Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Syntheses of naturally occuring, cytotoxic [7.7]paracyclophane, (–)-Cylindrocyclophane A and its enantiomer, and implications for the biological activity

Hiroyuki Yamakoshi, Fumiya Ikarashi, Masataka Minami, Masatoshi Shibuya, Tsutomu Sugahara, Naoki Kanoh, Hisatugu Ohori, Hiroyuki Shibata and Yoshiharu Iwabuchi*

Department of Organic Chemistry and Biophysical Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aobayama, Sendai 980-8578, Japan and Department of Clinical Oncology, Institute of Development, Aging and Cancer, Tohoku University, Sendai 980-8575, Japan.

Supporting Information

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General

All reactions were carried out under an atmosphere of argon unless otherwise specified. Anhydrous solvents were transferred via syringe to flame-dried glassware, which had benn cooled under a stream of dry nitrogen. Ethereal solvents and dichloromethane (anhydrous; Kanto Chemical Co., Inc) were used as received. All other solvents were dried and distilled by standard procedures. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials unless otherwise stated. Reagents were purchased at highest commercial quality and used without further purification unless otherwise stated.

Reaction were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as visualizing agent and *p*-anisaldehyde in ethanol/aqueous H_2SO_4/CH_3CO_2H for staining. Column chromatography was performed using solica gel 60 particle size 0.063-0.210 mm. The eluents employed are reported as volume / volume.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a JEOL JMN-AL400 (400 MHz), and a JEOL JNM-ECP-500 (500 MHz) spectrometers. Chemical shift (δ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS). Coupling constants (*J*) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded using a JEOL JMN-AL400 (100 MHz) and a JEOL JNM-ECP-500 (125 MHz) spectrometers. Chemical shift is reported in ppm relative to the center of $CDCl_3$ or CD_3OD.

Melting point were determined using Yazawa BY-2 melting point apparatus and are reported uncorrected. Infrared spectra were obtained on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrophitimeter at 4.0 cm^{-1} resolution and are reported in wavenumbers. Low and high resolution mass spectra were recorded on a JEOL JMS-DX303 or a JMS-700 using electron impact (EI). FAB mass spectra were recorded on a JEOL-JMS700 spectrometer using 3-nitrobenzyl alcohol as a matrix. Optical rotations were measured on a JASCO DIP-370 Digital Polarimeter using the sodium D line.

Synthesis of (–)-Cylindrocyclophane A

4-Formyl-2,6-dimethoxyphenyl trifluoromethanesulfonate 7a

To a solution of the syringaldehyde (4.0 g, 22 mmol) in CH_2Cl_2 was added pyridine (5.3 mL, 66 mmol), followed by trifluoromethanesulfonic anhydride (4.4 mL, 26 mmol) over 10 min. After sterring at room temperature for 30 min, the mixture was quenched by addition of H_2O and extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 2 / 5) to give **7a** (6.3 g, 92% yeild) as a colorless crystal; mp 108–110 °C ($CHCl_3$ / Hexane); FT-IR (neat) ν 1699, 1609, 1424, 1123 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.94 (1H, s), 7.17 (2H, s), 3.98 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 190.4, 153.2, 135.8, 132.0, 118.6 (1C, q, J = 321.2 Hz), 105.9, 56.6; MS (EI) *m/z* 314 (M^+), 181 (100%); HRMS (EI) *m/z* calcd for $C_{10}H_9F_3O_6S$ (M^+): 314.0072, found: 314.0052.

(*R*)-(1-Benzyloxybut-3-yn-2-yloxy)*tert*-butyldimethylsilane 8a

A mixture of the alcohol **8** (5.0 g, 28 mol), TBSCl (7.2 g, 48 mmol) and imidazole (3.3 g, 48 mmol) in DMF (56 mL) was stirred at room temperature for 50 min. The mixture was quenched by addition of H_2O and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 10) to give **8a** (7.8 g, 96% yeild) as a colorless oil; $[\alpha]_D^{23}$ +28.5 (*c* 0.46, $CHCl_3$); FT-IR (neat) ν 3309, 1252, 1130, 1104 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (5H, m), 4.62 (2H, s), 4.56 (1H, ddd, J = 7.0, 4.8, 2.0 Hz), 3.61 (1H, dd, J = 10.0, 4.8 Hz), 3.57 (1H, dd, J = 10.0, 7.0 Hz), 2.41 (1H, d, J = 2.0), 0.91 (9H, s), 0.14 (3H, s), 0.12 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.2, 128.3, 127.6, 127.6, 83.2, 74.4, 73.5, 73.0, 62.8, 25.7, 18.2, –4.8, –5.0; MS (FAB) *m/z* 291 [(M+H)$^+$], 91 (100%); HRMS (FAB) *m/z* calcd for $C_{17}H_{27}O_2Si$ [(M+H)$^+$]: 291.1786, found: 291.1749.

(*R*)-4-(4-Benzyloxy-3-*tert*-butyldimethylsilyloxybut-1-ynyl)-3,5-dimethoxybenzaldehyde 9

The triflate **7a** (500 mg, 1.6 mmol), $(PPh_3)_2PdCl_2$ (111 mg, 0.16 mmol), PPh_3 (125 mg, 0.48 mmol), Bu_4NI (1.2 g, 3.2 mmol), K_2CO_3 (660 mg, 4.8 mmol) and CuI (91 mg, 0.48 mmol) were charged in a 2-knecked, round-bottomed 50 mL flask equipped with a rubber septam and a condenser. To the flask was introduced a degassed solution of the

propargyl ether **8a** (600 mg, 2.1 mmol) in tetrahydropyrane (16 mL). The mixture was heated at 70 °C for 18 h. After cooling to room temperature, the mixture was filtered through a pad of Celite and the Celite layer was washed with Et_2O. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **9** (565 mg, 78% yeild) as a red oil; $[\alpha]_D^{30}$ –35.0 (*c* 1.13, $CHCl_3$); FT-IR (neat) ν 1698, 1574, 1462, 1230, 1130 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.91 (1H, s), 7.39-7.25 (5H, m), 7.01 (2H, s), 4.91 (1H, dd, *J* = 7.0, 5.0 Hz), 4.70 (2H, s), 3.89 (6H, s), 3.75 (1H, dd, *J* = 10.2, 5.0 Hz), 3.70 (1H, ddd, *J* = 10.2, 7.0, 2.8 Hz), 0.96 (9H, s), 0.22 (3H, s), 0.19 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.2, 138.4, 136.6, 128.2, 127.5, 127.4, 107.5, 104.3, 100.7, 76.7, 74.5, 73.4, 63.9, 56.1, 25.9, 18.4, –4.6, –4.9; MS (FAB) *m/z* 453 [$(M-H)^+$], 91 (100%); HRMS (FAB) *m/z* calcd for $C_{36}H_{33}O_5Si$ [$(M-H)^+$]: 453.6229, found: 453.2029.

(*R*)-1-Benzyloxy-4-(4-hydroxymethyl-2,6-dimethoxyphenyl)-but-3-yn-2-ol

To a solution of **9** (200 mg, 0.44 mmol) in MeOH (2.2 mL) was added $NaBH_4$ (10 mg, 0.26 mmol) at 0 °C and the mixture was stirred for 1 h. The reaction mixture was quenched with 1% aqueous HCl (2.2 mL) and MeOH was evaporated under reduced pressure. The residue was extracted AcOEt and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in THF (2.2 mL) and then, acetic acid (0.05 mL, 0.88 mol) and TBAF (1M in THF, 0.88 mL, 0.88 mmol) were added at 0 °C. The reaction mixture was stirred for 30 h at room temperature and extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 4 / 1) to give the diol (146 mg, 96% yeild) as a yellow oil; $[\alpha]_D^{33}$ +5.7 (*c* 0.96, $CHCl_3$); FT-IR (neat) ν 3376, 1574, 1459, 1416, 1126 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-7.26 (5H, m), 6.48 (2H, s), 4.87 (1H, dd, *J* = 7.0, 3.9 Hz), 4.70 (1H, d, *J* = 12.1 Hz), 4.65 (1H, d, *J* = 12.1 Hz), 4.64 (2H, s), 3.80 (6H, s), 3.79 (1H, ddd, *J* = 10.0, 3.9, 1.0 Hz), 3.72 (1H, ddd, *J* = 10.0, 7.0, 0.9 Hz), 3.01 (1H, brs), 2.30 (1H, brs); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.5, 143.6, 137.9, 128.4, 127.7, 127.6, 101.7, 995, 95.3, 76.7, 73.8, 73.4, 65.2, 62.6, 55.9; MS (EI) *m/z* 342 (M^+), 221 (100%); HRMS (EI) *m/z* calcd for $C_{20}H_{22}O_5$ (M^+): 342.1467, found: 342.1477.

(*R*)-1-Benzyloxy-4-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl) but-3-yn-2-ol 10

To a solution of the diol (108 mg, 0.31 mmol) in CH_2Cl_2 (1.6 mL) was added TBDPSCl (0.081 mL, 0.31 mmol), followed by Et_3N (0.087 mL, 0.63 mmol) and DMAP (7 mg, 0.063 mmol) at 0 °C. The mixture was stirred for 1h and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 2) to give **10** (140 mg, 77% yeild) as a colorless amorphous; $[\alpha]_D^{29}$ +4.9 (*c* 1.02, $CHCl_3$); FT-IR (neat) ν 3452, 1574, 1461, 1416, 1230, 1128 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (4H, m), 7.45-7.27 (11H, m), 6.50 (2H, s), 4.89 (1H, dd, *J* = 7.3, 3.7 Hz), 4.87 (2H, s), 4.72 (1H, d, *J* = 12.1 Hz), 4.66 (1H, d, *J* = 12.1 Hz), 3.82 (1H, dd, *J* = 9.9, 3.7 Hz), 3.79 (6H, s), 3.74 (1H, dd, *J* = 9.9, 7.3 Hz), 2.66 (1H, brs), 1.10 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 161.5, 143.5, 138.0, 135.5, 133.3, 129.8, 128.4, 127.8, 127.7, 127.6, 100.9, 98.9, 94.8, 76.7, 73.9, 73.4, 65.5, 62.7, 55.9, 26.8, 19.3; MS (EI) *m/z* 580 (M^+), 523 (100%); HRMS (EI) *m/z* calcd for $C_{36}H_{40}O_5Si$ (M^+): 580.2645, found: 580.2631.

(*R*,*E*)-1-Benzyloxy-4-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl) but-3-en-2-ol 6

To a solution of **10** (130 mg, 0.22 mmol) in THF (1.1 mL) was added LAH (10 mg, 0.27 mmol) at 0 °C. After stirring for 3 h at room temperature, another portion of LAH (10 mg, 0.27 mmol) was added at 0 °C. The reaction mixture was stirred for 3 h at room temperature and quenched by addition of H_2O. The mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (AcOEt / Hexane = 2 / 3) to give **6** (112 mg, 86% yeild) as a colorless oil. The chiral HPLC analysis showed the product to have >99% ee.; $[\alpha]_D^{31}$ –0.5 (*c* 1.11, $CHCl_3$); FT-IR (neat) ν 3450, 1607, 1577, 1455, 1420, 1111 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.45-7.26 (11H, m), 6.98 (1H, d, *J* = 16.2 Hz), 6.60 (1H, dd, *J* = 16.2, 6.7 Hz), 6.54 (2H, s), 4.75 (2H, s), 4.61 (2H, s), 4.51 (1H, m), 3.79 (6H, s), 3.63 (1H, dd, *J* = 9.6, 3.3 Hz), 3.49 (1H, dd, *J* = 9.6, 8.3 Hz), 2.47 (1H, brs), 1.10 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.2, 141.5, 137.9, 135.3, 133.1, 130.8, 129.5, 128.1, 127.7, 127.5, 127.4, 122.1, 112.0, 101.2, 74.4, 73.1, 72.9, 65.6, 55.4, 26.7, 19.2; MS (EI) *m/z* 582 (M^+), 461 (100%); HRMS (EI) *m/z* calcd for $C_{36}H_{42}O_5Si$ (M^+): 582.2802, found: 582.2755.

(*S*,*E*)-Ethyl 6-benzyloxy-3-(4-*tert*-butyldiphenylsilyloxy-methyl-2,6-dimethoxyphenyl)hex-4-enoate 5

A mixture of **6** (130 mg, 0.22 mmol) and *o*-NO_2PhOH (1.2 mg, 0.17 mmol) in triethyl orthoacetate (1.2 mL) was heated for 2 h at 140 °C. The mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, and aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **5** (86 mg, 72% yeild) as a yellowish oil. The chiral HPLC analysis showed the product to have >99% ee.; $[\alpha]_D^{31}$ +1.9 (*c* 0.99, $CHCl_3$); FT-IR (neat) ν 1731, 1672, 1609, 1585, 1455, 1426, 1367, 1116 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.42-7.19 (11H, m), 6.53 (2H, s), 6.08 (1H, dd, *J* = 15.4, 7.7 Hz), 5.63 (1H, dt, *J* = 15.4, 6.4 Hz), 4.74 (2H, s), 4.59 (1H, m), 4.44 (2H, s), 4.04 (2H, q, *J* = 7.1 Hz), 3.96 (2H, d, *J* = 6.4 Hz), 3.75 (6H, s), 2.97 (1H, dd, *J* = 15.0, 8.7 Hz), 2.78 (1H, dd, *J* = 15.0, 6.8 Hz), 1.15 (3H, t, *J* = 7.1 Hz), 1.11 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 172.6, 157.9, 141.0, 138.4, 135.4, 135.2, 129.6, 128.1, 127.6, 127.5, 127.3, 126.1, 116.9, 101.8, 71.3, 70.7, 65.5, 59.9, 55.6, 38.2, 34.6, 26.8, 19.3, 14.2; MS (EI) *m*/*z* 652 (M^+), 595 (100%); HRMS (EI) *m*/*z* calcd for $C_{40}H_{48}O_6Si$ (M^+): 652.3220, found: 652.3200.

(*S*,*E*)-6-Benzyloxy-3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl) hex-4-enal

To a solution of **5** (172 mg, 0.26 mmol) in toluene (3.6 mL) was added DIBAL (1.01 M in toluene, 0.21 mL, 0.32 mmol) at –78 °C, and stirred for 20 min at the same temperature. The mixture was quenched by addition of 0.5 N aqueous HCl and allowed to warm up to room temperature. The mixture was diluted with AcOEt and H_2O. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give the aldehyde (138 mg, 86% yeild) as a yellowish oil; $[\alpha]_D^{25}$ +0.6 (*c* 1.00, $CHCl_3$); FT-IR (neat) ν 1724, 1585, 1455, 1426, 1112 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.63 (1H, t, *J* = 2.4 Hz), 7.69-7.67 (4H, m), 7.43-7.24 (11H, m), 6.53 (2H, s), 6.08 (1H, dd, *J* = 15.4, 7.6 Hz), 5.64 (1H, dt, *J* = 15.4, 6.2 Hz), 4.73 (2H, s), 4.64 (1H, m), 4.47 (1H, d, *J* = 11.8 Hz), 4.43 (1H, d, *J* = 11.8 Hz), 3.97 (2H, d, *J* = 6.2 Hz), 3.75 (6H, s), 2.92 (1H, ddd, *J* = 16.3, 7.3, 2.4 Hz), 2.86 (1H, ddd, *J* = 16.3, 7.6, 2.4 Hz), 1.11 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.1, 157.8, 141.4, 138.3, 135.4, 135.0, 133.3, 129.6, 128.2, 127.7, 127.6, 127.4, 126.3, 116.2, 101.8, 71.7, 65.5, 55.6, 47.0, 32.6, 26.9, 19.4; MS (EI) *m*/*z* 608 (M^+), 551 (100%); HRMS (EI) *m*/*z* calcd for $C_{38}H_{44}O_5Si$ (M^+): 608.2958, found: 608.2973.

4{[(*S*,2*E*,6*Z*)-1-Benzyloxyocta-2,6-dien-4-yl]-3,5-dimethoxy-benzyloxy}-*tert*-butyldiphenylsilane 11

To a solution of ethyltriphenylphosphonium iodide (303 mg, 0.73 mmol) in THF (4.0 mL) was added KHMDS (0.7 M in toluene, 0.90 mL, 0.68 mmol) at –78 °C. After stirring for 20 min, a solution of the aldehyde (138 mg, 0.23 mmol) in THF (1.5 mL) was added dropwise *via* cannula. After stirring for 1 h at –78 °C, the reaction mixture was brought to 0 °C and quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give **11** (136 mg, 97% yeild) as a colorless oil; $[\alpha]_D^{25}$ +6.6 (*c* 0.96, $CHCl_3$); FT-IR (neat) ν 1608, 1585, 1455, 1426, 1111 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (4H, m), 7.43-7.24 (11H, m), 6.52 (2H, s), 6.15 (1H, dd, *J* = 15.4, 8.0 Hz), 5.58 (1H, dt, *J* = 15.4, 6.4 Hz), 5.39-5.33 (2H, m), 4.73 (2H, s), 4.49 (1H, d, *J* = 11.7 Hz), 4.45 (1H, d, *J* = 11.7 Hz), 4.06 (1H, m), 3.97 (2H, m), 3.74 (6H, s), 2.57 (2H, m), 1.55 (3H, d, *J* = 5.9), 1.10 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.0, 140.4, 138.5, 137.3, 135.5, 133.4, 129.6, 129.5, 128.2, 127.8, 127.6, 127.3, 125.4, 124.0, 118.4, 101.9, 71.3, 71.0, 65.5, 55.7, 38.3, 30.5, 26.9, 19.4, 13.0; MS (EI) *m*/*z* 620 (M^+), 565 (100%); HRMS (EI) *m*/*z* calcd for $C_{40}H_{48}O_4Si$ (M^+): 620.3322, found: 620.3311.

(*S*)-4-(4-*tert*-Butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl)octan-1-ol 12

To a solution of **11** (297 mg, 0.48 mmol) in THP (4.8 mL) was hydrogenated in the presence of Pd/C (30 mg) under atmospheric pressure of H_2 for 3 h. The reaction mixture was added $Pd(OH)_2$ (45 mg) in thrice at 3 h intervals. After stirring for 1 d, the reaction mixture was filtered through a pad of Celite and the Celite layer was washed with Et_2O. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **12** (243 mg, 95% yeild) as a colorless oil; $[\alpha]_D^{26}$ –0.5 (*c* 1.16, $CHCl_3$); FT-IR (neat) ν 3357, 1608, 1584, 1461, 1425, 1370, 1112 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.43-7.35 (6H, m), 6.51 (2H, s), 4.74 (2H, s), 3.72 (6H, s), 3.57 (2H, t, *J* = 6.6 Hz), 3.28 (1H, m),

1.89-1.78 (2H, m), 1.66-1.55 (2H, m), 1.47-1.32 (2H, m), 1.27-1.05 (5H, m), 1.11 (9H, s), 0.83 (3H, t, J = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.9, 135.5, 133.5, 129.6, 127.6, 119.4, 65.8, 65.6, 63.5, 34.8, 33.5, 31.6, 30.5, 29.7, 26.9, 22.9, 19.4, 15.3, 14.3, 14.2; MS (EI) m/z 534 (M^+), 379 (100%); HRMS (EI) m/z calcd for $C_{33}H_{46}O_4Si$ (M^+): 534.3165, found: 534.3167.

(*S*)-*tert*-Butyl[3,5-dimethoxy-4-(oct-1-en-4-yl)benzyloxy]-diphenylsilane

To a solution of **12** (120 mg, 0.22 mmol) in THF (1.2 mL) was added *o*-NO_2PhSeCN (153 mg, 0.67 mmol) and PBu_3 (0.17 mL, 0.67 mmol). After stirring for 3 h, the mixture was added 30% aqueous H_2O_2 (0.17 mL, 1.5 mmol) over 10 min at 0 °C. The reaction mixture was stirred for 8 h and diluted with Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give the alkene (109 mg, 94% yeild) as a colorless oil; $[\alpha]_D^{26}$ +0.8 (*c* 0.96, $CHCl_3$); FT-IR (neat) ν 1609, 1584, 1461, 1426, 1369, 1213, 1112 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.43-7.33 (6H, m), 6.51 (2H, s), 5.70 (1H, m), 4.92 (1H, dd, J = 17.1, 2.4 Hz), 4.82 (1H, dt, J = 10.2, 1.2 Hz), 4.75 (2H, s), 3.72 (6H, s), 3.36 (1H, m), 2.53 (1H, m), 2.43 (1H, m), 1.80 (1H, m), 1.60 (1H, m), 1.30-1.04 (4H, m), 1.11 (9H, s), 0.83 (3H, t, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.9, 139.0, 135.5, 133.5, 129.6, 127.7, 127.6, 119.5, 114.1, 102.0, 65.9, 65.7, 38.3, 35.1, 32.9, 30.5, 26.9, 22.9, 19.4, 14.2; MS (EI) m/z 516 (M^+), 475 (100%); HRMS (EI) m/z calcd for $C_{33}H_{44}O_3Si$ (M^+): 516.3060, found: 516.3047.

(*S*)-3,5-Dimethoxy-4-(oct-1-en-4-yl)methanol

To a solution of the silane (109 mg, 0.21 mmol) in THF (1.1 mL) was added TBAF (1.0 M in THF, 0.32 mL, 0.32 mmol) at room temperature. After stirring for 3 h, H_2O and AcOEt were added to the mixture. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 3 / 7) to give the alcohol (58 mg, 99% yeild) as a colorless solid; mp 39–41 °C; $[\alpha]_D^{24}$ –0.5 (*c* 0.98, $CHCl_3$); FT-IR (neat) ν 3323, 1583, 1455, 1421, 1213, 1135 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.52 (2H, s), 5.67 (1H, m), 4.90 (1H, d, J = 17.1 Hz), 4.80 (1H, d, J = 10.1 Hz), 4.61 (2H, s), 3.77 (6H, s), 3.37 (1H, m), 2.53 (1H, m), 2.41 (1H, m), 1.89 (1H, brs), 1.80 (1H, m), 1.59 (1H, m), 1.29-1.01 (4H, m), 0.81 (3H, t, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 139.6, 138.8, 120.4, 114.2, 102.9, 65.6, 55.7, 55.6, 38.1, 35.0, 32.8, 30.4, 22.9, 14.1; MS (EI) m/z 278 (M^+), 181 (100%); HRMS (EI) m/z calcd for $C_{17}H_{26}O_3$ (M^+): 278.1882, found: 278.1878.

(*S*)-3,5-Dimethoxy-4-(oct-1-en-4-yl)benzaldehyde 13

A mixture of the alcohol (58 mg, 0.21 mmol) and MnO_2 (180 mg, 2.1 mmol) in CH_2Cl_2 (4.2 mL) was stirred for 2 h at room temperature. The mixture was diluted with Et_2O, and filtered through a pad of Celite and the Celite layer was washed with Et_2O. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 3 / 7) to give **13** (55 mg, 97% yeild) as a colorless oil; $[\alpha]_D^{24}$ –5.3 (*c* 0.93, $CHCl_3$); FT-IR (neat) ν 1695, 1582, 1455, 1421, 1381, 1308, 1213, 1145 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.88 (1H, s), 7.04 (2H, s), 5.65 (1H, m), 4.89 (1H, d, J = 17.1 Hz), 4.80 (1H, d, J = 10.1 Hz), 3.85 (6H, s), 3.49 (1H, m), 2.57 (1H, m), 2.43 (1H, m), 1.85 (1H, m), 1.63 (1H, m), 1.29-0.99 (4H, m), 0.81 (3H, t, J = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.5, 138.1, 135.2, 128.7, 114.6, 105.1, 55.7, 55.5, 37.7, 35.6, 32.4, 30.3, 22.7, 14.0; MS (EI) m/z 276 (M^+), 179 (100%); HRMS (EI) m/z calcd for $C_{17}H_{24}O_3$ (M^+): 276.1725, found: 276.1745.

(4*R*,5*S*)-3-{(2*R*,3*R*)-3-[3,5-Dimethoxy-4-((*S*)-oct-1-en-4-yl)-phenyl]-3-hydroxy-2-methylpropionyl}-4-methyl-5-phenyl-oxazolidin-2-one 15

To a solution of **14** (59 mg, 0.22 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C was added Et_3N (0.09 mL, 0.65 mmol) and dibutylboron triflate (1.1 M in toluene, 0.51 mL, 0.56 mmol). After stirring for 1 h at 0 ºC, the mixture was cooled to –78 °C. Then, a solution of **13** (59 mg, 0.22 mmol) in CH_2Cl_2 (0.70 mL) was added and the mixture was stirred for 1 h at –78 °C and for 2.5 h at 0 °C. The mixture was quenched by additon of pH 7.0 phosphate buffer (1.8 mL) and MeOH (1.0 mL) at 0 °C, and then a mixture of MeOH (0.75 mL) and 30 % aqueous H_2O_2 (1.0 mL) at 0 °C. The resultant mixture was stirred for 1 h and the volatile material was evaporated under reduced pressure. The residue was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and

concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **15** (106 mg, 97% yeild) as a colorless solid; mp 53–54 °C; $[\alpha]_D^{24}$ –6.2 (*c* 0.93, $CHCl_3$); FT-IR (neat) ν 3498, 1780, 1696, 1638, 1582, 1455, 1367, 1195 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40-7.22 (5H, m), 6.58 (2H, s), 5.64 (1H, m), 5.32 (1H, d, *J* = 7.1 Hz), 4.91-4.85 (2H, m), 4.73 (1H, dd, *J* = 11.2, 1.0 Hz), 4.55 (1H, m), 4.21 (1H, m), 3.78 (6H, s), 3.36 (1H, m), 3.20 (1H, brs), 2.50 (1H, m), 2.41 (1H, m), 1.75 (1H, m), 1.60 (1H, m), 1.28 (3H, d, *J* = 6.8 Hz), 1.26-0.94 (4H, m), 0.85 (3H, d, *J* = 6.6 Hz), 0.77 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.7, 152.4, 140.3, 138.6, 132.8, 128.6, 128.5, 125.3, 120.4, 114.1, 102.2, 78.8, 75.1, 60.3, 55.0, 44.8, 37.9, 35.0, 32.8, 30.3, 22.7, 14.3, 14.1, 14.0, 11.7; MS (EI) *m/z* 509 (M^+), 468 (100%); HRMS (EI) *m/z* calcd for $C_{30}H_{39}NO_6$ (M^+): 509.2777, found: 509.2811.

(2*R*,3*R*)-3-{3,5-Dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-3-hydroxy-*N*-methoxy-*N*,2-dimethylpropionamide

To a suspension of HN(OMe)Me· HCl (41 mg, 0.42 mmol) in THF (0.47 mL) was added Me_3Al (1.03 M in hexane, 0.42 mL, 0.42 mmol) at 0 °C, and the mixture was stirred for 30 min. To this mixture was added **15** (72 mg, 0.14 mmol) in THF (0.47 mL) *via* cannula at –15 °C. The mixture was stirred for 15 min at –15 °C and then warmed to 0 °C. After stirring for 3 h at room temperature, the mixture was added dropwise *via* cannula into a stirred mixture of CH_2Cl_2 and 0.5 N aqueous HCl at 0 °C. The resulting two-phase mixture was stirred for 1 h at 0 °C. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 3 / 7) to give the amide (51 mg, 91% yeild) as a colorless solid; mp 77-80 °C; $[\alpha]_D^{25}$ –7.1 (*c* 0.84, $CHCl_3$); FT-IR (neat) ν 3421, 1638, 1582, 1456, 1421, 1134, 1114 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.54 (2H, s), 5.65 (1H, m), 4.98 (1H, d, *J* = 3.6 Hz), 4.89 (1H, ddd, *J* = 17.1, 2.4, 1.2 Hz), 4.78 (1H, dt, *J* = 10.0, 1.2 Hz), 4.04 (1H, s), 3.77 (6H, s), 3.61 (3H, s), 3.35 (1H, m), 3.17 (3H, s), 3.14 (1H, brs), 2.53 (1H, m), 2.44 (1H, m), 1.79 (1H, m), 1.59 (1H, m), 1.29-1.00 (4H, m), 1.14 (3H, d, *J* = 7.1 Hz), 0.81 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 177.5, 140.6, 138.9, 120.0, 114.1, 102.3, 77.2, 73.8, 61.5, 55.8, 41.5, 38.2, 35.0, 32.8, 31.9, 30.4, 22.8, 14.2, 11.0; MS (EI) *m/z* 393 (M^+), 352 (100%); HRMS (EI) *m/z* calcd for $C_{22}H_{35}NO_5$ (M^+): 393.2515, found: 393.2522.

(2*R*,3*R*)-3-{3,5-Dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-*N*-methoxy-*N*,2-dimethyl-3-triethylsilyloxypropionamide

To a suspension of the amide (62 mg, 0.16 mmol) in CH_2Cl_2 (3.2 mL) was added 2,6-lutidine (0.12 mL, 1.00 mmol), followed TESOTf (0.090 mL, 0.39 mmol) at 0 °C After stirring for 1.5 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give the silane (79 mg, 99% yeild) as a colorless oil; $[\alpha]_D^{26}$ –2.3 (*c* 1.06, $CHCl_3$); FT-IR (neat) ν 1657, 1607, 1583, 1456, 1421, 1098 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.53 (2H, s), 5.60 (1H, m), 4.83 (1H, dd, *J* = 17.1, 2.4 Hz), 4.74 -4.69 (2H, m), 3.73 (6H, s), 3.34 (1H, m), 3.20 (1H, brs), 3.16 (3H, s), 2.95 (3H, s), 2.51 (1H, m), 2.36 (1H, m), 1.80 (1H, m), 1.55 (1H, m), 1.31-0.92 (4H, m), 1.30 (3H, d, *J* = 6.6 Hz), 0.88 (9H, t, *J* = 7.8 Hz), 0.78 (3H, t, *J* = 7.3 Hz), 0.54 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 175.3, 142.8, 138.8, 119.7, 113.9, 102.9, 76.8, 61.0, 55.8, 45.0, 38.2, 34.9, 32.7, 31.5, 30.3, 22.8, 15.2, 14.2, 6.8, 4.8; MS (EI) *m/z* 507 (M^+), 466 (100%); HRMS (EI) *m/z* calcd for $C_{28}H_{49}NO_5Si$ (M^+): 507.3380, found: 507.3396.

(2*R*,3*R*)-3-{3,5-Dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-2-methyl-3-triethylsilyloxypropanal 16

To a stirred solution of the amide (79 mg, 0.16 mmol) in THF (0.79 mL) was added slowly DIBAL (1.01 M in toluene, 0.31 mL, 0.32 mmol) at –78 °C. After stirring for 3 h at the same temeperature, the mixture was quenched with 0.5 N aqueous HCl and then warmed to room temperature and diluted with Et_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give **16** (67 mg, 96% yeild) as a colorless oil; $[\alpha]_D^{26}$ +32.0 (*c* 0.93, $CHCl_3$); FT-IR (neat) ν 1726, 1639, 1606, 1584, 1455, 1419, 1213, 1100 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.72 (1H, d, *J* = 1.2 Hz), 6.46 (2H, s), 5.66 (1H, m), 5.03 (1H, d, *J* = 4.9 Hz), 4.88 (1H, ddd, *J* = 17.0, 2.4, 1.2 Hz), 4.79 (1H, ddd, *J* = 10.0, 2.3, 1.2 Hz), 3.76 (6H, s), 3.36 (1H, m), 2.63 (1H, m), 2.51 (1H, m), 2.41 (1H, m), 1.81 (1H, m), 1.60 (1H, m), 1.29-1.02 (4H, m), 1.09 (3H, d, *J* = 6.8 Hz), 0.86 (9H, t, *J* = 7.8 Hz), 0.81 (3H, t, *J* = 7.2 Hz), 0.53 (6H, q, *J* = 7.8 Hz); ^{13}C-NMR

(100 MHz, $CDCl_3$) δ 204.5, 141.2, 138.8, 120.2, 114.1, 102.4, 74.6, 54.7, 38.2, 35.1, 32.7, 30.4, 30.3, 22.8, 14.2, 8.6, 6.8, 6.7, 4.8; MS (EI) *m/z* 448 (M^+), 407 (100%); HRMS (EI) *m/z* calcd for $C_{26}H_{44}O_4Si$ (M^+): 448.3009, found: 448.3033.

(4*S*,5*R*,*E*)-Ethyl 5-{3,5-dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-4-methyl-5-triethylsilyloxypent-2-enoate

To a solution of triethyl phosphonoacetate (0.12 mL, 0.56 mmol) in THF (1.0 mL) was added NaH (60% in mineral oil, 21 mg, 0.52 mmol) at 0 °C. After stirring for 10 min, a solution of the aldehyde (167 mg, 0.37 mmol) in THF (0.90 mL) was added dropwise *via* cannula. After stirring for 30 min, H_2O was added to the mixture and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 99) to give the enoate (181 mg, 94% yeild) as a colorless oil; $[\alpha]_D^{25}$ +3.6 (*c* 1.33, $CHCl_3$); FT-IR (neat) ν 1722, 1653, 1606 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.93 (1H, dd, *J* = 15.6, 7.7 Hz), 6.40 (2H, s), 5.69 (1H, d, *J* = 15.6 Hz), 5.65 (1H, m), 4.86 (1H, dd, *J* = 17.1, 1.7 Hz), 4.77 (1H, d, *J* = 10.3 Hz), 4.49 (1H, d, *J* = 5.6 Hz), 4.15 (2H, qd, *J* = 7.1, 1.5 Hz), 3.74 (6H, s), 3.33 (1H, m), 2.59 (1H, m), 2.51 (1H, m), 2.38 (1H, m), 1.80 (1H, m), 1.59 (1H, m), 1.26 (3H, t, *J* = 7.1 Hz), 1.05 (3H, d, *J* = 6.6 Hz), 1.31-0.96 (4H, m), 0.87 (9H, t, *J* = 7.9 Hz), 0.80 (3H, t, *J* = 7.2 Hz), 0.52 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.5, 151.4, 141.8, 138.9, 120.8, 120.0, 114.0, 102.9, 78.2, 60.1, 45.1, 38.2, 35.1, 32.7, 30.4, 22.8, 14.4, 14.3, 14.2, 6.9, 6.8, 4.9, 4.8; MS (EI) *m/z* 518 (M^+), 391 (100%); HRMS (EI) *m/z* calcd for $C_{30}H_{50}O_5Si$ (M^+): 518.3428, found: 518.3409.

(4*S*,5*R*)-Mthyl 5-{3,5-dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-4-methyl-5-triethylsilyloxypentanoate

A mixture of the enoate (42 mg, 0.080 mmol) and magnesium turnings (20 mg, 0.8 mmol) in MeOH (0.40 mL) was stirred at 0 °C for 10 h. The mixture was diluted with hexane and Et_2O, and filtered through a pad of Celite. The filtrate was washed consecutively with 0.5 N aqueous HCl, saturated aqueous $NaHCO_3$, and brine, and dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 99) to give the ester (41 mg, 98% yeild) as a colorless oil; $[\alpha]_D^{26}$ +25.0 (*c* 1.26, $CHCl_3$); FT-IR (neat) ν 1741, 1639, 1607, 1583, 1455, 1420, 1135 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.43 (2H, s), 5.67 (1H, m), 4.88 (1H, d, *J* = 17.0 Hz), 4.78 (1H, d, *J* = 10.0 Hz), 4.35 (1H, d, *J* = 5.6 Hz), 3.58 (6H, s), 3.64 (3H, s), 3.33 (1H, m), 2.52 (1H, m), 2.38 (1H, m), 2.32 (1H, m), 2.23 (1H, m), 1.80 (1H, m), 1.78-1.56 (3H, m), 1.40 (1H, m), 1.38-1.02 (4H, m), 0.93 (3H, d, *J* = 6.6 Hz), 0.88 (9H, t, *J* = 7.9 Hz), 0.82 (3H, t, *J* = 7.2 Hz), 0.51 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.2, 142.9, 138.9, 119.7, 114.0, 103.1, 79.2, 51.5, 41.0, 38.3, 35.1, 32.7, 32.3, 30.4, 28.6, 22.9, 14.8, 14.2, 6.9, 4.9; MS (EI) *m/z* 506 (M^+), 391 (100%); HRMS (EI) *m/z* calcd for $C_{29}H_{50}O_5Si$ (M^+): 506.3428, found: 506.3413.

(1*R*,2*S*)-5-{3,5-Dimethoxy-4-[(*S*)-oct-1-en-4-yl]phenyl}-4-methyl-5-triethylsilyloxypentan-1-ol

To a solution of the ester (243 mg, 0.48 mmol) in THF (3.2 mL) was added LAH (22 mg, 0.58 mmol) at 0 °C. After stirring for 1.5 h at 0 °C, the mixture was quenched with 28% aqueous NH_3 and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give the alcohol (208 mg, 91% yeild) as a colorless oil; $[\alpha]_D^{27}$ +27.9 (*c* 1.00, $CHCl_3$); FT-IR (neat) ν 3335, 1639, 1607, 1583, 1455, 1419, 1135, 1099 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.43 (2H, s), 5.66 (1H, m), 4.88 (1H, d, *J* = 17.0 Hz), 4.78 (1H, d, *J* = 10.0 Hz), 4.32 (1H, d, *J* = 5.9 Hz), 3.75 (6H, s), 3.56 (2H, m), 3.33 (1H, m), 2.52 (1H, m), 2.40 (1H, m), 1.88-1.55 (4H, m), 1.48-1.01 (8H, m), 0.94 (3H, d, *J* = 6.6 Hz), 0.86 (9H, t, *J* = 7.9 Hz), 0.80 (3H, t, *J* = 7.2 Hz), 0.49 (6H, q, *J* = 7.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.2, 138.9, 119.6, 114.0, 103.1, 79.5, 63.2, 41.2, 38.3, 35.1, 32.7, 30.6, 30.4, 29.2, 22.8, 15.2, 14.2, 6.9, 4.9; MS (EI) *m/z* 478 (M^+), 391 (100%); HRMS (EI) *m/z* calcd for $C_{28}H_{50}O_4Si$ (M^+): 478.3478, found: 478.3480.

{(1*R*,2*S*)-1-[3,5-Dimethoxy-4-((*S*)-oct-1-en-4-yl)phenyl]-2-methylpent-4-enyloxy}triethylsilane 4

To a solution of the alcohol (49 mg, 0.10 mmol) in THF (0.52 mL) was added *o*-NO_2PhSeCN (47 mg, 0.21 mmol) and PBu_3 (0.050 mL, 0.21 mmol) at 0 °C. After stirring for 3 h, the mixture was added 30% aqueous H_2O_2 (0.080 mL, 0.67 mmol) over 10 min at 0 °C. The mixture was stirred for 8 h and diluted with Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine,

dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 24) to give **4** (44 mg, 93% yeild) as a colorless oil; $[\alpha]_D^{30}$ +31.9 (*c* 1.00, $CHCl_3$); FT-IR (neat) ν 1639, 1606, 1583, 1455, 1419, 1134 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.23 (2H, s), 5.81-5.60 (2H, m), 4.96 (2H, m), 4.87 (1H, d, *J* = 17.1 Hz), 4.78 (1H, d, *J* = 10.3 Hz), 4.35 (1H, d, *J* = 5.4), 3.75 (6H, s), 3.33 (1H, m), 2.54 (1H, m), 2.40 (1H, m), 2.12 (1H, m), 1.88-1.71 (3H, m), 1.60 (1H, m), 1.31-0.95 (4H, m), 0.91 (3H, d, *J* = 6.1 Hz), 0.86 (9H, t, *J* = 8.0 Hz), 0.80 (3H, t, *J* = 7.2 Hz), 0.50 (6H, q, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.2, 139.0, 137.7, 119.6, 115.5, 114.0, 103.2, 79.1, 41.4, 38.3, 37.9, 35.1, 32.8, 30.4, 22.9, 14.8, 14.2, 6.9, 5.0; MS (EI) *m/z* 460 (M^+), 419 (100%); HRMS (EI) *m/z* calcd for $C_{28}H_{48}O_3Si$ (M^+): 460.3373, found: 460.3364.

(+)-Cyclophane 17

A mixture of **4** (6.2 mg, 0.014 mmol) and Grubbs 2nd generation catalyst (4.0 mg, 0.0047 mmol) in dichloroethane (0.70 mL) was heated at 80 °C for 6 h. The solvent was evaporated and residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 99) to give **17** (2.3 mg, 40% yeild) as a colorless solid; mp 177-180 °C {lit.[6d] mp 176–178 °C}; $[\alpha]_D^{20}$ +26.9 (*c* 0.66, $CHCl_3$) {lit.[6d] $[\alpha]_D^{20}$ +22.0 (*c* 2.0, $CHCl_3$)}; The spectral data were identical with literature's data.[6d]

(-)-Diol

A mixture of **17** (2.2 mg, 0.003 mmol) and TBAF (1.0 M in THF, 0.02 mL, 0.015 mmol) in THF (0.11 mL) was stirred for 30 min. Then, saturated aqueous NH_4Cl and AcOEt were added to the mixture. The organic layer was separated, and the aqueous layer extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give the alcohol (1.2 mg, 74% yeild) as a colorless oil; mp 120-122 °C {lit.[6d] mp 124–126 °C}; $[\alpha]_D^{20}$ –145.9 (*c* 0.48, $CHCl_3$) {lit.[6d] $[\alpha]_D^{20}$ –131.4 (*c* 0.5, $CHCl_3$)}; The spectral data were identical with literature's data.[6d]

(-)-Tetra-*O*-methylcylindrocyclophane A 3

A mixture of the alcohol (15 mg, 0.076 mmol) and PtO_2 (0.8 mg) in EtOH (4.5 mL) was stirred under atmospheric pressure of H_2. After stirring for 1.5 h, the mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **3** (35 g, 99% yeild) as a colorless oil; mp 196-198 °C {lit.[6d] mp 195–197 °C}; $[\alpha]_D^{20}$ –8.44 (*c* 0.32, $CHCl_3$)}; The spectral data were identical with literature's data.[6d]

(-)-Cylindrocyclophane A (1)

To a solution of **3** (15 mg, 0.024 mmol) in 1-methyl-2-pyrrolidinone (3.0 mL) was added K_2CO_3 (20 mg, 0.14 mmol) followed by thiophenol (0.73 mL, 7.1 mmol). The reaction vessel was sealed and heated to 215 °C for 6 h, at which time it was diluted with AcOEt (30 mL) and pH 4 buffer (15 mL). The layer was separated and the aqueous layer was saturated with NaCl and extracted with AcOEt followed by 5% MeOH in CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **4** (12 mg, 85% yeild) as a white solid; mp 276-278 °C {lit.[6d] mp 276–278 °C}; $[\alpha]_D^{30}$ -24.7 (*c* 0.61, MeOH) {lit.[6d] $[\alpha]_D^{20}$ –20.7 (*c* 0.14, MeOH); FT-IR (neat) ν 3398, 1654, 1260, 1024 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 6.23 (2H, s), 6.05 (2H, s), 3.73 (2H, d, *J* = 9.4 Hz), 3.14 (2H, m), 2.03 (2H, m), 1.94 (2H, m), 1.53 (2H, m), 1.40-1.10 (12H, m), 1.07 (6H, d, *J* = 6.4 Hz), 1.15-0.79 (4H, m), 0.78 (6H, t, *J* = 7.1 Hz), 0.79-0.60 (8H, m); ^{13}C-NMR (125 MHz, CD_3OD) δ 158.9, 157.0, 143.9, 117.8, 109.0, 105.1, 81.6, 42.1, 36.9, 35.5, 35.3, 34.9, 31.7, 30.7, 29.9, 23.9, 17.0, 14.5; MS (FAB) *m/z* 607 [$(M+Na)^+$], 419 (100%); HRMS (FAB) *m/z* calcd for $C_{36}H_{56}O_6Na$ [$(M+Na)^+$]: 607.3935, found: 607.4001.

Synthesis of (+)-Cylindrocyclophane A

(*R*)-Ethyl 3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimeth-oxyphenyl)-6-hydroxyhexanoate 18

A mixture of **5** (1.30 g, 2.00 mmol) and Pd/C (130 mg) in THP (20 mL) was stirred under atmospheric pressure of H_2 for 3 h. To the mixture was added $Pd(OH)_2$ (195 mg) in thrice at 3 h intervals. After stirring for 1 d, the mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 2 / 3) to give **18** (1.92 g, 99% yeild) as a colorless oil; $[\alpha]_D^{27}$ –3.1 (*c* 1.16, $CHCl_3$); FT-IR (neat) ν 3418, 1730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.69 (4H, m), 7.44-7.36 (6H, m), 6.52 (2H, s), 4.73 (2H, s), 4.04 (2H, q, *J* = 5.8 Hz), 3.86 (1H, m), 3.75 (6H, s), 3.65-3.55 (2H, m), 2.82 (1H, dd, *J* = 15.4, 7.6 Hz), 2.72 (1H, dd, *J* = 15.4, 7.6 Hz), 1.93-1.87 (1H, m), 1.67 (1H, m), 1.46-1.36 (2H, m), 1.15 (3H, t, *J* = 5.8 Hz), 1.11 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.7, 158.7, 140.8, 135.6, 133.5, 129.7, 127.7, 117.6, 101.8, 65.5, 62.8, 59.9, 55.5, 38.7, 30.9, 30.8, 29.0, 26.8, 19.3, 14.1; MS (EI) *m/z* 564 (M^+), 461 (100%); HRMS (EI) *m/z* calcd for $C_{33}H_{44}O_6Si$ (M^+): 564.2907, found: 564.2919.

(*R*)-Ethyl 3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimeth-oxyphenyl)-6-oxohexanoate 19

To a solution of **18** (238 mg, 0.42 mmol) in CH_2Cl_2 (4.2 mL) was added $PhI(OAc)_2$ (203 mg, 0.63 mmol) and 1-Me-AZADO[18] (3.5 mg, 5 mol%) and the mixture was stirred for 4 h at room temperature. The reaction mixture was quenched with Na_2SO_3 and H_2O and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **19** (206 mg, 87% yeild) as a colorless oil; $[\alpha]_D^{28}$ –6.8 (*c* 1.16, $CHCl_3$); FT-IR (neat) ν 2716, 1730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.64 (1H, t, *J* = 1.3 Hz), 7.70-7.68 (4H, m), 7.44-7.36 (6H, m), 6.51 (2H, s), 4.74 (2H, s), 4.05 (2H, q, *J* = 5.8 Hz), 3.86 (1H, m), 3.74 (6H, s), 2.85 (1H, dd, *J* = 15.1, 7.1 Hz), 2.76 (1H, dd, *J* = 15.1, 7.1 Hz), 2.29 (1H, m), 2.21-2.13 (2H, m), 1.95 (1H, m), 1.16 (3H, t, *J* = 5.8 Hz), 1.11 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.2, 173.2, 158.7, 141.3, 135.6, 133.5, 129.7, 127.7, 116.2, 101.7, 65.5, 60.0, 55.5, 42.3, 38.6, 30.9, 26.8, 25.5, 19.3, 14.1; MS (EI) *m/z* 562 (M^+), 349 (100%); HRMS (EI) *m/z* calcd for $C_{33}H_{42}O_6Si$ (M^+): 562.2751, found: 562.2742.

(*R*)-Ethyl 3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimeth-oxyphenyl)hept-6-enoate

To a solution of methyltriphenylphosphonium bromide (155 mg, 0.44 mmol) in THF (1.4 mL) was added KHMDS (0.5 M in toluene, 0.77 mL, 0.38 mmol) at –78 °C. After stirring for 15 min, a solution of **19** (98 mg, 0.17 mmol) in THF (0.80 mL) was added dropwise *via* cannula. After stirring for 20 min at –78 °C, the mixture was brought to 0 °C and quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 12) to give the alkene (81 mg, 84% yeild) as a colorless oil; $[\alpha]_D^{28}$ –2.3 (*c* 1.16, $CHCl_3$); FT-IR (neat) ν 3071, 1733, 1639 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.44-7.35 (6H, m), 6.51 (2H, s), 5.80 (1H, m), 4.92 (1H, d, *J* = 17.1 Hz), 4.87 (1H, d, *J* = 10.1 Hz), 4.74 (2H, s), 4.03 (2H, q, *J* = 7.0 Hz), 3.85 (1H, m), 3.74 (6H, s), 2.76 (2H, m), 2.29 (1H, m), 1.96-1.80 (3H, m), 1.67 (1H, m), 1.13 (3H, t, *J* = 7.0 Hz), 1.10 (9H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.5, 158.8, 140.7, 139.3, 135.6, 133.6, 129.7, 127.7, 117.8, 113.8, 101.7, 65.6, 59.8, 55.6, 38.7, 32.6, 32.1, 31.3, 26.7, 19.3, 14.1; MS (EI) *m/z* 560 (M^+), 503 (100%); HRMS (EI) *m/z* calcd for $C_{34}H_{44}O_5Si$ (M^+): 560.2958, found: 560.2982.

(*R*)-Ethyl 3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl)heptanoate 20

A mixture of the alkene (802 mg, 1.43 mmol) and Pd/C (80 mg) in AcOEt (14 mL) was stirred under atmospheric pressure of H_2 for 1 h. The mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give **20** (789 mg, 98% yeild) as a colorless oil; $[\alpha]_D^{28}$ –2.3 (*c* 1.16, $CHCl_3$); FT-IR (neat) ν 1733 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (4H, m), 7.44-7.35 (6H, m), 6.51 (2H, s), 4.74 (2H, s), 4.02 (2H, q, *J* = 7.1 Hz), 3.80 (1H, m), 3.74 (6H, s), 2.74 (2H, m), 1.81 (1H, m), 1.58 (1H, m), 1.31-1.17 (4H, m), 1.13 (3H, t, *J* = 7.1 Hz), 1.10 (9H, s), 0.82 (3H, t, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 173.7, 158.8, 140.5, 135.6, 133.6, 129.7, 127.7, 118.4, 101.9, 65.6, 59.7, 55.6, 38.8, 32.9, 31.6, 30.1, 26.9, 22.9, 19.3,

14.1, 14.0; MS (EI) *m/z* 562 (M^+), 505 (100%); HRMS (EI) *m/z* calcd for $C_{34}H_{46}O_5Si$ (M^+): 562.8115, found: 562.3124.

(*R*)-3-(4-*tert*-butyldiphenylsilyloxymethyl-2,6-dimethoxyphenyl)heptanal

To a solution of **20** (76 mg, 0.14 mmol) in toluene (1.4 mL) was added DIBAL (1.01 M in toluene, 0.15 mL, 0.15 mmol) at –78 °C, and stirred for 1 h at the same temperature. The mixture was quenched with saturated aqueous NH_4Cl, and allowed to warm up to room temperature and diluted with AcOEt and H_2O. The organic layer was separated, and the aqueous layer was extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 9) to give the aldehyde (70 mg, 99% yeild) as a colorless oil; $[\alpha]_D^{29}$ −0.1 (*c* 1.11, $CHCl_3$); FT-IR (neat) ν 2713, 1723 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.60 (1H, t, *J* = 2.4 Hz), 7.70-7.68 (4H, m), 7.44-7.35 (6H, m), 6.52 (2H, s), 4.74 (2H, s), 3.86 (1H, m), 3.71 (6H, s), 2.81 (1H, ddd, *J* = 16.2, 8.4, 2.4 Hz), 2.68 (1H, ddd, *J* = 16.2, 6.5, 2.4 Hz), 1.84 (1H, m), 1.60 (1H, m), 1.31-1.13 (4H, m), 1.11 (9H, s), 0.84 (3H, t, *J* = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.3, 158.6, 140.9, 135.6, 133.5, 129.7, 127.7, 117.6, 101.8, 65.6, 55.5, 47.9, 33.1, 30.1, 29.6, 26.9, 22.6, 19.3, 14.0; MS (EI) *m/z* 518 (M^+), 461 (100%); HRMS (EI) *m/z* calcd for $C_{32}H_{42}O_4Si$ (M^+): 518.2852, found: 518.2872.

(*R*)-*tert*-Butyl[3,5-dimethoxy-4-(oct-1-en-4-yl)benzyloxy]-diphenylsilane

To a solution of methyltriphenylphosphonium bromide (1.01 g, 2.80 mmol) in THF (9.5 mL) was added KHMDS (0.5 M in toluene, 5.0 mL, 2.5 mmol) at –78 °C. After stirring for 15 min, a solution of the aldehyde (587 mg, 1.1 mmol) in THF (3.8 mL) was added dropwise *via* cannula. After stirring for 15 min at –78 °C, the reaction mixture was brought to 0 °C and quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20) to give the alkene (527 mg, 90% yeild) as a colorless oil; $[\alpha]_D^{28}$ –0.6 (*c* 0.62, $CHCl_3$). The spectral data were identical to those of the enantiomer.

(*S*)-4-Benzyl-3-{(2*S*,3*S*)-3-[3,5-dimethoxy-4-((*R*)-oct-1-en-4-yl)phenyl]-3-hydroxy-2-methylpropanoyl}oxazolidin-2-one 22

To a solution of **21** (22 mg, 0.094 mmol) in CH_2Cl_2 (0.40 mL) at 0 °C was added Et_3N (0.02 mL, 0.14 mmol) and dibutylboron triflate (1.0 M in toluene, 0.12 mL, 0.12 mmol). After stirring for 1 h at 0 ºC, the mixture was cooled to –78 °C. After addition of a solution of *ent*-**13** (12 mg, 0.043 mmol) in CH_2Cl_2 (0.50 mL) *via* cannula, the mixture was stirred for 30 min at –78 °C and for 2 h at 0 °C. The reaction was quenched by additon of pH 7.0 phosphate buffer (0.30 mL) and MeOH (0.20 mL) at 0 °C, and then a mixture of MeOH (0.15 mL) and 30 % aqueous H_2O_2 (0.20 mL) at 0 °C. The resultant mixture was stirred for 1 h and the volatile material was evaporated under reduced pressure. The residue was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **22** (18 mg, 83% yeild) as a colorless oil; $[\alpha]_D^{27}$ +50.4 (*c* 0.36, $CHCl_3$); FT-IR (neat) ν 3504, 1782, 1698, 1638 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (3H, m), 7.21-7.18 (2H, m), 6.55 (2H, s), 5.59 (1H, ddt, *J* = 17.0, 10.1, 7.0 Hz), 4.97 (1H, d, *J* = 4.6 Hz), 4.90 (1H, dd, *J* = 17.0, 2.4 Hz), 4.78 (1H, dt, *J* = 10.1, 1.1 Hz), 4.51 (1H, m), 4.17-4.11 (2H, m), 4.04 (1H, m), 3.77 (6H, s), 3.34 (1H, tt, *J* = 8.7, 6.3 Hz), 3.23 (1H, dd, *J* = 13.4, 3.4 Hz), 2.90 (1H, brs), 2.78 (1H, dd, *J* = 13.4, 9.6 Hz), 2.48 (1H, m), 2.37 (1H, m), 1.74 (1H, m), 1.60-1.54 (3H, m), 1.27-1.17 (5H, m), 0.80 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.6, 152.9, 140.1, 139.0, 135.0, 129.4, 129.0, 127.5, 120.5, 114.3, 102.2, 74.5, 66.1, 55.7, 44.5, 38.1, 37.8, 35.0, 32.8, 30.9, 30.4, 22.8, 14.1, 11.3, 10.4; MS (EI) *m/z* 509 (M^+), 179 (100%); HRMS (EI) *m/z* calcd for $C_{30}H_{39}NO_6$ (M^+): 509.2777, found: 509.2779.

Synthesis of a half-sized analogue

{(1*R*,2*S*)-1-[3,5-Dimethoxy-4-((*S*)-oct-1-en-4-yl)phenyl]-2-methylbut-3-enyloxy}triethylsilane

To a solution of methyltriphenylphosphonium bromide (119 mg, 0.29 mmol) in THF (1.0 mL) was added KHMDS (0.7 M in toluene, 0.39 mL, 0.28 mmol) at –78 °C. After stirring for 15 min, a solution of the aldehyde (41 mg, 0.092 mmol) in THF (0.90 mL) was added dropwise *via* cannula. After stirring for 15 min at –78 °C, the mixture was brought to 0 °C and quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20) to give the alkene (39 mg, 99% yeild) as a colorless oil; $[\alpha]_D^{28}$ +18.6 (*c* 0.73, $CHCl_3$); FT-IR (neat) ν 1639, 1607, 1584 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.44 (2H, s), 6.78-5.59 (2H, m), 4.94 (1H, d, *J* = 9.0 Hz), 4.92-4.82 (2H, m), 4.78 (1H, d, *J* = 10.3 Hz), 4.36 (1H, d, *J* = 6.3 Hz), 3.76 (6H, s), 3.34 (1H, m), 2.53 (1H, m), 2.48-2.32 (2H, m), 1.81 (1H, m), 1.59 (1H, m), 1.32-1.00 (4H, m), 1.04 (3H, t, *J* = 6.8 Hz), 0.87 (9H, t, *J* = 8.0 Hz), 0.80 (3H, t, *J* = 7.2 Hz), 0.50 (6H, q, *J* = 8.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.9, 141.4, 139.0, 119.8, 114.0, 113.9, 103.3, 79.2, 46.0, 38.3, 35.1, 32.7, 30.4, 22.8, 14.7, 14.1, 6.8, 4.9; MS (EI) *m/z* 446 (M^+), 391 (100%); HRMS (EI) *m/z* calcd for $C_{27}H_{46}O_3Si$ (M^+): 446.3216, found: 446.3214.

{(1*R*,2*S*)-1-[3,5-Dimethoxy-4-((*R*)-octan-4-yl)phenyl]-2-methylbutoxy}triethylsilane

A mixture of the alkene (35 mg, 0.076 mmol) and PtO_2 (1.0 mg) in EtOH (3.8 mL) was stirred under atmospheric pressure of H_2. After stirring for 1 h, the mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give the silane (35 g, 99% yeild) as a colorless oil; $[\alpha]_D^{24}$ +37.5 (*c* 0.69, $CHCl_3$); FT-IR (neat) ν 1606, 1582, 1455, 1420, 1218, 1137 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.43 (2H, s), 4.31 (1H, d, *J* = 6.2 Hz), 3.75 (6H, s), 3.27 (1H, m), 1.77 (2H, m), 1.75-1.50 (3H, m), 1.34-0.95 (6H, m), 0.98-0.78 (21H, m), 0.47 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 143.4, 120.3, 103.3, 79.4, 43.2, 36.1, 34.8, 33.3, 30.5, 30.3, 26.0, 22.9, 21.3, 14.4, 14.3, 14.1, 11.9, 6.8, 4.9; MS (EI) *m/z* 450 (M^+), 393 (100%); HRMS (EI) *m/z* calcd for $C_{27}H_{50}O_3Si$ (M^+): 450.7696, found: 450.3507.

{(1*R*,2*S*)-1-[3,5-Dimethoxy-4-((*R*)-octan-4-yl)phenyl]-2-methylbutan-1-ol 23

To a solution of the silane (34 mg, 0.075 mmol) in THF (0.38 mL) was added TBAF (1.0 M in THF, 0.23 mL, 0.23 mmol). After stirring for 3 h, H_2O and Et_2O were added to the mixture. The organic layer was separated, and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 5) to give **23** (22 mg, 88% yeild) as a colorless solid; $[\alpha]_D^{25}$ +11.9 (*c* 0.44, $CHCl_3$); FT-IR (neat) ν 3412, 1606, 1581, 1455, 1420, 1137 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.47 (2H, s), 4.44 (1H, d, *J* = 5.8 Hz), 3.77 (6H, s), 3.26 (1H, m), 1.82-1.61 (4H, m), 1.56-1.04 (10H, m), 0.96 (3H, d, *J* = 6.5 Hz), 0.89 (3H, t, *J* = 7.3 Hz), 0.81 (6H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.6, 121.0, 102.5, 78.5, 41.9, 36.0, 34.9, 33.3, 30.6, 26.0, 22.9, 21.4, 14.3, 14.1, 14.1, 11.7; MS (EI) *m/z* 336 (M^+), 279 (100%); HRMS (EI) *m/z* calcd for $C_{21}H_{36}O_3$ (M^+): 336.2664, found: 336.2655.

5-(4-Dimethoxymethyl-2,6-dimethoxyphenyl)nonane-5-ol

To a stirred solution of **24** (2.8 g, 10.4 mmol) in THF (52 mL) was slowly added *n*-BuLi (1.6 M in hexane, 14 mL, 22.8 mmol) at –78 °C. After stirring for 3 h at the same temperature, the mixture was quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 3) to give the alcohol (2.41 g, 66% yeild) as a colorless oil; FT-IR (neat) ν 3522, 1612, 1575, 1456, 1415, 1351, 1114 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.70 (2H, s), 6.07 (1H, s), 5.33 (1H, s), 3.83 (6H, s), 3.35 (6H, s), 2.16 (2H, td, *J* = 12.3, 4.4 Hz), 1.60 (1H, dd, *J* = 12.3, 4.4 Hz), 1.37 (2H, m), 1.30-1.19 (4H, m), 1.03 (2H, m), 0.83 (6H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 158.2, 137.6, 121.7, 104.3, 102.8, 80.1, 56.2, 52.8, 41.8, 26.4, 23.2, 14.0; MS (EI) *m/z* 353 (M^+), 297 (100%); HRMS (EI) *m/z* calcd for $C_{20}H_{33}O_5$ (M^+): 353.2328, found: 353.2342.

Olefin mixture 25

To a stirred solution of the alcohol (2.4 g, 6.8 mmol) and trimethyl orthoformate (0.75 mL, 6.8 mmol) in MeOH (23 mL) was added conc. aqueous HCl (0.10 mL) at –78 °C. After stirring for 3 h at –78 °C, the reaction mixture was warmed to 0 °C and quenched with the aqueous K_2CO_3 and diluted with Et_2O. The organic layer was separated, and aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure (*E*:*Z* = 2.2:1). Thermodynamically, *Z* olefin was preferentially afforded. Inseparable *Z* olefin could not be reduced on next step.

[3,5-Dimethoxy-4-(nonan-5-yl)phenyl]methanol

A mixture of **25** and Pd/C (228 mg) in AcOEt (68 mL) was stirred under atmospheric pressure of H_2. After stirring for 3 h, the mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. To this residue was added AcOH (10 mL) and H_2O (2 mL) and the mixture was stirred at 100 °C for 5 h. After cooling, the mixture was concentrated under reduced pressure. The residue was roughly purified by silica gel column chromatography (AcOEt / Hexane = 1 / 1) to give the aldehyde. To a solution of the aldehyde in THP (68 mL) was added LAH (258 mg, 6.8 mmol) at 0 °C. The mixture was stirred for 1 h at room temperature and quenched with H_2O. The reaction mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtered was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 2 / 3) to give the alcohol (1.04 g, 52% yeild) as a colorless oil; FT-IR (neat) ν 3324, 1583, 1455, 1421, 1137 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.54 (2H, s), 4.64 (2H, s), 3.78 (6H, s), 3.26 (1H, m), 1.75 (2H, m), 1.55 (2H, m), 1.30-0.98 (8H, m), 0.81 (6H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 159.1, 139.4, 121.5, 103.1, 68.5, 55.7, 35.1, 33.4, 30.5, 22.9, 14.1; MS (EI) *m/z* 294 (M^+), 181 (100%); HRMS (EI) *m/z* calcd for $C_{18}H_{30}O_3$ (M^+): 294.2195, found: 294.2192.

5-Hydroxymethyl-2-(nonan-5-yl)benzene-1,3-diol 26

To a solution of the alcohol in CH_2Cl_2 (18 mL) was slowly added BBr_3 (1.0 M in CH_2Cl_2, 4.4 mL, 4.4 mmol) at –78 °C. The mixture was warmed to room temperature and stirred for 12 h. The mixture was slowly poured into 10% aqueous NaOH and stirred for 1 h. The reaction mixture was quenched with 10% aqueous HCl and extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 1) to give **26** (215 g, 54% yeild) as a yellow oil; FT-IR (neat) ν 3389, 1591, 1430, 1019 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.34 (2H, s), 5.28 (2H, brs), 4.51 (2H, s), 3.09 (1H, m), 1.84 (2H, m), 1.65 (2H, m), 1.32-1.13 (8H, m), 0.82 (6H, t, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.7, 139.2, 117.6, 107.1, 64.8, 35.7, 33.5, 30.6, 22.8, 14.0; MS (EI) *m/z* 266 (M^+), 153 (100%); HRMS (EI) *m/z* calcd for $C_{16}H_{26}O_3$ (M^+): 266.1882, found: 266.1864.

3,5-Dihydroxy-4-(nonan-5-yl)benzaldehyde (27).

To a solution of **26** (320 mg, 1.2 mmol) in CH_2Cl_2 (7.1 mL) was slowly added $TEMPO^+Cl^-$ (322 mg, 1.7 mmol) at 0 °C. After stirring for 5 min, H_2O and $CHCl_3$ was added to the mixture. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 2) to give **27** (220 mg, 69% yeild) as a yellow oil; FT-IR (neat) ν 3398, 1680, 1588, 1433, 1025 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.78 (1H, s), 6.92 (2H, s), 5.57 (2H, brs), 3.26 (1H, m), 1.90 (2H, m), 1.77 (2H, m), 1.34-1.07 (8H, m), 0.83 (6H, t, *J* = 7.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 192.1, 156.1, 135.0, 126.2, 109.5, 36.3, 33.1, 30.5, 22.8, 14.0; MS (EI) m/z 264 (M^+), 151 (100%); HRMS (EI) *m/z* calcd for $C_{16}H_{24}O_3$ (M^+): 264.1725, found: 264.1692.

3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl) benzaldehyde 28

To a solution of **27** (19 mg, 0.072 mmol) in CH_2Cl_2 was added TBSCl (22 mg, 0.14 mmol) and imidazole (15 mg, 0.21 mmol). After sterring for 3 h, the mixture was quenched by addition of H_2O and extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 8) to give **28** (29 mg, 80% yeild) as

a colorless oil; FT-IR (neat) ν 1701, 1573, 1429, 1260, 1071 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.78 (1H, s), 6.91 (1H, s), 6.90 (1H, s), 3.32 (1H, m), 1.84 (2H, m), 1.64 (2H, m), 1.30-1.03 (8H, m), 1.03 (18H, s), 0.82 (6H, t, *J* = 7.1 Hz), 0.33 (6H, s), 0.28 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 191.6, 156.3, 155.6, 134.6, 134.3, 112.0, 111.8, 36.6, 32.8, 30.6, 26.2, 25.8, 22.9, 18.6, 18.3, 14.1, –3.6, –4.1; MS (EI) *m/z* 492 (M^+), 323 (100%); HRMS (EI) *m/z* calcd for $C_{28}H_{52}O_3Si_2$ (M^+): 492.3455, found: 492.3457.

(4*R*,5*S*)-3-{(2*R*,3*R*)-3-[3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl)phenyl]-3-hydroxy-2-methylpropanoyl}-4-methyl-5-phenyloxazolidin-2-one 29

To a solution of **14** (27 mg, 0.12 mmol) in CH_2Cl_2 (0.57 mL) at 0 °C was added Et_3N (0.03 mL, 0.22 mmol) and dibutylboron triflate (1.1 M in toluene, 0.15 mL, 0.15 mmol). After stirring for 1 h at 0 °C, the mixture was cooled to –78 °C. Then, a solution of **28** (28 mg, 0.06 mmol) in CH_2Cl_2 (0.30 mL) was added, and stirred for 1 h at the same temperature and for 2.5 h at 0 °C. The mixture was quenched by the additon of pH 7.0 phosphate buffer (1.8 mL) and MeOH (1.0 mL) at 0 °C, and then a mixture of MeOH (0.75 mL) and 30 % aqueous H_2O_2 (1.0 mL) at 0 °C. The resultant mixture was stirred for 1 h and the volatile material was evaporated under reduced pressure. The residue was extracted with Et_2O and the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 4) to give **29** (40 mg, 97% yeild) as a colorless oil; $[\alpha]_D^{23}$ −0.4 (*c* 0.55, $CHCl_3$); FT-IR (neat) ν 3410, 1781, 1427, 1016 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43-7.36 (3H, m), 7.26 (2H, d, *J* = 6.8 Hz), 6.50 (1H, s), 6.47 (1H, s), 5.51 (1H, d, *J* = 7.2 Hz), 4.93 (1H, d, *J* = 4.1 Hz), 4.69 (1H, m), 4.08 (1H, m), 3.21 (1H, m), 2.73 (1H, s), 1.77 (2H, m), 1.60 (2H, m), 1.21-1.09 (11H, m), 1.01 (18H, s), 0.88 (3H, d, *J* = 5.5 Hz), 0.81-0.77 (6H, m), 0.32 (3H, s), 0.30 (3H, s), 0.27 (3H, s), 0.24 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 176.1, 155.6, 154.8, 152.4, 139.1, 133.1, 128.8, 128.7, 125.5, 125.3, 109.2, 108.5, 78.9, 76.7, 73.7, 60.4, 54.9, 44.7, 35.9, 33.1, 33.0, 30.7, 30.7, 26.3, 25.9, 23.0, 23.0, 18.6, 18.3, 14.3, 14.2, 14.1, 14.1, 10.8, –3.5, –3.7, –3.9, –4.2; MS (EI) *m/z* 725 (M^+), 323 (100%); HRMS (EI) *m/z* calcd for $C_{41}H_{67}NO_6Si_2$ (M^+): 725.4507, found: 725.4493.

(4*R*,5*S*)-3-{(2*R*,3*R*)-3-[3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl)phenyl]-3-hydroxy-2-methyl-3-triethyl-silyloxypropanoyl}-4-methyl-5-phenyloxazolidin-2-one

To a suspension of **29** (40 mg, 0.055 mmol) in DMF (0.30 mL) was added TESCl (0.014 mL, 0.080 mmol), followed by imidazole (9.0 mg, 0.13 mmol). After stirring for 3 h, H_2O was added to the mixture and extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 6) to give the silane (46 mg, 99% yeild) as a colorless oil; $[\alpha]_D^{22}$ –15.0 (*c* 0.43, $CHCl_3$); FT-IR (neat) ν 1788, 1428, 1339, 1067 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (3H, m), 7.20 (2H, d, *J* = 5.3 Hz), 6.45 (1H, s), 6.42 (1H, s), 5.51 (1H, d, *J* = 6.8 Hz), 4.62 (1H, d, *J* = 7.5 Hz), 4.39 (1H, m), 4.09 (1H, m), 3.21 (1H, m), 1.77 (2H, m), 1.56 (2H, m), 1.29 (3H, d, J = 5.5 Hz), 1.28-0.96 (8H, m), 1.05 (18H, s), 0.88 (9H, d, *J* = 7.9 Hz), 0.83 (3H, d, *J* = 6.6 Hz), 0.71 (6H, m), 0.51 (6H, q, *J* = 7.9 Hz), 0.32 (3H, s), 0.30 (3H, s), 0.28 (3H, s), 0.25 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 174.7, 155.4, 154.6, 152.4, 141.0, 133.2, 128.6, 125.5, 125.0, 109.9, 109.3, 79.0, 55.4, 46.7, 35.9, 33.2, 33.0, 30.7, 30.7, 30.3, 26.3, 26.0, 23.0, 22.9, 18.6, 18.3, 14.3, 14.1, 14.0, 13.3, 6.7, 4.8, –3.4, –3.9, –3.9, –4.4; MS (EI) *m/z* 839 (M^+), 607 (100%); HRMS (EI) *m/z* calcd for $C_{47}H_{81}NO_6Si_3$ (M^+): 839.5372, found: 839.5361.

(2*S*,3*R*)-3-[3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl)phenyl]-2-methyl-3-triethylsilyloxypropane-1-ol 30

To a solution of the oxazolin-2-one (47 mg, 0.44 mmol) in THF was added $LiBH_4$ (10 mg, 0.26 mmol) at 0 °C. After sterring for 12 h, the mixture was quenched by addition of H_2O and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 6) to give **30** (34 mg, 88% yeild) as a colorless oil; $[\alpha]_D^{23}$ +31.6 (*c* 0.23, $CHCl_3$); FT-IR (neat) ν 3434, 1604, 1573, 1428, 1258, 1065 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.37 (1H, s), 6.34 (1H, s), 4.54 (1H, d, *J* = 4.8 Hz), 3.58 (1H, m), 3.41 (1H, m), 3.20 (1H, m), 2.72 (1H, s), 2.09 (1H, m), 1.81 (2H, m), 1.61 (2H, m), 1.22-0.87 (8H, m), 0.98 (18H, s), 0.85-0.78 (18H, m), 0.52 (6H, q, *J* = 7.9 Hz), 0.27 (6H, s), 0.22 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 155.3, 154.5, 139.3, 124.9, 110.4, 109.8, 78.8, 65.6, 42.2, 35.9, 33.1, 33.0, 30.7, 30.6, 26.3, 25.9, 23.0, 23.0, 18.6, 18.3, 14.2, 13.2, 6.7, 4.7, –3.6, –3.6, –4.0, –4.1; MS (EI) *m/z* 666 (M^+), 607 (100%); HRMS (EI) *m/z* calcd for $C_{37}H_{74}O_4Si_3$ (M^+): 666.4895, found: 666.4925.

(2*R*,3*R*)-3-[3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl)phenyl]-2-methyl-3-triethylsilyloxypropanal 31

To a solution of **30** (338 mg, 0.049 mmol) in CH_2Cl_2 (0.50 mL) was added $PhI(OAc)_2$ (9.0 mg, 0.074 mmol) and 1-Me-AZADO[18] (0.4 mg, 0.002 mmol) and mixture was stirred at ambient temperature for 2 h. The reaction mixture was quenched with Na_2SO_3 (solid) and H_2O and extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 10) to give **31** (23 mg, 70% yeild) as a colorless oil; $[\alpha]_D^{30}$ +12.3 (*c* 0.46, $CHCl_3$); FT-IR (neat) ν 1727, 1574, 1428, 1258, 1068 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 9.73 (1H, d, *J* = 1.4 Hz), 6.34 (1H, s), 6.32 (1H, s), 4.82 (1H, d, *J* = 5.0 Hz), 3.19 (1H, m), 2.57 (1H, m), 1.77 (2H, m), 1.60 (2H, m), 1.37-0.87 (8H, m), 1.06 (3H, d, *J* = 6.7 Hz), 1.00 (18H, s), 0.87-0.78 (15H, m), 0.51 (6H, q, *J* = 7.9 Hz), 0.27 (6H, s), 0.21 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.5, 140.0, 125.2, 109.8, 109.2, 74.7, 54.6, 35.9, 33.1, 32.9, 30.7, 30.6, 26.2, 25.9, 23.0, 22.9, 18.6, 18.3, 14.1, 8.9, 6.7, 4.8, –3.5, –3.6, –4.0, –4.1; MS (EI) m/z 664 (M^+), 607 (100%); HRMS (EI) *m/z* calcd for $C_{37}H_{72}O_4Si_3$ (M^+): 664.4738, found: 664.4727.

(2*S*,3*R*,*Z*)-3-[3,5-Bis-(*tert*-butyldimethylsilyloxy)-4-(nonan-5-yl)phenyl]-2-methyl-3-triethylsilyloxypent-3-ene.

To a solution of ethyltriphenylphosphonium iodide (72 mg, 0.17 mmol) in THF (2.0 mL) was added *n*-BuLi (1.6 M in hexane, 0.030 mL, 0.050 mmol) at –78 °C. After stirring for 20 min, a solution of **31** (23 mg, 0.035 mmol) in THF (2.0 mL) was added dropwise *via* cannula. After stirring for 1.5 h at –78 °C, the reaction mixture was brought to 0 °C and quenched with saturated aqueous NH_4Cl and diluted with Et_2O. The organic layer was separated, and the aqueous layer extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20) to give the alkene (17 mg, 72% yeild) as a colorless oil; $[\alpha]_D^{22}$ +40.9 (*c* 0.33, $CHCl_3$); FT-IR (neat) ν 1574, 1427, 1258, 1066 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.30 (1H, s), 6.29 (1H, s), 5.30 (1H, m), 5.12 (1H, dd, *J* = 10.9, 1.8 Hz), 4.14 (d, *J* = 6.8 Hz), 3.17 (1H, m), 2.65 (1H, m), 1.80 (2H, m), 1.57 (2H, m), 1.35 (dd, *J* = 6.8, 1.8 Hz), 1.36-0.97 (8H, m), 1.02 (18H, s), 0.86-0.75 (15H, m), 0.49 (6H, q, *J* = 7.9 Hz), 0.26 (6H, s), 0.21 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 154.8, 154.1, 142.0, 133.4, 123.9, 123.6, 110.3, 110.0, 79.0, 40.4, 35.8, 33.2, 33.1, 30.6, 26.3, 26.0, 23.0, 23.0, 18.6, 18.3, 16.9, 14.2, 12.9, 6.8, 4.9, –3.6, –4.1; MS (EI) *m/z* 647 [$(M-Et)^+$], 607 (100%); HRMS (EI) *m/z* calcd for $C_{37}H_{71}O_3Si_3$ [$(M-Et)^+$]: 647.4711, found: 647.4704.

1,3-Bis-(*tert*-butyldimethylsilyloxy)-2-[4-(nonan-5-yl)]-5-[(1R,2S)-(2-methyl-1-triethylsilyloxypentyl)]benzene.

A mixture of the alkene (17 mg, 0.025 mmol) and Pd/C (2.0 mg) in AcOEt (0.60 mL) was stirred under atmospheric pressure of H_2. After stirring for 3 h, the mixture was filtered through a pad of Celite and the Celite layer was washed with AcOEt. The combined filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 20) to give the pentane (16 mg, 94% yeild) as a colorless oil; $[\alpha]_D^{23}$ +20.9 (*c* 0.31, $CHCl_3$); FT-IR (neat) ν 1514, 1427, 1215 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.31 (1H, s), 6.29 (1H, s), 4.14 (1H, d, *J* = 6.3 Hz), 3.18 (1H, m), 1.79 (2H, m), 1.59 (2H, m), 1.32-0.90 (12H, m), 1.02 (18H, s), 0.90 (3H, d, *J* = 6.7 Hz), 0.87-0.78 (18H, m), 0.49 (6H, q, *J* = 7.8 Hz), 0.25 (6H, s), 0.21 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 142.2, 124.1, 110.4, 110.0, 79.3, 41.2, 35.9, 35.0, 33.2, 33.0, 30.7, 30.6, 26.3, 26.0, 23.0, 23.0, 20.3, 15.5, 14.2, 14.2, 6.8, 4.9, –3.5, –3.6, –4.0, –4.1; MS (EI) *m/z* 678 (M^+), 607 (100%); HRMS (EI) *m/z* calcd for $C_{39}H_{78}O_3Si_3$ (M^+): 678.5259, found: 678.5280.

Half-sized 32.

To a solution of the silane (7.0 mg, 0.010 mmol) in THF (0.10 mL) was added TBAF (1.0 M in THF, 0.15 mL, 0.15 mmol). After stirring for 48 h, H_2O and AcOEt was added to the mixture. The organic layer was separated, and the aqueous layer extracted with AcOEt. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (AcOEt / Hexane = 1 / 2) to give **32** (3.0 mg, 84% yeild) as a colorless oil; $[\alpha]_D^{26}$ +2.8 (*c* 0.12, MeOH); FT-IR (neat) ν 3367, 1620, 1591, 1428, 1376, 1015 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 6.23 (2H, s), 4.16 (1H, d, *J* = 6.5 Hz), 3.17 (1H, m), 1.96 (2H, m), 1.69 (1H, m), 1.52 (2H, m), 1.35-0.90 (12H, m), 0.92 (3H, d, *J* = 6.7 Hz), 0.83-0.79 (9H, m); ^{13}C-NMR (125 MHz, CD_3OD) δ 157.9, 143.8, 117.9, 106.5, 79.4, 41.0, 36.8, 36.4, 34.4, 31.7, 23.9, 21.3, 15.7, 14.6, 14.6; MS (EI) *m/z* 336 (M^+), 205 (100%); HRMS (EI) *m/z* calcd for $C_{21}H_{36}O_3$ (M^+): 336.2664, found: 336.2650.