Structure Elucidation of (+)-Amphidinolide A by Total Synthesis and NMR Chemical Shift Analysis

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To a solution of oxalyl chloride (1.50 mL, 2.18 g, 17.2 mmol) in CH_2Cl_2 (40 mL) at -78°C was added DMSO (2.50 mL, 2.75 g, 35.2 mmol), stirred for 15 min, and a solution of alcohol **12** (3.264 g, 10.6 mmol) in CH_2Cl_2 (35 mL) at -78°C was added via cannula. After 1 h at -78°C , triethylamine (7.4 mL, 5.4 g, 53 mmol) was added, the reaction mixture was stirred at -78°C for 15 min, warmed to room temperature, diluted with CH_2Cl_2 , washed with saturated NH_4Cl (2 x), brine (1 x), dried over MgSO_4 , filtered through a pad of silica gel, and concentrated to give the aldehyde which was used in the next step without further purification: ^1H NMR (500 MHz, CDCl_3) δ 9.75 (d, $J = 1.7$ Hz, 1H), 7.26 (d, $J = 8.8$ Hz, 2H), 6.88 (d, $J = 8.5$ Hz, 2H), 4.53 (s, 2H), 4.51 (m, 1H), 4.21 (m, 1H), 4.17 (dd, $J = 7.1, 1.7$ Hz, 1H), 3.81 (s, 3H), 3.79 (m, 1H), 3.62 (d, $J = 4.9$ Hz, 1H), 1.92-1.62 (m, 8H). To a solution of $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{OTBS}$ (4.849 g, 26.3 mmol) in THF (100 mL) at 0°C was added $n\text{-BuLi}$ (10.5 mL, 2.5 M in hexanes, 26.3 mmol), stirred for 15 min, cooled to -60°C , and $\text{ClTi}(\text{O}i\text{-Pr})_3$ (6.25 mL, 6.82 g, 26.2 mmol) was added. The solution was stirred at -60°C for 1.5 h, cooled to -78°C , and a solution of the aldehyde, prepared in the previous step, in THF (80 mL) at -78°C was added via cannula. The reaction mixture was stirred at -78°C for 1 h, warmed from -78°C to -50°C over 1 h, quenched with saturated NH_4Cl , warmed to room temperature, and diluted with ether and water. The aqueous phase was extracted with ether (6 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO_4 , concentrated, and used in the next step without further purification: ^1H NMR (500 MHz, CDCl_3) δ 7.26 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 4.55-4.52 (m, 2H), 4.49 (m, 1H), 3.86 (dd, $J = 7.3, 4.4$ Hz, 1H), 3.81-3.78 (m, 3H), 3.80 (s, 3H), 3.69 (t, $J = 7.3$ Hz, 2H), 3.62 (d, $J = 5.1$ Hz, 1H), 2.45 (d, $J = 4.6$ Hz, 1H), 2.38 (dddd, $J = 7.1, 7.1, 2.0, 2.0$ Hz, 1H), 1.88-1.65 (m, 8H), 0.89 (s, 9H), 0.08 (s, 6H). To a solution of the alkyne, prepared in the previous step, in THF (33 mL) at 0°C was added Red-Al® (5.6 mL, 65% wt in toluene, 18.7

mmol). The reaction mixture was warmed to room temperature, stirred for 6 h, quenched with aqueous potassium sodium tartrate, stirred for 20 min, and diluted with ether and water. The aqueous phase was extracted with Et₂O (5 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO₄, and concentrated. Purification by flash column chromatography on silica gel (20% to 30% to 50% EtOAc in petroleum ether) gave alkene **13** (2.636 g, 51%) and recovered alcohol **12** (747 mg, 23%) as colorless oils. Data for **13**: *R_f* = 0.29 (20% EtOAc in petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ 7.25 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.76 (dddd, *J* = 13.9, 6.8, 6.8, 1.2 Hz, 1H), 5.51 (ddd, *J* = 15.4, 6.1, 1.2 Hz, 1H), 4.51 (s, 2H), 4.18 (m, 1H), 4.07 (ddd, *J* = 7.3, 5.4, 5.4 Hz, 1H), 3.80 (s, 3H), 3.70 (dd, *J* = 7.6, 5.6 Hz, 1H), 3.62 (t, *J* = 6.8 Hz, 2H), 3.58 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.51 (dd, *J* = 10.0, 5.1 Hz, 1H), 2.57 (d, *J* = 2.9 Hz, 1H), 2.25 (q br, *J* = 6.8 Hz, 2H), 1.88-1.62 (m, 8H), 0.89 (s, 9H), 0.04 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 159.3, 130.1, 129.8, 129.7, 129.4, 119.3, 113.8, 81.2, 76.7, 73.2, 72.2, 70.4, 68.2, 55.2, 37.2, 37.1, 36.0, 25.9, 23.6, 23.3, 18.3, -5.3; IR (neat) 3458 (br), 2955, 1614, 1515, 1250, 1102 cm⁻¹; MALDIMS *m/z* 515.3 [M + Na]⁺; optical rotation [*α*]_D²⁷ +9.5° (*c* 1.0, CH₂Cl₂). Anal. Calcd for C₂₇H₄₄O₆Si: C, 65.82; H, 9.00. Found: C, 65.66; H, 8.87.

To a solution of alcohol **13** (3.038 g, 6.17 mmol) in CH₂Cl₂ (40 mL) at 0 °C was added NaHCO₃ (3.668 g, 43.7 mmol) and Dess-Martin reagent (3.559 g, 8.39 mmol). The reaction mixture was warmed to room temperature, stirred for 2 h, quenched with saturated Na₂SO₃, stirred for 15 min, and diluted with water. The aqueous phase was extracted with CH₂Cl₂ (5 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO₄, and concentrated. Purification by flash column chromatography on silica gel (5% to 10% to 15% EtOAc in petroleum ether) gave ketone **23** (2.613 g, 86%) as a colorless oil: *R_f* = 0.20 (10% EtOAc in petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.05 (ddd, *J* = 15.9, 7.2, 7.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.58 (ddd, *J* = 15.9, 1.5, 1.5 Hz, 1H), 4.54 (s, 2H), 4.30 (d, *J* = 7.0 Hz, 1H), 4.23 (ddd, *J* = 7.0, 5.8, 3.5 Hz, 1H), 3.80 (s, 3H), 3.73 (t, *J* = 6.4 Hz, 2H), 3.70 (dd, *J* = 10.7, 3.5 Hz, 1H), 3.60 (dd, *J* = 10.5, 5.6 Hz, 1H), 2.44 (ddd, *J* = 13.6, 6.6,

1.5 Hz, 2H), 1.91-1.67 (m, 8H), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.7, 159.2, 147.1, 130.0, 129.4, 126.5, 120.9, 113.8, 80.8, 77.5, 73.2, 69.9, 61.4, 55.3, 36.8, 36.7, 36.2, 25.9, 23.7, 23.3, 18.3, -5.3; IR (neat) 2959, 1691, 1252, 1103, 836 cm^{-1} ; EIMS m/z 277 (1), 213 (1), 145 (1), 137 (1), 121 (100); HREIMS calcd for $\text{C}_{27}\text{H}_{42}\text{O}_6\text{Si}$ 490.2751, found 490.2751; optical rotation $[\alpha]_D^{27} +6.0^\circ$ (c 1.0, CH_2Cl_2). Anal. Calcd for $\text{C}_{27}\text{H}_{42}\text{O}_6\text{Si}$: C, 66.09; H, 8.63. Found: C, 66.40; H, 8.62.

To a mixture of $\text{K}_3\text{Fe}(\text{CN})_6$ (17.96 g, 54.5 mmol), K_2CO_3 (7.57 g, 54.8 mmol), NaHCO_3 (4.62 g, 55.0 mmol), methanesulfonamide (1.720 g, 18.1 mmol), and $(\text{DHQ})_2\text{-PHAL}$ (369 mg, 0.47 mmol) at room temperature was added water (85 mL) and *tert*-butyl alcohol (45 mL). The reaction mixture was cooled to 0 $^\circ\text{C}$, $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (171 mg, 0.46 mmol) was added followed by a solution of alkene **23** (8.871 g, 18.1 mmol) in *tert*-butyl alcohol (40 mL). The reaction mixture was stirred at 0 $^\circ\text{C}$ for 22 h, quenched with Na_2SO_3 (80 g), warmed to room temperature, stirred for 1 h, and diluted with EtOAc and water. The aqueous phase was extracted with EtOAc (4 x) and the combined organic extracts were washed with 2 M NaOH (1 x), brine (1 x), dried over MgSO_4 , and concentrated to give the diol which was used in the next step without further purification: R_f = 0.46 (30% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, J = 7.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.55 (s, 2H), 4.52 (d br, J = 7.3 Hz, 1H), 4.48 (d, J = 6.8 Hz, 1H), 4.34 (ddd, J = 5.9, 5.9, 3.2 Hz, 1H), 3.95-3.85 (m, 3H), 3.80 (s, 3H), 3.75 (dd, J = 11.0, 3.2 Hz, 1H), 3.62 (dd, J = 10.8, 5.9 Hz, 1H), 3.45 (d, J = 6.8 Hz, 1H), 3.14 (d, J = 4.9 Hz, 1H), 2.03-1.66 (m, 10H), 0.89 (s, 9H), 0.08 (s, 6H). To a solution of the diol, prepared in the previous step, and 1,1-dimethoxycyclopentane (25 mL) in CH_2Cl_2 (190 mL) at 0 $^\circ\text{C}$ was added $\text{TsOH} \cdot \text{H}_2\text{O}$ (562 mg, 2.95 mmol). The reaction mixture was stirred at 0 $^\circ\text{C}$ for 2 h, diluted with ether, washed with saturated NaHCO_3 (1 x), brine (1 x), dried over MgSO_4 , and concentrated to give ketal **14** which was used in the next step without further purification: R_f = 0.68 (30% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.57-4.51 (m, 3H), 4.41 (d, J = 7.1 Hz, 1H), 4.26 (ddd, J = 9.3, 6.1, 3.2 Hz, 1H), 4.18 (ddd, J = 8.8,

7.1, 3.7 Hz, 1H), 3.80 (s, 3H), 3.79-3.72 (m, 3H), 3.62 (dd, $J = 10.7, 6.1$ Hz, 1H), 2.07-1.63 (m, 20H), 0.87 (s, 9H), 0.04 (s, 6H). To a suspension of methyltriphenylphosphonium bromide (13.08 g, 36.6 mmol) in THF (150 mL) at 0 °C was added NaHMDS (37 mL, 1.0 M in THF, 37 mmol), stirred at 0 °C for 15 min, warmed to room temperature, stirred for 1 h, cooled to 0 °C, and a solution of ketone **14**, prepared in the previous step, in THF (150 mL) at 0 °C was added via cannula. The reaction mixture was stirred at 0 °C for 11 h and diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO₄, and concentrated. Purification by flash column chromatography on silica gel (5% to 10% EtOAc in petroleum ether) gave alkene **24** (6.351 g, 60%) as a colorless oil: $R_f = 0.38$ (10% EtOAc in petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, $J = 8.2$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 5.34 (s, 2H), 4.55-4.49 (m, 2H), 4.25 (d, $J = 7.9$ Hz, 1H), 4.11 (d, $J = 8.1$ Hz, 1H), 4.03 (ddd, $J = 9.0, 6.4, 2.3$ Hz, 1H), 3.89 (ddd, $J = 8.9, 8.9, 2.6$ Hz, 1H), 3.80 (s, 3H), 3.78-3.66 (m, 3H), 3.50 (dd, $J = 10.8, 6.6$ Hz, 1H), 1.97-1.56 (m, 18H), 0.88 (s, 9H), 0.042 (s, 3H), 0.038 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.2, 143.4, 130.2, 129.3, 119.4, 118.6, 116.5, 113.7, 80.9, 80.6, 77.6, 77.2, 73.1, 69.4, 60.1, 55.2, 37.5, 37.4, 37.1 (2 carbons), 35.3, 25.9, 23.6, 23.4, 23.3 (2 carbons), 18.3, -5.3, -5.4; IR (neat) 2949, 1614, 1510, 1334, 1103 cm⁻¹; MALDIMS m/z 611.3 [M + Na]⁺; optical rotation [α]_D²⁵ -5.9° (*c* 1.0, CH₂Cl₂). Anal. Calcd for C₃₃H₅₂O₇Si: C, 67.31; H, 8.90. Found: C, 67.15; H, 8.70.

To a solution of ether **24** (7.987 g, 13.6 mmol) in THF (90 mL) at room temperature was added TBAF (20.4 mL, 1 M in THF, 20.4 mmol). The reaction mixture was stirred for 24 h, and diluted with ether and water. The aqueous phase was extracted with ether (4 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO₄, and concentrated. Purification by flash column chromatography on silica gel (30% to 50% EtOAc in petroleum ether) gave alcohol **25** (5.024 g, 78%) as a colorless oil: $R_f = 0.38$ (50% EtOAc in petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, $J = 8.7$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 5.38 (s, 1H), 5.36 (s, 1H), 4.51 (s, 2H), 4.27 (d, $J = 8.1$ Hz, 1H), 4.15 (d, $J = 8.2$ Hz, 1H), 4.02 (ddd, $J = 8.2, 6.3, 2.7$

Hz, 1H), 3.91 (ddd, $J = 8.4, 8.4, 3.4$ Hz, 1H), 3.79 (s, 3H), 3.78-3.75 (m, 2H), 3.66 (dd, $J = 10.7, 2.7$ Hz, 1H), 3.50 (dd, $J = 10.8, 6.3$ Hz, 1H), 2.44 (t, $J = 5.6$ Hz, 2H), 1.99-1.59 (m, 17H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.1, 143.0, 130.1, 129.35, 129.30, 119.5, 118.9, 117.2, 113.7, 80.9, 80.32, 80.30, 77.2, 73.1, 69.1, 60.8, 55.2, 37.5, 37.4, 37.1, 34.0, 23.5, 23.4, 23.2 (2 carbons); IR (neat) 3486 (br), 2951, 1611, 1516, 1108 cm^{-1} ; MALDIMS m/z 497.3 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{26} +4.4^\circ$ (c 1.0, CH_2Cl_2); Anal. Calcd for $\text{C}_{27}\text{H}_{38}\text{O}_7$: C, 68.33; H, 8.07. Found: C, 68.17; H, 7.90.

To a solution of oxalyl chloride (1.50 mL, 2.18 g, 17.2 mmol) in CH_2Cl_2 (50 mL) at -78°C was added DMSO (2.45 mL, 2.70 g, 34.5 mmol), stirred for 15 min, and a solution of alcohol **25** (5.083 g, 10.7 mmol) in CH_2Cl_2 (50 mL) at -78°C was added via cannula. After 1 h at -78°C , triethylamine (7.5 mL, 5.4 g, 54 mmol) was added, the reaction mixture was stirred at -78°C for 15 min, warmed to room temperature, diluted with CH_2Cl_2 , washed with saturated NH_4Cl (2 x), brine (1 x), dried over MgSO_4 , filtered through a pad of silica gel, and concentrated to give the aldehyde which was used in the next step without further purification: $R_f = 0.32$ (30% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 9.78 (dd, $J = 2.7, 1.6$ Hz, 1H), 7.26 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.43 (s, 1H), 5.32 (s, 1H), 4.54-4.49 (m, 2H), 4.30 (d, $J = 8.2$ Hz, 1H), 4.20 (ddd, $J = 8.2, 8.2, 3.2$ Hz, 1H), 4.16 (d, $J = 8.1$ Hz, 1H), 3.98 (ddd, $J = 8.6, 6.0, 2.7$ Hz, 1H), 3.80 (s, 3H), 3.64 (dd, $J = 10.7, 2.7$ Hz, 1H), 3.50 (dd, $J = 10.8, 6.0$ Hz, 1H), 2.86 (ddd, $J = 16.6, 3.1, 1.5$ Hz, 1H), 2.61 (ddd, $J = 16.6, 8.2, 2.6$ Hz, 1H), 1.92-1.61 (m, 16H). To a suspension of methyltriphenylphosphonium bromide (6.00 g, 16.8 mmol) in THF (65 mL) at 0°C was added $n\text{-BuLi}$ (6.70 mL, 2.5 M in hexanes, 16.8 mmol). The solution was stirred at 0°C for 30 min and a solution of the aldehyde, prepared in the previous step, in THF (65 mL) at room temperature was added via cannula. The reaction mixture was warmed to room temperature over 1 h, stirred at room temperature for 14 h, and diluted with ether and water. The aqueous phase was extracted with ether (5 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO_4 , and concentrated. Purification by flash column chromatography on silica gel

(5% to 10% to 20% EtOAc in petroleum ether) gave alkene **26** (3.990 g, 79%) as a colorless oil: R_f = 0.55 (20% EtOAc in petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 7.26 (d, J = 8.2 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.86 (dddd, J = 17.1, 13.6, 10.2, 6.9 Hz, 1H), 5.36 (s, 1H), 5.34 (s, 1H), 5.11 (dm, J = 17.2 Hz, 1H), 5.08 (dm, J = 10.2 Hz, 1H), 4.55-4.49 (m, 2H), 4.27 (d, J = 7.9 Hz, 1H), 4.15 (d, J = 7.9 Hz, 1H), 4.02 (ddd, J = 8.1, 6.4, 2.6 Hz, 1H), 3.85 (ddd, J = 7.9, 7.9, 3.8 Hz, 1H), 3.80 (s, 3H), 3.69 (dd, J = 10.7, 2.8 Hz, 1H), 3.50 (dd, J = 10.7, 6.6 Hz, 1H), 2.49 (m, 1H), 2.26 (ddd, J = 14.8, 7.5, 7.5 Hz, 1H), 1.94-1.56 (m, 16H); ^{13}C NMR (101 MHz, CDCl_3) δ 159.4, 143.7, 134.5, 130.4, 129.6, 119.7, 119.0, 117.5, 116.9, 113.9, 80.9, 80.7, 80.3, 77.4, 73.3, 69.6, 55.5, 37.8, 37.7, 37.41, 37.38, 36.5, 23.8, 23.7, 23.6 (2 carbons); IR (neat) 2959, 1614, 1515, 1103 cm^{-1} ; EIMS m/z 137 (2), 123 (2), 122 (4), 121 (100); HREIMS calcd for $\text{C}_{28}\text{H}_{38}\text{O}_6$ 470.2663, found 470.2668; optical rotation $[\alpha]_D^{24} +0.5^\circ$ (c 1.0, CH_2Cl_2). Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_6$: C, 71.46; H, 8.14. Found: C, 71.65; H, 7.98.

found 350.2090; optical rotation $[\alpha]_D^{24} -22^\circ$ (c 1.0, CH_2Cl_2). Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{O}_5$: C, 68.54; H, 8.63. Found: C, 68.70; H, 8.66.

To a solution of oxalyl chloride (40 μL , 58 mg, 0.46 mmol) in CH_2Cl_2 (2 mL) at -78°C was added DMSO (65 μL , 72 mg, 0.92 mmol), stirred for 15 min, and a solution of alcohol **15** (101 mg, 0.29 mmol) in CH_2Cl_2 (2 mL) at -78°C was added via cannula. After 1 h at -78°C , triethylamine (200 μL , 145 mg, 1.4 mmol) was added, the reaction mixture was stirred at -78°C for 15 min, warmed to 0°C , diluted with ether, washed with saturated NH_4Cl (2 x), brine (1 x), dried over MgSO_4 , filtered through a pad of silica gel, and concentrated to give the aldehyde which was used in the next step without further purification: $R_f = 0.19$ (20% EtOAc in petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 9.72 (d, $J = 2.0$ Hz, 1H), 5.87 (dddd, $J = 16.9, 13.6, 10.2, 6.9$ Hz, 1H), 5.51 (s, 1H), 5.32 (s, 1H), 5.16-5.10 (m, 2H), 4.66 (d, $J = 6.6$ Hz, 1H), 4.23 (dd, $J = 6.7, 2.0$ Hz, 1H), 4.20 (d, $J = 8.2$ Hz, 1H), 3.86 (ddd, $J = 7.6, 7.6, 3.8$ Hz, 1H), 2.46 (dm, $J = 14.8$ Hz, 1H), 2.28 (ddd, $J = 14.6, 6.9, 6.9$ Hz, 1H), 2.00-1.62 (m, 16H). To a solution of $(\text{MeO})_2\text{POC}(=\text{N}_2)\text{COMe}$ (277 mg, 1.44 mmol) in MeOH (1 mL) at 0°C was added K_2CO_3 (204 mg, 1.48 mmol). After 30 min, a solution of the aldehyde, prepared in the previous step, in MeOH (1.5 mL) at 0°C was added via cannula. The reaction mixture was warmed to room temperature over 1 h, stirred at room temperature for 24 h, and diluted with ether and water. The aqueous phase was extracted with ether (4 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO_4 , and concentrated. Purification by flash column chromatography on silica gel (5% to 10% EtOAc in petroleum ether) gave alkyne **16** (86 mg, 87%) as a colorless oil: $R_f = 0.45$ (10% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 5.87 (dddd, $J = 17.1, 13.7, 10.1, 6.8$ Hz, 1H), 5.44 (s, 1H), 5.33 (s, 1H), 5.15-5.08 (m, 2H), 4.58 (d, $J = 6.1$ Hz, 1H), 4.52 (dd, $J = 6.2, 2.2$ Hz, 1H), 4.17 (d, $J = 7.9$ Hz, 1H), 3.89 (ddd, $J = 7.7, 7.7, 3.8$ Hz, 1H), 2.50 (d, $J = 2.1$ Hz, 1H), 2.47 (m, 1H), 2.29 (dddd, $J = 14.7, 7.3, 7.3, 1.3, 1.3$ Hz, 1H), 2.06-1.61 (m, 16H); ^{13}C NMR (126 MHz, CDCl_3) δ 142.9, 134.1, 120.7, 119.1, 117.4, 116.1, 81.7, 81.2, 80.4, 79.5, 74.4, 70.6, 37.6, 37.1, 36.7, 36.6, 36.3, 23.9, 23.5, 23.4,

22.9; IR (neat) 3303, 2959, 1642, 1334, 1207, 1107 cm^{-1} ; ESIMS m/z 367.4 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]^{24}_{\text{D}} +1.6^\circ$ (c 1.0, CH_2Cl_2); Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_4$: C, 73.23; H, 8.19. Found: C, 73.35; H, 8.28.

A solution of alkyne **16** (576 mg, 1.67 mmol) and alkene **17** (2.581 g, 8.48 mmol) in DCE (4.3 mL) was degassed by bubbling argon through the solution for 15 min, the reaction mixture was heated to 50°C , and $\text{Cp}^*\text{Ru}(\text{MeCN})_3\text{PF}_6$ (87 mg, 0.17 mmol) was added in one portion. After 1 h, the reaction mixture was filtered through silica gel and concentrated. Purification by flash column chromatography on silica gel (3% to 6% to 9% EtOAc in petroleum ether) gave branched alkene **18** (251 mg, 23%), linear alkene **27** (94 mg, 9%) and recovered alkyne **16** (233 mg, 40%) as colorless oils. Data for **18**: $R_f = 0.30$ (10% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.6$ Hz, 2H), 7.62 (d, $J = 7.5$ Hz, 2H), 7.41 (dd, $J = 7.5, 7.5$ Hz, 2H), 7.32 (dd, $J = 7.4, 7.4$ Hz, 2H), 6.22-6.14 (m, 2H), 5.89 (dddd, $J = 17.1, 13.7, 10.1, 6.7$ Hz, 1H), 5.83 (s, 1H), 5.43 (s, 1H), 5.38 (s, 1H), 5.25 (s, 1H), 5.16-5.10 (m, 2H), 5.00 (s, 1H), 4.42 (d, $J = 7.2$ Hz, 2H), 4.32-4.24 (m, 3H), 4.18 (d, $J = 7.8$ Hz, 1H), 3.93 (ddd, $J = 7.7, 7.7, 3.8$ Hz, 1H), 3.03 (dd, $J = 16.6, 5.9$ Hz, 1H), 2.92 (dd, $J = 16.6, 6.7$ Hz, 1H), 2.52 (m, 1H), 2.31 (ddd, $J = 14.5, 7.5, 7.5$ Hz, 1H), 2.27 (s, 3H), 1.93-1.62 (m, 16H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.0, 153.0, 144.0, 143.3, 142.8, 141.3, 135.5, 134.4, 134.3, 127.7, 127.0, 125.1, 119.9, 119.0, 118.8, 117.8, 117.6, 117.2, 114.7, 83.0, 80.3, 80.2, 79.4, 65.7, 46.8, 37.6, 37.4, 37.30, 37.25, 36.3, 35.1, 23.5, 23.4 (2 carbons), 23.3, 13.9; IR (neat) 2959, 1715, 1613, 1147, 1107 cm^{-1} ; EIMS m/z 180 (21), 165 (20); HREIMS calcd for $\text{C}_{42}\text{H}_{48}\text{O}_6$ 648.3451, found 648.3456; optical rotation $[\alpha]^{24}_{\text{D}} +21^\circ$ (c 0.50, CH_2Cl_2). Data for **27**: $R_f = 0.26$ (10% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.77 (d, $J = 7.5$ Hz, 2H), 7.62 (d, $J = 7.5$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.5$ Hz, 2H), 6.19-6.13 (m, 2H), 5.93-5.80 (m, 2H), 5.83 (s, 1H), 5.56 (dd, $J = 15.4, 6.8$ Hz, 1H), 5.48-5.09 (m, 3H), 5.38 (s, 1H), 4.42 (d, $J = 7.2$ Hz, 1H), 4.30-4.06 (m, 5H), 3.91 (m, 1H), 2.95 (dd, $J = 5.9, 5.9$ Hz, 1H), 2.52 (dm, $J = 10.4$ Hz, 1H),

2.33-2.27 (m, 2H), 2.25 (s, 3H), 1.89-1.65 (m, 16H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.9, 152.9, 144.0, 142.7, 141.2, 134.7, 134.3, 134.2, 132.3, 128.2, 127.7, 127.0, 125.1, 119.9, 118.9, 118.8, 117.9, 117.2, 116.5, 81.9, 80.9, 80.01, 79.96, 65.7, 46.8, 37.6, 37.5, 37.3, 37.2, 36.4, 35.5, 23.50, 23.47, 23.4, 23.3, 13.8.

To a solution of ester **18** (310 mg, 0.48 mmol) in CH_2Cl_2 (14 mL) at room temperature was added piperidine (1.6 mL, 1.4 g, 16 mmol). After 3 h at room temperature, the reaction mixture was diluted with ether, water, and 1 M HCl. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO_4 , and concentrated. Purification by flash column chromatography on silica gel (30% to 50% EtOAc in petroleum ether) gave acid **28** (198 mg, 88%) as a colorless oil: R_f = 0.41 (40% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 6.18-6.14 (m, 2H), 5.88 (dddd, J = 17.1, 13.7, 10.3, 6.7 Hz, 1H), 5.74 (d, J = 0.9 Hz, 1H), 5.41 (s, 1H), 5.36 (s, 1H), 5.23 (s, 1H), 5.15-5.08 (m, 2H), 4.97 (d, J = 1.1 Hz, 1H), 4.29 (d, J = 8.4 Hz, 1H), 4.26 (d, J = 8.4 Hz, 1H), 4.16 (d, J = 7.7 Hz, 1H), 3.91 (ddd, J = 7.7, 7.7, 3.8 Hz, 1H), 3.02 (dd, J = 16.2, 4.5 Hz, 1H), 2.91 (dd, J = 16.1, 5.3 Hz, 1H), 2.51 (dm, J = 14.7 Hz, 1H), 2.31 (m, 1H), 2.29 (d, J = 1.0 Hz, 3H), 1.90-1.62 (m, 17H); ^{13}C NMR (126 MHz, CDCl_3) δ 172.0, 154.7, 143.2, 142.8, 135.5, 135.1, 134.3, 119.0, 118.8, 117.6, 117.4, 117.3, 114.8, 83.1, 80.3, 80.2, 79.4, 37.6, 37.4, 37.30, 37.25, 36.3, 35.1, 23.5, 23.41, 23.40, 23.3, 14.1; IR (neat) 3076 (br), 2959, 1682, 1610, 1107 cm^{-1} ; MALDIMS m/z 493.2 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{28} +28^\circ$ (c 0.50, CH_2Cl_2).

To ketal **28** (76 mg, 0.16 mmol) at room temperature was added acetic acid (1.5 mL) and water (500 μ L). The reaction mixture was heated to 40 °C for 20 h and concentrated to give the tetraol which was used in the next step without further purification. To a solution of the tetraol, prepared in the previous step, in THF (4 mL) at 0 °C was added *i*-Pr₂NEt (260 μ L, 193 mg, 1.5 mmol) and TESOTf (230 μ L, 269 mg, 1.0 mmol). The reaction mixture was stirred at 0 °C for 10 min, quenched with 1 M HCl, stirred for 10 min, and diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with saturated KH₂PO₄ (1 x), brine (1 x), dried over MgSO₄, and concentrated. Purification by flash column chromatography on silica gel (5% to 10% EtOAc in petroleum ether) gave silyl ether **19** (106 mg, 83%) as a colorless oil: *R*_f = 0.56 (30% EtOAc in petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ 6.20 (ddd, *J* = 15.6, 6.8, 6.8 Hz, 1H), 6.14 (d, *J* = 15.6 Hz, 1H), 5.82 (dddd, *J* = 17.0, 14.3, 10.3, 7.1 Hz, 1H), 5.40-5.39 (m, 2H), 5.09 (s, 1H), 5.05 (dd, *J* = 9.6, 2.0 Hz, 1H), 5.02 (d, *J* = 0.9 Hz, 1H), 4.79 (d, *J* = 1.3 Hz, 1H), 4.26 (d, *J* = 4.0 Hz, 1H), 4.23 (d, *J* = 3.8 Hz, 1H), 4.21 (d, *J* = 3.7 Hz, 1H), 3.80 (ddd, *J* = 7.9, 3.9, 3.9 Hz, 1H), 3.01 (dd, *J* = 17.5, 6.6 Hz, 1H), 2.95 (dd, *J* = 17.2, 6.6 Hz, 1H), 2.40 (dm, *J* = 14.2 Hz, 1H), 2.31 (d, *J* = 1.1 Hz, 3H), 2.30 (m, 1H), 2.14 (ddd, *J* = 15.4, 7.7, 7.7 Hz, 1H), 0.99-0.91 (m, 36H), 0.65-0.51 (m, 24H), exchangeable proton not listed; ¹³C NMR (126 MHz, CDCl₃) δ 171.6, 155.0, 148.7, 146.5, 136.4, 136.1, 135.0, 117.2, 116.9, 116.6, 112.9, 78.1, 75.9, 75.8, 75.0, 37.1, 35.4, 14.0, 7.1, 7.05, 7.04, 7.01, 5.4, 5.32, 5.28, 5.1; IR (neat) 2956, 1684, 1610, 1096, 738 cm⁻¹; optical rotation [α]_D²³ -1.3° (*c* 0.20, CH₂Cl₂).

To KN(TMS)₂ (6.4 mL, 0.47 M in DME, 3.0 mmol) at -78°C was added a solution of 5-((*S*)-2-methyl-butane-1-sulfonyl)-1-phenyl-1*H*-tetrazole (823 mg, 2.80 mmol) in DME (6 mL) at -78°C. The solution was stirred at -78°C for 1 h and a solution of aldehyde **29** (677 mg, 2.17 mmol) in DME (6 mL) at -78°C was added via cannula. The reaction mixture was warmed from -78°C to room temperature over 3 h, stirred at room temperature for 10 h, partially concentrated, and diluted with ether and water. The aqueous phase was extracted with ether (5 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO₄, and concentrated.

Chemical reaction scheme showing the conversion of compound **30** to compound **31**. Compound **30** is a complex molecule with a TMSO group, a TMS group, and a TBSO group. It is converted to compound **31**, which has a HO group instead of the TMSO group.

S11

To a solution of alkene **31** (272 mg, 1.39 mmol) in CH_2Cl_2 (11 mL) at -10°C was added $\text{VO}(\text{acac})_2$ (26 mg, 0.098 mmol) and *tert*-butyl hydroperoxide (840 μL , 5–6 M in decane, 4.2–5.0 mmol). The reaction mixture was stirred at -10°C for 6 h and quenched with saturated Na_2SO_3 . After stirring for 15 min, the reaction mixture was diluted with ether and water. The aqueous phase was extracted with ether (3 x) and the combined organic extracts were washed with brine (1 x), dried over MgSO_4 , and concentrated. Purification by flash column chromatography on silica gel (5% to 7.5% to 10% to 15% to 20% EtOAc in petroleum ether) gave a mixture of epoxides **20** (231 mg, 78%) and **32** (45 mg, 15%) as colorless oils. Data for **20**: R_f = 0.44 (20% EtOAc in petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 3.92 (t, J = 3.5 Hz, 1H), 2.85 (dd, J = 6.9, 1.8 Hz, 1H), 2.82 (t, J = 2.9 Hz, 1H), 2.39 (ddd, J = 16.8, 6.9, 2.6 Hz, 1H), 2.23 (ddd, J = 16.8, 7.2, 2.8 Hz, 1H), 2.00 (dd, J = 2.6, 2.1 Hz, 1H), 1.94 (m, 1H), 1.54–1.19 (m, 6H), 1.07 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 82.8, 70.3, 67.9, 59.8, 58.2, 36.7, 35.7, 35.2, 22.8, 20.0, 15.9, 14.2, 14.0; IR (neat) 3466 (br), 3312, 2959, 2361, 1460 cm^{-1} ; CIMS m/z 211.2 $[\text{M} + \text{H}]^+$; optical rotation $[\alpha]_D^{26} +2.0^\circ$ (c 0.25, CH_2Cl_2); Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$: C, 74.24; H, 10.54. Found: C, 74.24; H, 10.68. Data for **32**: R_f = 0.39 (20% EtOAc in petroleum ether); ^1H NMR (400 MHz, CDCl_3) δ 3.64 (t, J = 4.4 Hz, 1H), 2.91 (dd, J = 4.1, 2.4 Hz, 1H), 2.75 (dd, J = 6.9, 2.3 Hz, 1H), 2.37 (ddd, J = 16.8, 6.9, 2.6 Hz, 1H), 2.24 (ddd, J = 16.8, 6.6, 2.4 Hz, 1H), 2.00 (t, J = 2.4 Hz, 1H), 1.93 (m, 1H), 1.43–1.20 (m, 6H), 1.09 (d, J = 6.9 Hz, 3H), 1.01 (d, J = 6.4 Hz, 3H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 82.7, 72.1, 69.7, 61.0, 60.1, 37.1, 35.5, 35.1, 22.6, 20.2, 16.8, 14.2, 14.1; IR (neat) 3464 (br), 3310, 2951, 2353, 1462, 902 cm^{-1} ; CIMS m/z 211.2 $[\text{M} + \text{H}]^+$; optical rotation $[\alpha]_D^{27} +39^\circ$ (c 0.50, CH_2Cl_2); Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2$: C, 74.24; H, 10.54. Found: C, 73.99; H, 10.44.

To a solution of acid **19** (170 mg, 0.21 mmol) in PhMe (3.0 mL) at room temperature was added $[\text{RuCl}_2(p\text{-cymene})]_2$ (12 mg, 0.020 mmol) and ethoxyacetylene (60 μL , 50% wt. in hexanes, 0.34 mmol). The reaction mixture was stirred at room temperature for 2 h and concentrated under a stream of argon. A solution of alcohol **20** (108 mg, 0.51 mmol) in DCE (2.5 mL) was added via cannula followed by CSA (5.1 mg, 22 μmol). The reaction mixture was stirred at room temperature for 2 h, filtered through silica gel, and concentrated. Purification by flash column chromatography on silica gel (1% to 2% to 5% to 20% EtOAc in petroleum ether) gave ester **21** (108 mg, 51%) as a colorless oil: R_f = 0.36 (5% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 6.20-6.10 (m, 2H), 5.82 (dddd, J = 17.2, 14.4, 10.3, 7.3 Hz, 1H), 5.71 (s, 1H), 5.40-5.39 (m, 2H), 5.08 (s, 1H), 5.05 (dm, J = 9.0 Hz, 1H), 5.02 (d, J = 1.2 Hz, 1H), 4.79 (d, J = 1.5 Hz, 1H), 4.70 (dd, J = 6.7, 4.3 Hz, 1H), 4.26 (d, J = 4.0 Hz, 1H), 4.23 (d, J = 3.7 Hz, 1H), 4.21 (d, J = 3.5 Hz, 1H), 3.80 (ddd, J = 8.2, 3.9, 3.9 Hz, 1H), 3.00 (dd, J = 16.6, 5.7 Hz, 1H), 2.94 (dd, J = 17.2, 6.4 Hz, 1H), 2.82 (dd, J = 7.5, 2.2 Hz, 1H), 2.75 (dd, J = 6.7, 2.1 Hz, 1H), 2.40 (dm, J = 14.2 Hz, 1H), 2.34 (ddd, J = 15.9, 5.5, 2.7 Hz, 1H), 2.29 (d, J = 1.1 Hz, 3H), 2.19 (dd, J = 7.9, 2.7 Hz, 1H), 2.16-2.11 (m, 2H), 1.98 (t, J = 2.7 Hz, 1H), 1.49-1.22 (m, 5H), 1.14 (d, J = 6.6 Hz, 3H), 0.98-0.92 (m, 39H), 0.88 (t, J = 6.7 Hz, 3H), 0.65-0.55 (m, 24H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.1, 153.5, 148.8, 146.5, 136.5, 135.5, 135.0, 117.2, 117.0, 116.6, 112.8, 82.3, 78.0, 75.9, 74.9, 74.2, 69.9, 69.6, 62.6, 55.7, 37.1, 36.6, 35.4, 35.2, 35.0, 22.4, 20.0, 15.7, 15.6, 14.3, 14.2, 7.12, 7.09, 7.06, 7.0, 5.4, 5.30, 5.27, 5.1; IR (neat) 3312, 2946, 1714, 1605, 1146, 1094, 741 cm^{-1} ; ESIMS m/z 987.1 $[\text{M} + \text{H}]^+$; optical rotation $[\alpha]_D^{23}$ -18° (c 0.50, CH_2Cl_2).

To a solution of silyl ether **21** (45 mg, 0.046 mmol) in THF (1.0 mL) at room temperature was added 200 μL of a mixture of TBAF (2.0 mL, 1 M in THF, 2.0 mmol) and acetic acid (115 μL , 121 mg, 2.01 mmol). The reaction mixture was stirred at room temperature for 30 h and concentrated. Purification by flash column chromatography on silica gel (30% to 50% to 70% EtOAc in petroleum ether) gave tetraol **22** (19 mg, 79%) as an amorphous solid: R_f = 0.54

(EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 6.19-6.14 (m, 2H), 5.85 (dddd, $J = 16.8, 14.3, 10.6, 7.1$ Hz, 1H), 5.72 (d, $J = 1.0$ Hz, 1H), 5.34 (s, 1H), 5.32 (s, 1H), 5.23 (s, 1H), 5.17 (dm, $J = 7.2$ Hz, 1H), 5.14 (dd, $J = 1.1, 1.1$ Hz, 1H), 5.02 (d, $J = 1.0$ Hz, 1H), 4.71 (dd, $J = 4.2, 2.1$ Hz, 1H), 4.33-4.31 (m, 2H), 4.17 (d, $J = 4.9$ Hz, 1H), 3.83 (ddd, $J = 8.3, 4.6, 4.6$ Hz, 1H), 3.03 (dd, $J = 17.0, 4.9$ Hz, 1H), 2.92 (dd, $J = 16.6, 4.4$ Hz, 1H), 2.80 (dd, $J = 7.5, 2.1$ Hz, 1H), 2.75 (dd, $J = 6.5, 2.2$ Hz, 1H), 2.39 (dm, $J = 14.2$ Hz, 1H), 2.33 (ddd, $J = 16.2, 5.6, 2.8$ Hz, 1H), 2.26 (d, $J = 1.1$ Hz, 3H), 2.25 (dd, $J = 14.5, 8.1$ Hz, 1H), 2.18 (dd, $J = 4.3, 2.7$ Hz, 1H), 2.13 (m, 1H), 1.98 (t, $J = 2.7$ Hz, 1H), 1.48-1.21 (m, 5H), 1.13 (d, $J = 6.7$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H), 0.87 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.0, 152.9, 147.5, 146.3, 135.6, 134.24, 134.18, 118.5, 117.8, 116.7, 114.0, 82.2, 76.0, 74.8, 74.1, 73.0, 72.3, 69.8, 62.5, 55.6, 37.9, 36.6, 36.0, 35.2, 35.0, 22.5, 19.9, 15.6, 14.3, 14.2, 14.0; IR (neat) 3424 (br), 3297, 2917, 1716, 1607, 1236, 1150 cm^{-1} ; ESIMS m/z 553.3 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{29} +4.8^\circ$ (c 0.10, CH_2Cl_2).

A solution of alkyne **22** (15.6 mg, 0.029 mmol) in DCE (30 mL) was degassed by bubbling nitrogen through the solution for 15 min. The reaction mixture was heated to 50°C and $\text{Cp}^*\text{Ru}(\text{MeCN})_3\text{PF}_6$ (3.6 mg, 7.1 μmol) was added. After 6 h at 50°C , the reaction mixture was filtered through silica gel, and concentrated. Purification by flash column chromatography on silica gel (40% to 60% to 80% EtOAc in petroleum ether) gave diene **11** (5.2 mg, 33%) and recovered alkyne **22** (1.9 mg, 12%) as amorphous solids. Data for **11**: $R_f = 0.33$ (80% EtOAc in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 6.28 (d, $J = 15.4$ Hz, 1H), 6.10 (ddd, $J = 15.5, 9.6, 5.1$ Hz, 1H), 5.80 (s, 1H), 5.69 (dddd, $J = 15.3, 7.3, 7.3, 1.5$ Hz, 1H), 5.50 (dd, $J = 15.4, 4.8$ Hz, 1H), 5.49 (s, 1H), 5.38 (d, $J = 1.0$ Hz, 1H), 5.36 (d, $J = 1.0$ Hz, 1H), 5.21 (s, 1H), 4.88 (s, 1H), 4.79 (s, 1H), 4.72 (dd, $J = 6.1, 3.2$ Hz, 1H), 4.59 (s br, 1H), 4.43 (s br, 1H), 4.22 (s br, 1H), 4.06 (t br, $J = 3.8$ Hz, 1H), 3.21 (dd, $J = 14.9, 5.0$ Hz, 1H), 3.11 (dd, $J = 14.7, 9.3$ Hz, 1H), 2.85 (dd, $J = 6.2, 2.2$ Hz, 1H), 2.76 (dd, $J = 7.5, 2.2$ Hz, 1H), 2.76 (s br, 2H), 2.34 (dd, $J = 15.3, 5.0$ Hz, 1H), 2.27 (d, $J = 1.1$ Hz, 3H), 2.16 (m, 1H), 1.92 (dd, $J = 14.4, 9.2$ Hz, 1H), 1.53-1.24 (m, 5H), 1.06 (d, $J = 7.0$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.91 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101

MHz, CDCl₃) δ 165.8, 152.8, 147.2, 145.0, 144.8, 136.4, 134.8, 130.9, 130.6, 118.6, 116.1, 114.7, 112.9, 75.8, 74.7, 73.5, 72.5, 70.5, 61.8, 54.2, 39.7, 39.0, 36.7, 36.2, 35.4, 33.3, 20.0, 15.8, 14.9, 14.3, 13.9; IR (neat) 3438 (br), 2927, 1715, 1612, 1235, 1150, 850 cm⁻¹; ESIMS m/z 553.3 [M + Na]⁺; HRESIMS calcd for C₃₁H₄₆O₇Na [M⁺ + Na] 553.3141, found 553.3157; optical rotation [α]_D²⁴ +56° (*c* 0.05, CHCl₃).

Data for **4**: R_f = 0.31 (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 6.19 (d, J = 15.6 Hz, 1H), 6.08 (ddd, J = 14.9, 9.8, 3.8 Hz, 1H), 5.79 (s, 1H), 5.77-5.72 (m, 1H), 5.59 (s, 1H), 5.57 (s, 1H), 5.37 (s, 1H), 5.26 (d br, J = 16.2 Hz, 1H), 5.22 (s, 1H), 4.86 (s, 1H), 4.78 (s, 1H), 4.61 (dd, J = 6.2, 3.8 Hz, 1H), 4.28 (s, 1H), 4.23 (s, 1H), 4.20 (s, 1H), 3.83 (s, 1H), 3.22 (dd, J = 15.1, 4.4 Hz, 1H), 3.11 (dd, J = 15.3, 10.4 Hz, 1H), 2.97 (dd, J = 6.1, 2.1 Hz, 1H), 2.76 (dd, J = 13.6, 4.0 Hz, 1H), 2.69 (dd, J = 8.9, 2.1 Hz, 1H), 2.66 (dd, J = 14.2, 10.4 Hz, 1H), 2.51 (dd, J = 12.5, 2.5 Hz, 1H), 2.29 (s, 3H), 2.13 (m, 1H), 1.79 (dd, J = 12.7, 11.6 Hz, 1H), 1.44-1.22 (m, 5H), 1.01 (d, J = 6.4 Hz, 3H), 0.99 (d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H), exchangeable protons not listed; ¹³C NMR (126 MHz, CDCl₃) δ 165.6, 152.1, 146.6, 145.2, 143.7, 136.3, 133.8, 131.2, 130.2, 119.3, 115.4, 114.8, 110.6, 78.8, 76.4, 72.5, 69.6, 65.9, 61.0, 52.6, 41.3, 38.6, 36.4, 35.3, 35.2, 33.4, 20.2, 15.9, 15.3, 14.2, 13.6; IR (neat) 3293 (br), 1709, 1234, 1152 cm⁻¹; ESIMS m/z 553.3 [M + Na]⁺; optical rotation [α]_D²³ +55° (*c* 0.10, CH₂Cl₂).

Data for **5**: R_f = 0.38 (EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 6.19 (d, J = 15.4 Hz, 1H), 6.08 (ddd, J = 14.7, 8.1, 6.4 Hz, 1H), 5.81 (s, 1H), 5.72 (dddd, J = 15.4, 8.6, 7.0, 1.2 Hz, 1H), 5.49 (s, 1H), 5.48 (ddm, J = 15.6, 4.9 Hz, 1H), 5.44 (s, 1H), 5.34 (s, 1H), 5.24 (s, 1H), 4.83 (s, 1H), 4.75 (s, 1H), 4.60 (dd, J = 10.3, 5.5 Hz, 1H), 4.32 (s, 1H), 4.16 (s, 1H), 4.09 (m, 1H), 3.95

(s, 1H), 3.25 (dd, $J = 14.4, 6.4$ Hz, 1H), 3.02 (dd, $J = 5.6, 2.2$ Hz, 1H), 3.00 (dd, $J = 14.4, 8.2$ Hz, 1H), 2.76-2.74 (m, 2H), 2.72 (dd, $J = 6.7, 2.1$ Hz, 1H), 2.26 (d, $J = 1.0$ Hz, 3H), 2.17 (dd, $J = 12.9, 2.6$ Hz, 1H), 1.94 (m, 1H), 1.65 (dd, $J = 13.3, 9.6$ Hz, 1H), 1.47-1.21 (m, 5H), 1.04 (d, $J = 6.7$ Hz, 3H), 1.00 (d, $J = 6.6$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H), exchangeable protons not listed; ^{13}C NMR (101 MHz, CDCl_3) δ 165.9, 152.1, 146.9, 145.0, 144.9, 135.6, 134.7, 131.7, 130.2, 118.5, 115.6, 115.0, 113.5, 77.2, 76.1, 74.8, 74.3, 72.5, 72.3, 62.4, 58.4, 39.5, 39.2, 38.8, 35.4, 35.0, 33.6, 20.0, 16.4, 15.7, 14.2; IR (neat) 3286 (br), 2963, 1706, 1616, 1150 cm^{-1} ; ESIMS m/z 553.3 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{23} -65^\circ$ (c 0.10, CH_2Cl_2).

Data for **6**: $R_f = 0.30$ (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, $J = 15.9$ Hz, 1H), 6.08 (ddd, $J = 15.5, 7.0, 6.7$ Hz, 1H), 5.82 (s, 1H), 5.68 (ddd, $J = 15.4, 7.8, 6.6, 1.2$ Hz, 1H), 5.47 (s, 1H), 5.39 (s, 1H), 5.38 (dd, $J = 15.4, 5.4$ Hz, 1H), 5.32 (s, 1H), 5.20 (s, 1H), 4.85 (s br, 1H), 4.77 (s br, 1H), 4.67 (dd, $J = 6.1, 3.4$ Hz, 1H), 4.38 (d, $J = 4.3$ Hz, 1H), 4.17 (dd, $J = 4.0, 3.7$ Hz, 1H), 4.10 (d, $J = 4.3$ Hz, 1H), 3.89 (d, $J = 3.5$ Hz, 1H), 3.21 (dd, $J = 14.7, 6.5$ Hz, 1H), 2.98 (dd, $J = 14.5, 7.4$ Hz, 1H), 2.97 (dd, $J = 6.1, 2.2$ Hz, 1H), 2.73 (dd, $J = 13.9, 6.0$ Hz, 1H), 2.66 (dd, $J = 7.0, 2.2$ Hz, 1H), 2.63 (dd, $J = 14.7, 8.3$ Hz, 1H), 2.40 (dd, $J = 13.7, 3.9$ Hz, 1H), 2.25 (d, $J = 1.1$ Hz, 3H), 2.11 (m, 1H), 1.82 (dd, $J = 13.7, 10.1$ Hz, 1H), 1.43-1.20 (m, 5H), 1.01 (d, $J = 7.0$ Hz, 3H), 1.00 (d, $J = 6.5$ Hz, 3H), 0.91 (t, $J = 7.0$ Hz, 3H), exchangeable protons not listed; ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 152.4, 147.0, 145.1, 144.7, 133.4, 134.9, 131.5, 130.3, 118.3, 116.2, 115.0, 113.4, 76.4, 75.1, 74.1, 73.6, 72.2, 60.9, 55.8, 39.2, 38.3, 36.4, 35.4, 35.2, 34.1, 20.2, 16.7, 15.7, 14.4, 14.2; IR (neat) 3285, 2922, 1709, 1614, 1153 cm^{-1} ; ESIMS m/z 553.4 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{26} -42^\circ$ (c 0.10, CH_2Cl_2).

Data for **7**: $R_f = 0.41$ (10% MeOH in CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, $J = 15.5$ Hz, 1H), 6.08 (ddd, $J = 15.9, 6.8, 6.5$ Hz, 1H), 5.77 (s, 1H), 5.69 (ddd, $J = 14.2, 6.3, 6.3$ Hz, 1H), 5.48 (s, 1H), 5.41 (dd, $J = 15.5, 5.4$ Hz, 1H), 5.39 (s, 1H), 5.33 (s, 1H), 5.21 (s, 1H), 4.87 (s, 1H), 4.79 (s, 1H), 4.67 (dd, $J = 6.4, 3.2$ Hz, 1H), 4.38 (s br, 1H), 4.18 (s br, 1H), 4.12 (s br, 1H), 3.91 (s br, 1H), 3.21 (dd, $J = 14.9, 7.0$ Hz, 1H), 2.98 (dd, $J = 14.4, 7.1$ Hz, 1H), 2.84 (dd, $J = 6.2, 2.1$ Hz, 1H), 2.77 (dd, $J = 7.6, 2.2$ Hz, 1H), 2.74 (dd, $J = 14.8, 6.7$ Hz, 1H), 2.66 (dd, $J = 14.8, 7.3$ Hz, 1H), 2.26 (d br, $J = 14.0$ Hz, 1H), 2.24 (d, $J = 1.0$ Hz, 3H), 2.14 (m, 1H), 1.88 (dd, $J = 13.9, 9.2$ Hz, 1H), 1.51-1.25 (m, 5H), 1.05 (d, $J = 7.1$ Hz, 3H), 0.91 (t, $J = 7.0$ Hz, 3H), 0.89 (d, $J = 7.1$ Hz, 3H).

Data for **8**: $R_f = 0.38$ (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, $J = 15.6$ Hz, 1H), 6.03 (ddd, $J = 14.9, 9.8, 4.8$ Hz, 1H), 5.75 (ddd, $J = 15.3, 7.3, 6.4$ Hz, 1H), 5.72 (s, 1H), 5.53 (dd, $J = 15.6, 5.4$ Hz, 1H), 5.49 (s, 1H), 5.42 (s, 1H), 5.33 (s, 1H), 5.20 (s, 1H), 4.74 (s, 1H), 4.73 (s, 1H), 4.56 (dd, $J = 10.3, 5.6$ Hz, 1H), 4.36 (s br, 1H), 4.30 (s br, 1H), 4.27 (s br, 1H), 3.99 (s br, 1H), 3.16 (dd, $J = 14.4, 4.3$ Hz, 1H), 3.04 (dd, $J = 14.7, 9.9$ Hz, 1H), 2.91 (dd, $J = 5.7, 2.1$ Hz, 1H), 2.81 (dd, $J = 15.3, 7.0$ Hz, 1H), 2.70 (dd, $J = 7.6, 2.0$ Hz, 1H), 2.68 (m, 1H), 2.24 (s, 3H), 2.15 (dd, $J = 13.8, 4.8$ Hz, 1H), 2.01 (m, 1H), 1.76 (dd, $J = 13.9, 8.4$ Hz, 1H), 1.51-1.19 (m, 5H), 1.02 (d, $J = 6.7$ Hz, 3H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.89 (t, $J = 7.2$ Hz, 3H), exchangeable protons not listed; ^{13}C NMR (125 MHz, CDCl_3) δ 165.9, 152.9, 147.1, 145.0, 144.7, 136.0, 134.7, 131.5, 130.4, 118.3, 115.1, 114.7, 112.9, 76.1, 74.9, 73.5, 72.5, 70.8, 62.5, 57.8, 39.9, 38.4, 38.2, 36.6, 35.4, 33.3, 20.0, 16.2, 15.8, 14.2, 13.9; IR (neat) 3274 (br), 2829, 1719, 1610, 1231, 1144 cm^{-1} ; ESIMS m/z 553.4 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{26} +165^\circ$ (c 0.050, CH_2Cl_2).

Data for **9**: R_f = 0.37 (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 6.20 (d, J = 15.8 Hz, 1H), 6.08 (ddd, J = 14.5, 8.4, 5.6 Hz, 1H), 5.79 (s, 1H), 5.68 (dddd, J = 15.0, 8.3, 7.1, 1.3 Hz, 1H), 5.51 (s, 1H), 5.43 (s, 1H), 5.42 (dd, J = 15.4, 5.4 Hz, 1H), 5.37 (s, 1H), 5.24 (s, 1H), 4.84 (s, 1H), 4.76 (s, 1H), 4.62 (dd, J = 6.7, 3.5 Hz, 1H), 4.42 (d, J = 3.2 Hz, 1H), 4.28 (d, J = 3.2 Hz, 1H), 4.17 (t, J = 4.5 Hz, 1H), 4.02 (d, J = 3.9 Hz, 1H), 3.22 (dd, J = 14.5, 5.4 Hz, 1H), 2.94 (dd, J = 13.1, 8.9 Hz, 1H), 2.92 (dd, J = 7.0, 2.3 Hz, 1H), 2.74 (dd, J = 14.6, 5.1 Hz, 1H), 2.68 (dd, J = 7.6, 2.2 Hz, 1H), 2.67 (dd, J = 14.4, 7.7 Hz, 1H), 2.50 (dd, J = 13.3, 3.4 Hz, 1H), 2.26 (d, J = 1.1 Hz, 3H), 2.10 (m, 1H), 1.81 (dd, J = 13.4, 10.6 Hz, 1H), 1.53-1.25 (m, 5H), 0.98 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), exchangeable protons not listed; ^{13}C NMR (125 MHz, CDCl_3) δ 165.7, 152.3, 145.8, 145.4, 144.6, 135.5, 135.1, 131.1, 130.6, 118.7, 117.1, 115.7, 113.3, 77.2, 76.6, 73.5, 72.5, 70.9, 61.3, 54.5, 39.0, 38.4, 36.7, 36.5, 35.5, 33.4, 20.0, 16.02, 15.96, 14.2, 14.1; IR (neat) 3414 (br), 2961, 1710, 1612, 1150 cm^{-1} ; ESIMS m/z 553.5 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{27}$ -116° (c 0.020, CH_2Cl_2).

Data for **10**: R_f = 0.38 (EtOAc); ^1H NMR (500 MHz, CDCl_3) δ 6.27 (d, J = 15.5 Hz, 1H), 6.08 (ddd, J = 15.1, 10.0, 5.0 Hz, 1H), 5.85 (s, 1H), 5.68 (dddd, J = 15.4, 7.1, 7.1, 1.2 Hz, 1H), 5.49 (dd, J = 15.4, 5.0 Hz, 1H), 5.45 (s, 1H), 5.34 (s, 2H), 5.19 (s, 1H), 4.85 (s, 1H), 4.77 (s, 1H), 4.65 (dd, J = 6.7, 3.7 Hz, 1H), 4.62 (s br, 1H), 4.41 (s br, 1H), 4.20 (s br, 1H), 4.04 (s br, 1H), 3.20 (dd, J = 14.8, 4.4 Hz, 1H), 3.10 (dd, J = 14.9, 10.0, 1H), 2.92 (dd, J = 6.7, 2.2 Hz, 1H), 2.75-2.72 (m, 2H), 2.68 (dd, J = 7.5, 2.2 Hz, 1H), 2.51 (dd, J = 13.7, 3.4 Hz, 1H), 2.27 (d, J = 0.9 Hz, 3H), 2.12 (m, 1H), 1.85 (dd, J = 14.0, 10.5 Hz, 1H), 1.53-1.24 (m, 5H), 1.00 (d, J = 7.1 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), exchangeable protons not listed; ^{13}C NMR (125 MHz, CDCl_3) δ 165.9, 152.8, 147.7, 145.1, 144.8, 136.5, 134.8, 131.0, 130.4, 118.9, 115.6, 114.4, 113.2, 76.5, 75.7, 74.1, 72.4, 70.4, 61.2, 54.7, 39.1, 38.9, 36.7, 36.3, 35.4, 33.7, 20.0, 16.0, 15.8, 14.2, 13.8; IR (neat) 3424 (br), 2928, 1709, 1611, 1163 cm^{-1} ; ESIMS m/z 553.4 $[\text{M} + \text{Na}]^+$; optical rotation $[\alpha]_D^{27}$ +103° (c 0.10, CH_2Cl_2).

<u>Isomer 1</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.80	s	-	5.80	s	-
4	6.20	d	15.5	6.27	d	15.6
5	6.09	ddd	15.5, 10.3, 4.5	6.09	ddd	15.6, 8.8, 4.8
6a	3.22	dd	14.9, 4.5	3.20	dd	14.6, 4.8
6b	3.12	dd	14.9, 10.3	3.13	dd	14.6, 8.8
8	4.23	s br	-	4.42	s br	-
9	4.29	s br	-	4.58	s br	-
11	3.84	s br	-	4.09	s br	-
12	4.21	s br	-	4.22	s br	-
13	5.28	dd	15.3, 2.6	5.51	dd	15.4, 4.1
14	5.78-5.73	m		5.69	dt	15.4, 7.7, 7.7
15a	2.77	dd	13.9, 3.6	2.76	s br (2H)	
15b	2.67	dd	13.9, 10.3	2.76	s br (2H)	
17a	2.53	dd	12.9, 3.1	2.35	dd	14.0, 5.5
17b	1.78	dd	12.9, 10.8	1.92	dd	14.0, 9.5
18	2.18-2.13	m		2.17	m	
19	4.55	dd	7.1, 3.8	4.72	dd	5.9, 3.4
20	2.92	dd	7.1, 2.2	2.85	dd	5.9, 1.9
21	2.70	dd	7.5, 2.2	2.76	dd	1.9
22	1.70-1.26	m (5H)		1.38	m	
23	1.70-1.26	m (5H)		1.55-1.25	m (4H)	
24	1.70-1.26	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.92	t	7.1	0.91	t	6.8
26 (3H)	2.30	s	-	2.27	s	-
27a	5.45	s	-	5.36	s	-
27b	5.23	s	-	5.21	s	-
28a	5.59	s	-	5.49	s	-
28b	5.58	s	-	5.37	s	-
29a	4.87	s	-	4.88	s	-
29b	4.78	s	-	4.79	s	-
30 (3H)	0.99	d	7.1	1.06	d	7.0
31 (3H)	0.98	d	6.8	0.93	d	6.0

Figure 1. ^1H NMR data for **1** in CDCl_3

<u>Isomer 2</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.80	s	-	5.80	s	-
4	6.14	d	15.6	6.27	d	15.6
5	6.06	dt	15.4, 6.7, 6.7	6.09	ddd	15.6, 8.8, 4.8
6a	3.19	dd	14.4, 6.7	3.20	dd	14.6, 4.8
6b	2.96	dd	14.1, 7.2	3.13	dd	14.6, 8.8
8	4.09	d	4.6	4.42	s br	-
9	4.37	d	4.6	4.58	s br	-
11	3.88	d	3.3	4.09	s br	-
12	4.16	t	4.4, 4.4	4.22	s br	-
13	5.36	dd	15.4, 4.6	5.51	dd	15.4, 4.1
14	5.67	dt	14.1, 6.4, 6.4	5.69	dt	15.4, 7.7, 7.7
15a	2.71	dd	14.1, 6.7	2.76	s br (2H)	
15b	2.61	dd	14.1, 8.0	2.76	s br (2H)	
17a	2.41	dd	14.1, 3.6	2.35	dd	14.0, 5.5
19	4.58	dd	6.9, 3.3	4.72	dd	5.9, 3.4
20	2.90	dd	6.7, 3.1	2.85	dd	5.9, 1.9
21	2.66	dd	7.7, 2.1	2.76	dd	1.9
26 (3H)	2.23	s	-	2.27	s	-
27a	5.30	s	-	5.36	s	-
27b	5.18	s	-	5.21	s	-
28a	5.46	s	-	5.49	s	-
28b	5.37	s	-	5.37	s	-
29a	4.83	s	-	4.88	s	-
29b	4.75	s	-	4.79	s	-

Figure 2. ^1H NMR data for **2** in CDCl_3

Isomer 4				Natural Product		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.79	s	-	5.80	s	-
4	6.19	d	15.6	6.27	d	15.6
5	6.08	ddd	14.9, 9.8, 3.8	6.09	ddd	15.6, 8.8, 4.8
6a	3.22	dd	15.1, 4.4	3.20	dd	14.6, 4.8
6b	3.11	dd	15.3, 10.4	3.13	dd	14.6, 8.8
8	4.23	s br	-	4.42	s br	-
9	4.28	s br	-	4.58	s br	-
11	3.83	s br	-	4.09	s br	-
12	4.20	s br	-	4.22	s br	-
13	5.26	d br	16.2	5.51	dd	15.4, 4.1
14	5.77-5.72	m		5.69	dt	15.4, 7.7, 7.7
15a	2.76	dd	13.6, 4.0	2.76	s br (2H)	
15b	2.66	dd	14.2, 10.4	2.76	s br (2H)	
17a	2.51	dd	12.5, 2.5	2.35	dd	14.0, 5.5
17b	1.79	dd	12.7, 11.6	1.92	dd	14.0, 9.5
18	2.13	m		2.17	m	
19	4.61	dd	6.2, 3.8	4.72	dd	5.9, 3.4
20	2.97	dd	6.1, 2.1	2.85	dd	5.9, 1.9
21	2.69	dd	8.9, 2.1	2.76	dd	1.9
22	1.44-1.22	m (5H)		1.38	m	
23	1.44-1.22	m (5H)		1.55-1.25	m (4H)	
24	1.44-1.22	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.91	t	7.0	0.91	t	6.8
26 (3H)	2.29	s	-	2.27	s	-
27a	5.37	s	-	5.36	s	-
27b	5.22	s	-	5.21	s	-
28a	5.59	s	-	5.49	s	-
28b	5.57	s	-	5.37	s	-
29a	4.86	s	-	4.88	s	-
29b	4.78	s	-	4.79	s	-
30 (3H)	0.99	d	7.0	1.06	d	7.0
31 (3H)	1.01	d	6.4	0.93	d	6.0

Figure 3. ^1H NMR data for **4** in CDCl_3

Proton #	Isomer 5			Natural Product		
	δ_{H}	Mult.	J	δ_{H}	Mult.	J
2	5.81	s	-	5.80	s	-
4	6.19	d	15.4	6.27	d	15.6
5	6.08	ddd	14.7, 8.1, 6.4	6.09	ddd	15.6, 8.8, 4.8
6a	3.25	dd	14.4, 6.4	3.20	dd	14.6, 4.8
6b	3.00	dd	14.4, 8.2	3.13	dd	14.6, 8.8
8	4.32	s br	-	4.42	s br	-
9	4.16	s br	-	4.58	s br	-
11	3.95	s br	-	4.09	s br	-
12	4.09	m	-	4.22	s br	-
13	5.48	ddm	15.6, 4.9	5.51	dd	15.4, 4.1
14	5.72	dddd	15.4, 8.6, 7.0, 1.2	5.69	dt	15.4, 7.7, 7.7
15a	2.76-2.74	m (2H)		2.76	s br (2H)	
15b	2.76-2.74	m (2H)		2.76	s br (2H)	
17a	2.17	dd	12.9, 2.6	2.35	dd	14.0, 5.5
17b	1.65	dd	13.3, 9.6	1.92	dd	14.0, 9.5
18	1.94	m		2.17	m	
19	4.60	dd	10.3, 5.5	4.72	dd	5.9, 3.4
20	3.02	dd	5.6, 2.2	2.85	dd	5.9, 1.9
21	2.72	dd	6.7, 2.1	2.76	dd	1.9
22	1.47-1.21	m (5H)		1.38	m	
23	1.47-1.21	m (5H)		1.55-1.25	m (4H)	
24	1.47-1.21	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.92	t	7.2	0.91	t	6.8
26 (3H)	2.26	d	1.0	2.27	s	-
27a	5.34	s	-	5.36	s	-
27b	5.24	s	-	5.21	s	-
28a	5.49	s	-	5.49	s	-
28b	5.44	s	-	5.37	s	-
29a	4.83	s	-	4.88	s	-
29b	4.75	s	-	4.79	s	-
30 (3H)	1.04	d	6.7	1.06	d	7.0
31 (3H)	1.00	d	6.6	0.93	d	6.0

Figure 4. ^1H NMR data for **5** in CDCl_3

<u>Isomer 6</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.82	s	-	5.80	s	-
4	6.16	d	15.9	6.27	d	15.6
5	6.08	ddd	15.5, 7.0, 6.7	6.09	ddd	15.6, 8.8, 4.8
6a	3.21	dd	14.7, 6.5	3.20	dd	14.6, 4.8
6b	2.98	dd	14.5, 7.4	3.13	dd	14.6, 8.8
8	4.38	d	4.3	4.42	s br	-
9	4.10	d	4.3	4.58	s br	-
11	3.89	d	3.5	4.09	s br	-
12	4.17	dd	4.0, 3.7	4.22	s br	-
13	5.38	dd	15.4, 5.4	5.51	dd	15.4, 4.1
14	5.68	dddd	15.4, 7.8, 6.6, 1.2	5.69	dt	15.4, 7.7, 7.7
15a	2.73	dd	13.9, 6.0	2.76	s br (2H)	
15b	2.63	dd	14.7, 8.3	2.76	s br (2H)	
17a	2.40	dd	13.7, 3.9	2.35	dd	14.0, 5.5
17b	1.82	dd	13.7, 10.1	1.92	dd	14.0, 9.5
18	2.11	m		2.17	m	
19	4.67	dd	6.1, 3.4	4.72	dd	5.9, 3.4
20	2.97	dd	6.1, 2.2	2.85	dd	5.9, 1.9
21	2.66	dd	7.0, 2.2	2.76	dd	1.9
22	1.43-1.20	m (5H)		1.38	m	
23	1.43-1.20	m (5H)		1.55-1.25	m (4H)	
24	1.43-1.20	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.91	t	7.0	0.91	t	6.8
26 (3H)	2.25	d	1.1	2.27	s	-
27a	5.32	s	-	5.36	s	-
27b	5.20	s	-	5.21	s	-
28a	5.47	s	-	5.49	s	-
28b	5.39	s	-	5.37	s	-
29a	4.85	s	-	4.88	s	-
29b	4.77	s	-	4.79	s	-
30 (3H)	1.01	d	7.0	1.06	d	7.0
31 (3H)	1.00	d	6.5	0.93	d	6.0

Figure 5. ^1H NMR data for **6** in CDCl_3

Proton #	Isomer 7			Natural Product		
	δ_{H}	Mult.	J	δ_{H}	Mult.	J
2	5.77	s	-	5.80	s	-
4	6.16	d	15.6	6.27	d	15.6
5	6.08	ddd	15.9, 6.8, 6.5	6.09	ddd	15.6, 8.8, 4.8
6a	3.21	dd	14.9, 7.0	3.20	dd	14.6, 4.8
6b	2.98	dd	14.4, 7.1	3.13	dd	14.6, 8.8
8	4.38	s br	-	4.42	s br	-
9	4.12	s br	-	4.58	s br	-
11	3.91	s br	-	4.09	s br	-
12	4.18	s br	-	4.22	s br	-
13	5.41	dd	15.5, 5.4	5.51	dd	15.4, 4.1
14	5.69	ddd	14.2, 6.6, 6.3	5.69	dt	15.4, 7.7, 7.7
15a	2.74	dd	14.8, 6.7	2.76	s br (2H)	
15b	2.66	dd	14.8, 7.3	2.76	s br (2H)	
17a	2.26	d br	14.0	2.35	dd	14.0, 5.5
17b	1.88	dd	13.9, 9.2	1.92	dd	14.0, 9.5
18	2.14	m		2.17	m	
19	4.67	dd	6.4, 3.2	4.72	dd	5.9, 3.4
20	2.84	dd	6.2, 2.1	2.85	dd	5.9, 1.9
21	2.77	dd	7.6, 2.2	2.76	dd	1.9
22	1.51-1.25	m (5H)		1.38	m	
23	1.51-1.25	m (5H)		1.55-1.25	m (4H)	
24	1.51-1.25	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.91	t	7.0	0.91	t	6.8
26 (3H)	2.24	d	1.0	2.27	s	-
27a	5.33	s	-	5.36	s	-
27b	5.21	s	-	5.21	s	-
28a	5.48	s	-	5.49	s	-
28b	5.39	s	-	5.37	s	-
29a	4.87	s	-	4.88	s	-
29b	4.79	s	-	4.79	s	-
30 (3H)	1.05	d	7.1	1.06	d	7.0
31 (3H)	0.89	d	7.1	0.93	d	6.0

Figure 6. ^1H NMR data for **7** in CDCl_3

<u>Isomer 8</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.72	s	-	5.80	s	-
4	6.16	d	15.6	6.27	d	15.6
5	6.03	ddd	14.9, 9.8, 4.8	6.09	ddd	15.6, 8.8, 4.8
6a	3.16	dd	14.4, 4.3	3.20	dd	14.6, 4.8
6b	3.04	dd	14.7, 9.9	3.13	dd	14.6, 8.8
8	4.36	s br	-	4.42	s br	-
9	4.30	s br	-	4.58	s br	-
11	3.99	s br	-	4.09	s br	-
12	4.27	s br	-	4.22	s br	-
13	5.53	dd	15.6, 5.4	5.51	dd	15.4, 4.1
14	5.75	ddd	15.3, 7.3, 6.4	5.69	dt	15.4, 7.7, 7.7
15a	2.81	dd	15.3, 7.0	2.76	s br (2H)	
15b	2.68	m		2.76	s br (2H)	
17a	2.15	dd	13.8, 4.8	2.35	dd	14.0, 5.5
17b	1.76	dd	13.9, 8.4	1.92	dd	14.0, 9.5
18	2.01	m		2.17	m	
19	4.56	dd	10.3, 5.6	4.72	dd	5.9, 3.4
20	2.91	dd	5.7, 2.1	2.85	dd	5.9, 1.9
21	2.70	dd	7.6, 2.0	2.76	dd	1.9
22	1.51-1.19	m (5H)		1.38	m	
23	1.51-1.19	m (5H)		1.55-1.25	m (4H)	
24	1.51-1.19	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.89	t	7.2	0.91	t	6.8
26 (3H)	2.24	s	-	2.27	s	-
27a	5.33	s	-	5.36	s	-
27b	5.20	s	-	5.21	s	-
28a	5.49	s	-	5.49	s	-
28b	5.42	s	-	5.37	s	-
29a	4.74	s	-	4.88	s	-
29b	4.73	s	-	4.79	s	-
30 (3H)	1.02	d	6.7	1.06	d	7.0
31 (3H)	0.93	d	6.8	0.93	d	6.0

Figure 7. ^1H NMR data for **8** in CDCl_3

<u>Isomer 9</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.79	s	-	5.80	s	-
4	6.20	d	15.8	6.27	d	15.6
5	6.08	ddd	14.5, 8.4, 5.6	6.09	ddd	15.6, 8.8, 4.8
6a	3.22	dd	14.5, 5.4	3.20	dd	14.6, 4.8
6b	2.94	dd	13.1, 8.9	3.13	dd	14.6, 8.8
8	4.42	d	3.2	4.42	s br	-
9	4.28	d	3.2	4.58	s br	-
11	4.02	d	3.9	4.09	s br	-
12	4.17	t	4.5, 4.5	4.22	s br	-
13	5.42	dd	15.4, 5.4	5.51	dd	15.4, 4.1
14	5.68	dddd	15.0, 8.3, 7.1, 1.3	5.69	dt	15.4, 7.7, 7.7
15a	2.74	dd	14.6, 5.1	2.76	s br (2H)	
15b	2.67	dd	14.4, 7.7	2.76	s br (2H)	
17a	2.50	dd	13.3, 3.4	2.35	dd	14.0, 5.5
17b	1.81	dd	13.4, 10.6	1.92	dd	14.0, 9.5
18	2.10	m		2.17	m	
19	4.62	dd	6.7, 3.5	4.72	dd	5.9, 3.4
20	2.92	dd	7.0, 2.3	2.85	dd	5.9, 1.9
21	2.68	dd	7.6, 2.2	2.76	dd	1.9
22	1.53-1.25	m (5H)		1.38	m	
23	1.53-1.25	m (5H)		1.55-1.25	m (4H)	
24	1.53-1.25	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.90	t	7.2	0.91	t	6.8
26 (3H)	2.26	d	1.1	2.27	s	-
27a	5.37	s	-	5.36	s	-
27b	5.24	s	-	5.21	s	-
28a	5.51	s	-	5.49	s	-
28b	5.43	s	-	5.37	s	-
29a	4.84	s	-	4.88	s	-
29b	4.76	s	-	4.79	s	-
30 (3H)	0.98	d	6.6	1.06	d	7.0
31 (3H)	0.97	d	6.7	0.93	d	6.0

Figure 8. ^1H NMR data for **9** in CDCl_3

<u>Isomer 10</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.85	s	-	5.80	s	-
4	6.27	d	15.5	6.27	d	15.6
5	6.08	ddd	15.1, 10.0, 5.0	6.09	ddd	15.6, 8.8, 4.8
6a	3.20	dd	14.8, 4.4	3.20	dd	14.6, 4.8
6b	3.10	dd	14.9, 10.0	3.13	dd	14.6, 8.8
8	4.41	s br		4.42	s br	-
9	4.62	s br		4.58	s br	-
11	4.04	s br		4.09	s br	-
12	4.20	s br		4.22	s br	-
13	5.49	dd	15.4, 5.0	5.51	dd	15.4, 4.1
14	5.68	dddd	15.4, 7.1, 7.1, 1.2	5.69	dt	15.4, 7.7, 7.7
15a	2.75-2.72	m (2H)		2.76	s br (2H)	
15b	2.75-2.72	m (2H)		2.76	s br (2H)	
17a	2.51	dd	13.7, 3.4	2.35	dd	14.0, 5.5
17b	1.85	dd	14.0, 10.5	1.92	dd	14.0, 9.5
18	2.12	m		2.17	m	
19	4.65	dd	6.7, 3.7	4.72	dd	5.9, 3.4
20	2.92	dd	6.7, 2.2	2.85	dd	5.9, 1.9
21	2.68	dd	7.5, 2.2	2.76	dd	1.9
22	1.53-1.24	m (5H)		1.38	m	
23	1.53-1.24	m (5H)		1.55-1.25	m (4H)	
24	1.53-1.24	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.90	t	7.2	0.91	t	6.8
26 (3H)	2.27	d	0.9	2.27	s	-
27a	5.34	s	-	5.36	s	-
27b	5.19	s	-	5.21	s	-
28a	5.45	s	-	5.49	s	-
28b	5.34	s	-	5.37	s	-
29a	4.85	s	-	4.88	s	-
29b	4.77	s	-	4.79	s	-
30 (3H)	1.00	d	7.1	1.06	d	7.0
31 (3H)	0.97	d	6.8	0.93	d	6.0

Figure 9. ^1H NMR data for **10** in CDCl_3

<u>Isomer 11</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.80	s	-	5.80	s	-
4	6.28	d	15.4	6.27	d	15.6
5	6.10	ddd	15.5, 9.6, 5.1	6.09	ddd	15.6, 8.8, 4.8
6a	3.21	dd	14.9, 5.0	3.20	dd	14.6, 4.8
6b	3.11	dd	14.7, 9.3	3.13	dd	14.6, 8.8
8	4.43	s br	-	4.42	s br	-
9	4.59	s br	-	4.58	s br	-
11	4.06	t br	3.8	4.09	s br	-
12	4.22	s br	-	4.22	s br	-
13	5.50	dd	15.4, 4.8	5.51	dd	15.4, 4.1
14	5.69	dddd	15.3, 7.3, 7.3, 1.5	5.69	dt	15.4, 7.7, 7.7
15a	2.76	s br (2H)		2.76	s br (2H)	
15b	2.76	s br (2H)		2.76	s br (2H)	
17a	2.34	dd	15.3, 5.0	2.35	dd	14.0, 5.5
17b	1.92	dd	14.4, 9.2	1.92	dd	14.0, 9.5
18	2.16	m		2.17	m	
19	4.72	dd	6.1, 3.2	4.72	dd	5.9, 3.4
20	2.85	dd	6.2, 2.2	2.85	dd	5.9, 1.9
21	2.76	dd	7.5, 2.2	2.76	dd	1.9
22	1.53-1.24	m (5H)		1.38	m	
23	1.53-1.24	m (5H)		1.55-1.25	m (4H)	
24	1.53-1.24	m (5H)		1.55-1.25	m (4H)	
25 (3H)	0.91	t	7.1	0.91	t	6.8
26 (3H)	2.27	d	1.1	2.27	s	-
27a	5.36	d	1.0	5.36	s	-
27b	5.21	s	-	5.21	s	-
28a	5.49	s	-	5.49	s	-
28b	5.38	d	1.0	5.37	s	-
29a	4.88	s	-	4.88	s	-
29b	4.79	s	-	4.79	s	-
30 (3H)	1.06	d	7.0	1.06	d	7.0
31 (3H)	0.93	d	6.8	0.93	d	6.0

Figure 10. ^1H NMR data for **11** in CDCl_3

<u>Isomer 11</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.83	s	-	5.83	s	-
4	5.98	d	15.6	5.98	d	15.6
5	5.71	ddd	14.9, 8.9, 5.6	5.71	ddd	15.6, 8.9, 5.7
6a	2.88	m		2.87	m	
6b	2.88	m		2.87	m	
8	4.39	s br	-	4.38	s br	-
9	4.45	s br	-	4.44	s br	-
11	3.90	t br	3.9	3.89	s br	-
12	3.97	s br	-	3.98	s br	-
13	5.29	dd	15.3, 4.4	5.29	dd	15.4, 4.4
14	5.65	ddd	13.7, 7.4, 5.7	5.65	ddd	15.4, 7.4, 6.5
15a	2.63	dd	14.0, 7.1	2.63	dd	14.4, 7.4
15b	2.56	dd	14.2, 7.1	2.56	dd	14.4, 6.5
17a	2.36	dd	14.5, 4.4	2.36	dd	14.7, 6.2
17b	1.87	dd	14.4, 8.8	1.88	dd	14.7, 8.9
18	2.19	m		2.19	m	
19	4.92	dd	6.8, 3.1	4.92	dd	6.8, 3.1
20	2.79	dd	6.7, 2.1	2.79	dd	6.8, 2.0
21	2.85	dd	7.6, 2.0	2.85	dd	7.5, 2.0
22	1.48-1.12	m (5H)		1.24	m	
23	1.48-1.12	m (5H)		1.49-1.13	m (4H)	
24	1.48-1.12	m (5H)		1.49-1.13	m (4H)	
25 (3H)	0.85	t	7.2	0.85	t	7.3
26 (3H)	2.21	d	1.1	2.21	s	-
27a	5.46	s	-	5.45	s	-
27b	5.01	s br	-	5.01	s br	-
28a	5.43	t	1.3	5.42	t	1.3
28b	5.15	d	1.1	5.15	d	1.3
29a	4.86	s	-	4.86	s	-
29b	4.78	d	1.2	4.78	d	1.5
30 (3H)	1.09	d	7.0	1.09	d	7.0
31 (3H)	0.83	d	6.8	0.83	d	6.8

Figure 11. ^1H NMR data for **11** in C_6D_6

<u>Isomer 11</u>				<u>Natural Product</u>		
Proton #	δ_H	Mult.	J	δ_H	Mult.	J
2	5.85	s	-	5.85	s	-
4	6.36	d	15.4	6.35	d	15.4
5	6.14	ddd	15.1, 8.9, 5.9	6.14	ddd	15.4, 9.0, 5.9
6a	3.12-3.09	m (2H)		3.10	m	
6b	3.12-3.09	m (2H)		3.10	m	
8	4.21	s br	-	4.21	s br	-
9	4.46	s br	-	4.46	s br	-
11	3.99	d br	2.2	3.99	d	2.8
12	4.13	s br	-	4.14	s br	-
13	5.46	dd	15.3, 5.3	5.46	dd	15.6, 5.5
14	5.59	dddd	15.3, 7.7, 6.2, 1.5	5.59	ddd	15.6, 8.4, 5.8
15a	2.67	dd	14.5, 7.9	2.67	dd	14.3, 8.4
15b	2.75	dd	14.3, 6.2	2.75	dd	14.3, 5.8
17a	2.41	dd	13.9, 5.1	2.41	dd	14.3, 5.8
17b	1.92	dd	13.7, 8.8	1.92	dd	14.7, 8.5
18	2.14	m		2.14	m	
19	4.69	dd	5.7, 3.3	4.69	dd	5.7, 3.2
20	2.91	dd	5.7, 2.2	2.91	dd	5.7, 2.2
21	2.75	dd	7.6, 2.2	2.75	dd	7.4, 2.2
22	1.50-1.25	m (5H)		1.37	m	
23	1.50-1.25	m (5H)		1.50-1.25	m (4H)	
24	1.50-1.25	m (5H)		1.50-1.25	m (4H)	
25 (3H)	0.91	t	7.1	0.91	t	7.2
26 (3H)	2.25	d	1.2	2.25	s	-
27a	5.27	s	1.6	5.27	t	1.2
27b	5.10	s br	-	5.10	s br	-
28a	5.40	t	1.5	5.40	t	1.3
28b	5.34	s	-	5.35	s br	-
29a	4.85	s	-	4.85	s	-
29b	4.76	s br	-	4.76	s br	-
30 (3H)	1.06	d	7.1	1.06	d	7.1
31 (3H)	0.92	d	6.7	0.92	d	6.8

Figure 12. ^1H NMR data for **11** in CD_3OD

	<u>Isomer 11</u>	<u>Natural Product</u>
Carbon #	δ_C	δ_C
1	165.8	165.8
2	118.6	118.6
3	152.7	152.8
4	136.3	136.4
5	134.7	134.8
6	39.0	39.0
7	144.8	144.8
8	72.5	72.5
9	70.6	70.5
10	147.2	147.2
11	75.8	75.8
12	73.5	73.5
13	130.5	130.6
14	130.9	130.9
15	39.7	39.7
16	145.0	145.0
17	36.2	36.2
18	33.3	33.3
19	74.7	74.7
20	54.2	54.2
21	61.8	61.8
22	35.3	35.4
23	36.7	36.7
24	19.9	20.0
25	14.2	14.3
26	13.9	13.9
27	114.6	114.7
28	116.0	116.1
29	112.8	112.9
30	14.9	14.9
31	15.8	15.8

Figure 13. ^{13}C NMR data for **11** in CDCl_3

✓ 0417-43-01

STANDARD PROTON PARAMETERS

Pulse Sequence: zgpg30
Solvent: CDCl₃
Acquire temperature: 300 K
Pulse 60.0 degrees
Acq. time 4.000 sec
Fid length 8000.0 Hz
SFO 400.143400
OBSERVE H1 499.7485685 MHz
DATA PROCESSING
FT size 131072
Total time 28 min, 43 sec

PulseSequence: zspu1
Solvent: CCl₄
Ambient temperature
Mercury-100B5 "merc100"
Relax: delay 0.500 sec
Pulse 35.8 degrees
Acq. time 1.19 sec
Width 25000.0 Hz
24140 repetitions
OBSERVE: C13, 100.6081265 MHz
DECOUPLE: H1, 400.1135502 MHz
continuously on
VALT2-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 23 hr, 43 min, 20 sec