Supporting Information-I

Direct Amino Acid-Catalyzed Cascade Biomimetic Reductive Alkylations: Application to the Asymmetric Synthesis of Hajos-Parrish Ketone Analogues

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General Methods: The $^1$H NMR and $^{13}$C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for $^1$H NMR and relative to the central CDCl$_3$ resonance ($\delta = 77.0$) for $^{13}$C NMR. In the $^{13}$C NMR spectra, the nature of the carbons (C, CH, CH$_2$ or CH$_3$) was determined by recording the DEPT-135 experiment, and is given in parentheses. The coupling constants $J$ are given in Hz. Column chromatography was performed using Acme’s silica gel (particle size 0.063-0.200 mm). High-resolution mass spectra were recorded on micromass ESI-TOF MS. GCMS mass spectrometry was performed on Shimadzu GCMS-QP2010 mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300 and Thermo Nicolet FT/IR-5700. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. Mass spectra were recorded on either VG7070H mass spectrometer using EI technique or Shimadzu-LCMS-2010 A mass spectrometer. The X-ray diffraction measurements were carried out at 298 K on an automated Enraf-Nonius MACH 3 diffractometer using graphite monochromated, Mo-Kα ($\lambda = 0.71073$ Å) radiation with CAD4 software or the X-ray intensity data were measured at 298 K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($\lambda = 0.71073$ Å). For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of $p$-anisaldehyde (23 mL), conc. H$_2$SO$_4$ (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

Because of solubility problem of 2-alkyl-cyclopentane-1,3-diones 7a-x in CDCl$_3$, we have used three drops of CD$_3$OD.

Due to the keto-enol and enol-enol tautomerism in 2-alkyl or 2-aryl-cyclopentane-1,3-dione compounds, $^{13}$C NMR shows some of carbons (2 $\times$ CH$_2$ and 2 $\times$ C=O) are poor resolution even after more than 2000 scans in the solvent system of CDCl$_3$ or CDCl$_3$ + CD$_3$OD (three drops).

Materials: All solvents and commercially available chemicals were used as received.

General Experimental Procedures for the Cascade Reactions:

Amino Acid-Catalyzed Cascade Olefination/Hydrogenation Reactions with Cyclopentane-1,3-Dione: In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde 2, 0.3 mmol of CH-acid 1 and 0.3 mmol of Hantzsch ester 3 was added 1.0 mL of solvent, and then the catalyst amino acid 4a (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Tables 1 to 3. The crude reaction mixture was directly loaded on silica gel column with or without aqueous work-up and pure cascade products 7 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

Amino Acid-Catalyzed Robinson Annulation Reaction: In ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 2-alkyl-cyclopentane-1,3-diones 7 and 0.9 mmol of methyl vinyl ketone 9 was added 1.0 mL of DMSO solvent, and then the catalyst proline 4a (0.09 mmol, 30 mol%) was added and the
reaction mixture was stirred at 25 °C for 6 days. The crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure products 11 and 12 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**Amino Acid-Catalyzed One-Pot Double Cascade Olefination/Hydrogenation/Robinson Annulation Reactions:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde 2, 0.3 mmol of CH-acid 1 and 0.3 mmol of Hantzsch ester 3 was added 1.0 mL of dichloromethane, and then the catalyst amino acid 4a (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Scheme 3. After evaporation of the solvent completely, to the crude reaction mixture added 0.9 mmol of vinyl ketone 9, 1.0 mL of DMSO solvent and 0.09 mmol of L-proline 4a and the reaction mixture was stirred at room temperature for the 6 days. The crude reaction mixture was worked up with aqueous NH₄Cl solution and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure one-pot products 11 and 12 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**General Procedure for the Direct Organocatalytic One-Pot Synthesis of 2-Alkyl-3-Methoxy-Cyclopent-2-enones 13:** In an ordinary glass vial equipped with a magnetic stirring bar, to 0.9 mmol of the aldehyde 2, 0.3 mmol of CH-acid 1 and 0.3 mmol of Hantzsch ester 3 was added 1.0 mL of dichloromethane, and then the catalyst amino acid 4a (0.015 mmol, 5 mol%) was added and the reaction mixture was stirred at 25 °C for the time indicated in Scheme 2. After evaporation of the solvent completely, to the crude reaction mixture added an excess ethereal solution of diazomethane and the reaction mixture was stirred at room temperature for the 0.5 h. After evaporation of the solvent and excess diazomethane completely in fume hood, the crude reaction mixture was directly loaded on silica gel column with or without aqueous work-up and pure one-pot products 13 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

**General Procedure for the Dehydration of 7a-Alkyl-3a-Hydroxy-Hexahydro-Indene-1,5-Diones 11:** A solution of alcohol compound 11 (0.2 mmol) and 1N HClO₄ (0.4 mmol) in DMSO (1.0 mL) stirred at 90 °C for 0.5 to 1 h. After cooling, the reaction mixture washed with water and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na₂SO₄), filtered and concentrated. Pure products 10 were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).

2,2’-Phenylmethane-bis-[1,3-cyclopentanedione] (6a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 186 °C; IR (Neat): ν_max 3376, 2921, 1659, 1547, 1411, 1239 and 1213 cm⁻¹; ¹H NMR (CDCl₃) δ 9.77 (2H, br s, 2 x O-H), 7.21-7.09 (5H, m) [Ar-H]; 5.33 (1H, s, PhCH), 2.58 (8H, s, 4 x CH₂); ¹³C NMR
(CDCl₃, DEPT-135) δ 200.1 (2 x C, C=O), 139.6 (C), 128.3 (2 x CH), 126.9 (2 x CH), 126.3 (CH), 118.5 (2 x C), 30.5 (4 x CH₂), 30.0 (CH); LCMS m/z 285.00 (M+H⁺), calcd for C₁₇H₁₆O₄H 285.1049; Anal. calcd for C₁₇H₁₆O₄: C, 71.82; H, 5.67. Found: C, 71.731; H, 5.652%.

2,2’-Dicyclopentane-1,3-dione-methyl-2-(3-methyl-but-2-enyloxy)-benzene (6g): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 140 °C; IR (Neat): νmax 2924, 2723, 1659, 1590, 1412, 1354, 1275, 1226, 1118, 1020 and 754 cm⁻¹; ¹H NMR (CDCl₃) δ 7.90 (2H, br s, 2 x OH), 7.26 (1H, d, J = 7.2 Hz), 7.13 (1H, t, J = 8.0 Hz), 6.85 (1H, t, J = 8.0 Hz), 6.77 (1H, d, J = 8.0 Hz) [Ar-H]; 5.42 (1H, t, J = 6.4 Hz, olefinic-H), 5.37 (1H, s, PhCH), 4.45 (2H, d, J = 6.8 Hz, OCH₂CH=CH₂), 2.53 (8H, br s, 4 x CH₂), 1.77 (3H, s, CH₃), 1.70 (3H, s, CH₃); ¹³C NMR (CDCl₃, DEPT-135) δ 199.4 (2 x C, C=O), 155.8 (C), 137.5 (C), 128.34 (CH), 128.2 (C, OCH₂CH=CH₂), 127.7 (CH), 120.3 (CH), 119.8 (CH), 111.6 (CH), 65.1 (CH₂, OCH₂CH=CH₂), 30.4 (4 x CH₂), 25.7 (CH), 25.6 (CH₃), 18.1 (CH₃); LCMS m/z 369.00 (M+H⁺), calcd for C₂₂H₂₄O₅H 369.1624; Anal. calcd for C₂₂H₂₄O₅: C, 71.72; H, 6.57. Found: C, 71.668; H, 6.575%.

2-Benzyl-cyclopentane-1,3-dione (7a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 180 °C; IR (Neat): νmax 2923, 1571, 1565, 1473, 1434, 1396, 1368, 1321 and 1257 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.26-7.20 (4H, m), 7.15-7.13 (1H, m) [Ar-H]; 3.46 (2H, s, PhCH₂), 2.46 (4H, s); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 140.0 (C), 128.3 (2 x CH), 128.1 (2 x CH), 125.6 (CH), 117.3 (C), 30.2 (2 x CH₂), 26.7 (CH₃); HRMS m/z 211.0728 (M + Na⁺), calcd for C₁₂H₁₀O₂Na 211.0735.

2-Naphthalen-1-ylmethyl-cyclopentane-1,3-dione (7b): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 205 °C; IR (Neat): νmax 2971, 1569, 1335, 1318, 1282 (CH), 126.4 (CH), 125.7 (CH), 125.4 (CH), 125.2 (CH), 125.1 (CH), 124.0 (CH), 116.0 (C), 30.1 (2 x CH₂), 24.0 (CH₃); HRMS m/z 261.0882 (M + Na⁺), calcd for C₁₆H₁₄O₂Na 261.0891.

2-Naphthalen-2-ylmethyl-cyclopentane-1,3-dione (7c): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 220 °C; IR (Neat): νmax 2923, 2854, 2658, 1573, 1430, 1376, 1260, 1178, 1034, 818 and 754 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.76-7.67 (4H, m), 7.51-7.45 (2H, m), 7.36 (2H, m) [Ar-H]; 3.63 (2H, s, ArCH₂), 2.50 (4H, s, 2 x CH₂); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 137.6 (C), 133.4 (C), 131.8 (C), 127.5 (CH), 127.3 (3 x CH), 126.1 (CH), 125.5 (CH), 117.1 (C), 30.2 (2 x CH₂), 26.8 (CH₃); HRMS m/z 261.0880 (M + Na⁺), calcd for C₁₆H₁₄O₂Na 261.0891.
2-(4-Hydroxy-benzyl)-cyclopentane-1,3-dione (7d): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 194 °C; IR (Neat): ν max 3243, 1578, 1433, 1366, 1258, 1237, 1174, 1028 and 820 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.07 (2H, d, J = 8.4 Hz), 6.69 (2H, d, J = 8.4 Hz) [Ar-H]; 3.36 (2H, s, ArCH₂); 2.46 (4H, s, 2 x CH₂); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 154.4 (C), 131.1 (C), 129.1 (2 x CH), 117.7 (C), 114.8 (2 x CH), 30.1 (2 x CH₂), 25.7 (CH₂); HRMS m/z 227.0688 (M + Na⁺), calcd for C₁₂H₁₂O₃Na 227.0684.

2-(3-Hydroxy-benzyl)-cyclopentane-1,3-dione (7e): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; IR (Neat): ν max 3406, 3152, 2924, 1664, 1375, 1262, 1240, 1161 and 692 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.05 (1H, t, J = 8.0 Hz), 6.74 (1H, d, J = 7.6 Hz), 6.71 (1H, br s), 6.62 (1H, dd, J = 8.0, 1.6 Hz) [Ar-H]; 3.38 (2H, s, ArCH₂); 2.46 (4H, s, 2 x CH₂); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 156.4 (C), 141.5 (C), 129.1 (CH), 119.8 (CH), 117.2 (C), 115.1 (CH), 112.7 (CH), 30.2 (2 x CH₂), 26.5 (CH₂); HRMS m/z 227.0679 (M + Na⁺), calcd for C₁₂H₁₂O₃Na 227.0684.

2-(2-Hydroxy-benzyl)-cyclopentane-1,3-dione (7f): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 156 °C; IR (Neat): ν max 3237, 2923, 1727, 1584, 1540, 1372, 1301, 1260, 1174, 1101 and 661 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.20 (1H, d, J = 7.2 Hz), 7.08 (1H, t, J = 7.2 Hz), 6.96 (2H, m) [Ar-H]; 5.59 (1H, t, J = 7.2 Hz, OCH₂CH=CH₂), 4.65 (2H, d, J = 7.2 Hz, OCH₂CH=CH₂), 3.45 (2H, s, ArCH₂), 2.45-2.39 (4H, m), 1.86 (3H, s, CH₃), 1.80 (3H, s, CH₃); ¹³C NMR [CDCl₃, DEPT-135] δ 204.4 (C, O=O), 184.2 (C), 154.6 (C), 141.5 (C), 131.4 (CH), 128.5 (C), 127.7 (CH), 122.5 (CH), 117.7 (CH), 117.5 (C), 112.5 (CH), 66.1 (CH₂), 33.7 (CH₂), 26.5 (CH₂), 25.9 (CH₃), 21.2 (CH₂), 18.2 (CH₃); HRMS m/z 295.1299 (M + Na⁺), calcd for C₁₇H₂₀O₃Na 295.1310.

2-[2-(3-Methyl-but-2-enyloxy)-benzyl]-cyclopentane-1,3-dione (7g): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 95 °C; IR (Neat): ν max 2924, 1578, 1433, 1366, 1258, 1237, 1174, 1028 and 820 cm⁻¹; ¹H NMR (CDCl₃) δ 9.22 (1H, s, O-H), 7.35 (1H, dd, J = 7.6, 1.6 Hz), 7.20 (1H, dt, J = 8.0, 1.6 Hz), 6.96 (2H, m) [Ar-H]; 5.59 (1H, t, J = 7.2 Hz, OCH₂CH=CH₂), 4.65 (2H, d, J = 7.2 Hz, OCH₂CH=CH₂), 3.45 (2H, s, ArCH₂), 2.45-2.39 (4H, m), 1.86 (3H, s, CH₃), 1.80 (3H, s, CH₃); ¹³C NMR [CDCl₃, DEPT-135] δ 204.4 (C, O=O), 184.2 (C), 154.6 (C), 141.5 (C), 131.4 (CH), 128.5 (C), 127.7 (CH), 122.5 (CH), 117.7 (CH), 117.5 (C), 112.5 (CH), 66.1 (CH₂), 33.7 (CH₂), 26.5 (CH₂), 25.9 (CH₃), 21.2 (CH₂), 18.2 (CH₃); HRMS m/z 295.1299 (M + Na⁺), calcd for C₁₇H₂₀O₃Na 295.1310.

2-(3-Nitro-benzyl)-cyclopentane-1,3-dione (7h): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 202 °C; IR (Neat): ν max 2922, 1620, 1559, 1523, 1427, 1354, 1295, 1259, 1164, 1084, 1027, 802 and
716 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 8.09 (1H, s), 8.00 (1H, d, J = 7.6 Hz), 7.62 (1H, d, J = 7.6 Hz), 7.40 (1H, t, J = 8.0 Hz) [Ar-H]; 3.56 (2H, s, ArCH₂); 13C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 148.1 (C), 142.3 (C), 135.0 (CH), 128.9 (CH), 123.2 (CH), 120.8 (CH), 115.9 (C), 30.3 (2 x CH₂), 26.5 (CH₂); HRMS m/z 256.0591, calcd for C₁₂H₁₁NO₄Na 256.0586.

2-(2-Nitro-benzyl)cyclopentane-1,3-dione (7i): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 190 °C; IR (Neat): νmax 2550, 1570, 1521, 1339, 1257, 1189, 1036, 844 and 727 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.86 (1H, d, J = 8.0 Hz), 7.48 (1H, t, J = 7.2 Hz), 7.31 (2H, m) [Ar-H]; 3.81 (2H, s, ArCH₂), 2.53 (4H, s, 2 x CH₂); 13C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 149.2 (C), 134.1 (C), 132.5 (CH), 130.8 (CH), 126.6 (CH), 124.0 (CH), 114.4 (C), 30.0 (2 x CH₂), 23.4 (CH₂); HRMS m/z 234.0755, calcd for C₁₂H₁₁NO₄H 234.0766.

2-(3-Phenyl-allyl)cyclopentane-1,3-dione (7j) and 2-(3-Phenyl-propyl)-cyclopentane-1,3-dione (7j’): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (Neat): νmax 2928, 1724, 1609, 1520, 1435, 1401, 1375, 1255, 1158, 827 and 751 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops), 2:1 ratio of O/H product 7j and completely reduced product 7j’, major product 7j] δ 7.30-7.17 (5H, m) [Ar-H]; 6.39 (1H, d, J = 16.0 Hz), 6.29 (1H, td, J = 15.6, 6.8 Hz) [PhCH=CHCH₂]; 3.04 (2H, d, J = 6.0 Hz), 2.48 (4H, s, 2 x CH₂); 13C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135, 2:1 ratio of O/H product 7j and completely reduced product 7j’, major product 7j] δ 137.5 (C), 130.1 (CH), 128.3 (2 x CH), 126.80 (CH), 126.76 (CH), 125.9 (2 x CH), 115.8 (C), 30.4 (2 x CH₂), 24.3 (CH₂); ¹H NMR [CDCl₃ + CD₃OD (three drops), 2:1 ratio of O/H product 7j and completely reduced product 7j’, minor product 7j’] δ 7.33-7.10 (5H, m) [Ar-H]; 2.59 (2H, t, J = 8.0 Hz), 2.43 (4H, s, 2 x CH₂), 2.19 (2H, t, J = 8.0 Hz), 1.74 (2H, quintet, J = 8.0 Hz); 13C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135, 2:1 ratio of O/H product 7j and completely reduced product 7j’, minor product 7j’] δ 142.5 (C), 128.4 (CH), 128.1 (2 x CH), 125.5 (2 x CH), 117.8 (C), 35.7 (CH₂), 30.4 (2 x CH₂), 29.4 (CH₂), 20.7 (CH₂); HRMS (Q-top) m/z 215.1016 and 217.1190, calcd for C₁₄H₁₄O₂H 215.1072 and C₁₄H₁₆O₂H 217.1229.

2-[3-(2-Nitro-phenyl)-allyl]-cyclopentane-1,3-dione (7k) and 2-[3-(2-Nitro-phenyl)-propyl]-cyclopentane-1,3-dione (7k’): Purified by column chromatography using EtOAc/hexane and isolated as a solid. IR (Neat): νmax 3326, 2927, 1624, 1524, 1344, 1255, 1176 and 750 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 7.85 (1H, d, J = 8.4 Hz), 7.57 (1H, d, J = 8.0 Hz), 7.50 (1H, t, J = 7.2 Hz), 7.32 (1H, t, J = 7.6 Hz) [Ar-H]; 6.83 (1H, d, J = 16.0 Hz), 6.28 (1H, td, J = 15.2, 6.4 Hz) [ArCH=CHCH₂]; 3.11 (2H, d, J = 6.4 Hz), 2.53 (4H, s, 2 x CH₂); 13C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135, 2:1 ratio of O/H product 7k and completely reduced product 7k’, major product 7k] δ 147.4 (C), 133.2 (C), 132.9 (CH), 132.8 (CH), 128.5 S-6
(CH), 127.4 (CH), 125.0 (CH), 124.2 (CH), 115.0 (C), 30.3 (2 x CH₂), 24.5 (CH₂); ¹H NMR [CDCl₃ + CD₃OD (three drops), 2:1 ratio of O/H product 7k and completely reduced product 7k', minor product 7k”] δ 7.85 (1H, d, J = 8.4 Hz), 7.50 (1H, t, J = 7.2 Hz), 7.38 (1H, d, J = 8.0 Hz), 7.32 (1H, t, J = 7.6 Hz) [Ar-H]; 2.84 (2H, t, J = 8.0 Hz), 2.48 (4H, s, 2 x CH₂), 2.23 (2H, t, J = 8.0 Hz), 1.76 (2H, quintet, J = 8.0 Hz); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135; 2:1 ratio of O/H product 7k and completely reduced product 7k’, minor product 7k”] δ 149.1 (C), 137.3 (C), 132.7 (CH), 131.7 (CH), 126.6 (CH), 124.3 (CH), 117.1 (C), 32.3 (CH₂), 30.3 (2 x CH₂), 28.5 (CH₂), 20.6 (CH₂); HRMS (Q-top) m/z 260.0845 and 262.1007, calcd for C₁₄H₁₃NO₄H 260.0923 and C₁₄H₁₅NO₄H 262.1079.

2-Ethyl-cyclopentane-1,3-dione (7l): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 166 °C; IR (Neat): νmax 2971, 2931, 1530, 1545, 1348, 1267 and 1108 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.46 (4H, s, 2 x CΗ₂), 2.14 (2H, q, J = 7.2 Hz, CH₂CH₃), 0.99 (3H, t, J = 7.6 Hz, CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 119.6 (C), 30.1 (2 x CH₂), 14.0 (CH₂), 12.3 (CH₃); HRMS m/z 149.0571 (M + Na⁺), calcd for C₇H₁₀O₂Na 149.0578.

2-Propyl-cyclopentane-1,3-dione (7m): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 174 °C; IR (Neat): νmax 2951, 2870, 1547, 1535, 1458, 1473, 1430, 1345, 1258, 1244, 1113 and 998 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.48 (4H, s, 2 x CΗ₂), 2.10 (2H, t, J = 7.2 Hz, CH₂CH₂CH₃), 1.42 (2H, sextet, J = 7.2 Hz, CH₂CH₂CH₂CH₃), 0.88 (3H, t, J = 7.2 Hz, CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.2 (C), 30.3 (2 x CH₂), 22.8 (CH₂), 22.1 (CH₃), 13.8 (CH₃); HRMS m/z 141.0922 (M+H⁺), calcd for C₈H₁₂O₂H 141.0915.

2-Butyl-cyclopentane-1,3-dione (7n): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 150 °C; IR (Neat): νmax 2930, 2856, 1547, 1530, 1427, 1344, 1279, 1257, 1206, 1119 and 998 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.48 (4H, s, 2 x CH₂), 2.13 (2H, t, J = 7.6 Hz, CH₂CH₂CH₂CH₃), 1.40-1.26 (4H, m, CH₂CH₂CH₂CH₂CH₃), 1.40-1.26 (4H, m, CH₂CH₂CH₂CH₃), 0.89 (3H, t, J = 7.2 Hz, CH₂CH₂CH₂CH₂CH₃), 1.40-1.26 (4H, m, CH₂CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.5 (C), 30.2 (2 x CH₂), 30.1 (CH₂), 22.6 (CH₃), 20.7 (CH₂), 13.8 (CH₃); HRMS m/z 155.1078 (M+H⁺), calcd for C₉H₁₄O₂H 155.1072.

2-Pentyl-cyclopentane-1,3-dione (7o): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 136 °C; IR (Neat): νmax 2929, 2861, 1531, 1456, 1428, 1342, 1262, 1194, 1122, 999 and 663 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.46 (4H, br s, 2 x CH₂), 2.11 (2H, t, J = 8.0 Hz, CH₂CH₂CH₂CH₂CH₃), 1.40 (2H, quintet, J = 7.6 Hz, CH₂CH₂CH₂CH₂CH₃), 1.33-1.24 (4H, m, CH₂CH₂CH₂CH₂CH₃), 0.87 (3H, t, J = 6.8 Hz, CH₂CH₂CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.5 (C), 31.7 (CH₃), 30.3 (2 x CH₂), 27.6 (CH₃), 22.4 (CH₂), 20.9 (CH₂), 13.9 (CH₃); HRMS m/z 169.1224 (M + H⁺), calcd for C₉H₁₄O₂H 169.1228.
2-Hexyl-cyclopentane-1,3-dione (7p): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 240 °C; IR (Neat): νmax 2923, 2852, 1531, 1454, 1427, 1348, 1285, 1254, 1123, 1001 and 664 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.48 (4H, s, 2 × CH₂(CH₃)), 2.12 (2H, t, J = 7.2 Hz, CH₂CH(CH₃)CH₂CH₂CH₃), 1.38 (2H, quintet, J = 7.6 Hz, CH₂CH₂CH(CH₃)CH₂CH₃), 1.33-1.20 (6H, m, CH₂CH₂CH(CH₂CH₂)₂), 0.86 (3H, t, J = 6.8 Hz, CH₂CH₂CH(CH₂CH₂)₂); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.4 (C), 31.6 (CH₂), 30.4 (2 × CH₂), 29.2 (CH₂), 27.9 (CH₂), 22.5 (CH₂), 20.9 (CH₂), 13.9 (CH₃); LRMS m/z 183.00 (M + H⁺), calcd for C₁₁H₁₈O₂H 183.1307; Anal. calcd for C₁₁H₁₈O₂ (182.1307): C, 72.49; H, 9.95. Found: C, 72.584; H, 9.966%.

2-Heptyl-cyclopentane-1,3-dione (7q): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 128 °C; IR (Neat): νmax 2927, 2852, 1532, 1456, 1426, 1344, 1276, 1253, 1123 and 998 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.46 (4H, s, 2 × CH₂), 2.11 (2H, t, J = 8.0 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.39 (2H, quintet, J = 6.8 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.26 (8H, br s, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.87 (3H, t, J = 6.8 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.3 (C), 31.7 (CH₂), 30.2 (2 × CH₂), 29.4 (CH₂), 29.0 (CH₂), 27.9 (CH₂), 22.5 (CH₂), 20.8 (CH₂), 13.8 (CH₃); HRMS m/z 197.1543 (M + H⁺), calcd for C₁₂H₂₀O₂H 197.1541.

2-Octyl-cyclopentane-1,3-dione (7r): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 130 °C; IR (Neat): νmax 2918, 2850, 1532, 1462, 1428, 1347, 1290, 1261, 1124, 999 and 664 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.46 (4H, s, 2 × CH₂), 2.11 (2H, t, J = 7.2 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.39 (2H, quintet, J = 6.8 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.26 (10H, br s, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.87 (3H, t, J = 6.8 Hz, CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 118.4 (C), 31.8 (CH₂), 30.4 (2 × CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 27.9 (CH₂), 22.5 (CH₂), 20.9 (CH₂), 13.9 (CH₃); HRMS m/z 211.1697 (M + H⁺), calcd for C₁₃H₂₂O₂H 211.1698.

2-Isobutyl-cyclopentane-1,3-dione (7s): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 190 °C; IR (Neat): νmax 2929, 2496, 1552, 1427, 1350, 1313, 1258, 1124 and 998 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.48 (4H, s, 2 × CH₂), 2.00 (2H, d, J = 7.2 Hz, CH₂CH(Me₂)), 1.80 (1H, m, J = 6.8 Hz, CH₂CH(Me₂)), 0.85 [6H, d, J = 6.4 Hz, CH₂CH(CH₃)₂]; ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 117.4 (C), 30.1 (2 × CH₂), 29.7 (CH₂), 27.2 (CH), 22.2 (2 × CH₂); LRMS m/z 155.00 (M + H⁺), calcd for C₈H₁₀O₂H 155.0994; Anal. calcd for C₈H₁₀O₂ (154.0994): C, 70.10; H, 9.15. Found: C, 70.162; H, 9.180%.

2-(3-Methyl-butyl)-cyclopentane-1,3-dione (7t): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 138 °C; IR (Neat): νmax 2924, 2598, 1598, 1555, 1436, 1364, 1289, 1254 and 1128 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.47 (4H,
s, 2 x CH$_2$), 2.12 (2H, t, J = 8.0 Hz, CH$_2$CH$_2$CHMe$_2$), 1.51 (1H, m, J = 6.4 Hz, CH$_2$CH$_2$CHMe$_2$), 1.28 (2H, td, J = 12.4, 7.2 Hz, CH$_2$CH$_2$CHMe$_2$), 0.89 (6H, d, J = 6.4 Hz, CH$_2$CH$_2$CHMe$_2$); $^1$C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135] δ 118.5 (C), 36.7 (CH$_2$), 30.2 (2 x CH$_3$), 27.9 (CH), 22.2 (2 x CH$_3$), 18.8 (CH$_3$); LRMS m/z 169.05 (M + H$^+$), calcd for C$_{10}$H$_{16}$O$_2$H 169.11; Anal. calcd for C$_{10}$H$_{16}$O$_2$ (168.1150): C, 71.39; H, 9.59. Found: C, 71.392; H, 9.578%.

$^{(-)(3R)}$-(3,7-Dimethyl-oct-6-enyl)-cyclopentane-1,3-dione (7u): Purified by column chromatography using EtOAc/hexane and isolated as a solid. [$\alpha$]$_D^{25}$ = $-5.029^\circ$ (c = 1.075 g/100 mL, CHCl$_3$, 90%); Mp 70 ºC; IR (Neat): $\nu_{\text{max}}$ 2922, 1566, 1473, 1368, 1289 and 1256 cm$^{-1}$; $^1$H NMR [CDCl$_3$] δ 5.08 (1H, d, J = 6.8 Hz), 2.56 (4H, s, 2 x CH$_2$), 2.30-2.10 (2H, m), 2.08-1.80 (2H, m), 1.67 (3H, s, CH$_3$), 1.59 (3H, s, CH$_3$), 1.50-1.30 (3H, m), 1.30-1.20 (1H, m), 1.19-1.10 (1H, m), 0.89 (3H, d, J = 6.4 Hz, CH$_3$); $^1$C NMR [CDCl$_3$, DEPT-135] δ 198.5 (C, C=O), 130.9 (C), 125.0 (CH), 118.7 (C), 36.9 (CH$_2$), 35.0 (CH$_2$), 32.6 (CH), 30.5 (single sharp peak, 2 x CH$_2$), 25.7 (CH$_3$), 25.5 (CH$_2$), 19.3 (CH$_3$), 18.7 (CH$_2$), 17.6 (CH$_3$); LRMS m/z 237.10 (M + H$^+$), calcd for C$_{15}$H$_{24}$O$_2$H 237.18; Anal. calcd for C$_{15}$H$_{24}$O$_2$ (236.1776): C, 76.23; H, 10.24. Found: C, 76.217; H, 10.242%.$^1$H NMR [CDCl$_3$ + CD$_3$OD (three drops)] δ 5.09 (1H, d, J = 6.8 Hz), 2.47 (4H, s, 2 x CH$_2$), 2.20-2.05 (2H, m), 2.05-1.85 (2H, m), 1.67 (3H, s, CH$_3$), 1.59 (3H, s, CH$_3$), 1.50-1.30 (3H, m), 1.30-1.20 (1H, m), 1.19-1.10 (1H, m), 0.90 (3H, d, J = 6.4 Hz, CH$_3$); $^1$C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135] δ 130.8 (C), 125.0 (CH), 118.6 (C), 36.9 (CH$_2$), 34.8 (CH$_2$), 32.4 (CH), 30.3 (broad peak, poor resolution, 2 x CH$_2$), 25.6 (CH$_3$), 25.4 (CH$_2$), 19.2 (CH$_3$), 18.6 (CH$_2$), 17.5 (CH$_3$).

$^{(+)(3S)}$-(3,7-Dimethyl-oct-6-enyl)-cyclopentane-1,3-dione (7v): Purified by column chromatography using EtOAc/hexane and isolated as a solid. [$\alpha$]$_D^{25}$ = +7.463º (c = 0.55 g/100 mL, CHCl$_3$, 96%); Mp 70 ºC; IR (Neat): $\nu_{\text{max}}$ 2920, 1622, 1566, 1473, 1368, 1255, 1195, 1127, 904, 826 and 672 cm$^{-1}$; $^1$H NMR [CDCl$_3$] δ 5.08 (1H, d, J = 6.0 Hz), 2.56 (4H, s, 2 x CH$_2$), 2.30-2.10 (2H, m), 2.10-1.80 (2H, m), 1.66 (3H, s, CH$_3$), 1.58 (3H, s, CH$_3$), 1.50-1.30 (3H, m), 1.30-1.20 (1H, m), 1.20-1.05 (1H, m), 0.90 (3H, d, J = 6.0 Hz, CH$_3$); $^1$C NMR [CDCl$_3$, DEPT-135] δ 198.5 (C, C=O), 130.9 (C), 125.0 (CH), 118.7 (C), 36.9 (CH$_2$), 35.0 (CH$_2$), 32.5 (CH), 30.5 (2 x CH$_2$), 25.7 (CH$_3$), 25.5 (CH$_2$), 19.3 (CH$_3$), 18.7 (CH$_2$), 17.6 (CH$_3$); LRMS m/z 237.10 (M + H$^+$), calcd for C$_{15}$H$_{24}$O$_2$H 237.18; Anal. calcd for C$_{15}$H$_{24}$O$_2$ (236.1776): C, 76.23; H, 10.24. Found: C, 76.240; H, 10.243%.

2-Isopropyl-cyclopentane-1,3-dione (7w): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 216 ºC; IR (Neat): $\nu_{\text{max}}$ 2970, 2927, 2522, 1684, 1549, 1431, 1364, 1340, 1279 and 1120 cm$^{-1}$; $^1$H NMR [CDCl$_3$ + CD$_3$OD (three drops)] δ 2.74 (1H, heptet, J = 7.2 Hz, CHMe$_2$), 2.46 (4H, s, 2 x CH$_2$), 1.14 (6H, d, J = 7.2 Hz, 2 x CH$_3$, CHMe$_2$); $^1$C NMR [CDCl$_3$ + CD$_3$OD (three drops), DEPT-135] δ 122.9 (C), 30.3 (2 x CH$_2$), 22.6 (CH, CHMe$_2$), 20.0 (2 x CH$_3$, CHMe$_2$); LRMS m/z 141.05 (M + H$^+$), calcd for C$_{8}$H$_{12}$O$_{2}$H 141.08; Anal. calcd for C$_{8}$H$_{12}$O$_{2}$ (140.0837): C, 68.54; H, 8.63. Found: C, 68.578; H, 8.685%.
2-Cyclohexyl-cyclopentane-1,3-dione (7x): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 230 °C; IR (Neat): νmax 2930, 2854, 1552, 1440, 1382, 1350, 1282, 1255, 1140, 1096 and 654 cm⁻¹; ¹H NMR [CDCl₃ + CD₃OD (three drops)] δ 2.43 (4H, s, 2 x CH₂), 2.38-2.35 (1H, m), 1.80-1.67 (5H, m), 1.50 (2H, m), 1.26 (3H, m); ¹³C NMR [CDCl₃ + CD₃OD (three drops), DEPT-135] δ 122.3 (C), 32.8 (CH), 30.5 (2 x CH₂), 29.7 (2 x CH₃), 26.7 (2 x CH₂), 25.9 (CH₃); LRMS m/z 181.10 (M + H⁺), calcd for C₁₁H₁₆O₂H 181.1150; Anal. calcd for C₁₁H₁₆O₂ (180.1150): C, 73.30; H, 8.95. Found: C, 73.365; H, 8.919%.

(+)-7a-Benzyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/i-PrOH = 70:30, flow rate 0.5 mL/min, λ = 254 nm), tₐ = 61.6 min (major), tᵣ = 75.2 min (minor). [α]D²⁵ = +241.3° (c = 0.80 g/100 mL, CHCl₃, 90.6% ee); Mp 154 °C; IR (Neat): νmax 2925, 1729, 1664, 1453, 1250, 1077, 754 and 706 cm⁻¹; ¹H NMR (CDCl₃) δ 7.28 (3H, m), 7.08 (2H, m) [Ar-H]; 6.06 (1H, s, olefinic-H), 3.06 (2H, AB q, J = 12.8 Hz), 2.60-2.40 (3H, m), 2.30-2.22 (3H, m), 2.10-2.01 (1H, m), 1.84 (1H, dt, J = 13.6, 6.0 Hz); ¹³C NMR (CDCl₃, DEPT-135) δ 217.5 (C, C=O), 198.0 (C, C=O), 169.2 (C), 135.5 (C), 129.6 (2 x CH), 128.6 (2 x CH), 127.5 (CH), 125.1 (CH), 54.1 (C), 42.4 (CH₂), 36.9 (CH₂), 32.8 (CH₂), 29.2 (CH₃), 28.1 (CH₂); LRMS m/z 241.00 (M + H⁺), calcd for C₁₆H₁₆O₂H 241.1150; Anal. calcd for C₁₆H₁₆O₂ (240.1150): C, 79.97; H, 6.71. Found: C, 79.924; H, 6.718%.

(−)-7a-Benzyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/i-PrOH = 70:30, flow rate 0.5 mL/min, λ = 254 nm), tᵣ = 61.6 min (major), tₐ = 75.2 min (minor). [α]D²⁵ = −293.6° (c = 0.960 g/100 mL, CHCl₃, 90.2% ee).

(+)-7a-Ethyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10l): Purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/i-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm), tₐ = 62.0 min (minor), tᵣ = 89.0 min (major). [α]D²⁵ = +125.8° (c = 0.16 g/100 mL, CHCl₃, 90% ee); IR (Neat): νmax 2973, 2953, 1732, 1658, 1651, 1465, 1364, 1217, 1147 and 1086 cm⁻¹; ¹H NMR (CDCl₃) δ 5.98 (1H, s, olefinic-H), 3.10-2.93 (1H, m), 2.85-2.67 (2H, m), 2.47-2.38 (2H, m), 2.27 (1H, ddd, J = 14.0, 4.8, 2.4 Hz), 1.79-1.70 (4H, m), 0.98 (3H, t, J = 7.2 Hz, CH₃(2)); ¹³C NMR (CDCl₃, DEPT-135) δ 215.8 (C, C=O), 198.1 (C, C=O), 170.1 (C), 124.1 (CH), 52.6 (C), 35.8 (CH₂), 32.6 (CH₂), 27.1 (CH₂), 26.9 (CH₂), 25.8 (CH₂), 8.9 (CH₃); LRMS m/z 179.00 (M + H⁺), calcd for C₁₆H₁₄O₂H 179.0994; Anal. calcd for C₁₆H₁₄O₂ (178.0994): C, 74.13; H, 7.92. Found: C, 74.195; H, 7.928%.

(+)-7a-Propyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10m): Purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/i-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm), tᵣ = 62.0 min (minor), tₐ = 89.0 min (major). [α]D²⁵ = +125.8° (c = 0.16 g/100 mL, CHCl₃, 90% ee); IR (Neat): νmax 2973, 2953, 1732, 1658, 1651, 1465, 1364, 1217, 1147 and 1086 cm⁻¹; ¹H NMR (CDCl₃) δ 5.98 (1H, s, olefinic-H), 3.10-2.93 (1H, m), 2.85-2.67 (2H, m), 2.47-2.38 (2H, m), 2.27 (1H, ddd, J = 14.0, 4.8, 2.4 Hz), 1.79-1.70 (4H, m), 0.98 (3H, t, J = 7.2 Hz, CH₃(2)); ¹³C NMR (CDCl₃, DEPT-135) δ 215.8 (C, C=O), 198.1 (C, C=O), 170.1 (C), 124.1 (CH), 52.6 (C), 35.8 (CH₂), 32.6 (CH₂), 27.1 (CH₂), 26.9 (CH₂), 25.8 (CH₂), 8.9 (CH₃); LRMS m/z 179.00 (M + H⁺), calcd for C₁₆H₁₄O₂H 179.0994; Anal. calcd for C₁₆H₁₄O₂ (178.0994): C, 74.13; H, 7.92. Found: C, 74.195; H, 7.928%.
\( \lambda = 254 \text{ nm} \), \( t_R = 25.0 \text{ min} \) (major), \( t_R = 36.1 \text{ min} \) (minor). \( [\alpha]_{D}^{25} = +225.83^\circ \) \( (c = 0.36 \text{ g/100 mL}, \text{CHCl}_3, 94\% \text{ ee}) \); IR (Neat): \( \nu_{\text{max}} 2960, 2933, 2873, 1741, 1666, 1443, 1357, 1211 \text{ and } 1089 \text{ cm}^{-1} \); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 5.98 (1H, s, olefinic-\( H \)), 3.05-2.90 (1H, m), 2.85-2.65 (2H, m), 2.54-2.38 (2H, m), 2.28-2.23 (1H, m), 1.80-1.60 (3H, m), 1.45-1.32 (3H, m), 0.91 (3H, \( t, J = 7.2 \text{ Hz}, \text{CH}_2\text{CH}_3 \)); \(^1^3\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 216.1 (C, C=O), 198.2 (C, C=O), 170.1 (C), 124.1 (CH), 52.5 (C), 36.5 (CH\(_2\)), 35.9 (CH\(_2\)), 32.7 (CH\(_2\)), 27.0 (CH\(_3\)), 26.6 (CH\(_2\)), 17.9 (CH\(_3\)), 14.3 (CH\(_3\)); LRMS m/z 193.00 (M + H\(^{+}\)), calcd for C\(_{12}\)H\(_{16}\)O\(_2\)H 193.1150; Anal. calcd for C\(_{12}\)H\(_{16}\)O\(_2\) (192.1150): C, 74.97; H, 8.39. Found: C, 74.885; H, 8.406%.

\( (+)-7a\)-Butyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10n): Purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/i-PrOH = 70:30, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \), \( t_R = 20.0 \text{ min} \) (major), \( t_R = 25.2 \text{ min} \) (minor). \( [\alpha]_{D}^{25} = +148.3^\circ \) \( (c = 0.32 \text{ g/100 mL}, \text{CHCl}_3, 94.3\% \text{ ee}) \); IR (Neat): \( \nu_{\text{max}} 2957, 2933, 2869, 1742, 1666, 1461, 1358, 1246, 1209 \text{ and } 1095 \text{ cm}^{-1} \); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 5.98 (1H, s, olefinic-\( H \)), 3.03-2.93 (1H, m), 2.85-2.67 (2H, m), 2.53-2.37 (2H, m), 2.25 (1H, \( dd, J = 14.2, 5.2 \text{ Hz} \)), 1.80-1.62 (4H, m), 1.40-1.24 (4H, m), 0.90 (3H, \( J = 7.2 \text{ Hz}, \text{CH}_3 \)); \(^1^3\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 216.0 (C, C=O), 198.2 (C, C=O), 170.1 (C), 124.1 (CH), 52.4 (C), 35.9 (CH\(_2\)), 34.1 (CH\(_2\)), 32.8 (CH\(_2\)), 27.0 (CH\(_3\)), 26.59 (CH\(_2\)), 26.57 (CH\(_2\)), 23.0 (CH\(_3\)), 13.8 (CH\(_3\)); LRMS m/z 207.00 (M + H\(^{+}\)), calcd for C\(_{13}\)H\(_{18}\)O\(_2\)H 207.1307; Anal. calcd for C\(_{13}\)H\(_{18}\)O\(_2\) (206.1307): C, 75.69; H, 8.80. Found: C, 75.613; H, 8.794%.

\( 7a\)-Benzyl-3a-hydroxy-hexahydro-indene-1,5-dione (11a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 128 °C IR (Neat): \( \nu_{\text{max}} 3409 \) (O-H), 2925, 1723, 1715, 1447, 1288, 1155, 1080, 1056, 758 and 708 \text{ cm}^{-1} \); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.26 (5H, m) [Ph-\( H \)]; 3.07 (2H, AB q, \( J = 14.0 \text{ Hz}, \text{C}_2\text{H}_2\text{Ph} \)), 2.65-2.57 (3H, m), 2.51-2.37 (2H, m), 2.15 (2H, \( J = 6.8 \text{ Hz} \)), 2.10-2.04 (1H, m), 1.98-1.91 (1H, m), 1.84 (2H, \( t, J = 6.8 \text{ Hz} \)); \(^1^3\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 216.8 (C, C=O), 209.3 (C, C=O), 136.7 (C), 130.5 (2 x CH), 128.3 (2 x CH), 127.0 (CH), 82.0 (C, C-OH), 56.4 (C), 51.2 (CH\(_2\)), 37.1 (CH\(_2\)), 36.8 (CH\(_2\)), 34.2 (CH\(_2\)), 33.4 (CH\(_2\)), 27.4 (CH\(_2\)); LRMS m/z 259.00 (M + H\(^{+}\)), calcd for C\(_{16}\)H\(_{18}\)O\(_3\)H 259.1256; Anal. calcd for C\(_{16}\)H\(_{18}\)O\(_3\) (258.1256): C, 74.39; H, 7.02. Found: C, 74.406; H, 7.006%.

\( 7a\)-Ethyl-3a-hydroxy-hexahydro-indene-1,5-dione (11l): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): \( \nu_{\text{max}} 3456 \) (O-H), 2967, 2883, 1721, 1714, 1464, 1411, 1292, 1231, 1138 and 1062 \text{ cm}^{-1} \); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 2.65-2.46 (4H, m), 2.40-2.22 (3H, m), 2.20-2.08 (2H, m), 2.05-1.94 (1H, m), 1.85-1.76 (2H, m), 1.74-1.64 (1H, m), 0.97 (3H, \( J = 7.6 \text{ Hz} \)); \(^1^3\)C NMR (CDCl\(_3\), DEPT-135) \( \delta \) 217.2 (C, C=O), 209.6 (C, C=O), 82.3 (C, C-OH), 55.3 (C), 51.1 (CH\(_2\)), 37.1 (CH\(_2\)), 34.3 (CH\(_2\)), 33.2 (CH\(_2\)), 25.8 (CH\(_2\)), 22.9 (CH\(_2\)), 8.2 (CH\(_3\)); LRMS m/z 197.00 (M + H\(^{+}\)), calcd for C\(_{13}\)H\(_{16}\)O\(_3\)H 197.1099; Anal. calcd for C\(_{13}\)H\(_{16}\)O\(_3\) (196.1099): C, 67.32; H, 8.22. Found: C, 67.347; H, 8.259%.
3a-Hydroxy-7a-propyl-hexahydro-indene-1,5-dione (11m): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν\textsubscript{max} 3448 (O-H), 2960, 2930, 2870, 1715, 1414, 1211 and 1094 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 2.63-2.46 (4H, m), 2.39-2.24 (3H, m), 2.20-2.05 (2H, m), 2.00-1.94 (1H, m), 1.95-1.75 (1H, m), 1.70-1.56 (2H, m), 1.48-1.33 (2H, m), 0.94 (3H, t, J = 7.2 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, DEPT-135) δ 217.4 (C, C=O), 209.4 (C, C=O), 82.3 (C, C-OH), 55.3 (C), 51.0 (CH\textsubscript{2}), 37.2 (CH\textsubscript{2}), 34.3 (CH\textsubscript{2}), 33.2 (CH\textsubscript{2}), 32.5 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}), 17.1 (CH\textsubscript{2}), 14.8 (CH\textsubscript{3}); LRMS m/z 211.00 (M + H\textsuperscript{+}), calcd for C\textsubscript{12}H\textsubscript{18}O\textsubscript{3}H 211.1256; Anal. calcd for C\textsubscript{12}H\textsubscript{18}O\textsubscript{3} (210.1256): C, 68.54; H, 8.63. Found: C, 68.526; H, 8.619%.

7a-Butyl-3a-hydroxy-hexahydro-indene-1,5-dione (11n): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν\textsubscript{max} 3452 (O-H), 2957, 2868, 1715, 1413, 1219 and 1099 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 2.94 (1H, br s, O-H), 2.63-2.45 (3H, m), 2.40-2.26 (3H, m), 2.21-2.07 (2H, m), 2.00-1.93 (1H, m), 1.87-1.77 (1H, m), 1.73-1.53 (2H, m), 1.43-1.21 (4H, m), 0.91 (3H, t, J = 7.2 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, DEPT-135) δ 217.4 (C, C=O), 209.6 (C, C=O), 82.2 (C, C-OH), 55.2 (C), 51.0 (CH\textsubscript{2}), 37.2 (CH\textsubscript{2}), 34.3 (CH\textsubscript{2}), 33.2 (CH\textsubscript{2}), 30.0 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}), 25.8 (CH\textsubscript{2}), 23.4 (CH\textsubscript{2}), 13.9 (CH\textsubscript{3}); LRMS m/z 225.00 (M + H\textsuperscript{+}), calcd for C\textsubscript{13}H\textsubscript{20}O\textsubscript{3}H 224.1412; Anal. calcd for C\textsubscript{13}H\textsubscript{20}O\textsubscript{3} (224.1412): C, 69.61; H, 8.99. Found: C, 69.690; H, 8.969%.

2-Benzyl-2-(3-oxo-butyl)-cyclopentane-1,3-dione (12a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 114 °C. IR (Neat): ν\textsubscript{max} 2922, 2852, 1721, 1713, 1448, 1374, 1167, 758 and 707 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 7.24-7.21 (3H, m), 7.04-7.01 (2H, m) [Ph-H], 2.93 (2H, s, C\textsubscript{2}H\textsubscript{2}Ph), 2.54 (2H, AB q, J = 6.8 Hz), 2.45 (2H, t, J = 7.2 Hz), 2.10 (3H, s, CH\textsubscript{3}), 2.00 (2H, t, J = 7.2 Hz), 1.96 (2H, AB q, J = 6.8 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, DEPT-135) δ 217.1 (C, C=O), 209.6 (C, C=O), 82.2 (C, C-OH), 55.2 (C), 51.0 (CH\textsubscript{2}), 37.2 (CH\textsubscript{2}), 34.3 (CH\textsubscript{2}), 33.2 (CH\textsubscript{2}), 30.0 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}), 25.8 (CH\textsubscript{2}), 23.4 (CH\textsubscript{2}), 13.9 (CH\textsubscript{3}); LRMS m/z 259.00 (M + H\textsuperscript{+}), calcd for C\textsubscript{16}H\textsubscript{18}O\textsubscript{3}H 259.1256; Anal. calcd for C\textsubscript{16}H\textsubscript{18}O\textsubscript{3} (258.1256): C, 74.39; H, 7.02. Found: C, 74.403; H, 7.073%.

2-Ethyl-2-(3-oxo-butyl)-cyclopentane-1,3-dione (12l): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν\textsubscript{max} 2971, 2927, 1720, 1713, 1418, 1364, 1255, 1170 and 1089 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 2.88-2.66 (4H, m), 2.42 (2H, t, J = 6.8 Hz), 2.10 (3H, s, CH\textsubscript{3}), 1.88 (2H, t, J = 7.2 Hz), 1.65 (2H, q, J = 7.2 Hz), 0.80 (3H, t, J = 7.2 Hz); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, DEPT-135) δ 216.1 (2 x C, C=O), 207.9 (C, C=O), 59.7 (C), 37.5 (CH\textsubscript{2}), 35.6 (2 x CH\textsubscript{2}), 29.9 (CH\textsubscript{3}), 28.0 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}), 8.7 (CH\textsubscript{3}); LRMS m/z 197.00 (M + H\textsuperscript{+}), calcd for C\textsubscript{11}H\textsubscript{16}O\textsubscript{3}H 197.1099; Anal. calcd for C\textsubscript{11}H\textsubscript{16}O\textsubscript{3} (196.1099): C, 67.32; H, 8.22. Found: C, 67.322; H, 8.217%.

2-(3-Oxo-butyl)-2-propyl-cyclopentane-1,3-dione (12m): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν\textsubscript{max} 2962, 2932, 2875, 1720, 1715, 1420, 1364, 1170 and 1098 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 2.82-2.64 (4H, m),
2.42 (2H, t, $J = 7.2$ Hz), 2.09 (3H, s, CH$_3$), 1.88 (2H, t, $J = 7.2$ Hz), 1.58 (2H, m), 1.16 (2H, m), 0.84 (3H, t, $J = 7.2$ Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 216.3 (2 x C, C=O), 207.8 (C, C=O), 59.4 (C), 37.6 (CH$_2$), 37.1 (CH$_3$), 35.6 (2 x CH$_2$), 29.9 (CH$_3$), 27.1 (CH$_2$), 17.8 (CH$_2$), 14.3 (CH$_3$); LRMS m/z 211.00 (M + H$^+$), calcd for C$_{12}$H$_{18}$O$_3$H 211.1256; Anal. calcd for C$_{12}$H$_{18}$O$_3$ (210.1256): C, 68.54; H, 8.63. Found: C, 68.549; H, 8.658%.

2-Butyl-2-(3-oxo-butyl)-cyclopentane-1,3-dione (12n): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): $\nu$ max 2958, 2932, 2870, 1720, 1715, 1652, 1420, 1366, 1170 and 1100 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 2.85-2.65 (4H, m), 2.42 (2H, t, $J = 7.2$ Hz), 2.09 (3H, s, CH$_3$), 1.88 (2H, t, $J = 7.2$ Hz), 1.58 (2H, m), 1.30-1.20 (2H, m), 1.13-1.07 (2H, m), 0.84 (3H, t, $J = 7.2$ Hz); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 216.3 (2 x C, C=O), 207.8 (C, C=O), 59.3 (C), 37.6 (CH$_2$), 34.8 (CH$_2$), 29.9 (CH$_3$), 27.1 (CH$_2$), 26.5 (CH$_2$), 23.0 (CH$_3$), 13.6 (CH$_3$); LRMS m/z 225.00 (M + H$^+$), calcd for C$_{13}$H$_{20}$O$_3$H 225.1412; Anal. calcd for C$_{13}$H$_{20}$O$_3$ (224.1412): C, 69.61; H, 8.99. Found: C, 69.626; H, 9.015%.

2-Benzyl-3-methoxy-cyclopent-2-enone (13a): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): $\nu$ max 3027, 2919, 1685, 1623 (C=O), 1358, 1258, 1087, 1041 and 962 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.26-7.20 (4H, m), 7.17-7.13 (1H, m) [Ar-H]; 3.92 (3H, s, OC$_3$H$_3$), 3.45 (2H, s, PhCH$_2$), 2.64 (2H, t, $J = 4.8$ Hz), 2.44 (2H, m); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 204.1 (C, C=O), 185.0 (C), 140.1 (C), 128.4 (2 x CH), 128.1 (2 x CH), 125.7 (CH), 119.8 (C), 56.4 (CH$_3$, OCH$_3$), 33.4 (CH$_2$), 27.1 (CH$_2$), 24.5 (CH$_3$); LCMS m/z 203.10 (M + H$^+$), calcd for C$_{13}$H$_{14}$O$_2$H 203.0994; Anal. calcd for C$_{13}$H$_{14}$O$_2$ (202.0994): C, 77.20; H, 6.98. Found: C, 77.334; H, 6.966%.

2-Ethyl-3-methoxy-cyclopent-2-enone (13l): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): $\nu$ max 3471, 2966, 1683, 1621 (C=O), 1614, 1462, 1360, 1268, 1123, 1016, 914 and 618 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 3.95 (3H, s, OC$_3$H$_3$), 2.66 (2H, br t, $J = 4.4$ Hz), 2.43 (2H, br t, $J = 4.4$ Hz), 2.14 (2H, q, $J = 7.6$ Hz, CH$_2$CH$_3$), 0.98 (3H, t, $J = 7.6$ Hz, CH$_2$CH$_3$); $^{13}$C NMR (CDCl$_3$, DEPT-135) $\delta$ 204.8 (C, C=O), 184.3 (C), 122.1 (C), 56.2 (CH$_3$, OCH$_3$), 33.4 (CH$_2$), 24.4 (CH$_2$), 14.4 (CH$_2$), 12.5 (CH$_3$); LCMS m/z 141.15 (M + H$^+$), calcd for C$_8$H$_{12}$O$_2$H 141.0837; Anal. calcd for C$_8$H$_{12}$O$_2$ (140.0837): C, 72.80; H, 6.98. Found: C, 72.84; H, 6.83. Found: C, 68.536; H, 6.613%.

2-Isopropyl-3-methoxy-cyclopent-2-enone (13w): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): $\nu$ max 2960, 1683, 1621 (C=O), 1463, 1375, 1352, 1278, 1248, 1060 and 1033 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 3.92 (3H, s, OCH$_3$), 2.74 (1H, heptet, $J = 7.2$ Hz, CHMe$_2$), 2.64-2.62 (2H, m), 2.41-2.39 (2H, m), 1.11 (6H, d, $J = 7.2$ Hz, 2 x CH$_3$, CHMe$_2$); $^{13}$C NMR [CDCl$_3$, DEPT-135] $\delta$ 204.4 (C, C=O), 184.0 (C), 125.7 (C), 56.1 (CH$_3$, OCH$_3$), 33.5 (CH$_2$), 24.1 (CH$_2$), 22.8 (CH), 20.1 (2 x CH$_2$); LCMS m/z 155.10 (M + H$^+$), calcd for C$_9$H$_{14}$O$_2$H 155.0994; Anal. calcd for C$_9$H$_{14}$O$_2$ (154.0994): C, 70.10; H, 9.15. Found: C, 70.070; H, 9.164%.
Datablock: dbr43 (Product 7i)

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Temperature: 298 K  

Calculated  Reported

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Hall group  -P 2ybc  ?  
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Sum formula  C12 H11 N O4  C12 H11 N O4  

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Datablock dbr43 - ellipsoid plot
**Datablock: dbr47 (Product 10a)**

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**Datablock dbr47 - ellipsoid plot**