Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Total synthesis of decarestrictine I and botryolide B via RCM protocol

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Supporting Information: Representative experimental procedures, copies of ^{1}H and ^{13}C NMR of **1, 1(a)** and their intermediates.

General experimental details: Solvents were dried over standard drying agents and freshly distilled prior to use. All commercially available chemicals were used without further purification. All reactions were performed under Nitrogen. ^{1}H NMR (200 MHz, 300 MHz, 400 MHz and 500 MHz) and ^{13}C NMR (75 MHz) spectra were measured with a Varian Gemini FT-200 MHz spectrometer, Bruker Avance 300 MHz, Unity 400 MHz and Inova-500 MHz with tetramethylsilane as internal standard for solutions in deuteriochloroform. *J* values are given in Hz. Chemical shifts were reported in ppm relative to solvent signal. Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets); quin (quintet). All column chromatographic separations were performed using silica gel (Acme's, 60-120 mesh). Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 ºC in *vacuo*. IR spectra were recorded on at Perkin-Elmer IR-683 spectrophotometer with NaCl optics. Optical rotations were measured with JASCO DIP 300 digital polarimeter at 25 ºC. Mass spectra were recorded on CEC-21-11013 or Fannigan Mat 1210 double focusing mass spectrometers operating at a direct inlet system or LC/MSD Trap SL (Agilent Technologies).

(3*S*)-5-[1-*tert*-Butyl-1,1-diphenylsilyl]oxy-1-penten-3-ol (8)

To a suspension of trimethylsulfonium iodide (5.70 g, 27.7 mmol) in dry THF (20 mL) at -10 ^{o}C under nitrogen atmosphere was added *n*-BuLi (2.5M solution in hexane, 9.3 mL, 23.3 mmol). After 30 min., compound **7** (3.0 g, 9.3 mmol) in THF (10 mL) was introduced producing a milky suspension. The reaction was allowed to warm to 0 ^{o}C over 30 min. and then to room temperature and stirred for 4 h. The reaction was quenched with water (20 mL) at 0 ^{o}C, extracted with ethyl acetate (2 x 50 mL) and the combined organic

layer dried (Na_2SO_4). Chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane; 1:4) of the residue afforded **8** (2.2 g, 70%) as thick syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.60 (m, 4H, Ar-H), 7.43-7.33 (m, 6H, Ar-H), 5.90-5.78 (m, 1H, olefinic), 5.30-5.22 (m, 1H, olefinic), 5.10-5.04 (m, 1H, olefinic), 4.41-4.35 (m, 1H, -OCH), 3.89-3.76 (m, 2H, -OCH), 2.87 (br. s, 1H, OH), 1.78-1.71 (m, 2H, CH_2), 1.05 (s, 9H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 140.2, 136.2, 135.9, 129.9, 127.6, 127.1, 114.8, 73.1, 59.8, 39.4, 26.8, 18.9.

MS (ESI): 363 $(M+Na)^+$ **HRMS** ($C_{21}H_{28}O_2SiNa$) found: 363.1768 calculated: 363.1720.

Rotation value $[\alpha]_D^{25}$ = + 8.5 (*c* 0.67, $CHCl_3$).

Anal. Calcd. for $C_{21}H_{28}O_2Si$: C, 74.07, H, 8.29; Found: C, 74.12, H, 8.22.

***tert*-Butyl (3*S*)-3-[(4-methoxybenzyl)oxy]-4-pentenyloxy diphenylsilane (9)**

To a cooled (0 ^oC) solution of **8** (2.20 g, 6.5 mmol) in dry THF (20 mL), NaH (0.45 g, 19.5 mmol) was added, stirred for 30 min and treated with a solution of PMB-Br (1.56 g, 7.8 mmol) in dry THF (50 mL). After 6 h stirring at room temperature, the reaction mixture was quenched with saturated aq. NH_4Cl solution (8 mL) and extracted with EtOAc (2 x 10 mL). The organic layer was washed with water (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), evaporated under reduced pressure and the residue purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 1:9) to furnish **9** (2.50 g, 84%) as a yellow syrup.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65-7.58 (m, 4H, Ar-H), 7.39-7.28 (m, 6H, Ar-H), 7.13 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.76 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.78-5.65 (m, 1H, olefinic), 5.21-5.16 (m, 2H, olefinic), 4.49 (d, *J* = 11.3 Hz, 1H, -OCH_2Ph), 4.22 (d, *J* = 11.3 Hz, 1H, -OCH_2Ph), 4.0 (q, *J* = 7.7 Hz, 1H, -OCH), 3.83-3.72 (m, 4H, -OCH_3 and -OCH), 3.71-3.63 (m, 1H, -OCH), 1.88-1.64 (m, 2H, CH_2), 1.02 (s, 9H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9, 136.2, 135.5, 130.0, 129.5, 129.2, 128.9, 116.9, 113.8, 70.2, 59.9, 55.4, 38.7, 26.8, 19.3, 14.5

MS (ESI): 483 $(M+Na)^+$ **HRMS** ($C_{29}H_{36}O_3SiNa$) found: 483.2342. calculated: 483.2325.

Rotation value $[\alpha]_D^{25}$ = +36.8 (*c* 0.23, $CHCl_3$).

Anal. Calcd. for $C_{29}H_{36}O_3Si$: C, 75.61, H, 7.88; Found: C, 75.56, H, 7.90.

(3*S*)-3-[(4-Methoxybenzyl) oxy]-4-penten-1-ol (10)

To a stirred solution of compound **9** (2.5 g, 5.45 mmol) in dry THF under nitrogen atmosphere at 0 ºC tetrabutylammonium fluoride (5.45 mL, 5.45 mmol) was added and stirred for about 2 h. The reaction was quenched with saturated aq. NH_4Cl (10 mL) and extracted with EtOAc (3 x 15 mL). The combined organic layer was washed with brine (25 mL), dried (Na_2SO_4) and concentrated in *vaccuo*. The crude residue was purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 1:2) to furnish **10** (1.1 g, 91%) as a light yellow syrup.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.18 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.81 (d, *J* = 8.3 Hz, 2H, Ar-H), 5.82-5.70 (m, 1H, olefinic), 5.26-5.21 (m, 2H, olefinic), 4.51 (d, *J* = 11.3 Hz, 1H, -OCH_2Ph), 4.24 (d, *J* = 11.3 Hz, 1H, -OCH_2Ph), 3.96 (sext, *J* = 3.7, 12.0 Hz, 1H, -OCH) 3.78 (s, 3H, -OCH_3), 3.76-3.60 (m, 2H, -OCH_2), 2.33 (br. s, 1H, OH), 1.86-1.67 (m, 2H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 138.4, 129.3, 117.0, 113.6, 72.8, 70.7, 66.5, 55.5, 37.3, 25.9, 19.0 .

MS (ESI): 245 $(M+Na)^+$ **HRMS (**$C_{13}H_{18}O_3Na$) found: 245.1888 calculated: 245.1886.

Rotation value $[\alpha]_D^{25}$ **= -**87.6 (*c* 0.6, $CHCl_3$).

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.24, H, 8.16; Found: C, 70.30, H, 8.20.

(3*S*)-3-[(4-Methoxybenzyl) oxy]-4-pentenoic acid (4)

To a solution of oxalyl chloride (0.63 g, 4.95 mmol) in dry CH_2Cl_2 (10 mL) at -78 ^oC, dry DMSO (0.77 g, 9.9 mmol) was added dropwise and stirred for 10 min. A solution of **10** (1.0 g, 4.5 mmol) in dry CH_2Cl_2 (5 mL) was added and stirred for 1 h at -78 ^0C. It was quenched with Et_3N (2.73 g, 27.0 mmol) and diluted with CH_2Cl_2 (10 mL). The reaction mixture was washed with water (15 mL), brine (15 mL), dried (Na_2SO_4) and evaporated to furnish the corresponding aldehyde.

To a cooled (0 ^oC) solution of the above aldehyde (1.0 g, 4.4 mmol) in *t*-butanol (5 mL), 2-methyl-2-butene (1 mL) followed by a solution of $NaClO_2$ (0.58 g, 6.5 mmol) and NaH_2PO_4 (1.07 g, 6.5 mmol) in water (3 mL) was added and stirred at room

temperature for 6 h. The solvent was evaporated, residue dissolved in EtOAc (20 mL) and washed with water (15 mL), brine (15 mL) and dried (Na_2SO_4). Evaporation of solvent under reduced pressure and purification of residue by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 2:3) gave **4** (0.70 g, 66%) as a yellow syrup.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16 (d, 2H, *J* = 8.3 Hz, Ar-H), 6.78 (d, 2H, *J* = 8.3 Hz, Ar-H), 5.82-5.71 (m, 1H, olefinic), 5.34-5.23 (m, 2H, olefinic), 4.49 (d, 1H, *J* = 11.3 Hz, -$OCH_2C_6H_4$), 4.28 (d, 1H, *J* = 11.3 Hz, -$OCH_2C_6H_4$), 4.25-4.16 (m, 2H, -OCH and $OCH_2C_6H_4$), 3.78 (s, 3H, - OCH_3), 2.64 (dd, 1H, *J* = 8.3, 15.8 Hz, -CH_2), 2.51 (dd, 1H, *J* = 8.3, 15.8 Hz, 1H, -CH_2).

IR (neat): 3410, 2923, 2362, 1713, 1612, 1513 cm^{-1}.

MS (ESI): 259 $(M+Na)^+$ **HRMS (**$C_{13}H_{16}O_4Na$) found: 259.0949 calculated: 259.0940.

Rotation value [α]$_D^{25}$ **= -**32.3 (*c* 0.5, $CHCl_3$).

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 66.09, H, 6.83; Found: C, 66.15, H, 6.85.

(*Z*,5*R*)-5-[(4-Methoxybenzyl) oxy]-2-hexen-1-ol (12)

1M Solution of sodium borohydride (0.83 g, 22.1 mmol) was added to nickel acetate (3.65 g, 14.7 mmol) in EtOH at room temperature under hydrogen atmosphere. After 30 min. ethylenediamine (3.53 g, 58.8 mmol) was added. After 15 minutes compound **11** (3.50 g, 14.7 mmol) dissolved in EtOH was added. After 5 h reaction mixture was filtered through celite, washed with diethyl ether (2 x 50 mL). Organic layer was evaporated and purified by column chromatography (Silica gel 60-120 mesh, 3:7 EtOAc:*n*-hexane) to obtain **12** (2.50 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, 2H, *J* = 8.3 Hz, Ar-H), 6.82 (d, 2H, *J* = 8.3 Hz, Ar-H), 5.81-5.76 (m, 1H, olefinic), 5.58-5.51 (m, 1H, *J* = 8.3, 13.5, Hz, olefinic), 4.50 (d, 1H, *J* = 10.4 Hz, -$OCH_2C_6H_4$), 4.34 (d, 1H, *J* = 10.4 Hz, -$OCH_2C_6H_4$), 4.09-4.06 (m, 1H, -OCH_2), 3.98 (quin, *J* = 5.2 Hz, 1H, -OCH), 3.8-3.75 (s, 3H, -OCH_3), 3.50 (quin, *J* = 6.2, Hz, 1H, -OCH), 2.39-2.33 (m, 1H, CH_2), 2.23-2.17 (m, 1H, -CH_2), 1.63-1.45 (br. s, 1H, CH_2), 1.19 (d, *J* = 6.2 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.3, 129.8, 129.5, 128.7, 114.0,113.7, 71.7, 70.0, 60.2, 55.5, 54.4, 35.2, 20.0.

MS (ESI): 259 $(M+Na)^+$ **HRMS** ($C_{14}H_{20}O_3Na$) found: 259.1308 calculated: 259.1310.

Rotation value $[\alpha]_D^{25}$ = -26.3 (*c* 0.1, $CHCl_3$).

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.16, H, 8.53; Found: C, 71.20, H, 8.50.

((2*R*,3*S*)-3-(2*R*)-2-[(4-Methoxybenzyl)oxy]propyloxiran-2-yl) methanol (13)

To a stirred solution of (-)-DIPT (0.50 g, 2.1 mmol) in CH_2Cl_2 (20 mL) at -20 ^oC containing MS 4Å (4.0 g), sequentially $Ti(O^iPr)_4$ (0.30 g, 1.05 mmol) and cumene hydroperoxide (1.78 g, 11.6 mmol) were added and stirred for 20 min. A solution of **11** (2.50 g, 10.5 mmol) in CH_2Cl_2 (10 mL) was added and stirred for 5 h at -20 ^oC. The reaction mixture was quenched with 10% NaOH solution (1.25 g in 12 mL brine), stirred for 3 h and filtered. The organic layers were dried (Na_2SO_4), evaporated and the residue obtained was purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 2:3) to furnish **13** (2.50 g, 93%) as a yellow syrup.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.2 (d, 2H, *J* = 8.3 Hz, Ar-H), 6.82 (d, 2H, *J* = 8.3 Hz, Ar-H), 4.57 (d, 1H, *J* = 11.3 Hz, $-OCH_2C_6H_4$), 4.32 (d, 1H, *J* = 11.3 Hz, $-OCH_2C_6H_4$), 3.81-3.70 (m, 5H, $-OCH_3$ and $-OCH_2$), 3.37 (dd, *J* = 8.3, 12.0 Hz, 1H, -OCH), 3.06 (quin, *J* = 4.5 Hz, 1H, epoxide), 2.87-2.81 (m, 1H, epoxide), 1.95-1.87 (m, 1H, CH_2), 1.58-1.53 (m, 1H, CH_2), 1.25 (d, *J* = 6.0 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 129.3, 128.9, 114.2,113.7, 72.6, 70.2, 62.2, 58.9, 54.4, 38.9, 19.7.

MS (ESI): 275 $(M+Na)^+$ **HRMS (**$C_{14}H_{20}O_4Na$) found: 275.1266 calculated: 275.1259.

Rotation value $[\alpha]_D^{25}$ = -78.8 (*c* 0.35, $CHCl_3$).

IR (neat): 3422, 2870, 1453, 1217, 1154 cm^{-1}.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.65, H, 7.99; Found: C, 66.56, H, 7.98**.**

(2*S*,3*R*)-2-(2*R*)-2-[(4-Methoxybenzyl)oxy]propyl-3-vinyloxirane (14)

To a stirred solution of oxalyl chloride (1.36 g, 10.74 mmol) in dry CH_2Cl_2 (20 mL), DMSO (1.67 g, 21.4 mmol) was added at -78 ^oC and stirred at the same temperature for 0.5 h. A solution of alcohol **13** (2.50 g, 9.7 mmol) in CH_2Cl_2 (15 mL) was added at -78 ^oC and stirred for another 1 h at the same temperature. Et_3N (5.93 g, 58.5 mmol) was

added at -78 °C and stirred for further 15 min. The reaction mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4) and concentrated to give aldehyde in quantitative yield as pale yellow syrup, which was used as such for the next reaction.

To a solution of (methylenetriphenyl)phosphonium iodide (11.94 g, 29.5 mmol) in dry THF (30 mL), KO^{t}Bu (2.75 g, 24.6 mmol) was added at -10 ^{o}C and the mixture stirred for 4 h. Aldehyde (2.50 g, 9.84 mmol) in dry THF (30 mL) was added at 0 °C and the mixture stirred for 2 h. The reaction mixture was quenched with saturated NH_4Cl (20 mL) solution and extracted with EtoAc (2 x 30 mL). Combined extracts were washed with brine (20 mL), dried (Na_2SO_4), concentrated and crude residue was purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 1:9) to afford **14** (1.50 g, 62%) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2 (d, 2H, *J* = 8.3 Hz, Ar-H), 6.80 (d, 2H, *J* = 8.3 Hz, Ar-H), 5.74-5.62 (m, 1H, olefinic), 5.47 (d, 1H, *J* = 16.6 Hz, olefinic), 5.32 (d, 1H, *J* = 10.5 Hz, olefinic), 4.52 (d, 1H, *J* = 11.3 Hz, -$OCH_2C_6H_4$), 4.39 (d, 1H, *J* = 11.3 Hz, -$OCH_2C_6H_4$), 3.78 (S, 3H, -OCH_3), 3.73-3.62 (m, 1H, -OCH), 3.37 (q, *J* = 4.5 Hz, 1H, -OCH), 3.23-3.18 (m, 1H, -OCH), 1.81-1.71 (m, 1H, CH_2), 1.60-1.51 (m, 1H, CH_2), 1.23 (d, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 132.8, 129.8, 120.5, 113.7, 72.7, 70.2, 57.0, 56.3, 55.2, 35.8, 20.1.

IR (neat); 3049, 2932, 1614, 1512, 1454, 1375, 1090, 824 cm^{-1}.

MS (ESI): 271 $(M+Na)^+$ **HRMS** ($C_{15}H_{20}O_3Na$) found: 271.1317 calculated: 271.1310.

Rotation value $[\alpha]_D^{25}$ = -81.3 (*c* 0.15, $CHCl_3$).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.55, H, 8.12; Found: C, 72.60, H, 8.18.

(2*R*)-1-[(2*S*,3*R*)-3-Vinyloxiran-2-yl]propan-2-ol (5)

To a solution of **14** (1.50 g, 6.1 mmol) in aq. CH_2Cl_2 (10 mL; 19:1), DDQ (0.85 g, 6.7 mmol) was added and stirred at room temperature 1 h after it was quenched with saturated $NaHCO_3$ solution (10 mL), filtered and washed with CH_2Cl_2 (20 mL). The filtrate was washed with water (15 mL), brine (30 mL), dried (Na_2SO_4), evaporated under

reduced pressure and the residue purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 3:7) to furnish **5** (0.70 g, 90%) as a yellow syrup.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.79-5.63 (m, 1H, olefinic), 5.51-5.31 (m, 2H, olefinic), 4.10-3.98 (m, 1H, -OCH), 3.41-3.35 (m, 1H, epoxide), 3.22 (dt, J = 3.9, 11.7 Hz, 1H, epoxide), 2.2 (br. s, 1H, OH) 1.75-1.51 (m, 2H, CH_2), 1.23 (d, J = 6.2 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 132.3, 120.8, 66.4, 56.8, 55.9, 36.9, 23.5.

IR (neat): 3414, 2969, 2923, 1459, 1377, 1257, 1157 cm^{-1}.

MS (EI-MS, 70 eV): m/z (%): 129 (100), 111 (75), 87 (55), 69 (70), 43 (25).

Rotation value $[\alpha]_D^{25}$ = -84.5 (*c* 0.32, $CHCl_3$).

Anal. Calcd for $C_7H_{12}O_2$: C, 65.6, H, 9.44; Found: C, 65.55, H, 9.50.

(1*R*)-1-Methyl-2-[(2*S*,3*R*)-3-vinyloxiran-2-yl]ethyl(3*S*)-3-[(4-methoxybenzyl)oxy]-4-pentenoate (3)

To a solution of **4** (0.10 g, 0.4 mmol) and Et_3N (0.13 g, 1.2 mmol) in dry THF (3 mL) at 0 ^oC, 2,4,6-trichlorobenzoyl chloride (0.12 g, 0.5 mmol) was added dropwise and stirred at room temperature for 2 h. The reaction mixture was evaporated and residue dissolved in toluene (5 mL). A solution of **5** (0.05 g, 0.4 mmol) and DMAP (0.15 g, 1.3 mmol) in dry toluene (4 mL) was added to the reaction mixture and stirred for 4 h at room temperature. It was filtered through celite and washed with toluene (2 x 10 mL). The filtrate was evaporated and residue purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 1:10) to afford **3** (0.120 g, 83%) as a colorless syrup.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.17 (d, J = 8.3 Hz, 2H, Ar-H), 6.79 (d, J = 8.3 Hz, 2H, Ar-H), 5.81-5.59 (m, 2H, olefinic), 5.45-5.20 (m, 4H, olefinic), 5.11-5.00 (m, 1H, -OCH), 4.45 (d, J = 11.3 Hz, 1H, OCH_2-Ph), 4.27 (d, J = 11.3 Hz, 1H, OCH_2-Ph), 4.23-4.17 (m, 1H, -OCH), 3.77 (s, 3H, $-OCH_3$), 3.32-3.22 (m, 1H, epoxide), 3.08-3.01 (m, 1H, epoxide), 2.61-2.51 (m, 1H, $-CH_2$), 2.43-2.36 (m, 1H, CH_2), 1.82-1.62 (m, 2H, CH_2), 1.25 (d, J = 6.0 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 158.9, 137.2, 132.4, 132.0, 129.4, 129.2, 128.3, 120.8, 120.6, 118.1, 117.7, 114.3, 113.9, 76.9, 70.2, 69.0, 56.2, 55.2, 41.3, 33.8, 19.8.

MS (ESI): 369 $(M+Na)^+$ **HRMS** ($C_{20}H_{26}O_5Na$) found: 369.1888 calculated: 369.1886.

Rotation value $[\alpha]_D^{25}$ = -15.50 (*c* 0.45, $CHCl_3$).

IR (neat): 3449, 2926.8, 2858.5, 1732, 1612, 1177.7, 1117.3 cm^{-1}.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34, H, 7.56; Found: C, 69.40, H, 7.50.

(1a*S*,3*R*,7*S*,9a*R*)-7-[(4-Methoxybenzyl)oxy]-3-methyl-2,3,5,6,7,9a-hexahydro-1a*H*-oxireno[2,3-*d*]oxecin-5-one (2)

To a solution of **3** (0.12 g, 0.35 mmol) in CH_2Cl_2 (100 mL), 10 mol% Grubbs' II generation catalyst was added and stirred at reflux for 12 h under N_2 atmosphere. Most of the solvent was then distilled off and the concentrated solution was left to stir at room temperature for 2 h under air bubbling in order to decompose the catalyst. The reaction mixture was evaporated to dryness to give a brown residue which was purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 1:5) to give **2** as a thick syrup.

^{1}H NMR (200 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.77 (d, *J* = 8.7 Hz, 2H, Ar-H), 5.64 (ddd, *J* = 1.8, 8.3, 11.7 Hz, 1H, olefinic), 5.49-5.42 (m, 1H, olefinic), 5.19 (ddq, d, *J* = 1.8, 8.3, 11.7 Hz, 1H, -OCH), 4.49 (d, *J* = 11.3 Hz, 1H, OCH_2-Ph), 4.40-4.31 (m, 2H, -OCH and OCH_2-Ph), 3.75-3.69 (m, 4H, $-OCH_3$ and OCH), 3.24 (quin, *J* = 1.8, 5.8 Hz, 1H, epoxide), 2.83 (dt, *J* = 3.3, 10.5 Hz, 1H, epoxide), 2.60 (dd, *J* = 3.3, 10.3 Hz, 1H, $-CH_2$), 2.28 (t, *J* = 10.5 Hz, 1H, CH_2), 2.11-2.05 (m, 1H, CH_2), 1.28-1.16 (m, 4H, CH_2 and CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 159.2, 133.6, 133.2, 130.0, 129.7, 129.5, 129.4, 114.2, 113.8, 76.9, 71.9, 70.0, 66.8, 55.4, 54.4, 53.9, 41.2, 32.9, 29.6, 18.2.

IR (neat):3456.2, 2924, 2853, 2058, 1735.6, 1612.2, 1513, 1177.8, 1072 cm^{-1}.

MS (ESI): 341 $(M+Na)^+$ **HRMS** ($C_{18}H_{22}O_5Na$) found: 341.1367 calculated: 341.1364.

Rotation value $[\alpha]_D^{25}$ = -63.5 (*c* 0.34, $CHCl_3$).

Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91 .02, H, 6.97; Found: C, 67.85, H, 6.95.

Decarestrictine I (1)

To a solution of **2** (0.07 g, 0.2 mmol) in aq. CH_2Cl_2 (2 mL; 19:1), DDQ (0.042 g, 0.33 mmol) was added and stirred at room temperature 1 h after it was quenched with

saturated $NaHCO_3$ solution (2 mL), filtered and washed with CH_2Cl_2 (20 mL). The filtrate was washed with water (15 mL), brine (5 mL), dried (Na_2SO_4), evaporated under reduced pressure and the residue purified by column chromatography (Silica gel 60-120 mesh, EtOAc:*n*-hexane, 3:7) to furnish **1** (0.025 g, 69%) as a colorless syrup.

^{1}H NMR (200 MHz, $CDCl_3$): δ 5.95-5.82 (m, 2H, olefinic), 5.10-4.95 (m, 2H, OCH), 4.92-4.85 (m, 1H, -OCH), 3.90 (dt, *J* = 2.3, 4.6, 10.9 Hz, 1H, -OCH), 2.76-2.54 (sept, *J* = 7.8, 14.0 Hz, 1H, CH_2), 2.01 (dd, *J* = 2.3, 3.1 Hz, 2H, CH_2), 1.68-1.60 (m, 1H, CH_2), 1.25 (d, *J* = 6.2 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 132.2, 127.5, 92.6, 81.6, 73.7, 71.2, 42.5, 39.9, 21.9.

IR (neat): 3405.5, 2956.3, 2854, 1710, 1431.2, 1385, 1070 cm^{-1}.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.59, H, 7.12; Found: C, 60.55, H, 7.20.

MS: (EI-MS, 70 eV): m/z (%): 199 (27), 137 (15), 121 (62), 85 (65), 83 (95), 62 (100), 41 (80).

Rotation value $[\alpha]_D^{25}$ = -130.5 (*c* 0.30, CH_3OH).

(3*R*)-5-[1-(*tert*-Butyl)-1,1-diphenylsilyl]oxy-1-penten-3-ol (8a)

Adopted the same procedure as discussed earlier for the preparation of compound **8, 7a** (2.5 g, 7.71 mmol) gave **8a** (1.7 g, 65%).

Rotation value $[\alpha]_D^{25}$ = - 10.5 (*c* 0.8, $CHCl_3$).

***tert*-Butyl((3*R*)-3-[(4-methoxybenzyl)oxy]-4-pentenyloxy)diphenylsilane (9a)**

Adopted the same procedure as discussed earlier for the preparation of compound **9, 8a** (1.7 g, 5.03 mmol) gave **9a** (1.8 g, 78%).

Rotation value $[\alpha]_D^{25}$ = -33.8 (*c* 0.35, $CHCl_3$).

(3*R*)-3-[(4-Methoxybenzyl) oxy]-4-penten-1-ol (10a)

Adopted the same procedure as discussed earlier for the preparation of compound **10, 9a** (1.8 g, 3.93 mmol) gave **10a** (0.75 g, 85%) as a colorless syrup.

Rotation value $[\alpha]_D^{25}$= +82.4 (*c* 0.2, $CHCl_3$).

(3*R*)-3-[(4-Methoxybenzyl)oxy]-4-pentenoic acid (4a)

Adopted the same procedure as discussed earlier for the preparation of compound **4**, alcohol **10a** {0.75 g, 3.4 mmol) gave **4a** (0.50 g, 79% (over two steps)} as a syrup.

Rotation value $[\alpha]_D^{25}$= +36.3 (*c* 0.2, $CHCl_3$).

(1*R*)-1-Methyl-2-[(2*S*,3*R*)-3-vinyloxiran-2-yl]ethyl (3*R*)-3-[(4-methoxybenzyl)oxy]-4-pentenoate (3a).

Adopted the same procedure as discussed earlier for the preparation of compound **3**, **4a** and **5** (0.150 g, 0.63 mmol) gave **3a** (0.160 g, 74%) as a yellow syrup.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.14 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.77 (d, *J* = 8.5 Hz, 2H, Ar-H), 5.80-5.58 (m, 2H, olefinic), 5.40-5.20 (m, 4H, olefinic), 5.11-5.01 (m, 1H, -OCH), 4.49 (d, *J* = 10.9 Hz, 1H, OCH_2-Ph), 4.28 (d, *J* = 10.9 Hz, 1H, OCH_2-Ph), 4.21-4.15 (m, 1H, -OCH), 3.78 (s, 3H, OCH_3), 3.30 (q, *J* = 4.5, 6.7 Hz, 1H, epoxide), 3.10-3.01 (m, 1H, epoxide), 2.64-2.39 (m, 2H, CH_2), 1.84-1.65 (m, 2H, CH_2), 1.27 (d, *J* = 6 Hz, 3H, CH_3).
^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 159.3, 137.1, 132.4, 130.1, 129.2, 127.9, 121.0, 118.3, 113.8, 76.9, 70.1, 68.9, 56.2, 55.2, 41.3, 33.8, 19.8.
IR (neat): 3449, 2926.8, 2858.5, 1732.3, 1612, 1513, 1246, 1177 cm^{-1}.
MS (ESI): 369 $(M+Na)^+$ **HRMS (**$C_{20}H_{26}O_5Na$) found: 369.1668 calculated: 369.1670.
Rotation value $[\alpha]_D^{25}$ **= -**6.1 (*c* 0.35, $CHCl_3$).

(1a*S*,3*R*,7*R*,9a*R*)-7-[(4-Methoxybenzyl)oxy]-3-methyl-2,3,5,6,7,9a-hexahydro-1a*H*-oxireno[2,3-*d*]oxecin-5-one (2a).

Adopted the same procedure as discussed earlier for the preparation of compound **2**, **3a** (0.1 g, 0.29 mmol) gave **2a** (0.065 g, 70%) as a dark colored liquid.
^{1}H NMR (200 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.81 (d, *J* = 8.5 Hz, 2H, Ar-H), 5.69 (ddd, *J* = 1.5, 7.8, 10.9 Hz, 1H, olefinic), 5.49 (dd, *J* = 5.4, 11.7 Hz, 1H, olefinic), 5.29-5.16 (m, 1H, -OCH), 4.55 (d, *J* = 11.7 Hz, 1H, OCH_2-Ph) 4.48-4.35 (m,

2H, OCH_2-Ph and -OCH), 3.79 (s, 3H, CH_3), 3.30 (quin, *J* = 1.5, 5.4 Hz, 1H, -OCH), 2.89 (dt, *J* = 3.1, 10.9 Hz, 1H, epoxide), 2.64 (dd, *J* = 3.1, 10.1 Hz, 1H, epoxide), 2.34 (t, *J* = 10.9 Hz, 1H, CH_2), 2.19-2.10 (m, 1H, CH_2), 1.4 (m, 1H, CH_2), 1.27 (d, *J* = 6.2 Hz, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.0, 159.3, 135.2, 133.4, 129.9, 129.4, 113.8, 78.2, 70.8, 69.3, 57.2, 55.0, 53.5, 43.5, 32.4, 18.3.

IR (neat): 3453.6, 2924, 2853, 2058, 1735.8, 1612.5, 1513, 1177.7, 1072 cm^{-1}.

MS (ESI): 341 $(M+Na)^+$ **HRMS (**$C_{18}H_{22}O_5Na$) found: 341.1358 calculated: 341.1362.

Rotation value $[\alpha]_D^{25}$ = -165.5 (*c* 0.27, $CHCl_3$).

Botryolide B (1a)

Adopted the same procedure as discussed earlier for the preparation of compound **1**, **2a** (0.065 g, 0.21 mmol) gave **1a** (0.025 g, 90%) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.71 (ddd, *J* = 2.2, 8.3, 11.3 Hz, 1H, olefinic), 5.45 (dd, *J* = 1.5, 5.3, 12.0 Hz, 1H, olefinic), 5.29 (ddq, *J* = 1.5, 6.0, 11.3 Hz, 1H, -OCH), 4.93-4.85 (m, 1H, -OCH), 3.48 (quin, *J* = 1.5, 6.0 Hz, 1H, -OCH), 2.99 (dt, *J* = 3.7, 11.3 Hz, 1H, epoxide), 2.67 (dd, *J* = 3.0, 9.8 Hz, 1H, CH_2), 2.44 (t, *J* = 11.3 Hz, 1H, epoxide), 2.19 (ddd, *J* = 1.5, 3.0, 14.3 Hz, 1H, CH_2), 1.71 (b. s, 1H, OH), 1.29 (d, *J* = 6.0 Hz, 3H, CH_3), 1.25-1.23 (m, 1H, CH_2).

^{13}C NMR (75 MHz, $CDCl_3$): δ 170.1, 135.6, 128.0, 67.8, 67.7, 57.0, 53.5, 43.5, 38.0, 20.4.

IR (neat): 3422.6, 2924.8, 2854, 2358.4, 1732, 1513, 1432, 1351, 1275 cm^{-1}.

MS: (EI-MS, 70 eV): m/z (%): 198, 137 (15), 121 (62), 85 (65), 83 (95), 62 (100), 41 (80).

Rotation value $[\alpha]_D^{25}$ = -144.0 (*c* 0.25, $CHCl_3$).