Titanocene-Mediated Homolytic Opening of Epoxysilanes

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Dedicated to the memory of Professor *Hanns Fischer*, whose outstanding contribution to radical chemistry has made it an essential asset of modern chemistry

The titanocene(III) chloride mediated opening of silyloxiranes has been examined. Electron transfer from the metal leads to α-silyl radicals with total regiocontrol. The radicals could be trapped by various olefins, and the corresponding adducts were obtained in good yields (*Table*). Further substitution of the oxirane by alkyl groups proved detrimental to the reactions, but ring opening remained essentially regioselective.

Introduction. – Introduction of titanocene(III) chlorides as effective reagents for the homolytic opening of epoxides – leading to β-titanoxy alkyl radicals – is arguably one of the most-significant breakthroughs in radical chemistry of the past two decades. Indeed, *Nugent* and *RajanBabu* [1] reported in 1988 that titanocene(III) chloride can transfer one electron to oxiranes, which regioselectively leads to the most substituted β-titanoxyl radical after opening of the strained three-membered ring. *Gansäuer et al.* have shown that this system is amenable to asymmetric catalysis [2][3]. Those two outstanding contributions have opened vast new opportunities for chemists. Interest for this new system stems in no small part from the fact that it avoids the use of Sn derivatives – relying on nontoxic metals instead – and it creates radicals from oxiranes, which can be obtained easily, and using green reactions, too. The number of reports focusing on this particular aspect of Ti chemistry has thus soared over these last four years. Yet, research has so far been focused on mechanistic elucidations [4–7], variations of the catalysts [8–10], and the scope of the β-titanoxyl radical addition to unsaturated compounds [11][12] from intermolecular additions [13–15] and cyclizations [13][16][17] to polycyclization cascades leading to natural products [18–20] and other domino processes [21][22].

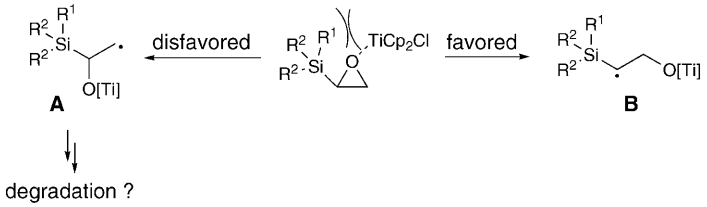
To the best of our knowledge, little attention has been given to the oxirane substitution beyond the initial determination of the opening's regioselectivity. Introduction of heteroatoms on the small ring might both modulate the reactivity and allow further functionalization after the radical step. In this respect, silicon groups are attractive candidates. Because of their steric bulk, they might direct the opening of the oxiranes toward the formation of α-silyl radicals, which could further react with olefins to create

various C,C bonds; *Tamao–Fleming* oxidation of the C–Si bond would afford the corresponding alcohols [23]. Overall, epoxysilanes are potential synthetic equivalents of β-hydroxy ketyl radicals and might provide an entry to polyhydroxylated compounds (*Scheme 1*). We report herein our progress along these lines.

Scheme 1. *Epoxysilanes as Potential Equivalents of β-Hydroxy Ketyl Radicals*

Results and Discussion. – We started our work with a series of monosubstituted silyloxiranes **1** (*Table*). Reactions were carried out using a stoichiometric amount of titanocene(IV) dichloride in the presence of powdered Zn and an acceptor (2 equiv.). In all cases, only formation of the α-silyl radical addition products (compounds **2**–**15**) were observed. The regiochemical outcome of the reaction is in agreement with what has been previously observed with nonsymmetric oxiranes. Indeed, opening is directed by nonbonding interactions during electron transfer, *i.e.*, on the Ti/oxirane complex (*Scheme 2*) [7].

Scheme 2. *Origin of the Regioselectivity of the Ring Opening of Epoxysilanes*

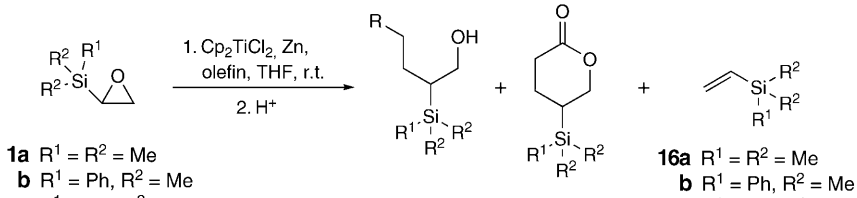


The absence of the minor regioisomer might be attributed to the increased steric hindrance brought by the silyl group. Although C–Si bonds are longer than C–C ones by 20%, steric control would still be effective (the total selectivity may also be the consequence of a degradation of regioisomer **A**, which is suitable for a *Brook* rearrangement). It has to be noted that stabilization of radicals by silyl groups is still a matter of debate [24] and might play also a role, even if the literature on homolytic openings of oxiranes by titanocene(III) complexes has excluded such a possibility for normal oxiranes [7][11].

Several olefins have been used throughout this study: acrylonitrile (*Table*, *Entries 1*, *5*, *10*, *11*, and *14*), vinylsulfones (*Entries 2* and *6*), or acrylates (*Entries 3*, *4*, *7–9*, *12*, and *13*). The yields were medium to good, reflecting those generally obtained with standard oxiranes. Lactonization was observed with methyl acrylates (*Entries 3*, *7*, *9*, and *12*), but we could get the opened product with the *tert*-butyl acrylates (*Entries 4*, *8*, and *13*). However, in those cases, the yields were lower. Maybe some of the adducts were lost upon acidic hydrolysis. We next looked at the substitution on silicon. Different combinations were tried, and all gave similar results. Heavier silyloxiranes gave some deoxygenated vinylsilanes **16b–e** (11–20%) [25]. This was not observed with oxirane **1a**, probably because of the volatility of **16a** (b.p. 55°).

We next studied the influence of further substitution on the oxirane moiety. Because our ultimate goal is to prepare polyhydroxylated compounds, we decided to

Table. *Titanocene-Mediated Homolytic Opening of Epoxysilanes.* Conditions: Cp_2TiCl_2 (2 equiv.), Zn dust (5 equiv.), olefin (2 equiv.).



1a $R^1 = R^2 = Me$
b $R^1 = Ph$, $R^2 = Me$
c $R^1 = Me$, $R^2 = Ph$
d $R^1 = R^2 = Ph$
e $R^1 = R^2 = i\text{-Pr}$

16a $R^1 = R^2 = Me$
b $R^1 = Ph$, $R^2 = Me$
c $R^1 = Me$, $R^2 = Ph$
d $R^1 = R^2 = Ph$
e $R^1 = R^2 = i\text{-Pr}$

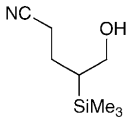
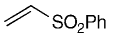
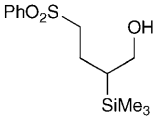
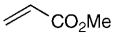
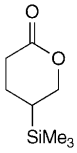
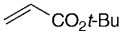
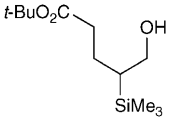
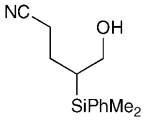
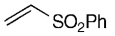
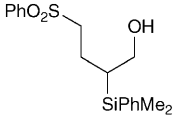
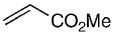
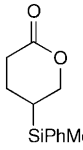
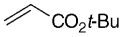
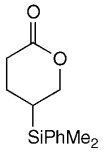
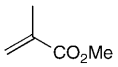
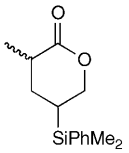
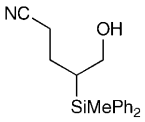
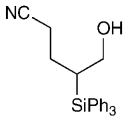
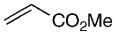
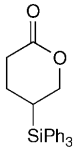
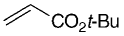
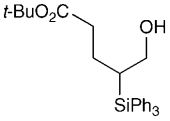
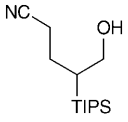
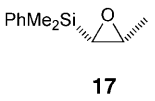
Entry	Substrate	Olefin	Product		Yield [%]	Side product (yield [%])
1	**1a**			**2**	73	–
2	**1a**			**3**	71	–
3	**1a**			**4**	84	–
4	**1a**			**5**	56	–
5	**1b**			**6**	75	–
6	**1b**			**7**	65	–
7	**1b**			**8**	60	**16b** (12)
8	**1b**			**9**	48	–

Table (cont.)

Entry	Substrate	Olefin	Product		Yield [%]	Side product (yield [%])
9	**1b**			**10**	60[a])	**16b** (12)
10	**1c**			**11**	57	**16c** (15)
11	**1d**			**12**	64	**16d** (14)
12	**1d**			**13**	62	**16d** (20)
13	**1d**			**14**	50	**16d** (14)
14[b])	**1e**			**15**	61	**16e** (11)

[a]) Diastereoisomer ratio (ds) *ca.* 1:1. [b]) Mn instead of Zn dust was used.

continue with a silyl moiety that could undergo oxidation. We opted for the phenyldimethylsilyl derivatives **17**–**19**, with different steric hindrance (*cis* and *trans* relative configurations, increased bulk).



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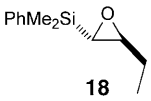

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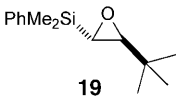
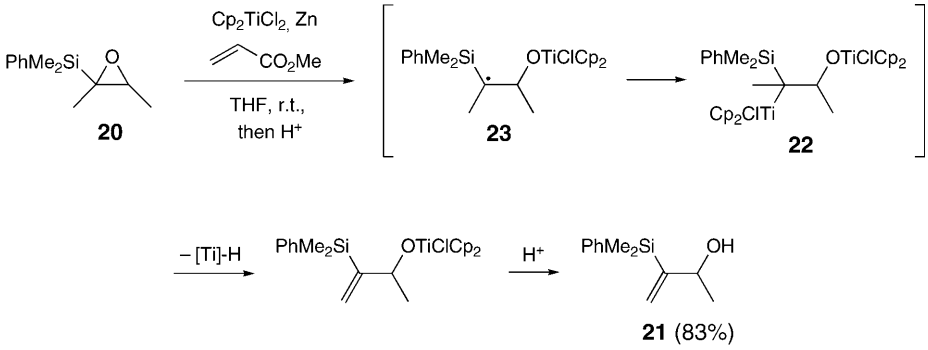


19

Unfortunately, no reaction proceeded as anticipated. Besides, the substrates' behavior toward different olefins was far from clear, and could not be rationalized. Complex mixtures were obtained, and the only observable products were, in some cases, acrylonitrile (the remaining starting material, up to 86%), and in other cases acrylates (an increased amount of deoxygenated products, up to 75%). Overall, it seems that increased steric hindrance is detrimental to the addition process. This was

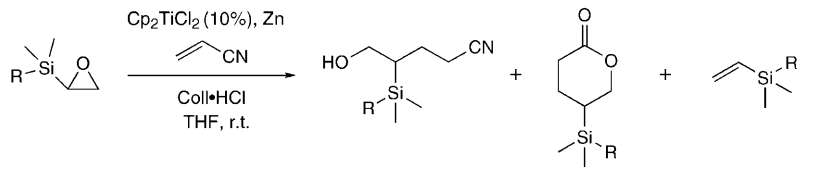
further confirmed in the case of the trisubstituted substrate **20** (*Scheme 3*). The only isolated product was the silylated allyl alcohol **21**, which was isolated in 83% yield. Its formation could be rationalized by a β-hydride elimination of the intermediate **22**, which would originate from the reduction of radical **23**. The latter could be too congested to allow the desired addition on the double bond. If this is the case, the opening of **20** would still be totally regioselective. Alternatively, the elimination could have been mediated by the *Lewis* acid ($ZnCl_2$) produced during the reduction of titanocene dichloride [26]. We are currently assessing this issue.

Scheme 3. *Possible Mechanism for the Reaction of* **20**



We finally examined the catalytic version (*Scheme 4*). To our surprise, the reactions with acrylonitrile were rather sluggish. The major products were the lactones arising from the acid-catalyzed or *Lewis* acid catalyzed activation of the nitrile moiety during the reaction. The overall yields were lower than with stoichiometric Ti complexes (maybe because of loss of an intermediate hydroxy carboxylic acid). Clearly, an optimization is required, but this shows nonetheless that catalysis is feasible.

Scheme 4. *Preliminary Examples of Catalytic Reactions*



1a R = Me	5 d:	**2** (26%)	**4** (38%)	**16a** (10%)
1b R = Ph	14 d:	**6** (4%)	**8** (39%)	**16b** (31%)

Conclusions. – Silyloxiranes can be regioselectively opened by titanocene(III) complexes. Provided steric hindrance on the oxirane moiety is not too important, addition of the resulting α-silyl radicals onto olefins can take place. Our initial work has shown that steric hindrance is a predominant factor. We could show that the system is amenable to catalysis. We are now focusing on establishing precisely the scope of the reaction,

notably by introducing trialkylsilyl vinyloxiranes [27]. This will be presented in due course.

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Experimental Part

General. Reactions were carried out under inert gas, with magnetic stirring, using redistilled, degassed solvents when necessary. THF was distilled from Na/benzophenone. Cp_2TiCl_2 (97%) was purchased from *Aldrich* and used as received. Manganese (Mn, −325 mesh; >99%) was purchased from *Strem* and used without further purification. Zn Dust (−325 mesh) was purchased from *Aldrich* and purified according to the following procedure: Zn (120 mg) was stirred for 1 min with aq. 2% HCl (300 ml). The acid was removed by filtration, and the powder was washed with aq. 2% HCl (300 ml), dist. H_2O (300 ml), 95% EtOH (400 ml), and Et_2O (200 ml). The material was finally thoroughly dried. Acrylonitrile was dried over $CaCl_2$ and distilled immediately before use. Methyl acrylate was purchased from *Aldrich*, washed repeatedly with aq. 1M NaOH, then with dist. H_2O, dried ($CaCl_2$), and distilled under reduced pressure before use. Phenyl vinyl sulfone (99%) and *tert*-butyl acrylate (>98%) were purchased from *Aldrich* and used without further purification. The starting silyloxiranes were prepared according to the literature [28].

Thin-layer chromatography (TLC) was performed on silica gel *60 F254* (*Merck*). *Geduran SI 60 A* silica gel (35–70 μm; *Merck*) was used for flash column chromatography (FC). The abbreviation 'PE' is used for petroleum ether. Melting points (m.p.) were measured with a *Reichert* hot-stage apparatus and are uncorrected. IR Spectra were recorded on a *Bruker Tensor 27 ATR diamant PIKE* spectrometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra were recorded at r.t. on 200/50 MHz *Bruker AC-200* and *ARX-200* spectrometers, on a 250/62.5 MHz *Bruker ARX-250* apparatus, and on 400/100 MHz *Bruker ARX-400* and *AVANCE-400* spectrometers, resp.; chemical shifts δ in ppm rel. to residual solvent signals of $CDCl_3$ (δ(H) 7.26, δ(C) 77.0), coupling constants J in Hz. High-resolution mass spectra (HR-MS) were recorded at *ICSN* (*CNRS*, Gif) on an LCT micromass apparatus (electrospray source). Elemental analyses were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie, and at *ICSN* (*CNRS*, Gif).

General Procedure (GP) *for Cp_2TiCl-Mediated Reactions.* Cp_2TiCl_2 (498 mg, 2.0 mmol, 2.0 equiv.) and Zn powder (296 mg, 5.0 mmol, 5.0 equiv.) were added to degassed THF (15 ml) at r.t. The mixture turned greenish, and the supernatant was cannulated to a degassed soln. of the starting silyloxirane (1.0 mmol, 1.0 equiv.) and the olefin acceptor (2.0 mmol, 2.0 equiv.). After completion of the reaction (*ca.* 30 min), the mixture was diluted with Et_2O (10 ml), and quenched with 10% aq. H_2SO_4 soln. (*ca.* 15 ml), washed twice with sat. aq. $NaHCO_3$ soln. (40 ml) and brine (20 ml), dried ($MgSO_4$), and concentrated *in vacuo*. The crude product was purified by FC (SiO_2) and, in some cases, separated from the corresponding vinylsilanes (see main text and the *Table*).

5-Hydroxy-4-(trimethylsilyl)pentanenitrile (**2**). Purified by FC (SiO_2; PE/Et_2O 60:40). Yield: 125 mg (73%). Yellow oil. IR (neat): 3445, 2950, 2240. ^1H-NMR (400 MHz, $CDCl_3$): 0.03 (*s*, Me_3Si); 0.97–1.03 (*m*, SiCH); 1.77–1.88 (*m*, CH_2CH_2CN); 2.53–2.58 (*m*, CH_2CN); 3.65 (*B* of *ABX*, J = 10.8, 8.1, 1 H of OCH_2); 3.89 (*A* of *ABX*, J = 10.8, 3.5, 1 H of OCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.5 (Me_3Si); 17.9 (CH_2CH_2CN); 24.6 (CH_2CN); 29.4 (SiCH); 63.6 (CH_2O); 120.4 (CN). HR-ESI-MS: 194.0988 ($[M+Na]^+$, $C_8H_{17}NNaOSi^+$; calc. 194.0977).

4-(Phenylsulfonyl)-2-(trimethylsilyl)butan-1-ol (**3**). Purified by FC (SiO_2; PE/AcOEt 70:30). Yield: 203 mg (71%). Orange oil. IR (neat): 3522, 2950, 1085. ^1H-NMR (400 MHz, $CDCl_3$): −0.01 (*s*, Me_3Si); 0.93–0.99 (*m*, SiCH); 1.81–1.88 (*m*, 1 H of CH_2CH_2CN); 1.93–1.99 (*m*, 1 H of CH_2CH_2CN); 3.16–3.24 (*m*, 1 H of CH_2SO_2); 3.38–3.45 (*m*, 1 H of CH_2SO_2), 3.59 (*B* of *ABX*, J = 10.8, 8.1, 1 H of

OCH_2); 3.84 (*A* of *ABX*, $J = 10.8, 3.5$, 1 H of OCH_2); 7.57–7.67 (*m*, 3 arom. H); 7.88–7.90 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.5 (Me_3Si); 21.2 ($CH_2CH_2SO_2$); 29.2 (SiCH); 56.5 (CH_2SO_2); 63.8 (CH_2O); 128.0 (arom. CH); 129.2 (arom. CH); 133.6 (arom. CH); 154.0 (arom. C). HR-ESI-MS: 309.0912 ($[M+Na]^+$, $C_{13}H_{22}NaO_3SSi^+$; calc. 309.0957). Anal. calc. for $C_{13}H_{22}O_3SSi$: C 54.51, H 7.74; found: C 54.06, H 7.71.

*Tetrahydro-5-(trimethylsilyl)-2*H*-pyran-2-one* (**4**). Purified by FC (SiO_2; PE/Et_2O 60:40). Yield: 145 mg (84%). Yellow oil. IR (neat): 2952, 1731, 1077. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.06 (*s*, Me_3Si); 1.21–1.28 (*m*, SiCH); 1.64–1.78 (*m*, 1 H of $CH_2CH_2C{=}O$); 1.90–1.99 (*m*, 1 H of $CH_2CH_2C{=}O$); 2.46 (*B* of *ABXY*, $J = 17.7, 10.0, 7.4$, 1 H of $CH_2C{=}O$); 2.63 (*A* of *ABXY*, $J = 17.7, 6.6, 3.5$, 1 H of $CH_2C{=}O$); 4.18 (*B* of *ABX*, $J = 12.9, 11.4$, 1 H of OCH_2); 4.46 (*A* of *ABX*, $J = 11.4, 2.3$, 1 H of OCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.4 (Me_3Si); 21.3 ($CH_2CH_2C{=}O$); 23.1 ($CH_2C{=}O$); 31.1 (SiCH); 72.3 (OCH_2); 171.5 (C=O). Anal. calc. for $C_8H_{16}O_2Si$: C 55.77, H 9.36; found: C 55.56, H 9.12.

1,1-Dimethylethyl 5-Hydroxy-4-(trimethylsilyl)pentanoate (**5**). Purified by FC (SiO_2; PE/Et_2O 70:30). Yield: 138 mg (56%). Yellow oil. IR (neat): 3434, 2952, 1726, 1148, 833. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.03 (*s*, Me_3Si); 0.78–0.85 (*m*, SiCH); 1.45 (*s*, Me_3C); 1.68–1.85 (*m*, $CH_2CH_2C{=}O$); 2.34 (*t*, $J = 7.3$, $CH_2C{=}O$); 3.63 (*B* of *ABX*, $J = 10.9, 7.6$, 1 H of OCH_2); 3.79 (*A* of *ABX*, $J = 10.9, 3.6$, 1 H of OCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.3 (Me_3Si); 22.2 ($CH_2CH_2C{=}O$); 28.1 (*t*-Bu); 30.2 (SiCH); 35.2 ($CH_2C{=}O$); 63.3 (OCH_2); 80.4 (Me_3C); 173.9 (C=O). Anal. calc. for $C_{12}H_{26}O_3Si$: C 58.49, H 10.63; found: C 58.75, H 10.51.

4-[Dimethyl(phenyl)silyl]-5-hydroxypentanenitrile (**6**). Purified by FC (SiO_2; PE/Et_2O 60:40). Yield: 175 mg (75%). Yellow oil. IR (neat): 3431, 2954, 2246, 814. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.34 (*s*, 3 H of Me_2Si); 0.35 (*s*, 3 H of Me_2Si); 1.22–1.27 (*m*, 1 H, SiCH); 1.73–1.90 (*m*, CH_2CH_2CN); 2.43–2.48 (*m*, CH_2CN); 3.66 (*B* of *ABX*, $J = 10.6, 7.8$, 1 H of OCH_2); 3.88 (*A* of *ABX*, $J = 10.6, 3.5$, 1 H of OCH_2); 7.32–7.41 (*m*, 3 arom. H); 7.48–7.56 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −4.3 (1 C of Me_2Si); −4.1 (1 C of Me_2Si); 17.6 (CH_2CH_2CN); 24.4 (CH_2CN); 29.1 (SiCH); 63.4 (CH_2O), 120.2 (CN), 128.1 (arom. CH); 129.5 (arom. CH); 133.7 (arom. CH); 136.9 (arom. C). HR-ESI-MS: 256.1100 ($[M+Na]^+$, $C_{13}H_{19}NNaOSi^+$; calc. 256.1134). Anal. calc. for $C_{13}H_{19}NOSi$: C 66.90, H 8.21, N 6.00; found: C 66.59, H 8.07, N 5.75.

2-[Dimethyl(phenyl)silyl]-4-(phenylsulfonyl)butan-1-ol (**7**). Purified by FC (SiO_2; PE/AcOEt 70:30). Yield: 227 mg (65%). Yellow oil. IR (neat): 3525, 3068, 2923, 1146, 818. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.29 (*s*, 3 H of Me_2Si); 0.30 (*s*, 3 H of Me_2Si); 1.15–1.23 (*m*, SiCH); 1.78–1.96 (*m*, $CH_2CH_2SO_2$); 3.10 (*B* of *ABXY*, $J = 13.9, 10.2, 5.9$, 1 H of CH_2SO_2); 3.29 (*A* of *ABXY*, $J = 13.9, 10.1, 5.0$, 1 H of CH_2SO_2); 3.59 (*B* of *ABX*, $J = 10.9, 8.3$, 1 H of OCH_2); 3.82 (*A* of *ABX*, $J = 10.9, 3.6$, 1 H of OCH_2); 7.31–7.40 (*m*, 3 arom. H); 7.41–7.45 (*m*, 2 arom. H); 7.50–7.56 (*m*, 2 arom. H); 7.61–7.66 (*m*, 1 arom. H); 7.81–7.84 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −4.2 (1 C of Me_2Si); −4.1 (1 C of Me_2Si); 21.2 ($CH_2CH_2SO_2$); 28.9 (SiCH); 56.1 (CH_2SO_2); 63.7 (OCH_2); 128.0 (arom. CH); 128.0 (arom. CH); 129.2 (arom. CH); 129.4 (arom. CH); 133.6 (arom. CH); 133.7 (arom. CH); 137.0 (arom. C); 139.1 (arom. C). HR-ESI-MS: 371.1074 ($[M+Na]^+$, $C_{18}H_{24}NaO_3SSi^+$; calc. 371.1113). Anal. calc. for $C_{18}H_{24}O_3SSi$: C 62.03, H 6.94; found: C 61.65, H 6.93.

*5-[Dimethyl(phenyl)silyl]tetrahydro-2*H*-pyran-2-one* (**8**). Purified by FC (SiO_2; PE/Et_2O 60:40). Yield: 141 mg (60%). Yellow oil. IR (neat): 2953, 1731, 813. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.35 (*s*, Me_2Si); 1.41–1.49 (*tt*, $J = 12.9, 4.5$, SiCH); 1.63–1.76 (*m*, 1 H of $CH_2CH_2C{=}O$); 1.87–1.98 (*m*, 1 H of $CH_2CH_2C{=}O$); 2.43 (*B* of *ABXY*, $J = 17.7, 10.2, 7.3$, 1 H of $CH_2C{=}O$); 2.58 (*A* of *ABXY*, $J = 17.7, 6.6, 3.8$, 1 H of $CH_2C{=}O$); 4.15 (*B* of *ABX*, $J = 12.9, 11.4$, 1 H of OCH_2); 4.42 (*A* of *ABX*, $J = 11.4, 4.5, 2.2$, 1 H of OCH_2); 7.35–7.42 (*m*, 3 arom. H); 7.44–7.49 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −5.1 (1 C of Me_2Si); −5.0 (1 C of Me_2Si); 21.3 ($CH_2CH_2C{=}O$); 23.0 ($CH_2C{=}O$); 31.0 (SiCH); 72.1 (OCH_2); 128.2 (arom. CH); 129.8 (arom. CH); 133.7 (arom. CH); 125.4 (arom. C); 171.4 (C=O).

1,1-Dimethylethyl 4-[Dimethyl(phenyl)silyl]-5-hydroxypentanoate (**9**). Purified by FC (SiO_2; PE/Et_2O 70:30). Yield: 148 mg (48%). Yellow oil. IR (neat): 3434, 2976, 1725, 1150, 814. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.33 (br. *s*, Me_2Si); 0.98–1.13 (*m*, SiCH); 1.42 (*s*, *t*-Bu); 1.63–1.82 (*m*, $CH_2CH_2C{=}O$); 2.28 (*t*, $J = 7.3$, $CH_2C{=}O$); 3.62 (*B* of *ABX*, $J = 11.1, 6.9$, 1 H of OCH_2); 3.77 (*A* of *ABX*, $J = 11.1, 3.9$, 1 H of OCH_2); 7.30–7.39 (*m*, 3 arom. H); 7.46–7.58 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −3.9 (1 C of Me_2Si); −3.8 (1 C of Me_2Si); 22.2 ($CH_2CH_2C{=}O$); 28.1 (Me_3C); 29.8 (SiCH); 35.1 ($CH_2C{=}O$); 63.0

(OCH_2); 80.4 (Me_2C); 127.9 (arom. CH); 129.1 (arom. CH); 133.9 (arom. CH); 138.0 (arom. C); 173.9 (C=O). HR-ESI-MS: 331.1682 ($[M+Na]^+$, $C_{17}H_{28}NaO_3Si^+$; calc. 331.1705). Anal. calc. for $C_{17}H_{28}O_3Si$: C 66.19, H 9.15; found: C 66.15, H 9.38.

*5-[Dimethyl(phenyl)silyl]tetrahydro-3-methyl-2*H*-pyran-2-one* (**10**). Purified by FC (SiO_2; PE/Et_2O 80:20). Yield: 149 mg (60%; mixture of inseparable diastereoisomers). Yellow oil. IR (neat): 2956, 1730, 1171, 818. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.31 (*s*, 1 C of Me_2Si of one isomer); 0.34 (*s*, 1 C of Me_2Si of one isomer); 0.35 (*s*, 1 C of Me_2Si of one isomer); 0.35 (*s*, 1 C of Me_2Si of one isomer); 1.18 (*d*, *J* = 6.8, *Me*CH, isomer *B*); 1.25 (*d*, *J* = 7.1, *Me*CH, isomer *A*); 1.35–1.45 (*m*, 1 H of CH_2CHC=O, isomer *A*); 1.50–1.64 (*m*, 1 H of CH_2CHC=O of isomer *B*, SiCH of isomer *A*); 1.59–1.69 (*m*, SiCH of isomer *B*); 1.94–2.04 (*m*, CH_2CHC=O, 1 H each of isomers *A* and *B*); 2.40–2.55 (*m*, CHC=O of isomers *A* and *B*); 4.14 (*B* of *ABX*, *J* = 12.6, 11.4, 1 H of OCH_2, isomer *B*); 4.18 (*B* of *ABX*, *J* = 12.4, 11.4, 1 H of OCH_2, isomer *A*); 4.29 (*A* of *ABX*, *J* = 11.4, 4.8, 1.3, 1 H of OCH_2, isomer *B*); 4.41 (*A* of *ABX*, *J* = 11.4, 4.8, 2.5, 1 H of OCH_2, isomer A); 7.31–7.43 (*m*, 6 arom. H, isomers *A* and *B*); 7.45–7.55 (*m*, 4 arom. H; isomers *A* and *B*). ^{13}C-NMR (75 MHz, $CDCl_3$): −5.1 (Me_2Si, three out of four isomers), −4.9 (Me_2Si, remaining isomer); 16.4 (*Me*CH, isomer *B*); 17.1 (MeCH, isomer *A*); 21.3 (SiCH, isomer *B*); 24.2 (SiCH, isomer *A*); 28.4 (CH_2CHC=O, isomer *B*); 30.5 (CH_2CHC=O, isomer *A*); 33.8 (Me*C*H, isomer *B*); 37.8 (Me*C*H, isomer *A*); 69.7 (OCH_2, isomer *B*); 72.6 (OCH_2, isomer *A*); 128.2 (arom. CH, isomers *A* and *B*); 129.8 (arom. CH., isomers *A* and *B*); 133.7 (arom. CH, isomers *A* and *B*); 135.5 (arom. C, isomers *A* and *B*); 174.4 (C=O, one isomer); 176.2 (C=O, one isomer). HR-ESI-MS: 271.1124 ($[M+Na]^+$, $C_{14}H_{20}NaO_2Si^+$; calc. 271.1130).

5-Hydroxy-4-[methyl(diphenyl)silyl]pentanenitrile (**11**). Purified by FC (SiO_2; PE/Et_2O 80:20). Yield: 168 mg (57%). Yellow oil. IR (neat): 3427, 3069, 2927, 2246, 1588, 1108. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.63 (*s*, MeSi); 1.66–1.73 (*m*, SiCH); 1.80–1.98 (*m*, CH_2CH_2CN); 2.48 (*t*-like, *J* = 7.6, CH_2CN); 3.69 (*B* of *ABX*, *J* = 10.8, 7.7, 1 H of OCH_2); 3.93 (*A* of *ABX*, *J* = 10.8, 3.3, 1 H of OCH_2); 7.34–7.44 (*m*, 6 arom. H); 7.48–7.59 (*m*, 4 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −5.4 (MeSi); 17.7 (CH_2CH_2CN); 24.5 (CH_2CN); 27.7 (SiCH); 63.3 (OCH_2); 120.2 (CN); 128.1 (arom. CH); 128.2 (arom. CH); 129.7 (arom. CH); 129.7 (arom. CH); 134.6 (arom. CH); 134.6 (arom. CH); 134.9 (arom. C); 134.9 (arom. C).

5-Hydroxy-4-(triphenylsilyl)pentanenitrile (**12**). Purified by FC (SiO_2; CH_2Cl_2/Et_2O 95:5). Yield: 229 mg (64%). Colorless solid. M.p. 126–128°. IR (neat): 3479, 3069, 2931, 2245, 1109. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.85–1.96 (*m*, SiCH); 2.03–2.18 (*m*, CH_2CH_2CN); 2.50–2.64 (*m*, CH_2CN); 3.77–3.81 (*m*, 1 H of OCH_2); 4.07–4.10 (*m*, 1 H of OCH_2); 7.36–7.49 (*m*, 9 arom. H); 7.50–7.64 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 17.9 (CH_2CH_2CN); 25.3 (CH_2CN); 27.2 (SiCH); 63.6 (OCH_2); 120.1 (CN); 128.2 (arom. CH); 129.9 (arom. CH); 133.1 (arom. C); 135.8 (arom. CH): HR-ESI-MS: 380.1448 ($[M+Na]^+$, $C_{23}H_{23}NNaOSi^+$; calc. 380.1447).

*Tetrahydro-5-(triphenysilyl)-2*H*-pyran-2-one* (**13**). Purified by FC (SiO_2; CH_2Cl_2/Et_2O 95:5). Yield: 222 mg (62%). Colorless solid. M.p. 144–147°. IR (neat): 2947, 1730, 1107. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.83–1.96 (*m*, SiCH); 2.13–2.30 (*m*, CH_2CH_2C=O); 2.46–2.61 (*m*, CH_2C=O); 4.26 (*B* of *ABX*, *J* = 12.8, 11.6, 1 H of OCH_2); 4.64 (*A* of *ABX*, *J* = 11.6, 4.6, 2.2, 1 H of OCH_2); 7.31–7.50 (*m*, 9 arom. H); 7.50–7.59 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 21.1 (SiCH); 21.7 (CH_2CH_2C=O); 30.9 (CH_2C=O); 71.8 (OCH_2); 128.4 (arom. CH); 130.2 (arom. CH); 132.0 (arom. C); 135.7 (arom. CH); 171.5 (C=O). HR-ESI-MS: 381.1278 ($[M+Na]^+$, $C_{23}H_{22}NaO_2Si^+$; calc. 381.1287).

1,1-Dimethylethyl 5-Hydroxy-4-(triphenylsilyl)pentanoate (**14**). Purified by FC (SiO_2; CH_2Cl_2/Et_2O 95:5). Yield: 216 mg (50%). Yellow oil. IR (neat): 3434, 2977, 1721, 1589, 1107. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.42 (*s*, *t*-Bu); 1.83–1.94 (*m*, SiCH, 1 H of CH_2CH_2C=O); 1.98–2.02 (*m*, OH); 2.06–2.13 (*m*, 1 H of CH_2CH_2C=O); 2.32–2.39 (*m*, CH_2C=O); 3.76–3.83 (*m*, 1 H of OCH_2); 3.96–4.03 (*m*, 1 H of OCH_2); 7.34–7.45 (*m*, 9 arom. H); 7.55–7.60 (*m*, 6 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): 23.4 (CH_2CH_2C=O); 28.1 (Me_3C); 35.3 (CH_2C=O); 63.1 (OCH_2); 80.5 (*t*-Bu); 128.0 (arom. CH); 129.6 (arom. CH); 133.9 (arom. C); 136.0 (arom. CH); 173.7 (C=O). HR-ESI-MS: 455.1997 ($[M+Na]^+$, $C_{27}H_{32}NaO_3Si^+$; calc. 455.2018). Anal. calc. for $C_{27}H_{32}O_3Si$: C 74.96, H 7.46; found: C 74.93, H 7.34.

5-Hydroxy-4-[tris(1-methylethyl)silyl]pentanenitrile (**15**). Purified by FC (SiO_2; CH_2Cl_2/AcOEt 90:10). Yield: 156 mg (61%). Colorless solid. M.p. 41–42°. IR (neat): 3501, 2942, 2866, 2249, 1006. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.03–1.16 (*m*, 3 i-Pr); 1.39–1.45 (*m*, 1 H, Si*CH*); 1.82–1.91 (*m*, 1 H of

CH_2CH_2CN); 1.99–2.06 (*m*, 1 H of CH_2CH_2CN); 2.63 (*B* of *ABXY*, $J=16.7$, 8.3, 8.3, 1 H of CH_2CN); 2.75 (*A* of *ABXY*, $J=16.7$, 8.2, 4.8, 1 H of CH_2CN); 3.75 (*B* of *ABX*, $J=10.7$, 9.7, 1 H of OCH_2); 4.02–4.05 (*m*, 1 H of OCH_2). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.0 (Me_2CH); 19.0 (Me_2CH); 19.1 (CH_2CH_2CN); 26.9 (CH_2CN); 27.2 (CH_2CHSi); 65.2 (CH_2O); 120.6 (CN). Anal. calc. for $C_{14}H_{29}NOSi$: C 65.82, H 11.44; found: C 65.82, H 11.55.

3-[Dimethyl(phenyl)silyl]but-3-en-2-ol (**21**). Purified by FC (SiO_2; PE/Et_2O 95:5). Yield: 171 mg (83%). Yellow oil. IR (neat): 3376, 3069, 2961, 1110. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.43 (3 H of Me_2Si); 0.44 (3 H of Me_2Si); 1.20 (*d*, $J=6.3$, *Me*CH); 4.45 (*q*, $J=6.3$, 1 H, OCH); 5.46 (br. *s*, 1 H of $=CH_2$); 5.90 (br. *s*, 1 H of $=CH_2$); 7.31–7.40 (*m*, 3 arom. H); 7.51–7.57 (*m*, 2 arom. H). ^{13}C-NMR (75 MHz, $CDCl_3$): −2.2 (1 C of Me_2Si); −2.1 (1 C of Me_2Si); 24.1 (*Me*CH); 71.7 (OCH); 124.7 ($=CH_2$); 127.9 (arom. CH); 129.1 (arom. CH); 133.9 (arom. CH); 138.4 (arom. C); 155.0 (=C). HR-ESI-MS: 229.1019 ($[M+Na]^+$, $C_{12}H_{18}NaOSi^+$; 229.1025). Anal. calc. for $C_{12}H_{18}OSi$: C 69.84, H 8.79; found: C 69.39, H 8.95.

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