K_2CO_3 (35 mg, 0.25 mmol), and MeOH (1.5 mL) was stirred for 19 h. The product was isolated in the usual way and chromatographed (SiO_2, 1.5 g, 100–200 mesh, toluene–acetone) to give aldehyde 4 (34 mg, 85%) as colorless oil: $[\alpha]^{19}_D$ +3.5° (c 2.14). NMR spectra of this product are identical with those of 2.

(2*R*,3*R*)-2,3-*O*-Isopropylidene-4-*O*-(triphenylmethyl)-erythrose (3). A solution of thioacetal 17 (152 mg, 0.274 mmol) in CH_2Cl_2 (2 mL) was treated with DIBALH (1 M in hexane, 0.9 mL) at −78 °C for 1 h. Workup and chromatography of the crude product (SiO_2, 2 g, toluene) gave aldehyde 3 (74 mg, 67%): mp 120–122 °C (acetone–hexane); $[\alpha]^{19}_D$ +87.5° (c 2.08). The NMR spectra of this product are identical with those of 1.

(2*R*,3*R*)-1,1-Bis(phenylthio)butane-2,3,4-triol Triacetate (18). (a) From D-(−)-Erythrose (19). A mixture of D-(−)-erythrose (88 mg), benzenethiol (0.5 mL), and concd HCl (0.5 mL) was stirred for 18 h. Solid $CaCO_3$ was added, and the mixture was diluted with MeOH (10 mL) and filtered. The filtrate was evaporated in vacuo. The residue was washed with hexane and dried whereupon it was treated wit pyridine (1 mL), Ac_2O (1 mL), and DMAP (10 mg) for 30 min. Workup and chromatography (SiO_2, 5 g, toluene–acetone) gave the derivative 18 (76 mg) as colorless oil: $[\alpha]^{19}_D$ +58.5° (c 1.91); IR (film) 1755 and 1220 (acetate) cm^{-1}; NMR δ_H 1.93, 2.00, and 2.01 (3 s, 3 each, CH_3), 4.16 (dd, 1, J = 4.8, 12.5 Hz, C_4 Ha), 4.34 (dd, 1, J = 2.7, 12.5 Hz, C_4 Hb), 4.50 (d, 1, J = 3.4, C_1 H), 5.50 (dd, 1, J = 3.4, 7.6 Hz, C_2 H), 5.59 (ddd, 1, J = 2.7, 4.8, 7.6 Hz, C_3 H), 7.2–7.6 (m, 10, arom H); δ_C 20.25, 20.36, 20.46 (Me), 61.3, 61.8 (C_1, C_4), 70.5, 72.4 (C_2, C_3), 128.3, 128.5 (C_p), 129.2 (C_m), 132.8, 133.7 (C_o), 133.8, 134.5 (C_{ipso}), 169.7, 170.7 (CO). Anal. Calcd for $C_{22}H_{24}O_6S_2$ (448.53): C, 58.91; H, 5.39; S, 14.30. Found: C, 59.13; H, 5.47; S, 14.16.

(b) From Compound 3. A mixture of aldehyde 3 (47 mg), benzenethiol (0.25 mL), and concd HCl (0.25 mL) was stirred for 14 h and worked up as described above. The crude product was treated with pyridine (0.2 mL), Ac_2O (0.2 mL), and DMAP (3 mg) for 2 h. Workup and chromatography (SiO_2, 1 g) of the crude product gave acetal 18 (40 mg, 76%) as colorless oil: $[\alpha]^{19}_D$ + 63.1° (c 2.06), showing the same spectral properties as the product described under a.

Reactions of Carbonyl Compounds with [(Trimethylsilyl)propargyl]diisobutyltelluronium Bromide Mediated by Different Strong Bases: Highly Regioselective Synthesis of (Trimethylsilyl)propargyl Alcohol and Highly Stereoselective Synthesis of *cis*-(Trimethylsilyl)alkynyl Epoxides†

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[(Trimethylsilyl)propargyl)]diisobutyltelluronium bromide (1), after being treated with alkyl- or aryllithium reagent, undergoes a lithium–tellurium exchange reaction via an unstable transient tetraorganyltellurium intermediate, and the in situ generated lithium species reacts with carbonyl compounds to give (trimethylsilyl)-propargyl alcohols 2 in high yields with high regioselectivity. However, when the telluronium salt 1 was treated with nonnucleophilic bases such as LDA or lithium 2,2,6,6-tetramethylpiperidide, the moderately stabilized silylated telluronium ylide formed. The silylated telluronium ylide reacted with carbonyl compounds to afford (trimethylsilyl)alkynyl epoxides 11 in good to excellent yields with high cis stereoselectivity.

Recently there has been a remarkable interest in the synthetic application of organotellurium reagents.[1] With the development of sulfonium, sulfoxonium, and selenonium ylides,[2] the application of several stabilized and moderately stabilized telluronium ylides in organic synthesis has been described.[3] In our previous paper, we found that diphenyltelluronium methylide—the first nonstabilized telluronium ylide generated from methyldiphenyltelluronium tetraphenylborate—reacted with aldehydes or ketones to form substituted oxiranes.[4] However, the reactions of trimethyl- and methyldiphenyltelluronium salts (precursors of nonstabilized telluronium ylides) with aromatic aldehydes gave secondary alcohols with the use of alkyl- or aryllithium reagent.[5] Later, we reported that the reactions of carbonyl compounds with benzyldibutyltelluronium bromide (precursor of semistabilized telluronium ylide) and dibutyl(cyanomethyl)-telluronium chloride (precursor of stabilized telluronium ylide) afforded homobenzylic alcohols and β-hydroxy nitriles respectively promoted by alkyl- or aryllithium reagent.[6] However, no report concerning the synthesis and reactions of a silylated telluronium ylide has appeared in the literature. We wish to report herein that reactions of carbonyl compounds with [(trimethylsilyl)propargyl]di-

† This paper is the 100th report on the application of elementoorganic compounds of 15th and 16th groups in organic synthesis. For the 99th report and preliminary communication, see: Zhou, Z. L.; Huang, Y. Z.; Shi, L. L. *J. Chem. Soc., Chem. Commun.* **1992**, 986.

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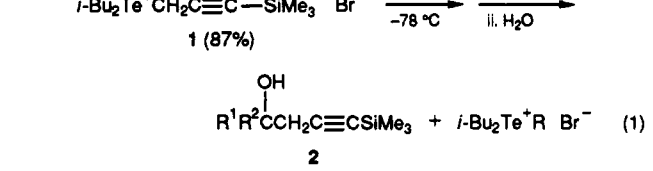
isobutyltelluronium bromide (1) (precursor of silylated telluronium ylide) mediated by lithium 2,2,6,6-tetramethylpiperidide (LiTMP) give *cis*-(trimethylsilyl)alkynyl epoxides in excellent yields, while those mediated by alkyl- or aryllithium reagent afford (trimethylsilyl)propargyl alcohols in high yields.

In the last decade, unsaturated organosilicon compounds have been extensively studied because of their interesting potential in selective organic synthesis.[7] Thus vinyl-[8] and dienylsilanes[9] have received much attention and their synthetic utility has been demonstrated in numerous carbon–carbon bond forming reaction. Alkynyltrimethylsilanes are also an important class of compounds and many useful transformations have been reported.[10]

3-Bromo-1-(trimethylsilyl)-1-propyne could be easily prepared from propargyl alcohol by treatment with 2 equiv of ethylmagnesium bromide and chlorotrimethylsilane, followed by bromination with phosphorus tribromide.[11] It reacted with diisobutyl telluride without solvent at room temperature under nitrogen to give [3-(trimethylsilyl)-2-propynyl]diisobutyltelluronium bromide (1) in 87% yield (eq 1).



Attempts to generate the silylated telluronium ylide by alkyl- or aryllithium reagent, similar to that of corresponding phosphonium and arsonium ylide, failed.[12] It was reported that the reactions of aldehydes and ketones with [3-(trimethylsilyl)-2-propynylidene]triphenylphosphorane and -arsorane, generated in situ from the corresponding phosphonium and arsonium salts, respectively, with *n*-butyllithium, gave terminal trimethylsilyl enynes.[12] However, the telluronium salt 1, after being treated with alkyl- or phenyllithium, reacted with carbonyl compounds to give alcohols, viz. 1-substituted-4-(trimethylsilyl)-3-butyn-1-ols 2 in excellent yields (eq 1), instead of the corresponding alkenes or epoxides, the products expected by analogy with the reactions of other heteroatom ylides.[13]

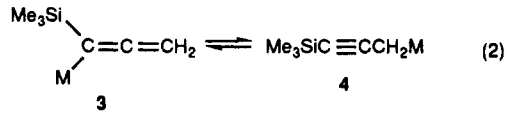
Table I. Highly Regioselective Synthesis of (Trimethylsilyl)propargyl Alcohols 2

entry	R^1	R^2	RLi	product	yield (%)[a]
1	C_6H_5	H	BuLi	**2a**	76
2	*p*-ClC_6H_4	H	BuLi	**2b**	87
3	*p*-ClC_6H_4	H	*t*-BuLi	**2b**	71
4	*p*-ClC_6H_4	H	MeLi	**2b**	85
5	*p*-ClC_6H_4	H	PhLi	**2b**	72
6	*p*-BrC_6H_4	H	BuLi	**2c**	84
7	*p*-FC_6H_4	H	BuLi	**2d**	88
8	*p*-MeC_6H_4	H	BuLi	**2e**	93
9	2-pyridyl	H	BuLi	**2f**	91
10	2-naphthyl	H	BuLi	**2g**	90
11	cyclohexyl	H	BuLi	**2h**	67
12	C_6H_5	CH_3	BuLi	**2i**	79
13	$-(CH_2)_5-$		BuLi	**2j**	80
14	$-(CH_2)_3CH{=}CH-$		BuLi	**2k**	82

[a] Isolated yield based on carbonyl compound.

The preparation of compounds 2 has been performed on a variety of structurally different carbonyl compounds to determine the scope of the reaction. Some experimental results are summarized in Table I and illustrate the efficiency, the applicability, and the scope of the present method. As shown in Table I, the reaction is of wide scope and works well with both enolizable and nonenolizable carbonyl compounds. As for β-monosubstituted α,β-enones, only a 1,2-addition product was isolated and no 1,4-adduct was detected (entry 14).

The importance of the propargylic anions in synthetic chemistry emerged from the recognition of their utility for the extension of the carbon chain and the facility in the interconversion of the functionality.[14] Their applicability in organic synthesis, however, has been limited because of the difficulties in controlling the regio- and stereoselectivities of the reaction. It is often pointed out that the propargylic anion may be in equilibrium with the allenic anion.[15] Thus, in the condensation with carbonyl compounds, two products—acetylenic and allenic alcohols—can be formed. Recently, considerable attention has been paid to the control of the propargyl–allenic equilibrium for practical synthetic purposes. In the specific case of the trimethylsilyl derivatives 3 and 4 (eq 2, M = metal) the



lithium reagent (M = Li) is particularly effective in adding to alkyl and allyl halides,[16] as well as to epoxides,[17] with regiocontrolled formation of propargylic products. However, in condensation with aldehydes it gave both allenic and acetylenic adducts as major products.[18] The derived cuprate (M = Cu) is recognized to enter into conjugate addition with similar results.[19] The Grignard reagent (M = MgX) also reacts in the propargylic form but adds to

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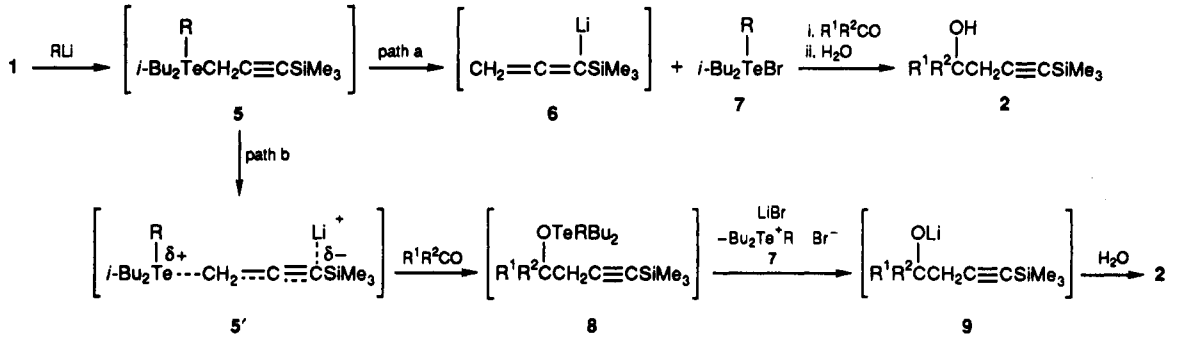
Scheme I



aldehydes and ketones only in low yield.[20] The reactions of titanium[21] and aluminum derivatives[22] (M = Ti, Al) with aldehydes both gave allenic adducts. Although the zinc derivative (M = Zn) reacts with carbonyl compounds in propargylic form, the yield is still limited.[22] Thus, this RLi-promoted, highly regioselective condensation of the telluronium salt 1 with carbonyl compounds is a novel alternative method for the synthesis of (trimethylsilyl)-propargyl alcohols.

It is noteworthy that, in the absence of RLi, the reaction did not take place at all under the same reaction conditions. Various alkyl- and aryllithium reagents such as *n*-BuLi, *t*-BuLi, MeLi, and PhLi could promote the reaction effectively (Table I). Instead of formation of a silylated telluronium ylide, as in the case of phosphonium or arsonium analogs,[12] an unstable tetraorganyltellurium intermediate (5) may be formed, as in the case of Bu_3TeI.[23] In the presence of LiBr, a lithium–tellurium exchange reaction, similar to that of diorganyl telluride, may take place.[24] The in situ generated lithium species 6 reacted with carbonyl compounds to give (trimethylsilyl)propargyl alcohols 2 as shown in Scheme I (path A). Another possibility (path B) has also been considered for this RLi-mediated reaction. The intermediate 5 may be polarized as in 5′ in the presence of Li^+ owing to the weakness of the Te–C bond. The anion formed from the cleavage of the tellurium–carbon bond of intermediate 5′ could then attack the carbonyl compound to form intermediate 8. Reaction of 8 with LiBr could lead to the stable telluronium salt 7 and intermediate 9, and hydrolysis of 9 would give rise to 2.

It is noteworthy that, in the PhLi-promoted reaction of the telluronium salt 1 with *p*-chlorobenzaldehyde, we did isolate the byproduct 7 as a colorless crystal before hydrolysis, viz. phenyldiisobutyltelluronium bromide, which gave satisfactory elemental analysis, ^1H NMR, FAB-MS.

It is of interest that the lithium–tellurium exchange reaction[25] could be avoided effectively by the use of a nonnucleophilic base, such as LDA, instead of the nucleophilic organolithium reagent. The telluronium salt 1, after being treated with LDA in THF at −78 °C under N_2, reacted with *p*-chlorobenzaldehyde to give *cis*-3-(4-chlorophenyl)-2-[(trimethylsilyl)ethynyl]oxirane in 55% yield (eq 3). To our surprise, the result is different from that of the reactions of carbonyl compounds with the corresponding phosphonium and arsonium ylides.[12]

Scheme II

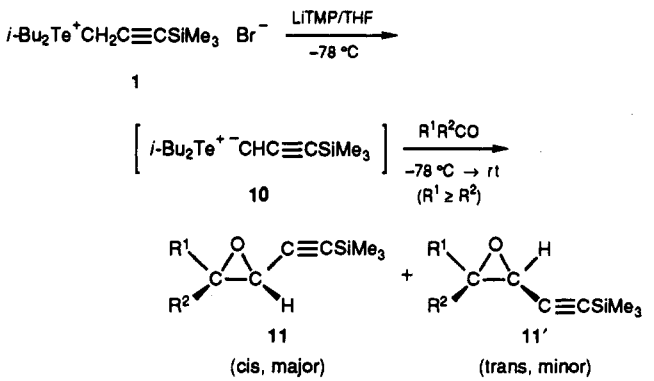
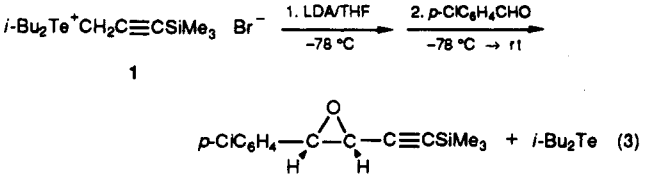


Table II. Highly Stereoselective Synthesis of *cis*-(Trimethylsilyl)alkynyl Epoxides 11

entry	R^1	R^2	product 11	cis/trans[a]	total yield (%)[b]
1	C_6H_5	H	11a	82:18	76
2	*p*-ClC_6H_4	H	11b	98:2	80
3	*p*-BrC_6H_4	H	11c	98:2	80
4	2-naphthyl	H	11d	81:19	95
5	4-PhC_6H_4	H	11e	88:12	95
6	cyclohexyl	H	11f	99:1	86
7	*n*-C_4H_9	H	11g	98:2	83
8	*n*-C_5H_{11}	H	11h	98:2	82
9	*n*-C_9H_{19}	H	11i	97:3	94
10	C_6H_5	CH_3	11j	86:14	96
11	C_6H_5	C_6H_5	11k		80

[a] Determined by 200-MHz ^1H NMR and/or NOE. [b] Isolated yields based on carbonyl compounds.



This significant result prompted us to explore more effective bases for the generation of the silylated telluronium ylide. We found that lithium 2,2,6,6-tetramethylpiperidide,[26] which is less nucleophilic and more basic than

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(25) The actual reactive species would probably be free lithium reagent 6 or polarized lithium reagent 5′ rather than tetraorganyltellurium intermediate 5, because only 1,2-addition to 2-cyclohexen-1-one occurred in the present system, quite similar to that in a ($CH_2C{\equiv}C$-TIPS)Li/THF system.[18] Furthermore, the reaction works well with acetophenone, which also indicates that the reactive species may be 5′ and/or 6.
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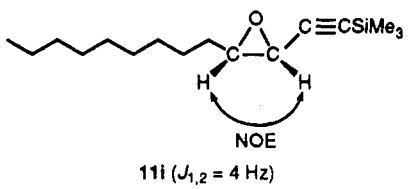
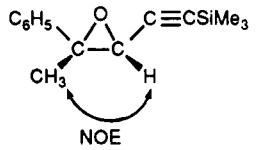
Scheme III

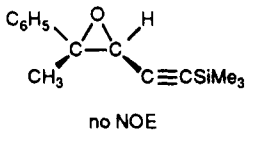


11i ($J_{1,2}$ = 4 Hz)

Scheme IV



11j (*cis*)



11j' (trans)

LDA, is more suitable for generating the silylated telluronium ylide **10**. Ylide **10** reacted with carbonyl compounds to afford (trimethylsilyl)alkynyl epoxides **11** in good yields with high cis stereoselectivity (Scheme II).

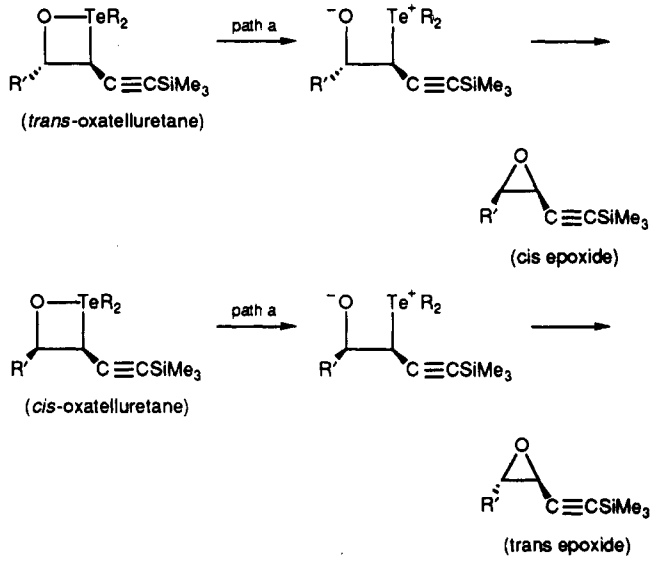
The results are shown in Table II.

As shown in Table II, we can see that this new method for the direct propargyl transfer to carbonyl compounds is of wide scope and occurs with high cis stereoselectivity. The reaction works well with both enolizable and nonenolizable carbonyl compounds, including aromatic aldehydes, aliphatic aldehydes, and ketones. The *cis*-oxirane was generally characterized by a coupling constant between the vicinal oxirane hydrogens of about 4 Hz observed in the ^{1}H NMR spectrum.[27] On the other hand, the *trans*-oxirane was characterized by a coupling constant of about 2 Hz.[27] To support this conclusion, we measured the NOEs of oxirane **11i** as shown in Scheme III. For irradiation of 1-H, the NOE of 2-H is 8.20; while when 2-H was irradiated, the NOE of 1-H is 10.00.

The configurations of oxiranes **11j** and **11j'** were determined by the NOE technique as shown in Scheme IV. For isomer **11j**: irradiation of 2-H resulted in an NOE of 5.72 for the methyl protons. When the methyl hydrogens were irradiated, the NOE of 2-H was 5.80; thus isomer **11j** must be cis. On the other hand, no NOE was observed for isomer **11j'**, so the configuration of **11j'** would be trans.

The mechanism illustrated in Scheme V would account for our results described above. We presume that the reaction proceeds via oxatelluretane similar to that of arsonium ylides.[28] It might be anticipated that *cis*-oxatelluretane is destabilized relative to *trans*-oxatelluretane due to the steric interaction between the (trimethylsilyl)ethynyl and R′ groups. *trans*-Oxatelluretane opens to the corresponding betaine through catalysis by the lithium salt present under the reaction conditions,[29] which collapses to the cis epoxide product (pathway a). The *cis*-oxatelluretane in the presence of lithium salt can open to the corresponding betaine, which subsequently collapses to trans epoxide products (pathway b). Apparently, the high cis stereoselectivity observed for the epoxide formation suggests that process a is highly favored over process b.

Scheme V[a]



[a] R = i-Bu$_2$.

cis-(Trimethylsilyl)alkynyl epoxides reported herein are expected to be useful in organic synthesis due to their novel structure and several functional groups. The epoxides can be reduced to cis terminal enynes,[30] which have attracted much attention due to their biological properties.[31] Furthermore, the epoxide ring can also be opened regiospecifically by nucleophilic reagent to yield potentially useful β-substituted alcohols.[32]

In summary, a novel method for direct synthesis of cis trimethylsilylalkynyl epoxides from carbonyl compounds has been described by the use of the silylated semistabilized telluronium ylide. However, the telluronium salt **1**, after being treated with alkyl- or aryllithium reagent, reacted with carbonyl compounds to give (trimethylsilyl)-propargyl alcohols in high yields with high regioselectivity.

It is expected that the above-described reaction will find considerable application to the synthesis of acyclic molecules having adjacent chiral centers. Further work in this area is now in progress in our laboratory.

Experimental Section

All reactions were carried out under N_2. THF was distilled from sodium and benzophenone under N_2. The NOEs were measured at 400 MHz. MS data were obtained with electron ionization.

Diisobutyl telluride[33] and LiTMP[26] were prepared according to the reported methods.

Synthesis of [3-(Trimethylsilyl)-2-propynyl]diisobutyltelluronium Bromide (1). Diisobutyl telluride (50 mmol) was syringed into 3-bromo-1-(trimethylsilyl)-1-propyne under N_2 without solvent. The mixture was stirred for 4 h at rt to afford

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a white crystal. mp 102–104 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 3.58 (s, 2 H), 3.00 (d, J = 7 Hz, 4 H), 2.30 (m, 2 H), 2.04 (d, J = 7.2 Hz, 6 H), 2.02 (d, J = 7.2 Hz, 6 H), 0.10 (s, 9 H); FAB-MS, m/e (rel intensity) 355 (C^+, ^{130}Te, 100), 353 (C^+, ^{128}Te, 93), 351 (C^+, ^{126}Te, 58), 298 (i-BuTe$^+$$CH_2C{\equiv}CSiMe_3$, ^{130}Te, 1), 296 (^{128}Te, 1), 294 (^{126}Te, 1), 244 (i-Bu_2Te^+, ^{130}Te, 4), 242 (^{128}Te, 4), 240 (^{126}Te, 3), 187 (i-BuTe$^+$, ^{130}Te, 3), 185 (^{128}Te, 3), 183 (^{126}Te, 3), 111 ($CH_2C{\equiv}CSiMe_3^+$, 3), 57 (28), 789 ([M + C]$^+$, ^{130}Te, 0.8), 787 (^{128}Te, 1.0), 785 (^{126}Te, 0.6); IR (KCl) 2950 (s), 2150 (s), 1380 (s), 1360 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{29}BrSiTe$: C, 38.84; H, 6.75; Br, 18.45. Found: C, 38.50; H, 6.77; Br, 18.52.

Highly Regioselective Synthesis of (Trimethylsilyl)propargyl Alcohols 2. The synthesis of 1-(4-chlorophenyl)-4-trimethyl-3-butyn-1-ol (**2b**) is a typical procedure. A solution of BuLi (0.6 mL, 1.5 mmol) in hexane was syringed into a solution of the telluronium salt **1** (0.65 g, 1.5 mmol) in dry THF (10 mL) at −78 °C under N_2. After 30 min, a solution of p-chlorobenzaldehyde (168.6 mg, 1.2 mmol) in THF (2 mL) was added dropwise at −78 °C, and the reaction mixture was allowed to warm to rt. After the reaction was complete (monitored by TLC), 1 mL of H_2O was added to the mixture, and the solution was stirred for another 1 h. The mixture was then extracted with ether (5 mL × 3). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. After flash chromatography on a silica gel column, **1-(4-chlorophenyl)-4-(trimethylsilyl)-3-butyn-1-ol (2b**, 265 mg) was obtained in 87% yield (GC shows >98% purity).

1-Phenyl-4-(trimethylsilyl)-3-butyn-1-ol (2a): 200 mg, 76%; pale yellow liquid;[34] ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.13 (s, 5 H), 4.60 (t, J = 6 Hz, 1 H), 3.05 (br s, OH), 2.42 (d, J = 6 Hz, 2 H), 0.03 (s, 9 H); EIMS m/z (rel intensity) 200 (M$^+$ − H_2O, 3), 185 (8), 179 (18), 107 (M$^+$ − $CH_2C{\equiv}C$ $SiMe_3$, 100), 85 (27), 73 (20); IR (neat) 3450 (vs), 2980 (m), 2200 (m) cm^{-1}.

1-(4-Chlorophenyl)-4-(trimethylsilyl)-3-butyn-1-ol (2b): 265 mg, 87% (BuLi); 215 mg, 71% (*t*-BuLi); 258 mg, 85% (MeLi); 218 mg, 71% (PhLi); colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.17 (s, 4 H), 4.62 (t, J = 7 Hz, 1 H), 2.89 (br s, OH), 2.44 (d, J = 7 Hz, 2 H), 0.06 (s, 9 H); EIMS m/z (rel intensity) 235 (M$^+$ − OH, 2), 213 (16), 141 (85), 112 (21), 97 (10), 73 (100); IR (neat) 3400 (vs), 2980 (m), 2190 (m) cm^{-1}. Anal. Calcd for $C_{13}H_{17}ClOSi$: C, 61.76; H, 6.78; Cl, 14.02. Found: C, 62.01; H, 6.90; Cl, 13.72.

1-(4-Bromophenyl)-4-(trimethylsilyl)-3-butyn-1-ol (2c): 303 mg, 85%; colorless liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.11 (m, 4 H), 4.47 (t, J = 6 Hz, 1 H), 3.58 (br s, OH), 2.35 (d, J = 6 Hz, 2 H), 0.0 (s, 9 H); EIMS m/e (rel intensity) 281 (M$^+$ − OH, ^{81}Br, 1), 279 (M$^+$ − OH, ^{79}Br, 1), 265 (3), 263 (3), 259 (20), 257 (21), 187 (24), 185 (100), 159 (9), 157 (10), 73 (87); IR (neat) 3350 (vs), 2950 (m), 2180 (w) cm^{-1}. Anal. Calcd for $C_{13}H_{17}BrOSi$: C, 52.53; H, 5.76; Br, 26.88. Found: C, 52.22; H, 5.78; Br, 26.88.

1-(4-Fluorophenyl)-4-(trimethylsilyl)-3-butyn-1-ol (2d): 250 mg, 88%; pale yellow liuqid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.34 (m, 4 H), 4.94 (t, J = 6 Hz, 1 H), 2.74 (d, J = 6 Hz, 2 H), 2.64 (br s, OH), 0.24 (s, 9 H); EIMS m/z (rel intensity) 235 (M$^+$ − 1, 1), 218 (M$^+$ − OH_2, 1), 197 (21), 125 (M$^+$ − $CH_2{\equiv}CSiMe_3$, 100), 112 (18), 97 (45), 73 (99); IR (neat) 3400 (vs), 2980 (s), 2200 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{17}FOSi$: C, 66.06; H, 7.25. Found: C, 65.56; H, 7.32.

1-(4-Methylphenyl)-4-(trimethylsilyl)-3-butyn-1-ol (2e): 260 mg, 93%; pale yellow liquid; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.17 (s, 4 H), 4.77 (t, J = 6 Hz, 2 H), 2.59 (d, J = 6 Hz, 2 H), 2.44 (br s, OH), 2.29 (s, 3 H), 0.13 (s, 9 H); EIMS m/z (rel intensity) 231 (M$^+$ − 1, 1), 214 (M$^+$ − OH_2, 1), 193 (8), 121 (M$^+$ − $CH_2C{\equiv}CSiMe_3$, 100), 105 (10), 93 (24), 73 (51); IR (neat) 3450 (vs), 2950 (m), 2180 (m) cm^{-1}. Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67; Found: C, 71.98; H, 8.69.

1-(2-Pyridyl)-4-(trimethylsilyl)-3-butyn-1-ol (2f): 240 mg, 91%; pale yellow liquid; ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.30 (m, 1 H), 7.40 (m, 3 H), 4.65 (t, J = 6 Hz, 1 H), 4.60 (br s, OH), 2.53 (d, J = 6 Hz, 2 H), 0.03 (s, 9 H); EIMS m/z (rel intensity) 220 (M$^+$ + 1, 100), 218 (M$^+$ − 1, 20), 204 (20), 166 (15), 108 (M$^+$ − $CH_2C{\equiv}CSiMe_3$, 19), 73 (6); IR (neat) 3300 (vs), 2950 (m), 2150 (m) cm^{-1}. Anal. Calcd for $C_{12}H_{17}NOSi$: C, 65.71; H, 7.81; N, 6.39. Found: C, 65.65; H, 7.80; N, 6.37.

1-(2-Naphthyl)-4-(trimethylsilyl)-3-butyn-1-ol (2g): 290 mg, 90%; colorless liquid; ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.80 (m, 4 H), 7.50 (m, 3 H), 5.02 (t, J = 6 Hz, 1 H), 2.86 (d, J = 6 Hz, 2 H), 2.50 (br s, OH), 0.13 (s, 9 H); EIMS m/z (rel intensity) 268 (M$^+$, 2), 267 (M$^+$ − 1, 1), 251 (M$^+$ − OH, 61), 229 (13), 157 (M$^+$ − $CH_2C{\equiv}CSiMe_3$, 100), 129 (76), 73 (95); IR (neat) 3350 (vs), 3010 (m), 2950 (m), 2180 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.77; H, 7.53.

1-Cyclohexyl-4-(trimethylsilyl)-3-butyn-1-ol (2h): 180 mg, 67% colorless liquid;[34] ^{1}H NMR (60 MHz, $CDCl_3$) δ 4.00 (m, 1 H), 2.43 (br s, 1 H, OH), 2.40 (d, J = 6 Hz, 2 H), 1.10–2.10 (m, 11 H), 0.15 (s, 9 H); EIMS m/z (rel intensity) 224 (M$^+$, 3), 207 (M$^+$ − OH, 46), 185 (73), 147 (98), 133 (81), 95 (100), 73 (66); IR (neat) 3400 (vs), 2900 (s), 2850 (m), 2150 (m) cm^{-1}.

1-Methyl-1-phenyl-4-(trimethylsilyl)-3-butyn-1-ol (2i): 210 mg, 79%; colorless liquid;[35] ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.25 (m, 5 H), 2.50 (br s, 1 H, OH), 2.42 (s, 2 H), 1.45 (s, 3 H), 0.03 (s, 9 H); IR (neat) 3350 (vs), 2090 (s), 2180 (s) cm^{-1}.

1-[(Trimethylsilyl)propargyl]cyclohexan-1-ol (2j): 202 mg, 80%; colorless liquid;[22] ^{1}H NMR (60 MHz, $CDCl_3$) δ 2.45 (s, 2 H), 1.72–3.15 (m, 10 H), 1.70 (br s, 1 H, OH), 0.10 (s, 9 H); IR (neat) 3350 (vs), 2950 (s), 2150 (s), 1250 (s), 840 (s) cm^{-1}.

1-[(Trimethylsilyl)propargyl]-2-cyclohexen-1-ol (2k): 205 mg, 82%; pale yellow liquid; ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.0 (m, 2 H), 2.40 (s, 2 H), 1.75–3.15 (m, 6 H), 1.70 (br s, 1 H, OH), 0.12 (s, 9 H); EIMS m/z (rel intensity) 217 (M$^+$ − 1, 0.14), 191 (M$^+$ − OH, 26), 97 (M$^+$ − $CH_2C{\equiv}CSiMe_3$, 100), 73 ($SiMe_3^{\cdot+}$, 19); IR (neat) 3400 (vs), 2950 (s), 2140 (s), 1250 (s), 840 (s) cm^{-1}.

Phenyldiisobutyltelluronium Bromide (7, R = Ph). This compound was prepared by a similar procedure to the synthesis of **2b** using PhLi. A solution of PhLi (0.6 mL, 0.6 mmol) in ether was syringed into a solution of the telluronium salt **1** (0.26 g, 0.6 mmol) in dry THF (5 mL) at −78 °C under N_2. After 30 min, a solution of p-chlorobenzaldehyde (70 mg, 0.5 mmol) in THF (1 mL) was added dropwise at −78 °C. The reaction mixture was allowed to warm to rt and stirred for another 2 h. THF was removed in vacuo and petroleum ether/ethyl acetate (9:1, 10 mL) was added. The white solid appeared in the bottom of the reaction tube. After filtration and washing of the residue with ether, phenyldiisobutyltelluronium bromide (**7**) (190 mg) was obtained in 79% yield: mp 136–138 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.60 (m, 5 H), 3.80 (dd, J_1 = 11 Hz, J_2 = 7 Hz, 2 H), 3.24 (dd, J_1 = 11 Hz, J_2 = 7 Hz, 2 H), 2.30 (m, 2 H), 1.14 (d, J = 7 Hz, 6 H), 1.02 (d, J = 7 Hz, 6 H); FAB-MS m/z (rel intensity) 321 (C^+, ^{130}Te, 100), 319 (C^+, ^{128}Te, 93), 317 (C^+, ^{126}Te, 59), 264 (i-BuTe$^+$Ph, ^{130}Te, 3), 262 (^{128}Te, 3), 260 (^{126}Te, 3), 187 (i-BuTe$^+$, ^{130}Te, 4), 185 (^{128}Te, 4), 183 (^{126}Te, 2), 721 ([M + C]$^+$, ^{130}Te, 1), 719 (^{128}Te, 2), 717 (^{126}Te, 1); IR (KBr) 3010 (m), 1570 (m), 1425 (m), 1380 (m), 1360 (s), 745 (s), 682 (s) cm^{-1}. Anal. Calcd for $C_{14}H_{23}BrTe$: C, 42.16; H, 5.81; Br, 20.03. Found: C, 41.92; H, 5.70; Br, 20.42.

Highly Stereoselective Synthesis of (Trimethylsilyl)ethynyl Epoxides 11. Typical procedure for the synthesis of 3-phenyl-2-[(trimethylsilyl)ethynyl]oxirane (**11a**). A solution of LiTMP (2 mL, 1.2 mmol) in THF was syringed into a solution of the telluronium salt **1** (0.53 g, 1.2 mmol) in dry THF (8 mL) at −78 °C under N_2. The solution turned red. After 30 min, a solution of benzaldehyde (106 mg, 1.0 mmol) in THF (2 mL) was added dropwise at −78 °C, and the reaction mixture was allowed to warm to rt. After the reaction was completed (monitored by TLC), 1 mL of H_2O was added to the mixture and it was stirred for 30 min more. The mixture was then extracted with ether (5 mL × 3). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. After column chromatography on silica gel (eluting with petroleum ether and 2% triethylamine) gave the desired 3-phenyl-2-[(trimethylsilyl)ethynyl]oxirane (**11a** and **11a'**) (165 mg) in 76% yield (GC shows >98% purity).

3-Phenyl-2-[(trimethylsilyl)ethynyl]oxirane: 165 mg, 76%; **11a** (cis isomer) pale yellow liquid ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ 7.35 (m, 5 H), 4.16 (d, J = 4 Hz, 1 H), 3.77 (d, J = 4 Hz, 1 H), 0.02 (s, 9 H); **11a'** (trans isomer) pale yellow liquid ^{1}H NMR (200 MHz, $(CD_3)_2CO$) δ 7.17 (m, 5 H), 3.88 (d, J = 2 Hz, 1 H), 3.33 (d, J = 2 Hz, 1 H), 0.02 (s, 9 H); mixture of **11a** and **11a'** EIMS

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m/z (rel intensity) 216 (M^+, 10), 201 (17), 185 (10), 141 (22), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 2960 (m), 2160 (m), 1250 (s), 1060 (s), 760 (s) cm^{-1}; HRMS m/z calcd for $C_{13}H_{16}OSi$ 216.0971, found 216.0990.

3-(4-Chlorophenyl)-2-[(trimethylsilyl)ethynyl]oxirane (11b): 200 mg, 80%; pale yellow liquid; ^1H NMR (60 MHz, CCl_4) δ 7.20 (s, 4 H), 3.90 (d, J = 4 Hz, 1 H), 3.50 (d, J = 4 Hz, 1 H), 0.03 (s, 9 H); ^{13}C NMR (90 MHz, $(CD_3)_3CO$/TMS) δ 135.0, 130.1, 129.0, 101.4, 92.8, 59.2, 49.1, 0.5; EIMS m/z (rel intensity) 325 ($M^+ + SiMe_3$, ^{37}Cl, 52), 323 ($M^+ + SiMe_3$, ^{35}Cl, 100), 252 (M^+, ^{37}Cl, 29), 250 (M^+, ^{35}Cl, 66), 235 (47), 215 (33), 141 (23), 73 (60); IR (neat) 2960 (m), 2150 (m), 1250 (s), 840 (s), 760 (s) cm^{-1}; HRMS m/z calcd for $C_{13}H_{15}{}^{35}ClOSi$ 250.0581, found 250.0580; calcd for $C_{13}H_{15}{}^{37}ClOSi$ 252.0551, found 252.0525.

3-(4-Bromophenyl)-2-[(trimethylsilyl)ethynyl]oxirane (11c): 236 mg, 80%; pale yellow liquid; ^1H NMR (200 MHz, C_6D_6) δ 7.28 (d, J = 8 Hz, 2 H), 7.02 (d, J = 8 Hz, 2 H), 3.41 (d, J = 4 Hz, 1 H), 3.28 (d, J = 4 Hz, 1 H), 0.09 (s, 9 H); EIMS m/z (rel intensity) 296 (M^+, ^{81}Br, 17), 294 (M^+, ^{79}Br, 15), 281 (15), 279 (13), 215 (15), 187 (19), 185 (15), 141 (23), 110 (28), 95 (66), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 2950 (m), 2150 (m), 1250 (s), 840 (vs), 770 (s) cm^{-1}; HRMS m/z calcd for $C_{13}H_{15}{}^{79}BrOSi$ 294.0076, found 294.0099; calcd for $C_{13}H_{15}{}^{81}BrOSi$ 296.0174, found 296.0154.

3-(2-Naphthyl)-2-[(trimethylsilyl)ethynyl]oxirane (11d): 253 mg, 95%; **11d** (cis isomer) pale yellow liquid ^1H NMR (200 MHz, C_6D_6) δ 7.3–7.8 (m, 7 H), 3.87 (d, J = 4 Hz, 1 H), 3.56 (d, J = 4 Hz, 1 H), 0.15 (s, 9 H); **11d'** (trans isomer) ^1H NMR (200 MHz, C_6D_6) δ 7.15–7.55 (m, 7 H), 4.06 (d, J = 2 Hz, 1 H), 3.21 (d, J = 2 Hz, 1 H), 0.20 (s, 9 H); EIMS m/z (rel intensity) 267 ($M^+ + 1$, 8), 266 (M^+, 35), 251 (22), 237 (64), 223 (23), 209 (25), 127 (22), 95 (26), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 3050 (m), 2150 (m), 1250 (s), 845 (vs), 810 (s) cm^{-1}; HRMS m/z calcd for $C_{17}H_{18}OSi$ 266.1130, found 266.1120.

3-(4-Biphenylyl)-2-[(trimethylsilyl)ethynyl]oxirane (11e): 297 mg, 95%; **11e** (cis isomer) mp 68–70 °C; ^1H NMR (200 MHz, CD_3COCD_3) δ 7.71 (m, 4 H), 7.50 (m, 5 H), 4.28 (d, J = 4 Hz, 1 H), 3.87 (d, J = 4 Hz, 1 H), 0.08 (s, 9 H); **11e'** (trans isomer) mp 70–72 °C; ^1H NMR (200 MHz, CD_3COCD_3) δ 7.70 (m, 4 H), 7.51 (m, 5 H), 4.14 (d, J = 2 Hz, 1 H), 3.60 (d, J = 2 Hz, 1 H), 0.20 (s, 9 H); EIMS m/z (rel intensity) 293 ($M^+ + 1$, 16), 292 (M^+, 58), 277 (26), 249 (20), 235 (23), 181 (14), 165 (37), 152 (16), 95 (29), 73 ($SiMe_3^{\bullet+}$, 100); IR (KCl) 2950 (s), 2150 (m), 1250 (s), 860 (m), 770 (s) cm^{-1}; HRMS m/z calcd for $C_{19}H_{20}OSi$ 292.1283, found 292.1290.

3-Cyclohexyl-2-[(trimethylsilyl)ethynyl]oxirane (11f): 190 mg, 86%; colorless liquid; ^1H NMR (200 MHz, CD_3COCD_3) δ 3.42 (d, J = 4 Hz, 1 H), 2.76 (dd, J_1 = 8 Hz, J_2 = 4 Hz, 1 H), 1.75 (m, 5 H), 1.25 (m, 6 H), 0.12 (s, 9 H); EIMS m/z (rel intensity) 295 ($M^+ + SiMe_3$, 29), 223 ($M^+ + 1$, 32), 222 (M^+, 11), 207 (30), 183 (58), 133 (99), 95 (66), 81 (100), 73 (60); IR (neat) 2800 (s), 2150 (m), 1250 (s), 845 (vs), 760 (m) cm^{-1}; HRMS m/z calcd for $C_{13}H_{12}OSi$ 222.1526, found 222.1525. Anal. Calcd for $C_{13}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 70.31; H, 9.85.

3-Butyl-2-[(trimethylsilyl)ethynyl]oxirane (11g): 163 mg, 83%; colorless liquid; ^1H NMR (200 MHz, C_6D_6) δ 3.19 (d, J = 4 Hz, 1 H), 2.64 (m, 1 H), 1.70 (m, 2 H), 1.30 (m, 4 H), 0.12 (s, 9 H); EIMS m/z (rel intensity) 197 ($M^+ + 1$, 9), 196 (M^+, 7), 195 ($M^+ - 1$, 9), 181 (50), 110 (42), 95 (70), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 2950 (s), 2150 (m), 1250 (s), 845 (s), 760 (s) cm^{-1}; HRMS calcd for $C_{11}H_{20}OSi$ 196.1284, found 196.1280.

3-Pentyl-2-[(trimethylsilyl)ethynyl]oxirane (11h): 172 mg, 82%; colorless liquid; ^1H NMR (200 MHz, CD_3COCD_3) δ 3.44 (d, J = 4 Hz, 1 H), 3.04 (m, 1 H), 1.3–1.6 (m, 8 H), 0.92 (t, J = 8 Hz, 3 H), 0.20 (s, 9 H); EIMS m/z (rel intensity) 211 ($M^+ + 1$, 2), 209 ($M^+ - 1$, 2), 195 (22), 183 (18), 147 (16), 110 (28), 75 (23), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 2950 (s), 2150 (m), 1250 (s), 845 (s), 760 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found: C, 68.49; H, 10.52.

3-Nonyl-2-[(trimethylsilyl)ethynyl]oxirane (11i): 205 mg, 94%; colorless liquid; ^1H NMR (200 MHz, CD_3COCD_3) δ 3.44 (d, J = 4 Hz, 1 H), 3.03 (m, 1 H), 1.3–1.6 (m, 16 H), 0.9 (t, J = 8 Hz, 3 H), 0.2 (s, 9 H); EIMS m/z (rel intensity) 267 ($M^+ + 1$, 2), 265 ($M^+ - 1$, 1), 251 (7), 193 (6), 110 (14), 95 (35), 73 ($SiMe_3^{\bullet+}$, 100); IR (neat) 2950 (s), 2150 (m), 1250 (s), 840 (s), 760 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.34; H, 11.35. Found: C, 72.11; H, 11.15.

3-Methyl-3-phenyl-2-[(trimethylsilyl)ethynyl]oxirane (11j): 220 mg, 96%: **11j** (cis isomer) colorless liquid ^1H NMR (200 MHz, C_6D_6) δ 7.46 (m, 2 H), 7.16 (m, 3 H), 3.30 (s, 1 H), 1.36 (s, 3 H), 0.05 (s, 9 H); **11j'** (trans isomer) 7.10–7.20 (m, 5 H), 3.24 (s, 1 H), 1.81 (s, 3 H), 0.20 (s, 9 H); EIMS m/z (rel intensity) 231 ($M^+ + 1$, 17), 230 (M^+, 60), 229 ($M^+ - 1$, 30), 215 ($M^+ - CH_3$, 100), 159 (13), 104 (31), 95 (15), 73 (39); IR (film) 3050 (w), 2950 (m), 2160 (m), 1250 (s), 850 (s), 760 (s) cm^{-1}; HRMS m/z calcd for $C_{14}H_{18}OSi$ 230.1127, found 230.1126.

3,3-Diphenyl-2-[(trimethylsilyl)ethynyl]oxirane (11k): 234 mg, 80%; pale yellow liquid; ^1H NMR (90 MHz, CD_3COCD_3) δ 7.30–7.24 (m, 10 H), 3.12 (s, 1 H), 0.03 (s, 9 H); EIMS m/z (rel intensity) 292 (M^+, 100), 277 (29), 165 (36), 105 (55), 73 (8); IR (neat) 3050 (w), 2950 (m), 2150 (m), 1250 (s), 840 (s), 760 (s) cm^{-1}; HRMS m/z calcd for $C_{19}H_{20}OSi$ 292.1260, found 292.1257.

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