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SCIENCE DIRECT®

Tetrahedron 59 (2003) 8979–8987

TETRAHEDRON

1,3-Polyol arrays via the stereoselective rearrangement of vinyl acetals

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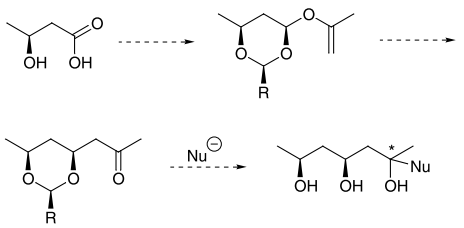
Received 24 February 2002; accepted 20 March 2003

Abstract—A series of 1,3-dioxanyl vinyl acetals were readily synthesized from the corresponding dioxanone by a reduction and in situ acylation followed by Petasis olefination. Treatment of these vinyl acetals with $BF_3{\cdot}OEt_2$ results in an O to C rearrangement to form *anti*-3,5-dihydroxyketones while a mixture of Me_3Al and $BF_3{\cdot}OEt_2$ provides the corresponding *syn* relationship via a stereoretentive rearrangement.

1. Introduction

Skipped polyol units are ubiquitous structural motifs in several important classes of natural products. For example, the polyene macrolide class of natural products is characterized by a conjugated polyene and skipped polyol unit.[1] Due to their important biological activity and structural complexity, numerous efforts have been directed at the development of an efficient synthetic method for stereoselective synthesis of 1,3-polyol segments.[2]

Recently, we have developed a Lewis acid-mediated highly stereoretentive rearrangement of vinyl acetals, wherein the selectivity is controlled by tight ion pairing in the solvent cage.[3] In many cases, either isomer can be prepared by simple choice of Lewis acid systems ($BF_3{\cdot}OEt_2$ or Me_3Al/$BF_3{\cdot}OEt_2$). In order to explore this unusual methodology fully, we have been interested in new methods for the stereoselective synthesis of skipped polyols employing the Lewis acid-promoted rearrangement of vinyl acetals. Herein we report that the Lewis acid-mediated rearrangement of dioxanyl-derived vinyl acetals is an effective method for the highly stereocontrolled synthesis of both *syn*- and *anti*-3,5-dihydroxy ketone units (Eq. (1)). The presence of two distinct acetal functionalities in these substrates was a potential cause for concern, but we expected to disfavor ring acetal binding by increasing the bulk of the R group. A subsequent diastereoselective addition to the newly formed ketone would provide a stereoselective entry to 1,3,5-triol fragments.



(1)

2. Results and discussion

2.1. Substrate synthesis

1,3-Dioxanones were efficiently prepared from β-hydroxy acids utilizing the protocol described by Crich et al.[4] Thus, reaction of a β-hydroxy acid and suitable aldehyde, isopropoxytrimethylsilane, and TMSOTf in the presence of 4 Å molecular sieves at −78°C to −15°C for 8 h afforded the corresponding 1,3-dioxanone in moderate to good yield after purification by silica gel chromatography (Scheme 1). The dioxanones are typically formed with better than 10:1 selectivity at the acetal carbon.

A one-pot reduction/acylation protocol developed by Rychnovsky[5] provides a general synthesis to the 4-acyloxy-1,3-dioxane required for this study. Yields for this reaction typically exceed 80% and the products are easily purified by flash silica gel chromatography. It should be noted that only trace product was formed if benzoyl chloride was used as an acylating agent. Finally, the acylation products were converted to the corresponding vinyl acetals in moderate to good yield by the action of Cp_2TiMe_2/Cp_2TiCl_2 at 80°C for 12 h.[6]

2.2. Stereoselective rearrangement of vinyl acetals

Initial attempts to effect the rearrangement of a vinyl acetal

Keywords: polyols; Lewis acids; diastereoselection.
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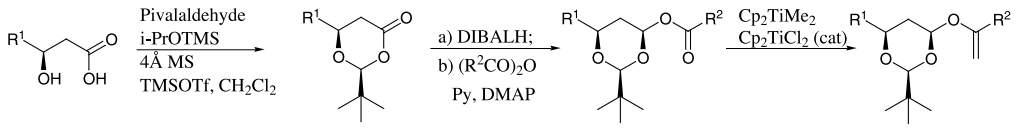
doi:10.1016/j.tet.2003.03.004



1

R^1 = Me (**a**), *n*-Hex (**b**), *cy*-Hex (**c**), *i*-Pr (**d**), Ph (**e**), $Ph(CH_2)_2$ (**f**)

R^2 = Ph (**a**), Me (**b**), Et (**c**)

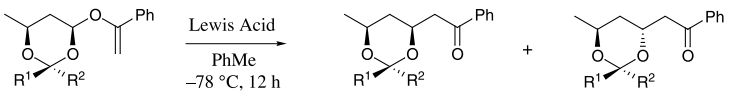
2a 42%
2b 94%
2c 83%
2d 67%
2e -
2f 53%

3aa 88%
3ba 85%
3ca 82%
3da 67%
3ea 41% (two steps)
3fa 86%
3fb 86%
3fc 85%

4aa 57%
4ba 75%
4ca 70%
4da 53%
4ea 56%
4fa 64%
4fb 61%
4fc 57%

Scheme 1.

Table 1. Effect of 2-substitutent on rearrangement



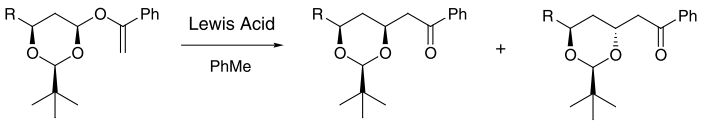
5a-d, 4aa *syn*-**6a-d**, *syn*-**7aa** *anti*-**6a-d**, *anti*-**7aa** (2)

Entry	Vinyl acetal	Product	*syn*/*anti* (isolated yield)[a]	
			$BF_3{\cdot}OEt_2$[b]	$Me_3Al/BF_3{\cdot}OEt_2$[c]
1	**5a** (R^1=Me, R^2=H)	**6a**	Many products	Many products
2	**5b** (R^1=Ph, R^2=H)	**6b**	Many products	Many products
3	**5c** (R^1=Me, R^2=Me)	**6c**	16:84 (65%)	Many products
4	**5d** (R^1=*i*-Pr, R^2=H)	**6d**	3:97 (92%)	90:10 (80%)
5	**4aa** (R^1=*t*-Bu, R^2=H)	**7aa**	2:98 (82%)	96:4 (90%)

[a] Selectivity determined by ^{1}H NMR analysis of the unpurified reaction mixture; isolated yield indicates analytically pure material of the major isomer.
[b] $BF_3{\cdot}OEt_2$ (1.2 equiv.) used as Lewis acid.
[c] Me_3Al (4.0 equiv.) and $BF_3{\cdot}OEt_2$ (1.2 equiv.) used as Lewis acid.

with a methyl group at the 2-position revealed that the $Me_3Al/BF_3{\cdot}OEt_2$ -mediated rearrangement produced many products. In the case of $BF_3{\cdot}OEt_2$, epimerization occurred at the dioxane ring acetal, complicating product analysis. These results are summarized in Table 1. Although isobutyraldehyde-derived dioxanyl acetal **5d** provided reasonable levels of selectivity in the rearrangement reaction (entry 4, Table 1), the larger *tert*-butyl group provided enough of a benefit to warrant its use. The use of $BF_3{\cdot}OEt_2$ as a Lewis acid provides the *anti* relationship selectively, while $Me_3Al/BF_3{\cdot}OEt_2$ provides *syn*. Relative stereochemistry was determined by nOe experiments. Having identified the *tert*-butyl group at the 2-position as providing optimal selectivities, the scope and limitations of

Table 2. Scope of the vinyl acetal rearrangement—dioxanyl fragment

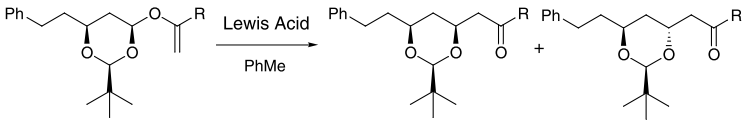


4aa-4fa *syn*-**7aa-7fa** *anti*-**7aa-7fa** (3)

Entry[a]	Vinyl acetal	Product	*syn*/*anti* (isolated yield)[b]	
			$BF_3{\cdot}OEt_2$[c]	$Me_3Al/BF_3{\cdot}OEt_2$[d]
1	**4aa** (R=Me)	**7aa** (R=Me)	2:98 (82%)	96:4 (90%)
2	**4ba** (R=*n*-Hex)	**7ba** (R=*n*-Hex)	2:98 (87%)	92:8 (90%)
3	**4ca** (R=*cy*-Hex)	**7ca** (R=*cy*-Hex)	2:98 (96%)	93:7 (87%)
4	**4da** (R=*i*-Pr)	**7da** (R=*i*-Pr)	2:98 (97%)	93:7 (85%)
5	**4ea** (R=Ph)	**7ea** (R=Ph)	2:98 (87%)	92:8 (81%)[e]
6	**4fa** (R=CH_2CH_2Ph)	**7fa** (R=CH_2CH_2Ph)	2:98 (91%)	98:2 (89%)[f]

[a] All reactions conducted in toluene at −78°C for 12 h on 0.1 mmol scale, unless otherwise stated.
[b] Selectivity determined by ^{1}H NMR analysis of the unpurified reaction mixture; isolated yield indicates analytically pure material of the major isomer.
[c] $BF_3{\cdot}OEt_2$(1.2 equiv.) used as Lewis acid.
[d] Me_3Al (4.0 equiv.) and $BF_3{\cdot}OEt_2$ (1.2 equiv.) used as Lewis acid.
[e] Reaction allowed to stir for 36 h.
[f] Reaction carried out on 1 mmol scale.

Table 3. Scope of the vinyl acetal rearrangement—enolate fragment



(4)

4fb-4fc *syn*-**7fb-7fc** *anti*-**7fb-7fc**

Entry[a]	Vinyl acetal	Product	Temp (°C)	*syn*/*anti* (isolated yield)[b]	
				$BF_3{\cdot}OEt_2$[c]	$Me_3Al/BF_3{\cdot}OEt_2$[d]
1	**4fb** (R=Me)	**7fb** (R=Me)	−78	17:83 (78%)	67:33 (ND)
2	**4fb** (R=Me)	**7fb** (R=Me)	−55	–	96:4 (89%)
3	**4fc** (R=Et)	**7fc** (R=Et)	−78	4:96 (91%)	78:22 (ND)
4	**4fc** (R=Et)	**7fc** (R=Et)	−55	–	92:8 (88%)

[a] All reactions conducted in toluene at the indicated temperature for 12 h, unless otherwise stated.
[b] Selectivity determined by ^1H NMR analysis of the unpurified reaction mixture; isolated yield indicates analytically pure material of the major isomer.
[c] $BF_3{\cdot}OEt_2$ (1.2 equiv.) used as Lewis acid.
[d] Me_3Al (4.0 equiv.) and $BF_3{\cdot}OEt_2$ (1.2 equiv.) used as Lewis acid.

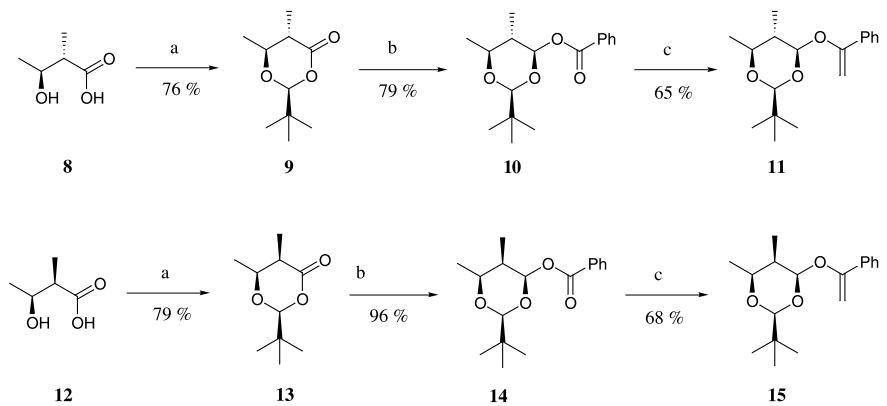
the rearrangement reaction were further studied with vinyl acetals containing this substituent (Table 2).

A variety of sterically and electronically dissimilar substituents at the 6-position could undergo rearrangement with high selectivity and good yield in the presence of $Me_3Al/BF_3{\cdot}OEt_2$ or $BF_3{\cdot}OEt_2$. When $Me_3Al/BF_3{\cdot}OEt_2$ was used, the rearrangement reaction leads to formation of *syn*-1,3 product. The use of $BF_3{\cdot}OEt_2$ provides the corresponding *anti* adduct. In the case of vinyl acetal **4fb**, warming the reaction temperature led to greatly improved selectivity, affording the *syn*-product in 96:4 selectivity (Table 3). This trend was further reinforced by vinyl acetal **4fc**, which rearranged at higher temperature with much better selectivity. This is consistent with our rationale of the stereochemistry of $Me_3Al/BF_3{\cdot}OEt_2$-mediated rearrangement of pyranyl vinyl acetals, where the selectivity could be controlled by tight ion pairing.[3] At higher temperature, tight ion pairing is favored relative to solvent-dissociated ions for entropic reasons.[7]

To further demonstrate the synthetic utility of our methodology, we investigated the rearrangement of 5-methyl vinyl acetals **11** and **15**. Mixed polypropionate-polyacetate arrays are common units in biologically important compounds.[8] Many elegant approaches have been developed, yet the construction of these units remains a challenge.[9] We envisioned that the Lewis-acid-mediated rearrangement of an appropriately substituted vinyl acetal could provide a new entry. To this end, we prepared the rearrangement precursors **11** and **15** employing routine synthetic sequences (Scheme 2).

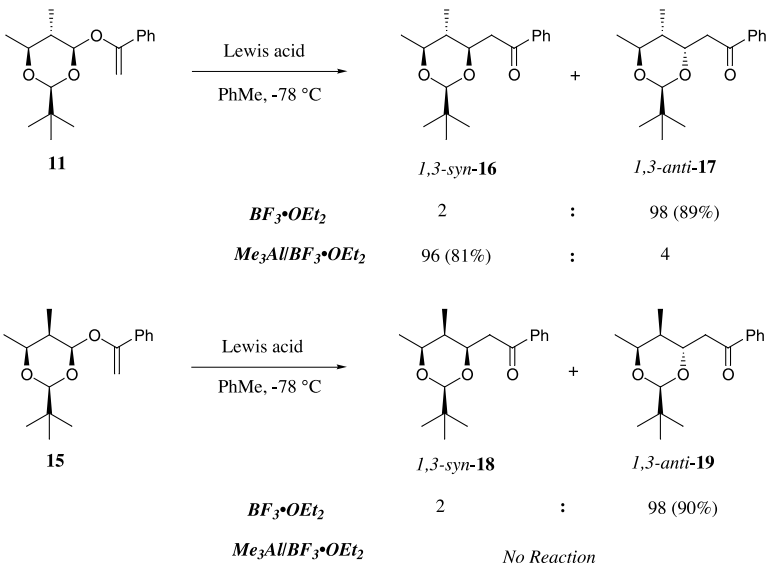
The diastereomeric vinyl acetals **11** and **15** were each subjected to the two sets of reaction conditions described above (Scheme 3). Substrate **11** bearing the 1,2-*anti* relationship underwent highly selective rearrangement, affording 1,3-*anti*-**17** in 98:2 selectivity using $BF_3{\cdot}Et_2O$ and 1,3-*syn*-**16** in 96:4 selectivity using $Me_3Al/BF_3{\cdot}OEt_2$. Rearrangement of substrate **15** was equally effective in the presence of $BF_3{\cdot}OEt_2$. The 1,3-*anti* isomer **19** was formed in 98:2 selectivity. However, treatment of this acetal with $Me_3Al/BF_3{\cdot}OEt_2$ resulted in no reaction, even at ambient temperature.

We believe that the lack of reactivity between substrate **15**

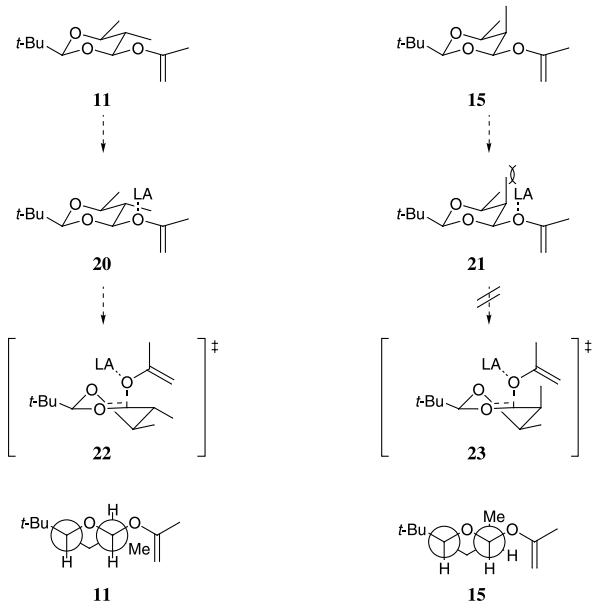


a) pivalaldehyde, i-PrOTMS, 4Å MS, TMSOTf, CH_2Cl_2; b) DIBALH; $(PhCO)_2O$, Py, DMAP; c) Cp_2TiMe_2, Cp_2TiCl_2.

Scheme 2.



Scheme 3.



Scheme 4.

and $Me_3Al/BF_3{\cdot}OEt_2$ may provide some insight as to the mechanism of ionization. Vinyl acetals **11** and **15** are presumably in chair conformations with the large *tert*-butyl group equatorial (Scheme 4). Coordination of Lewis acid to the enol ether oxygen forms **20** and **21**, respectively. The latter suffers from *syn*-pentane interactions with the axial methyl group, potentially disfavoring its formation altogether. Once the Lewis acid is coordinated to the enol ether oxygen, ionization of the enolate presumably has to occur at an axial position. We suggest that torsional strain with the *cis*-5-methyl group prevents this from occurring.

In conclusion, we have developed a new process for highly stereocontrolled synthesis of both *syn*- and *anti*-3,5-dihydroxy ketone units via O to C rearrangement of vinyl acetals. The reactions described here significantly expand the scope of stereoretentive O to C rearrangement of vinyl acetals. Further investigations of this reaction and applications to the efficient synthesis of stereochemically complex natural products are ongoing.

3. Experimental

3.1. General

All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Tetrahydrofuran, diethyl ether, and dichloromethane were degassed with argon and passed through two columns of neutral alumina. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Column chromatography was performed on EM Science silica gel 60 (230–400 mesh). Thin layer chromatography was performed on EM Science 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light, $KMnO_4$, aqueous ceric ammonium molybdate, or bromocresol green dips followed by heating.

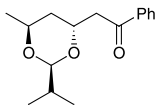
Melting points were measured with a MelTemp II melting point apparatus outfitted with a Fluke 51 thermocouple and are uncorrected. Infrared spectra were obtained on a Nicolet Avatar 320 FT-IR spectrometer. ^1H NMR and spectra were recorded on a Varian 300, 400, or 500 MHz spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from an internal standard [tetramethylsilane (TMS) or deuterated chloroform ($CDCl_3$)], multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet), integration, and coupling constant (Hz). ^{13}C NMR were recorded on a Varian 300, 400, or 500 MHz spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Mass spectra were obtained on Fisons VG Autospec.

Procedure A. General procedure for the $BF_3{\cdot}OEt_2$ mediated rearrangement of vinyl acetals: a flame-dried round bottom

flask containing a magnetic stir bar was charged with the vinyl acetal (0.11 mmol). Under an atmosphere of argon, toluene was added via syringe (0.5 mL) and the mixture cooled to the desired temperature. $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) was added to the solution via syringe and the reaction allowed to stir 12 h. Triethylamine (0.5 mL) was added to quench the reaction and the mixture was poured into saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with Ether (3×10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Diastereoselectivity was determined by ^1H NMR of the unpurified reaction mixture. Analytically pure material was obtained by column chromatography on silica gel.

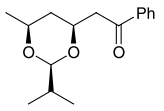
Procedure B. General procedure for the $Me_3Al/BF_3{\cdot}OEt_2$ mediated rearrangement of vinyl acetals: a flame-dried round bottom flask containing a magnetic stir bar was charged with the vinyl acetal (0.11 mmol) and toluene (0.5 mL). Under an atmosphere of argon, Me_3Al was added via syringe (0.22 mL, 2.0 M in PhMe, 0.44 mmol) at −78°C and allowed to stir 2 min at that temperature. $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) was then added to the solution via syringe and the reaction allowed to stir 12 h. Triethylamine (0.5 mL) was added to quench the reaction and the mixture was poured into saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with Ether (3×10 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated. Diastereoselectivity was determined by ^1H NMR of the unpurified reaction mixture. Analytically pure material was obtained by column chromatography on silica gel.

3.1.1. [2(2*S* *,4*R* *,6*S* *)]-2-(2-Isopropyl-6-methyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*anti*-6d).



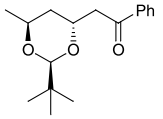
According to general procedure A, vinyl acetal (26.2 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 97:3 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**6d** (24.0 mg, 92%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.60 (m, 1H), 7.49 (m, 2H), 4.79–4.72 (m, 1H), 4.55 (d, 1H, *J*=5.4 Hz), 3.95 (m, 1H), 3.53 (dd, 1H, *J*=6.6, 15.6 Hz), 3.34 (dd, 1H, *J*=8.1, 15.3 Hz), 1.91 (m, 1H), 1.72 (m, 1H), 1.54 (m, 1H), 1.23 (d, 3H, *J*=6.3 Hz), 0.90 (d, 3H, *J*=6.6 Hz), 0.87 (d, 3H, *J*= 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$ δ 198.3, 137.1, 133.5, 128.9, 128.4, 99.5 689, 68.1, 40.5, 35.6, 33.0, 22.0, 17.4, 17.1; IR (NaCl, neat) 2970, 2931, 1683, 1449, 1373, 1301, 1280, 1213, 1165, 1124, 1076, 1002, 900, 756, 691 cm^{-1}; HRMS $(C_{16}H_{22}O_3+H)^+$ calcd 263.1647. Found 263.1655 (FAB+).

3.1.2. [2(2*S* *,4*S* *,6*S* *)]-2-(2-Isopropyl-6-methyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*syn*-6d).



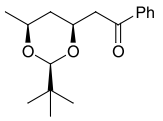
According to general procedure B, vinyl acetal (26.2 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 10:90 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/ hexane) afforded *syn*-**6d** (21.0 mg, 80%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.56 (m, 1H), 745 (m, 2H), 4.27–4.18 (m, 2H), 3.77 (m, 1H), 3.38 (dd, 1H, *J*=6.6, 16.2 Hz), 2.95 (dd, 1H, *J*=6.0, 16.2 Hz), 1.80–1.69 (m, 2H), 1.31 (m, 1H), 1.22 (d, 3H, *J*=6.3 Hz), 0.88 (d, 3H, *J*=6.9 Hz), 0.85 (d, 3H, *J*=6.9 Hz); ^{13}C NMR (*J*=75 MHz, $CDCl_3$) δ 198.5, 137.5, 133.4, 128.7, 128.5, 105.6, 73.2, 72.4, 45.0, 39.1, 32.9, 21.8, 17.6, 17.3; IR (NaCl, neat) 2969, 1686, 1449, 1380, 1350, 1193, 1164, 1121, 1108, 1065, 1028, 993, 962, 753, 690 cm^{-1}; HRMS $(C_{16}H_{22}O_3+H)^+$ calcd 263.1647. Found 263.1646 (FAB+).

3.1.3. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-methyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*anti*-7aa).



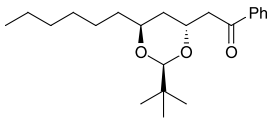
According to general procedure A, vinyl acetal (27.6 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purifi-cation by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7aa** (22.5 mg, 82%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.59 (m, 1H), 7.48 (m, 2H), 4.75 (m, 1H), 4.43 (s, 1H), 3.95 (m, 1H), 3.53 (dd, 1H, *J*=6.6, 15 Hz), 3.30 (dd, 1H, *J*=8.1, 15.3 Hz), 1.90–1.80 (m, 1H), 1.50 (ddd, 1H, *J*=1.5, 2.4, 13.5 Hz), 1.21 (d, 3H, *J*= 6 Hz), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 137.2, 133.3, 128.8, 128.3, 101.0, 68.9, 69.1, 40.6, 35.7, 35.0, 24.9, 22.1; IR (NaCl, neat) 2976, 2957, 2868, 1684, 1449, 1384, 1361, 1215, 1123, 1040, 995, 755, 691 cm^{-1}; HRMS $(C_{17}H_{24}O_3+H)^+$ calcd 277.1804. Found 277.1790 (FAB+).

3.1.4. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-methyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*syn*-7aa).



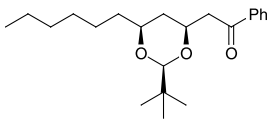
According to general procedure B, vinyl acetal (27.6 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 4:96 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7aa** (25.0 mg, 92%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 4.19 (m, 1H), 4.10 (s, 1H), 3.72 (m, 1H), 3.35 (dd, 1H, *J*=6.9, 15.9 Hz), 2.90 (dd, 1H, *J*=6.0, 15.6 Hz), 1.63 (ddd, 1H, *J*= 2.1, 2.1, 12.6 Hz), 1.28 (m, 1H), 1.19 (d, 3H, *J*=6.3 Hz), 0.82 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 137.7, 133.3, 128.7, 128.7, 107.1, 73.4, 72.3, 45.1, 39.1, 35.0, 24.9, 21.8; IR (NaCl, neat) 2976, 2958, 2909, 2869, 1685, 1449, 1385, 1361, 1152, 1123, 1048, 1002, 690 cm^{-1}; HRMS $(C_{17}H_{24}O_3+H)^+$ calcd 277.1804. Found 277.1799 (FAB+).

3.1.5. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-hexanyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*anti*-7ba).



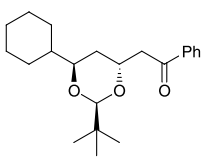
According to general procedure A, vinyl acetal (34.6 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7ba** (30.0 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.58 (m, 1H), 7.49 (m, 2H), 4.73 (m, 1H), 4.41 (s, 1H), 3.75 (m, 1H), 3.53 (dd, 1H, *J*=6.6, 15.6 Hz), 3.30 (dd, 1H, *J*=8.1, 15.3 Hz), 1.86 (m, 1H), 1.64–1.29 (m, 9H), 0.95–0.87 (m, 5H), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 137.2, 133.4, 128.9, 128.4, 101.1, 72.0, 69.0, 40.6, 36.3, 35.1, 34.2, 32.0, 29.4, 25.2, 24.8, 22.9, 14.3; IR (NaCl, neat), 2956, 2929, 2858, 1685, 1449, 1361, 1279, 1215, 1116, 1069, 996, 754, 691 cm^{-1}; HRMS $(C_{22}H_{34}O_3+H)^+$ calcd 347.2586. Found 347.2578 (FAB+).

3.1.6. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-hexanyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*syn*-7ba).



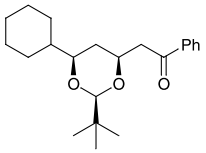
According to general procedure B, vinyl acetal (34.6 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 2:98 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7ba** (31.0 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 4.19 (m, 1H), 4.10 (s, 1H), 3.56 (m, 1H), 3.37 (dd, 1H, *J*=6.6, 15.3 Hz), 2.92 (dd, 1H, *J*=5.7, 15.9 Hz), 1.70–1.21 (m, 10H), 0.91–0.83 (m, 5H), 0.83 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 137.7, 133.3, 128.7, 128.7, 107.1, 76.2, 73.5, 45.2, 37.5, 36.1, 35.1, 32.0, 29.4, 25.2, 24.9, 22.8, 14.3; IR (NaCl, neat), 2956, 2929, 2858, 1687, 1449, 1361, 1350, 1209, 1114, 1077, 1051, 1001, 752, 690 cm^{-1}; HRMS $(C_{22}H_{34}O_3+H)^+$ calcd 347.2586. Found 347.2583 (FAB+).

3.1.7. [2(2*S* *,4*R* *,6*R* *)]-2-(2-*tert*-Butyl-6-cyclohexanyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*anti*-7ca).



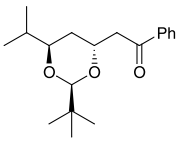
According to general procedure A, vinyl acetal (34.4 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7ca** (33.0 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.40 (m, 1H), 7.29 (m, 2H), 4.60–4.54 (m, 1H), 4.20 (s, 1H), 3.33 (dd, 1H, *J*=6.6, 15.3 Hz), 3.30 (m, 1H), 3.09 (dd, 1H, *J*=7.8, 15.3 Hz), 1.80–0.68 (m, 13H), 0.66 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 137.2, 133.3, 128.8, 128.3, 101.0, 76.2, 69.0, 43.1, 40.7, 35.3, 31.5, 28.8, 28.6, 26.9, 26.4, 26.2, 24.8; IR (NaCl, neat) 2926, 2853, 1684, 1449, 1214, 1113, 1062, 993, 754, 691 cm^{-1}; HRMS $(C_{22}H_{32}O_3+H)^+$ calcd 345.2430. Found 345.2420 (FAB+).

3.1.8. [2(2*S* *,4*S* *,6*R* *)]-2-(2-*tert*-Butyl-6-cyclohexanyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*syn*-7ca).



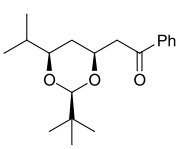
According to general procedure B, vinyl acetal (34.4 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 3:97 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7ca** (30.0 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (m, 2H), 7.41 (m, 1H), 7.29 (m, 2H), 3.99 (m, 1H), 3.91 (s, 1H), 3.20 (dd, 1H, *J*=6.9, 15.3 Hz), 3.13 (m, 1H), 2.76 (dd, 1H, *J*=5.7, 15.3 Hz), 1.78–0.70 (m, 13H), 0.65 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 138.0, 137.7, 133.3, 128.6, 106.9, 80.4, 73.6, 45.3, 42.9, 35.2, 34.6, 28.8, 28.6, 26.9, 26.4, 26.2, 24.9; IR (NaCl, neat) 2926, 2853, 1687, 1449, 1210, 1118, 1001, 753, 690 cm^{-1}; HRMS $(C_{22}H_{32}O_3+H)^+$ calcd 345.2430. Found 345.2435 (FAB+).

3.1.9. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-*iso*propyl-[1,3] dioxan-4-yl)-1-phenyl-ethanone (*anti*-7da).



According to general procedure A, vinyl acetal (30.4 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7da** (29.5 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.59 (m, 1H), 7.49 (m, 2H), 4.73 (m, 1H), 4.40 (s, 1H), 3.53 (dd, 1H, *J*=6.6, 15.3 Hz), 3.44 (m, 1H), 3.29 (dd, 1H, *J*=7.8, 15.3 Hz), 1.89 (m, 1H), 1.67 (m, 1H), 1.50 (m, 1H), 0.96 (d, 3H, *J*=6.6 Hz), 0.88 (d, 3H, *J*=6.9 Hz), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 137.3, 133.4, 128.9, 128.4, 101.0, 77.65, 68.9, 40.6, 35.2, 33.3, 31.3, 24.7, 18.3; IR (NaCl, neat) 2958, 1684, 1449, 1361, 1300, 1214, 1114, 1062, 1000, 754, 691 cm^{-1}; HRMS $(C_{19}H_{28}O_3+H)^+$ calcd 305.2117. Found 305.2106 (FAB+).

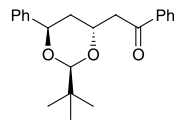
3.1.10. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-isopropyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*syn*-7da).



According to general procedure B, vinyl acetal (30.4 mg,

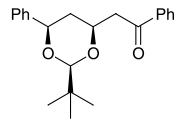
0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 3:97 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7da** (26.0 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 4.18 (m, 1H), 4.09 (s, 1H), 3.38 (dd, 1H, *J*=6.9, 15.3 Hz), 3.28 (m, 1H), 2.93 (dd, 1H, *J*=6.0, 15.6 Hz), 1.74–1.61 (m, 2H), 1.27 (m, 1H), 0.95 (d, 3H, *J*=6.9 Hz), 0.90 (d, 3H, *J*=6.3 Hz), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 137.7, 133.3, 128.7, 106.9, 81.0, 73.5, 45.3, 35.2, 34.4, 33.2, 24.9, 18.3, 18.3; IR (NaCl, neat) 2959, 1687, 1449, 1114, 1052, 1009, 753, 690 cm^{-1}; HRMS $(C_{19}H_{28}O_3+H)^+$ calcd 305.2117. Found 305.2105 (FAB+).

3.1.11. [2(2*S* *,4*R* *,6*R* *)]-2-(2-*tert*-Butyl-6-phenyl-[1,3]-dioxan-4-yl)-1-phenyl-ethanone (*anti*-7ea).



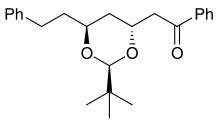
According to general procedure A, vinyl acetal (33.8 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7ea** (29.0 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02–7.99 (m, 2H), 7.60 (m, 1H), 7.53–7.48 (m, 2H), 7.37–7.27 (m, 5H), 4.93–4.80 (m, 2H), 4.64 (s, 1H), 3.66 (dd, 1H, *J*=6.9, 15.6 Hz), 3.44 (dd, 1H, *J*=7.8, 15.3 Hz), 2.12 (m, 1H), 1.76 (m, 1H), 0.92 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 142.6, 137.2, 133.5, 129.0, 128.5, 128.4, 127.6, 125.6, 101.0, 73.5, 69.1, 40.3, 36.2, 35.3, 24.8; IR (NaCl, neat), 2957, 1683, 1449, 1359, 1215, 1120 cm^{-1}; HRMS $(C_{21}H_{26}O_3+H)^+$ calcd 339.1960. Found 339.1976 (FAB+).

3.1.12. [2(2*S* *,4*S* *,6*R* *)]-2-(2-*tert*-Butyl-6-cyclohexanyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*syn*-7ea).



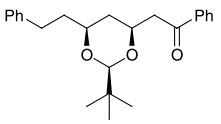
According to general procedure B, vinyl acetal (33.8 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C were stirred for 36 h to produce the product as a 2:98 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7ea** (27.0 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.97 (m, 2H), 7.57 (m, 1H), 7.50–7.44 (m, 2H), 7.38–7.23 (m, 5H), 4.72 (m, 1H), 4.39 (m, 1H), 4.34 (s, 1H), 3.41 (ddd, 1H, *J*=1.2, 6.6, 15.6 Hz), 2.97 (ddd, 1H, *J*=1.2, 6.0, 15.9 Hz), 1.99 (m, 1H), 1.52 (m, 1H), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.7, 142.6, 137.6, 133.4, 128.7, 128.6, 128.5, 127.5, 125.7, 107.5, 77.65, 73.5, 45.0, 39.7, 35.3, 25.0; IR (NaCl, neat), 2958, 1686, 1483, 1449, 1362, 1210, 1180, 1121, 1057, 1041 cm^{-1}; HRMS $(C_{22}H_{26}O_3+H)^+$ calcd 339.1960. Found 339.1969 (FAB+).

3.1.13. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*anti*-7fa).



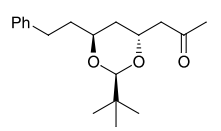
According to general procedure A, vinyl acetal (36.6 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7fa** (33.0 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96–7.92 (m, 2H), 7.60–7.55 (m, 1H), 7.49–7.45 (m, 2H), 7.31–7.26 (m, 2H), 7.21–7.16 (m, 3H), 4.73 (m, 1H), 4.40 (s, 1H), 3.74 (m, 1H), 3.47 (dd, 1H, *J*=6.6, 15.6 Hz), 2.60 (dd, 1H, *J*=7.5, 15.3 Hz), 2.84–2.62 (m, 2H), 1.88 (m, 2H), 1.70 (m, 1H), 1.47 (m, 1H), 0.89 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 142.4, 137.2, 133.4, 128.9, 128.7, 128.6, 128.4, 126.0, 101.0, 70.6, 68.9, 40.6, 37.9, 35.1, 34.1, 24.8; IR (NaCl, neat) 2955, 1684, 1449, 1360, 1123 cm^{-1}; HRMS $(C_{24}H_{30}O_3+H)^+$ calcd 367.2273. Found 367.2257 (FAB+).

3.1.14. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (*syn*-7fa).



According to general procedure B, vinyl acetal (36.6 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 4:96 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7fa** (31.0 mg, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.96 (m, 2H), 7.59–7.53 (m, 1H), 7.48–7.42 (m, 2H), 7.31–7.26 (m, 2H), 7.21–7.16 (m, 3H), 4.216 (m, 1H), 4.10 (s, 1H), 3..56 (m, 1H), 3.36 (dd, 1H, *J*=6.3, 15.3 Hz), 2.92 (dd, 1H, *J*=6.0, 15.9 Hz), 2.72 (m, 2H), 1.88 (m, 1H), 1.74 (m, 1H), 1.65 (m, 1H), 1.33 (m, 1H), 0.89 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.9, 142.3, 137.6, 133.3, 128.8, 128.7, 128.6, 128.5, 126.0, 107.0, 74.7, 73.3, 45.1, 37.7, 37.4, 35.2, 31.3, 24.9; IR (NaCl, neat) 2955, 2912, 1686, 1449, 1350, 1209, 1120, 1093, 1047, 1001, 752, 690 cm^{-1}; HRMS $(C_{24}H_{30}O_3+H)^+$ calcd 367.2273. Found 367.2266 (FAB+).

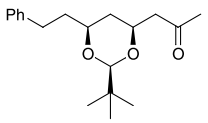
3.1.15. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-methyl-ethanone (*anti*-7fb).



According to general procedure A, vinyl acetal (30.4 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 84:16 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7fb** (23.6 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.16 (m, 5H), 4.60 (m, 1H), 4.30 (s, 1H), 3.65 (m, 1H), 3.01 (dd, 1H, *J*=8.4, 15.3 Hz), 2.73 (m, 2H), 2.56 (dd, 1H, *J*=6.9, 15.3 Hz),

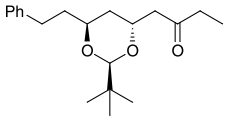
2.19 (s, 3H), 1.86 (m, 2H), 1.67 (m, 1H), 1.32 (m, 1H), 0.89 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 142.1, 128.7, 128.5, 125.9, 100.7, 70.3, 68.3, 45.8, 37.8, 35.1, 34.0, 31.2, 30.2, 24.8; IR (NaCl, neat), 2955, 1716, 1359, 1123, 1097 cm^{-1}; HRMS $(C_{19}H_{28}O_3+H)^+$ calcd 305.2117. Found 305.2114 (FAB+).

3.1.16. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-methyl-ethanone (*syn*-7fb).



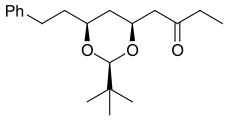
According to general procedure B, vinyl acetal (30.4 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −55°C produced the product as a 4:96 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7fb** (27.0 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.20–7.16 (m, 3H), 4.09 (s, 1H), 3.98 (m, 1H), 3.52 (m, 1H), 2.82–2.63 (m, 3H), 2.44 (dd, 1H, *J*=4.5, 14.7 Hz), 2.19 (s, 3H), 1.86 (m, 1H), 1.70 (m, 1H), 1.49 (m, 1H), 1.21 (m, 1H), 0.92 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 142.2, 128.7, 128.5, 126.0, 106.9, 74.7, 73.0, 49.9, 37.6, 37.1, 35.2, 31.4, 31.3, 25.0; IR (NaCl, neat), 2956, 1717, 1484, 1455, 1361, 1217, 1155, 1119, 1097, 1079, 1044, 1005 cm^{-1}; HRMS $(C_{19}H_{28}O_3+H)^+$ calcd 305.2117. Found 305.2121 (FAB+).

3.1.17. [2(2*S* *,4*R* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-ethyl-ethanone (*anti*-7fc).



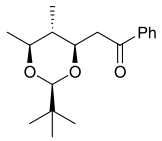
According to general procedure A, vinyl acetal (31.8 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 96:4 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *anti*-**7fc** (29.0 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.21–7.16 (m, 3H), 4.60 (m, 1H), 4.31 (s, 1H), 3.65 (m, 1H), 2.99 (dd, 1H, *J*=8.1, 14.1 Hz), 2.73 (m, 2H), 2.58–2.04 (m, 3H), 1.85 (m, 2H), 1.68 (m, 1H), 1.33 (m, 1H), 1.04 (t, *J*=7.2 Hz), 0.89 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1, 142.1, 128.6, 128.5, 125.9, 100.6, 70.4, 68.5, 44.6, 37.6, 36.4, 35.2, 34.2, 31.3, 24.9, 7.9; IR (NaCl, neat), 2976, 1715, 1455, 1360, 1123, 1074, 1040, 996 cm^{-1}; HRMS $(C_{20}H_{30}O_3+H)^+$ calcd 319.2273. Found 319.2266 (FAB+).

3.1.18. [2(2*S* *,4*S* *,6*S* *)]-2-(2-*tert*-Butyl-6-phenylethyl-[1,3]dioxan-4-yl)-1-ethyl-ethanone (*syn*-7fc).



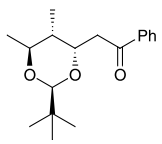
According to general procedure B, vinyl acetal (31.8 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −55°C produced the product as a 2:98 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded *syn*-**7fc** (28.0 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.25 (m, 2H), 7.20–7.16 (m, 3H), 4.08 (s, 1H), 3.98 (m, 1H), 3.51 (m, 1H), 2.82–2.63 (m, 3H), 2.57–2.37 (m, 3H), 1.86 (m, 1H), 1.69 (m, 1H), 1.50 (m, 1H), 1.23 (m, 1H), 1.04 (t, 3H, *J*=7.5 Hz), 0.91 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 142.2, 128.7, 128.5, 125.9, 106.9, 74.7, 73.1, 48.7, 37.6, 37.6, 37.2, 35.1, 31.3, 25.0, 7.7; IR (NaCl, neat), 2976, 2955, 2867, 1716, 1483, 1455, 1377, 1361, 1342, 1133, 1095, 1080, 1047, 1004, 748, 700 cm^{-1}; HRMS $(C_{20}H_{30}O_3+H)^+$ calcd 319.2273. Found 319.2277 (FAB+).

3.1.19. [2(2*S* *,4*S* *,5*S* *,6*S* *)]-2-(2-*tert*-Butyl-5-methyl-6-methyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (16).



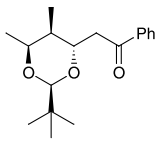
According to general procedure B, vinyl acetal (29.0 mg, 0.10 mmol), Me_3Al (0.22 mL, 0.44 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 4:96 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded **16** (23.5 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (m, 2H), 7.53 (m, 1H), 7.45 (m, 2H), 4.08 (s, 1H), 3.83 (m, 1H), 3.31 (m, 2H), 2.94 (dd, 1H, *J*=3.0, 14.1 Hz), 1.36 (m, 1H), 1.22 (d, 3H, *J*=6.0, Hz), 0.84 (d, 3H, *J*=6.6 Hz), 0.74 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 138.1, 133.1, 128.9, 128.5, 106.7, 79.4, 78.0, 42.7, 41.3, 34.9, 24.8, 19.6, 12.6; IR (NaCl, neat), 2976, 1686, 1449, 1362, 1260, 1145, 1124, 1093, 1048 cm^{-1}; HRMS $(C_{18}H_{26}O_3+H)^+$ calcd 291.1960. Found 291.1951 (FAB+).

3.1.20. [2(2*S* *,4*R* *,5*S* *,6*S* *)]-2-(2-*tert*-Butyl-5-methyl-6-methyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (17).



According to general procedure A, vinyl acetal (29.0 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded **17** (36.0 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 4.63 (m, 1H), 4.44 (s, 1H), 3.60 (m, 1H), 3.46 (dd, 1H, *J*=9.9, 15.0 Hz), 3.03 (dd, 1H, *J*=4.8, 15.0 Hz), 1.94 (m, 1H), 1.19 (d, 3H, *J*=6.0 Hz), 0.79 (d, 3H, *J*=7.2 Hz), 0.76 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 137.5, 133.2, 128.9, 128.4, 100.4, 73.5, 73.4, 39.0, 36.4, 34.8, 24.7, 19.6, 13.0; IR (NaCl, neat), 2975, 2959, 1684, 1448, 1359, 1287, 1216, 1136, 1123, 1090, 1045 cm^{-1}; HRMS $(C_{18}H_{26}O_3+H)^+$ calcd 291.1960. Found 291.1956 (FAB+).

3.1.21. [2(2*S* *,4*R* *,5*R* *,6*S* *)]-2-(2-*tert*-Butyl-5-methyl-6-methyl-[1,3]dioxan-4-yl)-1-phenyl-ethanone (19).



According to general procedure A, vinyl acetal (29.0 mg, 0.10 mmol) and $BF_3{\cdot}OEt_2$ (16 μL, 0.12 mmol, neat) at −78°C produced the product as a 98:2 mixture of isomers (*anti*/*syn*). Purification by column chromatography on silica gel (1% ethyl acetate/hexane) afforded **19** (26.0 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.59 (m, 1H), 7.49 (m, 2H), 4.44 (m, 1H), 4.44 (s, 1H), 4.09 (m, 1H), 3.56 (dd, 1H, J=6.9, 15.6 Hz), 3.33 (dd, 1H, J=7.5, 15.6 Hz), 1.40 (m, 1H), 1.15 (d, 3H, J=2.1 Hz), 1.13 (d, 3H, J=1.5 Hz), 0.85 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.5, 137.3, 133.4, 128.9, 128.4, 101.3, 75.9, 69.9, 40.2, 35.4, 35.0, 24.7, 18.9, 12.9; IR (NaCl, neat), 2977, 1684, 1449, 1328, 1283, 1216, 1083 cm^{-1}; HRMS $(C_{18}H_{26}O_3+H)^+$ calcd 291.1960. Found 291.1955 (FAB+).

Acknowledgements

We thank the National Institutes of General Medical Sciences (GM65047), Colorado State University, Merck Research Laboratories and Glaxo-SmithKline for partial support of this research. We thank Professor Scott Rychnovsky (UC-Irvine) for helpful discussions.

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