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Article

Aerobic Co- / N-hydroxysuccinimide- catalyzed oxidation of p-tolylsiloxanes to p-carboxyphenylsiloxanes: synthesis of functionalized siloxanes as promising building blocks for siloxane-based materials

Irina K. Goncharova, Kseniia P. Silaeva, Ashot V. Arzumanyan, Anton A. Anisimov, Sergey A. Milenin, Roman A. Novikov, Pavel N. Solyev, Yaroslav V. Tkachev, Alexander D. Volodin, Alexander A. Korlyukov, and Aziz M. Muzafarov

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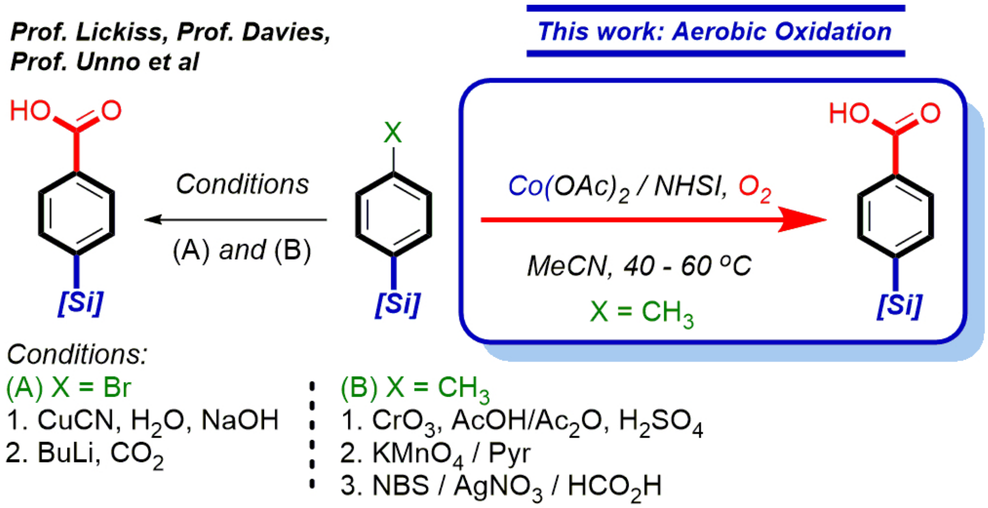

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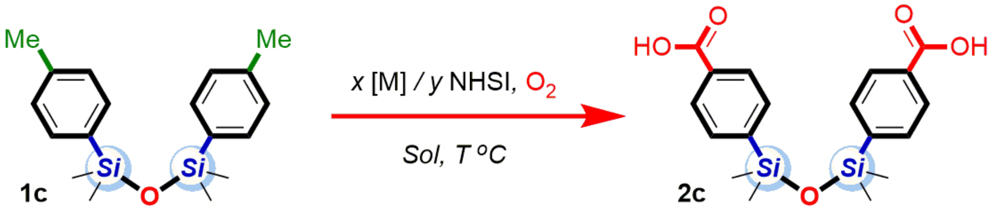

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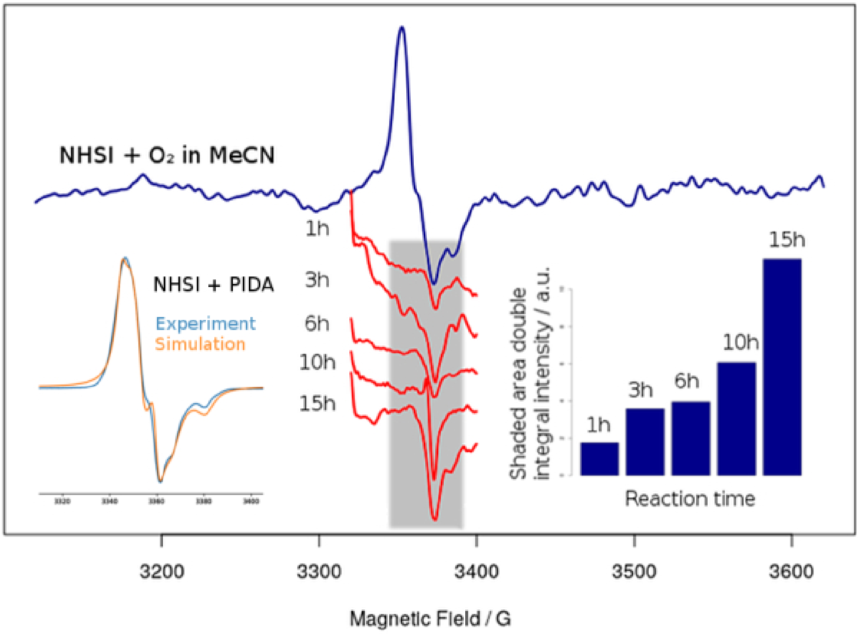

Figure 1

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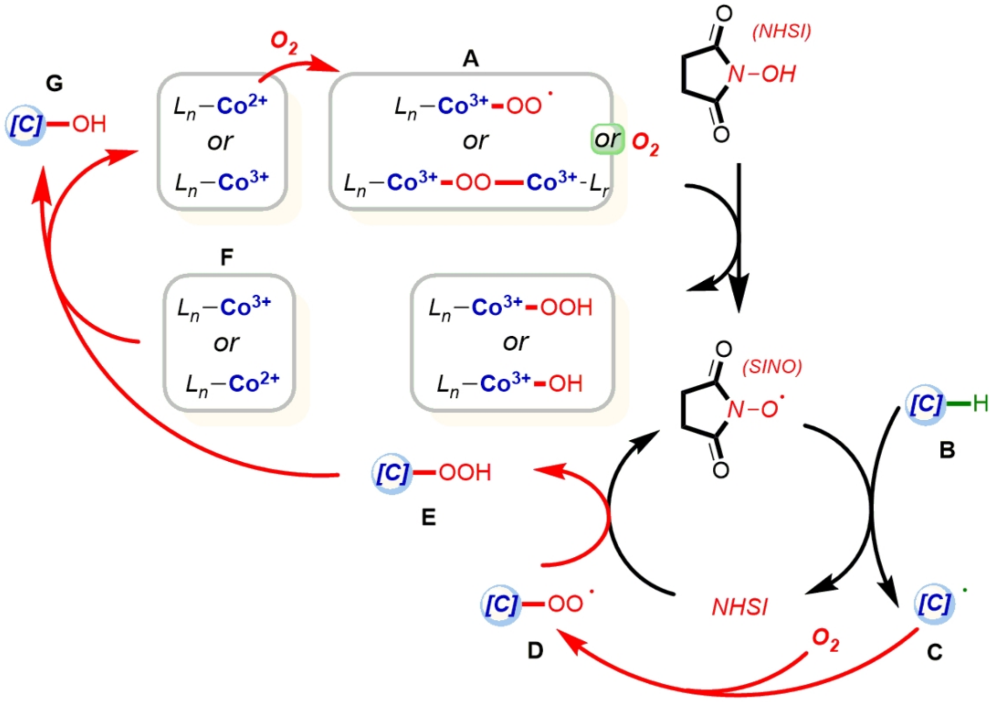

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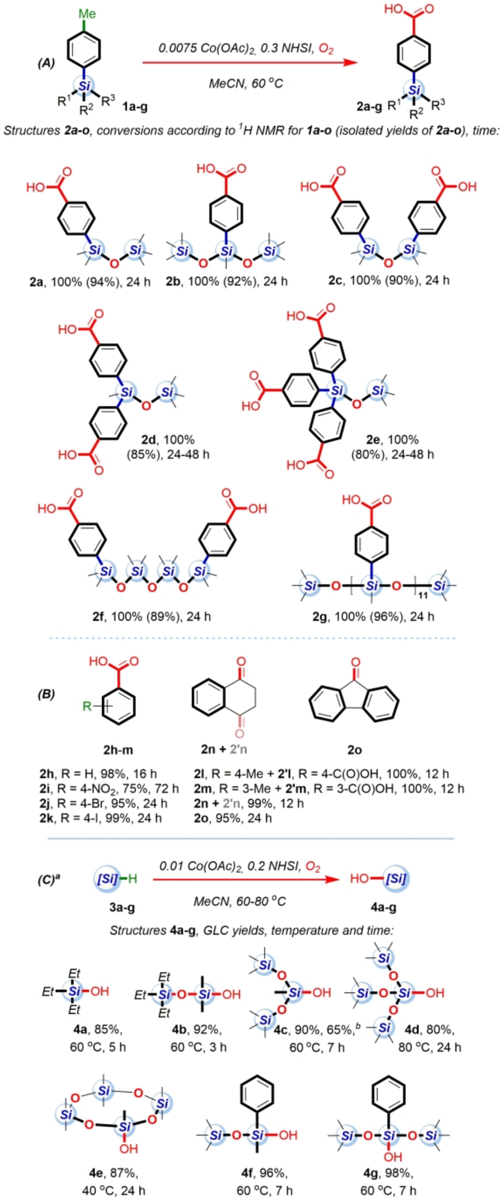

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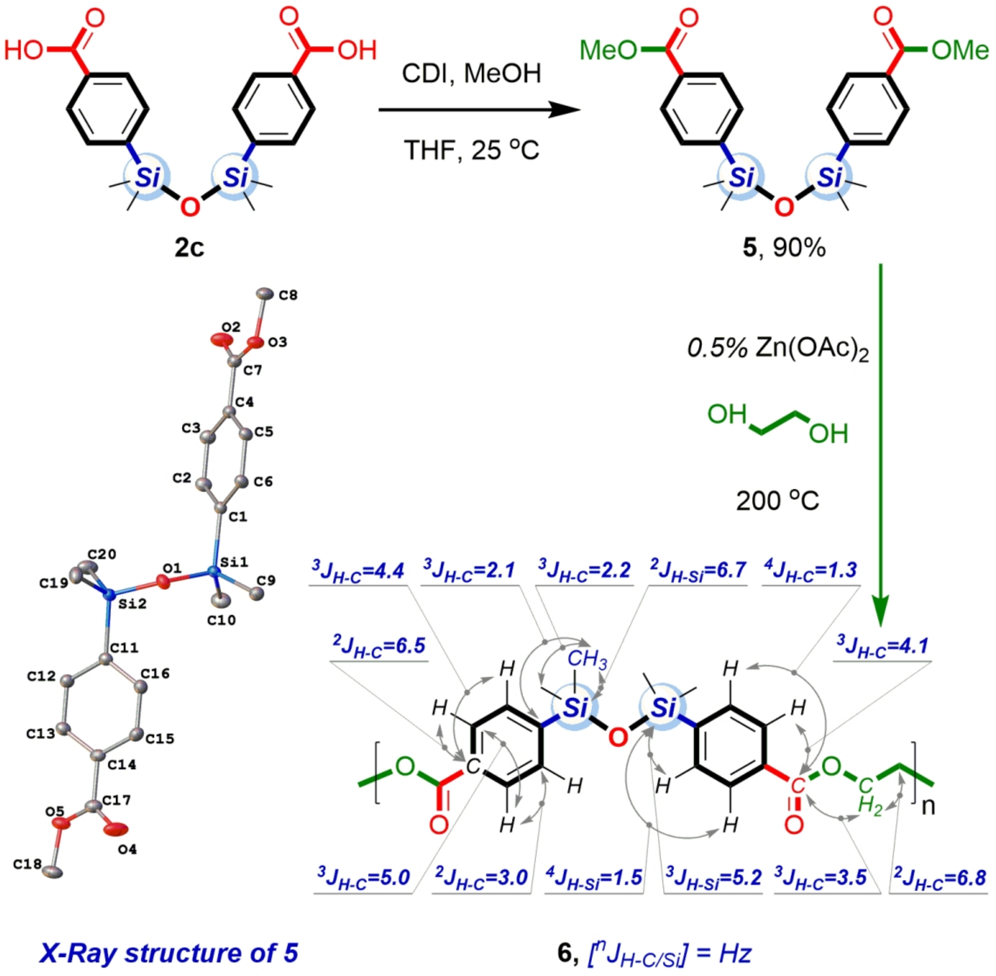

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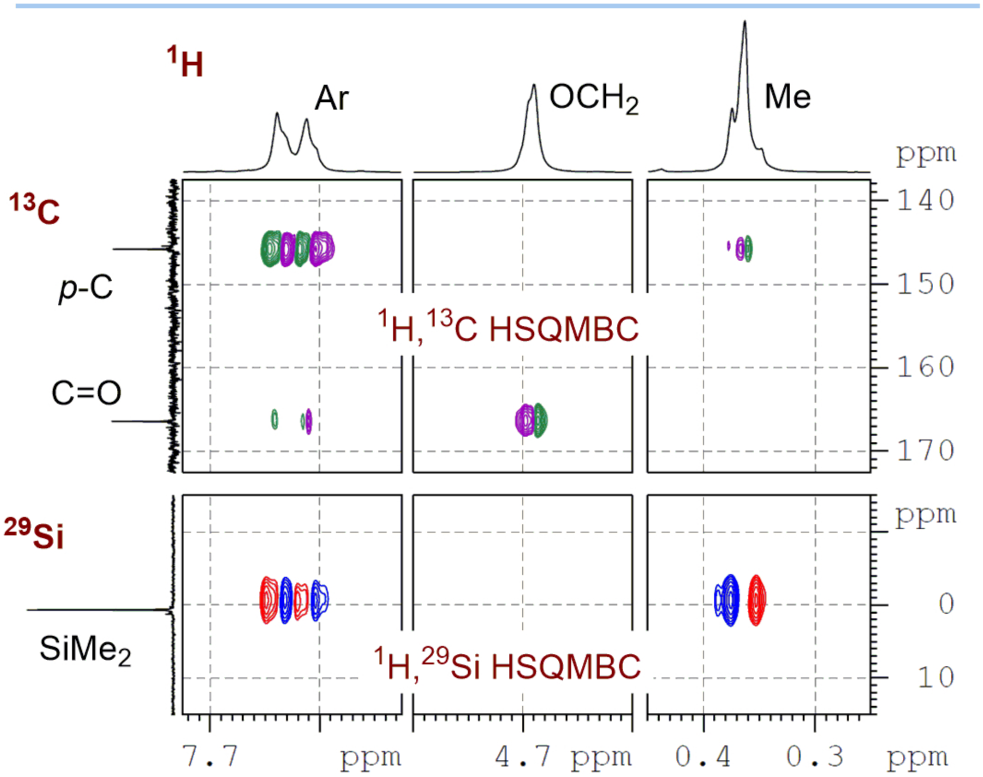

Scheme 4_bottom

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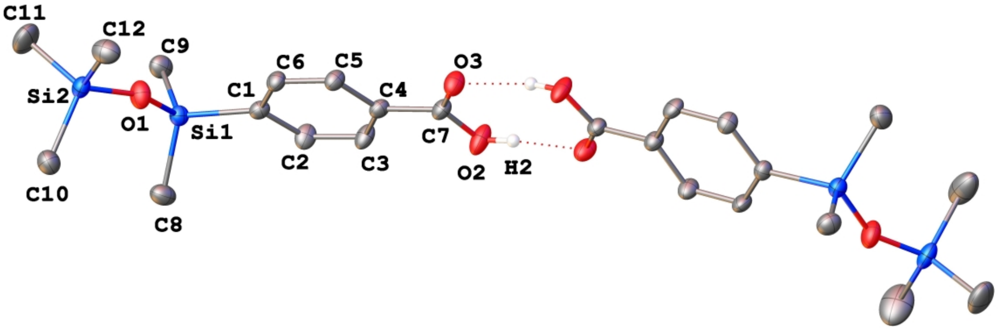

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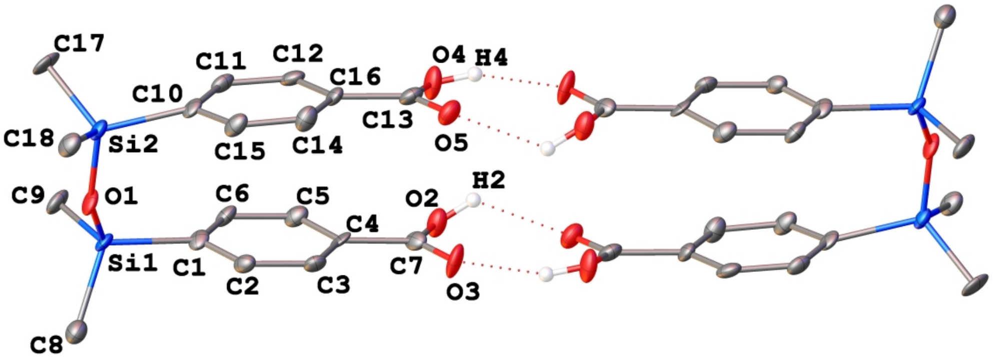
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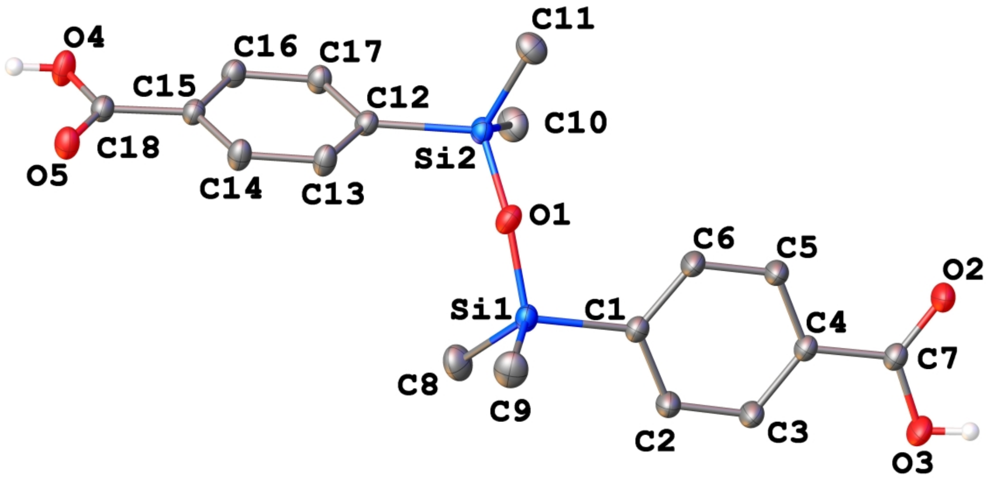
2'c_dimer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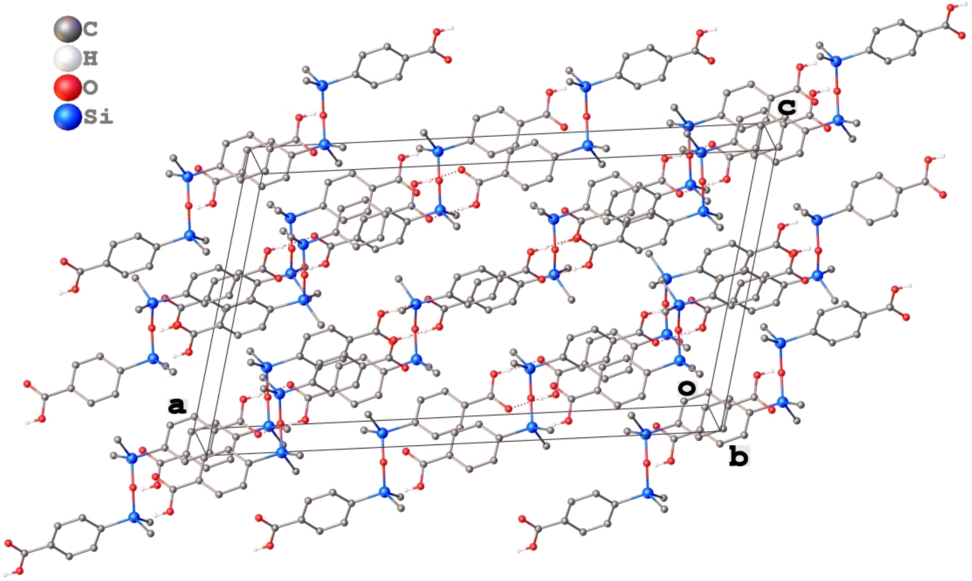

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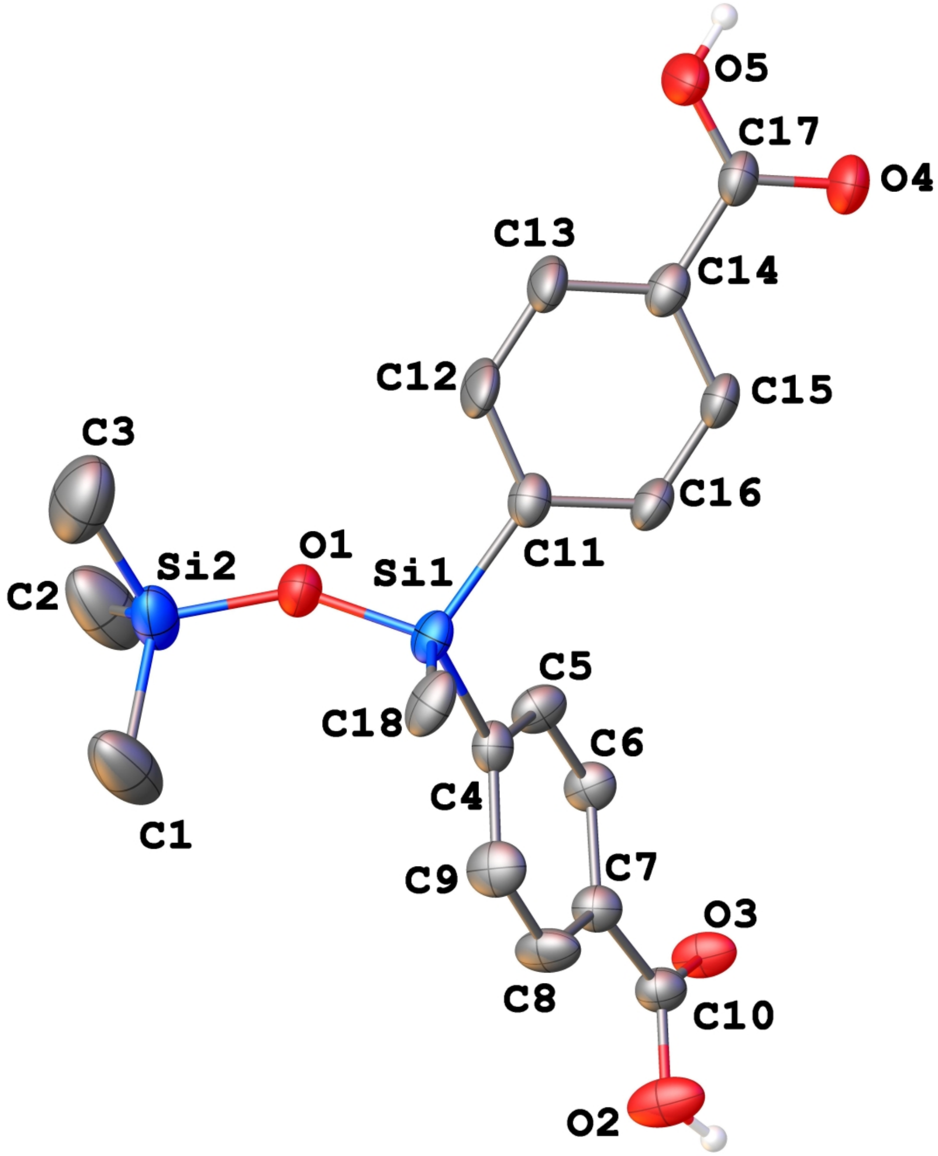
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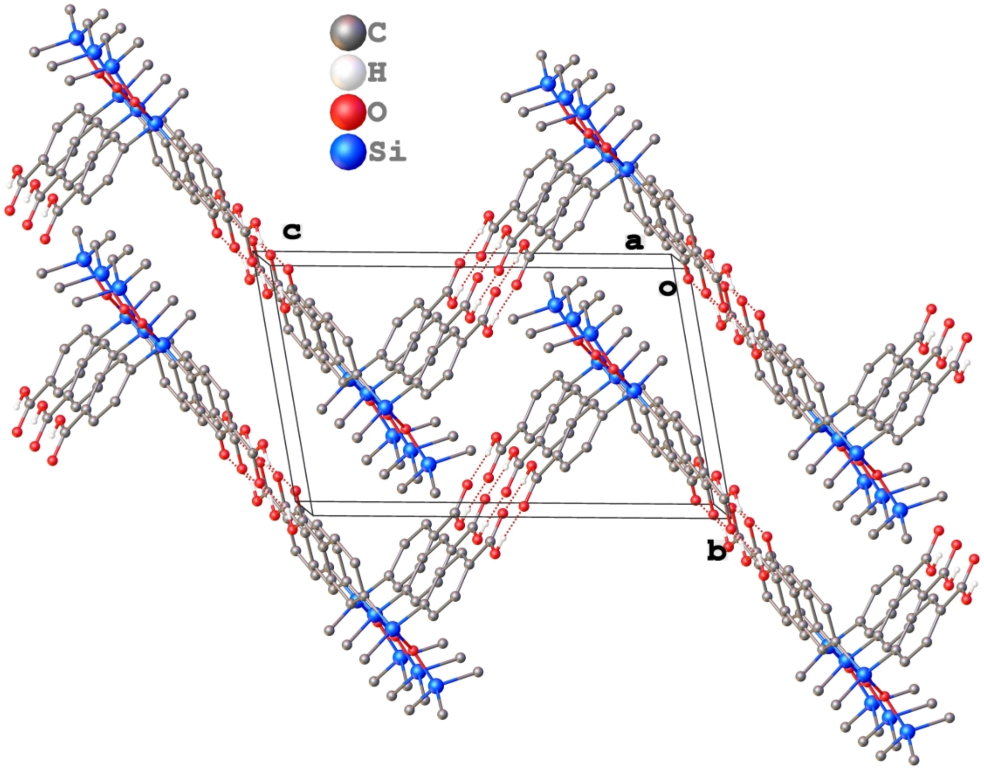

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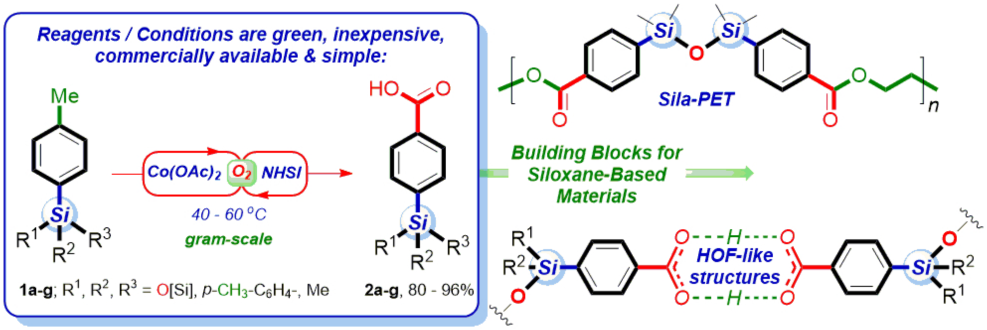

Graph. Abstr.

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Aerobic Co- / N-hydroxysuccinimide- catalyzed oxidation of *p*-tolylsiloxanes to *p*-carboxyphenylsiloxanes: synthesis of functionalized siloxanes as promising building blocks for siloxane-based materials.

Irina K. Goncharova,[a] Kseniia P. Silaeva,[a,b] Ashot V. Arzumanyan,*[a] Anton A. Anisimov,[a] Sergey A. Milenin,[c] Roman A. Novikov,[d,f] Pavel N. Solyev,[d] Yaroslav V. Tkachev,[d] Alexander D. Volodin,[a] Alexander A. Korlyukov[a,e] and Aziz M. Muzafarov[a,c]

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ABSTRACT: Synthesis of organosilicon products with a “polar” functional group within organic substituents is one of the most fundamentally and practically important challenges in today’s chemistry of silicones. In our study we suggest a solution to this problem, *viz.*, a high-efficiency preparative method based on aerobic Co / N-hydroxysuccinimide (NHSI) catalyzed oxidation of *p*-tolylsiloxanes to *p*-carboxyphenylsiloxanes. This approach is based on “green”, commercially available, simple and inexpensive reagents and employs mild reaction conditions: $Co(OAc)_2$ / NHSI catalytic system, O_2 as the oxidant, process temperature from 40 to 60 °C, atmospheric pressure. This reaction is a general and allows for synthesizing both mono- and di-, tri-, and poly(*p*-carboxyphenyl)siloxanes with *p*-carboxyphenyl groups at *1,1*-, *1,3*-, *1,5*- and *1,1,1*-positions. All the products were obtained and isolated in gram amounts (up to 5 g) and in high yields (80 – 96%), and characterized by NMR, ESI-HRMS, GPC, IR and X-Ray data: *p*-carboxyphenylsiloxanes in crystalline state form HOF-like structures. Furthermore, it was shown that the suggested method is applicable for the oxidation of organic alkylarene derivatives ($Ar–CH_3$, $Ar–CH_2–R$) to the corresponding acids and ketones (Ar–C(O)OH and Ar–C(O)–R), as well as hydride silanes ([Si]–H) to silanols ([Si]–OH). The possibility of synthesizing monomeric (methyl) and polymeric (siloxane-containing PET analogue, Sila-PET) esters based on *1,3*-bis(*p*-carboxyphenyl)disiloxane was studied. These processes occur with retention of the organosiloxane frame and allow one to obtain the corresponding products in 90 and 99% yields.

INTRODUCTION

Organosilicon compounds, and especially materials based thereon, *i.e.*, silicones (siloxanes), are among the most popular products that find use in the most important fields of today’s science, technology, medicine, aviation, aerospace industry and construction. This is due to the unique spectrum of the physicochemical properties of siloxanes: low glass transition point and high thermal stability (wide range of working temperatures), high hydrophobicity, gas permeability, biocompatibility, radiation stability, low dielectric constant, etc. [1]

The possibility of synthesizing hybrid and composite materials based on siloxanes with integration of the characteristics mentioned above allowed unique materials to be created. However, the potential of their application has not been revealed completely to date and continues to attract special attention of chemists and material scientists. This is due to one of the central problems of the modern chemistry of organosiloxanes, namely, the preparation of organosilicon products with a “polar” (–C(O)OH, –OH, $–NH_2$, etc.) functional group in an organic substituent.

The fact is that incorporation of a “polar” function into organosilicon compounds opens quite unique opportunities for their subsequent modification and preparation of new copolymers, [2] MOFs,[3] HOFs,[4] etc. In addition, modification by incorporation of polar groups would also allow other problems to be solved, namely, the low mechanical strength and “incompatibility” of silicones with organic polymers (polyesters, polyamides, etc.).[5]

Moreover, functionalized organosilicon monomers are promising building blocks in organic synthesis[6] where a new C–Hal, C–O, C–N or C–C bonds are to be created (Hiyama, Hiyama-Denmark couplings, etc., which occur through cleavage of a Si–C-bond).[7]

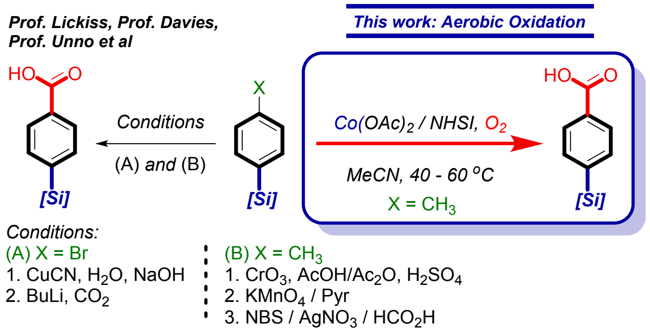
To date, only a few successful examples of incorporating “polar” functional groups into an organic substituent in siloxanes have been reported. On the one hand, these examples confirm the possibility of such a synthesis, but, on the other hand, they show the limitations of the real synthetic methods aimed at solving this problem. [8]

Using classical methods for synthesizing organosilicon monomers and subsequently, polymers based thereon do not allow one to obtain functionalized organosilicon substrates,[9,10] with rare exceptions.[11] As a rule, these methods are either suitable just for a narrow range of substrates, or being excessively time-consuming, require multiple stages involving the “attaching/removal” of protective groups, and present other disadvantages.

However, it might seem that “polar” functional groups can be easily incorporated into finished organosilicon products. Despite appearing to be simple, this problem has not been solved so far, except in rare cases.[12] The classic methods for the incorporation of functional groups into an organic substituent used in organic chemistry prove to be inefficient for organosilicon substrates due to relatively harsh reaction conditions where these substrates decompose with cleavage of Si–O, Si–Cl, Si–N and Si–C bonds to give hardly separable product mixtures, with ultimately low yields of the target product.

The most promising results were obtained in syntheses of such functionalized organosilicon compounds as *p*-carboxyphenylsiloxanes using following main approaches: (A) modification of *p*-bromophenylsiloxanes (Prof Davies, Prof. Lickiss et al);[12c,13] (B) oxidation of *p*-tolylsiloxanes (Prof. Unno et al; Scheme 1).[12a,14]

Scheme 1. The main approaches to the synthesis of *p*-carboxyphenylsiloxanes



These studies contributed considerably to the development of methods for the synthesis of *p*-carboxyphenylsiloxanes and confirmed the potential possibility of their synthesis and subsequent use in the design of new materials based on organosilicon building blocks: HOFs, MOFs, etc.[12c,13]

However, synthetic techniques presented in these works generally require the use of excess amounts of rather expensive and toxic reagents (these methods have not been implemented in a catalytic variant); or rather complex and time-consuming experimental techniques and harsh reaction conditions that have a degrading effect on the organosilicon core (using oxidants, acids, bases, etc.). All these factors generally impose restrictions on the synthetic approaches.

In one of our previous studies, we made an attempt to improve the conditions for synthesizing *p*-carboxyphenylsiloxanes using the $MnCl_2$/*t*BuOOH oxidizing system. It showed that this transformation is possible in the [M]-catalyzed version, though it was not very successful.[14 d]

Thus, the problem of development of new highly efficient methods for synthesizing *p*-carboxyphenylsiloxanes based on “green”, simple and available reagents/conditions[15] remains unresolved to date.

In recent years there have been an increasing number of publications on the oxidation of organic compounds involving molecular oxygen as a “green”, simple and available oxidant that allows one to obtain valuable products widely used in science, technology and medicine. Furthermore, a number of industrially important processes are based on aerobic oxidation: production of K/A oil, benzoic acid, terephthalic acid, phenol and acetone, Waker process, etc.[16] However, the processes indicated above generally occur with low selectivity and under rather drastic conditions (elevated temperature, high pressure, etc.).

Still, the use of the [M]-/Organo-catalyst combination allowed to solve these problems, *i.e.*, considerably soften the reaction conditions and achieve high regio- and chemoselectivity, in the aerobic liquid-phase oxidation of the C–H and Si–H groups.[17] In fact, this approach was utilized to implement the production of adamantanediol and –triol that are used as components of photoresist polymer materials. [17a,b] Moreover, we have shown in our recent study that it is principally possible to perform the aerobic M-/Organo-catalyzed oxidation of a Si–H group to a Si–OH group with retention of the organosiloxane core. [17g]

Thus, the purpose of this study was to develop a method of aerobic [M]-/Organo-catalyzed oxidation of *p*-tolylsiloxanes to *p*-carboxyphenylsiloxanes (Scheme 1).

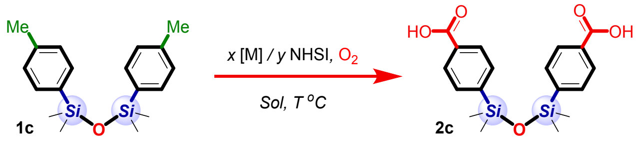
RESULTS AND DISCUSSION

At the first stage of our study, we performed a detailed optimization of the conditions of aerobic oxidation of *p*-tolylsiloxane **1c** to *p*-carboxyphenylsiloxane **2c**, then the optimum conditions were extended to other *p*-tolylsiloxanes **1a**-**b**,**d**-**g**. Additionally, we estimated the applicability of this method to organic toluene derivatives **1h**-**o** and hydride silanes **3a**-**g**. Furthermore, using certain *p*-carboxyphenylsiloxanes as examples, we showed that it is possible to use them as HOF-like structures and monomers for the synthesis of copolymers (Sila-PET).

Aerobic Co-/NHSI-catalyzed oxidation of p-tolylsiloxanes to p-carboxyphenyldsiloxanes

We chose the commercially available and inexpensive N-hydroxysuccinimide (NHSI) as organocatalyst, which was previously reported to be relatively low-active in [M]-free aerobic oxidation of alkylbenzenes,[17a] benzylamines, etc.[18] NHSI attracted our attention due to good solubility in aprotic and low-polar solvents (which is an important factor in operations with organosilicon substrates) and facility of separation from reaction products (p-carboxyphenylsiloxanes) in comparison with other organocatalysts. Commercially available forms of abundant metals were chosen as the [M]-catalysts (precatalysts).

Table 1. Effect of aerobic oxidation conditions of 1c on the yield of 2c[a]



Entry	[M]	Solvent	T, °C	p-$CH_3C_6H_4$[Si] / p-HO(O)CC_6H_4[Si] / byproducts, %
1	Cu(OAc)$_2$	MeCN	40	95/0/5[b]
2	Co(acac)$_2$	MeCN	40	100/0/0[b]
3	Co(OAc)$_2$	MeCN	40	11/77/12[b]
4	Co(OAc)$_2$	EtOAc	40	99/0/1[b]
5	Co(OAc)$_2$	MeCN	40	3/96/1[c]
6	Co(OAc)$_2$	MeCN	60	0/94/6,[c,d] 90[e]

[a] **1c** (0.318 mmol, 1 eq.), NHSI (0.064 – 0.254 mmol, 0.2 – 0.8 eq.), [M] (1.59 – 19.1 μmol, 0.005 – 0.06 eq.), MeCN (1 mL), 25 – 60 °C, 15 h, O_2 (1 atm). The yield of **2c** was determined by ^{1}H NMR. [b] Co(OAc)$_2$ (12.72 μmol, 0.04 eq.), NHSI (0.127 mmol, 0.4 eq.). [c] Co(OAc)$_2$ (4.77 μmol, 0.015 eq.), NHSI (0.191 mmol, 0.6 eq.). [d] 24 h. [e] Isolated yield of **2c**. For the scaled reactions the temperature of oxidation was increased leading to the increase in NHSI / p-HO(O)CC_6H_4[Si]-adduct content.

It was found that the type of the metal (M) and anion (X) in the precatalyst (MX_n = [M]) are the key factors in the process if the [M] / NHSI / O_2 oxidizing system is used for conversion of p-tolylsiloxane **1c** to p-carboxyphenylsiloxane **2c**. In fact, the conversion of p-$\boldsymbol{CH_3}C_6H_4$[Si] group to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] for reagent **2c** (according to ^{1}H NMR), with 0.04[M] / 0.4NHSI ratio in MeCN at 40 °C in 15 hours using $CuCl_2$, $MnCl_2$, $NiCl_2$, $FeCl_3$, $CrCl_3$, $CoCl_2$, Cu(OAc)$_2$, Mn(OAc)$_2$, Mn(OAc)$_3$, Ni(acac)$_2$, Fe(OAc)$_2$, Fe(OAc)$_2$, Cr(OAc)$_3$, Co(acac)$_2$, Co(acac)$_3$, $CoSO_4$ and CAN ($(NH_4)_2Ce(NO_3)_6$), was no higher than 1 – 2%, but it was 77% in the case of Co(OAc)$_2$ (Table 1; *Supp. Inf.*).

At the next stage, we performed screening of the Co(OAc)$_2$ / NHSI ratio within (0.005 – 0.06) / (0.2 – 0.8) equiv. It was found that the best Co(OAc)$_2$ / NHSI ratio is 0.015 / 0.6 equiv., which allows one to reach 96% conversion of the p-$\boldsymbol{CH_3}C_6H_4$[Si] group to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] (Table 1; *Supp. Inf.*).

The choice of solvent is also a key factor that affects the result of the process. In fact, the conversion of p-$\boldsymbol{CH_3}C_6H_4$[Si] group to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] in various solvents (AcOH, $MeNO_2$, EtOAc, EtOH, $HCCl_3$, 1,2-dichloroethane (DCE), octafluorotoluene (Tol-F8), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and their mixtures in various ratios), except for MeCN, does not exceed 2%. However, if the reaction mixture was diluted or concentrated twofold with respect to the original concentration (**1c** concentration ~ 0.32 M), the conversion of **1c** did not change considerably (4 – 6% decrease; Table 1; *Supp. Inf.*).

The process temperature is also among key factors: when the temperature was lowered from 40 to 25 – 30 °C, the conversion of p-$\boldsymbol{CH_3}C_6H_4$[Si] group to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] did not exceed 2%. Increasing the temperature from 40 to 60 °C lead to 100% conversion of p-$\boldsymbol{CH_3}C_6H_4$[Si] to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] group / byproducts, but the content of byproducts also increased from 1% (at 40 °C) to 6% (Table 1; *Supp. Inf.*).

Evolution of the effect of the process time (from 0 to 48 h) showed that the process involves an induction period. In fact, in the 0.015 Co(OAc)$_2$ / 0.6 NHSI system in MeCN at 60 °C, no conversion of substrate **1c** was observed during initial 3 h, however, conversion of p-$\boldsymbol{CH_3}C_6H_4$[Si] to p-$\boldsymbol{HO(O)C}C_6H_4$[Si] group / byproducts after 5 and 7 h already reached 56 and 93%, respectively. After that, the conversion was increasing, but sufficiently slower: 15 h – 99%; 24 and 48 h – 100%. This difference in conversion from 93 to 100%, which is small at first glance, is an important factor in syntheses of di-, tri- and polyfunctional substrates.

Apparently, the induction period is due to the formation of a reactive catalytic form from the precatalysts (Co(OAc)$_2$ and NHSI) and to the demand of a certain concentration of succinimido-N-oxyl radicals (SINO; "N–O•" radical) to be present in the reaction mixture, which are both initiators and carriers of the radical chain process by a mechanism similar to that reported by Prof. Ishii et al. (Figure 1, Scheme 2; *Supp. Inf.*).[17a]

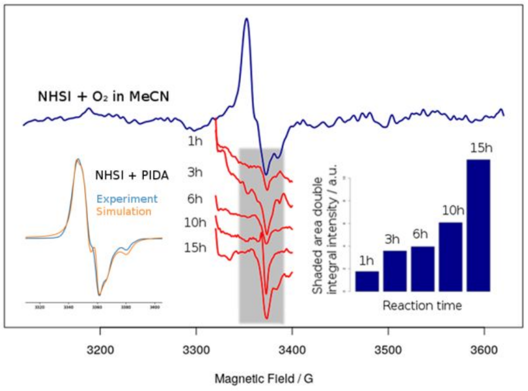
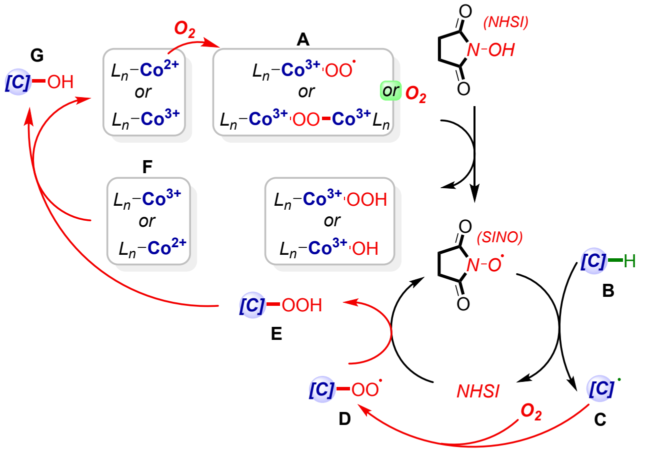


Figure 1. Free radical content of the reaction studied by EPR. Spectra of the reaction mixture samples (1h, 3h, 6h, 10h and 15h, red lines), and spectrum of SINO radical generated by treatment of NHSI with oxygen in MeCN (blue line). Double integral value of the signal region (shaded rectangle) depending on the reaction time is shown on the right inset. Spectrum of SINO generated by oxidation of NHSI with phenyliodine diacetate ($PhI(OAc)_2$; PIDA), and corresponding simulated spectrum (For simulation parameters see *Supp. Inf.*).

Electron Paramagnetic Resonance (EPR) spectra of reaction mixture samples display radical signal near *g*=2.005 (Figure 1, red line). The double integral intensity of the signal significantly increases in course of reaction (Figure 1, right inset). The signal shape is not well resolved and suffers from baseline distortion, so it is readily consistent with presence of detectable amounts of free SINO only at 15 hours after reaction start, where its width exceeds 28G, and the outer peak belonging to z-manifold appears on the right. Before 15h, it cannot be unequivocally attributed to SINO both due to its shape and offset in *g* factor (2.005 instead of expected 2.010, as observed in the spectrum of SINO radical generated by treatment of NHSI with O_2, blue line on Figure 1). The width of the rigid limit SINO spectrum has low limit set by double z-component of hyperfine splitting on ^{14}N nitrogen nucleus, estimated $2A_{zz}$ = 28G (found by simulation, left inset on Figure 1). These findings support the theory that free SINO radical formation is hampered on initial stages of reaction.

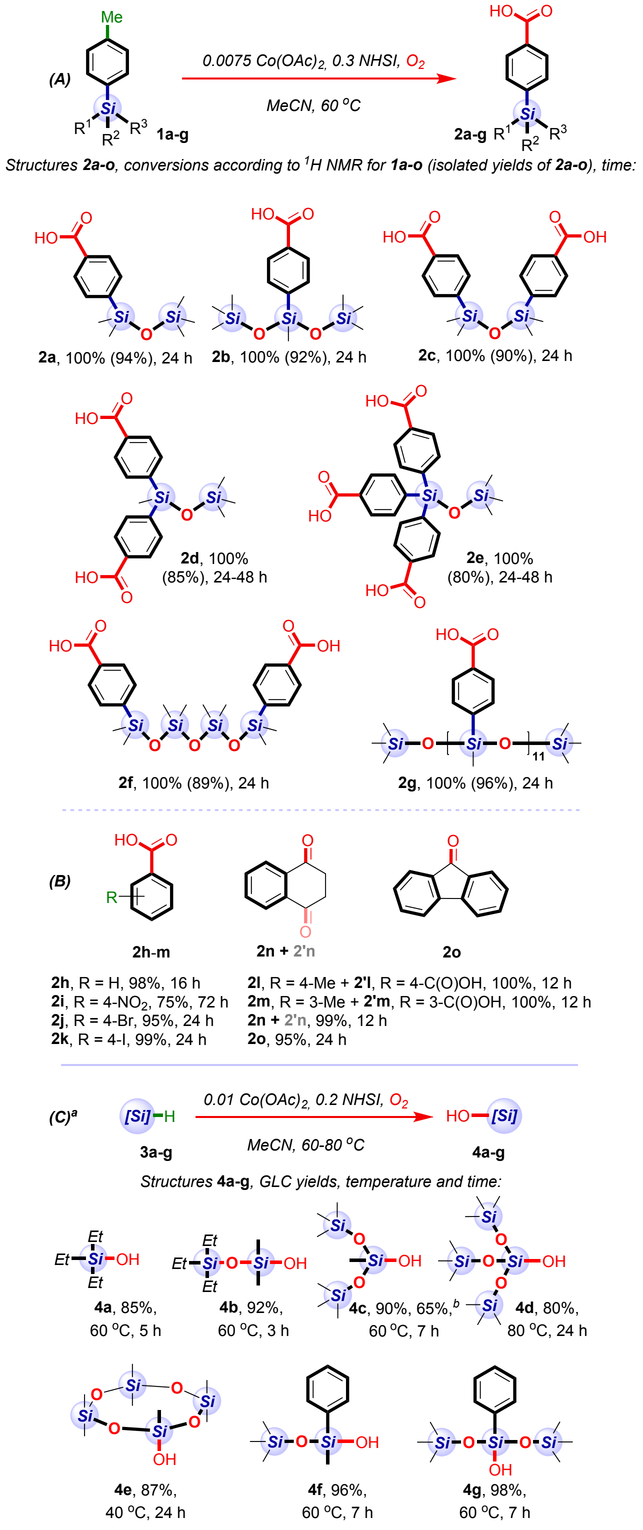
Based on these findings and literature data, radical mechanism of the oxidation was proposed.[17a] Accordingly, for the initiation of reaction, the SINO is formed by interaction of NHSI with complexes of [Co] **A**, or with O_2. Further interaction of SINO with the C–H group **B** (of $\boldsymbol{CH_3}C_6H_4$[Si]) leads to the regeneration of NHSI and the formation of the C-centered radical **C** ($\boldsymbol{\cdot CH_2}C_6H_4$[Si]), which then recombines with oxygen to give the peroxy radical D ($\boldsymbol{\cdot OOCH_2}C_6H_4$[Si]). The radical **D** when interacting with NHSI turns into the corresponding hydroperoxide **E** ($\boldsymbol{HOOCH_2}C_6H_4$[Si]), the subsequent interaction of which with the [Co] complexes **F** leads to the reduction of hydroperoxide **E** to the corresponding hydroxide **G**. This catalytic cycle can be repeated until complete oxidation of the corresponding C–H groups, with the formation of the final product – $\boldsymbol{HO(O)C}C_6H_4$[Si] (Scheme 2).

Scheme 2. The proposed reaction mechanism



The optimized conditions for **1c** oxidation were found to be applicable to the other *p*-tolylsiloxanes **1a-b, d-g** ((*A*), Scheme 3; *Supp. Inf.*).

Scheme 3. Synthesis of 2a–o and 4a-g from 1a–o and 3a-g, respectively[a]



(A) **1a-g** (6.36 mmol of Tol-groups, 1 eq.), NHSI (1.91 mmol, 0.3 eq. per Tol-group), $Co(OAc)_2$ (47.7 µmol, 0.0075 eq. per Tol-group), MeCN (2.5 mL), 60 °C, 24 – 48 h, under O_2 bubbling (≈ 5 – 7 mL / min).

(B) **1h-o** (0.636 mmol, 1 eq.), NHSI (0.191 mmol, 0.3 eq.), $Co(OAc)_2$ (4.77 µmol, 0.0075 eq.), MeCN (1 mL), 60 °C, 16 – 71 h, O_2 (1 atm).

(C) [a] **3a-g** (0.452 mmol, 1 eq.), NHSI (0.0905 mmol, 0.2 eq.), $Co(OAc)_2$ (2.26 µmol, 0.005 eq.), MeCN (1 mL), 25 °C, 24 h, O_2 (1 atm). [b] Isolated yield of **4c** after distillation under reduced pressure. The ratios of reagents were taken from our previous article.[17g]

This method makes it possible to oxidize *p*-tolylsiloxanes **1a-g** to *p*-carboxyphenylsiloxanes **2a-g** (the conversion is 100% according to ¹H NMR) with high regio-/chemoselectivity and with retention of the organosiloxane core: no cleavage of Si–O, Si–Me and Si–Ar bonds was observed.

The amphiphilic mono(*p*-carboxydiphenyl)di- (**2a**) and trisiloxanes (**2b**) obtained in high yields (94 and 92%) are of interest for synthesizing new types of siloxane surfactants and modifiers of organic polymers.[19]

We also estimated the applicability of the method not only for preparation of bifunctional *1,3*-bis(*p*-carboxyphenyl)disiloxane **2c**, but also “geminal” *1,1*-bis- (**2d** – 85%) and *1,1,1*-tris(*p*-carboxyphenyl)disiloxanes (**2e** – 80%) and “isolated” *1,7*-bis(*p*-carboxyphenyl)tetrasiloxane (**2f** – 89%). These products may be of interest in the syntheses of siloxane-containing copolymers and materials based thereon, as we discuss below.

Furthermore, the method proved to be suitable for synthesis of such a polyfunctional product as poly(*p*-carboxyphenyl)siloxane (**2g**) which can be obtained in 96% yield without degradation of the organosiloxane chain (determination of the average number of structural units in **1g** and **2g** (n ≈ 11) and the stability of the organosiloxane core under the reaction conditions was carried out according to ¹H NMR data). This is the first example of polymeric *p*-carboxyphenylsiloxanes. Polymers of this type may be promising for preparation of silicone elastomers, surfactants, electrolytes, self-healing, liquid-crystal and other materials. Furthermore, it is a way to the design of silicones with enhanced mechanical strength.

The suggested method can be scaled to obtain *p*-carboxyphenylsiloxanes **2a-g** in gram amounts (up to 5 g; *Supp. Inf.*) in 80 – 96% yields.

Aerobic Co-/NHSI-catalyzed oxidation of alkylarenes to benzoic acid and arylketone derivatives

Since liquid-phase aerobic oxidation is a powerful tool for producing industrially important organic compounds as mentioned above,[16,17] we also estimated the applicability of the suggested method for the oxidation of organic derivatives, *viz.*, alkylarenes **1h-o** (Ar–CH_3, Ar–CH_2–R) with various structures, to the corresponding derivatives **2h-o** (Ar–C(O)OH and Ar–C(O)–R) with conversions up to 95 – 100%. It is noted in early studies on the [M]-/Org-catalyzed oxidation of arylketones that donor substituents at the aromatic ring, unlike acceptor substituents, accelerate the oxidation process. In fact, conversion can decrease to 0% in the case of nitrotoluene.[16,17]**Error! Bookmark not defined.** However, the conversion of *p*-nitrotoluene under the suggested conditions is about 40% in 24 h and 75% in 3 days ((*B*), Scheme 3; *Supp. Inf.*).

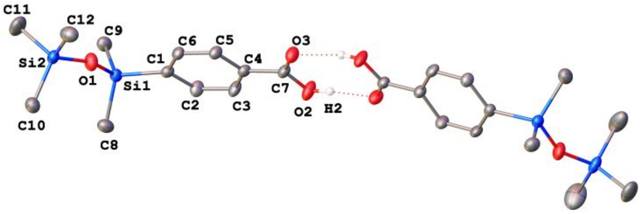
Aerobic Co-/NHSI-catalyzed oxidation of hydride silanes to silanols

Hydride silanes ([Si]–H) with various structures are also selectively oxidized to the corresponding silanols and siloxanols ([Si]–OH) with 80 - 98% conversion. As a rule, the Si–H group undergoes oxidation much more easily than the C–H group. The main difficulty in the synthesis of silanols lies in the subsequent side process, *i.e.*, condensation to give siloxanes (disiloxanes). However, silanols are rather stable under the suggested reaction conditions: for example, the fraction of disiloxane after 24 hours does not exceed 14% in the case of silanol **4c** (*(C)*, Scheme 3; *Supp. Inf.*).

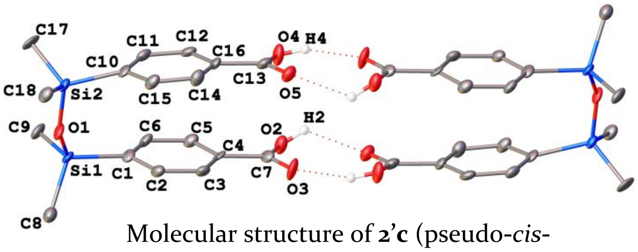
Determination of the structure and study of the properties of p-carboxyphenyldsiloxanes

Unlike the starting oil-like *p*-tolylsiloxanes **1a-d**,**f**,**g**, *p*-carboxyphenylsiloxanes **2a-g** are solid compounds at 25 ^{o}C, which is an additional confirmation that the intermolecular interactions are stronger. The structures of **2a-g** were confirmed by ^{1}H, ^{13}C, ^{29}Si and ^{1}H, ^{29}Si-HMBC NMR spectroscopy, IR spectroscopy, high resolution mass spectrometry (ESI-HRMS) for **2a-f** and X-Ray for **2a**,**c**,**d** and **1e** (Figure 2; *Supp. Inf.*).

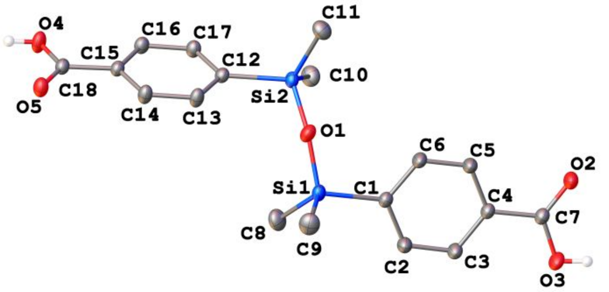
Like in the majority of carboxylic acid derivatives, the supramolecular structures of *p*-carboxyphenylsiloxanes **2a-d** are hydrogen-bonded systems: they are dimers (in the case of **2a** and **2’c** – pseudo-*cis*-conformation of **2c**), like in, *e.g.*, benzoic acid;[20] polymers, *i.e.*, HOF-like structures[4] (in the case of **2d** and **2”c** [12a] – pseudo-*trans*-conformation of **2c**) (Figure 2).



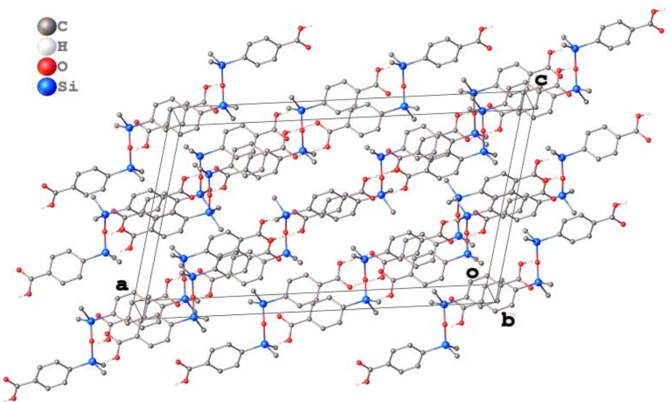
Molecular structure of **2a** (hydrogen-bonded dimer)



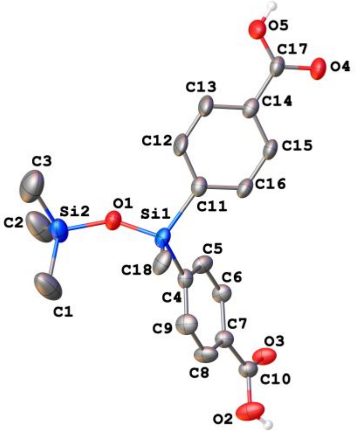
Molecular structure of **2’c** (pseudo-*cis*-conformation of **2c**; hydrogen-bonded dimer)



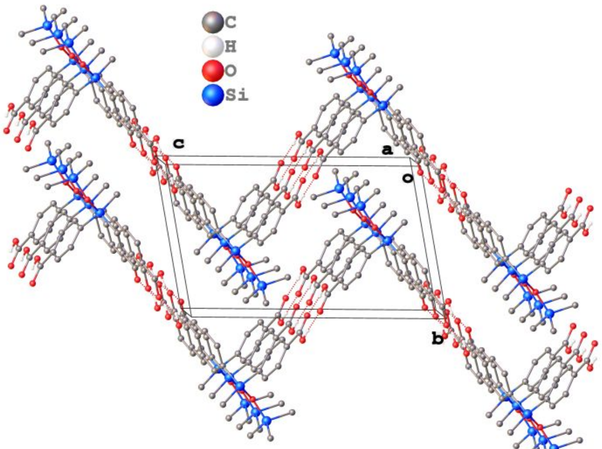
Molecular structure of **2”c** (pseudo-*trans*-conformation of **2c**)



Crystal packing of **2”c** (hydrogen-bonded polymer, HOF-like structure)



Molecular structure of **2d**



Crystal packing of **2d** (hydrogen-bonded polymer, HOF-like structure)

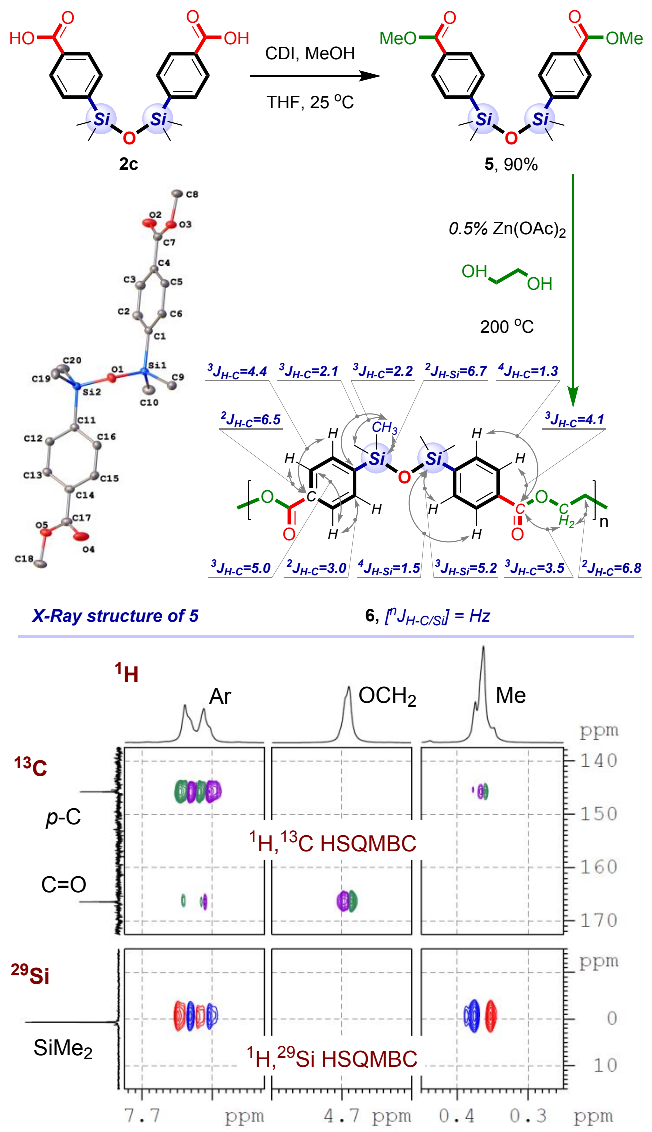
Figure 2. X-Ray structures of 2a,c,d. HOF-like structures

Bond lengths and angles in of **2a**, **2’c**, **2”c** and **2d** are typical for carbosiloxanes (Table 1s, *X-Ray Supp. Inf.*). Due to the presence of carboxylic groups in all the molecules studied, hydrogen bonds play a significant role in the stabilization of their crystal packing. Compounds **2’c** and **2”c**, being conformational polymorphs present the most interesting case. The conformational changes in the latter structures are related to changes in the mutual orientation of the Ar-groups, so molecules **2'c** and **2"c** are pseudo-*cis*- and pseudo-*trans*-isomers. According to theoretical calculations, the former is by 0.88 kJ/mol more favorable. As a consequence, H-bonded dimers are formed in the crystal packing of **2'c**, while in the case of **2"c**, infinite zigzag chains are present. The latter packing motif is also observed in the crystal of **2d**. Due to the presence of only one carboxylic group in **2a**, centrosymmetric dimers are formed by two independent molecules in the crystal. The parameters of H-bonds are presented in ESI. Additionally, the crystal packing of **2a**, **2'c**, **2"c**, **2d** was analyzed in terms of pairwise interactions (CE-B3LYP/6-31G(d,p) method). The energy of pairwise interactions related to O-H···O bonding in a crystal are 76.4 - 121.3 kJ/mol, whereas bonding between the chains or dimers related to other types of intermolecular bonds does not exceed 35 kJ/mol (*X-Ray Supp. Inf.*).

*Synthesis of monomeric (**5**) and polymeric (**6**) esters (Sila-PET) from p-carboxyphenyldsiloxane (**2c**). Determination of the structures of **5** and **6***

As mentioned above, functionalized siloxanes are important building blocks, in particular in syntheses of copolymers from organic and organosilicon monomers.[21] For example, our attention was attracted by the potential possibility of synthesizing a siloxane analogue of PET, a polymer produced on a large scale and used for the production of various materials, such as fibers, films for food packaging, and plastics used in building, medicine, electronics, etc.[22]

We studied the feasibility of synthesizing Sila-PET **6** from *p*-carboxyphenylsiloxane **2c** (Scheme 4).



Scheme 4. Synthesis of esters 5 and 6 (Sila-PET) from 2c (top); H-C and H-Si coupling constants for Sila-PET 6, and key fragments of ^{1}H,^{13}C and ^{1}H,^{29}Si HSQMBC spectra from it (bottom).

First, the dimethyl ester of *p*-carboxyphenylsiloxane **5** was obtained in 90% yield. Further, the reaction of **5** and ethylene glycol in the presence of catalytic amounts of $Zn(OAc)_2$ gave polymeric ester **6** – Sila-PET – in 99% yield. This process occurs with retention of the organosiloxane frame and allows one to obtain Sila-PET **6** with M_n = 9700, M_w = 14900 and PDI = 1.53 (PSS; *Supp. Inf.*).

Products **5** is a solid and **6** is glassy polymer. The structures of **5** and **6** were confirmed by ^{1}H, ^{13}C, ^{29}Si and ^{1}H, ^{29}Si-HMBC NMR spectroscopy, IR spectroscopy, high resolution mass spectrometry (ESI-HRMS) for **5**, GPC for **6** and X-Ray for **5** (Scheme 4, top; *Supp. Inf.*). The structure of Sila-PET **6** was additionally confirmed by a representative set of 2D NMR correlation techniques (COSY, NOESY, HSQC, HMBC, ^{1}H-^{29}Si-HMBC, DOSY). Moreover, the accurate determination of long-range H-C and H-Si spin-spin coupling constants was performed using ^{1}H,^{13}C and ^{1}H,^{29}Si HSQMBC and IPAP-HSQMBC 2D NMR experiments (coupling constants are shown on Scheme 4, bottom). Sila-PET **6** despite its high molecular weight has a highly ordered structure and gives narrow peaks in NMR spectra, which allows to accurately measure the coupling constants. Diffusion NMR experiment (DOSY) additionally shows a high molecular weight of the Sila-PET **6** in solutions.

CONCLUSION

A new highly efficient method for synthesizing organosilicon products with a "polar" functional group in organic substituents, *p*-carboxyphenylsiloxanes, has been suggested. The method is based on aerobic Co- / NHSI-catalyzed oxidation of *p*-tolylsiloxanes to *p*-carboxyphenylsiloxanes. This is the first preparative method for synthesizing such products implemented in a catalytic version and under mild and "green" reaction conditions.

This approach makes it possible to obtain monomeric, oligomeric and polymeric *p*-carboxyphenylsiloxanes with various structures in 80 – 96% yields. The method was also found suitable for the oxidation of organic derivatives, namely alkylarenes, and hydride silanes to the corresponding acids/ketones and silanols with high conversions (75 – 100%).

p-Carboxyphenylsiloxanes can become promising building blocks for synthesizing unique silicone materials, such as HOFs, MOFs, various copolymers, surfactants, etc. In fact, a siloxane analogue of PET (Sila-PET), obtained from one of the products (*1,3*-bis(*p*-carboxyphenyl)disiloxane), was taken as an example.

Thus, considering the simplicity and efficiency of the catalytic reaction and taking into account the commercial availability and low cost of the reagents used, this method has considerable prospects for application in the syntheses of new functionalized organic and organosilicon monomers, oligomers and polymers.

ASSOTIATED CONTENT

Supporting Information Available: Optimization and experimental procedures, spectral and X-Ray data are included in the supporting information. This material is available free of charge via the internet at http://pubs.acs.org.

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