# Selective Prins Reaction of Styrenes and Formaldehyde Catalyzed by 2,6-Di-*tert*-butylphenoxy(difluoro)borane

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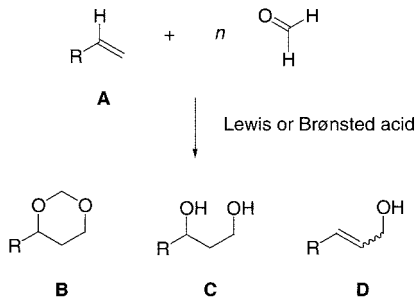
Dedicated to Professor George A. Olah on the occasion of his 75th birthday.

**Abstract:** The sterically congested Lewis acid **1** was used as a catalyst in the Prins reaction of various styrenes and formaldehyde. 4-Aryl-1,3-dioxanes **5** were selectively formed as the exclusive products of the reaction with styrenes **4a**–**i** and vinylthiophenes **4j**–**k**. The reaction proceeded in most cases with good to excellent yields (55–99%). Styrenes which carried a strongly electron-withdrawing group (CN, $CO_2Me$) did not react. The reaction with β-alkylstyrenes **6** was successful for the methyl substituted substrate **6a** and yielded (88%) *trans*-5-methyl-4-phenyl-1,3-dioxane (**7a**) preferentially (dr = 75:25). For steric reasons, other β-alkylstyrenes **6b**–**d** did not react. The remarkable stereodiscrimination attained by catalyst **1** was employed in the regioselective transformation of 4-propenylstyrene (**10**) to dioxane **11** (83% yield).

**Keywords:** carbocations, catalysis, chemoselectivity, electrophilic additions, Lewis acids

The Prins reaction[1,2] of alkenes **A** and formaldehyde can proceed to a variety of products depending on the reaction conditions (Scheme 1). Major products commonly observed include 1,3-dioxanes **B**, 1,3-diols **C** and allylic alcohols **D**. Homoallylic alcohols are also accessible from the same starting materials but they are often formed by a mechanistically different pathway (carbonyl-ene reaction).[3] Additional side reactions may further complicate the outcome of the reaction. In particular, a polymerization of the olefin which is induced by Lewis or Brønsted acids can severely interfere with the desired C–C-bond formation.




**Scheme 1**

We became interested in the Prins reaction because of its high synthetic versatility.[4] A double bond functionalization can be nicely combined with a C–C-bond formation in a single step provided there is a significant type selectivity for either product **B**, **C** or **D**. At least one stereogenic center is formed in the course of the reaction to **B** or **C**.[5]

Our major focus was to find suitable conditions for the conversion of styrenes to the corresponding 1,3-dioxanes. Ideally, we looked for a catalytic reaction system with the Lewis acid[6] being used in substoichiometric amounts.[7] Preliminary studies with $BF_3$ as the Lewis acidic catalyst and styrene as the alkene under various conditions revealed that the chemoselectivity of the $BF_3$-catalyzed reaction was not sufficient. Yields remained under 50% and many side reactions were observed. In search of less active, but more selective catalysts, we considered the use of sterically congested alkoxy- and aryloxyboron halides.[8] Recent synthetic studies by Meller et al.[9] had provided several boron compounds, e.g. **1**–**3** (Figure 1), which appeared interesting Lewis acids for our purpose. Whereas diaryloxyboron fluoride **2** and dialkoxyboron fluoride **3** turned out to be not sufficiently reactive the aryloxyboron difluoride **1** was found well suited to catalyze the Prins reaction of styrenes. Details of the reactions conducted by us are reported in this account.

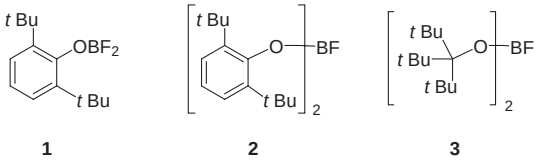



**Figure 1** Sterically congested Lewis acids[9] with a boron atom as the Lewis acidic center

Catalyst **1** is a liquid which can be purified by distillation in vacuo. It can be stored at –30 °C for several weeks without loosing its catalytic activity. Optimized reaction conditions which we used in all Prins reaction experiments included the use of paraformaldehyde [$(CH_2O)_n$] as the formaldehyde source and 1,4-dioxane as the solvent. A catalyst loading of 10 mol% turned out to be ideal. The use of a lower catalyst/substrate ratio (5 mol%) led to longer reaction times or to incomplete conversion. The selectivity (type selectivity and chemoselectivity) of the catalyzed reaction is remarkable. In all instances, the styrenes **4** were converted exclusively to the 1,3-dioxanes

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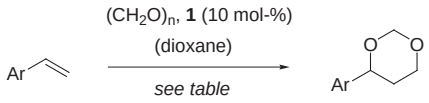
**5** (Scheme 2). Other side products were not observed. The reaction temperature had to be adjusted depending on the substituent on the styrenes (Table 1). The parent compound **4a** reacted at 80 °C and gave the corresponding dioxane **5a** in 95% yield. Electron-donating substituents with a negative Hammett constant[10] [**4b**, $\sigma_p$ (Me) = –0.14, **4c**, $\sigma_p$ (OMe) = –0.28] facilitated reactions at lower temperature. The reactive vinylthiophenes **4j** and **4k** also reacted under milder conditions (75 °C) and yielded the hitherto unknown 1,3-dioxanes **5j** and **5k**. Styrenes substituted with an electron-withdrawing group reacted less readily and required higher reaction temperatures. Reactions which were conducted at 100 °C with the *para*-substituted styrenes **4d** and **4i** [**4d**, $\sigma_p$ (Cl) = 0.22, **4i**, $\sigma_p$ (OAc) = 0.18] serve as examples.



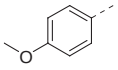
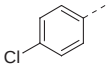
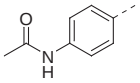
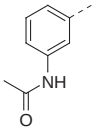
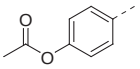

**4** **5**

**Scheme 2**

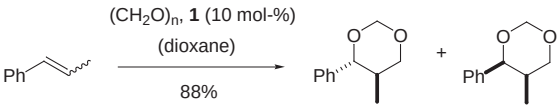
Varying the location of the chlorine substituents in the chlorostyrenes **4d–f** showed that an *ortho*-substituent does not significantly alter the outcome of the reaction. Both 2- (**4f**) and 4-chlorostyrene (**4d**) reacted smoothly to give the corresponding products in good yields. The lower reactivity of the *meta*-compound **4e** is attributed to the higher electron acceptor power of chlorine in *meta*-position [$\sigma_m$ (Cl) = 0.37]. Indeed, it appears as if the reactivity of the electrophile, which is presumably a formaldehyde-Lewis acid ($H_2CO$·**1**) complex, is sufficient to attack styrenes, the substituents of which exhibit a Hammett constant $\sigma \leq 0.40$. More deactivating substituents prohibit the reaction completely. Accordingly, 4-cyano [$\sigma_p$ (CN) = 0.71] and 4-methoxycarbonylstyrene [$\sigma_p$ ($CO_2$Me) = 0.44] did not react. It is unlikely that the failure of these reactions is due to a deactivation of the Lewis acid by carbonyl complexation as other esters **4i** and even amides **4g**, **4h** did react. Along these lines, the unsuccessful attempt to convert 4-vinylpyridine to its 1,3-dioxane derivative is easy to understand.

1-Phenylprop-1-ene (**6a**)[11] underwent a stereoselective Prins reaction under the typical reaction conditions. The *trans*-1,3-dioxane **7a** was formed in excess relative to the *cis*-isomer **8a** (dr = 75:25) (Scheme 3). The reaction proceeded not stereospecifically but in a stereoconvergent fashion, i.e. the diastereomeric ratio was not dependent on the configuration of the styrene. Experiments conducted with pure *trans*-**6a** and with a *cis*/*trans*-mixture resulted in identical yields and diastereoselectivities. The diastereoselectivity is higher than previously observed for the analogous Prins reaction promoted by Brønsted acids.[12] Depending on the acid and the reaction conditions diastereomeric ratios of dr = 64:36 to 37:63 have been reported.

**Table 1** Substitution Pattern, Reaction Conditions and Yields for the Conversion of Styrenes **4** to the Corresponding 1,3-Dioxanes **5** with Paraformaldehyde in Dioxane as the Solvent

| Substrate | Ar | Temp (°C) | Time (h)[a] | Product | Yield (%)[b] |
|---|---|---|---|---|---|
| **4a** |  | 80 | 12 | **5a** | 95 |
| **4b** |  | 80 | 12 | **5b** | 97 |
| **4c** |  | 70 | 8 | **5c** | 65 |
| **4d** |  | 100 | 24 | **5d** | 88 |
| **4e** |  | 110 | 48 | **5e** | 55 |
| **4f** |  | 110 | 48 | **5f** | 81 |
| **4g** |  | 80 | 12 | **5g** | 56 |
| **4h** |  | 110 | 24 | **5h** | 35 |
| **4i** |  | 100 | 12 | **5i** | 99 |
| **4j** |  | 75 | 12 | **5j** | 80 |
| **4k** |  | 75 | 6 | **5k** | 67 |

[a] Period of time after which the reaction was complete.
[b] Yield of isolated product after chromatographic purification.




**6a** d.r. = 75/25 **7a** **8a**

**Scheme 3**

The diastereomerically pure 1,3-dioxane **7a** was subjected to the typical Prins reaction conditions. An equilibration to compound **8a** was not observed. We therefore conclude that the products are formed in a kinetically controlled reaction, which proceeds irreversibly to the two diastereoisomers. A possible explanation for the preference in favor of **7a** is based on the generally accepted mechanism

of the Prins reaction. Accordingly, the styrene is attacked by an activated formaldehyde molecule (complex $H_2CO$·**1**) in the first reaction step. As a cyclization to a four-membered oxetane is disfavored, a second formaldehyde molecule is incorporated leading to a 1,3-dioxane. In the case of compound **6a**, a potential cyclization precursor is the chiral carbenium ion **9a**. The two faces of the carbenium ion are diastereotopic due to the adjacent stereogenic center. A differentiation results from the size difference of the hydrogen atom and the methyl group. The hydrogen atom adopts the pseudoaxial position in the transition state of the cyclization as depicted in Figure 2. The hypothesis of a carbenium ion intermediate is in line with the observed stereoconvergency of the reaction.

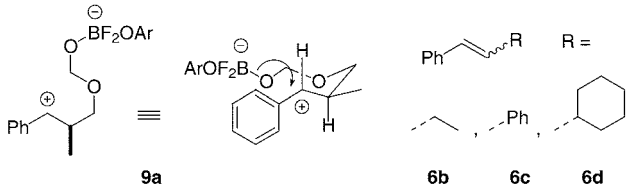
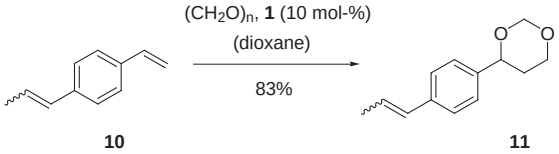



**Figure 2** Putative intermediate **9a** en route to the formation of compound **7a** and other β-alkylstyrenes **6b**–**d**

Due to the steric bulk of the Lewis acid **1**, a potential electrophilic complex $H_2CO$·**1** is sensitive towards the substitution pattern in β-substituted styrenes. Whereas 1-phenylprop-1-ene (**6a**)[11] showed reasonable reactivity (vide supra) other styrenes **6b**–**d** (Figure 2) did not react at all. In this respect, the Lewis acid allows for a differentiation between a methyl and an ethyl substituted styrene. Since compound **6a** reacted already significantly slower than the unsubstituted parent styrene (**4a**) we attempted a differentiation in a bifunctional substrate. To this end, compound **10** was prepared[13] as a mixture of diastereoisomers (*cis*/*trans* = 36:64). Upon subjecting this bifunctional substrate to the catalytic reaction conditions (Scheme 4) at 80 °C dioxane **11** was the exclusive reaction product (diastereomeric mixture, *cis*/*trans* = 36:64). The result supports the high selectivity, which can be achieved with Lewis acid **1**.




**Scheme 4**

In summary, the boron compound **1** was found to be an effective and selective catalyst for the Prins reaction of several styrenes. Due to its steric bulk, the catalyst allows for a decent diastereoselectivity and a remarkable site-selectivity in this reaction. Possible applications of these selectivities are currently studied more closely. In addition, chiral analogues of compound **1** are being prepared to evaluate enantioselective variants of the Prins reaction.

All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. All experiments were performed in Fluka p.a. solvents. The styrenes were either commercially available or they were prepared according to known protocols: acetamidostyrenes **4g**/**h**,[14] vinylthiophenes **4j**/**k**.[15] Common solvents for chromatography [$Et_2O$, pentane (P), EtOAc] were distilled prior to use. TLC was performed on aluminum sheets (0.2 mm silica gel 60 $F_{254}$) with detection by UV (254 nm) or by coloration with ceric ammonium molybdate (CAM). Flash chromatography[16] was performed on silica gel 60 (Merck, 230–400 mesh) (ca. 50 g for 1 g of material to be separated) with the indicated eluent. Melting points (uncorrected): Reichert hot bench. IR: Perkin Elmer 1600 FT-IR. MS: Varian CH7 (EI). HRMS: Finnigan MAT 95S or MAT 8200. GC-MS: Agilent 6890 (GC system), Agilent 5973 (Mass selective detector). $^1$H and $^{13}$C NMR: Bruker AMX-250 and AV-360. $^1$H and $^{13}$C NMR spectra were recorded at 303 K. Chemical shifts are reported relative to tetramethylsilane as an internal reference. The multiplicities of the $^{13}$C NMR signal were determined by DEPT experiments.

**Prins Reaction of Styrenes 4, 6a and 10; General Procedure**

A high pressure reaction vessel with gas inlet was charged with paraformaldehyde (0.45 g, 15.0 mmol), styrene **4**, **6a** or **10** (2.50 mmol) and 1,4-dioxane (20 mL). 2,6-Di-*tert*-butylphenoxy(difluoro)borane (**1**;[9] 0.13 mL, 0.25 mmol) was added under Ar. The mixture was heated for the time provided in Table 1 or in the corresponding paragraph (vide infra). After complete conversion, the reaction was quenched by the addition of $H_2O$ (10 mL) and the aqueous layer was extracted with $Et_2O$ (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried ($Na_2SO_4$), filtered and evaporated. The crude material was purified by flash chromatography to give the pure 1,3-dioxane.

**4-Phenyl-1,3-dioxane (5a)**

Yield: 0.39 g (95%); colorless oil; $R_f$ 0.30 (P–EtOAc, 95:5).

The analytical and spectral data were in full agreement with previously reported values.[17]

**4-(4-Methylphenyl)-1,3-dioxane (5b)**

Yield: 0.44 g (97%); colorless oil; $R_f$ 0.28 (P–EtOAc, 95:5).

The analytical and spectral data were in full agreement with previously reported values.[17]

**4-(4-Methoxyphenyl)-1,3-dioxane (5c)**

Yield: 0.31 g (65%), colorless solid; $R_f$ 0.12 (P–EtOAc, 95:5); mp 71 °C.

The analytical and spectral data were in full agreement with previously reported values.[17]

**4-(4-Chlorophenyl)-1,3-dioxane (5d)**

Yield: 0.44 g (88%); colorless oil; $R_f$ 0.26 (P–EtOAc, 95:5).

The analytical and spectral data were in full agreement with previously reported values.[17]

**4-(3-Chlorophenyl)-1,3-dioxane (5e)**

Yield: 0.27 g (55%), yellow oil; $R_f$ 0.17 (P–EtOAc, 95:5).

IR (film): 2920 (vs, $CH_{al}$), 2850 (s, $CH_{al}$), 1730 (w), 1650 (m, C=C), 1435 (m), 1365 (w), 1225 (s), 1175 (s), 1120 (m), 1030 (s), 785 $cm^{-1}$ (m).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.69–1.73 (m, 1 H, CHC*H*H), 1.98–2.09 (m, 1 H, CHCH*H*), 3.81–3.89 (m, 1 H, C*H*HO), 4.19 (dd, $^2J$ = 11.5 Hz, $^3J$ = 5.0 Hz, 1 H, CH*H*O), 4.61 (dd, $^3J$ = 11.4 Hz, $^3J$ = 2.5 Hz, 1 H, CH), 4.87 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.23 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.21–7.30 (m, 3 $H_{arom}$), 7.37 (s, 1 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 33.9 (t, CH*C*$H_2$), 66.7 (t, $CH_2O$), 77.8 (d, CH), 94.1 (t, $OCH_2O$), 123.7 (d, $CH_{arom}$), 126.0 (d, $CH_{arom}$), 127.9 (d, $CH_{arom}$), 129.7 (d, $CH_{arom}$), 134.4 (s, $C_{arom}$), 143.5 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 13.37 min): *m*/*z* (%) = 198 (12, $[M]^+$), 168 (5, $[M - CH_2O]^+$), 163 (2, $[M - Cl]^+$), 140 (100, $[M - (CH_2)_2OCH_2]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{10}H_{11}ClO_2$: 198.0448; found: 198.0446.

**4-(2-Chlorophenyl)-1,3-dioxane (5f)**
Yield: 0.40g (81%); colorless oil; $R_f$ 0.40 (P–EtOAc, 95:5).

IR (film): 2965 (w, $CH_{al}$), 2850 (s, $CH_{al}$), 1475 (m), 1370 (m), 1250 (m), 1175 (s), 1120 (s), 1025 (s), 985 (s), 755 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.84–1.94 (m, 2 H, CHC*H*$_2$), 3.86–3.93 (m, 1 H, C*H*HO), 4.15–4.20 (m, 1 H, CH*H*O), 4.92 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.03 (dd, $^3J$ = 9.6 Hz, $^3J$ = 3.9 Hz, 1 H, C*H*CH$_2$), 5.23 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.18–7.23 (m, 1 $H_{arom}$), 7.28–7.33 (m, 2 $H_{arom}$), 7.60 (dd, $^3J$ = 7.7 Hz, $^4J$ = 1.8 Hz, 1 $H_{arom}$).

$^{13}$C NMR (60.9 MHz, $CDCl_3$): δ = 32.7 (t, CH*C*$H_2$), 66.8 (t, $CH_2O$), 75.6 (d, CH), 94.2 (t, $OCH_2O$), 127.3 (d, 2 $CH_{arom}$), 128.6 (d, $CH_{arom}$), 129.2 (d, $CH_{arom}$), 131.1 (s, $C_{arom}$), 139.2 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 14.15 min): *m*/*z* (%) = 198 (7, $[M]^+$), 168 (4, $[M - CH_2O]^+$), 163 (2, $[M - Cl]^+$), 152 (48, $[M - OCH_2O]$), 140 (100, $[M - (CH_2)_2OCH_2]^+$), 117 (28, $[M - OCH_2O - Cl]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{10}H_{11}ClO_2$: 198.0448; found: 198.0447.

**4-(4-Acetamidophenyl)-1,3-dioxane (5g)**
Yield: 0.31 g (56%); colorless solid; $R_f$ 0.28 (P–EtOAc, 3:7); mp 146 °C.

IR (KBr): 3310 (s, br, NH), 1685 (s, C=O), 1605 (s), 1540 (s), 1320 (s), 1170 (s), 1080 (s), 1020 (s), 970 (s, br), 835 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.68 (d, $^2J$ = 13.2 Hz, 1 H, CHC*H*H), 1.99–2.11 (m, 1 H, CHCH*H*), 2.14 (s, 3 H, $CH_3$), 3.82–3.89 (m, 1 H, C*H*HO), 4.18 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.60 (dd, $^3J$ = 11.4 Hz, $^3J$ = 2.3 Hz, 1 H, CH), 4.88 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.19 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.30 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$), 7.48 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$), 7.57 (s, 1 H, NH).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 24.6 (q, $CH_3$), 33.8 (t, CH*C*$H_2$), 66.9 (t, $CH_2O$), 78.3 (d, CH), 94.1 (t, $OCH_2O$), 119.9 (d, $CH_{arom}$), 126.4 (d, $CH_{arom}$), 137.2 (s, $C_{arom}$), 137.4 (s, $C_{arom}$), 168.5 (s, CO).

GC-MS (EI, 70 eV, $t_R$ 20.30 min): *m*/*z* (%) = 221 (31, $[M]^+$), 179 (5, $[M - C_2H_2O]^+$), 163 (43, $[CH_2O(CH_2)_2]^+$), 121 (100, $[M - C_2H_2O - CH_2O(CH_2)_2]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{12}H_{15}NO_3$: 221.1052; found: 221.1052.

**4-(3-Acetamidophenyl)-1,3-dioxane (5h)**
Yield: 0.20 g (35%); yellow solid; $R_f$ 0.36 (P–EtOAc, 3:7); mp 108 °C.

IR (KBr): 3300 (s, br, NH), 2930 (w, $CH_{al}$), 2860 (w, $CH_{al}$), 1665 (s, C=O), 1605 (s), 1560 (s), 1445 (s), 1375 (m), 1170 (s), 1030 (s), 780 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.69 (d, $^2J$ = 13.4 Hz, 1 H, CHC*H*H), 1.96–2.09 (m, 1 H, CHCH*H*), 2.13 (s, 3 H, $CH_3$), 3.79–3.87 (m, 1 H, C*H*HO), 4.16 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.59 (dd, $^3J$ = 11.1 Hz, $^3J$ = 2.0 Hz, 1 H, CH), 4.85 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.16 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.08 (d, $^3J$ = 7.5 Hz, 1 $H_{arom}$), 7.27 (dd, $^3J$ = 8.2 Hz, $^3J$ = 7.5 Hz, 1 $H_{arom}$), 7.44 (d, $^3J$ = 8.2 Hz, 1 $H_{arom}$), 7.52 (s, 1 $H_{arom}$), 7.72 (s, 1 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 24.4 (q, $CH_3$), 33.8 (t, CH*C*$H_2$), 66.8 (t, $CH_2O$), 78.3 (d, CH), 94.0 (t, $OCH_2O$), 117.2 (d, $CH_{arom}$), 119.2 (d, $CH_{arom}$), 121.4 (d, $CH_{arom}$), 129.0 (d, $CH_{arom}$), 138.2 (s, $C_{arom}$), 142.4 (s, $C_{arom}$), 168.5 (s, CO).

GC-MS (EI, 70 eV, $t_R$ 20.00 min): *m*/*z* (%) = 221 (19, $[M]^+$), 179 (16, $[M - C_2H_2O]^+$), 175 (23, $[M - C_2H_2O]^+$), 163 (25, $[M - CH_2O(CH_2)_2]^+$), 133 (38, $[M - CH_2O - CH_3CONH]^+$), 121 (100, $[M - C_2H_2O - CH_2O(CH_2)_2]^+$), 107 (9, $[C_7H_7O]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{12}H_{15}NO_3$: 221.1052; found: 221.1051.

**4-(4-Acetoxyphenyl)-1,3-dioxane (5i)**
Yield: 0.55 g (99%); yellow solid; $R_f$ 0.30 (P–EtOAc, 9:1); mp 75 °C.

IR (KBr): 2970 (m, $CH_{al}$), 2785 (w, $CH_{al}$), 1760 (vs, br, C=O), 1605 (m), 1500 (s), 1370 (s), 1190 (vs, br), 1080 (s), 1020 (s) 810 $cm^{-1}$ (m).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.68–1.73 (m, 1 H, CHC*H*H), 2.00–2.12 (m, 1 H, CHCH*H*), 2.28 (s, 3 H, $CH_3$), 3.82–3.89 (m, 1 H, C*H*HO), 4.18 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.63 (dd, $^3J$ = 11.1 Hz, $^3J$ = 2.5 Hz, 1 H, CH), 4.75 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.19 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.07 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$), 7.37 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$),

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 21.1 (q, $CH_3$), 33.9 (t, CH*C*$H_2$), 66.8 (t, $CH_2O$), 78.1 (d, CH), 94.1 (t, $OCH_2O$), 121.5 (d, $CH_{arom}$), 126.8 (d, $CH_{arom}$), 139.0 (s, $C_{arom}$), 150.1 (s, $C_{arom}$), 169.4 (s, C=O).

GC-MS (EI, 70 eV, $t_R$ 16.60 min): *m*/*z* (%) = 222 (11, $[M]^+$), 180 (80, $[M - C_2H_2O]^+$), 134 (21, $[M - C_2H_2O - OCH_2O]^+$), 122 (100, $[M - C_2H_2O - CH_2O(CH_2)_2]^+$), 107 (8, $[C_7H_7O]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{12}H_{14}O_4$: 222.0892; found: 222.0891.

**4-(3-Thiophenyl)-1,3-dioxane (5j)**
Yield: 0.34 g (80%); colorless oil; $R_f$ 0.26 (P–EtOAc, 95:5).

IR (film): 3105 (w), 2960 (m, sh, $CH_{al}$), 2850 (s, $CH_{al}$), 2775 (s, $CH_{al}$), 1365 (m), 1170 (s), 1115 (s), 1085 (s), 1030 (s), 990 (s), 840 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.72–1.79 (m, 1 H, CHC*H*H), 2.08–2.19 (m, 1 H, CHCH*H*), 3.79–3.87 (m, 1 H, C*H*HO), 4.17 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.73 (dd, $^3J$ = 11.1 Hz, $^3J$ = 2.5 Hz, 1 H, CH), 4.86 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.16 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 7.09 (dd, $^3J$ = 8.4 Hz, $^4J$ = 1.1 Hz, 1 $H_{arom}$), 7.22–7.24 (m, 1 $H_{arom}$), 7.29 (dd, $^3J$ = 5.0 Hz, $^4J$ = 3.0 Hz, 1 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 33.1 (t, CH*C*$H_2$), 66.7 (t, $CH_2O$), 74.9 (d, CH), 94.0 (t, $OCH_2O$), 121.2 (d, $CH_{arom}$), 125.6 (d, $CH_{arom}$), 126.1 (s, $CH_{arom}$), 142.5 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 11.90 min): *m*/*z* (%) = 170 (12, $[M]^+$), 140 (6, $[M - CH_2O]^+$), 124 (78, $[M - OCH_2O]^+$), 112 (90, $[M - (CH_2)_2OCH_2]^+$), 97 (15, $[C_5H_5S]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_8H_{10}O_2S$: 170.0402; found: 170.0398.

**4-(2-Thiophenyl)-1,3-dioxane (5k)**
Yield: 0.21 g (67%); colorless oil; $R_f$ 0.22 (P–EtOAc, 95:5).

IR (film): 3105 (w), 2960 (m, sh, $CH_{al}$), 2850 (s, $CH_{al}$), 1370 (s), 1165 (s), 1115 (s), 1085 (s), 1020 (s, br), 980 (s), 830 (m), 705 $cm^{-1}$ (s, br).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.82–1.87 (m, 1 H, CHC*H*H), 2.17–2.29 (m, 1 H, CHCH*H*), 3.81–3.88 (m, 1 H, C*H*HO), 4.19 (dd,

$^3J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.87–4.92 (m, 2 H, CH, OC*H*HO), 5.16 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 6.97–7.02 (m, 2 $H_{arom}$), 7.27 (dd, $^3J$ = 5.0 Hz, $^4J$ = 1.3 Hz, 1 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 33.8 (t, CH*C*$H_2$), 66.5 (t, $CH_2O$), 74.4 (d, CH), 94.0 (t, $OCH_2O$), 124.0 (d, $CH_{arom}$), 125.1 (d, $CH_{arom}$), 126.5 (d, $CH_{arom}$), 144.3 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 11.80 min): *m*/*z* (%) = 170 (49, $[M]^+$), 138 (20, $[M – S]^+$), 124 (72, $[M – OCH_2O]^+$), 112 (90, $[M – (CH_2)_2OCH_2]^+$), 97 (100, $[C_5H_5S]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_8H_{10}O_2S$: 170.0402; found: 170.0399.

**5-Methyl-4-phenyl-1,3-dioxane (7a/8a)**

The reaction was conducted according to the general procedure with compound **6a** as the starting material. In one run diastereomerically pure *trans*-**6a**[11] was used. In another run a *cis*/*trans*-mixture of compound **6a**[11] (dr = 52:48) was employed as the substrate. In both runs, the product (0.39 g, 88%) was obtained as a mixture of *cis*- and *trans*-isomers (dr = 25:75), which could be separated by flash chromatography; yield: 0.39 g (88%); colorless oil; $R_f$ 0.32 (**7a**), 0.31 (**8a**) (P–EtOAc, 95:5). The analytical data were in full agreement with previously reported values.[18]

**4-(4-Prop-1-enylphenyl)-1,3-dioxane (11)**

The reaction was conducted according to the general procedure with a *cis*/*trans*-mixture (dr = 36:64) of compound **10**.[13] The product (0.59 g, 83%) was obtained as a mixture of *cis*/*trans*-isomers (dr = 36:64) which were separated by flash chromatography.

*cis*-Isomer (*cis*-**11**)

Yellow oil; $R_f$ 0.28 (P–EtOAc, 95:5).

IR (film): 2960 (m, br, $CH_{al}$), 2850 (s, $CH_{al}$), 1515 (w), 1370 (m), 1245 (m), 1170 (s), 1115 (s), 1030 (vs), 985 (s), 845 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.70–1.74 (m, 1 H, CHC*H*H), 1.88 (dd, $^3J$ = 7.3 Hz, $^4J$ = 1.8 Hz, 3 H, $CH_3$), 2.05–2.15 (m, 1 H, CHCH*H*), 3.84–3.91 (m, 1 H, C*H*HO), 4.20 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.64 (dd, $^3J$ = 11.1 Hz, $^3J$ = 2.5 Hz, 1 H, CH), 4.90 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.21 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 5.79 (dq, $^3J$ = 11.6 Hz, $^3J$ = 7.3 Hz, 1 H, = CH), 6.42 (dd, $^3J$ = 11.6 Hz, $^4J$ = 1.8 Hz, 1 H, = C*H*$CH_3$), 7.29 (d, $^3J$ = 8.2 Hz, 2 $H_{arom}$), 7.33 (d, $^3J$ = 8.2 Hz, 2 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 14.6 (q, $CH_3$), 33.8 (t, CH*C*$H_2$), 66.9 (t, $CH_2O$), 78.6 (d, CH), 94.2 (t, $OCH_2O$), 125.6 (d, $CH_{arom}$), 127.0 (d, = CH), 128.9 (d, $CH_{arom}$), 129.5 (d, =CH), 137.2 (s, $C_{arom}$), 139.5 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 16.40 min): *m*/*z* (%) = 204 (54, $[M]^+$), 189 (2, $[M – CH_3]^+$), 174 (2, $[M – CH_2O]^+$), 158 (18, $[M – OCH_2O]^+$), 146 (100, $[M – CH_2O(CH_2)_2]^+$), 129 (35, $[M – CH_3 – 2CH_2O]^+$), 117 (58, $[M – OCH_2O – CH_3(CH)_2]^+$), 91 (27, $[C_7H_7]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1149.

*trans*-Isomer (*trans*-**11**)

Colorless crystals; $R_f$ 0.27 (P–EtOAc, 95:5); mp 37 °C.

IR (film): 2960 (m, br, $CH_{al}$), 2850 (s, $CH_{al}$), 1515 (w), 1370 (m), 1245 (m), 1170 (s), 1115 (s), 1030 (vs), 985 (s), 845 $cm^{-1}$ (s).

$^1$H NMR (360 MHz, $CDCl_3$): δ = 1.67–1.72 (m, 1 H, CHC*H*H), 1.88 (dd, $^3J$ = 6.6 Hz, $^4J$ = 1.6 Hz, 3 H, $CH_3$), 2.03–2.15 (m, 1 H, CHCH*H*), 3.82–3.90 (m, 1 H, C*H*HO), 4.20 (dd, $^2J$ = 11.4 Hz, $^3J$ = 4.8 Hz, 1 H, CH*H*O), 4.61 (dd, $^3J$ = 11.3 Hz, $^3J$ = 2.5 Hz, 1 H, CH), 4.88 (d, $^2J$ = 6.4 Hz, 1 H, OC*H*HO), 5.21 (d, $^2J$ = 6.4 Hz, 1 H, OCH*H*O), 6.24 (dq, $^3J$ = 15.7 Hz, $^3J$ = 6.6 Hz, 1 H, =CH), 6.40 (dd, $^3J$ = 15.7 Hz, $^4J$ = 1.6 Hz, 1 H, =C*H*$CH_3$), 7.29 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$), 7.33 (d, $^3J$ = 8.4 Hz, 2 $H_{arom}$).

$^{13}$C NMR (90.6 MHz, $CDCl_3$): δ = 18.5 (q, $CH_3$), 33.8 (t, CH*C*$H_2$), 66.9 (t, $CH_2O$), 78.6 (d, CH), 94.2 (t, $OCH_2O$), 125.9 (d, $CH_{arom}$; d, =CH; d, $CH_{arom}$), 130.6 (d, =CH), 137.6 (s, $C_{arom}$), 139.8 (s, $C_{arom}$).

GC-MS (EI, 70 eV, $t_R$ 58 (33, $[M – OCH_2O]^+$), 146 (100, $[M – CH_2O(CH_2)_2]^+$), 129 (35, $[M – CH_3 – 2CH_2O]^+$), 117 (52, $[M – OCH_2O – CH_3(CH)_2]^+$), 91 (22, $[C_7H_7]^+$).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1142.

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