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Reagent-Controlled Stereoselective Synthesis of Lignan-Related Tetrahydrofurans

Steven M. Miles,[†] Stephen P. Marsden,*[,‡] Robin J. Leatherbarrow,[†] and William J. Coates[§]

Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AY, U.K., School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K., and GlaxoSmthKline, Third Avenue, Harlow, Essex CM19 5AW, U.K.

stevem@chem.leeds.ac.uk

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The reaction of ring-closing metathesis-derived cyclic allylsiloxanes **3** with aldehydes in the presence of a Lewis acid gives 2,3,4-trisubstituted tetrahydrofurans related to the furanolignan family of natural products. The reactions proceed with complete 3,4-*trans* stereoselectivity, whereas the C-2 stereochemistry depends on both the aldehyde and Lewis acid used. When boron trifluoride etherate is used with aliphatic or electronically neutral aryl aldehydes, the reactions favor the production of the 2,3-*cis* isomer **8**, whereas electron-rich aryl aldehydes lead to the 2,3-*trans* isomer **9** by Lewis acid-mediated isomerization of the kinetically favored *cis* isomer. The isomerization can be avoided by use of TMSOTf as a promoter, and hence, the stereochemistry can be tuned by appropriate choice of reagent. Cleavage of the pendant 3-ethenyl group installs the 3-hydroxymethyl group common to the furanolignans.

Introduction

Natural products of the furanolignan family display interesting and diverse biological activities, and as such are popular targets for total synthesis.[1] The core of these compounds is usually a 2,3,4-trisubstituted tetrahydrofuran. The majority of furanolignans have the substituents arranged with 2,3-*trans*, 3,4-*cis* stereochemistry, but other stereochemical arrangements are known. The 2,3-*trans*, 3,4-*trans* stereochemistry is found in the antimicrobial natural product sesaminone **1**,[2] for example, while the 2,3-*cis*, 3,4-*trans* stereochemistry is observed in sylvone **2** (Figure 1).[3]

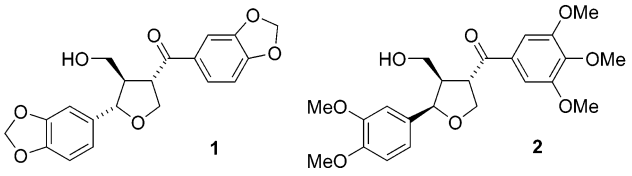

FIGURE 1. Representative furanofuran lignans.

We[4] and others[5] have previously reported the stereoselective synthesis of all-*cis*-2,3,5-trisubstituted tetrahydrofurans by the Lewis acid-mediated condensation of aldehydes with 7-substituted 1-oxa-2-silacyclohept-4-enes (cyclic allylsiloxanes). The latter species are readily derived from ring-closing olefin metathesis (RCM) of the corresponding acyclic homoallylic allylsilyl ethers.[6] Mechanistically, this reaction is presumably a form of silyl-modified Sakurai reaction, and the stereochemical outcome of the reaction is consistent with such a process.[7] We reasoned that a convergent synthesis of the gross skeleton of the furanolignans could potentially be realized in a convergent manner through a similar condensation sequence using the isomeric 6-substituted oxasilacyclohept-5-enes **3** in conjunction with an appropriate aldehyde **4**. Further, the resulting 3-vinyl substituent of the tetrahydrofuran **5** could serve as a direct precursor to the hydroxymethyl group of the furanoligan **6** (Scheme 1). This would provide a complementary synthetic approach to existing methods for the assembly of 2,3,4-trisubstituted tetrahydrofurans, which include 5-*exo*-radical cyclizations of substituted allyl bromoethyl ethers,[8] the reduction of aldol-derived substituted butyrolactones,[9] the rearrangement of 4,5-dihydro-1,3-dioxepins,[10] and the Lewis-acid promoted condensation of benzyloxyacetaldehyde derivatives with diazoesters.[11] We describe herein the successful reduction of this scheme to practice and discuss the stereochemical features of the reaction,

[†] Imperial College London.
[‡] University of Leeds.
[§] GlaxoSmithKline.

(1) Ward, R. S. *Nat. Prod. Rep.* **1999**, *16*, 75−96.
(2) Chiung, Y.-M.; Hayashi, H.; Matsumoto, H.; Otani, T.; Yoshida, K.; Huang, M.-Y.; Chen, R.-X.; Liu, J.-R.; Nakayama, M. *J. Antibiot.* **1994**, *47*, 487−491.
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(11) Angle, S. R.; Bernier, D. S.; Chann, K.; Jones, D. E.; Kim, M.; Neitzel, M. L.; White, S. L. *Tetrahedron Lett.* **1998**, *39*, 8195−8198.

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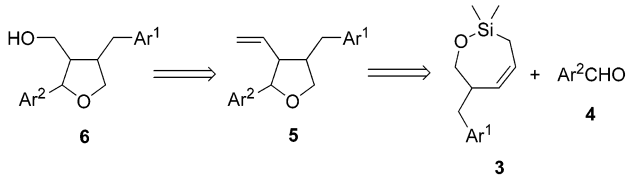
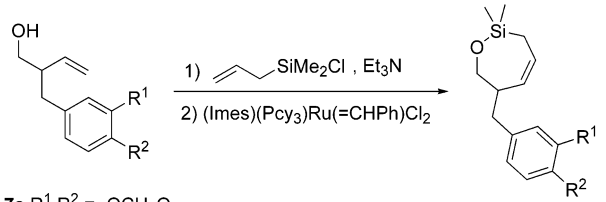
SCHEME 1. Retrosynthetic Analysis of Furanolignans 6



SCHEME 2. Synthesis of Substituted Allylsiloxanes



7a R^1,R^2 = -OCH_2O
7b R^1 = R^2 = H
7c R^1 = OMe, R^2 = H
7d R^1 = R^2 = OMe

3a 91%
3b 85%
3c 90%
3d 90%

which include the ability to tune the stereochemistry at C2 by appropriate choice of reagent.

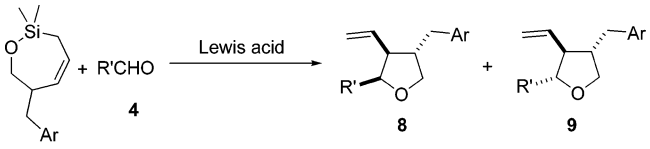
Results and Discussion

The requisite allylsiloxanes (**3a**−**d**) were prepared as shown in Scheme 2. The 2-substituted homoallylic alcohols (**7a**−**d**) were prepared in two steps from ethyl 3-butenoate according to Beckwith's general method (enolate alkylation with the appropriate benzylic bromide followed by $LiAlH_4$ reduction).[12] Etherification under standard conditions with allylchlorodimethylsilane followed by RCM with Grubbs' second-generation catalyst gave the target allylsiloxanes in excellent yield over two steps. With these materials in hand, we then investigated their cyclocondensation with a variety of aldehydes.

Treatment of the allylsiloxanes (**3a**−**d**) under our previously reported conditions[4] (1 equiv of aldehyde, 1 equiv of boron trifluoride etherate in dichloromethane at −78 °C and then warming to room temperature) with hexanal or benzaldehyde gave the expected tetrahydrofurans in good yield as an inseparable mixture of two diastereoisomers (ca. 5−10:1 ratio) which were identified as **8a**−**h** and **9a**−**h** (Table 1, entries 1−8). The major isomer **8** from these reactions was confirmed to have 2,3-*cis*, 3,4-*trans* stereochemistry, as predicted by our mechanistic model for the reaction (vide infra), whereas the minor isomer **9** was epimeric at C2. We next investigated the reactions of electron-rich aromatic aldehydes as the electrophilic reaction partner, i.e., those aldehydes which would give rise to compounds with appropriate substitution for furanolignan synthesis. The aldehydes chosen were piperonal, *p*-methoxybenzaldehyde, veratraldehyde, and vanillin (Table 1, entries 9−17). In all cases, the reactions were successful, although they were in general slightly lower yielding than the reactions with benzaldehyde or hexanal. This may be a consequence of the lower electrophilicity of the carbonyl groups in these substrates. However, more significantly, in all of these examples an unexpected reversal of stereoselectivity was observed whereby the major isomer from the reaction was now found to be the 2,3-*trans*, 3,4-*cis* isomer **9i**−**q**, with **8i**−**q** as the minor (<11%) component in the mixture.

(12) Beckwith, A. L. J.; Gerba, S. *Aust. J. Chem*. **1992**, *45*, 289−308.

TABLE 1. Condensation of Allylsiloxanes 3 with Aldehydes



entry	conditions[a]	silane	R′	yield (%)	products	ratio
1	A	**3a**	*n*-C_5H_{11}	76	**8a**, **9a**	91:9
2	A	**3a**	Ph	78	**8b**, **9b**	89:11
3	A	**3b**	*n*-C_5H_{11}	83	**8c**, **9c**	87:13
4	A	**3b**	Ph	81	**8d**, **9d**	84:16
5	A	**3c**	*n*-C_5H_{11}	67	**8e**, **9e**	90:10
6	A	**3c**	Ph	76	**8f**, **9f**	88:12
7	A	**3d**	*n*-C_5H_{11}	79	**8g**, **9g**	85:15
8	A	**3d**	Ph	68	**8h**, **9h**	87:13
9	A	**3a**	3,4-(OCH_2O)Ph	58	**8i**, **9i**	8:92
10	A	**3a**	4-MeO-Ph	50	**8j**, **9j**	8:92
11	A	**3a**	3,4-$(MeO)_2$-Ph	54	**8k**, **9k**	10:90
12	A	**3a**	3-MeO-4-HO-Ph	51	**8l**, **9l**	8:92
13	A	**3b**	3,4-(OCH_2O)-Ph	76	**8m**, **9m**	11:89
14	A	**3b**	4-MeO-Ph	68	**8n**, **9n**	8:92
15	A	**3c**	3,4-(OCH_2O)-Ph	52	**8o**, **9o**	8:92
16	A	**3c**	4-MeO-Ph	48	**8p**, **9p**	8:92
17	A	**3d**	3,4-(OCH_2O)-Ph	47	**8q**, **9q**	9:91
18	A	**3a**	3-MeO-Ph	74	**8r**, **9r**	82:18
19	B	**3a**	4-Me_2N-Ph	67	**8s**, **9s**	57:43
20	C	**3a**	3,4-(OCH_2O)-Ph	71	**8i**, **9i**	50:50
21	C	**3a**	4-MeO-Ph	67	**8j**, **9j**	39:61
22	D	**3a**	3,4-(OCH_2O)-Ph	73	**8i**, **9i**	90:10
23	D	**3b**	3,4-(OCH_2O)-Ph	74	**8m**, **9m**	93:7

[a] Conditions: (A) 1 equiv each RCHO and BF_3·OEt_2, CH_2Cl_2, −78 °C, 8 h, then rt; (B) as for A, but 2 equiv of BF_3·OEt_2; (C) as for A, using 0.91 equiv each of RCHO and BF_3·OEt_2; (D) 1 equiv each RCHO and TMSOTf, CH_2Cl_2, −78 °C, 3 h.

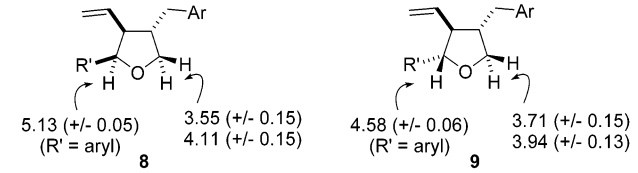


FIGURE 2. Diagnostic chemical shift patterns (in ppm) for diastereomeric tetrahydrofurans **8** and **9**.

The relative stereochemical assignments of the tetrahydrofurans were made as follows. Extensive NOE experiments on compounds **8a** and **8b** confirmed the 2,3-*cis*, 3,4-*trans* stereochemistry of this isomer, while the corresponding 2,3-*trans*, 3,4-*trans* stereochemistry of compounds **9** was made on the basis of NOE experiments on **9i** and the subsequent chemical correlation of this compound with a compound of known stereochemistry (vide infra). The stereochemistry of those tetrahydrofurans not subjected to NOE analysis was assigned with confidence on the basis of the strongly consistent and recognizable patterns of certain signals for each diastereoisomer in their ^1H NMR spectra. Specifically, as shown in Figure 2, the signals corresponding to the protons at C-5 in the 2,3-*cis* isomer **8** routinely present as a pair of signals (separated by 0.56 ± 0.04 ppm) flanking those

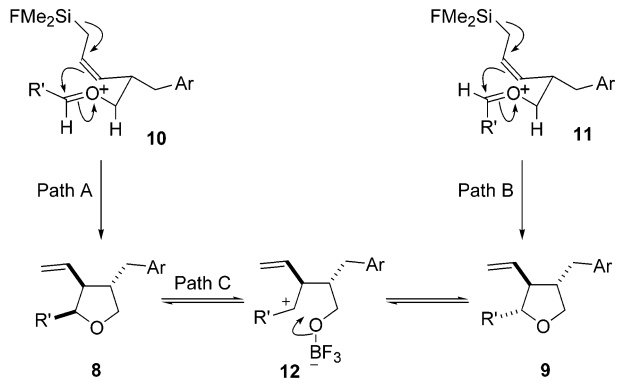


FIGURE 3. Possible mechanistic pathways leading to diastereomeric tetrahydrofurans **8** and **9**.

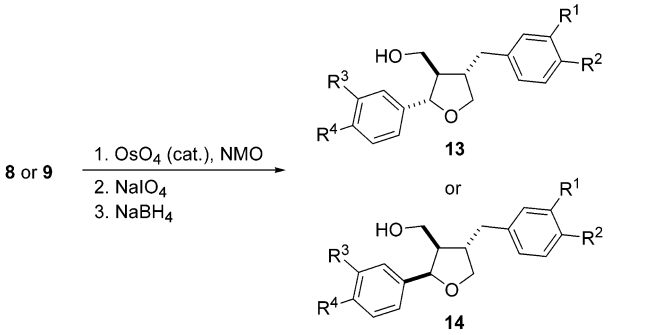
for the 2,3-*trans* isomer **9** (which are themselves separated by 0.23 ± 0.04 ppm). Further, the signal for H-2 in **8** (R′ = aryl) consistently appears over 0.5 ppm downfield of that for H-2 in isomer **9** (R′ = aryl), presumably due to anisotropic deshielding by the neighboring vinyl group (the H-2 signals for **8**/**9**, R′ = pentyl are generally obscured and hence no comparison can be made).

With these assignments of stereochemistry confidently in place, we looked to rationalize the divergence in the sense of diastereoselectivity for the different aldehydes. The predominant formation of 2,3-*cis*, 3,4-*trans* isomer **8** with hexanal and benzaldehyde can be rationalized by assuming that the reaction takes place by condensation of the siloxane oxygen with the aldehyde, leading to the formation of an (*E*)-oxonium ion **10** which undergoes cyclization through a chairlike transition state with all substituents equatorially disposed (path A, Figure 3). The switch in selectivity in favor of the 2,3-*trans*, 3,4-*trans* isomer **9** when electron-rich aldehydes are employed in the reaction could potentially arise through path B, namely Sakurai reaction between the allylsilane and a (*Z*)-configured oxonium ion **11**. This seems unlikely, however, given that the steric demands of the aldehydes have not greatly changed in the proximity of the oxonium ion. A second possibility is that the kinetic product of the reaction is still the 2,3-*cis*, 3,4-*trans* compound **8** but that under the Lewis acidic reaction conditions the tetrahydrofuran undergoes reversible ring-opening to a stabilized benzylic cation **12** (path C).[13] In this event, the more stable 2,3-*trans*, 3,4-*trans* isomer **9** would be expected to dominate.

Further experiments were carried out to provide support for this hypothesis. The reaction of 3-methoxybenzaldehyde (Table 1, entry 18), which would not offer significant stabilization to the proposed intermediate cation **12** and hence should not suffer significant epimerization, yields a mixture of diastereomeric products in which the 2,3-*cis*, 3,4-*trans* isomer **8r** does indeed dominate. Interestingly, the reaction of 4-(dimethylamino)-benzaldehyde gave an approximately equal mixture of isomers **8s** and **9s**, despite the expectation that this would lead to the most stable benzylic cation. However, it was found necessary to employ more than 1 equiv of Lewis acid to enable this reaction to proceed presumably

(13) A pathway invoked in the epimerization of C-aryl nucleosides. See, for example: Jiang, Y. L.; Stivers, J. T. *Tetrahedron Lett.* **2003**, *44*, 85−88.

SCHEME 3. Synthesis of Hydroxymethyl-Containing Lignan Skeleta



13a (93%) $R^1,R^2 = R^3,R^4 = -OCH_2O-$
13b (96%) $R^1,R^2 = -OCH_2O-$, $R^3,R^4 = OCH_3$
13c (96%) $R^1,R^2 = OCH_3$, $R^3,R^4 = -OCH_2O-$
14a (99%) $R^1,R^2 = R^3,R^4 = -OCH_2O-$

due to coordination of the Lewis acid to the anilinic nitrogen. This would negate the electron-donating effect of the dimethylamino substituent and hence reduce the rate of tetrahydrofuran cleavage. The use of reduced quantities of Lewis acid would be expected to lead to slower epimerization, and this was indeed observed (Table 1, entries 20 and 21). Finally, we suspected that the epimerization was taking place only at elevated temperatures. The tetrahydrofuran-forming reaction mediated by boron trifluoride is extremely slow at −78 °C, and hence, the reaction mixtures are slowly warmed to room temperature to effect complete reaction. Trimethylsilyl trifluoromethanesulfonate has been demonstrated to effect these reactions at −78 °C,[5] and we were delighted to find that the use of these alternative reaction conditions did indeed overturn the selectivity with electron-rich aldehydes, giving rise to predominantly the 2,3-*cis*, 3,4-*trans* isomers **8i**,**n** as the major product in those substrates examined (Table 1, entries 22 and 23). Significantly, this means that either stereoisomer **8** or **9** can now be obtained as the predominant product depending upon the selection of appropriate reaction conditions.

The conversion of the 2-ethenyl group to the hydroxymethyl functionality found in the furanolignans was then investigated. Ozonolysis was found not to be compatible with the oxidatively sensitive electron-rich aryl groups, but olefin cleavage could be achieved cleanly by a two-step sequence of osmium tetraoxide-mediated dihydroxylation followed by periodate cleavage of the resulting diol.[14] Reduction of the aldehyde with sodium borohydride gave the desired alcohols **13**/**14**, which are all epimers of known lignan natural products (Scheme 3).[15] Compound **13a** (4-epidihydrosesamin) has previously been prepared by Yoda,[9] and the agreement of our spectral data with their reported values allowed further confirmation of the stereochemical assignments above. In terms of efficiency, the Yoda synthesis of enantiopure **13a** requires 16 steps (1.8% overall yield) from com-

(14) Ishibashi, F.; Taniguchi, E. *Chem. Lett.* **1986**, 1771−1774.
(15) (a) Lin-Gen, Z.; Seligmann, O.; Lotter, H.; Wagner, H. *Phytochemistry* **1983**, *22*, 265−7. (b) Vidigal, M. C. S.; Cavalheiro, A. J.; Kato, M. J.; Yoshida, M. *Phytochemistry* **1995**, *40*, 1259−61. (c) Cuca, L. E.; Martinez, J. C.; Delle Monache, F. *Phytochemistry* **1998**, *47*, 1437−1439.

mercial dihydroxyacetone dimer,[9,16] whereas our synthesis of *rac*-**13a** proceeds in 37% overall yield over 8 total synthetic steps from ethyl 3-butenoate. Further, the availability of alcohols **7** in enantiomerically enriched form[17] means that application of our chemistry to either enantiomeric series should be straightforward.

In summary, we have developed an efficient, high-yielding and convergent synthesis of 2,3,4-trisubstituted tetrahydrofurans utilizing allylsiloxane/aldehyde condensation chemistry. The stereochemical outcome is dependent upon the aldehyde substituent and the choice of Lewis acid. The 2,3-*cis*, 3,4-*trans* isomer **8** can be obtained as the major product regardless of aldehyde substituent if the appropriate Lewis acid is chosen, whereas for electron-rich aldehydes the 2,3-*trans*, 3,4-*trans* isomer **9** can be accessed if conditions are chosen which permit equilibration through a stabilized benzylic cation. Conversion of the 3-ethenyl group to a hydroxymethyl group can be achieved in high yield, giving access to a range of natural lignan epimers.

Experimental Section

5-(2,2-Dimethyl-2,3,6,7-tetrahydro[1,2]oxasilepin-6-ylmethyl)benzo[1,3]dioxole (3a). To a stirred solution of allyldimethylchlorosilane (410 μL, 2.70 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a solution of homoallylic alcohol **7a** (567 mg, 2.75 mmol) and triethylamine (383 μL, 2.75 mmol) in CH_2Cl_2 (5 mL) dropwise. The reaction mixture was stirred at 0 °C for a further 90 min, whereupon saturated aqueous $NaHCO_3$ (12.5 mL) was added and the mixture was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic phase was washed with water (10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by rapid filtration through a plug of basic alumina (5.5 g alumina, 1.5 cm plug height, eluent 10% Et_2O in hexane followed by neat Et_2O flush) yielded the recovered alcohol starting material **7a** (74 mg) and the allyldimethylsilyl ether as a colorless oil (685 mg, 83%, 94% yield based on recovered starting material). To a solution of the allyldimethylsilyl ether (600 mg, 1.97 mmol) in toluene (99 mL) at 100 °C was added a solution of tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidine]ruthenium(IV) dichloride (84 mg, 98.5 μmol) in CH_2Cl_2 (6 mL) dropwise over 6 h (syringe pump). After a further 12 h at 100 °C, the reaction mixture was cooled and concentrated in vacuo. The residue was purified by filtration through a short pad of silica (eluent 5% Et_2O in hexane) to afford compound **3a** as a pale yellow oil (528 mg, 97%): IR (film, cm^{-1}) 3012, 2954, 1633, 1610; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (3H, s), 0.14 (3H, s), 1.38 (1H, dd, *J* 15.0, 8.5), 1.80 (1H, ddd, *J* 15.0, 6.0, 1.5), 2.50 (1H, dd, *J* 14.0, 8.0), 2.56 (1H, dd, *J* 14.0, 7.5), 2.85 (1H, m), 3.64 (1H, dd, *J* 11.0, 9.0), 3.84 (1H, dd, *J* 11.0, 3.0), 5.38 (1H, ddd, *J* 11.0, 6.0, 2.0), 5.76 (1H, dddd, *J* 11.0, 8.5, 6.0, 2.0), 5.92 (2H, s), 6.61 (1H, dd, *J* 8.0, 1.5,), 6.68 (1H, d, *J* 1.5), 6.72 (1H, d, *J* 8.0); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ −2.2 (q), −0.7 (q), 18.4 (t), 38.1 (t), 43.6 (d), 67.1 (t), 100.8 (t), 108.1 (d), 109.4 (d), 121.9 (d), 126.9 (d), 132.4 (d), 133.9 (s), 145.9 (s), 147.6 (s); MS (CI^+, NH_3) *m*/*z* 294 ([M + NH_4]$^+$, 44), 277 ([M + H]$^+$, 100), 141 (57), 135 (88); HRMS (CI^+, NH_3) for [M + H]$^+$ found 277.1263, $C_{15}H_{21}O_3Si$ requires 277.1260.

6-Phenylmethyl-2,2-dimethyl-2,3,6,7-tetrahydro[1,2]-oxasilepine (3b). Prepared according to the general procedure above, yield 85% over two steps: IR (film, cm^{-1}) 3086, 3063, 3026, 2956, 1634, 1604; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (3H, s), 0.15 (3H, s), 1.38 (1H, dd, *J* 15.0, 8.5), 1.80 (1H, ddd, *J* 15.0, 6.0, 2.0), 2.59 (1H, dd, *J* 14.0, 8.0), 2.64 (1H, dd, *J* 14.0, 7.5), 2.92 (1H, m), 3.66 (1H, dd, *J* 11.0, 9.0), 3.85 (1H, dd, *J* 11.0, 3.0), 5.40 (1H, ddd, *J* 10.5, 6.0, 2.0), 5.76 (1H, dddd, *J* 10.5, 8.0, 6.0, 2.0), 7.17−7.21 (3H, m), 7.26−7.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.2 (q), −0.7 (q), 18.3 (t), 38.4 (t), 43.4 (d), 67.1 (t), 126.1 (d), 126.8 (d), 128.4 (d), 129.1 (d), 132.5 (d), 140.1 (s); MS (CI^+, NH_3) *m*/*z* 250 ([M + NH_4]$^+$, 100), 233 ([M + H]$^+$, 15), 141 (13), 91 (12); HRMS (CI^+, NH_3) for [M + H]$^+$ found 233.1362, $C_{14}H_{21}OSi$ requires 233.1362.

6-(3-Methoxyphenylmethyl)-2,2-dimethyl-2,3,6,7-tetrahydro[1,2]oxasilepine (3c). Prepared according to the general procedure above, yield 90% over two steps: IR (film, cm^{-1}) 3011, 2954, 1633, 1602; ^1H NMR (400 MHz, $CDCl_3$) δ 0.12 (3H, s), 0.14 (3H, s), 1.38 (1H, dd, *J* 15.0, 8.5), 1.80 (1H, ddd, *J* 15.0, 6.0, 2.0), 2.56 (1H, dd, *J* 13.5, 8.0), 2.61 (1H, dd, *J* 13.5, 7.5), 2.92 (1H, m), 3.66 (1H, dd, *J* 11.0, 9.5), 3.79 (3H, s), 3.84 (1H, dd, *J* 11.0, 2.5), 5.40 (1H, ddd, *J* 10.5, 5.5, 2.0), 5.76 (1H, dddd, *J* 10.5, 8.5, 6.0, 2.0), 6.72−6.79 (3H, m), 7.19 (1H, apparent dt, *J* 7.5, 1.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.2 (q), −0.7 (q), 18.3 (t), 38.4 (t), 43.3 (d), 55.1 (q), 67.2 (t), 111.3 (d), 114.9 (d), 121.5 (d), 126.9 (d), 129.3 (d), 132.5 (d), 141.7 (s), 159.6 (s); MS (CI^+, NH_3) *m*/*z* 280 ([M + NH_4]$^+$, 100), 263 ([M + H]$^+$, 92), 141 (12), 121 (3); HRMS (CI^+, NH_3) for [M + H]$^+$ found 263.1473, $C_{15}H_{23}O_2Si$ requires 263.1467.

6-(3,4-Dimethoxyphenylmethyl)-2,2-dimethyl-2,3,6,7-tetrahydro[1,2]oxasilepine (3d). Prepared according to the general procedure above, yield 90% over two steps: IR (film, cm^{-1}) 3007, 2996, 2954, 1634, 1608; ^1H NMR (500 MHz, $CDCl_3$) δ 0.13 (3H, s), 0.15 (3H, s), 1.39 (1H, dd, *J* 15.0, 8.5), 1.79 (1H, ddd, *J* 15.0, 6.0, 2.0), 2.54 (1H, dd, *J* 14.0, 8.0), 2.59 (1H, dd, *J* 14.0, 8.0), 2.88 (1H, m), 3.66 (1H, dd, *J* 11.0, 9.0), 3.85 (1H, dd, *J* 11.0, 3.0), 3.85 (3H, s), 3.87 (3H, s), 5.40 (1H, ddd, *J* 11.0, 6.0, 2.0), 5.76 (1H, dddd, *J* 11.0, 8.5, 6.0, 2.0), 6.71 (1H, d, *J* 2.0), 6.72 (1H, dd, *J* 8.0, 2.0), 6.78 (1H, d, *J* 8.0); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.3 (q), −0.8 (q), 18.2 (t), 37.9 (t), 43.5 (d), 55.7 (q), 55.8 (q), 67.1 (t), 111.0 (d), 112.1 (d), 120.9 (d), 126.8 (d), 132.5 (d and s, 2 coincident peaks), 147.3 (s), 148.7 (s) [16C expected, 15C seen]; MS (CI^+, NH_3) *m*/*z* 310 ([M + NH_4]$^+$, 100), 293 ([M + H]$^+$, 22), 151 (19); HRMS (CI^+, NH_3) for [M + H]$^+$ found 293.1564, $C_{16}H_{25}O_3Si$ requires 293.1573.

5-[(3*SR*,4*SR*,5*SR*)-5-Pentyl-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (8a). To a solution of cyclic allylsiloxane **3a** (18 mg, 0.065 mmol) in DCM (0.6 mL) at −78 °C was added boron trifluoride diethyl etherate (8.0 μL, 0.065 mmol). After 5 min, hexanal (6.5 mg, 0.065 mmol in 0.1 mL DCM) was added dropwise. The solution was stirred at −78 °C for 8 h and then warmed slowly to room temperature with stirring over the next 14 h before the addition of brine (2 mL) and Et_2O (5 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 2 mL). The combined organic phases were washed with water (6 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography (5% Et_2O in hexane) yielded tetrahydrofurans **8a**/**9a** as a colorless oil (32 mg, 76%, 91:9 inseparable mixture): IR (film, cm^{-1}) 3075, 2956, 1634, 1605; ^1H NMR (signals for **8a**, 400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* 7.0), 1.25−1.46 (8H, m,), 2.28 (1H, m, 3′-H), 2.45 (1H, dd, *J* 14.0, 9.5), 2.46 (1H, m), 2.78 (1H, dd, *J* 14.0, 5.5), 3.42 (1H, dd, *J* 8.5, 7.5), 3.91 (1H, m), 3.96 (1H, dd, *J* 8.5, 7.5), 5.00 (1H, dd, *J* 17.0, 2.0), 5.05 (1H, dd, *J* 10.0, 2.0), 5.71 (1H, apparent dt, *J* 17.0, 10.0), 5.92 (2H, s), 6.59 (1H, dd, *J* 8.0, 1.5), 6.63 (1H, d, *J* 1.5), 6.71 (1H, d, *J* 8.0); signals for minor isomer **9a** visible at δ 0.90 (3H, t, *J* 6.5), 3.56 (1H, apparent t, *J* 8.0), 3.83 (1H, dd, *J* 8.5, 7.5), 6.61 (1H, d, *J* 1.5), 6.70 (1H, d, *J* 8.0); ^{13}C NMR (signals for **8a**, 75 MHz, $CDCl_3$) δ 14.1 (q), 22.7 (t), 26.2 (t), 31.6 (t), 32.0 (t), 38.4 (t), 46.9 (d), 53.0 (d), 72.3 (t), 81.6 (d), 100.9 (t), 108.2 (d), 109.1 (d), 116.4 (t), 121.5 (d), 134.2 (s), 137.4 (d), 145.9 (s), 147.7 (s); signals for minor isomer **9a** visible at δ 22.8 (t), 26.1 (t), 38.0 (t), 47.9 (d), 56.8 (d), 84.2 (d), 117.2 (t), 138.1 (s); MS (CI^+, NH_3) *m*/*z* 320 ([M + NH_4]$^+$, 100), 303 ([M + H]$^+$, 48), 285 (13),

(16) (a) Yoda, H.; Mizutani, M.; Takabe, K. *Synlett* **1998**, 855−856. (b) Yoda, H.; Mizutani, M.; Takabe, K. *Tetrahedron Lett.* **1999**, *40*, 4701−4702.

(17) Takekawa, Y.; Shishido, K. *J. Org. Chem.* **2001**, *66*, 8490−8503.

202 (9), 135 (24); HRMS (CI$^+$, NH_3) for $[M + H]^+$ found 303.1965, $C_{19}H_{27}O_3$ requires 303.1960.

5-[(3*SR*,4*SR*,5*RS*)-5-Phenyl-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (8b). Prepared according to the general procedure above, yield 48 mg, 78%, 89:11 inseparable mixture of **8b**/**9b**: IR (film, cm^{-1}) 3071, 3029, 2976, 1640, 1607, 1502, 1489, 1443, 1247, 1191, 1039, 925, 729; ^{1}H NMR (signals for **8b**, 400 MHz, $CDCl_3$) δ 2.35 (1H, m), 2.42 (1H, dd, *J* 13.0, 10.0), 2.78 (1H, apparent q, *J* 8.5), 2.83 (1H, dd, *J* 13.0, 3.5), 3.67 (1H, apparent t, *J* 8.5), 4.25 (1H, dd, *J* 8.5, 7.0), 4.92 (1H, dd, *J* 9.0, 3.0), 5.00 (1H, dd, *J* 16.5, 3.0), 5.07 (1H, ddd, *J* 16.5, 9.0, 8.5), 5.16 (1H, d, *J* 8.0), 5.93 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.5), 6.64 (1H, d, *J* 1.5), 6.73 (1H, d, *J* 8.0), 7.17−7.33 (5H, m); signals for minor isomer **9b** visible at δ 3.82 (1H, apparent t, *J* 8.0), 4.04 (1H, dd, *J* 8.5, 7.0), 4.63 (1H, d, *J* 9.0), 5.83 (1H, ddd, *J* 17.5, 10.0, 9.0), 6.72 (1H, d, *J* 8.0); ^{13}C NMR (signals for **8b**, 75 MHz, $CDCl_3$) δ 37.1 (t), 45.7 (d), 54.8 (d), 73.8 (t), 83.5 (d), 100.9 (t), 108.2 (d), 109.0 (d), 117.0 (t), 121.4 (d), 126.5 (d), 127.0 (d), 127.9 (d), 134.0 (s), 137.0 (d), 140.5 (s), 145.9 (s), 147.6 (s); signals for minor isomer **9b** visible at δ 37.5 (t), 48.1 (d), 59.5 (d), 73.4 (t), 85.8 (d), 118.1 (t), 125.9 (d), 127.4 (d), 128.2 (d), 136.6 (d), 141.6 (s); MS (CI$^+$, NH_3) *m*/*z* 326 ($[M + NH_4]^+$, 100), 309 ($[M + H]^+$, 48), 291 (19), 202 (18), 135 (21), 105 (6); HRMS (CI$^+$, NH_3) for $[M + H]^+$ found 309.1499, $C_{20}H_{21}O_3$ requires 309.1491.

(2*SR*,3*SR*,4*SR*)-2-Pentyl-4-phenylmethyl-3-vinyltetrahydrofuran (8c). Prepared according to the general procedure above, yield 19 mg, 83%, 87:13 inseparable mixture of **8c**/**9c**: IR (film, cm^{-1}) 3079, 3065, 3027, 2956, 1638, 1604; ^{1}H NMR (signals for **8c**, 500 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* 7.0), 1.24−1.46 (8H, m), 2.35 (1H, m), 2.49 (1H, ddd, *J* 10.0, 7.0, 6.5), 2.54 (1H, dd, *J* 14.0, 9.5), 2.87 (1H, dd, *J* 14.0, 5.5), 3.44 (1H, dd, *J* 8.5, 7.5), 3.93 (1H, ddd, *J* 8.5, 7.0, 4.5), 3.97 (1H, dd, *J* 8.5, 7.0), 4.99 (1H, ddd, *J* 17.0, 2.0, 0.5), 5.04 (1H, dd, *J* 10.0, 2.0), 5.72 (1H, apparent dt, *J* 17.0, 10.0), 7.13−7.21 (3H, m), 7.25−7.29 (2H, m); signals for minor isomer **9c** visible at δ 2.05 (1H, apparent q, *J* 9.0), 3.59 (1H, apparent t, *J* 8.0), 3.83 (1H, dd, *J* 8.0, 7.5); ^{13}C NMR (signals for **8c**, 75 MHz, $CDCl_3$) δ 14.1 (q), 22.7 (t), 26.2 (t), 31.6 (t), 32.0 (t), 38.7 (t), 46.7 (d), 53.1 (d), 72.3 (t), 81.6 (d), 116.4 (t), 126.1 (d), 128.5 (d), 128.8 (d), 137.4 (d), 140.4 (s); signals for minor isomer **9c** visible at δ 38.3 (t), 47.7 (d), 57.0 (d), 84.1 (d), 117.2 (t), 138.0 (d); MS (CI$^+$, NH_3) *m*/*z* 276 ($[M + NH_4]^+$, 73), 259 ($[M + H]^+$, 4), 241 (14), 167 (9), 158 (100), 91 (28); HRMS (CI$^+$, NH_3) for $[M + NH_4]^+$ found 276.2334, $C_{18}H_{30}NO$ requires 276.2327.

(2*RS*,3*SR*,4*SR*)-2-Phenyl-4-phenylmethyl-3-vinyltetrahydrofuran (8d). Prepared according to the general procedure above, yield 17 mg, 81%, 84:16 inseparable mixture of **8d**/**9d**: IR (film, cm^{-1}) 3083, 3063, 3003, 2976, 1640, 1603; ^{1}H NMR (signals for **8d**, 500 MHz, $CDCl_3$) δ 2.43 (1H, m), 2.52 (1H, dd, *J* 13.5, 10.0), 2.82 (1H, apparent q, *J* 8.5), 2.93 (1H, dd, *J* 13.5, 4.5), 3.70 (1H, apparent t, *J* 8.5), 4.26 (1H, dd, *J* 8.5, 7.0), 4.93 (1H, dd, *J* 9.5, 2.5,), 5.02 (1H, dd, *J* 17.0, 2.5), 5.10 (1H, dt, *J* 17.0, 9.5), 5.18 (1H, d, *J* 8.0), 7.15−7.34 (10H, m); signals for minor isomer **9d** visible at δ 2.37 (1H, m), 3.86 (1H, apparent t, *J* 8.0), 4.06 (1H, dd, *J* 8.5, 7.5), 4.64 (1H, d, *J* 9.5), 4.97 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.11 (1H, dd, *J* 10.5, 1.5), 5.78 (1H, ddd, *J* 17.0, 10.5, 9.0); ^{13}C NMR (signals for **8d**, 75 MHz, $CDCl_3$) δ 37.5 (t), 45.6 (d), 55.0 (d), 73.9 (t), 83.5 (d), 117.1 (t), 126.3 (d), 126.6 (d), 127.1 (d), 127.9 (d), 128.5 (d), 128.7 (d), 137.2 (d), 140.3 (s), 140.6 (s); signals for minor isomer **9d** visible at δ 37.9 (t), 48.0 (d), 59.7 (d), 73.5 (t), 85.9 (d), 118.1 (t), 125.9 (d), 127.5 (d), 128.3 (d), 136.7 (d); MS (CI$^+$, NH_3) *m*/*z* 282 ($[M + NH_4]^+$, 100), 265 ($[M + H]^+$, 8), 247 (16), 158 (22), 91 (19); HRMS (CI$^+$, NH_3) for $[M + H]^+$ found 265.1595, $C_{19}H_{21}O$ requires 265.1592.

(2*SR*,3*SR*,4*SR*)-4-(3-Methoxyphenylmethyl)-2-pentyl-3-vinyltetrahydrofuran (8e). Prepared according to the general procedure above, yield 18.7 mg, 67%, 90:10 inseparable mixture of **8e**/**9e**: IR (film, cm^{-1}) 3075, 3028, 2999, 2954, 1638, 1611, 1602; ^{1}H NMR (signals for **8e**, 400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* 6.5), 1.25−1.45 (8H, m), 2.35 (1H, m), 2.49 (1H, m), 2.52 (1H, dd, *J* 13.5, 6.0), 2.85 (1H, dd, *J* 13.5, 5.5), 3.44 (1H, dd, *J* 8.5, 7.5), 3.79 (3H, s), 3.93 (1H, m), 3.98 (1H, dd, *J* 8.5, 7.5), 5.01 (1H, dd, *J* 17.0, 2.0), 5.05 (1H, dd, *J* 10.0, 2.0), 5.73 (1H, apparent dt, *J* 17.0, 10.0), 6.69 (1H, s), 6.74 (1H, d, *J* 8.0), 6.74 (1H, d, *J* 8.0), 7.19 (1H, apparent t, *J* 8.0); signals for minor isomer **9e** visible at δ 0.90 (3H, t, *J* 7.0), 3.59 (1H, apparent t, *J* 8.5), 3.82 (3H, s), 3.84 (1H, dd, *J* 8.5, 7.5), 7.11 (1H, apparent t, *J* 8.0); ^{13}C NMR (signals for **8e**, 75 MHz, $CDCl_3$) δ 14.1 (q), 22.7 (t), 26.2 (t), 31.6 (t), 32.0 (t), 38.7 (t), 46.5 (d), 53.2 (d), 55.2 (q), 72.3 (t), 81.6 (d), 111.4 (d), 114.6 (d), 116.4 (t), 121.2 (d), 129.4 (d), 137.4 (d), 142.0 (s), 159.7 (s); signals for minor isomer **9e** visible at δ 26.0 (t), 31.4 (t), 31.8 (t), 39.1 (t), 47.6 (d), 57.0 (d), 108.2 (d); MS (CI$^+$, NH_3) *m*/*z* 306 ($[M + NH_4]^+$, 100), 289 ($[M + H]^+$, 53), 271 (26), 217 (3), 188 (8), 121 (6); HRMS (CI$^+$, NH_3) for $[M + H]^+$ found 289.2165, $C_{19}H_{29}O_2$ requires 289.2168.

(2*RS*,3*SR*,4*SR*)-4-(3-Methoxyphenylmethyl)-2-phenyl-3-vinyltetrahydrofuran (8f). Prepared according to the general procedure above, yield 24.6 mg, 76%, 88:12 inseparable mixture of **8f**/**9f**: IR (film, cm^{-1}) 3078, 3029, 3003, 1639, 1602; ^{1}H NMR (signals for **8f**, 400 MHz, $CDCl_3$) δ 2.41 (1H, m), 2.47 (1H, dd, *J* 13.0, 10.0), 2.81 (1H, apparent q, *J* 8.5), 2.90 (1H, dd, *J* 13.0, 4.0), 3.70 (1H, apparent t, *J* 8.5), 3.80 (3H, s), 4.27 (1H, dd, *J* 8.5, 7.0), 4.94 (1H, dd, *J* 9.0, 3.0), 5.02 (1H, dd, *J* 17.0, 3.0), 5.08 (1H, ddd, *J* 17.0, 9.0, 8.5), 5.17 (1H, d, *J* 8.0), 6.70 (1H, dd, *J* 2.0, 2.0), 6.74−6.78 (2H, m), 7.17−7.34 (6H, m); signals for minor isomer **9f** visible at δ 3.80 (3H, s), 3.85 (1H, apparent t, *J* 8.5), 4.07 (1H, dd, *J* 8.5, 7.5), 4.63 (1H, d, *J* 9.0), 4.97 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.11 (1H, dd, *J* 10.0, 1.5), 5.78 (1H, ddd, *J* 17.0, 10.0, 8.5); ^{13}C NMR (signals for **8f**, 75 MHz, $CDCl_3$) δ 37.6 (t), 45.5 (d), 55.0 (d), 55.2 (q), 73.9 (t), 83.5 (d), 111.4 (d), 114.7 (d), 117.0 (t), 121.1 (d), 126.6 (d), 127.1 (d), 127.9 (d), 129.5 (d), 137.2 (d), 140.6 (s), 141.9 (s), 159.8 (s); signals for minor isomer **9f** visible at δ 38.0 (t), 47.9 (d), 59.6 (d), 73.5 (t), 85.9 (d), 118.0 (t), 125.9 (d), 127.5 (d), 128.3 (d); MS (CI$^+$, NH_3) *m*/*z* 312 ($[M + NH_4]^+$, 100), 295 ($[M + H]^+$, 57), 277 (19), 188 (16), 121 (7), 105 (3); HRMS (CI$^+$, NH_3) for $[M + H]^+$ found 295.1693, $C_{20}H_{23}O_2$ requires 295.1698.

(2*SR*,3*SR*,4*SR*)-4-(3,4-Dimethoxyphenylmethyl)-2-pentyl-3-vinyltetrahydrofuran (8g). Prepared according to the general procedure above, yield 24.3 mg, 79%, 85:15 inseparable mixture of **8g**/**9g**: IR (film, cm^{-1}) 3076, 2997, 2954, 1638, 1609; ^{1}H NMR (signals for **8g**, 400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* 6.5), 1.25−1.46 (8H, m), 2.32 (1H, m), 2.45−2.52 (2H, m), 2.81 (1H, dd, *J* 14.0, 5.5), 3.44 (1H, dd, *J* 8.5, 7.5), 3.85 (3H, s), 3.85 (3H, s), 3.92 (1H, m), 3.98 (1H, dd, *J* 8.5, 7.5), 4.99 (1H, dd, *J* 17.0, 2.0), 5.05 (1H, dd, *J* 10.0, 2.0), 5.73 (1H, apparent dt, *J* 17.0, 10.0), 6.65 (1H, d, *J* 2.0), 6.68 (1H, dd, *J* 8.0, 2.0), 6.77 (1H, d, *J* 8.0); signals for minor isomer **9g** visible at δ 0.90 (3H, t, *J* 6.5), 2.86 (1H, dd, *J* 15.5, 4.5), 3.58 (1H, apparent t, *J* 8.0); ^{13}C NMR (signals for **8g**, 75 MHz, $CDCl_3$) δ 14.1 (q), 22.7 (t), 26.2 (t), 31.6 (t), 32.0 (t), 38.3 (t), 46.8 (d), 53.1 (d), 55.9 (q), 55.9 (q), 72.3 (t), 81.5 (d), 111.1 (d), 111.9 (d), 116.3 (t), 120.6 (d), 132.9 (s), 137.5 (d), 147.4 (s), 148.8 (s); signals for minor isomer **9g** visible at δ 22.8 (t), 26.0 (t), 47.8 (d), 56.9 (d), 72.4 (t), 84.2 (d), 110.7 (d), 132.6 (s), 138.1 (s), 147.1 (s); MS (CI$^+$, NH_3) *m*/*z* 336 ($[M + NH_4]^+$, 100), 319 ($[M + H]^+$, 7), 218 (7), 151 (8); HRMS (CI$^+$, NH_3) for $[M + NH_4]^+$ found 336.2544, $C_{20}H_{34}NO_3$ requires 336.2539.

(2*RS*,3*SR*,4*SR*)-4-(3,4-Dimethoxyphenylmethyl)-2-phenyl-3-vinyltetrahydrofuran (8h). Prepared according to the general procedure above, yield 15.1 mg, 68%, 87:13 inseparable mixture of **8h**/**9h**: IR (film, cm^{-1}) 3076, 3063, 3028, 3002, 1640, 1606; ^{1}H NMR (signals for **8h**, 400 MHz, $CDCl_3$) δ 2.38 (1H, m, 4-H), 2.46 (1H, dd, *J* 13.5, 10.0), 2.80 (1H, apparent q, *J* 8.5), 2.86 (1H, dd, *J* 13.5, 4.0), 3.70 (1H, apparent t, *J* 8.5), 3.87 (3H, s), 3.87 (3H, s), 4.26 (1H, dd, *J* 8.5, 7.0), 4.94 (1H, dd, *J* 9.5, 3.0), 5.02 (1H, dd, *J* 17.0, 3.0), 5.09 (1H, ddd, *J* 17.0, 9.5, 8.5), 5.17 (1H, d, *J* 8.0), 6.65 (1H, d, *J* 2.0), 6.70 (1H, dd, *J* 8.0, 2.0), 6.79 (1H d, *J* 8.0), 7.17−7.33 (5H, m); signals for minor isomer **9h** visible at δ 4.06 (1H, dd, *J* 8.5, 7.5), 4.64 (1H, d, *J* 9.0), 4.96 (1H, ddd, *J* 17.0, 1.5, 1.0), 5.11 (1H, dd, *J* 10.0,

1.5), 5.78 (1H, ddd, *J* 17.0, 10.0, 8.5); ^{13}C NMR (signals for **8h**, 100 MHz, $CDCl_3$) δ 37.1 (t), 45.7 (d), 55.0 (d), 55.9 (q, 2 coincident peaks), 73.9 (t), 83.5 (d), 111.2 (d), 111.9 (d), 117.1 (t), 120.6 (d), 126.6 (d), 127.1 (d), 127.9 (d), 132.8 (s), 137.2 (d), 140.6 (s), 147.5 (s), 148.8 (s) [19 C expected, 18 seen]; signals for minor isomer **9h** visible at δ 37.4 (t), 48.1 (d), 73.5 (t), 85.9 (d), 118.1 (t), 127.5 (d), 128.3 (d), 136.8 (d); MS (CI^+, NH_3) *m*/*z* 342 ($[M + NH_4]^+$, 100), 325 ($[M + H]^+$, 35), 307 (7), 218 (7), 151 (15); HRMS (CI^+, NH_3) for $[M + H]^+$ found 325.1801, $C_{21}H_{25}O_3$ requires 325.1804.

5-[(3*SR*,4*SR*,5*SR*)-5-(Benzo[1,3]dioxol-5-yl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (9i). Prepared according to the general procedure above, yield 20.4 mg, 58%, 92:8 inseparable mixture of **9i**/**8i**: IR (film, cm^{-1}) 3076, 2972, 1641, 1608; ^{1}H NMR (signals for **9i**, 400 MHz, $CDCl_3$) δ 2.28 (1H, apparent q, *J* 9.0), 2.37−2.48 (2H, m), 2.86 (1H, dd, *J* 18.5, 9.5), 3.79 (1H, apparent t, *J* 8.5), 4.02 (1H, dd, *J* 8.5, 7.5), 4.52 (1H, d, *J* 9.0), 4.97 (1H, dd, *J* 17.0, 1.0,), 5.10 (1H, dd, *J* 10.0, 1.0), 5.71 (1H, ddd, *J* 17.0, 10.0, 9.0), 5.93 (2H, s), 5.94 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.0), 6.64 (1H, d, *J* 1.0), 6.72 (1H, d, *J* 8.0), 6.75 (2H, apparent s,), 6.84 (1H, apparent s); signals for minor isomer **8i** visible at δ 2.72 (1H, apparent q, *J* 8.5), 3.62 (1H, apparent t, *J* 8.5), 4.20 (1H, dd, *J* 8.5, 7.0); ^{13}C NMR (signals for **9i**, 100 MHz, $CDCl_3$) δ 37.6 (t), 48.0 (d), 59.5 (d), 73.3 (t), 85.9 (d), 100.9 (t), 101.0 (t), 106.5 (d), 108.0 (d), 108.3 (d), 109.1 (d), 118.2 (t), 119.5 (d), 121.5 (d), 134.0 (s), 135.4 (s), 136.5 (d), 146.0 (s), 146.9 (s), 147.7 (s, 2 coincident peaks) [21 C expected, 20 seen]; signals for minor isomer **8i** visible at δ 37.1 (t), 45.7 (d), 55.0 (d), 73.8 (t), 83.4 (d), 107.2 (d), 107.8 (d), 117.2 (t), 119.8 (d), 134.7 (s), 137.1 (d); MS (CI^+, NH_3) *m*/*z* 370 ($[M + NH_4]^+$, 27), 353 ($[M + H]^+$, 100), 335 (30), 231 (45), 202 (18), 149 (74), 135 (37); HRMS (CI^+, NH_3) for $[M + H]^+$ found 353.1386, $C_{21}H_{21}O_5$ requires 353.1389.

5-[(3*SR*,4*SR*,5*SR*)-5-(4-Methoxyphenyl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (9j). Prepared according to the general procedure above, yield 20.0 mg, 50%, 92:8 inseparable mixture of **9j**/**8j**: IR (film, cm^{-1}) 3074, 2968, 1640, 1613; ^{1}H NMR (signals for **9j**, 400 MHz, $CDCl_3$) δ 2.32 (1H, apparent q, *J* 9.0), 2.42−2.49 (2H, m), 2.86 (1H, dd, *J* 18.5, 9.5), 3.79 (3H, s), 3.80 (1H, m), 4.02 (1H, dd, *J* 8.5, 7.0), 4.56 (1H, d, *J* 9.0), 4.95 (1H, d, *J* 17.0), 5.10 (1H, d, *J* 10.0), 5.73 (1H, ddd, *J* 17.0, 10.0, 8.5), 5.92 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.5), 6.63 (1H, d, *J* 1.5), 6.72 (1H, d, *J* 8.0), 6.86 (2H, d, *J* 9.0), 7.24 (2H, d, *J* 9.0); signals for minor isomer **8j** visible at δ 2.74 (1H, apparent q, *J* 8.5), 3.63 (1H, apparent t, *J* 8.5), 4.22 (1H, dd, *J* 8.5, 7.0), 7.09 (2H, d, *J* 8.5); ^{13}C NMR (signals for **9j**, 75 MHz, $CDCl_3$) δ 37.8 (t), 48.1 (d), 55.3 (q), 59.3 (d), 73.2 (t), 85.7 (d), 100.9 (t), 108.3 (d), 109.1 (d), 113.7 (d), 118.0 (t), 121.5 (d), 127.3 (d), 133.5 (s), 134.1 (s), 136.7 (d), 146.0 (s), 147.7 (s), 159.1 (s); signals for minor isomer **8j** visible at δ 37.2 (t), 45.8 (d), 55.0 (d), 55.3 (q), 73.8 (t), 83.3 (d), 113.4 (d), 117.0 (t), 127.7 (d), 132.8 (s), 134.2 (s), 137.3 (d), 158.7 (s); MS (CI^+, NH_3) *m*/*z* 356 ($[M + NH_4]^+$, 83), 339 ($[M + H]^+$, 100), 321 (8), 231 (89), 202 (15), 135 (48); HRMS (CI^+, NH_3) for $[M + H]^+$ found 339.1598, $C_{21}H_{23}O_4$ requires 339.1596.

5-[(3*SR*,4*SR*,5*SR*)-5-(3,4-Dimethoxyphenyl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (9k). Prepared according to the general procedure above, yield 16.1 mg, 54%, 90:10 inseparable mixture of **9k**/**8k**: IR (film, cm^{-1}) 3075, 2950, 1640, 1607; ^{1}H NMR (signals for **9k**, 400 MHz, $CDCl_3$) δ 2.32 (1H, apparent q, *J* 9.0), 2.41−2.49 (2H, m), 2.87 (1H, dd, *J* 18.5, 9.5), 3.81 (1H, apparent t, *J* 8.0), 3.87 (3H, s), 3.89 (3H, s), 4.03 (1H, dd, *J* 8.5, 7.5), 4.57 (1H, d, *J* 9.0), 4.98 (1H, dd, *J* 17.0, 1.0), 5.11 (1H, dd, *J* 10.0, 1.5), 5.75 (1H, ddd, *J* 17.0, 10.0, 9.0), 5.93 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.5), 6.65 (1H, d, *J* 1.5), 6.72 (1H, d, *J* 8.0), 6.81 (1H, d, *J* 8.0), 6.85 (1H, dd, *J* 8.0, 1.5), 6.87 (1H, d, *J* 1.5); signals for minor isomer **8k** visible at δ 2.73 (1H, apparent q, *J* 9.0), 3.63 (1H, apparent t, *J* 8.5), 3.85 (3H, s), 4.21 (1H, dd, *J* 8.5, 7.5), 5.92 (2H, s); ^{13}C NMR (signals for **9k**, 75 MHz, $CDCl_3$) δ 37.6 (t), 48.9 (d), 55.9 (q), 55.9 (q), 59.2 (d), 73.2 (t), 85.7 (d), 100.9 (t), 108.2 (d), 109.0 (d, 2 coincident peaks), 110.8 (d), 118.0 (t), 118.2 (d), 121.4 (d), 133.9 (s), 134.0 (s), 136.8 (d), 145.9 (s), 147.7 (s), 148.4 (s), 148.9 (s) [22 C expected, 21 seen]; signals for minor isomer **8k** visible at δ 37.1 (t), 122.0 (d); MS (CI^+, NH_3) *m*/*z* 386 ($[M + NH_4]^+$, 95), 369 ($[M + H]^+$, 91), 351 (11), 231 (100), 202 (10), 165 (64), 135 (17); HRMS (CI^+, NH_3) for $[M + NH_4]^+$ found 386.1965, $C_{22}H_{28}NO_5$ requires 386.1967.

4-[(2*SR*,3*SR*,4*SR*)-4-Benzo[1,3]dioxol-5-ylmethyl-3-vinyltetrahydrofuran-2-yl]-2-methoxyphenol (9l). Prepared according to the general procedure above, yield 11.6 mg, 51%, 92:8 inseparable mixture of **9l**/**8l**: IR (film, cm^{-1}) 3450 (br, OH), 3075, 1639, 1607; ^{1}H NMR (signals for **9l**, 400 MHz, $CDCl_3$) δ 2.31 (1H, apparent q, *J* 9.0), 2.41−2.48 (2H, m), 2.87 (1H, dd, *J* 18.5, 9.5), 3.81 (1H, apparent t, *J* 8.0), 3.89 (3H, s), 4.03 (1H, dd, *J* 8.5, 7.5), 4.54 (1H, d, *J* 9.0), 4.97 (1H, dd, *J* 17.0, 1.0), 5.10 (1H, dd, *J* 10.0, 1.5), 5.59 (1H, br s), 5.74 (1H, ddd, *J* 17.0, 10.0, 9.0), 5.93 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.5), 6.65 (1H, d, *J* 1.5), 6.72 (1H, d, *J* 8.0), 6.80 (1H, dd, *J* 8.0, 1.5), 6.85 (1H, d, *J* 1.5), 6.86 (1H, d, *J* 8.0); signals for minor isomer **8l** visible at δ 2.73 (1H, apparent q, *J* 9.0), 3.62 (1H, apparent t, *J* 8.5), 3.86 (3H, s), 4.22 (1H, dd, *J* 8.5, 7.0), 5.92 (2H, s); ^{13}C NMR (signals for **9l**, 75 MHz, $CDCl_3$) δ 37.7 (t), 48.0 (d), 55.9 (q), 59.2 (d), 73.2 (t), 85.8 (d), 100.9 (t), 108.2 (d′), 108.4 (d), 109.0 (d), 114.1 (d), 118.0 (t), 119.1 (d), 121.4 (d), 133.3 (s), 134.0 (s), 136.7 (d), 145.0 (s), 145.9 (s), 146.4 (s), 147.7 (s); signals for minor isomer **8l** visible at δ 37.1 (t), 45.9 (d), 54.9 (d), 73.7 (t), 83.3 (d), 109.2 (d), 109.5 (d), 113.9 (d), 116.8 (t), 119.5 (d), 122.0 (d), 132.5 (s), 137.4 (d), 139.1 (s), 144.6 (s); MS (CI^+, NH_3) *m*/*z* 372 ($[M + NH_4]^+$, 100), 355 ($[M + H]^+$, 94), 337 (14), 231 (88), 202 (14), 151 (63), 135 (18); HRMS (CI^+, NH_3) for $[M + H]^+$ found 355.1543, $C_{21}H_{23}O_5$ requires 355.1543.

5-[(2*SR*,3*SR*,4*SR*)-4-Phenylmethyl-3-vinyltetrahydrofuran-2-yl]benzo[1,3]dioxole (9m). Prepared according to the general procedure above, yield 18.6 mg, 76%, 89:11 inseparable mixture of **9m**/**8m**: IR (film, cm^{-1}) 3078, 3063, 3026, 2973, 1642, 1604; ^{1}H NMR (signals for **9m**, 500 MHz, $CDCl_3$) δ 2.33 (1H, apparent q, *J* 9.0), 2.49 (1H, m), 2.54 (1H, dd, *J* 12.5, 10.0), 2.96 (1H, dd, *J* 12.5, 3.0), 3.82 (1H, apparent t, *J* 8.5), 4.03 (1H, dd, *J* 8.5, 7.5), 4.54 (1H, d, *J* 9.0), 4.98 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.11 (1H, dd, *J* 10.0, 1.5), 5.74 (1H, ddd, *J* 17.0, 10.5, 9.0), 5.94 (2H, s), 6.75 (1H, d, *J* 8.0), 6.78 (1H, dd, *J* 8.0, 1.0), 6.85 (1H, d, *J* 1.0), 7.16 (2H, dd, *J* 7.5, 1.5), 7.19−7.31 (3H, m); signals for minor isomer **8m** visible at δ 2.40 (1H, m), 2.76 (1H, apparent q, *J* 9.0), 3.66 (1H, apparent t, *J* 9.0), 4.21 (1H, dd, *J* 8.5, 7.5), 4.96 (1H, dd, *J* 9.5, 2.0), 5.14 (1H, apparent dt, *J* 17.0, 9.5), 5.94 (2H, s), 6.65 (1H, dd, *J* 8.0, 1.5), 6.70 (1H, d, *J* 1.5), 6.74 (1H, d, *J* 8.0); ^{13}C NMR (signals for **9m**, 75 MHz, $CDCl_3$) δ 37.9 (t), 47.8 (d), 59.6 (d), 73.4 (t), 85.9 (d), 101.0 (t), 106.5 (d), 108.0 (d), 118.2 (t), 119.5 (d), 126.3 (d), 128.5 (d), 128.7 (d), 135.5 (s), 136.6 (d), 140.2 (s), 147.0 (s), 147.7 (s); signals for minor isomer **8m** visible at δ 37.4 (t), 45.6 (d), 55.1 (d), 73.9 (t), 83.4 (d), 107.2 (d), 107.8 (d), 117.2 (t), 119.8 (d), 137.1 (d), 146.5 (s), 147.4 (s); MS (CI^+, NH_3) *m*/*z* 326 ($[M + NH_4]^+$, 59), 309 ($[M + H]^+$, 100), 291 (38), 217 (4), 187 (12), 158 (8), 149 (60), 91 (11); HRMS (CI^+, NH_3) for $[M + H]^+$ found 309.1500, $C_{20}H_{21}O_3$ requires 309.1491.

(2*SR*,3*SR*,4*SR*)-2-(4-Methoxyphenyl)-4-phenylmethyl-3-vinyltetrahydrofuran (9n). Prepared according to the general procedure above, yield 16.6 mg, 68%, 92:8 inseparable mixture of **9n**/**8n**: IR (film, cm^{-1}) 3079, 3063, 3000, 1642, 1614; ^{1}H NMR (signals for **9n**, 400 MHz, $CDCl_3$) δ 2.35 (1H, apparent q, *J* 9.0), 2.48−2.58 (2H, m), 2.97 (1H, dd, *J* 18.5, 9.5), 3.81 (3H, s), 3.84 (1H, apparent t, *J* 8.5), 4.03 (1H, dd, *J* 8.5, 8.0), 4.58 (1H, d, *J* 9.0), 4.97 (1H, ddd, *J* 17.0, 1.5, 1.0), 5.10 (1H, dd, *J* 10.0, 1.5), 5.75 (1H, ddd, *J* 17.0, 10.0, 9.0), 6.87 (2H, d, *J* 8.5), 7.15−7.32 (7H, m, 2′-H); signals for minor isomer **8n** visible at δ 2.77 (1H, apparent q, *J* 9.0), 3.67 (1H, apparent t, *J* 8.5), 3.80 (3H, s), 4.23 (1H, dd, *J* 8.5, 7.0), 6.84 (2H, d, *J* 8.5); ^{13}C NMR (signals for **9n**, 75 MHz, $CDCl_3$) δ 38.0 (t), 47.8 (d), 55.3 (q), 59.5 (d), 73.3 (t), 85.7 (d), 113.7 (d), 118.0 (t), 126.2 (d), 127.3 (d), 128.5 (d), 128.7 (d), 133.5 (s), 136.7 (d), 140.3 (s), 159.1 (s); signals for minor isomer **8n** visible at δ 37.5 (t), 45.6 (d), 55.1 (d), 73.8 (t), 83.3 (d), 113.3 (d), 117.0 (t), 127.7

(d), 129.1 (d), 137.3 (d); MS (CI^+, NH_3) *m/z* 312 ($[M + NH_4]^+$, 82), 295 ($[M + H]^+$, 100), 277 (19), 203 (6), 187 (13), 158 (11), 135 (36), 91 (16); HRMS (CI^+, NH_3) for $[M + H]^+$ found 295.1694, $C_{20}H_{23}O_2$ requires 295.1698.

5-[(2*SR*,3*SR*,4*SR*)-4-(3-Methoxyphenylmethyl)-3-vinyltetrahydrofuran-2-yl]-benzo[1,3]dioxole (9o). Prepared according to the general procedure above, yield 19.8 mg, 52%, 92:8 inseparable mixture of **9o**/**8o**: IR (film, cm^{-1}) 3075, 1642, 1602; ^1H NMR (signals for **9o**, 500 MHz, $CDCl_3$) δ 2.31 (1H, apparent q, *J* 9.0), 2.47−2.52 (2H, m), 2.93 (1H, dd, *J* 18.5, 9.5), 3.80 (3H, s), 3.82 (1H, apparent t, *J* 8.5), 4.03 (1H, dd, *J* 8.5, 7.5), 4.53 (1H, d, *J* 9.0), 4.98 (1H, ddd, *J* 17.0, 2.0, 0.5), 5.11 (1H, dd, *J* 10.0, 2.0), 5.73 (1H, ddd, *J* 17.0, 10.0, 9.0), 5.94 (2H, s), 6.70 (1H, dd, *J* 2.0, 2.0), 6.74−6.77 (4H, m), 6.85 (1H, d, *J* 1.5), 7.20 (1H, apparent t, *J* 8.0); signals for minor isomer **8o** visible at δ 2.62 (1H, dd, *J* 13.5, 10.0), 2.75 (1H, apparent q, *J* 8.5), 3.65 (1H, apparent t, *J* 8.5), 4.22 (1H, dd, *J* 8.5, 7.0), 4.96 (1H, dd, *J* 10.0, 2.0), 5.93 (2H, s), 6.64 (1H, dd, *J* 8.0, 1.5), 7.21 (1H, apparent t, *J* 8.0); ^{13}C NMR (signals for **9o**, 75 MHz, $CDCl_3$) δ 37.9 (t), 47.7 (d), 55.2 (q), 59.6 (d), 73.4 (t), 85.8 (d), 101.0 (t), 106.5 (d), 108.0 (d), 111.4 (d), 114.5 (d), 118.2 (t), 119.5 (d), 121.0 (d), 129.5 (d), 135.4 (s), 136.5 (d), 141.8 (s), 147.0 (s), 147.7 (s), 159.7 (s); signals for minor isomer **8o** visible at δ 37.5 (t), 45.4 (d), 55.1 (d), 73.9 (t), 83.4 (d), 117.2 (t), 137.1 (d); MS (CI^+, NH_3) *m/z* 356 ($[M + NH_4]^+$, 100), 339 ($[M + H]^+$, 41), 321 (6), 217 (17), 188 (7); HRMS (CI^+, NH_3) for $[M + H]^+$ found 309.1582, $C_{21}H_{23}O_4$ requires 339.1596.

(2*SR*,3*SR*,4*SR*)-4-(3-Methoxyphenylmethyl)-2-(4-methoxyphenyl)-3-vinyltetrahydrofuran (9p). Prepared according to the general procedure above, yield 17.8 mg, 48%, 92:8 inseparable mixture of **9p**/**8p**: IR (film, cm^{-1}) 3075, 3028, 3000, 1642, 1614, 1601; ^1H NMR (signals for **9p**, 400 MHz, $CDCl_3$) δ 2.34 (1H, apparent q, *J* 9.0), 2.46−2.54 (2H, m), 2.94 (1H, dd, *J* 18.5, 9.5), 3.80 (3H, s), 3.80 (3H, s), 3.83 (1H, apparent t, *J* 8.5), 4.03 (1H, dd, *J* 8.5, 7.5), 4.57 (1H, d, *J* 9.0), 4.97 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.08 (1H, ddd, *J* 10.0, 1.5, 0.5), 5.74 (1H, ddd, *J* 17.0, 10.0, 8.5), 6.70 (1H, dd, *J* 2.0, 2.0) 6.74−6.77 (2H, m), 6.86 (2H, d, *J* 8.5), 7.20 (1H, apparent t, *J* 8.0), 7.25 (2H, d, *J* 8.5); signals for minor isomer **8p** visible at δ 2.76 (1H, apparent q, *J* 8.5), 3.66 (1H, apparent t, *J* 8.5), 4.23 (1H, dd, *J* 8.5, 7.0), 7.10 (2H, d, *J* 8.5); ^{13}C NMR (signals for **9p**, 75 MHz, $CDCl_3$) δ 38.0 (t), 47.7 (d), 55.2 (q), 55.3 (q), 59.5 (d), 73.3 (t), 85.6 (d), 111.4 (d), 113.3 (d), 113.7 (d), 118.0 (t), 121.1 (d), 127.3 (d), 129.5 (d), 133.5 (s), 136.7 (d), 141.9 (s), 159.1 (s), 159.7 (s); signals for minor isomer **8p** visible at δ 37.5 (t), 55.1 (d), 83.2 (d); MS (CI^+, NH_3) *m/z* 342 ($[M + NH_4]^+$, 73), 325 ($[M + H]^+$, 99), 307 (11), 217 (100), 188 (25), 135 (52), 121 (26); HRMS (CI^+, NH_3) for $[M + H]^+$ found 325.1805, $C_{21}H_{25}O_3$ requires 325.1804.

5-[(2*SR*,3*SR*,4*SR*)-4-(3,4-Dimethoxyphenylmethyl)-3-vinyltetrahydrofuran-2-yl]benzo[1,3]dioxole (8q). Prepared according to the general procedure above, yield 9.8 mg, 47%, 91:9 inseparable mixture of **9q**/**8q**: IR (film, cm^{-1}) 3072, 2995, 1640, 1607; ^1H NMR (signals for **9q**, 400 MHz, $CDCl_3$) δ 2.30 (1H, apparent q, *J* 9.0), 2.40−2.50 (2H, m), 2.89 (1H, dd, *J* 18.5, 9.5), 3.82 (1H, apparent t, *J* 8.5), 3.86 (3H, s), 3.87 (3H, s), 4.02 (1H, dd, *J* 8.5, 7.0), 4.53 (1H, d, *J* 9.0), 4.97 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.10 (1H, dd, *J* 10.0, 1.5), 5.73 (1H, ddd, *J* 17.0, 10.0, 8.5), 5.94 (2H, s), 6.65 (1H, d, *J* 2.0), 6.69 (1H, dd, *J* 8.0, 2.0), 6.75 (1H, apparent s), 6.75 (1H, apparent d, *J* 2.0), 6.78 (1H, d, *J* 8.0), 6.84 (1H, m); signals for minor isomer **8q** visible at δ 2.74 (1H, apparent q, *J* 8.5), 3.65 (1H, apparent t, *J* 8.5), 4.21 (1H, dd, *J* 8.5, 7.0), 4.96 (1H, dd, *J* 10.0, 2.5), 5.01 (1H, dd, *J* 17.0, 2.5), 5.94 (2H, s); ^{13}C NMR (signals for **9q**, 75 MHz, $CDCl_3$) δ 37.6 (t), 48.0 (d), 56.0 (q), 56.0 (q), 59.5 (d), 73.4 (t), 85.9 (d), 101.0 (t), 106.5 (d), 108.0 (d), 111.4 (d), 112.1 (d), 118.1 (t), 119.5 (d), 120.6 (d), 132.8 (s), 135.5 (s), 136.7 (d), 147.0 (s), 147.6 (s), 147.7 (s), 149.0 (s); signals for minor isomer **8q** visible at δ 37.0 (t), 45.7 (d), 73.8 (t), 83.4 (d), 107.2 (d), 107.8 (d), 117.1 (t), 119.8 (d), 134.7 (s), 137.2 (d); MS (CI^+, NH_3) *m/z* 386 ($[M + NH_4]^+$, 58), 369 ($[M + H]^+$, 12), 351 (3), 247 (29), 218 (19), 151 (64), 149 (100); HRMS (CI^+, NH_3) for $[M + H]^+$ found 369.1696, $C_{22}H_{25}O_5$ requires 369.1702.

5-[(3*SR*,4*SR*,5*RS*)-5-(3-Methoxyphenyl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (8r). Prepared according to the general procedure above, yield 13.9 mg, 74%, 82:18 inseparable mixture of **8r**/**9r**: IR (film, cm^{-1}) 3075, 1640, 1603; ^1H NMR (signals for **8r**, 400 MHz, $CDCl_3$) δ 2.35 (1H, m), 2.42 (1H, dd, *J* 13.0, 10.0), 2.77 (1H, apparent q, *J* 8.5), 2.83 (1H, dd, *J* 13.0, 4.0), 3.66 (1H, apparent t, *J* 8.5), 3.79 (3H, s), 4.24 (1H, dd, *J* 8.5, 7.0), 4.94 (1H, dd, *J* 9.5, 2.5), 5.01 (1H, dd, *J* 17.0, 2.5), 5.10 (1H, ddd, *J* 17.0, 9.5, 9.0), 5.13 (1H, d, *J* 8.0), 5.93 (2H, s), 6.60 (1H, dd, *J* 8.0, 1.5), 6.63 (1H, d, *J* 1.5), 6.73 (1H, d, *J* 8.0), 6.74−6.78 (3H, m), 7.21 (1H, apparent td, *J* 8.5, 1.0); signals for minor isomer **9r** visible at δ 3.81 (3H, s), 3.81 (1H, apparent t, *J* 8.0), 4.05 (1H, dd, *J* 8.5, 7.0), 4.61 (1H, d, *J* 9.0), 4.98 (1H, ddd, *J* 17.0, 1.5, 0.5), 5.77 (1H, ddd, *J* 17.0, 10.0, 8.5), 5.93 (2H, s), 6.72 (1H, d, *J* 8.0), 6.90 (2H, m); ^{13}C NMR (signals for **8r**, 75 MHz, $CDCl_3$) δ 37.1 (t), 45.7 (d), 54.8 (d), 55.2 (q), 73.8 (t), 83.4 (d), 100.9 (t), 108.2 (d), 109.0 (d), 112.2 (d), 112.3 (d), 117.0 (t), 119.0 (d), 121.4 (d), 128.9 (d), 134.0 (s), 137.1 (d), 142.3 (s), 145.9 (s), 147.7 (s), 159.4 (s); signals for minor isomer **9r** visible at δ 37.5 (t), 48.2 (d), 59.4 (d), 73.4 (t), 85.6 (d), 111.2 (d), 112.9 (d), 118.1 (t), 129.3 (d), 136.8 (d), 143.4 (s), 159.6 (s); MS (CI^+, NH_3) *m/z* 356 ($[M + NH_4]^+$, 100), 339 ($[M + H]^+$, 52), 321 (13), 202 (11), 135 (21); HRMS (CI^+, NH_3) for $[M + H]^+$ found 339.1596, $C_{21}H_{23}O_4$ requires 339.1596.

5-[(3*SR*,4*SR*,5*RS*)- and 5-[(3*SR*,4*SR*,5*SR*)-5-(4-Dimethylaminophenyl)-4-vinyltetrahydrofuran-3-ylmethyl]-benzo[1,3]dioxole (8s and 9s). Prepared according to the general procedure above, yield 14.3 mg, 67%, 57:43 inseparable mixture of **8s**/**9s**: IR (film, cm^{-1}) 3075, 2972, 1640, 1615; ^1H NMR (both diastereoisomers, asterisk denotes signal for minor isomer **9s**), 500 MHz, $CDCl_3$) δ 2.33−2.50 (2.4H, m, 3′-H), 2.72 (0.6H, apparent q, *J* 9.0), 2.80−2.91 (1H, m), 2.93 (3.6H, s), 2.94* (2.4H, s), 3.63 (0.6H, apparent t, *J* 8.5), 3.80* (0.4H, apparent t, *J* 8.0), 4.01* (0.4H, dd, *J* 8.0, 7.0), 4.22 (0.6H, dd, *J* 8.0, 6.5), 4.54* (0.4H, d, *J* 9.0), 4.94 (0.6H, dd, *J* 10.0, 2.0), 4.97* (0.4H, ddd, *J* 17.0, 2.0, 0.5), 5.00 (0.6H, dd, *J* 17.0, 2.0), 5.07* (0.4H, dd, *J* 10.5, 2.0), 5.09 (0.6H, d, *J* 8.5), 5.15 (0.6H, apparent dt, *J* 17.0, 9.5), 5.74* (0.4H, ddd, *J* 17.0, 10.0, 8.5), 5.93* (0.8H, s), 5.93 (1.2H, s), 6.60 (0.6H, dd, *J* 8.0, 1.5), 6.61* (0.4H, dd, *J* 8.0, 1.5), 6.64 (0.6H, d, *J* 1.5), 6.65* (0.4H, d, *J* 1.5), 6.68−6.74 (3H, m), 7.05 (1.2H, d, *J* 8.5), 7.20* (0.8H, d, *J* 9.0); ^{13}C NMR (both diastereoisomers, asterisk denotes signal for minor diastereoisomer, 125 MHz, $CDCl_3$) δ 37.2 (t), 37.8* (t), 40.8 (q), 45.8 (d), 48.0* (d), 55.1 (d), 58.8* (d), 73.0* (t), 73.7 (t), 83.6 (d), 86.0* (d), 100.9 (t), 108.2 (d), 109.1 (d), 112.2 (d), 112.6* (d), 116.7 (t), 117.6* (t), 121.5 (d), 127.1* (d), 127.5 (d), 128.7 (s), 129.2* (s), 134.2* (s), 134.3 (s), 137.0* (d), 137.6 (d), 145.9 (s), 147.7 (s), 149.7 (s), 150.2* (s) [38C expected, 31C seen]; MS (CI^+, NH_3) *m/z* 352 ($[M + H]^+$, 100); HRMS (CI^+, NH_3) for $[M + H]^+$ found 352.1913, $C_{22}H_{26}NO_3$ requires 352.1913.

5-[(3*SR*,4*SR*,5*RS*)- and 5-[(3*SR*,4*SR*,5*RS*)-5-(Benzo[1,3]-dioxol-5-yl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo-[1,3]dioxole (8i and 9i). Cyclic allylsilane **3a** (56.4 mg, 0.204 mmol) was reacted with piperonal in the presence of boron trifluoride diethyl etherate according to the general procedure described above, but employing 0.91 equiv each of $BF_3{\cdot}OEt_2$ and piperonal in place of the usual 1.0 equiv. Purification by flash chromatography (10% Et_2O in hexane) yielded tetrahydrofurans **8i** and **9i** as a colorless oil (9.8 mg, 71%, 50:50 inseparable mixture of **8i** and **9i**).

5-[(3*SR*,4*SR*,5*RS*)- and 5-[(3*SR*,4*SR*,5*RS*)-5-(4-Methoxyphenyl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo-[1,3]dioxole (8j and 9j). Cyclic allylsilane **3a** (10.0 mg, 0.036 mmol) was reacted with *p*-anisaldehyde in the presence of boron trifluoride diethyl etherate according to the general procedure described above, but employing 0.91 equiv each of $BF_3{\cdot}OEt_2$ and *p*-anisaldehyde in place of the usual 1.0 equiv. Purification by flash chromatography (10% Et_2O in hexane)

yielded tetrahydrofurans **8j** and **9j** as a colorless oil (8.2 mg, 67%, 39:61 inseparable mixture of **8j** and **9j**).

5-[(3*SR*,4*SR*,5*RS*)-5-(Benzo[1,3]dioxol-5-yl)-4-vinyltetrahydrofuran-3-ylmethyl]benzo[1,3]dioxole (8i). To a solution of cyclic allylsilane **3a** (24.7 mg, 0.089 mmol) in DCM (0.8 mL) at −78 °C was added trimethylsilyl trifluoromethanesulfonate (16.2 μL, 0.089 mmol). After 5 min, piperonal (13.4 mg, 0.089 mmol in 0.1 mL DCM) was added dropwise. The solution was stirred at −78 °C for 3 h before the addition of brine (3 mL) and Et_2O (7 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (3 × 3 mL). The combined organic phases were washed with water (8 mL), dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography (10% Et_2O in hexane) yielded tetrahydrofurans **8i** and **9i** as a colorless oil (22.9 mg, 73%, 90:10 inseparable mixture of **8i** and **9i**): IR (film, cm^{-1}) 3074, 3010, 2976, 1639, 1608; ^1H NMR (signals for **8i**, 400 MHz, $CDCl_3$) δ 2.32 (1H, m), 2.39 (1H, dd, *J* 13.0, 10.0), 2.72 (1H, apparent q, *J* 8.5), 2.82 (1H, dd, *J* 13.0, 4.0), 3.62 (1H, apparent t, *J* 8.5), 4.20 (1H, dd, *J* 8.5, 7.0), 4.95 (1H, dd, *J* 9.5, 2.5), 5.01 (1H, dd, *J* 17.0, 2.5), 5.07 (1H, d, *J* 8.0), 5.11 (1H, dt, *J* 17.0, 9.5), 5.93 (2H, s), 5.94 (2H, s), 6.59 (1H, dd, *J* 8.0, 1.5), 6.63 (1H, d, *J* 1.5), 6.64 (1H, dd, *J* 8.0, 1.5), 6.68 (1H, d, *J* 1.5), 6.73 (1H, d, *J* 8.0), 6.74 (1H, d, *J* 8.0); signals for minor isomer **9i** visible at δ 3.79 (1H, apparent t, *J* 8.5), 4.02 (1H, dd, *J* 8.5, 7.5), 4.52 (1H, d, *J* 9.0), 5.72 (1H, ddd, *J* 17.0, 10.0, 9.0); ^{13}C NMR (signals for **8i**, 75 MHz, $CDCl_3$) δ 37.1 (t), 45.7 (d), 55.0 (d), 73.8 (t), 83.4 (d), 100.9 (t, 2 coincident peaks), 107.2 (d), 107.8 (d), 108.3 (d), 109.0 (d), 117.2 (t), 119.8 (d), 121.5 (d), 134.0 (s), 134.7 (s), 137.1 (d), 146.0 (s), 146.5 (s), 147.4 (s), 147.7 (s) [21 C expected, 20 seen]; signals for minor isomer **9i** visible at δ 37.6 (t), 48.0 (d), 59.5 (d), 73.3 (t), 85.9 (d), 106.5 (d), 108.0 (d), 118.2 (t), 119.5 (d), 136.5 (d); MS (CI^+, NH_3) *m*/*z* 370 ($[M + NH_4]^+$, 100), 353 ($[M + H]^+$, 97), 335 (24), 231 (41), 202 (16), 149 (70), 135 (29); HRMS (CI^+, NH_3) for $[M + H]^+$ found 353.1398, $C_{21}H_{21}O_5$ requires 353.1389.

5-[(2*RS*,3*SR*,4*SR*)-4-Phenylmethyl-3-vinyltetrahydrofuran-2-yl]benzo[1,3]dioxole (8m). Cyclic allylsilane **3b** (22.4 mg, 0.096 mmol) was reacted with piperonal in the presence of trimethylsilyl trifluoromethanesulfonate according to the procedure described above. Purification by flash chromatography (5% Et_2O in hexane) yielded tetrahydrofurans **8m** and **9m** as a colorless oil (21.9 mg, 74%, 93:7 inseparable mixture of **8m** and **9m**): IR (film, cm^{-1}) 3074, 3026, 2976, 1640, 1604; ^1H NMR (signals for **8m**, 400 MHz, $CDCl_3$) δ 2.40 (1H, m), 2.49 (1H, dd, *J* 13.5, 10.0), 2.76 (1H, apparent q, *J* 9.0), 2.92 (1H, dd, *J* 13.5, 4.0), 3.66 (1H, dd, *J* 9.0, 8.5), 4.21 (1H, dd, *J* 8.5, 7.5), 4.97 (1H, dd, *J* 9.5, 2.5), 5.03 (1H, dd, *J* 17.0, 2.5), 5.09 (1H, d, *J* 8.0), 5.14 (1H, dt, *J* 17.0, 9.5), 5.94 (2H, s), 6.65 (1H, dd, *J* 8.0, 1.5), 6.70 (1H, d, *J* 1.5), 6.74 (1H, d, *J* 8.0), 7.15 (2H, dd, *J* 7.5, 1.5), 7.20−7.32 (3H, m); signals for minor isomer **9m** visible at δ 3.82 (1H, apparent t, *J* 8.5), 4.03 (1H, dd, *J* 8.5, 7.5), 4.54 (1H, d, *J* 9.0), 5.74 (1H, ddd, *J* 17.0, 10.5, 9.0); ^{13}C NMR (signals for **8m**, 75 MHz, $CDCl_3$) δ 37.4 (t), 45.6 (d), 55.1 (d), 73.9 (t), 83.4 (d), 100.9 (t), 107.2 (d), 107.8 (d), 117.2 (t), 119.8 (d), 126.3 (d), 128.5 (d), 128.9 (d), 134.7 (s), 137.1 (d), 140.3 (s), 146.5 (s), 147.4 (s); signals for minor isomer **9m** visible at δ 37.9 (t), 47.8 (d), 59.6 (d), 73.4 (t), 85.9 (d), 106.5 (d), 108.0 (d), 118.2 (t), 119.5 (d), 135.5 (s), 136.6 (d); MS (CI^+, NH_3) *m*/*z* 326 ($[M + NH_4]^+$, 100), 309 ($[M + H]^+$, 97), 291 (30), 217 (3), 187 (9), 158 (8), 149 (50), 91 (8); HRMS (CI^+, NH_3) for $[M + H]^+$ found 309.1494, $C_{20}H_{21}O_3$ requires 309.1491.

(2*SR*,3*RS*,4*SR*)-(2-Benzo[1,3]dioxol-5-yl-4-benzo[1,3]-dioxol-5-ylmethyltetrahydrofuran-3-yl)methanol (13a). To a stirred solution of vinyl tetrahydrofurans **9i** and **8i** (15 mg, 0.043 mmol, 92:8 diastereoisomeric mixture) in THF (0.5 mL) were added successively water (50 μL), *N*-methylmorpholine *N*-oxide hydrate (8.1 mg, 0.060 mmol), and osmium tetraoxide (8 μL of a 4% solution in water, 2.5 mol %). The reaction mixture was stirred at room temperature for 15 h, whereupon water (2 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was dried (Na_2SO_4) and concentrated in vacuo. The resulting crude diol was taken up in methanol (0.4 mL) and cooled to 0 °C, and a solution of sodium metaperiodate (10.9 mg, 0.051 mmol) in methanol−water (10:3, 0.82 mL) was added dropwise over 5 min. The resulting white suspension was warmed to room temperature and stirred for a further 70 min, whereupon the mixture was filtered and the solid was washed with CH_2Cl_2 (2 mL). The filtrate was diluted with CH_2Cl_2 (5 mL), and water (3 mL) was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (4 × 4 mL). The combined organic phases were combined, dried (Na_2SO_4), and concentrated in vacuo. The resulting crude aldehyde was taken up in CH_2Cl_2 (0.4 mL), and a solution of sodium borohydride (2.0 mg, 0.053 mmol) in methanol (0.2 mL) was added dropwise. The reaction mixture was stirred at room temperature for a further 30 min, whereupon water (1 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 3 mL). The combined organic phase was dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (50% Et_2O in hexane) yielded compound **13a** as a colorless oil (13 mg, 93% based upon isomeric content of starting material): IR (film, cm^{-1}) 3425 (br, OH), 1608; ^1H NMR (400 MHz, $CDCl_3$) δ 1.95 (1H, ddt, *J* 8.0, 7.0, 5.5), 2.45 (1H, apparent sextet, *J* 7.0), 2.66 (1H, dd, *J* 13.5, 8.5), 2.77 (1H, dd, *J* 13.5, 7.0), 3.62 (2H, d, *J* 5.5), 3.82 (1H, dd, *J* 8.5, 6.0), 3.94 (1H, dd, *J* 8.5, 7.5), 4.59 (1H, d, *J* 8.0), 5.93 (2H, s), 5.96 (2H, s), 6.62 (1H, dd, *J* 8.0, 1.5), 6.67 (1H, d, *J* 1.5), 6.73 (1H, d, *J* 8.0), 6.77 (1H, d, *J* 8.0), 6.83 (1H, dd, *J* 8.0, 1.5), 6.90 (1H, d, *J* 1.5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5 (t), 44.2 (d), 55.7 (d), 62.8 (t), 73.1 (t), 84.1 (d), 101.0 (t), 101.1 (t), 106.7 (d), 108.2 (d), 108.4 (d), 109.1 (d), 119.7 (d), 121.6 (d), 134.0 (s), 136.1 (s), 146.0 (s), 147.1 (s), 147.8 (s), 148.0 (s); MS (EI^+) *m*/*z* 356 (M^+, 74), 135 (100); HRMS (EI^+) for $[M]^+$ found 356.1248, $C_{20}H_{20}O_6$ requires 356.1260.

(2*SR*,3*RS*,4*SR*)-[4-Benzo[1,3]dioxol-5-ylmethyl-2-(3,4-dimethoxyphenyl)tetrahydrofuran-3-yl]methanol (13b). Vinyl tetrahydrofurans **9k** and **8k** (4.7 mg, 0.013 mmol, 90:10 diastereoisomeric mixture) were transformed to the corresponding hydroxymethyl tetrahydrofurans according to the procedure described above. Purification by flash chromatography (gradient 60% Et_2O in hexane to neat Et_2O) yielded compound **13b** as a colorless oil (4.1 mg, 96% based upon isomeric content of starting material): IR (film, cm^{-1}) 3444 (br, OH), 1608; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (1H, t, *J* 5.0), 2.00 (1H, ddt, *J* 8.0, 7.0, 5.5), 2.47 (1H, apparent sextet, *J* 7.0), 2.67 (1H, dd, *J* 13.5, 8.5), 2.78 (1H, dd, *J* 13.5, 7.0), 3.64 (2H, d, *J* 5.5), 3.84 (1H, dd, *J* 8.5, 6.0), 3.88 (3H, s), 3.91 (3H, s), 3.97 (1H, dd, *J* 8.5, 7.5), 4.63 (1H, d, *J* 8.0), 5.93 (2H, s), 6.61 (1H, dd, *J* 8.0, 1.5), 6.67 (1H, d, *J* 1.5), 6.73 (1H, d, *J* 8.0), 6.84 (1H, d, *J* 8.0), 6.92 (1H, dd, *J* 8.0, 2.0), 6.94 (1H, d, *J* 2.0); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.5 (t), 44.2 (d), 55.4 (d), 55.9 (q), 56.0 (q), 63.0 (t), 73.0 (t), 84.0 (d), 100.9 (t), 108.3 (d), 109.1 (d), 109.4 (d), 111.1 (d), 118.5 (d), 121.6 (d), 134.0 (s), 134.6 (s), 146.0 (s), 147.8 (s), 148.6 (s), 149.2 (s); MS (EI^+) *m*/*z* 372 (M^+, 65), 135 (100); HRMS (EI^+) for $[M]^+$ found 372.1582, $C_{21}H_{24}O_6$ requires 372.1573.

(2*SR*,3*RS*,4*SR*)-[2-Benzo[1,3]dioxol-5-yl-4-(3,4-dimethoxyphenylmethyl)tetrahydrofuran-3-yl]methanol (13c). Vinyl tetrahydrofurans **9p** and **8p** (5.1 mg, 0.014 mmol, 91:9 diastereoisomeric mixture) were transformed to the corresponding hydroxymethyl tetrahydrofurans according to the procedure described above. Purification by flash chromatography (gradient 60% to 70% Et_2O in hexane) yielded compound **13c** as a colorless oil (4.5 mg, 96% based upon isomeric content of starting material): IR (film, cm^{-1}) 3450 (br, OH), 3006, 1608; ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (1H, br s), 1.96 (1H, ddt, *J* 8.0, 7.0, 5.5), 2.50 (1H, apparent sextet, *J* 7.0), 2.70 (1H, dd, *J* 13.5, 8.5), 2.79 (1H, dd, *J* 13.5, 7.0), 3.63 (2H, d, *J* 5.5), 3.84 (1H, dd, *J* 8.5, 6.0), 3.86 (3H, s), 3.87 (3H, s), 3.95 (1H, dd, *J* 8.5, 7.5), 4.60 (1H, d, *J* 8.0), 5.95 (2H, s), 6.68 (1H, d, *J* 1.5), 6.71 (1H, dd, *J* 8.0, 1.5), 6.77 (1H, d, *J* 8.0), 6.79 (1H, d, *J* 8.0),

6.83 (1H, dd, *J* 8.0, 1.5), 6.90 (1H, d, *J* 1.5); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.4 (t), 44.2 (d), 55.8 (q), 56.0 (d & q, 2 coincident peaks), 62.9 (t), 73.1 (t), 84.1 (d), 101.1 (t), 106.7 (d), 108.2 (d), 111.3 (d), 112.0 (d), 119.7 (d), 120.7 (d), 132.8 (s), 136.2 (s), 147.1 (s), 147.6 (s), 148.0 (s), 149.0 (s) (21C expected, 20 seen); MS (EI$^+$) *m*/*z* 372 (M^+, 89), 151 (100); HRMS (EI$^+$) for $[M]^+$ found 372.1579, $C_{21}H_{24}O_6$ requires 372.1573.

(2*RS*,3*RS*,4*SR*)-(2-Benzo[1,3]dioxol-5-yl-4-benzo[1,3]-dioxol-5-ylmethyltetrahydrofuran-3-yl)methanol (14a). Vinyl tetrahydrofurans **8i** and **9i** (21.7 mg, 0.062 mmol, 50:50 diastereoisomeric mixture) were transformed to the corresponding hydroxymethyl tetrahydrofurans according to the procedure described above. Purification by flash chromatography (50% Et_2O in hexane) yielded compound **14a** as a colorless oil (10.8 mg, 99% based upon isomeric content of starting material): IR (film, cm^{-1}) 3433 (br, OH), 1608; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (1H, apparent quintet, *J* 6.5, 3-H), 2.44 (1H, apparent sextet, *J* 7.0, 4-H), 2.64 (1H, dd, *J* 14.0, 8.5, 5″-CH_aH), 2.82 (1H, dd, *J* 14.0, 6.5, 5″-CHH_b), 3.29 (2H, d, *J* 6.5, CH_2OH), 3.57 (1H, dd, *J* 8.5, 8.0, 5-H_aH), 4.18 (1H, dd, *J* 8.5, 7.5, 5-HH_b), 5.03 (1H, d, *J* 7.0, 2-H), 5.94 (2H, s, OCH_2O), 5.95 (2H, s, OCH_2O), 6.65 (1H, dd, *J* 8.0, 1.5, 6″-H), 6.69 (1H, d, *J* 1.5, 4″-H), 6.74 (1H, d, *J* 8.0, 7″-H), 6.78−6.79 (2H, m, 7′-H & 4′-H or 6′-H), 6.82 (1H, apparent s, 6′-H or 4′-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9 (t), 43.5 (d), 51.1 (d), 62.5 (t), 73.2 (t), 81.9 (d), 101.0 (t), 101.1 (t), 106.8 (d), 108.4 (d, 2 coincident signals), 109.1 (d), 119.2 (d), 121.6 (d), 133.3 (s), 133.8 (s), 146.1 (s), 147.0 (s), 147.8 (s), 147.9 (s) [20C expected, 19C seen]; MS (EI$^+$) *m*/*z* 356 (M^+, 90), 135 (100); HRMS (EI$^+$) for $[M]^+$ found 356.1251, $C_{20}H_{20}O_6$ requires 356.1260.

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Supporting Information Available: Experimental procedures and compound data for alcohols **7a**−**d** and NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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