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Scope and Limitation of the Microwave-Assisted Catalytic Wittig Reaction

Marcel Hoffmann,[a] Sunetra Deshmukh,[a] and Thomas Werner*[a]

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We have developed a microwave-assisted catalytic Wittig reaction. In this paper, we give full account of the scope and limitations of this reaction. A screening of various commercially available phosphine oxides as precatalysts revealed $Bu_3P{=}O$ to be the most promising candidate. We tested 10 silanes for the in situ reduction of the phosphine oxide to generate Bu_3P as the actual catalyst. Different epoxides were tested as masked bases. In this context, cyclohexene oxide as well as butylene oxide proved to be suitable. The reaction could be carried out at 125 °C, but higher yields and *E*/*Z* selectivities were obtained at 150 °C. Under the optimised reaction conditions, more than 40 examples for the conversion of various aldehydes into the corresponding alkenes are reported. The products were obtained in yields of up to 88 % with high *E* selectivities. Moreover, we also describe the further screening of several chiral phosphines as catalysts for the microwave-assisted enantioselective catalytic Wittig reaction.

Introduction

Carbon–carbon double bonds are ubiquitous structural elements in organic and natural product chemistry.[1] Numerous methods for their preparation have been developed.[2] Of these, especially carbonyl olefinations,[3] e.g., the Wittig reaction,[4] Peterson olefination,[5] or the Julia–Kocienski reaction,[6] as well as their numerous modifications, give versatile access to alkenes. Since its discovery in 1953 by Wittig and Geissler, the Wittig reaction has become the most recognised method for the chemo- and regioselective olefination of carbonyl groups.[4] This reaction has been extensively studied and used in synthesis,[7] even on industrial scale,[8] and a variety of reagents and modifications have emerged.[9] However, the formation of stoichiometric amounts of phosphine oxides represents the major disadvantage of the classic Wittig reaction, as it hampers atom economy and product purification.[10] To overcome these purification problems and to recycle the phosphine oxide by-product, many approaches on a laboratory scale as well as an industrial scale have been reported.[11] Nevertheless, the inert phosphine oxides are often discarded as waste products, as their reduction requires harsh reaction conditions or the use of highly toxic phosgene.[12]

An alternative strategy involving the in situ reduction of the phosphine oxide e.g., using silanes as reducing agents, might be economically and ecologically beneficial. A recently published life-cycle assessment by Huijbregts et al. indicates that a catalytic Wittig reaction can be more advantageous than the stoichiometric variant in terms of cumulative energy demand as well as greenhouse gas emissions.[10a] Indeed, organoarsenic,[13] organotellurium,[14] and organoantimony[15] compounds have been used for catalytic Wittig-type reactions, probably due to the fact that the corresponding oxides are considerably easier to reduce than phosphine oxides.[16]

The classic Wittig reaction occurs between a carbonyl compound, e.g., an aldehyde, and a phosphonium ylide to give the corresponding alkene and stoichiometric amounts of phosphine oxide as the by-product. The ylide is usually prepared before the olefination by alkylation of a suitable phosphine and subsequent deprotonation, which requires stoichiometric amounts of a suitable base.[9] A catalytic cycle would be based on the in situ reduction of the phosphine oxide by-product and recycling of the resulting phosphine as the catalyst. In 2009, O'Brien et al. reported the first catalytic Wittig reaction (CWR, in phosphine) and subsequently developed this approach further.[17]

For the chemoselective reduction of phosphine oxides, a stoichiometric amount of a reductant is needed, which must be carefully chosen to prevent possible side-reactions with either the substrates or the desired product. In this context, strong reductants like $LiAlH_4$,[18] borohydrides,[19] or DIBALH (diisobutylaluminium hydride),[20] which are known to reduce phosphine oxides, are unsuitable. Silanes are the reductants of choice, and they fulfill the requirements under various reaction conditions.[21] The reduction strategy has also been applied by other groups to the Appel, aza-Wittig, and Staudinger reactions.[22] Due to our interest in the synthesis and application of phosphorus-based organocatalysts, we recently turned our attention to this very exciting field.[23]

[a] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany
E-mail: Thomas.Werner@catalysis.de
http://www.catalysis.de/

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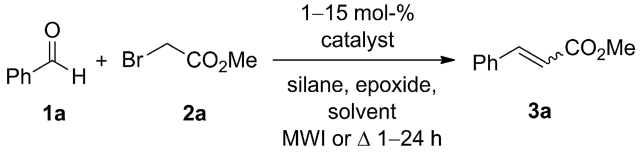
Results and Discussion

In this paper, we describe the impact of various reaction parameters as well as the influence of the silane and masked bases on the outcome of the reaction under microwave dielectric heating (MWI). We have significantly extended the substrate scope of the reaction. Based on our recently reported protocol,[23d] we chose the reaction of benzaldehyde (**1a**) and methyl bromoacetate (**2a**) to form methyl phenyl propenoate (**3a**) as model reaction (Scheme 1).



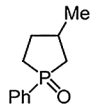
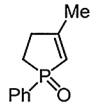
Scheme 1. Model reaction for the reaction optimisation.

Initially, we screened several phosphine oxides as well as Ph_3P as potential (pre)catalysts (Table 1). $Et_3P{=}O$ gave the desired product in only 5% yield (Table 1, entry 1). However, in the presence of $Bu_3P{=}O$, a promising 56% yield was achieved (Table 1, entry 2). Other (pre)catalysts proved to be less efficient (Table 1, entries 3–7). In the absence of any phosphine or phosphine oxide, no reaction was observed, and in the presence of $Bu_3P{=}O$ but using conventional heating only a 30% yield could be obtained (Table 1, entries 8 and 9). This demonstrates the positive effect of microwave dielectric heating. 1-Butanol and ethylene carbonate (EC) proved to be unsuitable solvents in the model reaction (Table 1, entries 10 and 11). The best result was achieved using dioxane as solvent (Table 1, entry 12). Decreasing the reaction temperature from 150 °C to 125 °C led to a significant decrease in yield (Table 1, entries 2 and 12). Commonly observed by-products in the reaction mixture were benzyl alcohol, originating from the reduction of **1a**, and methyl acetate, derived from the dehalogenation of **2a**.

We then tested various silanes as potential reducing agents for the in situ (re)generation of the phosphine catalyst (Table 2). In the phenylsilane series, $PhSiH_3$ proved to be the most efficient reducing agent (Table 2, entries 1–3). In the presence of 10 mol-% $Bu_3P{=}O$, the desired product was obtained in 56% yield. This could be improved to 66% yield by using 15 mol-% of the precatalyst. With lower amounts of $Bu_3P{=}O$, the yield decreased to 51%. The use of aliphatic silanes such as Et_3SiH, $t Bu_2SiH_2$, and $n HexSiH_3$ as reducing agents generally gave poor yields of the alkene of up to 9% (Table 2, entries 4–6). Similar results were obtained with alkoxy silanes (Table 2, entries 7–9). The readily available polymethylhydrosiloxane (PMHS) was potentially a useful reducing agent. Recently, Kegelvich et al. reported the reduction of phosphine oxides using PMHS under microwave as well as thermal conditions.[24] Unfortunately, PMHS proved to be inefficient as a reducing agent in the catalytic Wittig reaction under our conditions, and the desired products were formed in low yields of up to 11% (Table 2, entry 10).

Finally, we studied the possibility of using different epoxides as masked bases for the in situ yilde formation. The role of the epoxide as a masked base is shown in Scheme 2. The nucleophilic ring opening mediated by halogens is well recognised.[25] In our case, the bromide of the in situ formed phosphonium salt might act as the nucleophile. This would

Table 1. Effect of selected reaction parameters.[a]

Entry	$R_3P{=}O$	Solvent	t [h]	Yield **3a** [%][b]	E/Z[b]
1	$Et_3P{=}O$	toluene	1	5	85:15
2	$Bu_3P{=}O$	toluene	1	56 (24)[c]	86:14
3	$Cy_3P{=}O$	toluene	1	21	85:15
4	$Ph_3P{=}O$	toluene	1	10	84:16
5	Ph_3P	toluene	1	14	83:17
6[d]		toluene	1	<1	–
7		toluene	1	<1	–
8[e]	$Bu_3P{=}O$	toluene	24	30	>99:1
9	–	toluene	1	–	–
10	$Bu_3P{=}O$	1-butanol	1	7	86:14
11	$Bu_3P{=}O$	EC	1	–	–
12	$Bu_3P{=}O$	dioxane	2	67 (44)[c]	90:10

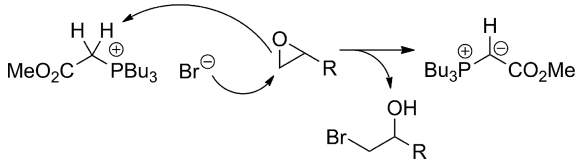
[a] Screening reactions were carried out on a 1.5 mmol scale. $R_3P{=}O$ (10 mol-%), benzaldehyde (**1a**; 1.0 equiv.), methyl bromoacetate (**2a**; 1.2 equiv.), $PhSiH_3$ (2.0 equiv.), butylene oxide (2.0 equiv.), solvent (0.75 mL), MWI 150 °C. [b] Yields and E/Z ratios were determined by GC with *n*-hexadecane as internal standard, and reactions were performed in duplicate. [c] 125 °C. [d] The phosphine oxide was used as a mixture of diastereoisomers (58:42 *dr*). [e] Conventional heating.

Table 2. Screening of silanes as reducing agents.[a]

Entry	Silane	Yield **3a** [%][b]	E/Z[b]
1	Ph_3SiH	0	–
2	Ph_2SiH_2	33	88:12
3	$PhSiH_3$	56 (66,[c] 51[d])	86:14
4	Et_3SiH	0	–
5	$t Bu_2SiH_2$	0	–
6	$n HexSiH_3$	5	86:14
7	$(MeO)_3SiH$	11	83:17
8	$(EtO)_3SiH$	5	76:24
9	$(EtO)_2MeSiH$	0	–
10	PMHS	9 (11)[e]	85:15

[a] Screening reactions were carried out on a 1.5 mmol scale. $Bu_3P{=}O$ (10 mol-%), benzaldehyde (**1a**; 1.0 equiv.), methyl bromoacetate (**2a**; 1.2 equiv.), silane (2.0 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 1 h. [b] Yields and E/Z ratios were determined by GC with *n*-hexadecane as internal standard, and reactions were performed in duplicate. [c] 15 mol-% Bu_3P. [d] 5 mol-%. [e] 3 h.

liberate an alcoholate, which, in turn, could act as a base to deprotonate the phosphonium salt and ultimately form the desired ylide. The corresponding halohydrin, formed in situ as a by-product, was detected by GC–MS analysis of the reaction mixture.



Scheme 2. Ylide formation using epoxides as masked bases.

Under the screening conditions, epoxides generally proved to be suitable masked bases (Table 3). Propylene oxide, butylene oxide, styrene oxide, and cyclohexene oxide all gave the desired product (i.e., **3a**) in moderate yields (Table 3, entries 1–4). The best results were obtained with butylene and cyclohexene oxides. Notably, in the presence of sodium carbonate or potassium carbonate, no reaction was observed (Table 3, entries 5 and 6).

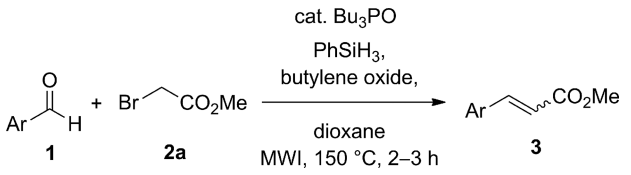
Table 3. Effect of various epoxides as masked bases.[a]

Entry	Epoxide	Yield **3a** [%][b]	*E*/*Z*[b]
1		41	87:13
2		56	85:15
3		45	84:16
4		56	86:14
5	Na_2CO_3	–	–
6	K_2CO_3	–	–

[a] Screening reactions were carried out on a 1.5 mmol scale. $Bu_3P{=}O$ (10 mol-%), benzaldehyde (**1a**; 1.0 equiv.), methyl bromoacetate (**2a**; 1.2 equiv.), $PhSiH_3$ (2.0 equiv.), epoxide (2.0 equiv.), dioxane (0.75 mL), 150 °C. [b] Yields and *E*/*Z* ratios were determined by GC with *n*-hexadecane as internal standard, and reactions were performed in duplicate.

Having established standard reaction conditions, we went on to investigate the substrate scope and limitations of the reaction. We started our study with aromatic aldehydes **1** bearing electron-donating or electron-withdrawing groups in the reaction with methyl bromoacetate (**2a**) to give the corresponding alkenes (i.e., **3a**–**3n**) (Table 4). The reactions were carried out in the presence of 10 or 15 mol-% $Bu_3P{=}O$ as the precatalyst, and slightly better results were usually achieved with the higher loading. Good yields of up to 78% were achieved for the reactions of benzaldehyde (**1a**), naphthyl derivatives **1b** and **1c**, and substrate **1d** (Table 4, entries 1–8). Alkyl-substituted benzaldehydes **1e**–**1h** and methoxy-substituted benzaldhydes **1i**–**1k** gave the desired products (i.e., **3e**–**3k**) in moderate to good yields (Table 4, entries 9–19). The reactions of substrates bearing electron-withdrawing groups (i.e., **1l**–**1n**) gave the corresponding olefination products in yields between 60 and 74% (Table 4, entries 20–23). The reaction was highly *E* selective for *meta*- and *para*-substituted substrates, while the selectivity for the corresponding *ortho*-substituted derivatives was slightly lower (e.g., compare Table 4, entry 20 with entries 22 and 23).

Table 4. Substrate scope and limitations for the reaction of aryl aldehydes **1a**–**1n** in the microwave-assisted catalytic Wittig reaction.[a]



Entry	Ar		$Bu_3P{=}O$ [mol-%]	Product	Yield [%][b]	*E*/*Z*[c]
1	Ph	**1a**	10	**3a**	69[d]	97:3
2			15		75	96:4
3	2-naphthyl	**1b**	10	**3b**	75	94:6
4			15		75	90:10
5	1-naphthyl	**1c**	10	**3c**	70	96:4
6			15		71	90:10
7	*p*-PhC_6H_4	**1d**	10	**3d**	68[d]	94:6
8			15		78	94:6
9	*p*-*t*BuC_6H_4	**1e**	10	**3e**	63[c]	97:3
10			15		67	94:4
11	*o*-MeC_6H_4	**1f**	15	**3f**	60	88:12
12	*m*-MeC_6H_4	**1g**	15	**3g**	60	90:10
13	*p*-MeC_6H_4	**1h**	15	**3h**	60	97:3
14	*o*-$MeOC_6H_4$	**1i**	10	**3i**	49	85:15
15			15		65	87:13
16	*m*-$MeOC_6H_4$	**1j**	10	**3ja**	76	92:8
17			15		75	90:10
18	*p*-$MeOC_6H_4$	**1k**	10	**3k**	57	94:6
19			15		56	95:5
20	*o*-$(CO_2Me)C_6H_4$	**1l**	15	**3l**	60	77:23
21	*m*-$(CO_2Me)C_6H_4$	**1m**	10	**3m**	74	93:7
22			15		69	95:5
23	*p*-$(CO_2Me)C_6H_4$	**1n**	15	**3n**	65	92:8

[a] Reaction conditions: $Bu_3P{=}O$ (10 or 15 mol-%), aldehyde **3** (2.0 M in dioxane; 1.0 equiv.), **2a** (1.2 equiv.), $PhSiH_3$ (1.5 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 2 h. [b] Isolated yields. [c] *E*/*Z* ratio was determined by ^1H NMR spectroscopy. [d] 3 h.

We than turned our attention to the reactions of halogen-functionalised aryl derivatives **1o**–**1u** (Table 5). Unfortunately, in all cases only moderate yields were obtained for the reaction with **2a** (Table 5, entries 1–7). It should be mentioned that for **1o**–**1t**, significant amounts of methyl cinnamate (**3a**) up to 20% were observed. This product might be formed from dehalogenation of either the substrate or the product. However, dehalogenation reactions of organic halides using $PhSiH_3$ usually require radical initiators and proceed by radical mechanisms.[26]

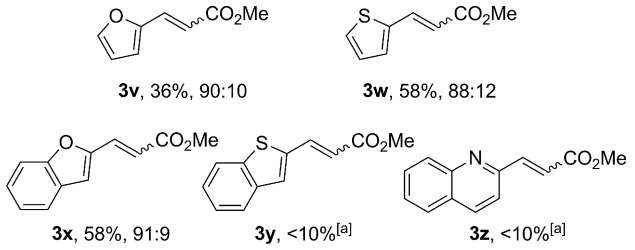
The reactions of heteroaromatic substrates **1v**–**1z** with methyl bromoacetate (**2a**) in the presence of $Bu_3P{=}O$

Table 5. Substrate scope and limitations for the reactions of **1o**–**1u**.[a]

Entry	Ar	Product	Yield [%][b]	*E*/*Z*[c]
1	*p*-FC_6H_4 (**1o**)	**3o**	52[d,e]	99:1
2	*o*-ClC_6H_4 (**1p**)	**3p**	52[e]	96:4
3	*m*-ClC_6H_4 (**1q**)	**3q**	52[d]	97:3
4	*p*-ClC_6H_4 (**1r**)	**3r**	50	95:5
5	*m*-BrC_6H_4 (**1s**)	**3s**	53[e]	99:1
6	*p*-BrC_6H_4 (**1t**)	**3t**	61	98:2
7	*o*-$(CF_3)C_6H_4$ (**1u**)	**3u**	54	73:27

[a] Reaction conditions: Bu_3P=O (15 mol-%), aldehyde **3** (2.0 M in dioxane; 1.0 equiv.), **2a** (1.2 equiv.), $PhSiH_3$ (1.5 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 2 h. [b] Isolated yields. [c] *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy. [d] 3 h. [e] Yield was determined by ^{1}H NMR spectroscopy with mesitylene as internal standard.

(15 mol-%) in the microwave at 150 °C for 2 h gave the corresponding products (i.e., **3v**–**3x**) in yields of 36–58% (Scheme 3). The reactions of **3y** and **3z** gave complex mixtures, and only traces of the desired products (i.e., **3y** and **3z**) could be detected.



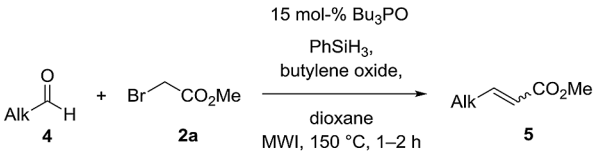
Scheme 3. Reaction of heteroaromatic substrates in the microwave-assisted catalytic Wittig reaciton. Reaction conditions: Bu_3P=O (15 mol-%), aldehyde **3** (2.0 M in dioxane; 1.0 equiv.), **2a** (1.2 equiv.), $PhSiH_3$ (1.5 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 2 h. [a] Determined by ^{1}H NMR spectroscopy with mesitylene as internal standard.

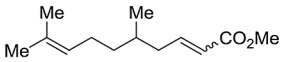
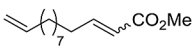
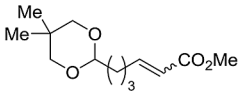
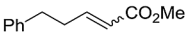
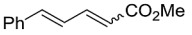
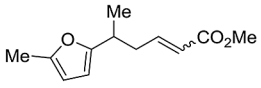
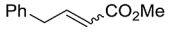
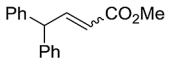
Finally, we evaluated the olefination of aliphatic aldehydes **4** with **2a** (Table 6). Again, the reaction proceeded with a high *E* selectivity in all cases. The desired products (i.e., **5a**–**5e**) were obtained in moderate to good yields (Table 6, entries 1–7). Surprisingly, furan derivative **5f** could even be obtained in 78% yield (Table 6, entry 8).

Products **5g** and **5h** were obtained as mixtures of double-bond isomers that could not be separated by column chromatography. We assume that a Michael addition and subsequent deprotonation, elimination sequence led to the corresponding double bond isomers, e.g., **7** (Scheme 4).

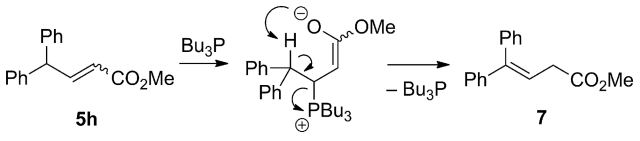
We turned our attention to alternative organohalides **2** as substrates in reaction with anisaldehyde **1j** (Table 7). When methyl chloroacetate (**2b**) was used instead of **2a**, the yield dropped from 76 to 68% (Table 7, entries 1 and 2). Iodide derivative **2c** gave the desired product (i.e., **3ja**) in a considerably lower yield (Table 7, entry 3). In these reactions, significant amounts of the dehalogenated by-product methyl acetate were observed. The reaction of α-chloroacetonitrile (**2d**) gave the desired product (i.e., **3jb**) in just 53% yield, whereas the bromo derivative (i.e., **2e**) led to **3jb** in a very good yield of 88% (Table 7, entries 4 and 5). In

Table 6. Substrate scope and limitations for the reaction of aliphatic aldehydes **4** in the microwave-assisted catalytic Wittig reaction.[a]



Entry	Product		Yield [%][b]	*E*/*Z*[c]
1		**5a**	57[d]	93:7
2		**5b**	83[d]	93:7
3			63[d,e]	94:6
4		**5c**	60	93:7
5		**5d**	63	93:7
6			74[e]	91:9
7		**5e**	52	95:5
8		**5f**	78	89:11
9			73[d,e]	88:12
10		**5g**	42	94:6
11		**5h**	48 (11)[f]	97:3
12			68[d,e] (21)[f]	97:3

[a] Reaction conditions: Bu_3P=O (10 or 15 mol-%), aldehyde **3** (2.0 M in dioxane; 1.0 equiv.), **2a** (1.2 equiv.), $PhSiH_3$ (1.5 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 2 h. [b] Isolated yields. [c] *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy. [d] 1 h. [e] 10 mol-%. [f] Yield was determined by ^{1}H NMR spectroscopy with mesitylene as internal standard, yield of the double bond isomer in parentheses.

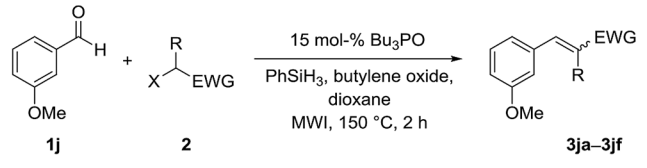


Scheme 4. Possible reaction sequence for the observed double bond isomerisation.

contrast, no product formation was observed in the presence of **2f**. When the sterically more demanding methyl 2-bromopropionate (**2g**) was used instead of **2a**, **3jc** was obtained in 53% yield (Table 7, entry 7). The reactions of **1j** with benzyl chlorides and bromides bearing electron-withdrawing groups (i.e., **2h**–**2l**) were also possible. However, the corresponding products were obtained only in low to moderate yields (Table 7, entries 8–12). Usually, the corresponding dehalogenated benzyl derivatives were observed in the GC–MS traces of the reaction mixtures.

At this point, the high complexity of the reaction mixture should be emphasised. The catalytic Wittig reaction in-

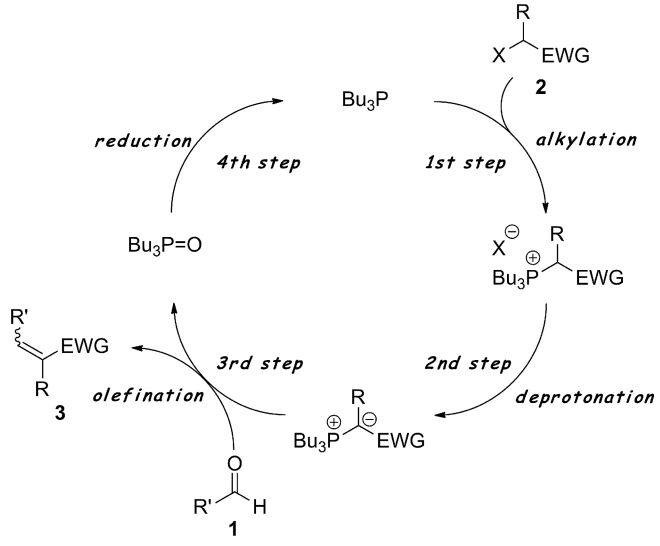
Table 7. Substrate scope and limitations for the reactions of anisaldehyde **1j** with organohalides **2** in the microwave-assisted catalytic Wittig reaction.[a] EWG = electron-withdrawing group.



Entry	Substrate **2**	Product	Yield [%][b]	*E*/*Z*[c]
1	**2a**, X = Br		76[d]	92:8
2	X, CO_2Me **2b**, X = Cl	**3ja**	68[d]	97:3
3	**2c**, X = I		24[d]	94:6
4	**2d**, X = Cl		53	81:19
5	X, CN **2e**, X = Br	**3jb**	88 (72)[d]	83:17 (84:16)
6	**2f**, X = I		0	–
7	Me, Br, CO_2Me **2g**	**3jc**	53 (42)[d]	86:14 (86:14)
8	X, CO_2Me **2h**, X = Cl	**3jd**	41 (36)[d]	95:5 (82:18)
9	**2i**, X = Br		26 (11)[d]	79:21 (87:13)
10	X, CF_3 **2j**, X = Cl	**3je**	55 (49)[d]	78:22 (79:21)
11	**2k**, X = Br		54	71:29
12	X, CF_3 **2l**	**3jf**	58	75:25

[a] Reaction conditions: $Bu_3P{=}O$ (15 mol-%), aldehyde **3** (2.0 M in dioxane; 1.0 equiv.), **2** (1.2 equiv.), $PhSiH_3$ (1.5 equiv.), butylene oxide (2.0 equiv.), MWI 150 °C, 2 h. [b] Isolated yields are given. [c] *E*/*Z* ratio determined by ^1H NMR spectroscopy. [d] 10 mol-%.

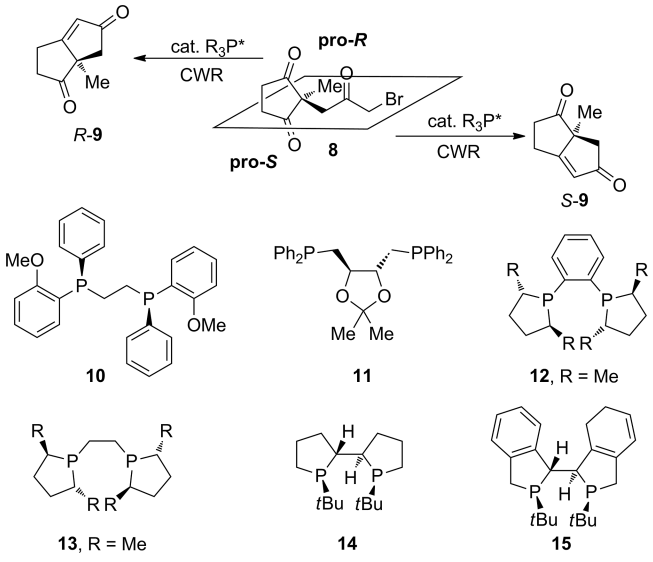
volves four steps that must occur simultaneously in a single reaction vessel (Scheme 5). The first step is the alkylation of the phosphine to give the corresponding phosphonium salt. Subsequent deprotonation gives rise to the ylide. Olefination of the aldehyde (i.e., **1**) gives the desired product (i.e., **2**) and produces the phosphine oxide as a by-product.



Scheme 5. The four steps of the catalytic Wittig reaction.

The key step to close the catalytic cycle is the subsequent reduction of this species to the phosphine. Assuming the last step occurs chemoselectively and under full conversion, step one (alkylation), step two (deprotonation), and the final olefination step have to proceed in ≥90% yield to obtain the desired product (i.e., **3**) in yields >70%. Even to obtain **3** in moderate yields of >50%, those steps have to proceed in an average of 80% yield.

Recently, we reported the first enantioselective catalytic Wittig reaction.[23e] Finally in this paper, we describe the microwave-assisted variant of this reaction. In this context, we examined the desymmetrisation of prochiral diketone **8** to give bicyclic olefin **9** in the presence of chiral phosphines **10**–**15** (Scheme 6). The reaction was carried out in the presence of 5 mol-% of the catalysts under microwave dielectric heating. The results of the screening are shown in Table 8.



Scheme 6. Desymmetrisation of prochiral ketone **8** in the catalytic Wittig reaction (CWR) under microwave dielectric heating using chiral phosphine catalysts. Reaction conditions: chiral phosphine **10**–**15** (5 mol-%), substrate **8** (1 mmol), $PhSiH_3$ (1.5 equiv.), 1,2-butylene oxide (2.0 equiv.), 1,4-dioxane (0.5 mL), MWI 150 °C (180 W), 2 h.

Table 8. Screening of chiral catalysts **8**–**13** for the enantioselective catalytic Wittig reaction.[a]

Entry	Cat.	Yield [%]	*ee* [%][b]	*er* (*R*/*S*)[b]
1	**10**	<20[d]	10	55:45
2	**11**	<20[d]	20	60:40
3	**12**	39[c]	62	81:19
4	**13**	63[b]	32	68:32
5	**14**	<5[d]	32	34:66
6	**15**	<20[d]	54	23:77

[a] Reaction conditions: chiral phosphine **10**–**15** (5 mol-%), substrate **8** (1 mmol), $PhSiH_3$ (1.5 equiv.), 1,2-butylene oxide (2.0 equiv.), 1,4-dioxane (0.5 mL), MWI 150 °C, 2 h. [b] The *ee* and *er* values were determined by chiral GC–MS. [c] Isolated yield after column chromatography. [d] The yields were determined by ^1H NMR spectroscopic analysis of the reaction mixture with mesitylene as internal standard.

(*R*,*R*)-DIPAMP {**10**; 1,2-bis[(2-methoxyphenyl)(phenylphosphino)]ethane} and (*R*,*R*)-DIOP [**11**; *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane] gave the desired product (i.e., **9**) in yields of <20%, and with enantioselectivities of 10 and 20%, respectively (Table 8, entries 1 and 2). Nevertheless, a moderate enantiomeric excess could be obtained in the presence of (*S*,*S*)-Me-DuPhos [**12**; 1,2-bis(2,5-dimethylphospholano)benzene; 5 mol-%], which gave an *ee* of 62% and an isolated yield of 39% (Table 8, entry 3). The use of (*R*,*R*)-Me-BPE (**13**; 1,2-bis(2,5-dimethylphospholano)ethane) gave the desired product (i.e., **9**) in 63% yield with an enantiomeric excess of 32% (Table 8, entry 4). This result indicates that both good yields and selectivities are generally possible. The use of catalysts **14** and **15**, both of which have a phospholane structure like **12** and **13**, gave comparable *ee*'s but low yields.

Conclusions

We have evaluated the scope and limitations of the microwave-assisted catalytic Wittig reaction. As well as screening various readily available (pre)catalysts, we could establish that in general epoxides are suitable masked bases for this reaction. Under the optimised reaction conditions, moderate to good isolated yields and excellent *E*/*Z* selectivities for aromatic, heteroaromatic, and aliphatic olefins were achieved. We investigated the influence of the catalyst loading for a variety of substrates. Furthermore, the scope with respect to the halide component was evaluated. 2-Bromoacetonitrile proved to be particularly suitable, giving the desired product in 88% yield. We have presented a putative reaction sequence that demonstrates the high overall efficiency of the process that is necessary to achieve reasonable yields. Moreover, we have also described further studies of our stereoselective catalytic Wittig reaction in terms of an intramolecular desymmetrisation using chiral bis-phosphines to give an enantiomerically enriched alkene with an *er* of 81:19.

Experimental Section

General Procedure (GP) for the Microwave-Assisted Catalytic Wittig Reaction: $Bu_3P{=}O$ (10–15 mol-%), the aldehyde (2 M in 1,4-dioxane; 1.5 mmol, 1.0 equiv.), the organohalide (1.8 mmol, 1.2 equiv.), $PhSiH_3$ (2.3 mmol, 1.5 equiv.), and 1,2-epoxybutane (3.0 mmol, 2.0 equiv.) were put into a microwave vial (10 mL) equipped with a stirrer bar. The vial was then purged with argon and sealed with a septum, and the reaction mixture was heated by microwave irradiation (MWI) at 150 °C for 1–3 h (150 W). The mixture was then cooled to 23 °C, and dioxane (10 mL) and satd. aq. NH_4F solution (3 mL) were added. The mixture was then stirred at 23 °C for a further 16 h. The mixture was diluted with H_2O (25 mL), and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, and the volatiles were removed in vacuo. The residue was purified by flash column chromatography [SiO_2, cyclohexane (CH)/ethyl acetate (EtOAc)].

Methyl (*E*)-Phenylpropenoate (3a):[17a,27] According to the GP, benzaldehyde (**1a**; 162 mg, 1.53 mmol), methyl bromoacetate (**2a**; 280 mg, 1.83 mmol), $Bu_3P{=}O$ (60 mg, 0.27 mmol, 15 mol-%), $PhSiH_3$ (248 mg, 2.29 mmol), and 1,2-epoxybutane (220 mg, 3.05 mmol) in dioxane (1 mL) were converted for 3 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3a** (186 mg, 75%, *E*/*Z* = 97:3) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 6.46 (d, *J* = 16.0 Hz, 1 H, CH), 7.38–7.43 (m, 3 H, ArH), 7.51–7.56 (m, 2 H, ArH), 7.72 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.56 (CH_3), 117.66 (CH), 127.95 (2 CH), 128.76 (2 CH), 130.17 (CH), 134.23 (C), 144.73 (CH), 167.27 (C=O) ppm.

Methyl (*E*)-3-(2-Naphthyl)propenoate (3b):[28] According to the GP, 2-naphthaldehyde (**1b**; 239 mg, 1.53 mmol), methyl bromoacetate (**2a**; 281 mg, 1.84 mmol), $Bu_3P{=}O$ (50 mg, 0.23 mmol, 15 mol-%), $PhSiH_3$ (248 mg, 2.30 mmol), and 1,2-epoxybutane (221 mg, 3.06 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3b** (242 mg, 75%, *E*/*Z* = 90:10) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, CH_3), 6.57 (d, *J* = 16.0 Hz, 1 H, CH), 7.48–7.54 (m, 2 H), 7.66–7.70 (m, 1 H), 7.80–7.91 (m, 4 H), 7.93–7.97 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.52 (CH_3), 117.71 (CH), 123.25 (CH), 126.50 (CH), 127.04 (CH), 127.59 (CH), 128.39 (CH), 128.48 (CH), 129.80 (CH), 131.65 (C), 133.06 (C), 134.03 (C), 144.70 (CH), 167.27 (C=O) ppm.

Methyl (*E*)-3-(1-Naphthyl)propenoate (3c):[28a,29] According to the GP, 1-naphthaldehyde (**1c**; 153 mg, 0.980 mmol), methyl bromoacetate (**2a**; 181 mg, 1.18 mmol), $Bu_3P{=}O$ (32 mg, 0.15 mmol, 15 mol-%), $PhSiH_3$ (159 mg, 1.47 mmol), and 1,2-epoxybutane (141 mg, 1.96 mmol) in dioxane (0.5 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3c** (147 mg, 71%, *E*/*Z* = 90:10) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.88 (s, 3 H, CH_3), 6.56 (d, *J* = 15.8 Hz, 1 H, CH), 7.48–7.66 (m, 3 H, ArH), 7.75–7.78 (m, 1 H, ArH), 7.85–7.93 (m, 2 H, ArH), 8.22 (m, 1 H, ArH), 8.56 (d, *J* = 15.8 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.55 (CH_3), 120.16 (CH), 123.12 (CH), 124.78 (CH), 125.23 (CH), 126.01 (CH), 126.66 (CH), 128.52 (CH), 130.35 (CH), 131.18 (C), 131.43 (C), 133.45 (C), 141.59 (CH), 167.06 (C=O) ppm.

Methyl (*E*)-3-[(1,1′-Biphenyl)-4-yl]acrylate (3d):[28a] According to the GP, 4-phenylbenzaldehyde (**1d**; 239 mg, 1.31 mmol), methyl bromoacetate (**2a**; 240 mg, 1.57 mmol), $Bu_3P{=}O$ (43 mg, 0.20 mmol, 15 mol-%), $PhSiH_3$ (213 mg, 1.97 mmol), and 1,2-epoxybutane (189 mg, 2.62 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3d** (243 mg, 78%, *E*/*Z* = 94:6) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CH_3), 6.49 (d, *J* = 16.0 Hz, 1 H, CH), 7.36–7.42 (m, 1 H, ArH), 7.44–7.50 (m, 2 H, ArH), 7.59–7.66 (m, 6 H, ArH), 7.75 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.64 (CH_3), 117.55 (CH), 126.95 (2 CH), 127.44 (2 CH), 127.78 (CH), 128.51 (2 CH), 128.83 (2 CH), 133.24 (C), 140.03 (C), 142.96 (C), 144.32 (CH), 167.38 (C=O) ppm.

Methyl (*E*)-3-(4-*tert*-Butylphenyl)propenoate (3e):[28a,30] According to the GP, 4-*tert*-butylbenzaldehyde (**1e**; 188 mg, 1.16 mmol), methyl bromoacetate (**2a**; 213 mg, 1.39 mmol), $Bu_3P{=}O$ (38 mg, 0.17 mmol, 15 mol-%), $PhSiH_3$ (188 mg, 1.74 mmol), and 1,2-epoxybutane (167 mg, 2.32 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3e** (170 mg, 67%, *E*/*Z* = 94:4) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.34 (s, 9 H, CH_3), 3.81 (s, 3 H, CH_3), 6.42 (d, *J* = 16.0 Hz, 1 H, CH), 7.41–7.50 (m, 4 H, ArH), 7.70 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.00 (3 CH_3), 34.71 (C), 51.43 (CH_3), 116.74 (CH), 125.71 (2 CH), 127.81 (2 CH), 131.50 (C), 144.62 (CH), 153.66 (C), 167.42 (C=O) ppm.

Methyl (*E*)-3-(2-Methylphenyl)-2-propenoate (3f):[17a,31] According to the GP, 2-methylbenzaldehyde (**1f**; 173 mg, 1.44 mmol), methyl bromoacetate (**2a**; 264 mg, 1.73 mmol), Bu_3P=O (47 mg, 0.22 mmol, 15 mol-%), $PhSiH_3$ (234 mg, 2.16 mmol), and 1,2-epoxybutane (208 mg, 2.88 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3f** (153 mg, 60%, *E*/*Z* = 88:12) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, CH_3), 3.87 (s, 3 H, CH_3), 6.43 (d, *J* = 15.9 Hz, 1 H, CH), 7.25–7.34 (m, 3 H, ArH), 7.59–7.63 (m, 1 H, ArH), 8.05 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.64 (CH_3), 51.53 (CH_3), 118.69 (CH), 126.22 (CH), 126.25 (CH), 129.91 (CH), 130.66 (CH), 133.21 (C), 137.51 (C), 142.38 (CH), 167.31 (C=O) ppm.

Methyl (*E*)-3-(3-Methylphenyl)-2-propenoate (3g):[32] According to the GP, 3-methylbenzaldehyde (**1g**; 118 mg, 0.982 mmol), methyl bromoacetate (**2a**; 180 mg, 1.18 mmol), Bu_3P=O (32 mg, 0.15 mmol, 15 mol-%), $PhSiH_3$ (159 mg, 1.47 mmol), and 1,2-epoxybutane (141 mg, 1.96 mmol) in dioxane (0.5 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3g** (104 mg, 60%, *E*/*Z* = 90:10) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 3.82 (s, 3 H, CH_3), 6.44 (d, *J* = 16.0 Hz, 1 H, CH), 7.19–7.23 (m, 1 H, ArH), 7.28–7.36 (m, 3 H, ArH), 7.68 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.18 (CH_3), 51.53 (CH_3), 117.43 (CH), 125.15 (CH), 128.62 (CH), 128.65 (CH), 131.02 (CH), 134.21 (C), 138.41 (C), 144.94 (CH), 167.37 (C=O) ppm.

Methyl (*E*)-3-(4-Methylphenyl)-2-propenoate (3h):[33] According to the GP, 4-methylbenzaldehyde (**1h**; 184 mg, 1.53 mmol), methyl bromoacetate (**2a**; 281 mg, 1.84 mmol), Bu_3P=O (50 mg, 0.23 mmol, 15 mol-%), $PhSiH_3$ (248 mg, 2.30 mmol), and 1,2-epoxybutane (221 mg, 3.06 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3h** (163 mg, 60%, *E*/*Z* = 97:3) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H, CH_3), 3.81 (s, 3 H, CH_3), 6.41 (d, *J* = 16.0 Hz, 1 H, CH), 7.19–7.21 (m, 2 H, ArH), 7.42–7.44 (m, 2 H, ArH), 7.68 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.41 (CH_3), 51.57 (CH_3), 116.65 (CH), 128.02 (2 CH), 129.57 (2 CH), 131.61 (C), 140.67 (C), 144.83 (CH), 167.58 (C=O) ppm. $C_{11}H_{12}O_2$ (176.21): calcd. C 74.98, H 6.86; found C 74.88, H 7.17.

Methyl (*E*)-3-(2-Methoxyphenyl)propenoate (3i):[28a] According to the GP, 2-methoxybenzaldehyde (**1i**; 158 mg, 1.16 mmol), methyl bromoacetate (**2a**; 213 mg, 1.39 mmol), Bu_3P=O (38 mg, 0.17 mmol, 15 mol-%), $PhSiH_3$ (188 mg, 1.74 mmol), and 1,2-epoxybutane (167 mg, 2.32 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3i** (144 mg, 65%, *E*/*Z* = 87:13) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 3.90 (s, 3 H, CH_3), 6.55 (d, *J* = 16.2 Hz, 1 H, CH), 6.87–7.00 (m, 2 H, ArH), 7.33–7.39 (m, 1 H, ArH), 7.50–7.53 (m, 1 H, ArH), 8.01 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.41 (CH_3), 55.27 (CH_3), 110.98 (CH), 118.11 (CH), 120.54 (CH), 123.15 (C), 128.73 (CH), 131.37 (CH), 140.11 (CH), 158.18 (C), 167.77 (C=O) ppm. $C_{11}H_{12}O_3$ (192.21): calcd. C 68.74, H 6.29; found C 68.24, H 6.24.

Methyl (*E*)-3-(3-Methoxyphenyl)propenoate (3ja):[34] According to the GP, 3-methoxybenzaldehyde (**1j**; 119 mg, 0.874 mmol), methyl bromoacetate (**2a**; 150 mg, 0.981 mmol), Bu_3P=O (27 mg, 0.12 mmol, 15 mol-%), $PhSiH_3$ (133 mg, 1.23 mmol), and 1,2-epoxybutane (118 mg, 1.64 mmol) in dioxane (0.4 mL) were converted for 3 h. Purification (SiO_2, CH/EtOAc, 10:1) gave **3ja** (125 mg, 75%, *E*/*Z* = 90:10) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 6.44 (d, *J* = 16.0 Hz, 1 H, CH), 6.93–6.96 (m, 1 H, ArH), 7.04–7.06 (m, 1 H, ArH), 7.12–7.14 (m, 1 H, ArH), 7.29–7.34 (m, 1 H, ArH), 7.67 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.53 (CH_3), 55.09 (CH_3), 112.86 (CH), 115.97 (CH), 117.94 (CH), 120.59 (CH), 129.74 (CH), 135.60 (C), 144.63 (CH), 159.76 (C), 167.18 (C=O) ppm.

(*E*)-3-(3-Methoxyphenyl)propenenitrile (3jb):[35] According to the GP, 3-methoxybenzaldehyde (**1j**; 208 mg, 1.53 mmol), bromoacetonitrile (**2e**; 220 mg, 1.84 mmol), Bu_3P=O (50 mg, 0.23 mmol, 15 mol-%), $PhSiH_3$ (248 mg, 2.30 mmol), and 1,2-epoxybutane (221 mg, 3.06 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 10:1) gave **3jb** (214 mg, 88%, *E*/*Z* = 83:17) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CH_3), 5.88 (d, *J* = 16.6 Hz, 1 H, CH), 6.94–7.14 (m, 3 H, CH), 7.30–7.44 (m, 2 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.21 (CH_3), 96.46 (CH), 112.34 (CH), 116.68 (CH), 117.97 (C), 119.80 (CH), 129.99 (CH), 134.66 (C), 150.31 (CH), 159.84 (C) ppm.

Methyl (*E*)-2-Methyl-3-(3-methoxyphenyl)propenoate (3jc): According to the GP, 3-methoxybenzaldehyde (**1j**; 162 mg, 1.19 mmol), methyl 2-brompropanoate (**2f**; 238 mg, 1.43 mmol), Bu_3P=O (39 mg, 0.18 mmol, 15 mol-%), $PhSiH_3$ (193 mg, 1.79 mmol), and 1,2-epoxybutane (172 mg, 2.38 mmol) in dioxane (0.6 mL) were converted for 1 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3jc** (129 mg, 53%, *E*/*Z* = 86:14) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 1.5 Hz, 3 H, CH_3), 3.83 (s, 6 H, CH_3), 6.86–6.91 (m, 1 H), 6.92–6.95 (m, 1 H), 6.98–7.02 (m, 1 H), 7.29–7.35 (m, 1 H), 7.67 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.02 (CH_3), 51.95 (CH_3), 55.09 (CH_3), 113.75 (CH), 114.97 (CH), 121.97 (CH), 128.43 (C), 129.26 (CH), 137.06 (C), 138.72 (CH), 159.34 (C), 168.95 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 206 (72) $[M]^+$, 175 (25) $[M - OMe]^+$, 146 (100) $[M - CO_2Me]^+$, 131 (22), 115 (33), 103 (28), 91 (23). HRMS (EI): calcd. for $C_{12}H_{14}O_3$ $[M]^+$ 206.0938; found 206.0937.

Methyl (*E*)-4-[2-(3-Methoxyphenyl)ethenyl]benzoate (3jd):[36] According to the GP, 3-methoxybenzaldehyde (**1j**; 178 mg, 1.31 mmol), methyl 4-(chloromethyl)benzoate (**2h**; 290 mg, 1.57 mmol), Bu_3P=O (43 mg, 0.20 mmol, 15 mol-%), $PhSiH_3$ (213 mg, 1.97 mmol), and 1,2-epoxybutane (189 mg, 2.68 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3jd** (143 mg, 0.533 mmol, 41%, *E*/*Z* = 95:5) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.87 (s, 3 H, CH_3), 3.94 (s, 3 H, CH_3), 6.87 (dd, *J* = 8.2, *J* = 0.8 Hz, 1 H, CH), 7.07–7.23 (m, 4 H), 7.30–7.32 (m, 1 H), 7.56–7.59 (m, 2 H), 8.02–8.05 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.96 (CH_3), 55.12 (CH_3), 111.90 (CH), 113.77 (CH), 119.38 (CH), 126.24 (2 CH), 127.70 (CH), 128.80 (C), 129.63 (CH), 129.90 (2 CH), 130.98 (CH), 138.05 (C), 141.58 (C), 159.80 (C), 166.73 (C=O) ppm.

(*E*)-1-(3-Methoxyphenyl)-2-(4-trifluoromethylphenyl)ethene (3je):[37] According to the GP, 3-methoxybenzaldehyde (**1j**; 182 mg, 1.43 mmol), 4-(trifluoromethyl)benzyl chloride (**2j**; 313 mg, 1.61 mmol), Bu_3P=O (44 mg, 0.20 mmol, 15 mol-%), $PhSiH_3$ (218 mg, 2.01 mmol), and 1,2-epoxybutane (193 mg, 2.68 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3je** (205 mg, 55%, *E*/*Z* = 78:22) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, CH_3), 6.63–6.73 (m, 1 H), 6.75–6.79 (m, 1 H), 6.97–7.06 (m, 4 H), 7.16–7.25 (m, 1 H), 7.47–7.55 (m, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.22 (CH_3), 112.00 (CH), 113.88 (CH), 119.44 (CH), 124.21 (q, $^1J_{C,F}$ = 272.0 Hz, C), 125.58 (q, $^3J_{C,F}$ = 3.8 Hz, 2 CH), 126.58 (2 CH), 127.35 (CH), 129.21 (q, $^2J_{C,F}$ = 32.5 Hz, C), 129.74 (CH), 131.05 (CH), 138.03 (C), 140.66 (C), 159.91 (C) ppm. MS (EI,

70 eV): *m*/*z* (%) = 278 (100) $[M]^+$, 262 (16), 209 (18) $[M - CF_3]^+$, 194 (20), 178 (20), 165 (46). $C_{16}H_{13}FO_3$ (272.27): calcd. C 69.06, H 4.71; found C 69.29, H 4.55.

(*E*)-1-(3-Methoxyphenyl)-2-(3-trifluoromethylphenyl)ethene (3jf): According to the GP, 3-methoxybenzaldehyde (**1j**; 221 mg, 1.62 mmol), 3-(trifluoromethyl)benzyl bromide (**2l**; 465 mg, 1.94 mmol), $Bu_3P{=}O$ (53 mg, 0.24 mmol, 15 mol-%), $PhSiH_3$ (263 mg, 2.43 mmol), and 1,2-epoxybutane (234 mg, 3.24 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3jf** (262 mg, 58%, *E*/*Z* = 75:25) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.00 (s, 3 H, CH_3), 6.72–7.04 (m, 2 H), 7.21–7.24 (m, 1 H), 7.27–7.35 (m, 1 H), 7.39–7.50 (m, 1 H), 7.56–7.69 (m, 3 H), 7.78–7.84 (m, 1 H), 7.90–7.92 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.07 (CH_3), 111.90 (CH), 113.76 (CH), 119.32 (CH), 123.03 (q, $^3J_{C,F}$ = 3.8 Hz, CH), 123.99 (q, $^3J_{C,F}$ = 3.8 Hz, CH), 124.16 (q, $^1J_{C,F}$ = 272.3 Hz, C), 127.27 (CH), 129.04 (CH), 129.51 (CH), 129.68 (CH), 130.33 (CH), 130.98 (q, $^2J_{C,F}$ = 32.1 Hz, C), 137.96 (C), 138.04 (C), 159.90 (C) ppm. MS (EI, 70 eV): *m*/*z* (%) = 278 (100) $[M]^+$, 277 (18), 262 (13), 209 (10) $[M - CF_3]^+$, 178 (15), 165 (33). HRMS (EI): calcd. for $C_{16}H_{13}F_3O$ $[M]^+$ 278.0913; found 278.0913.

Methyl (*E*)-3-(2-Methoxyphenyl)propenoate (3k):[38] According to the GP, 4-methoxybenzaldehyde (**1k**; 178 mg, 1.31 mmol), methyl bromoacetate (**2a**; 240 mg, 1.57 mmol), $Bu_3P{=}O$ (43 mg, 0.20 mmol, 15 mol-%), $PhSiH_3$ (213 mg, 1.97 mmol), and 1,2-epoxybutane (189 mg, 2.62 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3k** (141 mg, 56%, *E*/*Z* = 95:5) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3), 3.84 (s, 3 H, CH_3), 6.32 (d, *J* = 15.9 Hz, 1 H, CH), 6.89–6.93 (m, 2 H, ArH), 7.47–7.50 (m, 2 H, ArH), 7.66 (d, *J* = 15.9 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.45 (CH_3), 55.24 (CH_3), 114.23 (2 CH), 115.16 (CH), 127.01 (C), 129.63 (2 CH), 144.42 (CH), 161.31 (C), 167.64 (C=O) ppm. $C_{11}H_{12}O_3$ (192.21): calcd. C 68.74, H 6.29; found C 68.63, H 6.28.

Methyl (*E*)-3-(2-Methoxycarbonylphenyl)-2-propenoate (3l):[34,39] According to the GP, 2-(methoxycarbonyl)benzaldehyde (**1l**; 236 mg, 1.44 mmol), methyl bromoacetate (**2a**; 264 mg, 1.73 mmol), $Bu_3P{=}O$ (47 mg, 0.22 mmol, 15 mol-%), $PhSiH_3$ (234 mg, 2.16 mmol), and 1,2-epoxybutane (208 mg, 2.88 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 10:1) gave **3l** (192 mg, 60%, *E*/*Z* = 77:23) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 3.93 (s, 3 H, CH_3), 6.31 (d, *J* = 15.9 Hz, 1 H, CH), 7.33–7.61 (m, 3 H, ArH), 7.94–7.98 (m, 1 H, ArH), 8.45 (d, *J* = 15.9 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.64 (CH_3), 52.26 (CH_3), 120.53 (CH), 127.77 (CH), 129.27 (CH), 129.61 (C), 130.63 (CH), 132.25 (CH), 136.20 (C), 143.78 (CH), 166.84 (C=O), 166.99 (C=O) ppm.

Methyl (*E*)-3-(3-Methoxycarbonylphenyl)-2-propenoate (3m):[34] According to the GP, 3-(methoxycarbonyl)benzaldehyde (**1m**; 156 mg, 0.950 mmol), methyl bromoacetate (**2a**; 174 mg, 1.14 mmol), $Bu_3P{=}O$ (31 mg, 0.14 mmol, 15 mol-%), $PhSiH_3$ (154 mg, 1.43 mmol), and 1,2-epoxybutane (137 mg, 1.90 mmol) in dioxane (0.5 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 10:1) gave **3m** (144 mg, 69%, *E*/*Z* = 95:5) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 3.95 (s, 3 H, CH_3), 6.53 (d, *J* = 16.1 Hz, 1 H, CH), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.69–7.76 (m, 2 H, ArH), 8.21–8.22 (m, 1 H, ArH), 8.05 (d, *J* = 16.1 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.78 (CH_3), 52.29 (CH_3), 119.05 (CH), 128.93 (CH), 128.97 (CH), 130.78 (C), 131.02 (CH), 132.15 (CH), 134.66 (C), 143.57 (CH), 166.39 (C=O), 167.03 (C=O) ppm.

Methyl (*E*)-3-(4-Methoxycarbonylphenyl)-2-propenoate (3n):[40] According to the GP, 4-(methoxycarbonyl)benzaldehyde (**1n**; 200 mg, 1.22 mmol), methyl bromoacetate (**2a**; 224 mg, 1.46 mmol), $Bu_3P{=}O$ (40 mg, 0.18 mmol, 15 mol-%), $PhSiH_3$ (198 mg, 1.83 mmol), and 1,2-epoxybutane (176 mg, 2.44 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 5:1) gave **3n** (175 mg, 65%, *E*/*Z* = 92:8) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 3.94 (s, 3 H, CH_3), 6.53 (d, *J* = 16.1 Hz, 1 H, CH), 7.57–7.62 (m, 2 H, ArH), 7.72 (d, *J* = 16.1 Hz, 1 H, CH), 8.01–8.08 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.53 (CH_3), 51.94 (CH_3), 119.86 (CH), 127.62 (2 CH), 129.77 (2 CH), 131.06 (C), 138.25 (C), 143.06 (CH), 166.00 (C=O), 166.55 (C=O) ppm.

Methyl (*E*)-3-(4-Fluorophenyl)propenoate (3o):[41] According to the GP, 4-fluorobenzaldehyde (**1o**; 155 mg, 1.25 mmol), methyl bromoacetate (**2a**; 230 mg, 1.50 mmol), $Bu_3P{=}O$ (41 mg, 0.19 mmol, 15 mol-%), $PhSiH_3$ (202 mg, 1.87 mmol), and 1,2-epoxybutane (180 mg, 2.49 mmol) in dioxane (0.6 mL) were converted for 3 h. Purification (SiO_2, CH/EtOAc, 20:1) gave a mixture of **3o** (118 mg, 52%, *E*/*Z* = 99:1) and methyl 3-(4-fluorophenyl)propanoate (7 mg, 4%) as a colorless solid. Data for **3o**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 6.37 (d, *J* = 16.0 Hz, 1 H), 7.05–7.12 (m, 2 H, ArH), 7.49–7.55 (m, 2 H, ArH), 7.66 (d, *J* = 16.0 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.65 (CH_3), 115.96 (d, $J_{C,F}$ = 21.9 Hz, 2 CH), 117.46 (CH), 129.87 (d, $J_{C,F}$ = 8.5 Hz, 2 CH), 130.55 (d, $J_{C,F}$ = 3.4 Hz, C), 143.48 (CH), 163.83 (d, $J_{C,F}$ = 251.3 Hz, C), 167.23 (C=O) ppm.

Methyl (*E*)-3-(2-Chlorophenyl)propenoate (3p):[29,33a] According to the GP, 2-chlorobenzaldehyde (**1p**; 215 mg, 1.53 mmol), methyl bromoacetate (**2a**; 280 mg, 1.83 mmol), $Bu_3P{=}O$ (50 mg, 0.23 mmol, 15 mol-%), $PhSiH_3$ (248 mg, 2.29 mmol), and 1,2-epoxybutane (220 mg, 3.05 mmol) in dioxane (0.5 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave a mixture of **3p** (156 mg, 52%, *E*/*Z* = 96:4) and methyl 3-(2-chlorophenyl)-propanoate (9 mg, 3%) as a colorless oil. Data for **3p**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3), 6.41 (d, *J* = 16.0 Hz, 1 H, CH), 7.23–7.30 (m, 2 H, ArH), 7.38–7.42 (m, 1 H, ArH), 7.57–7.61 (m, 1 H, ArH), 8.08 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.75 (CH_3), 120.39 (CH), 127.01 (CH), 127.54 (CH), 130.09 (CH), 130.98 (CH), 132.58 (C), 134.86 (C), 140.52 (CH), 166.80 (C=O) ppm.

Methyl (*E*)-3-(3-Chlorophenyl)propenoate (3q):[29] According to the GP, 3-chlorobenzaldehyde (**1q**; 153 mg, 1.09 mmol), methyl bromoacetate (**2a**; 202 mg, 1.32 mmol), $Bu_3P{=}O$ (36 mg, 0.16 mmol, 15 mol-%), $PhSiH_3$ (178 mg, 1.64 mmol), and 1,2-epoxybutane (157 mg, 2.18 mmol) in dioxane (0.5 mL) were converted for 3 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3q** (112 mg, 52%, *E*/*Z* = 97:3) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 6.45 (d, *J* = 16.0 Hz, 1 H, CH), 7.32–7.42 (m, 3 H, ArH), 7.50–7.52 (m, 1 H, ArH), 7.63 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.74 (CH_3), 119.19 (CH), 126.16 (CH), 127.71 (CH), 130.05 (CH), 130.06 (CH), 134.82 (C), 136.11 (C), 143.13 (CH), 166.89 (C=O) ppm.

Methyl (*E*)-3-(4-Chlorophenyl)propenoate (3r):[42] According to the GP, 4-chlorobenzaldehyde (**1r**; 180 mg, 1.28 mmol), methyl bromoacetate (**2a**; 235 mg, 1.54 mmol), $Bu_3P{=}O$ (42 mg, 0.19 mmol, 15 mol-%), $PhSiH_3$ (111 mg, 1.02 mmol), and 1,2-epoxybutane (185 mg, 2.56 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3r** (127 mg, 50%, *E*/*Z* = 95:5) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, CH_3), 6.42 (d, *J* = 16.0 Hz, 1 H, CH), 7.35–7.39 (m, 2 H, ArH), 7.45–7.48 (m, 2 H, ArH), 7.65 (d, *J* = 16.0 Hz, 1 H, CH)

ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.51 (CH_3), 118.17 (CH), 128.93 (2 CH), 129.01 (2 CH), 132.65 (C), 135.94 (C), 143.11 (CH), 166.84 (C=O) ppm. $C_{10}H_9ClO_3$ (212.63): calcd. C 61.08, H 4.61, Cl 18.03; found C 60.99, H 4.33, Cl 17.90.

Methyl (*E*)-3-(3-Bromophenyl)propenoate (3s):[43] According to the GP, 3-bromobenzaldehyde (**1s**; 305 mg, 1.65 mmol), methyl bromoacetate (**2a**; 303 mg, 1.98 mmol), Bu_3P=O (54 mg, 0.25 mmol, 15 mol-%), $PhSiH_3$ (268 mg, 2.48 mmol), and 1,2-epoxybutane (238 mg, 3.30 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 10:1) gave a mixture of **3s** (224 mg, 53%, *E*/*Z* = 99:1) and methyl 3-(3-bromophenyl)propanoate (25 mg, 10%) as a colorless solid. Data for **3s**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 6.42 (d, *J* = 16.0 Hz, 1 H, CH), 7.22–7.26 (m, 1 H, ArH), 7.41–7.44 (m, 1 H, ArH), 7.48–7.50 (m, 1 H, ArH), 7.59 (d, *J* = 16.0 Hz, 1 H, CH), 7.63–7.67 (m, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.63 (CH_3), 119.09 (CH), 122.83 (C), 126.48 (CH), 130.19 (CH), 130.55 (CH), 132.85 (CH), 136.26 (C), 142.89 (CH), 166.69 (C=O) ppm.

Methyl (*E*)-3-(4-Bromophenyl)propenoate (3t):[43,44] According to the GP, 4-bromobenzaldehyde (**1t**; 305 mg, 1.65 mmol), methyl bromoacetate (**2a**; 303 mg, 1.98 mmol), Bu_3P=O (54 mg, 0.25 mmol, 15 mol-%), $PhSiH_3$ (268 mg, 2.48 mmol), and 1,2-epoxybutane (238 mg, 3.30 mmol) in dioxane (0.8 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3t** (244 mg, 61%, *E*/*Z* = 98:2) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, CH_3), 6.43 (d, *J* = 16.0 Hz, 1 H, CH), 7.37–7.41 (m, 2 H, ArH), 7.51–7.54 (m, 2 H, ArH), 7.63 (d, *J* = 16.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.66 (CH_3), 118.34 (CH), 124.41 (C), 129.31 (2 CH), 131.99 (2 CH), 133.13 (C), 143.31 (CH), 166.96 (C=O) ppm.

Methyl (*E*)-3-(2-Trifluoromethylphenyl)propenoate (3u):[45] According to the GP, 2-trifluoromethylbenzaldehyde (**1u**; 352 mg, 1.89 mmol), methyl bromoacetate (**2a**; 348 mg, 2.27 mmol), Bu_3P=O (62 mg, 0.28 mmol, 15 mol-%), $PhSiH_3$ (306 mg, 2.83 mmol) and 1,2-epoxybutane (272 mg, 3.77 mmol) in dioxane (0.5 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3u** (197 mg, 54%, *E*/*Z* = 73:27) as a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (s, 3 H, CH_3), 6.42 (d, *J* = 15.8 Hz, 1 H, CH), 7.40–7.74 (m, 4 H), 8.04–8.11 (m, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.87 (CH_3), 122.11 (CH), 123.86 (q, $^1J_{C,F}$ = 273.0 Hz, CF_3), 126.11 (q, $^3J_{C,F}$ = 5.6 Hz, CH), 127.84 (CH), 128.80 (q, $^2J_{C,F}$ = 30.4 Hz, C), 129.56 (CH), 132.06 (CH), 133.28 (C), 140.25 (d, $^3J_{C,F}$ = 2.0 Hz, CH), 166.48 (C=O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –58.56 ppm.

Methyl (*E*)-3-(2-Furyl)propenoate (3v):[40,46] According to the GP, 2-furylcarbaldehyde (**2v**; 83 mg, 0.86 mmol), methyl bromoacetate (**2a**; 158 mg, 1.03 mmol), Bu_3P=O (28 mg, 0.13 mmol, 15 mol-%), $PhSiH_3$ (140 mg, 1.29 mmol), and 1,2-epoxybutane (124 mg, 1.72 mmol) in dioxane (0.4 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3v** (47 mg, 36%, *E*/*Z* = 90:10) as an orange oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, CH_3), 6.32 (d, *J* = 15.7 Hz, 1 H, CH), 6.46–6.48 (m, 1 H, ArH), 6.60–6.63 (m, 1 H, ArH), 7.44 (d, *J* = 15.7 Hz, 1 H, CH), 7.48–7.49 (m, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.55 (CH_3), 112.19 (CH), 114.74 (CH), 115.33 (CH), 131.11 (CH), 144.67 (CH), 150.77 (C), 167.39 (C=O) ppm.

Methyl (*E*)-3-(2-Thienyl)propenoate (3w):[47] According to the GP, 2-thienylcarbaldehyde (**2w**; 140 mg, 1.25 mmol), methyl bromoacetate (**2a**; 229 mg, 1.50 mmol), Bu_3P=O (41 mg, 0.19 mmol, 15 mol-%), $PhSiH_3$ (203 mg, 1.88 mmol), and 1,2-epoxybutane (180 mg, 2.50 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 10:1) gave **3w** (123 mg, 58%, *E*/*Z* = 88:12) as a reddish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3 H, CH_3), 6.25 (d, *J* = 15.7 Hz, 1 H, CH), 7.04–7.08 (m, 1 H, ArH), 7.25–7.27 (m, 1 H, ArH), 7.37–7.39 (m, 1 H, ArH), 7.80 (d, *J* = 15.7 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.49 (CH_3), 116.34 (CH), 127.92 (CH), 128.32 (CH), 130.80 (CH), 137.11 (CH), 139.31 (C), 167.06 (C=O) ppm.

Methyl (*E*)-3-(2-Benzofuranyl)propenoate (3x):[48] According to the GP, benzofuran-2-carbaldehyde (**2x**; 161 mg, 1.10 mmol), methyl bromoacetate (**2a**; 202 mg, 1.32 mmol), Bu_3P=O (36 mg, 0.17 mmol), $PhSiH_3$ (179 mg, 1.65 mmol), and 1,2-epoxybutane (159 mg, 2.20 mmol) in dioxane (0.6 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **3x** (130 mg, 58%, *E*/*Z* = 91:9) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, CH_3), 6.59 (d, *J* = 15.6 Hz, 1 H, CH), 6.90–6.95 (m, 1 H, CH), 7.22–7.28 (m, 1 H, CH), 7.33–7.40 (m, 1 H, CH), 7.45–7.52 (m, 1 H, CH), 7.54–7.61 (m, 3 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.68 (CH_3), 111.10 (CH), 111.28 (CH), 118.31 (CH), 121.63 (CH), 123.20 (CH), 126.34 (CH), 128.20 (C), 131.33 (CH), 152.13 (C), 155.41 (C), 166.97 (C=O) ppm.

Methyl (*E*)-5,9-Dimethyldeca-2,8-dienoate (5a):[17a,17b] According to the GP, 3,7-dimethyloct-6-enal (**4a**; 159 mg, 1.03 mmol), methyl bromoacetate (**2a**; 189 mg, 1.24 mmol), Bu_3P=O (34 mg, 0.16 mmol, 15 mol-%), $PhSiH_3$ (167 mg, 1.55 mmol) and 1,2-epoxybutane (149 mg, 2.06 mmol) in dioxane (0.5 mL) were converted for 1 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5a** (124 mg, 57%, *E*/*Z* = 93:7) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.12–1.42 (m, 3 H, CH_2), 1.59–1.63 (m, 3 H, CH_3), 1.66–1.71 (m, 3 H, CH_3), 1.91–2.10 (m, 3 H, CH_2), 2.17–2.27 (m, 1 H, CH), 3.73 (s, 3 H, CH_3), 5.05–5.12 (m, 1 H), 5.82 (dt, *J* = 15.6, *J* = 1.5 Hz, 1 H, CH), 6.90–7.01 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.50 (CH), 19.34 (CH_3), 25.36 (CH_2), 25.57 (CH_3), 31.95 (CH_3), 36.54 (CH_2), 39.52 (CH_2), 51.20 (CH_3), 121.86 (CH), 124.27 (CH), 131.28 (C), 148.37 (CH), 166.86 (C=O) ppm.

Methyl (*E*)-Trideca-2,12-dienoate (5b):[49] According to the GP, 10-undecenal (**4b**; 282 mg, 1.67 mmol), methyl bromoacetate (**2a**; 307 mg, 2.01 mmol), Bu_3P=O (55 mg, 0.25 mmol), $PhSiH_3$ (272 mg, 2.51 mmol), and 1,2-epoxybutane (241 mg, 3.35 mmol) in dioxane (0.8 mL) were converted for 1 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5b** (312 mg, 83%, *E*/*Z* = 93:7) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.50 (m, 12 H, CH_2), 2.00–2.09 (m, 2 H, CH_2), 2.16–2.24 (m, 2 H, CH_2), 3.73 (s, 3 H, CH_3), 4.90–5.04 (m, 2 H, CH), 5.75–5.89 (m, 2 H, CH), 6.98 (dt, *J* = 15.6, *J* = 7.0 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.91 (CH_2), 28.80 (CH_2), 28.99 (CH_2), 29.01 (CH_2), 29.24 (CH_2), 29.26 (CH_2), 32.11 (CH_2), 33.69 (CH_2), 51.22 (CH_3), 114.05 (CH), 120.73 (CH), 139.00 (CH), 149.64 (CH), 167.03 (C=O) ppm.

Methyl (*E*)-6-(5,5-Dimethyl-1,3-dioxanyl)hex-2-enoate (5c): According to the GP, 4-(5,5-dimethyl-1,3-dioxanyl)butyraldehyde (**4c**; 397 mg, 2.13 mmol), methyl bromoacetate (**2a**; 392 mg, 2.56 mmol), Bu_3P=O (70 mg, 0.32 mmol, 15 mol-%), $PhSiH_3$ (346 mg, 3.20 mmol), and 1,2-epoxybutane (308 mg, 4.26 mmol) in dioxane (1.1 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5c** (310 mg, 60%, *E*/*Z* = 93:7) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.53–1.72 (m, 4 H, CH_2), 2.18–2.26 (m, 2 H, CH_2), 3.38–3.44 (m, 2 H, OCH_2), 3.56–3.61 (m, 2 H, OCH_2), 3.71 (s, 3 H, CH_3), 4.40–4.45 (m, 1 H, CH), 5.82 (dt, *J* = 15.6, *J* = 1.6 Hz, 1 H, CH), 6.96 (dt, *J* = 15.6, *J* = 6.9 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.62 (CH_3), 22.09 (CH_2), 22.76 (CH_3), 29.91 (C), 31.78 (CH_2), 33.97 (CH_2), 51.11 (CH_3), 76.95 (2 CH_2), 101.45 (CH), 120.96 (CH), 148.89 (CH), 166.77 (C=O) ppm. MS

(EI, 70 eV): *m*/*z* (%) = 242 (1) $[M]^+$, 141 (21), 125 (52), 115 (100), $[M - C_7H_{11}O_2]^+$, 81 (17), 69 (73), 56 (42). IR (ATR): $\tilde{\nu}$ = 2952 (m), 2846 (w), 1721 (vs), 1656 (m), 1436 (m), 1394 (w), 1312 (m), 1270 (s), 1195 (s), 1165 (s), 1132 (vs), 1110 (s), 1039 (m), 1017 (s), 980 (s), 940 (w), 923 (m), 855 (m), 817 (m), 784 (s), 719 (m), 665 (m) cm^{-1}. $C_{13}H_{22}O_4$ (242.31): calcd. C 64.44, H 9.15; found C 64.06, H 9.18.

Methyl (*E*)-5-Phenylpent-2-enoate (5d):[50] According to the GP, 3-phenylpropanal (**4d**; 191 mg, 1.42 mmol), methyl bromoacetate (**2a**; 261 mg, 1.70 mmol), $Bu_3P{=}O$ (31 mg, 0.14 mmol, 10 mol-%), $PhSiH_3$ (230 mg, 2.13 mmol), and 1,2-epoxybutane (205 mg, 2.84 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5d** (200 mg, 74%, *E*/*Z* = 91:9) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.50–2.59 (m, 2 H, CH_2), 2.76–2.82 (t, *J* = 7.7 Hz, 2 H, CH_2), 3.74 (s, 3 H, CH_3), 5.87 (dt, *J* = 15.7, *J* = 1.6 Hz, 1 H, CH), 7.03 (dt, *J* = 15.7, *J* = 6.8 Hz, 1 H, CH), 7.17–7.25 (m, 3 H, ArH), 7.27–7.34 (m, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.85 (CH_2), 34.29 (CH_2), 51.40 (CH_3), 121.41 (CH), 126.14 (CH), 128.29 (2 CH), 128.45 (2 CH), 140.70 (C), 148.33 (CH), 166.96 (C=O) ppm.

Methyl (*E*)-5-Phenylpentadienoate (5e):[51] According to the GP, 3-phenylpropenal (**5e**; 209 mg, 93% purity, 1.47 mmol), methyl bromoacetate (**2a**; 270 mg, 1.76 mmol), $Bu_3P{=}O$ (48 mg, 0.22 mmol, 15 mol-%), $PhSiH_3$ (239 mg, 2.21 mmol), and 1,2-epoxybutane (212 mg, 2.94 mmol) in dioxane (0.7 mL) were converted for 3 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5e** (143 mg, 52%, *E*/*Z* = 95:5) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, CH_3), 6.01 (d, *J* = 15.3 Hz, 1 H, CH), 6.88–6.91 (m, 2 H), 7.32–7.51 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.38 (CH_3), 120.65 (CH), 126.00 (CH), 127.06 (2 CH), 128.64 (2 CH), 128.91 (CH), 135.81 (C), 140.39 (CH), 144.67 (CH), 167.27 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 188 (21) $[M]^+$, 157 (17) $[M - OMe]^+$, 129 (100) $[M - CO_2Me]^+$. HRMS (EI): calcd. for $C_{12}H_{12}O_2$ $[M]^+$ 188.0832; found 188.0829.

Methyl (*E*)-5-(5-Methylfur-2-yl)hex-2-enoate (5f): According to the GP, 3-(5-methylfur-2-yl)butylaldehyde (**4f**; 224 mg, 1.47 mmol), methyl bromoacetate (**2a**; 270 mg, 1.76 mmol), $Bu_3P{=}O$ (48 mg, 0.22 mmol, 15 mol-%), $PhSiH_3$ (239 mg, 2.21 mmol), and 1,2-epoxybutane (212 mg, 2.94 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave **5f** (239 mg, 1.15 mmol, 78%, *E*/*Z* = 89:11) as a yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.25 (d, *J* = 7.0 Hz, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.33–2.44 (m, 1 H, CH_2), 2.55–2.65 (m, 1 H, CH_2), 2.89–3.00 (m, 1 H, CH), 3.73 (s, 3 H, CH_3), 5.83–5.88 (m, 3 H), 6.87–6.97 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.41 (CH_3), 18.51 (CH_3), 32.33 (CH), 38.22 (CH_2), 51.31 (CH_3), 104.62 (CH), 105.64 (CH), 122.41 (CH), 147.06 (CH), 150.36 (C), 156.95 (C), 166.78 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 208 (4) $[M]^+$, 109 (100) $[M - C_3H_4CO_2Me]^+$. IR (ATR): $\tilde{\nu}$ = 2951 (w), 1721 (vs), 1657 (m), 1613 (w), 1566 (w), 1436 (m), 1270 (m), 1216 (s), 1164 (vs), 1112 (m), 1019 (s), 957 (m), 940 (m), 780 (s), 720 (m) cm^{-1}. $C_{12}H_{16}O_3$ (208.26): calcd. C 69.21, H 7.74; found C 69.19, H 7.65.

Methyl (*E*)-4-Phenylbut-2-enoate (5g):[52] According to the GP, 3-phenylethanal (**4g**; 173 mg, 1.44 mmol), methyl bromoacetate (**2a**; 264 mg, 1.73 mmol), $Bu_3P{=}O$ (47 mg, 0.22 mmol, 15 mol-%), $PhSiH_3$ (234 mg, 2.16 mmol), and 1,2-epoxybutane (208 mg, 2.88 mmol) in dioxane (0.7 mL) were converted for 2 h. Purification (SiO_2, CH/EtOAc, 20:1) gave a mixture of **5g** (107 mg, 42%, *E*/*Z* = 94:6) and methyl 4-phenylbut-3-enoate (6 mg, 3%) as a yellowish oil. Data for **5g**: ^1H NMR (300 MHz, $CDCl_3$): δ = 3.54 (dd, *J* = 6.8, *J* = 1.5 Hz, 2 H, CH_2), 3.73 (s, 3 H, CH_3), 5.84 (dt, *J* = 15.6, *J* = 1.6 Hz, 1 H, CH), 7.08–7.36 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.33 (CH_2), 51.32 (CH_3), 121.81 (CH), 126.56 (CH), 128.57 (2 CH), 128.66 (2 CH), 137.51 (C), 147.48 (CH), 166.73 (C=O) ppm.

Methyl (*E*)-4-(4-Diphenyl)but-2-enoate (5h):[53] According to the GP, diphenylacetaldehyde (**4h**; 279 mg, 1.42 mmol), methyl bromoacetate (**2a**; 261 mg, 1.70 mmol), $Bu_3P{=}O$ (31 mg, 0.14 mmol), $PhSiH_3$ (230 mg, 2.13 mmol), and 1,2-epoxybutane (205 mg, 2.84 mmol) in dioxane (0.71 mL) were converted for 1 h. Purification (SiO_2, CH/EtOAc, 20:1) gave a colorless oil, a mixture of product **5h** (245 mg, 68%, *E*/*Z* = 97:3) and isomerised product methyl 4-(4-diphenyl)but-3-enoate (63 mg, 11%). Data for **5h**: ^1H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3 H, CH_3), 4.90 (d, *J* = 7.3 Hz, 1 H, CH), 5.76 (dd, *J* = 15.6, *J* = 1.5 Hz, 1 H, CH), 7.16–7.36 (m, 10 H, CH), 7.42–7.52 (m, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 51.44 (CH_3), 53.30 (CH), 122.42 (CH), 126.82 (2 CH), 128.48 (4 CH), 128.58 (4 CH), 141.36 (2 C), 150.06 (CH), 166.72 (C=O) ppm.

(*R*)-5-Methylbicyclo[3.3.0]oct-1-ene-3,6-dione (9):[23e] Ketone **8** (241 mg, 0.98 mmol), $PhSiH_3$ (159 mg, 1.47 mmol), 1,2-butylene oxide (141 mg, 1.96 mmol), and (*R*,*R*)-Me-BPE (**13**; 12.6 mg, 0.049 mmol, 5 mol-%) in 1,4-dioxane (0.5 mL) were converted for 20 h according to the GP to give alkene *R*-**9** (93 mg, 0.619 mmol, 63%, 32% *ee*) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 2.28–2.64 (m, 3 H, CH_2), 2.91–3.20 (m, 3 H, CH_2), 5.97 (s, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.19 (CH_3), 24.39 (CH_2), 38.25 (CH_2), 44.66 (CH_2), 56.74 (C), 126.12 (CH), 184.71 (C), 207.58 (C=O), 212.47 (C=O) ppm.

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