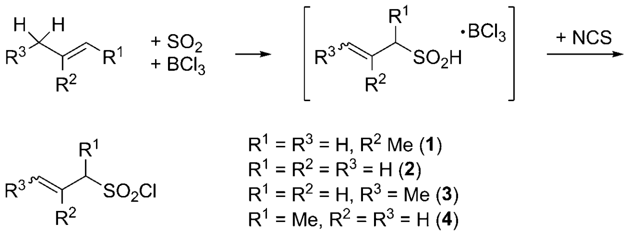
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201000705

The Catalyzed Desulfinylative Allylation of Carbonyl Compounds with Alk-2-enesulfonyl Chlorides and Silyl Alk-2-enesulfinates

Chandra M. R. Volla, Dean Marković, Sylvain Laclef, and Pierre Vogel*[a]

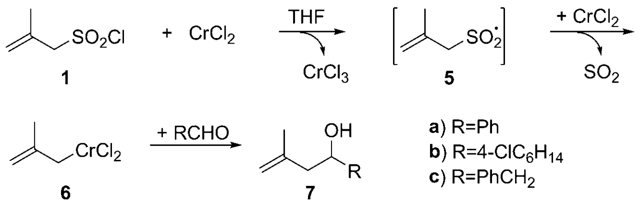
Carbon–carbon cross-coupling reactions are very important in the areas of material science and medicinal chemistry.[1] Transition-metal-catalyzed cross-coupling of organometallic reagents (nucleophiles) with halides or triflates (electrophiles) constitutes one of the most powerful methods for constructing C–C bonds.[2] Arene- and alkanesulfonyl chlorides are inexpensive and readily available compounds. We have shown that Stille, carbonylative Stille,[3] Suzuki–Miyaura,[4] Sonogashira–Hagihara,[5] Mizoroki–Heck,[6] and Negishi[7]-type cross-couplings can all be carried out by using sulfonyl chlorides as the electrophilic partners under desulfinylative conditions.[8] We have also shown that 2-methylprop-2-ene- (**1**), prop-2-ene- (**3**), and (*E*)-but-2-enesulfonyl chlorides (**4**) are useful electrophilic partners in desulfinylative palladium-catalyzed C–C coupling reactions with inexpensive Grignard reagents and sodium salts of malonic esters and methyl acetoacetate.[9] As these sulfonyl chlorides can be prepared in one-pot operations (Scheme 1) through a BCl_3-promoted ene reaction of the corresponding monoalkenes with sulfur dioxide,[10] substrates **1**–**4** have become powerful electrophilic allylating agents (without BCl_3, the ene reaction of simple monoalkenes with SO_2 is endergonic above −100 °C).[11] We have recently reported that iron catalysts can be used in the desulfinylative C–C cross-coupling reaction of Grignard reagents with alkane-, alkene-, and arenesulfonyl chlorides[12] and with alk-3-enesulfonyl chlorides.[13]



Scheme 1. The one-pot synthesis of alk-2-enesulfonyl chlorides.[10]

In 1977, Nozaki and co-workers[14] reported the chemoselective allylation of aldehydes with allyl halides mediated by $CrCl_2$. The reaction was then extended to the alkenylation[15] and alkynylation[16] of carbonyl compounds. Alkenyl triflates can also be used in this type of reaction under nickel catalysis.[17] The reaction requires two equivalents of $CrCl_2$ to reduce the allyl halides into allylchromium complexes[18] that then add to the carbonyl compounds, like other allyl–metal species, through a Zimmermann–Traxler-like transition state.[19] Alternative mechanisms implying radical intermediates[20] and oxidation/reduction equilibria (Oppenauer–Meerwein–Ponndorf–Verley-type mechanism) have been proposed.[21] These alternative mechanisms suggested to us that $CrCl_2$ might induce desulfinylation of alk-2-enesulfonyl chlorides generating allylchromium(III) intermediates that could be used as nucleophilic partners in carbonyl-compound allylation, thus creating umpolung[22] reactivity by converting allyl–SO_2Cl compounds (C-electrophile) into allyl–metal compounds (C-nucleophile; Scheme 2).

When we reacted 2-methylprop-2-enesulfonyl chloride (**1**) in THF at room temperature with a) benzaldehyde, b) *para*-



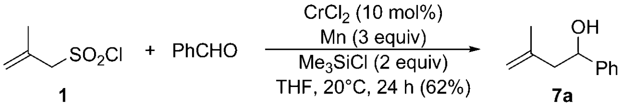
Scheme 2. The $CrCl_2$-mediated conversion of electrophilic sulfonyl chlorides into nucleophilic allylating agents.

---

[a] Dr. C. M. R. Volla, Dr. D. Marković, S. Laclef, Prof. P. Vogel
Laboratoire de glycochimie et de synthèse asymétrique (LGSA)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Batochime, CH 1015 Lausanne (Switzerland)
Fax: (+41) 21-693-93-75
E-mail: pierre.vogel@epfl.ch

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000705.

chlorobenzaldehyde, and c) phenylacetaldehyde in the presence of two equivalents of $CrCl_2$, the corresponding homoallylic alcohols **7a–c** were formed as the sole products of the reaction and isolated in 70, 63, and 55 % yields, respectively (Scheme 3). As with other Nozaki–Hiyama-type reactions, the stoichiometric $CrCl_2$ can be replaced by Mn (metal) and Me_3SiCl, allowing the use of $CrCl_2$ as a catalyst.[23] Indeed we found that **1** reacted with benzaldehyde in the presence of Mn (3 equiv) and Me_3SiCl (2 equiv) in THF at room temperature to afford **7a** in 62 % yield.



Scheme 3. $CrCl_2$-catalyzed reductive allylation of benzaldehyde with 2-methylprop-2-enesulfonyl chloride.

We then explored whether the toxic $CrCl_2$ could be removed completely. Since we have previously observed that alk-2-enesulfonyl chlorides undergo fast desulfinylation in the presence of palladium complexes,[9] generating electrophilic allylpalladium intermediates, we searched for reducing agents capable of converting these into C-nucleophiles (allylation by umpolung[24]). Our results are summarized in Table 1 for the reaction of **1** with benzaldehyde to give **7a**.

With metallic indium[25] (Table 1, entry 1) and $[Pd(Ph_3P)_4]$ as the catalyst, **7a** was not found in the crude reaction mixture after 24 h at 25 °C.[26] In hexane/toluene (4:1) with Et_2Zn and using either $[Pd(Ph_3P)_4]$ or $Pd(OAc)_2/nBu_3P$ (Table 1, entries 2 and 4, respectively) as the catalyst system the reaction led to the formation of homoallyl alcohol **7a** in good yields. If hexane alone was used as the solvent (Table 1, entry 5), the reaction was slower, whilst without a phosphane ligand in the reaction (Table 1, entries 3 and 7) the yield dropped. Interestingly, if $[PdCl_2(PhCN)_2]$ was used as the catalyst, $SnCl_2$ was a suitable reductant for this allylation by umpolung reaction (Table 1, entry 8).[27] As expected, if Et_2Zn or $SnCl_2$ were replaced by $ZnCl_2$, no allylation was observed (Table 1, entry 6).

Table 1. Palladium-catalyzed reductive and desulfinylative allylation of benzaldehyde with 2-methylprop-2-enesulfonyl chloride **1** at 25 °C.[a]

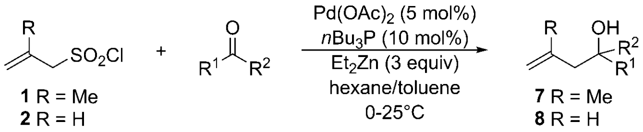
	Catalyst (5 mol %)/ ligand (10 mol %)	Reductant (3 equiv)	Solvent	t	Yield [%][b]
1	$[Pd(Ph_3P)_4]$	In	THF	24 h	–
2	$[Pd(Ph_3P)_4]$	Et_2Zn	hexane/toluene[c]	25 min	62
3	$[Pd_2(dba)_3]$[d]	Et_2Zn	hexane/toluene[c]	25 min	traces
4	$Pd(OAc)_2/(nBu_3P)$	Et_2Zn	hexane/toluene[c]	15 min	85
5	$Pd(OAc)_2/(nBu_3P)$	Et_2Zn	hexane	30 min	47
6	$Pd(OAc)_2/(nBu_3P)$	$ZnCl_2$	hexane/toluene[c]	24 h	–
7	$[PdCl_2(PhCN)_2]$	Et_2Zn	hexane/toluene[c]	30 min	15[e]
8	$[PdCl_2(PhCN)_2]$	$SnCl_2$	THF	24 h	65

[a] Conditions: **1** (1 mmol) and PhCHO (1.2 mmol) in solvent (5 mL). [b] Yield after purification by column chromatography on silica gel. [c] 4:1 hexane/toluene. [d] dba = dibenzylideneacetone. [e] Yield by ^1H NMR spectroscopy of the crude product.

We then applied the conditions with the best yield for the reaction (Table 1, entry 4) to various carbonyl compounds using both 2-methylprop-2-enesulfonyl chloride (**1**) and prop-2-enesulfonyl chloride (**2**). Our results are summarized in Table 2 and show the versatility of the method as a wide range of aliphatic and aromatic aldehydes and ketones can be allylated in good yields.

By using a mixture of (*E*)- and (*Z*)-but-2-enesulfonyl chloride (**3**; 3:1), we studied the regio- and diastereoselectivity of the allylation of benzaldehyde (Table 3). Under our standard conditions (Table 1, entry 4: $Pd(OAc)_2/nBu_3P$ in hexane/toluene), a 1:1:2 mixture of the three possible homo-

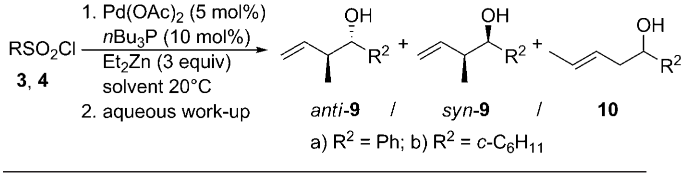
Table 2. Pd-catalyzed reductive and desulfinylative allylations of carbonyl compounds with **1** and **2**.[a]



	RSO_2Cl	Carbonyl compound	Yield [%][b]	Product	R^1	R^2
1	**1**	$4\text{-}ClC_6H_4CHO$	76	**7b**	H	$4\text{-}ClC_6H_4$
2	**1**	$4\text{-}EtC_6H_4CHO$	77	**7e**	H	$4\text{-}EtC_6H_4$
3	**1**	$4\text{-}MeOC_6H_4CHO$	68	**7d**	H	$4\text{-}MeOC_6H_4$
4	**1**	$PhCH_2CHO$	59	**7c**	H	$PhCH_2$
5	**1**	$n\text{-}C_{10}H_{21}CHO$	65	**7f**	H	$n\text{-}C_{10}H_{21}$
6	**1**	$c\text{-}C_6H_{11}CHO$	72	**7g**	H	$c\text{-}C_6H_{11}$
7	**1**	PhCOMe	65	**7h**	Me	Ph
8	**1**	PhCOPh	67	**7i**	Ph	Ph
9	**1**	cyclohexanone	63	**7j**	$-(CH_2)_5-$	
10	**2**	$4\text{-}PhC_6H_4CHO$	81	**8a**	H	$4\text{-}PhC_6H_4$
11	**2**	$4\text{-}PhOC_6H_4CHO$	75	**8b**	H	$4\text{-}PhOC_6H_4$
12	**2**	$PhCH_2CHO$	69	**8c**	H	$PhCH_2$
13	**2**	$4\text{-}FC_6H_4COPh$	72	**8d**	Ph	$4\text{-}FC_6H_4$
14	**2**	PhCOOMe	–	–	–	–

[a] Conditions: **1** (1 mmol) and the carbonyl compound (1.2 mmol) in hexane/toluene (4:1; 5 mL). [b] Isolated yield after flash column chromatography on silica gel.

Table 3. Regio- (**9** vs. **10**) and diastereoselectivity (*syn*-**9** vs. *anti*-**9**) of the reductive and desulfinylative Pd-catalyzed allylation of aldehydes with but-2-enesulfonyl (**3**) and 1-methylprop-2-enesulfonyl chloride (**4**).

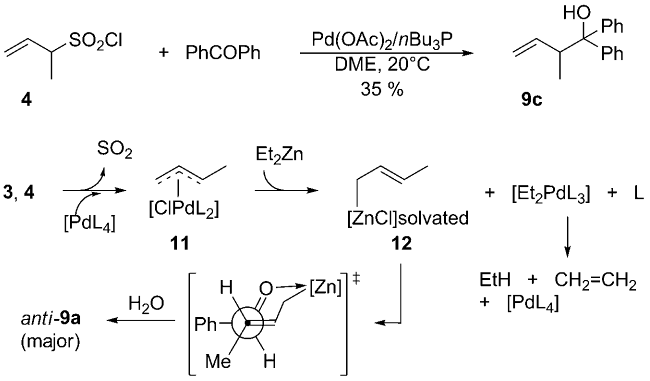


	RSO_2Cl	Aldehyde	Solvent	Yield [%][a]	Product ratio[b]	R^2
1	**3** or **4**	PhCHO	hexane/toluene	75	1:1:2	Ph
2	**3**	PhCHO	toluene	44	1:1:2	Ph
3	**3**	PhCHO	THF	69	2:1:0	Ph
4	**3** or **4**	PhCHO	DME	73	2.5:1:0	Ph
5	**3** or **4**	$c\text{-}C_6H_{11}CHO$	DME	68	2.3:1:0	$c\text{-}C_6H_{11}$

[a] Yield of the product mixture by flash column chromatography on silica gel. [b] The *anti*-**9**/*syn*-**9**/**10** product ratio was determined by ^1H NMR spectroscopy of the crude reaction mixture.

allylic alcohols *anti*-**9a**, *syn*-**9a**, and **10a** was obtained in a 75% combined yield (Table 3, entry 1).

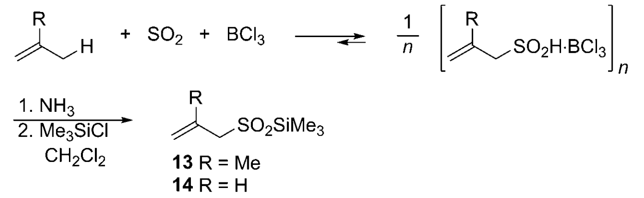
The same yield and product ratio were obtained if **4** was used instead of **3**, which supports the possible mechanism shown in Scheme 4 by implying the formation of the same but-2-en-1-yl–palladium intermediate **11** starting from either **3** or **4**. Transmetallation generates butenylzinc intermediate **12**, which allylates the carbonyl compounds. Interestingly, whereas the formation of homoallylic alcohol **10** competed with the generation of products **9** in non-polar solvents (Table 3, entries 1 and 2), product **10** was not visible if more polar solvents such as THF (Table 3, entry 3) or DME (Table 3, entries 4 and 5) were used. If [Pd(Ph$_3$P)$_4$] was used as the catalyst instead of Pd(OAc)$_2$/*n*Bu$_3$P, the product ratio was 1:1:1 (*syn*-**9**/*anti*-**9**/**10**). The reaction of 1-methylprop-2-enesulfonyl chloride **4** with benzophenone formed the corresponding homoallylic alcohol **9c** in 35% yield (Scheme 4).



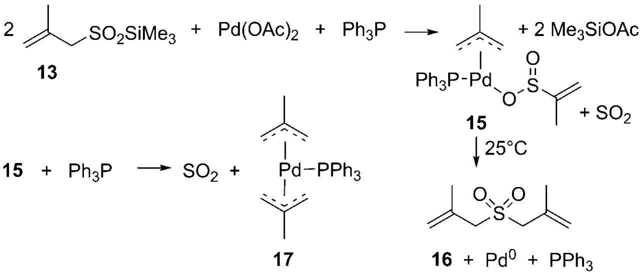
Scheme 4. A possible mechanism for the reductive (Et$_2$Zn) and desulfinylative allylation of benzaldehyde with alk-2-enesulfonyl chlorides; DME = dimethoxyethane.

β,γ-Unsaturated silyl sulfinyl esters can be obtained readily by an ene reaction of allylsilanes with SO$_2$[28] and as intermediates in the cocondensation of SO$_2$ with electron-rich 1,3-dienes and alkenes.[29,30] As these compounds can also be obtained by the H-ene reaction of alkenes with SO$_2$/BCl$_3$, followed by neutralization with NH$_3$ and reaction with silyl chlorides[10] (Scheme 5), we wondered whether these systems could be employed as nucleophilic allylating agents.

Preliminary studies within our group[31] have shown that silyl sulfinate **13** reacts with Pd(OAc)$_2$/Ph$_3$P to give allylpalladium complex **15** and Me$_3$SiOAc (Scheme 6). Complex **15** was then converted, at 25 °C, into sulfone **16**. On adding a further 0.5 equivalents of Ph$_3$P, **15** was converted into **17** and SO$_2$. These experiments suggested that silyl sulfinate **13** reacts with palladium, generating allylpalladium intermediates that could be used as nucleophilic allylating reagents.



Scheme 5. The preparation of β,γ-unsaturated silyl sulfinates through an H-ene reaction of SO$_2$·BCl$_3$.

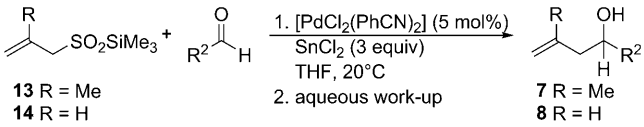


Scheme 6. Known reactions of Pd(OAc)$_2$/PPh$_3$ with β,γ-unsaturated silyl sulfinates.

If **13** or **14** were reacted with benzaldehyde and catalytic amounts of Pd(OAc)$_2$/*n*Bu$_3$P, the corresponding homoallylic alcohols **7a** (3-methyl-1-phenylbut-3-enol) and **8e** (1-phenylbut-3-enol) were formed in low yields (<10%). This failure suggests that a stronger Lewis acid must be added to enhance the electrophilicity of the aldehyde. After several unsuccessful attempts, we found that the use of [PdCl$_2$(PhCN)$_2$] as the precatalyst (5 mol%), in the presence of SnCl$_2$, in THF permitted the nucleophilic allylation of PhCHO with both sulfinates **13** and **14**, giving **7a** and **8e** in 75 and 71% yields, respectively (Table 4, entries 1 and 2). The reaction was extended to 4-chlorobenzaldehyde (Table 4, entry 3) and aliphatic aldehydes such as undecanal (Table 4, entry 4) and phenylacetaldehyde (Table 4, entry 5). Further work will have to be carried out to find a promoter that does not have to be used in excess, as was required here (3 equivalents of SnCl$_2$).

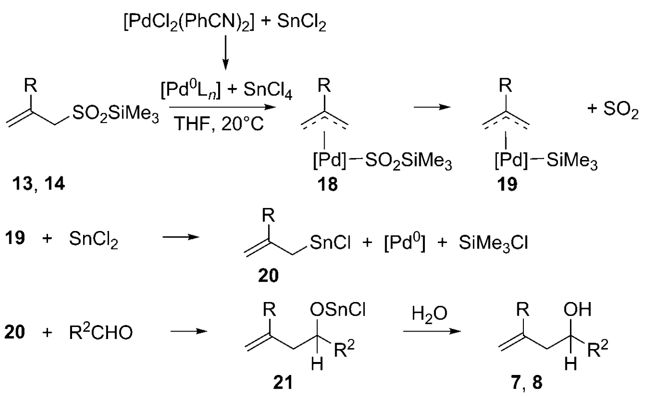
A possible mechanism for the allylation of aldehydes with silyl alk-2-enesulfinates is proposed in Scheme 7. After re-

Table 4. Pd-catalyzed desulfinylative allylation of aldehydes with trimethylsilyl 2-methylprop-2-enesulfinate (**13**) and trimethylsilyl prop-2-enesulfinate (**14**).



	Sulfinate	Aldehyde	Yield [%][a]	Product	R^2
1	**13**	PhCHO	75	**7a**	Ph
2	**14**	PhCHO	71	**8e**	Ph
3	**13**	4-ClC$_6$H$_4$CHO	67	**7b**	4-ClC$_6$H$_4$
4	**13**	*n*-C$_{10}$H$_{21}$CHO	72	**7f**	*n*-C$_{10}$H$_{21}$
5	**14**	PhCH$_2$CHO	58	**8f**	PhCH$_2$

[a] Yield of isolated product after flash column chromatography on silica gel.



Scheme 7. Possible mechanism for the Pd-catalyzed allylation of aldehydes with silyl alk-2-enesulfinates in the presence of SnCl$_2$.

duction of the Pd^{II} precatalyst into a Pd^0 catalyst, coordination of **13** or **14** by the latter and subsequent oxidative addition into the C−S bond generates allylpalladium intermediates of type **18**. Desulfinylation produces compound **19**, which undergoes Pd/Sn exchange to form allyltin intermediate **20**. This intermediate undergoes additions to aldehydes giving homoallyl alcoholates **21** that are hydrolyzed by aqueous work-up into products **7** or **8**.

Alk-2-enesulfonyl chlorides can be obtained easily by the H-ene reaction of monoalkenes with SO$_2$. We have demonstrated for the first time that these sulfonyl chlorides are suitable reagents for the palladium-catalyzed reductive and desulfinylative allylation of aldehydes and ketones. Alternatively, the allylations can occur by applying the Nozaki–Hiyama conditions, including those in which CrCl$_2$ is used as a catalyst in the presence of metallic Mn and trimethylsilyl chloride. Preliminary results demonstrate that silyl alk-2-enesulfinates can also be used as reagents in the desulfinylative allylation of aldehydes. Further work is underway to explore the scope of these new reactions.

Acknowledgements

We are grateful to the Swiss National Science Foundation (Grants 200020 124724 and 200021 119954) and the Roche Research Foundation (Basel) for generous financial support. We thank Dr. S. R. Dubbaka for useful discussions. We also thank Dr. L. Menin, F. Sepúlveda, and M. Rey for their technical help.

Keywords: allylation · ene reaction · palladium · sulfonyl chlorides · umpolung

[1] a) R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, New York, **1985**, p. 461; b) J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, New York, **1995**; c) *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1988**; d) *Transition Metals for Organic Synthesis*, 2nd ed. (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**; e) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; f) P. Knochel, I. Sapountzis, N. Gommermann in *Metal-Catalyzed Cross-Coupling* (Eds.: A. de Meijere, F. Dietrich), Wiley-VCH, Weinheim, **2004**, pp. 671–698.

[2] a) *Handbook of Functionalized Organometallics* (Ed.: P. Knochel), Wiley-VCH, Weinheim, **2005**; b) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; c) J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359–1469; d) R. Chinchilla, C. Najera, *Chem. Rev.* **2007**, *107*, 874–922; e) K. Tamao, T. Hiyama, E. Negishi, *J. Organomet. Chem.* **2002**, *653*, 1–4; f) T. Banno, Y. Hayakawa, M. Umeno, *J. Organomet. Chem.* **2002**, *653*, 288–291; g) O. Vechorkin, X. Hu, *Angew. Chem.* **2009**, *121*, 2981–2984; *Angew. Chem. Int. Ed.* **2009**, *48*, 2937–2940, and references therein.

[3] a) S. R. Dubbaka, P. Vogel, *J. Am. Chem. Soc.* **2003**, *125*, 15292–15293; b) S. R. Dubbaka, P. Steunenberg, P. Vogel, *Synlett* **2004**, 1235–1238.

[4] S. R. Dubbaka, P. Vogel, *Org. Lett.* **2004**, *6*, 95–98.

[5] S. R. Dubbaka, P. Vogel, *Adv. Synth. Catal.* **2004**, *346*, 1793–1797.

[6] a) S. R. Dubbaka, P. Vogel, *Chem. Eur. J.* **2005**, *11*, 2633–2641; b) S. R. Dubbaka, D. B. Zhao, Z. F. Fei, C. M. R. Volla, P. J. Dyson, P. Vogel, *Synlett* **2006**, 3155–3157.

[7] S. R. Dubbaka, P. Vogel, *Tetrahedron Lett.* **2006**, *47*, 3345–3348.

[8] S. R. Dubbaka, P. Vogel, *Angew. Chem.* **2005**, *117*, 7848–7859; *Angew. Chem. Int. Ed.* **2005**, *44*, 7674–7684.

[9] C. M. Rao Volla, S. R. Dubbaka, P. Vogel, *Tetrahedron* **2009**, *65*, 504–511.

[10] D. Marković, C. M. R. Volla, A. Alvarez, J. A. Sordo, P. Vogel, *Chem. Eur. J.* **2010**, *16*, 5969–5975.

[11] A. Alvarez, D. Marković, P. Vogel, J. A. Sordo, *J. Am. Chem. Soc.* **2009**, *131*, 9547–9561.

[12] C. M. Rao Volla, P. Vogel, *Angew. Chem.* **2008**, *120*, 1325–1327; *Angew. Chem. Int. Ed.* **2008**, *47*, 1305–1307.

[13] C. M. R. Volla, D. D. Marković, S. R. Dubbaka, P. Vogel, *Eur. J. Org. Chem.* **2009**, 6281–6288.

[14] Y. Okude, S. Hirano, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1977**, *99*, 3179–3181.

[15] K. Takai, K. Kimura, T. Kuroda, T. Hiyama, H. Nozaki, *Tetrahedron Lett.* **1983**, *24*, 5281–5284.

[16] K. Takai, T. Kuroda, S. Nakatsukasa, K. Oshima, H. Nozaki, *Tetrahedron Lett.* **1985**, *26*, 5585–5588.

[17] a) K. Takai, M. Tagashira, T. Kuroda, K. Oshima, K. Utimoto, H. Nozaki, *J. Am. Chem. Soc.* **1986**, *108*, 6048–6050; b) H. Jin, J. Uenishi, W. J. Christ, Y. Kishi, *J. Am. Chem. Soc.* **1986**, *108*, 5644–5646; c) A. Fürstner, *Chem. Rev.* **1999**, *99*, 991–1045.

[18] a) C. Chen, K. Tagami, Y. Kishi, *J. Org. Chem.* **1995**, *60*, 5386–5387; b) M. Bandini, P. G. Cozzi, A. Umani-Ronchi, *Angew. Chem.* **2000**, *112*, 2417–2420; *Angew. Chem. Int. Ed.* **2000**, *39*, 2327–2330; c) M. Bandini, P. G. Cozzi, P. Melchiorre, A. Umani-Ronchi, *Angew. Chem.* **1999**, *111*, 3558–3561; *Angew. Chem. Int. Ed.* **1999**, *38*, 3357–3359; d) A. I. Berkessel, D. Menche, C. A. Sklorz, M. Schroder, I. Paterson, *Angew. Chem.* **2003**, *115*, 1062–1065; *Angew. Chem. Int. Ed.* **2003**, *42*, 1032–1035; e) M. Giammaruco, M. Taddei, P. Ulivi, *Tetrahedron Lett.* **1993**, *34*, 3635–3638.

[19] C. T. Buse, C. H. Heathcock, *Tetrahedron Lett.* **1978**, *19*, 1685–1688.

[20] J. Mulzer, A. R. Strecker, L. Kattner, *Tetrahedron Lett.* **2004**, *45*, 8867–8870.

[21] a) H. S. Schrekker, K. Micskei, C. Hajdu, T. Patonay, M. W. G. De Bolster, L. A. Wessjohann, *Adv. Synth. Catal.* **2004**, *346*, 731–736; b) H. S. Schrekker, M. W. G. De Bolster, W. G. Martin, R. V. A. Orru, L. A. Wessjohann, *J. Org. Chem.* **2002**, *67*, 1975–1981.

[22] a) D. Seebach, *Angew. Chem.* **1969**, *81*, 690–700; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 639–649; b) D. Seebach, *Angew. Chem.* **1979**, *91*, 259–278; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 239–258.

[23] a) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 2533–2534; b) A. Fürstner, N. Shi, *J. Am. Chem. Soc.* **1996**, *118*, 12349–12357.

[24] a) B. M. Trost, J. W. Herndon, *J. Am. Chem. Soc.* **1984**, *106*, 6835–6837; with SmI$_2$ as the reductant: b) T. Tabuchi, J. Inanaga, M. Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 1195–1196; c) J. Inanaga, M.

Yamaguchi, *Tetrahedron Lett.* **1986**, *27*, 1195–1196; d) with $SnCl_2$ as the reductant: Y. Masuyama, R. Hayashi, K. Otake, Y. Kurusa, *Chem. Commun.* **1988**, 44–45; e) Y. Masuyama, J. P. Takahara, Y. Kurusu, *J. Am. Chem. Soc.* **1988**, *110*, 4473–4474; f) Y. Masuyama, J. P. Takahara, Y. Kurusu, *J. Am. Chem. Soc.* **1988**, *110*, 4473–4474; g) B. M. Trost, G. B. Tometzki, *J. Org. Chem.* **1988**, *53*, 915–917; h) Y. Masuyama, Y. Nimura, Y. Kurusu, *Tetrahedron Lett.* **1991**, *32*, 225–228; i) T. Ahiko, T. Ishiyama, N. Miyaura, *Chem. Lett.* **1997**, 811–812; j) D. Franco, D. Panyella, M. Rocamora, M. Gomez, J. C. Clinet, G. Müller, E. Dunach, *Tetrahedron Lett.* **1999**, *40*, 5685–5688; k) K. Masanari, I. Kiyama, T. Tomizawa, Y. Horino, S. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **1999**, *40*, 6795–6798; l) S. Araki, S. Kambe, K. Kameda, T. Hirashita, *Synthesis* **2003**, 751–754; m) M. Kimura, M. Shimizu, K. Shibata, M. Tazoe, Y. Tamaru, *Angew. Chem.* **2003**, *115*, 3514–3517; *Angew. Chem. Int. Ed.* **2003**, *42*, 3392–3395; n) G. Zanoni, S. Gladiali, A. Marchetti, P. Piccini, I. Tredici, G. Vidari, *Angew. Chem.* **2004**, *116*, 864–867; *Angew. Chem. Int. Ed.* **2004**, *43*, 846–849; o) O. A. Wallner, K. J. Szabó, *Org. Lett.* **2004**, *6*, 1829–1831; p) S.-F. Zhu, Y. Yang, L.-X. Wang, B. Liu, Q.-L. Zhou, *Org. Lett.* **2005**, *7*, 2333–2335; q) G. P. Howell, A. J. Minnaard, B. L. Feringa, *Org. Biomol. Chem.* **2006**, *4*, 1278–1283; r) G. Zanoni, A. Pontiroli, A. Marchetti, G. Vidari, *Eur. J. Org. Chem.* **2007**, 3599–3611; s) M. Gagliardo, N. Selander, N. C. Mehendale, G. van Koten, R. J. M. Klein Gebbink, K. J. Szabó, *Chem. Eur. J.* **2008**, *14*, 4800–4809; t) R. E. Grote, E. R. Jarvo, *Org. Lett.* **2009**, *11*, 485–488.

[25] a) S. Araki, K. Kameda, J. Tanaka, T. Hirashita, H. Yamamura, M. Kawai, *J. Org. Chem.* **2001**, *66*, 7919–7921; b) L. W. Chung, T. H. Chan, *Organometallics* **2005**, *24*, 1598–1607.

[26] S. R. Dubbaka, Ph.D. Thesis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, **2005**.

[27] a) Y. Masuyama, N. Kinugawa, Y. Kurusu, *J. Org. Chem.* **1987**, *52*, 3702–3704; b) T. Tabuchi, J. Inamaga, M. Yamaguchi, *Tetrahedron Lett.* **1987**, *28*, 215–216; c) B. M. Trost, R. Walchli, *J. Am. Chem. Soc.* **1987**, *109*, 3487–3488; d) K. Kasui, Y. Goto, T. Yajima, Y. Taniseki, K. Fugami, A. Tanaka, Y. Tamaru, *Tetrahedron Lett.* **1993**, *34*, 7919–7922.

[28] L. Bouchez, P. Vogel, *Synthesis* **2002**, 225–231.

[29] X. Huang, P. Vogel, *Synthesis* **2002**, 232–236.

[30] a) P. Vogel, M. Turks, L. Bouchez, D. Marković, A. Varela-Alvarez, J. A. Sordo, *Acc. Chem. Res.* **2007**, *40*, 931–942; b) P. Vogel, M. Turks, L. Bouchez, C. Craita, X. Huang, M. C. Murcia, F. Fonquerne, C. Didier, C. Flowers, *Pure Appl. Chem.* **2008**, *80*, 791–805; c) M. Turks, C. J. Exner, C. Hamel, P. Vogel, *Synthesis* **2009**, 1065–1074.

[31] X. Huang, C. Craita, P. Vogel, *J. Org. Chem.* **2004**, *69*, 4272–4275.

Received: March 19, 2010