Supporting Information for

Design of Highly Enantioselective Organocatalysts Based on Molecular Recognition

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General data: NMR spectra were recorded on a Bruker-300 MHz spectrometer. Elemental analysis was carried out using Carlo Erba-1106 Analyzer. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter at $\lambda = 589$ nm. FT-ICRMS spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AS, AD and OJ columns were purchased from Daicel Chemical Industries, LTD. Acetone was dried over anhydrous K_2CO_3 . Hexane and ethyl acetate for column chromatography were distilled before use.

The typical procedure for the preparation of 3a-g.

Typical procedure for the synthesis of Z-A: *N*-Carbobenzyloxy-L-proline (2.0 g, 8.0 mmol) and TEA (0.81 g, 8.0 mmol) were dissolved in THF (30 mL). The solution was cooled down to 0°C. To the solution was added ethylchloroformate (0.88 g, 8.0 mmol) dropwise for 15 min. After the solution was stirred for 30 min, amine (8.0 mmol) was added for 15 min. The resulting solution was stirred at 0 °C for 1 h and at room temperature for another 16 h, and then refluxed for 3 h. After cooled down to room temperature, the solution was diluted with ethyl acetate. After filtration and removal of solvent under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane: ethyl acetate = 2:1) to give Z-A .

Typical procedure for the synthesis of A: Compounds Z-A (1.0 g), 5 % Pd/C (0.1 g) and methanol (30 ml) were mixed in a 100 mL two-neck flask. After stirred under hydrogen (1 atm) for 1 h, the

solution was filtered. After removal of the solvent, the residue was purified through column chromatography on silica gel (eluent: hexane: ethyl acetate = 2:1) to give **A**.

Pyrrolidine-2-carboxylic acid pyridin-2-ylamide (3a): Yield: 64%, mp 45-50 °C; $[\alpha]_D^{26} = -61.5$

(c = 0.44, EtOAc); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.73 (m, 2H), 2.01 (m, 1H), 2.18 (m, 1H), 3.01 (m, 2H), 3.87 (m, 1H), 6.98 (m, 1H), 7.65 (m, 1H), 8.26 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 26.2, 30.9, 47.4, 61.1, 113.7, 119.7, 138.3, 148.0, 151.2, 174.4. HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{10}\text{H}_{13}\text{N}_3\text{O} + \text{H})^+$ requires m/z 192.1137, found m/z 192.1138.

Pyrrolidine-2-carboxylic acid (3-methyl-pyridin-2-yl)-amide (3b): Yield: 69%; $[\alpha]_D^{26} = -50.3$ (c =

0.56, EtOAc); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.77 (m, 2H), 2.07 (m, 1H), 2.21 (m, 1H), 2.24 (s, 1H), 3.05 (m, 2H), 3.90 (m, 1H), 7.03 (m, 1H), 7.50 (m, 1H), 8.27 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 17.8, 26.2, 30.8, 47.3, 60.9, 121.0, 126.8, 139.4, 146.1, 149.4, 173.4. HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O} + \text{Na})^+$ requires m/z 228.1113, found m/z 228.1117.

Pyrrolidine-2-carboxylic acid (4-methyl-pyridin-2-yl)-amide (3c): Yield: 76%; $[\alpha]_D^{26} = -70.4$ (c =

0.55, EtOAc); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.74 (m, 2H), 2.03 (m, 1H), 2.17 (m, 1H), 2.34 (s, 1H), 3.03 (m, 2H), 3.85 (m, 1H), 6.84 (m, 1H), 8.08-8.13 (m, 1H), 10.1 (brs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 21.2, 26.1, 30.8, 47.2, 60.9, 114.0, 120, 147.5, 149.6, 151.1, 174.3. HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O} + \text{Na})^+$ requires m/z 228.1113, found m/z 228.1121.

Pyrrolidine-2-carboxylic acid (5-methyl-pyridin-2-yl)-amide (3d): Yield: 62%; mp 63-68 °C;

$[\alpha]_D^{26} = -54.4$ (c = 0.36, EtOAc); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.73 (m, 2H), 2.01 (m, 1H), 2.18 (m, 1H), 2.26 (s, 1H), 3.01 (m, 2H), 3.85 (m, 1H), 7.48 (m, 1H), 8.08-8.14 (m, 2H), 10.1 (brs, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 17.8, 26.2, 30.8, 47.3, 60.9, 121.0, 126.8, 139.4, 146.1, 149.4, 173.4. HRMS (FT-ICRMS) exact mass calcd for $(\text{C}_{11}\text{H}_{15}\text{N}_3\text{O} + \text{Na})^+$ requires m/z 228.1113, found m/z 228.1119.

Pyrrolidine-2-carboxylic acid (6-methyl-pyridin-2-yl)-amide (3e): Yield: 73% mp 60-63 °C;

$[\alpha]_D^{26} = -39.2$ (c = 0.45, EtOAc); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.74 (m, 2H), 2.01 (m, 1H), 2.17 (m, 1H), 2.44 (s, 1H), 3.03 (m, 2H), 3.85 (m, 1H), 6.85 (d, $J = 7.5$ Hz, 1H), 7.55 (t, $J = 7.9$ Hz, 1H), 8.04 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 24.2, 26.3, 30.9, 47.4, 61.1, 110.5, 119.1, 138.5, 150.6, 156.9, 174.4. HRMS (FT-ICRMS)

exact mass calcd for $(C_{11}H_{15}N_3O + H)^+$ requires m/z 206.1293, found m/z 206.1299.

Pyrrolidine-2-carboxylic acid (4,6-dimethyl-pyridin-2-yl)-amide (3f): Yield: 81%; $[\alpha]_D^{26} = -48.8$

($c = 0.65$, EtOAc); 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.75 (m, 2H), 2.01 (m, 1H), 2.20 (m, 1H), 2.29 (s, 1H), 2.40 (s, 1H), 3.04 (m, 2H), 3.85 (m, 1H), 6.70 (s, 1H), 7.89 (s, 1H), 10.0 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.3, 24.0, 26.2,

31.0, 47.4, 61.1, 111.1, 120.4, 149.9, 150.6, 156.5, 174.3. HRMS (FT-ICRMS) exact mass calcd for $(C_{12}H_{17}N_3O + H)^+$ requires m/z 220.1450, found m/z 220.1435.

Pyrrolidine-2-carboxylic acid (6-acetylamino-pyridin-2-yl)-amide (3g): Yield: 75%; mp

175-179 $^{\circ}C$; $[\alpha]_D^{26} = -5.4$ ($c = 0.41$, EtOAc); 1H NMR (300 MHz, $CDCl_3$) δ (ppm)

1.74 (m, 2H), 2.02 (m, 1H), 2.17 (s, 1H), 2.20 (m, 1H), 2.95-3.08 (m, 2H), 3.86 (m, 1H), 7.64-7.69 (m, 1H), 7.84-7.93 (m, 2H), 9.95 (brs, 1H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ (ppm) 24.7, 26.3, 30.8, 47.4, 61.1, 109.2, 109.4, 140.7, 149.3, 149.7, 168.7, 174.1. HRMS (FT-ICRMS) exact mass calcd for $(C_{12}H_{16}N_4O_2 + H)^+$ requires m/z 249.1352, found m/z 249.1342.

Pyrrolidine-2-carboxylic acid pyridin-3-ylamide (3h): Yield: 72%; $[\alpha]_D^{26} = -10.8$ ($c = 0.36$,

EtOH); 1H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.78 (m, 2H), 2.05 (m, 1H), 2.20 (m, 1H), 2.90-3.15 (m, 2H), 3.88 (m, 1H), 7.26 (m, 1H), 8.22-8.32 (m, 2H), 8.60 (s, 1H);

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 26.4, 30.8, 47.5, 61.1, 123.7, 126.4, 134.7,

141.0, 145.1, 174.1. HRMS (FT-ICRMS) exact mass calcd for $(C_{10}H_{13}N_3O + H)^+$ requires m/z 192.1137, found m/z 192.1136.

General procedure for aldol reaction: To a mixture of anhydrous acetone (1 mL) and toluene (3 mL) was added the corresponding aldehyde (0.5 mmol) and catalyst (20 mol %) and the resulting mixture was stirred at 0 $^{\circ}C$ for 48 h. The reaction mixture was treated with CH_2N_2 solution in ether for 20min. After removal of solvent, the residue was purified through flash column chromatography on a silica gel (eluent: hexane: ethyl acetate = 7:1) to give the pure adducts.

2-Hydroxy-4-oxo-2-phenyl-pentanoic acid (5a): Yield: >99%; 1H NMR (300 MHz, $CDCl_3$) δ

(ppm) 2.20 (s, 3H), 3.00 (d, $J = 17.7$ Hz, 1H), 3.57 (d, $J = 17.7$ Hz, 1H), 7.28-7.38 (m, 3H), 7.50-7.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 30.6, 52.1, 124.9, 128.3,

128.5, 139.2, 176.9, 208.9. HRMS (FT-ICRMS) exact mass calcd for $(C_{11}H_{12}O_4-H)^-$ requires m/z 207.0657, found m/z 207.0668.

2-Hydroxy-4-oxo-2-phenyl-pentanoic acid methyl ester (6a): Yield: >99%; 1H NMR (300 MHz,

CDCl₃) δ (ppm) 2.20 (s, 3H), 3.00 (d, J = 17.6 Hz, 1H), 3.55 (d, J = 17.6 Hz, 1H), 3.75 (s, 3H), 7.29-7.38 (m, 3H), 7.54-7.57 (m, 2H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 30.7, 53.1, 53.2, 76.5, 124.9, 128.2, 128.6, 140.3, 174.5, 208.0. HRMS

(FT-ICRMS) exact mass calcd for (C₁₂H₁₄O₄ + Na)⁺ requires m/z 245.0790, found m/z 245.0781. Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak AS-H, i-PrOH/ Hexane= 30/70), UV 254 nm, flow rate 1.0 mL/min. *R*-isomer, t_R 6.3 min and *S*-isomer, t_R 5.6 min.

2-Hydroxy-4-oxo-2-thiophen-2-yl-pentanoic acid methyl ester (6b): Yield: 78%; ¹HNMR (300

MHz, CDCl₃) δ (ppm) 2.19 (s, 3H), 3.19 (d, J = 17.7 Hz, 1H), 3.51 (d, J = 17.7 Hz, 1H), 3.79 (s, 3H), 6.96 (m, 1H), 7.04 (m, 1H), 7.25 (m, 1H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 30.4, 53.3, 53.5, 74.9, 123.7, 125.4, 127.0, 144.9, 173.4, 206.5.

HRMS (FT-ICRMS) exact mass calcd for (C₁₀H₁₂O₄S + Na)⁺ requires m/z 251.0354, found m/z 251.0357. Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak AS-H, i-PrOH/ Hexane=30/70), UV 254 nm, flow rate 1.0 mL/min. *R*-isomer, t_R 9.75 min and *S*-isomer, t_R 7.76 min.

2-Furan-2-yl-2-hydroxy-4-oxo-pentanoic acid methyl ester (6c): Yield: >99%; ¹HNMR (300

MHz, CDCl₃) δ (ppm) 2.20 (s, 3H), 3.25 (d, J = 17.7 Hz, 1H), 3.48 (d, J = 17.7 Hz, 1H), 3.79 (s, 3H), 6.34 (t, J = 2.1 Hz, 2H), 7.36 (t, J = 1.2 Hz, 1H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 30.6, 49.4, 53.3, 72.9, 107.0, 110.5, 142.7, 152.5, 172.6,

206.2. HRMS (FT-ICRMS) exact mass calcd for (C₁₀H₁₂O₅ + Na)⁺ requires m/z 235.0582, found m/z 235.0578. Enantiomeric excess: 93%, determined by HPLC (Daicel Chiralpak AS-H, i-PrOH/ Hexane= 20/80), UV 254 nm, flow rate 1.0 mL/min. *R*-isomer, t_R 12.14 min and *S*-isomer, t_R 10.53 min.

2-Benzyl-2-hydroxy-4-oxo-pentanoic acid methyl ester (6d): Yield: 75%; ¹HNMR (300 MHz,

CDCl₃) δ (ppm) 2.14 (s, 3H), 2.80 (d, J = 17.4 Hz, 1H), 2.89 (d, J = 13.4 Hz, 1H), 2.97 (d, J = 13.4 Hz, 1H), 3.12 (d, J = 17.4 Hz, 1H), 3.70 (s, 3H), 7.16-7.19 (m, 2H),

7.25-7.31 (m, 1H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 30.7, 45.2, 50.8, 52.6, 75.8, 127.1, 128.2, 128.6, 130.2, 134.8, 175.0, 207.3. HRMS (FT-ICRMS) exact mass calcd for (C₁₃H₁₆O₄ + Na)⁺ requires m/z 259.0946, found m/z 259.0930. Enantiomeric excess: 98%, determined by chiral GC analysis (SUPELCO GAMMA DEX 225), Inject Temp 240 °C, Column Temp 117 °C, FID Oven Temp 260 °C, Inlet Pressure 10 Psi. *R*-isomer, t_R 12.7 min and *S*-isomer, t_R 13.2 min.

2-Hydroxy-2-methyl-4-oxo-pentanoic acid methyl ester (6e): Yield: 78%; ¹HNMR (300 MHz, CDCl₃) δ (ppm) 1.37 (s, 3H), 2.15 (s, 3H), 2.78 (d, *J* = 17.7 Hz, 1H), 3.13 (d, *J* = 17.7 Hz, 1H), 3.75 (s, 3H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 26.1, 30.5, 52.2, 52.7, 72.5, 176.2, 207.8. HRMS (FT-ICRMS) exact mass calcd for (C₇H₁₂O₄ + Na)⁺ requires *m/z* 183.0633, found *m/z* 183.0618. Enantiomeric excess: 92%, determined by chiral GC analysis (SUPELCO GAMMA DEX 225), Inject Temp 240 °C, Column Temp 117 °C, FID Oven Temp 260 °C, Inlet Pressure 10 Psi. *R*-isomer, *t_R* 8.1 min and *S*-isomer, *t_R* 8.6 min.

2-Ethyl-2-hydroxy-4-oxo-pentanoic acid methyl ester (6f): Yield: 85%; ¹HNMR (300 MHz, CDCl₃) δ (ppm) 0.87 (t, *J* = 7.5 Hz, 3H), 1.66 (q, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 2.81 (d, *J* = 17.4 Hz, 1H), 3.03 (d, *J* = 17.4 Hz, 1H), 3.75 (s, 3H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 7.4, 30.6, 32.2, 51.2, 52.6, 75.4, 175.7, 207.5. HRMS (FT-ICRMS) exact mass calcd for (C₈H₁₄O₄ + Na)⁺ requires *m/z* 197.0790, found *m/z* 197.0780. Enantiomeric excess: 95%, determined by chiral GC analysis (SUPELCO GAMMA DEX 225), Inject Temp 240 °C, Column Temp 110 °C, FID Oven Temp 260 °C, Inlet Pressure 10 Psi. *R*-isomer, *t_R* 11.7 min and *S*-isomer, *t_R* 12.0 min.

2-Hydroxy-2-isobutyl-4-oxo-pentanoic acid methyl ester (6g): Yield: 96%; ¹HNMR (300 MHz, CDCl₃) δ (ppm) 0.84 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 1.57 (d, *J* = 5.8 Hz, 2H), 1.75 (m, 1H), 2.14 (s, 3H), 2.83 (d, *J* = 17.4 Hz, 1H), 3.01 (d, *J* = 17.4 Hz, 1H), 3.75 (s, 3H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 23.4, 23.7, 24.3, 30.7, 47.6, 52.5, 52.6, 75.2, 176.1, 207.6. HRMS (FT-ICRMS) exact mass calcd for (C₁₀H₁₈O₄ + Na)⁺ requires *m/z* 225.1103, found *m/z* 225.1109. Enantiomeric excess: 96%, determined by chiral GC analysis (SUPELCO BETA DEX120), Inject Temp 240 °C, Column Temp 102 °C, FID Oven Temp 260 °C, Inlet Pressure 10 Psi. *R*-isomer, *t_R* 22.3 min and *S*-isomer, *t_R* 22.8 min.

Anti-Hydroxy-(2-oxo-cyclopentyl)-phenyl-acetic acid methyl ester (anti-6h): Yield: 20%; ¹HNMR (300 MHz, CDCl₃) δ (ppm) 1.58-2.32 (m, 6H), 3.31 (t, *J* = 9.2 Hz, 1H), 3.84 (s, 3H), 7.26-7.37 (m, 3H), 7.57-7.60 (m, 2H); ¹³CNMR (75 MHz, CDCl₃) δ (ppm) 20.3, 24.5, 38.9, 53.4, 56.6, 77.2, 125.6, 127.8, 128.2, 140.1, 175.0, 217.6. HRMS (FT-ICRMS) exact mass calcd for (C₁₄H₁₆O₄ + Na)⁺ requires *m/z* 271.0946, found *m/z* 271.0956. Enantiomeric excess: 81%, determined by HPLC (Daicel Chiralpak AS-H, i-PrOH/ Hexane = 30/70), UV 254 nm, flow rate 1.0 mL/min. *t_R* (major) 7.0 min and *S*-isomer, *t_R* (minor) 9.75 min.

Syn-Hydroxy-(2-oxo-cyclopentyl)-phenyl-acetic acid methyl ester (*syn*-6h): Yield: 40%;

^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.25-2.38 (m, 6H), 2.71 (m, 1H), 3.75 (s, 3H), 7.32-7.38 (m, 3H), 7.45-7.49 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 20.3, 26.5, 29.5, 38.9, 52.9, 56.7, 80.2, 125.2, 127.9, 128.1, 139.7, 173.6, 219.7. HRMS

(FT-ICRMS) exact mass calcd for $(\text{C}_{14}\text{H}_{16}\text{O}_4 + \text{Na})^+$ requires m/z 271.0946, found m/z 271.0954.

Enantiomeric excess: 24%, determined by HPLC (Daicel Chiralpak AS-H, i-PrOH/ Hexane=30/70),

UV 254 nm, flow rate 1.0 mL/min. t_R (major) 13.3 min and *S*-isomer, t_R (minor) 17.5 min.

General procedure for recycle reaction: To a mixture of anhydrous acetone (1 mL) and toluene (3 mL) was added the corresponding aldehyde (0.5 mmol) and catalyst (20 mol %) and the resulting mixture was stirred at 0°C for 48 h. After removal of solvent, the residue was solved in 5 mL water and then added saturated aqueous Na_2CO_3 until pH=8. The aqueous phase was extracted with ether (3x 5 mL). The combined organic layers were washed with brine and dried over anhydrous NaSO_4 . Removal of solvent recovers the catalyst. The aqueous phase was added 1N HCl until pH=6 and then extracted with EtOAc (3x 5ml). The combined organic layers were washed with brine and dried over anhydrous NaSO_4 . Removal of the solvent gave the aldol product in high purity. Its ee value was detected by HPLC after it was converted to the ester with CH_2N_2 .

¹H NMR Spectra of Racemic -hydroxyl Acids and Different Receptors

Crystallographic data for anti-3h

Table 1. Crystal data and structure refinement for y1972.

Identification code	y1972
Empirical formula	C ₁₄ H ₁₆ O ₄
Formula weight	248.27
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 5.814(1) Å alpha = 90 deg. b = 13.696(2) Å beta = 95.25(1) deg. c = 16.114(2) Å gamma = 90 deg.
Volume, Z	1277.80(33) Å ³ , 4
Density (calculated)	1.291 Mg/m ³
Absorption coefficient	0.094 mm ⁻¹
F(000)	528
Crystal size	0.50 x 0.34 x 0.12 mm
Theta range for data collection	1.95 to 25.50 deg.
Limiting indices	0 ≤ h ≤ 7, 0 ≤ k ≤ 16, -19 ≤ l ≤ 19
Reflections collected	2825
Independent reflections	2364 [R(int) = 0.0168]
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2364 / 0 / 166
Goodness-of-fit on F ²	0.979
Final R indices [I > 2σ(I)]	R1 = 0.0394, wR2 = 0.0740
R indices (all data)	R1 = 0.0814, wR2 = 0.0812
Extinction coefficient	0.0153(12)
Largest diff. peak and hole	0.148 and -0.109 e.Å ⁻³

Table 2. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for y1972. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	6948(2)	4844(1)	1543(1)	52(1)
O(2)	2688(2)	4852(1)	203(1)	55(1)
O(3)	2364(2)	3117(1)	1525(1)	57(1)
O(4)	5856(3)	2979(1)	1062(1)	71(1)
C(1)	2392(3)	5387(2)	781(1)	45(1)
C(2)	1566(4)	6422(2)	726(1)	67(1)
C(3)	1294(4)	6725(2)	1617(1)	64(1)
C(4)	3067(4)	6096(1)	2131(1)	57(1)
C(5)	2893(3)	5109(1)	1690(1)	41(1)
C(6)	4969(3)	4421(1)	1844(1)	41(1)
C(7)	5525(3)	4251(1)	2784(1)	42(1)
C(8)	7578(4)	4562(1)	3182(1)	52(1)
C(9)	8055(4)	4436(2)	4032(1)	68(1)
C(10)	6501(5)	3994(2)	4492(1)	73(1)
C(11)	4449(5)	3678(2)	4099(1)	76(1)
C(12)	3954(4)	3805(2)	3252(1)	63(1)
C(13)	4490(4)	3427(2)	1420(1)	47(1)
C(14)	1711(4)	2172(2)	1196(1)	71(1)

Table 3. Bond lengths [Å] and angles [deg] for y1972.

O(1)-C(6)	1.413(2)
O(1)-H(10)	0.8200
O(2)-C(1)	1.209(2)
O(3)-C(13)	1.333(2)
O(3)-C(14)	1.436(2)
O(4)-C(13)	1.194(2)
C(1)-C(2)	1.498(3)
C(1)-C(5)	1.517(2)
C(2)-C(3)	1.517(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.528(3)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.526(2)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-C(6)	1.534(2)
C(5)-H(5)	0.9800
C(6)-C(13)	1.536(3)

C(6)-C(7)	1.537(2)
C(7)-C(8)	1.370(2)
C(7)-C(12)	1.379(3)
C(8)-C(9)	1.384(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.362(3)
C(9)-H(9)	0.9300
C(10)-C(11)	1.369(3)
C(10)-H(10)	0.9300
C(11)-C(12)	1.381(3)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600

C(6)-O(1)-H(1O)	109.5
C(13)-O(3)-C(14)	117.22(17)
O(2)-C(1)-C(2)	126.58(18)
O(2)-C(1)-C(5)	124.37(18)
C(2)-C(1)-C(5)	109.02(17)
C(1)-C(2)-C(3)	105.34(17)
C(1)-C(2)-H(2A)	110.7
C(3)-C(2)-H(2A)	110.7
C(1)-C(2)-H(2B)	110.7
C(3)-C(2)-H(2B)	110.7
H(2A)-C(2)-H(2B)	108.8
C(2)-C(3)-C(4)	103.58(17)
C(2)-C(3)-H(3A)	111.0
C(4)-C(3)-H(3A)	111.0
C(2)-C(3)-H(3B)	111.0
C(4)-C(3)-H(3B)	111.0
H(3A)-C(3)-H(3B)	109.0
C(5)-C(4)-C(3)	103.59(16)
C(5)-C(4)-H(4A)	111.0
C(3)-C(4)-H(4A)	111.0
C(5)-C(4)-H(4B)	111.0
C(3)-C(4)-H(4B)	111.0
H(4A)-C(4)-H(4B)	109.0
C(1)-C(5)-C(4)	103.09(15)
C(1)-C(5)-C(6)	112.85(15)
C(4)-C(5)-C(6)	116.89(16)
C(1)-C(5)-H(5)	107.9
C(4)-C(5)-H(5)	107.9
C(6)-C(5)-H(5)	107.9
O(1)-C(6)-C(5)	110.23(14)

O(1)-C(6)-C(13)	109.31(16)
C(5)-C(6)-C(13)	111.40(15)
O(1)-C(6)-C(7)	107.22(15)
C(5)-C(6)-C(7)	110.06(15)
C(13)-C(6)-C(7)	108.51(15)
C(8)-C(7)-C(12)	118.27(19)
C(8)-C(7)-C(6)	120.67(18)
C(12)-C(7)-C(6)	121.05(18)
C(7)-C(8)-C(9)	120.8(2)
C(7)-C(8)-H(8)	119.6
C(9)-C(8)-H(8)	119.6
C(10)-C(9)-C(8)	120.8(2)
C(10)-C(9)-H(9)	119.6
C(8)-C(9)-H(9)	119.6
C(9)-C(10)-C(11)	118.8(2)
C(9)-C(10)-H(10)	120.6
C(11)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	120.8(2)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
C(7)-C(12)-C(11)	120.6(2)
C(7)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7
O(4)-C(13)-O(3)	124.3(2)
O(4)-C(13)-C(6)	124.66(19)
O(3)-C(13)-C(6)	111.04(17)
O(3)-C(14)-H(14A)	109.5
O(3)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
O(3)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Crystallographic data For 3c

Table 1. Crystal data and structure refinement for y1992.

Identification code	y1992
Empirical formula	C ₁₀ H ₁₂ O ₄ S
Formula weight	228.26
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.553(1) Å alpha = 90 deg. b = 10.746(2) Å beta = 90 deg. c = 13.435(2) Å gamma = 90 deg.
Volume, Z	1090.40(25) Å ³ , 4
Density (calculated)	1.390 Mg/m ³
Absorption coefficient	0.288 mm ⁻¹
F(000)	480
Crystal size	0.46 x 0.38 x 0.32 mm
Theta range for data collection	2.43 to 27.99 deg.
Limiting indices	-9<=h<=9, -14<=k<=14, -17<=l<=17
Reflections collected	3196
Independent reflections	2626 [R(int) = 0.0100]
Absorption correction	Empirical
Max. and min. transmission	0.7658 and 0.7352
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2626 / 0 / 138
Goodness-of-fit on F ²	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0826
R indices (all data)	R1 = 0.0478, wR2 = 0.0860
Absolute structure parameter	0.06(9)
Extinction coefficient	0.093(5)

Largest diff. peak and hole

0.170 and -0.151 e.Å⁻³Table 2. Atomic coordinates (x10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for y1992. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S	1500(1)	376(1)	6167(1)	58(1)
O(1)	1989(2)	643(1)	8309(1)	50(1)
O(2)	4245(3)	2012(1)	9712(1)	73(1)
O(3)	5692(2)	2346(1)	7414(1)	50(1)
O(4)	5448(2)	350(1)	7862(1)	65(1)
C(1)	750(3)	1187(2)	5158(2)	56(1)
C(2)	886(3)	2419(2)	5291(2)	56(1)
C(3)	1638(3)	2742(2)	6223(1)	47(1)
C(4)	2030(2)	1727(2)	6786(1)	37(1)
C(5)	2829(2)	1648(2)	7811(1)	35(1)
C(6)	2582(2)	2866(2)	8382(1)	37(1)
C(7)	3521(3)	2910(2)	9367(1)	41(1)
C(8)	3544(4)	4129(2)	9882(2)	63(1)
C(9)	4811(3)	1349(2)	7713(1)	39(1)
C(10)	7591(3)	2232(3)	7310(2)	67(1)

Table 3. Bond lengths [Å] and angles [deg] for y1992

S-C(1)	1.708(2)
S-C(4)	1.7207(19)
O(1)-C(5)	1.419(2)
O(1)-H(10)	0.8200
O(2)-C(7)	1.202(2)
O(3)-C(9)	1.324(2)
O(3)-C(10)	1.446(2)
O(4)-C(9)	1.194(2)
C(1)-C(2)	1.339(3)
C(1)-H(1)	0.9300
C(2)-C(3)	1.418(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.360(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.506(3)
C(5)-C(6)	1.529(2)
C(5)-C(9)	1.537(3)
C(6)-C(7)	1.502(3)
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700

C(7)-C(8)	1.482(3)
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(8)-H(8D)	0.9600
C(8)-H(8E)	0.9600
C(8)-H(8F)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(10)-H(10D)	0.9600
C(10)-H(10E)	0.9600
C(10)-H(10F)	0.9600
C(1)-S-C(4)	91.73(10)
C(5)-O(1)-H(1O)	109.5
C(9)-O(3)-C(10)	117.4(2)
C(2)-C(1)-S	111.94(16)
C(2)-C(1)-H(1)	124.0
S-C(1)-H(1)	124.0
C(1)-C(2)-C(3)	113.0(2)
C(1)-C(2)-H(2)	123.5
C(3)-C(2)-H(2)	123.5
C(4)-C(3)-C(2)	112.47(18)
C(4)-C(3)-H(3)	123.8
C(2)-C(3)-H(3)	123.8
C(3)-C(4)-C(5)	129.88(17)
C(3)-C(4)-S	110.89(14)
C(5)-C(4)-S	119.23(14)
O(1)-C(5)-C(4)	107.11(15)
O(1)-C(5)-C(6)	111.12(15)
C(4)-C(5)-C(6)	111.21(15)
O(1)-C(5)-C(9)	108.47(16)
C(4)-C(5)-C(9)	108.91(15)
C(6)-C(5)-C(9)	109.93(15)
C(7)-C(6)-C(5)	114.27(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
O(2)-C(7)-C(8)	121.64(18)
O(2)-C(7)-C(6)	121.95(17)
C(8)-C(7)-C(6)	116.39(17)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5

H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(8)-H(8D)	109.5
H(8A)-C(8)-H(8D)	141.1
H(8B)-C(8)-H(8D)	56.3
H(8C)-C(8)-H(8D)	56.3
C(7)-C(8)-H(8E)	109.5
H(8A)-C(8)-H(8E)	56.3
H(8B)-C(8)-H(8E)	141.1
H(8C)-C(8)-H(8E)	56.3
H(8D)-C(8)-H(8E)	109.5
C(7)-C(8)-H(8F)	109.5
H(8A)-C(8)-H(8F)	56.3
H(8B)-C(8)-H(8F)	56.3
H(8C)-C(8)-H(8F)	141.1
H(8D)-C(8)-H(8F)	109.5
H(8E)-C(8)-H(8F)	109.5
O(4)-C(9)-O(3)	125.19(19)
O(4)-C(9)-C(5)	124.49(18)
O(3)-C(9)-C(5)	110.30(16)
O(3)-C(10)-H(10A)	109.5
O(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(3)-C(10)-H(10D)	109.5
H(10A)-C(10)-H(10D)	141.1
H(10B)-C(10)-H(10D)	56.3
H(10C)-C(10)-H(10D)	56.3
O(3)-C(10)-H(10E)	109.5
H(10A)-C(10)-H(10E)	56.3
H(10B)-C(10)-H(10E)	141.1
H(10C)-C(10)-H(10E)	56.3
H(10D)-C(10)-H(10E)	109.5
O(3)-C(10)-H(10F)	109.5
H(10A)-C(10)-H(10F)	56.3
H(10B)-C(10)-H(10F)	56.3
H(10C)-C(10)-H(10F)	141.1
H(10D)-C(10)-H(10F)	109.5
H(10E)-C(10)-H(10F)	109.5

Symmetry transformations used to generate equivalent atoms:

anti-6h

Selected HPLC Spectra

rac-6c

ulas

Project Name: Defaults
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	tz-0	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	4/7/05 3:51:11 PM
Vial:	1	Acq. Method:	100A
Injection #:	1	Date Processed:	4/7/05 4:13:53 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	180.00 Minutes	Sample Set Name:

RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1 3.654	62375	0.30	7759	0.52
2 5.511	51177	0.24	6302	0.42
3 5.609	45616	0.22	5986	0.40
4 5.783	79122	0.38	6808	0.46
5 7.761	10267309	48.84	849426	56.87
6 9.750	10518572	50.03	617414	41.33

6c 93%ee

ulas

Project Name: Defaults
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name: tz-3
Sample Type: Unknown
Vial: 1
Injection #: 3
Injection Volume: 20.00 ul
Run Time: 180.00 Minutes

Acquired By: System
Date Acquired: 4/7/05 4:19:00 PM
Acq. Method: 100A
Date Processed: 4/7/05 4:31:37 PM
Channel Name: 2487Channel 1
Sample Set Name:

	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.813	119879	3.52	10756	4.85
2	9.850	3282265	96.48	211063	95.15

rac-6g

实验时间: 2005-04-08, 9:10:51

谱图文件: D:\1367\唐卓\05.04.08\4-dex120-240-260-102-10.org

报告时间: 2005-06-15, 15:25:45

计算方法: 面积归一法

使用仪器类型: 气相色谱
型号: VARIAN CP-30

检测器: FID

进样器: 分流

柱温: 恒温
温度(°C)

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		2.632	820.820	1689.585	0.6226
2		19.492	66.355	2838.860	1.0462
3		22.292	9919.061	133029.359	49.0231
4		22.878	9608.685	132675.813	48.8928
5		24.105	57.081	1127.182	0.4154
总计			20472.000	271360.799	100.0000

6g 96%ee

实验时间: 2005-04-08, 9:10:51
谱图文件: D:\1367\唐卓\05.04.08\4#.2.org

报告时间: 2005-06-15, 15:31:56
计算方法: 面积归一法

使用仪器类型: 气相色谱
型号: VARIAN CP-30

检测器: FID

进样器: 分流

柱温: 恒温
温度 (°C)

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		2.625	1531.441	3005.601	1.2922
2		22.253	17396.957	224671.719	96.5927
3		22.875	361.425	4919.746	2.1151
总计			19289.823	232597.065	100.0000

N2000 数据工作站

1

实验时间: 2005-04-18, 9:07:30

报告时间: 2005-06-15, 15:27:45

谱图文件: D:\1367\唐卓\05.04.18\消旋体DEX225-240-260-160.org

计算方法: 面积归一法

使用仪器类型: 气相色谱
型号: VARIAN CP-30

检测器: FID

进样器: 分流

柱温: 恒温
温度(°C)

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		5.318	1059.909	6199.050	1.0625
2		6.945	71.929	1756.736	0.3011
3		12.772	43858.934	291004.438	49.8794
4		13.252	43533.918	284456.375	48.7570
总计			88524.690	583416.599	100.0000

6d 98%ee

N2000 数据工作站

1

实验时间: 2005-04-18, 9:07:30
谱图文件: D:\1367\唐卓\05.04.18\样品1.mdy

报告时间: 2005-06-15, 15:28:35
计算方法: 面积归一法

使用仪器类型: 气相色谱
型号: VARIAN CP-30

检测器: FID

进样器: 分流

柱温: 恒温
温度(°C)

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		9.573	561.367	3260.871	1.3294
2		12.052	169.026	2298.222	0.9369
3		12.528	38809.773	238099.859	97.0674
4		13.007	348.093	1634.300	0.6663
总计			39888.260	245293.252	100.0000