Supporting Information

Manganese and Rhenium-catalyzed Selective Reduction of Esters to Aldehydes with Hydrosilanes

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1. General information

All reagents were obtained from commercial sources and used as received. All manipulations were performed with dried glassware using standard Schlenk techniques under an inert atmosphere of dry argon. Technical grade petroleum ether and ethyl acetate were used for column chromatography. Toluene, THF, pentane, and dichloromethane were dried over a LabSolv (Innovative Technology) solvent purification system and degassed by thaw-freeze cycle. Analytical TLC was performed on Merck $^{60}F_{254}$ silica gel plates (0.25 mm thickness). Column chromatography was performed silica gel (mesh size 40-63 μm, 60 Å).

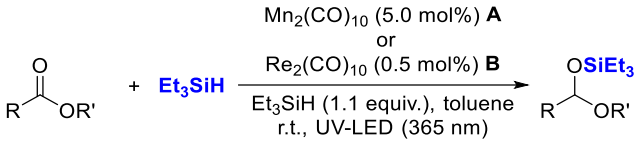
^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ at 298 K unless otherwise stated, on Bruker, AVANCE 400 and AVANCE 300 spectrometers. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were calibrated using the residual solvent signal as internal standard (^{1}H: $CDCl_3$ 7.26 ppm, C_6D_6 7.16 ppm ^{13}C: $CDCl_3$, central peak is 77.16 ppm C_6D_6 128.06 ppm). Chemical shift (δ) and coupling constants (*J*) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet, and br. for broad).

$Mn_2(CO)_{10}$, $Mn(CO)_5Br$, $CpMn(CO)_3$, $Re_2(CO)_{10}$ and $Re(CO)_5Br$ were purchased from Strem Chemicals.

High-resolution mass spectra were obtained using a Xevo G2 QTof (Waters) spectrometer (ESI positive mode) or GCT Premier (Waters) spectrometer (DCI-CH_4). Low-resolution mass spectra were obtained using a DSQ (Thermo Fisher Scientific) spectrometer (DCI-NH_3). Analysis were carried out by the corresponding facilities at the Institut de Chimie de Toulouse (ICT FR2599).

Irradiation were performed using a Rayonet RPR100 apparatus equipped with UV lamps (350 nm), a medium pressure mercury lamp (150 W) or homemade system equipped with 4*10W LEDs (365 nm).

2. Typical procedure for $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ catalyzed hydrosilylation of esters



Typical 0.5 mmol scale hydrosilylation reaction:

$Mn_2(CO)_{10}$ (9.7 mg, 5.0 mol%) (method **A**) or $Re_2(CO)_{10}$ (1.6 mg, 0.5 mol%) (method **B**) was charged in a 20 ml Schlenk tube under argon atmosphere, followed by toluene (1 mL), carboxylic ester (0.5 mmol), Et_3SiH (88 µL, 0.55 mmol, 1.1 equiv.), then the Schlenk tube was stirred at room temperature under UV-LED irradiation (365 nm, 4*10 W) for 9 h. The crude solution was then diluted with ethyl acetate (2.0 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with ethyl acetate (2×2.0 mL). The filtrate was evaporated and the crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent) to afford the desired product.

Typical 1 mmol scale hydrosilylation reaction:

$Mn_2(CO)_{10}$ (19.4 mg, 5.0 mol%) (method **A**) or $Re_2(CO)_{10}$ (3.2 mg, 0.5 mol%) (method **B**) was charged in a 20 ml Schlenk tube under argon atmosphere, followed by toluene (1 mL), carboxylic ester (1 mmol), Et_3SiH (176 µL, 1.1 mmol, 1.1 equiv.), then the Schlenk tube was stirred at room temperature under UV-LED irradiation (365 nm, 4*10 W) for 9 h. The crude solution was then diluted with ethyl acetate (2.0 mL) and filtered through a small pad of celite (2 cm in a Pasteur pipette). The celite was washed with ethyl acetate (2×2.0 mL). The filtrate was evaporated and the crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent) to afford the desired product.

Typical 1 mmol scale synthesis of aldehyde:

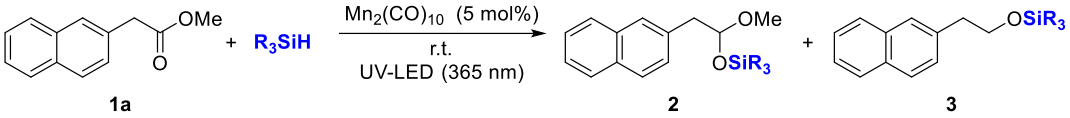
After irradiation, the reaction mixture was filtered through celite and evaporated. After hydrolysis of the crude mixture (1N HCl, 10 mL, THF 10 mL, 4 h) and extraction with Et_2O (3*20 mL), the crude residue was purified by column chromatography (SiO_2, mixture of petroleum ether/ethyl acetate as eluent) to afford the desired product.

“1 g scale” procedure:

The reduction of ethyl 1-naphthaleneacetate (1,0 g, 4,67 mmol) was performed according to general procedure ($Re_2(CO)_{10,}$ 15 mg, 0.5 mol%, Et_3SiH, 0.8 mL, 5.1 mmol, toluene 4 mL, hv 365 nm, 18 h). The reaction mixture was filtered through celite and evaporated. After hydrolysis of the crude mixture (1N HCl, 10 mL, THF 10 mL, 4 h) and extraction with Et_2O (3*20 mL), 1-naphthaleneacetaldehyde was isolated by bulb to bulb distillation (599 mg, 75% yield).

3. Tables of optimization

Table S1. Optimization of the parameters for the reduction of methyl 2-naphthylacetate **1a** with $Mn_2(CO)_{10}$ as catalyst.[a]



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

Entry	Silane (equiv.)	Time (h)	Conv. (%)	Selectivity (%) **2**	**3**
1	Et_3SiH (4)	3	**92**	**82**	18
2	Et_3SiH (3)	3	**82**	**99**	1
3	Et_3SiH (2)	3	**73**	**99**	1
4		6	**92**	**99**	1
5	Et_3SiH (1.1)	3	**60**	**99**	1
6		6	**70**	**99**	1
7		9	**90**	**99**	1
8	Et_2SiH_2 (3)	3	**41**	**49**	51
9	Ph_2SiH_2 (3)	3	**>99**	**1**	99
10	$PhSiH_3$ (3)	3	**>99**	**1**	99
11	TMDS (3)	3	**>99**	**1**	99
12	Ph_3SiH (1.1)	16	**0**	**-**	-
13	$MePh_2SiH$ (1.1)	16	**0**	**-**	-
14[b]	Et_3SiH (2)	6	**0**	-	-
15[c]	Et_3SiH (2)	6	**56**	99	1
16[d]	Et_3SiH (2)	6	**0**	-	-
17[e]	Et_3SiH (2)	9	**92**	99	1

18[f]	Et_3SiH (2)	1	**86**	85	15
19[g]	Et_3SiH (1.1)	9	**0**	-	-
20[h]	Et_3SiH (1.1)	9	**0**	-	-

[a] General conditions: In a Schlenk tube, $Mn_2(CO)_{10}$ (4.9 mg, 5 mol%), toluene (0.5 mL), silane, and **1a** (50 mg, 0.25 mmol) were added in that order, then stirred under irradiation (LED 365 nm, 40W) at r.t. (c.a. 30°C); Conversion of **1a** and yields of **2** and **3** detected by ^1H NMR.

[b] in the dark.

[c] visible light irradiation (400-800 nm, 30 W).

[d] at 100°C.

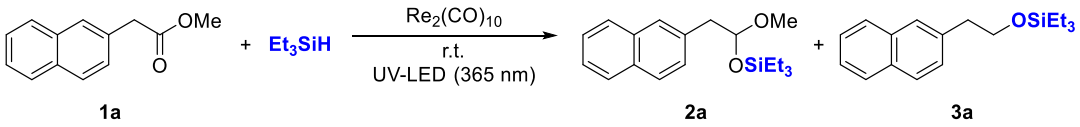
[e] UV irradiations (350 nm) in a Rayonet RPR100 apparatus.

[f] with UV lamp (medium pressure mercury lamp,150 W).

[g] $Mn(CO)_5Br$ (10 mol%) as catalyst.

[h] $CpMn(CO)_3$ (10 mol%) as catalyst.

Table S2. Optimization of the parameters for the reduction of methyl 2-naphthylacetate **1a** with $Re_2(CO)_{10}$ as catalyst.[a]



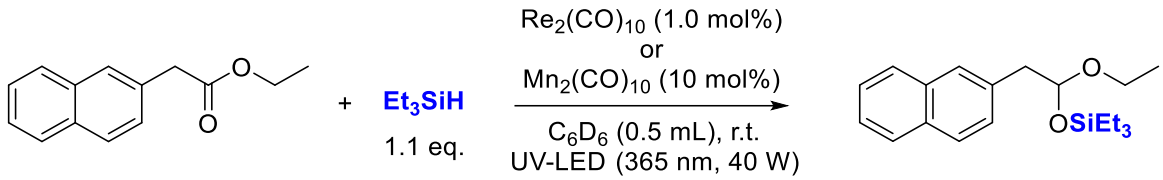
1a **2a** **3a**

Entry	$Re_2(CO)_{10}$ (mol%)	Silane (equiv.)	Time (h)	Conv. (%)	Selectivity (%)	
					2	**3**
1	0.5	Et_3SiH (4)	3	**75**	**96**	4
2			6	**>99**	**85**	15
3	0.5	Et_3SiH (1.1)	9	**96**	**99**	1
4	1	Et_3SiH (1.1)	6	**92**	**94**	6
5 [b]	1	Et_3SiH (1.1)	9	**72**	**87**	13
6	None	Et_3SiH (1.1)	9	**0**	**-**	-

[a] General conditions: In a Schlenk tube, $Re_2(CO)_{10}$, toluene (1 mL), silane, and **1a** (100 mg, 0.5 mmol) were added in that order, then stirred under irradiation (LED 365 nm, 40W) at r.t. (c.a. 30°C); Conversion of **1a** and yields of **2a** and **3a** detected by ^1H NMR.

[b] $Re(CO)_5Br$ (1 mol%) as catalyst

4. On-Off experiments monitored by ^{1}H NMR



1b **2b**

In an argon filled glove box, **1b** (0.1 mmol, 21.4 mg) and $Re_2(CO)_{10}$ (1.0 mol%, 0.7 mg) [or $Mn_2(CO)_{10}$ (10 mol%, 3.9 mg)] was charged into a Young NMR tube, C_6D_6 (0.5 mL), Et_3SiH (1.1 equiv., 18 µL) and toluene (internal standard, 0.066 mmol, 7 µL) were followed. ^{1}H NMR were performed in situ.

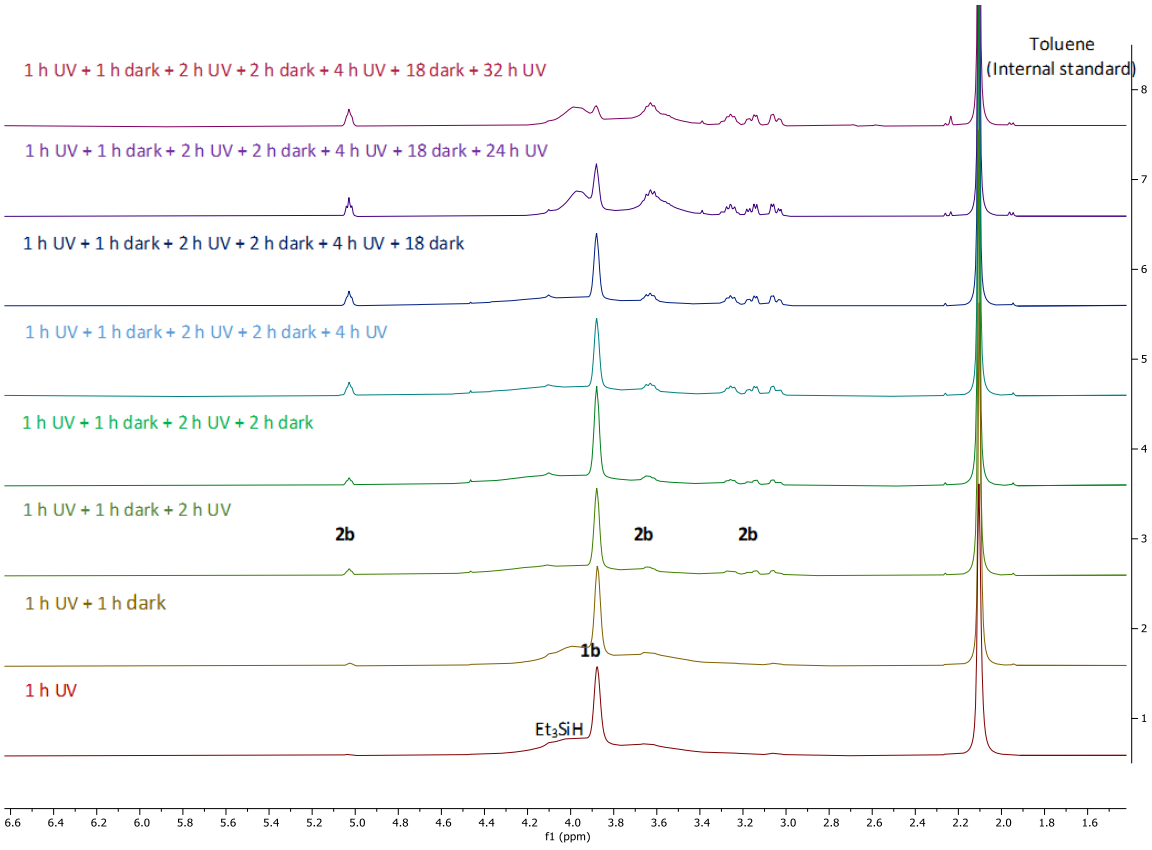


Figure S1: Monitoring over time of the "On-Off" experiment with $Mn_2(CO)_{10}$ as catalyst.

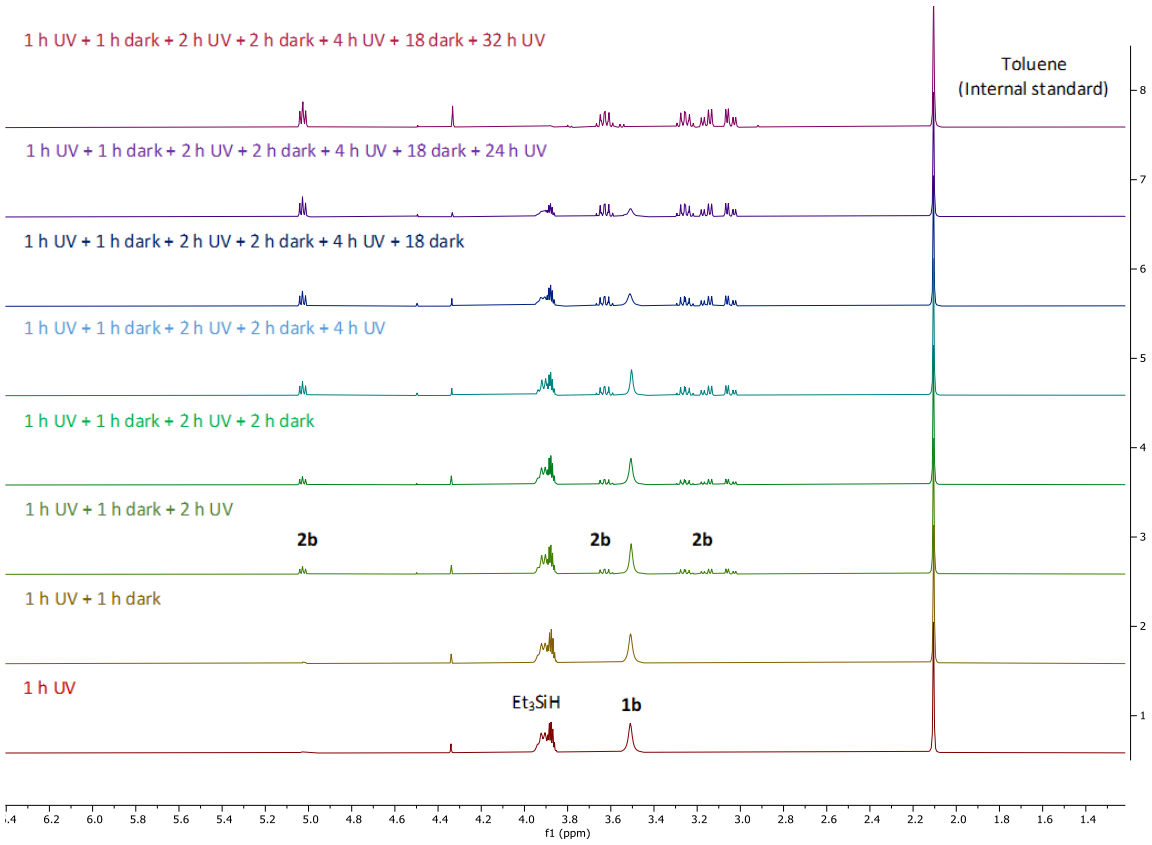
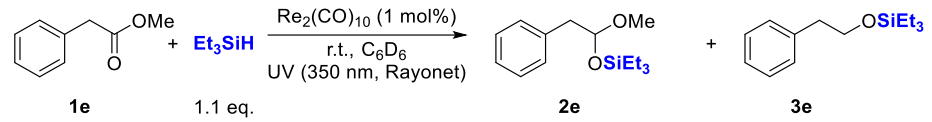


Figure S2: Monitoring over time of the "On-Off" experiment with $Re_2(CO)_{10}$ as catalyst.

5. Monitoring over time of the reduction of methyl 2-phenyl acetate **1e** catalyzed by $Re_2(CO)_{10}$.



1e **2e** **3e**

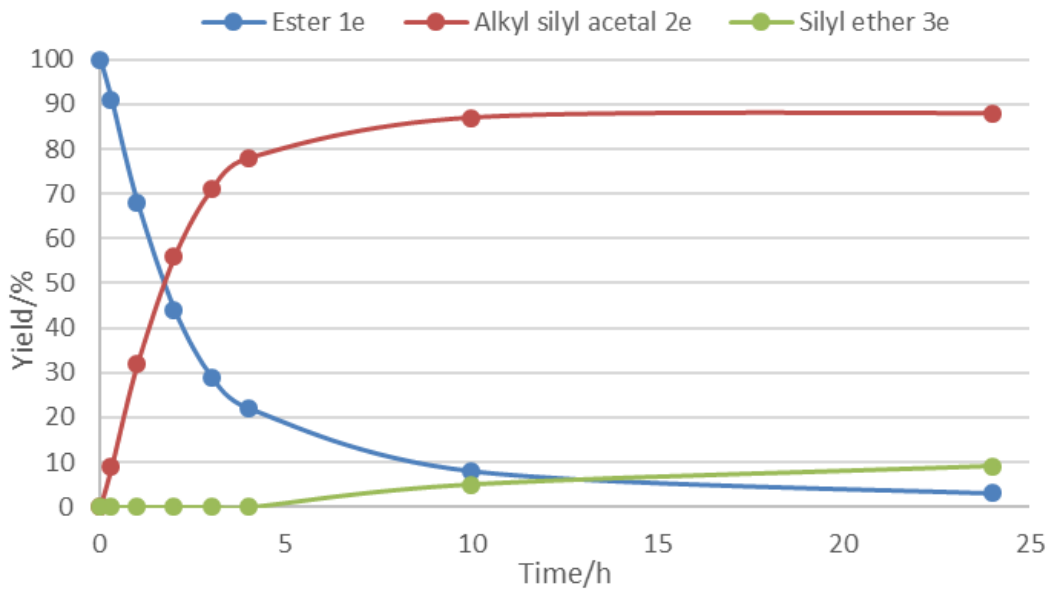
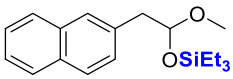


Figure S3. Kinetic monitoring of reaction between 2-phenylacetate **1e** and Et_3SiH catalyzed by $Re_2(CO)_{10}$.

6. Characterization data for the hydrosilylation products



The compound **2a** was prepared as described in the general procedure method **A** (129.8 mg) in 82% yield.

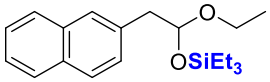
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 3H, CH_{Ar}), 7.67 (s, 1H, CH_{Ar}), 7.47 – 7.40 (m, 2H, CH_{Ar}), 7.38 (dd, J = 8.4, 1.6, 1H, CH_{Ar}), 4.94 (dd, J = 6.1, J = 4.7 Hz, 1H, CH), 3.34 (s, 3H, OCH_3), 3.11 (dd, J = 13.7, 6.1 Hz, 1H, CH_2), 3.00 (dd, J = 13.7, 4.7 Hz, 1H, CH_2), 0.94 (t, J = 8.0 Hz, 9H, CH_2CH_3), 0.60 (q, J = 8.2 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.9 (C_{Ar}), 133.6 (C_{Ar}), 132.4 (C_{Ar}), 128.4 (CH_{Ar}), 128.3 (CH_{Ar}) 127.76 (CH_{Ar}), 127.72(CH_{Ar}), 127.68 (CH_{Ar}), 126.0 (CH_{Ar}), 125.4 (CH_{Ar}), 99.9 (CH), 54.1 (OCH_3), 44.4 (CH_2), 6.9 (CH_2CH_3), 5.1 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.8.

HR MS (ESI): m/z calcd for $C_{18}H_{25}OSi$ ([M – OMe]$^+$) 285.1675, found 285.1679 (1 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{19}H_{32}O_2SiN$ ([M + NH_4]$^+$) 334.2, found 334.2.



The compound **2b** was prepared as described in the general procedure method **B** (155 mg) in 94% yield

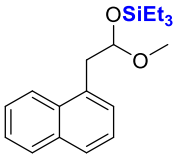
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 3H, CH_{Ar}), 7.68 (s, 1H, CH_{Ar}), 7.48 – 7.39 (m, 3H, CH_{Ar}), 5.00 (dd, J = 6.1, 4.7 Hz, 1H, CH), 3.74 (dq, J = 9.0, 7.0 Hz, 1H, OCH_2CH_3), 3.39 (dq, J = 9.1, 7.0 Hz, 1H, OCH_2CH_3), 3.13 (dd, J = 13.6, 6.1 Hz, 1H, CH_2), 3.00 (dd, J = 13.6, 4.7 Hz, 1H, CH_2), 1.16 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 0.94 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.59 (q, J = 8.2 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.1 (C_{Ar}), 133.6 (C_{Ar}), 132.4 (C_{Ar}), 128.6 (CH_{Ar}), 128.3 (CH_{Ar}), 127.71 (CH_{Ar}), 127.66 (CH_{Ar}), 127.64 (CH_{Ar}), 125.9 (CH_{Ar}), 125.4 (CH_{Ar}), 99.0 (CH), 62.3 (OCH_2CH_3), 44.8 (CH_2), 15.3 (OCH_2CH_3), 6.9 (CH_2CH_3), 5.1 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, $CDCl_3$) δ 17.69

HR MS (ESI): m/z calcd for $C_{20}H_{30}O_2SiNa$ ([M + Na]$^+$) 353.1913, found 353.1918 (1.4 ppm).

LR MS (DCI-NH_3, POS): m/z calcd for $C_{20}H_{34}O_2SiN$ ([M + NH_4]$^+$) 348.2, found 348.2.



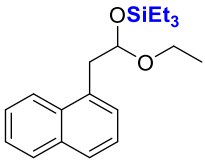
The compound **2c** was prepared as described in the general procedure method **A** (125.3 mg) in 79% yield

^{1}H NMR (400 MHz, C_6D_6) δ 8.14 (d, *J* = 8.3 Hz, 1H, C*H*$_{Ar}$), 7.67 (d, *J* = 8.5 Hz, 1H, C*H*$_{Ar}$), 7.58 (d, *J* = 8.2 Hz, 1H, C*H*$_{Ar}$), 7.37 – 7.32 (m, 2H, C*H*$_{Ar}$), 7.29 – 7.24 (m, 2H, C*H*$_{Ar}$), 5.11 (t, *J* = 5.4 Hz, 1H, C*H*), 3.46 (dd, *J* = 13.8, 5.2 Hz, 1H, C*H*$_2$), 3.38 (dd, *J* = 13.8, 5.5 Hz, 1H, C*H*$_2$), 3.14 (s, 3H, OC*H*$_3$), 0.88 (t, *J* = 7.9 Hz, 9H,CH_2C*H*$_3$), 0.47 (q, *J* = 8.2 Hz, 6H, C*H*$_2$CH$_3$).

^{13}C{^{1}HCH} NMR (101 MHz, C_6D_6) δ 134.5 (*C*$_{Ar}$), 134.2 (*C*$_{Ar}$), 133.2 (*C*$_{Ar}$), 129.1 (*C*H$_{Ar}$), 128.5 (*C*H$_{Ar}$), 127.6 (*C*H$_{Ar}$), 126.0 (*C*H$_{Ar}$), 125.72 (*C*H$_{Ar}$), 125.67 (*C*H$_{Ar}$), 124.6 (*C*H$_{Ar}$), 99.7 (*C*H), 53.3 (OCH$_3$), 41.3 (*C*H$_2$), 7.0 (s, CH_2*C*H$_3$)., 5.4 (s, *C*H$_2$CH$_3$).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.90

LR MS (DCI-NH_3): m/z calcd for $C_{12}H_{14}NO$ ([Aldehyde + NH_4]$^+$) 188.1, found 188.0.



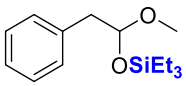
The compound was **2d** prepared as described in the general procedure method **B** (158.3 mg) in 96% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 8.17 (d, *J* = 8.4 Hz, 1H, C*H*$_{Ar}$), 7.67 (d, *J* = 7.6 Hz, 1H, C*H*$_{Ar}$), 7.59 (d, *J* = 8.2 Hz, 1H, C*H*$_{Ar}$), 7.39 – 7.32 (m, 2H, C*H*$_{Ar}$), 7.29 – 7.25 (m, 2H, C*H*$_{Ar}$), 5.18 (t, *J* = 5.4 Hz, 1H, C*H*), 3.60 (dq, *J* = 8.9, 7.0 Hz, 1H, OC*H*$_2$CH$_3$), 3.49 (dd, *J* = 13.8, 5.3 Hz, 1H, C*H*$_2$), 3.40 (dd, *J* = 13.8, 5.5 Hz, 1H, C*H*$_2$), 3.22 (dq, *J* = 8.8, 7.0 Hz, 1H, OC*H*$_2$CH$_3$), 1.03 (t, *J* = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 0.90 (t, *J* = 7.9 Hz, 9H, CH$_2$C*H*$_3$), 0.49 (q, *J* = 8.1 Hz, 6H, C*H*$_2$CH$_3$).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 134.5 (C_{Ar}), 134.4 (C_{Ar}), 133.2 (C_{Ar}), 129.1 (CH_{Ar}), 128.5 (CH_{Ar}), 127.5 (CH_{Ar}), 125.9 (CH_{Ar}), 125.70 (CH_{Ar}), 125.67 (CH_{Ar}), 124.8 (CH_{Ar}), 98.9 (*C*H), 61.8 (OCH_2CH_3), 41.8 (CH_2), 15.5 (OCH_2CH_3), 7.0 (CH_2CH_3), 5.5 (CH_2CH_3).

$^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6) δ 16.44

LR MS (DCI-NH_3): m/z calcd for $C_{12}H_{14}NO$ ([Aldehyde + NH_4]$^+$) 188.1, found 187.9.

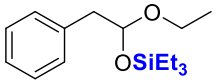


The compound **2e** was prepared as described in the general procedure method **A** (94.3 mg) in 71% yield.[1]

^1H NMR (400 MHz, C_6D_6) *δ* 7.23 – 7.20 (m, 2H, CH_{Ar}), 7.18 – 7.15 (m, 2H, CH_{Ar}), 7.10 – 7.06 (m, 1H, CH_{Ar}), 4.88 (t, *J* = 5.3, 1H, C*H*), 3.15 (s, 3H, OCH_3), 3.00 (dd, *J* = 13.5, 5.7 Hz, 1H, CH_2), 2.88 (dd, *J* = 13.5, 5.0 Hz, 1H, CH_2)., 0.96 (t, *J* = 8.0 Hz, 9H, CH_2CH_3), 0.56 (q, *J* = 8.0 Hz, 6H, CH_2CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) *δ* 137.9 (C_{Ar}), 130.2 (CH_{Ar}) , 128.5 (CH_{Ar}), 126.6 (CH_{Ar}), 100.2 (*C*H), 53.3 (OCH_3), 44.4 (CH_2), 7.1 (CH_2CH_3), 5.4 (CH_2CH_3).

$^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6) *δ* 16.68.

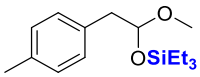


The compound **2f** was prepared as described in the general procedure method **B** (132.7 mg) in 95% yield. [2]

^1H NMR (400 MHz, C_6D_6) δ 7.24 – 7.22 (m, 2H, CH_{Ar}), 7.19 – 7.17 (m, 2H, CH_{Ar}) , 7.10 – 7.06 (m, 1H, CH_{Ar}), 4.95 (dd, *J* = 5.7, 5.0 Hz, 1H, C*H*), 3.61 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH_3), 3.25 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH_3), 3.02 (dd, *J* = 13.5, 5.8 Hz, 1H, CH_2), 2.90 (dd, *J* = 13.5, 4.9 Hz, 1H, CH_2), 1.07 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 0.97 (t, *J* = 8.0 Hz, 9H, CH_2CH_3), 0.58 (q, *J* = 8.0 Hz, 6H, CH_2CH_3).

$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ 138.0 (C_{Ar}), 130.2 (CH_{Ar}), 128.4 (CH_{Ar}), 126.6 (CH_{Ar}), 99.3 (*C*H), 61.8 (OCH_2CH_3), 44.9 (CH_2), 15.5 (OCH_2CH_3), 7.1 (CH_2CH_3), 5.5(CH_2CH_3).

$^{29}Si\{^1H\}$ NMR (80 MHz, C_6D_6) δ 16.79



The compound **2g** was prepared as described in the general procedure method **A** (112.2 mg) in 80% yield (95% purity according to ^{1}H NMR).

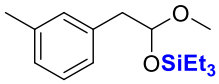
^{1}H NMR (300 MHz, C_6D_6) δ 7.17 (d, J = 7.8 Hz, 2H, CH_{Ar}), 7.01 (d, J = 7.8 Hz, 2H, CH_{Ar}), 4.90 (dd, J = 5.8, 4.9 Hz, 1H, CH), 3.17 (s, 3H, OCH_3), 3.01 (dd, J = 13.6, 5.8 Hz, 1H, CH_2), 2.89 (dd, J = 13.6, 4.9 Hz, 1H, CH_2), 2.13 (s, 3H, CH_3), 0.97 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.58 (q, J = 8.2 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 135.8 (C_{Ar}), 134.9 (C_{Ar}), 130.1 (CH_{Ar}), 129.2 (CH_{Ar}), 100.4 (CH), 53.4 (OCH_3), 44.1 (CH_2), 21.1 (CH_3), 7.1 (CH_2CH_3), 5.5 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.54.

HR MS (ESI): m/z calcd for $C_{15}H_{25}OSi$ ([M – OMe]$^+$) 249.1675, found 249.1679 (1.6 ppm).

LR MS (DCI-NH_3, POS): m/z calcd for $C_{16}H_{32}O_2SiN$ ([M + NH_4]$^+$) 298.2, found 298.2.



The compound **2h** was prepared as described in the general procedure method **B** (95.4 mg) in 68% yield.

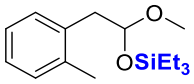
^{1}H NMR (400 MHz, C_6D_6) δ 7.13 – 7.11 (m, 1H, CH_{Ar}), 7.08 – 7.06 (m, 2H, CH_{Ar}), 6.93 (d, J = 7.2 Hz, 1H, CH_{Ar}), 4.91 (t, J = 5.4 Hz, 1H, CH), 3.17 (s, 3H, OCH_3), 3.01 (dd, J = 13.5, 5.6 Hz, 1H, CH_2), 2.90 (dd, J = 13.5, 5.1 Hz, 1H, CH_2), 2.16 (s, 3H, CH_3), 0.97 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.58 (t, J = 8.0 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 137.8 (C_{Ar}), 137.7 (C_{Ar}), 131.1 (CH_{Ar}), 128.4 (CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 100.3 (CH), 53.3 (OCH_3), 44.4 (CH_2), 21.4 (CH_3), 7.1 (CH_2CH_3), 5.5 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.55.

HR MS (ESI): m/z calcd for $C_{15}H_{25}OSi$ ([M – OMe]$^+$) 249.1675, found 249.1679 (1.6 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_9H_{14}NO$ ([Aldehyde+NH4]$^+$) 152.1, found 152.1.



The compound **2i** was prepared as described in the general procedure method **B** (105.2 mg) in 75% yield (> 95% purity according to ^{1}H NMR).

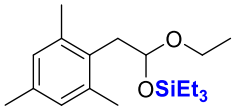
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 4H, CH_{Ar}), 4.87 (dd, *J* = 5.8, 5.2 Hz, 1H, C*H*), 3.33 (s, 3H, OCH_3), 2.97 (dd, *J* = 13.8, 5.8 Hz, 1H, CH_2), 2.87 (dd, *J* = 13.8, 5.2 Hz, 1H, CH_2), 2.35 (s, 3H, CH_3), 0.93 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 0.57 (q, *J* = 7.5 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 136.9 (C_{Ar}), 135.8 (C_{Ar}), 130.6 (CH_{Ar}), 130.2 (CH_{Ar}), 126.6 (CH_{Ar}), 125.8 (CH_{Ar}), 99.5 (*C*H), 54.0 (OCH_3), 41.2 (CH_2), 20.0 (CH_3), 6.9 (CH_2CH_3), 5.1 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.7.

HR MS (ESI): m/z calcd for $C_{15}H_{25}OSi$ ([M – OMe]$^{+}$) 249.1675, found 249.1680 (1 ppm).

LR MS (DCI-NH3): m/z calcd for $C_{16}H_{32}O_2SiN$ ([M + NH_4]$^{+}$) 298.2, found 298.2.



The compound **2j** was prepared as described in the general procedure method **B** (156.3 mg) in 97% yield.

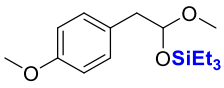
^{1}H NMR (400 MHz, C_6D_6) δ 6.79 (s, 2H, CH_{Ar}), 5.02 (t, *J* = 5.7 Hz, 1H, C*H*), 3.61 (dq, *J* = 8.9, 7.0 Hz, 1H, OCH_2CH$_3$), 3.20 (dq, J = 8.9, 7.0 Hz, 1H, OCH_2CH$_3$), 3.09 (dd, *J* = 13.7, 6.0 Hz, 1H, CH_2), 3.02 (dd, *J* = 13.7, 5.3 Hz, 1H, CH_2), 2.36 (s, 6H, CH_3), 2.15 (s, 3H, CH_3), 1.03 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 0.97 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.60 (q, J = 7.9 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 137.3 (C_{Ar}), 135.5 (C_{Ar}), 131.8 (C_{Ar}), 129.3 (CH_{Ar}), 98.8 (*C*H), 62.3 (OCH_2CH_3), 38.1 (CH_2), 21.0 (CH_3), 20.8 (CH_3), 15.5 (OCH_2CH_3), 7.1 (CH_2CH_3), 5.6 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.07.

HR MS (ESI): m/z calcd for $C_{13}H_{19}O$ ([M – $OSiEt_3$]$^{+}$) 191.1436, found 191.1437 (0.5 ppm): m/z calcd for $C_{11}H_{15}O$ ([Aldehyde + H]$^{+}$) 163.1122, found 163.1124 (1.2 ppm).

LR MS (DCI-NH_3, POS): m/z calcd for $C_{11}H_{18}NO$ ([Aldehyde + NH_4]$^{+}$) 180.1, found 180.1.



The compound **2k** was prepared as described in the general procedure method **A** (129.0 mg) in 87% yield.

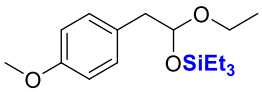
^{1}H NMR (300 MHz, C_6D_6) δ 7.17 – 7.14 (m, 2H, CH_{Ar}), 6.83 – 6.79 (m, 2H, CH_{Ar}), 4.87 (dd, J = 5.7, 4.9 Hz, 1H, CH), 3.32 (s, 3H, OCH_3), 3.18 (s, 3H, OCH_3), 2.99 (dd, J = 13.7, 5.8 Hz, 1H, CH_2), 2.87 (dd, J = 13.7, 4.9 Hz, 1H, CH_2), 0.98 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.59 (q, J = 8.2 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (75 MHz, C_6D_6) δ 159.0 (C_{Ar}), 131.1 (CH_{Ar}), 129.9 (C_{Ar}), 114.0 (CH_{Ar}), 100.4 (*C*H), 54.8 (O*C*H$_3$), 53.4 (O*C*H$_3$), 43.6 (*C*H$_2$), 7.1 (CH_2CH_3), 5.5 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.54.

HR MS (ESI): m/z calcd for $C_{15}H_{25}O_2Si$ ([M – OMe]$^+$) 265.1624, found 265.1628 (1.5 ppm).

LR MS (DCI-NH_3, POS): m/z calcd for $C_{16}H_{32}O_3SiN$ ([M + NH_4]$^+$) 314.2, found 314.2.



The compound **2l** was prepared as described in the general procedure method **A** (150.4 mg) in 97% yield.

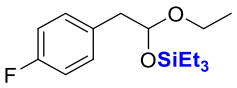
^{1}H NMR (400 MHz, C_6D_6) δ 7.17 – 7.13 (m, 2H, CH_{Ar}), 6.81 – 6.77 (m, 2H, CH_{Ar}), 4.93 (dd, J = 5.8, 4.9 Hz, 1H, CH), 3.62 (dq, J = 8.9, 7.0 Hz, 1H, OCH_2CH$_3$), 3.32 (s, 3H, OCH_3), 3.26 (dq, J = 8.9, 7.0 Hz, 1H, OCH_2CH$_3$), 2.99 (dd, J = 13.6, 5.9 Hz, 1H, CH_2), 2.86 (dd, J = 13.6, 4.8 Hz, 1H, CH_2), 1.08 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3), 0.98 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.59 (q, J = 7.8 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 158.9 (C_{Ar}), 131.1 (CH_{Ar}), 130.0 (C_{Ar}), 114.0 (CH_{Ar}), 99.6 (*C*H), 61.9 (O*C*H$_2$CH$_3$), 54.8 (O*C*H$_3$), 44.0 (*C*H$_2$), 15.5 (OCH$_2$*C*H$_3$), 7.1 (CH_2CH_3), 5.6 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.02

HR MS (ESI): m/z calcd for $C_9H_{11}O_2$ ([Aldehyde + H]$^+$) 151.0759, found 151.0751(5.2 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{17}H_{34}NO_3Si$ ([M + NH_4]$^+$) 328.2, found 328.1.



The compound **2m** was prepared as described in the general procedure method **B** (145.4 mg) in 97% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 7.01 – 6.97 (m, 2H, CH_{Ar}), 6.84 – 6.78 (m, 2H, CH_{Ar}), 4.81 (dd, *J* = 5.8, 4.9 Hz, 1H, C*H*), 3.57 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH$_3$), 3.21(dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH$_3$), 2.85 (dd, *J* = 13.6, 5.7 Hz, 1H, CH_2), 2.74 (dd, *J* = 13.6, 4.8 Hz, 1H, CH_2), 1.04 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3), 0.95 (t, J = 8.0 Hz, 9H, CH$_2$CH_3), 0.55 (q, J = 8.0 Hz, 6H, CH_2CH$_3$).

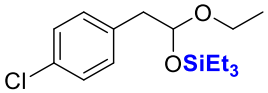
^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 162.2 (d, *J* = 243.7 Hz, C_{Ar}), 133.6 (d, *J* = 3.2 Hz, C_{Ar}), 131.7 (d, *J* = 7.7 Hz, CH_{Ar}), 115.1 (d, *J* = 21.0 Hz, CH_{Ar}), 99.0 (d, *J* = 1.1 Hz, *C*H), 61.9 (s, OCH_2CH$_3$), 43.9 (s, CH_2), 15.4 (s, OCH$_2$CH_3), 7.1 (s, CH$_2$CH_3), 5.5 (s, CH_2CH$_3$).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.29

^{19}F NMR (377 MHz, C_6D_6) δ -117.03.

HR MS (DCI-CH_4): m/z calcd for $C_{16}H_{26}FO_2Si$ ([M – H]$^+$) 297.1686, found 297.1691 (1.7 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{16}H_{31}FNO_2Si$ ([M + NH_4]$^+$) 316.2, found 316.1.

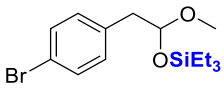


The compound **2n** was prepared as described in the general procedure. However, the acetal **2n** decomposed into the corresponding aldehyde **4h** during its purification on silica gel. ^{1}H NMR of crude mixture was used for the description of **2n**.

^{1}H NMR (300 MHz, C_6D_6) δ 7.14 – 7.11 (m, 2H, CH_{Ar}), 6.96 – 6.92 (m, 2H, CH_{Ar}), 4.81 (dd, *J* = 5.8, 4.8 Hz, 1H, C*H*), 3.56 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH$_3$), 3.19 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH$_3$), 2.83 (dd, *J* = 13.5, 5.8 Hz, 1H, CH_2), 2.71 (dd, *J* = 13.5, 4.8 Hz, 1H, CH_2), 1.04 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3), 0.95 (t, *J* = 8.0 Hz, 9H, CH$_2$CH_3), 0.56 (q, *J* =8.0 Hz, 6H, CH_2CH$_3$).

HR MS (ESI): m/z calcd for $C_{10}H_{12}ClO$ ([M – $OSiEt_3$]$^+$) 183.0577, found 183.0576 (0.5 ppm).m/z calcd for C_8H_8ClO ([Aldehyde + H]$^+$) 155.0264, found 155.0265 (0.6 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{16}H_{31}ClNO_2Si$ ([M + NH_4]$^+$) 332.2, found 332.1.



The compound **2o** was prepared as described in the general procedure method **A** (101.9 mg) in 59% yield.

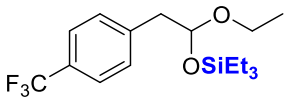
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H, CH_{Ar}), 7.12 – 7.08 (m, 2H, CH_{Ar}), 4.81 (dd, *J* = 5.9, 4.6 Hz, 1H, C*H*), 3.31 (s, 3H, OCH_3), 2.88 (dd, *J* = 13.7, 5.9 Hz, 1H, CH_2), 2.78 (dd, *J* = 13.7, 4.6 Hz, 1H, CH_2), 0.94 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 0.59 (q, *J* = 8.5, 8.0 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 136.3 (*C*$_{Ar}$), 131.6 (*C*H$_{Ar}$), 131.3 (*C*H$_{Ar}$), 120.4 (*C*$_{Ar}$), 99.4 (*C*H), 54.0 (O*C*H$_3$), 43.5 (*C*H_2), 6.9 (CH_2CH_3), 5.1 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 16.96.

HR MS (ESI): m/z calcd for $C_9H_{10}BrO$ ([M – $OSiEt_3$]$^+$) 212.9915, found 212.9915 (0 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{15}H_{29}BrO_2SiN$ ([M + NH_4]$^+$) 362.1, found 362.1.



The compound **2p** was prepared as described in the general procedure method **B** (131 mg) in 75% yield.

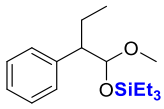
^{1}H NMR (400 MHz, C_6D_6) δ 7.36 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 7.05 (d, *J* = 8.0 Hz, 2H, CH_{Ar}), 4.81 (dd, *J* = 5.8, 4.7 Hz, 1H, C*H*), 3.55 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH_3), 3.18 (dq, *J* = 9.0, 7.0 Hz, 1H, OCH_2CH_3), 2.85 (dd, *J* = 13.5, 5.7 Hz, 1H, CH_2), 2.75 (dd, *J* = 13.5, 4.7 Hz, 1H, CH_2), 1.03 (t, *J* = 7.0 Hz, 3H, OCH_2CH_3), 0.94 (t, *J* = 8.0 Hz, 9H, CH_2CH_3)), 0.54 (q, *J* = 8.0 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.6 (s, *C*$_{Ar}$), 130.3 (s, *C*H$_{Ar}$), 128.8 (q, *J* = 32.3 Hz, *C*$_{Ar}$), 125.1 (q, *J* = 3.8 Hz, *C*H$_{Ar}$), 124.5 (q, *J* = 271.8 Hz, *C*F_3), 98.3 (s, *C*H), 62.3 (s, O*C*H_2CH_3), 44.3 (s, *C*H_2), 15.2 (s, OCH_2CH_3), 6.8 (s, CH_2CH_3), 5.1 (s, *C*H_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 18.04

^{19}F NMR (377 MHz, C_6D_6) δ -62.05

HR MS (ESI): m/z calcd for $C_9H_8F_3O$ ([Aldehyde + H]$^+$) 189.0522, found 189.0520 (1.0 ppm).



The compound **2q** was prepared as described in the general procedure method **A** (100.1 mg) in 68% yield.

The product is present a mixture of two diastereoisomers with a ratio 1 : 0.3 (M = major, m= minor)

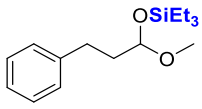
^{1}H NMR (400 MHz, C_6D_6) δ 7.28 – 7.06 (m, 5H, M+m, CH_{Ar}), 4.81 (d, *J* = 5.6 Hz, 1H, M, C*H*OCH$_3$), 4.77 (d, *J* = 5.1 Hz, m, C*H*OCH$_3$) 3.17 (s, 3H, m, OC*H*$_3$), 3.04 (s, 3H, M, OC*H*$_3$), 2.82 – 2.69 (m, 1H, M+m, C*H*), 2.22 – 2.01 (m, 1H, M+m, C*H*$_2$), 1.85 – 1.65 (m, 1H, M+m, C*H*$_2$), 1.00 (t, *J* = 7.9 Hz, 9H, M, CH$_2$C*H*$_3$), 0.93 (t, *J* = 7.9 Hz, 9H, m, CH$_2$C*H*$_3$), 0.83 (t, *J* = 7.4 Hz, 3H, m, C*H*$_3$), 0.82 (t, *J* = 7.4 Hz, 3H, M, C*H*$_3$), 0.63 (q, *J* = 8.0 Hz, 6H, M, C*H*$_2$CH$_3$), 0.54 (q, *J* = 8.1 Hz, 6H, m, C*H*$_2$CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 142.0 (m, *C*$_{Ar}$), 141.6 (M, *C*$_{Ar}$), 129.54 (m, *C*H$_{Ar}$), 129.51 (M, *C*H$_{Ar}$), 128.43 (m, *C*H$_{Ar}$), 128.35 (M, *C*H$_{Ar}$), 126.73 (m, *C*H$_{Ar}$), 126.62 (M, *C*H$_{Ar}$), 102.6 (M, *C*HOCH$_3$), 101.3 (m, *C*HOCH$_3$), 55.1 (m, C*H*), 54.3 (M,C*H*), 53.8 (M, OCH$_3$), 53.4 (m, OCH$_3$), 23.9 (M, C*H*$_2$), 23.0 (m, C*H*$_2$), 12.5 (m, *C*H$_3$), 12.3 (M, *C*H$_3$), 7.15 (M, CH$_2$*C*H$_3$), 7.07 (m, CH$_2$*C*H$_3$), 5.6 (M, *C*H$_2$CH$_3$), 5.3 (m, *C*H$_2$CH$_3$).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) *δ* 16.77, 15.97.

HR MS (ESI): m/z calcd for $C_{16}H_{27}OSi$ ([M – OMe]$^+$) 263.1831, found 263.1829 (0.8 ppm).

LR MS (DCI-NH$_3$): m/z calcd for $C_{17}H_{34}NO_2Si$ ([M + NH$_4$]$^+$) 312.2, found 312.2



The compound **2r** was prepared as described in the general procedure method **B** (102.4 mg) in 73% yield.

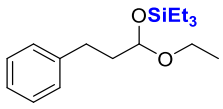
^{1}H NMR (300 MHz, C_6D_6) *δ* 7.21 – 7.18 (m, 4H, CH_{Ar}), 7.11 – 7.05 (m, 1H, CH_{Ar}), 4.72 (dd, *J* = 5.8, 4.4 Hz, 1H, C*H*), 3.22 (s, 3H, OC*H*$_3$), 2.78 (m, 2H, C*H*$_2$), 2.10 – 1.89 (m, 2H, C*H*$_2$), 1.02 (t, *J* = 7.9 Hz, 9H, CH$_2$C*H*$_3$), 0.64 (q, *J* = 8.2 Hz, 6H, C*H*$_2$CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) *δ* 142.0 (*C*$_{Ar}$), 128.4 (*C*H$_{Ar}$), 128.3 (*C*H$_{Ar}$), 125.7 (*C*H$_{Ar}$), 98.3 (*C*H), 52.9 (O*C*H$_3$), 38.9 (*C*H$_2$), 30.8 (*C*H$_2$), 6.7 (CH$_2$*C*H$_3$), 5.2 (*C*H$_2$CH$_3$).

$^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ 16.15.

HR MS (ESI): m/z calcd for $C_{15}H_{25}OSi$ ($[M - OMe]^+$) 249.1675, found 249.1670 (2 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{16}H_{32}NO_2Si$ ($[M + NH_4]^+$) 298.2, found 298.2.

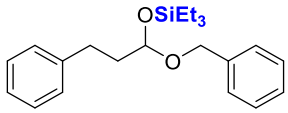


The compound **2s** was prepared as described in the general procedure method **A** (135.5 mg) in 92% yield. [2]

^{1}H NMR (300 MHz, C_6D_6) δ 7.21 – 7.18 (m, 4H, CH_{Ar}), 7.12 – 7.05 (m, 1H, CH_{Ar}), 4.81 (dd, J = 5.9, 4.3 Hz, 1H, CH), 3.72 – 3.62 (m, 1H, OCH_2CH$_3$), 3.36 – 3.22 (m, 1H, OCH_2CH$_3$), 2.83 – 2.77 (m, 2H, CH_2), 2.12 – 1.91 (m, 2H, CH_2), 1.16 (t, J = 7.0 Hz, 3H, OCH$_2$CH_3), 1.03 (t, J = 7.9 Hz, 9H, CH$_2$CH_3), 0.64 (q, J = 8.2 Hz, 6H, CH_2CH$_3$).

$^{13}C\{^{1}H\}$ NMR (75 MHz, C_6D_6) δ 142.5 (C_{Ar}), 128.8 (CH_{Ar}), 128.7 (CH_{Ar}), 126.1 (CH_{Ar}), 97.7 (CH), 61.8 (OCH$_2$CH$_3$), 39.8 (CH_2), 31.2 (CH_2), 15.6 (OCH$_2$CH$_3$), 7.2 (CH$_2$CH$_3$), 5.7 (CH_2CH$_3$).

$^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ 15.66.



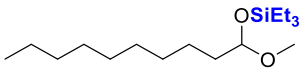
The compound **2t** was prepared as described in the general procedure method **B** (165.8 mg) in 93% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 4H, CH_{Ar}), 7.35 – 7.26 (m, 3H, CH_{Ar}), 7.23 – 7.16 (m, 3H, CH_{Ar}), 4.93 (dd, J = 6.3, 4.0 Hz, 1H, CH), 4.77 (d, J = 11.8 Hz, 1H, OCH_2Ph), 4.49 (d, J = 11.8 Hz, 1H, OCH_2Ph), 2.86 – 2.65 (m, 2H, CH_2), 2.12 – 1.83 (m, 2H, CH_2), 1.00 (t, J = 7.9 Hz, 9H, CH$_2$CH_3), 0.67 (q, J = 7.8 Hz, 6H, CH_2CH$_3$).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 142.1 (C_{Ar}), 138.6 (C_{Ar}), 128.5 (CH_{Ar}), 128.49 (CH_{Ar}), 128.47 (CH_{Ar}), 127.8 (CH_{Ar}), 127.6 (CH_{Ar}), 125.9 (CH_{Ar}), 97.1 (CH), 68.3 (OCH$_2$Ph), 39.5 (CH_2), 30.9 (CH_2), 7.0 (CH$_2$CH$_3$), 5.3 (CH_2CH$_3$).

$^{29}Si\{^{1}H\}$ NMR (80 MHz, C_6D_6) δ 17.1.

HR MS (DCI-CH_4): m/z calcd for $C_{22}H_{31}O_2Si$ ([M – H]$^+$) 355.2093, found 355.2103 (2.8 ppm).; m/z calcd for $C_{20}H_{27}O_2Si$ ([MH – C_2H_6]$^+$) 327.1780, found 327.1788 (2.4 ppm).



The compound **2u** was prepared as described in the general procedure method **B** (140.7 mg) in 93% yield.

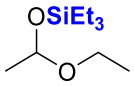
^{1}H NMR (400 MHz, C_6D_6) δ 4.76 (dd, J = 5.8, 4.6 Hz, 1H, C*H*), 3.23 (s, 3H, OCH_3), 1.83 – 1.64 (m, 2H, CH_2), 1.54-1.47 (m, 2H, CH_2); 1.31 – 1.26 (m, 12H, CH_2), 1.04 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.90 (t, J = 6.8 Hz, 3H, CH_3), 0.67 (q, J = 7.9 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 99.5 (*C*H), 53.1 (O*C*H$_3$), 37.6 (*C*H$_2$), 32.3 (*C*H$_2$), 30.2 (*C*H$_2$), 30.1 (*C*H$_2$), 30.0 (*C*H$_2$), 29.8 (*C*H$_2$), 25.0 (*C*H$_2$), 23.1 (*C*H$_2$), 14.4 (*C*H$_3$), 7.2 (CH_2CH_3), 5.7 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 15.7.

HR MS (ESI): m/z calcd for $C_{16}H_{35}OSi$ ([M – OMe]$^+$) 271.2457, found 271.2469 (4.4 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{17}H_{42}NO_2Si$ ([M + NH_4]$^+$) 320.3, found 320.3.

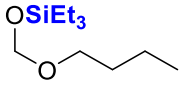


The compound **2v** was prepared as described in the general procedure method **A** (91.0 mg) in 89% yield. [3]

^{1}H NMR (400 MHz, C_6D_6) δ 4.91 (q, J = 5.1 Hz, 1H, C*H*), 3.71 – 3.64 (m, 1H, OCH_2CH$_3$), 3.32 – 3.24 (m, 1H, OCH_2CH$_3$), 1.33 (d, J = 4.8 Hz, 3H, CH_3), 1.14 (t, J = 7.0 Hz, 3H, OCH_2CH_3), 1.01 (t, J = 7.9 Hz, 9H, CH_2CH_3), 0.62 (q, J = 9.6, 8.7 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 95.2 (*C*H), 61.6 (O*C*H$_2$CH$_3$), 24.4 (*C*H$_3$), 15.6 (OCH_2CH_3), 7.1 (CH_2CH_3), 5.6 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 15.0.



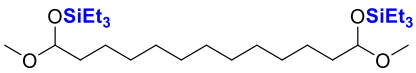
The compound **2w** was prepared as described in the general procedure method **B** (99.4 mg) in 91% yield.

^{1}H NMR (300 MHz, $CDCl_3$) δ 4.85 (s, 2H, OCH_2O), 3.55 (t, J = 6.6 Hz, 2H, OCH_2), 1.61 – 1.52 (m, 2H, CH_2), 1.44 – 1.32 (m, 2H, CH_2), 1.00-0.90 (m, 9H + 3H, CH_2CH_3 + CH_3), 0.64 (q, J = 8.3 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 90.0 (OCH_2O), 67.9 (OCH_2), 32.0 (CH_2), 19.5 (CH_2), 14.1 (CH_3), 6.8 (CH_2CH_3), 4.8 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, $CDCl_3$) δ 19.9.

LR MS (DCI-NH_3): m/z calcd for $C_{11}H_{30}NO_2Si$ ([M + NH_4]$^+$) 236.2, found 236,2.



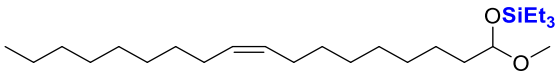
The compound **2x** was prepared as described in the general procedure method **B** (231.9 mg) in 92% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 4.77 (dd, J = 5.8, 4.5 Hz, 2H, CH), 3.23 (s, 6H, OCH_3), 1.84 – 1.64 (m, 4H, CH_2), 1.55 – 1.48 (m, 4H, CH_2), 1.34 – 1.28 (m, 14H, CH_2), 1.04 (t, J = 7.9 Hz, 18H, CH_2CH_3), 0.67 (q, J = 7.9 Hz, 12H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 99.5 (CH), 53.1 (OCH_3), 37.6 (CH_2), 30.17 (CH_2), 30.08 (CH_2), 30.06 (CH_2), 25.0 (CH_2), 7.2 (CH_2CH_3), 5.7 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 15.75.

LR MS (DCI-NH_3): m/z calcd for $C_{26}H_{58}O_3Si_2$ ([M - OMe + H]$^+$) 474.4, found 474.3.



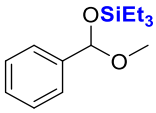
The compound **2y** was prepared as described in the general procedure method **B** (152.7 mg) in 74% yield.

^{1}H NMR (400 MHz, C_6D_6) δ 5.53 – 5.43 (m, 2H, C*H*=C*H*), 4.75 (dd, *J* = 5.7, 4.6 Hz, 1H, C*H*), 3.23 (s, 3H, OC*H*$_3$), 2.1 – 2.05 (m, 4H, C*H*$_2$), 1.80 – 1.62 (m, 2H, C*H*$_2$), 1.53 – 1.28 (m, 22H, C*H*$_2$), 1.04 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 0.91 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 0.66 (q, *J* = 7.9 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 130.2 (*C*H=*C*H), 99.5 (*C*H), 53.1 (O*C*H$_3$), 37.6 (*C*H$_2$), 32.3 (*C*H$_2$), 32.33 (*C*H$_2$), 30.26 (*C*H$_2$), 30.23 (*C*H$_2$), 30.04 (*C*H$_2$), 30.02 (*C*H$_2$), 30.00 (*C*H$_2$), 29.8 (*C*H$_2$), 29.7 (*C*H$_2$), 27.7 (*C*H$_2$), 25.0 (*C*H$_2$), 23.1 (*C*H$_2$), 14.4 (*C*H$_3$), 7.2 (CH_2CH_3), 5.7 (CH_2CH_3).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ 15.70.

LR MS (DCI-NH_3): m/z calcd for $C_{25}H_{56}O_2SiN$ ([M + NH_4]$^+$) 430.4, found 430.3.



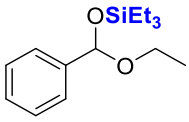
The compound **2z** was prepared as described in the general procedure method **A** (135.5 mg) in 86% yield. [4]

^{1}H NMR (400 MHz, C_6D_6) δ 7.57 – 7.55 (m, 2H, C*H*$_{Ar}$), 7.22 – 7.17 (m, 2H, C*H*$_{Ar}$), 7.13 – 7.09 (m, 1H, C*H*$_{Ar}$), 5.81 (s, 1H, C*H*), 3.15 (s, 3H, OC*H*$_3$), 0.98 (t, *J* = 7.9 Hz, 9H, CH_2CH_3), 0.63 (q, *J* = 8.0 Hz, 6H, CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 141.7 (*C*$_{Ar}$), 128.5 (*C*H$_{Ar}$), 128.4 (*C*H$_{Ar}$), 126.9 (*C*H$_{Ar}$), 98.0 (*C*H), 51.6 (O*C*H$_3$), 7.0 (CH_2CH_3), 5.4 (CH_2CH_3).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 18.57.

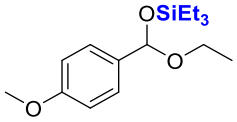
LR MS (DCI-NH_3): m/z calcd for $C_{13}H_{21}OSi$ ([M – OMe]$^+$) 221.1, found 221.1.



The compound **2z'** was prepared as described in the general procedure. However, the acetal **2z'** decomposed into the corresponding aldehyde **4m** during its purification on silica gel. NMR of crude mixture was used for the description of **2z'**.

^{1}H NMR (300 MHz, C_6D_6) δ 7.59 – 7.56 (m, 2H, CH_{Ar}), 7.23 – 7.17 (m, 2H, CH_{Ar}), 7.14 – 7.10 (m, 1H, CH_{Ar}), 5.85 (s, 1H, C*H*), 3.52 (dq, *J* = 9.2, 7.1 Hz, 1H, OCH_2CH$_3$), 3.42 (dq, *J* = 9.2, 7.0 Hz, 1H, OCH_2CH$_3$), 1.11 (t, *J* = 7.0 Hz, 3H, OCH$_2$CH_3), 0.99 (t, *J* = 7.9 Hz, 9H, CH$_2$CH_3), 0.64 (q, *J* = 7.9 Hz, 6H, CH_2CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 142.3 (*C*$_{Ar}$), 128.4 (*C*H$_{Ar}$), 128.3 (*C*H$_{Ar}$), 126.8 (*C*H$_{Ar}$), 97.5 (*C*H), 60.3 (O*C*H$_2$CH$_3$), 15.5 (OCH$_2$*C*H$_3$), 7.1 (CH$_2$*C*H$_3$), 5.4 (*C*H$_2$CH$_3$).



The compound **2aa** was prepared as described in the general procedure method **A** (133.5 mg) in 90% yield.

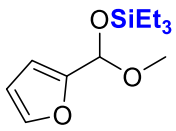
^{1}H NMR (400 MHz, C_6D_6) δ 7.48 (d, *J* = 8.6 Hz, 2H, CH_{Ar}), 6.80 (d, *J* = 8.7 Hz, 2H, CH_{Ar}), 5.84 (s, 1H, C*H*), 3.55 (dq, *J* = 9.0, 7.1 Hz, 1H, OCH_2CH$_3$), 3.43 (dq, *J* = 9.1, 7.0 Hz, 1H, OCH_2CH$_3$), 3.32 (s, 3H, OCH_3), 1.13 (t, *J* = 7.1 Hz, 3H, OCH$_2$CH_3), 1.00 (t, *J* = 7.9 Hz, 9H, CH$_2$CH_3), 0.65 (q, *J* = 7.9 Hz, 6H, CH_2CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ 160.2 (*C*$_{Ar}$), 134.6 (*C*$_{Ar}$), 128.0 (*C*H$_{Ar}$), 113.8 (*C*H$_{Ar}$), 97.4 (*C*H), 60.3 (O*C*H$_3$), 54.8 (O*C*H$_2$CH$_3$), 15.5 (OCH$_2$*C*H$_3$), 7.1 (CH$_2$*C*H$_3$), 5.5 (*C*H$_2$CH$_3$).

^{29}Si{^{1}H} NMR (80 MHz, C_6D_6) δ 17.65.

HR MS (ESI): m/z calcd for $C_{14}H_{23}O_2Si$ ([M – OEt]$^{+}$) 251.1467, found 251.1477 (4 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{14}H_{23}O_2Si$ ([M – OEt]$^{+}$)251.1, found 251.1.



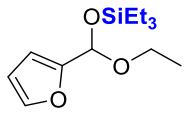
The compound **2ac** was prepared as described in the general procedure method **A** (94.5 mg) in 40% yield

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1H, CH_{Ar}), 6.38 (d, *J* = 3.3 Hz, 1H, CH_{Ar}), 6.36 – 6.31 (m, 1H, CH_{Ar}), 5.75 (s, 1H, C*H*), 3.32 (s, 3H, OCH_3), 0.96 (t, *J* = 7.9 Hz, 9H, CH$_2$CH_3), 0.65 (q, *J* = 7.8 Hz, 6H, CH_2CH$_3$).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.3 (*C*H$_{Ar}$), 110.1 (*C*H$_{Ar}$), 107.5 (*C*H$_{Ar}$), 92.4 (*C*H), 52.6 (O*C*H$_3$), 6.8 (CH$_2$*C*H$_3$), 4.9 (*C*H$_2$CH$_3$) (The signal of the quaternary carbon was not observed).

HR MS (DCI-CH_4): m/z calcd for $C_{11}H_{19}O_2S$ ([M – OMe]$^+$) 211.1154, found 211.1155 (0.5 ppm).

LR MS (DCI-NH_3): m/z calcd for $C_{11}H_{19}O_2S$ ([M – OMe]$^+$) 211.1, found 211.1.



The compound **2ad** was prepared as described in the general procedure method **A** (94.5 mg) in 96% yield.

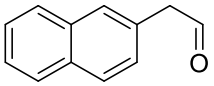
^{1}H NMR (400 MHz, C_6D_6) δ 7.09 (s, 1H, C*H*$_{Ar}$), 6.38 (d, *J* = 3.0 Hz, 1H, C*H*$_{Ar}$), 6.09 – 6.08 (m, 1H, C*H*$_{Ar}$), 5.90 (s, 1H, C*H*), 3.60 – 3.48 (m, 2H, OC*H*$_2$CH$_3$), 1.11 (t, *J* = 7.0 Hz, 3H, OCH$_2$C*H*$_3$), 1.00 (t, *J* = 7.9 Hz, 9H, CH$_2$C*H*$_3$), 0.65 (q, *J* = 7.9 Hz, 6H, C*H*$_2$CH$_3$).

^{13}C{^{1}H} NMR(101 MHz, C_6D_6) δ 155.0 (*C*$_{Ar}$), 142.0 (*C*H$_{Ar}$), 110.3 (*C*H$_{Ar}$), 107.5 (*C*H$_{Ar}$), 92.1 (*C*H), 60.6 (O*C*H$_2$CH$_3$), 15.4 (OCH$_2$*C*H$_3$), 7.0 (CH$_2$*C*H$_3$), 5.3 (*C*H$_2$CH$_3$).

^{29}Si{^{1}H} NMR (79 MHz, C_6D_6) δ 19.10.

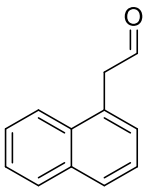
LR MS (DCI-NH_3): m/z calcd for $C_{11}H_{19}O_2Si$ ([M – OEt]$^+$) 211.1, found 211.1.

7. Characterization data for the aldehyde products



The compound **4a** was prepared as described in the general procedure method **A** (79 mg) in 93% yield.[5]

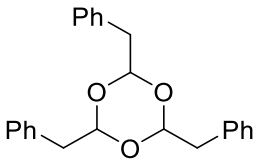
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (t, *J* = 2.4 Hz, 1H, C*H*=O), 7.87 – 7.81 (m, 3H, CH_{Ar}), 7.70 (br s, 1H, CH_{Ar}), 7.51 – 7.48 (m, 2H, CH_{Ar}), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H, CH_{Ar}), 3.86 (d, *J* = 2.4 Hz, 2H, CH_2).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.5 (*C*H=O), 133.8 (C_{Ar}), 132.7 (C_{Ar}), 129.4 (C_{Ar}), 128.9 (*C*H_{Ar}), 128.7 (*C*H_{Ar}), 127.9 (*C*H_{Ar}), 127.7 (*C*H_{Ar}), 127.6 (*C*H_{Ar}), 126.6 (*C*H_{Ar}), 126.2 (*C*H_{Ar}), 50.9 (*C*H_2).



The reduction of ethyl 1-naphthaleneacetate **1d** (1,0 g, 4,67 mmol) was performed according to general procedure ($Re_2(CO)_{10}$, 15 mg, 0.5 mol%, Et_3SiH, 0.8 mL, 5.1 mmol, toluene 4 mL, hv 365 nm, 18 h).The reaction mixture was filtered through celite and evaporated. After hydrolysis of the crude mixture(1N HCl, 10 mL, THF 10 mL, 4 h) and extraction with Et_2O (3*20 mL), 1-naphthaleneacetaldehyde **4b** was isolated by bulb to bulb distillation (599 mg, 75% yield).[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (t, *J* = 2.4 Hz, 1H, C*H*=O), 7.78 – 7.74 (m, 2H, CH_{Ar}), 7.71 (d, *J* = 8.2 Hz, 1H, CH_{Ar}), 7.44 – 7.39 (m, 2H, CH_{Ar}), 7.36 – 7.32 (m, 1H, CH_{Ar}), 7.27 (d, *J* = 6.9 Hz, 1H, CH_{Ar}), 3.96 (d, *J* = 2.4 Hz, 2H, CH_2).

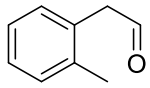
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.7 (*C*H=O), 134.0 (C_{Ar}), 132.4 (C_{Ar}), 129.0 (*C*H_{Ar}), 128.6 (*C*H_{Ar}), 128.50 (*C*H_{Ar}), 128.47 (C_{Ar}), 126.8 (*C*H_{Ar}), 126.2 (*C*H_{Ar}), 125.7 (*C*H_{Ar}), 123.6 (*C*H_{Ar}), 48.4 (*C*H_2).



The compound **4c'** was prepared as described in the general procedure method **B** (1 mmol scale, 90 mg) in 75% yield.[7] (The ^{1}H NMR before purification of the aldehyde **4c** is provided on Figure S97)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.22 (m, 15H, CH_{Ar}), 4.95 (t, *J* = 5.4 Hz, 3H, C*H*), 3.02 (d, *J* = 5.4 Hz, 6H, CH_2).

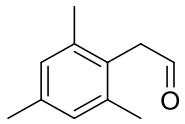
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.7 (C_{Ar}), 130.1 (CH_{Ar}), 128.3 (CH_{Ar}), 126.7 (CH_{Ar}), 101.9 (*C*H), 41.2 (CH_2).



The compound **4d** was prepared as described in the general procedure method **B** (1 mmol scale, 94.5 mg) in 70% yield.[8]

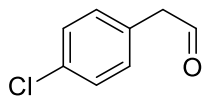
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (t, *J* = 2.2 Hz, 1H, C*H*=O), 7.18 – 7.07 (m, 4H, CH_{Ar}), 3.63 (d, *J* = 2.2 Hz, 2H, CH_2), 2.20 (s, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.4 (*C*H=O), 137.3 (C_{Ar}), 130.8 (CH_{Ar}), 130.7 (C_{Ar}), 130.6 (CH_{Ar}), 127.9 (CH_{Ar}), 126.6 (CH_{Ar}), 48.9 (CH_2), 19.8 (CH_3).



The compound **4e** was prepared as described in the general procedure method **B** (75 mg) in 93% yield.[9]

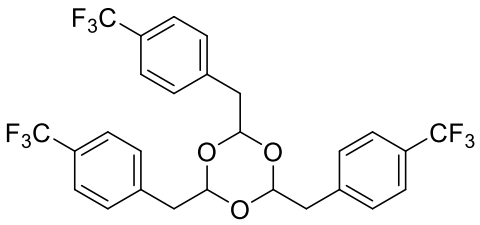
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (t, *J* = 2.1 Hz, 1H, C*H*=O), 6.83 (s, 2H, CH_{Ar}), 3.64 (d, *J* = 2.1 Hz, 2H, CH_2), 2.20 (s, 3H, CH_3), 2.17 (s, 6H, CH_3).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.2 (*C*H=O), 137.3 (C_{Ar}), 137.1 (C_{Ar}), 129.3 (CH_{Ar}), 126.3 (C_{Ar}), 44.9 (CH_2), 21.0 (CH_3), 20.5(CH_3).



The compound **4h** was prepared as described in the general procedure method **B** (1 mmol scale, 118 mg) in 76% yield.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (t, *J* = 2.1 Hz, 1H, C*H*=O), 7.27 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 7.08 (d, *J* = 8.3 Hz, 2H, CH_{Ar}), 3.61 (d, *J* = 2.1 Hz, 2H, CH_2).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 198.8 (*C*H=O), 131.1 (CH_{Ar}), 130.4 (C_{Ar}), 129.3 (CH_{Ar}), 128.5 (C_{Ar}), 49.9 (CH_2).



The compound **4i'** was prepared as described in the general procedure method **B** (1 mmol scale, 115 mg) in 61% yield. (The ^{1}H NMR before purification of the aldehyde **4i** is provided on Figure S106))

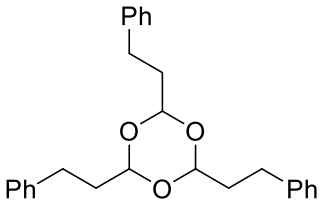
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 6H, CH_{Ar}), 7.20 (d, *J* = 8.6 Hz, 6H, CH_{Ar}), 4.89 (t, *J* = 5.2 Hz, 3H, C*H*), 2.96 (d, *J* = 5.2 Hz, 6H, CH_2).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 139.3 (s, C_{Ar}), 130.4 (s, CH_{Ar}), 129.3 (q, *J* = 32.5 Hz, C_{Ar}), 125.2 (q, *J* = 3.9 Hz, CH_{Ar}), 124.32 (q, *J* = 271.9 Hz, CF_3), 101.0 (s, *C*H), 40.7 (s, CH_2).

^{19}F NMR (377 MHz, $CDCl_3$) δ -62.58.

HR MS (DCI-CH_4): m/z calcd for $C_{27}H_{20}F_9O_3$ ($[M - H]^+$) 563.1269, found 563.1289 (3.5 ppm); m/z calcd for $C_{27}H_{21}F_8O_3$ ($[M - F]^+$) 545.1363, found 545.1366 (0.6 ppm).

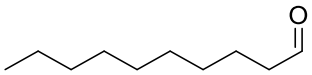
LR MS (DCI-NH_3, POS): m/z calcd for $C_{27}H_{25}F_9NO_3$ ($[M + NH_4]^+$) 582.1, found 582.1.



The compound **4j'** was prepared as described in the general procedure method **A** (1 mmol scale, 114.5 mg) in 85% yield.[10] (The ^{1}H NMR before purification of the aldehyde **4j** is provided on Figure S110)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 6H, CH_{Ar}), 7.13 – 7.10 (m, 9H, CH_{Ar}), 4.74 (t, *J* = 5.3 Hz, 3H, C*H*), 2.71-2.67 (m, 6H, CH_2), 1.98 – 1.93 (m, 6H, CH_2).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 141.5 (C_{Ar}), 128.6 (CH_{Ar}), 128.5 (CH_{Ar}), 126.1 (CH_{Ar}), 100.8 (*C*H), 35.8 (CH_2), 29.7 (CH_2).

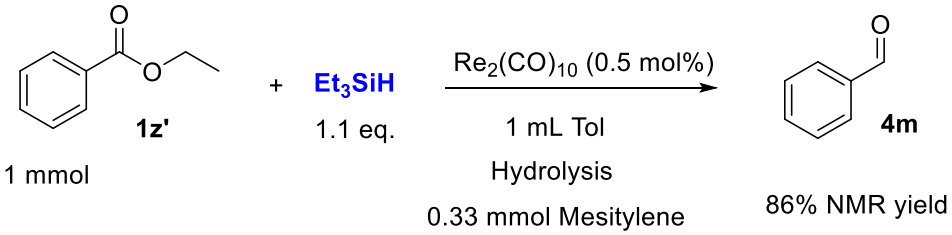


The compound **4k** was prepared as described in the general procedure method **B** (65 mg) in 83% yield.[11]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.9 Hz, 1H, C*H*=O), 2.41 (td, *J* = 7.3, 1.9 Hz, 2H, CH_2), 1.67 – 1.57 (m, 2H, CH_2), 1.35 – 1.23 (m, 12H, CH_2), 0.87 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 203.1 (*C*H=O), 44.1 (*C*H_2), 31.9 (*C*H_2), 29.52 (*C*H_2), 29.49 (*C*H_2), 29.38 (*C*H_2), 29.30 (*C*H_2), 22.8 (*C*H_2), 22.2 (*C*H_2), 14.2 (*C*H_3).

Typical synthesis of aldehyde monitored by ^{1}H NMR with mesitylene as internal standard



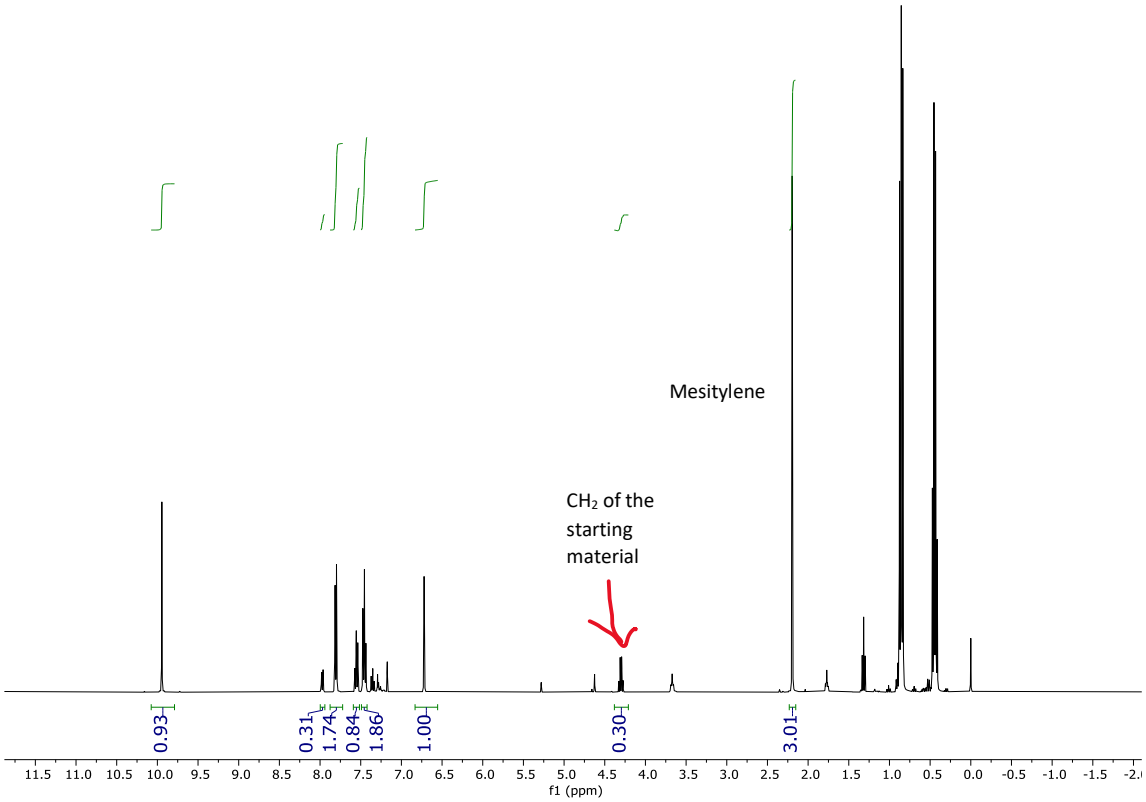
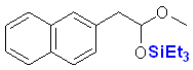


Figure S4: Crude ^{1}H NMR mixture after hydrolysis of compound **4m**.

8. NMR spectra of the hydrosilylation products



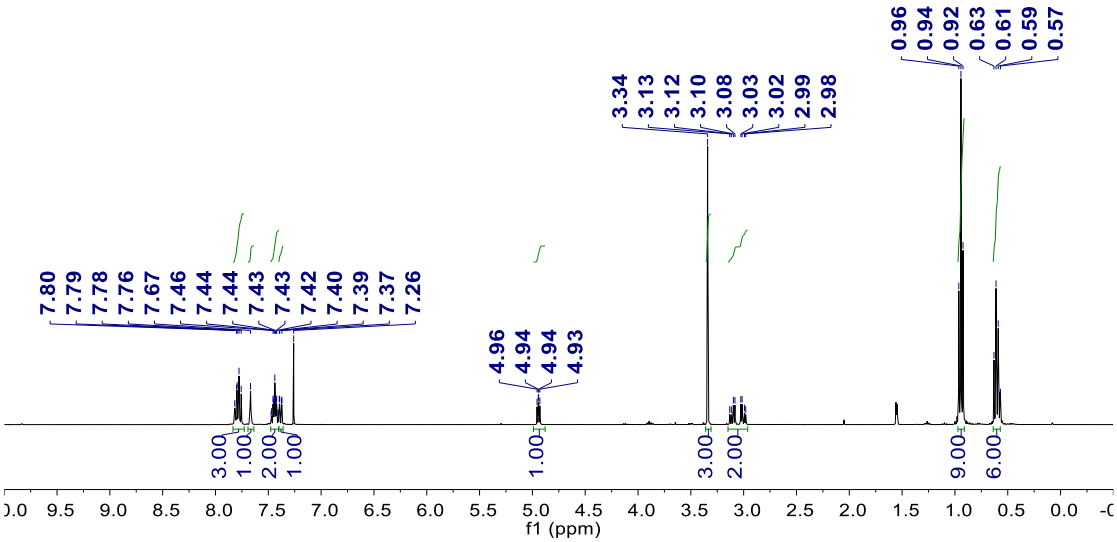
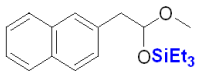


Figure S5: ^{1}H NMR spectrum of the compound **2a** in $CDCl_3$.



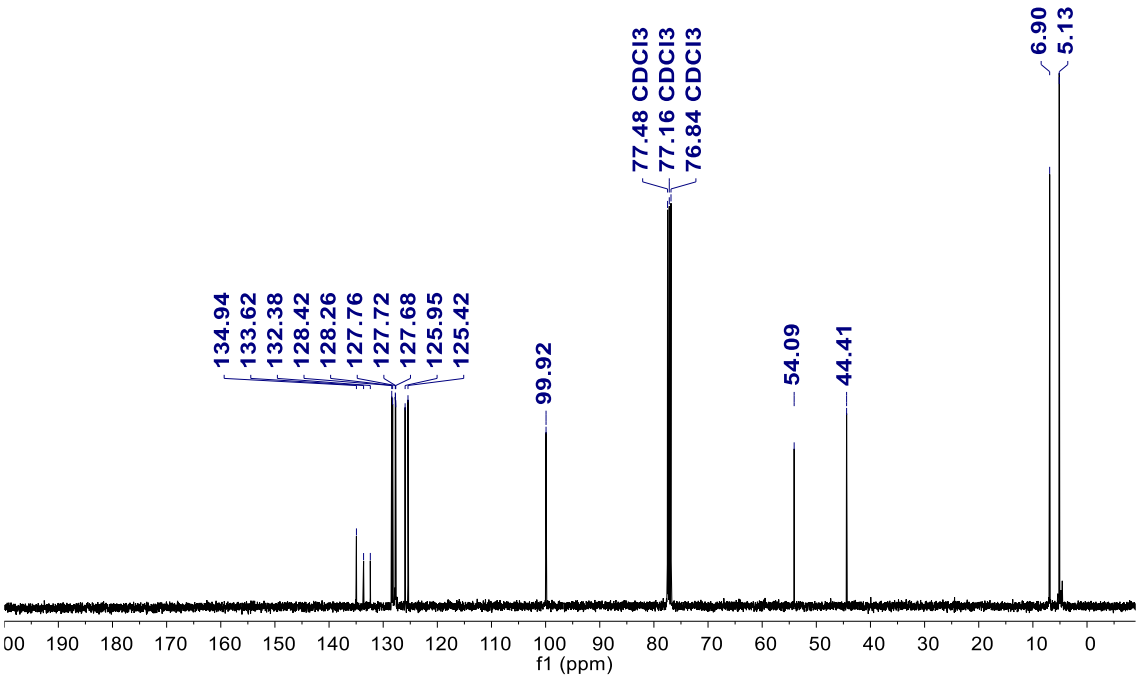
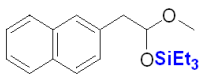


Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2a** in $CDCl_3$.



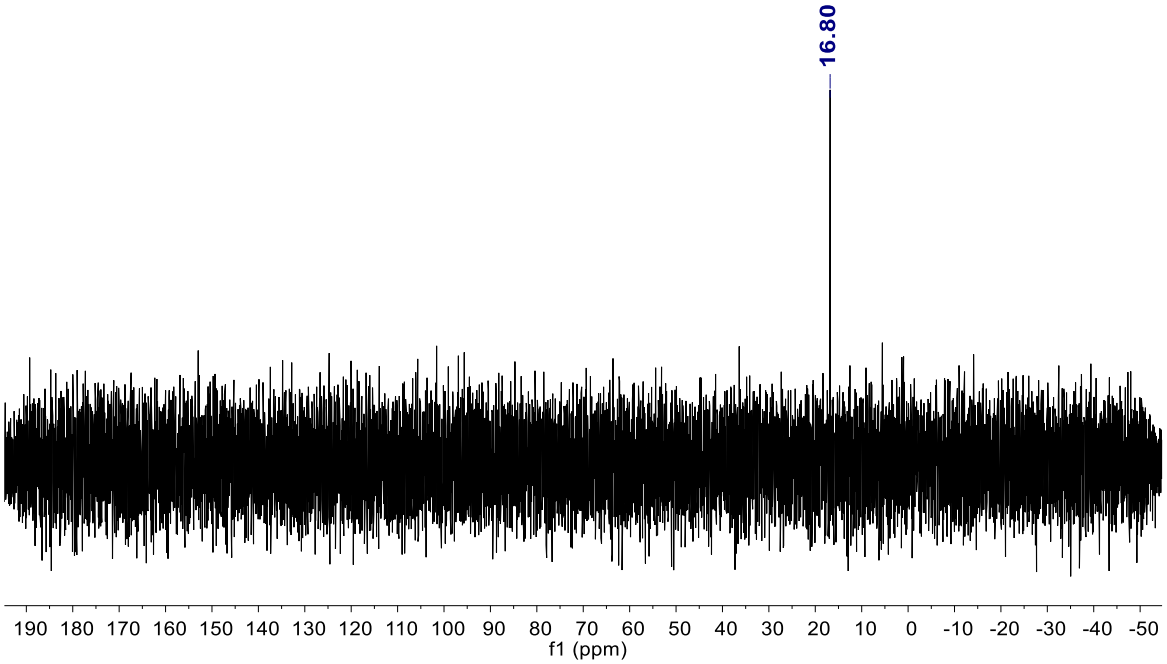


Figure S7: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2a** in C_6D_6.

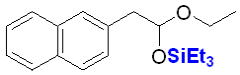


Figure S8: ^{1}H NMR spectrum of the compound **2b** in $CDCl_3$.

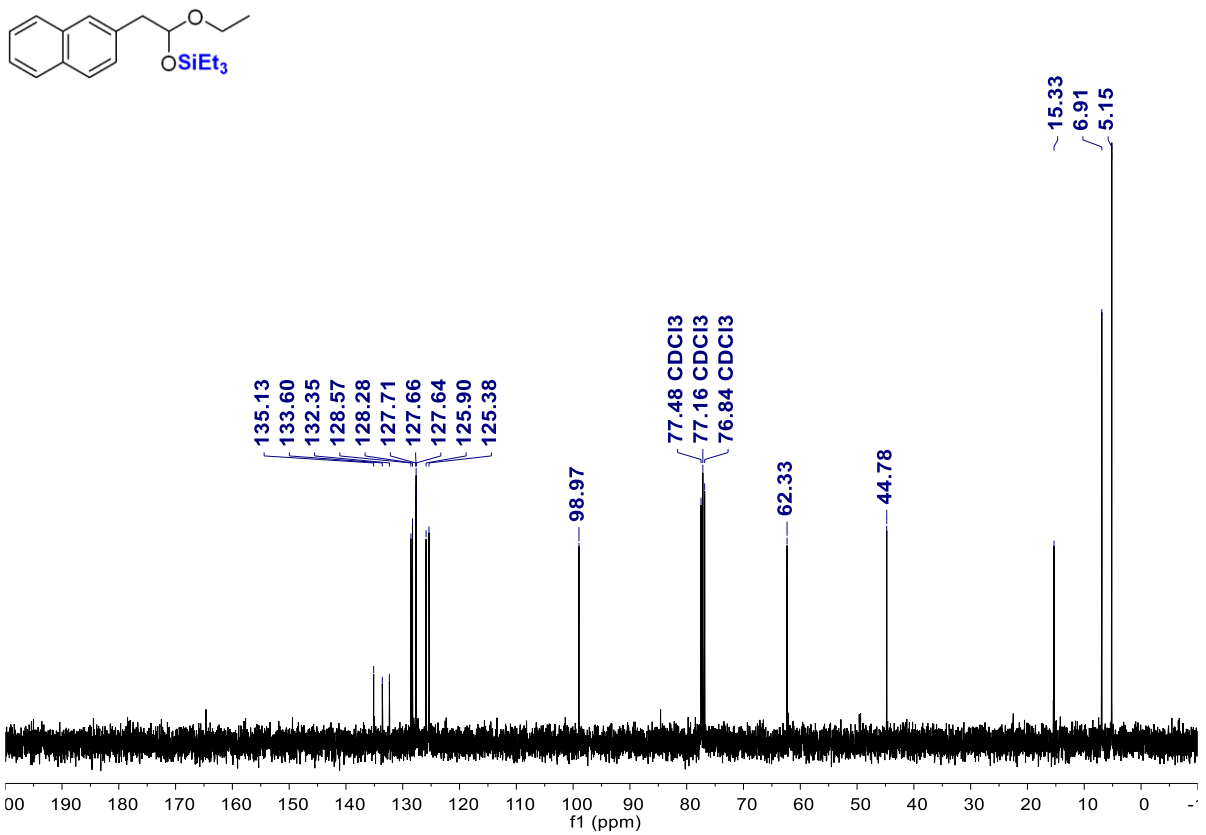


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2b** in $CDCl_3$.

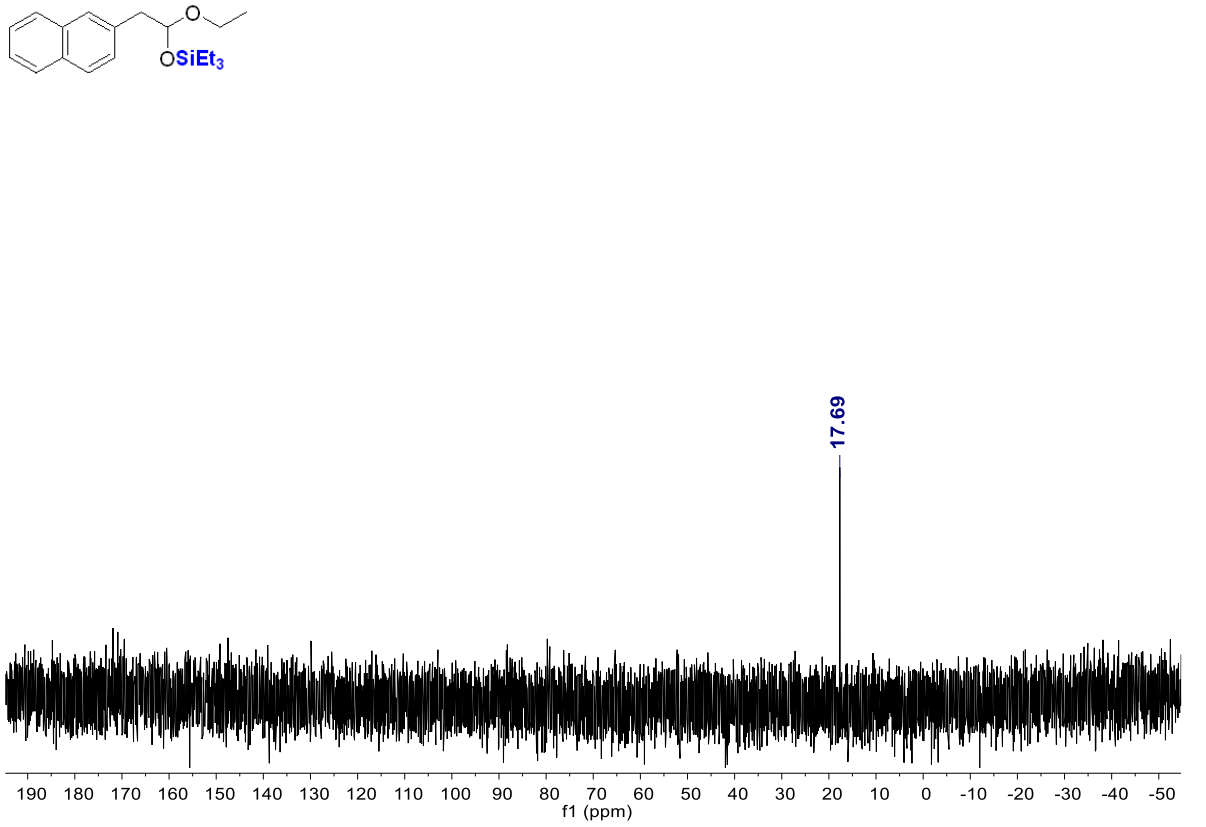


Figure S10: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2b** in $CDCl_3$.

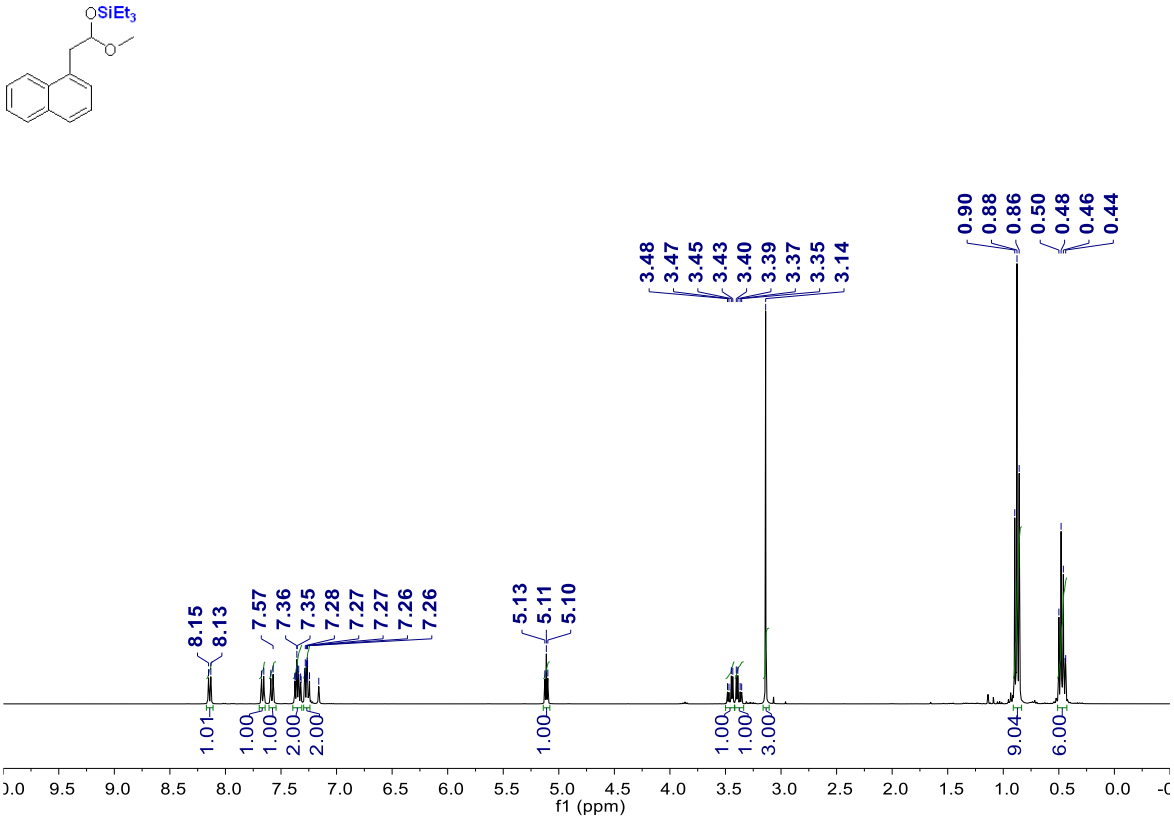


Figure S11: ^{1}H NMR spectrum of the compound **2c** in C_6D_6.

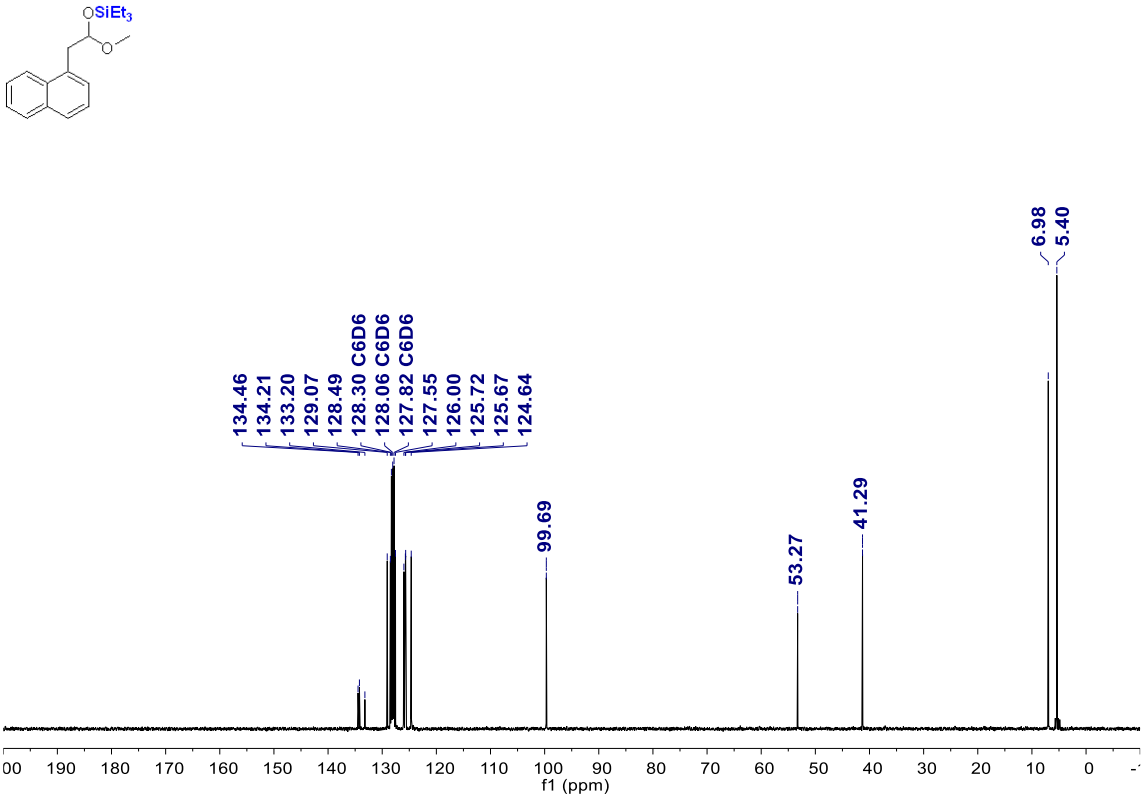


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2c** in C_6D_6.

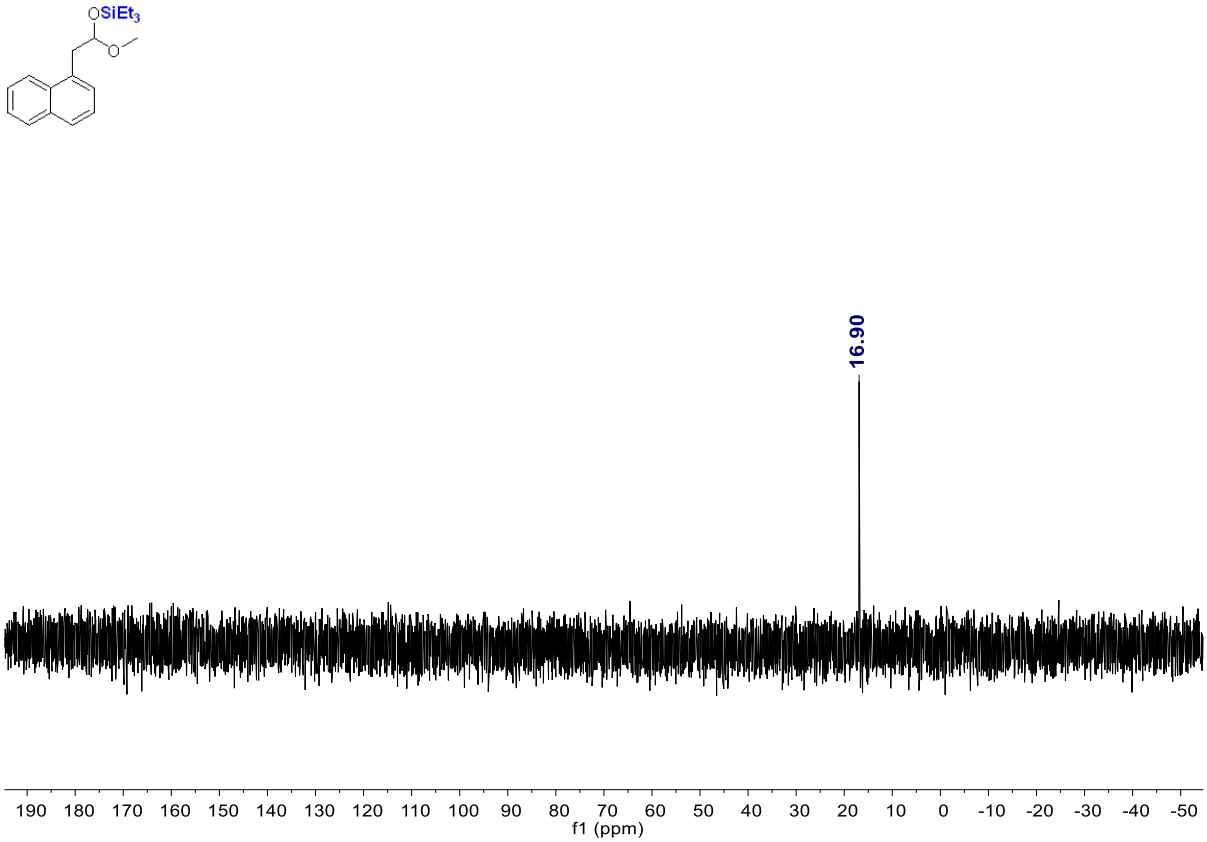


Figure S13: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2c** in C_6D_6

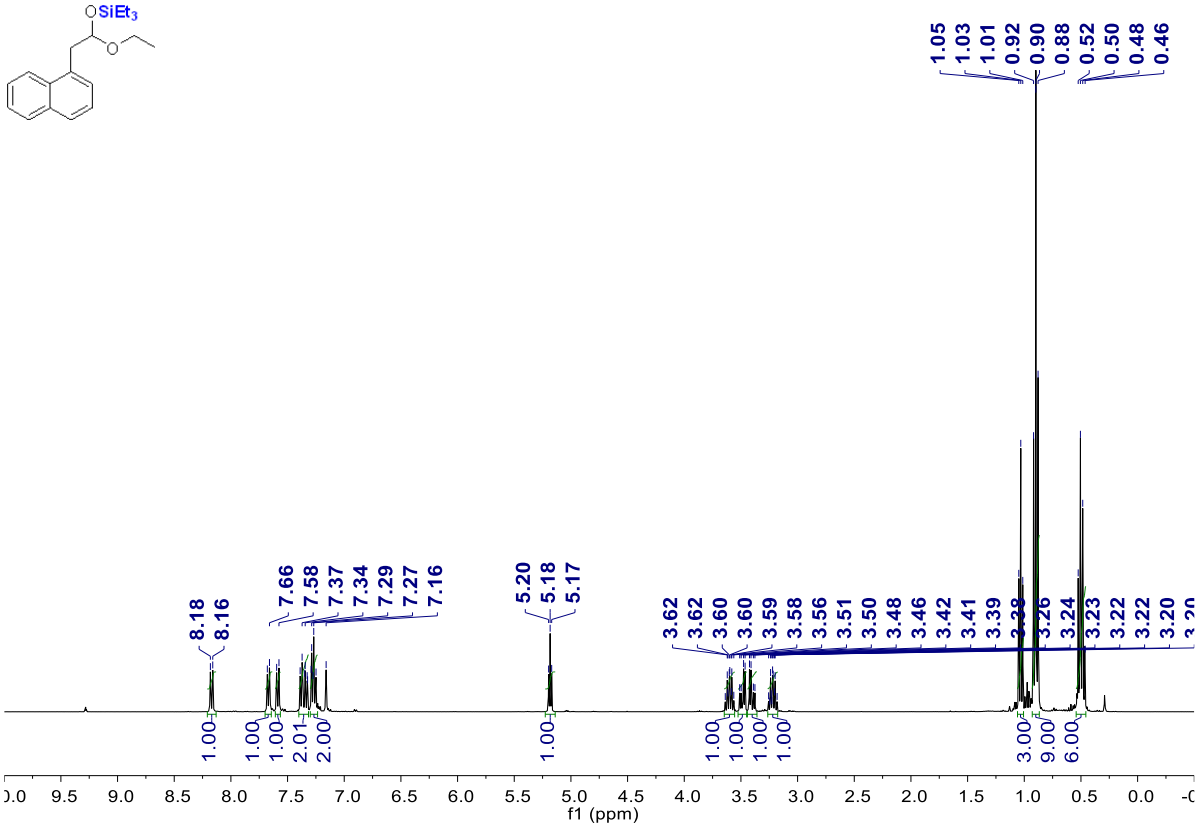


Figure S14: ^{1}H NMR spectrum of the compound **2d** in C_6D_6.

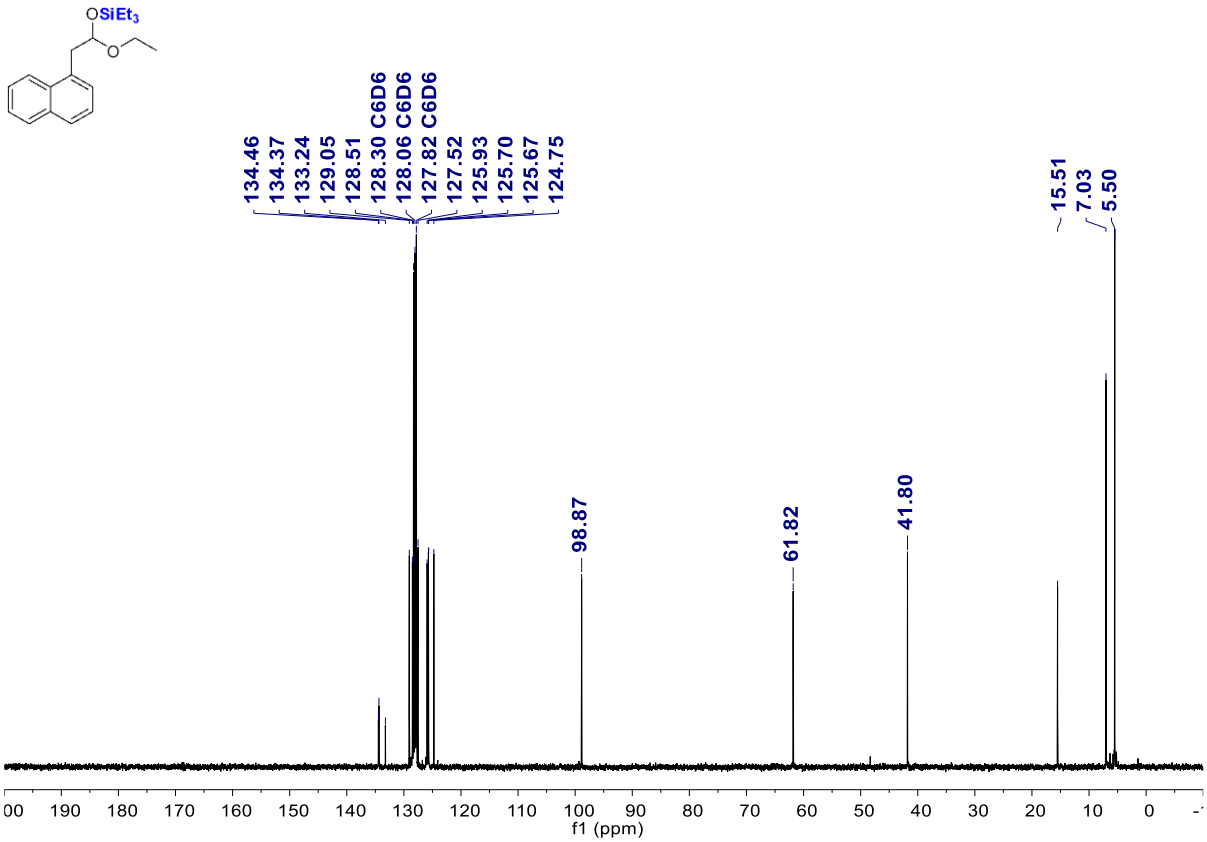


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2d** in C_6D_6.

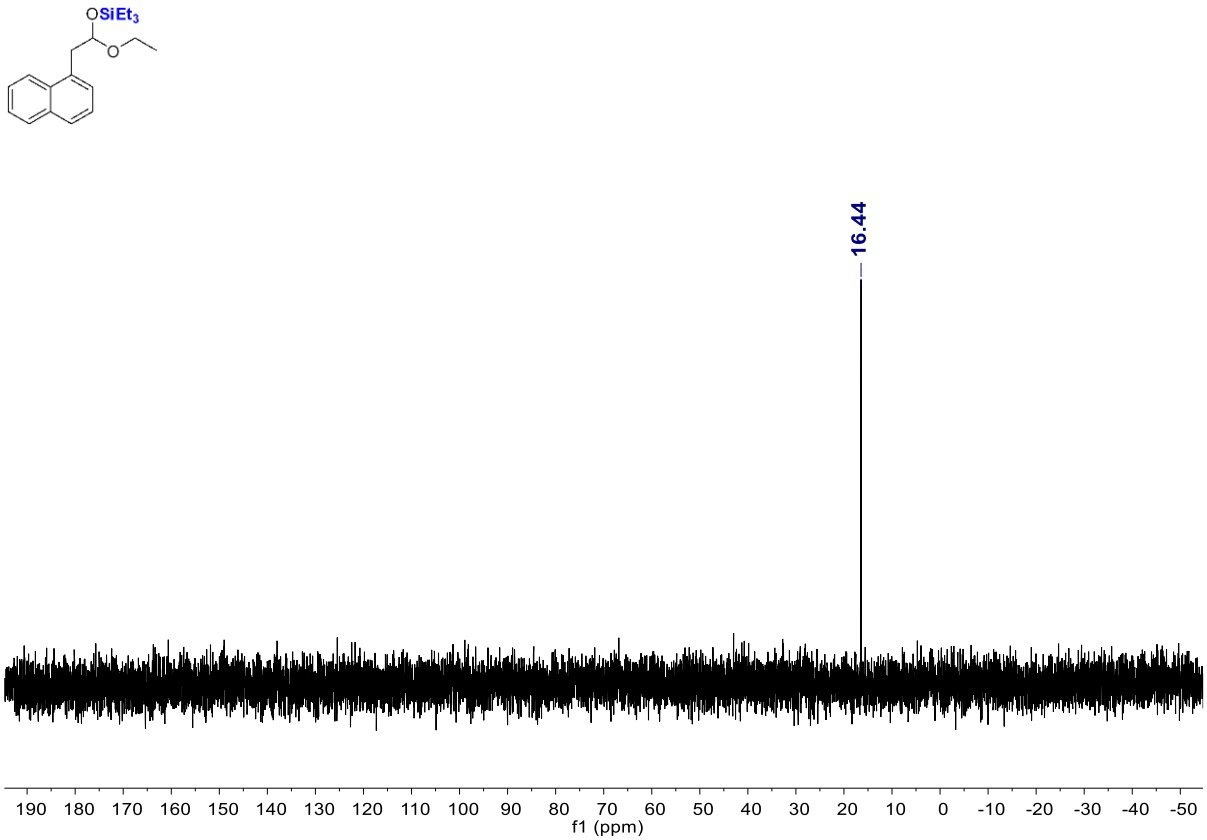
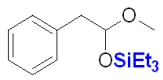


Figure S16: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2d** in C_6D_6



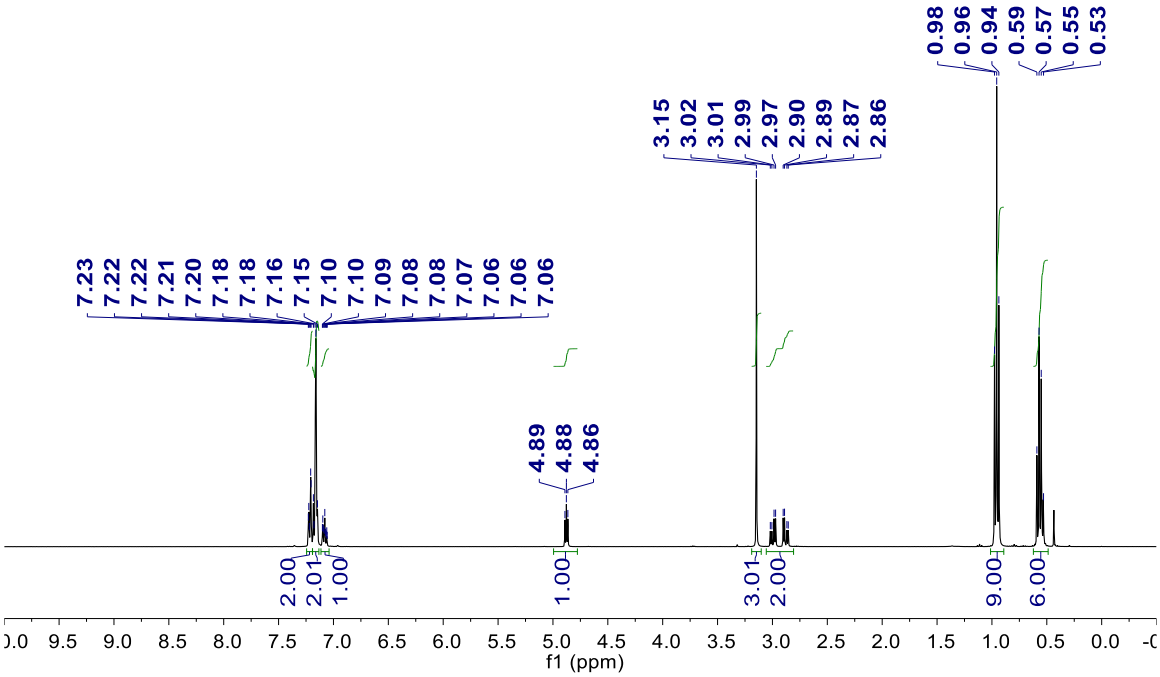


Figure S17: ^{1}H NMR spectrum of the compound **2e** in C_6D_6.

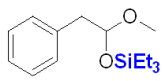
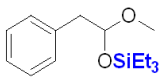


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2e** in C_6D_6.



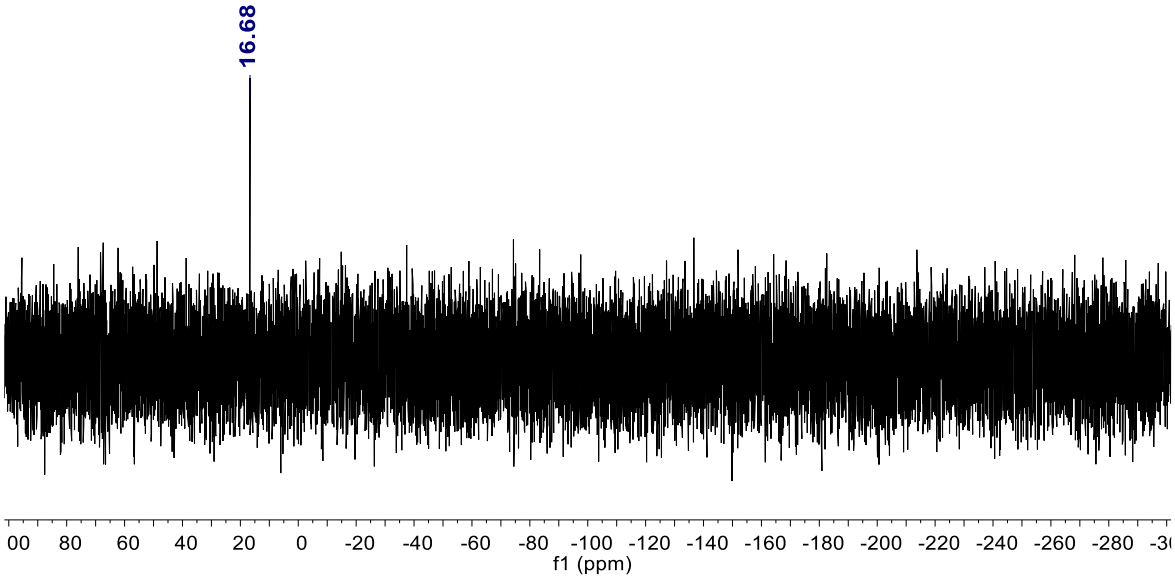
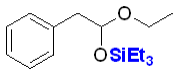


Figure S19: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2e** in C_6D_6.



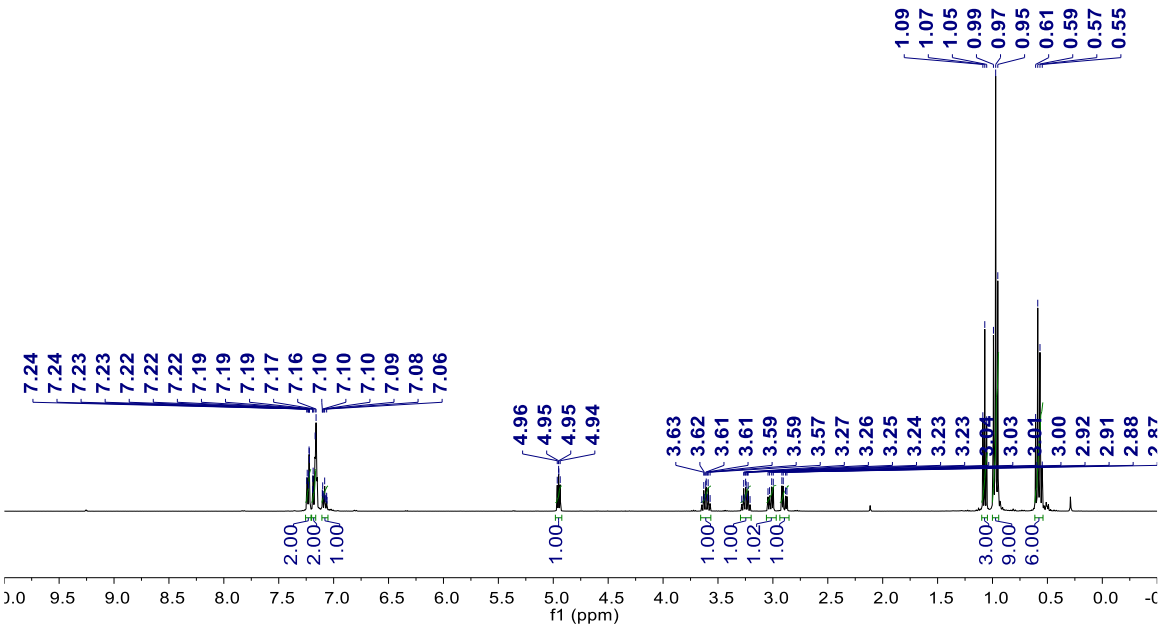


Figure S20: ^{1}H NMR spectrum of the compound **2f** in C_6D_6.

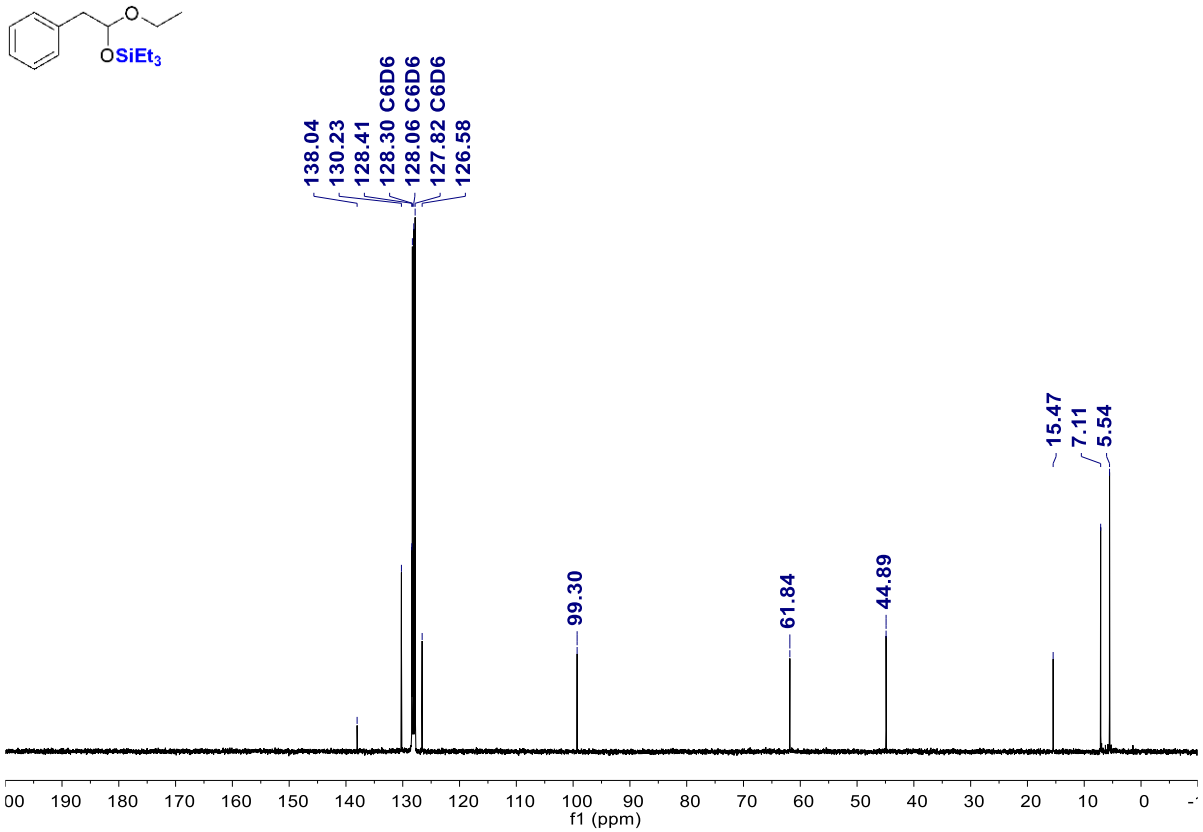


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2f** in C_6D_6.

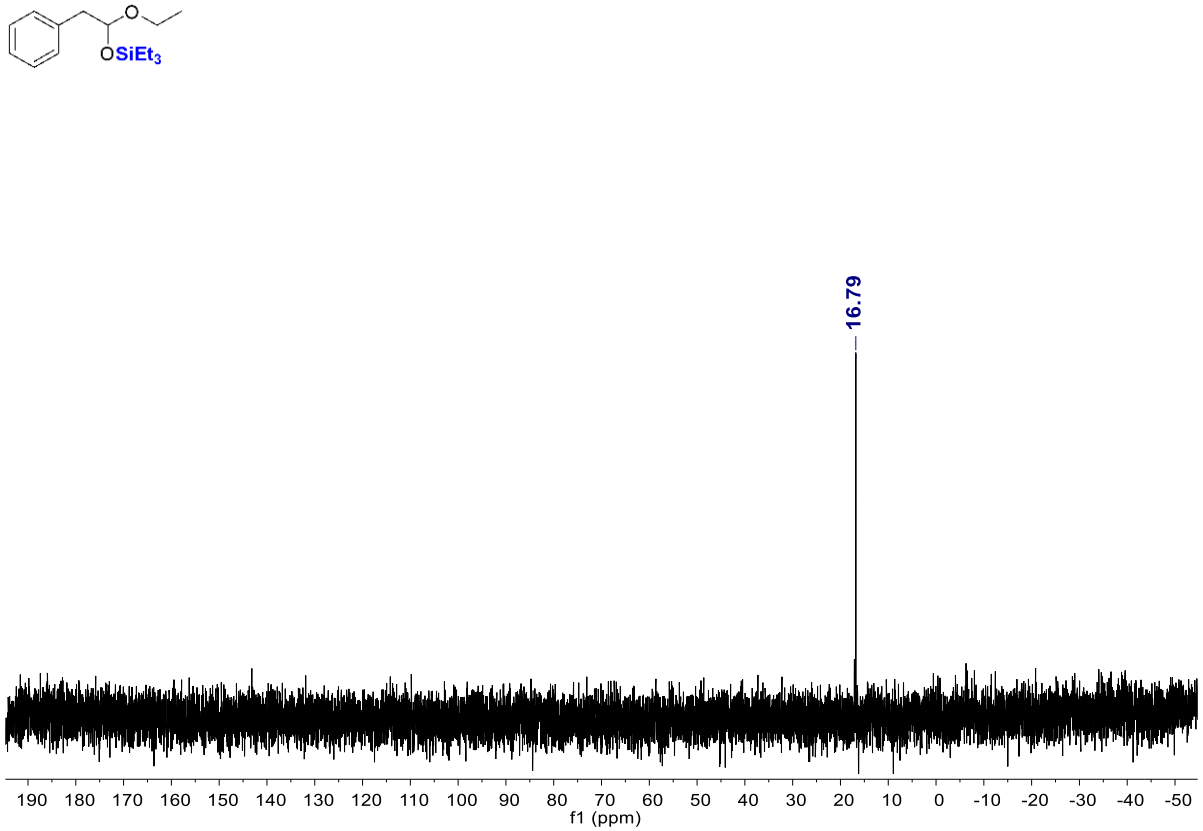


Figure S22: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2f** in C_6D_6

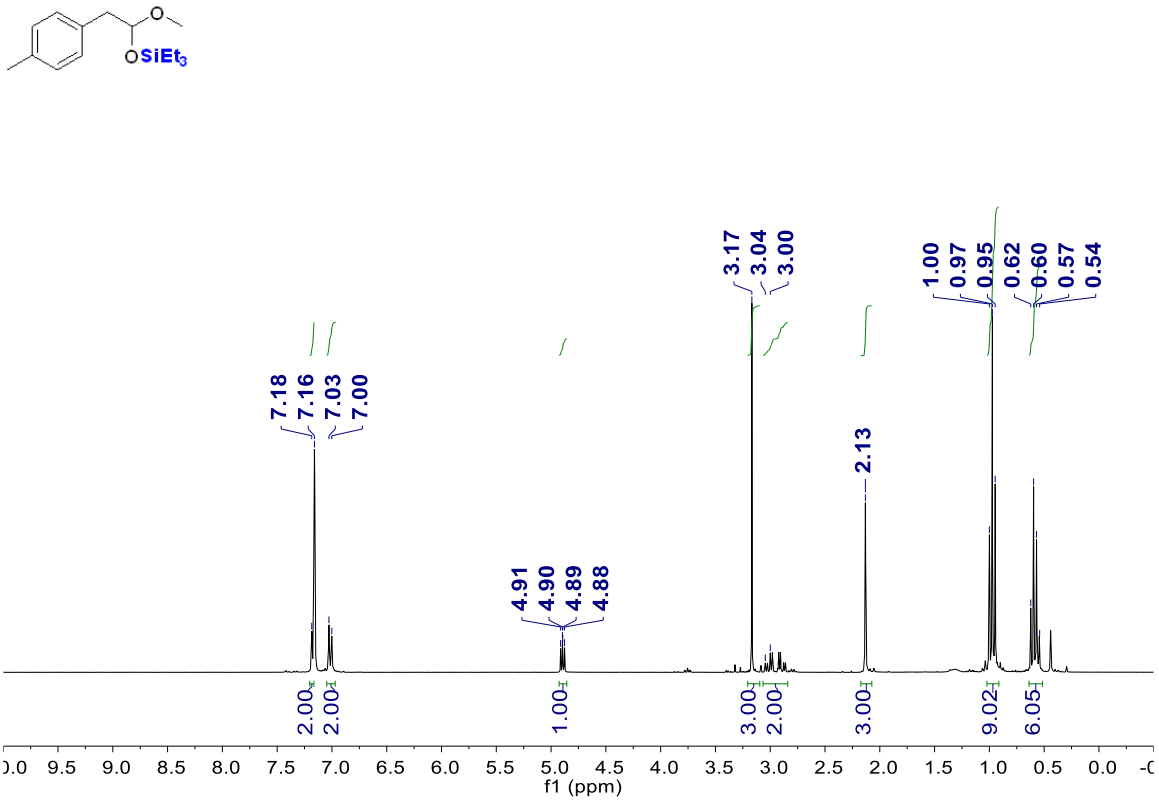


Figure S23: ^{1}H NMR spectrum of the compound **2g** in C_6D_6.

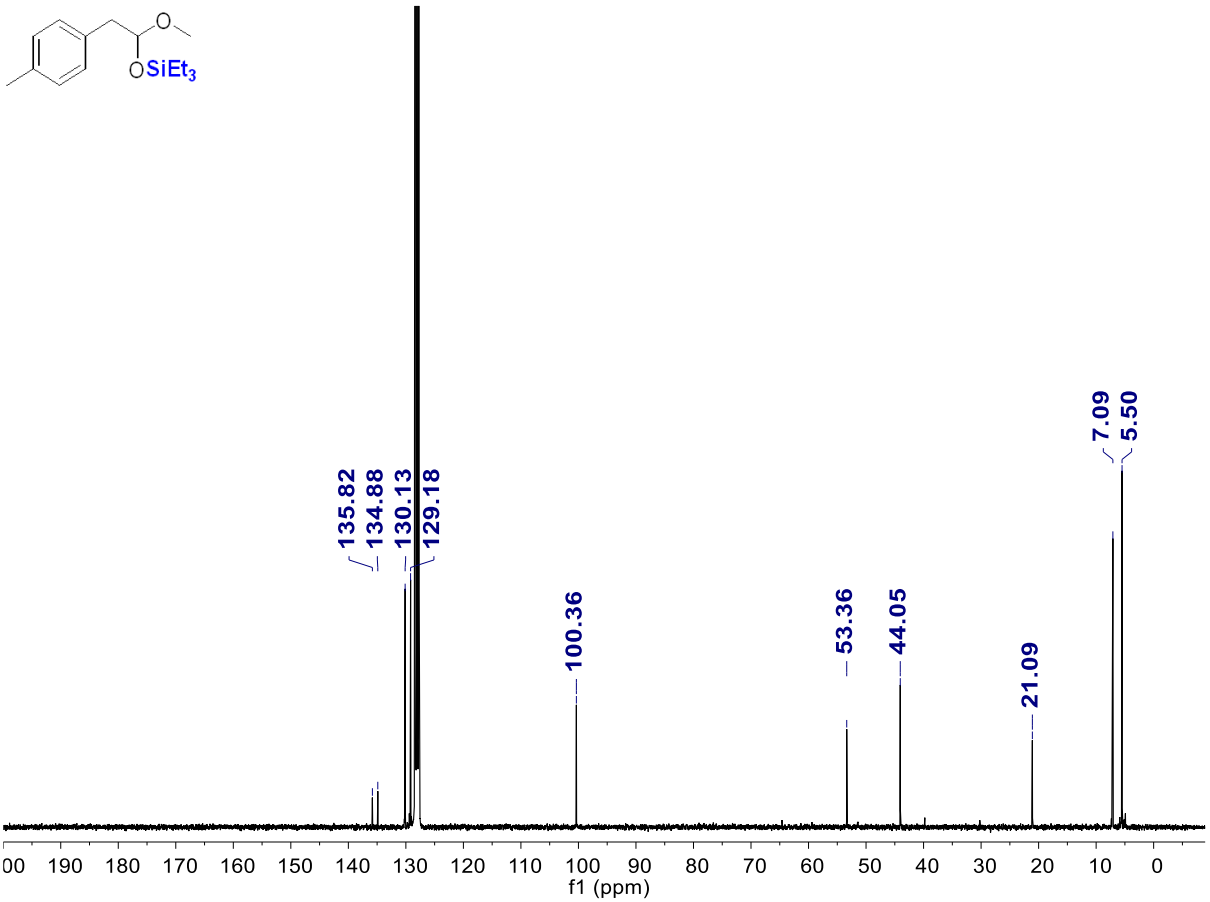
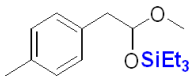


Figure S24: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2g** in C_6D_6.



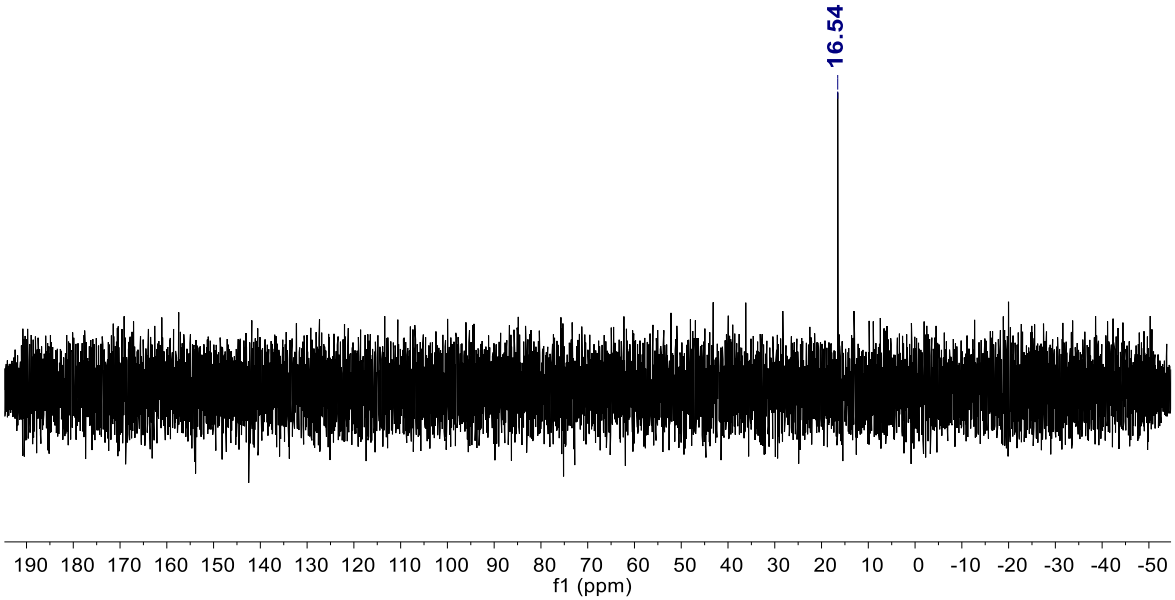
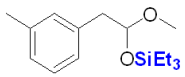


Figure S25: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2g** in C_6D_6.



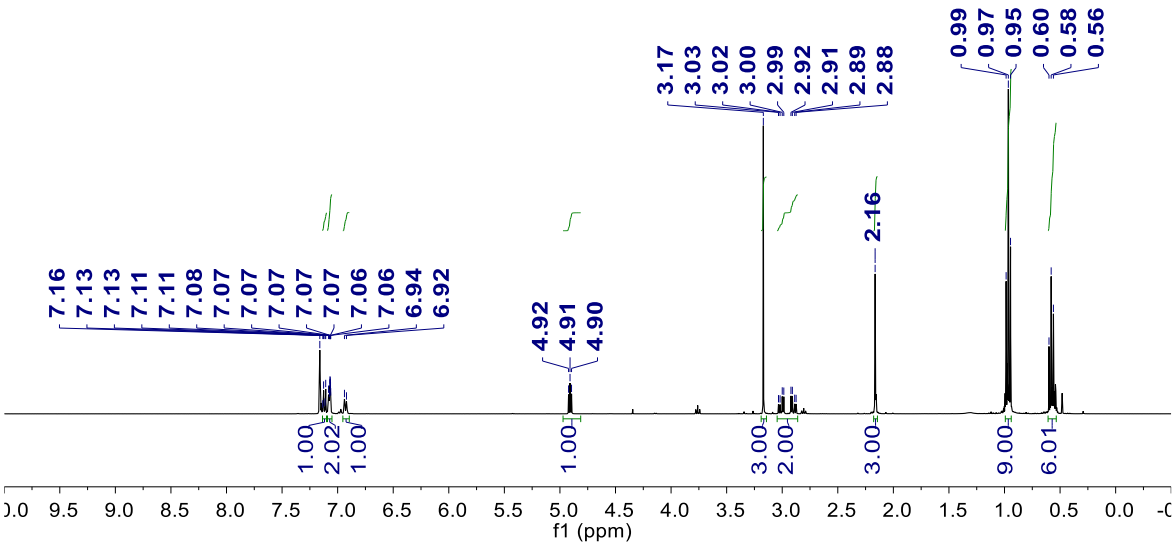
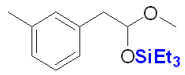


Figure S26: ^{1}H NMR spectrum of the compound **2h** in C_6D_6.



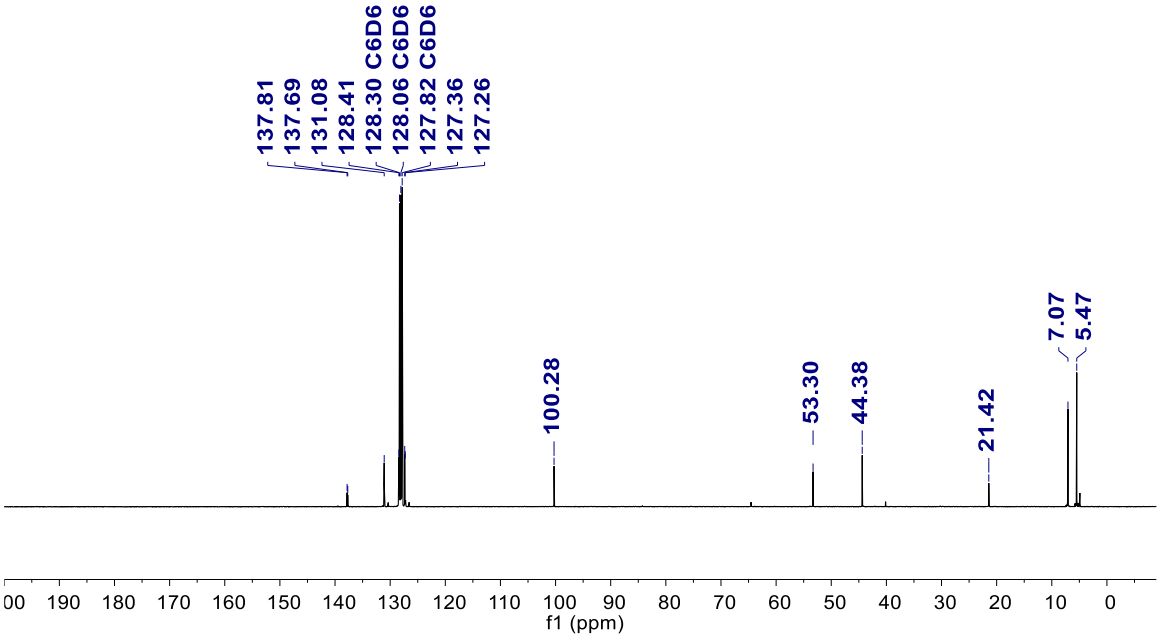
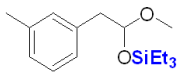


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2h** in C_6D_6.



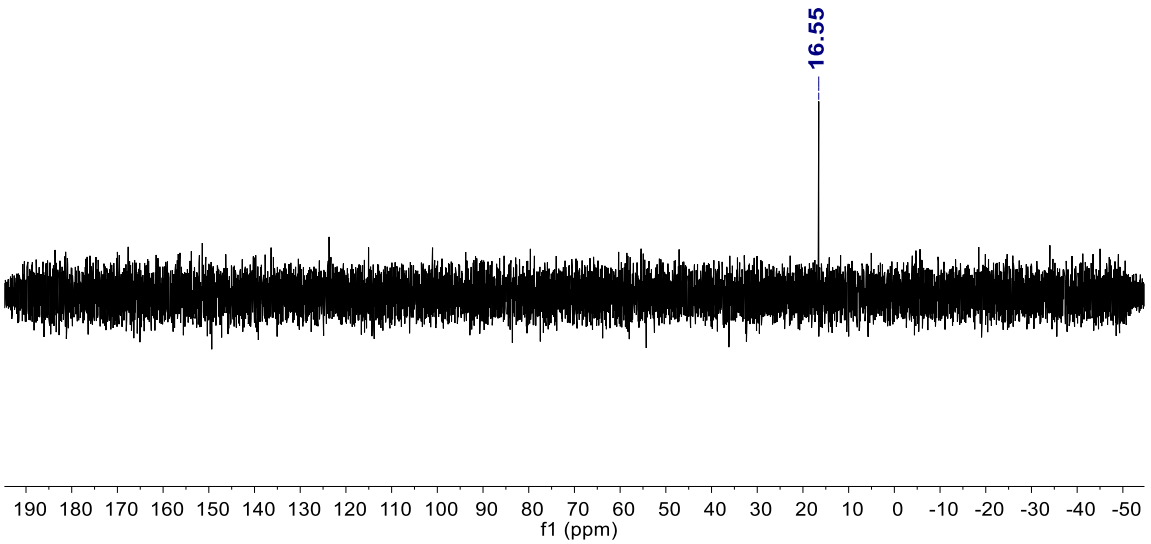


Figure S28: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2h** in C_6D_6.

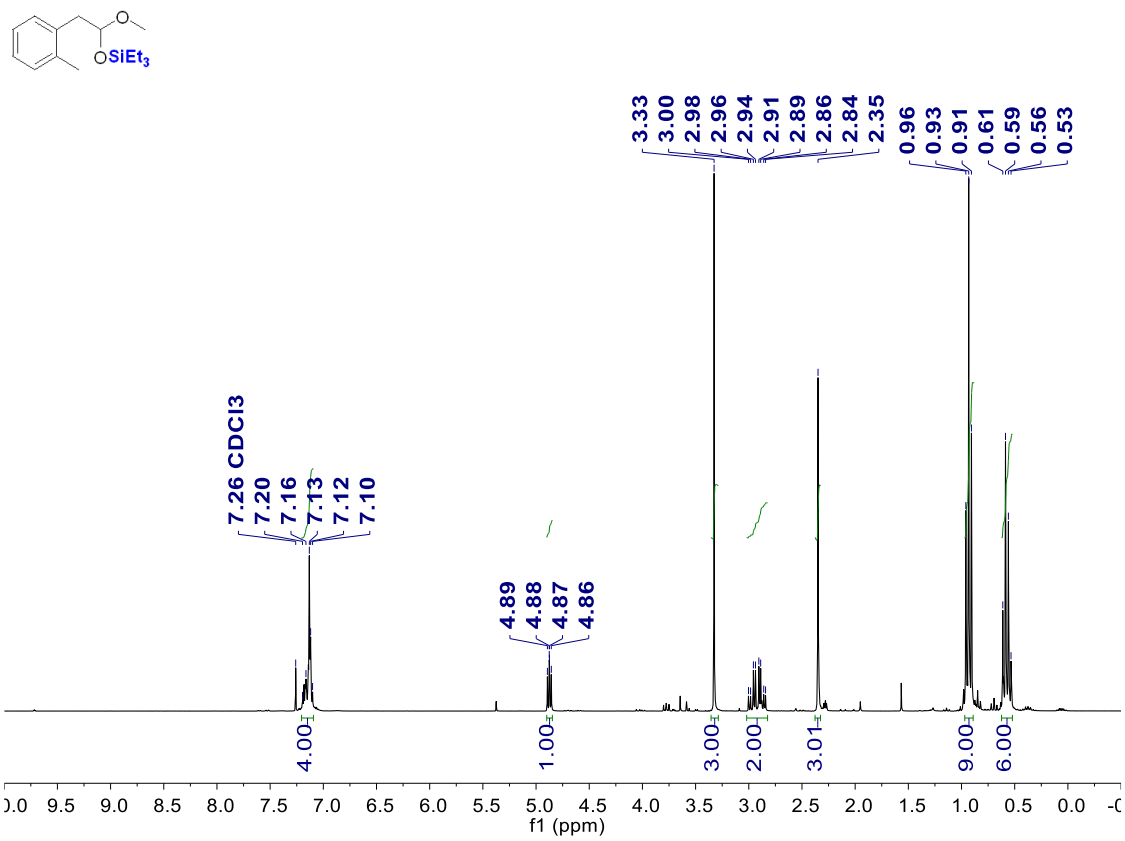


Figure S29: ^{1}H NMR spectrum of the compound **2i** in $CDCl_3$.

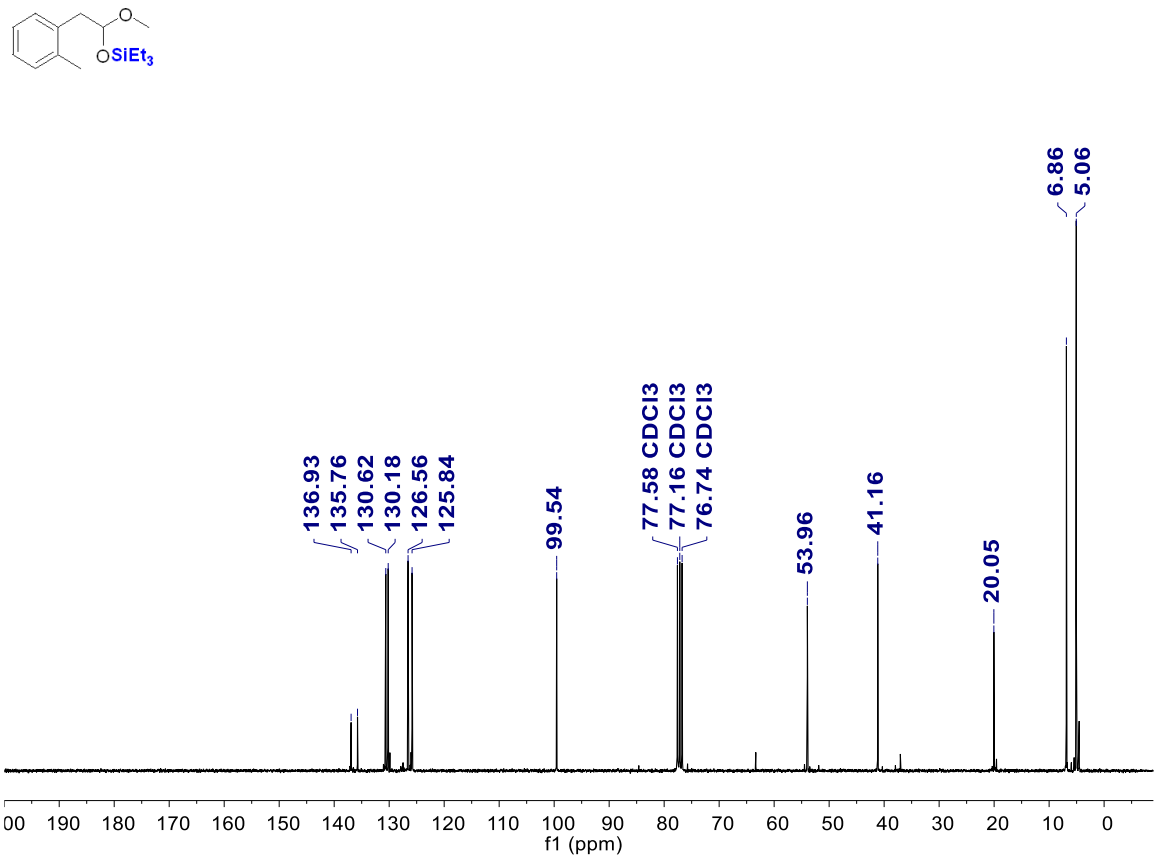
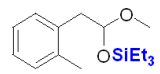


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2i** in $CDCl_3$.



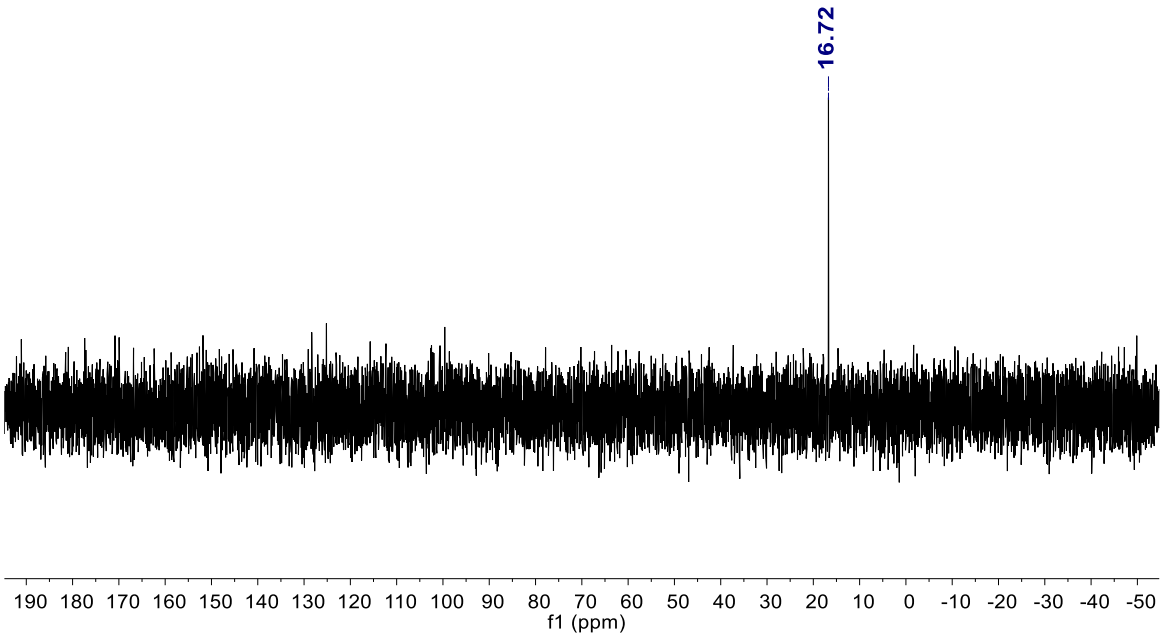
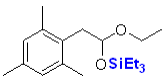


Figure S31: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2i** in C_6D_6.



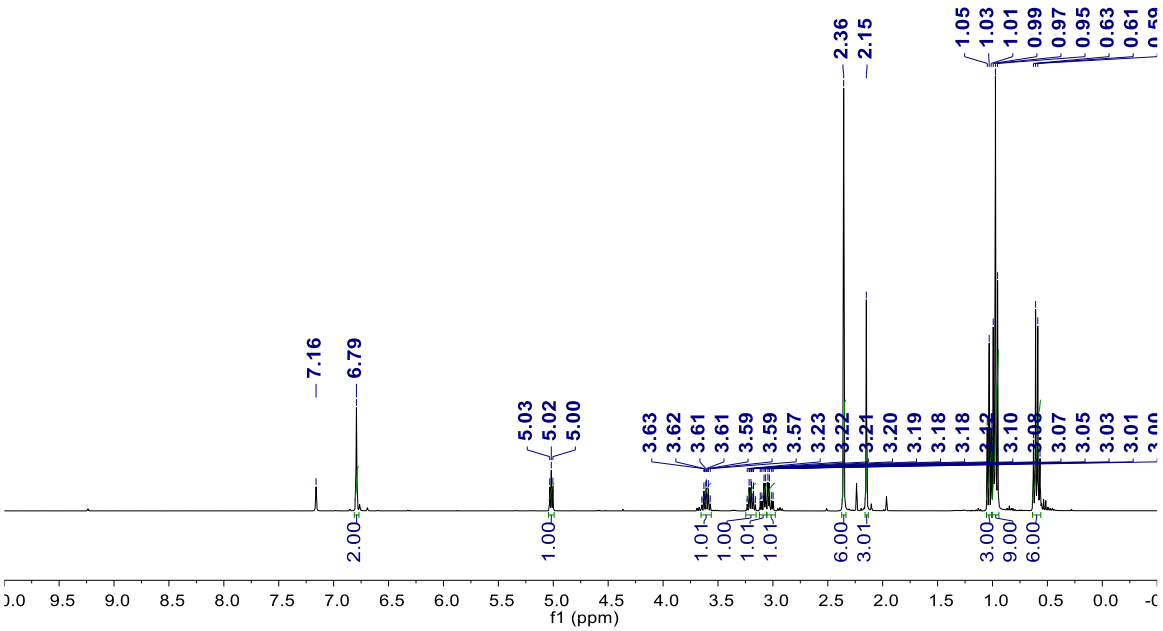
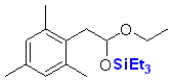


Figure S32: ^{1}H NMR spectrum of the compound **2j** in C_6D_6.



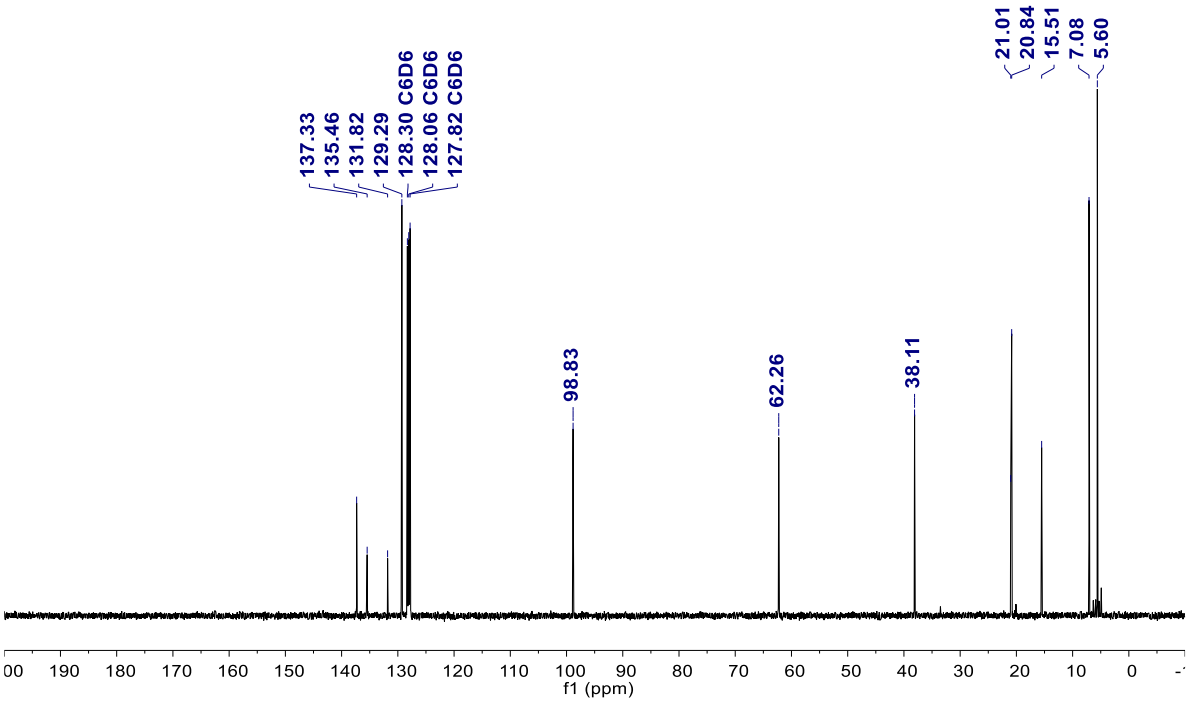
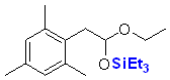


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2j** in C_6D_6.



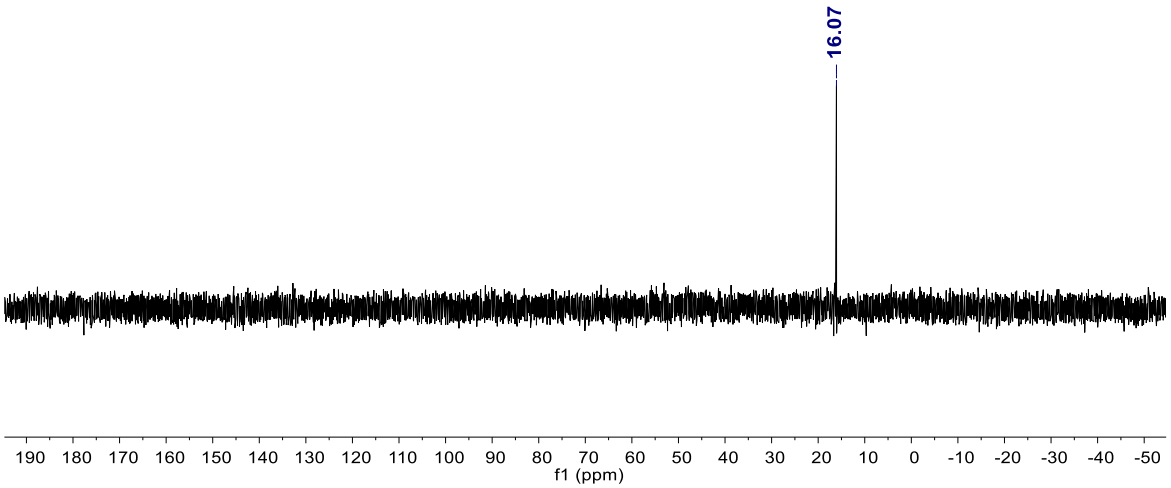
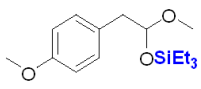


Figure S34: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2j** in C_6D_6



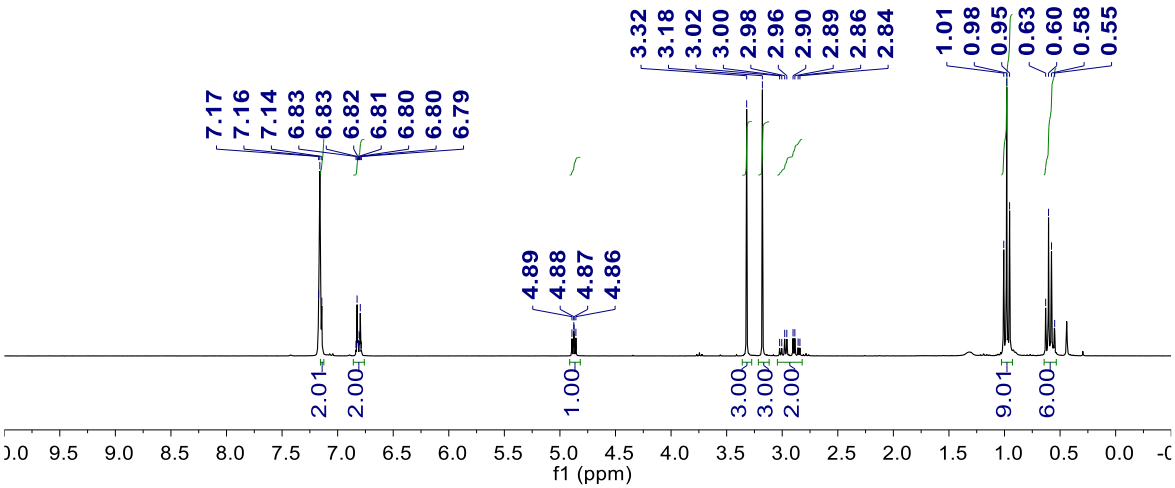
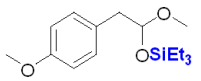


Figure S35: ^{1}H NMR spectrum of the compound **2k** in C_6D_6.



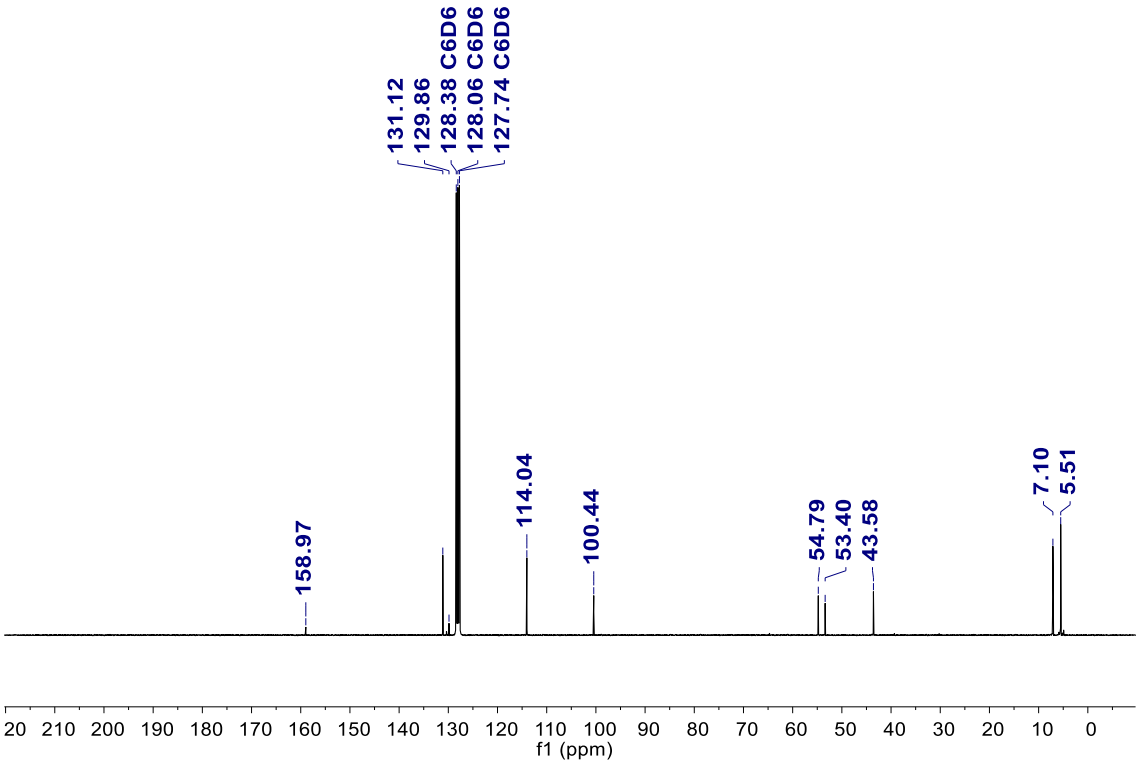
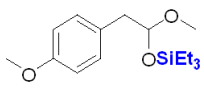


Figure S36: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2k** in C_6D_6.



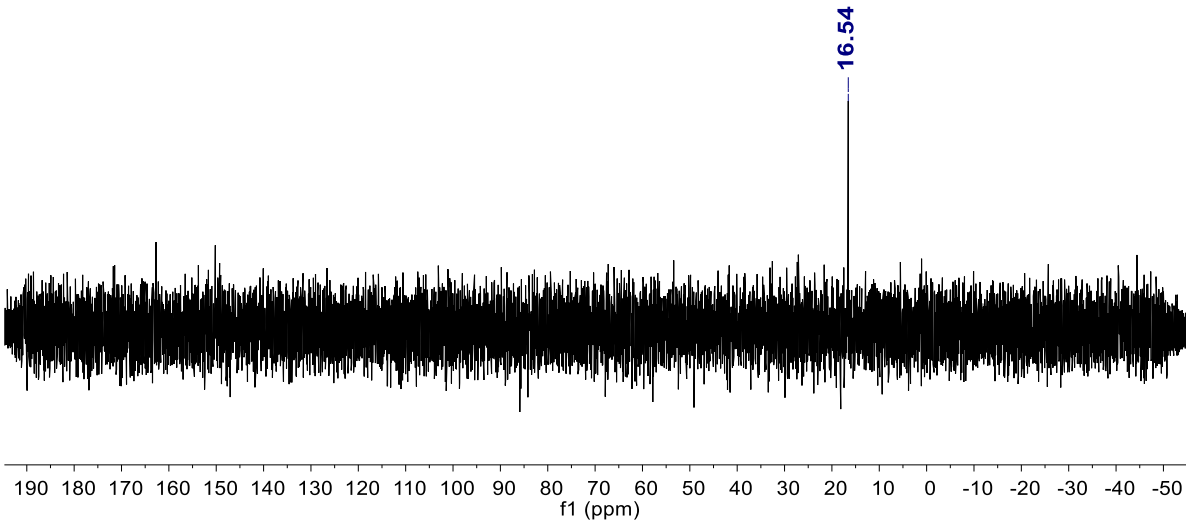
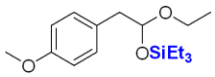


Figure S37: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2k** in C_6D_6.



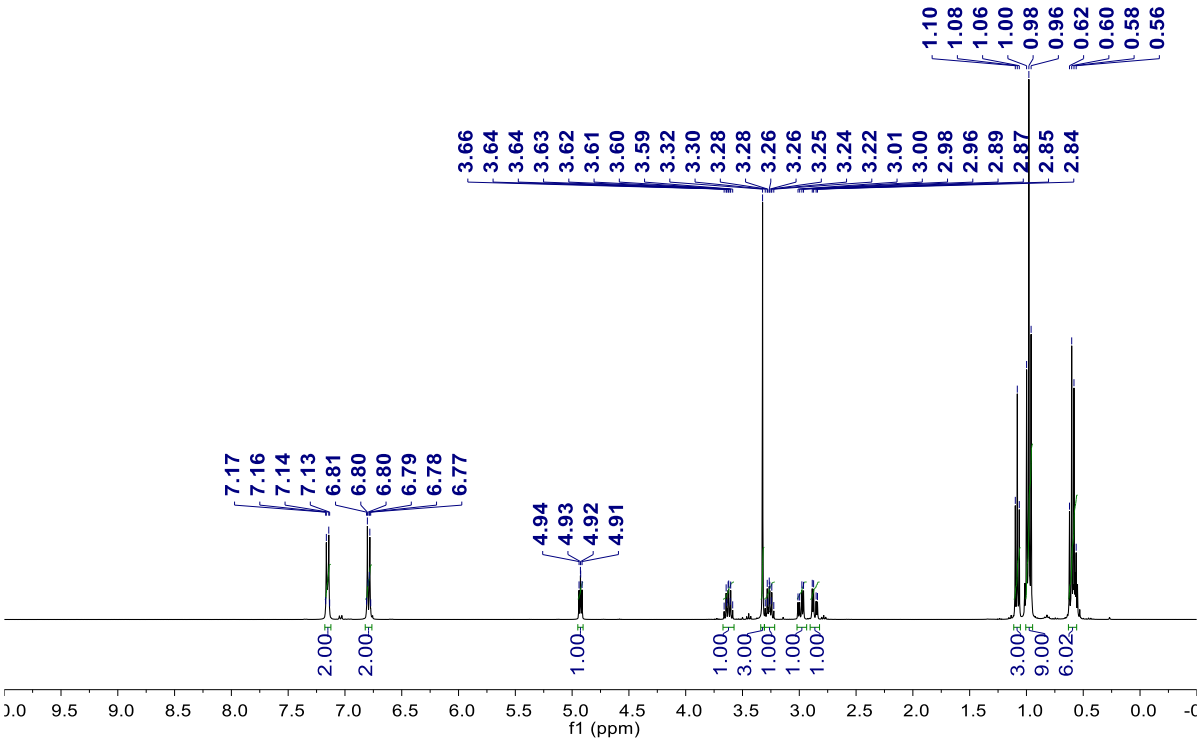


Figure S38: ^{1}H NMR spectrum of the compound **2l** in C_6D_6.

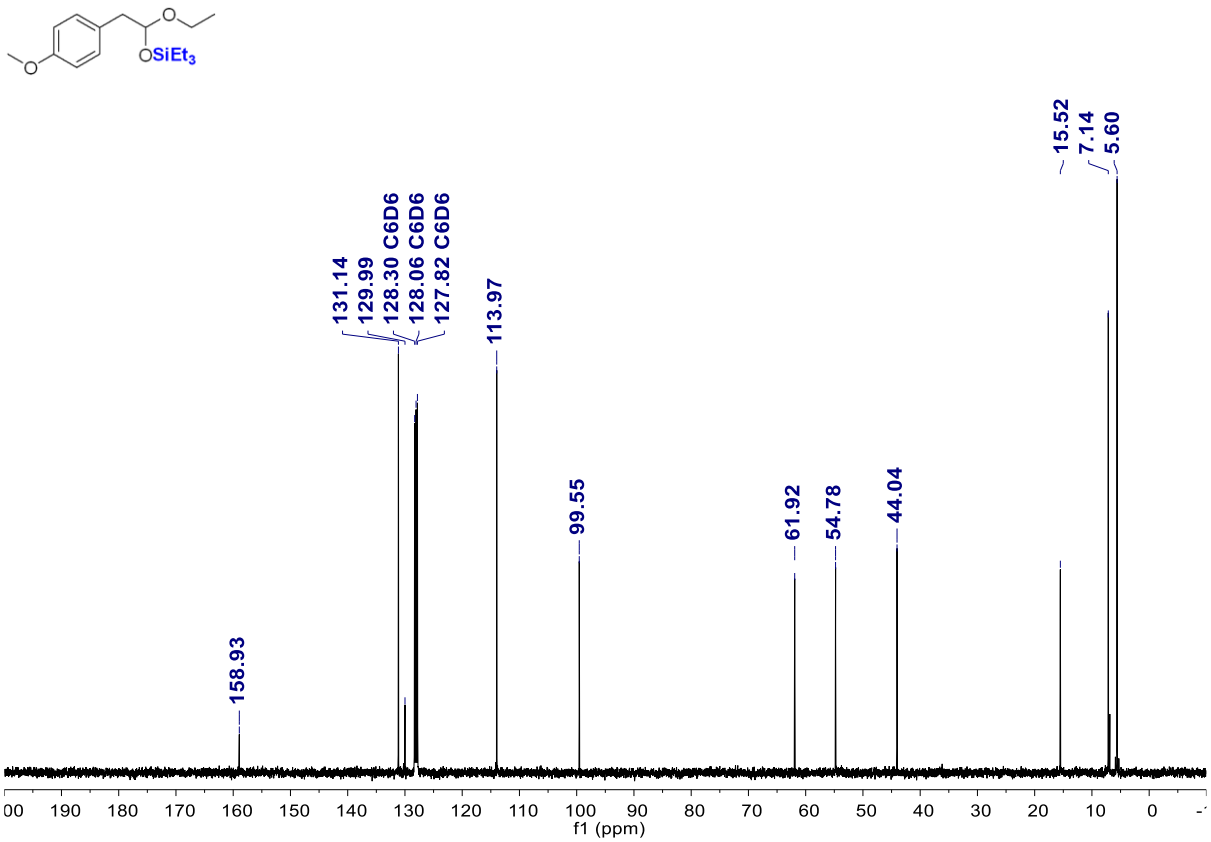


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2l** in C_6D_6.

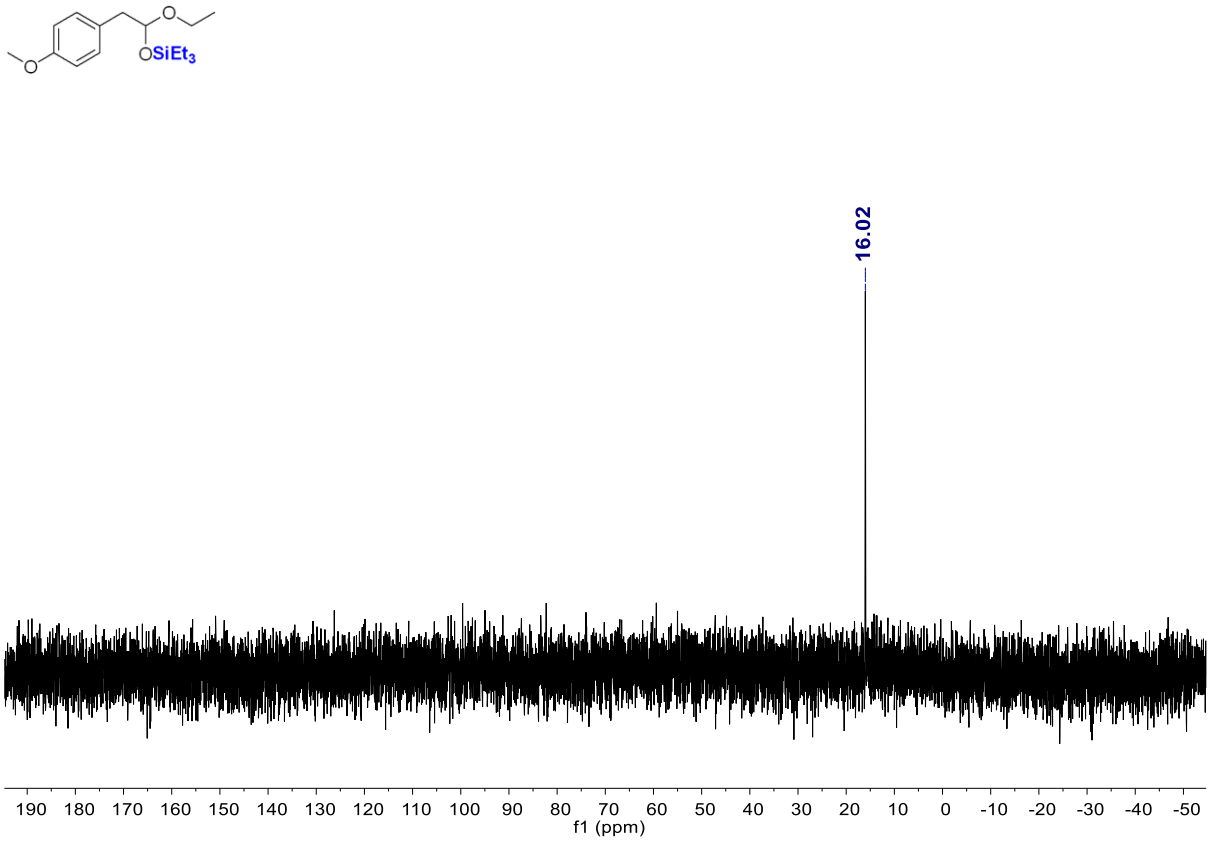
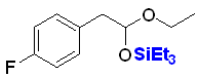


Figure S40: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2l** in C_6D_6



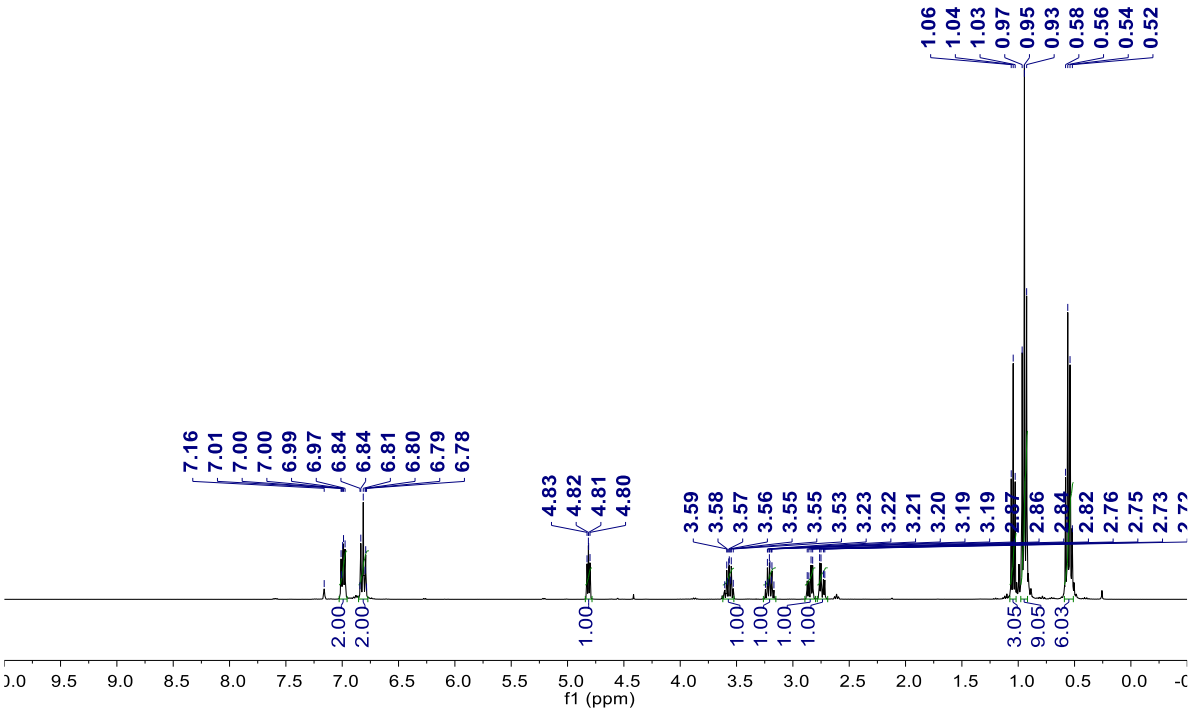


Figure S41: ^{1}H NMR spectrum of the compound **2m** in C_6D_6.

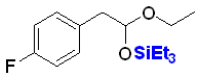
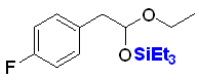


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2m** in C_6D_6.



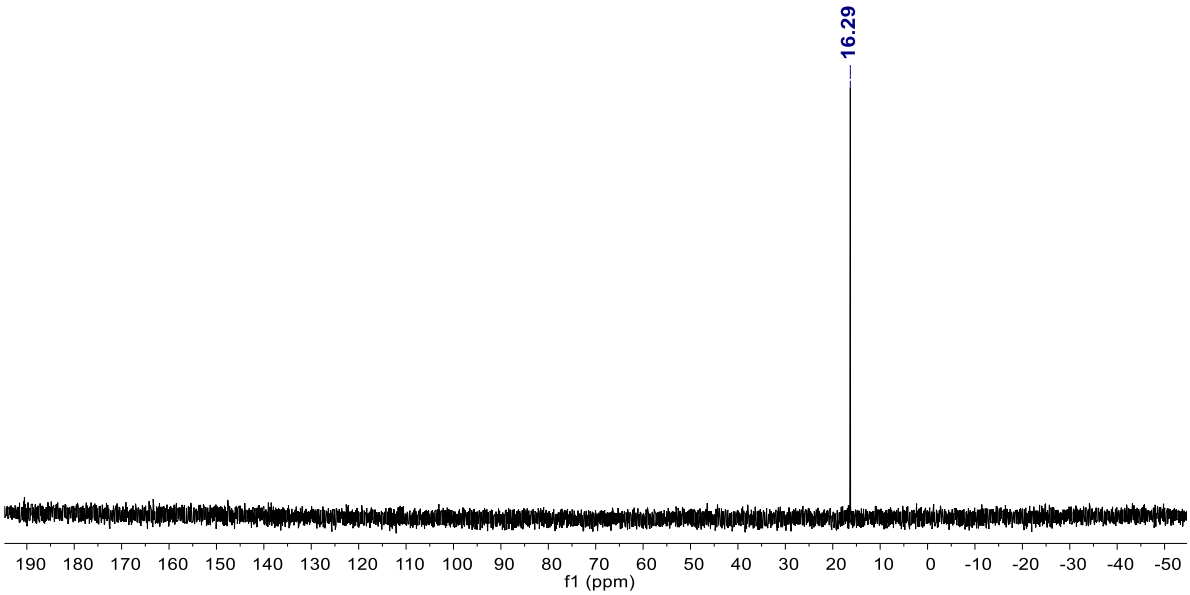
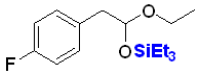


Figure S43: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2m** in C_6D_6



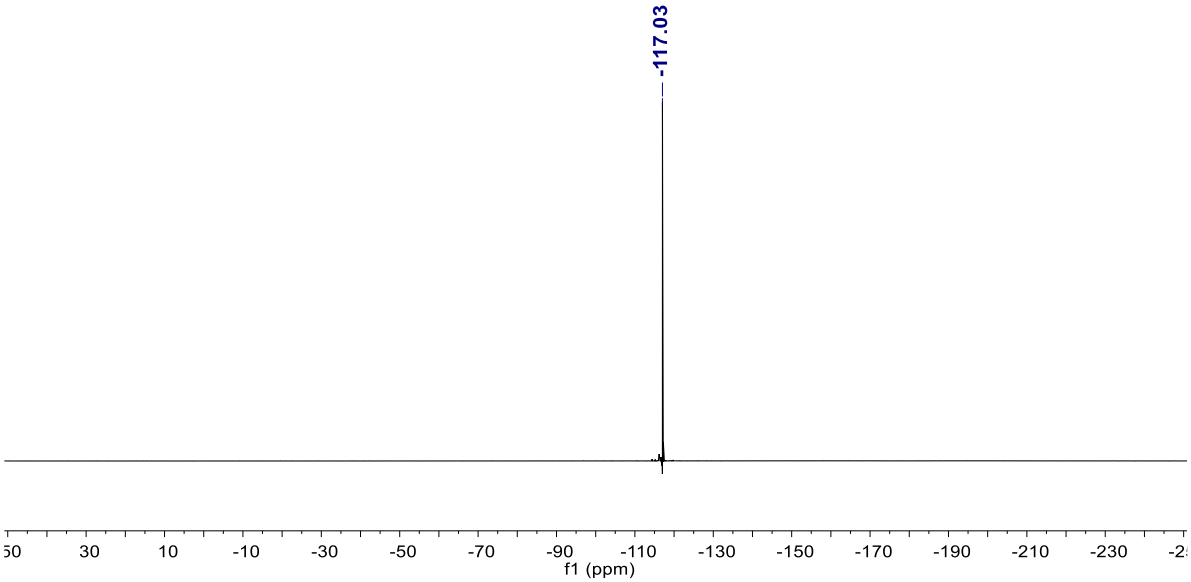


Figure S44: ^{19}F NMR spectrum of the compound **2m** in C_6D_6.

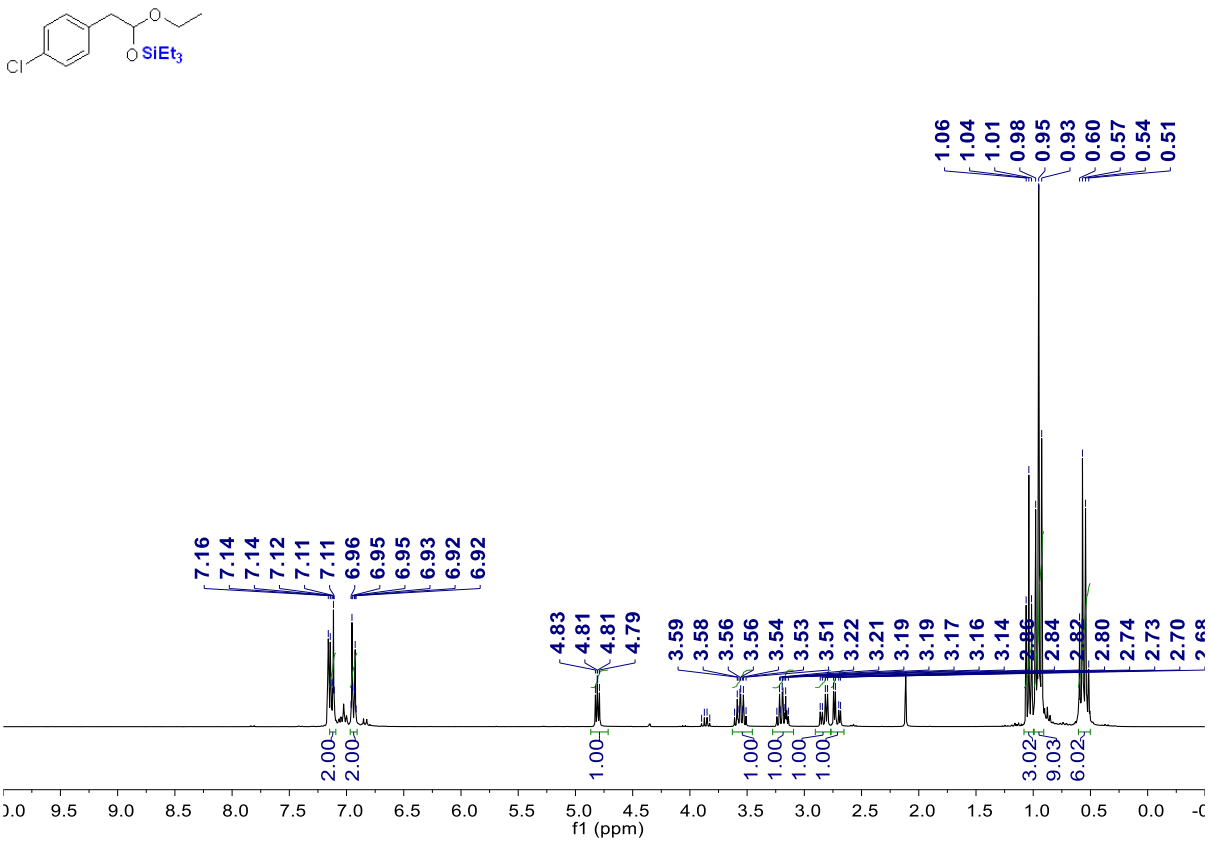


Figure S45: ^{1}H NMR spectrum of the compound **2n** in C_6D_6.

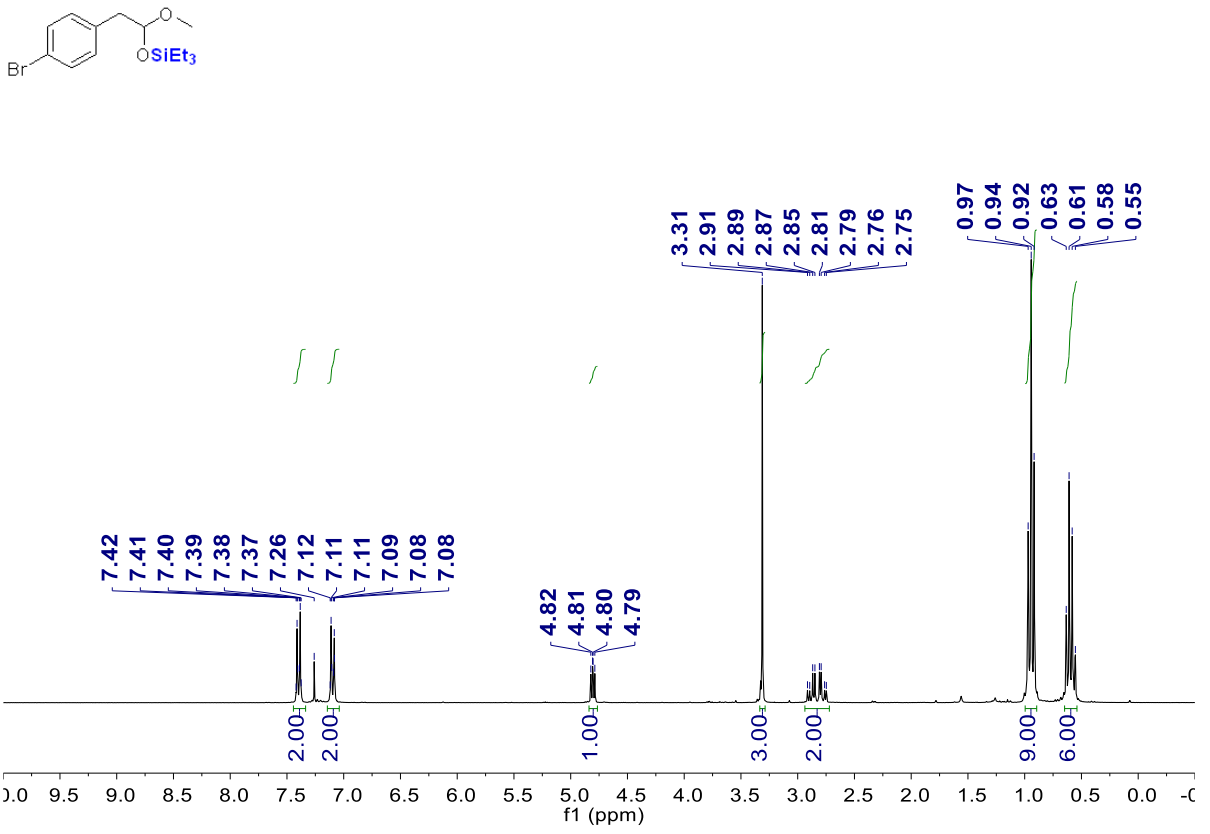
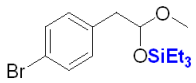


Figure S46: ^{1}H NMR spectrum of the compound **2o** in $CDCl_3$.



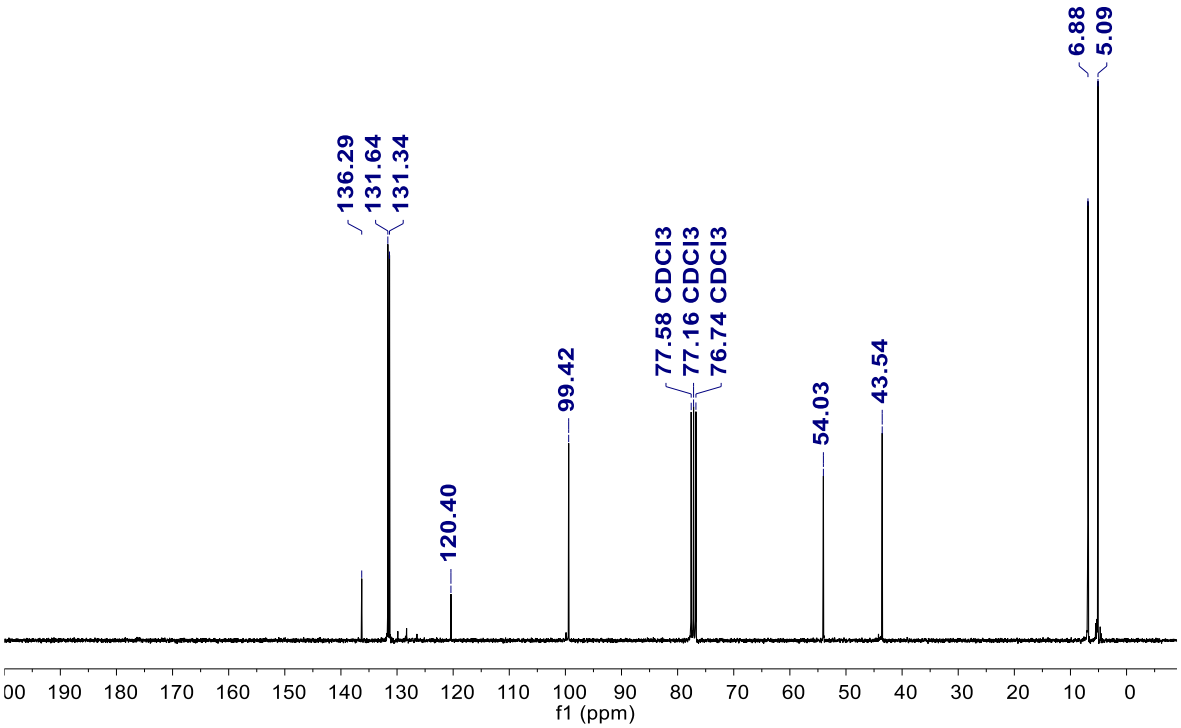
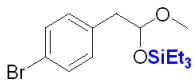


Figure S47: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2o** in $CDCl_3$.



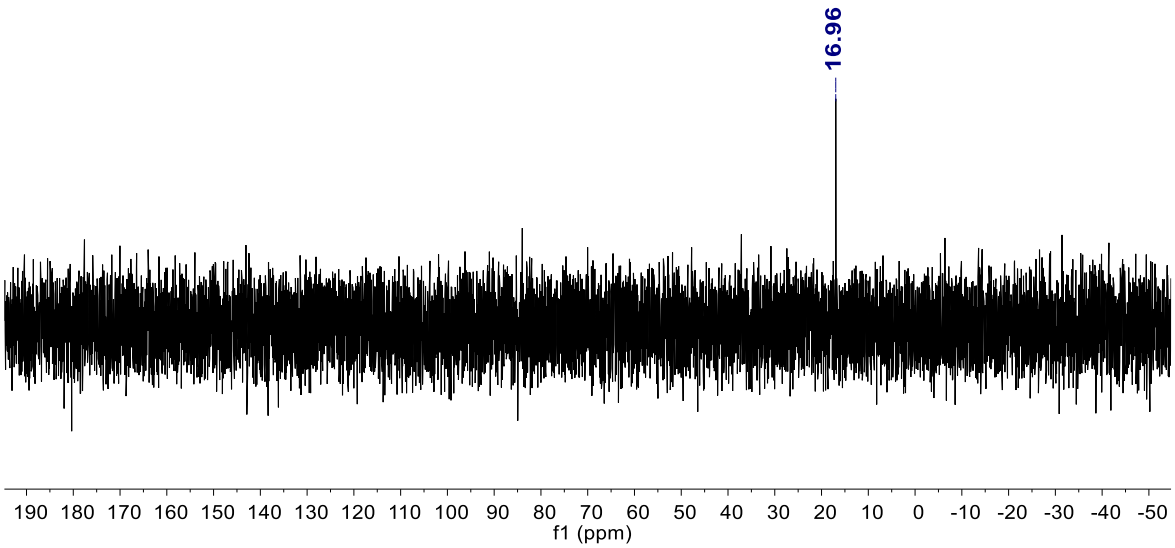
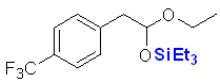


Figure S48: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2o** in C_6D_6.



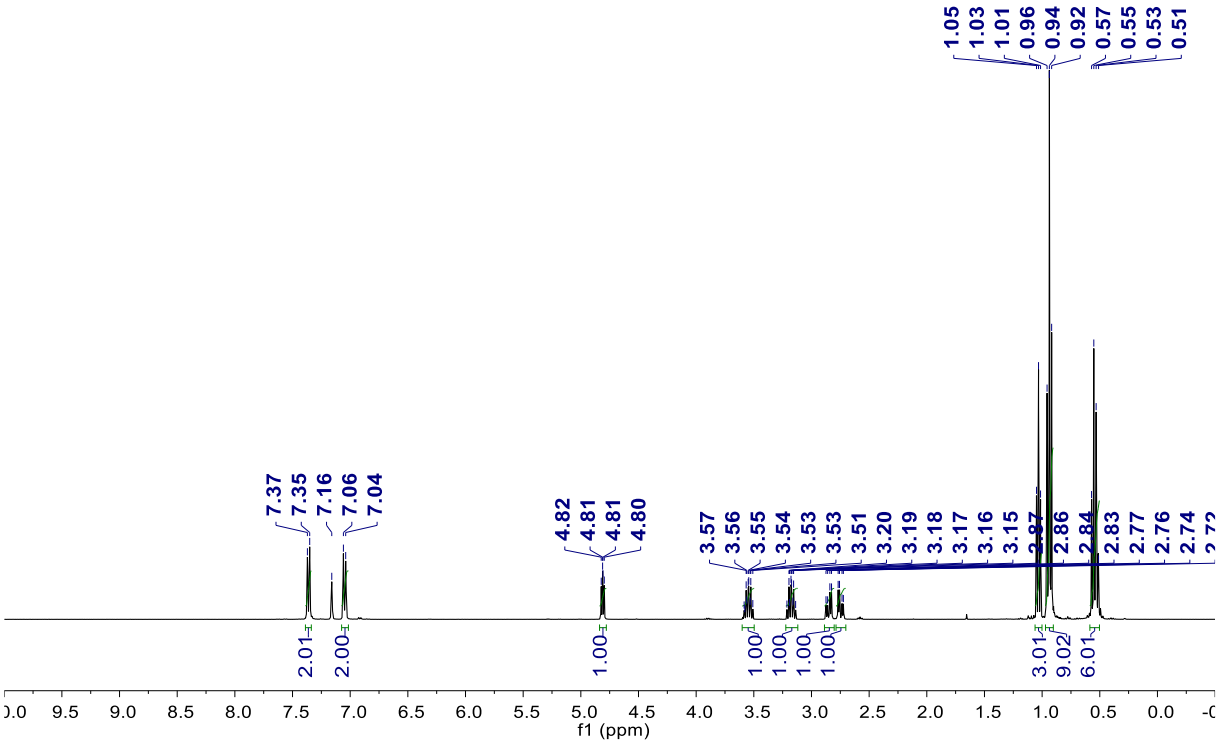
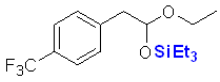


Figure S49: ^{1}H NMR spectrum of the compound **2p** in C_6D_6.



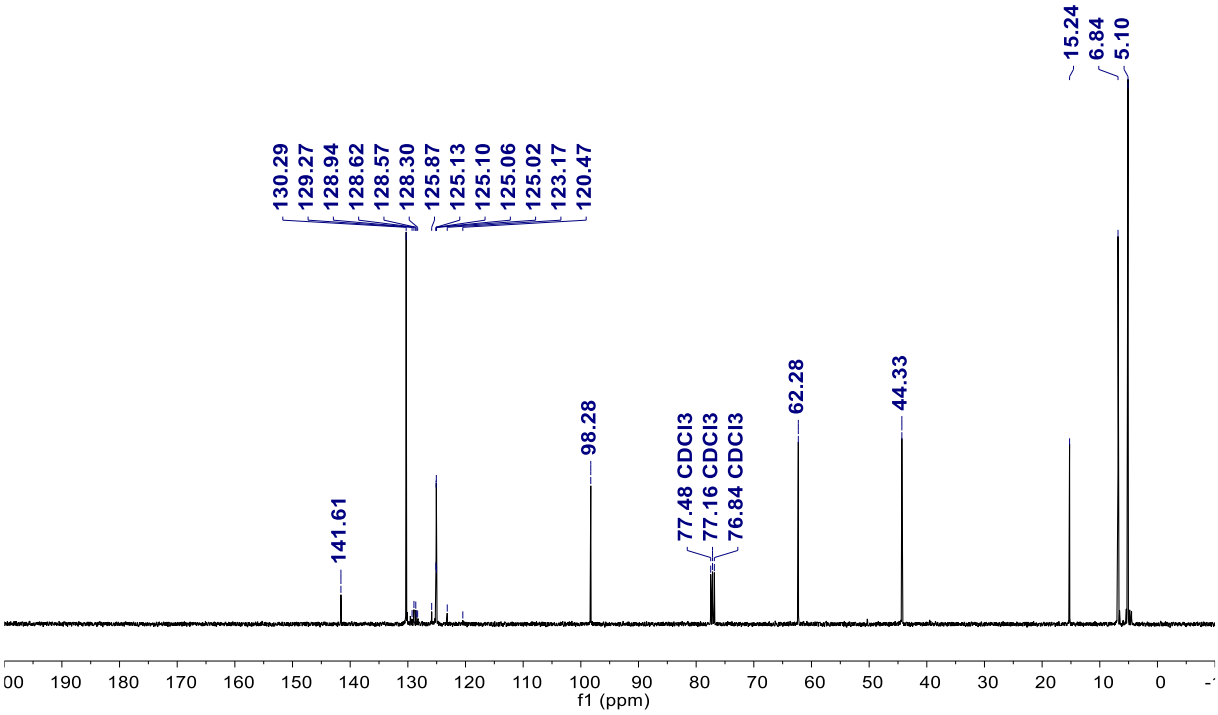
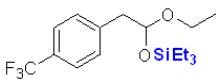


Figure S50: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2p** in $CDCl_3$.



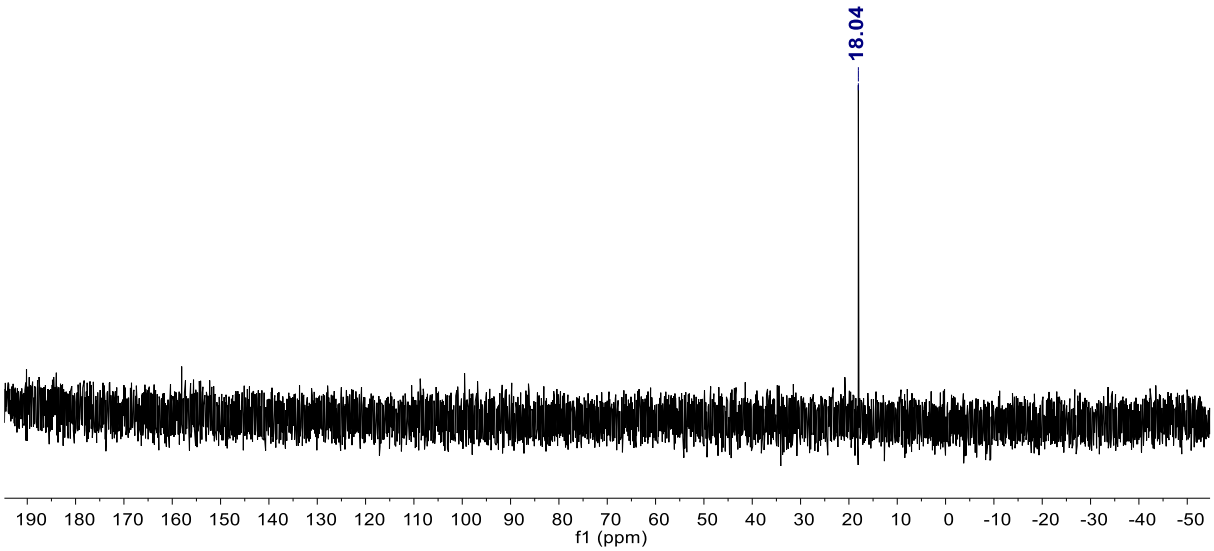
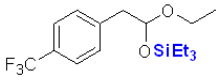


Figure S51: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2p** in C_6D_6



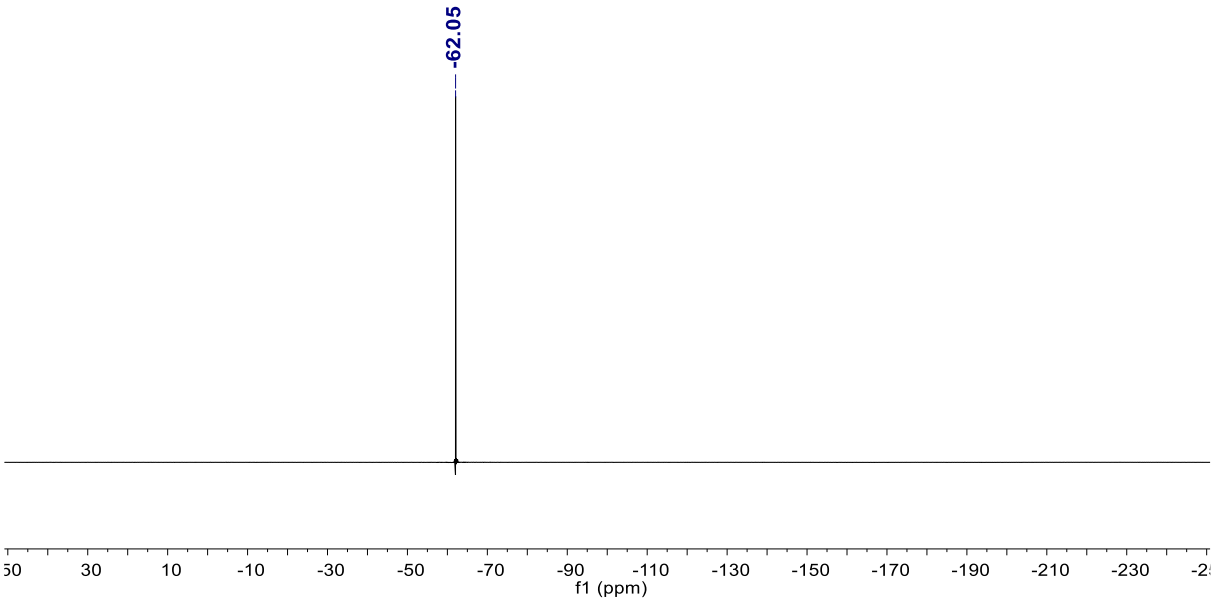


Figure S52: ^{19}F NMR spectrum of the compound **2p** in C_6D_6.

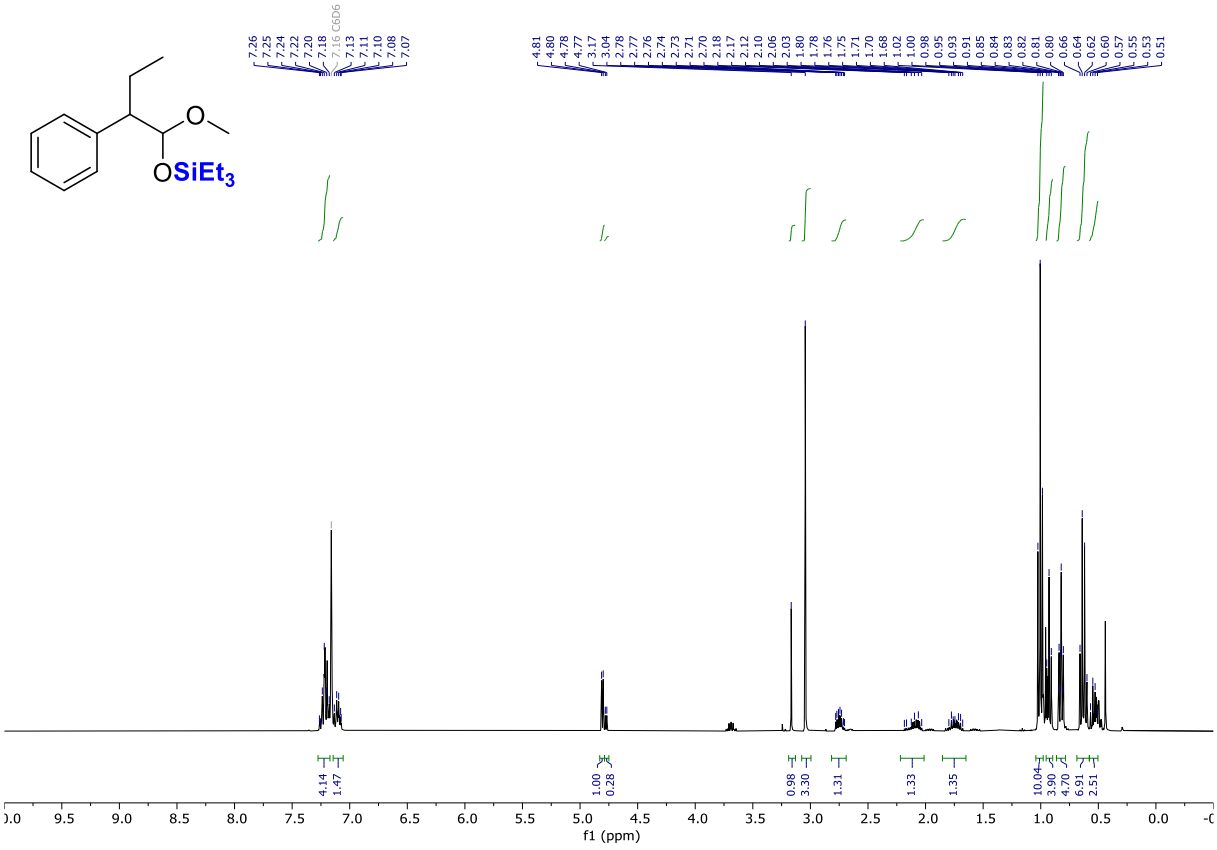


Figure S53: ^{1}H NMR spectrum of the compound **2q** in C_6D_6.

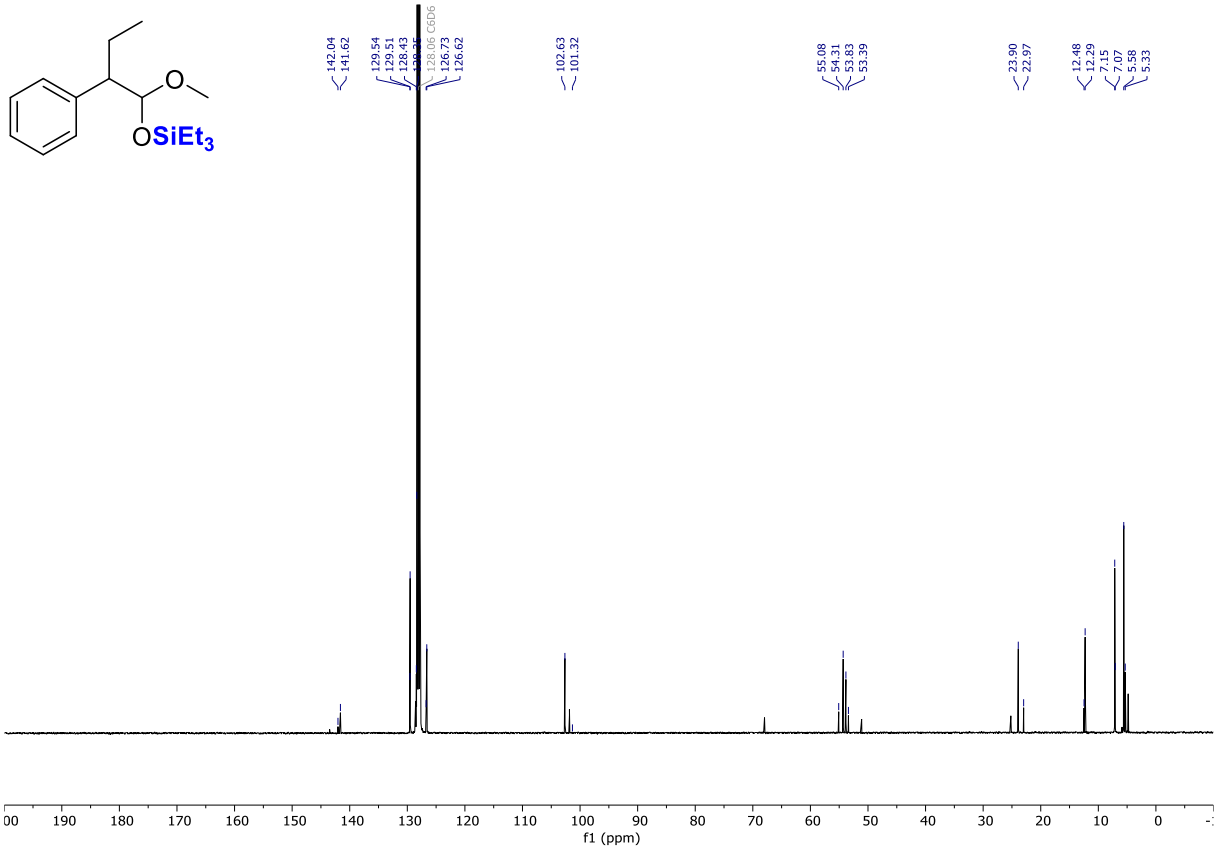
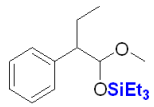


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2q** in C_6D_6.



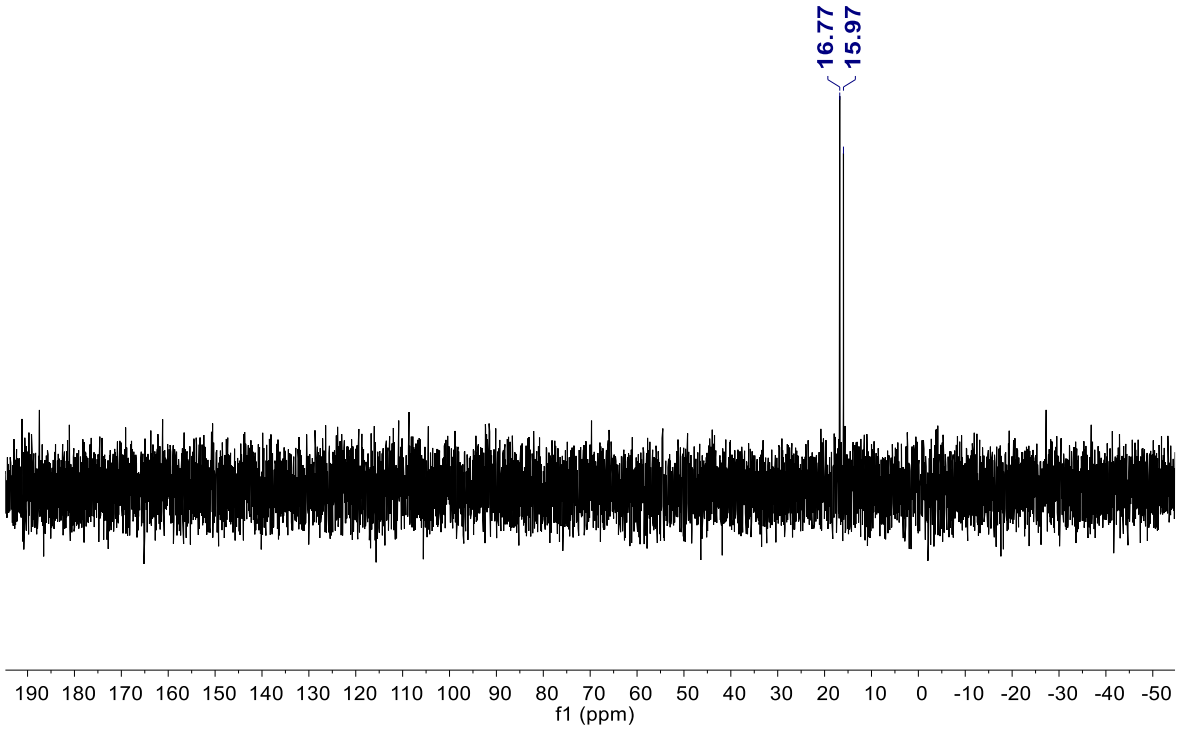
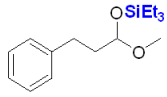


Figure S55: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2q** in $CDCl_3$.



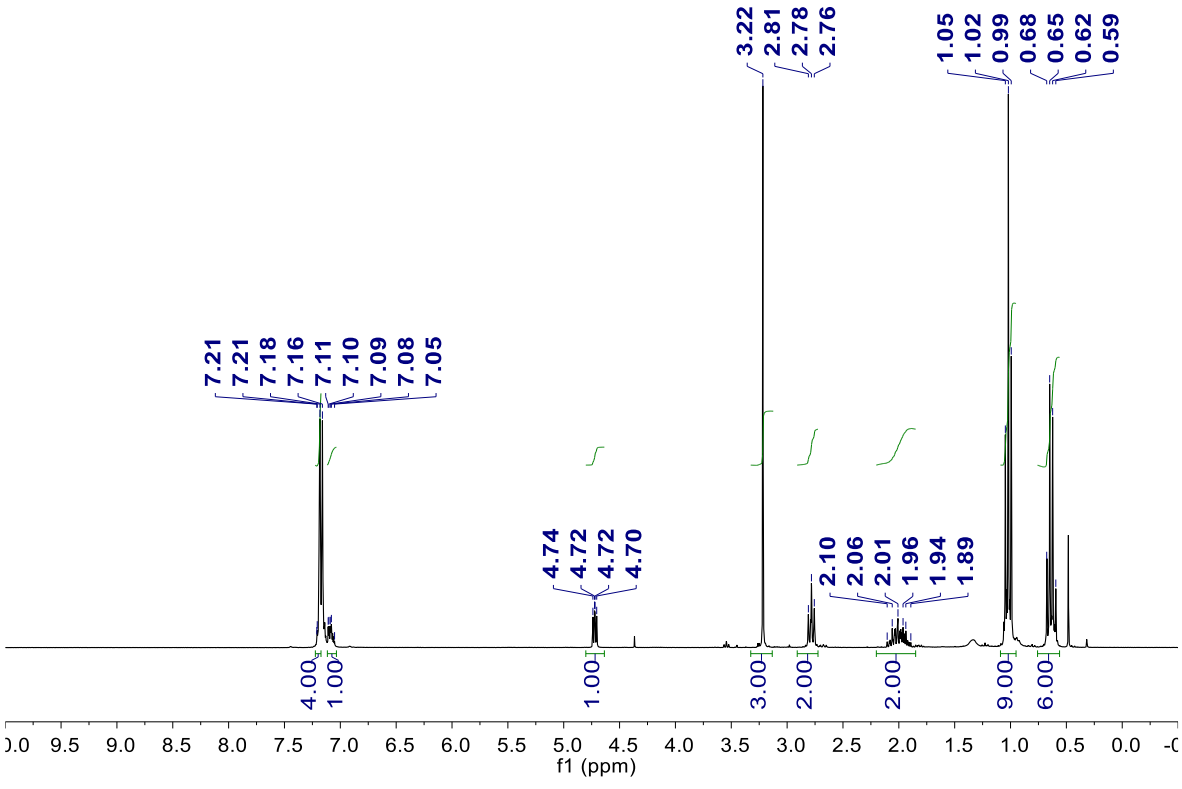


Figure S56: ^{1}H NMR spectrum of the compound **2r** in C_6D_6.

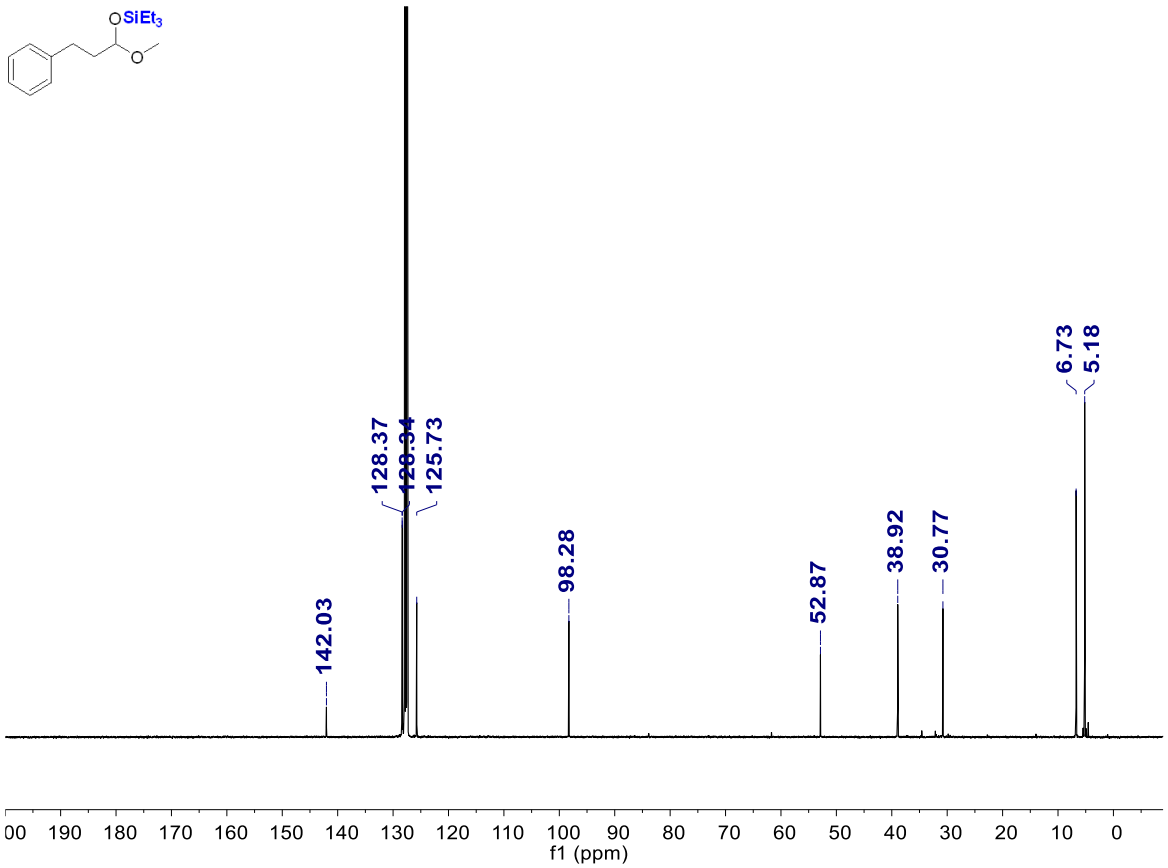


Figure S57: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2r** in C_6D_6.

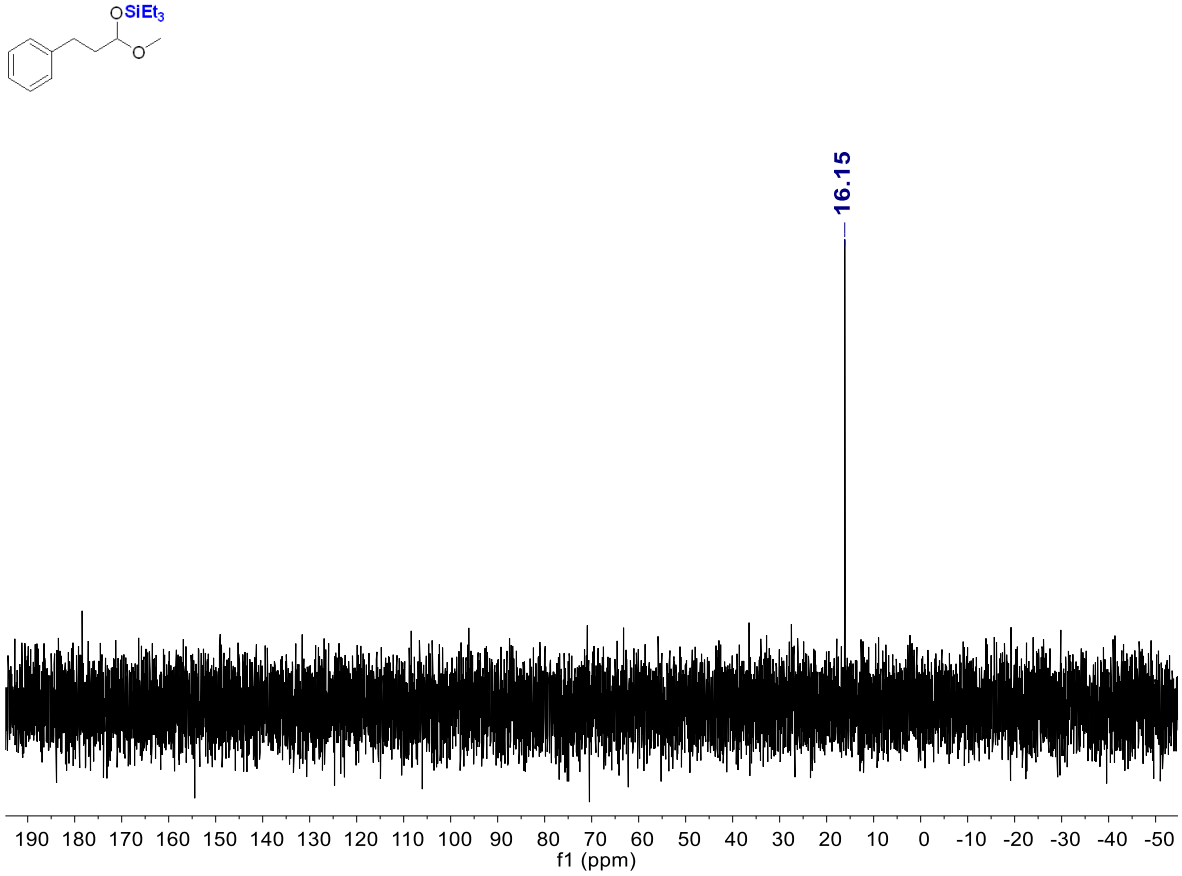


Figure S58: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2r** in C_6D_6.

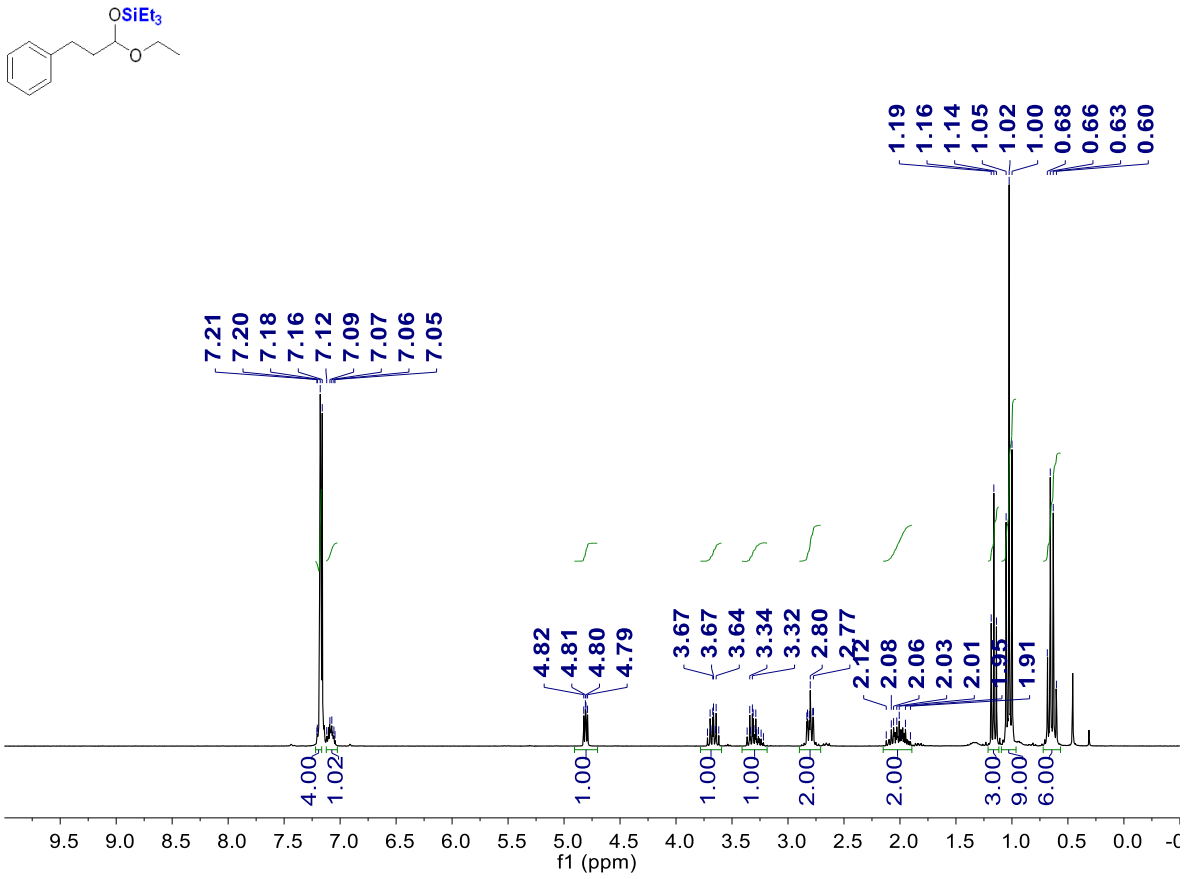


Figure S59: ^{1}H NMR spectrum of the compound **2s** in C_6D_6.

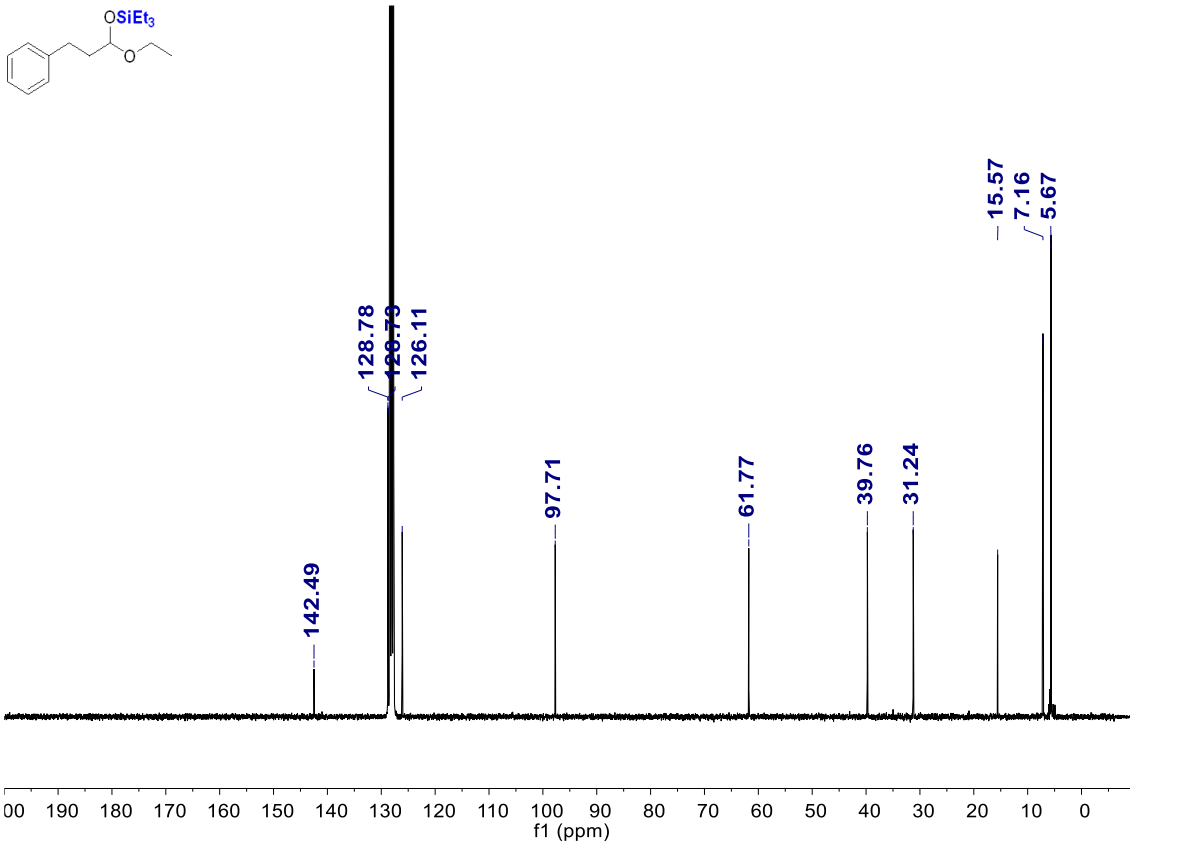
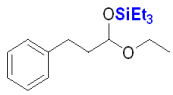


Figure S60: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2s** in C_6D_6.



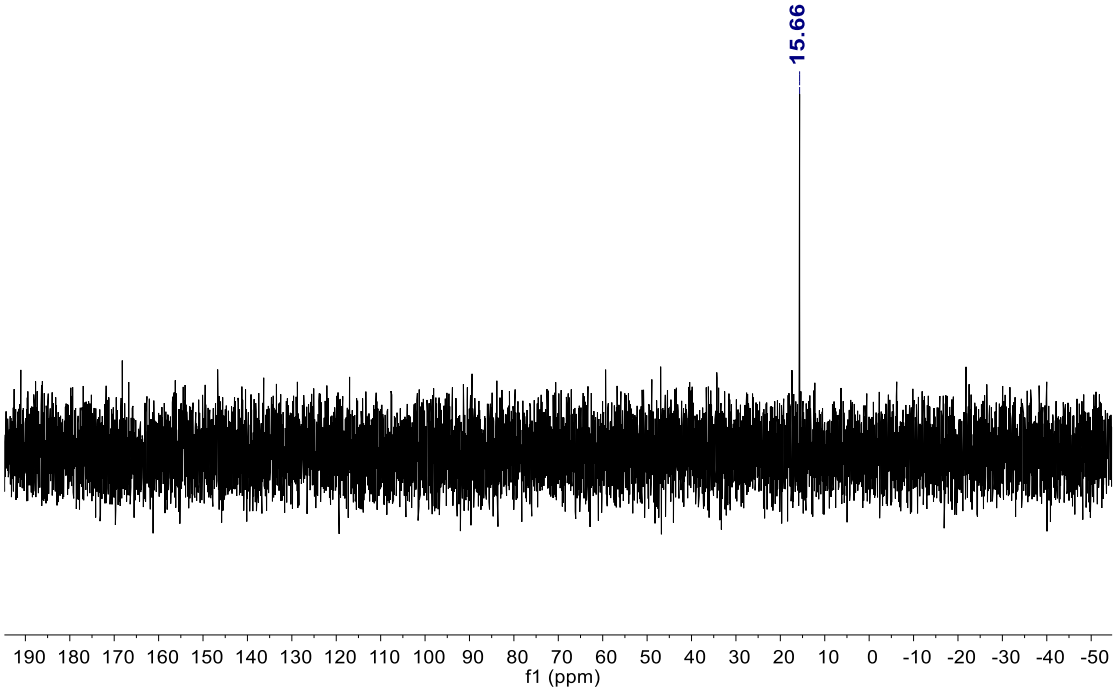
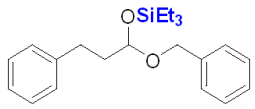


Figure S61: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2s** in C_6D_6.



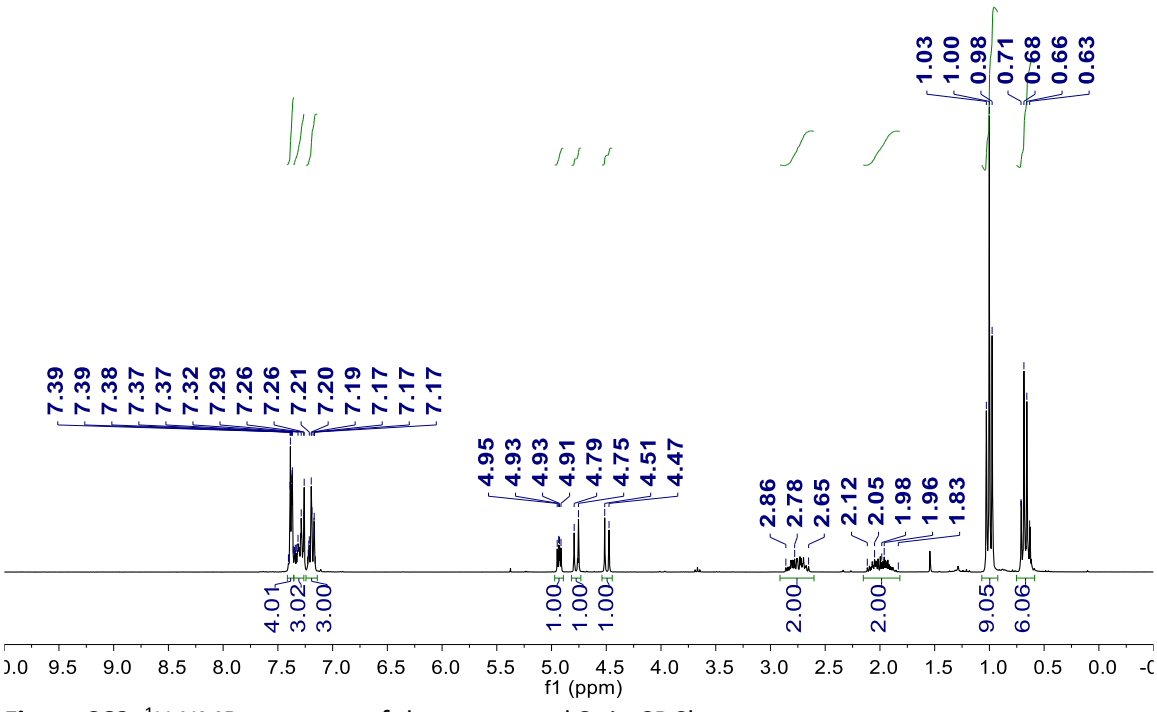
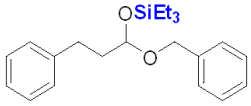


Figure S62: ^{1}H NMR spectrum of the compound **2t** in $CDCl_3$.



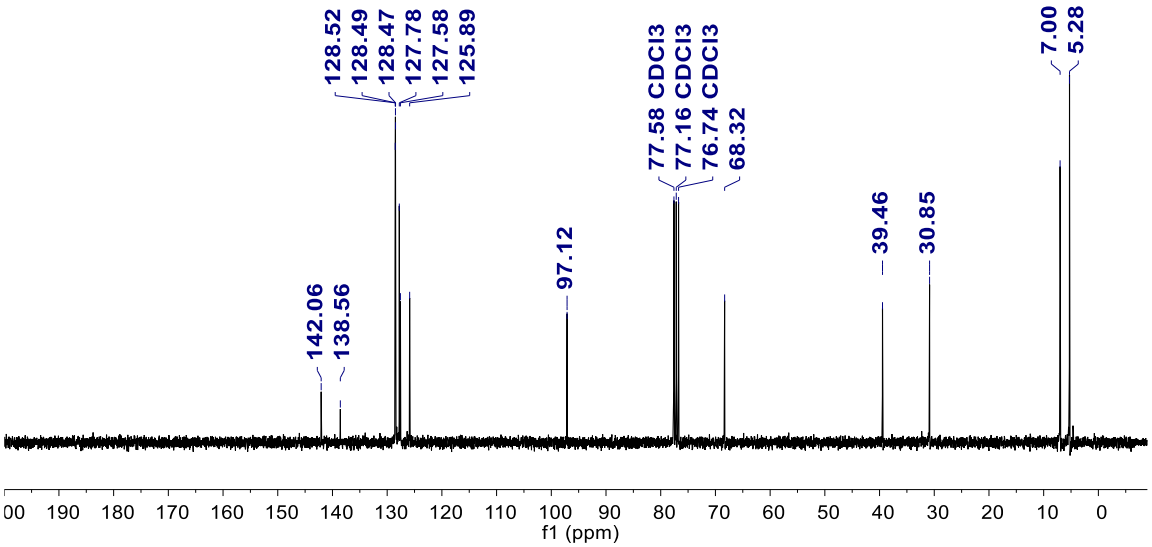
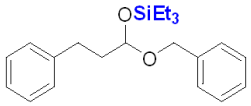


Figure S63: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2t** in $CDCl_3$.



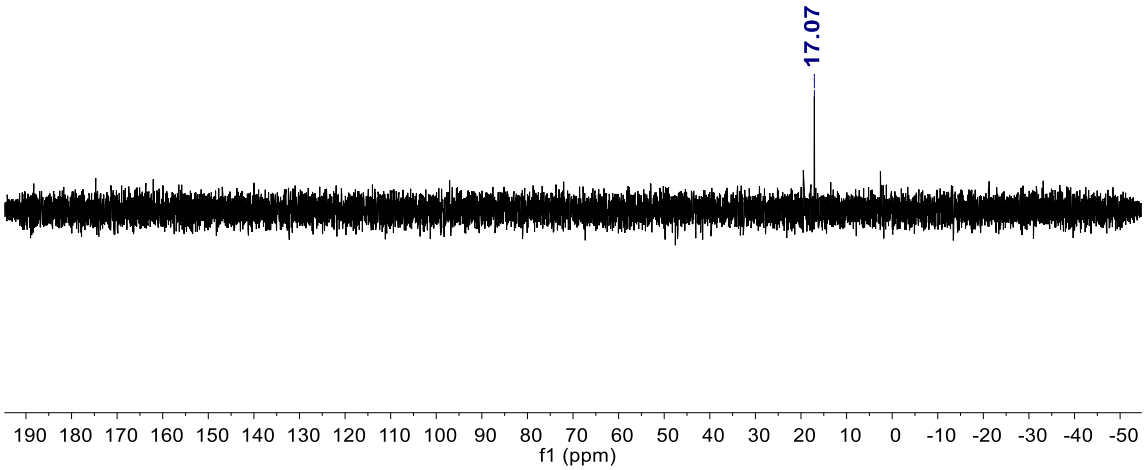


Figure S64: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2t** in C_6D_6.

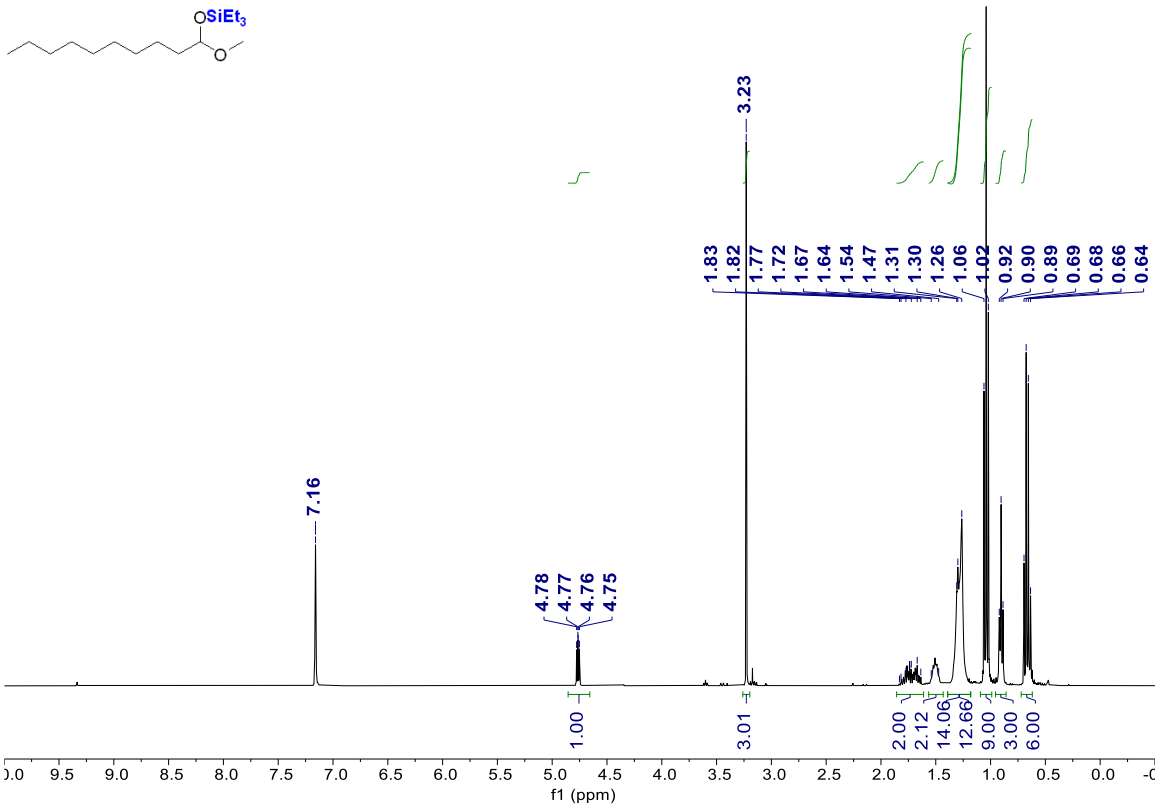


Figure S65: ^{1}H NMR spectrum of the compound **2u** in C_6D_6.

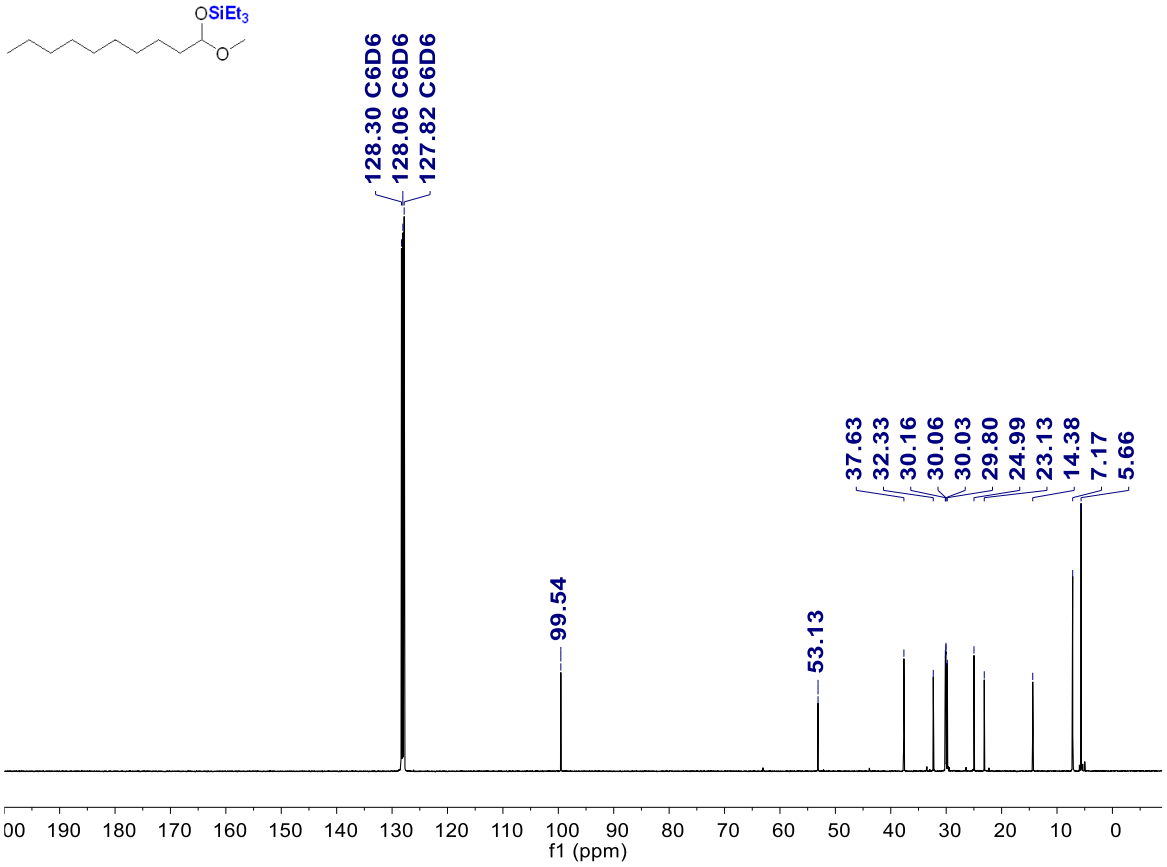
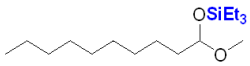


Figure S66: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2u** in C_6D_6.



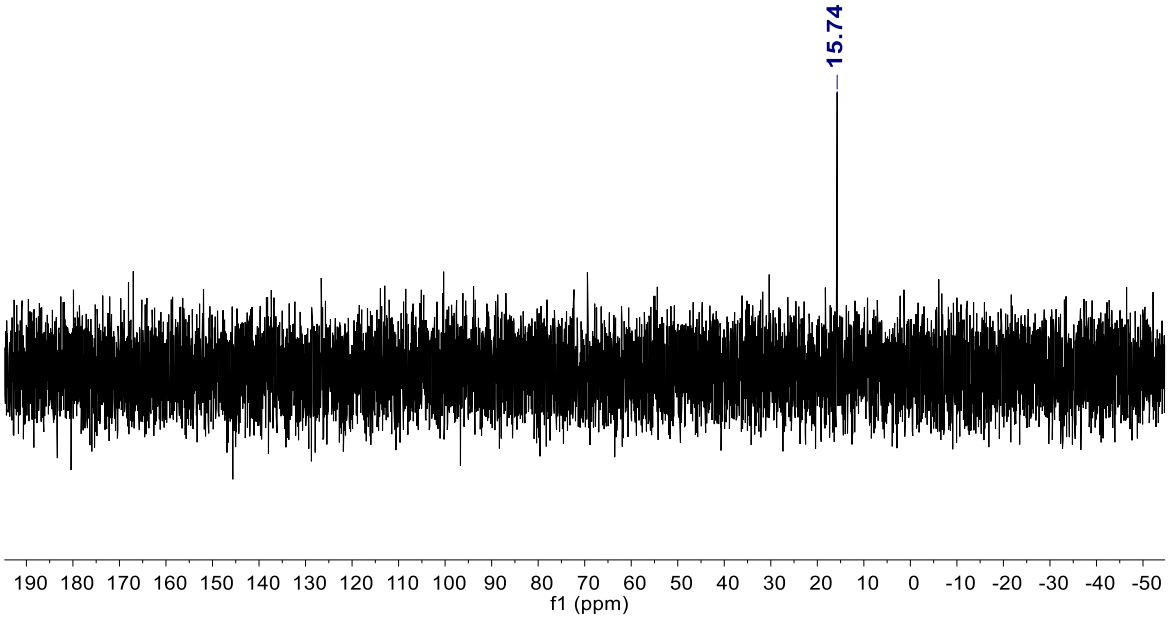
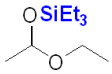


Figure S67: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2u** in C_6D_6.



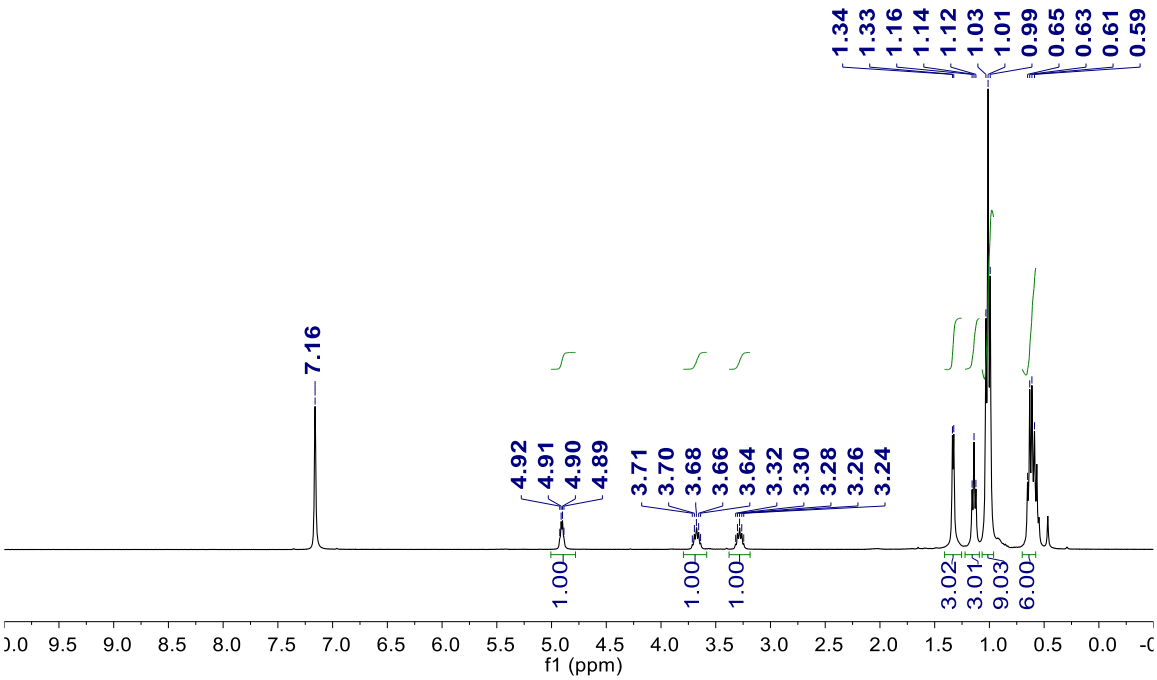


Figure S68: ^{1}H NMR spectrum of the compound **2v** in C_6D_6.

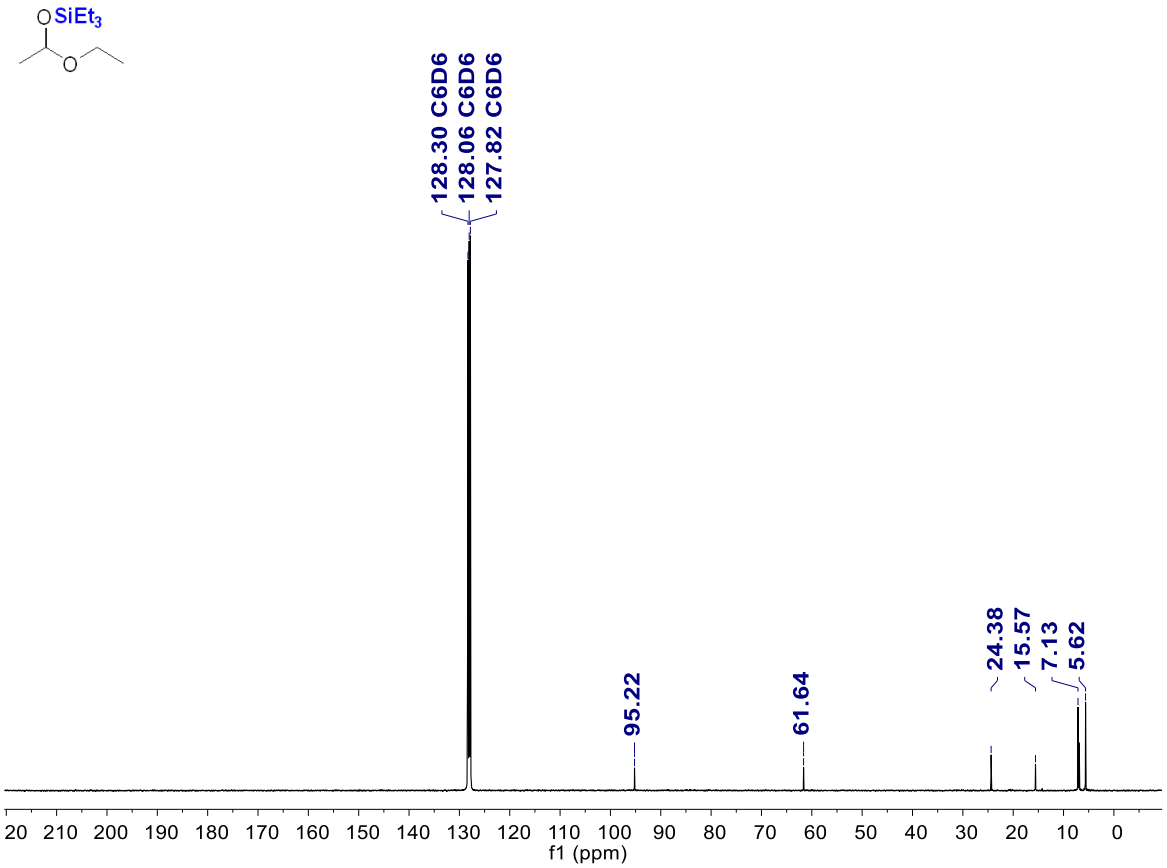


Figure S69: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2v** in C_6D_6.

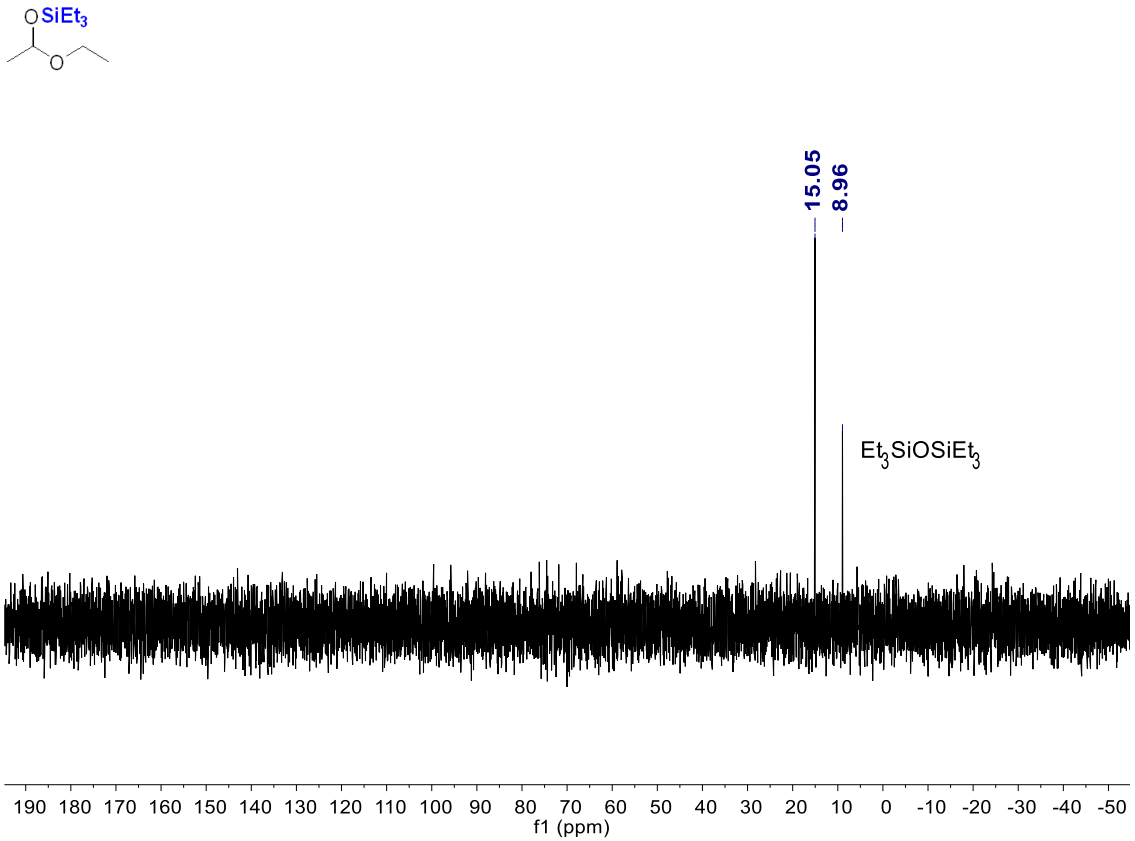
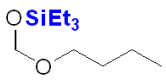


Figure S70: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2v** in $CDCl_3$.



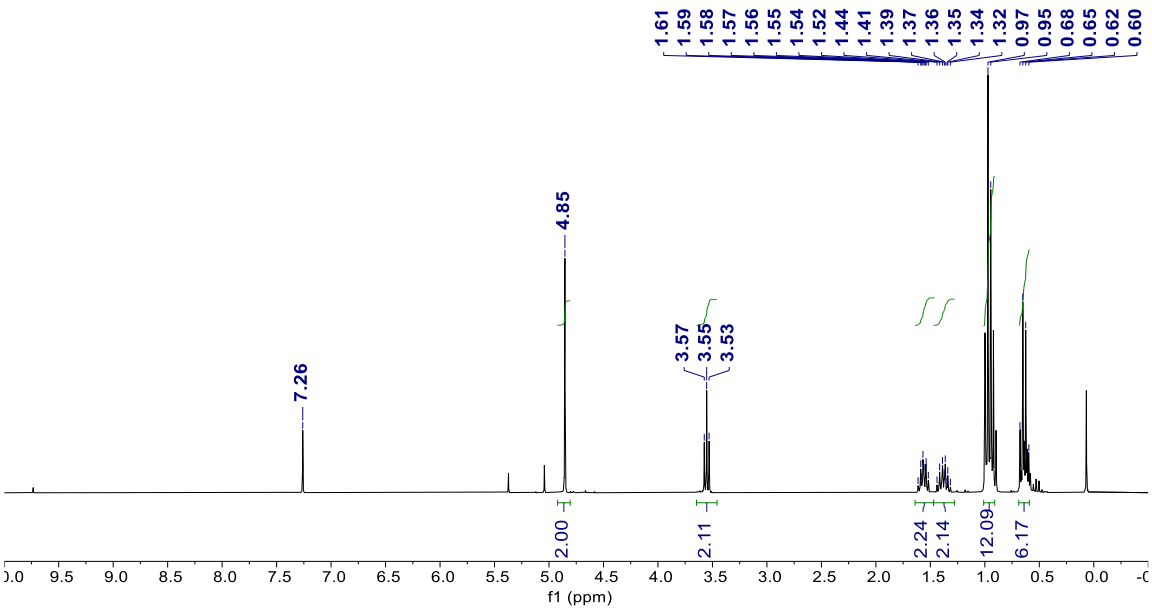
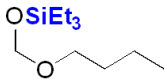


Figure S71: ^{1}H NMR spectrum of the compound **2w** in $CDCl_3$.



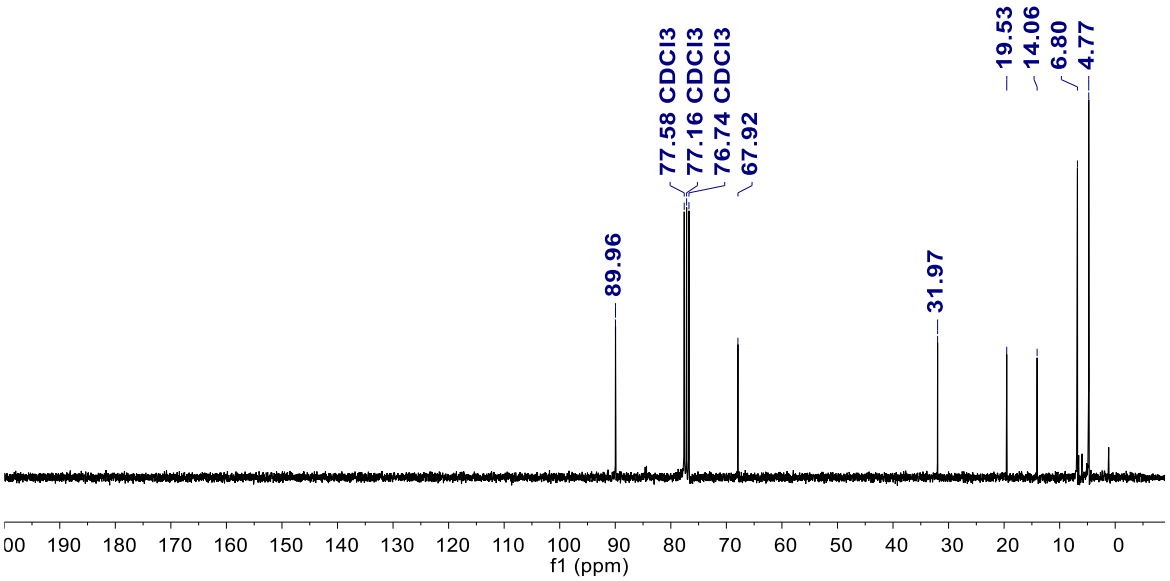
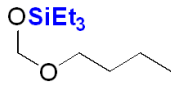


Figure S72: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2w** in $CDCl_3$.



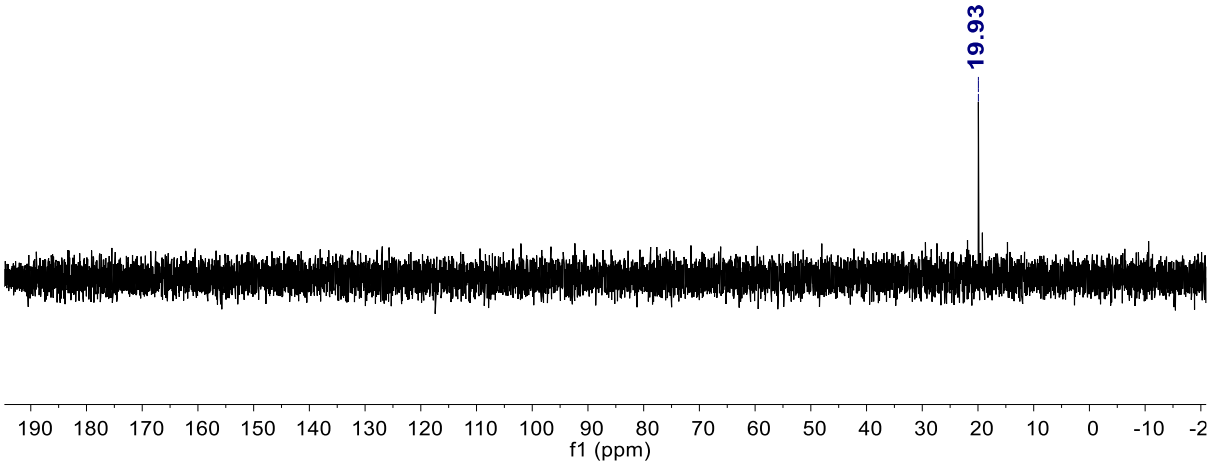
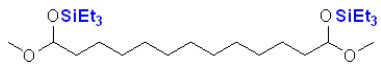


Figure S73: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2w** in $CDCl_3$.



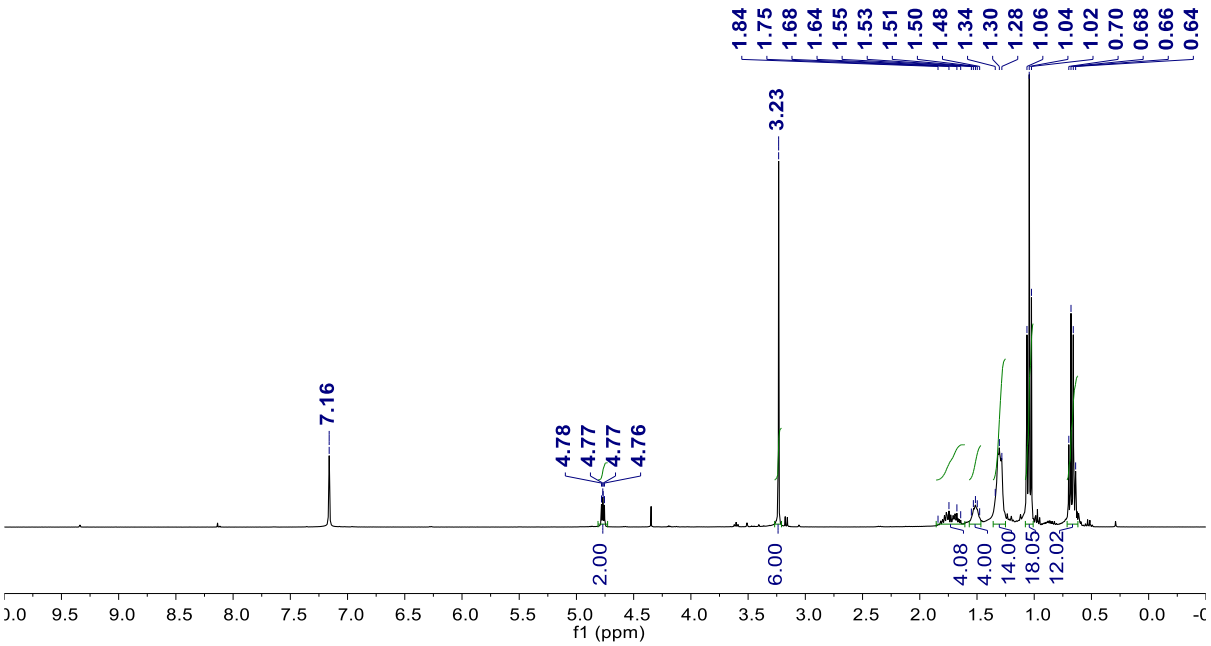


Figure S74: ^{1}H NMR spectrum of the compound **2x** in C_6D_6.

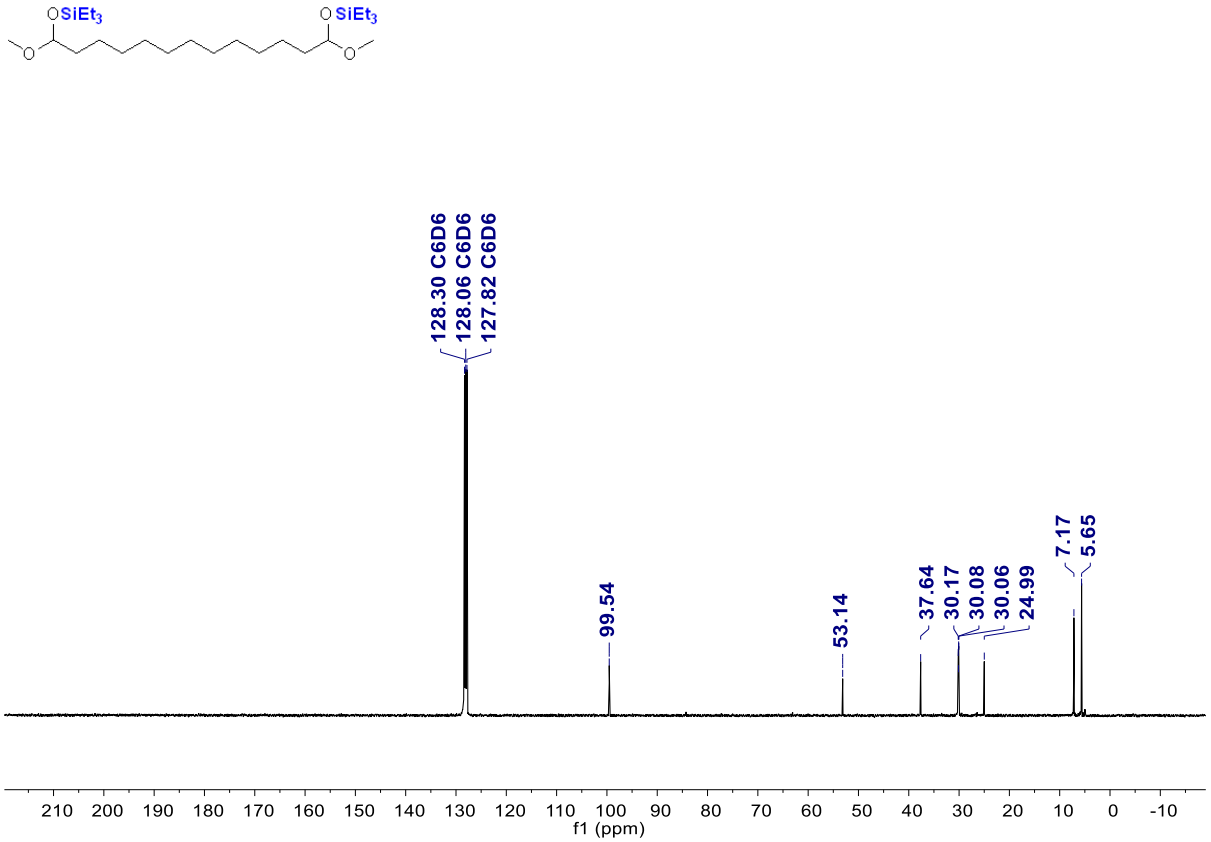


Figure S75: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2x** in C_6D_6.

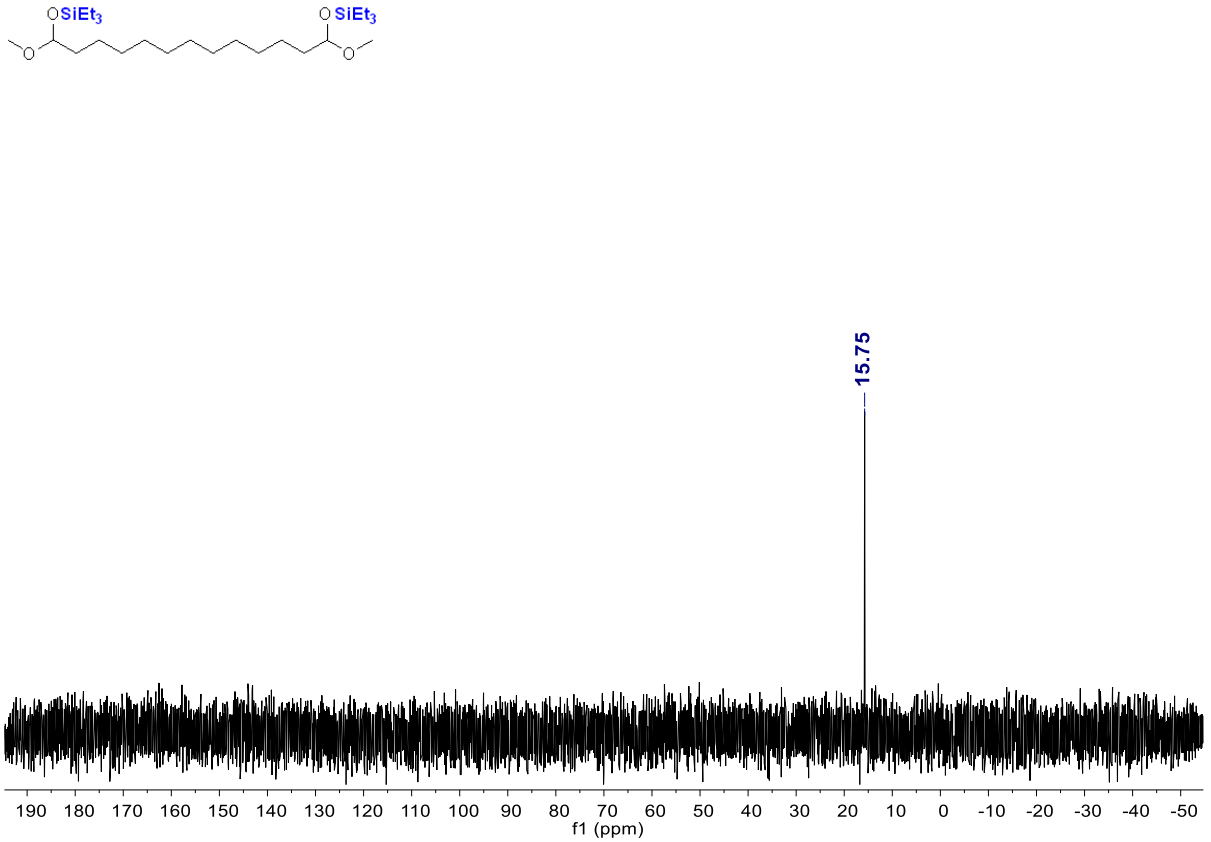


Figure S76: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2x** in C_6D_6

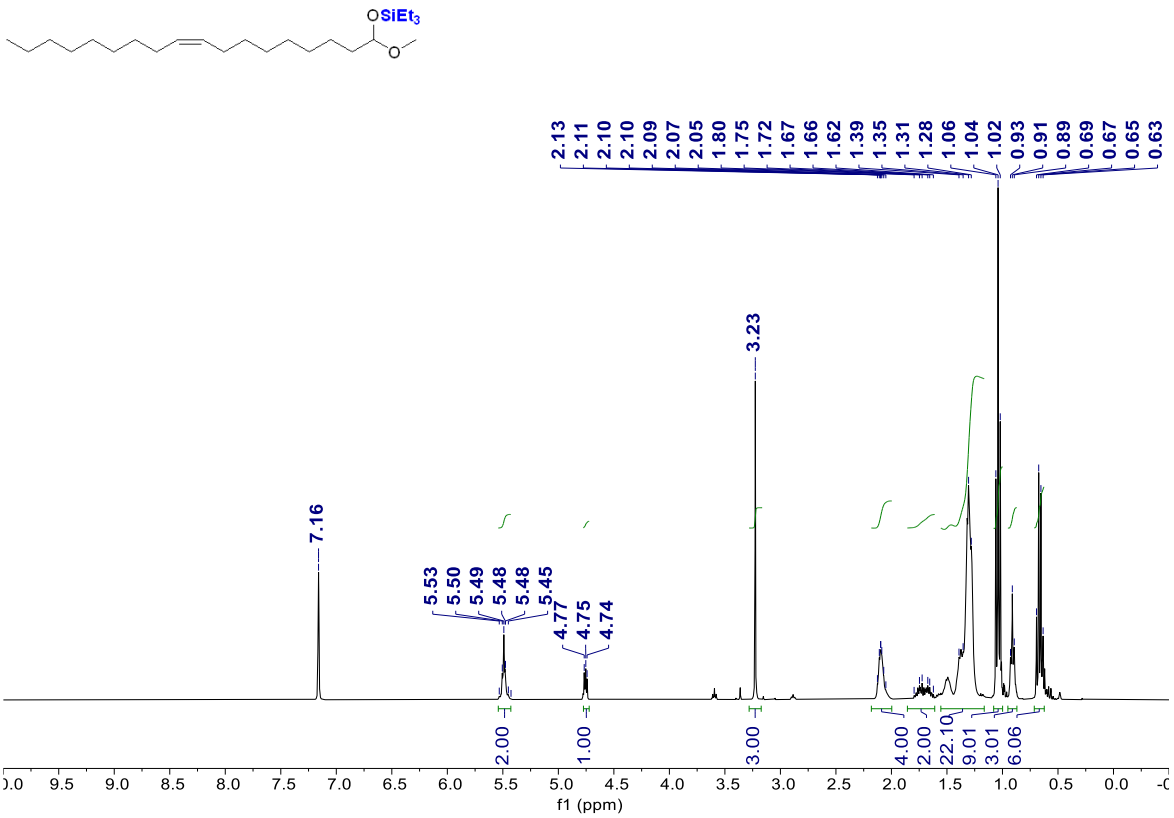


Figure S77: ^{1}H NMR spectrum of the compound **2y** in C_6D_6.

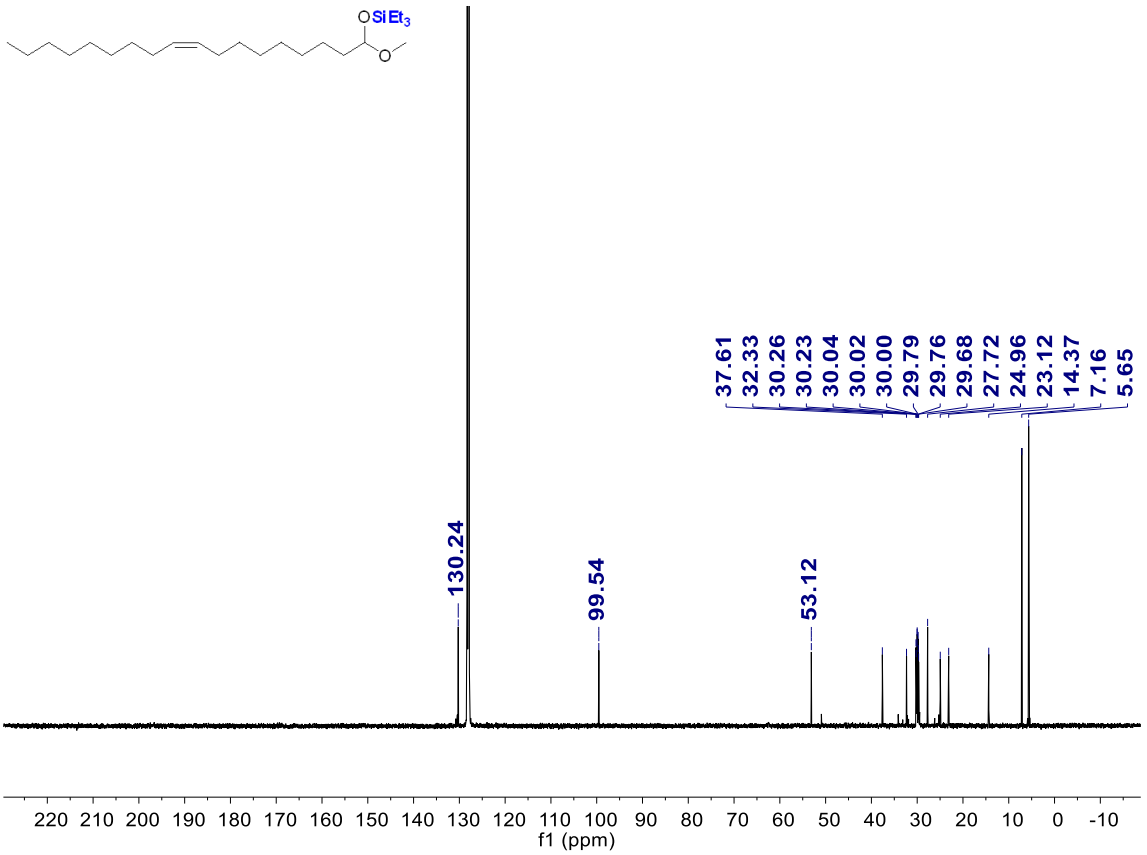


Figure S78: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2y** in C_6D_6.

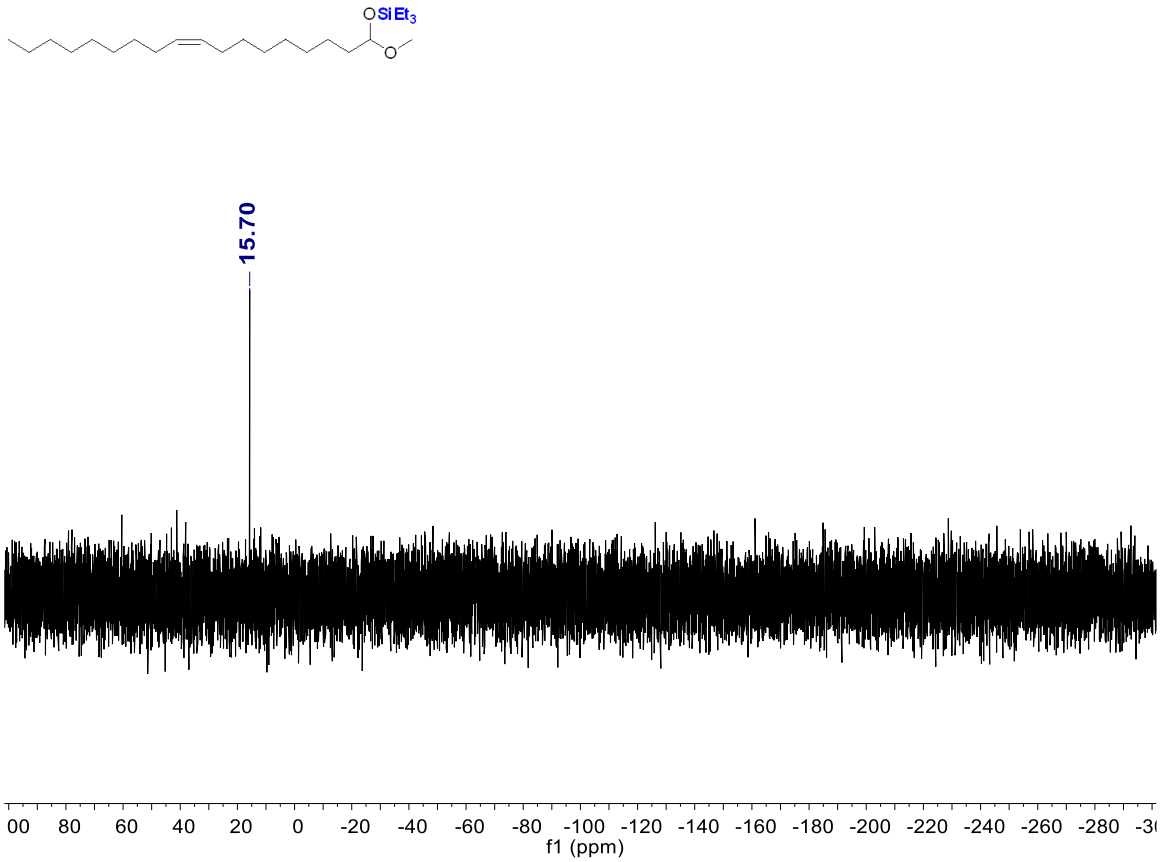


Figure S79: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2y** in C_6D_6.

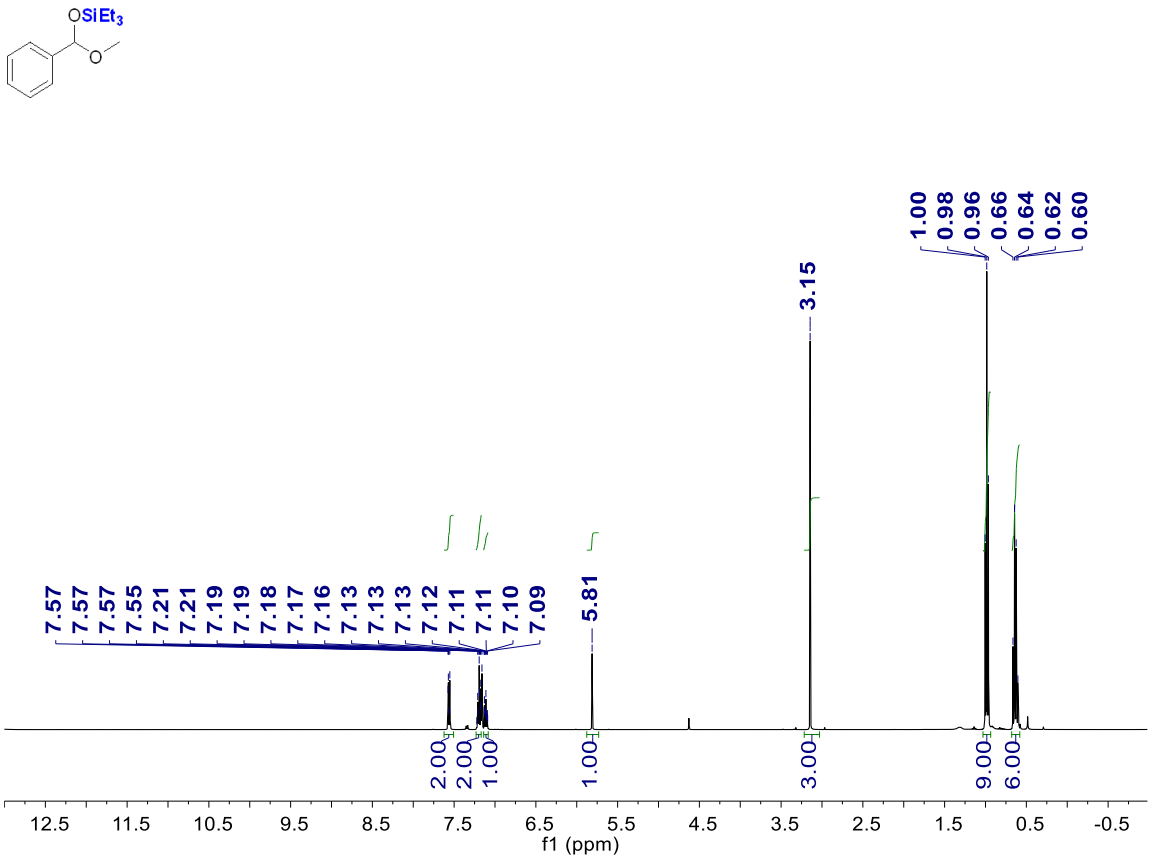


Figure S80: ^{1}H NMR spectrum of the compound **2z** in C_6D_6.

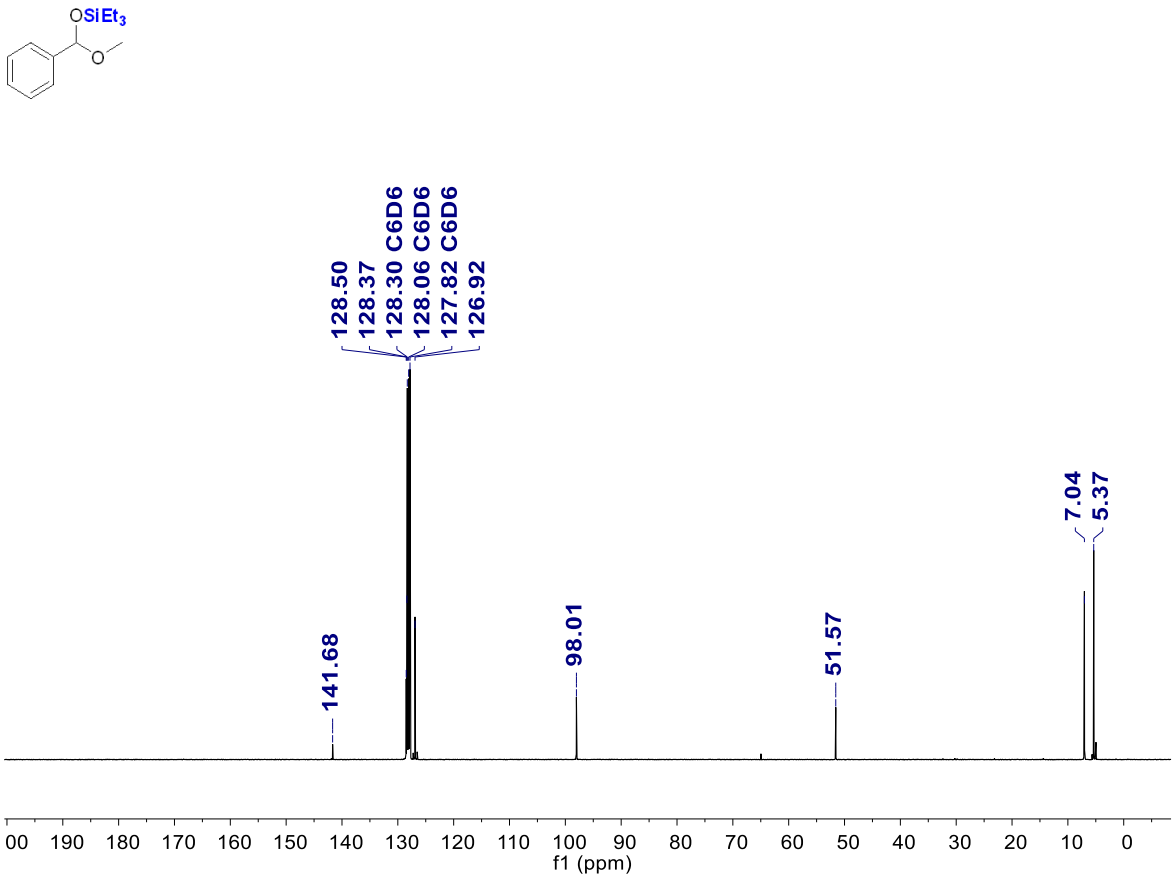


Figure S81: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2z** in C_6D_6.

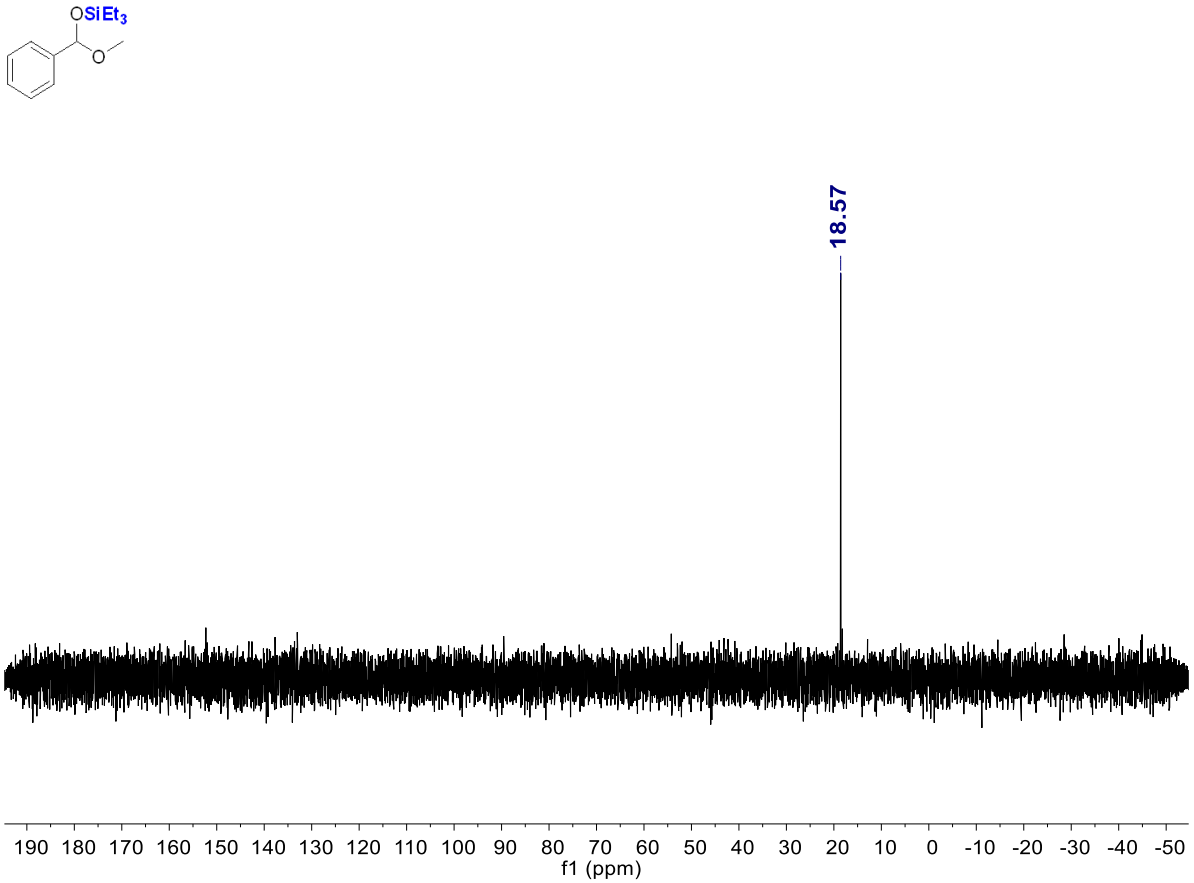


Figure S82: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2z** in C_6D_6.

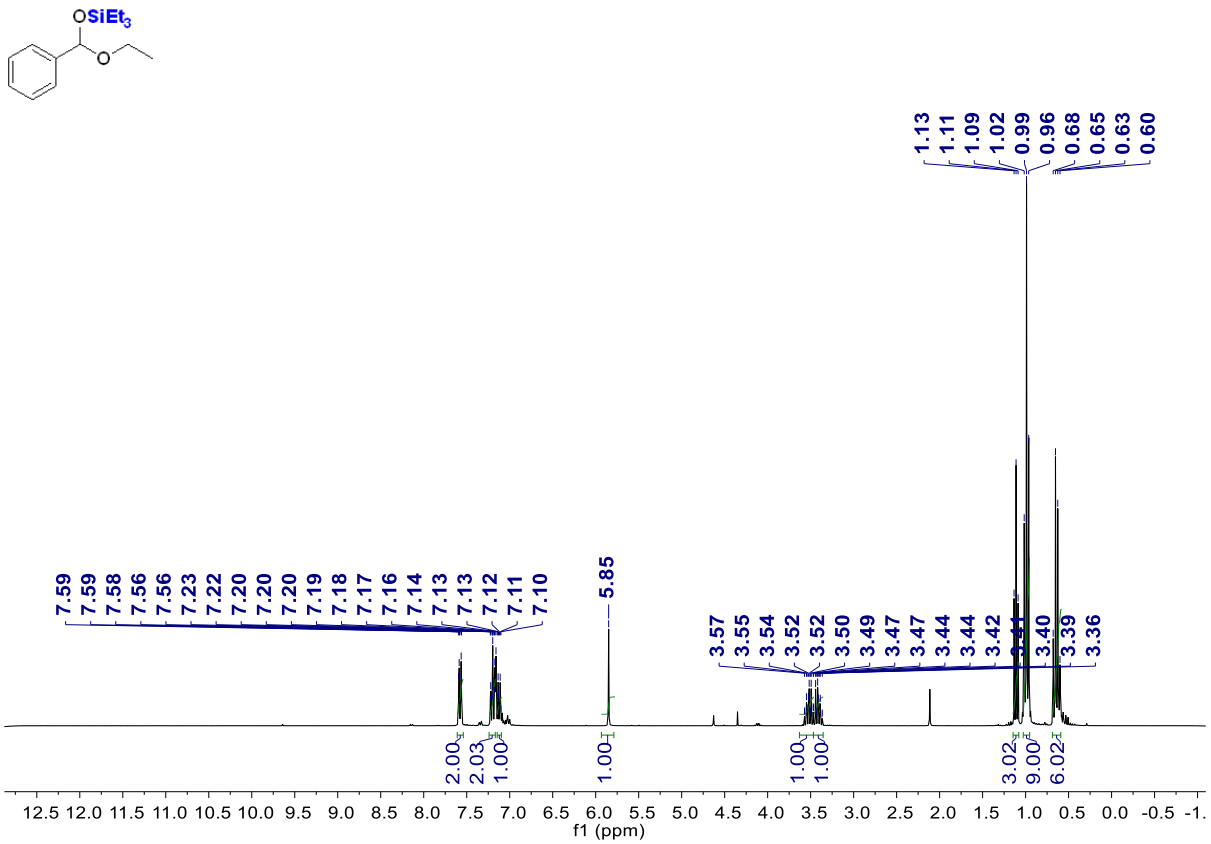


Figure S83: ^{1}H NMR spectrum of the compound **2z'** in C_6D_6. (Crude NMR mixture)

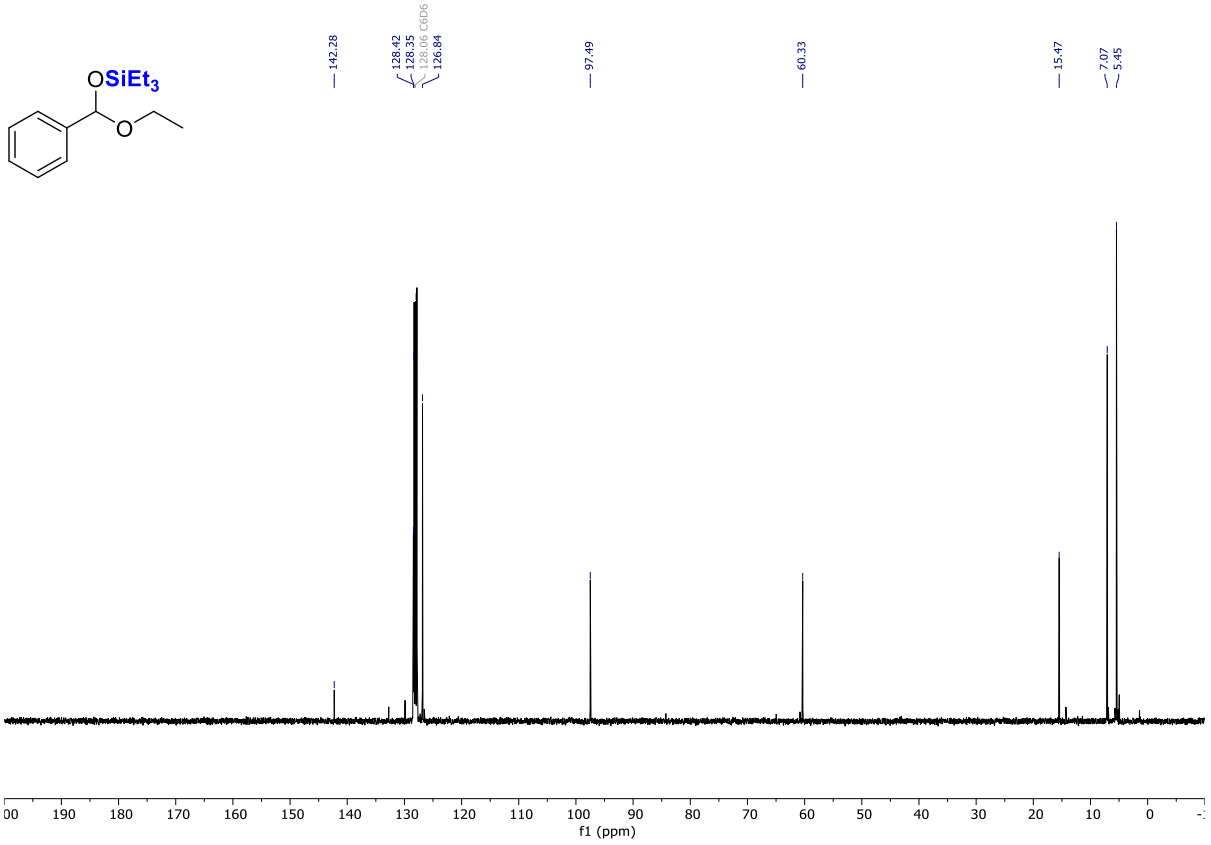


Figure S84: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2z'** in C_6D_6. (Crude NMR mixture)

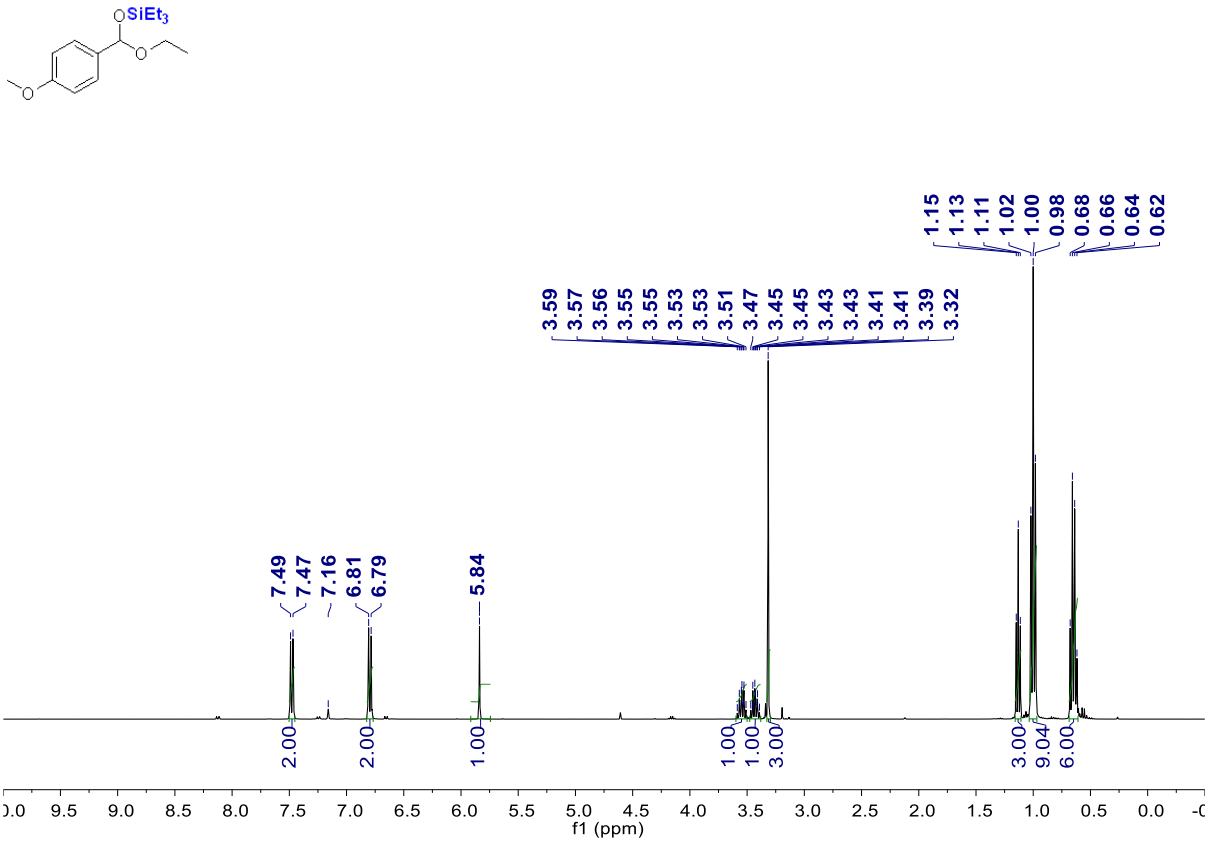


Figure S85: ^{1}H NMR spectrum of the compound **2aa** in C_6D_6.

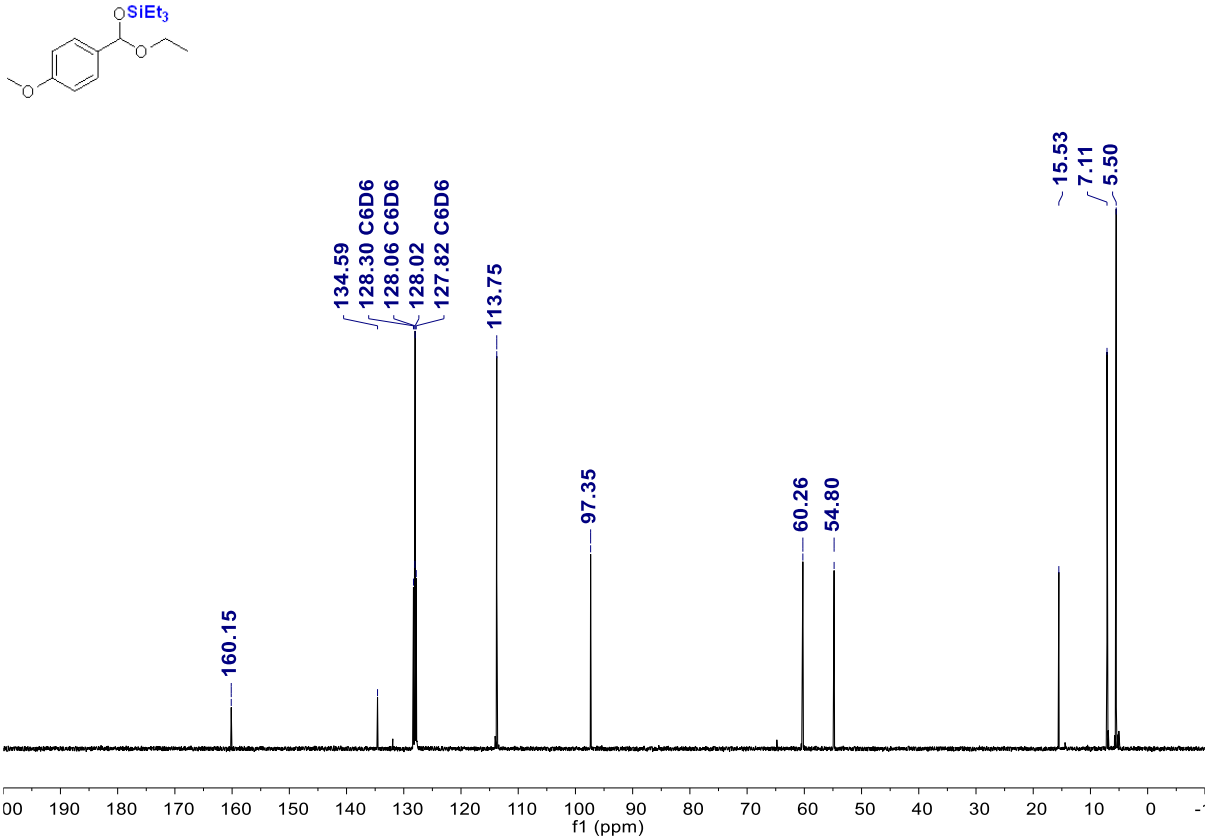
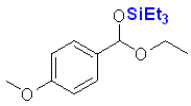


Figure S86: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2aa** in C_6D_6.



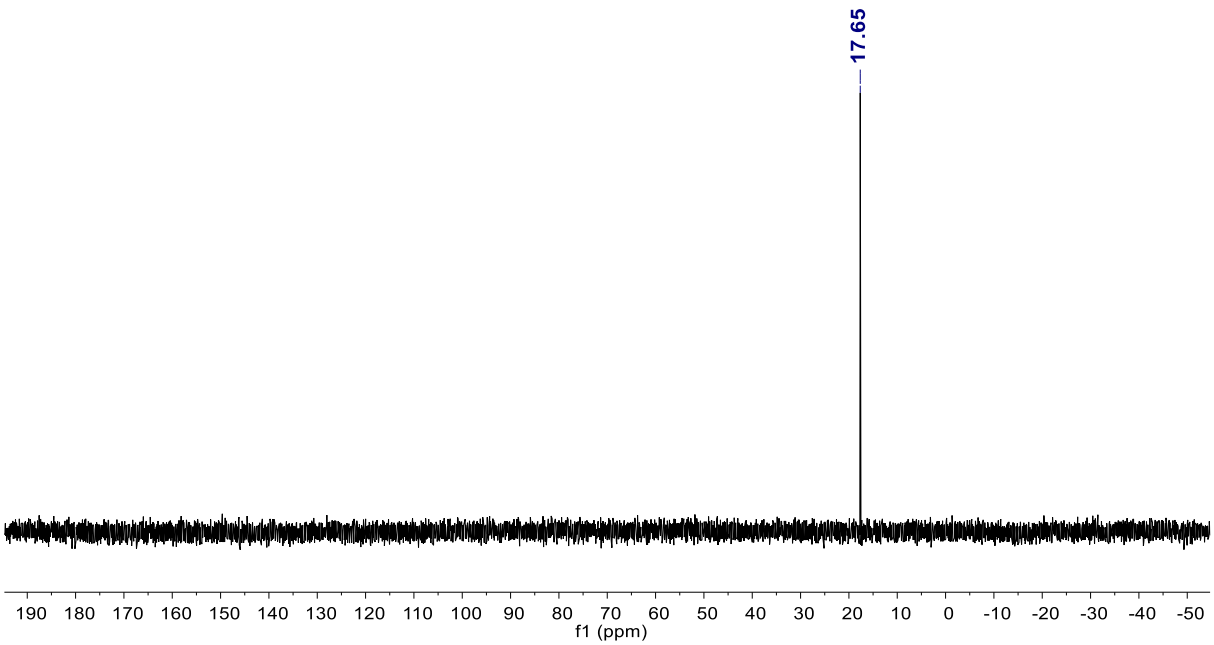


Figure S87: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2aa** in C_6D_6

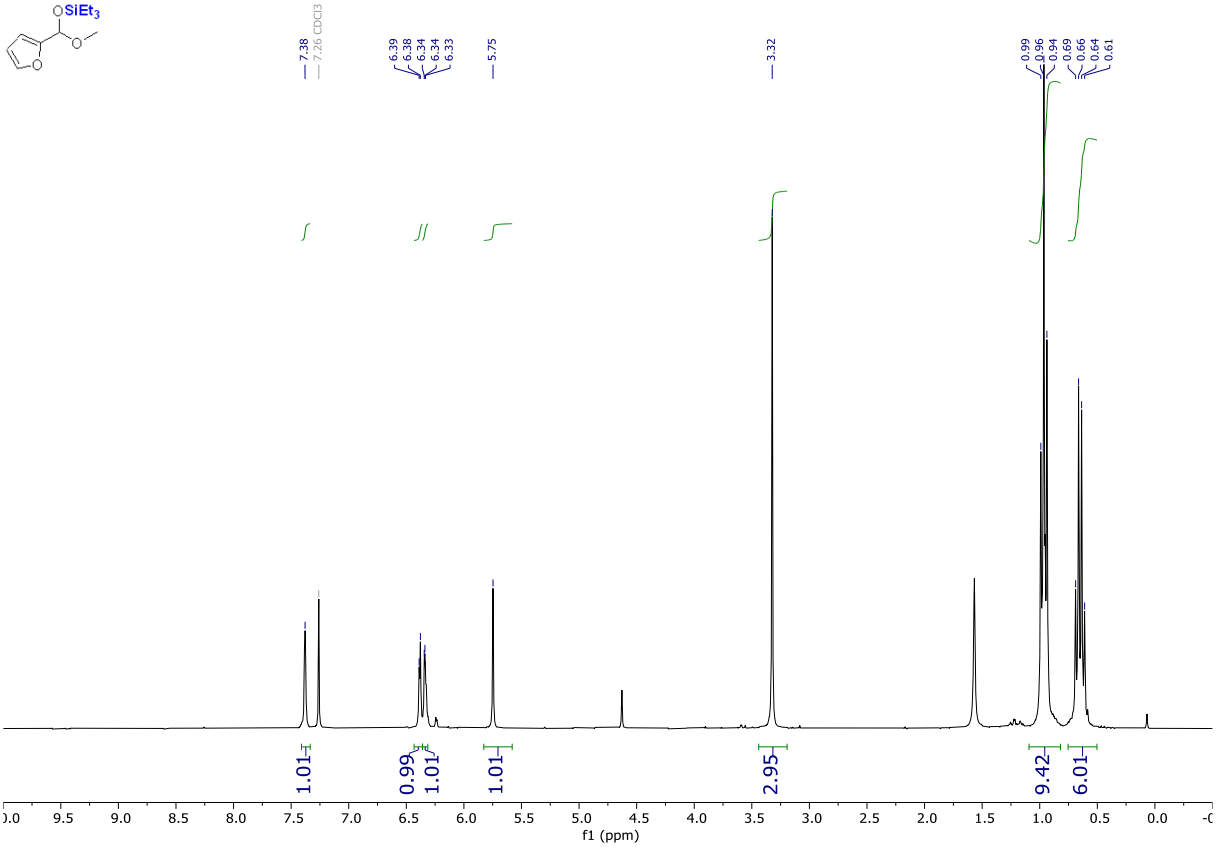


Figure S88: ^{1}H NMR spectrum of the compound **2ac** in $CDCl_3$.

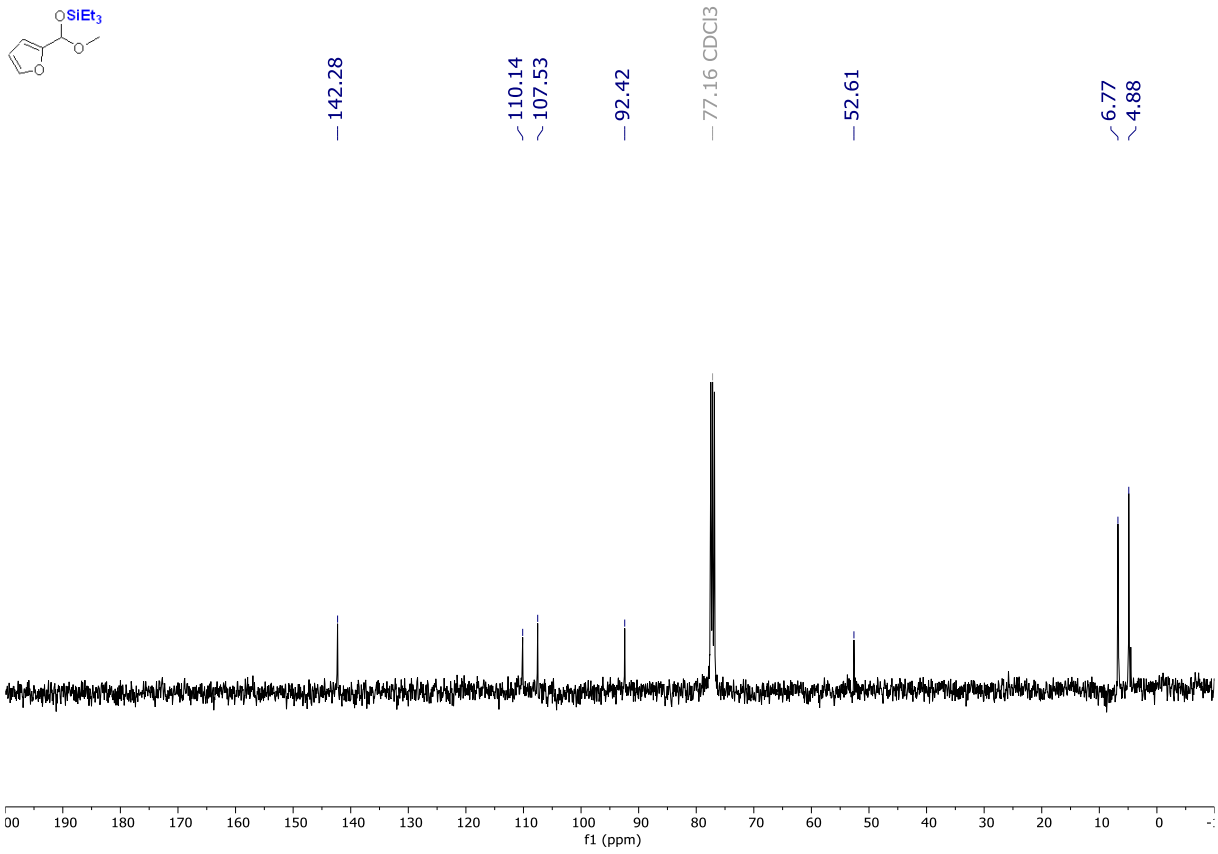


Figure S89: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2ac** in $CDCl_3$.

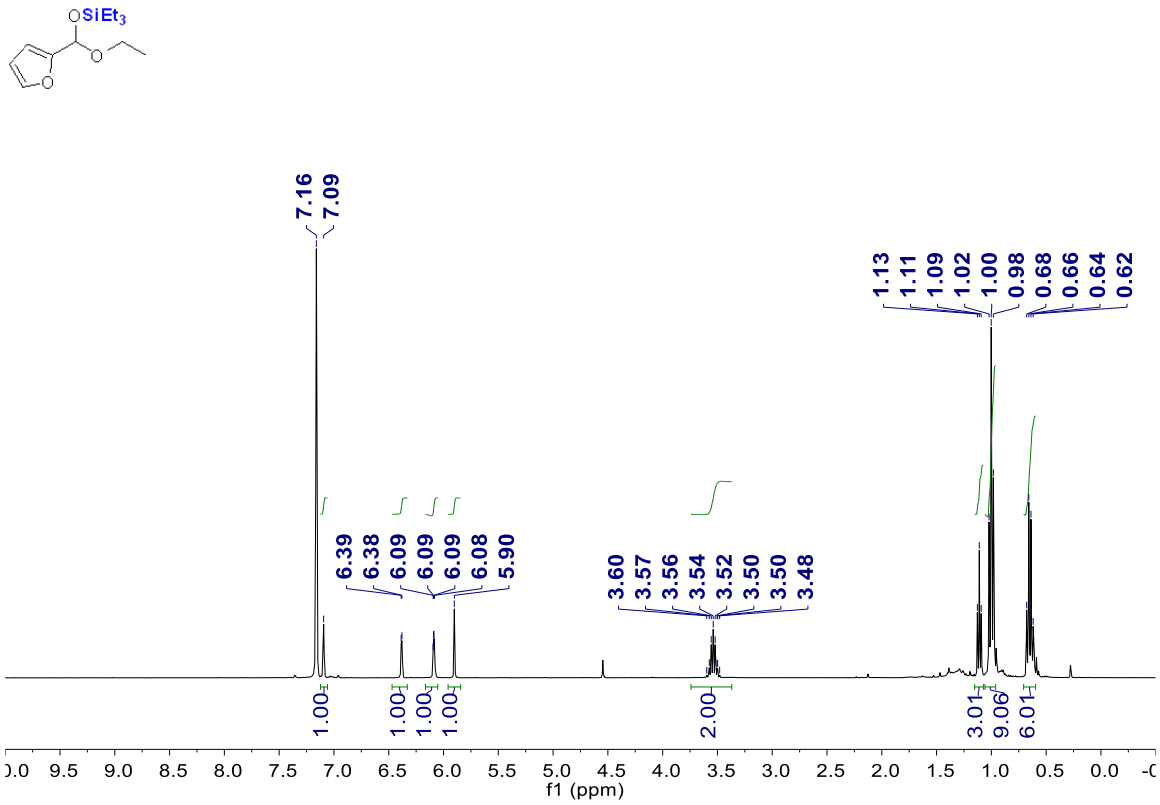


Figure S90: ^{1}H NMR spectrum of the compound **2ac** in C_6D_6.

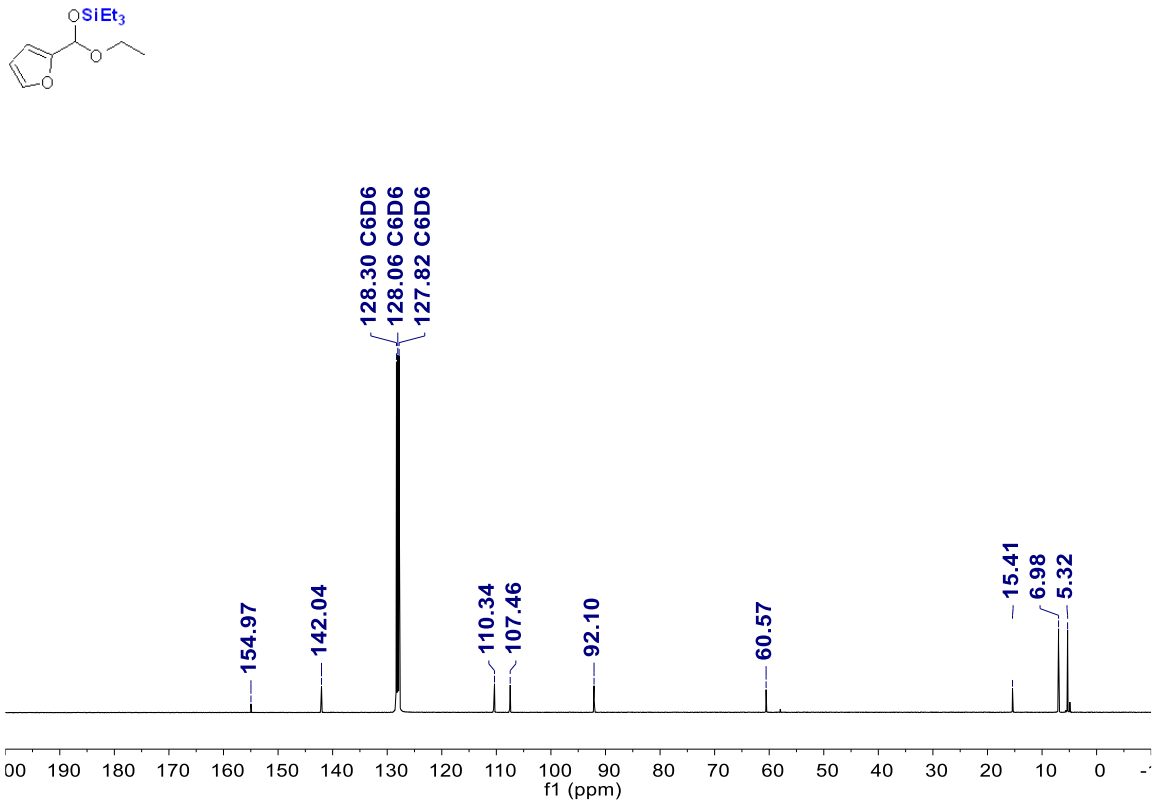


Figure S91: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **2ad** in C_6D_6.

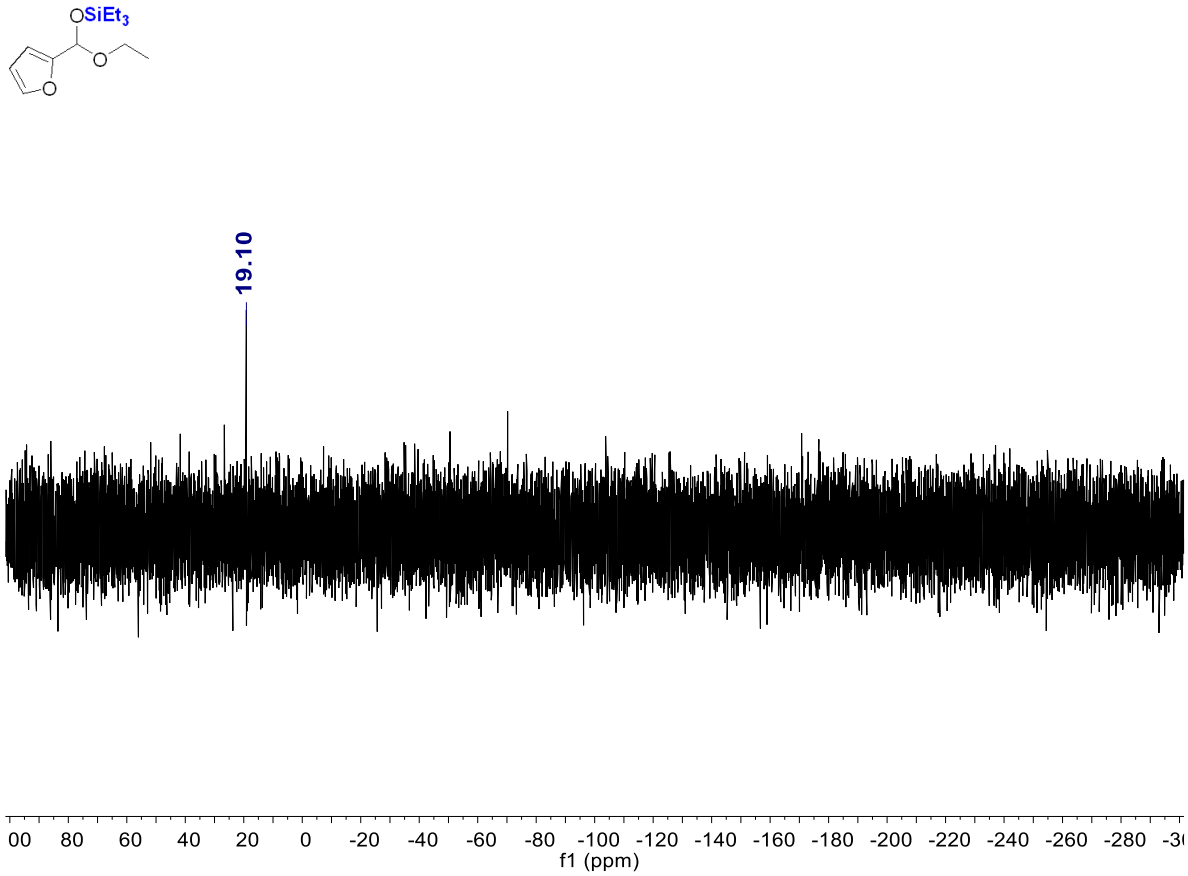
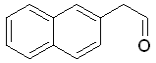


Figure S92: $^{29}Si\{^{1}H\}$ NMR spectrum of the compound **2ad** in C_6D_6.

9. NMR spectra of the aldehydes



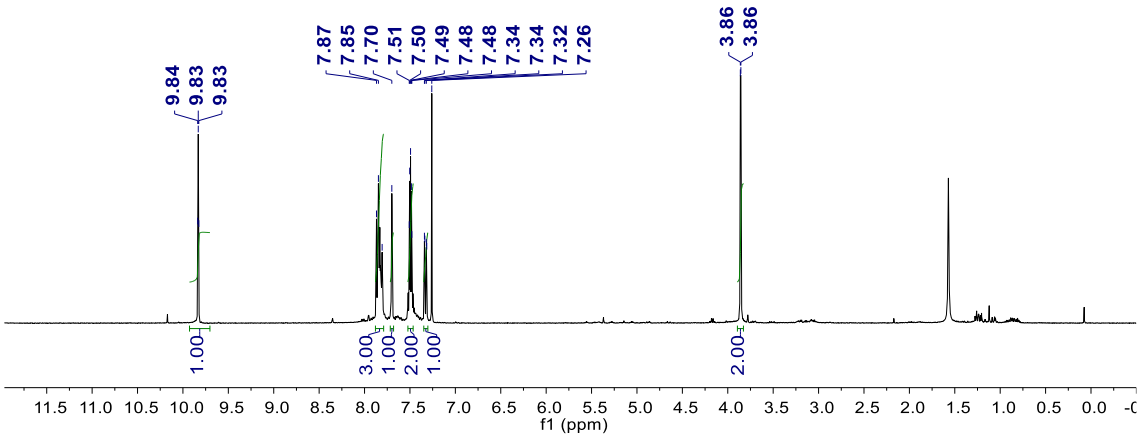
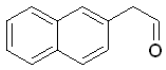


Figure S93: ^{1}H NMR spectrum of the compound **4a** in $CDCl_3$



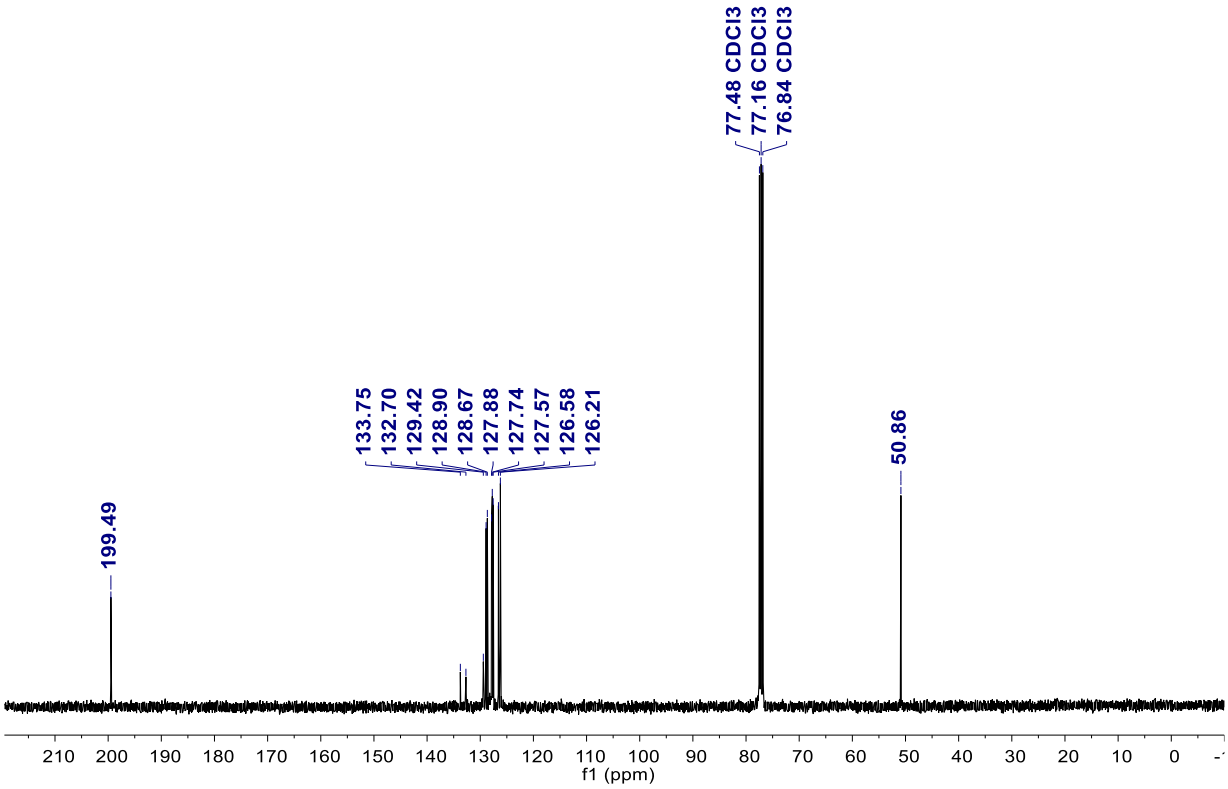


Figure S94: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4a** in $CDCl_3$.

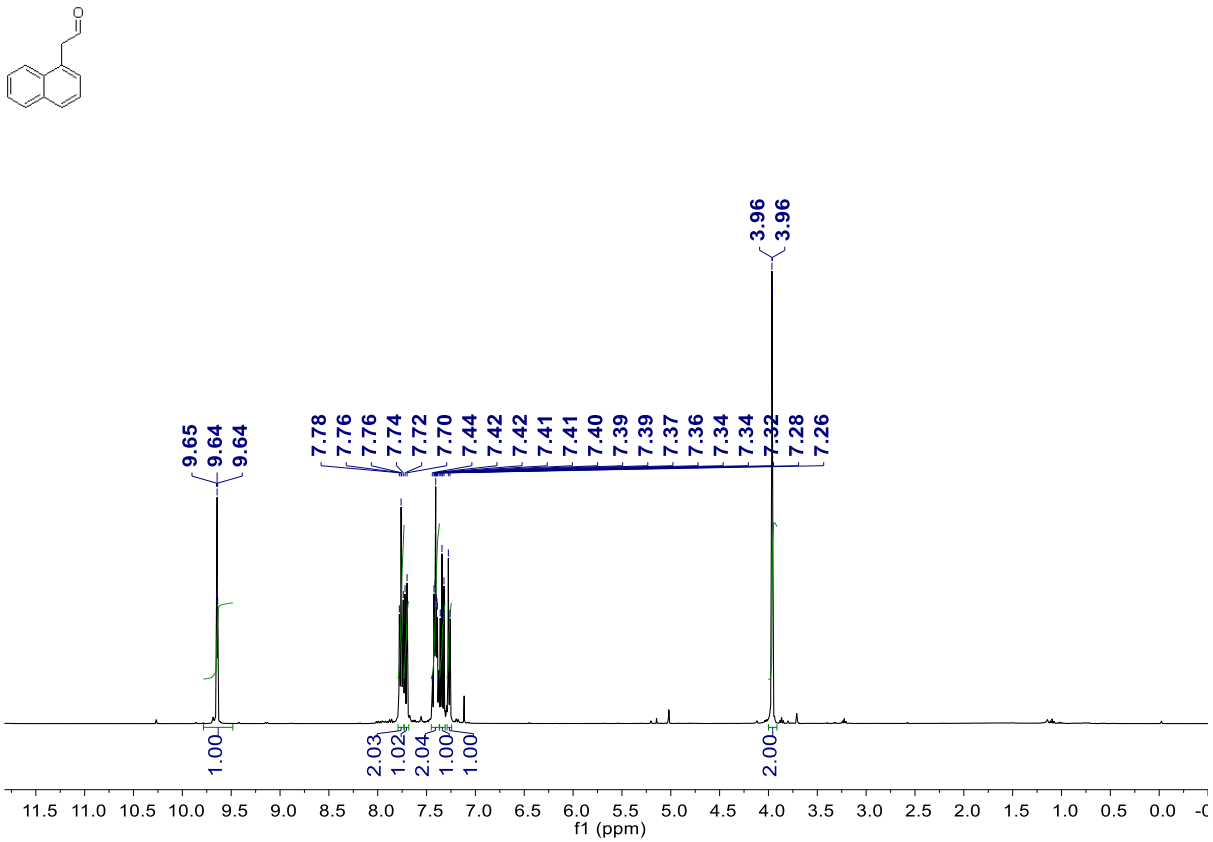


Figure S95: ^{1}H NMR spectrum of the compound **4b** in $CDCl_3$

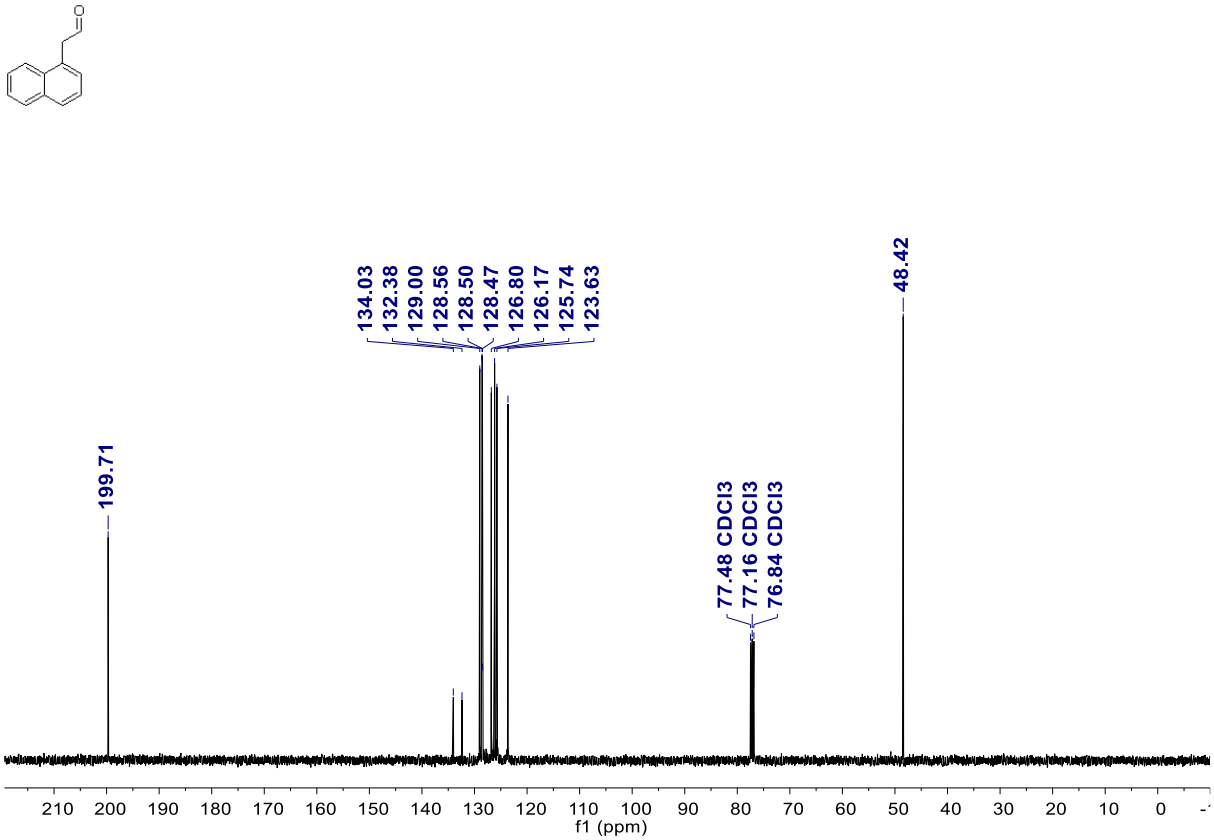


Figure S96: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4b** in $CDCl_3$.

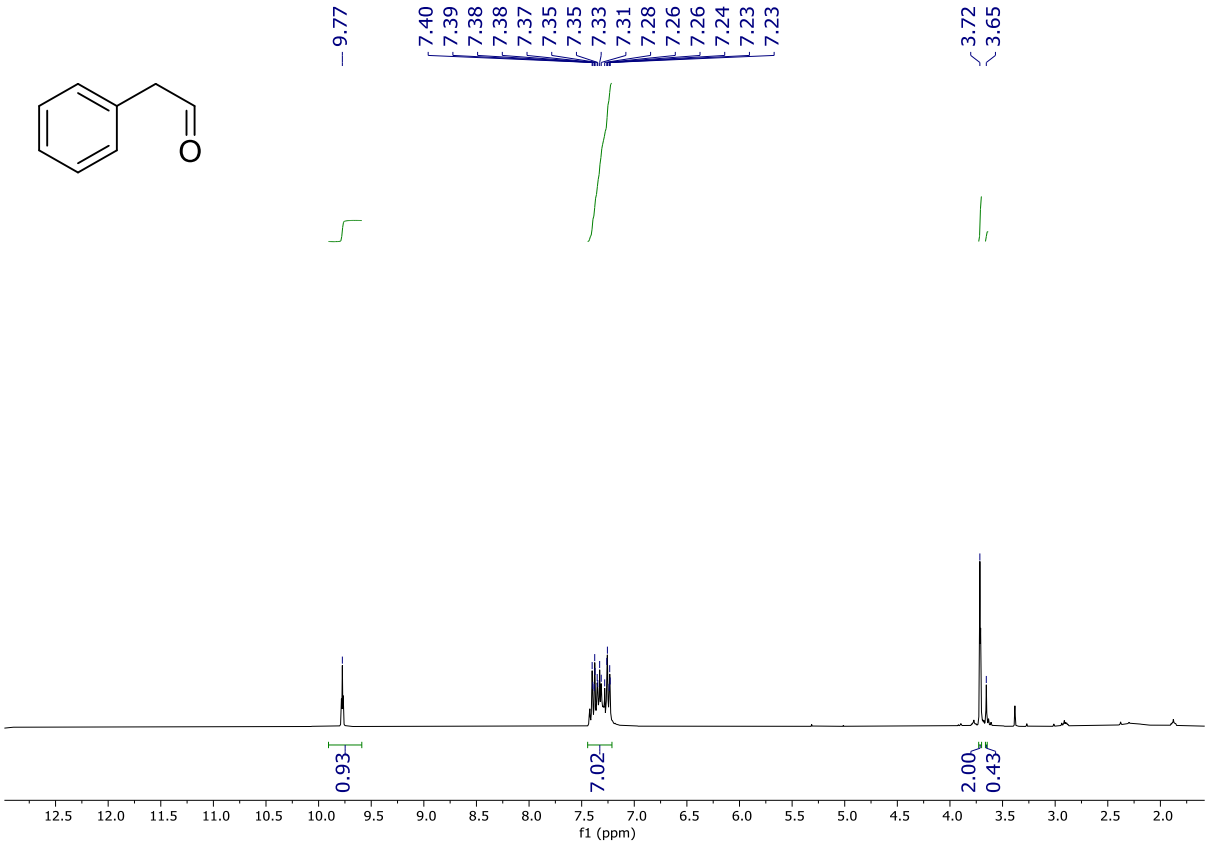
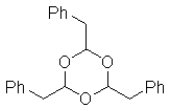


Figure S97: ^{1}H NMR spectrum of the compound **4c** in $CDCl_3$. (Crude mixture after hydrolysis)



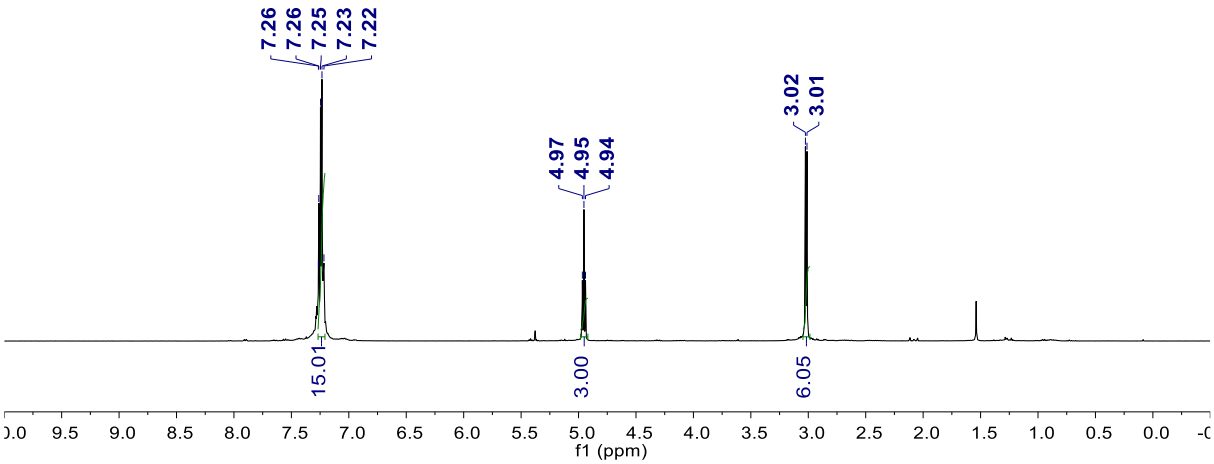
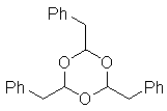


Figure S98: ^{1}H NMR spectrum of the compound **4c'** in $CDCl_3$



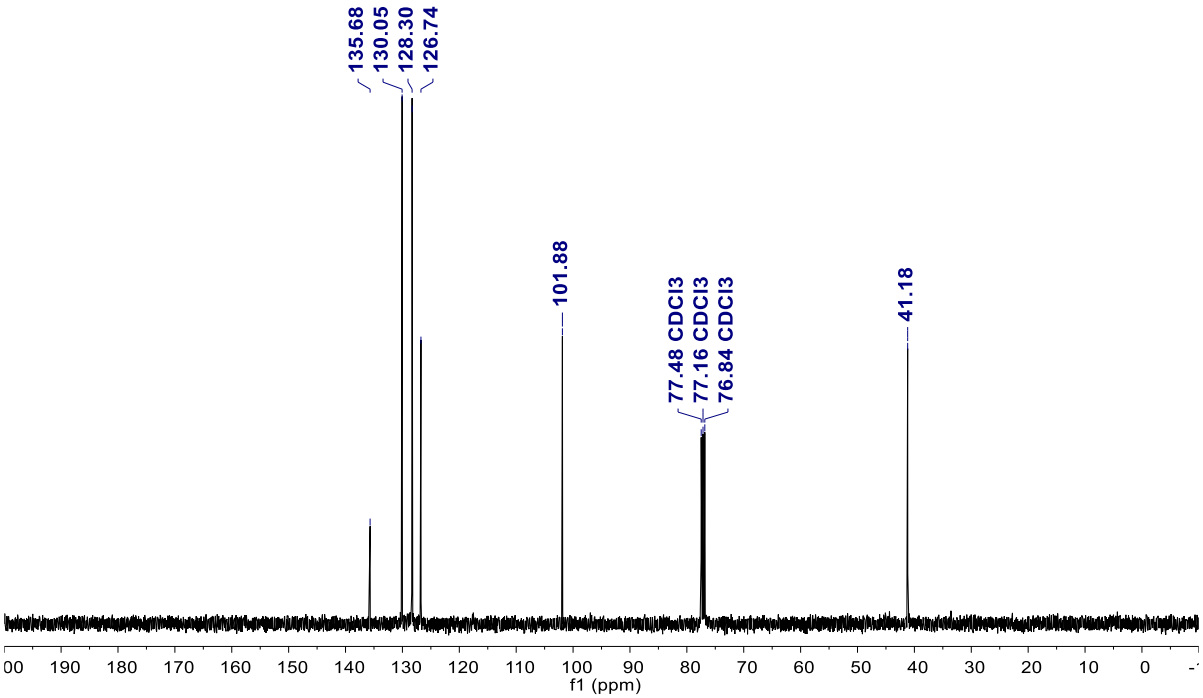
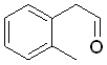


Figure S99: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4c'** in $CDCl_3$.



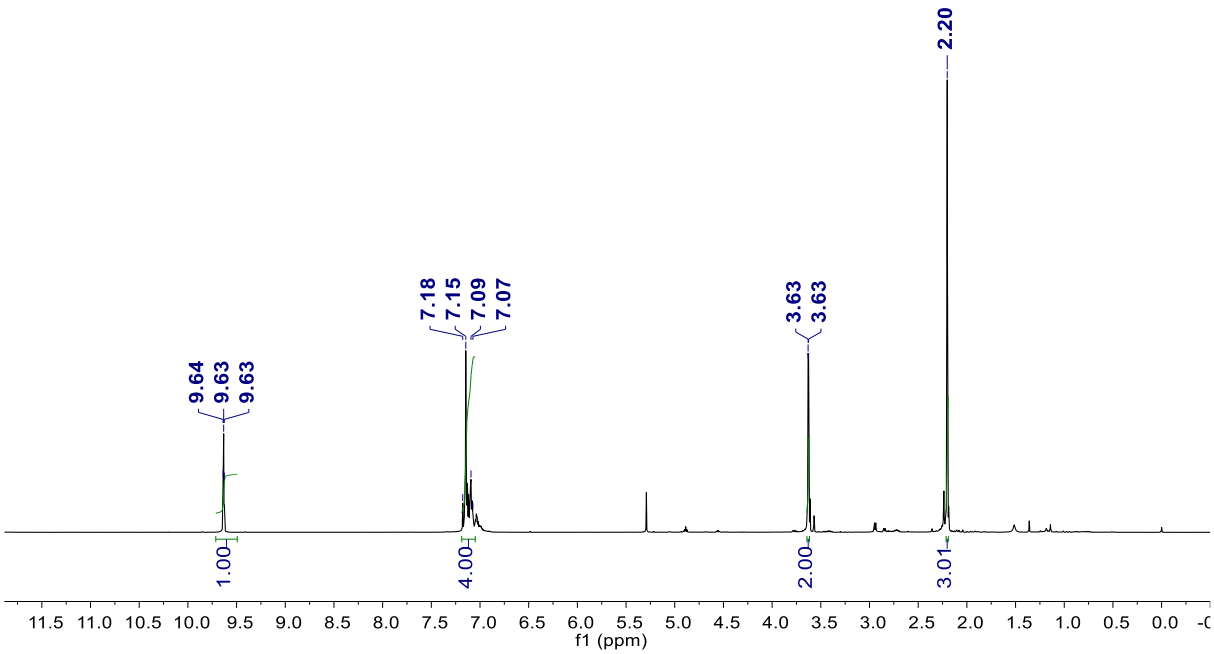
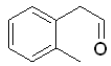


Figure S100: ^{1}H NMR spectrum of the compound **4d** in $CDCl_3$



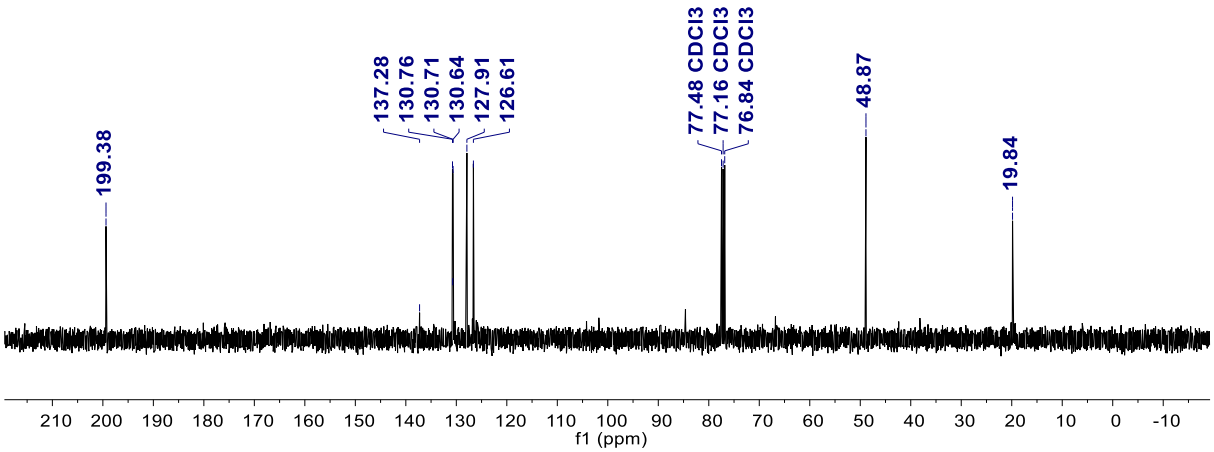
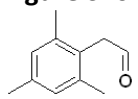


Figure S101: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4d** in $CDCl_3$.



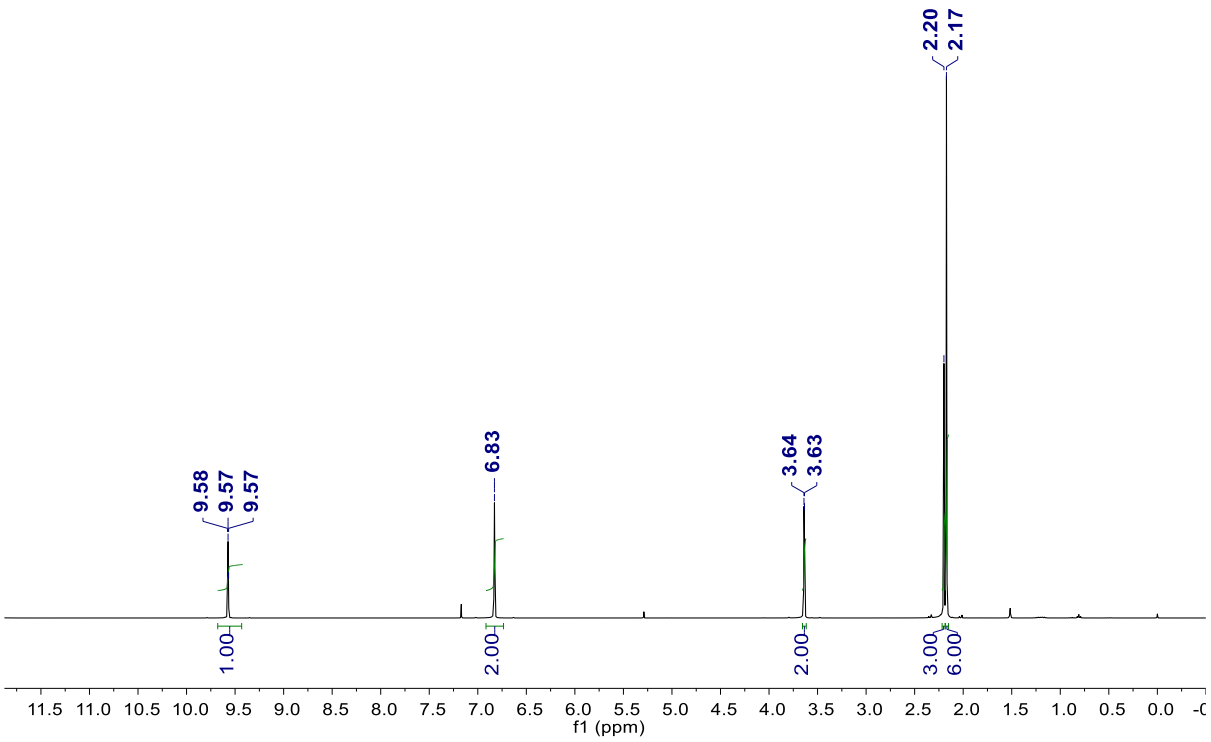


Figure S102: ^{1}H NMR spectrum of the compound **4e** in $CDCl_3$

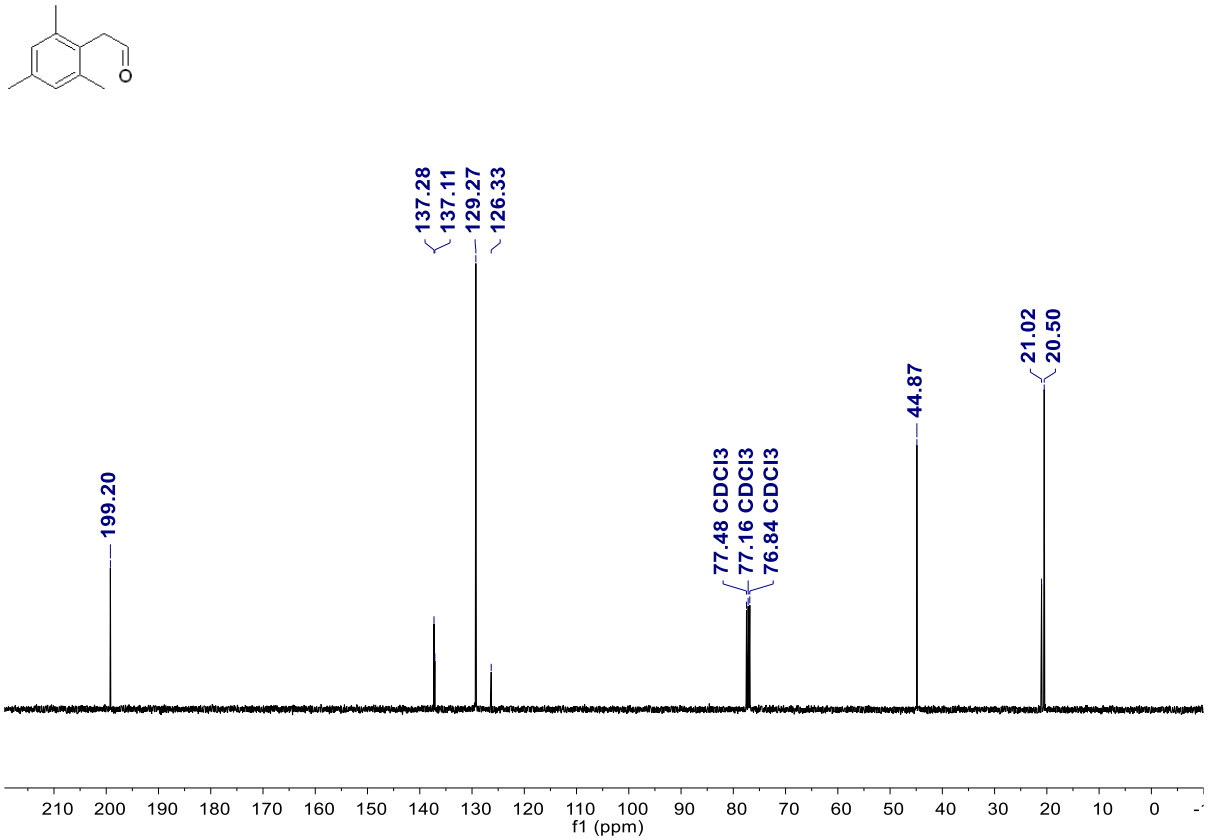


Figure S103: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4e** in $CDCl_3$.

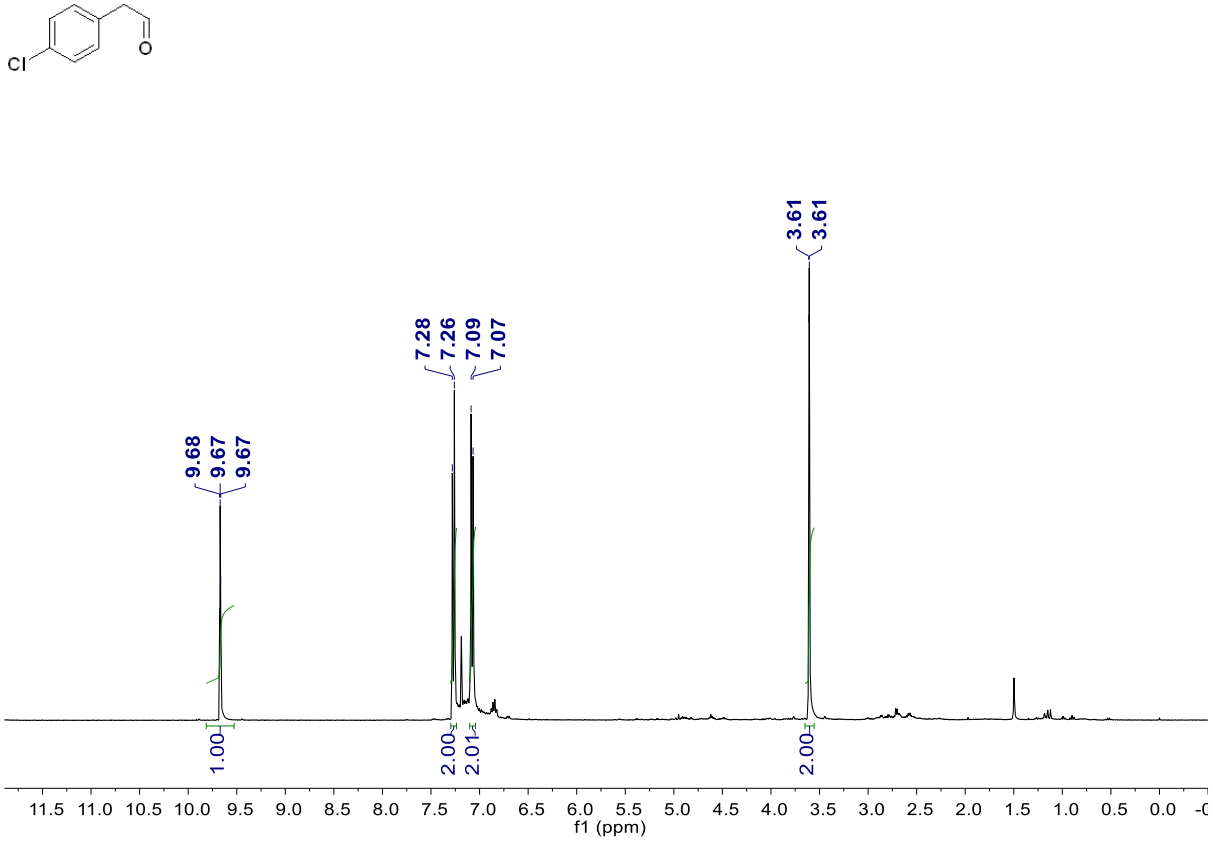


Figure S104: ^{1}H NMR spectrum of the compound **4h** in $CDCl_3$

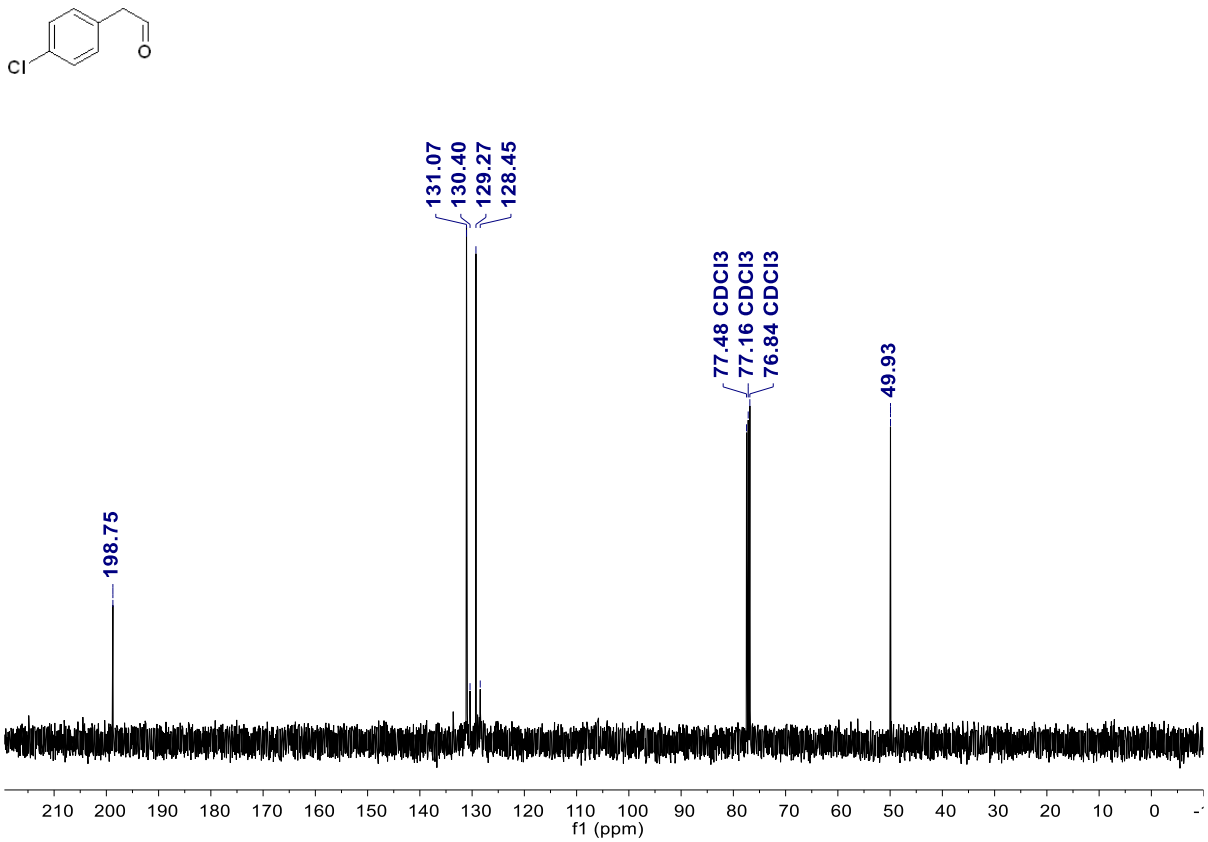


Figure S105: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4h** in $CDCl_3$.

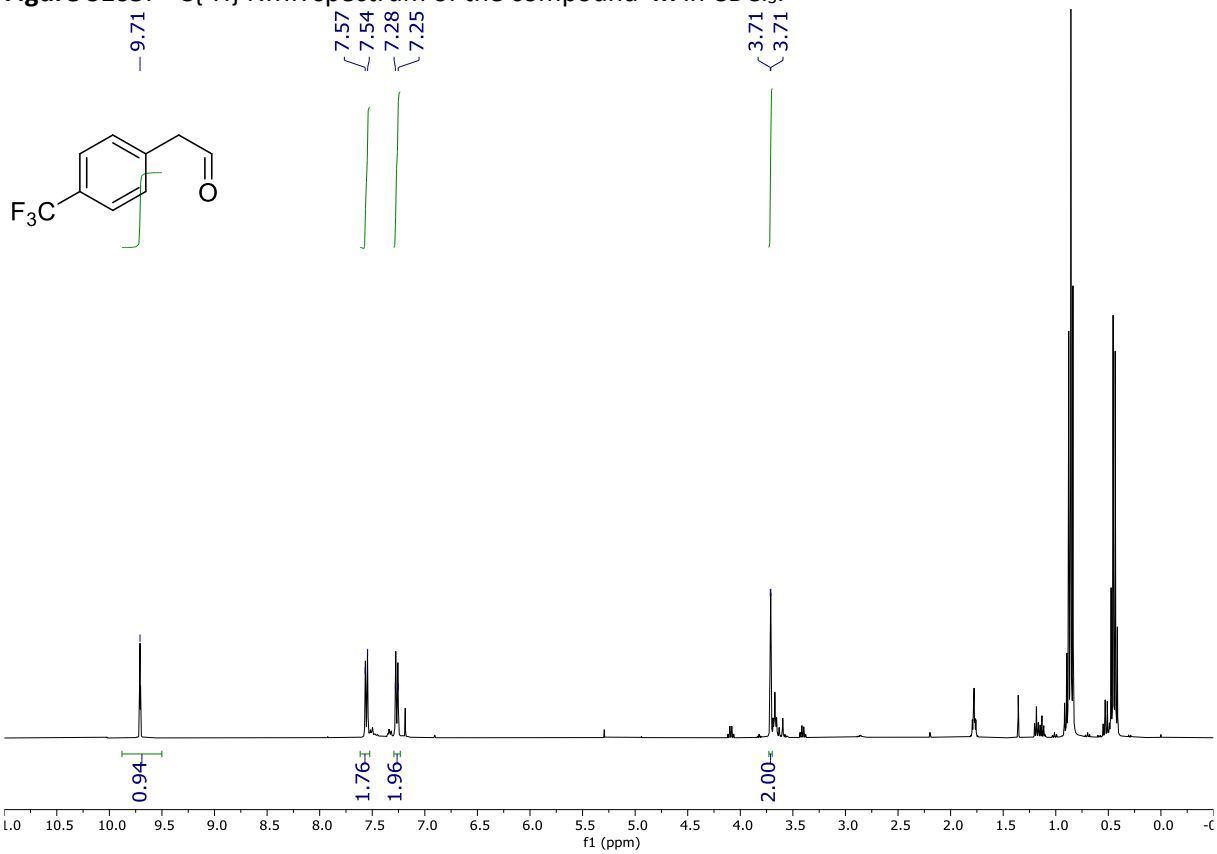
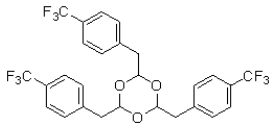


Figure S106: ^{1}H NMR spectrum of the compound **4i** in $CDCl_3$. (Crude mixture after hydrolysis)



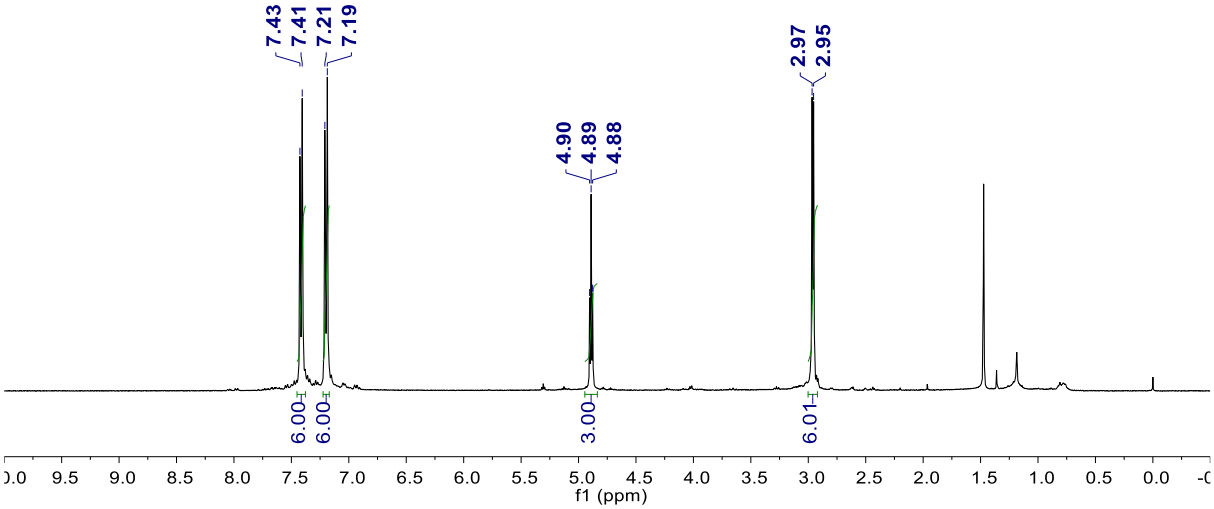
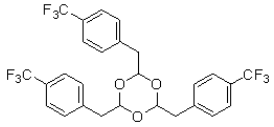


Figure S107: ^{1}H NMR spectrum of the compound **4i'** in $CDCl_3$



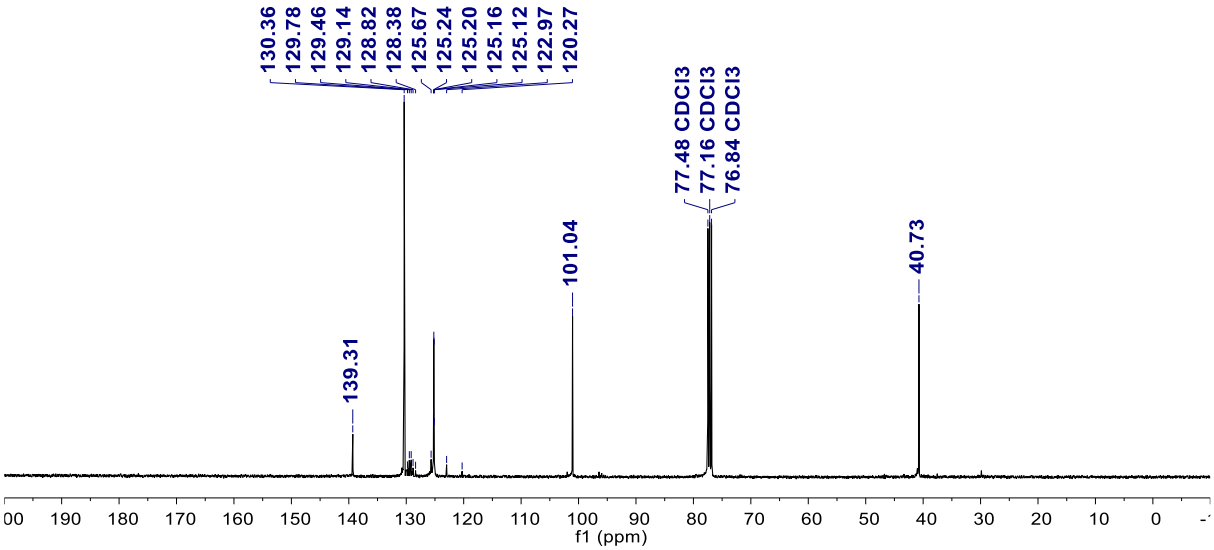
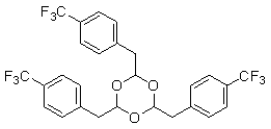


Figure S108: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4i'** in $CDCl_3$.



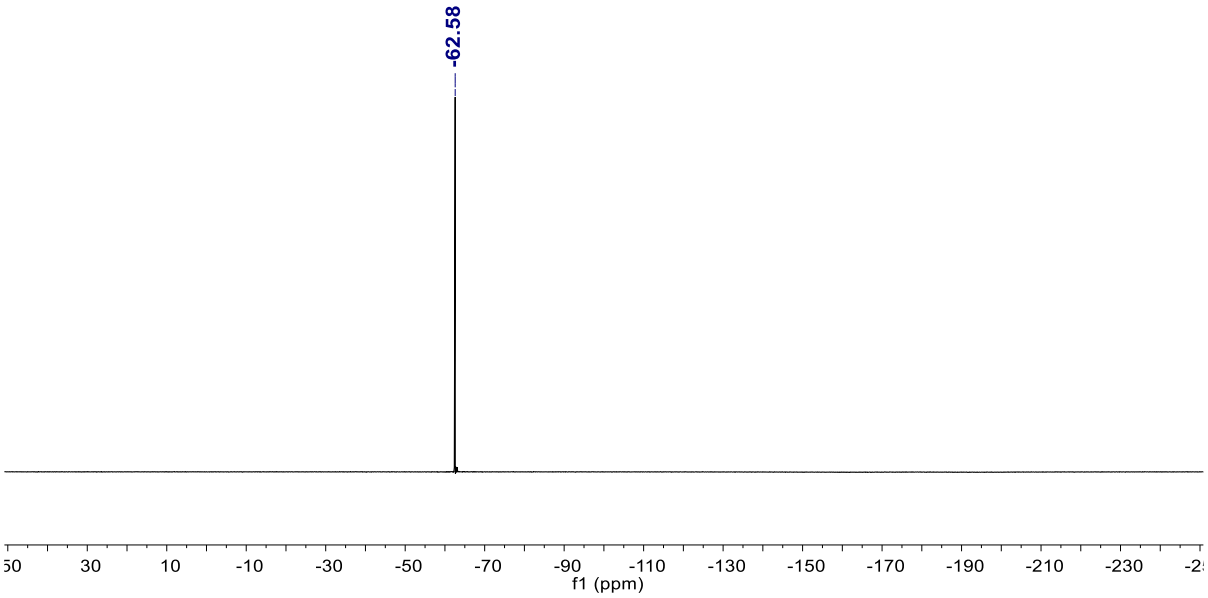


Figure S109: ^{19}F NMR spectrum of the compound **4i'** in $CDCl_3$.

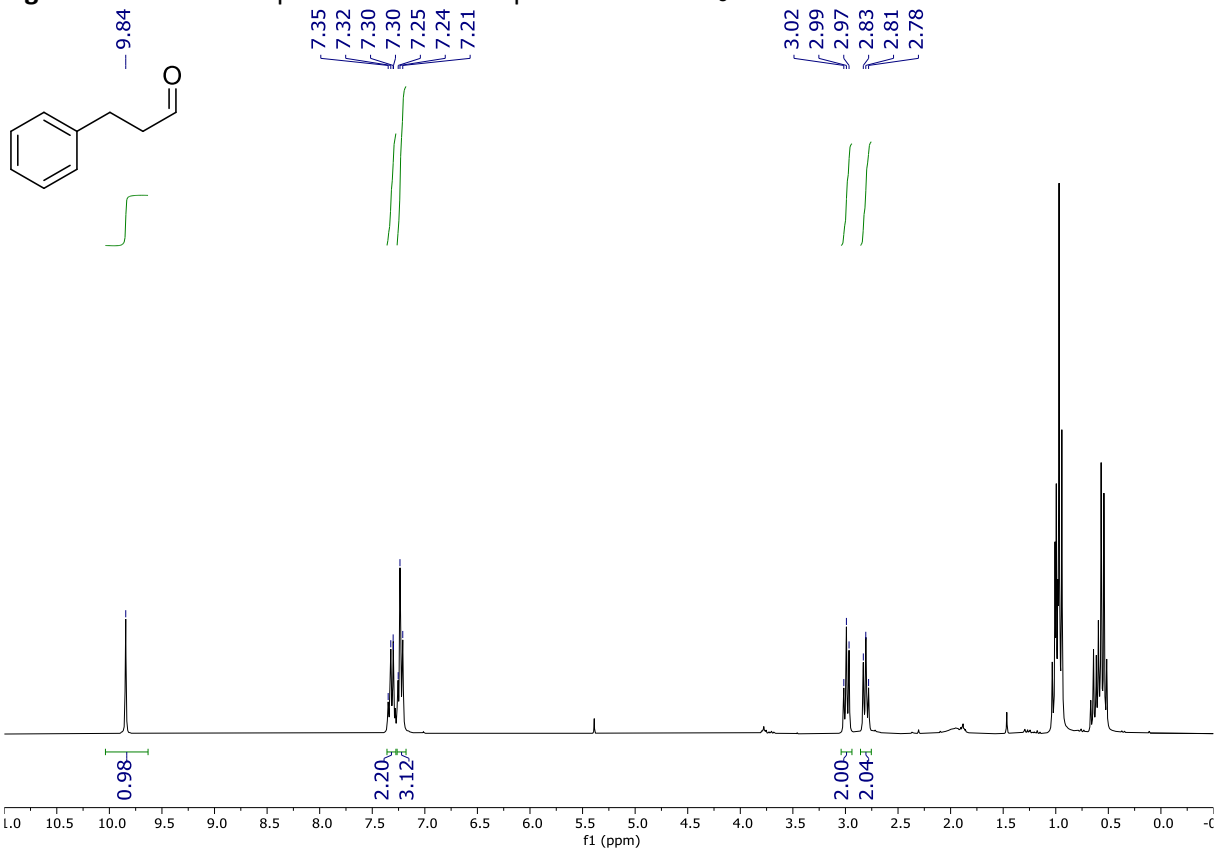
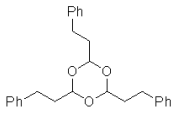


Figure S110: ^{1}H NMR spectrum of the compound **4j** in $CDCl_3$. (Crude mixture after hydrolysis)



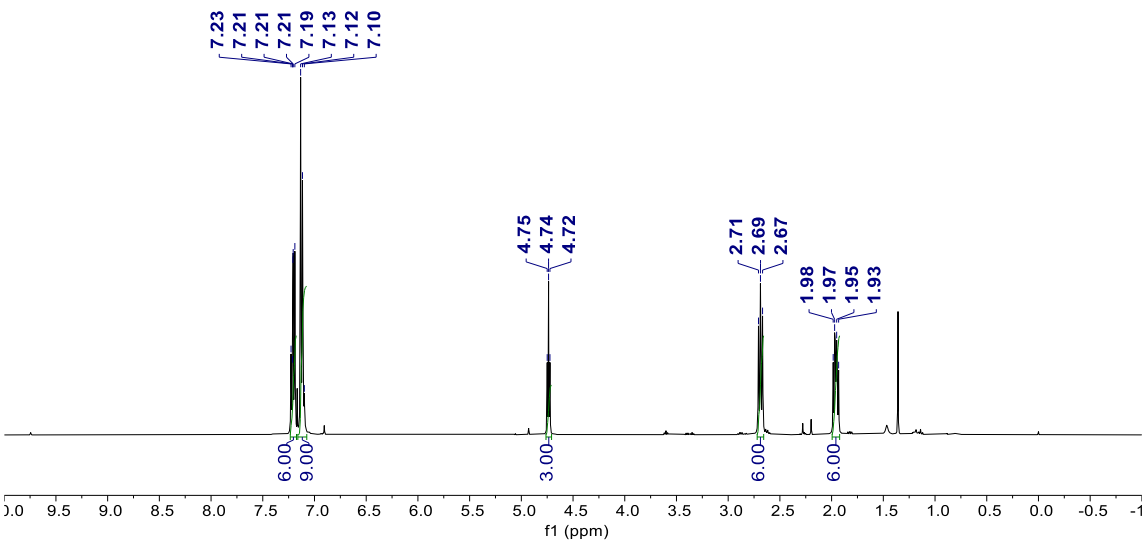
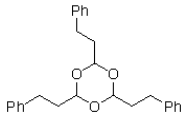


Figure S111: ^{1}H NMR spectrum of the compound **4j'** in $CDCl_3$



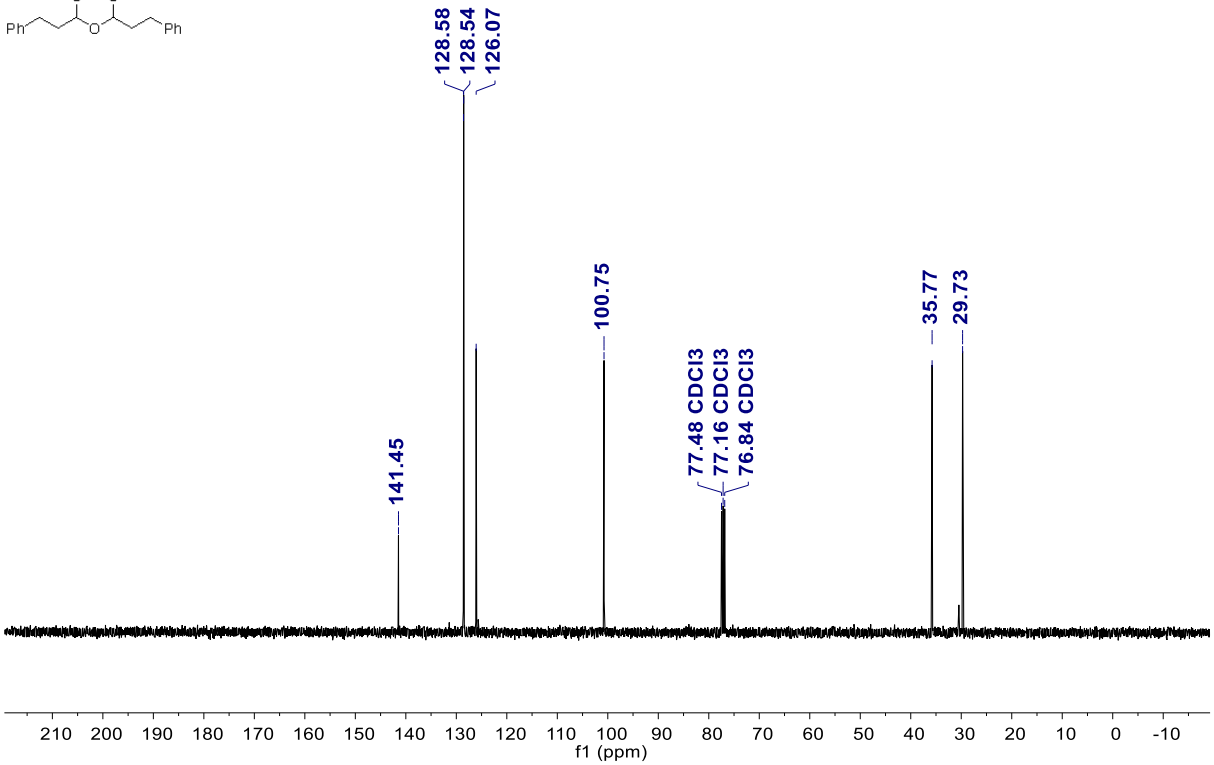
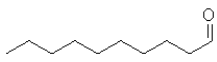


Figure S112: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4j'** in $CDCl_3$.



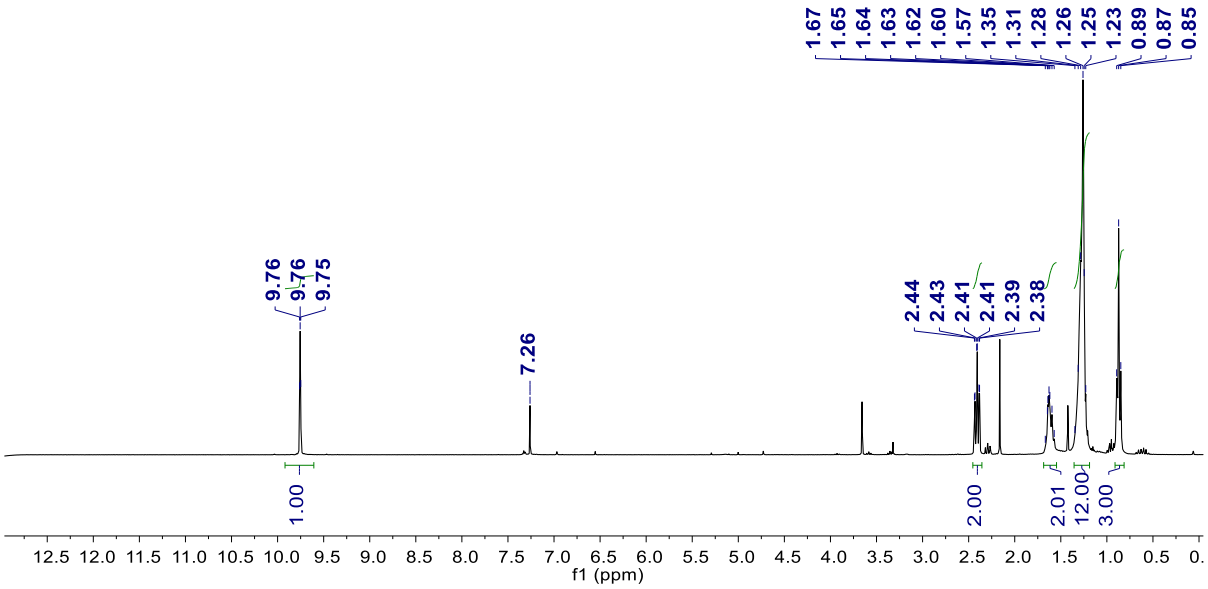
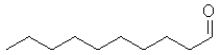


Figure S113: ^{1}H NMR spectrum of the compound **4k** in $CDCl_3$



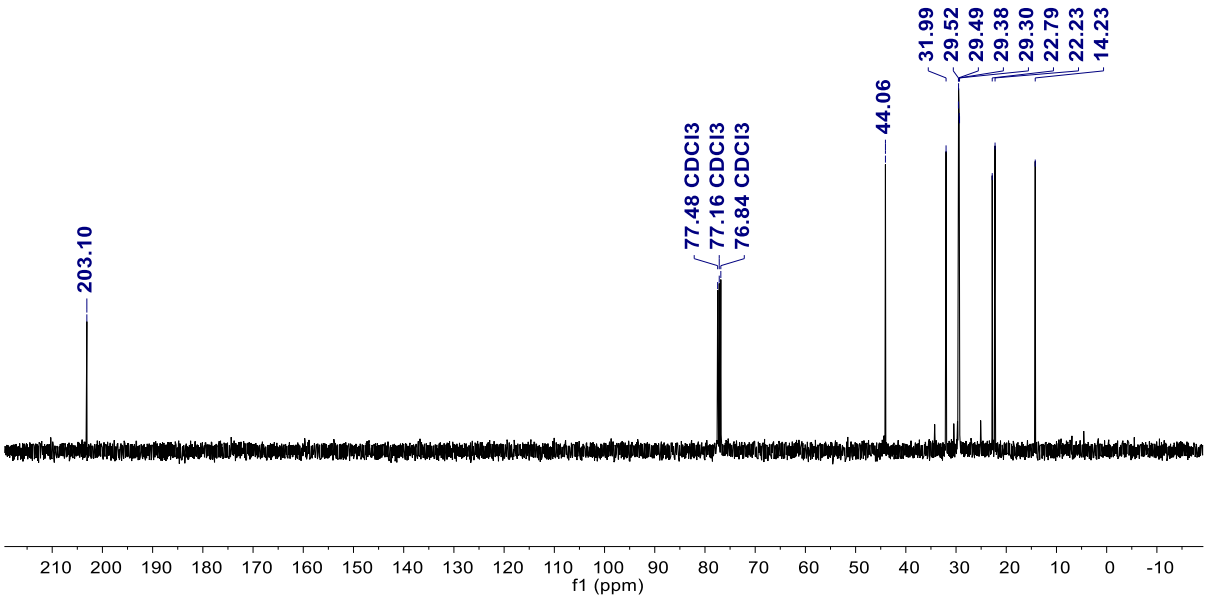


Figure S114: $^{13}C\{^{1}H\}$ NMR spectrum of the compound **4k** in $CDCl_3$.

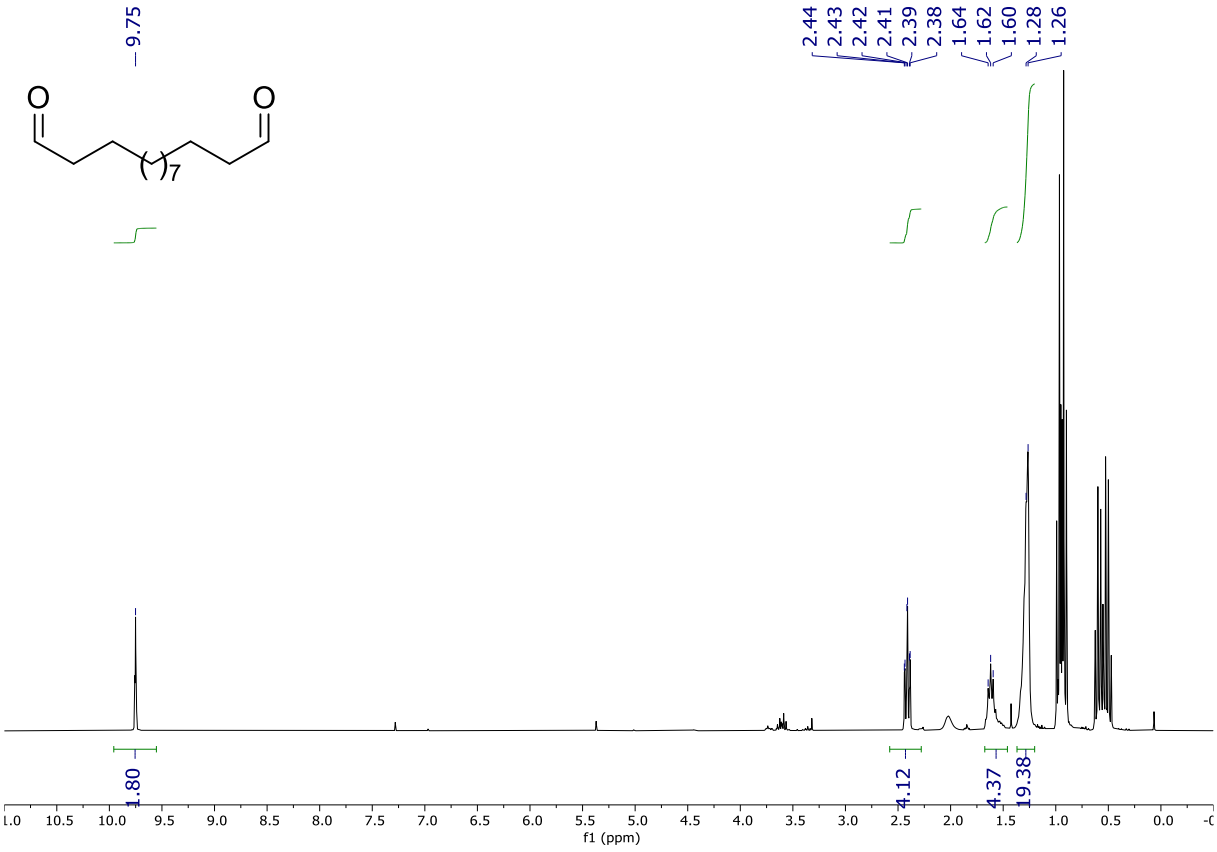
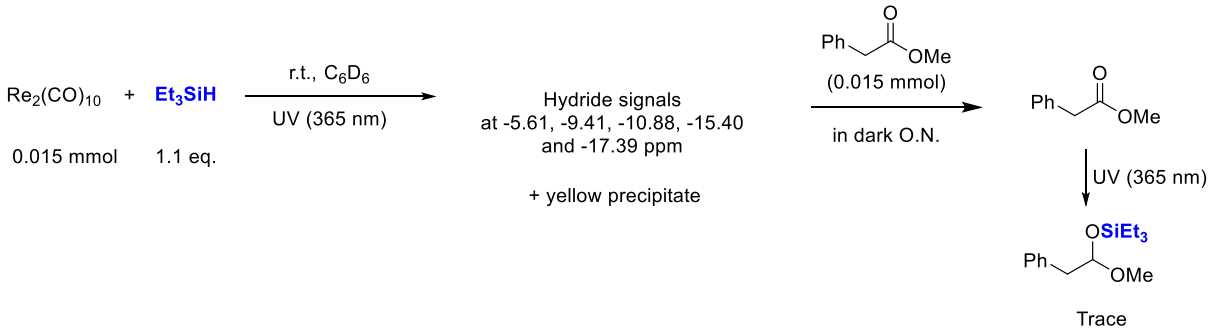


Figure S115: ^{1}H NMR spectrum of the compound **4l** in $CDCl_3$. (Crude mixture after hydrolysis)

10. Complementary data

1) Stoichiometric reactions between metal precursor and Et_3SiH



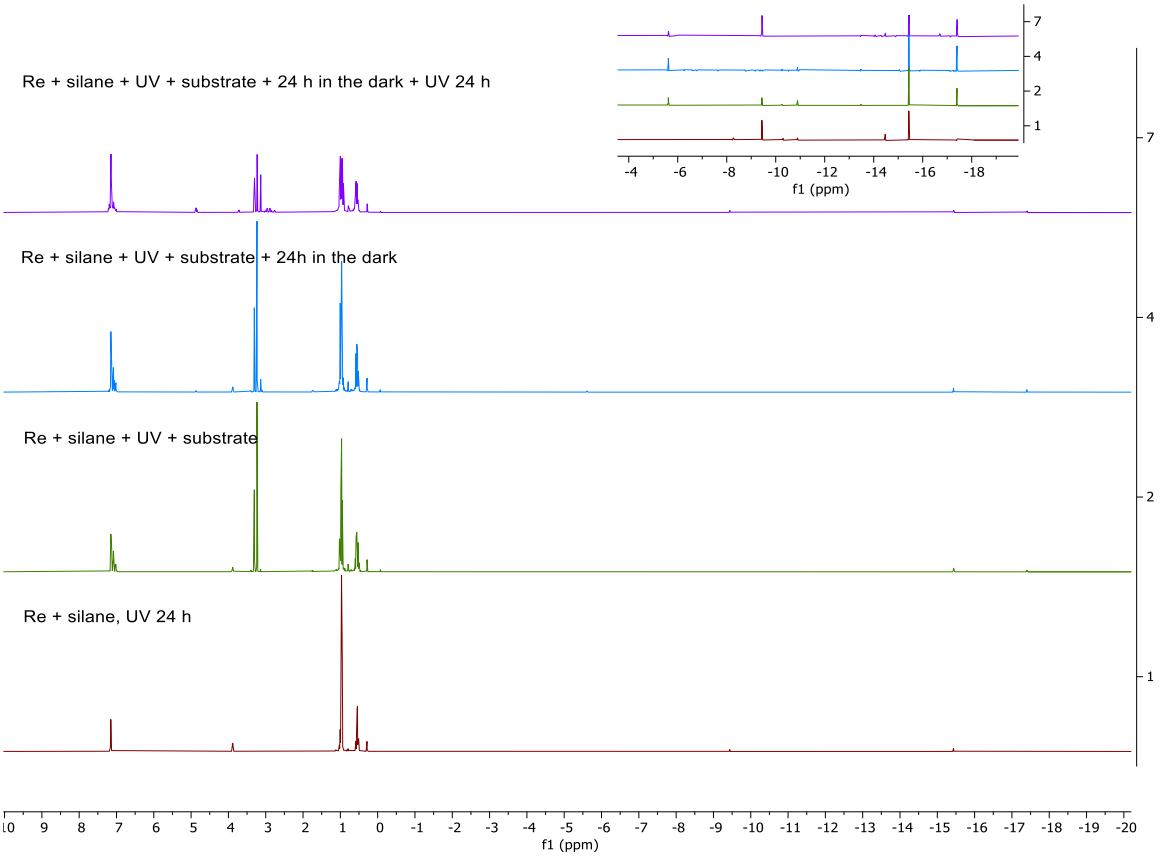


Figure S116 : : Monitoring over time of the reaction between $Re_2(CO)_{10}$ and Et_3SiH (1 equiv.).

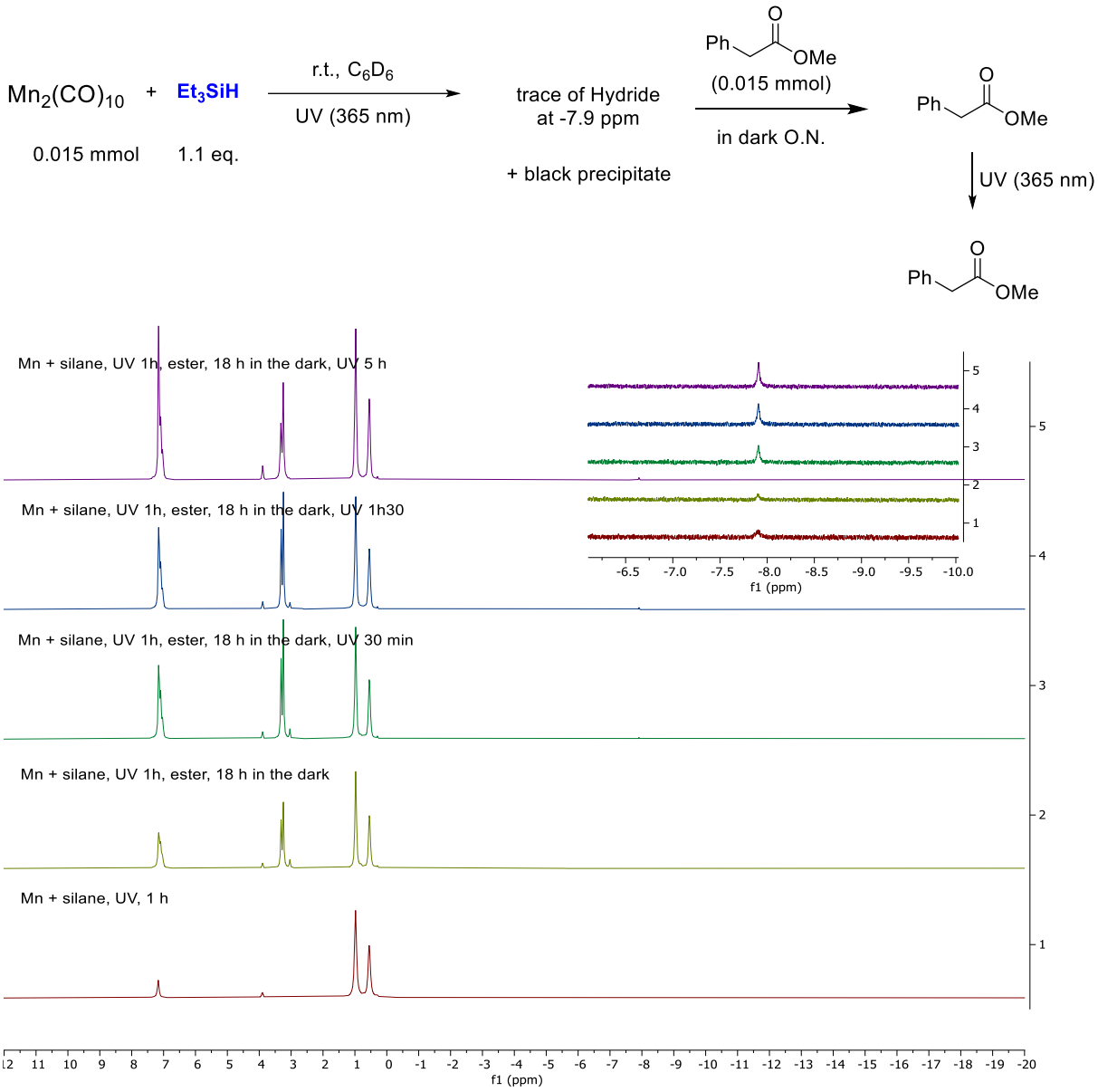
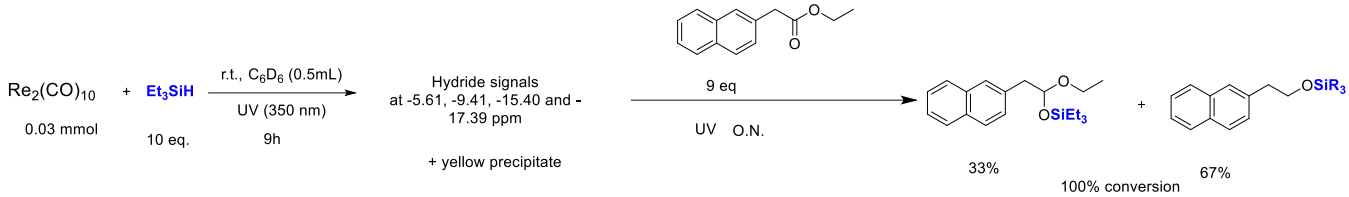


Figure S117: : Monitoring over time of the reaction between $Mn_2(CO)_{10}$ and Et_3SiH (1 equiv.).

2) Stoichiometric reactions of metal precursors with an excess of silane (10 equiv.)



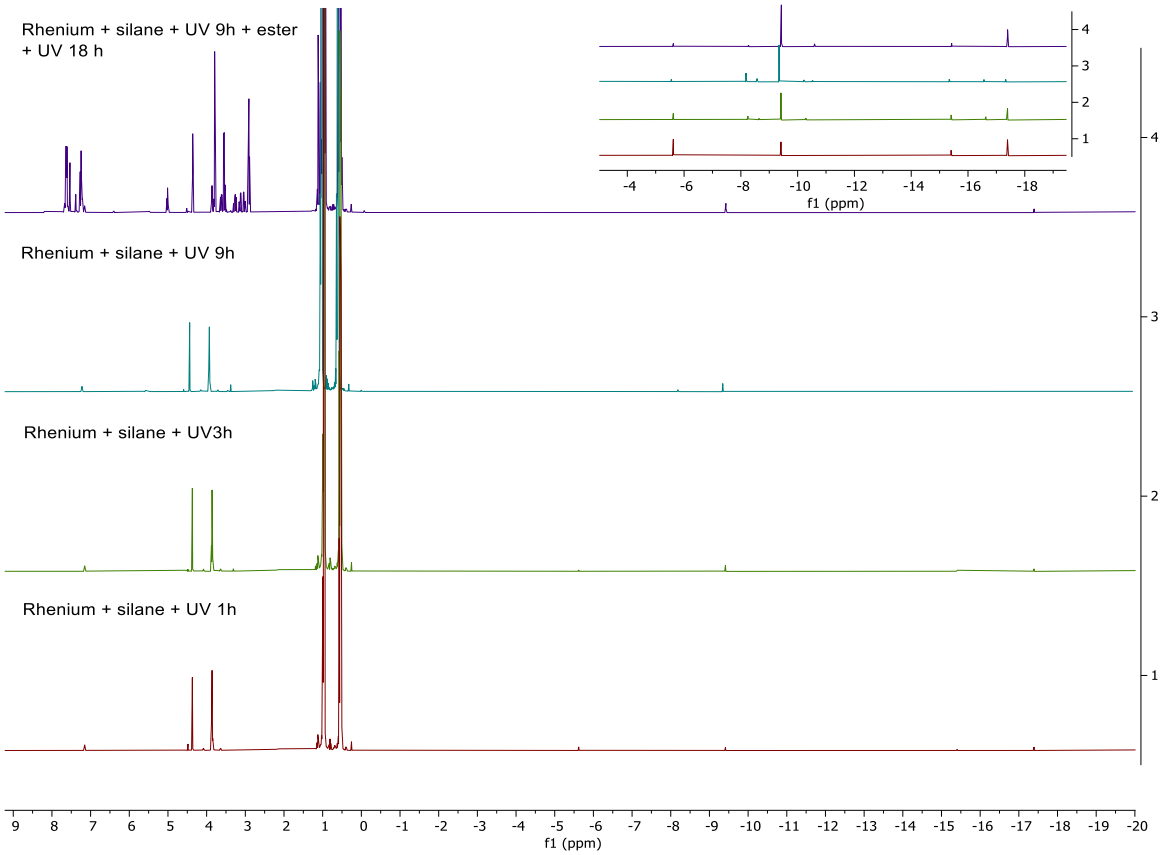


Figure S118: : Monitoring over time of the reaction between $Re_2(CO)_{10}$ and Et_3SiH (10 equiv.).

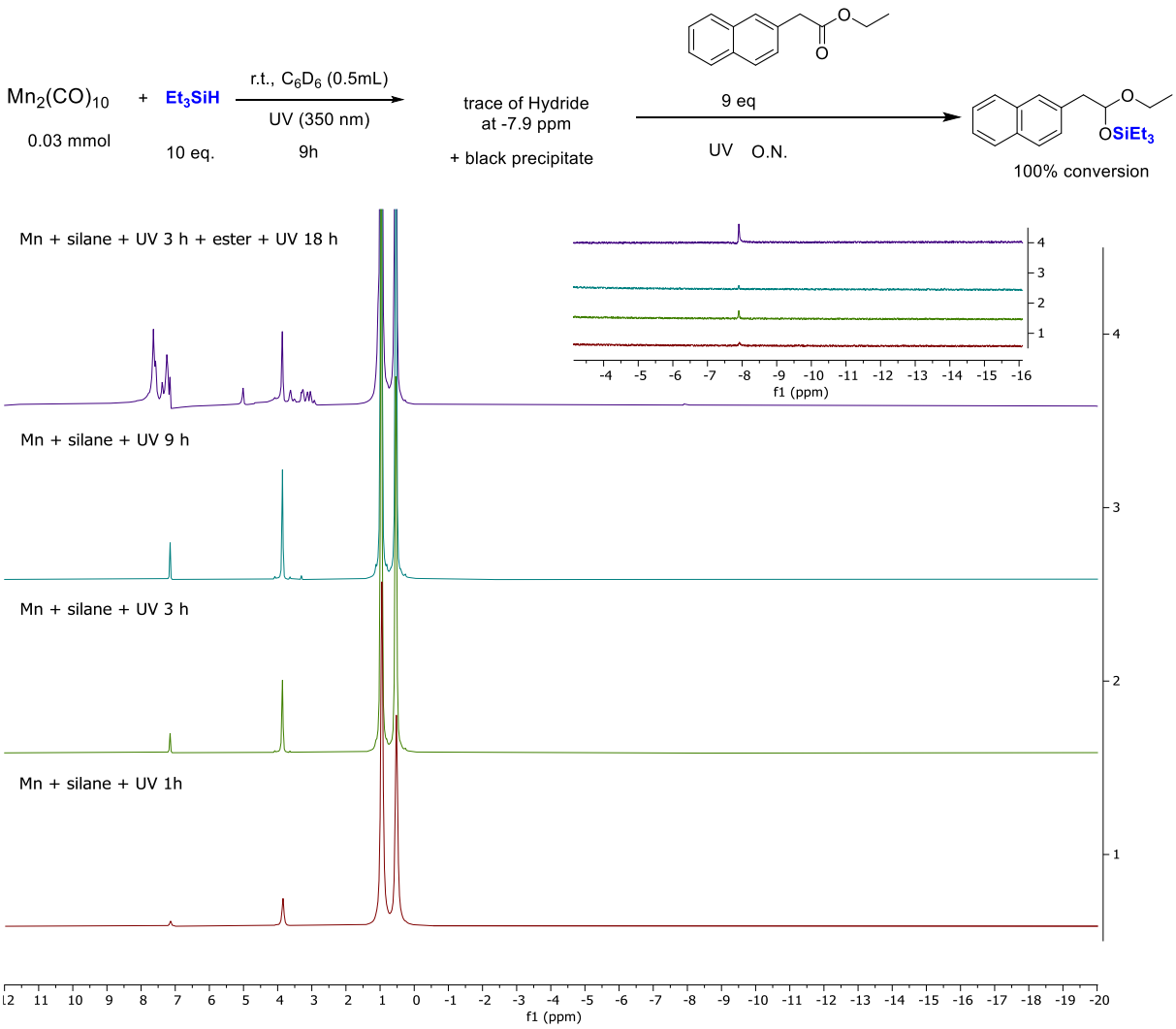


Figure S119: Monitoring over time of the reaction between $Mn_2(CO)_{10}$ and Et_3SiH (10 equiv.).

3) Catalytic reactions with high loading of catalyst

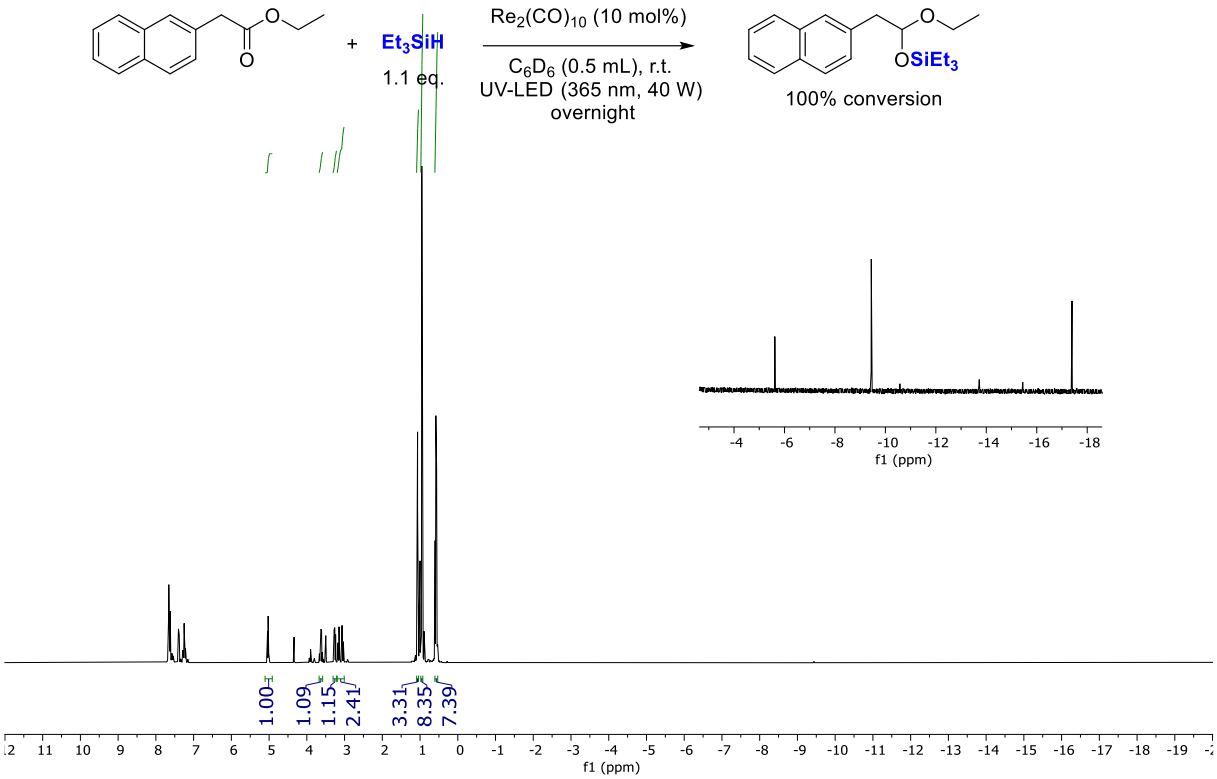


Figure S120: Crude NMR spectra of the catalytic mixture with 10 mol% $Re_2(CO)_{10}$

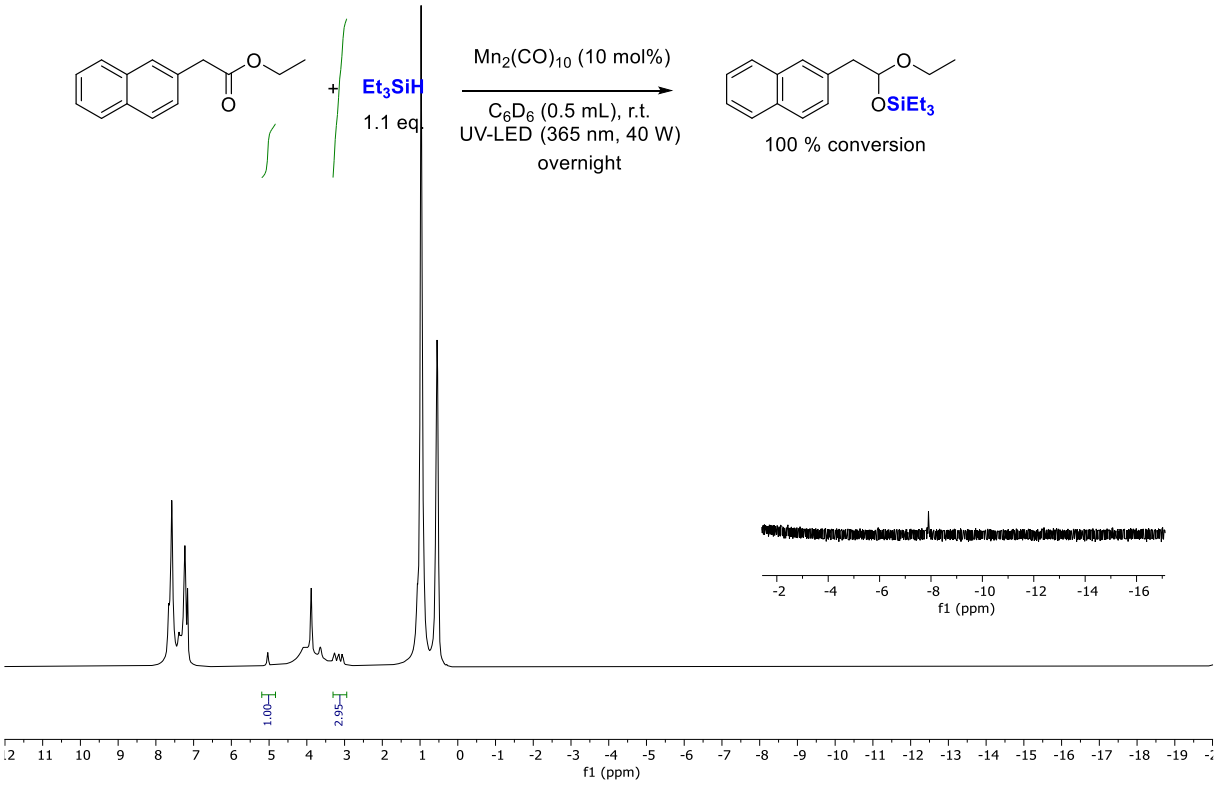


Figure S121: Crude NMR spectra of the catalytic mixture with 10 mol% $Mn_2(CO)_{10}$

4) Discussion

First, the catalytic reactions were found to be inhibited by the addition of TEMPO. The homolytic cleavage of decacarbonyl manganese and rhenium complexes into $[M(CO)_5]$ radicals upon irradiation has been studied in detail previously and reported. [12] Therefore, it is likely that the initiation step of the catalytic cycle is the homolytic cleavage of the metal pre-catalysts.

Second, stoichiometric reactions between metal precursors and Et_3SiH were performed under light irradiation (Figures S116-S119).

In the case of $Mn_2(CO)_{10}$, a very weak signal at -7.9 ppm was detected which could be attributed to $HMn(CO)_5$,, along with significant decomposition (black precipitate). When a stoichiometric amount of substrate was added, no product was detected with or without irradiation. (Figure S117)

In the case of $Re_2(CO)_{10}$, a series of signals was observed at negative chemical shifts, accompagnied by significant precipitation (yellow precipitate). Some of these signals have been previously reported by Fan[13], including $HRe(CO)_5$ (-5.7 ppm) and $HRe_2(CO)_9(SiEt_3)$ (-9.0 ppm) . After addition of a stoichiometric amount of substrate, very low conversion was detected after UV irradiation (Figure S116).

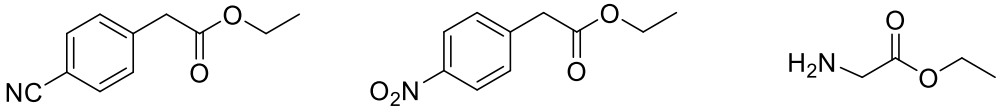
Then, the same stepwise experiments were conducted in the presence of 10 equiv. of silane. As in the previous case, hydrides were detected (Figures S118 and S119), but the catalytic activity was recovered after irradiation.

Finally, under catalytic conditions (i.e. in the presence of the substrate from the beginning of the reaction) but with 10 mol% of catalyst, crude NMR mixture analysis revealed the presence of hydride species after the full conversion of the ester (Figure S120 and S121).

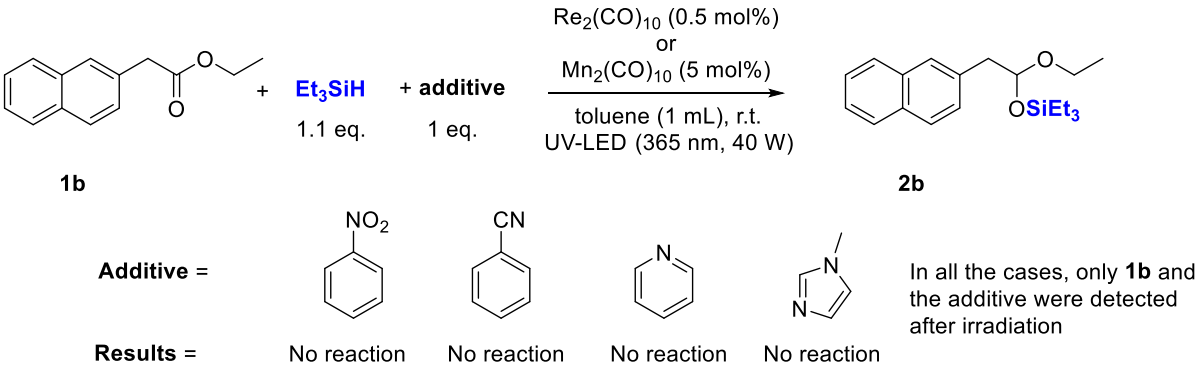
For manganese catalysis, based on our results, we assumed that the radical mechanism proposed by Wang[14] or by Zhang[15] is likely to operate in our case.

In the case of rhenium catalysis, it is likely that the mechanism proposed by Fan[13] is operating in our case, even if we have observed more hydride species than reported in their article.

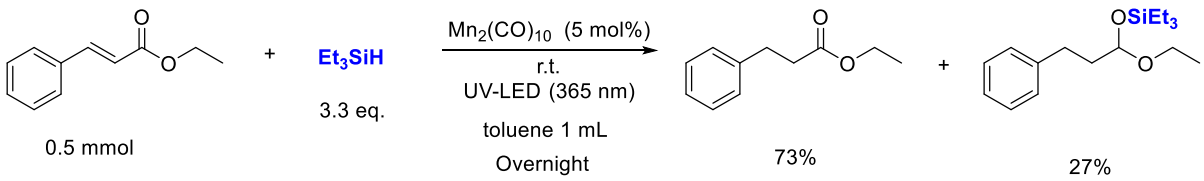
11. Limitations of the scope

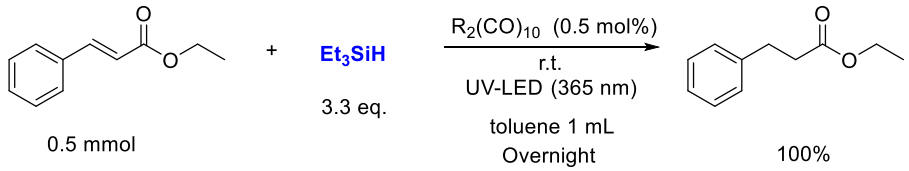


Scheme S1: Substrates that are not reduced neither by $Mn_2(CO)_{10}$ nor by $Re_2(CO)_{10}$ in the presence of Et_3SiH



Scheme S2: Competitive experiments





Scheme S3: Reduction of ethyl cinnamate

12. Reference

1. L. Schiavo, L. Lebedel, P. Massé, S. Choppin and G. Hanquet, *J. Org. Chem.*, 2018, **83**, 6247-6258.
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3. A. Y. Khalimon, W. E. Piers, J. M. Blackwell, D. J. Michalak and M. Parvez, *J. Am. Chem. Soc.*, 2012, **134**, 9601-9604.
4. a) M. Igarashi, R. Mizuno and T. Fuchikami, *Tetrahedron Lett.*, 2001, **42**, 2149-2151; b) S. Soualmi, M. Dieng, A. Ourari, D. Gningue-Sall and V. Jouikov, *Electrochimica Acta*, 2015, **158**, 457-469.
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