SUPPORTING INFORMATION

Enantioselective Route to Platensimycin: An Intramolecular Robinson Annulation Approach

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General materials and methods

All non-aqueous reactions were carried out in flame- and/or oven-dried glasswares using standard syringe-septum operations under argon atmosphere and magnetically stirred unless otherwise noted. All reactions were monitored by analytical thin-layer chromatography using Merck pre-coated silica gel plates with F₂₅₄ indicator. Visualization was accomplished by UV light (254 nm), potassium permanganate, phosphomolybdic acid, iodine, or *p*-anisaldehyde stains. Flash column chromatography was performed according to the method of Still using silica gel (mesh 230-400) supplied by Silicycle. Room temperature means 20±1 °C. All reactions were carried out with anhydrous solvents unless otherwise noted. Anhydrous THF (Ultra low water, 99.9%), dichloromethane, diethyl ether, acetonitrile and toluene were dried with an M BRAUN solvent purification system (A2 Alumina). Anhydrous grade 1,2-dichloroethane and dimethyl sulfide were purchased from Aldrich, anhydrous grade methanol, ethyl acetate, *N,N*-dimethylformamide were purchased from Acros, and used without further purification. All other reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification. Optical rotations were recorded on a JASCO DIP-1000 polarimeter and reported as follows: $[\alpha]_D^{25}$ °C (*c* = g/100 mL, solvent). Gas chromatography (GC) analysis was done with a Shimadzu model 17A instrument with a flame-ionization detector and a capillary column of PEG-Ht (25 m x 0.25 mm), or chiral column Chiraldex B-DP (20 m x 0.25 mm) using nitrogen as carrier gas. High-performance liquid chromatography (HPLC) was performed on Varian ProStar series equipped with a variable wavelength detector using a Chiralpak AD-H (0.46 cm × 25 cm) from Daicel, or a MICROSORB-Si-MV achiral column (2.14 cm × 25 cm) from Varian. Infrared spectra were recorded as thin films on sodium chloride plates using a Nicolet 20 SXB FTIR. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 400 (400 MHz ¹H, 100 MHz ¹³C), or a Bruker Avance 500 (500 MHz ¹H, 125 MHz ¹³C). Chemical shift values (δ) are reported in ppm (TMS δ = 0 ppm for ¹H; residual

chloroform $\delta = 77.0$ ppm for ^{13}C). The proton spectra are reported as follows δ (multiplicity, coupling constant J , number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad), etc. Low resolution mass spectra (LRMS) were obtained on a QSTAR (Applied SCIEX Biochemistry/MDS) spectrometer. High resolution mass spectra (HRMS) were recorded on a ThermoFinnigan LTQFT mass spectrometer using electrospray ionization (ESI) or a JEOL GCMate II mass spectrometer using electron impact ionization (EI) at the Mass Spectrometry Laboratory, Research Resources Center, University of Illinois at Chicago.

Synthetic procedures and characterization of products

Oxazaborolidine 10

To a dry, 100 mL round bottom flask equipped with a magnetic stirrer bar was charged (2*R*)-3-methyl-2-[(1-naphthyl)-amino]-1,1'-diphenyl-butan-1-ol¹ (1.14 g, 2.88 mmol, 1 eq), triphenylboroxine (299.3 mg, 0.96 mmol, 1/3 eq), and 40 mL of toluene. To this flask was connected a vigreux column followed by a 50 mL pressure-equalizing addition funnel (containing ~10 g of 4Å molecular sieves²), and a reflux condenser fitted with an argon balloon. The resulting solution was refluxed for 15 h using a CEM Discover[®] LabMate microwave synthesizer.³ (For a procedure using a conventional household microwave, see reference 1) The addition funnel stopcock was then closed and ~30 mL of toluene was removed from the reaction mixture. The reaction mixture was then allowed to cool to room temperature and the remaining toluene was removed *in vacuo* to afford valine-derived oxazaborolidine as clear oil. This compound can be safely stored in a Schlenk flask under inert atmosphere as a solution in toluene or dichloromethane at -20 °C for at least one month without any loss of catalytic activity. **IMPORTANT:** All operations should be conducted under inert atmosphere to avoid introduction of moisture which could lead to hydrolysis of this pre-catalyst.

¹ Futatsugi, K.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 1484-1487.

² Molecular sieves (pellets) were heated in a microwave for 60 seconds and then placed under vacuum for 15 minutes. This operation was repeated for two more times.

³ For more information see: <http://www.cem.com/synthesis/discoverLM.asp>

Ester 2

To a dry, 3-neck, 1L flask fitted with a mechanical stirrer was added 580 mL of CH₂Cl₂ and oxazaborolidine **10** (1.39 g, 2.88 mmol, 0.024 eq) in 10 mL CH₂Cl₂. After cooling to -78 °C, C₆F₅CHTf₂ **11** (1.07g, 2.4 mmol, 0.02 eq) in 10 mL CH₂Cl₂ was added dropwise. The resultant solution was stirred for 15 minutes. To this mixture was added methyl acrylate (10.33g, 120 mmol, 1 eq) dropwise. After 1-2 minutes, methylcyclopentadiene (28.8 g, 360 mmol, 3 eq) was added (1:1 (v/v) room temperature solution in CH₂Cl₂) using a syringe pump over 30 minutes. After stirring for 14 hours, the reaction was quenched by addition of 10 mL of triethylamine at -78 °C. The reaction mixture was allowed to warm to room temperature and the solvent was removed *in vacuo*. The crude product was transferred in a minimal amount of ether to a 2 L Erlenmeyer flask containing a large magnetic stirrer bar. 1.8 L of acetone was charged into the flask and the resulting solution was stirred vigorously for two hours or until the precipitated polymers became powder-like. The precipitate polymers were filtered off and the solvent removed *in vacuo*. To remove remaining polymers, the crude product was subjected to flash column chromatography. The column was flushed with hexanes until all polymers had been removed as indicated by TLC. Subsequently, 15:1 hexanes/ether was used as eluent to give the title compound **2** as a yellow oil (18.35 g, 92% yield). Enantiomeric excess of **2** was determined to be 99% by chiral GC analysis (B-DP column, 100 °C injection, 70 °C column, 40 kPa pressure, $t_{\text{major}} = 52.8$ min, $t_{\text{minor}} = 53.9$ min).

2: $R_f = 0.17$ (silica gel, hexanes: chloroform 3:1); $[\alpha]_D^{23\text{ }^\circ\text{C}} = -159.4$ ($c = 1.00$, CHCl₃); FT-IR (thin film): 2964, 1739, 1435, 1273, 1195, 1028 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 5.44$ (s, 1 H), 3.62 (s, 3H), 3.12-3.05 (m, 1H), 2.98-2.94 (m, 1H), 2.65 (s, 1H), 1.89-1.85 (m, 1H), 1.76 (d, $J = 1.6$ Hz, 1 H), 1.48-1.40 (m, 2H), 1.25 (d, $J = 8.2$ Hz, 1 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 175.4$, 148.1, 124.9, 51.4, 49.2, 47.2, 46.4, 45.2, 28.7, 15.6; LRMS (CI) calcd for C₁₀H₁₅O₂⁺ (M+H)⁺, 167.1, found 167.1.

Ketone 3

To a 350 mL THF solution of diisopropylamine (12.15 g, 120 mmol, 1.2 eq), was added a 2.5 M solution of *n*-BuLi in hexane (44 mL, 110 mmol,

1.1 eq) dropwise at -78 °C. The resulting mixture was allowed to stir for 30 minutes at this temperature. To this solution was added ester **2** (16.6 g, 100 mmol, 1 eq) in 20 mL of THF dropwise at -78 °C. The resulting mixture was allowed to stir for 45 minutes. To this solution was then added nitrosobenzene (11.25 g, 105 mmol, 1.05 eq) in 15 mL of THF dropwise at -78 °C. The resultant mixture was allowed to stir for two hours. The reaction was then quenched by addition of 75 mL of water. Subsequently, the biphasic mixture was placed on a rotary evaporator to remove THF. After >85% of THF had been removed, 100 mL of dioxane was added and the mixture was placed back on the rotary evaporator to remove remaining THF. Next, to the same flask was consecutively added, 150 mL of dioxane, 175 mL of water, and LiOH monohydrate (21 g, 500 mmol, 5 eq). The resultant solution was stirred for 20 h at 30-35 °C. The organic layer was then separated from the aqueous phase. The aqueous phase was extracted with ethyl acetate (5×). The combined extracts were dried over Na₂SO₄, filtered, and concentrated *in vacuo*. (Note: dioxane can be easily removed through co-distillation with ethyl acetate) ¹H NMR of the crude product indicated a 1.7:1 mixture of the corresponding *N*-phenyl imines. Purification by flash column chromatography with hexanes/ether (10:1) as eluent resulted in hydrolysis of the imines, giving the title compound as an orange oil (9.15 g, 75% yield).

3: R_f = 0.46 (silica gel, hexanes: EtOAc 3:1); [α]_D^{23 °C} = -1087.6 (*c* = 1.00, CHCl₃); FT-IR (thin film): 2967, 2935, 2872, 1744, 1607, 1573, 1441 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 5.56 (s, 1H), 2.94 (brs, 1H), 2.84 (brs, 1H), 2.15-2.12 (m, 1H), 1.95 (dd, *J* = 16.0, 3.0 Hz, 1H), 1.91 (d, *J* = 9.0 Hz, 1H), 1.85 (d, *J* = 1.5 Hz, 3H), 1.78 (dd, *J* = 16.5, 4.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 215.2, 153.9, 122.0, 56.2, 49.5, 44.4, 36.8, 16.3; LRMS (CI) calcd for C₈H₁₁O⁺ (M+H)⁺, 123.1, found 123.1.

Lactone 4

To a 30 mL Et₂O solution of ketone **3** (7.94 g, 65.0 mmol, 1 eq) was added a 27 mL aqueous solution of NaOH (3.12 g, 78.0 mmol, 1.2 eq). The biphasic mixture was rapidly stirred and cooled by an ice-water bath, then a 30% aqueous solution of H₂O₂ (8.6 mL, 84.5 mmol, 1.3 eq) was added through an pressure equalizing addition funnel over a period of 30 min, and then the reaction mixture was warmed up to room temperature for another 45 min. Trace amount of starting material

was left unreacted at this stage judging by TLC analysis (1:3 ethyl acetate/ hexanes). The mixture was cooled down again by an ice bath, and acidified by 14 mL 4 N H₂SO₄ till pH value of the aqueous phase was 1~2. Then, 2.5 g Na₂SO₃ was added **cautiously** to destroy excess peroxide. After extraction with 4×50 mL Et₂O, the combined organic phase was washed by 10 mL brine and dried over MgSO₄. Flash column with 2:7 ethyl acetate/ hexanes afforded lactone **4** (6.15 g, 68% yield) as a yellow oil.

Preparation of (±)-**4**: Add 200 mL toluene to a 500 mL round-bottom flask, and then cool it to -78 °C. Freshly cracked and fractionally distilled (oil bath up to 200 °C, boiling point about 73~76 °C) methyl cyclopentadiene monomer (39.2 mL, 400 mmol, 2.0 eq) and chloroacrylonitrile (16.0 mL, 200 mmol, 1.0 eq) (**Caution:** this material is known to be highly toxic) is added in this order and the mixture is stirred at -78 °C, followed by a 20 mL toluene solution of B(C₆F₅)₃ (1.024 g, 2 mmol, 0.01 eq) in one portion *via* cannula. Stirring is continued for 5 h at -78 °C and then the reaction mixture warmed up to r.t. over 0.5 h, followed by pouring into a solution obtained from 400 mL brine and 40 g sodium potassium tartrate. Layers are separated and the aqueous phase is extracted by 3 × 50 mL Et₂O. The combined organic solution is concentrated to give the crude Diels-Alder adduct, which is dissolved in 200 mL DMSO and then added a hot solution of KOH (28.0 g, 500 mmol, 2.5 eq) in 20 mL H₂O. Stir it overnight at r.t. for 13 h, and then dilute with 100 mL H₂O. Extract with 4 × 50 mL Et₂O, and dry over Na₂SO₄. After filtration and concentration, the crude mixture of ketones (±)-**3** and its regioisomer (20.0 g crude, less than 164 mmol, 1 eq) are dissolved in 70 mL Et₂O, and then mixed with a solution of NaOH (7.88 g, 197 mmol, more than 1.2 eq) in 67 mL H₂O. The biphasic mixture is vigorously stirred and cooled by an ice-water bath. A 30 % H₂O₂ solution (25.1 mL, 246 mmol, more than 1.5 eq) is added dropwise over 50 min, and stirring is continued at this temperature for another 1 h after addition is completed. The solution is acidified by dropwise addition of 17 mL HCl (12 M), and then 25 g solid Na₂SO₃ is slowly added portionwise to destroy excess oxidants (**Caution:** highly exothermic reaction). After warming up to r.t., the aqueous phase is saturated by solid NaCl and layers separated. The aqueous phase is extracted by 3 × 25 mL Et₂O. The combined organic phase is dried over Na₂SO₄. After filtration and concentration, flash column chromatography (silica gel,

hexanes to hexanes: EtOAc 2:1 gradient) affords lactone (**±**)-**4** (13.2 g, 48 % yield from chloroacrylonitrile) as a yellow oil. Alternative purification procedure involves distillation of the crude product at 3~4 mmHg with ~120 °C oil bath.

4: R_f = 0.20 (silica gel, hexanes: ethyl acetate 3:1); b.p. 99~102 °C (uncorrected), 3~4 mmHg; $[\alpha]_D^{20\text{ }^\circ\text{C}}$ = +89.5 (c = 0.98, CHCl_3); FT-IR (thin film): 3052, 2972, 2925, 2856, 1762, 1446, 1356, 1247, 1152, 1082, 935, 743 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3): δ = 5.94-5.92 (m, 1 H), 5.79-5.77 (m, 1 H), 2.93 (dd, J = 18.3, 10.1 Hz, 1 H), 2.79 (ddt, J = 17.2, 7.9, 2.2 Hz, 1 H), 2.71-2.68 (m, 1 H), 2.38 (dd, J = 18.3, 5.6 Hz, 1 H), 2.28 (dq, J = 17.2, 2.3 Hz, 1H), 1.54 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ = 176.4, 133.9, 133.3, 98.0, 41.6, 39.1, 37.1, 24.6; HRMS (ESI) calcd for $\text{C}_8\text{H}_{10}\text{O}_2\text{Na}^+$ ($\text{M}+\text{Na}$) $^+$ 161.0573, found 161.0570.

Vinyl lactones **5**

$\text{CuBr}\cdot\text{Me}_2\text{S}$ (5.45 g, 26.5 mmol, 1.2 eq) was added to a 500 mL round bottom flask, then dissolved with 22 mL Me_2S and 50 mL THF. After cooling down by a dry ice acetonitrile bath (bath temp: -40 °C ~ -45 °C, the colorless solution became a white suspension at this time), a 1.11 M THF solution of vinyl magnesium bromide (47.8 mL, 53.1 mmol, 2.4 eq) was added through syringe dropwise. After addition was complete, the black suspension was maintained at this temperature for 15 min. A solution of lactone **4** (3.05 g, 22.1 mmol, 1 eq) in 40 mL THF was transferred to the flask via cannula dropwise. The reaction mixture was allowed to gradually warm up to room temperature over 2 h, then quenched by 60 mL 1N HCl, and the organic layer separated, the aqueous layer was extracted further by 4×40 mL Et_2O . The combined organic phase was washed by 30 mL 1N HCl, 30 mL brine, and the brine washing was back extracted by 40 mL Et_2O . The combined organic phase was dried over MgSO_4 . After filtration and concentration, without further purification, this material was dissolved in 60 mL 1,2-dichloroethane, followed by addition of a solution of HNTf_2 (280 mg, 0.99 mmol, 0.045 eq) in 2 mL 1,2-dichloroethane at room temperature. This black solution was heated in a 70 °C oil bath for 45 min. Trace amount of starting material was left unreacted at this stage judging by TLC analysis (1:1 ethyl acetate/chloroform). After cooling down to room temperature, the solution was concentrated in vacuum and purified

by flash column with 1:7 ethyl acetate/ hexanes to afford vinyl lactones **5** (2.98 g, 81% yield) as a diastereomeric mixture, d.r. ~ 10:1 by ^1H NMR integration.

5: R_f = 0.60 (silica gel, chloroform: ethyl acetate 5:4); FT-IR (thin film): 3076, 2968, 2925, 2864, 1768, 1642, 1420, 1381, 1269, 1215, 1156, 1016, 953, 912 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): for major diastereomer, δ = 5.78-5.68 (m, 1 H), 5.05 (dt, J = 17.1, 1.5 Hz, 1 H), 4.98 (ddd, J = 10.3, 1.5, 1.0 Hz, 1 H), 2.94 (dd, J = 18.6, 10.3 Hz, 1 H), 2.83-2.70 (m, 1 H), 2.59 (tt, J = 9.9, 2.4 Hz, 1 H), 2.35 (dd, J = 18.6, 2.7 Hz, 1 H), 2.23 (ddd, J = 13.7, 5.9, 1.8 Hz, 1 H), 1.85-1.78 (m, 1 H), 1.69 (ddt, J = 13.3, 6.6, 1.9 Hz, 1 H), 1.51 (s, 3 H), 1.49-1.43 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 177.0, 139.7, 114.5, 95.0, 45.8, 43.0, 41.6, 40.5, 37.1, 25.4; HRMS(EI) calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2^+$ (M^+) 166.0994, found 166.0991.

Cyanides **6**

Lactone **5** (2.39 g, 14.4 mmol, 1 eq) was dissolved in 50 mL toluene and then cooled to $-78\text{ }^\circ\text{C}$ by a dry ice-acetone bath. DIBAL-H (14.5 mL, 1.0 M hexanes solution, 14.5 mmol, 1.01 eq) was added *via* a syringe pump over 30 min, and then stirring was continued at this temperature for another 30 min. Et_2AlCN (14.7 mL, 1.0 M toluene solution, 14.7 mmol, 1.02 eq) was added dropwise to this solution, followed by dropwise addition of $\text{BF}_3\cdot\text{OEt}_2$ (3.62 mL, 28.8 mmol, 2.0 eq). After 30 min, 10 mL EtOAc was added, and then the reaction mixture was warmed up to $0\text{ }^\circ\text{C}$ in an ice-water bath. A pre-mixed solution of 100 mL pH 7 phosphate buffer ($\sim 0.1\text{ M}$) and 20 mL 30% Rochelle's solution was poured into the reaction mixture, which was then vigorously stirred for 1.5 h till the two layers got clearly separated. The organic layer was separated, and the aqueous layer was extracted by $4 \times 30\text{ mL}$ EtOAc. The combined organic phase was washed by 20 mL brine, and then dried over Na_2SO_4 . Filtration, concentration and flash column chromatography (silica gel, hexanes: EtOAc 25:1 to 22:1 to 20:1 gradient) afforded cyanides **6** and its epimers **6'** (2.13 g total, 84% yield). Crude ^1H NMR shows the two pairs of anomers exit in 1:1 ratio. The stereochemistry assignments are based on the ^1H - ^1H NOESY spectrums, showing the existence of nOe effect between H-2 and methyl-6a in **6**, which is absent in **6'**. The undesired cyanide **6'** can be epimerized by the following procedures to give additional

material of the desired cyanide **6**: Dissolve **6** (63.9 mg, 0.361 mmol, 1 eq) in 1 mL THF and cool it to -78 °C by a dry ice-acetone bath, and then add LiHMDS (0.397 mL, 1.0 M in THF, 1.1 eq) dropwise. After 5 min, the dry ice-acetone bath is taken off, and the reaction mixture stirred at room temperature for 30 min. After quenching by 10 mL saturated NH₄Cl solution, it is extracted by 3 × 10 mL Et₂O and the combined organic phase is washed by 5 mL brine. After drying over MgSO₄, the crude NMR shows the ratio of **6** and **6'** is 2:3. Flash column chromatography (silica gel, hexanes: EtOAc 20:1) afforded cyanides **6** and its epimers **6'** (56.0 mg total, 87% yield).

6: *R_f* = 0.45 (silica gel, hexanes: ethyl acetate 3:1); FT-IR (thin film): 3081, 2965, 2864, 2361, 2337, 1641, 1456, 1378, 1146, 1070, 914 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): major diastereomer, δ = 5.78-5.71 (m, 1 H), 5.06 (dt, *J* = 17.2, 1.6 Hz, 1 H), 4.95 (ddd, *J* = 10.3, 1.6, 1.1 Hz, 1 H), 4.55 (t, *J* = 7.2 Hz, 1 H), 3.01-2.89 (m, 1 H), 2.67-2.58 (m, 1 H), 2.47-2.40 (m, 1 H), 2.13 (ddd, *J* = 13.5, 6.2, 1.4 Hz, 1 H), 2.05-1.98 (m, 1 H), 1.83-1.69 (m, 2 H), 1.37 (dd, *J* = 13.5, 11.7 Hz, 1 H), 1.30 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ = 140.6, 119.1, 113.9, 95.1, 66.0, 48.0, 45.9, 41.6, 39.7, 39.1, 24.9; HRMS(EI) calcd for C₁₁H₁₅NO⁺ (*M*⁺) 177.1154, found 177.1156.

6': *R_f* = 0.54 (silica gel, hexanes: ethyl acetate 3:1); ¹H NMR (400 MHz, CDCl₃): major diastereomer, δ = 5.76-5.67 (m, 1H), 5.02 (dt, *J* = 17.2, 1.4 Hz, 1H), 4.94 (ddd, *J* = 10.3, 1.5, 1.1 Hz, 1H), 4.75 (dd, *J* = 8.2, 3.6 Hz, 1H), 2.73-2.53 (m, 3H), 2.10-2.02 (m, 2H), 1.70-1.65 (m, 2H), 1.52 (s, 3H), 1.31 (dd, *J* = 13.6, 11.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 140.3, 120.2, 114.0, 95.6, 66.0, 47.5, 46.8, 41.5, 40.0, 38.9, 26.1.

Unsaturated ketones **7**

DIBAL-H (2.34 mL, 1.0 M hexanes solution, 2.34 mmol, 1.02 eq) was added to a 100 mL round-bottom flask, cooled to 0 °C by an ice-water bath, and then diluted with 8.5 mL Et₂O. *n*-BuLi (1.58 mL, 1.47 M hexanes solution, 2.32 mmol, 1.01 eq) was added to this solution dropwise. Stirring was continued for another 20 min, and the flask was then cooled down to -78 °C by a dry ice-acetone bath. A solution of cyanide **6** (406.6 mg, 2.29 mmol, 1 eq) in 17 mL Et₂O was transferred to the above mentioned solution *via* cannula. After 5 min, the dry ice-acetone bath was changed to an ice-water bath and stirring was continued for another

30 min. Trace amount of cyanide **6** was left unreacted at this stage judging by TLC analysis (1:3 ethyl acetate/ hexanes). The ice-water bath was changed back to a dry ice-acetone bath, and then 8.5 mL MeOH was added dropwise while gas generated in the flask. After 5 min, the dry ice-acetone bath was changed back to an ice-water bath and stirring was continued for another 60 min. Then 5.8 mL H₂SO₄ (1:17 aqueous solution) was added, and stirring was continued for another 30 min. The two layers were separated, and then the aqueous phase was extracted by 3 × 20 mL Et₂O. The combined organic phase was washed with 5 mL water and 5 mL brine, and then dried over MgSO₄. Filtration and concentration afforded the crude aldehyde product (*R_f* = 0.37, silica gel, hexanes: ethyl acetate 3:1), which was used in the next reaction immediately without further purification. The crude aldehyde product was dissolved in 14 mL THF and cooled to 0 °C by an ice-water bath. NaH (0.366 g, 60% dispersion in mineral oil, 9.16 mmol, 4 eq) was suspended with 23 mL THF, to which was added diethyl (2-oxopropyl)-phosphonate (1.76 mL, 9.16 mmol, 4 eq). Stirring was continued at room temperature for 15 min, generating a clear solution with no further gas evolving. This solution was transferred *via* cannula to the solution of the crude aldehyde product, and stirring was continued at 0 °C for another 30 min. Trace amount of aldehyde was left unreacted at this stage judging by TLC analysis (1:6 acetone/ benzene). The reaction was quenched by 50 mL saturated NH₄Cl solution. After dilution with 50 mL H₂O and extraction with 3 × 50 mL Et₂O, the combined organic phase was washed with 10 mL brine, and dried over MgSO₄. Filtration, concentration and flash column chromatography (silica gel, hexanes: EtOAc 6:1) afforded unsaturated ketones **7** (327.9 mg, 65% yield over two steps) as a mixture of two diastereomers.

7: *R_f* = 0.37 (silica gel, hexanes: ethyl acetate 3:1); FT-IR (thin film): 3078, 2962, 2921, 2863, 1699, 1679, 1640, 1448, 1432, 1373, 1359, 1300, 1256, 1212, 1166, 1106, 1047, 979, 912 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): major diastereomer, δ = 6.69 (dd, *J* = 16.0, 5.5 Hz, 1H), 6.28 (dd, *J* = 16.0, 2.0 Hz, 1H), 5.80-5.73 (m, 1H), 5.04 (dt, *J* = 17.0, 1.5 Hz, 1H), 4.94 (dq, *J* = 10.0, 1.0 Hz, 1H), 4.42-4.38 (m, 1H), 2.82-2.76 (m, 1H), 2.44-2.38 (m, 2H), 2.28 (s, 3H), 2.05 (ddd, *J* = 13.5, 6.0, 1.5 Hz, 1H), 1.64-1.54 (m, 2H), 1.38 (dd, *J* = 11.0, 5.0 Hz, 1H), 1.33 (s, 3H), 1.25 (dd, *J* = 13.0, 12.0 Hz, 1H); 198.6, 145.9, 140.9, 129.8, 113.6, 92.3, 76.4, 49.0, 46.3, 41.9, 41.3, 39.8, 27.1, 25.2; HRMS(EI) calcd for

$C_{14}H_{20}O_2^+ (M^+)$ 220.1463, found 220.1468.

Aldehydenone 8

Unsaturated ketone **7** (167.3 mg, 0.76 mmol, 1 eq) was dissolved in 6.6 mL CH_3CN and 1.1 mL H_2O , and then $RuCl_3$ (calculated as dihydrate, 6.5 mg, 0.027 mmol, 0.035 eq) was added. $NaIO_4$ (328.4 mg, 1.54 mmol, 2.02 eq) was added portionwise at room temperature during 1 h. Stirring was continued for another 1 h, and then the reaction was quenched by 40 mL saturated aqueous solution of $Na_2S_2O_3$. After extraction by 3×15 mL EtOAc, the combined organic phase was washed with 10 mL brine, and dried over Na_2SO_4 . Filtration, concentration and flash column chromatography (silica gel, hexanes: EtOAc 3:1) afforded 51.7 mg starting material **7** (31% recovery) and desired aldehydenone **8** (98.8 mg, 59% yield, 86 % based on recovered starting material) as a mixture of two diastereomers.

8: R_f = 0.35 (silica gel, hexanes: EtOAc 1:1); FT-IR (thin film): 2963, 2921, 2864, 2717, 1719, 1676, 1634, 1360, 1257 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): major diastereomer, δ = 9.68 (d, J = 2.5 Hz, 1H), 6.76 (dd, J = 16.0, 5.2 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 4.51-4.43 (m, 1H), 3.13-3.03 (m, 1H), 2.52-2.45 (m, 2H), 2.28 (s, 3H), 2.19 (ddd, J = 13.5, 6.6, 1.5 Hz, 1H), 2.01-1.94 (m, 1H), 1.76-1.61 (m, 2H), 1.44-1.40 (m, 1H), 1.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.9, 198.4, 145.4, 129.6, 92.2, 76.5, 50.4, 48.5, 41.3, 40.5, 34.1, 27.3, 24.7; HRMS(EI) calcd for $C_{13}H_{18}O_3^+ (M^+)$ 222.1256, found 222.1254.

Tetracyclic compound 9

Aldehydenone **8** (22.6 mg, 0.102 mmol, 1 eq) was dissolved in 2 mL DMF along with L-proline (11.7 mg, 0.102 mmol, 1 eq) and stirred at room temperature for 132 h. The yellow color solution was cooled by an ice bath, and then 1 mL 2N aqueous NaOH solution was added. After 10 min, the ice bath was taken off and stirring was continued for another 30 min at room temperature. The reaction was quenched by 10 mL saturated aqueous NH_4Cl solution and extracted by 3×15 mL Et_2O . The combined organic phase was washed with 2×5 mL brine, and dried

over MgSO₄. Filtration, concentration and flash column chromatography (silica gel, hexanes: EtOAc 3:1) afforded tetracyclic compound **9** and **9'** as inseparable diastereomeric mixture (19.7 mg total, 95% yield). Crude ¹H NMR shows the two isomers exit in 5:1 ratio favoring the desired compound **9**. An analytical sample of **9** was obtained by HPLC purification of this mixture (MICROSORB-Si-MV achiral column, hexane/EtOAc 1:1, 30 mL/min, collect ~ 5.4-6.4 min fractions). Enantiomeric excess of **9** was determined to be 99% by chiral HPLC analysis (Chiralpak AD-H, hexanes/isopropanol= 98:2, flow rate= 1 mL/min, *t*_{major}= 17.1 min, *t*_{minor}= 18.9 min), the racemic sample of (±)-**9** was obtained from (±)-**4** using the same synthetic procedures.

9: *R*_f = 0.36 (silica gel, hexanes: EtOAc 1:1); [*α*]_D^{26 °C} = -14.7 (*c* = 0.18, CHCl₃); FT-IR (thin film): 2952, 1678, 1448, 1378, 1326, 1281, 1248, 1137, 1082, 1037, 993, 820, 778 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 6.62 (d, *J* = 10.0 Hz, 1H), 5.94 (dd, *J* = 10.0, 0.5 Hz, 1H), 4.16 (dd, *J* = 3.4, 3.4 Hz, 1H), 2.44-2.27 (m, 4H), 1.97-1.92 (m, 2H), 1.89 (d, *J* = 11.6 Hz, 1H), 1.78-1.73 (m, 2H), 1.66 (d, *J* = 11.2 Hz, 1H), 1.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 199.1, 155.2, 128.9, 87.0, 79.0, 51.7, 46.2, 44.1, 42.7, 42.2, 37.9, 37.5, 23.1; LRMS (ESI) calcd for C₁₃H₁₆O₂Na⁺ (*M*+Na)⁺ 227.1, found 227.1.

Supporting Table. Preliminary organocatalyst screening for the Robinson annulation step.

Organocatalysts and solvents	d.r. (9 / 9') or notes
COOH (1 eq) in DMF	5 / 1
COOH (2 eq) in DMF	4.5 / 1
COOH (2 eq) in EtOH	1.4 / 1
COOH (1 eq) in DMF	3 / 1

Supporting Table (continued)

Organocatalysts and solvents	d.r. (9 / 9') or notes
(1 eq) in DMF	4 / 1
(1 eq) + (0.5 eq) in THF	2 / 1
(0.1 eq) in THF	no conversion
(1.2 eq) in DMF	no desired product

References with complete list of authors:

(1a) Wang, J.; Soisson, S. M.; Young, K.; Shoop, W.; Kodali, S.; Galgoci, A.; Painter, R.; Parthasarathy, G.; Tang, Y.; Cummings, R.; Ha, S.; Dorso, K.; Motyl, M.; Jayasuriya, H.; Ondeyka, J.; Herath, K.; Zhang, C.; Hernandez, L.; Alloco, J.; Basilio, Á.; Tormo, J. R.; Genilloud, O.; Vicente, F.; Pelaez, F.; Colwell, L.; Lee, S. H.; Michael, B.; Felcetto, T.; Gill, C.; Silver, L. L.; Hermes, J.; Bartizal, K.; Barrett, J.; Schmatz, D.; Becker, J. W.; Cully, D.; Singh, S. B. *Nature* **2006**, *441*, 358-361.

Current Data Parameters
 NAME 7514
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070514
 Time 20.27
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zg
 TD 48076
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.166670 Hz
 AQ 2.9999924 sec
 RG 128
 DW 62.400 usec
 DE 4.50 usec
 TE 300.0 K
 D1 5.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
 P1 9.50 usec
 PL1 0.00 dB
 SF01 500.1325006 MHz

F2 - Processing parameters

SI 65536
 SF 500.1300112 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00
 1D NMR plot parameters
 CX 20.00 cm
 F1P 11.000 ppm
 F1 5501.43 Hz
 F2P -1.000 ppm
 F2 -500.13 Hz
 PPMCM 0.60000 ppm/cm
 HZCM 300.07800 Hz/cm

Current Data Parameters
 NAME 7514
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070514
 Time 20.34
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zgpg
 TD 112780
 SOLVENT CDCl3
 NS 64
 DS 0
 SMH 30303.031 Hz
 FIDRES 0.266892 Hz
 AQ 1.8609200 sec
 RG 4096
 DW 16.500 usec
 DE 7.50 usec
 TE 300.0 K
 D1 4.0000000 sec
 d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
 P1 8.00 usec
 PL1 3.00 dB
 SF01 125.7728299 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
 NUC2 1H
 PCPD2 90.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 500.1338000 MHz

F2 - Processing parameters

SI 32768
 SF 125.7577940 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters

CX 20.00 cm
 F1P 200.000 ppm
 F1 25151.56 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.00000 ppm/cm
 HZCM 1257.57800 Hz/cm

B-DP column, 100 °C injection, 70 °C column, 40 kPa pressure, $t_{\text{major}} = 52.8$ min, $t_{\text{minor}} = 53.9$ min).

Current Data Parameters
 NAME carboketone
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070517
 Time 0.38
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zg
 TO 48076
 SOLVENT CDCl3
 NS 8
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.166670 Hz
 AQ 2.9999924 sec
 RG 64
 DW 62.400 usec
 DE 4.50 usec
 TE 300.0 K
 D1 3.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
 P1 9.50 usec
 PL1 0.00 dB
 SF01 500.1325006 MHz

F2 - Processing parameters
 SI 65536
 SF 500.1300064 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 10.083 ppm
 F1 5042.94 Hz
 F2P -1.032 ppm
 F2 -516.24 Hz
 PPMCM 0.55577 ppm/cm
 HZCM 277.95889 Hz/cm

2.942
2.939
2.839
2.144
2.134
2.129
2.125
1.980
1.974
1.948
1.941
1.920
1.902
1.847
1.844
1.801
1.792
1.768
1.759

5.557

7.275

Integral

0.9880
1.0676
1.1426
0.6076
0.7406
1.1874
3.3296
0.6906
0.4664

1.0000

Current Data Parameters

NAME 2carbonketone
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070517
Time 1.17
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TO 112780
SOLVENT CDC13
NS 397
DS 0
SWH 68965.516 Hz
FIDRES 0.614505 Hz
AQ 0.8177050 sec
RG 16384
DW 7.250 usec
DE 7.50 usec
TE 300.0 K
D1 4.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SF01 125.7671708 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1338000 MHz

F2 - Processing parameters

SI 32768
SF 125.7577852 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
F1P 283.568 ppm
F1 35660.83 Hz
F2P -31.980 ppm
F2 -4021.70 Hz
PPMCM 15.77737 ppm/cm
HZCM 1984.12659 Hz/cm

Current Data Parameters

NAME 7224
EXGNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070224
Time 10.13
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zg
TD 40538
SOLVENT CDCl3
NS 4
DS 0
SWH 7507.507 Hz
FIDRES 0.185197 Hz
AQ 2.6998808 sec
RG 128
DW 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 7.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 5.60 usec
PL1 0.00 dB
SF01 500.1322000 MHz

F2 - Processing parameters

SI 16384
SF 500.1300059 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCM 0.60000 ppm/cm
HZCM 300.07800 Hz/cm

Current Data Parameters

NAME 7223
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070224
Time 11.13
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg
TD 121208
SOLVENT CDCl3
NS 562
DS 0
SWH 30303.031 Hz
FIDRES 0.250008 Hz
AQ 1.9999820 sec
RG 2048
DM 16.500 usec
DE 7.50 usec
TE 300.0 K
D1 3.0000000 sec
d11 0.0300000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SF01 100.6268148 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 101.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 400.1324710 MHz

F2 - Processing parameters

SI 15384
SF 100.6127847 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 210.000 ppm
F1 21126.69 Hz
F2P -10.000 ppm
F2 -1006.13 Hz
PQCM 11.000000 ppm/cm
HZCM 1106.74060 Hz/cm

4

Current Data Parameters
NAME 7308
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070309
Time 16.24
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 25960
SOLVENT CDC13
NS 4
DS 0
SWH 4807.692 Hz
FIDRES 0.185196 Hz
AQ 2.6998899 sec
RG 90.5
DW 104.000 usec
DE 6.00 usec
TE 300.0 K
D1 3.00000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 10.50 usec
PL1 0.00 dB
SF01 400.1320007 MHz

F2 - Processing parameters

SI 32768
SF 400.1300057 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 11.000 ppm
F1 4401.43 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.60000 ppm/cm
HZCM 240.07800 Hz/cm

7.2684
5.7248
5.6993
5.0789
5.0752
5.0720
5.0361
5.0323
5.0291
4.9920
4.9896
4.9882
4.9859
4.9664
4.9639
4.9626
4.9602
2.9763
2.9505
2.9299
2.9041
2.5878
2.3795
2.3728
2.3331
2.3264
1.7995
1.5083
1.4920
1.4644
1.4630
1.4578
1.4280
0.0003

Integral

0.8415
0.9552
0.9338
0.9636
0.9421
1.0000
1.1911
1.0674
0.1362
0.1440
1.0371
1.0268
2.8693
0.3390
1.0119

ppm

Current Data Parameters

NAME 7308
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070309
Time 18.03
INSTRUM spect
PROBHD 5 mm GNP 1H
PULPROG zgdc
TD 121208
SOLVENT CDCl3
NS 1121
DS 0
SWH 30303.031 Hz
FIDRES 0.250008 Hz
AQ 1.9999820 sec
RG 4096
DM 16.500 usec
DE 7.50 usec
TE 300.0 K
D1 3.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 11.00 usec
PL1 -2.00 dB
SF01 100.6258087 MHz

===== CHANNEL f2 =====

CPOPRG2 waltz16
NUC2 1H
PCPD2 101.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 400.1324710 MHz

F2 - Processing parameters

SI 16384
SF 100.6127736 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 200.000 ppm
F1 20122.55 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 10.00000 ppm/cm
HZCM 1006.12769 Hz/cm

Current Data Parameters
 NAME 7308
 EXPNO 3
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070309
 Time 16.16
 INSTRUM spect
 PROBHD 5 mm QNP 1H
 PULPROG zg
 TD 25960
 SOLVENT CDCl3
 NS 4
 DS 0
 SMH 4807.692 Hz
 FIDRES 0.185196 Hz
 AQ 2.6998899 sec
 RG 35.9
 DW 104.000 usec
 DE 6.00 usec
 TE 300.0 K
 D1 3.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.50 usec
 PL1 0.00 dB
 SF01 400.1320007 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1300054 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 11.000 ppm
 F1 4401.43 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.60000 ppm/cm
 HZCM 240.07800 Hz/cm

Current Data Parameters
 NAME 730B
 EXPNO 6
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20070309
 Time 20.19
 INSTRUM spect
 PROBHD 5 mm GNP 1H
 PULPROG zgdc
 TD 121208
 SOLVENT CDCl3
 NS 677
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.250008 Hz
 AQ 1.9999820 sec
 RG 4096
 DW 16.500 usec
 DE 7.50 usec
 TE 300.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 11.00 usec
 PL1 -2.00 dB
 SF01 100.6256087 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 101.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 400.1324710 MHz

F2 - Processing parameters
 SI 16384
 SF 100.6127755 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 200.000 ppm
 F1 20122.55 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.00000 ppm/cm
 HZCM 1006.12781 Hz/cm

Current Data Parameters
NAME 7305
EXPNO 4
PROCNO 1

F2 - Acquisition Parameter

Date_ 20070310
Time 8.49
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TD 1024
SOLVENT CDCl3
NS 8
DS 16
SWH 1893.939 Hz
AQ 1.849500 Hz
RG 0.270300 sec
DE 4.00 Hz
TE 284.000 usec
DE 4.50 usec
TE 300.0 K
d0 0.0000300 sec
d1 5.40999985 sec
d8 2.81999993 sec
d9 0.00026395 sec
IN0 0.00026395 sec

***** CHANNEL f1 *****

NUC1 1H
P1 6.25 usec
PL1 0.00 dB
SF01 500.1315504 MHz

F1 - Acquisition parameter

NU0 2
TD 262144
SFO1 500.1315504 MHz
FIDRES 7.38853 Hz
SF 3.787 ppm

F2 - Processing parameter:

SI 1024
SF 500.1300861 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameter:

SI 512
MC2 TPPI
SF 500.1300861 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB 0

2D NMR plot parameters

CX2 15.00 cm
F2P0 4.861 ppm
F2L0 2431.22 Hz
F2PHI 1.074 ppm
F2H1 537.28 Hz
F1P0 4.861 ppm
F1L0 2431.31 Hz
F1PHI 1.074 ppm
F1H1 537.28 Hz
F2PMON 0.25546 ppm/cm
F2HON 126.26553 Hz/cm
F1PMON 0.25847 ppm/cm
F1HON 126.26860 Hz/cm

6

Current Data Parameters
 NAME 7308
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070309
 Time 16.08
 INSTRUM spect
 PROBHD 5 mm GNP 1H
 PULPROG zg
 TD 25960
 SOLVENT CDCl3
 NS 4
 DS 0
 SWH 4807.692 Hz
 FIDRES 0.185196 Hz
 AQ 2.6998899 sec
 RG 40.3
 DW 104.000 usec
 DE 6.00 usec
 TE 300.0 K
 D1 3.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
 P1 10.50 usec
 PL1 0.00 dB
 SF01 400.1320007 MHz

F2 - Processing parameters

SI 32768
 SF 400.1300054 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters

CX 20.00 cm
 F1P 11.000 ppm
 F1 4401.43 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.50000 ppm/cm
 HZCM 240.07800 Hz/cm

Current Data Parameters
 NAME 730B
 EXPNO 5
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070309
 Time 19.43
 INSTRUM spect
 PROBD 5 mm QNP 1H
 PULPROG zgpg30
 TD 121208
 SOLVENT CDCl3
 NS 282
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.250008 Hz
 AQ 1.9999820 sec
 RG 2048
 DW 16.500 usec
 DE 7.50 usec
 TE 300.0 K
 D1 3.00000000 sec
 d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
 P1 11.00 usec
 PL1 -2.00 dB
 SF01 100.6258087 MHz

===== CHANNEL f2 =====

CPCPRG2 waltz16
 NUC2 1H
 PCPD2 101.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 400.1324710 MHz

F2 - Processing parameters

SI 16384
 SF 100.6127755 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameters

CX 20.00 cm
 F1P 200.000 ppm
 F1 20122.55 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 10.00000 ppm/cm
 HZCM 1006.12781 Hz/cm

Current Data Parameters
NAME 7311
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070311
Time 15:31
INSTRUM spect
PROBHD 5 mm Multinu
PULPROG zgpg30
TO 1024
SOLVENT DMSO
NS 8
DS 16
SWH 2003.205 Hz
FIDRES 1.956295 Hz
AQ 0.2556404 sec
RG 48
DM 249.600 usec
DE 24.50 usec
TE 300.2 K
D0 0.000000 sec
D1 5.94899981 sec
D8 3.09599990 sec
D9 0.00024863 sec
TD 0

***** CHANNEL f1 *****
NUC1 ¹H
P1 6.20 usec
PL1 0.00 dB
SF01 500.1315754 MHz

F1 - Acquisition Parameters
NUC0 ²H
TD 512
SF01 500.1316 MHz
FIDRES 3.912118 Hz
SW 4.005 ppm

F2 - Processing parameters
SI 1824
SF 500.130078 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 512
MC2 TPPI
SF 500.1300134 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB 0

2D NMR Plot parameters
CZ2 15.00 cm
CY1 15.00 cm
FZ2L0 5.028 ppm
FZ2L1 2514.65 Hz
FZPH1 1.023 ppm
FZHL 511.45 Hz
F1PL0 5.028 ppm
F1LC 2514.51 Hz
F1PH1 1.023 ppm
F1HL 511.51 Hz
F2PMCM 0.26702 ppm/cm
F2HZCM 133.54698 Hz/cm
F1PMCM 0.26700 ppm/cm
F1HZCM 133.53362 Hz/cm

Current Data Parameters
NAME 7401
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070401
Time 10.01
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 32050
SOLVENT Aceton
NS 8
DS 0
SWH 8012.820 Hz
FIDRES 0.250010 Hz
AQ 1.9999700 sec
RG 128
DW 62.400 usec
DE 4.50 usec
TE 300.0 K
D1 3.00000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SF01 500.1325006 MHz

F2 - Processing parameters
SI 65536
SF 500.1300102 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ID NMR plot parameters
CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPHMC 0.60000 ppm/cm
HZCM 300.07800 Hz/cm

Current Data Parameters
NAME 7401
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070401
Time 10.36
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgpg30
TD 112780
SOLVENT CDCl3
NS 301
DS 0
SWH 27777.777 Hz
FIDRES 0.246301 Hz
AQ 2.0300901 sec
RG 8192
DM 18.000 usec
DE 7.50 usec
TE 300.0 K
D1 4.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SF01 125.7715724 MHz

===== CHANNEL f2 =====
CPOPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1338000 MHz

F2 - Processing parameters
SI 32768
SF 125.7577929 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters
CX 20.00 cm
F1P 220.000 ppm
F1 27666.71 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 11.00000 ppm/cm
HZCM 1383.33569 Hz/cm

Current Data Parameters
NAME 7412
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070412
Time 11.06
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zg
TD 40538
SOLVENT CDCl3
NS 8
DS 0
SMH 7507.507 Hz
FIDRES 0.185197 Hz
AQ 2.6998808 sec
RG 128
DM 66.600 usec
DE 4.50 usec
TE 300.0 K
D1 3.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
P1 9.50 usec
PL1 0.00 dB
SF01 500.1330008 MHz

F2 - Processing parameters

SI 65536
SF 500.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 20.00 cm
F1P 11.000 ppm
F1 5501.43 Hz
F2P -1.000 ppm
F2 -500.13 Hz
PPMCH 0.60000 ppm/cm
HZCM 300.07800 Hz/cm

Current Data Parameters
 NAME 7412
 EXPNO 2
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070412
 Time 11.14
 INSTRUM spect
 PROBD 5 mm GNP 1H
 PULPROG zgpg
 TD 112780
 SOLVENT CDC13
 NS 169
 DS 0
 SWH 30303.031 Hz
 FIDRES 0.268692 Hz
 AQ 1.8609200 sec
 RG 8192
 DM 16.500 usec
 DE 7.50 usec
 TE 300.0 K
 D1 4.00000000 sec
 d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
 P1 8.00 usec
 PL1 3.00 dB
 SF01 125.7728299 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz15
 NUC2 1H
 PCD2 90.00 usec
 PL2 120.00 dB
 PL12 19.00 dB
 SF02 500.1338000 MHz

F2 - Processing parameters

SI 32768
 SF 125.7577940 MHz
 MDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

1D NMR plot parameters

CX 20.00 cm
 F1P 220.000 ppm
 F1 27666.71 Hz
 F2P 0.000 ppm
 F2 0.00 Hz
 PPMCM 11.00000 ppm/cm
 HZCM 1383.33582 Hz/cm

Current Data Parameters
 NAME 7505
 EXPNO 1
 PROCNO 1

F2 - Acquisition Parameters

Date_ 20070505
 Time 18.42
 INSTRUM spect
 PROBHD 5 mm PABBI Z
 PULPROG zg
 TD 40538
 SOLVENT CDCl3
 NS 32
 DS 0
 SWH 7507.507 Hz
 FIDRES 0.185197 Hz
 AQ 2.6998808 sec
 RG 128
 DM 66.600 usec
 DE 4.50 usec
 TE 300.0 K
 D1 3.0000000 sec

===== CHANNEL f1 =====

NUC1 1H
 P1 5.80 usec
 PL1 0.00 dB
 SF01 499.8779993 MHz

F2 - Processing parameters

SI 32768
 SF 499.8750123 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters

CX 20.00 cm
 F1P 11.000 ppm
 F1 5498.63 Hz
 F2F -1.000 ppm
 F2 -499.87 Hz
 PPMCM 0.60000 ppm/cm
 HZCM 299.92499 Hz/cm

Current Data Parameters

NAME 7505
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date_ 20070505
Time 17.43
INSTRUM spect
PROBHD 5 mm QNP 1H
PULPROG zgdc
TD 112780
SOLVENT CDCl3
NS 1173
DS 0
SWH 30303.031 Hz
FIDRES 0.268692 Hz
AQ 1.8609200 sec
RG 2048
DK 16.500 usec
DE 7.50 usec
TE 300.0 K
D1 4.00000000 sec
d11 0.03000000 sec

===== CHANNEL f1 =====

NUC1 13C
P1 8.00 usec
PL1 3.00 dB
SF01 125.7728299 MHz

===== CHANNEL f2 =====

CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 500.1338000 MHz

F2 - Processing parameters

SF 32768
SF 125.7577931 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

1D NMR plot parameters

CX 20.00 cm
F1P 210.000 ppm
F1 26409.14 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 10.50000 ppm/cm
HZCM 1320.45679 Hz/cm

Data File: c:\star\2-7-07 4:25:18 pm -1.run
 Sample ID: Manual Sample
 Operator (Inj):
 Injection Date: 02/07/07 04:25:18 PM
 Run Mode: Analysis
 Peak Measurement: Peak Area
 Calibration Level: N/A
 Run Time (min): 20.827

Peak No	Result ()	Ret Time (min)	Time Offset (min)	Peak Area (counts)	Rel Ret Time	Sep. Code	Width 1/2 (sec)
1	52.8682	17.000	0.000	20336164	0.00	BB	20.8
2	47.1318	18.893	0.000	18129608	0.00	BB	24.0
	100.0000		0.000	38465772			

Data File: c:\star\data\5-14-071;07:07 pm.run
 Channel: 1 = 210.00 nm RESULTS
 Sample ID: Manual Sample
 Injection Method: c:\star\pingfan\pingfan pda.mth
 Run Time (min): 19.413
 Instrument (Inj): PDA
 Workstation:
 Verification Tolerance: N/A

Operator (Calc):
 Calc Date: 05/14/07 01:27:31 PM
 Times Calculated: 2
 Calculation Method: Analysis
 Instrument (Calc): PDA
 Run Mode:
 Peak Measurement: Peak Area
 Calculation Type: Percent
 Calibration Level: N/A

Peak No	Result ()	Ret. Time (min)
1	99.5414	17.133
2	0.4586	18.867
	100.0000	