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Hydroalumination of silylacetylenes: a novel and highly stereoselective synthesis of (*E*)-telluro(silyl)ketene acetals and their applications in Sonogashira cross-coupling reactions

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(*Z*)-1,4-Diorganyl-2-tri(organyl)silyl-1-buten-3-ynes

ABSTRACT

The hydroalumination of silylacetylenes with DIBAL-H followed by the addition of *n*-butyllithium generated in situ the (*Z*)-β-vinylorganosilane alanates intermediates, which were trapped with butyltellurenyl bromide (C_4H_9TeBr), furnishing exclusively the (*E*)-1-butyltelluro-1-tri(organyl)silyl-2-organyl-1-alkenes in 45–70% yields. These telluro(silyl)ketene acetals were utilized as substrates in Sonogashira cross-coupling Pd-catalyzed reactions, furnishing the (*Z*)-1,4-diorganyl-2-tri(organyl)silyl-1-buten-3-ynes with total control of regio- and stereochemistry in 62–80% yield.

Over the past four decades, the *syn*-hydroalumination of terminal alkynes with the commercially available di-(isobutyl)aluminum hydride (DIBAL-H) as reducing agent, has been established as a highly efficient and versatile methodology for the generation of (*E*)-vinylorganoaluminum intermediates following an *anti*-Markovinikov mechanism.[1] On the other hand, amazing results in the generation of alana intermediates with opposite regiochemistry such as α-vinylorganoaluminum were obtained via Ni-catalyzed hydroalumination of terminal alkynes with DIBAL-H.[2] This vinylorganoaluminum can be applied as a soft nucleophile to form new carbon–carbon bonds with high enantioselectivity in catalytic systems,[3] transmetalation processes[4] and to prepare vinyl halides, normally used as a substrate in cross-coupling reactions.[5]

Investigations involving the hydroalumination of disubstituted alkynes represented by selenoacetylenes[6] and thioacetylenes[7] with DIBAL-H and lithium di-(isobutyl)-*n*-butyl aluminate hydride (Zweifel's reagent), were carried out by our group. In these processes, the β-organylchalcogene vinylorganoaluminum intermediates were generated 'in situ' and then reacted with chalcogene electrophiles, furnishing the 1,1-bis(organylchalcogene)-1-alkenes.

The pioneer study by Eich and co-workers[8] described mechanistically the coordination of a Lewis base to the empty 3p orbital of the Al metal, permitting the total retention of configuration of the *Z*-vinylaluminum generated by the stereoselective *syn*-addition of DIBAL-H to silylacetylenes.

Recently, Hoveyda and co-workers[9] reported the reduction of silylacetylenes carried out with DIBAL-H in a solvent mixture of hexane/THF (5:1), furnishing the *cis*-vinyl metals which were applied in Cu-catalyzed cross coupling, aiming at the stereoselective total synthesis of the antifungal (−)-nyasol.

However, to the best of our knowledge, methodologies to prepare telluro(silyl)ketene acetals from Al/Te transmetalation and their applications in cross-coupling reactions have not yet been reported.

The hydroalumination of silylacetylenes **1a–g** with DIBAL-H in hexanes/ethyl ether furnished stereoselectively the (*Z*)-β-vinylorganosilane alanas **2a–g**. Subsequently, we investigated the addition of *n*-BuLi to **2a–g** at 0 °C to afford 'in situ' the novel 'ate complex' (*Z*)-β-vinylorganosilane alanate intermediates **3a–g** which were then trapped with butyltellurenyl bromide (C_4H_9TeBr),

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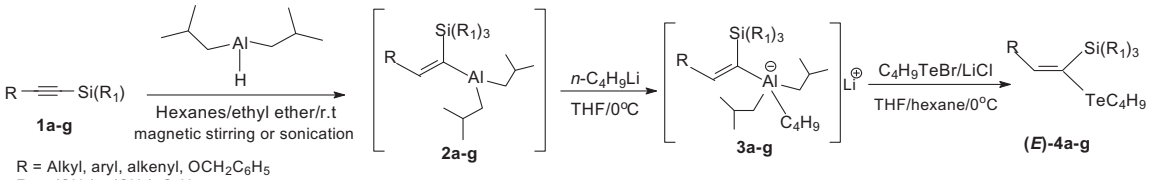
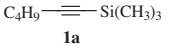
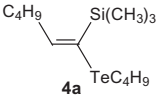
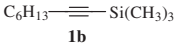
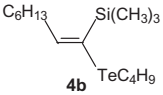
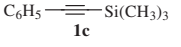
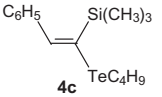
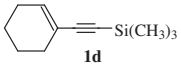
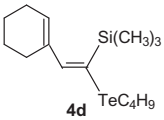
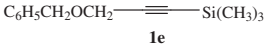
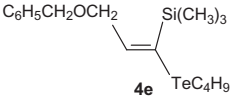
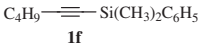
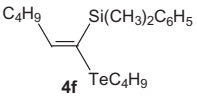
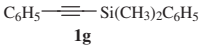
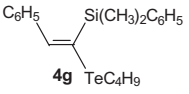
Table 1
Synthesis of (*E*)-telluro(silyl)ketene acetals[15–18]

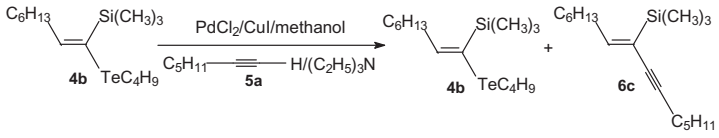


R = Alkyl, aryl, alkenyl, $OCH_2C_6H_5$
R_1 = $(CH_3)_3$, $(CH_3)_2C_6H_5$

Entry	Silylacetylene	Product[a]	Time[b] (h)	Yield[c] (%)
1	 **1a**	 **4a**	4.5	65
2	 **1b**	 **4b**	4.5	65
3	 **1c**	 **4c**	4.5	70
4	 **1d**	 **4d**	4.5	45
5	 **1e**	 **4e**	6.0	50
6	 **1f**	 **4f**	4.5	60
7	 **1g**	 **4g**	4.5	70

[a] Fully characterized by NMR (^1H, ^{13}C), microanalysis data.
[b] Reaction conditions: **1a–d** (1.0 mmol), **DIBAL-H** (1.5 mmol in hexane), ethyl ether (3.0 mL) at room temperature under magnetic stirring (2 h), *n*-BuLi (1.0 mmol)—30 min. at 0 °C, C_4H_9TeBr/LiCl (2.0 mmol)—2 h at 0 °C; **1e** (1.0 mmol), **DIBAL-H** (3.75 mmol in hexane), ethyl ether (4.5 mL) at room temperature under sonication (3.5 h), *n*-BuLi (1.5 mmol)—30 min. at 0 °C, C_4H_9TeBr/LiCl (2.0 mmol)—2 h at 0 °C; **1f–g** (1.0 mmol), **DIBAL-H** (1.5 mmol in hexane), ethyl ether (3.0 mL) at room temperature under sonication (2 h), *n*-BuLi (1.0 mmol)—30 min. at 0 °C, C_4H_9TeBr/LiCl (2.0 mmol)—2 h at 0 °C.
[c] Isolated yields after purification by chromatography using silica gel (230–400 mesh) using hexane (**4a–d, f–g**) and a mixture of ethyl acetate/hexane (0.5:9.5 v/v) as the mobile phase for **4e**.

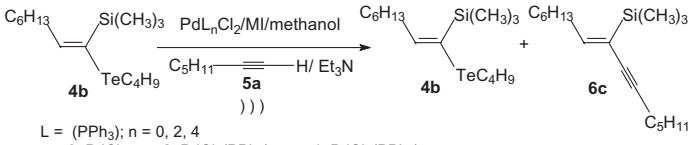
Table 2
Cross-coupling reaction of **4b** and 1-heptyne



Entry	$PdCl_2$(mol %)/CuI (mol %)	1-heptyne (equiv)	Time (h)	Rate[b] **4b**:**6c**
1[a]	20/20	2.0	8	1:4
2	20/20	1.0	18	1:4
3	20/20	2.5	18	1:4
4	20/20	3.0	18	1:4
5	20/10	3.0	18	1:4
6	30/30	2.0	64	0:1
7	20/20	3.0	72	0:1
8	30/30	3.0	48	0:1
9	20/20	2.0	72	0:1
10	30/30	3.0	36	0:1
11	20/20	2.0	48	0:1
12	20/20	3.0	36	1:5

[a] Reaction carried out as described in Ref. 12
[b] Ratio determined by ^1H NMR.

Table 3
Cross-coupling reaction of **4b** and 1-heptyne



L = (PPh_3); n = 0, 2, 4
n = 0, $PdCl_2$; n = 2, $PdCl_2(PPh_3)_2$; n = 4, $PdCl_2(PPh_3)_4$
M = Cu, Ag

Entry	PdL_nCl_2 (mol %)/MI (mol %)	Time (min)	Rate[a] **4b**:**6c**
1	$PdCl_2(PPh_3)_2$ (20 mol %)/CuI (30 mol %)	60	1:6
2	$PdCl_2(PPh_3)_2$ (20 mol %)/CuI (30 mol %)	90	0:1
3	$PdCl_2(PPh_3)_2$ (5 mol %)/CuI (10 mol %)	50	1:0
4	$PdCl_2$ (30 mol %)/AgI (30 mol %)	50	1:2
5	$PdCl_2$ (30 mol %)/AgI (30 mol %)	90	1:6
6	$PdCl_2$ (30 mol %)/AgI (30 mol %)	120	0:1
7	$PdCl_2$ (20 mol %)/AgI (20 mol %)	50	1:3
8	$PdCl_2$ (20 mol %/CuI(20 mol %)	50	0:1
9	$Pd(PPh_3)_4$ (5 mol %)/CuI (10 mol %)	50	1:0

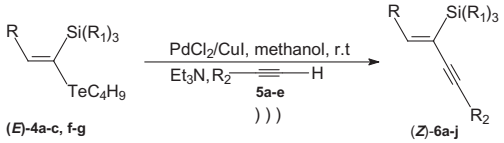
[a] Ratio determined by ^1H NMR.

furnishing exclusively the (***E***)-telluro(silyl)ketene acetals **4a–g** (Table 1). The addition of DIBAL-H to the triple bond of the silylacetylenes using a mixture of hexane/ethyl ether as solvent, occurred in a *cis*-fashion mechanism, transferring the organoaluminum moiety to the same C-sp^2 containing the trialkyl silyl group (Table 1).

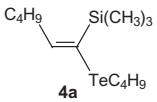
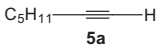
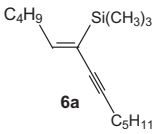
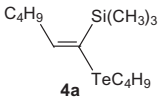
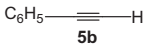
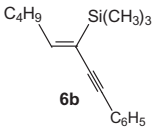
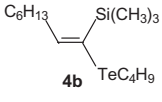
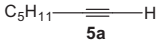
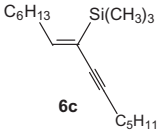
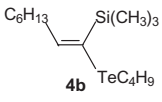
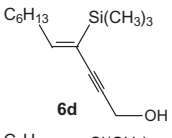
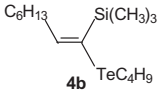
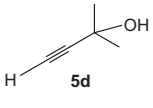
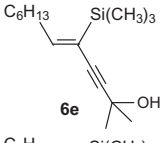
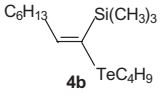
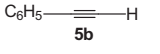
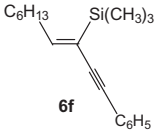
We believe that the ethyl ether acts as a Lewis base[8,9] playing an important role in the total control of the stereochemistry in the *cis*-hydroalumination of the silylacetylenes **1a–g**. However, these intermediates showed very low reactivity toward Al/Te transmetalation with electrophiles such as butyltellurenyl bromide (C_4H_9TeBr). So, the activation of the vinyl alanas type **2** was performed by the reaction with *n*-BuLi producing the highly reactive (***Z***)-β-vinylorganolsilane alanates **3a–g** which were then reacted with *n*-butyltellurenyl bromide leading to the (***E***)-telluro(silyl)ketene acetals **4a–g** in good yields (Table 1).

Among the methodologies applied to build new carbon–carbon bonds in mild conditions, the Pd-catalyzed cross-coupling reactions, described by Sonogashira and co-workers,[10] have been intensively explored.[11] However, the Sonogashira reaction involving telluro(silyl)ketene acetals as substrate has not been reported so far.

Table 4
Synthesis of (*Z*)-1,4-diorganyl-2-tri(organyl)silyl-1-buten-3-ynes[19–21]

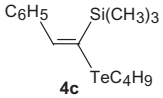
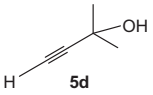
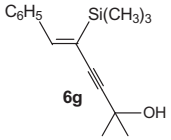
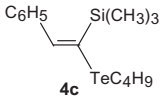
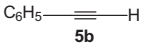
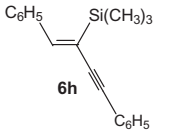
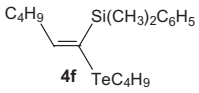
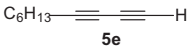
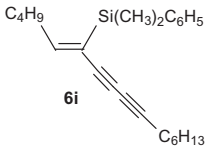
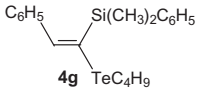
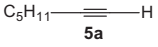
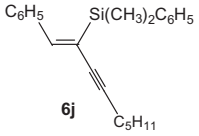


R_1 = $(CH_3)_3$, $(CH_3)_2C_6H_5$
R_2 = Alkyl, aryl, alkynyl, $(CH_3)_2(OH)C$, CH_2OH

Entry	(*E*)-Telluro(silyl)keteneacetal	1-alkyne	Product[a,b]	Time (min)	Yield[c] (%)
1				50	75
2				90	73
3				50	80
4				120	62
5				60	75
6				90	75

(*continued on next page*)

Table 4 (*continued*)

Entry	(*E*)-Telluro(silyl)keteneacetal	1-alkyne	Product[a,b]	Time (min)	Yield[c] (%)
7	 **4c**	 **5d**	 **6g**	60	70
8	 **4c**	 **5b**	 **6h**	90	68
9	 **4f**	 **5e**	 **6i**	90	68
10	 **4g**	 **5a**	 **6j**	50	72

[a] Fully characterized by NMR (^{1}H, ^{13}C), microanalysis data.
[b] Reaction conditions: **4a**–**c**,**f**–**g** (0.5 mmol), **5a**–**e** (1.0 mmol), triethylamine (1.0 mmol) in methanol (5.0 mL) at room temperature, catalytic system: $PdCl_2$ 20 mmol%/CuI 20 mmol %.
[c] Isolated yields after purification by chromatography using silica gel (230–400 mesh) in hexane (**6a**–**c**, **f**, **h**–**i**) or a mixture of ethyl acetate:hexane (1:9 v/v) as the mobile phase (**6d**–**e**, **g**).

Therefore, we examined the protocol described in the literature[12] to carry out the reaction of (***E***)-1-butyltelluro-1-tri(methyl)-silyl-1-octene (1.0 equiv) **4b** and 1-hepyne (2.0 equiv) in a catalytic system containing $PdCl_2$ (20 mol %), CuI (20 mol %) in methanol/triethylamine (5.0 mL/0.3 mL), which furnished the (***Z***)-8-tri(methyl)silyl-7-pentadecen-9-yne **6c**.

However, the reaction did not proceed to completion and an appreciable amount of the starting material **4b** was recovered intact, as detected by NMR (Entry 1, Table 2).

In order to increase the yield of the process, several reaction conditions were tested, and the relationship between $PdCl_2$/CuI, the amounts of 1-heptyne, and the reaction times needed to be modified (Table 2, entries 6–11) in comparison with the literature (Table 2, entry 1).[12] However, the reaction time needed to obtain the desired product **6c** remained long in all conditions tested (from 36 to 72 h).

Within the context of exploring a novel, efficient, and general methodology to prepare (***Z***)-1,4-diorganyl-2-tri(organyl)silyl-1-but-en-3-ynes from Sonogashira-type cross coupling, we studied the reaction of the (***Z***)-telluro(silyl)ketene acetals **4b** (1.0 equiv) and 1-heptyne (2.0 equiv) in a wide range of reaction conditions, under sonication (Table 3).

The best result was obtained when the (***E***)-telluro(silyl)ketene acetal **4b** (1.0 equiv) reacted with 1-heptyne **5a** (2.0 equiv) in the presence of $PdCl_2$ (20 mol %)/CuI (20 mol %) and methanol/triethylamine as solvent under sonication (50 min), to give only the (***Z***)-1,4-diorganyl-2-tri(methyl)-silyl-1-buten-3-ynes **6c**, in 80% yield (Entry 8, Table 3).

Next, we applied this improved reaction condition to perform the cross-coupling reaction using the (***E***)-telluro(silyl)ketene acetals **4a–f** and 1-alkynes **5a–e**, which were totally consumed after 50 to 120 min, affording the (***Z***)-1,4-diorganyl-2-(triorganyl)silyl-1-buten-3-ynes **6a–j** in good yields (Table 4).

The complete Sonogashira reaction mechanism using palladium as a catalyst and copper as a cocatalyst in homogeneous medium remains unknown.[11a,13] Our cross-coupling mechanism

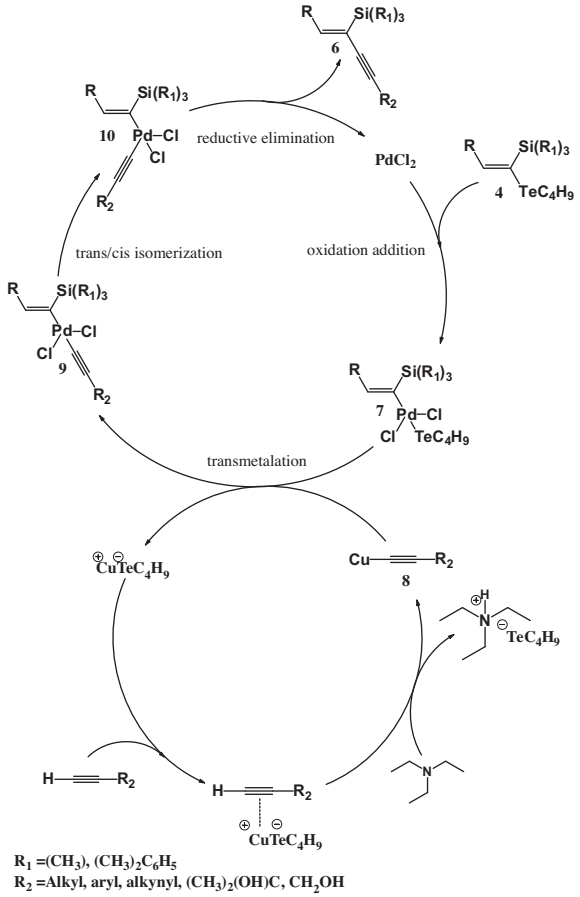


Figure 1. A plausible Sonogashira-type cross-coupling reaction mechanism

proposal, outlined in Figure1, involving the (***E***)-telluro(silyl)ketene acetals and 1-alkynes is similar to that described in the literature.[11a,11i] Therefore, the $PdCl_2$ must react with the vinyl compound **4** in a fast oxidative addition, producing the initial Pd-complex **7**. The next step in the Pd-cycle would connect with the cycle of the copper[14] and subsequent Pd/Cu transmetalation from the copper acetylide **8** (formed in the Cu-cycle) to give the Pd-species **9** which after *trans/cis* isomerization and reductive elimination will furnish the symmetrical and unsymmetrical (***Z***)-1,4-diorganyl-2-tri(organyl)-silyl-1-buten-4-ynes **6**, with regeneration of the catalyst (Fig. 1).

In summary, we describe herein the highly stereoselective synthesis of (***E***)-telluro(silyl)ketene acetals **4a–g** via Al/Te transmetalation of the novel 'ate complex' (***Z***)-β-vinylorganosilane alanates, which were generated by the hydroalumination of silylacetylene with DIBAL-H followed by the addition of *n*-BuLi. The (***E***)-telluro(silyl)ketene acetals were successfully applied in the Sonogashira cross-coupling reaction with 1-alkynes, using sonication to speed up the process, leading to the synthesis of the (***Z***)-1,4-diorganyl-2-tri(organyl)silyl-1-buten-3-ynes. The mechanism of the modified Sonogashira cross-coupling reaction is proposed.

Acknowledgments

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15. *Typical procedure for the synthesis of (E)-telluro(silyl)ketene acetals.*
To a two-neck 50 mL flask under nitrogen atmosphere, containing a solution of 1-trimethysilyl-2-organyl ethyne and DIBAL-H in ethyl ether/hexane, the mixture was stirred at 25 °C for the time and conditions shown in Table 1. The disappearance of the starting material was confirmed by TLC using hexane as eluent. The resulting solution was cooled to 0 °C and *n*-BuLi was transferred and the reaction stirred for 30 min. Then, a solution of butyl tellurenylbromide/lithium chloride [(C_4H_9TeBr/LiCl 2.0 mmol], prepared separately by the addition of bromine (0.070 g; 1.0 mmol) in hexane (5 mL) to a solution of dibutyl ditelluride[22] (0.368 g; 1.0 mmol) in THF (10 mL) cooled at 0 °C. Next, dry lithium chloride (0.084 g; 2.0 mmol) was added and the mixture stirred for 10 min. Then, the solution of butyltellurenyl-bromide/lithium chloride was added dropwise at 0 °C with a syringe to the (***Z***)-β-vinylorganolsilane alanates **3a–g** derivatives. The stirring was continued for an additional time shown in Table 1, and the mixture was transferred to an Erlenmeyer flask (500 mL) and diluted with ethyl acetate (20 mL), water (50 mL) and 95% ethanol (20 mL). Butyl bromide (1.0 mL) and finally $NaBH_4$ (until the mixture turned pale yellow) were added to transform dibutyl ditelluride to the corresponding telluride, which is more easily removed by distillation. After this treatment, the crude product was extracted with ethyl acetate (3 × 20 mL) and washed with brine (4 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$, and the solvent evaporated. After filtration through Celite using hexane as eluent, the product was concentrated under vacuum. Dibutyl telluride was removed by distillation from the crude product using a Kugelrohr apparatus (80 °C/0.01 mm Hg). Flash column chromatography (using silica gel 230–400 mesh and the appropriate mobile phase as shown in Table 1) of the residue furnished the (***E***)-telluro(silyl)ketene acetals as a yellow oil.
16. *(E)-1-Butyltelluro-1-trimethylsilyl-1-octene 4b*. Yield (65%), IR (neat, cm^{-1}): 2954, 1573, 1377, 1245, 690. ^1H NMR (300 MHz, in $CDCl_3$) 0.21 (s, 9 H); 0.86–0.94 (m, 6H); 1.27-1.42 (m, 10H); 1.73 (quint., *J* = 7.5 Hz, 2H); 2.18 (q, *J* = 7.5 Hz, 2H); 2.69 (t, *J* = 7.5 Hz, 2H); 6.81 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, in $CDCl_3$) 1.12; 7.17; 7.20; 13.42; 14.01; 22.57; 25.17; 28.87; 29.53; 31.71; 33.43; 35.94; 114.66; 156.76. Anal Calcd for $C_{15}H_{32}SiTe$: C, 48.91; H, 8.69; Found: C, 48.84; H 8.80.
17. *(E)-1-Butyltelluro-1-trimethylsilyl-2-phenyl ethene 4c*. Yield (70%), IR (neat, cm^{-1}) 3054, 3020, 2954, 2925, 1687, 1486, 1245, 835. ^1H NMR (300 MHz, in $CDCl_3$) 0.21 (s, 9H); 1.10 (t, *J* = 7.5 Hz, 2H); 1.58 (sext., *J* = 7.5 Hz, 2H); 1.99 (quint., *J* = 7.5 Hz, 2H); 3.01 (t, *J* = 7.5 Hz, 2 H); 7.33–7.47 (m, 5H), 8.03 (s, 1H). ^{13}C NMR (75 MHz, in $CDCl_3$) 1.12; 7.15; 8.28; 13.45; 25.16; 33.29; 123.57, 127.16; 127.70; 127.79; 127.82; 127.85; 127.88; 151.47. Anal Calcd for $C_{15}H_{14}SiTe$: C, 49.99; H 6.66; Found C, 48.82; H 6.91.
18. *(E)-1-Butytelluro-1-dimethyphenylsilyl-1-hexene 4f*. Yield (60%),%), IR (neat, cm^{-1}) 3064, 2954, 2957, 2158, 1591, 1472, 1247, 813, 698. ^1H NMR (300 MHz, in $CDCl_3$) 0.49 (s, 9H); 0.80 (t, *J* = 7.5 Hz, 3H); 0.89 (t, *J* = 7.5 Hz, 3H); 1.13–1.38 (m, 6H); 1.69 (quint., *J* = 7.5 Hz, 2H); 2.04 (q, *J* = 7.5 Hz, 2H); 2.63 (t, *J* = 7.5 Hz, 2H); 6.89 (t, *J* = 7.5 Hz, 1H); 7.32–7.57 (m, 5H). ^{13}C NMR (75 MHz, in $CDCl_3$) 0.70; 8.97; 13.45; 25.17; 33.14; 121.6; 127.23; 127.45; 127.61; 127.76; 127.94; 129.06; 130.1; 130.9; 131.1; 132.5; 133.98; 139.55; 141.47; 152.07. Anal Calcd for $C_{18}H_{30}SiTe$: C, 53.73, H 7.46; Found C, 53.55; H 7.54.
19. *Typical procedure for the synthesis of (Z)-1,4-diorganyl-2-tri(organyl)silyl-1-buten-3-ynes.*
To a two-neck flask under nitrogen atmosphere and magnetic stirring containing $PdCl_2$ (0.177; 0.1 mmol) and CuI (0.019 g; 0.1 mol) in methanol (5.0 mL) was added the (***E***)-telluro(silyl)ketene acetal **4** (0.5 mmol) and the solution stirred for 45 min. at 25 °C. Next, the 1-alkyne (1.0 mmol) and triethylamine (0.6 mL; 1.0 mmol) were transferred via syringe, and the reaction mixture stirred under sonication using an ultrasonic cleaner (Unique Ultrasonic Cleaner–USC800A) for the time shown in Table 4 at room temperature. Then, the crude product was extracted with hexanes (4 × 20 mL) and washed with brine (5 × 15 mL), the organic phase dried under $MgSO_4$, the solvent evaporated and the product concentrated under vacuum. Finally, the product was purified by flash chromatography (using silica gel 230–400 mesh and the appropriate mobile phase as shown in Table 4) furnishing the (***Z***)-1,4-diorganyl-2-tri(organyl)silyl-1-buten-3-ynes as a yellow oil.
20. *(Z)-1-hexyl-4-pentyl-2-trimethylsilyl-1-buten-3-yne 6a*. Yield (75%). IR (neat, cm^{-1}) 2956, 2927, 2856, 2358, 2341, 1247, 838. ^1H NMR (300 MHz, in $CDCl_3$) 0.20 (s, 9H); 0.86–0.92 (m, 7H); 1.28–1.55 (m, 13H); 2.15 (q, *J* = 7.7 Hz, 2H); 2.31 (t, *J* = 7.7 Hz, 2H); 6.55 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (75 MHz, in $CDCl_3$) 0.03; 14.05; 19.55; 22.23; 22.59; 28.87; 29.56; 31.16; 31.74; 32.35; 83.53; 90.30; 109.78; 153.16. Anal Calcd For $C_{16}H_{30}Si$: C, 76.67, H 11.98; Found C, 76.61; H 10.89.
21. *(Z)-4-trimethylsilyl-undec-3-en-2-yn-1-ol 6d*. Yield (62%). IR (neat, cm^{-1}) 3348, 2954, 2925, 2856, 2198, 1249, 840. ^1H NMR (300 MHz, in $CDCl_3$) 0.21 (s, 9H); 0.88 (t, *J* = 7.5 Hz, 3H); 1.28–1.38 (m, 8H); 1.64 (s, 1H); 2.18 (q, *J* = 7.5 Hz, 2H); 4.39 (s, 2H); 6.65 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (75 MHz, in $CDCl_3$) 0.17; 13.99; 22.54; 28.96; 29.35; 31.68; 32.50; 51.79; 87.22; 89.09; 108.77; 155.42. Anal Calcd for $C_{14}H_{25}SiO$: C, 70.76, H 10.54; Found C, 70.65; H 10.34.
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