Enantioselective Synthesis of (−)-Acetylapoaranotin

Haoxuan Wang, Clinton J. Regan, Julian A. Codelli, Paola Romanato, Angela L. A.
Puchlopek-Dermenci and Sarah E. Reisman*

The Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

*reisman@caltech.edu

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General Considerations. Unless otherwise stated, reactions were performed under a nitrogen atmosphere using freshly dried solvents. Tetrahydrofuran (THF), methylene chloride (CH₂Cl₂), acetonitrile (MeCN), dimethylformamide (DMF), and toluene (PhMe) were dried by passing through activated alumina columns. Triethylamine (Et₃N), and N,N-diisopropylethylamine (DIPEA) were distilled over calcium hydride prior to use. Unless otherwise stated, chemicals and reagents were used as received. All reactions were monitored by thin-layer chromatography using EMD/Merck silica gel 60 F254 pre-coated plates (0.25 mm) and were visualized by UV, p-anisaldehyde, or KMnO₄ staining. Flash column chromatography was performed as described by Still et al.¹ using silica gel (partical size 0.032-0.063) purchased from Silicycle. Optical rotations were measured on a Jasco P-2000 polarimeter using a 100 mm path-length cell at 589 nm. ¹H and ¹³C NMR spectra were recorded on a Varian 400 MR (at 400 MHz and 101 MHz, respectively), a Bruker 400 equipped with a cryoprobe (at 400 MHz and 101 MHz, respectively), a Varian Inova 500 (at 500 MHz and 126 MHz, respectively), or a Varian Inova 600 (at 600 MHz and 150 MHz, respectively), and are reported relative to internal CHCl₃ (¹H, δ = 7.26), CHDCl₂ (¹H, δ = 5.32), CD₃OD (¹H, δ = 3.31), MeCN-d2 (¹H, δ = 1.94), or DMSO-d5 (¹H, δ = 2.50), and CDCl₃ (¹³C, δ = 77.0), CD₂Cl₂ (¹³C, δ = 54.0), CD₃OD (¹³C, δ = 49.0), MeCN-d3 (¹³C, δ = 118.3), or DMSO-d6 (¹³C, δ = 40.0). Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicity and qualifier abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm⁻¹). HRMS were acquired using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), or mixed (MM) ionization mode. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing Chiralpak AD or Chiralcel OD-H columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm. Preparative HPLC was performed with an Agilent 1100 Series HPLC utilizing an Agilent Eclipse XDB-C18 5µm column (9.4 x 250 mm) or an Agilent Zorbax RX-SIL 5µm column (9.4 x 250 mm). Melting points were determined using a Büchi B-545 capillary melting point apparatus and the values reported are uncorrected.
Synthetic Procedures

Preparation of pyrrolidine 13

**Preparation of ethyl glycinate:** ethyl glycinate hydrochloride salt (3.0 g, 21.5 mmol) was suspended in 50 mL of CH$_2$Cl$_2$ and KOH (1.32 g, 1.2 equiv) in 100 mL H$_2$O was added with vigorous stirring. Saponification of the ethyl ester occurred readily, so it was important to accurately measure KOH. The layers were separated, and the aqueous layer was further extracted with CH$_2$Cl$_2$ (2 x 50 mL), dried over Na$_2$SO$_4$, and concentrated to yield 1.75 g (79% yield) of the free amine 12 (slightly volatile under high vacuum). The amine was used immediately to avoid dimerization.

**Generation of imine:** The free amine 12 (1.75 g, 17.0 mmol, 1.1 equiv) was dissolved in 35 mL CHCl$_3$. Silica gel (4.5 g, 0.3 g SiO$_2$ per mmol substrate) was added and the resulting suspension was cooled to 0 °C while open to the atmosphere. *Trans*-cinnamaldehyde 11 (1.9 mL, 15.0 mmol, 1.0 equiv) was added dropwise and the reaction was left to stir at 0 °C for an additional 3 hours, during which it turned from colorless to light yellow. The silica gel was removed via filtration and rinsed with 50 mL CHCl$_3$, and the resulting imine solution was used immediately.

**(1,3)-Dipolar cycloaddition reaction:** A round-bottom flasks was charged with CuI (287 mg, 1.5 mmol, 10 mol %), brucin-OL (647 mg, 1.5 mmol, 10 mol %), and 35 mL of CHCl$_3$. The resulting suspension was stirred at 0 °C under air. After a five-minute prestir, DBU (225 µL, 1.5 mmol, 10 mol %) was added and the solution was stirred vigorously for twenty minutes during which the solution went from cloudy brown to dark green. *N*-methoxy-*N*-methylacrylamide 10 (2.6 g, 22.6 mmol, 1.5 equiv) was then added, followed by the solution of imine (precooled to 0 °C and transferred via cannula over 5 min). The reaction was kept at 0 °C for 5 hours and then allowed to warm to room temperature over 7 hours. The reaction mixture was concentrated to half the volume and loaded directly onto SiO$_2$ and subjected to flash chromatography (50 : 45 : 5 hexanes : ethyl acetate : methanol) to afford 2.12 g (42% yield, 6.38 mmol) of 13 as a light yellow oil. The enantiomeric excess was determined to be 95% by chiral HPLC analysis (OD, 1 mL/min, 15% IPA in hexanes, λ = 254 nm): $t_R$(minor) = 13.3 min, $t_R$(major) = 24.7 min. [α]$_D^{25}$ = +152° (c = 0.90, CHCl$_3$); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.29 (m, 2H), 7.29 – 7.22 (m, 2H), 7.21 – 7.16 (m, 1H), 6.53 (d, $J$ = 15.7 Hz, 1H), 6.10 (dd, $J$ = 15.7, 8.3 Hz, 1H), 4.22 (qd, $J$ = 7.1, 3.2 Hz, 2H), 4.12 (t, $J$ = 7.9 Hz, 1H), 3.86 (t, $J$ = 8.4 Hz, 1H), 3.65 (s, 3H), 3.59 (q, $J$ = 7.7 Hz, 1H), 3.05 (s, 3H), 2.56 (s, 1H), 2.45 – 2.28 (m, 2H), 1.28 (t, $J$ = 7.1 Hz, 3H); $^{13}$C (126 MHz, CDCl$_3$) δ 173.7, 173.4, 136.6, 131.9, 128.3, 127.4, 126.4, 63.6, 61.3, 61.0, 59.8, 45.3, 33.2, 32.2, 14.1; FTIR (NaCl/thin film) 3340, 3298, 3057, 3024, 2979,
Preparation of Teoc-pyrrolidine 14

Pyrrolidine 13 (3.17 g, 9.54 mmol, 1.0 equiv) was suspended in H₂O (24 mL) and 1,4-dioxane (24 mL). Triethylamine (2.66 mL, 19.07 mmol, 2.0 equiv) was added followed by Teoc-OSu (3.71 g, 14.31 mmol, 1.5 equiv). The resulting solution was allowed to stir for 26 hours at room temperature. The solution was acidified with 60 mL 1M HCl then extracted with EtOAc (3 x 50 mL). The combined organic extracts were dried over MgSO₄ and concentrated to yield a light orange oil. Flash chromatography (10% to 60% EtOAc in hexanes) afforded Teoc-pyrrolidine 14, as a thick yellow oil (3.89 g, 8.16 mmol, 86% yield). [α]D₂₅ = +101° (c = 0.64, CHCl₃); ¹H NMR (400 MHz, CD₃CN, 60 °C) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 6.70 (dd, J = 15.8, 1.1 Hz, 1H), 6.05 (dd, J = 15.8, 7.6 Hz, 1H), 4.92 (t, J = 7.8 Hz, 1H), 4.30 (dd, J = 10.3, 7.6 Hz, 1H), 4.21 (qd, J = 7.1, 1.0 Hz, 1H), 4.18 – 4.12 (m, 2H), 3.75 (s, 3H), 3.61 (dt, J = 12.2, 7.4 Hz, 1H), 3.08 (s, 3H), 2.46 (q, J = 12.0 Hz, 1H), 2.33 (dt, J = 13.0, 7.2 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.97 (dd, J = 8.8, 7.5 Hz, 2H), 0.03 (s, 9H); ¹³C NMR (101 MHz, CD₃CN, compound exists as a 1:1 mixture of rotamers) δ 173.8, 173.5, 171.3, 155.8, 155.0, 137.8, 132.8, 129.6, 128.6, 127.7, 127.3, 127.2, 64.3, 64.2, 62.3, 62.0, 61.8, 61.7, 61.2, 59.7, 59.4, 46.6, 45.9, 32.8, 31.6, 30.6, 18.4, 18.3, 14.6, -1.4, -1.5; FTIR (NaCl, thin film): 2953, 2900, 1747, 1700, 1668, 1404, 1345, 1282, 1250, 1186, 1112, 1038, 1012, 961, 860, 838, 756, 694 cm⁻¹; HRMS (MM) calc’d for C₂₂H₃₃N₂O₆Si [M–C₂H₄+H]⁺ 449.2102, found 449.2110 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

Preparation of diene 9

Weinreb amide 14 (2.37 g, 4.97 mmol, 1.0 equiv) was dissolved in dry THF (42 mL) under N₂ and the solution was cooled to −78 °C. A solution of allyl Grignard (0.85M in THF, diluted with THF from commercially available reagent; 8.2 mL, 6.96 mmol, 1.4 equiv) was added slowly over the course of 4 hours using a syringe pump at −78 °C. Following the addition, the reaction was allowed to stir for another 10 minutes before being
quenched with 30 mL of AcOH/THF/H₂O (1:1:1) and warmed to room temperature. The reaction was then carefully basified with saturated NaHCO₃ solution until gas evolution ceased. The aqueous layer was then extracted with EtOAc (3 x 150 mL). The combined organic layers were washed with brine (200 mL) and dried over Na₂SO₄, filtered, and concentrated to give a yellow oil. Flash chromatography (5% to 30% EtOAc in hexanes) afforded diene 9, as a yellow oil (1.15 g, 2.51 mmol, 51% yield). [α]D²⁵ = −8° (c = 0.495, CHCl₃); ¹H NMR (400 MHz, CD₃CN, 60 °C) δ 7.39 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 6.77 (dd, J = 15.9, 0.9 Hz, 1H), 6.01 (ddd, J = 15.7, 8.1, 0.8 Hz, 1H), 5.95 – 5.77 (m, 1H), 5.16 – 5.10 (m, 1H), 5.12 – 5.07 (m, 1H), 4.97 (t, J = 8.0 Hz, 1H), 4.30 (dd, J = 9.8, 8.0 Hz, 1H), 4.20 (qt, J = 7.2, 1.2 Hz, 2H), 4.17 – 4.10 (m, 2H), 3.55 (dt, J = 1.1, 0.6 Hz, 1H), 3.26 (dt, J = 7.1, 0.7 Hz, 3H), 1.27 (td, J = 1.2, 1.2 Hz, 3H), 0.03 (d, J = 0.8 Hz, 9H); ¹³C NMR (101 MHz, CD₃CN, 60 °C) δ 205.5, 205.4, 173.6, 173.3, 155.6, 154.8, 137.5, 133.74, 133.68, 131.6, 129.7, 128.9, 128.8, 127.3, 126.6, 126.5, 119.1, 64.4, 64.3, 62.1, 62.0, 61.9, 61.7, 59.8, 59.5, 54.7, 54.1, 48.2, 30.5, 29.5, 18.4, 14.6, -1.47, -1.52; FTIR (NaCl, thin film): 3082, 3060, 3024, 2981, 2952, 2899, 1749, 1702, 1450, 1408, 1371, 1344, 1285, 1250, 1185, 1168, 1110, 1038, 962, 924, 860, 837, 751, 694 cm⁻¹; HRMS (MM) calc’d for C₂₃H₃₂NO₅Si [M–C₂H₄+H]⁺ 430.2044, found 430.2053 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

Preparation of ketone 15

To a 500 mL flame-dried flask was added diene 9 (1.15 g, 2.51 mmol, 1.0 equiv) and CH₂Cl₂ (250 mL). Hoveyda-Grubbs II catalyst (63 mg, 0.10 mmol, 4 mol %) was added and the resulting light green solution was allowed to stir at room temperature for 4 hours. The reaction was then quenched with DMSO (380 µL, 50 equiv) and stirred for another 22 hours. The reaction mixture was filtered through a silica gel plug, eluting with EtOAc, and the filtrate was concentrated to give a light brown oil. Flash chromatography (5% to 25% EtOAc in hexanes) afforded ketone 15, as a light brown oil (761 mg, 2.15 mmol, 86% yield). [α]D²⁵ = −117° (c = 0.63, CHCl₃); ¹H NMR (400 MHz, CD₃CN, 60 °C) δ 6.04 (dq, J = 10.2, 2.5 Hz, 1H), 5.80 (dt, J = 10.2, 3.7, 1.6 Hz, 1H), 4.79 (dt, J = 7.6, 2.3 Hz, 1H), 4.32 (dd, J = 8.3, 7.1 Hz, 1H), 4.24 – 4.15 (m, 2H), 4.12 (qd, J = 7.1, 1.1 Hz, 2H), 3.05 (q, J = 8.0 Hz, 1H), 2.99 – 2.80 (m, 2H), 2.45 – 2.26 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 8.3 Hz, 2H), 0.05 (s, 9H); ¹³C NMR (101 MHz, CD₃CN, 60 °C) δ 207.5, 173.3, 155.8, 128.1, 124.4, 64.7, 62.2, 61.2, 60.2, 51.0, 38.2, 32.8, 19.0, 14.8, -1.0; FTIR (NaCl, thin film): 3042, 2953, 2899, 1749, 1703, 1454, 1412, 1350, 1249, 1186, 1112, 1033, 988, 964, 946, 860, 838, 769, 695 cm⁻¹; HRMS (MM) calc’d for C₁₅H₂₄NO₅Si [M–C₂H₄+H]⁺ 326.1418, found 326.1419 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).
Preparation of enone 16

To ketone 15 (761 mg, 2.15 mmol, 1.0 equiv) in a 200 mL round-bottom flask was added freshly prepared DMDO acetone solution (0.0905 M, 48 mL, 4.30 mmol, 2.0 equiv) and the resulting solution was allowed to stir at room temperature for 90 minutes (the reaction was monitored by taking 1H NMR spectra of the reaction aliquots). The reaction was then concentrated and put under high vacuum for 90 minutes to remove the residual solvent. The crude material was then dissolved in toluene (215 mL) and mixed with silica gel (17.2 g). The resulting mixture was heated to 50 °C for 1 hour and cooled to room temperature. The mixture was filtered through a silica gel plug, eluting with EtOAc, and the filtrate was concentrated to give a light brown oil. Flash chromatography (5% to 40% EtOAc in hexanes) afforded enones 16 and 16', (6.5 : 1 mixture of diastereomers by 1H NMR, where 16 is the major diastereomer), as a thick colorless oil (630 mg, 1.71 mmol, 80% yield). The mixture of diastereomers was carried through the next reaction. Analytically pure products were isolated using preparative reverse phase HPLC (50% to 60% CH3CN in H2O over 10 minutes, tR(16) = 8.0-8.7 min, tR(16') = 9.5-10.0 min).

**Major diastereomer 16.** [α]D 25 = −23° (c = 1.925, CHCl3); 1H NMR (400 MHz, CDCl3) δ 6.85 (dd, J = 10.4, 2.1 Hz, 1H), 6.00 (dd, J = 10.4, 2.5 Hz, 1H), 4.91 (s, 1H), 4.78 (dt, J = 7.2, 2.3 Hz, 1H), 4.38 (dd, J = 8.6, 7.3 Hz, 1H), 4.33 (dd, J = 9.8, 7.6 Hz, 1H), 4.25 – 4.12 (m, 4H), 3.04 (dt, J = 12.8, 8.2 Hz, 1H), 2.65 (dt, J = 12.7, 7.6 Hz, 1H), 1.95 (td, J = 12.8, 9.7 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.01 – 0.88 (m, 2H), 0.02 (s, 9H); 13C NMR (101 MHz, CDCl3) δ 195.4, 171.7, 156.8, 150.5, 126.9, 70.0, 65.2, 65.1, 61.6, 59.2, 45.6, 32.8, 17.7, 14.1, -1.6; FTIR (NaCl, thin film): 3413, 2953, 2899, 1744, 1676, 1457, 1420, 1377, 1350, 1304, 1251, 1215, 1188, 1166, 1118, 1069, 1032, 960, 861, 839, 770, 695 cm⁻¹; HRMS (MM) calc’d for C15H24NO6Si [M–C2H4+H]+ 342.1367, found 342.1378 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

**Minor diastereomer 16’.** [α]D 25 = −58° (c = 0.405, CHCl3); 1H NMR (400 MHz, CD3CN, 60 °C) δ 7.08 (dd, J = 10.0, 5.9 Hz, 1H), 6.10 (d, J = 10.0 Hz, 1H), 4.70 – 4.56 (m, 1H), 4.39 (dd, J = 9.5, 7.9 Hz, 1H), 4.37 – 4.32 (m, 1H), 4.27 – 4.15 (m, 5H), 3.08 (dt, J = 12.0, 8.3 Hz, 1H), 2.62 (dt, J = 12.2, 8.2 Hz, 1H), 2.13 (app q, J = 11.6 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.10 – 0.90 (m, 2H), 0.06 (s, 9H); 13C NMR (101 MHz, CD3CN, compound exists as a mixture of rotamers) δ 198.7, 175.2, 155.7, 148.0, 147.2, 132.3, 131.9, 64.9, 63.2, 62.7, 61.6, 60.8, 60.4, 47.1, 46.7, 34.5, 33.9, 18.3, 14.4, -1.5; FTIR (NaCl, thin film): 3445, 2953, 2900, 1698, 1404, 1377, 1348, 1303, 1251, 1203, 1177, 1114, 1065, 1030, 999, 975, 942, 899, 853, 838, 769, 696 cm⁻¹; HRMS (MM) calc’d for C15H24NO6Si [M–C2H4+H]+ 342.1367, found 342.1376 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).
Preparation of TBS ether 8

A flame-dried 50 mL round-bottom flask was charged with enone 16/16’ (462 mg, 1.25 mmol, 1.0 equiv; as a 6.5 : 1 mixture of 16/16’) and dry CH₂Cl₂ (12 mL), which was cooled to –78 °C. 2,6-Lutidine (0.72 mL, 6.25 mmol, 5.0 equiv) was added, followed by slow addition of TBSOTf (0.57 mL, 2.50 mmol, 2.0 equiv). The resulting clear solution was allow to stir at –78 °C for 90 minutes. The reaction was quenched with pH 7 buffer (15 mL) and warmed to room temperature. The mixture was separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, filtered, and concentrated to give a colorless oil (extended drying under high vacuum removed the residual 2,6-lutidine, improving subsequent purification). Flash chromatography (1% to 18% EtOAc in hexanes) afforded TBS ether 8 as a single diastereomer, which was a colorless oil (425 mg, 0.825 mmol, 71% yield). [α]D²⁵ = +49° (c = 0.650, CHCl₃); ¹H NMR (400 MHz, CD₃CN, 60 °C) δ 6.79 (dd, J = 10.3, 2.8 Hz, 1H), 5.95 – 5.89 (m, 1H), 4.86 (br s, 1H), 4.43 – 4.37 (m, 2H), 4.22 (app q, J = 8.8 Hz, 1H), 4.18 – 4.04 (m, 3H), 2.96 (dt, J = 10.1, 7.5 Hz, 1H), 2.52 (dt, J = 12.9, 8.2 Hz, 1H), 2.11 (q, J = 10.5 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 8.5 Hz, 2H), 0.95 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H), 0.04 (s, 9H); ¹³C NMR (101 MHz, CD₃CN, 60 °C) δ 197.7, 173.6, 156.8, 151.9, 129.0, 69.4, 66.3, 64.8, 62.3, 61.3, 48.1, 33.4, 26.6, 19.0, 18.9, 14.9, -1.1, -4.0, -4.2; FTIR (NaCl, thin film): 2953, 2929, 2896, 2856, 1748, 1701, 1682, 1462, 1405, 1375, 1340, 1319, 1289, 1250, 1211, 1187, 1155, 1099, 1058, 985, 956, 939, 862, 829, 779 cm⁻¹; HRMS (MM) calc’d for C₂₁H₃₈NO₆Si₂ [M–C₂H₄+H]+ 456.2232, found 456.2231 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

Preparation of vinyl triflate S1²

A flame-dried 50 mL round-bottom flask was charged with TBS ether 8 (200 mg, 0.41 mmol, 1.0 equiv), dry THF (7.4 mL) and cooled to –78 °C. A solution of KHMDS (0.5M in toluene, 0.9 mL, 0.45 mmol, 1.1 equiv) was slowly added to the flask. The reaction solution turned dark red upon addition. The solution was stirred for 5 minutes before the addition of a THF solution of PhNTf₂ (162 mg, 0.45 mmol, 1.1 equiv; prepared by dissolving 180 mg in 1 mL THF and used 0.9 mL). The mixture was stirred for 2 hours before quenching with 1% NaOH solution (10 mL) and was warmed to room temperature. The mixture was separated and the organic layer was
washed with 1% NaOH solution (10 mL). The aqueous layer was extracted with diethyl ether (3 x 20 mL). The combined organic layers were washed with brine (50 mL), dried over Na₂SO₄, filtered, and concentrated to give a light yellow oil. Flash chromatography (1% to 8% EtOAc in hexanes) afforded vinyl triflate S₁, as a colorless oil (191 mg, 0.31 mmol, 75% yield; to avoid the decomposition of S₃, this intermediate was isolated and used immediately). [α]₀⁺²⁵ = +14° (c = 0.69, CH₂Cl₂); ¹H NMR (400 MHz, CD₂CN, 60 °C) δ 5.96 (d, J = 10.2 Hz, 1H), 5.87 (dd, J = 10.2, 2.3 Hz, 1H), 5.06 – 4.90 (m, 3H), 4.28 (dd, J = 10.9, 9.3, 7.4 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.09 (ddd, J = 10.8, 9.2, 7.1 Hz, 1H), 3.00 – 2.76 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.03 (ddd, J = 9.3, 7.0, 1.8 Hz, 2H), 0.93 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.05 (s, 9H); ¹³C NMR (101 MHz, CD₂CN, 60 °C) δ 172.8, 157.1, 140.7, 138.6, 132.1, 124.6, 121.7, 121.5, 115.1, 75.6, 67.8, 65.2, 64.6, 62.7, 31.9, 26.7, 19.1, 18.8, 14.8, -1.1, -4.0, -4.4 (one of the quartet of -CF₃ ¹³C NMR peaks is masked under the solvent peak; the other quartet peaks are underlined); FTIR (NaCl, thin film): 3426, 2954, 2930, 2898, 2857, 1750, 1722, 1709, 1423, 1403, 1361, 1334, 1295, 1251, 1123, 1142, 1104, 1037, 973, 943, 894, 839, 779, 769, 693, 619 cm⁻¹; HRMS (MM) calc’d for C₂₂H₃₇F₃NO₈SSi₂ [M–C₂H₄+H]⁺ 588.1725, found 588.1744 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

**Preparation of cyclic diene 7**

A flame-dried 50 mL round-bottom flask was charged with vinyl triflate S₁ (260 mg, 0.42 mmol, 1.0 equiv), Pd(OAc)₂ (19 mg, 0.084 mmol, 20 mol %), and PPh₃ (44 mg, 0.169 mmol, 40 mol %). The system was purged with N₂ and charged with dry DMF (8 mL), nBu₃N (0.50 mL, 2.11 mmol, 5.0 equiv), and formic acid (48 µL, 1.27 mmol, 3.0 equiv). The resulting yellow, clear solution was heated to 65 °C for 15 minutes, at which point the reaction turned black. It was then diluted with EtOAc (25 mL) and washed with 1M HCl (25 mL), H₂O (25 mL) and brine (25 mL). The aqueous layers were each extracted with ether (20 mL). The combined organic layers were then dried over Na₂SO₄, filtered, and concentrated to give a brown oil. Flash chromatography (1% to 10% EtOAc in hexanes) afforded cyclic diene 7, as a light yellow oil (165 mg, 0.35 mmol, 84% yield). [α]₀⁺²⁵ = +55° (c = 1.43, CHCl₃); ¹H NMR (400 MHz, CD₂CN, 60 °C) δ 5.88 – 5.81 (m, 1H), 5.81 – 5.73 (m, 1H), 5.65 (d, J = 9.6 Hz, 1H), 4.87 – 4.76 (m, 2H), 4.74 – 4.64 (m, 1H), 4.33 – 4.23 (m, 1H), 4.17 (qd, J = 7.1, 1.0 Hz, 2H), 4.07 (ddd, J = 10.8, 9.0, 7.3 Hz, 1H), 2.93 – 2.80 (m, 1H), 2.63 (d, J = 15.9 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.02 (ddd, J = 8.8, 7.1, 1.1 Hz, 2H), 0.93 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 9H); ¹³C NMR (101 MHz, CD₂CN, 60 °C) δ 173.5, 157.6, 142.0, 135.3, 125.6, 119.1, 76.7, 66.7, 64.7, 64.3, 62.3, 35.1, 26.8, 19.2, 18.9, 15.0, -1.0, -3.8, -4.3; FTIR (NaCl, thin film): 3049, 2954, 2928, 2897, 2855, 1750, 1722, 1699, 1472, 1398, 1361, 1329, 1290, 1261, 1254, 1234, 1194, 1142, 1037, 973, 943, 894, 839, 779, 769, 693, 619 cm⁻¹; HRMS (MM) calc’d for C₂₃H₃₉F₃NO₈SSi₂ [M–C₂H₄+H]⁺ 590.1725, found 590.1734 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).
1250, 1204, 1180, 1105, 1031, 958, 839, 776, 701, 670 cm⁻¹; HRMS (MM) calc’d for C₃₁H₃₈NO₅Si₂ [M–C₂H₄H⁺]⁺ 440.2283, found 440.2298 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

**Preparation of carboxylic acid 17**

Cyclic diene 7 (31.5 mg, 0.067 mmol, 1.0 equiv) was transferred to a 1-dram vial, to which was added Me₃SnOH (122 mg, 0.673 mmol, 10 equiv) and dry DCE (1.3 mL). The vial was sealed with a Teflon cap and heated to 80 °C for 26 hours. It was then cooled to room temperature and quenched with pH 2.5 buffer (2 mL). The mixture was separated and the aqueous layer was then extracted with EtOAc (6 x 2 mL). Combined organic layer was washed with brine (15 mL). It was then dried over Na₂SO₄, filtered, and concentrated to give a light brown oil. Flash chromatography (1% to 6% MeOH in CH₂Cl₂) afforded carboxylic acid 17, as a light brown oil (27.6 mg, 0.063 mmol, 94% yield). [α]D₂⁵ = +44° (c = 0.59, CHCl₃); ¹H NMR (500 MHz, CDCl₃, 45 °C) δ 5.87 – 5.77 (m, 2H), 5.69 (d, J = 9.5 Hz, 1H), 4.93 – 4.79 (m, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.58 (d, J = 14.4 Hz, 1H), 4.38 (d, J = 10.3 Hz, 1H), 4.09 (q, J = 9.5 Hz, 1H), 2.99 – 2.77 (m, 2H), 1.07 (dd, J = 9.6, 7.9 Hz, 2H), 0.90 (s, 9H), 0.04 (s, 3H), 0.04 (s, 12H); ¹³C NMR (101 MHz, CDCl₃, 45 °C) δ 175.1, 157.6, 139.4, 134.6, 124.3, 118.7, 75.4, 65.0, 64.6, 62.8, 32.8, 26.0, 18.2, 18.0, -1.5, -4.6, -5.1; FTIR (NaCl, thin film): 3121, 3051, 2954, 2928, 2897, 2856, 1747, 1699, 1471, 1418, 1360, 1335, 1250, 1178, 1107, 1042, 1020, 970, 957, 862, 838, 776, 700, 667, 627 cm⁻¹; HRMS (MM) calc’d for C₁₉H₃₄NO₅Si₂ [M–C₂H₄H⁺]⁺ 412.1970, found 412.1977 (detected fragment has undergone elimination of ethylene from the Teoc protecting group).

**Preparation of dipeptide 19**

To a 1-dram vial was transferred carboxylic acid 17 (27.6 mg, 0.063 mmol, 1.0 equiv) and amine 18 (23.4 mg, 0.069 mmol, 1.1 equiv), using CH₂Cl₂, and the mixture of starting materials was co-evaporated with benzene (1 mL). The mixture of starting materials was then dissolved in dry CH₂Cl₂ (1.2 mL), followed by the addition of Et₃N (88 µL, 0.628 mmol, 10 equiv) and BOP-Cl (80 mg, 0.314 mmol, 5 equiv). The reaction mixture was allowed to stir at room temperature for 24 hours and quenched with saturated NaHCO₃ (2 mL). The mixture was extracted with EtOAc (5 x 2 mL). The combined organic layers were washed with brine (10 mL), dried over
Na₂SO₄, filtered through a silica gel plug, and concentrated to give a mixture of white solid and light brown oil. Flash chromatography (1% to 5% EtOAc in hexanes) afforded dipeptide 19, as a colorless oil (42.2 mg, 0.055 mmol, 89% yield).  

\[ \alpha \] D\text{25} = +38° (c = 0.865, CHCl₃); \(^1\)H NMR \( \delta \) (400 MHz, CD₃CN) 6.48 (td, \( J = 2.5, 1.2 \) Hz, 1H), 6.23 (dd, \( J = 8.2, 2.2 \) Hz, 1H), 5.87 – 5.80 (m, 1H), 5.72 (qd, \( J = 2.2, 1.3 \) Hz, 1H), 5.67 (br s, 1H), 5.57 (d, \( J = 9.6 \) Hz, 1H), 5.47 (dd, \( J = 5.7, 3.0 \) Hz, 1H), 4.83 (dd, \( J = 10.1, 1.8 \) Hz, 1H), 4.79 (dd, \( J = 8.2, 1.9 \) Hz, 1H), 4.75 – 4.72 (m, 2H), 4.46 (dt, \( J = 7.9, 2.1 \) Hz, 1H), 4.28 – 4.18 (m, 1H), 4.13 (qd, \( J = 7.1, 0.7 \) Hz, 2H), 3.98 (tt, \( J = 16.4, 8.5 \) Hz, 1H), 2.87 (dddd, \( J = 15.8, 10.1, 2.6, 1.6 \) Hz, 1H), 2.68 (dq, \( J = 15.8, 1.6 \) Hz, 1H), 2.65 – 2.60 (m, 2H), 1.23 (t, \( J = 7.1 \) Hz, 3H), 1.03 – 0.98 (m, 2H), 0.93 (s, 9H), 0.85 (s, 9H), 0.15 (s, 3H), 0.06 (s, 3H), 0.02 (s, 9H), -0.08 (s, 3H), -0.10 (s, 3H); \(^{13}\)C NMR \( \delta \) (101 MHz, CD₃CN, 50 °C) 173.5, 173.3, 158.1, 145.7, 139.8, 137.3, 134.5, 126.2, 117.4, 116.9, 112.0, 75.8, 72.4, 67.7, 65.1, 64.2, 62.4, 61.7, 58.8, 35.4, 33.2, 26.8, 26.6, 19.1, 19.1, 19.0, 14.8, -1.2, -2.8, -4.1, -4.6, -5.1; FTIR (NaCl, thin film): 3049, 3014, 2954, 2929, 2895, 2856, 1747, 1717, 1694, 1652, 1472, 1463, 1428, 1393, 1348, 1329, 1315, 1250, 1213, 1179, 1139, 1094, 1039, 974, 949, 860, 837, 780, 756, 701, 667, 632 cm⁻¹; HRMS (MM) calc’d for C₃₈H₆₄N₂O₈Si₃Na [M+Na]⁺ 783.3863, found 783.3866.

**Preparation of DKP S2 (undesired reaction pathway)**

A 5 mL Schlenk tube was charged with TBAF•(tBuOH)₄ (4.8 mg, 0.009 mmol, 6 equiv) ⁴, followed by addition of dipeptide 19 (1.1 mg, 0.0014 mmol, 1.0 equiv) as a CH₃CN solution (0.16 mL). The resulting solution was degassed using the freeze-pump-thaw technique. The vessel was sealed and the solution frozen by submersion in a bath of liquid N₂. The vessel was then placed under vacuum for ca. five minutes before once again being sealed and allowed to thaw under static vacuum by removal from the liquid N₂ bath. This procedure was repeated three times before the head-space was finally backfilled with N₂, the vessel sealed, and the solution heated to 70 °C with stirring. After 1.5 hours, the reaction mixture was cooled to room temperature, diluted with saturated Na₂SO₄ solution, and extracted with EtOAc (5 x 0.5 mL). Each organic fraction was passed individually through a plug of SiO₂, which was then rinsed with excess EtOAc. The combined organic filtrates were concentrated in vacuo to provide the crude product, which was purified by preparative TLC (50% EtOAc in hexanes) afforded alcohol S2, as a white solid (0.2 mg, 0.0006 mmol, 43% yield).  

\[ \alpha \] D\text{25} = –331° (c = 0.355, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 8.08 (d, \( J = 7.9 \) Hz, 1H), 7.27 (t, \( J = 8.0 \) Hz, 2H), 7.13 (td, \( J = 7.5, 1.1 \) Hz, 1H), 6.53 (q, \( J = 2.0 \) Hz, 1H), 6.20 (dd, \( J = 8.2, 2.3 \) Hz, 1H), 5.41 (d, \( J = 4.5 \) Hz, 1H), 5.07 – 4.98 (m, 1H), 4.92 (dd, \( J = 8.0, 2.1 \) Hz, 1H), 4.87 (dd, \( J = 8.2, 2.0 \) Hz, 1H), 4.50 (td, \( J = 9.0, 1.7 \) Hz, 1H), 4.40 (ddt, \( J = 8.2, 4.3, 2.1 \) Hz, 1H), 3.61 (ddt, \( J = 16.6, 10.0, 1.2 \) Hz, 1H), 3.41 (dd, \( J = 16.5, 10.1 \) Hz, 1H), 3.06 (dt, \( J = 9.0, 1.7 \) Hz, 2H); \(^{13}\)C
NMR (101 MHz, CDCl₃) δ 168.3, 163.6, 140.4, 138.5, 137.7, 129.7, 128.0, 125.4, 125.0, 116.2, 110.4, 110.3, 71.5, 64.4, 61.0, 58.8, 33.2, 30.7; FTIR (NaCl, thin film): 3338, 3013, 2928, 2859, 1668, 1602, 1486, 1464, 1418, 1328, 1248, 1192, 1077, 1047, 978, 916, 860, 821, 755, 665, 625 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₅N₂O₃ [M–OH]⁺ 307.1077, found 307.1081 (detected fragment has undergone loss of hydroxyl anion).

Preparation of diol 20

In a 1-dram vial, dipeptide 19 (15.3 mg, 0.020 mmol, 1.0 equiv) was co-evaporated with benzene (1 mL) and the vial was purged with argon. THF (1.9 mL) was added into the vial, followed by dropwise addition of TBAF (1M solution in THF, 120 µL, 0.12 mmol, 6 equiv). The resulting clear orange solution was allowed to stir at room temperature for 7 hours before being quenched with saturated Na₂SO₄ solution, and extracted with EtOAc (7 x 2 mL). Each organic fraction was passed individually through a plug of SiO₂, which was rinsed with excess EtOAc. The combined organic filtrates were then concentrated in vacuo to provide the crude product. Flash chromatography (10% to 95% EtOAc in hexanes) afforded diol 20, as a white solid (3.2 mg, 0.009 mmol, 47% yield). [α]D25 = –456° (c = 0.17, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.53 (td, J = 2.5, 1.1 Hz, 1H), 6.19 (dd, J = 8.2, 2.3 Hz, 1H), 5.93 (s, 1H), 5.92 – 5.84 (m, 2H), 5.79 – 5.72 (m, 1H), 5.20 (d, J = 4.6 Hz, 1H), 4.90 (dd, J = 7.9, 2.1 Hz, 1H), 4.87 (dd, J = 8.2, 1.9 Hz, 1H), 4.81 – 4.73 (m, 1H), 4.73 – 4.63 (m, 2H), 4.45 (ddd, J = 10.2, 7.5, 2.2 Hz, 1H), 4.41 – 4.34 (m, 1H), 3.05 – 2.96 (m, 2H), 2.92 (ddt, J = 15.2, 10.7, 2.2 Hz, 1H), 2.81 (dddt, J = 17.8, 12.1, 2.5, 1.3 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 167.8, 167.7, 138.4, 137.8, 132.6, 130.2, 123.0, 119.1, 110.4, 109.6, 73.5, 71.3, 68.2, 64.2, 62.3, 58.0, 33.5, 32.6; FTIR (NaCl, thin film): 3253, 3048, 2923, 2851, 2787, 1667, 1622, 1441, 1386, 1350, 1284, 1267, 1250, 1236, 1206, 1187, 1132, 1084, 1047, 1002, 852, 823, 750, 736, 708, 629 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₇N₂O₄ [M–OH]⁺ 325.1183, found 325.1194 (detected fragment has undergone loss of hydroxyl anion).

Preparation of tetrasulfide 21

To a suspension of S₈ (20 mg, 0.078 mmol, 9.2 equiv) in THF (0.34 mL) at 0 °C under argon was added LiHMDS (1 M in THF, 340 µL, 0.34 mmol, 40 equiv) dropwise over 2 min. This solution was stirred for an
additional 5 min, and half of the solution was transferred using syringe dropwise to a THF solution (0.17 mL) of diol 20 (2.9 mg, 0.0085 mmol, 1.0 equiv) over 2 min. The reaction mixture was allowed to stir for 4 hours and quenched with saturated NaHCO₃ (2 mL), and then the mixture was extracted with EtOAc (4 x 2 mL). The combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated to give a yellow solid. Preparative TLC (60% EtOAc in hexanes) afforded tetrasulfide 21, as a yellow solid (0.9 mg, 0.0019 mmol, 23% yield). [α]D₂₅ = –375° (c = 0.045, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.54 (t, J = 2.3 Hz, 1H), 6.21 (dd, J = 8.2, 2.4 Hz, 1H), 5.98 – 5.91 (m, 1H), 5.92 – 5.86 (m, 1H), 5.79 (d, J = 9.8 Hz, 1H), 5.33 (s, 1H), 5.08 – 4.98 (m, 2H), 4.93 (dd, J = 8.3, 2.0 Hz, 1H), 4.78 (d, J = 13.3 Hz, 1H), 4.60 (d, J = 4.5 Hz, 1H), 4.46 (td, J = 4.9, 2.3 Hz, 1H), 3.30 – 3.19 (m, 2H), 3.03 (dd, J = 16.1, 3.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 170.3, 169.4, 138.9, 138.0, 131.0, 129.5, 122.9, 121.2, 110.4, 106.4, 78.1, 74.5, 72.7, 71.5, 70.1, 65.3, 41.5, 40.4; FTIR (NaCl, thin film): 3407, 2924, 2852, 1644, 1379, 1289, 1262, 1234, 1188, 1132, 1082, 1053, 971, 902, 861, 819, 744, 722, 622 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₆N₂O₅S₄Cl [M+Cl]– 502.9636, found 502.9633.

The major side product aromatic diketopiperazine 22 was also isolated as a yellow solid (0.5 mg, 0.0016 mmol, 17% yield). [α]D₂₅ = –365° (c = 0.055, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.46 (dt, J = 8.3, 0.9 Hz, 1H), 7.74 (dt, J = 7.8, 1.0 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.46 (ddd, J = 8.2, 7.3, 1.0 Hz, 1H), 6.61 (td, J = 2.5, 0.8 Hz, 1H), 6.22 (dd, J = 8.2, 2.3 Hz, 1H), 5.54 (br s, 1H), 5.04 (d, J = 7.9 Hz, 1H), 4.97 (dd, J = 8.2, 1.9 Hz, 1H), 4.69 (dd, J = 11.9, 6.4 Hz, 1H), 4.44 (d, J = 7.9 Hz, 1H), 3.20 (ddt, J = 14.0, 6.5, 1.2 Hz, 1H), 2.95 (ddt, J = 14.2, 12.0, 2.2 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 163.4, 158.1, 138.1, 138.0, 135.0, 129.2, 128.7, 128.5, 125.7, 122.9, 116.5, 115.6, 110.5, 109.4, 70.5, 64.3, 59.0, 34.7; FTIR (NaCl, thin film): 3391, 2926, 2854, 1713, 1695, 1652, 1634, 1588, 1575, 1446, 1390, 1362, 1336, 1312, 1284, 1252, 1212, 1192, 1182, 1135, 1079, 1046, 1006, 968, 844, 818, 789, 754, 667 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₆N₂O₃ [M–OH]+ 305.0931, found 305.0921 (detected fragment has undergone loss of hydroxyl anion).

Preparation of diacetate S3

To a stirred solution of diol 21 (1.3 mg, 2.8 µmol, 1.0 equiv) and DMAP (8.5 mg, 69 µmol, 25 equiv) in CH₂Cl₂ (0.28 mL) at 0 °C was added acetyl chloride (3.0 µL, 42 µmol). After 10 min, the ice bath was removed and the reaction mixture was allowed to warm to room temperature. After an additional 30 min, the reaction mixture was quenched with saturated NaHCO₃ (0.5 mL) and extracted five times with a mixture of hexanes and EtOAc (1 : 1). Each organic fraction was passed individually through a plug of SiO₂, which was subsequently rinsed with excess hexanes/EtOAc (1 : 1). The combined filtrates were concentrated in vacuo to provide the crude
product, which was purified by preparative TLC (60% EtOAc in hexanes) to afford diacetate S3, as a yellow solid (1.0 mg, 1.8 µmol, 66% yield). \([\alpha]_D^{25} = -327^\circ (c = 0.03, \text{CHCl}_3)\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 6.56 (t, J = 2.5 \text{ Hz}, 1\text{H}), 6.26 (dd, J = 8.2, 2.3 \text{ Hz}, 1\text{H}), 6.00 - 5.91 (m, 2\text{H}), 5.83 (d, J = 14.2 \text{ Hz}, 1\text{H}), 5.68 - 5.59 (m, 1\text{H}), 5.37 (d, J = 14.4 \text{ Hz}, 1\text{H}), 5.29 (d, J = 8.2 \text{ Hz}, 1\text{H}), 5.22 (dt, J = 8.4, 2.1 \text{ Hz}, 1\text{H}), 4.70 (dd, J = 8.2, 1.9 \text{ Hz}, 1\text{H}), 3.31 - 3.21 (m, 2\text{H}), 3.04 (dd, J = 16.5, 6.4 \text{ Hz}, 2\text{H}), 2.19 (s, 6\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 170.4, 170.4, 166.6, 165.8, 139.6, 138.6, 131.9, 128.8, 124.9, 120.9, 108.1, 106.0, 79.4, 75.4, 74.2, 71.1, 64.2, 60.7, 41.8, 41.2, 21.5, 21.4; FTIR (NaCl, thin film): 2923, 2854, 1734, 1685, 1369, 1293, 1236, 1187, 1135, 1046, 753, 710 cm\(^{-1}\); HRMS (LC-MM) calc’d for C\(_{20}\)H\(_{17}\)N\(_2\)O\(_5\)S\(_4\) [M–C\(_2\)H\(_3\)O\(_2\)]\(^+\) 493.0026, found 493.0015 (detected fragment has undergone loss of acetate anion).

Preparation of (–)-acetylapoaranotin (3)

A solution of diacetate S3 (1.0 mg, 1.8 µmol) in CH\(_2\)Cl\(_2\) (0.2 mL) was diluted with MeCN (6 mL), then treated with a solution of Et\(_3\)N in MeCN (0.08 µL, 0.6 µmol in 20 µL of MeCN), followed by 1,3-propanedithiol (18 µL, 0.18 mmol, 100 equiv). The resulting mixture was allowed to stand for 20 min, and was then washed with hexanes (5 x 5 mL, the final hexanes wash was back-extracted once with MeCN (15 mL) to ensure material recovery), and concentrated \(\text{in vacuo}\). The resulting residue was dissolved in CH\(_2\)Cl\(_2\)/PhMe and loaded onto a short plug of SiO\(_2\). Residual propanedithiol and other nonpolar impurities were eluted with 20% EtOAc in hexanes before the presumed dithiol intermediate was eluted with 50 to 100% EtOAc in hexanes. The collected fractions were concentrated \(\text{in vacuo}\). The resulting material was taken up in EtOAc (20 mL) and MeOH (20 mL). The resulting solution was sparged with O\(_2\) for 2 hours and allowed to stir for another 12 hours. The solution was then concentrated \(\text{in vacuo}\), and purified by preparative TLC (60% EtOAc in hexanes) to provide (–)-acetylapoaranotin (3) as a yellow solid (0.6 mg, 1.2 µmol, 69% yield). \([\alpha]_D^{25} = -281^\circ (c = 0.015, \text{CHCl}_3)\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 6.60 (dd, J = 2.2, 2.2 \text{ Hz}, 1\text{H}), 6.30 (dd, J = 8.2, 2.2 \text{ Hz}, 1\text{H}), 6.04 (d, J = 12.4 \text{ Hz}, 1\text{H}), 6.01 - 5.93 (m, 2\text{H}), 5.70 (ddd, J = 8.5, 2.0, 2.0 \text{ Hz}, 1\text{H}), 5.55 (d, J = 8.2 \text{ Hz}, 1\text{H}), 5.09 (dd, J = 8.8, 2.0 \text{ Hz}, 1\text{H}), 4.99 (d, J = 12.6 \text{ Hz}, 1\text{H}), 4.60 (dd, J = 8.3, 1.8 \text{ Hz}, 1\text{H}), 4.01 (d, J = 17.9 \text{ Hz}, 1\text{H}), 3.80 (d, J = 17.7 \text{ Hz}, 1\text{H}), 2.99 (ddd, J = 18.3, 1.7, 1.7 \text{ Hz}, 1\text{H}), 2.87 (d, J = 17.7 \text{ Hz}, 1\text{H}), 2.14 (s, 3\text{H}), 2.03 (s, 3\text{H}); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 170.5, 169.9, 163.1, 162.2, 141.1, 139.2, 132.2, 127.8, 124.5, 119.9, 113.4, 105.3, 78.2, 75.9, 73.9, 69.8, 64.5, 62.8, 36.1, 34.5, 21.3, 20.9; FTIR (NaCl, thin film): 2919, 2850, 1737, 1706, 1552, 1435, 1367, 1302, 1279, 1233, 1143, 1041, 962, 752, 720, 655 cm\(^{-1}\); HRMS (ESI) calc’d for C\(_{22}\)H\(_{20}\)N\(_2\)O\(_7\)S\(_2\)Na [M+Na]\(^+\) 511.0610, found 511.0621.
Preparation of dienol 23

Preparation of syn-diol 25
1380, 1314, 1253, 1145, 1068, 987, 875, 833, 794, 762, 712, 624 cm⁻¹; HRMS (MM) calc’d for C₉H₁₂NO₃ [M+H]⁺ 182.0812, found 182.0815.

The crude material was first dissolved in small amount of MeOH (ca. 0.1 mL) and co-evaporated with benzene to further remove water. It was then dissolved in DMF (0.3 mL). Under N₂, DIPEA (6 µL, 0.034 mmol, 6 equiv), and PyBroP (10.7 mg, 0.023 mmol, 4 equiv) were added in sequence. The resulting light brown solution was allowed to stir at room temperature for 22 hours. It was then quenched with saturated NaHCO₃ (1 mL). The mixture was separated and the aqueous layer was then extracted with CH₂Cl₂ (5 x 1 mL). The combined organic layers were washed with brine (5 mL), dried over Na₂SO₄, filtered, and concentrated to give a light brown oil. Preparative TLC (80% EtOAc in hexanes) afforded syn-diol 25, as a white solid (0.4 mg, 0.0012 mmol, 43% yield over 2 steps). [α]D²⁵ = +230° (c = 0.06, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 6.41 (d, J = 1.3 Hz, 1H), 5.93 (ddd, J = 9.5, 5.0, 2.8 Hz, 1H), 5.89 – 5.82 (m, 1H), 4.75 – 4.65 (m, 1H), 4.48 (dd, J = 13.2, 3.0 Hz, 1H), 4.41 (dd, J = 10.2, 6.6 Hz, 1H), 3.34 – 3.18 (m, 1H), 3.16 – 2.93 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.4, 133.4, 129.5, 123.6, 118.7, 71.8, 68.9, 60.5, 29.3; FTIR (NaCl, thin film): 3281, 2922, 2853, 1651, 1423, 1381, 1351, 1336, 1295, 1273, 1255, 1230, 1192, 1147, 1083, 1061, 721, 671 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₉N₂O₄ [M+H]⁺ 327.1339, found 327.1342.

Preparation of anti-diol 26

A 1-dram vial was charged with syn-diol 25 (1.2 mg, 0.0037 mmol, 1.0 equiv) and Cs₂CO₃ (48 mg, 0.147 mmol, 40 equiv). Dry MeOH (0.75 mL) was fully degassed by bubbling N₂ through and was added to the vial under N₂. The resulting mixture gradually turned into a clear yellow solution and was stirred for 30 minutes. It was then quenched with saturated NaHCO₃ (3 mL) and the mixture was extracted with EtOAc (5 x 3 mL). The combined organic layers were washed with brine (15 mL), dried over Na₂SO₄, filtered, and concentrated to give a white solid. Flash chromatography (20% to 100% EtOAc in hexanes) afforded anti-diol 26, as a white solid (0.8 mg, 0.0024 mmol, 67% yield). [α]D²⁵ = –159° (c = 0.075, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 6.00 (s, 1H), 5.96 – 5.86 (m, 2H), 5.76 (dt, J = 9.5, 1.4 Hz, 1H), 4.78 – 4.63 (m, 3H), 2.99 (dd, J = 15.5, 7.2 Hz, 1H), 2.88 (t, J = 13.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 168.2, 132.7, 130.0, 123.0, 119.0, 73.6, 68.1, 62.5, 32.2; FTIR (NaCl, thin film): 3305, 3039, 2924, 2853, 2713, 1626, 1553, 1447, 1381, 1354, 1330, 1290, 1265, 1237, 1201, 1139, 1087, 1057, 767, 710 cm⁻¹; HRMS (MM) calc’d for C₁₈H₁₉N₂O₄ [M+H]⁺ 327.1339, found 327.1336.
Table S1. Comparison of $^1$H NMR data for natural vs. synthetic (–)-acetylapoaranotin (3)

| Yang et al. Report, Natural (–)-acetylapoaranotin $^1$H NMR, 500 MHz, CDCl$_3$ | This Work, Synthetic (–)-acetylapoaranotin $^1$H NMR, 400 MHz, CDCl$_3$ | Chemical Shift Difference, $\Delta\delta$ |
|---|---|---|
| $\delta$ 6.61 (br ddd, $J = 2.5, 2.0, 2.0$ Hz, 1H) | $\delta$ 6.60 (dd, $J = 2.2, 2.2$ Hz, 1H) | 0.1 |
| 6.31 (dd, $J = 8.5, 2.0$ Hz, 1H) | 6.30 (dd, $J = 8.2, 2.2$ Hz, 1H) | 0.1 |
| 6.05 (br dm, $J = 13.2$ Hz, 1H) | 6.04 (d, $J = 12.4$ Hz, 1H) | 0.2 |
| 5.99 (m, 1H) | 6.01-5.93 (m, 2H) | 0.1 |
| 5.96 (m, 1H) | 5.96 (m, 1H) | 0.0 |
| 5.70 (ddd, $J = 8.5, 2.0, 2.0$ Hz, 1H) | 5.70 (ddd, $J = 8.5, 2.0, 2.0$ Hz, 1H) | 0.0 |
| 5.66 (br dm, $J = 13.2$ Hz, 1H) | 5.55 (d, $J = 8.2$ Hz, 1H) | 0.1 |
| 5.10 (br dddd, $J = 8.5, 2.0, 2.0, 1.5$ Hz, 1H) | 5.09 (dd, $J = 8.8, 2.0$ Hz, 1H) | 0.2 |
| 5.00 (br dm, $J = 13.2$ Hz, 1H) | 4.99 (d, $J = 12.6$ Hz, 1H) | 0.1 |
| 4.61 (dd, $J = 8.5, 2.0$ Hz, 1H) | 4.60 (d, $J = 8.3, 1.8$ Hz, 1H) | 0.1 |
| 4.02 (br ddd, $J = 18.0, 2.5, 1.5$ Hz, 1H) | 4.01 (d, $J = 17.9$ Hz, 1H) | 0.1 |
| 3.81 (dm, $J = 18.5$ Hz, 1H) | 3.80 (d, $J = 17.7$ Hz, 1H) | 0.1 |
| 2.99 (ddd, $J = 18.0, 2.0, 2.0$ Hz, 1H) | 2.99 (ddd, $J = 18.3, 1.7, 1.7$ Hz, 1H) | 0.1 |
| 2.88 (br dd, $J = 18.5, 1.5$ Hz, 1H) | 2.87 (d, $J = 17.7$ Hz, 1H) | 0.1 |
| 2.15 (s, 3H) | 2.14 (s, 3H) | 0.1 |
| 2.03 (s, 3H) | 2.03 (s, 3H) | 0.0 |

Table S2. Comparison of $^{13}$C NMR data for natural vs. synthetic (–)-acetylapoaranotin (3)

| Yang et al. Report, Natural (–)-acetylapoaranotin $^{13}$C NMR, 126 MHz, CDCl$_3$ | This Work, Synthetic (–)-acetylapoaranotin $^{13}$C NMR, 101 MHz, CDCl$_3$ | Chemical Shift Difference, $\Delta\delta$ |
|---|---|---|
| $\delta$ 170.5 | $\delta$ 170.5 | 0.0 |
| 170.0 | 169.9 | 0.1 |
| 163.1 | 163.1 | 0.0 |
| 162.2 | 162.2 | 0.0 |
| 141.2 | 141.1 | 0.1 |
| 139.2 | 139.2 | 0.0 |
| 132.2 | 132.2 | 0.0 |
| 127.8 | 127.8 | 0.0 |
| 124.5 | 124.5 | 0.0 |
| 119.9 | 119.9 | 0.0 |
| 113.4 | 113.4 | 0.0 |
| 105.3 | 105.3 | 0.0 |
| 78.2 | 78.2 | 0.0 |
| 75.9 | 75.9 | 0.0 |
| 73.9 | 73.9 | 0.0 |
| 69.8 | 69.8 | 0.0 |
| 64.5 | 64.5 | 0.0 |
| 62.9 | 62.8 | 0.1 |
| 36.1 | 36.1 | 0.0 |
| 34.5 | 34.5 | 0.0 |
| 21.3 | 21.3 | 0.0 |
| 21.0 | 20.9 | 0.1 |
Chiral HPLC Traces:

**Pyrrolidine 13: racemic**

![Chiral HPLC Trace](image1)

| Peak RetTime Type | Width | Area     | Height | Area     |
|------------------|-------|----------|--------|----------|
| #                | [min] | [min]    | [mAU]  | [mAU]    | %       |
| 1                | 13.323| 0.9322   | 1.86144e4 | 275.05743 | 50.1679 |
| 2                | 24.715| 1.7546   | 1.84898e4 | 144.25124 | 49.8321 |

**Pyrrolidine 13: enantioenriched, 95% ee**

![Chiral HPLC Trace](image2)

| Peak RetTime Type | Width | Area     | Height | Area     |
|------------------|-------|----------|--------|----------|
| #                | [min] | [min]    | [mAU]  | [mAU]    | %       |
| 1                | 16.027| 2.9130   | 475.44940 | 2.72031  | 2.4178  |
| 2                | 24.987| 2.1332   | 1.91891e4 | 149.92198 | 97.5822 |
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Enantioselective Synthesis of (–)-Acetylapoaranotin

Haoxuan Wang, Clinton J. Regan, Julian A. Codelli, Paola Romanato, Angela L. A. Puchlopek-Dermenci and Sarah E. Reisman*

The Warren and Katharine Schlinger Laboratory for Chemistry and Chemical Engineering, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

*reisman@caltech.edu

Supporting Information 2 (NMR Spectral Data):
WHX-7-197-F-RE-INDY-CDCL3

Sample Name:
WHX-7-197-F-RE-INDY-CDCL3
Data Collected on:
indy.caltech.edu-inova500
Archive directory:
/home/hxwang/vnmrsys/data
Sample directory:
WHX-7-197-F-RE-INDY-CDCL3
FidFile: WHX-7-197-F-RE-INDY-CDCL3

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 4 2015

Sample #11, Operator: hxwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.6749695 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 min 8 sec
Sample Name: WHX-7-197-F-RE-INDY-CDCL3

Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-197-F-RE-INDY-CDCL3
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jun 4 2015

Sample #11, Operator: hxwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1000 repetitions
OBSERVE C13, 125.6433872 MHz
DECOUPLE H1, 499.6774469 MHz
Power 36 dB continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 34 min
WHX-6-291-F3-Siena-CD3CN-60C

Sample Name: WHX-6-291-F3-Siena-CD3CN-60C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-6-291-F3-Siena-CD3CN-60C
FidFile: WHX-6-291-F3-Siena-CD3CN-60C-Proton

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 9 2015

Temp. 60.0 C / 333.1 K
Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970633 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 0 sec

4.04 0.95 1.00 1.01 1.03 1.03 2.04 2.02 3.04 1.08 3.01 1.03 1.07 3.08 2.09 8.95 ppm

14 (CD3CN, 60 °C)
Current Data Parameters
NAME WHX-6-291-F3-Flo-CD3CN-RT
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150510
Time 0.25
INSTRUM spect
PROBHD 5 mm CPPBBB BB
PULPFG 2qpg30
TD 65384
SOLVENT CD3CN
NS 3000
DS 4
SNH 24038.461 Hz
FIDRES 0.367651 Hz
AQ 1.3599873 sec
NG 72.02
DW 20.800 usec
DE 82.37 usec
TE 298.2 K
D1 1.0000000 sec
D11 0.0000000 sec
TD0 1

CHANNEL f1
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 36.0000000 W

CHANNEL f2
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 7.0000000 W
PLW12 0.1203300 W
PLW13 0.0974680 W

F2 - Processing parameters
SI 32768
SF 100.6126713 MHz
WDW EM
SSB 0
LB 1.00 Hz
GN 0
PC 1.40
Current Data Parameters
NAME: WHX-7-37-F-Flo-CD3CN-RT
EXPNO: 1
PROCNO: 1

F2 - Acquisition Parameters
Date: 20150509
Time: 19.46
INSTRUM: spect
PROBHD: 5 mm CPPBBO BB
FULLPROG: zg30
TD: 65536
SOLVENT: CD3CN
NS: 16
DS: 2
SWH: 8012.820 Hz
FIDRES: 0.122266 Hz
AQ: 4.0894465 sec
RG: 64.2
DW: 62.400 usec
DE: 10.00 usec
TE: 298.1 K
D1: 1.00000000 sec
TD0: 1

======== CHANNEL f1 ========
SFO1: 400.1324710 MHz
NUC1: 1H
P1: 11.70 usec
PLW1: 7.00000000 W

F2 - Processing parameters
SI: 65536
SF: 400.1300114 MHz
WDW: EM
SB: 0
LB: 0.30 Hz
GB: 1.00
PC: 1.00
Sample Name: WHX-7-37-F-Siena-CD3CN-60C-H
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-37-F-Siena-CD3CN-60C-H
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 9 2015

Temp. 60.0 C / 333.1 K
Sample #1, Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970637 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec

9 (CD3CN, 60 °C)
Current Data Parameters
NAME WHX-7-37-F-Flo-CD3CN-RT
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date  20150509
Time  21:49
INSTRUM spect
PROBHD  5 mm CPPBG BB
PULPROG zgpg30
TD  65384
SOLVENT CD3CN
NS  3000
DS  4
SNH  24038.461 Hz
FIDRES  0.367651 Hz
AQ  1.3599873 sec
RG  78.69
DW  20.800 usec
DE  82.37 usec
TE  298.1 K
D1  1.00000000 sec
D11  0.03000000 sec
TD0  1

======== CHANNEL f1 ========
SFO1  100.6228293 MHz
NUC1  13C
P1  10.00 usec
PLN1  36.00000000 W

======== CHANNEL f2 ========
SFO2  400.1316005 MHz
NUC2  1H
CPDPRG[2  waltz16
PCPD2  90.00 usec
PLN2  7.00000000 W
PLN12  0.12033000 W
PLN13  0.09746800 W

F2 - Processing parameters
SI  32768
SF  100.6126706 MHz
MDW  EM
SSB  0
LB  1.00 Hz
GN  0
PC  1.40
Sample Name: WHX-7-177-F-Siena-CD3CN
Data Collected on: May 11 2015
Temp. 25.0 C / 298.1 K
Sample #2, Operator: hwwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970641 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
Sample Name: WHX-7-177-F-Siena-CD3CN-65C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-177-F-Siena-CD3CN-65C
FidFile: WHX-7-177-F-Siena-CD3CN-65C-Proton

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 11 2015

Temperature: 65.0 °C / 338.1 K
Operator: hwwang
Relax. delay: 5.000 sec
Pulse: 45.0 degrees
Acq. time: 2.556 sec
Width: 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970633 MHz

DATA PROCESSING
FT size: 32768
Total time: 2 min 1 sec
WHX-7-177-F-Siena-CD3CN-65C

Sample Name:
WHX-7-177-F-Siena-CD3CN-65C
Data Collected on:
siena.caltech.edu-vmrs400
Archive directory:
/home/hwwang/vnmrsys/data
Sample directory:
WHX-7-177-F-Siena-CD3CN-65C
FidFile: WHX-7-177-F-Siena-CD3CN-65C-Carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: May 11 2015

Temp. 65.0 C / 338.1 K
Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
5000 repetitions
OBSERVE C13, 100.5289063 MHz
DECOUPLE H1, 399.7990538 MHz
Power 41 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 12 min

CO2Et
H
Teoc

15 (CD3CN, 65 °C)
Current Data Parameters
NAME WHX-7-70-HPLC-F1-Flo-CDCL3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150430
Time 21.11
INSTRUM spect
PROBHD 5 mm CPPBBO BB
FIDPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 30.29
DW 62.400000 usec
DE 10.00 usec
TE 298.1 K
D1 2.00000000 sec
TDO 1

-------------- CHANNEL f1 ------------
SFO1 400.1324710 MHz
NUC1 1H
P1 11.70 usec
PLW1 7.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300095 MHz
WGN EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Current Data Parameters
NAME WHX-7-70-HPLC-F1-Flo-CDCl3
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150430
Time 21.17
INSTRUM spect
PROBHD 5 mm CPPBBO BB
TD 65536
SOLVENT CDCl3
NS 128
DE 2
SNN 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 72.02
DW 20.800 usec
DE 82.37 usec
TE 298.1 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 18

======== CHANNEL f1 ========
SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLM1 36.00000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLM2 7.00000000 W
PLM12 0.12033800 W
PLM13 0.09746800 W

F2 - Processing parameters
SI 32768
SF 100.6127747 MHz
WDM EM
SSB 0
LB 1.00 Hz
PC 1.40
WHX-6–289-F-Flo CDCL3.2.ser

COSY of 16
HMBC of 16
WHX-6-296-HPLC-F2_Siena_CD3CN

Sample Name: WHX-6-296-HPLC-F2_Siena_CD3CN
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-6-296-HPLC-F2_Siena_CD3CN
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 1 2015

Sample #5, Operator: hwwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970641 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
Sample Name: WHX-6-296-HPLC-F2_Siena_CD3CN-60C

Data Collected on:
siena.caltech.edu-vnmrs400

Archive directory: /home/hwwang/vnmrsys/data

Sample directory: WHX-6-296-HPLC-F2_Siena_CD3CN-60C

FidFile: WHX-6-296-HPLC-F2-Siena-CD3CN-60C-re

Pulse Sequence: PROTON (s2pul)

Solvent: cd3cn

Data collected on: May 1 2015

Temp. 60.0 C / 333.1 K

Operator: hwwang

Relax. delay 5.000 sec

Pulse 45.0 degrees

Acq. time 2.556 sec

Width 6410.3 Hz

16 repetitions

OBSERVE H1, 399.7970633 MHz

DATA PROCESSING

Line broadening 0.3 Hz

FT size 32768

Total time 2 min 1 sec
Current Data Parameters
NAME WHX-6-296-HPLC-F2 Carbon Flo CDCL3
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20141109
Time 20.09
INSTRUM spect
PULPROG zgpg30
TD 65384
SOLVENT CD3CN
DS 2
DRS 24038.416 Hz
TDRRES 0.367551 Hz
AQ 1.039873 sec
RG 87.75
DM 20.880 usec
DE 82.37 usec
TX 298.0 K
D1 1.0000000 sec
D11 0.0300000 sec
TD0 19

======== CHANNEL f1 ========
SFO1 100.6228298 MHz
HUC1 13C
P1 10.00 usec
PLW1 36.0000000 W

======== CHANNEL f2 ========
SFO2 400.1316005 MHz
HUC2 1H
CP2PRG2 waltx16
PCPD2 90.00 usec
PLW2 7.000000000 W
PLW12 0.120330000 W
PLW13 0.097468000 W

F2 - Processing parameters
S1 32768
SF 100.6126704 MHz
MDW EN
DSB 0
LB 1.00 Hz
GB 0
PC 1.40
WHX-7-136-F_Siena_CD3CN

Sample Name: WHX-7-136-F_Siena_CD3CN
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-136-F_Siena_CD3CN
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: Feb 25 2015

Sample #3, Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970633 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
WHX-7-136-F-60C_Siena_CD3CN

Sample Name: WHX-7-136-F-60C_Siena_CD3CN
Data Collected on: siena.caltech.edu-vmr400
Archive directory: /home/hwwang/vmr400sys/data
Sample directory: WHX-7-136-F-60C_Siena_CD3CN
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: Feb 25 2015

Temp. 60.0 C / 333.1 K
Sample #3, Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970625 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 1 sec
Sample Name:
WHX-7-136-F-60C_Siena_CD3CN
Data Collected on:
siena.caltech.edu-vnmrs400
Archive directory:
/home/hwwang/vnmrsys/data
Sample directory:
WHX-7-136-F-60C_Siena_CD3CN
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: Feb 25 2015

Temp. 60.0 C / 333.1 K
Sample #8, Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
4200 repetitions
OBSERVE C13, 100.5289108 MHz
DECOUPLE H1, 399.7990538 MHz
Power 41 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 2 hr, 41 min
WHX-7-171-F1_Siena_CD3CN

Sample Name: WHX-7-171-F1_Siena_CD3CN
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory:/home/hwwang/vnmrsys/data
Sample directory: WHX-7-171-F1_Siena_CD3CN
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 6 2015

Temp. 25.0 C / 298.1 K
Sample #6, Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
8 repetitions
OBSERVE H1, 399.7970641 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 28 sec
Sample Name: WHX-7-171-F1_Siena_CD3CN-60C

Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-171-F1_Siena_CD3CN-60C
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 6 2015

Temp. 60.0 C / 333.1 K
Sample #6, Operator: hwwang

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970633 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 13 sec
WHX-7-171-F1_Siena_CD3CN-60C

Sample Name: WHX-7-171-F1_Siena_CD3CN-60C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-171-F1_Siena_CD3CN-60C
FidFile: WHX-7-171-F1_Siena_CD3CN-60C-carbon-BS160

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: May 6 2015

Temp. 60.0 C / 333.1 K
Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
5120 repetitions
OBSERVE C13, 100.5289093 MHz
DECOUPLE H1, 399.7990538 MHz
Power 41 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 25 min
WHX-7-172-F_Siena_CD3CN

Sample Name:  
WHX-7-172-F_Siena_CD3CN  
Data Collected on:  
siena.caltech.edu-vnmrs400  
Archive directory:  
/home/hwwang/vnmrsys/data  
Sample directory:  
WHX-7-172-F_Siena_CD3CN  
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)  
Solvent: cd3cn  
Data collected on: May 6 2015

Temp. 25.0 C / 298.1 K  
Sample #4, Operator: hwwang

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 2.556 sec  
Width 6410.3 Hz  
8 repetitions  
OBSERVE  N1, 399.7970645 MHz  
DATA PROCESSING  
FT size 32768  
Total time 0 min 28 sec
WHX-7-172-F_Siena_CD3CN-60C

Sample Name:
WHX-7-172-F_Siena_CD3CN-60C
Data Collected on:
siena.caltech.edu-vnmrs400
Archive directory:
/home/hwwang/vnmrsys/data
Sample directory:
WHX-7-172-F_Siena_CD3CN-60C
FidFile: WHX-7-172-F-Siena-CD3CN-60C-proton

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 6 2015

Temp. 60.0 C / 333.1 K
Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970633 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 1 sec
WHX-7-172-F_Siena_CD3CN-60C

Sample Name: WHX-7-172-F_Siena_CD3CN-60C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-172-F_Siena_CD3CN-60C
FidFile: WHX-7-172-F-Siena-CD3CN-60C-carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: May 6 2015

Temp. 60.0 C / 333.1 K
Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
4800 repetitions
OBSERVE C13, 100.5289078 MHz
DECOUPLE H1, 399.7990538 MHz
Power 41 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 6 hr, 25 min
WHX-7-189-re-INDY-CDCL3

Sample Name:
WHX-7-189-re-INDY-CDCL3
Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-189-re-INDY-CDCL3
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 21 2015

Sample #1, Operator: hxwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.6749701 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min 32 sec
Sample Name: WHX-7-189-F-Siena-CDCL3-45C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-189-F-Siena-CDCL3-45C
FidFile: WHX-7-189-F-Siena-CDCL3-45C-proton

Pulse Sequence: PROTON (p2p1)
Solvent: cdcl3
Data collected on: May 20 2015

Temp. 45.0 C / 318.1 K
Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7949397 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 1 sec
WHX-7-189-F-Siena-CDCL3-45C

Sample Name: WHX-7-189-F-Siena-CDCL3-45C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-189-F-Siena-CDCL3-45C
FidFile: WHX-7-189-F-Siena-CDCL3-45C-Carbon-4000

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 20 2015

Temp. 45.0 C / 318.1 K
Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
4000 repetitions
OBSERVE C13, 100.5285101 MHz
DECOUPLE H1, 399.7969389 MHz
Power 41 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
PT size 65536
Total time 3 hr, 12 min
WHX-7-192-F-Siena-CD3CN

Sample Name:
WHX-7-192-F-Siena-CD3CN
Data Collected on:
siena.caltech.edu-vnmrs400
Archive directory:
/home/hwwang/vnmrsys/data
Sample directory:
WHX-7-192-F-Siena-CD3CN
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 23 2015

Temp. 25.0 C / 298.1 K
Sample #4, Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970641 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 1 sec
Sample Name: WHX-7-192-F-Siena-CD3CN-50C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-192-F-Siena-CD3CN-50C
FidFile: WHX-7-192-F-Siena-CD3CN-50C-proton

Pulse Sequence: PROTON (s2pul)
Solvent: cd3cn
Data collected on: May 23 2015
Temp. 50.0 C / 323.1 K
Operator: hwwang

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.7970637 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 1 sec
Sample Name: WHX-7-192-F-Siena-CD3CN-50C
Data Collected on: siena.caltech.edu-vnmrs400
Archive directory: /home/hwwang/vnmrsys/data
Sample directory: WHX-7-192-F-Siena-CD3CN-50C
FidFile: WHX-7-192-F-Siena-CD3CN-50C-carbon

Pulse Sequence: CARBON (s2pul)
Solvent: cd3cn
Data collected on: May 23 2015

Temp. 50.0 C / 323.1 K
Operator: hwwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
3232 repetitions
OBSERVE C13, 100.5289215 MHz
DECOUPLE H1, 399.7990538 MHz
Power 41 dB continuously on
WALTZ-16 modulated

DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 12 min
Current Data Parameters
NAME  WHX-7-193-F1-Flo-CDCL3
EXPNO  1
PROCNO  1

F2 - Acquisition Parameters
Date_  20150523
Time  8.48
INSTRUM  spect
PROBND  5 mm CPPBBO BB
PULPNOS  zg30
TD  65536
SOLVENT  CDCl3
NS  16
DS  2
SWK  8012.820 Hz
FIDRES  0.122266 Hz
AQ  4.0894465 sec
RG  142.81
DW  62.400 usec
DE  10.00 usec
TE  295.0 K
D1  5.00000000 sec
TD0  1

------ CHANNEL f1 ------
SFO1  400.1324710 MHz
NUC1  1H
P1  11.70 usec
PLW1  7.00000000 W

F2 - Processing parameters
SI  65536
SF  400.1300100 MHz
WDW  EM
SSB  0
LB  0.30 Hz
GB  0
PC  1.00
Current Data Parameters
NAME    WHK-7-193-F1-Flo-CDCl3
EXPNO    2
PROCNO    1

F2 - Acquisition Parameters
Date_   20150523
Time    9:45
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
PULPG02  zppg30
TD       65536
SOLVENT  CDCl3
NS       1400
DS       4
SWW      24038.461 Hz
FIDRES   0.366798 Hz
AQ       1.3631488 sec
RG       37.97
DW       20.800 usec
DE       82.37 usec
TE       294.9 K
D1       1.0000000 sec
D11      0.0300000 sec
TD0      1

-------- CHANNEL f1 --------
SFO1    100.6228293 MHz
NUC1    13C
P1       10.00 usec
PLW1    36.0000000 W

-------- CHANNEL f2 --------
SFO2    400.1316005 MHz
NUC2    1H
CPDPRG[2] waltz16
PCPD2   90.00 usec
PLW2    7.0000000 W
PLW12   0.12033000 W
PLW13   0.09746800 W

F2 - Processing parameters
SI       32768
SF       100.6127735 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GR       0
PC       1.40
Current Data Parameters
NAME WHX-7-188-F-Chara-Flo-CDCL3
EXPDNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150519
Time  13.02
INSTRUM spect
PROBHD 5 mm CPPBBO SB
PULPROG x90
TD  65536
SOLVENT CDCl3
NS  16
DG  2
SWM  8012.820 Hz
FIDRES  0.122266 Hz
AQ 4.8894465 sec
DG  197.44
DW  62.400 usec
DE  10.00 usec
TE  294.9 K
D1 2.00000000 sec
TD0 1

---------- CHANNEL f1 ----------
SFO1  400.132471 MHz
NUC1  1H
P1 11.70 usec
PLW1  7.00000000 W

F2 - Processing parameters
SI  65536
SF  400.130010 MHz
NOW EM
SSB 0
LS  0.30 Hz
PC  1.00
### Current Data Parameters

**NAME** WHX-7-188-F-Chara-Flo-CDCL3

**PROCNO** 30

**F2 - Acquisition Parameters**

- **Date:** 20150519
- **Time:** 14:04
- **INSTRUM:** spect
- **PROBHD:** 5 mm CPPBRD BB
- **SOLOVENT:** CDCl3
- **NS:** 1450
- **DS:** 4
- **SWM:** 24038.461 Hz
- **FIDRES:** 0.367651 Hz
- **AQ:** 1.3599873 sec
- **RG:** 72.02
- **DW:** 20.800 usec
- **DE:** 82.37 usec
- **TE:** 295.0 K
- **D1:** 1.00000000 sec
- **D11:** 0.03000000 sec
- **TD0:** 1

#### CHANNEL f1

- **SFO1:** 100.628293 MHz
- **NUC1:** 13C
- **P1:** 10.00 usec
- **PLW1:** 36.00000000 W

#### CHANNEL f2

- **SFO2:** 400.1316005 MHz
- **NUC2:** 1H
- **CPDPRG[2]:** waltz16
- **PCPD02:** 90.00 usec
- **PLW2:** 7.00000000 W
- **PLW12:** 0.12033000 W
- **PLW13:** 0.09746800 W

**F2 - Processing parameters**

- **SI:** 32768
- **SF:** 100.6127728 MHz
- **WOW:** EM
- **SSB:** 0
- **LB:** 1.00 Hz
- **GB:** 0
- **PC:** 1.40
Current Data Parameters
NAME WHX-7-194-F3-Flo-CDCl3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150523
Time 23.04
INSTRUM spect
PROBHD 5 mm CPPBBB BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
tS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 197.44
DH 62.400 usec
de 10.00 usec
tE 295.0 K
tD1 5.00000000 sec
tD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
P1 11.70 usec
PLW1 7.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300101 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

S60
Current Data Parameters
NAME WHX-7-194-F3-Flo-CDCL3
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150523
Time 23.13
INSTRUM spect
PROBHD 5 mm CPPBBO BB
PULPNOG zppg30
TD 65384
SOLVENT CDCl3
NS 8960
DS 2
SNW 24038.461 Hz
FIDRES 0.367651 Hz
AQ 1.3599873 sec
RG 72.02
DW 20.800 usec
DE 82.37 usec
TE 295.0 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 70

SFO1 100.6228298 MHz
NUC1 13C
P1 10.00 usec
PLW1 36.00000000 W

SFO2 400.1316005 MHz
NUC2 1H
CPSPRG[2 waltz16
CPDPRD2 90.00 usec
PLW2 7.00000000 W
PLW12 0.12033000 W
PLW13 0.09746800 W

F2 - Processing parameters
SI 32768
SF 100.6127718 MHz
WDW EM
SSB 0
LB 1.00 Hz
GR 0
PC 1.40

--- CHANNEL f1 ---
--- CHANNEL f2 ---
Current Data Parameters
NAME: WHX-7-223-F1-Flo-CDCL3  
EXPNO: 1  
PROCNO: 1

F2 - Acquisition Parameters
Date: 20150624  
Time: 21:05  
INSTRM: spect  
PROBHD: 5 mm CPPBBO BB  
PULPROG: zg30  
TD: 65536  
SOLVENT: CDCl3  
NS: 16  
DS: 2  
SWH: 8012.820 Hz  
FIDRES: 0.122266 Hz  
AQ: 4.0894465 sec  
RG: 197.44  
DW: 62.400 usec  
DE: 10.00 usec  
TE: 294.9 K  
DI: 2.0000000 sec  
TD0: 1  

======== CHANNEL f1 ========  
SFO1: 400.1324710 MHz  
NUC1: 1H  
P1: 11.70 usec  
PLW1: 7.0000000 W  

F2 - Processing parameters  
SI: 65536  
SF: 400.1300100 MHz  
WDW: EM  
SSB: 0  
LB: 0.30 Hz  
GB: 0  
PC: 1.00
Current Data Parameters
NAME  WHX-7-223-F1-Fl-CDCL3
EXPNO  10
PROCNO  1

F2 - Acquisition Parameters
Date_ 20150624
Time  23.48
INSTRUM  spect
PROBHD  5 mm CPPBBD BB
PULPROG  zgpa30
TD  65384
SOLVENT  CDCl3
NS  4000
DS  4
SNH  24038.461 Hz
FIDRES  0.367651 Hz
AQ  1.3599873 sec
RG  55.48
DW  20.800 usec
DE  82.37 usec
TE  295.0 K
D1  1.0000000 sec
D11  0.0300000 sec
TD0  1

======== CHANNEL f1 ========
SFO1  100.6228293 MHz
NUC1  13C
P1  10.00 usec
PLIN1  36.0000000 W

======== CHANNEL f2 ========
SFO2  400.1316005 MHz
NUC2  1H
CPDP2G 2 waltz16
CPD2  90.00 usec
PLIN2  7.00000000 W
PLIN12  0.12033000 W
PLIN13  0.09746800 W

F2 - Processing parameters
SI  32768
SF  100.6127720 MHz
WDW  EM
SSB  0
LB  1.00 Hz
GB  0
PC  1.40
Sample Name: WHX-7-195-F-FID-CDCL3
Data Collected on: fid.caltech.edu-inova600
Archive directory:

Sample directory: FidFile: WHX-7-195-F-FID-CDCL3

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 26 2015

Temp. 25.0 C / 298.1 K
Operator: hxwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.705 sec
Width 9611.9 Hz
64 repetitions
OBSERVE H1, 599.6200960 MHz
DATA PROCESSING
FT size 32768
Total time 2 min 53 sec
Current Data Parameters
NAME     WHX-7-195-F-Flo-CDCl3
EXPNO    30
PROCNO   1

F2 - Acquisition Parameters
Date     20150525
Time     22.08
INSTRUM  spect
PROBHD   5 mm CPPBBO BB
FUPROG   zgge30
TD       65384
SOLVENT  CDCl3
NS       8960
DS       2
SWH      24038.461 Hz
FIDRES   0.367651 Hz
AQ       1.359873 sec
RG       72.02
DW       20.800 usec
DE       82.37 usec
TE       295.0 K
D1       1.00000000 sec
D11      0.03000000 sec
TD0      70

-------- CHANNEL f1 --------
SFO1     100.6228298 MHz
NUC1     13C
P1       10.00 usec
PLW1     36.00000000 W

-------- CHANNEL f2 --------
SFO2     400.1316005 MHz
NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2     7.00000000 W
PLW12    0.12033000 W
PLW13    0.09746800 W

F2 - Processing parameters
SI       32768
SF       100.6127718 MHz
WOW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
Current Data Parameters
NAME WHX-7-225-F-Flo-CDCl3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150627
Time 0.37
INSTRUM spect
PROBHD 5 mm CPPBBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 197.44
DW 62.400 usec
DE 10.00 usec
TE 298.9 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
F1 11.70 usec
PLW1 7.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300096 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

(–)-acetylapoaranotin (3)
Current Data Parameters
NAME WHX-T-225-F-Flo-CDCl3
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150627
Time 7.24
INSTRUM spect
PROBHD 5 mm CPPBB0 BB
PULPLOG zgpg30
TD 65384
SOLVENT CDCl3
NS 10000
DS 4
SWH 24038.461 Hz
FIDRES 0.367651 Hz
AQ 1.3599873 sec
RG 72.02
DW 20.800 usec
DE 82.37 usec
TE 294.9 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

------- CHANNEL f1 -------
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 36.00000000 W

------- CHANNEL f2 -------
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 7.00000000 W
PLW12 0.12033000 W
PLW13 0.09746800 W

F2 - Processing parameters
SI 32768
SF 100.6127721 MHz
WDW EM
SSB 0
LB 1.00 Hz
GR 0
PC 1.40

(-)-acetylapoaranotin (3)
Sample Name: WHX-7-173-F-INDY-CDCL3
Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-173-F-INDY-CDCL3
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 7 2015

Sample #19, Operator: hxwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.6749700 MHz

DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min 32 sec
WHX-7-173-F-INDY-CDCL3

Sample Name: WHX-7-173-F-INDY-CDCL3
Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-173-F-INDY-CDCL3
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 7 2015

Sample #20, Operator: hxwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
1500 repetitions
OBSERVE C13, 125.6433729 MHz
DECOUPLE H1, 499.6774469 MHz
Power 36 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 51 min
Current Data Parameters
NAME WHX-7-174-HPLC-F-Flo-MeOD
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 20150508
Time 19.49
INSTRUM spect
PROBHD 5 mm CPPBBO BB
FULFROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SNH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 127.09
DW 62.400 usec
DE 10.00 usec
TE 298.2 K
D1 5.00000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 400.1324710 MHz
NUC1 1H
Pl 11.70 usec
PLW1 7.00000000 W

F2 - Processing parameters
SI 65536
SF 400.1300078 MHz
DNW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

9 8 7 6 5 4 3 2 1 0 ppm

S70
Current Data Parameters
NAME: WHX-7-174-HPLC-F-Flo-MeOD
EXPNO: 2
PROCNO: 1

F2 - Acquisition Parameters
Date: 20150508
Time: 20.08
INSTRUM: spect
PROBHD: 5 mm CFFFBO BB
PULPROG: zpg20
TD: 65536
SOLVENT: MeOD
NS: 128
DS: 2
SNH: 24038.46 Hz
FIDRES: 0.366798 Hz
AQ: 1.3631488 sec
DG: 64.2
DW: 20.800 usec
DE: 82.37 usec
TE: 298.2 K
D1: 1.00000000 sec
D11: 0.0000000 sec
TD0: 11

======== CHANNEL f1 ========
SFO1: 100.6228298 MHz
NUC1: 13C
P1: 10.00 usec
PLW1: 36.0000000 W

======== CHANNEL f2 ========
SFO2: 400.1316005 MHz
NUC2: 1H
CPDPRG2: waltz16
PCPD2: 90.00 usec
PLW2: 7.0000000 W
PLW3: 0.12033000 W
PLW4: 0.09746800 W

F2 - Processing parameters
SI: 12768
SF: 100.6126282 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GN: 0
FC: 1.40
Current Data Parameters
NAME   WHX-7-175-F-Flo-CDC13
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20150510
Time   19.43
INSTRUM   spect
PROBHD   5 mm CPPBBO BB
PULPROG   zg30
TD   65536
SOLVENT   CDC13
NS   16
DS   2
SWH   8012.820 Hz
FIDRES   0.122266 Hz
AQ   4.0894465 sec
RG   197.44
DW   62.400 usec
DE   10.00 usec
TE   298.1 K
D1   1.00000000 sec
TD0   1

---------- CHANNEL f1 ----------
SFO1   400.1324710 MHz
NUC1   1H
P1   11.70 usec
PLW1   7.00000000 W

F2 - Processing parameters
SI   65536
SF   400.1300097 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00
Current Data Parameters
NAME WHK-7-175-F-Flo-CDCl3
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150510
Time 21.04
INSTRUM spect
PROBHD 5 mm CPBBBO BB
PULPROG zgpg30
TD 65384
SOLVENT CDCl3
NS 2000
DS 4
SWH 24038.461 Hz
FIDRES 0.367651 Hz
AQ 1.3599873 sec
RD 78.69
DW 20.800 usec
DE 82.37 usec
TB 298.2 K
D1 1.00000000 sec
D11 0.03000000 sec
TD0 1

--------- CHANNEL f1 ----------
SFO1 100.6228293 MHz
NUC1 13C
P1 10.00 usec
PLW1 36.00000000 W

--------- CHANNEL f2 ----------
SFO2 400.1316005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 7.00000000 W
PLW12 0.12033000 W
PLW13 0.09746800 W

F2 - Processing parameters
SI 32768
SF 100.6127706 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
WHX-7-180-F-INDY-CDCL3

Sample Name: WHX-7-180-F-INDY-CDCL3
Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-180-F-INDY-CDCL3
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 12 2015

Sample #47, Operator: hxwang

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 8000.0 Hz
8 repetitions
OBSERVE H1, 499.6749675 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min 32 sec
Sample Name: WHX-7-180-F-Charact-INDY-CDCL3
Data Collected on: indy.caltech.edu-inova500
Archive directory: /home/hxwang/vnmrsys/data
Sample directory: WHX-7-180-F-Charact-INDY-CDCL3
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 12 2015

Sample #49, Operator: hxwang
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.042 sec
Width 31446.5 Hz
5760 repetitions
OBSERVE C13, 125.6433700 MHz
DECOUPLE H1, 499.6774469 MHz
Power 36 dB continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 16 min