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ELECTRONIC SUPPORTING INFORMATION

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B E L O N G I N G TO T H E P A P E R

Total synthesis of (+)-bretonin B: Access to the (*E*,*Z*,*E*)-triene core by a late-stage Peterson elimination of a convergently assembled silyl ether

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General Information

All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under argon. Tetrahydrofuran (THF), diethyl ether (Et_2O) and dichloromethane (CH_2Cl_2) were purified using a SPS-800 solvent purification system (M. Braun). All other chemicals were either commercially available or prepared according to the cited references. TLC was performed on silica coated glass plates (silica gel 60 F_{254}) with detection by UV (254 nm), $KMnO_4$ (0.5% in water) or ceric ammonium molybdate (CAM) with subsequent heating.

Flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh) with the indicated eluent. Common solvents for chromatography [pentane, ethyl acetate, diethyl ether (Et_2O)] were distilled prior to use.

HPLC analyses was performed using the stationary phase Daicel, Chiralpak, AD-RH (analytical: 125 × 2.1 mm, 3 µm) employing acetonitrile/water as eluent and UV-detection at 20 °C.

IR: JASCO IR-4100 (ATR).

MS / HRMS: Finnigan MAT 8200 (EI) / Finnigan MSD 5973 (HR-EI) / Finnigan LCQ classic (ESI) / Thermo Finnigan LTQ FT (HRMS-ESI) / Thermo Sientific LTQ Orbitrap XL (HRMS-ESI).

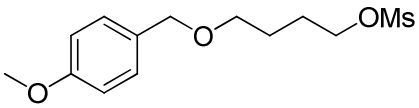
^1H and ^{13}C NMR: Bruker AV-250, Bruker AV-360, Bruker AV-500, Bruker AV-500cr. Chemical shifts are reported relative to solvent signals [$CDCl_3$ $\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.16 ppm]. The symbol * denotes an interconvertible assignment. Abbreviations for the multiplicities of ^1H NMR and ^{13}C NMR signals are s (singlet), d (duplet), t (triplet), q (quartet) p (pentet), and sext (sextet). The multiplicities of the ^{13}C NMR signal were determined by DEPT experiments, assignments are based on COSY, HMBC and HMQC experiments. ^1H or ^{13}C NMR signals are usually assigned using significant short sections of the molecular formular.

Specific rotations were measured using a Perkin-Elmer 241 MC Polarimeter.

UV-Vis: Perkin Elmer Lambda 35.

Experimental Procedures

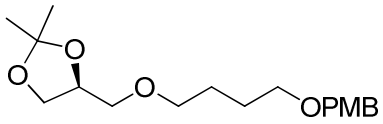
4-(4-Methoxybenzyloxy)butylmethanesulfonate (S1)



$C_{13}H_{20}O_5S$
MW: 288.36 g/mol

4-((4-Methoxybenzyl)oxy)butan-1-ol[1] (2.30 g, 10.9 mmol) in THF (50 mL) was cooled to 0 °C, and triethylamine (1.60 g, 15.8 mmol) and methanesulfonylchloride (1.33 g, 11.6 mmol) were successively added. After five hours at 0 °C saturated aqueous NH_4Cl (20 mL) was added and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with brine (15 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude product **S1** was directly submitted to the next step without any further purification.

(*S*)-4-((4-(4-Methoxybenzyloxy)butoxy)methyl)-2,2-dimethyl-1,3-dioxolane (6)



$C_{18}H_{28}O_5$
MW: 324.41 g/mol

(*S*)-(2,2-Dimethyl-1,3-dioxolan-4-yl)methanol[1] **5** (1.40 g, 10.6 mmol) was solved in DMF (120 mL) at 0 °C, before sodium hydride (467 mg, 11.6 mmol, 60% in mineral oil) was added portionwise. After one and a half hours the mesylate **S1** (10.9 mmol) in DMF (20 mL) was added dropwise. The suspension was stirred overnight at room temperature, before saturated aqueous NH_4Cl (100 mL) was added and the aqueous layer was extracted with diethyl ether (5 × 20 mL). The combined organic layers were washed with brine (50 mL), dried with Na_2SO_4 and concentrated *in vacuo*. After purification by flash chromatography (pentane/ether = 4/1) the desired ether **6** (2.73 g, 8.42 mmol, 79%) was isolated as slightly yellow oil.

TLC: R_f = 0.35 (pentane/Et_2O) [$KMnO_4$].

[1] Commercially available

Specific rotation: $[\alpha]_D^{20}$ = +7.6 (*c* = 1.6 $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2985 (w, CH), 2934 (w, CH), 2859 (w, CH), 2548 (w), 2159 (w), 2032 (w), 1612 (s), 1513 (s), 1244.83 (s), 1088 (s).

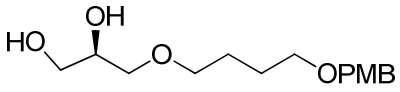
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.36 [s, 3 H, C(C*H*$_3$)(CH$_3$)], 1.41 [s, 3 H, C(C*H*$_3$)(CH$_3$)], 1.62-1.70 (m, 4 H, C*H*$_2$C*H*$_2$), 3.54-3.37 (m, 6 H, CH$_2$O), 3.72 (dd, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 6.5 Hz, 1 H, C*H*HOC), 3.80 (s, 3 H, OCH$_3$), 4.02 (dd, $^2J_{HH}$ = 8.1, $^3J_{HH}$ = 6.5 Hz, 1 H, CH*H*OC), 4.24 (*virt.* p, $^3J_{HH} \cong$ 6.0 Hz, 1 H, CHO), 4.42 (s, 2 H, C*H*$_2$Ar), 6.87 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H), 7.25 (*virt.* d, $J_{HH} \cong$ 8.5 Hz, 2 H, C_{ar}-H).

^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 25.6 (t, OCH$_2$*C*H$_2$CH$_2$), 26.5 [q, C(*C*H$_3$)(CH$_3$)], 26.5 (t, OCH$_2$*C*H$_2$CH$_2$), 26.9 [q, C(*C*H$_3$)(CH$_3$)], 55.4, (q, OCH$_3$), 67.1 (t, *C*H$_2$OC), 69.9 (t, *C*H$_2$OPMB), 71.6 (t, O*C*H$_2$CH$_2$), 72.0 (t, *C*H$_2$O), 72.7 (t, *C*H$_2$Ar) 74.9 (t, *C*H$_2$OC), 109.5 [s, *C*(CH$_3$)(CH$_3$)], 113.9 (d, C_{ar}-H), 129.3 (d, C_{ar}-H), 130.9 (s, C_{ar}-CH$_2$), 159.27 (s, C_{ar}-O).

MS (ESI): *m/z* (%) = 724 (5), 606 (9), 347 (100) [(M+Na)$^+$], 325 (15) [(M+H)$^+$], 282 (6).

HRMS (ESI) $C_{18}H_{28}O_5Na$ cald.: [(M+Na)$^+$] 347.18290
found: [(M+Na)$^+$] 347.18322.

(*S*)-3-(4-(4-Methoxybenzyloxy)butoxy)propan-1,2-diol (7)



$C_{15}H_{24}O_5$
MW: 284.35 g/mol

p-Toluenesulfonic acid (116 mg, 0.648 mmol) was added to the protected diol **6** (2.10 g, 6.48 mmol) in MeOH (14 mL). The solution was stirred for 3 hours at room temperature, followed by addition of solid $NaHCO_3$ to adjust pH = 8. The aqueous layer was extracted with ethyl acetate (8 × 40 mL). The combined organic layers were dried with Na_2SO_4 and concentrated *in vacuo* to yield the desired diol **7** (1.56 g, 5.83 mmol, crude 90%) as slightly yellow oil. The crude product was directly submitted to the next step without any further purification. For analytical data a small sample was purified by flash chromatography (EtOAc) to give viscous colourless oil.

TLC: R_f = 0.10 (EtOAc) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{20}$ = +1.3 (*c* = 1.1, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3383 (w, OH), 2931 (w, CH), 2858 (w, CH), 2159 (w), 1612 (s), 1512 (s), 1244 (s).

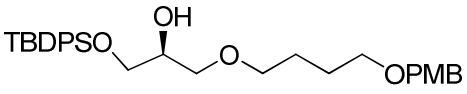
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.60-1.70 (m, 4 H, CH_2CH_2), 2.16 (br. s, 2 H, OH), 3.54-3.37 (m, 6 H, CH_2O), 3.62 (dd, $^2J_{HH}$ = 11.3, $^3J_{HH}$ = 5.2 Hz, 1 H, C*H*HOH), 3.69 (dd, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, CH*H*OH), 3.80 (s, 3 H, OCH_3), 3.80-3.84 (m, 1 H, CHO), 4.43 (s, 2 H, CH_2Ar), 6.88 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H), 7.26 (*virt.* d, $^3J_{HH} \cong$ 8.5 Hz, 2 H, C_{ar}-H).

^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 25.5 (t, $OCH_2CH_2CH_2$), 26.6 (t, $OCH_2CH_2CH_2$), 55.4 (q, OCH_3), 64.3 (t, CH_2OH), 69.9 (t, CH_2OPMB), 70.6 (t, OCH_2CH_2), 71.6 (t, CH_2OH), 72.5 (t, CH_2Ar), 72.7 (t, CH_2OC), 113.9 (d, C_{ar}-H), 129.4 (d, C_{ar}-H), 130.8 (s, C_{ar}-CH_2), 159.3 (s, C_{ar}-O).

MS (ESI): *m/z* (%) = 307 (90) [$(M+Na)^+$], 302 (32) [$(M+NaH_4)^+$], 285 (100), [$(M+H)^+$], 121 (35).

HRMS (ESI) $C_{15}H_{25}O_5$ cald.: [$(M+H)^+$] 285.16965
found: [$(M+H)^+$] 285.16963.

(*S*)-1-(4-Methoxyphenyl)-13,13-dimethyl-12,12-diphenyl-2,7,11-trioxa-12-silatetradecan-9-ol (8)



$C_{31}H_{42}O_5Si$
MW: 522.75 g/mol

The diol **7** (1.10 g, 3.97 mmol) in DMF (50 mL) was cooled to 0 °C, before imidazole (526 mg, 7.74 mmol) and *tert*-butyldiphenylsilyl chloride (1.17 g, 4.26 mmol) in DMF (20 mL) were added. The reaction mixture was warmed to room temperature overnight. Saturated aqueous NH_4Cl (30 mL) was added and the aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4. After filtration the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether: 7/3) to give the desired silylether **8** (1.81 g, 3.45 mmol, 87%) as colourless oil.

TLC: R_f = 0.72 (pentane/Et_2O 1/1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{20}$ = −2.8 (*c* = 1.4, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3467 (w, OH), 2929 (w, CH), 2857 (w, CH), 1612 (s), 1105 (s).

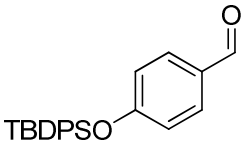
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.06 [s, 9 H, $SiC(CH_3)_3$], 1.60-167 (m, 4 H, CH_2CH_2), 3.40-3.55 (m, 6 H, CH_2O), 3.70 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, CH_2OSi), 3.80 (s, 3 H, OCH_3), 3.87 (*virt*. p, $^3J_{HH} \cong$ 5.4 Hz, 1 H, CHOH), 4.42 (s, 2 H, CH_2Ar), 6.87 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H), 7.25 (*virt.* d, $J_{HH} \cong$ 8.5 Hz, 2 H, C_{ar}-H), 7.35-7.42 [m, 6 H, $Si(C_6H_5)$], 7.62-7.68 [m, 4 H, $Si(C_6H_5)$].

^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.4 [q, $SiC(CH_3)_3$], 25.7 (t, $OCH_2CH_2CH_2$), 26.6 (t, $OCH_2CH_2CH_2$), 27.0 [s, $SiC(CH_3)_3$], 55.4 (q, OCH_3), 65.0 (t, CH_2OSi), 70.0 (t, CH_2OPMB), 70.9 (t, OCH_2CH_2), 71.4 (t, CH_2OH), 71.6 (t, CH_2Ar), 72.7 (t, CH_2OC), 113.9 (d, C_{ar}-H), 127.9 [d, $Si(C_6H_5)$], 129.3 (d, C_{ar}-H), 129.9 [d, $Si(C_6H_5)$], 130.9 (s, C_{ar}-CH_2), 133.4 [s, $Si(C_6H_5)$], 135.7 [d, $Si(C_6H_5)$], 159.3 (s, C_{ar}-O).

MS (ESI): *m/z* (%) = 1068 (25), 545 (100) [$(M+Na)^+$], 523 (25) [$(M+H)^+$].

HRMS (ESI) $C_{31}H_{42}O_5NaSi$ cald.: [$(M+Na)^+$] 545.26937
found: [$(M+Na)^+$] 545.27007.

4-((*tert*-Butyldiphenylsilyl)oxy)benzaldehyde (S2)



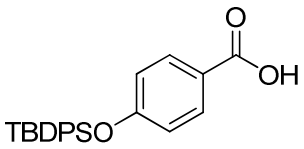
$C_{23}H_{24}O_2Si$
MW: 360.52 g/mol

4-Hydroxybenzaldehyde[2] (2.39 g, 19.6 mmol) and imidazole (3.33 g, 50.0 mmol) were solved in DMF (30 mL) followed by addition of *tert*-butyldiphenylsilyl chloride (7.01 g, 25.5 mmol). The solution was stirred for 15 hours at room temperature, before another portion of 4-hydroxybenzaldehyde (0.718 g, 5.88 mmol) was added. The solution was stirred again for five hours at room temperature. Saturated aqueous NH_4Cl (20 mL) was added and the aqueous layer was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were washed with brine (30 mL), dried with Na_2SO_4 and concentrated *in vacuo*. The crude product

[2] Commercially available

was purified by flash chromatography (pentane/diethyl ether: 9/1) to give the desired silylether **S2** (6.70 g, 18.6 mmol, 73%) as a colourless solid.

4-((*tert*-Butyldiphenylsilyl)oxy)benzoic acid (S3)

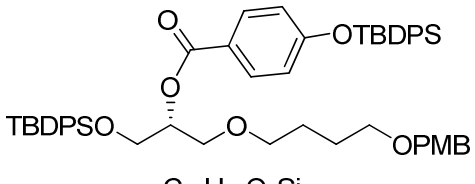


$C_{23}H_{24}O_3Si$
MW: 376.52

Aldehyde **S2** (19.4 g, 53.7 mmol) was solved in a mixture of *tert*-butanol (290 mL) and water (110 mL), before 2-methyl-2-butene (7.80 mL, 77.4 mmol), NaH_2PO_4 (2.87 g, 23.9 mmol) and $NaClO_2$ (6.50 g, 71.9 mmol) were added. After 36 hours at room temperature the reaction mixture was extracted with ethyl acetate (5 × 50 mL). The combined organic layers were washed with brine (50 mL), dried with Na_2SO_4 and concentrated *in vacuo*. After purification by flash chromatography (EtOAc) the desired benzoic acid **S3** (19.2 g, 51.2 mmol, 95%) was isolated as a white solid.

TLC: R_f = 0.10 (EtOAc) [UV].
m.p.: 162 °C.
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.13 [s, 9 H, $SiC(CH_3)_3$], 6.81 (*virt.* d, $J_{HH} \cong$ 8.8 Hz, 2 H, C_{ar}-H), 7.43-7.51 (m, 6 H, C_{ar}-H), 7.72 (d, $^3J_{HH}$ = 8.0 Hz, 4 H, C_{ar}-H), 7.88 (*virt.* d, $J_{HH} \cong$ 8.9 Hz, 2 H, C_{ar}-H).
^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.5 [q, $SiC(CH_3)_3$], 26.4 [s, $SiC(CH_3)_3$], 119.7 (d, C_{ar}-H(Benzoate)), 121.9 (s, C_{ar}-COOH), 127.9 [d, $Si(C_6H_5)$], 130.2 [d, $Si(C_6H_5)$], 132.2 [d, C_{ar}-H(Benzoate)], 132.3 [s, C_{ar}-Si],135.4[d, $Si(C_6H_5)$], 160.5 (s, C_{ar}-OTBDPS), 170.5 (s, COOH).

(*R*)-1-(4-Methoxyphenyl)-13,13-dimethyl-12,12-diphenyl-2,7,11-trioxa-12-silatetradecan-9-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (9)



$C_{54}H_{64}O_7Si_2$
MW: 881.25 g/mol

The secondary alcohol **8** (1.20 g, 2.30 mmol) together with benzoic acid **S3** (1.73 g, 4.59 mmol) and triphenylphosphine (1.21 g, 4.59 mmol) were solved in THF (60 mL) and cooled to 0 °C. To this solution diisopropyl azodicarboxylate (928 mg, 4.59 mmol) was added dropwise. After 30 minutes at 0 °C the solution was warmed up to room temperature and stirred overnight. After addition of saturated aqueous NH_4Cl (30 mL), the aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4. After filtration the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether: 9/1) to give the desired ester **9** (1.84 g, 2.10 mmol, 91%) as colourless oil.

TLC: R_f = 0.80 (pentane/Et_2O 1/1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{20}$ = –9.1 (*c* = 1.3 $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2931 (w, CH), 2857 (w, CH), 2159 (w), 1602 (s).

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.11 [s, 9 H, $SiC(CH_3)_3$], 1.70-1.76 (m, 4 H, CH_2CH_2), 3.40-3.55 (m, 4 H, CH_2O), 3.70 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, CH_2OSi), 3.79 (s, 3 H, OCH_3), 3.86 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, CH_2OCH_2), 4.38 (s, 2 H, CH_2Ar), 5.26 (*virt.* p, $^3J_{HH} \cong$ 4.8 Hz, 1 H, CHOCO), 6.76 (*virt.* d, $J_{HH} \cong$ 8.8 Hz, 2 H, C_{ar}-H), 6.85 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H), 7.16-7.26 (m, 4 H, C_{ar}-H), 7.26-7.46 (m, 10 H, C_{ar}-H), 7.61 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 4 H, C_{ar}-H), 7.68-7.70 (m, 4 H, C_{ar}-H), 7.78 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H).

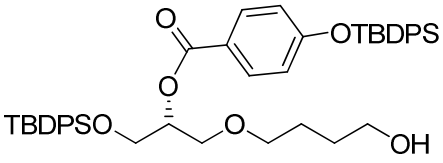
^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.4 [q, $SiC(CH_3)_3$], 19.6 [q, $SiC(CH_3)_3$], 25.5 (t, $OCH_2CH_2CH_2$), 26.6 (t, $OCH_2CH_2CH_2$), 26.9 [s, $SiC(CH_3)_3$], 55.4 (q, OCH_3), 62.9 (t, CH_2OSi), 69.1 (t, CH_2OPMB), 70.0 (t, OCH_2CH_2), 71.4 (t, CH_2O), 72.6 (t, CH_2Ar), 73.4 (t, CH_2OC), 113.9 (d, C_{ar}-H), 119.7 (d, C_{ar}-H(Benzoate)), 123.4 (s, C_{ar}-COO), 127.8 [d,

Si(C_6H_5)], 127.8 [d, Si(C_6H_5)], 128.1 (d, C_{ar}-H), 129.3 (d, C_{ar}-H(PMB)), 129.7 (d, C_{ar}), 129.9 (d, C_{ar}-H), 130.3 (d, C_{ar}-H), 130.9 (s, C_{ar}-CH_2), 131.7 (d, C_{ar}-H(Benzoate)), 132.4 (s, SiC_{ar}), 132.5 (s, SiC_{ar}), 135.6 (s, SiC_{ar}), 135.7 (d, C_{ar}), 159.3 (s, C_{ar}-OMe), 160.0 (s, C_{ar}-OTBDPS), 165.8 (s, COO).

MS (ESI): *m/z* (%) = 1181 (5), 903 (20) [$(M+Na)^+$], 881 (100) [$(M+H)^+$], 803 (33).

HRMS (ESI) $C_{54}H_{65}O_7Si_2$ cald.: [$(M+H)^+$] 881.42633
found:[$(M+H)^+$] 881.42782.

(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-hydroxybutoxy)propan-2-yl 4-(*tert*-butyl diphenylsilyloxy)benzoate (10)



$C_{46}H_{56}O_6Si_2$
MW: 761.10 g/mol

The protected alcohol **9** (1.92 g, 2.19 mmol) was solved in a mixture of dichloromethane (116 mL) and aqueous pH = 7 buffer (5.8 mL) and cooled to 0 °C. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (994 mg, 4.38 mmol) was added. After three hours at room temperature aqueous $NaHCO_3$ (40 mL) was added and the aqueous layer was extracted with dichloromethane (3 × 50 mL) and the combined organic layers were dried over Na_2SO_4. After filtration the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether: 1/1) to give the desired alcohol **10** (1.49 g, 1.96 mmol, 89%) as colourless oil.

TLC: R_f = 0.4 (pentane/Et_2O 1/1) [$KMnO_4$].

Specific rotation: $[\alpha]_D^{20} = -9.3$ (c = 1.2, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2930 (w, CH), 2857 (w, CH), 2525 (w), 1603 (s).

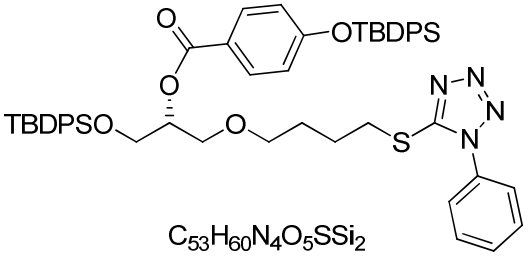
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.11 [s, 9 H, $SiC(CH_3)_3$], 1.50-1.65 (m, 4 H, CH_2CH_2), 3.40-3.55 (m, 2 H, CH_2OH), 3.70 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, CH_2OSi), 3.79 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, CH_2OCH_2), 3.86 (t, $^3J_{HH}$ = 4.6 Hz, 2 H, CH_2OCH_2), 5.26 (*virt*. p, $^3J_{HH} \cong$ 4.8 Hz, 1 H, CHOCO), 6.76 (*virt.* d, $J_{HH} \cong$ 8.8 Hz, 2 H, C_{ar}-H), 6.85 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H), 7.16-7.26 (m, 4 H, C_{ar}-H), 7.26-7.46 (m, 6 H, C_{ar}-H), 7.61 (d, $J_{HH} \cong$ 8.6 Hz, 4 H, C_{ar}-H), 7.65-7.72 (m, 4 H, C_{ar}-H), 7.78 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C_{ar}-H).

^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.2 [s, $SiC(CH_3)_3$], 19.5 [s, $SiC(CH_3)_3$], 26.4 (t, $OCH_2CH_2CH_2$), 26.4 [q, $SiC(CH_3)_3$], 26.7 [q, $SiC(CH_3)_3$], 29.9 (t, $OCH_2CH_2CH_2$), 62.6 (t, CH_2OSi), 69.1 (t, CH_2OC), 70.0 (t, OCH_2CH_2), 71.4 (t, CH_2OH), 73.1 (t, CH_2OC), 119.5 (d, C_{ar}-H(Benzoate)), 123.1 (s, C_{ar}-COO), 127.7 [d, $Si(C_6H_5)$], 127.9 [d, $Si(C_6H_5)$], 129.6 (d, C_{ar}-H), 130.1 (d, C_{ar}-H), 131.5 (d, C_{ar}-H(Benzoate)), 132.2 (s, SiC_{ar}), 133.2 (s, SiC_{ar}), 135.4 (s, SiC_{ar}), 135.5 (d, C_{ar}), 159.8 (s, C_{ar}-OTBDPS), 165.7 (s, COO).

MS (ESI): *m/z* (%) = 1284 (5), 799 (30) [$(M+Na)^+$], 761 (100) [$(M+H)^+$], 683 (90).

HRMS (ESI) $C_{46}H_{57}O_6S_{i2}$ cald.: $[(M+H)^+]$ 761.36882
found: $[(M+H)^+]$ 761.36870.

(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-(1-phenyl-*1H*-tetrazole-5-ylthio)butoxy) propan-2-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (11)



$C_{53}H_{60}N_4O_5SSi_2$
MW: 921.30 g/mol

The primary alcohol **10** (800 mg, 1.05 mmol) together with 1-phenyl-1*H*-tetrazole-5-thiol (374 mg, 2.10 mmol) and triphenylphosphine (413 mg, 1.58 mmol) were solved in THF (40 mL) and cooled to 0 °C. To this solution diisopropyl azodicarboxylate (225 mg, 1.11 mmol) was added dropwise. After 30 minutes at 0 °C the solution was warmed up to room temperature and stirred overnight. After addition of saturated aqueous NH_4Cl (30 mL), the aqueous layer was extracted with diethyl ether (3 × 20 mL) and the combined organic layers were dried over Na_2SO_4. After filtration the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether: 4/1) to give the desired ether **11** (871 mg, 0.95 mmol, 90%) as colourless oil.

TLC: R_f = 0.75 (pentane/Et_2O 1/1) [UV].

Specific rotation: $[\alpha]_D^{20} = -7.3$ (c = 1.3, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2930 (w, CH), 2857 (w, CH), 2519 (w), 2159 (w), 1714 (s), 1603 (s), 1109 (s).

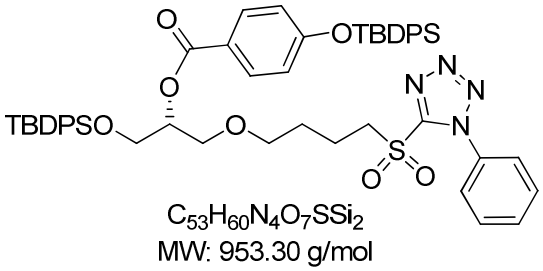
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.04 [s, 9 H, $SiC(CH_3)_3$], 1.15 [s, 9 H, $SiC(CH_3)_3$], 1.63-1.77 (m, 2 H, CH_2CH_2), 1.83-1.95 (m, 2 H, CH_2CH_2), 3.40 (t, $^3J_{HH}$ = 7.2 Hz, 2 H, CH_2S), 3.45-3.59 (m, 2 H, CH_2O), 3.74 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, $CHCH_2OCH_2$), 3.89 (d, $^3J_{HH}$ = 4.7 Hz, 2 H, $CHCH_2OSi$), 5.26 (*virt.* p, $^3J_{HH} \cong$ 5.0 Hz, 1 H, CHOCO), 6.80 (*virt.* d, $J_{HH} \cong$ 8.7 Hz, 2 H, C_{ar}-H), 7.23-7.49 (m, 12 H, C_{ar}-H), 7.54-7.61 (m, 5 H, C_{ar}-H), 7.61-7.67 (m, 4 H, C_{ar}-H), 7.71-7.77 (m, 4 H, C_{ar}-H), 7.82 (*virt.* d, $J_{HH} \cong$ 8.8 Hz, 2 H, C_{ar}-H).

^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.3 [s, Si*C*$(CH_3)_3$], 19.6 [s, Si*C*$(CH_3)_3$], 26.1 (t, $OCH_2CH_2CH_2$), 26.6 [q, SiC(CH_3)$_3$], 26.9 [q, SiC(CH_3)$_3$], 28.6 (t, $SCH_2CH_2CH_2$), 33.3 (t, SCH_2), 62.8 (t, CH_2OSi), 69.3 (t, OCH_2CH_2), 70.54 (t, CH_2O), 73.2 (d, *C*HOCOO), 119.7 (d, C_{ar}-H(Benzoate)), 123.2 (s, C_{ar}-COO), 123.9 (d, C_{ar}-H), 127.7 [d, Si(C_6H_5)], 127.8 [d, Si(C_6H_5)], 128.0 [d, Si(C_6H_5)], 129.8 [d, Si(C_6H_5)], 129.8 [d, Si(C_6H_5)], 129.9 (d, C_{ar}-H), 130.1 [d, Si(C_6H_5)], 130.2 (d, C_{ar}-H), 131.6 (d, C_{ar}-H(Benzoate)), 132.3 [d, Si(C_6H_5)], 132.3 [d, Si(C_6H_5)], 133.4 (s, C_{ar}-Si), 133.4 (s, C_{ar}-Si), 133.9 (s, C_{ar}-N), 135.6 (s, C_{ar}-Si), 135.5 [d, Si(C_6H_5)], 154.5 [d, Si(C_6H_5)], 160.0 (s, C_{ar}-OTBDPS), 165.7 (s, COO).

MS (ESI): *m/z* (%) = 959 (5) [$(M+K)^+$], 943 (25) [$(M+Na)^+$], 921 (100), [$(M+H)^+$], 282 (12).

HRMS (ESI) $C_{53}H_{61}N_4O_5SSi_2$ cald.: [$(M+H)^+$] 921.38957
found: [$(M+H)^+$] 921.39048.

(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-(1-phenyl-1*H*-tetrazole-5-ylsulfonyl)butoxy) propan-2-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (4)



A solution of thioether **11** (120 mg, 0.130 mmol) in dichloromethane (3 mL) was cooled to 0 °C, before *m*-chloroperbenzoic acid (68.8 mg, 0.40 mmol, 70%) was added. After 16 hours at room temperature saturated aqueous $Na_2S_2O_3$ (10 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 20 mL) and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (20 mL) and dried over Na_2SO_4. After filtration the solvent was removed *in vacuo*. The crude product was purified by flash chromatography (pentane/diethyl ether: 4/1) to give the desired sulfone **4** (110 mg, 0.115 mmol, 89%) as a low melting solid.

TLC: R_f = 0.60 (pentane/Et_2O 1/1) [UV].

m.p.: 42°C.

Specific rotation: $[\alpha]_D^{20}$ = +7.8 (*c* = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2956 (w), 2931 (w, CH), 2858 (w, CH), 1713 (s), 1603 (s), 1258 (s), 1111 (s).

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.11 [s, 9 H, $SiC(CH_3)_3$], 1.67-1.76 (m, 2 H, CH_2CH_2), 1.95-2.05 (m, 2 H, CH_2CH_2), 3.42-3.55 (m, 2 H, CH_2SO_2), 3.71 (d, $^3J_{HH}$ = 5.4 Hz, 2 H, $CHCH_2OCH_2$), 3.72-3.76 (m, 2 H, CH_2CH_2O), 3.85 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, $CHCH_2OSi$), 5.26 (*virt.* p, $^3J_{HH} \cong$ 5.1 Hz, 1 H, CHOCO), 6.76 (*virt.* d, $J_{HH} \cong$ 8.7 Hz, 2 H, C_{ar}-H), 7.17-7.41 (m, 10 H, C_{ar}-H), 7.42-7.47 (m, 2 H, C_{ar}-H), 7.55-7.65 (m, 7 H, C_{ar}-H), 7.65-7.75 (m, 6 H, C_{ar}-H), 7.77 (*virt.* d, $J_{HH} \cong$ 8.7 Hz, 2 H, C_{ar}-H).

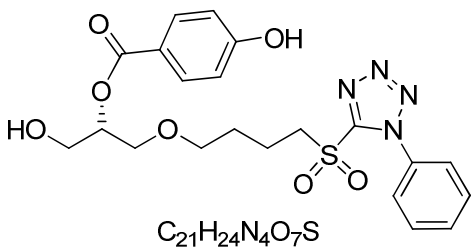
^{13}C-NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 19.4 [s, $SiC(CH_3)_3$], 19.6 [s, $SiC(CH_3)_3$], 19.6 (t, $SO_2CH_2CH_2CH_2$), 26.5 [q, $SiC(CH_3)_3$], 26.9 [q, $SiC(CH_3)_3$], 28.2 (t, $OCH_2CH_2CH_2$), 55.9 (t, SO_2CH_2), 62.8 (t, CH_2OSi), 69.5 (t, OCH_2CH_2), 70.5 (t, CH_2O), 73.0 (d, CHOCOO), 119.7 (d, C_{ar}-H(Benzoate)), 123.1 (s, C_{ar}-COO), 125.2 (d, C_{ar}-H), 127.7 [d, $Si(C_6H_5)$], 127.8 [d, $Si(C_6H_5)$], 128.0 [d, $Si(C_6H_5)$], 129.8 [d, $Si(C_6H_5)$], 129.8 [d, $Si(C_6H_5)$], 130.3 [d, $Si(C_6H_5)$], 131.6 (d, C_{ar}-H(Benzoate)), 131.7 (d, C_{ar}-H), 132.3 [d, $Si(C_6H_5)$], 132.3 [d, $Si(C_6H_5)$], 133.2 (s, C_{ar}-N), 133.3 (s, C_{ar}-Si), 133.3 (s, C_{ar}-Si), 135.5 [d, $Si(C_6H_5)$], 135.7 [d, $Si(C_6H_5)$], 153.5 (s, C_{ar}-SO_2), 160.0 (s, C_{ar}-OTBDPS), 165.8 (s, COO).

MS (ESI): *m/z* (%) = 991 (25) [$(M+Na)^+$], 953 (100) [$(M+H)^+$], 875 (6), 715 (20).

HRMS (ESI) $C_{53}H_{61}N_4O_7SSi_2$ cald.: [$(M+H)^+$] 953.37940
found: [$(M+H)^+$] 953.37994.

Confirmation of the enantiomeric purity of key building block 4:

Analysis of a racemic mixture of sulfone **4** on chiral HPLC (normal and reverse phase, various columns) did not lead to any separation of the enantiomers. Therefore, both silyl ethers in sulfone **4** were cleaved[3] to yield (*S*)-1-hydroxy-3-(4-(1-phenyl-1*H*-tetrazol-5-ylsulfonyl)butoxy)propan-2-yl 4-hydroxybenzoate (**S4**).



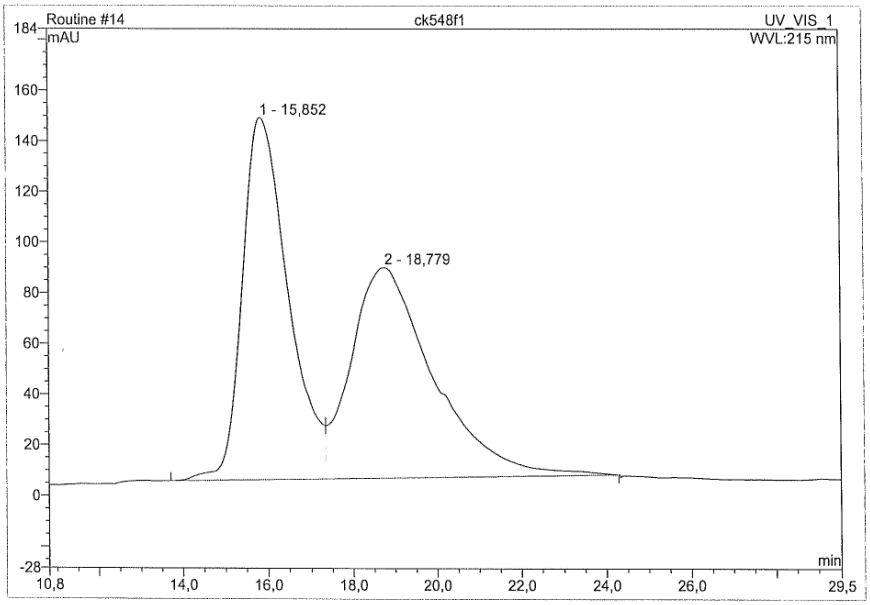
$C_{21}H_{24}N_4O_7S$
MW: 476.5029 g/mol

[3] Deprotection procedure according to the global deprotection of **2/2'** (see below).

HPLC analysis of diol **S4**:

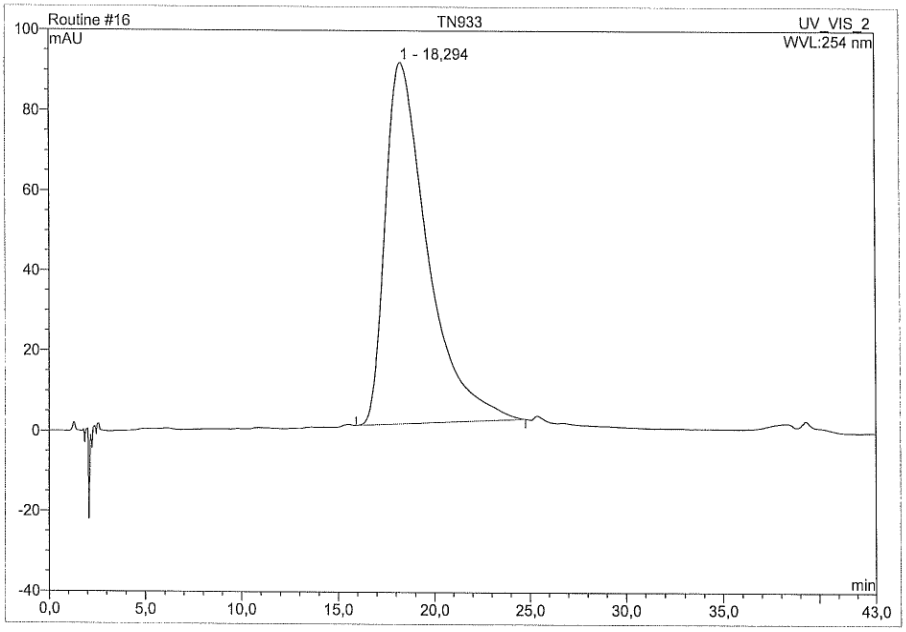
AD-RH, Acetonitrile/H_2O = 20/80 to 100/0, 30 min, 1 mL/min:

-racemic mixture of **S4**



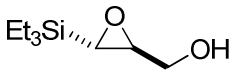
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount mg/ml	Type
1	15,85	n.a.	142,828	177,537	48,53	n.a.	BM
2	18,78	n.a.	83,043	188,285	51,47	n.a.	MB
Total:			225,871	365,822	100,00	0,000	

-enantiopure compound **S4**:



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount mg/ml	Type
1	18,29	n.a.	90,035	228,326	100,00	n.a.	BMB
Total:			90,035	228,326	100,00	0,000	

((2*S,3*S**)-3-(Triethylsilyl)oxiran-2-yl)methanol (*rac*-3)**



$C_9H_{20}O_2Si$
MW: 188.34 g/mol

Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate $[Rh(cod)_2]BF_4$ (6.09 mg, 15.0 µmol, 0.5 mol%) was added to a solution of triphenylphosphine (7.87 mg, 30.0 µmol, 1 mol%) in dry acetone (4.3 mL). The resulting yellow solution was stirred at room temperature for 5 min and propargyl alcohol (177 µL, 3.00 mmol) and freshly distilled triethylsilane (727 µL, 4.50 mmol) were then successively added. The reaction mixture was stirred at room temperature and the completion of the reaction was monitored by TLC. After 30 min, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 90/10) to afford (*E*)-3-(triethylsilyl)prop-2-en-1-ol **S5** (461 mg, 2.67 mmol, 89%) as a colourless oil and as a single regio- and diastereoisomer.

TLC: R_f = 0.18 (pentane/EtOAc = 95/5) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3321 (s, br, O-H), 2952 (s, C-H), 2910 (s, C-H), 2874 (s, C-H), 2361 (w), 2119 (w), 1620 (m, C=C), 1460 (m, C-H), 1416 (m, C=C), 1236 (m), 1198 (w), 1081 (m), 1009 (s), 786 (m), 717 (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.59 (q, $^3J_{HH}$ = 7.8 Hz, 6 H, C*H*$_2$CH$_3$), 0.95 (t, $^3J_{HH}$ = 7.8 Hz, 9 H, CH$_2$C*H*$_3$), 1.44 (br s, 1 H, O*H*), 4.21 (dd, $^3J_{HH}$ = 4.4 Hz, $^4J_{HH}$ = 1.7 Hz, 2 H, C*H*$_2$OH), 5.86 (dt, $^3J_{trans}$= 19.0 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, CH=C*H*Si), 6.22 (dt, $^3J_{trans}$= 19.0 Hz, $^3J_{HH}$ = 4.4 Hz, 1 H, C*H*=CHSi).

^{13}C NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 3.6 (t, *C*H$_2$CH$_3$), 7.5 (q, CH$_2$*C*H$_3$), 65.9 (t, *C*H$_2$OH), 125.9 (d, CH=*C*HSi), 146.2 (d, *C*H=CHSi).

MS (EI, 70 eV): *m*/z (%) = 143 (100) [(M – C_2H_5)$^+$], 141 (12), 115 (85) [(M – C_3H_5O)$^+$], 113 (20), 103 (21), 87 (35), 75 (32), 59 (26), 55 (18).

The data obtained matched those reported in the literature.[4]

[4] F. Le Bideau, F. Gilloir, Y. Nilsson, C. Aubert and M. Malacria, *Tetrahedron*, 1996, **52**, 7487-7510.

meta-Chloroperbenzoic acid (2.00 g, 8.73 mmol, 75% w/w) was added in several portions to a solution of (*E*)-3-(triethylsilyl)prop-2-en-1-ol **S5** (1.00 g, 5.81 mmol) in dichloromethane (30 mL), cooled to 0 °C. After 10 min, the reaction was allowed to reach room temperature and stirred at that temperature for 16 hours. The reaction was quenched with a saturated solution of $Na_2S_2O_3$ (20 mL), added dropwise at 0 °C. The biphasic mixture was stirred at room temperature for 30 min and a saturated solution of $NaHCO_3$ (20 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 30 mL) and the combined organic layers were washed with a saturated solution of $NaHCO_3$ (50 mL), dried on Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 7/3) to afford the desired product *rac*-**3** (1.05 g, 5.57 mmol, 96%) as a colourless oil and as a single diastereoisomer.

TLC: R_f = 0.26 (pentane/EtOAc = 9/1) [$KMnO_4$].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3404 (s, br, O-H), 2953 (s, C-H), 2911 (s, C-H), 2875 (s, C-H), 2357 (w), 1458 (m, C-H), 1415 (m), 1237 (m, C-O), 1101 (w), 1052 (s), 1015 (s), 974 (w), 862 (m, C-O), 798 (w), 718 (s).

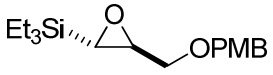
^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.55-0.69 (m, 6 H, CH_2CH$_3$), 0.99 (t, $^3J_{HH}$ = 7.9 Hz, 9 H, CH$_2$CH_3), 1.63 (t, $^3J_{HH}$ = 6.0 Hz, 1 H, O*H*), 2.32 (d, $^3J_{HH}$ = 3.7 Hz, 1 H, SiC*H*O), 3.07 (ddd, $^3J_{HH}$ = 4.6 Hz, $^3J_{HH}$ = 3.7 Hz, $^3J_{HH}$ = 2.4 Hz, 1 H, C*H*CH$_2$OH), 3.59 (ddd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 4.6 Hz, 1 H, C*H*HOH), 4.00 (ddd, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 5.9 Hz, $^3J_{HH}$ = 2.4 Hz, 1 H, CH*H*OH).

^{13}C NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 2.0 (t, *C*H$_2$CH$_3$), 7.4 (q, CH$_2$*C*H$_3$), 46.7 (d, Si*C*HO), 55.5 (d, *C*HCH$_2$OH), 63.6 (t, *C*H$_2$OH).

MS (EI, 70 eV): *m*/z (%) = 115 (5) [(M – $C_3H_5O_2$)$^+$], 103 (45), 91 (5), 87 (14), 75 (100), 73 (3) [(M – $C_5H_{15}Si$)$^+$], 71 (8), 59 (17), 57 (6), 55 (5).

The data obtained matched those reported in the literature.[4]

Triethyl ((2*S,3*S**)-3-((4-methoxybenzyloxy)methyl)oxiran-2-yl)silane (*rac*-12)**



$C_{17}H_{28}O_3Si$
MW: 308.49 g/mol

The primary alcohol *rac*-**3** (188 mg, 1.00 mmol) was solved in dichloromethane (8 mL) and cooled to 0°C, before *p*-methoxy-benzyl-2,2,2-trichloroacetimidate (297 mg, 1.05 mmol) and camphorsulfonic acid (23.0 mg, 0.100 mmol) were added. The solution was warmed up to room temperature and stirred for 16 hours. Saturated solution of $NaHCO_3$ (50 mL) was added and the aqueous layer was extracted with diethyl ether (3 × 40 mL). The combined organic layers were washed with brine (30 mL), dried on Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 4/1) to afford the desired product *rac*-**12** (152 mg, 0.810 mmol, 81%) as a colourless oil.

TLC: R_f = 0.33 (pentane/EtOAc = 95/5) [CAM, UV].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2953 (s, C-H), 2936 (s, C-H), 2910 (s, C-H), 2874 (s, C-H), 2832 (s, C-H), 1613 (m, C=C), 1512 (s), 1463 (m), 1247 (s, C-O), 1173 (m, C-O), 1089 (s), 1036 (s), 1015 (s), 734 (s), 718 (s).

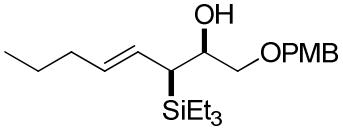
^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.55-0.66 (m, 6 H, CH_2CH$_3$), 0.98 (t, $^3J_{HH}$ = 7.8 Hz, 9 H, CH$_2$CH_3), 2.12 (d, $^3J_{HH}$ = 3.6 Hz, 1 H, SiC*H*O), 3.08 (ddd, $^3J_{HH}$ = 6.2 Hz, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$ = 2.7 Hz, 1 H, C*H*CH$_2$O), 3.36 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 6.2 Hz, 1 H, CHC*H*HO), 3.80 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 2.7 Hz, 1 H, CHCH*H*O), 3.81 (s, 3 H, OCH_3), 4.49 (d, $^2J_{HH}$ = 11.5 Hz, part of AB system, 1 H, C*H*HAr), 4.58 (d, $^2J_{HH}$ = 11.5 Hz, part of AB system, 1 H, CH*H*Ar), 6.87-6.91 (m, 2 H, C_{ar}-*H*), 7.27-7.30 (m, 2 H, C_{ar}-*H*).

^{13}C NMR (90.6 MHz, $CDCl_3$): δ (ppm) = 2.0 (t, *C*H$_2$CH$_3$), 7.4 (q, CH$_2$*C*H$_3$), 46.5 (d, Si*C*HO), 54.4 (d, *C*HCH$_2$O), 55.4 (q, O*C*H$_3$), 72.7 (t, *C*H$_2$Ar), 73.0 (t, CH*C*H$_2$O), 114.0 (d, C_{ar}), 129.5 (d, C_{ar}), 130.4 (s, C_{ar}), 159.4 (s, C_{ar}).

MS (EI, 70 eV): *m*/z (%) = 279 (3) [(M - C_2H_5)$^+$], 122 (11), 121 (100) [(M - $C_9H_{19}O_2Si$)$^+$], 115 (15) [$SiEt_3^+$].

HRMS (EI) $C_{15}H_{23}O_3Si$ calcd.: [(M - C_2H_5)$^+$] 279.1411
found: [(M - C_2H_5)$^+$] 279.1406.

(2*S,3*S**,4*E*)-1-(4-Methoxybenzyloxy)-3-(triethylsilyl)oct-4-en-2-ol** (*rac*-**13**)



$C_{22}H_{38}O_3Si$
MW: 378.62 g/mol

Preparation of (*E*)-1-bromopent-1-ene[5] (**S6**):

1-Pentyne (0.80 mL, 8.08 mmol) was added over 10 min to a suspension of the Schwartz' reagent Cp_2ZrHCl (2.50 g, 9.69 mmol) in dichloromethane (27 mL), cooled to 0 °C. The resulting mixture was stirred at room temperature for 45 min, yielding a clear yellow solution, and then cooled to −78 °C. Bromine (0.41 mL, 8.08 mmol) was added dropwise at −78 °C and the solution was stirred at that temperature for 15 min. An aqueous solution of HCl (15 mL, 1.0 M) was added dropwise at −78 °C and the resulting biphasic mixture was stirred at room temperature for 30 min. The aqueous layer was extracted with pentane (3 × 20 mL). The combined organic layers were washed with a saturated solution of $Na_2S_2O_3$ and $NaHCO_3$ (1:1, 50 mL), dried on $MgSO_4$ and carefully concentrated *in vacuo* (850 mbar, 40 °C). The crude product was submitted to Kugelrohr distillation (60 mmHg, 65 °C) to yield (*E*)-1-bromopent-1-ene as a mixture with dichloromethane. After dilution with pentane, a second Kugelrohr distillation (700 mbar, 40 °C) gave (*E*)-1-bromopent-1-ene **S6** (3.96 mmol, 49% corrected yield) as a 29:71 mixture with pentane.

TLC: R_f = 1.0 (pentane) [CAM].

^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CH_2CH_2CH_3$), 1.44 (*virt.* sext, $^3J_{HH}$ ≅ 7.3 Hz, 2 H, $CH_3CH_2CH_2$), 2.03 (*virt.* q, $^3J_{HH}$ ≅ 7.2 Hz, 2 H, $CH_3CH_2CH_2$), 6.02 (d, $^3J_{trans}$ = 14.0 Hz, 1 H, BrC*H*=CH), 6.19 (dt, $^3J_{trans}$ = 14.0 Hz, $^3J_{HH}$ = 7.1 Hz, 1 H, BrCH=C*H*).

Preparation of the alkenyl Grignard solution:

tert-Butyllithium (4.95 mL, 7.92 mmol) was added dropwise to a solution of the previously obtained (*E*)-1-bromopent-1-ene **S6** (3.96 mmol, 29:71 mixture with pentane) in diethyl ether (2.3 mL), cooled to −78 °C. The resulting milky solution was stirred at −78 °C for two hours and a solution of magnesium bromide diethyl etherate $MgBr_2{\cdot}OEt_2$ (1.12 g, 4.36 mmol) in diethyl ether (4.4 mL) was introduced dropwise at −78 °C. The resulting mixture was allowed to reach room temperature and stirred at that temperature for 1.25 hours, yielding a pale brown solution of (*E*)-pentenyl magnesium bromide, which was directly used in the next step.

[5] Commercially available

Copper-mediated ring-opening of epoxide *rac*-**12**:

The solution of (*E*)-pentenyl magnesium bromide was added dropwise to a suspension of copper(I) iodide (12.4 mg, 65.3 µmol, 10 mol%) in degassed THF (1.1 mL), cooled to −30 °C. The resulting thick yellow solution was vigorously stirred at −30 °C for 10 min and a solution of epoxide *rac*-**12** (200 mg, 0.650 mmol) in degassed THF (1.1 mL) was then added via cannula. The reaction was stirred at −30 °C and the completion of the reaction was monitored by TLC. After 20 min, the reaction was quenched with a saturated solution of NH_4Cl (2 mL), added dropwise at −30 °C. The biphasic mixture was allowed to reach room temperature and was stirred at that temperature for 20 min. The aqueous layer was extracted with diethyl ether (3 × 5 mL) and the combined organic layers were dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 9/1) to afford the desired product *rac*-**13** (185 mg, 0.489 mmol, 75%) as a colourless oil and as a single regio- and stereoisomer.

TLC: R_f = 0.44 (pentane/Et_2O= 9/1) [CAM, UV].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3570 (s, br, O-H), 2952 (m, C-H), 2904 (m, C-H), 2871 (m, C-H), 1615 (m, C=C), 1513 (s, C=C), 1461 (m, C=C), 1302 (m), 1246 (s), 1172 (m, C-O), 1092 (s, C-O), 1038 (m), 1006 (m), 968 (m), 820 (m, C-H), 727 (s).

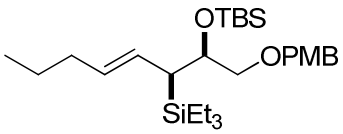
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.61 (q, $^3J_{HH}$ = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$), 0.88 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.95 (t, $^3J_{HH}$ = 8.0 Hz, 9 H, SiCH$_2$C*H*$_3$), 1.35 (*virt.* sext, $^3J_{HH}$ ≅ 7.3 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.87 (*virt.* t, $^3J_{HH}$ ≅ 9.8 Hz, 1 H, SiC*H*CH=CH), 1.95 (*virt.* q, $^3J_{HH}$ ≅ 7.2 Hz, 2 H, CH$_3$CH$_2$C*H*$_2$), 2.40 (s, 1 H, O*H*), 3.27 (dd, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 8.6 Hz, 1 H, CHC*H*HO), 3.60 (dd, $^2J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 2.5 Hz, 1 H, CHCH*H*O), 3.82 (s, 3 H, OC*H*$_3$), 3.88-3.92 (m, 1 H, C*H*OH), 4.46 (d, $^2J_{HH}$ = 11.5 Hz, part of AB system, 1 H, C*H*HAr), 4.48 (d, $^2J_{HH}$ = 11.5 Hz, part of AB system, 1 H, CH*H*Ar), 5.20 (dd, $^3J_{trans}$= 15.4 Hz, $^3J_{HH}$ = 9.9 Hz, 1 H, SiCHC*H*=CH), 5.28 (dt, $^3J_{trans}$= 15.3 Hz, $^3J_{HH}$ = 6.4 Hz, 1 H, SiCHCH=C*H*), 6.88-6.90 (m, 2 H, C$_{ar}$-*H*), 7.25-7.28 (m, 2 H, C$_{ar}$-*H*).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = 3.4 (t, Si*C*H$_2$CH$_3$), 7.8 (q, SiCH$_2$*C*H$_3$), 13.9 (q, CH$_2$CH$_2$*C*H$_3$), 23.0 (t, CH$_2$*C*H$_2$CH$_3$), 35.1 (t, *C*H$_2$CH$_2$CH$_3$), 35.4 (d, Si*C*HCH=CH), 55.4 (q, O*C*H$_3$), 71.6 (d, *C*HOH), 73.1 (t, *C*H$_2$Ar), 74.7 (t, CH*C*H$_2$O), 113.9 (d, *C*$_{ar}$), 127.7 (d, SiCH*C*H=CH), 129.5 (d, *C*$_{ar}$), 130.4 (s, *C*$_{ar}$), 130.4 (d, SiCHCH=*C*H), 159.4 (s, *C*$_{ar}$).

MS (ESI+): *m*/z (%) = 401 (100) [(M + Na)$^+$], 396 (88) [(M + NH_4)$^+$], 361 (24), 282 (21), 229 (31).

HRMS (ESI+): $C_{22}H_{38}O_3NaSi$ calcd.: $[(M + Na)^+]$ 401.2482
found: $[(M + Na)^+]$ 401.2485.

***tert*-Butyl(((1*S**,2*S**,3*E*)-1-(((4-methoxybenzyl)oxy)methyl)-2-(triethylsilyl)hept-3-en-1-yl)oxy)dimethylsilane (*rac*-14)**



$C_{28}H_{52}O_3Si_2$
MW: 492.88 g/mol

2,6-Lutidine (196 µL, 1.68 mmol) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (193 µL, 0.84 mmol) were successively added dropwise to a solution of alcohol *rac*-**13** (159 mg, 0.42 mmol) in dichloromethane (10 mL), cooled to −78 °C. The resulting mixture was stirred at −78 °C for three hours and was then allowed to reach room temperature overnight. The reaction was quenched with a saturated solution of NH_4Cl (10 mL) and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were washed with brine (40 mL), dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 99:1) to afford the desired product *rac*-**14** (198 mg, 0.402 mmol, 96%) as a colourless oil.

TLC: R_f = 0.26 (pentane/Et_2O = 99/1) [CAM, UV].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2952 (m, C-H), 2933 (m, C-H), 2875 (m, C-H), 2861 (m, C-H), 1615 (w, C=C), 1513 (m, C=C), 1466 (w, C=C), 1247 (s), 1093 (s, C-O), 1072 (s, Si-O), 1039 (m), 1005 (m), 970 (m), 831 (s), 773 (m), 722 (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.05 (s, 3 H, SiC*H*$_3$), 0.06 (s, 3 H, SiC*H*$_3$), 0.57 (q, $^3J_{HH}$ = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$), 0.89 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.89 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.93 (t, $^3J_{HH}$ = 7.9 Hz, 9 H, SiCH$_2$C*H*$_3$), 1.36 (*virt.* sext, $^3J_{HH} \cong$ 7.3 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.96 (m, 2 H, CH$_3$CH$_2$C*H*$_2$), 1.98 (m, 1 H, SiC*H*CH=CH), 3.39 (dd, $^2J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, CHC*H*HO), 3.44 (dd, $^2J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 4.4 Hz, 1 H, CHCH*H*O), 3.82 (s, 3 H, OCH$_3$), 3.97-4.02 (m, 1 H, C*H*OSi), 4.41 (d, $^2J_{HH}$ = 11.6 Hz, part of AB system, 1 H, C*H*HAr), 4.46 (d, $^2J_{HH}$ = 11.6 Hz, part of AB system, 1 H, CH*H*Ar), 5.27 (dt, $^3J_{trans}$= 15.0

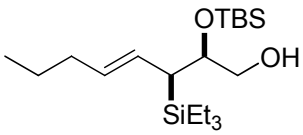
Hz, $^3J_{HH}$ = 6.4 Hz, 1 H, SiCHCH=C*H*), 5.34 (dd, $^3J_{trans}$= 15.1 Hz, $^3J_{HH}$ = 10.4 Hz, 1 H, SiCHC*H*=CH), 6.88 (*virt.* d, *J* ≅ 8.5 Hz, 2 H, C_{ar}-*H*), 7.26 (*virt.* d, *J* ≅ 8.7 Hz, 2 H, C_{ar}-*H*).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = -4.2 (q, Si*C*H$_3$), -4.2 (q, Si*C*H$_3$), 3.5 (t, Si*C*H$_2$CH$_3$), 7.8 (q, SiCH$_2$*C*H$_3$), 13.9 (q, *C*H$_3$CH$_2$CH$_2$), 18.4 [s, Si*C*(CH$_3$)$_3$], 23.1 (t, CH$_3$*C*H$_2$CH$_2$), 26.2 [q, SiC(*C*H$_3$)$_3$], 35.2 (t, CH$_3$CH$_2$*C*H$_2$), 37.3 (d, Si*C*HCH=CH), 55.4 (q, O*C*H$_3$), 72.9 (t, *C*H$_2$Ar), 74.3 (t, CH*C*H$_2$O), 74.3 (d, *C*HCH$_2$O), 113.7 (d, C_{ar}), 128.3 (d, SiCH*C*H=CH), 129.4 (d, C_{ar}), 130.4 (d, SiCHCH=*C*H), 130.8 (s, C_{ar}), 159.1 (s, C_{ar}).

MS (ESI+): *m*/z (%) = 515 (100) [(M + Na)$^+$], 510 (28) [(M + NH$_4$)$^+$], 396 (89), 361 (16), 282 (12), 229 (15).

HRMS (ESI+): $C_{28}H_{52}O_3NaSi_2$ calcd.: [(M + Na)$^+$] 515.3347
found: [(M + Na)$^+$] 515.3348

(2*S,3*S**,4*E*)-2-((*tert*-Butyl(dimethyl)silyl)oxy)-3-(triethylsilyl)oct-4-en-1-ol** (*rac*-**15**)



$C_{20}H_{44}O_2Si_2$
MW: 372.73 g/mol

2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (137 mg, 0.602 mmol) was added to a solution of PMB-protected alcohol *rac*-**14** (198 mg, 0.400 mmol) in a mixture of dichloromethane (12.7 mL) and phosphate buffer (pH=7, 0.7 mL). The resulting mixture was stirred at room temperature and the completion of the reaction was monitored by TLC. After 16 hours, the reaction was quenched with a saturated solution of $NaHCO_3$ (15 mL) and the aqueous layer was extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with brine (2 × 25 mL), dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 98:2) to afford the desired product *rac*-**15** (117 mg, 0.314 mmol, 78%) as a colourless oil.

TLC: R_f = 0.35 (pentane/Et_2O= 95/5) [CAM].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3445 (s, br, O-H), 2952 (m, C-H), 2928 (m, C-H), 2875 (m, C-H), 1461 (m, C=C), 1413 (w), 1364 (w), 1249 (m), 1067 (s, C-O), 1005 (m), 966 (s), 833 (s), 774 (s), 715 (s).

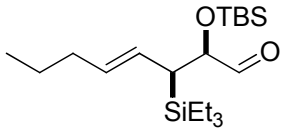
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.10 (s, 3 H, SiC*H*$_3$), 0.11 (s, 3 H, SiC*H*$_3$), 0.59 (q, $^3J_{HH}$ = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$), 0.91 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.96 (t, $^3J_{HH}$ = 7.9 Hz, 9 H, SiCH$_2$C*H*$_3$), 1.37 (*virt.* sext, $^3J_{HH}$ ≅ 7.3 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.88 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.2 Hz, 1 H, OH), 1.98 (*virt*. q, $^3J_{HH}$ ≅ 6.9 Hz, 2 H, CH$_3$CH$_2$C*H*$_2$), 2.07 (dd, $^3J_{HH}$ = 9.9 Hz, $^3J_{HH}$ = 4.7 Hz, 1 H, SiC*H*CH=CH), 3.54 (ddd, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 3.5 Hz, 1 H, CHC*H*HOH), 3.64 (ddd, $^2J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 4.0 Hz, 1 H, CHCH*H*OH), 3.92-3.95 (m, 1 H, C*H*OSi), 5.28 (dt, $^3J_{trans}$= 15.0 Hz, $^3J_{HH}$ = 6.6 Hz, 1 H, SiCHCH=C*H*), 5.33 (dd, $^3J_{trans}$= 15.1 Hz, $^3J_{HH}$ = 9.9 Hz, 1 H, SiCHC*H*=CH).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = -4.4 (q, Si*C*H$_3$), -3.8 (q, Si*C*H$_3$), 3.3 (t, Si*C*H$_2$CH$_3$), 7.8 (q, SiCH$_2$*C*H$_3$), 13.9 (q, *C*H$_3$CH$_2$CH$_2$), 18.4 [s, Si*C*(CH$_3$)$_3$], 23.1 (t, CH$_3$*C*H$_2$CH$_2$), 26.1 [q, SiC(*C*H$_3$)$_3$], 35.2 (t, CH$_3$CH$_2$*C*H$_2$), 37.1 (d, Si*C*HCH=CH), 65.4 (t, CH*C*H$_2$OH), 74.4 (d, *C*HCH$_2$OH), 126.7 (d, SiCH*C*H=CH), 131.4 (d, SiCHCH=*C*H).

MS (ESI+): *m*/z (%) = 395 [(M + Na)$^+$].

HRMS (ESI+): $C_{20}H_{44}O_2NaSi_2$ calcd.: [(M + Na)$^+$] 395.2772
found: [(M + Na)$^+$] 395.2774.

(2*S,3*S**,4*E*)-2-((*tert*-Butyl(dimethyl)silyl)oxy)-3-(triethylsilyl)oct-4-enal (*rac*-16)**



$C_{20}H_{42}O_2Si_2$
MW: 370.72 g/mol

Solid sodium hydrogencarbonate (2.04 mg, 24.3 µmol, 25 mol%) and Dess-Martin periodinane (61.8 mg, 146 µmol) were successively added to a solution of primary alcohol *rac*-**15** (36.2 mg, 97.0 µmol) in dichloromethane (4.8 mL). The resulting mixture was stirred at room temperature for two hours. The reaction was quenched with a saturated solution of $Na_2S_2O_3$ and $NaHCO_3$ (1/1, 5 mL) and stirred at room temperature for 30 min. The aqueous layer was then extracted with dichloromethane (3 × 5 mL) and the combined organic layers were dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pure pentane) to afford the desired product *rac*-**16** (33.8 mg, 91.2 µmol, 94%) as a colourless oil.

TLC: R_f = 0.27 (pure pentane) [UV, CAM].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2954 (m, C-H), 2930 (m, C-H), 2875 (m, C-H), 2859 (m, C-H), 1736 (s, C=O), 1463 (m, C=C), 1416 (w), 1378 (w), 1254 (m), 1090 (m, C-O), 1005 (m), 970 (w), 939 (w), 837 (s), 777 (s), 730 (m).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.07 (s, 3 H, SiCH_3), 0.10 (s, 3 H, SiCH_3), 0.60 (q, $^3J_{HH}$ = 7.7 Hz, 6 H, SiCH_2CH$_3$), 0.89 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, $CH_2CH_2CH_3$), 0.94 [s, 9 H, SiC(CH_3)$_3$], 0.94 (t, $^3J_{HH}$ = 7.7 Hz, 9 H, SiCH$_2$CH_3), 1.37 (*virt.* sext, $^3J_{HH} \cong$ 7.4 Hz, 2 H, $CH_3CH_2CH_2$), 1.95-1.99 (m, 2 H, $CH_3CH_2CH_2$), 2.12-2.15 (m, 1 H, SiC*H*CH=CH), 4.09 (dd, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 2.1 Hz,1 H, C*H*OSi), 5.30-5.35 (m, 1 H, SiCHCH=C*H*), 5.36 (dd, $^3J_{trans}$= 15.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1 H, SiCHC*H*=CH), 9.53 [d, $^3J_{HH}$ = 2.2 Hz, 1 H, C(O)H].

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = -4.4 (q, Si*C*H$_3$), -4.3 (q, Si*C*H$_3$), 3.5 (t, Si*C*H$_2$CH$_3$), 7.7 (q, SiCH$_2$*C*H$_3$), 13.8 (q, *C*H$_3$CH$_2$CH$_2$), 18.4 [s, Si*C*(CH$_3$)$_3$], 22.9 (t, CH$_3$*C*H$_2$CH$_2$), 26.0 [q, SiC(*C*H$_3$)$_3$], 35.0 (t, CH$_3$CH$_2$*C*H$_2$), 35.3 (d, Si*C*HCH=CH), 80.7 [d, *C*HC(O)H], 127.2 (d, SiCH*C*H=CH), 131.3 (d, SiCHCH=*C*H), 203.7 [d, *C*(O)H].

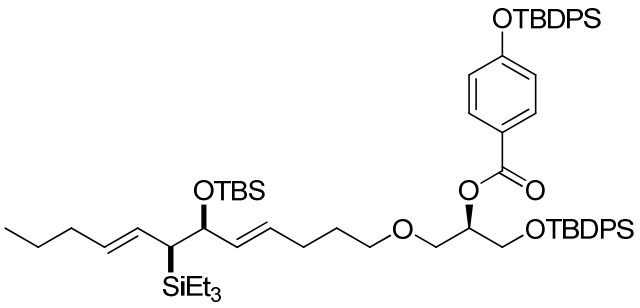
MS (ESI+): *m*/z (%) = 371 [(M + H)$^+$].

HRMS (ESI+): $C_{20}H_{43}O_2Si_2$ calcd.: [(M + H)$^+$] 371.2796
found: [(M + H)$^+$] 371.2801.

(1*R*)-2-(((4*E*,6*S*,7*S*,8*E*)-6-((*tert*-Butyl(dimethyl)silyl)oxy)-7-(triethylsilyl)dodeca-4,8-dien-1-yl)oxy)-1-(((*tert*-butyl(diphenyl)silyl)oxy)methyl)ethyl 4-(*tert*-butyl(diphenyl)silyl)oxy)benzoate (2)

and

(1*R*)-2-{[(4*E*,6*R*,7*R*,8*E*)-6-{[*tert*-butyl(dimethyl)silyl]oxy}-7-(triethylsilyl)dodeca-4,8-dien-1-yl]oxy}-1-({[*tert*-butyl(diphenyl)silyl]oxy}methyl)ethyl 4-{[*tert*-butyl(diphenyl)silyl]oxy}benzoate (2')



$C_{66}H_{96}O_6Si_4$
MW: 1097.81 g/mol

Potassium bis(trimethylsilyl)amide (KHMDS) (242 µL, 169 µmol, 0.7 M solution in toluene) was added dropwise to a solution of sulfone **4** (161 mg, 169 µmol) in THF (4 mL), cooled to −78 °C. The resulting bright yellow solution was stirred for 3 min at −78 °C and a solution of aldehyde *rac*-**16** (31.4 mg, 84.7 µmol) in THF (3 mL) was added via cannula. The reaction was stirred at −78 °C and the completion of the reaction was monitored by TLC. After 1 h, the reaction was quenched with a saturated solution of NH_4Cl (5 mL), added dropwise at −78 °C. The biphasic mixture was allowed to reach room temperature over 20 min and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic layers were dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 98/2→95/5) to afford the desired products **2** and **2'** (71.5 mg, 78.8 µmol, 93%) as a colourless oil. It is worthy to note that the ^{1}H- and ^{13}C-NMR spectra do not allow any distinction between **2** and **2'**.

TLC: R_f = 0.57 (pentane/Et_2O= 95/5) [CAM, UV].

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3071 (w, C-H), 2954 (m, C-H), 2931 (m, C-H), 2858 (m, C-H), 1718 (m, C=O), 1604 (m, C=C), 1509 (m, C=C), 1472 (w), 1428 (m), 1390 (w), 1361 (w), 1260 (s, C-O), 1164 (m), 1113 (s, C-O), 1055 (m), 1007 (w), 967 (m, O-Si), 913 (m), 852 (w), 822 (w), 772 (m), 735 (m), 700 (s).

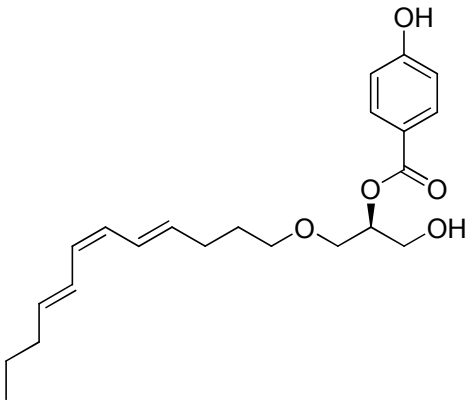
^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = -0.01 (s, 3 H, SiC*H*$_3$), 0.03 (s, 3 H, SiC*H*$_3$), 0.57 (q, $^3J_{HH}$ = 7.9 Hz, 6 H, SiC*H*$_2$CH$_3$), 0.88 [s, 9 H, SiC(C*H*$_3$)$_3$], 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, C*H*$_3$CH$_2$CH$_2$), 0.93 (t, $^3J_{HH}$ = 7.9 Hz, 9 H, SiCH$_2$C*H*$_3$), 1.02 [s, 9 H, SiC(C*H*$_3$)$_3$], 1.13 [s, 9 H, SiC(C*H*$_3$)$_3$], 1.35 (*virt.* sext, $^3J_{HH}$ ≅ 7.3 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.59-1.64 (m, 2 H, OCH$_2$C*H*$_2$CH$_2$), 1.89 (dd, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 4.7 Hz, 1 H, SiC*H*CH=CH), 1.96 (*virt.* q, $^3J_{HH}$ ≅ 7.1 Hz, 2 H, CH$_3$CH$_2$C*H*$_2$), 2.01-2.05 (m, 2 H, OCH$_2$CH$_2$C*H*$_2$), 3.40-3.51 (m, 2 H, OC*H*$_2$CH$_2$CH$_2$), 3.71 (dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 5.6 Hz, 1 H, SiOCH$_2$CHC*H*HO), 3.73 (dd, $^2J_{HH}$ = 10.8 Hz, $^3J_{HH}$ = 5.0 Hz, 1 H, SiOCH$_2$CHCH*H*O), 3.89 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, SiOC*H*$_2$CH), 4.22-4.27 (m, 1 H, SiCHC*H*OSi), 5.22 (dt, $^3J_{trans}$ = 15.0 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, CH$_3$CH$_2$CH$_2$C*H*=CH), 5.28 (*virt.* p, $^3J_{HH}$ ≅ 4.9 Hz, 1 H, SiOCH$_2$C*H*CH$_2$O), 5.34 (dd, $^3J_{trans}$ = 15.2 Hz, $^3J_{HH}$ = 10.5 Hz, 1 H, CH$_3$CH$_2$CH$_2$CH=C*H*), 5.43-5.50 (m, 2 H, OCH$_2$CH$_2$CH$_2$C*H*=CH and OCH$_2$CH$_2$CH$_2$CH=C*H*), 6.78 (*virt.* d, J_{HH} ≅ 8.7 Hz, 2 H, C$_{ar}$-*H*), 7.24-7.40 (m, 10 H, C$_{ar}$-*H*), 7.43-7.47 (m, 2 H, C$_{ar}$-*H*), 7.61-7.64 (m, 4 H, C$_{ar}$-*H*), 7.71-7.73 (m, 4 H, C$_{ar}$-*H*), 7.80 (*virt.* d, J_{HH} ≅ 8.7 Hz, 2 H, C$_{ar}$-*H*).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = -4.2 (q, Si*C*H_3), -3.9 (q, Si*C*H_3), 3.5 (t, Si*C*H_2CH_3), 7.9 (q, $SiCH_2$*C*H_3), 13.9 (q, *C*$H_3CH_2CH_2$), 18.4 [s, Si*C*$(CH_3)_3$], 19.4 [s, Si*C*$(CH_3)_3$], 19.6 [s, Si*C*$(CH_3)_3$], 23.2 (t, CH_3*C*H_2CH_2), 26.2 [q, SiC(*C*$H_3)_3$], 26.5 [q, SiC(*C*$H_3)_3$], 26.9 [q, SiC(*C*$H_3)_3$], 28.8 (t, OCH_2CH_2*C*H_2), 29.4 (t, OCH_2*C*H_2CH_2), 35.2 (t, *C*$H_2CH_2CH_3$), 40.2 (d, Si*C*HCHOSi), 62.8 (t, SiO*C*H_2CHCH_2O), 69.1 (t, SiOCH_2CH*C*H_2O), 71.2 (t, O*C*$H_2CH_2CH_2$), 73.3 (d, SiOCH_2*C*HCH_2O), 75.7 (d, SiCH*C*HOSi), 119.6 (d, *C*$_{ar}$), 123.3 (s, *C*$_{ar}$COO), 127.7 (d, *C*$_{ar}$), 127. 8 (d, *C*$_{ar}$), 128.0 (d, *C*$_{ar}$), 128.4 (d, $CH_3CH_2CH_2CH$=*C*H), 129.7 (d, *C*$_{ar}$), 129.7 (d, $CH_3CH_2CH_2$*C*H=CH), 129.8 (d, *C*$_{ar}$), 129.8 (d, $OCH_2CH_2CH_2$*C*H=CH), 130.3 (d, *C*$_{ar}$), 131.7 (d, *C*$_{ar}$), 132.3 (s, Si*C*$_{ar}$), 132.3 (s, Si*C*$_{ar}$), 133.4 (s, Si*C*$_{ar}$), 133.7 (d, $OCH_2CH_2CH_2CH$=*C*H), 135.5 (d, *C*$_{ar}$), 135.7 (d, *C*$_{ar}$), 159.9 (s, *C*$_{ar}$-OSi), 165.8 (s, *C*OO).

MS (ESI+): *m*/z (%) = 1120 (38) [$(M + Na)^+$], 966 (100) [$(M - C_6H_{15}OSi)^+$], 851 (32), 773 (5).

HRMS (ESI+): $C_{66}H_{96}O_6NaSi_4$ calcd.: [$(M + Na)^+$] 1119.6176
found: [$(M + Na)^+$] 1119.6181.

(+)-Bretonin B (1)



$C_{22}H_{30}O_5$
MW: 374.47 g/mol

HF·pyridine complex (180 µL, ~ 70% HF and 30% pyridine) was slowly added to a solution of the protected bretonin B **2/2'**(34.7 mg, 31.6 µmol) in THF (1.5 mL) and dry pyridine (370 µL). The resulting mixture was stirred at room temperature and the completion of the reaction was monitored by TLC. After 16 h, the reaction mixture was filtered on a pad of silica gel, eluting with diethyl ether. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 30/70) to afford of (+)-bretonin B (**1**) (28.4 mg, 28.4 µmol, 90%) as a highly viscous colourless oil.

TLC: R_f = 0.54 (pentane/Et_2O= 30/70) [UV, CAM].

Specific rotation: $[\alpha]_D^{20}$ = +4.4 (*c* = 1.0, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3299 (s, br, O-H), 3025 (w, C-H), 2956 (m, C-H), 2927 (m, C-H), 2871 (m, C-H), 1708 (m, C=O), 1686 (m, C=C), 1608 (m, C=C), 1592 (m, C=C), 1514 (w, C=C), 1445 (w), 1357 (w), 1310 (w), 1270 (s, C-O), 1165 (m, C-O), 1098 (m, C-O), 1042 (w), 963 (m, O-Si), 851 (w), 771 (m).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, C*H*$_3$CH$_2$CH$_2$), 1.43 (*virt*. sext, $^3J_{HH}$ ≅ 7.3 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.69-1.74 (m, 2 H, OCH$_2$C*H*$_2$CH$_2$), 2.10 (*virt*. q, $^3J_{HH}$ ≅ 7.0 Hz, 2 H, CH$_3$CH$_2$C*H*$_2$), 2.20 (*virt*. q, $^3J_{HH}$ ≅ 7.1 Hz, 2 H, OCH$_2$CH$_2$C*H*$_2$), 2.82 (br s, 1 H, OH), 3.49-3.59 (m, 2 H, OC*H*$_2$CH$_2$CH$_2$), 3.77 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, HOCH$_2$CHC*H*HO), 3.82 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, HOCH$_2$CHCH*H*O), 3.97 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 4.7 Hz, 1 H, HOC*H*HCHCH$_2$O), 4.00 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 4.2 Hz, 1 H, HOCH*H*CHCH$_2$O), 5.23 (*virt*. p, $^3J_{HH}$ ≅ 4.3 Hz, 1 H, HOCH$_2$C*H*CH$_2$O), 5.66 (dt, $^3J_{trans}$ = 15.3 Hz, $^3J_{HH}$ = 7.1 Hz, 1 H, OCH$_2$CH$_2$CH$_2$C*H*=CH), 5.71 (dt, $^3J_{trans}$ = 15.3

Hz, $^3J_{HH}$ = 7.1 Hz, 1 H, $CH_3CH_2CH_2CH$=CH), 5.83 (*virt.* t, $^3J_{HH} \cong$ 10.9 Hz, 1 H, $OCH_2CH_2CH_2CH$=CH-C*H*=CH), 5.87 (*virt.* t, $^3J_{HH} \cong$ 10.9 Hz, 1 H, $CH_3CH_2CH_2CH$=CH-C*H*=CH), 6.42-6.54 (m, 2 H, $OCH_2CH_2CH_2CH$=C*H*-CH, $CH_3CH_2CH_2CH$=C*H*-CH), 6.82 (*virt.* d, $J_{HH} \cong$ 8.7 Hz, 2 H, C_{ar}-*H*), 7.92 (*virt.* d, $J_{HH} \cong$ 8.7 Hz, 2 H, C_{ar}-*H*).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = 13.9 (q, $CH_2CH_2CH_3$), 22.7 (t, $CH_2CH_2CH_3$), 29.3 (t, $OCH_2CH_2CH_2$), 29.5 (t, $OCH_2CH_2CH_2$), 35.2 (t, $CH_2CH_2CH_3$), 63.5 (t, $HOCH_2CHCH_2O$), 70.6 (t, $HOCH_2CHCH_2O$), 71.4 (t, $OCH_2CH_2CH_2$), 73.2 (d, $HOCH_2CHCH_2O$), 115.4 (d, C_{ar}), 122.0 (s, $C_{ar}COO$), 125.9 (d, $CH_3CH_2CH_2CH$=CH), 126.6 (d, $OCH_2CH_2CH_2CH$=CH), 127.4 (d, $OCH_2CH_2CH_2CH$=CH-CH), 128.3 (d, $CH_3CH_2CH_2CH$=CH-CH), 132.3 (d, C_{ar}), 134.1 (d, $OCH_2CH_2CH_2CH$=CH), 135.8 (d, $CH_3CH_2CH_2CH$=CH), 160.7 (s, C_{ar}-OH), 166.3 (s, COO).

UV-Vis ($CHCl_3$): λ_{max} (nm) = 250 (shoulder, ε = 26419 M^{-1} cm^{-1}), 261 (37140), 271 (38249), 281 (25708).

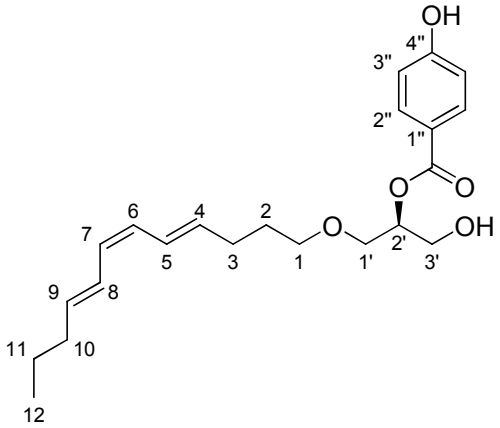
MS (ESI-): *m*/z (%) = 373 [$(M - H)^-$].

HRMS (ESI-): $C_{22}H_{29}O_5$ calcd.: [$(M - H)^-$] 373.2021
found: [$(M - H)^-$] 373.2023.

The data obtained matched those reported in the literature:[6]

[6] I. Mancini, G. Guella and F. Pietra, *Helv. Chim. Acta,* 1991, **74**, 941-950.

Comparison of the ^{1}H NMR data of 1 with those reported in the literature.[6]



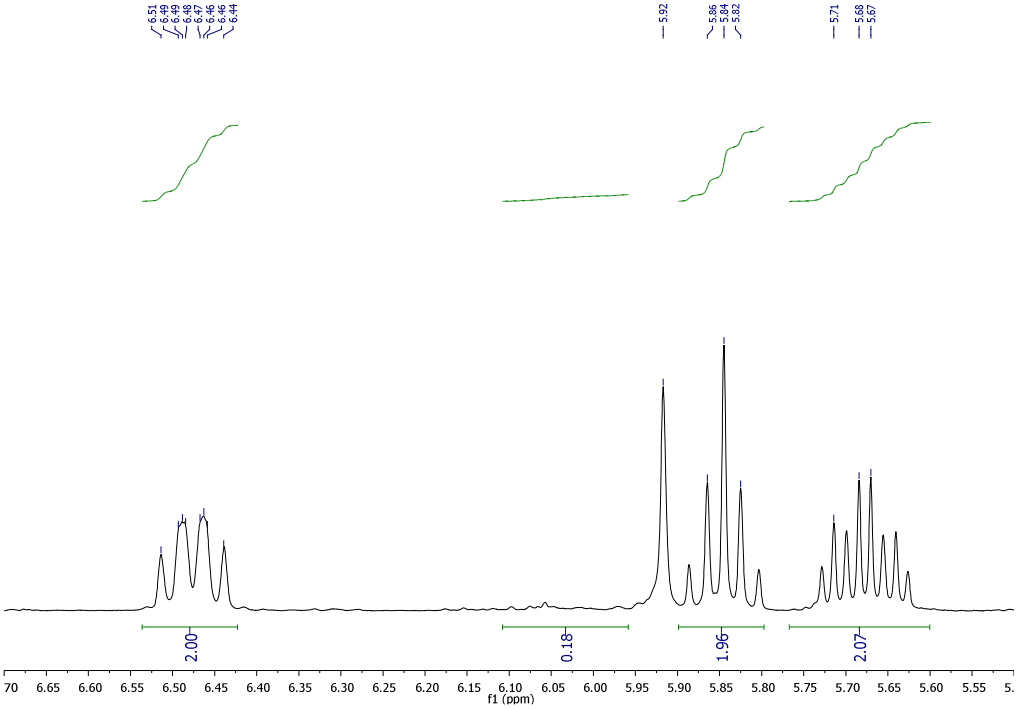
	Lit.[6] ($CDCl_3$, 300 MHz)	**1** ($CDCl_3$, 500 MHz)
2H-C(1)	3.50 (m)	3.49-3.59 (m)
2H-C(2)	1.68 (p, J = 7.2 Hz)	1.69-1.74 (m)
2H-C(3)	2.15 (q, J = 7.2 Hz)**	2.20 (*virt*. q, $^3J_{HH} \cong$ 7.1 Hz)
H-C(4)	5.65 (dt, J = 14.7 Hz, J = 7.0 Hz)*	5.66 (dt, $^3J_{trans}$= 15.3 Hz, $^3J_{HH}$ = 7.1 Hz)
H-C(5)	6.40-6.54 (m)	6.42-6.54 (m)
H-C(6)	5.83 (m)	5.83 (*virt*. t, $^3J_{HH} \cong$ 10.9 Hz)
H-C(7)	5.83 (m)	5.87 (*virt*. t, $^3J_{HH} \cong$ 10.9 Hz)
H-C(8)	6.40-6.54 (m)	6.42-6.54 (m)
H-C(9)	5.69 (dt, J = 14.7 Hz, J = 7.0 Hz)*	5.71 (dt, $^3J_{trans}$= 15.3 Hz, $^3J_{HH}$ = 7.1 Hz)
2H-C(10)	2.08 (q, J = 7.2 Hz)**	2.10 (*virt*. q, $^3J_{HH} \cong$ 7.0 Hz)
2H-C(11)	1.42 (sext, J = 7.2 Hz)	1.43 (*virt*. sext, $^3J_{HH} \cong$ 7.3 Hz)
3H-C(12)	0.90 (t, J = 7.2 Hz)	0.92 (t, $^3J_{HH}$ = 7.3 Hz)
2H-C(1')	3.75, 3.77 (AB of ABX, J(AB) = 10.5 Hz, J(AX) = 4.8 Hz, J(BX) = 5.1 Hz)	3.77 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, part of ABX system), 3.82 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 4.8 Hz, 1 H, part of ABX system)
H-C(2')	5.20 (p, J = 4.8 Hz)	5.23 (*virt*. p, $J \cong$ 4.3 Hz, 1 H)
2H-C(3')	3.92 (d, J = 4.8 Hz)	3.97 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 4.7 Hz, 1 H, part of ABX system), 4.00 (dd, $^2J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 4.2 Hz, 1 H, part of ABX system)
H-C(2'')	7.96 (d, J = 8.7 Hz)	7.92 (d, J_{HH} = 8.7 Hz)
H-C(3'')	6.85 (d, J = 8.7 Hz)	6.82 (d, J_{HH} = 8.7 Hz)

*, **: these assignments can be interchanged.

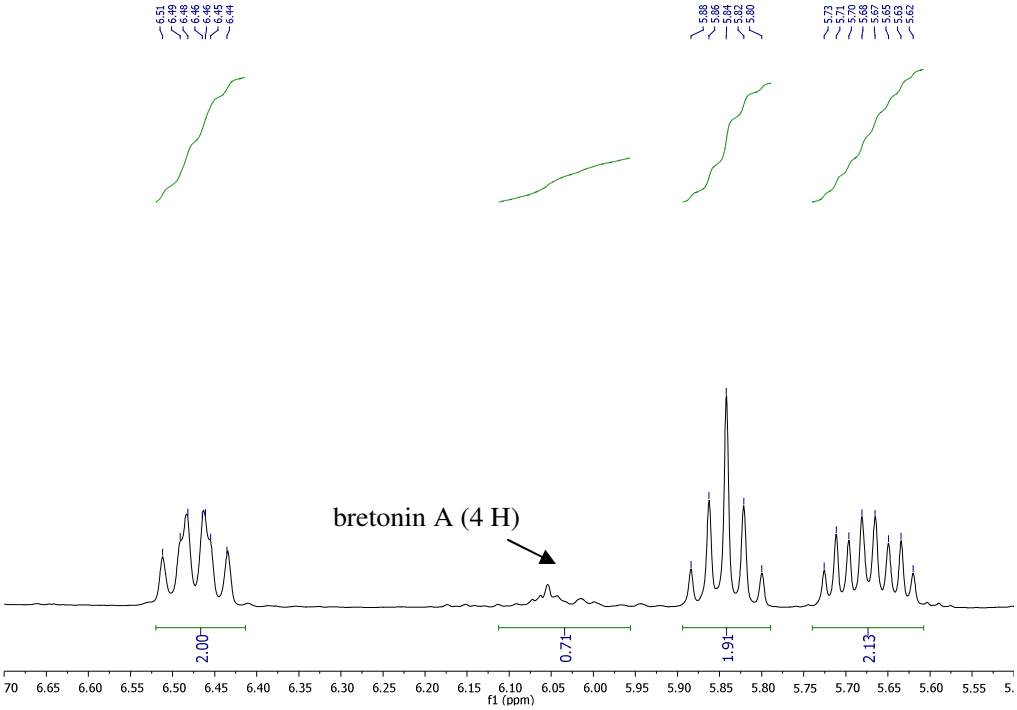
Isomerisation of bretonin B to bretonin A:

Upon standing at room temperature, an isomerisation of the (*E*,*Z*,*E*)-triene unit of bretonin B (**1**) to isomeric (*E*,*E*,*E*)-configured bretonin A was observed. For instance, evolution of a 97/3 mixture of isomers to a ratio <90/10 could be followed by ^{1}H-NMR spectroscopy (500 MHz, $CDCl_3$):

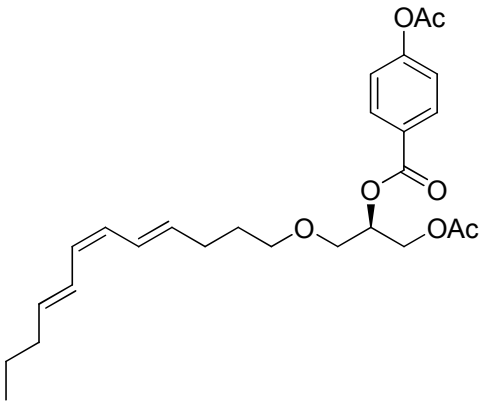
- (*E*,*Z*,*E*)/(*E*,*E*,*E*) > 97/3



- (*E*,*Z*,*E*)/(*E*,*E*,*E*) <90/10



(*R*)-2-(Acetyloxy)-1-{[(4*E*,6*Z*,8*E*)-dodeca-4,6,8-trien-1-yloxy]methyl}ethyl 4-(acetyloxy)benzoate (17)



$C_{26}H_{34}O_7$
MW: 458.54 g/mol

Pyridine (46.0 µL, 566 µmol) and acetic anhydride (27.0 µL, 283 µmol) were successively added to a solution of bretonin B (**1**) (10.6 mg, 28.3 µmol) in dichloromethane (1.1 mL). The resulting mixture was stirred at room temperature and the completion of the reaction was monitored by TLC. After 24 h, the reaction was quenched with a saturated solution of NH_4Cl (3 mL) and the aqueous layer was extracted with dichloromethane (3 × 5 mL). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (2 × 15 mL), dried on $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel (pentane/Et_2O: 75/25) to afford the desired bretonin B diacetate **17** (8.90 mg, 19.4 µmol, 69%) as a highly viscous colourless oil.

TLC: R_f = 0.29 (pentane/Et_2O= 75/25) [UV/CAM].

Specific rotation: $[\alpha]_D^{20} = -14.3$ (c = 1.1, $CHCl_3$).

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3025 (w, C-H), 2957 (m, C-H), 2929 (m, C-H), 2871 (m, C-H), 1744 (s, C=O), 1721 (s, C=O), 1638 (w, C=C), 1604 (m, C=C), 1504 (m, C=C), 1436 (w), 1414 (w), 1368 (m), 1271 (m, C-O), 1193 (s, C-O), 1161 (s, C-O), 1113 (m, C-O), 1100 (m, C-O), 1047 (w), 1016 (w), 965 (m, O-Si), 913 (w), 863 (w), 762 (m), 703 (m).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, C*H*$_3$CH$_2$CH$_2$), 1.43 (*virt*. sext, $^3J_{HH} \cong$ 7.4 Hz, 2 H, CH$_3$C*H*$_2$CH$_2$), 1.68 (*virt*. p, $^3J_{HH} \cong$ 6.6 Hz, 2 H, OCH$_2$C*H*$_2$CH$_2$), 2.06 [s, 3 H, OC(O)C*H*$_3$], 2.11 (*virt*. q, $^3J_{HH} \cong$ 7.3 Hz, 2 H, CH$_3$CH$_2$C*H*$_2$), 2.19 (*virt*. q, $^3J_{HH} \cong$ 7.5 Hz, 2 H, OCH$_2$CH$_2$C*H*$_2$), 2.34 [s, 3 H, OC(O)C*H*$_3$], 3.46-3.54 (m, 2 H, OC*H*$_2$CH$_2$CH$_2$),

3.66 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, AcOCH$_2$CHC*H*HO), 3.70 (dd, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, AcOCH$_2$CHCH*H*O), 4.36 (dd, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, AcOC*H*HCHCH$_2$O), 4.44 (dd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, AcOCH*H*CHCH$_2$O), 5.41-5.45 (m, 1 H, AcOCH$_2$C*H*CH$_2$O), 5.67 (dt, $^3J_{trans}$= 14.8 Hz, $^3J_{HH}$ = 7.1 Hz, 1 H, OCH$_2$CH$_2$CH$_2$C*H*=CH), 5.70 (dt, $^3J_{trans}$= 14.8 Hz, $^3J_{HH}$ = 7.2 Hz, 1 H, CH$_3$CH$_2$CH$_2$C*H*=CH), 5.83 (*virt*. t, $^3J_{HH} \cong$ 10.9 Hz, 1 H, OCH$_2$CH$_2$CH$_2$CH=CH-C*H*=CH), 5.87 (*virt*. t, $^3J_{HH} \cong$ 10.9 Hz, 1 H, CH$_3$CH$_2$CH$_2$CH=CH-C*H*=CH), 6.43-6.54 (m, 2 H, OCH$_2$CH$_2$CH$_2$CH=C*H*-CH, CH$_3$CH$_2$CH$_2$CH=C*H*-CH), 7.19 (*virt.* d, $J_{HH} \cong$ 8.8 Hz, 2 H, C$_{ar}$-*H*), 8.09 (*virt.* d, $J_{HH} \cong$ 8.6 Hz, 2 H, C$_{ar}$-*H*).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ (ppm) = 13.9 (q, CH$_2$CH$_2$*C*H$_3$), 21.0 [q, C(O)*C*H3], 21.3 [q, C(O)*C*H3], 22.7 (t, CH$_2$*C*H$_2$CH$_3$), 29.3 (t, OCH$_2$*C*H$_2$CH$_2$), 29.5 (t, OCH$_2$CH$_2$*C*H$_2$), 35.2 (t, *C*H$_2$CH$_2$CH$_3$), 63.2 (t, AcO*C*H$_2$CHCH$_2$O), 69.1 (t, AcOCH$_2$CH*C*H$_2$O), 71.2 (t, O*C*H$_2$CH$_2$CH$_2$), 71.3 (d, AcOCH$_2$*C*HCH$_2$O), 121.8 (d, *C*$_{ar}$), 126.0 (d, CH$_3$CH$_2$CH$_2$CH=*C*H), 126.4 (d, OCH$_2$CH$_2$CH$_2$CH=*C*H), 127.5 (d, OCH$_2$CH$_2$CH$_2$CH=CH-*C*H), 127.6 (s, *C*$_{ar}$COO), 128.2 (d, CH$_3$CH$_2$CH$_2$CH=CH-*C*H), 131.5 (d, *C*$_{ar}$), 134.3 (d, OCH$_2$CH$_2$CH$_2$*C*H=CH), 135.7 (d, CH$_3$CH$_2$CH$_2$*C*H=CH), 154.6 (s, *C*$_{ar}$-OAc), 165.2 (s, C$_{ar}$-*C*OO), 169.1 [s, *C*(O)CH$_3$], 170.9 [s, *C*(O)CH$_3$].

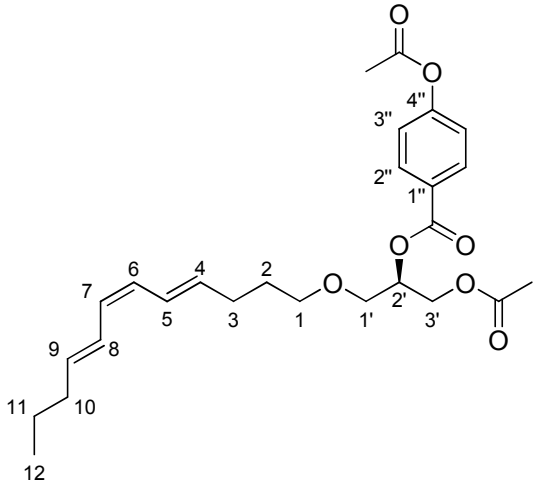
UV-Vis ($CHCl_3$): λ_{max} (nm) = 244 (shoulder, ε = 23639 M^{-1} cm^{-1}), 250 (shoulder, 24899), 262 (31553), 272 (37571), 282 (28359).

MS (ESI+): *m*/z (%) = 481 (47) [(M + Na)$^+$], 476 (100) [(M + NH$_4$)$^+$], 459 (61) [(M + H)$^+$], 399 (10) [(M - C$_2$H$_3$O$_2$)$^+$], 279 (52) [(M - C$_{12}$H$_{19}$O)$^+$].

HRMS (ESI+): C$_{26}$H$_{35}$O$_7$ calcd.: [(M + H)$^+$] 459.2377
found: [(M + H)$^+$] 459.2381.

The data obtained matched those reported in the literature.[6]

Comparison of the ^{1}H NMR data of 17 with those reported in the literature.[6]

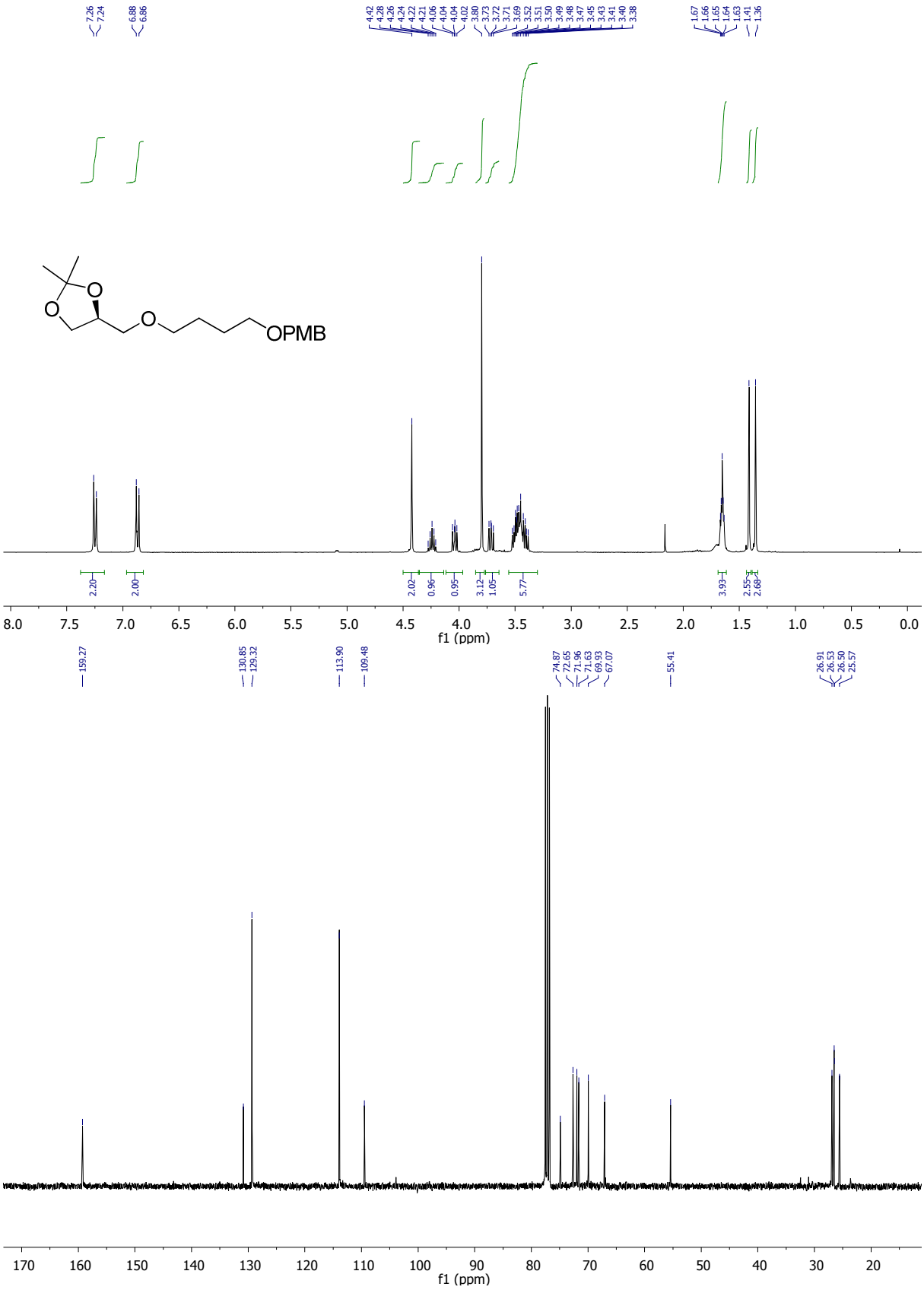


	Lit.[6] ($CDCl_3$, 300 MHz)	**17** ($CDCl_3$, 500 MHz)
2H-C(1)	3.48 (m)	3.46-3.54 (m)
2H-C(2)	1.63 (m)**	1.68 (*virt.* p, $^3J_{HH} \cong 6.6$ Hz)
2H-C(3)	2.05-2.12 (m)	2.19 (*virt.* q, $^3J_{HH} \cong 7.5$ Hz)
H-C(4)	5.66 (dt, J = 14.8 Hz, J = 7.2 Hz)*	5.67 (dt, $^3J_{trans}$= 14.8 Hz, $^3J_{HH}$ = 7.1 Hz)
H-C(5)	6.40-6.56 (m)	6.43-6.54 (m)
H-C(6)	5.84 (m)	5.83 (*virt.* t, $^3J_{HH} \cong 10.9$ Hz)
H-C(7)	5.84 (m)	5.87 (*virt.* t, $^3J_{HH} \cong 10.9$ Hz)
H-C(8)	6.40-6.56 (m)	6.43-6.54 (m)
H-C(9)	5.69 (dt, J = 14.8 Hz, J = 7.2 Hz)*	5.70 (dt, $^3J_{trans}$= 14.8 Hz, $^3J_{HH}$ = 7.2 Hz)
2H-C(10)	2.05-2.12 (m)	2.11 (*virt.* q, $^3J_{HH} \cong 7.3$ Hz)
2H-C(11)	1.40 (m)**	1.43 (*virt.* sext, $^3J_{HH} \cong 7.4$ Hz)
3H-C(12)	0.90 (t, J = 7.2 Hz)	0.92 (t, $^3J_{HH}$ = 7.3 Hz)
2H-C(1')	3.64, 3.67 (AB of ABX, J(AB) = 10.2 Hz, J(AX) = 5.1 Hz, J(BX) = 5.1 Hz)	3.66 (dd, $^2J_{HH}$ = 10.6 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, part of ABX system) 3.70 (dd, $^2J_{HH}$ = 10.7 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, part of ABX system)
H-C(2')	5.40 (m)	5.41-5.45 (m)
2H-C(3')	4.33, 4.41 (AB of ABX, J(AB) = 12.0 Hz, J(AX) = 3.9 Hz, J(BX) = 6.6 Hz)	4.36 (dd, $^2J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, part of ABX system) 4.44 (dd, $^2J_{HH}$ = 12.0 Hz, $^3J_{HH}$ = 3.6 Hz, 1 H, part of ABX system)
H-C(2'')	8.07 (d, J = 8.7 Hz)	8.09 (d, J_{HH} = 8.6 Hz)
H-C(3'')	7.17 (d, J = 8.7 Hz)	7.19 (d, J_{HH} = 8.8 Hz)
3H-CCO_2C(4'')	2.32 (s)	2.34 (s)
3H-CCO_2C(3')	2.04 (s)	2.06 (s)

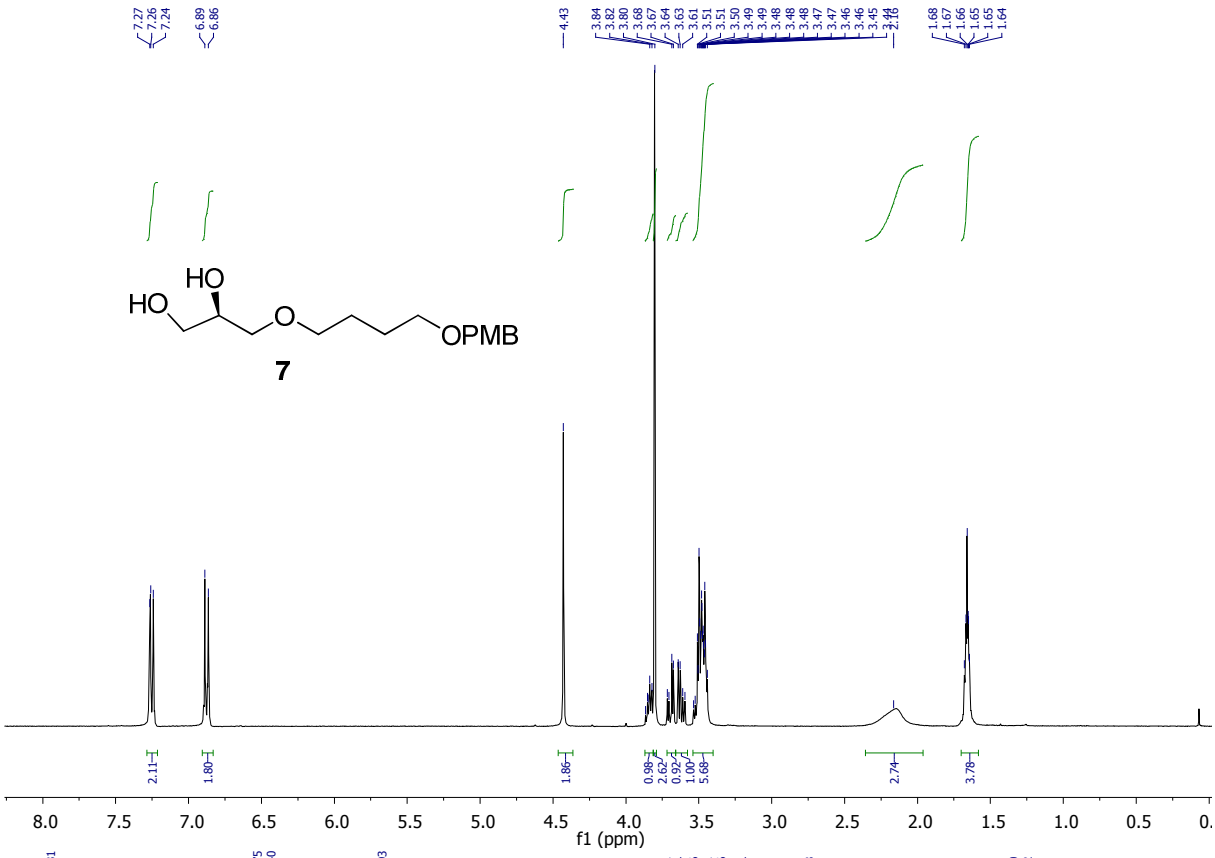
*, **: these assignments can be interchanged.

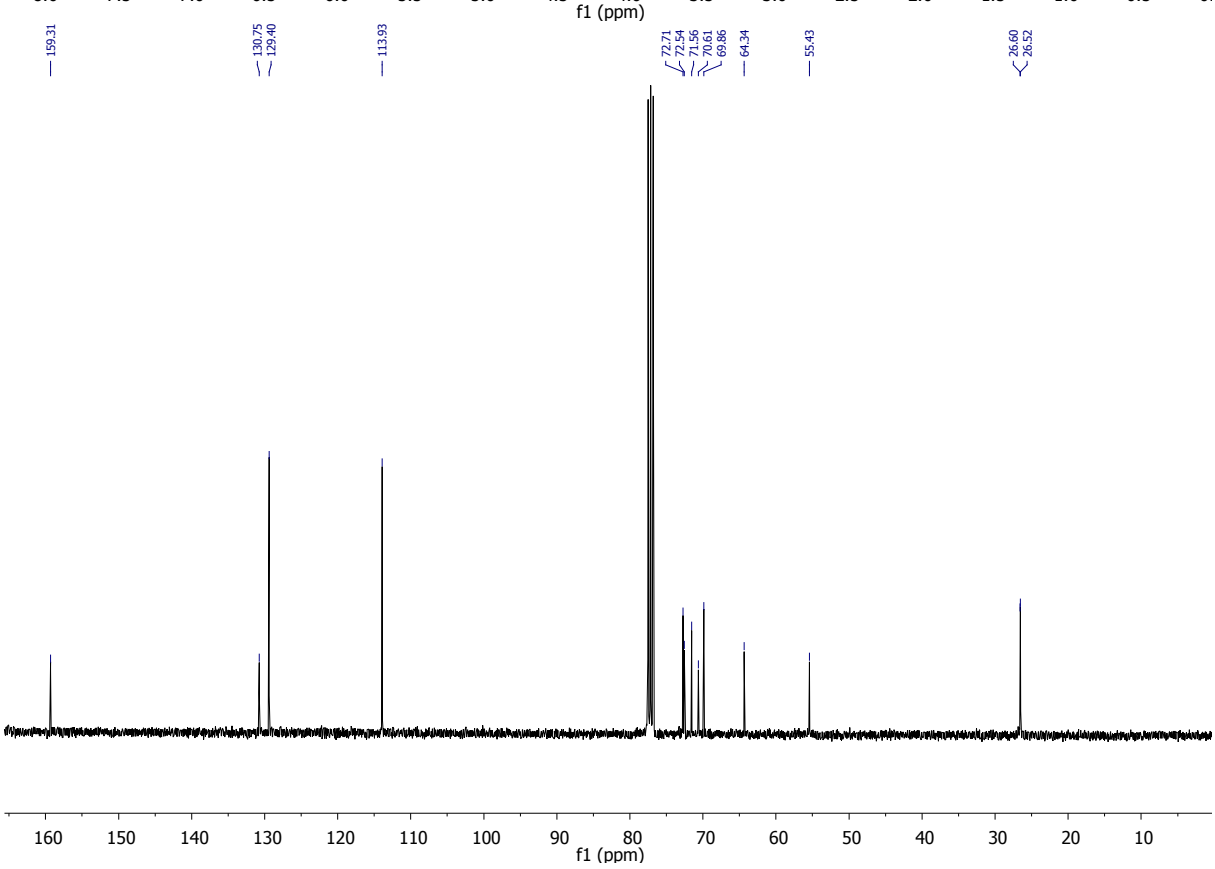
NMR spectra of new compounds

(*S*)-4-((4-(4-Methoxybenzyloxy)butoxy)methyl)-2,2-dimethyl-1,3-dioxolane (6)

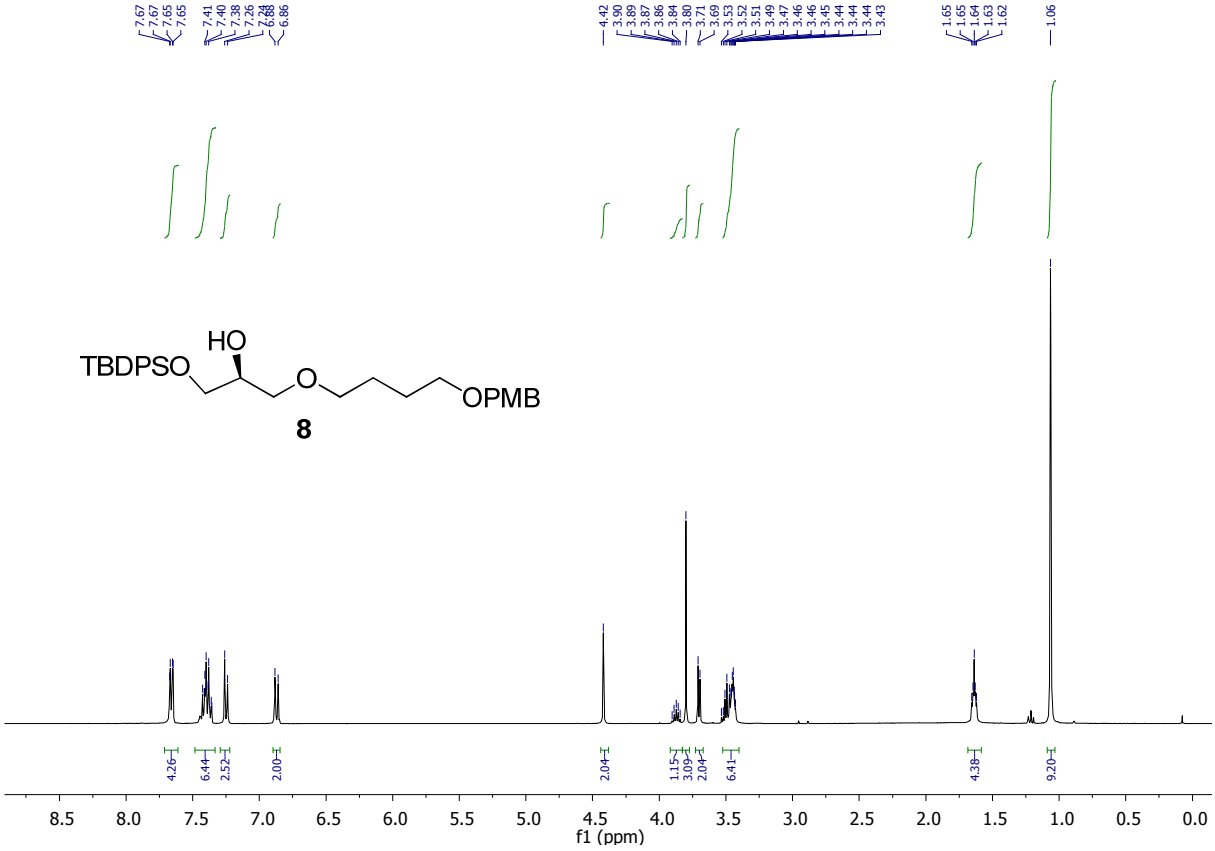


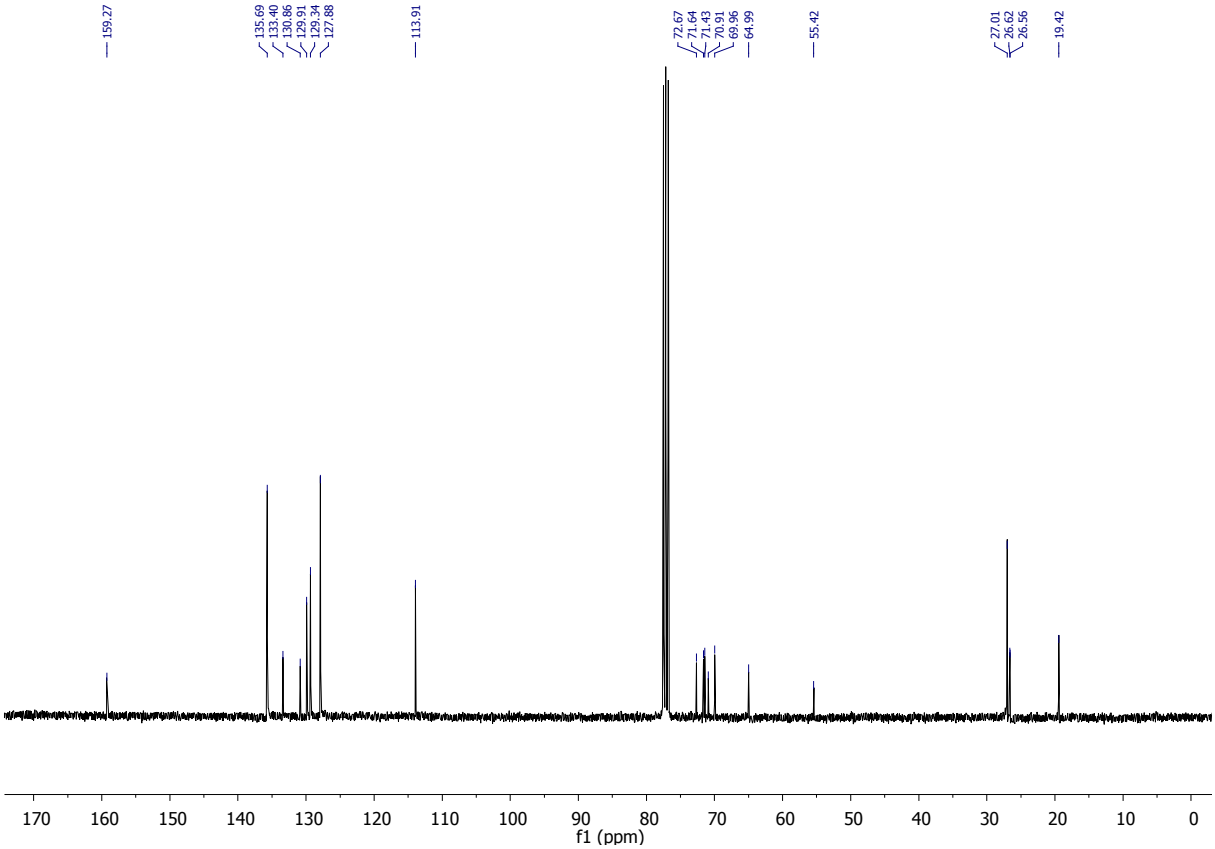
(*S*)-3-(4-(4-Methoxybenzyloxy)butoxy)propan-1,2-diol (7)



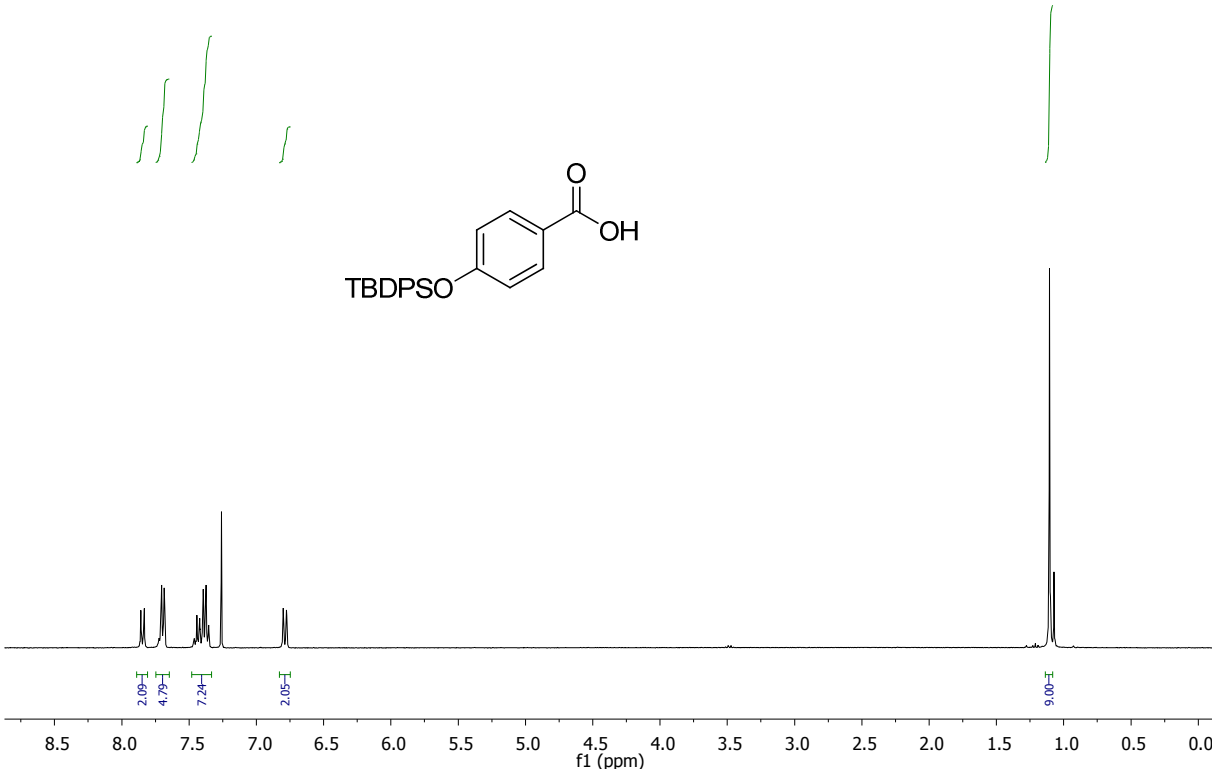


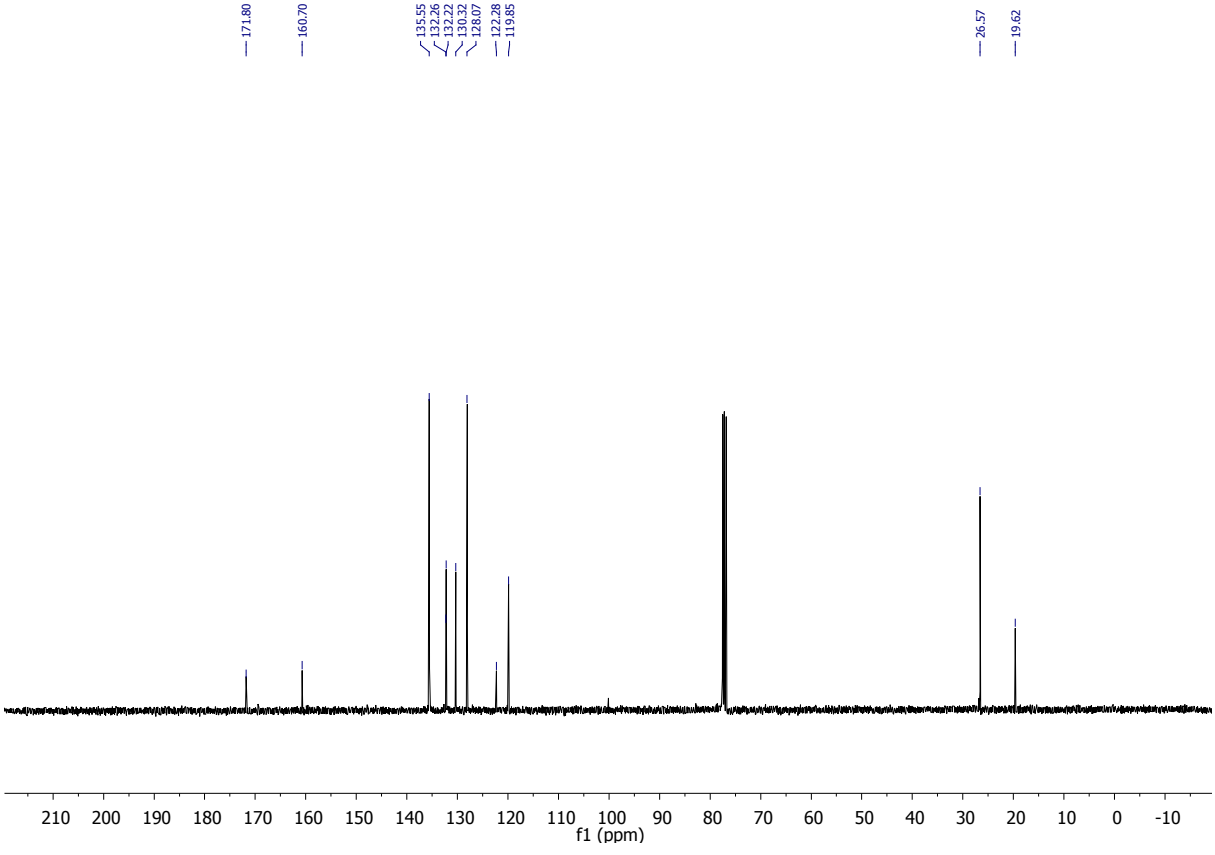
(*S*)-1-(4-Methoxyphenyl)-13,13-dimethyl-12,12-diphenyl-2,7,11-trioxa-12-silatetradecan-9-ol (8)



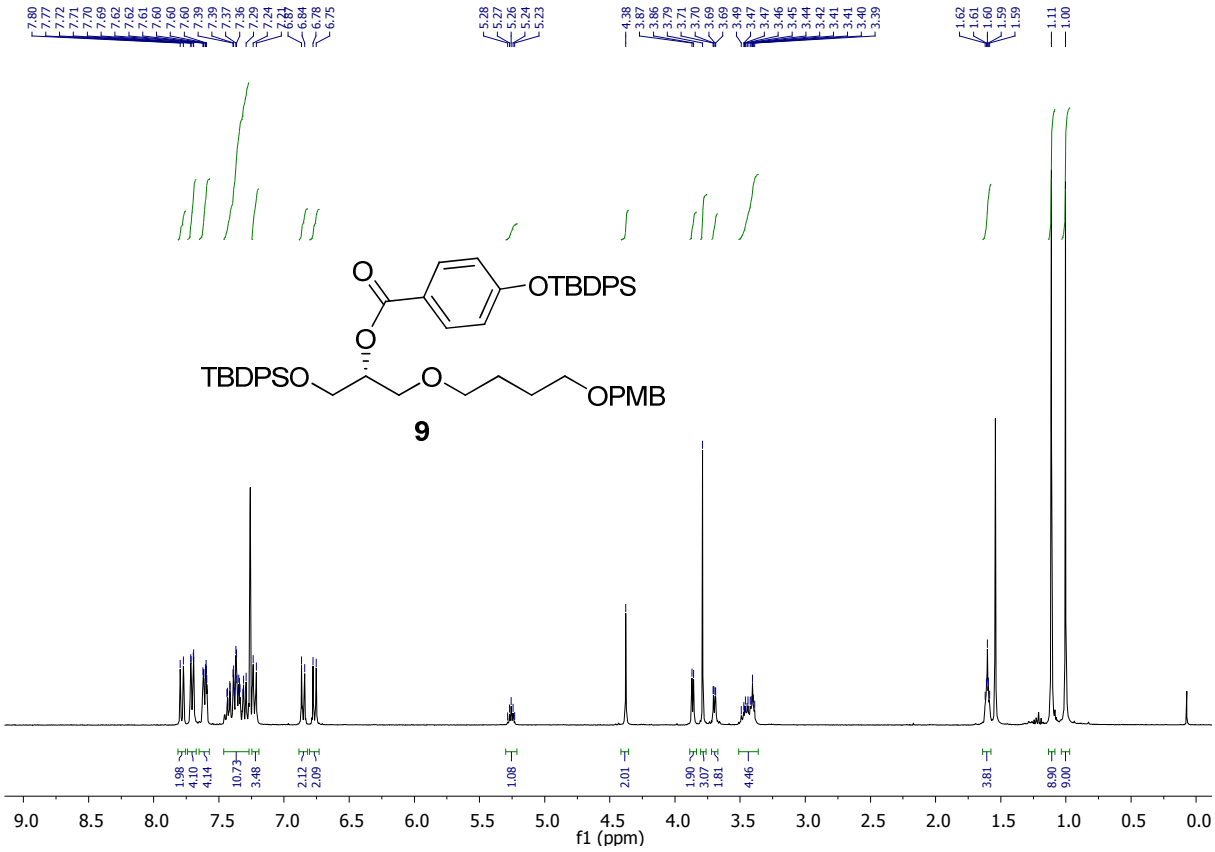


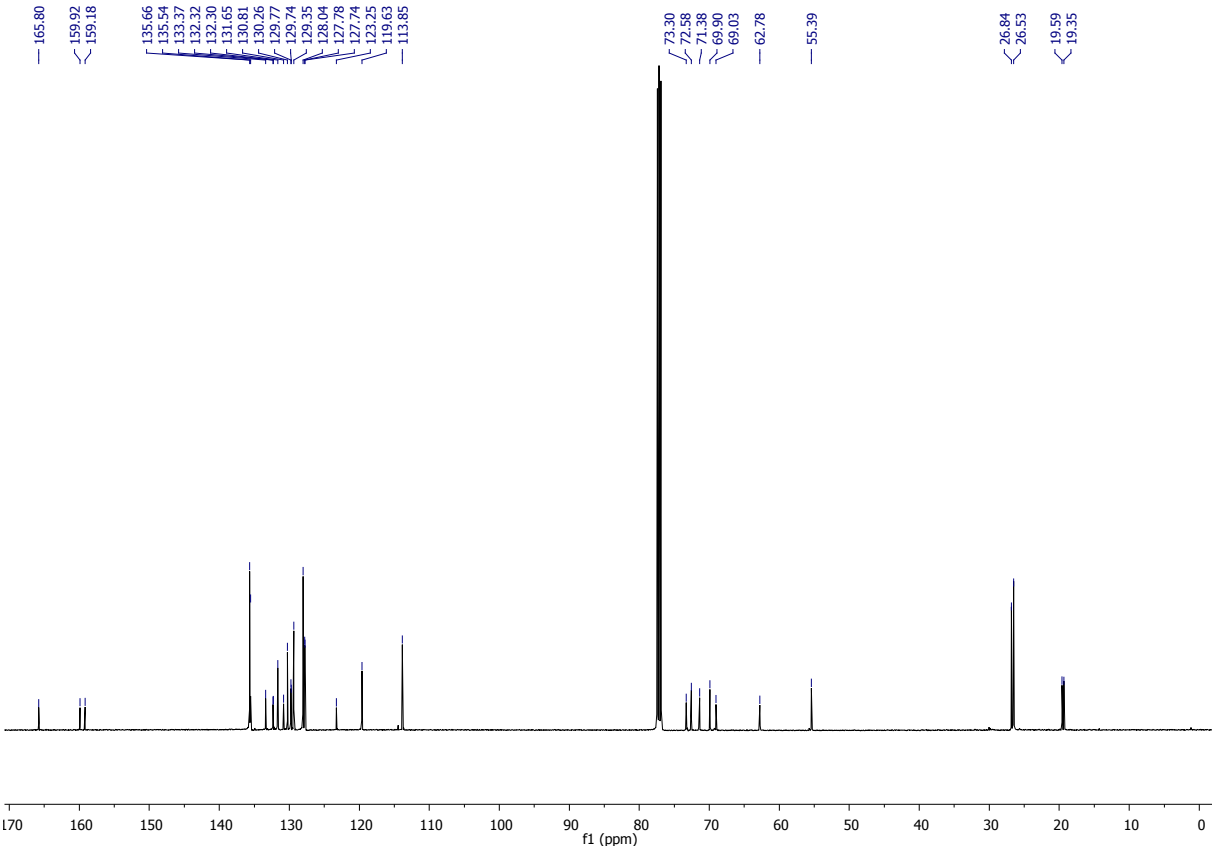
4-((*tert*-Butyldiphenylsilyl)oxy)benzoic acid (S3)



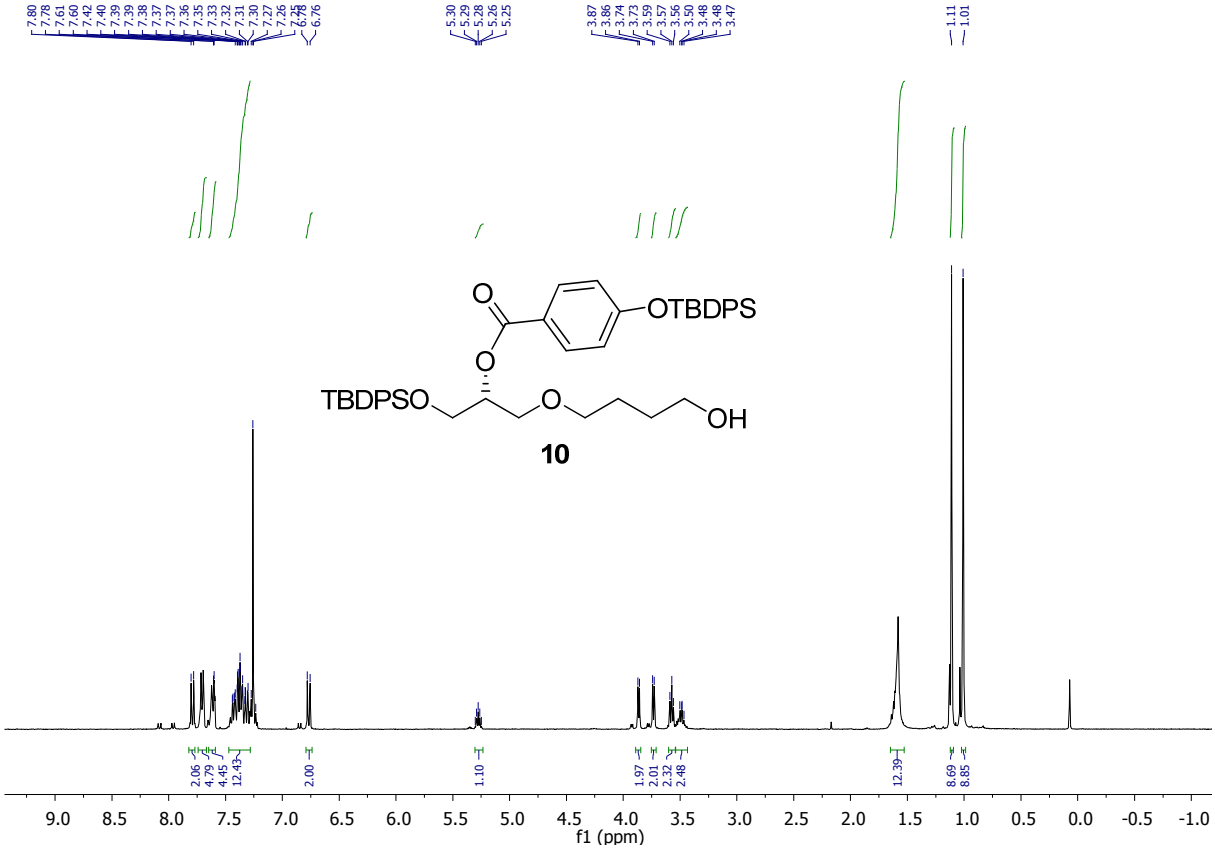


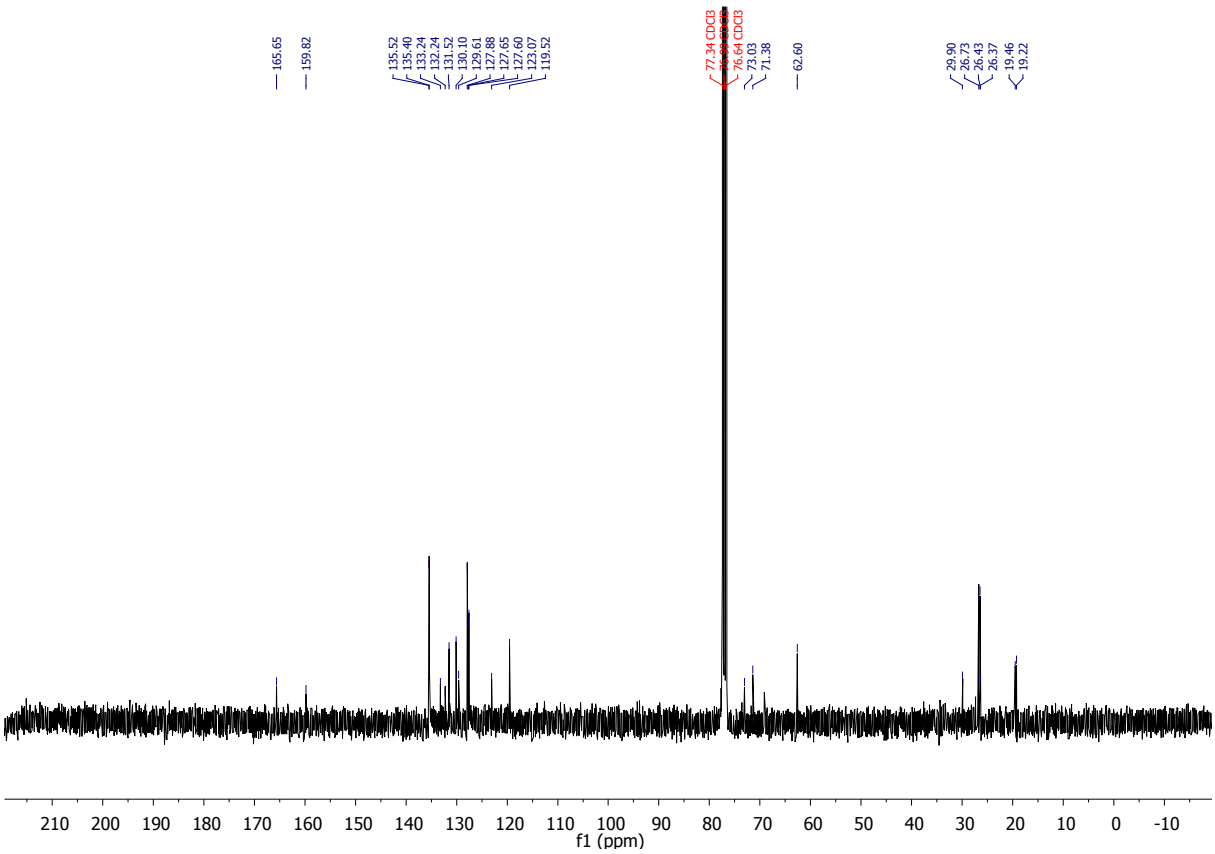
(*R*)-1-(4-Methoxyphenyl)-13,13-dimethyl-12,12-diphenyl-2,7,11-trioxa-12-silatetradecan-9-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (9)



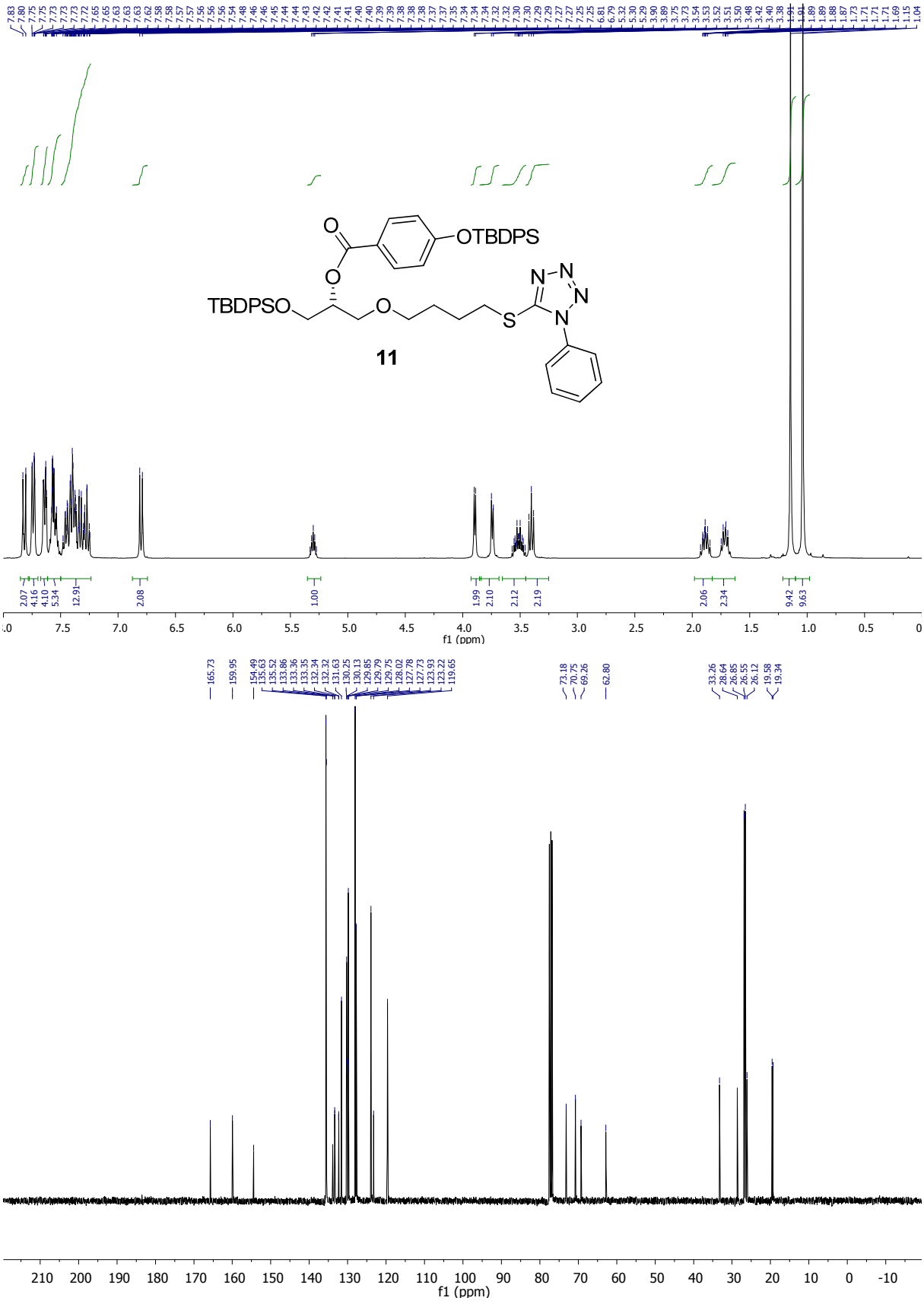


(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-hydroxybutoxy)propan-2-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (10)

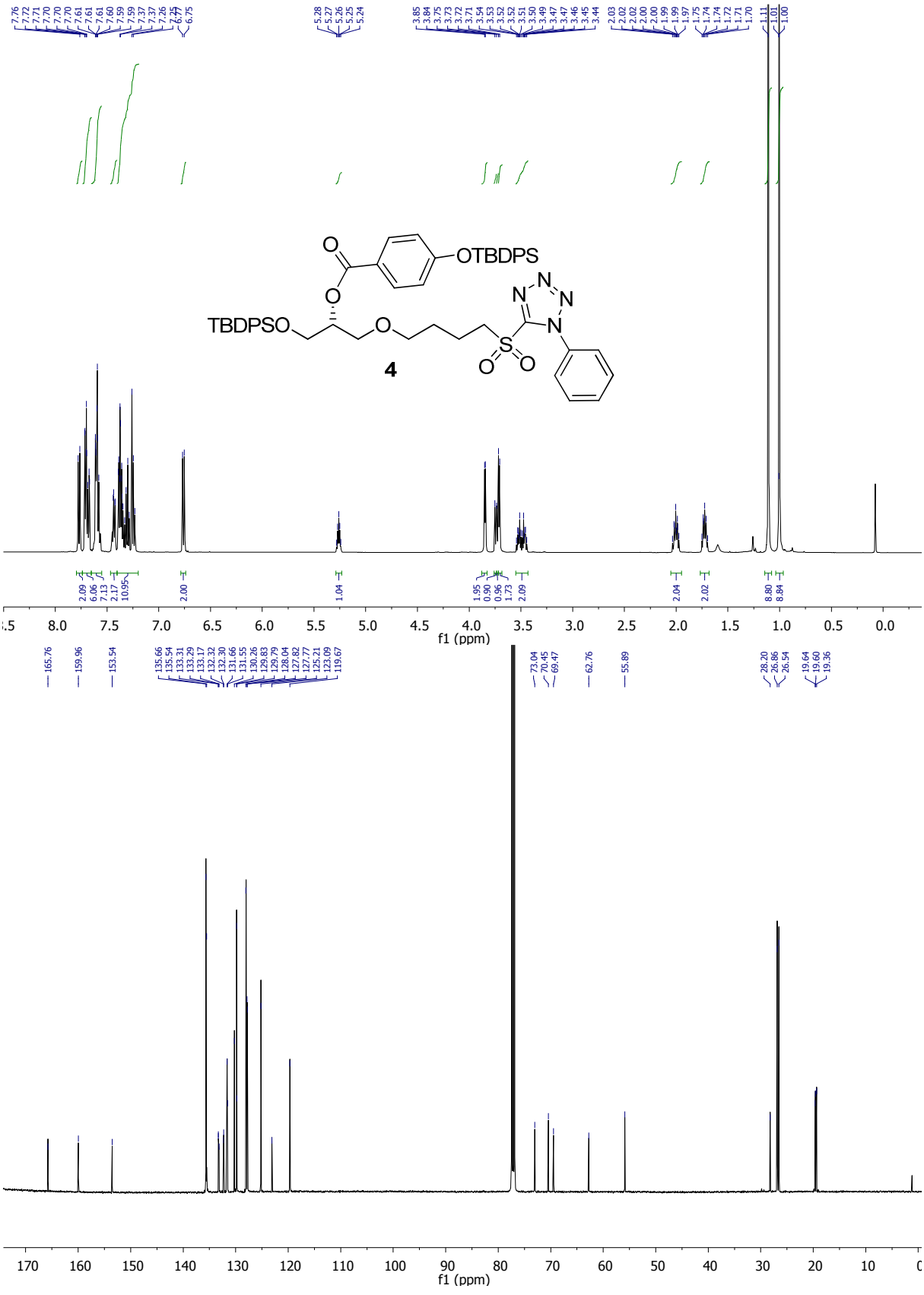




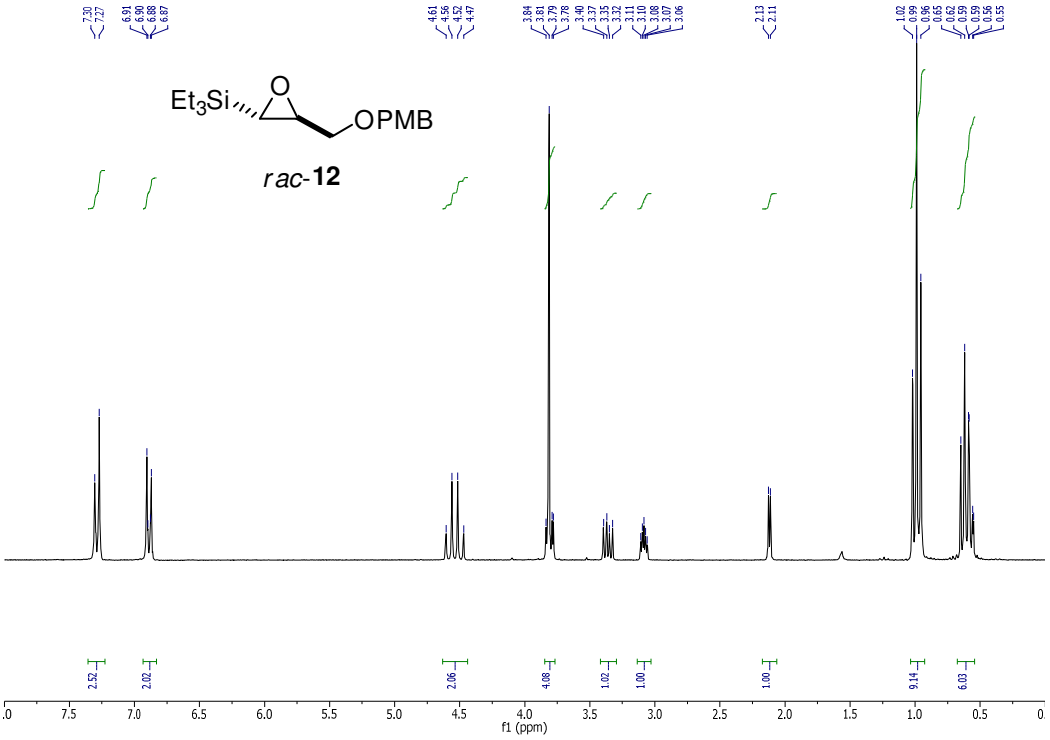
(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-(1-phenyl-*1H*-tetrazole-5-ylthio)butoxy)propan-2-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (11)

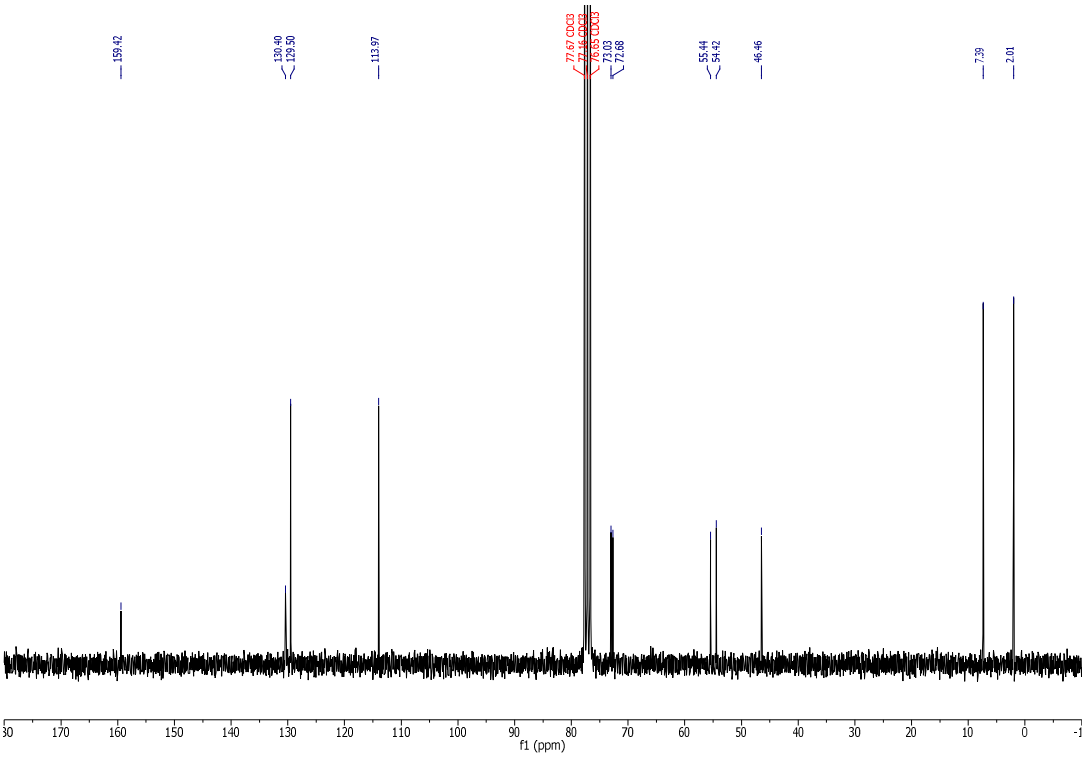


(*R*)-1-(*tert*-Butyldiphenylsilyloxy)-3-(4-(1-phenyl-1*H*-tetrazole-5-ylsulfonyl)butoxy)propan-2-yl 4-(*tert*-butyldiphenylsilyloxy)benzoate (4)

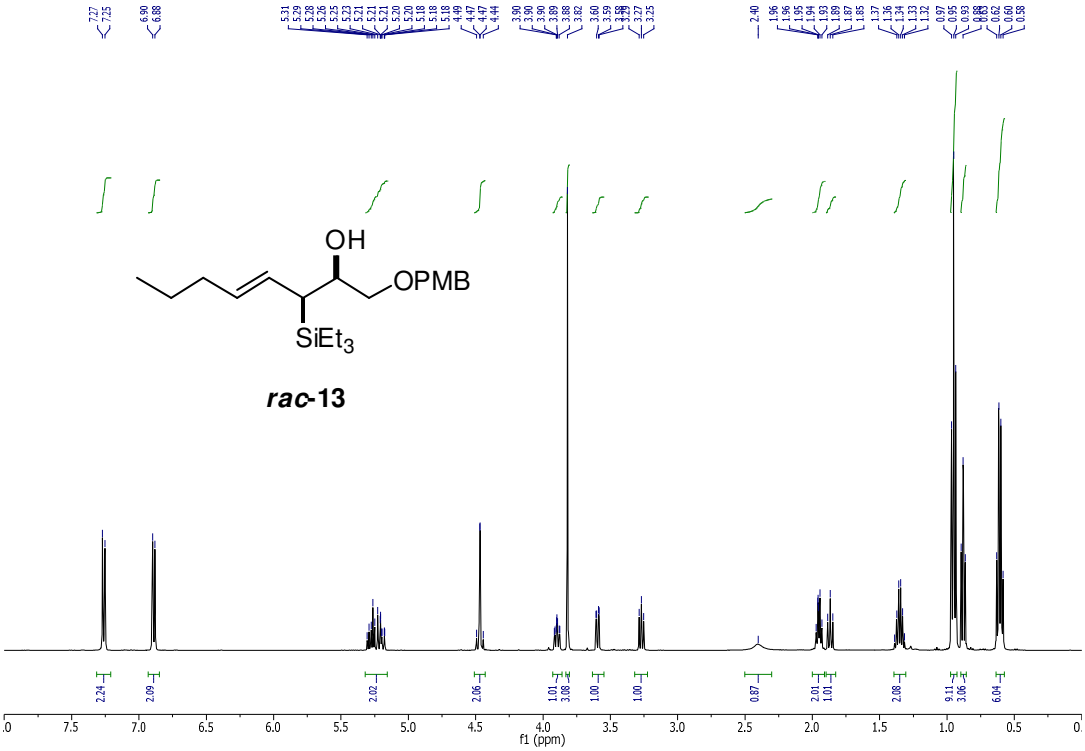


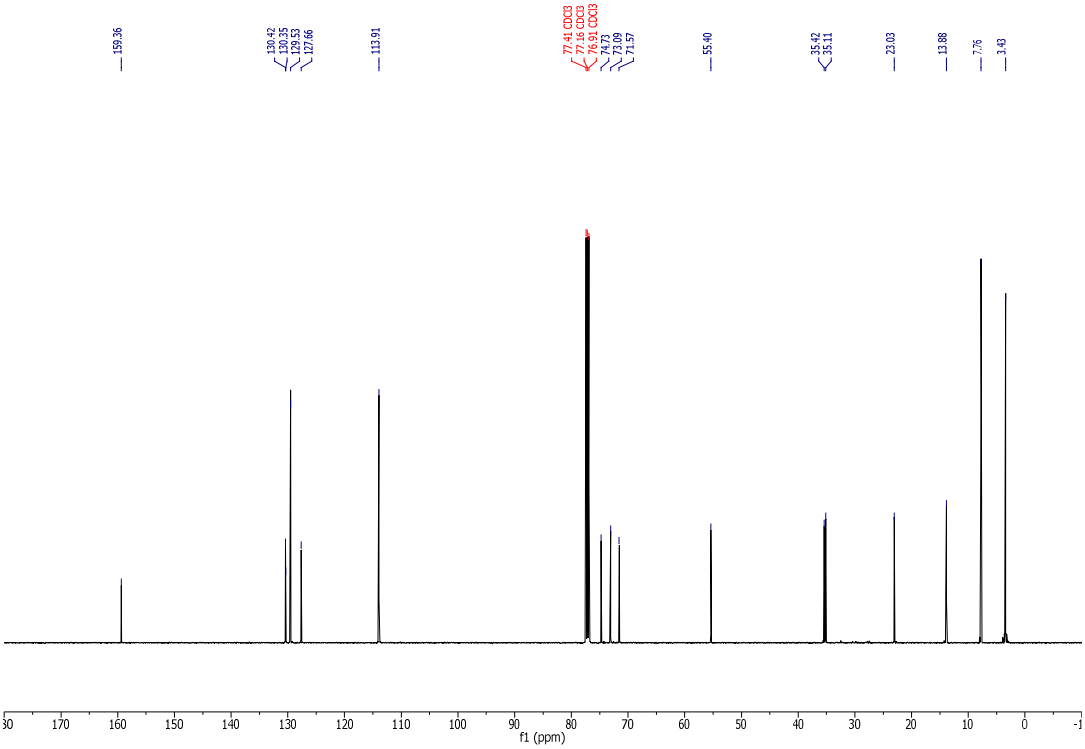
Triethyl ((2*S,3*S**)-3-((4-methoxybenzyloxy)methyl)oxiran-2-yl)silane (*rac*-12)**



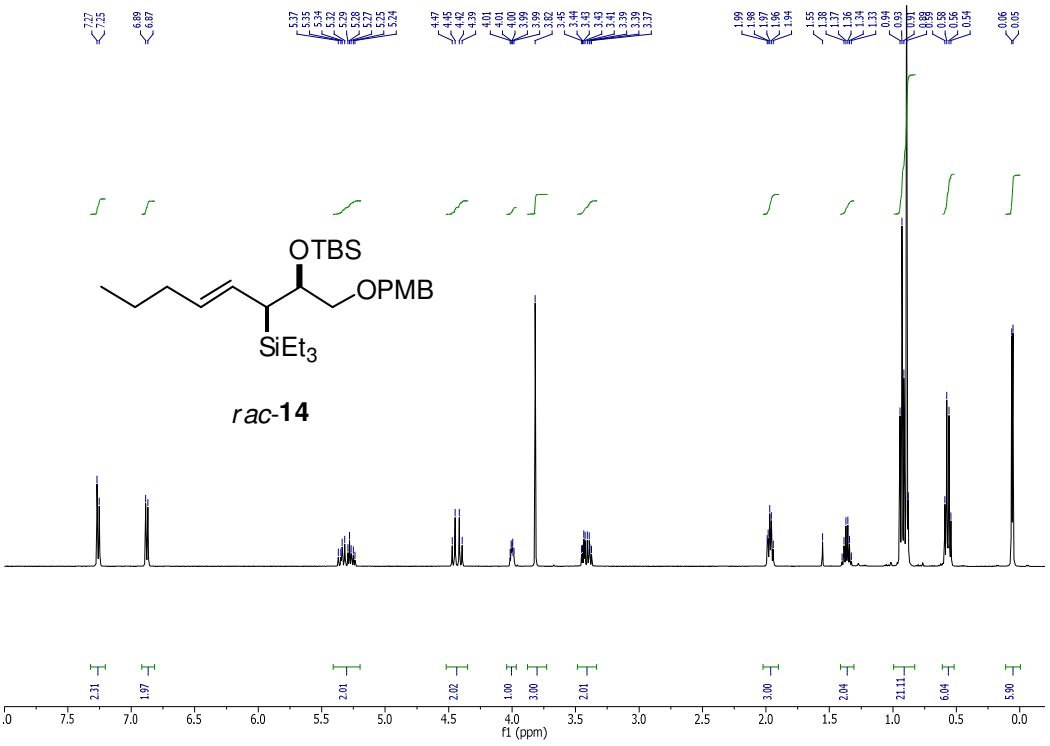


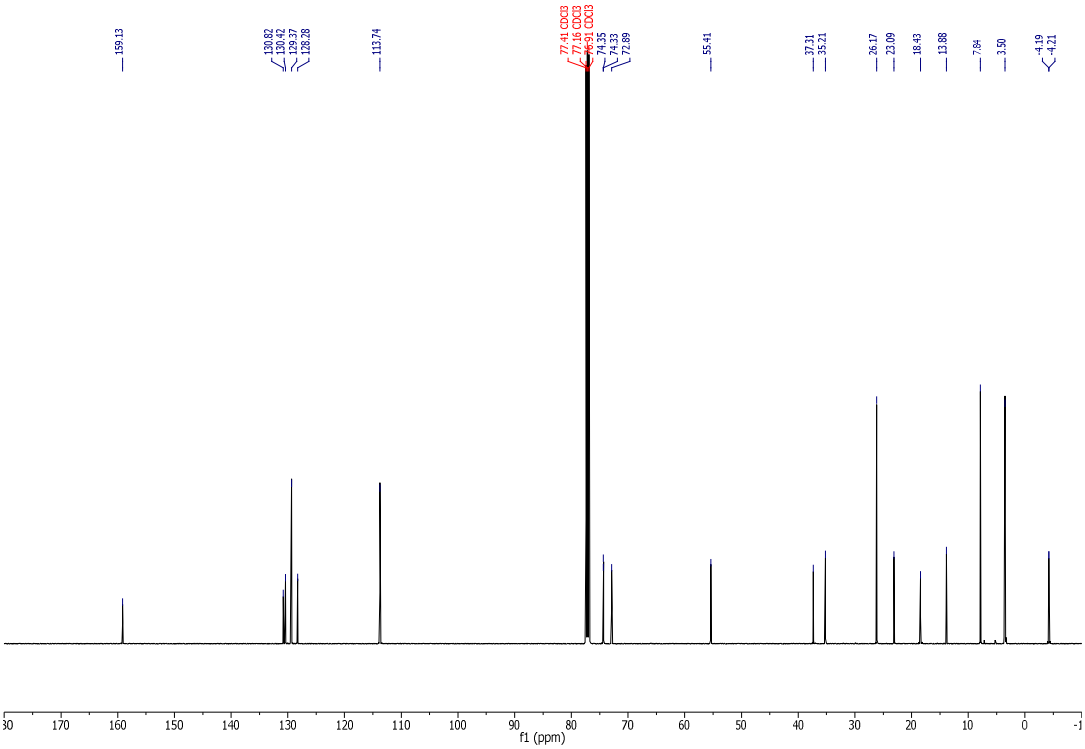
(2*S,3*S**,4*E*)-1-(4-Methoxybenzyloxy)-3-(triethylsilyl)oct-4-en-2-ol (*rac*-13)**



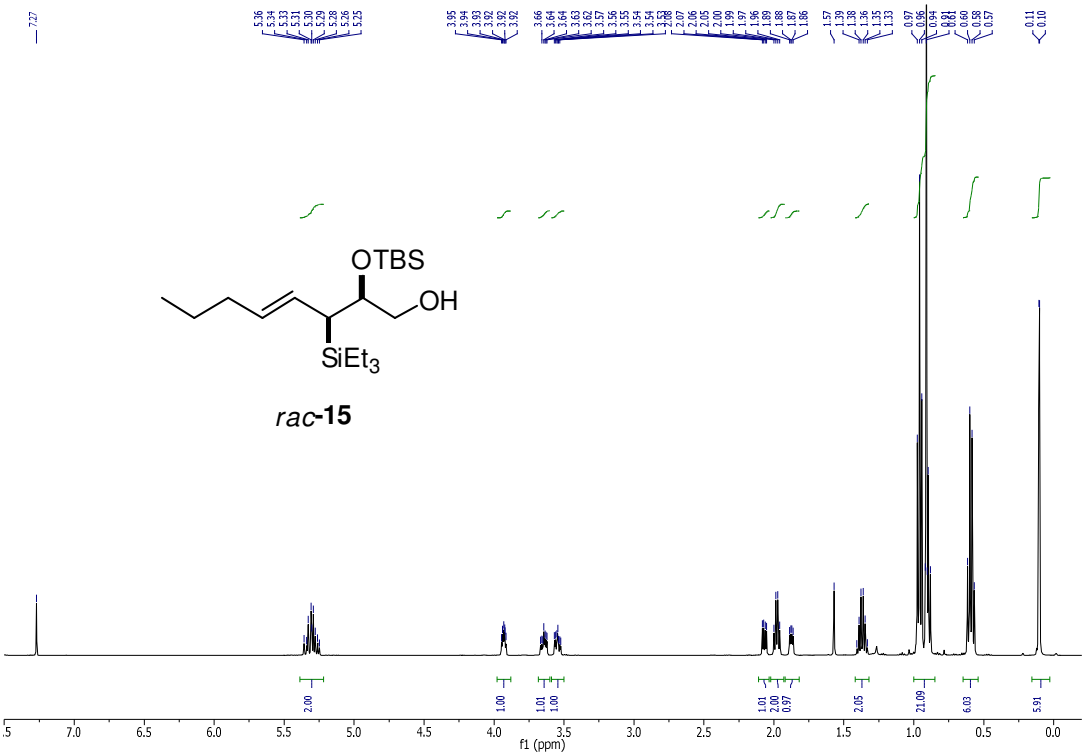


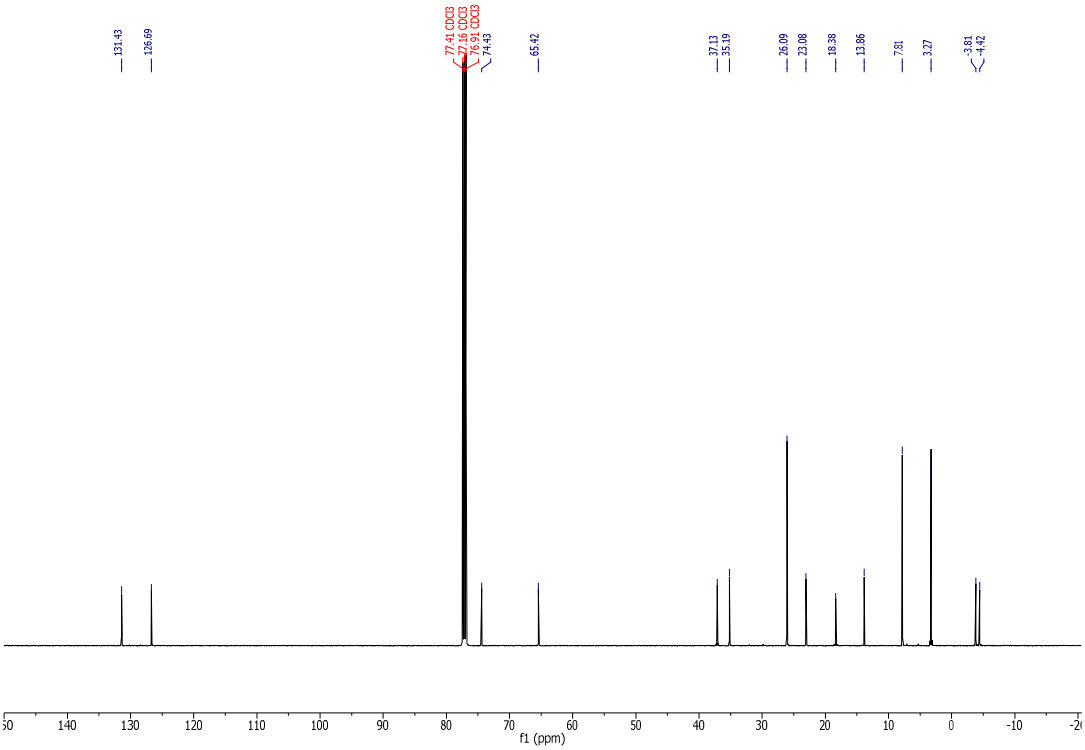
tert-Butyl(((1*S,2*S**,3*E*)-1-(((4-methoxybenzyl)oxy)methyl)-2-(triethylsilyl)hept-3-en-1-yl)oxy)dimethylsilane (*rac*-14)**



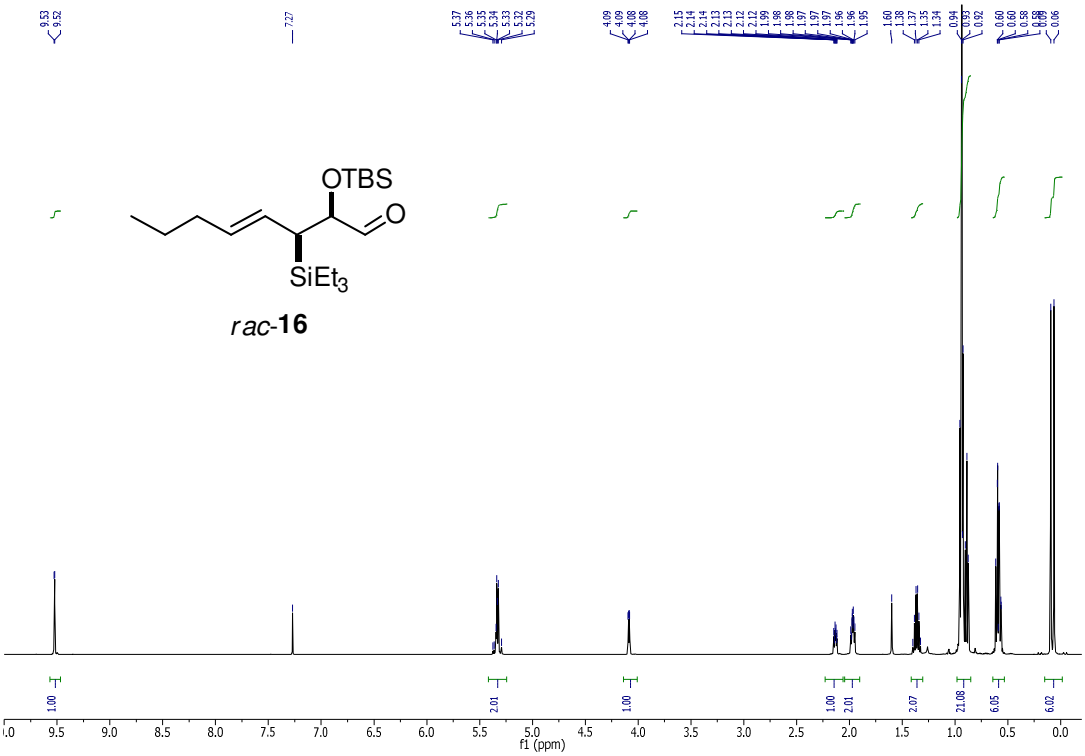


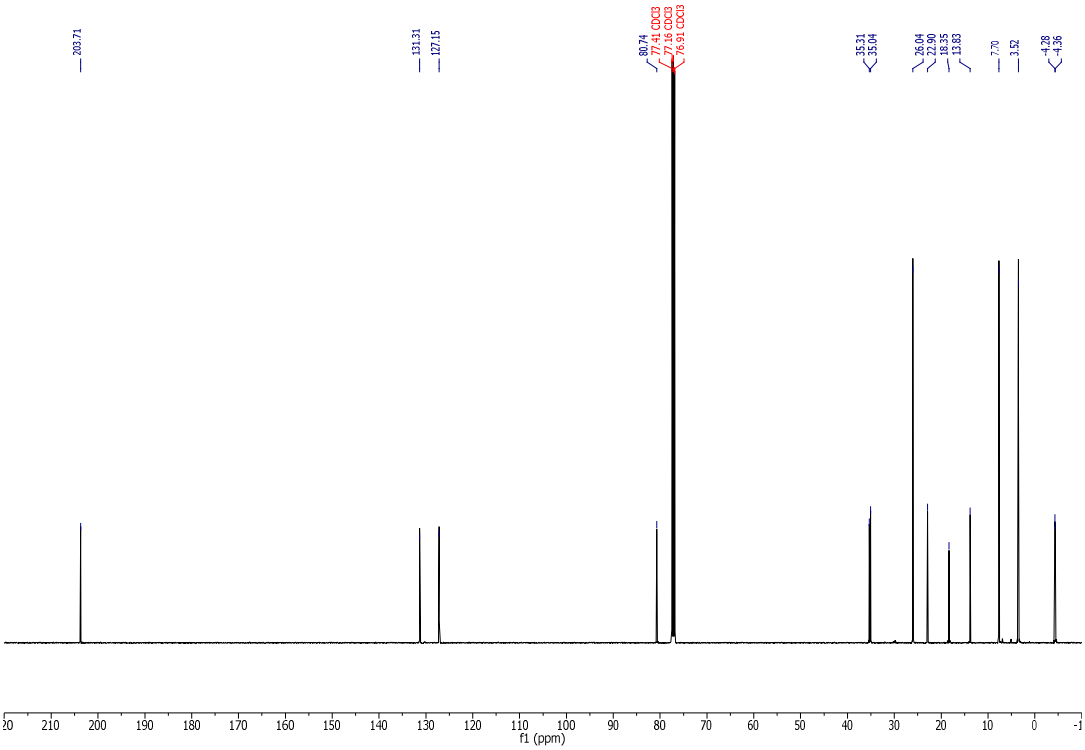
(2*S,3*S**,4*E*)-2-((*tert*-Butyl(dimethyl)silyl)oxy)-3-(triethylsilyl)oct-4-en-1-ol (*rac*-15)**





(2*S,3*S**,4*E*)-2-((*tert*-Butyl(dimethyl)silyl)oxy)-3-(triethylsilyl)oct-4-enal (*rac*-16)**

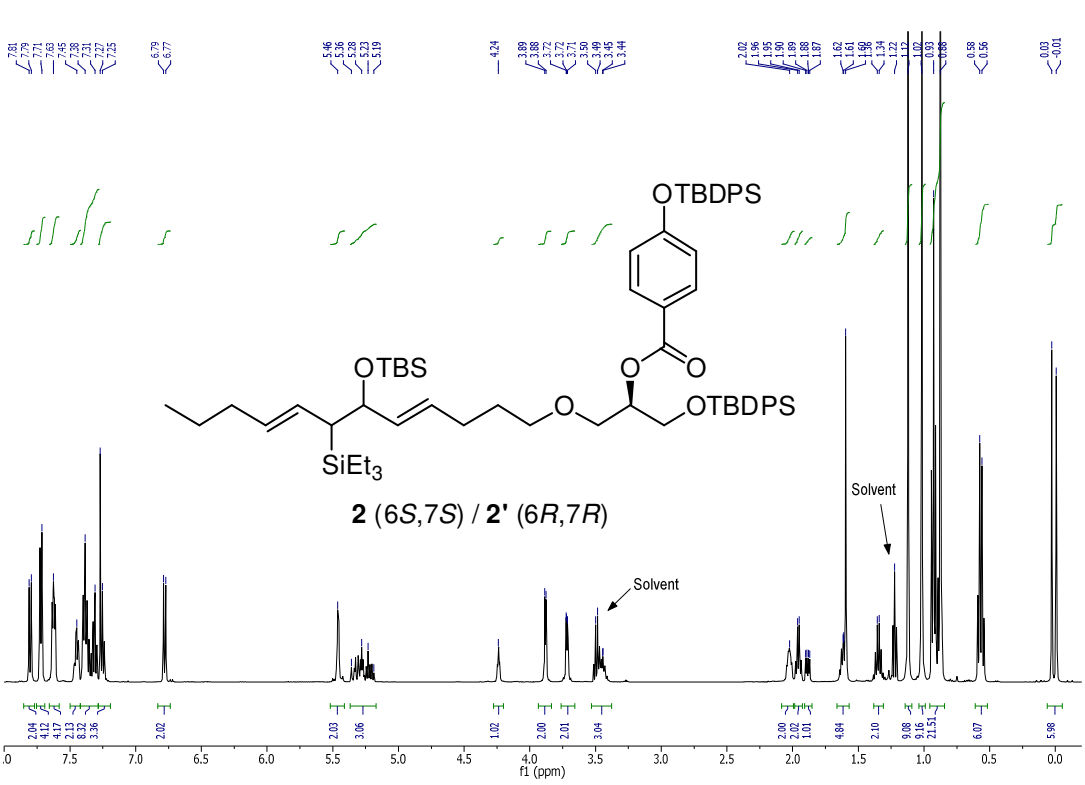


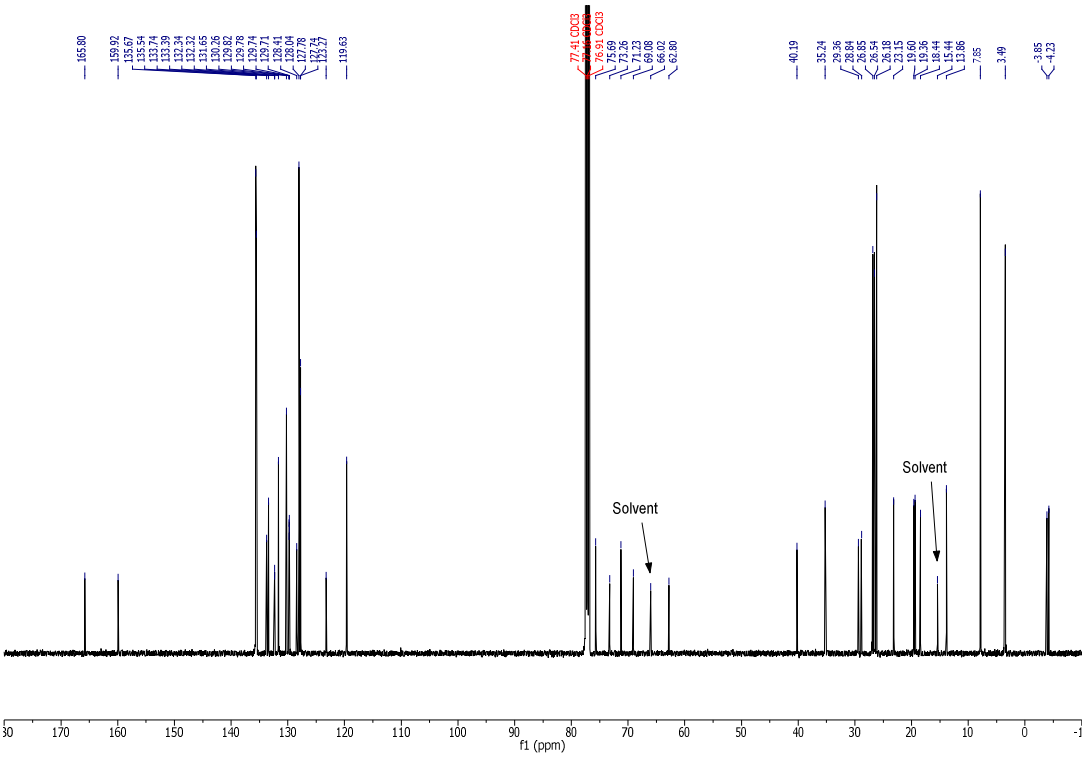


(1*R*)-2-(((4*E*,6*S*,7*S*,8*E*)-6-((*tert*-Butyl(dimethyl)silyl)oxy)-7-(triethylsilyl)dodeca-4,8-dien-1-yl)oxy)-1-(((*tert*-butyl(diphenyl)silyl)oxy)methyl)ethyl 4-(*tert*-butyl(diphenyl)silyl)oxy)benzoate (2)

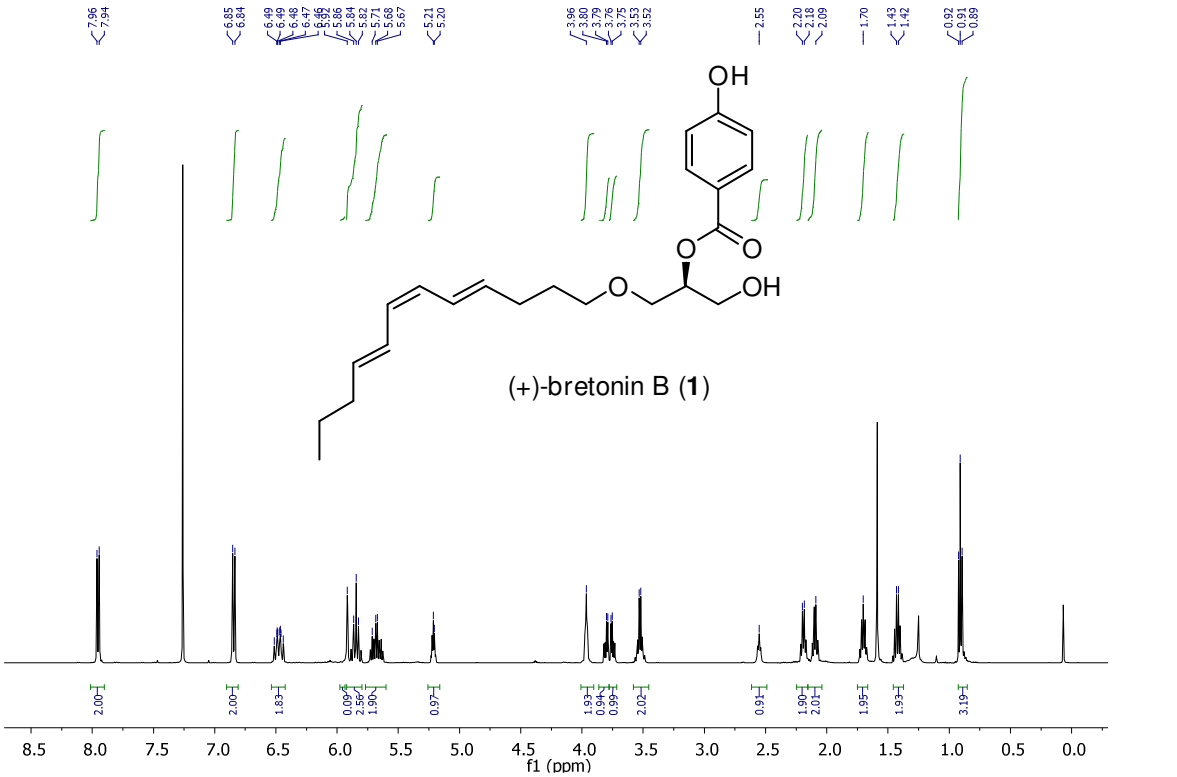
and

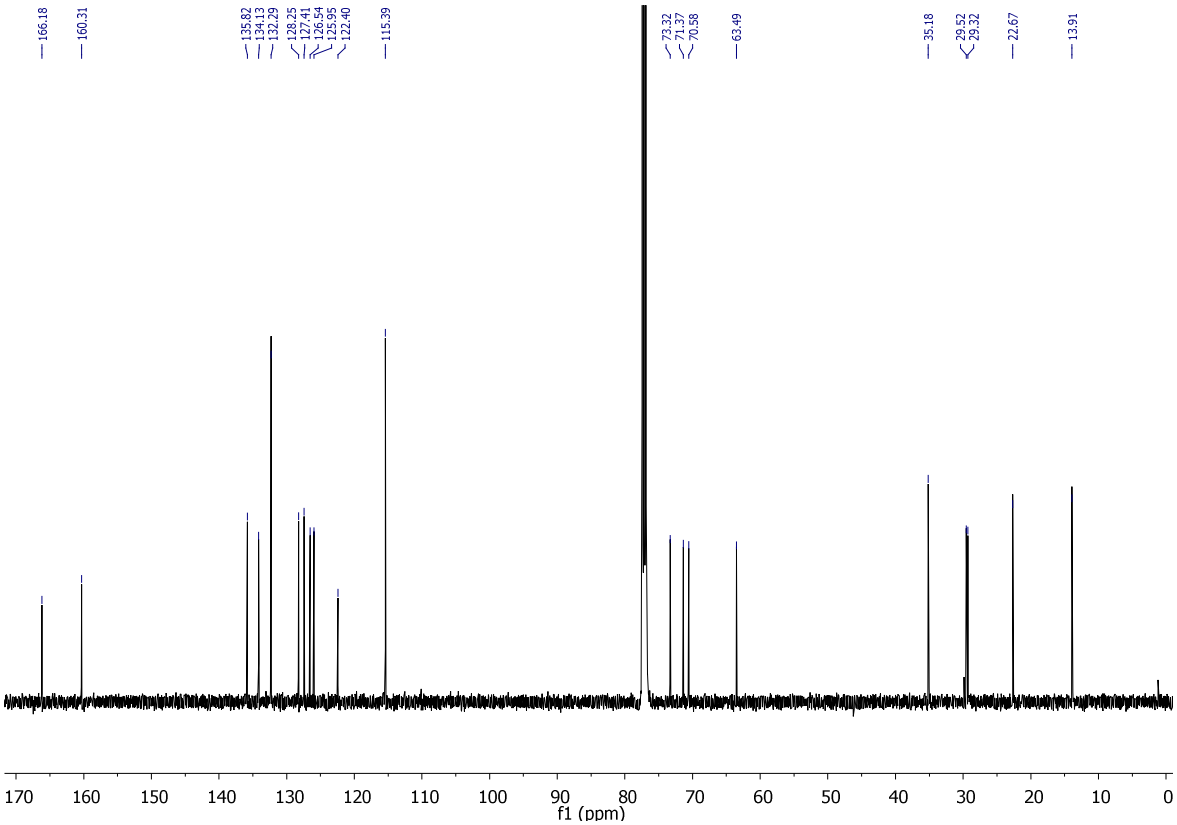
(1*R*)-2-{[(4*E*,6*R*,7*R*,8*E*)-6-{[*tert*-butyl(dimethyl)silyl]oxy}-7-(triethylsilyl)dodeca-4,8-dien-1-yl]oxy}-1-({[*tert*-butyl(diphenyl)silyl]oxy}methyl)ethyl 4-{[*tert*-butyl(diphenyl)silyl]oxy}benzoate (2')





(+)-Bretonin B (= (*S*)-2-{[(4*E*,6*Z*,8*E*)-Dodeca-4,6,8-trien-1-yl]oxy}-1-(hydroxymethyl)ethyl 4-hydroxybenzoate) (1)





(*R*)-2-(Acetyloxy)-1-{[(4*E*,6*Z*,8*E*)-dodeca-4,6,8-trien-1-yloxy]methyl}ethyl 4-(acetyloxy)benzoate (17)