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Cyclic 1,1-bis(silyl)alkenes—new building blocks for the stereoselective synthesis of unsymmetrical (*E*)-stilbenes and (*E*,*E*)-1,4-diarylbuta-1,3-dienes

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ABSTRACT

A new efficient synthetic protocol for the highly stereoselective synthesis of unsymmetrical (or symmetrical) (*E*)-stilbenes and (*E*,*E*)-1,4-diarylbuta-1,3-dienes based on sequential palladium-catalyzed Heck arylation–Hiyama *cross*-coupling reactions using cyclic *gem*-bis(silyl)ethene as alkenyl building block is reported.

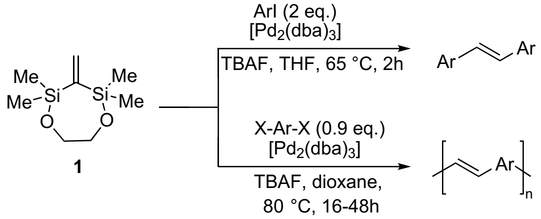
1. Introduction

Highly conjugated π-electron compounds such as stilbenes or aryl-substituted polyenes have gained a lot of attention because of their wide range of biological activities and potential therapeutic values.[1] The conjugated polyenes are essential in functional materials such as organic fluorescent probes, electroluminescent devices and nonlinear optical materials.[2] Of the available methods for preparation of stilbenes, the transition metal-catalyzed processes utilizing the C–C or C=C bond formation reactions are the most convenient, powerful and selective approaches. Indeed, most strategies developed so far involve palladium-catalyzed coupling reactions.[3] Among them, protocols based on the Heck,[4] Suzuki,[5] Stille[6] and Negishi[7] reactions stand out for their synthetic versatility and efficiency. Alternative transition metal-catalyzed syntheses involve the titanium-mediated McMurry coupling of aldehydes[8] and ruthenium-catalyzed cross-metathesis of substituted styrenes.[9]

A number of methodologies for the preparation of aryl-substituted 1,3-butadienes based on palladium-catalyzed cross-coupling of vinyl halides with alkenyl-substituted organometallic compounds of boron,[10] tin,[6a,11] zinc,[12] silicon[13] or zirconium[14] have been developed over the last two decades. The complementary synthetic routes involving bis-metallated 1,3-butadienyl building blocks are represented by palladium-catalyzed cross-coupling of aryl halides with 1,4-bis(silyl)-,[15] 2,3-bis(boryl)-,[16] 2-aryl-3-silyl-[17] or 1-boryl-4-stannylbuta-1,3-dienes.[18] An alternative approach based on cross-coupling reactions of organometallic reagents with bis-electrophilic buta-1,3-dienes has also been reported.[19]

The palladium-catalyzed and fluoride-promoted cross-coupling of unsaturated organosilicon compounds with aryl halides (Hiyama coupling) has been recently employed as a mild and efficient alternative to the well-established Stille and Suzuki reactions due to commercial availability, high stability and low toxicity of the silicon derivatives.[20] In view of the above advantages, several synthetic methodologies based on sequential hydrosilylation/Hiyama coupling,[21] Heck arylation/Hiyama coupling[22] or silylative coupling/Hiyama coupling[23] processes, in which unsaturated organosilicon precursors or intermediates have been utilized as versatile double bond equivalents in the iterative construction of π-conjugated systems, have been reported.

In the preliminary communication, we have reported that 2,2,4,4-tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane



Scheme 1. Synthesis of symmetrical (*E*)-stilbene derivatives using 2,2,4,4-tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane **1** as a platform.

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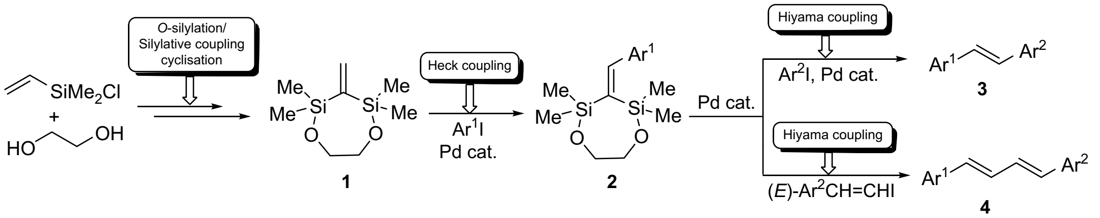
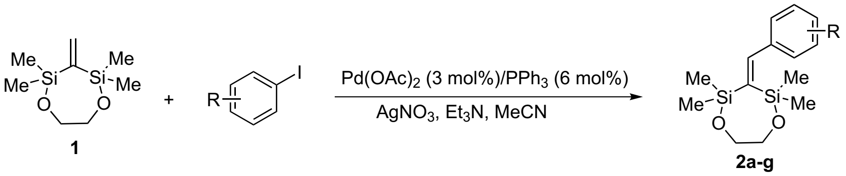


Scheme 2. Synthetic strategy for unsymmetrical (*E*)-stilbenes and (*E*,*E*)-1,4-diaryl-1,3-dienes.



Scheme 3. Pd-catalyzed Heck coupling of **1** with aryl iodides.

1, in the reaction with 2 equiv of aryl iodides, under standard cross-coupling conditions forms exclusively (instead of expected 1,1-diarylethenes) *cine*-substitution products with perfect stereoselectivity and almost quantitative yield.[24] A double bond of bis(silyl)alkene can thus be very efficiently grafted into aromatic structure, offering the potential of constructing symmetrical (*E*)-stilbene derivatives. The extension of this new silicon-assisted protocol for aryl dihalides has led to stereoselective synthesis of (*E*)-poly(arylenevinylene)s (Scheme 1).[24]

Since the starting compound **1** can be easily prepared with high yield in a two-step process from inexpensive chlorodimethylvinylsilane and ethylene glycol by silylation–ruthenium-catalyzed silylative coupling *exo*-cyclization sequence,[25] this novel bis(silyl)ethene transformation is expected to be an attractive alternative for the synthesis of unsymmetrically-substituted π-systems using sequential Pd-catalyzed C–H arylation (Heck coupling) and C–Si arylation (Hiyama coupling).

Therefore, herein we report our results on the use of cyclic 1,1-bis(silyl)ethene **1** as a new platform for the sequential installation of aryl groups onto C=C core, which leads to unsymmetrically-functionalized (*E*)-stilbenes and (*E*,*E*)-1,4-diaryl-substituted buta-1,3-dienes (Scheme 2).

2. Results and discussion

2.1. Heck coupling of cyclic 1,1-bis(silyl)ethene 1 with aryl iodides

Since we have recently reported an efficient procedure for the selective Heck coupling of acyclic 1,1-bis(silyl)ethenes with aryl and alkenyl iodides,[26] the coupling of **1** with aryl iodides was performed in the presence of palladium(II) acetate/triphenylphosphine as catalyst, using triethylamine and silver nitrate as iodine abstractor.[27] After several attempts, we found that the reaction of compound **1** (1 equiv) with 1 equiv of aryl iodide, 1 equiv of $AgNO_3$ and 1.5 equiv of Et_3N, in the presence of 3 mol % of $Pd(OAc)_2$ and 6 mol % of PPh_3, conducted in acetonitrile at 60 °C for 1 h, afforded exclusively the corresponding 2,2,4,4-tetramethyl-1,5-dioxa-3-benzylidene-2,4-disilacycloheptane derivatives (Scheme 3) in good yield (compounds **2a**–**g**, Table 1). The noteworthy features of these processes are that the formation of styrene and symmetrical stilbene derivatives (via desilylation) was completely suppressed, and the formation of biaryls (by *homo*-coupling of the aryl iodides) was not observed. Moreover, the Heck coupling occurred under mild conditions with a wide array of electronically (similar reaction rates were obtained with electron-rich and electron-poor aryl iodides) and structurally diverse aryl iodides (Table 1).

Table 1
Palladium-catalyzed Heck coupling of **1** with aryl iodides

R	Compound	Yield[a] (%)
H	**2a**	82
4-Ac	**2b**	72
4-NO_2	**2c**	67
3-MeO	**2d**	88
4-MeO	**2e**	80
4-Me	**2f**	85
4-Cl	**2g**	90

Reaction conditions: 60 °C, $[Pd(OAc)_2]:[PPh_3]:[AgNO_3]:[Et_3N]:[ArI]:[1]=0.03:0.06:1:1.5:1:1$.

[a] Isolated yields of chromatographically pure products.

The 2,2,4,4-tetramethyl-3-(4-acetyl)benzylidene-1,5-dioxa-2,4-disilacycloheptane **2b** proved to be a solid and yielded a crystal amenable to X-ray structure determination. Thermal-ellipsoid representation of molecule **2b** is shown in Figure 1. The conformation of the seven-membered ring in **2b** can be described as close to a 'pseudo-chair': five atoms C1, O3, C4, O6 and Si7 make an approximate plane while the remaining two: C5 and Si2 are significantly deviated in two opposite directions. To the best of our knowledge, this is the first structural characterization of a molecule containing such a seven-membered ring. In the crystal structure relatively strong C11–H11···O3(x, $y-1$, z) hydrogen bond connects the molecules into infinite chains along the [010] direction.

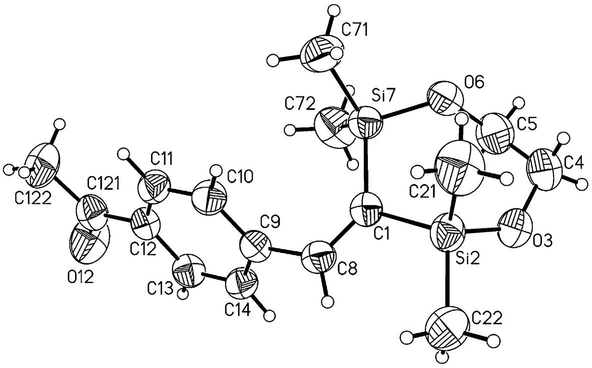
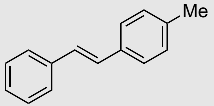
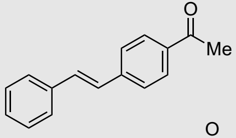
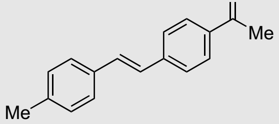
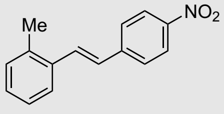
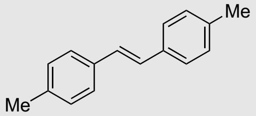
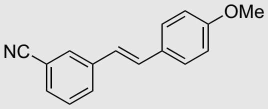
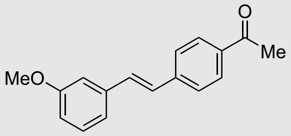
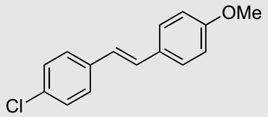


Figure 1. Perspective view of the molecule **2b**.[33] The anisotropic displacement ellipsoids were drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii.

Table 2
Synthesis of (*E*)-stilbenes

R^1	R^2	Product structure	Compound	Yield[a] (%)
H	4-Me		**3a**	86
4-Ac	H		**3b**	62
4-Me	4-Ac		**3c**	68
$4\text{-}NO_2$	2-Me		**3d**	62
4-Me	4-Me		**3e**	78
4-MeO	3-CN		**3f**	88
3-MeO	4-Ac		**3g**	92
4-Cl	4-MeO		**3h**	90

[**2**]:[ArI]:[TBAF]:[Pd]=1:0.9:2.4:0.01, THF, 60 °C.
[a] Isolated yields of products.

2.2. Synthesis of unsymmetrical (*E*)-stilbenes

Having established an efficient protocol for the Heck coupling of **1** with aryl iodides, we subsequently investigated the reactivity of thus-generated β-aryl-substituted cyclic 1,1-bis(silyl)ethenes **2a**–**g** towards selected aryl iodides under Hiyama cross-coupling conditions. Since trialkyl-substituted alkenylsilanes generally are extremely stable to chemical manipulation prior to fluoride activation, cyclic 1,1-bis(silyl)alkenes containing alkoxy groups **2a**–**g** seem to be essential for efficient reactivity.

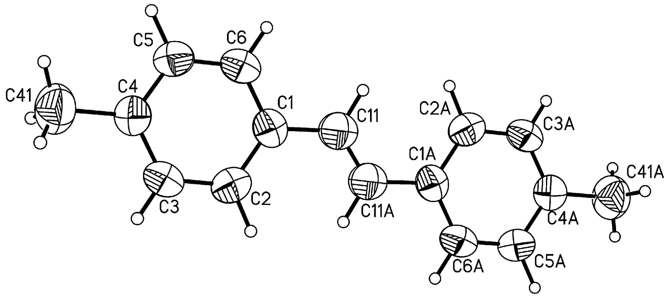


Figure 2. Perspective view of the molecule **3e**.[33] The anisotropic displacement ellipsoids were drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii. The letter A refers to the symmetry operation −*x*, 1−*y*, 1−*z*.

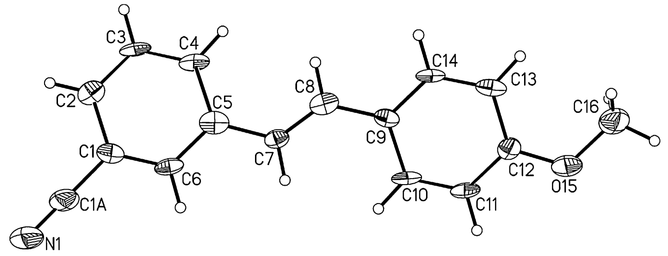


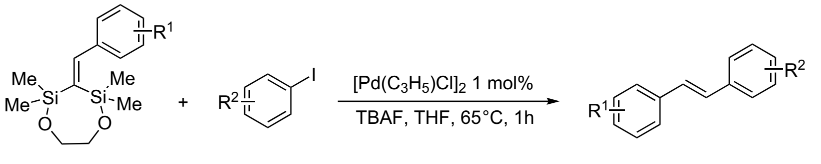
Figure 3. Perspective view of one of the symmetry-independent molecules of **3f** (A).[33] The anisotropic displacement ellipsoids were drawn at 50% probability level, hydrogen atoms are depicted as spheres with arbitrary radii.

Initial studies were carried out using 2,2,4,4-tetramethyl-3-benzylidene-1,5-dioxa-2,4-disilacycloheptane **2a** and 4-iodotoluene in the presence of allylpalladium(II) chloride dimer $[Pd(C_3H_5)Cl]_2$ catalyst (2 mol % Pd) and TBAF (2.4 equiv) as an activator. After several attempts, we found that its reaction with 2 equiv of aryl iodide conducted in THF at 60 °C for 1 h exclusively afforded the monosubstitution product—(*E*)-4-methylstilbene **3a**, as single stereoisomer. Although the protodesilylation of C–Si bonds mediated by TBAF in THF has been previously reported,[28] the simultaneous *ipso*-substitution and protodesilylation of geminally silylated alkenes under Hiyama cross-coupling conditions are unprecedented. To investigate the generality of this reaction, a series of cyclic 1,1-bis(silyl)-2-arylethenes (Heck coupling products) bearing various substituents in the aromatic ring were subjected to similar reaction conditions with commercially available functionalized aryl iodides. For the economical reasons, for further synthetic investigation we decided to decrease the necessary amount of the aryl iodide to 0.9 equiv, which additionally permitted avoiding the homo-coupling reaction of aryl iodides. In general, the reactions proceeded smoothly under mild conditions to give the corresponding unsymmetrical (*E*)-stilbenes in good yield (Table 2, Scheme 4).

Substituted (*E*)-stilbenes **3e** and **3f** proved to be solids and yielded crystals amenable to X-ray structure determination. Perspective views of these molecules are shown in Figures 2 and 3. The molecule **3e** occupies a special position in the space group *Pbca*: the middlepoint of the central C–C bond falls at the inversion centre; the molecule therefore has the C_i symmetry, and the phenyl rings are coplanar (Table 3). The crystal structure of **3f** contains two symmetry-independent molecules, of slightly different conformations. The dihedral angle between the least squares planes of the phenyl rings is 10.9(4)° in molecule A and 17.5(3)° in molecule B (Table 3).

2.3. Synthesis of unsymmetrical (*E*,*E*)-1,4-diarylbuta-1,3-dienes

A successful, simple and selective method of obtaining unsymmetrical (*E*)-stilbenes has prompted us to apply selected β-aryl-

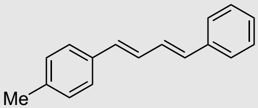
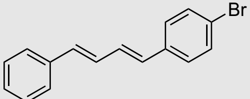
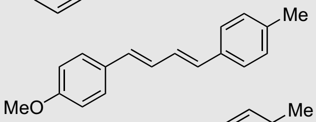
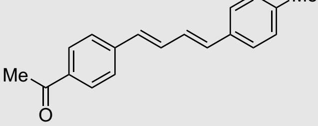


Scheme 4. Silicon-assisted synthesis of unsymmetrical (*E*)-stilbenes.

Table 3
Crystal data, data collection and structure refinement for **2b**, **3e** and **3f**

	2b	**3e**	**3f**
Formula	$C_{16}H_{24}O_3Si_2$	$C_{16}H_{16}$	$C_{16}H_{13}NO$
Formula weight	320.53	208.28	235.27
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_12_12_1$
a (Å)	13.752(2)	7.521(3)	7.1105(11)
b (Å)	9.083(1)	6.016(3)	11.1854(13)
c (Å)	14.571(1)	27.090(5)	30.944(3)
β (°)	92.41(1)	90	90
V (Å^3)	1818.4(4)	1225.7(8)	2461.1(6)
Z	4	4	8
D_x (g cm^{-3})	1.171	1.13	1.27
F (000)	688	448	992
μ (mm^{-1})	0.202	0.063	0.079
Θ range (°)	2.64–25.00	4.40–25.00	1.94–25.00
hkl range	$-14\leq h\leq 16$	$-8\leq h\leq 7$	$-8\leq h\leq 7$
	$-10\leq k\leq 9$	$-7\leq k\leq 7$	$-13\leq k\leq 13$
	$-17\leq l\leq 17$	$-31\leq l\leq 32$	$-36\leq l\leq 36$
Reflections			
Collected	8080	3225	14,786
Unique (R_{int})	3195 (0.020)	1060 (0.037)	4307 (0.118)
$R(F)$ [$I>2\sigma(I)$]	0.041	0.072	0.114
$wR(F^2)$ [$I>2\sigma(I)$]	0.114	0.120	0.272
Goodness of fit	1.08	1.07	1.06
max/min $\Delta\rho$ (e Å^{-3})	0.27/−0.22	0.32/−0.13	0.47/−0/39

Table 4
Synthesis of unsymmetrical (*E*,*E*)-1,4-diarylbuta-1,3-dienes

R^1	R^2	Product structure		(*E*,*E*)/(*Z*,*E*)	Yield[a] (%)
4-Me	H		**4a**	95/5	86
H	4-Br		**4b**	96/4	80
4-MeO	4-Me		**4c**	96/4	68
4-Ac	4-Me		**4d**	95/5	80

[**2**]:[ArCH═CHI]:[TBAF]:[Pd]═1:0.9:2.4:0.01, THF, 60 °C.
[a] Isolated yields of products.

substituted derivatives **2a**, **2b**, **2e** and **2f** in the synthesis of stereodefined (*E*,*E*)-1,4-diaryl-1,3-butadienes by their palladium-catalyzed Hiyama cross-coupling with (*E*)-styryl iodides. The optimal conditions established for the reactions of compounds **2a**–**g** with aryl iodides were applied to (*E*)-styryl iodides providing good yields (68–86%) of the desired unsymmetrical 1,4-diaryl-substituted buta-1,3-dienes (**4a**–**d**, Table 4). Thus, the coupling reactions were performed in THF using [Pd(C_3H_5)Cl]$_2$ (2 mol % Pd) as catalyst, in the presence of tetrabutylammonium fluoride (20% excess per silyl group) as the activator at 60 °C. It is worth noting that the Hiyama coupling processes proceeded in highly stereoselective manner to yield products containing (*E*,*E*)-dienes as predominant products, however, trace amounts of the respective (*E*,*Z*) isomers (4–5%) were also detected using the GC–MS method. Although the stereochemistry of dienes **4a**–**c** cannot be directly derived from the ^{1}H NMR spectra on the basis of the protons of the diene moiety, the analysis of spin systems by means of MestReC NMR software[19a] as well as comparison with literature data[15a,19a] allowed us to define a diene structure (Scheme 5).

3. Conclusions

In conclusion, a new application of cyclic 1,1-bis(silyl)ethene for the highly stereoselective construction of unsymmetrical (*E*)-stilbenes and (*E*,*E*)-1,4-diarylbuta-1,3-dienes based on sequential palladium-catalyzed Heck and Hiyama cross-coupling reactions is described. Further results on the application of this strategy to the synthesis of highly π-conjugated triene systems will be reported in due course.

4. Experimental

4.1. General

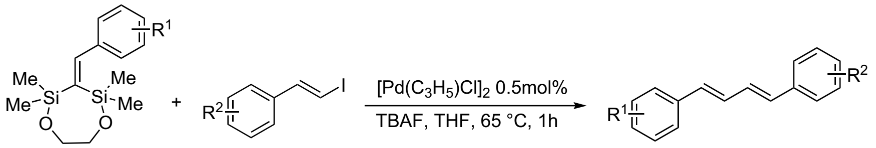
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian XL 300 spectrometer using $CDCl_3$ or as a solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Mass spectra of the products were determined by GC–MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finnigan Mat 800 ion trap detector. The Hiyama coupling reactions were performed under an atmosphere of deoxygenated and dried argon. Triethylamine was dried over CaH_2, distilled under argon and stored over molecular sieves type 4A. THF and acetonitrile as well as all the commercial materials were purchased from Aldrich and used without further purification. 2,2,4,4-Tetramethyl-1,5-dioxa-3-methylene-2,4-disilacycloheptane **1** was prepared using procedure described in literature.[25]

4.2. Representative procedure for Heck coupling of 1 with aryl iodides

A mixture consisting of 33.5 mg (0.15 mmol) of palladium(II) acetate, 78.6 mg (0.3 mmol) of triphenylphosphine, 0.85 g of silver nitrate (5 mmol), 5 mmol of aryl iodide, 5 mmol of cyclic 1,1-bis(silyl)ethene **1**, 1.05 mL (7.5 mmol) of triethylamine and 10 mL of acetonitrile was placed in 50 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 60 °C for 1 h. After cooling to room temperature, the solvent was evaporated and reaction mixture was extracted twice with 30 mL of hexane. The combined organic layers were dried ($MgSO_4$) and the crude product obtained was then purified by column chromatography (deactivated silica gel (5% Et_3N)/eluent—hexane) to give corresponding compounds **2a**–**g**.

*4.2.1. 2,2,4,4-Tetramethyl-3-benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2a**) (yield 82%)*

^{1}H NMR ($CDCl_3$) *δ* (ppm): 0.12 (s, 6H, $SiCH_3$), 0.36 (s, 6H, $SiCH_3$), 3.75–3.78 (m, 2H, CH_2O), 3.87–3.89 (m, 2H, CH_2O), 7.20–7.35 (m, 5H, Ph), 7.68 (s, 1H, –CH═). ^{13}C NMR ($CDCl_3$) *δ* (ppm): −1.3, 0.5, 65.8, 65.9, 127.7, 127.8, 128.6, 141.6, 148.8, 154.6. MS (EI) *m*/*z* (%): 278 (M$^+$ 1%), 263



Scheme 5. Silicon-assisted synthesis of unsymmetrical (*E*,*E*)-1,4-diarylbuta-1,3-dienes.

(100), 250 (18), 219 (20), 193 (16), 159 (10), 145 (24), 133 (65), 115 (14), 73 (20), 45 (15). HRMS calcd for $C_{14}H_{22}O_2Si_2$: 278.1158, found: 278.1161.

*4.2.2. 2,2,4,4-Tetramethyl-3-(4-acetyl)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2b**) (yield 72%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.11 (s, 6H, $SiCH_3$), 0.36 (s, 6H, $SiCH_3$), 2.61 (s, 3H, CH_3CO), 3.78–3.82 (m, 2H, CH_2O), 3.86–3.89 (m, 2H, CH_2O), 7.31 (d, 2H, Ar), 7.91 (d, 2H, Ar), 7.66 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.54, 0.48, 26.6, 65.9, 127.9, 128.2, 136.3, 152.3, 145.9, 153.0, 197.6. MS (EI) *m*/*z* (%): 320 (M^+ 10%), 305 (100), 262 (17), 201 (15), 187 (13), 151 (13), 141 (76), 133 (80), 115 (15), 75 (22), 73 (34). HRMS calcd for $C_{16}H_{24}O_3Si_2$: 320.1264, found: 320.1273.

*4.2.3. 2,2,4,4-Tetramethyl-3-(4-nitro)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2c**) (yield 67%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.11 (s, 6H, $SiCH_3$), 0.37 (s, 6H, $SiCH_3$), 3.76–3.78 (m, 2H, CH_2O), 3.87–3.89 (m, 2H, CH_2O), 7.36 (dd, 2H, *J*=8.8 Hz, Ar), 7.92–7.94 (m, 2H, Ar), 8.18 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.4, 0.7, 65.9, 66.0, 123.3, 124.8, 128.4, 138.6, 147.6, 151.2. MS (EI) *m*/*z* (%): 323 (M^+ 2%), 308 (75), 293 (12), 264 (80), 218 (15), 203 (18), 148 (50), 133 (100), 115 (48), 101 (30), 73 (20). HRMS calcd for $C_{14}H_{21}O_4Si_2N$: 323.1009, found: 323.0997.

*4.2.4. 2,2,4,4-Tetramethyl-3-(3-methoxy)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2d**) (yield 88%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.10 (s, 6H, $SiCH_3$), 0.38 (s, 6H, $SiCH_3$), 3.83 (s, 3H CH_3O), 3.86 (t, 2H, CH_2O), 7.22–7.30 (m, 4H, Ar), 7.67 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −6.6, −4.1, 50.0, 60.6, 60.7, 107.7, 108.0, 108.4, 115.0, 123.7, 137.3, 143.6, 149.2. MS (EI) *m*/*z* (%): 308 (M^+ 3), 293 (92), 265 (30), 249 (25), 193 (17), 175 (37), 133 (100), 115 (30), 73 (28), 59 (25), 45 (23). HRMS calcd for $C_{15}H_{24}O_3Si_2$: 308.1264, found: 308.1256.

*4.2.5. 2,2,4,4-Tetramethyl-3-(4-methoxy)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2e**) (yield 80%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.24 (s, 6H, $SiCH_3$), 0.41 (s, 6H, $SiCH_3$), 3.83 (s, 3H, CH_3O), 3.86–3.89 (m, 4H, CH_2O), 6.87–6.92 (dd, 2H, *J*=8.5 Hz), 7.09–7.12 (d, 2H, *J*=8.6), 7.67 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.4, 1.2, 55.2, 65.8, 65.8, 112.9, 113.3, 129.4, 130.5, 133.6, 154.5, 159.5. MS (EI) *m*/*z* (%): 308 (M^+ 1%), 293 (100), 250 (8), 266 (20), 191 (5), 159 (10), 133 (24), 115 (5), 73 (12). HRMS calcd for $C_{15}H_{24}O_3Si_2$: 308.1264, found: 308.1252.

*4.2.6. 2,2,4,4-Tetramethyl-3-(4-methyl)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2f**) (yield 85%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.22 (s, 6H, $SiCH_3$), 0.42 (s, 6H, $SiCH_3$), 2.42 (s, 3H, CH_3), 3.82–3.85 (m, 2H, CH_2O), 3.91–3.96 (m, 2H, CH_2O), 7.19 (s, 4H, Ar), 7.72 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.5, 0.4, 21.2, 65.8, 65.9, 127.8, 128.6, 137.2, 138.2, 147.5, 154.9. MS (EI) *m*/*z* (%): 277 (M^+-15, 100%), 234 (20), 208 (12), 160 (20), 133 (56), 115 (20), 73 (15). HRMS calcd for $C_{15}H_{24}O_2Si_2$, [M−15]: 277.1080, found: 277.1069.

*4.2.7. 2,2,4,4-Tetramethyl-3-(4-chloro)benzylidene-1,5-dioxa-2,4-disilacycloheptane (**2g**) (yield 90%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 0.12 (s, 6H, $SiCH_3$), 0.34 (s, 6H, $SiCH_3$), 3.82–3.86 (dt, 4H, CH_2O), 7.15 (d, 2H, *J*=8.1 Hz), 7.29 (d, 2H, *J*=8.5 Hz), 7.59 (s, 1H, –CH=). ^{13}C NMR ($CDCl_3$) δ (ppm): −1.4, 0.6, 65.9, 128.1, 129.0, 133.7, 139.5, 150.2, 153.0. MS (EI) *m*/*z* (%): 297 (M^+, 75%), 253 (55), 133 (35), 73 (25). HRMS calcd for $C_{14}H_{21}ClO_2Si_2$, [M−15]: 297.0534, found: 297.0537.

4.3. Representative procedure for the synthesis of (*E*)-stilbenes

The glass reactor (100 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated heating oil bath) was evacuated and flushed with argon. Respective compounds **2a**–**g** (5 mmol) and THF (20 mL) were added to the reactor. At room temperature 12 mmol of TBAF (1 M solution in THF) was added and the mixture was stirred for 10 min. After this time, 4.55 mmol of the respective aryl iodide and 18.3 mg (0.05 mmol) of $[Pd(C_3H_5)Cl]_2$ were added and the reaction mixture was stirred under argon for 1 h at 65 °C. After the reaction was completed (GC–MS analysis) the volatiles were evaporated under vacuum and the crude product was chromatographed on silica gel (eluent—hexane/ethyl acetate 10:1 for compounds **3a**–**f** or hexane/CH_2Cl_2 10:1 for **3g**–**h**) to afford the analytically pure products. The structures of synthesized (*E*)-stilbenes were confirmed by GC–MS and NMR spectroscopy matching data reported in the literature: (*E*)-4-methylstilbene (**3a**),[4g] (*E*)-4-acetylstilbene (**3b**),[4g] (*E*)-4-acetyl-4′-methylstilbene (**3c**),[5c] (*E*)-4,4′-dimethylstilbene (**3e**),[29a] (*E*)-4-acetyl-3′-methoxystilbene (**3g**)[9b] and 4-chloro-4′-methoxystilbene (**3h**).[29b]

*4.3.1. (E)-2-Methyl-4′-nitrostilbene (**3d**) (yield 62%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 2.46 (s, 3H, CH_3), 7.03 (d, 1H, *J*=16.1 Hz, CH=CH), 7.08 (d, 1H, *J*=16.1 Hz, CH=CH), 7.20–7.25 (m, 2H), 7.49–7.54 (m, 2H), 7.60–7.66 (m, 2H), 8.21–8.25 (m, 2H). ^{13}C NMR ($CDCl_3$) δ (ppm): 19.9, 124.1, 125.5, 126.3, 126.8, 127.5, 128.6, 130.6, 130.9, 135.2, 136.3, 144.0, 146.7. MS (EI) *m*/*z* (%): 239 (M^+, 100%), 223 (12), 207 (8), 192 (25), 178 (62), 165 (18), 115 (20), 63 (5). HRMS calcd for $C_{15}H_{13}NO_2$: 239.0946, found: 239.0969.

*4.3.2. (E)-3-Cyano-4′-methoxystilbene (**3f**) (yield 88%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 3.84 (s, 3H, OCH_3), 6.89–6.94 (m, 2H, Ar), 7.08 (d, 1H, *J*=16.2 Hz, CH=CH), 7.13 (d, 1H, *J*=16.2 Hz, CH=CH), 7.43–7.48 (m, 4H, Ar), 7.68–7.75 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$) δ (ppm): 55.4, 112.8, 114.2, 118.8, 123.9, 127.9, 129.0, 129.3, 129.5, 129.9, 130.2, 130.7, 138.8, 159.2. MS (EI) *m*/*z* (%): 235 (M^+, 100%), 219 (17), 204 (25), 190 (25), 165 (30), 152 (10), 140 (6), 89 (12), 63 (15). HRMS calcd for $C_{16}H_{13}NO$: 235.0997, found: 235.1006.

4.4. Representative procedure for the synthesis of (*E*,*E*)-1,4-diarylbuta-1,3-dienes

The glass reactor (100 mL, two-necked, round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, argon bubbling tube and thermostated heating oil bath) was evacuated and flushed with argon. Compound **2** (5 mmol) and THF (20 mL) were added to the reactor. At room temperature 12 mmol of TBAF (1 M solution in THF) was added and the mixture was stirred for 10 min. After this time, 4.55 mmol of the respective (*E*)-styryl iodide and 18.3 mg (0.05 mmol) of $[Pd(C_3H_5)Cl]_2$ were added and the reaction mixture was stirred under argon for 1 h at 65 °C. After the reaction was completed (GC–MS analysis) the volatiles were evaporated under vacuum and the crude product was chromatographed on silica gel (eluent—toluene) to afford the analytically pure products.

*4.4.1. (E,E)-1-(4-Methylphenyl)-4-phenylbuta-1,3-diene (**4a**) (yield 86%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 2.35 (s, 3H, CH_3), 6.62–6.69 (m, 2H, ArCH=C*H*), 6.87–6.95 (m, 2H, ArC*H*=CH), 7.13–7.22 (m, 2H), 7.30–7.36 (m, 3H), 7.42–7.45 (m, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.3, 126.2, 127.3, 128.2, 128.5, 129.3, 129.3, 132.1, 132.7, 134.5, 137.6, 137.4. MS (EI) *m*/*z* (%): 220 (M^+, 100%), 205 (96), 190 (20), 178 (10), 165 (8), 128 (32), 115 (24), 105 (35), 91 (30), 77 (20), 63 (18), 51 (22). HRMS calcd for $C_{17}H_{16}$: 220.1252, found: 220.1262.

*4.4.2. (E,E)-1-(4-Bromophenyl)-4-phenylbuta-1,3-diene (**4b**) (yield 80%)*

^{1}H NMR ($CDCl_3$) δ (ppm): 6.57–6.67 (m, 2H, ArCH=C*H*), 6.88–6.96 (m, 2H, ArC*H*=CH), 7.22–7.28 (m, 3H), 7.31–7.36 (m, 2H), 7.43–7.46 (m, 4H). ^{13}C NMR ($CDCl_3$) δ (ppm): 121.2, 126.3, 126.4, 127.7, 127.8, 128.7, 128.9, 129.9, 131.4, 131.7, 131.8, 133.5. MS (EI) *m*/*z* (%): 286 (M^+, 60%), 285 (58), 269 (8), 205 (100), 190 (25), 169 (22), 152 (8), 128 (25), 115 (15), 101 (22), 63 (20), 50 (20). HRMS calcd for $C_{16}H_{13}Br$ (^{79}Br): 284.0201, found: 284.0212.

4.4.3. (E,E)-1-(4-Methoxyphenyl)-4-(4-methylphenyl)buta-1,3-diene (**4c**) (yield 68%)

^{1}H NMR ($CDCl_3$) δ (ppm): 2.35 (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 6.58–6.62 (m, 2H), 6.76–6.80 (m, 1H), 6.84 (d, 1H, 15.6 Hz), 6.88 (d, 2H, J=8.1 Hz), 7.14 (m, 2H), 7.34 (d, 2H, J=8.1 Hz), 7.38 (d, 2H, J=8.1 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.2, 55.3, 114.2, 126.2, 127.4, 127.6, 128.2, 129.4, 129.5, 120.3, 131.6, 131.8, 134.7, 137.2, 159.2. MS (EI) *m*/*z* (%): 250 (M^+, 100%), 235 (30), 220 (22), 192 (10), 165 (8), 159 (10), 121 (10), 105 (15).

4.4.4. (E,E)-1-(4-Acetylphenyl)-4-(4-methylphenyl)buta-1,3-diene (**4d**) (yield 80%)

^{1}H NMR ($CDCl_3$) δ (ppm): 2.36 (s, 3H, CH_3), 2.60 (s, 3H, $COCH_3$), 6.48–6.62 (m, 2H), 6.90–7.02 (m, 2H), 7.12 (d, 2H, 7.6 Hz), 7.36 (d, 2H, J=8.0 Hz), 7.54 (m, 2H), 7.92 (d, 2H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.2, 26.3, 126.2, 126.8, 127.8, 128.8, 129.4, 130.6, 132.3, 134.1, 134.8, 135.6, 138.2, 143.0, 197.8. MS (EI) *m*/*z* (%): 262 (M^+, 40), 247 (100), 219 (62), 204 (30), 143 (10), 129 (12), 101 (10). HRMS calcd for $C_{19}H_{18}O$: 262.1357, found: 262.1366.

4.5. X-ray crystal structure analysis

Crystals of approximate dimensions $0.3\times0.3\times0.4$ mm^3 (**2b**), $0.02\times0.1\times0.4$ mm^3 (**3e**) and $0.02\times0.4\times0.4$ mm^3 (**3f**) were grown from the hexane solution. The crystals of **3e** and **3f** were obtained as very thin plates, this caused the relatively poor quality of the data—however the data are good enough for the structure analysis. The X-ray diffraction data were collected on Oxford Diffraction four-circle diffractometer equipped with CCD detector[30] at room temperature. The data were corrected for Lp and absorption effects.[31] The crystal data together with some experimental and refinement details are given in Table 3. The structures were solved by direct methods with SHELXS97[32] and refined by full-matrix least squares with SHELXL97.[32] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located from the ideal geometry[32] and refined as 'riding model'. The isotropic displacement parameters of hydrogen atoms were set at 1.2 (1.4 for methyl groups) times the equivalent displacement parameters of appropriate carrier atoms.

Crystallographic data (excluding structure factors) for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, No. CCDC-648155 (**2b**), CCDC-713055 (**3f**) and CCDC-713056 (**3e**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

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