Supporting Information for:

Stereoselective Synthesis of Highly Functionalized *C*-Glycosides based on the Acetal [1,2]- and [1,4]-Wittig Rearrangements

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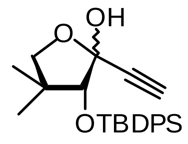
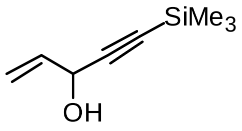


1

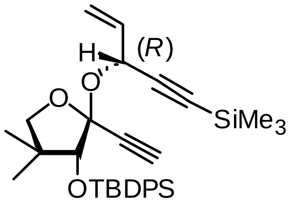
hemiketal **1**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.65 (m, 4H), 7.52-7.34 (m, 6H), 4.84 (s, 0.46H), 4.23 (s, 0.13H), 4.13 (s, 0.46H), 3.99 (s, 0.41H), 3.66 (d, J = 8.7 Hz, 0.46H), 3.60 (d, J = 8.52H, 0.41H), 3.57 (d, J = 0.41H), 3.48-3.40 (m, 0.26H), 3.44 (d, J = 8.7 Hz, 0.46H), 3.29 (s, 0.13H), 3.40 (dd, J = 11.5, 6.0 Hz, 0.13H), 3.13 (s, 0.41H), 2.75 (s, 0.41H), 2.49 (s, 0.46H), 1.17 (s, 4.14H), 1.16 (s, 3.69H), 1.15 (s, 1.17H), 1.12 (s, 1.23H), 0.96 (s, 0.39H), 0.95 (s, 0.39H), 0.76 (s, 1.38H), 0.68 (s, 1.38H), 0.45 (s, 1.23H).



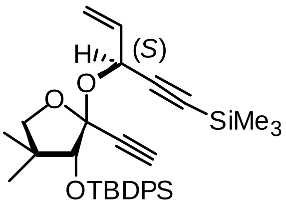
2

5-(trimethylsilyl)pent-5-en-4-yn-3-ol (2):
Alcohol **2** was prepared from acrolein and lithiated trimethylsilylacetilene in THF (91% yield). bp 50- 55 °C /12 mm Hg. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddd, J = 17.0, 10.1, 5.3 Hz, 1H), 5.48 (ddd, J = 17.0, 1.5, 1.2 Hz, 1H), 5.23 (dt, J = 10.1, 1.5 Hz, 1H), 4.87 (dddd, J = 6.4, 5.3, 1.5, 1.2 Hz, 1H), 1.92 (d, J = 6.4 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.53, 116.52, 103.92, 91.14, 63.56, -0.07; IR (neat, cm^{-1}) 3310, 3092, 3026, 2964, 2178, 1647, 1408, 1253, 1029, 988, 845.

***O*-glycoside 3:** MS 4A (3.00 g) was placed in two-necked flask and was flame-dried under reduced pressure. After the flask and its contents had been cooled down, the flask was purged with argon and alcohol **2** (0.30 g, 1.94 mmol) and hemiketal **1** (0.50g, 1.27 mmol) in 10 mL of CH_2Cl_2 was added. The resulting suspension was atirred at rt for 30 min and then Montmorillonite K 10 (2.00 g) was added. The resulting mixture was stirred at rt for 90 min, and then filtered through a pad of celite using Et_2O as eluent. The filtrate was evaporated under reduced pressure and the residue was purified by silica gel chromatography (hexane/Et_2O = 40:1 to 35:1) to afford 460 mg (68%) of ketal **3** as the diastereomer mixture {(1β,1'*R*)-**3**/(1β,1'*S*)-**3**/α-**3a**/α-**3b** = 47:40:5:7 by ^{1}H NMR }. The two isomers of (1β,1'*R*)-**3** and (1β,1'*S*)-**3** were separated by medium presure liquid chromatography on silica gel (hexane/Et_2O = 80:1).



(1β, 1'*R*)-**3**

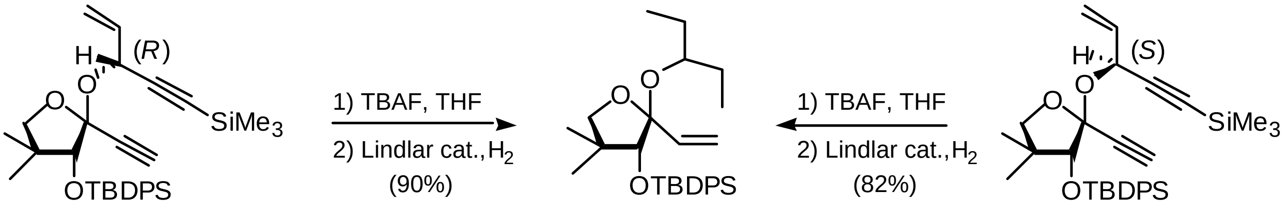


(1β, 1'*S*)-**3**

(1β,1'*R*)-**3**: Rf 0.60 (hexane/Et_2O=7:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (m, 4H), 7.45-7.30 (m, 6H), 5.89 (ddd, J = 17.1, 10.1, 5.0 Hz, 1H); 5.53 (dt, J = 17.1, 1.5 Hz, 1H), 5.26 (dt, J = 5.0, 1.5 Hz, 1H), 5.25 (dt, J = 10.1, 1.5 Hz, 1H), 4.14 (s, 1H), 3.62 (d, J = 8.6 Hz, 1H), 3.50 (d, J = 8.6 Hz, 1H), 2.71 (s, 1H), 1.13 (s, 9H), 1.04 (s, 3H), 0.33 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.56, 136.39, 135.22, 134.50, 133.38, 129.91, 129.71, 127.70, 127.43, 116.89, 107.11, 103.73, 90.22, 88.30, 79.33, 77.31, 76.63, 65.38, 44.26, 27.17, 21.64, 20.86, 19.39, -0.23; IR (KBr, cm^{-1}) 3282, 3068, 3054, 2172, 2122. (1β,1'*S*)- **3**: Rf 0.56 (hexane/Et_2O = 7:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82-7.74 (m, 4H), 7.46-7.34 (m, 6H), 5.91 (ddd, J = 17.1, 10.1, 5.4 Hz, 1H), 5.48 (dt, J = 10.1, 1.4 Hz, 1H), 5.32 (dt, J = 5.4, 1.4 Hz, 1H), 5.18 (dt, J = 10.1, 1.4 Hz, 1H), 4.05 (s, 1H), 3.47 (d, J = 8.2 Hz, 1H), 3.46 (d, J = 8.2 Hz, 1H), 2.83 (s, 1H), 1.16 (s, 9H), 1.06 (s, 3H), 0,24 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.74, 136.49, 136.26, 134.74,

132.94, 129.80, 129.70, 127.63, 127.60, 116.68, 106.38, 102.92, 91.12, 88.15, 79.04, 77.78, 76.57, 66.45, 43.34, 27.20, 21.56, 20.37, 19.45, -0.23; IR (neat, cm^{-1}) 3312, 3076, 3054, 3018, 2180, 2124, 1468, 1429, 1181, 1145, 1114, 1073, 1023, 990, 849.
Anal. calced for $C_{32}H_{42}O_3Si_2$ (mixture of β-anomers): C, 72.40; H, 7.98. Found: C, 72.21; H, 8.09.

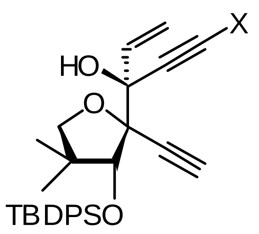
The stereochemistry of (1β,1'*R*)-**3** was determined by X-ray crystallography (CCDC 144556).
The β-configuration of (1β,1'*S*)-**3** was confirmed by the comparison of its derivative ketal **i** and the authentic sample which derived from (1β,1'*R*)-**3**



(1β,1'*R*)-**3** ketal **i** (1β,1'*S*)-**3**

ketal **i** : ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.68 (m, 4H), 7.47-7.32 (m, 6H), 5.93 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.56 (dd, *J* = 17.3, 2.3 Hz, 1H), 5.31 (dd, *J* = 10.7, 2.3 Hz, 1H), 4.19 (s, 1H), 3.53 (d, *J* = 8.5 Hz, 1H), 3.49 (qi, *J* = 5.7 Hz, 1H), 3.43 (d, *J* = 8.5 Hz, 1H), 1.44 (m, 4H), 1.10 (s, 9H), 0.91 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H), 0.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.03, 136.34, 134.96, 133.83, 129.81, 129.68, 127.62, 127.52, 116.64, 109.94, 89.46, 76.17, 74.13, 43.28, 27.24, 26.64, 22.48, 20.62, 19.57, 9.50, 8.99; IR (neat, cm^{-1}) 1591, 1464, 1429, 1191, 1110, 1064, 1033, 1015, 961, 936, 849, 700, 613

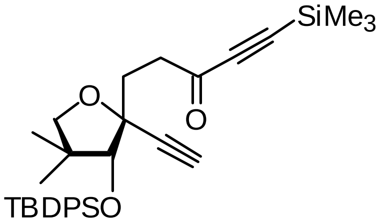
Rearrangement of (β, *R*)-**3:**
A solution of (β, *R*)-**3** (100 mg, 0.19 mmol) in 5 mL of THF was cooled to –78 °C and a solution of *n*-BuLi (0.38 mL of 1.50 M solution in hexane, 0.57 mmol) was added dropwise over a period of 2 min. The resulting mixture was stirred at –78 °C for 50 min. The reaction was quenched with sat. NH_4Cl aq. and the product was extracted with Et_2O. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (hexane/Et_2O = 5:1) to afford 50 mg (50%) of (1β,1'*S*)-**4a** (dr = >98:2< by ^{1}H NMR), 25 mg (28%) of (1β, 1'*S*)-**4b** (dr = >98:2< by ^{1}H NMR), and 17 mg (16%) of [1,4]-product **5.**



X=$SiMe_3$: (1β, 1'*S*)-**4a**
X=H: (1β, 1'*S*)-**4b**

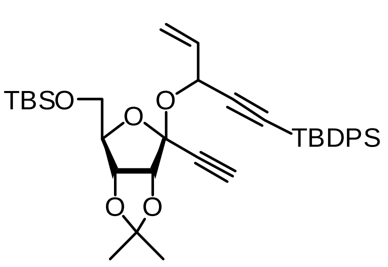
(1β, 1'*S*)-**4a:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78-7.69 (m, 4H), 7.47-7.34 (m, 6H), 5.69 (dd, *J* = 17.1, 10.2 Hz, 1H), 5.28 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.70 (dd, *J* = 10.1, 1.2 Hz, 1H), 4.25 (s, 1H), 3.63 (s, 2H), 3.05 (s, 1H), 2.81 (s, 1H), 1.35 (s, 3H), 1.14 (s, 9H), 0.68 (s, 3H), 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.81, 136.77, 134.65, 133.79, 133.46, 129.86, 129.63, 127.43, 127.17, 119.00, 104.01, 92.00, 87.20, 82.15, 81.25, 79.40, 77.83, 76.86, 44.12, 27.18, 22.15, 21.05, 19.61, -0.38; IR (neat, cm^{-1}) 3560, 3410, 3312, 2252, 2170, 2118, 1591, 1473, 1251, 1112, 1044, 980, 839. (1β, 1'*S*)-**4b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.71 (m, 4H), 7.48-7.23 (m, 6H), 5.68 (ddd, *J* = 17.1, 10.5, 0.8 Hz, 1H), 5.22 (dd, *J* = 17.1, 1.3 Hz, 1H), 4.87 (dd, *J* = 10.5, 1.3, 1H), 4.14 (s, 1H), 3.63 (d, *J* = 8.5 Hz, 1H), 3.43 (d, *J* = 8.5 Hz, 1H), 2.85 (s, 1H), 2.65 (d, *J* = 0.8 Hz, 1H), 2.38 (s, 1H), 1.33 (s, 3H), 1.13 (s, 9H), 0.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.91, 136.74, 134.67, 133.96, 133.39, 129.92, 129.69, 127.44, 127.32, 118.40, 86.49, 83.29, 81.63, 81.47, 79.19, 78.22, 75.98, 74.74, 43.76, 27.16, 22.43, 20.83, 19.56; IR (KBr, cm-1) 3452, 3300, 3074, 3046, 3022, 3004, 2122; Anal. calced for $C_{29}H_{34}O_3Si$: C, 75.94; H, 7.47. Found: C, 76.12; H, 7.66.

The stereochemistry of (1β, 1'*S*)-**4a** was determined by X-ray crystallography (CCDC 144557).


5

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.77-7.68 (m, 4H), 7.47-7.34 (m, 6H), 3.65 (d, J = 8.9 Hz, 1H), 3.58 (s, 1H), 3.36 (d, J = 8.9 Hz, 1H), 2.72 (ddd, J = 17.9, 9.9, 5.7 Hz, 1H), 2.63 (s,1H), 2.60 (ddd, J = 17.9, 9.9, 5.4 Hz, 1H), 1.78 (ddd, J = 14.1, 9.9, 5.4 Hz, 1H), 1.54 (ddd, J = 14.1, 9.9, 5.7 Hz, 1H), 1.18 (s, 3H), 1.13 (s, 9H), 0.71 (s, 3H), 0.22 (s, 9H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 186.68, 136.47, 136.35, 133.46, 133.28, 129.98, 129.93, 127.58, 127.52, 101.91, 97.22, 86.03, 82.95, 81.72, 78.13, 76.69, 42.54, 40.67, 33.23, 27.18, 25.79, 21.30, 19.54, -0.76; IR (neat, cm^{-1}) 3310, 2154, 1729, 1682, 1591, 1466, 1429, 1255, 1114, 1042, 847, 704.

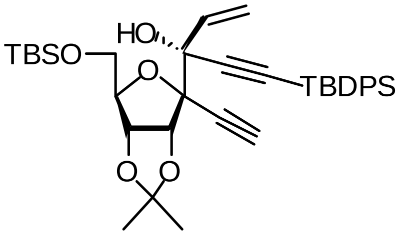
Preparation of β-6: This compound was prepared from ribose-derived hemiketal and 5-*tert*-butyldiphenylsilyl-1-penten-4-yn-3-ol as the diastereomer mixture [β-**6a**/β-**6b**/α-**6** = 35:48:17] by the same way as the prepararion of **3** (68% yield).

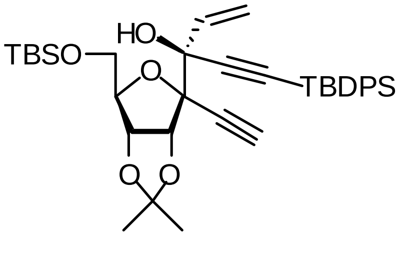

β-**6**

β-**6** (β-**6a**/β-**6b** = 63:37) ^{1}H NMR (300 MHz, CDCl$_3$) 7.85-7.76 (m, 4H), 7.44-7.30 (m, 6H), 6.06 (ddd, J = 17.1, 10.2, 5.1 Hz, 0.37H), 5.97 (ddd, J = 17.1, 10.1, 6.0 Hz, 0.63H), 5.62 (ddd J = 17.1, 1.5, 1.2 Hz, 0.37H), 5.59 (ddd, J = 17.1, 1.5, 1.2 Hz, 0.63H), 5.50 (dt, J = 5.1, 1.4 Hz, 0.37H), 5.35 (ddd, J = 6.0, 1.5, 1.2 Hz, 0.63H), 5.29 (ddd, J = 10.2, 1.5, 1.2 Hz, 0.37H), 5.28 (dt, J = 10.1, 1.3 Hz, 0.63H), 4.85 (dd, J = 5.9, 1.2 Hz, 0.37H), 4.76 (d, J = 5.9 Hz, 0.63H), 4.75 (d, J = 5.9 Hz, 0.63H), 4.69 (d, J = 5.9 Hz, 0.37H), 4.26 (m, 1H), 3.72 (dd, J = 10.5, 5.7 Hz, 0.37H), 3.67 (t, J = 10.5 Hz, 0.37H), 3.63 (dd, J = 10.2, 6.0 Hz, 0.63H), 3.58 (dd, J = 10.2, 9.3 Hz, 0.63H), 2.84 (s, 0.37H), 2.70 (s, 0.63H), 1.58 (s, 1.11H), 1.57 (s, 1.89H), 1.38 (s, 3H), 1.09 (s, 5.67H), 1.09 (s, 3.33H), 0.91 (s, 5.67H), 0.76 (s, 3.33H), 0.07 (s, 3.78H), -0.25 (s, 1.11H), -0.26 (s, 1.11H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 135.57, 135.55, 135.23, 135.12, 133.06, 133.03, 132.93, 132.88, 129.49, 129.47, 127.70, 127.67, 127.64, 117.74, 117.29, 113.31, 113.26, 106.77, 106.74, 105.92, 105.35, 87.56, 87.42, 87.39, 87.19, 87.14, 86.75, 82.53, 82.41, 77.66, 77.59, 76.97, 76.70, 66.22, 66.09, 64.16, 63.32, 27.04, 26.56, 26.53, 25.86, 25.70, 25.49, 25.47, 18.60, 18.56, 18.26, 17.92, -5.32, -5.38, -5.51, -5.65; IR (neat, cm^{-1}) 3308, 3292, 2180, 2128, 1253, 1112, 1079, 1011, 839, 702.

Preparation of 7 (Rearrangement of β-6):

A solution of β-**6** (205 mg, 0.325 mmol) in 9 mL of THF under argon was cooled at -78 °C and a solution of *n*-BuLi (0.65 mL of 1.51 M solution in hexane, 0.982 mmol) was added over a period of 3 min. The resulting mixture was stirred at -78 °C for 50 min. The reaction was quenched with sat. NH$_4$Cl aq. and the product was extracted with Et$_2$O. The combined organic phase was washed with brine, dried over Na$_2$SO$_4$, filtered, and the solvent was removed under reduced pressure. Purification by silica gel chromatography (hexane/iPr$_2$O = 3:1, Silica Gel 60N 40~100 μm) gave 191 mg of the mixture of **7** and [1,4]-product [(1β,1'*R*)-**7**/(1β,1'*S*)-**7**/[1,4]-product = 69:14:17].


(1β, 1'*R*)-**7**

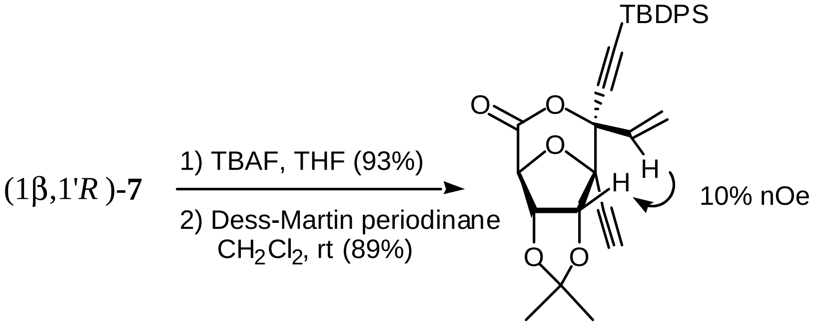


(1β,1'*R*)-**7:** ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.88-7.80 (m, 4H), 7.42-7.29 (m, 6H), 6.19 (ddd, J = 17.1, 10.5, 1.2 Hz, 1H), 5.83 (dd, J = 17.1, 1.5 Hz, 1H), 5.44 (dd, J = 10.5, 1.5 Hz, 1H), 4.83 (dd, J = 6.6, 4.8 Hz, 1H), 4.77 (d, J = 6.6 Hz, 1H), 4.56 (d, J = 1.2 Hz, 1H), 4.30 (ddd, J = 4.8, 2.4, 1.8 Hz, 1H), 3.99 (dd, J = 11.4, 2.4 Hz, 1H), 3.84 (dd, J = 11.4, 1.8 Hz, 1H), 2.73 (s, 1H), 1.63 (s, 3H), 1.38 (s, 3H), 1.09 (s, 9H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 135.79, 135.12, 133.30, 129.38, 127.57, 118.46, 114.58, 108.43, 88.10, 85.33, 85.27, 82.53, 80.56, 80.12, 77.86, 76.01, 63.01, 26.98, 26.93, 25.83, 25.62, 18.75, 18.38, -5.55, -5.73; IR (neat, cm^{-1}) 3312, 2172, 2120, 1431, 1259, 1214, 1158, 1112, 1081, 992, 837, 700.

(1β,1'*S*)-**7**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86-7.80 (m, 4H), 7.44-7.31

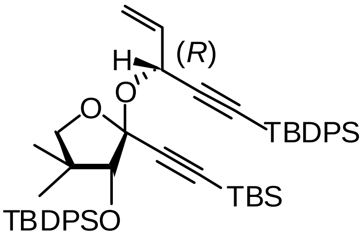
(m, 6H), 6.31 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.72 (dd, *J* = 17.1, 1.2 Hz, 1H), 5.40 (dd, *J* = 10.5, 1.2 Hz, 1H), 5.26 (d, *J* = 6.3 Hz, 1H), 4.88 (dd, *J* = 6.3, 5.7 Hz, 1H), 4.22 (ddd, *J* = 5.7, 2.4, 1.5 Hz, 1H), 4.11 (s, 1H), 3.96 (dd, *J* = 11.3, 2.4 Hz, 1H), 3.82 (dd, *J* = 11.3, 1.5 Hz, 1H), 2.70 (s, 1H), 1.63 (s, 3H), 1.39 (s, 3H), 1.11 (s, 9H), 0.93 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.29, 135.74, 132.89, 129.46, 127.60, 117.38, 114.22, 106.60, 88.28, 88.02, 85.85, 84.62, 79.85, 77.79, 76.45, 62.80, 27.32, 27.05, 26.00, 25.66, 18.83, 18.55, -5.42, -5.47; IR (neat, cm^{-1}) 3402, 3312, 2180, 2120, 1473, 1431, 1375, 1259, 1214, 1112, 1083, 837, 702; Anal. calced for $C_{37}H_{50}O_5Si_2$: C, 73.43; H, 7.99. Found: C, 70.12; H, 7.95.

The stereochemistry of (1β,1'*R*)-**7** was assigned by nOe experiment of lactone **ii** as shown below.



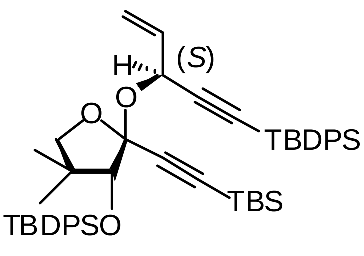
lactone **ii**

lactone **ii:** ^{1}H NMR (300 MHz, C_6D_6) δ 7.98-7.90 (m, 4H), 7.21-7.12 (m, 6H), 5.91 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.68 (dd, *J* = 17.1, 0.8 Hz, 1H), 5.56 (dd, *J* = 10.8, 0.8 Hz, 1H), 4.59 (d, *J* = 5.4 Hz, 1H), 4.58 (s, 1H), 4.29 (d, *J* = 5.4 Hz, 1H), 2.24 (s, 1H), 1.47 (s, 3H), 1.19 (s, 9H), 1.05 (s, 3H).



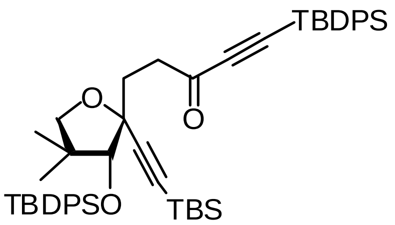
(1β,1'*R*)-**8**

(1β,1'*R*)-**8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.76 (m, 8H), 7.50-7.30 (s, 12H), 6.00 (ddd, *J* = 17.1, 10.5, 4.5 Hz, 1H), 5.67 (dt, *J* = 17.1, 1.5 Hz, 1H), 5.52 (dt, *J* = 4.5, 1.5 Hz, 1H), 5.31 (dt, *J* = 10.5, 1.5 Hz, 1H), 4.13 (s, 1H), 3.63 (d, *J* = 8.7 Hz, 1H), 3.49 (d, *J* = 8.7 Hz, 1H), 1.19 (s, 9H), 1.09 (s, 12H), 1.01 (s, 9H), 0.29 (s, 3H), 0.18 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.69, 137.00, 135.72, 135.50, 134.35, 133.59, 133.47, 129.91, 129.72, 129.46, 127.68, 127.41, 116.89, 108.32, 106.86, 101.46, 91.80, 88.16, 85.38, 77.37, 65.47, 43.63, 27.34, 26.95, 26.14, 21.85, 20.66, 19.42, 18.44, 16.41. -4.82; IR (neat, cm-1) 2252, 2178, 1642, 1591, 1429, 1394, 1363, 1334, 1296, 1253, 1228, 1180, 1110, 1071, 911, 841, 777, 741, 692, 609.



(1β,1'*S*)-**8**

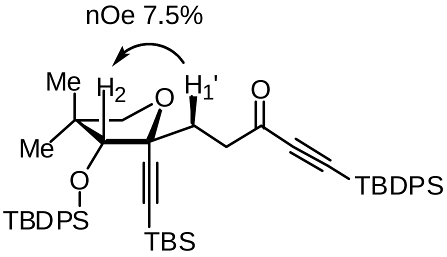
(1β,1'*S*)-**8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.75 (m, 8H), 7.46-7.34 (m, 9H), 7.28-7.15 (m, 3H), 6.07 (ddd, *J* = 17.4, 10.2, 5.1 Hz, 1H), 5.60 (ddd, *J* = 5.1, 1.5, 1.2 Hz, 1H), 5.59 (dt, *J* = 17.4, 1.5 Hz, 1H), 5.24 (dt, *J* = 10.2, 1.2 Hz, 1H), 4.06 (s, 1H), 3.49 (d, *J* = 9.2 Hz, 1H), 3.47 (d, *J* = 9.2 Hz, 1H), 1.14 (s, 9H), 1.13 (s, 9H), 1.10 (s, 3H), 0.99 (s, 9H), 0.25 (s, 3H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.35, 136.60, 136.25, 135.83, 134.66, 133.36, 133.34, 133.01, 129.81, 129.66, 129.52, 127.75, 127.53, 127.53, 116.66, 106.97, 106.60, 101.13, 92.70, 88.14, 86.26, 76.91, 66.83, 43.17, 27.30, 27.10, 26.13, 21.62, 20.21, 19.55, 18.51, 16.44, -4.81, -4.86; IR (neat, cm-1) 2250, 2178, 1642, 1591, 1429, 1394, 1363, 1340, 1294, 1253, 1226, 1183, 1110, 1075, 909, 777, 734, 700, 609; Anal. calced for $C_{51}H_{66}O_3Si_3$ (mixture of epimers): C, 75.50; H, 8.20. Found: C, 75.55; H, 8.08.

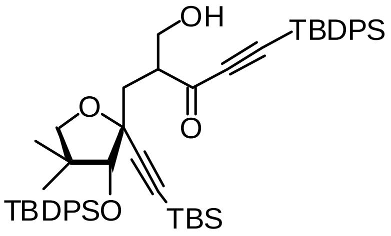


9

9: ^{1}H NMR (300 MHz, CDCl$_3$) 7.83-7.69 (m, 8H), 7.49-7.27 (m, 12H), 3.69 (d, *J* = 8.7 Hz, 1H), 3.52 (s, 1H), 3.37 (d, *J* = 8.7 Hz, 1H), 2.88 (ddd, *J* = 18.0, 9.9, 5.1 Hz, 1H), 2.75 (ddd, *J* = 18.0, 10.2, 5.4 Hz, 1H), 1.95 (ddd, *J* = 14.1, 10.2, 5.1 Hz, 1H), 1.61 (ddd, *J* = 14.1, 9.9, 5.4 Hz, 1H), 1.25 (s, 3H), 1.15 (s, 9H), 1.12 (s, 9H), 1.00 (s, 9H), 0.18 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 186.50, 136.48, 136.43, 135.56, 133.46, 133.38, 131.57, 131.54, 130.00, 127.96, 127.62, 127.55, 105.44, 104.66, 93.27, 92.63, 85.93, 81.56, 78.13, 42.33, 41.10, 33.19, 27.14, 26.93, 25.67, 21.37, 19.52, 18.64, -0.18; IR (neat, cm^{-1}) 2166, 1684, 1591, 1464, 1431, 1251, 1108, 1040, 940, 700.

The β-configuration of ketone **7** was assigned by nOe experiment as shown below.





10

10: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.85-7.69 (m, 8H), 7.48-7.30 (m, 12H), 4.25-4.14 (m, 0.40H), 4.03-3.94 (m, 0.40H), 3.89-3.82 (m, 1.20H), 3.74 (d, *J* = 8.7 Hz, 0.40H), 3.64 (d, *J* = 8.7 Hz, 0.60 H), 3.53 (s, 0.40H), 3.50 (s, 0.60H), 3.44 (d, *J* = 8.7 Hz, 0.40H), 3.33 (d, *J* = 8.7 Hz, 0.60H), 3.17 (m, 0.60H), 3.03 (m, 0.40H), 2.81 (m, 0.40H), 1.97 (dd, *J* = 14.7, 4.4 Hz, 0.40H), 1.83 (dd, *J* = 14.4, 6.8 Hz, 0.60H), 1.64 (m, 0.60H), 1.60 (dd, *J* = 14.4, 4.7 Hz, 0.60H), 1.54 (dd, *J* = 14.7, 9.6 Hz, 0.40H), 1.26 (s, 1.20H), 1.24 (s, 1.80H), 1.14 (s, 10.8H), 1.08 (s, 7.2H), 0.99 (s, 5.40H), 0.97 (s, 3.60H), 0.75 (s, 1.20H), 0.67 (s, 1.80H), 0.16 (s, 1.80H), 0.16 (s, 1.20H), 0.15 (s, 1.80H), 0.14 (s, 1.20H).