Supporting Information

3-Pyrrolidinecarboxylic Acid for Direct Asymmetric *anti*-Mannich-Type Reactions of Unmodified Ketones

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General: For thin layer chromatography (TLC), silica gel plates VWR GL60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (25 g), $\text{Ce}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (10 g), and conc. H_2SO_4 (60 mL) in H_2O (940 mL) followed by heating or by treatment with a solution of *p*-anisaldehyde (23 mL), conc. H_2SO_4 (35 mL), and acetic acid (10 mL) in ethanol (900 mL) followed by heating. Flash column chromatography was performed using Bodman silica gel 32-63, 60Å. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-500, Varian INOVA-400, or Varian Mercury-300. Proton chemical shifts are given in relative to tetramethylsilane (0.00 ppm) in CDCl_3 or to the residual proton signals of the deuterated solvent in CD_3OD (δ 3.31 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in CDCl_3 (δ 77.00 ppm) or CD_3OD (δ 49.00 ppm). High-resolution mass spectra were recorded on an Agilent ESI-TOF mass spectrometer. Enantiomeric excesses were determined by chiral-phase HPLC using a Hitachi instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

1. Solvent Screen

Table S1. Solvent Screen on the Mannich-Type Reaction between 3-Pentanone and *N*-PMP-Protected α -Imino Ethyl Glyoxylate Using (*R*)-3-Pyrrolidinecarboxylic Acid^a

entry	solvent	time	yield ^b (%)	dr ^c <i>anti:syn</i>	ee ^c (%)
1	DMSO	29 h	75	94:6	97
2	DMF	38 h	74	87:13	97
3	<i>N</i> -Methylpyrrolidone (NMP)	40 h	65	93:7	96
4	CHCl ₃	3 d	46	95:5	97
5	CH ₃ CN	3 d	51	97:3	95
6	Dioxane	3 d	30	74:26	71
7	THF	3 d	<10	ND	ND
8	AcOEt	3 d	<10	ND	ND
9	2-PrOH	18 h	90	97:3	98
10	EtOH	18 h	91	95:5	92
11	MeOH	32 h	79	96:4	87

^a Conditions: Ethyl (*E*)-2-(*p*-methoxyphenylimino)acetate (0.1 mmol, 1 equiv) was dissolved in a solvent (0.6 mL) and 3-pentanone (0.4 mL, 3.8 mmol, 38 equiv) was added, followed by (*R*)-3-pyrrolidinecarboxylic acid (*R*)-1 (0.02 mmol, 0.2 equiv, 20 mol% to the imine) at room temperature (25 °C). After stirring for the indicated time at the same temperature, the reaction mixture was worked up by addition of aqueous saturated ammonium chloride solution and was extracted with AcOEt (three or four times). The combined organic layers were dried over anhydrous MgSO₄, filtered, concentrated *in vacuo*, and purified by flash column chromatography (AcOEt/hexane = 1:10). For entries 9–11, the reaction mixture was concentrated *in vacuo* without work-up, and purified by flash column chromatography. The *anti*- and *syn*-diastereomers were not discriminated each other on TLC. ^b Isolated yield (containing *anti*- and *syn*-diastereomers). ^c The dr and ee of the isolated products were determined by chiral-phase HPLC using Daicel Chiralpak AS.

2-PrOH was the best solvent tested in terms of reaction rate, yield, less byproduct formation, *anti*-selectivity, and enantioselectivity. Although the reaction in DMSO and in 2-PrOH afforded similar diastereo- and enantioselectivities, the reaction rate in 2-PrOH was approximately 2-fold faster than that in DMSO and the reaction in 2-PrOH was clean or (less byproduct formation) than that in DMSO. An approximate order of the reaction rate of the product formation (from the solvent for faster reaction): EtOH, 2-PrOH >> DMSO, DMF, NMP, MeOH >> CH₃CN > CHCl₃ > Dioxane, THF, AcOEt.

2. Synthesis of catalysts

(R)-3-Pyrrolidinecarboxylic acid [(R)-1].^{1,2}

(R)-3-Pyrrolidinecarboxylic acid (also known as, (R)-pyrrolidine-3-carboxylic acid, (R)- β -proline) (CAS No. 72580-53-1) was prepared from (R)-1-N-Boc-beta-proline purchased from J & W Phamlab. To a solution of (R)-1-N-Boc-beta-proline (2.00 g, 9.3 mmol) in CH₂Cl₂ (10 mL) was added trifluoroacetic acid (TFA) (5 mL) at 0 °C, and the resulting mixture was stirred at room temperature over night. The mixture was concentrated in vacuo, dissolved in water, and loaded to Dowex 50WX8-100 ion-exchange resin (H⁺ form, activated with 0.1 M HCl). The resin was washed with water then eluted with 15% ammonium hydroxide and the eluted fractions were lyophilized. The resulting semi-solid was dissolved in MeOH-toluene and the solvents were removed in vacuo to give (R)-1 (1.07 g) as a colorless solid.

(S)-3-Pyrrolidinecarboxylic acid [(S)-1].^{1,2}

(S)-3-Pyrrolidinecarboxylic acid (also known as, (S)-pyrrolidine-3-carboxylic acid, (S)- β -proline) (CAS No. 72580-54-2) was prepared from (S)-1-N-Boc-beta-proline purchased from J & W Phamlab. To a solution of (S)-1-N-Boc-beta-proline (450 mg, 2.0 mmol) in CH₂Cl₂ (2 mL) was added TFA (2 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 3 h. The mixture was concentrated in vacuo, dissolved in water, and loaded to Dowex 50WX8-100 ion-exchange resin (H⁺ form, activated with 0.1 M HCl). The resin was washed with water then eluted with 15% ammonium hydroxide and the eluted fractions were lyophilized. The resulting semi-solid was dissolved in MeOH-toluene and the solvents were removed in vacuo to give (S)-1 (232 mg) as a colorless solid.

(S)-Trifluoro-N-(pyrrolidin-3-ylmethyl)methanesulfonamide [(S)-3].

Catalyst (S)-3 was prepared from (R)-3-aminomethyl-1-N-Boc-pyrrolidine purchased from Asta Tech, Inc.

(S)-1-N-Boc-3-[(trifluoromethylsulfonamido)methyl]pyrrolidine

To a solution of (R)-3-aminomethyl-1-N-Boc-pyrrolidine (500 mg, 2.5 mmol) and triethylamine (1.05 mL, 7.5 mmol) in anhydrous CH_2Cl_2 (40 mL) was slowly added trifluoromethanesulfonic anhydride (0.5 mL, 3 mmol) in anhydrous CH_2Cl_2 (6 mL) using a syringe pump over 1 h at 0 °C under N_2 .³ The resulting mixture was stirred over night at room temperature. The mixture was concentrated in vacuo and directly purified by flash column chromatography (EtOAc/hexane = 1/2–2/1) to afford (S)-1-N-Boc-3-[(trifluoromethylsulfonamido)methyl]pyrrolidine (556 mg, 67%) as a colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 1.42 (s, 9H), 1.65 (m, 1H), 2.01 (m, 1H), 2.46 (m, 1H), 3.04–3.53 (m, 6H), 7.05 (brs, 1/2H, NH), 7.30 (brs, 1/2H, NH). ^{13}C NMR (100 MHz, CDCl_3): δ 28.3, 28.7, 38.7, 39.3, 44.7, 45.2, 46.2, 46.3, 48.8, 49.0, 60.6, 65.2, 79.8, 79.9, 119.7 (q, J = 310 Hz), 154.7, 154.8.

(S)-Trifluoro-N-(pyrrolidin-3-ylmethyl)methanesulfonamide [(S)-3].

To a solution of (S)-1-N-Boc-3-[(trifluoromethylsulfonamido)methyl]pyrrolidine (332 mg, 1.00 mmol) in CH_2Cl_2 (2 mL) was added triethylamine (1 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 3 h. The mixture was concentrated in vacuo, dissolved in water, and loaded to Dowex 50WX8-100 ion-exchange resin (H^+ form, activated with 0.1 M HCl). The resin was washed with water then eluted with 15% ammonium hydroxide. The eluted fractions were lyophilized to afford (S)-3 (197 mg, 85%) as a colorless solid. ^1H NMR (500 MHz, CD_3OD): δ 1.78 (m, 1H), 2.09 (m, 1H), 2.47 (m, 1H), 3.01–3.08 (m, 2H), 3.13–3.20 (m, 2H), 3.27–3.31 (m, 2H). ^{13}C NMR (125 MHz, CD_3OD): δ 29.0, 41.3, 46.7, 48.9, 50.1, 123.5 (q, J = 327 Hz), HRMS: calcd for $\text{C}_6\text{H}_{12}\text{F}_3\text{N}_2\text{O}_2\text{S}$ (MH^+)

233.0566, found 233.0575. $[\alpha]_D^{25}$ -7.2 (c 0.47, C₂H₅OH).

3. Preparation of *N*-PMP-protected α -imino esters.

Ethyl (*E*)-2-(*p*-methoxyphenylimino)acetate⁴. A mixture of glyoxylic acid ethyl ester (polymer form 45-50% in toluene, 10 mL, about 45 mmol), *p*-anisidine (5.54 g, 45 mmol), and molecular sieves 4 Å (50 g) in anhydrous toluene (250 mL) was stirred at room temperature for 2–6 h. After filtration through celite, the mixture was concentrated in vacuo to afford the imine. The imine was used for the Mannich-type reactions without further purification.

Allyl (*E*)-2-(*p*-methoxyphenylimino)acetate,⁵⁻⁷ *tert*-butyl (*E*)-2-(*p*-methoxyphenylimino)acetate,^{8,9} and isopropyl (*E*)-2-(*p*-methoxyphenylimino)acetate.⁴ Glyoxylic acid esters were prepared by the reported procedures.⁵⁻⁹ A mixture of a glyoxylic acid ester (12 mmol) and *p*-anisidine (11.5 mmol) in CH₂Cl₂ (30 mL) was stirred at room temperature for 30 min. The mixture was concentrated in vacuo to afford the imine. The imine was used without further purification.

4. Direct asymmetric *anti*-Mannich-type reactions of unmodified ketones

General procedure for the (*R*)-1-catalyzed Mannich-type reactions between unmodified ketones and α -imino esters (Table 2).

The reactions were performed in a closed system (a vial with a cap). An inert atmosphere of nitrogen or argon was not necessary. *N*-PMP-protected α -imino ester (0.5 mmol, 1.0 equiv) was dissolved in 2-PrOH (1.0 mL) and ketone (5.0 mmol, 10 equiv) was added to the solution, followed by catalyst (*R*)-1 (0.05 mmol, 0.1 equiv). After stirring at room temperature (25 °C) for the indicated time in the Table, the reaction mixture was concentrated in vacuo and purified by flash column chromatography. The *anti*- and *syn*-isomers of the Mannich product shown in Table 2 were not discriminated on TLC each other (see below for preparation of ($\pm$)-*anti*- and *syn*-products). The diastereomeric ratio was determined by ¹H NMR of the isolated product. The enantiomeric excess of the *anti*-product was determined by chiral-phase HPLC analysis (see **Figures S1-S4**). The chiral-phase HPLC analysis was also used for the determination of the diastereomeric ratio as indicated.

General procedure for the (*R*)-1-catalyzed Mannich-type reactions between unmodified cyclic ketones and α -imino esters (Table 3).

The reactions were performed in a closed system (a vial with a cap). An inert atmosphere of nitrogen or argon was not necessary. *N*-PMP-protected α -imino ester (0.5 mmol, 1.0 equiv) was dissolved in 2-PrOH (1.0 mL) and ketone (1.0 mmol, 2.0 equiv) was added to the solution, followed by catalyst (*R*)-**1** (0.05 mmol, 0.1 equiv or 0.025 mmol, 0.05 equiv). After stirring at room temperature (25 °C) for 10–16 h, the reaction mixture was concentrated in vacuo and purified by flash column chromatography. The *anti*- and *syn*-isomers of the Mannich product shown in Table 3 were not discriminated on TLC each other, except **11** and **17**. The diastereomeric ratio was determined by ¹H NMR of the isolated product. The enantiomeric excess of the *anti*-product was determined by chiral-phase HPLC analysis.

Synthesis of ($\pm$)-*anti*- and ($\pm$)-*syn*-Mannich products (see Scheme S1 and Figure S3, S4)

Racemic standards of the *anti*-Mannich products were synthesized by using ($\pm$)-3-pyrrolidinecarboxylic acid (CAS No. 59378-87-9) purchased from J & W Pharmed as catalysts. Racemic standards of the *syn*-Mannich products were synthesized by using ($\pm$)-proline as catalyst. Alternatively, a racemic mixture of the diastereomers and enantiomers was synthesized using pyrrolidine-trifluoroacetic acid as catalyst.

Scheme S1: Synthesis of ($\pm$)-*anti*- and ($\pm$)-*syn*-Mannich products.

Figure S1. HPLC chart of the Mannich product (*2S*, *3R*)-*anti*-4 generated by the (*R*)-1-catalyzed reaction.

Figure S2. HPLC chart of the imidazole isomerization of (*2S*, *3R*)-*anti*-4.

Figure S3. HPLC chart of the Mannich product *syn*- **4** generated using (±)-proline.

Figure S4. HPLC chart of the Mannich product **4** generated using pyrrolidine-trifluoroacetic acid: A mixture of diastereomers and enantiomers.

Ethyl (2*S*,3*R*)-2-(*p*-methoxyphenylamino)-3-methyl-4-oxohexanoate (4).

^1H NMR (400 MHz, CDCl_3): δ 1.06 (t, 3H, $J = 7.3$ Hz, COCH_2CH_3), 1.17 (d, 3H, $J = 7.2$ Hz, COCHCH_3), 1.21 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 2.54 (dq, 2H, $J = 0.8$ Hz, 7.2 Hz, COCH_2CH_3), 3.02 (quintet, 1H, $J = 7.1$ Hz, COCHCH_3), 3.73 (s, 3H, OCH_3), 4.09-4.17 (m, 3H, CHNHPMP , OCH_2CH_3), 4.19 (brd, 1H, $J = 7.5$ Hz, CHNHPMP), 6.65 (d, 2H, $J = 9.0$ Hz, ArH), 6.76 (d, 2H, $J = 9.0$ Hz, ArH), ^{13}C NMR (100 MHz, CDCl_3): 7.5, 13.4, 14.1, 34.9, 48.4, 55.6, 60.8, 61.2, 114.8, 115.8, 140.8, 153.0, 172.8, 212.2. HRMS: calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_4$ (MH^+) 294.1700, found 294.1698. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 20.0 min, t_R (*anti* minor enantiomer) = 37.7 min. See **Figures S1-S4**. $[\alpha]_D^{25}$ -27.8 (c 2.9, CHCl_3 , 98% ee).

Imidazole isomerization¹⁰ of the *anti*-4 obtained from the (*R*)-1-catalyzed reaction afforded the *syn*-product possessing a (2*S*,3*S*) configuration, which was the product of the (*S*)-proline-catalyzed reaction.¹¹ (See **Figure S1** and **Figure S2**). This result confirmed that the major *anti*-product 4 generated from the (*R*)-1-catalyzed reaction had a (2*S*,3*R*) configuration.

***tert*-Butyl (2*S*,3*R*)-2-(*p*-methoxyphenylamino)-3-methyl-4-oxohexanoate (5)**

^1H NMR (500 MHz, CDCl_3): δ 1.07 (t, 3H, $J = 7.2$ Hz, COCH_2CH_3), 1.15 (d, 3H, $J = 7.1$ Hz, COCHCH_3), 1.38 (s, 9H, $\text{CH}(\text{CH}_3)_3$), 2.54 (dq, 1H, $J = 0.8$ Hz, 7.2 Hz, COCHHCH_3), 2.59 (dq, 1H, $J = 0.8\text{Hz}$, 7.2Hz, COCHHCH_3), 2.97 (quintet, 1H, $J = 7.1$ Hz, COCHCH_3), 3.73 (s, 3H, OCH_3), 4.10 (brs, 1H, CHNHPMP), 4.15 (d, 1H, $J = 5.9$ Hz, CHNHPMP), 6.64 (d, 2H, $J = 9.0$ Hz, ArH), 6.76 (d, 2H, $J = 9.0$ Hz, ArH), ^{13}C NMR (125 MHz, CDCl_3): δ 7.5, 12.7, 27.9, 34.7, 48.3, 55.6, 60.9, 82.1, 114.7, 115.6, 140.8, 152.9, 171.5, 211.9. HRMS: calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_4$ (MH^+) 322.2013, found 322.2015. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 99:1, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 10.3 min; t_R (*anti* minor enantiomer) = 17.9 min. $[\alpha]_D^{25}$ -45.0 (c 2.1, CHCl_3 , 95%

ee).

Ethyl (2*S*,3*R*)-3-ethyl-2-(*p*-methoxyphenylamino)-4-oxoheptanoate (6)

^1H NMR (500 MHz, CDCl_3): δ 0.90 (t, 3H, $J = 7.4$ Hz, $\text{COCH}_2\text{CH}_2\text{CH}_3$), 0.92 (t, 3H, $J = 7.4$ Hz, $\text{COCHCH}_2\text{CH}_3$), 1.18 (t, 3H, $J = 7.1$ Hz, OCH_2CH_3), 1.54-1.76 (m, 4H, $\text{COCH}_2\text{CH}_2\text{CH}_3$, $\text{COCHCH}_2\text{CH}_3$), 2.44 (dt, 1H, $J = 7.1$ Hz, 17.5 Hz, $\text{COCHHCH}_2\text{CH}_3$), 2.49 (dt, 1H, $J = 7.1$ Hz, 17.5 Hz, $\text{COCHHCH}_2\text{CH}_3$), 2.87 (dt, 1H, $J = 6.3$ Hz, 8.3 Hz, $\text{COCHCH}_2\text{CH}_3$), 3.72 (s, 3H, OCH_3), 4.08-4.17 (m, 4H, OCH_2CH_3 , CHNHPMP , CHNHPMP), 6.62 (d, 2H, $J = 9.0$ Hz, ArH), 6.75 (d, 2H, $J = 9.0$ Hz, ArH), ^{13}C NMR (125 MHz, CDCl_3): δ 11.9, 13.6, 14.1, 16.6, 22.0, 45.5, 55.5, 55.6, 59.6, 61.1, 114.7, 115.7, 140.9, 153.0, 173.2, 212.1. HRMS: calcd for $\text{C}_{18}\text{H}_{28}\text{NO}_4$ (MH^+) 322.2013, found 322.2014. HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 90:10, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 7.7 min; t_R (*anti* minor enantiomer) = 9.4 min.

Ethyl (2*S*,3*R*)-2-(*p*-methoxyphenylamino)-3-methyl-4-oxopentanoate (7)

Figure S5. X-ray crystal structure of (2*S*,3*R*)-7. (The Flack parameter is -0.4(19), indicating that this structure shows relative stereochemistry.)

^1H NMR (400 MHz, CDCl_3): δ 1.19 (d, 3H, $J = 7.1$ Hz, COCHCH_3), 1.21 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 2.22 (s, 3H, CH_3CO), 3.02 (quintet, 1H, $J = 7.1$ Hz, COCHCH_3), 3.74 (s, 3H, OCH_3), 4.08-4.22 (m, 4H, CHNHPMP , OCH_2CH_3 , CHNHPMP), 6.65 (d, 2H, $J = 8.9$ Hz, ArH), 6.76 (d, 2H, $J = 8.9$ Hz, ArH). ^{13}C NMR (125 MHz, CDCl_3): δ 13.0, 14.1, 28.6, 49.4, 55.7, 60.5, 61.3, 114.8, 115.8, 140.7, 153.1, 172.5, 209.5. HRMS: calcd for $\text{C}_{15}\text{H}_{22}\text{NO}_4$ (MH^+) 280.1543, found 280.1542. HPLC (Daicel Chiralcel AS-H, hexane/*i*-PrOH = 96:4, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 17.1 min; t_R (*anti* minor enantiomer) = 28.9 min. $[\alpha]_D^{25}$ -20.7 (c 1.4, CHCl_3 , 99% ee).

Ethyl (2S,3R)-3-ethyl-2-(p-methoxyphenylamino)-4-oxopentanoate (8)

^1H NMR (500 MHz, CDCl_3): δ 0.93 (t, 3H, $J = 7.4$ Hz, $\text{COCHCH}_2\text{CH}_3$), 1.19 (t, 3H, $J = 7.1$ Hz, OCH_2CH_3), 1.57-1.76 (m, 2H, $\text{CH}_3\text{CH}_2\text{CHCO}$), 2.20 (s, 3H, COCH_3), 2.88 (m, 1H, $\text{COCHCH}_2\text{CH}_3$), 3.73 (s, 3H, OCH_3), 4.10-4.17 (m, 4H, CHNHPMP , OCH_2CH_3 , CHNHPMP), 6.63 (d, 2H, $J = 8.9$ Hz, ArH), 6.75 (d, 2H, $J = 8.9$ Hz, ArH); ^{13}C NMR (125 MHz, CDCl_3): δ 11.9, 14.1, 21.8, 30.0, 55.6, 56.4, 59.5, 61.2, 114.8, 115.7, 140.8, 153.1, 173.0, 210.0. HRMS: calcd for $\text{C}_{16}\text{H}_{24}\text{NO}_4$ (MH^+) 294.1700, found 294.1687. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 8.1 min; t_R (*anti* minor enantiomer) = 9.9 min.

Ethyl (2S, 3R)-3-allyl-2-(p-methoxyphenylamino)-4-oxopentanoate (9)

^1H NMR (400 MHz, CDCl_3): δ 1.20 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 2.20 (s, 3H, COCH_3), 2.35 (m, 1H, $\text{CHHCH}=\text{CH}_2$), 2.46 (m, 1H, $\text{CHHCH}=\text{CH}_2$), 3.10 (q, 1H, $J = 6.8$ Hz, CH_3COCH), 3.73 (s, 3H, OCH_3), 4.10-4.20 (m, 4H, CHNHPMP , OCH_2CH_3 , CHNHPMP), 5.06-5.11 (m, 2H, $\text{CH}_2=\text{CH}$), 5.75 (m, 1H, $\text{CH}_2=\text{CH}$), 6.63 (d, 2H, $J = 8.9$ Hz, ArH), 6.75 (d, 2H, $J = 8.9$ Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 30.4, 32.8, 54.2, 55.6, 59.3, 61.3, 114.7, 115.8, 118.0, 134.5, 140.9, 153.0, 172.9, 209.5. HRMS: calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_4$ (MH^+) 306.1700, found 306.1690. HPLC (Daicel Chiralpak As, hexane/*i*-PrOH = 90:10, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* minor enantiomer) = 8.6 min, t_R (*anti* major enantiomer) = 10.5 min.

Ethyl (2S,3R)-3-acetyl-6-chloro-2-(p-methoxyphenylamino)hexanoate (10)

^1H NMR (400 MHz, CDCl_3): δ 1.21 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 1.70-1.86 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$), 2.23 (s, 3H, COCH_3), 2.97 (m, 1H, COCHCH_2), 3.51 (t, 2H, $J = 6.1$ Hz, CH_2Cl), 3.74 (s, 3H, OCH_3), 4.09-4.18 (m, 4H, CHNHPMP , OCH_2CH_3 , CHNHPMP), 6.63 (d, 2H, $J = 8.9$ Hz, ArH), 6.76 (d, 2H, $J = 8.9$ Hz, ArH). ^{13}C NMR (125 MHz, CDCl_3): δ 14.2, 25.4, 29.7, 30.1, 44.3, 54.1, 55.7, 59.6, 61.4, 114.8, 115.8, 140.5, 153.2, 172.6, 209.2. HRMS: calcd for $\text{C}_{17}\text{H}_{25}\text{ClNO}_4$ (MH^+) 342.1467, found 342.1466. HPLC (Daicel Chiralpak AD, hexane/*i*-PrOH = 94:6, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* minor enantiomer) = 19.6 min; t_R (*anti* major enantiomer) = 25.5 min.

Ethyl (2*S*, 1'*R*)-2-(*p*-methoxyphenylamino)-2-(2'-oxocyclohexyl)acetate (11)

^1H NMR (400 MHz, CDCl_3): δ 1.21 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 1.61-1.79 (m, 2H, CH_2), 1.87-1.97 (m, 2H, CH_2), 2.02-2.14 (m, 2H, CH_2), 2.28-2.46 (m, 2H, $\text{CH}_2\text{CH}_2\text{CO}$), 3.08-3.13 (m, 1H, CH_2CHCO), 3.73 (s, 3H, OCH_3), 3.99 (brs, 1H, NH), 4.15 (m, 2H, OCH_2CH_3), 4.24 (m, 1H, CHNHPMP), 6.63 (d, 2H, $J = 8.8$ Hz, ArH), 6.76 (d, 2H, $J = 8.8$ Hz, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 24.5, 26.8, 30.5, 41.8, 53.6, 55.7, 59.1, 61.2, 114.7, 115.6, 142.1, 152.7, 173.0, 210.9. HRMS: calcd for $\text{C}_{17}\text{H}_{24}\text{NO}_4$ (MH^+) 306.1700, found 306.1697. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 12.7 min; t_R (*anti* minor enantiomer) = 19.0 min. $[\alpha]_D^{25} +29.1$ (c 2.0, CHCl_3 , 96% ee).

Isopropyl (2*S*, 1'*R*)-2-(*p*-methoxyphenylamino)-2-(2'-oxocyclohexyl)acetate (12)

^1H NMR (500 MHz, CDCl_3): δ 1.14 (d, 3H, $J = 6.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, 3H, $J = 6.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.63-1.78 (m, 2H, CH_2), 1.87-1.98 (m, 2H, CH_2), 2.02-2.13 (m, 2H, CH_2), 2.28-2.45 (m, 2H, $\text{CH}_2\text{CH}_2\text{CO}$), 3.07 (m, 1H, CH_2CHCO), 3.73 (s, 3H, OCH_3), 3.96 (brd, 1H, $J = 3.8$ Hz), 4.21 (brs, 1H), 4.99 (septet, 1H, $J = 6.3$ Hz, $\text{CH}(\text{CH}_3)_2$), 6.63 (d, 2H, $J = 8.9$ Hz, ArH), 6.75 (d, 2H, $J = 8.9$ Hz, ArH); ^{13}C NMR (125 MHz, CDCl_3): δ 21.7, 24.5, 26.9, 30.5, 41.8, 53.5, 55.7, 59.2, 68.8, 114.7, 115.7, 142.2, 152.8, 172.5, 210.8. HRMS: calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_4$ (MH^+) 320.1856, found 320.1854. HPLC

(Daicel Chiralpak AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, λ = 254 nm): t_R (*anti* major enantiomer) = 8.6 min; t_R (*anti* minor enantiomer) = 14.1 min. $[\alpha]_D^{25} +37$ (c 1.0, CHCl₃, 94% ee).

***tert*-Butyl (2*S*,1'*R*)-2-(*p*-methoxyphenylamino)-2-(2'-oxocyclohexyl)acetate (13)**

The absolute stereochemistry of product **13** generated by the (*R*)-**1** catalyzed reaction was determined to be (2*S*, 1'*R*) by the X-ray structural analysis. (The Flack parameter is 0.0(14).)

Figure S6. X-ray crystal structure of (2*S*,1'*R*)-**13**.

¹H NMR (500 MHz, CDCl₃): δ 1.38 (s, 9H, OC(CH₃)₃), 1.62-1.76 (m, 2H, CH₂), 1.85-1.95 (m, 2H, CH₂), 1.99-2.13 (m, 2H, CH₂), 2.27-2.44 (m, 2H, CH₂CH₂CO), 3.02 (m, 1H, CH₂CHCO), 3.73 (s, 3H, OCH₃), 3.92 (brs, 1H, NH), 4.17 (m, 1H, CHNHPMP), 6.61 (d, 2H, J = 8.9 Hz, ArH), 6.74 (d, 2H, J = 8.9 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 24.4, 26.8, 27.9, 30.3, 41.7, 53.4, 55.6, 59.4, 81.5, 114.7, 115.4, 142.3, 152.6, 172.0, 210.7. HRMS: calcd for C₁₉H₂₈NO₄ (MH⁺) 334.2013, found 334.2012. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, λ = 254 nm): t_R (*anti* major enantiomer) = 5.9 min; t_R (*anti* minor enantiomer) = 8.4 min. $[\alpha]_D^{25} +23.7$ (c 3.5, CHCl₃, 95% ee).

Allyl (2*S*,1'*R*)-2-(*p*-methoxyphenylamino)-2-(2'-oxocyclohexyl)acetate (14)

¹H NMR (500 MHz, CDCl₃): δ 1.63-1.78 (m, 2H, CH₂), 1.89-1.97 (m, 2H, CH₂), 2.02-2.14 (m, 2H, CH₂), 2.29-2.45 (m, 2H, CH₂CH₂CO), 3.13 (m, 1H, CH₂CHCO), 3.73 (s, 3H, OCH₃), 4.02 (brs, 1H, NH), 4.25 (m, 1H, CHNHPMP), 4.58 (m, 2H, OCH₂CH=CH₂), 5.17-5.21 (m, 2H, OCH₂CH=CH₂), 5.84 (m, 1H, OCH₂CH=CH₂), 6.63 (d, 2H, J = 9.0 Hz, ArH), 6.76 (d, 2H, J = 9.0 Hz, ArH); ¹³C NMR (100 MHz, CDCl₃): δ 24.6, 26.8, 30.5, 41.8, 53.6, 55.7, 59.0, 65.7, 114.8, 115.6, 118.2, 131.8, 142.1,

152.8, 172.7, 210.9. HRMS: calcd for $C_{18}H_{24}NO_4$ (MH^+) 318.1700, found 318.1701. HPLC (Daicel Chiralpak AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, λ = 254 nm): t_R (*anti* major enantiomer) = 12.6 min; t_R (*anti* minor enantiomer) = 18.7 min. $[\alpha]_D^{25} +25.9$ (c 1.4, $CHCl_3$, 95% ee).

Ethyl (2*S*,3'*R*)-2-(*p*-methoxyphenylamino)-2-(4'-oxotetrahydrothiopyran-3'-yl)acetate (15)

1H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 2.67-2.80 (m, 2H, $COCH_2CH_2S$), 2.88-3.00 (m, 3H, CH_2SCHH), 3.14 (dd, J = 10.0 Hz, 13.5 Hz, CH_2SCHH), 3.37 (dt, 1H, J = 5.0 Hz, 10.0 Hz, $COCHCH_2S$), 3.73 (s, 3H, OCH_3), 4.10-4.20 (m, 3H, NH , OCH_2CH_3), 4.25 (m, 1H, $CHNHPMP$), 6.65 (d, 2H, J = 8.9 Hz, ArH), 6.76 (d, 2H, J = 8.9 Hz, ArH), ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1, 29.8, 32.8, 43.7, 55.2, 55.7, 59.0, 61.4, 114.8, 115.9, 141.4, 153.1, 172.2, 208.0. HRMS: calcd for $C_{16}H_{22}NO_4S$ (MH^+) 324.1264, found 324.1263. HPLC (Daicel Chiralcel AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, λ = 254 nm): t_R (*anti* major enantiomer) = 32.4 min; t_R (*anti* minor enantiomer) = 46.0 min. $[\alpha]_D^{25} +48.0$ (c 2.6, $CHCl_3$, 99% ee).

Ethyl (2*S*, 3'*S*)-2-(*p*-methoxyphenylamino)-2-(4'-oxotetrahydropyran-3'-yl)acetate (16)

1H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, 3H, J = 7.2 Hz, OCH_2CH_3), 2.48 (dt, 1H, J = 3.9 Hz, 14.8 Hz, $COCHHCH_2$), 2.57-2.65 (m, 1H, $COCHHCH_2$), 3.24 (m, 1H, $COCHCH_2O$), 3.74 (s, 3H, OCH_3), 3.81 (ddd, 1H, J = 3.9 Hz, 9.9 Hz, 11.4 Hz, $CHHOCH_2$), 3.91 (dd, 1H, J = 9.0 Hz, 11.3 Hz, $CHHOCH_2$), 4.06-4.25 (m, 6H, CH_2OCH_2 , $CHNHPMP$, OCH_2CH_3 , $CHNHPMP$), 6.62 (d, 2H, J = 8.8 Hz, ArH), 6.77 (d, 2H, J = 8.8 Hz, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.10, 42.08, 53.8, 55.7, 56.4, 61.5, 67.8, 70.1, 114.8, 115.9, 141.3, 153.2, 172.1, 206.2. HRMS: calcd for $C_{16}H_{22}NO_5$ (MH^+) 308.1492, found 308.1492. HPLC (Daicel Chiralcel AS, hexane/*i*-PrOH = 80:20, 1.0 mL/min, λ = 254 nm): t_R (*anti* major enantiomer) = 16.8 min; t_R (*anti* minor enantiomer) = 21.4 min.

Ethyl (2*S*,1'*R*)-2-(*p*-methoxyphenylamino)-2-(5',5'-ethylenedioxy-2'-oxocyclohexyl)acetate (17)

^1H NMR (400 MHz, CDCl_3): δ 1.21 (t, 3H, $J = 7.2$ Hz, OCH_2CH_3), 1.94-2.13 (m, 3H), 2.29 (t, 1H, $J = 13.1$ Hz), 2.38-2.43 (m, 1H), 2.63-2.72 (m, 1H), 3.45-3.51 (m, 1H), 3.73 (s, 3H, OCH_3), 3.91 (brs, 1H, NH), 4.00-4.09 (m, 4H, $\text{OCH}_2\text{CH}_2\text{O}$), 4.14 (m, 2H, OCH_2CH_3), 4.21 (m, 1H, CHNHPMP), 6.62 (d, 2H, $J = 8.8$ Hz, ArH), 6.75 (d, 2H, $J = 8.8$ Hz, ArH). ^{13}C NMR (100 MHz, CDCl_3): δ 14.1, 33.9, 37.6, 38.0, 50.0, 55.7, 59.0, 61.3, 64.7, 64.8, 107.5, 114.8, 115.9, 142.1, 152.9, 172.7, 209.6. HRMS: calcd for $\text{C}_{19}\text{H}_{26}\text{NO}_6$ (MH^+) 364.1755, found 364.1756. HPLC (Daicel Chiralcel AS, hexane/*i*-PrOH = 90:10, 1.0 mL/min, $\lambda = 254$ nm): t_R (*anti* major enantiomer) = 25.3 min; t_R (*anti* minor enantiomer) = 31.0 min. $[\alpha]_D^{25} +18.1$ (c 1.0, CHCl_3 , 97% ee).

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Date:
1 Apr 2006

Document's Title:
MestReC1

Spectrum Title:
ZHL-1280MeOD_28Nov2005

Frequency (MHz):
(f1) 300.144

Original Points Count:
(f1) 9596

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 1.9979

Spectral Width (ppm):
(f1) 16.003

Pulse Program:
Unknown

Temperature:
25

Number of Scans:
40

Acq. Date:
Nov 28 2005

Date:
31 Mar 2006

Document's Title:
MestReC1

Spectrum Title:
ZHL-2041-b7-c3_06Jan2006

Frequency (MHz):
(f1) 399.739

Original Points Count:
(f1) 23946

Actual Points Count:
(f1) 32768

Acquisition Time (sec):
(f1) 3.7440

Spectral Width (ppm):
(f1) 16.000

Pulse Program:
Unknown

Temperature:
29

Number of Scans:
8

Acq. Date:
Jan 6 2006

Date:
3 Apr 2006

Document's Title:
ZHL-2047moreHNMR.mrc

Spectrum Title:
None

Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
64

Acq. Date:
Sat Apr 01 01:12:59 PM

Date:
3 Apr 2006
Document's Title:
ZHL-2047f orcaJACSCNMR.mrc

Spectrum Title:
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Frequency (MHz):
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Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
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Spectral Width (ppm):
(f1) 250.031
Pulse Program:
ZGPG45
Temperature:
298.16
Number of Scans:
4901
Acq. Date:
Sat Apr 01 10:54:58 PV

Date:

4 Mar 2006

Document's Title:

ZHL-2073B.mrc

Spectrum Title:

ZHL-2073B_03Feb2006

Frequency (MHz):

(f1) 399.739

Original Points Count:

(f1) 23946

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 3.7440

Spectral Width (ppm):

(f1) 16.000

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

8

Acq. Date:

Feb 3 2006

Date:

4 Mar 2006

Document's Title:

CARBON.fid

Spectrum Title:

ZHL-2073D-car_04Feb2006

Frequency (MHz):

(f1) 100.525

Original Points Count:

(f1) 30135

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 1.1994

Spectral Width (ppm):

(f1) 249.945

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

1000

Acq. Date:

Feb 4 2006

Date:
 28 Mar 2006
Document's Title:
 2165f or JACS.mrc
Spectrum Title:
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Frequency (MHz):
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Original Points Count:
 (f1) 16384
Actual Points Count:
 (f1) 16384
Acquisition Time (sec):
 (f1) 2.7263
Spectral Width (ppm):
 (f1) 12.016
Pulse Program:
 ZG30
Temperature:
 298.16
Number of Scans:
 64
Acq. Date:
 Fri Mar 24 07:02:52 PM

Date:
28 Mar 2006

Document's Title:
1

Spectrum Title:
None

Frequency (MHz):
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Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 32768

Acquisition Time (sec):
(f1) 0.5210

Spectral Width (ppm):
(f1) 250.031

Pulse Program:
ZGPG45

Temperature:
298.16

Number of Scans:
488

Acq. Date:
Fri Mar 24 05:36:42 PM

Date:
28 Mar 2006

Document's Title:
ZHL-2155doeJACS.mrc

Spectrum Title:
None

Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
32

Acq. Date:
Tue Mar 21 12:13:21 AV

Date:

28 Mar 2006

Document's Title:

ZHL-2155.mrc

Spectrum Title:

None

Frequency (MHz):

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Original Points Count:

(f1) 16384

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 0.5210

Spectral Width (ppm):

(f1) 250.031

Pulse Program:

ZGPG45

Temperature:

298.16

Number of Scans:

256

Acq. Date:

Tue Mar 21 12:30:42 AM

Date:
25 Apr 2006
Document's Title:
ZHL-2189x-crystal.mrc

Spectrum Title:
None
Frequency (MHz):
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Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 16384
Acquisition Time (sec):
(f1) 2.7263
Spectral Width (ppm):
(f1) 12.016
Pulse Program:
ZG30
Temperature:
298.16
Number of Scans:
64
Acq. Date:
Tue Apr 25 11:08:56 AM

Date:
28 Mar 2006
Document's Title:
ZHL-2159 for JACS.mrc

Spectrum Title:
None
Frequency (MHz):
(f1) 125.770
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.5210
Spectral Width (ppm):
(f1) 250.031
Pulse Program:
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Temperature:
298.16
Number of Scans:
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Acq. Date:
Wed Mar 22 06:59:07 PM

Date:
28 Mar 2006

Document's Title:
ZHL-1120.mrc

Spectrum Title:
ZHL-1120_17Jul2005

Frequency (MHz):

(f1) 399.739

Original Points Count:

(f1) 23946

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 3.7440

Spectral Width (ppm):

(f1) 16.000

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

8

Acq. Date:

Jul 17 2005

Date:
28 Mar 2006

Document's Title:
ZHL-2153.mrc

Spectrum Title:
None

Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
16

Acq. Date:
Mon Mar 20 06:23:54 PM

Date:
2 May 2006
Document's Title:
ZHL-2153CNMRagain.mrc

Spectrum Title:
None
Frequency (MHz):
(f1) 125.770
Original Points Count:
(f1) 16384
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 0.5210
Spectral Width (ppm):
(f1) 250.031
Pulse Program:
ZGPG45
Temperature:
298.16
Number of Scans:
418
Acq. Date:
Mon Mar 20 06:50:01 PV

Date:
15 Mar 2006
Document's Title:
ZHL-2083Bf or JACS.mrc

Spectrum Title:
ZHL-2083B_04Feb2006

Frequency (MHz):
(f1) 399.739
Original Points Count:
(f1) 23946
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.7440
Spectral Width (ppm):
(f1) 16.000
Pulse Program:
Unknown
Temperature:
29

Number of Scans:
8

Acq. Date:
Feb 4 2006

Date:

15 Mar 2006

Document's Title:

ZHL-2083car.mrc

Spectrum Title:

ZHL-2083B-car-feb_04Feb2006

Frequency (MHz):

(f1) 100.525

Original Points Count:

(f1) 30135

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 1.1994

Spectral Width (ppm):

(f1) 249.945

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

2000

Acq. Date:

Feb 4 2006

Date:
28 Mar 2006

Document's Title:
ZHL-2162.mrc

Spectrum Title:
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Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
16

Acq. Date:
Wed Mar 22 07:50:57 PM

Date:
28 Mar 2006

Document's Title:
ZHL-2163.mrc

Spectrum Title:
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Frequency (MHz):
(f1) 125.770

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 32768

Acquisition Time (sec):
(f1) 0.5210

Spectral Width (ppm):
(f1) 250.031

Pulse Program:
ZGPG45

Temperature:
298.16

Number of Scans:
576

Acq. Date:
Wed Mar 22 08:13:11 PM

Date:

4 Mar 2006

Document's Title:

ZHL-2089.mrc

Spectrum Title:

ZHL-2089HNMR_06Feb2006

Frequency (MHz):

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Actual Points Count:

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Acquisition Time (sec):

(f1) 3.7440

Spectral Width (ppm):

(f1) 16.000

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

8

Acq. Date:

Feb 6 2006

Date:

4 Mar 2006

Document's Title:

ZHL-2089car.mrc

Spectrum Title:

ZHL-2089car_06Feb2006

Frequency (MHz):

(f1) 100.525

Original Points Count:

(f1) 30135

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 1.1994

Spectral Width (ppm):

(f1) 249.945

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

1000

Acq. Date:

Feb 6 2006

Date:

27 Mar 2006

Document's Title:

ZHL-1191-c1-c5.mrc

Spectrum Title:

ZHL-1119-c1-cosy_14Jul2005

Frequency (MHz):

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Original Points Count:

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Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 3.7440

Spectral Width (ppm):

(f1) 16.000

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

8

Acq. Date:

Jul 14 2005

Date:
15 Mar 2006

Document's Title:
ZHL-2136f or JACS.mrc

Spectrum Title:
None

Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
32

Acq. Date:
Tue Mar 07 07:43:56 PM

Date:

2 May 2006

Document's Title:

ZHL-2136Car.mrc

Spectrum Title:

None

Frequency (MHz):

(f1) 125.770

Original Points Count:

(f1) 16384

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 0.5210

Spectral Width (ppm):

(f1) 250.031

Pulse Program:

ZGPG45

Temperature:

298.16

Number of Scans:

840

Acq. Date:

Tue Mar 07 08:35:16 PM

Date:
27 Apr 2006

Document's Title:
MestReC1

Spectrum Title:
None

Frequency (MHz):
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Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
8

Acq. Date:
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Date:

3 May 2006

Document's Title:

1

Spectrum Title:

None

Frequency (MHz):

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Original Points Count:

(f1) 16384

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 0.5210

Spectral Width (ppm):

(f1) 250.031

Pulse Program:

ZGPG45

Temperature:

298.16

Number of Scans:

379

Acq. Date:

Thu Mar 16 08:56:24 PM

Date:
15 Mar 2006

Document's Title:
ZHL-2091.mrc

Spectrum Title:
None

Frequency (MHz):
(f1) 500.133

Original Points Count:
(f1) 16384

Actual Points Count:
(f1) 16384

Acquisition Time (sec):
(f1) 2.7263

Spectral Width (ppm):
(f1) 12.016

Pulse Program:
ZG30

Temperature:
298.16

Number of Scans:
16

Acq. Date:
Sat Mar 04 08:00:02 PM

Date:

15 Mar 2006

Document's Title:

ZHL-2091Acar.mrc

Spectrum Title:

None

Frequency (MHz):

(f1) 125.770

Original Points Count:

(f1) 16384

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 0.5210

Spectral Width (ppm):

(f1) 250.031

Pulse Program:

ZGPG45

Temperature:

298.16

Number of Scans:

1000

Acq. Date:

Sat Mar 04 08:25:45 PM

Date:
12 Apr 2006
Document's Title:
ZHL-2093A for JACS.mrc

Spectrum Title:
ZHL-2093A_08Feb2006

Frequency (MHz):
(f1) 399.739
Original Points Count:
(f1) 23946
Actual Points Count:
(f1) 32768
Acquisition Time (sec):
(f1) 3.7440
Spectral Width (ppm):
(f1) 16.000
Pulse Program:
Unknown
Temperature:
29

Number of Scans:
8

Acq. Date:
Feb 8 2006

Date:

27 Apr 2006

Document's Title:

CARBON.fid

Spectrum Title:

ZHL-2093C-caragain_08Feb2006

Frequency (MHz):

(f1) 100.525

Original Points Count:

(f1) 30135

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 1.1994

Spectral Width (ppm):

(f1) 249.945

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

1000

Acq. Date:

Feb 8 2006

Date:

4 Mar 2006

Document's Title:

ZHL-2085.mrc

Spectrum Title:

ZHL-2085-c5-c10_05Feb2006

Frequency (MHz):

(f1) 399.739

Original Points Count:

(f1) 23946

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 3.7440

Spectral Width (ppm):

(f1) 16.000

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

8

Acq. Date:

Feb 5 2006

Date:

4 Mar 2006

Document's Title:

ZHL-2085car.mrc

Spectrum Title:

ZHL-2085-c5-c10-car_05Feb2006

Frequency (MHz):

(f1) 100.525

Original Points Count:

(f1) 30135

Actual Points Count:

(f1) 32768

Acquisition Time (sec):

(f1) 1.1994

Spectral Width (ppm):

(f1) 249.945

Pulse Program:

Unknown

Temperature:

29

Number of Scans:

2000

Acq. Date:

Feb 5 2006

Figure S7. Ortep diagram of the structure (2*S*, *R*)-*anti*-7. The non-hydrogen atoms are drawn as 30% probability Ellipsoids.

Figure S8. Unit cell packing diagram for (2*S*, 3*R*)-*anti*-7.

Figure S9. Ortep diagram of the structure (2S, 1'R)-anti-13. The non-hydrogen atoms are drawn as 30% probability Ellipsoids.

Figure S10. Unit cell packing diagram for (2S, 1'R)-anti-13.