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Synthesis of six-membered cyclic siloxanes via enyne metathesis with a ruthenium catalyst generated in situ

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Abstract

The catalytic system in situ generated by combination of $[RuCl_2(p\text{-cymene})]_2$ as a ruthenium source, 1,3-bis(mesityl)imidazolinium chloride ($MesH_2ImCl$) as a bulky electron-releasing carbene precursor and cesium carbonate as a base, is shown to be an efficient catalyst for the metathesis reaction of propargylic allylsilyl ethers R^1–C≡CCR_2–O–$SiMe_2$–CH_2CH=CH_2. The metathesis products, the cyclic siloxanes, were obtained after complete conversion of the enynes in 67–87% isolated yields. These six-membered ring compounds contain the 1,3-diene unit that is used in Diels–Alder reaction and give access to heterobicyclic derivatives. The resulting cyclic siloxanes are selectively opened under oxidative conditions with H_2O_2 to afford allylic diols, with fluoride to form conjugated triene and under hydrogenation conditions with Pd/C catalyst to give a tetrasubstituted alkene.

Keywords: Enyne metathesis; Ruthenium catalyst; Imidazolinium salt; Cyclic siloxanes; Allylsilanes

1. Introduction

The silicon atom is often used in organic chemistry as a temporary connecting atom between two moieties due to the easy preparation of its derivatives and the facile subsequent removal of the silicon element [1]. This strategy joined with the use of the ring closing alkene metathesis reaction, for the formation of cyclic allylsilanes, has already given access to 3-vinyltetrahydrofurans [2], allylic alcohols [3] or allylic diols [4]. Moreover, enyne metathesis produces cyclic products with two conjugated double bonds that are able to react in Diels–Alder reactions to produce bicyclic derivatives [4a,5].

This potential has motivated the search of more active alkene or enyne metathesis catalysts. First, $Ru(Cl)_2$(=CHPh)$(PCy_3)_2$ was used for enyne metathesis of substrates containing O [6] and N [7] heteroatoms. Then, the salts $[Ru(Cl)$=C=C=$CPh)_2(PCy_3)(p\text{-cymene})]X$ appeared to be efficient catalysts for the metathesis reaction from O-containing enynes [8] and fluorinated aminoesters [9]. Recently, the substitution of one tricyclohexylphosphine of the Grubbs catalyst by an electron-rich diaminocarbene [10] gave access to more efficient catalysts for ring closing metathesis [11], cross-metathesis [12] or ene–yne cross-metathesis [13]. This was due to the easiness to prepare a variety of stable carbene–metal complexes containing a very electron-releasing imidazolylidene or imidazolinylidene ligand [14]. The syntheses of all

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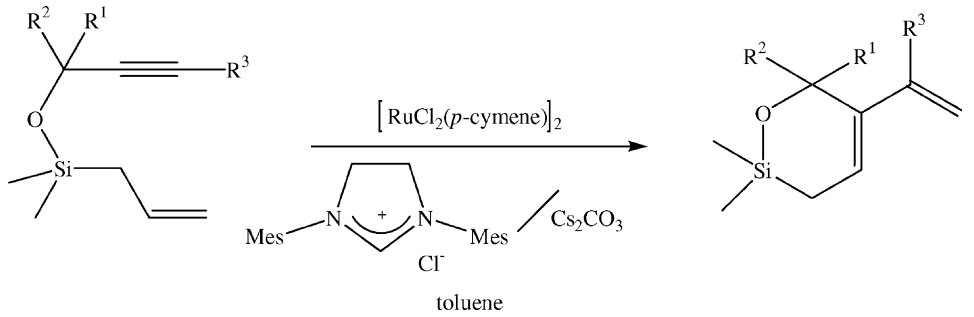


Scheme 1.

these catalysts require several organometallic steps and purifications under inert atmosphere. With the aim to simplify the metathesis catalyst preparation, in situ generated catalysts were made by the one step combination of a ruthenium source with an imidazolylidene [15] or imidazolinylidene [16] carbene precursor. They are efficient catalysts for both enyne metathesis [15,16], and ring opening metathesis of cyclooctene [17], and for diene ring closing metathesis in the presence of terminal alkyne [18,19].

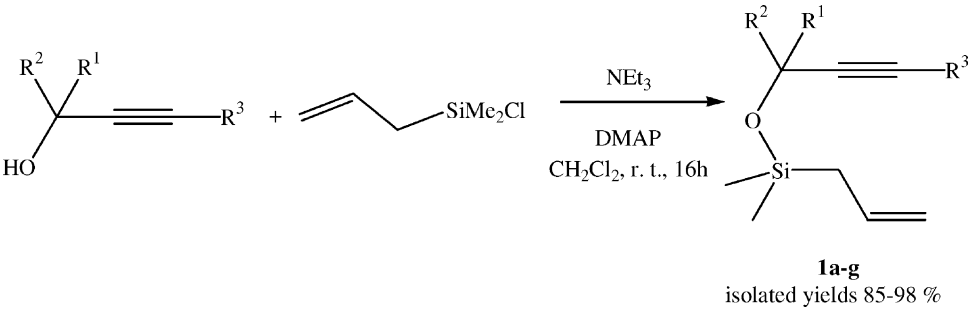
We now report the use of the in situ generated catalytic system (catalytic system **A**) composed of commercially available and stable reagents: the dimeric $[RuCl_2(p\text{-cymene})]_2$ as ruthenium source, the 1,3-bis(mesityl)imidazolinium chloride ($MesH_2ImCl$) as carbene precursor and cesium carbonate as a base, for the metathesis of simple enynes containing the propargylic and allylsilyl ether functionalities (Scheme 1). We show that the six-membered ring metathesis products possessing the 1,3-diene structure can be used in Diels–Alder reactions and that their "O-$SiMe_2$" unit that can be easily removed to afford diols, trienes or tetrasubstitued alkenes. The preliminary description of this enyne metathesis catalytic system has been reported [16].

2. Results

2.1. Preparation of the enynes *1a–h*

The enynes containing an allylsilane group **1a–h** were easily obtained from propargylic alcohol and allyldimethylchlorosilane (1.1 eq.) in the presence of triethylamine (2 eq.) and a catalytic amount of 4-dimethylaminopyridine (DMAP) in CH_2Cl_2 for 16 h at room temperature (Scheme 2). The products **1a–g** were obtained in good isolated yields (>85%) for various alkyl or phenyl substituents (Table 1). These enynes have a terminal alkyne end (**1a–d**) or are disubstituted alkynes with a phenyl (**1e**), butyl (**1f**) or ether (**1g**) group.

Under similar conditions, starting from 3-hexyn-2,5-diol and 2.2 eq. of allyldimethylchlorosilane, it was possible to obtain the bis(allyl)siloxane **1h** in 80% isolated yield (Scheme 3).



Scheme 2.

Table 1
Preparation of the enynes **1a**–**g**[a]

Enyne	R^1	R^2	R^3	Isolated yield (%)
1a	Me	Ph	H	95
1b	$-(CH_2)_5-$	$-(CH_2)_5-$	H	96
1c	Me	$CH_2CH(CH_3)_2$	H	92
1d	Ph	Ph	H	98
1e	Me	Me	Ph	85
1f	$-(CH_2)_5-$		^{n}Bu	95
1g	$-(CH_2)_5-$		CH_2OCH_3	90

[a] An amount of 5 mmol of propargylic alcohol; 5.5 mmol of $Me_2(CH_2{=}CHCH_2)SiCl$; 10 mmol of NEt_3; 0.5 mmol of DMAP in 10 ml of CH_2Cl_2, RT, 16 h.

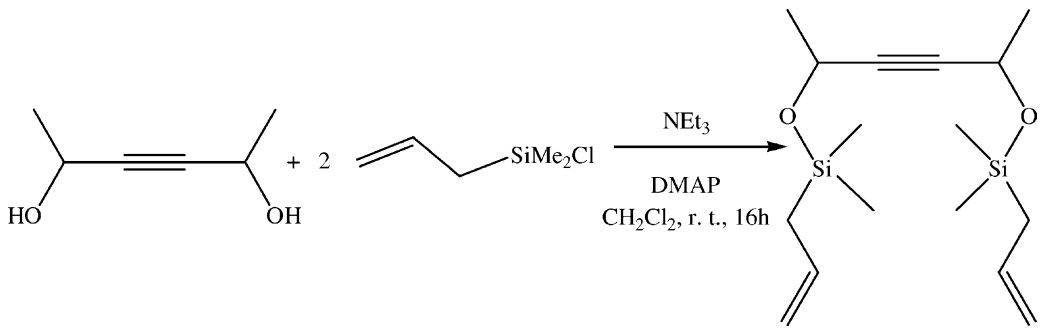
2.2. Ruthenium-catalysed ring closing metathesis of enynes *1a–h*: preparation of cyclic allylsiloxanes *3a–h*

By contrast to the easy general, high yield preparation of a variety of mixed arene–carbene complexes of the type $RuCl_2$(imidazolinylidene)(arene) by reaction of $[RuCl_2(arene)]_2$ with electron-rich tetraamino olefins [20], the preparation of {$RuCl_2$[1,3-bis(mesityl)imidazolin-2-ylidene](*p*-cymene)} complex starting from $[RuCl_2(p\text{-cymene})]_2$, $MesH_2ImCl$ and NaH led to poor yield, whereas that of the {$RuCl_2$[1,3-bis(mesityl)imidazol-2-ylidene](*p*-cymene)} complex takes place [21]. To overcome this problem and on the basis of our previous experience with the utilization of a catalytic system generated in situ from $[RuCl_2(p\text{-cymene})]_2$, 1,3-bis(mesityl)imidazolium chloride (MesImCl) and Cs_2CO_3 [15], we attempted to generate in situ a catalytic system composed of $[RuCl_2(p\text{-cymene})]_2$ (**2**), $MesH_2ImCl$ and Cs_2CO_3 in the molar ratio of 1/2/4 (catalytic system **A**).

The use of $MesH_2ImCl$ salt as carbene precursor led to a more efficient catalytic system as compared to the MesImCl salt. For example, in the presence of the catalyst **A**, prepared from 5 mol% of $[RuCl_2(p\text{-cymene})]_2$ (**2**) and $MesH_2ImCl$ salt in refluxing toluene, the enyne **1f** was completely converted into **3h**, whereas when the MesImCl salt was used after the same reaction time only 60% of **1f** was converted (Scheme 4).

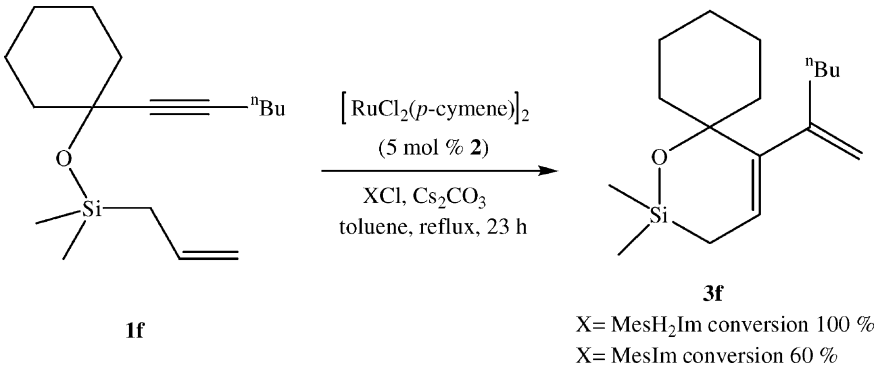
Thus, the catalytic system **A** was selected for the selective transformation of the enynes **1a**–**h**. With the enynes containing a terminal triple bond (R^3 = H) and bearing alkyl or aryl substituents at the propargylic position (**1a**–**d**), the metathesis reaction was achieved within 15–16 h at 80 °C using 2.5 mol% of $[RuCl_2(p\text{-cymene})]_2$ (**2**) and the metathesis products (**3a**–**d**) were isolated in 34–87% yield (Table 2, Scheme 5). The poor recovery of the diene **3c** was due to its decomposition over silica during the flash chromatography, but not to a low conversion of **1c**.

The metathesis reaction of enynes containing a disubstituted triple bond ($R^3 \neq$ H) (**1e**–**g**) required more drastic conditions. For example, with the enyne **1e** (R^3 = Ph), the complete conversion was obtained only after 48 h at 80 °C using catalyst **A** based on 2.5 mol% of $[RuCl_2(p\text{-cymene})]_2$ (**2**). The use of catalyst **A** based on 5 mol% of $[RuCl_2(p\text{-cymene})]_2$ (**2**) in refluxing toluene with enynes **1f** ($R^3 = {}^n$Bu) and **1g** ($R^3 = CH_2OCH_3$) gave a full conversion into the metathesis products **3f** and **3g** after 23 h (Table 2).



1h
isolated yield 80 %

Scheme 3.



1f

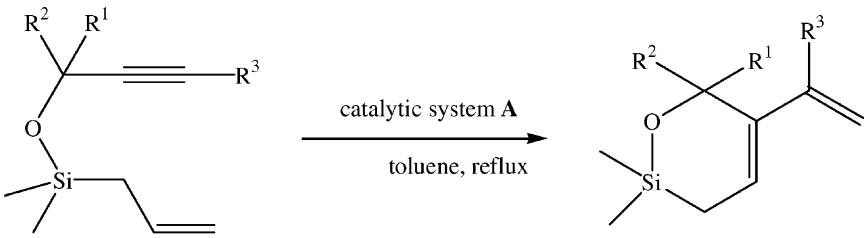
3f
X= $MesH_2Im$ conversion 100 %
X= MesIm conversion 60 %

Scheme 4.

Table 2
Enyne metathesis with the catalytic system **A**[a]

Product	R^1	R^2	R^3	**2** (mol%)	*T* (°C)	*t* (h)	Isolated yield (%)[b]
3a	Me	Ph	H	2.5	80	16	81
3b	$-(CH_2)_5-$	$-(CH_2)_5-$	H	2.5	80	16	87
3c	Me	$CH_2CH(CH_3)_2$	H	2.5	80	15	34[c]
3d	Ph	Ph	H	2.5	80	15	70
3e	Me	Me	Ph	2.5	80	48	75
3f	$-(CH_2)_5-$		^{n}Bu	5	110	23	72
3g	$-(CH_2)_5-$		CH_2OCH_3	5	110	23	67

[a] An amount of 1 mmol of enyne **1**, 5 ml of toluene, catalytic system **A**: 2.5 mol% of ruthenium complex **2** and based on a molar ratio of $[RuCl_2(p\text{-cymene})]_2$ (**2**)/$MesH_2ImCl/Cs_2CO_3$: 1/2/4.
[b] Complete conversion.
[c] Degradation over silica during purification.



1a-g

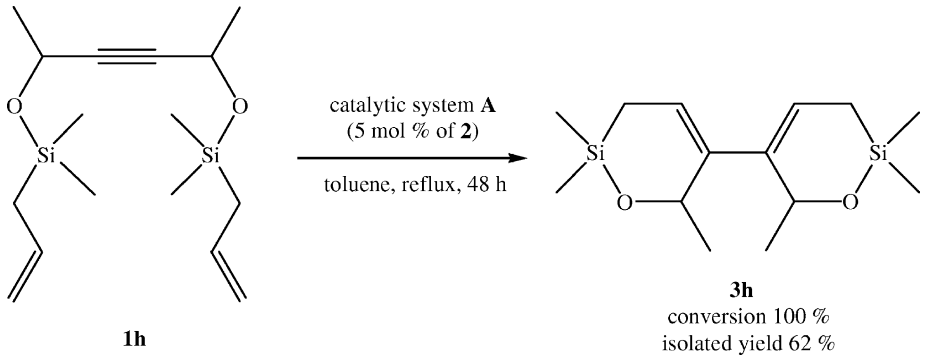
3a-g
conversion 100 %
isolated yield 34-87 %

Scheme 5.

This catalytic system **A** was also active for dienyne metathesis. After 48 h in refluxing toluene with catalyst **A** based on 5 mol% of $[RuCl_2(p\text{-cymene})]_2$ (**2**), the compound **1h** gave the bicyclic product **3h** in complete conversion and 62% isolated yield. The conjugated diene was obtained as a mixture of two diastereoisomers in the ratio 62/38 (Scheme 6).

*2.3. Involvement of the 1,3-diene unit of compounds **3** in Diels–Alder reaction: formation of bicyclic products **4a–d***

The metathesis products (**3a–d**) which present a 1,3-diene unit, are well suited for a Diels–Alder reaction [4a,5,9,15,16] to give rise to the formation of



Scheme 6.

heterobicyclic products. After 5 h in refluxing toluene, the dienes **3b** and **3d** in the presence of 2 eq. of diethylacetylene dicarboxylate (DEAD) selectively led to the Diels–Alder products **4b** and **4d**, in 41 and 61% isolated yield, respectively (Scheme 7).

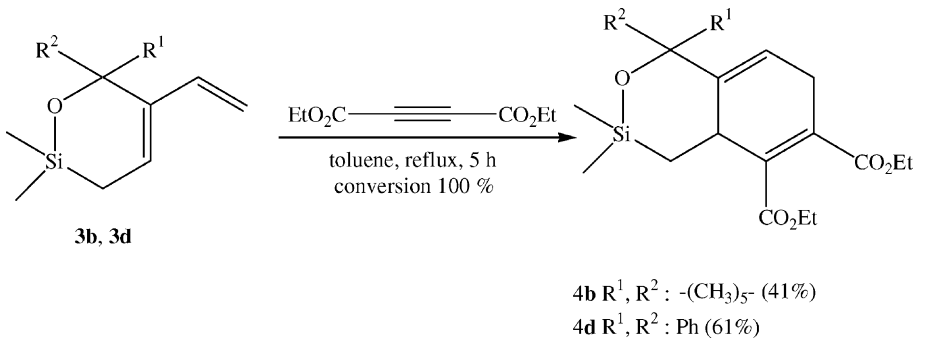
To perform the Diels–Alder reaction, it was not necessary to isolate the diene **3**. Indeed, the catalytic metathesis and Diels–Alder reactions could be successively carried out (Scheme 8). The enynes **1a** and **1c** were first transformed into the metathesis products **3a** and **3c** by the catalytic system **A** (2.5 mol% of $[RuCl_2(p\text{-cymene})]_2$) at 80 °C for 16 h in toluene. Then, in the same flask, 2 eq. of DEAD were added and the reaction mixture was refluxed for 5 h. The Diels–Alder products **4a** (78%) and **4c** (61%) were isolated as a mixture of two diastereoisomers in the ratio 72/28 and 50/50, respectively, as determined by ^{1}H NMR.

Table 3
Oxidation of the Diels–Alder products **4a–d**[a] into the aromatic bicyclic compounds **5a–d**[a]

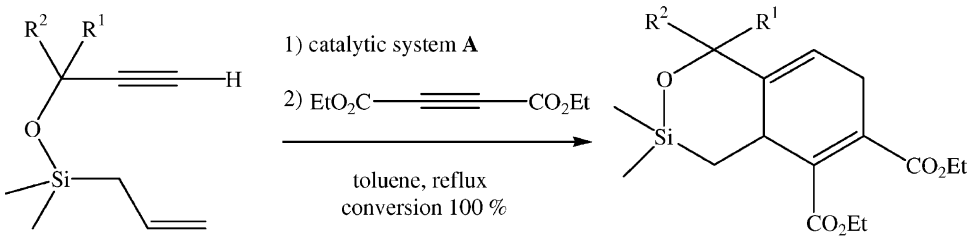
Oxidation product	R^1	R^2	Isolated yield (%)
5a	Me	Ph	86
5b	$-(CH_2)_5-$		90
5c	Me	$CH_2CH(CH_3)_2$	80
5d	Ph	Ph	85

[a] An amount of 0.2 mmol of **4**, 0.6 mmol of DDQ, 5 ml of toluene, reflux, 15 h.

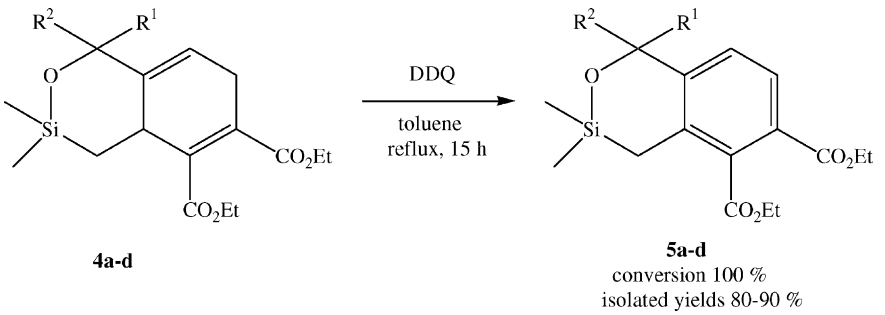
The bicyclic products (**4a–d**) could be oxidized with 3 eq. of 2,3-dichloro-5,6-dicyanoquinone (DDQ) [22] in refluxing toluene for 15 h (Scheme 9). After complete conversion, the aromatic bicyclic compounds **5a–d** were isolated in good yields (80–90%; Table 3).



Scheme 7.



Scheme 8.

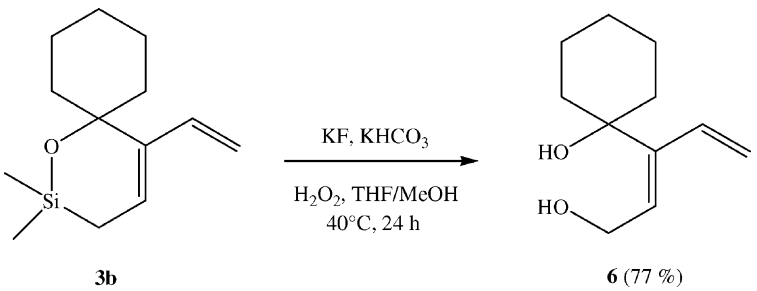


Scheme 9.

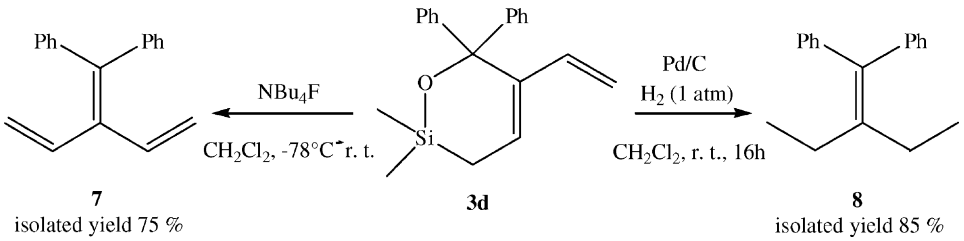
*2.4. Selective transformation of the cyclic siloxanes into diols, trienes and tetrasubstituted alkenes **6–8***

Another property of the metathesis products **3** in addition to the 1,3-diene unit is to possess a cyclic allylsilane functionality which can be opened. For instance, under Tamao oxidation conditions [23], cyclic allylsilanes are known to give allylic diols [4]. The metathesis product **3b** was thus, oxidized with an excess of H_2O_2 in a THF/MeOH mixture in the presence of 5 eq. of KF, 2.3 eq. of $KHCO_3$ at 40 °C for 24 h. The allylic diol **6** was isolated in 77% yield (Scheme 10). Consequently, this simple reaction shows the potential of the metathesis compounds for the access to optically active 1,4-diols from easily accessible optically active propargyl alcohols.

Another way to cleave cyclic allylsilane deals with the use a fluorine anion in order to obtain allylic alcohol and the corresponding dehydrated diene [3a]. The cyclic allylsilane **3d** in CH_2Cl_2 was reacted at



Scheme 10.



Scheme 11.

−78 °C with 3 eq. of tetrabutylammonium fluoride in THF. Under these conditions desilylation and complete selective dehydration took place, and the conjugated triene **7** was isolated in 75% yield (Scheme 11).

This cyclic allylsilane **3d** was also hydrogenated in the presence of 10 mol% of Pd/C under an atmosphere of hydrogen in CH_2Cl_2 and selectively led, after 16 h at room temperature, to the tetrasubstituted alkene **8** which was isolated in 85% yield (Scheme 11). Under these catalytic conditions, the product **8** corresponds to the hydrogenation of the more reactive monosubstituted double bonds of the triene **7**.

3. Conclusion

The use of the ruthenium catalyst **A**, in situ generated, resulting from the three component combination: the air stable and commercially available complex $[RuCl_2(p\text{-cymene})]_2$ as a ruthenium precursor, the $MesH_2ImCl$ salt as a carbene precursor and cesium carbonate as a base, constitutes an efficient enyne metathesis catalyst. The enynes containing an allylsilane with this in situ generated catalyst provide access to six-membered heterocyclic compounds. The conjugated diene unit of these cyclic siloxanes can be involved in a Diels–Alder reaction to form bicyclic derivatives. The potential of these cyclic allylsilanes has been shown by their selective transformations into either diol, triene or tetrasubstituted alkene.

The efficiency of the in situ prepared catalyst is expected to be based on the direct formation of a $[RuX_2(imidazolinylidene)]$ coordinatively unsaturated ruthenium species, by displacement of the arene ligand on coordination of the bulky carbene. Indeed, $[RuCl_2(p\text{-cymene})]_2$ was known to easily loose the *p*-cymene group on addition of the bulky phosphine PCy_3 and the ruthenium species could thus, trap an alkyne to produce the $RuCl_2(=C=CHR)(PCy_3)_2$ complex [24,25]. The bulkyness of the imidazolinylidene ligand and especially its electron-releasing capability [14] is likely to preclude the coordination of a second carbene but to stabilize a coordinatively unsaturated ruthenium species allowing the coordination of the enyne.

This enyne-metathesis-three-component-catalytic system opens the way to a variety of new catalysts in situ prepared by association of: (i) a metal moiety (here a source of $[RuCl_2]$); (ii) a suitable ligand able to control the reaction and protect the catalytic species (here a bulky electron-rich carbene ligand); (iii) the reagents allowing, whenever it is necessary, this carbene ligand formation previously to coordination.

4. Experimental

General: ^1H and ^{13}C NMR spectra were recorded with a Brucker DPX 200 spectrometer—GC–MS spectra were obtained with a CE instruments GC 8000 top chromatograph (capillary column OV1, 25 m × 0.35 mm, 0.1–0.15 μm) coupled with an Automass II Finnigan MAT (75 eV) mass spectrometer. Elemental microanalyses were carried out by the CNRS Analysis Center in Villeurbanne. Organic solvents were dried and distilled prior to use.

*4.1. General procedure for the preparation of enynes **1a–h***

*4.1.1. For enynes **1a–g***

In a Schlenk tube $Me_2(CH_2{=}CHCH_2)SiCl$ (0.83 ml, 5.5 mmol) was added dropwise to a stirred solution of propargylic alcohol (5 mmol), NEt_3 (1.40 ml, 10 mmol) and DMAP (61 mg, 0.5 mmol) in CH_2Cl_2 (10 ml). The reaction mixture was stirred at

room temperature for 16 h. Distilled water (10 ml) was then added to the reaction, the aqueous layer was extracted with CH_2Cl_2 (10 ml). The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/9). The enynes **1a**–**g** were obtained in 85–98% isolated yield.

1a: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.12 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.14 (s, 3H, Si(C$\underline{H}_3$)$_2$); 1.67 (ddt, 2H, $^2J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.1 Hz, SiC$\underline{H}_2$); 1.72 (s, 3H, C$\underline{H}_3$); 2.68 (s, 1H, C≡C–$\underline{H}$); 4.83 (dm, 1H, $^3J_{HH}$ = 11.1 Hz, *cis* CH=C$\underline{H}_2$); 4.85 (dm, 1H, $^3J_{HH}$ = 16.8 Hz, *trans* CH=C$\underline{H}_2$); 5.64–5.90 (m, 1H, C$\underline{H}$=CH$_2$); 7.18–7.40 (m, 3H, *meta* and *para* arom. CH); 7.55–7.63 (m, 2H, *ortho* arom. CH).

^{13}C NMR (50.329 MHz, $CDCl_3$), δ ppm: −0.5, −0.4 (2CH$_3$, Si(C$\underline{H}_3$)$_2$); 26.0 (SiC$\underline{H}_2$); 35.9 (C$\underline{H}_3$); 71.2 (Si–O–$\underline{C}$); 74.3 (C≡$\underline{C}$–H); 87.5 (C≡$\underline{C}$–H); 113.5 (C$\underline{H}_2$=CH); 125.0, 127.4, 128.1 (arom. $\underline{C}$H); 134.5 (CH$_2$=$\underline{C}$H); 146.3 (*ipso* $\underline{C}$).

GC–MS (relative intensity): 244 ([*M*]$^+$,<1); 228 (30); 227 (20); 204 (37); 203 (86); 201 (61); 186 (13); 184 (15); 176 (13); 134 (10); 129 (56); 128 (63); 127 (71); 126 (78); 125 (14); 114 (12); 104 (16); 103 (12); 102 (29); 101 (36); 100 (29); 99 (14); 98 (19); 87 (10); 86 (17); 85 (23); 84 (25); 83 (65); 82 (100); 79 (13); 78 (25); 77 (92); 76 (88); 73 (20); 71 (14); 70 (15); 63 (16); 62 (19); 61 (32); 60 (41); 59 (78); 58 (61); 55 (13); 54 (12); 53 (11); 52 (18); 51 (82); 50 (58); 47 (34); 46 (36); 45 (47); 44 (43); 43 (44); 42 (27); 41 (24); 40 (11); 39 (32); 38 (15).$C_{15}H_{20}OSi$ (244.2): calculated C 69.90, H 8.10; found C 71.06, H 8.16.

1b: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.17 (s, 6H, Si(C$\underline{H}_3$)$_2$); 1.10–1.95 (m, 10H, 5C$\underline{H}_2$); 1.67 (dm, 2H, $^2J_{HH}$ = 8.1 Hz, SiC$\underline{H}_2$); 2.46 (s, 1H, C≡C–$\underline{H}$); 4.82 (dm, 1H, $^3J_{HH}$ = 10.0 Hz, *cis* CH=C$\underline{H}_2$); 4.87 (dm, 1H, $^3J_{HH}$ = 12.0 Hz, *trans* CH=C$\underline{H}_2$); 5.68–5.91 (m, 1H, C$\underline{H}$=CH$_2$).

^{13}C NMR (50.329 MHz, $CDCl_3$), δ ppm: −0.2 (2CH$_3$, Si(C$\underline{H}_3$)$_2$); 22.8, 26.5, 41.1 (5C$\underline{H}_2$); 25.2 (SiC$\underline{H}_2$); 69.6 (Si–O–$\underline{C}$); 73.5 (C≡$\underline{C}$–H); 87.9 (C≡$\underline{C}$–H); 113.3 (C$\underline{H}_2$=CH); 134.4 (CH$_2$=$\underline{C}$H).

GC–MS (relative intensity): 222 ([*M*]$^+$,1); 183 (18); 182 (56); 181 (56); 179 (10); 165 (10); 156 (21); 155 (100); 139 (53); 113 (19); 105 (11); 101 (10); 99 (15); 97 (10); 91 (18); 85 (31); 84 (21); 83 (92); 82 (11); 81 (55); 79 (30); 78 (14); 77 (52); 76 (58); 74 (12); 73 (11); 71 (20); 69 (18); 67 (22); 65 (20); 61 (53); 60 (16); 59 (90); 55 (38); 53 (33); 51 (16); 47 (41); 45 (53); 43 (37); 41 (44); 39 (41); 29 (17); 28 (18); 27 (15).

1c: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.17 (s, 6H, Si(C$\underline{H}_3$)$_2$); 0.94 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$); 1.44 (s, 3H, C$\underline{H}_3$–C); 1.54 (d, 2H, $^3J_{HH}$ = 5.8 Hz, C–C$\underline{H}_2$); 1.67 (dm, 2H, $^2J_{HH}$ = 8.1 Hz, SiC$\underline{H}_2$); 1.90 (m, 1H, C$\underline{H}$(CH$_3$)$_2$); 2.41 (s, 1H, C≡C–$\underline{H}$); 4.82 (dm, 1H, $^3J_{HH}$ = 10.1 Hz, *cis* CH=C$\underline{H}_2$); 4.84 (dm, 1H, $^3J_{HH}$ = 18.0 Hz, *trans* CH=C$\underline{H}_2$); 5.64–5.91 (m, 1H, C$\underline{H}$=CH$_2$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.2, −0.1 (2CH$_3$, Si(C$\underline{H}_3$)$_2$); 24.4 (2CH$_3$, CH(C$\underline{H}_3$)$_2$); 24.9 (C$\underline{H}$(CH$_3$)$_2$); 26.2 (SiC$\underline{H}_2$); 31.8 (C–C$\underline{H}_3$); 53.2 (C–C$\underline{H}_2$); 69.5 (Si–O–$\underline{C}$); 72.4 (C≡$\underline{C}$–H); 88.6 (C≡$\underline{C}$–H); 113.3 (C$\underline{H}_2$=CH); 134.7 (CH$_2$=C$\underline{H}$).

GC–MS (relative intensity): 224 ([*M*]$^+$,<1); 184 (18); 183 (88); 169 (10); 168 (27); 167 (100); 157 (13); 141 (37); 129 (11); 128 (30); 127 (82); 126 (11); 125 (27); 115 (36); 113 (19); 111 (12); 109 (16); 107 (48); 101 (41); 100 (11); 99 (73); 97 (18); 93 (17); 91 (13); 85 (30); 84 (23); 83 (88); 77 (36); 76 (51); 74 (12); 73 (14); 71 (22); 69 (12); 67 (12); 61 (32); 60 (11); 59 (68); 55 (16); 53 (12); 46 (11); 44 (32); 42 (49); 40 (14); 37 (18); 25 (14).

$C_{13}H_{24}OSi$ (224.2): calculated C 67.30, H 10.78; found C 67.91, H 10.71.

1d: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.09 (s, 6H, Si(C$\underline{H}_3$)$_2$); 1.56 (dm, 2H, $^2J_{HH}$ = 8.1 Hz, SiC$\underline{H}_2$); 2.89 (s, 1H, C≡C–$\underline{H}$); 4.86 (dm, 1H, $^3J_{HH}$ = 9.6 Hz, *cis* CH=C$\underline{H}_2$); 4.87 (dm, 1H, $^3J_{HH}$ = 16.3 Hz, *trans* CH=C$\underline{H}_2$); 5.65–5.91 (m, 1H, C$\underline{H}$=CH$_2$); 7.14–7.35 (m, 6H, *meta* and *para* arom. C$\underline{H}$); 7.50–7.61 (m, 4H, *ortho* arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.0 (2CH$_3$, Si(C$\underline{H}_3$)$_2$); 26.4 (SiC$\underline{H}_2$); 76.1 (Si–O–$\underline{C}$); 77.7 (C≡$\underline{C}$–H); 86.8 (C≡$\underline{C}$–H); 114.3 (C$\underline{H}_2$=CH); 126.5, 127.9, 128.5 (10 arom. $\underline{C}$H); 134.6 (CH$_2$=$\underline{C}$H); 146.6 (2 *ipso* $\underline{C}$).

GC–MS (relative intensity): 306 ([*M*]$^+$,1); 266 (23); 265 (86); 192 (21); 191 (100); 190 (29); 189 (42); 165 (23); 83 (12); 59 (10).

$C_{20}H_{22}OSi$ (306.2): calculated C 77.35, H 7.53; found C 77.88, H 7.36.

1e: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.38 (s, 6H, Si(C$\underline{H}_3$)$_2$); 1.70 (s, 6H, C≡C$\underline{H}_3$)$_2$); 1.88 (dm, 2H, $^2J_{HH}$ = 8.0 Hz, SiC$\underline{H}_2$); 5.00 (dm,

1H, $^3J_{HH}$ = 9.1 Hz, *cis* CH=C$\underline{H}_2$); 5.02 (dm, 1H, $^3J_{HH}$ = 17.3 Hz, *trans* CH=C$\underline{H}_2$); 5.81–6.10 (m, 1H, C$\underline{H}$=CH$_2$); 7.29–7.44 (m, 3H, *meta* and *para* arom. C$\underline{H}$); 7.45–7.59 (m, 2H, *ortho* arom C$\underline{H}$).

NMR ^{13}C (50.329 MHz, $CDCl_3$) δ ppm: −0.1 (2CH_3, Si($\underline{C}H_3$)$_2$); 26.2 (Si$\underline{C}H_2$); 33.2 (2CH_3, C($\underline{C}H_3$)$_2$); 67.1 (Si–O–$\underline{C}$); 83.3 (C≡$\underline{C}$–Ph); 94.4 ($\underline{C}$≡C–Ph); 113.6 ($\underline{C}H_2$=CH); 123.2 (*ipso* $\underline{C}$); 128.3, 128.5, 131.5 (5 arom. $\underline{C}$H); 134.6 (CH$_2$=$\underline{C}$H).

GC–MS (relative intensity): 258 ([*M*]$^+$,3); 243 (21); 219 (25); 218 (81); 201 (23); 185 (16); 183 (10); 161 (44); 160 (100); 145 (17); 144 (27); 143 (12); 142 (43); 141 (91); 139 (14); 131 (21); 129 (58); 128 (26); 127 (67); 126 (21); 117 (18); 116 (38); 109 (11); 105 (24); 103 (39); 102 (29); 101 (27); 99 (22); 97 (10); 91 (22); 89 (11); 85 (10); 83 (10); 78 (15); 77 (78); 76 (65); 74 (17); 71 (15); 65 (15); 63 (15); 61 (33); 60 (10); 59 (59); 51 (16); 46 (10); 44 (34); 43 (39); 40 (13); 37 (17).

$C_{16}H_{22}OSi$ (258.2): calculated C 73.56, H 8.61; found C 73.15, H 8.69.

1f: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.13 (s, 6H, Si($C\underline{H}_3$)$_2$); 0.87 (t, 3H, $^3J_{HH}$ = 6.9 Hz, $C\underline{H}_3CH_2$); 1.10–1.82 (m, 14H, 5$C\underline{H}_2$ and $CH_3C\underline{H}_2C\underline{H}_2CH_2$); 1.65 (dm, 2H, $^2J_{HH}$ = 8.1 Hz, Si$C\underline{H}_2$); 2.17 (t, 2H, $^3J_{HH}$ = 6.8 Hz, $C\underline{H}_2$–C≡C); 4.79 (dm, 1H, $^3J_{HH}$ = 10.0 Hz, *cis* CH=C$\underline{H}_2$); 4.82 (dm, 1H, $^3J_{HH}$ = 17.0 Hz, *trans* CH=C$\underline{H}_2$); 5.62–5.92 (m, 1H, C$\underline{H}$=CH$_2$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.3 (2CH_3, Si($\underline{C}H_3$)$_2$); 13.5 ($\underline{C}H_3CH_2$); 18.4 ($\underline{C}H_2$–C≡C); 22.0 ($CH_3\underline{C}H_2$); 23.1, 25.4, 41.5 (5$\underline{C}H_2$); 26.26 (Si$\underline{C}H_2$); 30.8 ($\underline{C}H_2CH_2$–C≡C); 69.8 (Si–O–$\underline{C}$); 84.2 (CH$_2$–$\underline{C}$≡C); 85.3 (CH$_2$–C≡$\underline{C}$); 112.9 ($\underline{C}H_2$=CH); 134.7 (CH$_2$=$\underline{C}$H).

GC–MS (relative intensity): 278 ([*M*]$^+$,1); 240 (23); 239 (46); 222 (25); 220 (12); 218 (11); 197 (21); 196 (83); 195 (17); 194 (11); 182 (11); 180 (14); 170 (11); 168 (15); 166 (24); 164 (17); 162 (29); 158 (18); 157 (55); 155 (13); 153 (32); 152 (38); 151 (18); 141 (26); 140 (42); 137 (18); 133 (11); 127 (32); 125 (11); 123 (11); 121 (20); 119 (27); 115 (13); 113 (12); 111 (23); 110 (11); 109 (41); 107 (20); 105 (35); 101 (17); 99 (55); 98 (13); 97 (44); 96 (25); 95 (27); 93 (26); 92 (13); 91 (56); 89 (10); 85 (30); 84 (12); 83 (76); 82 (13); 81 (48); 80 (14); 79 (88); 78 (28); 77 (100); 76 (91); 74 (18); 73 (26); 71 (40); 69 (27); 67 (68); 66 (15); 65 (36); 63 (11); 61 (57); 60 (16); 57 (12); 55 (68); 53 (27); 51 (10); 44 (37); 42 (39); 40 (48); 37 (17); 25 (17).

$C_{17}H_{30}OSi$ (278.2): calculated C 68.28, H 10.34; found C 68.78, H 10.45.

1g: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.16 (s, 6H, Si($C\underline{H}_3$)$_2$); 1.10–1.89 (m, 10H, 5$C\underline{H}_2$); 1.66 (dm, 2H, $^2J_{HH}$ = 8.1 Hz, Si$C\underline{H}_2$); 3.36 (s, 3H, $C\underline{H}_3$–O); 4.12 (s, 2H, O–$C\underline{H}_2$); 4.82 (ddt, 1H, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 2.4 Hz, *cis* CH=C$\underline{H}_2$); 4.84 (ddt, 1H, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 1.1 Hz, *trans* CH=C$\underline{H}_2$); 5.66–5.92 (m, 1H, C$\underline{H}$=CH$_2$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.2 (2CH_3, Si($\underline{C}H_3$)$_2$); 23.0, 26.2, 41.1 (5$\underline{C}H_2$); 25.2 (Si$\underline{C}H_2$); 57.4 ($\underline{C}H_3$–O); 59.9 (O–$\underline{C}H_2$); 69.9 (Si–O–$\underline{C}$); 81.0 (CH$_2$–$\underline{C}$≡C); 90.5 (CH$_2$–C≡$\underline{C}$); 113.2 ($\underline{C}H_2$=CH); 134.6 (CH$_2$=$\underline{C}$H).

GC–MS (relative intensity): 266 ([*M*]$^+$,<1); 225 (11); 224 (50); 193 (10); 192 (42); 155 (10); 154 (43); 91 (20); 90 (12); 89 (26); 88 (17); 77 (12); 75 (46); 74 (16); 71 (10); 69 (10); 67 (14); 65 (14); 61 (27); 60 (14); 59 (100); 55 (28); 53 (20); 51 (12); 47 (23); 45 (66); 43 (27); 41 (80); 39 (34); 29 (15); 28 (13).

$C_{15}H_{26}OSi$ (250.2): calculated C 66.18, H 9.73; found C 65.68, H 9.69.

Enyne **1h**: In a Schlenk tube Me$_2$(CH$_2$=CHCH$_2$)SiCl (1.66 ml, 11 mmol) was added dropwise to a stirred solution of 3-hexyne-2,5-diol (571 mg, 5 mmol), NEt_3 (2.80 ml, 20 mmol) and DMAP (122 mg, 1 mmol) in CH_2Cl_2 (15 ml). The reaction mixture was stirred at room temperature for 16 h. Distilled water (10 ml) was then added to the reaction, the aqueous layer was extracted with CH_2Cl_2 (10 ml). The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/9). The dienyne **1h** was obtained in 80% isolated yield.

1h: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.14 (s, 12H, Si($C\underline{H}_3$)$_2$); 1.37 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $C\underline{H}_3CH$); 1.65 (dm, 4H, $^3J_{HH}$ = 8.0 Hz, Si$C\underline{H}_2$); 4.53 (qm, 2H, $^3J_{HH}$ = 6.6 Hz, $CH_3C\underline{H}$); 4.85 (dm, 2H, $^3J_{HH}$ = 10.0 Hz, *cis* CH=C$\underline{H}_2$); 4.87 (dm, 2H, $^3J_{HH}$ = 17.0 Hz, *trans* CH=C$\underline{H}_2$); 5.64–5.91 (m, 2H, C$\underline{H}$=CH$_2$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −2.1, −2.0 (4CH_3, Si($\underline{C}H_3$)$_2$); 24.7 (Si$\underline{C}H_2$); 25.1 ($\underline{C}H_3CH$);

58.5 ($CH_3\underline{C}H$); 85.5 ($\underline{C}\equiv\underline{C}$); 113.3 ($\underline{C}H_2$=CH); 133.6 ($CH_2$=$\underline{C}$H).

GC–MS (relative intensity): 282 ([*M*]$^+$,<1); 175 (10); 174 (20); 157 (23); 151 (11); 150 (12); 149 (66); 141 (12); 135 (30); 134 (34); 131 (19); 121 (29); 119 (27); 117 (15); 115 (12); 114 (20); 111 (10); 110 (21); 109 (47); 105 (21); 99 (29); 97 (14); 93 (49); 92 (45); 91 (12); 83 (15); 79 (33); 77 (26); 76 (11); 75 (100); 73 (38); 71 (17); 69 (19); 61 (18); 59 (53); 44 (18); 42 (16).

*4.2. General procedure for the metathesis reaction and the formation of **3a–h***

In a Schlenk tube under an argon atmosphere, the catalytic system **A** {[$RuCl_2$(*p*-cymene)]$_2$ (**2**), $MesH_2ImCl$ (2 mol eq.) and Cs_2CO_3 (4 mol eq.) (5 or 10 mol% of Ru)}, 1 mmol of enyne and 5 ml of degassed toluene were introduced. The reaction mixture was then heated at 80 °C for enynes **3a–e** or at 110 °C for enynes **3f–h**. The solvent was removed under vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/9). The metathesis products **3a–h** were obtained in 34–87% isolated yield.

3a: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.17 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.21 (s, 3H, Si($C\underline{H}_3$)$_2$); 1.56 (d, 1H, $^3J_{HH}$ = 6.5 Hz, Si$C\underline{H}_2$); 1.60 (d, 1H, $^3J_{HH}$ = 5.6 Hz, Si$C\underline{H}_2$); 1.72 (s, 3H, $C\underline{H}_3$); 4.85 (dd, 1H, $^3J_{HH}$ = 10.3 Hz, $^2J_{HH}$ = 2.0 Hz, *cis* CH=C$\underline{H}_2$); 5.18 (dd, 1H, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 2.0 Hz, *trans* CH=C$\underline{H}_2$); 6.12 (ddd, 1H, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 10.8 Hz, $^4J_{HH}$ = 1.1 Hz, C$\underline{H}$=CH_2); 6.18 (dd, 1H, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 5.6 Hz, C=$\underline{C}$H–CH_2); 7.15–7.38 (m, 3H, *meta* and *para* arom. C$\underline{H}$); 7.38–7.72 (m, 2H, *ortho* arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.6, 0.8 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.5 (Si$\underline{C}H_2$); 29.7 ($\underline{C}H_3$); 78.6 (Si–O–$\underline{C}$); 113.7 ($\underline{C}H_2$=CH); 122.7 (C=$\underline{C}$H–CH_2); 126.0, 126.9, 128.0 (5 arom. $\underline{C}$H); 138.2 (CH_2=$\underline{C}$H); 145.6 (*ipso* $\underline{C}$); 147.3 (CH_2=CH–$\underline{C}$).

GC–MS (relative intensity): 244 ([*M*]$^+$,37); 229 (24); 170 (12); 169 (11); 168 (15); 167 (13); 156 (15); 155 (89); 154 (16); 153 (27); 152 (10); 143 (10); 142 (31); 141 (18); 129 (32); 128 (32); 127 (13); 115 (25); 109 (13); 91 (15); 77 (25); 76 (13); 75 (100); 59 (10).

3b: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.11 (s, 6H, Si($C\underline{H}_3$)$_2$); 0.75–2.05 (m, 10H, 5$C\underline{H}_2$); 1.28 (d, 2H, $^3J_{HH}$ = 5.3 Hz, Si$C\underline{H}_2$); 4.85 (dd, 1H, $^3J_{HH}$ = 10.6 Hz, $^2J_{HH}$ = 1.8 Hz, *cis* CH=C$\underline{H}_2$); 5.18 (dd, 1H, $^3J_{HH}$ = 17.2 Hz, $^2J_{HH}$ = 1.8 Hz, CH *trans* =C$\underline{H}_2$); 5.91 (t, 1H, $^3J_{HH}$ = 5.3 Hz, C=C$\underline{H}$–CH_2); 6.27 (ddm, 1H, $^3J_{HH}$ = 17.2 Hz, $^3J_{HH}$ = 10.6 Hz, CH_2=C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.7 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.0 (Si$\underline{C}H_2$); 21.4, 25.6, 37.2 ($5CH_2$); 75.9 (Si–O–$\underline{C}$); 113.5 ($\underline{C}H_2$=CH); 120.9 (C=$\underline{C}$H–CH_2); 138.3 (CH_2=$\underline{C}$H); 147.2 (CH_2=CH–$\underline{C}$).

GC–MS (relative intensity): 222 ([*M*]$^+$,34); 180 (20); 179 (95); 167 (29); 166 (95); 165 (59); 151 (20); 147 (13); 146 (31); 133 (12); 131 (27); 119 (22); 118 (20); 117 (27); 109 (15); 106 (19); 105 (50); 104 (10); 103 (12); 97 (10); 95 (14); 93 (15); 92 (23); 91 (99); 85 (21); 83 (17); 82 (12); 81 (29); 80 (34); 79 (83); 78 (35); 77 (100); 76 (92); 74 (20); 73 (14); 72 (13); 71 (10); 69 (22); 68 (11); 67 (47); 66 (23); 65 (49); 63 (14); 61 (54); 60 (14); 59 (73); 58 (13); 57 (10); 56 (10); 55 (37); 53 (42); 52 (14); 51 (21); 47 (60); 45 (58); 44 (17); 43 (46); 42 (10); 41 (78); 40 (14); 39 (57); 29 (27); 28 (25); 27 (32).

3c: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.12 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.15 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.83 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH($C\underline{H}_3$)$_2$); 0.91 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH($C\underline{H}_3$)$_2$); 1.28 (s, 3H, C–$C\underline{H}_3$); 1.33 (dm, 2H, $^3J_{HH}$ = 6.7 Hz, Si$C\underline{H}_2$); 1.43 (d, 2H, $^3J_{HH}$ = 6.5 Hz, $C\underline{H}_2$CH(CH_3)$_2$); 1.52–1.75 (m, 1H, C$\underline{H}$(CH_3)$_2$); 4.87 (dd, 1H, $^3J_{HH}$ = 10.6 Hz, $^2J_{HH}$ = 2.0 Hz, *cis* CH=C$\underline{H}_2$); 5.22 (dd, 1H, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 2.0 Hz, *trans* CH=C$\underline{H}_2$); 6.00 (dd, 1H, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.8 Hz, C=C$\underline{H}$–CH_2); 6.16 (ddm, 1H, $^3J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 10.6 Hz, CH_2=C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.3, 0.9 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 12.9 (Si$\underline{C}H_2$); 24.4, 24.6 ($2CH_3$, CH($\underline{C}H_3$)$_2$); 24.6 ($\underline{C}$H(CH_3)$_2$); 30.4 (C–$\underline{C}H_3$); 50.7 ($\underline{C}H_2$CH(CH_3)$_2$); 78.3 (Si–O–$\underline{C}$); 113.6 ($\underline{C}H_2$=CH); 121.3 (C=$\underline{C}$H–CH_2); 138.4 (CH_2=$\underline{C}$H); 145.3 (CH_2=CH–$\underline{C}$).

GC–MS (relative intensity): 224 ([*M*]$^+$,48); 211 (12); 210 (35); 209 (100); 182 (13); 181 (36); 171 (13); 170 (30); 169 (74); 165 (14); 164 (18); 153 (14); 152 (64); 150 (29); 148 (15); 138 (15); 137 (10); 136 (16); 134 (24); 132 (25); 124 (17); 123 (10); 122 (20); 114 (11); 108 (19); 107 (13); 106 (16); 105 (10); 104 (10); 95 (13); 94 (14); 93 (23); 92 (19); 91 (24); 90 (17); 85 (13); 84 (11); 83 (17); 82

(12); 81 (12); 80 (13); 79 (48); 78 (26); 77 (54); 76 (57); 74 (57); 73 (24); 72 (17); 71 (10); 69 (16); 67 (22); 66 (16); 65 (42); 63 (11); 61 (54); 60 (22); 59 (13); 58 (18); 57 (19); 55 (46); 54 (11); 53 (53); 52 (15); 51 (23); 47 (12); 46 (15); 45 (13); 44 (35); 42 (20); 40 (19); 39 (25); 31 (10); 29 (43); 28 (15); 27 (36).

3d: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.12 (s, 6H, Si($C\underline{H}_3$)$_2$); 1.30 (d, 2H, $^3J_{HH}$ = 6.3 Hz, $SiC\underline{H}_2$); 4.68 (dd, 1H, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 1.9 Hz, *cis* CH=C$\underline{H}_2$); 5.20 (dd, 1H, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 1.9 Hz, *trans* CH=C$\underline{H}_2$); 5.69 (ddd, 1H, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 10.5 Hz, $^4J_{HH}$ = 0.8 Hz, CH_2=C$\underline{H}$); 6.40 (td, 1H, $^3J_{HH}$ = 6.3 Hz, $^4J_{HH}$ = 0.8 Hz, C=C$\underline{H}$–CH_2); 7.03–7.54 (m, 10H, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.7 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 14.6 (Si$\underline{C}H_2$); 83.5 (Si–O–$\underline{C}$); 112.8 ($\underline{C}H_2$=CH); 125.1 (C=$\underline{C}$H–CH_2); 127.3, 127.9, 128.3 (10 arom. $\underline{C}$H); 139.6 (CH_2=$\underline{C}$H); 146.1 (CH_2=CH–$\underline{C}$); 146.7 (2 *ipso* $\underline{C}$).

GC–MS (relative intensity): 306 ([*M*]$^+$,<1); 266 (19); 265 (70); 192 (20); 191 (100); 190 (22); 189 (37); 165 (21); 83 (13); 59 (10).

$C_{20}H_{22}OSi$ (306.2): calculated C 78.38, H 7.24; found C 78.56, H 7.50.

3e: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.24 (s, 6H, Si($C\underline{H}_3$)$_2$); 1.18 (s, 6H, C≡C$\underline{H}_3$)$_2$); 1.49 (d, 2H, $^3J_{HH}$ = 5.7 Hz, $SiC\underline{H}_2$); 5.07 (d, 1H, $^2J_{HH}$ = 2.1 Hz, *cis* CH=C$\underline{H}_2$); 5.33 (d, 1H, $^2J_{HH}$ = 2.1 Hz, *trans* CH=C$\underline{H}_2$); 5.87 (t, 1H, $^3J_{HH}$ = 5.7 Hz, C=$\underline{C}$H–CH_2); 7.10–7.30 (m, 5H, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.9 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.2 (Si$\underline{C}H_2$); 31.0 ($2CH_3$, C($\underline{C}H_3$)$_2$); 75.6 (Si–O–$\underline{C}$); 115.4 ($\underline{C}H_2$=CPh); 124.7 (C=$\underline{C}$H–CH_2); 127.6, 127.9, 128.3 (5 arom. $\underline{C}$H); 141.3 (*ipso* $\underline{C}$); 148.3 (CH_2=CPh–$\underline{C}$); 151.8 (CH_2=$\underline{C}$Ph).

GC–MS (relative intensity): 258 ([*M*]$^+$,10); 244 (11); 243 (44); 200 (24); 185 (11); 183 (13); 169 (26); 167 (17); 156 (11); 155 (12); 154 (10); 153 (11); 141 (23); 129 (10); 128 (20); 117 (17); 115 (32); 91 (14); 77 (18); 76 (12); 75 (100); 42 (10).

3f: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.11 (s, 6H, Si($C\underline{H}_3$)$_2$); 0.87 (t, 3H, $^3J_{HH}$ = 6.8 Hz, $C\underline{H}_3CH_2$); 1.10–1.85 (m, 16H, 5C$\underline{H}_2$ and $CH_3C\underline{H}_2C\underline{H}_2C\underline{H}_2$); 1.26 (d, 2H, $^3J_{HH}$ = 5.7 Hz, $SiC\underline{H}_2$); 4.62 (d, 1H, $^2J_{HH}$ = 2.6 Hz, C$\underline{H}_2$=C); 4.76 (dt, 1H, $^2J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 1.3 Hz, C$\underline{H}_2$=C); 5.48 (t, 1H, $^3J_{HH}$ = 5.7 Hz, C=C$\underline{H}$–CH_2).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.7 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 12.8 (Si$\underline{C}H_2$); 14.1 ($\underline{C}H_3CH_2$); 21.6, 25.6, 37.2 ($5CH_2$ cyclohexyl); 22.5 ($CH_3\underline{C}H_2$); 30.9 ($CH_3CH_2\underline{C}H_2$); 37.6 (CH_2=C–$\underline{C}H_2$); 75.8 (Si–O–$\underline{C}$); 112.6 ($\underline{C}H_2$=C); 121.8 (C=$\underline{C}$H–CH_2); 150.8 (CH_2=C–$\underline{C}$=CH); 152.1 (CH_2=$\underline{C}$).

GC–MS (relative intensity): 278 ([*M*]$^+$,10); 250 (22); 249 (76); 237 (24); 236 (100); 235 (35); 194 (10); 193 (37); 180 (21); 179 (48); 75 (30); 74 (20); 59 (23); 55 (20); 53 (11); 47 (14); 45 (13); 43 (21); 41 (44); 39 (13); 29 (17); 28 (11); 27 (13).

3g: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.11 (s, 6H, Si($C\underline{H}_3$)$_2$); 0.91–1.89 (m, 10H, 5C$\underline{H}_2$); 1.28 (d, 2H, $^3J_{HH}$ = 5.7 Hz, $SiC\underline{H}_2$); 3.35 (s, 3H, C$\underline{H}_3$–O); 3.85 (t, 2H, $^4J_{HH}$ = 1.4 Hz, O–C$\underline{H}_2$); 4.84 (dt, 1H, $^2J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 1.1 Hz, C$\underline{H}_2$=C); 5.09 (dt, 1H, $^2J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 2.3 Hz, C$\underline{H}_2$=C); 5.58 (t, 1H, $^3J_{HH}$ = 5.7 Hz, C=C$\underline{H}$–CH_2).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.7 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 12.8 (Si$\underline{C}H_2$); 21.5, 25.5, 37.2 ($5CH_2$ cyclohexyl); 58.1 ($\underline{C}H_3$–O); 75.9 (Si–O–$\underline{C}$); 76.1 (O–$\underline{C}H_2$); 113.0 ($\underline{C}H_2$=C); 123.6 (C=$\underline{C}$H–CH_2); 147.6 (CH_2=C–$\underline{C}$=CH); 148.1 (CH_2=$\underline{C}$).

GC–MS (relative intensity): 266 ([*M*]$^+$,22); 251 (16); 237 (22); 236 (75); 235 (64); 223 (39); 221 (14); 210 (10); 209 (19); 195 (15); 194 (10); 193 (32); 191 (15); 180 (17); 179 (50); 178 (12); 176 (36); 166 (10); 164 (20); 152 (10); 144 (12); 130 (19); 117 (10); 116 (19); 91 (11); 90 (19); 89 (11); 88 (20); 79 (10); 78 (11); 77 (16); 76 (15); 75 (43); 74 (28); 67 (11); 65 (11); 61 (11); 59 (50); 58 (15); 55 (28); 53 (21); 47 (29); 45 (100); 44 (12); 43 (29); 41 (38); 39 (19); 29 (14); 27 (11).

3h was obtained as a mixture of two diastereoisomers. Major diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.04, 0.08 (s, 12H, Si($C\underline{H}_3$)$_2$); 1.21–1.34 (m, 4H, $SiC\underline{H}_2$); 1.21 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $C\underline{H}_3CH$); 4.54 (q, 2H, $^3J_{HH}$ = 6.6 Hz, $CH_3C\underline{H}$); 5.65 (dd, 2H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 5.3 Hz, C$\underline{H}$=C).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.8, 1.0 ($4CH_3$, Si($\underline{C}H_3$)$_2$); 12.7 (Si$\underline{C}H_2$); 24.1 ($\underline{C}H_3CH$); 70.3 ($CH_3\underline{C}H$); 121.1 ($\underline{C}$H=C); 145.9 ($\underline{C}$=CH).

GC–MS (relative intensity): 282 ([*M*]$^+$,24); 268 (12); 267 (46); 193 (49); 179 (14); 155 (25); 154 (43); 150 (13); 148 (13); 147 (13); 141 (26); 139 (11); 135 (27); 134 (42); 133 (100); 132 (12); 131 (16); 128 (18); 121 (11); 120 (24); 119 (42); 118 (12); 117 (50);

115 (25); 109 (10); 107 (11); 106 (27); 105 (69); 104 (12); 103 (34); 93 (13); 92 (24); 91 (76); 85 (11); 77 (26); 76 (16); 75 (63); 73 (26); 65 (10); 61 (15); 59 (36); 44 (14); 42 (15).

Minor diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.16, 0.17 (s, 12H, Si($C\underline{H}_3$)$_2$); 1.21–1.34 (m, 4H, $SiC\underline{H}_2$); 1.28 (d, 6H, $^3J_{HH}$ = 6.6 Hz, $C\underline{H}_3CH$); 4.56 (q, 2H, $^3J_{HH}$ = 6.6 Hz, $CH_3C\underline{H}$); 5.65 (dd, 2H, $^3J_{HH}$ = 5.2 Hz, $^3J_{HH}$ = 5.3 Hz, $C\underline{H}$=C).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.6, −0.4 ($4CH_3$, Si($\underline{C}H_3$)$_2$); 12.7 ($Si\underline{C}H_2$); 24.1 ($\underline{C}H_3CH$); 71.5 ($CH_3\underline{C}H$); 120.8 ($\underline{C}$H=C); 144.8 ($\underline{C}$=CH).

GC–MS (relative intensity): 282 ([*M*]$^+$,8); 267 (26); 193 (24); 155 (15); 154 (25); 149 (32); 141 (13); 134 (22); 133 (67); 120 (13); 119 (100); 117 (26); 115 (13); 106 (14); 105 (35); 103 (17); 92 (13); 91 (41); 79 (10); 77 (14); 75 (89); 73 (14); 59 (20).

*4.3. General procedure for the preparation of Diels–Alder products **4b** and **4d***

In a Schlenk tube, 0.5 mmol of diene **3b** or **3d**, DEAD (0.16 ml, 1 mmol) and 5 ml of toluene were introduced. The reaction mixture was heated at reflux for 5 h. The solvent was removed in vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/5). The Diels–Alder products **4b** and **4d** were obtained, respectively in 41 and 61% isolated yield.

4b: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.08 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.16 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.65 (dm, 1H, $^2J_{HH}$ = 13.5 Hz, $C\underline{H}_2$Si); 1.16 (dm, 1H, $^2J_{HH}$ = 13.5 Hz, $SiC\underline{H}_2$); 0.76–2.05 (m, 10H, $5C\underline{H}_2$); 1.28 (t, 3H,$^3J_{HH}$ = 7.0 Hz, $CO_2CH_2C\underline{H}_3$); 1.30 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 2.90 (ddd, 1H, $^2J_{HH}$ = 23.2 Hz, $^3J_{HH}$ = 4.9 Hz, $^5J_{HH}$ = 4.9 Hz, $C\underline{H}_2$–CH=C); 3.09 (ddd, 1H, $^2J_{HH}$ = 23.2 Hz, $^3J_{HH}$ = 6.2 Hz, $^4J_{HH}$ = 2.7 Hz, $C\underline{H}_2$–CH=C); 3.36–3.53 (m, 1H, Si–CH_2–$C\underline{H}$); 4.18 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.26 (q, 2H, $^3J_{HH}$ = 7.0 Hz, $CO_2C\underline{H}_2CH_3$); 5.53–5.59 (m, 1H, CH_2–$C\underline{H}$=C).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 2.0 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.8, 14.0 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 21.6, 21.8, 25.9, 36.9, 38.9 ($\underline{C}H_2$ cyclohexyl); 22.9 ($Si\underline{C}H_2$); 27.7 (C=C–$\underline{C}H_2$–CH); 32.5 (Si–CH_2–$\underline{C}$H); 61.0 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 76.0 (Si–O–$\underline{C}$); 115.2 (C=$\underline{C}$H–CH_2); 129.4 (C=$\underline{C}$–CH_2–CH); 140.3 ($\underline{C}$=C–CH_2–CH); 144.6 (CH=$\underline{C}$–CH); 167.7, 168.1 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 392 ([*M*]$^+$,23); 349 (25); 348 (15); 347 (46); 346 (74); 320 (16); 319 (53); 318 (38); 317 (100); 303 (19); 293 (14); 291 (12); 289 (10); 276 (13); 275 (47); 247 (25); 246 (12); 245 (15); 221 (14); 219 (32); 203 (28); 202 (10); 201 (12); 193 (15); 175 (10); 173 (13); 149 (14); 129 (19); 128 (16); 115 (19); 103 (15); 91 (18); 79 (13); 77 (35); 76 (19); 75 (94); 73 (32); 61 (12); 59 (15); 55 (23); 45 (14); 43 (10); 41 (13); 29 (65); 28 (15).

4d: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.01 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.31 (s, 3H, Si($C\underline{H}_3$)$_2$); 0.81 (dm, 1H, $^2J_{HH}$ = 14.0 Hz, $C\underline{H}_2$Si); 0.87 (dm, 1H, $^2J_{HH}$ = 14.0 Hz, $SiC\underline{H}_2$); 1.22 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.26 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CO_2CH_2C\underline{H}_3$); 2.91–3.07 (m, 2H, $C\underline{H}_2$–CH=C); 3.30–3.53 (m, 1H, Si–CH_2–$C\underline{H}$); 4.15 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CO_2C\underline{H}_2CH_3$); 4.22 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 5.05 (dd, 1H, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 3.5 Hz, CH_2–$C\underline{H}$=C); 7.02–7.50 (m, 10H, arom. $C\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.5, 1.3 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 14.0, 14.1 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 23.0 ($Si\underline{C}H_2$); 28.0 (C=C–$\underline{C}H_2$–CH); 34.5 (Si–CH_2–$\underline{C}$H); 61.0, 61.2 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 85.6 (Si–O–$\underline{C}$); 123.8 (C=$\underline{C}$H–CH_2); 126.8, 127.3, 127.5, 127.5, 127.9, 128.0 (10 arom. $\underline{C}$H); 129.9 (C=$\underline{C}$–CH_2–CH); 139.8 ($\underline{C}$=C–CH_2–CH); 142.5, 144.5 (2 *ipso* $\underline{C}$); 146.0 (CH=$\underline{C}$–CH); 167.6 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 476 ([*M*]$^+$,3); 431 (13); 430 (16); 401 (10); 400 (10); 399 (28); 371 (17); 353 (18); 326 (11); 325 (20); 255 (11); 254 (11); 253 (26); 252 (17); 241 (10); 240 (10); 239 (20); 221 (28); 220 (11); 219 (26); 193 (13); 179 (15); 178 (19); 177 (10); 165 (26); 149 (11); 75 (22); 45 (14); 44 (11); 43 (10); 29 (100); 28 (21); 27 (12).

*4.4. General procedure for the preparation of Diels–Alder products **4a** and **4c***

In a Schlenk tube under an argon atmosphere, the catalytic system **A** {[$RuCl_2$(*p*-cymene)]$_2$ (**2**) (7.6 mg, 1.25×10^{-2} mmol), $MesH_2ImCl$ (7.8 mg, 2.5×10^{-2} mmol) and Cs_2CO_3 (16.3 mg, 5×10^{-2} mmol)}, 0.5 mmol of enyne and 2.5 ml of degassed toluene were introduced. The reaction mixture was then heated at 80 °C for 16 h. The complete conversion was observed by GC–MS and 0.16 ml (1 mmol) of

DEAD was added to the crude reaction. The reaction mixture was heated at reflux for 5 h. The solvent was removed under vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/5). The Diels–Alder products **4a** and **4c** were obtained, respectively in 79 and 61% isolated yield and as a mixture of two diastereoisomers in the ratio, respectively 72/28 and 50/50.

4a was obtained as a mixture of two diastereoisomers. Major diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.20 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.27 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.74 (dm, 1H, $^2J_{HH}$ = 13.6 Hz, C$\underline{H}_2$Si); 0.81 (dm, 1H, $^2J_{HH}$ = 13.6 Hz, SiC$\underline{H}_2$); 1.25 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.32 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.76 (s, 3H, C$\underline{H}_3$); 2.79 (d, 1H, $^3J_{HH}$ = 4.4 Hz, C$\underline{H}_2$–CH=C); 2.88 (d, 1H, $^3J_{HH}$ = 4.5 Hz, C$\underline{H}_2$–CH=C); 3.67–3.83 (m, 1H, Si–CH_2–C$\underline{H}$); 4.18 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.22 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.84 (dd, 1H, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 4.5 Hz, CH_2–C$\underline{H}$=C); 7.15–7.42 (m, 5H, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 1.2, 1.3 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 14.1, 14.1 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 22.9 (Si$\underline{C}H_2$); 28.1 (C=C–$\underline{C}H_2$–CH); 28.7 ($\underline{C}H_3$); 32.8 (Si–CH_2–$\underline{C}$H); 61.0, 61.2 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 80.4 (Si–O–$\underline{C}$); 119.9 (C=$\underline{C}$H–CH_2); 125.1, 126.7, 127.7 (5 arom. $\underline{C}$H); 130.1 (*ipso* $\underline{C}$); 139.3 (C=$\underline{C}$–CH_2–CH); 143.4 ($\underline{C}$=C–CH_2–CH); 146.4 (CH=$\underline{C}$–CH); 167.8, 167.9 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 414 ($[M]^+$,<1); 353 (22); 326 (17); 297 (12); 253 (13); 221 (17); 219 (19); 193 (16); 191 (14); 179 (18); 178 (31); 177 (12); 165 (16); 163 (10); 149 (14); 135 (11); 133 (11); 128 (11); 121 (10); 115 (20); 105 (18); 103 (22); 91 (13); 77 (32); 76 (11); 75 (100); 73 (16).

Minor diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.15 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.16 (s, 3H, Si(C$\underline{H}_3$)$_2$); 1.23 (dm, 1H, $^2J_{HH}$ = 14.5 Hz, C$\underline{H}_2$Si); 1.27 (dm, 1H, $^2J_{HH}$ = 14.5 Hz, SiC$\underline{H}_2$); 1.19 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.30 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.56 (s, 3H, C$\underline{H}_3$); 2.68 (d, 1H, $^3J_{HH}$ = 4.0 Hz, C$\underline{H}_2$–CH=C); 2.93–3.09 (m, 1H, Si–CH_2–C$\underline{H}$); 3.12 (d, 1H, $^3J_{HH}$ = 4.1 Hz, C$\underline{H}_2$–CH=C); 4.13 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.27 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 5.98 (dd, 1H, $^3J_{HH}$ = 4.0 Hz, $^3J_{HH}$ = 4.1 Hz, CH_2–C$\underline{H}$=C); 7.15–7.42 (m, 5H, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.6, 2.3 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.9, 14.0 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 23.2 (Si$\underline{C}H_2$); 28.0 (C=C–$\underline{C}H_2$–CH); 31.9 ($\underline{C}H_3$); 33.2 (Si–CH_2–$\underline{C}$H); 61.1, 63.0 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 79.9 (Si–O–$\underline{C}$); 118.3 (C=$\underline{C}$H–CH_2); 125.1, 126.9, 128.0 (5 arom. $\underline{C}$H); 129.4 (*ipso* $\underline{C}$); 140.2 (C=$\underline{C}$–CH_2–CH); 142.5 ($\underline{C}$=C–CH_2–CH); 146.9 (CH=$\underline{C}$–CH); 167.7, 167.7 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 414 ($[M]^+$,<1); 341 (10); 325 (27); 297 (17); 263 (12); 221 (16); 219 (22); 193 (15); 191 (15); 179 (14); 178 (25); 177 (10); 165 (14); 149 (15); 133 (10); 128 (16); 121 (10); 115 (19); 105 (30); 103 (21); 91 (12); 77 (29); 76 (11); 75 (100); 73 (17); 42 (11).

4c was obtained as a mixture of two diastereoisomers. Major diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.06 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.11 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.55 (d, 1H, $^2J_{HH}$ = 13.7 Hz, C$\underline{H}_2$Si); 0.62 (d, 1H, $^2J_{HH}$ = 13.7 Hz, C$\underline{H}_2$Si); 0.83 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH(C$\underline{H}_3$)$_2$); 0.91 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CH(C$\underline{H}_3$)$_2$); 1.24 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CO_2CH_2C\underline{H}_3$); 1.27 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.32 (d, 2H, $^3J_{HH}$ = 7.0 Hz, C$\underline{H}_2$CH(CH_3)$_2$); 1.51 (s, 3H, C–C$\underline{H}_3$); 1.70–1.98 (m, C$\underline{H}$(CH_3)$_2$); 2.88 (ddm, 1H, $^2J_{HH}$ = 23.0 Hz, $^3J_{HH}$ = 6.4 Hz, C$\underline{H}_2$–CH=C); 3.07 (ddd, 1H, $^2J_{HH}$ = 23.0 Hz, $^3J_{HH}$ = 6.0 Hz, $^5J_{HH}$ = 2.7 Hz, C$\underline{H}_2$–CH=C); 3.27–3.53 (m, 1H, Si–CH_2–C$\underline{H}$); 4.17 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.19 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CO_2C\underline{H}_2CH_3$); 5.45–5.56 (m, 1H, CH_2–C$\underline{H}$=C).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.5, 2.1 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 13.9, 14.1 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 22.5 (Si$\underline{C}H_2$); 24.0, 24.6 ($2CH_3$, C$\underline{H}$(CH_3)$_2$); 25.0 ($\underline{C}$H(CH_3)$_2$); 27.9 (C=C–$\underline{C}H_2$–CH); 28.3 (Si–CH_2–$\underline{C}$H); 29.5 (C–$\underline{C}H_3$); 49.3 ($\underline{C}H_2$CH(CH_3)$_2$); 61.1 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 78.5 (Si–O–$\underline{C}$); 115.1 (C=$\underline{C}$H–CH_2); 128.9 (C=$\underline{C}$–CH_2–CH); 140.1 ($\underline{C}$=C–CH_2–CH); 143.7 (CH=$\underline{C}$–CH); 167.6, 167.8 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 394 ($[M]^+$,<1); 347 (11); 337 (25); 336 (57); 335 (100); 291 (10); 290 (43); 263 (23); 262 (95); 234 (18); 220 (10); 218 (19); 192 (12); 191 (14); 190 (53); 176 (12); 160 (12); 75 (35); 74 (13); 59 (12); 45 (15); 44 (12); 43 (48); 41 (28); 29 (69); 28 (16); 27 (13).

Minor diastereoisomer ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.06 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.12 (s, 3H, Si(C$\underline{H}_3$)$_2$); 0.57 (d, 1H, $^2J_{HH}$ = 13.7 Hz,

$C\underline{H}_2Si$); 0.63 (d, 1H, $^2J_{HH}$ = 13.7 Hz, $C\underline{H}_2Si$); 0.92 (d, 3H, $^3J_{HH}$ = 6.4 Hz, $CH(C\underline{H}_3)_2$); 0.91 (d, 3H, $^3J_{HH}$ = 6.7 Hz, $CH(C\underline{H}_3)_2$); 1.24 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CO_2CH_2C\underline{H}_3$); 1.28 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.32 (d, 2H, $^3J_{HH}$ = 7.0 Hz, $C\underline{H}_2CH(CH_3)_2$); 1.53 (s, 3H, C–$C\underline{H}_3$); 1.70–1.98 (m, $C\underline{H}(CH_3)_2$); 2.89 (ddm, 1H, $^2J_{HH}$ = 23.0 Hz, $^3J_{HH}$ = 6.4 Hz, $C\underline{H}_2$–CH=C); 3.07 (ddd, 1H, $^2J_{HH}$ = 23.0 Hz, $^3J_{HH}$ = 6.0 Hz, $^5J_{HH}$ = 2.7 Hz, $C\underline{H}_2$–CH=C); 3.27–3.53 (m, 1H, Si–CH_2–$C\underline{H}$); 4.18 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.24 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CO_2C\underline{H}_2CH_3$); 5.45–5.56 (m, 1H, CH_2–$C\underline{H}$=C).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.5, 2.4 ($2CH_3$, $Si(\underline{C}H_3)_2$); 13.9, 14.1 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 22.6 ($Si\underline{C}H_2$); 24.7, 24.7 ($2CH_3$, $CH(\underline{C}H_3)_2$); 25.4 ($\underline{C}H(CH_3)_2$); 28.0 (C=C–$\underline{C}H_2$–CH); 33.3 (Si–CH_2–$\underline{C}H$); 32.7 (C–$\underline{C}H_3$); 52.1 ($\underline{C}H_2CH(CH_3)_2$); 61.1 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 78.6 (Si–O–$\underline{C}$); 116.4 (C=$\underline{C}$H–CH_2); 129.5 (C=$\underline{C}$–CH_2–CH); 140.5 ($\underline{C}$=C–CH_2–CH); 143.9 (CH=$\underline{C}$–CH); 168.1, 168.2 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 394 ($[M]^+$,<1); 378 (15); 377 (26); 348 (10); 347 (14); 337 (25); 336 (54); 335 (100); 332 (12); 331 (15); 304 (17); 290 (34); 263 (17); 262 (76); 234 (15); 220 (15); 218 (22); 192 (12); 190 (34); 176 (11); 75 (21); 74 (11); 45 (10); 43 (29); 41 (15); 29 (43); 28 (10).

*4.5. General procedure for the preparation of the aromatic products **5a–d***

In a Schlenk tube, 0.2 mmol of Diels–Alder product **4a–d**, 139 mg (0.6 mmol) of DDQ and 5 ml of toluene were introduced. The reaction mixture was heated at reflux for 15 h. The solvent was removed in vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/4). The products **5a–d** were obtained in 80–90% isolated yield.

5a: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: −0.04 (s, 3H, $Si(C\underline{H}_3)_2$); 0.26 (s, 3H, $Si(C\underline{H}_3)_2$); 1.34 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CO_2CH_2C\underline{H}_3$); 1.38 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.44 (d, 1H, $^2J_{HH}$ = 14.9 Hz, $C\underline{H}_2Si$); 1.87 (s, 3H, $C\underline{H}_3$); 1.88 (d, 1H, $^2J_{HH}$ = 14.9 Hz, $C\underline{H}_2Si$); 4.34 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.35 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CO_2C\underline{H}_2CH_3$); 5.55 (d, 1H, $^3J_{HH}$ = 8.2 Hz, arom. C$\underline{H}$); 7.11–7.30 (m, 5H, arom. C$\underline{H}$); 7.88 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.6, 0.4 ($2CH_3$, $Si(\underline{C}H_3)_2$); 14.1, 14.3 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 17.8 ($Si\underline{C}H_2$); 33.5 ($\underline{C}H_3$); 61.4 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 80.1 (Si–O–$\underline{C}$); 125.4, 127.1, 128.2 (arom. Ph $\underline{C}$H); 127.3 (CH=$\underline{C}$–CO_2); 128.3, 129.0 (arom. $\underline{C}$H); 135.0 (CH–C=$\underline{C}$–CO_2); 137.0 (C=$\underline{C}$–CH_2–Si); 147.4 (*ipso* $\underline{C}$); 149.0 (Si–O–C–$\underline{C}$); 165.6, 169.5 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 412 ($[M]^+$,<1); 337 (14); 335 (30); 324 (30); 323 (100); 261 (25); 218 (11); 191 (14); 190 (10); 189 (15); 178 (11); 165 (13); 105 (15); 77 (18); 75 (73).

$C_{23}H_{28}O_5Si$ (412.3): calculated C 65.20, H 6.67; found C 65.30, H 6.74.

5b: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.12 (s, 6H, $Si(C\underline{H}_3)_2$); 1.32 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.34 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.44–1.90 (m, 10H, $5C\underline{H}_2$); 2.01 (s, 2H, $C\underline{H}_2Si$); 4.29 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.39 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 7.38 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom. C$\underline{H}$); 7.77 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.4 ($2CH_3$, $Si(\underline{C}H_3)_2$); 14.1, 14.2 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 16.3 ($Si\underline{C}H_2$); 21.9, 25.6, 38.4 ($5\underline{C}H_2$); 61.3, 61.4 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 76.8 (Si–O–$\underline{C}$); 125.4, 127.1 (2 arom. $\underline{C}$H); 126.1 (CH=$\underline{C}$–CO_2); 132.7 (C=$\underline{C}$–CO_2); 137.8 (C=$\underline{C}$–CH_2–Si); 151.5 (Si–O–C–$\underline{C}$=CH); 166.6, 169.9 ($2\underline{C}O_2CH_2$).

GC–MS (relative intensity): 390 ($[M]^+$,71); 349 (15); 348 (47); 347 (100); 346 (28); 345 (36); 344 (19); 318 (13); 317 (44); 316 (19); 315 (54); 275 (20); 274 (20); 273 (54); 247 (22); 245 (16); 232 (12); 231 (21); 230 (14); 229 (42); 203 (19); 202 (15); 201 (26); 128 (18); 115 (16); 77 (19); 76 (12); 75 (99); 29 (28).

5c: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.04 (s, 3H, $Si(C\underline{H}_3)_2$); 0.17 (s, 3H, $Si(C\underline{H}_3)_2$); 0.79 (d, 3H, $^3J_{HH}$ = 6.1 Hz, $CH(C\underline{H}_3)_2$); 0.81 (d, 3H, $^3J_{HH}$ = 6.3 Hz, $CH(C\underline{H}_3)_2$); 1.31 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.34 (t, 3H, $^3J_{HH}$ = 7.2 Hz, $CO_2CH_2C\underline{H}_3$); 1.52 (s, 3H, C–$C\underline{H}_3$); 1.61 (d, 2H, $^3J_{HH}$ = 7.1 Hz, $C\underline{H}_2CH(CH_3)_2$); 1.62–1.86 (m, 1H, $C\underline{H}(CH_3)_2$); 1.97 (s, 1H, Si–$C\underline{H}_2$); 1.99 (s, 1H, Si–$C\underline{H}_2$); 4.29 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.39 (q, 2H, $^3J_{HH}$ = 7.2 Hz, $CO_2C\underline{H}_2CH_3$); 7.26 (d, 1H, $^3J_{HH}$ = 8.2 Hz, arom. C$\underline{H}$); 7.76 (d, 1H, $^3J_{HH}$ = 8.2 Hz, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 0.2, 0.3 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 14.1, 14.2 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 16.2 (Si$\underline{C}H_2$); 24.6 ($\underline{C}H(CH_3)_2$); 24.7 ($2CH_3$, $CH(\underline{C}H_3)_2$); 31.2 (C–$\underline{C}H_3$); 52.4 ($\underline{C}H_2CH(CH_3)_2$); 61.3, 61.4 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 79.4 (Si–O–$\underline{C}$); 126.1 (CH=$\underline{C}$–CO_2); 126.7, 126.8 (2CH, arom. $\underline{C}$H); 132.4 (C=$\underline{C}$–CO_2); 138.1 (Si–CH_2–$\underline{C}$); 150.3 (Si–O–C–$\underline{C}$=CH); 165.6, 169.8 ($2\underline{C}O_2CH_2$).

GC–MS (relative intensity): 392 ($[M]^+$,<1); 336 (28); 335 (100); 334 (11); 262 (15); 261 (66); 189 (10); 115 (11); 75 (23); 42 (10).

$C_{21}H_{32}O_5Si$ (392.2): calculated C 65.18, H 8.08; found C 64.87, H 8.10.

5d: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.18 (s, 6H, Si($C\underline{H}_3$)$_2$); 1.32 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.34 (t, 3H, $^3J_{HH}$ = 7.1 Hz, $CO_2CH_2C\underline{H}_3$); 1.75 (s, 2H, $C\underline{H}_2$Si); 4.31 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 4.39 (q, 2H, $^3J_{HH}$ = 7.1 Hz, $CO_2C\underline{H}_2CH_3$); 6.61 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom. C$\underline{H}$); 7.02–7.14 (m, 4H, arom. C$\underline{H}$); 7.19–7.32 (m, 6H, arom. C$\underline{H}$); 7.64 (d, 1H, $^3J_{HH}$ = 8.3 Hz, arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: −0.1 ($2CH_3$, Si($\underline{C}H_3$)$_2$); 14.2, 14.2 ($2CH_3$, $CO_2CH_2\underline{C}H_3$); 18.0 (Si$\underline{C}H_2$); 61.4, 61.5 ($2CH_2$, $CO_2\underline{C}H_2CH_3$); 85.4 (Si–O–$\underline{C}$); 126.0, 129.9 (2 arom. $\underline{C}$H); 127.3 (CH=$\underline{C}$–CO_2); 127.6, 128.0, 128.1 (10 arom Ph $\underline{C}$H); 134.7 (C=$\underline{C}$–CO_2); 136.8 (C=$\underline{C}$–CH_2–Si); 146.0 (2 *ipso* $\underline{C}$); 149.5 (CH=$\underline{C}$–CO_2); 165.7, 169.6 (2C=O, $\underline{C}O_2CH_2$).

GC–MS (relative intensity): 474 ($[M]^+$,7); 429 (12); 428 (11); 399 (24); 398 (34); 326 (12); 325 (12); 324 (25); 323 (45); 322 (87); 292 (17); 254 (13); 253 (30); 252 (44); 251 (26); 250 (12); 241 (11); 240 (10); 239 (21); 219 (13); 218 (41); 164 (21); 75 (16); 45 (11); 29 (100); 28 (38); 27 (15).

$C_{28}H_{30}O_5Si$ (474.3): calculated C 71.05, H 7.02; found C 70.96, H 7.29.

4.6. Formation of the allylic diol **6**

In a Schlenk tube, 111 mg (0.5 mmol) of allylsilane **3b**, 145 mg (2.5 mmol) of KF, 115 mg (1.15 mmol) of $KHCO_3$, 5 ml of THF and 2.3 ml (20 mmol) of H_2O_2 (30%) were introduced. The reaction mixture was heated at 40 °C for 24 h. After cooling at room temperature, the organic product was extracted with diethyl ether (3 ml × 10 ml). The combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (diethyl ether). The allylic diol **6** was obtained in 77% isolated yield.

6: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 0.92–1.75 (m, 10H, $5C\underline{H}_2$); 3.29 (s, 2H, 2 O$\underline{H}$); 4.30 (d, 2H, $^3J_{HH}$ = 6.7 Hz, $HOC\underline{H}_2$); 4.91 (dd, 1H, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 2.0 Hz, *cis* CH=C$\underline{H}_2$); 5.22 (dd, 1H, $^3J_{HH}$ = 16.7 Hz, $^2J_{HH}$ = 2.0 Hz, *trans* CH=C$\underline{H}_2$); 5.71 (t, 1H, $^3J_{HH}$ = 6.7 Hz, $HOCH_2C\underline{H}$); 6.29 (dd, 1H, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 16.7 Hz, C$\underline{H}$=CH_2).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 21.4, 25.3, 36.6 ($5CH_2$); 59.4 ($HO\underline{C}H_2$); 74.8 (HO$\underline{C}$); 115.2 (CH=$\underline{C}H_2$); 126.1 ($HOCH_2\underline{C}$H=C); 138.3 ($\underline{C}$H=CH_2); 149.9 (CH=$\underline{C}$).

4.7. Formation of the triene **7**

In a Schlenk tube, 1.5 ml (1.5 mmol) of tetrabutylammonium fluoride (1 M in THF) was added to a stirred solution of 153 mg (0.5 mmol) of allylsilane **3d** and 10 ml of CH_2Cl_2 at −78 °C. The reaction mixture was slowly allowed to room temperature. After stirring for an additional 15 min at this temperature, the solvents were removed in vacuum and the crude product was purified by flash chromatography (diethyl ether/pentane: 1/3). The triene **7** was obtained in 75% isolated yield.

7: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 5.31 (dd, 2H, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 1.9 Hz, 2 *cis* CH=C$\underline{H}_2$); 5.55 (dd, 2H, $^3J_{HH}$ = 17.7 Hz, $^2J_{HH}$ = 1.9 Hz, 2 *trans* CH=C$\underline{H}_2$); 6.48 (dd, 2H, $^3J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 11.2 Hz, 2C$\underline{H}$=CH_2); 6.92–7.37 (m, 10 arom. H).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 118.8 (2CH=$\underline{C}H_2$); 127.2, 127.8, 131.1 (10 arom. $\underline{C}$H); 135.1 ($\underline{C}$CH=CH_2); 135.8 (2CH=CH_2); 141.8 ($Ph_2\underline{C}$=C); 142.2 (2 *ipso* $\underline{C}$).

GC–MS (relative intensity): 232 ($[M]^+$,89); 231 (29); 229 (11); 228 (11); 227 (7); 226 (9); 218 (16); 217 (68); 216 (57); 215 (100); 213 (8); 206 (6); 205 (28); 204 (83); 203 (66); 202 (80); 200 (9); 192 (15); 191 (73); 190 (19); 189 (34); 179 (10); 178 (22); 177 (5); 176 (10); 167 (6); 166 (8); 165 (29); 164 (7); 163 (7); 155 (20); 154 (21); 153 (29); 152 (22); 151 (9); 142 (5); 141 (29); 139 (7); 129 (10); 128 (31); 127

(10); 126 (5); 117 (9); 116 (5); 115 (24); 114 (6); 113 (6); 108 (12); 107 (6); 104 (6); 103 (7); 102 (9); 101 (19); 95 (6); 91 (31); 89 (13); 88 (8); 87 (6); 78 (12); 77 (33); 76 (13); 75 (11); 74 (7); 65 (10); 63 (18); 62 (5); 51 (28); 50 (8); 39 (21); 28 (19); 27 (19).

*4.8. Formation of the tetrasubstituted olefin **8***

In a Schlenk tube under an argon atmosphere, 153 mg (0.5 mmol) of allylsilane **3d**, 15 mg of Pd/C and 5 ml of degassed CH_2Cl_2 were introduced. The Schlenk tube was purged three times with hydrogen. The reaction mixture was stirred for 16 h at room temperature under 1 atm of hydrogen. The reaction was filtered on celite and the solvent was removed in vacuum. The product **8** was obtained in 75% isolated yield.

8: ^{1}H NMR (200.130 MHz, $CDCl_3$), δ ppm: 1.10 (t, 6H, $^3J_{HH} = 7.5$ Hz, $2CH_2C\underline{H}_3$); 2.24 (q, 4H, $^3J_{HH} = 7.5$ Hz, $2C\underline{H}_2CH_3$); 7.12–7.46 (m, 10 arom. C$\underline{H}$).

^{13}C NMR (50.329 MHz, $CDCl_3$) δ ppm: 13.6 ($2CH_2\underline{C}H_3$); 24.6 ($2CH_2CH_3$); 126.2 128.0, 129.4 (10 arom. $\underline{C}$H); 137.4 (C=$\underline{C}$$CH_2CH_3$); 142.2 ($Ph_2\underline{C}$=C); 143.6 (2 *ipso* $\underline{C}$).

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