

Stereoselective Synthesis of *trans*-2-Ethynyl-3-hydroxytetrahydropyran Derivatives

Eleuterio Alvarez, Ricardo Pérez, Milagros Rico, Rosa M^a Rodríguez, M^a Candelaria Suárez, and Julio D. Martín*

Instituto Universitario de Bio-Organica "Antonio González", Universidad de La Laguna-CSIC, Carretera Vieja de La Esperanza, 2; 38206 La Laguna, Tenerife, Spain

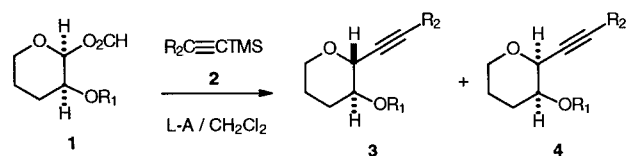
Fax: +34-(22)-630099

Received 12 August 1996

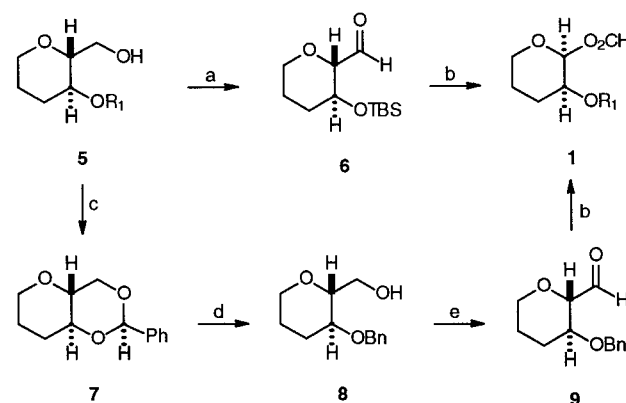
Abstract: *Trans*-substituted tetrahydropyrans with an acetylenic moiety at C-2 were synthesized from 2-formyloxy-3-(*tert*-butyldimethylsilyloxy)-tetrahydropyran by reaction with substituted silylacetylenes in the presence of a Lewis acid.

In the course of our studies towards the convergent synthesis of ciguatoxin and related compounds,¹ we required a simple method for the construction of β -C-glycosyl derivatives. Stereoselective reduction of C-2 hemiketals has been extensively investigated for alkynyl substituents, affording excellent yields of β -C-glycosides.² A procedure involving α -selective introduction of acetylenic groups to glucals followed by epimerization through dicobalt hexacarbonyl complex has also been reported recently.^{3,4}

We wish to disclose in this letter our results dealing mainly with the synthesis of *trans*-2-ethynyl-3-hydroxytetrahydropyran derivatives, **3**, by C₂-alkynylation of **1** with substituted silylacetylenes in the presence of a Lewis acid (Scheme 1). The synthesis of **1** (R₁ = TBS and R₁ = Bn) is briefly summarized in Scheme 2. Diol **5** (R₁ = H)⁵ was converted into **5** (R₁ = TBS) by silylation of both hydroxy groups with excess of TBSCl in DMF and selective deprotection at the primary position by removal of the TBS group with 0.2 equiv of CSA in MeOH at 0 °C. Oxidation of **5** (R₁ = TBS) under Swern conditions gave aldehyde **6** which was further treated with *m*-CPBA to yield **1** (R₁ = TBS) (65 % overall yield).



Scheme 1



Reagents and conditions: (a) From **5**, R₁ = TBS: 4.0 equiv of SO₃·pyridine, 7.0 equiv of Et₃N, 6:1 CH₂Cl₂:DMSO, 25 °C, 4 h, 84%; (b) 4.0 equiv of *m*-CPBA, CH₂Cl₂, 0 °C, 3 h, 77%; (c) from **5**, R₁ = H: 1.5 equiv of PhCH(OMe)₂, 0.01 equiv of CSA, DMF, 50 °C, 4 h, 92%; (d) 10.0 equiv of DIBAL, CH₂Cl₂, 0 °C, 30 h, 94%; (e) 3.0 equiv of oxalyl chloride, 9.0 equiv of DMSO, 15.0 equiv of Et₃N, CH₂Cl₂, -78 °C, 30 min, 77%.

Scheme 2

For the synthesis of **1** (R₁ = Bn), diol **5** (R₁ = H) was selectively protected, by means of 1,3-benzylidene ketalization followed by DIBAL reduction to give **8**. Oxidation of **8** under Swern conditions gave aldehyde **9** which was further oxidized to formate **1** (R₁ = Bn) by treatment with *m*-CPBA [51% overall yield from **5** (R₁ = H)].

Table 1

Entry	Conditions ^a	Substrate	Reagent	Products (Ratio) ^b	Yield (%) ^c
1	A	1 , R ₁ = TBS	2 , R ₂ = H	3a : 4a (0:100)	60
2	B	1 , R ₁ = TBS	2 , R ₂ = H	3a : 4a (0:100)	73
3	A	1 , R ₁ = TBS	2 , R ₂ = TMS	3b : 4b (66:34)	74
4	B	1 , R ₁ = TBS	2 , R ₂ = TMS	3b : 4b (80:20)	68
5	A	1 , R ₁ = TBS	2 , R ₂ = Me	3c : 4c (70:30)	81
6	B	1 , R ₁ = TBS	2 , R ₂ = Me	3c : 4c (100:0)	67
7	A	1 , R ₁ = TBS	2 , R ₂ = C ₃ H ₇	3d : 4d (80:20)	66
8	B	1 , R ₁ = TBS	2 , R ₂ = C ₃ H ₇	3d : 4d (90:10)	72
9	A	1 , R ₁ = TBS	2 , R ₂ = C ₆ H ₅	3e : 4e (80:20)	64
10	B	1 , R ₁ = TBS	2 , R ₂ = C ₆ H ₅	3e : 4e (95:5)	71

^a Method A: 1.0 equiv TiCl₄, CH₂Cl₂, -78 °C to -20 °C; Method B: 1.0 equiv SnCl₄, CH₂Cl₂, -78 °C to -20 °C. ^b Compounds **3** and **4** could be separated by silica gel chromatography in pure form. Ratio was determined on the basis of the isolated amount of each compound, **3** and **4**. ^c The specific yields are isolated yields of **3** and **4**.

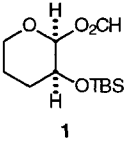
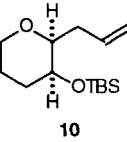
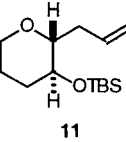
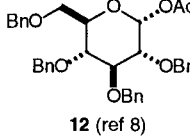
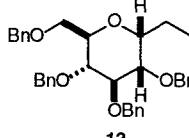
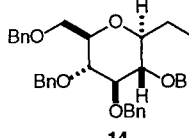
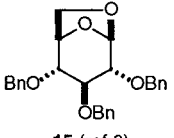
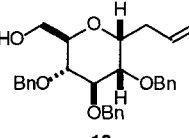
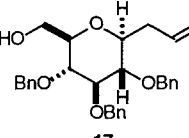
While the two differently substituted substrates **1** (R₁ = TBS and Bn) were tried out with a variety of Lewis acids (e.g. TMSOTf, TiCl₄, SnCl₄, BF₃·Et₂O and ZnBr₂), solvents, reaction temperatures and times, a very simple procedure which called for the dropwise addition of TiCl₄ (or SnCl₄) solution (1.0 equiv, 1 M in CH₂Cl₂) to a cooled (-78 °C) mixture of **1** (R₁ = TBS)⁶ and substituted silylacetylene (2.0 equiv) in CH₂Cl₂ proved to be the most satisfactory. The reaction mixture was allowed to warm up to -20 °C and was stirred for 15-30 min. Work-up and chromatography afforded C₂-alkynylated products (Table 1). The stereochemistry assigned to compounds **3a-e** and **4a-e** was supported by the coupling constants (J_{ab}) between C-2 and C-3 protons determined by analysis of the ¹H NMR spectra and set out in Table 2.^{7,10}

Table 2. ¹H NMR Data Coupling Constants

Compound	J _{ab} (Hz)	Compound	J _{ab} (Hz)
3a (R = H)	7.7 ⁷	4a (R = H)	4.2
3b (R = TMS)	8.2	4b (R = TMS)	4.2
3c (R = Me)	8.0	4c (R = Me)	4.5
3d (R = C ₃ H ₇)	8.8	4d (R = C ₃ H ₇)	4.2
3e (R = C ₆ H ₅)	7.9	4e (R = C ₆ H ₅)	4.3

With regard to the stereochemistry of this alkynylation process, Table 1 clearly shows that when terminal substituted silylacetylenes **2** (R₂ ≠ H) were used, the reaction appeared superficially to take on more of

Table 3

Compound ^a	Products	<i>cis:trans</i> (ratio)	Yield (%)
 1	 10	 11	10:11 (1:5) 93
 12 (ref 8)	 13	 14	13:14 (≥10:1) 80
 15 (ref 9)	 16	 17	16:17 (≥10:1) 55

^a Reaction conditions: Dropwise addition of TMSOTf soln (1.0 equiv, 1 M in CH₂Cl₂) to a cooled (-78 °C) mixture of activated pyranoside and allyltrimethylsilane (1.5 equiv) in CH₂Cl₂. The reaction mixture was allowed to warm to -20 °C and stirred for 30 min.

the character of an S_N2 process (entries 3 - 10). In these cases, an efficient blocking of one face of the oxane ring by the TBSO group forced the silylacetylenes to approach from the back giving preferentially *trans*-substituted compounds. The trimethylsilyl acetylene itself (2, R₂ = H), on the other hand, showed a preference for forming a product in which the C-2 stereochemistry was retained (entries 1 and 2, Table 1).

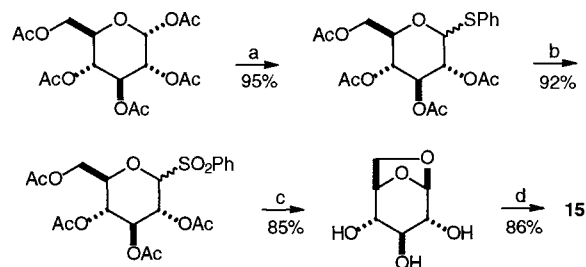
Along this line, it is worth adding that the treatment of 1 (R₁ = TBS) with allyltrimethylsilane gave a good yield (93%) of C₂-allylated products, *cis:trans* (1:5) ratio, under reaction conditions in which activated glucopyranosides are stereoselective to α-allylation (Table 3).

Acknowledgement. Financial support from the Ministry of Education and Science, Spain (PB92-0487) and the EU (Contract CH-CT92-0049) is gratefully acknowledged.

References and Notes

- (1) For previous studies from our group, see: Alvarez, E.; Pérez, R.; Rodríguez, R.M.; Martín, J.D. *J. Org. Chem.* **1996**, *61*, 3003.
- (2) (a) Lewis, M.D.; Cha, J.K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Rouzand, D.; Sinaÿ, P. *J.C.S., Chem. Commun.* **1983**, 1353. (c) Giannis, A.; Sandhoff, K. *Tetrahedron Lett.* **1985**, 26, 1479. (d) Daly, S.M.; Armstrong, R.W. *Tetrahedron Letts.* **1989**, *30*, 5713. (e) Sutherlin, D.P.; Armstrong, R.W. *Tetrahedron Lett.* **1993**, *34*, 4897.
- (3) (a) Ichikawa, Y.; Isobe, M.; Konobe, M.; Goto, T. *Carbohydrate Research* **1987**, *171*, 193. (b) Isobe, M.; Tsukiyama, Y. *Tetrahedron Lett.* **1992**, *33*, 7911. (c) Tsukiyama, T.; Peters, S.C.; Isobe, M. *Synlett.* **1993**, 413. (d) Hosokawa, S.; Isobe, M. *Synlett.* **1995**, 1179.
- (4) (a) Tanaka, S.; Tsukiyama, T.; Isobe, M. *Tetrahedron Lett.* **1993**, *34*, 5757. (b) Tanaka, S.; Isobe, M. *Tetrahedron* **1994**, *50*, 5633.
- (5) Nicolaou, K.C.; Hwang, C.-K.; Marron, B.E.; De Frees, S.A.; Couladouros, E.A.; Abe, Y.; Carroll, P.J.; Snyder, J.P. *J. Am. Chem. Soc.* **1990**, *112*, 3040.
- (6) Formate ester 1 (R₁ = TBS or Bn) was chosen on the basis of the compatibility of this group with TiCl₄ and SnCl₄ which precluded hydrolysis of the ester during the reaction process.
- (7) The *trans*-isomer 3a was synthesized via dibromoolefination of aldehyde 6 followed by treatment with 2.0 equiv of *n*-BuLi in THF: Corey, E.J.; Fuchs, P.L. *Tetrahedron Lett.* **1972**, 3769.

- (8) Compound 12 was prepared by acylation (Ac₂O/cat DMAP cat/TEA/CH₂Cl₂) of 2,3,4,6-tetrabenzylglucopyranose.
- (9) 2,3,4-Tribenzyl-1,6-anhydro-D-glucopyranose (15) was prepared from α-D (+) glucose pentaacetate in 64% overall yield as illustrated below:



Reagents and conditions: (a) 1.5 equiv of PhSTMS, 1.2 equiv of TMSOTf, CH₂Cl₂, 0-25 °C, 6 h, 95%, [ca. α:β (5:1) stereoselectivity]; (b) 3.0 equiv of *m*-CPBA, 3.0 equiv of NaHCO₃, EtOAc, 0-25 °C, 12 h, 92%; (c) 3.0 of NaOMe, MeOH, 0-25 °C, 2 h, 85%; (d) 3.1 equiv of NaH, 3.1 equiv of BnBr, cat. *n*-Bu₄NI, THF, 0 °C, 12 h, 86%.

For a comparative study with reported methods for synthesis of 1,6-anhydro-D-glucopyranose, see: Zottola, M.A.; Alonso, R.; Vite, G.D.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 6123, and references quoted therein.

- (10) All products gave spectroscopic data consistent with the proposed structures. For example, 1 (R₁ = TBS): oil; [α]_D +17.7° (c 0.94, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 8.12 (s, 1H), 5.63 (d, 1H, J = 4.4 Hz), 3.89 (ddd, 1H, J = 11.4, 7.7, 3.3 Hz), 3.66 (ddd, 1H, J = 11.4, 3.6, 3.2 Hz), 3.62 (ddd, 1H, J = 8.0, 4.3, 3.1 Hz), 1.96 (m, 2H), 1.64 (m, 1H), 1.50 (m, 1H), 0.91 (s, 9H), 0.07 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 160.1 (d), 96.1 (d), 67.5 (d), 64.5 (t), 29.1 (t), 26.1 (q), 21.8 (t), 18.4 (s), -4.4 (q); HRMS Calcd for C₁₁H₂₂O₂Si (M⁺-CO₂H): 215.14673; Found: 215.14336. 3 (R₁ = TBS, R₂ = H): oil; [α]_D +29.3° (c 1.2, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ 3.91 (dddd, 1H, J = 11.4, 4.2, 3.8, 1.2 Hz), 3.87 (dd, 1H, J = 7.7, 2.0 Hz), 3.61 (ddd, 1H, J = 9.1, 7.7, 4.2 Hz), 3.39 (ddd, 1H, J = 11.4, 10.1, 2.8 Hz), 2.42 (d, 1H, J = 2.1 Hz), 2.04 (dddd, 1H, J = 13.1, 5.1, 4.2, 3.8, 1.1 Hz), 1.72 (br ddd, 1H, J = 11.8, 4.2, 3.8 Hz), 1.62 (m, 1H), 1.45 (dddd, 1H, J = 13.1, 11.2, 9.1, 4.2 Hz), 0.89 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 82.1 (d), 73.7 (s), 72.8 (d), 70.3

(d), 66.7 (t), 32.1 (t), 25.7 (q), 24.0 (t), 18.0 (s), - 4.5 (q), - 4.6 (q); HRMS Calcd for $C_{13}H_{23}O_2Si$ (M^+-H): 239.14673; Found: 239.14638. **4** ($R_1 = TBS$, $R_2 = H$): oil; $[\alpha]_D -79.1^\circ$ (c 0.46, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 4.48 (dd, 1H, $J = 4.2$, 1.7 Hz), 3.86 (ddd, 1H, $J = 11.4$, 10.7, 2.6 Hz), 3.76 (ddd, 1H, $J = 9.0$, 4.7, 4.2 Hz), 3.59 (dddd, 1H, $J = 11.5$, 4.3, 3.4, 0.9 Hz), 2.44 (d, 1H, $J = 2.2$ Hz), 1.78 (m, 3H), 1.59 (m, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 80.3 (s), 75.7 (s), 70.8 (d), 68.5 (d), 63.2 (t), 29.5 (t), 26.2 (q), 24.2 (t), 18.5 (s), - 4.20 (q), - 4.30 (q); HRMS Calcd for $C_{13}H_{23}O_2Si$ (M^+-H): 239.14673; Found: 239.14663. **3** ($R_1 = TBS$, $R_2 = TMS$): oil; $[\alpha]_D +34.6^\circ$ (c 0.43, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 3.91 (dddd, 1H, $J = 11.4$, 3.1, 2.8, 1.4 Hz), 3.83 (d, 1H, $J = 8.2$ Hz), 3.56 (ddd, 1H, $J = 9.7$, 8.3, 4.4 Hz), 3.36 (ddd, 1H, $J = 11.4$, 10.3, 3.8 Hz), 2.05 (m, 1H), 1.63 (m, 2H), 1.43 (m, 1H), 0.90 (s, 9H), 0.15 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.2 (s), 91.0 (s), 74.1 (d), 70.8 (d), 67.6 (t), 33.1 (t), 26.2 (q), 24.8 (t), 18.5 (s), 0.2 (q), - 4.0 (q), - 4.1 (q); HRMS Calcd for $C_{16}H_{32}O_2Si_2$ (M^+): 312.19409; Found: 312.19396. **4** ($R_1 = TBS$, $R_2 = TMS$): oil; $[\alpha]_D -14.4^\circ$ (c 1.35, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 4.42 (d, 1H, $J = 4.2$ Hz), 3.87 (ddd, 1H, $J = 11.6$, 9.1, 2.7 Hz), 3.75 (ddd, 1H, $J = 8.0$, 4.2, 3.8 Hz), 3.57 (dddd, 1H, $J = 11.4$, 5.0, 4.7, 1.1 Hz), 1.78 (m, 3H), 1.49 (m, 1H), 0.90 (s, 9H), 0.17 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.4 (s), 92.3 (s), 71.5 (d), 68.4 (d), 64.1 (t), 29.9 (t), 26.1 (q), 23.6 (q), 18.4 (s), 0.3 (q), - 4.2; (q); HRMS Calcd for $C_{11}H_{23}O_2Si$ (M^+-tBu): 255.21442; Found: 255.21454. **3** ($R_1 = TBS$, $R_2 = CH_3$): oil; $[\alpha]_D +31.4^\circ$ (c 1.0, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 3.89 (dddd, 1H, $J = 11.4$, 4.3, 2.9, 1.4 Hz), 3.81 (dd, 1H, $J = 8.0$, 2.0 Hz), 3.55 (ddd, 1H, $J = 9.5$, 8.0, 4.3 Hz), 3.36 (ddd, 1H, $J = 11.4$, 10.6, 3.1 Hz), 2.02 (m, 1H), 1.84 (d, 3H, $J = 2.1$ Hz), 1.62 (m, 2H), 1.44 (m, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 82.1 (s), 78.1 (s), 73.8 (d), 71.3 (d), 67.3 (t), 32.9 (t), 26.1 (q), 24.9 (t), 18.5 (s), 4.0 (q), - 4.2 (q), - 4.3 (q); HRMS Calcd for $C_{14}H_{25}O_2Si$ (M^+-H): 253.16238; Found: 253.16336. **4** ($R_1 = TBS$, $R_2 = CH_3$): oil; $[\alpha]_D -77.7^\circ$ (c 0.53, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 4.38 (dd, 1H, $J = 4.5$, 2.0 Hz), 3.87 (ddd, 1H, $J = 11.5$, 9.1, 2.7 Hz), 3.74 (ddd, 1H, $J = 8.1$, 4.2, 3.9 Hz), 3.54 (dddd, 1H, $J = 11.4$, 4.8, 3.9, 0.9 Hz), 1.87 (d, 3H, $J = 2.2$ Hz), 1.76 (m, 3H), 1.50 (m, 1H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 83.5 (s), 75.9 (s), 71.3 (d), 68.9 (d), 63.9 (t), 29.9 (t), 26.2 (q), 23.7 (t), 18.6 (s), - 4.0 (q), - 4.3 (q); HRMS Calcd for $C_{14}H_{25}O_2Si$ (M^+-H): 253.16238; Found: 253.15980. **3** ($R_1 = TBS$, $R_2 = C_3H_7$): oil; $[\alpha]_D +58^\circ$ (c 0.17, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 3.90 (dddd, 1H, $J = 11.4$, 4.4, 4.2, 1.1 Hz), 3.86 (ddd, 1H, $J = 8.8$, 1.8, 1.8 Hz), 3.54 (ddd, 1H, $J = 9.3$, 7.9, 4.3 Hz), 3.38 (ddd, 1H, $J = 11.3$, 10.5, 3.0 Hz), 2.20 (ddd, 2H, $J = 7.2$, 7.1, 2.0 Hz), 2.00 (dddd, 1H, $J = 12.6$, 7.5, 4.0, 3.5 Hz), 1.66 (m, 1H), 1.61 (m, 1H), 1.53 (m, 2H), 1.43 (m, 1H), 0.98 (dd, 3H, $J = 7.4$, 7.4 Hz), 0.90 (br s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 86.7 (s), 78.4 (s), 73.4 (d), 70.8 (d), 66.8 (t), 32.4 (t), 25.8 (q), 24.3 (t),

21.9 (t), 20.8 (t), 13.6 (s), - 4.5 (q), - 4.6 (q); HRMS Calcd for $C_{16}H_{30}O_2Si$ (M^+): 282.20151; Found: 282.20174. **4** ($R_1 = TBS$, $R_2 = C_3H_7$): oil; $[\alpha]_D -52^\circ$ (c 0.10, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 4.45 (dd, 1H, $J = 4.2$, 1.8 Hz), 3.87 (ddd, 1H, $J = 11.5$, 10.0, 2.8 Hz), 3.72 (ddd, 1H, $J = 8.8$, 4.2, 4.0 Hz), 3.55 (ddd, 1H, $J = 11.5$, 5.0, 3.8 Hz), 2.21 (ddd, 2H, $J = 7.0$, 7.0, 2.0 Hz), 1.56 (m, 4H), 1.54 (m, 2H), 1.00 (dd, 3H, $J = 7.4$, 7.3 Hz), 0.90 (s, 9H), 0.08 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 87.8 (s), 70.8 (d), 68.5 (d), 63.0 (t), 29.3 (t), 25.7 (q), 23.6 (t), 22.1 (t), 20.8 (t), 18.1 (s), 13.5 (q), - 4.6 (q); HRMS Calcd for $C_{16}H_{30}O_2Si$ (M^+): 282.20151; Found: 282.19677. **3** ($R_1 = TBS$, $R_2 = C_6H_5$): oil; $[\alpha]_D +38.1^\circ$ (c 0.53, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 2H), 7.29 (m, 3H), 4.09 (d, 1H, $J = 7.9$ Hz), 3.98 (ddd, 1H, $J = 11.4$, 3.3, 3.1 Hz), 3.69 (ddd, 1H, $J = 9.2$, 7.9, 4.3 Hz), 3.45 (ddd, 1H, $J = 11.2$, 10.5, 3.2 Hz), 2.09 (dddd, 1H, $J = 8.0$, 7.7, 4.0, 3.6 Hz), 1.74 (m, 1H), 1.68 (m, 1H), 1.50 (m, 1H), 0.92 (br s, 9H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7 (d), 128.2 (d), 128.1 (d), 122.8 (s), 87.5 (s), 85.5 (s), 73.7 (d), 70.6 (d), 67.1 (t), 32.5 (t), 29.7 (t), 25.8 (q), 18.1 (s), - 4.4 (q), - 4.5 (q); HRMS Calcd for $C_{19}H_{28}O_2Si$ (M^+): 316.18586; Found: 316.18665. **4** ($R_1 = TBS$, $R_2 = C_6H_5$): oil; $[\alpha]_D -49^\circ$ (c 0.17, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 2H), 7.31 (m, 3H), 4.68 (d, 1H, $J = 4.3$ Hz), 3.94 (ddd, 1H, $J = 11.6$, 10.0, 2.5 Hz), 3.85 (ddd, 1H, $J = 9.0$, 4.9, 4.2 Hz), 3.63 (ddd, 1H, $J = 11.1$, 4.6, 4.2 Hz), 1.88 (m, 1H), 1.76 (m, 2H), 1.57 (m, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7 (d), 128.2 (d), 128.1 (d), 123.1 (s), 87.2 (s), 85.8 (s), 71.2 (d), 68.4 (d), 63.4 (t), 29.5 (t), 29.3 (t), 25.9 (q), 23.6 (s), - 4.6 (q); HRMS Calcd for $C_{19}H_{28}O_2Si$ (M^+): 316.18586; Found: 316.18445. **10**: oil; $[\alpha]_D -10.8^\circ$ (c 0.63, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 5.84 (dddd, 1H, $J = 17.1$, 10.2, 7.0, 6.9 Hz), 5.09 (dddd, 1H, $J = 17.2$, 3.3, 3.3, 1.5 Hz), 5.04 (ddd, 1H, $J = 10.2$, 1.0, 1.0 Hz), 3.95 (dddd, 1H, $J = 11.3$, 4.0, 2.2, 1.9 Hz), 3.67 (br s, 1H), 3.43 (ddd, 1H, $J = 11.6$, 11.4, 2.4 Hz), 3.32 (ddd, 1H, $J = 8.1$, 5.3, 1.4 Hz), 2.36 (ddd, 1H, $J = 14.4$, 8.4, 6.8 Hz), 2.17 (ddd, 1H, $J = 14.4$, 6.8, 5.6 Hz), 1.98 (m, 1H), 1.84 (m, 1H), 1.63 (m, 1H), 1.31 (m, 1H), 0.92 (s, 9H), 0.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0 (d), 116.8 (t), 80.2 (d), 68.1 (t), 67.7 (d), 36.7 (t), 31.7 (t), 26.3 (q), 21.0 (t), 18.6 (s), - 4.0 (q), - 4.4 (q); HRMS Calcd for $C_{13}H_{25}O_2Si$ (M^+-CH_3): 241.16238; Found: 241.16109. **11**: oil; $[\alpha]_D +7.3^\circ$ (c 1.54, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$): δ 5.90 (dddd, 1H, $J = 17.2$, 10.2, 7.2, 6.4 Hz), 5.10 (ddd, 1H, $J = 17.2$, 3.4, 1.7 Hz), 5.06 (ddd, 1H, $J = 10.2$, 2.1, 1.2 Hz), 3.89 (dddd, 1H, $J = 11.3$, 4.0, 2.0, 1.8 Hz), 3.32 (ddd, 1H, $J = 11.4$, 11.4, 4.5 Hz), 3.28 (m, 1H), 3.10 (ddd, 1H, $J = 8.7$, 8.6, 2.8 Hz), 2.58 (dddd, 1H, $J = 14.6$, 6.1, 3.0, 1.6, 1.4 Hz), 2.12 (dddd, 1H, $J = 14.6$, 7.3, 7.3, 1.1 Hz), 2.02 (m, 1H), 1.64 (m, 2H), 1.43 (m, 1H), 0.88 (m, 9H), 0.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0 (d), 116.8 (t), 82.7 (d), 71.3 (d), 68.3 (t), 37.0 (t), 34.0 (t), 26.2 (q), 26.1 (t), 18.3 (s), - 3.5 (q); HRMS Calcd for $C_{13}H_{25}O_2Si$ (M^+-CH_3): 241.16238; Found: 241.16584.