Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information for

Silylation of O–H Bonds by Catalytic Dehydrogenative and Decarboxylative Coupling of Alcohols with Silyl Formates

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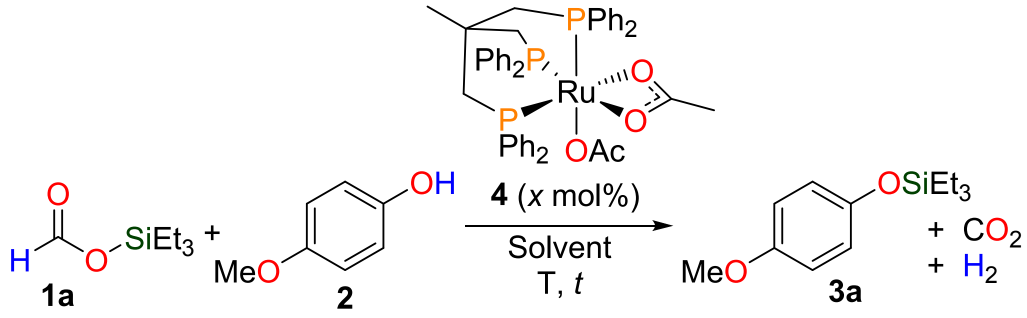
1. Experimental details

a) General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and/or using Schlenk lines. Glassware was dried overnight at 120 ºC or flame-dried under vacuum before use. ^{1}H and ^{13}C were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to solvent impurities. Tetrahydrofuran (THF), d_8-tetrahydrofuran (d_8-THF) and d_6-benzene were dried over a sodium(0)/benzophenone mixture and vacuum-distilled before use. CD_3CN and CD_2Cl_2 were dried over CaH_2 and vacuum-distilled before use. Chlorosilanes TESCl (TES = triethylsilyl), TMSCl (TMS = trimethylsilyl), TEOSCl (TEOS = triethoxysilyl), DPMSCl (DPMS = diphenylmethylsilyl), TIPSCl (TIPS = triisopropylsilyl), TBDMSCl (TBDMS = tertiobutyldimethylsilyl), and triethylsilane were obtained from Aldrich and used as received. Triethylamine was purchased from Carlo Erba and was distilled and degassed prior to use. Benzyl alcohol was washed with sodium carbonate, dried with magnesium sulfate and distilled under reduced pressure prior to use. Other alcohols were purchased from Aldrich and used as received. The complex [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (triphos: 1,1,1-tris(diphenylphosphinomethyl)ethane) as well as the silyl formates **1a-f** were prepared according to previously reported procedures.[1]

2. Optimization of the reaction conditions

Table S1: Optimization of the reaction conditions for the dehydrogenative coupling between silyl formate **1a** and phenol **2**.



Solvent	*x*	Equiv. **1a**	T (°C)	*t*[a]	Yield[b] (%)
CD_2Cl_2	1	1.4	70	30 min	>95
C_6D_6	1	1.4	70	30 min	>95
THF-d_8	1	1.4	70	30 min	>95
CD_3CN	1	1.4	70	30 min	>95
CD_3CN	0.5	1.4	70	1,5 h	>95
CD_3CN	2	1.4	70	15 min	>95
CD_3CN	0	1.4	70	1 h	<5
CD_3CN	0	1.4	70	100 h	15
CD_3CN	1	1.4	25	6 h	< 5
CD_3CN	1	1.4	50	3 h	>95
CD_3CN	1	1.2	70	40 min	>95
CD_3CN	1	1.05	70	1,5 h	>95

Reaction conditions: 4-methoxyphenol (**2**) (0.1 mmol), solvent (0,4 mL, 0.25 M). [a] time to reach full conversion of **2**. [b] Yields were determined by ^1H NMR analysis of the crude mixture using mesitylene as an internal standard.

3. General procedures for the dehydrogenative and decarboxylative coupling of alcohols with silyl formates

a) Alcohol silylation: general procedure for NMR-scale experiments

In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (0.9 mg , 1 µmol, 1 mol%) followed by d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous yellow solution were sequentially added the alcohol (0.1 mmol, 1 equiv.), silyl formate (0.12 mmol, 1.2 equiv.) and mesitylene (10 µL, 0.072mmol) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). At this temperature, all the reactions were generally complete within 1 h with silyl formates **1a-e**. Yields of silyl ethers were determined by ^{1}H NMR integration versus mesitylene as an internal standard (δ_H = 6.79 and 2.24 ppm in d_3-MeCN).

Representative ^{1}H NMR spectra for the dehydrogenative coupling of 4-methoxy-phenol (**2)** with $\mathrm{Et_3SiOCHO}$ (**1a**) are given in Figure S1 (^{1}H).

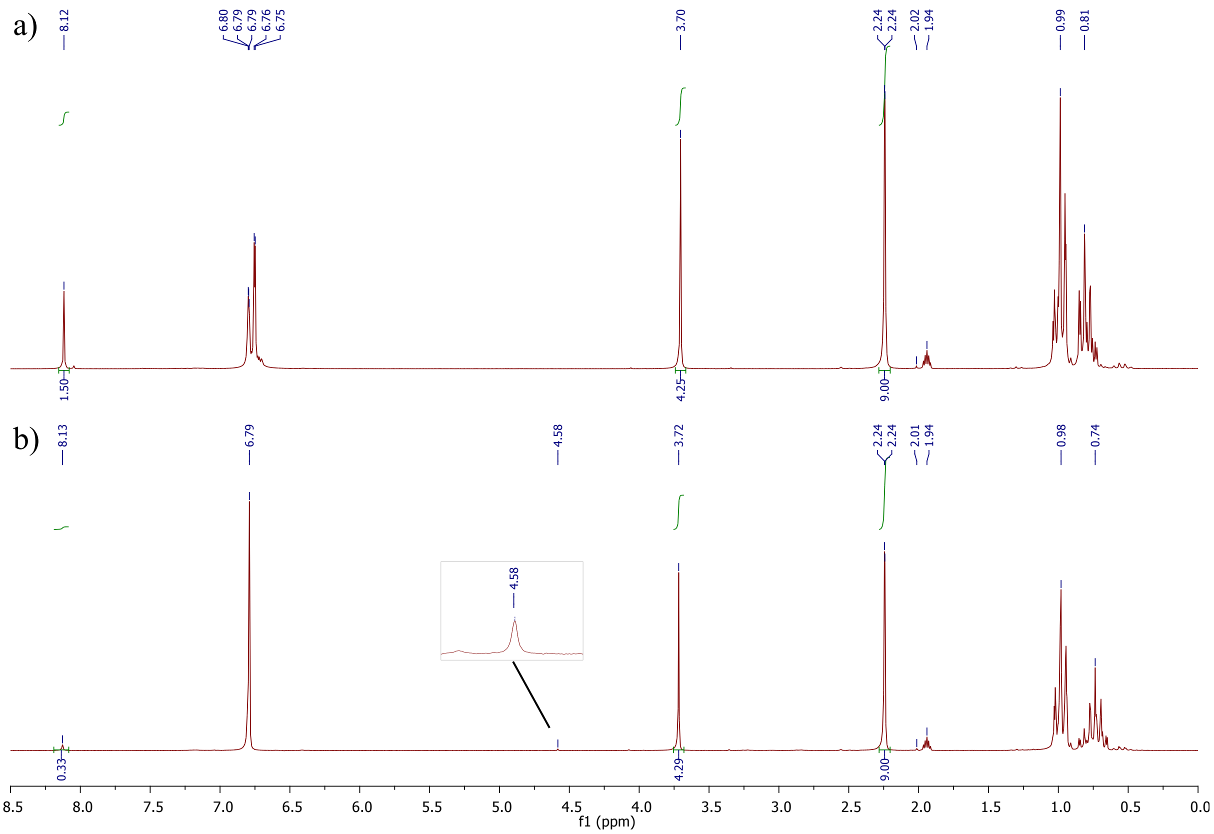


Figure S1: Representative ^{1}H NMR spectra obtained in $\mathrm{CD_3CN}$ for the dehydrogenative coupling of 4-methoxyphenol (2) with $\mathrm{Et_3SiOCHO}$ (1a). a) Crude reaction mixture before heating; t = 0. b) Crude reaction mixture after heating 30 min at 70 °C. Yield: > 95%.

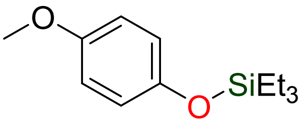
The formation of known silyl ethers **3a**[2], **3b**[3], **3d**[4], **5b**[5], **5d**[6], **8a**[7], **8b**[8] **8d**[1], **9a**[9], **10a**[10], **11a**[11], **12b**[12], **13a**[13], **16a**[14], **17b**[15], **18a**[16], **19a**[17], **25a**[3], **26b**[18] and **20b** (commercially available) was confirmed by ^{1}H and/or ^{13}C NMR analysis, and their spectroscopic data were identical to those reported in the literature.

b) Alcohols silylation: general procedure for preparative scale experiments

Up-scaled experiments were additionally carried out for unknown silyl ethers **3a**, **3c**, **3e**, **6a**, **7a, 14a, 15b, 21a**, **22a**, **23a**, and **24b** according to the following procedure:

In a glovebox, a flame-dried 10 mL Schlenk flask equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (4.3 mg, 5 µmol, 1 mol%) followed by MeCN (2 mL, $C = 0.25$ M). To the resulting homogeneous yellow solution was sequentially added the alcohol (0.5 mmol, 1 equiv.) and silyl formate (1.2 equiv.). The flask was sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature) for 1 h. The volatiles were then removed under vacuum and the resulting crude mixture was purified by column chromatography on silica gel.

c) Characterization of new silyl ethers



(3a)

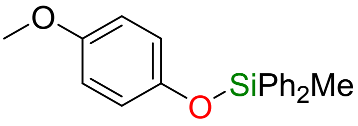
Colorless oil

97% isolated yield (116 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CD$_3$CN) δ 6.77 (m, 4H), 3.76 (s, 3H), 0.99 (t, $J = 7.7$ Hz, 9H), 0.74 (q, $J = 7.7$ Hz, 6H).

^{13}C NMR (50 MHz, CD$_3$CN) δ 154.02, 149.23, 120.49, 114.42, 55.59, 6.64, 4.87.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{13}H_{23}O_2Si^+$ 239.1462; found : 239.1461.



(3c)

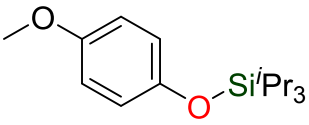
Colorless oil

96 % isolated yield (153 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.67 (m, 2H), 7.65 – 7.01 (m, 8H), 6.82 – 6.66 (m, 4H), 3.73 (s, 3H), 0.74 (s, 3H).

^{13}C NMR (50 MHz, CDCl$_3$) δ 156.87, 151.41, 138.20, 137.06, 132.76, 130.64, 123.20, 117.10, 58.24, 0.02.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{20}H_{21}O_2Si^+$ 321.1305; found : 321.1305.



(3e)

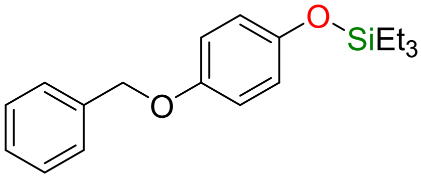
Colorless oil

97 % isolated yield (137 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 6.84 – 6.72 (m, 4H), 3.75 (s, 3H), 1.29 – 0.92 (m, 18H).

^{13}C NMR (50 MHz, CDCl$_3$) δ 156.45, 152.45, 123.05, 117.03, 58.27, 20.58, 15.24.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{16}H_{29}O_2Si^+$ 281.1931; found : 281.1931.



(6a)

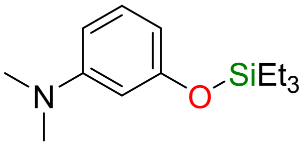
Colorless oil

90 % isolated yield (140 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.56 – 7.18 (m, 5H), 6.92 – 6.70 (m, 4H), 5.00 (s, 2H), 1.09 – 0.83 (m, 9H), 0.71 (m, 6H).

^{13}C NMR (50 MHz, CDCl$_3$) δ 155.97, 152.16, 139.95, 131.20, 130.55, 130.22, 123.17, 118.23, 73.21, 9.31, 7.56.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{19}H_{27}O_2Si^+$ 315.1775; found : 315.1775.



(7a)

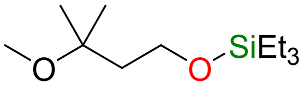
Colorless oil

98 % isolated yield (123 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.07 (t, *J* = 8.4 Hz, 1H), 6.31 (m, 3H), 2.92 (s, 6H), 1.15 – 0.91 (m, 9H), 0.77 (dd, *J* = 11.2, 4.8 Hz, 6H).

^{13}C NMR (50 MHz, CDCl$_3$) δ 159.16, 154.65, 132.18, 110.88, 108.63, 107.25, 43.26, 9.38, 7.71.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{14}H_{26}NOSi^+$ 252.1778; found : 252.1778.



(14a)

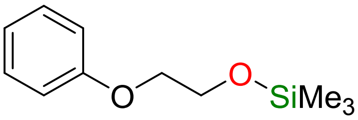
Colorless oil

88 % isolated yield (102 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 3.78 – 3.60 (m, 2H), 3.18 (s, 3H), 1.85 – 1.67 (m, 2H), 1.16 (s, 6H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.70 – 0.45 (m, 6H)

^{13}C NMR (50 MHz, CDCl$_3$) 76.42, 61.70, 51.80, 44.84, 28.14, 9.46, 7.02.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{12}H_{29}O_2Si^+$ 233.1931; found : 233.1931.



(15b)

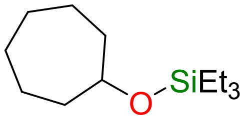
Colorless oil

86 % isolated yield (107 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, CDCl$_3$) δ 7.28 (dd, *J* = 10.6, 5.2 Hz, 2H), 6.93 (dd, *J* = 12.1, 4.8 Hz, 3H), 3.99 (m, 4H), 0.17 (s, 9H).

^{13}C NMR (50 MHz, CDCl$_3$) δ 161.47, 132.09, 123.39, 117.15, 80.31, 64.08, 2.31.

HRMS (ESI) *m/z* $[M + Na]^+$ calcd. for $C_{11}H_{18}O_2SiNa^+$ 233.0968; found : 233.0969.

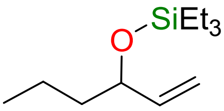

(**21a**)

Colorless oil

52 % isolated yield (60 mg), 100:0 petroleum ether/AcOEt

^{1}H NMR (200 MHz, $CDCl_3$) δ 4.09 – 3.54 (m, 1H), 2.08 – 1.13 (m, 14H), 0.94 (dd, *J* = 10.2, 5.4 Hz, 9H), 0.60 (dd, *J* = 11.4, 4.4 Hz, 6H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 75.89, 40.68, 30.61, 25.41, 9.57, 7.50.

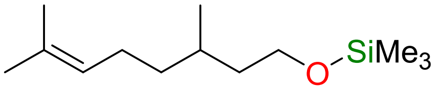

(**22a**)

Colorless oil

41 % isolated yield (87.4 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.21 – 4.89 (m, 2H), 4.07 (m, 1H), 1.66 – 1.16 (m, 7H), 0.98 – 0.83 (m, 9H), 0.55 (m, 6H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 144.54, 116.19, 76.38, 43.04, 21.18, 16.76, 9.52, 9.47, 9.05, 7.55.


(**23a**)

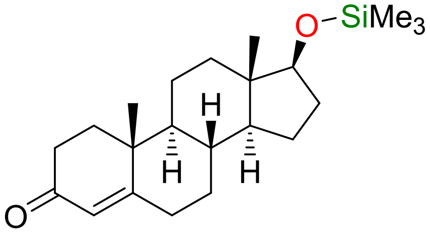
Colorless oil

86 % isolated yield (231 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.10 (dd, *J* = 4.9, 3.6 Hz, 1H), 3.78 – 3.42 (m, 2H), 1.97 (d, *J* = 6.8 Hz, 2H), 1.62 (m, 8H), 1.25 (m, 4H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.11 (s, 9H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 133.81, 127.50, 63.56, 42.44, 39.87, 31.81, 28.40, 28.11, 22.23, 20.30, 2.21.

HRMS (ESI) *m/z* [M –TMS + H]$^+$ calcd. for $C_{10}H_{21}O^+$ 157.1587; found : 157.1589.


(**24b**)

White powder

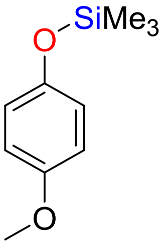
97 % isolated yield (361 mg), 95:5 petroleum ether/AcOEt

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.72 (s, 1H), 3.54 (t, *J* = 8.1 Hz, 1H), 2.54 – 2.18 (m, 4H), 2.10 – 1.19 (m, 12H), 1.18 (s, 2H), 0.96 (ddt, *J* = 15.5, 10.4, 4.6 Hz, 4H), 0.74 (s, 2H), 0.07 (s, 9H).

^{13}C NMR (50 MHz, $CDCl_3$) δ 202.08, 173.98, 126.44, 84.04, 56.67, 52.78, 45.49, 41.29, 39.30, 38.36, 38.30, 36.61, 35.47, 34.22, 33.38, 26.05, 23.28, 20.04, 13.90, 2.83.

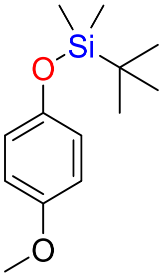
HRMS (ESI) *m/z* [M + H]$^+$ calcd. for $C_{14}H_{25}O_2Si^+$ 361.2557; found : 361.2557.

d) Selected resonances for known silyl ethers and esters



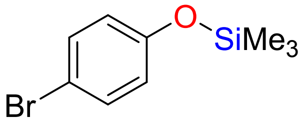
(3b)

^{1}H NMR (200 MHz, CD_3CN) δ 6.80 (s, 4H), 3.73 (s, 3H), 0.22 (s, 9H).



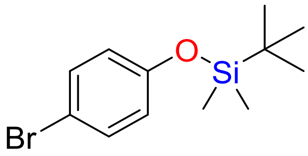
(3d)

^{1}H NMR (200 MHz, CD_3CN) δ 6.79 (m, 4H), 3,71 (s, 3H), 1.11 – 0.95 (m, 15H).



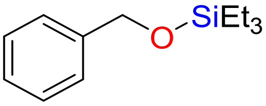
(5b)

^{1}H NMR (200 MHz, CD_3CN) δ 7.41 – 7.34 (m, 2H), 6.94 – 6.61 (m, 2H), 0.25 (s, 9H).



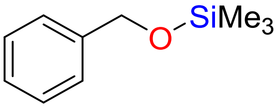
(5d)

^{1}H NMR (200 MHz, CD_3CN) δ 7.36 (d, *J* = 8.9 Hz, 2H), 6.81 (m, 2H), 0.97 (m, 9H), 0.19 (m, 6H).



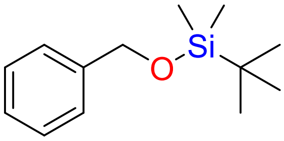
(**8a**)

^{1}**H NMR (200 MHz, CD$_3$CN)** δ 7.38 – 7.23 (m, 5H), 4.73 (s, 2H), 1.14 – 0.89 (m, 9H), 0.87 – 0.41 (m, 6H). **HRMS (ESI)** *m/z* $[M + H]^+$ calcd. for $C_{13}H_{23}OSi^+$ 239.1462; found : 239.1461.



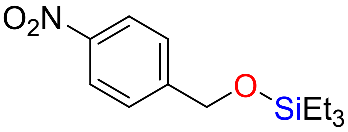
(**8b**)

^{1}**H NMR (200 MHz, CD$_3$CN)** δ 7.33 (m, 5H), 4.69 (s, 2H), 0.14 (s, 9H).



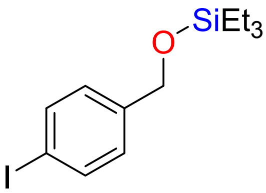
(**8d**)

^{1}**H NMR (200 MHz, CD$_3$CN)** δ 7.33 (m, 5H), 4.69 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H),



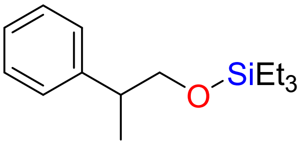
(**9a**)

^{1}**H NMR (200 MHz, CD$_3$CN)** δ 8.16 (m, 2H), 7.55 (m, 2H), 4.85 (s, 3H), 1.20 – 0.88 (m, 9H), 0.73 (m, 6H).



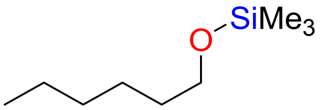
(**10a**)

^{1}**H NMR (200 MHz, CD$_3$CN)** δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H), 4.68 (s, 2H), 0.97 (td, *J* = 7.5, 1.8 Hz, 9H), 0.75 – 0.38 (m, 6H).



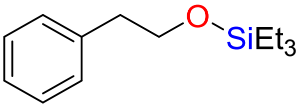
(**11a**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 7.41 – 7.07 (m, 5H), 3.80 – 3.58 (m, 2H), 2.87 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.12 – 0.68 (m, 9H), 0.68 – 0.41 (m, 6H).



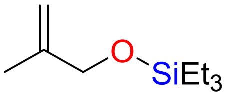
(**12b**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 3.57 (t, *J* = 6.4 Hz, 2H), 1.47 (m, 2H), 1.30 (m, 6H), 1.01 – 0.77 (m, 3H), 0.09 (s, 9H).



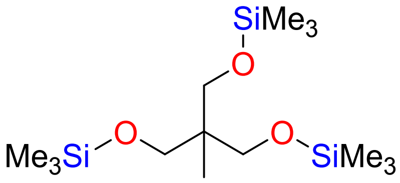
(**13a**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 7.43 – 7.09 (m, 5H), 3.82 (t, *J* = 6.9 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 1.16 – 0.87 (m, 9H), 0.65 – 0.40 (m, 6H).



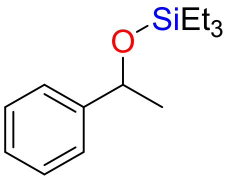
(**16a**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 5.06 – 4.89 (m, 1H), 4.79 (m, 1H), 4.13 – 3.93 (m, 2H), 1.69 (m, 3H), 1.12 – 0.87 (m, 9H), 0.87 – 0.42 (m, 6H).



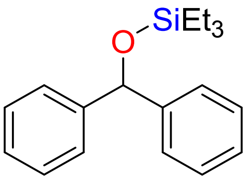
(**17b**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 3.36 (s, 6H), 0.77 (s, 3H), 0.08 (s, 27H).



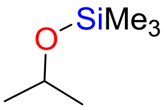
(**18a**)

^{1}H NMR (200 MHz, CD$_3$CN) δ 7.48 – 7.12 (m, 5H), 4.92 (q, *J* = 6.3 Hz, 1H), 1.38 (d, *J* = 6.3 Hz, 3H), 0.93 (m, 9H), 0.66 – 0.37 (m, 6H).



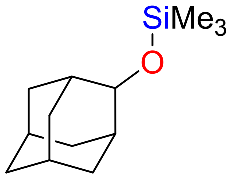
(19a)

^{1}H NMR (200 MHz, CD$_3$CN) δ 7.47 – 7.10 (m, 10H), 5.86 (s, 1H), 1.14 – 0.43 (m, 15H).



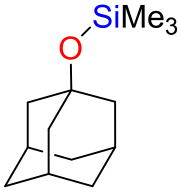
(20b)

^{1}H NMR (200 MHz, CD$_3$CN) δ 4.00 (hept., *J* = 6.0 Hz, 1H), 1.11 (d, *J* = 6.1 Hz, 6H), 0.08 (s, 9H).



(25a)

^{1}H NMR (200 MHz, CD$_3$CN) δ 3.88 (m, 1H), 2.12 (d, *J* = 12.2 Hz, 2H), 1.73 (m, 10H), 1.46 (d, *J* = 11.9 Hz, 2H), 0.10 (s, 9H).



(26b)

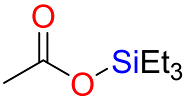
^{1}H NMR (200 MHz, CD$_3$CN) δ 2.07 (s, 6H), 1.73 (m, 3H), 1.61 (m, 3H), 0.09 (s, 6H).

4. General procedures for the dehydrogenative coupling of carboxylic acids

a) Carboxylic acid triethylsilylation: general procedure for NMR-scale experiments

In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (0.9 mg , 1 µmol, 1 mol%) followed by d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous yellow solution were sequentially added the carboxylic acid (0.1 mmol, 1 equiv.), triethylsilyl formate **1a** (1.2 equiv.) and mesitylene (10 µL, 0.072 mmol) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). At this temperature, all the reactions were generally complete within 3h. Yields of silyl ethers were determined by ^{1}H NMR integration versus mesitylene as an internal standard (δ_H = 6.79 and 2.24 ppm in d_3-MeCN).

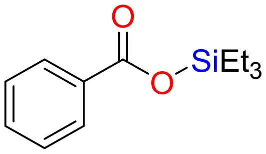
The formation of known silyl acetate (**27a**)[19] and benzoate (**28a**)[20], were confirmed by ^{1}H and/or ^{13}C NMR analysis, and their spectroscopic data were identical to those reported in the literature.



(**27a**)

^{1}H NMR (200 MHz, CD_3CN) δ 2.01 (s, 3H), 0.97 (m, 9H), 0.88 – 0.67 (m, 6H).

^{13}C NMR (50 MHz, CD_3CN) δ 172.33, 22.70, 6.73, 5.07.



(**28a**)

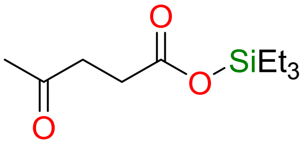
^{1}H NMR (200 MHz, CD_3CN) δ 8.04 (d, J = 7.2 Hz, 2H), 7.53 (m, 3H), 1.21 – 0.58 (m, 15H).

^{13}C NMR (50 MHz, CD_3CN) δ 167.20, 138.59, 132.35, 130.80, 129.47, 6.88, 5.26.

b) Dehydrogenative coupling between levulinic acid and triethylsilyl formate

In a glovebox, a flame-dried 10 mL Schlenk flask equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (4.3 mg, 5 µmol, 1 mol%) followed by MeCN (2 mL, C = 0.25 M). To the resulting homogeneous yellow solution was sequentially added levulinic acid (0.5 mmol, 50.9 µL;1 equiv.) and **1a** (1.4 equiv.). The flask was sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature) for 3 h. The volatiles were removed *in vacuo*, the crude reaction mixture was diluted with anhydrous ether (*ca.* 1 mL) in a glovebox and filtered over a sintered glass funnel through a pad of celite.

The volatiles were then removed under vacuum. The silyl ester **29a** was obtained in 70 % yield (80 mg) as a pale yellow oil highly sensitive to moisture.



(**29a**)

Pale yellow oil
70 % isolated yield (80 mg)
^{1}H NMR (200 MHz, CD_3CN) δ 2.67 (m, 2H), 2.56 – 2.39 (m, 2H), 2.10 (s, 3H), 1.04 – 0.87 (m, 9H), 0.85 – 0.56 (m, 6H).
^{13}C NMR (50 MHz, CD_3CN) δ 207.83, 173.97, 38.66, 30.11, 29.86, 6.69, 5.06.

5. Functional group tolerance: additional examples

Additional experiments were also carried out to further assess the functional group tolerance of the dehydrogenative and decarboxylative silylation of alcohols with triethylsilyl formate **1a**. In addition to the functional groups mentioned in the main text, protic functionalities such as the amino or acetamido groups are well-tolerated during the silylation of phenols **30** and **31** (Figure S2). Triethylsilylation of the O–H bond can be performed selectivity as the dehydrogenative silylation or the formylation of the nitrogen atoms are not observed. Moreover, the carbonyl of the amide in **31** remains untouched under the reaction conditions.

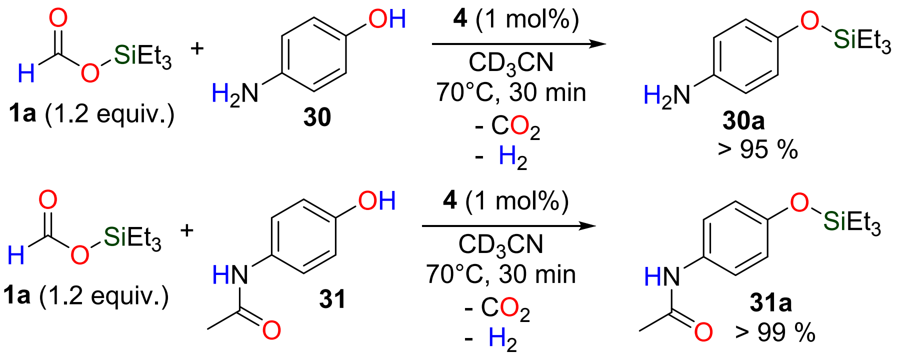


Figure S2: Dehydrogenative silylation of 4-aminophenol (**30**) and 4-acetamidophenol (**31**).

In agreement with our previous report on the transfer hydrosilylation of aldehydes with silyl formates catalyzed by complex **4**,[1] the aldehyde functional group was found reactive under the applied reaction conditions. For example, in the presence of **1a** (1.2 equiv.), isovanilin **32** bearing both a formyl and an hydroxyl on the aromatic ring gave a mixture of mono- and bis-silylated products (Figure S3). Notably, the major product obtained at full conversion of **1a** was the phenol **32a'** resulting from the exclusive transfer hydrosilylation of the aldehyde. Adding one more molar equivalent of **1a** to the previous mixture leads to the formation of the bis-silyl ether **32a''** in quantitative yield (determined by NMR spectroscopy).

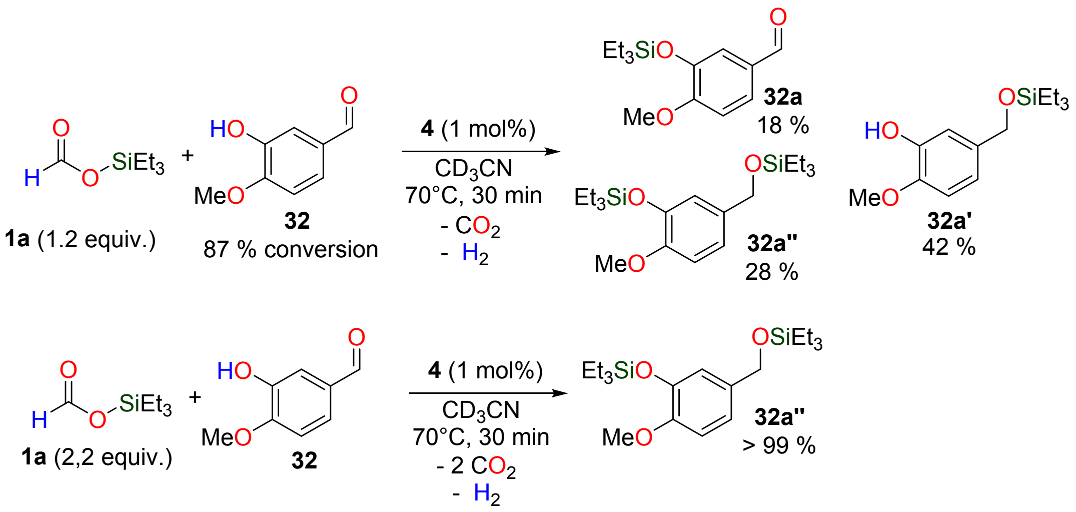


Figure S3: Outcome of the dehydrogenative silylation of 2-hydroxy-3-methoxybenzaldehyde (isovanilin, **32**) with silyl formate **1a** (1.2 and 2.2 equiv.).

The somewhat fragile epoxide functionality, which readily undergoes ring opening under basic conditions, was also tolerated as illustrated by the quantitative silylation of benzyl alcohol **8** with **1a** (1.2 equiv.) in the presence of 1 molar equivalent of styrene oxide (**33** in Fig. S4). The latter remains unreacted under the applied reaction conditions.

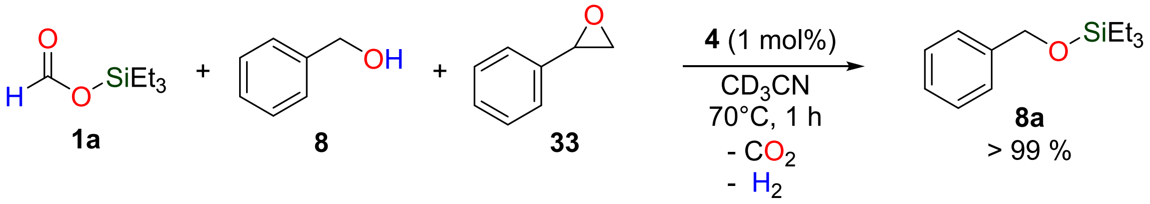


Figure S4: Silylation of benzyl alcohol in the presence of 1 equiv. of styrene oxide (**33**).

Unsaturated groups such as the imine (in aldimine **34**, Fig. S5) or alkynyl (in **35**, Fig. S6) are also stable under the transfer silylation conditions.

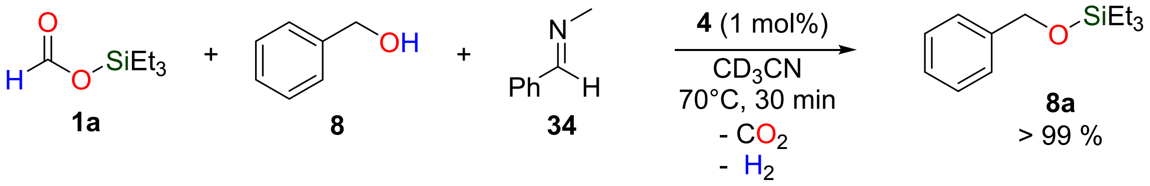


Figure S5: Silylation of benzyl alcohol in the presence of 1 equiv. of *N*-benzylidenemethylamine (**34**).

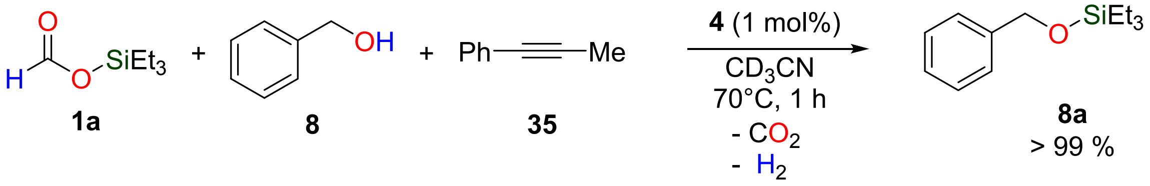


Figure S6: Silylation of benzyl alcohol in the presence of 1 equiv. of 1-phenyl-1-propyne (**35**).

In conclusion, with the exception of the aldehyde functional group, the dehydrogenative silylation protocol is chemoselective of alcohols and phenols and tolerates various unsaturated or fragile functionalities introduced either in an intra- or intermolecular fashion.

6. Competitive silylation of primary and secondary alcohols

In order to evaluate the relative kinetics of silylation of primary and secondary alcohols, an intermolecular competition experiment was carried out between benzyl alcohol (**8**) and related 1-phenylethanol (**18**) with 1.2 molar equivalent of silyl formate **1a** (limiting reagent). With 1 mol% of complex **4**, the full conversion of **1a** was obtained after 30 min at 70 °C and the silyl ether **8a** was the major product formed in 88 % yield (relative to the initial amount of **8**). The dehydrogenative silylation of **18** was *ca.* 3 times slower and the protected secondary alcohol was only 32 % silylated.

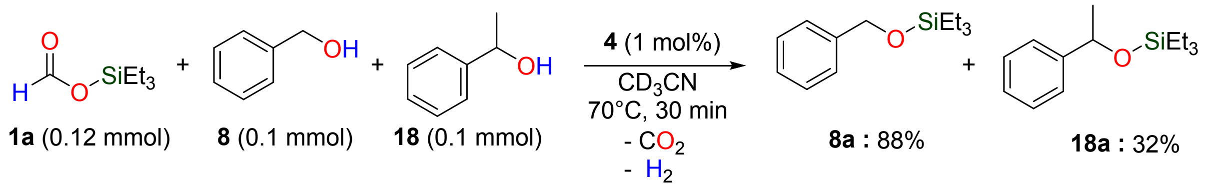


Figure S7: Competitive silylation of benzyl alcohol and 1-phenylethanol in the presence of triethylsilyl formate.

7. NMR spectra of isolated silyl ethers

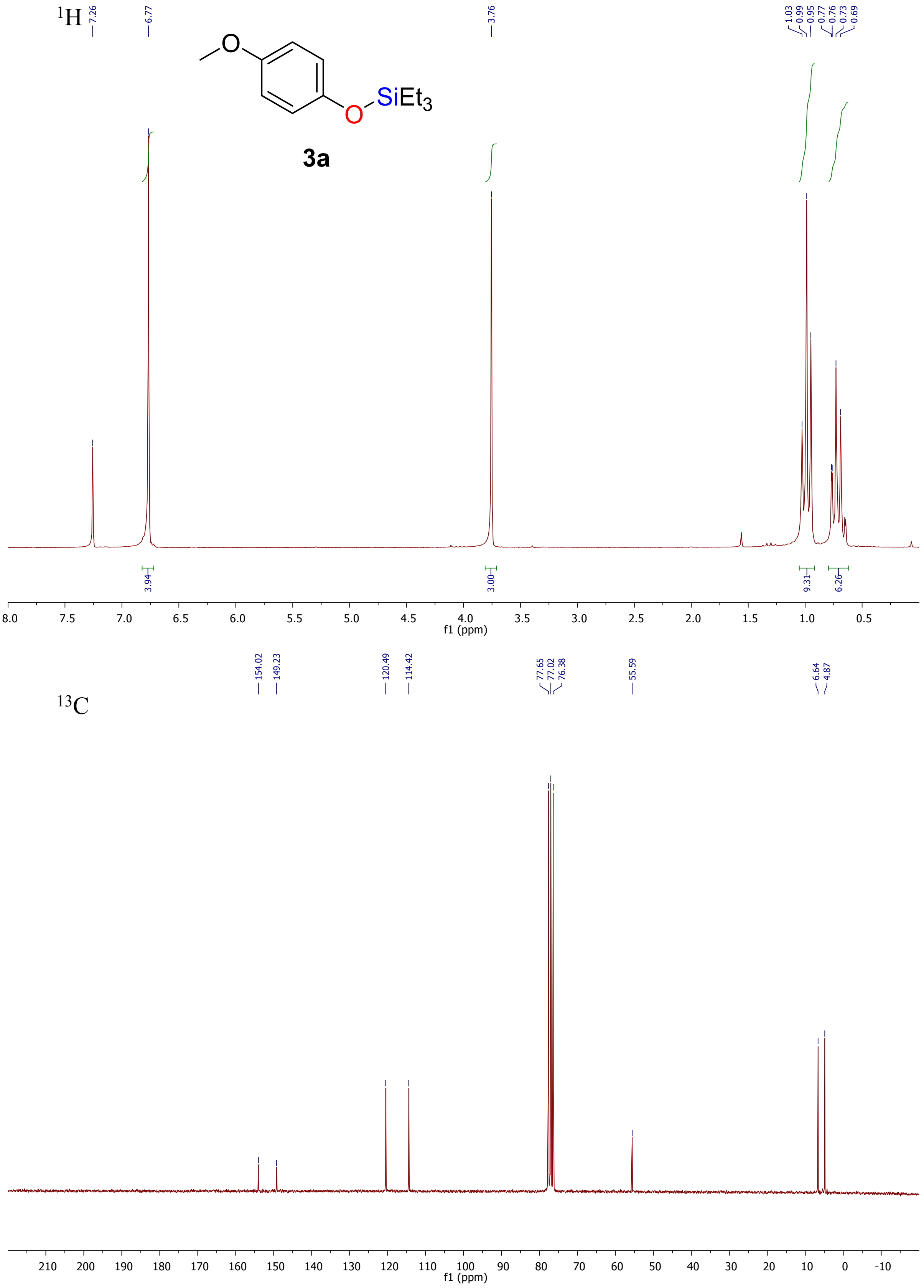


Figure S8: ^{1}H and ^{13}C NMR spectra of **3a** in $CDCl_3$

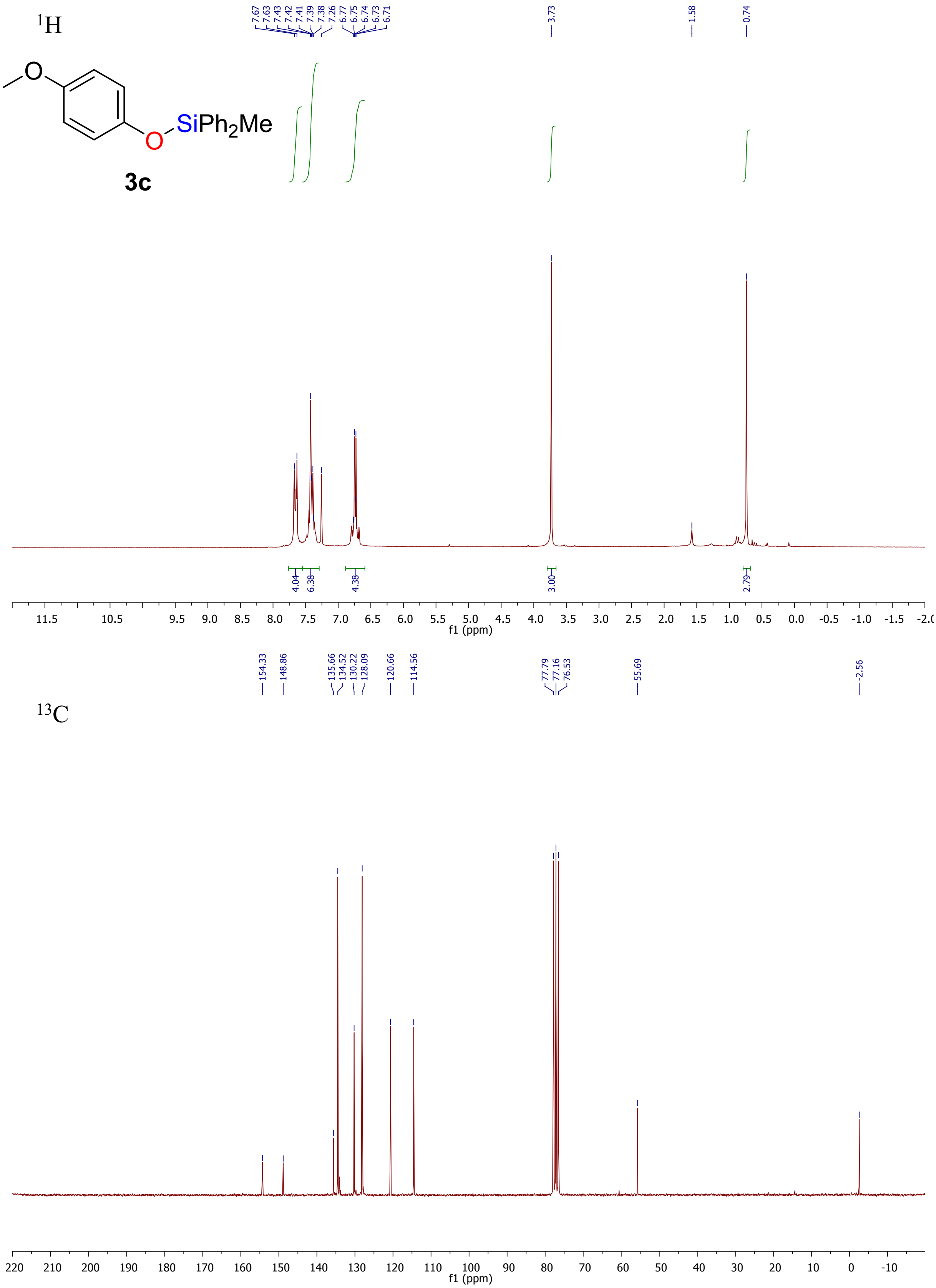
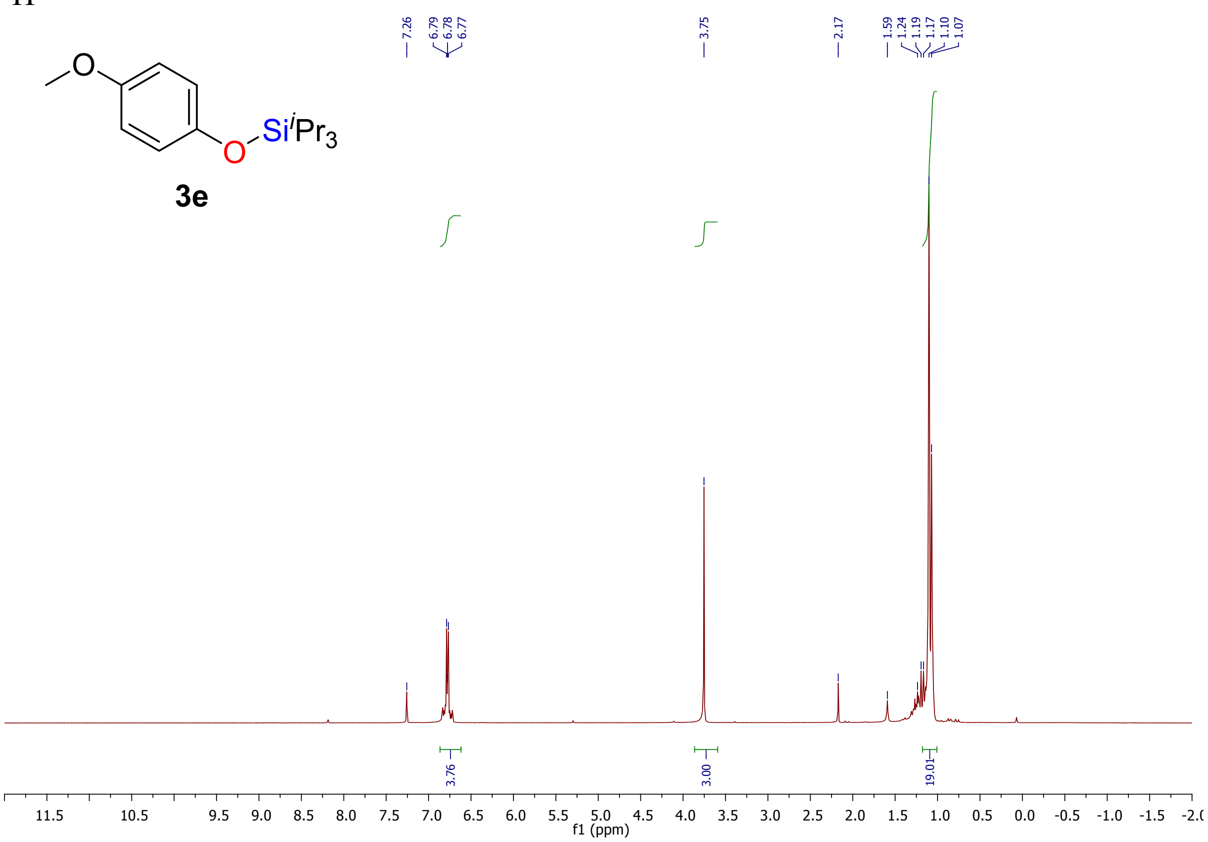


Figure S9: ^{1}H and ^{13}C NMR spectra of **3c** in $CDCl_3$

^{1}H



^{13}C

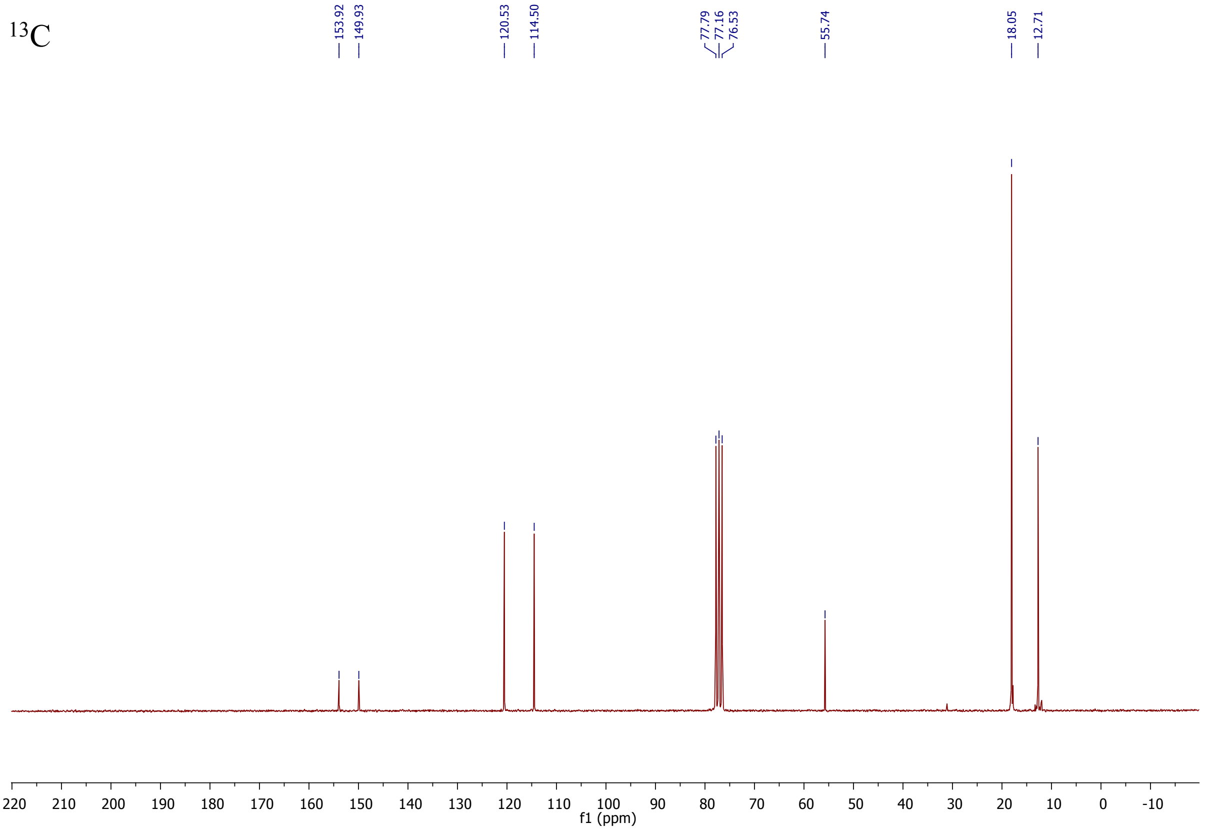


Figure S10: ^{1}H and ^{13}C NMR spectra of **3e** in CDCl$_3$

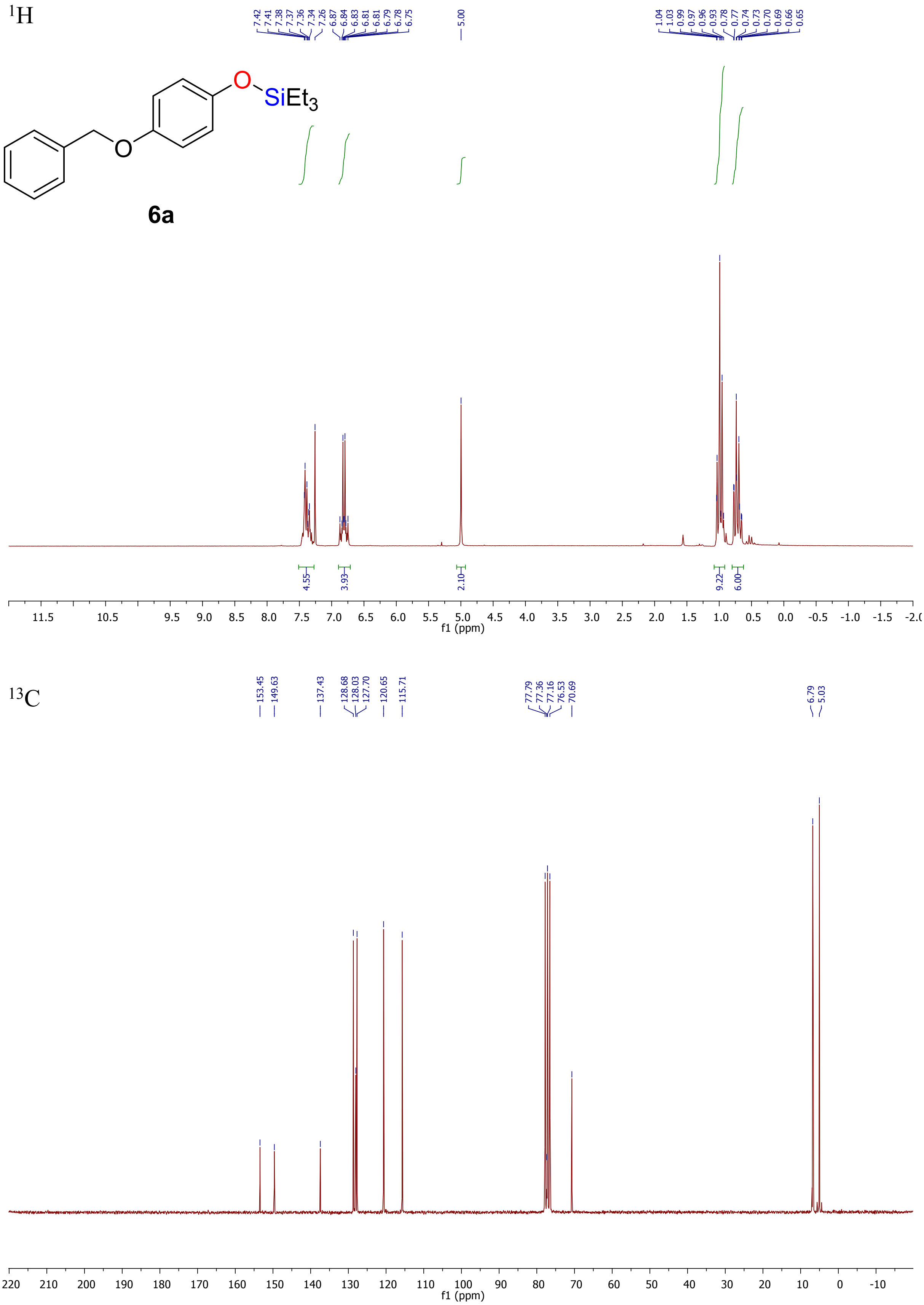


Figure S11: ^{1}H and ^{13}C NMR spectra of **6a** in $CDCl_3$

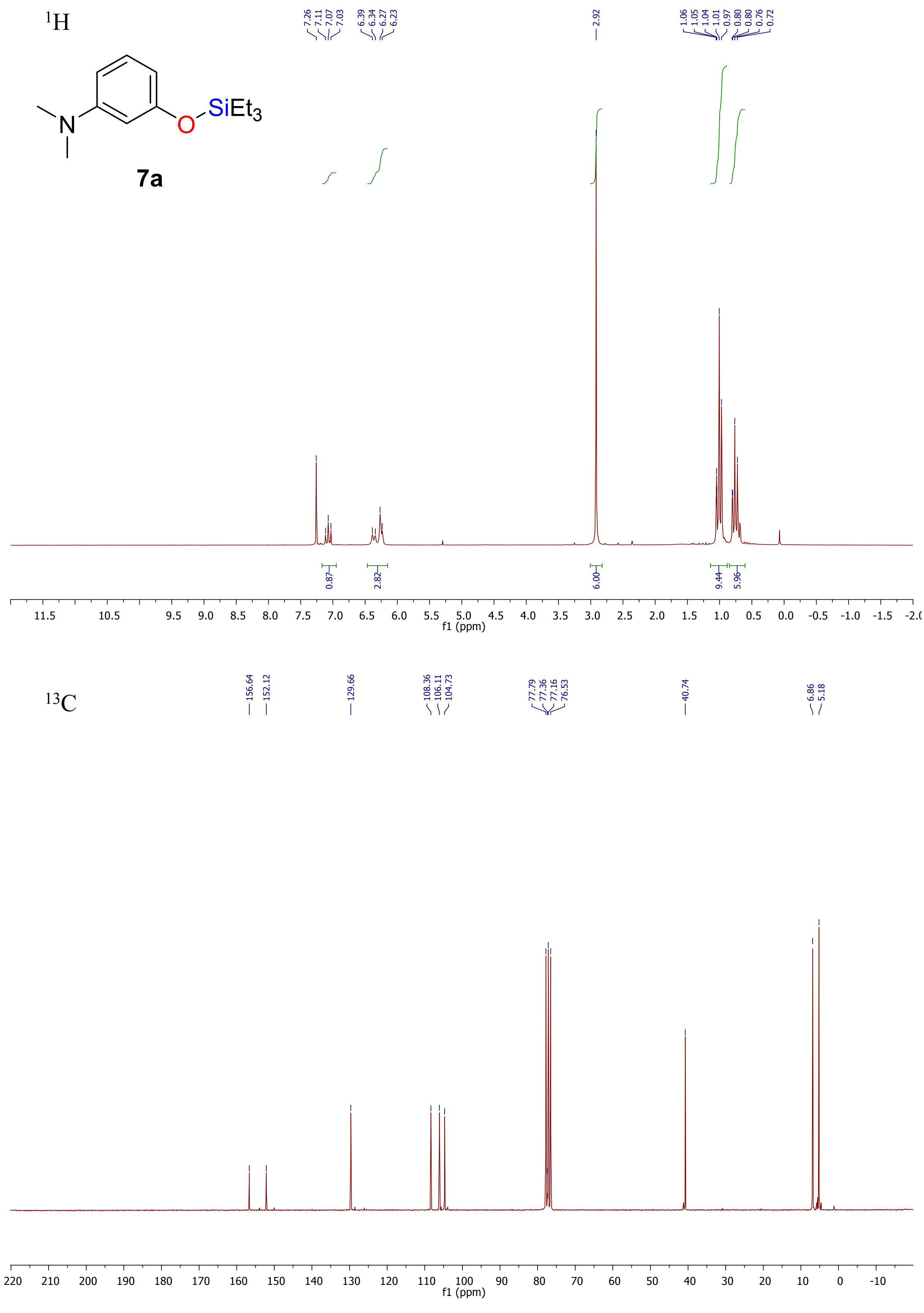


Figure S12: ^{1}H and ^{13}C NMR spectra of **7a** in CDCl$_3$

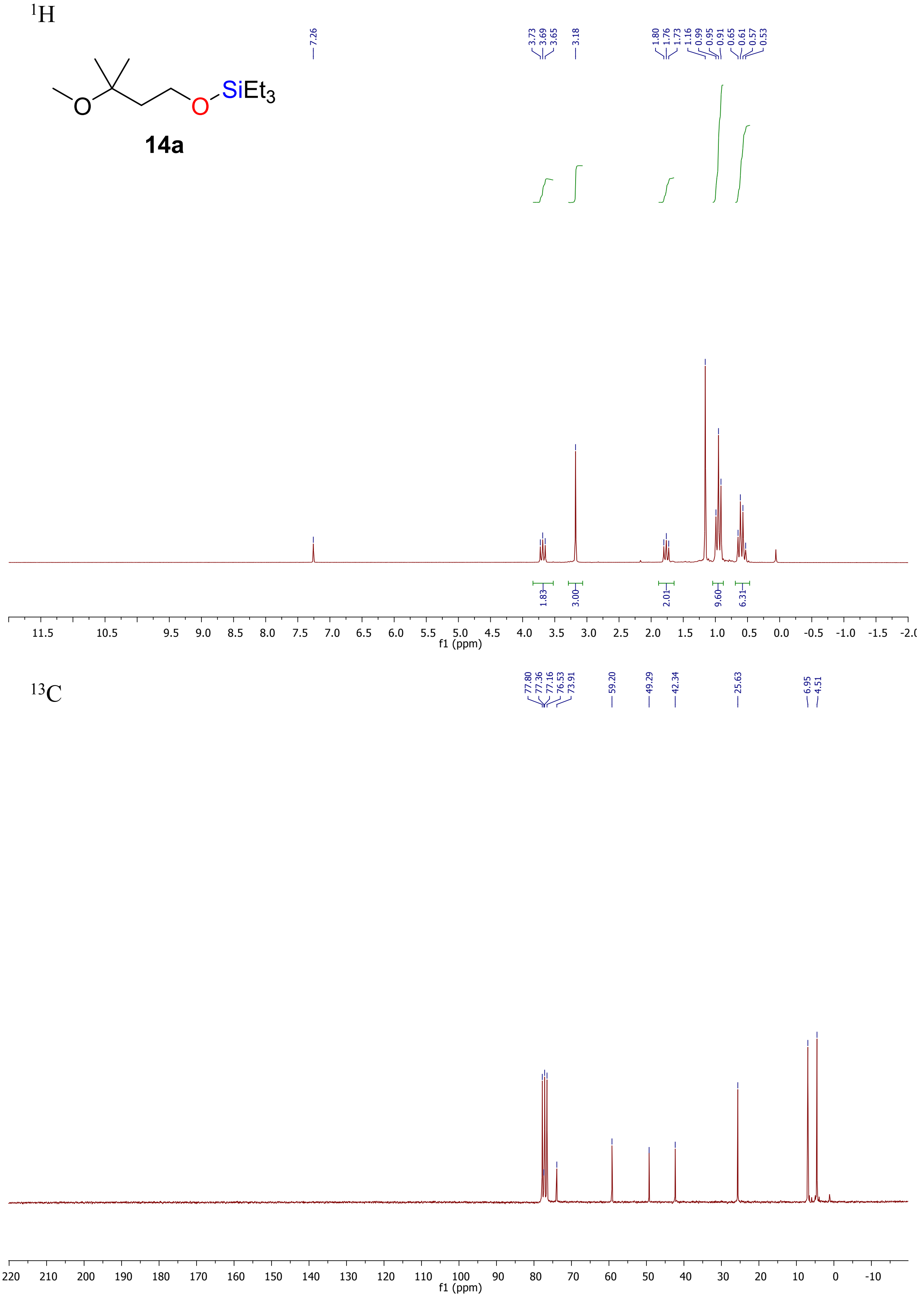


Figure S13: ^1H and ^{13}C NMR spectra of **14a** in $CDCl_3$

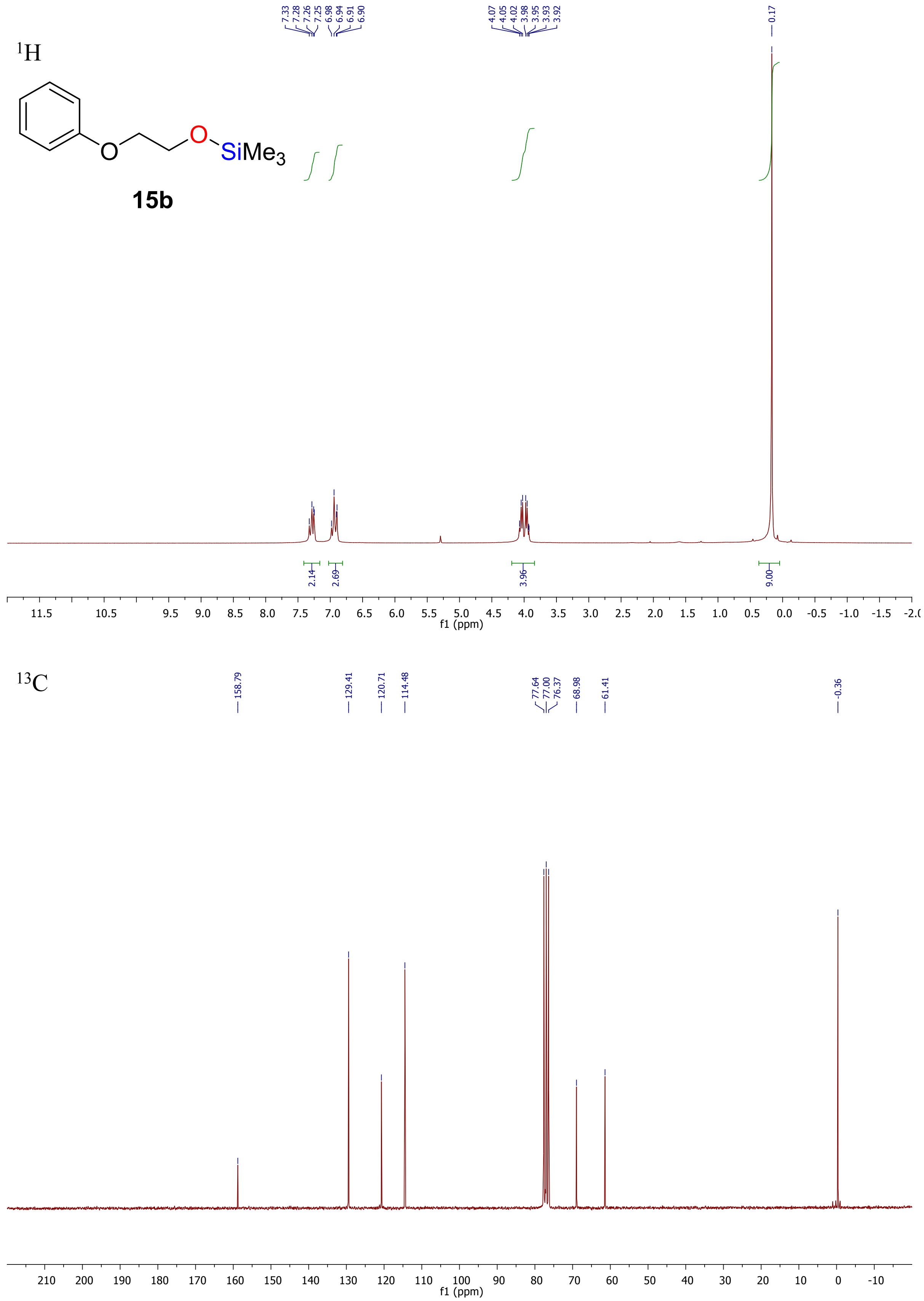


Figure S14: ^{1}H and ^{13}C NMR spectra of **15b** in $CDCl_3$

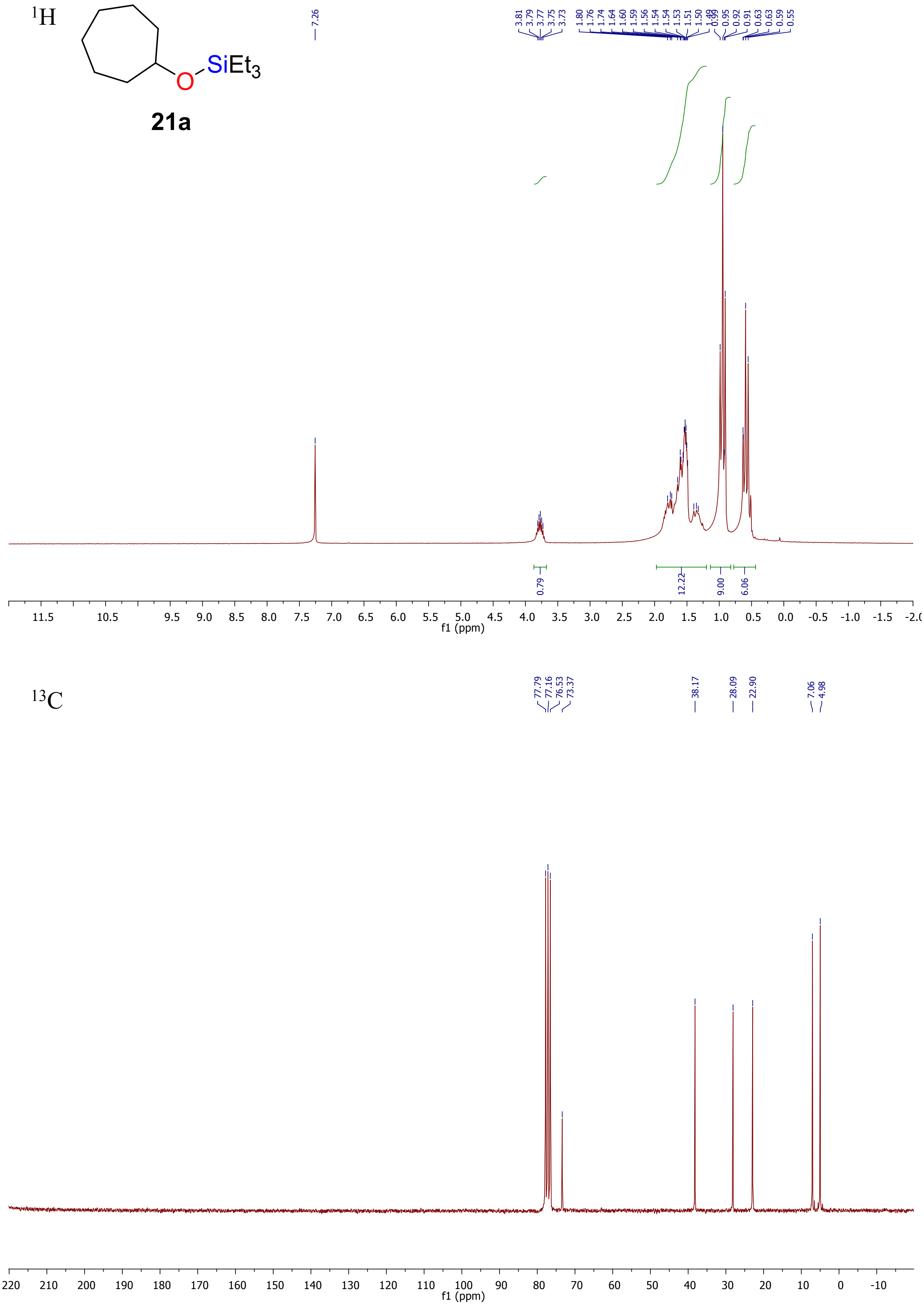


Figure S15: ^{1}H and ^{13}C NMR spectra of **21a** in CDCl$_3$

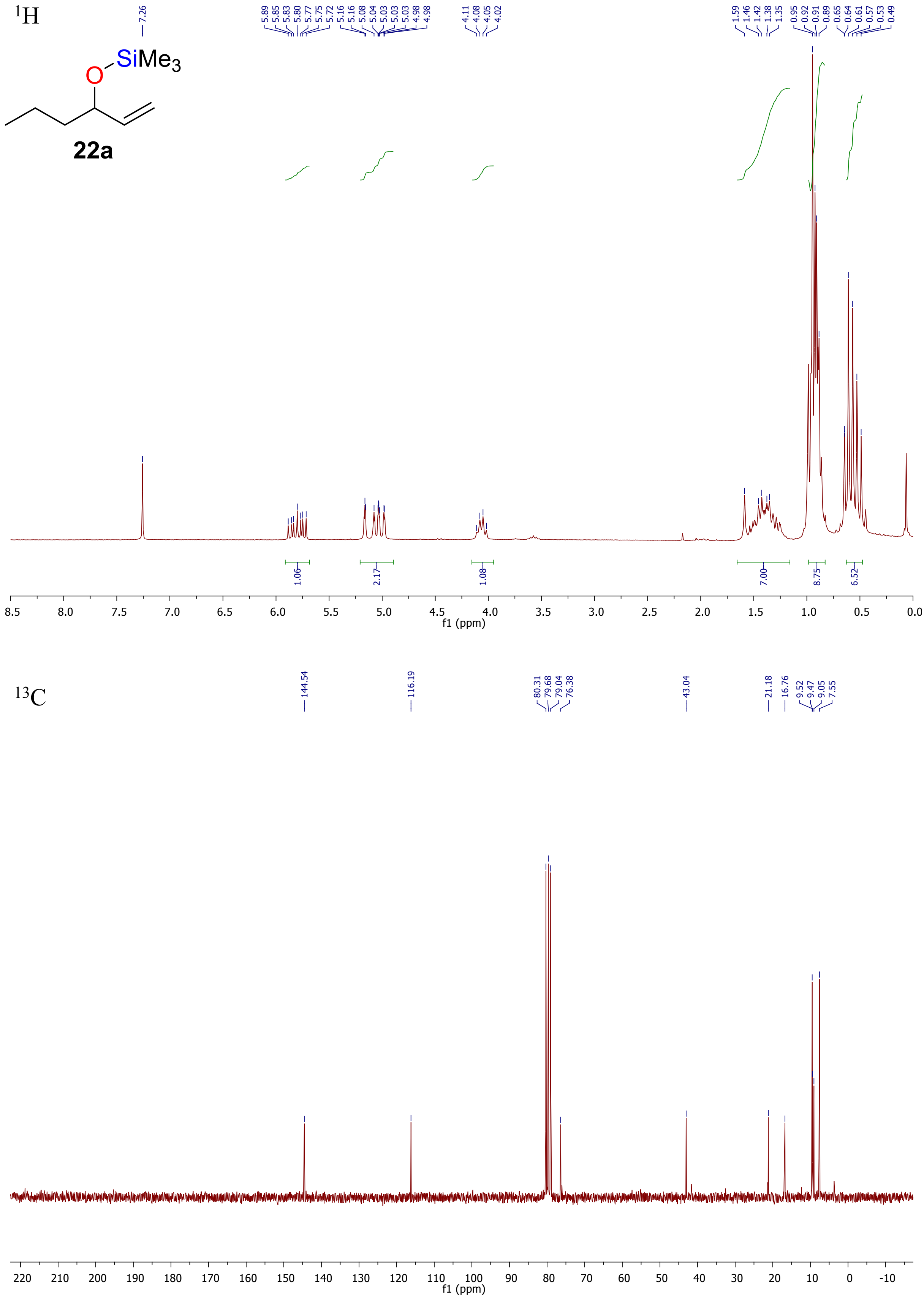


Figure S16: ^{1}H and ^{13}C NMR spectra of **22a** in $CDCl_3$

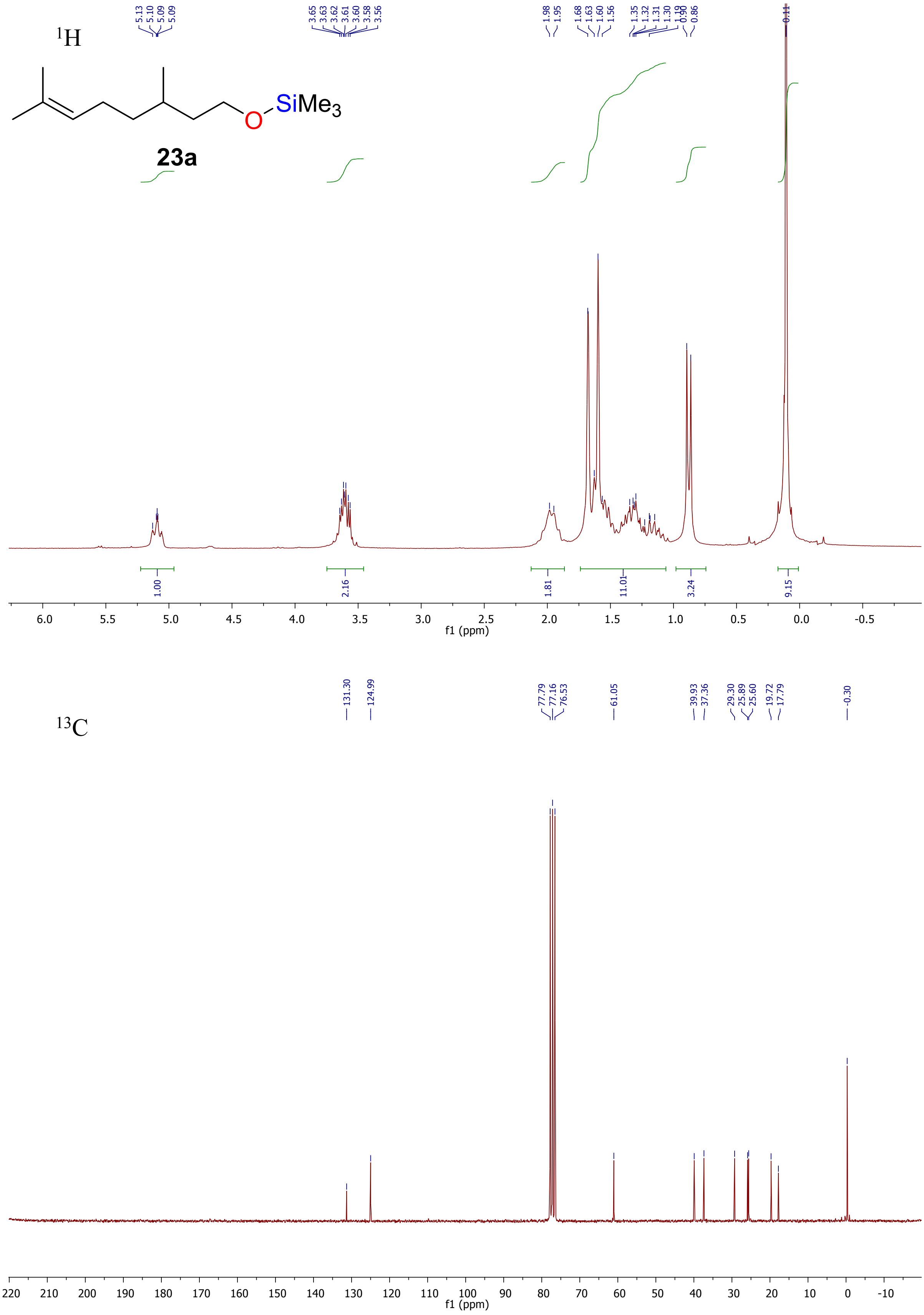
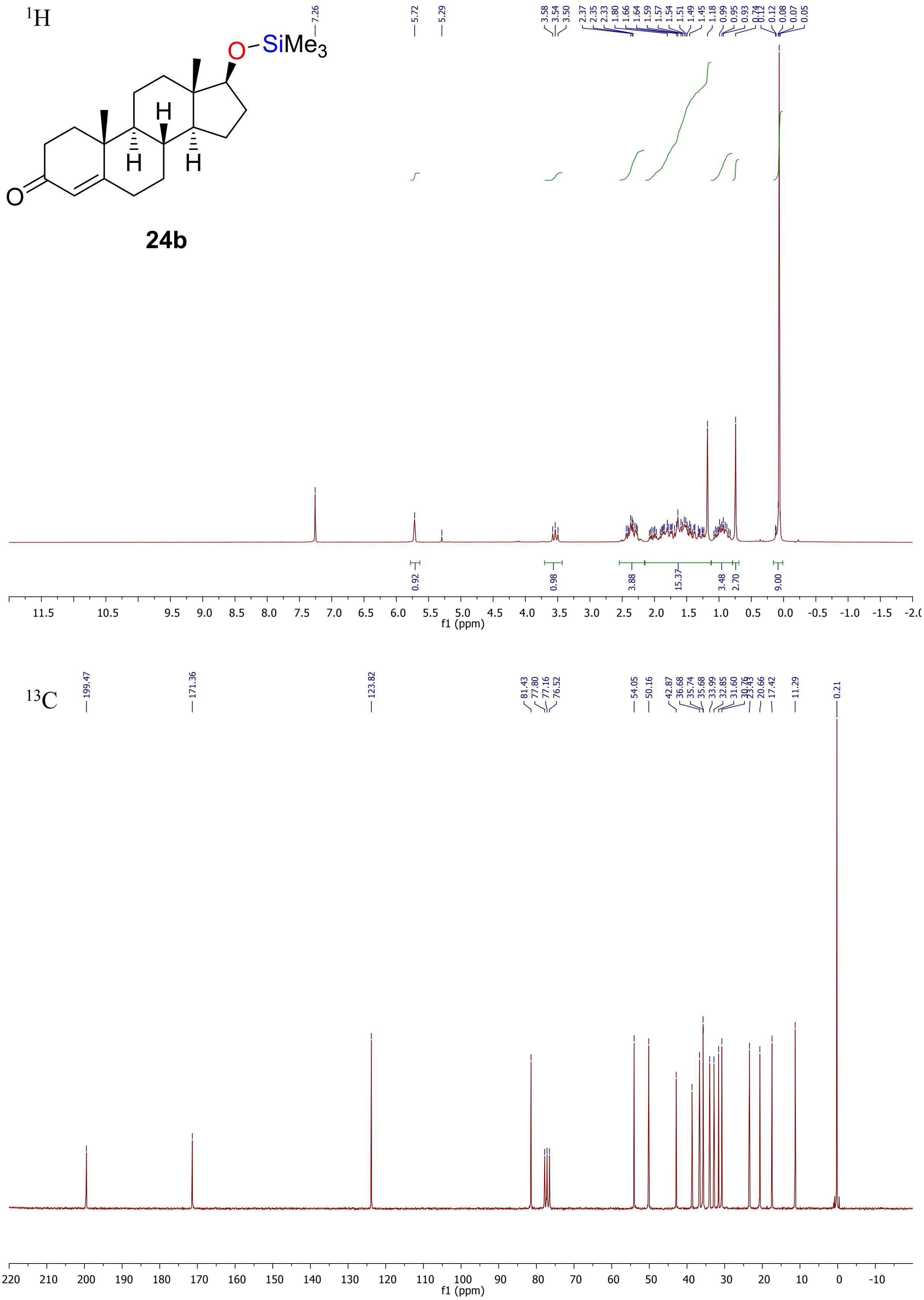
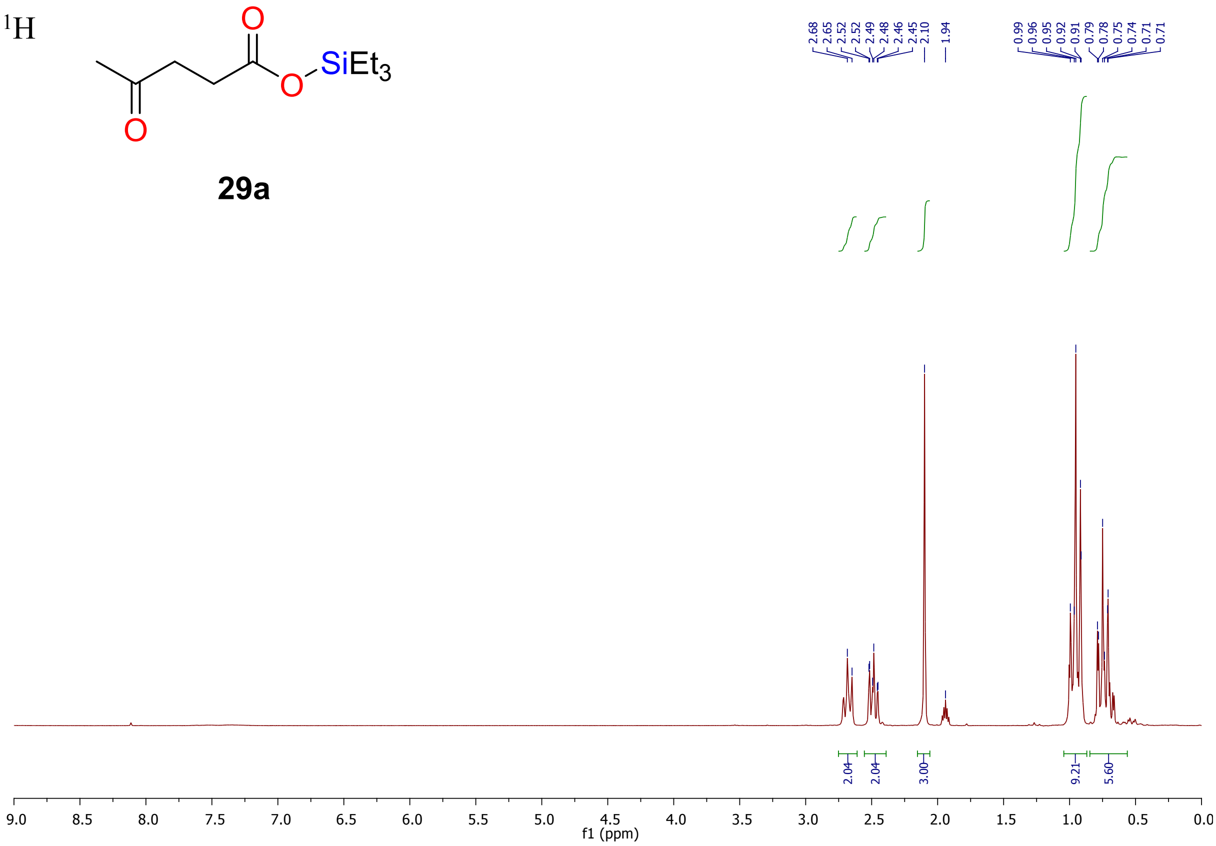


Figure S17: ^{1}H and ^{13}C NMR spectra of **23a** in $CDCl_3$



24b

Figure S18: ^{1}H and ^{13}C NMR spectra of **24b** in $CDCl_3$



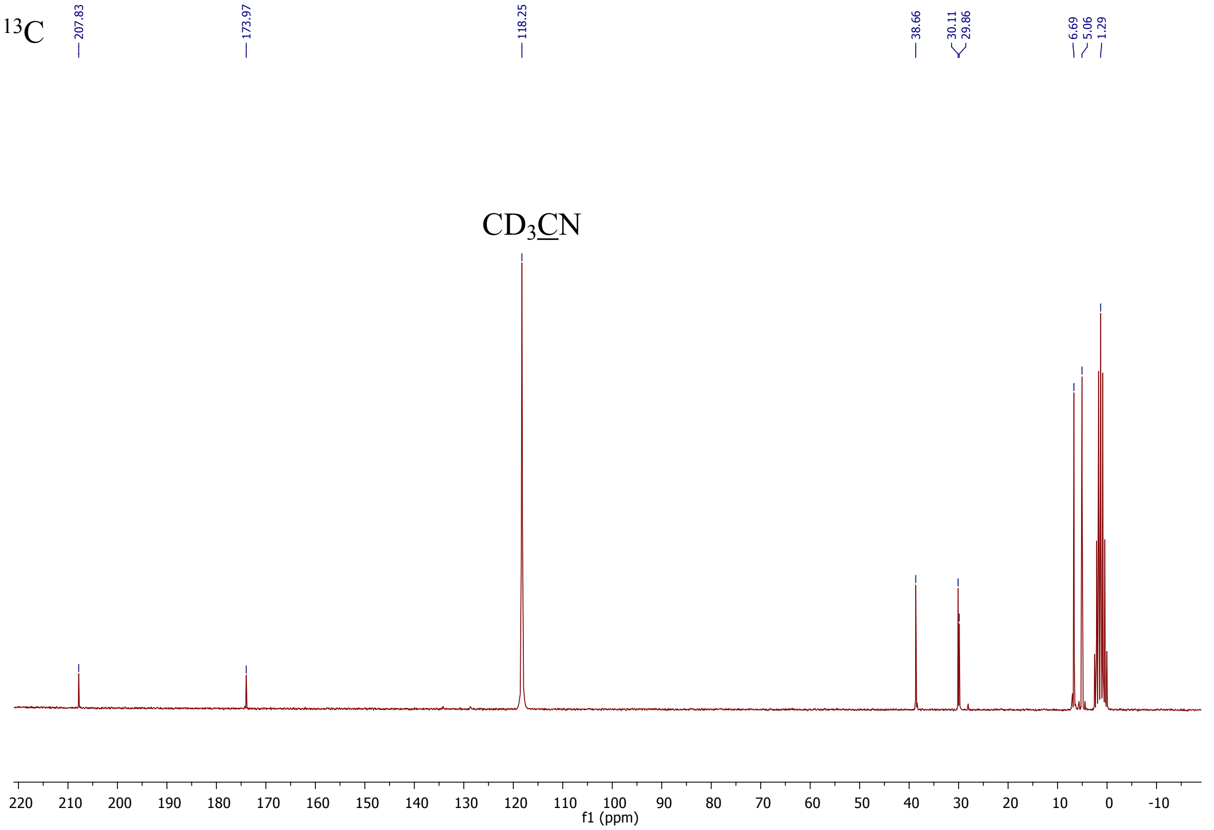
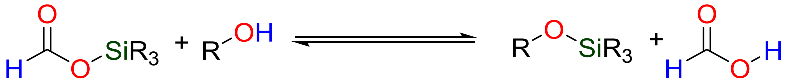


Figure S19: ^{1}H and ^{13}C NMR spectra of **29a** in CD_3CN

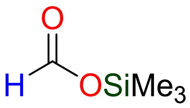
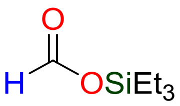
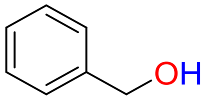
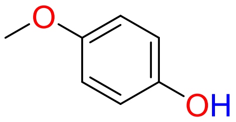
8. Experimental mechanistic investigations

a) Equilibrium between silylformates and silylethers

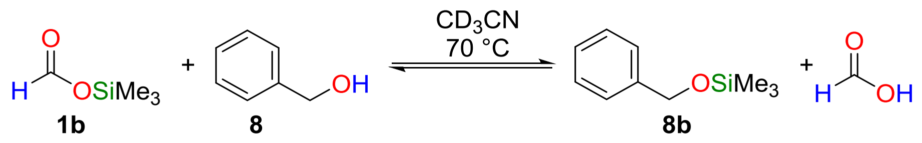


In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with the alcohol (0.1 mmol, 1 equiv.) and d_3-MeCN (0.4 mL, $C = 0.25$ M). To the resulting homogeneous solution was added the silyl formate reagent (0.1 mmol, 1 equiv.). The NMR tube was then sealed and immersed in a pre-heated oil bath at 70 °C (oil temperature), leading to the partial displacement of the formate anion by an alkoxide anion at the silicon center. The equilibrium was reached after 7 days (ca. 170 h) at 70 °C (see figure S24) and the corresponding $K^0_{(343K)}$ equilibrium constants (Table 2) were calculated based on the equilibrium concentrations as determined from NMR spectroscopy (representative spectra are reported in Figures S20-S23). The equilibrium constants are reported at 343 K though the NMR measurement were made at room temperature because of the slow kinetics of the equilibration process (see Figure S24).

Table 2: Equilibrium constants (K^0_{343}) between alcohols and silylformates at 70 °C in acetonitrile.

		
	6.6	5.0
	2.4	1.7

Equilibrium mixture obtained after mixing benzyl alcohol (**8**) and trimethylsilyl formate (**1b**).



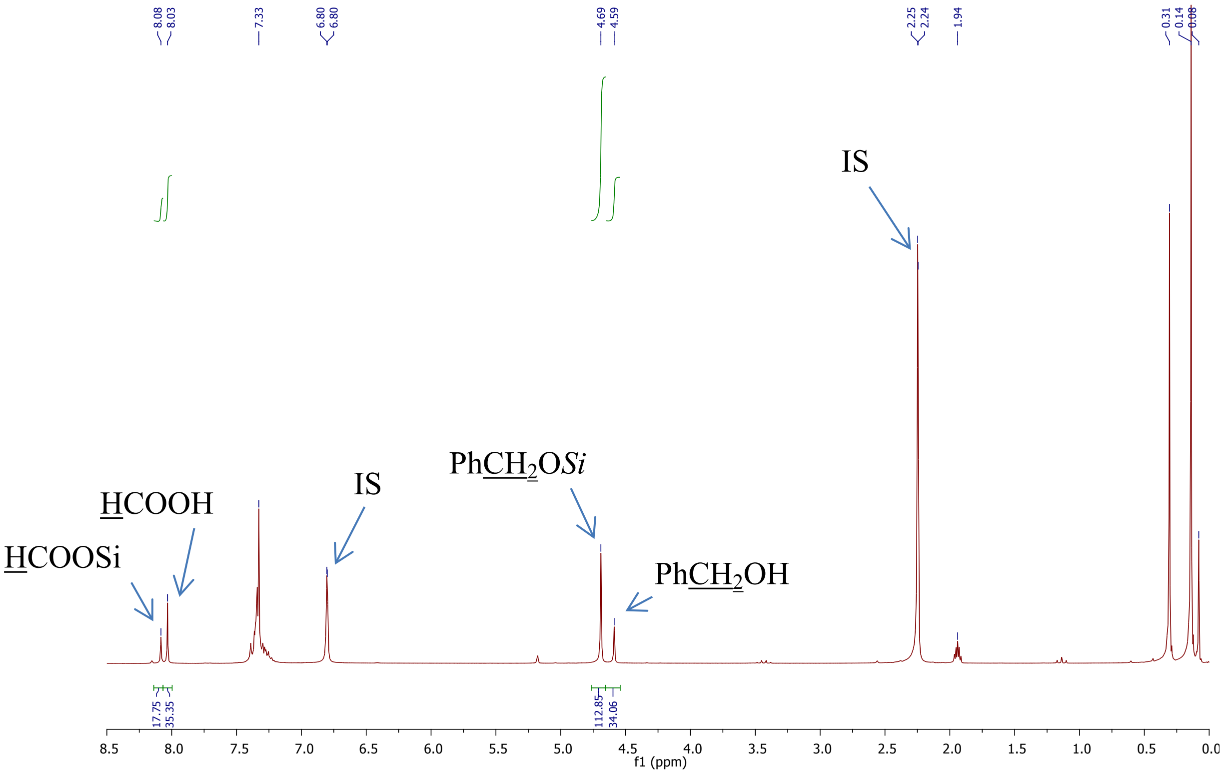
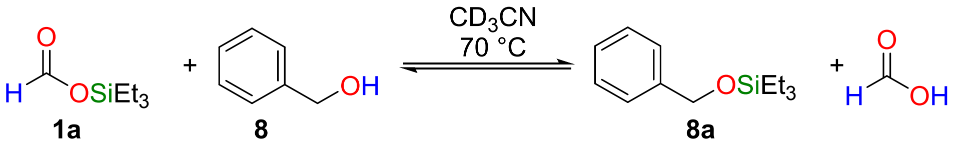


Figure S20: ^{1}H NMR spectrum of the reaction between trimethylsilyl formate (**1b**) and benzyl alcohol after 7 days at 70 °C (relaxation delay (d_1) of 60 sec.). (IS = internal standard, mesitylene)

Equilibrium mixture obtained after mixing benzyl alcohol (**8**) and triethylsilyl formate (**1a**).



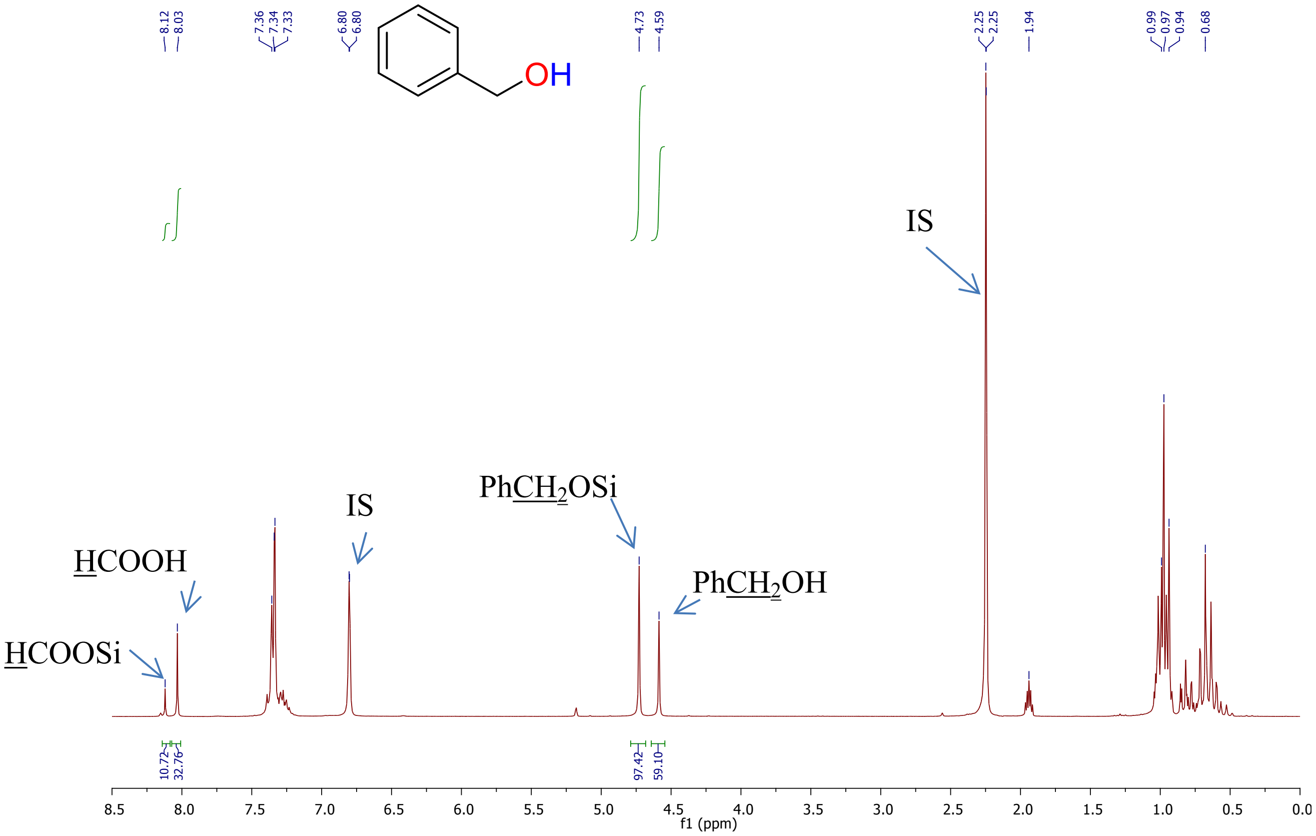
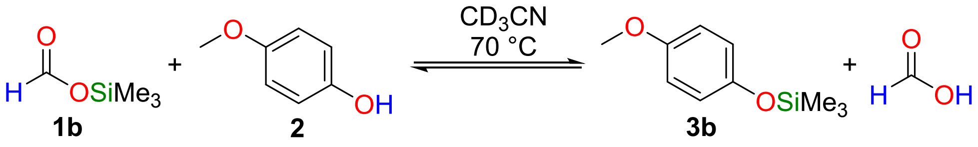


Figure S21: ^{1}H NMR spectrum of the reaction between triethylsilyl formate (**1a**) and benzyl alcohol after 7 days at 70 °C (relaxation delay (d_1) of 60 sec.). (IS = internal standard, mesitylene)

Equilibrium mixture obtained after mixing 4-methoxyphenol (**2**) and trimethylsilyl formate (**1b**).



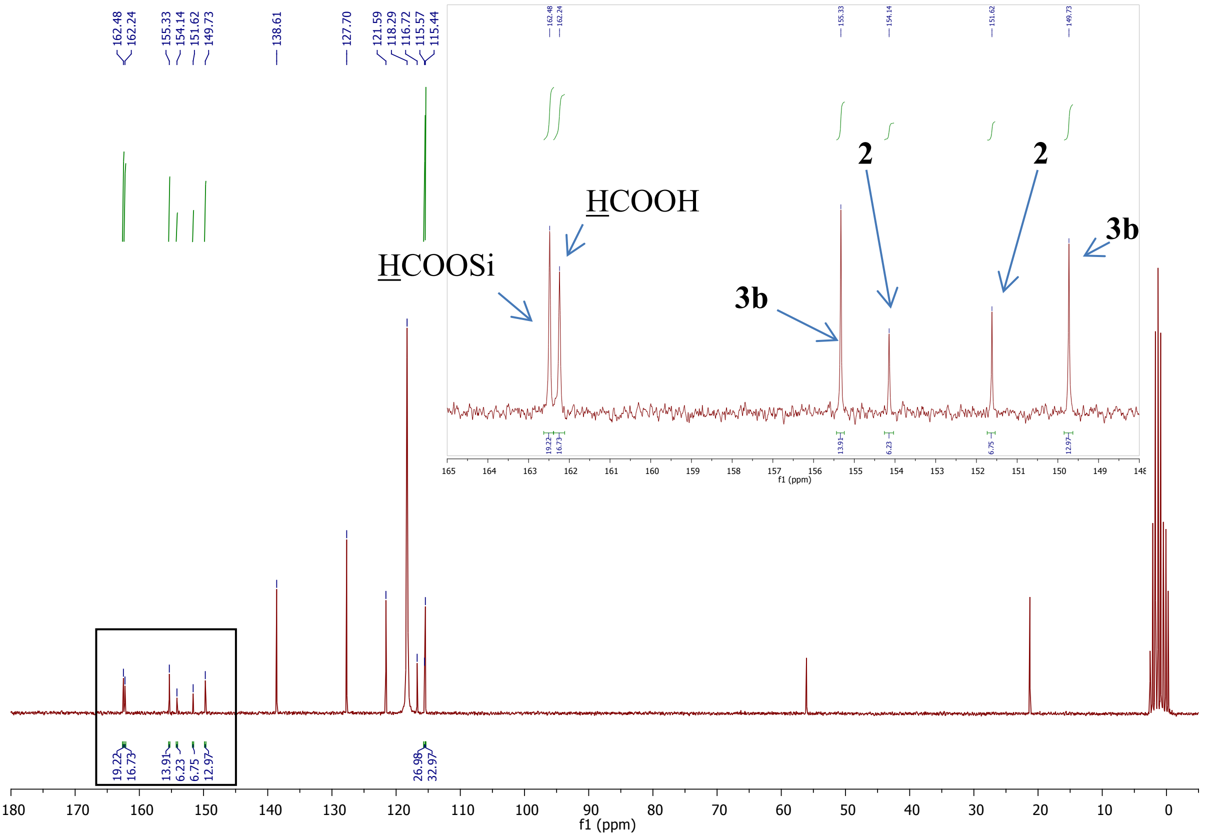
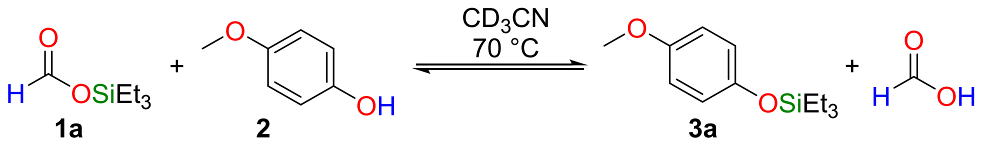


Figure S22: ^{13}C NMR spectrum of the reaction between trimethylsilyl formate (**1b**) and 4-methoxyphenol (**2**) after 7 days at 70 °C (relaxation delay (d_1) of 100 sec.). (IS = internal standard, mesitylene)

Equilibrium mixture obtained after mixing 4-methoxyphenol (**2**) and triethylsilyl formate (**1a**).



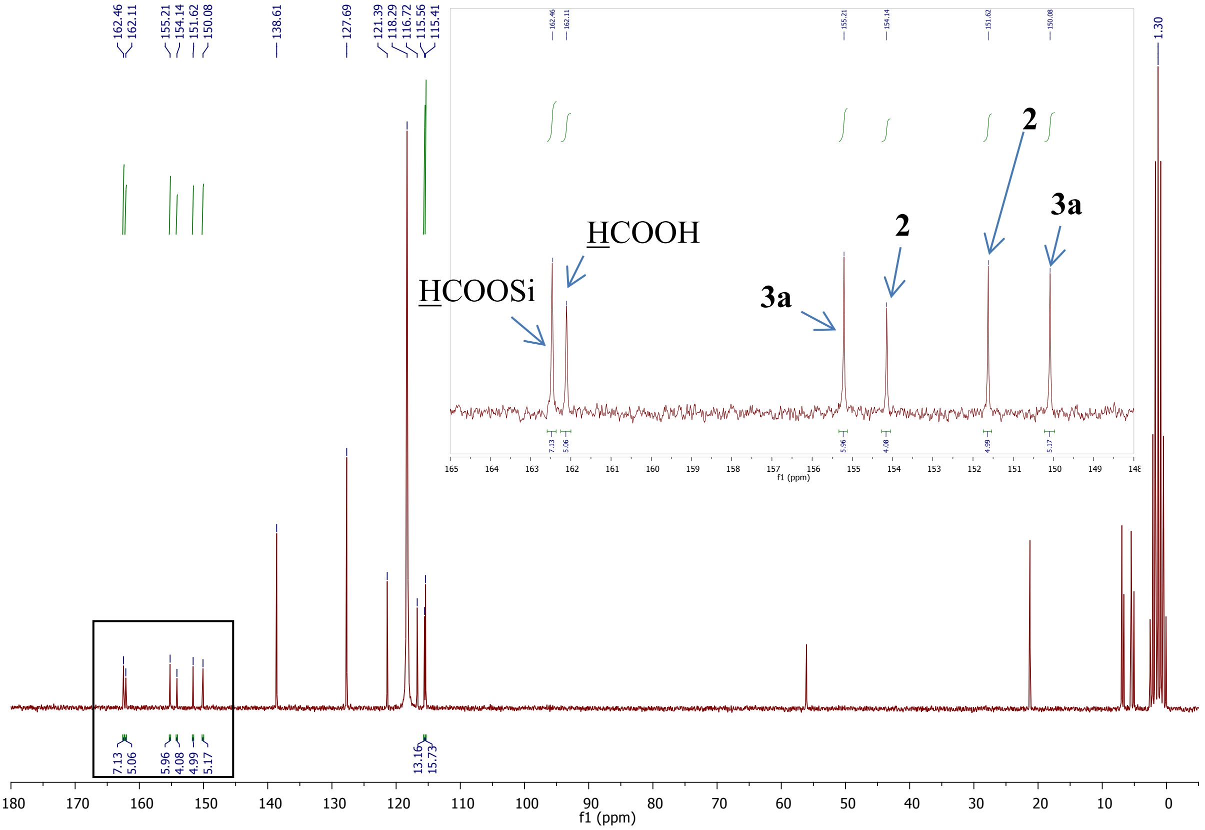


Figure S23: ^{13}C NMR spectrum of the reaction between triethylsilyl formate (**1a**) and 4-methoxyphenol (**2**) after 7 days at 70 °C (relaxation delay (d_1) of 100 sec.). (IS = internal standard, mesitylene)

b) Kinetic studies

For the kinetic investigations, in a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with 4-methoxyphenol (**2**) (0.1 mmol, 1 equiv.) followed by d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous solution was added the silyl formate (**1a**) (0.14 mmol, 1.4 equiv.). The tube was then sealed, brought out of the glovebox and the reaction was monitored regularly by ^{1}H NMR (relaxation delay d_1 set to 30 sec). In the event that heating was required, the tube was immersed in a pre-heated oil bath at 70 °C (oil temperature) and brought out of the oil bath during the time of the analysis (time not added to the heating time).

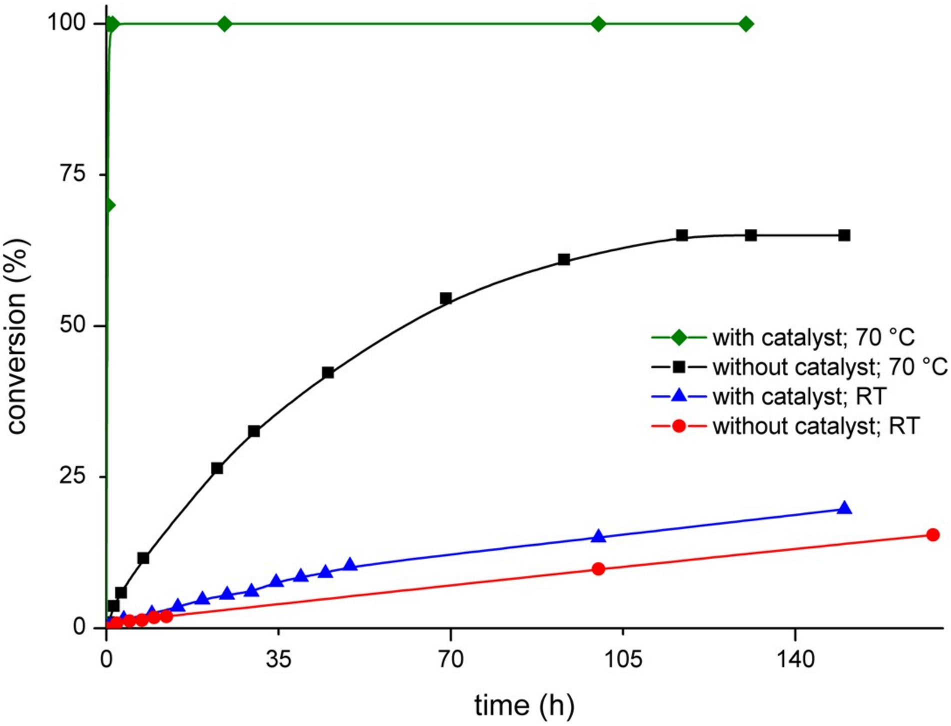
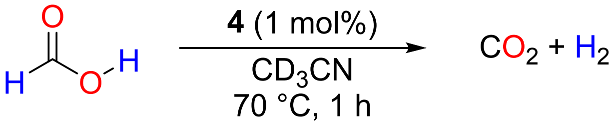


Figure S24: Influence of the temperature and the catalyst on the equilibrium between silylformates and silylethers

c) Decomposition of formic acid (HCO_2H) catalyzed by complex 4

CAUTION: *Full decomposition of formic acid in a sealed tube generates a high internal pressure.*



In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (0.9 mg, 1 µmol, 1 mol%,) followed by d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous yellow solution were added formic acid (3.8 µL, 0.1 mmol, 1 equiv.) and mesitylene (10 µL, 0.072 mmol) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). The NMR tube was periodically cooled down to RT and the reaction was monitored by NMR spectroscopy. The full conversion of formic acid was reached after 1 h at 70 °C (Figure S25).

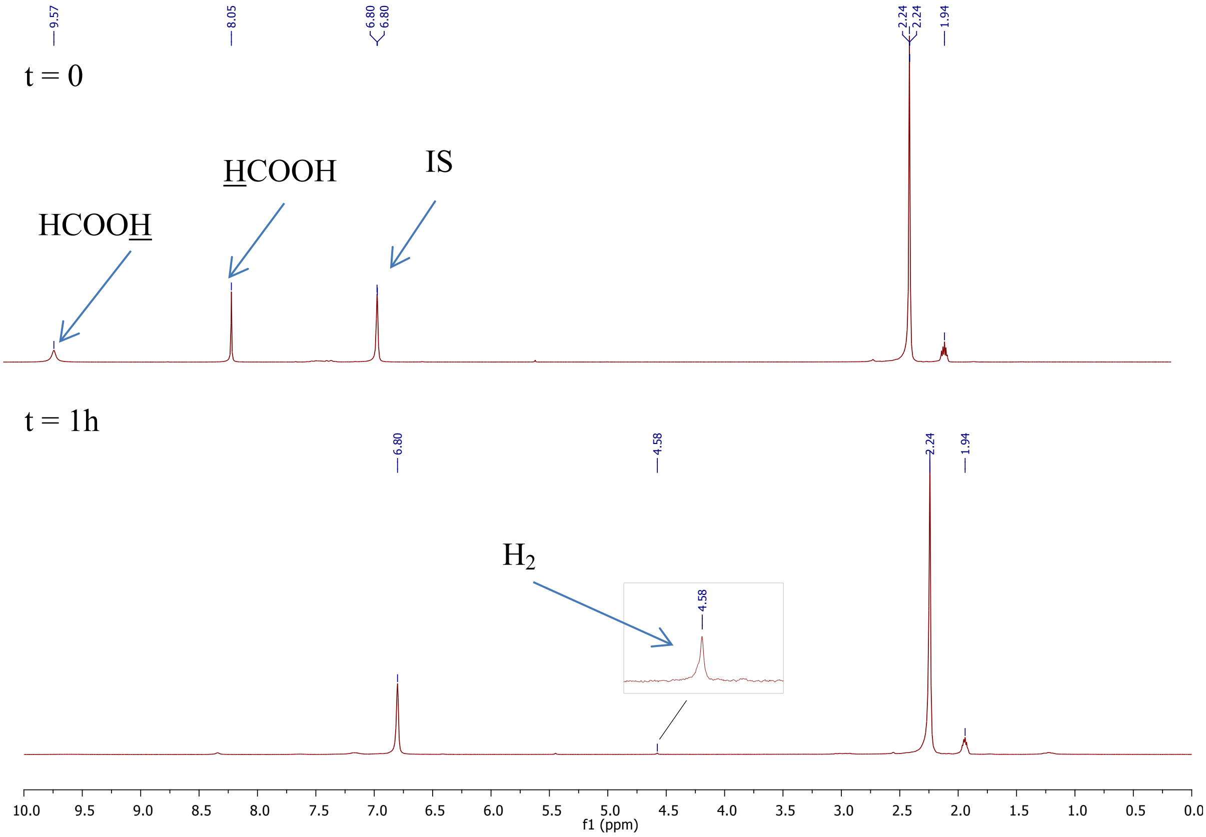
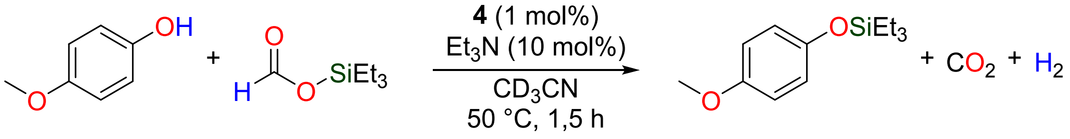


Figure S25: Crude of reaction at t = 0 (up) and t = 1 h at 70 °C (bottom)

d) Reaction between triethylsilyl formate and 4-(methoxy)phenol in presence of Et_3N



2 **1a** **3a**

In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (0.9 mg, 1 µmol, 1 mol%,) and d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous yellow solution were sequentially added the 4-methoxyphenol (**2**) (12.4 mg, 0.1 mmol, 1 equiv.), triethylsilyl formate (**1a**) (25 µL, 0.14 mmol, 1.4 equiv.), triethylamine (10.4 µL, 0.01 mmol, 10 mol%) and mesitylene (10 µL, 0.072 mmol) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 50 °C (oil temperature). The reaction was complete after 1.5 h, whereas 3 h are required in the absence of triethylamine.

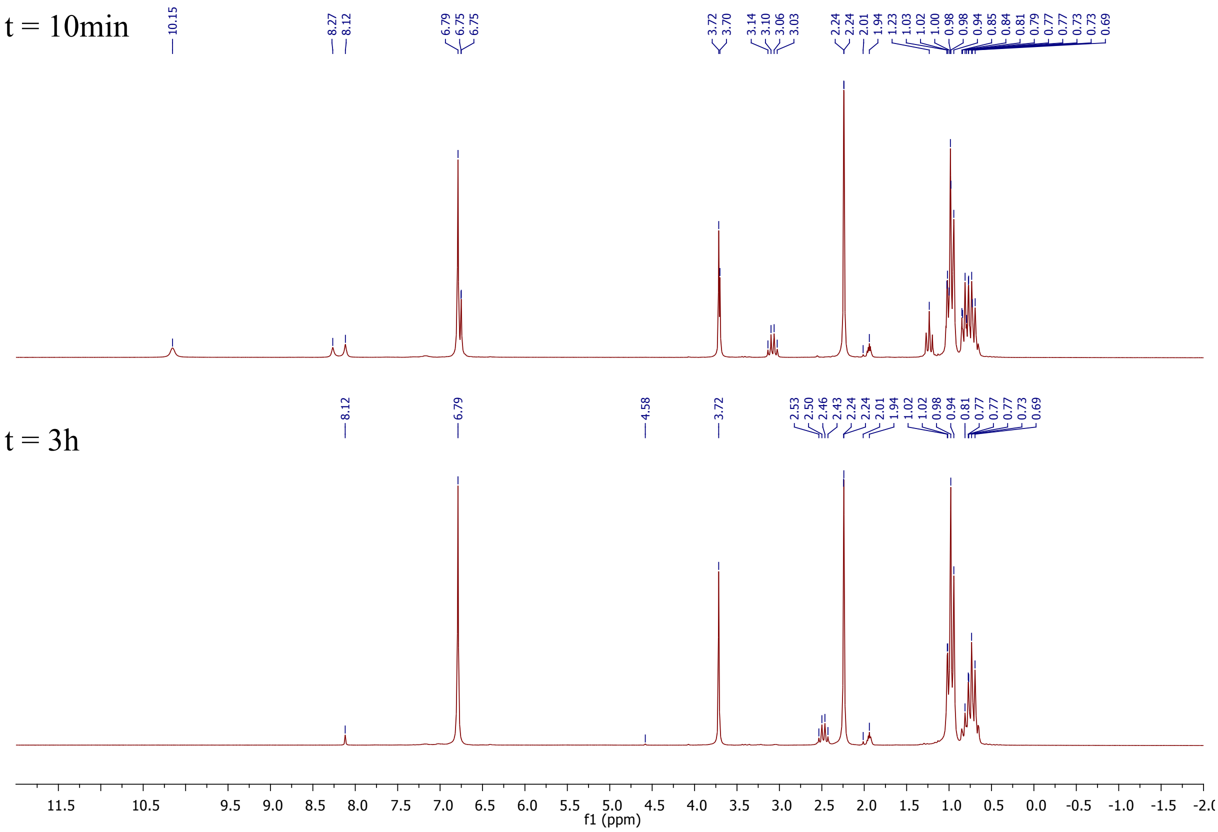
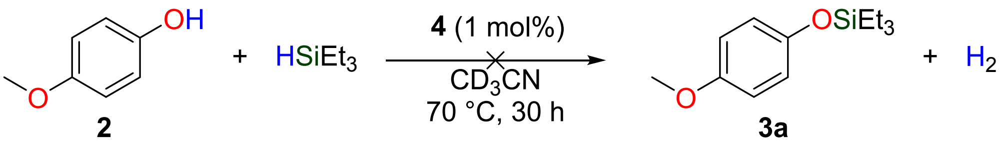


Figure S26: Crude NMR spectra (^1H) after 10 min at room temperature (top) and after 3 h at 50 °C (bottom) for the silylation of **2** with **1a**, in the presence of 1 mol% **4**.

Note that in the presence of a catalytic amount of triethylamine (TEA), the equilibrium between free phenol (**2**) and the corresponding silyl ether (**3a**) is reached almost instantaneously at room temperature. The basicity of TEA may indeed be highly beneficial to catalyse the proton transfer between the free alcohol and the silyl formate, which is otherwise very slow (see Fig. S24, red curve) at RT. As a consequence, care must be taken to avoid trace amount of basic impurities for mechanistic investigations.

e) Reaction of triethylsilane with 4-methoxyphenol



In a glovebox, a flame-dried 2.5-mL NMR tube equipped with a J-Young valve was charged with [Ru(κ^1-OAc)(κ^2-OAc)(κ^3-triphos)] (**4**) (0.9 mg, 1 µmol, 1 mol%) and d_3-MeCN (0.4 mL, C = 0.25 M). To the resulting homogeneous yellow solution were sequentially added 4-methoxyphenol (**2**) (12.4mg, 0.1 mmol, 1 equiv.), triethylsilane (24µL, 0.15mmol, 1.5 equiv.) and mesitylene (10 µL, 0.072mmol) as an internal standard. The tube was then sealed, brought out of the glovebox and immersed in a pre-heated oil bath at 70 °C (oil temperature). No reaction was noted and the reagents were recovered unreacted after 30 h at 70 °C, thereby showing that the catalytic system is unable to perform the dehydrogenative silylation of **2** with hydrosilanes.

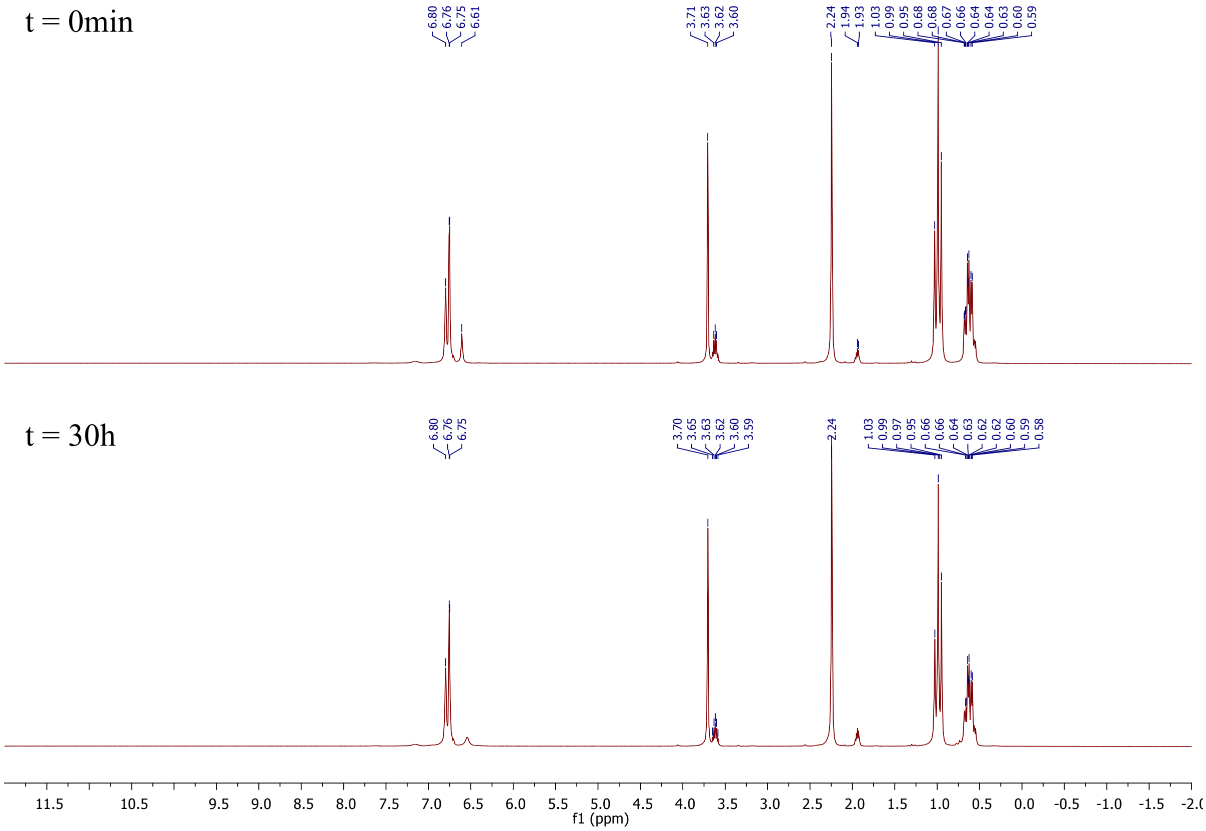


Figure S27: Crude NMR spectra (^{1}H) after 10 min at room temperature (top) and after 30 h at 70 °C (bottom) for the tentative silylation of **2** with $HSiEt_3$, in the presence of 1 mol% **4**.

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