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# Novel Route to Silanetriols and Silanediols based on Acetoxysilylalkoxides

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Silanols • Hydrolysis • Acetoxysilylalkoxides • Structural study • CO<sub>2</sub> Conversion.

#### Abstract

An easy and versatile method for the preparation of molecular alkoxysilanols as molecular organosilicates based on acetoxysilylalkoxides (ASA,  $(RO)(tBuO)_nSi(OAc)_{3-n}$  or  $(AcO)_{3-n}(tBuO)_nSi-O-R-O-Si(OtBu)_n(OAc)_{3-n}$ , R = organic group; n = 0 or 1) is presented. These ASA precursors are prepared from silicon tetraacetate and suitable alcohols and are cleanly hydrolyzed in water to the corresponding alkoxysilanols in the absence of a base or organic solvents. The compounds were characterized by common spectroscopic methods including X-Ray structural analysis. Alkoxysilanols were tested in the catalytic conversion of CO<sub>2</sub> to styrene carbonate and show quantitative conversion within 15 hours at 60 °C and 1 atm of CO<sub>2</sub>.

#### 1. Introduction

Organosilanols combine in their molecule  $Si(OH)_n$  (n = 1–3) moiety, which provides remarkable hydrogen-bonding capabilities and tunable acidity, with an organic residue providing structural modularity and solubility [1–3]. Thus their final properties can be easily adjusted according to the desired application. Therefore, it is not surprising that they have found many applications in both academia and industry. The most significant are cross-coupling reactions, synthesis of hybrid organicinorganic materials with long-range order [4–9], molecular recognition [10–12], environmentally friendly surfactants based on organosilanetriols [13]; as well as unique bioisosteres, that do not have stable carbon analogues, and are used in improving the advance of new therapeutic agents [14–19]. Furthermore, discrete alkoxysilanols (RO)<sub>n</sub>Si(OH)<sub>4–n</sub> (n = 2, 3) with a silicon atom immediately coordinated to four oxygen atoms as in silica materials, have been used in the preparation of molecular models to understand the local active sites on the surface of heterogeneous catalysts [20–12]. More recently organosilanediols have been applied in enantioselective hydrogen-bond donor catalysis (HBD) [23–26] and the binary catalytic system silanediol/TBAI has been described by Cokoja *et al.* [27] as a "potential metal-free system that bridges the gap between metal containing and organic catalysts".

Despite the above-mentioned promising applications, wider use of organosilanols is hampered by the available synthetic methods [1–3,28,29]. The most important are based on the hydrolysis of organochlorosilanes [2,3,28] or organoalkoxysilanes [29,30] ( $R_nSiCl_{(4-n)}$  and  $R_nSiOR'_{(4-n)}$ ; R'= Me, Et, n = 1–3 respectively), synthesized from SiCl<sub>4</sub> or tetramethoxy- or tetraethoxysilanes and organometallic reagents. Eventually, they can also be prepared using catalytic hydrosilylation of dienes, starting from HSiCl<sub>3</sub> or HSi(OR)<sub>3</sub> (R = Me, Et) [31]. These precursors are converted to the corresponding silanols by hydrolysis. However, each precursor type has its disadvantages. The hydrolysis of the chlorosilanes produces HCl, which causes condensation of the silanols and thus it has to be trapped using stoichiometric amounts of a base such as aniline or pyridine. However, an excess of

the base can also cause decomposition of the products [2,3,28]. The hydrolysis of alkoxysilanes produces alcohols that by themselves do not accelerate the condensation of the silanols, but this hydrolysis requires acidic catalysis and long reaction times (up to 34 days!), which always results in a partial condensation and thus product loss [29,30]. Finally, both methods require, especially in the case of silanols with two or three OH groups, large quantities of organic solvent to dilute the reagents and thus protect the silanols from condensation. In addition, the synthesis of alkoxysilanols (RO)<sub>n</sub>Si(OH)<sub>4-n</sub> starts from the respective chloro derivatives (RO)<sub>n</sub>SiCl<sub>4-n</sub> and is even more problematic than the synthesis of silanols with Si–C bonds, due to the low stability of the Si–OR bond under the synthetic conditions [32]. However, they feature higher potential as a catalyst for HBD due to the higher acidic character of their OH groups [33].

These facts prompted us to pursue a new sustainable synthetic pathway, which would afford stable alkoxysilanols  $(RO)_nSi(OH)_{4-n}$  (n = 1, 2) under mild conditions. Therefore, we envisioned that the use of acetoxysilylalkoxides (ASA) prepared from Si(OAc)<sub>4</sub> and suitable tertiary alcohols as organic moiety would represent a facile and efficient strategy for the preparation of alkoxysilanols. Although the hydrolysis of some acetoxysilyl derivatives to the corresponding silanols have been in a limited extent explored earlier, they used additional reagents such as carbonates or emulsifiers and in general had low yields and thus did not became more widespread. [3] Unlike their chlorosilanes analogues the ASA compounds are more stable and easier to handle but at the same time still more reactive than alkoxysilanes, as the AcO<sup>-</sup> is a better leaving group. Furthermore, Pohl and Osterholtz [34] determined that the condensation rate of alkylsilanetriols has a minimum at the pH of 4.5. This is just slightly lower than the pK<sub>a</sub> of the acetic acid (4.76 at 25 °C). Therefore, we hypothesized that the acetic acid formed during the hydrolysis would, in fact, stabilize the proposed alkoxysilanols from forming undesired condensation by-products. A further advantage of this procedure would be that the released acetic acid is biodegradable and much less corrosive than HCl and thus the use of a base during the hydrolysis could be avoided.

Herein, we report a base- and organic solvent-free synthesis of molecular air-stable alkoxysilanols, with tailored HB capabilities from acetoxylsilylalkoxides in an aqueous medium. Furthermore, preliminary results of their catalytic activity in the conversion of  $CO_2$  into cyclic carbonate as a function of the steric protection and the number of silanol groups are also reported.

#### 2. Results and Discussion

#### 2.1. Synthetic aspects and spectral characterization

To prepare the ASA precursors, tertiary diols 1,4-bis(diethylhydroxymethyl)benzene and 3,6-diethyl-4octyne-3,6-diol were reacted with Si(OAc)<sub>4</sub> as the silicon source, in toluene to yield the corresponding bis(triacetoxylsilyl)alkoxides **1** and **2**. In the case of the bulkier alcohols Ph<sub>3</sub>COH and (*4R*,5*R*)-TADDOL (TADDOL = (*4R*,5*R*)-2,2-dimethyl- $\alpha$ , $\alpha$ , $\alpha$ ', $\alpha$ '-tetraphenyldioxolane-4,5-dimethanol), reflux in toluene was necessary to obtain full conversion either to the cyclic chiral  $\kappa^2$ -O,O'-(diacetoxylsilyl)-(*4R*,5*R*)-TADDOLate **3** or triacetoxylsilyltriphenylmethanolate **4** (Schemes 1 and 2). Furthermore, the compounds **1** and **4** can be directly reacted with *t*BuOH to yield the corresponding diacetoxylsilylalkoxides **5** and **6**. This allows an efficient control of the number of remaining acetate groups attached to each silicon center. With the exception of **5**, which it is colorless oil, all acetoxysilyl derivatives are off-white crystalline powders that are soluble in polar organic solvents and toluene.

These ASA derivatives were suspended directly in ice-cold water, stirred for 2–15 min and the corresponding alkoxysilanols 7–12 (Scheme 3), with one or two  $OSi(OH)_n$  (n = 2, 3) groups, were filtered off as white precipitates in good yields (71–96 %). A mixture of water and few drops of ethylacetate were used to prevent the oily 5 from sticking to the glass walls during its hydrolysis to 7. In the case of 6, ammonia was used to accelerate its hydrolysis to 11. All compounds were fully characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR and IR spectroscopy, elemental analysis, and mass spectrometry. In addition, the molecular structures of most of the compounds were determined by single crystal X-ray diffraction (see Supporting Information). The formation of the ASA compounds 1–6 was confirmed by





Scheme 2 Synthesis of chiral compounds 3 and 12 from (4R,5R)-TADDOL



Scheme 3 Acetoxysilyl derivatives and the corresponding hydrolyzed alkoxysilanols

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (<sup>1</sup>H:  $\delta$  1.52–2.10 ppm, <sup>13</sup>C:  $\delta$  21.8–23.0 for *CH*<sub>3</sub>COO<sup>-</sup>,  $\delta$  167.7–168.6 ppm for *C*=O). Additionally, in comparison with Si(OAc)<sub>4</sub> ( $\tilde{v}$  1760 cm<sup>-1</sup>), these compounds shifted to lower wavenumbers ( $\tilde{v}$  1739–1752 cm<sup>-1</sup>) in the bands associated with C=O stretching vibration. All silanediols are soluble in polar organic solvents and toluene; however, their silanetriols analogues are soluble only in highly polar solvents such as DMSO and only sparingly in THF. This can be explained by the higher polarity of the OH moieties in the silanetriol group and, thus, higher strength of the

present hydrogen bonds (vide infra). These inductive effects, associated with substituents such as OH and OR in organosilanol compounds, are supported by <sup>1</sup>H NMR spectroscopy where the signals corresponding to the OH groups are in the range of  $\delta$  5.90–6.89 ppm. Furthermore, the corresponding normalized integrals match with the number of the OH groups expected for each silanol. Also, in <sup>29</sup>Si NMR spectra, the sharp signals of the silanols shifted up-field with each consecutive substitution of the OH moiety by OR groups Si(OH)<sub>4</sub> (<sup>29</sup>Si:  $\delta$  –72 ppm) [35], ROSi(OH)<sub>3</sub> (<sup>29</sup>Si:  $\delta$  –78.3 to –80.9 ppm), (RO)(*t*BuO)Si(OH)<sub>2</sub> (<sup>29</sup>Si:  $\delta$  –83.8 to –87.0 ppm). The retention of organic moieties in the molecular alkoxysilanols after the hydrolysis process was confirmed by elemental analysis and NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C) where the signals corresponding to the organic moieties remained present; while those for the acetate groups, were essentially absent (see Supporting Information). Also, the absence of any condensation by-products in the alkoxysilanols was corroborated by the lack of the band corresponding to the siloxane bridge Si-Q-Si ( $\tilde{V}$  1060–1220 cm<sup>-1</sup>) in their FT-IR spectra [28]. Moreover, the shift to upper wavenumber of the broad band attributed to OH groups in 7 and 11 ( $\tilde{V}$ 3373 and 3381 cm<sup>-1</sup>) compared to their respective alkoxysilanetriol analogues 8 and 10 ( $\tilde{V}$  3128 and 3312 cm<sup>-1</sup>), clearly evidences the influence of the number of OH groups attached to the same silicon center and on the strength of the hydrogen bond interactions in solid state. This behavior was also supported by X-ray structural analysis. Additionally, these findings seem to have important implications in the relative catalytic activity of the silanols in HBD (vide infra).

The relative thermal stability of alkoxy(bis-silanetriol) **8** and its analogous alkoxy(bis-silanediol) **7** was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC). **8** and **7** were thermally stable up to 161.6 and 72.4 °C respectively. The TG-DSC curves exhibited single stage decomposition for **8**; while **7** decomposes in a multistage process. For both compounds, the final product at 450 °C is a slightly impure silica (for more details see the Supporting Information).

2.2. Description of molecular and crystal structures of compounds 1 - 4, 6 - 8, 10 - 12

The molecular structures of the (acetoxylsilyl)alkoxides 1 - 4, 6, alkoxysilanediols 7, 11 and 12, and the alkoxysilanetriols 8 and 10, were determined by single crystal X-ray diffraction. Crystals suitable for X-ray diffraction studies were obtained either from saturated toluene (1, 2) and THF (3, 4, 6, 7, 8, 10) solutions at -24 °C; while single crystals of 11 and 12 were grown either from DMSO (11. DMSO) or wet dichloromethane solutions ( $11 \cdot H_2O$  and  $12 \cdot CH_2Cl_2$ ) by slow solvent evaporation. In a neat form, 8 always precipitates as a microcrystalline powder and all attempts to grow bigger crystals failed. Nonetheless, it has been shown that silanetriols can be co-crystallized with organic diamines due to strong hydrogen-bonding interaction [36,37]. Hence, 8 was co-crystallized with two equivalents of DABCO (DABCO = diazabicyclo[2.2.2]octane). Compounds 2, 4, 6 - 8 and  $11 \cdot H_2O$  crystallized in the triclinic  $P\overline{1}$  space group, compounds 3 and 12 in the orthorhombic  $P2_12_12$  and  $P2_12_12_1$  space groups, respectively, while the rest of the compounds crystallized in monoclinic space groups: C2 (1),  $P2_1/n$ (10) or C2/c (11·DMSO). The asymmetric unit contains half a molecule (2, 3, 6, 8), one molecule (4, 7, 10 - 12) or one complete and two halves of a molecule, together with one molecule of DABCO (8·2DABCO), THF (10·THF), DMSO (11·DMSO), H<sub>2</sub>O (11·H<sub>2</sub>O) or CH<sub>2</sub>Cl<sub>2</sub> (12·CH<sub>2</sub>Cl<sub>2</sub>). The molecular structures of all compounds are shown in Figure 1, while selected crystallographic details are listed in Tables 1 and 2. In all compounds, the SiO<sub>4</sub> unit has a distorted tetrahedral geometry with angles ranging from 99.3(1)° to 116.1(1)°. The Si–O bond distances are only slightly influenced by the different substituents, as the values for the Si–O(C) (1.578(2)-1.641(1) Å), Si–OAc (1.640(1)-1.654(1) Å)Å) and Si–OH bonds (1.607(1)–1.624(1) Å) fall in a very narrow range. However, the Si–OAc bond lengths are always slightly longer (0.03 Å) than the corresponding Si–OH distances due to both the electronic effect of the acetate groups and their larger steric bulk, but show no variation compared to the parent silicon tetraacetate (Si–OAc = 1.624 Å) [38]. These values are comparable to those in related silicate based silanols  $[Ph_2Si(\mu-O)Si(OH)_2(\mu-O)]_2$ ,  $Me_2Si[(\mu-O)SiMe_2(\mu-O)]_2Si(OH)_2$ and

 $[(tBuO)_3Si(\mu-O)Si(OH)_2](\mu-O)$  (Si-O(C) 1.608 – 1.612 Å, Si–OH (1.592 – 1.625 Å, O-Si-O 104.7 – 112.4 °),[39a–c] but one of the Si–OH (1.625 Å) bond lengths in  $[(Mes*O)_2Si(OH)_2]\cdot 2THF$  is significantly longer.[39d] Selected bond lengths and angles for compounds 1 - 4, 6 - 8 and 10 - 12 are listed in Table 3, while Table 4 contains details of the above-described hydrogen bonds. While the acetates are isolated molecules in the crystal, the silanols are always aggregated by strong Hydrogenbonding interaction. Overall, five different hydrogen-bonding patterns (I–V) were observed, as a function of the steric bulk of the organic groups and the number of OH groups per silicon atom that regulates the degree of self-association and were described using the graph set analysis (Figure 2) [40].

	1 <sup>c</sup>	2	-3 <sup>d</sup>	4	6
Empirical formula	$C_{28}H_{42}O_{14}Si_2$	$C_{24}H_{38}O_{14}Si_2$	C35H34O8Si	$C_{25}H_{24}O_7Si$	C27H30O6Si
Formula mass (g/mol)	658.79	606.72	610.71	464.53	478.60
Space group	C2	$P\overline{1}$	P21212	$P\overline{1}$	$P\overline{1}$
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda$ (Å)	1.54178	1.54178	1.54178	0.71073	0.71073
<i>a</i> (Å)	20.3982(4)	9.0912(2)	13.4373(3)	9.9282(4)	8.6997(2)
<i>b</i> (Å)	13.8584(4)	9.1134(2)	9.5065(2)	10.7649(4)	9.0317(2)
<i>c</i> (Å)	24.3524(6)	9.3268(2)	11.8659(3)	13.0781(5)	17.0129(4)
α (°)	90	87.784(1)	90	110.8963(7)	99.2568(5)
β (°)	94.712(2)	83.045(1)	90	97.5728(8)	90.5947(5)
γ (°)	90	76.746(2)	90	110.4489(7)	109.8012(5)
$V(\text{\AA}^3)$	6860.8(3)	746.58(3)	1515.77(6)	1169.85(8)	1238.31(5)
Crystal size (mm)	0.207 x 0.200 x 0.178	0.165 x 0.141 x 0.124	0.123 x 0.118 x 0.097	0.373 x 0.350 x 0.251	0.300 x 0.280 x 0.219
Ζ	8	1	2	2	2
$\rho_{\text{calc.}}(\text{g·cm}^{-3})$	1.276	1.349	1.338	1.319	1.284
$\mu (\mathrm{mm}^{-1})$	1.486	1.658	1.131	0.144	0.135
F(000)	2800	322	644	488	508
$\boldsymbol{\theta}$ range for data collection	1.820 to 67.747	4.777 to 67.711	3.725 to 69.967	1.743 to 26.369	2.432 to 26.371
(°) No. of reflections	48551	8081	18442	19964	37746
No. of independent	12124 (0.0195)	2608 (0.0198)	2885 (0.0228)	4801 (0.0243)	5062 (0.0191)
reflections $(R_{int})$ No. of data/restraints/parameters	12124 / 1 / 813	2608/0/186	2885 / 0 / 202	4801 / 130 / 330	5062/0/312
Goodnes-on-fit (GOF) on $F^2$	1.055	1.066	1.059	1.029	1.028
$R_{1}^{a}, wR_{2}^{b} (I > 2\sigma(I))$	0.0402, 0.1081	0.0412, 0.1231	0.0270	0.0309, 0.0784	0.0296, 0.0766
$R_{1}^{a}$ , $wR_{2}^{b}$ (all data)	0.0407, 0.1088	0.0468, 0.1286	0.0709	0.0341, 0.0807	0.0311, 0.0778
Largest diff. peak/hole $(e \cdot \hat{A}^{-3})$	0.541 / -0.269	0.407 / -0.309	0.201 / -0.250	0.306 / -0.355	0.356/-0.342
ĊCDĆ	1453225	1453226	1453230	1453228	1453229

Table 1. Crystal data and structure refinement details for compounds 1 - 4, 6

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|. {}^{b}wR_{2} = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{\frac{1}{2}}. {}^{c} \text{ Flack parameter } 0.487(4). {}^{d}\text{ Flack parameter : } -0.008(5).$ 



Figure 1. Molecular structures of 1 - 4, 6 - 8·DABCO, 10·THF, 11·DMSO and 12·CH<sub>2</sub>Cl<sub>2</sub> with thermal ellipsoids set at 50 % probability level. Carbon bound hydrogen atoms and solvating solvent molecules were eliminated for the sake of clarity.

### Table 2. Selected crystallographic data for compounds 7, 8, 10 – 12.

	7	8-2DABCO	10. THF	11.DMSO	$11 \cdot H_2O$	$12 \cdot CH_2Cl_2^c$
Empirical formula	$C_{24}H_{46}O_8Si_2$	$C_{28}H_{54}N_4O_8Si_2$	C23H26O5Si	C <sub>25</sub> H <sub>32</sub> O <sub>5</sub> SSi	C23H27O4.5Si	$C_{32}H_{32}Cl_2O_6Si$
Formula mass (g/mol)	518.79	630.93	410.53	472.65	403.53	611.56
Space group	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$	C2/c	$P\overline{1}$	P212121
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
<i>a</i> (Å)	7.1203(2)	8.5208(4)	12.3488(3)	30.6391(6)	8.8728(3)	9.2264(2)
<i>b</i> (Å)	10.0366(3)	9.8696(5)	8.9576(2)	8.7736(2)	10.2369(3)	13.6523(3)
<i>c</i> (Å)	10.5331(3)	11.7679(6)	19.5820(4)	20.1977(4)	12.7680(4)	23.0659(6)
α (°)	102.7633(5)	103.7594(11)	90	90	113.0905(6)	90
β (°)	95.1489(5)	97.5810(11)	107.9408(5)	113.6567(4)	95.8921(6)	90
γ (°)	103.8582(5)	113.1915(11)	90	90	91.7488(6)	90
$V(\text{\AA}^3)$	704.63(4)	854.90(7)	2060.75(8)	4973.19(18)	1057.99(6)	2905.42(12)
Crystal size (mm)	0.417 x 0.301 x	0.189 x 0.052 x	0.286 x 0.218 x	0.296 x 0.261 x	0.289 x 0.207 x	0.251 x 0.248 x
Crystal size (mm)	0.206	0.040	0.184	0.239	0.163	0.226
Ζ	1	1	4	8	2	4
$\rho_{\rm calc.} (\rm g \cdot \rm cm^{-3})$	1.223	1.226	1.323	1.263	1.267	1.398
$\mu (\mathrm{mm}^{-1})$	0.168	0.154	0.146	0.211	0.139	0.310
<i>F</i> (000)	282	342	872	2016	430	1280
$\theta$ range for data collection (°)	2.005 to 26.368	1.841 to 26.371	1.733 to 26.370	2.095 to 26.369	1.747 to 26.372	1.733 to 27.483
No. of reflections	13531	16864	20204	22388	17675	64011
No. of independent reflections	2872 (0.0159)	3500 (0.0390)	4200 (0.0250)	5078 (0.0240)	4316 (0.0210)	6660 (0.0192)
$(R_{\rm int})$	2072 10 11/5	2500 / 2 / 201	1200 1251 1215	5050 / 105 / 220	1016 150 1011	(((0.102.140)
No. Of	28/2/0/165	3500/3/201	420072517317	50/8/10//330	4316//3/311	6660/93/406
Goodnes-on-fit (GOE) on $F^2$	1.025	1.018	1.025	1.033	1.033	1.049
$R^{a} w R^{b} (I > 2\sigma(I))$	0.0292. 0.0748	0.0335. 0.0786	0.0346. 0.0892	0.0310. 0.0800	0.0414. 0.1083	0.0210. 0.0561
$R_1^{a}$ , $wR_2^{b}$ (all data)	0.0303.0.0756	0.0436. 0.0844	0.0378, 0.0916	0.0346. 0.0828	0.0446.0.1109	0.0213, 0.0563
I argest diff neak/hole (e, $Å^{-3}$ )	0.3710.310	0.3410.252	0.3790.372	0.383 / -0.321	0.488 / -0.522	0.295/-0.197
CCDC	1453233	1453231	1453232	1453234	1453235	1453236

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|. {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{\frac{1}{2}, c}$  Flack parameter: 0.008(6)



Figure 2. Hydrogen-bonding patterns found in compounds  $12 \cdot CH_2Cl_2$  (I),  $11 \cdot DMSO$  (II),  $11 \cdot H_2O$  (III),  $10 \cdot THF$  (IV) and 7 (V).

In this study, the TADDOL derivative 12 contains the bulkiest organic group, which resulted in the formation of only a single hydrogen-bond. Thus the proton from one Si–OH group coordinates to the oxygen atom from the second Si–OH group belonging to a neighboring molecule of 12 to form an extended chain C(4) a (Figure 2, motif I). The proton of this accepting OH group is involved in an H··· $\pi$  interaction. In the case of 11·H<sub>2</sub>O, the characteristic Si–OH···H homodimer ring pattern  $R_2^2(8)$ usually found in organosilanediols structures is present, and the water molecule serves as O-H donor to interconnect these  $R_2^2(8)$  synthons (Figure 2, motif III). On the contrary, when 11 was crystalized from DMSO, two molecules of this solvent were included in the structure and break the strong Si-OH···H homodimer  $R_2^2(8)$  to give heterosynthon formed by discrete solvated rings  $R_4^2(12)$  abab (Figure 2, motif II). The oxygen atom in DMSO acts as hydrogen-bond acceptor supressing the formation of the extended network. In 10, the tBuO group present in 11 is replaced by a third OH group leading to a higher acidity and lower steric protection. Thus, 10 presents a modulated equilibrium between solvent interaction and self-association through (Si-OH···O-Si) hydrogen-bonding; hence, the THF breaks one of the two hydrogen bonds involved in the  $R_2^2(8)$  synthon to give an interconnected ring pattern  $R_3^2(10)$  abc; which is classified as third level graph-set. Also, this could be described on a binary-level through hydrogen bonding chains C(4) b and  $C_2^1(6)$  ac (Figure 2, Motif IV). In the case of alkoxy(bis-silanols) 7 and 8, the organic group acts as bridging moiety between two silicate centers, resulting in higher order structures than in the monosilicate analogs. For the compound 7, the selfassociation produces a zig-zag interconnected  $C_2^2(26)[R_2^2(8)]$  chain formed of alternated ring homodimers  $(R_2^2(8) aa, R_2^2(8) bb)$  between silicate centers; where the organic "spacer" allows the multiple macrocyclic rings, without the inclusion of solvent molecules (Figure 2, Motif V). In the case of alkoxy(bis-silanetriol) co-crystal 8.2DABCO the interaction of diamine with 8 creates a macrocyclic 2D system  $R_4^4(36)$  bcbc ( $d_{Si \dots Si} = Si(1) - Si(1a)$  10.51 Å and Si(1) - Si(1c) 9.86 Å). We observed three different OH···A (A = O, N) hydrogen-bonds per Si(OH)<sub>3</sub> unit with O···A distances of 2.780(1) Å,

 $[O(2)-H(2)\cdots(O4)]; 2.742(2)$  Å,  $[O(3)-H(3)\cdots(N2)]; 2.658(2)$  Å,  $[O(4)-H(4)\cdots(N1)]$ , respectively. In the crystal lattice, the self-association between adjacent alkoxy(bis-silanetriol) molecules creates a chain  $C_2^2(26)[R_2^2(8)]$  along the *c* axis. These chains are linked by DABCO pillars  $C_4^4(36)$  bccb to give two-dimensional ABABAB stacking type formed by diamin $\cdots$  silanol alternating layers (Figure 3).

Table 3. Selected bond distances (	Å) and angles (°) for compounds $1-4$	6 - 8 and $10 - 12$ .
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	Si–O <sub>Ac</sub>	Si–O <sub>spacer</sub>	$Si-O_{tBu}$	Si-OH	<0-Si-0	<0-Si-0
mono- and bis	s(triacetoxy	silyl)alkoxid	les			
4	1.642(1)	1.590(1)	-	-	114.09(5)	100.84(4)
1	1.648(2)	1.578(2)	_	-	114.14(13)	104.06(13)
2	1.640(1)	1.588(1)	_	-	114.72(7)	102.35(7)
(diacetoxysily	l)alkoxides					
6	1.654(1)	1.608(1)	1.597(1)		114.83(4)	103.24(4)
3	1.642(1)	1.611(1)	_	-	116.06(6)	99.34(6)
alkoxymono-	and bis(sila	mediols)				
$12 \cdot CH_2Cl_2$	_	1.616(1)		1.608(1)	112.01(6)	105.35(6)
11·DMSO	_	1.628(1)	1.676(1)	1.617(1)	113.05(5)	103.47(5)
11·H <sub>2</sub> O	-	1.618(1)	1.637(1)	1.620(1)	113.68(6)	106.59(6)
7	_	1.613(1)	1.641(1)	1.607(1)	112.83(4)	106.90(4)
alkoxymono-	and bis(sila	metriols)				
10·THF	-	1.618(1)	-	1.624(1)	113.82(5)	104.17(6)
8-2DABCO	-	1.632(1)	-	1.622(1)	113.22(6)	105.04(5)



Figure 3. Detail of the hydrogen bonded layer formed by 8 and DABCO in 8.2DABCO.

Compound	H-bond	D-H (Å)	H···A (Å)	D…A (Å)	<dha (°)<="" th=""><th>Symmetry code</th></dha>	Symmetry code
7	$O(2)-H(2)\cdots O(4)$	0.81(1)	1.91(1)	2.715(1)	171.6(2)	-x+1,-y+1,-z
	O(3)−H(3)····O(2)	0.82(1)	1.92(1)	2.721(1)	169.0(2)	-x+2,-y+1,-z
11. DMSO	O(3)−H(3)····O(5)	0.82(1)	1.96(2)	2.773(1)	170.7(2)	-x+1/2,-y+3/2,-z+1
	$O(4)-H(4)\cdots O(5)$	0.81(1)	1.89(2)	2.678(1)	167.2(2)	-x+1/2,-y+3/2,-z+1
$11 \cdot H_2O$	O(3)−H(3)····O(5)	0.86(2)	1.77(2)	2.600(3)	161.0(5)	-x+1,-y+1,-z+1
	$O(4)-H(4)\cdots O(2)$	0.86(2)	1.88(2)	2.731(2)	172.0(2)	-x+1,-y+1,-z+1
	$O(5)-H(5)\cdots O(4)$	0.82(2)	2.06(2)	2.870(3)	168.0(4)	-x+2,-y+1,-z+1
12	O(5)−H(5)···O(6)	0.81(2)	1.94(2)	2.744(2)	171.0(2)	x+1/2,-y+3/2,-z+1
10	O(2)−H(2)····O(5)	0.83(1)	1.85(2)	2.670(2)	170.0(2)	-x+1,y+1/2,-z+3/2
	O(3)−H(3)····O(2)	0.83(1)	2.08(1)	2.908(2)	173.0(2)	-x+1,y+1/2,-z+3/2
	$O(4)-H(4)\cdots O(5)$	0.83(1)	1.99(3)	2.780(3)	158.0(2)	-x+1,y-1/2,-z+3/2
8·2DABCO	$O(2)-H(2)\cdots O(4)$	0.83(1)	1.95(1)	2.780(2)	173.2(2)	-x+1,-y+1,-z+1
	O(3)−H(3)····N(2)	0.83(1)	1.91(1)	2.742(2)	171.7(2)	-x+1,-y+1,-z
	$O(4)-H(4)\cdots N(1)$	0.84(1)	1.84(1)	2.658(2)	162.6(2)	x,y+1,z

**Table 4.** Geometric parameters for the hydrogen-bonds in the crystal structures of compounds [Å and °]

#### 2.3. Catalytic studies

These results clearly demonstrate the advantage of this synthetic method, since it is possible to easily modulate the steric and/or electronic effects around the silicon atom. Therefore, the acidity of the OH groups and, consequently, the number and strength of hydrogen bonds are tunable. This should have a direct effect on the activity of Si–OH groups in HBD organocatalysis. To evaluate this hypothesis, the organocatalytic cycloaddition of  $CO_2$  with styrene oxide (SO) to yield styrene carbonate (SC) was tested using selected alkoxysilanols in the presence of tetrabutylammonium iodide (TBAI) as a nucleophile source (Scheme 4).

The synergic effect between onium salts such as phosphonium and ammonium halides and Si–OH groups in the catalytic cycloaddition of  $CO_2$  to epoxides has been reported previously [41–44]. However, most of them operate as a heterogeneous catalyst where silica is used as silanol source

acting as a support to immobilize the onium salts. Although, this approach facilitates the separation and recycling of the catalyst; traditionally, most of them require harsh reaction conditions, such as high pressure and temperature. As an alternative, the use of molecular bis(1-naphtyl)silanediol in the presence of tetrabutylammonium halides as co-catalysts has been reported [45]. This is a homogeneous system that under mild conditions affords excellent yield in the CO<sub>2</sub> coupling with SO. Unfortunately, the major drawback of this is the catalyst synthesis and recovery. Thus the binary systems (10 mol% organosilanol/TBAI) were used under solvent free and mild reaction conditions (60 °C, 15 h, using a balloon of  $CO_2$ ). Quantitative conversions (93% – >99%, Table 5) were observed, even though SO is a rather difficult substrate due to the lack of electron-withdrawing substituents, which would facilitate the nucleophilic attack on the epoxide ring. In addition, SO's high viscosity reduces the diffusion of  $CO_2$  in the reaction media. In the absence of alkoxysilanol, only 31% of SO was converted to SC (entry 1), while, a conversion of 93% was observed for 8 (entry 2); in the case of 7 and 10–12), conversions above 98% were obtained (entries 3 to 6). Nonetheless, the results seem to be counterintuitive since it is generally assumed that the most acidic silanols are the best catalysts. Nevertheless, 8 presented the lowest conversion, even when it is one of the most acidic alkoxysilanol in this study and contains six hydroxyl groups per molecule. This behavior can be rationalized in terms of the strong self-association present in 8, which reduces the availability of catalytically active hydroxyl groups as well as the solubility of such compound in



Scheme 4. Catalytic cycloadition of CO<sub>2</sub> to styrene oxide

**Table 5.** Conversion of styrene oxide (SO) and  $CO_2$  into styrene carbonate (SC) using the binary catalytical alkoxysilanol/TBAI system.

Entry	Catalyst	Yield $(\%)^{a,b}$	Entry	Catalyst	Yield $(\%)^{a,b}$
1	-	31	4	10	$>99(96)^c, 85^d$
2	8	93	5	11	>99
3	7	99	6	12	98

<sup>a</sup> Each experiment was repeated 3 times and the average yield is reported; <sup>b</sup> reported yields are based on <sup>1</sup>H NMR spectroscopic analysis using toluene as internal standard (selectivity > 99% for SC), <sup>c</sup> yield obtained after 12 h, <sup>d</sup> yield obtained with only 5 mol % **10**/TBAI.

the reaction media. In comparison, 7 showed better catalytic performance, even though the substitution of two OH groups by two tBuO moieties lowers its acidity. Nonetheless, this substitution significantly increases the solubility of 7 and the steric protection around the silicon atom. Consequently, this reduces its self-association and increases the availability of the OH groups in the catalytic process. Therefore, a balance between solubility and acidity is essential for an optimum catalytic performance. Finally, 10 showed practically quantitative conversion after 12 h. However, with regards to a sustainable and economical process for potential applications, the recycling of the catalysts plays an important role. Therefore, the mixture of 10 and TBAI was recycled by filtration through the addition of diethyl ether/hexane (1:2) mixture, which dissolves the SC preferentially. Moreover, 10 can be used in three consecutive runs with only 13% activity loss in the third cycle. However, slight catalyst leaching effects were observed. Although 8 shows only 93% of conversion, it is insoluble in diethyl ether and thus easily recyclable. Nonetheless, after the second run, we observed significant loss of activity. This fact could be explained due to its higher tendency to undergo self-condensation under reaction conditions (Figure 4). Furthermore, the binary catalytic system **10**/TBAI can be easily recycled through filtration as heterogeneous catalysts and its

catalytic performance in the cycloaddition of CO<sub>2</sub> with SO to SC is comparable with that reported for bis(1-naphtyl)silanediol and others homogeneous HB organocatalysts reported in the literature.[27,46]



Figure 4. Comparative yields of SC obtained after three consecutive runs using recycled catalysts 8 and 10.

#### 3. Conclusion

To summarize, acetoxylsilylalkoxides (ASA) offer a straightforward, scalable and cost-efficient synthetic pathway towards alkoxysilanols. Such pathway eliminates the main disadvantages of the current synthetic methods, such as large quantities of organic solvent, the use of a base, and long reaction times. Additionally, it allows a stepwise tuning of the steric and electronic environment of the silicon atom; the precise control of the number of OH groups attached to each silicon atom, as well as their Bronsted acidity and consequently their hydrogen bonding capabilities. Therefore, their organocatalytic properties can be easily tailored, as observed in the cycloaddition of  $CO_2$  with styrene oxide, to form styrene carbonate in the presence of TBAI. We also demonstrated that the hydrogen-bonding interactions between alkoxy(bis-silanetriol) and DABCO allow the formation of

higher order structures with great potential in the synthesis of hybrid ordered materials. Such studies are currently underway in our research group. Finally, compound **8** is to the best of our knowledge the first structurally characterized silicate- alkoxy(bis-silanetriol).

#### 4. Experimental Section

#### 4.1. General methods

The syntheses of the ASA compounds (1-6) were performed under a dried dinitrogen atmosphere using Schlenk and glove-box techniques. The solvents were purchased from Sigma-Aldrich and dried prior use with an MBraun SPS solvent purification system using Grubs' columns. *tert*-Butyl alcohol was dried with Na and distilled before use; tetrabutylammonium iodide (TBAI) was purchased from Sigma-Aldrich and recrystallized from a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture. The Ph<sub>3</sub>COH, DABCO and styrene oxide, were purchased from Sigma-Aldrich and used without further purification, whereas Si(OAc)<sub>4</sub>, 1,4-bis(diethylhydroxymethyl)benzene and 3,6-diethyl-4-octyne-3,6-diol were prepared according to the literature procedures [47–50].  $C_6D_6$  was distilled from a Na/K alloy and degassed before use, whereas CDCl<sub>3</sub> was dried with P<sub>4</sub>O<sub>10</sub> and degassed before use. DMSO-d<sub>6</sub> was purchased from ABCR and used as received. Industrial grade extra dry CO<sub>2</sub> was purchased from INFRA S.A. de C.V. and used as received. NMR spectroscopic data were recorded on a Bruker Avance III 300 MHz spectrometer and referenced to residual signals of the deuterated solvent for <sup>1</sup>H and <sup>13</sup>C nuclei, or TMS as an external standard for the <sup>29</sup>Si spectra. Electron impact mass spectrometry (EI-MS) and chemical ionization mass spectrometry were carried on a Shimadzu GCMS-QP2010 Plus using direct injection in the detection range of m/z 20 – 1090. Elemental analyses (C, H, N) were determined on an Elementar MicroVario Cube analyzer. FT-IR spectra

were recorded on a Bruker ALPHA FTIR spectrometer placed inside a glove-box using the ATR technique with a diamond window in the range of 500 – 4000 cm<sup>-1</sup>. Melting points were measured in sealed capillaries on a Büchi B-540 melting point apparatus. DSC/TG measurements were carried on a Netzsch STA 449 F3 Jupiter with the heating rate of 10 °C/min from room temperature to 450 °C. The measurements were performed with a constant flow of dinitrogen gas (50 mL/min), using 5 mm aluminum crucible. Savitzky-Golay smoothing algorithm was employed for TG and DSC curves.

4.2. Preparation of compounds 1 - 12.

**1,4-[(AcO<sub>3</sub>Si)OCEt<sub>2</sub>]C<sub>6</sub>H<sub>4</sub> (1). A solution of 1,4-bis(diethylhydroxymethyl)benzene** (0.50 g, 2.00 mmol) in toluene (5 mL) was added dropwise to a suspension of silicon tetraacetate (1.06 g, 4.01 mmol) in toluene (10 mL). The reaction mixture was stirred for 4 h. Afterwards, all volatiles were removed under reduced pressure to afford the product as a white solid. Yield: 1.19 g, 1.81 mmol, 90%. M.p. 115 – 117 °C. Single crystals of compound **1** were grown from a saturated toluene solution at –25 °C. Elemental analysis (%) Calcd for C<sub>28</sub>H<sub>42</sub>O<sub>14</sub>Si<sub>2</sub> (658.80 g·mol<sup>-1</sup>): C 51.05, H 6.43; Found: C 50.67, H 6.26. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  2980, 2941 (w, C–H, CH<sub>3</sub>, CH<sub>2</sub>), 1739 (s, C=O), 951 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 0.85 (t, 6H, <sup>3</sup>*J*<sub>H–H</sub> = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.73 (s, 9H, OCC*H*<sub>3</sub>), 1.93 (dq, 2H, <sup>2</sup>*J*<sub>H–H</sub> = 14.5 Hz, <sup>3</sup>*J*<sub>H–H</sub> = 7.3 Hz, CH<sub>2</sub>), 2.13 (dq, 2H, <sup>2</sup>*J*<sub>H–H</sub> = 14.5 Hz, <sup>3</sup>*J*<sub>H–H</sub> = 7.3 Hz, CH<sub>2</sub>D<sub>6</sub>):  $\delta$  (ppm) 8.3 (CH<sub>2</sub>CH<sub>3</sub>), 22.0 (OCCH<sub>3</sub>), 35.7 (CH<sub>2</sub>CH<sub>3</sub>), 87.2 (CEt<sub>2</sub>), 125.9, 141.9 (*o*, *i*, *C* of Ar), 168.0 (*C*=O). <sup>29</sup>Si NMR (59.63 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) –101.4. EI-MS: m/z (%) 629 (9) [M – Et]<sup>+</sup>, 407 (100) [M – Et – Si(OAc)<sub>3</sub> – OH]<sup>+</sup>.

**1,2-[(AcO<sub>3</sub>Si)OCEt<sub>2</sub>]C<sub>2</sub> (2).** A solution of 3,6-diethyl-4-octyne-3,6-diol (0.50 g, 2.50 mmol) in toluene (5 mL) was added dropwise to a suspension of silicon tetraacetate (1.33 g, 5.05 mmol) in

toluene (10 mL). The reaction was stirred for 4 h. Afterwards, all volatiles were removed under reduced pressure to afford the product as a white solid. Yield: 1.36 g, 2.24 mmol, 90%. M.p. 49 – 51 °C. Single crystals of compound **2** were grown from a saturated toluene solution at –25 °C. Elemental analysis (%) Calcd for C<sub>24</sub>H<sub>38</sub>O<sub>14</sub>Si<sub>2</sub> (606.72 g·mol<sup>-1</sup>): C 47.51, H 6.31; Found: C 47.31, H 6.31. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  2983, 2946 (w, C–H, CH<sub>3</sub>, CH<sub>2</sub>), 1744 (s, C=O), 947 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 1.12 (t, 6H, <sup>3</sup>*J*<sub>H–H</sub> = 7.4 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.78 (s, 9H, OCC*H*<sub>3</sub>), 1.97 – 1.82 (m, 4H, C*H*<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 8.8 (CH<sub>2</sub>CH<sub>3</sub>), 22.1 (OCCH<sub>3</sub>), 35.0 (*C*H<sub>2</sub>CH<sub>3</sub>), 78.4 (*C*=*C*), 86.6 (*C*Et<sub>2</sub>), 167.9 (*C*=O). <sup>29</sup>Si NMR (59.63 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –99.2. EI-MS: m/z (%) 577 (1) [M – Et]<sup>+</sup>, 547 (2) [M – AcO]<sup>+</sup>, 517 (3) [M – AcO – C<sub>2</sub>H<sub>6</sub>]<sup>+</sup>, 355 (12) [M – Si(AcO)<sub>3</sub> – Et – H<sub>2</sub>O]<sup>+</sup>.

*O*,*O*'-TADDOL-Si(OAc)<sub>2</sub> (3). A solution of (*4R*,5*R*)-2,2-dimethyl-α,α,α',α'-tetraphenyldioxolane-4,5-dimethanol (TADDOL) (0.40 g, 0.86 mmol) in toluene (10 mL) was added to a suspension of silicon tetraacetate Si(OAc)<sub>4</sub> (0.23 g, 0.86 mmol) in toluene (5 mL) and the reaction mixture was heated under reflux over a period of 3 h. Afterwards, all volatiles were removed under reduced pressure and the product was isolated as a white solid. Yield: 0.41 g, 0.67 mmol, 78%. M.p. 263 °C. Elemental Analysis (%) Calcd for C<sub>35</sub>H<sub>34</sub>O<sub>8</sub>Si (610.73 g·mol<sup>-1</sup>): C 68.83, H 5.61; Found: C 68.36, H 5.90. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  1752 (m, C=O), 937 (m, Si–O). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 0.52 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 1.78 (s, 6H, CH<sub>3</sub>CO), 5.24 (s, 2H, Ph<sub>2</sub>CCHO), 7.13 – 7.38 (m, 16H, CH of Ph), 7.58 (d, 4H, <sup>3</sup>J<sub>H-H</sub> = 7.9 Hz, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, CDCl<sub>3</sub>): δ (ppm) 22.1 (CH<sub>3</sub>CO), 27.0 (C(CH<sub>3</sub>)<sub>2</sub>), 80.9 (Ph<sub>2</sub>CCHO), 84.3 (CPh<sub>2</sub>), 114.3 (C(CH<sub>3</sub>)<sub>2</sub>), 127.1, 127.1, 127.3, 127.7, 128.1, 129.1, 141.3, 146.0 (C of Ph), 168.2 (C=O). <sup>29</sup>Si NMR (59.63 MHz, CDCl<sub>3</sub>): δ (ppm) –94.3. EI-MS: m/z (%) 610 (16) [M]<sup>+</sup>, 510 (21.5) [M – C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>]<sup>+</sup>.

Ph<sub>3</sub>COSi(OAc)<sub>3</sub> (4). To a mixture of triphenylmethanol (1.00 g, 3.84 mmol) and silicon tetraacetate

(1.01 g, 3.84 mmol) was added toluene (20 mL). The reaction mixture was heated under reflux over a period of 3 h. Afterwards, all volatiles were removed under reduced pressure, to afford the product as a white solid. Yield: 1.52 g, 3.27 mmol, 85%. M.p. > 350 °C. Single crystals of compound **4** were grown from a saturated THF solution at -35 °C. Elemental analysis (%) Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>7</sub>Si (464.55 g·mol<sup>-1</sup>): C 64.64, H 5.21; Found: C 64.30, H 5.26. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  3059, 3023 (w, C–H, Ph), 1749 (s, C=O), 955 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.52 (s, 9H, OCCH<sub>3</sub>), 7.11 – 6.99 (m, 3H, CH of Ph), 7.26 – 7.12 (m, 6H, CH of Ph), 7.70 (d, 6H, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  (ppm) 21.8 (OCCH<sub>3</sub>), 88.7 (CPh<sub>3</sub>), 127.8, 128.2, 129.0, 145.5 (*p*, *m*, *o*, *i*, *C* of Ph) 167.7 (*C*=O). <sup>29</sup>Si NMR (59.63 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) – 101.8. EI-MS: m/z (%): 464 (21) [M]<sup>+</sup>, 421 (100) [M – Ac]<sup>+</sup>, 387 (17) [M – Ph]<sup>+</sup>.

**1,4-[{(AcO)**<sub>2</sub>(*t***BuO**)**Si}OCEt**<sub>2</sub>]**C**<sub>6</sub>**H**<sub>4</sub> (5). *t*BuOH (3 mL) was added to **1** (1.00 g, 1.52 mmol) and the reaction mixture was stirred over a period of 12 h. All volatiles were removed under reduced pressure and the product was isolated as a colorless oil. Yield: 0.87 g, 2.64 mmol, 87%. Elemental analysis (%) Calcd for C<sub>32</sub>H<sub>54</sub>O<sub>12</sub>Si<sub>2</sub> (686.93 g·mol<sup>-1</sup>): C 55.95, H 7.92; Found: C 55.65, H 7.88. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  2975, 2937 (w, C–H, CH<sub>3</sub>, CH<sub>2</sub>), 1743 (s, C=O), 984 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.69 (t, 6H, <sup>3</sup>*J*<sub>H–H</sub> = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.37 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.84 – 2.05 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 2.10 (s, 6H, OCCH<sub>3</sub>), 7.28 (s, 2H, Ar*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.2 (CH<sub>2</sub>CH<sub>3</sub>), 23.0 (OCCH<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 35.0 (CH<sub>2</sub>CH<sub>3</sub>), 76.2 (*C*(CH<sub>3</sub>)<sub>3</sub>), 85.3 (*C*Et<sub>2</sub>), 125.4, 142.0 (*o*, *i*, *C* of Ar), 168.6 (*C*=O). <sup>29</sup>Si NMR (59.63 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) – 104.8, EI-MS: m/z (%) 657 (55) [M – Et]<sup>+</sup>, 627 (10) [M – AcO]<sup>+</sup>, 613 (30) [M – *t*BuO]<sup>+</sup>.

 $Ph_3COSi(OtBu)(OAc)_3$  (6) *t*BuOH (3 mL) was added to 4 (1.00 g, 2.15 mmol) and the reaction mixture was stirred over a period of 12 h. Afterwards, all volatiles were removed under reduced pressure and the product was isolated as a white solid. Yield: 0.70 g, 1.46 mmol, 68%. M.p. 87 – 89

°C. Elemental analysis (%) Calcd for C<sub>27</sub>H<sub>30</sub>O<sub>6</sub>Si (478.61 g·mol<sup>-1</sup>): C 67.76, H 6.32; Found: C 67.58, H 6.50. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  3057 (w, C–H, Ph), 2982, 2937, (w, C–H, CH<sub>3</sub>), 1740 (s, C=O), 951 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.88 (s, 6H, OCCH<sub>3</sub>), 7.22 – 7.32 (m, 9H, CH of Ph), 7.38 – 7.42 (m, 6H, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 22.7 (OCCH<sub>3</sub>), 31.0 (C(CH<sub>3</sub>)<sub>3</sub>), 76.2 (C(CH<sub>3</sub>)<sub>3</sub>), 87.2 (CPh<sub>3</sub>), 127.3, 127.7, 128.8, 145.5 (*p*, *m*, *o*, *i*, *C* of Ph) 168.3 (*C*=O). <sup>29</sup>Si NMR (59.63 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) –105.1. EI-MS: m/z (%) 478 (5) [M]<sup>+</sup>, 421 (44) [M – *t*Bu]<sup>+</sup>, 401 (18) [M – Ph]<sup>+</sup>, 243 (96) [Ph<sub>3</sub>C]<sup>+</sup>.

**1,4-[{(HO)<sub>2</sub>(***t***BuO)Si}OCEt<sub>2</sub>]C<sub>6</sub>H<sub>4</sub> (7). 5 (0.20 g, 0.29 mmol) was added to a mixture of water (5 mL) and ethyl acetate (10 drops, 0 °C) and stirred for 15 min. The solvents were decanted and the product was isolated as white solid. Single crystals were obtained by slow evaporation of THF solution at ambient temperature. Yield: 0.09 g, 0.17 mmol, 87%. M.p. 160 – 161 °C. Elemental analysis (%) Calcd for C<sub>24</sub>H<sub>46</sub>O<sub>8</sub>Si<sub>2</sub> (518.79 g·mol<sup>-1</sup>): C 55.51, H 8.86; Found: C 55.09, H 8.72. FT-IR (ATR) (cm<sup>-1</sup>) \tilde{V} 3373 (s, SiO–H), 2975, 2935 (w, –CH<sub>3</sub>, –CH<sub>2</sub>), 961 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, DMSO-***d***<sub>6</sub>): \delta (ppm) 0.59 (t, 6H, <sup>3</sup>***J***<sub>H-H</sub> = 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.29 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>) 1.70 – 2.08 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), 6.19 (s, 2H, Si(OH)<sub>2</sub>), 7.26 (s, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSO-***d***<sub>6</sub>): \delta (ppm) 8.3 (CH<sub>2</sub>CH<sub>3</sub>), 31.3 (C(CH<sub>3</sub>)<sub>3</sub>), 34.5 (CH<sub>2</sub>CH<sub>3</sub>), 71.2 (C(CH<sub>3</sub>)<sub>3</sub>), 81.0 (CEt<sub>2</sub>), 124.8, 142.9 (***o***,** *i***,** *C* **of Ar). <sup>29</sup>Si NMR (59.63 MHz, DMSO-***d***<sub>6</sub>): \delta (ppm) –85.5. EI-MS: m/z (%) 489 (100) [M – Et]<sup>+</sup>.** 

**1,4-[(HO)<sub>3</sub>SiOCEt<sub>2</sub>]C<sub>6</sub>H<sub>4</sub> (8). 1** (0.35 g, 0.53 mmol) was suspended in cold distilled water (5 mL). The reaction mixture was vigorously stirred at 0 °C for 10 min. Afterwards, the white powder was collected via filtration and washed with cold water (2 x 2 mL) in order to remove the remanent acetic acid. Yield: 0.20 g, 0.50 mmol, 93%. M.p. > 350 °C (dec). Elemental analysis (%) Calcd for  $C_{16}H_{30}O_8Si_2$  (406.58 g·mol<sup>-1</sup>): C 47.27, H 7.44; Found: C 46.90, H 7.30. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$ 

3128 (s, SiO–H), 2972, 2937 (w, C–H, CH<sub>3</sub>, CH<sub>2</sub>), 918 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, DMSOd<sub>6</sub>):  $\delta$  (ppm) 0.59 (t, 6H, <sup>3</sup>J<sub>H–H</sub> = 7.3 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.76 – 2.04 (m, 4H, CH<sub>2</sub>), 6.04 (s, 3H, Si(OH)<sub>3</sub>), 7.26 (s, 2H, Ar*H*). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) 8.4 (CH<sub>2</sub>CH<sub>3</sub>), 34.7 (CH<sub>2</sub>CH<sub>3</sub>), 80.6 (CEt<sub>2</sub>), 124.9, 143.0 (*o*, *i*, *C* of Ar). <sup>29</sup>Si NMR (59.63 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) –79.4. EI-MS: m/z (%) 377 (6) [M – Et]<sup>+</sup>.

**1.4-**[(HO)<sub>3</sub>SiOCEt<sub>2</sub>]C<sub>2</sub> (9). 2 (0.33 g, 0.54 mmol) was suspended in cold distilled water (1.5 mL). The reaction mixture was vigorously stirred at 0 °C for 2 min. Afterwards, the white powder was collected via filtration and washed with cold water (2 x 1 mL) in order to remove the remanent acetic acid. Yield: 0.14 g, 0.40 mmol, 75%. M.p. > 350 °C (dec). Elemental analysis (%) Calcd for  $C_{12}H_{26}O_8Si_2$  (354.50 g·mol<sup>-1</sup>): C 40.66, H 7.39; Found: C 39.42, H 7.23. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$ 3145 (s, SiO-H), 2972, 2940 (w, C-H, CH<sub>3</sub>, CH<sub>2</sub>), 928 (s, Si-O). <sup>1</sup>H NMR (300.53 MHz, DMSO $d_6$ ):  $\delta$  (ppm) 0.94 (t, 6H,  ${}^{3}J_{H-H} = 7.3$  Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.59 – 1.74 (m, 4H, CH<sub>2</sub>), 6.18 (s, 3H, Si(OH)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 8.9 (CH<sub>2</sub>CH<sub>3</sub>), 34.3 (CH<sub>2</sub>CH<sub>3</sub>), 73.3 (C=C), 85.9 (*C*Et<sub>2</sub>). <sup>29</sup>Si NMR (59.63 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) –78.3. EI-MS: m/z (%) 325 (5) [M – Et]<sup>+</sup>. Ph<sub>3</sub>COSi(OH)<sub>3</sub> (10). 4 (0.32 g, 0.69 mmol) was suspended in cold distilled water (10 mL). The reaction mixture was vigorously stirred at 0 °C for 10 min. Afterwards, the white powder was collected via filtration and washed with cold water (2 x 2 mL) in order to remove the remanent acetic acid. Yield: 0.20 g, 0.59 mmol, 85%. M.p. 95 - 97 °C. Elemental analysis (%) Calcd for  $C_{19}H_{18}O_4Si$  (338.43 g·mol<sup>-1</sup>): C 67.43, H 5.36; Found: C 66.39, H 5.12. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$ 3312 (s, SiO-H), 3057 (w, C-H, Ph), 928, 898 (s, Si-O). <sup>1</sup>H NMR (300.53 MHz, DMSO- $d_6$ ):  $\delta$ (ppm) 5.90 (s, 3H, Si(OH)<sub>3</sub>), 7.18 – 7.32 (m, 15H, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSOd<sub>6</sub>): δ (ppm) 84.1 (CPh<sub>3</sub>), 126.6, 127.3, 128.2, 147.1 (p, m, o, i, C of Ph). <sup>29</sup>Si NMR (59.63 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) -80.9. EI-MS: m/z (%) 338 (1) [M]<sup>+</sup>.

Ph<sub>3</sub>COSi(OtBu)(OH)<sub>3</sub> (11). Hydrolysis route 1: 7 (1.00 g, 2.08 mmol) was suspended in a mixture of cold distilled water (20 mL) and concentrated ammonia solution (1 mL) and stirred at room temperature for 15 min. Subsequently, the product was extracted with ethylacetate and isolated after removing all volatiles. Yield: 0.53 g, 0.13 mmol, 65%. Hydrolysis route 2: 7 (1.00 g, 2.08 mmol) was suspended in cold distilled water (20 mL) and stirred at room temperature for 15 hours. Subsequently, the product was isolated as a white powder via filtration. Yield: 0.58 g, 0.14 mmol, 71%. Single crystals of compound 11 were grown: a) from a DMSO solution by slow solvent evaporation at ambient temperature b) by slow evaporation of wet dichloromethane solution. M.p. 73 – 75 °C. Elemental analysis (%) Calcd for  $C_{23}H_{26}O_4Si$  (394.54 g·mol<sup>-1</sup>): C 63.53, H 6.80; Found: C 61.91, H 6.67. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  3381 (m, SiO–H), 2973 (w, C–H, CH<sub>3</sub>), 928 (s, Si–O). <sup>1</sup>H NMR (300.53 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 1.03 (s, 9H, C(CH\_3)\_3), 6.12 (s, 2H, Si(OH)\_2), 7.18 - 7.32 (m, 15H, CH of Ph).  ${}^{13}C{}^{1}H{}$  NMR (75.57 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 31.1 (C(CH\_3)\_3), 71.2 (C(CH<sub>3</sub>)<sub>3</sub>), 84.4 (OCPh<sub>3</sub>), 126.6, 127.2, 128.4, 147.0 (p, m, o, i, C of Ph). <sup>29</sup>Si NMR (59.63 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) -87.0. EI-MS: m/z (%) 394 (5) [M]<sup>+</sup>, 379 (8) [M - Me]<sup>+</sup>, 337 (100) [M - tBu]<sup>+</sup>,  $317 (80) [M - Ph]^+$ .

*O*,*O*<sup>\*</sup>-TADDOL-Si(OH)<sub>2</sub> 12. 3 (0.31 g, 0.51 mmol) was suspended in cold distilled water (10 mL) and stirred for 10 min. Then the white solid was filtered off and washed once with 5 mL of water. Yield: 0.26 g, 0.49 mmol, 96%). M.p. 204 °C (dec). Elemental Analysis (%) Calcd for  $C_{31}H_{30}O_6Si \cdot 0.66(CH_2Cl_2)$  (583.25 g·mol<sup>-1</sup>) C 65.21, H 5.41. Found: C 65.13, H 5.49. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  3577 (s, SiO–H), 939 (m, Si–O). <sup>1</sup>H NMR (300.53 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 0.51 (s, 6H, C(CH\_3)<sub>2</sub>), 4.89 (s, 2H, Ph<sub>2</sub>CCHO), 6.89 (s, 2H, SiOH), 7.22 – 7.51 (m, 20H, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 26.8 (C(CH\_3)<sub>2</sub>), 80.9 (Ph<sub>2</sub>CCHO, CPh<sub>2</sub>), 112.5 (C(CH\_3)<sub>2</sub>), 126.6, 126.8, 126.9, 127.1, 127.9, 128.9, 142.5, 147.0 (C of Ph). <sup>29</sup>Si NMR (59.63 MHz, DMSO-

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 $d_6$ ):  $\delta$  (ppm) -83.8. EI-MS: m/z (%) 526 (8) [M]<sup>+</sup>, 468 (3.5) [M - (CH<sub>3</sub>)<sub>2</sub>C=O]<sup>+</sup>.

**8-2DABCO.** A solution of diazabicyclo[2.2.2]octane (DABCO, 0.11 g, 0.98 mmol) in THF (2 mL) was added to a solution of **8** (0.20 g, 0.49 mmol) in THF (5 mL) and the mixture was stirred for 15 min. The white precipitate was filtered off. Crystals of **8-2DABCO** were grown from a saturated THF solution at -25 °C. Yield: 0.24 g 0.37 mmol, 76%. M.p. >350 °C (dec). Elemental analysis (%) Calcd for Si<sub>2</sub>N<sub>4</sub>O<sub>8</sub>C<sub>28</sub>H<sub>54</sub> (630.52 g·mol<sup>-1</sup>) C 53.34, N 8.88, H 8.56; Found: C 52.65, N 8.52, H 8.47. FT-IR (ATR) (cm<sup>-1</sup>)  $\tilde{V}$  2958, 2881 (w, C–H, CH<sub>3</sub>, CH<sub>2</sub>), 927 (s, Si–O).

4.3. General procedure for the catalytic cycloaddition of  $CO_2$  to styrene oxide.

A 10 mL reaction vial was charged with the racemic mixture of styrene oxide (1 equiv SO, 0.11 g, 0.88 mmol), tetrabutylammonium iodide (0.1 equiv, 0.033 g, 0.088 mmol), and silanol catalyst which were used as obtained from the synthesis (0.1 equiv, 0.088 mmol). The vial was purged once with CO<sub>2</sub>. Afterwards, it was put under a positive pressure with a balloon of CO<sub>2</sub>, and the reaction mixture was stirred for 15 h at 60 °C. The conversion degree was determined using <sup>1</sup>H NMR spectroscopy using toluene as internal standard (1 equiv, 0.081 g, 0.88 mmol), and DMSO-*d*<sub>6</sub> as the deuterated solvent. Silanol catalyst and TBAI were precipitated in diethyl ether; the mixture was filtered and the volatiles were removed from the filtrate to yield the product. The NMR spectroscopic data for the product SC match those reported in the literature [45]. <sup>1</sup>H NMR (300.53 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 4.42 (apparent t, 1H, *J*<sub>H-H</sub> = 8.3 Hz), 4.89 (apparent t, 1H, *J*<sub>H-H</sub> = 8.3 Hz), 5.86 (apparent t, 1H, *J*<sub>H-H</sub> = 8.0 Hz), 7.30 – 7.57 (m, 5H, CH of Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (75.57 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) 70.9, 77.8, 126.7, 128.9, 129.4, 136.3, 154.8.

#### 4.4. X-Ray Crystallography

Single crystals were mounted on a Bruker APEX DUO diffractometer equipped with an Apex II

CCD detector at 100 K. Frames were collected using omega scans and integrated with SAINT [51]. Multi-scan absorption correction (SADABS) [51] was applied. The structures were solved by direct methods (SHELXS) [52] or using intrinsic phasing (SHELXT) [53] and refined using full-matrix least-squares on  $F^2$  with SHELXL [54] using the ShelXle GUI [55]. Weighted *R* factors,  $R_w$  and all goodness-of-fit indicators, are based on  $F^2$ . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the C–H bonds were placed in idealized positions, whereas the hydrogen atoms from the OH moieties in **7**, **8·2DABCO**, **11·DMSO**, **11·H**<sub>2</sub>**O** and **12** were localized from the difference electron density map and their position was refined with  $U_{iso}$  fied to the parent atom with distance restraints (DFIX or SADI). The disordered groups and solvent molecules (**4** 1 x CH<sub>3</sub>C(O); **10·THF** 1 x THF; **11·DMSO** 1 x DMSO; **11·H**<sub>2</sub>**O** 1 x *t*Bu, 1 x OH; **12** 1 x CH<sub>2</sub>Cl<sub>2</sub>) were refined using geometry (SADI, SAME) and  $U_{ij}$  restraints (SIMU, RIGU) implemented in SHELXL [54]. The Flack parameter for compound **1** 0.487(4) suggests that an inversion center could be present, but the structure cannot be refined neither in the *C2/c* or *C2/m* space group. Thus this unusual value is caused by the presence of racemic twinning.

The molecular graphics were prepared using GRETEP, POV-RAY and GIMP [56]. CCDC-1453225, 1453226, 1453228 – 1453236 contain the supplementary crystallographic data for this of Copies ' the paper. data can be obtained free of charge via http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### **Author contributions**

The manuscript was written through contributions of all authors. All authors have given approval to

the final version of the manuscript.

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#### Supplementary data

CCDC-1453225, 1453226, 1453228 – 1453236 contain the supplementary crystallographic data for Copies of can be obtained free of this the data charge paper. via http://www.ccdc.cam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

#### References

- [1] V. Chandrasekhar, R. Boomishankar, S. Nagendran, Chem. Rev. 104 (2004) 5847–5910.
- [2] R. Pietschnig, S. Spirk, Coord. Chem. Rev. 323 (2016) 87–106.
- [3] P. D. Lickiss, In Advances in Inorganic Chemistry; The synthesis and structure of Organosilanols, Vol. 42, Academic Press inc. (1995), 147–262.
- [4] J. Alauzun, A. Mehdi, C. Reyé, R.J.P. Corriu, J. Mater. Chem. 15 (2005) 841–843.
- [5] G. Cerveau, S. Chappellet, R.J.P. Corriu, J. Mater. Chem. 13 (2003) 2885–2889.
- [6] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, Nature 416 (2002) 304–307.
- [7] M.P. Kapoor, Q. Yang, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 15176–15177.

- [8] K. Kuroda, A. Shimojima, K. Kawahara, R. Wakabayashi, Y. Tamura, Y. Asakura, M. Kitahara, Chem. Mater. 26 (2014) 211–220.
- [9] L.D. Carlos, V. de Z. Bermudez, V.S. Amaral, S.C. Nunes, N.J.O. Silva, R.A. Sa Ferreira, J.C.V. Santilli, D. Ostrovskii, Adv. Mater. 19 (2007) 341–348.
- [10] S. Kondo, Y. Bie, M. Yamamura, Org. Lett. 15 (2013) 520–523.
- [11] M. Yamamura, S. Kondo, M. Unno, Tetrahedron Lett. 55 (2014) 646–649.
- [12] S. Kondo, T. Harada, R. Tanaka, M. Unno, Org. Lett. 8 (2006) 4621-4624.
- [13] N. Hurkes, H.M.A. Ehmann, M. List, S. Spirk, M. Bussiek, F. Belaj, R. Pietschnig, Chem. Eur. J. 20 (2014) 1–7.
- [14] M. Blunder, N. Hurkes, S. Spirk, M. List, R. Pietschnig, Bioorg. Med. Chem. Lett. 21 (2011) 363–365.
- [15] K. Franz, S.O. Wilson, J. Med. Chem. 56 (2013) 388-405.
- [16] J.L.H. Madsen, T.L. Andersen, S. Santamaria, H. Nagase, J.J. Enghild, T. Skrydstrup, J. Med. Chem. 55 (2012) 7900–7908.
- [17] S.M. Sieburth, C.A. Chen, Eur. J. Org. Chem. (2006) 311–322.
- [18] S. Singh, S.M. Sieburth, Org. Lett. 14 (2012) 4422–4425.
- [19] M. wa Mutahi, T. Nittoli, L. Guo, S.McN. Sieburth, J. Am. Chem. Soc. 124 (2002) 7363– 7375.
- [20] D.A. Ruddy, J. Jarupatrakorn, R.M. Rioux, J.T. Miller, M.J. Mcmurdo, J.L. Mcbee, K.A.Tupper, T.D. Tilley, Chem. Mater. 20 (2008) 6517–6527.
- [21] C. Copéret, A. Comas-Vives, M.P. Conley, D.P. Estes, A. Fedorov, V. Mougel, H. Nagae, F. Núñez-Zarur, P.A. Zhizhko, Chem. Rev. 116 (2016) 323–421.
- [22] D. Pinkert, C. Limberg, Chem. Eur. J. 20 (2014) 9166–9175.

- [23] G. Schafer, J.M. Wieting, T.J. Fisher, A.E. Mattson, Angew. Chem. Int. Ed. 52 (2013) 11321– 11324.
- [24] N.T. Tran, S.O. Wilson, A.K. Franz, Org. Lett. 14 (2012) 186–189.
- [25] J.M. Wieting, T.J. Fisher, A.G. Schafer, M.D. Visco, J.C. Gallucci, A.E. Mattson, Eur. J. Org. Chem. (2015) 525–533.
- [26] S.O. Wilson, N.T. Tran, A.K. Franz, Organometallics 31 (2012) 6715–6718.
- [27] M. Cokoja, M.E. Wilhelm, M.H. Anthofer, W.A. Herrmann, F.E. Kühn, ChemSusChem 8 (2015) 2436–2454.
- [28] J. Suzuki, A. Shimojima, Y. Fujimoto, K. Kuroda, Chem. Eur. J. 14 (2008) 973–980.
- [29] G. Cerveau, S. Chappellet, R.J.P. Corriu, B. Dabiens, J.L. Bideau, Organometallics 21 (2002) 1560–1564.
- [30] G. Cerveau, R.J.P. Corriu, B. Dabiens, J.L. Bideau, Angew. Chem. Int. Ed. 39 (2000) 4533–4537.
- [31] Y. Nakajima, S. Shimada, RSC Adv. 5 (2015) 20603–20616.
- [32] B. Arkles, Y. Pan, G.L. Larson, M. Singh, Chem. Eur. J. 20 (2014) 9442–9450.
- [33] M. Liu, N.T. Tran, A.K. Franz, J.K. Lee, J. Org. Chem. 76 (2011) 7186–7194.
- [34] F.D. Osterholtz, E.R. Pohl, Kinetics and Mechanism of Aqueous Hydrolysis and Condensation of alkyltrialkoxysilanes. In Molecular characterization of composite interfaces, Proceedings of the (ACS) Symposium on Polymer Composites: Interfaces, Washington, March 1983, H. Ishida, G. Kumar, Eds., Plenum Press: New York (1985) 157–170.
- [35] C.J. Brinker, G.W. Scherer, Sol-Gel Science The Physics and Chemistry of Sol-Gel Processing, Academic Press: San Diego (1990).
- [36] G. Prabusankar, R. Murugavel, R.J. Butcher, Organometallics 23 (2004) 2305–2314.

- [37] K. Krekić, N.F. Hurkes, C. Bruhn, F. Belaj, R. Pietschnig, Z. Anorg. Allg. Chem. 642 (2016) 302–305.
- [38] L. Wicke, E. Alig, L. Hans-Wolfram, M. Bolte, Acta Crystallogr. E58 (2002) 0927–0928.
- [39] a) V.E. Shklover, I.L. Dubchak, Yu.T. Struchkov, E.S. Khinku, A.A. Zhdanov, J. Struc. Chem. 22 (1981) 225–229; b) C. Wendler, H. Reinke, H. Kelling, J. Organomet. Chem. 626 (2001) 53–58; c) R. Rulkens, M.P. Coles, T.D. Tilley, J. Chem. Soc., Dalton Trans. (2000) 627–628; d) S. Spirik, M. Nieger, G. N. Rechberger, R. Pietschnig, Appl. Organomet. Chem. 20 (2006) 683–686.
- [40] J. Bernstein, R. E. Davis, L. Shimoni, N. L. Chang, Angew. Chem. Int. Ed. 34 (1995) 1555– 1573.
- [41] J. Wang, J. Leong, Y. Zhang, Green Chem. 16 (2014) 4515–4519.
- [42] J. Q. Wang, D. L. Kong, J. Y. Chen, F. Cai, L. N. He, J. Mol. Catal. A: Chem. 249 (2006) 143–148.
- [43] M. M. Dharman, H. J. Choi, D. W. Kim, D. W. Kim, D. W. Park, Catal. Today 164 (2011) 544–547.
- [44] T. Takahashi, T. Watahik, S. Kitazume, H. Yasuda, T. Sakakura, Chem. Commun. (2006) 1664–1666.
- [45] M. Hardman-Baldwin, A.E. Mattson, ChemSusChem 7 (2014) 3275–3278.
- [46] a) M.E. Wilhelm, M.H. Anthofer, M. Cokoja, L.I.E.Markovits, W.A. Herrmann, F.E. Kühn, Chemsuschem 7 (2014) 1357–1360. b) C.J. Whiteoak, A. Nova, F. Maseras, A.W. Kleij, Chemsuschem 5 (2012) 2032–2038.
- [47] J.H. Balthis, E.G. Rochow, D.G. White, In Inorganic Syntheses; J.C. Bailar, Ed.; Silicon Tetraacetate, Vol. 4, Part. IV; Wiley & Sons: Hoboken, NJ (2007) pp 45–47.

- [48] Y.K. Kang, P. Deria, M.J. Therien, Synthesis of poly-(p-aryleneethynylene)s in neat water under aerobic conditions. U.S. Patent 0326150 A1, December 31, 2009.
- [49] D.T. McQuade, J. Kim, T.M. Swager, J. Am. Chem. Soc. 122 (2000) 5885-5886.
- [50] J. Mortier, M. Vaultier, F. Carreaux, D. Jean-Marc, J. Org. Chem. 63 (1998) 3515-3516.
- [51] SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
- [52] SHELX, G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112–122.
- [53] G.M. Sheldrick, Acta Crystallogr. A71 (2015) 3-8.
- [54] G.M. Sheldrick, Acta Crystallogr. C71 (2015) 3-8.

- [55] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, J. Appl. Cryst. 44 (2011) 1281–1284.
- [56] a) LMGP-Suite Suite of Programs for the interpretation of X-ray Experiments, J. Laugier, B. Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France. WWW: http://www.inpg.fr/LMGP and <a href="http://www.ccp14.ac.uk/tutorial/lmgp/">http://www.inpg.fr/LMGP</a> and <a href="http://www.inpg.fr/LMGP">http://www.inpg.fr/LMGP</a> and </a> and



#### **TOC synopsis**

Acetoxysilylalkoxides (ASA) can be easily hydrolyzed to the corresponding silanols in the absence of organic solvent and a base. These ASA precursors are readily prepared from silicon tetraacetate and alcohols. The compounds were characterized by common spectroscopic methods including X-Ray diffraction and some were tested in the catalytic conversion of CO<sub>2</sub> to styrene carbonate.