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-Nonious MACH 3 diffractometer using graphite monochromated, Mo-Kα (λ = 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 (λ = 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_2SO_4 (35 mL), acetic acid (10 mL), and ethanol (900 mL) followed by heating.

- ***Because of solubility problem of 2-alkyl-cyclopenatane-1,3-diones 7a-x in $CDCl_3$, we have used three drops of CD_3OD.***
- ***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 x CH_2 and 2 x C=O) are poor resolution even after more than 2000 scans in the solvent system of $CDCl_3$ or $CDCl_3$ + CD_3OD (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).

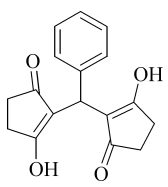
Amino Acid-Catalyzed Robinson Annulation Reaction: In ordinary glass vial equipped with a magnetic stirring bar, to 0.3 mmol of 2-alkyl-cyclopentane-1,3-diones **7** and 0.9 mmol of methyl vinyl ketone **9** was added 1.0 mL of DMSO solvent, and then the catalyst proline **4a** (0.09 mmol, 30 mol%) was added and the

reaction mixture was stirred at 25 °C for 6 days. The crude reaction mixture was worked up with aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), 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 methyl 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 NH_4Cl solution and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), 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).

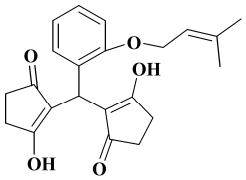
General Procedure for the Dehydration of 7a-Alkyl-3a-Hydroxy-Hexahydro-Indene-1,5-Diones 11: A solution of alcohol compound **11** (0.2 mmol) and 1N $HClO_4$ (0.4 mmol) in DMSO (1.0 ml) stirred at 90 °C for 0.5 to 1 h. After cooling, the reaction mixture washed with water and the aqueous layer was extracted with dichloromethane (3 x 20 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated. Pure products **10** were obtained by column chromatography (silica gel, mixture of hexane/ethyl acetate).



6a

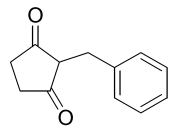
2,2'-Phenylmethylene-bis-[1,3-cyclopentanedione] (6a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 186 °C; IR (Neat): ν_{max} 3376, 2921, 1659, 1547, 1411, 1239 and 1213 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.77 (2H, br s, 2 x O-H), 7.21-7.09 (5H, m) [Ar-H]; 5.33 (1H, s, PhC*H*), 2.58 (8H, s, 4 x CH_2); ^{13}C NMR

($CDCl_3$, 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 CH_2), 30.0 (CH); LCMS m/z 285.00 ($M+H^+$), calcd for $C_{17}H_{16}O_4H$ 285.1049; Anal. calcd for $C_{17}H_{16}O_4$ (284.1049): C, 71.82; H, 5.67. Found: C, 71.731; H, 5.652%.



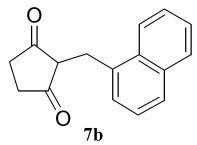
6g

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): ν_{max} 2924, 2723, 1659, 1590, 1412, 1354, 1275, 1226, 1118, 1020 and 754 cm^{-1}; ^1H NMR ($CDCl_3$) 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* = 7.6 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, PhC*H*), 4.45 (2H, d, *J* = 6.8 Hz, OCH_2CH=CMe_2), 2.53 (8H, br s, 4 x CH_2), 1.77 (3H, s, CH_3), 1.70 (3H, s, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 199.4 (2 x C, C=O), 155.8 (C), 137.5 (C), 128.34 (CH), 128.2 (C, $OCH_2CH=CMe_2$), 127.7 (CH), 120.3 (CH), 119.8 (CH), 117.9 (2 x C), 111.6 (CH), 65.1 (CH_2, OCH_2CH=CMe_2), 30.4 (4 x CH_2), 25.7 (CH), 25.6 (CH_3), 18.1 (CH_3); LCMS m/z 369.00 ($M+H^+$), calcd for $C_{22}H_{24}O_5H$ 369.1624; Anal. calcd for $C_{22}H_{24}O_5$ (368.1624): C, 71.72; H, 6.57. Found: C, 71.668; H, 6.575%.



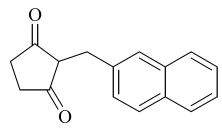
7a

2-Benzyl-cyclopentane-1,3-dione (7a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 180 °C; IR (Neat): ν_{max} 2923, 1571, 1565, 1473, 1434, 1396, 1368, 1321 and 1257 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.26-7.20 (4H, m), 7.15-7.13 (1H, m) [Ar-H]; 3.46 (2H, s, PhCH_2), 2.46 (4H, s); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 26.7 (CH_2); HRMS m/z 211.0728 ($M + Na^+$), calcd for $C_{12}H_{12}O_2Na$ 211.0735.



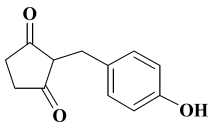
7b

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): ν_{max} 2971, 1569, 1365, 1259, 1179 and 779 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 8.23 (1H, d, *J* = 8.4 Hz), 7.82 (1H, d, *J* = 7.6 Hz), 7.69 (1H, t, *J* = 5.2 Hz), 7.51-7.45 (2H, m), 7.36 (2H, m) [Ar-H]; 3.90 (2H, s, ArCH_2), 2.47 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 135.1 (C), 133.5 (C), 131.8 (C), 128.2 (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 CH_2), 24.0 (CH_2); HRMS m/z 261.0882 ($M + Na^+$), calcd for $C_{16}H_{14}O_2Na$ 261.0891.

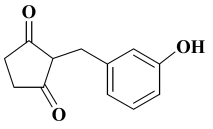


7c

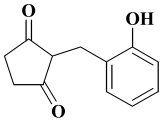
2-Naphthalen-2-ylmethyl-cyclopentane-1,3-dione (7c): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 220 °C; IR (Neat): ν_{max} 2923, 2854, 2658, 1573, 1430, 1376, 1260, 1178, 1034, 818 and 754 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.76-7.67 (4H, m), 7.43-7.30 (3H, m) [Ar-H]; 3.63 (2H, s, ArCH_2), 2.50 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (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), 124.8 (CH), 117.1 (C), 30.2 (2 x CH_2), 26.8 (CH_2); HRMS m/z 261.0880 ($M + Na^+$), calcd for $C_{16}H_{14}O_2Na$ 261.0891.


7d

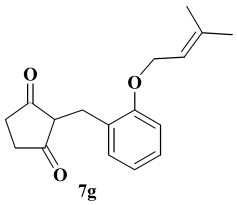
2-(4-Hydroxy-benzyl)-cyclopentane-1,3-dione (7d): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 194 °C; IR (Neat): ν_{max} 3243, 1578, 1433, 1366, 1258, 1237, 1174, 1028 and 820 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.07 (2H, d, *J* = 8.4 Hz), 6.69 (2H, d, *J* = 8.4 Hz) [Ar-H]; 3.36 (2H, s, ArC*H*$_2$), 2.46 (4H, s, 2 x C*H*$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 25.7 (CH_2); HRMS m/z 227.0688 (M + Na^+), calcd for $C_{12}H_{12}O_3Na$ 227.0684.


7e

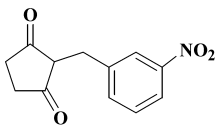
2-(3-Hydroxy-benzyl)-cyclopentane-1,3-dione (7e): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 160 °C; IR (Neat): ν_{max} 3406, 3152, 2924, 1664, 1375, 1262, 1240, 1161 and 692 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.05 (1H, t, *J* = 8.0 Hz), 6.74 (1H, 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, ArC*H*$_2$), 2.46 (4H, s, 2 x C*H*$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 26.5 (CH_2); HRMS m/z 227.0679 (M + Na^+), calcd for $C_{12}H_{12}O_3Na$ 227.0684.


7f

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 [$CDCl_3$ + CD_3OD (three drops)] δ 7.20 (1H, d, *J* = 7.2 Hz), 7.08 (1H, t, *J* = 7.2 Hz), 6.88 (1H, d, *J* = 8.0 Hz), 6.81 (1H, t, *J* = 7.2 Hz) [Ar-H]; 3.42 (2H, s, ArC*H*$_2$), 2.47 (4H, s, 2 x C*H*$_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 197.5 (C, *C*=O), 153.7 (C), 130.6 (CH), 127.7 (CH), 126.6 (C), 120.6 (CH), 117.8 (C), 116.7 (CH), 30.1 (2 x CH_2), 21.7 (CH_2); HRMS m/z 227.0685 (M + Na^+), calcd for $C_{12}H_{12}O_3Na$ 227.0686.

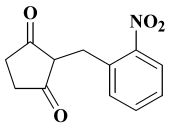

7g

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, 1570, 1432, 1374, 1324, 1262, 1244, 1223, 1190, 1108, 1021 and 753 cm^{-1}; **^1H NMR ($CDCl_3$)** 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, OCH_2CH=CMe_2), 4.65 (2H, d, *J* = 7.2 Hz, OCH_2CH=CMe_2), 3.45 (2H, s, ArC*H*$_2$), 2.45-2.39 (4H, m), 1.86 (3H, s, CH_3), 1.80 (3H, s, CH_3); **^{13}C NMR ($CDCl_3$, DEPT-135)** δ 204.4 (C, *C*=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 (CH_2, OCH_2CH=CMe_2), 33.7 (CH_2), 26.5 (CH_2), 25.9 (CH_3), 21.2 (CH_2), 18.2 (CH_3); HRMS m/z 295.1299 (M + Na^+), calcd for $C_{17}H_{20}O_3Na$ 295.1310.


7h

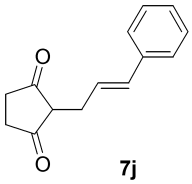
2-(3-Nitro-benzyl)-cyclopentane-1,3-dione (7h): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 202 °C; IR (Neat): ν_{max} 2922, 1620, 1559, 1523, 1427, 1354, 1295, 1259, 1164, 1084, 1027, 802 and

716 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (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, ArCH_2), 2.52 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 26.5 (CH_2); HRMS m/z 256.0591, calcd for $C_{12}H_{11}NO_4Na$ 256.0586.



7i

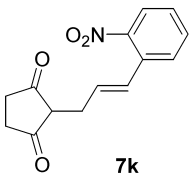
2-(2-Nitro-benzyl)-cyclopentane-1,3-dione (7i): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 190 °C; IR (Neat): ν_{max} 2550, 1570, 1521, 1339, 1257, 1189, 1036, 844 and 727 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 7.86 (1H, d, *J* = 8.0 Hz), 7.48 (1H, t, *J* = 7.2 Hz), 7.31 (2H, m) [Ar-H]; 3.81 (2H, s, ArCH_2), 2.53 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 23.4 (CH_2); HRMS m/z 234.0755, calcd for $C_{12}H_{11}NO_4H$ 234.0766.



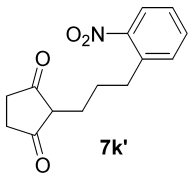
7j

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): ν_{max} 2928, 1724, 1609, 1520, 1435, 1401, 1375, 1255, 1158, 827 and 751 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (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) [PhC*H*=C*H*CH_2]; 3.04 (2H, d, *J* = 6.0 Hz), 2.48 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 CH_2), 24.3 (CH_2).; ^1H NMR [$CDCl_3$ + CD_3OD (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 CH_2), 2.19 (2H, t, *J* = 8.0 Hz), 1.74 (2H, quintet, *J* = 8.0 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 (CH_2), 30.4 (2 x CH_2), 29.4 (CH_2), 20.7 (CH_2); HRMS (Q-top) m/z 215.1016 and 217.1190, calcd for $C_{14}H_{14}O_2H$ 215.1072 and $C_{14}H_{16}O_2H$ 217.1229.

7j'



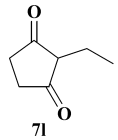
7k



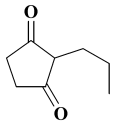
7k'

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): ν_{max} 3326, 2927, 1624, 1524, 1344, 1255, 1176 and 750 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops), 2:1 ratio of O/H product **7k** and completely reduced product **7k'**, major product **7k**] 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) [ArC*H*=C*H*CH_2]; 3.11 (2H, d, *J* = 6.4 Hz), 2.53 (4H, s, 2 x CH_2); ^{13}C NMR [$CDCl_3$ + CD_3OD (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

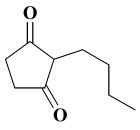
(CH), 127.4 (CH), 125.0 (CH), 124.2 (CH), 115.0 (C), 30.3 (2 x CH_2), 24.5 (CH_2).; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops), 2:1 ratio of O/H product **7k** and completely reduced product **7k'**, minor product **7k'**] δ 7.85 (1H, d, *J* = 8.4 Hz), 7.50 (1H, t, *J* = 7.2 Hz), 7.38 (1H, d, *J* = 8.0 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 CH_2), 2.23 (2H, t, *J* = 8.0 Hz), 1.76 (2H, quintet, *J* = 8.0 Hz); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 (CH_2), 30.3 (2 x CH_2), 28.5 (CH_2), 20.6 (CH_2); HRMS (Q-top) m/z 260.0845 and 262.1007, calcd for $C_{14}H_{13}NO_4H$ 260.0923 and $C_{14}H_{15}NO_4H$ 262.1079.


7l

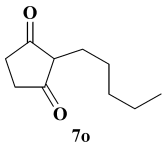
2-Ethyl-cyclopentane-1,3-dione (7l): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 166 °C; IR (Neat): ν_{max} 2971, 2931, 1530, 1545, 1348, 1267 and 1108 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.46 (4H, s, 2 x C*H*$_2$), 2.14 (2H, q, *J* = 7.2 Hz, C*H*$_2$CH$_3$), 0.99 (3H, t, *J* = 7.6 Hz, CH$_2$C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 119.6 (C), 30.1 (2 x CH_2), 14.0 (CH_2), 12.3 (CH_3); HRMS m/z 149.0571 (M + Na$^+$), calcd for $C_7H_{10}O_2Na$ 149.0578.


7m

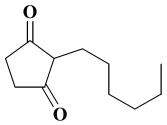
2-Propyl-cyclopentane-1,3-dione (7m): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 174 °C; IR (Neat): ν_{max} 2951, 2870, 1547, 1535, 1458, 1473, 1430, 1345, 1258, 1244, 1113 and 998 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.48 (4H, s, 2 x C*H*$_2$), 2.10 (2H, t, *J* = 7.2 Hz, C*H*$_2$CH$_2$CH$_3$), 1.42 (2H, sextet, *J* = 7.2 Hz, CH$_2$C*H*$_2$CH$_3$), 0.88 (3H, t, *J* = 7.2 Hz, CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 118.2 (C), 30.3 (2 x CH_2), 22.8 (CH_2), 22.1 (CH_2), 13.8 (CH_3); HRMS m/z 141.0922 (M+H$^+$), calcd for $C_8H_{12}O_2H$ 141.0915.


7n

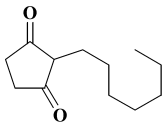
2-Butyl-cyclopentane-1,3-dione (7n): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 150 °C; IR (Neat): ν_{max} 2930, 2856, 1547, 1530, 1427, 1344, 1279, 1257, 1206, 1119 and 998 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.48 (4H, s, 2 x C*H*$_2$), 2.13 (2H, t, *J* = 7.6 Hz, C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.40-1.26 (4H, m, CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.89 (3H, t, *J* = 7.2 Hz, CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 118.5 (C), 30.2 (2 x CH_2), 30.1 (CH_2), 22.6 (CH_2), 20.7 (CH_2), 13.8 (CH_3); HRMS m/z 155.1078 (M + H$^+$), calcd for $C_9H_{14}O_2H$ 155.1072.


7o

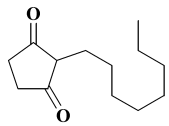
2-Pentyl-cyclopentane-1,3-dione (7o): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 136 °C; IR (Neat): ν_{max} 2929, 2861, 1531, 1456, 1428, 1342, 1262, 1194, 1122, 999 and 663 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.46 (4H, br s, 2 x C*H*$_2$), 2.11 (2H, t, *J* = 8.0 Hz, C*H*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.40 (2H, quintet, *J* = 7.6 Hz, CH$_2$C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.33-1.24 (4H, m, CH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_3$), 0.87 (3H, t, *J* = 6.8 Hz, CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_3$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 118.5 (C), 31.7 (CH_2), 30.3 (2 x CH_2), 27.6 (CH_2), 22.4 (CH_2), 20.9 (CH_2), 13.9 (CH_3); HRMS m/z 169.1224 (M + H$^+$), calcd for $C_{10}H_{16}O_2H$ 169.1228.


7p

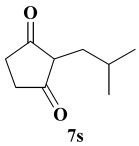
2-Hexyl-cyclopentane-1,3-dione (7p): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 240 °C; IR (Neat): ν_{max} 2923, 2852, 1531, 1454, 1427, 1348, 1285, 1254, 1123, 1001 and 664 cm^{-1}; ^1H NMR [$CDCl_3 + CD_3OD$ (three drops)] δ 2.48 (4H, s, 2 x CH_2), 2.12 (2H, t, J = 7.2 Hz, CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.38 (2H, quintet, J = 7.6 Hz, CH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.33-1.20 (6H, m, CH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 0.86 (3H, t, J = 6.8 Hz, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3); ^{13}C NMR [$CDCl_3 + CD_3OD$ (three drops), DEPT-135] δ 118.4 (C), 31.6 (CH_2), 30.4 (2 x CH_2), 29.2 (CH_2), 27.9 (CH_2), 22.5 (CH_2), 20.9 (CH_2), 13.9 (CH_3); LRMS m/z 183.00 (M + H^+), calcd for $C_{11}H_{18}O_2H$ 183.1307; Anal. calcd for $C_{11}H_{18}O_2$ (182.1307): C, 72.49; H, 9.95. Found: C, 72.584; H, 9.966%.


7q

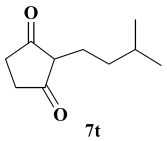
2-Heptyl-cyclopentane-1,3-dione (7q): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 128 °C; IR (Neat): ν_{max} 2927, 2852, 1532, 1456, 1426, 1344, 1276, 1253, 1123 and 998 cm^{-1}; ^1H NMR [$CDCl_3 + CD_3OD$ (three drops)] δ 2.46 (4H, s, 2 x CH_2), 2.11 (2H, t, J = 8.0 Hz, CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.39 (2H, quintet, J = 6.8 Hz, CH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.26 (8H, br s, CH$_2$CH$_2$CH_2CH_2CH_2CH_2CH$_3$), 0.87 (3H, t, J = 6.8 Hz, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 118.3 (C), 31.7 (CH_2), 30.2 (2 x CH_2), 29.4 (CH_2), 29.0 (CH_2), 27.9 (CH_2), 22.5 (CH_2), 20.8 (CH_2), 13.8 (CH_3); HRMS m/z 197.1543 (M + H^+), calcd for $C_{12}H_{20}O_2H$ 197.1541.


7r

2-Octyl-cyclopentane-1,3-dione (7r): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 130 °C; IR (Neat): ν_{max} 2918, 2850, 1532, 1462, 1428, 1347, 1290, 1261, 1124, 999 and 664 cm^{-1}; ^1H NMR [$CDCl_3 + CD_3OD$ (three drops)] δ 2.46 (4H, s, 2 x CH_2), 2.11 (2H, t, J = 7.2 Hz, CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.39 (2H, quintet, J = 6.8 Hz, CH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.26 (10H, br s, CH$_2$CH$_2$CH_2CH_2CH_2CH_2CH_2CH$_3$), 0.87 (3H, t, J = 6.8 Hz, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3); ^{13}C NMR [$CDCl_3 + CD_3OD$ (three drops), DEPT-135] δ 118.4 (C), 31.8 (CH_2), 30.4 (2 x CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 27.9 (CH_2), 22.5 (CH_2), 20.9 (CH_2), 13.9 (CH_3); HRMS m/z 211.1697 (M + H^+), calcd for $C_{13}H_{22}O_2H$ 211.1698.

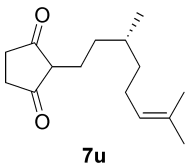

7s

2-Isobutyl-cyclopentane-1,3-dione (7s): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 190 °C; IR (Neat): ν_{max} 2929, 2496, 1552, 1427, 1350, 1313, 1258, 1124 and 998 cm^{-1}; ^1H NMR [$CDCl_3 + CD_3OD$ (three drops)] δ 2.48 (4H, s, 2 x CH_2), 2.00 (2H, d, J = 7.2 Hz, CH_2CHMe$_2$), 1.80 (1H, m, J = 6.8 Hz, CH$_2$CHMe$_2$), 0.85 [6H, d, J = 6.4 Hz, CH$_2$CH(CH_3)$_2$]; ^{13}C NMR [$CDCl_3 + CD_3OD$ (three drops), DEPT-135] δ 117.4 (C), 30.1 (2 x CH_2), 29.7 (CH_2), 27.2 (CH), 22.2 (2 x CH_3); LRMS m/z 155.00 (M + H^+), calcd for $C_9H_{14}O_2H$ 155.0994; Anal. calcd for $C_9H_{14}O_2$ (154.0994): C, 70.10; H, 9.15. Found: C, 70.162; H, 9.180%.

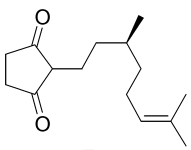

7t

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): ν_{max} 2924, 2598, 1598, 1555, 1436, 1364, 1289, 1254 and 1128 cm^{-1}; ^1H NMR [$CDCl_3 + CD_3OD$ (three drops)] δ 2.47 (4H,

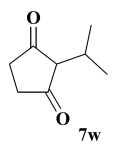
s, 2 x CH_2), 2.12 (2H, t, J = 8.0 Hz, $CH_2CH_2CHMe_2$), 1.51 (1H, m, J = 6.4 Hz, $CH_2CH_2CHMe_2$), 1.28 (2H, td, J = 12.4, 7.2 Hz, $CH_2CH_2CHMe_2$), 0.89 (6H, d, J = 6.4 Hz, $CH_2CH_2CHMe_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 118.5 (C), 36.7 (CH_2), 30.2 (2 x CH_2), 27.9 (CH), 22.2 (2 x CH_3), 18.8 (CH_2); LRMS m/z 169.05 (M + H^+), calcd for $C_{10}H_{16}O_2H$ 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%.


7u

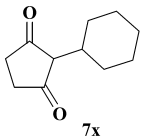
(–)-(3*R*)-2-(3,7-Dimethyl-oct-6-enyl)-cyclopentane-1,3-dione (7u): Purified by column chromatography using EtOAc/hexane and isolated as a solid. $[\alpha]_D^{25}$ = –5.029° (*c* = 1.075 g/100 mL, $CHCl_3$, 90%); Mp 70 °C; IR (Neat): ν_{max} 2922, 1566, 1473, 1368, 1289 and 1256 cm^{-1}; **^{1}H NMR [$CDCl_3$]** 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); **^{13}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 $C_{15}H_{24}O_2H$ 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_3OD (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); **^{13}C NMR [$CDCl_3$ + CD_3OD (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).


7v

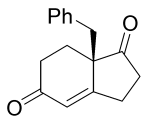
(+)-(3*S*)-2-(3,7-Dimethyl-oct-6-enyl)-cyclopentane-1,3-dione (7v): Purified by column chromatography using EtOAc/hexane and isolated as a solid. $[\alpha]_D^{25}$ = +7.463° (*c* = 0.55 g/100 mL, $CHCl_3$, 96%); Mp 70 °C; IR (Neat): ν_{max} 2920, 1622, 1566, 1473, 1368, 1255, 1195, 1127, 904, 826 and 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); **^{13}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 $C_{15}H_{24}O_2H$ 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%.


7w

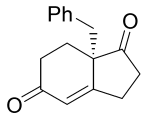
2-Isopropyl-cyclopentane-1,3-dione (7w): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 216 °C; IR (Neat): ν_{max} 2970, 2927, 2522, 1721, 1684, 1549, 1431, 1364, 1340, 1279 and 1120 cm^{-1}; ^{1}H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.74 (1H, heptet, J = 7.2 Hz, $CHMe_2$), 2.46 (4H, s, 2 x CH_2), 1.14 (6H, d, J = 7.2 Hz, 2 x CH_3, $CHMe_2$); ^{13}C NMR [$CDCl_3$ + CD_3OD (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 $C_8H_{12}O_2H$ 141.08; Anal. calcd for $C_8H_{12}O_2$ (140.0837): C, 68.54; H, 8.63. Found: C, 68.578; H, 8.685%.


7x

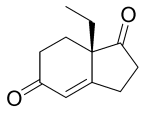
2-Cyclohexyl-cyclopentane-1,3-dione (7x): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 230 °C; IR (Neat): ν_{max} 2930, 2854, 1552, 1440, 1382, 1350, 1282, 1255, 1140, 1096 and 654 cm^{-1}; ^1H NMR [$CDCl_3$ + CD_3OD (three drops)] δ 2.43 (4H, s, 2 x C*H*$_2$), 2.38-2.35 (1H, m), 1.80-1.67 (5H, m), 1.50 (2H, m), 1.26 (3H, m); ^{13}C NMR [$CDCl_3$ + CD_3OD (three drops), DEPT-135] δ 122.3 (C), 32.8 (CH), 30.5 (2 x CH_2), 29.7 (2 x CH_2), 26.7 (2 x CH_2), 25.9 (CH_2); LRMS m/z 181.10 (M + H^+), calcd for $C_{11}H_{16}O_2H$ 181.1150; Anal. calcd for $C_{11}H_{16}O_2$ (180.1150): C, 73.30; H, 8.95. Found: C, 73.365; H, 8.919%.


(+)-**10a**

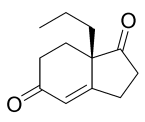
(+)-7a-Benzyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 70:30, flow rate 0.5 mL/min, λ = 254 nm), t_R = 61.6 min (major), t_R = 75.2 min (minor). $[\alpha]_D^{25}$ = +241.3° (*c* = 0.80 g/100 mL, $CHCl_3$, 90.6% ee); Mp 154 °C; IR (Neat): ν_{max} 2925, 1729, 1664, 1453, 1406, 1250, 1208, 1077, 754 and 706 cm^{-1}; ^1H NMR ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$, 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 (CH_2), 36.9 (CH_2), 32.8 (CH_2), 29.2 (CH_2), 28.1 (CH_2); LRMS m/z 241.00 (M + H^+), calcd for $C_{16}H_{16}O_2H$ 241.1150; Anal. calcd for $C_{16}H_{16}O_2$ (240.1150): C, 79.97; H, 6.71. Found: C, 79.924; H, 6.718%.


(–)-**10a**

(-)-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), t_R = 61.6 min (minor), t_R = 75.2 min (major). $[\alpha]_D^{25}$ = –293.6° (*c* = 0.960 g/100 mL, $CHCl_3$, 90.2% ee).

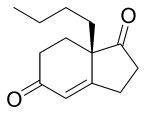

10l

(+)-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), t_R = 62.0 min (minor), t_R = 89.0 min (major). $[\alpha]_D^{25}$ = +125.8° (*c* = 0.16 g/100 mL, $CHCl_3$, 90% ee); IR (Neat): ν_{max} 2973, 2953, 1732, 1658, 1651, 1465, 1364, 1217, 1147 and 1086 cm^{-1}; ^1H NMR ($CDCl_3$) 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, CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 215.8 (C, C=O), 198.1 (C, C=O), 170.1 (C), 124.1 (CH), 52.6 (C), 35.8 (CH_2), 32.6 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 25.8 (CH_2), 8.9 (CH_3); LRMS m/z 179.00 (M + H^+), calcd for $C_{11}H_{14}O_2H$ 179.0994; Anal. calcd for $C_{11}H_{14}O_2$ (178.0994): C, 74.13; H, 7.92. Found: C, 74.195; H, 7.928%.

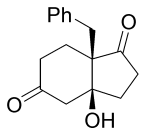

10m

(+)-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,

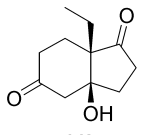
λ = 254 nm), t_R = 25.0 min (major), t_R = 36.1 min (minor). $[\alpha]_D^{25}$ = +225.83° (*c* = 0.36 g/100 mL, $CHCl_3$, 94% ee); IR (Neat): ν_{max} 2960, 2933, 2873, 1741, 1666, 1443, 1357, 1211 and 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.98 (1H, s, olefinic-*H*), 3.05-2.90 (1H, m), 2.85-2.65 (2H, m), 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 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 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_2), 26.6 (CH_2), 17.9 (CH_2), 14.3 (CH_3); LRMS m/z 193.00 ($M + H^+$), calcd for $C_{12}H_{16}O_2H$ 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%.


10n

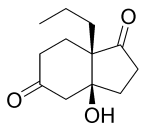
(+)-7a-Butyl-2,3,7,7a-tetrahydro-6H-indene-1,5-dione (10n): Purified by column chromatography using EtOAc/hexane and isolated as an oil. The ee was determined by chiral-phase HPLC using a Daicel Chiralpak AS-H column (hexane/*i*-PrOH = 70:30, flow rate 1.0 mL/min, λ = 254 nm), t_R = 20.0 min (major), t_R = 25.2 min (minor). $[\alpha]_D^{25}$ = +148.3° (*c* = 0.32 g/100 mL, $CHCl_3$, 94.3% ee); IR (Neat): ν_{max} 2957, 2933, 2869, 1742, 1666, 1461, 1358, 1246, 1209 and 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 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 Hz), 1.80-1.62 (4H, m), 1.40-1.24 (4H, m), 0.90 (3H, t, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 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_2), 26.59 (CH_2), 26.57 (CH_2), 23.0 (CH_2), 13.8 (CH_3); LRMS m/z 207.00 ($M + H^+$), calcd for $C_{13}H_{18}O_2H$ 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%.


11a

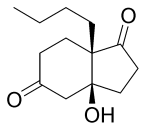
7a-Benzyl-3a-hydroxy-hexahydro-indene-1,5-dione (11a): Purified by column chromatography using EtOAc/hexane and isolated as a solid. Mp 128 °C IR (Neat): ν_{max} 3409 (O-H), 2925, 1723, 1715, 1447, 1288, 1155, 1080, 1056, 758 and 708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (5H, m) [Ph-*H*]; 3.07 (2H, AB q, *J* = 14.0 Hz, CH_2Ph), 2.65-2.57 (3H, m), 2.51-2.37 (2H, m), 2.15 (2H, t, *J* = 6.8 Hz), 2.10-2.04 (1H, m), 1.98-1.91 (1H, m), 1.84 (2H, t, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 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 $C_{16}H_{18}O_3H$ 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%.


11l

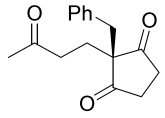
7a-Ethyl-3a-hydroxy-hexahydro-indene-1,5-dione (11l): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν_{max} 3456 (O-H), 2967, 2883, 1721, 1714, 1464, 1411, 1292, 1231, 1138 and 1062 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65-2.46 (4H, m), 2.40-2.22 (3H, m), 2.20-2.08 (2H, m), 2.05-1.94 (1H, m), 1.85-1.76 (2H, m), 1.74-1.64 (1H, m), 0.97 (3H, t, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 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 $C_{11}H_{16}O_3H$ 197.1099; Anal. calcd for $C_{11}H_{16}O_3$ (196.1099): C, 67.32; H, 8.22. Found: C, 67.347; H, 8.259%.


11m

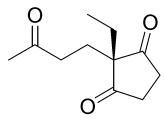
3a-Hydroxy-7a-propyl-hexahydro-indene-1,5-dione (11m): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν_{max} 3448 (O-H), 2960, 2930, 1720, 1715, 1414, 1211 and 1094 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.63-2.46 (4H, m), 2.39-2.24 (3H, m), 2.20-2.05 (2H, m), 2.00-1.94 (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); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 217.4 (C, C=O), 209.4 (C, C=O), 82.3 (C, C-OH), 55.3 (C), 51.0 (CH_2), 37.2 (CH_2), 34.3 (CH_2), 33.2 (CH_2), 32.5 (CH_2), 26.4 (CH_2), 17.1 (CH_2), 14.8 (CH_3); LRMS m/z 211.00 (M + H^+), calcd for $C_{12}H_{18}O_3H$ 211.1256; Anal. calcd for $C_{12}H_{18}O_3$ (210.1256): C, 68.54; H, 8.63. Found: C, 68.526; H, 8.619%.


11n

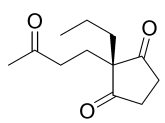
7a-Butyl-3a-hydroxy-hexahydro-indene-1,5-dione (11n): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν_{max} 3452 (O-H), 2957, 2868, 1720, 1715, 1651, 1413, 129, 1178 and 1099 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.94 (1H, br s, O-H), 2.63-2.45 (3H, m), 2.40-2.26 (3H, 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); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 217.4 (C, C=O), 209.6 (C, C=O), 82.2 (C, *C*-OH), 55.2 (C), 51.0 (CH_2), 37.2 (CH_2), 34.3 (CH_2), 33.2 (CH_2), 30.0 (CH_2), 26.4 (CH_2), 25.8 (CH_2), 23.4 (CH_2), 13.9 (CH_3); LRMS m/z 225.00 (M + H^+), calcd for $C_{13}H_{20}O_3H$ 224.1412; Anal. calcd for $C_{13}H_{20}O_3$ (224.1412): C, 69.61; H, 8.99. Found: C, 69.690; H, 8.969%.


12a

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_{max} 2922, 2852, 1721, 1713, 1448, 1407, 1374, 1167, 758 and 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24-7.21 (3H, m), 7.04-7.01 (2H, m) [Ph-*H*]; 2.93 (2H, s, CH_2Ph), 2.54 (2H, AB q, *J* = 6.8 Hz), 2.45 (2H, t, *J* = 7.2 Hz), 2.10 (3H, s, CH_3), 2.00 (2H, t, *J* = 7.2 Hz), 1.96 (2H, AB q, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 217.1 (2 x C, C=O), 207.6 (C, C=O), 135.1 (C), 129.7 (2 x CH), 128.6 (2 x CH), 127.3 (CH), 61.1 (C), 42.9 (CH_2), 37.8 (CH_2), 36.3 (2 x CH_2), 29.9 (CH_3), 28.4 (CH_2); LRMS m/z 259.00 (M + H^+), calcd for $C_{16}H_{18}O_3H$ 259.1256; Anal. calcd for $C_{16}H_{18}O_3$ (258.1256): C, 74.39; H, 7.02. Found: C, 74.403; H, 7.073%.

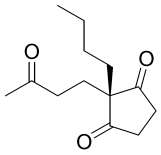

12l

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_{max} 2971, 2927, 1720, 1713, 1418, 1364, 1255, 1170 and 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.88-2.66 (4H, m), 2.42 (2H, t, *J* = 6.8 Hz), 2.10 (3H, s, CH_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); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 216.1 (2 x C, C=O), 207.9 (C, C=O), 59.7 (C), 37.5 (CH_2), 35.6 (2 x CH_2), 29.9 (CH_3), 28.0 (CH_2), 26.4 (CH_2), 8.7 (CH_3); LRMS m/z 197.00 (M + H^+), calcd for $C_{11}H_{16}O_3H$ 197.1099; Anal. calcd for $C_{11}H_{16}O_3$ (196.1099): C, 67.32; H, 8.22. Found: C, 67.322; H, 8.217%.


12m

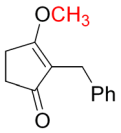
2-(3-Oxo-butyl)-2-propyl-cyclopentane-1,3-dione (12m): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): IR (Neat): ν_{max} 2962, 2932, 2875, 1720, 1715, 1420, 1364, 1170 and 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82-2.64 (4H, m),

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) δ 216.3 (2 x C, C=O), 207.8 (C, C=O), 59.4 (C), 37.6 (CH_2), 37.1 (CH_2), 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 $C_{12}H_{18}O_3H$ 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%.



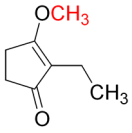
12n

2-Butyl-2-(3-oxo-butyl)-cyclopentane-1,3-dione (12n): Purified by column chromatography using EtOAc/hexane and isolated as an oil. IR (Neat): ν_{max} 2958, 2932, 2870, 1720, 1715, 1652, 1420, 1366, 1170 and 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 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) δ 216.3 (2 x C, C=O), 207.8 (C, C=O), 59.3 (C), 37.6 (CH_2), 35.6 (2 x CH_2), 34.8 (CH_2), 29.9 (CH_3), 27.1 (CH_2), 26.5 (CH_2), 23.0 (CH_2), 13.6 (CH_3); LRMS m/z 225.00 (M + H^+), calcd for $C_{13}H_{20}O_3H$ 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%.



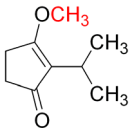
13a

2-Benzyl-3-methoxy-cyclopent-2-enone (13a): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 3027, 2919, 1685, 1623 (C=O), 1358, 1258, 1087, 1041 and 962 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.26-7.20 (4H, m), 7.17-7.13 (1H, m) [Ar-H]; 3.92 (3H, s, OC*H*$_3$), 3.45 (2H, s, PhC*H*$_2$), 2.64 (2H, t, *J* = 4.8 Hz), 2.44 (2H, m); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 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, O*C*H$_3$), 33.4 (CH_2), 27.1 (CH_2), 24.5 (CH_2); LCMS m/z 203.10 (M + H^+), calcd for $C_{13}H_{14}O_2H$ 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%.



13l

2-Ethyl-3-methoxy-cyclopent-2-enone (13l): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 3471, 2966, 1683, 1621 (C=O), 1614, 1462, 1360, 1268, 1123, 1016, 914 and 618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (3H, s, OC*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, C*H*$_2$CH$_3$), 0.98 (3H, t, *J* = 7.6 Hz, CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, DEPT-135) δ 204.8 (C, C=O), 184.3 (C), 122.1 (C), 56.2 (CH_3, O*C*H$_3$), 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 $C_8H_{12}O_2H$ 141.0837; Anal. calcd for $C_8H_{12}O_2$ (140.0837): C, 68.54; H, 8.63. Found: C, 68.536; H, 8.613%.



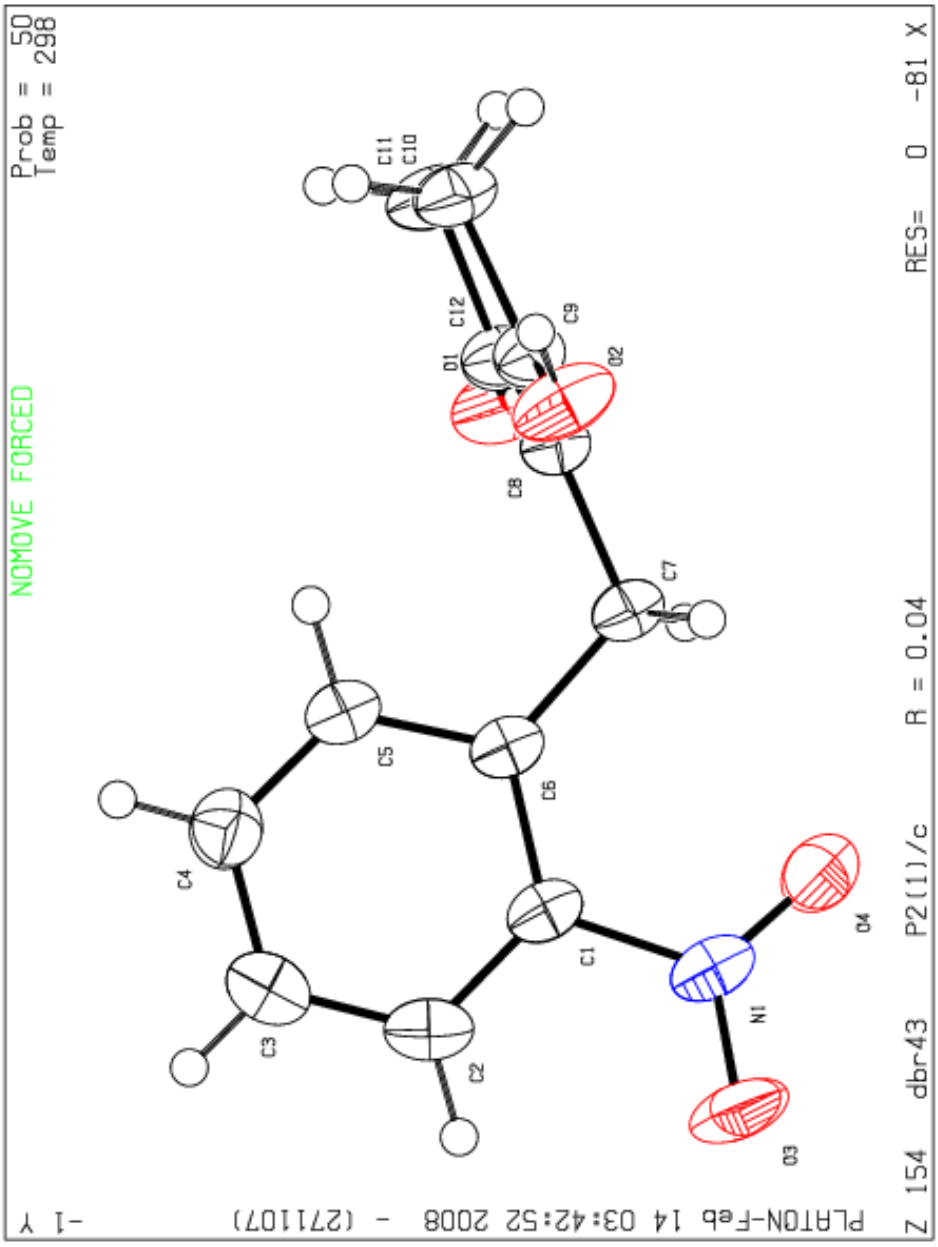
13w

2-Isopropyl-3-methoxy-cyclopent-2-enone (13w): Purified by column chromatography using EtOAc/hexane and isolated as oil. IR (Neat): ν_{max} 2960, 1681, 1612 (C=O), 1463, 1375, 1352, 1278, 1248, 1060 and 1033 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.92 (3H, s, OC*H*$_3$), 2.74 (1H, heptet, *J* = 7.2 Hz, C*H*Me$_2$), 2.64-2.62 (2H, m), 2.41-2.39 (2H, m), 1.11 (6H, d, *J* = 7.2 Hz, 2 x CH_3, CH*Me*$_2$); ^{13}C NMR [$CDCl_3$, DEPT-135] δ 204.4 (C, C=O), 184.0 (C), 125.7 (C), 56.1 (CH_3, O*C*H$_3$), 33.5 (CH_2), 24.1 (CH_2), 22.8 (CH), 20.1 (2 x CH_3); LCMS m/z 155.10 (M + H^+), calcd for $C_9H_{14}O_2H$ 155.0994; Anal. calcd for $C_9H_{14}O_2$ (154.0994): C, 70.10; H, 9.15. Found: C, 70.070; H, 9.164%.

Datablock: dbr43 (Product 7i)


```
Bond precision:      C-C = 0.0028 A               Wavelength=0.71073
Cell:        a=10.805(4)    b=12.994(5)     c=7.924(3)
             alpha=90       beta=110.696(6) gamma=90
Temperature: 298 K
                   Calculated                     Reported
Volume             1040.7(7)                      1040.8(6)
Space group        P 21/c                         P2(1)/c
Hall group         -P 2ybc                        ?
Moiety formula     C12 H11 N O4                   C12 H11 N O4
Sum formula        C12 H11 N O4                   C12 H11 N O4
Mr                 233.22                         233.22
Dx,g cm-3          1.488                          1.488
Z                  4                              4
Mu (mm-1)          0.113                          0.113
F000               488.0                          488.0
F000'              488.28
h,k,lmax           13,15,9                        13,15,9
Nref               2008                           2007
Tmin,Tmax          0.976,0.998                    0.942,0.998
Tmin'              0.951
Correction method= AbsCorr=EMPIRICAL
Data completeness= Ratio =
1.000                          Theta(max)= 25.840
R(reflections)= 0.0422( 1390)      wR2(reflections)= 0.1157( 2007)
S = 1.021             Npar= 155
```

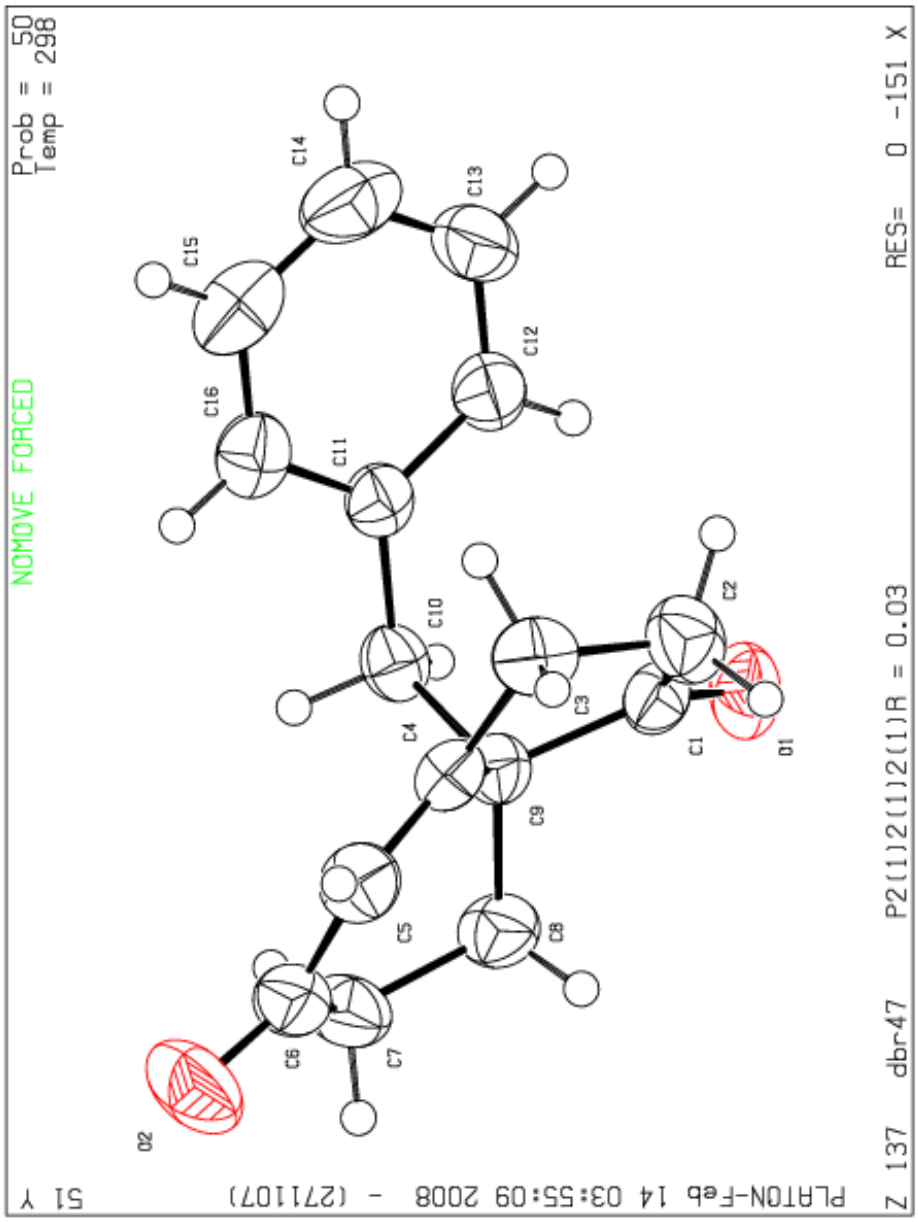
Datablock dbr43 - ellipsoid plot

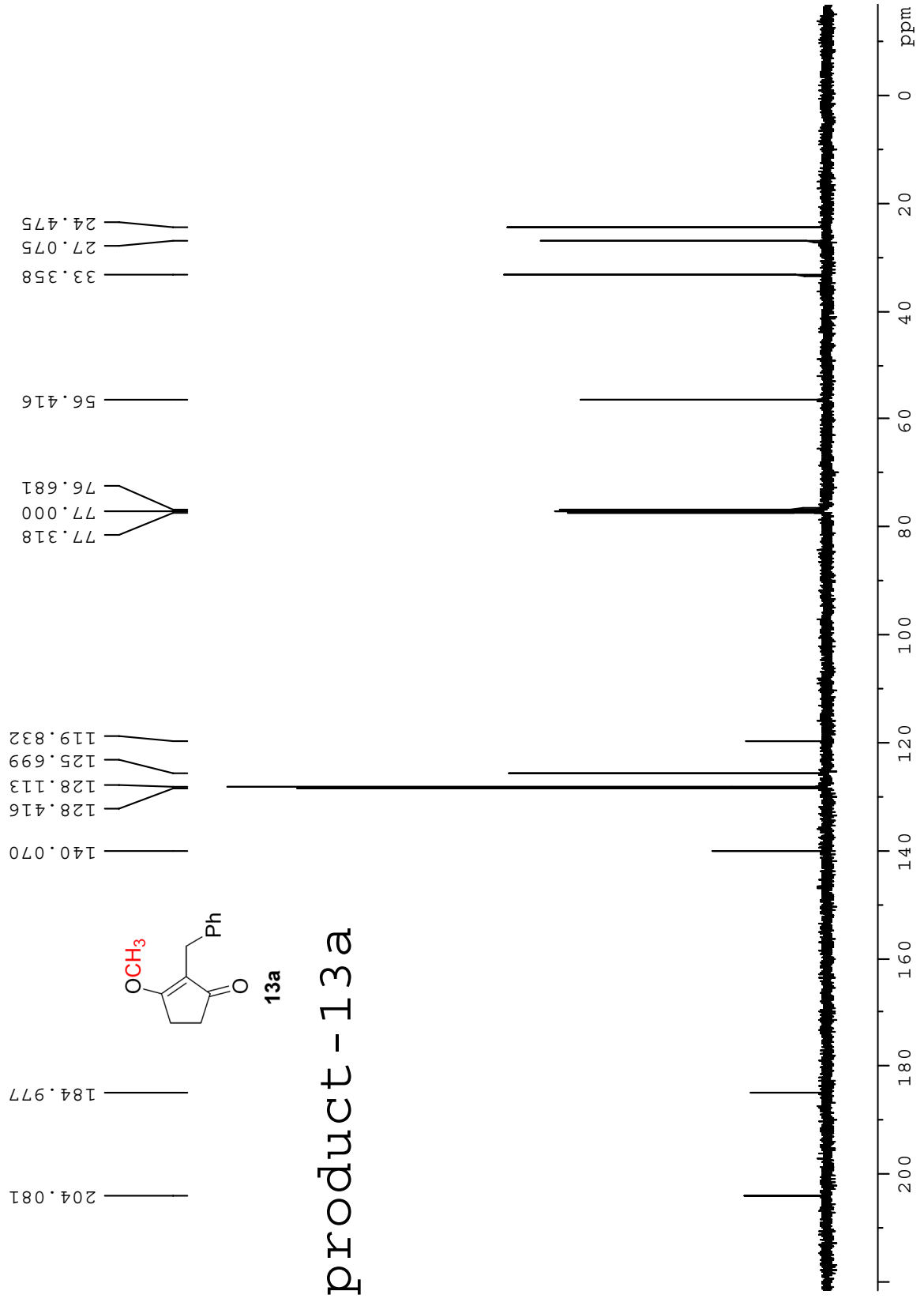

Prob = 50
Temp = 298
NOMOVE FORCED
C11
C10
C12
C9
O1
O2
C8
C7
C5
C6
C4
C1
O4
N1
C3
C2
O3
PLATON-Feb 14 03:42:52 2008 - (271107)
-1 Y
Z 154 dbr43 P2(1)/c R = 0.04
RES= 0 -81 X

Datablock: dbr47 (Product 10a)


```
Bond precision:      C-C = 0.0029 A              Wavelength=0.71073
Cell:        a=7.0365(9)    b=11.9831(16)  c=15.178(2)
             alpha=90       beta=90        gamma=90
Temperature: 298 K
                   Calculated                    Reported
Volume             1279.8(3)                     1279.8(3)
Space group        P 21 21 21                    P2(1)2(1)2(
Hall group         P 2ac 2ab                     ?
Moiety formula     C16 H16 O2                    ?
Sum formula        C16 H16 O2                    C16 H16 O2
Mr                 240.29                        240.29
Dx,g cm-3          1.247                         1.247
Z                  4                             4
Mu (mm-1)          0.081                         0.081
F000               512.0                         512.0
F000'              512.24
h,k,lmax           8,14,18                       8,14,18
Nref               1327( 2261)                   1326
Tmin,Tmax          0.969,0.984                   0.953,0.984
Tmin'              0.953
Correction method= AbsCorr=MULTI-SCAN
Data completeness= 1.00(0.59)  Theta(max)= 25.000
R(reflections)= 0.0332( 1258)     wR2(reflections)= 0.0880( 1326)
S = 1.061             Npar= 163
```

Datablock dbr47 - ellipsoid plot


Prob = 50
Temp = 298
NOMOVE FORCED
RES= 0 -151 X
Z 137 dbr47 P2(1)2(1)2(1)R = 0.03
PLATON-Feb 14 03:55:09 2008 - (271107)
S1 Y
C14
C13
C15
C12
C16
C11
C10
C2
C3
C4
C1
O1
C9
C5
C8
C6
C7
O2


product-13a
13a
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O
O
204.081
184.977
140.070
128.416
128.113
125.699
119.832
77.318
77.000
76.681
56.416
33.358
27.075
24.475
ppm
0
20
40
60
80
100
120
140
160
180
200