Supporting Information

for

Studies Toward Australifungin. A Synthesis Dilemma of Regioselective Keto-Enol Tautomerization

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General Methods

Solvents and Reagents

Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled under argon from sodium-benzophenone ketyl immediately before use. Methylene chloride (CH_2Cl_2) and toluene were distilled from calcium hydride. Hexanes and ethyl acetate (EtOAc) were distilled prior to their use for chromatography.

Triethylamine (Et_3N), *N,N*-diisopropylethylamine (*i*-Pr_2NEt), pyridine, and trimethylsilyl chloride were distilled from calcium hydride immediately prior to use. Cuprous iodide (CuI) was continuously washed with ether over 2 days with a Soxhlet extractor, dried under vacuum and stored in the dark. Potassium *tert*-butoxide was sublimed and *tert*-butyl acetate was dried over K_2CO_3 and activated 4 Å molecular sieves prior to use. Purification of *meta*-chloroperbenzoic acid was accomplished by dissolution in CH_2Cl_2, washing repeatedly with pH 7 buffer (5 washes), and drying over anhydrous Na_2SO_4 before being concentrated to a solid which was then used without subsequent recrystallization. *Tert*-butanol was dried by gently stirring a slightly warmed volume over activated 3 Å molecular sieves. Dess–Martin periodinane was prepared from 2-iodobenzoic acid by oxidation to IBX according to Santagostino[1] and then converted to the periodinane according to Ireland.[2] All other reagents were used as provided by the chemical supplier. Reactions were typically carried out in flame or oven dried glassware under a positive atmosphere of dry argon.

Chromatography

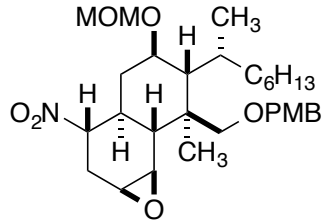
Analytical thin layer chromatography (TLC) was performed on precoated (0.25 mm thickness) glass plates (E. Merck, silica gel 60F-254). Developed plates were visualized by UV light (254 nm) and stained with either an acidic ethanolic solution of *p*-anisaldehyde or an acidic solution of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ and ceric sulfate followed by heating. Preparative chromatography was performed using flash column chromatography with Kieselgel-60 (230-400 mesh) silica gel (E. Merck). Compounds were applied directly to silica gel and eluted under a positive pressure of in-house air. Removal of solvents from samples (*in vacuo*) was accomplished using a Büchi rotary-evaporator at aspirator pressure. All non-volatile compounds were evacuated to constant weight under high vacuum (0.2–0.5 mm Hg) at room temperature.

Physical Data

Optical rotations were measured on a Perkin-Elmer 241 polarimeter at wavelength 589 nm (sodium, D-line) using a standard 10 cm cell (1mL volume). Specific rotations, $[\alpha]_D^{temp}$, are reported in degree·mL/(g·dm) at the specified temperature. Concentrations (c) are given in grams per 100 mL of the specified solvent. Proton (^{1}H-NMR) and carbon (^{13}C-NMR) nuclear magnetic resonance spectra were recorded on Varian Gemini 300, Varian VXR-400, Varian Inova-400 and Varian Inova-500 spectrometers. The chemical shifts are reported in parts per million (δ, ppm) downfield from tetramethylsilane (TMS) using residual $CHCl_3$ (δ 7.26 ppm) as an internal reference. Coupling constants are reported in Hertz (Hz) and the data is presented in the following form: chemical shift (multiplicity, coupling constants, number of protons) for each resonance. Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m,

[1] Frigerio, M.; Santagostino, M.; Sputore, S. *J. Org. Chem.* **1999**, *64*, 4537–4538.
[2] Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.

multiplet; br, broad. All carbon chemical shifts are reported in δ using $CDCl_3$ as an internal reference (δ 77.16 ppm). Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR as a neat film or as the residue of a dichloromethane solution as indicated. Infrared spectral data are reported in wavenumbers (cm^{-1}) and calibrated to the 1601 cm^{-1} absorption of polystyrene film. High resolution mass spectra were recorded on a Thermo Electron MAT 95XP mass spectrometer by use of electron ionization (EI), chemical ionization (CI), or electrospray ionization (ESI).



Compound 5
[Scheme 1, Step 1]

Epoxide 5 – To a solution of nitro-olefin **4** (477 mg, 0.912 mmol) and 4,4'-thiobis(6-*tert*-butyl-*m*-cresol) (3.1 mg, 0.027 mmol) in methylene chloride (3.0 mL) at 0 °C was added *m*-chloroperbenzoic acid (472 mg, 2.736 mmol) portionwise over 4.5 h (4 equal portions). The cooling bath was removed after the addition of the initial portion and the solution was allowed to come to room temperature. After the reaction was complete by TLC analysis (approx. 6 h) anhydrous KF (318 mg, 5.47 mmol) was added and the heterogeneous mixture was stirred for 5 min before 1:1 ether-pentane (12 mL) was added and mixture then filtered through Celite. The filtrant was washed with 1:1 ether-pentane (24 mL) and the resulting filtrate was washed in a separatory funnel with 2 x 50 mL of a solution of 5 mL saturated Na_2SO_3, 50 mL of pH 7 buffer and 45 mL of water. The aqueous layer was extracted with ether (20 mL) and the organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (25 g SiO_2), eluting with gradient of 10:1–1:1 hexanes-ethyl acetate, provided epoxide **5** (411 mg, 0.770 mmol, 84%) as a colorless viscous oil (NMR shows **4** present in small amounts).

For epoxide **5**:

R_f 0.38 (4:1 hexanes-EtOAc);

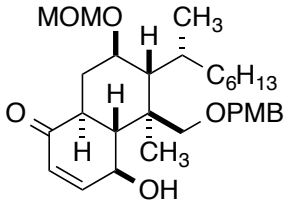
$[\alpha]_D^{20}$ –11.4 (*c* 0.62, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 2H), 6.89–6.86 (m, 2H), 4.64–4.60 (m, 2H), 4.51–4.35 (m, 3H), 3.81 (s, 3H), 3.64 (td, *J* = 11.0, 4.8 Hz, 1H), 3.50–3.32 (m, 2H), 3.31 (s, 3H), 3.04 (d, *J* = 4.0 Hz, 1H), 2.71 (ddd, *J* = 14.0, 4.4, 1.6 Hz, 1H), 2.32 (ddd, *J* = 13.6, 11.2, 2.0 Hz, 1H), 2.05–1.94 (m, 2H), 1.82–1.71 (m, 2H), 1.63–1.56 (m, 1H), 1.46–1.06 (m, 12H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.76 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.3, 130.4, 129.23, 113.8, 96.3, 86.7, 76.2, 73.0, 71.8, 56.0, 55.4, 52.0, 50.3, 43.8, 42.7, 35.3, 35.2, 32.5, 32.2, 32.0, 30.7, 29.9, 28.9, 28.8, 22.9, 22.8, 14.2;

IR (film) 3415 (br), 2954, 2924, 2853, 1612, 1586, 1551, 1513, 1463, 1377, 1032, 1248, 1209, 1172, 1137, 1097, 1039, 916, 823 cm^{-1};

HRMS (CI+) calc. for $C_{30}H_{46}O_7N$ $[M - H]^+$ 532.3269. Found: 532.3260.



Compound 6
[Scheme 1, Step 2]

Enone 6: Epoxide **5** (499.7 mg, 0.936 mmol) was dissolved in dry THF (6.2 mL) and cooled to 10 °C. Solid potassium *tert*-butoxide (157.6 mg, 1.40 mmol) was added and the mixture was allowed to stir for 10 min during which the solution turned a bright yellow. A solution of dimethyldioxirane (freshly dried over anhydrous Na_2SO_4) was added in an amount until the solution turned colorless (~37 mL of a 0.05 M solution). The reaction mixture was allowed to stir for an additional 10 min at 10 °C before sequentially adding ether (40 mL), and a 1:1:1 solution of saturated $Na_2S_2O_3$, pH 7 buffer, and water (total 30 mL). The mixture was then stirred vigorously for 15 min and then poured into a separatory funnel. The layers separated and the aqueous layer back extracted with ether (2 x 40 mL). The combined organic layers were then washed with saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was then redissolved in dry 1:1 THF-*t*-BuOH (10 mL) and a cooled to –10 °C before adding a solution of potassium *tert*-butoxide in 1:1 THF-*t*-BuOH (1.5 mL, 0.1 M, 0.15 mmol) dropwise. The mixture was allowed to stir until TLC indicated the more polar component was completely formed. Ethyl acetate (50 mL) and pH 7 buffer (50 mL) were added and the layers separated. The aqueous layer was extracted with ethyl acetate (50 mL) and the combined organic layers were then washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (25 g SiO_2) eluting with gradient of 16:1–1:1 hexanes-EtOac provided enone **6** (373 mg, 0.742 mmol, 79%) as a clear colorless oil along with starting material **5** (35.2 mg) and epi-**5** (27.8 mg).

For ketone **6**:

R_f 0.21 (2:1 hexanes-EtOAc);

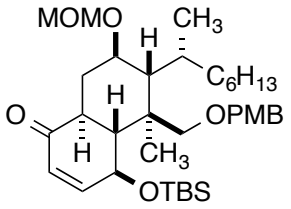
$[\alpha]_D^{23}$ +33.8 (*c* 0.87, $CHCl_3$);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.28–7.17 (m, 2H), 6.90–6.82 (m, 2H), 6.77 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.91 (dd, *J* = 10.1, 1.9 Jz, 1H), 4.71 (d, *J* = 8.9 Hz, 1H), 4.65–4.53 (m, 2H), 4.42 (dd, *J* = 22.2, 11.0 Hz, 3H), 3.77 (s, 3H), 3.70 (td, *J* = 9.7, 4.2 Hz, 1H), 3.59 (d, *J* = 10.0 Hz, 1H), 3.52–3.45 (m, 1H), 3.36 (s, *J* = 8.0 Hz, 3H), 2.69–2.56 (m, 1H), 2.15–1.99 (m, 2H), 1.60–1.48 (m, 1H), 1.47–1.05 (m, 12H), 0.99 (d, *J* = 12.7 Hz, 3H), 0.91–0.82 (m, 6H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.4, 159.6, 153.0, 129.8, 129.0, 126.8, 114.0, 95.6, 75.2, 74.9, 73.1, 66.7, 56.1, 55.3, 53.2, 51.7, 43.4, 41.6, 32.6, 32.5, 32.0, 31.6, 29.9, 28.9, 22.7, 22.6, 14.2, 13.1;

IR (film) 3415 (br), 2954, 2929, 2872, 1678, 1612, 1513, 1465, 1382, 1302, 1248, 1101, 1040, 820 cm^{-1};

HRMS (ES+) calc. for $C_{30}H_{46}O_6Na$ $[M+Na]^+$ 525.3192. Found: 525.3199.



Compound 6a
[Scheme 1, Step 6]

TBS ether 6a: In a flame dried round-bottomed flask fitted with a magnetic stirbar was placed alcohol **6** (73.4 mg, 0.146 mmol) dissolved in dry CH_2Cl_2 (3 mL). An argon atmosphere over the reaction mixture was generated and the reaction cooled to –40 °C. At this point 2,6-lutidine (70 μL, 0.601 mmol) was added via syringe followed by TBSOTf (40 μL, 0.174 mmol) which was also added via syringe. After a 4 h, additional quantities of 2,6-lutidine (70 μL, 0.601 mmol) and TBSOTf (40 μL, 0.174 mmol) were added. After another 2 h, the reaction mixture was quenched by the addition water (6 mL) and the cooling bath removed. After approximately 15 min the mixture was poured into ether (12 mL). The layers were separated and the aqueous layer extracted with ether (2 x 6 mL). The combined organic portion was washed with brine (15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo. The residue was then purified by flash chromatography (5 g SiO_2, 12:1–4:1 hexanes-EtOAc) afforded silyl ether **6a** (74.1 mg, 0.120 mmol, 84%) as a clear colorless oil.

For TBS ether **6a**:

R_f 0.41 (4:1 hexanes-EtOAc);

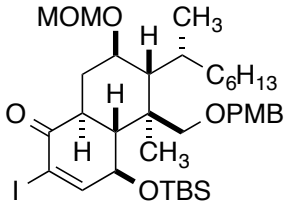
$[\alpha]_D^{23}$ +68.4 (*c* 0.95, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (m, 2H), 6.86–6.84 (m, 2H), 6.79 (d, J = 10.8 Hz, 1H), 5.89 (dd, J = 10.4 Hz, 1.6 Hz, 1H), 4.76 (A of AB, J_{AB} = 6.6 Hz, 1H), 4.68 (B of AB, J_{AB} = 6.6 Hz, 1H), 4.55 (d, J = 9.6 Hz, 1H), 4.45 (A of AB, J_{AB} = 11.2 Hz, 1H), 4.31 (B of AB, J_{AB} = 11.2 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.61 (td, J = 11.2 Hz, 4.0 Hz, 1H), 3.41 (s, 3H), 3.35 (d, J = 9.2 Hz, 1H), 2.72 (dt, J = 12.8, 4.0 Hz, 1H), 2.46 (dd, J = 12.8, 9.2 Hz, 1H), 2.06 (td, J = 12.8, 3.6 Hz, 1H), 1.86 (d, J = 11.2 Hz, 1H), 1.61–1.54 (m, 2H), 1.46–1.37 (m, 2H), 1.34–1.11 (m, 8H), 1.06 (d, J = 6.8 Hz, 3H), 0.96 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H), 0.83 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 199.9, 159.1, 155.8, 131.3, 129.1, 126.9, 113.8, 96.2, 76.3, 73.5, 72.6, 56.4, 55.4, 50.2, 49.3, 44.3, 44.2, 32.8, 32.2, 31.4, 30.1, 29.9, 29.2, 26.2, 23.3, 22.8, 18.3, 14.3, 13.4, –3.1, –3.9;

IR (film) 2954, 2926, 2855, 1682, 1514, 1463, 1384, 1362, 1249, 1171, 1075, 1043, 995, 854, 835 cm^{-1};

HRMS (ES+) calc. for $C_{36}H_{60}O_6SiNa$ $[M+Na]^+$ 639.4057. Found: 639.4076.



Compound 7
[Scheme 1, Step 4]

α-Iodoketone 7: In a flame dried round-bottomed flask fitted with a magnetic stirbar and covered with aluminum foil was placed enone **6a** (97.6 mg, 0.158 mmol) dissolved in dry pyridine (260 μL) and CCl_4 (260 μL). To the solution was added 4-dimethylaminopyridine (27.0 mg, 0.22 mmol) and solid elemental iodine (200.7 mg, 0.791 mmol) which was added portionwise over 2 min. After a further 4 h, a 1:1:1 solution of saturated $Na_2S_2O_3$:saturated $NaHCO_3$:H_2O (15 mL) was added and the mixture vigorously stirred for 15 min. The mixture was then poured into ether (20 mL) and shaken. The layers were separated and the aqueous layer extracted with ether (2 x 10 mL). The combined organic portion was washed with dilute HCl (40 mL, 0.1 N HCl) and saturated $NaHCO_3$ (2 x 60 mL) and then dried over anhydrous Na_2SO_4. The mixture was then filtered and concentrated in vacuo and the residue purified by flash chromatography (15 g SiO_2, 15:1–6:1 hexanes-EtOAc) afforded iodide **7** (110.3 mg, 0.1485 mmol, 94%) as a clear pale yellow oil.

For α-iodo ketone **7**:

R_f 0.53 (4:1 hexanes-EtOAc);

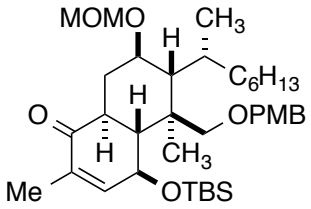
$[\alpha]_D^{22}$ +30.1 (*c* 1.42, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.6 Hz, 1H), 7.24–7.21 (m, 2H), 6.87–6.85 (m, 2H), 4.75–4.68 (m, 2H), 4.56 (dd, J = 9.4, 1.4 Hz, 1H), 4.44 (A of AB, J_{AB} = 11.2 Hz, 1H), 4.30 (B of AB, J_{AB} = 11.2 Hz, 1H), 4.06 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.60 (td, J = 10.8, 4.0 Hz, 1H), 3.40 (s, 3H), 3.33 (d, J = 9.2 Hz, 1H), 2.78 (dt, J = 13.0, 4.0 Hz, 1H), 2.50 (dd, J = 13.2, 9.6, Hz, 1H), 2.20 (td, J = 12.8 Hz, 4.0 Hz, 1H), 1.85 (d, J = 11.2 Hz, 1H), 1.58–1.55 (m, 1H), 1.41–1.08 (m, 11H), 1.05 (d, J = 7.2 Hz, 3H), 0.97 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 0.82 (s, 3H), 0.21 (s, 3H), 0.18 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 193.4, 163.5 ,159.1, 131.0, 129.1, 113.7, 101.1, 96.4, 76.15, 74.1, 73.2, 72.6, 56.2, 55.4, 50.0, 49.2, 44.1, 42.9, 33.8, 32.7, 32.1, 31.3, 30.0, 29.1, 26.1, 23.2, 22.8, 18.3, 14.2, 13.4, –3.2, –4.0;

IR (film) 2953, 2927, 2854, 1683, 1610, 1513, 1464, 1362, 1303, 1250, 1080, 1040, 831 cm^{-1};

HRMS (ES+) calc. for $C_{36}H_{59}IO_6SiNa$ $[M+Na]^+$ 765.3023. Found: 765.3052.



Compound 8
[Scheme 1, Step 5]

Enone 8: In a flame dried round-bottomed flask fitted with a magnetic stirbar was placed iodide **7** (160.1 mg, 0.216 mmol) dissolved in dry DMF (2.1 mL). The solution was then degassed briefly by stirring under high vacuum and backfilled with argon before $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (8.8 mg, 0.0108 mmol), CuI (6.2 mg, 0.0323 mmol), and Me_4Sn (208 μL, 1.51 mmol) were added. The flask was then fitted with a reflux condenser and the reaction warmed to 60 °C. After 1 h the reaction was complete and the mixture was then poured into half saturated NaCl solution (15 mL). Ether was added and the layers separated and the aqueous layer extracted again with ether (2 x 15 mL). The combined organic portion was washed with half saturated NaCl (20 mL) and then dried over anhydrous $MgSO_4$. The mixture was then filtered and concentrated in vacuo and the residue purified by flash chromatography (12 g SiO_2, 16:1–6:1 hexanes-EtOAc) affording enone **8** (127.1 mg, 0.2012 mmol, 94%) as a clear colorless oil.

For enone **8**:

R_f 0.50 (4:1 hexanes-EtOAc);

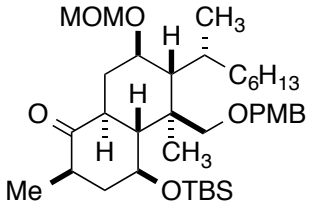
$[\alpha]_D^{23}$ +48.0 (*c* 0.65, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (m, 2H), 6.88–6.86 (m, 2H), 6.54 (s, 1H), 4.76 (A of AB, J_{AB} = 6.6 Hz, 1H), 4.69 (B of AB, J_{AB} = 6.6 Hz, 1H), 4.50 (td, J = 9.4, 1.8 Hz, 1H), 4.45 (A of AB, J_{AB} = 11.3 Hz, 1H), 4.31 (B of AB, J_{AB} = 11.3 Hz, 1H), 4.13 (d, J = 9.2 Hz, 1H), 3.80 (s, 3H), 3.61 (td, J = 11.1, 4.1 Hz, 1H), 3.41 (s, 3H), 3.34 (d, J = 9.2 Hz, 1H), 2.74 (td, J = 13.1, 3.9 Hz, 1H), 2.39 (dd, J = 12.9, 9.4 Hz, 1H), 2.02 (td, J = 12.5, 3.7 Hz, 1H), 1.85 (d, J = 11.3 Hz, 1H), 1.74 (s, 3H), 1.61–1.52 (m, 1H), 1.48–1.38 (m, 1H), 1.32–1.12 (m, 10H), 1.06 (d, J = 6.8 Hz, 3H), 0.96 (s, 9H), 0.88 (t, J = 6.6 Hz, 3H), 0.82 (s, 3H), 0.19 (s, 3H), 0.16 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.0, 159.0, 150.7, 133.1, 129.1, 113.7, 96.3, 76.5, 73.5, 72.6, 71.8, 56.3, 55.4, 50.1, 49.5, 44.2, 44.0, 33.1, 32.8, 32.2, 31.3, 30.1, 29.9, 29.2, 26.3, 23.3, 22.8, 18.3, 15.5, 14.3, 13.5, –3.1, –3.8;

IR (film) 2955, 2927, 2855, 1676, 1613, 1513, 1465, 1364, 1301, 1249, 1080, 1044, 858, 836, 777 cm^{-1};

HRMS (CI+) calc. for $C_{37}H_{61}O_6Si$ $[M - H]^+$ 629.4232. Found: 629.4219.



Compound 9
[Scheme 1, Step 6]

Ketone 9: In a flame dried round-bottomed flask fitted with a magnetic stirbar was placed enone **8** (89.9 mg, 0.142 mmol) dissolved in EtOAc (7.2 mL). Pd/C (20 mg, 5% w/w, 140 mg/mmol enone) was added and the mixture degassed by applying vacuum and backfilling with argon before charging the flask with hydrogen using vacuum and backfilling from a ballon. The mixture was then stirred vigorously under a hydrogen filled balloon for 12 h. The balloon was removed and the mixture purged of hydrogen by applying vacuum and back filling with argon several times. The mixture was then passed through a plug of silica (2 g) with EtOAc washing (3 x 5 mL) and the filtrates concentrated in vacuo to afford ketone **9** (87.7 mg, 0.139 mmol, 98%) as a clear colorless oil.

For ketone **9**:

R_f 0.50 (4:1 hexanes-EtOAc);

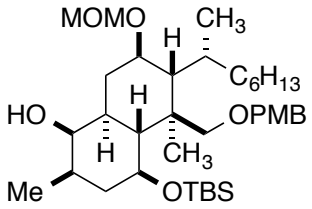
$[\alpha]_D^{22}$ +13.7 (*c* 0.52, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (m, 2H), 6.86–6.84 (m, 2H), 4.72, (A of AB, J_{AB} = 6.8 Hz, 1H), 4.66 (B of AB, J_{AB} = 6.8 Hz, 1H), 4.43 (A of AB, J_{AB} = 11.6 Hz, 1H), 4.30 (B of AB, J_{AB} = 11.6 Hz, 1H), 4.21 (d, J = 9.2 Hz, 1H), 4.11–4.04 (m, 1H), 3.80 (s, 3H), 3.53 (td, J = 11.2 Hz, 4.0 Hz, 1H), 3.39 (d, J = 9.2 Hz, 1H), 2.43–2.31 (m, 2H), 2.16–2.03 (m, 3H), 1.86 (d, J = 11.6 Hz, 1H), 1.58–1.46 (m, 2H), 1.45–1.20 (m, 11H), 1.04 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.6 Hz, 3H), 0.92–0.82 (m, 15H), 0.14 (s, 3H), 0.13 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 211.5, 159.0, 131.4, 129.0, 113.7, 96.3, 76.8, 73.1, 73.0, 72.5, 56.3, 55.4, 50.3, 49.9, 45.4, 44.7, 44.5, 42.1, 32.8, 32.5, 32.2, 31.5, 30.1, 29.1, 26.3, 23.2, 22.8, 18.3, 14.6, 14.3, 12.7, –3.4, –3.7;

IR (film) 2954, 2926, 2854, 1718, 1513, 1462, 1248, 1083, 1039, 852, 843 cm^{-1};

HRMS (ES+) calc. for $C_{37}H_{64}O_6SiNa$ $[M+Na]^+$ 655.4370. Found: 655.4379.



Compound 9a
[Scheme 1, Step 7]

Alcohol 9a: To a 50 mL round-bottom flask containing ketone **9** (218 mg, 0.344 mmol) under argon was added THF (11.1 mL, 0.03 M). The reaction mixture was cooled to –78 °C, followed by the addition of L-selectride® (1.38 mL, 1.38 mmol, 1 M in THF). The solution was stirred at –78 °C until no starting material remained by TLC, approximately 2.5 h. At which time a solution of NaOH (7.5 mL, 1.0 M) and 30% H_2O_2 (6.0 mL) was added to the reaction mixture at –78 °C and warmed to 0 °C and stirred for 1h. The solution was diluted with H_2O (15 mL) and EtOAc (50 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with H_2O (1 x 50 mL), saturated NH_4Cl (1 x 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash column chromatography (95:5–3:1 hexanes-EtOAc) to afford **9a** (195 mg, 0.307 mmol, 90%) as a colorless oil.

For alcohol **9a**:

R_f 0.29 (4:1 hexanes-EtOAc);

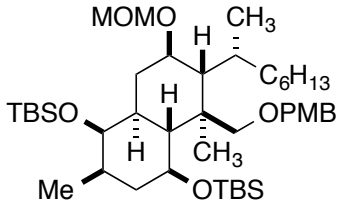
$[\alpha]_D^{20}$ +23.7 (*c* 0.35, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26–7.25 (m, 2H), 6.87–6.85 (m, 2H), 4.70 (A of AB, J_{AB} = 6.8 Hz, 1H), 4.68 (B of AB, J_{AB} = 6.8 Hz, 1H), 4.47 (A of AB, J_{AB} = 11.5 Hz, 1H), 4.31 (B of AB, J_{AB} = 11.5 Hz, 1H), 4.22 (d, J = 7.2 Hz, 1H), 3.80 (s, 3H), 3.62–3.55 (m, 2H), 3.41–3.36 (m, 4H), 3.29 (d, J = 9.0 Hz, 1H), 2.02–1.96 (m, 2H), 1.88 (d, J = 11.0 Hz, 1H), 1.60–1.08 (m, 17H), 1.03 (d, J = 7.0 Hz, 3H), 0.96 (m, 3H), 0.92–0.84 (m, 15H), 0.73 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.9, 131.8, 129.1, 113.7, 96.5, 77.7, 75.2, 74.7, 74.3, 72.6, 56.1, 55.4, 50.8, 43.5, 41.9, 39.7, 39.6, 37.3, 35.1, 32.9, 32.2, 31.5, 30.2, 29.1, 26.4, 23.2, 22.8, 18.4, 17.9, 14.3, 13.1, –3.3, –3.7;

IR (film) 3446 (br), 2958, 2923, 2851, 1613, 1514, 1463, 1377, 1249, 1083, 1042, 834 cm^{-1};

HRMS (ES+) calc. for $C_{37}H_{66}O_6SiNa$ $[M+Na]^+$ 657.4526. Found: 657.4528.



Compound 10
[Scheme 1, Step 8]

Bis-TBS Ether 10: To a 50 mL round-bottom flask containing alcohol **9a** (256 mg, 0.403 mmol) under argon was added CH_2Cl_2 (8.1 mL, 0.016 M) and 2,6-di-*tert*-butylpyridine (0.712 mL, 3.22 mmol). The reaction mixture was cooled to –40 °C, followed by the addition of TBSOTf (0.612 mL, 0.575 mmol). The solution was allowed to slowly warm to –10 °C over 30 min and then recooled to –40 °C. The reaction mixture was quenched by the addition of saturated $NaHCO_3$ (15 mL) and the cooling bath removed. After 20 min the solution was diluted with EtOAc (50 mL) and H_2O (15 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–95:5 hexanes–ethyl acetate) provided **10** (309 mg, 0.395 mmol, 98%) as a colorless oil.

For TBS ether **10**:

R_f 0.54 (6:1 hexanes-EtOAc);

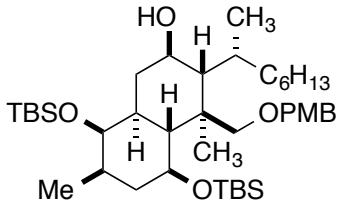
$[\alpha]_D^{23}$ +37.0 (*c* 0.35 CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.26–7.23 (m, 2H), 6.85–6.83 (m, 2H), 4.68 (s, 2H), 4.45 (A of AB, J_{AB} = 11.6 Hz), 4.31 (m, 2H), 3.80 (s, 3H), 3.58 (td, J = 10.0, 4.0 Hz, 1H), 3.50 (td, J = 11.2, 4.0 Hz, 1H), 3.43 (br s, 1H), 3.37 (s, 3H), 3.28 (d, J = 9.2 Hz, 1H), 2.18 (dd, J = 11.6, 10.0 Hz, 1H), 1.90–1.85 (m, 2H), 1.68–1.14 (m, 16H), 1.03 (d, J = 6.8 Hz, 3H), 0.91–0.85 (m, 24H), 0.73 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.6, 132.3, 128.6, 113.6, 96.9, 78.7, 76.3, 75.3, 74.3, 72.3, 56.0, 55.4, 50.7, 43.6, 41.6, 41.0, 40.0, 39, 36.4, 33.0, 32.2, 31.6, 30.2, 29.2, 26.5, 23.3, 22.9, 19.3, 18.7, 18.4, 14.3, 13.0, –2.9, –3.1, –3.4, –3.4;

IR (film) 2954, 2928, 2855, 1617, 1514, 1463, 1361, 1249, 1172, 1147, 1099, 1045, 1000, 921, 935, 773 cm^{-1};

HRMS (ES+) calc. for $C_{43}H_{80}O_6Si_2Na$ $[M+Na]^+$ 771.5391. Found: 771.5414.



Compound 11
[Scheme 2, Step 1]

Alcohol 11:To a 50 mL round-bottom flask containing MOM ether **10** (150 mg, 0.192 mmol) under argon was added CH_2Cl_2 (12.0 mL, 0.016 M) and 2,6-di-tert-butylpyridine (0.424 mL, 1.92 mmol). The reaction mixture was cooled to –78 °C, followed by the addition of *B*-bromocatecholborane (0.612 mL, 0.575 mmol, 0.94 M in CH_2Cl_2). The solution was stirred at –78 °C until no starting material remained by TLC, at which time the mixture was poured into a 1:1 mixture of THF/pH 7 buffer (100 mL) and agitated briefly. Et_2O (100 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (100 mL) and the combined organic layers washed with saturated $NaHCO_3$ (75 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was then purified by flash column chromatography (98:2–6:1 hexanes-EtOAc) to afford alcohol **11** (127 mg, 0.180 mmol, 94%) as a colorless oil.

For alcohol **11**:

R_f 0.48 (6:1 hexanes-EtOAc);

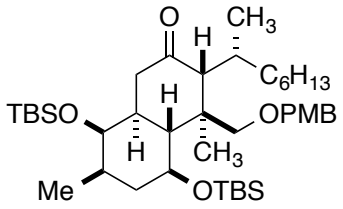
$[\alpha]_D^{20}$ +21.0 (*c* 0.14, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.25–7.23 (m, 2H), 6.85–6.83 (m, 2H), 4.43 (A of AB, J_{AB} = 11.6 Hz, 1H), 4.33–4.29 (m, 2H), 3.80 (s, 3H), 3.69 (m, 1H), 3.58 (td, *J* = 10.0, 4.0 Hz, 1H), 3.43 (br s, 1H), 3.27 (d, *J* = 9.2 Hz, 1H), 2.17 (dd, *J* = 11.6, 9.8 Hz, 1H), 1.69–1.05 (m, 19H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.90–0.85 (m, 24H), 0.73 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), 0.03 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.7, 132.3, 128.6, 113.6, 94.6, 76.1, 75.3, 74.2, 72.3, 69.9, 55.4, 53.0, 43.7, 42.0, 41.6, 41.3, 40.1, 36.4, 33.1, 30.1, 29.1, 26.5, 23.9, 22.9, 19.3, 18.7, 18.4, 14.3, 13.0, –2.9, –3.0, –3.4;

IR (film) 3483 (br), 2954, 2927, 2855, 1614, 1513, 1463, 1378, 1301, 1248, 1171, 1140, 1064, 1040, 927, 882, 834, 774 cm^{-1};

HRMS (CI+) calc. for $C_{41}H_{77}O_5Si_2$ $[M+H]^+$ 705.5304. Found: 705.5326.



Compound 12
[Scheme 2, Step 2]

Ketone 12: In a flame dried round-bottomed flask fitted with a magnetic stirbar was placed alcohol **11** (5.1 mg, 0.0071 mmol) dissolved in dry CH_2Cl_2 (150 μL). To this was added powdered 4 Å activated molecular sieves and the mixture was allowed to stir for 5 min. *N*-methylmorpholine-*N*-oxide (1.3 mg, 0.011 mmol) and tetra-*N*-propylammonium perruthenate (0.2 mg, 0.0006 mmol) were added. The mixture was allowed to stir for 30 min before the the reaction mixture was taken up and filtered through a plug of Celite® and concentrated in vacuo. The residue was then purified by flash column chromatography (1.5 g SiO_2, 50:1–20:1 hexanes-EtOAc) to afford ketone **12** (4.2 mg, 0.0058 mmol, 80%) as a clear colorless oil.

For ketone **12**:

R_f 0.52 (6:1 hexanes–EtOAc);

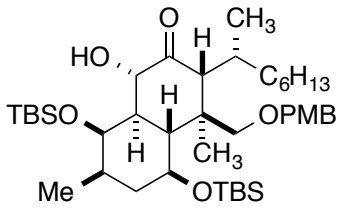
$[\alpha]_D^{21}$ +24.1 (*c* 0.29, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.24–7.22 (m, 2H), 6.86–6.84 (m, 2H), 4.51 (A of AB, J = 11.6 Hz, 1H), 4.39 (d, J = 8.8 Hz, 1H), 4.30 (B of AB, J = 11.6 Hz, 1H), 3.81 (s, 3H), 3.66 (td, J = 10.0, 4.0 Hz, 1H), 3.39 (br s, 1H), 3.19 (d, J = 8.8 Hz, 1H), 2.86 (br s, 1H), 2.60–2.50 (m, 2H), 1.95 (dd, J = 12.4, 4.8 Hz, 1H), 1.72–1.05 (m, 15H), 0.93–0.85 (m, 30H), 0.11 (s, 3H), 0.10 (s, 3H), 0.05 (s, 3H), 0.01 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 214.8, 209.0, 170.3, 131.8, 128.7, 113.6, 75.4, 74.7,74.3, 72.2, 59.8, 55.4, 48.3, 47.4, 44.5, 43.2, 40.1, 35.9, 34.1, 32.2, 30.8, 29.5, 26.5, 26.4, 22.9, 20.8, 19.3, 18.8, 18.5, 14.7, 14.3, –2.7, –3.1, –3.5, –4.8;

IR (film) 2955, 2923, 2856, 1715, 1616, 1513, 1463, 1380, 1249, 1170, 1063, 1040, 1004, 884, 835, 774 cm^{-1};

HRMS (ES+) calc. for $C_{41}H_{74}O_5Si_2Na$ $[M+Na]^+$ 725.4973. Found: 725.4993.



Compound 13
[Scheme 2, Step 3]

Ketol 13: A flame-dried 25 mL round-bottom flask charged with a magnetic stir bar was evacuated and back-filled with argon. A THF (3.0 mL) solution of **ketone 12** (228 mg, 0.324 mmol) was slowly added down the sides of the flask to a lithium diisopropylamide (3.89 mL, 3.89 mmol, 1.0 M in THF) solution at –78 °C. Additional THF (3.5 mL) was used to rinse the remaining ketone into the reaction flask. The solution was allowed to stir at –78 °C for 2 h before freshly distilled TMSCl (0.62 mL, 4.86 mmol) was added dropwise via syringe over 5 min. The mixture was allowed to stir for 3 h at –78 °C. A solution of pH 7 buffer (75 mL) was cooled in an Erlenmeyer flask to 0 °C and then the silyl enol ether solution was poured into the cooled buffer solution and agitated briefly. Pentane (150 mL) was added to the quenched reaction mixture and the layers were separated. The aqueous layer was extracted with pentane (2 x 100 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to provide a yellow oil. The crude product was used in the following reaction without purification. To a 50 mL round-bottom flask containing the crude silyl enol ether was added CH_2Cl_2 (15.4 mL, 0.021 M). The reaction mixture was cooled to 0 °C, followed by addition of anhydrous $NaHCO_3$ (544 mg, 6.48 mmol) and m-chloroperoxybenzoic acid (227 mg, 1.30 mmol). The reaction was stirred at 0 °C for 1 h, at which time a 10% solution of Na_2SO_3 (25 mL) was added and the solution was stirred for an additional 15 min while warming to room temperature. The solution was diluted with H_2O (15 mL) and CH_2Cl_2 (75 mL). The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with saturated NaHCO3 (1 x 50 mL) and saturated NaCl (1 x 50 mL). The organic layer was then dried over anhydrous Na_2SO_4, filtered and concentrated to provide a yellow oil. The crude product was used in the following reaction without purification. To a 50 mL round-bottom flask containing the crude TMS ether was added CH_2Cl_2 (16.2 mL, 0.02 M) and MeOH (0.77 mL, 0.42 M). The reaction mixture was cooled to 0 °C, followed by addition of camphorsulfonic acid (7.5 mg, 0.0324 mmol). The reaction was stirred at 0 °C until no starting material remained by TLC, approximately 1 h 15 min. A saturated solution of $NaHCO_3$ (20 mL) was added to the reaction at 0 °C. The solution was diluted with H_2O (20 mL) and CH_2Cl_2 (75 mL). The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (95:5–9:1 hexanes–ethyl acetate) provided ketol **13** (201 mg, 0.279 mmol, 86% over 2 steps) as a colorless oil.

For ketol **13**:

R_f 0.62 (6:1 hexanes-EtOAc);

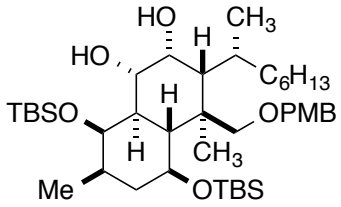
$[\alpha]^{D}_{23}$ +12.0 (c 1.20, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.28–7.19 (m, 2H), 6.88–6.82 (m, 2H), 4.52 (A of AB, J_{AB} = 11.4 Hz, 1H), 4.46 (d, J = 8.8, 1H), 4.30 (B of AB, J_{AB} = 11.3 Hz, 1H), 3.97 (bs, 1H) 3.93 (dd, J = 10.5, 3.4 Hz, 1H), 3.81 (s, 3H), 3.62 (ddd, J = 10.4, 10.4, 3.8 Hz, 1H), 3.60 (d, J = 3.7 Hz, 1H), 3.19 (d, J = 8.8 Hz, 1H), 2.86 (bs, 1H), 2.69 (dd, J = 11.7, 9.7 Hz, 1H), 1.83– 0.77 (m, 24H), 0.92 (s, 9H), 0.91 (s, 9H), 0.84 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 214.6, 158.9, 131.5, 128.7, 113.7, 74.8, 73.9, 73.7, 72.2, 71.1, 57.3, 55.4, 54.0, 49.4, 41.7, 40.1, 35.7, 33.9, 32.2, 30.6, 29.8, 29.4, 26.5, 26.4, 22.8, 20.4, 19.2, 18.8, 18.4, 14.5, 14.3, –2.9, –3.1, –3.7, –4.4;

IR (film) 3468, 2955, 2928, 2856, 1712, 1721, 1613, 1514, 1463, 1385, 1251, 1065, 1040, 988, 836, 775 cm^{-1};

HRMS (ESI+) calc. for $C_{41}H_{74}O_6Si_2Na$ $[M+Na]^+$ 741.4916. Found 741.4955.



Compound 13a
[Scheme 2, Step 4]

Diol 13a: To a 100 mL round-bottom flask containing **13** under argon was added MeOH (36.1 mL, 0.02 M). The solution was cooled to 0 °C and $NaBH_4$ (682 mg, 18.0 mmol) was added in two equal portions to the reaction. The reaction mixture was stirred at 0 °C until no starting material was present by TLC, approximately 1 h. A saturated solution of NH_4Cl (30 mL) was added slowly to the reaction at 0 °C, followed by stirring for 15 min while warming to room temperature. The solution was diluted with H_2O (15 mL) and EtOAc (75 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with saturated NaCl (1 x 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–9:1 hexanes–ethyl acetate) provided diol **13a** (460 mg, 0.638 mmol, 88%) as a viscous colorless oil.

For diol **13a**:

R_f 0.34 (6:1 hexanes-EtOAc);

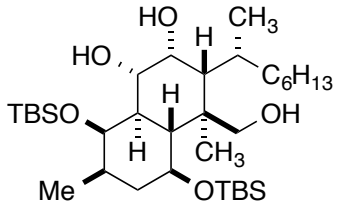
[α]D 23 +32.7 (c 0.80, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.23–7.17 (m, 2H), 6.86–6.81 (m, 2H), 4.43 (A of AB, J_{AB} = 11.7 Hz, 1H), 4.28 (B of AB, J_{AB} = 11.7 Hz, 1H), 4.27 (d, J = 9.0 Hz, 1H), 4.12–4.09 (m, 1H), 4.04 (bs, 1H), 3.80 (s, 3H), 3.70 (ddd, J = 10.5, 10.5, 4.1 Hz, 1H), 3.36 (ddd, J = 11.0, 8.3, 2.8 Hz, 1H), 3.20 (d, J = 8.9 Hz, 1H), 2.29 (dd, J = 11.6, 9.8 Hz, 1H), 1.95–0.81 (m, 26H), 1.84 (d, J = 8.3 Hz, 1H), 1.01 (s, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.8, 132.1, 128.8, 113.6, 75.3, 74.8, 72.4, 71.4, 71.2, 70.3, 55.5, 47.0, 44.5, 41.5, 40.9, 40.3, 36.2, 35.2, 32.3, 30.5, 30.0, 29.4, 26.6, 26.5, 22.9, 21.5, 19.5, 18.8, 18.5, 15.7, 14.3, –3.0, –3.2, –3.5, –4.0;

IR (film) 3445, 2955, 2928, 2856, 1614, 1514, 1463, 1386, 1301, 1249, 1171, 1089, 1063, 1037, 984, 940, 911, 831, 774, 674 cm^{-1};

HRMS (ESI+) calc. for $C_{41}H_{76}O_6Si_2Na$ $[M+Na]^+$ 743.5073. Found 743.5093.



Compound 14
[Scheme 2, Step 5]

Triol 14: To a 100 mL round-bottom flask containing diol **13a** was added a 1:1 solution of CH_2Cl_2:pH 7 buffer (31.9 mL, 0.02 M). The solution was cooled to 0 °C, DDQ (434 mg, 1.91 mmol) was added to the reaction and the mixture was allowed to warm to room temperature. After stirring for 5 h, a saturated solution of $NaHCO_3$ (30 mL) was added to the reaction mixture at 0 °C. The solution was diluted with H_2O (15 mL) and EtOAc (75 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–9:1 hexanes–ethylacetate) provided triol **14** (354 mg, 0.589 mmol, 92%) as a white foam.

For triol **14**:

R_f 0.34 (6:1 hexanes-EtOAc);

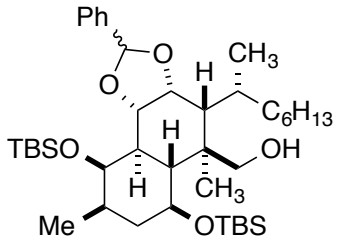
$[\alpha]^{D}_{23}$ +33.0 (c 0.74, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.21–4.16 (m, 1H), 4.04 (bs, 1H), 3.84 (ddd, *J* = 10.2, 10.2, 5.7 Hz, 1H), 3.64 (dd, *J* = 12.3, 4.8 Hz, 1H), 3.50 (dd, *J* = 11.2, 11.2 Hz, 1H), 3.40 (ddd, *J* = 11.0, 8.0, 3.5 Hz, 1H), 2.59 (dd, *J* = 10.7, 4.8 Hz, 1H), 1.99–0.84 (m, 25H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.99 (s, 3H), 0.94 (s, 9H), 0.91 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H), 0.13 (s, 3H), 0.09 (s, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 72.2, 71.6, 71.5, 69.9, 66.8, 48.4, 43.3, 43.1, 42.3, 38.3, 35.0, 35.0, 32.2, 31.7, 29.9, 29.3, 26.6, 26.5, 22.9, 21.7, 19.5, 19.0, 18.5, 16.1, 14.3, –3.1, –3.3, –3.6, –3.7;

IR (film) 3455, 2956, 2929, 2858, 1472, 1388, 1255, 1095, 1044, 983, 906, 836, 812, 775, 674 cm^{-1};

HRMS (ESI+) calc. for $C_{33}H_{68}O_5Si_2Na$ $[M+Na]^+$ 623.4497. Found 623.4504.



Compound 14a
[Scheme 2, Step 6]

Benzyl acetal 14a: To a 25 mL round-bottom flask containing triol **14** under argon was added CH_2Cl_2 (7.2 mL, 0.02 M), 4Å molecular sieves (260 mg), benzaldehyde dimethyl acetal (0.064 mL, 0.429 mmol) and PTSA•H_2O (8.0 mg, 0.043 mmol). The reaction mixture was stirred at room temperature until no starting material remained by TLC, approximately 13 minutes. A saturated solution of $NaHCO_3$ (10 mL) was added to the reaction. The solution was diluted with H_2O (15 mL) and EtOAc (50 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 75 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–95:5 hexanes–ethyl acetate) provided benzyl acetal **14a** (95 mg, 0.138 mmol, 96%) as a viscous colorless oil.

For 1:1.6 diastereomeric mixture of benzyl acetal **14a**:

R_f 0.61 (6:1 hexanes-EtOAc);

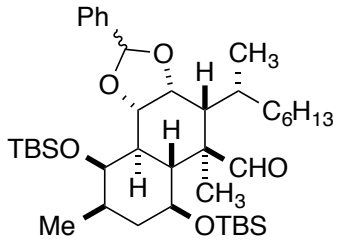
$[\alpha]^{D}_{23}$ +11.7 (c 0.78, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.53–7.28 ($m_{major/minor}$, 5H), 6.08 (s_{minor}, 1H), 5.79 (s_{major}, 1H), 4.43 (dd_{major}, J = 5.5, 3.2 Hz, 1H), 4.26 (dd_{minor}, J = 4.9, 3.0 Hz, 1H), 4.18–4.12 (m_{minor}, 1H), 4.06 (dd_{major}, J = 9.3, 5.6 Hz, 1H), 3.99 (bs_{minor}, 1H), 3.94–3.85 (m_{minor}, 1H), 3.87 (bs_{major}, 1H), 3.83 (ddd_{major}, J = 10.6, 9.1, 6.0 Hz, 1H), 3.63–3.45 ($m_{major/minor}$, 2H), 3.14–3.02 ($m_{major/minor}$, 1H), 2.17–1.96 ($m_{major/minor}$, 1H), 1.93–0.82 ($m_{major/minor}$, 22H), 1.10 (d_{major}, J = 6.8 Hz, 3H), 1.02 (s_{major}, 3H), 0.96 (s_{major}, 9H), 0.96 (s_{minor}, 9H), 0.93 (s_{minor}, 9H), 0.92 (s_{major}, 9H), 0.21 (s_{minor}, 3H), 0.20 (s_{major}, 3H), 0.17 (s_{major}, 3H), 0.15 (s_{major}, 3H), 0.15 (s_{minor}, 3H), 0.15 (s_{minor}, 3H), 0.11 (s_{minor}, 3H), 0.08 (s_{major}, 3H);

^{13}C-NMR (125 MHz, $CDCl_3$) δ 141.2, 139.5, 128.8, 128.4, 128.3, 126.7, 126.1, 103.6, 101.7, 77.9, 76.3, 75.2, 74.6, 71.6, 71.5, 69.9, 66.1, 46.6, 46.5, 44.9, 43.9, 43.6, 42.5, 41.9, 37.7, 37.6, 34.9, 34.8, 34.4, 34.3, 32.4, 32.2, 32.1, 31.9, 29.9, 29.8, 29.1, 26.6, 26.5, 22.9, 21.3, 21.1, 19.6, 18.9, 18.6, 15.9, 15.5, 14.4, –3.1, –3.2, –3.3, –3.5, –3.6;

IR (film) 3534, 2955, 2929, 2858, 1463, 1388, 1362, 1257, 1218, 1160, 1093, 1051, 1005, 987, 875, 836, 812, 774, 723, 692, 680, 634 cm^{-1};

HRMS (ESI+) calc. for $C_{40}H_{72}O_5Si_2Na$ $[M+Na]^+$ 711.4810. Found 711.4821.



Compound 15
[Scheme 3, Step 7]

Aldehyde 15: To a 25 mL round-bottom flask containing benzyl acetal **14a** (173 mg, 0.251 mmol) under argon was added CH_2Cl_2 (5.0 mL, 0.05 M) and powdered 4 Å molecular sieves (270 mg). The reaction mixture was cooled to 0 °C, followed by addition of NMO (60 mg, 0.512 mmol) and TPAP (10 mg, 0.244 mmol). The solution was warmed to room temperature and stirred for 24 h. The reaction mixture was diluted with EtOAc and filtered through a plug of silica gel using EtOAc as the eluent and concentrated in vacuo. The crude NMR still showed the presence of alcohol, therefore the crude mixture was resubjected under the same conditions as previously described. The resulting residue was then purified by flash chromatography (98:2–95:5 hexanes–ethyl acetate) to provide aldehyde **15** (168 mg, 0.244 mmol, 97%) as a viscous colorless oil.

For 1:1.6 diastereomeric mixture of aldehyde **15**:

R_f 0.56 & 0.48 (95:5 hexanes-EtOAc; developed 2x);

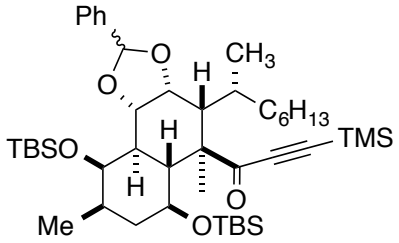
$[\alpha]^{D}_{23}$ +16.6 (c 0.93, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.42 (s_{major}, 1H), 9.41 (s_{minor}, 1H), 7.54–7.30 ($m_{major/minor}$, 5H), 6.09 (s_{minor}, 1H), 5.84 (s_{major}, 1H), 4.40 (dd_{major}, J = 5.3, 2.9 Hz, 1H), 4.28 (dd_{minor}, J = 9.3, 4.8 Hz, 1H), 4.23 (dd_{minor}, J = 4.7, 2.7 Hz, 1H), 4.14 (dd_{major}, J = 9.2, 5.3 Hz, 1H), 3.99 (bs_{minor}, 1H), 3.87 (bs_{major}, 1H), 3.64 (ddd_{minor}, J = 9.7, 9.7, 4.7 Hz, 1H), 3.55 (ddd_{major}, J = 10.2, 10.2, 4.7 Hz, 1H), 1.98–1.90 ($m_{major/minor}$, 1H), 1.80–0.84 ($m_{major/minor}$, 22H), 1.29 (s_{minor}, 3H), 1.23 (s_{major}, 3H), 0.97 ($s_{major/minor}$, 9H), 0.89 (s_{minor}, 9H), 0.87 (s_{major}, 9H), 0.82 (d_{major}, J = 6.6 Hz, 1H), 0.75 (d_{minor}, J = 6.6 Hz, 1H), 0.21 (s_{minor}, 3H), 0.19 (s_{major}, 3H), 0.12 (s_{minor}, 3H), 0.09 (s_{major}, 3H), 0.08 (s_{minor}, 3H), 0.07 (s_{minor}, 3H), 0.05 (s_{major}, 3H), 0.05 (s_{major}, 3H);

^{13}C-NMR (125 MHz, $CDCl_3$) δ 205.3, 140.5, 139.0, 128.8, 128.4, 128.3, 128.1, 126.4, 125.9, 103.6, 101.6, 76.5, 75.3, 74.0, 73.2, 72.3, 72.2, 70.0, 69.9, 49.8, 47.8, 47.6, 45.6, 45.5, 44.1, 41.4, 37.2, 37.1, 35.6, 35.5, 34.1, 34.0, 32.0, 31.9, 31.8, 29.7, 29.6, 27.4, 27.3, 26.4, 26.3, 26.1, 22.7, 21.4, 19.4, 18.7, 18.2, 14.1, 11.5, 11.3, –3.0, –3.3, –3.4, –3.9;

IR (film) 2955, 2929, 2857, 1727, 1471, 1463, 1407, 1384, 1361, 1254, 1218, 1155, 1137, 1095, 1065, 1006, 992, 940, 909, 870, 837, 812, 776, 724, 696 cm^{-1};

HRMS (ESI+) calc. for $C_{40}H_{70}O_5Si_2Na$ $[M+Na]^+$ 709.4654. Found 709.4651.



Compound 16
[Scheme 3, Step 9]

TMS–Ynone 16: To a flame-dried 50 mL round-bottom flask charged with a magnetic stir bar, evacuated and back-filled with argon was added trimethylsilyl acetylene (1.04 mL, 7.32 mmol) and THF (7.3 mL). The solution was cooled to –78 °C, followed by the addition of *n*-BuLi (3.47 mL, 6.11 mmol, 1.76 M) and the reaction was allowed to stir for 40 min at –78 °C. A THF (4.0 mL) solution of aldehyde **15** (168 mg, 0.244 mmol) was slowly added down the sides of the flask to the TMS lithium acetylide solution at – 78 °C. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stirred for 18 h. A saturated solution of NH_4Cl (15 mL) was added to the reaction at 0 °C. The solution was diluted with H_2O (25 mL) and EtOAc (75 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 75 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to provide a yellow oil. The crude product was used in the following reaction without purification. To a 50 mL round-bottom flask containing crude alcohol under argon was added CH_2Cl_2 (12.2 mL, 0.02 M). The reaction was cooled to 0 °C, followed by the addition of $NaHCO_3$ (210 mg, 2.44 mmol) and Dess-Martin periodinane (311 mg, 0.732 mmol) to the reaction mixture. The solution was warmed to room temperature and stirred for 20 h. The mixture was cooled to 0 °C and saturated $NaHCO_3$ (15 mL) and saturated $Na_2S_2O_3$ (20 mL) were added. The mixture was warmed to room temperature and stirred for 15 min. The solution was diluted with H_2O (15 mL) and Et_2O (70 mL). The layers were then separated and the aqueous layer was extracted with Et_2O (2 x 75 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–95:5 hexanes–ethyl acetate) provided TMS–ynone **16** (175 mg, 0.223 mmol, 92% over 2 steps) as a viscous colorless oil.

For 1:1.3 diastereomeric mixture of TMS–ynone **16**:

R_f 0.63 & 0.57 (95:5 hexanes-EtOAc; developed 2x);

$[\alpha]^{D}_{23}$ +30.4 (c 0.57, CH_2Cl_2);

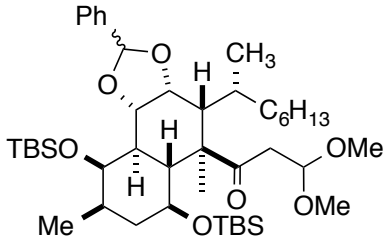
^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.47–7.30 ($m_{major/minor}$, 5H), 6.09 (s_{minor}, 1H), 5.83 (s_{major}, 1H), 4.40 (dd_{major}, J = 5.2, 3.0 Hz, 1H), 4.29 (dd_{minor}, J = 9.4, 4.6 Hz, 1H), 4.22 (dd_{minor} , J = 4.7, 2.7 Hz, 1H), 4.18 (dd_{major}, J = 9.1, 5.1 Hz, 1H), 4.01 (bs_{minor}, 1H), 3.89 (bs_{major}, 1H), 3.56 (ddd_{minor}, J = 10.2, 10.2, 4.4 Hz, 1H), 3.46 (ddd_{major}, J = 10.3, 10.3, 4.5 Hz, 1H), 2.52–2.41 ($m_{major/minor}$, 1H), 2.04 (dd_{major}, J = 2.9, 2.9 Hz, 1H), 1.94 (dd_{minor}, J = 2.3, 2.3 Hz, 1H), 1.85–1.75 ($m_{major/minor}$, 1H), 1.70–0.81 ($m_{major/minor}$, 23H), 1.26 (s_{minor}, 3H),

1.20 (s_{major}, 3H), 1.00 (s_{major}, 9H), 0.99 (s_{minor}, 9H), 0.89 (s_{minor}, 9H), 0.87 (s_{major}, 9H), 0.23 (s_{minor}, 3H), 0.22 (s_{major}, 3H), 0.21 (s_{major}, 9H), 0.19 (s_{minor}, 9H), 0.13 (s_{minor}, 3H), 0.11 (s_{major}, 3H), 0.06 (s_{minor}, 3H), 0.03 (s_{minor}, 3H), 0.02 (s_{major}, 3H), 0.00 (s_{major}, 3H);

^{13}C-NMR (125 MHz, $CDCl_3$) δ 191.5, 140.6, 139.1, 128.7, 128.3, 128.1, 126.3, 125.9, 103.8, 101.9, 101.8, 96.9, 75.8, 75.7, 74.4, 72.6, 72.1, 71.9, 70.1, 70.0, 53.6, 47.0, 46.9, 46.8, 46.6, 44.8, 42.3, 37.6, 37.5, 35.5, 34.6, 32.6, 32.1, 32.0, 29.7, 29.6, 28.5, 26.5, 26.3, 22.7, 22.6, 21.3, 19.6, 19.5, 18.7, 18.2, 14.2, 11.4, 11.3, –0.6, –2.8, –3.7, –3.8, –4.1;

IR (film) 2956, 2928, 2857, 1672, 1463, 1407, 1385, 1360, 1252, 1155, 1133, 1096, 1179, 1067, 1005, 940, 840, 812, 775, 697, 677, 629, 574 cm^{-1};

HRMS (ESI+) calc. for $C_{45}H_{78}O_5Si_2Na$ $[M+Na]^+$ 805.5049. Found 805.5090.



Compound 16a
[Scheme 3, Step 10]

Dimethyl Acetal 16a: To a culture tube containing TMS–ynone **16** (98 mg, 0.125 mmol) under argon was added anhydrous MeOH (6.3 mL, 0.02 M) and K_2CO_3 (346 mg, 2.50 mmol). The reaction was heated to 65 °C and stirred for 20 h. The solution was cooled to room temperature and diluted with H_2O (50 mL) and EtOAc (100 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with H_2O (1 x 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–95:5 hexanes–ethyl acetate) provided dimethyl acetal **16a** (95 mg, 0.123 mmol, 98%) as a viscous colorless oil.

For 1:1.6 diastereomeric mixture of dimethyl acetal **16a**:

R_f 0.67 (6:1 hexanes-EtOAc);

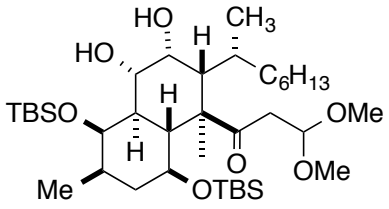
$[\alpha]^{D}_{23}$ +28.9 (c 0.71, CH_2Cl_2);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.49–7.30 ($m_{major/minor}$, 5H), 6.08 (s_{minor}, 1H), 5.84 (s_{major}, 1H), 4.97–4.92 ($m_{major/minor}$, 1H), 4.40 (dd_{major}, J = 5.0, 2.8 Hz, 1H), 4.28–4.21 (m_{minor}, 1H), 4.28–4.21 (m_{minor}, 1H), 4.13 (dd_{major}, J = 9.1, 5.1 Hz, 1H), 4.01 (bs_{minor}, 1H), 3.89 (bs_{major}, 1H), 3.63 (m_{minor}, 1H), 3.50–3.38 (m_{major}, 1H), 3.41 (s_{major}, 3H), 3.39 (s_{minor}, 3H), 3.33 (s_{major}, 3H), 3.32 (s_{minor}, 3H), 3.00–2.88 ($m_{major/minor}$, 1H), 2.88–2.79 ($m_{major/minor}$, 1H), 2.30–2.19 ($m_{major/minor}$, 1H), 1.92–1.79 ($m_{major/minor}$, 1H), 1.71–0.79 ($m_{major/minor}$, 24H), 1.28 (s_{minor}, 3H), 1.23 (s_{major}, 3H), 0.99 (s_{major}, 9H), 0.98 (s_{minor}, 9H), 0.87 (s_{minor}, 9H), 0.85 (s_{major}, 9H), 0.21 ($s_{major/minor}$, 3H), 0.13 (s_{minor}, 3H), 0.11 (s_{major}, 3H), 0.05 (s_{minor}, 3H), 0.05 (s_{minor}, 3H), 0.02 (s_{major}, 3H), 0.02 (s_{major}, 3H);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 209.7, 209.6, 140.7, 139.2, 128.8, 128.5, 128.4, 128.3, 126.4, 126.0, 104.0, 103.4, 102.1, 77.4, 76.0, 75.7, 74.7, 73.1, 73.0, 72.6, 70.7, 70.5, 56.5, 56.4, 53.6, 53.0, 46.7, 46.6, 45.4, 44.2, 43.9, 42.7, 41.4, 38.6, 38.5, 35.9, 35.8, 34.9, 34.8, 32.6, 32.5, 32.2, 32.1, 29.9, 29.8, 29.2, 29.1, 26.5, 26.4, 22.8, 21.0, 20.9, 19.5, 18.8, 18.5, 18.4, 14.3, 12.5, 12.4, –2.6, –3.7, –3.8, –4.3;

IR (film) 2955, 2929, 2857, 1708, 1463, 1385, 1294, 1254, 1218, 1154, 1125, 1195, 1095, 1064, 1006, 947, 870, 812, 777, 744, 696, 671, 575 cm^{-1};

HRMS (ESI+) calc. for $C_{44}H_{78}O_7Si_2Na$ [M+Na]+ 797.5178. Found 797.5181.



Compound 17
[Scheme 3, Step 11]

Diol 17: To a 50 mL round-bottom flask containing benzyl acetal **16a** (95 mg, 0.123 mmol) dissolved in EtOAc (9.4 mL, 0.013 M) was added Pd/C (206 mg, 5% w/w). The mixture was degassed by applying vacuum and backfilling with argon before charging the flask with hydrogen using vacuum and backfilling from a balloon. The mixture was then stirred vigorously under a hydrogen filled balloon for 18 h. The balloon was removed and the mixture was purged of hydrogen by applying vacuum and back filling with argon several times. The reaction mixture was diluted with EtOAc and filtered through a plug of silica gel using EtOAc as the eluent and concentrated in vacuo. Purification by flash chromatography (95:5–6:1 hexanes–ethyl acetate) provided diol **17** (76 mg, 0.111 mmol, 90%) as a white solid.

For diol **17**:

R_f 0.38 (6:1 hexanes-EtOAc);

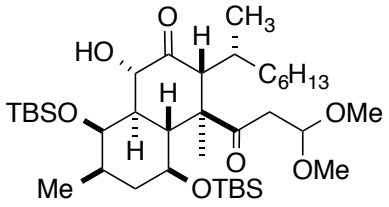
$[\alpha]^{D}_{23}$ +40.4 (c 0.75, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.91 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.19 (bs, 1H), 4.06 (bs, 1H), 3.53 (ddd, *J* = 10.1, 10.1, 4.9 Hz, 1H), 3.45 (ddd, *J* = 11.2, 8.6, 3.2 Hz, 1H), 3.36 (s, 3H), 3.28 (s, 3H), 2.90 (dd, *J* = 16.9, 8.3 Hz, 1H), 2.74 (dd, *J* = 16.9, 1.8 Hz, 1H), 2.32 (dd, *J* = 11.0, 11.0 Hz, 1H), 2.06 (d, *J* = 8.6 Hz, 1H), 1.92 (d, *J* = 3.1 Hz, 1H), 1.88 (ddd, *J* = 11.2, 11.2, 4.5 Hz, 1H), 1.71–0.80 (m, 24H), 0.96 (s, 9H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.83 (s, 9H), 0.15 (s, 3H), 0.09 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H);

^{13}C-NMR (125 MHz, $CDCl_3$) δ 209.9, 103.2, 72.8, 71.0, 69.8, 56.2, 54.3, 52.5, 48.5, 44.0, 43.7, 41.2, 38.6, 35.7, 35.2, 32.4, 32.1, 29.9, 29.3, 26.5, 26.3, 22.8, 20.9, 19.5, 18.9, 18.4, 14.2, 13.6, –3.3, –3.8, –3.9, –4.2;

IR (film) 3483, 2955, 2929, 2858, 1706, 1463, 1380, 1255, 1193, 1125, 1096, 1061, 1038, 1006, 985, 948, 885, 837, 813, 777, 679 cm^{-1};

HRMS (ESI+) calc. for $C_{37}H_{74}O_7Si_2Na$ $[M+Na]^+$ 709.4865. Found 709.4899.



Compound 19
[Scheme 3, Step 1]

Ketol 19: To a culture tube containing diol **17** (35 mg, 0.051 mmol) under argon was added anhydrous DMSO (5.1 mL, 0.01 M) and IBX (143 mg, 0.509 mmol). The reaction was stirred at room temperature for 16 h. The reaction mixture was diluted with H_2O (20 mL) and EtOAc (50 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with H_2O (2 x 30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (98:2–9:1 hexanes–ethyl acetate) provided ketol **19** (31 mg, 0.045 mmol, 89%) as a viscous colorless oil.

For ketol **19**:

R_f 0.69 (4:1 hexanes-EtOAc);

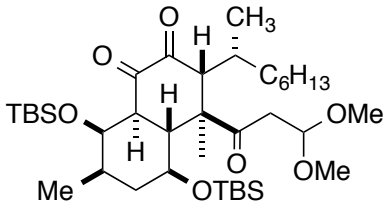
$[\alpha]^{D}_{23}$ –2.9 (c 0.75, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.94 (dd, *J* = 8.1, 1.9 Hz, 1H), 4.03 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.98 (bs, 1H), 3.57 (d, *J* = 3.5 Hz, 1H), 3.47 (ddd, *J* = 9.8, 9.8, 4.7 Hz, 1H), 3.38 (s, 3H), 3.34 (s, 3H), 3.05 (dd, *J* = 17.0, 8.2 Hz, 1H), 2.95 (dd, *J* = 17.0, 2.0 Hz, 1H), 2.57 (bs, 1H), 1.69– 0.79 (m, 24H), 1.01 (s, 9H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.86 (s, 9H), 0.15 (s, 3H), 0.12 (s, 3H), 0.03 (s, 3H), 0.01 (s, 3H);

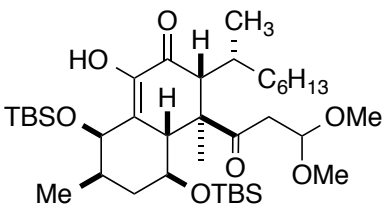
^{13}C-NMR (125 MHz, $CDCl_3$) δ 211.3, 205.3, 102.9, 73.9, 72.9, 70.8, 58.7, 57.9, 56.2, 53.7, 53.0, 44.7, 41.2, 38.8, 35.9, 32.9, 32.2, 31.4, 29.7, 29.2, 26.5, 26.3, 22.9, 20.2, 19.3, 18.8, 18.4, 14.3, 12.1, –3.0, –3.7, –4.3, –4.4;

IR (film) 3479, 2955, 2929, 2857, 1716, 1463, 1385, 1298, 1254, 1164, 1125, 1061, 1039, 1007, 988, 876 cm^{-1};

HRMS (ESI+) calc. for $C_{37}H_{72}O_7Si_2Na$ $[M+Na]^+$ 707.4709. Found 707.4681.



Compound 20
[Scheme 3, Step 2]



Compound 21
[Scheme 3, Step 2]

Diketone 20/Keto-Enol 21: To a culture tube containing ketol **19** (15 mg, 0.219 mmol) under argon was added CH_2Cl_2 (2.7 mL, 0.008 M), sodium acetate (23 mg, 0.280 mmol) and powdered 4 Å molecular sieves (100 mg). The reaction mixture was stirred for 5 min and then PCC (23 mg, 0.105 mmol) was added. The reaction was stirred until no starting material remained by TLC. The reaction mixture was diluted with Et_2O and filtered through a plug of silica gel using Et_2O as the eluent and concentrated in vacuo. The resulting residue was then purified by flash chromatography (98:2–9:1 hexanes–ethyl acetate) to provide keto-enol **21** (12 mg, 0.176 mmol, 80%) as a colorless oil.

For diketone **20**:

R_f 0.60 (6:1 hexanes-EtOAc);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.98 (dd, *J* = 6.5, 3.6 Hz, 1H), 4.50 (bs, 1H), 3.57 (ddd, *J* = 9.4, 9.4, 3.6 Hz, 1H), 3.41 (s, 3H), 3.34 (s, 3H), 3.24 (dd, *J* = 11.6, 9.8 Hz, 1H), 3.07–3.01 (m, 2H), 2.82 (bs, 1H), 2.16 (dd, *J* = 11.6, 1.2 Hz, 1H), 1.69–0.77 (m, 26H), 0.90 (s, 9H), 0.88 (s, 9H), 0.13 (s, 3H), 0.07 (s, 3H), 0.05 (s, 3H), –0.02 (s, 3H).

For keto-enol **21**:

R_f 0.60 (6:1 hexanes-EtOAc);

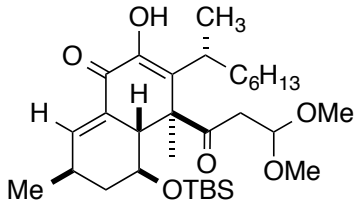
$[\alpha]^{D}_{23}$ –7.1 (c 0.38, CH_2Cl_2);

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.23 (s, 1H), 4.93 (dd, *J* = 7.7, 2.3 Hz, 1H), 4.72 (d, *J* = 1.9 Hz, 1H), 3.63 (ddd, *J* = 10.9, 10.9, 3.7 Hz, 1H), 3.40 (s, 3H), 3.36 (s, 3H), 3.27 (d, *J* = 10.0 Hz, 1H), 3.00 (dd, *J* = 16.9, 7.8 Hz, 1H), 2.88 (dd, *J* = 17.0, 2.4 Hz, 1H), 2.60 (s, 1H), 1.78–0.84 (m, 27H), 1.15 (s, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), –0.06 (s, 3H);

13C-NMR (125 MHz, $CDCl_3$) δ 206.9, 194.9, 141.6, 125.3, 103.2, 72.6, 66.9, 56.2, 54.6, 53.8, 46.0, 42.4, 37.2, 34.3, 33.5, 32.1, 31.8, 29.9, 29.8, 29.4, 26.3, 25.9, 22.9, 21.9, 18.5, 18.4, 17.8, 14.3, 14.2, –3.6, –3.9, –4.7, –5.1;

IR (film) 3411, 2955, 2929, 2857, 1712, 1685, 1663, 1463, 1377, 1289, 1258, 1201, 1124, 1090, 1056, 1028, 938, 889, 836, 814, 778, 720, 666 cm^{-1};

HRMS (ESI+) calc. for $C_{37}H_{70}O_7Si_2Na$ $[M+Na]^+$ 705.4552. Found 705.4540.



Compound 27
[Scheme 3, Step 3]

Keto-enol 27: To a plastic culture tube containing keto-enol **21** (4 mg, 0.0059 mmol) was added THF (0.700 mL, 0.008 M). The reaction was cooled to 0 °C and HF•pyridine (0.050 mL of a 70% HF/30% pyridine) was added dropwise. The reaction was stirred for 72 h at room temperature. A saturated solution of $NaHCO_3$ (5 mL) was added to the reaction mixture at 0 °C. The solution was diluted with H_2O (10 mL) and EtOAc (30 mL). The layers were then separated and the aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Purification by flash chromatography (9:1–6:1 hexanes–ethyl acetate) provided keto-enol **27** (1.0 mg, 0.0018 mmol, 31%; at 50% conversion) as a colorless oil.

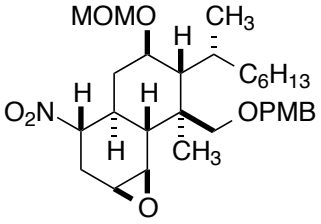
For keto-enol **27**:

R_f 0.55 (6:1 hexanes-EtOAc);

^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.97–6.94 (m, 1H), 6.59 (s, 1H), 4.91 (dd, *J* = 7.1, 3.1 Hz, 1H), 3.93 (ddd, *J* = 11.8, 9.0, 3.2 Hz, 1H), 3.43 (s, 3H), 3.36 (s, 3H), 3.27–3.20 (m, 1H), 3.09 (dd, *J* = 17.7, 3.1 Hz, 1H), 2.97 (dd, *J* = 17.6, 7.2 Hz, 1H), 2.53–2.40 (m, 1H), 2.02 (ddd, *J* = 13.0, 4.4, 4.4 Hz, 1H), 1.95–1.78 (m, 2H), 1.43–1.04 (m, 16H), 1.13 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.87 (t, 7.1 Hz, 3H), 0.09 (s, 3H), 0.07 (s, 3H);

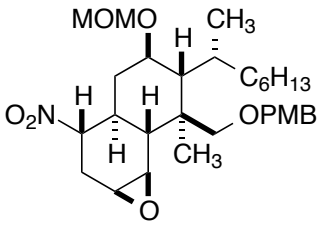
HRMS (ESI+) calc. for $C_{31}H_{54}O_6SiNa$ $[M+Na]^+$ 573.3582. Found 573.3560.

	Parameter	Value
1	Title	jck-3-295
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	48
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0031
13	Acquisition Date	2006-11-13T09:17:05
14	Spectrometer Frequency	400.12
15	Spectral Width	6402.0
16	Lowest Frequency	-809.0
17	Nucleus	1H
18	Acquired Size	12824
19	Spectral Size	65536



Compound 5
[Scheme 1, Step 1]

	Parameter	Value
1	Title	jck-3-295-c13dept135sp2
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	c13dept
8	Number of Scans	1400
9	Receiver Gain	60
10	Relaxation Delay	0.6000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2006-11-13T19:03:06
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1496.8
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768

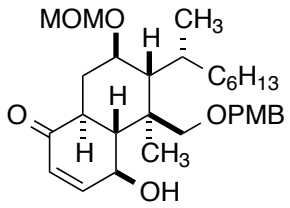


Compound 5
[Scheme 1, Step 1]

159.34 130.39 129.40 113.85 97.36 86.94 77.47 77.15 76.83 75.43 72.86 71.76 56.20 55.39 53.17 52.15 49.07 44.86 42.21 34.49 34.21 33.26 32.47 32.17 30.88 29.80 29.27 22.81 21.28 16.55 14.27

f1 (ppm)

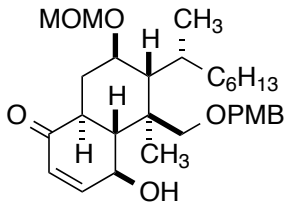
	Parameter	Value
1	Title	jck-4-207
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	8
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2008-02-15T15:59:38
14	Spectrometer Frequency	399.71
15	Spectral Width	6000.6
16	Lowest Frequency	-993.2
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 6
[Scheme 1, Step 2]

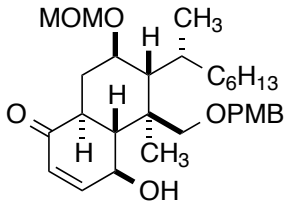
199.39 159.60 152.98 129.78 128.99 126.81 113.98 95.57 77.47 77.15 76.83 75.19 74.85 73.11 66.70 56.12 55.27 53.17 51.71 43.43 41.59 32.63 32.58 32.00 31.57 29.84 28.86 22.70 22.64 14.17 13.11

	Parameter	Value
1	Title	jck-4-207-13Cdept135
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	c13dept
8	Number of Scans	1024
9	Receiver Gain	20
10	Relaxation Delay	0.6000
11	Pulse Width	0.0000
12	Acquisition Time	1.1994
13	Acquisition Date	2008-02-15T17:03:20
14	Spectrometer Frequency	100.52
15	Spectral Width	25000.0
16	Lowest Frequency	-3005.4
17	Nucleus	13C
18	Acquired Size	29984
19	Spectral Size	65536



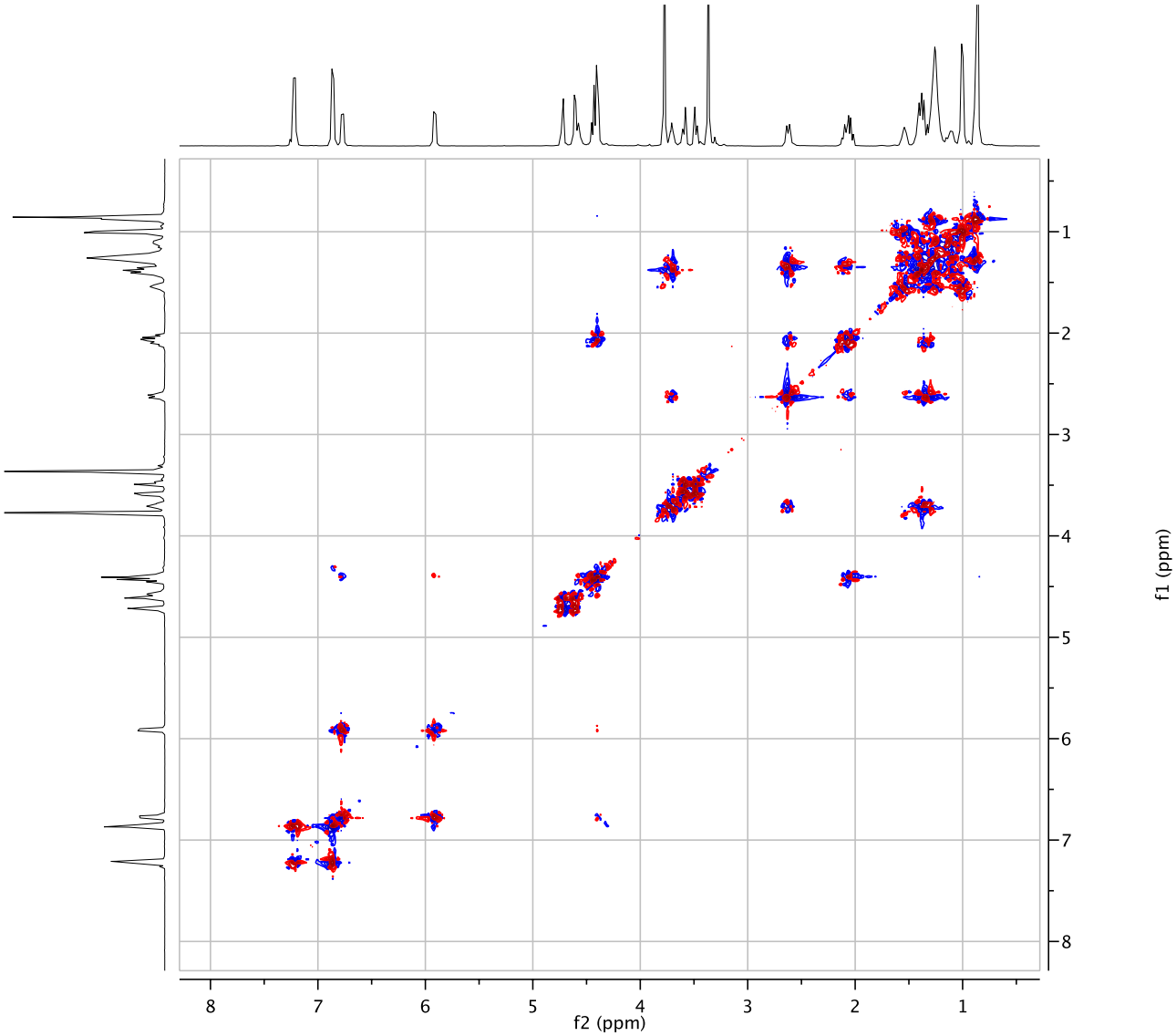
Compound 6
[Scheme 1, Step 2]

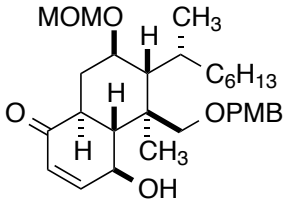
f1 (ppm)



Compound 6
[Scheme 1, Step 2]

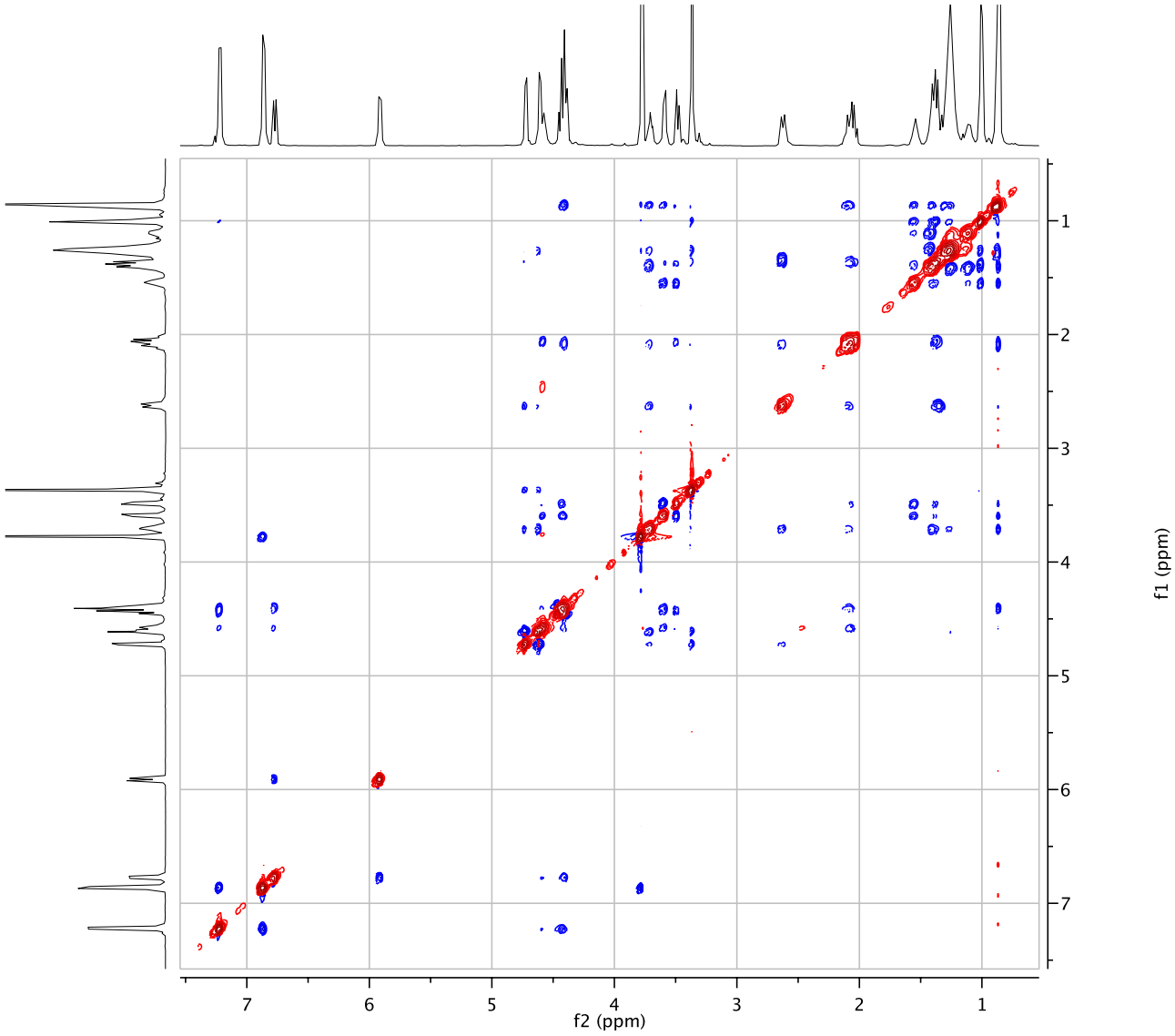
	Parameter	Value
1	Title	jck-4-207-2dgdqcosy
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	d2o
6	Temperature	25.0
7	Pulse Sequence	iugdqcosy
8	Number of Scans	4
9	Receiver Gain	20
10	Relaxation Delay	1.0000
11	Pulse Width	670.0000
12	Acquisition Time	0.1277
13	Acquisition Date	2008-02-15T01:48:51
14	Spectrometer Frequency	(499.81, 499.81)
15	Spectral Width	(4009.8, 4009.8)
16	Lowest Frequency	(132.7, 132.7)
17	Nucleus	(1H, 1H)
18	Acquired Size	(512, 200)
19	Spectral Size	(512, 512)



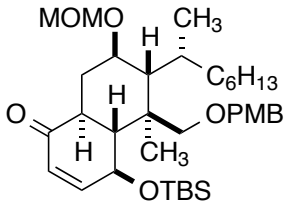


Compound 6
[Scheme 1, Step 2]

	Parameter	Value
1	Title	jck-4-207-noesy
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	d2o
6	Temperature	25.0
7	Pulse Sequence	iunoesy
8	Number of Scans	4
9	Receiver Gain	20
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.2554
13	Acquisition Date	2008-02-15T02:58:38
14	Spectrometer Frequency	(499.81, 499.81)
15	Spectral Width	(4009.8, 4009.8)
16	Lowest Frequency	(132.7, 132.7)
17	Nucleus	(1H, 1H)
18	Acquired Size	(1024, 200)
19	Spectral Size	(1024, 1024)

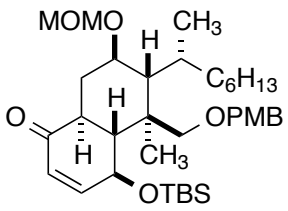


	Parameter	Value
1	Title	jck-3-117-1H
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	20
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0029
13	Acquisition Date	2005-09-24T23:08:46
14	Spectrometer Frequency	400.12
15	Spectral Width	3019.6
16	Lowest Frequency	11.8
17	Nucleus	1H
18	Acquired Size	6048
19	Spectral Size	65536



Compound 6a
[Scheme 1, Step 6]

	Parameter	Value
1	Title	jck-3-117-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	6000
9	Receiver Gain	60
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2005-09-24T23:12:33
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1491.5
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768



Compound 6a
[Scheme 1, Step 6]

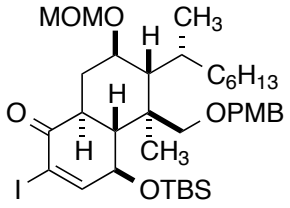
199.91 159.11 155.81 131.31 129.11 126.90 113.80 96.22 77.52 77.40 77.20 76.88 76.30 73.49 72.63 72.10 56.46 55.46 50.24 49.38 44.39 44.28 32.81 32.76 32.23 31.41 30.17 29.90 29.19 26.27 23.32 22.89 18.31 14.32 13.50 3.08 -3.81

3000 2500 2000 1500 1000 500 0

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

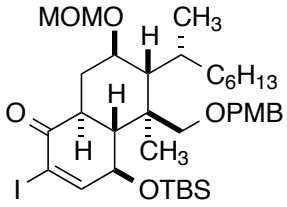
f1 (ppm)

	Parameter	Value
1	Title	jck-4-86
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	36
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0031
13	Acquisition Date	2007-03-20T18:03:47
14	Spectrometer Frequency	400.12
15	Spectral Width	6402.0
16	Lowest Frequency	-810.0
17	Nucleus	1H
18	Acquired Size	12824
19	Spectral Size	65536



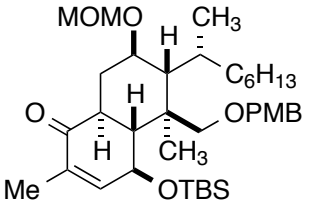
Compound 7
[Scheme 1, Step 4]

	Parameter	Value
1	Title	jck-4-86-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	1489
9	Receiver Gain	60
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2007-03-20T18:08:37
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1503.6
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768



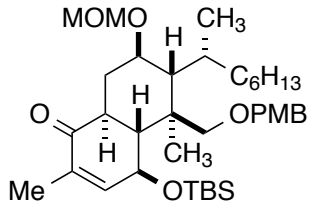
Compound 7
[Scheme 1, Step 4]

	Parameter	Value
1	Title	jck-4-69
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	32
9	Receiver Gain	48
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0031
13	Acquisition Date	2007-02-13T11:08:00
14	Spectrometer Frequency	400.12
15	Spectral Width	6402.0
16	Lowest Frequency	-810.4
17	Nucleus	1H
18	Acquired Size	12824
19	Spectral Size	65536



Compound 8
[Scheme 1, Step 5]

	Parameter	Value
1	Title	jck-4-69-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	15000
9	Receiver Gain	60
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2007-02-13T20:27:26
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1524.4
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768



Compound 8
[Scheme 1, Step 5]

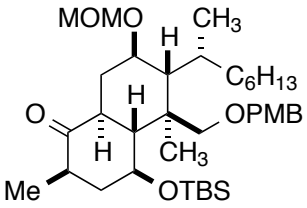
200.01 159.02 150.67 133.09 131.31 129.04 113.72 96.25 77.47 77.35 77.16 76.84 76.49 73.52 72.57 71.77 56.34 55.41 50.09 49.46 44.15 44.03 33.13 32.79 32.18 31.30 30.13 29.86 29.15 26.28 23.30 22.84 18.29 15.46 14.28 13.48 -3.09 -3.76

5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

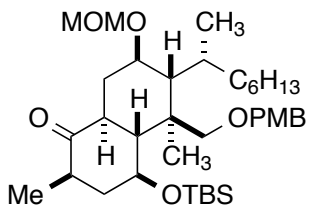
f1 (ppm)

	Parameter	Value
1	Title	jck-4-89
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	20
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0032
13	Acquisition Date	2007-04-06T21:15:02
14	Spectrometer Frequency	400.12
15	Spectral Width	3507.4
16	Lowest Frequency	-319.6
17	Nucleus	1H
18	Acquired Size	7026
19	Spectral Size	65536

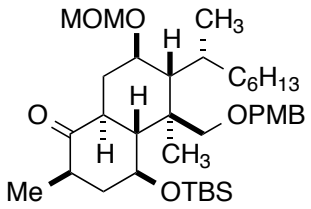


Compound 9
[Scheme 1, Step 6]

	Parameter	Value
1	Title	jck-4-89-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	11740
9	Receiver Gain	60
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2007-04-06T21:22:58
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1497.5
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768

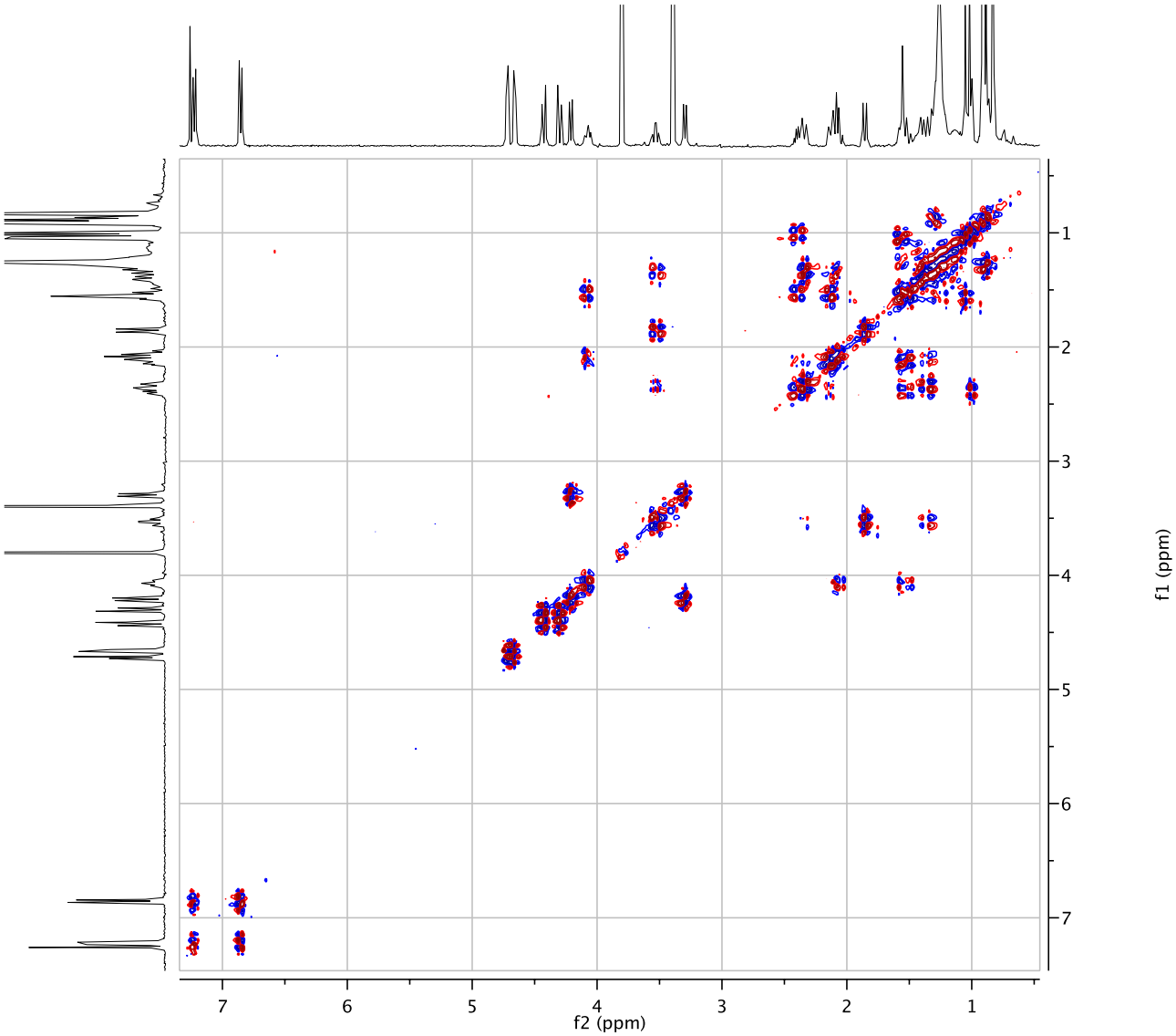


Compound 9
[Scheme 1, Step 6]

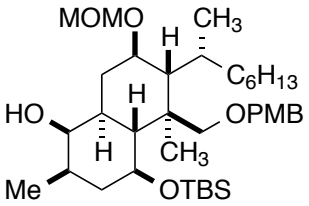


Compound 9
[Scheme 1, Step 6]

	Parameter	Value
1	Title	jck-4-89-2dgdqcosy
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gDQCOSY
8	Number of Scans	8
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1460
13	Acquisition Date	2007-04-07T01:48:46
14	Spectrometer Frequency	(400.12, 400.12)
15	Spectral Width	(3507.4, 3507.4)
16	Lowest Frequency	(-319.6, -319.6)
17	Nucleus	(1H, 1H)
18	Acquired Size	(512, 200)
19	Spectral Size	(512, 512)

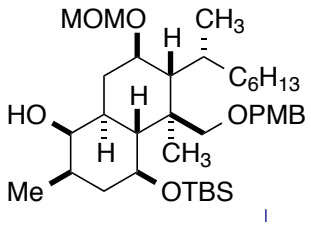


	Parameter	Value
1	Title	jck-4-204-B
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	52
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2008-02-18T11:36:43
14	Spectrometer Frequency	399.71
15	Spectral Width	6000.6
16	Lowest Frequency	-993.5
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 9a
[Scheme 1, Step 7]

	Parameter	Value
1	Title	jck-4-204-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	d2o
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	15000
9	Receiver Gain	30
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.3005
13	Acquisition Date	2008-02-19T07:58:51
14	Spectrometer Frequency	125.69
15	Spectral Width	30165.9
16	Lowest Frequency	-1887.0
17	Nucleus	13C
18	Acquired Size	39230
19	Spectral Size	131072

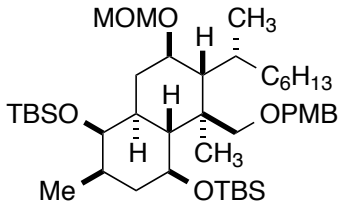


Compound 9a
[Scheme 1, Step 7]

158.87 131.77 129.05 113.63 96.48 77.63 77.36 77.11 76.90 76.86 75.14 74.63 74.22 72.51 56.04 55.38 50.76 43.48 41.89 39.64 39.60 37.27 35.10 32.87 32.14 31.45 30.12 29.82 29.08 26.38 23.18 22.80 18.35 17.83 14.24 13.06 -3.35 -3.73

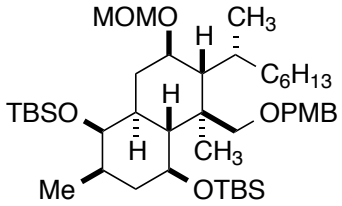
f1 (ppm)

	Parameter	Value
1	Title	jck-4-227-A
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	4
9	Receiver Gain	46
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2008-03-28T22:02:43
14	Spectrometer Frequency	399.71
15	Spectral Width	6000.6
16	Lowest Frequency	-993.2
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 10
[Scheme 1, Step 8]

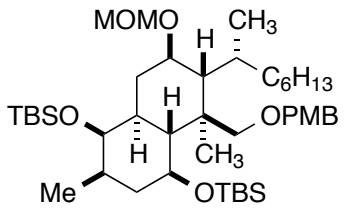
	Parameter	Value
1	Title	jck-4-227-A-13Cdept135
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	c13dept
8	Number of Scans	8192
9	Receiver Gain	20
10	Relaxation Delay	0.6000
11	Pulse Width	0.0000
12	Acquisition Time	0.6554
13	Acquisition Date	2008-03-29T03:58:52
14	Spectrometer Frequency	100.52
15	Spectral Width	25000.0
16	Lowest Frequency	-2989.2
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768



Compound 10
[Scheme 1, Step 8]

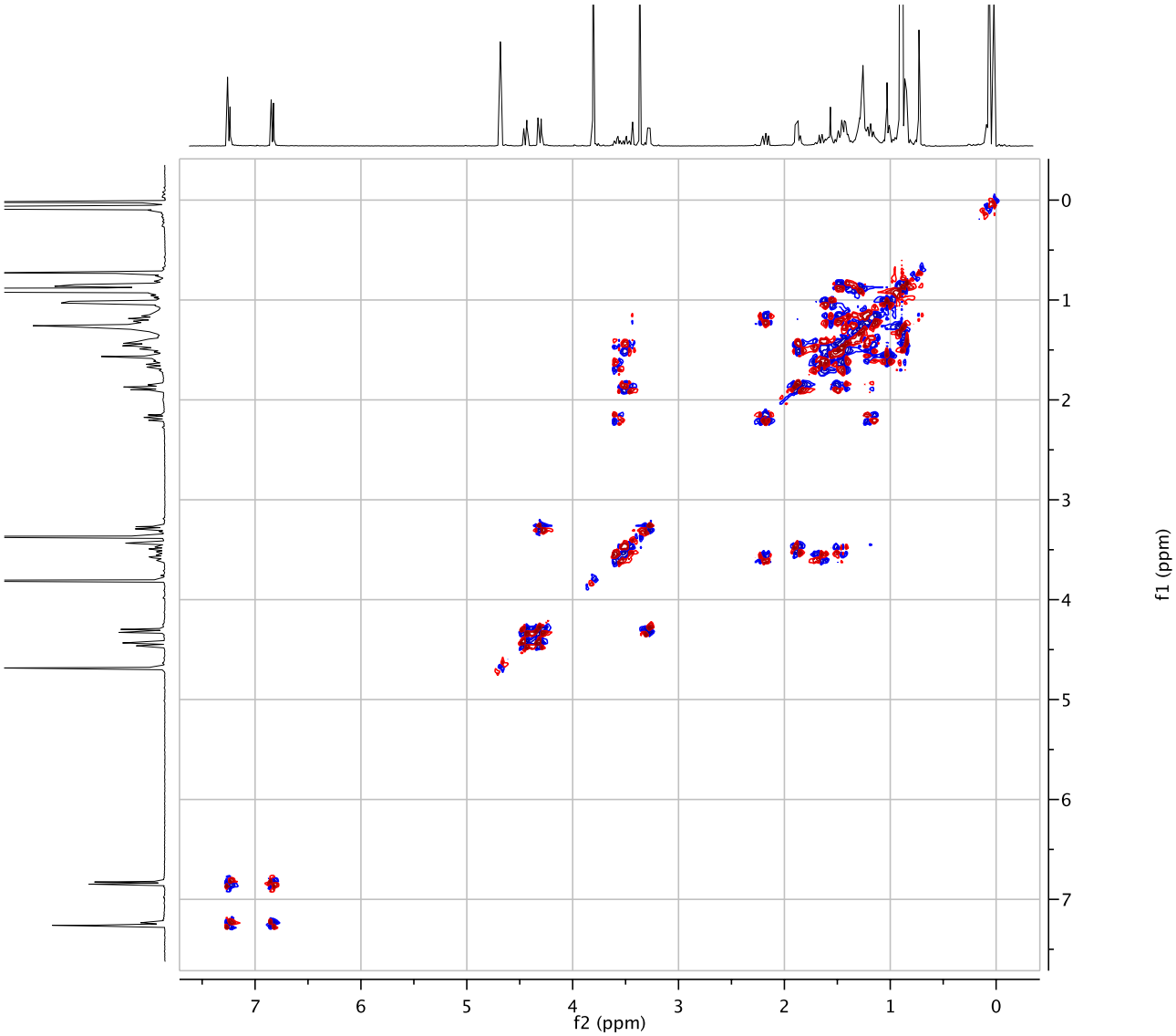
158.68
132.38
128.70
128.63
113.61
96.93
78.75
77.53
77.41
77.21
76.90
76.34
75.37
74.37
72.31
56.05
55.47
50.72
43.61
41.61
41.09
40.07
39.05
36.43
33.09
32.26
31.69
30.29
29.91
29.26
26.53
23.40
22.92
19.39
18.74
18.49
14.35
13.09
-2.81
-3.09
-3.33
-3.37

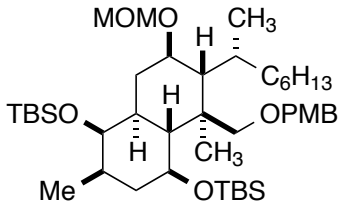
f1 (ppm)



Compound 10
[Scheme 1, Step 8]

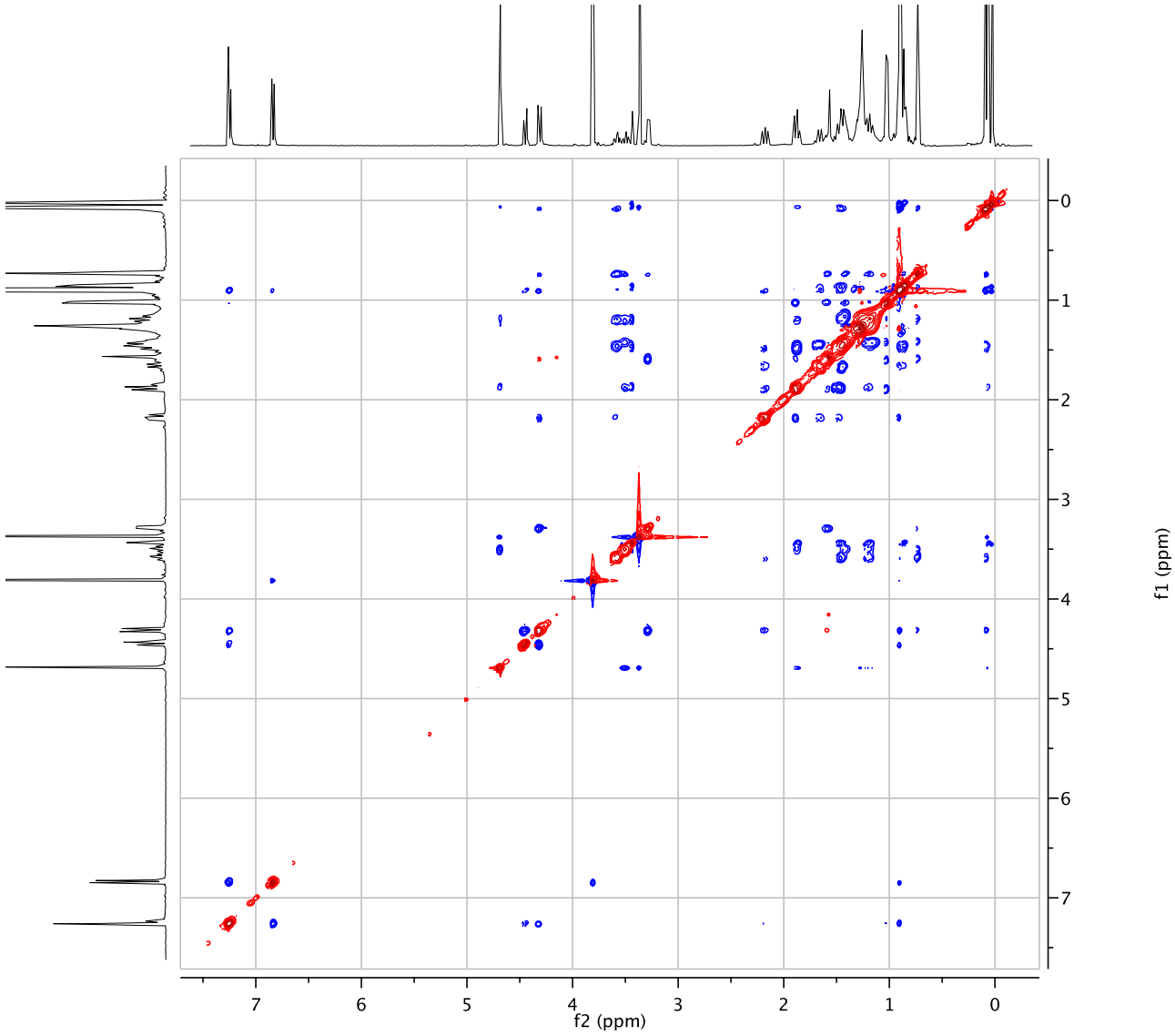
	Parameter	Value
1	Title	jck-4-227-A-2dgdqcosy
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gDQCOSY
8	Number of Scans	4
9	Receiver Gain	48
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1571
13	Acquisition Date	2008-03-31T22:45:36
14	Spectrometer Frequency	(400.12, 400.12)
15	Spectral Width	(3258.1, 3258.1)
16	Lowest Frequency	(-171.6, -171.6)
17	Nucleus	(1H, 1H)
18	Acquired Size	(512, 200)
19	Spectral Size	(512, 512)



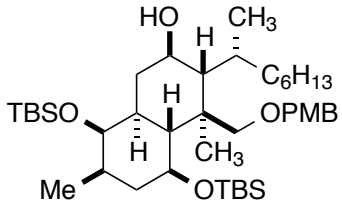


Compound 10
[Scheme 1, Step 8]

	Parameter	Value
1	Title	jck-4-227-A-noesy
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	iunoesy
8	Number of Scans	4
9	Receiver Gain	48
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.3143
13	Acquisition Date	2008-03-31T23:57:02
14	Spectrometer Frequency	(400.12, 400.12)
15	Spectral Width	(3258.1, 3258.1)
16	Lowest Frequency	(-171.6, -171.6)
17	Nucleus	(1H, 1H)
18	Acquired Size	(1024, 200)
19	Spectral Size	(1024, 1024)

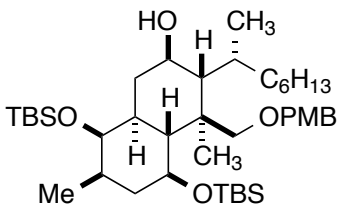


	Parameter	Value
1	Title	jck-4-246-C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	58
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2008-05-28T14:13:49
14	Spectrometer Frequency	400.11
15	Spectral Width	6000.6
16	Lowest Frequency	-992.1
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 11
[Scheme 2, Step 1]

	Parameter	Value
1	Title	JCK-4-235-B-13C
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	24000
9	Receiver Gain	60
10	Relaxation Delay	1.5000
11	Pulse Width	0.0000
12	Acquisition Time	0.6554
13	Acquisition Date	2008-05-05T08:10:34
14	Spectrometer Frequency	100.52
15	Spectral Width	25000.0
16	Lowest Frequency	-2989.2
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768

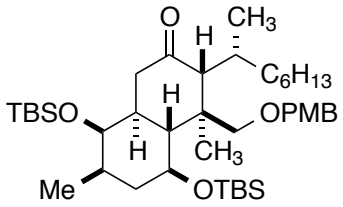


Compound 11
[Scheme 2, Step 1]

158.73 132.30 128.64 113.63 77.52 77.41 77.32 77.21 76.89 76.20 75.36 74.32 72.34 69.98 55.48 53.07 43.71 42.06 41.63 41.39 40.12 36.42 33.19 32.27 31.39 30.18 29.91 29.20 26.53 23.99 22.92 19.34 18.76 18.50 14.33 13.08 -2.82 -2.98 -3.36

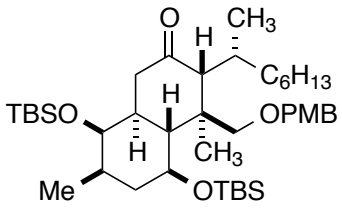
f1 (ppm)

	Parameter	Value
1	Title	jck-4-252-A
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	16
9	Receiver Gain	58
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2008-05-29T16:03:22
14	Spectrometer Frequency	400.11
15	Spectral Width	6000.6
16	Lowest Frequency	-992.3
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 12
[Scheme 2, Step 2]

	Parameter	Value
1	Title	jck-4-252-A-13Cdept135
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	c13dept
8	Number of Scans	18000
9	Receiver Gain	20
10	Relaxation Delay	0.6000
11	Pulse Width	0.0000
12	Acquisition Time	0.6554
13	Acquisition Date	2008-05-31T11:05:16
14	Spectrometer Frequency	100.52
15	Spectral Width	25000.0
16	Lowest Frequency	-2989.4
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768

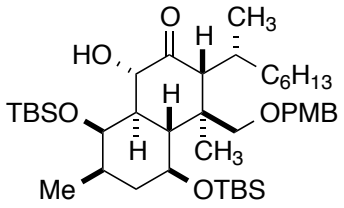


Compound 12
[Scheme 2, Step 2]

214.89 158.83 128.71 113.68 94.62 77.51 77.43 77.20 76.86 76.88 75.48 74.72 74.33 72.21 59.88 55.46 48.35 47.40 44.51 43.18 40.08 35.97 34.13 32.22 30.86 29.90 29.56 26.50 26.42 22.90 20.81 19.30 18.78 18.48 14.76 14.32 -2.65 -3.04 -3.48 -3.59

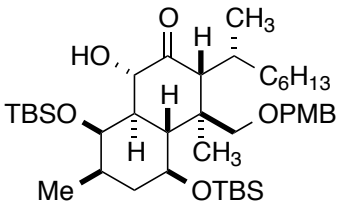
f1 (ppm)

	Parameter	Value
1	Title	I-Ick-299H_B_f15-21
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	0
9	Receiver Gain	36
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2009-06-22T20:02:48
14	Spectrometer Frequency	400.11
15	Spectral Width	6000.6
16	Lowest Frequency	-997.8
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 13
[Scheme 2, Step 3]

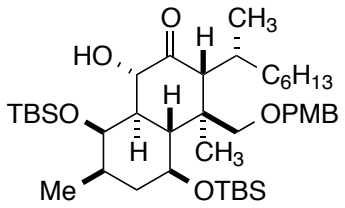
	Parameter	Value
1	Title	l-lck-299C_B_f15-21_C13
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	0
9	Receiver Gain	60
10	Relaxation Delay	3.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2009-06-22T20:21:47
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1492.1
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768



Compound 13
[Scheme 2, Step 3]

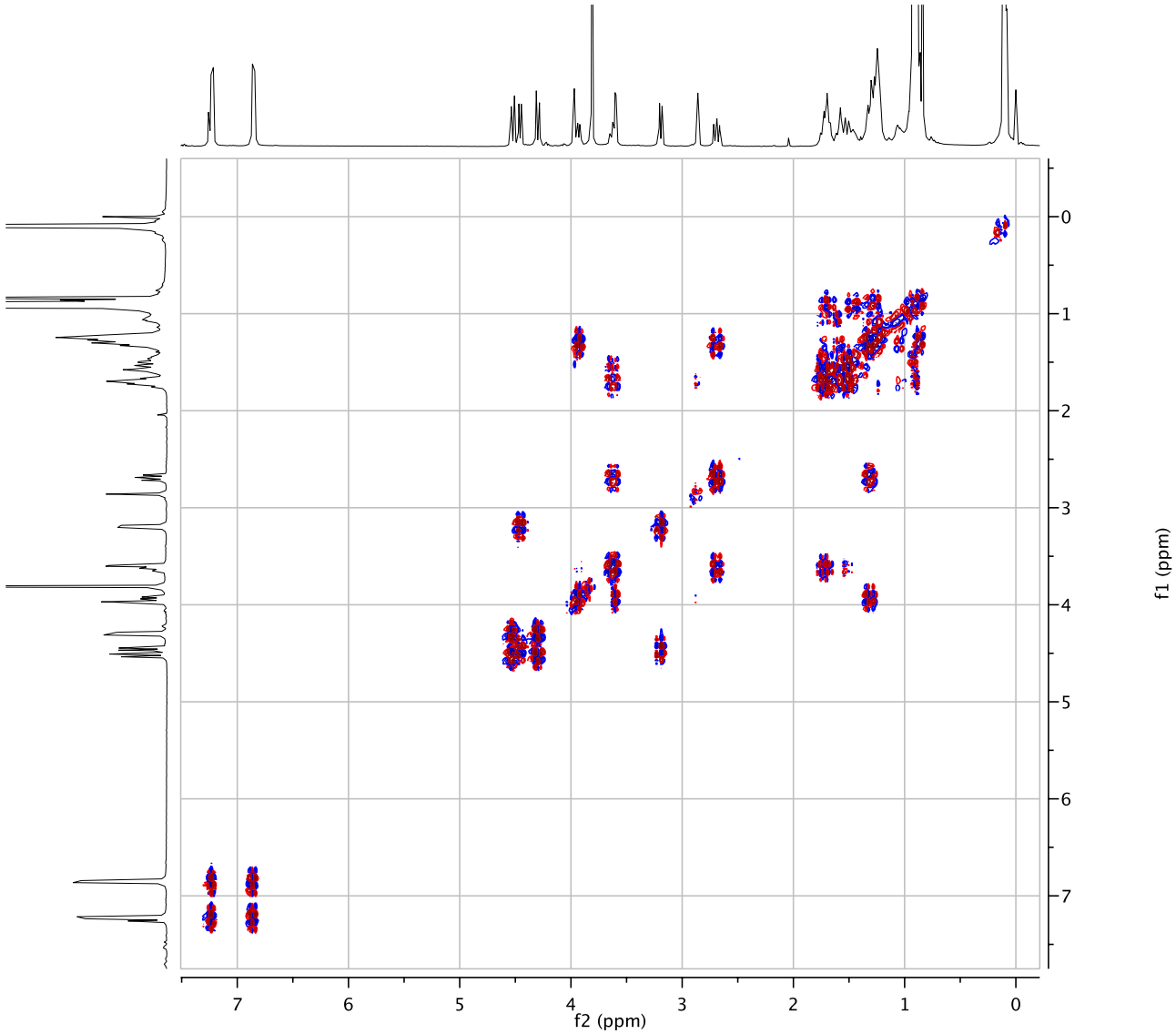
214.69 158.98 131.60 128.81 113.73 77.53 77.42 77.22 76.90 74.83 73.99 73.76 72.29 71.19 57.38 55.47 54.07 49.46 41.79 40.14 35.71 33.96 32.22 30.66 29.88 29.49 26.52 26.45 22.91 20.47 19.25 18.84 18.51 14.57 14.33 -2.84 -3.01 -3.66 -4.30

f1 (ppm)

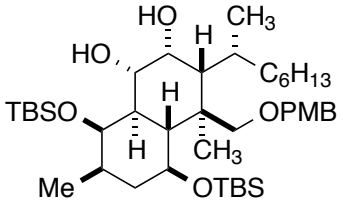


Compound 13
[Scheme 2, Step 3]

	Parameter	Value
1	Title	I-lck-299H_B_f15-21_gDQCOSY
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gDQCOSY
8	Number of Scans	0
9	Receiver Gain	36
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1706
13	Acquisition Date	2009-06-22T20:21:19
14	Spectrometer Frequency	(400.11, 400.11)
15	Spectral Width	(6000.6, 6000.6)
16	Lowest Frequency	(-997.8, -997.8)
17	Nucleus	(1H, 1H)
18	Acquired Size	(1024, 200)
19	Spectral Size	(1024, 1024)

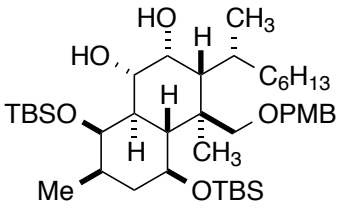


	Parameter	Value
1	Title	II-lck-077H_B_f41-4
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	20.0
7	Pulse Sequence	s2pul
8	Number of Scans	0
9	Receiver Gain	36
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.7304
13	Acquisition Date	2009-09-02T10:32:17
14	Spectrometer Frequency	400.11
15	Spectral Width	6000.6
16	Lowest Frequency	-999.5
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 13a
[Scheme 2, Step 4]

	Parameter	Value
1	Title	II-lck-077C_B_f41-4_C13
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	20.0
7	Pulse Sequence	s2pul
8	Number of Scans	0
9	Receiver Gain	60
10	Relaxation Delay	3.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.6513
13	Acquisition Date	2009-09-04T20:03:29
14	Spectrometer Frequency	100.62
15	Spectral Width	25157.2
16	Lowest Frequency	-1491.7
17	Nucleus	13C
18	Acquired Size	16384
19	Spectral Size	32768

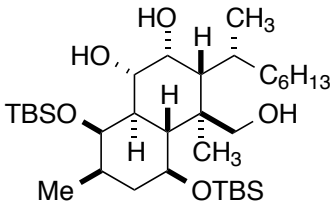


Compound 13a
[Scheme 2, Step 4]

158.80 132.12 128.78 113.64 77.54 77.43 77.23 76.91 75.31 74.78 72.43 71.40 71.22 70.30 55.47 47.03 44.51 41.49 40.85 40.28 36.21 35.19 32.27 30.53 30.00 29.45 26.61 26.46 22.91 21.47 19.52 18.83 18.55 15.69 14.34 -3.00 -3.18 -3.46 -3.97

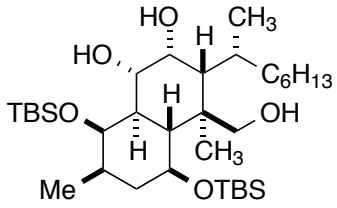
f1 (ppm)

	Parameter	Value
1	Title	III-lck-099H_f15-19_col2_forCOSY_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	24
9	Receiver Gain	52
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.9824
13	Acquisition Date	2010-05-29T14:24:11
14	Spectrometer Frequency	499.81
15	Spectral Width	4132.4
16	Lowest Frequency	-209.9
17	Nucleus	1H
18	Acquired Size	8192
19	Spectral Size	65536

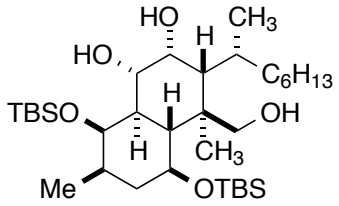


Compound 14
[Scheme 2, Step 5]

	Parameter	Value
1	Title	III-lck-007-013C_prod_C13_vxr
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	1696
9	Receiver Gain	60
10	Relaxation Delay	3.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.3033
13	Acquisition Date	2010-03-27T14:03:19
14	Spectrometer Frequency	100.57
15	Spectral Width	25141.4
16	Lowest Frequency	-1508.9
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

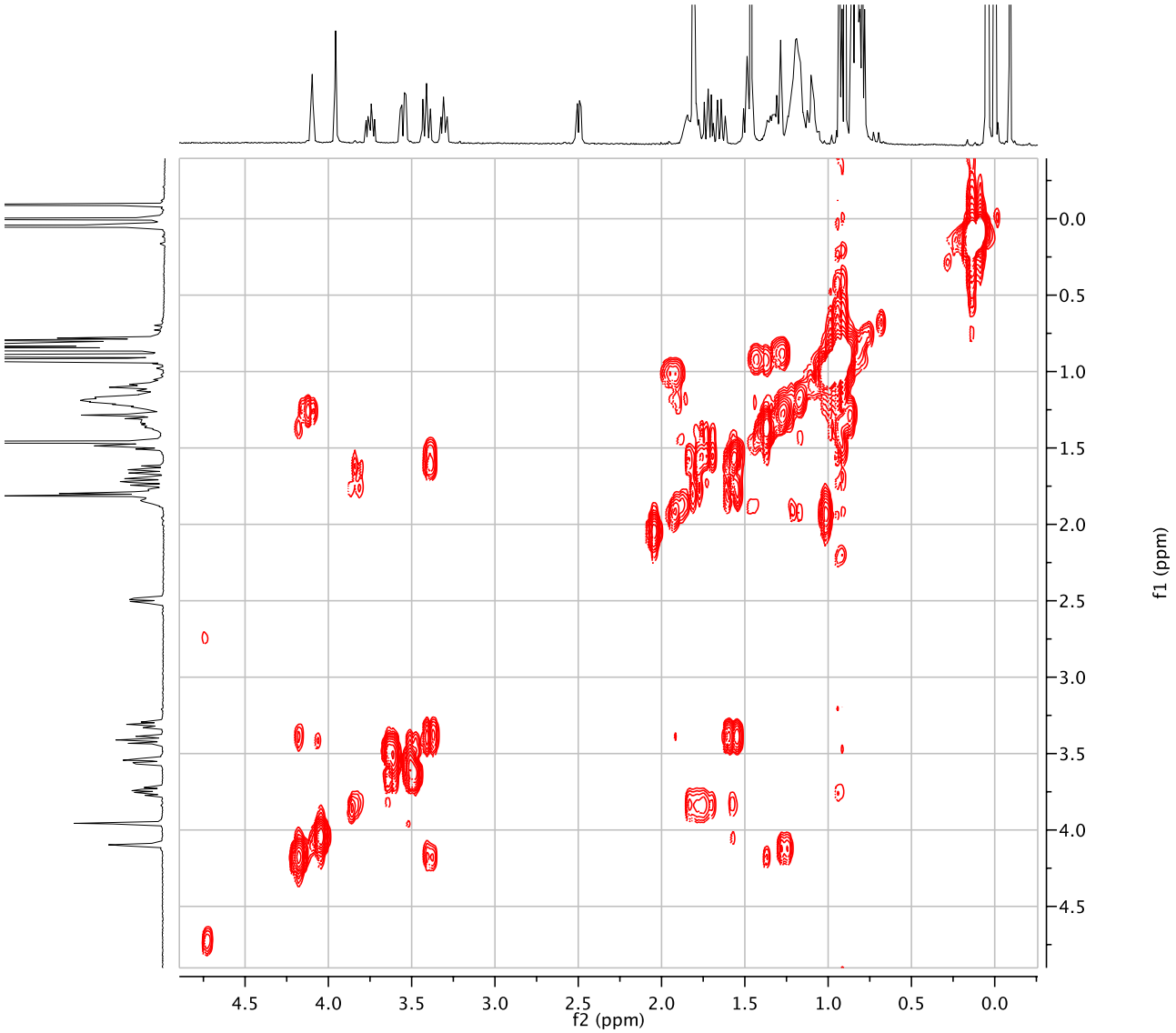


Compound 14
[Scheme 2, Step 5]

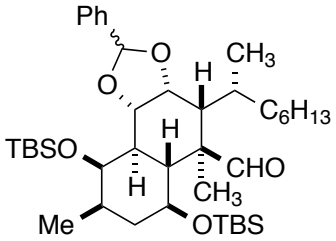


Compound 14
[Scheme 2, Step 5]

	Parameter	Value
1	Title	IV-lck-149H_f14-20_wD2O_COSY
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gCOSY
8	Number of Scans	4
9	Receiver Gain	58
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1500
13	Acquisition Date	2011-05-21T19:23:52
14	Spectrometer Frequency	(400.11, 400.11)
15	Spectral Width	(3472.4, 3472.4)
16	Lowest Frequency	(-240.4, -240.4)
17	Nucleus	(1H, 1H)
18	Acquired Size	(521, 128)
19	Spectral Size	(1024, 1024)

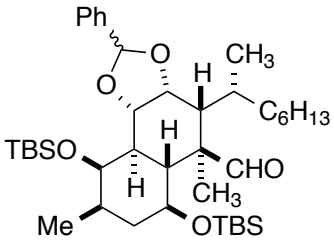


	Parameter	Value
1	Title	III-lck-115H_f14-17_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	48
9	Receiver Gain	46
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0488
13	Acquisition Date	2010-06-16T10:59:21
14	Spectrometer Frequency	499.81
15	Spectral Width	7996.8
16	Lowest Frequency	-999.6
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



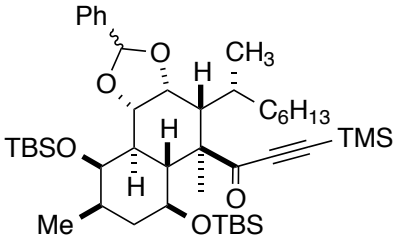
Compound 15
[Scheme 3, Step 7]

	Parameter	Value
1	Title	III-lck-115C_f14-17_C13_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	904
9	Receiver Gain	60
10	Relaxation Delay	4.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0428
13	Acquisition Date	2010-06-16T09:39:22
14	Spectrometer Frequency	125.69
15	Spectral Width	31421.8
16	Lowest Frequency	-1886.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



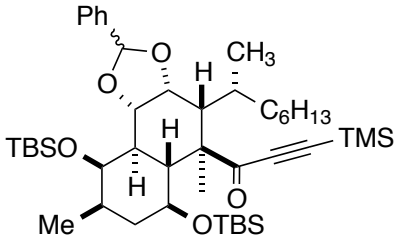
Compound 15
[Scheme 3, Step 7]

	Parameter	Value
1	Title	III-lck-119H_f9-13_forCOSY
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	40
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.3861
13	Acquisition Date	2010-06-21T12:39:31
14	Spectrometer Frequency	400.11
15	Spectral Width	3433.2
16	Lowest Frequency	-214.2
17	Nucleus	1H
18	Acquired Size	8192
19	Spectral Size	65536



Compound 16
[Scheme 3, Step 9]

	Parameter	Value
1	Title	III-lck-119C_f9-13_C13_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	844
9	Receiver Gain	60
10	Relaxation Delay	4.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0428
13	Acquisition Date	2010-06-19T11:39:13
14	Spectrometer Frequency	125.69
15	Spectral Width	31421.8
16	Lowest Frequency	-1886.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



Compound 16
[Scheme 3, Step 9]

191.52 191.47

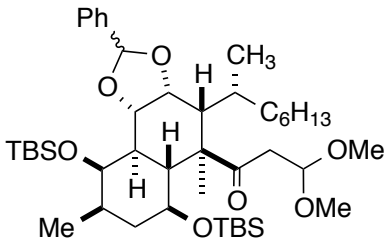
140.65 139.09 128.71 128.30 128.28 128.11 126.30 125.90 103.85 101.86 101.83 96.89 77.28 77.23 77.03 76.77 75.80 75.66 74.44 72.58 72.08 71.93 70.13 70.03 53.66 53.64 47.03 46.95 46.85 46.64 44.83 42.33 37.64 37.54 35.52 35.47 34.65 34.58 32.65 32.58 32.10 31.96 29.68 29.64 28.53 28.49 26.53 26.51 26.27 22.67 22.65 21.33 19.55 19.52 18.74 18.72 18.27 18.25 14.17 11.40 11.27 -0.59 -0.61 -2.80 -2.81 -3.68 -3.81 -3.97

7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

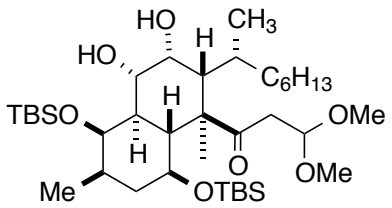
f1 (ppm)

	Parameter	Value
1	Title	IV-lck-159H_crude_i500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	26.0
7	Pulse Sequence	s2pul
8	Number of Scans	24
9	Receiver Gain	58
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0488
13	Acquisition Date	2011-05-29T16:26:48
14	Spectrometer Frequency	499.81
15	Spectral Width	7996.8
16	Lowest Frequency	-999.6
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



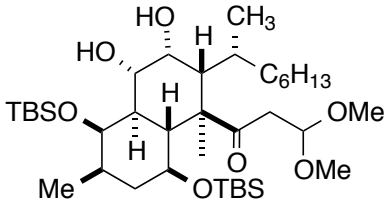
Compound 16a
[Scheme 3, Step 10]

	Parameter	Value
1	Title	III-lck-123H_B_f30-43_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	36
9	Receiver Gain	26
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0488
13	Acquisition Date	2010-06-29T09:31:31
14	Spectrometer Frequency	499.81
15	Spectral Width	7996.8
16	Lowest Frequency	-999.6
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536



Compound 17
[Scheme 3, Step 11]

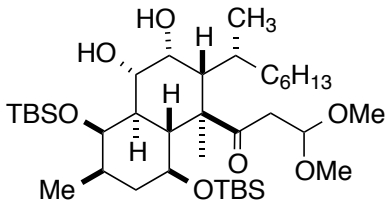
	Parameter	Value
1	Title	III-lck-123C_B_f30-43_C13_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	1260
9	Receiver Gain	60
10	Relaxation Delay	3.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0428
13	Acquisition Date	2010-06-29T09:36:14
14	Spectrometer Frequency	125.69
15	Spectral Width	31421.8
16	Lowest Frequency	-1886.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536



Compound 17
[Scheme 3, Step 11]

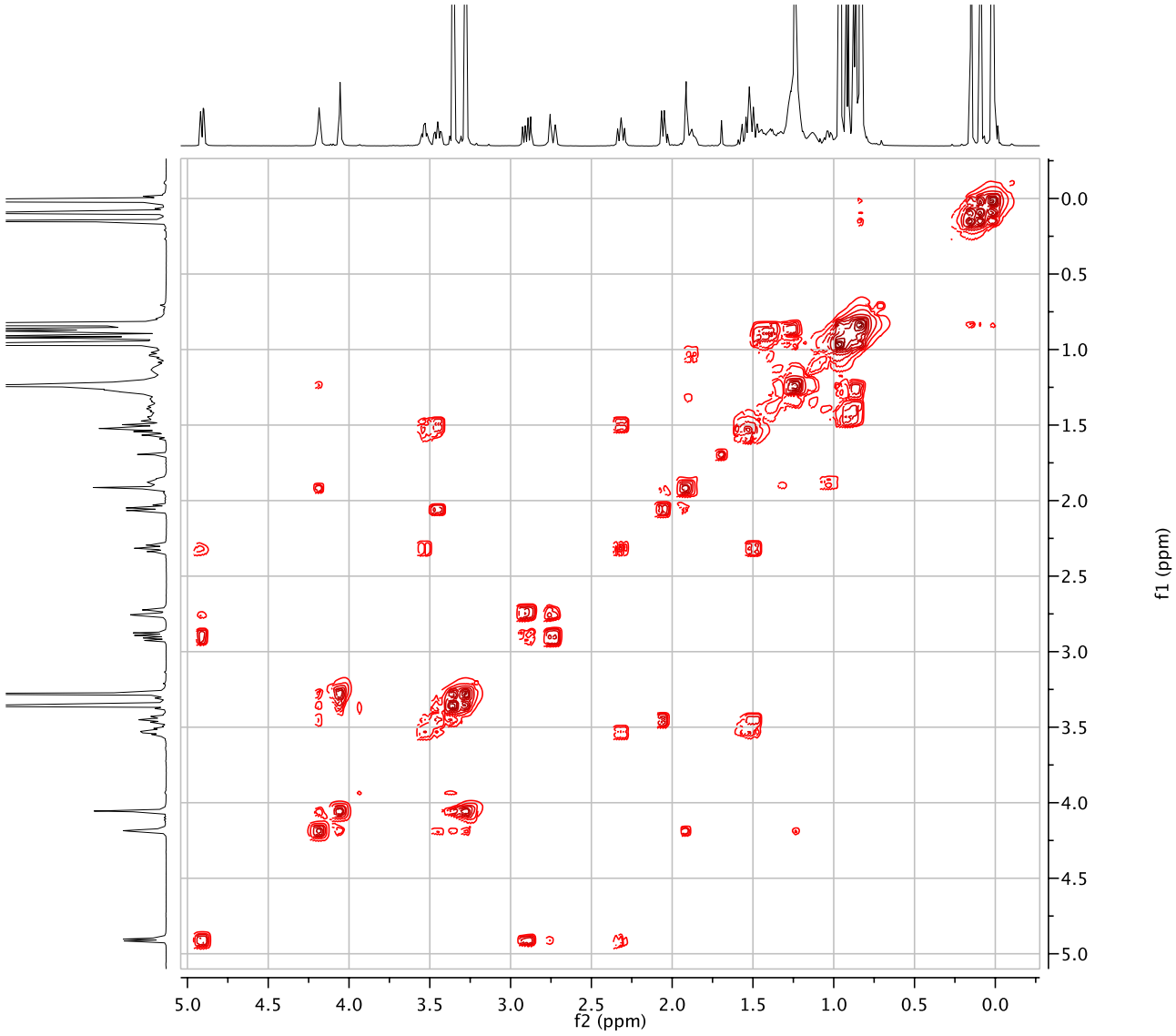
209.75
103.02
77.27
77.22
77.02
76.77
72.69
70.88
69.70
69.68
56.03
54.19
52.41
48.37
43.85
43.52
41.09
38.45
35.54
35.07
32.30
31.98
29.78
29.12
26.34
26.18
22.64
20.81
19.36
18.71
18.29
14.10
13.41
-3.39
-3.90
-4.03
-4.34

f1 (ppm)

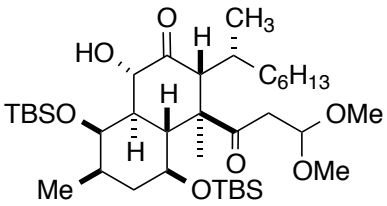


Compound 17
[Scheme 3, Step 11]

	Parameter	Value
1	Title	III-lck-123H_B_f30-43_COSY_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gCOSY
8	Number of Scans	4
9	Receiver Gain	26
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1499
13	Acquisition Date	2010-06-29T11:17:39
14	Spectrometer Frequency	(499.81, 499.81)
15	Spectral Width	(4088.5, 4088.5)
16	Lowest Frequency	(-219.9, -219.9)
17	Nucleus	(1H, 1H)
18	Acquired Size	(613, 128)
19	Spectral Size	(1024, 1024)

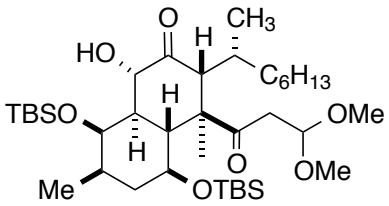


	Parameter	Value
1	Title	III-lck-127H_f19-27_forC13_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	32
9	Receiver Gain	36
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	2.0488
13	Acquisition Date	2010-07-04T09:44:15
14	Spectrometer Frequency	499.81
15	Spectral Width	7996.8
16	Lowest Frequency	-999.6
17	Nucleus	1H
18	Acquired Size	16384
19	Spectral Size	65536

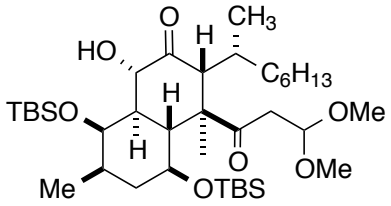


Compound 19
[Scheme 3, Step 1]

	Parameter	Value
1	Title	III-lck-127C_f19-27_C13_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	s2pul
8	Number of Scans	4544
9	Receiver Gain	60
10	Relaxation Delay	3.0000
11	Pulse Width	0.0000
12	Acquisition Time	1.0428
13	Acquisition Date	2010-07-04T09:57:02
14	Spectrometer Frequency	125.69
15	Spectral Width	31421.8
16	Lowest Frequency	-1886.6
17	Nucleus	13C
18	Acquired Size	32768
19	Spectral Size	65536

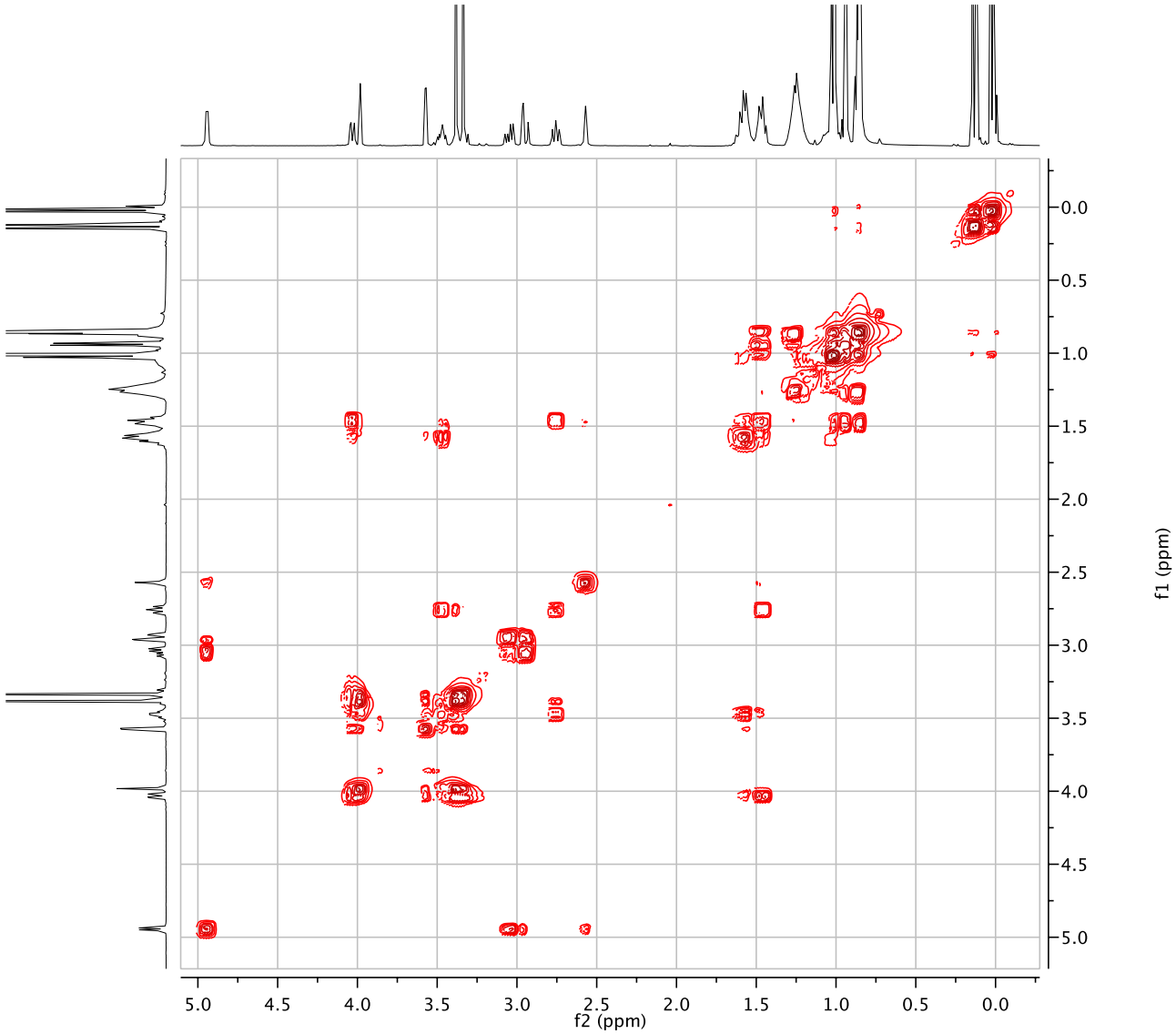


Compound 19
[Scheme 3, Step 1]

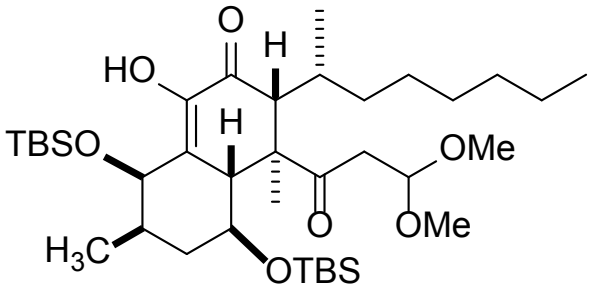


Compound 19
[Scheme 3, Step 1]

	Parameter	Value
1	Title	III-lck-127H_19-27_COSY_vi500
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gCOSY
8	Number of Scans	4
9	Receiver Gain	32
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1500
13	Acquisition Date	2010-07-04T15:21:01
14	Spectrometer Frequency	(499.81, 499.81)
15	Spectral Width	(4152.0, 4152.0)
16	Lowest Frequency	(-229.4, -229.4)
17	Nucleus	(1H, 1H)
18	Acquired Size	(623, 128)
19	Spectral Size	(1024, 1024)



Parameters		
	Parameter	Value
1	Title	SAB-4-292
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Number of Scans	64
8	Receiver Gain	30
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Time	1.7046
12	Acquisition Date	2015-10-30T19:27:06
13	Spectrometer Frequency	599.80
14	Spectral Width	9611.9
15	Lowest Frequency	-1192.2
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536

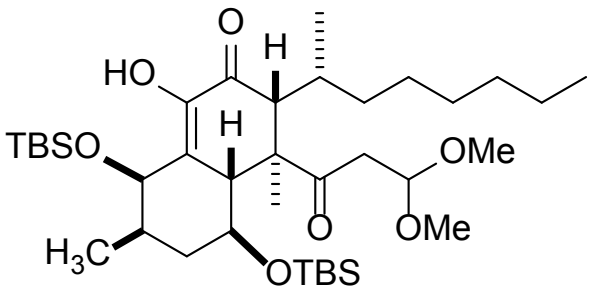


Compound 21
[Scheme 3]

206.94
194.85
141.61
125.26
103.24
77.42
77.16 cdcl3
76.90
72.55
66.90
56.19
54.59
53.79
46.03
42.41
37.17
34.31
33.47
32.08
31.80
29.76
29.36
26.28
26.01
22.85
21.89
18.48
18.42
17.76
14.26
1.18
-3.63
-3.95
-4.74
-5.14

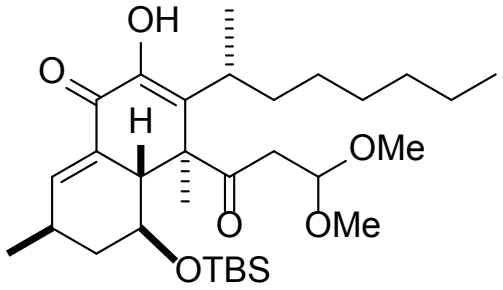
Williams and Tantillo, et al.

Parameters		
	Parameter	Value
1	Title	SAB-4-292-C2
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Number of Scans	20112
8	Receiver Gain	60
9	Relaxation Delay	1.5000
10	Pulse Width	0.0000
11	Acquisition Time	1.0428
12	Acquisition Date	2015-12-01T18:49:10
13	Spectrometer Frequency	125.69
14	Spectral Width	31421.8
15	Lowest Frequency	-1882.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

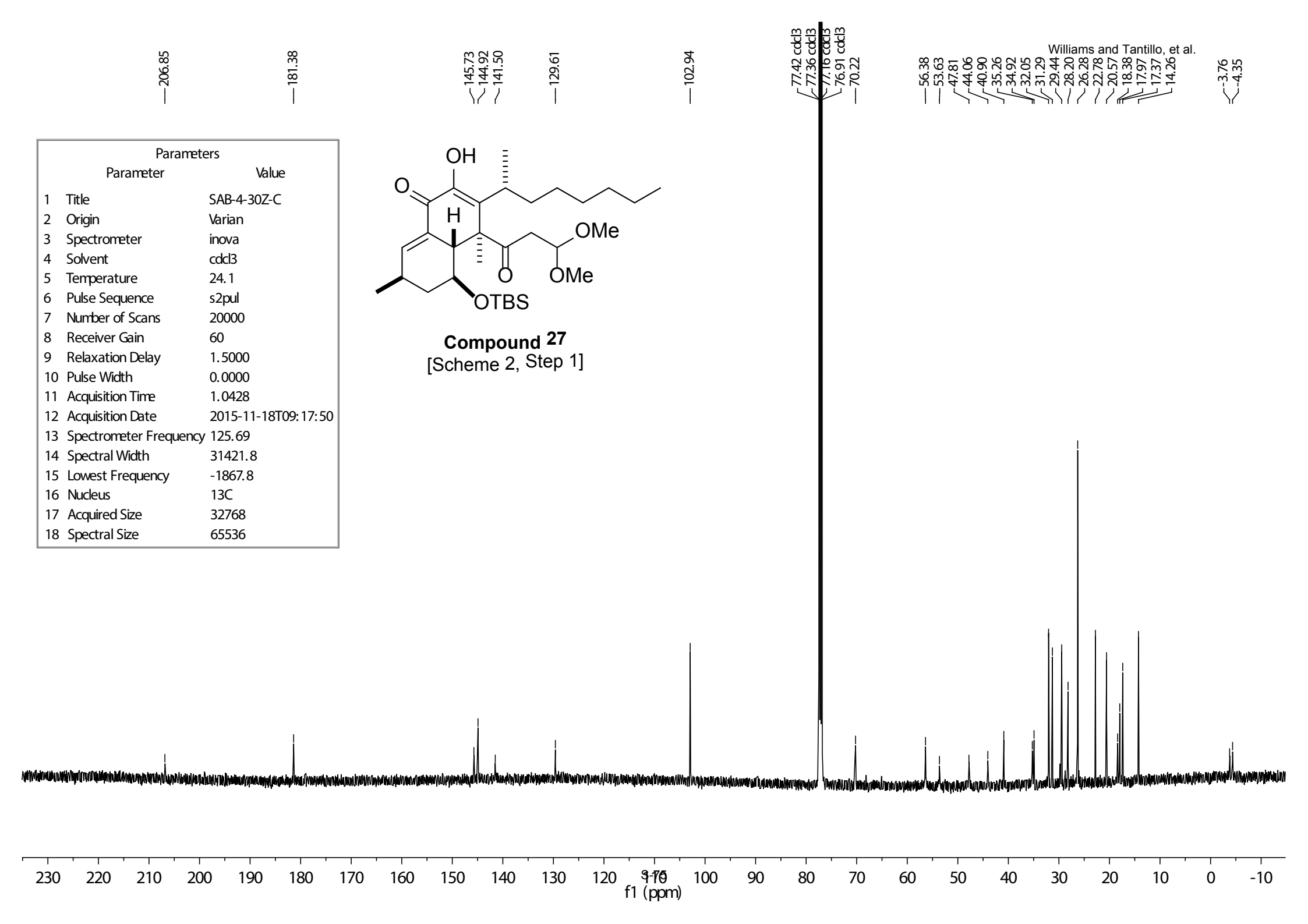


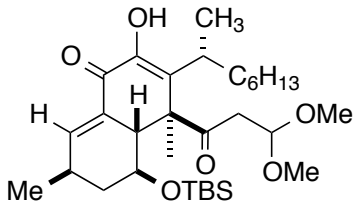
Compound 21
[Scheme 3]

Parameters		
	Parameter	Value
1	Title	SAB-4-302-2
2	Origin	Varian
3	Spectrometer	inova
4	Solvent	cdcl3
5	Temperature	25.0
6	Pulse Sequence	s2pul
7	Number of Scans	32
8	Receiver Gain	50
9	Relaxation Delay	1.0000
10	Pulse Width	0.0000
11	Acquisition Time	1.7046
12	Acquisition Date	2015-12-01T18:35:59
13	Spectrometer Frequency	599.78
14	Spectral Width	9611.9
15	Lowest Frequency	-1197.7
16	Nucleus	1H
17	Acquired Size	16384
18	Spectral Size	65536



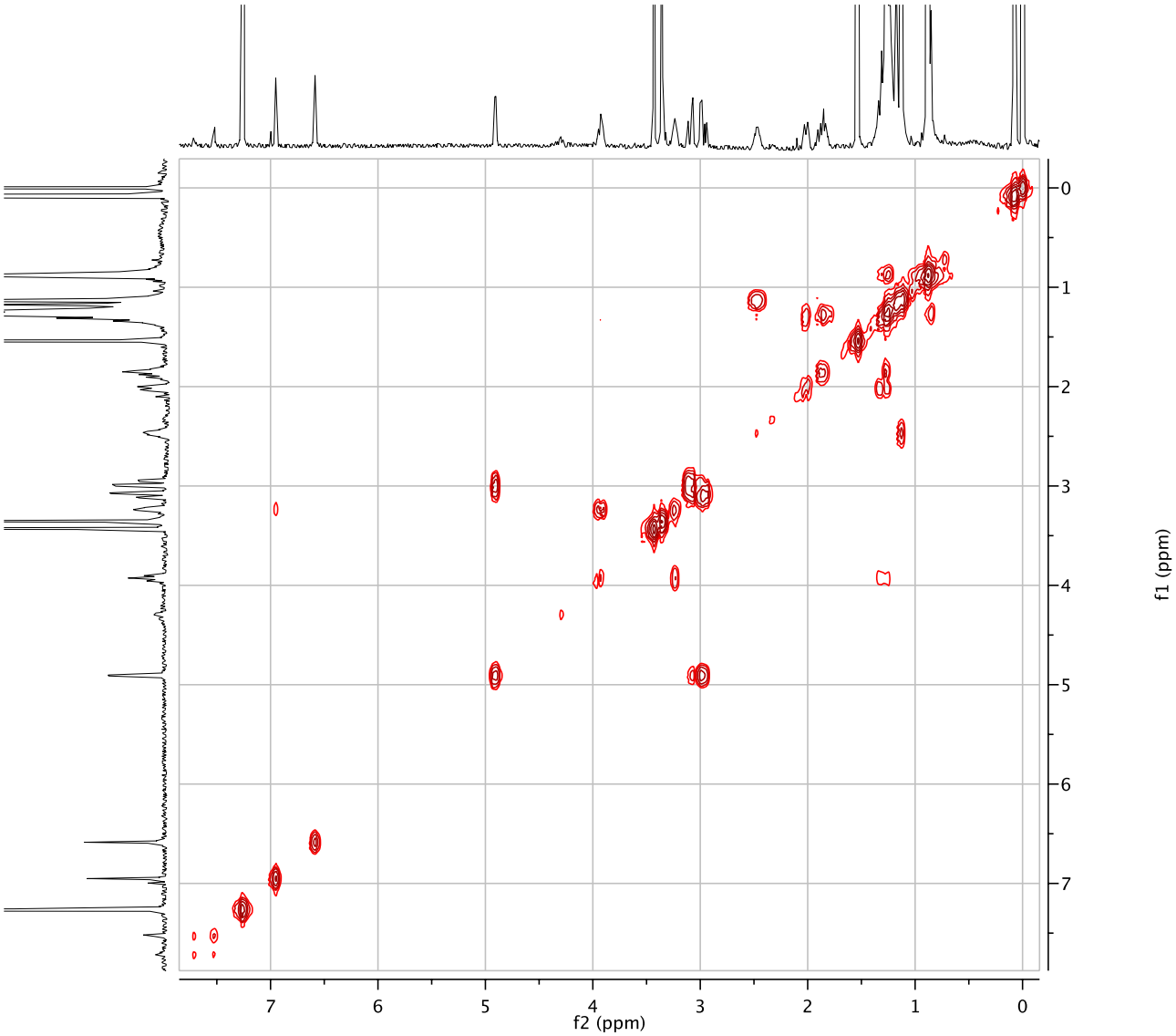
Compound 27
[Scheme 2, Step 1]


206.85
181.38
145.73
144.92
141.50
129.61
102.94
77.42 cdcl3
77.36 cdcl3
77.16 cdcl3
76.91 cdcl3
70.22
56.38
53.63
47.81
44.06
40.90
35.26
34.92
32.05
31.29
29.44
28.20
26.28
22.78
20.57
18.38
17.97
17.37
14.26
-3.76
-4.35
Williams and Tantillo, et al.
Parameters
Parameter Value
1 Title SAB-4-30Z-C
2 Origin Varian
3 Spectrometer inova
4 Solvent cdcl3
5 Temperature 24.1
6 Pulse Sequence s2pul
7 Number of Scans 20000
8 Receiver Gain 60
9 Relaxation Delay 1.5000
10 Pulse Width 0.0000
11 Acquisition Time 1.0428
12 Acquisition Date 2015-11-18T09:17:50
13 Spectrometer Frequency 125.69
14 Spectral Width 31421.8
15 Lowest Frequency -1867.8
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
OH
O
H
OMe
O
OMe
OTBS
Compound 27
[Scheme 2, Step 1]
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

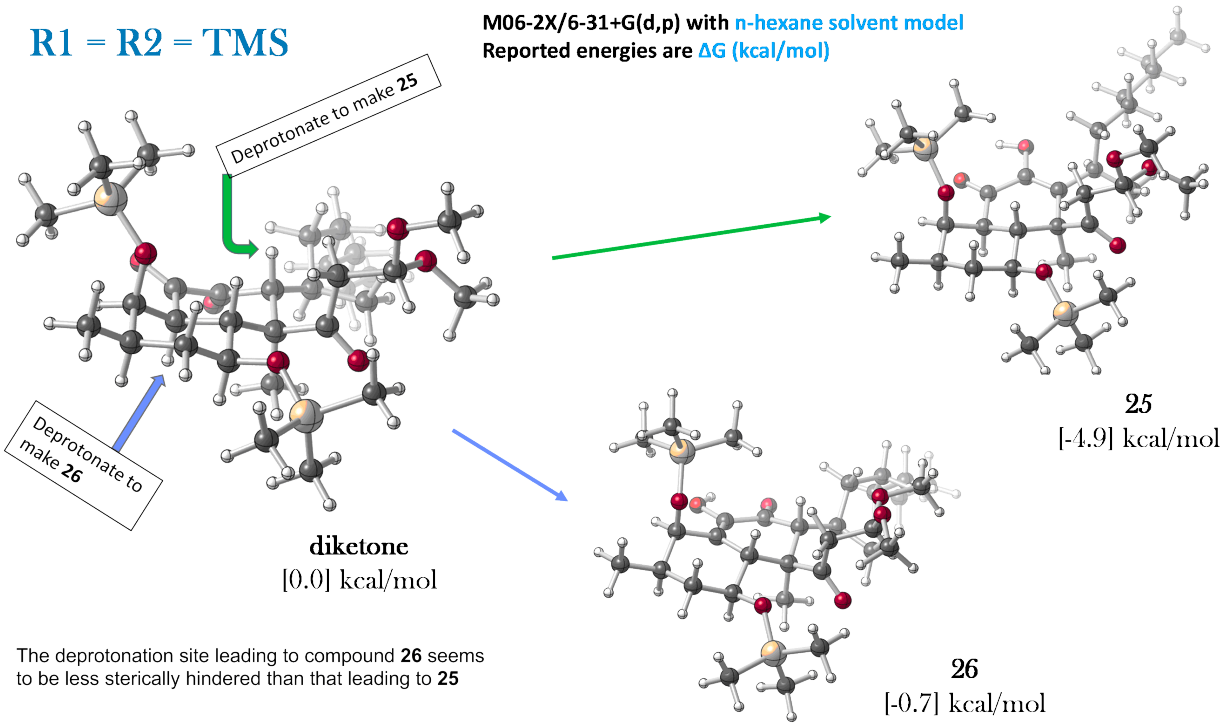


Compound 27
[Scheme 3, Step 3]

	Parameter	Value
1	Title	III-lck-179H_bttm_spot_COSY
2	Origin	Varian
3	Spectrometer	inova
4	Author	jcklein
5	Solvent	cdcl3
6	Temperature	25.0
7	Pulse Sequence	gCOSY
8	Number of Scans	4
9	Receiver Gain	60
10	Relaxation Delay	1.0000
11	Pulse Width	0.0000
12	Acquisition Time	0.1499
13	Acquisition Date	2010-09-11T13:46:35
14	Spectrometer Frequency	(400.11, 400.11)
15	Spectral Width	(3416.2, 3416.2)
16	Lowest Frequency	(-228.9, -228.9)
17	Nucleus	(1H, 1H)
18	Acquired Size	(512, 128)
19	Spectral Size	(512, 512)



Additional Computational data:



The deprotonation site leading to compound **26** seems to be less sterically hindered than that leading to **25**

Cartesian coordinates for the computed structures mentioned in the main text:

Routecard includes: m062x/6-31+g(d,p) scrf=(smd,solvent=n-hexane)

1

```
     Imaginary Frequencies: none found
     Zero-point correction = 0.571920 (Hartree/Particle)

     Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
     Sum of electronic and thermal Free Energies =
          -1348.487062 hartrees (-846189.11627562 kcal/mol)

C           -3.633393   -2.038665   -0.181123
C           -2.390346   -1.445940    0.502652
C           -2.193115    0.047600    0.197410
C           -3.467596    0.800397    0.634424
C           -4.681954    0.238689   -0.094453
C           -4.887578   -1.248722    0.190024
C           -0.864089    0.602790    0.818646
C           -1.169951   -2.238894    0.123842
C            0.148279   -1.585165    0.177529
C            0.342274   -0.273751    0.445186
C           -6.124439   -1.798259   -0.513766
C           -0.976884    0.682395    2.353067
C           -0.652425    2.011678    0.237697
C           -0.416624    2.157147   -1.180300
C           -0.221567    3.395331   -1.708920
C            1.800112    0.199417    0.456324
C            2.394635    0.163971   -0.975914
C            3.907250    0.405486   -1.037776
C            4.739902   -0.565777   -0.201177
```

C	6.242127	-0.398390	-0.423938
C	7.090531	-1.336055	0.433324
C	8.587443	-1.155578	0.195047
C	2.122491	1.548274	1.111447
O	-3.478450	-2.010310	-1.593659
O	-3.424824	2.185401	0.336952
O	-1.226680	-3.416765	-0.216376
O	1.188850	-2.425438	-0.059742
O	-0.703248	3.004278	0.986879
O	-0.222512	4.515548	-1.012966
H	-2.515302	-1.584639	1.588778
H	-3.749388	-3.077448	0.154528
H	-3.613927	0.652435	1.716987
H	-5.563599	0.809330	0.215733
H	-4.550657	0.399793	-1.172188
H	-5.017739	-1.374575	1.275612
H	-2.123025	0.148824	-0.893886
H	-6.262200	-2.863269	-0.297829
H	-7.023143	-1.267342	-0.184565
H	-6.032359	-1.682193	-1.597039
H	-0.037949	0.995655	2.808632
H	-1.735936	1.404026	2.664916
H	-1.232249	-0.296849	2.765573
H	1.893286	0.931633	-1.575886
H	2.173940	-0.805988	-1.431148
H	4.215141	0.319110	-2.088160
H	4.142014	1.435975	-0.741222
H	4.524946	-0.422547	0.867044
H	4.444362	-1.597688	-0.438782
H	6.474617	-0.568818	-1.484749
H	6.526080	0.642250	-0.209789
H	6.805683	-2.375142	0.222150
H	6.861733	-1.161113	1.492780
H	9.181102	-1.826618	0.823172
H	8.845080	-1.361012	-0.849830
H	8.897689	-0.128611	0.417651
H	1.893472	2.392307	0.453242
H	1.609984	1.712303	2.059921
H	3.195484	1.587827	1.321300
H	2.325697	-0.576691	1.029024
H	0.803602	-3.299534	-0.243509
H	-2.851115	2.647481	0.961213
H	-2.891558	-2.735445	-1.842696
H	-0.407664	4.258638	-0.069456
H	-0.399063	1.292233	-1.830376
H	-0.042623	3.546095	-2.771372

22 Imaginary Frequencies: none found
Zero-point correction = 0.572237 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-1348.481264 hartrees (-846185.47797264 kcal/mol)

C	3.573197	-2.048858	0.470276
C	2.226142	-1.428441	0.160452
C	2.177284	0.069480	-0.056555
C	3.310752	0.475055	-1.037011
C	4.657552	-0.070562	-0.586666
C	4.651640	-1.595443	-0.511792
C	0.768212	0.609240	-0.509144
C	1.118169	-2.184778	0.162986

C	-0.238411	-1.592259	0.104953
C	-0.359829	-0.089426	0.314794
C	6.020196	-2.159445	-0.141963
C	0.525031	0.368340	-2.005486
C	0.770707	2.117151	-0.198940
C	0.818818	2.570049	1.175500
C	0.837911	3.903233	1.449069
C	-1.842301	0.334599	0.107862
C	-2.617062	-0.016385	1.394014
C	-4.135093	0.181069	1.326953
C	-4.815402	-0.578562	0.187812
C	-6.339217	-0.480033	0.238275
C	-7.032482	-1.217264	-0.906590
C	-8.553167	-1.096722	-0.849607
C	-2.113722	1.791002	-0.277150
O	3.981958	-1.630154	1.776026
O	3.452873	1.881718	-1.122064
O	1.140886	-3.536079	0.284155
O	-1.189549	-2.347766	-0.018460
O	0.762336	2.938658	-1.134402
O	0.804878	4.857772	0.541967
H	3.485025	-3.140828	0.441056
H	3.087038	0.053595	-2.028592
H	5.416783	0.275227	-1.296241
H	4.906782	0.352122	0.394807
H	4.357742	-1.992024	-1.494929
H	2.442533	0.546091	0.899947
H	-0.108905	0.047048	1.379272
H	5.991871	-3.252195	-0.072483
H	6.763421	-1.887588	-0.897986
H	6.351164	-1.767363	0.823471
H	-0.507538	0.601812	-2.275993
H	1.163601	0.988981	-2.636426
H	0.710853	-0.679949	-2.259892
H	-2.214903	0.605221	2.208124
H	-2.413703	-1.060061	1.658012
H	-4.561823	-0.155163	2.280937
H	-4.378516	1.248718	1.249007
H	-4.467654	-0.190954	-0.779658
H	-4.511590	-1.634412	0.221874
H	-6.699392	-0.880181	1.196726
H	-6.634635	0.579024	0.217105
H	-6.744897	-2.276358	-0.879763
H	-6.667185	-0.822199	-1.863496
H	-9.031886	-1.629604	-1.676740
H	-8.945115	-1.511316	0.085739
H	-8.865477	-0.047923	-0.902824
H	-1.860833	2.485275	0.531865
H	-1.583352	2.106985	-1.176648
H	-3.181241	1.909086	-0.485957
H	-2.228932	-0.295546	-0.701941
H	0.218930	-3.837740	0.219018
H	3.395665	-2.037802	2.424659
H	2.722153	2.269177	-1.620958
H	0.783866	4.401408	-0.342522
H	0.851027	1.872913	2.001500
H	0.878520	4.277098	2.469903

23 Imaginary Frequencies: none found
Zero-point correction = 0.656143 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =

-1503.384254 hartrees (-943388.65322754 kcal/mol)

C	-3.821132	-2.232682	-0.554563
C	-2.578722	-1.863714	0.274606
C	-2.330000	-0.349097	0.334906
C	-3.596385	0.324921	0.900232
C	-4.806507	-0.003879	0.035747
C	-5.062779	-1.509706	-0.036996
C	-1.014151	0.011758	1.106871
C	-1.372125	-2.569142	-0.279535
C	-0.043033	-1.991872	-0.028642
C	0.181583	-0.813369	0.597294
C	-6.291304	-1.837267	-0.880271
C	-1.184989	-0.231463	2.616681
C	-0.750544	1.518959	0.865279
C	-0.669098	2.023358	-0.559948
C	0.052266	3.356581	-0.654178
C	1.790675	4.134056	0.790775
C	0.618045	4.979292	-2.257642
C	1.658660	-0.456561	0.786179
C	2.270151	0.003920	-0.562692
C	3.802025	0.077203	-0.571984
C	4.501884	-1.209541	-0.133854
C	6.004578	-1.194407	-0.409870
C	6.718268	-2.457737	0.067658
C	8.215529	-2.440721	-0.229192
C	2.039463	0.511503	1.909400
O	-3.627208	-1.872638	-1.915295
O	-3.487482	1.741446	0.938505
O	-1.450484	-3.616586	-0.914494
O	0.983736	-2.768848	-0.463126
O	-0.675827	2.292737	1.801232
O	1.379882	3.212118	-0.203979
O	0.020917	3.723593	-2.000821
H	-2.723517	-2.255843	1.294271
H	-3.977076	-3.316719	-0.478727
H	-3.783658	-0.062248	1.914119
H	-5.678675	0.508989	0.455277
H	-4.643756	0.397259	-0.973002
H	-5.230399	-1.879939	0.985950
H	-2.217581	-0.012643	-0.704448
H	-6.461790	-2.918294	-0.926275
H	-7.186766	-1.371571	-0.457028
H	-6.162004	-1.471835	-1.902483
H	-0.271452	0.004027	3.159388
H	-1.969568	0.399984	3.041928
H	-1.434212	-1.278949	2.806999
H	-1.698953	2.157780	-0.910903
H	-0.194217	1.292667	-1.221889
H	-0.451886	4.122951	-0.042391
H	2.840643	3.919699	1.001995
H	1.706341	5.171200	0.439884
H	1.201853	4.012909	1.707955
H	1.693244	4.957774	-2.046537
H	0.465462	5.192477	-3.316802
H	0.142126	5.771336	-1.661179
H	1.882217	0.995898	-0.809098
H	1.948454	-0.693715	-1.344097
H	4.112366	0.319924	-1.596938
H	4.147606	0.914480	0.048828
H	4.343482	-1.376979	0.940841
H	4.041714	-2.065704	-0.647686
H	6.173929	-1.068637	-1.488621
H	6.456341	-0.317424	0.076376

H	6.257734	-3.332690	-0.409516
H	6.558524	-2.575550	1.147482
H	8.706338	-3.352900	0.123703
H	8.401327	-2.356716	-1.305610
H	8.702812	-1.589247	0.258662
H	1.697162	1.531368	1.721496
H	1.674919	0.188527	2.886758
H	3.131146	0.543865	1.980378
H	2.131054	-1.418157	1.021433
H	0.584227	-3.553580	-0.875598
H	-3.009908	2.021370	1.729408
H	-3.048020	-2.532074	-2.318024

24 Imaginary Frequencies: none found
Zero-point correction = 0.656902 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-1503.375174 hartrees (-943382.95543674 kcal/mol)

C	-3.634576	-2.330132	-0.843378
C	-2.289909	-1.809138	-0.381083
C	-2.248490	-0.432548	0.243661
C	-3.392035	-0.292167	1.280448
C	-4.734039	-0.702384	0.695242
C	-4.715443	-2.154778	0.221928
C	-0.851464	-0.033329	0.848785
C	-1.172318	-2.508740	-0.625376
C	0.179641	-1.943368	-0.402688
C	0.303657	-0.452604	-0.116709
C	-6.080502	-2.610351	-0.285730
C	-0.634946	-0.686680	2.220459
C	-0.868777	1.504848	0.973481
C	-1.156117	2.356521	-0.256954
C	-0.180440	3.518198	-0.430679
C	1.943429	3.962281	-1.337362
C	-1.476900	5.475473	-0.228021
C	1.784527	-0.143882	0.263114
C	2.584606	-0.028656	-1.050666
C	4.102796	0.098468	-0.891735
C	4.741612	-1.030038	-0.081851
C	6.268580	-0.995452	-0.115296
C	6.916853	-2.112482	0.700741
C	8.441893	-2.074195	0.646909
C	2.058551	1.078316	1.142825
O	-4.047229	-1.584245	-1.992325
O	-3.516866	1.056932	1.708702
O	-1.181179	-3.760279	-1.148252
O	1.134097	-2.693302	-0.538291
O	-0.734235	2.053766	2.049999
O	0.865345	3.048512	-1.219434
O	-0.780005	4.604267	-1.095547
H	-3.543863	-3.391401	-1.102171
H	-3.182725	-0.944487	2.139948
H	-5.499927	-0.561416	1.465386
H	-4.982523	-0.039550	-0.143195
H	-4.420258	-2.793459	1.067517
H	-2.507570	0.277788	-0.555095
H	0.097434	0.026751	-1.088696
H	-6.042857	-3.643606	-0.647079
H	-6.825179	-2.558462	0.514744
H	-6.415061	-1.975845	-1.110893

H	0.398670	-0.575498	2.552309
H	-1.261322	-0.238533	2.995082
H	-0.858466	-1.757389	2.175870
H	-2.164540	2.753663	-0.090472
H	-1.170626	1.794128	-1.192331
H	0.198143	3.862885	0.549662
H	2.740328	3.445203	-1.875264
H	1.643819	4.854548	-1.895040
H	2.312677	4.260990	-0.345932
H	-0.798328	5.925412	0.509340
H	-1.909568	6.262435	-0.847250
H	-2.287015	4.961907	0.307637
H	2.202715	0.847547	-1.593065
H	2.375697	-0.909637	-1.668398
H	4.547330	0.107839	-1.895919
H	4.363074	1.064991	-0.439708
H	4.407115	-0.976144	0.963535
H	4.386448	-1.996580	-0.466573
H	6.610456	-1.065025	-1.157793
H	6.620267	-0.022894	0.258758
H	6.558750	-3.081770	0.330264
H	6.582390	-2.038038	1.743664
H	8.887153	-2.881739	1.235995
H	8.800476	-2.176140	-0.383275
H	8.824985	-1.125166	1.038041
H	1.816389	2.008395	0.621555
H	1.521757	1.065222	2.091413
H	3.126421	1.103320	1.381436
H	2.148263	-1.024553	0.805957
H	-0.253731	-4.049846	-1.192130
H	-3.437202	-1.774232	-2.715399
H	-2.870574	1.254101	2.398367

25TMS-TMS Imaginary Frequencies: none found
Zero-point correction = 0.859882 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-2320.441503 hartrees (-1456100.24754753 kcal/mol)

Si	-3.359432	-3.198591	-0.799338
Si	-1.881038	3.856520	1.581985
C	-2.736228	2.445769	-0.683082
C	-1.598119	1.660519	-1.358382
C	-1.437713	0.278334	-0.717904
C	-2.755658	-0.489708	-0.925830
C	-3.931011	0.279967	-0.319530
C	-4.061948	1.702544	-0.870197
C	-0.165596	-0.485525	-1.206304
C	-0.322546	2.455034	-1.317639
C	0.952107	1.747125	-1.126863
C	1.086798	0.400818	-1.065623
C	-5.215358	2.455253	-0.214598
C	-0.319211	-0.905782	-2.677492
C	-0.007405	-1.754174	-0.330475
C	-0.026111	-1.582693	1.176803
C	0.565617	-2.775424	1.901957
C	2.355542	-4.170415	1.159602
C	0.843302	-3.595608	4.087296
C	2.532028	-0.096626	-0.975597
C	3.084885	0.134760	0.455059
C	4.589589	-0.119227	0.599190
C	5.471605	0.714009	-0.329855

C	6.962552	0.502726	-0.072104
C	7.860923	1.330633	-0.989016
C	9.346321	1.086638	-0.734510
C	2.853153	-1.521120	-1.439009
C	-0.042054	3.635875	1.884654
C	-2.795616	3.772113	3.214011
C	-2.240319	5.465142	0.692818
C	-2.662405	-4.467665	0.380149
C	-5.228406	-3.084670	-0.656071
C	-2.912286	-3.613286	-2.572187
O	-2.470133	2.555588	0.700447
O	-2.646075	-1.758999	-0.313390
O	-0.303706	3.672915	-1.466715
O	2.034708	2.569813	-1.102610
O	0.116660	-2.852281	-0.834891
O	1.936686	-2.889284	1.597368
O	0.375782	-2.543336	3.267999
H	-1.854311	1.556894	-2.424920
H	-2.797551	3.441296	-1.143986
H	-2.928470	-0.603660	-2.010963
H	-4.855817	-0.278637	-0.503949
H	-3.784887	0.322504	0.767280
H	-4.244076	1.649182	-1.954197
H	-1.329538	0.453521	0.359745
H	-5.313760	3.465732	-0.626364
H	-6.164995	1.934046	-0.372106
H	-5.047468	2.540595	0.863747
H	0.576932	-1.401462	-3.047839
H	-1.144813	-1.610628	-2.794515
H	-0.503394	-0.028712	-3.304885
H	-1.073745	-1.475167	1.476422
H	0.494580	-0.667313	1.478578
H	0.056193	-3.707750	1.606868
H	3.430868	-4.105621	0.978406
H	2.173456	-4.940157	1.921385
H	1.846363	-4.454176	0.230576
H	1.932393	-3.698874	4.019601
H	0.572238	-3.345610	5.114367
H	0.366870	-4.548532	3.812963
H	2.565095	-0.537798	1.144478
H	2.864796	1.166080	0.753882
H	4.866332	0.100024	1.638886
H	4.806883	-1.185495	0.450577
H	5.257566	0.466391	-1.378788
H	5.222836	1.778161	-0.209572
H	7.190108	0.748219	0.975049
H	7.203137	-0.563258	-0.197067
H	7.632238	2.395467	-0.850772
H	7.622677	1.096451	-2.034901
H	9.974407	1.698651	-1.388996
H	9.610524	1.326375	0.301473
H	9.605709	0.036358	-0.908376
H	2.560100	-2.267746	-0.698753
H	2.392769	-1.777703	-2.394283
H	3.936150	-1.601164	-1.576640
H	3.083052	0.587184	-1.633552
H	0.189607	2.591230	2.125545
H	0.556204	3.924857	1.015435
H	0.287070	4.248180	2.732364
H	-2.434702	4.534756	3.913079
H	-3.870652	3.927620	3.072723
H	-2.657858	2.793712	3.687026
H	-1.921368	6.309921	1.314764
H	-1.701048	5.528299	-0.257651

H	-3.311481	5.588984	0.497268
H	-2.780872	-4.145724	1.420717
H	-3.167335	-5.433443	0.267080
H	-1.596385	-4.615569	0.177742
H	-5.656032	-2.401478	-1.398552
H	-5.676906	-4.070747	-0.826785
H	-5.538623	-2.746745	0.338450
H	-3.205942	-2.826540	-3.276682
H	-1.837531	-3.793299	-2.676420
H	-3.438258	-4.526638	-2.875697
H	1.697278	3.470594	-1.247630

26TMS-TMS Imaginary Frequencies: none found
Zero-point correction = 0.860248 (Hartree/Particle)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
Sum of electronic and thermal Free Energies =
-2320.434841 hartrees (-1456096.06707591 kcal/mol)

Si	-3.241012	-3.062219	-1.473889
Si	-2.198422	3.623969	1.774776
C	-2.597327	2.533887	-0.716048
C	-1.304035	1.758111	-0.843945
C	-1.345739	0.281375	-0.532079
C	-2.559114	-0.379470	-1.225446
C	-3.848326	0.398541	-0.979128
C	-3.744221	1.845882	-1.457169
C	-0.005970	-0.485183	-0.824290
C	-0.150087	2.393353	-1.083058
C	1.162623	1.728849	-0.916208
C	1.200291	0.346543	-0.274509
C	-5.055896	2.602669	-1.272261
C	0.179346	-0.736721	-2.324532
C	-0.080308	-1.828766	-0.065264
C	-0.421659	-1.832547	1.422139
C	0.504575	-2.717746	2.248238
C	2.630306	-2.644080	3.255937
C	-0.943840	-4.309676	3.221818
C	2.660790	-0.194948	-0.379644
C	3.463081	0.430184	0.780938
C	4.971700	0.164026	0.763284
C	5.669287	0.578914	-0.532051
C	7.190202	0.461934	-0.447798
C	7.899006	0.815069	-1.754166
C	9.417378	0.693538	-1.653363
C	2.877805	-1.709429	-0.404014
C	-0.488403	3.006115	2.254463
C	-3.328609	3.578517	3.263773
C	-2.074480	5.344613	1.044388
C	-2.958729	-4.426594	-0.229620
C	-5.066521	-2.880831	-1.874788
C	-2.301605	-3.402298	-3.058838
O	-2.941094	2.601912	0.664868
O	-2.667561	-1.687983	-0.696659
O	-0.078984	3.715454	-1.385551
O	2.158684	2.367960	-1.221418
O	0.098071	-2.888173	-0.630982
O	1.585253	-1.925356	2.622937
O	-0.118785	-3.182390	3.424042
H	-2.456126	3.545784	-1.117696
H	-2.375428	-0.418326	-2.311718
H	-4.671426	-0.109958	-1.493689

H	-4.070869	0.380907	0.095102
H	-3.474380	1.850009	-2.523923
H	-1.569982	0.205455	0.542616
H	0.988014	0.539543	0.791777
H	-4.961534	3.644770	-1.597113
H	-5.858241	2.138558	-1.854411
H	-5.349084	2.601173	-0.218377
H	1.191777	-1.081778	-2.544137
H	-0.505983	-1.504551	-2.684153
H	0.006213	0.181851	-2.894908
H	-1.446812	-2.218062	1.471676
H	-0.416228	-0.840570	1.879693
H	0.845896	-3.588450	1.657917
H	3.447274	-1.937931	3.416846
H	2.302667	-3.050075	4.217654
H	2.984178	-3.464589	2.615552
H	-0.392523	-5.125950	2.734430
H	-1.277442	-4.641291	4.206508
H	-1.826640	-4.069813	2.614567
H	3.040007	0.043893	1.718794
H	3.302851	1.514829	0.777510
H	5.423367	0.714485	1.599423
H	5.175362	-0.897087	0.959651
H	5.312244	-0.042228	-1.365108
H	5.391365	1.612908	-0.780601
H	7.561208	1.115967	0.354227
H	7.459418	-0.564172	-0.157540
H	7.628964	1.838460	-2.045600
H	7.529190	0.158412	-2.552530
H	9.906330	0.949187	-2.598400
H	9.813834	1.361772	-0.880968
H	9.712214	-0.328442	-1.390692
H	2.592355	-2.171320	0.544849
H	2.339914	-2.213761	-1.206542
H	3.943568	-1.905928	-0.558986
H	3.061791	0.202396	-1.319306
H	-0.488572	1.923320	2.427786
H	0.266332	3.239408	1.495953
H	-0.170406	3.483840	3.189120
H	-2.958457	4.236689	4.057704
H	-4.339628	3.903881	2.997734
H	-3.398907	2.565130	3.673133
H	-1.684402	6.048553	1.788691
H	-1.396674	5.363307	0.184094
H	-3.055043	5.710829	0.719807
H	-3.525660	-4.245477	0.689978
H	-3.274630	-5.396248	-0.630573
H	-1.892316	-4.491949	0.014388
H	-5.244363	-2.153549	-2.674793
H	-5.467366	-3.842440	-2.217858
H	-5.644923	-2.573840	-0.996827
H	-2.358402	-2.576140	-3.776757
H	-1.248525	-3.613492	-2.847728
H	-2.730837	-4.284000	-3.550540
H	0.863758	3.917217	-1.516583

25TBS-TMS

HF = -2439.0868687 hartrees (-1530551.40097794 kcal/mol)

Si	2.293432	4.184622	-0.587810
Si	2.473397	-3.320960	0.536817
C	2.808965	-1.401472	-1.476900
C	1.478161	-0.772384	-1.925394

C	1.111747	0.417055	-1.032447
C	2.225858	1.469950	-1.174819
C	3.583202	0.875316	-0.793401
C	3.937579	-0.374326	-1.603905
C	-0.327360	0.965845	-1.293405
C	0.394309	-1.813739	-1.954480
C	-0.970061	-1.433426	-1.559353
C	-1.360766	-0.175818	-1.242798
C	5.274978	-0.965539	-1.169665
C	-0.403676	1.650047	-2.668415
C	-0.646307	2.006902	-0.190660
C	-0.447387	1.592589	1.255167
C	-1.188991	2.494260	2.222436
C	-3.282346	3.584021	1.860209
C	-1.408533	2.858316	4.534314
C	-2.859890	-0.017276	-0.974959
C	-3.214215	-0.597152	0.419374
C	-4.718115	-0.694684	0.699001
C	-5.504911	-1.527304	-0.312461
C	-6.975903	-1.682131	0.069912
C	-7.778522	-2.515113	-0.927672
C	-9.250863	-2.636725	-0.542786
C	-3.499002	1.364347	-1.147326
C	3.422337	-3.464049	2.149638
C	3.205958	-4.496555	-0.723507
C	0.647344	-3.654563	0.785022
C	1.478336	5.061253	0.845621
C	4.153100	4.445710	-0.581802
C	1.602748	4.787214	-2.223274
C	4.804970	-2.796438	2.030385
C	2.673350	-2.806454	3.323601
C	3.655043	-4.941979	2.514565
O	2.705842	-1.795795	-0.123794
O	1.928536	2.566130	-0.333285
O	0.601374	-2.965370	-2.324187
O	-1.861716	-2.458372	-1.621532
O	-1.032863	3.122767	-0.475417
O	-2.578641	2.365396	2.027923
O	-0.824949	2.081462	3.508144
H	1.603734	-0.439355	-2.968083
H	3.020032	-2.269693	-2.116361
H	2.266244	1.798430	-2.228779
H	4.357349	1.639541	-0.927460
H	3.554943	0.620957	0.273755
H	3.999103	-0.102409	-2.668495
H	1.145753	0.044524	-0.001048
H	5.529952	-1.848576	-1.765933
H	6.083340	-0.236597	-1.285730
H	5.233095	-1.264291	-0.117386
H	-1.411659	2.000212	-2.885863
H	0.251445	2.522810	-2.703363
H	-0.112319	0.949805	-3.456811
H	0.625007	1.660057	1.465619
H	-0.745567	0.550491	1.414002
H	-0.904489	3.549172	2.073969
H	-4.336260	3.324887	1.735827
H	-3.182148	4.235726	2.738396
H	-2.932067	4.120852	0.970271
H	-2.497929	2.739036	4.553105
H	-0.994752	2.502364	5.479266
H	-1.158252	3.922606	4.412012
H	-2.772476	0.044472	1.188139
H	-2.767178	-1.593893	0.508936
H	-4.843570	-1.138882	1.695282

H	-5.154673	0.311070	0.763066
H	-5.447116	-1.067488	-1.308762
H	-5.040825	-2.519613	-0.405839
H	-7.047477	-2.142458	1.065680
H	-7.432823	-0.685543	0.158539
H	-7.332144	-3.515339	-1.002336
H	-7.694168	-2.063632	-1.924932
H	-9.806774	-3.248797	-1.259539
H	-9.360410	-3.097375	0.445312
H	-9.727797	-1.651017	-0.503885
H	-3.288094	2.020852	-0.301260
H	-3.193527	1.869109	-2.065061
H	-4.584693	1.235739	-1.201794
H	-3.326815	-0.681618	-1.713036
H	3.183472	-5.531258	-0.363696
H	2.653056	-4.457258	-1.668284
H	4.249539	-4.239265	-0.935000
H	0.504918	-4.681248	1.142556
H	0.212652	-2.979039	1.528597
H	0.086560	-3.553424	-0.151064
H	1.758743	4.601522	1.799812
H	1.769600	6.116855	0.882152
H	0.389523	5.012453	0.739094
H	4.632528	4.002911	-1.462127
H	4.379697	5.518619	-0.594647
H	4.619229	4.018832	0.312624
H	1.975589	4.210021	-3.077297
H	0.508654	4.750998	-2.227043
H	1.906312	5.828766	-2.384506
H	-1.369182	-3.230084	-1.950418
H	4.682263	-1.739175	1.920673
H	5.376366	-2.999608	2.911934
H	5.316940	-3.186673	1.175690
H	3.035373	-1.809387	3.463938
H	1.625788	-2.778428	3.107432
H	2.838488	-3.374649	4.215107
H	2.719921	-5.462004	2.509947
H	4.314003	-5.386702	1.798400
H	4.092890	-5.004104	3.488901

26TBS-TMS

HF = -2439.0730899 hartrees (-1530542.75464315 kcal/mol)

Si	2.114381	4.166856	-1.126440
Si	2.707495	-3.122732	0.563545
C	2.611538	-1.472522	-1.631724
C	1.190656	-0.971256	-1.488138
C	0.992502	0.382266	-0.849029
C	1.975307	1.410591	-1.454334
C	3.406070	0.881320	-1.483189
C	3.518990	-0.421877	-2.272547
C	-0.490689	0.899861	-0.863858
C	0.155212	-1.765771	-1.786309
C	-1.230488	-1.437116	-1.380803
C	-1.451118	-0.259902	-0.437693
C	4.960761	-0.913256	-2.357697
C	-0.888634	1.419011	-2.249666
C	-0.581485	2.038399	0.176502
C	-0.080125	1.798092	1.597696
C	-1.054747	2.278021	2.667139
C	-3.001391	1.555934	3.775644
C	0.173818	3.892068	3.877710
C	-2.989100	-0.021786	-0.314255
C	-3.524260	-1.029898	0.724363

C	-5.048137	-1.083248	0.872808
C	-5.799026	-1.349817	-0.431706
C	-7.295626	-1.569764	-0.217749
C	-8.070185	-1.777319	-1.518012
C	-9.563269	-1.995891	-1.287119
C	-3.484959	1.385466	0.025021
C	3.907237	-3.410650	1.982605
C	2.831380	-4.527026	-0.664914
C	0.966849	-2.927698	1.228040
C	1.726754	5.149097	0.414454
C	3.884276	4.455059	-1.683678
C	0.954366	4.632862	-2.521936
C	5.365909	-3.199108	1.536370
C	3.789010	-4.864249	2.477250
C	3.621956	-2.492493	3.185602
O	3.116500	-1.758425	-0.330569
O	1.898171	2.571326	-0.647906
O	0.297016	-2.979609	-2.378760
O	-2.118618	-2.188771	-1.754959
O	-1.016586	3.133278	-0.116973
O	-1.919792	1.218761	2.923678
O	-0.399119	2.602069	3.872183
H	2.616052	-2.383510	-2.244321
H	1.665462	1.639392	-2.487235
H	4.056558	1.645758	-1.922890
H	3.741981	0.717053	-0.451692
H	3.135255	-0.256047	-3.290409
H	1.319300	0.273937	0.196191
H	-1.087008	-0.625843	0.538416
H	5.025322	-1.859665	-2.905922
H	5.591562	-0.181223	-2.871773
H	5.366311	-1.074060	-1.354550
H	-1.965808	1.586129	-2.313499
H	-0.403183	2.370024	-2.469840
H	-0.613816	0.697719	-3.026384
H	0.854467	2.367511	1.663377
H	0.150767	0.752559	1.814382
H	-1.616629	3.164188	2.317710
H	-3.649344	0.678679	3.826193
H	-2.647809	1.808167	4.779854
H	-3.571885	2.402138	3.366952
H	-0.571225	4.661139	3.630242
H	0.549643	4.069615	4.886722
H	1.011042	3.973455	3.171979
H	-3.076582	-0.771750	1.694276
H	-3.166813	-2.032341	0.460775
H	-5.291791	-1.879081	1.589341
H	-5.421695	-0.153028	1.321301
H	-5.660504	-0.506636	-1.122458
H	-5.363951	-2.227772	-0.929768
H	-7.445191	-2.440691	0.436288
H	-7.716002	-0.706363	0.318388
H	-7.649640	-2.637707	-2.054724
H	-7.921853	-0.904904	-2.167810
H	-10.100324	-2.141306	-2.229430
H	-9.738400	-2.879376	-0.663346
H	-10.011017	-1.135889	-0.776937
H	-3.184395	1.685109	1.032514
H	-3.144764	2.147922	-0.675447
H	-4.579255	1.385988	-0.006501
H	-3.413387	-0.285556	-1.289988
H	2.558300	-5.480711	-0.199681
H	2.163464	-4.361933	-1.516636
H	3.851559	-4.622010	-1.051804

H	0.643954	-3.847408	1.729590
H	0.909470	-2.114272	1.959424
H	0.254226	-2.718727	0.422142
H	2.418150	4.898709	1.226337
H	1.809459	6.225417	0.226094
H	0.701485	4.939868	0.740176
H	4.102087	3.966025	-2.639700
H	4.057955	5.528991	-1.823574
H	4.605518	4.095582	-0.941926
H	1.081721	4.007034	-3.412604
H	-0.088711	4.572669	-2.195572
H	1.153715	5.667727	-2.826445
H	-0.600523	-3.339244	-2.487049
H	5.386539	-2.569794	0.671246
H	5.917345	-2.735799	2.327675
H	5.807336	-4.144750	1.300143
H	2.762469	-5.090712	2.676817
H	4.161071	-5.528281	1.725231
H	4.361347	-4.983720	3.373385
H	4.352588	-1.711510	3.219382
H	2.646630	-2.064316	3.084097
H	3.668434	-3.063715	4.089176

Full *Gaussian09* Citation:

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