.M. *Can. J. Chem*. **1975**, *53*, 1281-1290.
[6] Bienvenue,A. *J. Am. Chem. Soc.* **1973**, *95*, 7345-7353.
[7] Bienvenue,A.; Dubois,J. E. *Bull. Soc. Chim. Fr.* **1969**, 391-396.
[8] Jessup, P. J.; Petty, C. B.; Roos, J.; Overman, L. E. *Org. Synth.* **1980**, *59*, 1-9.
[9] Marvel; Woolford *J. Org. Chem*. **1958**, *23*,1658.
[10] Polonski, T. *Org. Magn. Reson.* **1984**, *22*, 176-179.
[11] Naef, R.; Seebach, D. *Helv. Chim. Acta* **1985**, *85*, 135-143.

(CI) exact mass calc'd for ($C_{16}H_{16}N_2O$) requires *m/z* 252.1263, found *m/z* 252.1265. $[\alpha]_D$ = - 8.6 (c = 1.0, $CHCl_3$). The relative stereochemistry of catalyst **3** was confirmed by nOe studies.

(2*S*, 5*S*)-5-Benzyl-3-methyl-2-phenyl-imidazolidin-4-one (catalyst 4). A solution of (*S*)-phenylalanine methyl amide (5.0 g, 28.1 mmol), benzaldehyde (3.14 mL, 30.9 mmol), and *p*-toluenesulfonic acid monohydrate (535 mg, 2.8 mmol) dissolved in 40 mL of methanol was heated to 50 °C for 24 hours. Concentration of the reaction mixture followed by silica gel chromatography (3:1 ethyl acetate:hexanes) afforded the title compound in 32% yield (2.38 g, 8.9 mmol) and the more quickly eluting (2*R*, 5*S*) isomer in 58% yield (4.32 g, 16.2 mmol). IR (film) 3479, 3331, 3085, 3061, 3030, 2921, 2861, 2242, 1959, 1891, 1815, 1696, 1603, 1494, 1475, 1436, 1370, 1335, 1282, 1206, 1098, 1028, 1002, 920.0, 760.0, 743.2, 700.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 8H, ArH), 6.82 (m, 2H, ArH), 5.10 (m, 1H, NCHN), 3.84 (dd, *J* = 4.5, 4.5 Hz, 1H, CHCO), 3.22 (dd, *J* = 14.1, 5.7 Hz, 1H, one of CH_2Ph), 3.11 (dd, *J* = 14.1, 4.5 Hz, 1H, one of CH_2Ph), 2.52 (s, 3H, CH_3), 1.87 (br s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 138.8, 137.1, 130.1, 129.7, 129.2, 129.1, 127.4, 127.1, 60.7, 37.2, 27.5; HRMS (CI) exact mass calc'd for ($C_{17}H_{18}N_2O$) requires *m/z* 266.1419, found *m/z* 266.1421. $[\alpha]_D$ = - 101.8 (c = 1.0, $CHCl_3$). The enantiopurity of the catalyst was confirmed (>99% ee) by HPLC analysis (AD column, 10% isopropanol in hexanes, 1 mL/min, 254 nm); (2*S*, 5*S*) isomer t_r = 17.1 min, (2*R*, 5*R*) isomer t_r = 15.5 min. The relative stereochemistry of catalyst **4** was confirmed by nOe studies. It should be noted that longer reaction times, higher temperatures, or an excess of benzaldehyde can lead to significant racemization of the catalyst.[12]

(2*S*, 5*S*)-5-Benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (catalyst 5). In an inert atmosphere glovebox, samarium (III) trifluoromethanesulfonate (1.20 g, 2.0 mmol)

[12] For an insight into this racemization, see: Rios, A.; Crugeiras, J.; Amyes, T. L.; Richard, J. P. *J. Am. Chem. Soc.* **2001**, *123*, 7949-7950.

was added to a flame-dried 250 mL 3-neck round bottom flask fitted with a glass stopper, a septum, and a vacuum hose adapter followed by powdered 4Å molecular sieves (4.0 g). Following removal from the glove-box, the reaction was placed under nitrogen and (*S*)-phenylalanine methyl amide (8.91 g, 50 mmol) was added as a solution in 80 mL of tetrahydrofuran immediately followed by freshly distilled (77 ^{o}C, 14 mmHg, Vigreaux collumn) clear, colorless 5-methylfurfural (3.98 mL, 40 mmol). After stirring for 29 hours at room temperature, the reaction mixture was filtered through a plug of silica with dichloromethane, concentrated and purified by silica gel chromatography (1:1 ethyl acetate:hexanes) to afford the title compound as a clear, colorless oil in 46% yield (4.93 g, 18.2 mmol) and the faster eluting (2*R*, 5*S*) isomer as a pale yellow oil in 38% yield (4.10 g, 15.2 mmol). IR (film) 3482, 3325, 2922, 2862, 1695, 1563, 1495, 1477, 1453, 1402, 1326, 1267, 1218, 1098, 1021, 1006, 956.8, 938.9, 791.1, 734.4, 701.5 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H, PhH), 6.11 (m, 1H, C**H**CHCCH$_3$), 5.89 (m, 1H, CHC**H**CCH$_3$), 5.19 (s, 1H, NCHN), 3.79 (dd, *J* = 7.2, 4.5 Hz, 1H, CHCONMe), 3.26 (dd, *J* = 14.4, 4.5 Hz, 1H, one of CH_2Ph), 3.09 (dd, *J* = 14.1, 7.5 Hz, 1H, one of CH_2Ph), 2.64 (s, 3H, NCH_3), 2.21 (s, 3H, $ArCH_3$), 2.10 (br s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 153.5, 148.5, 137.3, 129.6, 128.9, 127.0, 111.2, 106.6, 71.3, 60.5, 37.8, 27.4, 14.0; HRMS (CI) exact mass calc'd for ($C_{16}H_{18}N_2O_2$) requires *m/z* 270.1368, found *m/z* 270.1368. $[\alpha]_D$ = – 156.5 (c = 1.0, $CHCl_3$). The enantiopurity of the catalyst was confirmed (>99% ee) by HPLC analysis (AD column, 5% isopropanol in hexanes, 1 mL/min, 254 nm); (2*S*, 5*S*) isomer t_r = 22.9 min, (2*R*, 5*R*) isomer t_r = 25.7 min. The relative stereochemistry of catalyst **5** was confirmed by nOe studies.

General Procedure (A: propenyl ketones): A 10-ml roundbottomed flask equipped with a magnetic stir bar and containing (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (**5**) (0.2 eq.) was either charged with H_2O (3-7*M*) or no solvent and cooled to 0 °C. To the resulting suspension was added the α,β-unsaturated ketone (1.0 eq.) followed by

70% aqueous perchloric acid (0.2 eq.). After stirring for 5 minutes, freshly distilled, pre-chilled cyclopentadiene (1.5 eq.) was added dropwise. The resulting biphasic mixture was stirred at constant temperature until complete consumption of the α,β-unsaturated ketone was observed as determined by TLC or GLC analysis. The reaction mixture was then diluted with the appropriate eluent, and then purified directly by silica gel chromatography.

General Procedure (B: ethyl vinyl ketone): (2*S*, 5*S*)-5-Benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (**5**) was taken up in absolute ethanol (1-2*M*) and cooled to the appropriate temperature (–20 to –40 °C) with stirring. Ethyl vinyl ketone (1.0 eq.) was added to that chilled solution, followed by dropwise addition of 70% aqueous perchloric acid down the side of the flask. After stirring for 5 minutes, the diene (1.25-1.5 eq.) was added and the resulting solution was stirred at constant temperature until complete consumption of the α,β-unsaturated ketone was observed as determined by TLC or GLC analysis. The reaction mixture was then diluted with the appropriate eluent, and then purified directly by silica gel chromatography.

1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hept-5-en-2-yl]-ethanone (Table 2, entry 1). Prepared according to general procedure A from 3-penten-2-one (68 μL, 0.70 mmol), cyclopentadiene (69 μL, 0.84 mmol), 70% aqueous perchloric acid (12.1 μL, 0.14 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (37.8 mg, 0.14 mmol) in water (175 μL) for 2.5 hours at 0 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a colorless oil in 85% yield (89 mg, 0.59 mmol); 14:1 *endo*:*exo*, *endo* 61% ee. IR (film) 3061, 2962, 2871, 1708, 1461, 1426, 1359, 1333, 1267, 1183, 1170, 114, 1095, 1055, 906.8, 797.8, 719.4, 654.5, 597.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.21 (dd, *J* = 6.0, 3.3 Hz, 1H, C**H**=CH), 5.90 (dd, *J* = 5.7, 2.7 Hz, 1H, CH=C**H**), 3.13 (m, 1H, C**H**CH=CH), 2.44 (m, 1H, C**H**CH=CH), 2.42 (dd, *J* = 4.8, 3.9 Hz, 1H, CHCO), 2.10 (s,

3H, CH_3CO), 1.86 (m, 1H, C**H**CH_3), 1.57 (m, 1H, C(H)**H**), 1.43 (m, 1H, C(H)**H**), 1.14 (d, *J* = 6.9 Hz, 3H, CHC**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 138.8, 132.6, 61.9, 49.3, 46.6, 46.5, 35.9, 29.5, 21.4; HRMS (CI) exact mass calc'd for ($C_{10}H_{14}O$) requires *m/z* 150.1045, found *m/z* 150.1041. $[\alpha]_D$ = + 70.4 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (120 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 6.9 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 6.3 min, *exo* isomers t_r = 5.7, 5.5 min.

1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one (Table 2, entry 2). Prepared according to general procedure A from 4-hexen-3-one (70 µL, 0.61 mmol), cyclopentadiene (75 µL, 0.91 mmol), 70% aqueous perchloric acid (10.5 µL, 0.12 mmol) and (2*S*, 5*S*)-5-Benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (30.7 mg, 0.12 mmol) in water (203 µL) for 22 hours at 0 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a colorless oil in 89% yield (88.7 mg, 0.54 mmol); 25:1 *endo*:*exo*, *endo* 90% ee. Product ratios were determined by GLC analysis (150 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 3.7 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 3.6 min, *exo* isomers t_r = 3.4, 3.5 min. H NMR, ^{13}C NMR, and IR data [1]were consistent with previously reported values.[13] $[\alpha]_D$ = + 101.7 (c = 1.0, $CHCl_3$).

Determination of the absolute stereochemistry of 1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one by chemical correlation to (1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde. (1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde[14] was treated with ethylmagnesium chloride followed by tetrapropylammonium perruthenate and 4-methylmorpholine *N*-oxide to afford 1-

[13] Zhu, Z.; Espenson, J. H.; *J. Am. Chem. Soc*. **1997**, *119*, 3507-3512.
[14] Ahrendt, K. A.; Borths, C. J.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2000**, *122*, 4243-4244.

[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one; $[\alpha]_D$ = + 105.5 (c = 1.0, $CHCl_3$). The product was identical in all respects to the title compound.

1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one (Table 2, entry 3). Prepared according to general procedure A from oct-2-en-4-one (89 μL, 0.60 mmol), cyclopentadiene (74 μL, 0.90 mmol), 70% aqueous perchloric acid (10.3 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32.4 mg, 0.12 mmol) neat for 34 hours at 0 °C. Purification by silica gel chromatography (19:1 hexanes:ethyl acetate) provided the title compound as a colorless oil in 83% yield (95.7 mg, 0.50 mmol); 22:1 *endo*:*exo*, *endo* 92% ee. IR (film) 3061, 2958, 2871, 1707, 1462, 1409, 1375, 1332, 1267, 1137, 1045, 904.4, 801.4, 715.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 5.4, 3.0 Hz, 1H, C**H**=CH), 5.87 (dd, *J* = 5.7, 2.7 Hz, 1H, CH=C**H**), 3.10 (br s, 1H, C**H**CH=CH), 2.43 (m, 1H, C**H**CH=CH), 2.39 (m, 3H, CHCO and CH_2CO), 1.86 (m, 1H, C**H**CH_3), 1.57-1.20 (m, 6H, $COCH_2C\mathbf{H_2}C\mathbf{H_2}$, and $CHC\mathbf{H_2}CH$), 1.12 (d, *J* = 6.9 Hz, 3H, $CHC\mathbf{H_3}$), 0.87 (dd, *J* = 7.5, 7.5 Hz, 3H, $CH_2C\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.3, 138.6, 132.6, 61.2, 49.3, 46.6, 41.7, 35.9, 26.2, 22.8, 21.4, 14.3; HRMS (CI) exact mass calc'd for ($C_{13}H_{20}O$) requires *m/z* 192.1514, found *m/z* 192.1509. $[\alpha]_D$ = + 89.3 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 6.1 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 5.9 min, *exo* isomers t_r = 5.5, 5.6 min.

Determination of the absolute stereochemistry of 1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one by correlation from (1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde. (1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde[15] was treated with *n*-butyllithium followed by tetrapropylammonium perruthenate and 4-methylmorpholine *N*-oxide to afford 1-[(1*R*, 2*R*, 3*S*,

4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one; $[\alpha]_D$ = + 87.4 (c = 1.0, $CHCl_3$). The product was identical in all respects to the title compound.

4-Methyl-1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one (Table 2, entry 4). Prepared according to general procedure A from 7-methyloct-2-en-4-one (82 µL, 0.50 mmol), cyclopentadiene (62 µL, 0.75 mmol), 70% aqueous perchloric acid (8.6 µL, 0.10 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (27 mg, 0.10 mmol) in water (167 µL) for 38 hours at 0 °C. Purification by silica gel chromatography (19:1 hexanes:ethyl acetate) provided the title compound as a colorless oil in 86% yield (89 mg, 0.43 mmol); 20:1 *endo*:*exo*, *endo* 92% ee. IR (film) 3061, 2957, 2870, 1708, 1462, 1367, 1332, 1269, 1141, 1107, 1064, 904.7, 799.8, 716.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.20 (dd, *J* = 5.7, 3.0 Hz, 1H, C**H**=CH), 5.87 (dd, *J* = 5.7, 2.7 Hz, 1H, CH=C**H**), 3.11 (m, 1H, C**H**CH=CH), 2.43 (m, 1H, C**H**CH=CH), 2.39 (m, 3H, CHCO and CH_2CO), 1.86 (m, 1H, C**H**CH_3), 1.58-1.37 (m, 5H, $COCH_2C\mathbf{H}_2C\mathbf{H}$, $CHC\mathbf{H}_2CH$), 1.13 (d, *J* = 6.9 Hz, 3H, $CH_2C\mathbf{H}_3$), 0.86 (d, *J* = 6.3 Hz, 6H, $CH(C\mathbf{H}_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 138.6, 132.6, 61.2, 49.3, 46.6, 40.0, 35.9, 32.9, 28.1, 22.8, 22.7, 21.4; HRMS (CI) exact mass calc'd for ($C_{14}H_{22}O$) requires *m/z* 206.1671, found *m/z* 206.1671. $[\alpha]_D$ = + 89.4 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 7.4 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 7.1 min, *exo* isomers t_r = 6.6, 6.8 min.

Determination of the absolute stereochemistry of 4-methyl-1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one by correlation with (1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde. (1*R*, 2*R*, 3*S*, 4*R*)-3-Methylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde[15] was treated with (3-methyl-butyl)-magnesiumbromide followed by tetrapropylammonium perruthenate and 4-methylmorpholine *N*-

oxide to afford 4-methyl-1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-methylbicyclo[2.2.1]hept-5-en-2-yl]-pentan-1-one ; $[\alpha]_D$ = + 81.2 (c = 1.0, $CHCl_3$). The product was identical in all respects to the title compound.

2-Methyl-1-[3-methylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one (Table 2, entry 5). Prepared according to general procedure A from 2-methylhex-4-en-3-one (66 μL, 0.50 mmol), cyclopentadiene (62 μL, 0.75 mmol), 70% aqueous perchloric acid (8.6 μL, 0.10 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (27 mg, 0.10 mmol) in water (125 μL) for 48 hours at 0 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a colorless oil in 24% yield (22 mg, 0.12 mmol) as well as 29 mg recovered 2-methyl-hex-4-en-3-one; 8:1 *endo*:*exo*, *endo* 0% ee. IR (film) 3062, 2965, 2872, 1707, 1573, 1464, 1381, 1364, 1333, 1264, 1224, 1177, 1129, 1102, 1043, 1009, 908.1, 801.7, 724.5. 694.3 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.23 (dd, *J* = 6.0, 3.3 Hz, 1H, C**H**=CH), 5.84 (dd, *J* = 6.0, 2.7 Hz, 1H, CH=C**H**), 3.10 (m, 1H, C**H**CH=CH), 2.73 (dq, 1H, C**H**$(CH_3)_2$), 2.61 (dd, *J* = 4.5, 3.3, 1H, C**H**CO), 2.46 (m, 1H, C**H**CH=CH), 1.87 (ddq, *J* = 6.6, 1.8, 1.8 Hz, 1H, C**H**CHCO), 1.59 (m, 1H, one of CH_2), 1.44 (m, 1H, one of CH_2), 1.13 (d, *J* = 7.2 Hz, 3H, C**H$_3$**CHCHCO), 1.07 (d, *J* = 7.2 Hz, 3H, one of (C**H$_3$**)$_2$CH), 1.03 (d, *J* = 6.9 Hz, 3H, one of (C**H$_3$**)$_2$CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.3, 138.6, 132.5, 59.2, 49.4, 46.9, 46.8, 39.7, 35.9, 21.3, 19.4, 18.7; HRMS (CI) exact mass calc'd for ($C_{12}H_{18}O$) requires *m/z* 178.1358, found *m/z* 178.1356. $[\alpha]_D$ = 0.0 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); *endo* isomers t_r = 3.8 min, 3.7 min, *exo* isomers t_r = 3.6, 3.5 min.

1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-Propylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one (Table 2, entry 6). Prepared according to general procedure A from oct-4-en-3-one (112 μL, 0.75 mmol),

cyclopentadiene (93 μL, 1.13 mmol), 70% aqueous perchloric acid (12.9 μL, 0.15 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (40.5 mg, 0.15 mmol) in water (150 μL) for 32 hours at 0 °C. Purification by silica gel chromatography (15:1 pentane:ether) provided the title compound as a colorless oil in 84% yield (120 mg, 0.62 mmol); 15:1 *endo*:*exo*, *endo* 92% ee. IR (film) 3060, 2961, 2872, 1710, 1459, 1413, 1377, 1333, 1216, 1106, 1017, 935.7, 904.3, 716.7 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.22 (dd, *J* = 6.0, 3.3 Hz, 1H, C**H**=CH), 5.84 (dd, *J* = 5.4, 2.7 Hz, 1H, CH=C**H**), 3.12 (m, 1H, C**H**CH=CH), 2.57 (m, 1H, C**H**CH=CH), 2.45 (m, 3H, CH_2CO and CHCO), 1.83 (m, 1H, C**H**(nPr)), 1.59-1.19 (br m, 6H, $CH_3C\mathbf{H}_2C\mathbf{H}_2$, and CHC$\mathbf{H}_2$CH), 1.02 (dd, *J* = 6.0, 6.0 Hz, 3H, CH_3), 0.89 (dd, *J* = 7.2, 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 138.8, 132.4, 59.5, 47.3, 47.2, 46.6, 41.4, 38.7, 35.1, 22.3, 14.7, 8.3; HRMS (CI) exact mass calc'd for ($C_{13}H_{20}O$) requires *m/z* 192.1514, found *m/z* 192.1512. $[\alpha]_D$ = + 91.5 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 6.0 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 5.6 min, *exo* isomers t_r = 5.1, 5.4 min.

1-[(1*R*, 2*R*, 3*S*, 4*R*)-3-Isopropylbicyclo[2.2.1]hept-5-en-2-yl]-propan-1-one (Table 2, entry 7). Prepared according to general procedure A from 6-methylhept-4-en-3-one (89 μL, 0.60 mmol), cyclopentadiene (99 μL, 1.2 mmol), 70% aqueous perchloric acid (10.3 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32 mg, 0.12 mmol) in water (120 μL) for 2.5 days at 0 °C. Then, an additional 1.2 mmol of cyclopentadiene was added and the mixture was allowed to stir for an additional 3.5 days at 0 °C. Purification by silica gel chromatography (18:1 pentane:ether) provided the title compound as a colorless oil in 78% yield (90 mg, 0.47 mmol); 6:1 *endo*:*exo*, *endo* 90% ee. For the purpose of characterization, the more quickly eluting *exo* diastereomer was removed by silica gel chromatography as above. IR (film) 3057, 2961, 2869, 1709, 1460, 1367, 1334, 1136, 1028, 904.2, 716.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.26 (dd, *J* = 5.7, 3.3 Hz, 1H, C**H**=CH), 5.79 (dd, *J* = 5.7, 2.7 Hz, 1H,

CH=C**H**), 3.14 (m, 1H, C**H**CH=CH), 2.77 (m, 1H, C**H**CH=CH), 2.63 (dd, *J* = 3.6, 3.6 Hz, 1H, CHCO), 2.49 (m, 2H, CH_2CO), 1.40 (m, 3H, C**H**$(CH_3)_2$ and CHC**H**$_2$CH), 1.05 (d, *J* = 7.5 Hz, 3H, one of CH(C**H**$_3)_2$), 0.99 (dd, *J* = 4.8, 4.8 Hz, 3H, CH_2C**H**$_3$), 0.84 (d, *J* = 7.5 Hz, 3H, one of CH(C**H**$_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6, 139.6, 131.9, 57.8, 49.1, 47.4, 47.2, 45.5, 35.2, 33.1, 22.7, 22.2, 8.5; HRMS (CI) exact mass calc'd for ($C_{13}H_{20}O$) requires *m/z* 192.1514, found *m/z* 192.1513. $[\alpha]_D$ = + 20.1 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (162 °C, 23 psi); (1*R*, 2*R*, 3*S*, 4*R*) *endo* isomer t_r = 4.4 min, and (1*S*, 2*S*, 3*R*, 4*S*) *endo* isomer t_r = 4.2 min, *exo* isomers t_r = 3.9, 4.1 min.

1-[(1*R*, 2*S*)-2-Methoxycyclohex-3-en-1-yl]-propan-1-one (Table 3, entry 1). Prepared according to general procedure B from ethyl vinyl ketone (59 μL, 0.59 mmol), 1-methoxybutadiene (75 μL, 0.74 mmol) added via syringe pump over 12 hours, 70% aqueous perchloric acid (10.2 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32 mg, 0.12 mmol) in ethanol (590 μL) for 3.5 days at –30 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a single diastereomer (as judged by GLC analysis) in 88% yield (88 mg, 0.52 mmol) and 92% ee. IR (film) 3027, 2975, 2937, 2879, 2821, 1715, 1452, 1432, 1375, 1211, 1191, 1129, 1108, 1084, 917.8, 889.2 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (m, 2H, CH=CH), 4.06 (m, 1H, C**H**OCH_3), 3.30 (s, 1H, OCH_3), 2.53 (m, 3H, CH_2CO and CHCO), 2.20 (m, 1H, one of C**H**$_2$CH=CH), 1.85 (m, 3H, C**H**$_2$CHCOEt and one of C(H)**H**CH=CH), 1.05 (dd, *J* = 7.2, 7.2 Hz, 3H, CH_2C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 133.2, 124.5, 73.0, 56.7, 51.8, 33.8, 25.6, 18.7, 8.1; HRMS (CI) exact mass calc'd for $[M - CH_3OH]^+$ ($C_9H_{12}O_0$) requires *m/z* 136.0888, found *m/z* 136.0889. $[\alpha]_D$ = + 16.7 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (100 °C, 23 psi); (1*R*, 2*S*) *endo* isomer t_r = 29.6 min, and (1*S*, 2*R*) *endo* isomer t_r = 32.6 min, *exo* isomers t_r = 19.1, 19.4 min.

Benzyl (1*S*, 6*R*)-6-propionylcyclohex-2-en-1-ylcarbamate (Table 3, entry 2). Concentrated (70% aqueous) perchloric acid (431 μL, 5.0 mmol) was added slowly to a stirring solution of ethyl vinyl ketone (2.49 mL, 25.0 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (1.35 g, 5.0 mmol) pre-chilled to –30 °C. Then, buta-1,3-dienyl-carbamic acid benzyl ester (4.47g, 31.3 mmol) was added dropwise over 15 minutes as a solution in 12.5 mL of absolute ethanol. After stirring for 3.5 days, the reaction was diluted with ether (150 mL), washed successively with 1N HCl (50 mL), water (50 mL) and brine (25 mL). The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford a pale brown oil. Purification by silica gel (8:1 hexanes:ethyl acetate) afforded the title compound as a single diastereomer (as judged by HPLC analysis) in 91% yield (5.17g, 22.7 mmol) and 98% ee. The combined aqueous extracts were treated with solid K_2CO_3, extracted with 3 x 50 mL portions of $CHCl_3$, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to afford a 91% recovery of (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (1.23 g, 4.55 mmol) after silica gel chromatography. IR (film) 3411, 3329, 3064, 3031, 2974, 2938, 2879, 2836, 1956, 1872, 1711, 1523, 1455, 1409, 1376, 1331, 1278, 1236, 1164, 1120, 1060, 1028, 988.9, 973.1, 775.6, 736.0, 697.9 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (m, 5H, ArH), 5.82 (m, 1H, C**H**=CH), 5.70 (m, 1H, CH=C**H**), 5.04 (m, 3H, CH_2Ph and NH), 4.63 (m, 1H, C**H**NH), 2.86 (ddd, *J* = 10.2, 3.9, 3.9 Hz, 1H, CHCO), 2.70 (dq, *J* = 18.0, 7.2 Hz, 1H, one of CH_2CO), 2.43 (dq, *J* = 17.7, 7.2 Hz, 1H, one of CH_2CO), 2.10-1.65 (m, 4H, C$\mathbf{H_2}$C$\mathbf{H_2}$), 1.00 (dd, *J* = 6.9, 6.9 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 155.9, 136.6, 130.1, 128.7, 128.2, 128.1, 126.9, 67.0, 50.4, 46.9, 34.8, 24.2, 20.7, 8.0; HRMS (CI) exact mass calc'd for ($C_{17}H_{21}NO_3$) requires *m/z* 287.1521, found *m/z* 287.1519. $[\alpha]_D$ = + 122.0 (c = 1.0, $CHCl_3$). Product ratios were determined by HPLC analysis (OD-H column, 3% ethanol in hexanes, 1 mL/min, 254 nm); (1*S*, 6*R*) *endo* isomer t_r = 12.5 min, and (1*R*, 6*S*) *endo* isomer t_r = 11.3 min, *exo* isomers t_r = 8.6, 9.2 min.

1-[(1*R*)-4-Phenylcyclohex-3-en-1-yl]-propan-1-one (Table 3, entry 3). Prepared according to general procedure B from ethyl vinyl ketone (48 μL, 0.48 mmol), 1-(methylene-allyl)-benzene (83 μL, 0.60 mmol), 70% aqueous perchloric acid (8.2 μL, 0.10 mmol), (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (26 mg, 0.10 mmol), and 14.4 mg of anhydrous calcium chloride (as dessicant) in ethanol (160 μL) for 4 days and 10 hours at –40 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a single regioisomer (as judged by GLC analysis) in 92% yield (94 mg, 0.44 mmol) and 90% ee. IR (film) 3030, 2975, 2935, 2838, 1975, 1879, 1809, 1709, 1598, 1495, 1444, 1410, 1376, 1343, 1213, 1126, 1061, 1020, 958.4, 918.1, 868.1, 806.5, 743.2, 694.8 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H, ArH), 6.12 (m, 1H, C=CH), 2.54 (m, 7H, CH_2CO, CHCO, C**H**$_2$CH, and allylic C**H**$_2$CH_2), 2.12 (m, 1H, C(H)**H**), 1.73 (m, 1H, C(H)**H**), 1.08 (dd, *J* = 7.2, 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.2, 141.9, 136.4, 128.5, 127.1, 125.2, 123.0, 46.4, 34.4, 28.2, 27.5, 25.7, 8.2; HRMS (CI) exact mass calc'd for ($C_{15}H_{18}O$) requires *m/z* 214.1358, found *m/z* 214.1356. $[\alpha]_D$ = + 67.2 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); (*R*) isomer t_r = 62.4 min, and (*S*) isomer t_r = 60.8 min, regioisomers t_r = 49.6, 50.2 min.

1-[(1*R* , 2*S*)-2,4-Dimethylcyclohex-3-en-1-yl]-propan-1-one (Table 3, entry 4). Prepared according to general procedure B from ethyl vinyl ketone (59 μL, 0.59 mmol), *trans*-2-methyl-1,3-pentadiene (94 μL, 0.89 mmol), 70% aqueous perchloric acid (10.2 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32 mg, 0.12 mmol) in ethanol (590 μL) for 4.5 days at –30 °C. Purification by silica gel chromatography (9:1 pentane:ether) provided the title compound as a single diastereomer (as judged by GLC analysis) in 90% yield (90 mg, 0.54 mmol) and 90% ee. IR (film) 2964, 2937, 2874, 2833, 1711, 1452, 1377, 1343, 1227, 1195, 1123, 1038, 984.2, 886.0, 841.6 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ

5.37 (m, 1H, C**H**=CCH_3), 2.60 (m, 2H, CHCO and C**H**CH_3), 2.50 (dq, *J* = 17.4, 7.5 Hz, 1H, C(H)**H**CO), 2.37 (dq, *J* = 17.4, 7.5 Hz, 1H, C(H)**H**CO), 1.94 (m, 2H, =CCH_2), 1.68 (m, 2H, C$\mathbf{H_2}$CH), 1.64 (s, 3H, C$\mathbf{H_3}$C=CH), 1.05 (dd, *J* = 7.5, 7.5 Hz, 3H, CH_2C$\mathbf{H_3}$), 0.76 (dd, *J* = 6.9, 6.9 Hz, 3H, C$\mathbf{H_3}$CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 133.7, 126.3, 50.5, 34.6, 31.7, 30.2, 23.8, 19.0, 16.8, 8.1. $[\alpha]_D$ = + 16.7 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (100 °C, 23 psi); (1*R*, 2*S*) *endo* isomer t_r = 21.3 min, and (1*S*, 2*R*) *endo* isomer t_r = 20.4 min, *exo* isomers t_r = 15.4, 16.6 min.

1-[(1*R*)-4-Methylcyclohex-3-en-1-yl]-propan-1-one (Table 3, entry 5). Prepared according to general procedure B from ethyl vinyl ketone (70 μL, 0.70 mmol), isoprene (140 μL, 1.40 mmol), 70% aqueous perchloric acid (12.1 μL, 0.14 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (38 mg, 0.14 mmol) neat for 3 days at –20 °C. Then, another portion of isoprene (100 μL, 1.00 mmol) was added and the solution was allowed to stir for an additional 3 days. Purification by silica gel chromatography (10:1 pentane:ether) provided the title compound as a single regioisomer (as judged by GLC analysis) in 79% yield (84 mg, 0.55 mmol) and 85% ee. IR (film) 2967, 2928, 2836, 1710, 1452, 1413, 1377, 1343, 1217, 1149, 1126, 952.6, 915.1, 871.9, 800.0 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.34 (m, 1H, C=CH), 2.46 (m, 3H, CH_2CO and CHCO), 2.09 (m, 2H, C$\mathbf{H_2}$CH=C(CH_3)), 1.94 (m, 2H, C$\mathbf{H_2}$C(CH_3)=CH), 1.86 (m, 1H, one of CH_2C$\mathbf{H_2}$CH), 1.54 (m, 1H, one of CH_2C$\mathbf{H_2}$CH), 0.99 (dd, *J* = 7.5, 7.5 Hz, 3H, CH_2C$\mathbf{H_3}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 133.8, 119.6, 46.6, 34.1, 29.9, 27.6, 25.4, 23.7, 8.1; HRMS (CI) exact mass calc'd for ($C_{10}H_{16}O$) requires *m/z* 152.1201, found *m/z* 152.1201. $[\alpha]_D$ = + 37.8 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (100 °C, 23 psi); (*R*) isomer t_r = 16.1 min, and (*S*) isomer t_r = 15.4 min.

Determination of the absolute stereochemistry of 1-[(1*R*)-4-methylcyclohex-3-en-1-yl]-propan-1-one by correlation from (1*R*)-4-methyl-3-cyclohexene-1-carboxaldehyde. (1*R*)-4-Methyl-3-cyclohexene-1-carboxaldehyde[15] was treated with ethylmagnesium bromide followed by tetrapropylammonium perruthenate and 4-methylmorpholine *N*-oxide to afford 1-[(1*R*)-4-methylcyclohex-3-en-1-yl]-propan-1-one; $[\alpha]_D$ = + 41.3 (c = 1.0, $CHCl_3$). The product was identical in all respects to the title compound.

(1*R*, 2*R*, 6*R*, 7*R*)-Tricyclo[5.2.1.0~2,6~]dec-8-en-3-one (Table 4, entry 1). Prepared according to general procedure A from 2-cyclopenten-1-one (50 µL, 0.60 mmol), cyclopentadiene (74 µL, 0.90 mmol), 70% aqueous perchloric acid (10.3 µL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32.4 mg, 0.12 mmol) in water (150 µL) for 12 hours at 0 °C. Purification by silica gel chromatography (5:1 pentane:ether) provided the title compound as a volatile white powder in 81% yield (72 mg, 0.49 mmol); 15:1 *endo*:*exo*, *endo* 48% ee. IR (film) 3058, 2964, 2941, 2868, 1730, 1475, 1402, 1341, 1318, 1225, 1172, 1129, 1090, 1040, 936.0, 902.3, 840.8, 804.2, 732.8 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.22 (dd, *J* = 5.7, 2.7 Hz, 1H, C**H**=CH), 6.11 (dd, *J* = 5.7, 3.0 Hz, 1H, CH=C**H**), 3.19 (m, 1H, C**H**CH=CH), 3.00 (m, 1H, C**H**CH=CH), 2.97 (m, 1H, C**H**CO), 2.85 (m, 1H, C(H)**H**CO), 2.02 (m, 4H, C**H**CH_2CH_2, C(H)**H**CO, and CHC$\mathbf{H_2}$CH), 1.48 (m, 2H, C$\mathbf{H_2}CH_2CO$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 222.6, 136.3, 135.0, 54.7, 52.6, 47.8, 47.4, 41.6, 40.9, 23.1; HRMS (CI) exact mass calc'd for ($C_{10}H_{12}O$) requires *m/z* 148.0888, found *m/z* 148.0887. $[\alpha]_D$ = + 122.3 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (140 °C, 23 psi); (1*R*, 2*R*, 6*R*, 7*R*) *endo* isomer t_r = 7.1 min, and (1*S*, 2*S*, 6*S*, 7*S*) *endo* isomer t_r = 6.7 min, *exo* isomers t_r = 6.1 min.

(1*R*, 2*R*, 7*R*, 8*R*)-Tricyclo[6.2.1.0~2,7~]undec-9-en-3-one (Table 4, entry 2). Prepared according to general procedure A from 2-cyclohexen-1-one (58 µL, 0.60 mmol),

cyclopentadiene (74 μL, 0.90 mmol), 70% aqueous perchloric acid (10.3 μL, 0.12 mmol), and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32.4 mg, 0.15 mmol) in water (150 μL) for 17 hours at 0 °C. Purification by silica gel chromatography (5:1 pentane:ether) provided the title compound as a colorless oil in 81% yield (79 mg, 0.49 mmol); 12:1 *endo*:*exo*, *endo* 63% ee. For the purposes of characterization, the *endo* isomer was separated from the *exo* isomer by silica gel chromatography. IR (film) 3061, 2961, 2935, 2867, 1701, 1570, 1453, 1406, 1358, 1337, 1315, 1236, 1172, 1115, 1018, 910.6, 823.8, 779.2, 733.6, 561.5 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.15 (dd, *J* = 5.7, 3.0 Hz, 1H, C**H**=CH), 5.99 (dd, *J* = 5.7, 3.0 Hz, 1H, CH=C**H**), 3.24 (m, 1H, C**H**CH=CH), 2.85 (m, 1H, C**H**CH=CH), 2.66 (m, 2H, CH(H)CO and CHCO), 2.30 (m, 1H, one of CH_2CO), 1.79 (m, 4H, CHC**H**CH_2, $COCH_2C\mathbf{H_2}$ and one of CHCHC$\mathbf{H_2}$), 1.42 (ddd, *J* = 8.4, 1.8, 1.8 Hz, 1H, one of CHC$\mathbf{H_2}$CH), 1.28 (m, 1H, one of CHC$\mathbf{H_2}$CH), 0.73 (m, 1H, one of CHCHC$\mathbf{H_2}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.7, 137.8, 135.1, 52.0, 48.7, 46.8, 45.5, 41.7, 39.7, 28.4, 22.2; HRMS (CI) exact mass calc'd for ($C_{11}H_{14}O$) requires *m/z* 162.1045, found *m/z* 162.1049. $[\alpha]_D$ = + 120.6 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (130 °C, 23 psi); (1*R*, 2*R*, 7*R*, 8*R*) *endo* isomer t_r = 13.4 min, and (1*S*, 2*S*, 7*S*, 8*S*) *endo* isomer t_r = 13.2 min, *exo* isomers t_r = 11.7, 12.3 min.

(1*R*, 2*R*, 8*R*, 9*R*)-Tricyclo[7.2.1.0~2,6~]dodec-10-en-3-one (Table 4, entry 3). Prepared according to general procedure A from 2-cyclohepten-1-one (67 μL, 0.60 mmol), cyclopentadiene (74 μL, 1.13 mmol), 70% aqueous perchloric acid (10.2 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32.4 mg, 0.12 mmol) in water (150 μL) for 28 hours at 0 °C. Purification by silica gel chromatography (5:1 pentane:ether) provided the title compound as a colorless oil in 85% yield (90 mg, 0.51 mmol); 18:1 *endo*:*exo*, *endo* 90% ee. IR (film) 2958, 2930, 2862, 1700, 1455, 1405, 1335, 1289, 1246, 1166, 1125, 1066, 949.6, 912.0, 860.4, 776.5, 722.9, 580.5, 554.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.39 (dd, *J* = 5.4, 2.7 Hz, 1H, C**H**=CH), 5.91 (dd, *J* = 5.4, 3.0 Hz, 1H, CH=C**H**), 3.17

(dd, *J* = 10.2, 3.3 Hz, 1H, CHCO), 2.99 (m, 1H, C**H**CH=CH), 2.70 (m, 1H, C**H**CH=CH), 2.44 (m, 2H, CH_2CO), 2.21 (m, 1H, C**H**CHCO), 1.96-1.28 (br m, 7H, CHC$\mathbf{H_2}$CH, $COCH_2C\mathbf{H_2}C\mathbf{H_2}$, and one of CHCHC$\mathbf{H_2}$), 0.74 (m, 1H, one of CHCHC$\mathbf{H_2}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.9, 137.7, 132.5, 58.6, 48.9, 48.1, 45.1, 43.0, 41.8, 30.8, 27.6, 23.2; HRMS (CI) exact mass calc'd for ($C_{12}H_{16}O$) requires *m/z* 176.1201, found *m/z* 176.1201. $[\alpha]_D$ = + 9.1 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (140 °C, 23 psi); (1*R*, 2*R*, 8*R*, 9*R*) *endo* isomer t_r = 13.2 min, and (1*S*, 2*S*, 8*S*, 9*S*) *endo* isomer t_r = 12.8 min, *exo* isomers t_r = 11.8, 15.0 min.

(1*R*, 2*R*, 9*R*, 10*R*)-Tricyclo[8.2.1.0~2,6~]tridec-11-en-3-one (Table 4, entry 4). Prepared according to general procedure A from 2-cycloocten-1-one (82 μL, 0.60 mmol), cyclopentadiene (74 μL, 1.13 mmol), 70% aqueous perchloric acid (10.2 μL, 0.12 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (32.4 mg, 0.12 mmol) in water (240 μL) for 72 hours at 0 °C. Purification by silica gel chromatography (19:1 pentane:ether) provided the title compound as a colorless oil in 83% yield (95 mg, 0.50 mmol); 6:1 *endo*:*exo*, *endo* 91% ee. IR (film) 3060, 2928, 2856, 1701. 1454, 1338, 1290, 1222, 1175, 1073, 1019, 895.9, 838.2, 716.9 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.49 (dd, *J* = 5.4, 2.7 Hz, 1H, C**H**=CH), 5.98 (dd, *J* = 5.4, 2.7 Hz, 1H, CH=C**H**), 3.29 (dd, *J* = 8.1, 3.3 Hz, 1H, CHCO), 2.90 (m, 1H, C**H**CH=CH), 2.72 (m, 1H, C**H**CH=CH), 2.49 (m, 2H, CH_2CO), 2.15 (m, 1H, C**H**CHCO), 1.82 (m, 2H, $COCH_2C\mathbf{H_2}$), 1.63 (m, 1H, one of $COCH_2CH_2C(H)\mathbf{H}$), 1.32 (m, 3H, $COCH_2CH_2C(H)\mathbf{H}$, and $CHCH_2C\mathbf{H_2}$), 1.08 (m, 1H, CHC(H)**H**), 0.78 (m, 1H, , CHC(H)**H**); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.9, 137.9, 132.0, 56.0, 50.9, 49.5, 48.3, 48.0, 47.4, 31.3, 30.9, 28.5, 23.6. $[\alpha]_D$ = – 69.9 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (150 °C, 23 psi); (1*R*, 2*R*, 9*R*, 10*R*) *endo* isomer t_r = 12.8 min, and (1*S*, 2*S*, 9*S*, 10*S*) *endo* isomer t_r = 12.4 min, *exo* isomers t_r = 11.2, 10.6 min.

(1*R*, 2*R*, 16*S*, 17*R*)-Tricyclo[15.2.1.0~2,16~]eicos-18-en-3-one (Table 4, entry 5). Prepared according to general procedure A from *trans*-2-cyclopentadecen-1-one (100 mg, 0.45 mmol), cyclopentadiene (56 µL, 0.67 mmol), 70% aqueous perchloric acid (7.8 µL, 0.09 mmol) and (2*S*, 5*S*)-5-benzyl-3-methyl-2-(5-methyl-furan-2-yl)-imidazolidin-4-one (24.3 mg, 0.09 mmol) in water (150 µL) for 72 hours at 0 °C. Purification by flash chromatography (9:1 ethyl acetate:hexanes) provided the title compound as a clear, colorless crystalline solid in 88% yield (114 mg, 0.50 mmol); 5:1 *endo*:*exo*, *endo* 93% ee. IR (film) 3052, 2922, 2854, 1698, 1456, 1368, 1331, 1225, 1126, 1084, 1016, 905.5, 884.9, 714.4 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (dd, *J* = 5.4, 2.7 Hz, 1H, C**H**=CH), 5.86 (dd, *J* = 5.4, 2.7 Hz, 1H, CH=C**H**), 3.09 (m, 1H, C**H**CH=CH), 2.61 (m, 2H, CHCO and one of CH_2CO), 2.52 (m, 1H, C**H**CH=CH), 2.41 (m, 1H, one of CH_2CO), 2.27 (m, 1H, C**H**CHCO), 1.81-1.24 (br m, 22H, $(CH_2)_{11}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.6, 138.5, 132.6, 59.6, 48.4, 47.2, 46.7, 41.5, 41.3, 36.3, 28.0, 27.9, 27.7, 27.2, 26.8, 26.8, 26.7, 26.7, 26.0, 23.6. $[\alpha]_D$ = + 22.2 (c = 1.0, $CHCl_3$). Product ratios were determined by GLC analysis (200 °C, 23 psi); (1*R*, 2*R*, 16*S*, 17*S*) *endo* isomer t_r = 20.1 min, and (1*S*, 2*S*, 16*R*, 17*R*) *endo* isomer t_r = 19.6 min, *exo* isomers t_r = 19.0, 18.6 min. The *trans* relative stereochemistry of C-16 and C-17 was confirmed by the presence of an nOe between the C-16 methine proton and the two C-19 protons.