Remarkable Influence of Secondary Catalyst Site on Enantioselective Desymmetrization of Cyclopentenedione

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SUPPORTING INFORMATION: PART A

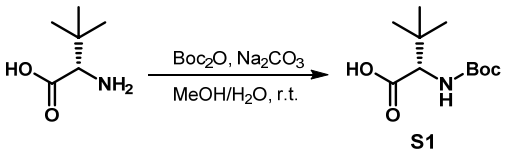
General: Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, ν_{max} in cm^{-1} and the bands are characterized as broad (br), strong (s), medium (m), and weak (w). NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR) and 100 MHz (for ^{13}C-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26, CD_3OD: δ 3.31 for ^{1}H-NMR and $CDCl_3$: δ 77.16, CD_3OD: δ 49.00 for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectrometry was performed on Micromass Q-TOF Micro instrument. Optical rotations were measured on JASCO P-2000 polarimeter. Melting points were measured using ANALAB μ-Thermocal 10 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Enantiomeric ratios were determined by Shimadzu LC-20AD HPLC instrument and SPD-20A UV/Vis detector using stationary phase chiral columns (25 cm × 0.46 cm) in comparison with authentic racemic compounds.

Unless stated otherwise, all reactions were carried out with distilled and dried solvents under an atmosphere of nitrogen or argon, oven (120 °C) dried glassware with standard vacuum-line techniques. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 or 100-200 mesh). Catalyst **I** and **II** were synthesized according to previously reported procedure.[1] α-Angelica lactone was

purchased from Alfa Aesar and used as received and the other butenolides were synthesized according to previously reported procedure.[1,2]

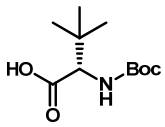
General procedure 1: Preparation of *N*-Boc-(*S*)-*tert*-leucine (S1):

N-Boc-(*S*)-*tert*-leucine was prepared according to the modified literature procedure.[3]



S1

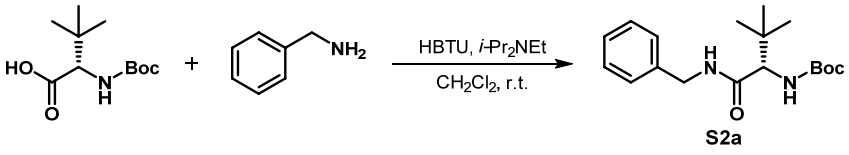
To a solution of (*S*)-*tert*-leucine (1.50 g, 11.43 mmol, 1.0 equiv.) and Na_2CO_3 (1.33 g, 12.57 mmol, 1.1 equiv.) in 45 mL MeOH/H_2O (1:1), was added di-*tert*-butyl dicarbonate (2.70 g, 12.57 mmol, 1.1 equiv.) and the resulting mixture was stirred at r.t. for 20 h. Methanol was removed *in vacuo*. The aqueous solution was acidified with sat. citric acid solution (pH~4) and extracted with CH_2Cl_2 (4 × 30 mL) and Et_2O (2 × 20 mL). The combined layer was washed with brine (2 × 25 mL), dried over anh. Na_2SO_4 and concentrated to obtain a colorless amorphous solid (2.6 g, 11.24 mmol, 98% yield). This was used in the next step without any further purification.



Compound S1: ^{1}H-NMR (400 MHz, CD_3OD): δ 3.95 (s, 1H), 1.45 (s, 9H), 1.00 (s, 9H); **^{13}C-NMR (100 MHz, CD_3OD):** δ 174.9, 158.0, 80.5, 63.4, 34.9, 28.7, 27.1.

General procedure 2: Preparation of *tert*-butyl (*S*)-(1-(benzylamino)-3,3-dimethyl-1-oxobutan-2-yl)carbamate (S2a):

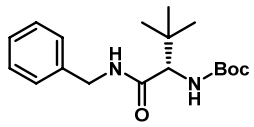
tert-Butyl (*S*)-(1-(benzylamino)-3,3-dimethyl-1-oxobutan-2-yl)carbamate was prepared according to the modified literature procedure.[4]



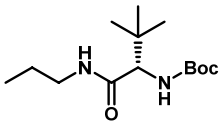
S2a

In an oven-dried 25 mL 2-necked round-bottom flask, *N*-Boc-(*S*)-*tert*-leucine (200 mg, 0.865 mmol, 1.0 equiv.) and HBTU (361 mg, 0.951 mmol, 1.1 equiv.) were taken with 10.0 ml of dry CH_2Cl_2 under argon. Diisopropylethylamine (0.2 mL, 1.038 mmol, 1.2 equiv.), followed by benzylamine (0.17 mL, 0.951 mmol, 1.1 equiv.) were added and the mixture was stirred at r.t.

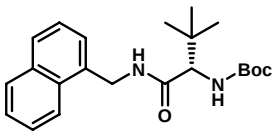
for 18 h. The reaction mixture was diluted with Et_2O (15 ml), washed with 1 M aqueous HCl (2 × 25 mL), sat. $NaHCO_3$ (2 × 20mL) and brine (2 × 20 mL). The organic phase was dried over anh. Na_2SO_4 and concentrated to obtain a pale yellow oil (276 mg, 0.861 mmol, >99% yield). This was used in the next step without any further purification.



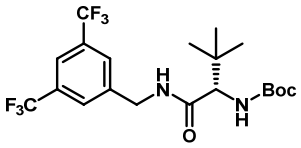
Compound S2a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 5H), 6.46 (br s, 1H), 5.34 (d, *J* = 8.5 Hz, 1H), 4.47 (dd, *J* = 14.8, 5.8 Hz, 1H), 4.35 (dd, *J* = 14.8, 5.8 Hz, 1H), 3.89 (d, *J* = 8.5 Hz, 1H), 1.39 (s, 9H), 0.99 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.1, 156.0, 138.1, 128.7, 127.9, 127.5, 79.8, 62.5, 43.6, 34.6, 28.4, 26.7.



Compound S2b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.02 (br s, 1H), 5.31 (d, *J* = 9.0 Hz, 1H), 3.79 (d, *J* = 9.0 Hz, 1H), 3.28-3.20 (m, 1H), 3.17-3.08 (m, 1H), 1.56-1.45 (m, 2H), 1.41 (s, 9H), 0.97 (s, 9H), 0.89 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.9, 156.0, 79.6, 62.5, 41.2, 34.5, 28.4, 26.7, 22.9, 11.5.

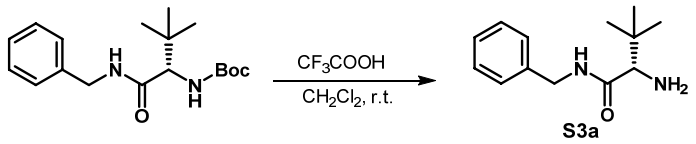


Compound S2c: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.53-7.46 (m, 2H), 7.42-7.36 (m, 2H), 6.18 (br s, 1H), 5.33 (d, *J* = 8.5 Hz, 1H), 4.95 (dd, *J* = 14.4, 5.3 Hz, 1H), 4.77 (dd, *J* = 14.4, 5.3 Hz, 1H), 3.82 (d, *J* = 8.5 Hz, 1H), 1.38 (s, 9H), 0.96 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 170.9, 155.9, 133.9, 133.3, 131.4, 128.8, 128.7, 126.8, 126.6, 126.1, 125.5, 123.6, 79.8, 62.6, 41.7, 34.6, 28.4, 26.7.

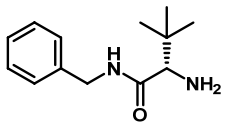


Compound S2d: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.74 (s, 2H), 7.15 (br s, 1H), 5.34 (d, *J* = 9.2 Hz, 1H), 4.62 (dd, *J* = 15.4, 5.8 Hz, 1H), 4.45 (dd, *J* = 15.4, 5.8 Hz, 1H), 3.96 (d, *J* = 9.2 Hz, 1H), 1.38 (s, 9H), 1.01 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 171.8, 156.2, 141.3, 131.9 (q, *J* = 33 Hz), 127.7, 123.3 (q, *J* = 272 Hz), 121.4, 80.1, 62.5, 42.6, 34.5, 28.3, 26.7.

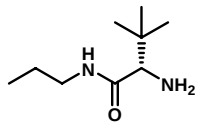
General procedure 3: Preparation of (*S*)-2-amino-*N*-benzyl-3,3-dimethylbutanamide (S3a): (*S*)-2-Amino-*N*-benzyl-3,3-dimethylbutanamide was prepared according to the modified literature procedure.[4]



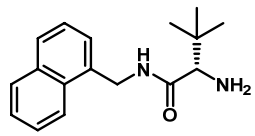
In an oven-dried 25 mL round-bottom flask, *tert*-Butyl (*S*)-(1-(benzylamino)-3,3-dimethyl-1-oxobutan-2-yl)carbamate (250 mg, 0.780 mmol, 1.0 equiv.) was taken with 3.0 mL of dry CH_2Cl_2 under argon. Trifluoroacetic acid (0.6 mL, 7.80 mmol, 10.0 equiv.) was added to it and the resulting solution was stirred at r.t. for 1 h. The reaction was cooled to 0 °C and carefully quenched with 20% aqueous Na_2CO_3 solution (10 mL). Chloroform (15 mL) was added to it and the organic phase was separated from aqueous phase. Organic phase was washed with 20% aqueous Na_2CO_3 solution (2 × 10 mL), brine (2 × 10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a brown oil (170 mg, 0.771 mmol, 98% yield). This was used in the next step without any further purification.



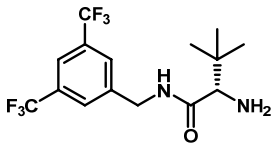
Compound S3a: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34-7.25 (m, 5H), 7.06 (br s, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 3.14 (s, 1H), 1.60 (br s, 2H), 1.00 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.6, 138.6, 128.8, 128.0, 127.5, 64.5, 43.3, 38.7, 26.9.



Compound S3b: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.75 (br s, 1H), 3.26-3.15 (m, 2H), 3.12 (br s, 1H), 1.56-1.47 (m, 2H), 0.99 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 172.0, 64.5, 40.9, 34.1, 26.8, 23.0, 11.6.



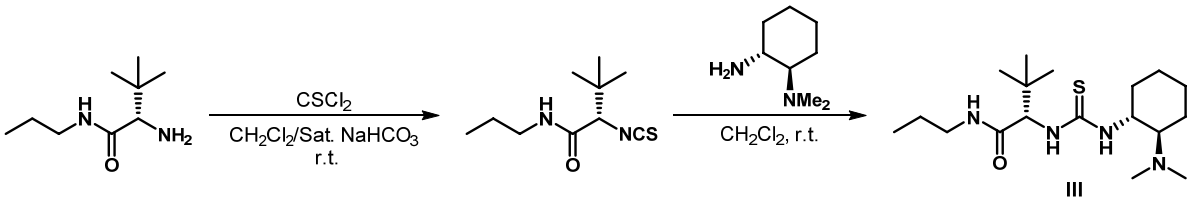
Compound S3c: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.54-7.47 (m, 2H), 7.44-7.39 (m, 2H), 7.03 (br s, 1H), 4.87 (d, *J* = 5.5 Hz, 2H), 3.10 (s, 1H), 1.54 (br s, 2H), 0.97 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 173.3, 133.9, 131.5, 128.8, 128.6, 126.8, 126.6, 126.0, 125.4, 123.8, 64.5, 41.3, 34.3, 26.8.



Compound S3d: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 7.73 (s, 2H), 7.58 (br s, 1H), 4.59 (dd, *J* = 15.4, 6.3 Hz, 1H), 4.49 (dd, *J* = 15.4, 6.3 Hz, 1H), 3.18 (s, 1H), 0.99 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 174.2, 141.7, 131.9 (q, *J* = 33 Hz), 127.8, 123.3 (q, *J* = 272 Hz), 121.4, 64.3, 42.2, 34.4, 26.8.

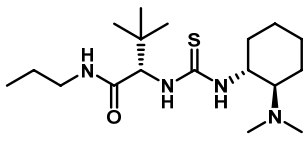
Preparation of bifunctional thiourea catalysts III, IV and V:

General procedure 4: Preparation of catalyst III:



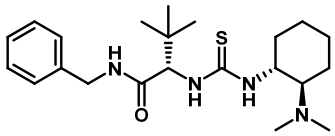
In a 50 mL round bottom-flask (*S*)-2-amino-3,3-dimethyl-*N*-propylbutanamide (300 mg, 1.74 mmol, 1.0 equiv.) was taken with 10 mL CH_2Cl_2 and 10 mL of sat. aqueous $NaHCO_3$ solution and cooled to 0 °C. The stirring was stopped and thiophosgene (0.16 mL, 2.09 mmol, 1.2 equiv.) was added to the organic phase with a syringe. The resulting orange mixture was vigorously stirred at 0 °C for 30 min. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and the organic phase was separated from aqueous phase. Aqueous phase was again extracted with CH_2Cl_2 (2× 10 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated to get a yellowish thick oil (300 mg, 1.40 mmol, 80%). This was used immediately for the thiourea formation without further purification or characterization.

In an oven-dried 25 mL round-bottom flask (1*R*,2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine (166 mg, 1.16 mmol, 1.0 equiv.) was taken with 1.5 mL of dry CH_2Cl_2 under argon. A solution of (*S*)-2-isothiocyanato-3,3-dimethyl-*N*-propylbutanamide (300 mg, 1.40 mmol, 1.2 equiv.) in 1.0 mL of dry CH_2Cl_2 was added slowly and the resulting mixture was stirred at r.t. for 12 h. Solvent was removed *in vacuo* and the residue was purified by silica-gel (100-200 mesh) column chromatography using 100:2:1 CH_2Cl_2/MeOH/Et_3N as eluent to afford an off-white amorphous solid (205 mg, 0.574 mmol, 49% yield).

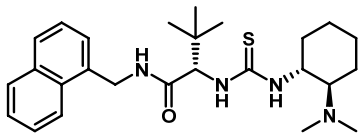


Catalyst III: Off-white amorphous solid; **m.p.** 65-66 °C; **FT-IR (Thin film):** 3056 (w), 2936 (m), 2870 (m), 1651 (s), 1647 (s), 1541 (s), 1457 (m), 1373 (m), 1339 (w), 1233 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.18 (s, 1H), 7.51 (s, 1H), 6.74 (s, 1H), 4.47 (d, *J* = 7.1 Hz, 1H), 3.30 (s, 1H), 3.21-

3.16 (m, 2H), 2.76 (s, 6H), 2.23 (s, 1H), 2.08-2.06 (m, 1H), 1.95-1.93 (m, 1H), 1.78-1.76 (m, 1H), 1.57-1.48 (m, 2H), 1.43-1.35 (m, 5H), 1.08 (s, 9H) 0.90 (t, J = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 182.7, 171.2, 67.7, 53.6, 53.5, 46.0, 41.3, 39.8, 34.0, 32.8, 27.4, 24.3, 23.0, 22.9, 11.7; **HRMS (ESI+):** Calcd. for $C_{18}H_{37}N_4OS$ ($[M+H]^+$): 357.2688, Found: 357.2685; **Optical rotation:** $[\alpha]_D^{24}$ +7.2 (*c* 1.0, $CHCl_3$).



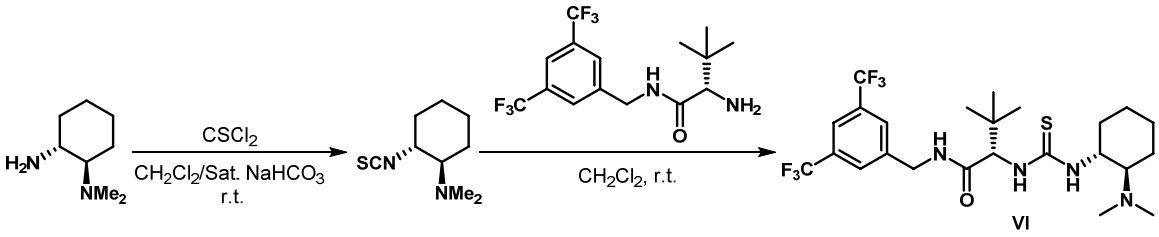
Catalyst IV: Purified by silica gel column chromatography (100:2:1 CH_2Cl_2/MeOH/Et_3N); Off-white amorphous solid (307 mg, 0.758 mmol, 57% yield); **m.p.** 70 °C; **FT-IR (Thin film):** 3065 (w), 2933 (s), 2860 (m), 1653 (s), 1648 (s), 1542 (s), 1456 (m), 1363 (m), 1341 (w), 1234 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.28-7.21 (m, 6H), 6.93 (s, 1H), 6.79 (s, 1H), 4.79 (br s, 1H), 4.48 (dd, J = 14.8, 6.2 Hz, 1H), 4.26 (dd, J = 14.8, 6.2 Hz, 1H), 2.54-2.49 (m, 1H), 2.38-2.36 (m, 1H), 2.24 (s, 6H), 1.87-1.82 (m, 2H), 1.71-1.68 (m, 1H), 1.31-1.17 (m, 5H), 1.05 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 182.6, 171.2, 138.2, 128.6, 127.9, 127.3, 66.8, 66.5, 55.3, 43.4, 40.1, 34.7, 33.0, 27.1, 24.9, 24.6, 22.2; **HRMS (ESI+):** Calcd. for $C_{22}H_{37}N_4OS$ ($[M+H]^+$): 405.2688, Found: 405.2689; **Optical rotation:** $[\alpha]_D^{24}$ –17.0 (*c* 1.0, $CHCl_3$).



Catalyst V: Purified by silica gel column chromatography (100:2:1 CH_2Cl_2/MeOH/Et_3N); Off-white amorphous solid (230 mg, 0.505 mmol, 27% yield); **m.p.** 142-144 °C; **FT-IR (Thin film):** 2937 (s), 2865 (w), 1651 (s), 1645 (s), 1539 (s), 1368 (m), 1304 (s), 1232; **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.11 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.72-7.70 (m, 2H), 7.56 (d, J = 6.5 Hz, 1H), 7.52-7.43 (m, 3H), 7.38-7.34 (m, 2H), 5.17 (d, J = 5.1 Hz, 1H), 4.62-4.57 (m, 2H), 3.06-2.99 (m, 1H), 2.14 (s, 6H), 1.83-1.70 (m, 3H), 1.26-1.20 (m, 6H), 1.09 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 182.5, 171.0, 134.5, 133.6, 131.5, 128.3, 128.0, 127.1, 126.6, 126.0, 125.4, 124.5, 67.7, 67.4, 53.6, 41.1, 38.9, 34.1, 32.7, 29.7, 27.5, 24.2, 22.6; **HRMS (ESI+):** Calcd. for $C_{26}H_{39}N_4OS$ ($[M+H]^+$): 455.2845, Found: 455.2848; **Optical rotation:** $[\alpha]_D^{24}$ –25.9 (*c* 1.0, $CHCl_3$).

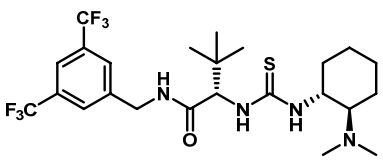
Preparation of bifunctional thiourea catalysts VI and VIa:

General procedure 5: Preparation of catalyst VI:



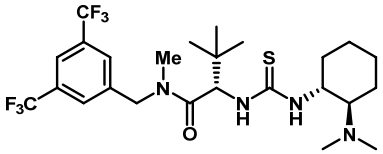
In a 50 mL round bottom-flask (1*R*,2*R*)-*N*,*N*-dimethylcyclohexane-1,2-diamine (185 mg, 1.30 mmol, 1.0 equiv.) was taken with 8 mL CH_2Cl_2 and 8 mL of sat. aqueous $NaHCO_3$ solution and cooled to 0 °C. The stirring was stopped and thiophosgene (0.12 mL, 1.56 mmol, 1.2 equiv.) was added to the organic phase with a syringe. The resulting orange mixture was vigorously stirred at 0 °C for 30 min. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and the organic phase was separated from aqueous phase. Aqueous phase was again extracted with CH_2Cl_2 (2× 10 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated to get a yellowish thick oil (239 mg, 1.30 mmol, quantitative yield). This was used immediately for the thiourea formation without further purification or characterization.

In an oven-dried 25 mL round-bottom flask (*S*)-2-amino-*N*-(3,5-bis(trifluoromethyl)benzyl)-3,3-dimethylbutanamide (356 mg, 1.00 mmol, 1.0 equiv.) was taken with 1.0 mL of dry CH_2Cl_2 under argon. A solution of (1*R*,2*R*)-2-isothiocyanato-*N*,*N*-dimethylcyclohexan-1-amine (239 mg, 1.30 mmol, 1.3 equiv.) in 1.0 mL of dry CH_2Cl_2 was added slowly and the resulting mixture was stirred at r.t. for 40 h. Solvent was removed *in vacuo* and the residue was purified by silica-gel (100-200 mesh) column chromatography using 100:2:1 CH_2Cl_2/MeOH/Et_3N as eluent to afford an off-white amorphous solid. The solid was dissolved in 10 mL of CH_2Cl_2 and washed with water (2 × 15 mL), brine (2 × 15 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure to obtain a better quality catalyst (340 mg, 0.628 mmol, 62% yield).

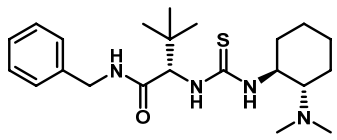


Catalyst VI: Off-white amorphous solid; **m.p.** 82-84 °C; **FT-IR (Thin film):** 2934 (m), 2861 (w), 1653 (m), 1647 (m), 1542 (m), 1379 (m), 1278 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (s, 2H), 7.73 (s, 1H), 7.09 (br s, 2H), 6.63 (br s, 1H), 4.56 (dd, *J* = 15.5, 6.0 Hz, 1H), 4.46 (dd, *J* = 15.5, 6.0 Hz, 1H), 3.80 (br s, 1H), 2.42-2.34 (m, 2H), 2.20 (s, 6H), 1.88-1.81 (m, 2H), 1.71-1.68

(m, 1H), 1.32-1.15 (m, 4H), 1.05 (s, 9H), 0.91-0.87 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 182.8, 171.9, 142.0, 131.5 (q, *J* = 33 Hz), 127.9, 122.0 (q, *J* = 273 Hz), 120.8 (q, *J* = 3.8 Hz), 67.5, 54.0, 42.4, 39.6, 34.2, 32.9, 29.7, 27.4, 26.8, 24.4, 22.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{35}F_6N_4OS$ ($[M+H]^+$): 541.2436, Found: 541.2433; **Optical rotation:** $[\alpha]_D^{24}$ –29.8 (*c* 1.0, $CHCl_3$).



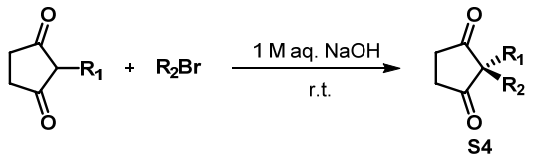
Catalyst VIa: Purified by silica gel column chromatography (100:2:1 CH_2Cl_2/MeOH/Et_3N); Light brown oil (203 mg, 0.366 mmol, 40% yield); **FT-IR (Thin film):** 2934 (s), 2863 (m), 1634 (s), 1538 (m), 1379 (m), 1352 (m), 1279 (s) 1135 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (s, 1H), 7.73 (s, 2H), 7.11 (br s, 1H), 6.86 (br s, 1H), 5.32 (d, *J* = 8.5 Hz, 1H), 4.75 (d, *J* = 14.9 Hz, 1H), 4.60 (d, *J* = 14.9 Hz, 1H), 3.25 (s, 3H), 2.23 (s, 6H), 2.51-2.47 (m, 1H), 2.33-2.30 (m, 1H), 1.88-1.85 (m, 1H), 1.81-1.78 (m, 1H), 1.70-1.67 (m, 1H), 1.25-1.18 (m, 5H), 1.03 (s, 9H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 183.0, 173.4, 139.9, 131.9 (q, *J* = 33 Hz), 128.2, 123.3 (q, *J* = 273 Hz), 121.4 (q, *J* = 3.8 Hz), 66.9, 60.8, 55.5, 51.1, 40.0, 36.7, 35.6, 33.2, 26.9, 25.0, 24.7, 21.9; **HRMS (ESI+):** Calcd. for $C_{25}H_{37}F_6N_4OS$ ($[M+H]^+$): 555.2592, Found: 555.2596; **Optical rotation:** $[\alpha]_D^{23}$ +10.3 (*c* 1.0, $CHCl_3$).

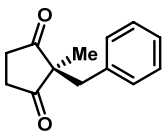


Purified by silica gel column chromatography (100:2:1 CH_2Cl_2/MeOH/Et_3N); Off-white amorphous solid (168 mg, 0.415 mmol, 41% yield); **m.p.** 68-70 °C; **FT-IR (Thin film):** 3065 (w), 2933 (s), 2860 (m), 1651 (s), 1540 (s), 1455 (m), 1363 (m), 1241 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.33-7.24 (m, 6H), 6.55 (s, 1H), 6.40 (s, 1H), 4.79 (br s, 1H), 4.47 (dd, *J* = 14.8, 6.2 Hz, 1H), 4.33 (dd, *J* = 14.8, 6.2 Hz, 1H), 2.26 (s, 6H), 2.23-2.13 (m, 2H), 1.91-1.70 (m, 3H), 1.28-1.15 (m, 4H), 1.05 (s, 9H), 1.01-0.99 (m, 1H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 183.3, 170.8, 138.0, 128.7, 127.8, 127.4, 67.7, 66.6, 57.2, 43.5, 41.0, 34.9, 33.1, 26.9, 25.5, 25.0, 24.6; **HRMS (ESI+):** Calcd. for $C_{22}H_{37}N_4OS$ ($[M+H]^+$): 405.2688, Found: 405.2688; **Optical rotation:** $[\alpha]_D^{23}$ –47.8 (*c* 1.0, $CHCl_3$).

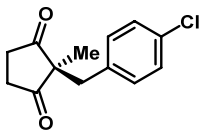
General procedure 6: Preparation of 2,2-disubstituted cyclopentane-1,3-dione (S4):

2,2-Disubstituted cyclopentane-1,3-diones are synthesized by benzylation or allylation of corresponding 2-substituted cyclopentane-1,3-dione according to modified literature procedure.[5]

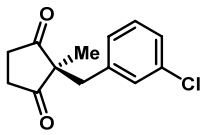




Compound S4a: 2-Methyl cyclopentane-1,3-dione (1.5 g, 13.37 mmol, 1.0 equiv.) was taken with 15.0 mL of 1 M aq. NaOH solution and the suspension was stirred at r.t. for 10 min. To this mixture was added benzyl bromide (3.2 mL, 26.75 mmol, 2.0 equiv.) at once and the resulting biphasic solution was stirred vigorously at r.t. After being stirred for 36 h, the reaction mixture was diluted with 20 mL of EtOAc, organic phase was separated from aqueous phase, aqueous phase was back-extracted with EtOAc (2 × 10mL). The combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (15% EtOAc in petroleum ether) to obtain a white solid (2.42 g, 11.96 mmol, 89% yield); **m.p.** 49-50 °C; **FT-IR (Thin film):** 2971 (w), 2925 (w), 1764 (w), 1718 (s), 1449 (m), 1415 (w), 1370 (w), 1323 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.24-7.19 (m, 3H), 7.04-7.02 (m, 2H), 2.95 (s, 2H), 2.57-2.51 (m, 2H), 2.08-2.01 (m, 2H), 1.20 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.6, 135.9, 129.7, 128.7, 127.3, 58.4, 43.2, 35.9, 20.1.

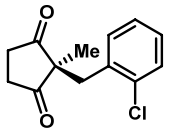


Compound S4b: Purified by silica gel column chromatography (15% EtOAc in petroleum ether); White solid (540 mg, 2.28 mmol, 51% yield); **m.p.** 85-87 °C; **FT-IR (Thin film):** 2975 (m), 2929 (m), 2860 (w), 1762 (m), 1718 (s), 1489 (m), 1448 (m), 1410 (m), 1371 (m), 1324 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.19-7.16 (m, 2H), 6.97-6.95 (m, 2H), 2.91 (s, 2H), 2.64-2.57 (m, 2H), 2.15-2.08 (m, 2H), 1.18 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.1, 134.5, 133.3, 131.2, 128.8, 58.3, 41.6, 35.8, 20.5.

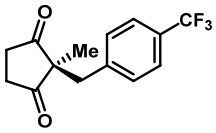


Compound S4c: Purified by silica gel column chromatography (15% EtOAc in petroleum ether); Colorless oil (162 mg, 0.684 mmol, 33% yield); **FT-IR (Thin film):** 2922 (w), 2850 (w), 1722 (s), 1588 (s), 1431 (w), 1323 (m), 1202 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.18-7.12 (m, 2H), 7.03 (s, 1H), 6.92-6.91 (m, 1H),

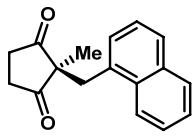
2.91 (s, 2H), 2.69-2.54 (m, 2H), 2.22-2.08 (m, 2H), 1.19 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.8, 138.0, 134.5, 129.9, 129.8, 128.0, 127.6, 58.2, 41.7, 35.8, 20.6.



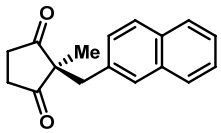
Compound S4d: Purified by silica gel column chromatography (15% EtOAc in petroleum ether); Colorless oil (254 mg, 1.07 mmol, 48% yield); **FT-IR (Thin film):** 2970 (w), 2927 (w), 1764 (m), 1725 (s), 1474 (s), 1449 (w), 1371 (w), 1328 (m), 1280 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.32 (m, 1H), 7.18-7.16 (m, 2H), 7.11-7.09 (m, 1H), 3.10 (s, 2H), 2.67-2.49 (m, 4H), 1.18 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.9, 134.7, 133.4, 132.0, 130.0, 128.9, 126.9, 57.2, 39.1, 35.7, 18.6.



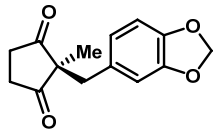
Compound S4e: Purified by silica gel column chromatography (15% EtOAc in petroleum ether); Colorless oil (103 mg, 0.38 mmol, 8.5% yield); **FT-IR (Thin film):** 2920 (w), 1612 (s), 1415 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, J = 7.9 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 3.01 (s, 2H), 2.72-2.57 (m, 2H), 2.21-2.07 (m, 2H), 1.22 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.6, 140.2, 130.3, 129.6 (q, J = 32 Hz), 125.5 (q, J = 4 Hz), 124.1 (q, J = 271 Hz), 58.3, 41.4, 35.7, 20.9.



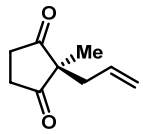
Compound S4f: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Colorless oil (735 mg, 2.91 mmol, 65% yield); **FT-IR (Thin film):** 2920 (m), 2870 (w), 1724 (s), 1604 (s), 1416 (m), 1199 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, J = 8.5 Hz, 1H), 7.80-7.78 (m, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.52-7.43 (m, 2H), 7.36-7.32 (m, 1H), 7.21-7.20 (m, 1H), 3.46 (s, 2H), 2.46-2.31 (m, 2H), 1.86-1.71 (m, 2H), 1.29 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.6, 133.8, 132.1, 131.7, 128.7, 128.4, 128.3, 126.4, 126.0, 125.3, 124.2, 58.3, 39.8, 36.1, 19.9.



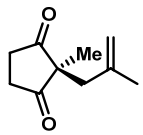
Compound S4g: Purified by silica gel column chromatography (15% EtOAc in petroleum ether); Colorless solid (680 mg, 2.69 mmol, 60% yield); **m.p.** 72-74 °C; **FT-IR (Thin film):** 2969 (w), 2920 (w), 1722 (s), 1598 (m), 1321 (w), 1269 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78-7.74 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.51 (s, 1H), 7.47-7.41 (m, 2H), 7.16 (dd, J = 8.4 Hz, 1.7 Hz, 1H), 3.12 (s, 2H), 2.60-2.45 (m, 2H), 2.08-1.94 (m, 2H), 1.25 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.5, 133.5, 133.4, 132.5, 128.5, 128.3, 127.9, 127.8, 127.7, 126.3, 126.1, 58.6, 43.2, 35.9, 20.4.



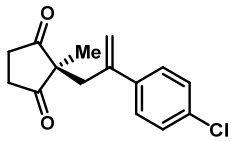
Compound S4h: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); White solid (850 mg, 3.45 mmol, 77% yield); **m.p.** 119-120 °C; **FT-IR (Thin film):** 2967 (w), 2916 (w), 1722 (s), 1502 (m), 1489 (m), 1444 (m), 1238 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 6.64 (d, *J* = 7.8 Hz, 1H), 6.51-6.47 (m, 2H), 5.89 (s, 2H), 2.86 (s, 2H), 2.64-2.50 (m, 2H), 2.23-2.09 (m, 2H), 1.15 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.5, 147.7, 146.8, 129.5, 122.9, 110.1, 108.4, 101.1, 58.5, 42.7, 35.9, 20.1.



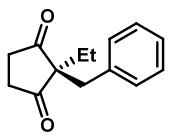
Compound S4i: Colorless oil (265 mg, 1.74 mmol, 98% yield); **FT-IR (Thin film):** 2979 (m), 2931 (m), 2873 (w), 1763 (m), 1724 (s), 1641 (w), 1452 (m), 1418 (m), 1371 (m), 1320 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 5.62-5.52 (m, 1H), 5.07-5.02 (m, 2H), 2.78-2.62 (m, 4H), 2.33 (d, *J* = 7.4 Hz, 2H), 1.10 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.3, 131.6, 119.6, 56.8, 40.2, 35.5, 18.9.



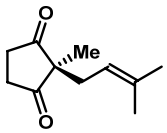
Compound S4j: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Colorless oil (200 mg, 1.20 mmol, 27% yield); **FT-IR (Thin film):** 2972 (m), 2928 (m), 1763 (m), 1725 (s), 1645 (s), 1453 (m), 1420 (m), 1373 (m), 1290 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 4.77 (s, 1H), 4.53 (s, 1H), 2.80-2.63 (m, 4H), 2.39 (s, 2H), 1.60 (s, 3H), 1.10 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.8, 140.8, 115.1, 56.9, 43.8, 35.7, 24.2, 20.7.



Compound S4k: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Colorless oil (115 mg, 0.503 mmol, 11% yield); **FT-IR (Thin film):** 2927 (w), 1723 (s), 1684 (m), 1490 (w), 1418 (w), 1262 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.27-7.25 (m, 2H), 7.22-7.20 (m, 2H), 5.23 (s, 1H), 5.03 (s, 1H), 2.91 (s, 2H), 2.62-2.55 (m, 2H), 2.30-2.23 (m, 2H), 1.12 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.6, 143.2, 138.4, 134.2, 128.6, 128.3, 118.3, 56.6, 41.9, 35.6, 21.1.

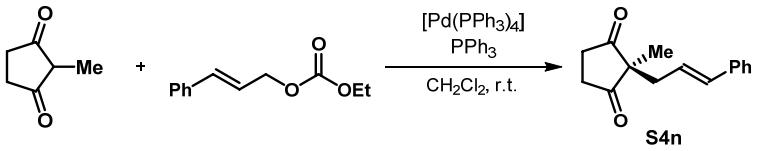


Compound S4l: Purified by silica-gel column chromatography (3-5% EtOAc in petroleum ether); White solid (204 mg, 0.943 mmol, 60% yield); **m.p.** 43-44 °C; **FT-IR (Thin film):** 2968 (m), 2922 (m), 1721 (s), 1496 (w), 1417 (m), 1350 (w), 1247 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.22-7.15 (m, 3H), 7.01-6.99 (m, 2H), 2.92 (s, 2H), 2.45-2.39 (m, 2H), 2.01-1.95 (m, 2H), 1.80 (q, *J* = 7.5 Hz, 2H), 0.77 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 218.3, 135.8, 129.7, 128.7, 127.2, 63.7, 42.5, 36.9, 29.4, 9.4.



Compound S4m: Purified by silica gel column chromatography (8% EtOAc in petroleum ether); Colorless oil (210 mg, 1.16 mmol, 26% yield); **FT-IR (Thin film):** 2972 (m), 2930 (m), 1723 (s), 1454 (m), 1418 (w), 1377 (m), 1315 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 4.91 (t, *J* = 7.7 Hz, 1H), 2.74-2.60 (m, 4H), 2.30 (d, *J* = 7.7 Hz, 2H), 1.64 (s, 3H), 1.55 (s, 3H), 1.08 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.1, 136.8, 117.2, 57.1, 35.7, 35.5, 25.9, 18.5, 17.8.

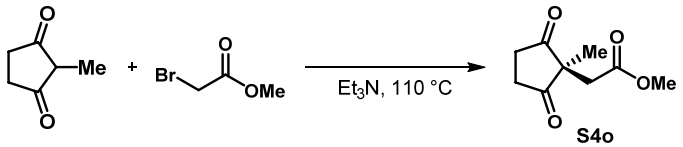
General procedure 7: Preparation of 2-cinnamyl-2-methylcyclopentane-1,3-dione (S4n):



In an oven and vacuum-dried 25 mL round-bottom flask cinnamyl ethyl carbonate (501 mg, 2.43 mmol, 1.0 equiv.) was taken with 10.0 mL of freshly distilled CH_2Cl_2 under positive argon pressure. To this solution was added 2-methyl-cyclopentane-1,3-dione (300 mg, 2.67 mmol, 1.1 equiv.), triphenylphosphine (127 mg, 0.48 mmol, 0.20 equiv.) followed by tetrakis(triphenylphosphine)palladium (0) (140 mg, 0.121 mmol, 0.05 equiv.) and the resulting solution was stirred at r.t. for 15 min. Solvent was removed under vacuum and the residue was purified by silica gel column chromatography (15% EtOAc in petroleum ether) to obtain a white solid (501 mg, 2.19 mmol, 90% yield); **m.p.** 63-65 °C; **FT-IR (Thin film):** 2973 (w), 2928 (m), 1760 (w), 1722 (s), 1449 (m), 1418 (w), 1319 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.28-7.25 (m, 4H), 7.23-7.21 (m, 1H), 6.40 (d, *J* = 15.7 Hz, 1H), 6.01-5.93 (m, 1H), 2.79-2.62 (m, 4H), 2.50 (d, *J* = 7.6 Hz, 2H), 1.15 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.5, 136.7, 134.8, 128.7, 127.8, 126.4, 122.8, 57.2, 39.3, 35.5, 19.1.

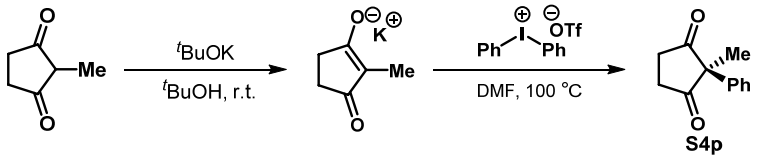
General procedure 8: Preparation of methyl 2-(1-methyl-2,5-dioxocyclopentyl)acetate (S4o):

Methyl 2-(1-methyl-2,5-dioxocyclopentyl)acetate (**S4o**) was synthesized according to modified literature procedure.[5]



In an oven and vacuum-dried 50 mL round-bottom flask, equipped with reflux condenser, 2-methyl-cyclopentane-1,3-dione (500 mg, 4.459 mmol, 1.0 equiv.) was taken with 2.5 mL of distilled triethylamine under positive argon pressure and methyl 2-bromoacetate (2.1 mL, 22.29 mmol, 5.0 equiv.) was added and the resulting solution was stirred at 110 °C. After 18 h reaction mixture was cooled to r.t., diluted with 10 mL of EtOAc and 5 mL of distilled water. Organic phase was separated from aqueous phase, aqueous phase was back-extracted with EtOAc (2 × 5 mL). Combined organic phase was washed with 1 M aq. HCl solution (2 × 10 mL), brine (2 × 10 mL), dried over anh. Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (15-20% EtOAc in petroleum ether) to obtain a colorless oil (160 mg, 0.868 mmol, 19% yield); **FT-IR (Thin film):** 2954 (m), 2924 (m), 1646 (s), 1417 (m), 1260 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** 3.58 (s, 3H), 2.92 (s, 2H), 2.86 (s, 4H), 1.07 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.2, 172.1, 52.9, 52.4, 40.1, 34.8, 20.0.

General procedure 9: Preparation of 2-methyl-2-phenylcyclopentane-1,3-dione (S4p):

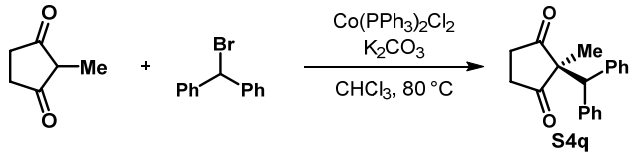


In an oven and vacuum dried round-bottom flask 2-methyl-cyclopentane-1,3-dione (100 mg, 0.89 mmol, 1.0 equiv.) was taken with 8.0 mL of *tert*-butanol under positive argon pressure, potassium *tert*-butoxide (120 mg, 1.07 mmol, 1.2 equiv.) was added and the resulting suspension was stirred at r.t. for 2 h. Solvent was removed under vacuum, the residue was taken with 8.0 mL of dry DMF, diphenyliodonium triflate (920 mg, 2.14 mmol, 2.4 equiv.) was added and the resulting solution was stirred at 100 °C. After 7 h reaction mixture was cooled to r.t., quenched with 10 mL of distilled water and 15 mL of EtOAc was added. Organic phase was separated from aqueous phase, aqueous phase was back-extracted with EtOAc (2 × 10 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The ridue was purified by silica gel column chromatography (5-7% EtOAc in petroleum ether) to obtain a colorless thick oil (102 mg, 0.541 mmol, 60% yield); **FT-IR (Thin film):** 2927 (m), 2869 (m), 1718 (s), 1523 (m), 1262 (m), 1186 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.36-7.26 (m, 3H),

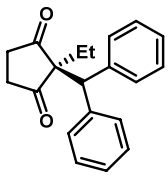
7.22-7.20 (m, 2H), 2.94-2.69 (m, 4H), 1.43 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 213.2, 137.0, 129.5, 128.2, 126.5, 62.2, 35.4, 19.9.

General procedure 10: Preparation of 2-benzhydryl-2-methylcyclopentane-1,3-dione (S4q):

2-Benzhydryl-2-methylcyclopentane-1,3-dione (**S4q**) was synthesized according to modified literature procedure.[6]

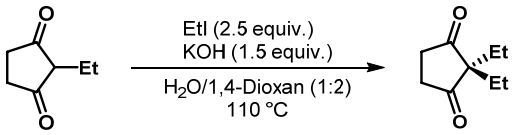


In an oven and vacuum-dried round-bottom flask, equipped with reflux condenser, K_2CO_3 (613 mg, 4.44 mmol, 2.0 equiv.) was taken and heated at 180 °C under vacuum for 3 h, cooled to r.t. and purged with argon. To this was added 2-methyl-cyclopentane-1,3-dione (250 mg, 2.22 mmol, 1.0 equiv.), benzhydryl bromide (823 mg, 3.33 mmol, 1.5 equiv.), $Co(PPh_3)_2Cl_2$ (290 mg, 0.44 mmol, 0.20 equiv.) followed by 11.0 mL of dry $CHCl_3$ and the resulting solution was stirred at 80 °C under argon. After being stirred for 24 h, reaction mixture was cooled to r.t., quenched with 5 mL of distilled water and diluted with 10 mL of CH_2Cl_2. Organic phase was separated from aqueous phase, aqueous phase was back extracted with CH_2Cl_2 (2 × 10 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (2-4% EtOAc in toluene) to obtain a 1:1 mixture of desire product and benzhydrol (310 mg). This mixture was used in next step without further purification or characterization.



Compound S4r: Purified by silica gel column chromatography (2% EtOAc in petroleum ether); White solid (135 mg, 0.461 mmol, 58% yield); **m.p.** 114-115 °C; **FT-IR (Thin film):** 2970 (m), 2920 (m), 1720 (s), 1598 (w), 1496 (m), 1451 (m), 1416 (m), 1254 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.45-7.43 (m, 4H), 7.28-7.24 (m, 4H), 7.21-7.17 (m, 2H), 4.32 (s, 1H), 2.49-2.35 (m, 2H), 2.10-1.99 (m, 2H), 1.72 (q, *J* = 7.5 Hz, 2H), 0.65 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 218.8, 139.7, 129.6, 128.7, 127.2, 65.8, 58.7, 37.3, 28.8, 9.5.

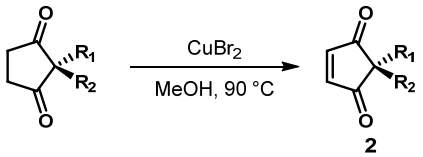
General procedure 11: Preparation of 2,2-diethylcyclopentane-1,3-dione (S4s):

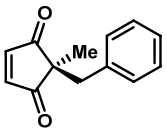


In a 10 mL round-bottom flask, equipped with reflux condenser, 2-ethyl-cyclopentane-1,3-dione (250mg, 1.98 mmol, 1.0 equiv.) and KOH (166 mg, 2.97 mmol, 1.5 equiv.) were taken with 3.0 mL of H_2O/1,4-dioxan (1:2). To this solution was added ethyl iodide (0.4 mL, 4.95 mmol, 2.5 equiv.) and the resulting solution was refluxed at 110 °C. After 12 h, another 1.5 equiv. of KOH and 2.5 equiv. of ethyl iodide was added and reflux was continued for another 12 h. Reaction mixture was cooled to r.t., diluted with 5 mL of CH_2Cl_2 and 5 mL of H_2O and the organic phase was separated from aqueous phase. Aqueous phase was back-extracted with CH_2Cl_2 (2 × 5 mL), combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (3:1 CH_2Cl_2/petroleum ether) to obtain a colorless oil (122 mg, 0.791 mmol, 40% yield); **FT-IR (Thin film):** 2969 (m), 2929 (m), 1720 (s), 1521 (m), 1212 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 2.69 (s, 4H), 1.66 (q, *J* = 7.5 Hz, 4H), 0.75 (t, *J* = 7.5 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 217.7, 62.3, 36.5, 28.0, 9.2.

General procedure 12: Preparation of 2,2-disubstituted cyclopentene-1,3-dione (2):

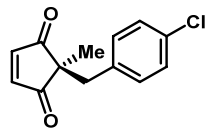
2,2-Disubstituted cyclopentene-1,3-diones (**2**) were synthesized according to modified literature procedure.[7]



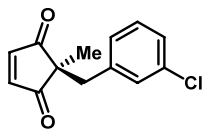


Compound 2a: To a solution of 2-benzyl-2-methylcyclopentane-1,3-dione (2.41 g, 11.92 mmol, 1.0 equiv.) in 86 mL of MeOH was added copper(II) bromide (5.86 g, 26.22 mmol, 2.2 equiv.) and the resulting brown solution was stirred at 90 °C under argon atmosphere. After 1 h the reaction mixture was cooled to r.t., quenched with 20 mL of distilled water followed by 20 mL of 1 M aq. HCl solution, 50 mL of Et_2O was added and the organic phase was separated from aqueous phase. Aqueous phase was back-extracted

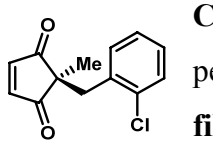
with Et_2O (2 × 20 mL). The combined organic phase was dried over anh. $MgSO_4$ and concentrated under reduced pressure. The crude reaction mixture was purified by silica-gel column chromatography (10% EtOAc in petroleum ether) to obtain a yellow crystalline solid (2.15 g, 10.73 mmol, 90% yield); **m.p.** 116-117 °C; **FT-IR (Thin film):** 2990 (w), 2929 (m), 1735 (m), 1701 (s), 1449 (m), 1374 (m), 1330 (m), 1246 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.16-7.12 (m, 3H), 6.96 (s, 2H), 6.92-6.90 (m, 2H), 2.97 (s, 2H), 1.24 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.3, 148.8, 135.6, 129.8, 128.4, 127.1, 52.6, 40.9, 19.4.



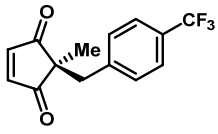
Compound 2b: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Yellow crystalline solid (442 mg, 1.88 mmol, 86% yield); **m.p.** 103-104 °C; **FT-IR (Thin film):** 2973 (m), 2930 (m), 1734 (m), 1699 (s), 1490 (w), 1327 (m), 1259 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.13-7.09 (m, 2H), 7.01 (s, 2H), 6.87-6.84 (m, 2H), 2.94 (s, 2H), 1.23 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.1, 148.9, 134.1, 133.1, 131.2, 128.6, 52.5, 39.9, 19.6.



Compound 2c: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Yellow oil (117 mg, 0.498 mmol, 84% yield); **FT-IR (Thin film):** 2932 (w), 2856 (w), 1750 (m), 1735 (m), 1699 (s), 1570 (m), 1452 (w), 1323 (m), 1255 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.13-7.06 (m, 2H), 7.03 (s, 2H), 6.92-6.91 (m, 1H), 6.82-6.79 (m, 1H), 2.94 (s, 2H), 1.24 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.9, 148.9, 137.6, 134.3, 129.9, 129.7, 128.1, 127.4, 52.4, 40.2, 16.6.

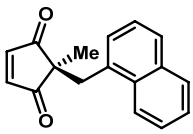


Compound 2d: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Yellow oil (132 mg, 0.562 mmol, 57% yield); **FT-IR (Thin film):** 3066 (m), 2931 (w), 1702 (s), 1457 (m), 1330 (m), 1282 (w), 1207 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.29-7.27 (m, 1H), 7.15-7.09 (m, 4H), 7.06-7.03 (m, 1H), 3.15 (s, 2H), 1.26 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.4, 148.4, 134.6, 133.5, 132.0, 130.0, 128.7, 126.7, 51.5, 37.6, 18.5.

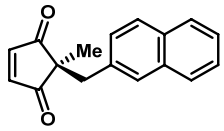


Compound 2e: Purified by silica gel column chromatography (5-10% EtOAc in petroleum ether); Yellow thick oil (69 mg, 0.26 mmol, 69% yield); **FT-IR (Thin film):** 2918 (m), 1611 (s), 1409 (w), 1124 (w); **^{1}H-NMR (400 MHz,**

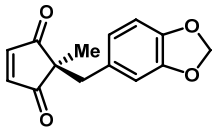
$CDCl_3$): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 2H), 3.02 (s, 2H), 1.26 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.8, 148.9, 139.7, 130.2, 129.5 (q, *J* = 32.4), 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272 Hz), 52.4, 40.1, 19.8.



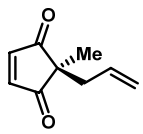
Compound 2f: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow crystalline solid (610 mg, 2.43 mmol, 90% yield); **m.p.** 100-101 °C; **FT-IR (Thin film):** 2966 (w), 2929 (w), 1733 (w), 1702 (s), 1455 (m), 1324 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.51-7.47 (m, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.84 (s, 2H), 3.52 (s, 2H), 1.36 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.4, 148.7, 134.0, 132.1, 131.6, 128.8, 128.6, 128.0, 126.1, 125.8, 125.2, 124.8, 52.7, 37.2, 19.5.



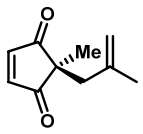
Compound 2g: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow crystalline solid (575 mg, 2.29 mmol, 92% yield); **m.p.** 164-165 °C; **FT-IR (Thin film):** 2967 (w), 2927 (w), 1733 (w), 1702 (s), 1455 (w), 1324 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74-7.70 (m, 2H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.42-7.40 (m, 3H), 7.05-7.02 (m, 1H), 6.91 (s, 2H), 3.15 (s, 2H), 1.30 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.4, 148.9, 133.2, 133.2, 132.4, 128.6, 128.1, 127.9, 127.8, 127.6, 126.2, 125.9, 52.7, 41.1, 19.5.



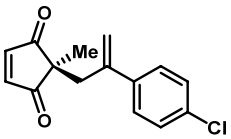
Compound 2h: Purified by silica gel column chromatography (5-10% EtOAc in petroleum ether); Yellow crystalline solid (720 mg, 2.94 mmol, 88% yield); **m.p.** 75-76 °C; **FT-IR (Thin film):** 2969 (w), 2917 (w), 1743 (m), 1702 (s), 1502 (s), 1490 (m), 1444 (m), 1326 (m), 1239 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.02 (s, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.38-6.35 (m, 2H), 5.84 (s, 2H), 2.88 (s, 2H), 1.19 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.4, 148.9, 147.5, 146.6, 129.3, 123.0, 110.1, 108.2, 101.0, 52.7, 40.6, 19.3.



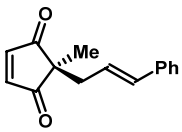
Compound 2i: Purified by silica gel column chromatography (10% EtOAc in petroleum ether); Yellow oil (152 mg, 1.01 mmol, 62% yield); **FT-IR (Thin film):** 2924 (m), 1645 (s), 1262 (m), 1101 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.22 (s, 2H), 5.53-5.42 (m, 1H), 5.03-4.97 (m, 2H), 2.37 (d, *J* = 7.5 Hz, 2H), 1.14 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.3, 148.5, 131.5, 119.8, 50.7, 38.8, 18.7.



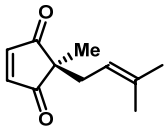
Compound 2j: Purified by silica gel column chromatography (5% Et_2O in petroleum ether); Yellow oil (140 mg, 0.85 mmol, 37% yield); **FT-IR (Thin film):** 2920 (w), 2853 (w), 1622 (s), 1396 (m), 1120 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.21 (s, 2H), 4.70 (s, 1H), 4.54 (s, 1H), 2.39 (s, 2H), 1.48 (s, 3H), 1.12 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.4, 148.6, 140.2, 116.4, 51.1, 42.8, 23.9, 19.9.



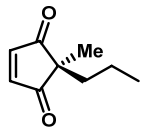
Compound 2k: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow solid (85 mg, 0.326 mmol, 53% yield); **m.p.** 58-60 °C; **FT-IR (Thin film):** 2925 (s), 2854 (m), 1700 (s), 1458 (m), 1323 (m), 1246 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.21-7.19 (m, 2H), 7.09-7.07 (m, 2H), 6.97 (s, 2H), 5.15 (s, 1H), 4.99 (s, 1H), 2.90 (s, 2H), 1.16 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.7, 148.4, 142.9, 138.5, 133.9, 129.2, 128.5, 119.1, 51.2, 40.4, 19.7.



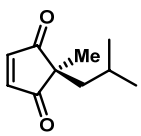
Compound 2l: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow crystalline solid (390 mg, 1.72 mmol, 80% yield); **m.p.** 64-65 °C; **FT-IR (Thin film):** 2970 (w), 2930 (w), 1745 (m), 1705 (s), 1492 (m), 1451 (m), 1323 (m), 1238 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34-7.20 (m, 7H), 6.35 (d, *J* = 15.6 Hz, 1H), 5.90-5.83 (m, 1H), 2.53 (d, *J* = 7.6 Hz, 2H), 1.19 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.3, 148.5, 136.7, 134.5, 128.5, 127.6, 126.3, 122.8, 51.0, 37.9, 18.7.



Compound 2m: Purified by silica gel column chromatography (5% Et_2O in petroleum ether); Yellow oil (59 mg, 0.33 mmol, 40% yield); **FT-IR (Thin film):** 2925 (w), 1641 (s), 1402 (w), 1171 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.21 (s, 2H), 4.78 (t, *J* = 7.8 Hz, 1H), 2.35 (d, *J* = 7.8 Hz, 2H), 1.57 (s, 3H), 1.53 (s, 3H), 1.12 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.9, 148.6, 136.4, 117.5, 50.9, 33.5, 25.9, 18.7, 17.7.

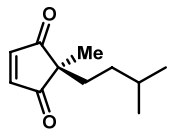


Compound 2n: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow oil (110 mg, 0.722 mmol, 41% yield); **FT-IR (Thin film):** 2961 (m), 2921 (m), 1633 (s), 1412 (m), 1259 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.21 (s, 2H), 1.62-1.58 (m, 2H), 1.10 (s, 3H), 1.06-0.99 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.2, 148.4, 50.7, 37.0, 19.2, 18.3, 14.4.

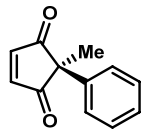


Compound 2o: Purified by silica gel column chromatography (5% Et_2O in petroleum ether); Yellow oil (45 mg, 0.270 mmol, 44% yield); **FT-IR (Thin film):**

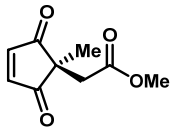
2921 (m), 1633 (s), 1400 (w), 1121 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.26 (s, 2H), 1.67 (d, *J* = 6.6 Hz, 2H), 1.20 (m, 1H), 1.13 (s, 3H), 0.74 (d, *J* = 6.6 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.1, 148.3, 50.5, 43.7, 25.5, 24.0, 21.5.



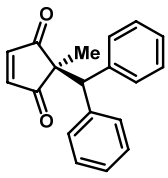
Compound 2p: Purified by silica gel column chromatography (5% Et_2O in petroleum ether); Light yellow oil with slight Et_2O as solvent impurity (60 mg, 0.332 mmol, 46% yield); **FT-IR (Thin film):** 2922 (m), 1633 (s), 1401 (m), 1259 (m), 1119 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.23 (s, 2H), 1.67-1.63 (m, 3H), 1.41-1.36 (m, 2H), 1.13 (s, 3H), 0.79 (d, *J* = 6.6 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.3, 148.4, 50.6, 33.7, 32.8, 28.4, 22.3, 19.3.



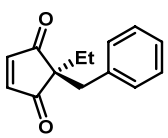
Compound 2q: Purified by silica gel column chromatography (2-4% EtOAc in petroleum ether); Yellow oil (122 mg, 0.655 mmol, 89% yield); **FT-IR (Thin film):** 2930 (m), 1637 (s), 1406 (m), 1262 (m), 1089 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.34 (s, 2H), 7.32-7.26 (m, 5H), 1.57 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.1, 148.5, 136.8, 128.9, 127.9, 126.5, 54.6, 19.8.



Compound 2r: Purified by silica gel column chromatography (5% EtOAc in petroleum ether); Yellow crystalline solid (110 mg, 0.603 mmol, 74% yield); m.p. 74-76 °C; **FT-IR (Thin film):** 2957 (m), 2933 (m), 1707 (s), 1437 (m), 1353 (m), 1210 (s); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.29 (s, 2H), 3.57 (s, 3H), 2.88 (s, 2H), 1.16 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.8, 170.9, 147.6, 52.1, 47.9, 37.5, 20.7.

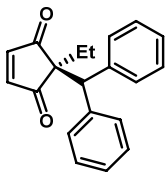


Compound 2s: Purified by silica gel column chromatography (2% EtOAc in petroleum ether); Yellow crystalline solid (110 mg, 0.398 mmol, 40% yield over 2 steps); **m.p.** 112-113 °C; **FT-IR (Thin film):** 2969 (w), 2879 (m), 1700 (s), 1459 (m), 1322 (w), 1259 (m), 1232 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.41-7.39 (m, 4H), 7.26-7.22 (m, 4H), 7.18-7.14 (m, 2H), 6.98 (s, 2H), 4.37 (s, 1H), 1.17 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.6, 148.6, 139.6, 129.7, 128.6, 127.1, 57.4, 55.2, 18.9.

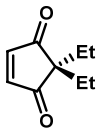


Compound 2t: Purified by silica-gel column chromatography (2-4% EtOAc in petroleum ether); Yellow crystalline solid (130 mg, 0.607 mmol, 65% yield); **m.p.** 116-117 °C; **FT-IR (Thin film):** 2966 (w), 2937 (m), 1700 (s), 1449 (m), 1447 (m), 1322 (w), 1248 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.16-7.12 (m, 3H), 7.02 (s, 2H),

6.91-6.89 (m, 2H), 2.96 (s, 2H), 1.83 (q, J = 7.5 Hz, 2H), 0.72 (t, J = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.7, 150.3, 135.5, 129.9, 128.4, 127.0, 57.7, 40.4, 27.7, 9.1.



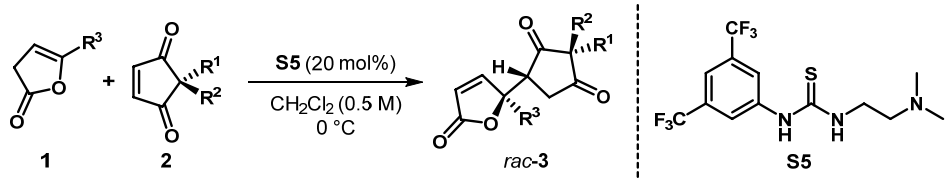
Compound 2u: Purified by silica gel column chromatography (1% EtOAc in petroleum ether); Yellow crystalline solid (72 mg, 0.248 mmol, 58% yield); **m.p.** 135-137 °C; **FT-IR (Thin film):** 2967 (w), 2929 (m), 1700 (s), 1439 (m), 1330 (m), 1231 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.40-7.39 (m, 4H), 7.25-7.21 (m, 4H), 7.17-7.13 (m, 2H), 7.03 (s, 2H), 4.33 (s, 1H), 1.76 (q, J = 7.5 Hz, 2H), 0.60 (t, J = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 207.9, 150.3, 139.6, 129.7, 128.6, 127.0, 60.4, 57.5, 26.6, 9.2.



Compound 2v: Purified by silica gel column chromatography (10% CH_2Cl_2 in petroleum ether); Yellow oil (60 mg, 0.394 mmol, 50% yield); **FT-IR (Thin film):** 2961 (w), 2929 (m), 1704 (s), 1518 (s), 1161 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.30 (s, 2H), 1.69 (q, J = 7.5 Hz, 4H), 0.68 (t, J = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 208.6, 150.0, 56.0, 27.1, 9.1. [*Caution*: Compound **2v** is volatile and hence solvent should be removed below 35 °C temperature and low pressure after work-up and column.]

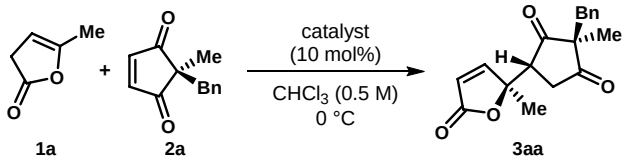
General procedure 13: Preparation of racemic desymmetrized products (*rac*-3):

Racemic products were prepared using the achiral bifunctional catalyst **S5**.

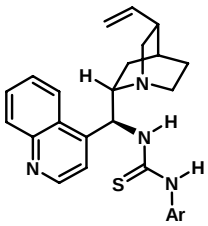


In a glass-vial **2** (0.133 mmol, 1.2 equiv.) and **S5** (0.022 mmol, 0.2 equiv.) was taken with 0.1 mL of CH_2Cl_2 under positive argon pressure and the mixture was cooled to 0 °C. To this was added a solution of **1** (0.111 mmol, 1.0 equiv.) in 0.1 mL of CH_2Cl_2 and the resulting solution was stirred at 0 °C until TLC reveals the complete consumption of **1**. The crude mixture was purified by preparative TLC (Merck silica-gel 60 F_{254} pre-coated plates of 0.25 mm thickness) to obtain the racemic desymmetrized products (*rac*-**3**).

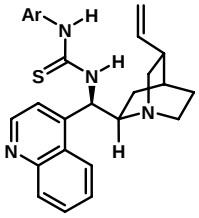
Catalyst optimization for enantioselective desymmetrization of 2-benzyl-2-methylcyclopent-4-ene-1,3-dione (2a):



1a 1.0 equiv. **2a** 1.5 equiv. **3aa**

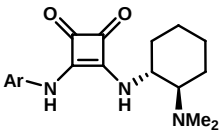


50 h, 18:1 dr
84% yield, 34:66 er

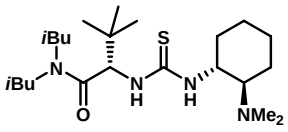


50 h, 16:1 dr
80% yield, 62.5:37.5 er

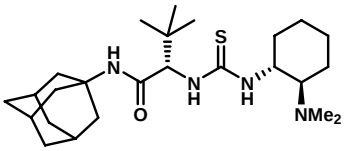
Ar = 3,5-$(CF_3)_2C_6H_3$



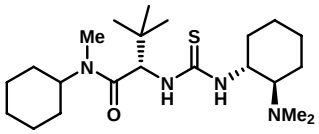
72 h, 2:1 dr
80% yield, 58:42 er



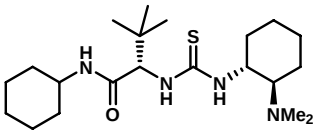
68 h, >20:1 dr
80% yield, 57.5:42.5 er



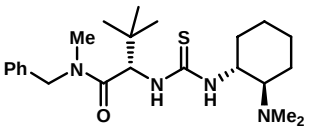
48 h, >20:1 dr
92% yield, 69:31 er



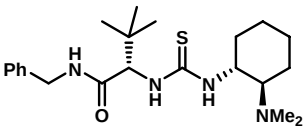
48 h, >20:1 dr
87% yield, 51:49 er



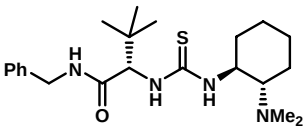
48 h, 10:1 dr
94% yield, 84.5:15.5 er



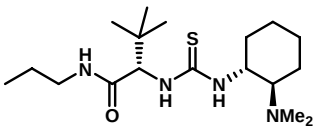
72 h, 15:1 dr
80% yield, 53:47 er



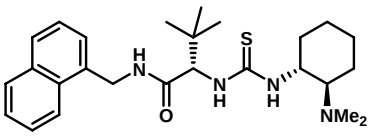
40 h, >20:1 dr
92% yield, 96:4 er



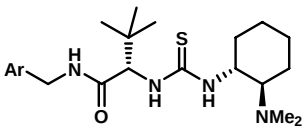
48 h, 4:1 dr
80% yield, 28:72 er



50 h, >20:1 dr
92% yield, 86:14 er

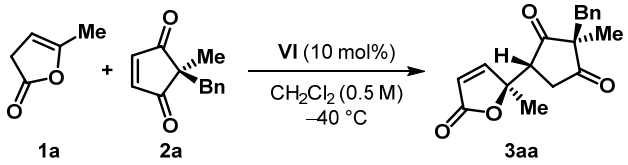


60 h, >20:1 dr
55% yield, 93:7 er

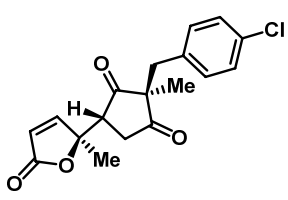


17 h, >20:1 dr
94% yield, 97:3 er

Typical procedure for the catalytic enantioselective desymmetrization of prochiral 2-benzyl-2-methylcyclopent-4-ene-1,3-dione 2a:

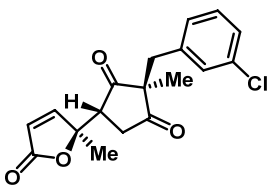


In an oven and vacuum-dried Schlenk tube 2-benzyl-2-methylcyclopent-4-ene-1,3-dione **2a** (48.0 mg, 0.240 mmol, 1.2 equiv.) and catalyst **VI** (10.8 mg, 0.020 mmol, 0.10 equiv.) were taken with 0.2 mL CH_2Cl_2 under a positive argon pressure and the mixture was cooled to –40 °C. A solution of α-Angelica lactone **1a** (18 μL, 0.20 mmol, 1.0 equiv.) in 0.2 mL of CH_2Cl_2 was added to it and the resulting mixture was stirred at –40 °C until TLC (30% EtOAc in petroleum ether) revealed complete conversion of **1a** (22 h). The reaction mixture was brought to r.t. and purified by silica-gel flash column chromatography (25% EtOAc in petroleum ether) to obtain **3aa** as a colorless thick oil (56 mg, 0.188 mmol, 94% yield); **FT-IR (Thin film):** 2933 (m), 2871(w), 1752 (s), 1577 (w), 1443 (m), 1219 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 5.6 Hz, 1H), 7.21-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.03 (d, *J* = 5.6 Hz, 1H), 3.00 (d, *J* = 12.8 Hz, 1H), 2.92 (d, *J* = 12.8 Hz, 1H), 2.44 (dd, *J* = 17.9, 6.3 Hz, 1H), 2.19-2.07 (m, 2H), 1.43 (s, 3H), 1.24 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.3, 214.6, 171.3, 159.6, 135.5, 129.5, 128.8, 127.6, 120.9, 87.4, 59.6, 53.8, 44.0, 38.5, 20.2, 19.9; **HRMS (ESI+):** Calcd. for $C_{18}H_{18}O_4Na$ ($[M+Na]^+$): 321.1103, Found: 321.1103; **Optical rotation:** $[\alpha]_D^{24}$ +32.2 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak ID column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 13.4 min, τ_{major} = 14.7 min). See Supporting Information: Part B for HPLC chromatograms. [*Caution*: Products **3** are sensitive to silica-gel and rapid chromatographic purification is necessary to ensure high yield.]

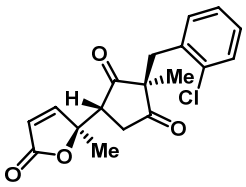


Compound 3ab: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (62 mg, 0.186 mmol, 94% yield); **FT-IR (Thin film):** 2931 (m), 1761 (s), 1725 (s), 1492 (m), 1455 (m), 1374 (w), 1249 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 5.6 Hz, 1H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.04 (d, *J* = 5.6 Hz, 1H), 2.93 (d, *J* = 13.0 Hz, 1H), 2.88 (d, *J* = 13.0 Hz, 1H), 2.43 (dd, *J* = 16.8, 5.3 Hz, 1H), 2.26-2.14 (m, 2H), 1.47 (s, 3H), 1.22 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.8, 214.1, 171.2,

159.3, 134.0, 133.5, 131.0, 128.9, 121.2, 87.4, 59.4, 53.3, 42.3, 38.2, 20.6, 20.2; **HRMS (ESI+):** Calcd. for $C_{18}H_{17}ClO_4Na$ ($[M+Na]^+$): 355.0713, Found: 355.0719; **Optical rotation:** $[\alpha]_D^{21}$ +13.2 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 98.5:1.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 9.5 min, τ_{major} = 11.6 min). See Supporting Information: Part B for HPLC chromatograms.

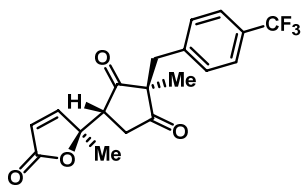


Compound 3ac: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); White solid (65 mg, 0.195 mmol, 97% yield); m.p. 86-87 °C; **FT-IR (Thin film):** 2924 (m), 1759 (s), 1725 (s), 1596 (w), 1572 (w), 1450 (w), 1374 (w), 1321 (w), 1205 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 5.6 Hz, 1H), 7.17-7.11 (m, 2H), 6.96 (s, 1H), 6.86-6.84 (m, 1H), 6.04 (d, *J* = 5.6 Hz, 1H), 2.93 (d, *J* = 13.0 Hz, 1H), 2.87 (d, *J* = 12.7 Hz, 1H), 2.49-2.40 (m, 1H), 2.26-2.18 (m, 2H), 1.47 (s, 3H), 1.22 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.5, 213.8, 171.2, 159.4, 137.6, 134.5, 130.0, 129.6, 127.9, 127.8, 121.1, 87.3, 59.2, 53.5, 42.5, 38.2, 20.4, 20.2; **HRMS (ESI+):** Calcd. for $C_{18}H_{17}ClO_4Na$ ($[M+Na]^+$): 355.0713, Found: 355.0713; **Optical rotation:** $[\alpha]_D^{24}$ +23.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 15.1 min, τ_{major} = 44.8 min). See Supporting Information: Part B for HPLC chromatograms.

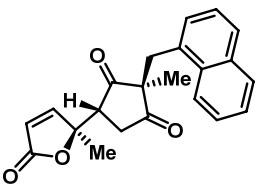


Compound 3ad: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); White solid (58 mg, 0.174 mmol, 87% yield); m.p. 143-145 °C; **FT-IR (Thin film):** 2932 (m), 2871(w), 1759 (s), 1726 (s), 1572 (w), 1455 (w), 1373 (w), 1337 (w), 1277 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 5.6 Hz, 1H), 7.32-7.30 (m, 1H), 7.21-7.15 (m, 2H), 7.09-7.07 (m, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 3.09 (s, 2H), 2.76-2.57 (m, 3H), 1.41 (s, 3H), 1.21 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 213.4, 213.0, 171.4, 159.9, 134.6, 132.8, 132.2, 130.0, 129.3, 127.1, 120.8, 87.5, 58.3, 53.7, 39.9, 38.5, 19.7, 18.4; **HRMS (ESI+):** Calcd. for $C_{18}H_{17}ClO_4Na$ ($[M+Na]^+$): 355.0713, Found: 355.0710; **Optical rotation:** $[\alpha]_D^{24}$ +10.2 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20

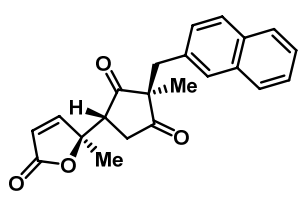
°C, 210 nm, τ_{minor} = 21.5 min, τ_{major} = 40.8 min). See Supporting Information: Part B for HPLC chromatograms.



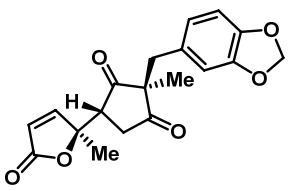
Compound 3ae: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (38 mg, 0.103 mmol, 94% yield); **FT-IR (Thin film):** 2929 (m), 1763 (s), 1727 (s), 1457 (w), 1420 (w), 1375 (m), 1326 (s), 1250 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 5.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 5.6 Hz, 1H), 3.00 (d, *J* = 7.3 Hz, 2H), 2.45 (dd, *J* = 17.8, 6.6 Hz, 1H), 2.30-2.16 (m, 2H), 1.51 (s, 3H), 1.27 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.4, 213.6, 171.2, 159.2, 139.8, 130.2, 129.7 (q, *J* = 33 Hz), 125.6 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 271 Hz), 121.3, 87.3, 59.3, 53.3, 42.2, 38.0, 20.7, 20.6; **HRMS (ESI+):** Calcd. for $C_{19}H_{17}F_3O_4Na$ ($[M+Na]^+$): 389.0977, Found: 389.0978; **Optical rotation:** $[\alpha]_D^{24}$ +21.1 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IC column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{major} = 10.5 min, τ_{minor} = 15.5 min). See Supporting Information: Part B for HPLC chromatograms.



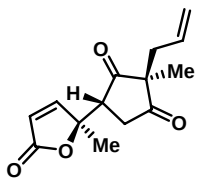
Compound 3af: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); White solid (66 mg, 0.189 mmol, 94% yield); m.p. 116-117 °C; **FT-IR (Thin film):** 2929 (m), 2856 (w), 1763 (s), 1725 (s), 1596 (w), 1455 (w), 1373 (w), 1323 (w), 1212 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.78-7.76 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.50-7.42 (m, 3H), 7.33-7.29 (m, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 5.87 (d, *J* = 5.6 Hz, 1H), 3.45 (s, 2H), 2.30 (dd, *J* = 18.9, 7.1 Hz, 1H), 1.88 (dd, *J* = 18.9, 11.2 Hz, 1H), 1.78 (dd, *J* = 11.2, 7.1 Hz, 1H), 1.33 (s, 3H), 1.30 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.5, 171.2, 159.5, 133.8, 131.6, 131.4, 128.8, 128.6, 128.4, 126.5, 126.1, 125.3, 123.9, 120.5, 87.2, 59.5, 53.9, 40.5, 38.8, 19.8, 19.7; **HRMS (ESI+):** Calcd. for $C_{22}H_{20}O_4Na$ ($[M+Na]^+$): 371.1259, Found: 371.1259; **Optical rotation:** $[\alpha]_D^{24}$ –1.7 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 15.0 min, τ_{major} = 22.1 min). See Supporting Information: Part B for HPLC chromatograms.



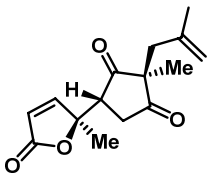
Compound 3ag: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (68 mg, 0.195 mmol, 97% yield); **FT-IR (Thin film):** 2924 (m), 1761 (s), 1725 (s), 1601 (w), 1451 (m), 1372 (m), 1321 (w), 1216 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76-7.71 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 5.6 Hz, 1H), 7.45-7.43 (m, 3H), 7.10-7.07 (m, 1H), 5.97 (d, *J* = 5.6 Hz, 1H), 3.14 (d, *J* = 12.8 Hz, 1H), 3.09 (d, *J* = 12.8 Hz, 1H), 2.38 (dd, *J* = 16.0, 4.1 Hz, 1H), 2.14-2.06 (m, 2H), 1.44 (s, 3H), 1.30 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.6, 171.2, 159.4, 133.3, 133.0, 132.4, 128.5, 128.4, 127.8, 127.7, 127.4, 126.5, 126.2, 121.0, 87.4, 59.6, 53.4, 43.9, 38.4, 20.5, 20.1; **HRMS (ESI+):** Calcd. for $C_{22}H_{20}O_4Na$ ($[M+Na]^+$): 371.1259, Found: 371.1256; **Optical rotation:** $[\alpha]_D^{24}$ –12.3 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 22.3 min, τ_{major} = 27.2 min). See Supporting Information: Part B for HPLC chromatograms.



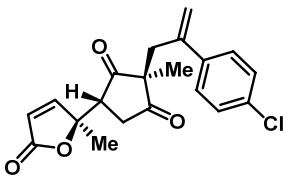
Compound 3ah: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (64 mg, 0.186 mmol, 93% yield); **FT-IR (Thin film):** 2919 (w), 2781 (w), 1759 (s), 1727 (s), 1606 (w), 1505 (m), 1489 (m), 1444 (m), 1373 (m), 1322 (w), 1244 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.63 (d, *J* = 5.6 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.42-6.39 (m, 2H), 6.03 (d, *J* = 5.6 Hz, 1H), 5.88 (s, 2H), 2.87 (d, *J* = 13.0 Hz, 1H), 2.81 (d, *J* = 13.0 Hz, 1H), 2.50-2.41 (m, 1H), 2.29-2.20 (m, 2H), 1.43 (s, 3H), 1.18 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.3, 214.6, 171.3, 159.6, 147.8, 146.9, 128.9, 122.7, 120.9, 109.8, 108.4, 101.1, 87.4, 59.6, 53.7, 43.5, 38.4, 20.2, 19.8; **HRMS (ESI+):** Calcd. for $C_{19}H_{18}O_6Na$ ($[M+Na]^+$): 365.1001, Found: 365.1001; **Optical rotation:** $[\alpha]_D^{24}$ +8.9 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (85:15 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 29.2 min, τ_{major} = 42.0 min). See Supporting Information: Part B for HPLC chromatograms.



Compound 3ai: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (44 mg, 0.177 mmol, 88% yield); **FT-IR (Thin film):** 2924 (w), 2854 (w), 1755 (s), 1727 (s), 1644 (m), 1455 (m), 1373 (m), 1217 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 5.57-5.47 (m, 1H), 5.07-5.01 (m, 2H), 2.91 (dd, *J* = 10.6, 8.1 Hz, 1H), 2.81 (dd, *J* = 19.0, 10.6 Hz, 1H), 2.65 (dd, *J* = 19.0, 8.1 Hz, 1H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.49 (s, 3H), 1.13 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.1, 213.4, 171.4, 159.8, 131.1, 121.0, 120.5, 87.5, 57.8, 53.5, 41.0, 38.0, 20.2, 18.6. [^{1}H and ^{13}C peaks correspond to major diastereoisomer]; **HRMS (ESI+):** Calcd. for $C_{14}H_{16}O_4Na$ ($[M+Na]^+$): 271.0946, Found: 271.0946; **Optical rotation:** $[\alpha]_D^{25}$ +47.8 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 55.5 min, τ_{major} = 63.9 min). See Supporting Information: Part B for HPLC chromatograms.

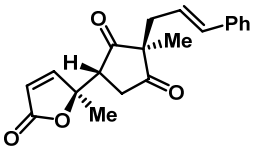


Compound 3aj: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (43 mg, 0.164 mmol, 81% yield); **FT-IR (Thin film):** 2976 (w), 2933 (w), 1749 (s), 1733 (s), 1540 (m), 1456 (m), 1213 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 5.6 Hz, 1H), 6.09 (d, *J* = 5.6 Hz, 1H), 4.77 (s, 1H), 4.55 (s, 1H), 2.91 (dd, *J* = 10.8, 8.3 Hz, 1H), 2.81 (dd, *J* = 19.0, 10.8 Hz, 1H), 2.64 (dd, *J* = 19.0, 8.3 Hz, 1H), 2.37 (q, *J* = 13.4 Hz, 2H), 1.57 (s, 3H), 1.50 (s, 3H), 1.13 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.5, 213.9, 171.5, 159.8, 140.5, 121.0, 115.8, 87.5, 58.1, 54.0, 44.9, 38.2, 24.2, 20.2, 20.1; **HRMS (ESI+):** Calcd. for $C_{15}H_{18}O_4Na$ ($[M+Na]^+$): 285.1103, Found: 285.1105; **Optical rotation:** $[\alpha]_D^{24}$ +45.2 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 9.9 min, τ_{major} = 12.9 min). See Supporting Information: Part B for HPLC chromatograms.

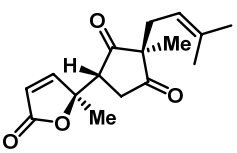


Compound 3ak: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (40 mg, 0.111 mmol, 74% yield); **FT-IR (Thin film):** 2929 (w), 2855 (w), 1761 (s), 1726 (s), 1491 (w), 1458 (m), 1375(m), 1216 (m); **^{1}H-NMR (400 MHz,**

$CDCl_3$): δ 7.57 (d, *J* = 5.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.17-7.14 (m, 2H), 6.03 (d, *J* = 5.6 Hz, 1H), 5.24 (s, 1H), 5.04 (s, 1H), 2.93-2.85 (m, 2H), 2.48-2.45 (m, 2H), 2.40-2.33 (m, 1H), 1.38 (s, 3H), 1.15 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.2, 213.3, 171.4, 159.7, 142.6, 138.0, 134.4, 128.7, 128.3, 120.8, 118.9, 87.3, 57.7, 53.9, 42.6, 38.2, 20.5, 19.6; **HRMS (ESI+):** Calcd. for $C_{20}H_{19}ClO_4Na$ ($[M+Na]^+$): 381.0870, Found: 381.0868; **Optical rotation:** $[\alpha]_D^{24}$ +15.9 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 18.7 min, τ_{major} = 36.6 min). See Supporting Information: Part B for HPLC chromatograms.

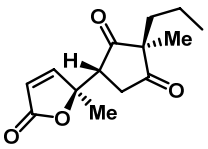


Compound 3al: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (56 mg, 0.172 mmol, 86% yield); **FT-IR (Thin film):** 2977 (w), 2931 (w), 1759 (s), 1724 (s), 1537 (w), 1455 (w), 1317(w), 1211 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 5.6 Hz, 1H), 7.27-7.23 (m, 3H), 7.22-7.21 (m, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 5.91 (dt, *J* = 15.7, 7.4 Hz, 1H), 2.90 (dd, *J* = 10.8, 7.6 Hz, 1H), 2.79 (dd, *J* = 19.0, 10.8 Hz, 1H), 2.64 (dd, *J* = 19.0, 7.6 Hz, 1H), 2.50 (d, *J* = 7.4 Hz, 2H), 1.52 (s, 3H), 1.20 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.2, 213.6, 171.3, 159.6, 136.4, 135.3, 128.7, 127.9, 126.3, 122.1, 121.1, 87.5, 58.1, 53.2, 40.1, 38.0, 20.4, 18.8; **HRMS (ESI+):** Calcd. for $C_{20}H_{20}O_4Na$ ($[M+Na]^+$): 347.1259, Found: 347.1258; **Optical rotation:** $[\alpha]_D^{24}$ +4.9 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 13.4 min, τ_{major} = 17.2 min). See Supporting Information: Part B for HPLC chromatograms.

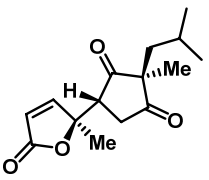


Compound 3am: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (24 mg, 0.086 mmol, 78% yield); **FT-IR (Thin film):** 2934 (m), 2872 (w), 1759 (s), 1726 (s), 1541 (w), 1456 (w), 1374 (w), 1217 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 4.87 (t, *J* = 7.8 Hz, 1H), 2.88 (dd, *J* = 10.8, 7.4 Hz, 1H), 2.81 (dd, *J* = 18.6, 10.8 Hz, 1H), 2.66 (dd, *J* = 18.6, 7.4 Hz, 1H), 2.31 (d, *J* = 7.8 Hz, 2H), 1.63 (s, 3H), 1.53 (s, 3H), 1.46 (s, 3H), 1.12 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.9, 214.1, 171.5, 159.9,

137.5, 120.9, 116.7, 87.6, 58.2, 53.8, 38.3, 36.3, 26.0, 20.0, 18.3, 17.9; **HRMS (ESI+):** Calcd. for $C_{16}H_{20}O_4Na$ ($[M+Na]^+$): 299.1259, Found: 299.1259; **Optical rotation:** $[\alpha]_D^{24}$ +22.4 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 96.5:3.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 17.6 min, τ_{major} = 42.7 min). See Supporting Information: Part B for HPLC chromatograms.

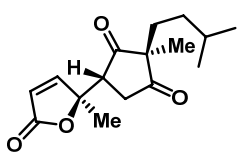


Compound 3an: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Colorless thick oil (36 mg, 0.144 mmol, 72% yield); **FT-IR (Thin film):** 2962 (w), 2932 (w), 1759 (s), 1723 (s), 1633 (m), 1415 (m), 1231 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 5.6 Hz, 1H), 6.09 (d, *J* = 5.6 Hz, 1H), 2.99 (dd, *J* = 10.8, 8.0 Hz, 1H), 2.88 (dd, *J* = 19.0, 10.8 Hz, 1H), 2.66 (dd, *J* = 19.0, 8.0 Hz, 1H), 1.58-1.52 (m, 2H), 1.48 (s, 3H), 1.22-1.01 (m, 2H), 1.10 (s, 3H), 0.81 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.6, 213.9, 171.4, 159.9, 120.9, 87.6, 57.9, 53.4, 38.9, 37.9, 20.0, 18.4, 18.0, 14.3; **HRMS (ESI+):** Calcd. for $C_{14}H_{18}O_4Na$ ($[M+Na]^+$): 273.1103, Found: 273.1102; **Optical rotation:** $[\alpha]_D^{25}$ +41.6 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 17.3 min, τ_{major} = 20.4 min). See Supporting Information: Part B for HPLC chromatograms.

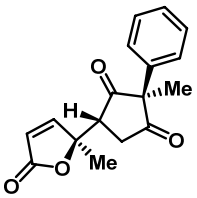


Compound 3ao: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless thick oil (23 mg, 0.087 mmol, 78% yield); **FT-IR (Thin film):** 2960 (m), 2929 (m), 1761 (s), 1724 (s), 1457 (m), 1374 (w), 1249 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 5.6 Hz, 1H), 6.11 (d, *J* = 5.6 Hz, 1H), 3.05 (dd, *J* = 10.9, 8.6 Hz, 1H), 2.90 (dd, *J* = 19.2, 10.9 Hz, 1H), 2.68 (dd, *J* = 19.2, 8.6 Hz, 1H), 1.69-1.55 (m, 3H), 1.53 (s, 3H), 1.13 (s, 3H), 0.76 (d, *J* = 6.7 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.5, 213.8, 171.5, 159.9, 121.0, 87.6, 57.5, 53.4, 45.5, 37.6, 25.3, 23.9, 23.8, 20.9, 20.2; **HRMS (ESI+):** Calcd. for $C_{15}H_{20}O_4Na$ ($[M+Na]^+$): 287.1259, Found: 287.1258; **Optical rotation:** $[\alpha]_D^{24}$ +47.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (85:15 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210

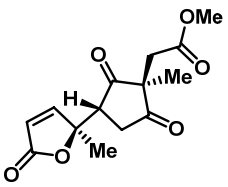
nm, τ_{minor} = 10.3 min, τ_{major} = 30.6 min). See Supporting Information: Part B for HPLC chromatograms.



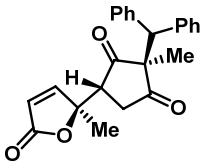
Compound 3ap: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless thick oil (26 mg, 0.093 mmol, 84% yield); **FT-IR (Thin film):** 2957 (m), 2872 (m), 1759 (s), 1724 (s), 1456 (m), 1374 (w), 1249 (m), 1213 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.78 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 5.6 Hz, 1H), 2.99 (dd, *J* = 10.8, 8.0 Hz, 1H), 2.89 (dd, *J* = 19.0, 10.8 Hz, 1H), 2.68 (dd, *J* = 19.0, 8.0 Hz, 1H), 1.65-1.57 (m, 2H), 1.49 (s, 3H), 1.42-1.36 (m, 1H), 1.11 (s, 3H), 1.03-0.92 (m, 2H), 0.80 (d, *J* = 6.6 Hz, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.7, 213.9, 171.5, 159.9, 121.0, 87.6, 57.8, 53.5, 37.9, 34.9, 33.3, 28.4, 22.3, 22.2, 20.0, 18.5; **HRMS (ESI+):** Calcd. for $C_{16}H_{22}O_4Na$ ($[M+Na]^+$): 301.1416, Found: 301.1417; **Optical rotation:** $[\alpha]_D^{24}$ +48.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 8.2 min, τ_{major} = 28.8 min). See Supporting Information: Part B for HPLC chromatograms.



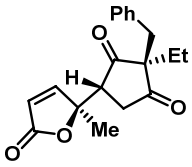
Compound 3aq: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); White solid (51 mg, 0.179 mmol, 89% yield); m.p. 145-146 °C; **FT-IR (Thin film):** 2934 (m), 2872 (w), 1751 (s), 1578 (w), 1441 (m), 1272 (w), 1245 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, *J* = 5.6 Hz, 1H), 7.36-7.27 (m, 3H), 7.17-7.15 (m, 2H), 6.10 (d, *J* = 5.6 Hz, 1H), 3.19 (dd, *J* = 11.6, 6.9 Hz, 1H), 3.07 (dd, *J* = 19.0, 11.6 Hz, 1H), 2.77 (dd, *J* = 19.0, 6.9 Hz, 1H), 1.50 (s, 3H), 1.45 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 211.0, 210.4, 171.4, 159.8, 136.6, 129.6, 128.4, 126.2, 120.9, 87.6, 63.4, 52.8, 38.2, 19.9, 19.6; **HRMS (ESI+):** Calcd. for $C_{17}H_{16}O_4Na$ ($[M+Na]^+$): 307.0946, Found: 307.0949; **Optical rotation:** $[\alpha]_D^{25}$ –6.3 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak IE column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 13.1 min, τ_{major} = 19.3 min). See Supporting Information: Part B for HPLC chromatograms.



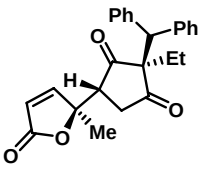
Compound 3ar: Purified by silica gel flash column chromatography (25-30% EtOAc in petroleum ether): Colorless thick oil (51 mg, 0.182 mmol, 90% yield); **FT-IR (Thin film):** 2957 (m), 2925 (m), 1760 (s), 1728 (s), 1455 (m), 1379 (w), 1352 (m), 1253 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 5.5 Hz, 1H), 6.11 (d, *J* = 5.5 Hz, 1H), 3.56 (s, 3H), 3.32-3.26 (m, 1H), 2.92 (d, *J* = 7.3 Hz, 2H), 2.88-2.79 (m, 1H), 2.51 (dd, *J* = 18.9, 9.1 Hz, 1H), 1.67 (s, 3H), 1.11 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 213.5, 213.1, 172.3, 171.7, 159.8, 121.1, 87.6, 52.6, 52.5, 52.4, 41.2, 37.0, 21.4, 19.4 [^{1}H and ^{13}C Peaks correspond to major diastereoisomer]; **HRMS (ESI+):** Calcd. for $C_{14}H_{16}O_6Na$ ($[M+Na]^+$): 303.0845, Found: 303.0844; **Optical rotation:** $[\alpha]_D^{25}$ +73.2 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 97:3 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 14.3 min, τ_{major} = 36.3 min). See Supporting Information: Part B for HPLC chromatograms.



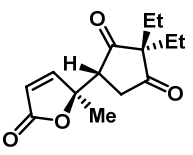
Compound 3as: Purified by silica gel flash column chromatography (20-25% EtOAc in petroleum ether); Colorless thick oil (40 mg, 0.107 mmol, 96% yield); **FT-IR (Thin film):** 2927 (m), 1761 (s), 1723 (s), 1623 (w), 1451 (m), 1373 (w), 1219 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.68 (d, *J* = 5.6 Hz, 1H), 7.42-7.36 (m, 4H), 7.30-7.20 (m, 6H), 6.04 (d, *J* = 5.6 Hz, 1H), 4.32 (s, 1H), 2.50 (dd, *J* = 19.1, 8.0 Hz, 1H), 2.24 (dd, *J* = 19.1, 11.2 Hz, 1H), 2.10 (dd, *J* = 11.2, 8.0 Hz, 1H), 1.44 (s, 3H), 1.14 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.7, 214.9, 171.4, 159.7, 139.3, 139.2, 129.5, 129.4, 128.8, 127.5, 120.9, 87.4, 61.7, 59.0, 54.0, 38.5, 20.0, 19.8; **HRMS (ESI+):** Calcd. for $C_{24}H_{22}O_4Na$ ($[M+Na]^+$): 397.1416, Found: 397.1412; **Optical rotation:** $[\alpha]_D^{25}$ +2.9 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using a Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 7.7 min, τ_{major} = 10.1 min). See Supporting Information: Part B for HPLC chromatograms.



Compound 3at: Purified by silica gel flash column chromatography (20-25% EtOAc in petroleum ether); Colorless thick oil (52 mg, 0.166 mmol, 83% yield); **FT-IR (Thin film):** 2923 (m), 2853 (w), 1756 (s), 1723 (s), 1604 (w), 1455 (w), 1373 (w), 1224 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 5.6 Hz, 1H), 7.592-7.52 (m, 3H), 7.30-7.28 (m, 2H), 6.33 (d, *J* = 5.6 Hz, 1H), 3.36 (d, *J* = 12.7 Hz, 1H), 3.15 (d, *J* = 12.7 Hz, 1H), 2.71-2.68 (m, 2H), 2.19-2.07 (m, 3H), 1.78 (s, 3H), 1.16 (t, *J* = 7.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.1, 214.6, 171.5, 159.9, 135.3, 129.5, 128.8, 127.6, 120.6, 87.4, 64.8, 54.3, 43.1, 39.6, 28.8, 19.9, 9.4. [^{1}H and ^{13}C Peaks correspond to major diastereoisomer]; **HRMS (ESI+):** Calcd. for $C_{19}H_{20}O_4Na$ ($[M+Na]^+$): 335.1259, Found: 335.1258; The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 10.1 min, τ_{major} = 17.3 min). See Supporting Information: Part B for HPLC chromatograms.

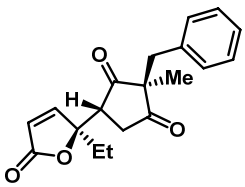


Compound 3au: Purified by silica gel flash column chromatography (20-25% EtOAc in petroleum ether); Colorless thick oil (36 mg, 0.093 mmol, 83% yield); **FT-IR (Thin film):** 2920 (m), 2855 (w), 1735 (s), 1417 (w), 1372 (w), 1201 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 5.6 Hz, 1H), 7.50-7.48 (m, 2H), 7.32-7.17 (m, 8H), 6.00 (d, *J* = 5.6 Hz, 1H), 4.31 (s, 1H), 2.52-1.34 (m, 2H), 1.86-1.81 (m, 1H), 1.70-1.64 (m, 2H), 1.45 (s, 3H), 0.68 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.5, 214.7, 171.3, 159.7, 139.1, 139.1, 129.5, 129.0, 128.7, 128.6, 127.4, 127.3, 120.3, 87.2, 67.0, 58.6, 54.5, 39.8, 28.1, 19.5, 9.3; **HRMS (ESI+):** Calcd. for $C_{25}H_{24}O_4Na$ ($[M+Na]^+$): 411.1572, Found: 411.1575; **Optical rotation:** $[\alpha]_D^{25}$ –28.0 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 7.6 min, τ_{major} = 15.9 min). See Supporting Information: Part B for HPLC chromatograms.

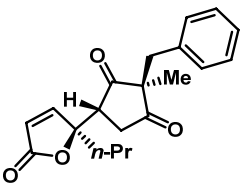


Compound 3av: Purified by silica gel flash column chromatography (20-25% EtOAc in petroleum ether); Colorless thick oil (24 mg, 0.095 mmol, 86% combined yield of both diasteroisomers); **FT-IR (Thin film):** 2973 (m), 2838 (w), 1758 (s), 1720 (s), 1523 (m), 1231 (w), 1162 (m); **^{1}H-NMR (400 MHz, $CDCl_3$):** [Major diastereomer]**:** δ 7.85 (d, *J* = 5.6 Hz, 1H), 6.09 (d, *J* = 5.6 Hz, 1H), 2.97-2.87 (m, 2H), 2.65-2.58

(m, 1H), 1.72-1.57 (m, 4H), 1.52 (s, 3H), 0.78-0.73 (m, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.4, 213.7, 171.6, 160.1, 120.8, 87.6, 63.3, 53.8, 39.0, 28.6, 26.4, 19.9, 9.2, 9.0; **HRMS (ESI+):** Calcd. for $C_{14}H_{18}O_4Na$ ($[M+Na]^+$): 273.1103, Found: 273.1107; **Optical rotation:** $[\alpha]_D^{25}$ +47.9 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 89:11 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak ID column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 13.8 min, τ_{major} = 20.2 min). See Supporting Information: Part B for HPLC chromatograms.

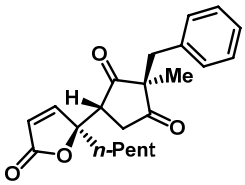


Compound 3ba: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless amorphous solid (60 mg, 0.192 mmol, 96% yield); m.p. 130-132 °C; **FT-IR (Thin film):** 2925 (m), 2855(w), 1763 (s), 1725 (s), 1603 (w), 1455 (w), 1372 (w), 1322 (w), 1201 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.46 (d, *J* = 5.6 Hz, 1H), 7.21-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.09 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.7 Hz, 1H), 2.91 (d, *J* = 12.7 Hz, 1H), 2.40 (dd, *J* = 18.1, 6.5 Hz, 1H), 2.20-2.08 (m, 2H), 2.05-1.98 (m, 1H), 1.81-1.71 (m, 1H), 1.24 (s, 3H), 0.72 (t, *J* = 7.4 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 157.8, 135.5, 129.5, 128.9, 127.6, 122.3, 90.4, 59.7, 53.1, 44.1, 38.4, 25.7, 19.9, 7.5; **HRMS (ESI+):** Calcd. for $C_{19}H_{20}O_4Na$ ($[M+Na]^+$): 335.1259, Found: 335.1260; **Optical rotation:** $[\alpha]_D^{24}$ +52.8 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 12.4 min, τ_{major} = 33.7 min). See Supporting Information: Part B for HPLC chromatograms.

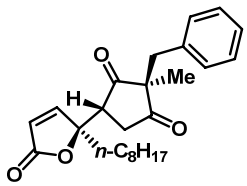


Compound 3ca: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless amorphous solid (61 mg, 0.186 mmol, 93% yield); m.p. 164-165 °C; **FT-IR (Thin film):** 2956 (m), 2933 (m), 2870 (w), 1748 (s), 1733 (s), 1522 (m), 1396 (w), 1212 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 5.6 Hz, 1H), 7.26-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.06 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.92 (d, *J* = 12.8 Hz, 1H), 2.41 (dd, *J* = 16.4, 4.7 Hz, 1H), 2.17-2.06 (m, 2H), 1.95-1.87 (m, 1H), 1.72-1.64 (m, 1H), 1.24 (s, 3H), 1.15-1.03 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 158.1, 135.5, 129.5, 128.9, 127.6, 122.0, 90.1, 59.7, 53.4, 44.1, 38.4, 34.7, 19.9, 16.7, 14.0; **HRMS (ESI+):**

Calcd. for $C_{20}H_{22}O_4Na$ ($[M+Na]^+$): 349.1416, Found: 349.1416; **Optical rotation:** $[\alpha]_D^{25}$ +61.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 9.1 min, τ_{major} = 15.6 min). See Supporting Information: Part B for HPLC chromatograms.

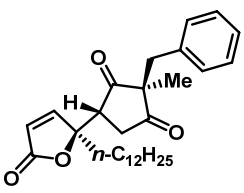


Compound 3da: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless amorphous solid (70 mg, 0.197 mmol, 98% yield); m.p. 110-112 °C; **FT-IR (Thin film):** 2954 (m), 2929 (m), 2871 (w), 1747 (s), 1733 (s), 1522 (m), 1317 (w), 1295 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 5.6 Hz, 1H), 7.25-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.91 (d, *J* = 12.8 Hz, 1H), 2.41 (dd, *J* = 17.3, 5.7 Hz, 1H), 2.17-2.05 (m, 2H), 1.95-1.87 (m, 1H), 1.75-1.67 (m, 1H), 1.24-1.20 (m, 4H), 1.22 (s, 3H), 1.10-1.00 (m, 2H), 0.83 (t, *J* = 6.5 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 158.4, 135.5, 129.5, 128.9, 127.6, 122.0, 90.2, 59.7, 53.4, 44.1, 38.4, 32.7, 31.7, 22.9, 22.4, 19.9, 13.9; **HRMS (ESI+):** Calcd. for $C_{22}H_{26}O_4Na$ ($[M+Na]^+$): 377.1729, Found: 377.1728; **Optical rotation:** $[\alpha]_D^{25}$ +68.3 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 8.7 min, τ_{major} = 11.6 min). See Supporting Information: Part B for HPLC chromatograms.

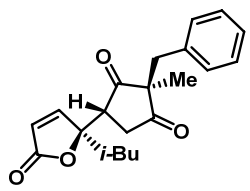


Compound 3ea: Purified by silica gel flash column chromatography (15% EtOAc in petroleum ether); Colorless thick oil (65 mg, 0.164 mmol, 82% yield); **FT-IR (Thin film):** 2930 (m), 2851 (w), 1747 (s), 1732 (s), 1524 (s), 1243 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 5.6 Hz, 1H), 7.21-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.91 (d, *J* = 12.8 Hz, 1H), 2.41 (dd, *J* = 17.2, 5.5 Hz, 1H), 2.17-2.05 (m, 2H), 1.94-1.87 (m, 1H), 1.74-1.67 (m, 1H), 1.28-1.20 (m, 10H), 1.24 (s, 3H), 1.10-0.97 (m, 2H), 0.85 (t, *J* = 6.6 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 158.1, 135.5, 129.5, 128.9, 127.6, 122.0, 90.2, 59.7, 53.4, 44.1, 38.4, 32.7, 31.8, 29.5, 29.4, 29.2, 23.3, 22.7, 19.9, 14.2; **HRMS (ESI+):** Calcd. for $C_{25}H_{32}O_4Na$ ($[M+Na]^+$): 419.2198, Found: 419.2196; **Optical rotation:** $[\alpha]_D^{25}$ +73.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was

determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 7.0 min, τ_{major} = 8.1 min). See Supporting Information: Part B for HPLC chromatograms.

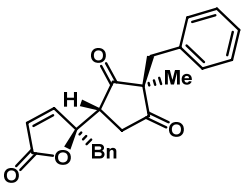


Compound 3fa: Purified by silica gel flash column chromatography (15% EtOAc in petroleum ether); Colorless thick oil (79 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 2925 (s), 2854 (m), 1764 (s), 1726 (s), 1454 (m), 1372 (w), 1322 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 5.6 Hz, 1H), 7.21-7.19 (m, 3H), 6.98-6.96 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.91 (d, *J* = 12.8 Hz, 1H), 2.40 (dd, *J* = 17.4, 5.8 Hz, 1H), 2.17-2.05 (m, 2H), 1.94-1.87 (m, 1H), 1.74-1.67 (m, 1H), 1.28-1.19 (m, 21H), 1.07-0.96 (m, 2H), 0.86 (t, *J* = 6.2 Hz, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 158.1, 135.5, 129.5, 128.8, 127.6, 122.0, 90.2, 59.7, 53.4, 44.1, 38.4, 32.7, 32.0, 29.7, 29.6, 29.5, 29.5, 29.4, 23.3, 22.8, 19.9, 14.2; **HRMS (ESI+):** Calcd. for $C_{29}H_{40}O_4Na$ ($[M+Na]^+$): 475.2824, Found: 475.2823; **Optical rotation:** $[\alpha]_D^{24}$ +60.6 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 95.5:4.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (97:3 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 10.2 min, τ_{major} = 11.5 min). See Supporting Information: Part B for HPLC chromatograms.

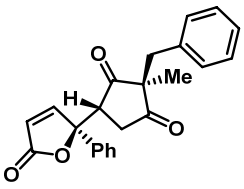


Compound 3ga: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless amorphous solid (68 mg, 0.199 mmol, 99% yield); m.p. 163-165 °C; **FT-IR (Thin film):** 2957 (m), 2923 (m), 2872 (w), 1744 (s), 1736 (s), 1648 (m), 1219 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 5.6 Hz, 1H), 7.25-7.19 (m, 3H), 6.97-6.95 (m, 2H), 6.07 (d, *J* = 5.6 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.90 (d, *J* = 12.8 Hz, 1H), 2.48-2.38 (m, 1H), 2.15-2.02 (m, 2H), 1.89-1.84 (m, 1H), 1.59-1.54 (m, 1H), 1.41-1.34 (m, 1H), 1.23 (s, 3H), 0.84-0.81 (m, 6H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.2, 214.7, 171.6, 158.4, 135.4, 129.5, 128.9, 127.6, 121.8, 90.3, 59.7, 54.4, 44.1, 41.2, 38.5, 24.5, 23.8, 23.7, 19.9; **HRMS (ESI+):** Calcd. for $C_{21}H_{24}O_4Na$ ($[M+Na]^+$): 363.1572, Found: 363.1572; **Optical rotation:** $[\alpha]_D^{24}$ +60.4 (*c* 2.0, $CHCl_3$) for an enantiomerically enriched sample with 99:1 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210

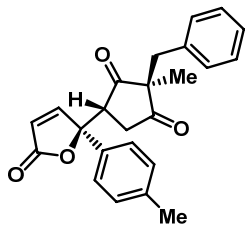
nm, τ_{minor} = 7.7 min, τ_{major} = 11.8 min). See Supporting Information: Part B for HPLC chromatograms.



Compound 3ha: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless thick oil (74 mg, 0.197 mmol, 98% yield); **FT-IR (Thin film):** 2926 (m), 2855(w), 1771 (s), 1725 (s), 1604 (w), 1496 (w), 1454 (w), 1321 (w), 1225 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, *J* = 5.6 Hz, 1H), 7.24-7.19 (m, 6H), 7.10-7.08 (m, 2H), 7.02-7.00 (m, 2H), 5.90 (d, *J* = 5.6 Hz, 1H), 3.38 (d, *J* = 13.6 Hz, 1H), 3.19 (d, *J* = 13.6 Hz, 1H), 3.02 (d, *J* = 12.8 Hz, 1H), 2.96 (d, *J* = 12.8 Hz, 1H), 2.32-2.24 (m, 2H), 2.16-2.01 (m, 1H), 1.31 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 215.1, 214.3, 171.1, 157.5, 135.6, 133.7, 130.5, 129.6, 128.8, 128.6, 127.5, 127.5, 122.4, 89.8, 59.7, 50.9, 43.8, 40.2, 38.2, 20.2; **HRMS (ESI+):** Calcd. for $C_{24}H_{22}O_4Na$ ($[M+Na]^+$): 397.1416, Found: 397.1412; **Optical rotation:** $[\alpha]_D^{24}$ +123.1 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 98:2 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 14.0 min, τ_{major} = 23.5 min). See Supporting Information: Part B for HPLC chromatograms.

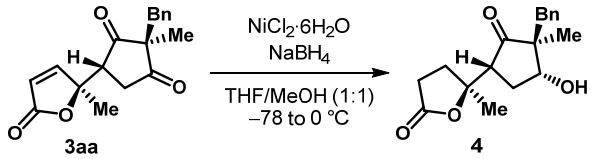


Compound 3ia: Purified by silica gel flash column chromatography (20% EtOAc in petroleum ether); Colorless thick oil (63 mg, 0.174 mmol, 87% yield); **FT-IR (Thin film):** 2928 (m), 2866 (w), 1763 (s), 1578 (m), 1438 (w), 1317 (w), 1214 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.31 (d, *J* = 5.7 Hz, 1H), 7.35-7.29 (m, 3H), 7.30-7.26 (m, 2H), 7.22-7.20 (m, 3H), 6.96-6.94 (m, 2H), 6.08 (d, *J* = 5.7 Hz, 1H), 2.93 (d, *J* = 12.8 Hz, 1H), 2.84 (d, *J* = 12.8 Hz, 1H), 2.57 (dd, *J* = 15.8, 4.9 Hz, 1H), 2.39-2.28 (m, 2H), 0.85 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.8, 214.4, 170.8, 158.4, 135.3, 135.3, 129.5, 129.1, 129.0, 128.9, 127.6, 126.2, 120.0, 89.6, 59.8, 57.9, 43.7, 38.2, 19.6; **HRMS (ESI+):** Calcd. for $C_{23}H_{20}O_4Na$ ($[M+Na]^+$): 383.1259, Found: 383.1259; **Optical rotation:** $[\alpha]_D^{24}$ +131.5 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 90:10 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (75:25 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 6.8 min, τ_{major} = 9.2 min). See Supporting Information: Part B for HPLC chromatograms.



Compound 3ja: Purified by silica gel flash column chromatography (25% EtOAc in petroleum ether); Off-white solid (63 mg, 0.168 mmol, 84% yield); **m.p.** 127-129 °C; **FT-IR (Thin film):** 2924 (m), 2854 (w), 1769 (s), 1727 (s), 1604 (w), 1495 (w), 1452 (w), 1319 (w), 1212 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 8.29 (d, *J* = 5.7 Hz, 1H), 7.21-7.19 (m, 3H), 7.16-7.11 (m, 4H), 6.95-6.93 (m, 2H), 6.05 (d, *J* = 5.7 Hz, 1H), 2.92 (d, *J* = 12.8 Hz, 1H), 2.84 (d, *J* = 12.8 Hz, 1H), 2.56 (dd, *J* = 15.8, 4.7 Hz, 1H), 2.37-2.33 (m, 2H), 2.29 (s, 3H), 0.86 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 214.9, 214.6, 170.9, 158.6, 139.1, 135.3, 132.3, 129.7, 129.5, 128.8, 127.6, 126.1, 119.7, 89.7, 59.8, 57.9, 43.8, 38.3, 21.1, 19.6; **HRMS (ESI+):** Calcd. for $C_{24}H_{22}O_4Na$ ($[M+Na]^+$): 397.1416, Found: 397.1416; **Optical rotation:** $[\alpha]_D^{25}$ +138.1 (*c* 3.0, $CHCl_3$) for an enantiomerically enriched sample with 95:5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak AD-H column (90:10 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 10.9 min, τ_{major} = 16.9 min). See Supporting Information: Part B for HPLC chromatograms.

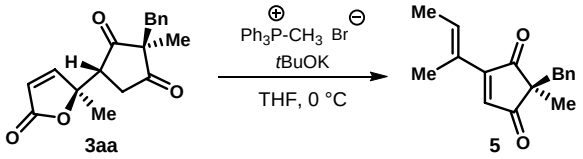
Procedure for selective reduction of 3aa:



In an oven and vacuum dried 10 mL 2-necked round-bottom flask, **3aa** (50 mg, 0.167 mmol, 1.0 equiv.) was taken with 1.6 mL of dry MeOH and THF (1:1) under positive argon pressure and the mixture was cooled to –78 °C. To this mixture was added $NiCl_2.6H_2O$ (79.7 mg, 0.335 mmol, 2.0 equiv.) followed by $NaBH_4$ (25.3 mg, 0.668 mmol, 4.0 equiv.) at –78 °C and the mixture was warmed to 0 °C. After stirring for 1 h at 0 °C, reaction mixture was quenched with 5 mL sat. NH_4Cl solution and diluted with 5 mL EtOAc. Organic phase was separated from aqueous phase, aqueous phase was back-extracted with EtOAc (2 × 5 mL). Combined organic phase was dried over anh. Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel flash column chromatography (40% EtOAc in petroleum ether) to obtain a colorless thick oil (38 mg, 0.125 mmol, 75% yield); **FT-IR (Thin film):** 2924 (m), 2853(w), 1756 (s), 1738 (s), 1632 (w), 1434 (w), 1228 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.30-7.21 (m, 3H), 7.13-7.11 (m, 2H), 4.19-4.18 (m, 1H), 2.95 (d, *J* = 13.5 Hz,

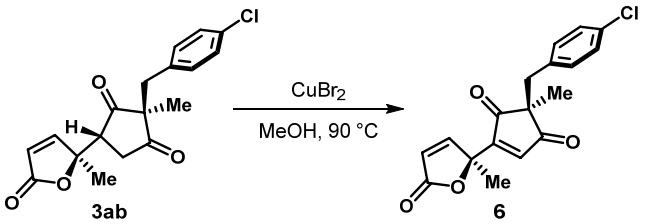
1H), 2.72 (d, J = 13.5 Hz, 1H), 2.67-2.49 (m, 2H), 2.38-2.15 (m, 4H), 1.82-1.74 (m, 2H), 1.39 (s, 3H), 1.03 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 216.7, 176.5, 137.2, 130.1, 128.7, 126.9, 85.7, 71.1, 56.5, 54.9, 41.6, 33.6, 30.4, 28.6, 23.0, 16.2; **HRMS (ESI+):** Calcd. for $C_{18}H_{22}O_4Na$ ($[M+Na]^+$): 325.1416, Found: 325.1416; **Optical rotation:** $[\alpha]_D^{21}$ +91.3 (*c* 2.0, $CHCl_3$).

Procedure for base-mediated decarboxylation of 3aa:



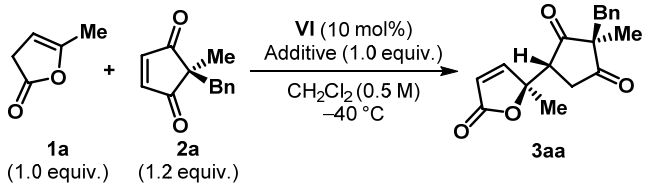
In an oven and vacuum-dried 2-necked round-bottom flask, methyltriphenylphosphonium bromide (71.8 mg, 0.201 mmol, 1.2 equiv.) was taken with 1.6 mL of freshly distilled THF under positive argon pressure and the suspension was cooled to 0 °C. Potassium *tert*-butoxide (20.6 mg, 0.184 mmol, 1.1 equiv.) was added and the resulting yellow solution was stirred at 0 °C for 1 h. To this solution was added **3aa** (50 mg, 0.167 mmol, 1.0 equiv.) and stirred for 10 min at 0 °C. The reaction mixture was warmed to r.t., diluted with 10 mL petroleum ether. The solid formed was filtered and the filtrate was concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography (2% EtOAc in petroleum ether) to obtain a yellow crystalline solid (36 mg, 0.141 mmol, 85% yield); **m.p.** 85-87 °C; **FT-IR (Thin film):** 2920 (m), 2851(w), 1693 (s), 1616 (m), 1557 (w), 1451 (w), 1330 (w), 1292 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.13-7.11 (m, 3H), 7.06 (q, J = 7.0 Hz, 1H), 6.94-6.92 (m, 2H), 6.55 (s, 1H), 2.96 (s, 2H), 1.81 (d, J = 7.0 Hz, 3H), 1.70 (s, 3H), 1.24 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 206.8, 205.9, 157.7, 138.7, 136.0, 129.8, 128.3, 127.4, 126.9, 54.3, 41.4, 19.8, 15.2, 14.2; **HRMS (ESI+):** Calcd. for $C_{17}H_{18}O_2Na$ ($[M+Na]^+$): 277.1204, Found: 277.1201; **Optical rotation:** $[\alpha]_D^{25}$ +142.7 (*c* 1.0, $CHCl_3$) for an enantiomerically enriched sample with 97.5:2.5 er. The enantiomeric ratio was determined by HPLC analysis using Daicel Chiralpak ID column (99:1 *n*-Hexane/EtOH, 1.0 mL/min, 20 °C, 210 nm, τ_{minor} = 5.7 min, τ_{major} = 6.1 min). See Supporting Information: Part B for HPLC chromatograms.

Procedure for Cu(II)-mediated oxidation of 3ab:



In an oven-dried 10 mL round-bottom flask, equipped with reflux condenser, a solution of **3ab** (60 mg, 0.180 mmol, 1.0 equiv.) in 1.8 mL of dry MeOH was added copper(II) bromide (88.6 mg, 0.397 mmol, 2.2 equiv.) and the resulting solution was stirred at 90 °C for 5 h. The reaction mixture was cooled to r.t., quenched with 2.0 mL of distilled water and 2.0 mL of 1 M aqueous HCl solution, 5.0 mL of Et_2O was added and the organic phase was separated from aqueous phase. Aqueous phase was back-extracted with Et_2O (2 × 5 mL), combined organic phase was dried over anh. $MgSO_4$ and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel flash column chromatography (25% EtOAc in petroleum ether) to obtain a yellow solid (53 mg, 0.160 mmol, 88% yield); **m.p.** 132-134 °C; **FT-IR (Thin film):** 2922 (m), 2873 (w), 1768 (s), 1738 (m), 1700 (s), 1602 (w), 1453 (m), 1375 (w), 1333 (w), 1242 (w); **^{1}H-NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 5.6 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.95 (s, 1H), 6.76 (d, *J* = 8.3 Hz, 2H), 5.89 (d, *J* = 5.6 Hz, 1H), 2.98 (d, *J* = 13.1 Hz, 1H), 2.88 (d, *J* = 13.1 Hz, 1H), 1.66 (s, 3H), 1.27 (s, 3H); **^{13}C-NMR (100 MHz, $CDCl_3$):** δ 205.0, 204.1, 170.6, 161.2, 155.7, 142.6, 133.7, 133.3, 130.9, 128.6, 120.4, 85.2, 53.9, 40.6, 23.6, 19.1; **HRMS (ESI+):** Calcd. for $C_{18}H_{15}ClO_4Na$ ($[M+Na]^+$): 353.0557, Found: 353.0556; **Optical rotation:** $[\alpha]_D^{25}$ –198.2 (*c* 2.0, $CHCl_3$).

General procedure for the robustness screening of the catalytic enantioselective desymmetrization of 2-benzyl-2-methylcyclopent-4-ene-1,3-dione (2a):



In an oven and vacuum-dried Schlenk tube 2-benzyl-2-methylcyclopent-4-ene-1,3-dione **2a** (26.6 mg, 0.133 mmol, 1.2 equiv.), additive (0.111 mmol, 1.0 equiv.) and catalyst **VI** (6.0 mg,

0.011 mmol, 0.10 equiv.) were taken with 0.1 mL CH_2Cl_2 under a positive argon pressure and the mixture was cooled to –40 °C. A solution of α-Angelica lactone **1a** (10 μL, 0.111 mmol, 1.0 equiv.) in 0.1 mL of CH_2Cl_2 was added to it and the resulting mixture was stirred at –40 °C until TLC (30% EtOAc in petroleum ether) revealed complete conversion of **1a**. The reaction mixture was brought to r.t., solvent was removed under vacuum and the additive remaining was calculated by ^{1}H-NMR analysis of the crude reaction mixture. The crude product was purified by silica-gel flash column chromatography.

References:

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7. K. Aikawa, T. Okamoto, K. Mikami, *J. Am. Chem. Soc.*, 2012, **134**, 10329.

Single crystal X-ray diffraction analysis of 3ad:

A single crystal of **3ad** (obtained from 1:1 petroleum ether/EtOAc at 0 °C) was mounted and the diffraction data were collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table 1. Crystal data and structure refinement for 3ad

Identification code	**3ad**	
Empirical formula	$C_{18}H_{17}ClO_4$	
Formula weight	332.77	
Temperature	296(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 663.48(9) pm	α = 90°
	b = 1164.31(15) pm	β = 99.155(8)°
	c = 1077.97(14) pm	γ = 90°
Volume	0.82212(19) nm^3	
Z	2	
Density (calculated)	1.344 Mg/m^3	
Absorption coefficient	0.250 mm^{-1}	
F(000)	348	
Crystal size	0.42 × 0.12 × 0.11 mm^3	
Theta range for data collection	1.91 to 30.58°	
Index ranges	$-9 \le h \le 9, -16 \le k \le 11, -12 \le l \le 15$	
Reflections collected	17575	
Independent reflections	4329 [R_{int} = 0.0433]	

Completeness to Θ = 30.58°	99.8 %
Absorption correction	Empirical
Max. and min. transmission	0.989 and 0.986
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4329 / 1 / 210
Goodness-of-fit on F^2	1.011
Final R indices [I > 2 σ (I)]	$R1 = 0.0407,\ \omega R2 = 0.0785$
R indices (all data)	$R1 = 0.0775,\ \omega R2 = 0.0906$
Absolute structure parameter	0.02(5)
Largest diff. peak and hole	0.149 and –0.158 e.Å^{-3}

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2 × 10^{-1}) for 3ad. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Cl(1)	-5163(1)	-6879(1)	-4005(1)	72(1)
O(1)	-3729(3)	-9307(1)	2237(2)	87(1)
O(2)	-5691(2)	-7787(1)	1651(1)	50(1)
O(3)	-9596(2)	-6028(2)	-133(2)	77(1)
O(4)	-4917(2)	-8537(1)	-1484(1)	55(1)
C(1)	-3905(4)	-8284(2)	2173(2)	59(1)
C(2)	-5481(3)	-6541(2)	1686(2)	46(1)
C(3)	-5904(3)	-6117(2)	316(2)	39(1)
C(4)	-8034(3)	-6472(1)	-323(2)	43(1)
C(5)	-7932(3)	-7463(1)	-1226(2)	39(1)
C(6)	-8843(3)	-7021(2)	-2568(2)	47(1)
C(7)	-8714(3)	-7867(2)	-3603(2)	48(1)
C(8)	-10266(4)	-8677(2)	-3938(2)	64(1)
C(9)	-10187(5)	-9474(2)	-4861(3)	80(1)

C(10)	-8550(6)	-9499(3)	-5481(3)	90(1)
C(11)	-6995(5)	-8714(2)	-5203(2)	75(1)
C(12)	-7107(3)	-7903(2)	-4276(2)	54(1)
C(13)	-5659(3)	-7677(1)	-1127(2)	37(1)
C(14)	-4509(3)	-6660(2)	-526(2)	43(1)
C(15)	-9070(3)	-8513(2)	-843(2)	52(1)
C(16)	-3340(4)	-6388(2)	2303(2)	64(1)
C(17)	-2467(4)	-7371(2)	2592(3)	71(1)
C(18)	-6975(4)	-6046(2)	2477(2)	77(1)

Table 3. Bond lengths [pm] and angles [°] for 3ad

Cl(1)-C(12)	174.6(2)
O(1)-C(1)	119.9(2)
O(2)-C(1)	135.7(3)
O(2)-C(2)	145.7(2)
O(3)-C(4)	120.5(2)
O(4)-C(13)	120.6(2)
C(1)-C(17)	145.2(3)
C(2)-C(16)	148.0(3)
C(2)-C(18)	152.0(3)
C(2)-C(3)	154.0(3)
C(3)-C(4)	152.7(3)
C(3)-C(14)	153.3(2)
C(3)-H(3)	98.00
C(4)-C(5)	151.8(2)
C(5)-C(13)	151.5(3)
C(5)-C(15)	152.8(2)
C(5)-C(6)	156.3(3)
C(6)-C(7)	150.1(3)

C(6)-H(6A)	97.00
C(6)-H(6B)	97.00
C(7)-C(12)	138.2(3)
C(7)-C(8)	140.2(3)
C(8)-C(9)	136.7(4)
C(8)-H(8)	93.00
C(9)-C(10)	136.3(5)
C(9)-H(9)	93.00
C(10)-C(11)	137.6(4)
C(10)-H(10)	93.00
C(11)-C(12)	138.5(3)
C(11)-H(11)	93.00
C(13)-C(14)	149.8(3)
C(14)-H(14A)	97.00
C(14)-H(14B)	97.00
C(15)-H(15A)	96.00
C(15)-H(15B)	96.00
C(15)-H(15C)	96.00
C(16)-C(17)	129.8(3)
C(16)-H(16)	93.00
C(17)-H(17)	93.00
C(18)-H(18A)	96.00
C(18)-H(18B)	96.00
C(18)-H(18C)	96.00

C(1)-O(2)-C(2)	109.85(16)
O(1)-C(1)-O(2)	121.2(2)
O(1)-C(1)-C(17)	131.1(2)
O(2)-C(1)-C(17)	107.73(19)
O(2)-C(2)-C(16)	102.27(15)
O(2)-C(2)-C(18)	108.87(17)

C(16)-C(2)-C(18)	111.52(19)
O(2)-C(2)-C(3)	107.03(15)
C(16)-C(2)-C(3)	114.07(15)
C(18)-C(2)-C(3)	112.37(17)
C(4)-C(3)-C(14)	102.94(14)
C(4)-C(3)-C(2)	111.08(15)
C(14)-C(3)-C(2)	113.60(15)
C(4)-C(3)-H(3)	109.7
C(14)-C(3)-H(3)	109.7
C(2)-C(3)-H(3)	109.7
O(3)-C(4)-C(5)	124.25(18)
O(3)-C(4)-C(3)	124.49(17)
C(5)-C(4)-C(3)	111.26(14)
C(13)-C(5)-C(4)	102.99(15)
C(13)-C(5)-C(15)	112.24(15)
C(4)-C(5)-C(15)	111.10(15)
C(13)-C(5)-C(6)	110.71(14)
C(4)-C(5)-C(6)	107.06(14)
C(15)-C(5)-C(6)	112.24(16)
C(7)-C(6)-C(5)	114.37(15)
C(7)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6A)	108.7
C(7)-C(6)-H(6B)	108.7
C(5)-C(6)-H(6B)	108.7
H(6A)-C(6)-H(6B)	107.6
C(12)-C(7)-C(8)	116.1(2)
C(12)-C(7)-C(6)	123.41(19)
C(8)-C(7)-C(6)	120.44(19)
C(9)-C(8)-C(7)	122.2(2)
C(9)-C(8)-H(8)	118.9
C(7)-C(8)-H(8)	118.9

C(10)-C(9)-C(8)	119.8(3)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	120.5(3)
C(9)-C(10)-H(10)	119.8
C(11)-C(10)-H(10)	119.8
C(10)-C(11)-C(12)	119.1(3)
C(10)-C(11)-H(11)	120.5
C(12)-C(11)-H(11)	120.5
C(7)-C(12)-C(11)	122.2(2)
C(7)-C(12)-Cl(1)	120.12(17)
C(11)-C(12)-Cl(1)	117.61(19)
O(4)-C(13)-C(14)	126.02(16)
O(4)-C(13)-C(5)	124.48(17)
C(14)-C(13)-C(5)	109.50(14)
C(13)-C(14)-C(3)	105.52(13)
C(13)-C(14)-H(14A)	110.6
C(3)-C(14)-H(14A)	110.6
C(13)-C(14)-H(14B)	110.6
C(3)-C(14)-H(14B)	110.6
H(14A)-C(14)-H(14B)	108.8
C(5)-C(15)-H(15A)	109.5
C(5)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(5)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(2)	111.20(19)
C(17)-C(16)-H(16)	124.4
C(2)-C(16)-H(16)	124.4
C(16)-C(17)-C(1)	108.9(2)

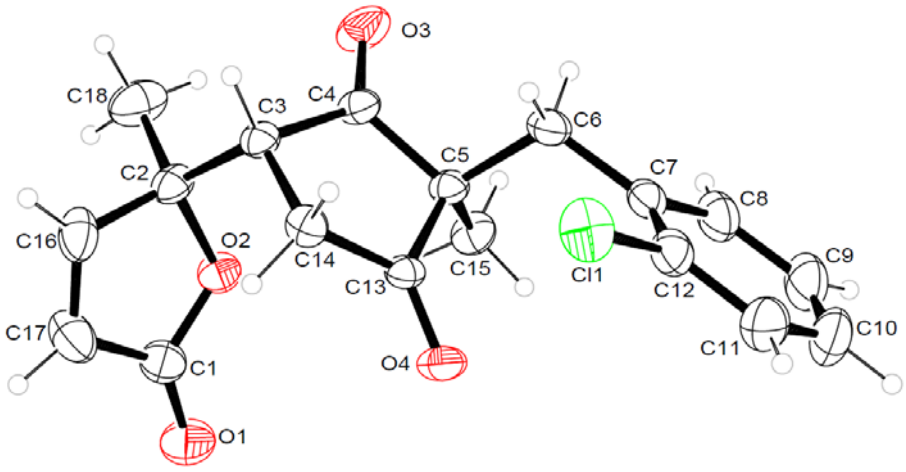
C(16)-C(17)-H(17)	125.5
C(1)-C(17)-H(17)	125.5
C(2)-C(18)-H(18A)	109.5
C(2)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(2)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 3ad. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	72(1)	81(1)	64(1)	8(1)	13(1)	-17(1)
O(1)	120(2)	43(1)	92(1)	9(1)	-6(1)	14(1)
O(2)	59(1)	31(1)	57(1)	6(1)	5(1)	-7(1)
O(3)	44(1)	74(1)	115(1)	-40(1)	17(1)	10(1)
O(4)	60(1)	43(1)	62(1)	0(1)	11(1)	19(1)
C(1)	72(2)	47(1)	56(1)	10(1)	3(1)	4(1)
C(2)	62(1)	30(1)	48(1)	2(1)	12(1)	-3(1)
C(3)	42(1)	28(1)	46(1)	0(1)	7(1)	-4(1)
C(4)	41(1)	33(1)	56(1)	-3(1)	10(1)	1(1)
C(5)	37(1)	30(1)	50(1)	-1(1)	5(1)	0(1)
C(6)	43(1)	36(1)	60(1)	4(1)	-1(1)	3(1)
C(7)	53(1)	38(1)	47(1)	5(1)	-9(1)	1(1)
C(8)	66(1)	56(1)	62(1)	1(1)	-13(1)	-11(1)
C(9)	96(2)	62(2)	71(2)	-10(1)	-20(2)	-18(1)
C(10)	135(3)	68(2)	59(2)	-20(1)	-11(2)	3(2)

C(11)	98(2)	76(2)	52(1)	-3(1)	11(1)	12(2)
C(12)	63(1)	51(1)	45(1)	5(1)	0(1)	-1(1)
C(13)	42(1)	31(1)	38(1)	6(1)	7(1)	6(1)
C(14)	36(1)	45(1)	48(1)	2(1)	8(1)	-4(1)
C(15)	54(1)	40(1)	64(1)	-1(1)	12(1)	-12(1)
C(16)	83(2)	51(1)	51(1)	3(1)	-9(1)	-21(1)
C(17)	66(2)	68(2)	72(2)	18(1)	-13(1)	-5(1)
C(18)	114(2)	62(1)	62(2)	6(1)	40(2)	17(2)



ORTEP representation of the X-ray structure of enantiopure **3ad** (thermal ellipsoids at 30% probability)

Single crystal X-ray diffraction analysis of 5:

A single crystal of **5** (obtained from petroleum ether at 0 °C) was mounted and the diffraction data were collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table 5. Crystal data and structure refinement for 5

Identification code	**5**	
Empirical formula	$C_{17}H_{18}O_2$	
Formula weight	236.42	
Temperature	296(2) K	
Wavelength	71.073 pm	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 656.9(8) pm	α = 90°
	b = 1328.6(17) pm	β = 90°
	c = 1705(2) pm	γ = 90°
Volume	1.49(1) nm^3	
Z	4	
Density (calculated)	1.055 Mg/m^3	
Absorption coefficient	0.070 mm^{-1}	
F(000)	473	
Crystal size	0.26 × 0.24 × 0.21 mm^3	
Theta range for data collection	1.94 to 27.77°	
Index ranges	$-8 \le h \le 8, -16 \le k \le 17, -22 \le l \le 22$	
Reflections collected	20390	
Independent reflections	3369 [R_{int} = 0.0516]	

Completeness to Θ = 27.77°	95.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3369 / 0 / 175
Goodness-of-fit on F^2	0.920
Final R indices [I > 2 σ (I)]	$R1$ = 0.0474, ωR2 = 0.1237
R indices (all data)	$R1$ = 0.0825, ωR2 = 0.1513
Absolute structure parameter	–0.01(8)
Largest diff. peak and hole	0.136 and –0.161 e. Å^{-3}

Table 6. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2 × 10^{-1}) for 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	12942(4)	21054(2)	18264(2)	78(1)
O(2)	13862(3)	19269(1)	16809(1)	84(1)
C(2)	12761(7)	21513(2)	19611(2)	114(2)
C(3)	13818(6)	21494(2)	18914(3)	105(1)
C(4)	10976(3)	20636(2)	18292(1)	58(1)
C(5)	9997(4)	20192(2)	17572(1)	61(1)
C(6)	10495(3)	19059(2)	17393(1)	51(1)
C(7)	9971(3)	18359(2)	18073(1)	47(1)
C(8)	11851(3)	17777(1)	18324(1)	43(1)
C(9)	11950(3)	16995(1)	18937(1)	47(1)
C(10)	10319(3)	16797(2)	19383(1)	56(1)
C(11)	10194(5)	16001(2)	20011(1)	80(1)
C(12)	10879(7)	21083(2)	19651(2)	106(1)
C(13)	9973(5)	20647(2)	18998(2)	78(1)
C(14)	12775(3)	18866(2)	17299(1)	56(1)
C(15)	13408(3)	18095(2)	17866(1)	54(1)
C(16)	13958(4)	16442(2)	19033(2)	70(1)

O(16)	8259(2)	18282(1)	18345(1)	77(1)
C(17)	9323(4)	18717(2)	16659(1)	69(1)

Table 7. Bond lengths [pm] and angles [°] for 5

C(1)-C(3)	137.9(4)
C(1)-C(4)	140.7(4)
C(1)-H(1)	93.00
O(2)-C(14)	122.3(3)
C(2)-C(12)	136.3(5)
C(2)-C(3)	137.7(5)
C(2)-H(2)	93.00
C(3)-H(3)	93.00
C(4)-C(13)	137.3(4)
C(4)-C(5)	150.6(3)
C(5)-C(6)	157.0(4)
C(5)-H(5A)	97.00
C(5)-H(5B)	97.00
C(6)-C(7)	152.7(3)
C(6)-C(14)	152.8(4)
C(6)-C(17)	153.8(3)
C(7)-O(16)	122.0(3)
C(7)-C(8)	151.8(3)
C(8)-C(15)	135.4(3)
C(8)-C(9)	147.6(3)
C(9)-C(10)	134.0(3)
C(9)-C(16)	151.8(3)
C(10)-C(11)	150.7(3)
C(10)-H(10)	93.00
C(11)-H(11A)	96.00

C(11)-H(11B)	96.00
C(11)-H(11C)	96.00
C(12)-C(13)	138.9(5)
C(12)-H(12)	93.00
C(13)-H(13)	93.00
C(14)-C(15)	146.9(3)
C(15)-H(15)	93.00
C(16)-H(16A)	96.00
C(16)-H(16B)	96.00
C(16)-H(16C)	96.00
C(17)-H(17A)	96.00
C(17)-H(17B)	96.00
C(17)-H(17C)	96.00

C(3)-C(1)-C(4)	121.5(3)
C(3)-C(1)-H(1)	119.2
C(4)-C(1)-H(1)	119.2
C(12)-C(2)-C(3)	119.5(3)
C(12)-C(2)-H(2)	120.2
C(3)-C(2)-H(2)	120.2
C(2)-C(3)-C(1)	119.5(4)
C(2)-C(3)-H(3)	120.3
C(1)-C(3)-H(3)	120.3
C(13)-C(4)-C(1)	117.8(3)
C(13)-C(4)-C(5)	121.0(2)
C(1)-C(4)-C(5)	121.3(2)
C(4)-C(5)-C(6)	116.46(18)
C(4)-C(5)-H(5A)	108.2
C(6)-C(5)-H(5A)	108.2
C(4)-C(5)-H(5B)	108.2
C(6)-C(5)-H(5B)	108.2

H(5A)-C(5)-H(5B)	107.3
C(7)-C(6)-C(14)	101.46(17)
C(7)-C(6)-C(17)	109.02(19)
C(14)-C(6)-C(17)	110.85(19)
C(7)-C(6)-C(5)	112.89(18)
C(14)-C(6)-C(5)	112.65(19)
C(17)-C(6)-C(5)	109.71(18)
O(16)-C(7)-C(8)	126.88(18)
O(16)-C(7)-C(6)	123.18(18)
C(8)-C(7)-C(6)	109.92(16)
C(15)-C(8)-C(9)	126.50(18)
C(15)-C(8)-C(7)	107.06(18)
C(9)-C(8)-C(7)	126.42(16)
C(10)-C(9)-C(8)	120.31(18)
C(10)-C(9)-C(16)	122.59(19)
C(8)-C(9)-C(16)	117.11(18)
C(9)-C(10)-C(11)	125.7(2)
C(9)-C(10)-H(10)	117.1
C(11)-C(10)-H(10)	117.1
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(2)-C(12)-C(13)	121.5(3)
C(2)-C(12)-H(12)	119.2
C(13)-C(12)-H(12)	119.2
C(4)-C(13)-C(12)	120.2(3)
C(4)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9

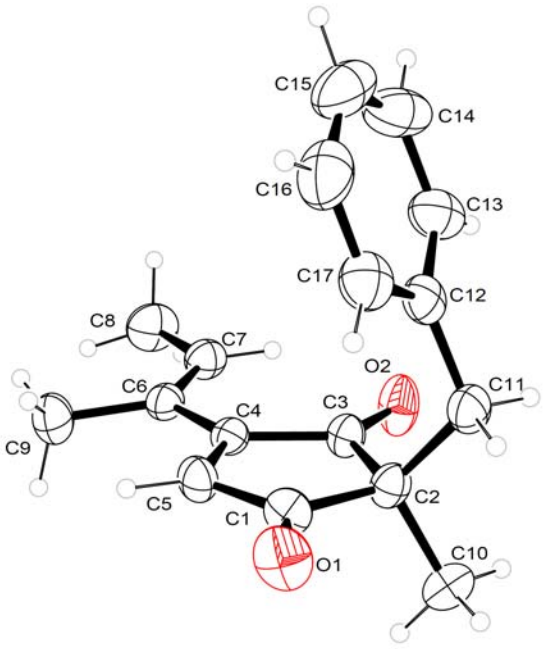
O(2)-C(14)-C(15)	126.2(2)
O(2)-C(14)-C(6)	124.8(2)
C(15)-C(14)-C(6)	108.96(18)
C(8)-C(15)-C(14)	112.55(19)
C(8)-C(15)-H(15)	123.7
C(14)-C(15)-H(15)	123.7
C(9)-C(16)-H(16A)	109.5
C(9)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(9)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(6)-C(17)-H(17A)	109.5
C(6)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(6)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 8. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 5. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	79(2)	63(2)	91(2)	3(1)	-3(2)	-1(1)
O(2)	73(1)	90(1)	89(1)	26(1)	30(1)	-5(1)
C(2)	182(4)	63(2)	97(2)	2(2)	-64(3)	5(2)
C(3)	99(2)	74(2)	143(3)	-7(2)	-43(2)	0(2)
C(4)	68(1)	43(1)	62(1)	10(1)	1(1)	8(1)

C(5)	64(1)	62(1)	56(1)	10(1)	-1(1)	9(1)
C(6)	49(1)	56(1)	47(1)	10(1)	-1(1)	-1(1)
C(7)	38(1)	52(1)	52(1)	6(1)	0(1)	-4(1)
C(8)	39(1)	44(1)	45(1)	-3(1)	-2(1)	-4(1)
C(9)	52(1)	42(1)	47(1)	-3(1)	-7(1)	-1(1)
C(10)	63(1)	54(1)	50(1)	4(1)	-1(1)	-1(1)
C(11)	106(2)	71(2)	63(1)	17(1)	5(2)	-4(1)
C(12)	191(4)	68(2)	59(2)	2(1)	1(2)	14(2)
C(13)	105(2)	61(2)	68(2)	3(1)	9(2)	4(1)
C(14)	53(1)	56(1)	59(1)	3(1)	10(1)	-7(1)
C(15)	39(1)	62(1)	61(1)	1(1)	4(1)	3(1)
C(16)	67(1)	65(1)	79(2)	9(1)	-2(1)	14(1)
O(16)	41(1)	104(1)	85(1)	36(1)	9(1)	6(1)
C(17)	76(1)	79(2)	53(1)	3(1)	-10(1)	-7(1)



ORTEP representation of the X-ray structure of enantiopure **5** (thermal ellipsoids at 30% probability)

Single crystal X-ray diffraction analysis of 6:

A single crystal of **6** (obtained from 1:1 petroleum ether/EtOAc at r.t.) was mounted and the diffraction data were collected at 100 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structures were solved by direct methods using the SHELX-97 and refined by full-matrix least-squares on F^2. Empirical absorption corrections were applied with SADABS. All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table 9. Crystal data and structure refinement for 6

Identification code	**6**	
Empirical formula	$2 \times (C_{18}H_{15}ClO_4)$	
Formula weight	661.50	
Temperature	100(2) K	
Wavelength	71.073 pm	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 646.5(5) pm	α = 90.000(5)°
	b = 1692.7(5) pm	β = 90.000(5)°
	c = 2914.3(5) pm	γ = 90.000(5)°
Volume	3.19(1) nm^3	
Z	4	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	0.257 mm^{-1}	
F(000)	1376	
Crystal size	$0.28 \times 0.26 \times 0.24$ mm^3	
Theta range for data collection	1.39 to 30.61°	
Index ranges	$-9 \le h \le 9$, $-23 \le k \le 24$, $-41 \le l \le 41$	
Reflections collected	67766	
Independent reflections	9766 [R_{int} = 0.0984]	

Completeness to Θ = 30.61°	99.6 %
Max. and min. transmission	0.9409 and 0.9315
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9766 / 0 / 423
Goodness-of-fit on F^2	1.002
Final R indices [I > 2 σ (I)]	$R1$ = 0.0514, ωR2 = 0.1001
R indices (all data)	$R1$ = 0.0791, ωR2 = 0.1106
Absolute structure parameter	0.00(5)
Largest diff. peak and hole	0.352 and –0.275 e.Å^{-3}

Table 10. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (pm^2 × 10^{-1}) for 6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C(1)	14185(4)	1528(1)	-444(1)	23(1)
C(2)	13530(4)	1747(1)	-9(1)	24(1)
C(3)	14860(4)	1670(1)	358(1)	20(1)
C(4)	16873(4)	1376(1)	299(1)	19(1)
C(5)	17509(4)	1194(1)	-146(1)	22(1)
C(6)	16195(4)	1267(1)	-517(1)	24(1)
C(7)	18213(4)	1202(1)	709(1)	20(1)
C(8)	17856(3)	361(1)	909(1)	16(1)
C(9)	19195(4)	210(2)	1331(1)	23(1)
C(10)	15561(3)	250(1)	1007(1)	16(1)
C(11)	14652(3)	-262(1)	649(1)	15(1)
C(12)	16138(3)	-563(1)	383(1)	14(1)
C(13)	18191(3)	-243(1)	528(1)	17(1)
C(14)	15913(3)	-1145(1)	-4(1)	14(1)
C(15)	17046(4)	-1911(1)	103(1)	20(1)
C(16)	16517(3)	-799(1)	-462(1)	17(1)

C(17)	14900(4)	-779(1)	-739(1)	20(1)
C(18)	13106(3)	-1100(1)	-491(1)	18(1)
C(19)	16785(4)	-2344(1)	3126(1)	22(1)
C(20)	17518(4)	-1772(1)	2832(1)	24(1)
C(21)	16311(4)	-1544(1)	2462(1)	23(1)
C(22)	14372(4)	-1875(1)	2386(1)	21(1)
C(23)	13636(4)	-2420(1)	2705(1)	24(1)
C(24)	14829(4)	-2667(2)	3076(1)	25(1)
C(25)	13211(4)	-1712(1)	1947(1)	23(1)
C(26)	13824(4)	-2296(1)	1562(1)	19(1)
C(27)	12612(4)	-2134(2)	1119(1)	27(1)
C(28)	16156(4)	-2272(1)	1479(1)	19(1)
C(29)	17053(4)	-3044(1)	1612(1)	19(1)
C(30)	15570(3)	-3547(1)	1739(1)	17(1)
C(31)	13518(4)	-3150(1)	1715(1)	19(1)
C(32)	15802(3)	-4387(1)	1894(1)	18(1)
C(33)	14624(4)	-4967(1)	1591(1)	23(1)
C(34)	15278(4)	-4456(1)	2396(1)	19(1)
C(35)	16932(4)	-4652(1)	2635(1)	21(1)
C(36)	18662(4)	-4771(1)	2315(1)	22(1)
O(1)	19845(2)	-423(1)	361(1)	26(1)
O(2)	14642(2)	540(1)	1331(1)	22(1)
O(3)	13722(2)	-1310(1)	-60(1)	16(1)
O(4)	11354(2)	-1206(1)	-618(1)	24(1)
O(5)	17095(3)	-1708(1)	1327(1)	24(1)
O(6)	11872(3)	-3454(1)	1807(1)	27(1)
O(7)	17979(2)	-4597(1)	1879(1)	19(1)
O(8)	20399(3)	-4993(1)	2384(1)	31(1)
Cl(1)	12460(1)	1576(1)	-902(1)	32(1)
Cl(2)	18352(1)	-2683(1)	3571(1)	34(1)

Table 11. Bond lengths [pm] and angles [°] for 6

C(1)-C(2)	138.8(3)
C(1)-C(6)	138.9(4)
C(1)-Cl(1)	174.1(2)
C(2)-C(3)	137.8(3)
C(2)-H(2)	95.00
C(3)-C(4)	140.3(3)
C(3)-H(3)	95.00
C(4)-C(5)	139.4(3)
C(4)-C(7)	150.6(3)
C(5)-C(6)	138.0(3)
C(5)-H(5)	95.00
C(6)-H(6)	95.00
C(7)-C(8)	155.6(3)
C(7)-H(7A)	99.00
C(7)-H(7B)	99.00
C(8)-C(13)	152.4(3)
C(8)-C(10)	152.2(3)
C(8)-C(9)	152.6(3)
C(9)-H(9A)	98.00
C(9)-H(9B)	98.00
C(9)-H(9C)	98.00
C(10)-O(2)	121.8(3)
C(10)-C(11)	147.8(3)
C(11)-C(12)	133.5(3)
C(11)-H(11)	95.00
C(12)-C(13)	149.4(3)
C(12)-C(14)	150.5(3)
C(13)-O(1)	121.3(3)

C(14)-O(3)	145.3(3)
C(14)-C(16)	150.8(3)
C(14)-C(15)	152.2(3)
C(15)-H(15A)	98.00
C(15)-H(15B)	98.00
C(15)-H(15C)	98.00
C(16)-C(17)	132.1(3)
C(16)-H(16)	95.00
C(17)-C(18)	147.1(3)
C(17)-H(17)	95.00
C(18)-O(4)	120.5(3)
C(18)-O(3)	136.5(3)
C(19)-C(20)	137.7(3)
C(19)-C(24)	138.5(4)
C(19)-Cl(2)	174.2(2)
C(20)-C(21)	138.5(3)
C(20)-H(20)	95.00
C(21)-C(22)	139.1(3)
C(21)-H(21)	95.00
C(22)-C(23)	139.2(3)
C(22)-C(25)	151.1(3)
C(23)-C(24)	139.2(3)
C(23)-H(23)	95.00
C(24)-H(24)	95.00
C(25)-C(26)	154.7(3)
C(25)-H(25A)	99.00
C(25)-H(25B)	99.00
C(26)-C(31)	152.6(3)
C(26)-C(28)	152.7(3)
C(26)-C(27)	153.5(3)
C(27)-H(27A)	98.00

C(27)-H(27B)	98.00
C(27)-H(27C)	98.00
C(28)-O(5)	121.6(3)
C(28)-C(29)	148.1(3)
C(29)-C(30)	133.5(3)
C(29)-H(29)	105(2)
C(30)-C(31)	148.8(3)
C(30)-C(32)	149.9(3)
C(31)-O(6)	121.1(3)
C(32)-O(7)	145.2(3)
C(32)-C(34)	150.6(3)
C(32)-C(33)	152.6(3)
C(33)-H(33A)	98.00
C(33)-H(33B)	98.00
C(33)-H(33C)	98.00
C(34)-C(35)	131.8(3)
C(34)-H(34)	95.00
C(35)-C(36)	147.1(3)
C(35)-H(35)	95.00
C(36)-O(8)	120.1(3)
C(36)-O(7)	137.7(3)

C(2)-C(1)-C(6)	120.6(2)
C(2)-C(1)-Cl(1)	119.57(19)
C(6)-C(1)-Cl(1)	119.80(19)
C(3)-C(2)-C(1)	119.6(2)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	121.1(2)
C(2)-C(3)-H(3)	119.4
C(4)-C(3)-H(3)	119.4

C(5)-C(4)-C(3)	117.8(2)
C(5)-C(4)-C(7)	121.7(2)
C(3)-C(4)-C(7)	120.33(19)
C(6)-C(5)-C(4)	121.8(2)
C(6)-C(5)-H(5)	119.1
C(4)-C(5)-H(5)	119.1
C(5)-C(6)-C(1)	119.0(2)
C(5)-C(6)-H(6)	120.5
C(1)-C(6)-H(6)	120.5
C(4)-C(7)-C(8)	112.95(18)
C(4)-C(7)-H(7A)	109.0
C(8)-C(7)-H(7A)	109.0
C(4)-C(7)-H(7B)	109.0
C(8)-C(7)-H(7B)	109.0
H(7A)-C(7)-H(7B)	107.8
C(13)-C(8)-C(10)	101.14(17)
C(13)-C(8)-C(9)	113.24(18)
C(10)-C(8)-C(9)	112.39(18)
C(13)-C(8)-C(7)	108.69(17)
C(10)-C(8)-C(7)	109.12(18)
C(9)-C(8)-C(7)	111.71(17)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(10)-C(11)	126.0(2)
O(2)-C(10)-C(8)	124.9(2)
C(11)-C(10)-C(8)	109.09(18)
C(12)-C(11)-C(10)	110.3(2)

C(12)-C(11)-H(11)	124.9
C(10)-C(11)-H(11)	124.9
C(11)-C(12)-C(13)	109.74(18)
C(11)-C(12)-C(14)	127.95(19)
C(13)-C(12)-C(14)	122.31(18)
O(1)-C(13)-C(12)	125.39(19)
O(1)-C(13)-C(8)	125.8(2)
C(12)-C(13)-C(8)	108.78(17)
O(3)-C(14)-C(16)	103.21(16)
O(3)-C(14)-C(12)	107.68(16)
C(16)-C(14)-C(12)	112.65(17)
O(3)-C(14)-C(15)	109.15(18)
C(16)-C(14)-C(15)	112.83(18)
C(12)-C(14)-C(15)	110.88(17)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(14)	110.22(19)
C(17)-C(16)-H(16)	124.9
C(14)-C(16)-H(16)	124.9
C(16)-C(17)-C(18)	108.29(19)
C(16)-C(17)-H(17)	125.9
C(18)-C(17)-H(17)	125.9
O(4)-C(18)-O(3)	121.2(2)
O(4)-C(18)-C(17)	130.1(2)
O(3)-C(18)-C(17)	108.60(19)
C(20)-C(19)-C(24)	121.7(2)
C(20)-C(19)-Cl(2)	119.6(2)

C(24)-C(19)-Cl(2)	118.66(18)
C(19)-C(20)-C(21)	119.1(2)
C(19)-C(20)-H(20)	120.5
C(21)-C(20)-H(20)	120.5
C(20)-C(21)-C(22)	121.3(2)
C(20)-C(21)-H(21)	119.4
C(22)-C(21)-H(21)	119.4
C(23)-C(22)-C(21)	118.0(2)
C(23)-C(22)-C(25)	121.1(2)
C(21)-C(22)-C(25)	120.6(2)
C(22)-C(23)-C(24)	121.8(2)
C(22)-C(23)-H(23)	119.1
C(24)-C(23)-H(23)	119.1
C(19)-C(24)-C(23)	118.0(2)
C(19)-C(24)-H(24)	121.0
C(23)-C(24)-H(24)	121.0
C(22)-C(25)-C(26)	111.78(18)
C(22)-C(25)-H(25A)	109.3
C(26)-C(25)-H(25A)	109.3
C(22)-C(25)-H(25B)	109.3
C(26)-C(25)-H(25B)	109.3
H(25A)-C(25)-H(25B)	107.9
C(31)-C(26)-C(28)	101.50(19)
C(31)-C(26)-C(27)	110.47(19)
C(28)-C(26)-C(27)	111.50(18)
C(31)-C(26)-C(25)	111.06(18)
C(28)-C(26)-C(25)	110.51(19)
C(27)-C(26)-C(25)	111.40(19)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5

C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
O(5)-C(28)-C(29)	126.4(2)
O(5)-C(28)-C(26)	124.9(2)
C(29)-C(28)-C(26)	108.77(19)
C(30)-C(29)-C(28)	110.8(2)
C(30)-C(29)-H(29)	133.1(11)
C(28)-C(29)-H(29)	115.1(11)
C(29)-C(30)-C(31)	109.8(2)
C(29)-C(30)-C(32)	128.1(2)
C(31)-C(30)-C(32)	122.08(19)
O(6)-C(31)-C(30)	125.5(2)
O(6)-C(31)-C(26)	125.5(2)
C(30)-C(31)-C(26)	109.00(19)
O(7)-C(32)-C(30)	108.66(17)
O(7)-C(32)-C(34)	103.21(18)
C(30)-C(32)-C(34)	110.11(18)
O(7)-C(32)-C(33)	107.94(18)
C(30)-C(32)-C(33)	112.73(18)
C(34)-C(32)-C(33)	113.63(19)
C(32)-C(33)-H(33A)	109.5
C(32)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(32)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(35)-C(34)-C(32)	110.5(2)
C(35)-C(34)-H(34)	124.7
C(32)-C(34)-H(34)	124.7
C(34)-C(35)-C(36)	108.4(2)

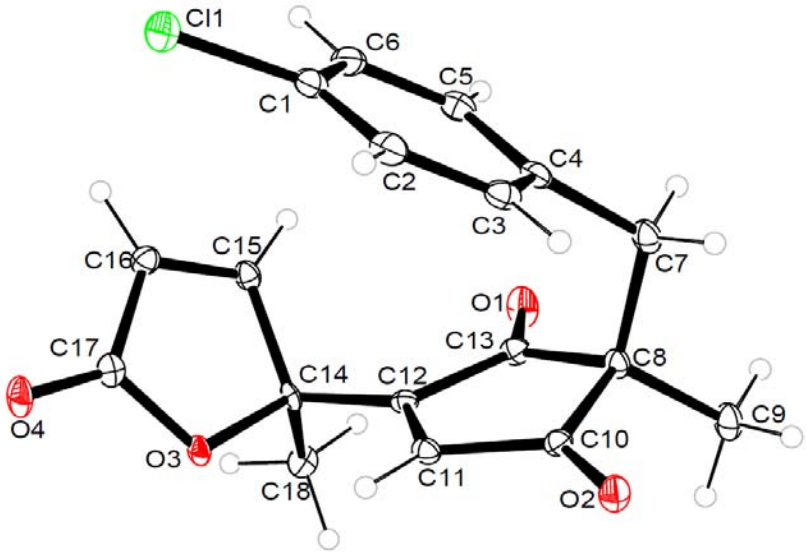
C(34)-C(35)-H(35)	125.8
C(36)-C(35)-H(35)	125.8
O(8)-C(36)-O(7)	121.5(2)
O(8)-C(36)-C(35)	130.3(2)
O(7)-C(36)-C(35)	108.2(2)
C(18)-O(3)-C(14)	109.68(16)
C(36)-O(7)-C(32)	109.57(17)

Symmetry transformations used to generate equivalent atoms:

Table 12. Anisotropic displacement parameters ($pm^2 \times 10^{-1}$) for 6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	23(1)	19(1)	26(1)	4(1)	-4(1)	-5(1)
C(2)	21(1)	21(1)	31(1)	4(1)	0(1)	-1(1)
C(3)	22(1)	16(1)	23(1)	1(1)	4(1)	-1(1)
C(4)	18(1)	15(1)	22(1)	2(1)	1(1)	-4(1)
C(5)	19(1)	21(1)	27(1)	1(1)	3(1)	-3(1)
C(6)	27(1)	23(1)	21(1)	3(1)	3(1)	-4(1)
C(7)	15(1)	24(1)	22(1)	-3(1)	0(1)	-5(1)
C(8)	12(1)	19(1)	16(1)	-3(1)	0(1)	-2(1)
C(9)	16(1)	29(1)	23(1)	-3(1)	-4(1)	-2(1)
C(10)	14(1)	17(1)	16(1)	1(1)	0(1)	-1(1)
C(11)	12(1)	16(1)	18(1)	1(1)	-1(1)	-1(1)
C(12)	11(1)	16(1)	14(1)	2(1)	-1(1)	0(1)
C(13)	14(1)	21(1)	17(1)	0(1)	0(1)	-1(1)
C(14)	9(1)	17(1)	17(1)	-1(1)	-2(1)	-2(1)
C(15)	23(1)	18(1)	20(1)	-2(1)	-1(1)	6(1)
C(16)	14(1)	20(1)	17(1)	-3(1)	2(1)	-2(1)

C(17)	23(1)	21(1)	15(1)	1(1)	2(1)	-1(1)
C(18)	16(1)	19(1)	18(1)	-5(1)	1(1)	2(1)
C(19)	27(1)	23(1)	17(1)	-2(1)	-4(1)	4(1)
C(20)	27(1)	20(1)	24(1)	-6(1)	1(1)	-1(1)
C(21)	29(1)	17(1)	22(1)	-1(1)	2(1)	-1(1)
C(22)	22(1)	20(1)	21(1)	-1(1)	2(1)	5(1)
C(23)	18(1)	29(1)	24(1)	-1(1)	4(1)	0(1)
C(24)	30(1)	28(1)	18(1)	0(1)	3(1)	-2(1)
C(25)	21(1)	20(1)	28(1)	4(1)	-2(1)	5(1)
C(26)	18(1)	21(1)	19(1)	4(1)	-3(1)	-2(1)
C(27)	25(1)	29(1)	26(1)	11(1)	-8(1)	-7(1)
C(28)	23(1)	19(1)	15(1)	2(1)	-2(1)	-1(1)
C(29)	16(1)	22(1)	17(1)	0(1)	1(1)	-1(1)
C(30)	19(1)	19(1)	12(1)	-1(1)	0(1)	-1(1)
C(31)	20(1)	22(1)	15(1)	3(1)	-1(1)	-1(1)
C(32)	12(1)	21(1)	21(1)	1(1)	2(1)	1(1)
C(33)	26(1)	19(1)	24(1)	-2(1)	-2(1)	-4(1)
C(34)	19(1)	16(1)	21(1)	1(1)	5(1)	-2(1)
C(35)	25(1)	20(1)	20(1)	3(1)	3(1)	0(1)
C(36)	20(1)	17(1)	29(1)	4(1)	2(1)	-1(1)
O(1)	10(1)	40(1)	30(1)	-11(1)	2(1)	2(1)
O(2)	17(1)	28(1)	19(1)	-7(1)	2(1)	-1(1)
O(3)	9(1)	21(1)	17(1)	-3(1)	-2(1)	-2(1)
O(4)	12(1)	37(1)	24(1)	-7(1)	-4(1)	1(1)
O(5)	24(1)	23(1)	26(1)	5(1)	1(1)	-7(1)
O(6)	15(1)	28(1)	38(1)	10(1)	-1(1)	-3(1)
O(7)	17(1)	19(1)	22(1)	2(1)	4(1)	2(1)
O(8)	17(1)	34(1)	41(1)	11(1)	1(1)	5(1)
Cl(1)	31(1)	35(1)	30(1)	4(1)	-9(1)	-5(1)
Cl(2)	37(1)	39(1)	26(1)	4(1)	-11(1)	-1(1)



ORTEP representation of the X-ray structure of enantiopure **6** (thermal ellipsoids at 30% probability)