J1230-1

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SUPPORTING INFORMATION

Supplementary Material

The First Enantioselective Total Synthesis of a Naturally Occurring Dolabellane; Revision of Absolute Configuration

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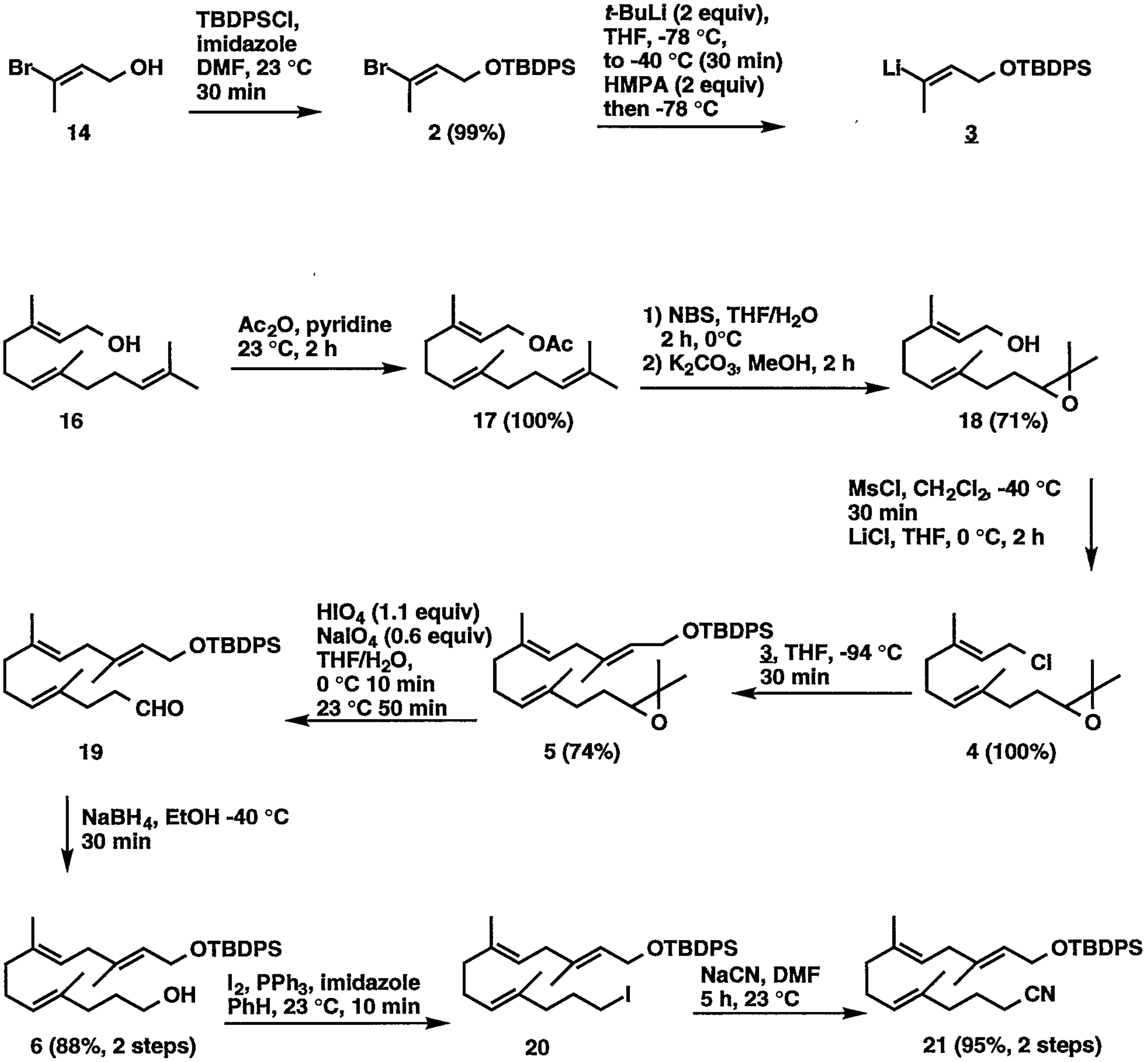

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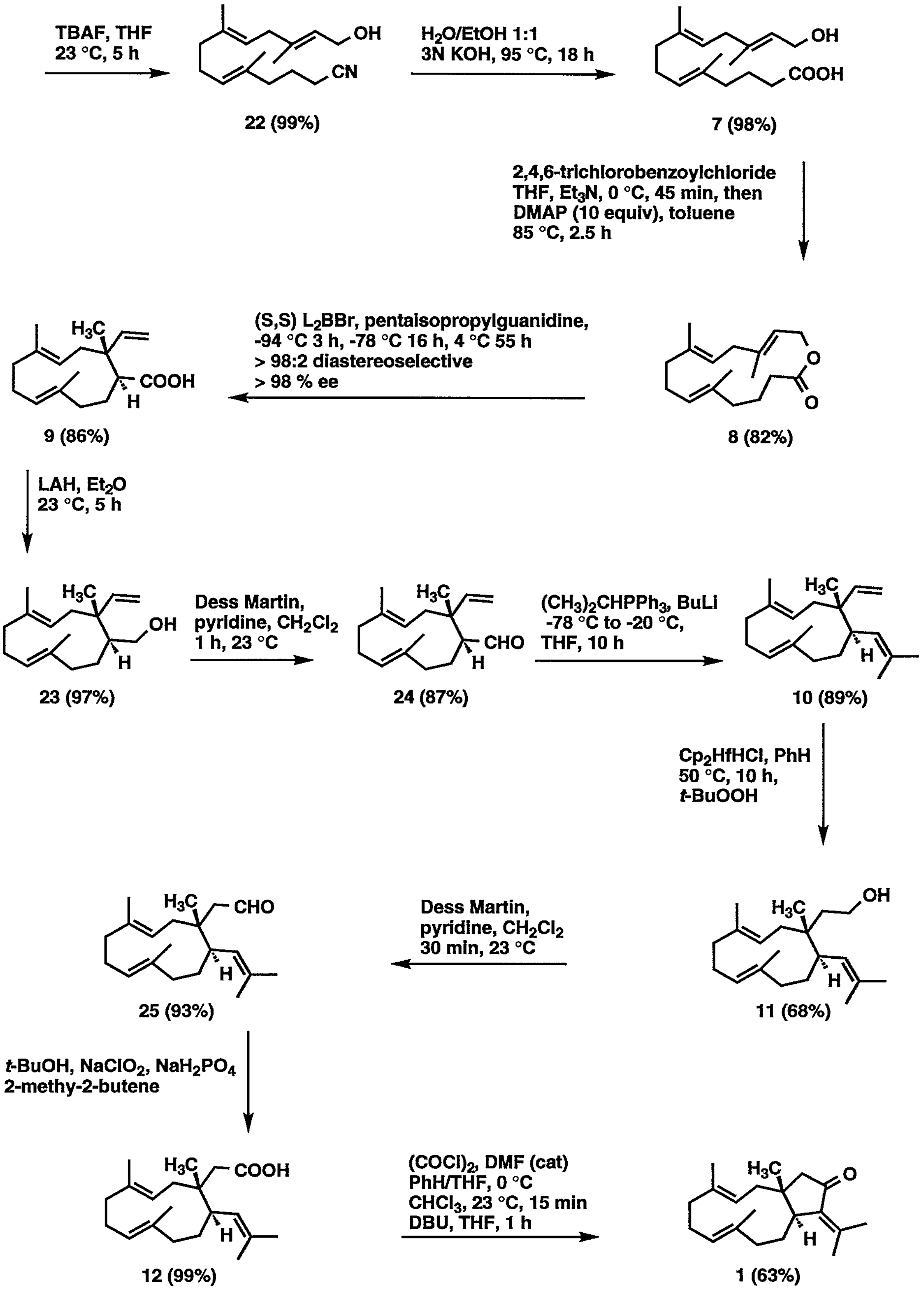
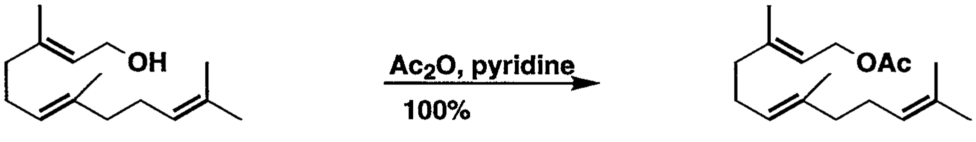

TBAF, THF
23 °C, 5 h
OH
CN
22 (99%)
H2O/EtOH 1:1
3N KOH, 95 °C, 18 h
OH
COOH
7 (98%)
2,4,6-trichlorobenzoylchloride
THF, Et3N, 0 °C, 45 min, then
DMAP (10 equiv), toluene
85 °C, 2.5 h
O
O
8 (82%)
(S,S) L2BBr, pentaisopropylguanidine,
-94 °C 3 h, -78 °C 16 h, 4 °C 55 h
> 98:2 diastereoselective
> 98 % ee
H3C
COOH
H
9 (86%)
LAH, Et2O
23 °C, 5 h
H3C
OH
H
23 (97%)
Dess Martin,
pyridine, CH2Cl2
1 h, 23 °C
H3C
CHO
H
24 (87%)
(CH3)2CHPPh3, BuLi
-78 °C to -20 °C,
THF, 10 h
H3C
H
10 (89%)
Cp2HfHCl, PhH
50 °C, 10 h,
t-BuOOH
H3C
OH
H
11 (68%)
Dess Martin,
pyridine, CH2Cl2
30 min, 23 °C
H3C
CHO
H
25 (93%)
t-BuOH, NaClO2, NaH2PO4
2-methy-2-butene
H3C
COOH
H
12 (99%)
(COCl)2, DMF (cat)
PhH/THF, 0 °C
CHCl3, 23 °C, 15 min
DBU, THF, 1 h
H3C
O
H
1 (63%)

Procedures

14 **2**

Allyl alcohol **14** (868 mg, 5.75 mmol) was taken up in dimethylformamide (5 mL) and was treated with imidazole (587 mg, 8.62 mmol) and *t*-butyldiphenylchlorosilane (1.79 mL, 6.90 mmol) at 23 °C. The reaction was allowed to stir for 30 minutes. The product was partitioned into hexane (100 mL) and water (20 mL). The organics were washed with saturated sodium bicarbonate (20 mL) and brine (20 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give a clear colorless oil as a crude product (2.54 g). The product was purified on silica gel (200 g) eluting with hexane (1 L) followed by hexane-ethyl acetate 95:5 to give pure silyl ether **2** (2.20 g, 99% y): R_f sm: 0.11; prod: 0.58 (Hex-EtOAc 9:1); FTIR (thin film) 3071, 3049, 2958, 2930, 2892, 2857, 1654, 1472, 1469, 1428, 1375, 1112, 1087, 1044, 1007, 998, 822 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.43 (m, 6H), 6.05 (t, 1H, J=6.9 Hz), 4.13 (d, 2H, J=6.7 Hz), 2.04 (s, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 133.4, 131.3, 129.8, 127.7, 127.6, 61.1, 26.8, 23.6, 19.2; HRMS (EF-CI) [m+NH_4]/z calc'd 406.1202, found 406.1213



16 **17**

Farnesol **16** (20.0 g, 89.9 mmol) was taken up in pyridine (65 ml) and was treated with acetic anhydride (34.0 ml, 360 mmol) at 23 °C for two hours. The mixture was then poured into ice water (500 ml) and the product was extracted into diethyl ether (500 ml). The organics were washed with citric acid (2X, 150 ml, 20%), water (150 ml), saturated sodium bicarbonate (2X,

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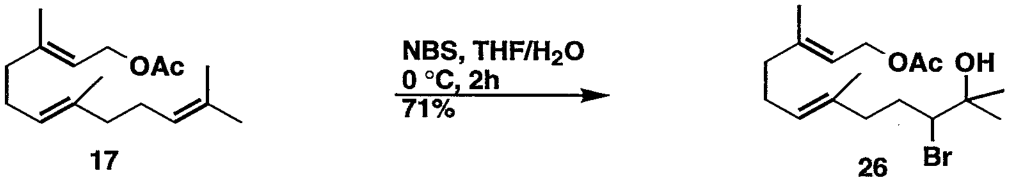
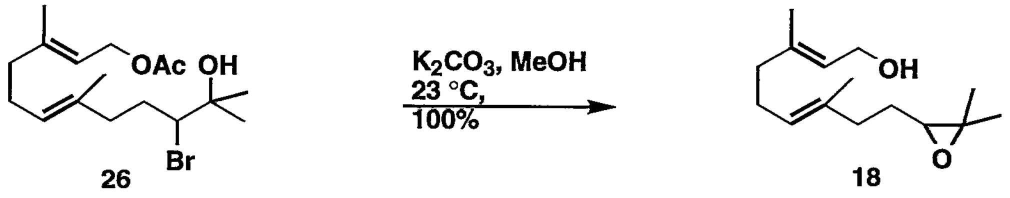
150 ml) and finally saturated sodium chloride (150 ml). The organics were dried over sodium sulfate and evaporated *in vacuo* to give farnesol acetate **17** as a clear oil (23.8 g, 100% y): R_f sm 0.13, p 0.38 (Hex-EtOAc 5:1); ^1H NMR (500 MHz, $CDCl_3$) d 5.34 (t, 1H), 5.09 (m, 2H), 4.59 (d, 2H, 7Hz), 2.12-2.06 (m, 6H), 2.05 (s, 3H), 1.99-1.96 (m, 2H), 1.71 (s, 3H), 1.68 (s, 3H), 1.60 (s, 6H)



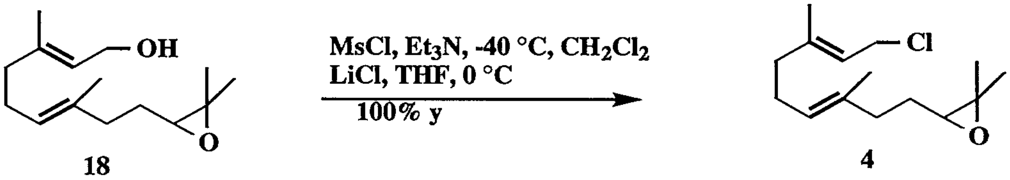
17

26

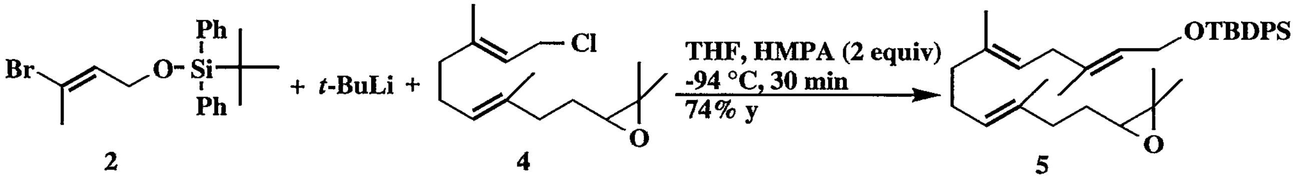
Farnesol acetate **17** (23.8 g, 90 mmol) was taken up in tetrahydrofuran (2.1 L) and cooled to 0 °C. To this was added water (1.6 L) until the solution became cloudy. N-bromosuccinimide (17.6 g) was then added in small portions over 1 hour and the reaction was allowed to stir for another hour at 0 °C. The tetrahydrofuran was evaporated *in vacuo* at ~5 °C (two hours) and the suspension was extracted with 20% diethyl ether in hexane (4X, 500 ml). The organic fractions were combined, dried over magnesium sulfate and reduced *in vacuo* to give a clear yellow oil as crude product. The oil was purified by flash chromatography (1 kg SiO_2; 2 vol 10% EtOAc in hexane, 4 vol 20% EtOAc in hexane) to give pure bromohydrin **26** as a clear colorless oil (23 g, 71% y): R_f sm 0.60, p 0.16 (Hex-EtOAc 5:1); FTIR (thin film) 3460 (br), 2977, 2935, 2853, 1730, 1725, 1445, 1433, 1383, 1366, 1232, 1023, 956 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) d 5.40 (tq, 1H, J = 6.4, 1.3 Hz), 5.21 (tq, 1H, J = 7.0, 1.1 Hz), 4.61 (dd, 2H, J = 6.9, 0.4 Hz), 3.83 (dd, 1H, J = 11.3, 1.8 Hz), 2.82 (m, 1H), 2.11 (dt, 1H, J = 13.8, 8.0 Hz), 2.03 (m, 3H), 1.92 (t, 2H, J = 7.5Hz), 1.90-1.82 (m, 2H), 1.82-1.80 (m, 1H), 1.73-1.65 (m 1H), 1.69 (s, 3H), 1.49 (s, 3H), 1.44 (s, 3H, J = 0.4 Hz) 1.17 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 141.8, 133.5, 125.2, 118.5, 72.3, 70.2, 61.3, 39.3, 38.1, 31.9, 26.4, 26.1, 26.06, 21.0, 16.4, 15.8; HRMS (EF-CI) $[m+NH_4]/z$ calc'd 378.1644 , found 378.1636



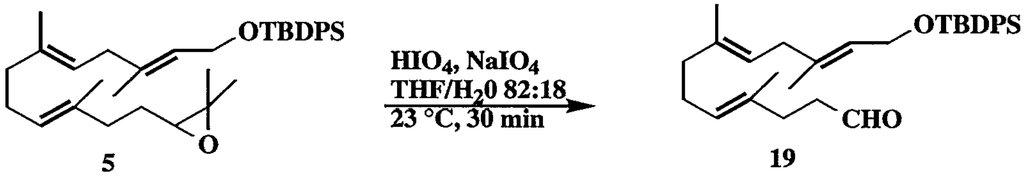
In a 1 L round bottom flask, bromohydrin **26** (22.9 g, 63.4 mmol) was taken up in anhydrous methanol (500 ml) and was treated with potassium carbonate (22.1 g, 160 mmol). The reaction was stirred for two hours at 23 °C. The solvent was removed *in vacuo* and the residue was taken up in diethyl ether (300 mL) to form a white suspension. The suspension was filtered through a plug of tightly packed celite which was washed three times with diethyl ether. The combined ether fractions were washed with saturated sodium chloride, dried over sodium sulfate and concentrated *in vacuo* to give epoxide **18** as a clear colorless oil (15.1 g, 100% y): R_f sm 0.25, p 0.12 (Hex-EtOAc 4:1); FTIR (thin film) 3420 (br), 2961, 2924, 2859, 1667,1440, 1378, 1323, 1249, 1121, 1007, 871 cm^{-1}; ^1H NMR (500 MHz, C_6D_6) 5.41 (t, 1H, J = 6.5 Hz), 5.20 (t, 1H, J = 6.7 Hz,), 4.01 (d, 2H, J = 6.5 Hz), 2.55 (t, 1H, J = 6.1 Hz), 2.12-2.03 (m, 4H), 1.98 (t, 2H, J = 7.3 Hz,), 1.56-1.49 (m, 2H), 1.52 (s, 3H,), 1.47 (s, 3H), 1.15 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 134.2, 124.5, 123.8, 64.1, 59.1, 58.4, 39.3, 36.2, 27.2, 26.1, 24.8, 18.7, 16.2, 15.9; HRMS (EF-CI) [m+NH_4]/z calc'd 256.2277, found 256.2271



Epoxy farnesol **18** (1.05 g, 4.4 mmol) was taken up in methylene chloride (20 mL) and tetrahydrofuran (10 mL) and was cooled to -40 °C. Mesyl chloride (0.409 mL, 5.28 mmol) was added followed by triethylamine (0.736 mL, 5.28 mmol). The solution quickly became a thick slurry. The reaction was allowed to stir at -40 °C for 30 minutes. Tetrahydrofuran (35 mL) was then added as was anhydrous lithium chloride (1.87 g). The reaction was allowed to warm and stir at 0 °C for 2 hours. The reaction mixture was partitioned between 10% ethyl acetate/hexane (300 mL) and water (50 mL). The organics were shaken with a brine(50 mL)/sodium bicarbonate(10 mL) mixture for five minutes. The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give pure chloride **4** as a clear colorless oil (1.13 g, 100% y). The isolated product was found to be pure and was used without further purification: R_f sm: 0.03; prod: 0.45 (Hex-EtOAc 9:1); FTIR (thin film) 2961, 2925, 2856, 1662, 1449, 1377, 1323, 1252, 1122, 899.4, 873.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.45 (t, 1H), 5.13 (t, 1H), 4.10 (d, 2H), 2.70 (t, 1H), 2.08 (m, 6H), 1.72 (s, 3H), 1.65 (m, 2H), 1.62 (s, 3H), 1.30 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 134.6, 124.0, 120.3, 64.0, 58.2, 41.0, 39.2, 36.2, 27.3, 26.0, 24.8, 18.7, 16.0, 15.96; HRMS (EF-CI) [$m+NH_4$]/z calc'd 274.1938, found 274.1932

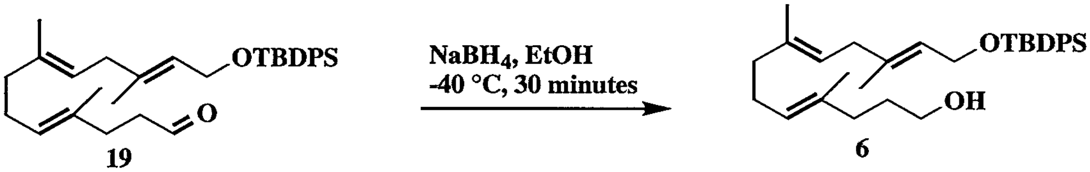


t-Butyl lithium (851 µL, 1.74 M, 1.48 mmol) was added to tetrahydrofuran (2.2 mL) at -78 °C. Vinyl bromide **2** (317 mg, 0.814 mmol) was then added via cannula in tetrahydrofuran (2x250 µL). The reaction was warmed and stirred at -40 °C for 30 minutes. Hexamethylphosphoramide (258 µL, 1.48 mmol) was then added and the reaction was cooled to -94 °C in a hexane/liquid nitrogen bath (allow 20 minutes for cooling, 45 minutes for larger scale). Allyl chloride **4** (95 mg, 0.37 mmol) was then added via cannula in precooled (-78 °C) tetrahydrofuran (2x250 µL). The reaction was allowed to stir at -94 °C for 30 minutes. The reaction was quenched by addition of saturated sodium bicarbonate (3-5 mL) and the frozen slurry was allowed to warm to ~0°C. The product was partitioned into 10% ethyl acetate in hexane (50 mL) and water (20 mL). The organics were washed with brine, dried over sodium sulfate and the solvent was removed *in* *vacuo* to give a clear colorless oil as a crude product . The product was purified on silica (40 g) gel eluting with hexane-ethyl acetate-triethyl amine 98:2:0.2 (500 mL) then 96:4:0.2 (500 mL) to give pure **5** (146 mg, 74% y): R_f sm(**2**): 0.62; sm(**4**): 0.10; prod: 0.14 (Hex-EtOAc 9:1); FTIR (thin film) 2959, 2929, 2897, 2856, 1472, 1446, 1377, 1111, 1054 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.40 (m, 6H), 5.39 (t, 1H, J=6.3 Hz), 5.18 (t, 1H, J=6.8 Hz), 5.12 (t, 1H, J=7.3 Hz), 4.22 (d, 2H, J=6.3 Hz), 2.70 (t, 1H, J=6.2 Hz), 2.64 (d, 2H, J=7.3 Hz), 2.12-2.03 (m, 6H), 1.63-1.59 (m, 2H), 1.62 (s, 3H), 1.61 (s, 3H), 1.41 (s, 3H), 1.30 (s, 3H), 1.25 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.5, 135.6, 134.1, 129.5, 127.6, 124.9, 123.9, 121.9, 64.2, 61.2, 58.3, 39.7, 37.9, 36.3, 27.5, 26.9, 26.7, 24.9, 19.2, 18.8, 16.4, 16.0; HRMS (EF-CI) [m+]/z calc'd 530.3580, found 530.3561

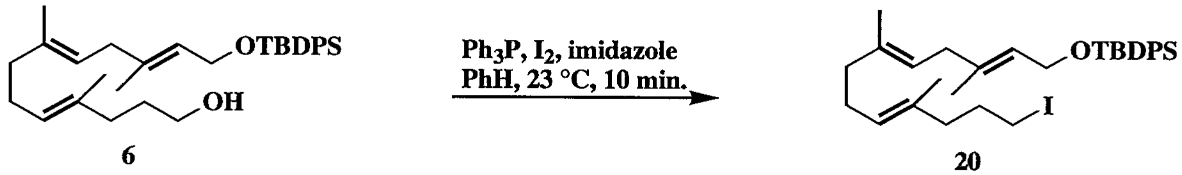


Epoxide **5** (612 mg, 1.153 mmol) was taken up in tetrahydrofuran (7.0 mL) and water (1.5 mL) and was cooled to 0 °C. Sodium periodate (140 mg, 0.656 mmol) and periodic acid dihydrate (290 mg, 1.27 mmol) were added. The reaction was allowed to warmed to 23 °C and was stirred for 30 minutes. The reaction was quenched with saturated sodium bicarbonate (5 mL). The product was extracted into 50% ethyl acetate in hexane (100 mL) and was washed with brine (20 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give aldehyde **19** as a clear colorless oil (580 mg, ~95% pure by crude ^{1}H NMR, total isolated yield over 2 steps is reported). The product was used without further purification: R_f sm: 0.37; prod: 0.29 (Hex-EtOAc 9:1); FTIR (thin film) 3070, 3048, 2958, 2929, 2896, 2856, 1726, 1472, 1427, 1364 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (t, 1H), 7.70 (m, 5H), 7.40 (m, 6H), 5.39 (t, 1H), 5.12 (m, 2H), 4.22 (d, 2H, J=6.2 Hz), 2.65 (d, 2H, J=7.3 Hz), 2.49 (t, 2H, J=7.6 Hz), 2.31 (t, 2H, J=7.4 Hz), 2.12-2.01 (m, 4H), 1.62 (s, 3H), 1.60 (s, 3H), 1.41 (s, 3H), 1.04 (s, 9H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 202.7, 136.6, 136.4, 135.7, 134.1, 133.0, 129.5, 127.6, 125.4, 124.0, 122.1, 61.3, 42.2, 39.6, 37.9, 31.9, 26.9, 26.6, 19.2, 16.5, 16.2, 16.0; HRMS (EF-CI) $[m+NH_4]/z$ calc'd 506.3454, found 506.3454

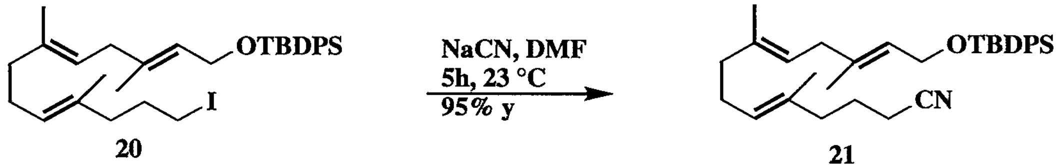


To a stirred solution of sodium borohydride (65.4 mg, 1.73 mmol) in ethanol (24 mL) at -42 °C was added aldehyde **19** (564 mg, 1.15 mmol) in ethanol (4 x 1.0 mL). The mixture was stirred at -42 °C for 30 minutes. Acetone (1.0 mL) was added to quench excess boron reagent and the reaction was allowed to stir at -42 °C for 1 hour. The reaction was allowed to warm to 23 °C and solvents were removed *in vacuo*. The resulting slurry was taken up in sodium sulfate (sat'd, 50 mL). The product was then extracted into 1:1 ethyl acetate/hexane (100 mL) and was washed with sodium chloride (sat'd, 25 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give a clear, colorless oil as a crude product (586 mg). The product was purified by silica gel chromatography (25 g) eluting with 9:1 hexane-ethyl acetate (200 mL) then 4:1 hexane-ethyl acetate (200 mL) to give alcohol **6** (497 mg, 88% over 2 steps) as a clear, colorless oil: R_f sm: 0.42; prod: 0.17 (Hex-EtOAc 4:1); FTIR (thin film) 3320, 3071, 2957, 2931, 2857, 1472, 1428, 1383, 1111, 1056, 823 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 4H), 7.39 (m, 6H), 5.38 (t, 1H), 5.16 (t, 1H), 5.12 (t, 1H), 4.22 (d, 2H, J=6.0 Hz), 3.61 (dt, 2H, J_1=5.7 Hz, J_2=6.4 Hz), 2.64 (d, 2H, J=7.3 Hz), 2.08 (m, 6H), 1.66 (m, 2H), 1.62 (s, 3H), 1.60 (s, 3H), 1.40 (s, 3H), 1.33, (t, 1H, J=5.6 Hz), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.4, 135.5, 134.6, 134.0 129.4, 127.5, 124.5, 123.7, 121.9, 62.6, 61.1, 39.6, 37.8, 35.9, 30.6, 26.8, 26.4, 19.1, 16.4, 15.9, 15.8; HRMS (EF-CI) $[m+NH_4]/z$ calc'd 508.3611, found 508.3590



6 **20**

A stirring solution of alcohol **6** (449 mg, 0.915 mmol) in benzene (5.5 mL) at 23 °C was treated with triphenylphosphine (312 mg, 1.19 mmol), imidazole (112 mg, 1.65 mmol), and iodine (279 mg, 1.10 mmol). The reaction was allowed to stir for 10 minutes, was diluted with diethyl ether (10 mL) and was decanted into a separatory funnel with extensive ether washes (5x5 mL). The organics were washed with water (15 mL), 20% citric acid (15 mL), saturated sodium bicarbonate (15 mL) and brine (15 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give an oily solid. This was taken up in hexane (30 mL) and was filtered through a plug of celite. The solvent was again removed to give iodide **20** as a clear pale yelow oil that was used without further purification: R_f sm: 0.06; prod: 0.61 (Hex-EtOAc 9:1); FTIR (thin film) 3070, 3049, 3025, 2959, 2930, 2897, 2856, 1472, 1462, 1428, 1383, 1360, 1217, 1166, 1111, 1055, 1029, 998, 823 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 4H, Ar), 7.40 (m, 6H, Ar), 5.42 (t, 1H, J=6.4 Hz), 5.20 (t, 1H, J=6.9 Hz), 5.15 (t, 1H, J=7.3 Hz), 4.25 (d, 2H, 6.3 Hz), 3.15 (t, 2H, J=7.0 Hz), 2.67 (d, 2H, J=7.3 Hz), 2.15-2.07 (m, 6H), 1.92 (quin, 2H, J=7.1 Hz), 1.63 (s, 3H), 1.61 (s, 3H), 1.44 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 136.4, 135.6, 134.1, 132.9, 129.5, 127.6, 125.8, 123.9, 122.1, 61.2, 40.0, 39.7, 37.9, 31.6, 26.9, 26.6, 19.2, 16.5, 16.0, 15.9, 6.6; MS (EF-CI) [m+NH_4]/z calc'd 618, found 618



20 **21**

To a stirring solution of iodide **20** (550 mg (theoretical), 0.915 mmol) in dimethylformamide (25 mL) was added sodium cyanide (67 mg, 1.37 mmol). The reaction was allowed to stir for 5 hours at 23 °C. The reaction was quenched with saturated sodium bicarbonate (50 mL). The

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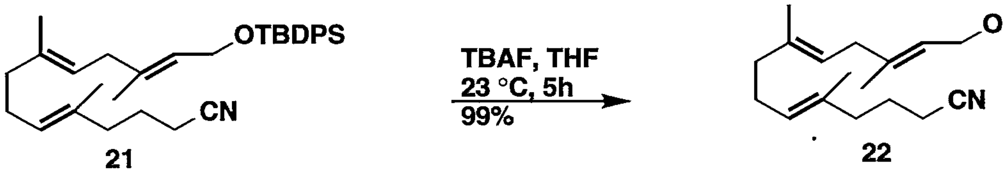
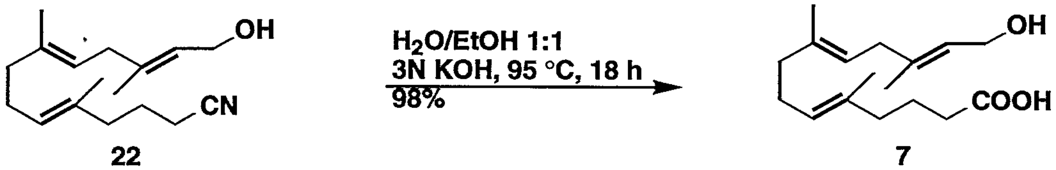
product was extracted into ethyl acetate (200 mL). The organics were washed with saturated sodium bicarbonate (25 mL) and brine (25 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give a clear yellow oil . The product was purified on silica gel (25 g) eluting with 95:5 hexane-ethyl acetate (100 mL) then 9:1 hexane-ethyl acetate (250 mL) to give nitrile **21** as a clear colorless oil (434 mg, 95% y over 2 steps): R_f sm: 0.61; prod: 0.24 (Hex-EtOAc 9:1); FTIR (thin film) 3071, 3050, 3029, 2997, 2931, 2877, 2857, 2246, 1671, 1589, 1471, 1445, 1428, 1384, 1361, 1111, 1055, 1028, 998, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.40 (m, 6H), 5.38 (t, 1H, J=6.3 Hz), 5.18 (t, 1H, J=6.9 Hz), 5.12 (t, 1H, J=7.4 Hz), 4.22 (d, 2H, J=6.3 Hz), 2.64 (d, 2H, J=7.3 Hz), 2.26 (t, 2H, J=7.2 Hz), 2.13-2.03 (m, 6H), 1.74 (quin, 2H, J=7.2 Hz), 1.61 (s, 3H), 1.59 (s, 3H), 1.41 (s, 3H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 136.3, 135.6, 134.1, 132.4, 129.5, 127.6, 126.5, 123.9, 122.1, 119.8, 61.2, 39.6, 38.2, 37.9, 26.9, 26.5, 23.4, 19.2, 16.5, 16.2, 16.0, 15.6; HRMS (EF-EI) [m+]/z calc'd 499.3271, found 499.3259



Silyl ether **21** (384.7 mg, 0.770 mmol) was taken up in tetrahydrofuran (9.2 mL) and was treated with *t*-butylammoniumfluoride (1M, 2.30 mL, 2.3 mmol). The reaction was allowed to stir at 23 °C for 5 hours. The tetrahydrofuran was removed *in vacuo* and the product was partitioned between saturated sodium bicarbonate (15 mL) and ethyl acetate (50 mL). The organics were washed with saturated sodium chloride (15 mL), dried over sodium sulfate and the solvent was removed *in vacuo*. The product was purified on silica gel (10 g) eluting with hexane-ethyl acetate (2:1) to give pure alcohol **22** (199 mg, 99% y): R_f sm: 0.61; prod: 0.21 (Hex-EtOAc 2:1); FTIR (thin film) 3363, 2960, 2919, 2874, 2855, 2247, 1672, 1441, 1430, 1000 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (tq, 1H, J = 7, 1.4), 5.16 (m, 2H), 4.14 (d, 2H, J = 7.0), 2.69 (d, 2H, J = 7.3), 2.28 (t, 2H, J = 7.1), 2.11 (m, 4H), 2.04 (t, 2H, J = 7.1), 1.75 (quin, 2H, J = 7.2), 1.61 (s, 3H), 1.59 (s, 3H), 1.58 (s, 3H), 1.03 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 136.5, 132.4, 126.4, 123.2, 121.8, 119.8, 59.4, 39.5, 38.2, 37.9, 26.3, 23.3, 16.5, 16.2, 15.9, 15.6; HRMS (EF-EI) [m+]/z calc'd 261.2093, found 291.2106



22 **7**

Nitrile **22** (77.9 mg, 0.298 mmol) was taken up in ethanol (3.75 mL) and water (3.75 mL) in a teflon reaction vessel and was treated with potassium hydroxide (418 mg, 7.45 mmol). The vessel was sealed and heated to 95 °C in an oil bath for 18 hours. The ethanol was removed *in vacuo* and the residue was diluted with water (10 mL), washed with hexane (5 mL) and was acidified with hydrochloric acid (3N) until cloudy. The product was extracted into ethyl acetate (3 x 25 mL). The organics were combined and washed with saturated sodium chloride. The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give a clear colorless oil. The product was purified on silica gel (4 g) eluting with acetic acid-ethyl acetate (1:99) to give pure carboxylic acid **7** (82.3 mg, 98% y): R_f sm: 0.88; prod: 0.51 (EtOAc/HOAc 99:1); FTIR (thin film) 3290 (br), 2916, 2858, 1708, 1674, 1440, 1410, 1382, 1237, 1237, 1083, 988, 959 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (tq, 1H, J = 7.1, 1.3 Hz), 5.13 (t, 1H, J = 7.3 Hz), 5.11 (t, 1H, J = 6.9 Hz), 4.15 (d, 2H, J = 7.0 Hz), 2.69 (d, 2H, J = 7.3 Hz), 2.29 (t, 2H, J = 7.4 Hz), 2.10 (m, 2H), 2.01 (m, 4H), 1.73 (quin, 2H, J = 7.3 Hz), 1.65 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 139.2, 136.5, 133.7, 125.0, 122.7, 121.7, 59.0, 39.5, 38.6, 37.8, 33.2, 26.1, 22.6, 16.3, 15.8, 15.7; HRMS (EF-CI) [m+NH_4]/z calc'd 298.2382, found 298.2376

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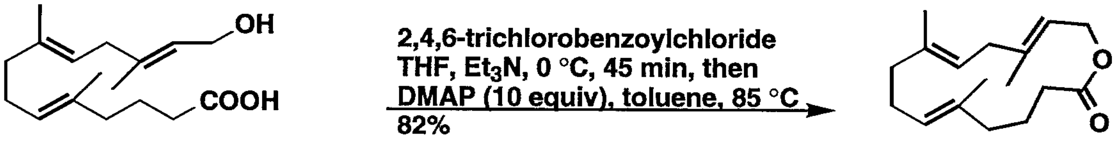
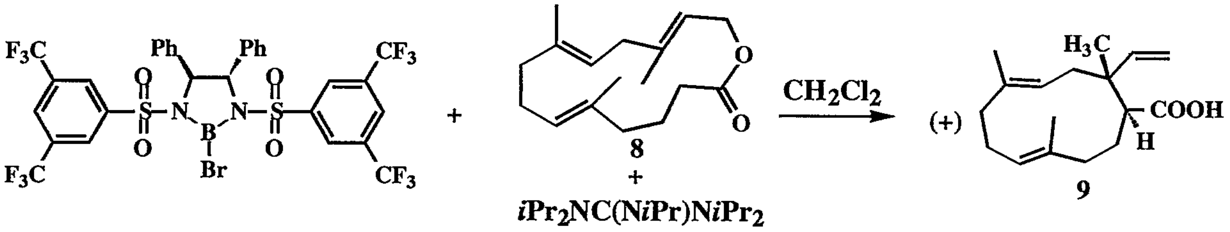
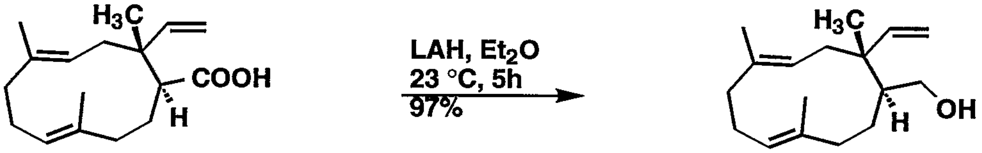


7 **8**

Hydroxy acid **7** (1.91 g, 6.81 mmol) was taken up in tetrahydrofuran (40 mL) and was cooled to 0 °C. To the reaction was added sequentially triethylamine (1.14 mL, 8.17 mmol) and 2,4,6-trichlorobenzoylchloride (1.12 mL, 7.15 mmol). The reaction was allowed to stir at 0 °C for 1 hour. Tetrahydrofuran (10 mL) was added slowly to maintain reaction temperature near 0 °C followed by the slow addition of toluene (40 mL). This reaction mixture (at 0 °C) was then slowly added over 2 hours via cannula to a solution of dimethylaminopyridine (8.31 g, 68.1 mmol, dried at 75 °C for 1 hour at 1mm Hg) in toluene (400 mL) stirring rapidly at 85 °C. Solids remained in the addition flask and were washed with toluene (10 mL) and the solution was also added via cannula. The receiving reaction vessel was then stirred for an additional 30 minutes at 85 °C and was then allowed to cool to 23 °C. The solvent was removed *in vacuo*. The product was extracted into 20% ethyl acetate-hexane (350 mL) and was washed with citric acid (20%, 100 mL), saturated sodium bicarbonate (100 mL), and brine (100 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* to give a clear colorless oil (1.8 g, 88:12 monomer/dimer by crude ^{1}H NMR). The product was purified on silica gel (150 g) eluting with pentane-diethyl ether (98:2) to give pure lactone **8** (1.46 g, 82% y): R_f sm: 0; prod: 0.28 (Hex-EtOAc 9:1); FTIR (thin film) 2975, 2924, 2852, 1735, 1441, 1381, 1257, 1234, 1201, 1175, 1145 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.19 (m, 2H), 5.04 (m, 1H), 4.69 (d, 2H, J = 6.6 Hz), 2.63 (d, 2H, J = 7.6 Hz), 2.25 (m, 2H), 2.13 (m, 4H), 2.06 (t, 2H, J = 7.7 Hz), 1.69 (m, 2H), 1.69 (s, 3H), 1.55 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.2, 140.0, 136.1, 134.2, 124.5, 123.0, 119.5, 60.7, 39.0, 37.8, 36.8, 33.2, 24.0, 23.5, 17.6, 15.3, 14.8; HRMS (EF-EI) [m+]/z calc'd 262.1933, found 262.1942

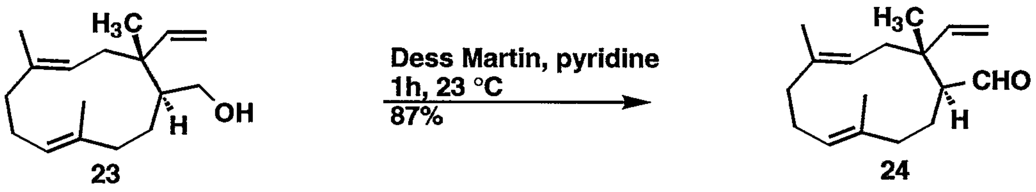


The bis-(3,5-ditrifluoromethyl)benzenesulfonamide of (S,S)-1,2-diphenyl-1,2-diaminoethane (431 mg) was dried under vacuum (0.5 mm Hg) at 70 °C for 12 hrs. It was then taken up in dichloromethane (15 mL) under nitrogen at 23 °C. Freshly distilled tribromoborane (from sodium, 103 μL) was then added and the reaction was allowed to stir at 23 °C for 24 hours. The mixture was concentrated under house vacuum (~25 mm Hg) through calcium chloride and sodium hydroxide traps to give a white solid. The residue was again taken up in dichloromethane (15 mL) and was reduced *in vacuo*. The remaining white solid was evacuated under high vacuum (0.5 mm Hg) and flushed with nitrogen three times and was then taken up in dichloromethane (10.5 mL). The solution was then cooled to -94 °C. A solution of lactone **8** (114 mg) in dichloromethane (4.5 mL) was treated with pentaisopropylguanidine (795 μL) and the solution was also cooled to -94 °C. The Lewis acid solution was then added to the lactone solution at -94 °C over a 5-10 minute period. The reaction was kept at -94 °C for 3 hours, at -78 °C for 12 hours, followed by 55 hours at 4 °C. The reaction was diluted with ether (100 mL) and was washed with aqueous citric acid (20%, 50 mL). The product was extracted into 1N potassium hydroxide (4 x 20 mL). The basic aqueous fractions were combined, washed with diethyl ether (20 mL), and acidified to pH~4 with 3N hydrochloric acid. The product was extracted with 10 % ethyl acetate in hexane (100 mL). The organics were dried over sodium sulfate and reduced *in vacuo* to give **9** as a white solid (98 mg, 86%) that was a single isomer by 500 MHz ^{1}H NMR. The diastereoselectivity was determined by integration of a doublet at 2.72 ppm for the "trans" isomer (measuring 100) and comparing to a baseline resolved doublet at 2.63 ppm for the "cis" isomer (measuring 1.8) to give >98% diastereoselectivity. Enantioselectivity of >98% ee was determined by reduction of the crude product **9** with lithium aluminum hydride to give alcohol **23** followed by chiral HPLC analysis using a chiracel OD column (see below): R_f sm: 0.64; prod: 0.48 (Hex-EtOAc/HOAc 60:40:1); FTIR (thin film) 3200-2600 (br), 3082, 2967, 2919, 2856, 1702, 1450, 1414, 1233, 912 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.05 (dd, 1H, J = 10.8, 17.4 Hz), 5.02 (dd, 1H, J = 0.9, 17.4 Hz), 5.01 (m, 1H), 4.98 (dd, 1H, J = 0.9, 10.8 Hz), 4.93 (dd, 1H, J = 5.5, 9.6 Hz), 2.71 (d, 1H, J = 10.0 Hz), 2.29 (m, 1H), 2.18-2.02 (m, 6H), 1.85 (m, 1H), 1.73 (t, 1H, J = 12.0 Hz), 1.60 (s, 3H), 1.49 (s, 3H), 1.20 (t, 1H, J = 12.4 Hz), 1.11 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.0, 144.8, 136.0, 135.7, 125.1, 122.6, 111.7, 49.5, 42.0, 39.2, 38.1, 36.6, 27.0, 25.1, 20.0, 17.8, 15.8; HRMS (EF-EI) [m+]/z calc'd 262.1933, found 262.1940; $[\alpha]_D$ = +16.4, c = 1.92 mg/mL $CHCl_3$

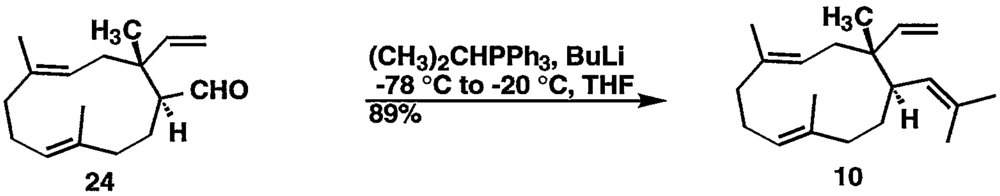


9 **23**

Carboxylic acid **9** (62.4 mg, 0.238 mmol) was taken up in diethyl ether (2.6 mL) and was treated with lithium aluminum hydride (1M, 1.32 mL, 1.32 mmol) at 23 °C. The reaction was allowed to stir for 5 hours at 23 °C. The reaction was diluted with diethyl ether (2.6 mL) and was quenched by the addition of water (50 mL), 15% sodium hydroxide (50 mL) and water (150 mL) and was stirred for 30 minutes. The product was filtered through a plug of celite with diethyl ether washes and the solvent was removed *in vacuo* to give alcohol **23** as a clear colorless oil (57.3 mg, 97% y) that was completely pure by ^{1}H NMR. Enantiomeric excess can be readily determined by HPLC on a Chiracel OD column detecting at 215 nm (1% isopropanol in hexane; (-) **23** 12 min; (+) **23** 28 min) and was found to be >98% ee by integration: R_f sm: 0.2; prod: 0.37 (Hex-EtOAc 4:1); FTIR (thin film) 3380 (br), 2965, 2918, 2856, 1452, 1032, 1002, 909 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (dd, 1H, J = 10.9, 17.6 Hz), 5.06 (dd, 1H, J = 1.3, 17.6 Hz), 5.03 (dd, 1H, J = 1.4, 10.8 Hz), 5.03 (m, 1H), 4.90 (dd, 1H, J = 5.2, 10.7 Hz), 3.63 (dd, 1H, J = 7.2, 11.8 Hz), 3.42 (dd, 1H, J = 3.3, 11.7 Hz), 2.34-1.96 (m, 6H), 1.89-1.80 (m, 3H, 1.72 (m, 1H), 1.56 (s, 3H), 1.47 (s, 3H), 1.08 (m, 2H), 0.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.9, 136.6, 134.5, 124.9, 123.0, 110.9, 64.7, 44.4, 42.1, 39.2, 38.7, 37.9, 25.5, 25.2, 19.3, 17.3, 15.9; HRMS (EF-EI) [m+]/z calc'd 248.2140, found 248.2146; mp = 47 °C; $[\alpha]_D$ = +21.6, c = 3.08 mg/mL CHCl3

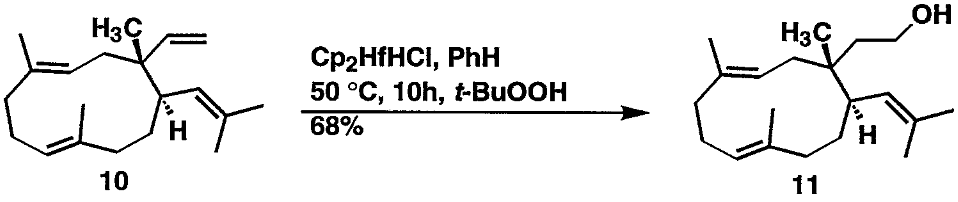


Alcohol **23** (110.8 mg, 0.446 mmol) was taken up in methylenechloride (12 mL), treated with pyridine (0.433 mL) and then with Dess Martin (567 mg). The reaction was complete after 45 minutes. The reaction was diluted with hexane (20 mL) filtered through celite and reduced *in vacuo*. Some solids from Dess Martin remained. The product was taken up in hexane and filtered a second time through celite. Concentration *in vacuo* gave aldehyde **24** as a clear colorless oil (95.3 mg, 87% y): R_f sm: 0.37; prod: 0.41 (Hex-EtOAc 9:1); FTIR (thin film) 2962, 2922, 2854, 1719, 1452, 1378, 916 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.64 (d, 1H, J = 2.8 Hz), 6.11 (dd, 1H, J = 10.9, 17.5 Hz), 5.07 (d, 1H, J = 10.9 Hz), 5.02 (d, 1H, J = 17.6 Hz), 5.01 (m, 1H), 4.85 (dd, 1H, J = 6.0, 9.8 Hz), 2.55 (dt, 1H, J = 9.1, 2.0 Hz), 2.3-1.9 (m, 7H), 1.83 (m, 1H), 1.66 (m, 1H), 1.55 (s, 3H), 1.47 (s, 3H), 1.07 (m, 1H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 205.7, 144.6, 136.0, 135.8, 125.2, 122.4, 112.7, 54.9, 41.8, 39.2, 38.5, 37.1, 25.0, 22.0, 20.7, 17.4, 15.9; HRMS (EF-EI) [m+]/z calc'd 246.1984, found 246.1993, $[\alpha]_D$ = +90.0, c = 3.06, CHCl3



J1230-16

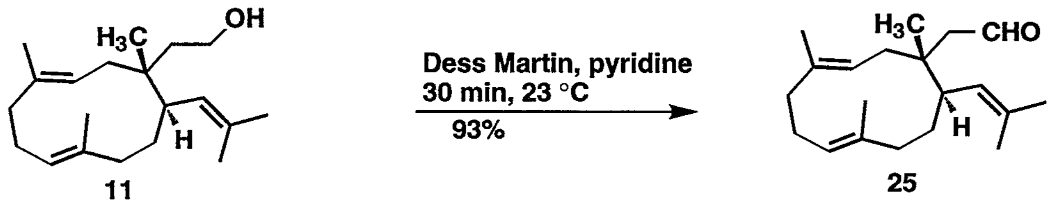
Isopropyltriphenyl phosphonium Iodide (538 mg, 1.245 mmol) was taken up in tetrahydrofuran (12.0 mL) and was cooled to -78 °C and was treated with *n*-butyllithium (1.6M, 700 µL). The reaction was allowed to warm to 0 °C to give a deep red solution and was stirred for 45 minutes. The reaction was cooled to -78 °C and aldehyde **24** (69.0 mg, 0.280 mmol) was added as a solution in tetrahydrofuran via canula (3 x 1mL). The reaction was then stored at -20 °C for 10 hours. The reaction was quenched by adding saturated sodium carbonate (5 mL) and the red color was quenched. The tetrahydrofuran was removed *in vacuo* and the product was extracted into hexane (30 mL) and was washed with water (10 mL), citric acid (10 mL), saturated sodium bicarbonate (10 mL) and brine (10 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo* . The product was purified on silica gel (2 g) eluting with hexane to give pure **10** as a clear colorless oil (68.0 mg, 89% y): R_f sm: 0; prod: 0.32 (Hexane); FTIR (thin film) 2969, 2923, 2857, 1445, 1380 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93 (dd, 1H, J = 11.1, 17.4 Hz), 5.00 (d, 1H, J = 9.4 Hz), 4.93 (dt, 1H, J = 10.6, 1.3 Hz), 4.89 (dd, 1H, J = 11.0, 2.5 Hz), 4.86 (dd, 1H, J = 8.2, 1.6 Hz), 4.83 (s, 1H), 2.50 (m, 1H), 2.36 (m, 1H), 2.19 (m, 2H), 2.01 (m, 3H), 1.83 (m, 1H), 1.72 (s, 3H), 1.68 (s, 3H), 1.61 (m, 1H), 1.59 (s, 3H), 1.13 (m, 2H), 0.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147. 2, 137.4, 134.0, 131.6, 127.8, 124.2, 123.7, 109.8, 42.9, 41.3, 39.3, 37.1, 36.4, 29.5, 26.0, 25.2, 20.5, 18.9, 17.8, 15.8; HRMS (EF-EI) [m+]/z calc'd 272.2504, found 272.2508; $[\alpha]_D = +18.6$, c = 1.00, $CHCl_3$



To hafnocene chloride hydride (382 mg, 1.10 mmol) was added tetraene **10** (74.5 mg, 0.273 mmol) in benzene (2 x 2.5 mL) via canula. The reaction vessel was wrapped in aluminum foil and was heated to 50 °C for 10 hours. The reaction was then cooled to 4 °C, diluted with benzene (5 mL), and was treated with anhydrous *t*-butylhydroperoxide (3M in octane, 735 µL,

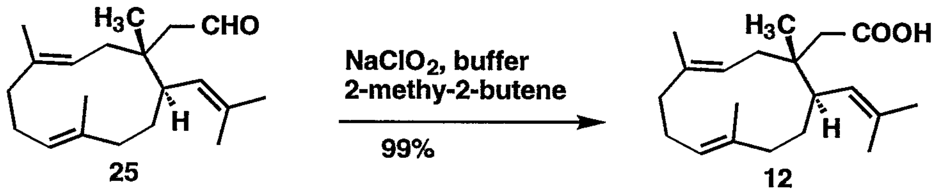
J1230-17

2.2 mmol). The reaction was allowed to stir and warm to 23 °C for 45 minutes. The reaction was quenched with citric acid (20%, 25mL) and was extracted into 10% ethyl acetate in hexane (100 mL). The organics were washed with saturated sodium bicarbonate (2 x 25 mL) and brine (25 mL). The organics were dried over sodium sulfate and the solvent was removed *in vacuo.* The product was purified on silica gel (5 g) eluting with hexane-ethyl acetate (9:1, 50 mL; 4:1 50 mL) to give pure alcohol **11** as a clear colorless oil (54.3 mg, 68% y): R_f sm: 0.68; prod: 0.23 (Hex-EtOAc 4:1); FTIR (thin film) 3330 (br), 2965, 2925, 2857, 1455, 1448, 1375, 1045, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.91 (m, 3H), 3.64 (t, 2H, J = 7.6 Hz), 2.33 (m, 2H), 2.21 (m, 1H), 2.18-1.93 (m, 3H), 1.89-1.78 (m, 2H), 1.74 (s, 3H), 1.71 (s, 3H), 1.57 (m, 4H), 1.52 (s, 3H), 1.47 (s, 3H), 1.08 (m, 2H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 134.5, 131.9, 127.5, 123.6, 123.4, 60.1, 43.2, 40.5, 39.3, 38.6, 36.4, 34.0, 28.8, 26.2, 25.3, 20.5, 19.0, 17.8, 16.0; HRMS (EF-EI) [m+]/z calc'd 290.2610, found 290.2601, $[\alpha]_D$ = +16.6, c = 1.27, $CHCl_3$



Alcohol **11** (13.9 mg, 0.0479 mmol) was taken up in methylenechloride (1.2 mL) and was treated with pyridine (46 µL, 0.575 mmol) and then with Dess Martin reagent (61 mg, 0.144 mmol). The reaction was allowd to stir for 10 minutes and was then diluted with hexane (4 mL), filtered through celite and reduced *in vacuo.* Some solids from Dess Martin remained. The product was taken up in hexane (5 mL) and filtered a second time through celite. Concentration *in vacuo* gave aldehyde **25** as a clear colorless oil (12.9 mg, 93% y): R_f sm: 0.23; prod: 0.45 (Hex-EtOAc 4:1); FTIR (thin film) 2966, 2919, 2856, 1714, 1445, 1381 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.74 (t, 1H, J = 3.1 Hz), 4.99 (d, 1H, J = 10.7 Hz), 4.93 (d, 1H, J = 9.5 Hz), 4.86 (d, 1H, J = 11.5 Hz), 2.46-2.32 (m, 3H), 2.28-2.13 (m, 3H), 2.10-1.97 (m, 3H), 1.86 (m, 1H), 1.71 (s, 3H), 1.66

(s, 3H), 2.60 (m, 1H), 1.60 (s, 3H), 1.12 (m, 2H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 137.2, 135.3, 134.1, 127.2, 123.8, 122.3, 52.4, 42.5, 40.6, 39.3, 36.7, 36.3, 28.9, 26.0, 25.2, 20.6, 18.9, 17.8, 16.0; HRMS (EF-CI) [m+NH_4]/z calc'd 306.2797, found 306.2809, $[\alpha]_D$ = +36.1, c = 1.58, CHCl3



Aldehyde **25** (12.9 mg, 0.0447 mmol) was taken up in *t*-butyl alcohol (0.6 mL), 20% monosodium phosphate (0.3 mL) and 2-methyl-2-butene (0.5 mL). To this mixture was added sodium chlorite (41 mg, 0.45 mmol). The reaction was allowed to stir rapidly for 30 minutes. The reaction was diluted with 1:1 hexane-ethyl acetate (25 mL) and with 10% monosodiumphosphate (10 mL). The organics were reduced *in vacuo*, taken up in lithium hydroxide (1M, 25 mL) and the aqueous was washed with hexane (15 mL). The aqueous was acidified with 3N hydrochloric acid until cloudy and 20% monosodiumphosphate (2 mL) was added. The product was extracted into 1:1 hexane-ethyl acetate (25 mL). The organics were washed with brine (5 mL) dried over sodium sulfate and the solvent was removed *in vacuo* to give carboxylic acid **12** as a clear colorless oil (13.5 mg, 99% y): R_f sm: 0.45; prod: 0.29 (Hex-EtOAc 4:1); FTIR (thin film) 3200-2600 (br), 2967, 2924, 2856, 1703, 1444, 1383 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.95 (m, 2H), 4.86 (m, 1H), 2.4-2.0 (m, 9H), 1.82 (m, 1H), 1.73 (s, 3H), 1.70 (s, 3H), 1.58 (s, 3H), 1.58 (m, 1H), 1.48 (s, 3H), 1.10 (m, 2H), 0.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.1, 137.2, 134.7, 133.1, 127.0, 123.8, 122.9, 42.9, 42.4, 39.9, 39.3, 36.3, 34.4, 29.0, 26.1, 25.2, 20.2, 18.9, 17.8, 16.0; HRMS (EF-EI) [m+]/z calc'd 304.2402, found 304.2404, $[\alpha]_D$ = +42.1, c = 1.22, CHCl3

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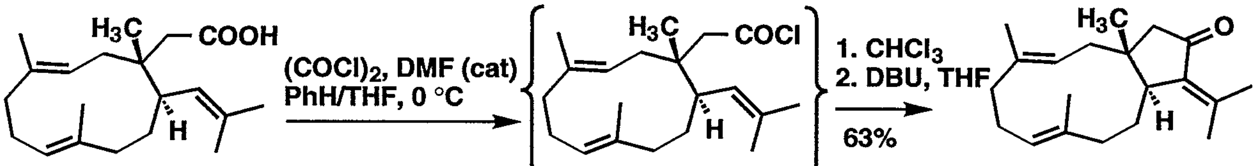
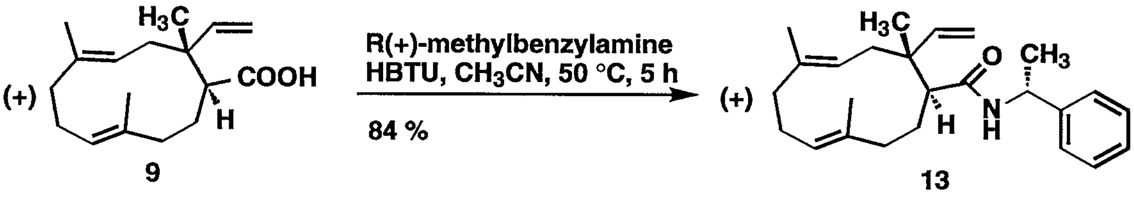


12 1

Carboxylic acid **12** (13.5 mg, 0.0443 mmol) was taken up in tetrahydrofuran (0.15 mL) and benzene (0.70 mL) and was cooled to 0 °C. The reaction was treated with oxalyl chloride (8 mL, 0.0887 mmol) and with dimethylformamide (1 mL, 0.014 mml). The reaction was allowed to stir for 30 minutes at 0 °C . The reaction was diluted with benzene (1 mL) and was frozen in a -78 °C bath. The frozen mixture was reduced *in vacuo*. The residue was taken up in chloroform (1 mL) and was maintaned at 23 °C for 15 minutes. Formation of cyclized product was observed by ^{1}H NMR and IR. The reaction mixture was then poured into saturated sodium bicarbonate (5 mL) and the products were extracted into dichloromethane (10 mL). The organic phase was dried over sodium sulfate, concentrated and then brought up in tetrahydrofuran. The mixture of isomers was treated with DBU (5 µL) and was allowed to stir for 1 hour at 23 °C. The reaction mixture was then concentrated, brought up in 10% ethyl acetate in hexane (15 mL). The organics were washed with 20% citric acid (5 mL) and saturated sodium bicarbonate (5 mL). The organics were dried over sodium sulfate and concentrated *in vacuo*. The product was purified on silica gel (1 g) eluting with hexane (10 mL) hexane-ethyl acetate (97:3, 10 mL), (95:5, 20 mL), to give pure Dolabellatrienone **1** (8.0 mg, 63% y). Racemic Dolabellatrienone (**1**) was readily resolved into its enatiomers by chiral HPLC using a Whelk-O 1 column eluting with 1% isopropanol in hexane (17 and 23 min). Synthetic (+) **1** was analyzed under the same conditions and was found to be opically pure (a single peak at 17 min, >98% ee).: R_f sm: 0.23 (Hex-EtOAc 4:1); prod: 0.24 (Hex-EtOAc 9:1); FTIR (thin film) 2972, 2957, 2920, 2851, 1703, 1621, 1441, 1181 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.23 (dd, 1H, J = 11.3, 5.1 Hz), 4.92 (d, 1H, J = 10.4 Hz), 2.83 (d, 1H, J = 11.6 Hz), 2.40-2.08 (m, 9H), 2.21 (s, 3H), 1.83 (s, 3H), 1.64 (s, 3H), 1.65-1.45 (m, 3H), 1.44 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 207.4, 148.3, 137.9, 135.7, 131.4, 130.3, 124.8, 54.8, 41.5, 41.0, 40.1, 39.8, 38.1, 28.0, 24.5, 24.3, 23.2, 21.4, 16.1, 15.5; HRMS (EF-EI) [m+]/z calc'd 286.2297, found 286.2301, $[\alpha]_D$ = +25, c = 0.52, $CHCl_3$



Carboxylic acid **9** (22 mg) was taken up in acetonitrile (650 µL) and was treated with R(+)-methylbenzylamine (50 µL) and with o-benzotriazol-1-yl-N,N,N',N'-tetramethyluronium hexafluorophosphate (64 mg). At room temperature, only anhydride was formed (1812 cm^{-1}). However, the reaction was heated to 50 °C for 5 hours to complete amide formation. The reaction was cooled to 23 °C, and was diluted with 10% ethyl acetate/ hexane (15 mL). The organics were washed with 20% citric acid (5 mL) and saturated sodium bicarbonate (5 mL). The organics were dried over sodium sulfate and concentrated *in vacuo*. The product was purified by crystallization from dichloromethane and hexane to give the product amide **13** as a white solid (25.7 mg, 84% y). X-ray quality crystals were grown from a chloroform-heptane bilayer at 23 °C over 48 hours: R_f sm: 0.25; prod: 0.2 (Hex-EtOAc 4:1); FTIR (thin film) 3300, 2982, 2921, 2856, 1635, 1531 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 6.00 (dd, 1H, J = 10.8, 17.5 Hz), 5.53 (bd, 1H, J = 7.8 Hz), 5.15 (quin, 1H, J = 7.3 Hz), 5.03 (d, 1H, J = 17.5 Hz), 4.99 (d, 1H, J = 10.8 Hz), 4.97 (d, 1H, J = 10 Hz), 4.79 (dd, 1H, J = 3.9, 11.0 Hz), 2.37-1.97 (m, 8H), 1.57 (s, 3H), 1.60-1.50 (m, 2H), 1.48 (s, 3H), 1.47 (d, 3H, J = 7.3 Hz), 1.12 (s, 3H), 1.07 (t, 1H, 11.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 145.1, 143.4, 136.9, 135.4, 128.6, 127.2, 126.2, 124.3, 111.9, 51.6, 48.5, 42.4, 39.3, 37.4, 37.1, 26.7, 25.1, 21.4, 20.7, 17.9, 15.9; HRMS (EF-EI) [m+]/z calc'd 365.2719, found 365.2724; mp = 202 °C; $[\alpha]_D$ = +33, c = 0.59, $CHCl_3$

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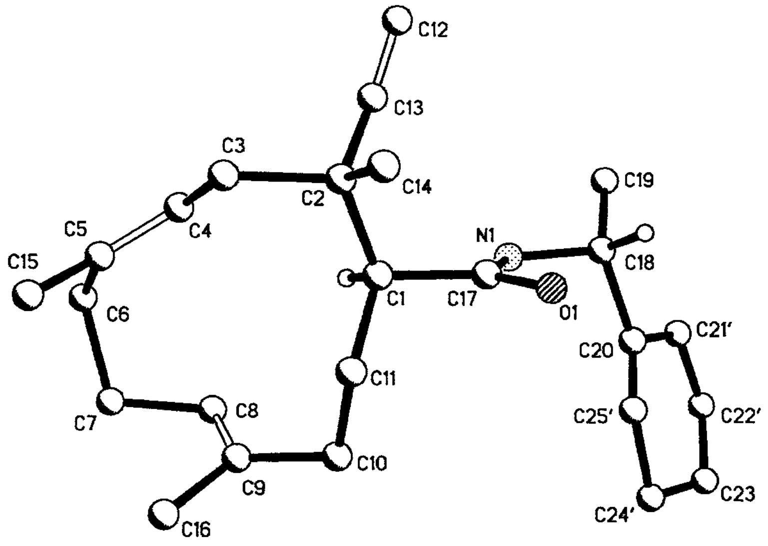

X-ray structure of (+)-amide **13**