Methyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl-Derived γ-Silyloxy Allylic Stannanes as Reagents for S_E2' Additions to Aldehydes†

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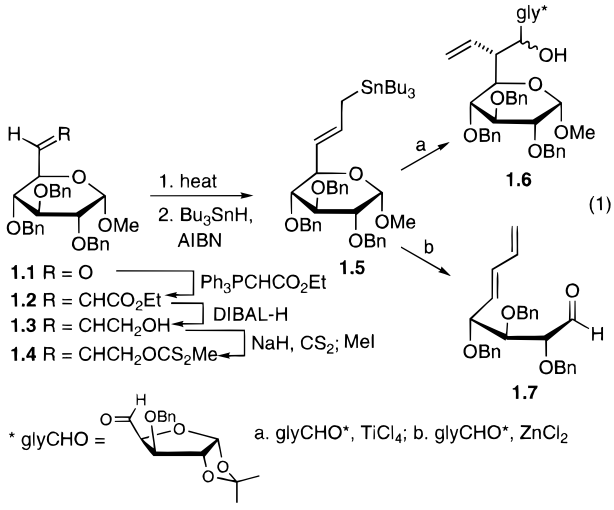
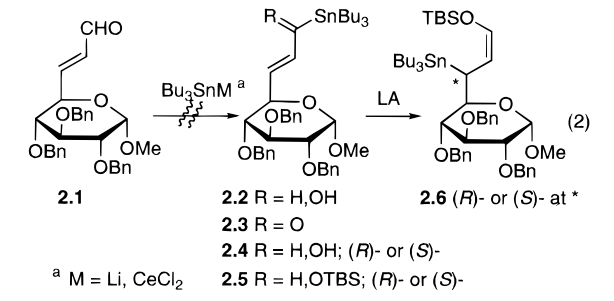
The methyl α-D-glucopyranoside allylic stannanes **3.1** and **3.2** were prepared from the 3-(5-pyranosyl)-2-propenal **2.1** and the cuprate $Bu_3Sn(Bu)CuCNLi_2$, followed by trapping of the derived enolate with TBSCl. The major stannane, **3.1**, underwent BF_3-promoted addition to 2-nonynal to afford a single *syn* adduct **4.1** in 70−90% yield. The minor stannane, **3.2**, gave rise to a 70:30 mixture of adduct **4.1** and the diastereomeric *syn* adduct **5.1** under these conditions. The stereochemistry of the adduct **4.1** was proven by degradation of the *bis*-TBS derivative **4.2** to aldehyde **4.3**, prepared independently from the (*R*,Z)-γ-OTBS crotyl stannane **4.4** and 2-nonynal along similar lines. Analogous degradation of the adducts **4.1** and **5.1** led to a *ca.* 65:35 mixture of aldehydes **4.3** and its enantiomer. Accordingly, it can be surmised that the addition of stannane **3.2** to 2-nonynal takes place mainly by a *syn* S_E2' pathway. BF_3-promoted additions to enal **6.1** proceeded as expected. Stannane **3.1** afforded the *syn* adduct **6.2** in 87−97% yield, and stannane **3.2** gave rise to a 9:1 mixture of *syn* and *anti* adducts **7.1** and **7.4** in 70−80% yield.

In the past several years we have developed a synthetic approach to carbohydrates through additions of nonracemic γ-alkoxy and silyloxy allylic stannanes, and related metallo species, to aldehydes.[1] The approach has proven successful for differentially protected precursors of the diastereomeric hexoses as well as higher sugars, such as lincosamine and destomic acid.[2] Studies to date have employed relatively simple stannanes derived from crotonaldehyde. It was of interest to investigate the synthesis and use of more complex γ-alkoxyallylic stannanes as possible reagents for the preparation of higher carbohydrates and C-disaccharides.[3]

Several years ago Jarosz and Fraser-Reid described the preparation of stannane **1.5** from the protected glucose derivative **1.1** (eq 1).[4] Attempts to effect addition to 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-pentadialdo-1,4-furanose (glyCHO), in the presence of $ZnCl_2$, led to 1,4-elimination affording diene **1.7** as the only product. When $TiCl_4$ was employed as the Lewis acid promoter, the adduct **1.6** was secured in 55% yield as a *ca.* 80:20 mixture of *anti* and *syn* diastereomers.

For the present studies we employed enal **2.1**, obtained from allylic alcohol **1.3** by Swern oxidation, as the stannane precursor. It was our intent to prepare the diastereomeric γ-silyloxy allylic stannanes **2.6**, in the usual way, through addition of Bu_3SnLi to enal **2.1** followed by *in situ* oxidation to the acylstannane **2.3** then reduction with (*S*)- or (*R*)-BINAL-H and silylation of the resulting (*R*)- or (*S*)-α-hydroxy stannane **2.4**. Subsequent 1,3-isomerization with one of several possible Lewis acids would afford the (*Z*)-γ-silyloxy allylic stannanes **2.6**.[1]





Enal **2.1** proved surprisingly unreactive toward Bu_3SnLi under the usual conditions. Only traces of adducts **2.2** could be isolated along with considerable unreacted enal. Attempts to facilitate the addition through use of the cerium reagent and through alternative methodology for preparation of the Bu_3SnLi reagent were unsuccessful. We therefore explored an alternative route involving 1,4-addition of $Bu_3Sn(Bu)CuCNLi_2$ to enal **2.1** followed by trapping of the derived enolate with TBSCl.[5] This approach proved successful. The silyloxy stannanes **3.1** and **3.2** were obtained as a separable 2.5:1 mixture in up to 80% yield.

† Dedicated to Clayton H. Heathcock on the occasion of his 60th birthday.

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1996.

(1) For recent reviews, see (a) Marshall, J. A. *Chemtracts-Org. Chem.* **1992**, *5*, 75. (b) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.

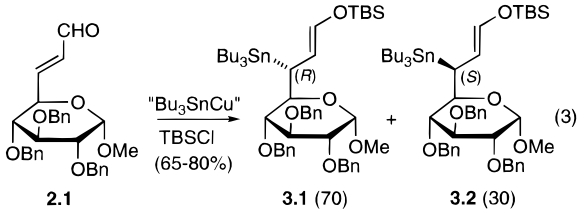
(2) (a) Marshall, J. A.; Beaudoin, S.; Lewinski, K. *J. Org. Chem.* **1993**, *58*, 5876. (b) Marshall, J. A.; Seletsky, B. M.; Luke G. P. *J. Org. Chem.* **1994**, *59*, 3413. (c) Marshall, J. A.; Beaudoin, S. *J. Org. Chem.* **1994**, *59*, 6614. (d) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1996**, *61*, 105. (e) Marshall, J. A.; Beaudoin, S. *J. Org. Chem.* **1996**, *61*, 581.

(3) For possible applications, see Armstrong, R. W.; Sutherlin, D. P. *Tetrahedron Lett.* **1994**, *35*, 7743.

(4) Jarosz, S.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 4011. For a related approach to disaccharides, see Roush, W. R.; VanNieuwenhze, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 8536.

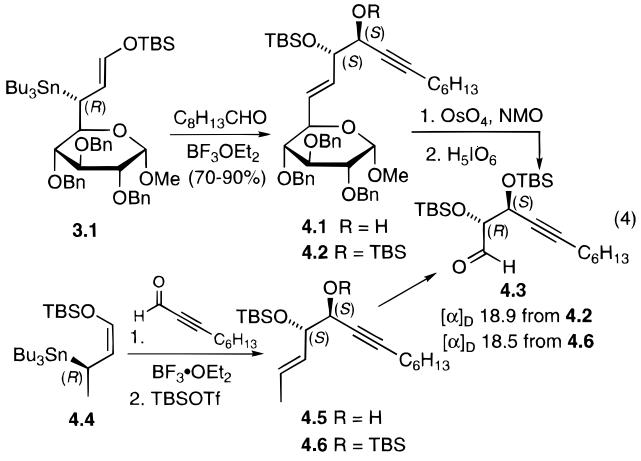
(5) Marshall, J. A.; Welmaker, G. S. *J. Org. Chem.* **1992**, *57*, 7158.

S0022-3263(96)00162-4 CCC: $12.00

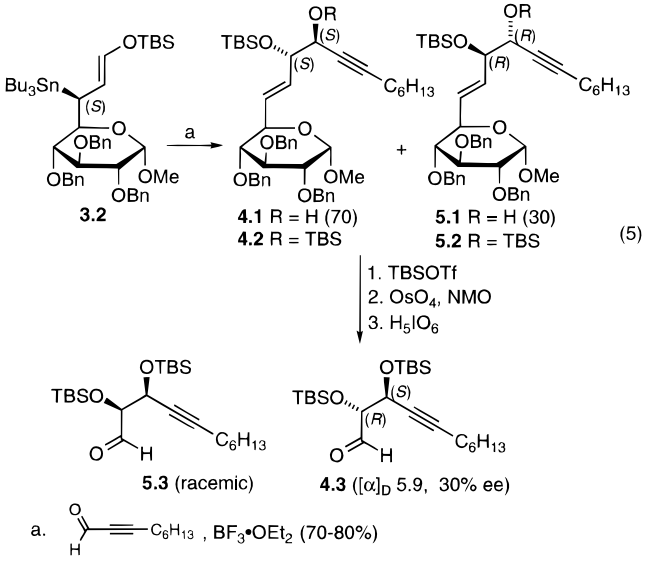


Unexpectedly, these stannanes failed to react with crotonaldehyde and related conjugate aldehydes under our standard conditions with $BF_3{\cdot}OEt_2$ as the promoter.[1] In all cases the stannanes were recovered unchanged. Attempts to effect $MgBr_2$-promoted addition to 2-(benzyloxy)propanal were also unsuccessful.[6] In that case, a small amount of elimination product (see eq 1) was isolated along with recovered stannane.

Success was finally realized with a more reactive aldehyde, 2-nonynal. Addition of stannane **3.1**[7] led to a single product in up to 90% yield. Retrospectively[7] we would expect stannane **3.1** to afford the (*S*,*S*)-adduct **4.1** based on transition state considerations.[1] Confirmation of this expectation was secured through a two-step oxidative cleavage of the double bond of the *bis*-TBS ether **4.2** to give aldehyde **4.3**. An authentic sample of this aldehyde was prepared by a parallel cleavage of the *bis*-TBS ether **4.6**, derived from the adduct **4.5** of stannane **4.4** and 2-nonynal (eq 4).[8]



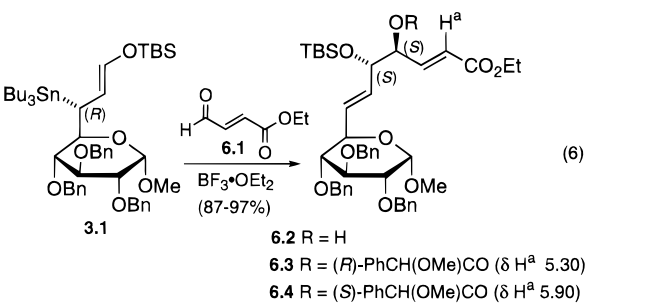
Addition of stannane **3.2** to 2-nonynal proceeded more rapidly than that of **3.1** under comparable conditions. The product, obtained in 70−80% yield, consisted of a 70:30 mixture, presumably stereoisomers, according to analysis of the ^1H and ^{13}C NMR spectra. Remarkably, the major isomer showed spectral characteristics identical to those of **4.1**, the adduct of stannane **3.1** and 2-nonynal! The derived mixture of *bis*-TBS ethers likewise displayed the predominant spectral characteristics of **4.2** derived from stannane **3.1**. Oxidative cleavage of this mixture, as before, afforded what appeared to be a single aldehyde according to NMR analysis. Futhermore, the spectra were identical to those of aldehyde **4.3**. Thus the addition of stannane **3.2** to 2-nonynal would appear to have produced the diastereomeric *syn* adducts **4.1** and **5.1** rather than a *syn:anti* mixture as might have been expected from past experience.[9] The optical rotation of the derived aldehyde **4.3**, $[\alpha]_D$ 5.9, is in close agreement with that expected from a 65:35 mixture of (*R*,*S*) and (*S*,*R*) enantiomers based on the value measured for **4.3** ($[\alpha]_D$ 18.9) secured from adduct **4.1** (see eq 4).



As added support for the foregoing conclusion, we compared the ^1H NMR spectrum of an authentic sample of the *anti*-*bis*-OTBS aldehyde **5.3** with that of **4.3**.[9,10] As expected, the two spectra were clearly different.

On the basis of exclusive formation of adduct **4.1** from stannane **3.1** and 2-nonynal and mechanistic considerations,[1] we can assign the (*R*) configuration to the allylic stereocenter of **3.1**. However, the anomalous behavior of stannane **3.2** weakens the arguments for this assignment. For this reason, and as a prelude to synthetic applications in the higher sugar and C-disaccharide areas, we examined additions to aldehyde **6.1**, prepared by selective ozonolysis of ethyl sorbate.[11]

The addition of stannane **3.1** proceeded smoothly under the usual BF_3 conditions affording a single adduct **6.2** in high yield. Evidence for the expected (*S*) configuration at the carbinyl stereocenter was secured through ^1H NMR analysis of the (*R*)- and (*S*)-*O*-methyl mandelates **6.3** and **6.4**.[12] The vinylic protons, especially H^a, showed the expected shielding in the (*R*)-mandelate **6.3** (eq 6).



(6) Marshall, J. A; Jablonowski, J. A.; Luke, G. P. *J. Org. Chem.* **1994**, *59*, 7825.

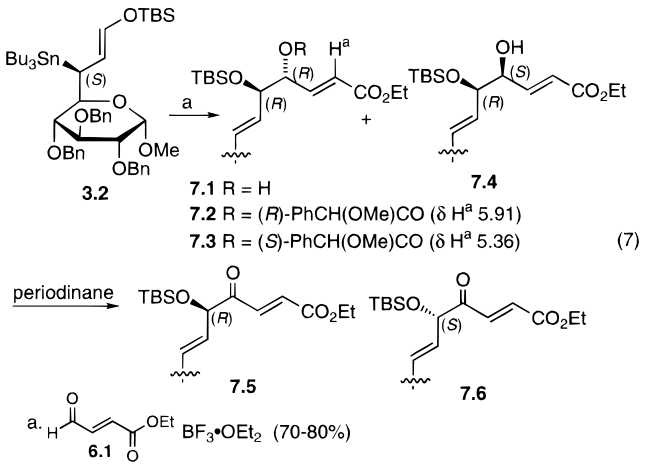
(7) At this point the configuration was not known. For clarity of the discussion we will show the configurations that were later proved.

(8) The configuration of the analogous 2-heptynal adduct has been shown to be (*S*,*S*).[5]

(9) To achieve economy of the space the adducts are shown in a hairpin projection rather than the usual zig-zag arrangement. It is the latter form from which the terms "*syn*" and "*anti*" are derived. We apologize for any confusion resulting from this presentation.

(10) Marshall, J. A.; Hinkle, K. W. *J. Org. Chem.* **1995**, *60*, 1920. We are indebted to Albert Garofalo for a sample of this material.

Stannane **3.2** afforded an 85:15 mixture of two adducts upon addition to aldehyde **6.1**. These were identified as *syn*/*anti* diastereomers through oxidation to a single ketone **7.5**.[13] This ketone showed distinct spectral differences from its epimer **7.6**, secured through oxidation of alcohol **6.2**. The expected (*R*) configuration at the carbinyl center was confirmed by analysis of the *O*-methyl mandelates **7.2** and **7.3**. In this case the vinylic proton H^a of the (*S*)-mandelate **7.3** was profoundly shielded (eq 7).



Aldehyde **6.1** thus displays typical matched−mismatched characteristics with stannanes **3.1** and **3.2**. In view of previous findings with (*E*)-γ-silyloxy allylic stannanes,[5,14] it seems safe to assume that adducts **6.2** and **7.1** are *syn* diastereomers.[9]

The unprecedented BF_3-promoted *syn* S_E2' addition of stannane **3.2** to 2-nonynal[15] as a major reaction pathway is not readily explained. Assuming Yamamoto acyclic transition states, as depicted in Figure 1,[16] it is unclear why the arrangement represented by **C** should not be preferred for this addition, particularly since **A** adequately accounts for the exclusive formation of adducts **4.1** and **6.2** from stannane **3.1** and the appropriate aldehydes. Even though the glycoside substituent of these stannanes would appear to be relatively remote from the reaction center, it obviously could play a role. *A priori* we might expect it to influence both the preferred orientation of the allylic stannane with respect to the glycoside appendage (rotation about the C5/C6 bond) and the facial approach to the π system of the stannane by the aldehyde. The apparent preference for **B** over **C** by 2-nonynal may reflect these factors. However it is quite surprising that enal **6.1** is not similarly influenced, as apparently little or no product from it and stannane **3.2** is formed *via* **B**.[17]

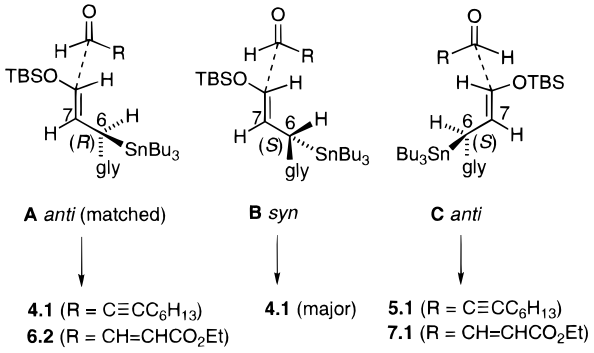


Figure 1. Yamamoto transition states leading to syn adducts.

Nonetheless, given the intrinsically lower reactivity of γ-oxygenated allylic stannanes compared to their non-oxygenated counterparts,[18] and in consideration of previous results (eq 1),[4] it is remarkable that the stereochemically homogeneous adducts **4.1** and **6.2** can be obtained in 90% or higher yield. The latter adducts, and appropriate analogues of the former, represent potentially useful precursors of complex unnatural higher sugars and C-disaccharides.[19]

Experimental Section[20]

Enal 2.1. To a stirring solution of 2.8 mL (32 mmol) of oxalyl chloride in 100 mL of dry CH_2Cl_2 cooled to −78 °C was added 3.0 mL (43 mmol) of DMSO. The mixture was stirred at −78 °C for 20 min, and a solution of 10.4 g (21.3 mmol) of allylic alcohol **1.3**[4] in 25 mL of dry CH_2Cl_2 was slowly added. The reaction mixture was stirred at −78 °C for 30 min, and then 12.0 mL (85.1 mmol) of Et_3N was added. The mixture was warmed to 0 °C for 20 min, and then diluted with Et_2O and washed with 10% HCl, saturated aqueous $NaHCO_3$, and brine. The organic extract was dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 10.7 g of a thick yellow syrup. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 8.99 g (86%) of aldehyde **2.1** as a cloudy, colorless syrup. $[\alpha]_D$ 112.7 (*c* 2.3, THF). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.33(d, J = 8.0 Hz, 1H), 7.34−7.26(m, 15H), 6.65(dd, J = 15.8, 4.1 Hz, 1H), 6.28(m, 1H), 4.98, 4.83(ABq, J_{AB} = 10.9 Hz, 2H), 4.87, 4.54(ABq, J_{AB} = 11.3 Hz, 2H), 4.80, 4.66(ABq, J_{AB} = 12.6 Hz, 2H), 4.60(d, J = 3.6 Hz, 1H), 4.31(m, 1H), 4.03(dd(apparent t), J = 9.2 Hz, 1H), 3.51(dd, J = 9.7, 3.6 Hz, 1H), 3.34(s, 3H), 3.25(dd(apparent t), J = 9.5 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 193.1, 152.3, 138.4, 137.8, 137.4, 131.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 98.1, 82.0, 80.8, 79.7, 75.9, 75.3, 73.5, 69.0, 55.5. IR(neat) 3085, 3029, 2907, 2730, 1952, 1874, 1811, 1692, 1495, 1452, 1097.

Methyl 2,3,4-Tri-*O*-benzyl-6-deoxy-6-(tri-*n*-butylstannyl)-6-[(*E*)-2-(*tert*- butyldimethylsilyloxy)vinyl]-α-D-glucopyranoside (3.1 and 3.2). To a stirred suspension of 1.75 g (19.6 mmol) of CuCN in 100 mL of dry THF cooled to −78 °C was added 15.0 mL (38.9 mmol) of 2.59 M *n*-BuLi in hexanes. The reaction mixture was warmed slightly until a faint yellow color appeared and the suspension dissolved. The mixture was again cooled to −78 °C, and 10.4 mL (38.6 mmol) of Bu_3SnH was added. The resulting bright yellow solution was stirred at −78 °C for 25 min. A solution of 8.58 g (17.6 mmol) of conjugated aldehyde **2.1** in 50 mL of dry THF was slowly added, and the mixture was stirred for 30 min before 10.6 g (70.2 mmol) of TBSCl was added. After stirring at −78 °C for 30 min, the reaction mixture was quenched and diluted

(11) Veysoglu, T.; Mitscher, L. A.; Swayze, J. K. *Synthesis* **1980**, 807.
(12) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.
(13) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. Ireland, R. E.; Liu, L. *J. Org. Chem.* **1993**, *58*, 2899.
(14) Marshall, J. A.; Jablonowski, J. A.; Elliott, L. M. *J. Org. Chem.* **1995**, *60*, 2662.
(15) Fortes, C. C.; Garrote, C. F. D. *Synth. Commun.* **1993**, *23*, 2869.
(16) Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Norihika, M.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. For a recent review, see Yamamoto, Y.; Shida, N. *Advances in Detailed Reaction Mechanisms*; JAI Press: Greenwich, CT, 1994; Vol. 3, pp 1−44.
(17) The glycoside substituent may not be the crucial factor in this addition as we have found that the reaction of (*R*,*E*)-3-[(tri-*n*-butylstannyl)-1-(*tert*-butyldimethylsilyl)oxy]-1-propene to 2-heptynal affords the *syn* adduct of only 20% ee. In contrast, addition of this stannane to (*E*)-2-heptenal gives the *syn* adduct of >95% ee.[14]
(18) Marshall, J. A.; Jablonowski, J. A.; Welmaker, G. S. *J. Org. Chem.* **1996**, *61*, 2904.
(19) For a preliminary disclosure of some of these results, see ref 14.
(20) For typical experimental protocols, see Marshall, J. A.; Wang, X-j. *J. Org. Chem.* **1991**, *56*, 960.

with a 1:1 solution of 3% NH_4OH and saturated NH_4Cl. The mixture was warmed to ambient temperature and diluted with Et_2O, and the layers were separated. The aqueous layer was extracted with Et_2O, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 25.7 g of a pale yellow oil. Chromatography on silica gel first with hexanes to remove Bu_6Sn_2, then 5% EtOAc−hexanes afforded 7.99 g (51%) of stannane **3.1** and 3.69 g (24%) of stannane **3.2** as clear, colorless oils.

Stannane 3.1: $[\alpha]_D$ −3.7 (*c* 1.1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.29 (m, 15 H), 6.05 (d, J = 12.0 Hz, 1H), 5.15 (dd(apparent t), J = 12.0 Hz, 1H), 4.94, 4.75 (ABq, J_{AB} = 10.8 Hz, 2H), 4.88, 4.66 (ABq, J_{AB} = 11.6 Hz, 2H), 4.77, 4.66 (ABq, J_{AB} = 12.1 Hz, 2H), 4.54 (d, J = 3.5 Hz, 1H), 3.94 (dd(apparent t), J = 9.4 Hz, 1H), 3.76 (dd, J = 9.4, 2.1 Hz, 1H), 3.53 (dd-(apparent t), J = 9.2 Hz, 1H), 3.44 (dd, J = 3.5, 6.3 Hz, 1H), 3.38 (s, 3H), 2.51 (dd, J = 9.7, 2.2 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 139.1, 139.0, 138.5, 138.4, 128.4, 128.4, 128.0, 127.9, 127.8, 127.5, 127.5, 127.4, 127.4, 110.3, 98.8, 82.0, 80.4, 80.0, 75.6, 74.7, 73.4, 73.3, 65.8, 56.3, 29.3, 29.2, 29.1, 27.8, 27.5, 27.2, 26.2, 25.8, 18.3, 15.3, 13.7, 10.9, 10.9, 9.4, 7.9, 7.9, −5.0, −5.2. Anal. Calcd for $C_{48}H_{74}O_6SiSn$: C, 64.50; H, 8.34. Found: C, 64.64; H, 8.37.

Stannane 3.2: $[\alpha]_D$ 23.5 (*c* 1.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.29 (m, 15H), 6.11 (d, J = 11.8 Hz, 1H), 5.20 (dd-(apparent t), J = 11.6 Hz, 1H), 4.94, 4.76 (ABq, J_{AB} = 11.2 Hz, 2H), 4.87, 4.61 (ABq, J_{AB} = 11.9 Hz, 2H), 4.76, 4.64 (ABq, J_{AB} = 11.8 Hz, 2H), 4.44 (d, J = 3.5 Hz, 1H), 3.93 (dd(apparent t), J = 9.3 Hz, 1H), 3.78 (dd, J = 9.6, 2.4 Hz, 1H), 3.44 (dd, J = 6.2, 3.6 Hz, 1H), 3.36 (s, 3H), 3.07 (dd(apparent t), J = 9.3 Hz, 1H), 2.36 (dd, J = 11.3, 2.4 Hz, 1H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ 138.9, 138.6, 138.2, 137.3, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.6, 128.5, 113.6, 97.7, 82.6, 82.1, 80.3, 75.7, 75.1, 74.6, 73.3, 55.3, 30.5, 29.4, 29.3, 29.2, 27.8, 27.5, 27.2, 25.7, 18.3, 13.7, 11.7, 10.2, 8.7, −5.1, −5.2. Anal. Calcd for $C_{48}H_{74}O_6SiSn$: C, 64.50; H, 8.34. Found: C, 64.68; H, 8.37.

2-Nonynal Adduct 4.1 A. From Stannane 3.1. To a solution of 0.017 g (0.12 mmol) of 2-nonynal[15] in 1 mL of dry CH_2Cl_2 cooled to −78 °C was added 0.021 mL (0.168 mmol) of $BF_3{\cdot}OEt_2$ with stirring. After 10 min, a solution of 0.057 g (0.063 mmol) of stannane **3.1** in 1 mL of dry CH_2Cl_2 was slowly added. The reaction mixture was stirred at −78 °C for 1.5 h, then quenched with saturated aqueous $NaHCO_3$. The mixture was warmed to ambient temperature and extracted with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 0.068 g of a pale yellow oil. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 0.018 g (27%) of recovered stannane and 0.027 g (77%) of the adduct **4.1** as a pale yellow syrup. $[\alpha]_D$ 11.9 (*c* 4.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.36−7.25 (m, 15H), 5.86 (m, 2H), 4.94, 4.79 (ABq, J_{AB} = 10.9 Hz, 2H), 4.78, 4.66 (ABq, J_{AB} = 12.3 Hz, 2H), 4.78, 4.61 (ABq, J_{AB} = 10.8 Hz, 2H), 4.58 (d, J = 3.6 Hz, 1H), 4.12−4.05 (m, 3H), 3.97 (dd(apparent t), J = 9.3 Hz, 1H), 3.51 (dd, J = 9.7, 3.6 Hz, 1H), 3.34 (s, 3H), 3.21 (dd(apparent t), J = 9.4 Hz, 1H), 2.53 (d, J = 5.3 Hz, 1H), 2.13 (m, 2H), 1.49−1.21 (m, 11H), 0.87 (s, 9H), 0.08 (s, 3H), 0.02 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 138.8, 138.2, 131.5, 129.8, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 126.6, 97.9, 86.7, 82.4, 81.9, 79.9, 78.4, 76.5, 75.8, 75.0, 73.4, 69.7, 66.5, 55.0, 31.3, 28.6, 28.5, 25.8, 22.5, 18.8, 18.2, 14.0, −4.1, −4.8. IR (neat) 3472, 3030, 2929, 2226, 1453. Anal. Calcd for $C_{45}H_{62}O_7Si$: C, 72.72; H, 8.41. Found: C, 72.82; H, 8.42.

B. From Stannane 3.2. The above procedure was followed with 0.093 g (0.67 mmol) of 2-nonynal,[15] 0.085 mL (0.69 mmol) of $BF_3{\cdot}OEt_2$, and 0.474 g (0.530 mmol) of stannane **3.2**. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 0.314 g (80%) of a 70:30 mixture of adducts **4.1**/**5.1** as a pale yellow syrup, $[\alpha]_D$ 12.3 (*c* 0.62, $CHCl_3$). Recovered stannanes from this and the previous experiment were unchanged.

***Bis*-TBS Ether 4.2.** To a stirring solution of 0.242 g (0.326 mmol) of alcohol **4.1** (from stannane **3.1**) in 7.0 mL of dry CH_2Cl_2 cooled to 0 °C was added 0.140 mL (1.20 mmol) of 2,6-lutidine followed by 0.270 mL (1.18 mmol) of TBSOTf. The reaction mixture was stirred for 25 min, quenched with H_2O, and extracted with Et_2O. The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was removed by distillation under reduced pressure to afford 0.282 g of a light yellow oil. Chromatography on silica gel with 10% EtOAc−hexanes as the eluant afforded 0.255 g (91%) of the TBS ether **4.2** as a pale yellow oil. $[\alpha]_D$ 6.4 (*c* 2.2, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.35−7.25 (m, 15H), 6.08 (dd, J = 15.6, 4.2 Hz, 1H), 5.85 (dd, J = 16.1, 5.2 Hz, 1H), 4.92, 4.79 (ABq, J_{AB} = 10.8 Hz, 2H), 4.78, 4.66 (ABq, J_{AB} = 12.2 Hz, 2H), 4.73, 4.67 (ABq, J_{AB} = 10.7 Hz, 2H), 4.60 (d, J = 3.6 Hz, 1H), 4.18−4.08 (m, 3H), 3.96 (dd(apparent t), J = 9.3 Hz, 1H), 3.51 (dd, J = 9.7, 3.6 Hz, 1H), 3.35 (s, 3H), 3.23 (dd(apparent t), J = 9.3 Hz, 1H), 2.04 (m, 2H), 1.41−1.19 (m, 11H), 0.90−0.83 (m, 18H), 0.09−0.00 (m, 12H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 138.7, 138.2, 138.2, 132.4, 128.7, 128.3, 128.2, 128.2, 127.9, 127.9, 127.9, 127.7, 127.7, 127.4, 97.8, 86.5, 82.6, 81.8, 79.9, 79.4, 76.0, 75.8, 74.9, 73.3, 70.2, 67.9, 54.9, 31.4, 28.6, 26.0, 22.6, 18.9, 18.5, 18.3, 14.2, −4.3, −4.4, −4.5, −4.6. Anal. Calcd for $C_{51}H_{76}O_7Si_2$: C, 71.45; H, 8.94. Found: C, 71.37; H, 8.99.

The above procedure was employed with 430 mg (0.579 mmol) of adducts **4.1**/**5.1**, from stannane **3.2**, 12 mL of dry CH_2Cl_2, 0.236 mL (2.03 mmol) of 2,6-lutidine, and 0.466 mL (2.03 mmol) of TBSOTf affording the *bis*-TBS ethers **4.2**/**5.2** (418 mg) in 84% yield.

(+)- (2*R*,3*S*)-2,3-*Bis*-[(*tert*-Butyldimethylsilyl)oxy-4-undecynal (4.3). To a stirring solution of 0.233 g (0.272 mmol) of olefin **4.2** (from stannane **3.1**) in 7.0 mL of a 9:2:1 solution of acetone, *t*-BuOH, and H_2O at room temperature were added 0.166 g (1.42 mmol) of NMO and 0.495 mL (0.046 mmol) of 2.5% OsO_4 in *t*-BuOH. The reaction mixture was stirred at room temperature for 44 h and quenched with saturated aqueous $NaHSO_3$. The mixture was diluted and extracted with EtOAc. The combined organic extracts were washed with brine, dried over $MgSO_4$, and filtered, and the solvent was removed by distillation under reduced pressure to afford 0.251 g of a brown syrup. Chromatography on silica gel with 15% EtOAc−hexanes as the eluant afforded 0.100 g (0.112 mmol, 41%) of the diol product as a pale yellow oil. This oil was dissolved in 3.0 mL of THF and treated with 0.080 g (0.351 mmol) of H_5IO_6 with stirring. The reaction mixture, which quickly formed a white precipitate, was quenched after 7 min with H_2O, diluted, and extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 0.093 g of a yellow oil. Chromatography on silica gel with 15% EtOAc−hexanes as the eluant afforded 0.020 g (42%) of the *bis*-TBS aldehyde **4.3** as a clear, colorless oil. $[\alpha]_D$ +18.9 (*c* 2.0, THF). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 9.67 (d, J = 1.7 Hz, 1H), 4.54 (m, 1H), 3.95 (dd, J = 7.0, 2.1 Hz, 1H), 2.16 (m, 2H) 1.55−1.19 (m, 11H), 0.90−0.85 (m, 18H), 0.12 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H), 0.07 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 201.7, 88.0, 80.6, 78.0, 64.9, 31.3, 29.7, 28.5, 28.3, 25.7, 22.5, 18.7, 18.3, 18.1, 14.0, −4.5, −4.8, −4.8, −4.9.

The above procedure was employed with 392 mg (0.457 mmol) of olefins **4.2**/**5.2** derived from stannane **3.2**, 12 mL of a 9:2:1 solution of acetone, *t*-BuOH, and H_2O, 165 mg (1.41 mmol) of NMO, and 0.480 mL (0.045 mmol) of 2.5% OsO_4 in *t*-BuOH, affording 129 mg of diol in 32% yield. This oil was treated with 0.101 g (0.444 mmol) of H_5IO_6 as described above, affording 0.046 g (84%) of aldehyde **4.3** of 30% ee as a pale yellow oil. $[\alpha]_D$ 5.9 (*c* 4.6, THF).

B. From Adduct 4.5. The above procedure was followed with 0.249 g (0.567 mmol) of olefin **4.6**, affording 0.106 g (40%) of the tetraol as a pale yellow oil after chromatography. This oil was treated with 0.070 g of H_5IO_6 as described above, affording 0.059 g (61%) of aldehyde **4.3** as a pale yellow oil. $[\alpha]_D$ 18.5 (*c* 1.7, THF).

(*E*)- (4*S*,5*S*)-4-[(*tert*-Butyldimethylsilyl)oxy]-2-tridecen-6-yn-5-ol (4.5). To a stirring solution of 0.087 g (0.63 mmol) of 2-nonynal[15] in 5.0 mL of dry CH_2Cl_2 cooled to −78 °C was added 0.076 mL (0.62 mmol) of $BF_3{\cdot}OEt_2$. The reaction mixture was stirred at −78 °C for 15 min, and then a solution of 0.246 g (0.521 mmol) of stannane **4.4**[5] in 4.0 mL of dry

CH_2Cl_2 was added. The reaction mixture was stirred at −78 °C for 5 min and then quenched with saturated aqueous $NaHCO_3$ and warmed to rt. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 0.352 g of a pale yellow oil. Chromatography on silica gel with 5% EtOAc−hexanes as the eluant afforded 0.137 (81%) of the alcohol **4.5** as a pale yellow oil. $[\alpha]_D$ 1.1 (*c* 1.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.72−5.64 (m, 1H), 5.48−5.42 (m, 1H), 4.09−4.05 (m, 1H), 4.01 (dd, *J* = 6.5 Hz, 1H), 2.56 (d, 1H), 2.19−2.15 (m, 2H), 1.68 (dd, *J* = 6.5, 1.5 Hz, 3H), 1.50−1.23 (m, 11H), 0.91−0.72 (m, 9H), 0.07 (s, 3H), 0.03 (s, 3H). ^{13}C-NMR (CDCl3, 100 MHz) δ 130.1, 128.6, 86.2, 78.4, 76.5, 66.5, 31.1, 28.3, 27.6, 26.6, 25.6, 22.3, 18.5, 17.9, 17.5, 17.3, 13.8, 13.5, −4.3, −5.0. IR (neat) 3455, 2958, 2929, 2230, 1671. Anal. Calcd for $C_{19}H_{36}O_2Si$: C, 70.31; H, 11.18. Found: C, 70.57; H, 11.19.

(*E*)- (4*S*,5*S*)-4,5-*Bis*-[(*tert*-Butyldimethylsilyl)oxy]-2-tridecen-6-yne (4.6). The procedure described for TBS ether **4.2** was followed with 0.217 g (0.669 mmol) of alcohol **4.5**, 0.094 mL of 2,6 lutidine, and 0.184 mL of TBSOTf to afford 0.286 g of a pale yellow oil. Chromatography on silica gel with 10% EtOAc−hexanes as eluant afforded 0.249 g (85%) of the TBS ether **4.6** as a pale yellow oil. $[\alpha]_D$ 13.2 (*c* 3.1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 5.67−5.50 (m, 2H), 4.16−4.14 (m, 1H), 3.96 (dd(apparent t), *J* = 6.3 Hz, 1H), 2.17−2.13 (m, 2H), 1.68 (d, *J* = 6.3 Hz, 3H), 1.53−1.23 (m, 11H), 0.90−0.84 (m, 18H), 0.10−0.00 (m, 12H). ^{13}C-NMR (CDCl3, 100 MHz) δ 130.8, 127.7, 86.3, 79.8, 68.2, 31.6, 28.8, 28.7, 26.1, 22.8, 19.0, 18.6, 18.4, 18.0, 14.2, −4.6, −4.7, −4.8, −4.9. Anal. Calcd for $C_{25}H_{50}O_2Si_2$: C, 68.42; H, 11.48. Found: C, 68.30; H, 11.47.

Adduct 6.2. The procedure for the preparation of alcohol **4.1** was employed with 0.200 g (1.56 mmol) of aldehyde **6.1**,[11] 45 mL of dry CH_2Cl_2, 0.575 mL (4.68 mmol) of $BF_3{\cdot}OEt_2$, and 0.927 g (1.04 mmol) of stannane **3.1,** affording 0.042 g (4.5%) of recovered stannane **3.1** and 0.553 g (73%) of adduct **6.2** as a clear, colorless syrup. $[\alpha]_D$ 22.5 (*c* 1.1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.36−7.24 (m, 15H), 6.86 (m, 1H), 6.08 (m, 1H), 5.80 (m, 2H), 4.96−4.54 (m, 7H), 4.15-4.02 (m, 3H), 3.99−3.94 (m, 1H), 3.51 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.34 (s, 3H), 3.21 (dd(apparent t), *J* = 9.4 Hz, 1H), 2.59 (d, *J* = 5.5 Hz, 1H), 2.15 (s, 3H), 1.23 (t, 3H), 0.83 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 166.0, 146.2, 138.6, 138.1, 138.0, 130.5, 130.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.4, 122.0, 97.9, 82.4, 81.9, 79.8, 76.2, 75.7, 75.0, 74.1, 73.4, 69.2, 60.4, 60.3, 55.0, 31.6, 25.8, 22.7, 18.2, 14.3, 14.3, 14.2, −3.9, −4.7. IR (neat) 3479, 2927, 1718, 1656, 1452. Anal. Calcd for $C_{42}H_{56}O_9Si$: C, 68.82; H, 7.70. Found: C, 68.91; H, 7.73.

Adduct 7.1. The above procedure was followed with 0.053 g (0.43 mmol) of aldehyde **6.1**, 0.105 mL (0.0854 mmol) of $BF_3{\cdot}OEt_2$, and 0.258 g (0.289 mmol) of stannane **3.2** to afford 0.123 g (70%) of the adducts **7.1**/**7.4** as a clear, colorless syrup after chromatography on silica gel. $[\alpha]_D$ 23.4 (*c* 2.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.36−7.26 (m, 15H), 6.87 (dd, *J* = 15.7, 3.9 Hz, 1H), 6.05 (dd, *J* = 15.7, 1.7 Hz, 1H), 5.81 (dd-(apparent t), *J* = 3.6 Hz, 2H), 4.84−4.56 (m, 7H), 4.17−4.03 (m, 5H), 3.98 (dd(apparent t), *J* = 9.3 Hz, 1H), 3.52 (dd, *J* = 9.7, 3.6 Hz, 1H), 3.35 (s, 3H), 3.20 (dd(apparent t), *J* = 9.3 Hz, 1H), 2.48 (d, *J* = 5.5 Hz, 1H), 1.24 (t, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 166.0, 146.3, 138.5, 138.1, 138.0, 131.4, 130.2, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 121.9, 97.9, 82.2, 81.8, 79.9, 75.9, 75.8, 74.9, 74.0, 73.4, 69.9, 60.3, 55.2, 25.9, 18.2, 14.3, −3.9, −4.7. IR (neat) 3478, 3062, 2924, 2361, 2340, 1716, 1657, 1454. Anal. Calcd for $C_{42}H_{56}O_9Si$: C, 68.82; H, 7.70. Found: C, 68.66; H, 7.79.

(*R*)-Mandelate 6.3. To a stirring solution of 0.051 g (0.070 mmol) of alcohol **6.2** in 1.0 mL of dry CH_2Cl_2 at rt was added 0.017 g (0.082 mmol) of DCC, 0.027 g (0.16 mmol) of (*R*)- (−)-α-methoxyphenylacetic acid, and a catalytic amount of DMAP. The reaction mixture was stirred at rt for 3 days, and then hexane was added and the mixture filtered to remove the white precipitate that formed. The filtrate was washed with 10% HCl, saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford 0.055 g of a clear, colorless oil. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 0.045 g (74%) of the mandelate **6.3** as a clear, colorless oil. $[\alpha]_D$ −8.7 (*c* 3.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.43−7.25 (m, 20H), 6.71 (dd, J = 15.8, 4.6 Hz, 1H), 5.79 (m, 2H), 5.37 (m, 1H), 5.30 (dd, J = 15.8, 1.5 Hz, 1H), 4.98−4.56 (m, 8H), 4.23 (dd(apparent t), J = 6.0 Hz, 1H), 4.14−3.95 (m, 4H), 3.53 (dd, J = 9.6, 3.5 Hz, 1H), 3.38 (s, 3H), 3.35 (s, 3H), 3.19 (dd(apparent t), J = 9.4 Hz, 1H), 1.29−1.17 (m, 3H), 0.99−0.78 (m, 9H), 0.08 (s, 3H), 0.01 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.2, 165.2, 141.2, 138.6, 138.1, 135.7, 130.4, 129.5, 128.9, 128.7, 128.3, 128.2, 128.2, 128.0, 127.8, 127.5, 127.4, 127.4, 127.2, 122.5, 97.8, 82.4, 81.9, 79.8, 75.7, 75.5, 74.9, 73.4, 69.2, 60.3, 57.3, 55.0, 25.8, 18.1, 14.2, −4.3, −4.8.

(*S*)-Mandelate 6.4. The above procedure was employed with 50 mg (0.068 mmol) of alcohol **6.2**, 1 mL of CH_2Cl_2, 21 mg (0.10 mmol) of DCC, 23 mg (0.14 mmol) of (*S*)- (+)-α-methoxyphenylacetic acid, and a catalytic amount of DMAP. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 47 mg (80%) of mandelate **6.4** as a pale yellow oil. $[\alpha]_D$ 7.4 (*c* 4.9, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.44−7.25 (m, 20H), 6.87 (dd, J = 15.8, 5.0 Hz, 1H), 5.90 (dd, J = 15.8, 1.9 Hz, 1H), 5.66−5.37 (m, 3H), 4.97−4.51 (m, 8H), 4.16−3.89 (m, 5H), 3.48 (dd, J = 9.6, 3.5 Hz, 1H), 3.40 (s, 3H), 3.31 (s, 3H), 3.09 (dd(apparent t), J = 9.2 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H), 0.82 (s, 9H), −0.01 (s, 3H), −0.07 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.3, 165.4, 141.6, 138.6, 138.2, 138.1, 135.8, 129.7, 129.6, 128.7, 128.6, 128.4, 128.2, 128.2, 128.0, 127.8, 127.4, 127.1, 123.1, 97.7, 82.4, 82.2, 81.9, 79.7, 75.7, 75.6, 74.7, 73.3, 72.7, 69.2, 60.5, 57.4, 55.0, 25.8, 18.1, 14.3, −4.4, −4.9.

(*R*)-Mandelate 7.2. The above procedure was employed with 62 mg (0.085 mmol) of alcohol **7.1**, 1 mL of CH_2Cl_2, 27 mg (0.13 mmol) of DCC, 24 mg (0.14 mmol) of (*R*)- (−)-α-methoxyphenylacetic acid, and a catalytic amount of DMAP affording 68 mg (91%) of mandelate **7.2** as a clear, colorless oil. $[\alpha]_D$ 21.6 (*c* 5.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.41−7.24 (m, 20H), 6.90 (dd, J = 15.8, 4.6 Hz, 1H), 5.91 (dd, J = 15.8, 1.5 Hz, 1H), 5.64−5.33 (m, 3H), 4.97−4.47 (m, 8H), 4.23−3.89 (m, 5H), 3.50 (dd, J = 9.6, 3.5 Hz, 1H), 3.38 (s, 3H), 3.33 (s, 3H), 3.08 (dd(apparent t), J = 9.4 Hz, 1H), 1.23 (t, J = 7.1 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 3H), −0.03 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.4, 165.4, 141.2, 138.6, 138.1, 135.8, 129.9, 129.2, 128.8, 128.6, 128.4, 128.2, 128.0, 127.9, 127.6, 127.5, 127.2, 123.0, 97.8, 82.8, 82.3, 81.8, 79.8, 75.8, 75.4, 75.0, 73.4, 72.3, 69.6, 60.5, 57.4, 55.1, 25.8, 18.1, 14.2, −4.4, −4.9.

(*S*)-Mandelate 7.3. The above procedure was employed with 60 mg (0.082 mmol) of alcohol **7.1**, 1 mL of CH_2Cl_2, 28 mg (0.14 mmol) of DCC, 24 mg (0.14 mmol) of (*S*)- (+)-α-methoxyphenylacetic acid, and a catalytic amount of DMAP affording 66 mg (92%) of mandelate **7.3** as a clear, colorless oil. $[\alpha]_D$ 43.2 (*c* 5.9, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.37−7.25 (m, 20H), 6.74 (dd, J = 16.0, 4.4 Hz, 1H), 5.93−5.70 (m, 2H), 5.39−5.33 (m, 2H), 4.98−4.55 (m, 8H), 4.30 (dd-(apparent t), J = 5.4 Hz,), 4.14−3.96 (m, 5H), 3.54 (dd, J = 9.6, 3.5 Hz, 1H), 3.38 (s, 3H), 3.35 (s, 3H), 3.17 (dd(apparent t), J = 9.2 Hz, 1H), 1.19 (t, J = 7.1 Hz, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.2, 165.3, 141.0, 138.6, 138.1, 138.0, 135.7, 130.1, 129.5, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.8, 127.6, 127.5, 127.1, 122.6, 97.9, 82.8, 82.3, 81.8, 79.9, 75.8, 75.4, 75.1, 73.4, 72.7, 69.7, 60.3, 57.2, 55.1, 25.8, 18.2, 14.3, 14.1, −4.4, −4.7.

Ketone 7.6. To a stirring solution of 0.102 g (0.139 mmol) of alcohol **6.2** in 1.2 mL of dry CH_2Cl_2 at rt was added 0.116 g (0.274 mmol) of Dess−Martin periodinane reagent.[13] The reaction mixture, which quickly turned a pale, milky green color, was stirred at rt for 1 h. To this stirring mixture was added a solution of 0.180 g (1.14 mmol) of $Na_2S_2O_3$ in saturated aqueous $NaHCO_3$. The mixture was stirred at rt until two clear layers were formed. The reaction mixture was diluted with Et_2O, and the layers were separated. The aqueous layer was extracted with Et_2O. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford 0.116 g of a pale yellow oil. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 0.79 g (77%) of ketone **7.6** as a clear yellow syrup. $[\alpha]_D$ −10.6 (*c* 0.46, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.45 (d, J =

15.8 Hz, 1H), 7.38−7.21 (m, 15H), 6.74 (d, J = 16.2 Hz, 1H), 6.14-5.85 (m, 2H), 4.98−4.53 (m, 9H), 4.26−4.14 (m, 3H), 3.99 (dd(apparent t), J = 9.2 Hz, 1H), 3.53 (dd, J = 9.6, 3.5 Hz, 1H), 3.37 (s, 3H), 3.22 (dd(apparent t), J = 9.4 Hz, 1H), 1.28 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 198.2, 165.7, 139.3, 138.7, 138.6, 135.0, 132.8, 130.9, 129.2, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 128.1, 128.0, 98.6, 82.9, 82.3, 80.3, 79.4, 78.0, 75.5, 73.9, 70.5, 61.7, 55.8, 26.3, 18.7, 14.6, −4.2, −4.5. IR (neat) 3029, 2929, 2858, 1718, 1621, 1493, 1453.

Ketone 7.5. The above procedure was employed with 0.046 g (0.063 mmol) of alcohols **7.1**/**7.4**, 0.057 g (0.13 mmol) of Dess−Martin periodinane reagent,[13] 2.5 mL of dry CH_2Cl_2, and 0.070 g of $Na_2S_2O_3$. Chromatography on silica gel with 20% EtOAc−hexanes as the eluant afforded 0.038 g (83%) of ketone **7.5** as a clear yellow syrup. $[\alpha]_D$ +59.5 (*c* 3.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.47 (d, J = 15.8 Hz, 1H), 7.35−7.23 (m, 15H), 6.77 (d, J = 15.8 Hz, 1H), 6.09-5.81 (m, 2H), 4.98−4.51 (m, 9H), 4.23−4.12 (m, 3H), 3.98 (dd(apparent t), J = 9.2 Hz, 1H), 3.52 (dd, J = 9.4, 3.7 Hz, 1H), 3.36 (s, 3H), 3.19 (dd(apparent t), J = 9.4 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.91 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 197.5, 165.0, 138.6, 138.0, 137.9, 134.4, 132.2, 132.1, 130.4, 128.7, 128.7, 128.4, 128.3, 128.0, 127.8, 127.6, 127.5, 127.3, 98.0, 82.5, 82.5, 81.6, 81.5, 79.8, 79.7, 79.1, 77.4, 77.3, 76.6, 76.5, 75.8, 75.7, 75.2, 73.4, 70.2, 61.2, 61.1, 55.3, 55.2, 25.7, 25.7, 18.2, 14.1, −4.7, −4.9.

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Supporting Information Available: ^{1}H NMR spectra for key intermediates (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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