CP/MAS NMR spectrum. This work was partly supported by a Grant-In-Aid for Specially Promoted Research (No. 62065005) from the ministry of Education, Science, and Culture of Japan.

Registry No. **1a**, 1066-45-1; **1a**-HMPA, 65941-34-6; **1b**, 1461-22-9; **1c**, 639-58-7; **2a**, 130063-57-9; **2b**, 98217-98-2; **2c**, 130063-58-0; **3**, 59094-54-1; **4**, 130063-59-1; **5a**, 130063-60-4; **5b**, 130063-61-5; **5c**, 130063-62-6; **6a**, 130063-64-8; **6b**, 130063-66-0; **6c**, 130063-68-2; **7a**, 130063-70-6; **7b**, 130063-72-8; **7c**, 130063-74-0; TAS-F, 59218-87-0; methoxytriphenylstannane, 1091-26-5; 2,6-dimethylphenol, 576-26-1; methoxytributylstannane, 1067-52-3; (2,6-dimethylphenoxy)trimethylsilane, 16286-54-7.

Supplementary Material Available: Tables of atomic parameters, anisotropic temperature factors, and complete bond angles and distances for **6a** and **7c** in X-ray crystallographic analyses, actual far-IR spectra of **1c**, **2c**, and **7c**, a Mössbauer spectrum of **7c**, CP/MAS ^{13}C NMR spectra of **2c**, **6a**, and **7c**, and lists of NMR parameters ($^1J(^{119}Sn-^{13}C)$ and $\delta(Sn-C_\alpha)$ values) in acetonitrile-d_3 for the various ratios of **3**/**2a** and **4**/**2a** (17 pages); listings of observed and calculated structure factors for **6a** and **7c** (24 pages). Ordering information is given on any current masthead page.

Preparation and Reactions of Functionalized Benzylic Organometallics of Zinc and Copper[†]

Scott C. Berk, Ming Chang P. Yeh, Nakcheol Jeong, and Paul Knochel*

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

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The reaction of zinc dust with primary or secondary benzylic halides **1** bearing various functional groups such as an ester, halide, cyano, or even a ketone group, in THF or, in the case of benzylic chlorides, in THF:DMSO (4:1), furnishes the corresponding zinc organometallics **2** in high yields. The reaction is accompanied by less than 10% of Wurtz coupling products. The benzylic copper organometallics **3**, obtained after a transmetalation of **2** with the THF-soluble copper salt CuCN·2LiCl at −20 °C, react in excellent yields (70–95%) with various electrophiles such as acid chlorides, enones, aldehydes, allylic bromides, ethyl propiolate, and tributyltin chloride, leading to the polyfunctional molecules of type **4**.

Introduction

Unlike allylic organometallics,[1] benzylic organometallic compounds have found relatively few synthetic applications. This is certainly due in part to the difficulties encountered in their preparation. Special experimental reaction conditions are often required to minimize the formation of Wurtz coupling products.[2] The formation of benzylic magnesium derivatives is best achieved by reacting magnesium anthracene[3] with benzylic chlorides or, less efficiently, with benzylic bromides. The direct metalation is achieved in high yields only in special cases[4] and often requires the use of strong bases, which can lead to the formation of ring-metalated products.[5] Benzyltin derivatives,[6] benzylic ethers[7] and thioethers,[8] and benzylic selenides[9] have also been used to prepare in most cases nonfunctionalized benzylic lithium compounds. Previously,[10] we reported a general preparation of functionalized primary benzylic zinc bromides by the reaction of benzylic bromides with zinc in THF.[11] The corresponding benzylic copper derivatives obtained after a transmetalation with CuCN·2LiCl were found to be versatile reagents that react with a variety of organic electrophiles (see Scheme I). Further work showed that this preparation of benzylic copper and zinc organometallics had a very broad scope and could be extended to the preparation of secondary benzylic zinc derivatives. We wish to report herein a full account of our results.

Results and Discussion

The slow addition (1 drop/5–10 s) of a 1.0–2.0 M THF solution of a primary benzylic bromide **1** (R = H; X = Br) at 0–5 °C to a stirred mixture of 1.2–1.5 equiv of cut zinc foil (Alfa, 99.9% pure) that was previously activated with 1,2-dibromoethane[12] leads to the complete formation of the corresponding benzylic zinc organometallic **2** after 2–3 h of stirring at 5 °C. Capillary GLC analysis of a hydrolyzed aliquot containing an internal standard indicates a yield

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[†] Dedicated to the memory of Professor John K. Stille.

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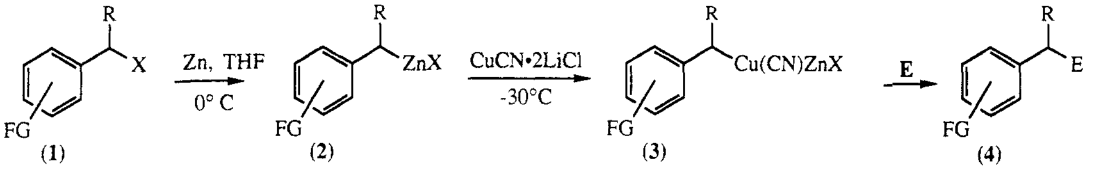
Scheme I[a]



[a] FG = COR, COOR, OAc, OMe, CN, Cl, I; X = Br, Cl; R = H, Me, Bu, 2-cyanoethyl; E = allylic bromides, acid chlorides, tributyltin chloride, enones, aldehydes.

of over 90%. The reaction was accompanied by the formation of less than 10% of Wurtz coupling products. Subsequently, we found that the use of zinc *dust* (Aldrich, -325 mesh) almost completely eliminates the formation of coupling products and furthermore does not require the dibromoethane activation (see Experimental Section). Secondary benzylic bromides show a high tendency to undergo homocoupling reactions, and depending on the substrate, 5-50% of dimerization products are obtained, even with the use of zinc dust. For example, whereas the reaction of zinc dust with 1-bromo-1-phenylpentane (**1k**, 0 °C, 0.5 M solution) leads to the desired benzylic zinc bromide in high yield with less than 5% of homocoupling products, the reaction of 1-bromo-1-phenylethane gives, under the same reaction conditions, more than 22% of Wurtz coupling products. In the latter cases, the use of the corresponding benzylic *chloride* in a 4:1 mixture of THF:DMSO[13] as the solvent at temperatures between 25 and 35 °C (22-24-h reaction times) was found to be very advantageous. Thus, 1-chloro-1-phenylethane (**1j**) could be converted under these conditions to the corresponding zinc compound in 90% yield with less than 5% of coupling products. Similarly, we observed that 1,4-diacetoxy-2-(bromomethyl)naphthalene reacts with zinc to give extensive dimerization (more than 34% by GLC analysis). However, the corresponding chloride **1i** reacts in THF at 65 °C (3 h) to afford the corresponding zinc derivative without the formation of significant amounts of dimer. The use of a THF:DMSO (4:1) mixture as solvent allows for the lowering of the reaction temperature to 45 °C (3-h reaction time) and leads to the suppression of Wurtz coupling products. All the functionalized benzylic zinc organometallics prepared showed a good thermal stability (no noticeable decomposition at 30 °C for several days); however, they are readily oxidized by air and hydrolyzed in a wet atmosphere. Their generation shows a remarkably good functional group tolerance, allowing the formation of zinc organometallics containing halide, ester, ketone, and cyano groups. The reactivity of the benzylic zinc organometallics **2** toward organic electrophiles is very low and can be dramatically increased by a transmetalation to the corresponding copper derivatives **3**. This transmetalation is best performed by adding the benzylic zinc organometallic to a THF solution of $CuCN{\cdot}2LiCl$[12b] at -40 °C. The transformation is complete after warming the reaction mixture to -20 °C for a few minutes. The copper species **3** is very stable below -20 °C but undergoes a slow reductive dimerization at higher temperatures. Various electrophiles react with the benzylic copper organometallics affording a variety of highly functionalized organic compounds **5-36** (see Table I), usually in excellent yields. Allylic bromides react very rapidly with the reagents **3** (addition at -70 °C, then 15 min at 0 °C), and furnish the desired allylated products in almost quantitative yields (see entries 5, 9, 13, 17, 22, 24, and 32). Michael additions to various enones and unsaturated aldehydes proceed smoothly. The benzylic zinc copper reagents show a reactivity very similar to that of alkylcopper derivatives[12b] for 1,4-addition, in contrast to allylic zinc copper organometallics, which lead to complex reaction mixtures.[14] All the Michael additions were performed in the presence of Me_3SiCl[15] to enhance the speed of the 1,4-addition and to avoid the polymerization of the enone. The presence of lithium salts also seems to be essential for the success of the reaction[12b] (see entries 2, 3, 6, 7, 11, 16, 20, and 29). The reaction is sensitive to steric hindrance, and β,β'-disubstituted enones do not react under these conditions. The β-disubstituted 2-chloro-1-cyclohexene-1-carboxaldehyde (**37**[16]) gives only the 1,2-addition product **8** (compare entries 3 and 4). The more reactive 3-iodo-2-cyclohexen-1-one,[17] however, gives only the 1,4-addition, elimination products (see entries 7 and 11). Whereas ethylenic and acetylenic esters do not react efficiently, ethyl propiolate yielded the desired addition compound **29** (79% yield, see entry 25) accompanied by 17% of the double-bond migration product. Aliphatic and aromatic aldehydes react in the presence of $BF_3{\cdot}OEt_2$[18] (2 equiv, -70 to -30 °C, 1-12 h at -30 °C) to provide the corresponding alcohols in excellent yields (see entries 1, 4, 8, 10, 14, 23, and 27). The reaction of acid chlorides with the copper reagent **3** occurs under mild conditions (-20 °C, 8-16 h) and furnishes polyfunctional ketones (see entries 15, 18, 30, and 31). This copper(I)-catalyzed coupling reaction efficiently complements the corresponding palladium(0) coupling reaction.[19] Finally, the reaction of tributyltin chloride with the reagents **3** allows for an easy preparation of new polyfunctional benzylic tin organometallics (see entries 12, 19, 21, and 26). Other electrophiles such as ketones, alkyl halides, and epoxides give a mixture of products or do not react at all.

Conclusion

The reaction conditions described in this report allow a practical and high-yield preparation of a variety of highly functionalized benzylic zinc and copper organometallics.

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These copper derivatives display a high reactiviy toward a variety of organic electrophiles such as acid chlorides, enones, aldehydes, allylic bromides, and ethyl propiolate, leading to the products in high yields (see Table I). The ability of these benzylic organometallics to tolerate many important functional groups combined with their good reactivity should make them useful reagents in organic synthesis.

Experimental Section

General Considerations. Unless otherwise indicated, all reactions were carried out under an inert (argon) atmosphere. Solvents (THF and diethyl ether) were dried and freshly distilled from sodium/benzophenone. The zinc foil used was from Alfa Products (0.25 mm, 99.9% pure). The zinc dust was obtained from Aldrich Chemical Co. (-325 mesh). Reactions were monitored by gas-liquid phase chromatography (GLC) or thin-layer chromatography (TLC) analysis 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 ether/saturated aqueous NH_4Cl mixture. 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 a nitrogen atmosphere on sodium chloride plates on a Nicolet 5DXB FT-IR spectrometer. Infrared frequencies are reported in wavenumber units (cm^{-1}). Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on a Bruker WM-300 (300 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as δ in units of parts per million (ppm) relative to an internal reference of tetramethylsilane (δ 0.00). Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were recorded on a Bruker WM-300 (75.5 MHz) nuclear magnetic resonance spectrometer. Chemical shifts are reported as δ in units of parts per million relative to chloroform-*d* (δ 77.0) as an internal reference. Mass spectra (MS) and exact mass calculations were recorded on a VG-70-250 S mass spectrometer. The ionization methods used were desorption chemical ionization (CI) and electron impact ionization (EI). Spectra are reported in units of mass to charge and relative intensity.

Starting Materials. The benzylic bromides **1a**, **1c**, and **1f** are available from Aldrich Chemical Co. Benzylic chloride **1j** is available from American Tokyo Kasai, Inc. All other benzylic halides were prepared as described below. The starting materials were purified by vacuum distillation or flash chromatography before use.

2-Iodobenzyl Bromide[20] (1b). To a 250-mL, single-necked, round-bottomed flask, a solution of 2-iodobenzyl chloride (8.83 g, 35 mmol) in 30 mL of acetone was added to LiBr (6.02 g, 70 mmol), and the mixture was heated to reflux for 1.5 h. The acetone was then evaporated, and CH_2Cl_2 was added. The mixture was filtered to remove the insoluble salts, and the solution was dried over $MgSO_4$. Removal of the solvent by rotary evaporation afforded 9.58 g (92% yield) of **1b**: IR (CH_2Cl_2) 3054 (s), 2987 (m), 1471 (m), 1441 (s), 1422 (s), 1262 (s), 1224 (s), 1014 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.86 (d, 1 H, J = 6 Hz), 7.48 (d, 1 H, J = 6 Hz), 7.33 (t, 1 H, J = 6 Hz), 6.98 (t, 1 H, J = 6 Hz), 4.60 (s, 2 H).

4-Acetoxy-3-methoxybenzaldehyde.[21] To a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel was added vanillin (15.2 g, 100 mmol), pyridine (15 mL), and 4-(dimethylamino)pyridine (DMAP, 0.6 g, 5 mmol) in 10 mL of dry ether. The solution was cooled in an ice bath, and acetic anhydride (10.2 g, 100 mmol) in 5 mL of dry ether was added dropwise. The reaction mixture was then warmed to room temperature. After 1.5 h, the reaction mixture was added to an ether/dilute HCl mixture. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and concentrated to afford, in over 99% purity, 17.54 g (90% yield) of 4-acetoxy-3-methoxybenzaldehyde: IR (CH_2Cl_2) 3055 (s), 3012 (m), 2854 (m), 2337 (m), 1769 (s), 1702 (s), 1602 (s), 1503 (s), 1465 (s), 1422 (s), 1390 (s), 1370 (s), 1269 (s), 1203 (s), 1147 (s), 1120 (s), 1032 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.95 (s, 1 H), 7.48 (m, 2 H), 7.22 (d, 1 H, J = 8.1 Hz), 3.91 (s, 3 H), 2.35 (s, 3 H).

4-Acetoxy-3-methoxybenzyl Alcohol.[22] $NaBH_4$ (0.76 g, 20 mmol) was added to a stirred solution of 4-acetoxy-3-methoxybenzaldehyde (8 g, 40 mmol) in 30 mL of ethanol/CH_2Cl_2 (10:1) at -20 °C under argon. After 30 min, the reduction was complete as shown by TLC, and the reaction was quenched with acetic acid (6 g, 100 mmol). The reaction mixture was then added to a water/ether mixture and separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated to afford 4-acetoxy-3-methoxybenzyl alcohol quantitatively in over 99% purity: IR (neat) 3400 (vs), 1764 (s), 1606 (m), 1510 (se, 1466 (m), 1421 (s), 1371 (s), 1276 (s), 1208 (s), 1152 (s), 1121 (m), 1034 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (m, 2 H), 7.42 (d, 1 H, J = 8.1 Hz), 5.16 (s, 2 H), 4.35 (s, 3 H), 2.85 (s, 3 H), 2.60 (s, 1 H).

4-Acetoxy-3-methoxybenzyl Bromide (1d). In a three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel, PBr_3 (3.9 mL, 40 mmol) was added dropwise to a solution of 4-acetoxy-3-methoxybenzyl alcohol (8 g, 40 mmol) in 40 mL of dry ether at -20 °C. After 30 min, the reaction mixture was added to an ice water/hexane mixture and separated. The aqueous layer was extracted with hexane, and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated to afford 8.3 g (80% yield) of **1d**: IR (CH_2Cl_2) 3055 (s), 2987 (m), 1765 (s), 1509 (s), 1465 (m), 1421 (s), 1271 (s), 1205 (s), 1155 (s), 1035 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.98 (m, 3 H), 4.74 (s, 2 H), 3.85 (s, 3 H), 2.31 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 168.8, 150.8, 136.5, 124.3, 122.9, 121.3, 113.2, 55.96, 33.12, 20.63; MS (EI) 39 (7), 43 (12), 51 (4), 65 (6), 78 (4), 94 (5), 107 (5), 122 (9), 137 (100), 216 (9), 218 (9), 258 (3); exact mass calcd for $C_{10}H_{11}O_3Br$ 257.9892, observed 257.9898.

3-(Cyclohexanecarbonyl)benzyl Chloride. Cut zinc foil (3.84 g, 60 mmol) in 3 mL of dry THF was added to a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. 1,2-Dibromoethane (0.2 mL) and trimethylsilyl chloride (0.2 mL) were then added, and the mixture was heated with a heat gun until soaplike bubbles of ethylene indicated activation. Iodocyclohexane (10.5 g, 50 mmol) in 20 mL of dry THF was then added dropwise, and the mixture was stirred overnight at 45 °C. In a separate three-necked flask equipped with an argon inlet, a thermometer, and a rubber septum, dry LiCl (3.8 g, 90 mmol) was combined with CuCN (4.0 g, 45 mmol) in 20 mL of dry THF. The solution was stirred at 0 °C for 30 min and then cooled to -70 °C. The cyclohexylzinc iodide reagent was then added dropwise, and the mixture was warmed to 0 °C for 30 min. The mixture was then recooled to -70 °C, and 3-(chloromethyl)benzoyl chloride (3.82 g, 36 mmol) was added slowly. After addition, the reaction mixture was allowed to warm to 0 °C. After 2 h, the reaction mixture was worked up, affording 7.49 g (94% yield) of 3-(cyclohexanecarbonyl)benzyl chloride, which was used without further purification: crude ^1H NMR ($CDCl_3$, 300 MHz) δ 7.96 (s, 1 H), 7.88 (d, 1 H, J = 9.0 Hz), 7.57 (d, 1 H, J = 9.0 Hz), 7.45 (t, 1 H, J = 9.0 Hz), 4.63 (s, 2 H), 3.28 (m, 1 H), 2.05-1.65 (m, 5 H), 1.65-1.20 (m, 5 H).

3-(Cyclohexanecarbonyl)benzyl Bromide (1e). In a 50-mL round-bottomed flask equipped with a reflux condenser, 3-(cyclohexanecarbonyl)benzyl chloride (6.6 g, 28 mmol) was combined with lithium bromide (4.82 g, 56 mmol) in 22 mL of acetone and heated to reflux. After 45 min, the acetone was evaporated and hexane/CH_2Cl_2 (5:1) was added. The insoluble lithium salts were filtered off, and the solvent was removed. Lithium bromide (6.6 g, 28 mmol) was added in 20 mL of acetone, and the mixture was again heated to reflux. This process was repeated twice. The

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Table I. Products 5–36 Obtained by the Reaction of the Benzylic Copper Organometallics 3 with Electrophiles

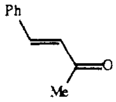
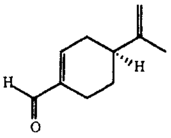
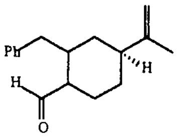
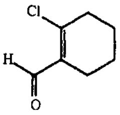
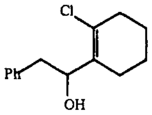
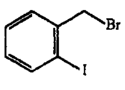
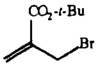
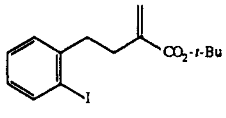
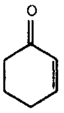
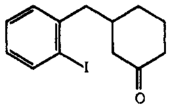
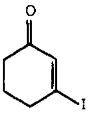
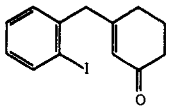
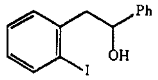
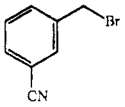
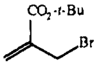
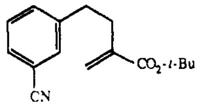
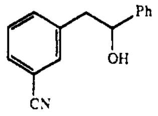
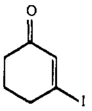
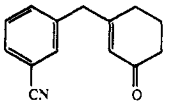
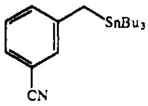
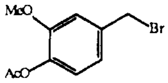
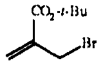
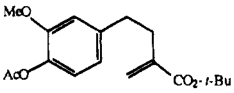
		reaction conditions for the organozinc formation					
entry	benzylic halide	proc	solv	temp °C, time h	electrophile	products 5–36	yield,[a] %
1	$PhCH_2Br$ **1a**	A	THF	5, 2	$CH_3CH_2CH_2CHO$	$PhCH_2CH(OH)CH_2CH_2CH_3$ **5**	94
2	**1a**	A	THF	5, 2		$PhCH_2CH(Ph)CH_2COCH_3$ **6**	91
3	**1a**	A	THF	5, 2		 **7**	72
4	**1a**	A	THF	5, 2	 **37**	 **8**	70
5	 **1b**	A	THF	5, 1		 **9**	97
6	**1b**	A	THF	5, 1		 **10**	93
7	**1b**	A	THF	5, 1		 **11**	85
8	**1b**	A	THF	5, 1	PhCHO	 **12**	93
9	 **1c**	A	THF	5, 2		 **13**	97
10	**1c**	A	THF	5, 2	PhCHO	 **14**	94
11	**1c**	A	THF	5, 2		 **15**	84
12	**1c**	B	THF	5, 2	Bu_3SnCl	 **16**	86
13	 **1d**	A	THF	10, 3		 **17**	98

Table I (Continued)

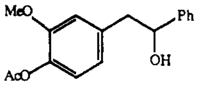
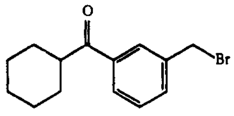
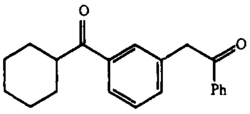
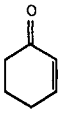
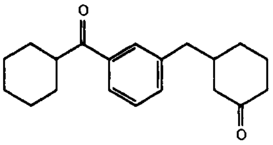
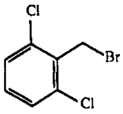
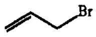
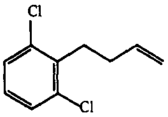
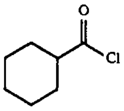
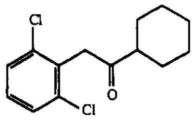
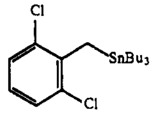
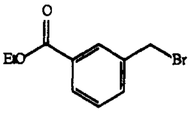
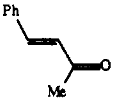
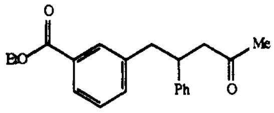
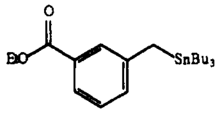
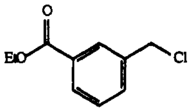
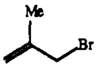
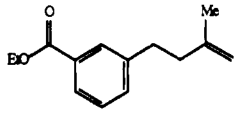
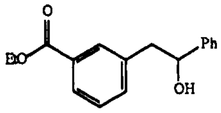
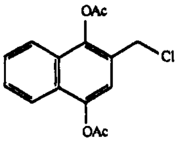
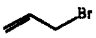
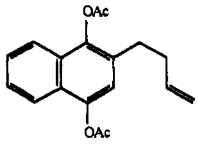
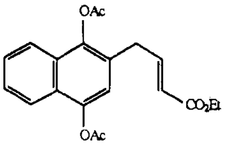
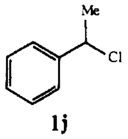
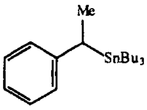
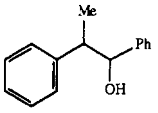
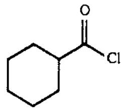
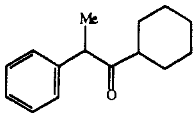
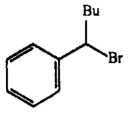
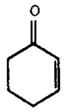
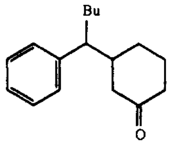
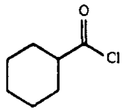
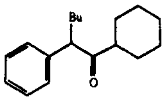
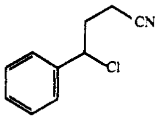
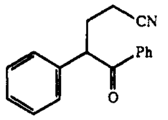
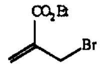
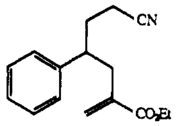
		reaction conditions for the organozinc formation					
entry	benzylic halide	proc	solv	temp °C, time h	electrophile	products **5–36**	yield,[a] %
14	**1d**	A	THF	10, 3	PhCHO	 **18**	85
15	 **1e**	A	THF	5, 2	PhCOCl	 **19**	90
16	**1e**	A	THF	5, 2		 **20**	95
17	 **1f**	A	THF	5, 1		 **21**	96
18	**1f**	A	THF	5, 1		 **22**	92
19	**1f**	B	THF	5, 1	Bu_3SnCl	 **23**	84
20	 **1g**	B	THF	5, 2		 **24**	92
21	**1g**	B	THF	5, 2	Bu_3SnCl	 **25**	88
22	 **1h**	*b*	THF	35–45, 48		 **26**	87
23	**1h**	*b*	THF	35–45, 48	PhCHO	 **27**	97
24	 **1i**	A	THF	65, 3		 **28**	82

Table I (Continued)

entry	benzylic halide	reaction conditions for the organozinc formation: proc	solv	temp °C, time h	electrophile	products 5–36	yield,[a] %
25	1i	C	THF:DMSO (4:1)	45, 3	$H-\equiv-CO_2Et$	 **29**	79
26	 **1j**	C	THF:DMSO (4:1)	25, 24	Bu_3SnCl	 **30**	92
27	1j	C	THF:DMSO (4:1)	25, 24	PhCHO	 **31**	96
28	1j	C	THF:DMSO (4:1)	25, 24		 **32**	93
29	 **1k**	B	THF	5, 4		 **33**	94
30	1k	B	THF	5, 4		 **34**	92
31	 **1l**	C	THF:DMSO (4:1)	25, 22	PhCOCl	 **35**	83
32	1l	C	THF:DMSO (4:1)	25, 22		 **36**	92

[a] All indicated yields are isolated yields. Satisfactory spectral data (IR, ^{1}H and ^{13}C NMR, and high-resolution mass spectra) were obtained for all new compounds. [b] Special reaction conditions. See Experimental Section.

final reaction yielded 7 g (89% yield) of **1e**: IR (neat) 2933 (s), 2853 (s), 1680 (s), 1601 (m), 1449 (s), 1371 (m), 1312 (m), 1289 (s), 1260 (s), 1212 (s), 1189 (m), 1161 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.94 (s, 1 H), 7.86 (d, 1 H, J = 9.0 Hz), 7.58 (d, 1 H, J = 9.0 Hz), 7.44 (t, 1 H, J = 9.0 Hz), 4.53 (s, 2 H), 3.25 (m, 1 H), 2.00–1.65 (m, 5 H), 1.65–1.25 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 208.7, 138.4, 137.0, 133.1, 129.1, 128.6, 128.2, 45.71, 32.60, 29.37, 25.94, 25.80; MS (EI) 41 (31), 49 (79), 63 (11), 84 (64), 90 (47), 118 (37), 169 (12), 171 (11), 187 (19), 199 (100), 225 (16), 280 (16); exact mass calcd for $C_{14}H_{17}OBr$ 280.0463, obsd 280.0467.

Ethyl 3-(Chloromethyl)benzoate[23] (1h). Ethanol (12 mL, 200 mmol), DMAP (1.2 g, 10 mmol), and pyridine (30 mL) in 20 mL of dry ether were combined in a three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. The solution was cooled to 0 °C, and 3-(chloromethyl)benzoyl chloride (28.4 mL, 200 mmol) in 10 mL of dry ether was added dropwise. After addition, the reaction mixture was warmed to room temperature and added to a dilute HCl/ether mixture. The organic layer was then washed with distilled water and brine, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by vacuum distillation (bp 112 °C, 0.1 mmHg) afforded 33.3 g (83% yield) of **1h**: IR (neat) 2982 (m), 1717 (s), 1446 (m), 1367 (m), 1290 (s), 1204 (s), 1107 (s), 1081 (m), 1024 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (s, 1 H), 7.99 (d, 1 H, J = 7.8 Hz), 7.57 (d, 1 H, J = 7.8 Hz), 7.42 (t, 1 H, J = 7.8 Hz), 4.61 (s, 2 H), 4.38 (q, 2 H, J = 7.2 Hz), 1.39 (t, 3 H, J = 7.2 Hz).

Ethyl 3-(Bromomethyl)benzoate[24] (1g). In a round-bottomed flask equipped ith a reflux condenser and a nitrogen inlet, ethyl 3-(chloromethyl)benzoate (**1h**, 5.96 g, 30 mmol) in 50 mL

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[23] Karrer, F. Ger. Patent 2,418,343, Nov. 7, 1974; *Chem. Abstr. 82*, P 111769v.

[24] Dawson, M.; et al. *J. Med. Chem.* **1984**, *27*, 1516.

of toluene was added to a saturated aqueous solution of potassium bromide (35 g, 300 mmol) and tetrabutylammonium chloride (1.67 g, 6 mmol). The reaction mixture was then heated to reflux for 4 h. The reaction mixture was cooled, and the aqueous layer was removed and replaced with fresh potassium bromide/tetrabutylammonium chloride solution. The reaction mixture was heated to reflux for another 2 h, and the aqueous layer was again replaced as above. After refluxing for another 2 h, the reaction mixture was separated, the aqueous layer was extracted with ether, and the combined organic layers were dried, filtered, and concentrated. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 4.32 g (60% yield) of **1g**: IR (neat) 2895 (m), 1719 (s), 1612 (m), 1414 (s), 1367 (s), 1312 (s), 1276 (s), 1178 (s), 1102 (s), 1021 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.06 (s, 1 H), 7.99 (d, 1 H, J = 7.8 Hz), 7.57 (d, 1 H, J = 7.8 Hz), 7.42 (t, 1 H, J = 7.8 Hz), 4.49 (s, 2 H), 4.37 (q, 2 H, J = 7.1 Hz), 1.39 (t, 3 H, J = 7.1 Hz).

1,4-Diacetoxy-2-(chloromethyl)naphthalene (1i). A 500-mL separatory funnel was charged with 2-methyl-1,4-naphthoquinone (15 g, 87.1 mmol) in 100 mL of ether and sodium hydrosulfite $Na_2S_2O_4$ (30.0 g, 172.3 mmol) in 100 mL of water. The separatory funnel was shaken thoroughly until the etheral layer became colorless. The organic layer was washed three times with 70 mL of water, three times with 70 mL of brine, dried over $MgSO_4$, and concentrated on a rotary evaporator. The crude mixture of 2-methyl-1,4-naphthohydroquinone[25] (15.3 g) was then diluted with 200 mL of CH_2Cl_2 in a 500-mL round-bottomed flask. The reaction mixture was cooled to 0 °C and charged with acetic anhydride (12.0 g, 100 mmol), triethylamine (10.6 g, 105 mmol), and 4-(dimethylamino)pyridine (DMAP, 0.61 g, 5.0 mmol). The reaction was allowed to stir at 0 °C for 1 h and at 23 °C for 40 h. The reaction was then quenched with 20 mL of saturated aqueous NH_4Cl. The mixture was washed three times with water and three times with brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. Recrystallization of the residue (hexane/ethyl acetate) afforded 10.6 g of 2-methyl-1,4-naphthohydroquinone diacetate: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, 1 H, J = 6.6 Hz), 7.74 (d, 1 H, J = 7.0 Hz), 7.50 (m, 1 H), 7.15 (s, 1 H), 2.48 (s, 3 H), 2.46 (s, 3 H), 2.33 (s, 3 H). A 250-mL round-bottomed flask was charged with 10.0 g (35.5 mmol) of the diacetate, *N*-bromosuccinimide (7.58 g, 42.6 mmol), and AIBN (0.23 g, 1.42 mmol) in 50 mL of CCl_4. The reaction was allowed to reflux for 5 h. After cooling, the reaction was diluted with 100 mL of ethyl acetate. The solution was filtered through a bed of Celite and concentrated on a rotary evaporator. Purification of the residue by flash chromatography (hexane:ethyl acetate = 1:1) gave 7.56 g (29.3 mmol) of 1,4-diacetoxy-2-(bromomethyl)-naphthalene as pale pink crystals: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (m, 1 H), 7.48 (m, 1 H), 7.56 (m, 2 H), 7.34 (s, 1 H), 4.53 (s, 2 H), 2.54 (s, 3 H), 2.48 (s, 3 H). A 250-mL round-bottomed flask was charged with the bromide (23.7 g, 70 mmol), 50 mL of saturated aqueous NaCl, 50 mL of toluene, and 0.5 g of tetrabutylammonium chloride. The reaction mixture was heated to 100 °C for 4 h. The aqueous layer was decanted, and the mixture was again charged with 50 mL of saturated aqueous NaCl and 0.5 g of tetrabutylammonium chloride. The solution was heated again at 100 °C for 4 h. This procedure was repeated once more. The organic layer was then washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was recrystallized from hexane/ethyl acetate to afford 15.2 g (51.96 mmol, 74% yield) of **1i**: IR (Nujol) 2955 (s), 2925 (s), 2855 (s), 1763 (s), 1465 (m), 1377 (m), 1367 (m), 1200 (s), 1183 (s), 1175 (m), 1160 (m), 1066 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (m, 1 H), 7.76 (m, 1 H), 7.62 (m, 2 H), 7.48 (s, 1 H), 4.53 (s, 2 H), 2.56 (s, 3 H), 2.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 168.8, 168.6, 144.6, 142.4, 127.7, 127.5, 127.3, 127.2, 125.6, 121.9, 121.5, 118.7, 40.61, 20.69, 20.30; MS (EI) 43 (100), 76 (7), 105 (9), 115 (22), 144 (6), 172 (78), 208 (56), 250 (14), 292 (4); exact mass calcd for $C_{15}H_{13}O_4Cl$ 292.0502, obsd 292.0508.

α-Butylbenzyl Alcohol.[26] A three-necked flask equipped with an argon inlet, a thermometer, and an additional funnel was charged with benzaldehyde (5.3 g, 50 mmol) in 10 mL of dry THF. The solution was cooled to −70 °C, and a 1.6 M solution of *n*-butyllithium in hexane (37.5 mL, 60 mmol) was added dropwise slowly. After addition, the reaction mixture was warmed to room temperature and quenched with an ammonium chloride/ether mixture. The organic layer was washed with sodium bicarbonate, ammonium chloride, and water. The aqueous layer was extracted twice with ether, and the combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by vacuum distillation (bp 155 °C, 50 mmHg) afforded 7.95 g (100% yield) of α-butylbenzyl alcohol: IR (neat) 3360 (s), 3029 (m), 2956 (s), 2932 (s), 2872 (s), 2869 (s), 1455 (s), 1041 (s), 1031 (s), 1012 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34–7.22 (m, 5 H), 4.58 (t, 1 H, J = 6.7 Hz), 2.29 (s, 1 H), 1.78–1.65 (m, 2 H), 1.36–1.18 (m, 4 H), 0.87 (t, 3 H, J = 7.0 Hz).

α-Butylbenzyl Bromide (1k). A three-necked flask equipped with an argon inlet, a thermometer, and a rubber septum was charged with α-butylbenzyl alcohol (7.95 g, 50 mmol) in 50 mL of dry ether. The solution was cooled to 0 °C, and phosphorus tribromide (2.9 mL, 30 mmol) was added dropwise. After addition, the reaction mixture was warmed to room temperature and quenched with an ice water/hexane mixture. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. Purification of the residue by vacuum distillation (bp 61 °C, 0.1 mmHg) yielded 4.97 g (73% yield) of **1k**: IR (neat) 3031 (m), 2961 (s), 2931 (s), 2872 (s), 2861 (s), 1494 (m), 1465 (m), 1455 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58–7.21 (m, 5 H), 4.98 (t, 1 H, J = 7.5 Hz), 2.35–2.15 (m, 2 H), 1.56–1.40 (m, 4 H), 0.88 (t, 3 H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 142.4, 128.7, 128.3, 127.3, 55.80, 39.80, 30.41, 22.06, 13.88; MS (EI) 41 (6), 51 (4), 65 (4), 77 (7), 91 (100), 104 (17), 117 (11), 147 (83), 202 (1); exact mass calcd for $C_{11}H_{15}Br$ 226.0357, obsd 226.0359.

3-Iodopropionitrile.[27] A 250-mL, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet was charged with 3-chloropropionitrile (17.9 g, 200 mmol) in 100 mL of acetone. Sodium iodide (45 g, 350 mmol) was added, and the reaction mixture was stirred at reflux overnight. The acetone was then removed on a rotary evaporator, CH_2Cl_2 was added, and the sodium chloride was filtered out. Evaporation of the CH_2Cl_2 by rotary evaporation and purification of the residue by vacuum distillation (bp 96–98 °C, 10 mmHg) afforded 32.5 g (90% yield) of 3-iodopropionitrile: IR (neat) 3034 (m), 2956 (m), 2918 (m), 2253 (s), 1427 (s), 1414 (s), 1327 (m), 1252 (s), 1185 (s), 1175 (s) cm^{-1}; ^{1}H NMR (THF-d_8, 300 MHz) δ 3.33 (t, 2 H, J = 6.8 Hz), 3.05 (t, 2 H, J = 6.8 Hz).

2-Cyanoethylzinc Iodide.[28] Cut zinc foil (2.57 g, 48 mmol) in 2 mL of dry THF was added to a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. 1,2-Dibromoethane (0.16 mL) and trimethylsilyl chloride (0.16 mL) were then added, and the mixture was heated with a heat gun until soaplike bubbles of ethylene indicated activation. At room temperature, a solution of 3-iodopropionitrile (7.24 g, 40 mmol) in 14 mL of THF was added dropwise (1 drop/5–10 s). The reaction mixture was stirred at room temperature until GLC analysis showed complete conversion to the zinc reagent (ca. 4 h).

4-Hydroxy-4-phenylbutyronitrile.[29] In a three-necked flask equipped with an argon inlet, a thermometer, and a rubber septum, dry LiCl (3.06 g, 72 mmol) was combined with CuCN (3.24 g, 36 mmol) in 20 mL of dry THF. The mixture was cooled to −30 °C and (2-cyanoethyl)zinc bromide solution (36 mmol) was added. After 15 min, the copper reagent was cooled to below −70 °C (dry ice/acetone bath). $BF_3{\cdot}OEt_2$ (8.9 mL, 72 mmol) was added dropwise, with the temperature maintained below −60 °C. After the solution recooled to below −70 °C, benzaldehyde (3.07 g, 39 mmol) was added dropwise. The reaction mixture was then warmed slowly to room temperature overnight and worked up. Purification of the residue by flash chromatography (ethyl acetate:hexane = 1:1) afforded 4.39 g (94% yield) of 4-hydroxy-4-phenylbutyronitrile: IR (neat) 3418 (s), 2954 (s), 2934 (s), 2247 (s), 1770 (s), 1736 (s), 1494 (s), 1454 (s), 1423 (s), 1375 (s), 1331 (s), 1301 (s), 1272 (s), 1251 (s), 1216 (s), 1178 (s), 1090 (s), 1064 (s), 1027 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.27 (m, 5

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H), 4.71 (t, 1 H, J = 6.5 Hz), 3.02 (s, 1 H), 2.48–2.31 (m, 2 H), 1.99–1.94 (m, 2 H).

4-Chloro-4-phenylbutyronitrile[30] (11). A three-necked flasked equipped with a nitrogen inlet, a thermometer, and an addition funnel was charged with a solution of thionyl chloride (2.4 mL, 32 mmol) in 4 mL of benzene. A solution of 4-hydroxy-4-phenylbutyronitrile (4.67 g, 29 mmol) in 9 mL of benzene was added dropwise at room temperature. The reaction mixture was stirred until evolution of HCl and SO_2 ceased and then quenched by adding it to an ice water/ether mixture. The organic layer was then separated, decolorized over activated charcoal, dried over $MgSO_4$, filtered, and concentrated. Purification of the residue by flash chromatography (ether:hexane = 2:3) afforded 2.77 g (53% yield) of **11**: IR (neat) 3034 (m), 2938 (m), 2248 (s), 1494 (s), 1455 (s), 1437 (s), 1423 (s), 1250 (s), 1201 (m), 1002 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.36 (m, 5 H), 4.97 (t, 1 H, J = 7.0 Hz), 2.66–2.27 (m, 4 H).

1-Chloro-2-formylcyclohexene[16] (37). A 250-mL round-bottomed flask was charged with cyclohexanone (32.0 g, 0.327 mmol), *N*,*N*-dimethylformamide (59.9 g, 0.816 mmol), and 150 mL of CH_2Cl_2. The reaction was cooled to 0 °C, and $POCl_3$ (125 g, 0.816 mmol) was added dropwise. The reaction mixture was then washed with water and brine, dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The residue was distilled in vacuo (bp 30 °C, 0.1 mmHg) to afford 38.7 g of **37**: ^1H NMR ($CDCl_3$, 300 MHz) δ 10.12 (s, 1 H), 2.58 (m, 2 H), 2.25 (m, 2 H), 1.72 (m, 2 H), 1.57 (m, 2 H).

Preparation of Benzylic Zinc Halides. General Procedures. Procedure A. Cut zinc foil (approximately 5-mm^2 pieces, 2.30 g, 36 mmol) in 3 mL of dry THF was added to a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. 1,2-Dibromoethane (150 mg) was then added, and the mixture was heated with a heat gun until evolution of soaplike bubbles of ethylene and darkening of the zinc surface indicated activation. The mixture was cooled to 0–5 °C (ice bath), and a solution of the benzylic bromide **1** (30 mmol) in 15 mL of THF was added dropwise (1 drop/5–10 s). The reaction mixture was stirred at 5 °C until GLC analysis showed that the starting material was completely consumed (1–4 h).

Procedure B. Zinc dust (0.67 g, 10.5 mmol) in 1 mL of dry THF was added to a three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. The mixture was cooled in an ice bath, and a solution of the benzylic bromide **1** (7 mmol) in 7 mL of dry THF was added dropwise (1 drop/5–10 s). The reaction mixture was stirred at 5 °C until GLC analysis showed that the starting material was completely consumed (1–4 h).

Procedure C. Zinc dust (1.34 g, 21 mmol) in 1.5 mL of dry THF was added to a three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. A solution of the benzylic chloride **1** (7 mmol) in 5.5 mL of dry THF and 1.5 mL of DMSO was added dropwise at room temperature. The reaction mixture was stirred at room temperature until GLC analysis showed complete conversion of the starting material to the zinc organometallic (22–24 h).

Preparation of Benzylic Copper Derivatives from Benzylic Zinc Halides by Transmetalation. In a three-necked flask equipped with an argon inlet, a thermometer, and a rubber septum, heat-dried LiCl (1.14 g, 27 mmol) was combined with CuCN (1.21 g, 13.5 mmol) in 10.5 mL of dry THF. The mixture was cooled to −40 °C, and the benzylic organozinc reagent **2** (14.7 mmol, prepared as described above) was added to the copper solution by cannula. The mixture was allowed to warm to −20 °C for 5 min and then cooled to −78 °C (dry ice/acetone bath). The copper reagent **3** was then ready to react with various organic electrophiles as described below.

Reactions of Benzylic Copper Derivatives with Organic Electrophiles. 1-Phenyl-2-pentanol (5). Benzylzinc bromide was prepared from benzyl bromide (**1a**, 2.57 g, 15 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with less than 2% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), $BF_3 \cdot OEt_2$ (3.32 mL, 27 mmol) was added at −70 °C dropwise, maintaining the temperature below −60 °C. Butanal (0.792 g, 11 mmol) was then added dropwise at −70 °C. The reaction mixture was then warmed slowly to −30 °C and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 2:3) afforded 1.69 g (94% yield) of **5**. IR (neat) 3432 (s), 3063 (m), 3028 (m), 2984 (s), 2872 (s), 1495 (m), 1081 (m), 1031 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.4–7.2 (m, 5 H), 3.86 (m, 1 H), 2.9–2.6 (m, 2 H), 1.71 (s, 1 H), 1.6–1.4 (m, 4 H), 0.98 (t, 3 H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 138.7, 129.4, 128.4, 126.3, 72.31, 44.06, 38.93, 18.88, 14.00; MS (EI) 39 (8), 43 (14), 51 (4), 55 (23), 65 (10), 73 (5), 77 (5), 92 (100), 103 (5), 115 (1), 121 (3), 164 (1); exact mass calcd for $C_{11}H_{16}O$ 164.1201, obsd 164.1202.

4,5-Diphenyl-2-pentanone (6). Benzylzinc bromide was prepared from benzyl bromide (**1a**, 2.23 g, 13 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with less than 2% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), a solution of *trans*-4-phenyl-3-buten-2-one (1.46 g, 10 mmol), Me_3SiCl (3.0 mL, 24 mmol), and 3 mL of dry THF was added dropwise at −70 °C, and the reaction mixture was allowed to warm to room temperature overnight. The reaction was then worked up as usual, and purification of the residue by flash chromatography (hexane:ether = 4:1) afforded 2.16 g (91% yield) of **6**: IR (neat) 3061 (m), 3027 (m), 2924 (m), 1716 (s), 1495 (m), 1453 (m), 1357 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.3–7.0 (m, 10 H), 3.45 (quint, 1 H, J = 7.5 Hz), 2.87 (d 2 H, J = 7.5 Hz), 2.8–2.6 (m, 2 H), 1.96 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 207.3, 143.8, 139.6, 129.1, 128.3, 128.1, 127.5, 126.4, 126.0, 49.07, 43.07, 42.93, 30.48; MS (CI–isobutane) 77 (7), 81 (4), 94 (1), 119 (2), 136 (1), 163 (3), 180 (3), 221 (2), 239 (100), 256 (32); exact mass calcd for $C_{17}H_{19}O$ 239.1436, obsd 239.1419.

2-(Phenylmethyl)-4-isopropenyl-1-formylcyclohexane (7). Benzylzinc bromide was prepared from benzyl bromide (**1a**, 1.24 g, 7.2 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with less than 2% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), a solution of perillaldehyde (Aldrich, 0.75 g, 5 mmol), Me_3SiCl (1.0 mL, 8 mmol), and 1 mL of dry THF was then added dropwise, and the reaction mixture was allowed to warm to −40 °C for 4 h and then stirred at 0 °C for 3 h. The reaction was then worked up as usual, and purification of the residue by flash chromatography (hexane:ethyl acetate = 9:1) afforded 0.87 g (72% yield) of **7** as a mixture of two diastereoisomers (4:1 ratio): IR (neat) 3084 (s), 3026 (s), 3000 (s), 2959 (s), 1720 (s), 1703 (s), 1643 (s), 1496 (s), 1453 (s), 1031 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 9.72 (s, 1 H), 7.3–7.1 (m, 5 H), 4.68 (s, 2 H), 2.67–2.48 (m, 4 H), 2.23 (m, 1 H), 1.98 (m, 2 H), 1.61 (m, 2 H), 1.48 (s, 3 H), 1.3 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 204.6, 180.2, 149.5, 140.5, 140.3, 129.0, 128.9, 128.3, 126.1, 125.8, 109.1, 108.8, 58.3, 53.5, 46.3, 38.4, 37.9, 23.6, 22.5, 20.9, 20.6, 18.2; MS (EI) 41 (23), 67 (18), 81 (24), 91 (100), 117 (84), 133 (20), 151 (43), 224 (7), 242 (13); exact mass calcd for $C_{17}H_{22}O$ 242.1670, obsd 242.1666.

1-Chloro-2-(1-hydroxy-2-phenylethyl)cyclohex-1-ene (8). Benzylzinc bromide was prepared from benzyl bromide (**1a**, 1.59 g, 9 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with less than 2% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), aldehyde **37** (1.0 g, 8.0 mmol) was added. The reaction mixture was stirred at −60 °C for 3 h and then at 23 °C for 2 days. The reaction was quenched with saturated aqueous NH_4Cl at 0 °C and worked up as usual. Purification of the residue by flash chromatography (hexane:ethyl acetate = 8:1) afforded 1.32 g (70% yield) of **8**: IR (CH_2Cl_2) 3589 (s), 3542 (s), 3524 (s), 3054 (m), 2941 (m), 1658 (w), 1454 (w), 1265 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.2–7.6 (m, 5 H), 5.0 (m, 1 H), 2.83 (m, 2 H), 2.2–2.4 (m, 4 H), 2.1 (m, 1 H), 1.8–1.6 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 138.0, 134.4, 129.2, 128.2, 127.3, 126.3, 72.2, 40.9, 33.9, 24.5, 23.7, 21.9; MS (CI − NH_4^+) 254 (MNH_4^+, 9), 236 (100)219 (40), 201 (22), 183 (34), 141 (6), 91 (22), 81 (18); exact mass calcd for $C_{14}H_{17}ClONH_4^+$ 254.1306, obsd 254.1312.

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***tert*-Butyl 4-(2-Iodophenyl)-2-methylenebutyrate (9).** (2-Iodobenzyl)zinc bromide was prepared from 2-iodobenzyl bromide (**1b**, 2.98 g, 10 mmol) according to procedure A. GLC analysis showed complete conversion in 1 h with less than 3% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), *tert*-butyl α-(bromomethyl)acrylate (1.76 g, 7.2 mmol) was added dropwise at −70 °C. The reaction mixture was warmed slowly to 0 °C and worked up as usual. Purification of the residue by flash chromatography (hexane:ether = 9:1) afforded 2.50 g (97% yield) of **9**: IR (neat) 3003 (m), 2976 (s), 2931 (m), 1710 (s), 1628 (m), 1466 (s), 1368 (s), 1254 (s), 1158 (s), 1140 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80 (d, 1 H, J = 7.9 Hz), 7.30–7.15 (m, 2 H), 6.87 (t, 1 H, J = 7.9 Hz), 6.08 (s, 1 H), 5.46 (s, 1 H), 2.89 (t, 2 H, J = 8.2 Hz), 2.58 (t, 2 H, J = 8.2 Hz), 1.51 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 165.4, 141.2, 139.4, 129.6, 128.3, 127.8, 124.6, 100.6, 80.57, 40.02, 32.48, 28.14, 0.42; MS (CI – isobutane) 129 (3), 175 (11), 217 (3), 285 (4), 303 (100), 359 (19); exact mass calcd for $C_{15}H_{20}O_2I$ 359.0508, obsd: 359.0516.

3-(2-Iodobenzyl)cyclohexanone (10). The (2-iodobenzyl)-copper reagent (9 mmol) was prepared as indicated in the synthesis of **9**. 2-Cyclohexen-1-one (0.70 g, 7.2 mmol) and Me_3SiCl (2.2 mL, 18 mmol) were then added at −70 °C. The mixture was allowed to warm to room temperature overnight and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 2.11 g (93% yield) of **10**: IR (neat) 2935 (s), 2864 (s), 1711 (s), 1550 (m), 1467 (s), 1446 (s), 1225 (s), 1009 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, 1 H, J = 7.9 Hz), 7.23 (t, 1 H, J = 7.6 Hz), 7.12 (d, 1 H, J = 7.6 Hz), 6.98 (t, 1 H, J = 7.7 Hz), 2.85–2.65 (m, 2 H), 2.45–2.00 (m, 6 H), 2.00–1.80 (m, 1 H), 1.70–1.35 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 210.9, 142.1, 139.6, 130.3, 128.0, 100.9, 47.45, 47.06, 41.32, 39.39, 30.85, 25.00, 0.31; MS (EI) 41 (74), 55 (52), 63 (13), 69 (83), 77 (10), 90 (35), 97 (65), 107 (4), 115 (26), 129 (91), 145 (6), 169 (4), 187 (100), 217 (21), 234 (5), 256 (14), 314 (16); exact mass calcd for $C_{13}H_{15}IO$ 314.0168, obsd 314.0166.

3-(2-Iodobenzyl)-2-cyclohexen-1-one (11). The (2-iodobenzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **9**. 3-Iodo-2-cyclohexen-1-one (1.60 g, 7.2 mmol) in 2 mL of dry THF was then added dropwise at −70 °C. After addition, the reaction mixture was allowed to warm slowly to −30 °C. After 2 h, the reaction mixture was worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 2:3) afforded 1.90 g (85% yield) of **11**: IR (neat) 2919 (m), 1668 (s), 1627 (m), 1465 (m), 1432 (m), 1012 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (d, 1 H, J = 7.9 Hz), 7.30 (t, 1 H, J = 7.5 Hz), 7.17 (d, 1 H, J = 7.6 Hz), 6.94 (t, 1 H, J = 7.7 Hz), 5.63 (s, 1 H), 3.65 (s, 2 H), 2.40–2.33 (m, 4 H), 2.06–1.97 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 199.6, 163.4, 140.9, 130.5, 128.6, 127.3, 101.4, 65.82, 48.56, 37.34, 29.88, 22.60, 15.25; MS (EI) 39 (19), 51 (8), 67 (14), 77 (7), 90 (11), 102 (3), 115 (10), 129 (100), 141 (4), 157 (12), 167 (3), 185 (9), 217 (3), 312 (29); exact mass calcd for $C_{13}H_{13}IO$ 312.0011, obsd 312.0012.

1-Phenyl-2-(2-iodophenyl)ethanol (12). The (2-iodobenzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **9**. Benzaldehyde (0.77 g, 7.3 mmol) and $BF_3\cdot OEt_2$ (2.2 mL, 18 mmol) were then added at −70 °C. The mixture was warmed slowly to −30 °C overnight and worked up as usual. Purification of the residue by flash chromatography (hexane:ether = 4:1) afforded 2.18 g (93% yield) of **12**: IR ($CDCl_3$) 3153 (s), 2992 (m), 2966 (m), 2921 (m), 2358 (s), 2320 (s), 1795 (s), 1722 (m), 1676 (s), 1563 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, 1 H, J = 7.9 Hz), 7.45–7.15 (m, 7 H), 6.92 (t, 1 H, J = 7.9 Hz), 5.1–4.9 (m, 1 H), 3.2–3.0 (m, 2 H), 1.93 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 143.8, 140.4, 139.6, 131.3, 128.4, 128.2, 127.1, 125.7, 101.3, 73.33, 50.40, 0.63; MS (EI) 39 (8), 51 (11), 63 (7), 79 (55), 90 (17), 107 (100), 152 (1), 165 (2), 178 (3), 218 (93), 307 (1), 324 (1); exact mass calcd for $C_{14}H_{13}IO$ 324.0011, obsd 324.0029.

***tert*-Butyl 4-(3-Cyanophenyl)-2-methylenebutyrate (13).** (3-Cyanobenzyl)zinc bromide was prepared from 3-cyanobenzyl bromide (**1c**, 1.95 g, 10 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with no detectable Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), *tert*-butyl α-(bromomethyl)acrylate (1.67 g, 7.2 mmol) was added at −78 °C. The reaction mixture was allowed to warm slowly to 0 °C and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 1.83 g (97% yield) of **13**: IR (neat) 2978 (s), 2933 (m), 2230 (s), 1709 (s), 1632 (m), 1483 (m), 1368 (s), 1318 (m), 1208 (s), 1152 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50–7.37 (m, 4 H), 6.07 (s, 1 H), 5.42 (s, 1 H), 2.82 (t, 2 H, J = 7.8 Hz), 2.57 (t, 2 H, J = 7.8 Hz), 1.51 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.2, 142.8, 140.7, 132.4, 131.0, 129.0, 128.3, 124.1, 118.6, 111.7, 80.7, 33.80, 33.11, 27.59; MS (EI) 41 (22), 51 (2), 57 (100), 63 (4), 77 (3), 89 (9), 103 (1), 116 (28), 129 (4), 142 (2), 155 (18), 184 (21), 201 (15), 257 (2); exact mass calcd for $C_{16}H_{19}NO_2$ 257.1416, obsd 257.1406.

1-Phenyl-2-(3-cyanophenyl)ethanol (14). The (3-cyanobenzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **13**. Benzaldehyde (0.76 g, 7.2 mmol) and $BF_3\cdot OEt_2$ (2.2 mL, 18 mmol) were then added at −70 °C. After warming to −30 °C (ca. 30–45 min), the reaction was complete by GLC analysis. The usual workup and purification of the residue by flash chromatography (ether:hexane = 1:9) afforded 1.50 g (94% yield) of **14**: IR (neat) 3451 (s), 3063 (m), 3038 (m), 2976 (m), 2876 (m), 2229 (s), 1623 (m), 1588 (m), 1483 (s), 1453 (s), 1049 (s), 1029 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.25 (m, 9 H), 4.85 (m, 1 H), 3.1–2.9 (m, 2 H), 2.06 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 143.3, 139.6, 134.1, 133.1, 130.1, 128.9, 128.5, 128.0, 125.8, 118.8, 112.2, 74.88, 45.11; MS (EI) 39 (6), 51 (9), 63 (4), 79 (40), 89 (7), 107 (100), 117 (19), 203 (1), 223 (2); exact mass calcd for $C_{15}H_{13}NO$ 223.0997, obsd 223.1000.

3-(3-Cyanobenzyl)-2-cyclohexen-1-one (15). The (3-cyanobenzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **13**. 3-Iodo-2-cyclohexen-1-one (1.60 g, 7.2 mmol) in 5 mL of dry THF was then added dropwise at −70 °C. After addition, the reaction mixture was allowed to warm up slowly to −30 °C, stirred overnight, and then worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 3:2) afforded 1.28 g (84% yield) of **15**: IR (neat) 2947 (m), 2229 (s), 1668 (s), 1627 (s), 1428 (s), 1373 (m), 1349 (m), 1252 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.60–7.40 (m, 4 H), 5.79 (s, 1 H), 3.56 (s, 2 H), 2.38 (t, 2 H, J = 5.9 Hz), 2.27 (t, 2 H, J = 5.9 Hz), 1.99 (quint, 2 H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 198.9, 162.7, 138.4, 133.5, 132.4, 130.8, 129.2, 127.0, 118.4, 112.7, 43.78, 37.30, 29.46, 22.43; MS (EI) 39 (40), 67 (39), 89 (10), 116 (11), 140 (14), 154 (44), 183 (100), 211 (80); exact mass calcd for $C_{14}H_{13}NO$ 211.0997, obsd 211.0997.

(3-Cyanobenzyl)tributyltin (16). (3-Cyanobenzyl)zinc bromide was prepared from 3-cyanobenzyl bromide (**1c**, 1.52 g, 7.8 mmol) according to procedure B. GLC analysis showed complete conversion in 2 h with no detectable Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), tributyltin chloride (1.82 g, 5.6 mmol) was added dropwise at −78 °C. The reaction mixture was allowed to warm slowly. After 3 h, TLC analysis showed no more starting material, and the reaction mixture was then worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 1.89 g (86% yield) of **16**: IR (neat) 2957 (s), 2927 (s), 2872 (s), 2852 (s), 2229 (m), 1593 (m), 1577 (m), 1480 (m), 1464 (m), 1241 (m), 1080 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.24–7.16 (m, 4 H), 2.29 (s, 2 H), 1.48–1.17 (m, 15 H), 0.91–0.78 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 145.9, 131.3, 130.0, 129.0, 126.6, 119.3, 112.3, 28.83, 27.25, 18.33, 13.59, 9.55; MS (EI) 41 (27), 49 (68), 57 (12), 63 (8), 84 (14), 116 (74), 121 (54), 179 (100), 211 (4), 235 (73), 350 (4), 407 (6); exact mass calcd for $C_{20}H_{33}NSn$ 407.1635, obsd 407.1621.

***tert*-Butyl 4-(4-Acetoxy-3-methoxyphenyl)-2-methylenebutyrate (17).** 4-Acetoxy-(3-methoxybenzyl)zinc bromide was prepared from 4-acetoxy-3-methoxybenzyl bromide (**1d**, 2.24 g, 8.6 mmol) according to procedure A. GLC analysis showed complete conversion in 3 h with 8% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), *tert*-butyl α-(bromomethyl)acrylate (1.43 g, 6.2 mmol) was added at −78 °C, and the reaction mixture was warmed slowly to 0 °C. The reaction mixture was then worked up as usual, and purification of the residue by flash chromatography (hexane:ether = 3:2) afforded 1.94 g (98% yield) of **17**: IR ($CDCl_3$) 3188 (m), 3150 (m), 2254 (s), 1760 (s), 1705 (s), 1647 (m), 1603 (m), 1510 (s), 1465 (s), 1458 (s), 1370 (s), 1281 (s), 1258 (s), 1221 (s), 1200 (s), 1153 (s), 1122 (s), 1038 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 6.95–6.90 (m, 1 H), 6.8–8.7 (m, 2 H), 6.08 (s, 1 H), 5.47 (s, 1 H), 3.81 (s, 3 H), 2.8–2.7 (m, 2 H), 2.6–2.5 (m, 2 H), 2.31 (s, 3 H), 1.52 (s, 9 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 169.0, 166.2, 150.8, 141.5, 140.5, 137.9, 124.3, 122.4, 120.5, 112.7, 80.53, 55.79, 35.08, 34.03, 28.07, 20.61; MS (EI) 43 (27), 51 (2), 57 (25), 65 (3), 77 (4), 91 (2), 107 (3), 117 (4), 137 (100), 143 (3), 161 (1), 189 (1), 205 (10), 222 (29), 247 (4), 264 (2), 278 (7), 320 (2); exact mass calcd for $C_{18}H_{24}O_5$ 320.1624, obsd 320.1631.

1-Phenyl-2-(4-acetoxy-3-methoxyphenyl)ethanol (18). The (4-acetoxy-3-methoxybenzyl)copper reagent (7.7 mmol) was prepared as indicated in the synthesis of **17**. Benzaldehyde (0.61 g, 5.8 mmol) and $BF_3{\cdot}OEt_2$ (1.9 mL, 15.4 mmol) were then added at −70 °C. The mixture was warmed slowly to −30 °C and worked up as usual after 4 h. Purification of the residue by flash chromatography (hexane:CH_2Cl_2:ether = 9:9:2) afforded 1.40 g (85% yield) of **18**: IR (CH_2Cl_2) 3600 (m), 3512 (m), 3062 (s), 2998 (s), 2551 (s), 2893 (m), 2319 (m), 1763 (s), 1609 (s), 1425 (s), 1376 (s), 1263 (s), 1207 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.40–7.25 (m, 5 H), 6.94 (d, 1 H, J = 8.0 Hz), 6.76 (d, 1 H, J = 8.0 Hz), 6.70 (s, 1 H), 4.86 (t, 1 H, J = 6.7 Hz), 3.73 (s, 3 H), 2.98 (d, 2 H, J = 6.7 Hz), 2.29 (s, 3 H), 2.09 (s, 1 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 169.1, 150.2, 143.8, 138.5, 137.0, 128.4, 127.6, 125.9, 122.6, 121.7, 113.9, 75.09, 55.78, 45.87, 20.56; MS (EI) 39 (7), 43 (36), 51 (8), 55 (4), 65 (4), 79 (28), 94 (6), 107 (34), 123 (9), 137 (100), 149 (2), 180 (36), 286 (1); exact mass calcd for $C_{17}H_{18}O_4$ 286.1205, obsd 286.1217.

3-(Cyclohexanecarbonyl)benzyl Phenyl Ketone (19). (3-(Cyclohexanecarbonyl)benzyl)zinc bromide was prepared from 3-(cyclohexanecarbonyl)benzyl bromide (**1e**, 3.11 g, 10 mmol) according to procedure A. GLC analysis showed complete conversion in 2 h with no detectable Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), benzoyl chloride (0.98 g, 7.2 mmol) in 2 mL of dry THF was added dropwise at −60 °C. The reaction mixture was warmed slowly to −20 °C overnight and then worked up as usual. Purification of the residue by flash chromatography (hexane:CH_2Cl_2 = 1:4) afforded 1.99 g (90% yield) of **19**: IR (neat) 2932 (s), 2855 (s), 1679 (s), 1597 (m), 1582 (m), 1448 (s), 1334 (s), 1315 (m), 1237 (m), 1209 (s), 1161 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.02 (d, 2 H, J = 7.4 Hz), 7.83 (s, 2 H), 7.6–7.4 (m, 5 H), 4.36 (s, 2 H), 3.30–3.15 (m, 1 H), 1.95–1.65 (m, 5 H), 1.6–1.2 (m, 5 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 203.6, 197.1, 137.2, 136.8, 135.2, 133.9, 133.4, 129.5, 128.9, 128.8, 128.6, 126.9, 45.68, 45.14, 29.43, 25.97, 25.83; MS (EI) 41 (9), 55 (9), 65 (1), 77 (25), 84 (13), 105 (100), 119 (3), 133 (9), 149 (2), 163 (4), 187 (6), 223 (16), 306 (3); exact mass calcd for $C_{21}H_{22}O_2$ 306.1620, obsd 306.1628.

3-(3-(Cyclohexanecarbonyl)benzyl)cyclohexanone (20). The (3-(cyclohexanecarbonyl)benzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **19**. 2-Cyclohexen-1-one (0.70 g, 7.2 mmol) and Me_3SiCl (2.2 mL, 18 mmol) were then added at −70 °C. The mixture was allowed to warm to room temperature overnight and worked up as usual. Purification of the residue by flash chromatography (CH_2Cl_2) afforded 2.03 g (95% yield) of **20**: IR (neat) 2932 (s), 2855 (s), 2275 (m), 1711 (s), 1678 (s), 1600 (m), 1588 (m), 1449 (s), 1375 (m), 1313 (m), 1254 (s), 1227 (m), 1161 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.85–7.65 (m, 2 H), 7.45–7.25 (m, 2 H), 3.35–3.20 (m, 1 H), 2.69 (t, 2 H, J = 6.9 Hz), 2.4–2.2 (m, 3 H), 2.15–1.95 (m, 3 H), 1.9–1.1 (m, 13 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 211.1, 203.9, 140.1, 136.7, 133.4, 128.8, 128.6, 126.3, 47.66, 45.70, 42.80, 41.33, 40.73, 30.89, 29.45, 25.96, 25.83, 24.99; MS (EI) 41 (100), 47 (21), 55 (81), 69 (20), 84 (70), 91 (39), 97 (28), 119 (27), 129 (35), 171 (16), 187 (13), 201 (13), 215 (65), 243 (18), 280 (11), 298 (15); exact mass calcd for $C_{20}H_{26}O_2$ 298.1933, obsd 298.1938.

4-(2,6-Dichlorophenyl)-1-butene (21). (2,6-Dichlorobenzyl)zinc bromide was prepared from 2,6-dichlorobenzyl bromide (**1f**, 2.42 g, 10 mmol) according to procedure A. GLC analysis showed complete conversion in 1 h with 7% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), allyl bromide (0.87 g, 7.2 mmol) was added at −70 °C, and the mixture was allowed to warm slowly to −20 °C. The reaction was worked up as usual after 2 h. Purification of the residue by vacuum distillation (bp 49–50 °C, 0.1 mmHg) afforded 1.40 g (96% yield) of **21**: IR (neat) 3088 (m), 3003 (m), 2971 (m), 1663 (s), 1588 (m), 1563 (s), 1461 (s), 1438 (s), 1194 (m), 1087 (s), 1002 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.27 (d, 2 H, J = 9 Hz), 7.06 (t, 1 H, J = 9 Hz), 6.00–5.85 (m, 1 H), 5.15–4.95 (m, 2 H), 3.04 (t, 2 H, J = 6 Hz), 2.36 (quart., 2 H, J = 6 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 138.0, 137.6, 135.4, 128.2, 127.6, 115.3, 32.22, 30.28; MS (EI) 39 (8), 51 (5), 63 (7), 75 (6), 89 (8), 101 (3), 123 (7), 159 (100), 200 (8); exact mass calcd for $C_{10}H_{10}Cl_2$ 200.0160, obsd 200.0149.

Cyclohexyl 2,6-Dichlorobenzyl Ketone (22). The (2,6-dichlorobenzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **21**. Cyclohexanecarbonyl chloride (1.18 g, 7.2 mmol) was then added dropwise at −70 °C. The reaction mixture was then warmed slowly to −20 °C, stirred overnight, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:19) afforded 1.81 g (92% yield) of **22**: IR (CDCl$_3$) 2934 (s), 2906 (s), 2857 (s), 2254 (s), 1715 (s), 1565 (m), 1468 (s), 1319 (m), 1142 (m), 1089 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.29 (d, 2 H, J = 8.0 Hz), 7.13 (t, 1 H, J = 8.7 Hz), 4.13 (s, 2 H), 2.57–2.48 (m, 1 H), 1.99–1.64 (m, 5 H), 1.48–1.19 (m, 5 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 208.0, 136.2, 132.3, 128.6, 128.0, 50.74, 43.28, 28.70, 25.88, 25.67; MS (EI) 41 (19), 55 (42), 83 (100), 111 (42), 159 (6), 270 (1); exact mass calcd for $C_{14}H_{16}Cl_2O$ 270.0578, obsd 270.0572.

(2,6-Dichlorobenzyl)tributyltin (23). (2,6-Dichlorobenzyl)zinc bromide was prepared from 2,6-dichlorobenzyl bromide (**1f**, 1.69 g, 7 mmol) according to procedure B. GLC analysis showed complete conversion in 2 h with 1% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), tributyltin chloride (1.63 g, 5 mmol) was added at −70 °C, and the reaction mixture was allowed to warm slowly to room temperature. The usual workup and purification of the residue by flash chromatography (hexane) afforded 1.88 g (84% yield) of **23**: IR (neat) 2957 (s), 2927 (s), 2872 (s), 2854 (s), 1558 (m), 1464 (m), 1434 (s), 1376 nm), 1214 (m), 1078 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.19 (d, 2 H, J = 7.9 Hz), 6.87 (t, 1 H, J = 7.9 Hz), 2.58 (s, 2 H), 1.48–1.21 (m, 15 H), 0.88–0.82 (m, 12 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 141.2, 132.6, 127.6, 124.0, 28.91, 27.31, 15.93, 13.63, 10.83. Anal. Calcd for $C_{19}H_{32}Cl_2Sn$: C, 50.71; H, 7.17; Cl, 15.75. Found: C, 50.65; H, 7.36; Cl, 15.69.

Ethyl 3-(4-Oxo-2-phenylpentyl)benzoate (24). (3-(Carboethoxy)benzyl)zinc bromide was prepared from 3-(carboethoxy)benzyl bromide (**1g**, 1.69 g, 7 mmol) according to procedure B. GLC analysis showed complete conversion in 2 h with less than 1% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), *trans*-4-phenyl-3-buten-2-one (0.88 g, 6 mmol) was added in the presence of Me_3SiCl (1.9 mL, 15 mmol) at −70 °C. The mixture was allowed to warm to −5 °C overnight and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 1.71 g (92% yield) of **24**: IR (neat) 2990 (m), 1719 (s), 1610 (m), 1452 (m), 1416 (m), 1367 (m), 1309 (m), 1278 (s), 1178 (s), 1102 (s), 1022 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.87 (m, 2 H), 7.26–7.06 (m, 7 H), 4.33 (q, 2 H, J = 7.1 Hz), 3.46 (quint, 1 H, J = 8.0 Hz), 2.97–2.75 (m, 4 H), 2.01 (s, 3 H), 1.37 (t, 3 H, J = 7.1 Hz); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 207.3, 166.6, 145.1, 143.3, 131.4, 130.2, 129.5, 129.2, 128.5, 128.2, 127.6, 126.7, 60.80, 49.27, 42.95, 42.73, 30.59, 14.32; MS (CI - isobutane) 75 (5), 105 (3), 123 (100), 137 (19), 147 (6), 245 (3), 265 (3), 311 (11); exact mass calcd for $C_{20}H_{23}O_3$ 311.1647, obsd 311.1654.

3-(Carbethoxy)benzyltributyltin (25). The (3-(carboethoxy)benzyl)copper reagent (6.3 mmol) was prepared as indicated in the synthesis of **24**. Tributyltin chloride (1.63 g, 5 mmol) was then added at −70 °C. The reaction mixture was allowed to warm slowly to room temperature and then worked up as usual after 2 h. Purification of the residue by flash chromatography (hexane:ether = 9:1) afforded 1.98 g (88% yield) of **25**: IR (neat) 2957 (s), 2927 (s), 2872 (s), 2854 (s), 1720 (s), 1583 (m), 1464 (m), 1440 (m), 1301 (m), 1275 (s), 1200 (s), 1099 (s), 1024 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.67–7.63 (m, 2 H), 7.24–7.15 (m, 2 H), 4.34 (q, 2 H, J = 7.1 Hz), 2.34 (s, 2 H), 1.46–1.18 (m, 15 H), 0.91–0.78 (m, 15 H); ^{13}C NMR (CDCl$_3$, 75.5 MHz) δ 167.1, 144.3, 131.4, 130.6, 128.3, 128.0, 124.3, 60.71, 29.04, 27.31, 18.24, 14.34, 13.62, 9.46; MS (EI) 41 (19), 77 (18), 91 (13), 105 (88), 119 (61), 135 (7), 163 (13), 179 (100), 235 (68), 291 (50), 339 (4), 397 (1), 454 (2); exact mass calcd for $C_{22}H_{38}O_2Sn$ 454.1894, obsd 454.1901.

Ethyl 3-(3-Methylenebutyl)benzoate (26). Cut zinc foil (1.92 g, 30 mmol) in 3 mL of dry THF was added to a dry, three-necked flask equipped with an argon inlet, a thermometer, and an addition funnel. 1,2-Dibromoethane (150 mg) was then added, and the mixture heated with a heat gun until soaplike bubbles of ethylene indicated activation. The mixture was cooled to room temperature, and a solution of ethyl 3-(chloromethyl)benzoate (**1h**, 2.98 g, 15 mmol) in 15 mL of THF was added dropwise. After the addition, the reaction mixture was heated to 35 °C and stirred overnight. After 22 h, GLC showed 60% conversion. The reaction mixture was warmed to 45 °C and stirred for an additional 26 h (48 h total). GLC analysis showed complete conversion with no detectable Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), 2-(bromomethyl)propene (1.30 g, 10.8 mmol) was added at -70 °C. The reaction mixture was allowed to warm slowly to 0 °C and then worked up as usual after 2 h. Purification of the residue by vacuum distillation (bp 85 °C, 0.1 mmHg) afforded 1.90 g (87% yield) of **26**: IR (neat) 2981 (m), 2937 (m), 1719 (s), 1445 (m), 1368 (m), 1283 (s), 1197 (s), 1106 (s), 1083 (m), 1024 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.88 (m, 2 H), 7.36 (m, 2 H), 4.73 (d, 2 H, J = 12 Hz), 4.37 (q, 2 H, J = 7.1 Hz), 2.81 (t, 2 H, J = 8.1 Hz), 2.33 (t, 2 H, J = 8.1 Hz), 1.77 (s, 3 H), 1.40 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.7, 144.8, 142.3, 132.8, 130.5, 129.3, 128.1, 127.0, 110.5, 60.71, 39.25, 33.89, 22.37, 14.19; MS (EI) 39 (6), 51 (3), 65 (3), 77 (9), 91 (13), 103 (3), 119 (33), 128 (5), 135 (19), 145 (49), 163 (100), 173 (18), 189 (6), 218 (10); exact mass calcd for $C_{14}H_{18}O_2$ 218.1307, obsd 218.1305.

Ethyl 3-(2-Phenyl-2-hydroxyethyl)benzoate (27). The (3-(carboethoxy)benzyl)copper reagent (9 mmol) was prepared as indicated in the synthesis of **26**. Benzaldehyde (0.74, 7 mmol) and $BF_3·OEt_2$ (1.8 mL, 14 mmol) were then added at -70 °C. The mixture was warmed slowly to -20 °C, stirred overnight, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:2) afforded 1.83 g (97% yield) of **27**: IR (neat) 3490 (s), 3017 (m), 1717 (s), 1446 (m), 1368 (m), 1282 (s), 1200 (s), 1107 (s), 1085 (m), 1050 (m), 1027 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (m, 2 H), 7.28 (m, 7 H), 4.83 (t, 1 H, J = 6.6 Hz), 4.30 (q, 2 H, J = 7.1 Hz), 3.00 (d, 2 H, J = 6.6 Hz), 2.59 (s, 1 H), 1.34 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.6, 143.8, 138.6, 134.1, 130.5, 128.3, 128.2, 127.6, 127.5, 127.0, 125.9, 75.02, 60.84, 45.52, 14.19; MS (EI) 51 (3), 79 (20), 91 (23), 107 (19), 118 (15), 136 (38), 164 (100), 225 (11), 253 (1), 270 (1); exact mass calcd for $C_{17}H_{18}O_3$ 270.1256, obsd 270.1264.

2-(But-3-enyl)-1,4-diacetoxynaphthalene (28). (1,4-Diacetoxynaphthyl)zinc chloride was prepared from 1,4-diacetoxy-2-(chloromethyl)naphthalene (1.6 mmol) according to procedure A with heating at 65 °C for 3 h. GLC analysis showed complete conversion with less than 5% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), allyl bromide (0.17 g, 1.42 mmol) was added at -78 °C. The reaction was allowed to warm to 0 °C with stirring for 3 h and then worked up as usual. Purification of the residue by flash chromatography (hexane:ethyl acetate = 10:1) afforded 0.348 g (82% yield) of **28**: IR (CH_2Cl_2) 3074 (s), 2999 (s), 2979 (s), 2936 (s), 2867 (s), 1765 (s), 1641 (s), 1604 (s), 1509 (s), 1463 (s), 1434 (s), 1367 (s), 1287 (s), 1192 (s), 1159 (s), 1091 (s), 1062 (s), 1009 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.81 (d, 1 H, J = 6.7 Hz), 7.73 (d, 1 H, J = 5.8 Hz), 7.49 (m, 2 H), 7.18 (s, 1 H), 5.88 (m, 1 H), 5.08 (d, 1 H, J = 14.1 Hz), 5.02 (d, 1 H, J = 8.5 Hz), 2.71 (m, 2 H), 2.50 (s, 3 H), 2.48 (s, 3 H), 2.46 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.2, 144.3, 141.8, 137.4, 130.0, 126.9, 126.1, 121.4, 121.3, 119.4, 115.3, 104.0, 33.5, 29.8, 20.8, 20.5; MS (EI) 45 (27), 73 (17), 105 (9), 173 (58), 214 (100), 298 (11); exact mass calcd for $C_{18}H_{18}O_4$ 298.1205, obsd 298.1198.

2-(3-Carbethoxy-2-propenyl)-1,4-diacetoxynaphthalene (29). (1,4-Diacetoxynaphthyl)zinc chloride was prepared from 1,4-diacetoxy-2-(chloromethyl)naphthalene (13 mmol) according to procedure C with heating at 45 °C for 3 h. GLC analysis showed complete conversion with less than 3% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), ethyl propiolate (1.02 mL, 10 mmol) was added at -78 °C. The reaction was allowed to stir at -50 °C for 14 h and then at -30 °C for 3 h. Workup and purification of the residue by flash chromatography (hexane:ethyl acetate = 3:1, then 2:1) afforded 0.51 g (14% yield) of the double-bond-isomerized product and 2.55 g (79% yield) of the desired product **29**: IR ($CDCl_3$) 2984 (m), 1766 (s), 1715 (s), 1656 (w), 1603 (w), 1368 (s), 1277 (m), 1191 (s), 1158 (m), 1065 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.82 (d, 1 H, J = 1.9 Hz), 7.54 (d, 1 H, J = 0.8 Hz), 7.54 (m, 2 H), 7.11 (s, 1 H), 7.07 (dt, 1 H, J = 15.6, 6.7 Hz), 5.86 (d, 1 H, J = 15.6 Hz), 4.17 (q, 2 H, J = 7.1 Hz), 3.55 (d, 2 H, J = 6.7 Hz), 2.46 (s, 3 H), 2.45 (s, 3 H), 1.26 (t, 3 H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 168.7, 168.5, 165.4, 144.5, 141.9, 127.1, 126.9, 126.4, 126.3, 126.0, 123.0, 121.3, 60.0, 32.8, 20.5, 20.1, 13.9; MS (EI) 43 (84), 77 (7), 105 (14), 115 (14), 141 (9), 152 (5), 174 (32), 191 (10), 197 (35), 226 (100), 272 (47), 314 (21), 356 (4); exact mass calcd for $C_{20}H_{20}O_6$ 356.1260, obsd 356.1254.

(α-Methylbenzyl)tributyltin (30). (α-Methylbenzyl)zinc chloride was prepared from α-methylbenzyl chloride (**1j**, 0.98 g, 7 mmol) according to procedure C. GLC analysis showed complete conversion in 24 h with 3% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), tributyltin chloride (1.63 g, 5 mmol) was added at -78 °C. The reaction mixture was allowed to warm slowly to room temperature and then worked up as usual after 2 h. Purification of the residue by flash chromatography (hexane:ether = 9:1) afforded 1.83 g (92% yield) of **30**: IR (neat) 2957 (s), 2928 (s), 2871 (s), 2856 (s), 1600 (m), 1492 (m), 1457 (m), 1376 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.23 (t, 2 H, J = 7.6 Hz), 7.04 (m, 3 H), 2.73 (q, 1 H, J = 7.6 Hz), 1.60 (d, 3 H, J = 7.6 Hz), 1.44–1.24 (m, 15 H), 0.91–0.78 (m, 12 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 149.1, 128.3, 125.7, 123.3, 29.12, 27.49, 26.96, 17.46, 13.65, 8.87; MS (EI) 41 (23), 49 (66), 57 (24), 69 (5), 77 (17), 84 (53), 105 (78), 121 (40), 135 (4), 147 (5), 171 (6), 179 (100), 197 (6), 225 (15), 235 (74), 283 (5), 291 (81), 339 (15), 396 (1); exact mass calcd for $C_{20}H_{36}Sn$ 396.1839, obsd 396.1851.

1,2-Diphenylpropanol[32] (31). The (α-methylbenzyl)copper reagent (14 mmol) was prepared as indicated in the synthesis of **30**. Benzaldehyde (1.17 g, 11 mmol) and $BF_3·OEt_2$ (2.7 mL, 22 mmol) were then added at -70 °C. After addition, the reaction mixture was warmed slowly to -30 °C, stirred for 4 h, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:9) afforded 2.25 g (96% yield) of **31** as a 1:1 mixture of diastereoisomers: IR (neat) 3435 (s), 3062 (s), 3029 (s), 2972 (s), 2875 (m), 1494 (s), 1452 (s), 1388 (m), 1023 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.11 (m, 10 H), 4.63 (d, 1 H, J = 8.7 Hz), 3.00 (quint, 1 H, J = 7.9 Hz), 1.87 (s, 1 H), 1.06 (d, 3 H, J = 7.1 Hz).

1-Cyclohexyl-2-phenylpropanone (32). The (α-methylbenzyl)copper reagent (8.5 mmol) was prepared as indicated in the synthesis of **30**. Cyclohexanecarbonyl chloride (1.00 g, 6.8 mmol) was then added -70 °C. The reaction mixture was then warmed to -20 °C, stirred for 8 h, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:19) afforded 1.37 g (93% yield) of **32**: IR (neat) 2973 (m), 2931 (s), 2654 (s), 1709 (s), 1495 (m), 1451 (s), 1373 (m), 1145 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.15 (m, 5 H), 3.89 (q, 1 H, J = 6.9 Hz), 2.45–2.35 (m, 1 H), 1.00–1.85 (m, 13 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 213.8, 140.8, 128.8, 128.0, 127.0, 51.13, 49.51, 29.47, 28.35, 25.91, 25.79, 25.31, 18.18; MS (EI) 77 (8), 83 (100), 91 (3), 105 (24), 111 (36), 216 (3); exact mass calcd for $C_{15}H_{20}O$ 216.1514, obsd 216.1519.

3-(α-Butylbenzyl)cyclohexanone (33). (α-Butylbenzyl)zinc bromide was prepared from α-butylbenzyl bromide (**1k**, 1.58 g, 7 mmol) according to procedure B. GLC analysis showed complete conversion in 3 h with 5% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), 2-cyclohexen-1-one (0.48 g, 5 mmol) and Me_3SiCl (1.5 mL, 12.6 mmol) were added at -70 °C. The mixture was allowed to warm to -20 °C overnight and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:4) afforded 1.15 g (94% yield) of **33** as a 3:1 mixture of diastereoisomers: IR (neat) 3027 (m), 2956 (s), 2931 (s), 2669 (s), 2661 (s), 1713 (s), 1495 (m), 1466 (m), 1452 (m), 1237 (m), 1228 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29–7.08 (m,

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(32) Kingsbury, C. A.; Best, D. C. *Tetrahedron Lett.* **1967**, *16*, 1499.

5 H), 2.60–1.91 (m, 6 H), 1.79–1.43 (m, 4 H), 1.33–1.12 (m, 4 H), 1.12–0.97 (m, 2 H), 0.80 (t, 3 H, *J* = 7.3 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 211.8, 143.1, 128.5, 128.2, 126.3, 51.44, 46.93, 44.38, 41.36, 32.25, 29.82, 28.83, 25.20, 22.65, 15.22; MS (EI) 41 (25), 55 (11), 69 (11), 91 (100), 97 (17), 105 (9), 115 (4), 147 (25), 244 (3); exact mass calcd for $C_{17}H_{24}O$ 244.1827, obsd 244.1824.

1-Cyclohexyl-2-phenylhexanone (34). The (α-butylbenzyl)copper reagent (6.3 mmol) was prepared as indicated in the synthesis of **33**. Cyclohexanecarbonyl chloride (0.66 g, 4.5 mmol) was then added at −70 °C. The reaction mixture was then warmed to −20 °C, stirred overnight, and worked up as usual. Purification of the residue by flash chromatography (ether:hexane = 1:19) afforded 1.07 g (92% yield) of **34**: IR (neat) 2934 (s), 2854 (s), 1710 (s), 1493 (m), 1485 (m), 1452 (s), 1370 (m), 1144 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33–7.19 (m, 5 H), 3.76 (t, 1 H, *J* = 7.5 Hz), 2.32–2.42 (m, 1 H), 2.07–1.58 (m, 6 H), 1.49–1.07 (m, 10 H), 0.84 (t, 3 H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 213.5, 139.5, 128.7, 128.4, 127.0, 57.31, 50.28, 32.74, 29.93, 29.15, 28.27, 25.93, 25.83, 25.34, 22.66, 13.90; MS (EI) 41 (12), 55 (19), 83 (100), 91 (37), 104 (4), 111 (34), 146 (5), 202 (3), 258 (2); exact mass calcd for $C_{18}H_{26}O$ 258.1984, obsd 258.1977.

3,4-Diphenyl-4-oxobutyronitrile (35). (α-(2-Cyanoethyl)benzyl)zinc chloride was prepared from α-(2-cyanoethyl)benzyl chloride (**11**, 1.08 g, 6 mmol) according to procedure C. GLC analysis showed complete conversion in 22 h with 5% Wurtz coupling. After the transmetalation to the corresponding copper reagent by the addition of CuCN·2LiCl (as indicated above), benzoyl chloride (0.61 g, 4.3 mmol) was added at −60 °C. The reaction mixture was then warmed to −20 °C, stirred for 8 h, and worked up as usual. Purification of the residue by flash chromatography (hexane:ethyl acetate = 9:1) afforded 0.89 g (83% yield) of **35**: IR (Nujol) 2954 (s), 2926 (s), 2855 (s), 2235 (m), 1677 (s), 1452 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.95 (d, 2 H, *J* = 8.4 Hz), 7.47–7.25 (m, 8 H), 4.73 (t, 1 H, *J* = 7.0 Hz), 2.42–2.36 (m, 2 H), 2.26–2.16 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 198.2, 137.6, 136.1, 133.3, 129.4, 128.8, 128.6, 128.2, 127.8, 119.3, 51.95, 29.02, 15.14; MS (EI) 41 (8), 49 (17), 65 (4), 77 (8), 84 (12), 91 (28), 104 (19), 117 (20), 122 (4), 128 (7), 144 (100), 157 (5), 171 (11), 183 (8), 211 (6), 257 (2); exact mass calcd for $C_{16}H_{19}NO_2$ 257.1416, obsd 257.1405.

Ethyl 6-Cyano-4-phenyl-2-methylenehexanoate (36). The (α-(2-cyanoethyl)benzyl)copper reagent (5.4 mmol) was prepared as indicated in the synthesis of **35**. Ethyl α-(bromomethyl)acrylate (0.83 g, 4.3 mmol) was then added at −70 °C. The reaction mixture was allowed to warm slowly to 0 °C and then worked up as usual. Purification of the residue by flash chromatography (CH_2Cl_2:hexane = 3:2) afforded 1.02 g (92% yield) of **36**: IR (neat) 2934 (m), 2249 (m), 1714 (s), 1453 (m), 1326 (m), 1304 (m), 1195 (s), 1140 (s), 1028 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.12 (m, 5 H), 6.09 (s, 1 H), 5.34 (s, 1 H), 4.18 (q, 2 H, *J* = 7.1 Hz), 3.0–2.87 (m, 1 H), 2.71–2.57 (m, 2 H), 2.23–1.84 (m, 4 H), 1.29 (t, 3 H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.8, 141.9, 138.1, 128.7, 127.6, 127.0, 126.8, 119.3, 60.64, 43.87, 38.97, 31.22, 15.25, 14.06; MS (EI) 40 (6), 51 (7), 77 (28), 105 (100), 115 (4), 143 (4), 181 (3), 249 (1); exact mass calcd for $C_{17}H_{15}NO$: 249.1154, obsd 249.1151.

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Lewis Acid Promoted, Cobalt-Catalyzed, and Phase-Transfer-Catalyzed Carbonylation of Iodoarenes and Iodoalkanes†

Jong-Tae Lee and Howard Alper*

Department of Chemistry, Ottawa–Carleton Chemistry Institute, University of Ottawa,
Ottawa, Ontario, Canada K1N 6N5

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Iodoarenes and iodoalkanes can be carbonylation to carboxylic acids under mild conditions using cobalt chloride or acetate, potassium cyanide, base, and PEG-400 as the phase-transfer agent. The reaction is promoted by Lewis acids such as boron trifluoride etherate, with ferrous chloride as a copromoter.

The carbonylation of iodoarenes to carboxylic acids has attracted considerable attention in recent years. Examples include the palladium(II)-catalyzed carbonylation of iodoarenes using K_2CO_3 and *N*,*N*-dimethylformamide,[1] the ruthenium trichloride catalyzed reaction at elevated temperatures and pressures using lithium carbonate as a base and lithium iodide as a promoter,[2] and the nickel cyanide,

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† Dedicated to the memory of John Stille, who made outstanding contributions to organometallic and polymer chemistry, including the area of carbonylation reactions.

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