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Hydrosilylation of alkynylsilanes utilizing organolanthanide and Group 3 metallocene complexes

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Abstract

The organolanthanide- and Group 3 metallocene-catalyzed hydrosilylation of alkynylsilanes has been found to provide (*Z*)-1,1-bis(silyl)alkenes. In particular, $Cp^*_2YMe{\cdot}THF$ (**1**), $[Cp^{TMS}_2YMe]_2$ (**2**), and $[Cp^{TMS}_2LuMe]_2$ (**3**) were shown to be regioselective for the hydrosilylation of various alkynylsilanes (Fig. 1). The process was evaluated for diverse substitution patterns and functional groups on the pendant alkyl chain. Silyl ethers and halogens are stable to the catalytic process, affording excellent chemo- and regioselectivities. Competition between 'aryl-directed' and 'silyl-directed' processes was observed upon hydrosilylation of (phenylethynyl)dimethylsilane. © 2002 Published by Elsevier Science B.V.

Keywords: Organolanthanide; Organoyttrium; Catalysis; Hydrosilylation; Alkynylsilane; Bis(silyl)alkene

1. Introduction

Organolanthanide metallocenes and Group 3 complexes have proven to be efficient and selective catalysts for the functionalization of unsaturated organic molecules [1]. Originally developed as olefin polymerization catalysts [2–5], their reactivity has been exploited for the hydrogenation, [6–10] hydrosilylation, [11–22] hydroamination, [23–31] hydroboration, [32–34] and hydrophosphination [35] of substrates containing one or more double or triple bonds. The transformations catalyzed by organolanthanide and Group 3 organometallics are generally high yielding and highly selective, thereby enhancing their synthetic utility.

Previous efforts in our laboratory have revealed that the organoyttrium species $Cp^*_2YMe{\cdot}THF$ serves as an effective precatalyst for the regioselective hydrosilylation of internal unsymmetrical alkynes [13,36–38]. The regioselectivity is derived from a combination of catalyst and alkyne steric constraints (Scheme 1) [13].

Hydrosilylation of terminal alkynes is an appealing transformation that provides access to easily functionalized alkenylsilanes. Alkenylsilanes thus generated can be protodesilylated [39–41] or transformed into haloalkenes with retention or inversion at the sp^2 center

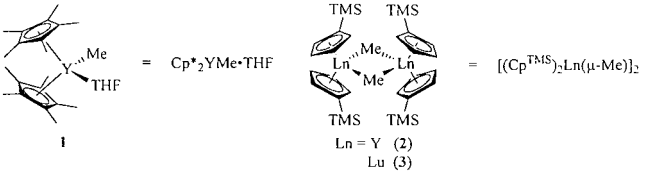
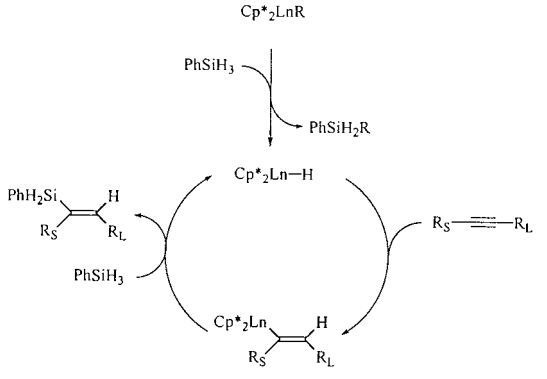


Fig. 1. Lanthanocene complexes.



Scheme 1. Catalytic cycle for the hydrosilylation of unsymmetrical, internal alkynes.

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[42–47]. Recently, Hatanaka and Hiyama [48,49], Denmark [50–52], and DeShong [53] have demonstrated the palladium(0)-catalyzed cross-coupling reactions of alkenylsilanes, an attractive alternative to the use of toxic (organostannane) or air-sensitive (organoborane) coupling partners [54].

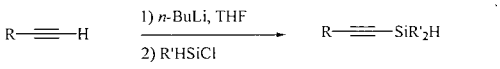
Unfortunately, terminal alkynes cannot be subjected to lanthanide catalysis because of the acidity of the alkyne [55–57]. Protection of the alkyne as the corresponding alkynylsilane allows a 'pseudo' proton to occupy the terminal position. Hydrosilylation of the resultant alkynylsilane provides some insight into the steric and electronic influence of directing groups on mechanistically associated organolanthanide-catalyzed processes.

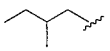
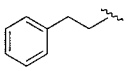
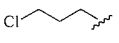
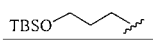
2. Results and discussion

2.1. Substrate preparations

Using a standard deprotonation/silylation protocol, various alkynylsilanes were prepared (Table 1) [58,59]. Using the same technique, the trimethylsilyl- (**4e**) and trimethylstannylalkynes (**4f**) were prepared in 99 and 76% yield, respectively.

Table 1
Preparation of substrates



R	R'	product	% isolated yield
n-Oct	Me	**4a**	87
	i-Pr	**4b**	77
	t-Bu	**4c**	85
	Ph	**4d**	85
	Me	**5a**	31
	i-Pr	**5b**	56
	Me	**6a**	35
	i-Pr	**6b**	32
	Me	**7**	79
	Me	**8**	29
	Me	**9**	48

2.2. Hydrosilylation of alkynylsilanes

Alkynylsilanes **4a–e** and alkynylstannane **4f** were surveyed for reactivity with catalysts **1–3** in simple hydrosilylation reactions. Generally, the reactions were run at higher temperatures and for longer reaction times in comparison to the hydrosilylation of alkenes and internal, unsymmetrical alkynes [11–22]. Under these more forcing conditions, polymerization, hydrogenation, and isomerization became notable side reactions. The data is summarized in Table 2. Surprisingly, the major regioisomer, in all cases, was the (*Z*)-1,1-bis(silyl)alkene. The regiochemistry of the major product was determined by analysis of the splitting pattern of the olefinic proton resonances and confirmed with decoupling experiments.

The results demonstrate the degree to which substrate and catalyst structure influenced the reactions. Increasing the size of the silyl group (from **4a** to **4b**) enhances the regioselectivity of the hydrosilylation reactions with **3**. More interesting is the effect of the catalyst upon the reaction. Typically, the use of a more sterically demanding catalyst, such as **1**, required higher reaction temperatures and/or longer reaction times. The bulky ligand about the metal center obstructed approach of the substrate to the metal. Under these more forcing conditions, the dehydrogenative coupling of phenylsilane and concomitant release of molecular hydrogen is effectively activated [6]. As a result, competing hydrogenation and isomerization side reactions were significant, and lower yields were obtained. The use of the less hindered yttrium complex **2** allowed the hydrosilylation of hindered alkynylsilane **4c** at 40 °C. The ability to 'tune' the reactivity of a given complex is demonstrated by the increased selectivity observed using lutetium catalyst **3**. Regioselectivities improve from 7.2:1 for the hydrosilylation of **4a** with catalyst **2**, to 32:1 when this change of the metal center is executed.

The hydrosilylation of alkynes with propargylic and homopropargylic substitution was also studied (Table 3). Branching at the β-position provided enough steric influence to afford complete regioselectivity, as evidenced by the hydrosilylation of **5b**. Propargylic substitution, however, seemed to interfere with the reaction, as reflected by the longer reaction times and higher reaction temperatures required for hydrosilylation of **6a** and **6b**. Regioselectivities of these reactions remained to be governed predominantly by the catalyst used.

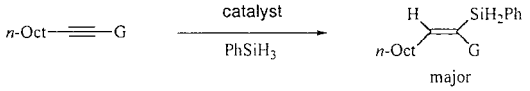
To study the electronic aspects of the hydrosilylation reaction further, aryl substitution on the alkyne was varied (Table 4). Hydrosilylation of (phenylethynyl)-dimethylsilane (**13**) demonstrated an expected loss of regioselectivity in comparison to hydrosilylations of **7**. By interacting with the Lewis-acidic metal center, the conjugated phenyl ring directed the metal to the benzylic position upon insertion into the alkyne [11,60,61].

Moving the phenyl group to the homopropargylic site (**7**) reestablished regioselectivity for the (*Z*)-1,1-bis(silyl)alkene, but in low yields. These attenuated yields might be attributed to polymerization of the styrene derivatives generated in the reaction. In comparison with results previously discussed (Tables 2 and 3), it appears that a homopropargylic aryl group has an adverse effect upon the efficiency of the hydrosilylation of silylalkynes.

Functional group compatibility was briefly investigated (Table 5). Halogens can undergo metal–halogen exchange with organolanthanide catalysts [63]. Moreover, heteroatoms, such as oxygen, nitrogen, and sulfur, are known to coordinate to the metal center, lowering the catalytic turnover [6,8,22]. As illustrated in Table 5, hydrosilylation of dimethylsilyl protected alkynes containing a silyl ether or chlorine moiety is highly chemo- and regioselective, although requiring longer reaction times in comparison to the hydrocarbon analogs. Unfortunately, the reactions failed to proceed to completion, despite the prolonged reaction period. Presumably, the heterosubstituents disrupt the catalytic cycle, slowly causing the reaction to halt. Furthermore, decomposition of the substrate was evident upon hydrosilylation of **8**.

As previously mentioned, the major regioisomer resulting from the hydrosilylation of silylalkynes was the (*Z*)-1,1-bis(silyl)alkene. If steric effects dictated the regioselectivity of the reaction (Eq. 1, path a), the (*E*)-1,2-bis(silyl)alkene would result. However, the major products resulting from our investigations mandate that the alkyne insertion into the metal–hydride bond proceeds to place the metal next to silicon, the more encumbered group (path b). The preference for metal placement at the α-position is rationalized by the α-directive effect of silicon. Earlier studies have indicated that the C–C bond of alkynylsilanes is polarized such that the more electronegative carbon is next to silicon and the more electropositive carbon is at the β-position [64,65]. The polarization of the C–C bond is a consequence of dative π-bonding from carbon to silicon. Thus, upon insertion into the metal–hydride bond, the Lewis-acidic lanthanide adds to the more Lewis-basic site. Increasing the size of the alkyl group on silicon adds electron density to the α-carbon, thereby enhancing regioselectivity of the hydrosilylation reaction. The

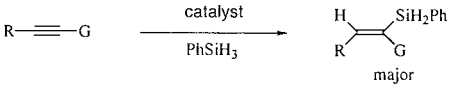
Table 2
Results for hydrosilylation reaction of alkynylsilanes [a]

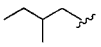


G	Catalyst [b]	Conditions (°C, h)	Product	% isolated yield	Selectivity [c] major:minor
$SiMe_2H$ (**4a**)	**1**	50, 48	**10a**	67	18:1
$SiMe_2H$ (**4a**)	**2**	r.t., 4	**10a**	52	7.2:1
$SiMe_2H$ (**4a**)	**3**	r.t., 24	**10a**	77	32:1
Si^iPr_2H (**4b**)	**1**	100, 24	**10b**	– [d,e]	–
Si^iPr_2H (**4b**)	**2**	r.t., 5	**10b**	84	27:1
Si^iPr_2H (**4b**)	**3**	r.t., 24	**10b**	71	>50:1
Si^tBu_2H (**4c**)	**1**	100, 72	**10c**	nr	–
Si^tBu_2H (**4c**)	**2**	40, 24	**10c**	59	>50:1
Si^tBu_2H (**4c**)	**3**	100, 48	**10c**	[f]	–
$SiPh_2H$ (**4d**)	**1**	100, 72	**10d**	– [d,e]	–
$SiPh_2H$ (**4d**)	**2**	40, 72	**10d**	40	>50:1
$SiMe_3$ (**4e**)	**1**	100, 24	**10c**	nr	–
$SiMe_3$ (**4e**)	**2**	50, 24	**10c**	– [g,h]	–
$SnMe_3$ (**4f**)	**1**	100, 24	**10f**	– [d,h]	–
$SnMe_3$ (**4f**)	**2**	100, 24	**10f**	nr	–

[a] Cyclohexane was used as the solvent. All reactions at r.t. were performed in a sealed glovebox. All heated reactions were performed in a sealed tube initially prepared in a glovebox.
[b] Catalyst **1**: $Cp_2^*YMe{\cdot}THF$; **2**: $[Cp_2^{TMS}YM3]_2$; and **3**: $[Cp_2^{TMS}LuMe]_2$.
[c] Regioselectivity was determined by GC analysis of the crude product.
[d] Starting material was not completely consumed.
[e] Hydrogenation and/or isomerization was observed.
[f] Reaction proceeded to 10% conversion as indicated by GC analysis.
[g] No starting material.
[h] Complex mixture of products as indicated by GC analysis.

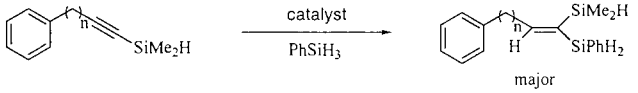
Table 3
Results for hydrosilylation reaction of alkynylsilanes with propargylic and homopropargylic substitution[a]



R	G	catalyst[b]	conditions	product	% isolated yield	selectivity[c] major:minor
	$SiMe_2H$ (**5a**)	**1**	100 °C, 48 h[d]	**11a**	22	11:1
"	"	**2**	75 °C, 2 h[d]	"	68	9:1
"	"	**3**	50 °C, 4 h[d]	"	52	35:1
"	$Sii\text{-}Pr_2H$ (**5b**)	**1**	100 °C, 4 d[d]	**11b**	—[f]	--
"	"	**2**	50 °C, 20 h[e]	"	82	>100:1
"	"	**3**	50 °C, 12 h[e]	"	73	exclusive
	$SiMe_2H$ (**6a**)	**1**	100 °C, 72 h[d]	**12a**	52	2:1
"	"	**2**	40 °C, 24 h[e]	"	71	22:1
"	"	**3**	100 °C, 48 h[e]	"	47	21:1
"	$Sii\text{-}Pr_2H$ (**6b**)	**1**	100 °C, 72 h[d]	**12b**	36[f]	4:1
"	"	**2**	50 °C, 72 h[d]	"	58	10:1
"	"	**3**	100 °C, 24 h[d]	"	58	26:1

[a] All heated reactions were performed in a sealed tube initially prepared in a glovebox. [b] Catalyst **1**: $Cp^*_2YMe{\cdot}THF$; **2**: $[Cp^{TMS}_2YMe]_2$; **3**: $[Cp^{TMS}_2LuMe]_2$. [c] Regioselectivity was determined by GC analysis of the crude product. [d] Cyclohexane was used as the solvent. [e] Toluene was used as the solvent. [f] Hydrogenation and/or isomerization was observed.

Table 4
Results for hydrosilylation reaction of alkynylsilanes with aryl substitution [a]

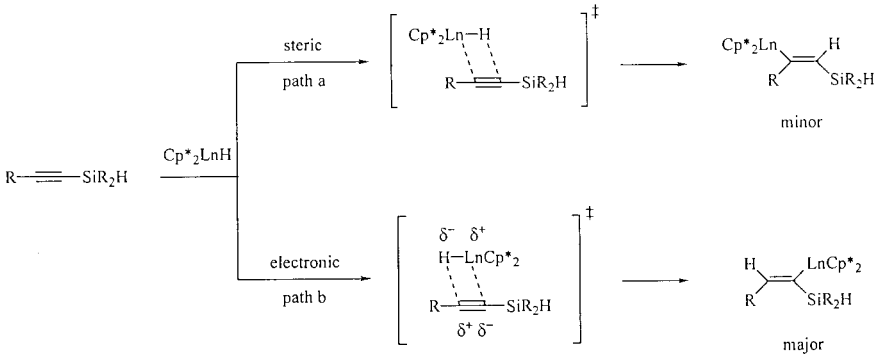


n	Catalyst [b]	Conditions	Product	% isolated yield	Selectivity[c] major:minor
0 (**13**)	**1**	100 °C, 4 d	**14a**	36	3:2
0 (**13**)	**2**	60 °C, 24 h; 80 °C, 12 h	**14a**	75[d]	1:1
0 (**13**)	**3**	50 °C, 24 h	**14a**	77	10:1
2 (**7**)	**1**	100 °C, 5 d	**15a**	28	8:1
2 (**7**)	**2**	100 °C, 5 d	**15a**	28	37:1
2 (**7**)	**3**	100 °C, 2 d	**15a**	27	43:1

[a] All heated reactions were performed in NMR tubes equipped with a J-Young valve [62]. Reactions were performed in C_6D_6 and monitored by ^{1}H-NMR for completion. Polymerization was also observed.
[b] Catalyst **1**: $Cp^*_2YMe{\cdot}THF$; **2**: $[Cp^{TMS}_2YMe]_2$; and **3**: $[Cp^{TMS}_2LuMe]_2$.
[c] Regioselectivity was determined by GC analysis of the crude product.
[d] Isolated as a mixture of diastereomers.

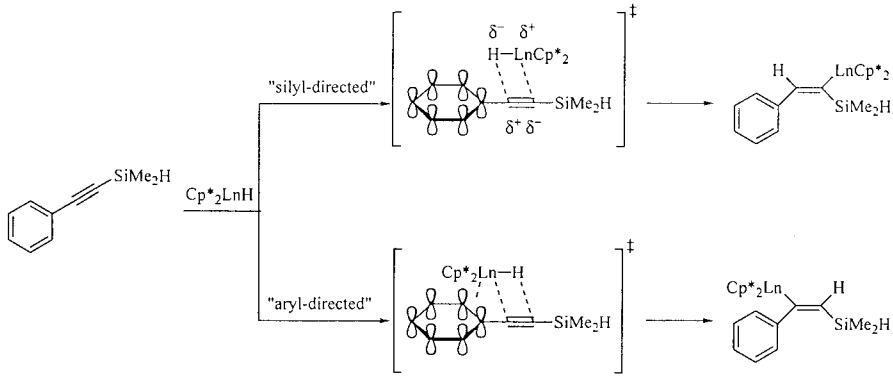
α-directive effect of silicon has been observed in the hydroalumination [64] and the hydroborations of (1-trimethylsilyl)alkynes [66–69].

With regard to the hydrosilylation of (phenylethynyl)dimethylsilane, the aryl group directs the lanthanide to the benzylic position by serving as a Lewis



(1)

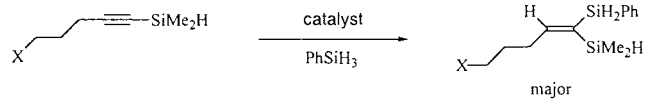
base (Eq. 2) [11,60]. The competition between the 'aryl-directed' and 'silyl-directed' processes results in the observed loss of selectivity [11,60].



(2)

In conclusion, the organolanthanide- and Group 3 metallocene-catalyzed hydrosilylation of alkynylsilanes has been studied and found to provide the (*Z*)-1,1-bis(silyl)alkene with good to excellent regioselectivity. The more 'open' organometallics, **2** and **3**, have been shown to be efficient precatalysts for the transformation. Regioselectivity of the reaction was induced predominantly by the electronics of the alkynylsilane moiety. Propargylic substitution provides enough steric influence to afford essentially one regioisomer. The process is tolerant of silylethers and halogens within the substrate. Finally, combining aryl and silyl substitution on the alkyne results in opposing directing forces, with a concomitant loss of regioselectivity.

Table 5
Results for hydrosilylation reaction of functionalized alkynylsilanes [a]



X	Catalyst [b]	Conditions (°C, h)	Product	% isolated yield	Selectivity [c] major:minor
Cl (**8**)	**2**	50, 72	**16**	35 [d,e]	52:1
Cl (**8**)	**3**	50, 19	**16**	70 [e,f]	50:1
TBSO (**9**)	**2**	50, 72	**17**	44 [g]	21:1
TBSO (**9**)	**3**	50, 88	**17**	82 [h]	>470:1

[a] All heated reactions were performed in sealed tubes originally prepared in a glove box. Toluene was used as the solvent.
[b] Catalyst **1**: $Cp^*_2YMe{\cdot}THF$; **2**: $[Cp^{TMS}_2YMe]_2$; and **3**: $[Cp^{TMS}_2LuMe]_2$.
[c] Regioselectivity was determined by GC analysis of the crude product.
[d] ^{1}H-NMR indicated 18% starting material in the crude mixture.
[e] Decomposition observed.
[f] ^{1}H-NMR indicated 3% starting material in the crude reaction mixture.
[g] ^{1}H-NMR indicated 17% starting material in the crude reaction mixture.
[h] ^{1}H-NMR indicated 8% starting material in the crude reaction mixture.

3. Experimental

3.1. Materials and methods

All NMR spectra were recorded on a 300 or 500 MHz spectrometer. All catalytic experiments were performed in a nitrogen-filled glovebox or in a sealed reaction vessel initially prepared in the glovebox. The organolanthanide complexes **1** [70], **2** and **3** [71] were prepared according to literature procedures. The following compounds were synthesized according to literature procedures: ethynylcyclohexane [72], **4j** [13], **4k** [13], and 5-(*tert*-butyldimethylsiloxy)-1-pentyne [73]. Diethyl ether and THF were distilled from sodium–benzophenone ketyl immediately before use. Cyclohexane and benzene-d_6 were distilled from sodium–benzophenone ketyl and stored in a glovebox. Phenylsilane (Aldrich), phenylmethylsilane (Gelest), and toluene were distilled from sodium metal, freeze–pump–thaw–degassed, and stored in a glovebox. 4-Methyl-1-hexyne (ChemSampCo.), 4-phenyl-1-butyne (Aldrich), and 5-chloro-1-pentyne (Acros) were used as received with no further purification. (Phenylethynyl)dimethylsilane (Aldrich) was distilled from powdered 4 Å mol sieves, degassed, and stored in a glovebox. All products synthesized were found to be $>95\%$ pure by capillary GC analysis unless otherwise indicated.

3.2. Preparation of 1-(dimethylsilyl)-1-decyne (4a). (general procedure for the preparation of 1-substituted alkynes)

To a THF solution of 1-decyne (2.56 g, 18.5 mmol) at 0 °C was added a 1.6 M solution of *n*-butyllithium in hexanes (14.0 ml, 22.4 mmol) via syringe. The mixture was stirred at 0 °C for 45 min before adding chlorodimethylsilane (3.00 g, 31.0 mmol) via syringe. The reaction was allowed to warm to room temperature (r.t.) overnight. The reaction was quenched with pH 7 buffer solution (1 ml), dried over $MgSO_4$, filtered through a pad of silica, and concentrated in vacuo. The crude material was Kugelrohr distilled to provide the title compound in 87% yield: oven temperature (ot) 115–130 °C/15–20 mmHg; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.10–4.07 (m, 1H), 2.19 (td, $J = 1.0$, 7.2 Hz, 2H), 1.52–1.46 (m, 2H), 1.38–1.31 (m, 2H), 1.29–1.22 (m, 8H), 0.86 (t, $J = 7.2$ Hz, 3H), 0.18 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 109.26, 81.23, 31.82, 29.15, 29.05, 28.81, 28.50, 22.65, 19.90, 14.08, −2.73; IR (neat, cm^{-1}): 2136.9, 2177.0; HRMS: calc. for $C_{12}H_{23}Si$ $[M-H]^+$: 195.1564; found: 195.1566; EILRMS; m/z: 181 (7), 98 (100), 59 (93).

3.3. 1-(Diisopropylsilyl)-1-decyne (4b)

1-(Diisopropylsilyl)-1-decyne (**4b**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by flash chromatography and Kugelrohr distilled to provide the title compound in 77% yield: ot 80–85 °C/0.1 mmHg; R_f 0.50 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.65 (s, 1H), 2.23 (td, $J = 1.0$, 7.0 Hz, 2H), 1.54–1.48 (m, 2H), 1.41–1.36 (m, 2H), 1.31–1.21 (m, 8H), 1.03 (t, $J = 8.5$ Hz, 12H), 1.00–0.91 (m, 2H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 110.49, 77.63, 31.82, 29.20, 29.03, 28.72, 28.63, 22.67, 19.89, 18.49, 18.22, 14.09; IR (neat, cm^{-1}): 2174.0, 2117.7; HRMS: calc. for $C_{16}H_{32}Si$: 252.2273; found: 252.2268; EILRMS; m/z: 252 (22), 209 (100), 111 (80), 97 (82).

3.4. 1-(Di-tert-butylsilyl)-1-decyne (4c)

1-(Di-*tert*-butylsilyl)-1-decyne (**4c**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by Kugelrohr distillation to provide the title compound in 85% yield: ot 90–100 °C/0.1 mmHg; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.54 (s, 1H), 2.23 (td, $J = 0.9$, 7.0 Hz, 2H), 1.54–1.48 (m, 2H), 1.42–1.37 (m, 2H), 1.29–1.25 (m, 8H), 1.03 (s, 18H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 110.03, 78.55, 31.81, 29.21, 29.02, 28.72, 28.65, 28.11, 22.66, 19.85, 18.44, 14.11; IR (neat, cm^{-1}): 2174.0, 2112.2; HRMS: calc. for $C_{18}H_{36}Si$: 280.2586; found: 280.2579; EILRMS; m/z: 280 (15), 223 (100), 195 (95).

3.5. 1-(Diphenylsilyl)-1-decyne (4d)

1-(Diphenylsilyl)-1-decyne (**4d**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by flash chromatography to provide the title compound in 85% yield: R_f 0.15 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.69–7.66 (m, 4H), 7.44–7.36 (m, 6H), 5.15 (s, 1H), 2.35 (td, $J = 1.1$, 7.1 Hz, 2H), 1.63–1.57 (m, 2H), 1.47–1.42 (m, 2H), 1.33–1.28 (m, 8H), 0.97–0.88 (m, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 135.07, 132.82, 129.89, 128.00, 112.94, 77.43, 31.81, 29.18, 29.05, 28.85, 28.40, 22.67, 20.14, 14.11; IR (neat, cm^{-1}): 2175.5, 2138.6; HRMS; calc. for $C_{22}H_{28}Si$: 320.1960; found: 320.1934; EILRMS; m/z: 320 (22), 183 (92), 105 (100).

3.6. 1-(Trimethylsilyl)-1-decyne (4e)

1-(Trimethylsilyl)-1-decyne (**4e**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by Kugelrohr distillation to provide the title compound in 99% yield. The NMR spectra closely matched the data reported in the literature [74]: ot 37–43 °C/0.1 mmHg.

3.7. 1-(Trimethylstannyl)-1-decyne (4f)

1-(Trimethylstannyl)-1-decyne (**4f**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by Kugelrohr distillation to provide the title compound in 76% yield. The NMR spectra closely matched the data reported in the literature [75]: ot 65–75 °C/0.1 mmHg.

3.8. 1-(Dimethylsilyl)-4-methyl-1-hexyne (5a)

1-(Dimethylsilyl)-4-methyl-1-hexyne (**5a**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 31% yield: R_f 0.51 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.13–4.10 (m, 1H), 2.22 (dd, $J = 5.7$, 16.9 Hz, 1H), 2.11 (dd, $J = 7.1$, 16.9 Hz, 1H), 1.62–1.56 (m, 1H), 1.49–1.41 (m, 1H), 1.28–1.20 (m, 1H), 0.98 (d, $J = 6.7$ Hz, 3H), 0.90 (t, $J = 7.5$ Hz, 3H), 0.23 (d, $J = 3.7$ Hz, 3H), 0.22 (d, $J = 3.7$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 108.16, 82.19, 34.18, 28.69, 26.90, 19.02, 11.46, −2.69; IR (neat, cm^{-1}): 2176.4, 2136.9; EILRMS; m/z: 153 (100), 139 (19), 83 (10).

3.9. 1-(Diisopropylsilyl)-4-methyl-1-hexyne (5b)

1-(Diisopropylsilyl)-4-methyl-1-hexyne (**5b**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 56% yield: R_f 0.58 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.68 (br s, 1H), 2.25 (ddd, $J = 1.1$, 5.6, 16.9 Hz, 1H), 2.16 (ddd, $J = 1.2$, 6.9, 16.8 Hz, 1H), 1.64–1.57 (m, 1H), 1.51–1.42 (m, 1H), 1.31–1.22 (m, 1H), 1.07 (d, $J = 6.9$ Hz, 6H), 1.06 (d, $J = 7.1$ Hz, 6H), 1.03–0.95 (m, 2H), 1.00 (d, $J = 6.7$ Hz, 3H), 0.90 (t, $J = 7.4$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 109.16, 78.57, 34.25, 28.64, 26.82, 19.06, 18.50, 18.21, 11.45, 10.93; IR (neat, cm^{-1}): 2173.9, 2117.2, 1461.9; HRMS: calc. for $C_{13}H_{26}Si$: 210.1804; found: 210.1805; CILRMS; m/z: 209 (100), 167 (54).

3.10. 2-Cyclohexyl-1-(dimethylsilyl)-1-ethyne (6a)

2-Cyclohexyl-1-(dimethylsilyl)-1-ethyne (**6a**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 35% yield: R_f 0.46 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.14–4.11 (m, 1H), 2.42–2.38 (m, 1H), 1.82–1.79 (m, 2H), 1.74–1.68 (m, 2H), 1.53–1.39 (m, 3H), 1.33–1.27 (m, 3H), 0.22 (d, $J = 3.7$ Hz, 3H), 0.21 (d, $J = 3.7$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 113.36, 80.73, 32.48, 30.07, 25.81, 24.80, −2.62; IR (neat, cm^{-1}): 2173.3, 1449.0; EILRMS; m/z: 151 (100), 138 (31), 83 (54).

3.11. 2-Cyclohexyl-1-(diisopropylsilyl)-1-ethyne (6b)

2-Cyclohexyl-1-(diisopropylsilyl)-1-ethyne (**6b**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 32% yield: R_f 0.57 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.68 (br s, 1H), 2.48–2.44 (m, 1H), 1.81–1.78 (m, 2H), 1.75–1.69 (m, 2H), 1.53–1.47 (m, 3H), 1.39–1.29 (m, 3H), 1.07 (d, $J = 7.0$ Hz, 6H), 1.06 (d, $J = 7.5$ Hz, 6H), 1.03–0.92 (m, 2H); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 114.65, 77.17, 32.55, 29.97, 25.89, 24.57, 18.52, 18.23, 10.91; IR (neat, cm^{-1}): 2173.4, 2116.5, 1462.2, 1448.5; HRMS; calc. for $C_{14}H_{25}Si$ $[M-H]^+$: 221.1726; found: 221.1729; CILRMS; m/z: 221 (100), 179 (51).

3.12. 1-(Dimethylsilyl)-4-phenyl-1-butyne (7)

1-(Dimethylsilyl)-4-phenyl-1-butyne (**7**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 79% yield: R_f 0.26 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.39–7.30 (m, 2H), 7.25–7.21 (m, 3H), 4.16–4.11 (m, 1H), 2.87 (t, $J = 7.6$ Hz, 2H), 2.56–2.52 (m, 2H), 0.24 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 140.49, 128.47, 128.36, 126.33, 108.20, 82.29, 34.96, 22.21, −2.81; IR (neat, cm^{-1}): 2177.2, 2135.3; HRMS; calc. for $C_{12}H_{16}Si$: 188.1021; found: 188.1012; CILRMS; m/z: 187 (88), 173 (91), 129 (100).

3.13. 5-Chloro-1-(dimethylsilyl)-1-pentyne (8)

To a THF solution of 5-chloro-1-pentyne in THF (2.51 g, 24.5 mmol) at −15 °C was added a 1.52 M solution of *n*-butyllithium in hexanes (17.9 ml, 27.2 mmol) via syringe. The mixture warmed to 0 °C and then was cooled to −15 °C for 15 min before adding chlorodimethylsilane (2.43 g, 25.7 mmol) via syringe. The reaction was complete after 20 min, as indicated by TLC. The reaction was quenched with pH 7 buffer solution (1 ml), dried over $MgSO_4$, filtered through a pad of silica and concentrated in vacuo. The crude material was purified by column chromatography to provide the title compound in 29% yield: R_f 0.31 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.12–4.09 (m, 1H), 3.65 (t, $J = 6.4$ Hz, 2H), 2.43 (dt, $J = 1.0$, 6.9 Hz, 2H), 1.99–1.95 (m, $J = 6.6$ Hz, 2H), 0.22 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 106.68, 82.64, 43.48, 31.15, 17.29, −2.88; IR (neat, cm^{-1}); 2177.2, 2137.5; EILRMS; m/z: 145 (2), 93 (100), 83 (10), 63 (11), 59 (8).

3.14. 5-(tert-Butyldimethylsiloxy)-1-(dimethylsilyl)-1-pentyne (9)

5-(*tert*-Butyldimethylsiloxy)-1-(dimethylsilyl)-1-pentyne (**9**) was prepared according to the general procedure for the preparation of **4a**. The crude material was purified by column chromatography to provide the title compound in 48% yield: R_f 0.15 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 4.11–4.10 (m, 1H), 3.69 (t, $J = 6.1$ Hz, 2H), 2.32 (t, $J = 7.0$ Hz, 2H), 1.72 (m, 2H), 0.90 (s, 9H), 0.21 (d, $J = 3.8$ Hz, 6H), 0.06 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 108.69, 81.55, 61.43, 31.42, 25.93, 18.33, 16.30, −2.75, −5.73; IR (neat, cm^{-1}) 2178.3, 2136.7; HRMS; calc. for $C_{13}H_{28}OSi_2$: 256.1679; found: 256.1669; CILRMS; m/z: 255 (70), 199 (100).

3.15. (Z)-1-(Dimethylsilyl)-1-(phenylsilyl)-1-decene (10a). (representative procedure for the hydrosilylation of an alkyne with organolanthanide catalysts)

In a sealed tube initially prepared in the glovebox, Cp_2^*YMe·THF (10 mg, 4.9 mol%) was dissolved in cyclohexane (1.0 ml). To this solution was added **4a** (89 mg, 0.45 mmol) and phenylsilane (60 mg, 0.55 mmol). The reaction was stirred at 50 °C for 48 h. The reaction was filtered through a small plug of silica to remove the catalyst and concentrated by rotary evaporation. The crude product was purified by flash chromatography and Kugelrohr distillation to provide the title compound in 67% yield: ot 85–95 °C/0.1 mmHg; R_f 0.50 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.55–7.53 (m, 2H), 7.40–7.33 (m, 3H), 6.95 (t, $J = 7.0$ Hz, 1H), 4.61 (s, 2H), 4.35–4.32 (m, 1H), 2.32 (q, $J = 7.4$ Hz, 2H), 1.47–1.41 (m, 2H), 1.34–1.24 (m, 10H), 0.90 (t, $J = 7.0$ Hz, 3H), 0.12 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 164.94, 135.46, 133.12, 130.17, 129.45, 127.88, 35.73, 31.88, 29.48, 29.33, 29.26, 29.08, 22.70, 14.12, −2.90; IR (neat, cm^{-1}); 2132.2; EILRMS; m/z: 259 (53), 135 (100), 121 (92); Anal. Calc. for $C_{18}H_{32}Si_2$: C, 70.97; H, 10.59; Found: C, 71.10; H, 10.76.

3.16. (Z)-1-(Diisopropylsilyl)-1-(phenylsilyl)-1-decene (10b)

(*Z*)-1-(Diisopropylsilyl)-1-(phenylsilyl)-1-decene (**10b**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at r.t. in the glovebox. The reaction was complete after 5 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 84% yield: R_f 0.64 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56–7.54 (m, 2H), 7.38–7.32 (m, 3H), 6.94 (t, $J = 6.9$ Hz, 1H), 4.60 (s, 2H), 3.79 (t, $J = 3.8$ Hz, 1H), 2.27 (q, $J = 7.5$ Hz, 2H), 1.41–1.37 (m, 2H), 1.29–1.21 (m, 10H), 1.09–1.00 (m, 2H), 0.99 (d, $J = 6.6$ Hz, 6H), 0.91 (d, $J = 6.9$ Hz, 6H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 165.72, 135.70, 132.96, 129.42, 127.82, 127.22, 36.74, 31.86, 29.46, 29.36, 29.23, 29.06, 22.69, 19.26, 19.11, 14.12, 11.54; IR (neat, cm^{-1}): 2126.9; HRMS: calc. for $C_{17}H_{33}Si_2$: 317.2121; found: 317.2104; EILRMS; m/z: 317 (100), 275 (11), 149 (36); Anal. Calc. for $C_{20}H_{40}Si_2$: C, 73.25; H, 11.18; Found: C, 72.99; H, 11.37.

3.17. (Z)-1-(Di-tert-butylsilyl)-1-(phenylsilyl)-1-decene (10c)

(*Z*)-1-(Di-*tert*-butylsilyl)-1-(phenylsilyl)-1-decene (**10c**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 40 °C in a sealed tube. The reaction was complete after 24 h as indicated by GC analysis. Workup and purification by flash chromatography and Kugelrohr distillation gave the title compound in 59% yield. The product was found to be >90% pure by GC analysis: ot 90–100 °C/0.1 mmHg; R_f 0.65 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.56–7.54 (m, 2H), 7.39–7.30 (m, 3H), 6.92 (t, $J = 7.1$ Hz, 1H), 4.72 (s, 2H), 2.39 (q, $J = 7.3$ Hz, 1H), 2.26–2.19 (m, 1H), 1.43–1.20 (m, 13H), 1.03–0.95 (m, 18H), 0.87 (t, $J = 6.8$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 167.97, 135.81, 135.37, 129.45, 127.93, 127.73, 34.93, 31.85, 29.67, 29.42, 29.30, 29.24, 29.10, 28.74, 22.68, 19.59, 19.27, 14.11; IR (neat, cm^{-1}) 2122.0; HRMS; calc. for $C_{24}H_{44}Si_2$ $[M - {}^tBu]^+$: 331.2277; found: 331.2246; EILRMS; m/z: 331 (100), 121 (84); Anal. Calc. for $C_{24}H_{44}Si_2$: C, 74.15; H, 11.41; Found: C, 74.54; H, 11.26.

3.18. (Z)-1-(Diphenylsilyl)-1-(phenylsilyl)-1-decene (10d)

(*Z*)-1-(Diphenylsilyl)-1-(phenylsilyl)-1-decene (**10d**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 50°C in a sealed tube. The reaction was complete after 48 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 40% yield: R_f 0.15 (hexanes); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.47–7.45 (m, 5H), 7.37–7.21 (m, 11H), 7.16 (t, $J = 6.9$ Hz, 1H), 5.29 (s, 1H), 4.53 (s, 2H), 2.23 (q, $J = 7.5$ Hz, 2H), 1.30–1.11 (m, 12H), 0.87 (t, $J = 6.9$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 167.76, 135.64, 135.52, 133.55, 132.52, 129.48, 129.35, 127.82, 127.73, 126.67, 36.79, 31.79, 29.31, 29.15, 28.66, 22.65, 14.12; IR (neat, cm^{-1}): 2124.1; HRMS; calc. for $C_{28}H_{36}Si_2$: 428.2356; found: 428.2328; EILRMS; m/z: 350 (11), 183 (100), 139 (90); Anal. Calc. for $C_{28}H_{36}Si_2$: C, 78.44; H, 8.46; Found: C, 78.54; H, 8.69.

3.19. (Z)-1-(Dimethylsilyl)-4-methyl-1-(phenylsilyl)-1-hexene (**11a**)

(*Z*)-1-(Dimethylsilyl)-4-methyl-1-(phenylsilyl)-1-hexene (**11a**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 4 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 52% yield: R_f 0.66 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.64–7.51 (m, 2H), 7.45–7.33 (m, 3H), 6.99 (t, $J = 7.0$ Hz, 1H), 4.63 (s, 2H), 4.39–4.32 (m, 1H), 2.42–2.32 (m, 1H), 2.23–2.15 (m, 1H), 1.62–1.51 (m, 1H), 1.47–1.36 (m, 1H), 1.27–1.17 (m, 1H), 0.93 (d, $J = 6.9$ Hz, 3H), 0.92 (t, $J = 7.6$ Hz, 3H), 0.14 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 164.08, 135.45, 133.17, 131.05, 129.45, 127.90, 42.49, 34.92, 29.40, 19.18, 11.54, −2.94; IR (neat, cm^{-1}): 2124, 1570.0; HRMS; calc. for $C_{15}H_{25}Si_2$ $[M-H]^+$: 261.1495; found: 261.1498; EILRMS; *m*/*z*: 261 (100), 201 (22), 185 (37).

3.20. (Z)-1-(Diisopropylsilyl)-4-methyl-1-(phenylsilyl)-1-hexene (**11b**)

(*Z*)-1-(Diisopropylsilyl)-4-methyl-1-(phenylsilyl)-1-hexene (**11b**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 20 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 82% yield: R_f 0.67 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.57–7.55 (m, 2H), 7.39–7.31 (m, 3H), 6.99 (t, $J = 6.9$ Hz, 1H), 4.62 (s, 2H), 3.84 (t, $J = 3.7$ Hz, 1H), 2.35–2.29 (m, 1H), 2.18–2.12 (m, 1H), 1.54–1.46 (m, 1H), 1.41–1.32 (m, 1H), 1.22–1.12 (m, 1H), 1.11–1.03 (m, 2H), 1.01, (d, $J = 6.6$ Hz, 6H), 0.92 (d, $J = 6.9$ Hz, 6H), 0.89–0.86 (m, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 165.09, 135.71, 133.02, 129.45, 128.42, 127.85, 43.22, 35.06, 29.45, 19.25, 19.18, 19.17, 19.16, 11.56, 11.50; IR (neat, cm^{-1}); 2124.3, 1567.5; HRMS; calc. for $C_{19}H_{33}Si_2$ $[M-H]^+$: 317.2121; found: 317.2106; EILRMS; *m*/*z*: 317 (100), 275 (39), 257 (10), 241 (37).

3.21. (Z)-2-Cyclohexyl-1-(dimethylsilyl)-1-(phenylsilyl)-1-ethene (**12a**)

(*Z*)-2-Cyclohexyl-1-(dimethylsilyl)-1-(phenylsilyl)-1-ethene (**12a**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 40 °C in a sealed tube. The reaction was complete after 24 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 71% yield: R_f 0.62 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53–7.51 (m, 2H), 7.39–7.32 (m, 3H), 6.73 (t, $J = 9.5$ Hz, 1H), 4.58 (s, 2H), 4.31–4.28 (m, 1H), 2.43–2.30 (m, 1H), 1.76–1.72 (m, 2H), 1.68–1.64 (m, 3H), 1.33–1.24 (m, 2H), 1.21–1.11 (m, 3H), 0.11 (d, $J = 3.8$, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 170.09, 135.43, 133.19, 129.42, 127.87, 127.50, 44.59, 32.28, 25.84, 25.53, −2.58; IR (neat, cm^{-1}) 2123.8, 1571.1; HRMS; calc. for $C_{16}H_{25}Si_2$ $[M-H^+]$: 273.1495; found: 273.1496; EILRMS; *m*/*z*: 273 (100), 259 (16).

3.22. (Z)-2-Cyclohexyl-1-(diisopropylsilyl)-1-(phenylsilyl)-1-ethene (**12b**)

(*Z*)-2-Cyclohexyl-1-(diisopropylsilyl)-1-(phenylsilyl)-1-ethene (**12b**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 72 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 58% yield: R_f 0.66 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.60–7.54 (m, 2H), 7.41–7.34 (m, 3H), 6.77 (t, $J = 9.5$ Hz, 1H), 4.62 (s, 2H), 3.79 (t, $J = 3.3$ Hz, 1H), 2.40–2.32 (m, 1H), 1.75–1.72 (m, 2H), 1.69–1.64 (m, 3H), 1.32–1.23 (m, 2H), 1.21–1.10 (m, 3H), 1.09–1.04 (m, 2H), 1.03, (d, $J = 5.4$ Hz, 6H), 0.94 (d, $J = 6.4$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 170.58, 135.69, 133.00, 129.40, 127.80, 127.47, 45.49, 32.18, 25.86, 25.51, 19.19, 19.13, 11.52; IR (neat, cm^{-1}): 2126.4, 1570.1; HRMS; calc. for $C_{20}H_{33}Si_2$ $[M-H]^+$: 329.2121; found: 329.2126; EILRMS; *m*/*z*: 329 (100), 253 (21).

3.23. (Z)-1-(Dimethylsilyl)-2-phenyl-1-(phenylsilyl)-1-ethene (**14**)

(*Z*)-1-(Dimethylsilyl)-2-phenyl-1-(phenylsilyl)-1-ethene (**14**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}LuMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 24 h as indicated by ^{1}H-NMR analysis. Workup and purification by flash chromatography gave the title compound in 77% yield: R_f 0.45 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.62–7.60 (m, 2H), 7.40–7.28 (m, 8H), 4.76 (s, 2H), 4.38–4.35 (m, 1H), 0.10 (d, $J = 3.5$ Hz, 3H), 0.08 (d, $J = 3.5$ Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 160.12, 140.32, 135.64, 135.32, 132.55, 129.70, 128.40, 128.03, 127.97, 127.28, −2.70; IR (neat, cm^{-1}): 2124.3, 1552.8; HRMS; calc. for $C_{16}H_{19}Si_2$ $[M-H]^+$: 267.1025, found: 267.1036; EILRMS; *m*/*z*: 267 (100), 253 (14).

3.24. (Z)-1-(Dimethylsilyl)-4-phenyl-1-(phenylsilyl)-1-butene (**15**)

(*Z*)-1-(Dimethylsilyl)-4-phenyl-1-(phenylsilyl)-1-butene (**15**) was prepared according to the general

procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}YMe]_2$ at 100 °C in a sealed tube. The reaction was complete after 5 days as indicated by ^{1}H-NMR analysis. Workup and purification by flash chromatography gave the title compound in 28% yield: R_f 0.34 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.50–7.48 (m, 2H), 7.43–7.32 (m, 3H), 7.29–7.23 (m, 2H), 7.22–7.14 (m, 3H), 6.97–6.95 (t, $J = 6.9$ Hz, 1H), 4.59 (s, 2H), 4.34–4.28 (m, 1H), 2.76–2.73 (m, 2H), 2.66–2.61 (m, 2H), 0.07 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 163.07, 141.35, 135.49, 132.79, 131.59, 129.49, 128.36, 125.95, 37.40, 35.36, −3.05; IR (neat, cm^{-1}) 2123.7, 1571.0; HRMS; calc. for $C_{18}H_{23}Si_2$ $[M-H]^+$: 295.1338, found: 295.1331; EILRMS; m/z: 295 (100), 219 (50).

3.25. (*Z*)-5-Chloro-1-(dimethylsilyl)-1-(phenylsilyl)-1-pentene (**16**)

(*Z*)-5-Chloro-1-(dimethylsilyl)-1-(phenylsilyl)-1-pentene (**16**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}LuMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 19 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 70% yield: R_f 0.37 (petroleum ether 40–60); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.53–7.52 (m, 2H), 7.40–7.33 (m, 3H), 6.87 (t, $J = 7.0$ Hz, 1H), 4.60 (s, 2H), 4.38–4.32 (m, 1H), 3.55 (t, $J = 6.6$ Hz, 2H), 2.50–2.46 (m, 2H), 1.95–1.89 (m, 2H), 0.13 (d, $J = 3.8$ Hz, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 161.80, 135.48, 132.87, 132.67, 129.60, 127.97, 44.31, 32.78, 31.98, −3.03; IR (neat, cm^{-1}): 2124.3, 1573.1; HRMS; calc. for $C_{13}H_{20}ClSi_2$ $[M-H]^+$: 267.0792; found: 267.0785; EILRMS; m/z: 267 (100), 207 (13), 191 (30).

3.26. (*Z*)-5-(*tert*-Butyldimethylsiloxy)-1-(dimethylsilyl)-1-(phenylsilyl)-1-pentene (**17**)

(*Z*)-5-(*tert*-Butyldimethylsiloxy)-1-(dimethylsilyl)-1-(phenylsilyl)-1-pentene (**17**) was prepared according to the general procedure for the preparation of **10a** using 5 mol% $[Cp_2^{TMS}LuMe]_2$ at 50 °C in a sealed tube. The reaction was complete after 88 h as indicated by GC analysis. Workup and purification by flash chromatography gave the title compound in 82% yield: R_f 0.24 (98:2 hexanes:EtOAc); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.40–7.32 (m, 3H), 6.94 (t, $J = 7.0$ Hz, 1H), 4.59 (s, 2H), 4.34–4.29 (m, 1H), 3.63 (t, $J = 6.4$ Hz, 2H), 2.40–2.36 (m, 2H), 1.68–1.63 (m, 2H), 0.90 (s, 9H), 0.12 (d, $J = 3.8$ Hz, 6H), 0.05 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$); δ 164.06, 135.46, 133.00, 130.84, 129.48, 127.91, 62.59, 32.27, 32.21, 18.33, −2.97, −5.30; IR (neat, cm^{-1}): 2124.0, 1572.7; HRMS; calc. for $C_{19}H_{35}OSi_3$ $[M-H]^+$: 363.1996; found: 363.1997; EILRMS; m/z: 363 (100), 349 (57), 307 (69), 287 (26).

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