Intramolecular Alkyne Carbomercuration by Allylic Silanes: A New Carbon−Carbon Bond-Forming Reaction

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Intramolecular alkyne carbomercuration (IAC) of alkynyl-tethered enol silanes is a mild, versatile, and high-yielding method for the formation of cyclic products bearing a mercuric-functionalized exocyclic alkene β to a carbonyl group.[1] The vinyl mercurial moiety of the products is synthetically valuable because it may be stereoselectively transformed into a variety of additional functional groups.[2] This synthetic utility has been demonstrated in the total syntheses of several structurally diverse natural products.[3−6] The configuration of the vinyl mercurial product, whether the mercuric substituent is syn or anti with respect to the carbonyl, is a diagnostic indicator of plausible mechanistic pathways leading from enol silane to carbomercuration product. Strict syn addition of the α-carbon and mercuric salt to the alkyne was originally postulated to occur from either an intermediate α-carbonyl mercurial or an *O*-mercury enolate.[1,7] However, because only anti vinyl mercurial products have since been observed from IAC reactions of enol silanes containing terminally unsubstituted alkynes,[3−5] α-carbonyl mercurial or *O*-mercury enolate intermediates may be unnecessary. This suggested that other types of latent carbon nucleophiles besides enol derivatives might also undergo efficient intramolecular alkyne carbomercuration to tethered, electrophilically activated alkynes. In particular, replacement of the enol silane oxygen by carbon provides a test for the intermediacy of enol derived organomercurials in the IAC process. The utility of alkynyl-tethered *allylic silanes* for unprecedented intramolecular carbon−carbon bond formation upon mercuric salt activation was therefore examined. This has resulted in the stereoselective formation of functionalized carbo- and heterocycles and means to control the *E*/*Z* configuration of the vinyl mercurial products. Details of these initial studies are reported here.

A few representative alkynyl-tethered allylic silanes were synthesized conveniently from the corresponding ketones or aldehydes using a common key phosphine intermediate, $TMSCH_2CH_2{=}PPh_3$.[8] Treatment of alkynyl aldehydes **1**,[9] **2**,[10] and **3**[11] or methyl ketone **4**[12] with in situ prepared $TMSCH_2CH_2{=}PPh_3$ gave allylic silanes **5**−**8**, respectively, each as a 1:1, *E*:*Z* alkene mixture (Scheme 1). Methyl- and trimethylsilyl-substituted alkynes **9** and **10** were prepared from **8** in quantitative yields, whereas terminally unsubstituted and methyl-substituted alkynyl (*Z*)-allylic silanes (**11** and **12**, respectively) were obtained in several steps from acetol.

Separate treatment of the alkynyl-tethered allylic silanes (**5**−**12**) with $HgCl_2$ (1.1 equiv) and HMDS (0.2 equiv) in CH_2Cl_2 (0.2 M) at room temperature did indeed promote intramolecular carbon−carbon bond formation in all but one case (Table 1). After the indicated reaction time, the vinyl mercurial products were isolated by silica gel column chromatography in the yields indicated in Table 1. Five-exo ring formation proceeded smoothly (14−19 h) from **5** and **8**−**12** to give the exocyclic vinyl mercurial products **13** and **16**−**18**, respectively, in moderate yields (entries 1 and 4−8). Six-exo ring formation leading from **6** to **14** was lower yielding (36%, entry 2) and accompanied by chloromercuration of the alkyne of **6**. Attempted formation of a seven membered carbocycle (**15**) from **7** was unsuccessful. Instead, mercuric chloride addition across the alkyne again occurred, while the allylic silane moiety remained intact (entry 3).

In general, the standard conditions used for the IAC reactions of silyl enol ethers provided the best results for carbon−carbon bond formation of the allylic silanes examined here. Attempts to increase the yields of the cyclizations by heating the reaction mixtures or using different types of mercuric salts or solvents (diethyl ether, acetonitrile, or THF) were unsuccessful. The use of hexamethyldisilazane was found to be beneficial, aiding the suspension of the mercuric salt and serving as an acid scavenger.[1] Both the allylic silane and alkyne moiety of **5** were unreactive toward $HgBr_2$ and HgI_2 under the standard reaction conditions. However, introduction of HgF_2, either as the salt or generated in situ from $HgCl_2$ and TBAF, led to rapid (<5 min) addition of mercuric and fluoride ions to the triple bond[13] but without disruption of the allylic silane moiety. Methyl substitution of either the alkene or alkyne allowed the cyclizations to proceed in yields comparable to those of the unsubstituted substrates (entries 4−8). However, trimethylsilyl substitution of the alkyne (**10**) dramatically impacted both the rate (45 h, entry 6) and stereoselectivity of the reaction, yet provided a comparable yield of cyclized product (**18*Z***). Substrates bearing allylic propargylic ether linkages (**11** and **12**) led to tetrahydrofuran products (**19** and **20**, entries 7 and 8).

All of these reactions are highly stereoselective; each carbomercuration product was obtained as only a single alkene stereoisomer. Although direct spectroscopic evidence to assign the vinyl mercurial configurations of **13** and **14** was not obtained, the vinyl configurations of **16**−**20** were determined by NOE experiments using the allylic methyl substituent as a secure spectroscopic handle. In the vinyl mercurial products **16*E*** and **19**, derived from terminally unsubstituted alkynes **8** and **11**, respectively, the newly formed carbon−carbon bond and mercuric salt are anti (entries 4 and 7). Terminal methyl-substituted alkynes **9** and **12** also gave anti products (entries 5 and 8), and it is therefore likely that **13** and **14** are also anti vinyl mercurials. However,

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Scheme 1

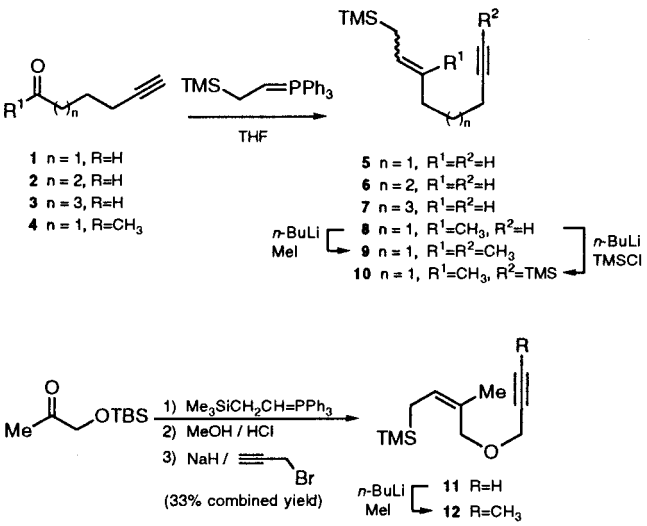
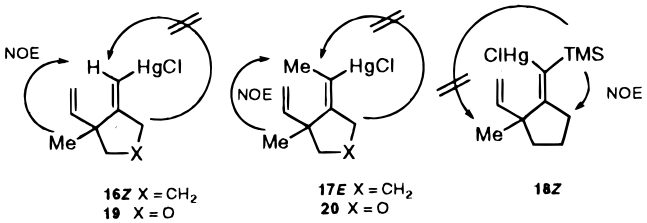


Table 1

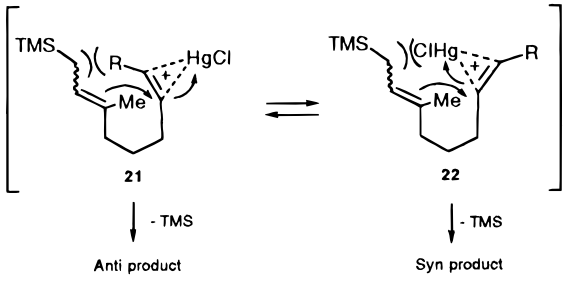
Entry[a]	Substrates	Reaction Time	Products / Yields[b]
1	**5** n=1	14 h	**13** 65 %
2	**6** n = 2	18 h	**14** 36 %
3	**7** n = 3	18 h	**15** 0%[c]
4	**8** R = H	14 h	**16*E*** 56% **16*Z*** 0%
5	**9** R = Me	19 h	**17*E*** 40% **17*Z*** 0%
6	**10** R = TMS	45 h	**18*E*** 0% **18*Z*** 50%
7	**11** R = H	14 h	**19** 48%
8	**12** R = Me	15 h	**20** 41%

[a] Standard reaction conditions were used (see text). [b] Isolated yields. [c] Only chloromercuration adducts were obtained (see text).

terminal substitution of the alkyne with a trimethylsilyl group led to complete reversal of stereoselectivity (entry 6, **10** → **18*Z***). Here, net syn addition of mercuric chloride and the allylic moiety to the alkyne places the vinyl trimethylsilyl group anti to the newly formed carbon−carbon bond in **18*Z***. The (*Z*)-selectivity observed in the carbomercuration of **10** is analogous to that reported previously in the IAC reaction of a (trimethylsilyl)alkynyl-tethered silyl enol ether.[7]



The anti selectivity in the cyclizations of methyl and terminally unsubstituted alkynes **8**, **9**, **11**, and **12** is consistent with simple trans addition of the nucleophilic β-allyl silane carbon to a mercuric salt-complexed alkyne, analogous to anti selective silyl enol ether IAC reactions.[3−5] It is interesting and synthetically useful that simple trimethylsilyl substitution of the starting alkyne led exclusively to a syn vinyl mercurial product (**18*Z***). Although further studies are required to define the basis of this reversal in stereoselectivity, contributing factors may include steric interactions or more unique silicon characteristics such as relative electropositivity and β-carbocation stabilization potential. Stereoselectivity may derive from partitioning of an sp^2-like carbomercurinium intermediate between anti (**21**) and syn (**22**) orientations with respect to the tethered nucleophile. Minimization of steric interactions in this model would help to define which conformer undergoes carbon−carbon bond formation, via either cis or trans addition[14] of carbon and mercury across the activated alkyne. Because the allyilc silane moiety of **7** was unchanged under prolonged IAC reaction conditions, it is unlikely that an allylic organomercurial is generated en route to **18*Z***.



Carbon−carbon bond formation using this novel nucleophile−electrophile pair complements alternative methods available for the synthesis of similar carbocycles.[15−17] The dramatic silicon effect observed here provides a practical means for controling the configuration of the functionalized exocyclic alkene, and the synthetic versatility of the vinyl mercurial[2] and vinyl silane[18−20] products may provide access to a wide range of additional functionality. This work also suggests that electrophilically activated alkynes may be useful in a broader variety of carbon−carbon bond-forming reactions. Although the yields of the allylic silane IAC reactions reported here are modest when compared to those of analogous ketone silyl enol ether-based reactions,[1,3−5] substantial improvements may result from modifying the substitution on silicon to increase the nucleophilicity of the allylic silane moiety.[21] The results of these and further studies to define basis of the observed stereoselectivity and extend the scope of this methodology will be reported in due course.

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Experimental Section

General Procedures. Unless otherwise noted, all reactions were carried out under Ar or N_2 in oven-dried glassware using standard syringe, cannula, and septa techniques. Diethyl ether and THF were distilled under N_2 from Na/benzophenone ketyl. Hexamethyldisilazane and CH_2Cl_2 were distilled under N_2 from CaH_2, and dimethylformamide was distilled from BaO. Other solvents were used as received. NaI, $HgCl_2$, and triphenylmethylphosphonium bromide were dried under vacuum (0.3 Torr, ca. 6−12 h) immediately prior to use. Silica gel column chromatography was performed using Baker flash silica gel 60 (40 μm) or ICN Silitech 69 (63−200 μm) and the solvent systems indicated. Analytic and preparative TLC was performed with 0.25 or 0.50 mm EM silica gel 60 F_{254} plates, respectively. NMR spectra were obtained in $CDCl_3$ and are referenced to residual $CHCl_3$ at 7.24 ppm (^{1}H) and 77.0 ppm (^{13}C). The mass spectrometers used show deviations of less than 5 ppm.

(*E*,*Z*)-1-(Trimethylsilyl)-2-octen-7-yne (5). Pyridinium chlorochromate (4.30 g, 20.0 mmol) was added to a stirred rt solution of 5-hexyn-1-ol (982 mg, 10.0 mmol) in CH_2Cl_2 (30 mL). After 1 h, the mixture was filtered through a pad of silica gel, and the filtrate was concentrated to give crude 5-hexynal[9] (**1** , 960 mg, ca. 10.0 mmol) as an oil: ^{1}H NMR (200 MHz) δ 9.83 (t, J = 1.2 Hz, 1H), 2.50-2.20 (m, 4H), 1.97 (t, J = 2.0 Hz, 1H), 1.60 (m, 2H). To a magnetically stirred 0 °C suspension of methyltriphenylphosphonium bromide (4.64 g, 13.0 mmol) in THF (10 mL) was added *n*-BuLi (5.60 mL, 2.50 M in hexanes, 14.0 mmol) under Ar. The resulting dark red solution was allowed to warm to rt and stir for 1 h. A mixture of NaI (3.90 g, 13 mmol) and (chloromethyl)trimethylsilane (1.82 mL, 13.0 mmol) in THF (10 mL) was heated under reflux for 1 h and then cooled to rt before the above phosphorylidene solution was added via cannula. The resulting mixture was stirred at rt for 14 h under Ar and then cooled to 0 °C before *n*-BuLi (5.20 mL, 2.50 M in hexanes, 13.0 mmol) was added.[8] After being stirred for 30 min, the mixture was cooled to −78 °C and a solution of crude **1** (960 mg, ca. 10.0 mmol) in THF (10 mL) was added slowly. The resulting mixture was allowed to warm to rt and stir over 14 h. Aqueous NH_4Cl was added, the mixture was extracted with hexanes, and the combined organic extract was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered, and concentrated. Silica gel column chromatography of the residue (hexanes−ethyl acetate, 10:1, v/v) gave **5** (318 mg, 1.80 mmol, 18% yield) as a colorless oil: IR (neat) 3309, 2117, 1644, 1248 cm^{-1}; ^{1}H NMR (500 MHz, E/Z = 1:1) δ 5.43 (m, 1H), 5.24 (m, 1H), 2.19 (dt, J = 2.5, 7.0 Hz, 2H), 2.09 (m, 2H), 1.94 (t, J = 2.5 Hz, 1H), 1.59 (m, 2H), 1.47 (d, J = 8.5 Hz, 2H), 0.00 (s, 4.5H), and −0.01 (s, 4.5H); HRMS calcd for $C_{11}H_{20}Si$ (M^+) 180.1335, found 180.1329.

(*E*,*Z*)-1-(Trimethylsilyl)-2-nonen-8-yne (6). Neat 1,3-diaminopropane (APA, 160 mL) was added to NaH (7.20 g, 300 mmol) under Ar, and the mixture was heated at 70 °C for 30 min. The resulting solution was cooled to rt, and 3-heptyn-1-ol (12.6 g, 100 mmol) was added dropwise. After 40 min, an ice−water mixture was added, and the resulting mixture was extracted repeatedly with ether. The combined ether extract was washed with H_2O, dilute aqueous HCl, H_2O, and a saturated aqueous NaCl solution. Drying over Na_2SO_4, filtration, and concentration gave crude 6-heptyn-1-ol[10] (13.0 g, ca. 100% yield): ^{1}H NMR (300 MHz) δ 3.65 (t, J = 6.3 Hz, 2H), 2.22 (dt, J = 2.4, 6.6 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 1.70−1.40 (m, 7H). To a stirred rt solution of crude 6-heptyn-1-ol (2.82 g, ca. 25.0 mmol) in CH_2Cl_2 (100 mL) was added PDC (18.8 g, 50.0 mmol). After 2 h, the mixture was filtered through a pad of silica gel, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give 6-heptynal[10] (**2**, 1.75 g, 16.1 mmol, 64% yield for two steps): ^{1}H NMR (200 MHz) δ 9.80 (t, J = 1.4 Hz, 1H), 2.49 (m, 2H), 2.23 (m, 2H), 1.96 (t, J = 2.0 Hz, 1H), 1.80-1.50 (m, 4H).

Using the same procedure as described for the preparation of **5** above (ca. 1.3 equiv of phosphorylidene), **2** (1.43 g, 13.0 mmol) gave **6** (1.81 g, 6.08 mmol, 46% yield) as a colorless oil after silica gel column chromatography (hexanes−ethyl acetate, 10:1, v/v): IR (neat) 3311, 2119, 1645, 1248 cm^{-1}; ^{1}H NMR (500 MHz, E/Z = 1:1): δ 5.39 (m, 1H), 5.24 (m, 1H), 2.19 (dt, J = 2.5, 7.0 Hz, 2H), 1.98 (m, 2H), 1.93 (t, J = 2.5 Hz, 1H), 1.54 (m, 2H), 1.45 (m, 4H), 0.00 (s, 4.5H), and −0.01 (s, 4.5H); HRMS calcd for $C_{12}H_{26}NSi$ ($M + NH_4$)$^+$ 212.1834, found 212.1832.

(*E*,*Z*)-1-(Trimethylsilyl)-2-decen-9-yne (7). Neat 1,3-diaminopropane (APA, 160 mL) was added to NaH (7.61 g, 317 mmol) under Ar, and the mixture was heated at 70 °C for 30 min. The resulting solution was cooled to rt, and 2-octyn-1-ol (5.00 g, 39.6 mmol) was added dropwise. After 40 min, an ice−water mixture was added, and the resulting mixture was extracted repeatedly with ether. The combined ether extract was washed with H_2O, dilute aqueous HCl, H_2O, and a saturated aqueous NaCl solution. Drying over Na_2SO_4, filtration, and concentration gave crude 7-octyn-1-ol (4.51 g): ^{1}H NMR (200 MHz) δ 3.60 (t, J = 6.60 Hz, 2H), 2.12 (m, 2H), 1.90 (t, J = 2.2 Hz, 1H), 1.60-1.24 (m, 9H). To a rt solution of crude 7-octyn-1-ol (2.52 g, ca. 20.0 mmol) in CH_2Cl_2 (50 mL) was added PDC (15.0 g, 40.0 mmol). After 2 h, the mixture was filtered through a pad of silica gel, the filtrate was concentrated, and the residue purified by silica gel column chromatography to give 7-octynal (**3**, 1.00 g, 8.00 mmol, 40% yield from 2-octyn-1-ol): ^{1}H NMR (200 MHz) δ 9.82 (t, J = 1.2 Hz, 1H), 2.49 (m, 2H), 2.23 (m, 2H), 1.96 (t, J = 2.0 Hz, 1H), 1.81−1.21 (m, 6H). Using the same procedure as described in the preparation of **5** above (ca. 1.3 equiv of phosphorylidene), **3** (911 mg, 7.33 mmol) gave **7** (1.15 g, 5.53 mmol, 30% yield) as a colorless oil after silica gel column chromatography (hexanes−ethyl acetate, 10:1, v/v): IR (neat) 3309, 2118, 1647, 1248 cm^{-1}; ^{1}H NMR (500 MHz, E/Z = 1:1) δ 5.36 (m, 1H), 5.22 (m, 1H), 2.17 (m, 2H), 1.96 (m, 2H), 1.91 (m, 1H), 1.52 (m, 2H), 1.45−1.32 (m, 6H), −0.01 (s, 4.5H), and −0.02 (s, 4.5H); HRMS calcd for $C_{13}H_{28}NSi$ ($M + NH_4$)$^+$ 226.1991, found 226.1995.

(*E*,*Z*)-1-(Trimethylsilyl)-3-methyl-2-octen-7-yne (8). To a stirred solution of crude **1**[9] (19.20 g, ca. 200 mmol, prepared from 5-hexyn-1-ol as described in the synthesis of **5** above) in THF (250 mL) was added slowly a solution of methylmagnesium bromide (80 mL, 3 M in ether, 240 mmol) at −78 °C and under Ar. After 3 h, aqueous HCl (1 N) was added until the reaction mixture was at neutral pH, and the mixture was extracted with ether. The combined organic extract was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered, and concentrated to give crude 6-heptyn-2-ol (11.0 g, ca. 100 mmol, ca. 50% yield from **1**): ^{1}H NMR (200 MHz) δ 3.64 (m, 1H), 2.20 (m, 2H), 1.80 (t, J = 2.4 Hz, 1H), 1.65−1.30 (m, 5H), 1.10 (d, J = 6.4 Hz, 3H). To a rt solution of crude 6-heptyn-2-ol (11.0 g, ca. 100 mmol) in CH_2Cl_2 (200 mL) was added PDC (45.1 g, 120 mmol). After 14 h, the mixture was filtered through a pad of silica gel, the filtrate was concentrated, and the residue was purified by silica gel column chromatography to give 6-heptyn-2-one (**4**, 3.90 g, 36.0 mmol, 36% yield) as a clear oil: ^{1}H NMR (200 MHz) δ 2.52 (t, J = 6.4 Hz, 2H), 2.11 (s, 3H), 1.83 (t, J = 2.4 Hz, 1H), 1.51 (m, 2H). Using the same procedure as described for the preparation of **5** above (ca. 1.3 equiv of phosphorylidene), 6-heptyn-2-one (**4**, 2.00 g, 18.0 mmol) gave **8** (1.30 g, 6.70 mmol, 37% yield) as a colorless oil after silica gel column chromatography (hexanes−ethyl acetate, 10:1, v/v): IR (neat) 3313, 2120, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $E/Z \approx$ 1:1) δ 5.17 (m, 1H), 2.13 (m, 2H), 2.08 (m, 2H), 1.93 (m, 1H), 1.65 and 1.52 (s, ∼1:1, 3H), 1.54 (m, 2H), 1.37 (d, J = 8.4 Hz, 2H), −0.03 (bs, 9H); HRMS calcd for $C_{12}H_{22}Si$ (M^+) 194.1488, found 194.1491.

(*E*,*Z*)-1-(Trimethylsilyl)-3-methyl-2-nonen-7-yne (9). To a 0 °C stirred solution of **8** (194 mg, 1.00 mmol) in THF (2 mL) were added sequentially *n*-BuLi (420 μL, 2.50 M in hexanes, 1.05 mmol) and methyl iodide (125 μL, 2.00 mmol) under Ar. After 14 h, the solution was diluted with hexanes (ca. 5 mL) and filtered through a pad of silica gel. Concentration of the filtrate gave **9** (208 mg, 1.00 mmol, ca. 100% yield) as a colorless oil: IR (neat) 2170, 1247 cm^{-1}; ^{1}H NMR (500 MHz, $E/Z \approx$ 1:1) δ 5.16 (m, 1H), 2.11 (m, 2H), 2.04 (m, 2H), 1.77 (bs, 3H), 1.66 and 1.52 (s, ∼1:1, 3H), 1.55 (m, 2H), 1.39 (m, 2H), −0.02 (bs, 9H); HRMS calcd for $C_{13}H_{24}Si$ (M^+) 208.1649, found 208.1647.

(*E*,*Z*)-1,8-Bis(trimethylsilyl)-3-methyl-2-octen-7-yne (10). To a stirred 0 °C solution of **8** (194 mg, 1.00 mmol) in THF (2 mL) were added sequentially *n*-BuLi (420 μL, 2.50 M in hexanes, 1.05 mmol) and TMSCl (253 μL, 2.00 mmol) under Ar. After 14 h, the solution was diluted with hexanes (ca. 5 mL) and filtered through a pad of silica gel. Concentration of the filtrate under reduced pressure gave **10** (267 mg, 1.00 mmol, ca. 100% yield) as a colorless oil: IR (neat) 2175, 1248 cm^{-1}; ^{1}H NMR (300 MHz, $E/Z \approx$ 1:1): δ 5.16 (m, 1H), 2.17 (m, 2H), 2.06 (m, 2H), 1.64 and

1.52 (s, 3H), 1.56 (m, 2H), 1.38 (m, 2H), 0.12 (bs, 9H), −0.03 (bs, 9H); HRMS calcd for $C_{15}H_{30}Si_2$ (M^+) 266.1886, found 266.1885.

1-((*tert*-Butyldimethylsilyl)oxy)propan-2-one (11a). To a stirred 0 °C solution of acetol (7.40 g, 100 mmol) in CH_2Cl_2 (200 mL) were added sequentially TBSCl (16.6 g, 110 mmol), imidazole (13.6 g, 200 mmol), and DMAP (122 mg, 1 mmol). After 1 h, saturated aqueous NH_4Cl was added and the mixture was extracted with CH_2Cl_2. The combined organic extract was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (170 g of silica gel, hexanes−ethyl acetate, 10:1, v/v) gave **11a** (11.76 g, 62.0 mmol, 62% yield) as an oil: IR (neat): 1734, 1717 cm^{-1}; ^1H NMR (500 MHz) δ 4.13 (s, 2H), 2.15 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz) δ 209.2, 69.5, 25.9, 25.6 (3C), 18.2, −5.4 (2C); HRMS calcd for $C_9H_{21}O_2Si$ $(M + H)^+$ 189.1310, found 189.1318.

(*Z*)-2-Methyl-4-(trimethylsilyl)-2-buten-1-ol (11b). To a stirred 0 °C suspension of methyltriphenylphosphonium bromide (14.28 g, 40.0 mmol) in THF (100 mL) was added *n*-BuLi (17.2 mL, 2.50 M in hexanes, 43.1 mmol) under Ar. The resulting dark red solution was allowed to warm to rt and stir for 1 h. A mixture of NaI (12.0 g, 40.0 mmol) and (chloromethyl)trimethylsilane (5.60 mL, 40.0 mmol) in THF (10 mL) was heated under reflux for 1 h and then cooled to rt before the above solution was added via cannula. The resulting mixture was stirred at rt for 14 h under Ar and then cooled to 0 °C before *n*-BuLi (17.2 mL, 2.50 M in hexanes, 40.0 mmol) was added.[8] After being stirred for 30 min, the mixture was cooled to −78 °C and a solution of **11a** (6.58 g, 35.0 mmol) in THF (100 mL) was added slowly. The resulting mixture was allowed to warm to rt and stir over 14 h. Saturated aqueous NH_4Cl was added, the mixture was extracted with hexanes, and the combined organic extract was washed with a saturated aqueous NaCl solution, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was dissolved in methanol (100 mL), and 12 M aqueous HCl (0.5 mL) was added. After 10 min of stirring, solid $NaHCO_3$ (ca. 5 g) was added, and the resulting mixture was filtered and concentrated. Silica gel column chromatography (hexanes−ethyl acetate, 5:1, v/v) of the residue gave **11b** (3.70 g, 23.4 mmol, 67% yield) as a pale yellow oil: IR (neat) 3332, 1653, 1248 cm^{-1}; ^1H NMR (300 MHz) δ 5.30 (t, J = 9.0 Hz, 1H), 4.06 (s, 2H), 1.77 (s, 3H), 1.44 (d, J = 9.0 Hz, 2H), −0.03 (s, 9H); NOE (500 MHz) irradiation of the C2-H methylene protons resonance at δ 4.06 gave a 2.1% enhancement of the C2-H methylene protons resonance at δ 1.44; ^{13}C NMR (75 MHz) δ 131.6, 124.3, 61.3, 21.2, 18.6, −1.8; HRMS calcd for $C_8H_{18}OSi$ (M^+) 158.1127, found 158.1127.

(*Z*)-2-Methyl-4-(trimethylsilyl)-2-butenyl 2-Propynyl Ether (11). To a stirred 0 °C solution of **11b** (1.15 g, 7.28 mmol) in THF (20 mL) were added sequentially NaH (239 mg, 9.46 mmol) and tetra-*n*-butylammonium iodide (37 mg, 0.10 mmol) under Ar. After 1 h, propargyl bromide (1.45 mL, 80% solution in toluene, 13.1 mmol) was added and the mixture was allowed to warm to rt and stir for 14 h. Hexanes (ca. 30 mL) was added, and the suspension was filtered through a pad of silica gel. Concentration of the filtrate and silica gel column chromatography (hexanes−ethyl acetate, 10:1, v/v) of the residue gave **11** (1.08 g, 5.51 mmol, 76% yield) as a pale yellow oil: IR (neat) 3310, 2119, 1248 cm^{-1}; ^1H NMR (300 MHz) δ 5.43 (t, J = 9.0 Hz, 1H), 4.08 (d, J = 2.1 Hz, 2H), 4.02 (s, 2H), 2.41 (t, J = 2.1 Hz, 1H), 1.74 (s, 3H), 1.50 (d, J = 9.0 Hz, 2H), −0.00 (s, 9H); ^{13}C NMR (75 MHz) δ 128.4, 126.4, 80.2, 74.0, 67.7, 56.5, 21.6, 18.7, −1.8; HRMS calcd for $C_{11}H_{20}OSi$ (M^+) 196.1283, found 196.1287.

(*Z*)-2-Methyl-4-(trimethylsilyl)-2-butenyl 2-*n*-Butynyl Ether (12). To a stirred 0 °C solution of **11** (589 mg, 3.00 mmol) in THF (10 mL) were added sequentially *n*-BuLi (1.26 mL, 2.5 M in hexanes, ca. 3.2 mmol) and methyl iodide (0.374 mL, 6.00 mmol) under Ar. After 14 h, hexanes (ca. 15 mL) was added and the suspension was filtered through a pad of silica gel. Concentration of the filtrate and silica gel column chromatography (hexanes−ethyl acetate, 10:1, v/v) of the reside gave **12** (631 mg, 3.00 mmol, 100% yield) as a pale yellow oil: IR (neat) 1659, 1451, 1247 cm^{-1}; ^1H NMR (300 MHz) δ 5.38 (t, J = 9.0 Hz, 1H), 4.00 (q, J = 2.1 Hz, 2H), 3.96 (s, 2H), 1.83 (t, J = 2.1 Hz, 3H), 1.71 (s, 3H), 1.48 (d, J = 9.0 Hz, 2H), −0.03 (s, 9H); ^{13}C NMR (75 MHz) δ 128.9, 125.9, 81.9, 75.6, 67.6, 57.1, 21.6, 18.7, 3.5, −1.8; HRMS calcd for $C_{12}H_{22}OSi$ (M^+) 210.1439, found 210.1434.

Vinyl Mercurial 13. To a stirred rt solution of **5** (87 mg, 482 μmol) and HMDS (20 μL, 96 μmol) in CH_2Cl_2 (2 mL) was added $HgCl_2$ (144 mg, 530 μmol). After 14 h, the reaction mixture was concentrated and the residue subjected to preparative silica gel TLC (hexanes−ethyl acetate, 5:1) to give **13** (109 mg, 318 μmol, 65% yield) as a colorless gum: IR ($CDCl_3$) 1640, 1636, 1449, 1248, 905 cm^{-1}; ^1H NMR (300 MHz) δ 5.69 (m, 1H), 5.64 (m, 1H), 5.05 (ddd, J = 10.8, 1.8, 0.6 Hz, 1H), 5.04 (ddd, J = 16.2, 1.8, 0.9 Hz, 1H), 3.14 (m, 1H), 2.54 (m, 2H), 2.00 (m, 1H), 1.80 (m, 1H), 1.60 (m, 2H); ^{13}C NMR (125 MHz) δ 164.5, 140.0, 125.4, 115.5, 51.6, 37.5, 34.5, 24.3; HRMS calcd for C_8H_{11}-HgCl (M^+) 344.0255, found 344.0258.

Vinyl Mercurial 14. To a stirred rt solution of **6** (194 mg, 1.00 mmol) and HMDS (42 μL, 0.20 mmol) in CH_2Cl_2 (3 mL) was added $HgCl_2$ (299 mg, 1.10 mmol). After 18 h, the reaction mixture was concentrated and the residue purified by silica gel column chromatography (hexanes−ethyl acetate, 5:1, v/v) to give **14** (ca. 129 mg, 360 μmol, ca. 36% yield) and partially characterized mercuric salt−alkyne adducts (ca. 147 mg) as a colorless gum: IR ($CDCl_3$) 1649, 1635, 1447, 1248, 901 cm^{-1}; ^1H NMR (300 MHz) δ 5.95 (m, 1H), 5.40 (m, 1H), 5.13 (d, J = 17.0 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 2.97 (m, 1H), 2.48 (m, 2H), 2.45-1.48 (m, 6H); HRMS calcd for $C_9H_{13}HgCl$ $(M + H)^+$ 359.0490, found 359.0491.

[(*E*)-(2-Methyl-2-vinylcyclopentylidene)methyl]-mercuric Chloride (16*E*). Treatment of **7** (97 mg, 0.50 mmol) with $HgCl_2$ (150 mg, 550 μmol) and HMDS (21 μL, 0.10 mmol) in CH_2Cl_2 (2 mL) and isolation as described for **13** above gave **16*E*** (100 mg, 280 μmol, 56% yield) as a colorless gum: IR ($CDCl_3$) 1631, 1613, 1455, 905 cm^{-1}; ^1H NMR (500 MHz) δ 5.80 (dd, J = 17.0, 10.5 Hz, 1H), 5.66 (t, J = 2.5 Hz, 1H), 5.00 (dd, J = 17.0, 1.0 Hz, 1H), 4.98 (dd, J = 10.5, 1.0 Hz, 1H), 2.61 (dt, J = 2.5, 7.5 Hz, 2H), 1.81 (m, 1H), 1.70 (m, 2H), 1.62 (m, 1H), 1.17 (s, 3H); NOE (500 MHz) irradiation of the (allylic methyl) ^1H resonance at δ 1.17 gave a 2.5% NOE enhancement of the (*syn* vinyl) ^1H resonance at δ 5.66; ^{13}C NMR (125 MHz) δ 168.1, 145.7, 125.0, 111.6, 51.3, 41.3, 37.7, 25.6, 22.1; HRMS calcd for $C_9H_{13}HgCl$ (M^+) 358.0412, found 358.0388.

[(*E*)-1-(2-Methyl-2-vinylcyclopentylidene)-1-ethyl]mercuric Chloride (17*E*). Treatment of **8** (104 mg, 500 μmol) with $HgCl_2$ (150 mg, 550 μmol) and HMDS (21 μL, 0.10 mmol) in CH_2Cl_2 (2 mL) for 19 h and isolation as described for **13** above gave **17*E*** (74 mg, 0.20 mmol, 40% yield) and uncharacterized alkyne addition products (18 mg, 38 μmol) as a colorless gum: IR ($CDCl_3$) 1632, 1615, 1247, 902 cm^{-1}; ^1H NMR (500 MHz) δ 5.88 (dd, J = 17.0, 10.5 Hz, 1H), 5.01 (dd, J = 17.0, 1.5 Hz, 1H), 4.98 (dd, J = 10.5, 1.5 Hz, 1H), 2.57 (m, 2H), 2.00 (t, J = 2.0 Hz, 3H), 1.78-1.62 (m, 4H), 1.27 (s, 3H); NOE (500 MHz) irradiation of the (allylic methyl) ^1H resonance at δ 1.27 gave a 1.8% NOE enhancement of the (*syn* vinyl methyl) ^1H resonance at δ 2.00; HRMS calcd for $C_{10}H_{15}HgCl$ (M^+) 372.0569, found 372.0574.

[(*Z*)-(2-Methyl-2-vinylcyclopentylidene)(trimethylsilyl)methyl]mercuric Chloride (18*Z*). Treatment of **10** (95 mg, 0.36 mmol) with $HgCl_2$ (107 mg, 392 μmol) and HMDS (15 μL, 71 μmol) in CH_2Cl_2 (2 mL) for 45 h and isolation as described for **13** above gave **18*Z*** (78 mg, 0.18 mmol, 50% yield) as a colorless gum: IR ($CDCl_3$) 1628, 1574, 1250 cm^{-1}; ^1H NMR (500 MHz) δ 5.68 (dd, J = 17.0, 10.5 Hz, 1H), 5.34 (d, J = 10.5 Hz, 1H), 5.27 (d, J = 17.0 Hz, 1H), 2.72 (m, 1H), 2.55 (m, 1H), 1.84-1.61 (m, 4H), 1.11 (s, 3H), 0.15 (s, 9H); NOE (500 MHz) irradiation of the (TMS) ^1H resonance at δ 0.15 gave a 2.3% NOE enhancement of the allylic methylene ^1H resonances at δ 2.72 and 2.55; ^{13}C NMR (125 MHz) δ 175.5, 148.1, 140.1, 118.0, 52.6, 40.4, 35.2, 24.4, 23.2, 1.29; HRMS calcd for $C_{12}H_{21}SiHgCl$: 430.0807, found 430.0806.

[(*E*)-(4-Methyl-4-vinyl-3-furylidene)methyl]mercuric Chloride (19). Treatment of **11** (196 mg, 1.00 mmol) with $HgCl_2$ (299 mg, 1.10 mmol) and HMDS (42 μL, 0.20 mmol) in CH_2Cl_2 (2 mL) and isolation as described for **13** above gave **19** (173 mg, 482 μmol, 48% yield) as a colorless gum: IR ($CDCl_3$) 1653, 1558, 905 cm^{-1}; ^1H NMR (500 MHz) δ 5.87 (dd, J = 2.5, 2.5 Hz, 1H), 5.82 (dd, J = 17.0, 10.5 Hz, 1H), 5.16 (d, J = 17.0 Hz, 1H), 5.13 (d, J = 10.5 Hz, 1H), 4.53 (dd, J = 13.5, 2.5 Hz, 1H), 4.48 (dd, J = 13.5, 2.5 Hz, 1H), 3.84 (d, J = 8.5 Hz, 1H), 3.70 (d, J = 8.5 Hz, 1H), 1.26 (s, 3H); NOE (500 MHz) irradiation

of the (allylic methyl) ^{1}H resonance at δ 1.26 gave a 2.1% NOE enhancement of the (vinyl) ^{1}H resonance at δ 5.87; ^{13}C NMR (125 MHz) δ 164.5, 141.4, 123.0, 114.1, 80.4, 73.6, 51.6, 22.4; HRMS calcd for $C_8H_{11}OHgCl$ 359.0201, found 359.0194.

[(*E*)-1-(4-Methyl-4-vinyl-3-furylidene)-1-ethyl]mercuric Chloride (20). Treatment of **12** (210 mg, 1.00 mmol) with $HgCl_2$ (299 mg, 1.10 mmol) and HMDS (42 μL, 0.20 mmol) in CH_2Cl_2 (5 mL) for 15 h and isolation as described for **13** above gave **20** (153 mg, 410 μmol, 41% yield) as a colorless gum: IR ($CDCl_3$) 1625, 905 cm^{-1}; ^{1}H NMR (500 MHz) δ 5.83 (dd, J = 17.0, 10.5 Hz, 1H), 5.16 (d, J = 10.5 Hz, 1H), 5.10 (d, J = 17.0 Hz, 1H), 4.26 (m, 2H), 3.54 (d, J = 11.0 Hz, 1H), 3.39 (d, J = 11.0 Hz, 1H), 1.84 (m, 3H), 1.15 (s, 3H); NOE (500 MHz) irradiation of the (vinyl methyl) ^{1}H resonance at δ 1.84 gave a 2.0% NOE enhancement of the (allylic methyl) ^{1}H resonance at δ 1.15; ^{13}C NMR (125 MHz) δ 144.3, 143.4, 141.7, 114.7, 74.1, 70.7, 44.8, 23.9, 20.0; HRMS calcd for $C_9H_{14}OHgCl$ $[M + H]^+$ 375.0430, found 375.0393.

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Supporting Information Available: ^{1}H NMR spectra for compounds **5**−**11a**, **11b**, **11**−**14**, **16*E***, and **18*Z***−**20** and ^{13}C NMR spectra for compounds **5**−**7**, **11a**, **11b**, **11**−**13**, **16**, **18**, and **19** (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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