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

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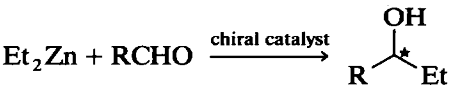
Abstract

Two new methods of preparation of functionalized diorganomercurials have been developed. The first method involves a substitution reaction of $(ICH_2)_2Hg$ with zinc-copper reagents FG-RCu(CN)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 $Cl(H)ZrCp_2$ to (*E*)-5-chloropentenylzinc bromide in CH_2Cl_2 (25°C, 1 min) affords a 1,1-bimetallic of zinc and zirconium $Cl(CH_2)_4CH(ZnBr)ZrCp_2(Cl)$ 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 [1l,m].



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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.

$$\underset{\mathbf{2}}{(\text{FG-R})_2\text{Hg}} + \text{Zn} \xrightarrow[3\text{–}5\ \text{h}]{\text{toluene, } 110^\circ\text{C}} \underset{\mathbf{1}}{(\text{FG-R})_2\text{Zn}} \qquad (2)$$

$$\underset{\mathbf{3}}{2\text{FG-RCu(CN)ZnX}} + \underset{\mathbf{4}}{\text{XCH}_2\text{MetL}_n} \longrightarrow \underset{\mathbf{5}}{\text{FG-RCH}_2\text{MetL}_n} \qquad (3)$$

$$\underset{\mathbf{3}}{2\text{FG-RCu(CN)ZnI}} + \underset{\mathbf{7}}{(\text{ICH}_2)_2\text{Hg}} \xrightarrow[15\ \text{h}]{\text{DMF–THF, } -60^\circ\text{C}} \underset{\mathbf{6}\ (74\text{–}98\%)}{(\text{FG-RCH}_2)_2\text{Hg}} \qquad (4)$$

FG = ester, nitrile, ketone, phosphonate, halide, boronic ester, carbon-metal bond (metal = zinc or copper)
R: primary or secondary alkyl, benzyl

$$\underset{\mathbf{11}}{2\text{FG-RZnI}} + \text{Hg}_2\text{Cl}_2 \xrightarrow[2\ \text{h}]{\text{THF, } -50^\circ\text{C to } 20^\circ\text{C}} \underset{\mathbf{2}\ (61\text{–}89\%)}{(\text{FG-R})_2\text{Hg}} + \text{ZnCl}_2 + \text{ZnI}_2 + \text{Hg}^{(0)} \qquad (5)$$

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

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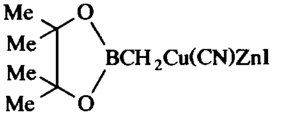
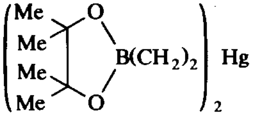
* Reference number with an asterisk indicates a note in the list of references.

Table 1

Polyfunctional dialkylmercurials **6** prepared by the reaction of $(ICH_2)_2Hg$ (**7**) with the highly functionalized copper-zinc organometallics FG-RCu(CN)ZnX (**3**)

Entry	Cu-Zn reagent **3a–j** [b]		Dialkylmercury **6a–j**		Yield (%) [a]
1	BuCu(CN)ZnI	3a	$(Pent)_2Hg$	**6a**	87
2	c-HexCu(CN)ZnI	**3b**	$(c\text{-}HexCH_2)_2Hg$	**6b**	95
3	$PhCH_2Cu(CN)ZnBr$	**3c** [c]	$(PhCH_2CH_2)_2Hg$	**6c**	98
4	$AcO(CH_2)_3Cu(CN)ZnI$	**3d**	$(AcO(CH_2)_4)_2Hg$	**6d**	87
5	$EtO_2C(CH_2)_3Cu(CN)ZnI$	**3e**	$(EtO_2C(CH_2)_4)_2Hg$	**6e**	98
6	$NC(CH_2)_3Cu(CN)ZnI$	**3f**	$(NC(CH_2)_4)_2Hg$	**6f**	96
7	$Cl(CH_2)_4Cu(CN)ZnI$	**3g**	$(Cl(CH_2)_5)_2Hg$	**6g**	95
8	$PhCO(CH_2)_3Cu(CN)ZnI$	**3h**	$(PhCO(CH_2)_4)_2Hg$	**6h**	95
9	$(EtO)_2(O)P(CH_2)_2Cu(CN)ZnBr$	**3i** [c]	$((EtO)_2(O)P(CH_2)_3)_2Hg$	**6i**	74 [d]
10		**3j** [c]		**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 $(FG\text{-}R)_2Hg$ and *ca.* 2% of $(FG\text{-}R\text{-}CH_2CH_2)_2Hg$. [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 $((EtO)_2(O)P(CH_2)_2)_2Hg$ and 5% of $((EtO)_2(O)P(CH_2)_4)_2Hg$.

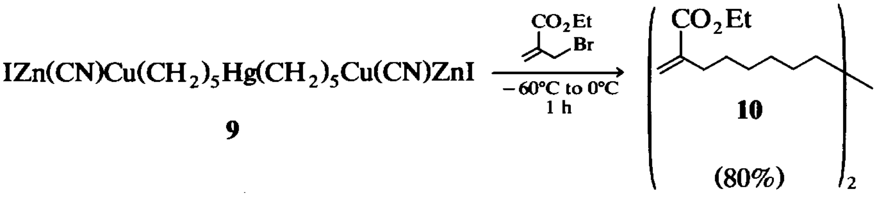
choice of DMF as a co-solvent was crucial for the success of the reaction, since the use of THF alone leads to appreciable amounts of non-homologated dialkylmercury compounds $(FG\text{-}R)_2Hg$ (*ca.* 16%). However, the use of a DMF/THF mixture (*ca.* 5 : 1) combined with a low reaction temperature leads to dialkylmercurials **6** contaminated by < 3% of the non-homologated dialkylmercury $(FG\text{-}R)_2Hg$ and < 3% of the double methylene homologated dialkylmercury $(FG\text{-}R\text{-}CH_2CH_2)_2Hg$. The less reactive aryl- and alkynyl-copper derivatives **3**, as also the copper amides (R_2NCu) 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).

$$IZn(CN)Cu(CH_2)_4Cu(CN)ZnI \xrightarrow[-60°C,\ 15\ h]{(ICH_2)_2Hg\ 7}$$

8

$$IZn(CN)Cu(CH_2)_5Hg(CH_2)_5Cu(CN)ZnI \quad (6a)$$

9



9

10

(80%)

(6b)

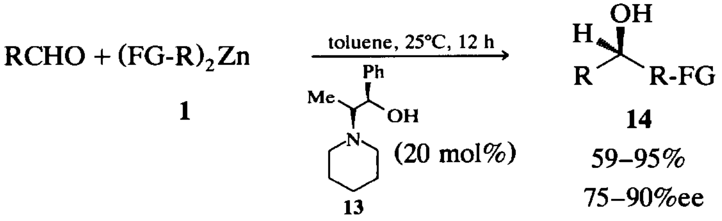
Table 2

Polyfunctional diorganomercurials **2** prepared by the reaction of Hg_2Cl_2 with the highly functionalized zinc organometallics FG-RZnX (**11**)

Entry	FG-RZnX	11	Diorganomercurial	2	Yield (%) [a]
1	BuZnI	**11a**	Bu_2Hg	**2a**	89
2	$Cl(CH_2)_4ZnI$	**11b**	$(Cl(CH_2)_4)_2Hg$	**2b**	76
3	$NC(CH_2)_5ZnI$	**11c**	$(NC(CH_2)_5)_2Hg$	**2c**	82
4	$EtO_2C(CH_2)_4ZnI$	**11d**	$(EtO_2C(CH_2)_4)_2Hg$	**6e**	87
b5	$AcO(CH_2)_4ZnI$	**11e**	$(AcO(CH_2)_4)_2Hg$	**6d**	61
6	$HC{\equiv}C(CH_2)_3ZnI$	**11f**	$(HC{\equiv}C(CH_2)_3)_2Hg$	**2d**	70
7	$PhCH_2ZnBr$	**11b**	$(PhCH_2)_2Hg$	**2e**	78
8	$CH_3CH(OPiv)(CH_2)_3ZnI$	**11h**	$(CH_3CH(OPiv)(CH_2)_3)_2Hg$	**2f**	84
9	(*E*)-HexCH=CHLi	**11i**	(*E*)-$(HexCH{=}CH)_2Hg$	**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 $(FG\text{-}R)_2Hg$ and *ca.* 2% of $(FG\text{-}R\text{-}CH_2CH_2)_2Hg$.

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] Hg_2Cl_2 (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 Bu_2Hg, **2a**, prepared by the mercurous chloride method, as well as $(Hex)_2Hg$ **12a**, and $((CH_3)_2CH(CH_2)_2)_2Hg$ **12b**, obtained by the reaction of the corresponding magnesium reagent with $HgBr_2$ 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-piperidinyl)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



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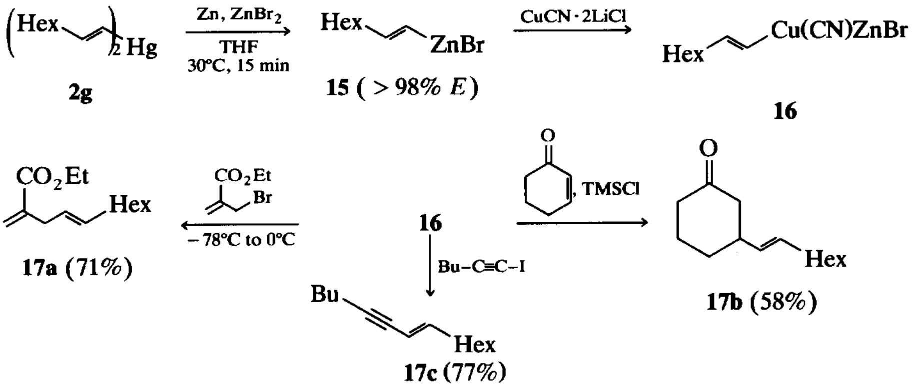
NMR analysis of the (*S*)-(+)-O-acetylmandelic ester [13]. Treatment of the ester-substituted dialkylzinc $(EtOOC(CH_2)_4)_2Zn$ prepared from the functionalized dialkylmercurial **6e**, with benzaldehyde did not give the desired product under our

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	$(FG\text{-}R)_2Hg$		Reaction conditions [a] (h, °C)	Aldehyde	Product		Yield (%) [b]	ee (%) [c]
1	Bu_2Hg	**2a**	(2, 110)	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*)-(*E*)-PhCH=CH(OH)Bu	**14c**	95	76
4	Hex_2Hg	**12a**	(6, 110)	PhCHO	(*S*)-PhCH(OH)Hex	**14d**	95	90
5	$(Me_2CH(CH_2)_2)_2Hg$	**12b**	(5, 110)	PhCHO	(*S*)-PhCH(OH)$(CH_2)_2CH(CH_3)_2$	**14e**	86	90

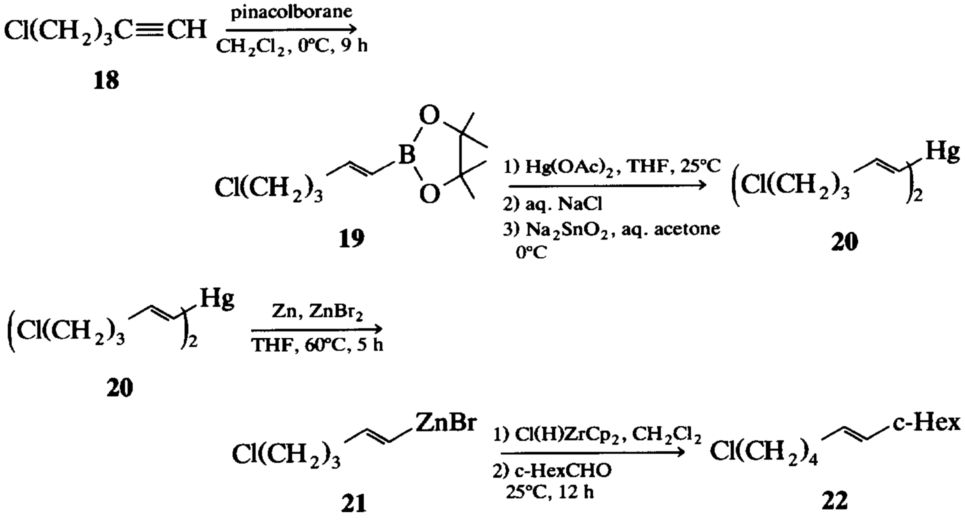
[a] Reaction conditions used for the preparation of the dialkylzinc 1. [b] Isolated yield of analytically pure alcohol. [c] The enantiomeric excess has been determined by ^{1}H-NMR analysis of the (*S*)-(+)-O-acetylmandelic ester of **14**.



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 transmetallation 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 transmetallation reaction and avoids the need to use high reaction temperatures, which lead to partial loss of the stereochemistry. Addition to CuCN · 2 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



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) $Hg(OAc)_2$ (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 ($H(Cl)ZrCp_2$ (1 equiv.) 25°C, 1 min.) gave an intermediate 1,1-bimetallic reagent of zinc and zirconium ($RCH(ZnBr)ZrCp_2Cl$) [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 $(FG\text{-}R)_2Hg$. 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], (1S,2R)-(–)-1-

phenyl-2-(1-piperidinyl)-propan-1-ol [12], $H(Cl)ZrCp_2$ [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°C, litt. [4h–j], 80–82°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 $FG\text{-}RI/FG\text{-}RCH_2I/FG\text{-}R(CH_2)_2I$ 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°C at 0.25 mm Hg $FG\text{-}RI/FG\text{-}CH_2I/FG\text{-}R(CH_2)_2I$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 1/98/1; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{14}H_{26}Hg$: 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 3.7/95/1.3; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{16}H_{18}Hg$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 2.5/95/2.5; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{12}H_{22}HgO_4$ calcd.: 432.1224. Anal. Found: C, 33.43; H, 5.19. $C_{12}H_{22}HgO_4$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 2.5/95/2.5; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{14}H_{26}HgO_4$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 2.5/95/2.5; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{10}H_{16}N_2Hg$ calcd.: 366.1020.

Bis-(5-chloropentyl)mercury (***6g***). 1.03 g (95%) as a colorless oil, purified by flash chromatography (hexane), FG-RI/FG-RCH_2I/FG-$R(CH_2)_2I$ ratio 0/100/0; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{10}H_{20}Cl_2Hg$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 3/94/3; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{22}H_{26}HgO_2$: 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 5/90/5; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{14}H_{32}HgP_2O_6$ 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 2.5/95/2.5; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.25 (s, 24H), 1.21 (t, 4H, $J = 7.5$ Hz), 1.02 (t, 4H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$, 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 $C_{16}H_{32}B_2HgO_4$: 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-RCH_2I/FG-$R(CH_2)_2I$ ratio 0/100/0. ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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, CH_4): 597 ($MC_2H_5^+$, 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 $C_{22}H_{38}HgO_4H$: 569.25555. Found: 569.2526.

Typical procedure for the preparation of dialkylmercurials $(FG\text{-}R)_2Hg$ (2) by the reaction of FG-RZnX (11) with Hg_2Cl_2

A dry, three-necked flask equipped with an argon inlet, a magnetic stirring bar and a low temperature thermometer was charged with Hg_2Cl_2 (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 NH_4Cl (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 dialkymercurials 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. $C_8H_{18}Hg$ 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. $C_8H_{16}Cl_2Hg$ calcd.: 384.0335. Anal. Found: C, 25.12; H, 4.24; Cl, 18.32. $C_8H_{16}Cl_2Hg$ 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. $C_{12}H_{20}N_2Hg$ 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. $C_{10}H_{14}HgH$ 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. $C_{14}H_{14}Hg$ 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. $C_{20}H_{38}O_2HgH$ 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 (MH^+, 3.7), 330 (100), 235 (5), 111 (10), 81 (9). HRMS Found: 425.2131. $C_{16}H_{30}^{202}HgH$ calcd.: 425.2132. Anal. Found: C, 45.62; H, 7.07. $C_{16}H_{30}Hg$ 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. $[\alpha]_D^{25} = -36.67°$ ($c = 2.19$, benzene) 90% ee, m.p. 31–32°C; determined by converting **14a** into the O-acetylmandelic ester derivative [13] performing a ^{1}H NMR analysis. ^{1}H 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), $[\alpha]_D^{25} = -16.31°$ ($c = 1.98$, C_6H_6); 90% ee. ^{1}H 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), $[\alpha]_D^{25} = +3.52°$ ($c = 3.95$, benzene) 76% ee; ^{1}H 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) $[\alpha]_D^{25} = -27.79°$ ($c = 4.80$, benzene); 90% ee. ^{1}H 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; $[\alpha]_D^{25} = -33.23°$ ($c = 3.41$, benzene) 90% ee. ^{1}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}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}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}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. $C_{14}H_{24}O_2$ 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}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}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 $C_{14}H_{20}O$: 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}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}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. $C_{14}H_{24}$ 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 $BH_3 \cdot Me_2S$ (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. $C_{11}H_{20}BClO_2$ 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 $Hg(OAc)_2$ (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 $Hg(OAc)_2$ (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 $SnCl_2 \cdot H_2O$ (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. $C_{10}H_{16}Cl_2HgH$ 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 CH_2Cl_2 (10 mL). A slurry of $Cp_2Zr(H)(Cl)$ (2.57 g, 10 mmol) in CH_2Cl_2 (8 mL) was then added at once, followed *immediately* by a solution of cyclohexanecarboxaldehyde (0.90 g, 8 mmol) in CH_2Cl_2 (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 $\sim$ 99.9:0.1). IR (neat): 2945 (s), 2908 (s), 1748 (s), 948 (m), 736 (s), 703 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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. $C_{12}H_{21}Cl$ calcd.: 200.1643.

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