Heck Reaction of Protected Allyl Alcohols with Aryl Bromides Catalyzed by a Tetraphosphanepalladium Complex

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A range of aryl bromides undergo a Heck vinylation reaction with a protected allyl alcohol in the presence of $[PdCl(C_3H_5)]_2$/*cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphanylmethyl)cyclopentane as a catalyst. The reactivity of these allyl alcohol derivatives using a variety of protecting groups has been studied. The best results in terms of substrate/catalyst ratio were obtained with a THP protecting group. In most cases, the major isomer obtained was the (*E*)-cinnamyl alcohol derivative. The reaction tolerates several functionalities, such as trifluoromethyl, methoxy, dimethylamino, acetyl, formyl or nitrile. Furthermore, this catalyst can be used at low loadings, even for reactions with sterically hindered substrates.

Introduction

The Heck reaction is one of the most widely used palladium-catalyzed methodologies in organic synthesis. The efficiency of several catalysts for the reaction of aryl halides with acrylates or styrene derivatives has been studied in detail.[1–6] The Heck reaction between an allyl alcohol or protected allyl alcohol and an aryl halide has attracted less attention; however, this is a powerful method for the synthesis of 3-arylpropionaldehyde derivatives. Most of the results described with allyl alcohols were obtained in the presence of expensive aryl iodides.[7–26] Few results have been described in the presence of aryl bromides.[27] 3-Arylpropionaldehyde derivatives are generally thermally unstable in organic solvents and the elevated temperatures required for the coupling of aryl bromides with an allyl alcohol generally lead to the decomposition of the product. The use of protected allyl alcohol derivatives should therefore lead to more satisfactory results with these aryl bromides; however few results have been described with such substrates.[28,29]

In order to find stable and efficient palladium catalysts, we have prepared the tetrapodal phosphane ligand *cis*,*cis*,*cis*-1,2,3,4-tetrakis(diphenylphosphanylmethyl)cyclopentane or Tedicyp (Figure 1)[30] in which the four diphenylphosphanylalkyl groups are stereospecifically bound to the same face of the cyclopentane ring. We have already reported the results obtained in allylic substitution,[30] in Suzuki cross-coupling,[31,32] in Sonogashira[33] and Heck[34–42] reactions using Tedicyp as ligand. For example, a TON of 69 000 for the coupling of 4-bromobenzophenone with hex-1-en-3-ol has been reported.[41] For this reaction the corresponding ketone was selectively obtained. Here, in order to further establish the requirements for a successful Heck reaction, we wish to report on the reaction of a protected allyl alcohol with a variety of aryl bromides using Tedicyp as the ligand (Figure 1).

Figure 1. The structure of Tedicyp.

Results and Discussion

For this study, based on previous results,[34] DMF was chosen as the solvent and potassium carbonate as the base. The reactions were generally performed at 130 °C under argon in the presence of a 1:2 $[Pd(C_3H_5)Cl]_2$/Tedicyp ratio as catalyst. Seven isomers can be obtained from this reaction (Scheme 1): the three branched isomers coming from the attack at the central carbon of the allyl alcohol derivative [*gem*-branched **a** and (*Z*/*E*)-branched **b**] and the four linear isomers coming from the attack at the terminal carbon of the allyl alcohol derivative [(*E*)-allyl **c**, (*Z*)-allyl **d**, (*E*)-enol **e**, (*Z*)-enol **f**]. The formation of this mixture is probably due to the involvement of both the available β-hydrogen atoms of the $[PdCH(CH_2Ar)(CH_2OR^2)]$ intermediate in the elimination step of the catalytic cycle.

First we studied the reactivity of allyloxytrimethylsilane and allyloxy-*tert*-butyldimethylsilane. In the presence of al-

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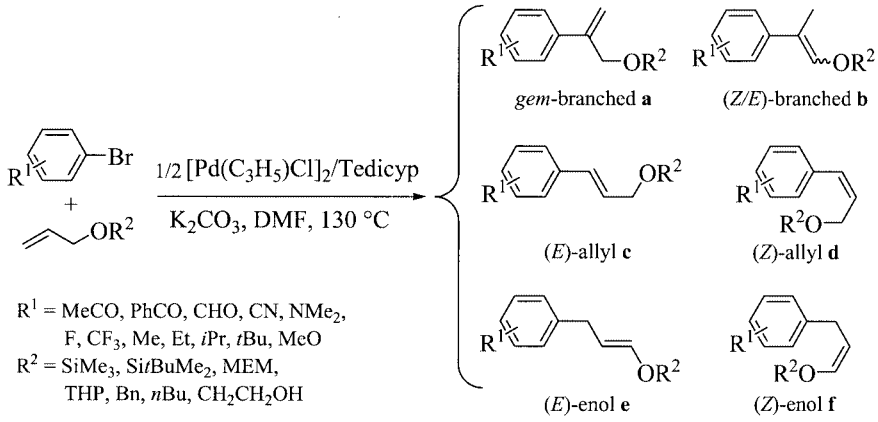

Scheme 1.

Table 1. Heck reaction with allyloxy-*tert*-butyldimethylsilane (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	1000	0:0:100:0:0:0	**1c**	74
2	4-$HCOC_6H_4Br$	100	0:0:100:0:0:0	**2c**	54[b]
3	4-$CF_3C_6H_4Br$	250	0:0:100:0:0:0	**3c**	31[b]
4	4-*t*BuC_6H_4Br	100	0:0:100:0:0:0	**4c**	40[b]
5	4-$MeOC_6H_4Br$	100	0:0:100:0:0:0	**5c**	32[b]
6	2,4,6-$Me_3C_6H_2Br$	100	18:0:82:0:0:0	**6a**, **6c**	44[b]
7	3-bromopyridine	100	22:0:78:0:0:0	**7a**, **7c**	72
8	3-bromoquinoline	100	0:0:100:0:0:0	**8c**	76

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated relative to Pd atom; aryl bromide (1 equiv.), allyloxy-*tert*-butyldimethylsilane (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, complete conversion of the aryl bromide, isolated yield of the mixture of isomers. [b] The formation of side-products was also observed.

lyloxytrimethylsilane, 4-*tert*-butylbromobenzene and 1 mol-% catalyst complete conversion of the aryl bromide was observed, although the formation of [3-(4-*tert*-butylphenyl)allyloxy]trimethylsilane was not detected. The trimethylsilane protecting group is not stable under the reaction conditions (90 °C, K_2CO_3) and the 3-(4-*tert*-butylphenyl)propionaldehyde decomposes. Next, we studied the reaction with allyloxy-*tert*-butyldimethylsilane (Table 1). With this alkene the vinylation products were obtained using 1–0.1% catalyst. In most cases the (*E*)-allyl isomer **c** (Scheme 1) was obtained selectively together with decomposition products. The reaction proceeds with electron-poor aryl bromides such as 4-bromoacetophenone or 4-bromobenzaldehyde and also with electron-rich aryl bromides such as 4-bromoanisole (entries 1–5, Table 1). With two substrates (3-bromopyridine and 1-bromo-2,4,6-trimethylbenzene) the formation of the *gem*-branched **a** isomer was also observed (entries 6 and 7, Table 1). With this protecting group the (*E*)- and (*Z*)-enol isomers **e**, **f** were not observed. These isomers are probably unstable under the reactions conditions.

Next we studied the reactivity and the selectivity of the reaction using MEM as protecting group on the allyl alcohol (Table 2). The reaction was possible with a high substrate/catalyst ratio in the presence of 4-bromoacetophenone (entries 1 and 2, Table 2). On the other hand, with electron-rich aryl bromides lower reaction rates were observed and 0.4% catalyst was used (entries 3 and 6, Table 2). In all cases we obtained mixtures of regio- and stereoisomers. In general the major isomer was the (*E*)-allyl **c**. Up to 79% of this isomer was obtained for the reaction with 4-*tert*-butylbromobenzene, but the presence of the two isomers (*E*)-enol **e** and (*Z*)-enol **f** was also observed. These two isomers were obtained in larger quantities with 1-bromo-2,4,6-trimethylbenzene. This sterically congested substrate led to the formation of (*E*)-allyl **c**, (*E*)-enol **e** and (*Z*)-enol **f** in a 38:38:24 ratio, thus indicating that the β-hydrogen elimination of the [PdCH(CH_2Ar)(CH_2OR^2)] intermediate is easier with the CH_2OR^2 substituent, probably for steric reasons.

Subsequently we studied the reaction of 2-allyloxytetrahydropyran with aryl bromides. The THP protecting group gave better results than those obtained with MEM. For example, the reaction of 4-bromoacetophenone gave a mixture of adducts in 91% yield in the presence of 0.01% catalyst (entry 1, Table 3). With 4-*tert*-butylbromobenzene, a TON of 34 000 was obtained with THP (entries 10 and 11, Table 3). Under similar reactions conditions with MEM as protecting group a TON of 40 was obtained. Having demonstrated that 2-allyloxytetrahydropyran can be efficiently reacted with aryl bromides, we investigated the scope of the coupling reaction using substituted aryl bromides and heteroaryl bromides. The results presented in Table 3 show a minor substituent effect of the aryl bromide on the reaction rate. Electron-withdrawing groups in the aryl bromides support the reaction, while electron-donating groups are slightly unfavourable. For example, turnover numbers of

Table 2. Heck reaction with 3-(2-methoxyethoxymethoxy)propene (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	1000	0:0:60:0:18:22	**9c**–**f**	88
2	4-$MeCOC_6H_4Br$	10 000	0:0:71:0:10:19	**9c**–**f**	10[b]
3	4-*t*BuC_6H_4Br	250	0:0:79:0:9:12	**10c**–**f**	91
4	4-*t*BuC_6H_4Br	1000	0:0:79:0:9:12	**10c**–**f**	32[b]
5	4-$MeOC_6H_4Br$	250	1:7:54:0:18:20	**11a**–**f**	92
6	2,4,6-$Me_3C_6H_2Br$	250	0:0:38:0:38:24	**12c**–**f**	86

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated with respect to Pd atom; aryl bromide (1 equiv.), 3-(2-methoxyethoxymethoxy)propene (1.2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, isolated yield of the mixture of isomers. [b] GC and NMR conversions.

3300–10 000 can be achieved with this catalyst for activated substrates such as 4-bromobenzophenone, 4-bromobenzaldehyde, 4-(trifluoromethyl)bromobenzene and 4-bromobenzonitrile (entries 2–8, Table 3). On the other hand, with deactivated 4-bromoanisole or 4-(dimethylamino)bromobenzene, we obtained TONs of 940 and 670, respectively (entries 12–14, Table 3). With these substrates the linear isomers **c**, **d**, **e** and **f** were obtained with 86–96% selectivity. Among them the (*E*)-allyl **c** isomer was obtained in 52–71% selectivity.

Next, we studied the influence of one *ortho* substituent on the aryl bromide. 2-Bromoacetophenone led to a lower TON (225) than *para*-substituted bromoacetophenone (entry 17, Table 3). 2-Fluorobromobenzene, 2-bromotoluene

Table 3. Heck reaction with 2-allyloxytetrahydropyran (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	10 000	5:2:58:5:12:18	**13a**–**f**	91
2	4-$PhCOC_6H_4Br$	1000	1:3:64:0:16:16	**14a**–**f**	88
3	4-$PhCOC_6H_4Br$	10 000	1:3:64:0:16:16	**14a**–**f**	33[b]
4	4-$HCOC_6H_4Br$	10 000	4:1:64:2:9:20	**15a**–**f**	90
5	4-$CF_3C_6H_4Br$	1000	5:0:71:2:10:12	**16a**–**f**	93
6	4-$CF_3C_6H_4Br$	10 000	5:0:68:2:11:14	**16a**–**f**	72[b]
7	4-CNC_6H_4Br	1000	4:3:58:2:11:22	**17a**–**f**	93
8	4-CNC_6H_4Br	10 000	4:3:58:2:11:22	**17a**–**f**	82[b]
9	4-FC_6H_4Br	10 000	8:1:61:2:14:14	**18a**–**f**	90
10	4-*t*BuC_6H_4Br	10 000	7:6:58:2:13:14	**19a**–**f**	94
11	4-*t*BuC_6H_4Br	100 000	7:6:58:2:13:14	**19a**–**f**	34[b]
12	4-$MeOC_6H_4Br$	1000	10:4:54:2:15:15	**20a**–**f**	92
13	4-$NMe_2C_6H_4Br$	250	8:6:67:6:7:6	**21a**–**f**	83
14	4-$NMe_2C_6H_4Br$	1000	9:7:67:3:7:7	**21a**–**f**	67[b]
15	2-bromo-6-methoxynaphthalene	1000	6:6:69:3:8:8	**22a**–**f**	91
16	2-bromo-6-methoxynaphthalene	10 000	8:8:69:3:8:4	**22a**–**f**	73[b]
17	2-$MeCOC_6H_4Br$	250	7:0:61:7:11:14	**23a**–**f**	90
18	2-FC_6H_4Br	1000	6:0:36:2:27:29	**24a**–**f**	94
19	2-FC_6H_4Br	10 000	5:0:41:4:24:26	**24a**–**f**	88[b]
20	2-MeC_6H_4Br	1000	0:0:59:0:19:22	**25c**–**f**	92
21	1-bromonaphthalene	10 000	6:4:36:0:25:29	**26a**–**f**	92
22	1-bromonaphthalene	100 000	5:4:44:0:23:24	**26a**–**f**	57[b]
23	2,6-$F_2C_6H_3Br$	1000	0:0:17:0:47:36	**27c**–**f**	94
24	2,6-$F_2C_6H_3Br$	10 000	0:0:16:0:44:40	**27c**–**f**	86[b]
25	2,4,6-$Me_3C_6H_2Br$	1000	0:0:34:0:42:34	**28c**–**f**	88
26	2,6-Et_2-4-MeC_6H_2Br	1000	0:0:45:0:25:30	**29c**–**f**	87
27	2,6-Et_2-4-MeC_6H_2Br	10 000	0:0:56:0:18:26	**29c**–**f**	33[b]
28	9-bromoanthracene	1000	0:0:6:0:46:48	**30c**–**f**	88
29	9-bromoanthracene	10 000	0:0:6:0:48:46	**30c**–**f**	78[b]
30	2,4,6-*i*$Pr_3C_6H_2Br$	100	0:0:0:0:50:50	**31e**–**f**	79
31	2,4,6-*i*$Pr_3C_6H_2Br$	1000	0:0:0:0:50:50	**31e**–**f**	55[b]
32	3-bromopyridine	10 000	8:0:62:3:12:15	**32a**–**f**	90
33	3-bromopyridine	100 000	7:0:57:1:15:20	**32a**–**f**	29[b]
34	3-bromoquinoline	10 000	7:0:67:5:8:13	**33a**–**f**	92
35	2-bromothiophene	250	9:0:60:7:14:10	**34a**–**f**	85
36	2-bromothiophene	1000	10:0:59:8:11:12	**34a**–**f**	75[b]
37	3-bromothiophene	10 000	21:9:64:0:3:3	**35a**–**f**	86
38	4-CN-C_6H_4Cl	250	6:1:55:0:14:24	**17a**–**f**	64

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated with respect to Pd atom; aryl bromide (1 equiv.), 2-allyloxytetrahydropyran (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, isolated yield of the mixture of isomers. [b] GC and NMR conversions.

or 1-bromonaphthalene led to higher TONs of 920–57 000, thus indicating that the low TON obtained with 2-bromoacetophenone does not comes from steric reasons, but is more likely due to poisoning of the catalyst. We then studied the reactivity of di-*ortho*-substituted aryl bromides. Even in the presence of highly congested substrates such as 9-bromoanthracene, 2,4,6-trimethylbromobenzene or 2,6-diethyl-4-methylbromobenzene satisfactory TONs were obtained (1000–7800; entries 25–29, Table 3). A very high regioselectivity (94%) in favour of formation of the isomers **e** and **f** was observed in the presence of 9-bromoanthracene. This selectivity in favour of the formation of the isomers **e** and **f** was complete (100%) with 1-bromo-2,4,6-triisopropylbenzene but a lower TON was obtained (550; entries 25–29, Table 3). We also studied the reactivity of heteroaryl bromides. Pyridines are π-electron-deficient heterocycles, whereas thiophenes and furans are rich in π-electrons. Oxidative addition to palladium should be faster with π-electron-deficient heterocycles; however, we observed similar reaction rates with 3-bromopyridine, 3-bromoquinoline and 3-bromothiophene (entries 32–34 and 37, Table 3). These observations suggest that the oxidative addition of the aryl or heteroaryl bromide is not the rate-limiting step of the reaction with this catalyst. On the other hand the TON obtained for the reaction with 2-bromothiophene (750) indicates that with this α-substituted heteroaryl bromide, a possible interaction between the hetero element and the palladium complex seems to be deleterious for the reaction (entries 35 and 36, Table 3).

Benzyl groups are also very useful protecting groups in organic synthesis, so we performed a few reactions with allyl benzyl ether (Table 4). The reactions rates using this allyl ether are similar to those observed with 2-allyloxytetrahydropyran. 4-Bromoacetophenone and 4-*tert*-butylbromobenzene led to the expected mixtures of adducts in good yields in the presence of 0.01–0.001% catalyst (entries 1–4, Table 4). The selectivities are slightly different than with THP as protecting group − larger amounts of (*E*)-enol **e** and (*Z*)-enol **f** were observed. With 2-bromobenzonitrile up to 84% of these two enol isomers was obtained (entries 6 and 7, Table 4). In most cases, only traces of the branched isomer were detected. The reaction also proceeds in good yield with heteroaromatic substrates (entries 10–15, Table 4).

Finally, we performed several reactions with 3-butoxypropene and 2-allyloxyethanol (Table 5 and Table 6). With these two substituents on the allyl alcohol the deprotection of the allyl isomers **c** and **d** to give cinnamyl derivatives should be not simple. However, the deprotection of the enols **e** and **f** should be easy and would lead selectively to the aldehydes. In the presence of 4-bromoacetophenone, 4-*tert*-butylbromobenzene or 4-bromoanisole, 3-butoxypropene gave the expected mixture of products in good yields with high substrate/catalyst ratios (Table 5). The two enol isomers **e** and **f** were obtained with 42–65% selectivity. 2-Allyloxyethanol is a commercially available and very cheap substituted allyl alcohol. We observed that this alkene also reacts with aryl bromides (Table 6). The best selectivity in favour of the formation of the enol isomers **e** and **f** (73%) was obtained with the electron-poor aryl bromide 4-bromoacetophenone.

Conclusions

In summary, we have established that the Tedicyp–palladium system is an efficient catalyst for the reaction of protected allyl alcohols with aryl bromides. In the presence of allyloxytrimethylsilane, decomposition of the products was observed. Better results were obtained with allyloxy-*tert*-butyldimethylsilane as alkene. The cinnamyl derivatives were obtained selectively, although in low yields in some cases, due to partial decomposition of the products. The use of MEM, THP and Bn as protecting groups led to the expected adducts, but higher substrate/catalyst ratios were needed with THP or Bn as protecting groups. Both the steric hindrance and the electronic properties of the aryl bromide have an effect on the reaction rates and the selectivi-

Table 4. Heck reaction with allyloxymethylbenzene (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	10 000	0:0:35:10:22:33	**36c**–**f**	92
2	4-$MeCOC_6H_4Br$	100 000	1:0:32:14:20:33	**36a**–**f**	36[b]
3	4-$tBuC_6H_4Br$	10 000	0:0:47:0:23:30	**37c**–**f**	90
4	4-$tBuC_6H_4Br$	100 000	0:0:52:0:23:25	**37c**–**f**	87[b]
5	4-$MeOC_6H_4Br$	10 000	7:2:50:3:20:18	**38a**–**f**	91
6	2-CNC_6H_4Br	250	2:0:14:0:37:47	**39a**–**f**	89
7	2-CNC_6H_4Br	1000	1:3:15:4:35:42	**39a**–**f**	50[b]
8	2,4,6-$Me_3C_6H_2Br$	250	0:0:40:0:31:29	**40c**–**f**	87
9	2,4,6-$Me_3C_6H_2Br$	1000	0:0:34:0:36:30	**40c**–**f**	34[b]
10	3-bromopyridine	10 000	7:0:36:2:22:33	**41a**–**f**	92
11	3-bromopyridine	100 000	4:0:32:0:27:37	**41a**–**f**	27[b]
12	2-bromothiophene	250	0:0:46:8:22:24	**42c**–**f**	89
13	2-bromothiophene	1000	0:0:48:9:20:23	**42c**–**f**	75[b]
14	3-bromothiophene	250	0:0:44:0:25:31	**43c**–**f**	89
15	3-bromothiophene	1000	0:0:44:0:21:35	**43c**–**f**	68[b]

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated with respect to Pd atom; aryl bromide (1 equiv.), allyloxymethylbenzene (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, isolated yield of the mixture of isomers. [b] GC and NMR conversions.

Table 5. Heck reaction with 3-butoxypropene (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	1000	5:3:37:0:24:31	**44a**–**f**	93
2	4-$MeCOC_6H_4Br$	10 000	5:3:37:0:24:31	**44a**–**f**	77[b]
3	4-*t*BuC_6H_4Br	1000	8:4:37:0:26:25	**45a**–**f**	90
4	4-*t*BuC_6H_4Br	10 000	8:4:41:2:24:21	**45a**–**f**	82[b]
5	4-$MeOC_6H_4Br$	10 000	10:3:47:1:22:17	**46a**–**f**	92
6	4-$MeOC_6H_4Br$	100 000	12:3:41:2:23:19	**46a**–**f**	27[b]
7	2,4,6-$Me_3C_6H_2Br$	100	4:0:38:0:28:30	**47a**–**f**	89
8	2,4,6-$Me_3C_6H_2Br$	250	3:0:32:0:34:31	**47a**–**f**	48[b]

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated with respect to Pd atom; aryl bromide (1 equiv.), 3-butoxypropene (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, isolated yield of the mixture of isomers. [b] GC and NMR conversions.

Table 6. Heck reaction with 2-allyloxyethanol (Scheme 1).

Entry[a]	ArBr	Substrate/catalyst ratio	*gem*-Branched **a**/(*Z*,*E*)-branched **b**/(*E*)-allyl **c**/(*Z*)-allyl **d**/(*E*)-enol **e**/(*Z*)-enol **f**	Product	Yield [%]
1	4-$MeCOC_6H_4Br$	1000	2:0:25:0:33:40	**48a**–**f**	83
2	4-$MeCOC_6H_4Br$	10 000	2:0:25:0:33:40	**48a**–**f**	13[b]
3	4-*t*BuC_6H_4Br	1000	1:13:32:0:26:28	**49a**–**f**	84
4	4-*t*BuC_6H_4Br	10 000	1:13:32:0:26:28	**49a**–**f**	73[b]
5	4-$MeOC_6H_4Br$	1000	2:18:32:0:22:26	**50a**–**f**	100[b]
6	4-$MeOC_6H_4Br$	10 000	2:18:32:0:22:26	**50a**–**f**	80
7	2,4,6-$Me_3C_6H_2Br$	50	70:0:0:0:22:8	**51a**–**f**	38[c]

[a] Conditions: catalyst see ref.[30]; substrate/catalyst ratio calculated with respect to Pd atom; aryl bromide (1 equiv.), 2-allyloxyethanol (2 equiv.), K_2CO_3 (2 equiv.), DMF, 130 °C, 20 h, isolated yield of the mixture of isomers. [b] GC and NMR conversions. [c] The formation of mesitylene was also observed.

ties, but even the *o*,*o*-disubstituted aryl bromide substrates provide the desired products. In most cases the linear isomers were obtained with high selectivity (70–100%). The ratio between the cinnamyl and enol isomers depends on the protecting group and the substituents on the aryl bromide. In the course of these reactions, only minor variations of the proportions of isomers formed were observed. With sterically congested aryl bromides larger amounts of the enol isomers were observed. Several reactions were performed with as little as 0.01% catalyst. Due to the high price of palladium, the practical advantage of such low catalyst loadings can become increasingly important for industrial processes. The functional group tolerance is remarkable: substituents such as fluoro, trifluoromethyl, methyl, methoxy, acetyl, formyl, benzoyl, dimethylamino and nitrile on the aryl bromide have been used successfully. Even though mixtures of isomers are generally obtained, this procedure should be a powerful method to access 3-arylpropionaldehyde and 3-arylpropan-1-ol derivatives by hydrogenation of the mixture of isomers.

Experimental Section

General Remarks: All reactions were run under argon using standard Schlenk techniques. Analytical grade DMF was used as received. Potassium carbonate (99+) was used without drying. The reactions were followed by GC and NMR spectroscopy for high-boiling-point substrates and by GC for low-boiling-point substrates. GC/mass spectra were recorded with a Varian Saturn 2100T spectrometer. ^1H and ^{13}C NMR spectra were recorded with a Bruker 300 MHz spectrometer in $CDCl_3$ solutions. Chemical shift are reported in ppm relative to $CDCl_3$ (δ = 7.25 ppm for ^1H and δ = 77 ppm for ^{13}C). 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 by GC and from the ^1H NMR spectrum of the crude mixtures. Ratios of regio- and stereoisomers were determined by GC and NMR spectroscopy.

General Procedure for the Coupling of Protected Alk-1-en-3-ols with Aryl Bromides: Treatment of a mixture of the aryl bromide (10 mmol) and K_2CO_3 (2.76 g, 20 mmol) with the protected allyl alcohol (12–20 mmol) at the appropriate temperature for 20 h in DMF (10 mL) in the presence of the Tedicyp-palladium complex (see Tables 1–6 for the substrate/catalyst ratio and other experimental conditions) under argon afforded the corresponding mixture of products after addition of water, extraction with dichloromethane or diethyl ether, separation, drying ($MgSO_4$), evaporation and filtration through silica gel. The major isomer was purified by chromatography on silica gel.

(*E*)-1-(4-Acetylphenyl)-3-(*tert*-butyldimethylsilanyloxy)propene (1c): ^1H NMR: δ = 0.10 (s, 6 H, MeSi), 0.93 (s, 9 H, *t*BuSi), 2.58 (s, 3 H, MeCO), 4.37 (dd, *J* = 4.6, 1.7 Hz, 2 H, CH_2), 6.41 (dt, *J* = 15.9, 4.6 Hz, 1 H, C*H*=), 6.65 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.44 (d, *J* = 8.4 Hz, 2 H, Ar), 7.90 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = –5.23, 18.4, 25.9, 26.54, 63.5, 126.4, 128.1, 128.7, 132.3, 135.8, 141.9, 197.6 ppm. $C_{17}H_{26}O_2Si$ (290.5): calcd. C 70.29, H 9.02; found C 70.47, H 8.87. MS (EI, 70 eV): *m*/*z* (%) = 290 (2) [M^+].

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(4-formylphenyl)propene (2c): ^1H NMR: δ = 0.10 (s, 6 H, MeSi), 0.94 (s, 9 H, *t*BuSi), 4.38 (dd, *J* = 4.5, 1.8 Hz, 2 H, CH_2), 6.45 (dt, *J* = 15.9, 4.5 Hz, 1 H, C*H*=), 6.67 (dt, *J* = 15.9, 1.8 Hz, 1 H, C*H*=), 7.51 (d, *J* = 8.2 Hz, 2 H, Ar), 7.82 (d, *J* = 8.2 Hz, 2 H, Ar), 9.96 (s, 1 H, CHO) ppm. ^{13}C NMR: δ = –5.24, 18.4, 25.9, 63.5, 126.8, 128.0, 130.1, 133.1, 135.2, 143.3, 191.7 ppm. $C_{16}H_{24}O_2Si$ (276.4): calcd. C 69.51, H 8.75; found C 69.24, H 8.61. MS (EI, 70 eV): *m*/*z* (%) = 276 (1) [M^+].

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(4-trifluoromethylphenyl)propene (3c): ^{1}H NMR: δ = 0.11 (s, 6 H, MeSi), 0.94 (s, 9 H, *t*BuSi), 4.37 (dd, J = 4.6, 1.6 Hz, 2 H, CH_2), 6.37 (dt, J = 15.9, 4.6 Hz, 1 H, C*H*=), 6.64 (d, J = 15.9 Hz, 1 H, C*H*=), 7.46 (d, J = 8.2 Hz, 2 H, Ar), 7.57 (d, J = 8.2 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = –5.2, 18.5, 26.0, 63.5, 124.7 (q, $J_{C,F}$ = 271.3 Hz), 125.5 (q, $^3J_{C,F}$ = 4.0 Hz), 126.5, 127.9, 129.1 (q, $^2J_{C,F}$ = 32.7 Hz), 132.0, 140.7 ppm. $C_{16}H_{23}F_3OSi$ (316.4): calcd. C 60.73, H 7.33; found C 60.99, H 7.48. MS (EI, 70 eV): *m*/*z* (%) = 316 (1) [M$^+$].

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(4-*tert*-butylphenyl)propene (4c): ^{1}H NMR: δ = 0.11 (s, 6 H, MeSi), 0.95 (s, 9 H, *t*BuSi), 1.32 (s, 9 H, Me), 4.35 (dd, J = 5.1, 1.6 Hz, 2 H, CH_2), 6.25 (dt, J = 15.8, 5.1 Hz, 1 H, C*H*=), 6.57 (dt, J = 15.8, 1.6 Hz, 1 H, C*H*=), 7.33 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = –5.1, 18.5, 26.0, 31.3, 34.5, 64.0, 125.4, 126.1, 128.4, 129.3, 134.3, 150.4 ppm. $C_{19}H_{32}OSi$ (304.5): calcd. C 74.93, H 10.59; found C 74.87, H 10.41. MS (EI, 70 eV): *m*/*z* (%) = 304 (2) [M$^+$].

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(4-methoxyphenyl)propene (5c): ^{1}H NMR: δ = 0.10 (s, 6 H, MeSi), 0.93 (s, 9 H, *t*BuSi), 3.80 (s, 3 H, MeO), 4.32 (dd, J = 5.3, 1.6 Hz, 2 H, CH_2), 6.14 (dt, J = 15.8, 5.3 Hz, 1 H, C*H*=), 6.52 (d, J = 15.8 Hz, 1 H, C*H*=), 6.84 (d, J = 9.0 Hz, 2 H, Ar), 7.31 (d, J = 9.0 Hz, 2 H, Ar) ppm. Compound **5c** was characterised by deprotection.[46]

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(2,4,6-trimethylphenyl)propene (6c): ^{1}H NMR: δ = 0.12 (s, 6 H, MeSi), 0.95 (s, 9 H, *t*BuSi), 2.27 (s, 9 H, Me), 4.38 (dd, J = 4.9, 1.8 Hz, 2 H, CH_2), 5.79 (dt, J = 16.1, 4.9 Hz, 1 H, C*H*=), 6.55 (d, J = 16.1 Hz, 1 H, C*H*=), 6.86 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = –5.13, 18.4, 20.2, 20.9, 25.9, 64.0, 126.8, 127.9, 128.5, 133.8, 133.9, 135.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 290 (2) [M$^+$]. Compound **6c** was characterised by deprotection.[43] Characteristic bands of isomer **6a**: δ = 4.92 (d, J = 2.1 Hz, 1 H, C*H*=), 5.60 (d, J = 2.1 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(3-pyridyl)propene (7c): ^{1}H NMR: δ = 0.11 (s, 6 H, MeSi), 0.94 (s, 9 H, *t*BuSi), 4.36 (dd, J = 4.6, 1.8 Hz, 2 H, CH_2), 6.36 (dt, J = 15.9, 4.6 Hz, 1 H, C*H*=), 6.59 (dt, J = 15.9, 1.8 Hz, 1 H, C*H*=), 7.22 (dd, J = 8.0, 4.0 Hz, 1 H, Ar), 7.67 (d, J = 8.0 Hz, 1 H, Ar), 8.44 (d, J = 4.0 Hz, 1 H, Ar), 8.58 (s, 1 H, Ar) ppm. ^{13}C NMR: δ = –5.23, 18.4, 25.9, 63.5, 123.4, 125.6, 131.6, 132.7, 132.8, 148.3, 148.4 ppm. $C_{14}H_{23}NOSi$ (249.4): calcd. C 67.42, H 9.29; found C 67.70, H 9.42. MS (EI, 70 eV): *m*/*z* (%) = 249 (1) [M$^+$]. Characteristic bands of isomer **7a**: δ = 4.50 (d, J = 1.4 Hz, 1 H, C*H*=), 5.45 (d, J = 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(*tert*-Butyldimethylsilanyloxy)-1-(3-quinolyl)propene (8c): ^{1}H NMR: δ = 0.13 (s, 6 H, MeSi), 0.96 (s, 9 H, *t*BuSi), 4.41 (dd, J = 4.5, 1.6 Hz, 2 H, CH_2), 6.51 (dt, J = 15.9, 4.5 Hz, 1 H, C*H*=), 6.76 (dt, J = 15.9, 1.6 Hz, 1 H, C*H*=), 7.53 (dd, J = 8.0, 1.2 Hz, 1 H, Ar), 7.64 (d, J = 8.0 Hz, 1 H, Ar), 7.8 (dd, J = 8.0, 1.2 Hz, 1 H, Ar), 7.98–8.15 (m, 2 H, Ar), 8.99 (d, J = 2.1 Hz, 1 H, Ar) ppm. ^{13}C NMR: δ = –5.22, 18.4, 25.9, 63.6, 125.9, 126.8, 127.7, 128.0, 129.0, 129.2, 130.0, 131.7, 132.3, 147.4, 149.4 ppm. $C_{18}H_{25}NOSi$ (299.5): calcd. C 72.19, H 8.41; found C 72.04, H 8.57. MS (EI, 70 eV): *m*/*z* (%) = 299 (1) [M$^+$].

(*E*)-1-(4-Acetylphenyl)-3-(2-methoxyethoxymethoxy)propene (9c): ^{1}H NMR: δ = 2.56 (s, 3 H, MeCO), 3.38 (s, 3 H, CH_3), 3.57 (t, J = 4.4 Hz, 2 H, CH_2), 3.72 (t, J = 4.4 Hz, 2 H, CH_2), 4.27 (dd, J = 5.6, 1.3 Hz, 2 H, CH_2), 4.78 (s, 2 H, CH_2), 6.40 (dt, J = 15.9, 5.6 Hz, 1 H, C*H*=), 6.66 (d, J = 15.9 Hz, 1 H, C*H*=), 7.43 (d, J = 8.4 Hz, 2 H, Ar), 7.89 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 26.5, 59.0, 66.9, 67.7, 71.8, 94.9, 126.5, 128.7 (2 C), 131.0, 136.1, 141.3, 197.4 ppm. $C_{15}H_{20}O_4$ (264.3): calcd. C 68.16, H 7.63; found C 68.40, H 7.51. MS (EI, 70 eV): *m*/*z* (%) = 264 (20) [M$^+$ – 89]. Characteristic bands of isomer **9e**: δ = 5.21 (dt, J = 12.3, 7.4 Hz, 1 H, C*H*=), 6.35 (dt, J = 12.3, 1.2 Hz, 1 H, C*H*=) ppm; **9f**: δ = 4.67 (dt, J = 7.5, 6.2 Hz, 1 H, C*H*=), 6.29 (dt, J = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-*tert*-Butylphenyl)-3-(2-methoxyethoxymethoxy)propene (10c): ^{1}H NMR: δ = 1.30 (s, 9 H, Me), 3.40 (s, 3 H, CH_3), 3.58 (t, J = 4.7 Hz, 2 H, CH_2), 3.73 (t, J = 4.7 Hz, 2 H, CH_2), 4.24 (dd, J = 6.3, 1.4 Hz, 2 H, CH_2), 4.78 (s, 2 H, CH_2), 6.24 (dt, J = 15.9, 6.3 Hz, 1 H, C*H*=), 6.60 (d, J = 15.9 Hz, 1 H, C*H*=), 7.35 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = 31.3, 34.6, 59.0, 66.9, 68.0, 71.8, 94.6, 124.7, 125.5, 126.2, 132.5, 133.9, 150.8 ppm. $C_{17}H_{26}O_3$ (278.4): calcd. C 73.34, H 9.41; found C 73.12, H 9.24. MS (EI, 70 eV): *m*/*z* (%) = 189 (90) [M$^+$ – 89]. Characteristic bands of isomer **10e**: δ = 5.22 (dt, J = 12.3, 6.5 Hz, 1 H, C*H*=), 6.31 (d, J = 12.3 Hz, 1 H, C*H*=) ppm; **10f**: δ = 4.71 (q, J = 6.4 Hz, 1 H, C*H*=), 6.25 (d, J = 6.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(2-Methoxyethoxymethoxy)-1-(4-methoxyphenyl)propene (11c): ^{1}H NMR: δ = 3.39 (s, 3 H, CH_3), 3.58 (t, J = 4.8 Hz, 2 H, CH_2), 3.73 (t, J = 4.8 Hz, 2 H, CH_2), 3.77 (s, 3 H, MeO), 4.22 (dd, J = 6.2, 1.3 Hz, 2 H, CH_2), 4.78 (s, 2 H, CH_2), 6.14 (dt, J = 15.9, 6.2 Hz, 1 H, C*H*=), 6.56 (d, J = 15.9 Hz, 1 H, C*H*=), 6.84 (d, J = 8.8 Hz, 2 H, Ar), 7.31 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 55.2, 59.0, 66.9, 68.1, 71.8, 94.6, 114.0, 123.3, 127.7 (2 C), 132.4, 159.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 252 (2) [M$^+$]. Compound **11c** was characterised by deprotection.[43] Characteristic bands of isomer **11a**: δ = 5.26 (d, J = 1.1 Hz, 1 H, C*H*=), 5.43 (d, J = 1.1 Hz, 1 H, C*H*=) ppm; **11b**: δ = 6.58 (q, J = 1.4 Hz, 1 H, C*H*=) ppm; **11e**: δ = 5.21 (dt, J = 12.4, 7.5 Hz, 1 H, C*H*=), 6.29 (dt, J = 12.4, 1.3 Hz, 1 H, C*H*=) ppm; **11f**: δ = 4.69 (dt, J = 7.5, 6.3 Hz, 1 H, C*H*=), 6.24 (dt, J = 6.3, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(2-Methoxyethoxymethoxy)-1-(2,4,6-trimethylphenyl)propene (12c): ^{1}H NMR: δ = 2.26 (s, 9 H, Me), 3.40 (s, 3 H, CH_3), 3.58 (t, J = 4.6 Hz, 2 H, CH_2), 3.75 (t, J = 4.6 Hz, 2 H, CH_2), 4.27 (dd, J = 6.0, 1.3 Hz, 2 H, CH_2), 4.81 (s, 2 H, CH_2), 5.77 (dt, J = 16.3, 6.0 Hz, 1 H, C*H*=), 6.57 (d, J = 15.9 Hz, 1 H, C*H*=), 6.85 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = 20.9 (3C), 59.0, 66.9, 68.2, 71.8, 94.5, 128.5, 130.4, 130.5, 133.5, 135.8, 136.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 175 (100) [M$^+$ – 89]. Compound **12c** was characterised by deprotection.[44] Characteristic bands of isomer **12e**: δ = 5.10 (dt, J = 12.5, 6.3 Hz, 1 H, C*H*=), 6.10 (dt, J = 12.5, 1.3 Hz, 1 H, C*H*=) ppm; **12f**: δ = 4.40 (q, J = 7.0 Hz, 1 H, C*H*=), 6.18 (dt, J = 6.2, 1.7 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-Acetylphenyl)-3-(tetrahydropyran-2-yloxy)propene (13c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 2.56 (s, 3 H, MeCO), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.18 (ddd, J = 13.5, 6.0, 1.0 Hz, 1 H, CH_2CH=), 4.38 (ddd, J = 13.5, 5.1, 1.4 Hz, 1 H, CH_2CH=), 4.69 (t, J = 3.3 Hz, 1 H, CH), 6.42 (dt, J = 15.9, 5.3 Hz, 1 H, C*H*=), 6.65 (d, J = 15.9 Hz, 1 H, C*H*=), 7.44 (d, J = 8.3 Hz, 2 H, Ar), 7.88 (d, J = 8.3 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.3, 26.5, 30.5, 62.2, 67.3, 98.1, 126.4, 128.6, 129.2, 130.6, 136.0, 141.4, 197.4 ppm. $C_{16}H_{20}O_3$ (260.3): calcd. C 73.82, H 7.74; found C 73.74, H 7.65. MS (EI, 70 eV): *m*/*z* (%) = 260 (5) [M$^+$]. Characteristic bands of isomer **13a**: δ = 5.40 (d, J = 1.3 Hz, 1 H, C*H*=), 5.54 (d, J = 1.3 Hz, 1 H, C*H*=) ppm; **13b**: δ = 6.82 (q, J = 1.2 Hz, 1 H, C*H*=) ppm; **13d**: δ = 5.90 (dt, J = 12.1, 6.5 Hz, 1 H, C*H*=), 6.92 (d, J = 12.1 Hz, 1 H, C*H*=) ppm; **13e**: δ = 5.14 (dt, J = 12.4, 7.6 Hz, 1 H, C*H*=), 6.37 (d, J = 12.4 Hz, 1 H, C*H*=) ppm; **13f**: δ = 4.67 (q, J = 6.3 Hz, 1 H, C*H*=), 6.33 (dt, J = 6.3, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-Benzoylphenyl)-3-(tetrahydropyran-2-yloxy)propene (14c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.16 (ddd, J = 13.4, 6.1, 1.1 Hz, 1 H,

CH_2CH=), 4.44 (ddd, J = 13.4, 5.1, 1.4 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.3 Hz, 1 H, CH), 6.44 (dt, J = 15.9, 5.6 Hz, 1 H, CH=), 6.65 (d, J = 15.9 Hz, 1 H, CH=), 7.39–7.61 (m, 5 H, Ar), 7.71–7.81 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.5, 62.2, 67.3, 98.0, 126.2, 128.2, 129.1, 129.8, 130.5, 130.7, 132.2, 136.3, 137.7, 140.9, 196.0 ppm. $C_{21}H_{22}O_3$ (322.4): calcd. C 78.23, H 6.88; found C 78.03, H 6.96. MS (EI, 70 eV): m/z (%) = 322 (5) [M$^+$]. Characteristic bands of isomer **14a**: δ = 5.42 (s, 1 H, CH=), 5.57 (s, 1 H, CH=) ppm; **14b**: δ = 6.85 (q, J = 1.2 Hz, 1 H, CH=) ppm; **14e**: δ = 5.17 (dt, J = 12.2, 7.6 Hz, 1 H, CH=), 6.40 (d, J = 12.2 Hz, 1 H, CH=) ppm; **14f**: δ = 4.63 (q, J = 6.3 Hz, 1 H, CH=), 6.27 (d, J = 6.3 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-Formylphenyl)-3-(tetrahydropyran-2-yloxy)propene (15c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.17 (ddd, J = 13.7, 6.0, 1.1 Hz, 1 H, CH_2CH=), 4.44 (ddd, J = 13.7, 5.1, 1.6 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.2 Hz, 1 H, CH), 6.46 (dt, J = 15.9, 5.8, 5.1 Hz, 1 H, CH=), 6.69 (d, J = 15.9 Hz, 1 H, CH=), 7.52 (d, J = 8.3 Hz, 2 H, Ar), 7.81 (d, J = 8.3 Hz, 2 H, Ar), 9.96 (s, 1 H, CHO) ppm. ^{13}C NMR: δ = 20.2, 26.2, 31.3, 63.1, 68.0, 98.9, 127.7, 130.9, 130.8, 131.3, 136.2, 143.7, 192.5 ppm. $C_{15}H_{18}O_3$ (246.3): calcd. C 73.15, H 7.37; found C 72.97, H 7.29. MS (EI, 70 eV): m/z (%) = 246 (5) [M$^+$]. Characteristic bands of isomer **15a**: δ = 5.53 (s, 1 H, CH=), 5.65 (s, 1 H, CH=) ppm; **15b**: δ = 6.94 (q, J = 1.3 Hz, 1 H, CH=) ppm; **15e**: δ = 5.22 (dt, J = 12.4, 7.6 Hz, 1 H, CH=), 6.38 (d, J = 12.4 Hz, 1 H, CH=) ppm; **15f**: δ = 4.68 (q, J = 6.3 Hz, 1 H, CH=), 6.36 (d, J = 6.3 Hz, 1 H, CH=) ppm.

(*E*)-3-(Tetrahydropyran-2-yloxy)-1-(4-trifluoromethylphenyl)propene (16c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.17 (ddd, J = 13.4, 6.1, 1.2 Hz, 1 H, CH_2CH=), 4.40 (ddd, J = 13.4, 5.1, 1.2 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.3 Hz, 1 H, CH), 6.40 (dt, J = 15.9, 5.7 Hz, 1 H, CH=), 6.40 (d, J = 15.9 Hz, 1 H, CH=), 7.46 (d, J = 8.3 Hz, 2 H, Ar), 7.55 (d, J = 8.3 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.3, 67.3, 98.1, 124.2 (q, $J_{C,F}$ = 271.9 Hz), 125.5 (q, $^3J_{C,F}$ = 4.0 Hz), 126.6, 128.9, 129.3 (q, $^2J_{C,F}$ = 32.1 Hz), 130.4, 140.3 ppm. $C_{15}H_{17}F_3O_2$ (286.3): calcd. C 62.93, H 5.99; found C 62.99, H 6.05. MS (EI, 70 eV): m/z (%) = 286 (2) [M$^+$]. Characteristic bands of isomer **16a**: δ = 5.49 (d, J = 1.2 Hz, 1 H, CH=), 5.59 (d, J = 1.2 Hz, 1 H, CH=) ppm; **16d**: δ = 5.99 (dt, J = 12.1, 6.3 Hz, 1 H, CH=), 6.60 (d, J = 12.1 Hz, 1 H, CH=) ppm; **16e**: δ = 5.23 (dt, J = 12.2, 7.6 Hz, 1 H, CH=), 6.38 (dt, J = 12.2, 0.8 Hz, 1 H, CH=) ppm; **16f**: δ = 4.67 (q, J = 6.3 Hz, 1 H, CH=), 6.25 (dt, J = 6.3, 1.5 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-Cyanophenyl)-3-(tetrahydropyran-2-yloxy)propene (17c): ^{1}H NMR: δ = 1.43–1.98 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–3.95 (m, 1 H, CH_2O), 4.16 (dd, J = 13.8, 6.0 Hz, 1 H, CH_2CH=), 4.42 (dd, J = 13.8, 5.1 Hz, 1 H, CH_2CH=), 4.68 (t, J = 3.3 Hz, 1 H, CH), 6.42 (dt, J = 16.1, 5.6 Hz, 1 H, CH=), 6.63 (d, J = 16.1 Hz, 1 H, CH=), 7.44 (d, J = 8.2 Hz, 2 H, Ar), 7.63 (d, J = 8.2 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.3, 30.5, 62.3, 67.1, 98.2, 110.7, 118.9, 126.8, 129.8, 130.3, 132.3, 141.3 ppm. $C_{15}H_{17}NO_2$ (243.3): calcd. C 74.05, H 7.04; found C 73.84, H 7.00. MS (EI, 70 eV): m/z (%) = 243 (2) [M$^+$]. Characteristic bands of isomer **17a**: δ = 5.50 (s, 1 H, CH=), 5.61 (s, 1 H, CH=) ppm; **17b**: δ = 6.88 (q, J = 1.1 Hz, 1 H, CH=) ppm; **17d**: δ = 6.02 (dt, J = 12.0, 6.4 Hz, 1 H, CH=), 6.56 (d, J = 12.0 Hz, 1 H, CH=) ppm; **17e**: δ = 5.18 (dt, J = 12.4, 7.6 Hz, 1 H, CH=), 6.38 (d, J = 12.4 Hz, 1 H, CH=) ppm; **17f**: δ = 4.64 (q, J = 6.3 Hz, 1 H, CH=), 6.35 (dt, J = 6.3, 1.4 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-Fluorophenyl)-3-(tetrahydropyran-2-yloxy)propene (18c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.13 (ddd, J = 12.9, 6.6, 1.2 Hz, 1 H, CH_2CH=), 4.37 (ddd, J = 12.9, 5.6, 1.2 Hz, 1 H, CH_2CH=), 4.69 (t, J = 3.3 Hz, 1 H, CH), 6.22 (dt, J = 15.9, 6.1 Hz, 1 H, CH=), 6.58 (d, J = 15.9 Hz, 1 H, CH=), 7.01 (m, 2 H, Ar), 7.35 (m, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.2, 67.5, 97.9, 115.4 (d, $^2J_{C,F}$ = 31.6 Hz), 125.7 (d, $^5J_{C,F}$ = 2.2 Hz), 127.9 (d, $^3J_{C,F}$ = 8.0 Hz), 131.0, 132.9 (d, $^4J_{C,F}$ = 3.3 Hz), 162.3 (d, $J_{C,F}$ = 246.7 Hz) ppm. MS (EI, 70 eV): m/z (%) = 236 (1) [M$^+$]. Compound **18c** was characterised by deprotection.[45] Characteristic bands of isomer **18a**: δ = 5.36 (d, J = 1.3 Hz, 1 H, CH=), 5.46 (d, J = 1.3 Hz, 1 H, CH=) ppm; **18b**: δ = 6.65 (q, J = 1.3 Hz, 1 H, CH=) ppm; **18d**: δ = 5.85 (dt, J = 11.7, 6.3 Hz, 1 H, CH=), 6.54 (d, J = 11.7 Hz, 1 H, CH=) ppm; **18e**: δ = 5.23 (dt, J = 12.2, 7.6 Hz, 1 H, CH=), 6.35 (dt, J = 12.2, 1.3 Hz, 1 H, CH=) ppm; **18f**: δ = 4.67 (q, J = 6.4 Hz, 1 H, CH=), 6.29 (dt, J = 6.4, 1.3 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-*tert*-Butylphenyl)-3-(tetrahydropyran-2-yloxy)propene (19c): ^{1}H NMR: δ = 1.31 (s, 9 H, Ar), 1.40–2.00 (m, 6 H, CH_2), 3.45–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.13 (ddd, J = 12.6, 6.6, 1.2 Hz, 1 H, CH_2CH=), 4.37 (ddd, J = 12.6, 5.5, 1.5 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.4 Hz, 1 H, CH), 6.18 (dt, J = 15.9, 5.8 Hz, 1 H, CH=), 6.56 (d, J = 15.9 Hz, 1 H, CH=), 7.33 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = 19.5, 25.5, 30.6, 31.3, 34.5, 62.2, 67.7, 97.7, 125.2, 125.4, 126.2, 132.2, 134.0, 150.7 ppm. $C_{18}H_{26}O_2$ (274.4): calcd. C 78.79, H 9.55; found C 78.58, H 9.61. MS (EI, 70 eV): m/z (%) = 274 (1) [M$^+$]. Characteristic bands of isomer **19a**: δ = 5.28 (d, J = 1.5 Hz, 1 H, CH=), 5.44 (d, J = 1.5 Hz, 1 H, CH=) ppm; **19b**: δ = 6.67 (q, J = 1.5 Hz, 1 H, CH=) ppm; **19d**: δ = 5.76 (dt, J = 12.1, 6.3 Hz, 1 H, CH=), 6.85 (d, J = 12.1 Hz, 1 H, CH=) ppm; **19e**: δ = 5.22 (dt, J = 12.4, 7.6 Hz, 1 H, CH=), 6.32 (dt, J = 12.4, 0.8 Hz, 1 H, CH=) ppm; **19f**: δ = 4.67 (q, J = 6.3 Hz, 1 H, CH=), 6.25 (dt, J = 6.3, 1.5 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-Methoxyphenyl)-3-(tetrahydropyran-2-yloxy)propene (20c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.45–3.60 (m, 1 H, CH_2O), 3.78 (s, 3 H, MeO), 3.80–4.00 (m, 1 H, CH_2O), 4.13 (ddd, J = 12.6, 6.8, 1.5 Hz, 1 H, CH_2CH=), 4.37 (ddd, J = 12.6, 5.8, 1.3 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.5 Hz, 1 H, CH), 6.18 (dt, J = 15.9, 5.8 Hz, 1 H, CH=), 6.56 (d, J = 15.9 Hz, 1 H, CH=), 6.83 (d, J = 8.7 Hz, 2 H, Ar), 7.32 (d, J = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 55.1, 62.1, 67.7, 97.7, 113.8, 123.6, 127.6, 129.5, 132.0, 159.1 ppm. MS (EI, 70 eV): m/z (%) = 248 (5) [M$^+$]. Compound **20c** was characterised by deprotection.[43] Characteristic bands of isomer **20a**: δ = 5.29 (d, J = 1.3 Hz, 1 H, CH=), 5.44 (d, J = 1.3 Hz, 1 H, CH=) ppm; **20b**: δ = 6.62 (q, J = 1.3 Hz, 1 H, CH=) ppm; **20d**: δ = 5.77 (dt, J = 11.9, 6.3 Hz, 1 H, CH=), 6.77 (d, J = 11.9 Hz, 1 H, CH=) ppm; **20e**: δ = 5.24 (dt, J = 12.2, 7.6 Hz, 1 H, CH=), 6.33 (dt, J = 12.2, 0.8 Hz, 1 H, CH=) ppm; **20f**: δ = 4.67 (q, J = 6.3 Hz, 1 H, CH=), 6.28 (dt, J = 6.3, 1.5 Hz, 1 H, CH=) ppm.

(*E*)-1-(4-Dimethylaminophenyl)-3-(tetrahydropyran-2-yloxy)propene (21c): ^{1}H NMR: δ = 1.50–2.00 (m, 6 H, CH_2), 2.95 (s, 6 H, Me), 3.44–3.58 (m, 1 H, CH_2O), 3.85–3.95 (m, 1 H, CH_2O), 4.12 (ddd, J = 12.3, 7.0, 1.0 Hz, 1 H, CH_2CH=), 4.36 (ddd, J = 12.3, 5.9, 1.3 Hz, 1 H, CH_2CH=), 4.70 (t, J = 3.6 Hz, 1 H, CH), 6.11 (dt, J = 15.7, 6.5 Hz, 1 H, CH=), 6.53 (d, J = 15.7 Hz, 1 H, CH=), 7.07 (d, J = 8.2 Hz, 2 H, Ar), 7.28 (d, J = 8.2 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.5, 25.5, 30.7, 40.4, 62.2, 68.1, 97.6, 112.3, 121.3, 125.2, 127.5, 132.9, 150.1 ppm. $C_{16}H_{23}NO_2$ (261.3): calcd. C 73.53, H 8.87; found C 73.67, H 8.99. MS (EI, 70 eV): m/z (%) = 261 (60) [M$^+$]. Characteristic bands of isomer **21a**: δ = 5.21 (s, 1 H, CH=), 5.41 (s, 1 H, CH=) ppm; **21b**: δ = 6.60 (s, 1 H, CH=) ppm; **21d**: δ = 5.68 (dt, J = 11.9, 6.3 Hz, 1 H, CH=) ppm; **21e**: δ = 5.23 (dt, J = 12.3, 5.5 Hz, 1 H, CH=), 6.33 (d, J = 12.3 Hz, 1 H, CH=) ppm; **21f**: δ = 4.73 (q, J = 6.2 Hz, 1 H, CH=), 6.26 (d, J = 6.2 Hz, 1 H, CH=) ppm.

(*E*)-1-(6-Methoxynaphthalen-2-yl)-3-(tetrahydropyran-2-yloxy)propene (22c): ^{1}H NMR: δ = 1.50–2.00 (m, 6 H, CH_2), 3.50–3.60 (m, 1 H, CH_2O), 3.90 (s, 3 H, MeO), 3.80–4.00 (m, 1 H, CH_2O), 4.20 (ddd, J = 12.8, 6.6, 1.1 Hz, 1 H, CH_2C*H*=), 4.57 (ddd, J = 12.8, 5.6, 1.5 Hz, 1 H, CH_2C*H*=), 4.45 (t, J = 3.5 Hz, 1 H, CH), 6.39 (dt, J = 15.9, 6.2 Hz, 1 H, C*H*=), 6.76 (d, J = 15.9 Hz, 1 H, C*H*=), 7.07–7.16 (m, 2 H, Ar), 7.58 (dd, J = 8.7, 1.5 Hz, 1 H, Ar), 7.64–7.72 (m, 3 H, Ar) ppm. ^{13}C NMR: δ = 19.5, 25.4, 30.6, 55.2, 62.2, 67.8, 97.9, 105.8, 118.9, 124.2, 125.2, 126.2, 127.0, 128.9, 129.4, 132.2, 132.5, 134.1, 157.7 ppm. $C_{19}H_{22}O_3$ (298.4): calcd. C 76.48, H 7.43; found C 76.27, H 7.33. MS (EI, 70 eV): *m*/*z* (%) = 298 (40) [M$^+$]. Characteristic bands of isomer **22a**: δ = 5.48 (s, 1 H, C*H*=), 5.67 (s, 1 H, C*H*=) ppm; **22b**: δ = 6.85 (q, J = 1.3 Hz, 1 H, C*H*=) ppm; **22d**: δ = 5.94 (dt, J = 12.0, 6.0 Hz, 1 H, C*H*=), 6.73 (d, J = 12.0 Hz, 1 H, C*H*=) ppm; **22e**: δ = 5.36 (dt, J = 12.2, 6.6 Hz, 1 H, C*H*=), 6.43 (dt, J = 12.2, 1.2 Hz, 1 H, C*H*=) ppm; **22f**: δ = 4.76 (q, J = 6.2 Hz, 1 H, C*H*=), 6.33 (d, J = 6.2 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(2-Acetylphenyl)-3-(tetrahydropyran-2-yloxy)propene (23c): ^{1}H NMR: δ = 1.45–2.00 (m, 6 H, CH_2), 2.56 (s, 3 H, MeCO), 3.45–3.65 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.18 (ddd, J = 13.2, 6.5, 1.4 Hz, 1 H, CH_2C*H*=), 4.41 (ddd, J = 13.2, 5.3, 1.7 Hz, 1 H, CH_2C*H*=), 4.72 (t, J = 3.4 Hz, 1 H, CH), 6.19 (dt, J = 16.0, 6.0 Hz, 1 H, C*H*=), 7.12 (d, J = 16.0 Hz, 1 H, C*H*=), 7.31 (td, J = 6.3, 1.3 Hz, 1 H, Ar), 7.43 (td, J = 6.4, 1.3 Hz, 1 H, Ar), 7.53–7.66 (m, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.5, 25.5, 29.9, 30.6, 62.3, 67.7, 98.0, 127.2, 127.8, 128.6, 129.2, 130.7, 131.4, 136.7, 137.6, 202.1 ppm. $C_{16}H_{20}O_3$ (260.3): calcd. C 73.82, H 7.74; found C 73.99, H 7.61. MS (EI, 70 eV): *m*/*z* (%) = 260 (1) [M$^+$]. Characteristic bands of isomer **23a**: δ = 5.07 (s, 1 H, C*H*=), 5.45 (s, 1 H, C*H*=) ppm; **23b**: δ = 6.62 (s, 1 H, C*H*=) ppm; **23d**: δ = 5.92 (dt, J = 12.0, 6.0 Hz, 1 H, C*H*=), 6.95 (d, J = 12.0 Hz, 1 H, C*H*=) ppm; **23e**: δ = 5.21 (dt, J = 12.4, 7.6 Hz, 1 H, C*H*=), 6.31 (d, J = 12.4 Hz, 1 H, C*H*=) ppm; **23f**: δ = 4.71 (q, J = 6.4 Hz, 1 H, C*H*=), 6.27 (d, J = 6.0 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(2-Fluorophenyl)-3-(tetrahydropyran-2-yloxy)propene (24c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.17 (ddd, J = 13.2, 6.3, 1.3 Hz, 1 H, CH_2C*H*=), 4.43 (ddd, J = 13.2, 5.3, 1.5 Hz, 1 H, CH_2C*H*=), 4.71 (t, J = 3.2 Hz, 1 H, CH), 6.39 (dt, J = 16.0, 6.3 Hz, 1 H, C*H*=), 6.79 (d, J = 16.0 Hz, 1 H, C*H*=), 6.95–7.25 (m, 3 H, Ar), 7.46 (dt, J = 7.6, 2.0 Hz, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.2, 67.7, 98.0, 115.6 (d, $^2J_{C,F}$ = 22.4 Hz), 124.0 (d, $^3J_{C,F}$ = 3.5 Hz), 124.5 (d, $^3J_{C,F}$ = 3.4 Hz), 124.7, 127.5 (d, $^3J_{C,F}$ = 4.0 Hz), 128.7, 128.8 (d, $^2J_{C,F}$ = 12.6 Hz), 160.7 (d, $J_{C,F}$ = 248.9 Hz). $C_{14}H_{17}FO_2$ (236.3): calcd. C 71.16, H 7.25; found C 70.94, H 7.04. MS (EI, 70 eV): *m*/*z* (%) = 236 (2) [M$^+$]. Characteristic bands of isomer **24a**: δ = 5.41 (s, 1 H, C*H*=), 5.56 (s, 1 H, C*H*=) ppm; **24d**: δ = 5.98 (dt, J = 12.1, 6.0 Hz, 1 H, C*H*=), 6.63 (d, J = 12.1 Hz, 1 H, C*H*=) ppm; **24e**: δ = 5.23 (dt, J = 12.3, 7.6 Hz, 1 H, C*H*=), 6.38 (d, J = 12.3 Hz, 1 H, C*H*=) ppm; **24f**: δ = 4.68 (q, J = 6.4 Hz, 1 H, C*H*=), 6.32 (dt, J = 6.4, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(2-Methylphenyl)-3-(tetrahydropyran-2-yloxy)propene (25c): ^{1}H NMR: δ = 1.50–2.00 (m, 6 H, CH_2), 2.35 (s, 3 H, Me), 3.45–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.19 (ddd, J = 12.6, 6.6, 1.5 Hz, 1 H, CH_2C*H*=), 4.42 (ddd, J = 12.6, 5.6, 1.3 Hz, 1 H, CH_2C*H*=), 4.70 (t, J = 3.3 Hz, 1 H, CH), 6.18 (dt, J = 15.6, 6.6 Hz, 1 H, C*H*=), 6.84 (d, J = 15.6 Hz, 1 H, C*H*=), 7.10–7.25 (m, 3 H, Ar), 7.40–7.50 (m, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.5, 19.7, 25.5, 30.6, 62.3, 67.8, 97.8, 125.7, 126.0, 127.3, 127.5, 130.1, 130.2, 135.4, 135.9 ppm. $C_{15}H_{20}O_2$ (232.3): calcd. C 77.55, H 8.68; found C 77.71, H 8.80. MS (EI, 70 eV): *m*/*z* (%) = 232 (1) [M$^+$]. Characteristic bands of isomer **25e**: δ = 5.18 (dt, J = 12.3, 7.2 Hz, 1 H, C*H*=), 6.31 (m, 1 H, C*H*=) ppm; **25f**: δ = 4.63 (q, J = 6.3 Hz, 1 H, C*H*=), 6.31 (m, 1 H, C*H*=) ppm.

(*E*)-1-(Naphthalen-1-yl)-3-(tetrahydropyran-2-yloxy)propene (26c): ^{1}H NMR: δ = 1.50–2.20 (m, 6 H, CH_2), 3.55–3.75 (m, 1 H, CH_2O), 3.90–4.15 (m, 1 H, CH_2O), 4.32 (ddd, J = 13.1, 6.5, 1.4 Hz, 1 H, CH_2C*H*=), 4.57 (ddd, J = 13.1, 5.5, 1.8 Hz, 1 H, CH_2C*H*=), 4.82 (t, J = 3.4 Hz, 1 H, CH), 6.39 (dt, J = 15.7, 6.3 Hz, 1 H, C*H*=), 7.37–7.60 (m, 4 H, Ar and C*H*=), 7.66 (d, J = 6.8 Hz, 1 H, Ar), 7.81 (d, J = 8.3 Hz, 1 H, Ar), 7.84–7.92 (m, 1 H, Ar), 8.13–8.23 (m, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.2, 67.7, 97.9, 123.7, 123.8, 125.5, 125.6, 125.9, 127.8, 128.4, 129.1, 129.2, 131.1, 133.5, 134.5 ppm. $C_{18}H_{20}O_2$ (268.3): calcd. C 80.56, H 7.51; found C 80.40, H 7.32. MS (EI, 70 eV): *m*/*z* (%) = 268 (15) [M$^+$]. Characteristic bands of isomer **26a**: δ = 5.32 (q, J = 1.8 Hz, 1 H, C*H*=), 5.80 (q, J = 1.8 Hz, 1 H, C*H*=) ppm; **26b**: δ = 6.63 (q, J = 1.5 Hz, 1 H, C*H*=) ppm; **26e**: δ = 5.47 (dt, J = 12.4, 7.3 Hz, 1 H, C*H*=), 6.45 (dt, J = 12.4, 1.5 Hz, 1 H, C*H*=) ppm; **26f**: δ = 4.78 (q, J = 6.5 Hz, 1 H, C*H*=), 6.35 (d, J = 6.0 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(2,6-Difluorophenyl)-3-(tetrahydropyran-2-yloxy)propene (27c): ^{1}H NMR: δ = 1.45–2.00 (m, 6 H, CH_2), 3.45–3.60 (m, 1 H, CH_2O), 3.85–4.00 (m, 1 H, CH_2O), 4.17 (dd, J = 13.6, 4.1 Hz, 1 H, CH_2C*H*=), 4.43 (dd, J = 13.6, 3.4 Hz, 1 H, CH_2C*H*=), 4.71 (t, J = 3.5 Hz, 1 H, CH), 6.60–6.65 (m, 1 H, C*H*=), 6.68 (d, J = 16.4 Hz, 1 H, C*H*=), 6.85 (t, J = 8.2 Hz, 2 H, Ar), 7.46 (tt, J = 8.4, 6.3 Hz, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.1, 68.1, 98.0, 111.4 (dd, $^2J_{C,F}$ = 18.1, 6.3 Hz), 114.1 (t, $^2J_{C,F}$ = 15.5 Hz), 118.1, 128.0 (t, $^3J_{C,F}$ = 11.0 Hz), 133.3 (t, $^3J_{C,F}$ = 7.7 Hz), 160.9 (dd, $J_{C,F}$ = 251.3, 8.1 Hz). $C_{14}H_{16}F_2O$ (254.3): calcd. C 66.13, H 6.34; found C 65.97, H 6.47. MS (EI, 70 eV): *m*/*z* (%) = 254 (1) [M$^+$]. Characteristic bands of isomer **27e**: δ = 5.20 (dt, J = 12.5, 7.4 Hz, 1 H, C*H*=), 6.40 (d, J = 12.5 Hz, 1 H, C*H*=) ppm; **27f**: δ = 4.61 (q, J = 6.2 Hz, 1 H, C*H*=), 6.23 (dt, J = 6.2, 1.5 Hz, 1 H, C*H*=). Compounds **27e** and **27f** were characterised by deprotection. 3-(2,6-Difluorophenyl)propionaldehyde: ^{1}H NMR: δ = 2.72 (t, J = 7.8 Hz, 2 H, CH_2), 2.99 (t, J = 7.8 Hz, 2 H, CH_2), 6.84 (t, J = 8.0 Hz, 2 H, Ar), 7.15 (tt, J = 8.0, 6.6 Hz, 1 H, Ar), 9.79 (s, 1 H, CHO) ppm. ^{13}C NMR: δ = 15.1, 43.0, 111.1 (dd, $^2J_{C,F}$ = 17.8, 8.0 Hz), 115.8 (t, $^2J_{C,F}$ = 20.1 Hz), 127.9 (t, $^3J_{C,F}$ = 10.4 Hz), 161.4 (dd, $J_{C,F}$ = 246.7, 8.6 Hz), 200.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 170 (100) [M$^+$].

(*E*)-3-(Tetrahydropyran-2-yloxy)-1-(2,4,6-trimethylphenyl)propene (28c): ^{1}H NMR: δ = 1.45–2.00 (m, 6 H, CH_2), 2.27 (s, 9 H, Me), 3.45–3.65 (m, 1 H, CH_2O), 3.75–4.05 (m, 1 H, CH_2O), 4.21 (ddd, J = 12.9, 6.6, 1.3 Hz, 1 H, CH_2C*H*=), 4.42 (ddd, J = 12.9, 5.6, 1.5 Hz, 1 H, CH_2C*H*=), 4.74 (t, J = 3.4 Hz, 1 H, CH), 5.79 (dt, J = 16.2, 6.6 Hz, 1 H, C*H*=), 6.57 (d, J = 16.2 Hz, 1 H, C*H*=), 6.85 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.6, 20.9, 21.3, 25.5, 30.7, 62.4, 67.9, 97.6, 128.5, 129.6, 130.0, 130.8, 135.9, 136.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 260 (10) [M$^+$]. Compound **28c** was characterised by deprotection.[44] Characteristic bands of isomer **28e**: δ = 5.13 (dt, J = 12.6, 6.3 Hz, 1 H, C*H*=), 6.23 (dt, J = 12.6, 1.3 Hz, 1 H, C*H*=) ppm; **28f**: δ = 4.43 (q, J = 6.5 Hz, 1 H, C*H*=), 6.18 (dt, J = 6.5, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(2,6-Diethyl-4-methylphenyl)-3-(tetrahydropyran-2-yloxy)propene (29c): ^{1}H NMR: δ = 1.15 (t, 6 H, Me), 1.50–2.00 (m, 6 H, CH_2), 2.30 (s, 3 H, Me), 2.62 (q, 4 H, CH_2), 3.45–3.60 (m, 1 H, CH_2O), 3.85–4.00 (m, 1 H, CH_2O), 4.21 (ddd, J = 12.9, 6.6, 1.2 Hz, 1 H, CH_2C*H*=), 4.38 (ddd, J = 12.9, 5.3, 1.5 Hz, 1 H, CH_2C*H*=), 4.74 (t, J = 3.5 Hz, 1 H, CH), 5.74 (dt, J = 16.2, 6.6 Hz, 1 H, C*H*=), 6.63 (d, J = 16.2 Hz, 1 H, C*H*=), 6.88 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = 15.3, 19.6, 21.1, 25.5, 26.7, 30.7, 62.4, 67.6, 97.5, 126.7, 129.6, 130.9, 132.9, 136.5, 142.1 ppm. $C_{19}H_{28}O_2$ (288.4):

calcd. C 79.12, H 9.78; found C 79.25, H 9.89. MS (EI, 70 eV): *m*/*z* (%) = 288 (8) [M$^+$]. Characteristic bands of isomer **29e**: δ = 5.19 (dt, *J* = 12.6, 6.3 Hz, 1 H, C*H*=), 6.23 (dt, *J* = 12.6, 1.0 Hz, 1 H, C*H*=) ppm; **29f**: δ = 4.46 (q, *J* = 6.4 Hz, 1 H, C*H*=), 6.24 (dt, *J* = 6.4, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(Anthracen-9-yl)-1-(tetrahydropyran-2-yloxy)propene (30e and 30f): Characteristic bands observed before hydrolysis: **30e**: ^{1}H NMR: δ = 5.47 (dt, *J* = 12.5, 6.4 Hz, 1 H, C*H*=), 6.37 (dt, *J* = 12.5, 1.5 Hz, 1 H, C*H*=) ppm; **30f**: δ = 4.78 (q, *J* = 6.6 Hz, 1 H, C*H*=), 6.31 (dt, *J* = 6.6, 1.6 Hz, 1 H, C*H*=) ppm; **30e** and **30f** were characterised by deprotection. 3-(Anthracen-9-yl)propionaldehyde: ^{1}H NMR: δ = 2.95 (td, *J* = 8.0, 1.2 Hz, 2 H, CH_2), 3.94 (t, *J* = 8.0 Hz, 2 H, CH_2), 7.42–7.57 (m, 4 H, Ar), 8.02 (d, *J* = 7.8 Hz, 2 H, Ar), 8.19 (d, *J* = 7.8 Hz, 2 H, Ar), 8.37 (s, 1 H, Ar), 9.95 (s, 1 H, CHO) ppm.

(*E*)-1-(Tetrahydropyran-2-yloxy)-3-(2,4,6-triisopropyl)propene (31e and 31f): Characteristic bands observed before hydrolysis: **31e**: ^{1}H NMR: δ = 5.22 (dt, *J* = 12.4, 6.1 Hz, 1 H, C*H*=), 6.11 (dt, *J* = 12.4, 1.5 Hz, 1 H, C*H*=) ppm; **31f**: δ = 4.47 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.21 (dt, *J* = 6.3, 1.8 Hz, 1 H, C*H*=) ppm; **31e** and **31f** were characterised by deprotection. 3-(2,4,6-Triisopropylphenyl)propionaldehyde: ^{1}H NMR: δ = 1.70 (d, *J* = 6.8 Hz, 18 H, CH_3), 2.55 (td, *J* = 8.0, 0.8 Hz, 2 H, CH_2), 2.88 (sept, *J* = 6.8 Hz, 1 H, CH), 3.01 (td, *J* = 8.0, 1.2 Hz, 2 H, CH_2), 3.09 (sept, *J* = 6.8 Hz, 2 H, CH), 7.01 (s, 2 H, Ar), 9.88 (t, *J* = 1.2 Hz, 1 H, CHO) ppm. ^{13}C NMR: δ = 19.8, 24.0, 24.4, 29.2, 34.1, 45.8, 121.1, 131.1, 146.4, 146.8, 201.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 260 (10) [M$^+$].

(*E*)-1-(3-Pyridyl)-3-(tetrahydropyran-2-yloxy)propene (32c): ^{1}H NMR: δ = 1.45–2.10 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.15 (ddd, *J* = 13.4, 5.8, 1.0 Hz, 1 H, CH_2C*H*=), 4.41 (ddd, *J* = 13.4, 5.3, 1.3 Hz, 1 H, CH_2C*H*=), 4.69 (t, *J* = 3.3 Hz, 1 H, CH), 6.37 (dt, *J* = 16.2, 5.8 Hz, 1 H, C*H*=), 6.61 (d, *J* = 16.2 Hz, 1 H, C*H*=), 7.18–7.26 (m, 1 H, Ar), 7.69 (dd, *J* = 8.0, 1.7 Hz, 1 H, Ar), 8.45 (br. s, 1 H, Ar), 8.59 (br. s, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.5, 62.3, 67.3, 98.1, 123.4, 128.2, 128.5, 132.8, 135.7, 148.4, 148.6 ppm. $C_{13}H_{17}NO_2$ (219.3): calcd. C 71.21, H 7.81; found C 71.04, H 7.94. MS (EI, 70 eV): *m*/*z* (%) = 219 (2) [M$^+$]. Characteristic bands of isomer **32a**: δ = 5.47 (s, 1 H, C*H*=), 5.57 (s, 1 H, C*H*=) ppm; **32d**: δ = 5.95 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=) ppm; **32e**: δ = 5.20 (dt, *J* = 12.4, 7.6 Hz, 1 H, C*H*=) ppm; **32f**: δ = 4.66 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.34 (dt, *J* = 6.1, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(3-Quinolyl)-3-(tetrahydropyran-2-yloxy)propene (33c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.19 (ddd, *J* = 13.4, 6.1, 1.3 Hz, 1 H, CH_2C*H*=), 4.46 (ddd, *J* = 13.4, 5.3, 1.3 Hz, 1 H, CH_2C*H*=), 4.71 (t, *J* = 3.3 Hz, 1 H, CH), 6.50 (dt, *J* = 16.0, 5.6 Hz, 1 H, C*H*=), 6.76 (d, *J* = 16.0 Hz, 1 H, C*H*=), 7.49 (dd, *J* = 8.1, 1.2 Hz, 1 H, Ar), 7.62 (d, *J* = 8.3 Hz, 1 H, Ar), 7.75 (dd, *J* = 8.1, 1.3 Hz, 1 H, Ar), 8.06 (d, *J* = 8.9 Hz, 2 H, Ar), 9.00 (d, *J* = 2.3 Hz, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.3, 30.5, 62.2, 67.4, 98.1, 126.8, 127.7, 127.9, 128.5, 128.6, 129.1, 129.2, 129.7, 132.4, 147.4, 149.3 ppm. $C_{17}H_{19}NO_2$ (269.3): calcd. C 75.80, H 7.11; found C 75.69, H 7.21. MS (EI, 70 eV): *m*/*z* (%) = 269 (7) [M$^+$]. Characteristic bands of isomer **33a**: δ = 5.50 (s, 1 H, C*H*=), 5.61 (s, 1 H, C*H*=) ppm; **33d**: δ = 6.09 (dt, *J* = 11.9, 6.1 Hz, 1 H, C*H*=), 6.61 (d, *J* = 11.9 Hz, 1 H, C*H*=) ppm; **33e**: δ = 5.27 (dt, *J* = 12.1, 7.6 Hz, 1 H, C*H*=), 6.42 (dt, *J* = 12.1, 1.2 Hz, 1 H, C*H*=) ppm; **33f**: δ = 4.75 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.39 (dt, *J* = 6.1, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(Tetrahydropyran-2-yloxy)-1-(2-thienyl)propene (34c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.10 (ddd, *J* = 13.1, 6.6, 1.3 Hz, 1 H, CH_2C*H*=), 4.35 (ddd, *J* = 13.1, 5.6, 1.5 Hz, 1 H, CH_2C*H*=), 4.69 (t, *J* = 3.4 Hz, 1 H, CH), 6.14 (dt, *J* = 15.7, 5.6 Hz, 1 H, C*H*=), 6.75 (d, *J* = 15.7 Hz, 1 H, C*H*=), 6.90–6.96 (m, 2 H, Ar), 7.14 (dd, *J* = 3.8, 2.5 Hz, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.1, 67.2, 97.8, 124.2, 125.3, 125.7 (2 C), 127.3, 141.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 224 (2) [M$^+$]. Compound **34c** was characterised by deprotection.[45] Characteristic bands of isomer **34a**: δ = 5.27 (s, 1 H, C*H*=), 5.54 (s, 1 H, C*H*=) ppm; **34d**: δ = 5.78 (dt, *J* = 12.1, 6.1 Hz, 1 H, C*H*=), 6.52 (dt, *J* = 12.1, 1.5 Hz, 1 H, C*H*=) ppm; **34e**: δ = 5.29 (dt, *J* = 12.2, 7.6 Hz, 1 H, C*H*=), 6.42 (d, *J* = 12.1 Hz, 1 H, C*H*=) ppm; **34f**: δ = 4.75 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.30 (dt, *J* = 6.3, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(Tetrahydropyran-2-yloxy)-1-(3-thienyl)propene (35c): ^{1}H NMR: δ = 1.40–2.00 (m, 6 H, CH_2), 3.40–3.60 (m, 1 H, CH_2O), 3.80–4.00 (m, 1 H, CH_2O), 4.13 (ddd, *J* = 12.8, 6.7, 1.3 Hz, 1 H, CH_2C*H*=), 4.39 (ddd, *J* = 12.8, 5.7, 1.5 Hz, 1 H, CH_2C*H*=), 4.71 (t, *J* = 3.4 Hz, 1 H, CH), 6.18 (dt, *J* = 15.9, 6.7 Hz, 1 H, C*H*=), 6.67 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.13–7.17 (dd, *J* = 2.9, 1.2 Hz, 1 H, Ar), 7.19–7.23 (dd, *J* = 5.0, 1.2 Hz, 1 H, Ar), 7.23–7.28 (m, 1 H, Ar) ppm. ^{13}C NMR: δ = 19.4, 25.4, 30.6, 62.2, 67.5, 97.8, 122.1, 125.0, 125.8, 125.9, 126.6, 139.4 ppm. $C_{12}H_{16}O_2S$ (224.3): calcd. C 64.25, H 7.19; found C 63.97, H 7.00. MS (EI, 70 eV): *m*/*z* (%) = 224 (4) [M$^+$]. Characteristic bands of isomer **35a**: δ = 5.33 (s, 1 H, C*H*=), 5.53 (s, 1 H, C*H*=) ppm; **35b**: δ = 6.83 (q, *J* = 1.3 Hz, 1 H, C*H*=) ppm; **35e**: δ = 5.27 (dt, *J* = 12.4, 7.6 Hz, 1 H, C*H*=), 6.36 (dt, *J* = 12.4, 1.3 Hz, 1 H, C*H*=) ppm; **35f**: δ = 4.71 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.29 (dt, *J* = 6.3, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-Acetylphenyl)-3-benzyloxypropene (36c): ^{1}H NMR: δ = 2.58 (s, 3 H, MeCO), 4.22 (dd, *J* = 5.7, 1.6 Hz, 2 H, CH_2), 4.59 (s, 2 H, CH_2), 6.45 (dt, *J* = 16.1, 5.7 Hz, 1 H, C*H*=), 6.68 (d, *J* = 16.1 Hz, 1 H, C*H*=), 7.26–7.40 (m, 5 H, Ar), 7.46 (d, *J* = 7.8 Hz, 2 H, Ar), 7.91 (d, *J* = 7.8 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 27.0, 70.8, 72.9, 126.9, 128.1, 128.2, 128.9, 129.1, 129.6, 131.3, 136.5, 138.4, 141.8, 198.0 ppm. $C_{18}H_{18}O_2$ (266.3): calcd. C 81.17, H 6.81; found C 81.01, H 6.98. MS (EI, 70 eV): *m*/*z* (%) = 266 (6) [M$^+$]. Characteristic bands of isomer **36a**: δ = 5.48 (s, 1 H, C*H*=), 5.66 (s, 1 H, C*H*=) ppm; **36d**: δ = 6.03 (dt, *J* = 12.1, 6.1 Hz, 1 H, C*H*=), **36e**: 5.02 (dt, *J* = 12.5, 7.4 Hz, 1 H, C*H*=), 6.47 (d, *J* = 12.5 Hz, 1 H, C*H*=) ppm; **36f**: δ = 4.61 (dt, *J* = 7.5, 6.3 Hz, 1 H, C*H*=), 6.20 (dt, *J* = 6.3, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(4-*tert*-butylphenyl)propene (37c): ^{1}H NMR: δ = 1.20 (s, 9 H, Ar), 4.07 (d, *J* = 6.1 Hz, 2 H, CH_2), 4.44 (s, 2 H, CH_2), 6.18 (dt, *J* = 16.0, 6.1 Hz, 1 H, C*H*=), 6.50 (d, *J* = 16.0 Hz, 1 H, C*H*=), 7.11–7.33 (m, 9 H, Ar) ppm. ^{13}C NMR: δ = 31.2, 34.5, 70.8, 71.9, 125.2, 125.4, 126.2, 127.5, 127.7, 128.3, 132.4, 133.9, 138.3, 150.7 ppm. $C_{20}H_{24}O$ (280.4): calcd. C 85.67, H 8.63; found C 85.40, H 8.51. MS (EI, 70 eV): *m*/*z* (%) = 189 (40) [M$^+$ – 91]. Characteristic bands of isomer **37e**: δ = 4.98 (dt, *J* = 12.8, 7.5 Hz, 1 H, C*H*=), 6.36 (d, *J* = 12.8 Hz, 1 H, C*H*=) ppm; **37f**: δ = 4.53 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.04 (d, *J* = 6.3 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(4-methoxyphenyl)propene (38c): ^{1}H NMR: δ = 3.81 (s, 3 H, MeO), 4.19 (dd, *J* = 6.3, 1.2 Hz, 2 H, CH_2), 4.58 (s, 2 H, CH_2), 6.22 (dt, *J* = 15.9, 6.3 Hz, 1 H, C*H*=), 6.59 (d, *J* = 15.9 Hz, 1 H, C*H*=), 6.87 (d, *J* = 8.7 Hz, 2 H, Ar), 7.35 (d, *J* = 8.7 Hz, 2 H, Ar), 7.26–7.40 (m, 5 H, Ar) ppm. ^{13}C NMR: δ = 55.2, 70.9, 72.0, 113.9, 123.7, 127.6, 127.7, 127.8, 128.4, 129.4, 132.2, 138.3, 159.3 ppm. MS (EI, 70 eV): *m*/*z* (%) = 254 (10) [M$^+$]. Compound **38c** was characterised by deprotection.[43] Characteristic bands of isomer **38a**: δ = 5.27 (d, *J* = 1.1 Hz, 1 H, C*H*=), 5.47 (d, *J* = 1.1 Hz, 1 H, C*H*=) ppm; **38b**: δ = 6.52 (q, *J* = 1.3 Hz, 1 H, C*H*=) ppm; **38d**: δ = 5.90 (dt, *J* = 12.1, 6.1 Hz, 1 H, C*H*=), **38e**: 5.08 (dt, *J* = 12.5, 7.4 Hz, 1 H, C*H*=), 6.48 (d, *J* = 12.5 Hz, 1 H,

C*H*=) ppm; **38f**: δ = 4.66 (d, *J* = 6.2 Hz, 1 H, C*H*=), 6.17 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(2-cyanophenyl)propene (39c): ^{1}H NMR: δ = 4.25 (dd, *J* = 5.8, 1.5 Hz, 2 H, CH_2), 4.59 (s, 2 H, CH_2), 6.51 (dt, *J* = 15.9, 5.8 Hz, 1 H, C*H*=), 6.99 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.26–7.40 (m, 6 H, Ar), 7.53 (t, *J* = 7.4 Hz, 1 H, Ar), 7.59–7.66 (m, 2 H, Ar) ppm. ^{13}C NMR: δ = 70.3, 72.6, 111.1, 117.8, 125.8, 127.7, 127.8, 127.9 (2 C), 128.5, 131.7, 132.7, 133.0, 137.9, 140.0 ppm. $C_{17}H_{15}NO$ (249.3): calcd. C 81.90, H 6.06; found C 82.11, H 6.19. MS (EI, 70 eV): *m*/*z* (%) = 249 (1) [M$^+$]. Characteristic bands of isomer **39a**: δ = 5.53 (s, 1 H, C*H*=), 5.70 (s, 1 H, C*H*=) ppm; **39b**: δ = 6.93 (q, *J* = 1.3 Hz, 1 H, C*H*=) ppm; **39d**: δ = 6.19 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=), 6.87 (d, *J* = 12.0 Hz, 1 H, C*H*=) ppm; **39e**: δ = 5.01 (dt, *J* = 12.6, 7.5 Hz, 1 H, C*H*=), 6.51 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **39f**: δ = 4.62 (q, *J* = 6.3 Hz, 1 H, C*H*=), 6.20 (dt, *J* = 6.3, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(2,4,6-trimethylphenyl)propene (40c): ^{1}H NMR: δ = 2.29 (s, 3 H, Me), 2.31 (s, 6 H, Me), 3.89 (dd, *J* = 6.1, 1.5 Hz, 2 H, CH_2), 4.63 (s, 2 H, CH_2), 5.85 (dt, *J* = 16.3, 6.1 Hz, 1 H, C*H*=), 6.61 (d, *J* = 16.3 Hz, 1 H, C*H*=), 6.89 (s, 2 H, Ar), 7.26–7.40 (m, 5 H, Ar) ppm. ^{13}C NMR: δ = 20.9 (3C), 71.1, 71.8, 127.6, 127.8, 128.4, 128.5, 130.4, 130.9, 133.5, 135.8, 136.2, 138.4 ppm. $C_{19}H_{22}O$ (266.4): calcd. C 85.67, H 8.32; found C 85.41, H 8.22. MS (EI, 70 eV): *m*/*z* (%) = 266 (1) [M$^+$]. Characteristic bands of isomer **40e**: δ = 5.02 (dt, *J* = 12.6, 6.4 Hz, 1 H, C*H*=), 6.32 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **40f**: δ = 4.39 (q, *J* = 6.5 Hz, 1 H, C*H*=), 6.12 (dt, *J* = 6.5, 1.3 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(3-pyridyl)propene (41c): ^{1}H NMR: δ = 4.20 (dd, *J* = 5.6, 1.3 Hz, 2 H, CH_2), 4.58 (s, 2 H, CH_2), 6.38 (dt, *J* = 16.1, 5.6 Hz, 1 H, C*H*=), 6.63 (d, *J* = 16.1 Hz, 1 H, C*H*=), 7.26–7.40 (m, 6 H, Ar), 7.70 (dt, *J* = 8.0, 1.9 Hz, 1 H, Ar), 8.40–8.65 (m, 2 H, Ar) ppm. ^{13}C NMR: δ = 70.3, 72.5, 102.7, 123.4, 127.5, 127.7, 127.8, 128.4, 128.5, 132.8, 138.0, 148.3, 148.6 ppm. $C_{15}H_{15}NO$ (225.3): calcd. C 79.97, H 6.71; found C 80.20, H 6.74. MS (EI, 70 eV): *m*/*z* (%) = 225 (1) [M$^+$]. Characteristic bands of isomer **41a**: δ = 5.42 (s, 1 H, C*H*=), 5.57 (s, 1 H, C*H*=) ppm; **41d**: δ = 5.96 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=), 6.89 (d, *J* = 12.0 Hz, 1 H, C*H*=) ppm; **41e**: δ = 4.97 (dt, *J* = 12.7, 7.4 Hz, 1 H, C*H*=), 6.43 (d, *J* = 12.7 Hz, 1 H, C*H*=) ppm; **41f**: δ = 4.58 (dt, *J* = 7.4, 6.1 Hz, 1 H, C*H*=), 6.18 (dt, *J* = 6.1, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(2-thienyl)propene (42c): ^{1}H NMR: δ = 4.18 (dd, *J* = 6.0, 1.2 Hz, 2 H, CH_2), 4.59 (s, 2 H, CH_2), 6.19 (dt, *J* = 15.8, 6.0 Hz, 1 H, C*H*=), 6.69 (d, *J* = 15.8 Hz, 1 H, C*H*=), 6.91–7.09 (m, 2 H, Ar), 7.11–7.21 (m, 1 H, Ar), 7.26–7.49 (m, 5 H, Ar) ppm. ^{13}C NMR: δ = 70.3, 72.2, 124.3, 125.5, 125.7 (2 C), 127.3, 127.6, 127.7, 128.4, 138.2, 141.8 ppm. $C_{14}H_{14}OS$ (230.3): calcd. C 73.01, H 6.13; found C 72.87, H 6.01. MS (EI, 70 eV): *m*/*z* (%) = 230 (1) [M$^+$]. Characteristic bands of isomer **42d**: δ = 5.84 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=), 6.69 (d, *J* = 12.0 Hz, 1 H, C*H*=) ppm; **42e**: δ = 5.12 (dt, *J* = 12.5, 7.3 Hz, 1 H, C*H*=), 6.51 (d, *J* = 12.5 Hz, 1 H, C*H*=) ppm; **42f**: δ = 4.70 (dt, *J* = 7.4, 6.1 Hz, 1 H, C*H*=), 6.18 (dt, *J* = 6.1, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Benzyloxy-1-(3-thienyl)propene (43c): ^{1}H NMR: δ = 4.17 (dd, *J* = 6.0, 1.3 Hz, 2 H, CH_2), 4.57 (s, 2 H, CH_2), 6.18 (dt, *J* = 15.9, 6.0 Hz, 1 H, C*H*=), 6.65 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.11–7.51 (m, 8 H, Ar) ppm. ^{13}C NMR: δ = 70.7, 72.1, 122.2, 125.1, 125.9, 126.0, 126.8, 127.6, 127.7, 128.4, 138.3, 139.4 ppm. $C_{14}H_{14}OS$ (230.3): calcd. C 73.01, H 6.13; found C 72.78, H 6.22. MS (EI, 70 eV): *m*/*z* (%) = 230 (3) [M$^+$]. Characteristic bands of isomer **43e**: δ = 5.10 (dt, *J* = 12.7, 7.3 Hz, 1 H, C*H*=), 6.46 (d, *J* = 12.7 Hz, 1 H, C*H*=) ppm; **43f**: δ = 4.67 (dt, *J* = 7.4, 6.1 Hz, 1 H, C*H*=), 6.16 (dt, *J* = 6.1, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-Acetylphenyl)-3-butoxypropene (44c): ^{1}H NMR: δ = 0.93 (t, *J* = 7.2 Hz, 3 H, Me), 1.38 (sext., *J* = 7.2 Hz, 2 H, CH_2), 1.50–1.70 (m, 2 H, CH_2), 2.57 (s, 3 H, MeCO), 3.49 (t, *J* = 6.5 Hz, 2 H, CH_2), 4.14 (dd, *J* = 5.5, 1.3 Hz, 2 H, CH_2), 6.41 (dt, *J* = 16.0, 5.5 Hz, 1 H, C*H*=), 6.64 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.44 (d, *J* = 8.5 Hz, 2 H, Ar), 7.90 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 13.9, 19.3, 26.5, 31.8, 70.5, 71.0, 126.5, 128.7, 129.6, 130.5, 136.0, 141.5, 197.5 ppm. $C_{15}H_{20}O_2$ (232.3): calcd. C 77.55, H 8.68; found C 77.31, H 8.58. MS (EI, 70 eV): *m*/*z* (%) = 232 (46) [M$^+$]. Characteristic bands of isomer **44a**: δ = 5.44 (s, 1 H, C*H*=), 5.62 (s, 1 H, C*H*=) ppm; **44b**: δ = 6.81 (s, 1 H, C*H*=) ppm; **44e**: δ = 4.89 (dt, *J* = 12.6, 7.4 Hz, 1 H, C*H*=), 6.35 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **44f**: δ = 4.52 (dt, *J* = 7.5, 6.2 Hz, 1 H, C*H*=), 6.08 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Butoxy-1-(4-*tert*-butylphenyl)propene (45c): ^{1}H NMR: δ = 0.92 (t, *J* = 7.3 Hz, 3 H, Me), 1.31 (s, 9 H, Me), 1.25–1.45 (m, 2 H, CH_2), 1.50–1.65 (m, 2 H, CH_2), 3.46 (t, *J* = 6.5 Hz, 2 H, CH_2), 4.15 (dd, *J* = 6.0, 1.2 Hz, 2 H, CH_2), 6.24 (dt, *J* = 15.9, 6.0 Hz, 1 H, C*H*=), 6.57 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.32 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = 13.9, 19.4, 31.3, 31.9, 34.6, 70.1, 71.5, 125.4, 125.7, 126.2, 132.0, 134.0, 150.7 ppm. $C_{17}H_{26}O$ (246.4): calcd. C 82.87, H 10.64; found C 82.61, H 10.81. MS (EI, 70 eV): *m*/*z* (%) = 246 (43) [M$^+$]. Characteristic bands of isomer **45a**: δ = 5.27 (d, *J* = 1.3 Hz, 1 H, C*H*=), 5.47 (d, *J* = 1.3 Hz, 1 H, C*H*=) ppm; **45b**: δ = 6.47 (q, *J* = 1.2 Hz, 1 H, C*H*=) ppm; **45d**: δ = 5.74 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=), **45e**: 4.95 (dt, *J* = 12.6, 7.4 Hz, 1 H, C*H*=), 6.37 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **45f**: δ = 4.58 (dt, *J* = 7.5, 6.2 Hz, 1 H, C*H*=), 6.07 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Butoxy-1-(4-methoxyphenyl)propene (46c): ^{1}H NMR: δ = 0.93 (t, *J* = 7.2 Hz, 3 H, Me), 1.25–1.55 (m, 2 H, CH_2), 1.55–1.85 (m, 2 H, CH_2), 3.47 (t, *J* = 6.5 Hz, 2 H, CH_2), 3.80 (s, 3 H, MeO), 4.17 (dd, *J* = 6.1, 1.3 Hz, 2 H, CH_2), 6.16 (dt, *J* = 15.9, 6.1 Hz, 1 H, C*H*=), 6.55 (d, *J* = 15.9 Hz, 1 H, C*H*=), 6.85 (d, *J* = 8.7 Hz, 2 H, Ar), 7.33 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 13.8, 19.2, 31.7, 55.1, 70.0, 71.4, 113.8, 124.1, 127.5, 129.5, 131.6, 159.1 ppm. $C_{14}H_{20}O_2$ (220.3): calcd. C 76.33, H 9.15; found C 76.17, H 9.30. MS (EI, 70 eV): *m*/*z* (%) = 220 (70) [M$^+$]. Characteristic bands of isomer **46a**: δ = 5.24 (d, *J* = 1.2 Hz, 1 H, C*H*=), 5.43 (d, *J* = 1.2 Hz, 1 H, C*H*=) ppm; **46b**: δ = 6.41 (q, *J* = 1.4 Hz, 1 H, C*H*=) ppm; **46d**: δ = 5.77 (dt, *J* = 12.0, 6.0 Hz, 1 H, C*H*=), **46e**: 4.94 (dt, *J* = 12.5, 7.4 Hz, 1 H, C*H*=), 6.36 (d, *J* = 12.5 Hz, 1 H, C*H*=) ppm; **46f**: δ = 4.56 (dt, *J* = 7.4, 6.2 Hz, 1 H, C*H*=), 6.07 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-Butoxy-1-(2,4,6-trimethylphenyl)propene (47c): ^{1}H NMR: δ = 0.96 (t, *J* = 7.2 Hz, 3 H, Me), 1.30–1.55 (m, 2 H, CH_2), 1.55–1.75 (m, 2 H, CH_2), 2.23–2.41 (m, 9 H, Me), 3.53 (t, *J* = 6.5 Hz, 2 H, CH_2), 4.18 (dd, *J* = 5.9, 1.4 Hz, 2 H, CH_2), 5.80 (dt, *J* = 16.3, 6.0 Hz, 1 H, C*H*=), 6.57 (d, *J* = 16.3 Hz, 1 H, C*H*=), 6.88 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = 13.9, 19.4, 19.6, 20.8, 31.9, 69.9, 71.7, 128.5, 129.8, 131.4, 133.6, 135.8, 136.1 ppm. $C_{16}H_{24}O$ (232.3): calcd. C 82.70, H 10.41; found C 82.46, H 10.24. MS (EI, 70 eV): *m*/*z* (%) = 232 (14) [M$^+$]. Characteristic bands of isomer **47a**: δ = 5.04 (d, *J* = 2.0 Hz, 1 H, C*H*=), 5.65 (d, *J* = 2.0 Hz, 1 H, C*H*=) ppm; **47e**: δ = 5.22 (dt, *J* = 12.7, 6.4 Hz, 1 H, C*H*=), 6.35 (dt, *J* = 12.7, 1.4 Hz, 1 H, C*H*=) ppm; **47f**: δ = 4.69 (q, *J* = 6.7 Hz, 1 H, C*H*=), 6.39 (dt, *J* = 6.2, 1.7 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-Acetylphenyl)-3-(2-hydroxyethoxy)propene (48c): ^{1}H NMR: δ = 1.79 (br. s, 1 H, OH), 2.57 (s, 3 H, MeCO), 3.61 (t, *J* = 4.6 Hz, 2 H, CH_2), 3.76 (t, *J* = 4.6 Hz, 2 H, CH_2), 4.21 (dd, *J* = 5.7, 1.3 Hz, 2 H, CH_2), 6.40 (dt, *J* = 16.1, 5.7 Hz, 1 H, C*H*=), 6.65 (d, *J* = 16.0 Hz, 1 H, C*H*=), 7.44 (d, *J* = 8.3 Hz, 2 H, Ar), 7.89 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 26.5, 61.8, 71.4, 71.6,

126.5, 128.7, 128.8, 131.1, 136.1, 141.2, 197.5 ppm. $C_{13}H_{16}O_3$ (220.2): calcd. C 70.89, H 7.32; found C 70.97, H 7.41. MS (EI, 70 eV): *m*/*z* (%) = 220 (100) [M^+]. Characteristic bands of isomer **48a**: δ = 5.44 (d, *J* = 1.1 Hz, 1 H, C*H*=), 5.63 (d, *J* = 1.1 Hz, 1 H, C*H*=) ppm; **48e**: δ = 4.92 (dt, *J* = 12.5, 7.4 Hz, 1 H, C*H*=), 6.38 (dt, *J* = 12.5, 1.2 Hz, 1 H, C*H*=) ppm; **48f**: δ = 4.58 (dt, *J* = 7.5, 6.2 Hz, 1 H, C*H*=), 6.12 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-1-(4-*tert*-Butylphenyl)-3-(2-hydroxyethoxy)propene (49c): ^{1}H NMR: δ = 1.58 (s, 9 H, Me), 2.61 (br. s, 1 H, OH), 3.86 (t, *J* = 4.7 Hz, 2 H, CH_2), 4.03 (t, *J* = 4.4 Hz, 2 H, CH_2), 4.46 (d, *J* = 6.1 Hz, 2 H, CH_2), 6.53 (dt, *J* = 15.9, 6.1 Hz, 1 H, C*H*=), 6.86 (d, *J* = 15.9 Hz, 1 H, C*H*=), 7.60 (m, 4 H, Ar) ppm. ^{13}C NMR: δ = 31.2, 34.5, 61.8, 71.2, 71.8, 124.8, 125.4, 126.2, 132.6, 133.7, 150.9 ppm. $C_{15}H_{22}O$ (234.3): calcd. C 76.88, H 9.46; found C 76.69, H 9.35. MS (EI, 70 eV): *m*/*z* (%) = 234 (2) [M^+]. Characteristic bands of isomer **49a**: δ = 5.32 (d, *J* = 0.9 Hz, 1 H, C*H*=), 5.55 (d, *J* = 0.9 Hz, 1 H, C*H*=) ppm; **49b**: δ = 6.52 (q, *J* = 1.3 Hz, 1 H, C*H*=) ppm; **49e**: δ = 5.02 (dt, *J* = 12.6, 7.4 Hz, 1 H, C*H*=), 6.42 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **49f**: δ = 4.68 (dt, *J* = 7.6, 6.2 Hz, 1 H, C*H*=), 6.13 (dt, *J* = 6.2, 1.5 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(2-Hydroxyethoxy)-1-(4-methoxyphenyl)propene (50c): ^{1}H NMR: δ = 2.22 (br. s, 1 H, OH), 3.60 (t, *J* = 4.6 Hz, 2 H, CH_2), 3.71 (t, *J* = 4.6 Hz, 2 H, CH_2), 3.86 (s, 3 H, MeO), 4.46 (dd, *J* = 6.2, 1.2 Hz, 2 H, CH_2), 6.15 (dt, *J* = 16.0, 6.2 Hz, 1 H, C*H*=), 6.55 (d, *J* = 16.0 Hz, 1 H, C*H*=), 6.85 (d, *J* = 8.8 Hz, 2 H, Ar), 7.31 (d, *J* = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR: δ = 55.2, 62.9, 71.2, 71.9, 114.0, 123.4, 127.7, 129.3, 132.5, 159.4 ppm. $C_{12}H_{16}O_3$ (208.2): calcd. C 69.21, H 7.74; found C 68.94, H 7.64. MS (EI, 70 eV): *m*/*z* (%) = 208 (75) [M^+]. Characteristic bands of isomer **50a**: δ = 5.20 (d, *J* = 0.8 Hz, 1 H, C*H*=), 5.42 (d, *J* = 0.8 Hz, 1 H, C*H*=) ppm; **50b**: δ = 6.41 (q, *J* = 1.4 Hz, 1 H, C*H*=) ppm; **50e**: δ = 4.97 (dt, *J* = 12.6, 7.3 Hz, 1 H, C*H*=), 6.35 (d, *J* = 12.6 Hz, 1 H, C*H*=) ppm; **50f**: δ = 4.62 (dt, *J* = 7.5, 6.2 Hz, 1 H, C*H*=), 6.08 (dt, *J* = 6.2, 1.4 Hz, 1 H, C*H*=) ppm.

(*E*)-3-(2-Hydroxyethoxy)-2-(2,4,6-trimethylphenyl)propene (51a): ^{1}H NMR: δ = 1.64 (br. s, 1 H, OH), 2.15–2.35 (m, 9 H, Me), 3.65 (t, *J* = 4.8 Hz, 2 H, CH_2), 3.71 (t, *J* = 4.8 Hz, 2 H, CH_2), 4.05 (t, *J* = 1.7 Hz, 2 H, CH_2), 4.98 (q, *J* = 1.7 Hz, 1 H, C*H*=), 5.56 (q, *J* = 1.7 Hz, 1 H, C*H*=), 6.86 (s, 2 H, Ar) ppm. ^{13}C NMR: δ = 19.7, 20.8, 61.9, 72.1, 73.2, 113.7, 128.1, 128.7, 135.7, 136.6, 144.9 ppm. $C_{14}H_{20}O_2$ (220.3): calcd. C 76.33, H 9.15; found C 76.01, H 9.18. MS (EI, 70 eV): *m*/*z* (%) = 220 (27) [M^+]. Characteristic bands of isomer **50e**: δ = 4.84 (dt, *J* = 12.6, 6.3 Hz, 1 H, C*H*=), 6.15 (dt, *J* = 12.6, 1.4 Hz, 1 H, C*H*=) ppm; **50f**: δ = 4.33 (q, *J* = 6.6 Hz, 1 H, C*H*=), 5.95 (dt, *J* = 6.2, 1.7 Hz, 1 H, C*H*=) ppm.

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[1] R. F. Heck, *Vinyl Substitution with Organopalladium Intermediates*, in *Comprehensive Organic Synthesis*, vol. 4 (Eds.: B. M. Trost, I. Fleming), Pergamon: Oxford, **1991**.
[2] A. de Meijere, F. Meyer, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379.
[3] M. T. Reetz, *Transition Metal Catalysed Reactions* (Eds.: S. G. Davies, S.-I. Murahashi), Blackwell Science, Oxford, **1999**.
[4] I. Beletskaya, A. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009.
[5] N. Withcombe, K. K. Hii (Mimi), S. Gibson, *Tetrahedron* **2001**, *57*, 7449.
[6] A. Littke, G. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
[7] T. Jeffery, *J. Chem. Soc., Chem. Commun.* **1984**, 1287.
[8] T. Jeffery, *Tetrahedron Lett.* **1991**, *32*, 2121.
[9] J.-L. Reymond, G. K. Jahangiri, C. Stoudt, R. A. Lerner, *J. Am. Chem. Soc.* **1993**, *115*, 3909.
[10] C. J. Barnett, T. M. Wilson, *Heterocycles* **1993**, *35*, 925.
[11] J.-L. Reymond, Y. Chen, *J. Org. Chem.* **1995**, *60*, 6970.
[12] S.-K. Kang, H.-W. Lee, S.-B. Jang, T.-H. Kim, S.-J. Pyun, *J. Org. Chem.* **1996**, *61*, 2604.
[13] G. Pattenden, P. Wiedenau, *Tetrahedron Lett.* **1997**, *38*, 3647.
[14] D. Bruyère, G. Gaignard, D. Bouyssi, G. Balme, J.-M. Lancelin, *Tetrahedron Lett.* **1997**, *38*, 827.
[15] J. Li, A. W.-H. Mau, C. R. Strauss, *Chem. Commun.* **1997**, 1275.
[16] S. Sengupta, S. K. Sadhukhan, *Tetrahedron Lett.* **1998**, *39*, 1237.
[17] E. C. Taylor, B. Liu, *Tetrahedron Lett.* **1999**, *40*, 4023.
[18] J.-R. Labrosse, C. Poncet, P. Lhoste, D. Sinou, *Tetrahedron: Asymmetry* **1999**, *10*, 1069.
[19] S. E. Gibson, J. O. Jones, R. McCague, M. J. Tozer, N. J. Whitcombe, *Synlett* **1999**, 954.
[20] D. Villemin, B. Nechab, *J. Chem. Res. Synopsis* **2000**, 429.
[21] S. Bouquillon, B. Ganchegui, B. Estrine, F. Hénin, J. Muzart, *J. Organomet. Chem.* **2001**, *634*, 153.
[22] H. Zhao, M.-Z. Cai, R.-H. Hu, C.-S. Song, *Synth. Commun.* **2001**, *31*, 3665.
[23] C. Kapplinger, R. Beckert, *Synthesis* **2002**, 1843.
[24] L. F. Tietze, K. Kahle, T. Raschke, *Chem. Eur. J.* **2002**, *8*, 401.
[25] A. Padwa, A. Zanka, M. P. Cassidy, J. M. Harris, *Tetrahedron* **2003**, *59*, 4939.
[26] S. B. Solabannavar, V. B. Helavi, U. V. Desai, R. B. Mane, *Synth. Commun.* **2003**, *33*, 361.
[27] S. E. Watson, *Synth. Commun.* **1998**, *28*, 1897.
[28] K. Ono, K. Fugami, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **1994**, *35*, 4133.
[29] T. Fukuyama, X. Chen, G. Peng, *J. Am. Chem. Soc.* **1994**, *116*, 3127.
[30] D. Laurenti, M. Feuerstein, G. Pèpe, H. Doucet, M. Santelli, *J. Org. Chem.* **2001**, *66*, 1633.
[31] M. Feuerstein, D. Laurenti, C. Bougeant, H. Doucet, M. Santelli, *Chem. Commun.* **2001**, 325.
[32] E. Peyroux, F. Berthiol, H. Doucet, M. Santelli, *Eur. J. Org. Chem.* **2004**, 1075.
[33] M. Feuerstein, F. Berthiol, H. Doucet, M. Santelli, *Org. Biomol. Chem.* **2003**, *1*, 2235.
[34] M. Feuerstein, H. Doucet, M. Santelli, *J. Org. Chem.* **2001**, *66*, 5923.
[35] M. Feuerstein, H. Doucet, M. Santelli, *Synlett* **2001**, 1980.
[36] M. Feuerstein, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2002**, *43*, 2191.
[37] F. Berthiol, M. Feuerstein, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2002**, *43*, 5625.
[38] F. Berthiol, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 1221.
[39] F. Berthiol, H. Doucet, M. Santelli, *Synlett* **2003**, 841.
[40] I. Kondolff, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 8487.
[41] I. Kondolff, H. Doucet, M. Santelli, *Synlett* **2004**, 1561.
[42] F. Berthiol, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2004**, *45*, 5633.
[43] G. Pandey, A. Krishna, *J. Org. Chem.* **1988**, *53*, 2364.
[44] E. Medina, A. Moyano, M. A. Pericas, A. Riera, *Helv. Chim. Acta* **2000**, *83*, 972.
[45] R. Takeuchi, N. Ue, K. Tanabe, K. Yamashita, N. Shiga, *J. Am. Chem. Soc.* **2001**, *123*, 9525.

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