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Carbometallation of 1,4-Bis(trimethylsilyl)butadiyne with Trimethylaluminium Using a Bis(cyclopentadienyl)metal Dichloride Catalyst

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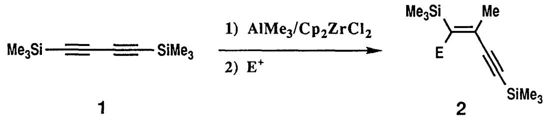
Carbometallation of 1,4-bis(trimethylsilyl)-1,3-butadiyne with trimethylaluminium in the presence of a bis(cyclopentadienyl)zirconium dichloride or bis(cyclopentadienyl)titanium dichloride catalyst afforded (*E*)-2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne selectively after aqueous workup. Treatment of the intermediate organoaluminium compound with an electrophile like D_2O, *N*-bromosuccinimide, *N*-chlorosuccinimide, or acetyl chloride gave the same hydrocarbon possessing D, Br, Cl, or CH_3CO at C-1. The reaction using a bis(cyclopentadienyl)vanadium dichloride catalyst gave rise to (*Z*)-1,2-dimethyl-1,4-bis(trimethylsilyl)-1-buten-3-yne in a single step.

Butadiyne is the smallest hydrocarbon which contains two conjugated carbon–carbon triple bonds. It is produced as a by-product during the transformation of natural gas to acetylene. Due probably to the intrinsically explosive nature, its application to organic synthesis has been limited. In contrast, its disilyl derivative, 1,4-bis(trimethylsilyl)butadiyne (**1**),1) is a crystalline compound thermally stable enough. Sublimation of **1** at 200 °C is easily carried out without any troubles. The compound **1** is readily available by silylation of butadiyne2) or oxidative coupling of trimethylsilylacetylene3,4) and now commercially available. The disilyl diacetylene **1** should be the stable model compound of its mother conjugated diyne. In addition, the two silyl groups of the products may be replaced by various functional groups. At the outset of our study, the disilyl diacetylene **1** had been used widely in organic synthesis as a C_4 building block through a 4-trimethylsilylbutadiynyl anion.5—8) The resulting diyne moiety was easily reduced to an enyne or a diene system.9—18) The Diels–Alder reaction is another type of synthetic use of **1**.19,20) We report herein that the zirconium-catalyzed carbometallation21—24) of **1** with trimethylaluminium allows us to introduce methyl group at C(2) and various electrophiles as well as methyl group at C(1) in a stereoselective manner.25)



(1)

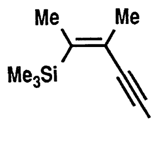
E^+ = H_2O	**2a**	(E = H)	69%	
D_2O	**2b**	(E = D)	60%	
NBS	**2c**	(E = Br)	56%	
NCS	**2d**	(E = Cl)	47%	
AcCl	**2e**	(E = Ac)	44%	(2:1 stereoisomeric mixture)

The reaction conditions reported by Negishi and his coworkers21) were slightly modified and employed for our reaction. Reaction of **1** with trimethylaluminium in the presence of a catalytic amount of bis(cyclopentadienyl)zirconium dichloride and quenching with 1 M (1 M=1 mol dm^{-3}) sodium hydroxide aqueous solution gave (*E*)-2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (**2a**) as an isolable product in 69% yield (Eq. 1). The stereochemistry of **2a** was assigned as such on the basis of ^{13}C NMR and ^{1}H NMR. $^3J(\underline{H}C{=}C\underline{C}H_3)$ observed for **2a** is 12.2 Hz which is typical for (*E*) allylic coupling (cf. (*E*)>10 Hz; (*Z*)<8 Hz).26) Allylic coupling constant $J(\underline{H}C{=}CC\underline{H}_3)=1.1$ Hz also supports the (*E*) configuration (cf. 1.5 Hz for (*E*) and 2 Hz for (*Z*)).27) To determine the regiochemistry of the Me group, **2a** was treated with 57% hydriodic acid28) in benzene-d_6. The disilylated product exhibited olefinic signals at δ=5.00 and 5.35 typical to terminal methylene. Various solvents and a series of catalysts of type Cp_2MtlCl_2 were screened for the reaction, and the results are summarized in Table 1. With 1 equiv of Cp_2ZrCl_2 **2a** was obtained in 66% yield (Run 1). We examined the amount of the catalyst and the reaction temperature and found the best yield 75% was achieved by the reaction with 19 mol% of the Zr-catalyst at 40—50 °C. Large amount of the catalyst at the reflux temperature did not give **2a** (Run 3). Hereby dimethylated product **3** formed which consisted of (*E*) and (*Z*) isomers of 1:2 ratio. When 1.3 mol% of the Zr-catalyst was employed, heating at reflux was needed (Run 4). Of various solvents tested, 1,2-dichloroethane was found to be the best for the carbometallation. In diethyl ether or hexane solvent, the reaction did not proceed at all (Runs 5 and 6). The reaction with trimethylgallium or triethylaluminium in place of trimethylaluminium gave only starting material or a complex mixture of products (Runs 7—10). For the reaction using a titanium catalyst Cp_2TiCl_2, the reaction temperature of dichloromethane reflux was pertinent, and **2a** was obtained in 38% yield (Run 12). At higher temperatures a complex mixture of products resulted (Run 13). Triethylaluminium did not give the corresponding carbometallation product with the titanium catalyst (Runs 14 and 15). Bis(cyclopenta-

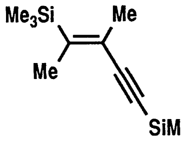
Table 1. Carbometallation of **1**

Run	R_3Mtl	Cp_2MtlCl_2 (mol%)	Solvent	Conditions	Yield/%[a,b] **2a**	Yield/%[a,b] **3**(*E*:*Z*)
1	Me_3Al	Cp_2ZrCl_2 (100)	$ClCH_2CH_2Cl$	R.t. 21 h and then 50 °C 1 h	66	
2	Me_3Al	Cp_2ZrCl_2 (19)	$ClCH_2CH_2Cl$	40—50 °C 10 h	75	
3	Me_3Al	Cp_2ZrCl_2 (20)	$ClCH_2CH_2Cl$	Reflux 20 h	tr	15(1:2)
4	Me_3Al	Cp_2ZrCl_2 (1.3)	$ClCH_2CH_2Cl$	Reflux 10 h	69	
5	Me_3Al	Cp_2ZrCl_2 (4.5)	Et_2O	Reflux 35 h	nr	
6	Me_3Al	Cp_2ZrCl_2 (17)	n-C_6H_{14}	Reflux 12 h	nr	
7	Me_3Ga	Cp_2ZrCl_2 (19)	$ClCH_2CH_2Cl$	40—50 °C 10 h and then reflux 20 h	nr	
8	Et_3Al	Cp_2ZrCl_2 (100)	$ClCH_2CH_2Cl$	0 °C 24 h	c	
9	Et_3Al	Cp_2ZrCl_2 (3.4)	$ClCH_2CH_2Cl$	R.t. 13 h	nr	
10	Et_3Al	Cp_2ZrCl_2 (3.4)	$ClCH_2CH_2Cl$	Reflux 4 h	c	
11	Me_3Al	Cp_2TiCl_2 (100)	CH_2Cl_2	R.t. 14 h	6	3(*Z*)
12	Me_3Al	Cp_2TiCl_2 (19)	CH_2Cl_2	Reflux 18 h	38	
13	Me_3Al	Cp_2TiCl_2 (20)	$ClCH_2CH_2Cl$	Reflux 10 h	c	
14	Et_3Al	Cp_2TiCl_2 (100)	CH_2Cl_2	R.t. 2 h	nr	
15	Et_3Al	Cp_2TiCl_2 (100)	CH_2Cl_2	Reflux 0.5 h	c	
16	Me_3Al	Cp_2VCl_2 (5.7)	$ClCH_2CH_2Cl$	Reflux 19 h		27(*Z*)
17	Me_3Al	Cp_2VCl_2 (13)	$ClCH_2CH_2Cl$	Reflux 10 h		10(*Z*)

a) Isolated yield. Except the runs of nr, the conversions were more than 80%. b) tr: trace; nr: no reaction; c: complex mixture.



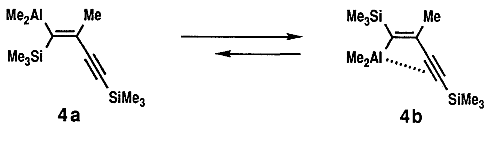
(*Z*)-**3**



(*E*)-**3**

dienyl)vanadium dichloride was found to catalyze the dimethylation to give (*Z*)-**3** (27% yield) instead of **2a** in a single step (Run 16). This type of vicinal dimethylation is unprecedented. Probably, the vanadium catalyst promoted the reductive elimination of an intermediary methyl alkenyl metal species.

The zirconium catalyzed methylation of **1** afforded, as shown in Eq. 1, a trans carbometallation product. The results contrast sharply to the well established stereochemistry of the carbometallation of alkynes using Cp_2ZrCl_2[21] or Cp_2TiCl_2.[22] The unusual stereochemical results may be ascribed to a facile isomerization of an initially produced (*Z*)-alkenylaluminum species **4a** to an (*E*)-isomer **4b** thanks to the intramolecular coordination effect of the acetylenic bond nearby the aluminium metal (Eq. 2). Similar trans stereochemistry is observed often in the carboalumination of 1-silyl-3-alken-1-ynes.[29] In the vanadium catalyzed carbometallation reaction giving the dimethylation product (*Z*)-**3**, the reductive elimination of **4a** should be faster than the configurational isomerization to **4b**.



(2)

The intermediate **4b** was allowed to react with various electrophiles. Quenching **4b** with D_2O, *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), or acetyl chloride (AcCl) afforded the corresponding 1-substituted 2-methyl-1,4-bis(trimethylsilyl)-1-buten-3-yne (**2b**, **2c**, **2d**, or **2e**).

The reaction of **4b** with excess copper(I) chloride at room temperature gave an (*E*)-dimethylated product (*E*)-**3**. Upon the reaction of **4b** with copper(II) chloride a chlorinated product **2d** (43%), the dimethylated derivative (*E*)-**3** (12%), and a trace amount of dimerization product **5** were produced.[30]

$$(E)\text{-}3 \xleftarrow[\text{2) CuCl}]{\text{1) AlCl}_3/\text{Cp}_2\text{ZrCl}_2} 1 \xrightarrow[\text{2) CuCl}_2]{\text{1) AlCl}_3/\text{Cp}_2\text{ZrCl}_2} 2d + (E)\text{-}3 \qquad (3)$$

The 1-substituted 2-methyl-1,4-disilyl-1-buten-3-ynes herein synthesized stereoselectively are expected to be versatile synthetic building blocks for a stereodefined conjugated C_4 homologation.

Experimental

Melting points and boiling points are given in °C and are uncorrected. Bulb-to-bulb distillation was carried out using a Shibata glass tube oven GTO 250R, and boiling points were determined by measurement of the bath temperature and given in °C/Torr (1 Torr=133.322 Pa). ^1H NMR spectra were obtained with a Varian EM-390, a Hitachi R-90, or a Bruker AM-400 spectrometer, chemical shifts being given in ppm units, ^{13}C NMR spectra with a Varian XL-100 or a Bruker AM-400 spectrometer. IR spectra were recorded with a JASCO A-202 machine. MS were recorded with a RMU-6MG spectrometer under 70 eV. High resolution mass spectra were recorded with a Hitachi M-80A spectrometer.

GLC assays were performed with a Shimadzu GC-7A chromatograph equipped with TCD or a Hitachi 163 gas chromatograph using FID, preparative GLC with an Ohkura Model-802T chromatograph equipped with TCD. TLC analyses were performed using Merck silica gel 60 F$_{254}$ glass plates (0.25 mm). Preparative TLC (1.2 mm thick) were prepared from Merck Kiesel-gel PF$_{254}$. The TLC mobility of a given component is described by its R_f value. Column chromatography was carried out with silica gel (Wakogel C-200) at atmospheric pressure.

(*E*)-1,4-Bis(trimethylsilyl)-2-methyl-1-buten-3-yne (2a). To a solution of bis(cyclopentadienyl)zirconium dichloride (2.0 mg, 7×10^{-3} mmol) in 1,2-dichloroethane (1 ml) was added trimethylaluminium (2.0 M hexane solution, 0.83 ml, 1.66 mmol), and the solution was stirred for 0.5 h at room temperature. Then a 1,2-dichloroethane (2 ml) solution of 1,4-bis(trimethylsilyl)butadiyne (**1**) (101 mg, 0.52 mmol) was added, and the mixture was heated to reflux for 10 h. Sodium hydroxide aqueous solution (1 M, 3 ml) was added at 0 °C, and the mixture was filtered through a Celite layer and washed with saturated sodium chloride aqueous solution (20 ml) and extracted with diethyl ether (20 ml). The ethereal extract was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Purification by preparative TLC (hexane, R_f 0.65) gave **2a** 75.5 mg (69% yield) as a colorless oil. Bp 75 °C/0.5 Torr. ^{1}H NMR (CDCl$_3$) δ=0.12 (s, 9 H), 0.17 (s, 9 H), 1.93 (d, J=1.1 Hz, 3 H), 6.05 (q, J=1.1 Hz, 1 H); ^{13}C NMR (CDCl$_3$) δ=−0.4 (q, J=119 Hz, Si$\underline{\mathrm{C}}$H$_3$), 0.0 (q, J=119 Hz, Si$\underline{\mathrm{C}}$H$_3$), 22.5 (dq, J=12.2 and 127 Hz, C(2)-$\underline{\mathrm{C}}$H$_3$), 91.2 (br m, $\underline{\mathrm{C}}$(4)), 109.0 (br m, $\underline{\mathrm{C}}$(3)), 134.0 (br s, $\underline{\mathrm{C}}$(2)), 139.3 (br d, J=134 Hz, $\underline{\mathrm{C}}$(1)); IR (neat) 2960, 2140, 1575, 1305, 1250, 1160, 1000, 850, 760, 700, 640, 550 cm^{-1}; MS m/z (rel intensity) 210 (M$^+$, 18), 196 (12), 195 (58), 156 (18), 155 (100), 137 (12), 163 (12), 97 (12), 73 (38). Found: C, 62.87; H, 10.79%. Calcd for C$_{11}$H$_{22}$Si$_2$: C, 62.78; H, 10.54%.

Protodesilylation of 2a. The butenyne **2a** (53 mg, 0.25 mmol), benzene-d_6 (0.5 ml), and 57% hydriodic acid aqueous solution (33 µl) were sealed in an NMR-tube. After 1 h the mixture showed ^{1}H NMR (C$_6$D$_6$) δ=1.70 (br s, 3 H), 1.90 (br s, 1 H), 5.00 (m, 1 H), 5.35 (m, 1 H).

(*E*)-1,4-Bis(trimethylsilyl)-1-deuterio-2-methyl-1-buten-3-yne (2b). The butadiyne **1** (94.6 mg, 0.49 mmol) was allowed to react with trimethylaluminium (1.5 mmol) under the same conditions as above, and deuterium oxide (0.4 ml) was added at 0 °C. The mixture was stirred for 1.5 h at room temperature and then worked up. Purification by preparative TLC (hexane, R_f 0.65) gave **2b** 61.7 mg (60% yield) as a colorless oil, bp 70 °C/0.4 Torr. ^{1}H NMR (CDCl$_3$) δ=0.13 (s, 9 H), 0.19 (s, 9 H), 1.93 (s, 3 H); IR (neat) 2970, 2150, 1580, 1250, 1230, 840, 760, 695, 670, 635, 550, 510 cm^{-1}; MS m/z (rel intensity) 211 (M$^+$, 15), 196 (55), 156 (18), 155 (100), 73 (43). Found: m/z 211.1307. Calcd for C$_{11}$H$_{21}$DSi$_2$: M, 211.1321.

(*E*)-1,4-Bis(trimethylsilyl)-1-bromo-2-methyl-1-buten-3-yne (2c). The butadiyne **1** (0.79 g, 4.0 mmol) was allowed to react with trimethylaluminium (2 M hexane solution, 8 ml, 16 mmol) and Cp$_2$ZrCl$_2$ (39.5 mg, 0.13 mmol) in 1,2-dichloroethane (13 ml). *N*-Bromosuccinimide (3.2 g, 17 mmol) was added to the reaction mixture at −40 °C. The mixture was stirred at 0 °C for 0.5 h, and worked up. Purification by column chromatography (hexane, R_f 0.65) gave **2c** 0.66 g (56% yield) as a colorless oil, bp 100 °C/0.5 Torr. ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 9 H), 0.28 (s, 9 H), 1.98 (s, 3 H); ^{13}C NMR (CDCl$_3$) δ=−0.14 (septuple q, J=2 and 120 Hz, Si$\underline{\mathrm{C}}$H$_3$), 0.50 (septuple q, J=2 and 120 Hz, Si$\underline{\mathrm{C}}$H$_3$), 22.45 (q, J=129 Hz, C(2)$\underline{\mathrm{C}}$H$_3$), 100.5 (decuplet, J=3 Hz, $\underline{\mathrm{C}}$(4)), 106.1 (q, J=5 Hz, $\underline{\mathrm{C}}$(3)), 132.1 (q, J=7 Hz, $\underline{\mathrm{C}}$(2)), 134.7 (br m, $\underline{\mathrm{C}}$(1)); IR (neat) 2990, 2170, 1560, 1260, 1210, 850, 765, 700, 640, 570, 530 cm^{-1}; MS m/z (rel intensity) 290 (M$^+$+2, 8), 288 (M$^+$, 8), 122 (13), 121 (100), 97 (6), 73 (56), 45 (8). Found: m/z 288.0348 and 290.0359. Calcd for C$_{11}$H$_{21}$BrSi$_2$: M, 288.0360 and M+2, 290.0359.

(*E*)-1,4-Bis(trimethylsilyl)-1-chloro-2-methyl-1-buten-3-yne (2d). This compound was prepared in a similar manner. Bp 90 °C/0.5 Torr. ^{1}H NMR (CDCl$_3$) δ=0.22 (s, 9 H), 0.27 (s, 9 H), 1.98 (s, 3 H); IR (neat) 2970, 2140, 1570, 1250, 1220, 840, 760, 640 cm^{-1}; MS m/z (rel intensity) 246 (M$^+$+2, 6), 244 (M$^+$, 15), 174 (5), 123 (4), 122 (13), 121 (100), 97 (6), 93 (8), 74 (6), 73 (63), 45 (12). Found: C, 53.91; H, 8.72; Cl, 14.52%. Calcd for C$_{11}$H$_{21}$ClSi$_2$: C, 53.95; H, 8.64; Cl, 14.48%.

3,6-Bis(trimethylsilyl)-4-methyl-3-hexen-5-yn-2-one (2e). The butadiyne **1** (106 mg, 0.55 mmol) was allowed to react with trimethylaluminium under the same conditions as for **2a**. Acetyl chloride (0.4 ml, 5.6 mmol) was added to the reaction mixture at 0 °C, and the whole was stirred for 2 h. Workup and purification by preparative TLC (hexane/ethyl acetate=7/1) gave **2e** 41 mg (R_f 0.64) and 20 mg (R_f 0.61) as a colorless oil in totally 44% yield. Stereochemical assignment of each product could not be made.

Major Isomer: ^{1}H NMR (CDCl$_3$) δ=0.15 (s, 9 H), 0.18 (s, 9 H), 1.95 (s, 3 H), 2.28 (s, 3 H); IR (neat) 2980, 2160, 1695, 1570, 1355, 1255, 890, 845, 760, 650 cm^{-1}; MS m/z (rel intensity) 252 (M$^+$, 13), 238 (16), 237 (34), 221 (15), 179 (21), 163 (16), 147 (37), 133 (19), 97 (16), 75 (25), 73 (100), 45 (21), 43 (13); Found: m/z 252.1372. Calcd for C$_{13}$H$_{24}$OSi$_2$: M, 252.1364.

Minor Isomer: ^{1}H NMR (CDCl$_3$) δ=0.21 (s, 9 H), 0.25 (s, 9 H), 1.85 (s, 3 H), 2.18 (s, 3 H); IR (neat) 2970, 2150, 1690, 1570, 1350, 1250, 1200, 890, 840, 760, 660 cm^{-1}; MS m/z (rel intensity) 252 (M$^+$, 11), 238 (14), 237 (55), 179 (21), 163 (14), 147 (31), 133 (13), 121 (15), 97 (17), 75 (27), 73 (100), 45 (19), 43 (17). Found: m/z 252.1371. Calcd for C$_{13}$H$_{24}$OSi$_2$: M, 252.1364.

(*E*)-1,4-Bis(trimethylsilyl)-3-methyl-3-penten-1-yne ((*E*)-3). The butadiyne **1** (102 mg, 0.52 mmol) was allowed to react with trimethylaluminium as before, and the resulting mixture was treated with copper(I) chloride (0.4 g, 4.0 mmol) at room temperature, and the whole was stirred for 0.5 h. Workup and purification by preparative TLC (hexane, R_f 0.65) gave (*E*)-**3** 79 mg (67% yield) as a colorless oil, bp 80 °C/0.5 Torr. ^{1}H NMR (CDCl$_3$) δ=0.15 (s, 9 H), 0.20 (s, 9 H), 1.95 (s, 6 H); ^{1}H NMR (C$_6$D$_6$) δ=0.15 (s, 9 H), 0.32 (s, 9 H), 2.03 (q, J=1.5 Hz, 3 H), 2.19 (q, J=1.5 Hz, 3 H); IR (neat) 2970, 2140, 1570, 1440, 1405, 1250, 960, 840, 755, 690, 650, 530 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ=−0.2 (septuple q, J=2 and 119 Hz, Si$\underline{\mathrm{C}}$H$_3$), 0.3 (septuple q, J=2 and 120 Hz, Si$\underline{\mathrm{C}}$H$_3$), 22.1 (q, J=127 Hz, $\underline{\mathrm{C}}$H$_3$), 22.7 (qq, J=1 and 128 Hz, $\underline{\mathrm{C}}$H$_3$), 97.9 (decuplet, J=2.5 Hz, $\underline{\mathrm{C}}$(1)), 106.6 (m, $\underline{\mathrm{C}}$(2)), 126.8 (m, $\underline{\mathrm{C}}$(3)), 145.6 (m, $\underline{\mathrm{C}}$(4)); MS m/z (rel intensity) 224 (M$^+$, 17), 209 (43), 155 (75), 151 (15), 150 (18), 136 (16), 121 (18), 97 (18), 73 (100), 45 (19). Found: C, 64.15; H, 10.56%. Calcd for C$_{12}$H$_{24}$Si$_2$: C, 64.20; H, 10.78%.

(*Z*)-1,4-Bis(trimethylsilyl)-3-methyl-3-penten-1-yne ((*Z*)-3). To a 1,2-dichloroethane (2 ml) solution of bis(cyclopentadienyl)vanadium dichloride (8.0 mg, 0.03 mmol) was added trimethylaluminum (2.0 M hexane solution, 1.2 ml, 2.4 mmol), and the solution was stirred for 0.5 h at room temperature. The diacetylene **1** (108 mg, 0.56 mmol) dissolved in 1,2-dichloroethane (1.5 ml) was added to the reaction mixture. The resulting mixture was heated under reflux for 19 h. Workup and purification by preparative TLC (hexane, R_f 0.65) gave (Z)-**3** 34 mg (27% yield) as a colorless oil, bp 80 °C/0.5 Torr. ^{1}H NMR ($CDCl_3$) δ=0.17 (s, 9 H), 0.19 (s, 9 H), 1.73 (q, J=1.1 Hz, 3 H), 1.87 (q, J=1.1 Hz, 3 H); ^{1}H NMR (C_6D_6) δ=0.30 (s, 9 H), 0.42 (s, 9 H), 1.68 (q, J=1.1 Hz, 3 H), 1.91 (q, J=1.1 Hz, 3 H); IR (neat) 2960, 2140, 1570, 1440, 1410, 1250, 840, 755, 690, 665, 645, 630 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ=−0.8 (septuple q, J=2 and 119 Hz, $Si\underline{C}H_3$), −0.1 (septuple q, J=2 and 120 Hz, $Si\underline{C}H_3$), 18.3 (q, J=127 Hz, $\underline{C}H_3$), 20.5 (qq, J=1 and 128 Hz, $\underline{C}H_3$), 94.8 (decuplet, J=2 Hz, $\underline{C}$(1)), 109.4 (m, $\underline{C}$(2)), 127.0 (m, $\underline{C}$(3)), 146.4 (m, $\underline{C}$(4)); MS m/z (rel intensity) 224 (M$^+$, 22), 209 (52), 179 (25), 155 (100), 151 (15), 150 (22), 136 (17), 97 (16), 73 (71), 45 (12). Found: m/z 224.1389. Calcd for $C_{12}H_{24}Si_2$: M, 224.1415.

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