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Synthesis of α-silylcarboxylic acids

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ABSTRACT

New α-silylacetic acids have been prepared following a general and convenient procedure of a one-pot reaction between trimethylsilylacetate and different chlorosilanes. New derivatives of diphenyl(methyl) silylacetic acid were prepared by a direct alkylation of its dianion with benzyl-, allyl-, and alkyl halides and trimethylchlorogermane to afford new α-silylcarboxylic acids.

1. Intoduction

Over the past decades, organosilicon compounds have reached considerable importance in synthetic organic chemistry. They are readily available and fairly stable compared to other organometallic compounds and are widely utilized not only as various functional materials, but also as valuable synthetic organic reagents owing to their unique chemical and physical properties.[1] As a result, organosilicon compounds are widely used in polymer and dendrimer synthesis,[2] bioorganic and drug design chemistry,[3,4] electrochemistry[5] and also in new type of reactions, such as cross coupling,[6] cross metathesis,[7] and Lewis acid-catalyzed reactions.[8]

α-Silylcarboxylic acids are important intermediates in organic synthesis. They are widely used for various biological purposes, such as preparing diethyl malonate labeled at each carboxyl carbon,[9] synthesizing α,β-unsaturated thiol esters,[10] and α-silyl thioesters.[11] In addition, the dianion of trimethylsilylacetic acid provides a highly efficient route for the preparation of α,β-unsaturated acids and butyrolactones.[12] Recently, α-silylcarboxylic acids have been utilized in the electrochemical synthesis of useful disilylalkanes of type $R_3SiCH_2CH_2SiR_3$ by the Kolbe anodic oxidation of their carboxylate anions.[13]

Since the first report of the synthesis of trimethylsilylacetic acid by Sommer and co-workers in 1949,[14] other attempts to synthesize similar acids have been hampered by low yields, lack of selectivity, and relatively high cost of the reagents used. Recently, our group developed a useful method for the preparation of various α-silylacetic acids of the type $R_1R_2R_3SiCH_2CO_2H$ by treating trimethylsilylacetate with LDA followed by quenching with chlorosilanes.[15] This method was found to be convenient, reproducible, efficient, and quite general for using different kinds of silyl substituents, as illustrated in Table 1 (entries 1–6).

Table 1
Synthesis of new α-silylacetic acids

Entry	Chlorosilane	Product	Yield[a], %
1[b]	Me_3SiCl	$Me_3SiCH_2CO_2H$ (**1**)	72
2[b]	*n*-Pr_3SiCl	*n*-$Pr_3SiCH_2CO_2H$ (**2**)	70
3[b]	*i*-Pr_3SiCl	*i*-$Pr_3SiCH_2CO_2H$ (**3**)	62
4[b]	Ph_3SiCl	$Ph_3SiCH_2CO_2H$ (**4**)	70
5[b]	$Me_2(Ph)SiCl$	$Me_2(Ph)SiCH_2CO_2H$ (**5**)	75
6[b]	$Ph_2(Me)SiCl$	$Ph_2(Me)SiCH_2CO_2H$ (**6**)	78
7	$Me_2(CH_2Cl)SiCl$	$Me_2(CH_2Cl)SiCH_2CO_2H$ (**7**)	68
8	$Me_2(C_6H_{11})SiCl$	$Me_2(C_6H_{11})SiCH_2CO_2H$ (**8**)	60
9	$Me_2(CH_2Ph)SiCl$	$Me_2(CH_2Ph)SiCH_2CO_2H$ (**9**)	72
10	$Me(Vinyl)PhSiCl$	$Me(Vinyl)PhSiCH_2CO_2H$ (**10**)	74
11	$Ph_2(Vinyl)SiCl$	$Ph_2(Vinyl)SiCH_2CO_2H$ (**11**)	80
12	$(Vinyl)_3SiCl$	$(Vinyl)_3SiCH_2CO_2H$ (**12**)	71
13	$[(Me)Si(Ph)Cl]_2O$	$[(Me)Si(Ph)CH_2CO_2H]_2O$ (**13**)	30

[a] Isolated yield.
[b] Taken from Ref. 15.

2. Results and discussion

The present work describes the synthesis and characterization of new α-silylacetic acids and their utility in the preparation of

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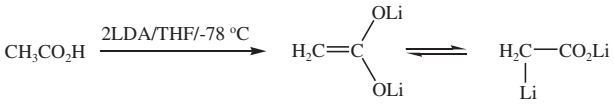
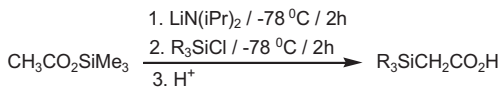
novel derivatives of α-silylcarboxylic acids. The synthesis is based on the well-known property of trimethylsilyl esters of carboxylic acids that they are readily hydrolyzed under very mild acidic conditions.[16] Trimethylsilylacetate ($CH_3CO_2SiMe_3$) was chosen as the starting material and was treated with 1 equiv of LDA to give the anticipated lithium enolate salt. Apparently, the early work of Ainsworth and Kuo indicated that a keto–enol equilibrium between two organolithium species (Scheme 1) was observed and as a result, equal amounts of *O*- and *C*-silyl derivatives were formed upon silylation.[16]



Scheme 1. Keto–enol equilibrium between two organolithium species.

However, we have found in our laboratory that the yield of the *C*-silylated products increases relative to the *O*-silylated one when the lithium enolote salt is allowed to stand at −78 °C for 2 h prior to quenching it with an alkylchlorosilane. On the other hand, if the enolate salt is immediately quenched at −78 °C, the yield of the *C*-silylated product is reduced significantly, whereas that of the O-silylation product increases. We also found that after adding an alkylchlorosilane, a continuous cooling of the reaction mixture at −78 °C for an additional 2 h was necessary to maintain a high yield of the *C*-silylated products. It seems that the rate of silylation at the carbon is slow at this low temperature, and therefore, a rapid heating to room temperature shifts the equilibrium toward O-silylation, resulting in a decrease in the yield of *C*-silylated products. Progress toward understanding the reactivity of the synthetically important lithium enolates relies on the ability to characterize their aggregation states in solutions. Mechanistic studies of enolate alkylations have afforded diverse hypotheses. The reaction could proceed via dimer[17] or tetramer-based[18] forms. Recently, it has been shown that C-alkylation of β-amino esters proceeds via hexameric enolates, which exist as such both in the solid-state and in THF solutions.[19]

It is noteworthy that recent work has proven that the hexameric enolate of β-amino esters undergo C-alkylation directly without deaggregation.[20] In addition, Hudrlik and co-workers reported on an unusual O→C migration of the trimethylsilyl group under similar experimental conditions.[21] It is conceivable that the 2 h reaction time before quenching (as described above) is required to obtain the desired aggregation state that allows efficient C-silylation at a low temperature. By employing the experimental conditions described above (Scheme 2), we have synthesized different types of known and novel α-silylacetic acids in good isolated yields, as is shown in Table 1 (entries 1–12).

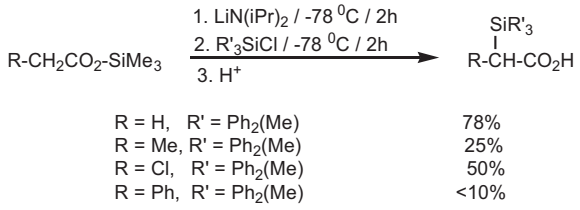


Scheme 2. Experimental conditions for α-silylation of trimethylsilylacetate.

The observation that C-silylation of the *tert*-butylester of acetic acid (analogue of trimethylsilylacetate) is quite sensitive to the bulkiness of the silyl group or 'softness' of the electrophilic silicon moiety is well known.[22] Now it can be seen that by using trimethylsilylacetate as the starting material and applying the experimental conditions mentioned above, the outcome of the reaction is not sensitive to the nature of the silyl group, whether it is an alkyl, phenyl or vinyl substituent. In addition, it can be observed (Table 1, entries 2–4) that the reaction is not sensitive to the bulkiness of the silyl substituents because the yields of the corresponding α-silylated acetic acids were still good. Interestingly, it is quite remarkable that the vinyl groups (entries 10–12) remain intact and do not undergo polymerization. As a result, different kinds of α-silylacetic acids were successfully synthesized and isolated by this new method. Moreover, some of these compounds (entries 7, 10–12) are functionalized, allowing further chemical transformations to new organosilyl derivatives.

A successful attempt to prepare a new α,α′-disilyldicarboxylic acid under the same experimental conditions by the use of 1,3-bis (dichlorosilyl)siloxane as reagent (entry 13) and 2 equiv of trimethylsilylacetate has been performed. Due to its relatively polar property, **13** was easily separated from the other major product, trimethysilylacetic acid, without further purification (see Experimental section for compound **13**). Apparently, its yield was low (entry 13) due to an O→C migration of the trimethylsilyl group to afford trimethysilylacetic acid. The reason for that is not clear yet. However, it should be noted that this type of migration was observed in all other reaction but to a minor extent. In any case, the reaction in entry 13 demonstrates the formation of a new class of α,α′-disilyldicarboxylic acids linked by a siloxyl moiety and no further attempts were made to optimize its yield.

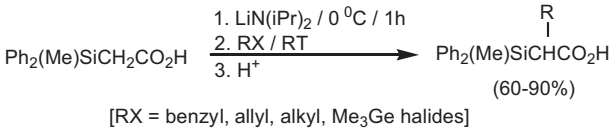
After the successful preparation of α-silylacetic acids from trimethylsilylacetate, we attempted the reaction with trimethylsilyl esters of other carboxylic derivatives of the type $RCH_2CO_2SiMe_3$ (R=Me, Cl, Ph) in order to prepare new derivatives of α-silylcarboxylic acids. The α-silylation of these esters was examined with diphenylmethylchlorosilane, which was preferred over trimethylchlorosilane due to its being a 'softer' acid (it has a stronger electronic withdrawing effect) and therefore, more reactive toward the carbon terminus of the ambient nucleophile. Consequently, C-silylation is predominant with diphenylmethylchlorosilane, whereas O-silylation is favored with trimethylchlorosilane.[22] However, there are other factors to be considered (inductive and steric effects). For example, it is noteworthy that silylation of the trimethylsilyl ester of propionic acid under the same experimental conditions gave the desired product in a low yield (Scheme 3). This trend could be explained either due to the inductive effect exerted by the methyl group that destabilizes the carbanion intermediate, or by a steric effect. On the other hand, it is conceivable that Cl and Ph substituents in trimethylsilyl esters of chloroacetic and phenylacetic acids should stabilize a carbanion at the α position, aiming toward higher yields of the desired *C*-silylated products. Surprisingly, the yield of the product from $ClCH_2CO_2SiMe_3$ decreased compared to that obtained from $CH_3CO_2SiMe_3$, while that from $PhCH_2CO_2SiMe_3$ was less then 10% (Scheme 3).



Scheme 3. α-Silylation of trimethylsilyl esters of carboxylic acids.

In spite of the few examples, the above results could indicate that in the latter two cases the inductive effect plays a minor role compared with steric effects. As a consequence, it is possible that the yield of the *C*-silylated product is dictated mostly by the bulkiness of the group attached to the carbon at the α position that increases in the order: H>Cl>Me>Ph.

In order to synthesize α-substituted silylcarboxylic acids in good yields, we have utilized an alternative route of direct alkylation of their dianions. The dianion of a carboxylic acid is a good nucleophile and the most nucleophilic site is at the α carbanionic position. However, in general, the limitation in alkylation of metalated straight-chain acids lies in their partial solubility in THF. In order to overcome this problem, hexamethylphosphoramide (HMPA) was used by others, previously.[23] Interestingly, we have found that the dianion of diphenyl(methyl)silylacetic acid is readily dissolved in THF. Moreover, a silyl group at the α position to carbanions has an electron accepting effect and therefore should stabilize it ('the α-effect').[24] Consequently, such an effect contributes to the stabilization of the α-carbanions of α-silylcarboxylic acids, and this could cause them to be more nucleophilic and reactive toward electrophiles. Earlier it was reported that the dianion of trimethylsilylacetic acid is readily alkylated with benzyl, allyl, and primary alkyl halides.[12] Similarly, we have found that the dianion of diphenyl(methyl)silylacetic acid [$Ph_2(Me)SiCH_2CO_2H$] is also readily alkylated to give new α-silylcarboxylic acids in good yields, as illustrated in Scheme 4 and Table 2 (entries 1–5). Alkylation of the dianion of diphenyl(methylsilyl)acetic acid can be representative for other type of α-silylacetic acids (especially for those containing phenylsilyl moieties) and may be utilized for the preparation of new α-silylcarboxylic acid derivatives.



Scheme 4. Alkylation of dianion of $Ph_2(Me)SiCH_2CO_2H$.

Thus, as it is shown in Table 2, the dianion of diphenyl(methylsilyl) acetic acid is readily alkylated with benzyl- and allylbromides to give α-silyl products in excellent yields (entries 1 and 2). Also, good results are obtained with common primary alkyl iodides including less reactive β-branched primary alkyl iodides (Table 2, entries 3 and 4). However, its reaction with isopropyl iodide provides only 40% of the desired alkylated product. In order to improve the yield of this product, an excess of isopropyl iodide (5 equiv) was used to obtain the same product in moderate yield (60%, entry 5).

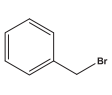
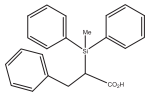
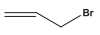
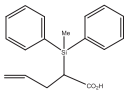
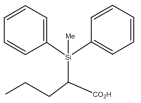
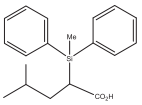
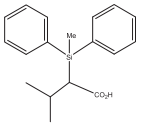
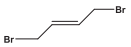
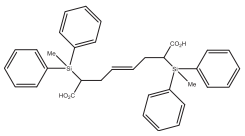
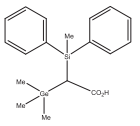
The decrease in the yield of the alkylated product upon using a secondary alkyl iodide is not surprising since it is well established that alkylation of acid dianions with secondary and tertiary halides mostly causes elimination.[25] However, in our case, interestingly, the major product from alkylation of the dianion with a secondary alkyl halide is an α-alkylated product.

Previously, it was shown that the orientation of *O*- and C-silylation of dilithiated carboxylic acids depends on the steric bulk of the alkyl group attached to the α position of the carboxylate anion.[26] Indeed, treatment of the dianion of diphenyl(methyl)silylacetic acid with 2 equiv of trimethylchlorosilane at −78 °C afforded only *O*-silylated product. However, germylation of the same dianion using 2 equiv of trimethylchlorogermane under the same experimental conditions yielded the C-alkylation product in a good isolated yield, as is illustrated in Table 2 (entry 7). This interesting compound is an example of producing new class of α-silyl-α-germylacetic acids.

After the successful preparation of a new generation of α-silylcarboxylic acids by alkylation of its dianion, we have attempted to prepare new α,α′-disilyldicarboxylic acid by the same method. For this purpose (*E*)-1,4-dibromo-2-butene was used as the alkylating agent, as illustrated in Table 2 (entry 6) and in Scheme 5.

After the alkylation and work up procedure, a mixture of two isomers of **19** (**a** and **b**) was obtained in 3/1 ratio, as determined by

Table 2
Synthesis of new α-silylcarboxylic acids

Entry	RX	Product		Yield[a], %
1			(**14**)	90
2			(**15**)	85
3			(**16**)	81
4			(**17**)	72
5[b]			(**18**)	60
6			(**19**)	75[c]
7			(**20**)	87

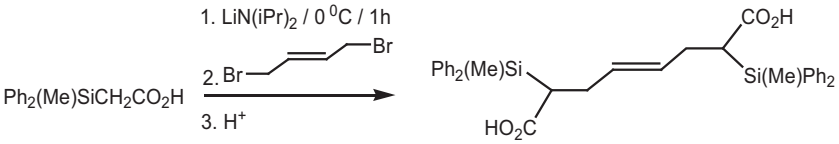
[a] Isolated yield.
[b] An excess of alkyl iodide was used.
[c] This product involves a mixture of two isomers in 3/1 ratio and one of them was characterized by X-ray (vide infra).

^1H and ^{13}C NMR spectroscopy. Both isomers have the same molecular ion mass, as detected by MALDI-TOF measurements. Therefore, it is reasonable to assume that the two isomers are diastereoisomers of the obtained dicarboxylic acid derivative, which contains two chiral centers (however, the possibility that the cis isomer is also formed cannot entirely be ruled out). Recrystallization of **19** from a mixture of hexane/ethyl acetate gave good quality crystals of a major isomer (**19a**) whose structure has been determined by X-ray analysis (vide infra) and ^1H and ^{13}C NMR spectroscopy.

2.1. Molecular structure of compound 19a

Colorless crystals suitable for X-ray crystallography were obtained by dissolving a mixture of the two isomers in ethyl acetate, followed by addition of hexane at ambient temperature and slow evaporation of the solvents. Single crystal X-ray diffraction analysis reveals that the major isomer (**19a**) in the solid-state packs in the monoclinic *P*2/*n* space group with crystal cell parameters: *Z*=4, dc=1.186; *a*=14.302 (15) Å, *b*=14.388 (15) Å, *c*=15.819 (17) Å, *α*=90°, *β*=103.64 (6)°, *γ*=90°, *R*1=0.0574.

Interestingly, the X-ray structure shows that **19a** crystallizes in the unit cell as a mixture of *trans*-enantiomers (*R*,*R*) and (*S*,*S*) interlinked by O–H···O intermolecular hydrogen bonds. The molecular structure of **19a** is shown in Fig. 1 with selected bond lengths and angles given in the figure caption.



Scheme 5. Alkylation of dianion by (*E*)-1,4-dibromo-2-butene.

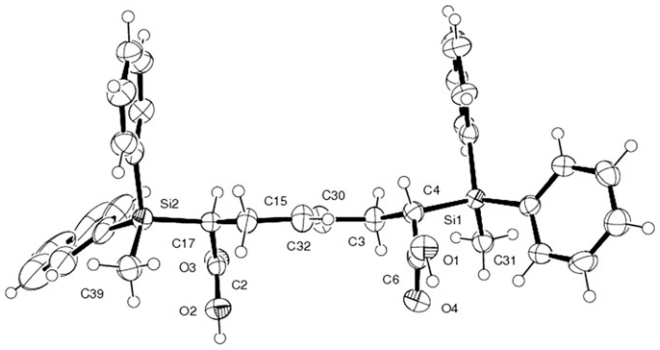


Fig. 1. ORTEP diagram of major isomer **19a**. Selected bond lengths [Å] and bond angels [deg]: C4-Si1 1.933(3); C4-C6 1.500(4); C6-O4 1.247(4); C6-O1 1.317(4); C3-C4 1.538(4); C(3)-C(30) 1.527(5); C30-C32 1.294(5); C32-C30-C3 128.4(3); C30-C3-C4 115.8(3); C6-C4-C3 112.6(3); C6-C4-Si1 111.0(2); C3-C4-Si1 108.7(2); O4-C6-O1 122.1(3); O4-C6-C4 121.9(3); O1-C6-C4 121.9(3).

In summary, we have successfully prepared new α-silylacetic acids in good isolated yields by a convenient and reproducible method. Novel α-alkyl,α-silylcarboxylic acids were prepared by alkylation of the dianions of α-silylacetic acids that should allow the easy way for the synthesis of highly branched α-silylcarboxylic acids. In addition, two new types of α,α′-disilyldicarboxylic acids were synthesized and characterized.

3. Experimental section

3.1. General

Reagents and solvents were used as received from commercial sources (Sigma–Aldrich, BioLab, Gelest (chlorosilanes)). Anhydrous tetrahydrofuran was dried over sodium–benzophenone under nitrogen and fractionally distilled. Diisopropylamine was dried over CaH_2 and fractionally distilled. Chloroacetic acid was crystallized from chloroform and dried over P_2O_5 in a vacuum desiccator. Reactions were conducted under an atmosphere of dry nitrogen in over-dried glassware. All air-sensitive liquids were transferred using standard syringe needle techniques under an atmosphere of argon. NMR spectra ^1H (500.13 MHz), ^{13}C (125.76 MHz), and ^{29}Si (99.36 MHz) were collected using a Bruker Avance DMX-500 MHz or Bruker ARX-200 MHz (for ^1H (200 MHz)) spectrometers. The chemical shifts are given in parts per million relative to the residual proton signal of the solvent ($CDCl_3$) 7.26 ppm (^1H) and $CDCl_3$ 77.0 ppm (^{13}C) and then referenced to $(CH_3)_4Si$ (0.00 ppm); *J* values are given in Hertz. Molecular mass of materials was determined by (HRESI MS) Thermo Scientific LTQ Orbitrap XL ETD equipped with Electrospay Ionization (ESI-MS) and by (MALDI-TOF) Bruker Daltonics (Reflex IV). Mass spectral data were reported in units of mass to charge (*m*/*z*). IR spectra were recorded using Impact 410 spectrometer. Single crystal X-ray diffraction measurements were performed on a Bruker Smart Apex on D8-Goniometer at low temperature (114 K).

3.2. General procedure for the synthesis of α-silylacetic acids

A general procedure for the synthesis of diphenyl(methyl)silylacetic acid (**6**) is representative for all α-silylacetic acids of type $R_1R_2R_3SiCH_2CO_2H$. Diisopropylamine (24.0 mmol, 3.4 mL) and anhydrous tetrahydrofuran (40 mL) were added to an oven-dried round-bottomed flask (250 mL) equipped with a magnetic stirring bar. The mixture was cooled to −78 °C prior to drop-wise addition of *n*-butyllithium 1.6 M (24.0 mmol, 15.0 mL). The mixture was warmed at room temperature for 15 min and cooled again to −78 °C. Trimethylsilylacetate ($CH_3CO_2SiMe_3$) (21.0 mmol, 3.2 mL) was added drop-wise to the cooled solution of LDA over 15 min and the reaction mixture was stirred for 2 h at −78 °C. Then diphenylmethylchlorosilane (24.0 mmol, 5.0 mL) in dry THF (5 mL) was added drop-wise to the solution over 10 min. The reaction mixture was then stirred at −78 °C for two additional hours and allowed to reach room temperature overnight. A solution of brine (30 mL) was added and the reaction mixture was carefully acidified with 1 N HCl to pH=1. The aqueous layer was extracted with diethyl ether (30 mL×3) and the combined organic extracts were washed with water (20 mL×2), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residual product was crystallized from hexane to give *diphenylmethylsilylacetic acid* (**6**) (4.2 g, 78%). Mp: 104–105 °C. NMR and MS spectrums of acids (**1**–**6**) were published in our previous work (see Ref. 15). The above procedure for **6** was also applied to **7**–**13**.

*3.2.1. Dimethyl(chloromethyl)silylacetic acid (**7**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and dimethyl (chloromethyl)chlorosilane (24 mmol, 3.1 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/acetone (9/1–8/2; v/v) that afforded product **7** (2.3 g, 68%) as a white solid. Mp: 42–44 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 0.28 (s, 6H, Si(CH_3)$_2$), 2.06 (s, 2H, SiCH_2-CO_2H), 2.89 (s, 2H, SiCH_2Cl), 10.92 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −4.60 (Si(CH_3)$_2$), 24.30 (SiCH_2CO_2H), 29.21 (SiCH_2Cl), 179.35 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) 5.92. IR (KBr): ν (SiCH_2CO_2H) at 1690 and 3150 cm^{-1}. HRMS (ESI positive mode): *m*/*z* calcd for $C_5H_{11}ClO_2Si$ $[M+Na]^+$: 189.0109; found 189.0109.

*3.2.2. Dimethyl(cyclohexyl)silylacetic acid (**8**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and dimethyl (chloromethyl)chlorosilane (23 mmol, 4.3 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/acetone (9/1–8/2; v/v) that afforded product **8** (2.4 g, 60%) as a white solid. Mp: 52–54 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 6H, Si(CH_3)$_2$), 0.70–0.75 (m, 1H, cyclohexyl), 1.06–1.13 (m, 2H, cyclohexyl), 1.18–1.24 (m, 3H, cyclohexyl), 1.68–1.75 (m, 5H, cyclohexyl), 1.90 (s, 2H, SiCH_2CO_2H), 10.47 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.13 (Si (CH_3)$_2$), 24.13 (SiCH_2CO_2H), 25.29, 26.75, 26.96, 27.81 (Si-cyclohexyl), 180.47 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) 5.41. IR (KBr): ν (SiCH_2CO_2H) at 1686 and 2913 cm^{-1}. HRMS (ESI positive mode): *m*/*z* calcd for $C_{10}H_{20}O_2Si$ $[M+Na]^+$: 223.1130; found 223.1123.

*3.2.3. Dimethyl(benzyl)silylacetic acid (**9**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and dimethyl (benzyl)chlorosilane (23 mmol, 4.5 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/acetone (9/1–8/2; v/v) that afforded product **9** (2.98 g, 72%), as a white solid. Mp:

45–47 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.24 (s, 6H, Si(CH_3)$_2$), 2.03 (s, 2H, SiCH_2CO_2H), 2.34 (s, 2H, SiCH_2Ph), 7.15–7.22 (m, 3H, Ph), 7.32–7.36 (m, 2H, Ph), 10.97 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −3.49 (Si (CH_3)$_2$), 25.09 (SiCH_2Ph), 25.14 (SiCH_2CO_2H), 124.45, 128.23, 128.38, 138.66 (Ph), 179.53 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) 4.55. IR (KBr): ν (SiCH_2CO_2H) at 1691 and 2967 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{11}H_{16}O_2Si$ [M+Na]$^+$: 231.0812; found 231.0804.

*3.2.4. Methyl(phenyl)vinylsilylacetic acid (**10**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and methyl (phenyl)vinylchlorosilane (23 mmol, 4.1 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/acetone (9/1; v/v) that afforded product **10** (3.05 g, 74%), as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.54 (s, 3H, SiCH_3), 2.23 (d, ^2J=16.0 Hz, 1H, SiCH_2CO_2H), 2.26 (d, ^2J=16.0 Hz, 1H, SiCH_2CO_2H), 5.87 (dd, ^3J=3.5 Hz, ^2J=20.0 Hz, 1H, SiCH=CH_2), 6.18 (dd, ^3J=3.5 Hz, ^2J=14.5 Hz, 1H, SiCH=CH_2), 6.34 (dd, ^2J=14.5 Hz, ^2J=20.0 Hz, 1H, SiCH=CH_2), 7.39–7.42 (m, 3H, Ph), 7.57–7.58 (m, 2H, Ph), 10.91 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −4.67 (SiCH_3), 25.28 (SiCH_2CO_2H), 128.04, 129.85, 134.08, 134.22, 134.73, 135.33 (Ph+Vinyl), 179.38 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −11.07. IR (neat): ν (SiCH_2CO_2H) at 1696 and 3053 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{11}H_{14}O_2Si$ [M+Na]$^+$: 229.0655; found 229.0648.

*3.2.5. Diphenyl(vinyl)silylacetic acid (**11**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and diphenyl(vinyl)chlorosilane (23 mmol, 5.1 mL). After standard work up procedure the residual product was crystallized from hexane to give product **11** (4.3 g, 80%) as a white solid. Mp: 95–97 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (s, 2H, SiCH_2CO_2H), 5.80 (dd, ^3J=3.5 Hz, ^2J=20 Hz, 1H, SiCH=CH_2), 6.24 (dd, ^3J=3.5 Hz, ^2J=14.5 Hz, 1H, SiCH=CH_2), 6.48 (dd, ^2J=14.5 Hz, ^2J=20.0 Hz, 1H, SiCH=CH_2), 7.30–7.53 (m, 6H, 2Ph), 7.54–7.55 (m, 4H, 2Ph), 10.75 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) 24.18 (SiCH_2CO_2H), 127.93, 129.95, 132.34, 132.58, 135.15, 137.35 (Ph+vinyl), 178.88 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −16.11. IR (KBr): ν (SiCH_2CO_2H) at 1696 and 2957 cm^{-1}. MS (MALDI-TOF): m/z calcd for $C_{16}H_{16}O_2Si$ [M+Na$^+$]: 291.082; found 291.750; [M+K$^+$]: 307.056; found 307.671.

*3.2.6. Trivinylsilylacetic acid (**12**).* Trimethylsilylacetate (20 mmol, 3.0 mL) was reacted with LDA (24 mmol) and trivinylchlorosilane (23 mmol, 3.6 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/acetone (9/1; v/v) that afforded product **12** (2.39 g, 71%), as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 2H, SiCH_2CO_2H), 5.81–5.94 (m, 3H, Si(CH=CH_2)$_3$), 6.13–6.19 (m, 6H, Si(CH=CH_2)$_3$), 10.36 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) 23.98 (SiCH_2CO_2H), 132.16 (Si(CH=CH_2)$_3$), 136.28 (Si(CH=CH_2)$_3$), 178.86 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −21.76. IR (neat): ν (SiCH_2CO_2H) at 1690 and 2950 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_8H_{12}O_2Si$ [M+Na]$^+$: 191.0499; found 191.0497.

*3.2.7. 1,3-Bis-(1,3-diphenyl-1,3-dimethyl)siloxanedioic acid (**13**).* Trimethylsilylacetate (16 mmol, 2.4 mL) in dry THF (30 mL) was reacted with LDA (18 mmol), and 1,3-dichloro-1,3-diphenyl-1,3-dimethyl-disiloxane (7.3 mmol, 2.1 mL), in dry THF (5 mL), added drop-wise to a cooled solution of enolate. After standard work up procedure the crude product was purified by washing it in the solution of hexane/ethyl acetate (95/5; v/v). The pure product precipitated as small white crystals, which were collected by vacuum filtration and dried to give product **13** (0.82 g, 30%), as a white solid. Mp: 117–120 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 2.13 (s, 6H, 2SiCH_3), 2.20 (d, 2H, ^2J=12.0 Hz, SiCH_2CO_2H), 2.26 (d, ^2J=12.0 Hz, 2H, SiCH_2CO_2H), 7.33–7.40 (m, 6H, 2Ph), 7.58–7.60 (m, 4H, 2Ph), 10.96 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, CD_3OD) −0.71 (SiCH_3), 28.72 (SiCH_2CO_2H), 128.93, 131.11, 134.42, 137.58 (Ph), 175.96 (SiCH_2CO_2H). ^{29}Si NMR (100 MHz, CD_3OD) −4.94. IR (KBr): ν (SiCH_2CO_2H) at 1690 and 2972 cm^{-1}, (SiOSi) 1090 cm^{-1}. MS (MALDI-TOF): m/z calcd for $C_{18}H_{22}O_5Si_2$ [M+Na$^+$]: 397.090; found 397.061; [M+K$^+$]; 413.064, found 413.027.

3.3. General procedure for the synthesis of alkylated α-silylcarboxylic acids

General procedure for the synthesis of *α-diphenyl(methyl)silylhydrocynnamic acid* (**14**) is representative for all α-silylcarboxylic acids of type Ph_2(Me)SiCH(R)CO_2H.

Diisopropylamine (14.8 mmol, 2.1 mL) and anhydrous tetrahydrofuran (30 mL) were added to an oven-dried round-bottomed flask (100 mL) equipped with a magnetic stirring bar. The mixture was cooled to −78 °C prior to drop-wise addition of *n*-butyllithium 1.6 M (14.8 mmol, 9.3 mL). The mixture was warmed to room temperature for 15 min and cooled to 0 °C. Diphenyl(methyl)silylacetic acid (6.75 mmol, 1.73 g) in dry THF (5 mL) was added drop-wise over 10 min to the LDA solution and the mixture was stirred for 1.5 h at the same temperature to complete the formation of the dianion. Then benzylbromide (7.42 mmol, 0.88 mL) was added drop-wise over 2 min to the dianion solution and the mixture was stirred overnight at room temperature. The reaction mixture was diluted with hexane (20 mL) and the organic phase washed twice with a solution of brine (30 mL×2). The aqueous phase was carefully acidified with 1 N HCl to pH=2 and then extracted with diethyl ether (20 mL×3). The combined organic extracts were washed with water (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residual product was crystallized from hexane to give *α-diphenyl(methyl)silylhydrocynnamic acid* (**14**) (2.1 g, 90%), as a white solid. Mp: 119–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (s, 3H, SiCH_3), 2.76 (dd, ^2J=14.5 Hz, ^3J=2.5 Hz, 1H, SiCHCH_2), 2.93 (dd, ^2J=12.0 Hz, ^3J=2.5 Hz, 1H, SiCHCH_2), 3.11 (dd, 1H, ^2J=12.0 , 14.5 Hz, 1H, SiCHCH_2), 7.09–7.62 (m, 15H, 3Ph), 11.35 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.25 (SiCH_3), 33.08 (PhCH_2Si), 38.32 (Si$CHCO_2$H), 126.14, 127.98, 128.06, 128.39, 129.87, 129.93, 133.49, 133.91, 134.74, 134.80, 134.92, 141.53 (2Ph), 179.50(CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −5.29. IR (KBr): ν (SiCHCO_2H) at 1683 and 3055 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{22}H_{22}O_2Si$ [M+Na]$^+$: 369.1287; found 369.1275. The above procedure for **14** was also applied to **15**–**20**.

*3.3.1. α-Diphenyl(methyl)silyl-4-pentenoic acid (**15**).* Diphenyl (methyl)silylacetic acid (6.98 mmol, 1.79 g) was reacted with LDA (15.4 mmol) and allylbromide (7.68 mmol, 0.66 mL). After standard work up procedure the crude product was crystallized from hexane to give acid (**15**) (1.76 g, 85%) as a white solid. Mp: 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68 (s, 3H, SiCH_3), 2.16–2.21 (m, 1H, CH_2=CHCH_2CH), 2.51–2.59 (m, 1H, CH_2=CHCH_2CH), 2.71 (dd, ^3J=7.5 , 9.0 Hz, 1H, CH_2=CHCH_2CH), 4.97–5.04 (m, 2H, CH_2=CHCH_2), 5.75–5.83 (m, 1H, CH_2=CHCH_2), 7.26–7.45 (m, 10H, 2Ph), 11.59 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.26 (SiCH_3), 31.29 (CH_2=CHCH_2CH), 35.85 (CH_2=CHCH_2CH), 115.27 (CH_2=CH), 127.94, 127.99, 129.84, 133.57, 133.92, 134.43, 134.72, 134.88, 137.27 (2Ph+CH_2=CH), 180.53 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −5.29. IR (KBr): ν (SiCHCO_2H) at 1679 and 2962 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{18}H_{20}O_2Si$ [M+Na]$^+$: 319.1130; found 319.1120.

*3.3.2. α-Diphenyl(methyl)silylvaleric acid (**16**).* Diphenyl(methyl) silylacetic acid (4.36 mmol, 1.12 g) was reacted with LDA (9.6 mmol) and propyliodide (4.80 mmol, 0.47 mL). After standard work up procedure the crude product was crystallized from

hexane to give acid (**16**) (1.05 g, 81%), as a white solid. Mp: 82–83 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.67 (s, 3H, SiCH_3), 0.85 (t, ^3J=7.5 Hz, 3H, $CH_2CH_2CH_3$) 1.23–1.30 (m, 1H, $CHCH_2CH_2CH_3$), 1.37–1.47 (m, 2H, $CHCH_2CH_2CH_3$), 1.81–1.88 (m, 1H, $CHCH_2CH_2CH_3$), 2.60 (dd, ^3J=12.0 , 11.5 Hz, $CHCH_2CH_2CH_3$), 7.26–7.42 (m, 6H, 2Ph), 7.53–7.57 (m, 4H, 2Ph), 11,11 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.34 (SiCH_3), 13.61 (CH_2CH_3), 23.54 (CH_2CH_3), 29.56 ($CH_2CH_2CH_3$), 36.17 ($CHCO_2H$), 127.86, 127.93, 129.70, 129.74, 134.01, 134.35, 134.73, 134.88 (2Ph), 180.86 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −5.76. IR (KBr): ν (SiCHCO_2H) at 1667 and 2975 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{18}H_{22}O_2Si$ $[M+Na]^+$: 321.1287; found 321.1275.

*3.3.3. α-Diphenyl(methyl)silyl-4-methylvaleric acid (**17**).* Diphenyl (methyl)silylacetic acid (4.98 mmol, 1.28 g) was reacted with LDA (11.0 mmol) and 1-iodo-2-methylpropane (5.48 mmol, 0.63 mL). After standard work up procedure the crude product was crystallized from hexane to give acid (**17**) (1.12 g, 72%), as a white solid. Mp: 84–86 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.06 (s, 3H, SiCH_3), 0.25 (d, ^3J=7.0 Hz, 3H, $CH(CH_3)_2$), 0.26 (d, ^3J=7.0 Hz, 3H, $CH(CH_3)_2$), 0.62–0.67 (m, 1H, $CH_2CH(CH_3)_2$), 1.04–1.08 (m, 1H, $CH_2CH(CH_3)_2$), 1.36–1.43 (m, 1H, $CH_2CH(CH_3)_2$), 2.28 (dd, ^3J=13.0 , 13.0 Hz, 1H, $CHCO_2H$), 7.35–7.45 (m, 6H, 2Ph), 7.56–7.61 (m, 4H, 2Ph), 11.05 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.39 (SiCH_3), 21.19 ($CH(CH_3)_2$), 22.99 ($CH(CH_3)_2$), 28.60 ($CH_2CH(CH_3)_2$), 34.36 ($CH_2CH(CH_3)_2$), 36.19 ($CHCO_2H$), 127.85, 127.94, 129.69, 129.75, 133.91, 134.35, 134.72, 134.88 (2Ph), 181.52 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −5.15. IR (KBr): ν (SiCHCO_2H) at 1676 and 2957 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{19}H_{24}O_2Si$ $[M+Na]^+$: 335.1443; found 335.1434.

*3.3.4. α-Diphenyl(methyl)silyl-3-methyl-butanoic acid (**18**).* Diphenyl-(methyl)silylacetic acid (2.14 mmol, 0.55 g) was reacted with LDA (4.7 mmol) and excess of 2-iodo-propane (10.7 mmol, 1.1 mL). After standard work up procedure the crude product was purified by a silica gel flash column chromatography by eluting with hexane/ethyl acetate (7/3; v/v) that afforded product **18** (0.64 g, 60%), as a white solid. Mp: 130–131 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73 (s, 3H, SiCH_3), 0.83 (d, ^3J=6.6 Hz, 3H, $CH(CH_3)_2$), 1.02 (d, ^3J=6.4 Hz, 3H, $CH(CH_3)_2$), 2.14–2.25 (m, 1H, $CH(CH_3)_2$), 2.40 (d, ^3J=10.2 Hz, 1H, SiCH), 7.33–7.40 (m, 6H, 2Ph), 7.58–7.63 (m, 4H, 2Ph), 10.94 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$), −4.42 (SiCH_3), 22.95 ($CH(CH_3)_2$), 23.45 ($CH(CH_3)_2$), 28.51 ($CH(CH_3)_2$), 45.02 (SiCH), 127.76, 127.80, 127.85, 129.55, 134.61, 134.71, 134.78, 134.82 (2Ph), 181.55 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) -11.35. IR (KBr): ν (SiCHCO_2H) at 1678 and 2955 cm^{-1}. MS (MALDI-TOF): m/z calcd for $C_{18}H_{22}O_5Si_2$ [M+Na]: 321.129; found 321.184.

*3.3.5. (E)-2R(S),7R(S)-Bis(diphenyl(methyl)silyl)oct-4-enedioic acid (**19a**).* Diphenyl(methyl)silylacetic acid (2.83 mmol, 0.73 g) was reacted with LDA (6.23 mmol) in dry THF (20 mL) and *trans*-1,4-dibromo-2-butene (1.32 mmol, 0.28 g) in dry THF (3 mL), added drop-wise over 5 min to a cool solution of dianion. After standard work up procedure the crude product was washed with warm hexane (20 mL), then collected by vacuum filtration and dried to give a mixture of two isomers in 3/1 ratio (0.55 g, 75%), as determined by ^{1}H NMR. Recrystallization of this compound from a mixture of hexane/ethyl acetate gave a good quality of colorless crystals of major isomer **19a**. Mp: 184–185 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60 (s, 6H, SiCH_3), 1.97 (d, ^3J=13.5 Hz, 2H, CH2CH), 2.26–2.31 (m, 2H, CH_2CH), 2.65 (dd, ^2J=2.0 Hz, ^3J=12.5 Hz, 2H, CH_2CH), 5.31 (t, ^3J=3.0 Hz, 2H, CH=CH), 7.26–7.51 (m, 20H, 4Ph), 10.57 (br, 2H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −4.91 (SiCH_3), 30.00 (CH_2CH), 36.07(CH_2CH), 127.94, 127.94, 129.74, 129.78, 129.94, 133.68, 134.14, 134.77, 134.98 (2Ph, CH=CH), 180.80 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −10.29. IR (KBr): ν (SiCHCO_2H) at 1681 and 3055 cm^{-1}. MS (MALDI-TOF): m/z calcd for $C_{34}H_{36}O_4Si_2$ $[M-H+Na]^+$: 586.197; found 586.529; $[M-H+K^+]$: 602.171, found 602.479. For isomer **19b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (s, 6H, SiCH_3), 2.03–2.08 (m, 2H, CH_2CH, overlapped with **19a**), 2.34–2.40 (m, 2H, CH_2CH, overlapped with **19a**), 2.67 (dd, ^2J=2.0 Hz, ^3J=10.0 Hz, 2H, CH_2CH), 5.48 (t, ^3J=3.0 Hz, 2H, CH=CH), 7.26–7.51 (m, 20H, 4Ph, overlapped with **19a**), 10.57 (br, 2H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −5.29 (SiCH_3), 29.41 (CH_2CH), 36.40 (CH_2CH), 127.90, 129.72, 129.94, 129.91, 133.62, 133.74, 134.08, 134.72, 134.89, 134.92 (2Ph, CH=CH), 180.80 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −10.29.

*3.3.6. α-Trimethylgermyl-α-diphenyl(methyl)silylacetic acid (**20**).* A procedure similar for that for **14** was used with the following modifications. Diphenyl(methyl)silylacetic acid (2.02 mmol, 0.52 g) was reacted with LDA (4.44 mmol) in dry THF (20 mL). The generated dianion was cooled to −78 °C. Then trimethylchlorogermane (4.44 mmol, 0.55 mL) was added drop-wise to the solution over 10 min. The reaction mixture was stirred at −78 °C for 1.5 h and allowed to reach room temperature overnight. A solution of brine (30 mL) was added and the reaction mixture was carefully hydrolyzed with 1 N HCl to pH=1. The aqueous layer was extracted with diethyl ether (30 mL×3) and the combined organic extracts were washed with water (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residual product was crystallized from hexane to give acid (**20**) (0.67 g, 87%). Mp: 68–70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9H, Ge(CH_3)$_3$), 0.77 (s, 3H, SiCH_3), 2.27 (s, 1H, SiCHGe), 7.31–7.60 (m, 10H, 2Ph), 9.47 (br, 1H, CO_2H). ^{13}C NMR (125 MHz, $CDCl_3$) −3.51(SiCH_3), −0.44 (Ge(CH_3)$_3$), 27.84 (SiCHGe), 127.74, 127.86, 129.30, 129.52, 134.49, 134.59, 136.06, 136.56 (2Ph), 181.23 (CO_2H). ^{29}Si NMR (100 MHz, $CDCl_3$) −13.78. IR (KBr): ν (Si(Ge) $CHCO_2H$) at 1653 and 3045 cm^{-1}. HRMS (ESI positive mode): m/z calcd for $C_{18}H_{24}GeO_2Si$ $[M+Na]^+$: 395.0660; found 395.0648.

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Supplementary data

CIF files giving crystallographic data including a full list of interatomic bond lengths and angles for the reported isomer **19a** are deposited at CCDC 796633. Copies of ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra of compounds **7**–**20** are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.12.020. These data include MOL files and InChIKeys of the most important compounds described in this article.

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