Supporting Information

Synthetic And Mechanistic Studies Of The Retro-Claisen Rearrangement 4. An Application To The Total Synthesis of (+)-Laurenyne.

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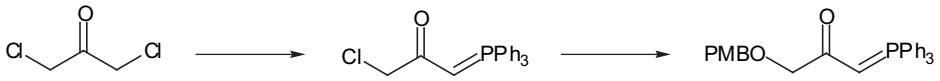
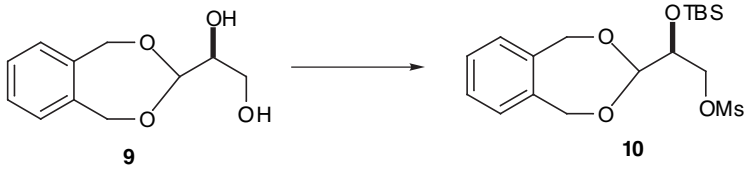


8

1-(4-Methoxyphenylmethoxy)-3-(triphenylphosphanylidene)-propan-2-one (8). To a solution of 1,3-dichloroacetone (63.50 g, 0.5 mol) in 800 mL THF was added triphenylphosphine (262.29 g, 0.5 mol). The solution was heated at reflux for 24 h before cooling to room temperature. The precipitate was collected by filtration and washed with 2 x 100 mL THF. The solid was then dissolved in 200 mL methanol. A solution of sodium carbonate (26.49 g, 0.25 mol) in 200 mL water was added resulting in a heavy white precipitate. After stirring at room temperature for a further 5 min, 600 mL distilled water was added. The resulting suspension was stirred for another 5 min, then allowed to stand at room temperature for 1 h. The precipitate was collected by filtration and dissolved in 400 mL of dichloromethane. The dichloromethane solution was dried over $MgSO_4$ and concentrated to afford 163 g of the chloro ylide (92 %) as a white solid, mp 178-180 °C (Lit[1] mp 179-180 °C).

A flame dried 1L round bottom flask was charged with *para*-methoxybenzyl alcohol (27.6 g, 0.2 mol) and 100 mL freshly distilled THF. An 8.0 g portion of 60% (wgt %) NaH (0.2 mol) was added slowly. After the addition was complete, a solution of the above chloro ylide (35.4 g, 0.1 mol) in 100 mL THF was added. The resulting solution was heated at reflux overnight. The reaction mixture was cooled to room temperature and concentrated to afford crude ylide **8** as a yellow semi-solid. Purification via silica gel chromatography eluting sequentially with 50 % ethyl acetate in hexane and 100% THF afforded 41.0 g of pure **8**[2] (90%) as a slightly yellow to colorless solid having mp 121-122°C: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (dd, J_1 = 12.6 Hz, J_2 = 8.1 Hz, 6H), 7.45 (t, J = 7.4 Hz, 3H), 7.35 (m, 6H), 7.27 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 4.75 (s, 2H), 4.23 (d, J = 25.6 Hz, 1H), 4.01 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.2, 158.5, 132.5, 131.6, 130.0, 128.9, 128.4, 126.2 (d), 113.1, 74.4, 72.3, 54.6, 49.1 (d); IR ($CHCl_3$): 3056, 2936, 1612, 1586, 1535, 1514, 1437, 1400, 1248 cm^{-1}.

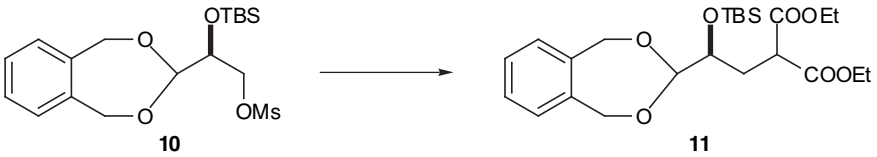
HRMS(EI). Calcd for $C_{29}H_{28}O_3P$ (M^++H): m/z 455.1776. Found: m/z 455.1776.



9 10

3-[(1*S*)-2-Methanesulfoxy-1-*tert*-butyldimethylsilanyoxyl]ethyl-1,5-dihydro-3H-2,4-benzodioxepine (10). Diol **9**[3] (12 g, 15.1 mmol) was dissolved in 35 mL of anh pyridine. The solution was then cooled to -20 °C and 6.87 g of neat CH_3SO_2Cl (60.0 mmol) was added dropwise over 5 min. The resulting suspension was vigorously stirred while warming to 0 °C for 2 h. While cooling at 0 °C, the reaction mixture was treated portionwise with 18.13 g of neat TBSOTf (68.6 mmol). Stirring was continued at 0 °C for an additional 2 h after the addition was complete. The reaction mixture was then diluted with 300 mL ether. The ether solution was washed successively with 50 mL portions of 1 M aq HCl solution until the aqueous phase was acidic then finally with 50 mL sat sodium bicarbonate solution. The ethereal layer was dried over magnesium sulfate and concentrated to give the mesylate **10** (19.76 g, 86%) as a white solid having mp 80-81 °C and $[\alpha]_D^{25}$ - 14.9 ($CHCl_3$, *c* 1.11): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.20 (m, 4H), 4.92 (s, 4H), 4.86 (d, J = 3.2 Hz, 1H), 4.42 (dd, J_1 = 10.3 Hz, J_2 = 2.6 Hz, 1H), 4.27 (dd, J_1 = 10.2 Hz, J_2 = 6.2 Hz, 1H), 4.00 (ddd, J_1 = 5.7 Hz, J_2 = 3.4 Hz, J_3 = 2.7 Hz, 1H), 3.02 (s, 3H), 0.96 (s, 9H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 138.7, 127.74, 127.71, 127.61, 127.56, 108.1, 73.2, 72.6, 71.8, 71.1, 37.0, 25.7, 18.1, -4.6, -4.9; IR ($CHCl_3$): 3054, 2956, 2856, 1462, 1360, 1265, 1177 cm^{-1}.

HRMS. Calcd for $C_{18}H_{31}O_6SSi$ (M^++H): *m/z* 403.1611. Found: *m/z* 403.1626.

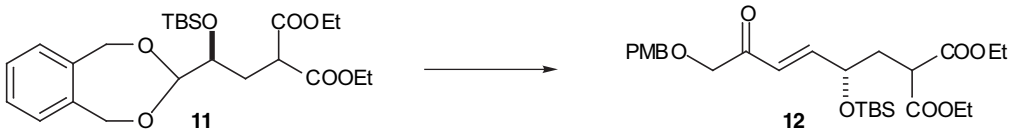


10 11

Diethyl 2-[(2*S*)-2-(*tert*-Butyldimethylsilyloxy)-2-(5,9-dihydro-6,8-dioxabenzocyclohepten-7-yl)-ethyl]-malonate (11). A flame dried l L round bottom flask fitted with a condenser was charged with 6.67 g of 60% NaH (0.167 mol) and 100 mL of dry N,N-dimethylformamide (DMF). Neat diethyl malonate (26 g, 0.164 mol) was then added slowly to the reaction mixture (a cold water bath may be needed to control the exothermic reaction which releases large amounts of hydrogen gas). After the addition was complete, a solution of mesylate **13** (22 g, 54.73 mmol) in 100 mL dry DMF was added in one portion. The homogeneous mixture was heated in a 155 °C oil bath for 40 h then cooled to room temperature. The entire reaction mixture was then transferred to a column containing 500 g of silica gel and eluted with10% EtOAc in hexanes to give 23.3 g of **11** (93%) as a colorless liquid having $[\alpha]_D^{25}$ = -2.4 ($CHCl_3$, *c* 0.615); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 - 7.16 (m, 4H), 4.96 - 4.92 (m, 4H), 4.68 (d, J = 5.6 Hz, 1H), 4.24 - 4.15 (m, 4H), 3.81 (m, 1H), 3.68 (dd, J_1 = 9.5 Hz, J_2 = 4.9 Hz, 1H), 2.38 - 2.31 (m, 1H), 2.10 - 2.04 (m, 1H), 1.31 - 1.25 (m, 6H), 0.91 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9,

169.4, 139.1, 127.5, 127.4, 110.1, 72.3, 70.9, 61.3, 47.8, 32.0, 25.9, 18.3, 14.0 –4.2, -5.0; IR ($CHCl_3$): 3155, 2984, 1728, 1372, 1257, 912, 734 cm^{-1}.

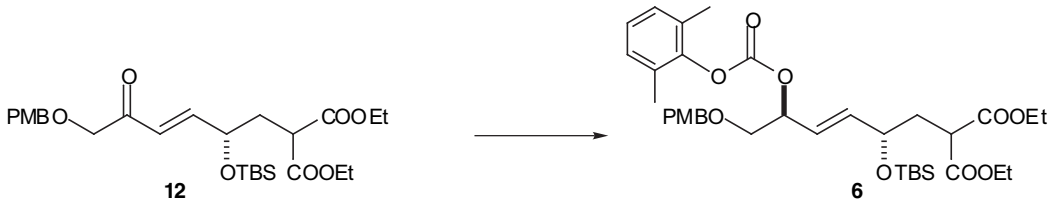
HRMS. Calcd for $C_{24}H_{39}O_7Si$ (M^++H): *m/z* 467.2465, Found *m/z* 467.2473.



Diethyl (2*S*)-2-[2-(*tert*-Butyldimethylsilyloxy)-6-(4-methoxyphenylmethoxy)-5-oxo-hex-3-enyl] malonate (12). Benzylidene acetal **11** (19 g, 40.77 mmol) was dissolved in 100 mL of EtOAc, 25 g of 5% Pd-C was added, and the resulting mixture hydrogenated under 50 psi of H_2 in a Parr apparatus for 2 days. The catalyst was removed by filtration through Celite, and the filtrate was concentrated to give the aldehyde **7** which was generally taken to the next operation without further purification. On small scale, the aldehyde **7** could be isolated in 95% yield.

The crude aldehyde **7**, prepared as above, was dissolved in 250 mL of $CHCl_3$ and treated with 24.12 g of ylide **8** (53.00 mmol). The resulting solution was heated at reflux for 7 h then cooled to room temperature. After concentration *in vacuo*, the residue was purified by chromatography on silica gel with elution by 20% ethyl acetate in hexanes to provide 19.2 g (90%) of enone **12** as a colorless liquid having $[\alpha]_D^{25}$ = -3.9 ($CHCl_3$, *c* 0.946): ^{1}H NMR (400MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.83 (dt, J_1 =16.0 Hz, J_2 = 4.8 Hz, 1H), 6.45 (dd, J_1 = 16.0 Hz, J_2 = 1.5 Hz, 1H), 4.52 (s, 2H), 4.41 (dt, J_1 = 5.1 Hz, J_2 = 4.8 Hz, 1H), 4.20-4.10 (m, 5H), 3.80 (s, 3H), 3.50 (m, 2H), 2.22-2.05 (m, 2H), 1.28-1.21 (m, 6H), 0.88 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 169.5, 159.4, 148.3, 129.6, 129.1, 124.7, 113.7, 73.8, 72.9, 69.4, 61.5, 55.2, 47.7, 35.6, 25.7, 17.2, 14.0, -4.6, -5.2; IR ($CHCl_3$): 2932, 1727, 1612, 1513, 1465, 1253, 911 cm^{-1}.

HRMS Calcd for $C_{27}H_{42}NaO_8Si$ (M^++ Na): *m/z* 545.2547. Found: *m/z* 545.2540.

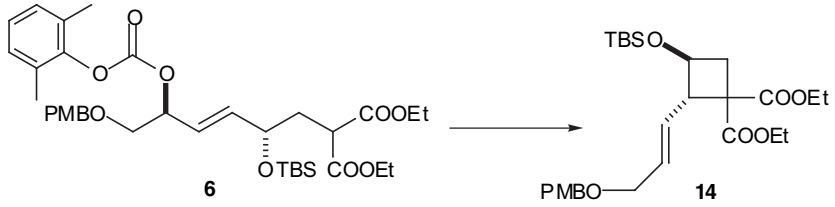


Diethyl (2*S*, 6*S*)-2-[2-(*tert*-Butyldimethylsilyloxy)-5-(2,6-dimethylphenoxycarbonyloxy)-6-(4-methoxyphenylmethoxy)-hex-3-enyl] malonate (6). A flame-dried 500 mL round bottom flask was charged with a solution of the CH_3-oxazaborolidine catalyst derived from (S)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (1.52g, 5.21 mmol), 80 mL anh dichloromethane and 3.91 mL of neat (10 M) BH_3•$S(CH_3)_2$ complex (39.1 mmol). After the catalyst solution had been cooled to -20 °C, a solution of

13.60 g of enone **12** (26.05 mmol) in 120 mL anh CH_2Cl_2 was added slowly dropwise via an additional funnel over 13 h, and the funnel was rinsed with 20 mL anh dichloromethane. After stirring the reaction mixture at -20 °C for an additional 30 min, 15 mL of methanol was added slowly. The solution was warmed to room temperature slowly and concentrated *in vacuo*. A second 15 mL portion of of methanol was then added and the mixture concentrated to give the crude alcohol **13** which was utilized without further purification. A small sample of alcohol **13** was isolated and converted to the corresponding Mosher ester whose de was shown to be greater than 98% by ^{1}H NMR analysis.

Crude alcohol **13**, prepared as described above, was dissolved in 100 mL of anh THF. A catalytic amount of DMAP (10 mg) and 6.17 g of pyridine (17.15 mmol) were then added followed by 9.59 g of 2,6-dimethylphenyl chloroformate (52.10 mmol). The resulting heavy white precipitate was stirred at room temperature for 2 h then diluted with 300 mL of diethyl ether. The mixture was washed with 100 mL of 1 M aq HCl solution, dried over anh $MgSO_4$, concentrated *in vacuo* to afford the crude carbonate **6**. Purification of crude **6** by chromatography on silica gel with eluting by 10% EtOAc in hexanes providing 14.53 g of carbonate **6** (83% over two steps) as a colorless liquid having $[\alpha]_D^{25}$ = +10.4 ($CHCl_3$, *c* 0.747); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.07 (s, 3H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.87 (dd, J_1 = 5.2 Hz, J_2 = 0.6 Hz, 1H), 5.76 (dd, J_1 = 6.5 Hz, J_2 = 0.7 Hz, 1H), 5.45 (m, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J*= 11.6 Hz, 1H), 4.27-4.16 (m, 5H), 3.83 (s, 3H), 3.65 - 3.53 (m, 3H), 2.21 (s, 6H), 2.13 - 2.07 (m, 2H), 1.27 (m, 6H), 0.91 (s, 9H) 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 159.2, 152.3, 148.3, 137.3, 130.2, 129.8, 129.2, 128.6, 126.0, 124.6, 113.7, 76.7, 72.8, 70.8, 70.1, 61.4, 61.3, 55.2, 47.7, 36.5, 25.7, 18.1, 16.0, 14.0, -4.3, -5.2; IR ($CHCl_3$): 2957, 1749, 1728, 1613, 1513, 1371, 1256, 1181, 910 cm^{-1}.

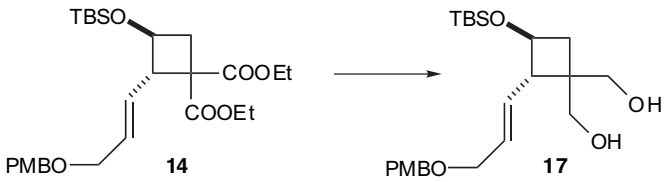
HRMS. Calcd for $C_{36}H_{52}NaO_{10}Si$ (M^++ Na): *m/z* 695.3227. Found: *m/z* 695.3204.



Diethyl (2*S*, 3*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-[3-(4-methoxyphenylmethoxy)-propenyl]-cyclobutane-1,1-dicarboxylate (14). A solution of 2.90 g of carbonate **6** (4.32 mmol) in 30 mL freshly distilled toluene was cautiously treated with 0.518 g of 60% NaH (12.95 mmol). The resulting suspension was heated at 120 °C in an oil bath for 0.5 h then cooled to 0 °C in an ice bath. The reaction mixture was then quenched with 0.2 mL of water and the entire mixture directly transferred to a column of 150 g of silica gel and eluted with a 3-step gradient of 0 - 10% EtOAc in hexanes which provided 1.49 g (75%) of the cyclobutane diethyl ester **14** as a colorless liquid having $[\alpha]_D^{25}$ = -19.4 ($CHCl_3$, *c* 1.24): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.79 (dt, J_1 = 15.5 Hz, J_2 = 5.3 Hz, 1H), 5.68 (dd, *J* = 15.6 Hz, J_2 = 7.3 Hz, 1H), 4.41 (s, 2H), 4.32-4.15 (m, 5H), 3.99 (d, *J* = 5.4 Hz, 2H),

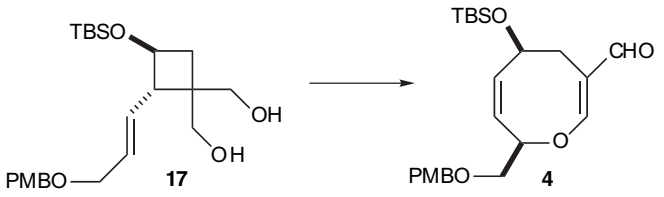
3.85 (s, 3H), 3.43 (t, J = 7.5 Hz, 1H), 2.87 (dd, J_1 = 11.4 Hz, J_2 = 7.4 Hz, 1H), 2.10 (dd, J_1 = 11.4Hz, J_2 = 7.7 Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H), 0.88 (s, 9H) 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 170.2, 159.1, 131.4, 130.5, 130.0, 129.3, 113.7, 71.8, 71.2, 69.8, 61.3, 61.2, 55.2, 54.1, 50.9, 38.3, 25.7, 17.9, 14.0, -4.6, -4.8; IR ($CHCl_3$): 2974,1729, 1613, 1513, 1252, 1181, 1115, 1080 cm^{-1}.

HRMS. Calcd for $C_{27}H_{42}NaO_7Si$ (M^++ Na): m/z 529.2598. Found: m/z 529.2625.



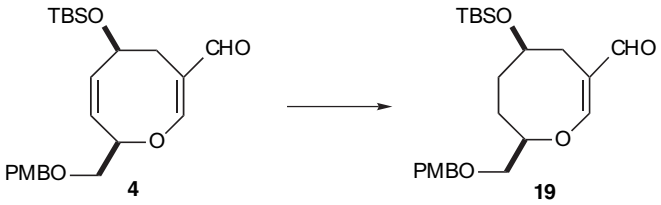
(2*S*, 3*S*)-{3-(*tert*-Butyldimethylsilyloxy)-1-hydroxymethyl-2-[3-(4-methoxyphenylmethoxy)-propenyl]-cyclobutyl}-methanol (17). A flame dried 250 mL round bottom flask was charged with a solution of 5.06 g of diester **14** (10 mmol) in 100 mL freshly distilled anh THF. The solution was cooled to 0 °C and 0.76 g of solid lithium aluminum hydride (LAH) (20 mmol) was added portionwise slowly. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stir for 2 h. The reaction mixture was then recooled to 0 °C and quenched with minimum amount of water which resulted in a white precipitate of hydrated aluminum oxide. The resulting suspension was filtered through a celite pad and the pad was washed thoroughly with ethyl acetate until no diol could be detected in the filtrate by TLC analysis (generally 8 washes with 75 mL of ethyl acetate was sufficient.). The combined filtrate was concentrated and the residue dried azotropically by two cycles of dissolution in 150 mL of toluene and concentration *in vacuo*. Purification of the residue via silica gel chromatography with elution by 50% EtOAc in hexanes provided 3.90 g (92%) of the diol **20** having $[\alpha]_D^{25}$ = + 28.7 ($CHCl_3$, c 0.703): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.75 (dd, J_1 = 15.6 Hz, J_2 = 7.7 Hz, 1H), 5.66 (dt, J_1 = 15.7 Hz, J_2 = 5.7 Hz, 1H), 4.42 (s, 2H), 4.13 (dd, J_1 = 7.4 Hz, J_1 = 7.4 Hz, 1H), 3.97 (d, J = 5.7 Hz, 2H), 3.79 (s, 3H), 3.73-3.59 (m, 4H), 3.23 (s(br), 2H), 2.62 (t, J = 7.4 Hz, 1H), 2.13 (dd, J_1 = 9.4 Hz, J_2 = 7.6 Hz, 1H), 1.60 (dd, J_1 = 11.5 Hz, J_2 = 7.6 Hz,1H), 0.86 (s, 9H), 0.03(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 131.3, 130.1, 129.3, 128.1, 113.7, 71.5, 70.9, 70.1, 67.8, 66.0, 55.1, 52.9, 40.2, 35.8, 25.7, 17.9, -4.6, -4.7; IR ($CHCl_3$): 3416, 3053, 2985, 2956, 1514, 1464, 1265, 1095, 1035, 909 cm^{-1}.

HRMS. Calcd for $C_{23}H_{38}NaO_5Si$ (M^++ Na): m/z 445.2386. Found: m/z 445.2371.

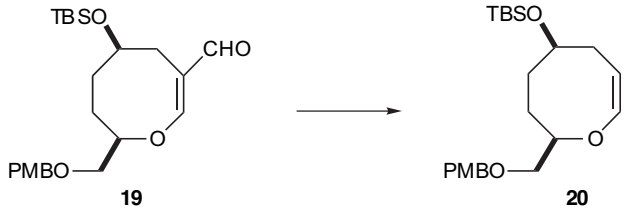


(5*S*, 8*R*)-5-(*tert*-Butyldimethylsilyloxy)-8-(4-methoxyphenylmethoxymethyl)-5,8-dihydro-4H-oxocine-3-carbaldehyde (4). A 100 mL round bottom flask was charged with Dess-Martin periodinane (1.70 g, 4 mmol), polyvinyl pyridine (1.05 g, 10 mmol) and 15 mL of anh dichloromethane. The resulting suspension was stirred for 10 min at room temperature. A solution of 0.422 g of diol **17** (1 mmol) in 15 mL anh dichloromethane was then added and the mixture stirred at room temperature for 1 h.. The reaction mixture was then diluted with 30 mL of pentane and the resulting precipitate was removed by filtration. The collected solids were washed twice with 20 mL of pentane/dichloromethane (2:1 v/v). The combined filtrates were washed with a saturated aqueous solution of 4.70 g $NaHCO_3$ (56 mmol) and 6.94 g of $Na_2S_2O_3$ (28 mmol). The organic phase was then dried over $MgSO_4$ and concentrated. Purification by silica gel chromatography with elution by 20% EtOAc in hexane afforded 0.375 g (90%) of principally dialdehyde **18** as a pale yellow oil. Analysis by ^{1}H NMR revealed that the product was a mixture of dialdehyde **18** (95%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.99 (s,1H), 9.93 (s, 1H), 7.24 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 5.73 (dt, J_1 = 15.7 Hz, J_2 = 5.2 Hz, 1H), 5.63 (dd, J_1 = 15.7 Hz, J_2 = 8.1 Hz, 1H), 4.40 (s, 2H), 4.37 (dt, J_1 = 7.6, Hz, J_2 = 7.4 Hz, 1H), 3.95 (d, J = 5.4 Hz, 2H), 3.81 (s, 3H), 3.28 (t, J = 7.6 Hz, 1H), 2.65 (dd, J_1 = 11.5 Hz, J_2= 7.3 Hz, 1H), 2.18 (dd, J_1 = 9.6 Hz, J_2 = 6.8 Hz, 1H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), and dihydrooxocene **4** (5%).

The above sample of dialdehyde **18** (0.395 g, 0.90 mmol) was dissolved in 25 mL $CHCl_3$ and heated at reflux (in an 80 °C oil bath) for 4 h and then at 45 °C for 12 h. The solution was concentrated and the residue purified by chromatography on silica gel with elution by 20% EtOAc in hexanes to give 0.30 g of dihydrooxocene **4** (77%) and 0.075 g of recovered dialdehyde **18** (19%). The recovered dialdehyde **18** was resubjected to the equilibrating condition affording a total of 0.365 g (92%) of the thermally sensitive dihydrooxocene **4** after recycling having $[\alpha]_D^{25}$ = - 42.4 ($CHCl_3$, *c* 0.8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.25 (s,1H), 7.29 (d, J = 8.8 Hz, 2H), 7.02 (s,1H), 6.92 (d, J = 8.5 Hz, 2H), 5.95 (dt, J_1 = 11.8 Hz, J_2 =1.1 Hz, 1H), 5.52 (m, 1H), 5.41 (m, 1H), 4.73 (s(br),1H), 4.62 (d, J = 11.7 Hz, 1H), 4.52 (d, J = 11.7 Hz, 1H), 3.83 (s, 3H), 3.66 (m, 2H), 3.13 (d, J = 15.5 Hz, 1H), 2.73 (d, J = 15.3 Hz, 1H), 0.89 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 166.1, 159.5, 141.7, 129.5, 121.6, 118.3, 113.9, 73.6, 73.4, 71.8, 71.7, 55.3, 28.4, 25.9, 18.3, -4.8, -5.2; IR ($CHCl_3$): 2954, 1681, 1617, 1513, 1463, 1251, 1230, 908, 733 cm^{-1}; LRMS: *m/z* 418.6 (M^++ Na).



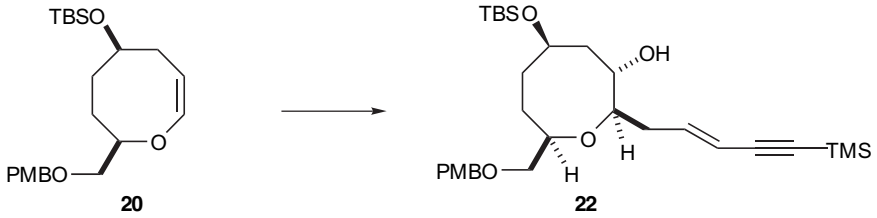
(5*S*, 8*R*)-5-(*tert*-Butyldimethylsilyloxy)-8-(4-methoxyphenylmethoxymethyl)-5,6,7,8-tetrahydro-4H-oxocine-3-carbaldehyde (19). The dihydrooxocene **4** (3.94 g, 9.43 mmol) was dissolved in 50 mL anh toluene in a 500 mL Parr flask. A 0.436 g sample (0.47 mmol, 5 mol%) of Wilkinson's catalyst ($Rh(PPh_3)_3Cl$) was added. The resulting solution was shaken under 45 psi of H_2 in a Parr apparatus for 30 h. The resulting solution was directly transferred to a column of 200 g of silica gel with elution sequentially by 100% hexane (to remove toluene) and 25% EtOAc in hexanes to afford 3.56 g of aldehyde **19** (91%) as a pale yellow oil having $[\alpha]_D^{25}$ = +25.3 ($CHCl_3$, *c* 1.185): ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.18 (s,1H), 6.88 (d, *J* = 8.5 Hz, 2H), 4.82(m, 1H), 4.51 (dt, J_1 = 10.6 Hz, J_2 = 6.7 Hz, 2H), 4.10 (m, 1H), 3.79 (s, 3H), 3.51 (dd, J_1 = 10.5 Hz, J_2 = 6.7 Hz, 1H), 3.44 (dd, J_1 = 10.5 Hz, J_2 = 3.2 Hz, 1H), 3.03 (dd, J_1 = 15.5 Hz, J_2 = 2.2 Hz, 1H), 2.50 (dd, J_1 = 15.4 Hz, J_2 = 1.9 Hz, 1H), 1.78-1.63 (m, 4H), 0.84 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 168.6, 159.2, 129.2, 129.1, 117.2, 113.7, 77.8, 73.0, 72.5, 71.4, 55.1, 30.2, 28.8, 27.2, 25.6, 17.9, -5.0, -5.1; IR ($CHCl_3$): 2954, 2930, 2857, 1675, 1613, 1514, 1463, 1353, 1240, 1106, 1076, 908 cm^{-1}; LRMS: *m*/*z* 420.1 (M^++ Na).



(2*R*, 5*S*)-2-(4-Methoxyphenylmethoxymethyl)-5-*tert*-butyldimethylsilyloxy-3,4,5,6-tetrahydro-2H-oxocine (20). A flame-dried 500 mL round bottom flask equipped with a reflux condenser capped by a rubber septum was charged with $[Rh(COD)Cl]_2$ (58.32 mg, 0.118 mmol, 2mol%) and 1,3-bis-(diphenylphosphino)-propane (0.212 g, 0.514 mmol, 8.69 mol%) in a glovebox. The flask was transferred to a hood, placed under an Ar atmosphere, and xylene (40 mL, dried over 4Å MS and deoxygenated by purging with Ar) was added via syringe through the rubber septum of the reflux condenser. The resulting solution was heated in 90-100 °C oil bath for 1 h during which time a bright yellow precipitate was formed. A solution of aldehyde **19** (2.49 g, 5.92 mmol) in 300 mL xylene (dried and deoxygenated as above) was then added via syringe through the rubber septum of the reflux condenser. The solution was brought to reflux in a 170 °C oil bath and heated for 96 h. The reaction mixture was then cooled to room temperature and most of the xylene was distilled off at atmosphere pressure under Ar. The residual liquid was purified

by chromatography on silica gel with elution sequentially by 100% hexane (to remove residual xylenes) and 10% EtOAc in hexanes to afford 2.08 g of vinyl ether **20** (90%) as a colorless oil having $[\alpha]_D^{25}$ = +29.1 ($CHCl_3$, *c* 0.635): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.15 (d, *J* = 6.1 Hz, 1H), 4.93 (dt, *J* = 7.0 Hz, 1H), 4.51 (dt, *J* = 11.7 Hz, 2H), 4.12 (m, 1H), 4.00 (m, 1H), 3.82 (s, 3H), 3.55 (dd, J_1 = 10.0 Hz, J_2 = 6.9 Hz, 1H), 3.40 (dd, J_1 = 10.0 Hz, J_2 = 4.7 Hz, 1H), 2.41-2.26 (m, 2H), 1.83-1.77 (m, 3H), 1.64-1.59 (m, 1H), 0.91 (s, 9H), 0.08 (m, 3H), 0.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.9, 130.2, 129.3, 113.7, 112.3, 78.4, 72.9, 71.83, 71.79, 55.2, 33.4, 33.2, 25.8, 25.2, 18.1, -4.8; IR ($CHCl_3$): 3154, 2954, 2931, 1613, 1513, 1472, 1250, 1093, 912 cm^{-1}.

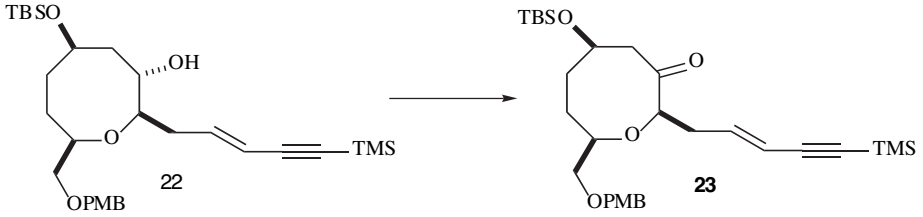
HRMS. Calcd for $C_{22}H_{37}O_4Si$ (M^++ H): *m/z* 393.2461. Found: *m/z* 393.2447.



(2*R*, 3*S*, 5*S*, 8*R*)-5-(*tert*-Butyldimethylsilyloxy)-8-(4-methoxyphenylmethoxymethyl)-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-oxocan-3-ol (22). A solution of 0.784 g of vinyl ether **20** (2 mmol) in 20 mL dry CH_2Cl_2 was cooled to -78 °C and a solution of dimethyldioxirane in acetone precooled to -78 °C was added dropwise until starting material was consumed based upon TLC analysis. The resulting mixture was then concentrated at 0 °C *in vacuo*. The flask was then attached to a high vacuum pump and dry benzene (20 mL) was added at 0 °C and concentrated using the high vacuum pump. This process was repeated once more and the residue was dissolved in 20 mL of anh THF and cooled to -78 °C. A solution of the hydrazone anion was prepared *in situ* by treatment of 1.72 g of acetaldehyde N,N-dimethylhydrazone (20 mmol) in 25 mL THF with 10 mL of a 2 M solution of LDA in THF dropwise at -78 °C, warmed to 0 °C and stirred at that temperature for 2 h, then recooled to -78 °C. This -78 °C solution of the hydrazone anion was added to the -78 °C solution of the epoxide prepared above dropwise via cannula. After the addition was complete, the solution was warmed to -25 °C over 2 h. Analysis by TLC showed complete consumption of the epoxide. The reaction mixture was quenched with 50 mL sat aq NH_4Cl solution. The phases were separated and the aqueous phase was extracted three times with 100 mL portions of ether. The combined organic phases were dried over $MgSO_4$, concentrated, and the residual acetaldehyde N,N-dimethylhydrazone removed under high vacuum. The residue was redissolved in 20 mL of 1:1 THF-water buffered to pH = 4.5 with a little acetic acid-sodium acetate and 0.422 g of periodic acid (2.2 mmol) was added. The resulting solution was stirred at room temperature for 3 h then quenched with 5 mL of sat sodium bicarbonate solution. The reaction mixture was then extracted with three times with 30 ml of ether. The combined organic phases were dried over $MgSO_4$ and concentrated to afford 0.82 g the crude hemiacetal **21** (91%) which was utilized in the next step without further purification.

A flame-dried 100 mL round bottom flask was charged with 2.47 g (5.44 mmol) of 1-trimethylsilyl-1-propyn-3-yltriphenylphosphonium bromide and 25 mL of anh THF. The suspension was cooled to -78 °C and 2.60 mL of *n*-BuLi (2 M in hexanes, 5.2 mmol) was added dropwise to generate a deep red solution of the ylide. The solution was allowed to stir at -40 °C for 30 min before recooling to -78 °C. A solution of 0.82 g of hemiacetal **21** (1.814 mmol) in 20 mL dry THF was then added dropwise over 5 min. After the addition was complete, the reaction mixture was stirred at 0 °C for 4 h then treated with 0.20 mL of methanol. The reaction mixture was stirred was for an additional 1 h at 0 °C then quenched with 30 mL sat aq NH_4Cl solution and the mixture extracted three times with 50 mL portions of ether. The combined organic phases was dried over $MgSO_4$ and concentrated *in vacuo*. Analysis of this crude material by ^1H NMR showed the E / Z selectivity to be > 15:1. The crude material was purified by chromatography on silica gel eluting with 20% EtOAc in hexanes to provide 0.85 g of alcohol **22** (78%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.37 (dt, J_1 = 16.0 Hz, J_2 = 7.4 Hz, 1H), 5.61 (d, J = 16.0 Hz, 1H), 4.52 (d, J = 11.6 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.03 (m, 1H), 3.81 (s, 3H), 3.70 (m, 2H), 3.40 (dd, J_1 = 9.9 Hz, J_2 = 6.3 Hz, 1H), 3.32 (dd, J_1 = 9.9 Hz, J_2 = 5.1 Hz, 1H), 3.27 (ddd, J_1 = 8.7 Hz, J_2 = 5.3 Hz, J_3 = 3.2 Hz, 1H), 2.54 (m, 1H), 2.25 (m, 1H), 2.14 (dd, J_1 = 14.8 Hz, J_2 = 8.4 Hz, 1H), 2.00-1.83 (m, 3H), 1.76-1.70 (m, 1H), 1.62 (m, 2H), 0.88 (s, 9H), 0.16 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 142.5, 130.5, 129.3, 113.7, 111.8, 104.1, 93.0, 81.7, 79.8, 73.4, 73.0, 71.9, 68.0, 55.2, 41.7, 38.6, 32.7, 25.8, 25.6, 18.1, 0.0, -4.71, -4.73; IR ($CHCl_3$): 3621, 2956, 1612, 1586, 1513, 1464, 1361, 1250, 1083, 912, 738 cm^{-1}.

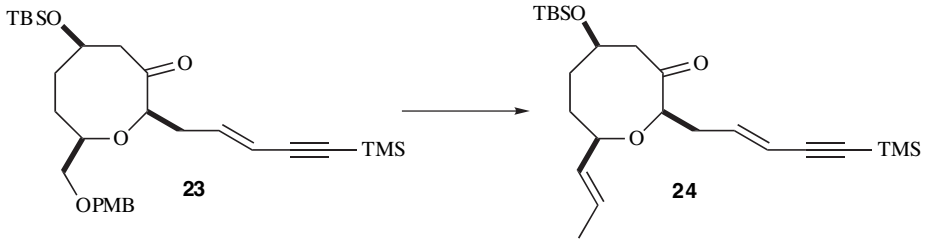
HRMS. Calcd for $C_{30}H_{51}O_5Si_2$ (M^++H): *m/z* 547.3275. Found: *m/z* 547.3272.



(2*R*, 5*S*, 8*R*)-5-(*tert*-Butyldimethylsilyloxy)-8-(4-methoxyphenylmethoxymethyl)-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-oxocan-3-one (23). To a solution of 0.60 g of alcohol **22** (1.097 mmol) in 40 mL dichloromethane was added 0.26 g of pyridine (3.291 mmol) followed by 0.93 g of Dess-Martin periodinane (2.194 mmol). The resulting solution was stirred at room temperature for 2 h then 5 g silica gel was added, the volatiles removed *in vacuo*. After the solid residue was transferred to a column, elution with 10% EtOAc in hexanes provided 0.54 g of ketone **26** (90%) as a colorless oil having $[\alpha]_D^{25}$ = + 49.7 ($CHCl_3$, *c* 0.507): ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.16 (dt, J_1 = 15.9 Hz, J_2 = 7.7 Hz , 1H), 5.55 (d, J = 15.9 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 4.52 (d, J = 11.6 Hz, 1H), 3.83 (m, 1H), 3.79 (s, 3H), 3.61-3.53 (m, 3H), 3.42 (dd, J_1 = 8.7 Hz, J_2 = 5.5 Hz, 1H), 3.25 (t, J = 10 Hz, 1H), 2.35 (dd, J_1 = 15.4 Hz, J_2 = 7.4 Hz, 2H), 2.25 (dd, J_1 = 9.5 Hz, J_2 = 4.4 Hz, 1H), 1.84 -1.70 (m, 2H), 1.64 -1.57 (m, 1H), 1.36 -1.30 (m, 1H), 0.88 (s, 9H), 0.17 (s, 9H), 0.07 (s, 3H), 0.06 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.4, 159.2, 139.4, 130.2, 129.22, 113.8, 112.8, 103.3, 93.8, 85.3, 80.6, 73.0, 72.2, 71.1, 55.1, 46.4, 36.5, 31.8, 25.7, 23.8, 18.0, -0.1, -4.87, -4.92; IR ($CHCl_3$) 2955, 2134, 1712, 1613, 1514, 1463, 1376, 1302, 1250, 1086, 842 cm^{-1}.

HRMS. Calcd for $C_{30}H_{49}O_5Si_2$ (M^++H): *m/z* 545.3119. Found: *m/z* 545.3097.



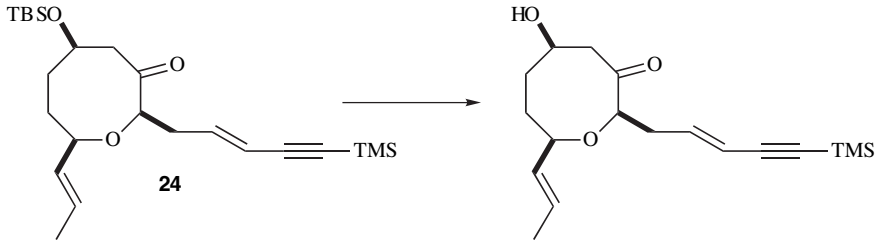
(2*R*, 5*S*, 8*R*)-5-(*tert*-Butyldimethylsilyloxy)-8-[(1*E*)-1-propenyl]-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl)-oxocan-3-one (24). A solution of 0.53 g of PMB ether **23** (0.973 mmol) in 35 mL dichloromethane / water (20:1) was treated with 0.331 g of solid DDQ (1.458 mmol). The resulting solution was stirred at room temperature for 2 h until TLC analysis (20% EtOAc/hexanes) showed no starting material. Silica gel (5 g) was added and the solvents evaporated. The solids were transferred to a column (dry column packing) and eluted sequentially with 10% EtOAc in hexanes and 25% EtOAc in hexanes afforded the expected alcohol which was not characterized further but directly utilized in the next transformation.

The above sample of alcohol was dissolved in 30 mL dichloromethane and pyridine (0.46 g, 5.835 mmol) and Dess-Martin periodinane (0.827 g, 1.945 mmol) were added sequentially. The resulting suspension was stirred at room temperature for 2 h. Silica gel (4 g) was added and the volatiles removed *in vacuo*. The solids were transferred to a column and eluted with 10% ethyl acetate in hexanes affording the expected aldehyde intermediate which was not characterized further but directly utilized in the next transformation.

A flame-dried 50 mL round bottom flask was charged with 1.106 g of $CrCl_2$ (9 mmol) in a glove box and sealed with a septum. The flask was transferred to a hood and placed under an Ar atmosphere. A solution of the above sample of aldehyde and 0.761 g of 1,1- diiodoethane (2.7 mmol) in 20 mL of anh THF was added. The resulting solution was stirred at room temperature for about 4 h until no starting material was left as determined by TLC analysis (20% EtOAc/hexanes). The reaction was quenched with 10 mL sat NH_4Cl solution and the mixture extracted three times with 30 mL portions of ether. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. Purification via silica gel chromatography with elution by 10% EtOAc in hexanes provided 0.29 g of ketone **24** (70 % yield over three steps) as a colorless oil having $[\alpha]_D^{25}$ = + 73.3 ($CHCl_3$, *c* 0.409): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.19 (dt, J_1 =15.9 Hz, J_2 =7.3 Hz, 1H), 5.81-5.74 (m, 1H), 5.58 (d, *J*=15.9 Hz, 1H), 5.50 (ddd, J_1 = 5.5 Hz, J_2 = 4.7 Hz, J_3 = 1.5 Hz, 1H), 3.99 (s(br), 1H), 3.80 (m, 1H), 3.56 (dd, J_1 = 8.0 Hz, J_2 = 5.1 Hz, 1H), 3.28 (t, *J* = 10.0 Hz, 1H), 2.45-2.31 (m, 2H), 2.28 (dd, J_1 = 9.4 Hz, J_2 = 3.9 Hz, 1H), 1.82 (m, 1H), 1.75 (d, *J* = 6.4 Hz, 3H), 1.65 (d, *J* = 8.4 Hz, 2H), 1.27 (m, 1H), 0.90 (s, 9H), 0.19 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H);

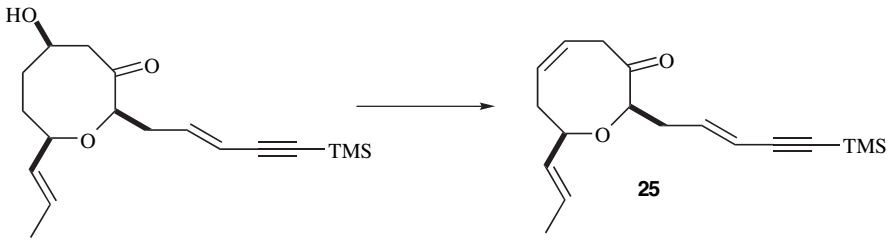
^{13}C NMR (100 MHz, $CDCl_3$): δ 214.8, 139.5, 130.6, 126.9, 112.8, 103.3, 93.9, 84.5, 80.5, 73.0, 47.1, 36.6, 31.4, 27.0, 25.7, 18.0, 17.9, -0.1, -4.9; IR ($CHCl_3$): 2955, 2931, 2857, 2149, 1710, 1461, 1376, 1250, 1082, 1006, 966, 841, 776 cm^{-1}.

HRMS. Calcd for $C_{24}H_{43}O_3Si_2$ (M^++H): *m/z* 435.2751. Found: *m/z* 435.2757.



(2*R*, 5*S*, 8*R*)-5-Hydroxy-8-[(1*E*)1-propenyl]-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-oxocan-3-one. A solution of 0.29 g of the silyl ether **24** (0.668 mmol) in 40 mL acetonitrile was cooled to 0 °C and 1 mL of 48% HF was added. The mixture was stirred for about 3 h until no starting material was left as determined by TLC analysis (20% EtOAc / hexanes). Silica gel (4 g) was then added and the volatiles were removed *in vacuo*. After transfer of the solids to a column, elution by 20% ethyl acetate in hexanes afforded 0.205 g of the title alcohol (97%) as a colorless oil having $[\alpha]_D^{25}$ = + 97.0 ($CHCl_3$, *c* 0.395): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (dt, J_1 =16.0 Hz, J_2 = 8.4 Hz, 1H), 5.76 (m, 1H), 5.57 (d, *J* =16.0 Hz, 1H), 5.51 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 4.02(s(br), 1H), 3.84 (m, 1H), 3.59 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 3.22(t, *J* = 10.1 Hz, 1H), 2.40 (m, 3H), 2.23 (s(br), 1H), 1.81 (dd, J_1 = 10.9 Hz, J_2 = 6.7 Hz, 2H), 1.75 (d, *J* = 6.5 Hz, 3H), 1.69 (d, *J* = 6.4 Hz, 1H), 1.45 (m, 1H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.3, 139.2, 130.2, 127.3, 113.0, 103.2, 94.0, 84.3, 80.2, 72.0, 47.1, 36.5, 30.6, 27.0, 17.9, -0.1; IR ($CHCl_3$): 3608, 3154, 2961, 2253, 2133, 1794, 1708, 1451, 1380, 1302, 1250, 1091, 908 cm^{-1}.

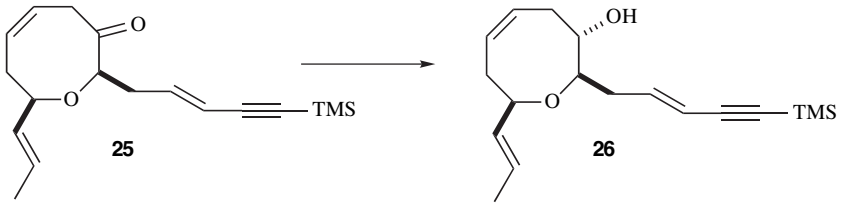
HRMS. Calcd for $C_{18}H_{29}O_3Si$ (M^++H): *m/z* 321.1886. Found: *m/z* 321.1891.



(2*R*, 8*R*)-8-[(1*E*)-1-Propenyl]-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-7,8-dihydro-4H-oxocin-3-one (25). A solution of 0.190 g of (2*R*, 5*S*, 8*R*)-5-hydroxy-8-[(1*E*)1-propenyl]-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-oxocan-3-one (0.594 mmol) in 25 mL anh dichloromethane was treated successively with 0.18 g NEt_3 (1.78 mmol) and 68 mg of MsCl (1.19 mmol). The resulting solution was stirred at room temperature for 2 h, then 0.18 g of DBU (1.19 mmol) was added. The reaction mixture was

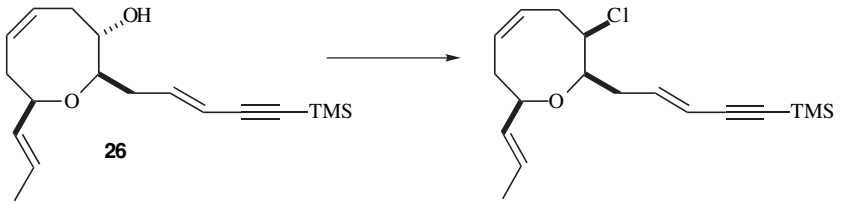
stirred for a further 6 h at room temperature. Silica gel (3 g) was then added and the volatiles removed *in vacuo*. After transfer of the solid residue to a column, elution with 10% EtOAc in hexanes afforded 0.153 g of enone **25** (85%) as a colorless liquid having $[\alpha]_D^{25}$ = + 304.0 ($CHCl_3$, *c* 0.444): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (dt, J_1 =16.0 Hz, J_2 = 7.4 Hz, 1H), 5.83 (dd,J_1 =16.0 Hz, J_2 = 8.5 Hz, 1H), 5.73 (ddd, J_1 =14.8 Hz, J_2 = 13.1 Hz, J_3 = 6.5 Hz, 1H), 5.65 (m, 1H), 5.56 (d, *J* =16.0 Hz, 1H), 5.55 (m, 1H), 3.98 (dd, J_1 = 7.3 Hz, J_2 = 4.0 Hz, 1H), 3.91(dt, J_1 = 4.9 Hz, J_2 = 3.0 Hz, 1H), 2.80 (dd, J_1 = 12.5 Hz, J_2 = 6.6 Hz, 1H), 2.49 (m, 1H), 2.04-2.42 (m, 4H), 1.72 (d, *J* = 6.5 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.4, 140.7, 131.2, 128.8, 127.1, 125.9, 112.7, 103.6, 93.4, 84.3, 84.1, 41.4, 36.1, 33.8, 17.8, -0.1; IR ($CHCl_3$): 3026, 2959, 2134, 1720, 1643, 1547, 1512, 1439, 1390, 1250, 1106, 959, 913 cm^{-1}.

HRMS. Calcd for $C_{18}H_{27}O_2Si$ (M^++H): *m/z* 303.1780. Found: *m/z* 303.1772.



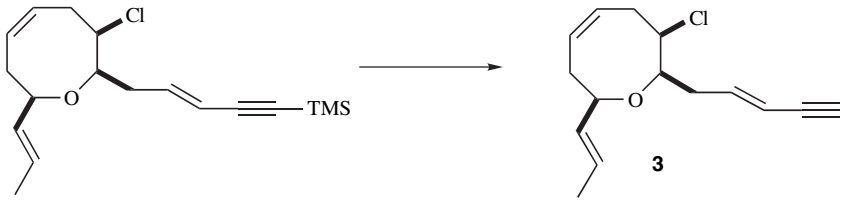
(2*R*, 3*S*, 8*R*)-8-[(1*E*)-1-Propenyl]-2-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-3,4,7,8-tetrahydro-2H-oxocin-3-ol (26). A flame-dried 10 mL flask was charged with a solution of the *n*-Bu-oxazaborolidine catalyst derived from (*R*)-(+)-α,α-diphenyl-2-pyrrolidinemethanol (4.77 mg, 0.015 mmol) and catecholborane (10.80 mg, 0.09 mmol) in 1 mL dry toluene. The catalyst solution was then cooled to –20 °C, and a solution of 9 mg of ketone **25** (0.03 mmol) in 5 mL anh toluene was added over 4 h via a syringe pump. After the addition was complete, the reaction mixture was stirred at –20 °C for 5 h. then quenched with 1 mL methanol and concentrated. ^{1}H NMR analysis of the crude product revealed an α/β ratio of 5:1 at the newly formed carbinol center. Separation of the crude mixture via silica gel chromatography with elution by 20% EtOAc in hexanes provided 7 mg of the α alcohol **26** (78%) as a colorless oil having $[\alpha]_D^{25}$ = - 20.6 ($CHCl_3$, *c* 0.253): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.26 (dt, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 1H), 5.93 (m, 1H), 5.83 (m,1H), 5.70 (m, 1H), 5.58 (d, *J* = 16.0 Hz, 1H), 5.50 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 1H), 3.80 (t, *J* = 8.1 Hz, 1H), 3.72 (m,1H), 3.35 (ddd, J_1 = 9.0, J_2 = 9.0 Hz, J_3 = 3.0 Hz, 1H), 2.85 (ddd, J_1 = 10.6 Hz, J_2 = 9.4 Hz, J_3 = 2.4 Hz, 1H), 2.53 (m, 1H), 2.36 (m, 1H), 2.03-2.24 (m, 3H), 1.71 (d, *J* = 6.5 Hz, 3H), 1.40 (s(br), 1H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 131.9, 130.0, 128.0, 126.8, 112.2, 104.0, 82.3, 81.8, 75.5, 37.4, 34.4, 32.5, 29.6, 17.9, 0.0; IR ($CHCl_3$): 3440, 2930, 1580, 1458, 1302, 1249, 1099 cm^{-1}.

HRMS. Calcd for $C_{18}H_{29}O_2Si$ (M^++H): *m/z* 305.1937. Found: *m/z* 305.1922.



(2*R*, 3*R*, 8*R*)-7-Chloro-2-[(1*E*)-1-propenyl]-8-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-3,4,7,8-tetrahydro-2H-oxocine. To a solution of 6 mg of α alcohol **26** (0.02 mmol) in 2 mL dry toluene was added 74 mg of trioctylphosphine (0.2 mmol), 30.8 mg of CCl_4 (0.2 mmol) and 45.5 mg of triethylbenzyl ammonium chloride (0.2 mmol). The solution was stirred at room temperature for 5 min then heated in a 70 °C oil bath for 6 h. The solution was cooled to room temperature and silica gel (2 g) was added. The volatiles were removed *in vacuo*. After transfer of the residue to a column, elution by 10% EtOAc in hexanes provided the crude products. Analysis by ^{1}H NMR revealed the mixture was comprised of 67% of the desired β chloride and 33% a diene resulting from elimination with traces of the epimeric α chloride. Separation of the mixture by preparative TLC with elution by 3% ether in hexane provided 3.8 mg of **26** (60%), and 1.8 mg of the diene. (2*R*, 3*R*, 8*R*)-7-Chloro-2-[(1*E*)-1-propenyl]-8-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-3,4,7,8-tetrahydro-2H-oxocine was obtained as a colorless oil having $[\alpha]_D^{25}$ = + 15.2 ($CHCl_3$, *c* 0.355): ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.14 (dt, J_1 = 16.0 Hz, J_2 = 7.5 Hz, 1H), 5.93 (m, 1H), 5.75-5.66 (m, 2H), 5.61 (d, J = 16 Hz, 1H), 5.53 (ddd, J_1 = 15.3 Hz, J_2 = 8.0 Hz, J_3 = 1.5 Hz, 1H), 3.96 (ddd, J_1 = 11.4 Hz, J_2 = 4.8 Hz, J_3 =1.6 Hz, 1H), 3.83 (ddd, J_1 = 7.9 Hz, J_2 = 5.2 Hz, J_3 = 2.3 Hz, 1H), 3.76 (dd, J_1 = 11.0 Hz, J_2 = 9.5 Hz, 1H), 2.98 (dt, J_1 =12.0 Hz, J_2 = 12.0 Hz, 1H), 2.56-2.45 (m, 3H), 2.27 (m, 1H), 2.16 (ddd, J_1 = 14.1 Hz, J_2 = 8.5 Hz, J_3 = 1.1 Hz, 1H), 1.70 (d, J = 6.2 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 131.8, 131.2, 128.5, 126.9, 112.7, 93.2, 81.7, 79.1, 77.3, 64.9, 38.0, 34.8, 34.4, 17.8, -0.1; IR ($CHCl_3$): 3026, 2925, 2854, 2360, 2134, 1445, 1249, 1085, 962, 843 cm^{-1}.

HRMS. Calcd for $C_{18}H_{28}ClOSi$ (M^+(^{35}Cl)+H) *m/z* 323.1598. Found: *m/z* 323.1602.



(2*R*, 7*R*, 8*R*)-7-Chloro-2-[(1*E*)-1-propenyl]-8-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-3,4,7,8-tetrahydro-2H-oxocine [(+)- Laurenyne] (3). To a solution of 3 mg of (2*R*, 3*R*, 8*R*)-7-chloro-2-[(1*E*)-1-propenyl]-8-[(2*E*)-5-trimethylsilylpent-2-en-4-ynyl]-3,4,7,8-tetrahydro-2H-oxocine (0.0093 mmol) in 2 mL methanol was added a 0.5 mL suspension of K_2CO_3 in methanol (5% w/v). The resulting reaction mixture was stirred at room temperature for 2 h. Silica gel (1 g) was added to the mixture and the volatiles were removed *in vacuo*. After transfer of the residue to a column, elution by 10% EtOAc in hexanes

afforded 2.2 mg of (+)-Laurenyne (**3**) (97%) as a white solid having mp 78-79 °C and $[\alpha]_D^{25}$ + 17.9 ($CHCl_3$, *c* 0.145) [Lit.[4] $[\alpha]_D^{25}$ + 22.6 ($CHCl_3$, *c* 0.235); Lit.[5] $[\alpha]_D^{24}$ - 18.8 ($CHCl_3$, *c* 2.0)]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (dt, J_1 = 15.9 Hz, J_2 = 7.9 Hz, 1H), 5.90 (dt, J_1 = 15.9 Hz, J_2 = 7.6 Hz, 1H), 5.74-5.65 (m, 2H), 5.60-5.52 (m, 2H), 3.96 (ddd, J_1 = 11.5, J_2 = 4.8 Hz, J_3 = 2.5 Hz, 1H), 3.85 (ddd, J_1 = 8.7 Hz, J_2 = 4.8 Hz, J_3 = 2.5 Hz, 1H), 3.76 (dd, J_1 = 9.3 Hz, J_2 = 7.0 Hz, 1H), 2.97 (dt, J_1 = 11.4 Hz, J_2 = 11.4 Hz, 1H), 2.82 (d, *J* = 2.0 Hz, 1H), 2.60-2.45 (m, 3H), 2.26 (m, 1H), 2.16 (ddd, J_1 = 14.1 Hz, J_2 = 8.5 Hz, J_3 = 1.4 Hz, 1H), 1.70 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 131.8, 131.2, 128.5, 126,8, 111.6, 82.2, 81.7, 79.0, 76.3, 65.0, 38.1, 34.8, 34.4, 17.8; IR ($CHCl_3$): 3292, 3014, 2917, 1732, 1556, 1538, 1446, 1382, 1324, 1084, 1037, 972 cm^{-1}.

HRMS. Calcd for $C_{15}H_{20}ClO$ (M^+(^{35}Cl)+H) *m/z* 251.1203. Found: *m/z* 251.1197.

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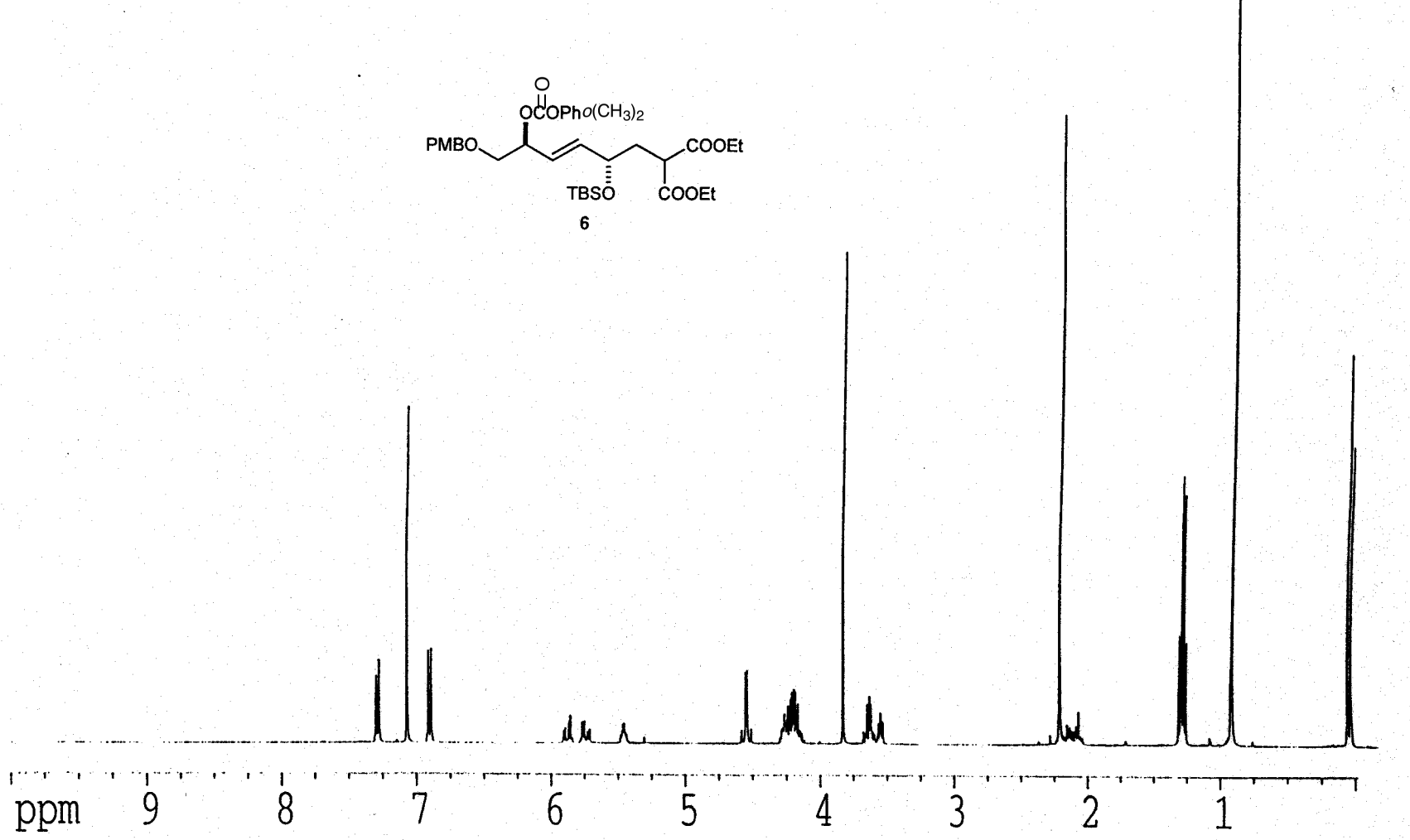
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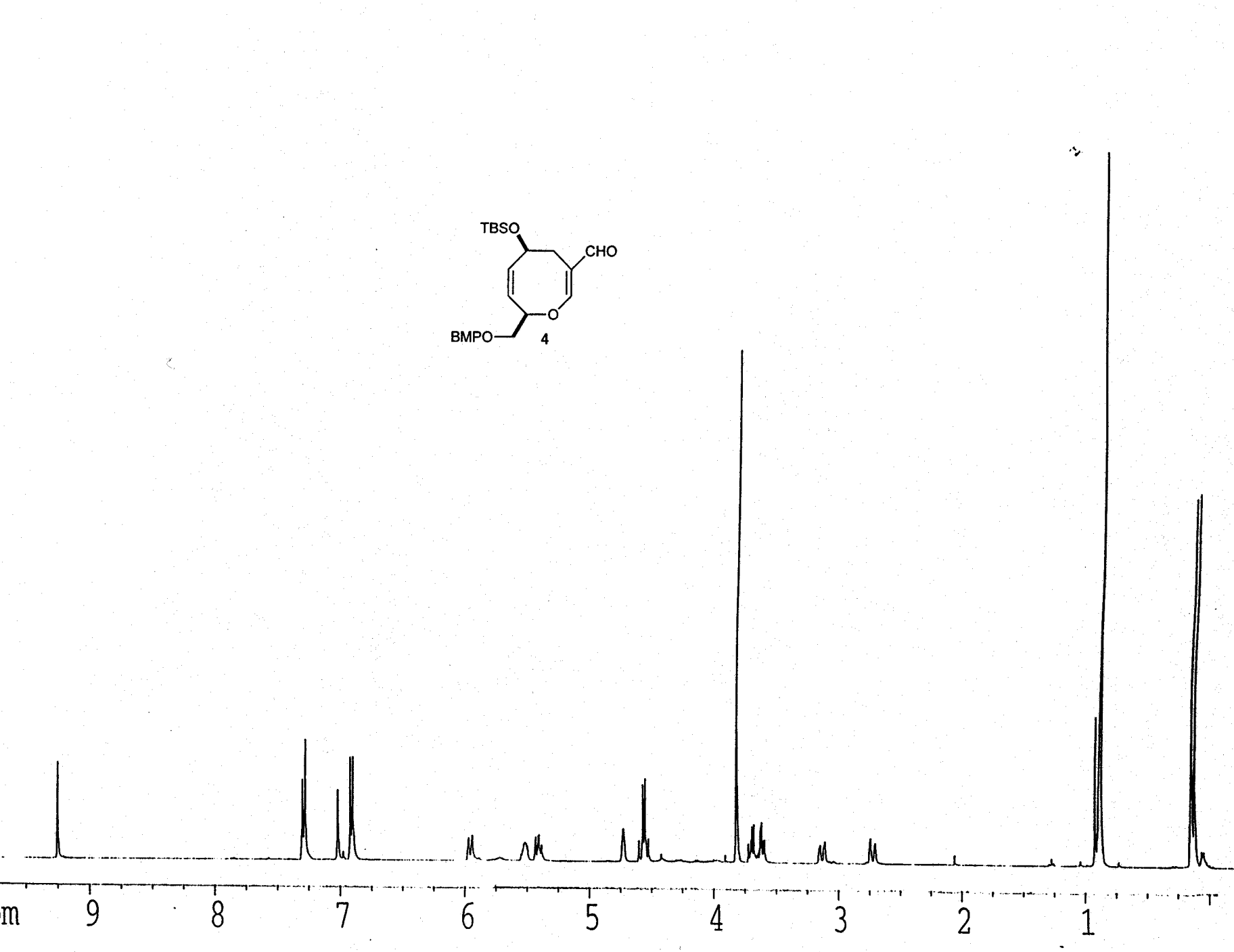
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