Nickel-Catalyzed Preparations of Functionalized Organozincs

Stephan Vettel, Andrea Vaupel, and Paul Knochel*

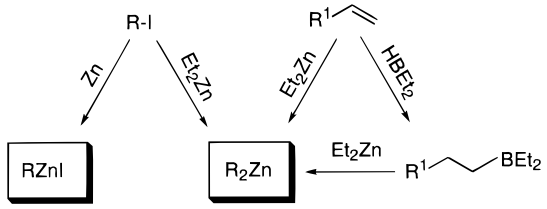
Fachbereich Chemie der Philipps-Universität Marburg, D-35032 Marburg, Germany

Received May 3, 1996[⊗]

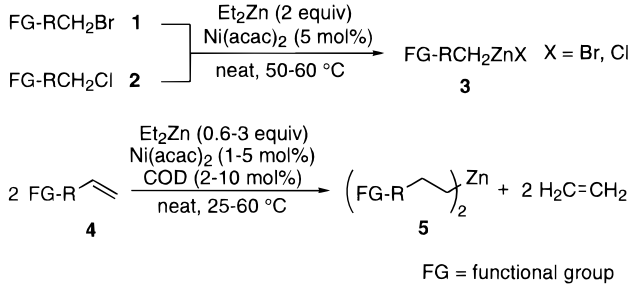
The reaction of primary alkyl bromides or chlorides with diethylzinc in the presence of $Ni(acac)_2$ (5 mol %) furnishes the corresponding alkylzinc halides (X = Br, Cl) via a halogen-zinc exchange reaction. The treatment of terminal alkenes with diethylzinc (neat, 25−60 °C) in the presence of $Ni(acac)_2$ as a catalyst (1−5 mol %) and 1,5-cyclooctadiene (COD) affords the corresponding dialkylzincs via a hydrozincation reaction. Whereas the conversion for simple alkenes bearing a remote functionality reaches 40 to 63%, the hydrozincation of allylic, homoallylic alcohols and allylic amines proceeds very efficiently (85−95% conversion). All the zinc organometallics obtained react with various electrophiles (allylic halides, enones, acid chlorides, alkynyl halides, ethyl propiolate) after transmetalation with CuCN·2LiCl. In the presence of the chiral catalyst **12**, the dialkylzincs prepared add to aldehydes with high enantioselectivity.

Organozincs are an important class of organometallics for organic synthesis[1] and organometallic synthesis.[2] Diorganozincs have also found extensive applications in asymmetric synthesis,[3] since they add to aldehydes in the presence of a chiral catalyst with high enantioselectivity.[3,4] They can be prepared by transmetalation from organomagnesium[4k] or zirconocene reagents,[5] by an iodine−zinc exchange,[4a] or by a boron−zinc exchange.[6] This last method is the most general and most versatile (Scheme 1). Recently, we have shown that the presence of transition metal salts strongly accelerates the iodine-zinc exchange and modifies even the nature of organometallic produced.[7−10]

Scheme 1



Scheme 2



Thus, the copper(I)-catalyzed iodine−zinc exchange reaction provides diorganozincs,[7] whereas a palladium(II)-[8] or manganese(II)[9]-catalyzed iodine− or bromine−zinc exchange leads to organozinc halides. Also, nickel(II) has proven to be an excellent catalyst for the iodine− and bromine−zinc exchange.[10] Herein we show that this high catalytic activity allows the conversion of primary alkyl bromides of type **1** and primary alkyl chlorides of type **2** to the corresponding alkylzinc halides **3**. The nickel catalysis also allows a formal hydrozincation of terminal alkenes **4**, providing in this case dialkylzincs **5** (Scheme 2).[11] Herein, we describe the scope and limitations of these new preparations of functionalized zinc organometallics as well as some applications in asymmetric synthesis.

Our first observations have shown that primary alkyl bromides and chlorides ($FG-RCH_2CH_2X$) react with Et_2Zn in the presence of $Ni(acac)_2$ (5 mol %) without solvent furnishing the corresponding alkylzinc halides in ca. 70−80% yield. The reaction is accompanied by ca. 10% of the protonated product $FG-RCH_2CH_3$ and ca. 10% of the elimination product $FG-RCH{=}CH_2$. Variation of the nature of the nickel catalyst shows that a range of nickel-

* To whom correspondence should be addressed. E-mail: Knochel@ps1515.chemie.uni-marburg.de.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) (a) Knochel, P.; Singer, R. *Chem. Rev.* **1993**, 2117. (b) Knochel, P. *Synlett* **1995**, 393.

(2) (a) Stadtmüller, H.; Knochel, P. *Organometallics* **1995**, *14*, 3163. (b) Dötz, K. H.; Christoffers, C.; Knochel, P. *J. Organomet. Chem.* **1995**, *489*, C84. (c) Schwink, L.; Vettel, S.; Knochel, P. *Organometallics* **1995**, *14*, 5000.

(3) (a) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833. (b) Noyori, T.; Kitamura, M. *Angew. Chem* **1991**, *103*, 34; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49. (c) Knochel, P.; Vettel, S.; Eisenberg, C. *Appl. Organomet. Chem.* **1995**, *9*, 175.

(4) (a) Rozema, M. J.; AchyuthaRao, S.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956. (b) Brieden, W.; Ostwald, R.; Knochel, P. *Angew. Chem* **1993,** *105*, 629; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 582. (c) Knochel, P.; Brieden,W.; Eisenberg, C.; Rozema, M. J. *Tetrahedron Lett.* **1993**, *34*, 5881. (d) Nowotny, S.; Vettel, S.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 4539. (e) Eisenberg, C.; Knochel, P. *J. Org. Chem.* **1994**, *59*, 3760. (f) Vettel, S.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 5849. (g) Ostwald, R.; Chavant, P.-Y.; Stadtmüller, H.; Knochel, P. *J. Org. Chem.* **1994**, *59*, 4143. (h) Schwink, L.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 9007. (i) Lütjens, H.; Nowotny, S.; Knochel, P. *Tetrahedron: Asymmetry* **1995**, *6*, 2675. (j) Seebach, D.; Behrendt, L.; Felix, D. *Angew. Chem.* **1991**, *103*, 991; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1008. (k) Bussche-Hünnefeld, J. L. v. d.; Seebach, D. *Tetrahedron* **1992**, *48*, 5719. (l) Oppolzer, W.; Radinov, R. N. *Tetrahedron Lett.* **1991**, *32*, 5777. (m) Oppolzer, W.; Radinov, R. N. *Helv. Chim. Acta* **1992**, *75*, 170. (n) Oppolzer, W.; Radinov, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 1593.

(5) Wipf, P.; Xu, W. *Tetrahedron Lett.* **1994**, *35* , 5197.

(6) (a) Langer, F.; Waas, J. R.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 5261. (b) Langer, F.; Devasagayaraj, A.; Chavant, P.-Y.; Knochel, P. *Synlett* **1994**, 410.

(7) Rozema, M. J.; Eisenberg, C.; Lütjens, H.; Ostwald, R.; Belyk, K.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 3115.

(8) (a) Stadtmüller, H.; Lentz, R.; Dörner, W.; Stüdemann, T.; Tucker, C. E.; Knochel, P. *J. Am. Chem. Soc.* **1993**, *115*, 7027. (b) Stadtmüller, H.; Tucker, C. E.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1993**, *34*, 7911.

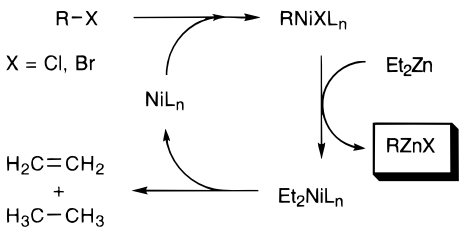
(9) Klement, I.; Chau, K.; Cahiez, G.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 1177.

(10) (a) Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1994**, *35*, 8349. (b) Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 231.

(11) Vettel, S.; Vaupel, A.; Knochel, P. *Tetrahedron Lett.* **1995**, *36*, 1023.

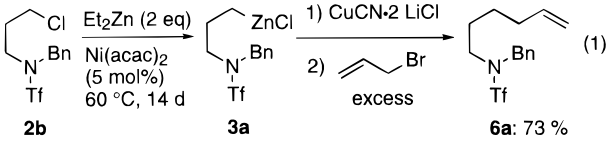
S0022-3263(96)00808-0 CCC: $12.00

Scheme 3



(II) complexes (e.g., $NiCl_2$, $NiCl_2(PPh_3)_2$, $NiCl_2 \cdot 4PPh_3$, Ni(mesal)$_2$[12]) are appropriate catalysts. However, the best conditions for performing a zinc−halogen exchange consist of treating neat a primary alkyl bromide with Ni(acac)$_2$ (5 mol %) and Et_2Zn (2 equiv) at 55 °C. The conversion to the corresponding zinc reagent is complete within a few hours (1.5−2 h). With less Et_2Zn, more protonated and elimination product was formed. A possible catalytic cycle is shown in Scheme 3. Under the reductive conditions, Ni(0) is formed catalytically from Ni(acac)$_2$ and Et_2Zn. This nickel(0) species undergoes an insertion reaction into the alkyl halide. The alkyl group is transmetalated to zinc, and the resulting diethyl nickel complex is reduced to Ni(0) with the concomitant formation of ethylene and ethane (Scheme 3).

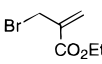
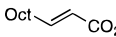
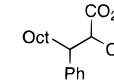
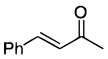
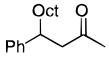
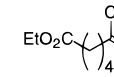
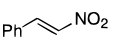
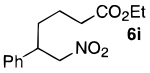
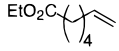
By using an alkyl chloride as substrate, longer reaction times are required. Thus, *n*-octyl chloride (**2a**) is converted to octylzinc chloride after a reaction time of 72 h at 60 °C (95% conversion). The presence of a functional group further reduces the reaction rate, and the chlorotriflamide **2b** leads to the corresponding zinc reagent **3a** after 14 d at 60 °C. After transmetalation with CuCN·2LiCl[13] to the copper−zinc species, an excess of allyl bromide was added, leading to the desired product **6a** in 73% isolated yield (eq 1). This procedure is general, and



various alkylzinc bromides or chlorides prepared in this way were reacted with electrophiles (iodine, ethyl (2-bromomethyl)acrylate,[14] ethyl propiolate, benzoyl chloride, diethyl benzylidenemalonate, benzylideneacetone, nitrostyrene) to furnish the expected products **6b**−**j** in satisfactory yields (Table 1). At the high reaction temperatures required for this insertion reaction no alkyl coupling was observed.[15]

After some experimentation, we found that terminal olefins of type **4** are converted to diorganozincs of type **5** with diethylzinc in the presence of a catalytic amount of Ni(acac)$_2$ (1−5 mol %) (Scheme 2). The reaction is only catalytic with respect to Ni(II) if halogen-free nickel salts are used like Ni(acac)$_2$ or Ni(mesal)$_2$. Not only Ni(II) can be used, but *in situ* generated Ni(0)-complexes (Ni(acac)$_2$−*i*-Bu$_2$AlH−COD) or Ni(COD)$_2$ also give similar results. The addition of 1,5-cyclooctadiene (COD; 1−2 mol %) has a positive effect leading to a better reproducibility of the reactions. Furthermore, a higher stability of the nickel catalytic system is achieved in this way. The performance of the reaction in a solvent like toluene leads to polymerization; with THF no reaction was observed. In DMF the same conversion as without solvent is observed; however, more protonated product is formed. This hydrozincation[16] allows an expeditive functionalization of unactivated double bonds. Ni(acac)$_2$ (1 mol %) in the presence of COD proved again to be the best catalytic system. Contrary to the halogen−zinc exchange, this reaction reaches maximum conversions between 40 and 63% with simple terminal alkenes. No reaction was observed with internal olefins. Functionalized alkenes bearing a remote functional group like an ester (**4b**) or a triflamide (**6a**) display a similar behavior affording the corresponding diorganozinc (50−60 °C, 3 h). All these diorganozincs can be trapped after transmetalation using CuCN·2LiCl with various electrophiles leading to the products **6c**,**d**,**f** and **7a**−**f** (Table 2). Satisfactory yields can be reached by adding ca. 0.35−0.55 equiv of the electrophile based on the starting alkene taken as one equivalent. The mechanism of the reaction may be analogous to the nickel-catalyzed hydromagnesation reported by Felkin and Marko,[17] although the presence of COD may lead to more complex reaction

Table 1. Products 6b−j Obtained by the Halogen−Zinc Exchange Reaction (X = Br or Cl) Using Et_2Zn and Ni(acac)$_2$ (5 mol %), Followed by Transmetalation with CuCN·2LiCl and Subsequent Reaction with an Electrophile (0.7 equiv Based on Haloalkane)

alkyl halide **1** or **2**	electrophile	product of type **6**		yield (%)[a]
Oct-Br **1a**	I_2	Oct-I	**6b**	68
1a (**2a**)			**6c**	79 (56)[b]
1a			**6d**	64
1a	PhCOCl	PhCOOct	**6e**	54
1a (**2a**)			**6f**	65 (68)[b]
1a			**6g**	71 [c]
 **1b**			**6h**	62
1b			**6i**	51 [c]
1b			**6j**	65 [d]

[a] Isolated yield of analytically pure products based on electrophile. [b] Yield obtained using 1-chlorooctane **2a**. [c] 0.5 equiv of electrophile. [d] 4 equiv of electrophile, yield based on bromoalkane.

(12) mesal = *N*-methylsalicylaldimino. (a) Klemm, W.; Raddatz, K.-H. *Z. Anorg. Allgem. Chem.* **1942**, *250*, 207. (b) Lardicci, L.; Giacomelli, G. P.; Salvadori, P.; Pino, P. *J. Am. Chem. Soc.* **1971**, *93*, 5794.

(13) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390.

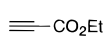
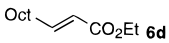
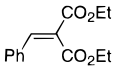
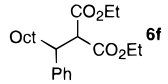
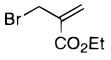
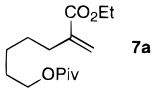
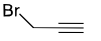
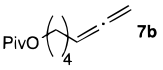
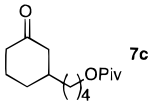
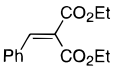
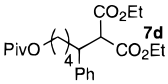
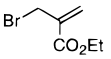
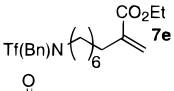
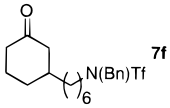
(14) Villieras, J.; Rambaud, M. *Synthesis* **1982**, 924.

(15) Devasagayaraj, A.; Stüdemann, T.; Knochel, P. *Angew. Chem.* **1995**, *107*, 2952; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2723.

(16) For other hydrozincation reactions see: (a) Dzhemilev, U. M.; Vostrikova, O. S.; Sultanov, R. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, *5*, 1195. Dzhemilev, U. M.; Vostrikova, O. S.; Tolsstikov, G. A. *J. Organomet. Chem.* **1986**, *304*, 17. (c) Gao, Y.; Urabe, H.; Sato, F. *J. Org. Chem.* **1994**, *59*, 5521. (d) Gao, Y.; Harada, K.; Hata, T.; Urabe, H.; Sato, F. *J. Org. Chem.* **1995**, *60*, 290.

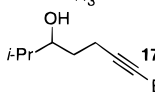
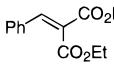
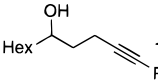
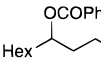
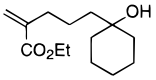
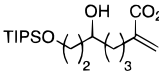
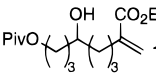
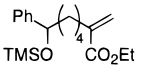
(17) (a) Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735. (b) Chuit, C.; Felkin, H.; Frajerman, C.; Roussi, G.; Swierczewski, G. *J. Chem. Soc., Chem. Commun.* **1968**, 1604. (c) Farady, L.; Bencze, L.; Marko, L. *J. Organomet. Chem.* **1967**, *10*, 505. (d) Farady, L.; Marko, L. *J. Organomet. Chem.* **1971**, *28*, 159.

Table 2. Products 6c,d,f and 7a−f Obtained by the Hydrozincation of Terminal Alkenes 4 with Et_2Zn in the Presence of $Ni(acac)_2$, Followed by Transmetalation with CuCN·2LiCl and Subsequent Reaction with an Electrophile (0.9 equiv of Electrophile Based on Rest R of the Zinc Compound)

alkene **4**	electrophile	product	yield (%)[a]
n-Hex **4a**		 **6c**	74
4a		 **6d**	60
4a		 **6f**	72
PivO **4b**		 **7a**	90
4b		 **7b**	68 [b]
4b		 **7c**	69 [c]
4b		 **7d**	87
6a N(Bn)Tf		 **7e**	82
6a		 **7f**	52 [c]

[a] Isolated yield of analytically pure products based on electrophile. [b] 1.2 equiv of electrophile, yield based on zinc compound. [c] 2 equiv of TMSCl, 0.7 equiv of electrophile based on rest R of the zinc compound.

Table 3. Products 17a−l Obtained by the Hydrozincation of Allylic and Homoallylic Alcohols 14a−f with Et_2Zn in the Presence of $Ni(acac)_2$, Followed by Transmetalation with CuCN·2LiCl and Subsequent Reaction with an Electrophile

alcohol **14**	electrophile	product of type **17**	yield (%)[a]
14a		 **17a**	63
14a		 **17b**	68
14a	I_2	 **17c**	76[b]
14a	t-BuCOCl	 **17d**	61[b]
14a		 **17e**	64[c]
14b		 **17f**	71
14b	PhCOCl	 **17g**	65[b]
14c		 **17h**	66
14d		 **17i**	62
14e		 **17j**	63
14f	I_2	 **17k**	70[b]
14f		 **17l**	72

[a] Isolated yield of analytically pure products based on alkene. [b] No TMSCl was added. [c] The TMS group of **17e** has been removed by treatment with Bu_4NF in THF.

pathways.[18] Thus, the reaction of Et_2Zn with $Ni(acac)_2$ may provide an ethylnickel(II) complex **8** that gives, after β-hydride elimination, the nickel(II) hydride **9**. A ligand exchange from ethylene to the alkene **4** furnishes the nickel−olefin complex **10**, which undergoes an insertion reaction (hydronickelation)[19] to give the alkylnickel(II) complex **11**. A transmetalation of **11** with Et_2Zn transfers the hydrometalated alkene fragment from nickel to zinc, affording the dialkylzinc **5** (Scheme 4).[20]

The moderate conversion for simple terminal alkenes may be explained by the reversibility of the hydrometalation reaction. Thus, heating of pure dioctylzinc prepared by boron−zinc exchange with a catalytic amount of $Ni(acac)_2$ (5 mol %) and COD (10 mol %) for 3 h at 50 °C affords 5% of 1-octene as shown by GC analysis. The diorganozincs prepared by hydrozincation enantioselectively add to aldehydes in the presence of catalytic amounts of (*R*,*R*)-1,2-bis(trifluoromethanesulfonamido)-cyclohexane (**12**)[21] (5−8 mol %) and Ti(O*i*-Pr)$_4$ (1.25−2 equiv) in toluene affording functionalized secondary alcohols **13a**−**c** in 89−95% ee (Scheme 5).

As noticed by Felkin[17] and others,[22] the hydrometalation of allylic and homoallylic alcohols is easier than the hydrometalation of unfunctionalized alkenes. We have used a range of allylic and homoallylic alcohols as substrates for the hydrozincation procedure and were pleased to find that a good conversion was obtained in these reactions. The treatment of allylic or homallylic alcohols of type **14** with Et_2Zn (3 equiv) and COD (10 mol %) in the presence of $Ni(acac)_2$ (5 mol %) for 4−6 h at 40 °C furnishes the hydrozincated products **15** with a conversion greater than 85%. Attempts to use the zinc reagents **15** for quenching experiments were disappointing due to their too low reactivity resulting from the

(18) Keim, W.; Behr, A.; Kraus, G. *J. Organomet. Chem.* **1983**, *251*, 377.

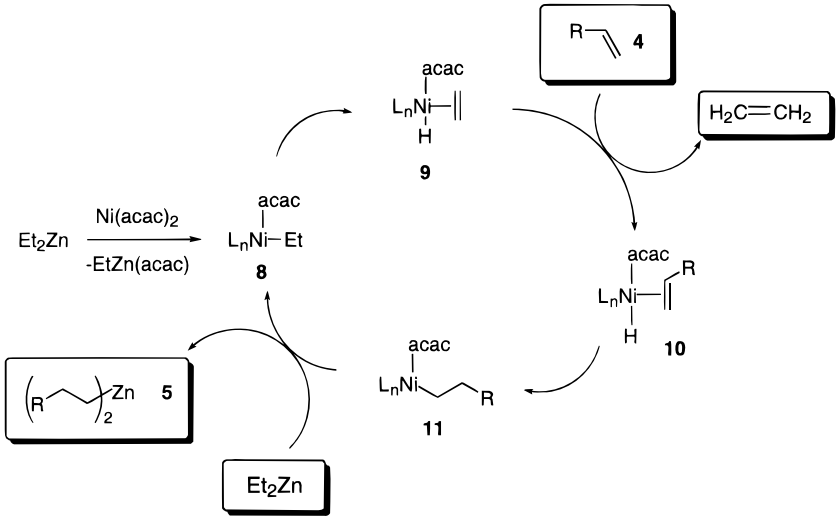
(19) (a) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (b) Sato, Y.; Takimoto, M.; Mori, M. *Tetrahedron Lett.* **1996**, *37*, 887.

(20) For an alternative mechanism involving Ni(0) see: Eisch, J. J.; Sexsmith, S. R.; Fichter, K. C. *J. Organomet. Chem.* **1990**, *382*, 273.

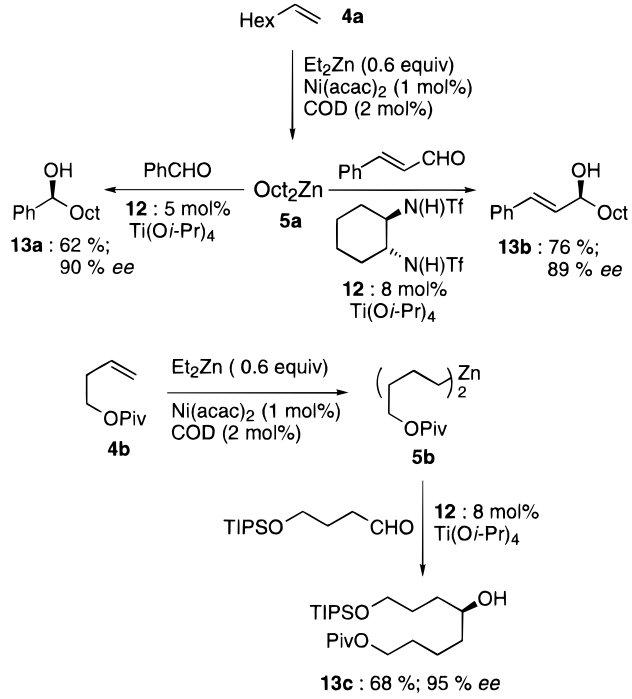
(21) (a) Yoshioka, M.; Kawakita, T.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 1657. (b) Takahashi, H.; Kawakita, T.; Yoshioka, M.; Kobayashi, S.; Ohno, M. *Tetrahedron Lett.* **1989**, *30*, 7095. (c) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691.

(22) (a) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1978**, *160*, C8. (b) Hoveyda, A. H.; Xu, Z. *J. Am. Chem. Soc.* **1991**, *113*, 5079. (c) Hoveyda, A. H.; Xu, Z.; Morken, J. P.; Houri, A. F. *J. Am. Chem. Soc.* **1991**, *113*, 8950. (d) Hoveyda, A. H.; Morken, J. P.; Houri, A. F.; Xu, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6692. (e) Houri, A. F.; Didiuk, M. T.; Xu, Z.; Horan, N. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1993**, *115*, 6614.

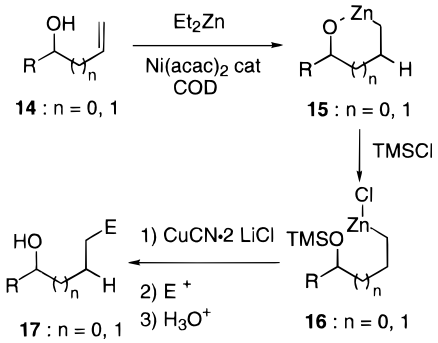
Scheme 4



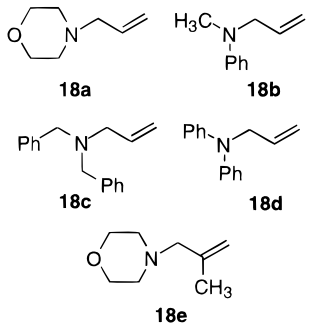
Scheme 5



Scheme 6

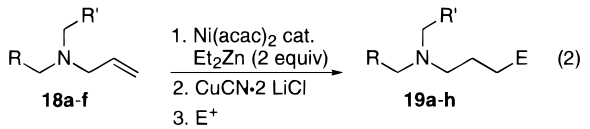


Scheme 7



chelation of zinc with oxygen.[23] In order to increase this reactivity TMSCl (2.0 equiv) was added. The high affinity of silicon for oxygen should result in the opening of the zinc metalacycle **15** and affords the alkylzinc chloride **16** in which the alcoholate function has been protected as a TMS-ether (Scheme 6). After addition of CuCN·2LiCl and an electrophile such as allylic bromide, diethyl benzylidenemalonate, iodine, acid chlorides, or an alkynyl bromide,[24] the expected products **17a**−**l** were obtained in 61−76% isolated yields (Table 3). The hydrozincation of allylic amine derivatives was also investigated. The most reactive amine, *N*-allylmorpholine **18a**, undergoes a quantitative hydrozincation within 1 h at rt. Depending on the steric hindrance at nitrogen, a rate decrease was observed (Scheme 7).

Unfortunately, the introduction of a substitution at position 2 hampers the hydrozincation (**18e** in Scheme 7). After a transmetalation with CuCN·2LiCl, the resulting amino-substituted zinc-copper organometallics react with several electrophiles (alkynyl bromide, allylic halide, ethyl propiolate, and diethyl benzylidenemalonate) to yield polyfunctional amines **19a**−**h** in 62−76% overall yield (eq 2 and Table 4).

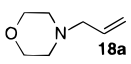
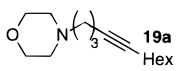
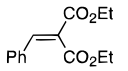
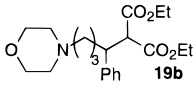
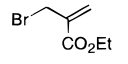
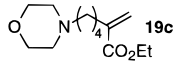
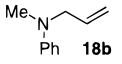
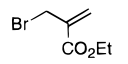
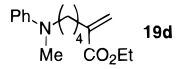
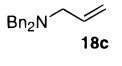
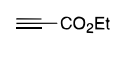
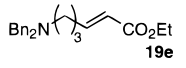
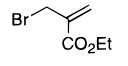
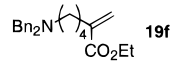
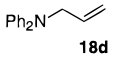
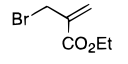
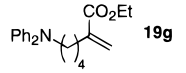
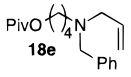
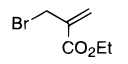
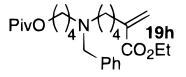


(2)

In summary, we have reported several new nickel-catalyzed preparations of functionalized dialkylzincs. Whereas the nickel-catalyzed bromine− and chlorine−zinc exchange reaction provides alkylzinc halides, the hydrozincation of alkenes furnishes dialkylzincs that can be added with excellent enantioselectivity to aldehydes. The conversion of the hydrozincation is independent of

(23) Klumpp, G. W. *Red. Trav. Chim. Pays-Bas* **1986**, *105*, 1.
(24) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1989**, *30*, 4799.

Table 4. Products 19a−h Obtained by the Hydrozincation of Allylic Amines 18a−e with Et_2Zn in the Presence of $Ni(acac)_2$, Followed by Transmetalation with CuCN·2LiCl and Subsequent Reaction with an Electrophile

allylic amine of type **18**	electrophile	product of type **19**	yield (%)[a]
 **18a**		 **19a**	64
18a		 **19b**	68
18a		 **19c**	76
 **18b**		 **19d**	74
 **18c**		 **19e**	65
18c		 **19f**	66
 **18d**		 **19g**	62
 **18e**		 **19h**	62

[a] Isolated yield of analytically pure products based on alkene.

the excess of Et_2Zn but strongly depends on the nature of the alkene. Conversions of alkenes bearing a remote functionality reach 40−63%, whereas with allylic and homoallylic alcohols as well as tertiary allylic amines conversions of the hydrozincation lay between 85−95%. Although less general and practical than the boron−zinc exchange reaction for the preparation of functionalized dialkylzincs, this method provides an efficient one-step preparation of functionalized organozincs bearing a hydroxy or amino function in the allylic position starting from alkenes.

Experimental Section

General Considerations. Unless otherwise indicated, all reactions were carried out under argon. Solvents (THF, toluene) were dried and freshly distilled over sodium/benzophenone. Reactions were monitored by gas−liquid-phase chromatography (GC) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots.

Starting Materials. The following starting materials were prepared according to literature procedures: ethyl (2-bromomethyl)acrylate,[14] 3-(*N*-benzyl-*N*-(trifluoromethyl)sulfonamido)propyl chloride (**2b**),[4g] 4-methyl-1-penten-3-ol (**14a**),[25] 1-nonen-3-ol (**14b**),[26] 1-ethenyl-1-cyclohexanol (**14c**),[26] 1-phenyl-3-buten-1-ol (**14f**),[27] *N*-allylmorpholine (**18a**),[28] *N*-allyl-*N*-methyl-*N*-phenylamine (**18b**),[29] *N*-allyl-*N*,*N*-dibenzylamine (**18c**),[30] *N*-allyl-*N*,*N*-diphenylamine (**18d**),[29] 1-bromo-1-butyne,[31] 1-bromo-1-octyne,[32] and 1-bromo-2-phenylacetylene.[33] The preparation of 3-butenyl pivalate (**4b**), 5-[(triisopropylsilyl)oxy]-1-penten-3-ol (**14d**), 4-hydroxy-5-hexenyl pivalate (**14e**), and (*N*-benzyl-*N*-allyl)-4-aminobutyl pivalate (**18e**) is described in the supporting information.

Preparation of Products 6a−j from Haloalkanes 1−2. Typical Procedure for the Preparation of Alkylzinc Halides 3 and Their Reaction with Electrophiles. A 50 mL two-necked flask equipped with an argon inlet, a magnetic stirring bar, and a septum cap was charged with $Ni(acac)_2$ (51 mg, 0.20 mmol, 5 mol %) followed by 1-bromoalkane (4.00 mmol). The mixture was cooled to 0 °C, and Et_2Zn (0.82 mL, 8.0 mmol, 2 equiv) was added dropwise. After completion of the addition, the cooling bath was removed and the reaction mixture was stirred in a preheated oil bath at 55 °C for 2 h. **Caution**: Large amounts of gas are produced in the reaction especially for large scale reactions! The excess of Et_2Zn was distilled off *in vacuo*. The black residue was dissolved in THF (2 mL) and cooled to −60 °C, and a solution of CuCN·2LiCl (CuCN: 322 mg, 3.6 mmol; LiCl: 305 mg, 7.2 mmol) in THF (4 mL) was added. The electrophile (2.80 mmol, 0.7 equiv) was added, and the reaction mixture was warmed to the temperature described. It was diluted with ether (20 mL) and was quenched by addition of a saturated aqueous NH_4Cl solution (30 mL). The aqueous layer was extracted with ether (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography (hexanes/ether 9:1) to afford the product.

Typical Procedure for the Allylation of Alkylzinc Halides 3. (*N*-Benzyltrifluoromethanesulfonamido)hex-5-ene (6a). The zinc compound was prepared as described above. It was dissolved in THF, and a solution of CuCN·2LiCl (10 mol %) in THF was added at −60 °C. Allyl bromide (3.2 equiv) was added, and the reaction mixture was warmed to 0 °C overnight. After usual workup, the residual oil was purified by flash chromatography (hexanes/ether 9:1) to afford the product **6a** (73% yield) as a colorless liquid. IR (neat): 2940 (m), 1390 (s), 1230 (s), 1195 (s), 1140 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.42−7.33 (m, 5H), 5.69 (ddt, J = 6.7, 10.6, 16.8 Hz, 1H), 4.99−4.86 (m, 2H), 4.52 (br, 2H), 3.28 (t, J = 7.8 Hz, 2H), 1.96 (m, 2 H), 1.57−1.41 (m, 2H), 1.28 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 137.7, 134.5, 128.9, 128.5, 128.4, 120.2 (q, J_{CF} = 321 Hz), 115.0, 52.0, 48.0, 32.9, 27.1, 25.5. MS (EI): 321 (M^+, 23), 91 (100). Anal. Calcd for $C_{14}H_{18}F_3NO_2S$ (321.364): C, 52.33; H, 5.65; N, 4.36. Found: C, 52.38; H, 5.55; N, 4.40.

1-Iodooctane (6b). The octyl zinc iodide was prepared as above from 1-bromooctane (579 mg, 3.00 mmol). It was dissolved in THF (3 mL) and cooled to −70 °C and a solution of iodine (1.14 g, 4.5 mmol) in THF (5 mL) added. The reaction mixture was warmed to −10 °C within 1 h. It was diluted with ether (30 mL) and quenched with water (20 mL) and aqueous saturated NaS_2O_3. The aqueous layer was extracted with ether (2 × 20 mL). The combined organic layer was washed with brine (20 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography (hexanes) to afford the product **6b** (488 mg, 2.03 mmol, 68% yield) as a colorless liquid. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 3.15 (t, J = 7.0 Hz, 2H), 1.79 (quint, J = 7.1 Hz, 2H), 1.47−1.17 (m, 10H), 0.85 (t, J = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 33.5, 31.7, 30.4, 29.0, 28.4, 22.6, 14.0, 7.1 (identical with commercially available material from Aldrich).

Ethyl 2-Nonylacrylate (6c). (a) Ethyl (2-bromomethyl)-acrylate[14] (0.7 equiv) was used as electrophile; reaction conditions: −60 to 0 °C 2 h, 2 h at 0 °C; hexanes/ether 9:1, 79% yield, yellowish oil. IR (neat): 2925 (s), 2860 (s), 1720 (s), 1180 (s), 1150 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.09 (d, J = 1.3 Hz, 1H), 5.47 (dt, J = 1.3, 1.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.26 (dd, J = 7.1, 7.6 Hz, 2H), 1.43 (m, 2H), 1.30−1.24

(25) Midland, M. M.; Koops, R. W. *J. Org. Chem.* **1990**, *55*, 5058.
(26) Smith, J. G.; Drozda, S. E., Petraglia, S. P.; Quinn, N. R.; Rice, E. M.; Taylor, B. S.; Viswanathan, M. *J. Org. Chem.* **1984**, *49*, 4112.
(27) Smith, G. G.; Voorhees, K. J. *J. Org. Chem.* **1970**, *35*, 2182.
(28) Bergbreiter, D. E.; Chen, B.; Lynch, T. J. *J. Org. Chem.* **1983**, *48*, 4179.
(29) Barnah, J. B.; Samuelson, A. G. *Tetrahedron* **1991**, *45*, 9449.
(30) Garro-Helion, F.; Merzouk, A.; Guibé, F. *J. Org. Chem.* **1993**, *58*, 6109.
(31) Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1990**, 985.
(32) Correia, J. *J. Org. Chem.* **1992**, *57*, 4555.
(33) Vogel, A. *Textbook of Practical Organic Chemistry*; 4th ed.; Longman: London, 1981; p 352.

(m, 12H), 1.27 (t, J = 7.2 Hz, 3H), 0.85 (t, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.3, 141.2, 124.0, 60.4, 31.86, 31.84, 29.5, 29.4, 29.3, 29.2, 28.4, 22.6, 14.2, 14.0. MS (EI): 226 (M^+, 3), 115 (100), 55 (71), 43 (74), 41 (71). Anal. Calcd for $C_{14}H_{26}O_2$ (226.360): C, 74.29; H, 11.58. Found: C, 74.34; H, 11.82.

(b) The procedure described for the preparation of **6c** was followed with 1-chlorooctane **2a** (60 °C, 3 d). Ethyl (2-bromomethyl)acrylate[14] (0.7 equiv) was used as electrophile; reaction conditions: −40 to 0 °C, overnight; hexanes/ether 9:1, 56% yield, yellowish oil.

(*E*)-Ethyl Undec-2-enoate (6d). Ethyl propiolate (0.7 equiv) was used as electrophile; reaction conditions: 0 °C, 3.5 h; hexanes/ether 9:1, 64% yield, yellowish liquid. IR (neat): 2920 (s), 1720 (s), 1265 (m), 980 (w). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.93 (dt, J = 15.6, 7.0 Hz, 1H), 5.77 (dt, J = 15.6, 1.6 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.16 (ddt, J = 7.4, 7.1, 1.5 Hz, 2H), 1.42 (quint, J = 7.1 Hz, 2H), 1.30−1.23 (m, 10H), 1.25 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 6.7 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.7, 149.3, 121.2, 60.0, 32.1, 31.8, 29.3, 29.13, 29.10, 28.0, 22.6, 14.2, 14.0. MS (EI): 212 (M^+, 1), 101 (95), 73 (75), 55 (100), 43 (94). Anal. Calcd for $C_{13}H_{24}O_2$ (212.333): C, 73.54; H, 11.39. Found: C, 73.34; H, 11.10.

Octyl Phenyl Ketone (6e). Benzoyl chloride (0.7 equiv) was used as electrophile; reaction conditions: −60 to −10 °C, overnight; hexanes/ether 20:1−10:1, 54% yield, colorless liquid. IR (neat): 2920 (s), 1685 (s), 750 (m), 690 (m). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.97−7.92 (m, 2H), 7.53−7.43 (m, 3H), 2.94 (dd, J = 7.2, 7.6 Hz, 2H), 1.72 (quint, J = 7.0 Hz, 2H), 1.38−1.17 (m, 10H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 200.4, 137.0, 132.8, 128.5, 128.0, 38.5, 31.8, 29.4, 29.3, 29.1, 24.3, 22.6, 14.0. MS (EI): 218 (M^+, 4), 120 (94), 105 (100). Anal. Calcd for $C_{15}H_{22}O$ (218.340): C, 82.52; H, 10.16. Found: C, 82.35; H, 10.05.

Ethyl 2-Carbethoxy-3-phenylundecanoate (6f). (a) Diethyl benzylidenemalonate (0.7 equiv) was as electrophile; reaction conditions: −60 to 0 °C, overnight; hexanes/ether 9:1, 65% yield, colorless oil. IR (neat): 2925 (s), 1670 (m), 1255 (s), 1185 (m), 755 (s), 700 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.21−7.17 (m, 2H), 7.13−7.08 (m, 3H), 4.16 (q, J = 7.1 Hz, 2 H), 3.79 (q, J = 7.1 Hz, 2H), 3.55 (d, J = 10.8 Hz, 1H), 3.28, (dt, J = 10.8, 4.0 Hz, 1H), 1.65−1.52 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H), 1.24−1.05 (m, 12H), 0.84 (t, J = 7.1 Hz, 3H), 0.77 (t, J = 6.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 168.4, 167.8, 141.0, 128.3, 128.1, 126.7, 61.3, 60.9, 58.9, 45.6, 33.9, 31.7, 29.2 (2 C), 29.1, 26.9, 22.5, 14.0, 13.9, 13.6. MS (EI): 362 (M^+, 8), 202 (51), 190 (55), 91 (100). Anal. Calcd for $C_{22}H_{34}O_4$ (362.510): C, 72.89; H, 9.45. Found: C, 73.08; H, 9.40.

(b) The procedure described for the preparation of **6c** was followed with 1-chlorooctane **2a**. Diethyl benzylidenemalonate (0.5 equiv) was used as electrophile; reaction conditions: −40 to −5 °C, overnight; hexanes/ether 9:1, 68% yield, colorless oil.

4-Phenyldodecan-2-one (6g). Benzylideneacetone (0.5 equiv) was used as electrophile; reaction conditions: −60 to 0 °C, overnight; hexanes/ether 9:1, 71% yield, colorless oil. IR (neat): 2925 (s), 1705 (s), 1360 (s), 700 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.30−7.25 (m, 2H), 7.19−7.15 (m, 3H), 3.18−3.07 (m, 1H), 2.71 (d, J = 7.4 Hz, 2H), 1.99 (s, 3H), 1.69−1.51 (m, 2H), 1.35−1.01 (m, 12H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 207.4, 144.5, 128.3, 127.3, 126.4, 50.7, 41.2, 36.3, 31.7, 30.3, 29.4, 29.3, 29.1, 27.2, 22.5, 13.9. MS (EI): 260 (M^+, 2), 202 (64), 147 (75), 91 (57), 43 (100). Anal. Calcd for $C_{18}H_{28}O$ (260.421): C, 83.02; H, 10.84. Found: C, 82.90, H, 10.95.

Ethyl 6-Carbethoxyhept-6-enoate (6h). Ethyl (2-bromomethyl)acrylate[13] (0.7 equiv) was used as electrophile; reaction conditions: −40 to 0 °C, overnight; hexanes/ether 20:1−9:1, 62% yield, colorless liquid. IR (neat): 2940 (m), 1720 (s), 1630 (m), 1300 (br), 810 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.07 (d, J = 1.4 Hz, 1H), 5.46 (dt, J = 1.4, 1.4 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 4.06 (q, J = 7.2 Hz, 2H), 2.25 (m, 2H), 2.25 (t, J = 7.3 Hz, 2H), 1.59 (quint, J = 7.5 Hz, 2H), 1.53−1.39 (m, 2H), 1.23 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 173.2, 166.8, 140.4, 124.2, 60.3, 59.9, 33.8, 31.3, 27.7, 24.3, 14.0, 13.9. MS (EI): 183 (64), 154 (69), 81 (100). Anal. Calcd for $C_{12}H_{20}O_4$ (228.288): C, 63.14; H, 8.83. Found: C, 62.85; H, 9.02.

Ethyl 6-Nitro-5-phenylhexanoate (6i). Nitrostyrene (0.5 equiv) was used as electrophile; reaction conditions: −40 to −5 °C, overnight; hexanes/ether 20:1−9:1, 51% yield, yellowish oil. IR (neat): 1720 (s), 1545 (s), 1375 (s), 1200 (s), 700 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.31−7.21 (m, 3H), 7.16−7.10 (m, 2H), 4.50 (dd, J = 2.6, 7.6 Hz, 2H), 4.04 (q, J = 7.1 Hz, 2H), 3.40 (m, 1H), 2.21 (m, 2H), 1.72−1.64 (m, 2H), 1.52−1.41 (m, 2H), 1.17 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 172.8, 138.9, 128.9, 127.6, 127.4, 80.6, 60.2, 44.0, 33.6, 32.2, 22.2, 14.1. MS (EI): 218 (25), 131 (100), 91 (76). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.309): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.11; H, 7.31; N, 5.42.

Ethyl Hept-6-enoate (6j). Allyl bromide (4 equiv) was used as electrophile (see **6a**); reaction conditions: −60 to 0 °C, overnight; Kugelrohr distillation, 65% yield, colorless liquid. IR (neat): 2940 (m), 1730 (s), 1260 (s), 1170 (m), 905 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.73 (ddt, J = 17.0, 10.3, 6.7 Hz, 1H), 4.98−4.87 (m, 2H), 4.06 (q, J = 7.2 Hz, 2H), 2.24 (t, J = 7.5 Hz, 2H), 2.01 (m, 2H), 1.58 (m, 2H), 1.36 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 173.5, 138.3, 114.5, 60.0, 34.1, 33.2, 28.3, 24.3, 14.1. MS (EI): 156 (M^+, 3), 88 (100), 55 (82), 41 (90). Anal. Calcd for $C_9H_{16}O_2$ (156.225): C, 69.19; H, 10.32. Found: C, 68.95; H, 10.64.

Preparation of Products 7a−i from Terminal Alkenes 4. Typical Procedure for the Hydrozincation of Alkenes 4 and Their Reaction with Electrophiles. Ethyl 2-Nonylacrylate (6c). A 50 mL two-necked flask equipped with an argon inlet, a magnetic stirring bar, and a septum cap was charged with $Ni(acac)_2$ (26 mg, 0.10 mmol, 1 mol %) and COD (22 mg, 0.20 mmol, 2 mol %), followed by the alkene **4a** (1.12 g, 10.0 mmol). The mixture was cooled to 0 °C, and Et_2Zn (0.61 mL, 6.0 mmol, 0.6 equiv) was dropwise added. The cooling bath was removed, and the reaction mixture was stirred in a preheated oil bath at 50−60 °C for 3 h. **Caution**: Large amounts of gas are produced in the reaction especially for large scale reactions! The conversion was checked by iodolysis of an aliquot of the reaction mixture (40−45%). The excess of Et_2Zn and unreacted olefin was distilled off *in vacuo*, yielding dioctylzinc (2.25 mmol). The black residue was dissolved in THF (3 mL) and added to a cooled solution of CuCN·2LiCl (CuCN: 403 mg, 4.50 mmol; LiCl: 382 mg, 9.00 mmol) in THF (4 mL) at −60 °C. The mixture was stirred for 10 min at rt and cooled back to −60 °C. Ethyl (2-bromomethyl)acrylate[14] (773 mg, 4.00 mmol, 0.9 equiv) was added, and the reaction mixture was warmed to −10 °C overnight. It was diluted with ether (30 mL) and quenched by addition of a saturated aqueous NH_4Cl solution (50 mL). The aqueous layer was extracted with ether (3 × 50 mL). The combined organic layer was washed with brine (50 mL), dried ($MgSO_4$), and filtered. The solvent was evaporated, and the residual oil was purified by flash chromatography (hexanes/ether 9:1) to afford the product **6c** (665 mg, 2.94 mmol, 74% yield) as a yellowish oil (see above for the spectral data).

(*E*)-Ethyl Undec-2-enoate (6d). Ethyl propiolate (0.9 equiv) was used as electrophile; reaction conditions: −60 to −5 °C, overnight; hexanes/ether 9:1, 60% yield, yellowish oil (see above for the spectral data).

Ethyl 2-Carbethoxy-3-phenylundecanoate (6f). Diethyl benzylidenemalonate (0.9 equiv) was used as electrophile; reaction conditions: −60 to 0 °C, overnight; hexanes/ether 9:1, 72% yield, colorless oil (see above for the spectral data).

Ethyl 2-(5-Pivaloxypentyl)acrylate (7a). The hydrozincation procedure described for the preparation of **6c** was followed with alkene **4b** (45% conversion), yielding bis(4-pivaloxybutyl)zinc (1.13 mmol). Ethyl (2-bromomethyl)acrylate[14] (0.9 equiv) was used as electrophile; reaction conditions: −60 to −10 °C, overnight; hexanes/ether 9:1, 90% yield, colorless oil. IR (neat): 2940 (m), 1720 (s), 1160 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.08 (s, 1H), 5.46 (s, 1H), 4.15 (q, J = 7.1 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 2.26 (t, J = 7.2 Hz, 2H), 1.60−1.28 (m, 6H), 1.25 (t, J = 7.1 Hz, 3H), 1.14 (s, 9 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 178.5, 167.1, 140.7, 124.3, 64.1, 60.5, 38.6, 31.6, 28.3, 27.9, 27.1, 25.4, 14.1. MS (EI): 168 (24), 95 (44), 57 (100). Anal. Calcd for $C_{15}H_{26}O_4$ (270.369): C, 66.64; H, 9.69. Found: C, 66.36; H, 9.98.

5,6-Heptadienyl pivalate (7b). Propargyl bromide (1.2 equiv, 80% in toluene) as electrophile; reaction conditions: −60 to −10 °C, overnight; hexanes/ether 20:1−9:1, 68% yield, colorless liquid. IR (neat): 3000 (m), 1955 (m), 1710 (s), 1150 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 5.05 (m, 1H), 4.64 (dd, J = 3.2, 3.2 Hz, 1H), 4.61 (dd, J = 3.2, 3.2 Hz, 1H), 4.02 (t, J = 6.6 Hz, 2H), 2.00 (m, 2H), 1.60 (m, 2H), 1.37 (m, 2H), 1.16 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 208.5, 178.5, 89.5, 74.8, 64.1, 38.6, 28.0, 27.7, 27.1, 25.3. MS (EI): 103 (12), 79 (62), 57 (100). Anal. Calcd for $C_{12}H_{20}O_2$ (196.290): C, 77.43; H, 10.27. Found: C, 74.23; H, 10.39.

3-(4-Pivaloxybutyl)cyclohexanone (7c). The hydrozincation procedure described for the preparation of **6c** was followed with alkene **4b**, yielding bis(4-pivaloxybutyl)zinc (1.85 mmol). The black residue was dissolved in THF (4 mL) and cooled to −60 °C, and a solution of CuCN·2LiCl (CuCN: 331 mg, 3.70 mmol; LiCl: 315 mg, 7.40 mmol) in THF (4 mL) was added. The mixture was stirred for 10 min at rt and cooled back to −60 °C. After 10 min, TMSCl (804 mg, 7.40 mmol, 2 equiv) was added, and after further 10 min cyclohexenone (250 mg, 2.60 mmol, 0.7 equiv) was added dropwise. The reaction mixture was warmed to −10 °C overnight and worked up as usual. The solvent was removed in vacuo, and the residue was diluted with THF (50 mL). Aqueous HCl (10%, 5 mL) was slowly added, and the reaction mixture was stirred for 30 min at rt. It was diluted with ether (30 mL) and neutralized with 2 N NaOH (20 mL). The aqueous layer was extracted twice with ether (20 mL) and washed with brine (20 mL). The combined organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated. The residual oil was purified by flash chromatography (hexanes/ether 9:1 to 4:1) to afford the product **7c** (458 mg, 1.80 mmol, 69% yield) as a colorless liquid. IR (neat): 2930 (m), 1725 (s), 1715 (s), 1155 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 3.96 (t, J = 6.4 Hz, 2H), 2.40−2.10 (m, 3H), 2.09−1.40 (m, 7H), 1.38−1.20 (m, 5H), 1.10 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 211.5, 178.3, 63.9, 47.9, 41.3, 38.7, 38.5, 35.9, 31.0, 28.4, 27.0, 25.0, 22.8. MS (EI): 152 (17), 97 (93), 57 (100). Anal. Calcd for $C_{15}H_{26}O_3$ (254.370) : C, 70.83; H, 10.30. Found: C, 70.64; H, 10.52.

Ethyl 2-Carbethoxy-3-phenyl-7-pivaloxyheptanoate (7d). Diethyl benzylidenemalonate (0.9 equiv) was used as electrophile; reaction conditions: −60 to 0 °C, overnight; hexanes/ether 4:1−1:1, 87% yield, yellowish oil. IR (neat): 2950 (m), 1750 (s), 1730 (s), 1260 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.23−7.11 (m, 5H), 4.18 (q, J = 7.2 Hz, 2H), 3.87 (t, J = 6.4 Hz, 2H), 3.81 (q, J = 7.2 Hz, 2H), 3.57 (q, J = 11.0 Hz, 1H), 3.30 (dt, J = 3.6, 10.7 Hz, 1H), 1.65−1.39 (m, 4H), 1.23 (t, J = 7.2 Hz, 3H), 1.12−1.03 (m, 2H), 1.05 (s, 9H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 178.3, 168.3, 167.6, 140.4, 128.2, 128.1, 126.8, 63.7, 61.4, 60.9, 58.6, 45.3, 38.5, 33.3, 28.1, 27.0, 23.2, 14.0, 13.5. MS (EI): 406 (M^+, 6), 161 (30), 144 (100), 57 (78). Anal. Calcd for $C_{23}H_{34}O_6$ (406.501) : C, 67.96; H, 8.43. Found: C, 67.72; H, 8.61.

Ethyl 2-[7-(*N*-Benzyltrifluoromethanesulfonamido)-heptyl]acrylate (7e). The hydrozincation procedure described for the preparation of **6c** was followed with alkene **6a** (63% conversion), yielding bis[6-(*N*-benzyltrifluormethanesulfonamido)hexyl]zinc (1.85 mmol). Ethyl (2-bromomethyl)-acrylate[14] (251 mg, 1.30 mmol, 0.7 equiv) was used as electrophile; reaction conditions: −60 to −30 °C, overnight; hexanes/ether 20:1−9:1, 82% yield, colorless oil. IR (neat): 2930 (m), 1710 (s), 1395 (s), 1225 (s), 1195 (s), 1145 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.35 (m, 5H), 6.11 (d, J = 1.0 Hz, 1H), 5.47 (d, J = 1.0 Hz, 1H), 4.50 (bs, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.23 (t, J = 7.8 Hz, 2H), 2.24 (t, J = 8.4 Hz, 2H), 1.72−1.10 (m, 10H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 167.2, 140.9, 134.4, 128.9, 128.5, 128.3, 124.1, 120.1 (q, J_{CF} = 322 Hz), 60.5, 51.9, 48.1, 31.7, 29.7, 28.7, 28.1, 27.6, 26.2, 14.1. MS (EI): 390 (2), 302 (47), 91 (100). Anal. Calcd for $C_{20}H_{28}F_3NO_4S$ (435.508): C, 55.16; H, 6.48; N, 3.22. Found: C, 55.0; H, 6.65; N, 3.38.

3-[6-(*N*-Benzyltrifluoromethanesulfonamido)hexyl]-cyclohexanone (7f). Cyclohexenone (0.7 equiv; TMSCl, 2 equiv) as electrophile (see preparation of **7c**); reaction conditions: −60 °C to rt, overnight; hexanes/ether 9:1−4:1, 52% yield, colorless oil. IR (neat): 2930 (m), 1705 (m), 1395 (s), 1225 (s), 1195 (s). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.29 (m, 5H), 4.45 (bs, 2H), 3.18 (t, J = 7.8 Hz, 2H), 2.44−2.14 (m, 3H), 2.13−0.94 (m, 16H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 212.0, 134.4, 128.8, 128.5, 128.3, 120.1 (q, J_{C-F} = 322 Hz), 51.9, 48.1, 41.4, 38.9, 36.3, 31.2, 28.9, 27.6, 26.3, 26.1, 25.2. MS (EI): 286 (64), 91 (100). Anal. Calcd for $C_{20}H_{28}F_3NO_3S$ (419.509): C, 57.26; H, 6.73 ; N, 3.34. Found: C, 56.99; H, 6.44; N, 3.53.

Typical Procedure for the Preparation of Chiral Alcohols 13a−c. (*S*)-(−)-1-Phenyl-1-nonanol (13a). The procedure described for the preparation of **7a** was followed with alkene **4a**, yielding dioctylzinc (4.2 mmol) that was diluted with toluene (3 mL). In a 50 mL two-necked flask equipped with an argon inlet, a magnetic stirring bar, and a septum cap a mixture of (*R*,*R*)-1,2-bis(trifluoromethanesulfonamido)cyclohexane (**12**) (32 mg, 0.083 mmol, 5 mol %) and Ti(O*i*-Pr)$_4$ (1.0 mL, 3.4 mmol, 2 equiv) in toluene (1.5 mL) was heated to 50 °C for 30 min. The resulting clear solution was cooled to −50 °C, and dioctylzinc in toluene was slowly added. After 45 min, benzaldehyde (193 mg, 1.82 mmol) was added and the reaction mixture was allowed to warm to −20 °C overnight. It was diluted with ether (20 mL) and quenched with saturated aqueous NH_4Cl. Aqueous HCl (10%) was added until a clear solution resulted. The aqueous layer was extracted with ether (3 × 10 mL) and treated with 2 N NaOH (20 mL) to remove the catalyst. The combined organic layer was dried ($MgSO_4$) and concentrated. The resulting residue was purified by flash chromatography (hexanes/ether 4:1) to afford the product **13a** (247 mg, 1.12 mmol, 62% yield, 90% ee) as a colorless oil. $[\alpha]^{25}_D$ = −23.8 (c = 2.5, $CHCl_3$). IR (neat): 3350 (br), 2920 (s), 2860 (s), 1030 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.33−7.24 (m, 5H), 4.60 (t, J = 6.0 Hz, 1H), 2.29 (bs, 1H), 1.83−1.63 (m, 2H), 1.42−1.19 (m, 16H), 0.89 (t, J = 6.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 145.0, 128.3, 127.3, 125.9, 74.6, 39.0, 31.9, 29.5 (2 C), 29.3, 25.8, 22.6, 14.0. MS (EI): 220 (M^+, 1), 107 (100). Anal. Calcd for $C_{15}H_{24}O$ (220.356): C, 81.76; H, 10.98. Found: C, 81.68; H, 11.15.

The enantiomeric excess was determined in ^{1}H-NMR of the corresponding (*S*)-*O*-acetyl mandelate.[34]

(*E*)-(*S*)-(+)-1-Phenylundec-1-en-3-ol (13b). The reaction was run as above with catalyst **12** (8 mol %), Ti(O*i*-Pr)$_4$ (1.25 equiv), and cinnamaldehyde; −45 °C stirred overnight; hexanes/ether 4:1−1:1, 76% yield, 89% ee, colorless oil. $[\alpha]^{25}_D$ = +3.9 (c = 2.0, $CHCl_3$). IR (neat): 3340 (br), 2920 (s), 745 (m), 695 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.23 (m, 5H), 6.42 (d, J = 15.9 Hz, 1H), 6.13 (dd, J = 6.8, 15.9 Hz, 1H), 4.11 (m, 1H), 2.41 (bs, 1H), 1.54−1.38 (m, 2H), 1.37−1.10 (m, 12H), 0.79 (t, J = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 136.7, 132.6, 129.9, 128.4, 127.4, 126.3, 72.9, 37.3, 31.8, 29.52, 29.48, 29.2, 25.4, 22.6, 14.0. MS (EI): 246 (M^+, 4), 228 (22), 133 (100), 91 (56). Anal. Calcd for $C_{17}H_{26}O$ (246.394): C, 82.87; H, 10.64. Found: C, 82.61; H, 10.55.

The enantiomeric excess was determined in ^{1}H-NMR of the corresponding (*S*)-*O*-acetyl mandelate.[34]

(*S*)-(+)-5-Hydroxy-8-[(triisopropylsilyl)oxy]octyl Pivalate (13c). The reaction was run as above with catalyst **12** (8 mol %) and Ti(O*i*-Pr)$_4$ (2 equiv) in toluene (2 mL). 4-[(Triisopropylsilyl)oxy]butanal[4f] was added at −50 °C and allowed to warm to −10 °C overnight; hexanes/ether 4:1−1:1, 68% yield, 95% ee, colorless oil. $[\alpha]^{25}_D$ = +0.8 (c = 15.7, C_6H_6). IR (neat): 3450 (br), 2865 (s), 1725 (s), 1290 (s), 765 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.01 (t, J = 6.5 Hz, 2H), 3.70 (t, J = 5.5 Hz, 2H), 3.58 (m, 1H), 2.75 (d, J = 4.0 Hz, 1H), 1.68−1.56 (m, 5H), 1.50−1.36 (m, 5H), 1.15 (s, 9H), 1.11−0.96 (m, 21H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 178.5, 71.1, 64.3, 63.7, 38.6, 36.9, 34.8, 29.2, 28.6, 27.1, 22.1, 17.9, 11.9. MS (EI): 359 (6), 215 (44), 109 (80), 57 (100). Anal Calcd for $C_{22}H_{46}O_4Si$ (402.692) C, 65.62; H, 11.51. Found: C, 65.59; H, 11.43.

The enantiomeric excess was determined in ^{1}H-NMR of the corresponding (*S*)-*O*-acetyl mandelate.[34]

Preparation of Products 17a−l from Allylic and Homoallylic Alcohols 14a−f. Typical Procedure for the Hydrozincation of Allylic and Homoallylic Alcohols 14a−f. Ethyl 2-(4-Hydroxy-5-methylhexyl)acrylate (17a). A 25 mL three-necked flask equipped with an argon inlet, a magnetic stirring bar, an internal thermometer, and a septum cap was charged with Ni(acac)$_2$ (66 mg, 0.25 mmol, 5 mol %)

(34) Parker, D. *J. Chem. Soc., Perkin Trans. 2* **1983**, 83.

and COD (54 mg, 0.5 mmol, 10%), followed by the allylic alcohol **14a** (0.5 g, 5.0 mmol). The mixture was cooled to −78 °C, and Et_2Zn (1.5 mL, 15.0 mmol, 3 equiv) was added dropwise. After completion of the addition, the cooling bath was removed and the reaction mixture was warmed gradually to 40 °C. It was stirred at this temperature for 5 h, and the excess Et_2Zn was distilled off *in vacuo*. THF (5 mL) was added to the reaction mixture and was distilled off again. This procedure was repeated twice. The black residue was dissolved in THF (5 mL) and cooled to −78 °C. At this temperature, TMSCl (1.2 mL, 10.0 mmol) was added, and the reaction mixture was allowed to warm to rt within 12 h. It was cooled back to −78 °C, and a solution of CuCN·2LiCl (CuCN: 0.45 g, 5.0 mmol; LiCl: 0.42 g, 10.0 mmol) in THF (8 mL) was added. The mixture was stirred for 5 min at 0 °C and was cooled back to −78 °C. Ethyl (2-bromomethyl)acrylate[14] (0.98 g, 5.0 mmol, 1.0 equiv) was added, and the reaction mixture was warmed to 0 °C within 1 h. It was diluted with ether (30 mL) and quenched by addition of a saturated aqueous NH_4Cl solution (50 mL). Precipitated copper salts were dissolved by addition of small portions of aqueous NH_3 solution. The aqueous layer was separated and extracted with ether (3 × 50 mL). The combined organic layer was dried ($MgSO_4$) and filtered, and the solvent was evaporated. The residual oil was purified by flash chromatography (hexanes/ether 9:1) to afford the product **17a** (0.74 g, 3.14 mmol, 63% yield) as a colorless oil. IR (neat): 3410 (s, br), 2920 (vs), 1720 (vs), 1620 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.07 (s, 1H), 5.46 (s, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.30 (bs, 1H), 2.26 (m, 2H), 1.72 (m, 1H), 1.56 (m, 2H), 1.43 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H), 0.83 (d, J = 6.8 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.2, 140.7, 124.3, 76.2, 60.4, 33.5, 31.6, 24.8, 18.7, 17.0, 14.1. MS (EI): 171 (26), 125 (100), 97 (41), 41 (28). Anal. Calcd for $C_{12}H_{22}O_3$ (214.24): C, 67.29; H, 10.28. Found: C, 67.20; H, 10.32.

2-Methyl-6-nonyn-3-ol (17b). 1-Bromo-1-butyne (1.3 equiv) was used as electrophile; reaction conditions: −60 °C, 2 d; hexanes/ether 9:1−4:1, 68% yield, colorless liquid. IR (neat): 3450 (s, br), 2950 (vs), 2350 (w), 1720 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.36 (m, 1H), 2.16 (m, 2H), 2.03 (m, 3H), 1.55 (m, 3H), 1.52 (m, 2H), 1.42 (m, 1H), 0.99 (t, J = 7.5 Hz, 3H), 0.68 (d, J = 7.0 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 82.2, 79.0, 75.8, 33.6, 32.9, 18.4, 17.2, 15.5, 14.1, 12.2. MS (EI): 121 (18), 111 (43), 55 (83), 41 (100). Anal. Calcd for $C_{10}H_{18}O$ (154.22): C, 77.87; H, 11.75. Found: C, 77.62; H, 11.88.

1-Iodo-4-methylpentan-3-ol (17c). The zinc reagent was directly quenched by the addition of iodine (3 equiv) dissolved in THF at −78 °C; hexanes/ether 19:1, 76% yield, yellow oil. IR (neat): 3350 (s, br), 2900 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.48 (m, 1H), 3.32 (m, 2H), 1.89 (m, 2H), 1.70 (m, 1H), 1.54 (d, J = 5.2 Hz, 1H), 0.92 (d, J = 6.7 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 76.3, 37.7, 33.5, 18.6, 17.4, 4.2. MS (EI): 227 (M^+, 13), 185 (38), 73 (100), 57 (40). Anal. Calcd for $C_6H_{13}IO$ (227.15): C, 31.72; H, 5.73. Found: C, 32.01; H, 5.65.

5,5-Dimethyl-1-isopropyl-4-oxohexyl Pivalate (17d). The intermediate zinc alcoholate was not protected with TMSCl, and after transmetalation with CuCN·2LiCl, pivaloyl chloride (2.4 equiv) was added as electrophile. Reaction conditions: −78 to −5 °C, 2 d; hexanes/ether 9:1, 61% yield, colorless oil. IR (neat): 2940 (vs), 1715 (vs), 1705 (vs), 1283 (s), 1160 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.63 (m, 1H), 2.40 (m, 2H), 1.77 (m, 2H), 1.65 (m, 1H), 1.13 (s, 9H), 1.05 (s, 9H), 0.83 (d, J = 6.1 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 215.1, 178.1, 77.3, 44.1, 39.0, 32.6, 31.8, 27.3, 26.5, 25.5. MS (EI): 185 (8), 129 (42), 57 (100). Anal. Calcd for $C_{16}H_{30}O_3$ (270.37): C, 71.11; H, 11.11. Found: C, 70.94; H, 11.20.

Ethyl 2-Carbethoxy-6-hydroxy-7-methyl-3-phenyloctanoate (17e). Diethyl benzylidene malonate (1.0 equiv) was used as electrophile; after usual workup the crude product was dissolved in THF and treated with a 1 M solution of Bu_4NF in THF at 0 °C (3 h); hexanes/ether 1:1, 64% yield, yellow oil. IR (neat): 3480 (s, br), 2970 (s), 1720 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.17 (m, 5H), 4.17 (q, J = 6.5 Hz, 2H), 3.80 (m, 2H), 3.56 (d, J = 10.9 Hz, 1H), 3.31 (m, 2H), 1.74 (m, 1H), 1.55 (m, 2H), 1.43 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H), 1.10 (m, 1H), 0.86 (m, 3H), 0.73 (t, J = 6.8 Hz, 3H), 0.68 (t, J = 6.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 168.3, 167.4, 140.7, 128.2, 126.7, 76.5, 61.4, 58.7, 45.7, 33.4, 31.0, 30.4, 18.8, 13.9. MS (EI): 259 (26), 189 (100), 147 (54), 69 (21). Anal. Calcd for $C_{20}H_{30}O_5$ (350.41): C, 68.57; H, 8.57. Found: C, 68.53; H, 8.30.

1-Phenyl-1-undecyn-5-ol (17f). 1-Bromo-2-phenylacetylene (2 equiv) as electrophile; reaction conditions: −53 °C, 2 d; hexanes/ether 9:1−4:1, 71% yield, colorless oil. IR (neat): 3350 (vs, br), 2910 (vs), 2850 (s), 1600 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.40 (m, 5H), 3.76 (m, 1H), 2.54 (t, J = 7.2 Hz, 2H), 2.02 (s, br, 1H), 1.68 (m, 2H), 1.49 (m, 2H), 1.29 (m, 2H), 0.91 (t, J = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 131.6, 128.3, 127.7, 123.9, 89.9, 81.1, 71.1, 37.5, 36.1, 31.9, 29.4, 25.7, 22.7, 16.1, 14.2. MS (EI): 159 (100), 128 (41), 91 (15), 43 (19). Anal. Calcd for $C_{17}H_{24}O$ (244.35): C, 83.56; H, 9.89. Found: C, 83.65; H, 10.02.

1-Hexyl-4-oxo-4-phenylbutyl Benzoate (17g). The intermediate zinc alcoholate was not protected with TMSCl, and after transmetalation with CuCN·2LiCl, benzoyl chloride (2.4 equiv) as electrophile was added. Reaction conditions: −78 to −5 °C, 24 h; hexanes/ether 9:1−4:1, 65% yield, colorless oil. IR (neat): 2920 (m), 1712 (s), 1690 (s), 1290 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.02 (d, J = 7.2 Hz, 2H), 7.99 (d, J = 7.1 Hz, 2H), 7.39 (m, 6H), 5.24 (m, 1H), 3.07 (t, J = 7.5 Hz, 2H), 2.14 (m, 2H), 1.72 (m, 2H), 1.33 (m, 8H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 199.4, 166.4 136.9, 133.0, 132.9, 130.6, 129.6, 128.6, 128.4, 74.6, 34.7, 31.8, 29.3, 28.8, 25.4, 22.6, 14.3. MS (EI): 248 (6), 247 (36), 105 (100), 77 (20). Anal. Calcd for $C_{23}H_{28}O_3$ (352.42): C, 78.39; H, 8.00. Found: C, 78.24; H, 7.94.

1-(4-Carbethoxy-4-pentenyl)cyclohexan-1-ol (17h). Ethyl (2-bromomethyl)acrylate[14] (1.2 equiv) as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ether 4:1, 66% yield, colorless oil. IR (neat): 3440 (s, br), 2930 (vs), 2850 (s), 1715 (vs), 1620 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.00 (s, 1H), 5.40 (s, 1H), 4.07 (q, J = 7.2 Hz, 2H), 2.17 (t, J = 7.6 Hz, 2H), 1.35 (m, 15H), 1.16 (t, J = 7.6 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.3, 140.9, 124.3, 71.2, 60.6, 41.9, 37.7, 37.5, 32.2, 25.9, 22.3, 22.0, 21.8, 14.2. MS (EI): 197 (6), 142 (73), 99 (100), 81 (49). Anal. Calcd for $C_{14}H_{24}O_3$ (240.30): C, 70.00; H, 10.05. Found: C, 70.01; H, 10.24.

Ethyl 2-[4-Hydroxy-6-[(triisopropylsilyl)oxy]hexyl]-acrylate (17i). Ethyl (2-bromomethyl)acrylate[14] (1.5 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ether 9:1, 62% yield, colorless oil. IR (neat): 3450 (m, br), 2910 (vs), 1715 (vs), 1295 (m), 1150 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.06 (s, 1H), 5.45 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.92 (m, 1H), 3.87 (m, 2H), 3.59 (s, 1H), 2.24 (m, 2H), 1.56 (m, 3H), 1.48 (m, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.01 (s, 21H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.1, 140.7, 124.2, 71.9, 63.3, 60.4, 38.3, 36.9, 31.6, 24.2, 17.8, 14.0, 11.8. MS (EI): 329 (4), 131 (69), 119 (100), 107 (96). Anal. Calcd for $C_{20}H_{46}O_4Si$ (344.44): C, 64.97; H, 10.82. Found: C, 64.88; H, 10.96.

Ethyl 2-(4-Hydroxy-7-pivaloxyheptyl)acrylate (17j). Ethyl (2-bromomethyl)acrylate[14] (1.0 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ether 4:1−1:1, 63% yield, colorless oil. IR (neat): 3450 (m, br), 2950 (s), 1715 (vs), 1620 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.07 (s, 1H), 5.47 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.00 (t, J = 10.0 Hz, 2H), 3.57 (s, 1H), 2.24 (m, 2H), 1.97 (m, 1H), 1.68−1.43 (m, 8H), 1.37 (t, J = 7.1 Hz, 3H), 1.12 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 178.5, 167.2, 140.6, 124.4, 70.8, 64.3, 60.5, 38.6, 36.8, 33.6, 31.6, 27.1, 24.8, 24.4, 14.4. MS (EI): 250 (5), 125 (40), 71 (81), 57 (100). Anal. Calcd for $C_{17}H_{30}O_5$ (314.33): C, 64.95; H, 9.61. Found: C, 64.88; H, 9.66.

4-Iodo-1-phenylbutan-1-ol (17k). Iodine (3 equiv) was used as electrophile; reaction conditions: −78 °C to rt, 1 h; hexanes/ether 95:5, 70% yield, yellow oil. IR (neat): 3355 (s, br), 2910 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.32 (m, 5H), 4.64 (t, J = 6.5 Hz, 1H), 3.13 (m, 2H), 1.83 (m, 5H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 144.7, 129.0, 128.2, 126.3, 73.9, 40.1, 30.2, 7.4. MS (EI): 148 (100), 147 (97), 105 (95), 77 (26). Anal. Calcd for $C_{10}H_{13}IO$ (275.19): C, 43.64; H, 4.73. Found: C, 43.82; H, 4.64.

Ethyl 2-[5-Phenyl-5-[(trimethylsilyl)oxy]pentyl]acrylate (17l). Ethyl (2-bromomethyl)acrylate[14] (1.1 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ether 9:1, 72% yield, colorless oil. IR (neat): 2920 (s), 2880 (m), 1710 (vs), 1630 (m). ^{1}H-NMR ($CDCl_3$, 300

MHz): δ 7.26 (m, 5H), 6.11 (s, 1H), 5.43 (s, 1H), 4.58 (dd, J = 7.7 Hz, 5.0 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.25 (t, J = 6.9 Hz, 2H), 1.63 (m, 2H), 1.45 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 0.00 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.1, 145.5, 140.9, 128.1, 127.3, 125.7, 124.1, 74.8, 60.3, 40.4, 31.7, 28.3, 25.4, 14.1, 0.0. MS (EI): 180 (21), 179 (100), 73 (47). Anal. Calcd for $C_{19}H_{30}O_3Si$ (334.37): C, 68.26; H, 8.98. Found: C, 68.48; H, 9.10.

Preparation of Products 19a−h from Allylic Amines 18a−d,f. Typical Procedure for the Hydrozincation of Allylic Amines 18a−d,f. *N*-4-Undecynylmorpholine (19a). A 25 mL three-necked flask equipped with an argon inlet, a magnetic stirring bar, and an internal thermometer was charged with $Ni(acac)_2$ (66 mg, 0.25 mmol, 5 mol %), COD (54 mg, 0.50 mmol, 10 mol %), and the amine **18a** (636 mg, 5.0 mmol). The resulting green suspension was cooled to −78 °C, and Et_2Zn (1.0 mL, 10.0 mmol, 2 equiv) was added. After completion of the addition, the cooling bath was removed and the reaction mixture was allowed to warm to rt and stirred for 1 h. After complete conversion of the starting material, THF (5 mL) was added. The solvent and excess of Et_2Zn was removed *in vacuo*. This procedure was repeated twice, and the resulting pure zinc compound was redissolved in THF (2 mL). After the mixture was cooled to −60 °C a solution of CuCN·2LiCl (CuCN: 0.45 g, 5.0 mmol; LiCl: 0.42 g, 10 mmol) in THF (5 mL) was added, and the reaction mixture was warmed to 0 °C for 10 min. It was cooled again to −78 °C, and 1-bromo-1-octyne (1.12 g, 6.0 mmol, 1.2 equiv) was added as electrophile. The mixture was warmed to −60 °C and stirred for 4 d. It was worked up as above and purified by flash chromatography (hexanes/ether 2:1 to 100% ether) to afford the product **19a** (769 mg, 3.2 mmol, 64% yield) as a colorless oil. IR (neat): 2920 (vs), 2880 (s), 2805 (m), 1460 (m), 1105 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 3.57 (m, 4H), 2.29 (m, 6H), 2.02 (m, 4H), 1.53 (m, 2H), 1.29 (m, 8H), 0.74 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 80.3, 79.3, 66.8, 57.8, 53.6, 31.2, 28.9, 28.3, 25.9, 22.4, 18.5, 16.5, 13.8. MS (EI): 180 (9), 166 (52), 100 (100), 56 (10). Anal. Calcd for $C_{15}H_{27}NO$ (237.39): C, 75.90; H, 11.46; N, 5.89. Found: C, 75.73; H, 11.44; N, 6.09.

***N*-(5,5-Dicarbethoxy-4-phenylpentyl)morpholine (19b).** Diethyl benzylidenemalonate (1.2 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 2 d; hexanes/ether 2:1 to 100% ether, 68% yield, yellow oil. IR (neat): 3100 (vs), 1735 (vs), 1450 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.24 (m, 5H), 4.20 (q, J = 7.1 Hz, 2H), 3.82 (q, J = 7.1 Hz, 2H), 3.60 (m, 5H), 2.25 (m, 7H), 1.63 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.21 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 168.3, 167.7, 140.6, 128.4, 128.2, 126.9, 66.8, 61.4, 60.9, 58.7, 58.5, 53.6, 45.5, 31.7, 23.9, 14.0, 13.6. MS (EI): 377 (M^+, 3), 304 (13), 100 (100), 42 (13). Anal. Calcd for $C_{21}H_{31}NO_5$ (377.38): C, 66.83; H, 8.27; N, 3.71. Found: C, 66.61; H, 8.49; N, 3.94.

***N*-(5-Carbethoxy-5-hexenyl)morpholine (19c).** Ethyl (2-bromomethyl)acrylate[14] (1.0 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ ether 1:1 to 100% ether, 76% yield, yellow oil. IR (neat): 2915 (s), 2850 (s), 2800 (m), 1705 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.96 (s, 1H), 5.34 (s, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.52 (t, J = 4.7 Hz, 4H), 2.24 (m, 4H), 2.14 (m, 4H), 1.32 (m, 4H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.9, 140.6, 124.1, 66.8, 60.3, 58.6, 53.6, 31.6, 25.9, 21.1, 14.0. MS (EI): 241 (M^+, 4), 196 (5), 100 (100). Anal. Calcd for $C_{13}H_{23}NO_3$ (241.29): C, 64.71; H, 9.59; N, 5.80. Found: C, 64.69; H, 9.80; N, 5.90.

***N*-(5-Carbethoxy-5-hexenyl)-*N*-methylaniline (19d).** Ethyl (2-bromomethyl)acrylate[14] (1.0 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ ether 19:1−9:1, 74% yield, yellow oil. IR (neat): 2915 (s), 1705 (vs), 1600 (s), 1500 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.23 (dd, J = 8.1, 7.1 Hz, 2H), 6.69 (d, J = 8.2 Hz, 3H), 6.16 (s, 1H), 5.52 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.33 (t, J = 6.9 Hz, 2H), 2.86 (s, 3H), 2.35 (m, 2H), 1.53 (m, 4H), 1.31 (t, J = 7.8 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.2, 149.4, 140.8, 129.2, 124.6, 116.0, 112.2, 60.6, 52.6, 38.4, 31.9, 26.4, 26.1, 14.3. MS (EI): 261 (M^+, 12), 120 (100). Anal. Calcd for $C_{16}H_{23}NO_2$ (261.32): C, 73.53; H, 8.86; N, 5.36. Found: C, 73.26; H, 8.72; N, 5.46.

***(E)*-Ethyl 6-(*N*,*N*-dibenzylamino)hex-2-enoate (19e).** Ethyl propiolate (1.0 equiv) was used as electrophile; reaction conditions: −78 to −10 °C, 12 h; hexanes/ether 9:1, 65% yield), colorless oil. IR (neat): 2830 (m), 2700 (s), 1720 (vs), 1660 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.32 (m, 10H), 6.87 (dt, J = 15.2, 6.9 Hz, 1H), 5.96 (d, J = 15.7 Hz, 1H), 4.13 (q, J = 7.2 Hz, 2H), 3.51 (s, 4H), 2.39 (t, J = 6.7 Hz, 2H), 2.12 (m, 2H), 1.61 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 166.5, 148.9, 138.1, 128.8, 127.1, 121.3, 60.0, 58.4, 52.7, 29.8, 25.6, 14.3. MS (EI): 337(M^+, 2), 210 (66), 91(100). Anal. Calcd for $C_{22}H_{27}NO_2$ (337.41): C, 78.31; H, 8.58; N, 4.15. Found: C, 78.07; H, 8.82; N, 4.09.

Ethyl 2-[4-(*N*,*N*-Dibenzylamino)butyl]acrylate (19f). Ethyl (2-bromomethyl)acrylate[14] (1.2 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ ether 99:1−95:5, 66% yield, yellow oil. IR (neat): 2990 (vs), 2900 (s), 1720 (vs). ^{1}H-NMR ($CDCl_3$, 300MHz): δ 7.44 (m, 10 H), 6.17 (s, 1H), 5.49 (s, 1H), 4.23 (q, J = 7.1 Hz, 2H), 3.61 (s, 4H), 2.49 (t, J = 6.6 Hz, 2H), 2.28 (t, J = 7.4 Hz, 2H), 1.54 (m, 4H), 1.33 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.2, 140.9, 139.9, 128.7, 128.1, 126.9, 124.2, 60.4, 58.3, 53.0, 31.6, 26.5, 25.8, 14.2. MS (EI): 210 (93), 91 (100). Anal. Calcd for $C_{23}H_{29}NO_2$ (351.43): C, 78.60; H, 8.31; N, 3.98. Found: C, 78.90; H, 8.50; N, 3.88.

Ethyl 2-[4-(*N*,*N*-Diphenylamino)butyl]acrylate (19g). Ethyl (2-bromomethyl)acrylate[14] (1.0 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h, 62% yield, colorless oil. IR (neat): 2930 (vs), 1710 (vs), 1595 (vs), 1505 (vs). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.25 (m, 4H), 6.97 (m, 6H), 6.13 (s, 1H), 5.48 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.70 (t, J = 7.4 Hz, 2H), 2.32 (t, J = 7.6 Hz, 2H), 1.71 (m, 2H), 1.56 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 167.3, 148.3, 140.9, 129.4, 124.7, 121.3, 121.1, 60.7, 52.3, 31.8, 27.3, 26.2, 14.4. MS (EI): 323 (M^+, 22), 183 (14), 182 (100). Anal. Calcd for $C_{21}H_{25}NO_2$ (323.38): C, 77.99; H, 7.78; N, 4.33. Found: C, 78.12; H, 7.81; N, 4.33.

Ethyl 2-[4-[*N*-Benzyl-*N*-(4-pivaloxybutyl)amino]butyl]-acrylate (19h). Ethyl (2-bromomethyl)acrylate[14] (1.0 equiv) was used as electrophile; reaction conditions: −78 to 0 °C, 1 h; hexanes/ether 4:1 to 100% ether, 62% yield, colorless oil. IR (neat): 2820 (s), 1710 (vs), 1185 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.31 (m, 5H), 6.13 (s, 1H), 5.49 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 4.04 (t, J = 6.2 Hz, 2H,), 3.55 (s, 2H), 2.43 (m, 3H), 2.26 (m, 2H), 1.60 (m, 7H), 1.33 (t, J = 7.1 Hz, 3H), 1.20 (s, 9H). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 178.5, 167.3, 141.0, 140.1, 128.8, 128.3, 126.7, 124.3, 64.3, 60.5, 58.7, 53.6, 53.4, 38.7, 31.7, 27.2, 26.7, 26.6, 23.6, 14.2. MS (EI): 276 (42), 274 (31), 91 (100), 57 (18). Anal. Calcd for $C_{21}H_{37}NO_4$ (367.47): C, 68.63; H, 10.14; N, 3.81. Found: C, 68.55; H, 10.03; N, 3.91.

Acknowledgment. We thank the DFG (SFB 260) and the Fonds der Chemischen Industrie for generous financial support. We thank WITCO AG, BASF AG, BAYER AG, Chemetall, Sipsy, and Chiroscience for the generous gift of chemicals.

Supporting Information Available: Text giving experimental procedures and analytical data for compounds **4b**, **14d**,**e**, **18e**, **6**, **7**, **13**, **17**, and **19** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO960808V