

Journal of Organometallic Chemistry, 438 (1992) 11–27
 Elsevier Sequoia S.A., Lausanne
 JOM 22818

Preparation of polyfunctional diorganomercurials and their transmetallation to diorganozincs. Applications to the preparation of optically active secondary alcohols

Michael J. Rozema, Duddu Rajagopal, Charles E. Tucker and Paul Knochel¹

The Willard H. Dow Laboratories, Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055 (USA)

(Received March 6, 1992)

Abstract

Two new methods of preparation of functionalized diorganomercurials have been developed. The first method involves a substitution reaction of $(\text{ICH}_2)_2\text{Hg}$ with zinc-copper reagents $\text{FG-RCu}(\text{CN})\text{ZnI}$ in THF/DMF at -60°C . Functional groups such as an ester, nitrile, ketone, phosphonate, halide, and boronic ester are tolerated in this reaction. The second method involves a reductive transmetallation between polyfunctional organozinc halides and mercurous chloride (Hg_2Cl_2). This very convenient procedure provides a rapid route to various functionalized diorganomercurials in good yields (61–89% yield). The synthetic utility of these mercury organometallics is demonstrated. Their transmetallation with zinc dust (toluene, 80°C , 3–5 h) affords dialkylzincs which add enantioselectively to aldehydes in the presence of a catalytic amount (20 mol%) of the norephedrine derivative **13**. This transmetallation can also be used to prepare stereoselectively (*E*)-alkenylzinc halides (>98% *E*). Addition of $\text{Cl}(\text{H})\text{ZrCp}_2$ to (*E*)-5-chloropentenylzinc bromide in CH_2Cl_2 (25°C , 1 min) affords a 1,1-bimetallic of zinc and zirconium $\text{Cl}(\text{CH}_2)_4\text{CH}(\text{ZnBr})\text{ZrCp}_2(\text{Cl})$ which reacts stereoselectively with an aldehyde providing the (*E*)-disubstituted olefin (49% yield; 100% *E*).

Introduction

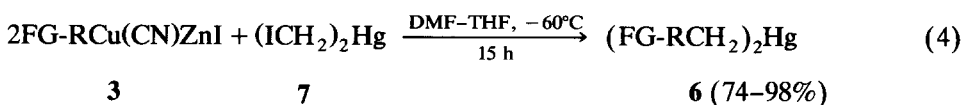
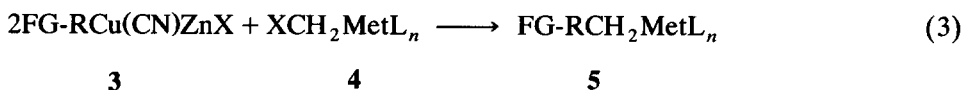
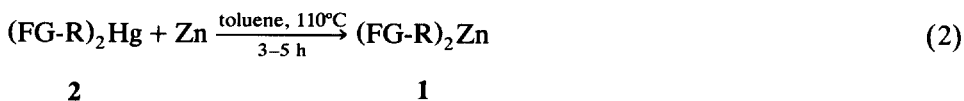
The preparation of optically pure secondary alcohols using the catalytic asymmetric addition of diethylzinc to aldehydes has been the subject of much study (eq. 1) [1]. However, extension to the use of other dialkylzincs has been limited [1,2] since no general route to these reagents was available. It should also be pointed out that alkylzinc halides cannot generally be used for the asymmetric addition to aldehydes since poor enantioselectivities are observed with these reagents [11,m].



Correspondence to: Professor P. Knochel.

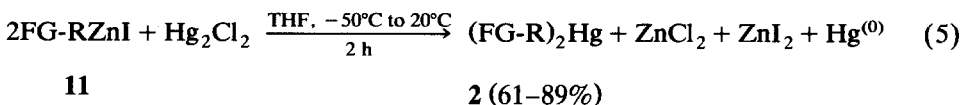
¹ Present address: Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse, W-3550 Marburg, Germany.

We report here a new approach to diorganozincs **1** involving transmetallation of diorganomercurials **2** with zinc dust (eq. 2). We also report two new methods of preparation of polyfunctional diorganomercurials. The first is a methylene homologation reaction (eqs. 3 and 4), and the second a reductive transmetallation of functionalized organozinc halides (eq. 5). Synthetic applications using the polyfunctional zinc reagents **1** for asymmetric synthesis, and for the preparation of 1,1-bimetallics will be described.



FG = ester, nitrile, ketone, phosphonate, halide, boronic ester, carbon-metal bond (metal = zinc or copper)

R: primary or secondary alkyl, benzyl



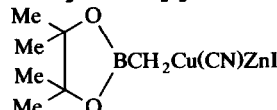
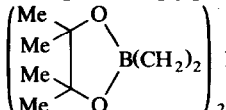
Results and discussion

The availability of a wide range of organic functionalities in organometallic compounds considerably extends the synthetic potential of these reagents in both organic and organometallic synthesis. Polyfunctional copper-zinc organometallics **3** bearing a variety of functionalities are now readily available [3], and their reactions with halomethyl [4] organometallics **4** would afford new functionalized organometallic derivatives of type **5** *via* a substitution reaction [5*] (eq. 3). A condition for the success of this reaction is that the carbon-metal bond (C-Met) must not undergo transmetallation with copper or zinc salts. We described here the first application of the general equation 3 in the preparation of polyfunctional dialkylmercury [6*] derivatives of type **6** (eq. 4). Thus the addition of bis(iodomethyl)mercury [4h-j] **7** (1.0 equiv.) to a DMF/THF solution of FG-RCu(CN)ZnX **3** (3.0 equiv.) at -60°C (15 h) affords the corresponding dialkylmercury compounds **6** in excellent yields (74-98%; Table 1) [7*]. Primary or secondary alkylcopper or benzylic copper reagents undergo the reaction smoothly (see entries 1-3). More importantly, the reaction displays a remarkable functional group tolerance and dialkylmercurials bearing an ester, cyano, ketone, phosphonate, halide or boronic ester group can be prepared (entries 4-10 of Table 1). The

* Reference number with an asterisk indicates a note in the list of references.

Table 1

Polyfunctional dialkylmercurials **6** prepared by the reaction of $(\text{ICH}_2)_2\text{Hg}$ (**7**) with the highly functionalized copper-zinc organometallics $\text{FG-RCu}(\text{CN})\text{ZnX}$ (**3**)

Entry	Cu-Zn reagent 3a-j ^b	Dialkylmercury 6a-j	Yield (%) ^a
1	BuCu(CN)ZnI	3a (Pent) ₂ Hg	6a 87
2	c-HexCu(CN)ZnI	3b (c-HexCH ₂) ₂ Hg	6b 95
3	PhCH ₂ Cu(CN)ZnBr	3c ^c (PhCH ₂ CH ₂) ₂ Hg	6c 98
4	AcO(CH ₂) ₃ Cu(CN)ZnI	3d (AcO(CH ₂) ₄) ₂ Hg	6d 87
5	EtO ₂ C(CH ₂) ₃ Cu(CN)ZnI	3e (EtO ₂ C(CH ₂) ₄) ₂ Hg	6e 98
6	NC(CH ₂) ₃ Cu(CN)ZnI	3f (NC(CH ₂) ₄) ₂ Hg	6f 96
7	Cl(CH ₂) ₄ Cu(CN)ZnI	3g (Cl(CH ₂) ₅) ₂ Hg	6g 95
8	PhCO(CH ₂) ₃ Cu(CN)ZnI	3h (PhCO(CH ₂) ₄) ₂ Hg	6h 95
9	(EtO) ₂ (O)P(CH ₂) ₂ Cu(CN)ZnBr	3i ^c ((EtO) ₂ (O)P(CH ₂) ₃) ₂ Hg	6i 74 ^d
10			6j 85

^a Unless otherwise indicated, all yields refer to isolated yields of chromatographed or distilled organomercury compounds having a purity of 95% or higher. The impurities are *ca.* 2% of (FG-R)₂Hg and *ca.* 2% of (FG-R-CH₂CH₂)₂Hg. ^b The organozinc halide has been prepared in DMF unless otherwise indicated. ^c This organozinc halide has been prepared in THF (see ref. 1). ^d This product has a purity of 90% and is contaminated with 5% of ((EtO)₂(O)P(CH₂)₂)₂Hg and 5% of ((EtO)₂(O)P(CH₂)₄)₂Hg.

choice of DMF as a co-solvent was crucial for the success of the reaction, since the use of THF alone leads to appreciable amounts of non-homologated dialkylmercury compounds (FG-R)₂Hg (*ca.* 16%). However, the use of a DMF/THF mixture (*ca.* 5:1) combined with a low reaction temperature leads to dialkylmercurials **6** contaminated by < 3% of the non-homologated dialkylmercury (FG-R)₂Hg and < 3% of the double methylene homologated dialkylmercury (FG-R-CH₂CH₂)₂Hg. The less reactive aryl- and alkynyl-copper derivatives **3**, as also the copper amides (R₂NCu) and lithium enolates, did not react with bis(iodomethyl)mercury **7** in a satisfactory manner. Of special interest was the reaction of **7** with the 1,4-dicopper-zinc reagent **8**, which led with high selectivity to the trimetallic derivative **9** (eq. 6a). The allylation of **9** with an excess of ethyl α -(bromomethyl)acrylate gave the bis-acrylate **10** in 80% isolated yield (eq. 6b).

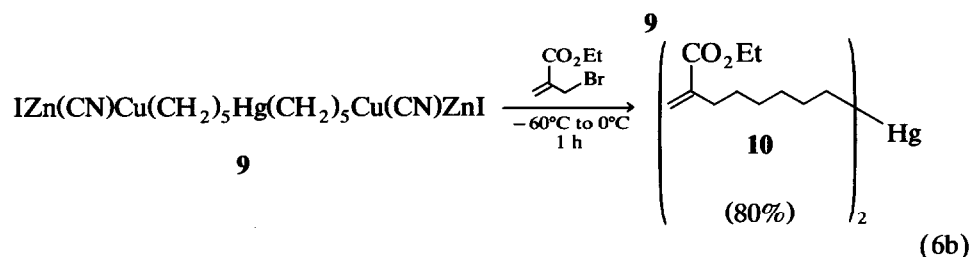
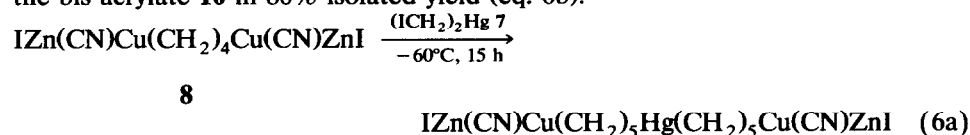


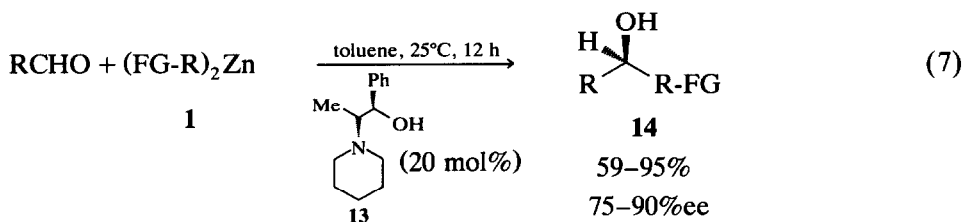
Table 2

Polyfunctional diorganomercurials **2** prepared by the reaction of Hg₂Cl₂ with the highly functionalized zinc organometallics FG-RZnX (**11**)

Entry	FG-RZnX	11	Diorganomercurial	2	Yield (%) ^a
1	BuZnI	11a	Bu ₂ Hg	2a	89
2	Cl(CH ₂) ₄ ZnI	11b	(Cl(CH ₂) ₄) ₂ Hg	2b	76
3	NC(CH ₂) ₅ ZnI	11c	(NC(CH ₂) ₅) ₂ Hg	2c	82
4	EtO ₂ C(CH ₂) ₄ ZnI	11d	(EtO ₂ C(CH ₂) ₄) ₂ Hg	6e	87
b5	AcO(CH ₂) ₄ ZnI	11e	(AcO(CH ₂) ₄) ₂ Hg	6d	61
6	HC≡C(CH ₂) ₃ ZnI	11f	(HC≡C(CH ₂) ₃) ₂ Hg	2d	70
7	PhCH ₂ ZnBr	11b	(PhCH ₂) ₂ Hg	2e	78
8	CH ₃ CH(OPiv)(CH ₂) ₃ ZnI	11h	(CH ₃ CH(OPiv)(CH ₂) ₃) ₂ Hg	2f	84
9	(<i>E</i>)-HexCH=CHLi	11i	(<i>E</i>)-(HexCH=CH) ₂ Hg	2g	61

^a Unless otherwise indicated, all yields refer to isolated yields of chromatographed or distilled organomercury compounds having a purity of 95% or higher. The impurities are *ca.* 2% of (FG-R)₂Hg and *ca.* 2% of (FG-R-CH₂CH₂)₂Hg.

During this work, we also attempted the transmetallation of alkylzinc halides with mercuric chloride [7*], and observed a very incomplete reaction. However, upon treating a THF suspension of mercurous chloride [8] Hg₂Cl₂ (1 equiv.) cooled to -50°C with a THF solution of an organozinc reagent [3] FG-RZnI **11** (2.5 equiv.) we observed the formation of a grey precipitate of Hg⁽⁰⁾. After the reaction mixture had been stirred at 25°C for 2 h, the corresponding diorganomercurials **2** were isolated in 61–89% yield (eq. 5 and Table 2). The reaction tolerates the presence of an ester, chloride, terminal alkyne [9] or nitrile. It also proceeds very well with a benzylzinc bromide (entry 7 of Table 2) and with an (*E*)-alkenyllithium. In the latter case, the addition of (*E*)-octenyllithium [10] has to be done at -90°C and gives the pure (*E*)-dialkenylmercurial **2g** (> 98% *E*; entry 9 of Table 2). The Bu₂Hg, **2a**, prepared by the mercurous chloride method, as well as (Hex)₂Hg **12a**, and ((CH₃)₂CH(CH₂)₂)₂Hg **12b**, obtained by the reaction of the corresponding magnesium reagent with HgBr₂ in THF, were converted to the corresponding dialkylzinc **1** by refluxing the dialkylmercurial **2** with zinc dust (10 equiv.) in toluene for 3–5 h [11]. The reaction of these dialkylzincs with an aldehyde (0.6 equiv.) in the presence of (1*S*, 2*R*)-(-)-1-phenyl-2-(1-piperidiny)propan-1-ol **13** (0.2 equiv.) at 25°C for 12 h gave the secondary alcohols **14a–e** in 59–95% yield and with a high enantioselectivity [12] (76–90% ee; see Table 3 and eq. 7). The enantiomeric excess of the alcohols **14** was determined by ¹H



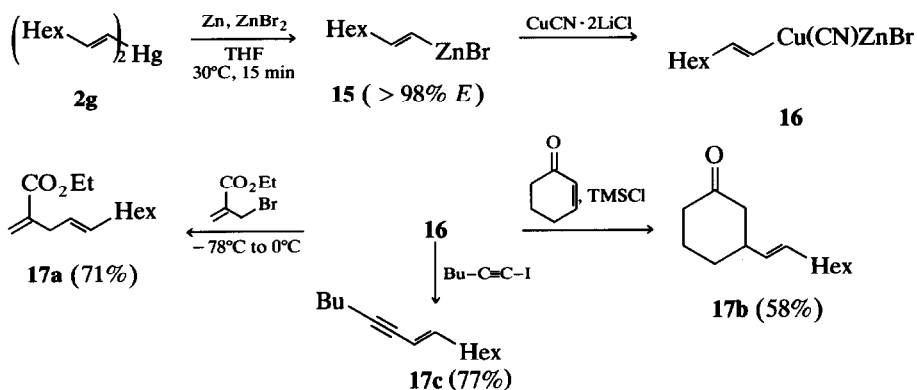
NMR analysis of the (*S*)-(+)-O-acetylmandelic ester [13]. Treatment of the ester-substituted dialkylzinc (EtOOC(CH₂)₄)₂Zn prepared from the functionalized dialkylmercurial **6e**, with benzaldehyde did not give the desired product under our

Table 3

Optically active secondary alcohols 14a–e obtained by the addition of dialkylzinc 1 prepared from the corresponding dialkylmercurials with aldehydes in the presence of 20 mol% of the amino-alcohol 13

Entry	(FG-R) ₂ Hg	Reaction conditions ^a (h, °C)	Aldehyde	Product	Yield (%) ^b	ee (%) ^c	
1	Bu ₂ Hg	2a	PhCHO	(S)-PhCH(OH)Bu	14a	82	90
2	2a	(2, 110)	c-HexCHO	(S)-c-HexCH(OH)Bu	14b	59	90
3	2a	(2, 110)	(E)-PhCH=CHCHO	(S)-(<i>E</i>)-PhCH=CH(OH)Bu	14c	95	76
4	Hex ₂ Hg	12a	PhCHO	(S)-PhCH(OH)Hex	14d	95	90
5	(Me ₂ CH(CH ₂) ₂) ₂ Hg	12b	PhCHO	(S)-PhCH(OH)(CH ₂) ₂ CH(CH ₃) ₂	14e	86	90

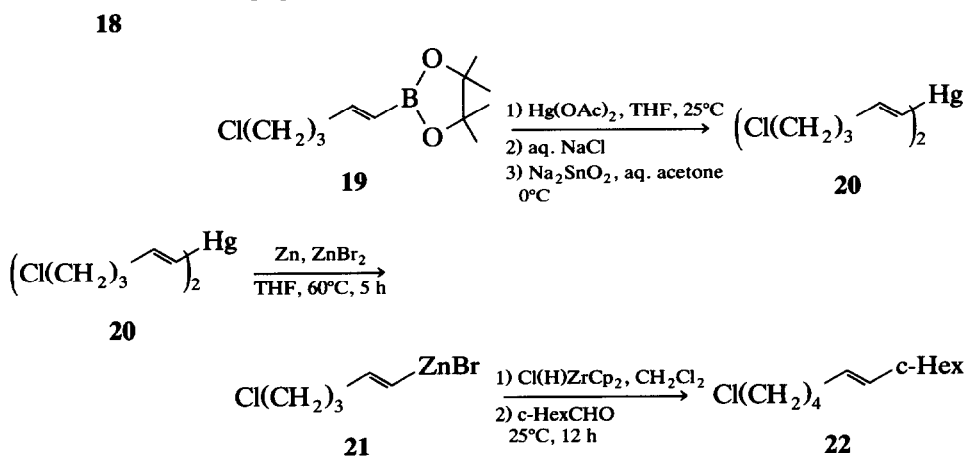
^a Reaction conditions used for the preparation of the dialkylzinc 1. ^b Isolated yield of analytically pure alcohol. ^c The enantiomeric excess has been determined by ¹H-NMR analysis of the (S)-(+)-O-acetylmandelic ester of 14.



Scheme 1

reaction conditions, showing that this chiral catalyst apparently does not tolerate the presence of functional groups. Whereas the direct insertion of zinc into (*E*)-octenyl iodide gives an *E/Z* mixture of octenylzinc iodides **15** (*E:Z*, ca. 65:35) [14], we found that the transmetalation of (*E*)-dioctenylmercury (**2g**) with zinc dust in the presence of zinc bromide gave **15** with >98% stereochemical purity (Scheme 1). The presence of ZnBr_2 catalyzes the transmetalation reaction and avoids the need to use high reaction temperatures, which lead to partial loss of the stereochemistry. Addition to $\text{CuCN} \cdot 2\text{LiCl}$ [3] to the reaction mixture gave the copper reagent **16**, which can be allylated with ethyl α -(bromomethyl)acrylate (-78°C to 0°C , 0.5 h) to give the dienic ester **17a** (>98% *E*) in 71% yield. Reaction of **16** with cyclohexenone in the presence of Me_3SiCl (2 equiv.; -78°C to 25°C , 12 h) gave the 3-substituted ketone **17b** in 58% yield. The coupling of **16** with 1-iodohexyne gave the alkyne **17c** (-70°C to -60°C , 18 h; 77%).

Preparation of a functionalized alkenylzinc bromide by this method is also possible. 5-Chloro-1-hexyne **18** was hydroborated with pinacolborane [15a] (2 $\text{Cl}(\text{CH}_2)_3\text{C}\equiv\text{CH} \xrightarrow[\text{CH}_2\text{Cl}_2, 0^\circ\text{C, 9 h}]{\text{pinacolborane}}$



Scheme 2

equiv.; CH_2Cl_2 , 0°C , 9 h) to afford the pinacol boronic ester **19** (99% *E*; 85% yield). The conversion of **19** into the bis-(alkenyl)mercury **20** by standard methods ((i) $\text{Hg}(\text{OAc})_2$ (1.0 equiv.), THF, 25°C , 0.25 h; (ii) saturated aqueous NaCl; (iii) Na_2SnO_2 (0.5 equiv.); acetone, H_2O , 0°C , 15 h)) proceeded in 61% overall yield. Treatment of **20** with Zn in the presence of ZnBr_2 (THF, 50°C , 5 h) gave the alkenylzinc bromide **21**, which after hydrozirconation ($\text{H}(\text{Cl})\text{ZrCp}_2$ (1 equiv.) 25°C , 1 min.) gave an intermediate 1,1-bimetallic reagent of zinc and zirconium ($\text{RCH}(\text{ZnBr})\text{ZrCp}_2\text{Cl}$) [**15b**]. The addition of cyclohexanecarboxaldehyde (0.8 equiv., 25°C , 12 h) led to a smooth olefination reaction, affording the (*E*)-chloroolefin **22** stereospecifically in moderate yields (49%; 100% *E*; Scheme 2).

Conclusion

We have reported two new preparations of polyfunctionalized dialkylmercurials $(\text{FG-R})_2\text{Hg}$. The transmetallation of these mercury organometallics with zinc furnishes dialkylzincs which add enantioselectively to aldehydes. Also, alkenylzinc bromides [16] can be obtained with high stereoselectivity and transmetallated to copper reagents which react satisfactorily with an enone or an alkynyl or allylic halide. An alkenylzinc bromide has also been hydrozirconated to give a 1,1-bimetallic of zirconium and zinc. This reagent reacts stereospecifically with an aldehyde to afford a pure (*E*)-olefin.

Experimental section

Unless otherwise indicated, all reactions were carried out under argon. Solvents (THF and diethyl ether) were dried over and freshly distilled from sodium/benzophenone. The zinc dust was obtained from Aldrich Chemical Company, Inc. (-325 mesh). Reactions were monitored by GLC or TLC (thin layer chromatography) of aliquots taken from the reaction mixture and quenched with saturated aqueous NH_4Cl . Unless otherwise indicated, the reactions were worked up as follows: the reaction mixture was added to a stirred mixture of ether and saturated aqueous NH_4Cl . The mixture was then filtered to remove the insoluble salts, and the two layers were separated. The aqueous layer was extracted twice with ether. The combined ethereal extracts were then washed with distilled water and saturated sodium chloride, dried over MgSO_4 and filtered, and the solvent was removed by rotary evaporation.

Fourier transform infrared spectra (FT-IR) were recorded under nitrogen on sodium chloride plates on a Nicolet 5DXB FT-IR spectrometer; IR frequencies are reported in wave number units (cm^{-1}). The ^1H NMR spectra were recorded on a Bruker WM-300 (300 MHz) spectrometer. Chemical shifts are reported as δ values ppm relative to internal tetramethylsilane. Coupling constants are reported in Hertz (Hz). ^{13}C NMR spectra were recorded on a Bruker WM-300 (75.5 MHz) spectrometer. Chemical shifts are reported as δ values (ppm) relative to chloroform-*d* (δ 77.0) as an internal reference. Mass spectra (MS) and exact mass data were recorded on a VG-70-250 S mass spectrometer. Chemical ionization (CI) and electron impact ionization (EI) were used, as indicated.

The starting materials, the zinc-copper organometallics **3a-h** [3] **3i** [17] and **3j** [18], ethyl α -(bromomethyl)acrylate [19], (*E*)-1-octenyl iodide [20], (1*S*,2*R*)-(-)-1-

phenyl-2-(1-piperidiny)-propan-1-ol [12], $\text{H}(\text{Cl})\text{ZrCp}_2$ [21], were prepared by published methods.

Preparation of bis(iodomethyl)mercury [4h-j]

To a solution of diiodomethane (40.2 g, 150 mmol) in 50 mL THF was added diethylzinc (7.6 mL, 74 mmol) at such a rate that the temperature remained below -60°C (ca. 10 min.). After 30 min stirring at this temperature, the mixture was warmed to 0°C and stirred for an additional 30 min. This solution of bis(iodomethyl)zinc was then transferred *via* a cannula to a solution of mercuric bromide (18.0 g, 50 mmol) in 30 mL THF cooled to -20°C . The mixture was allowed to warm to room temperature, then stirred for 16 h, and added to a mixture of saturated ammonium chloride solution (200 mL) and benzene (200 mL). The aqueous layer was extracted twice more with benzene (200 mL). The organic layers were combined, washed with saturated aqueous sodium thiosulfate (100 mL), and dried over magnesium sulfate. After evaporation of the solvent, the product was recrystallized from chloroform to give 19.3 g (80%) of bis(iodomethyl)mercury (m.p. $79-80^\circ\text{C}$, litt. [4h-j], $80-82^\circ\text{C}$).

Preparation of functionalized alkylzinc iodides in DMF

A solution of the alkyl iodide (10 mmol) in dry DMF (3 mL) was added to a suspension of cut zinc foil (Alfa, 1.3 g, 20 mmol) previously activated with dibromoethane (200 mg) in DMF (2 mL). During the addition, the reaction temperature rose to 35°C . The formation of the alkylzinc halide was complete after 1–2 h of stirring at 25°C , as indicated by the GLC analysis of hydrolyzed aliquots.

Preparation of functionalized copper derivatives FG-RCu(CN)ZnX 3 and their conversion to methylene homologated polyfunctional dialkylmercury compounds of type 6

The DMF solution of the alkylzinc halide prepared as above was added at -40°C to a solution of CuCN (1.78 g, 20 mmol) and LiCl (1.68 g, 40 mmol) in a mixture of dry DMF (40 mL) and dry THF (10 mL). The resulting white suspension was warmed to 0°C and after 5 min. cooled to -60°C . Bis (iodomethyl)mercury (1.45 g, 3 mmol) was added from a powder funnel. After 15 h at -60°C , the excess of the copper-zinc organometallic was decomposed with methanol (2 mL), and the mixture warmed to 0°C and worked up as usual. The resulting crude oil was purified by distillation or flash chromatography to afford pure dialkylmercury 6 in 74–98% yield (Table 1).

Determination of FG-RI / FG-RCH₂I / FG-R(CH₂)₂I ratios by iodolysis

Iodine (100 mg) was added to a solution of dialkylmercury (10 mg) in ether (1 mL), followed after 5 min. by a saturated aqueous sodium thiosulfate (1 mL). The layers were separated and the organic layer analyzed by GLC (DB5, 15 m column) to determine the product ratio.

Products 6a–6j (Table 1)

Dipentylmercury (6a) [22]. 890 mg (87%) as a colorless oil, b.p. $56-59^\circ\text{C}$ at 0.25 mm Hg FG-RI/FG-CH₂I/FG-R(CH₂)₂I ratio 2.5/95/2.5; ^1H NMR (CDCl_3 , 300 MHz): δ 1.84 (t, 2H, $J = 7.3$ Hz), 1.35–1.29 (m, 4H), 1.05 (t, 2H, $J = 7.4$ Hz), 0.89 (t, 3H, $J = 6.8$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 44.4, 37.8, 28.4, 22.5, 14.1.

Bis-(cyclohexylmethyl)mercury (6b). 1.10 g (95%) as a colorless oil, purified by flash chromatography (hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 1/98/1; ¹H NMR (CDCl₃, 300 MHz): δ 2.27–2.09 (m, 2H), 1.85–1.55 (m, 8H), 1.30–0.81 (m, 12H), 1.03 (d, 4H, *J* = 6.1 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 54.1, 39.3, 38.8, 26.8, 26.3; IR (neat) 2892 (s), 1445 (s), 1290 (m), 1168 (m), 888 (m) cm⁻¹. Mass (EI, 70 eV): 396 (*M*⁺, 5), 97 (100), 55 (40), 41 (8). HRMS calculated for C₁₄H₂₆Hg: 396.1741. Found: 396.1730.

Bis-(2-phenylethyl)mercury (6c). 1.20 g (98%) as a colorless oil; purified by flash chromatography (hexane) FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 3.7/95/1.3; ¹H NMR (CDCl₃, 300 MHz): δ 7.31–7.26 (m, 4H), 7.19–7.17 (m, 6H), 3.05 (t, 4H, *J* = 7.8 Hz), 1.29 (t, 4H, *J* = 7.8 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 147.4, 128.5, 128.0, 125.5, 45.0, 34.8; IR (neat): 3059 (m), 3022 (s), 2998 (s), 1600 (m), 1493 (s), 1451 (s), 749 (s), 698 (s). Mass (EI, 70 eV): 412 (*M*⁺, 4), 182 (34), 105 (100), 91 (100), 84 (24), 77 (27), 65 (12), 51 (15), 49 (32). HRMS Found: 412.1127. C₁₆H₁₈Hg calcd.: 412.1115.

Bis-(4-acetoxybutyl)mercury (6d). 1.12 g (87%) as a colorless oil; purified by flash chromatography (10% ethyl acetate in hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 2.5/95/2.5; ¹H NMR (CDCl₃, 300 MHz): δ 4.08 (t, 4H, *J* = 6.8 Hz), 2.05 (s, 6H), 1.92–1.82 (m, 4H), 1.70–1.58 (m, 4H), 1.06 (t, 4H, *J* = 7.61 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 170.8, 64.2, 43.3, 33.9, 24.9, 20.7; IR (neat): 2926 (s), 2851 (s), 1737 (s), 1365 (s), 1246 (s), 1033 (m) cm⁻¹. MS (EI, 70 eV): 432 (*M*⁺, 1), 115 (43), 101 (10), 86 (12), 61 (23), 55 (87), 43 (100). HRMS calculated for Found: 432.1227. C₁₂H₂₂HgO₄ calcd.: 432.1224. Anal. Found: C, 33.43; H, 5.19. C₁₂H₂₂HgO₄ calcd.: C, 33.44; H, 5.14%.

Bis-(4-carboethoxybutyl)mercury (6e). 1.35 g (98%) as a colorless oil, bulb to bulb distillation (bath 250°C, 0.1 mmHg), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 2.5/95/2.5; ¹H NMR (CDCl₃, 300 MHz): δ 4.12 (q, 4H, *J* = 7.2 Hz), 2.31 (t, 4H, *J* = 7.4 Hz), 1.89–1.79 (m, 4H), 1.70–1.60 (m, 4H), 1.25 (t, 6H, *J* = 7.1 Hz), 1.02 (t, 4H, *J* = 7.5 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 173.7, 59.9, 43.4, 34.0, 30.2, 28.2, 14.1; IR (neat): 2979 (s), 2927 (s), 2851 (s), 1737 (s), 1181 (s), 1036 (s) cm⁻¹. Mass (EI, 70 eV): 460 (*M*⁺, 2.9), 129 (83), 115 (17), 101 (100), 86 (20), 83 (42), 59 (19), 55 (41), 49 (30), 43 (15), 41 (17). HRMS Found 460.1536. C₁₄H₂₆HgO₄ calcd.: 460.1537.

Bis-(4-cyanobutyl)mercury (6f). 1.05 g (96%) as a colorless oil; purified by flash chromatography (10% ethyl acetate in hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 2.5/95/2.5; ¹H NMR (CDCl₃, 300 MHz): δ 2.35 (t, 4H, *J* = 7.0 Hz), 1.98–1.88 (m, 4H), 1.71–1.62 (m, 4H), 1.05 (t, 4H, *J* = 7.8 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 119.7, 41.9, 30.0, 27.4, 16.2; IR (neat) 2924 (s), 2854 (s), 2244 (s), 1424 (m) cm⁻¹. Mass (EI, 70 eV): 366 (*M*⁺, 3), 86 (11), 82 (100), 55 (62), 54 (40), 49 (17), 43 (17), 41 (37). HRMS Found: 366.1031. C₁₀H₁₆N₂Hg calcd.: 366.1020.

Bis-(5-chloropentyl)mercury (6g). 1.03 g (95%) as a colorless oil, purified by flash chromatography (hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 0/100/0; ¹H NMR (CDCl₃, 75.5 MHz): δ 3.54 (t, 4H, *J* = 6.8 Hz), 1.91–1.75 (m, 4H), 1.55–1.42 (m, 4H), 1.07 (t, 4H, *J* = 7.5 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 45.2, 43.9, 32.4, 28.0; IR (neat) 2924 (s), 2844 (s), 1457 (m), 722 (m), 598 (m). Mass (EI, 70 eV): 412 (*M*⁺, 0.1), 70 (14), 69 (100), 54 (14), 41 (46). HRMS Found: 412.0657. C₁₀H₂₀Cl₂Hg calcd.: 412.0648.

Bis-(4-benzoylbutyl)mercury (6h). 1.49 g (85%) as a white solid (m.p. 38–39°C),

purified by flash chromatography (4% ethyl acetate in hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 3/94/3; ¹H NMR (CDCl₃, 300 MHz): δ 2.98 (t, 4H, *J* = 7.2 Hz), 1.96–1.82 (m, 4H), 1.80–1.62 (m, 4H), 1.09 (t, 4H, *J* = 7.4 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 200.6, 137.2, 132.7, 128.5, 128.0, 43.7, 38.4, 29.8, 28.5. IR (neat): 3058 (m), 2924 (s), 1679 (s), 1586 (s), 1370 (s), 1205 (s), 1002 (m), 688 (s) cm⁻¹. Mass (EI, 70 eV): 524 (*M*⁺, 0.4), 161 (53), 105 (100), 77 (28), 51 (6). HRMS calculated for C₂₂H₂₆HgO₂: 524.1639. Found: 524.1667.

Bis-(3-diethylphosphonopropyl)mercury (**6i**). 1.24 g (74%) as a colorless oil, purified by flash chromatography (5% methanol in ethyl acetate), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 5/90/5; ¹H NMR (CDCl₃, 75.5 MHz): δ 4.15–4.02 (m, 8H), 2.14–2.04 (m, 4H), 1.82–1.71 (m, 4H), 1.32 (t, 12H, *J* = 7.06 Hz), 1.26–1.06 (m, 4H); ¹³C NMR (CDCl₃, 75.5 MHz): 60.95 (d, *J*(P,C) = 6.1 Hz), 43.94 (d, *J*(P,C) = 16.9 Hz), 30.60 (d, *J*(P,C) = 136.3 Hz), 21.42 (d, *J*(P,C) = 4.8 Hz), 16.16 (d, *J*(P,C) = 5.4 Hz). IR (neat): 2981 (s), 2905 (s), 1391 (m), 1233 (s), 1027 (s), 788 (m) cm⁻¹. Mass (EI, 70 eV): 560 (*M*⁺, 6), 272 (12), 257 (11), 244 (14), 193 (12), 179 (95), 152 (86), 138 (44), 109 (86), 97 (25), 91 (22), 81 (59), 65 (28), 55 (17), 41 (48). HRMS Found: 560.1390. C₁₄H₃₂HgP₂O₆ calcd.: 560.1380.

Bis-(2-pinacolborylethyl)mercury (**6j**). 1.30 g (85%) as a colorless oil, purified by flash chromatography (5% ethyl acetate in hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 2.5/95/2.5; ¹H NMR (CDCl₃, 300 MHz): δ 1.25 (s, 24H), 1.21 (t, 4H, *J* = 7.5 Hz), 1.02 (t, 4H, *J* = 7.5 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 82.7, 34.9, 24.7, 9.3. IR (neat): 2977 (s), 2901 (s), 1370 (s), 1165 (s), 964 (m). Mass (EI, 70 eV): 512 (*M*⁺, 11), 195 (17), 169 (13), 155 (22), 141 (11), 127 (11), 83 (100), 69 (17), 57 (17), 55 (33), 49 (13), 41 (34). HRMS calculated for C₁₆H₃₂B₂HgO₄: 512.2193. Found: 512.2202.

Bis-(7-carboethoxy-7-octenyl)mercury (**10**). 400 mg (80%) as a colorless oil, purified by flash chromatography (1% ethyl acetate in hexane), FG-RI/FG-RCH₂I/FG-R(CH₂)₂I ratio 0/100/0. ¹H NMR (CDCl₃, 300 MHz): δ 6.12 (s, 2H), 5.50 (s, 1H), 4.20 (q, 4H, *J* = 7.1 Hz), 2.29 (t, 4H, *J* = 7.5 Hz), 1.85–1.80 (m, 4H), 1.48–1.20 (m, 12H), 1.30 (t, 6H, *J* = 7.1 Hz), 1.04 (bt, 4H, *J* = 7.4 Hz); ¹³C NMR (CDCl₃, 75.5 MHz): δ 167.4, 141.3, 124.0, 60.4, 44.3, 35.2, 31.9, 29.0, 28.6, 28.4, 14.2; IR (neat) 2925 (s), 1718 (s), 1629 (m), 1463 (m), 1031 (m), 733 (s) cm⁻¹. Mass (CI, CH₄): 597 (MC₂H₅⁺, 3), 569 (MH⁺, 1), 387 (12), 385 (37), 213 (11), 203 (11), 201 (11), 185 (57), 183 (98), 169 (12), 157 (20), 137 (49), 123 (11), 115 (12), 109 (100), 95 (19), 83 (18). HRMS calculated for C₂₂H₃₈HgO₄H: 569.25555. Found: 569.2526.

Typical procedure for the preparation of dialkylmercurials (FG-R)₂Hg (2) by the reaction of FG-RZnX (11) with Hg₂Cl₂

A dry, three-necked flask equipped with an argon inlet, a magnetic stirring bar and a low temperature thermometer was charged with Hg₂Cl₂ (1.89 g, 4 mmol) and flushed with argon. Dry THF (20 mL) was added and the resulting suspension was cooled to -50°C. A THF solution of the organozinc halide FG-RZnX (10 mmol) prepared as previously described [3] was added dropwise. A grey precipitate was formed immediately and the mixture was stirred for 0.5 h at -50°C and then allowed to reach room temperature. After 2 h stirring, the mixture was treated with aqueous NH₄Cl (100 mL) and extracted with ether (3 × 50 mL). The combined organic layers were washed successively with water (100 mL) and brine (100

mL) and dried over MgSO_4 . Evaporation of the solvents and purification of the resulting crude oil by flash chromatography afforded the pure dialkylmercurial **2**.

Polyfunctional dialkylmercurials 2a–2g (Table 2).

Dibutylmercury 2a. 1.12 g (89%) as a colorless oil; purified by flash chromatography (hexane). ^1H NMR (CDCl_3 , 300 MHz): δ 1.9–1.78 (m, 4H), 1.41–1.3 (m, 4H), 1.05 (t, 4H, $J = 7.4$ Hz), 0.9 (t, 6H, $J = 7.3$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 44.1, 31.1, 28.4, 14.0; IR (neat): 2954 (s), 2921 (s), 2869 (s), 2846 (s), 1453 (s), 1377 (s), 1240 (s), 1069 (s) cm^{-1} . Mass (EI, 70 eV): 316 (M^+ , 6.7), 257 (1.2), 228 (1.3), 202 (1.0), 86 (2.9), 57 (100), 41 (30). HRMS Found: 316.113. $\text{C}_8\text{H}_{18}\text{Hg}$ calcd.: 316.1114.

Bis-(4-chlorobutyl)mercury 2b. 1.16 g (76%) as a colorless liquid; purified by flash chromatography (hexane): ^1H NMR (CDCl_3 , 300 MHz): δ 3.55 (t, 4H, $J = 6.6$ Hz), 2.0–1.85 (m, 4H), 1.85–1.6 (m, 4H), 1.05 (t, 4H, $J = 6.6$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 44.7, 42.7, 37.8, 25.8; IR (neat): 2950 (s), 2926 (bs), 2851 (s), 721 (s), 649 (s) cm^{-1} ; Mass (EI, 70 eV): 384 (M^+ , 5), 91 (60), 84 (39), 55 (100), 49 (46), 41 (19). HRMS Found: 384.0318. $\text{C}_8\text{H}_{16}\text{Cl}_2\text{Hg}$ calcd.: 384.0335. Anal. Found: C, 25.12; H, 4.24; Cl, 18.32. $\text{C}_8\text{H}_{16}\text{Cl}_2\text{Hg}$ calcd.: C, 25.04; H, 4.20; Cl, 18.47%.

Bis-(5-cyanopentyl)mercury 2c. 1.27 g (82%) as a colorless oil; purified by flash chromatography (8% ethyl acetate: hexane); ^1H NMR (CDCl_3 , 300 MHz): δ 2.35 (t, 4H, $J = 7.0$ Hz), 1.80–1.90 (m, 4H), 1.61–1.75 (m, 4H), 1.42–1.58 (m, 4H), 1.07 (t, 4H, $J = 7.6$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 119.4, 43.4, 33.9, 27.6, 24.9, 16.8; IR (neat): 2925 (bs), 2846 (s), 2244 (s), 1457 (s), 1424 (s) cm^{-1} ; Mass (EI, 70 eV): 394 (M^+ , 3.4), 96 (100), 69 (29), 55 (32), 41 (17). HRMS Found: 394.1324. $\text{C}_{12}\text{H}_{20}\text{N}_2\text{Hg}$ calcd.: 394.1332.

Bis-(4-pentynyl)mercury 2d. 0.93 g (70%) as a colorless liquid; purified by flash chromatography (hexane); ^1H NMR (CDCl_3 , 300 MHz): δ 2.28–2.17 (m, 8H), 2.05 (t, 2H, $J = 2.5$ Hz), 1.07 (t, 4H, $J = 7.1$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 86.4, 69.5, 40.6, 28.7, 22.6; IR (neat): 3301 (bs), 2910 (bs), 2850 (s), 2112 (s), 1427 (s), 1334 (s), 1240 (s) cm^{-1} ; Mass (EI, 70 eV): 337 (M^+ , 0.1), 308 (2.7), 297 (0.2), 269 (9.5), 106 (4.2), 84 (26), 67 (100), 49 (33.8). HRMS Found: 337.0866. $\text{C}_{10}\text{H}_{14}\text{HgH}$ calcd.: 337.0880.

Bis-(benzyl)mercury 2e. 1.19 g (78%) as a white crystalline solid, m.p. 109°C; purified by flash chromatography; ^1H NMR (CDCl_3 , 300 MHz): δ 7.24–7.13 (m, 4H), 7.1–6.92 (m, 6H), 2.43 (s, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 144.3, 128.2, 128.1, 127.9, 123.1, 46.6; IR (KBr): 3058 (bs), 3028 (s), 2982 (s), 1600 (m), 1490 (s), 1458 (s), 749 (s), 695 (s) cm^{-1} ; Mass (EI, 70 eV): 384 (M^+ , 2), 182 (10), 104 (4), 91 (100), 65 (16). HRMS Found: 384.0807. $\text{C}_{14}\text{H}_{14}\text{Hg}$ calcd.: 384.0801.

Bis-(4-pivaloyloxypentyl)mercury 2f. 1.82 g (84% as a colorless liquid; purified by flash chromatography (15% ethyl acetate: hexane). ^1H NMR (CDCl_3 , 300 MHz): δ 4.85–4.93 (m, 2H), 1.45–1.9 (m, 8H), 1.2 (m, 24H), 1.04 (t, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 177.8, 70.2, 43.7, 41.5, 38.6, 27.1, 24.4, 19.8; IR (neat): 2974 (s), 2932 (s), 2873 (s), 2854 (s), 1724 (s), 1480 (s), 1459 (s), 1378 (s), 1285 (s), 1167 (s), 1124 (s) cm^{-1} ; Mass (CI with ammonia): 545 (M^+ , 14.1), 518 (12.7), 390 (52.2), 316 (73.3), 197 (100), 171 (78), 132 (6.8), 102 (18), 85 (23). HRMS Found: 545.2556. $\text{C}_{20}\text{H}_{38}\text{O}_2\text{HgH}$ calcd.: 545.2554.

(E)-Bis-(1-octenyl)mercury 2g. 1.01 g (61%) as a colorless liquid, Kugelrohr distillation (250°C, 0.1 mmHg). ^1H NMR (CDCl_3 , 300 MHz): δ 6.2 (dt, 2H,

$J(1,2) = 18.8$ Hz, $J(1,3) = 1.4$ Hz), 5.78 (dt, 2H, $J(2,3) = 6.3$ Hz), 2.1–2.2 (m, 4H), 1.19–1.45 (m, 16H), 0.9 (t, 6H, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 158.2, 150.2, 37.7, 31.8, 29.3, 28.9, 22.6, 14.1; IR (neat): 2957 (s), 2923 (s), 2871 (s), 2853 (s), 1597 (s), 1471 (s), 986 (s) cm^{-1} ; Mass (CI with ammonia): 425 ($M\text{H}^+$, 3.7), 330 (100), 235 (5), 111 (10), 81 (9). HRMS Found: 425.2131. $\text{C}_{16}\text{H}_{30}\text{HgH}$ calcd.: 425.2132. Anal. Found: C, 45.62; H, 7.07. $\text{C}_{16}\text{H}_{30}\text{Hg}$ calcd.: C, 45.43; H, 7.16%.

Dihexylmercury **12a** and bis-(3-methylbutyl)mercury **12b** were prepared from the corresponding organomagnesium bromide according to ref. 7 in 72% and 67% yield respectively.

General method of preparation of enantiomerically enriched secondary alcohols; preparation of (S)-1-phenylpentanol (14a).

A three-necked flask equipped with a thermometer, a septum, and a magnetic stirring bar was charged with zinc dust (3.25 g, 50 mmol (Aldrich –325 mesh)) and flushed with argon. Dibromoethane (ca. 200 mg) in dry THF (5 mL) was added and the mixture was heated for a few seconds to reflux with a heat gun (three times). Chlorotrimethylsilane (ca. 0.1 mL) was added and the zinc suspension was stirred for 5 min. The stirring was stopped and the zinc powder allowed to settle out. The THF was removed with a syringe and the zinc dust washed twice with THF (5 mL) to remove any zinc salts and dried *in vacuo* by heating with a heat gun (ca. 10 min, 0.1 mmHg). A solution of dibutylmercury (1.57 g, 5.0 mmol) in toluene (2 mL) was added and the mixture was refluxed for 2 hours at 110°C. The resulting solution of dibutylzinc was added from a syringe to *N,N*-dibutyl (1*R*, 2*S*)-(+)-norephedrine [14] (158 mg, 0.6 mmol) in toluene (0.6 mL). The solution was warmed slowly to 40°C and then cooled to room temperature. Benzaldehyde (310 mg, 3 mmol) was added and the mixture was stirred overnight at 25°C. After the usual work-up and evaporation of the solvents, the residue was purified by flash chromatography (ethyl acetate: hexane, 5:95) to afford (*S*)-1-phenylpentanol (400 mg, 82% yield), see ref. 1t. $[\alpha]_{\text{D}}^{25} = -36.67^\circ$ ($c = 2.19$, benzene) 90% ee, m.p. 31–32°C; determined by converting **14a** into the *O*-acetylmandelic ester derivative [13] performing a ^1H NMR analysis. ^1H NMR (CDCl_3 , 300 MHz): δ 7.36–7.24 (m, 5H), 4.70–4.64 (m, 1H), 1.83–1.70 (m, 3H), 1.43–1.24 (m, 4H), 0.89 (brt, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 145.1, 128.3, 127.4, 125.9, 74.5, 38.7, 27.9, 22.5, 13.9.

(*S*)-(-)-1-Cyclohexylpentanol (**14b**) [23]. Purified by flash chromatography (ethyl acetate: hexane, 2:98), $[\alpha]_{\text{D}}^{25} = -16.31^\circ$ ($c = 1.98$, C_6H_6); 90% ee. ^1H NMR (CDCl_3 , 300 MHz): δ 3.39–3.34 (m, 1H), 1.85–1.71 (m, 3H), 1.70–1.62 (m, 2H), 1.55–0.98 (m, 15H), 0.88 (brt, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 75.6, 43.5, 33.6, 29.1, 28.0, 27.6, 26.4, 26.2, 26.1, 22.6, 13.7.

(*S*)-(+)-1-Phenyl-1-hepten-3-ol (**14c**) [24]. Purified by flash chromatography (ethyl acetate: hexane, 5:95), $[\alpha]_{\text{D}}^{25} = +3.52^\circ$ ($c = 3.95$, benzene) 76% ee; ^1H NMR (CDCl_3 , 300 MHz): δ 7.41–7.21 (m, 5H), 6.57 (d, 1H, $J = 15.9$ Hz), 6.23 (dd, 1H, $J = 6.8$ Hz, $J = 15.9$ Hz), 4.30–4.26 (m, 1H), 1.68–1.56 (m, 3H), 1.44–1.32 (m, 4H), 0.92 (brt, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 132.8, 130.1, 128.5, 127.5, 126.4, 72.9, 37.1, 27.6, 22.6, 13.9.

(*S*)-(-)-1-Phenylheptanol (**14d**) [25]. Purified by flash chromatography (ethyl acetate: hexane, 2:98) $[\alpha]_{\text{D}}^{25} = -27.79^\circ$ ($c = 4.80$, benzene); 90% ee. ^1H NMR (CDCl_3 , 300 MHz): δ 7.38–7.25 (m, 5H), 4.68–4.64 (m, 1H), 1.85–1.67 (m, 3H), 1.48–1.15 (m, 8H), 0.88 (brt, 3H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 144.9, 128.2, 127.2, 125.8, 74.5, 39.0, 31.7, 29.1, 25.7, 22.5, 13.9.

(*S*)-(-)-5-Methyl-1-phenylpentanol (**14e**) [26]. Purified by flash chromatography (ethyl acetate:hexane, 5:95), m.p. 32–34°C; $[\alpha]_D^{25} = -33.23^\circ$ ($c = 3.41$, benzene) 90% ee. $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 7.43–7.25 (m, 5H), 4.67–4.62 (m, 1H), 1.83–1.76 (m, 3H), 1.60–1.51 (m, 1H), 1.39–1.29 (m, 1H), 1.27–1.12 (m, 1H), 0.88 (d, 3H, $J = 1.6$ Hz), 0.86 (d, 3H, $J = 1.6$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 145.0, 128.2, 127.2, 125.9, 74.6, 36.8, 34.8, 27.9, 22.4.

Preparation of (E)-octenylzinc bromide (15) from (E)-bis-(octenyl)mercury 2g and its reactions with electrophiles

A dry, three-necked flask equipped with an argon inlet, a low temperature thermometer, an addition funnel and a magnetic stirring bar was charged with zinc dust (650 mg, 10 mmol) and flushed with argon. The zinc powder was activated as described above with dibromoethane (*ca.* 200 mg) and chlorotrimethylsilane (*ca.* 0.1 mL) in dry THF (2 mL). *E*-Dioctenylmercury (422 mg, 1 mmol) in THF (1 mL) was added dropwise at 25°C. After 15 min of stirring at 25–30°C, the GLC analysis of a hydrolyzed reaction aliquot indicates complete formation of the alkenylzinc bromide (**15**). The mixture was diluted with THF (2 mL) and allowed to settle. The THF solution of **15** was transferred with a syringe to a solution of CuCN (0.18 g, 2 mmol) and LiCl (0.169 g, 4 mmol) in THF (4 mL) at –60°C. The mixture was warmed to 0°C and then cooled to –60°C. The electrophile (0.7 equiv.) was added and the formation of the product was monitored by GLC analysis of an aliquot. The mixture was then worked up, and the residue purified by flash chromatography.

(*E*)-Ethyl-2-(non-2-enyl)-propenoate (**17a**). 0.22 g (71%) as a colorless oil. Purified by flash chromatography (1% ethyl acetate:hexane). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 6.15 (m, 1H), 5.53 (m, 1H), 5.32–5.53 (m, 2H), 4.2 (q, 2H, $J = 7.1$ Hz), 3.0 (d, 2H, $J = 5$ Hz), 2.05 (m, 2H), 1.4–1.19 (m, 11H), 0.9 (t, 3H, $J = 7.1$ Hz); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 166.9, 140.1, 133.1, 126.2, 124.3, 60.4, 34.6, 32.4, 31.6, 29.3, 28.7, 22.5, 14.1, 13.9; IR (neat) 2979 (s), 2958 (s), 2926 (s), 2873 (s), 2853 (s), 1720 (s), 1633 (s), 1322 (s), 1115 (s), 970 (s) cm^{-1} . Mass (EI, 70 eV): 224 (10), 181 (4), 151 (22), 139 (100), 111 (84), 79 (62), 55 (48), 41 (47); HRMS Found: 224.1781. $\text{C}_{14}\text{H}_{24}\text{O}_2$ calcd.: 224.1776.

(*E*)-3-(octenyl)-cyclohexan-1-one (**17b**). 0.17 g (58%) as a colorless oil. Purified by flash chromatography (5% ethyl acetate:hexane). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 5.3–5.5 (m, 2H), 1.8–2.5 (m, 7H), 1.37–1.78 (m, 2H), 1.18–1.42 (m, 10H), 0.9 (t, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 210.9, 132.8, 129.9, 47.6, 41.4, 41.1, 32.3, 31.6, 31.5, 29.3, 28.6, 24.8, 22.5, 13.96. IR (neat): 2955 (s), 2908 (s), 2870 (s), 2855 (s), 1715 (s), 1465 (s), 1447 (s), 1221 (s), 966 (s) cm^{-1} . Mass (EI, 70 eV): 208 (M^+ , 9), 193 (2), 150 (3.6), 123 (40), 110 (100), 95 (38), 81 (23), 67 (34), 55 (39), 41 (28). HRMS calculated for $\text{C}_{14}\text{H}_{20}\text{O}$: 208.1827. Found: 208.1832.

Tetradec-7-en-5-yne (**17c**). 0.20 g (77%) as a colorless oil. Purified by flash chromatography (3% ethyl acetate:hexane). $^1\text{H NMR}$ (CDCl_3 , 300 MHz): δ 6.05 (dt, 1H), 5.45 (m, 1H), 2.3 (m, 2H), 2.02–2.11 (m, 2H), 1.57–1.18 (m, 12H), 0.88–0.95 (m, 6H); $^{13}\text{C NMR}$ (CDCl_3 , 75.5 MHz): δ 143.1, 109.9, 88.5, 79.2, 32.9, 31.6, 31.0, 28.8, 28.7, 22.5, 21.9, 19.0, 14.0, 13.5. IR (neat): 3020 (s), 2959 (s), 2873 (s), 2733 (s), 2210 (s), 1486 (s), 1432 (s), 1378 (s), 1301 (s), 725 (s) cm^{-1} . Mass (EI, 70 eV): 192 (M^+ , 26), 135 (8.3), 121 (12), 107 (28), 93 (100), 79 (91), 67 (27), 55 (23), 41 (27). HRMS Found: 192.1881. $\text{C}_{14}\text{H}_{24}$ calcd.: 192.1878.

5-Chloro-1-pentenylpinacolborane (19). A three-necked flask equipped with a thermometer, a nitrogen inlet, and an addition funnel was charged with pinacol (2.36 g, 20 mmol) in dry CH_2Cl_2 (2 mL) and cooled to 0°C . A solution of $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (20 mmol, 10.0 M solution in Me_2S) was added dropwise, causing effervescence. The mixture was stirred for 1 h at 0°C and then warmed to 25°C and stirred until no further evolution of hydrogen was observed (*ca.* 1 h). The resulting clear solution was cooled to 0°C and 5-chloro-1-pentyne (1.02 g, 10 mmol) was slowly added. The mixture was warmed to 25°C and stirred for 7 h. GLC analysis of an aliquot showed that the reaction was complete. Ether (150 mL) was added and the resulting solution was poured into a separatory funnel containing saturated aqueous NH_4Cl (250 mL). The organic phase was washed quickly with saturated aqueous NH_4Cl (100 mL) and dried over MgSO_4 . The solvent was evaporated under vacuum to leave a residue, which was purified by flash chromatography (hexane:ether, 97:3) providing **19** as a clear oil (1.95 g; 85% yield). GLC analysis indicates an *E/Z* ratio of 99:1. IR (neat): 2979 (s), 2934 (m), 1640 (s), 1386 (s), 1372 (s), 1323 (s), 1165 (s), 997 (m), 849 (s) cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 6.63–6.52 (dt, 1H, $J = 6.4$ Hz, $J = 17.9$ Hz), 5.50–5.44 (d, 1H, $J = 17.9$ Hz), 3.55–3.50 (t, 2H, $J = 6.7$ Hz), 2.34–2.26 (q, 2H, $J = 7.0$ Hz), 1.94–1.84 (p, 2H, $J = 6.9$ Hz), 1.26 (s, 12H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 151.7, 83.0, 44.0, 32.6, 31.1, 24.7; MS (EI): 41 (73), 69 (100), 85 (48), 109 (37), 144 (55), 153 (95), 215 (68), 230 (27), 341 (6), 355 (6), 415 (3), 429 (5). Exact mass. Found: 230.1256. $\text{C}_{11}\text{H}_{20}\text{BClO}_2$ calcd.: 230.1245.

Bis-(5-chloro-1-pentenyl)mercury (20).

(a) **Preparation of 5-chloro-1-pentenylmercury chloride** [27]. A three-necked flask equipped with a stirring bar, a thermometer, an argon inlet, and an addition funnel was charged with $\text{Hg}(\text{OAc})_2$ (4.78 g, 15 mmol), and flushed with argon. Dry THF (15 mL) and 5-chloro-1-pentenylpinacolborane (**19**) (3.44 g, 15 mmol) were successively added. The mixture was stirred until complete dissolution of $\text{Hg}(\text{OAc})_2$ (0.25 h). The resulting solution was diluted with ether (200 mL) and added to a brine solution (100 mL). The layers were separated and the organic layer was dried over MgSO_4 . The solvent was removed *in vacuo* to leave a white solid, which was used without further purification.

(b) **Preparation of bis-(5-chloro-1-pentenyl)mercury (20)** [28]. A three-necked flask equipped with a stirring bar, a thermometer, an argon inlet, and an addition funnel was charged with $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ (1.86 g, 8.1 mmol), NaOH (3.84 g, 96 mmol) and water (30 mL). The mixture was cooled to 0°C and 5-chloro-1-pentenylmercury chloride (*ca.* 15 mmol) in acetone (0.28 M) was added. After 8 h at 0°C , a grey solid formed. The clear supernatant liquid was separated and the solid washed with acetone (5×50 mL). The combined acetone solutions were concentrated and the residue was purified by flash chromatography (hexane) to yield the bis-(5-chloro-1-pentenyl)mercury (**20**) (1.86 g, 61% yield) as a clear oil. IR (neat): 2956 (s), 2930 (s), 1470 (s), 1251 (s), 1078 (s), 1011 (m), 973 (m), 866 (m); ^1H NMR (CDCl_3 , 300 MHz): δ 6.28–6.20 (dt, 2H, $J = 1.5$ Hz, $J = 18.2$ Hz), 5.77–5.65 (dt, 2H, $J = 6.1$ Hz, $J = 18.2$ Hz), 3.58–3.52 (t, 4H, $J = 7.2$ Hz), 2.44–2.30 (m, 4H), 1.96–1.83 (m, 4H); ^{13}C NMR (CDCl_3 , 75.5 MHz): δ 161.5, 159.7, 159.4, 147.8, 147.6, 145.4, 44.5, 44.0, 34.6, 34.4, 32.0, 31.9; MS (EI): 86 (14), 92 (4), 120 (6), 322 (100), 362 (0.2), 373 (0.3), 409 (0.6); Exact mass. Found: 409.0400. $\text{C}_{10}\text{H}_{16}\text{Cl}_2\text{HgH}$ calcd.: 409.0414.

(*E*)-5-Chloro-1-cyclohexyl-1-pentene (22). A three-necked flask equipped with a thermometer, an addition funnel, a stirring bar, and an argon inlet was charged with zinc dust (1.96 g, 30 mmol) and activated as described above in THF (3 mL). A solution of bis-(5-chloro-1-pentenyl)mercury (20) (2.04 g, 5 mmol) in THF (5 mL) was added at 50°C and the mixture was stirred for 5 h at this temperature. The zinc dust was allowed to settle and the resulting clear solution transferred to another three-necked flask filled with the same equipment. The solvent was removed under vacuum and the resulting white solid was redissolved in dry CH₂Cl₂ (10 mL). A slurry of Cp₂Zr(H)(Cl) (2.57 g, 10 mmol) in CH₂Cl₂ (8 mL) was then added at once, followed *immediately* by a solution of cyclohexanecarboxaldehyde (0.90 g, 8 mmol) in CH₂Cl₂ (3 mL). The mixture was stirred for 14 h at 25°C. After the usual work-up and evaporation of the solvent, the residue obtained was purified by flash chromatography (hexane) to yield 5-chloro-1-cyclohexyl-1-pentene (0.79 g, 49% yield) as a clear oil. GLC analysis indicated an *E* : *Z* ratio of ~ 99.9 : 0.1. IR (neat): 2945 (s), 2908 (s), 1748 (s), 948 (m), 736 (s), 703 (m) cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 5.41–5.23 (m, 2H), 3.57–3.51 (t, 2H, *J* = 6.9 Hz), 2.04–1.96 (q, 2H, *J* = 7.1 Hz), 1.96–1.81 (m, 1H), 1.18–1.54 (m, 6H), 1.54–1.43 (m, 2H), 1.42–0.94 (m, 6H); ¹³C NMR (CDCl₃, 75.5 MHz): δ 137.3, 126.9, 44.9, 40.7, 33.3, 32.1, 31.8, 26.9, 26.3, 26.1; MS (EI): 41 (83), 55 (92), 67 (100), 81 (62), 96 (48), 109 (50), 200 (8), 202 (3). Exact mass. Found: 200.1655. C₁₂H₂₁Cl calcd.: 200.1643.

References and notes

- (a) N. Oguni and T. Omi, *Tetrahedron Lett.*, 25 (1984) 2823; (b) N. Oguni, Y. Matsuda and T. Kaneko, *J. Am. Chem. Soc.*, 110 (1988) 7877; (c) K. Soai, A. Ookawa, K. Ogawa and T. Kaba, *J. Chem. Soc., Chem. Commun.*, (1987) 467; (d) K. Soai, S. Yokoyama, K. Ebihara and T. Hayasaka, *J. Chem. Soc., Chem. Commun.*, (1987) 1690; (e) K. Soai, A. Ookawa, T. Kaba and K. Ogawa, *J. Am. Chem. Soc.*, 109 (1987) 7111; (f) K. Soai, S. Niwa, Y. Yamada and H. Inoue, *Tetrahedron Lett.*, 28 (1987) 4841; (g) K. Soai, M. Nishi and Y. Ito, *Chem. Lett.*, (1987) 2405; (h) K. Soai, S. Niwa and M. Watanabe, *J. Org. Chem.*, 53 (1988) 927; (i) K. Soai and S. Niwa, *Chem. Lett.*, (1989) 481; (j) K. Soai, M. Watanabe and M. Koyano, *J. Chem. Soc., Chem. Commun.*, (1989) 534; (k) M. Kitamura, S. Okada, S. Suga and R. Noyori, *J. Am. Chem. Soc.*, 111 (1989) 4028; (l) E.J. Corey, P.-W. Yuen, F.J. Hannon and D.A. Wierda, *J. Org. Chem.*, 55 (1990) 784; (m) E.J. Corey and F.J. Hannon, *Tetrahedron Lett.*, 28 (1987) 5233; (n) N.N. Joshi, M. Srebnik and H.C. Brown, *Tetrahedron Lett.*, 30 (1989) 5551; (o) S. Itsuno and J.M.J. Frechet, *J. Org. Chem.*, 52 (1987) 4140; (p) W. Oppolzer and R.N. Radinov, *Tetrahedron Lett.*, 29 (1988) 5645; (q) C. Bolm, M. Zehnder and D. Bur, *Angew. Chem., Int. Ed. Engl.*, 29 (1990) 205; (r) S. Itsuno, Y. Sakurai, K. Ito, T. Maruyama, S. Nakahama and J.M.J. Frechet, *J. Org. Chem.*, 55 (1990) 304; (s) For catalytic asymmetric addition of diethylzinc to aldehydes catalyzed by titanates: M. Yoshioka, T. Kawakita and M. Ohno, *Tetrahedron Lett.*, 30 (1989) 1657; (t) H. Takahashi, T. Kawakita, M. Yoshioka, S. Kobayashi and M. Ohno, *Tetrahedron Lett.*, 30 (1989) 7095; (u) B. Schmidt and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 99; (v) *ibid.*, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 1321; (w) W. Oppolzer and R.N. Radinov, *Tetrahedron Lett.*, 32 (1991) 5777; for excellent reviews see: (x) D.A. Evans, *Science*, 240 (1988) 420; (y) R. Noyori and M. Kitamura, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 49.
- (a) D. Seebach, L. Behrendt and D. Felix, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 1008; (b) A.K. Beck, B. Bastani, D.A. Plattner, W. Petter, D. Seebach, H. Braunschweiger, P. Gysi and L. La Vecchia, *Chimia*, 45 (1991) 238.
- (a) P. Knochel, M.C.P. Yeh, S.C. Berk and J. Talbert, *J. Org. Chem.*, 53 (1988) 2390; (b) S.C. Berk, P. Knochel and M.C.P. Yeh, *J. Org. Chem.*, 53 (1988) 5789; (c) T.N. Majid and P. Knochel, *Tetrahedron Lett.*, 31 (1990) 4413; (d) T.-S. Chou and P. Knochel, *J. Org. Chem.*, 55 (1990) 4791 and references cited therein.
- i: (a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, 11 (1972) 473; (b) J. Villieras, *Bull. Soc. Chim. Fr.*, (1967) 1511; (c) J. Villieras, B. Kirschleger, R. Tarhouni and M. Rambaud, *Bull. Soc. Chim. Fr.*,

- (1986) 470; (d) J. Villieras, R. Tarhouni, B. Kirschleger and M. Rambaud, *Bull. Soc. Chim. Fr.*, (1985) 825; (e) J. Villieras, M. Rambaud, B. Kirschleger and R. Tarhouni, *Bull. Soc. Chim. Fr.*, (1985) 837; (f) H. Siegel, *Top. Curr. Chem.*, 106 (1982) 55; Mg: (g) J. Villieras, *Bull. Soc. Chim. Fr.*, (1967) 1520; Ge, Sn, Pb, Hg, Zn: (h) D. Seyferth, H. Dertouzos and L.J. Todd, *J. Organomet. Chem.*, 4 (1965) 18; (i) D. Seyferth and S.B. Andrews, *J. Organomet. Chem.*, 30 (1971) 151; (j) D. Seyferth, S.B. Andrews and R.L. Lambert, Jr., *J. Organomet. Chem.*, 37 (1972) 69; Fe: (k) P.W. Jolly and R. Pettit, *J. Am. Chem. Soc.*, 88 (1966) 5044; (l) R.B. King and D.M. Braitsch, *J. Organomet. Chem.*, 54 (1973) 9; (m) T.C. Flood, F.J. DiSanti and D.L. Miles, *Inorg. Chem.*, 15 (1976) 1910; Co: (n) G. Albertin, S. Antoniutti and E. Bordignon, *Organometallics*, 9 (1990) 2177; (o) W.L. Olson, D.A. Nagaki and L.F. Dahl, *Organometallics*, 5 (1986) 630; (p) V. Galamb, G. Palyi, R. Boese and G. Schmid, *Organometallics*, 6 (1987) 861; Rh: (q) T.B. Marder, W.C. Fultz, J.C. Calabrese, R.L. Harlow and D. Milstein, *J. Chem. Soc., Chem. Commun.*, (1987) 1543; Pd: (r) R. McCrindle, G.J. Arsenault, R. Farwaha, A.J. McAlees and D.W. Sneddon, *J. Chem. Soc., Dalton Trans.*, (1989) 761; Pt: (s) C.A. Ghilardi, S. Midollini, S. Moneti, A. Orlandini and J.A. Ramirez, *J. Chem. Soc., Chem. Commun.*, (1989) 304; Mo, W: (t) M.L.H. Green, M. Ishaq and R.N. Whiteley, *J. Chem. Soc. (A)*, (1967) 1508; B: (u) H.C. Brown, N.R. DeLue, Y. Yamamoto and K. Maruyama, *J. Org. Chem.*, 42 (1977) 3252; (v) D.S. Matteson and G.D. Schaumberg, *J. Org. Chem.*, 31 (1966) 726; (w) D.S. Matteson, *Chem. Rev.*, 89 (1989) 1535; Al: (x) H. Hoberg, *Liebigs Ann. Chem.*, 703 (1967) 1.
- 5 The reaction of lithium or magnesium carbenoids with other organometallics has been reported: (a) J. Villieras, A. Reliquet and J.F. Normant, *Organomet. Chem.*, 144 (1978) 263; (b) *ibid.*, *Synthesis*, (1978) 27; (c) E. Negishi and K. Akiyoshi, *J. Am. Chem. Soc.*, 110 (1988) 646; (d) E. Negishi, K. Akiyoshi, B. O'Connor, K. Takagi and G. Wu, *J. Am. Chem. Soc.*, 111 (1989) 3089; (e) K. Ramig, M. Bhupathy and T. Cohen, *J. Org. Chem.*, 54 (1989) 4404; (f) T. Harada, D. Hara, K. Hattori and A. Oku, *Tetrahedron Lett.*, 29 (1988) 3821; (g) T. Harada, K. Hattori, T. Katsuhira and A. Oku, *Tetrahedron Lett.*, 30 (1989) 6035; (h) T. Harada, T. Katsuhira, K. Hattori and A. Oku, *Tetrahedron Lett.*, 30 (1989) 6039; (i) P. Charreau, M. Julia and J.-N. Verpeau, *J. Organomet. Chem.*, 379 (1989) 201; (j) R.C. Hahn and J. Tompkins, *Tetrahedron Lett.*, 31 (1990) 937; Related "carbenoid" reagents undergo similar reactions with electrophiles: (k) P. Kocienski, S. Wadman and K. Cooper, *J. Am. Chem. Soc.*, 111 (1989) 2363; (l) J.A. Miller, *J. Org. Chem.*, 54 (1989) 998; (m) C.P. Casey, P.C. Vosejпка and J.A. Gavney, *J. Am. Chem. Soc.*, 112 (1990) 4083; (n) P. Knochel, N. Jeong, M.J. Rozema and M.C.P. Yeh, *J. Am. Chem. Soc.*, 111 (1989) 6474; (o) P. Knochel and S. Achyutha Rao, *J. Am. Chem. Soc.*, 112 (1990) 6146; see also ref. 2m.
- 6 Some alkylmercury halides bearing functional groups have been reported: (a) R.C. Larock and H.C. Brown, *J. Am. Chem. Soc.*, 92 (1970) 2467; (b) J. Drouin, M.-A. Boaventura and J.-M. Conia, *J. Am. Chem. Soc.*, 107 (1985) 1726; (c) R.C. Larock, *Angew. Chem., Int. Ed. Engl.*, 17 (1978) 28; (d) I. Ryu, K. Matsumoto, M. Ando, S. Murai and N. Sonoda, *Tetrahedron Lett.*, (1980) 4283; (e) R.C. Larock, *Organomercury Compounds in Organic Synthesis*, Springer-Verlag, Berlin, New York, 1985.
- 7 Organomagnesium halides are readily transmetalated to the corresponding diorganomercurials: (a) P. Pfeiffer and P. Truskier, *Chem. Ber.*, 37 (1904) 1125; (b) H. Gilman and R.E. Brown, *J. Am. Chem. Soc.*, 52 (1930) 3314; (c) D.O. Cowan and H.S. Mosher, *J. Org. Chem.*, 27 (1962) 1.
- 8 S.C. Cohen, D.E. Fenton, A.J. Tomlinson and A.G. Massey, *J. Organomet. Chem.*, 6 (1966) 301.
- 9 H.P. Knoess, M.T. Furlong, M.J. Rozema and P. Knochel, *J. Org. Chem.*, 56 (1991) 5976.
- 10 G. Cahiez, D. Bernard and J.F. Normant, *Synthesis*, (1976) 245.
- 11 (a) E. Frankland and B.F. Dupa, *Liebigs Ann. Chem.*, 130 (1864) 104; (b) E. Frankland and B.F. Dupa, *J. Chem. Soc.*, 17 (1864) 30; (c) A. Marquardt, *Chem. Ber.*, 21 (1888) 2035.
- 12 K. Soai, M. Okudo and M. Okamoto, *Tetrahedron Lett.*, 32 (1991) 95.
- 13 D. Parker, *J. Chem. Soc., Perkin Trans. II*, (1983) 83.
- 14 T.N. Majid and P. Knochel, *Tetrahedron Lett.*, 31 (1990) 4413.
- 15 (a) C.E. Tucker, J. Davidson and P. Knochel, *J. Org. Chem.*, 57 (1992) 3482; (b) C.E. Tucker and P. Knochel, *J. Am. Chem. Soc.*, 113 (1991) 9888.
- 16 Aromatic mercury derivatives can also be converted to the corresponding zinc and copper reagents. Thus, the treatment of diphenylmercury with zinc (THF, 60°C, 2 h) in the presence of ZnBr₂ affords phenylzinc bromide which after addition of CuCN·LiCl and ethyl propiolate (0.7 equiv.; -50°C to 0°C, 6 h) gives ethyl cinnamate (92% yield, 99% E).
- 17 C. Retherford, T.-S. Chou, R.M. Schelkun and P. Knochel, *Tetrahedron Lett.*, 31 (1990) 1833.
- 18 P. Knochel, *J. Am. Chem. Soc.*, 112 (1990) 7431.
- 19 J. Villieras and M. Rambaud, *Synthesis*, (1982) 924.

- 20 (a) G. Zweifel and W. Lewis, *J. Org. Chem.*, 43 (1978) 2739; (b) G. Zweifel and J.A. Miller, *Org. React.*, 32 (1984) 375.
- 21 S.L. Buchwald, S.J. LaMaire, R.B. Nielsen, B.T. Watson and S.M. King, *Tetrahedron Lett.*, 28 (1987) 3895.
- 22 J. Casanova, H.R. Rogers and K.L. Servis, *Org. Magn. Reson.*, 7 (1975) 57.
- 23 D. Seebach, H.O. Kalinowski, B. Bastani, G. Crass, H. Daum, H. Dorr, N.P. Dupreez, V. Ehrig, W. Langer, C. Nussler, H.A. Oei and M. Schmidt, *Helv. Chim. Acta*, 60 (1977) 301.
- 24 M. Masnyk and J. Wicha, *Tetrahedron Lett.*, 29 (1988) 2497.
- 25 K. Tomioka, M. Kakajima and K. Koga, *Tetrahedron Lett.*, 28 (1987) 1291.
- 26 J. Furukawa, S. Iwasaki and S. Okuda, *Tetrahedron Lett.*, 24 (1983) 5257.
- 27 R.C. Larock, S.K. Gupta and H.C. Brown, *J. Am. Chem. Soc.*, 94 (1972) 4371.
- 28 A.N. Nesmaynov and L.G. Makarova, in *Methods of Elemento-Organic Chemistry*, Vol. 4, *The Organic Compounds of Mercury*, North-Holland, Amsterdam, 1967.