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Direct Synthesis of Protected Arylacetaldehydes by Tetrakis(phosphane)-palladium-Catalyzed Arylation of Ethyleneglycol Vinyl Ether

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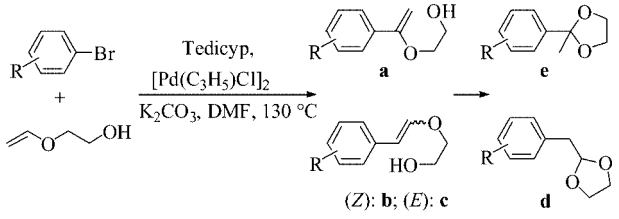
A range of aryl bromides undergo Heck reaction with ethylene glycol vinyl ether, in the presence of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphanyl)methyl]cyclopentane as catalyst, to give regioselectively protected arylacetaldehydes in good yields. The β-arylation products were obtained in with 93–100 % selectivity with electron-poor aryl bromides or heteroaryl bromides. Furthermore, this catalyst can be used at low loading, even for reactions with sterically hindered aryl bromides. The aryl vinyl ether intermediates undergo subsequent ketalisation to give the corresponding 2-benzyl-1,3-dioxolane derivatives.

Introduction

The palladium-catalysed functionalisation of aromatic halides with alkenes has become an important method in preparative organic chemistry.[1–6] As a C–C bond-forming process, the Heck arylation of alkenes inherently holds powerful synthetic potential if its regio- and stereoselectivity can be controlled.[7] Nevertheless, the arylation of electron-rich olefins such as enol ethers is often limited by poor α/β regioselectivity.[8–12] Highly α-regioselective arylations in the presence of *n*-butyl vinyl ether have been reported by Cabri et al. and Hallberg et al. in the presence of $Pd(OAc)_2$/dppp.[13–16] In some procedures, TlOAc was added in order to improve the regioselectivity of the reaction. The reaction performed in ionic liquids as solvent also leads selectively to α-arylation.[17] On the other hand, the use of poly(ethylene glycol) as solvent with $Pd(OAc)_2$ as catalyst leads selectively to the β-arylated products.[18] It has been demonstrated that the regioselectivity of the addition of organopalladium intermediates can be influenced by coordinating groups adjacent to the substrate double bond.[19–24] For example, Hallberg et al. have described that the nitrogen-containing vinyl ether [2-(dimethylamino)ethoxy]ethene undergoes regioselective β-arylation with several aryl halides in the presence of palladium acetate.[19,21] On the other hand, in the presence of ethylene glycol vinyl ether with $Pd(OAc)_2$/dppp as catalyst, they obtained selective α-arylations to give aryl vinyl ethers, which undergo subsequent ketalisation to form selectively the isomer **e** shown in Scheme 1.[24] Surprisingly, to the best of our knowledge, selective β-arylation in the presence of ethylene glycol vinyl ether has never been described.



Scheme 1.

In order to obtain stable and efficient palladium catalysts, we have prepared the tetrakis(phosphane) ligand *cis*,*cis*,*cis*-1,2,3,4-tetrakis[(diphenylphosphanyl)methyl]cyclopentane (Tedicyp;[25] Figure 1) in which four diphenylphosphanyl groups are stereospecifically bound to the same face of a cyclopentane ring. We have already reported the results obtained in allylic substitutions,[25] Suzuki cross-couplings[26] and Sonogashira alkynylations[27] with this ligand. We have also reported several results obtained for the Heck vinylation reaction:[28–39] we observed that *n*-butyl vinyl ether, in the presence of the tetrakis(phosphane) and $[Pd(C_3H_5)Cl]_2$, gave high reaction rates and moderate to good regioselectivities in favour of β-arylation,[30] although in many cases these selectivities were not high enough to provide a useful process for the preparation of arylacetaldehydes. The control of regioselectivity with the aid of interactions between substrate and catalyst is a continuing challenge in catalysis. In order to improve the selectivity of the reaction with vinyl ethers in favour of the β-addition with our catalyst, we decided to investigate arylation reactions with enol ethers containing a coordinating substitu-

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ent. We have already reported preliminary results with ethylene glycol vinyl ether and aryl bromides.[39] Here, we wish to describe the results obtained with alcohol-containing substrates derived from ethyl vinyl ether with a variety of aryl and heteroaryl halides using **1** as ligand.

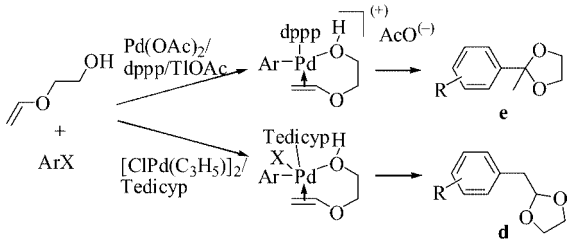
Figure 1. Structure of Tedicyp.

Results and Discussion

The Heck reaction between ethylene glycol vinyl ether and aryl bromides should lead to the three products **a**, **b** and **c** (Scheme 1). Attack on the substituted carbon atom of the vinyl ether would give product **a**, and attack on the terminal carbon atom products **b** and **c**. However, in the course of this reaction, we also observed the intramolecular cyclisation of these arylalkenols **a**–**c** (Scheme 1) to give the corresponding derivatives 2-benzyl-1,3-dioxolane (**d**) and 2-methyl-2-phenyl-1,3-dioxolane (**e**). This ketal formation is probably not palladium-catalysed, but arises through internal nucleophilic attack of the hydroxy group.[40,41]

First, we investigated the Heck reaction of 4-bromoacetophenone and 1-bromo-4-fluorobenzene with ethylene glycol vinyl ether in the presence of the system Pd/Tedicyp (Scheme 1, Table 1). The results show a strong influence of the reaction conditions on the regioselectivity and on the rate of the reaction. 4-Bromoacetophenone and ethylene glycol vinyl ether, with K_2CO_3 or Cs_2CO_3 as base, in DMF, give the isomer **1d** with high selectivity (93%; Table 1, Entries 1 and 2). Mixtures of isomers were obtained in the presence of NaOAc, Na_2CO_3, $NaHCO_3$ or KF (Table 1, Entries 3–6). Next, we studied the influence of the solvent (Table 1, Entries 7–11). High selectivities in favour of the formation of isomer **1d** were observed in NMP or DMAC. The reaction also proceeds in diglyme or xylene, but lower selectivities were observed. No reaction was observed when ethylene glycol was used. We then studied the selectivity using K_2CO_3 or Cs_2CO_3 as base and DMF, NMP or DMAC as solvent for the reaction with 1-bromo-4-fluorobenzene (Table 1, Entries 12–15). With this substrate, the best selectivity in favour of isomer **2d** (57%) was obtained with DMF and K_2CO_3 (Table 1, Entry 12).

In the presence of ethylene glycol vinyl ether and 4-bromobenzophenone with $Pd(OAc)_2$ (3%) and dppp (6%) as catalyst and NEt_3 and TlOAc in DMF, Hallberg et al. obtained selective α-arylation.[24] Under our reactions conditions {$[Pd(C_3H_5)Cl]_2$/Tedicyp (0.01%) with K_2CO_3 in DMF} we selectively obtained the β-arylation of ethylene glycol vinyl ether. Cabri has rationalised the regiochemical outcome dictated by bidentate ligands in terms of generation of cationic organopalladium complexes.[23] The difference or regioselectivity between these two catalysts might come from different (aryl)Pd(enol) intermediates (Scheme 2). The $Pd(OAc)_2$/dppp catalyst in the presence of TlOAc probably generates a cationic organopalladium complex by halide abstraction, which promotes the α-arylation. Our $[Pd(C_3H_5)Cl]_2$/Tedicyp system probably stabilizes a neutral Pd complex, which favours the formation of the β-arylated products.



Scheme 2.

In order to determine the scope and limitations of this reaction under the operating conditions {$[Pd(C_3H_5)Cl]_2$/

Table 1. Tedicyp/palladium-catalysed selective synthesis of protected arylacetaldehydes from ethylene glycol vinyl ether. Influence of the base and solvent on the selectivity (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	Base	Solvent	Ratio of isomers **a/b/c/d/e**	Product	Yield [%]
1	4-bromoacetophenone	10000	K_2CO_3	DMF	0:0:0:93:7	**1d**,**e**	87[b]
2	4-bromoacetophenone	1000	Cs_2CO_3	DMF	0:0:0:93:7	**1d**,**e**	100
3	4-bromoacetophenone	1000	NaOAc	DMF	0:14:39:29:18	**1b**–**e**	100
4	4-bromoacetophenone	1000	Na_2CO_3	DMF	17:1:2:79:1	**1a**–**e**	100
5	4-bromoacetophenone	1000	$NaHCO_3$	DMF	15:29:30:21:5	**1a**–**e**	100
6	4-bromoacetophenone	1000	KF	DMF	14:29:29:25:3	**1a**–**e**	100
7	4-bromoacetophenone	1000	K_2CO_3	NMP	0:0:0:93:7	**1d**,**e**	55
8	4-bromoacetophenone	1000	K_2CO_3	DMAC	0:0:0:93:7	**1d**,**e**	100
9	4-bromoacetophenone	1000	K_2CO_3	xylene	10:1:1:87:1	**1a**–**e**	100
10	4-bromoacetophenone	1000	K_2CO_3	ethylene glycol	–	–	0
11	4-bromoacetophenone	1000	K_2CO_3	diglyme	16:14:14:54:2	**1a**–**e**	57
12	1-bromo-4-fluorobenzene	250	K_2CO_3	DMF	0:0:0:57:43	**2d**,**e**	52[b]
13	1-bromo-4-fluorobenzene	250	NaOAc	DMF	0:15:42:8:35	**2b**–**e**	100
14	1-bromo-4-fluorobenzene	250	Cs_2CO_3	DMF	36:2:1:57:4	**2a**–**e**	100
15	1-bromo-4-fluorobenzene	250	K_2CO_3	DMAC	12:19:40:25:4	**2a**–**e**	72

[a] Conditions: catalyst see ref.[25], aryl halide (1 equiv.), ethylene glycol vinyl ether (1.2 equiv.), base (2 equiv.), 130 °C, 20 h. GC yields of the mixture of isomers. Ratio of isomers determined by GC and ^{1}H NMR spectroscopy of the crude mixtures. [b] Isolated yields of isomer **d**.

Tedicyp, DMF, K_2CO_3, 130 °C}, the coupling with ethylene glycol vinyl ether was applied to several *para*-substituted aryl bromides (Table 2), *meta*- and *ortho*-substituted aryl bromides (Table 3) and also to heteroaryl bromides (Table 4).

With *para*-substituted aryl bromides, we obtained good regioselectivities in favour of β-arylation with electron-poor aryl bromides such as 4-bromobenzophenone, methyl 4-bromobenzoate, 4-bromobenzonitrile, 1-bromo-4-nitrobenzene or 1-bromo-4-(trifluoromethyl)benzene (Table 2, En-

Table 2. Tedicyp/palladium-catalysed selective synthesis of protected arylacetaldehydes from ethylene glycol vinyl ether and *para*-substituted aryl halides (Scheme 1).

Entry[a]	ArX	Substrate/catalyst ratio	Ratio of isomers **a/b/c/d/e**	Product	Yield of **d** [%]
1	4-bromobenzaldehyde	10000	0:0:0:97:3	**3d**,**e**	91
2	4-bromobenzophenone	10000	0:0:0:94:6	**4d**,**e**	89
3	methyl 4-bromobenzoate	10000	0:0:0:97:3	**5d**,**e**	88
4	4-bromopropiophenone	10000	5:0:0:95:0	**6a**,**d**	93
5	4-bromobenzonitrile	10000	0:0:0:98:2	**7d**,**e**	92
6	1-bromo-4-nitrobenzene	1000	0:0:0:98:2	**8d**,**e**	87
7	1-bromo-4-(trifluoromethyl)benzene	10000	0:0:0:94:6	**9d**,**e**	90
8	bromobenzene	100	0:13:41:13:33	**10b**–**e**	89[b]
9	iodobenzene	100	0:10:11:57:22	**10b**–**e**	52
10	iodobenzene	100	0:26:44:8:22	**10b**–**e**	100[c,d]
11	1-bromo-4-*tert*-butylbenzene	250	0:10:29:27:34	**11b**–**e**	87[b]

[a] Conditions: catalyst see ref.[25], aryl halide (1 equiv.), ethylene glycol vinyl ether (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. Isolated yields of isomer **d**. Ratio of isomers determined by GC and ^{1}H NMR spectroscopy of the crude mixtures. [b] Yield of the mixture containing all the isomers **a**–**e**. [c] GC and NMR conversions. [d] NaOAc was used as base.

Table 3. Tedicyp–palladium catalysed selective synthesis of protected aryl acetaldehydes from ethylene glycol vinyl ether and *meta*- and *ortho*-substituted aryl bromides (Scheme 1 and Scheme 3).

Entry[a]	ArX	Substrate/catalyst ratio	Ratio of isomers **a/b/c/d/e**	Product	Yield of **d** [%]
1	1-bromo-3,5-bis(trifluoromethyl)benzene	10000	0:0:0:97:3	**12d**,**e**	90
2	1-bromo-4-nitro-3-(trifluoromethyl)benzene	10000	0:0:0:97:3	**13d**,**e**	89
3	3-bromoacetophenone	10000	0:0:0:96:4	**14d**,**e**	90
4	3-bromobenzaldehyde	10000	0:0:0:93:7	**15d**,**e**	91
5	1-bromo-3-nitrobenzene	250	5:0:0:95:0	**16a**,**d**	84
6	1-bromo-3-(trifluoromethyl)benzene	10000	0:0:0:94:6	**17d**,**e**	89
7	2-bromo-6-methoxynaphthalene	1000	29:6:17:48:0	**18a**–**d**	44
8	2-bromobenzaldehyde	250	0:0:0:96:4	**19d**,**e**	77
9	2-bromobenzonitrile	1000	3:0:0:97:0	**20a**,**d**	91
10	1-bromo-2-(trifluoromethyl)benzene	10000	0:0:0:94:6	**21d**,**e**	88
11	methyl 2-bromobenzoate	100	0:0:0:97:3	**22d**,**e**	77
12	1-bromo-3,4-difluorobenzene	250	0:0:0:85:15	**23d**	79
13	1-bromo-2,4-difluorobenzene	1000	0:0:0:80:20	**24d**,**e**	74
14	1-bromo-2-fluorobenzene	250	0:0:0:74:26	**25d**,**e**	61
15	1-bromo-2-methylbenzene	100	17:6:15:62:0	**26a**–**d**	57
16	1-bromonaphthalene	1000	0:0:0:78:22	**27d**,**e**	74
17	9-bromoanthracene	1000	0:0:0:90:10	**28d**,**e**	79
18	1,2-dibromobenzene	100	not determined	**29dd**	51

[a] Conditions: catalyst see ref.[25], aryl bromide (1 equiv.), ethylene glycol vinyl ether (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. Isolated yields of isomer **d**. Ratio of isomers determined by GC and ^{1}H NMR spectroscopy of the crude mixtures.

Table 4. Tedicyp/palladium-catalysed selective synthesis of protected arylacetaldehydes from ethylene glycol vinyl ether and heteroaryl bromides (Scheme 1 and Scheme 3).

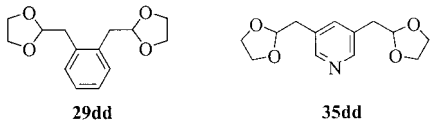
Entry[a]	ArX	Substrate/catalyst ratio	Ratio of isomers **a/b/c/d/e**	Product	Yield of **d** [%]
1	3-bromopyridine	1000	12:0:0:88:0	**30a**,**d**	83
2	4-bromopyridine	1000	3:0:0:97:0	**31a**,**d**	88
3	3-bromoquinoline	10000	10:0:0:90:0	**32a**,**d**	85
4	4-bromoisoquinoline	1000	12:0:0:88:0	**33a**,**d**	81
5	5-bromopyrimidine	1000	0:0:0:100:0	**34d**	76
6	3,5-dibromopyridine	250	not determined	**35dd**	78
7	5-bromo-2-furaldehyde	250	0:1:0:99:0	**36b**,**d**	78

[a] Conditions: catalyst see ref.[25], aryl halide (1 equiv.), ethylene glycol vinyl ether (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. Isolated yields of isomer **d**. Ratio of isomers determined by GC and ^{1}H NMR spectroscopy of the crude mixtures.

tries 1–7). The β-selectivities observed were in the range 94–98%. Moreover, most of these reactions were performed with high substrate/catalyst ratios (up to 10000). On the other hand, the reaction performed with the electron-rich aryl bromide 1-bromo-4-*tert*-butylbenzene led to a lower selectivity. With this substrate, a larger amount of α-arylated product was obtained (34%; Table 2, Entry 11). Bromobenzene or iodobenzene also led to mixtures of α- and β-arylated products (Table 2, Entries 8–10), thus indicating that the lower regioselectivities observed with electron-rich aryl bromides are not due to a slower oxidative addition of the aryl halide, but more likely to the electronic properties of the Ar(X)Pd(CH_2=$CHOCH_2CH_2OH$) intermediates. With electron-deficient aryl bromides, the complete intramolecular cyclisation of the arylalkenes **a**, **b** and **c** (Scheme 1) was generally observed to give the corresponding ketal products 2-benzyl-1,3-dioxolane (**d**) and 2-methyl-2-phenyl-1,3-dioxolane (**e**). On the other hand, when 1-bromo-4-*tert*-butylbenzene was used, mixtures of cyclised and linear products were obtained.

We then studied the influence of the presence of *meta* and *ortho* substituents of the aryl bromides on the regioselectivity of the addition and on the reaction rates. As expected, similar selectivities and reaction rates were obtained with the *meta*-substituted aryl bromides. 3-Bromoacetophenone, 3-bromobenzaldehyde and 1-bromo-3-(trifluoromethyl)benzene with ethylene glycol vinyl ether gave isomers **d** in 93–96% selectivities in the presence of 0.01% catalyst (Table 3, Entries 3, 4 and 6). 1-Bromo-3,5-bis(trifluoromethyl)benzene and 1-bromo-4-nitro-3-(trifluoromethyl)benzene also gave isomers **d** in high selectivities (97%) and high TONs (9000 and 8900; Table 3, Entries 1 and 2, respectively); *ortho* substituents on the aryl bromides have a more important effect on the regioselectivities of the addition and on the reaction rates. With electron-poor 2-bromobenzaldehyde, 2-bromobenzonitrile, 1-bromo-2-(trifluoromethyl)benzene or methyl 2-bromobenzoate high selectivities in favour of isomer **d** were obtained in all cases (94–97%) but the TONs were low in some cases (77–8800; Table 3, Entries 8–11). In order to determine the relative influence of electronic and steric factors on the regioselectivity of this reaction, we also performed the coupling with 1-bromo-3,4-difluorobenzene, 1-bromo-2,4-difluorobenzene, 1-bromo-2-fluorobenzene and 1-bromo-2-methylbenzene (Table 3, Entries 12–15). With these four substrates selectivities of 85, 80, 74 and 83% in favour of β-addition products were obtained, respectively. The sterically hindered substrates 1-bromonaphthalene and 9-bromoanthracene gave the β-arylated products in 78 and 90% selectivities, respectively (Table 3, Entries 16 and 17). These results indicate that the regioselectivity of the addition is partially controlled by steric factors. The reaction using 1,2-dibromobenzene led to the corresponding protected 1,2-bis(2-oxoethyl)benzene **29dd** in satisfactory yield [Table 3 (Entry 18) and Scheme 3].

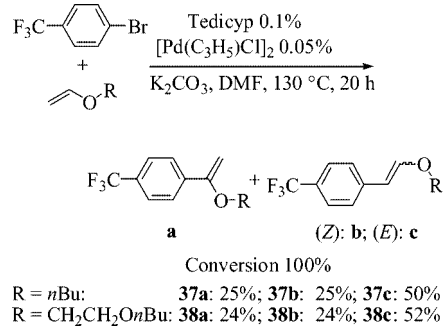
Next, we studied the reaction with heteroaryl bromides (Table 4). Pyridines or quinolines are π-electron-deficient, so we should expect similar results with bromopyridines or



Scheme 3.

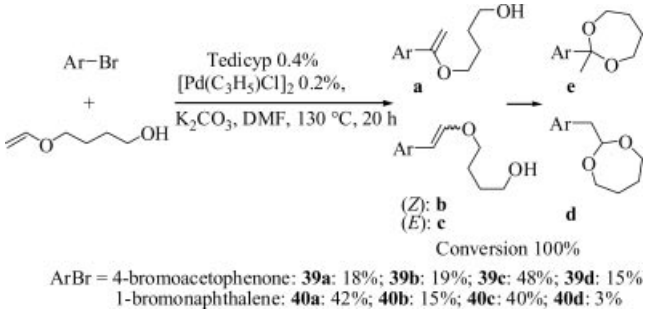
bromoquinolines as with electron-poor aryl bromides. With 3-bromopyridine, 3-bromoquinoline and 4-bromoisoquinoline selectivities of 88, 90 and 88% in favour of β-arylation were obtained, respectively (Table 4, Entries 1, 3 and 4). The highest selectivities with heteroaromatic substrates were observed with 4-bromopyridine, 5-bromopyrimidine and 5-bromo-2-furaldehyde (97, 100 and 99% respectively; Table 4, Entries 2, 5 and 7). Even 3,5-dibromopyridine gave a satisfactory yield of the corresponding protected dialdehyde **35dd** (Table 4, Scheme 3, Entry 6).

In order to determine if an ether function instead of an alcohol on the vinyl ether would have an effect on the control of the regioselectivity of the addition, we performed the reaction in the presence of ethylene glycol *n*-butyl vinyl diether and *n*-butyl vinyl ether with 1-bromo-4-(trifluoromethyl)benzene (substrate/catalyst ratio 1000; Scheme 4). We observed that very similar mixtures of isomers were obtained and in both cases large amounts of α-arylated products were formed (24 and 25%, respectively). With this aryl bromide, the formation of only 6% of α-arylated product **e** was observed in the presence of ethylene glycol vinyl ether (Table 2, Entry 7).



Scheme 4.

We also studied the selectivity of this reaction with 4-(vinyloxy)butan-1-ol (Scheme 5). Two aryl bromides were used, but in both cases mixtures of isomers were obtained. 4-Bromoacetophenone gave the intramolecularly ketalized



Scheme 5.

Table 5. Palladium-catalysed synthesis of protected arylacetaldehydes from ethylene glycol vinyl ether and aryl bromides using dppb as ligand.

Entry[a]	ArX	$[Pd(C_3H_5)Cl]_2$/dppb ratio	Substrate/catalyst ratio	Ratio of isomers **a/b/c/d/e**	Product	Yield
1	4-bromoacetophenone	1:2	1000	8:0:0:92:0	**1a**,**d**	100
2	4-bromoacetophenone	1:2	10000	8:0:0:92:0	**1a**,**d**	17
3	4-bromoacetophenone	1:4	1000	7:0:0:93:0	**1a**,**d**	100
4	1-bromo-4-fluorobenzene	1:2	100	23:13:19:42:3	**2a**–**e**	100
5	1-bromo-4-fluorobenzene	1:2	250	26:14:24:27:9	**2a**–**e**	69
6	1-bromo-4-fluorobenzene	1:4	250	16:3:12:42:27	**2a**–**e**	33[b]
7	9-bromoanthracene	1:2	100	37:0:0:55:8	**28a**,**d**,**e**	27[b,c]
8	9-bromoanthracene	1:2	250	0:0:0:78:22	**28d**,**e**	34[b,c]
9	9-bromoanthracene	1:4	250	14:0:0:78:8	**28a**,**d**,**e**	26[b,d]

[a] Conditions: catalyst: $[Pd(C_3H_5)Cl]_2$/dppb, aryl halide (1 equiv.), ethylene glycol vinyl ether (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h. GC yields of the mixture of isomers. Ratio of isomers determined by GC and ^{1}H NMR spectroscopy of the crude mixtures. [b] Isolated yields of isomer **d**. [c] The formation of 35% of anthracene was also observed. [d] The formation of 46% of anthracene was also observed.

isomer **39d** in 15% selectivity. The linear (*Z*) and (*E*) isomers **39b** and **39c** were obtained in 19 and 48% selectivity, respectively, together with 18% of the branched isomer **39a**. 1-Bromonaphthalene gave a larger amount of the branched isomer **40a** (42%). These results indicate that the position of the alcohol function on the (vinyloxy)alkanol has a large effect on the control of the regioselectivity of this reaction.

Finally, we compared our catalyst with the system PPh_3 (4 equiv.)/$[Pd(C_3H_5)Cl]_2$ (1 equiv.) for the reaction of ethylene glycol vinyl ether with 9-bromoanthracene. In the presence of 0.4% catalyst, the ratio of products **b+c+d/a+e** was 72:28 instead of 90:10 with Tedicyp/$[Pd(C_3H_5)Cl]_2$. Moreover, using PPh_3 as ligand, compound **28d** was isolated in a very low yield (21%), and a very important debromination of 9-bromoanthracene was observed. The major product of this reaction was anthracene. We also studied the reactivity and selectivity of this reaction using the bidentate ligand dppb. With the system dppb (2 or 4 equiv.)/$[Pd(C_3H_5)Cl]_2$ (1 equiv.) as catalyst, satisfactory results in terms of substrate/catalyst ratio and also of selectivity were obtained with 4-bromoacetophenone (Table 5, Entries 1–3). On the other hand with 1-bromo-4-fluorobenzene or 9-bromoanthracene low yields of isomers **2d** or **28d** were obtained due to the formation of mixtures of isomers or debromination of 9-bromoanthracene (Table 5, Entries 4–9). The difference of reactivity and selectivity between PPh_3, dppb and our tetradentate ligand probably arises from the stability of the catalysts.

Conclusions

In summary, we have established that the Tedicyp/palladium system provides a convenient catalyst for the synthesis of protected arylacetaldehyde derivatives by coupling of aryl bromides with ethylene glycol vinyl ether followed by intramolecular ketalisation. The electronic control of the regioselectivity of the addition encountered with *n*-butyl vinyl ether appears to be partially suppressed by an adjacent alcohol function on the vinyl ether. This alcohol function appears to be capable of coordinating to the palladium catalyst. Anchoring the enol to the metal atom by an alcohol function probably imposes a conformational change in the structure of the (aryl)Pd(enol) intermediate and stabilizes a neutral Pd complex, thus favouring the formation of the β-arylated products. Therefore, the reaction with ethylene glycol vinyl ether is one of the Heck substrate directed reactions. Both the steric hindrance and the electronic properties of the aryl bromide have an effect on the reaction rates and the selectivities. The best selectivities in favour of β-arylations were observed with electron-poor or sterically congested aryl bromides. With bromobenzene or electron-rich aryl bromides, mixtures or regioisomers were observed. In all cases, only traces (<1%) of homocoupling products were observed with this catalyst. Apart from achieving excellent regiocontrol, another advantage is the remarkable functional group tolerance: substituents such as fluoro, trifluoromethyl, acetyl, formyl, benzoyl, carboxylate, nitro or nitrile on the aryl bromide have been used successfully. Ethylene glycol vinyl ether is commercially available, and the reaction can be performed with as little as 0.01% catalyst with several substrates, so this catalyst appears to be the most active and stable one reported so far for this reaction. Due to the high price of palladium, the practical advantage of such low catalyst loadings can become increasingly important for industrial processes.

Experimental Section

General Remarks: All reactions were run under argon in Schlenk tubes using vacuum lines. DMF, DMAC, NMP, xylene, diglyme and ethylene glycol (analytical grade) were not distilled before use. K_2CO_3 (99+%), Cs_2CO_3 (97%), Na_2CO_3 (99%), $NaHCO_3$ (99%), NaOAc (99%), ethylene glycol vinyl ether (97%) and commercial aryl halides were used without purification. The reactions were monitored by GC and NMR spectroscopy for high-boiling-point substrates and by GC for low-boiling-point substrates. GC MS data were recorded with a Varian Saturn 2100T spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (^{1}H: δ = 7.25 ppm; ^{13}C: δ = 77.0 ppm). Flash chromatography was performed on silica gel (230–400 mesh). GC and NMR conversions in the tables are conversions of the aryl halides into the mixture of products calculated from the GC and

^{1}H NMR spectrum of the crude mixtures. Ratios of isomers were determined by GC and NMR spectroscopy.

Preparation of the Pd/Tedicyp Catalyst:[25] An oven-dried 40-mL Schlenk tube, equipped with a magnetic stirring bar, was charged with $[Pd(C_3H_5)Cl]_2$ (4.2 mg, 11.6 μmol) and Tedicyp (20 mg, 23.2 μmol) under argon. Anhydrous DMF (2.5 mL) was then added and the solution was stirred at room temperature for 10 min. The appropriate amount of catalyst (see tables) was transferred into the mixture of aryl halide, alkene and base.

General Procedure for the Coupling of Enol Ethers with Aryl Halides: The reaction of the aryl halide (1 mmol), K_2CO_3 (0.276 g, 2 mmol) and the enol ether (1.2 mmol) in DMF (5 mL) in the presence of the Tedicyp/palladium complex (see tables for substrate/catalyst ratio) under argon at 130 °C during 20 h afforded the corresponding mixture of products after addition of water, extraction with dichloromethane or diethyl ether, drying ($MgSO_4$) and concentration. The major isomer was purified by chromatography on silica gel.

2-(4-Acetylbenzyl)-1,3-dioxolane (1d): The reaction of 4-bromoacetophenone (0.199 g, 1 mmol), K_2CO_3 (0.276 g, 2 mmol) and ethylene glycol vinyl ether (0.106 g, 1.2 mmol) in DMF (5 mL) in the presence of the Tedicyp/palladium complex (0.1 μmol) under argon at 130 °C for 20 h afforded the corresponding coupling product **1d** after extraction with diethyl ether, drying ($MgSO_4$), concentration and filtration through silica gel (diethyl ether/pentane, 1:4) in 87% (0.179 g) isolated yield. White solid. M.p. 55 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.1 Hz, 2 H, Ar), 7.36 (d, J = 8.1 Hz, 2 H, Ar), 5.08 (t, J = 5.1 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 3.02 (d, J = 5.1 Hz, 2 H, CH_2CH), 2.56 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.8, 141.7, 135.6, 129.9, 128.3, 103.9, 65.0, 40.6, 26.5 ppm. $C_{12}H_{14}O_3$ (206): calcd. C 69.88, H 6.84; found C 69.62, H 6.63. MS (EI, 70 eV): m/z (%) = 206 (19) [M$^+$]. Before purification, traces of 2-(4-acetylphenyl)-2-methyl-1,3-dioxolane (**1e**) were present along with **1a**–**c**. **1e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.3 Hz, 2 H, Ar), 7.55 (d, J = 8.3 Hz, 2 H, Ar), 4.03 (m, 2 H, CH_2CH_2), 3.75 (m, 2 H, CH_2CH_2), 2.57 (s, 3 H, Me), 1.62 (s, 3 H, Me) ppm. **1a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.80 (d, J = 3.2 Hz, 1 H, C=CH_2), 4.36 (d, J = 3.2 Hz, 1 H, C=CH_2) ppm. (*Z*)-**1b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.31 (d, J = 7.1 Hz, 1 H, C=CH), 5.18 (d, J = 7.1 Hz, 1 H, C=CH) ppm. (*E*)-**1c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.09 (d, J = 13.0 Hz, 1 H, C=CH), 5.78 (d, J = 13.0 Hz, 1 H, C=CH) ppm.

2-(4-Fluorobenzyl)-1,3-dioxolane (2d): Isomer **2d** was obtained in 52% (0.095 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20 (dd, J = 8.5 and 5.5 Hz, 2 H, Ar), 6.97 (dd, J = 8.5 and 8.5 Hz, 2 H, Ar), 5.01 (t, J = 4.7 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 2.92 (d, J = 4.7 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.8 (d, J = 244.4 Hz), 131.7 (d, J = 2.9 Hz), 131.1 (d, J = 8.0 Hz), 115.1 (d, J = 21.2 Hz), 104.4, 65.0, 39.9 ppm. $C_{10}H_{11}FO_2$ (182): calcd. C 65.92, H 6.09; found C 65.73, H 6.17. MS (EI, 70 eV): m/z (%) = 182 (1) [M$^+$]. Before purification, 2-(4-fluorophenyl)-2-methyl-1,3-dioxolane (**2e**) and **2a**–**c** were also present. **2e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (dd, J = 8.5 and 5.5 Hz, 2 H, Ar), 7.00 (dd, J = 8.5 and 8.5 Hz, 2 H, Ar), 4.03 (m, 2 H, CH_2CH_2), 3.76 (m, 2 H, CH_2CH_2), 1.63 (s, 3 H, Me) ppm. **2a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.56 (d, J = 2.9 Hz, 1 H, C=CH_2), 4.17 (d, J = 2.9 Hz, 1 H, C=CH_2) ppm. (*Z*)-**2b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.17 (d, J = 7.1 Hz, 1 H, C=CH), 5.13 (d, J = 7.1 Hz, 1 H, C=CH). (*E*)-**2c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.77 (d, J = 13.0 Hz, 1 H, C=CH) ppm.

2-(4-Formylbenzyl)-1,3-dioxolane (3d): Isomer **3d** was obtained in 91% (0.175 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.98 (s, 1 H, CHO), 7.81 (d, J = 8.3 Hz, 2 H, Ar), 7.43 (d, J = 8.3 Hz, 2 H, Ar), 5.08 (t, J = 4.8 Hz, 1 H, CH_2CH), 3.96–3.82 (m, 4 H, CH_2CH_2), 3.04 (d, J = 4.8 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 143.3, 134.9, 130.4, 129.7, 103.8, 65.0, 40.8 ppm. $C_{11}H_{12}O_3$ (192): calcd. C 68.74, H 6.29; found C 68.52, H 6.12. MS (EI, 70 eV): m/z (%) = 192 (100) [M$^+$]. Before purification, traces of 2-(4-formylphenyl)-2-methyl-1,3-dioxolane (**3e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.04 (m, 2 H, CH_2CH_2), 3.75 (m, 2 H, CH_2CH_2), 1.63 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **3d**.

2-(4-Benzoylbenzyl)-1,3-dioxolane (4d): Isomer **4d** was obtained in 89% (0.239 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.2 Hz, 2 H, Ar), 7.76 (d, J = 8.2 Hz, 2 H, Ar), 7.56 (t, J = 7.2 Hz, 1 H, Ar), 7.45 (t, J = 7.2 Hz, 2 H, Ar), 7.37 (d, J = 8.2 Hz, 2 H, Ar), 5.10 (t, J = 4.8 Hz, 1 H, CH_2CH), 3.97–3.82 (m, 4 H, CH_2CH_2), 3.04 (d, J = 4.8 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.4, 141.1, 137.7, 135.8, 132.2, 130.1, 129.9, 129.6, 128.2, 104.0, 65.0, 40.7 ppm. $C_{17}H_{16}O_3$ (268): calcd. C 76.10, H 6.01; found C 75.99, H 5.89. MS (EI, 70 eV): m/z (%) = 268 (100) [M$^+$]. Before purification, traces of 2-(4-benzoylphenyl)-2-methyl-1,3-dioxolane (**4e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (m, 2 H, CH_2CH_2), 3.79 (m, 2 H, CH_2CH_2), 1.67 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **4d**.

Methyl 4-[(1,3-Dioxolan-2-yl)methyl]benzoate (5d): Isomer **5d** was obtained in 88% (0.195 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.2 Hz, 2 H, Ar), 7.31 (d, J = 8.2 Hz, 2 H, Ar), 5.06 (t, J = 4.3 Hz, 1 H, CH_2CH), 3.95–3.75 (m, 4 H, CH_2CH_2), 3.88 (s, 3 H, OMe), 2.99 (d, J = 4.3 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 141.6, 129.7, 129.6, 128.3, 103.9, 64.9, 51.9, 40.6 ppm. $C_{12}H_{14}O_4$ (222): calcd. C 64.85, H 6.35; found C 64.99, H 6.14. Before purification, traces of methyl 4-(2-methyl-1,3-dioxolan-2-yl)benzoate (**5e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **5d**.

2-(4-Propionylbenzyl)-1,3-dioxolane (6d): Isomer **6d** was obtained in 93% (0.205 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.1 Hz, 2 H, Ar), 7.31 (d, J = 8.1 Hz, 2 H, Ar), 5.04 (t, J = 4.3 Hz, 1 H, CH_2CH), 3.95–3.75 (m, 4 H, CH_2CH_2), 2.98 (d, J = 4.3 Hz, 2 H, CH_2CH), 2.93 (q, J = 7.2 Hz, 2 H), 1.17 (t, J = 7.2 Hz, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.4, 141.4, 135.2, 129.8, 127.9, 103.9, 64.9, 40.5, 31.5, 8.1 ppm. $C_{13}H_{16}O_3$ (220): calcd. C 70.89, H 7.32; found C 70.98, H 7.15. Before purification, traces of 1-(2-hydroxyethoxy)-1-(4-propionylphenyl)ethene (**6a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (d, J = 3.2 Hz, 1 H, C=CH_2), 4.31 (d, J = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **6d**.

2-(4-Cyanobenzyl)-1,3-dioxolane (7d): [42] Isomer **7d** was obtained in 92% (0.174 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.3 Hz, 2 H, Ar), 7.38 (d, J = 8.3 Hz, 2 H, Ar), 5.07 (t, J = 4.5 Hz, 1 H, CH_2CH), 3.93–3.80 (m, 4 H, CH_2CH_2), 3.02 (d, J = 4.5 Hz, 2 H, CH_2CH). Before purification, traces of 2-(4-cyanophenyl)-2-methyl-1,3-dioxolane (**7e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **7d**.

2-(4-Nitrobenzyl)-1,3-dioxolane (8d): [43] Isomer **8d** was obtained in 87% (0.182 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 8.7 Hz, 2 H, Ar), 7.42 (d, J = 8.7 Hz, 2 H, Ar), 5.09 (t, J = 4.4 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 3.06 (d, J

= 4.4 Hz, 2 H, CH_2CH). Before purification, traces of 2-methyl-2-(4-nitrophenyl)-1,3-dioxolane (**8e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **8d**.

2-[4-(Trifluoromethyl)benzyl]-1,3-dioxolane (9d): [44] Isomer **9d** was obtained in 90% (0.209 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.2 Hz, 2 H, Ar), 7.38 (d, J = 8.2 Hz, 2 H, Ar), 5.07 (t, J = 4.8 Hz, 1 H, CH$_2$C*H*), 3.95–3.80 (m, 4 H, CH_2CH_2), 3.02 (d, J = 4.8 Hz, 2 H, CH_2CH). Before purification, traces of 2-methyl-2-[4-(trifluoromethyl)phenyl]-1,3-dioxolane (**9e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05 (m, 2 H, CH_2CH_2), 3.75 (m, 2 H, CH_2CH_2), 1.64 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **9d**.

2-Benzyl-1,3-dioxolane (10d): [24] Isomer **10d** was obtained in 52% (0.85 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.10 (m, 5 H, Ar), 5.04 (t, J = 4.8 Hz, 1 H, CH$_2$C*H*), 3.95–3.75 (m, 4 H, CH_2CH_2), 2.95 (d, J = 4.8 Hz, 2 H, CH_2CH). Before purification, the presence of (*Z*)-2-(2-phenylvinyloxy)ethanol (**10b**), (*E*)-2-(2-phenylvinyloxy)ethanol (**10c**) and 2-methyl-2-phenyl-1,3-dioxolane (**10e**) was also observed. **10b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.23 (d, J = 7.1 Hz, 1 H, C=C*H*), 5.25 (d, J = 7.1 Hz, 1 H, C=C*H*) ppm. **10c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, J = 13.0 Hz, 1 H, C=C*H*), 5.87 (d, J = 13.0 Hz, 1 H, C=C*H*) ppm. **10e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.3 Hz, 2 H, Ar), 7.35–7.25 (m, 3 H, Ar), 4.03 (m, 2 H, CH_2CH_2), 3.75 (m, 2 H, CH_2CH_2), 1.64 (s, 3 H, Me) ppm. The other peaks were hidden.

2-(4-*tert*-Butylbenzyl)-1,3-dioxolane (11d)[42] and Products 11b, 11c and 11e: A mixture of isomers **11b**–**e** was obtained in 87% (0.191 g) isolated yield. **11d**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.1 Hz, 2 H, Ar), 7.19 (d, J = 8.1 Hz, 2 H, Ar), 5.03 (t, J = 4.9 Hz, 1 H, CH$_2$C*H*), 3.95–3.82 (m, 4 H, CH_2CH_2), 2.92 (d, J = 4.9 Hz, 2 H, CH_2CH), 1.28 (s, 9 H, *t*Bu) ppm. **11b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.20 (d, J = 7.0 Hz, 1 H, C=C*H*), 5.26 (d, J = 7.0 Hz, 1 H, C=C*H*) ppm. **11c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27 (d, J = 8.3 Hz, 2 H, Ar), 7.15 (d, J = 8.3 Hz, 2 H, Ar), 6.97 (d, J = 13.0 Hz, 1 H, C=C*H*), 5.87 (d, J = 13.0 Hz, 1 H, C=C*H*), 1.29 (s, 9 H, *t*Bu) ppm. **11e**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.68 (s, 3 H, Me) ppm. The other peaks were hidden.

2-[3,5-Bis(trifluoromethyl)benzyl]-1,3-dioxolane (12d): Isomer **12d** was obtained in 90% (0.270 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72 (s, 1 H, Ar), 7.71 (s, 2 H, Ar), 5.09 (t, J = 4.4 Hz, 1 H, CH$_2$C*H*), 3.90–3.80 (m, 4 H, CH_2CH_2), 3.08 (d, J = 4.4 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.4, 131.3 (q, J = 32.3 Hz), 130.1, 123.2 (q, J = 273.1 Hz), 120.6 (q, J = 4.0 Hz), 103.2, 65.1, 40.1 ppm. $C_{12}H_{10}F_6O_2$ (300): calcd. C 48.01, H 3.36; found C 47.89, H 3.42. MS (EI, 70 eV): m/z (%) = 299 (6) [M$^+$]. Before purification, traces of 2-methyl-2-[3,5-bis(trifluoromethyl)phenyl]-1,3-dioxolane (**12e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.65 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **12d**.

2-[4-Nitro-3-(trifluoromethyl)benzyl]-1,3-dioxolane (13d): Isomer **13d** was obtained in 89% (0.247 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 1 H, Ar), 7.72 (s, 1 H, Ar), 7.61 (d, J = 8.3 Hz, 1 H, Ar), 5.10 (t, J = 4.1 Hz, 1 H, CH$_2$C*H*), 3.85 (m, 4 H, CH_2CH_2), 3.09 (d, J = 4.1 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7, 141.9, 134.4, 129.4 (q, J = 5.2 Hz), 124.9, 123.4 (q, J = 33.9 Hz), 121.8 (q, J = 273.6 Hz), 102.8, 65.1, 39.9 ppm. $C_{11}H_{10}F_3NO_4$ (277): calcd. C 47.66, H 3.64; found C 47.36, H 3.51. MS (EI, 70 eV): m/z (%) = 277 (3) [M$^+$]. Before purification, traces of 2-methyl-2-[4-nitro-3-(trifluoromethyl)phenyl]-1,3-dioxolane (**13e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.06 (m, 2 H, CH_2CH_2), 3.76 (m, 2 H, CH_2CH_2), 1.65 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **13d**.

2-(3-Acetylbenzyl)-1,3-dioxolane (14d): Isomer **14d** was obtained in 90% (0.186 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (s, 1 H, Ar), 7.80 (d, J = 7.8 Hz, 1 H, Ar), 7.46 (d, J = 7.8 Hz, 1 H, Ar), 7.38 (t, J = 7.8 Hz, 1 H, Ar), 5.06 (t, J = 4.8 Hz, 1 H, CH$_2$C*H*), 3.94–3.78 (m, 4 H, CH_2CH_2), 3.00 (d, J = 4.8 Hz, 2 H, CH_2CH), 2.57 (s, 3 H, Me) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.1, 137.1, 136.6, 134.5, 129.5, 128.4, 126.6, 104.1, 64.9, 40.3, 26.6 ppm. $C_{12}H_{14}O_3$ (206): calcd. C 69.88, H 6.84; found C 69.69, H 6.61. MS (EI, 70 eV): m/z (%) = 206 (3) [M$^+$]. Before purification, traces of 2-(3-acetylphenyl)-2-methyl-1,3-dioxolane (**14e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.08 (s, 1 H, Ar), 7.89 (d, J = 7.8 Hz, 1 H, Ar), 7.69 (d, J = 7.8 Hz, 1 H, Ar), 7.44 (t, J = 7.8 Hz, 1 H, Ar), 4.06 (m, 2 H, CH_2CH_2), 3.77 (m, 2 H, CH_2CH_2), 2.61 (s, 3 H, Me), 1.64 (s, 3 H, Me) ppm.

2-(3-Formylbenzyl)-1,3-dioxolane (15d): Isomer **15d** was obtained in 91% (0.175 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.96 (s, 1 H, CHO), 7.75 (s, 1 H, Ar), 7.71 (d, J = 7.3 Hz, 1 H, Ar), 7.52 (d, J = 7.3 Hz, 1 H, Ar), 7.42 (t, J = 7.3 Hz, 1 H, Ar), 5.06 (t, J = 4.8 Hz, 1 H, CH$_2$C*H*), 3.92–3.76 (m, 4 H, CH_2CH_2), 3.01 (d, J = 4.8 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.3, 137.1, 136.3, 135.9, 131.0, 128.8, 127.9, 103.9, 64.9, 40.2 ppm. $C_{11}H_{12}O_3$ (192): calcd. C 68.74, H 6.29; found C 68.45, H 6.09. MS (EI, 70 eV): m/z (%) = 192 (3) [M$^+$]. Before purification, traces of 2-(3-formylphenyl)-2-methyl-1,3-dioxolane (**15e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.02 (s, 1 H, CHO), 4.06 (m, 2 H, CH_2CH_2), 3.77 (m, 2 H, CH_2CH_2), 1.65 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **15d**.

2-(3-Nitrobenzyl)-1,3-dioxolane (16d): Isomer **16d** was obtained in 84% (0.176 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (s, 1 H, Ar), 8.09 (d, J = 7.6 Hz, 1 H, Ar), 7.60 (d, J = 7.6 Hz, 1 H, Ar), 7.45 (t, J = 7.6 Hz, 1 H, Ar), 5.09 (t, J = 4.4 Hz, 1 H, CH$_2$C*H*), 3.94–3.80 (m, 4 H, CH_2CH_2), 3.06 (d, J = 4.4 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 138.0, 136.1, 129.0, 124.7, 121.7, 103.5, 65.1, 40.1 ppm. $C_{10}H_{11}NO_4$ (209): calcd. C 57.41, H 5.30; found C 57.11, H 5.12. Before purification, traces of 2-[1-(3-nitrophenyl)vinyloxy]ethanol (**16a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.79 (d, J = 3.2 Hz, 1 H, C=CH_2), 4.38 (d, J = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **16d**.

2-[3-(Trifluoromethyl)benzyl]-1,3-dioxolane (17d):[25] Isomer **17d** was obtained in 89% (0.207 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.35 (m, 4 H, Ar), 5.08 (t, J = 4.5 Hz, 1 H, CH$_2$C*H*), 3.95–3.75 (m, 4 H, CH_2CH_2), 3.01 (d, J = 4.5 Hz, 2 H, CH_2CH). Before purification, traces of 2-[3-(trifluoromethyl)phenyl]-2-methyl-1,3-dioxolane (**17e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05 (m, 2 H, CH_2CH_2), 3.76 (m, 2 H, CH_2CH_2), 1.65 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **17d**.

2-(6-Methoxynaphthalen-2-ylmethyl)-1,3-dioxolane (18d): Isomer **18d** was obtained in 44% (0.107 g) isolated yield. White solid. M.p. 57 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.63 (m, 3 H, Ar), 7.38 (dd, J = 8.3, 1.7 Hz, 1 H, Ar), 7.15–7.09 (m, 2 H, Ar), 5.14 (t, J = 4.3 Hz, 1 H, CH$_2$C*H*), 3.97–3.82 (m, 4 H, CH_2CH_2), 3.90 (s, 3 H, MeO), 3.09 (d, J = 4.3 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.3, 133.4, 131.3, 129.1, 129.0, 128.6, 128.0, 126.7, 118.7, 105.6, 104.7, 65.0, 55.2, 40.7 ppm. $C_{15}H_{16}O_3$ (244): calcd. C 73.75, H 6.60; found C 73.89, H 6.41. Before purification, traces of **18a**–**c** were also observed. **18a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (d, J = 3.2 Hz, 1 H, C=CH_2), 4.28 (d,

J = 3.2 Hz, 1 H, C=CH_2) ppm. **18b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.26 (d, J = 7.2 Hz, 1 H, C=CH), 5.34 (d, J = 7.2 Hz, 1 H, C=CH) ppm. **18c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.98 (d, J = 12.6 Hz, 1 H, C=CH) ppm. The other peaks were hidden by those of compound **18d**.

2-(2-Formylbenzyl)-1,3-dioxolane (19d):[44] Isomer **19d** was obtained in 77% (0.148 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.27 (s, 1 H, CHO), 7.86 (dd, J = 7.5 and 1.3 Hz, 1 H, Ar), 7.52 (td, J = 7.5 and 1.6 Hz, 1 H, Ar), 7.41 (td, J = 7.5 and 1.3 Hz, 1 H, Ar), 7.86 (d, J = 7.5 Hz, 1 H, Ar), 5.12 (t, J = 4.6 Hz, 1 H, CH_2CH), 3.85–3.76 (m, 4 H, CH_2CH_2), 3.41 (d, J = 4.6 Hz, 2 H, CH_2CH). Before purification, traces of 2-(2-formylphenyl)-2-methyl-1,3-dioxolane (**19e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **19d**.

2-(2-Cyanobenzyl)-1,3-dioxolane (20d): Isomer **20d** was obtained in 91% (0.172 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.8 Hz, 1 H, Ar), 7.51 (t, J = 7.5 Hz, 1 H, Ar), 7.42 (d, J = 7.5 Hz, 1 H, Ar), 7.31 (t, J = 7.6 Hz, 1 H, Ar), 5.16 (t, J = 4.8 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 3.17 (d, J = 4.8 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 132.6, 132.4, 131.0, 127.1, 118.1, 113.6, 103.3, 65.0, 39.1 ppm. $C_{11}H_{11}NO_2$ (189): calcd. C 69.83, H 5.86; found C 69.56, H 5.90. MS (EI, 70 eV): m/z (%) = 190 (15) [M$^+$]. Before purification, traces of 2-[1-(2-cyanophenyl)vinyloxy]ethanol (**20a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.65 (d, J = 3.2 Hz, 1 H, C=CH_2), 4.43 (d, J = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **20d**.

2-[2-(Trifluoromethyl)benzyl]-1,3-dioxolane (21d): Isomer **21d** was obtained in 88% (0.204 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.0 Hz, 1 H, Ar), 7.49 (m, 2 H, Ar), 7.32 (t, J = 8.0 Hz, 1 H, Ar), 5.07 (t, J = 4.9 Hz, 1 H, CH_2CH), 4.00 (m, 2 H, CH_2CH_2), 3.86 (m, 2 H, CH_2CH_2), 3.14 (d, J = 4.9 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.7, 132.5, 131.6, 129.1 (q, J = 29.6 Hz), 126.7, 125.9 (q, J = 5.5 Hz), 124.8 (q, J = 274.3 Hz), 103.9, 64.9, 37.4 ppm. $C_{11}H_{11}F_3O_2$ (232): calcd. C 56.90, H 4.77; found C 57.05, H 4.65. MS (EI, 70 eV): m/z (%) = 231 (6) [M$^+$]. Before purification, traces of 2-methyl-2-[2-(trifluoromethyl)phenyl]-1,3-dioxolane (**21e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **21d**.

Methyl 2-(1,3-Dioxolan-2-ylmethyl)benzoate (22): Isomer **22d** was obtained in 77% (0.171 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.5 Hz, 1 H, Ar), 7.44 (t, J = 7.5 Hz, 1 H, Ar), 7.33 (d, J = 8.2 Hz, 1 H, Ar), 7.29 (t, J = 7.5 Hz, 1 H, Ar), 5.12 (t, J = 4.9 Hz, 1 H, CH_2CH), 3.88 (s, 3 H, Me), 3.87–3.77 (m, 4 H, CH_2CH_2), 3.37 (d, J = 4.9 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.2, 137.4, 132.5, 131.7, 130.6, 130.4, 126.7, 104.3, 64.9, 51.9, 38.3 ppm. $C_{12}H_{14}O_4$ (222): calcd. C 64.85, H 6.35; found C 64.74, H 6.18. Before purification, traces of methyl 2-(2-methyl-1,3-dioxolan-2-yl)benzoate (**22e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.77 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **22d**.

2-(3,4-Difluorobenzyl)-1,3-dioxolane (23d): Isomer **23d** was obtained in 79% (0.158 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.15–6.90 (m, 3 H, Ar), 5.02 (t, J = 4.7 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 2.90 (d, J = 4.7 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1 (dd, J = 247.5 and 12.6 Hz), 149.2 (dd, J = 246.4 and 12.6 Hz), 132.9 (dd, J = 6.1 and 3.9 Hz), 125.7 (dd, J = 6.1 and 3.9 Hz), 118.6 (d, J = 17.0 Hz), 116.8 (d, J = 17.0 Hz), 103.9, 65.0, 39.8 ppm. $C_{10}H_{10}F_2O_2$ (200): calcd. C 60.00, H 5.04; found C 59.84, H 4.79. MS (EI, 70 eV): m/z (%) = 200 (3) [M$^+$]. Before purification, traces of 2-(3,4-difluorophenyl)-2-methyl-1,3-dioxolane (**23e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.03 (m, 2 H, CH_2CH_2), 3.74 (m, 2 H, CH_2CH_2), 1.60 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **23d**.

2-(2,4-Difluorobenzyl)-1,3-dioxolane (24d): Isomer **24d** was obtained in 74% (0.148 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m, 1 H, Ar), 6.81 (m, 2 H, Ar), 5.10 (t, J = 4.7 Hz, 1 H, CH_2CH), 3.98–3.84 (m, 4 H, CH_2CH_2), 2.99 (d, J = 4.7 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6 (dd, J = 246.7 and 11.5 Hz), 161.2 (dd, J = 247.9 and 12.0 Hz), 132.6 (dd, J = 9.8 and 5.3 Hz), 118.8 (dd, J = 16.1 and 4.0 Hz), 110.9 (dd, J = 10.7 and 3.5 Hz), 103.6 (t, J = 25.2 Hz), 103.3, 65.0, 33.1 ppm. $C_{10}H_{10}F_2O_2$ (200): calcd. C 60.00, H 5.04; found C 59.76, H 5.09. MS (EI, 70 eV): m/z (%) = 200 (3) [M$^+$]. Before purification, traces of 2-(2,4-difluorophenyl)-2-methyl-1,3-dioxolane (**24e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): 4.04 (m, 2 H, CH_2CH_2), 1.71 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **24d**.

2-(2-Fluorobenzyl)-1,3-dioxolane (25d): Isomer **25d** was obtained in 61% (0.111 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (td, J = 7.3 and 1.7 Hz, 1 H, Ar), 7.20 (t, J = 7.6 Hz, 1 H, Ar), 7.10–6.97 (m, 2 H, Ar), 5.11 (t, J = 4.7 Hz, 1 H, CH_2CH), 3.95–3.80 (m, 4 H, CH_2CH_2), 3.00 (d, J = 4.7 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.3 (d, J = 245.5 Hz), 131.9 (d, J = 4.6 Hz), 128.4 (d, J = 8.6 Hz), 123.9 (d, J = 4.0 Hz), 123.1 (d, J = 15.5 Hz), 115.1 (d, J = 22.4 Hz), 103.5, 65.0, 33.8 ppm. $C_{10}H_{11}FO_2$ (182): calcd. C 65.92, H 6.09; found C 65.64, H 6.07. Before purification, 2-(2-fluorophenyl)-2-methyl-1,3-dioxolane (**25e**) was also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.59 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **25d**.

2-(2-Methylbenzyl)-1,3-dioxolane (26d):[45] Isomer **26d** was obtained in 57% (0.102 g) isolated yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.00 (m, 4 H, Ph), 5.04 (t, J = 4.9 Hz, 1 H, CH_2CH), 3.97–3.80 (m, 4 H, CH_2CH_2), 2.98 (d, J = 4.9 Hz, 2 H, CH_2CH), 2.34 (s, 3 H, Me). Before purification, the presence of **26a**–**c** was also observed. **26a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35 (d, J = 2.1 Hz, 1 H, C=CH_2), 4.21 (d, J = 2.1 Hz, 1 H, C=CH_2) ppm. **26b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.29 (d, J = 7.2 Hz, 1 H, C=CH), 5.38 (d, J = 7.2 Hz, 1 H, C=CH) ppm. **26c**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.84 (d, J = 12.6 Hz, 1 H, C=CH), 6.01 (d, J = 12.6 Hz, 1 H, C=CH) ppm. The other peaks were hidden by those of compound **26d**.

2-(Naphthalen-1-yl)methyl-1,3-dioxolane (27d): Isomer **27d** was obtained in 74% (0.159 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.3 Hz, 1 H, Ar), 7.87 (d, J = 8.0 Hz, 1 H, Ar), 7.78 (d, J = 7.0 Hz, 1 H, Ar), 7.57–7.42 (m, 4 H, Ar), 5.25 (t, J = 4.9 Hz, 1 H, CH_2CH), 3.99 (m, 2 H, CH_2CH_2), 3.84 (m, 2 H, CH_2CH_2), 3.47 (d, J = 4.9 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.8, 132.4, 132.3, 128.6, 127.8, 127.4, 125.8, 125.4 (2C), 123.9, 104.2, 64.9, 37.7 ppm. $C_{14}H_{14}O_2$ (214): calcd. C 78.48, H 6.59; found C 78.56, H 6.71. MS (EI, 70 eV): m/z (%) = 214 (63) [M$^+$]. Before purification, traces of 2-methyl-2-(naphthalen-1-yl)-1,3-dioxolane (**27e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10 (m, 2 H, CH_2CH_2), 1.90 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **27d**.

2-(Anthracen-9-yl)methyl-1,3-dioxolane (28d): Isomer **28d** was obtained in 79% (0.209 g) isolated yield. White solid. M.p. 93 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (s, 1 H, Ar), 8.37 (d, J = 8.3 Hz, 2 H, Ar), 8.01 (d, J = 8.3 Hz, 2 H, Ar), 7.56–7.43 (m, 4 H, Ar), 5.32 (t, J = 4.8 Hz, 1 H, CH_2CH), 4.04 (d, J = 4.8 Hz, 2 H,

CH_2CH), 4.01 (m, 2 H, CH_2CH_2), 3.81 (m, 2 H, CH_2CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.5, 130.7, 129.0, 128.3, 126.8, 125.6, 125.9, 124.8, 104.2, 65.0, 32.7 ppm. $C_{18}H_{16}O_2$ (264): calcd. C 81.79, H 6.10; found C 81.89, H 6.19. MS (EI, 70 eV): *m*/*z* (%) = 264 (31) [M^+]. Before purification, traces of 2-(anthracen-9-yl)-2-methyl-1,3-dioxolane (**28e**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.10 (m, 2 H, CH_2CH_2), 2.25 (s, 3 H, Me) ppm. The other peaks were hidden by those of compound **28d**.

1,2-Bis(1,3-dioxolan-2-ylmethyl)benzene (29dd): Isomer **29dd** was obtained in 51% (0.228 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30–7.15 (m, 4 H, Ar), 5.06 (t, *J* = 4.3 Hz, 2 H, CH_2C*H*), 3.97–3.77 (m, 8 H, CH_2CH_2), 3.08 (d, *J* = 4.3 Hz, 4 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.0, 130.8, 126.7, 104.7, 64.9, 37.5 ppm. $C_{14}H_{18}O_4$ (250): calcd. C 67.18, H 7.25; found C 67.30, H 7.35.

2-(Pyrid-3-ylmethyl)-1,3-dioxolane (30d): Isomer **30d** was obtained in 83% (0.137 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.48 (d, *J* = 2.1 Hz, 1 H, Ar), 8.76 (dd, *J* = 5.0 and 1.7 Hz, 1 H, Ar), 7.57 (dt, *J* = 7.9 and 1.7 Hz, 1 H, Ar), 7.19 (dd, *J* = 7.9 and 5.0 Hz, 1 H, Ar), 5.05 (t, *J* = 4.3 Hz, 1 H, CH_2C*H*), 3.90–3.75 (m, 4 H, CH_2CH_2), 2.94 (d, *J* = 4.3 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.8, 147.8, 137.5, 131.5, 123.1, 103.6, 65.0, 37.7 ppm. $C_9H_{11}NO_2$ (165): calcd. C 65.44, H 6.71; found C 65.21, H 6.82. MS (EI, 70 eV): *m*/*z* (%) = 165 (17) [M^+]. Before purification, traces of 2-[1-(pyrid-3-yl)vinyloxy]ethanol (**30a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (d, *J* = 3.2 Hz, 1 H, C=CH_2), 4.31 (d, *J* = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **30d**.

2-(Pyrid-4-ylmethyl)-1,3-dioxolane (31d): Isomer **31d** was obtained in 88% (0.145 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (d, *J* = 6.1 Hz, 2 H, Ar), 7.01 (d, *J* = 6.1 Hz, 2 H, Ar), 4.88 (t, *J* = 4.5 Hz, 1 H, CH_2C*H*), 3.60–3.75 (m, 4 H, CH_2CH_2), 2.78 (d, *J* = 4.5 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4, 144.9, 125.0, 103.3, 64.9, 39.8 ppm. $C_9H_{11}NO_2$ (165): calcd. C 65.44, H 6.71; found C 65.18, H 6.60. Before purification, traces of 2-[1-(pyrid-4-yl)vinyloxy]ethanol (**31a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.84 (d, *J* = 3.2 Hz, 1 H, C=CH_2), 4.38 (d, *J* = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **31d**.

2-(Quinol-3-ylmethyl)-1,3-dioxolane (32d): Isomer **32d** was obtained in 85% (0.183 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.82 (d, *J* = 2.1 Hz, 1 H, Ar), 8.07 (d, *J* = 8.1 Hz, 1 H, Ar), 8.04 (d, *J* = 2.1 Hz, 1 H, Ar), 7.77 (d, *J* = 8.1 Hz, 1 H, Ar), 7.65 (t, *J* = 8.1 Hz, 1 H, Ar), 7.50 (t, *J* = 8.1 Hz, 1 H, Ar), 5.15 (t, *J* = 4.1 Hz, 1 H, CH_2C*H*), 3.90–3.75 (m, 4 H, CH_2CH_2), 3.13 (d, *J* = 4.1 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4, 146.9, 136.3, 129.0, 128.9, 128.7, 127.6, 127.4, 126.4, 103.6, 65.0, 37.8 ppm. $C_{13}H_{13}NO_2$ (215): calcd. C 72.54, H 6.09; found C 72.72, H 6.00. MS (EI, 70 eV): *m*/*z* (%) = 215 (52) [M^+]. Before purification, traces of 2-(1-quinol-3-yl-vinyloxy)ethanol (**32a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.88 (d, *J* = 3.2 Hz, 1 H, C=CH_2), 4.42 (d, *J* = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **32d**.

2-(Isoquinol-4-ylmethyl)-1,3-dioxolane (33d): Isomer **33d** was obtained in 81% (0.174 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.12 (s, 1 H, Ar), 8.44 (s, 1 H, Ar), 8.04 (d, *J* = 8.1 Hz, 1 H, Ar), 7.91 (d, *J* = 8.1 Hz, 1 H, Ar), 7.69 (t, *J* = 8.1 Hz, 1 H, Ar), 7.55 (t, *J* = 8.1 Hz, 1 H, Ar), 5.18 (t, *J* = 4.7 Hz, 1 H, CH_2C*H*), 3.92–3.74 (m, 4 H, CH_2CH_2), 3.33 (d, *J* = 4.7 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7, 144.2, 135.1, 130.1, 128.4, 128.0, 126.7, 125.6, 123.3, 103.7, 64.9, 34.7 ppm. $C_{13}H_{13}NO_2$ (215): calcd. C 72.54, H 6.09; found C 72.33, H 5.97. MS (EI, 70 eV): *m*/*z* (%) = 215 (90) [M^+]. Before purification, traces of 2-[(1-isoquinol-4-yl)vinyloxy]ethanol (**33a**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.56 (d, *J* = 3.2 Hz, 1 H, C=CH_2), 4.47 (d, *J* = 3.2 Hz, 1 H, C=CH_2) ppm. The other peaks were hidden by those of compound **33d**.

2-(Pyrimid-5-ylmethyl)-1,3-dioxolane (34d): Isomer **34d** was obtained in 76% (0.126 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.09 (s, 1 H, Ar), 8.65 (s, 2 H, Ar), 5.09 (t, *J* = 4.0 Hz, 1 H, CH_2C*H*), 3.82 (m, 4 H, CH_2CH_2), 2.95 (d, *J* = 4.0 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.0 (2C), 157.0, 129.2, 102.5, 65.2, 35.0 ppm. $C_8H_{10}N_2O_2$ (166): calcd. C 57.82, H 6.07; found C 57.92, H 5.88. MS (EI, 70 eV): *m*/*z* (%) = 166 (71) [M^+].

3,5-Bis(1,3-dioxolan-2-ylmethyl)pyridine (35dd): Isomer **35dd** was obtained in 78% (0.196 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 2 H, Ar), 7.45 (s, 1 H, Ar), 4.98 (t, *J* = 4.3 Hz, 2 H, CH_2C*H*), 3.85–3.65 (m, 8 H, CH_2CH_2), 2.85 (d, *J* = 4.3 Hz, 4 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.8, 138.7, 130.8, 103.5, 64.8, 37.4 ppm. $C_{13}H_{17}NO_4$ (251): calcd. C 62.14, H 6.82; found C 62.31, H 6.70.

5-(1,3-Dioxolan-2-ylmethyl)furan-2-carbaldehyde (36d): Isomer **36d** was obtained in 78% (0.142 g) isolated yield. Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.54 (s, 1 H, CHO), 7.17 (d, *J* = 3.4 Hz, 1 H, Ar), 6.39 (d, *J* = 3.4 Hz, 1 H, Ar), 5.19 (t, *J* = 4.3 Hz, 1 H, CH_2C*H*), 4.00–3.80 (m, 4 H, CH_2CH_2), 3.08 (d, *J* = 4.3 Hz, 2 H, CH_2CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.2, 157.7, 152.2, 122.8, 110.8, 101.7, 65.1, 33.9 ppm. $C_9H_{10}O_4$ (182): calcd. C 59.34, H 5.53; found C 59.14, H 5.71. Before purification, traces of (*Z*)-5-[2-(2-hydroxyethoxy)vinyl]furan-2-carbaldehyde (**36b**) were also observed. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.44 (d, *J* = 7.2 Hz, 1 H, C=C*H*) ppm. The other peaks were hidden by those of compound **36d**.

37a–c: 37a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.70 (d, *J* = 1.9 Hz, 1 H, =CH_2), 4.28 (d, *J* = 1.9 Hz, 1 H, =CH_2) ppm. **37b**: δ = 6.29 (d, *J* = 7.0 Hz, 1 H, =CH), 5.21 (d, *J* = 7.0 Hz, 1 H, =CH) ppm. **37c**: δ = 7.07 (d, *J* = 12.8 Hz, 1 H, =CH), 5.82 (d, *J* = 12.8 Hz, 1 H, =CH) ppm.

38a–c: 38a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.75 (d, *J* = 1.5 Hz, 1 H, =CH_2), 4.31 (d, *J* = 1.5 Hz, 1 H, =CH_2) ppm. **38b**: δ = 6.35 (d, *J* = 7.0 Hz, 1 H, =CH), 5.24 (d, *J* = 7.0 Hz, 1 H, =CH) ppm. **38c**: δ = 7.11 (d, *J* = 13.0 Hz, 1 H, =CH), 5.85 (d, *J* = 13.0 Hz, 1 H, =CH) ppm.

39a–d: 39a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.74 (d, *J* = 1.5 Hz, 1 H, =CH_2), 4.19 (d, *J* = 1.5 Hz, 1 H, =CH_2) ppm. **39b**: δ = 6.30 (d, *J* = 7.0 Hz, 1 H, =CH), 5.23 (d, *J* = 7.0 Hz, 1 H, =CH) ppm. **39c**: δ = 7.10 (d, *J* = 12.0 Hz, 1 H, =CH), 5.83 (d, *J* = 12.0 Hz, 1 H, =CH) ppm. **39d**: δ = 4.83 (t, *J* = 5.5 Hz, 1 H, CH_2C*H*) ppm. **39e** was not detected.

40a–d: 40a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (d, *J* = 1.5 Hz, 1 H, =CH_2), 4.34 (d, *J* = 1.5 Hz, 1 H, =CH_2) ppm. **40b**: δ = 5.84 (d, *J* = 7.0 Hz, 1 H, =CH) ppm. **40c**: δ = 6.89 (d, *J* = 12.0 Hz, 1 H, =CH), 6.45 (d, *J* = 12.0 Hz, 1 H, =CH) ppm. **40d**: δ = 5.01 (t, *J* = 5.5 Hz, 1 H, CH_2C*H*) ppm. **40e** was not detected.

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