cation (where OEt is replaced by H in **18**) was recently carried out in our laboratories.[27] The ^{1}H downfield shifts experienced by **5** in the presence of PhOH (Experimental Section) are nearly the same as those induced by CF_3CO_2H (Table IX).

For comparison with **5** (Table VI), Et_2O and $Si(OEt)_4$ were also reacted with acids (Table IX). The downfield ^{1}H shifts relative to the unprotonated compounds are in the order $Si(OEt)_4$ < **5** < Et_2O, which accords with the basicity order of these compounds (see next section).

Phenol OH Infrared Shifts. A measure of the basicity of a series of similar bases can be obtained from the shift of the OH stretching frequency of phenol.[28] In Table I are collected the relevant IR data for a series of silatranes and several other compounds for comparison. The data in this table imply the approximate basicity order $(Me_3Si)_2O$ < MeCN < $Si(OMe)_4$ < $Si(OEt)_4$ < **11** < **12** ≅ **10** < **4** < **9** ≅ **5**, **8**, Me_3SiOMe < Et_2O. Restricting our attention to the ethers in this ordering ($(Me_3Si)_2O$ < $(RO)_3SiOR$ < **12** < **4** < **5** < Me_3SiOMe < Et_2O) we see that silatranyl moieties are more basic than an $(RO)_3Si$ group, undoubtedly owing to the coordinate nature of the $N_{ax} \rightarrow Si$ bond. Whether π interaction involving silicon 3d orbitals in the ether linkages play a role here is still controversial.[29] Silatrane **8** must be hydrogen bonding at O_{eq} while **4**, **5**, and **9** could be doing so at either or both oxygen sites. In the cases of **4** and **5**, the axial oxygen may be preferentially involved in hydrogen bonding on the bases of the ^{1}H NMR spectroscopic argument made in the previous section for **5** in the presence of PhOH and on our structural determination of **7**. The decreasing basicity order **8** > **10** > **11** can be attributed to the corresponding increasing electron-withdrawing ability of the axial hydrocarbon substituent.

Conclusions. Polarization of the axial oxygen in alkoxysilatranes such as **4** and **5** by strong hydrogen bonding (**7**) or alkylation (**6**(BF_4)) leads to significant shortening (~0.1–0.2 Å) of the transannular SiN_{ax} bond and lengthening (up to 0.17 Å) of the SiO_{ax} link. The conclusion reached by others[1] that silatranes in which the Si atom is coplanar with the equatorial oxygens will exhibit an SiN_{ax} bond length of 1.83 Å is apparently not valid for **6**(BF_4) in which coplanarity is realized within experimental error and in which the SiN_{ax} bond length (1.965 Å) though the shortest thus far reported for a silatrane is >0.1 Å longer than the predicted[1] 1.83 Å. Consistent with the crystal structures of our new silatranes **6**(BF_4) and **7**, solution ^{1}H and solution and solid-state ^{13}C NMR chemical shifts for several hydrogen bonded, protonated, and alkylated alkoxysilatranes indicate electrophilic attack at the O_{ax} site. Where the axial group is a phenyl (**11**) or where the equatorial atoms are nitrogens (**17**), the solution NMR data suggest equatorial atom protonation. For compounds featuring O_{ax} and O_{eq} atoms (e.g., **5**) ^{1}H NMR studies as a function of acid concentration suggest equilibria involving protonation of both sites. The observed basicity order $(Me_3Si)_2O$ < $Si(OMe)_4$ < **4** < **5** ≅ Me_3SiOMe < Et_2O derived from phenol ν(OH) shift data is consistent with the order $(H_3Si)_2O$ < H_3SiOCH_3 < H_3COCH_3,[26] with the added feature that a silatranyl group bound to an OR group is more basic than a similarly bound $(RO)_3Si$ moiety, whereas it is less basic than a Me_3Si or Et group linked to an OR group.

Acknowledgment. The authors are grateful to the National Science Foundation for grant support for this research and to Dr. A. Naiini for experimental assistance.

Supplementary Material Available: Tables of thermal parameters, bond lengths, bond angles, and general displacement expressions (24 pages); tables of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

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Stereospecific Preparation of Polyfunctional Olefins by the Carbometalation of Alkynes with Polyfunctional Zinc–Copper Organometallics. Stereospecific Preparation of Five-Membered Carbocycles by Intramolecular Carbocupration

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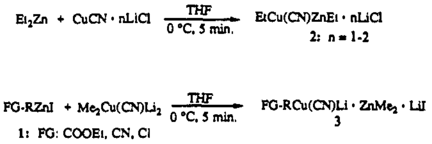
Abstract: The addition of copper reagents prepared by transmetalation from polyfunctional organozinc iodides to reactive alkynes such as 1-(methylthio)-1-hexyne, phenylacetylene and acetylene, leads to stereochemically well-defined (syn addition), highly functionalized alkenylcopper reagents that after protonation, allylation, iodolysis, or stannylation afford stereochemically pure di-, tri-, and tetrasubstituted olefins. A similar intramolecular carbocupration has allowed the preparation of highly substituted five-membered carbocycles. Compared to lithium- or magnesium–copper reagents, the highly functionalized copper reagents can contain an ester, nitrile, or chloride function. However, they display a lower reactivity than the lithium- or magnesium–copper reagents and do not react with unactivated terminal alkynes.

The carbocupration of alkynes by lithium- and magnesium-copper reagents is one of the most efficient ways for preparing stereoisomerically pure di-, tri-, or tetrasubstituted double bonds.[1] The reaction proceeds generally in good yields and is highly regio- and stereoselective. However, the method has some synthetic limitations: internal alkynes are usually unreactive[2] toward carbocupration; and aryl- alkenyl-,[3] allyl-, and alkynylcopper

Scheme I



$$Et_2Zn + CuCN \cdot nLiCl \xrightarrow[0\ °C,\ 5\ min.]{THF} \underset{\mathbf{2}:\ n = 1\text{-}2}{EtCu(CN)ZnEt \cdot nLiCl}$$

$$\underset{\mathbf{1}:\ FG:\ COOEt,\ CN,\ Cl}{FG\text{-}RZnI} + Me_2Cu(CN)Li_2 \xrightarrow[0\ °C,\ 5\ min.]{THF} \underset{\mathbf{3}}{FG\text{-}RCu(CN)Li \cdot ZnMe_2 \cdot LiI}$$

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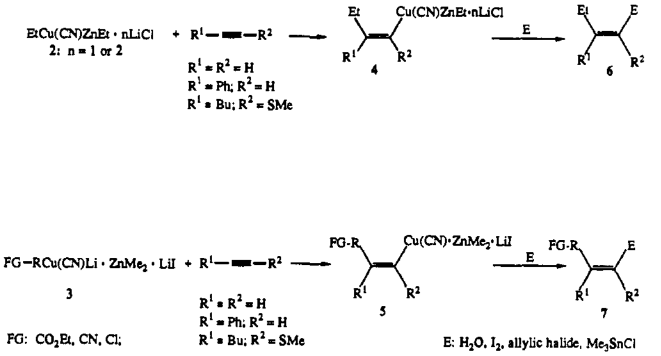
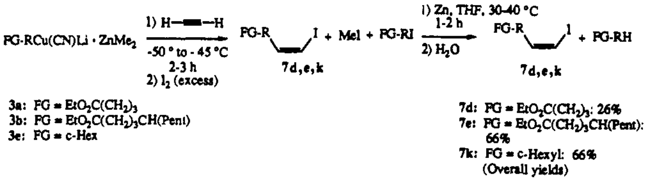
[1] (a) Normant, J. F.; Bourgain, M. *Tetrahedron Lett.* **1971**, 2583. (b) For an excellent review, see: Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841. (c) Normant, J. F.; Alexakis, A. In *Mod. Synth. Methods*; Scheffold, R., Ed.; Verlag Salle and Sauerländer: Frankfurt, 1983; 139. (d) Alexakis, A.; Cahiez, G.; Normant, J. F. *Org. Synth.* **1984**, *62*, 1.

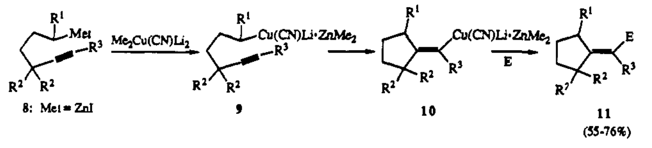
Scheme II



Scheme III



Scheme IV



derivatives do not add to acetylene or other alkynes. Also the methylcupration[4] of alkynes is a very sluggish reaction, whereas the carbocupration of alkynes with *secondary* alkylcopper compounds has been found to be in some cases less regio- and stereoselective.[4a,5] Finally, only a small number of *functionalized* copper reagents[6] has been used successfully.

In this work, we wish to report the first carbocupration of alkynes using *polyfunctionalized* zinc–copper reagents.[7] Diethylzinc or polyfunctional alkylzinc halides **1**, are transmetalated with CuCN·*n*LiCl ($n = 1, 2$) or $Me_2Cu(CN)Li_2$[8] in THF (0 °C, 5 min) respectively leading to copper reagents tentatively formulated as EtCu(CN)ZnEt·*n*LiCl **2** and FG-RCu(CN)Li·$ZnMe_2$·LiI **3** (Scheme I). The presence of zinc salts was found to strongly modify the reactivity of the carbon–copper bond, and reagents **2** and **3** are best considered to be mixed clusters of copper, zinc, and lithium. These new copper reagents do not add efficiently to unactivated internal alkynes or terminal alkynes due to their lower reactivity, and either no reaction or deprotonation of the alkyne is observed. However, in the case of more reactive alkynes such as 1-(methylthio)-1-hexyne, phenylacetylene, or acetylene, a syn addition occurs smoothly, leading to stereochemically pure alkenylcopper derivatives of types **4** and **5** that can be quenched by electrophiles (E) such as water, iodine, allylic halides, and trimethyltin chloride, leading to stereoisomerically pure (>99% pure by ^{1}H NMR and GC analyses) di-, tri-, and tetrasubstituted olefins of types **6** and **7** (Scheme II and Table I). Thus, 1-(methylthio)-1-hexyne (0.5 equiv) undergoes a very clean syn addition of the copper reagent EtCu(CN)ZnEt·*n*LiCl **2** (1.0 equiv), affording an alkenylcopper of type **4** (THF, 0 °C, 1 h; entries 1–4 of Table I). The presence of lithium chloride is crucial for the success of the carbometalation, the alkenylcopper **4** being unstable in its absence and forming the homocoupling dimer. With a reactive terminal alkyne such as phenylacetylene, the carbometalation is performed at −20 °C (entry 5). At higher temperature, the competitive deprotonation of the alkyne becomes an important side reaction. All the alkenylcopper of type **4** reacts with electrophiles in good yields (67–92%), furnishing the stereoisomerically pure olefins **6a–e**. Of special interest, compared to copper reagents prepared from lithium and magnesium organometallics, is the wide range of functional groups that can be present in these reagents (ester, nitrile, chloride; Table I). It was found that the addition of $(CH_3)_2Cu(CN)Li_2$ converts the organozinc halides **1** into copper reagents of type **3**, which add efficiently to several classes of alkynes (Scheme I). The copper–zinc reagents FG-RCu(CN)ZnI react with 1-(methylthio)-1-hexyne[9] very slowly and incompletely (45% conversion after 48 h at 45 °C); we also noticed that the addition of lithium salts to the reagents **3** slows down the carbometalation reaction. However, in their absence the addition of **3a** (1 equiv) to 1-(methylthio)-1-hexyne (0.6 equiv) is complete within 2 h at 25 °C, giving an alkenylcopper reagent of type **5** bearing an ester function in the side chain (FG-R). Protonation, allylation, or iodolysis (3–4 equiv) affords the pure ester-substituted vinylic thioethers **7a–c** in good yields (75–92%; entries 6–8). Various other zinc–copper reagents bearing ester, nitrile, or chloride groups (**3b**, **3c**, and **3d**) add to 1-(methylthio)-1-hexyne in a similar way, leading after protonation to the polyfunctional vinylic thioethers **7f–h** (60–75%; entries 11-13). The more reactive secondary copper–zinc reagent **3e** undergoes the carbometalation even at 5 °C (3 h), giving after allylation the thioether **7i** in 79% yield. Acetylene itself displays an interesting behavior. With a primary zinc–copper reagent such as **3a**, the addition proceeds at −50 °C, but only a maximum of 35% conversion could be achieved. The use of other copper salts such as $(vinyl)_2Cu(CN)(MgX)_2$, CuI·2LiCl, CuCN·LiCl, $Me_2Cu(CN)Li_2$ (catalytic amount) to prepare the organocopper derivatives, the use of ether as a solvent, or higher reaction temperatures did not improve the low conversion (35% conversion); the competitive metalation of acetylene was certainly responsible for this incomplete reaction. The best result was obtained by bubbling acetylene (3 equiv) through a THF solution of the copper reagent **3a** at −50 to −40 °C and stirring the reaction mixture for 2.5 h at −40 to −50 °C. Secondary alkyl zinc–copper reagents such as **3b** and **3e** react with acetylene with far better conversions (83–85% conversion). After the addition of an excess of iodine, a mixture of the alkyl iodide and the desired alkenyl iodide **7d–e** and **7k** was obtained. After workup, the crude mixture of iodides was treated with zinc in THF (3–4 M THF solution, 30–40 °C, 1-2 h), affording the alkylzinc iodide, whereas the alkenyl iodide remained unaffected (alkenyl iodides are only converted to the corresponding zinc organometallics in DMF at elevated temperatures). After protonation, the unreacted pure alkenyl iodides

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(2) Highly activated alkynes such as acetylenic acetals and ketals are useful substrates for carbocupration reactions: (a) Alexakis, A.; Commerçon, A.; Coulentianos, C.; Normant, J. F. *Tetrahedron* **1984**, *40*, 715; see also ref 1a. (b) Crandall, J. K.; Collonges, F. *J. Org. Chem.* **1976**, *41*, 4089.

(3) Some alkenylcopper derivatives bearing an alkyl substituent in position 1 undergo carbocupration reactions: (a) Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 5151. (b) Furber, M.; Taylor R. J. K.; Burford, S. C. *Tetrahedron Lett.* **1985**, *26*, 3285.

(4) (a) Westmijze, H.; Meijer, J.; Bos, T. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 299, 304. (b) Westmijze, H.; Kleijin, H.; Vermeer, P. *Tetrahedron Lett.* **1977**, 2023. (c) Iyer, R. S.; Helquist, P. *Org. Synth.* **1986**, *64*, 1. (d) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 1345, 3888.

(5) Achyutha Rao, S.; Periasamy, M. *Tetrahedron Lett.* **1988**, *29*, 4313.

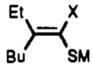
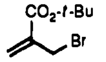
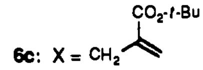
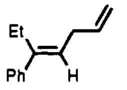
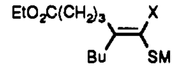
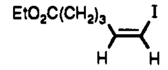
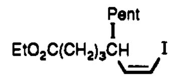
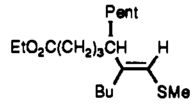
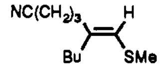
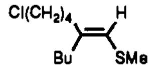
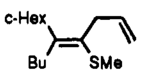
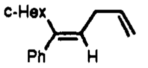
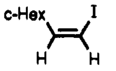
(6) (a) Alexakis, A.; Cahiez, G.; Normant, J. F. *Synthesis* **1979**, 826. (b) Gardette, M.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1982**, *23*, 5155. (c) Gardette, M.; Jabri, N.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1984**, *40*, 2741. (d) Gardette, M.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1985**, *41*, 5887.

(7) The highly functionalized copper reagents FG-RCu(CN)ZnX are versatile reagents forming new carbon–carbon bonds in a very efficient way: (a) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. (b) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1988**, *29*, 2395. (c) Yeh, M. C. P.; Knochel, P.; Butler, W. M.; Berk, S. C. *Tetrahedron Lett.* **1988**, *29*, 6693. (d) Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* **1988**, *53*, 5789. (e) Yeh, M. C. P.; Knochel, P.; Santa, L. E. *Tetrahedron Lett.* **1988**, *29*, 3887. (f) Knochel, P.; Chou, T.-S.; Chen, H. G.; Rozema, M. J. *J. Org. Chem.* **1989**, *54*, 5202. (g) Knochel, P. *J. Am. Chem. Soc.* **1990**, *112*, 7431.

(8) (a) Lipshutz, B. H. *Synthesis* **1987**, 325. (b) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005. (c) Lipshutz, B. H. *Synthesis* **1990**, 119.

(9) Alexakis, A.; Cahiez, G.; Normant, J. F.; Villieras, J. *Bull. Soc. Chim. Fr.* **1977**, 693.

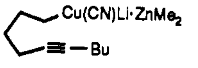
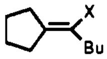
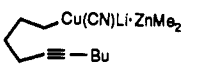
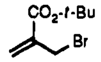
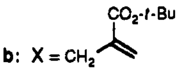
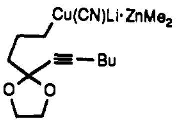
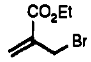
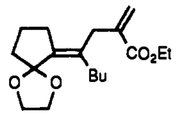
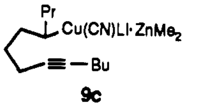
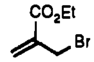
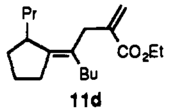
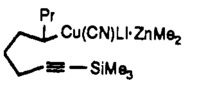
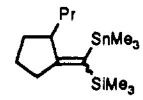
Table I. Carbometalation of Alkynes with Polyfunctional Zinc–Copper Reagents and Reactions of the Intermediate Alkenyl Copper–Zinc Derivatives with Electrophiles

entry	zinc–copper reagent	alkyne	carbometalation reaction conditions (°C, h)	electrophile	products	yield (%)[a]
1	**2**	Bu—≡—SMe	(0, 1)	H_2O	 **6a**: X = H	92
2	**2**	Bu—≡—SMe	(0, 1)	allyl bromide	**6b**: X = allyl	74
3	**2**	Bu—≡—SMe	(0, 1)		 **6c**: X = CH_2	78
4	**2**	Bu—≡—SMe	(0, 1)	$(CH_3)_3SnCl$	**6d**: X = $Sn(CH_3)_3$	81
5	**2**	Ph—≡—H	(−20, 12)	allyl bromide	 **6e**	67
6	**3a** (FG-R: $EtO_2C(CH_2)_3$)	Bu—≡—SMe	(25, 2)	H_2O	 **7a**: X = H	92
7	**3a**	Bu—≡—SMe	(25, 2)	allyl bromide	**7b**: X = allyl	70
8	**3a**	Bu—≡—SMe	(25, 3)	I_2	**7c**: X = I	75
9	**3a**	H—≡—H	(−45, 3)	I_2	 **7d**	26[b]
10	**3b** (FG-R: $EtO_2C(CH_2)_3CH(Pent)CH_2$)	H—≡—H	(−45, 3)	I_2	 **7e**	66[b]
11	**3b**	Bu—≡—SMe	(25, 6)	H_2O	 **7f**	75
12	**3c** (FG-R: $(NC(CH_2)_3)$)	Bu—≡—SMe	(0, 3)	H_2O	 **7g**	60
13	**3d** (FG-R: $Cl(CH_2)_4$)	Bu—≡—SMe	(25, 1)	H_2O	 **7h**	66
14	**3e** (FG-R: c-Hex)	Bu—≡—SMe	(5, 3)	allyl bromide	 **7i**	79
15	**3e**	Ph—≡—H	(−20, 15)	allyl bromide	 **7j**	69
16	**3e**	H—≡—H	(−45, 3)	I_2	 **7k**	66[b]

[a] All yields refer to isolated yields of analytically pure compounds. Satisfactory spectral data (IR, ^1H and ^{13}C NMR, mass spectra, and high-resolution mass spectra) were obtained for all new compounds. [b] See Scheme III and text.

can be easily purified by distillation or flash chromatography (Scheme III). Whereas the primary zinc–copper reagent **3a** is converted via this process to the vinylic iodide **7d** in only 26% overall yield (entry 9), the secondary reagents **3b** and **3e** afforded the pure *Z*-vinylic iodides in satisfactory overall yields (66%; entries 10 and 16). Finally, the addition of the secondary zinc–copper reagent **3e** to phenylacetylene at −20 °C (15 h) affords the desired alkenylcopper derivative that after allylation furnishes the 1,4-diene **7j** in 69% yield (entry 15). For primary alkylcopper reagents, the deprotonation of phenylacetylene was found to be an appreciable side reaction (carbometalation product/phenylacetylene deprotonation ratios: 1/1). Unactivated terminal alkynes such as hexyne or trimethylalkynylsilanes do not undergo carbocupration reactions with both types of reagents **2** and **3**, which certainly limits the synthetic applications of the reagents **2** and **3** in intermolecular carbometalations. In strong contrast, we found that intramolecular carbometalation reactions using zinc–copper organometallics proceed more readily than reactions using lithium- or magnesium–copper compounds. Thus, whereas various phenyl-substituted alkynes of type **8** (R_3 = Ph; Met = Li,[10] MgX,[11] AlR_2,[12] ZnX[13] or Cu[14]) bearing a carbon-metal bond in the δ position are known to undergo carbometalation reactions, in the absence of the phenyl-activating group (R_3 = alkyl), only a few succesful intramolecular carbometalations have been reported.[10-15]

Table II. Intramolecular Carbometalation of Copper–Zinc Organometallics and Trapping of the Resulting Five-Membered Carbocycles by Electrophiles

entry	zinc–copper reagent	carbometalation reaction conditions	electrophile	product	yield (%)[a]
1	 **9a**	25 °C, 15 h	H_2O	 **11a**: X = H	55
2		25 °C, 15 h		**11b**:  X = CH_2	76
3	 **9b**	25 °C, 1.5 h		 **11c**	60
4	 **9c**	25 °C, 2 h		 **11d**	57
5	 **9d**	25 °C, 2 h	Me_3SnCl	 **11e**: mixture of stereoisomers (74:26)	63

[a] All yields refer to isolated yields of analytically pure compounds. Satisfactory spectral data (IR, ^1H and ^{13}C NMR, mass spectra, and high-resolution spectra) were obtained for all new compounds.

We found that the zinc organometallics **8** (Met = ZnI) prepared via the direct insertion of zinc to the corresponding iodides (Zn dust (2–3 equiv), THF, 45 °C, 2–6 h) undergo, after transmetalation to the copper derivatives **9**, a clean intramolecular carbocupration reaction leading to the alkenylcopper reagent **10**, which after quenching with an electrophile (H_2O, allylic bromide, or Me_3SnCl) gives stereochemically pure *exo*-alkylidenecyclopentane derivatives of type **11** in satisfactory overall yields (55–76%; Scheme IV and Table II). Thus, whereas 5-decynylzinc iodide (**8a**) ($R_1 = R_2 = H$; $R_3 = Bu$) remains unchanged at 35 °C for several hours,[16] the addition of $Me_2Cu(CN)Li_2$[8] (1 equiv) leads to the cyclized alkenyl organocopper reagent **10a** ($R_1 = R_2 = H$; $R_3 = Bu$; THF, 25 °C, 15 h). After protonation, volatile pentylidenecyclopentane (**11a**) is isolated in 55% yield (entry 1 of Table II), whereas the allylation of **10a** with *tert*-butyl α-(bromomethyl)acrylate[17] gives the desired product **11b** (76% yield; entry 2 of Table II). Interestingly, the acetylenic ketal function present in **9b** does not interfere with the cyclization reaction that is complete within 1.5 h at 25 °C, affording after allylation with ethyl α-(bromomethyl)acrylate the protected *exo*-alkylidenecyclopentanone **11c** in 60% yield (entry 3). Secondary lithium organometallics are difficult to prepare,[10,18] whereas secondary alkylzinc halides are readily obtained under mild conditions (THF, 30–35 °C, 12 h) and in high yields. This has allowed us to generate the secondary copper reagents **9c** and **9d**, which after cyclization and respectively allylation and stannylation afforded the cyclopentane derivatives **11d** and **11e** in 57% and 63% yield (entries 4 and 5). As expected,[19] the 1-silyl-1-stannylmethylene cyclopentane derivative **11e** was obtained as a mixture of stereoisomers (74:26 ratio). Attempts to produce four- or six-membered rings by this methodology were not successful.

Conclusion

The regio- and stereospecific addition of zinc–copper organometallics of types **2** and **3** to reactive alkynes such as 1-(methylthio)-1-hexyne, phenylacetylene, or acetylene gives intermediate alkenylcopper derivatives that are allylated, protonated, or stannylated in satisfactory to good yields. Compared to the carbocupration using organolithium or -magnesium derived copper reagents, the use of zinc–copper reagents allows the addition of *highly functionalized organometallics* containing an ester, a nitrile, or a halide to alkynes. Less reactive alkynes such as simple terminal alkynes or internal alkynes do not react efficiently with the zinc–copper reagents **2** or **3**. In contrast, the intramolecular addition of zinc–copper organometallics to nonactivated internal alkynes occurs readily, leading to five-membered carbocycles having a stereochemically well defined *exo*-alkenylcopper functionality that reacts with electrophiles such as allylic bromides, water, and trimethyltin chloride in good yields. The high stereoselectivity of these carbometalations (>99% syn addition in all cases) should make these reactions useful for the construction

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of polyfunctional stereochemically well defined alkenes.

Experimental Section

General Considerations. Unless otherwise indicated, all reactions were carried out under an inert atmosphere (argon). Solvents (THF and diethyl ether) were dried and freshly distilled from sodium/benzophenone. The zinc dust was obtained from Aldrich Chemical Co., Inc. (−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 Brucker 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 (ppm) 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.

Preparation of Starting Materials. Diethylzinc was purchased from Aldrich. 1-(Methylthio)-1-hexyne was prepared according to the literature[20] with THF as solvent (90% yield). The alkyl iodides, ethyl 4-iodobutryate and 4-iodobutyronitrile, were prepared from the corresponding commerically available alkyl chorides by a Finkelstein reaction (NaI (1.5 equiv), acetone, reflux 10–14 h). Iodocyclohexane and 1-chloro-4-iodobutane were purchased from Lancaster Synthesis Ltd.

Ethyl 5-Iododecanoate.[21] A dichloromethane solution of ethyl 5-hydroxydecanoate (**7e**) (1.51 g, 7 mmol in 7 mL of dry CH_2Cl_2) was added to a solution of triphenylphosphine (3.15 g, 12 mmol), imidazole (0.82 g, 12 mmol), and iodine (3.05 g, 12 mmol) in 30 mL of dry CH_2Cl_2 at room temperature. GLC analysis showed that the reaction was completed after 3 h of stirring. The precipitate was filtered off and the solvent was evaporated under reduced pressure. The crude resulting oil was purified by flash chromatography (solvent, hexane), affording 2.05 g (90% yield) of ethyl 5-iododecanoate: IR (neat) 2926 (br s), 1732 (s), 1458 (s), 1374 (s), 1249 (m), 1034 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.13 (q, 2 H, *J* = 6.0 Hz), 2.35 (t, 2 H, *J* = 6 Hz), 1.95–1.62 (m, 6 H), 1.58–1.22 (m, 10 H), 0.9 (t, 3 H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 172.9, 60.1, 40.5, 39.7, 38.5, 33.3, 30.9, 29.0, 24.8, 22.3, 14.1, 13.8; MS (CI, methane) 119 (3), 136 (2.5), 153 (12), 199 (100), 281 (2.4), 327 $[M + H]^+$ (24), 344 $[M + NH_4]^+$ (15); exact mass calcd for $C_{12}H_{23}O_2IH$ 327.0821, obsd 327.0817 $[M + H]^+$. The same method[21] was used to prepare 10-iodo-5-tridecyne (88% yield) and 6-iodo-1-(trimethylsilyl)nonyne (91% yield).

10-Iodo-5-tridecyne. Flash column chromatography (hexane): IR (neat) 2928 (br s), 1464 (s), 1433 (s), 1326 (s), 1186 (s) cml–^{1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.2–4.1 (m, 1 H), 2.25–2.1 (m, 4 H), 2.0–1.35 (m, 12 H), 0.99–0.89 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 80.7, 79.1, 42.7, 39.5, 38.7, 31.1, 28.8, 22.6, 21.8, 18.3, 17.9, 13.5, 13.1; MS (CI, ammonia) 81 (100), 95 (98), 109 (85), 123 (86), 137 (42), 179 (52), 324 $[M + NH_4]^+$ (5.5); exact mass calcd for $C_{13}H_{23}INH_4$ 324.1188, obsd 324.1181 $[M + NH_4]^+$.

6-Iodo-1-(trimethylsilyl)nonyne. Flash column chromatography (hexane): IR (neat) 2899 (br s), 2175 (s), 1463 (s), 1432 (s), 1249 (s), 841 (s), 759 (s), 638 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.03–3.93 (m, 1 H), 2.1 (t, 2 H, *J* = 6 Hz), 1.8–1.2 (m, 8 H), 0.88 (t, 3 H, *J* = 6 Hz), 0.0 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 106.5, 85.1, 42.8, 39.4, 38.3, 28.3, 22.7, 19.0, 13.2, 0.186; MS (CI, ammonia) 90 (100), 107 (22), 121 (13), 136 (67), 153 (3), 212 (4), 228 (10), 282 (4), 323 $[M + H]^+$ (7), 340 $[M + NH_4]^+$ (36); exact mass calcd for $C_{12}H_{23}SiIH$ 323.0692, obsd 323.0703 $[M + H]^+$.

1-Iodo-5-decyne.[22] A mixture of 1-chloro-5-decyne[12b] (8.72 g, 50 mmol) and sodium iodide (22.5 g, 150 mmol) in 35 mL of acetone was heated at reflux for 12 h, affording 1-iodo-5-decyne (10.5 g, 80% yield): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.2 (t, 2 H, *J* = 6 Hz), 2.22–2.1 (m, 4 H), 2.0–1.9 (m, 2 H), 1.6–1.5 (m, 2 H), 1.49–1.35 (m, 4 H), 0.9 (t, 3 H, *J* = 6.5 Hz) in accord with the literature data.[22b]

1-Iodo-4-oxo-5-decyne. A solution of 1-chloro-4-oxo-5-decyne[23] (4 g, 21 mmol) and sodium iodide (9 g, 60 mmol) in 10 mL of acetone was heated at reflux for 5 h. The cooled reaction mixtures was diluted with hexane and filtered, and the solvent was removed by evaporation. After addition of fresh sodium iodide (9 g, 60 mmol) and 10 mL of acetone, the reaction mixture was heated at reflux for another 4 h. After the same workup, the crude oil was purified by flash chromatography (solvent, hexane/ether, 100:95/0:5) to give 4.25 g (purity, 91.5%) and 0.55 g (purity, 72%) of 1-iodo-4-oxo-5-decyne (72% yield), which was used directly for the next reaction step (ketalization): ^1H NMR ($CDCl_3$, 300 MHz) δ 3.22 (t, 2 H, *J* = 6 Hz), 2.68 (t, 2 H, *J* = 6 Hz), 2.38 (t, 2 H, *J* = 6 Hz), 2.2–2.1 (m, 2 H), 1.65–1.5 (m, 2 H), 1.5–1.4 (m, 2 H), 0.95 (t, 3 H, *J* = 6.5 Hz).

Ketalization of 1-Iodo-4-oxo-5-decyne.[24] **Preparation of 2-(1-Hexynyl)-2-(3-iodopropyl)-1,3-dioxolane.** To a mixture of 1-iodo-4-oxo-5-decyne (4 g, 14.4 mmol, purity, 91%) and 1,2-bis(trimethylsiloxy)ethane[24] (6.18 g, 30 mmol) in 6 mL of dry CH_2Cl_2 was added at −78 °C a catalytic amount of trimethylsilyl trifluoromethanesulfonate (80 mg, 0.36 mmol). The reaction mixture was warmed to −30 °C and stirred 12 h at this temperature, warmed to −20 °C, and stirred for 3 h. The reaction mixture was poured into an aqueous solution of saturated $NaHCO_3$. After extraction with CH_2Cl_2 (2 × 100 mL), the organic layer was washed with brine, dried over $MgSO_4$, and filtered. After evaporation of the solvents, the crude residual oil was purified by flash chromatography, affording two fractions: 3.82 g (>95% pure by GLC analysis) and 0.47 g (>86% pure) of the desired ketal (95% yield).

2-(1-Hexynyl)-2-(3-iodopropyl)1,3-dioxolane: IR (neat) 2939 (br s), 2236 (s), 1430 (m), 1245 (m), 1100 (s), 1027 (m), 982 (s), 893 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 4.1–4.01 (m, 2 H), 4.0–3.9 (m, 2 H), 3.28 (t, 2 H, *J* = 6 Hz), 2.22 (t, 2 H, *J* = 6 Hz), 2.15–1.95 (m, 4 H), 1.56–1.32 (m, 4 H), 0.93 (t, 2 H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 102.4, 84.9, 77.7, 64.3, 40.0, 30.2, 28.2, 21.7, 17.9, 13.3, 6.1; MS (EI) 41 (12), 79 (8), 109 (7), 153 (100), 195 (5), 241 (2), 280 (0.4), 323 (0.1); exact mass calcd for $C_{12}H_{19}O_2IH$ 323.0508, obsd 323.0505.

General Procedure for the Preparation of Alkylzinc Iodides FG-RZnI 1. A dry 100-mL, three-necked flask was equipped with a magnetic stirring bar and a 25-mL pressure-equalizing addition funnel bearing a rubber septum, a three-way stopcock, and a thermometer. The air in the flask was replaced by argon and charged with zinc dust (1.95 g, 30 mmol). The flask was again flushed three times with argon, and 1,2-dibromoethane (ca. 200 mg, ca. 1 mmol) in 2 mL of THF was injected with a syringe. The zinc suspension was heated gently with a heat gun until ebullition of the solvent was observed. The reaction mixture was stirred for a few minutes and heated again. The process was repeated three times, after which chlorotrimethylsilane (0.15 mL, 1.2 mmol) was injected through the addition funnel. The reaction mixture was stirred for 10 min and the alkyl iodide (10 mmol in 4 mL of THF) was added dropwise over 20 min between 25 and 40 °C. The reaction mixture was stirred a few hours at 40 °C (2–6 h depending on the structure of the alkyl iodide). The advancement of the reaction was monitored by GLC analysis of hydrolyzed reaction aliquots. The excess zinc was allowed to settle for 1.5 h and the clear alkylzinc iodide solution was ready to use. Less than 3–4% of the starting iodide was remaining and a yield of 90% of alkylzinc iodide was assumed.

Preparation of EtCu(CN)ZnEt·2LiCl (2). A mixture of lithium chloride (0.85 g, 20 mmol; dried under vacuum at 130 °C for 2 h) and copper cyanide (0.89 g, 10 mmol) was dissolved in 10 mL of THF under argon. The resulting yellow-greenish solution was cooled to −60 °C and diethylzinc (1.02 mL, 10 mmol) was added. The reaction mixture was allowed to warm up to 0 °C and was stirred at this temperature for 5 min.

General Procedure of the Carbometalation of Alkynes with EtCu(CN)ZnEt·2LiCl (2) and Subsequent Trapping of the Resulting Alkenylcopper with Electrophiles. To a THF solution of **2** (10 mmol) prepared as described above was added at −60 °C 1-(methylthio)-1-hexyne (0.64

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g, 5 mmol). The reaction mixture was warmed to 0 °C, and the formation of the alkenylcopper was complete within 1 h at 0 °C. In the case of phenylacetylene (0.612 g, 6 mmol), the carbocupration was complete after the reaction mixture was stirred for 12 h at −20 °C (higher reaction temperatures led to the deprotonation of phenylacetylene). The reaction was then cooled to −60 °C and an excess of an electrophile (20 mmol) such as water, allyl bromide, *tert*-butyl α-(bromomethyl)acrylate, or trimethyltin chloride was added and the reaction mixture was warmed to 0 °C and allowed to stir for 1 h at this temperature. The completion of the reaction was monitored by GLC analysis. The reaction mixture was poured into a saturated aqueous solution of ammonium chloride (50 mL), diluted ammonium hydroxide (50 mL), and diluted with ether (100 mL). The two layers were separated, and the aqueous layer was extracted with ether (2 × 100 mL). The combined ether phases were washed with water (100 mL) and brine solution (100 mL) and dried over $MgSO_4$. After filtration and evaporation of the solvent, the crude resulting product was purified by either distillation or flash chromatography, affording the pure products (>98% pure by GLC analysis) in 67–92% yield.

General Procedure for the Preparation of the Zinc–Copper Reagents FG–RCu(CN)Li·ZnMe$_2$·LiI 3, Their Reaction with Phenylacetylene or **1-(Methylthio)-1-hexyne, and Trapping with an Electrophile.** A THF solution of the alkylzinc iodide FG–RZnI **1** (10 mmol) was added at −70 °C via syringe to a THF solution of $Me_2Cu(CN)Li_2$ that was prepared from methyllithium (12.5 mL, 20 mmol) and CuCN (0.9 g, 10 mmol) in 5 mL of THF.[8] The resulting solution was warmed to 0 °C and stirred at this temperature for 5 min. The alkyne (phenylacetylene or 1-(methylthio)-1-hexyne (6 mmol)) was added at −70 °C and the reaction mixture was warmed to −20 °C in the case of phenylacetylene and 25 °C in the case of 1-(methylthio)-1-hexyne. The completion of the carbometalation was checked by GLC analysis of hydrolyzed reaction samples (see Tables I and II for the reaction time). After complete formation of the alkenylcopper–zinc reagent, the reaction mixture was cooled to −60 °C and an excess of the electrophile (H_2O, allyl bromide, *tert*-butyl α-(bromomethyl)acrylate, trimethyltin chloride; iodine; 3 equiv) was added. The reaction mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. The reaction was worked up as described above, and the crude resulting oil was purified by flash chromatography, affording pure products (>98% pure by GLC analysis).

Carbocupration of Acetylene with FG–RCu(CN)Li·ZnMe$_2$LiI 3. A THF solution of the zinc–copper reagent **3** (10 mmol) was prepared as described above. The addition funnel was replaced by a gas inlet and the reaction mixture was cooled to −60 °C. Acetylene (800 mL, 35 mmol) was slowly bubbled through the clear reaction mixture, which rapidly turns to a red-brown color. During the addition of acetylene the reaction temperature was kept between −45 and −40 °C. After the end of the addition, the reaction mixture was stirred 1 h at −40 °C. A conversion of only 35% was observed in the case of a primary alkyl reagent **3**, whereas a secondary alkyl reagent **3** led to conversion of 83–85%. Attempts to improve this carbometalation by raising or lowering the reaction temperature by using other copper salts such as $(CH_2{=}CH)_2Cu(CN)MgX)_2$, CuI·2LiCl, CuCN·LiCl, $Me_2Cu(CN)Li_2$ (catalytic amount) or by using ether instead of THF did not improve the conversion. The reaction mixture was cooled to −70 °C and iodine (8.8 g, 35 mmol in 10 mL of THF) was added. The reaction mixture was allowed to warm to 0 °C and was worked up as described above. The crude mixture of the desired alkenyl iodide and alkyl iodide (see Scheme III) was dissolved in 4 mL of THF and added to a zinc suspension (2 g, 30 mmol) activated as described above in 2 mL of THF. The reaction mixture was warmed to 40 °C, leading to the formation of the alkylzinc iodide. After 2–3 h at 40 °C the reaction mixture was cooled to 25 °C, and quenched with an aqueous saturated solution of ammonium chloride. After the usual workup, the crude residual oil was distilled under reduced pressure, affording the pure (*Z*)-alkenyl iodides **7d,e,k** in respectively 26%, 66%, and 66% yields.

Physical and Spectroscopic Data of 6a–d, 7a–k, and 11a–e. (*Z*)-2-Ethyl-1-hexenyl methyl sulfide (6a): distilled under reduced pressure at 45–47 °C (1.5 mmHg); IR (neat) 2923 (br s), 1640 (s), 839 (s), 807 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.55 (s, 1 H), 2.25 (s, 3 H), 2.17 (t, 2 H, J = 9 Hz), 2.1 (q, 2 H, J = 7 Hz), 1.45–1.3 (m, 4 H), 1.05 (t, 3 H, J = 6 Hz), 0.95 (t, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 142.3, 119.2, 31.8, 29.7, 29.3, 22.6, 17.1, 13.8, 12.4; MS (EI) 41 (39), 55 (33), 67 (37), 69 (33), 81 (30), 101 (32), 115 (100), 158 (65); exact mass calcd for $C_9H_{18}S$ 158.1129, obsd 158.1138.

(*Z*)-1-Allyl-2-ethyl-1-hexenyl methyl sulfide (6b): distilled under reduced pressure at 65–67 °C (0.5 mmHg); IR (neat) 3078 (s), 2920 (br s), 1638 (s), 1466 (s), 991 (s), 965 (s), 944 (s), 910 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.92–5.80 (m, 1 H), 5.15–5.0 (m, 2 H), 3.1 (d, 2 H, J = 5.5 Hz), 2.36 (t, 2 H, J = 6 Hz), 2.15 (s, 3 H), 2.10 (q, 2 H, J = 6 Hz), 1.45–1.30 (m, 4 H), 1.0–0.89 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.5, 136.1, 125.4, 114.8, 35.3, 33.2, 30.8, 25.5, 22.8, 15.5, 13.9, 13.1; MS (EI) 41 (100), 55 (44), 61 (45), 79 (91), 91 (35), 107 (44), 155 (32), 183 (13), 198 (50); exact mass cacld for $C_{12}H_{22}S$ 198.1442, obsd 198.1427.

(*Z*)-*tert*-Butyl 2-[3-ethyl-2-(methylthio)-2-heptenyl]acrylate (6c): flash column chromatography (hexane/ether, 49:1): IR (neat) 2926 (br s), 1710 (s), 1632 (s), 1254 (s), 1140 (s), 950 (s), 852 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.15 (s, 1 H), 5.48 (s, 1 H), 3.25 (s, 2 H), 2.38 (t, 2 H, J = 6 Hz), 2.1 (s, 3 H), 2.05 (q, 2 H, J = 5.5 Hz), 1.52 (s, 9 H), 1.45–1.30 (m, 4 H), 1.0–0.9 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.2, 145.3, 139.0, 124.3, 123.7, 80.3, 32.9, 32.3, 30.7, 27.9, 27.8, 25.7, 22.8, 15.4, 13.8, 13.0; MS (EI) 41 (78), 57 (100), 79 (16), 107 (14), 123 (14), 157 (41), 194 (10), 225 (8), 241 (6), 298 (8); exact mass calcd for $C_{17}H_{30}SO_2$ 298.1966, obsd 298.1967.

(*E*)-2-Ethyl-1-(trimethylstannyl)hexenyl methyl sulfide (6d): distilled under reduced pressure at 93–96 °C (0.6 mmHg); IR (neat) 2727 (br s), 1564 (s), 1436 (s), 769 (s), 711 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.5 (t, 2 H, J = 7 Hz), 2.15 (q, 2 H, J = 6 Hz), 2.08 (s, 3 H), 1.4–1.3 (m, 4 H), 1.05 (t, 3 H, J = 7 Hz), 0.94 (t, 3 H, J = 7 Hz), 0.28 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 162.4, 131.4, 32.6, 31.5, 22.9, 19.6, 14.2, 14.0, −6.3; MS (EI) 41 (42), 49 (60), 67 (47), 84 (42), 109 (70), 135 (35), 157 (49), 161 (47), 163 (69), 165 (82), 193 (50), 195 (79), 197 (100), 263 (19), 265 (23), 280 (18), 305 (20), 307 (28), 320 (18), 322 (24); exact mass calcd for $C_{12}H_{26}S^{120}Sn$ 322.0777, obsd 322.0781.

(*E*)-5-Phenyl-1,4-heptadiene (6e): distilled under reduced pressure at 63–65 °C (0.7 mmHg); IR (neat) 3080 (s), 3058 (s), 3021 (s), 2969 (s), 2933 (s), 2874 (s), 1640 (s), 1600 (s), 1491 (s), 1443 (m), 991 (s), 912 (s), 757 (s), 697 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.4–7.2 (m, 5 H), 5.96–5.82 (m, 1 H), 5.7–5.6 (m, 1 H), 5.15–5.0 (m, 2 H), 2.95 (t, 2 H, J = 7 Hz), 2.5 (q, 2 H, J = 6 Hz), 0.98 (t, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 142.9, 136.9, 131.6, 128.1, 126.5, 126.3, 124.9, 114.7, 32.6, 23.0, 13.4; MS (EI) 39 (35), 51 (20), 77 (20), 91 (34), 115 (41), 128 (62), 143 (100), 172 (27); exact mass calcd for $C_{13}H_{16}$ 172.1252, obsd 172.1248.

(*E*)-Ethyl 5-butyl-6-(methylthio)-5-hexenoate (7a): flash column chromatography (hexane/ether, 49:1): IR (neat) 2928 (br s), 1732 (s), 1642 (s), 1457 (s), 1260 (m), 1096 (s), 1028 (s), 805 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.6 (s, 1 H), 4.15 (q, 2 H, J = 6 Hz), 2.23 (t, 2 H, J = 6 Hz), 2.22 (s, 3 H), 2.15–2.04 (m, 4 H), 1.8–1.69 (m, 2 H), 1.4–1.3 (m, 4 H), 1.25 (t, 3 H, J = 6 Hz), 0.92 (t, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 173.0, 139.0, 121.1, 59.8, 35.5, 33.4, 31.3, 29.4, 22.9, 22.4, 16.9, 14.0, 13.6; MS (EI) 41 (91), 45 (48), 55 (65), 61 (50), 67 (54), 81 (66), 101 (53), 108 (100), 141 (50), 154 (55), 196 (18), 244 (31); exact mass calc for $C_{13}H_{24}SO_2$ 244.1497, obsd 244.1490.

(*E*)-Ethyl 5-butyl-6-(methylthio)-5,8-nonadienoate (7b): flash column chromatography (hexane/ether, 49:1); IR (neat) 3064 (s), 2927 (br s), 1736 (s), 1638 (s), 1445 (s), 1186 (m), 1028 (m), 911 (s), 733 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.9–5.78 (m, 1 H), 5.15–5.0 (m, 2 H), 4.15 (q, 2 H, J = 6.5 Hz), 3.1 (d, 2 H, J = 6 Hz), 2.4–2.26 (m, 4 H), 2.18 (s, 3 H), 2.12–2.05 (m, 2 H), 1.75–1.62 (m, 2 H), 1.45–1.32 (m, 4 H), 1.28 (t, 3 H, J = 6.5 Hz), 0.9 (t, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 172.9, 141.5, 135.8, 126.9, 114.8, 59.9, 35.1, 33.8, 33.3, 31.7, 30.6, 23.7, 22.6, 15.3, 14.0, 13.7; MS (EI) 41 (77), 49 (92), 55 (57), 79 (77), 105 (75), 107 (69), 119 (67), 121 (55), 147 (52), 149 (54), 181 (51), 191 (44), 223 (39), 243 (89), 284 (100); exact mass calcd for $C_{16}H_{28}SO_2$ 284.1810, obsd 284.1817.

(*Z*)-Ethyl 5-butyl-6-iodo-6-(methylthio)-5-hexenoate (7c): flash column chromatography (hexane/ethyl acetate, 49:1); IR (neat) 2924 (br s), 1726 (s), 1458 (m), 1175 (m), 1098 (m), 811 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.15 (q, 2 H, J = 6 Hz), 2.52–2.45 (m, 2 H), 2.36–2.3 (m, 4 H), 2.25 (s, 3 H), 1.8–1.68 (m, 2 H), 1.45–1.30 (m, 4 H), 1.26 (t, 3 H, J = 6 Hz), 0.9 (t, 3 H, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 173.0, 154.3, 92.8, 60.2, 41.9, 33.9, 33.8, 30.7, 22.7, 22.4, 22.2, 14.2, 13.8; MS (EI) 41 (45), 55 (41), 95 (36), 107 (100), 149 (54), 195 (36), 243 (33), 291 (10), 370 (9); exact mass calcd for $C_{13}H_{23}SiO_2$ 370.0463, obsd 370.0457.

(*Z*)-Ethyl 6-iodo-5-hexenoate (7d): flash column chromatography (hexane/ether, 49:1); IR (neat) 3040 (s), 2935 (br s), 1727 (s), 1610 (s), 1418 (m), 1247 (m), 1049 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.2 (d, 1 H, J = 6.5 Hz), 6.2–6.1 (m, 1 H), 4.15 (q, 2 H, 6.5 Hz), 2.35 (t, 2 H, J = 6.5 Hz), 2.25–2.15 (m, 2 H), 1.82–1.7 (m, 2 H), 1.25 (t, 3 H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 172.9, 139.9, 83.1, 60.1, 33.9, 33.3, 23.1, 14.1; MS (CI, ammonia) 95 (3), 99 (4), 141 (30), 269 $[M + H]^+$ (10), 286 $[M + NH_4]^+$ (100); exact mass calcd for $C_8H_{13}O_2IH$ 269.0038, obsd 269.0025.

(*Z*)-Ethyl 7-iodo-5-pentyl-6-heptenoate (7e): flash column chromatography (hexane/ether, 49:1); IR (neat) 3040 (s), 2927 (br s), 1738 (s), 1640 (s), 1457 (s), 1373 (s), 1247 (m), 1033 (s), 711 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.24 (d, 1 H, J = 6.25 Hz), 5.9–5.85 (m, 1 H), 4.15

(q, 2 H, 6.5 Hz), 2.5–2.35 (m, 1 H), 2.32–2.26 (m, 2 H), 1.68–1.58 (m, 2 H), 1.5–1.2 (m, 13 H), 0.9–0.8 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 173.3, 145.4, 81.9, 60.0, 44.0, 34.3, 34.2, 33.8, 31.9, 26.4, 22.4, 22.3, 14.1, 13.9; MS (CI, ammonia) 81 (42), 95 (41), 109 (23), 137 (42), 161 (45), 179 (100), 225 (78), 353 $[M + H]^+$ (54), 370 $[M + NH_4]^+$ (55); exact mass calcd for $C_{14}H_{25}O_2IH$ 353.0977, obsd 353.0969.

(*E*)-Ethyl 6-butyl-7-(methylthio)-5-pentyl-6-heptenoate (7f): flash column chromatography (hexane/ether, 49:1); IR (neat) 2927 (br s), 1739 (s), 1464 (s), 1245 (m), 1114 (s), 1033 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.55 (s, 1 H), 4.12 (q, 2 H, *J* = 6.5 Hz), 2.3–2.2 (m, 5 H), 2.04–1.94 (m, 2 H), 1.6–1.5 (m, 2 H), 1.4–1.2 (m, 18 H), 0.95–0.85 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 173.3, 142.7, 121.4, 59.9, 47.0, 34.3, 34.0, 33.4, 31.9, 30.5, 30.4, 27.0, 23.1, 22.9, 22.4, 17.3, 14.1, 13.9, 13.7; MS (EI) 41 (100), 43 (72), 55 (82), 101 (56), 121 (37), 163 (27), 213 (84), 257 (41), 280 (14), 328 (27); exact mass calcd for $C_{19}H_{36}O_2S$ 328.2436, obsd 328.2433.

(*E*)-5-Butyl-6-(methylthio)-5-hexenenitrile (7g): flash column chromatography (hexane); IR (neat) 2923 (br s), 2246 (s), 1617 (s), 1428 (m), 1341 (s), 803 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.5 (s, 1 H), 2.18 (t, 2 H, *J* = 6 Hz), 2.09 (s, 3 H), 2.05 (t, 2 H, *J* = 6 Hz), 1.95 (t, 2 H, *J* = 6.2 Hz), 1.65–1.55 (m, 2 H), 1.25–1.1 (m, 4 H), 0.75 (t, 3 H, *J* = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 137.3, 122.5, 119.1, 34.9, 31.1, 29.4, 23.4, 22.4, 17.0, 16.2, 13.6; MS (EI) 41 (65), 49 (43), 67 (33), 79 (32), 101 (66), 122 (21), 154 (100), 197 (50); exact mass calcd for $C_{11}H_{19}SN$ 197.1238, obsd 197.1244.

(*E*)-2-Butyl-6-chloro-1-hexenyl methyl sulfide (7h): distilled under reduced pressure at 103–105 °C (0.6 *m*mHg); IR (neat) 2929 (br s), 1620 (s), 1457 (m), 1311 (m), 910 (s), 804 (s), 733 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.6 (s, 1 H), 3.55 (t, 2 H, *J* = 6.25 Hz), 2.25 (s, 3 H), 2.18–2.05 (m, 4 H), 1.82–1.72 (m, 2 H), 1.6–1.5 (m, 2 H), 1.4–1.25 (m, 4 H), 0.92 (t, 3 H, *J* = 5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 139.8, 120.7, 44.7, 35.6, 32.1, 31.5, 29.6, 25.0, 22.6, 17.2, 13.8; MS (EI) 41 (42), 55 (35), 67 (27), 81 (24), 95 (26), 101 (100), 143 (26), 177 (45), 179 (20), 220 (54); exact mass calcd for $C_{11}H_{21}S^{35}Cl$ 220.1052, obsd 220.1044.

(*E*)-1-Allyl-2-cyclohexyl-1-hexenyl methyl sulfide (7i): distilled under reduced pressure at 112–115 °C (0.4 mmHg); IR (neat) 3078 (s), 2911 (br s), 1637 (s), 1465 (m). 990 (s), 954 (s), 909 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.9–5.78 (m, 1 H), 5.1–5.0 (m, 2 H), 3.08 (d, 2 H, *J* = 5.5 Hz), 2.48–2.4 (m, 1 H), 2.25 (t, 2 H, *J* = 8 Hz), 2.15 (s, 3 H), 1.78–1.6 (m, 4 H), 1.5–1.1 (m, 10 H), 0.9 (t, 3 H, *J* = 6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 147.4, 136.6, 125.8, 114.5, 42.8, 35.3, 32.4, 31.5, 30.5, 26.7, 26.2, 23.2, 15.4, 13.7; MS (EI) 41 (100), 55 (52), 67 (33), 79 (33), 91 (24), 105 (14), 147 (8), 195 (23), 209 (6), 237 (12), 252 (25); exact mass calcd for $C_{16}H_{28}S$ 252.1911, obsd 252.1922.

(*E*)-1-Cyclohexyl-1-phenyl-1,4-pentadiene (7j): distilled under reduced pressure at 112–115 °C (0.6 mmHg); IR (neat) 3078 (s), 3057 (s), 3019 (s), 2927 (s), 2852 (s), 1637 (s), 1595 (s), 1490 (s), 1448 (s), 991 (s), 910 (s), 767 (s), 701 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.3–7.0 (m, 5 H), 5.95–5.8 (m, 1 H), 5.76 (t, 1 H, *J* = 7 Hz), 5.1–4.94 (m, 2 H), 2.98–2.9 (m, 2 H), 2.65–2.5 (m, 1 H), 1.8–1.55 (m, 5 H), 1.35–1.0 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 147.6, 143.8, 137.2, 128.6, 127.3, 126.1, 125.8, 114.6, 40.6, 32.1, 31.9, 26.8, 26.1; MS (EI) 41 (61), 55 (38), 81 (37), 91 (68), 115 (40), 129 (52), 143 (100), 172 (21), 185 (8), 226 (18); exact mass calcd for $C_{17}H_{22}$ 226.1721, obsd 226.1717.

(*Z*)-2-Cyclohexyl-1-iodoethylene (7k): flash column chromatography (hexane); IR (neat) 3060 (s), 2923 (br s), 1608 (s), 1446 (s), 1276 (m), 955 (s), 888 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.1–5.86 (m, 2 H), 2.38–2.28 (m, 1 H), 1.8–1.61 (m, 5 H), 1.4–1.08 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 146.0, 79.4, 43.4, 31.2, 25.8, 25.4; MS (EI) 41 (45), 55 (32), 67 (100), 79 (11), 109 (47), 180 (5), 236 (21); exact mass calcd for $C_{18}H_{13}I$ 236.0062, obsd 236.0049.

Pentylidenecyclopentane (11a): flash column chromatography (hexane); IR (neat) 2929 (br s), 1648 (s), 1434 (m), 1350 (s), 1020 (s), 950 (s) 850 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.3–5.2 (m, 1 H), 2.25–2.12 (m, 4 H), 2.0–1.9 (m, 2 H), 1.7–1.54 (m, 4 H), 1.35–1.25 (m, 4 H), 0.92–0.86 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 142.8, 120.3, 33.5, 32.0, 29.3, 28.5, 26.47, 26.41, 22.4, 14.0; MS (EI) 41 (61), 55 (27), 67 (100), 82 (47), 95 (91), 109 (6), 138 (27); exact mass calcd for $C_{10}H_{18}$ 138.1408, obsd 138.1407.

3-Carbethoxy-3-butenylidenecyclopentane (11b): flash column chromatography (hexane); IR (neat) 2930 (br s), 1713 (s), 1629 (s), 1478 (m), 1287 (m), 1137 (m), 941 (s), 852 (s), 817 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.3 (s, 1 H), 5.35 (s, 1 H), 2.95 (s, 2 H), 2.8 (t, 2 H, *J* = 6.5 Hz), 2.16 (t, 2 H, *J* = 6.5 Hz), 1.98 (t, 2 H, *J* = 6.5 Hz), 1.7–1.6 (m, 4 H), 1.52 (s, 9 H), 1.38–1.25 (m, 4 H), 0.9 (t, 3 H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.9, 140.2, 139.6, 126.6, 122.7, 80.1, 34.8, 33.0, 30.4, 30.35, 30.31, 28.0, 26.8, 26.6, 22.8, 13.9; MS (EI) 41 (30), 49 (36), 57 (40), 67 (32), 81 (77), 95 (61), 137 (100), 165 (31), 177 (15), 205 (19), 222 (61), 278 (6); exact mass calcd for $C_{18}H_{30}O_2$ 278.2245, obsd 278.2241.

(*E*)-6-(1-Butyl-3-carbethoxy-3-butenylidene)-1,4-dioxospiro[4.4]nonane (11c): flash column chromatography (hexane/ether, 24:1); IR (neat) 2929 (br s), 1724 (s), 1674 (s), 1628 (s), 1441 (m), 1300 (m), 1172 (m), 1063 (m), 943 (s), 819 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.2 (s, 1 H), 5.5 (s, 1 H), 4.22 (q, 2 H, *J* = 6.25 Hz), 4.1–4.0 (m, 2 H), 3.98–3.9 (m, 2 H), 3.05 (s, 2 H), 2.28 (t, 2 H, *J* = 6.5 Hz), 2.15 (t, 2 H, *J* = 6.5 Hz), 1.84 (t, 2 H, *J* = 6.5 Hz), 1.65–1.55 (m, 2 H), 1.4–1.25 (m, 7 H), 0.9 (t, 3 H, *J* = 6.25 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 167.2, 137.2, 136.9, 135.7, 124.2, 115.1, 63.7, 60.5, 38.1, 35.6, 31.0, 30.8, 29.9, 23.3, 21.4, 14.0, 13.8; MS (EI): 41 (41), 55 (44), 79 (22), 99 (100), 161 (14), 195 (83), 207 (16), 235 (14), 265 (20), 279 (4), 308 (7); exact mass calcd for $C_{18}H_{28}O_2$ 308.1987, obsd 308.2003.

(*Z*)-1-(1-Butyl-3-carbethoxy-3-butenylidene)-2-propylcyclopentane (11d): flash column chromatography (hexane); IR (neat) 2929 (br s), 1720 (s), 1628 (s), 1485 (m), 1323 (m), 1173 (m), 1096 (s), 1029 (s), 943 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.16 (s, 1 H), 5.93 (s, 1 H), 4.24 (q, 2 H, *J* = 6 Hz), 3.16–2.9 (dd, 2 H, *J* = 17.3 Hz, *J* = 60 Hz), 2.56–2.5 (m, 1 H), 2.29 (t, 2 H, *J* = 8 Hz), 1.96–1.84 (m, 2 H), 1.7–1.5 (m, 4 H), 1.4–1.15 (m, 11 H), 0.98–0.82 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 167.5, 144.6, 139.2, 126.0, 124.2, 60.4, 41.3, 36.6, 33.9, 32.2, 31.1, 30.4, 29.2, 23.6, 22.7, 21.0, 14.1, 14.0; MS (EI) 41 (35), 55 (24), 67 (33), 81 (42), 95 (27), 109 (33), 123 (42), 179 (100), 247 (6), 292 (5); exact mass calcd for $C_{19}H_{32}O_2$ 292.2402, obsd 292.2404.

(*E*)- and (*Z*)-2-Propyl-1-[(trimethylsilyl)(trimethylstannyl)methylene]cyclopentane (11e): flash column chromatography (hexane); IR (neat) 2931 (br s), 1618 (s), 1562 (s), 1450 (m), 1250 (s), 877 (m), 764 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.4–2.15 (m, 3 H), 1.65–1.30 (m, 4 H), 1.29–1.02 (m, 4 H), 0.8 (t, 3 H, *J* = 6 Hz), 0.01–(−0.1) (m, 18 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 176.5, 166.4, 128.9, 116.8, 49.0, 47.7, 45.4, 42.3, 40.2, 38.8, 36.1, 33.0, 32.9, 32.3, 31.7, 30.1, 24.6, 24.5, 24.4, 20.8, 19.7, 19.5, 17.1, 14.6, 2.0, 1.9, 1.8, −0.1, −4.7, −10.8; MS (CI, methane) 119 (4), 136 (15), 165 (19), 178 (27), 179 (17), 180 (48), 181 (22), 182 (63), 207 (12), 319 (11), 341 (40), 342 (29); 343 (75), 344 (39), 345 (100), 346 (21), 347 (17), 357 (24), 358 (22), 359 (46), 360 (31), 361 $[M + H]^+$ (60); exact mass calcd for $C_{15}H_{32}{}^{120}SnSiH$ 361.1373, obsd 361.1357.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for the compounds synthesized (52 pages). Ordering information is given on any current masthead page.