Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for
Stable carboxylic acid derivatized alkoxy silanes

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Expected side reactions:

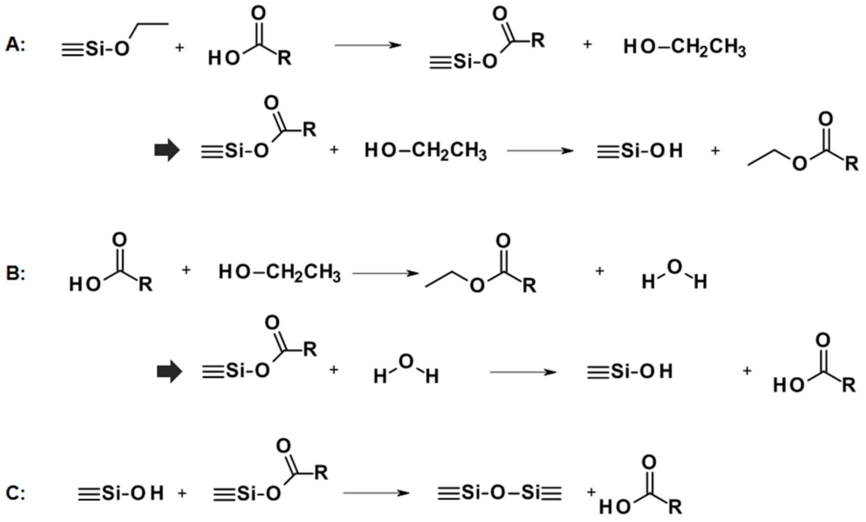


Fig. 1 Summary of the expected reactions between trialkoxysilanes and carboxylic acids.

Experimental Details

- **Materials**

Triethoxysilane (97%, ABCR), trimethoxysilane (95%, Aldrich), 4-pentenoic acid (97%, Aldrich), 3-butenoic acid (97%, Aldrich), 9-decenoic acid (≥ 90%, Aldrich), and platinum(IV) oxide (Aldrich) were used as received.

- **Characterization**

The ^{1}H-NMR, ^{13}C-NMR, and spin-lock ^{29}Si-NMR spectra of the carboxylic acid derivatives were measured on a Bruker AMX 400 spectrometer (Bruker BioSpin, USA). The ^{1}H-NMR spectra were recorded with 400.1 MHz, the ^{13}C-NMR spectra with 100.6 MHz, and the spin-lock ^{29}Si-NMR spectra with 79.5 MHz and a lock time of 150 ms, respectively. For the hydrolysis experiments, the ^{1}H-NMR spectra were taken on a Bruker DPX AVANCE 300 spectrometer with 300.13 MHz. IR-ATR (infrared spectroscopy in the attenuated total reflection mode) spectra were recorded on a Bruker VERTEX 70 spectrometer and MS (mass spectrometry) spectra on a Finnisam MAT SSQ 7000.

- **Typical procedure: Hydrosilylation of carbenoic acids with trialkoxysilanes and PtO_2 as catalyst**

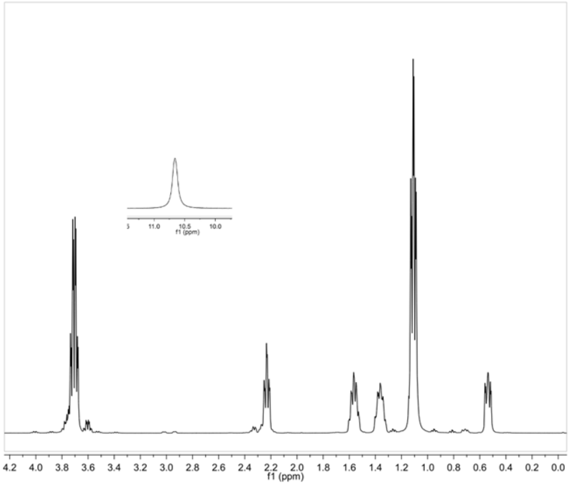
The hydrosilylated products were synthesized in a solvent-free hydrosilylation reaction with PtO_2 as catalyst. The general procedure was as follows: 0.05 mol of trialkoxysilane was added slowly via a dropping funnel to an icecold suspension of 0.05 mol of the carbenoic acid and 0.05 mmol platinum(IV) oxide. The respective amounts of the carbenoic acids and the silanes are listed in table1. After stirring the mixture for 6 h at 0 °C and 12 h at room temperature and filtration over a polytetrafluoroethylene syringe filter the product could be obtained as a light brown coloured liquid.

The colour results from colloidal Pt(0) particles, which can be removed by the addition of charcoal and dunning filtration. Since the product was not further purified, no quantitative yield was determined.

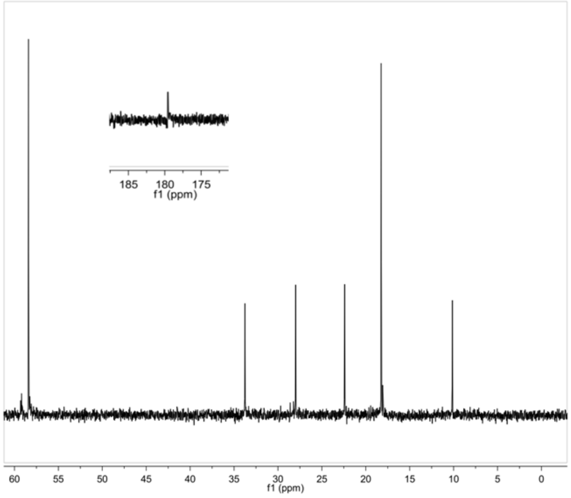
sample	*n (carbenoic acid) [mol]*	*V (carbenoic acid) [mL]*	*n (silane) [mol]*	*V (silane) [mL]*
4-(trimethoxysilyl)butanoic acid	0.05	4.3	0.05	6.4
4-(triethoxysilyl)butanoic acid	0.05	4.3	0.05	9.2
5-(trimethoxysilyl)pentanoic acid	0.05	5.1	0.05	6.4
5-(triethoxysilyl)pentanoic acid	0.05	5.1	0.05	9.2
10-(trimethoxysilyl)decanoic acid	0.05	9.3	0.05	6.4
10-(triethoxysilyl)decanoic acid	0.05	9.3	0.05	9.2

5-(triethoxysilyl)pentanoic acid

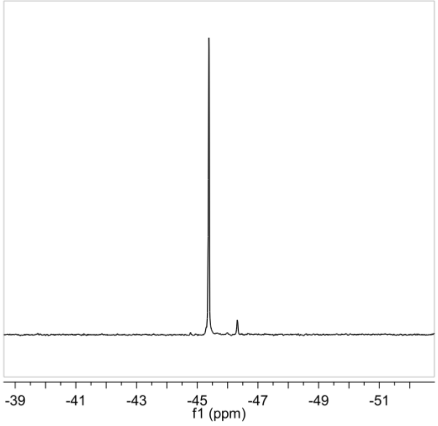
^{1}H-NMR (400.1 MHz, $\mathrm{CDCl_3}$): δ[ppm] = 0.53-0.58 (m, 2H, $\mathrm{SiC}\underline{H}_2$), 1.11-1.15 (m, 9H, $\mathrm{SiOCH_2C}\underline{H}_3$), 1.34-1.42 (m, 2H, $\mathrm{SiCH_2C}\underline{H}_2$), 1.55-1.62 (m, 2H, $\mathrm{SiCH_2CH_2C}\underline{H}_2$), 2.23-2.27 ($\mathrm{SiCH_2CH_2CH_2C}\underline{H}_2$) 3.58-3.63 (ethanol), 3.70-3.78 (m, 6H, $\mathrm{SiOC}\underline{H}_2\mathrm{CH_3}$), 10.68 (s, 1H, $\mathrm{CH_2COO}\underline{H}$).



^{13}C-NMR (100.6 MHz, $\mathrm{CDCl_3}$): δ[ppm] = 10.14 ($\mathrm{Si}\underline{C}\mathrm{H_2}$), 18.07 (ethanol), 18.24 ($\mathrm{SiOCH_2}\underline{C}\mathrm{H_3}$), 22.40 ($\mathrm{SiCH_2}\underline{C}\mathrm{H_2}$), 27.98 ($\mathrm{SiCH_2CH_2}\underline{C}\mathrm{H_2}$), 33.75 ($\mathrm{SiCH_2CH_2CH_2}\underline{C}\mathrm{H_2}$), 58.40 ($\mathrm{SiO}\underline{C}\mathrm{H_2CH_3}$), 59.19 (ethanol), 179.55 ($\mathrm{CH_2}\underline{C}\mathrm{OOH}$).



^{29}Si-NMR spin lock (79.5 MHz, CDCl$_3$): δ[ppm] = -45.38, -46.32.



IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1737 (CO of an ester, m), 1709 (CO of a carboxylic acid, s).

MS (Cl): calculated for (C$_{11}$H$_{24}$SiO$_5$) = 264; found: *m/z* = 265 [M+H]$^+$, 247 [M-OH]$^+$, 219 [M-EtOH]$^+$, 189 [M-C$_2$H$_5$]$^+$, 163 [M-C$_5$H$_9$O$_2$]$^+$.

4-(trimethoxysilyl)butanoic acid

^{1}H-NMR (400.1 MHz, DMSO-d6): δ[ppm] = 0.39-0.47 (m, 2H, SiC$\underline{H}_2$), 1.40-1.41 (m, 2H, SiCH$_2$C$\underline{H}_2$), 2.09-2.14 (m, 2H, SiCH$_2$CH$_2$C$\underline{H}_2$), 3.15 (s, 0.8H, methanol), 3.29 (s, 9H, SiOC$\underline{H}_3$), 3.39 (s, 0.4H, CH$_2$COOC$\underline{H}_3$), 9.57 (s, 1H, CH$_2$COO$\underline{H}$).

^{13}C-NMR (100.6 MHz, DMSO-d6): δ[ppm] = 7.51 (Si$\underline{C}$H$_2$), 8.87, 17.23 (SiCH$_2\underline{C}$H$_2$), 35.30 (SiCH$_2$CH$_2\underline{C}$H$_2$), 48.14 (methanol), 48.93 (SiO$\underline{C}$H$_3$), 49.62 (methanol), 176.53 (CH$_2\underline{C}$OOH).

^{29}Si-NMR spin lock (79.5 MHz, DMSO-d6): δ[ppm] = -42.7, -44.0.

IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1736 (CO of an ester, m), 1708 (CO of a carboxylic acid, s).

4-(triethoxysilyl)butanoic acid

^{1}H-NMR (400.1 MHz, DMSO-d6): δ[ppm] = 0.52-0.56 (m, 2H, SiC$\underline{H}_2$), 1.05-1.10 (m, 9H, SiOCH$_2$C$\underline{H}_3$), 1.60-1.62 (m, 2H, SiCH$_2$C$\underline{H}_2$), 2.22-2.26 (m, 2H, SiCH$_2$CH$_2$C$\underline{H}_2$), 3.52-3.60 (m, 0.4H, ethanol), 3.64-3.71 (m, 6H, SiOC$\underline{H}_2$CH$_3$), 10.34 (s, 1H, CH$_2$COO$\underline{H}$).

^{13}C-NMR (100.6 MHz, DMSO-d6): δ[ppm] = 9.64 ($Si\underline{C}H_2$), 17.68 (ethanol), 17.85 ($SiOCH_2\underline{C}H_3$), 18.06 ($SiCH_2\underline{C}H_2$), 36.49 ($SiCH_2CH_2\underline{C}H_2$), 57.95 (ethanol), 58.07 ($SiO\underline{C}H_2CH_3$), 178.59 ($CH_2\underline{C}OOH$).

^{29}Si-NMR spin lock (79.5 MHz, DMSO-d6): δ[ppm] = -45.9, -46.1.

IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1737 (CO of an ester, m), 1709 (CO of a carboxylic acid, s).

5-(trimethoxysilyl)pentanoic acid

^{1}H-NMR (400.1 MHz, CDCl$_3$): δ[ppm] = 0.54-0.58 (m, 2H, $SiC\underline{H_2}$), 1.31-1.39 (m, 2H, $SiCH_2C\underline{H_2}$), 1.50-1.60 (m, 2H, $SiCH_2CH_2C\underline{H_2}$), 2.21-2.25 (m, 2H, $SiCH_2CH_2CH_2C\underline{H_2}$), 3.34 (s, 1H, methanol), 3.45 (s, 9H, $SiOC\underline{H_3}$), 3.48 (s, 1H, $CH_2COOC\underline{H_3}$), 9.43 (s, 1H, $CH_2COO\underline{H}$).

^{13}C-NMR (100.6 MHz, CDCl$_3$): δ[ppm] = 8.87 ($Si\underline{C}H_2$), 22.21 ($SiCH_2\underline{C}H_2$), 27.94 ($SiCH_2CH_2\underline{C}H_2$), 33.69 ($SiCH_2CH_2CH_2\underline{C}H_2$), 50.15 (methanol), 50.49 ($SiO\underline{C}H_3$), 179.12 ($CH_2\underline{C}OOH$).

^{29}Si-NMR spin lock (79.5 MHz, CDCl$_3$): δ[ppm] = -41.9, -43.5.

IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1737 (CO of an ester, m), 1708 (CO of a carboxylic acid, s).

10-(trimethoxysilyl)decanoic acid

^{1}H-NMR (400.1 MHz, CDCl$_3$): δ[ppm] = 0.46-0.50 (m, 2H, $SiC\underline{H_2}$), 1.05-1.20 (m, 10H, $-C\underline{H_2}-$), 1.21-1.32 (m, 2H, $SiCH_2C\underline{H_2}$), 1.44-1.48 (m, 2H, $SiCH_2CH_2C\underline{H_2}$), 2.15-2.19 ($SiCH_2CH_2CH_2C\underline{H_2}$), 3.29 (methanol), 3.40-3.45 (m, 9H, $SiOC\underline{H_3}$), 10.75 (s, 1H, $CH_2COO\underline{H}$).

^{13}C-NMR (100.6 MHz, CDCl$_3$): δ[ppm] = 9.01 ($Si\underline{C}H_2$), 22.47 ($-\underline{C}H_2-$), 24.65 ($-\underline{C}H_2-$), 29.01, 32.97 ($-\underline{C}H_2-$), 33.93 ($-\underline{C}H_2-$), 50.27 ($SiO\underline{C}H_3$), 51.06 (methanol), 179.25 ($CH_2\underline{C}OOH$).

^{29}Si-NMR spin lock (79.5 MHz, CDCl$_3$): δ[ppm] = -41.4, -43.0.

IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1738 (CO of an ester, m), 1708 (CO of a carboxylic acid, s).

10-(triethoxysilyl)decanoic acid

^{1}H-NMR (400.1 MHz, CDCl$_3$): δ[ppm] = 0.52-0.56 (m, 2H, $SiC\underline{H_2}$), 1.12-1.16 (m, 9H, $SiOCH_2C\underline{H_3}$), 1.20-1.29 (m, 10H, $-C\underline{H_2}-$), 1.31-1.38 (m, 2H, $SiCH_2C\underline{H_2}$), 1.50-1.60 (m, 2H, $SiCH_2CH_2C\underline{H_2}$), 2.23-2.27 ($SiCH_2CH_2CH_2C\underline{H_2}$) 3.70-3.78 (m, 6H, $SiOC\underline{H_2}CH_3$), 10.67 (s, 1H, $CH_2COO\underline{H}$).

^{13}C-NMR (100.6 MHz, CDCl$_3$): δ[ppm] = 10.43 ($Si\underline{C}H_2$), 18.33 ($SiOCH_2\underline{C}H_3$), 22.80 ($-\underline{C}H_2-$), 29.15 ($-\underline{C}H_2-$), 33.20 ($-\underline{C}H_2-$), 34.17 ($-\underline{C}H_2-$), 58.39 ($SiO\underline{C}H_2CH_3$), 179.84 ($CH_2\underline{C}OOH$).

^{29}Si-NMR spin lock (79.5 MHz, CDCl$_3$): δ[ppm] = -44.5, -45.5.

IR-ATR: $\tilde{\nu}$ [cm^{-1}] = 1736 (CO of an ester, m), 1709 (CO of a carboxylic acid, s).

Triethoxysilane

^{1}H-NMR (400.1 MHz, $CDCl_3$): δ[ppm] = 1.14-1.18 (t, 9H, $\mathrm{Si(OCH_2C\underline{\mathit{H}}_3)_3}$), 3.58-3.64 (ethanol), 3.74-3.79 (q, 6H, $\mathrm{Si(OC\underline{\mathit{H}}_2CH_3)_3}$), 4.20 (s, 1H, $\mathrm{\underline{\mathit{H}}Si(OCH_2CH_3)_3}$.

^{13}C-NMR (100.6 MHz, $CDCl_3$): δ[ppm] = 18.3 ($\mathrm{SiOCH_2\underline{C}H_3}$), 18.4 (ethanol), 58.4 ($\mathrm{SiO\underline{C}H_2CH_3}$), 58.3 (ethanol).

General Procedure of the Hydrolysis Studies by ^{1}H-NMR Spectroscopy

0.2 mmol of the corresponding silane was mixed with 0.6 mL acetone-d6 in an NMR sample tube. After recording a ^{1}H-NMR spectrum of the sample, 0.1 mL diluted hydrochloric acid (0.01 M, pH = 2) or 0.1 mL distilled water (pH = 4.5) was added and 60 s after the addition, the first ^{1}H-NMR spectrum was recorded. Subsequently, a spectrum was recorded every 30 s.

For the evaluation, the kinetic equation $A_t = A_0 * e^{-kt}$ for first-order reactions was used. A_0 corresponds to the integral intensity of the ethoxy signals before the catalysis of hydrolysis and condensation reactions and A_t to the signal intensity at the corresponding time t after the addition of the catalyst. For the determination of the rate constant, the equation was converted into the linear equation: $\ln(A_0/A_t) = kt$. Through a plot of $\ln(A_0/A_t)$ against the time t, the rate constant can be obtained directly from the slope of the line.