Electronic Supplementary Information

Efficient reductive depolymerization of hardwood and softwood lignins with Brookhart's iridium(III) catalyst and hydrosilanes

Louis Monsigny,[a] Elias Feghali,[a] Jean-Claude Berthet,[a] and Thibault Cantat*[, a]

Table of contents

I) General considerations

Syntheses and manipulations of the compounds were conducted under ultra-high purity argon atmosphere with rigorous exclusion of air and water, using Schlenk-vessel and vacuum-line techniques and/or glove boxes. Glassware was dried overnight at 75 ºC before use. The ^{1}H, and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker DPX 200 MHz instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). Unless otherwise noted, reagents were purchased from commercial suppliers and the liquids dried over 4 Å molecular sieves prior to use. Molecular sieves (Aldrich) were activated by drying under dynamic vacuum at 250 °C for 48 h. The reagents used for lignin extractions were: acetic acid ($\geq$ 99.85 %), formic acid ($\geq$ 96.0 %), ethanol ($\geq$ 99.8 %), methanol (99.8 %), acetone (99.5 %) and HCl (37%). Dichloromethane (and d_2-CH_2Cl_2) and chlorobenzene (and d_5-C_6H_5Cl) were dried over CaH_2 and distilled before use. Deuterated solvants were obtained from Eurisotop and the non-deuterated organic solvents from Carlo Erba. The hydrosilanes and siloxanes (Et_2SiH_2, Ph_3SiH, Ph_2SiH_2, $(EtO)_3SiH$, PMHS and TMDS) were purchased from Aldrich, stored in the gloves box and used without further purification. Mass spectrometer data were collected on a Shimadzu GCMS-QP2010 Ultra gas chromatograph mass spectrometer equipped with a Supelco SLBTM-ms fused silica capillary column (30 m x 0.25 mm x 0.25 µm). $B(C_6F_5)_3$ was supplied from Aldrich, degassed and stored under argon in the gloves box. Brookhart's catalyst was synthesized from reported procedure but protonation to form the cationic species $[(^t\text{BuPOCOP})\text{IrH(THF)}][B(C_6F_5)_4]$ (^{t}BuPOCOP = $1,3\{^t\text{Bu}_2\text{PO}\}_2(C_5H_3)$; [**1**]$[B(C_6F_5)_4]$, M = 1351 g/Mol) was carried out in THF instead of acetone.[1] Compounds **5a** and **5b** were prepared according to the method of Ellman et *al.*[2] Compounds **7** and **9** were synthesized following literature.[3] Softwood and hardwood lignin samples were extracted from wood sawdust following Formacell process described by

Delmas *et al*.[4] In all cases, wood sawdust were used as starting materials and dried overnight under vacuum at 60 ºC before use. In all cases, sawdust pieces had a length less than 2 cm and a thickness of less than 0.1 cm.

Methane was observed *in situ* in ^{1}H NMR but not quantified.

Methane: **^{1}H NMR** (200 MHz, C_6D_5Cl) δ_H(ppm) = 0.15 (s)

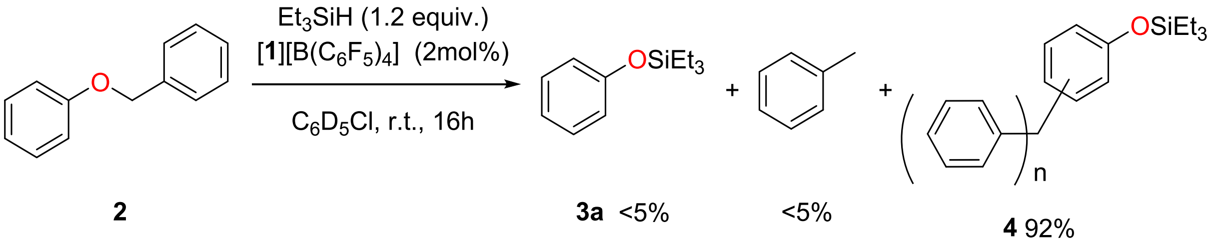
Siloxane was observed *in situ* in ^{13}C NMR but not quantified. (^{1}H NMR observation is not possible because Et_3Si signals of the silylated ether $ROSiEt_3$ and the hydrosilane Et_3SiH are overlaping)

$Et_3SiOSiEt_3$: **^{13}C NMR** (200 MHz, C_6D_5Cl) $\boldsymbol{\delta_C}$(ppm) = 6.8, 6.5.

II) Typical procedures for the catalytic hydrosilylation of lignin model molecules

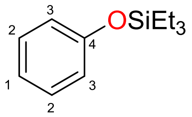
II.a) Hydrosilylation of (benzyloxy)benzene (**2**)

Equation 1



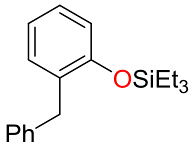
In an NMR tube equipped with a J. Young valve, Et_3SiH (19.1 µL, 0.12 mmol, 1.2 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **2** (18.2 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred at RT for 16 h during which no change of color was observed. The reaction was monitored by ^{1}H NMR and the spectra showed the formation of the ortho-isomer (2-benzylphenoxy)triethylsilane **4** as the major product (ratio ortho/para: 9/1) together with triethyl(phenoxy)silane **3a** (<5%) and toluene (<5%).

Characterization of triethyl(phenoxy)silane (**3a**)



^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm): 7.22 (dd, 2H, ^3J = 8.0 Hz and 7.8 Hz, H_2); 6.93 (t, 1H, ^3J = 8 Hz, H_1); 6,85 (d, 2H, ^3J = 7.8 Hz, H_3), 0.99 (t, 9H, ^3J = 8 Hz, CH_3-CH_2-Si); 0.74 (m, 6H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 155.6, 129.5, 121.3, 120.0, 6.4, 4.9. **SM-EI (m/z):** 209 (8), 208 (46), 180 (25), 179 (100), 152 (24), 151 (98), 149 (10), 123 (64), 121 (46), 79 (12), 77 (28).

Characterization of (2-benzylphenoxy)triethylsilane (*o*-**4**)



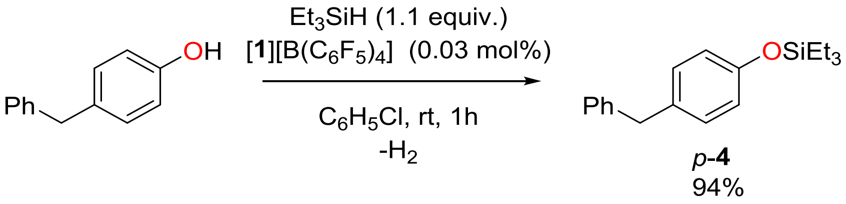
^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm) = 7.38–6.89 (m, 9H, ArH), 4.26 (s, 2H, CH_2), 1.17 (t, 9H, ^{3}J = 8 Hz, *CH_3*-CH_2-Si), 0.96–0.71 (m, 6H, *CH_2*-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** =153.7, 140.2, 131.0, 129.6, 129.0, 128.5, 127.4, 125.9, 121.3, 118.4, 36.7, 6.74, 5.40.

NB: The products *o*-**4** and *p*-**4** can easily be identified in ^{13}C NMR by the distinct chemical shift of the methylene groups: **δ_C**[-CH_2- (*o*-**4**)] = 36.7 and **δ_C**[-CH_2- (*p*-**4**)] = 41.3.

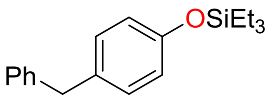
The mixture of the ortho and the para isomer of the (benzylphenoxy)triethylsilane **4** could not be separated by classical flash chromatography on silica gel. Consequently, the isomers of **4** have been synthetized independently:

In a 10 mL round bottom flask equipped with a magnetic stirring bar under inert atmosphere, Et_3SiH (176 µL, 127.9 mg, 1.1 mmol, 1.1 eq.) was added to 2-(benzyl)phenol or 4-(benzyl)phenol (184 mg, 1 mmol, 1 eq.) and [**1**][$B(C_6F_5)_4$] (5.0 mg, 4 µmol, 0.03 mol%) in C_6H_5Cl (2 ml). The mixture was stirred at room temperature until the end of the gas release (1h). The solvent was then evaporated off under vacuum and the crude solid residue purified by flash chromatography on silica gel (using a pentane/AcOEt (95:5) mixture as eluent). Evaporation of the solvents of the collected fractions afforded pure *p*-**4** or *o*-**4** in 94% and 92% yield respectively.

Equation 2



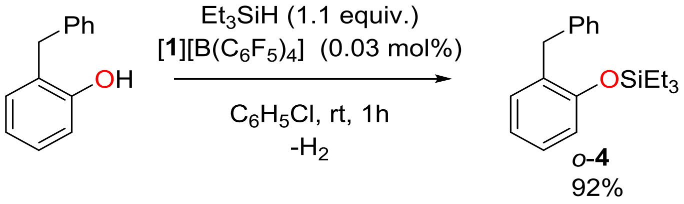
Characterization of (4-benzylphenoxy)triethylsilane (*p*-4)



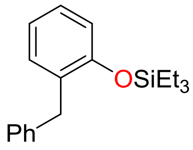
Colorless oil, 281 mg, 94% yield

^{1}H NMR (CD_2Cl_2, 298 K) δ_H(ppm) : δ 7.34 - 7.19 (m, 5H), 7.07 (d; 2H, ^3J = 8.3 Hz), 6.80 (d; 2H, ^3J = 8.3 Hz), 3.92 (s; 2H), 1.02 (t, 9H, ^3J = 7.7 Hz, CH_3-CH_2-Si), 0.74 (m, 6H, CH_2-Si).; **^{13}C NMR (CD_2Cl_2, 298 K) δ_C(ppm)** :154.28, 142.21, 134.44, 130.12, 129.15, 128.78, 126.32, 120.19, 41.44, 6.81, 5.28.

Equation 3



Characterization of (2-benzylphenoxy)triethylsilane (*o*-4)



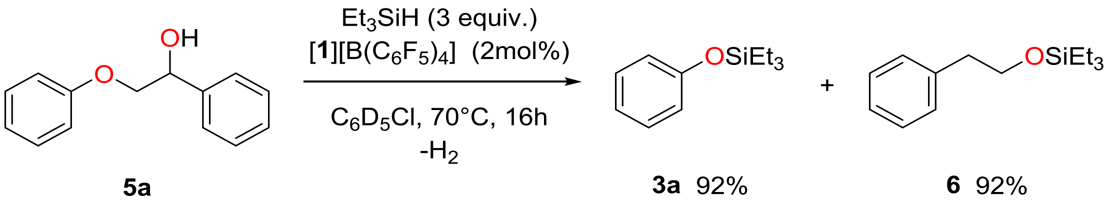
Limpid brown oil, 275 mg, 92 % yield

^{1}H NMR (CD_2Cl_2, 298 K) δ_H(ppm) = 7.35 - 7.21 (m, 5H), 7.18 - 7.11 (m, 2H), 6.96 – 4.87 (m; 2H), 4.02 (s, 2H), 1.03 (t, J = 7.6 Hz, 9H), 0.93 – 0.70 (m, 6H). **^{13}C NMR (CD_2Cl_2, 298 K) δ_C(ppm)** =154.1, 141.8, 132.2, 131.1, 129.3, 128.6, 127.7, 126.2, 121.4, 118.7, 36.7, 6.9, 5.7.

HRMS (ESI) *m/z* $[M + H]^+$ calcd. for $C_{19}H_{27}OSi^+$ 299.1826; found : 299.1834.
$[M + Na]^+$ calcd. for $C_{19}H_{26}OSiNa^+$ 321.1645; found : 321.1644.

II.b) Hydrosilylation of 2-phenoxy-1-phenylethan-1-ol (**5a**)

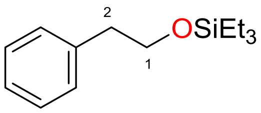
Equation 4



In an NMR tube equipped with a J. Young valve, Et_3SiH (47.8 µL, 0.3 mmol, 3.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **5a** (21.4 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by ^{1}H NMR and the spectra showed only the formation of triethyl(phenoxy)silane **3a** (92%) and triethyl(phenylethoxy)silane **6** (92%).

The ^{1}H NMR yields of compounds **3a** and **6** were confirmed with GC-MS analyses.

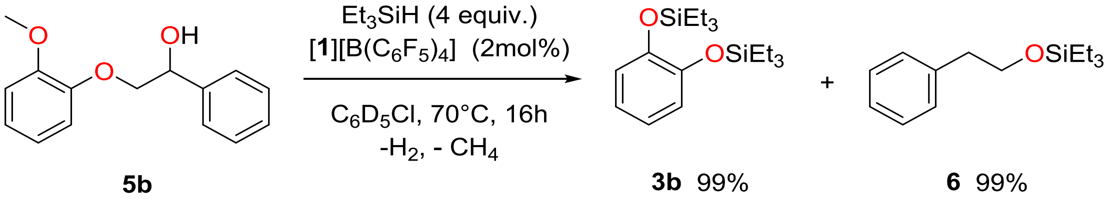
Characterization of triethyl(phenylethoxy)silane (**6**)



^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 7.32–7.15 (m, 5H); 3.83 (t; 2H, ^3J = 7.5 Hz, H_1); 2.85 (t, 2H, ^3J = 7.5 Hz, H_2), 0.97 (t, 9H, ^3J = 8 Hz, CH_3-CH_2-Si); 0.58 (m, 6H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 140.1, 129.9, 128.9, 126.8, 64.1, 39.9, 7.3, 5.1. **SM-EI (m/z):** 208 (19), 207 (100), 179 (7), 161 (12), 117 (10), 115 (7), 105 (23), 103 (12), 87 (11), 75 (21), 59 (10), 47 (6).

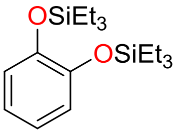
II.c) Hydrosilylation of 2-(2-methoxyphenoxy)-1-phenylethan-1-ol (**5b**)

Equation 5



In an NMR tube equipped with a J. Young valve, Et_3SiH (63.8 µL, 0.4 mmol, 4.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **5b** (24.4 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the reagents and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by ^{1}H NMR and the spectrum showed the quantitative formation of 1,2-bis((triethylsilyl)oxy)benzene **3b** and triethyl(phenylethoxy)silane **6**. The ^{1}H NMR yields of compounds **3b** and **6** were confirmed with GC-MS analyses.

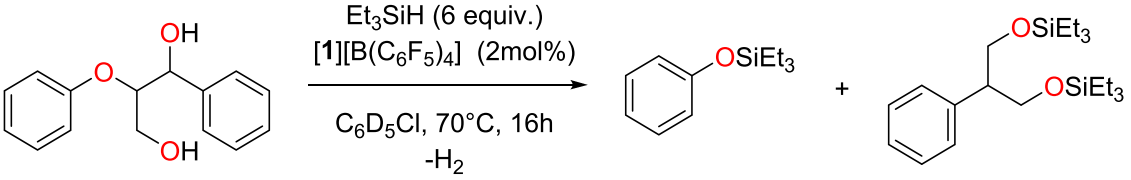
Characterization of 1,2-bis((triethylsilyl)oxy)benzene (**3b**)



^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 6.85–6.77 (m, 4H); 1.05–0.89 (m, 18H, *CH_3*-CH_2-Si); 0.85–0.69 (m, 12H, *CH_2*-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 147.8, 121.9, 121.0, 7.1, 5.4. **SM IE (m/z)** : 339 (8), 338 (12), 309 (23), 116 (12), 115 (100), 87 (56), 77 (1), 59 (25).

II.d) Reaction of hydrosilylation of 2-phenoxy-1-phenylpropane-1,3-diol (**7**)

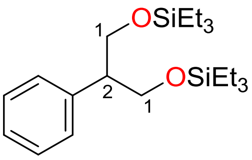
Equation 6



7 **3a** 99% **8** 83%

In an NMR tube equipped with a J. Young valve, Et_3SiH (95.7 µL, 0.6 mmol, 6.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **7** (24.4 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was then heated at 70°C for 16 h without any change of color. The reaction was monitored by ^{1}H NMR and the spectra showed the quantitative formation of triethyl(phenoxy)silane **3a** and of 2-methylhydroxy-1-phenylethanol **8** (83%) with traces of triethyl(3-phenylpropoxy)silane. The yield of **3a** was quantitative according to GC/MS analysis.

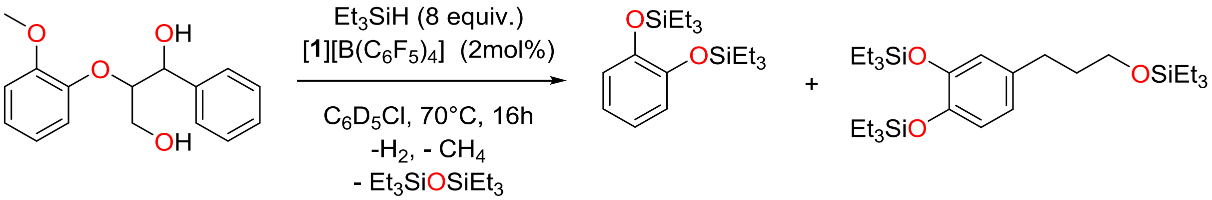
Characterisation of 2-methylhydroxy-1-phenylethanol (**8**)



^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 7.13–6.99 (m, 5H), 4.21 (d, 4H, ^3J = 6.0 Hz, H_1), 3.16 (q, 1H, ^3J = 6.0 Hz, H_2), 1.19–1.13 (m, 18H, CH_3-CH_2-Si), 0.84–0.72 (m, 12H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 148.8, 128.6, 128.1, 126.5, 63.6, 51.1, 6.9, 4.5.

II.e) Hydrosilylation of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy) propane-1,3-diol (**9**)

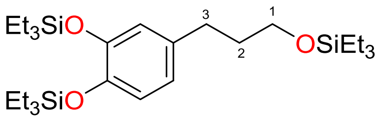
Equation 7



9 **3b** 99% **10G** 87%

In an NMR tube equipped with a J. Young valve, Et_3SiH (127.6 µL, 0.8 mmol, 8.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **9** (33.4 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred until complete dissolution of the starting materials and the end of the gas release. The tube was heated at 70°C for 16 h without any change of color. The reaction was monitored by ^{1}H NMR and the spectra showed the quantitative formation of 1,2-bis((triethylsilyl)oxy)benzene **3b** and **10G** (87%). The ^{1}H NMR yields of compounds **3b** and **10G** were confirmed with GC-MS analysis.

Characterization of compound **10G**



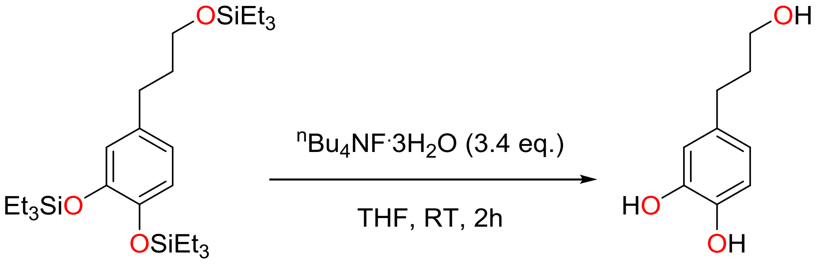
^{1}H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 7.13–6.99 (m, 3H); 3.83 (t, 2H, ^3J = 7.6 Hz, H_1); 2.84 (t, 2H, ^3J = 7.6 Hz, H_3), 2.03 (q, 2H, ^3J = 7.6 Hz, H_2), 1.23–1.16 (m, 27H, CH_3-CH_2-Si); 0.82–0.70 (m, 18H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 147.7, 145.2, 136.5, 121.7, 121.3, 120.7, 62.0, 35.0, 31.7, 6.9, 6.8, 5.2, 5.2, 4.8. **SM IE (m/z)**: 511 (8), 510 (18) 337 (19), 235 (24), 207 (36), 116 (10), 115 (84), 89 (31), 88 (10), 87 (100), 86 (5), 59 (34), 32 (16).

III) Typical procedure for the hydrolysis of silylated aromatic compounds

The procedure for the hydrolysis of silylated aromatic compounds **10G** and **10S** are identical and the reaction is exemplified with compound **10G**, as followed :

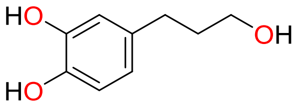
Under inert atmosphere (Argon), ^{n}Bu$_4$NF·3H$_2$O (1.08 g; 3.4 mmol, 3.4 equiv.) was added slowly to a solution of **10G** (511.0 mg; 1.0 mmol, 1 equiv.) in 4 mL of THF. The colorless solution was stirred at room temperature. After for 2 h, the solvent was evaporated off under vacuum and the solid residue was chromatographed on a silica gel column by using a mixture of pentane and ethyl acetate as eluent (2:8 pentane/AcOEt). Compound **10G’** was obtained pure as a colorless oil (141.3 mg; 0.9 mmol; 84 %).

Equation 8



10G **10G'** 84%

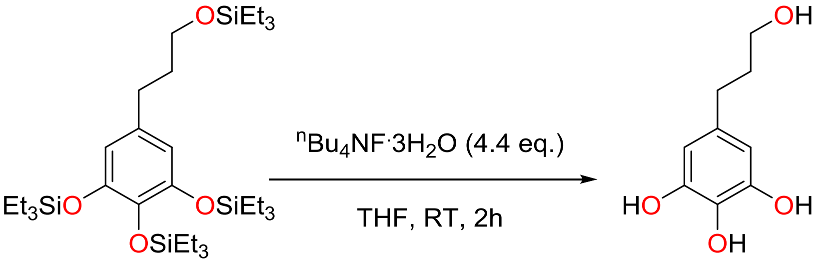
Characterization of compound **10G’**



^{1}H NMR (D$_2$O, 298 K) δ_H(ppm) = 6.88-6.57 (3H, m, Ar-H), 4.79 (3H, br.s, OH), 3.54 (2H, t, ^3J = 6.6 Hz, CH$_2$-O), 2.50 (2H, t, ^3J = 7.6 Hz, Ar-CH$_2$), 1.75 (2 H, quint, ^3J = 6.9 Hz, Ar-CH$_2$-CH$_2$).

^{13}C NMR (D$_2$O, 298 K) δ_C(ppm) = 143.9, 141.8, 135.3, 120.6, 116.2, 61.1, 33.3, 30.6

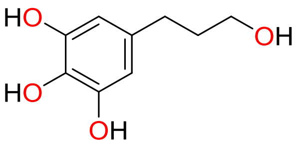
Equation 9



10S **10S'** 94%

From **10S** (640.0 mg; 1.0 mmol, 1 equiv.) with ${}^{n}Bu_4NF\cdot 3H_2O$ (1.4 mg; 4.4 mmol, 4.4 equiv.)

Characterization of compound (**10S'**)

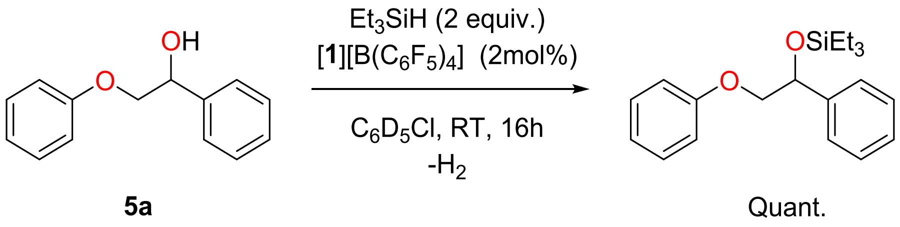


10S' (173.2 mg, 94% yield)

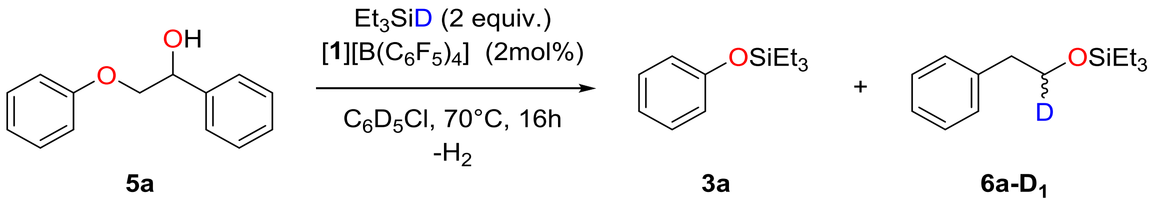
^{1}H NMR (D_2O, 298 K) δ_H(ppm) = 6.36 (2H, s, Ar-H), 4.79 (4H, br.s, OH), 3.54 (2H, t, ^3J = 6.7 Hz, CH_2-O), 2.45 (2H, t, ^3J = 7.5 Hz, Ar-CH_2), 1.73 (2 H, quint, ^3J = 7.1 Hz, Ar-CH_2-CH_2).

^{13}C NMR (D_2O, 298 K) δ_C(ppm) = 145.4, 135.1, 130.0, 108.1, 61.1, 33.2, 30.8

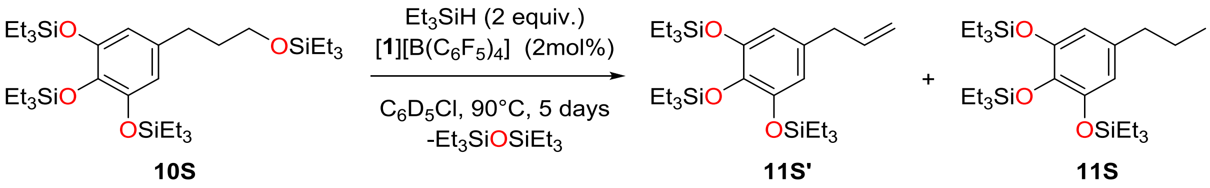
IV) Supplementary equations



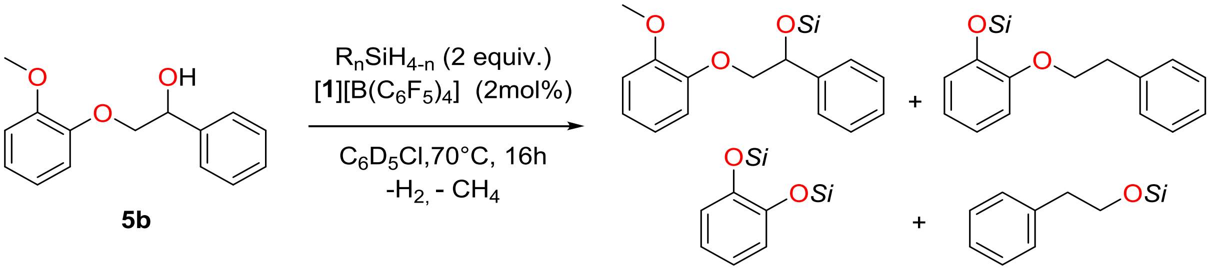
See page S16



See page S17



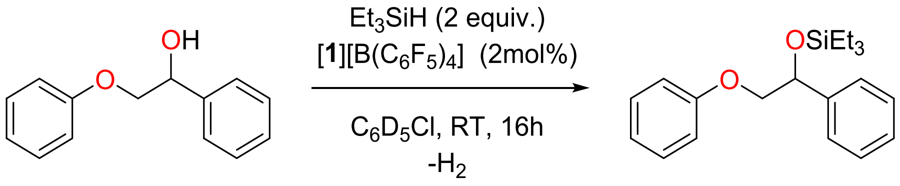
See page S18



See page S19

IV.a) Attempts of reduction of **5a** at room temperature

Equation 10

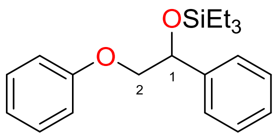


5a quant.

In an NMR tube equipped with a J. Young valve, Et_3SiH (34.4 µL, 0.2 mmol, 2.0 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **5a** (21.4 mg, 0.10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred for 16 h at RT without any change of color. The reaction was monitored by ^1H NMR and ^{13}C NMR and the spectra showed only the quantitative formation of the silylated derivative of **5a**.

In order to further reduce compound **5a**, as in equation 2, heating for hours at 70°C is required. This is consistent with the findings of Brookhart *et al.* for bulky substrates.[5]

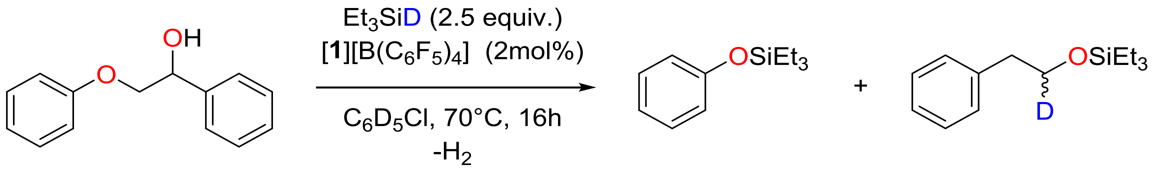
Characterisation of triethyl(2-phenoxy-1-phenylethoxy)silane



^1H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 7.52–7.29 (m, 5H), 7.08–6.84 (m, 5H), 5.14 (t, 1H, J = 5.8 Hz, H_1), 3.96 (m, 2H, H_2), 1.08–1.01 (m, 9H, CH_3-CH_2-Si); 0.73–0.56 (m, 6H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm)** : 159.2, 142.4, 129.5, 128.3, 127.8, 126.3, 120.7, 114.5, 74.0 (C_2), 73.7 (C_1), 6.9, 5.0.

IV.b) Labelling experiments on **5a** with Et_3SiD

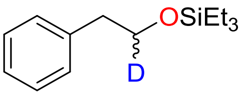
Equation 11



5a **3a** **6-D$_1$**

In an NMR tube equipped with a J. Young valve, Et_3SiD (29.2 mg, 0.25 mmol, 2.5 equiv.) and mesitylene (13.9 µL, 0.10 mmol, 1.0 equiv., used as an internal standard) were added to a mixture of **5a** (21.4 mg, 0,10 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 2.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred for 16 h without any change of color. The reaction was monitored by ^1H NMR and ^{13}C NMR and the spectra showed only the quantitative formation of the labelled derivative **6-D$_1$**.

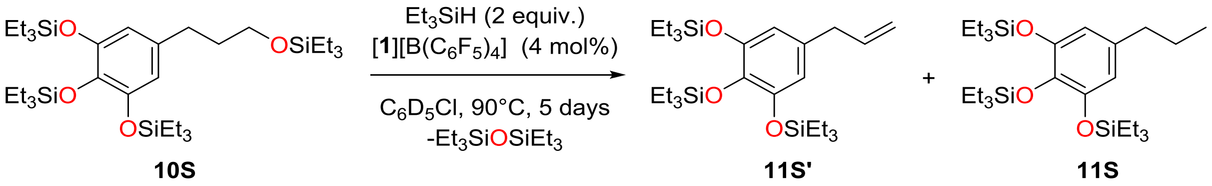
Characterisation of triethyl(2-phenyloxy-1-phenylethoxy)silane (**6-D$_1$**)



^1H NMR (C_6D_5Cl, 298 K) δ_H(ppm) : 7.32–7.15 (m, 5H); 3.83 (broad t; 1H, ^3J = 6.6 Hz, HD); 2.85 (broad d, 2H, ^3J = 6.6 Hz, H), 0.97 (t, 9H, ^3J = 8 Hz, CH_3-CH_2-Si); 0.58 (m, 6H, CH_2-Si); **^{13}C NMR (C_6D_5Cl, 298 K) δ_C(ppm) :** 140.1, 129.9, 128.9, 126.8, 64.3 , 39.9, 7.3, 5.1.

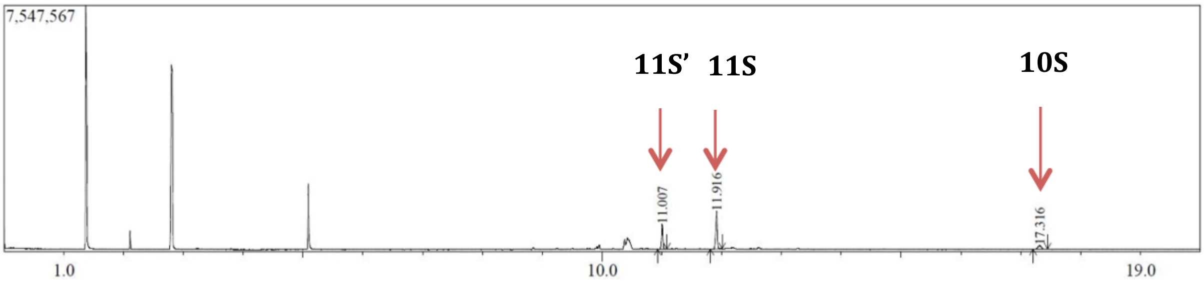
IV.c) Catalytic reduction of **10S** into **11S** and **11S’** with Et_3SiH

Equation 12



In an NMR tube equipped with a J. Young valve, Et_3SiH (16 µL, 0.1 mmol, 2 equiv.) was added to a mixture of **10S** (32 mg, 0.05 mmol, 1.0 equiv.) and [**1**][$B(C_6F_5)_4$] (2.7 mg, 0.002 mmol, 4.0 mol%) in C_6D_5Cl (0.3 mL). The clear orange solution was stirred 5 days at 90°C without any change of color. Reduction to the propylcatechol derivatives **11S’** and **11S** was effective but the reaction incomplete. As observed by Brookhart *et al*, elimination of Et_3SiOH on the pendant chain produced the corresponding alkene that can be further reduced into **11S** by the neutral [(^{t}BuPOCOP)IrH_2] dihydride complex formed *in situ*.[6] NMR and GC-MS spectra confirmed the formation of compounds **11S** (tr = 11.916 minutes) and **11S’** (tr = 11.007 minutes). However, purification of **11S’** and **11S** compounds by flash chromatography on a column was difficult due to their similar chemical properties.

Scheme 1: GC-MS chromatogram of the reduction of **10S** with Et_3SiH

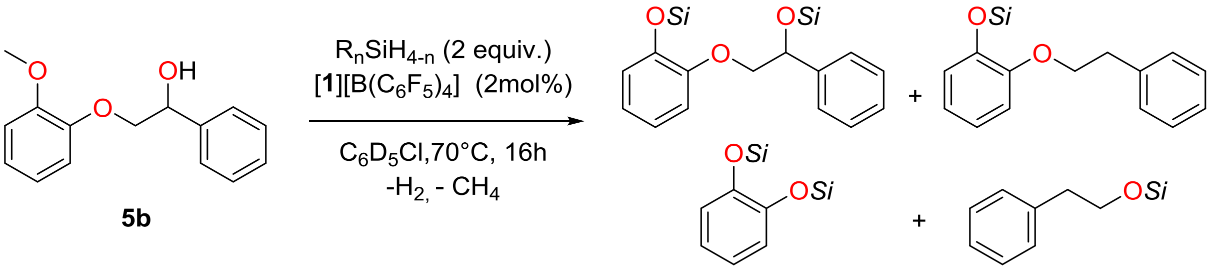


11S’: **SM IE (m/z):** 508 (21), 365, 364 (25), 363 (42), 336 (18), 335 (29), 116 (7), 115 (54), 88 (10), 87 (100), 59 (43).

11S: **SM IE (m/z)**: 510 (8), 339 (27), 338 (35), 337 (32), 116 (10), 115 (82), 88 (9); 87 (100), 59 (36).

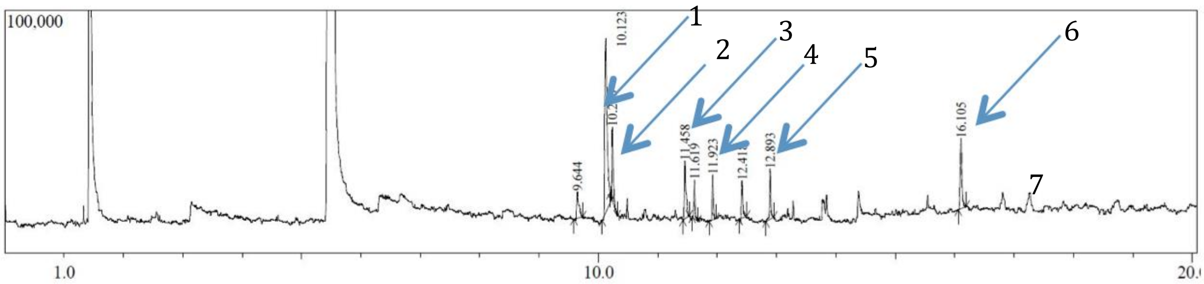
IV.d) Reduction of model **5b** with a variety of hydrosilanes

Equation 13

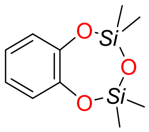


Compound **5b** was treated under the conditions of equation 4 with a variety of hydrosilanes (Et_2SiH_2, Ph_3SiH, Ph_2SiH_2, $(EtO)_3SiH$, PMHS and TMDS). The n values and the number of equiv. silane correspond to 4 Si-H per molecule of **5b**. Its hydrosilylation was observed by NMR spectroscopy which spectra showed the formation of an intricate mixture of silylated products impeding the determination of the yields.

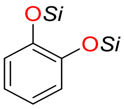
Scheme 2: GC-MS chromatogram of the hydrosilylation of **5b** with TMDS



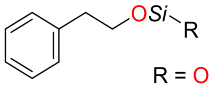
1



2

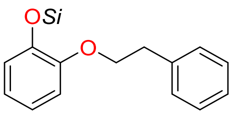


3,4,

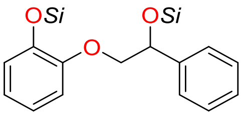


R = OSiHMe$_2$
OSiMe$_2$ OCH$_2$-CH$_2$-Ph, ...

5



6



7 Friedel-Craft alkylation products

V) Typical procedures for the catalytic hydrosilylation of lignins

V.a) Typical procedures for the catalytic hydrosilylation of softwood lignins

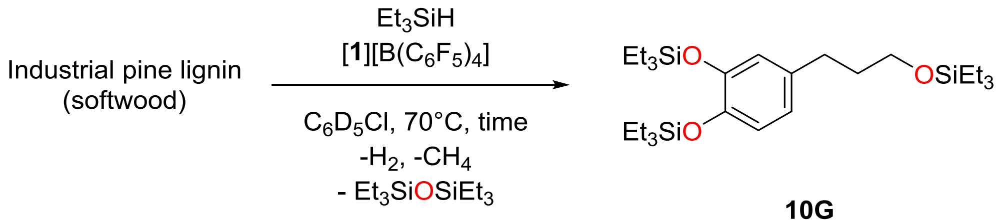
The procedure is detailed for the conversion of industrial pine lignin (extracted with the Formacell process) into **10G** by using Et_3SiH as reductant. Norway spruce, Lebanese cedar and Pacific red cedar similarly afforded compound **10G** in yields ranging from 11 to 120 wt%. In the same manner, hardwood lignin of the evergreen oak, hybrid plane, common beech and black poplar essences gave the two compounds **10G** and **10S** in yields varying from 20 to 42 wt% and 61 to 130 wt%, respectively.

In a 50 mL round bottom flask equipped with a magnetic stirring bar under inert atmosphere, Et_3SiH (600 mg, 5.2 mmol, 300 wt% from lignin) was added to 200 mg of lignin (~0.2 mmol lignin (Mn ~ 980 g/mole, $N_{aromatic} = 5$), ~1.0 mmol of aromatic units) and [**1**][$B(C_6F_5)_4$] (40.0 mg, 0.03 mmol, 20 wt% from lignin) in C_6H_5Cl (2 ml). The mixture was stirred at room temperature until complete dissolution of the starting materials and the end of the gas release. After 20 min, the solid has completely disappeared and the initial red-orange solution turned brown. The clear solution was then stirred at 70 °C for 24-48 h. The solvent was then evaporated off under vacuum and the crude solid residue purified by flash chromatography on silica gel (using pentane/CH_2Cl_2 (8:2) mixture as the eluent). All the by-products and in particular the potential diaromatic molecules were retained in the column. Evaporation of the solvent (*ca* 500 ml) of the collected fractions afforded pure **10G** as a colorless oil (100 wt%, 202 mg).

Yields are given in weight percent (wt%) which correspond to the weight of silylated monolignols derivatives over the weight in lignin (wt of **10S** or **10G**)/(wt of lignin). (See Section VII.a)

V.b) Optimization of the conditions for the industrial pine lignin

Equation 14



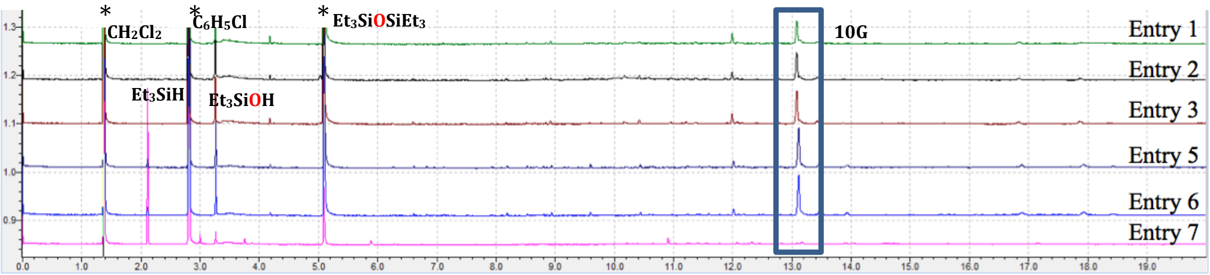
10G

Table 1: Attempts at optimizing the depolymerization of industrial pine lignin. The tests have been led on 40 mg (≈ 0.2 mmol in aromatic units) of industrial pine lignin.

Entry	[**1**][B(C_6F_5)$_4$] (wt%)	**Et$_3$SiH** (wt%)	**Temperature** (°C)	**Time** (h)	**10G** (wt%) (GC Yield)
1[a]	50	273	70	16	65
2[a]	25	273	90	24	99
3[a]	25	300	70	24	120
4[a]	20	273	70	24	110
5[a]	20	273	70	36	120
6[a]	10	300	70	48	120
7[a]	5	400	70	72	-

[a] Detection of other unidentified volatile products

Scheme 3: GC-MS chromatograms of the depolymerization residues of industrial pine lignin



The optimal conditions for the depolymerization of industrial pine lignin were: 10 wt% of [**1**][B(C_6F_5)$_4$], 273 wt% of Et_3SiH, 70 °C, 48 h, solvent = C_6H_5Cl
The peak at 12 mn is not attributed.

V.c) Depolymerization of softwood lignins

Equation 15

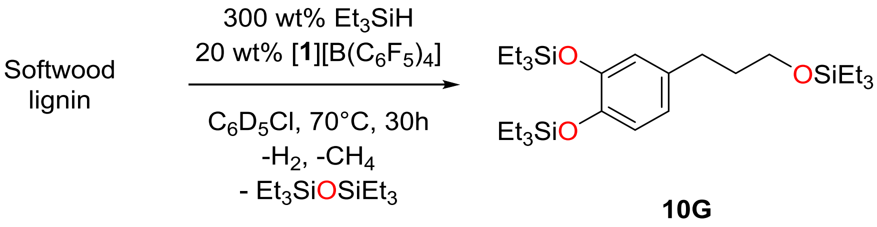
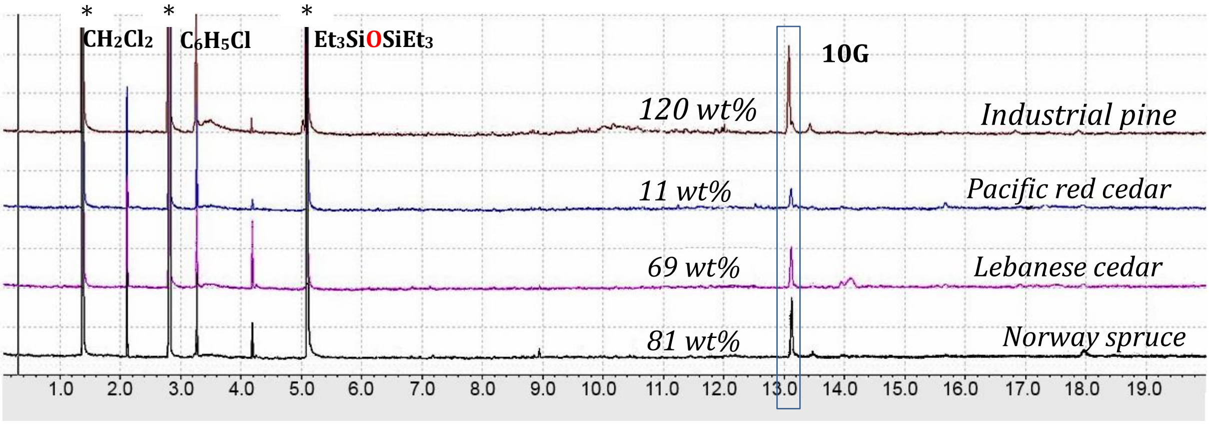


Table 2: Results Summary of softwood lignin depolymerization

Softwood lignin	**Et_3SiH** (wt%)	**10G** (wt%)	**Yield**[c]
Industrial pine	300	120 [a]	46 %
Norway spruce	300	81 [b]	31 %
Lebanese cedar	300	69 [a]	27 %
Pacific red cedar	300	11 [b]	4 %

[a] Detection of other unidentified volatile products. [b] No other major volatile products were detected. [c] Molar yield is calculated with respect to **10G** (see section VII.b).

Scheme 4: GC-MS chromatograms of the crude depolymerization residues of softwood lignins obtained from Eq. 15



V.d) Optimization of the depolymerization conditions for black poplar lignin

Equation 16

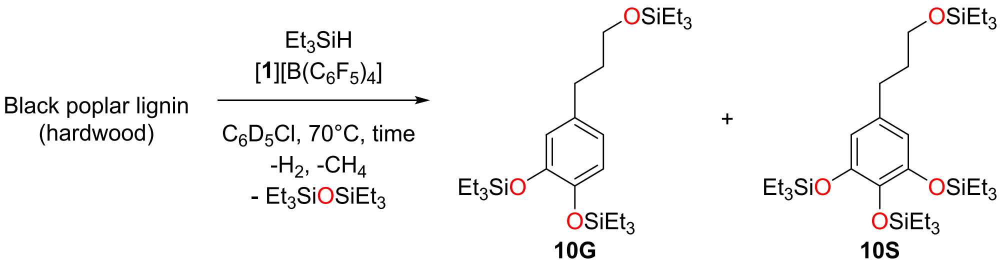
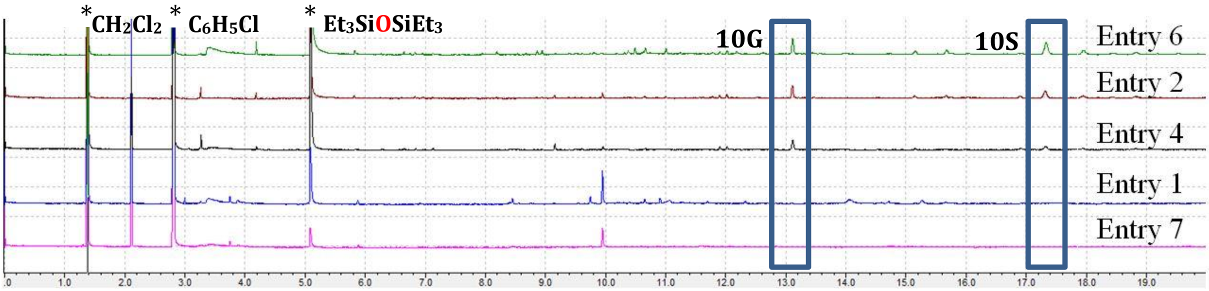


Table 3: Attempts at optimization for depolymerization of black poplar lignin (40 mg ≈ 0.2 mmol).

Entry	[**1**][B(C_6F_5)$_4$] (wt%)	**Et_3SiH** (wt%)	**Temperature** (°C)	**Time** (h)	**10G** (wt%)	**10S** (wt%)
1[a]	50	273	25	72	-	-
2[b]	50	273	70	16	36	55
3[b]	25	273	70	16	13	9
4[b]	25	300	90	24	30	26
5[b]	20	300	70	48	24	17
6[b]	20	300	70	36	22	61
7 [a]	10	300	70	48	-	-

[a] Detection of other unidentified volatile products. [b] No other major volatile products were detected.

Scheme 5: GC-MS chromatograms of the depolymerization residues of black poplar lignin



Optimized conditions for the depolymerization of black poplar lignin: 20 wt% of [**1**][B(C_6F_5)$_4$], 300 wt% of Et_3SiH, 70°C, 48 h, solvent = C_6H_5Cl. The peak at 10 mn is not attributed.

V.e) Depolymerization of hardwood lignins

Equation 17

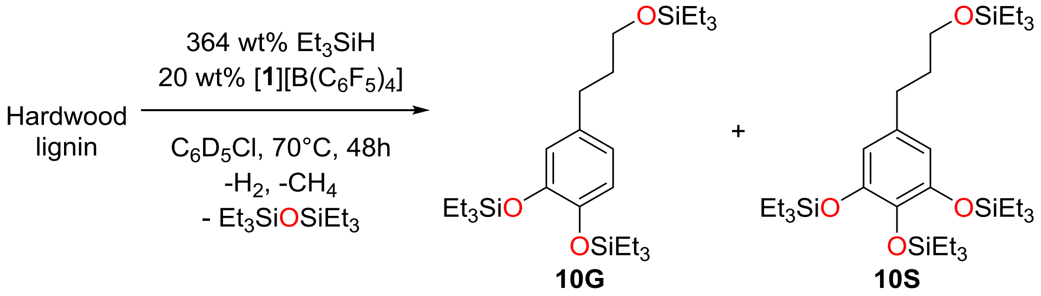
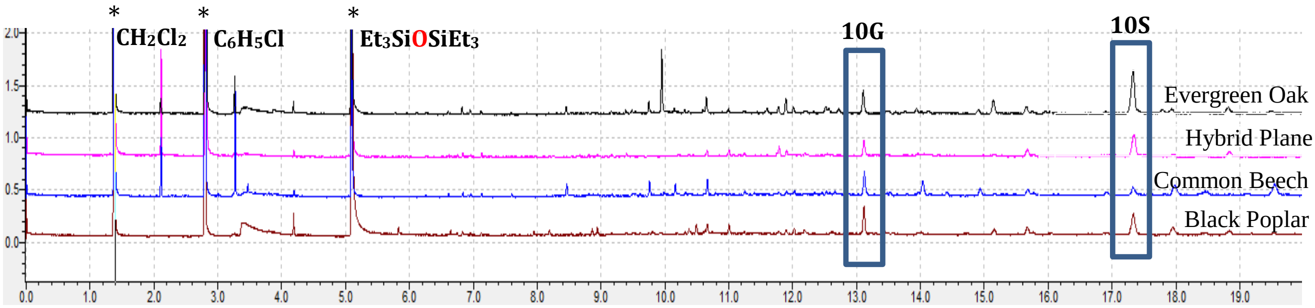


Table 4: Results Summary of hardwood lignin depolymerization

Hardwood Lignin	**Et_3SiH** (wt%)	**Time** (h)	**10G** (wt%)	**10S** (wt%)	**Yield**[c]
Evergreen Oak[b]	364	36	32	130	58 %
Hydrid Plane[a]	364	48	36	94	47 %
Common Beech[a]	364	48	42	83	46 %
Black Poplar[b]	364	36	20	80	36 %

[a] Detection of other unidentified volatile products. [b] No other major volatile products were detected. [c] Calculation of the yield is based on the **10G** and **10S** yields (see assumptions in section VII.b)

Scheme 6: GC-MS chromatogram of the depolymerization of hardwood lignin



VI) Characterizations of softwood and hardwood lignins.

Elemental analysis and SEC analyses of lignin have been previously reported in the following publication: E. Feghali, G. Carrot, P. Thuéry, C. Genre, T. Cantat, *Energy Environ. Sci.*, **2015**, 8, 2734.[7a]

VI.a) Elemental analyses

Table 5: Elemental analyses of extracted lignin samples and proposed chemical formulas

Species	C(%)	H(%)	O(%)	S(%)	H/C	O/C	Proposed chemical formula (in C10)	Proposed chemical formula (in C11)
Industrial pine	62.45	5.86	31.69	0.00	1.1	0.4	**C**10.00**H**11.26**O**3.81	**C**11.00**H**12.39**O**4.18
Parasol pine	61.97	5.94	32.09	0.00	1.2	0.4	**C**10.00**H**11.50**O**3.88	**C**11.00**H**12.65**O**4.27
Norway spruce	61.47	5.67	32.86	0.00	1.1	0.4	**C**10.00**H**11.07**O**4.01	**C**11.00**H**12.18**O**4.41
Hybrid plane	59.42	5.69	34.89	0.00	1.1	0.4	**C**10.00**H**11.49**O**4.40	**C**11.00**H**12.64**O**4.84
Evergreen oak	58.31	5.62	35.66	0.00	1.2	0.5	**C**10.00**H**11.56**O**4.59	**C**11.00**H**12.72**O**5.05

With the approximation that softwood lignins are exclusively composed of **G** residues, the general theoretical formula of the lignin polymer would be $[C_{10}H_{12}O_4]_n$ (Mw = 196.20 g/mol). (**G** residues represent about 90% of the of the total residues)[8]

With the approximation that hardwood lignins are exclusively composed of **S** residues, the general formula of the lignin polymer would be $[C_{11}H_{14}O_5]_n$ (Mw = 226.23 g/mol).

VI.b) Size Exclusion Chromatography (SEC)

Table 6: Summary of the SEC analysis results

Sample	**Extraction method**	**M_n ($g.mol^{-1}$)**	**M_w ($g.mol^{-1}$)**	**M_w/M_n**
Industrial pine	Formacell	1099	1829	1.66
Parasol pine	Formacell	952	1709	1.79
Evergreen oak	Formacell	952	1657	1.74

According to the SEC analyses, formation of reduced monomers is not observed. (Cf reference 7a)

VI.c) 2D NMR spectroscopy

HSQC NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. The central DMSO solvent peak was used as internal reference (δ_C 39.5, δ_H 2.49 ppm). The ^{13}C–^{1}H correlation experiment was an HSQC sequence started with the Bruker standard pulse sequence ‘hsqcetgpsi2’ (phase-sensitive gradient-edited-2D HSQC). HSQC experiments were performed at 10°C using the following parameters: acquired from 12 to -1 ppm in F2 (1H), 200 to 0 ppm in F1 (13C). The semi quantitative (Relative Quantitative Method) 2D-HSQC spectra were performed in accordance with the original reference as reported before.[9] Data analysis was performed using MestReNova software (version 6.0.2-5475) and TopSpin 3.5. The 2D HSQC NMR correlations were in agreement with those described in the literature for organosolv lignin.[10]

NB: The abundances of different linkages were estimated from the $C_\alpha{-}H_\alpha$ correlations in the following region spectra (side chain region): 2.5-6 ppm in F2 (^{1}H) and 40-100 ppm in F1 (^{13}C). In the aromatic region, $C_2{-}H_2$, $C_6{-}H_6$ correlations from **G**, and **S** lignin units were used to estimate their relative abundances in hardwood lignin as previously described.[9a]

VI.c.1) 2D NMR HSQC spectra of lignins

Figure 1: Partial 2D HSQC NMR spectra of Norway spruce lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

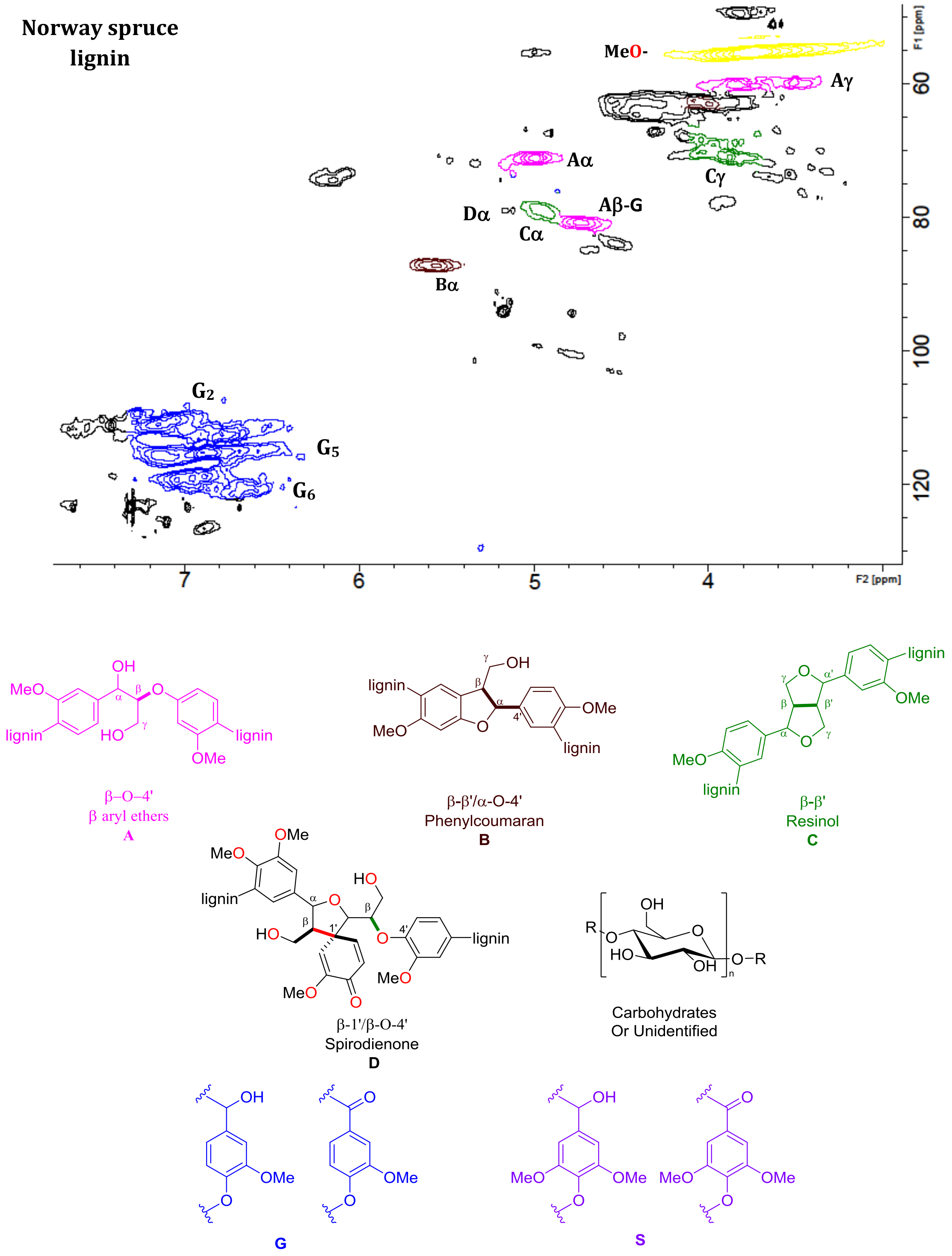


Figure 2: Partial 2D HSQC NMR spectra of pacific red cedar lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

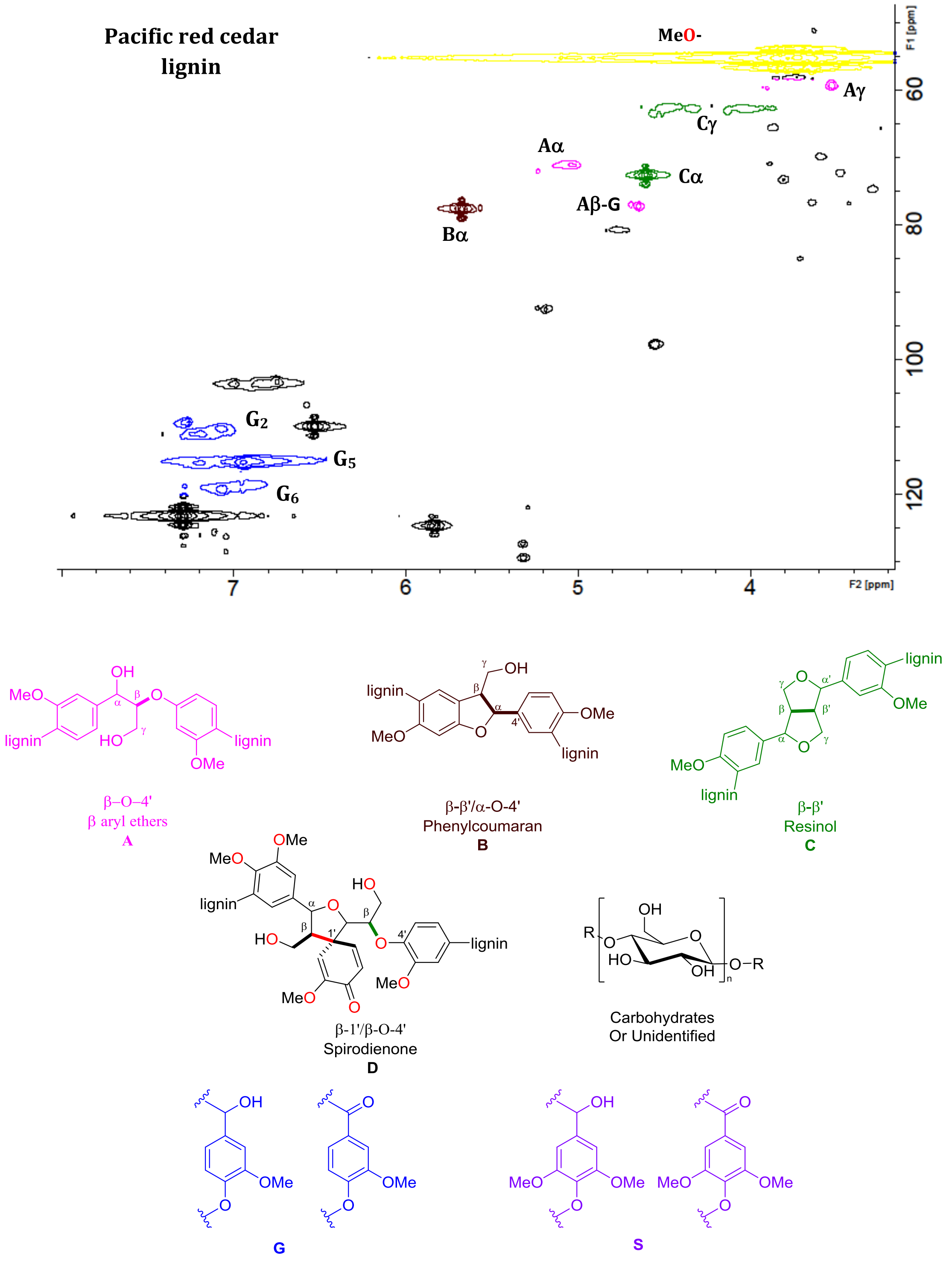


Figure 3: Partial 2D HSQC NMR spectra of Lebanese cedar lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

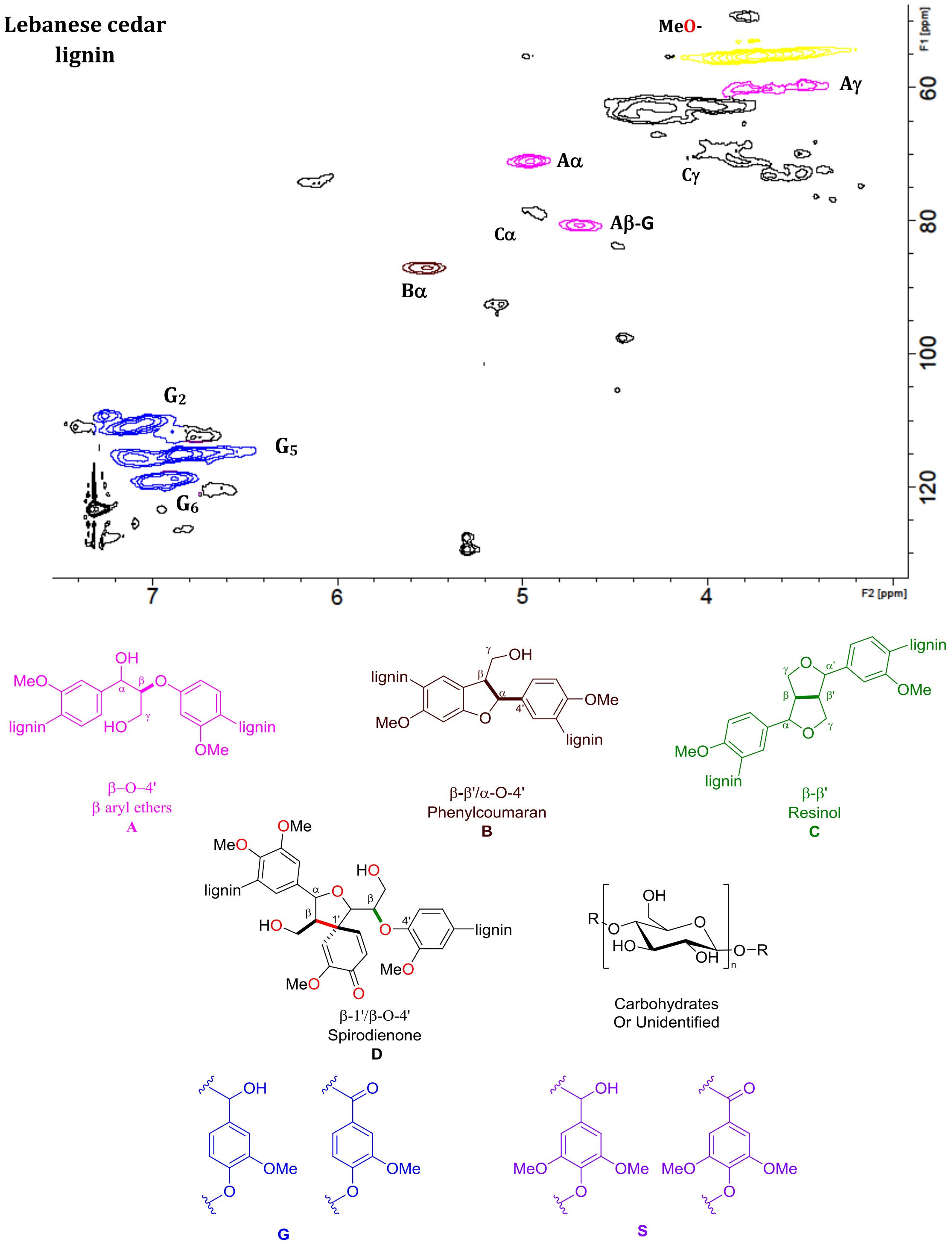


Figure 4: Partial 2D HSQC NMR spectra of industrial pine lignin extracted with the Formacell process (in 4:1 DMSO-d$_6$/pyridine-d$_5$).

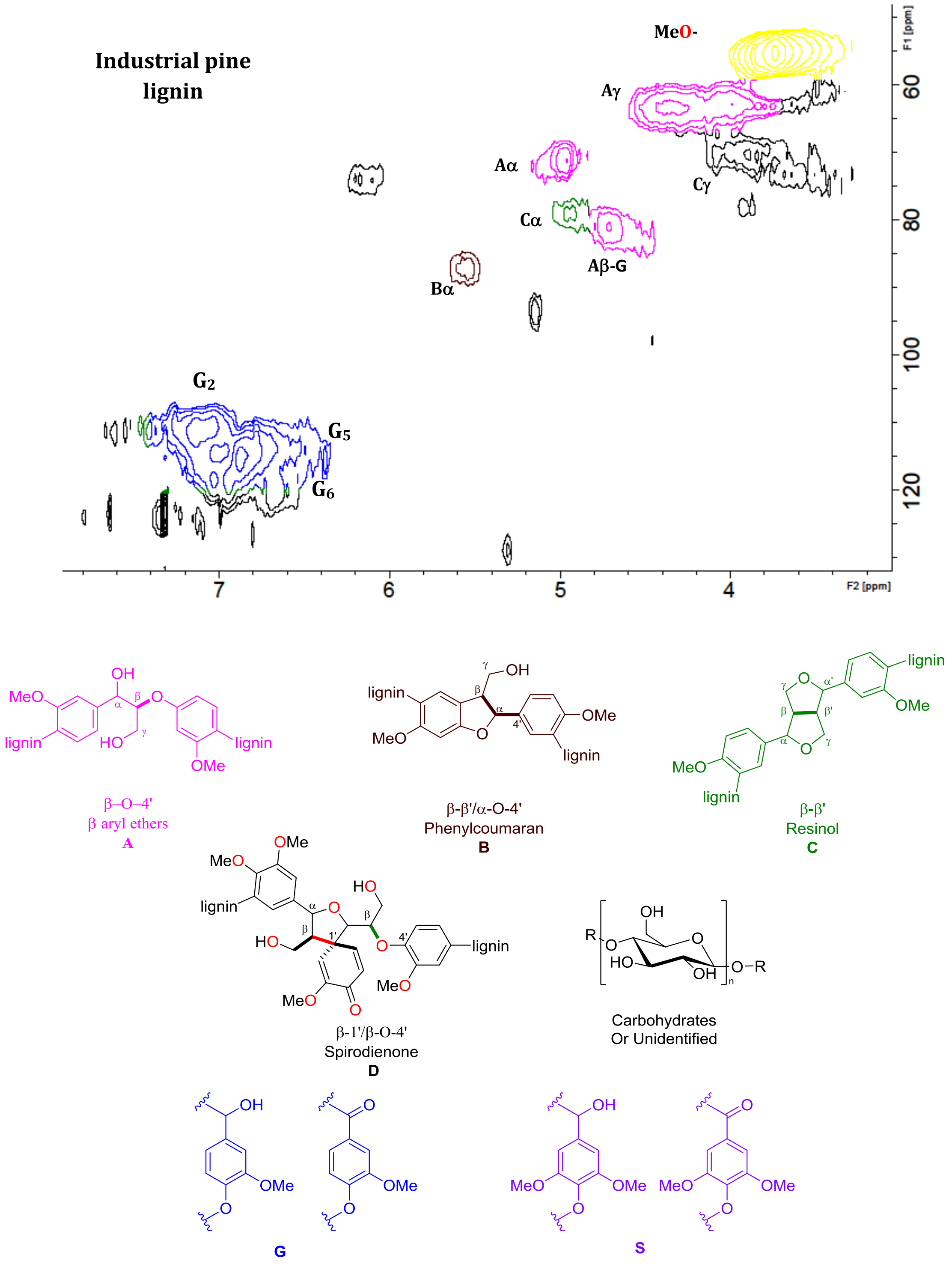


Figure 5: Partial 2D HSQC NMR spectra of common beech lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

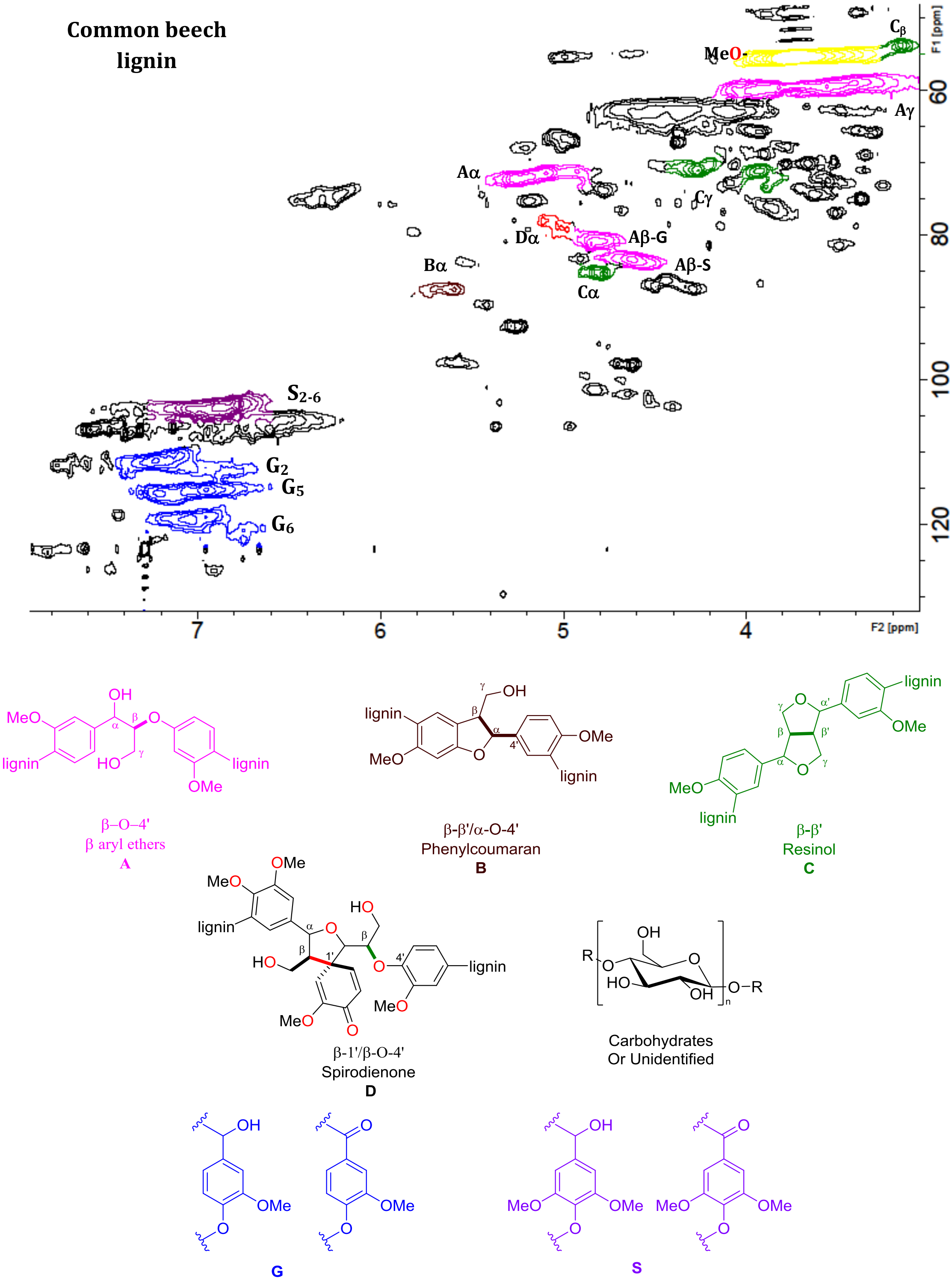


Figure 6: Partial 2D HSQC NMR spectra of black poplar lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

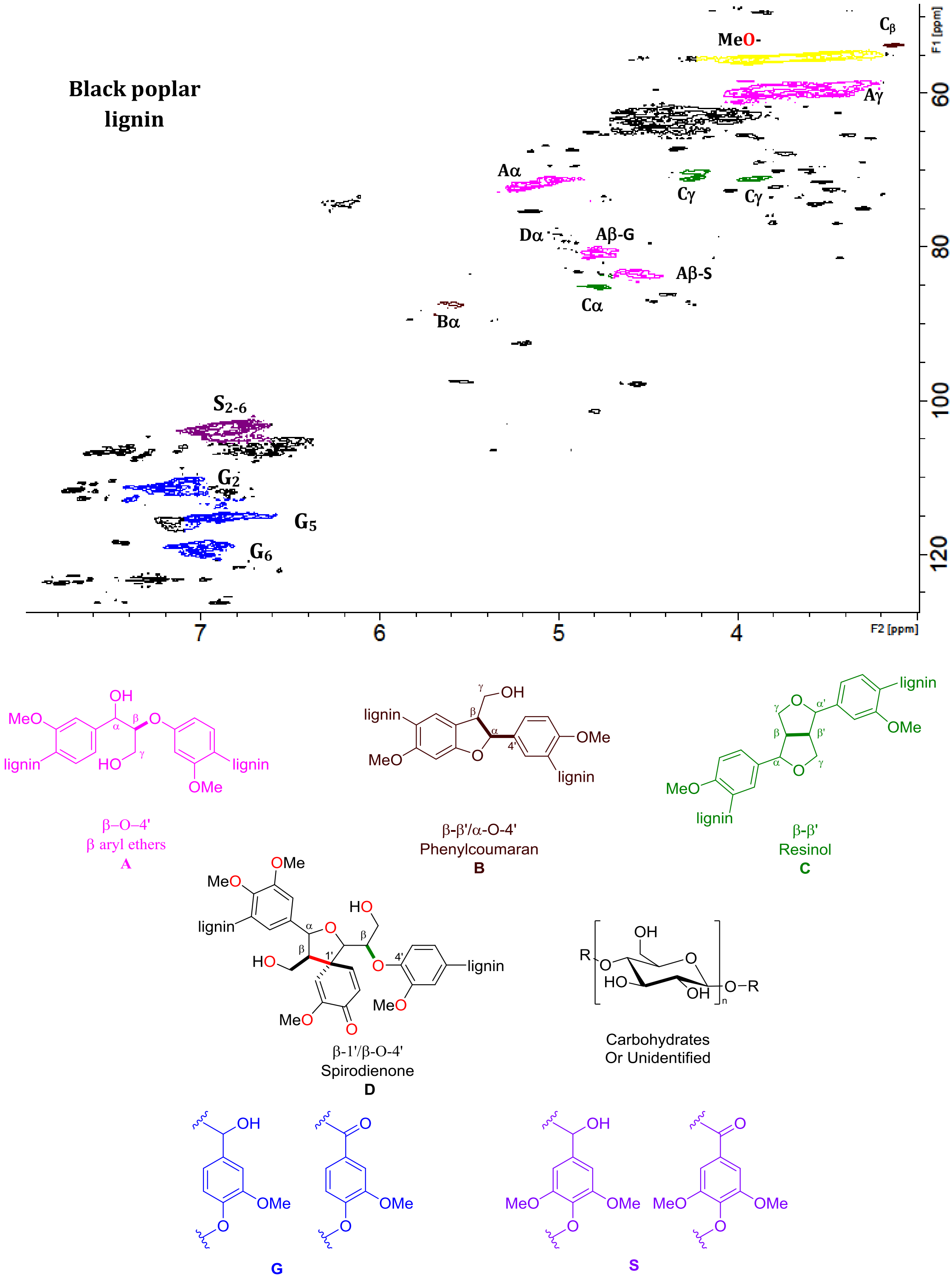


Figure 7: Partial 2D HSQC NMR spectra of evergreen oak extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5)

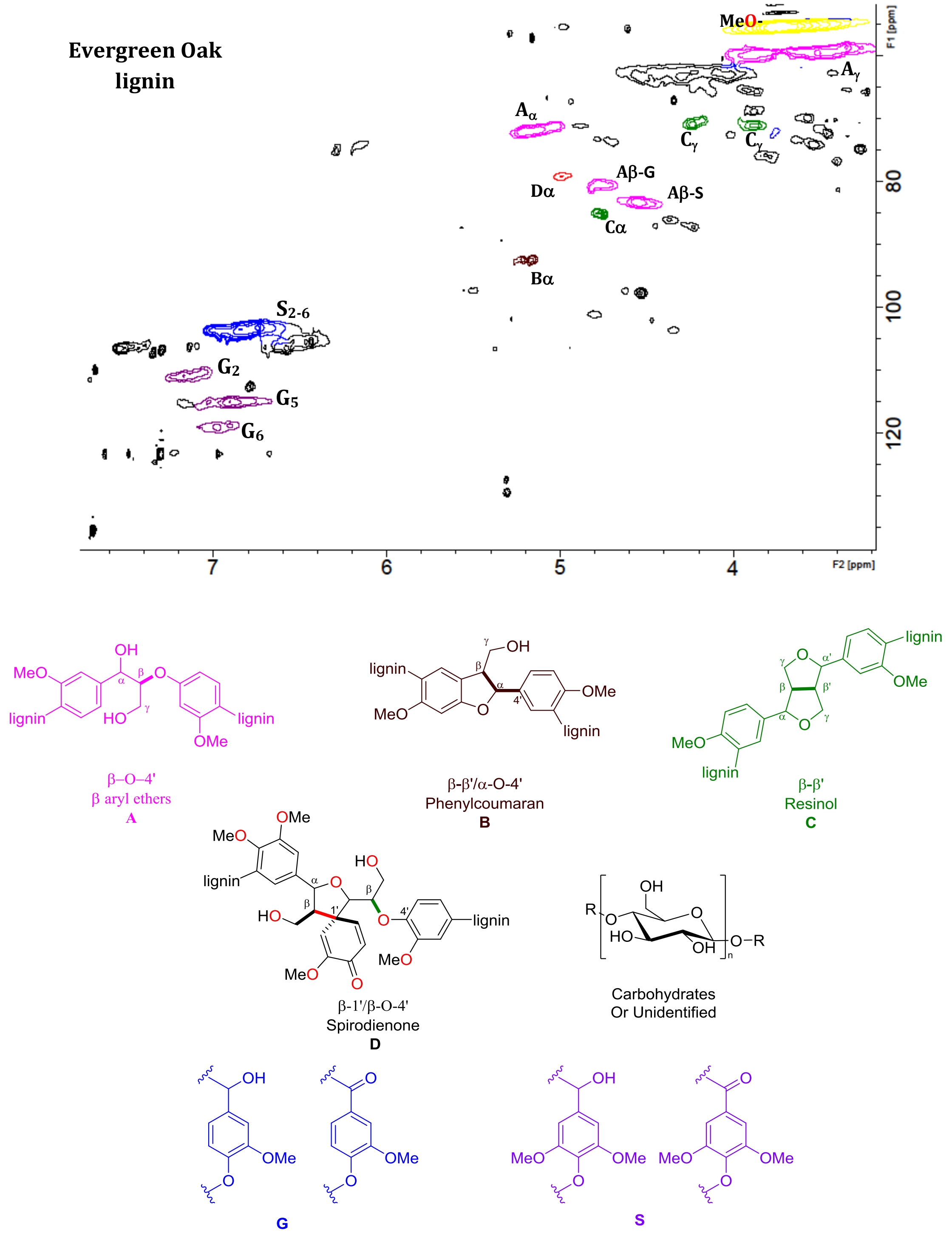
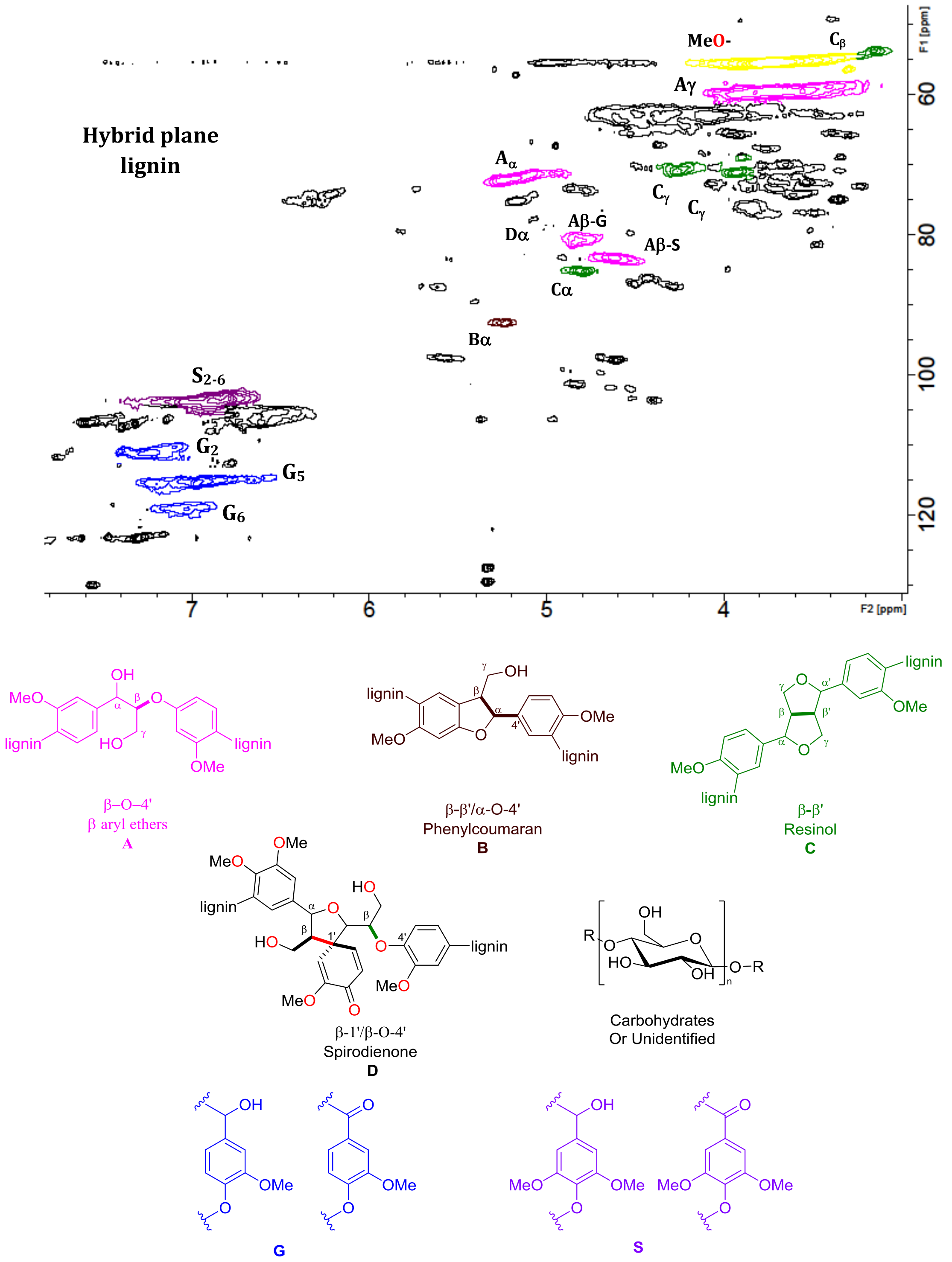


Figure 8: Partial 2D HSQC NMR spectra of hybrid plane extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).



VI.c.2) 2D NMR HSQC of lignins: examples

Figure 9: Quantitative integration of partial 2D HSQC NMR spectra of Pacific red cedar lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

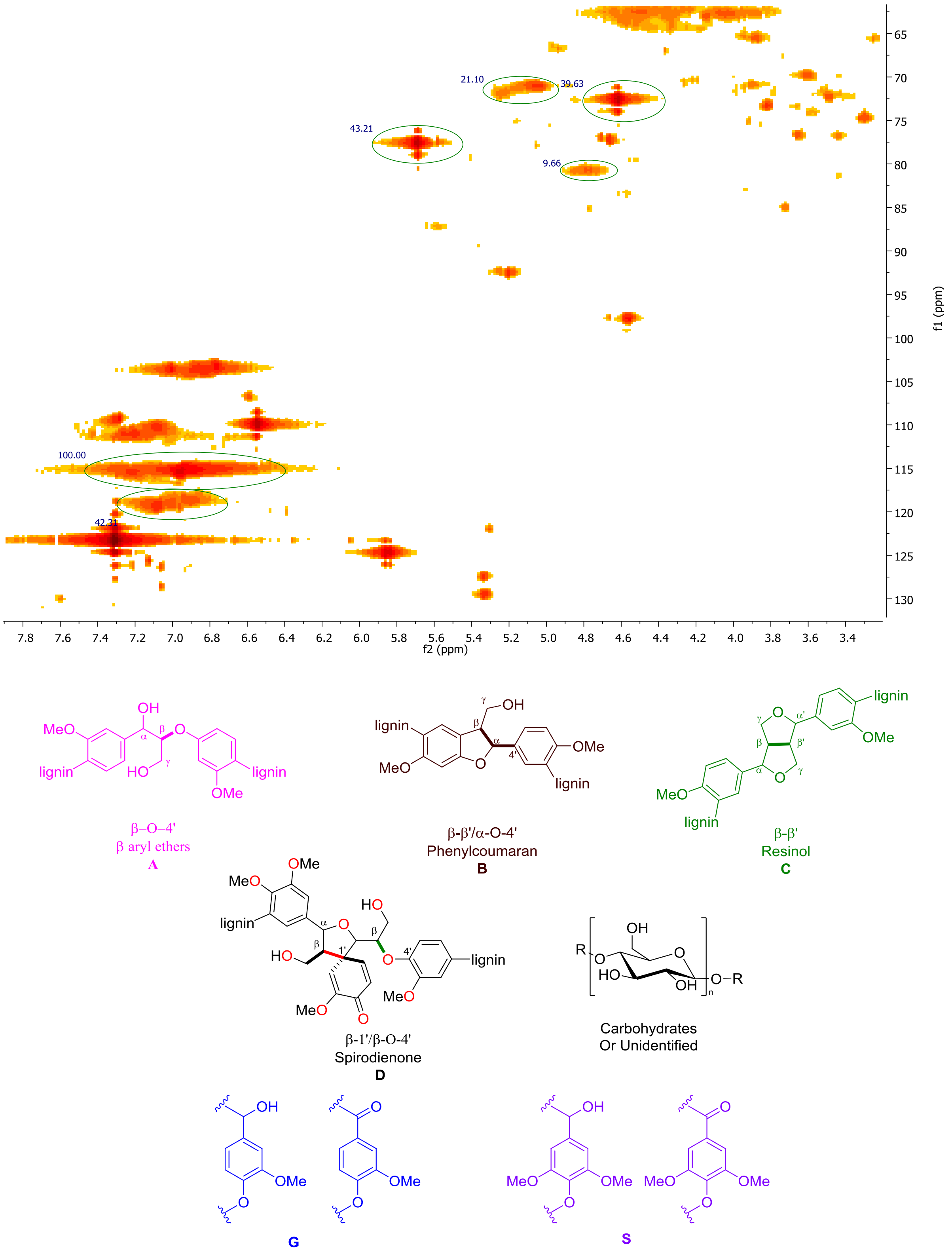


Figure 10: Quantitative integration of partial 2D HSQC NMR spectra of black poplar lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

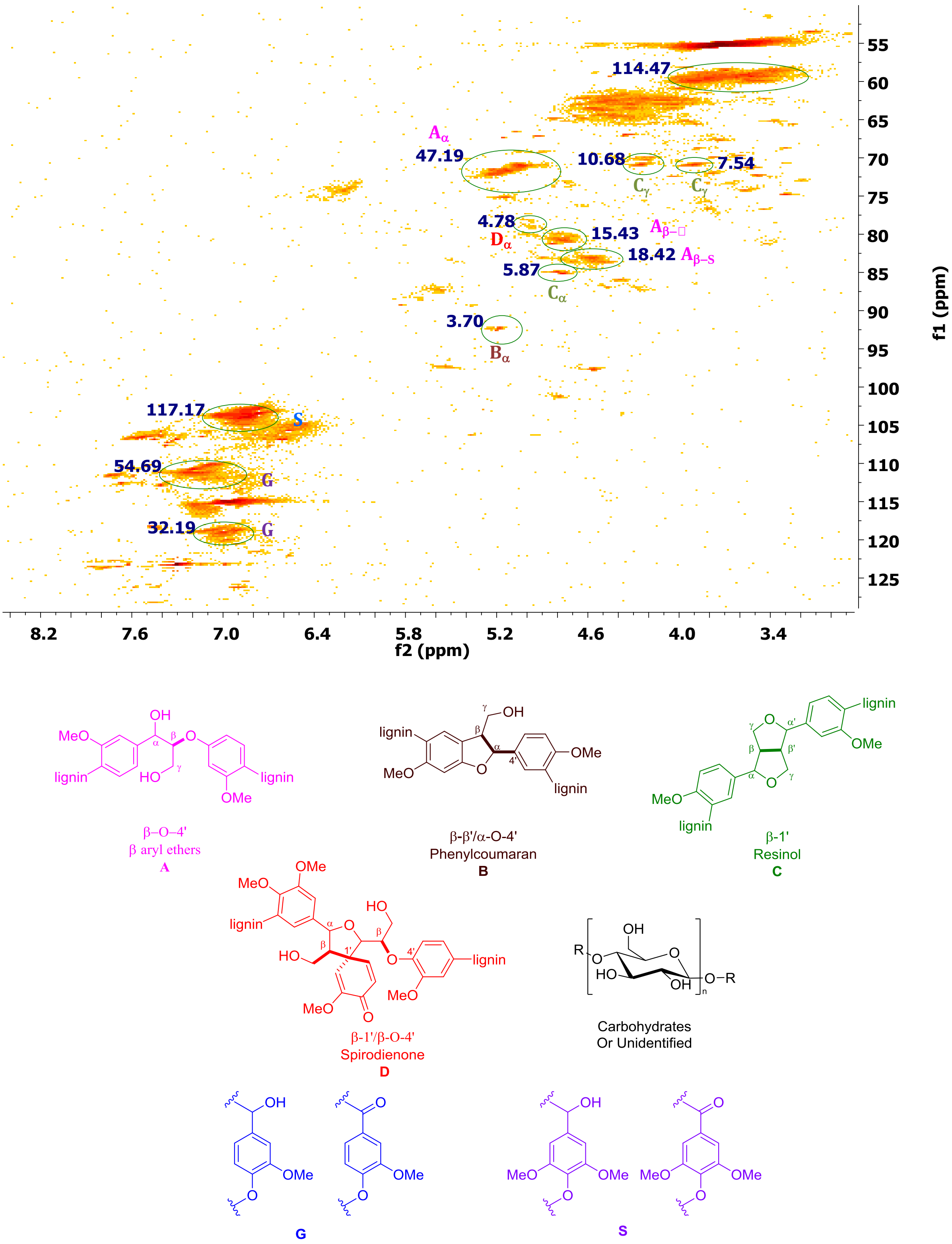


Figure 11: Quantitative integration of partial 2D HSQC NMR spectra of hybrid plane lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

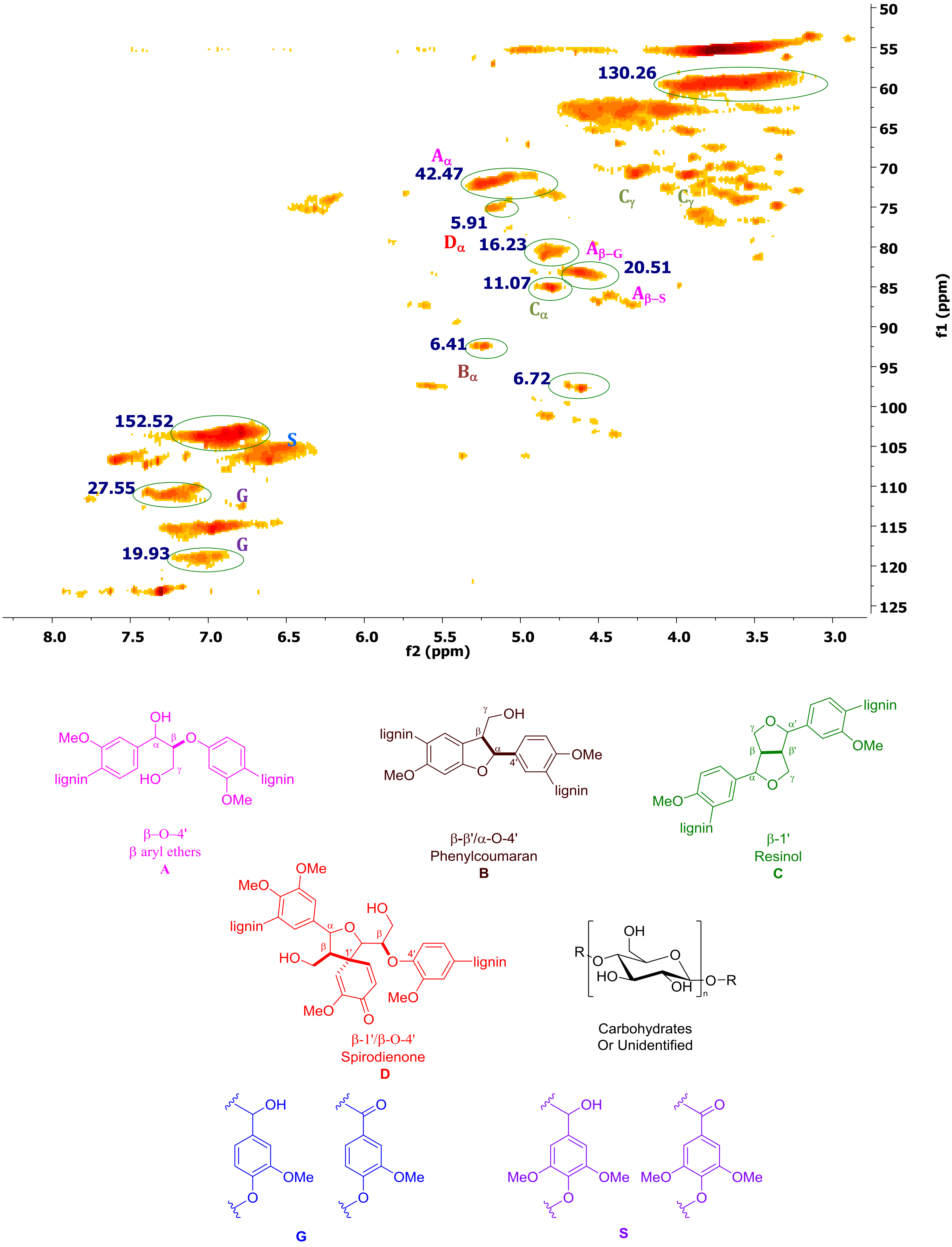


Figure 12: Integration of partial 2D HSQC NMR spectra of evergreen oak lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).

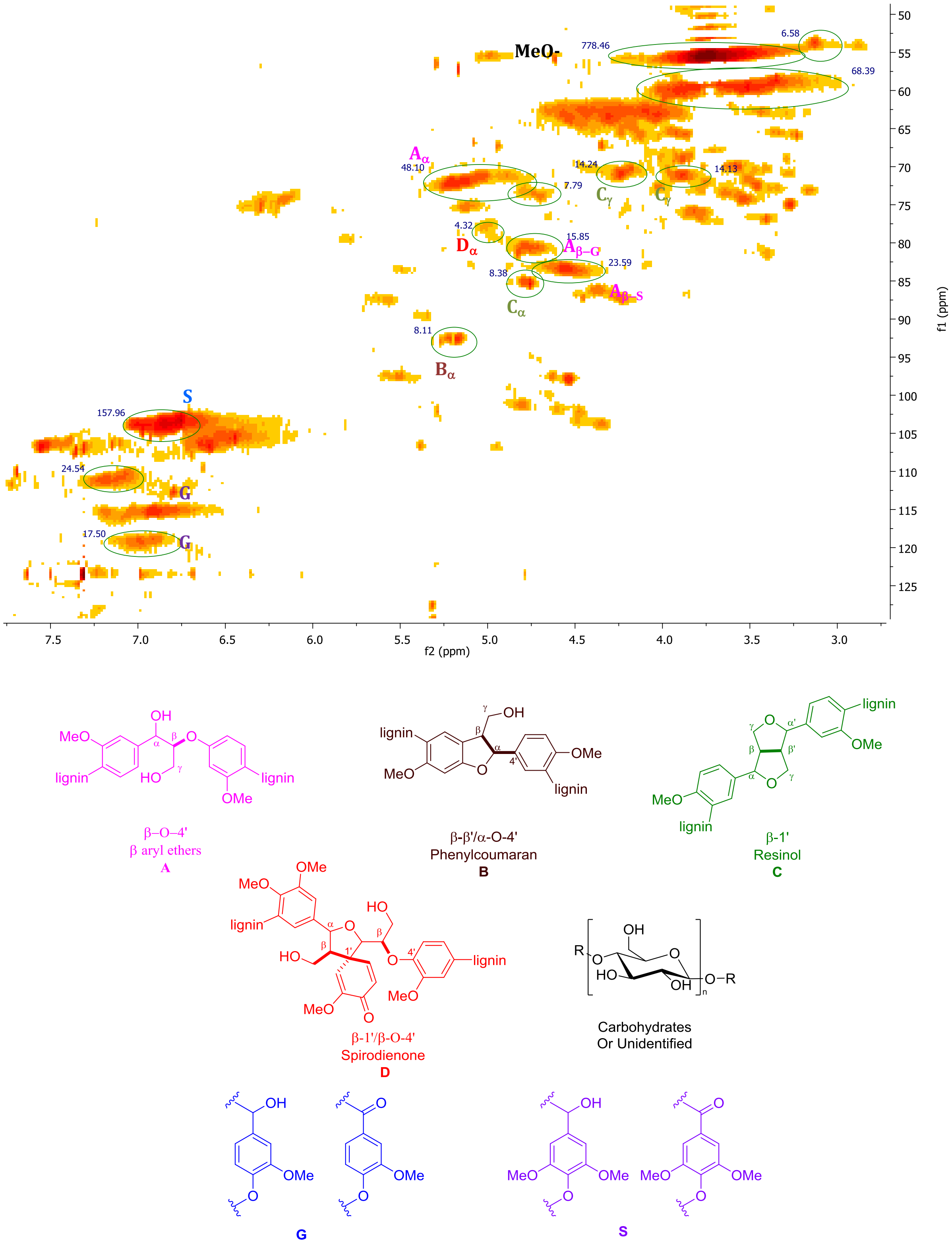
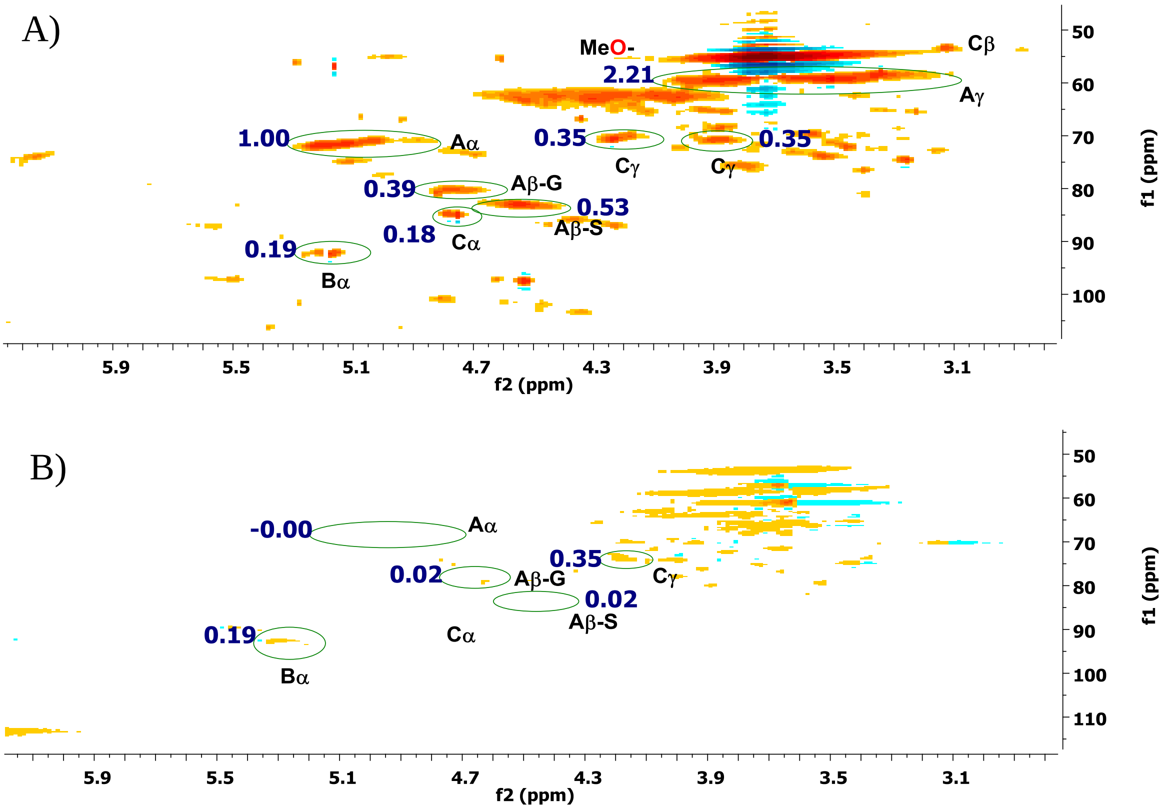
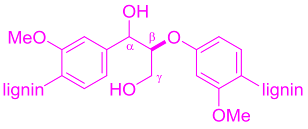


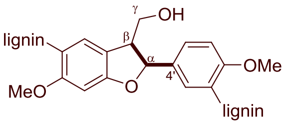
Figure 13: Quantitative integration of partial 2D HSQC NMR spectra of :

A) Evergreen oak lignin extracted with the Formacell process (in 4:1 DMSO-d_6/pyridine-d_5).
B) Crude of the depolymerization reaction of evergreen oak lignin in C_6H_5Cl/C_6D_6

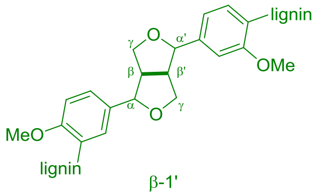




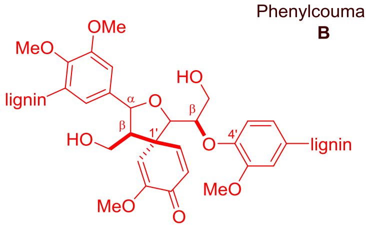
β–O–4'
β aryl ethers
A



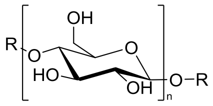
β-β'/α-O-4'
Phenylcoumaran
B



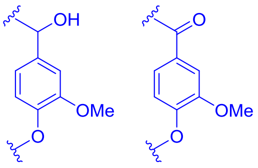
β-1'
Resinol
C



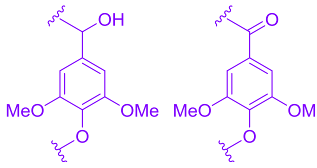
β-1'/β-O-4'
Spirodienone
D



Carbohydrates
Or Unidentified



G



S

VI.c.3) Summary of 2D HSQC NMR informations

The abundances of different linkages were estimated from the integration of $C_\alpha{-}H_\alpha$ correlations in the side chain region: 2.5-6 ppm in F2 (^1H) and 40-100 ppm in F1 (^{13}C). In the aromatic region, $C_2{-}H_2$, $C_6{-}H_6$ correlations from **G**, and **S** lignin units were used to estimate their relative abundances in hardwood lignin as previously described.[9a]

β-O-4 linkages which will be used further have been estimated with two classical approaches:

Approach 1: The integration of Cα-Hα correlation of each linkage was calibrated with respect to the integration of the C_2-H_2 and C_6-H_6 correlations of the G and S aromatic units. The linkages are expressed per 100 aromatics.

Approach 1: The integration of C_α-H_α correlation of each linkage was calibrated with respect to the integration of the C_2-H_2 and C_6-H_6 correlations of the G and S aromatic units. The linkages are expressed per 100 aromatics. (see figures 9-12)

Approach 2: The amount of each lignin linkage is estimated relatively to the total amount of interunit linkages (in the side chain region). The sum of the integrations of C_α-H_α correlations of each linkage (A, B, C and D) is arbitrarily calibrated to 100, *e.g.* A + B + C + D = 100.

For example, $A\% = \frac{A}{\mathrm{A+B+C+D}}$

Table 7: Summary of the 2D HSQC NMR results of the content of main linkages in lignins expressed per 100 aromatics (and expressed as Percentage of Total Side Chains.)

	β-aryl-ether units (β-O-4′, **A**)	Phenylcoumaran structures (β-5′,**B**)	Resinol structures (β-β′, **C**)	Spirodienone (β-1′, **D**)	**S/G** Ratio
Softwood lignins					
Industrial Pine	35.1 (63 %)[a]	13.7 (25 %)	6.9 (12 %)	-	-
Norway Spruce	30.2 (46 %)	19.7 (30 %)	15.7 (24 %)	-	-
Lebanese Cedar	38.9 (59 %)	20.6 (31 %)	6.7 (10 %)	-	-
Pacific Red Cedar	21.1 (20 %)	43.2 (41 %)	39.6 (39 %)	-	-
Hardwood lignins					
Evergreen Oak	48.10 (70 %)	8.11 (12 %)	8.4 (12 %)	4.3 (6 %)	75/25
Black Poplar	47.2 (76 %)	3.70 (6 %)	5.9 (10 %)	4.8-(8 %)	69/31
Hybrid Plane	42.5 (65 %)	6.4 (10 %)	11.1 (17 %)	5.6 (8 %)	68/32
Common Beech	43.7 (65 %)	6.0 (9.0 %)	12.2 (18 %)	5.23(8 %)	63/37

[a] in parentheses: percentage based on the total side chains linkages observed in HSQC (A + B + C + D = 100)

VII) Definition of the yield, theoretical yield and efficiency in the depolymerization of lignin

VII.a) Experimental yield

For a product X, the experimental yield $R(X)_{exp}$ (in wt%) is defined as the mass of isolated silylated product over the initial mass of lignin :

$$\boxed{\mathrm{R(X)exp} = \frac{\mathrm{m\ (silylated\ compound)}}{\mathrm{m(lignin)}} \times\ 100}$$

VII.b) Experimental molar yield

For a product X, the experimental molar yield $Rmol(X)_{exp}$ is expressed as the molar number of isolated silylated product over the molar number of the aromatics units in lignin :

$$\boxed{\mathrm{Rmol(X)exp} = \frac{\mathrm{n\ (silylated\ compound)}}{\mathrm{n(monomer\ in\ lignin)}} \times\ 100}$$

For example, if we consider that industrial pine lignin (IPL) is only composed of the G residues (Mw(G) = 196.2 g.mol^{-1}). For 100 mg of IPL, thus the molar number of monoaromatic units in lignin is:

$$\mathrm{n(IPLmonomer)} = 100.10^{-3}/196.2 = 0.51\ \mathrm{mmol.}$$

We recover 120 mg of **10G**, (Mw(**10G**) = 510.98):

$$\mathrm{n}(\mathbf{10G}) = 120.10^{-3}/510.98 = 0.23\ \mathrm{mmol.}$$

$$\mathrm{Rmol(X)exp} = \frac{\mathrm{n\ (10G)}}{\mathrm{n(IPLmonomer)}} \times\ 100 = \frac{0.23}{0.51} \times\ 100 = 46\ \%$$

VII.c) Theoretical yield

Calculation of the theoretical yield in monomeric aromatics and the efficiency of wood lignin depolymerization have been previously reported by our group.[7a] This calculation is based on a fine description of the considered lignin. Size exclusion chromatography, 2D NMR and elemental analysis were performed to characterize industrial pine and evergreen oak lignins. We have previously presented these characterizations.[7a] Here, we proposed a revised and more precise method for the calculation of the efficiency in hardwood lignin by considering the yields in both **G** and **S** aromatics.

NB: In the following sections, the percentage P of cleavable linkages in lignin (*i.e.* aryl-O-alkyl bonds) is approximated to the percentage of β-O-4 linkages determined by HSQC NMR.[12, 13]

The percentage of β-O-4 linkages estimated by the approach 1 (see VI.c.3) does not fit with the model for the calculation of the theoretical yield. We thus only considered the result from the approach 2 (See summary and discussions S55-56).

VII.c.1) Theoretical yield for softwood lignins

This statistical reasoning on the theoretical yield in monomeric aromatics products as well as determination of the efficiency are based on a fine description of the softwood lignin preparation[7a] and lie on some assumptions:

- We have shown that the degree of polymerization of lignin is very low when obtained by the Formacell organosolv process; a softwood lignin is thus considered as a linear polymer containing a unique oxidized **G** residue ($(MeO)_2PhC(O)CH_2CH_2OH$) (DP (degree of polymerization) = 5±1, M_w(**G**) = 196.2 g/mol). [7a]
- The percentages of cleavable linkages in softwood lignins strongly depend on the wood sources. However, softwood lignins classically contain 40-60% of cleavable linkages (aryl-O-alkyl bonds).[8-13] In the following demonstration, the percentage of C-O cleavable linkages, *eg* P = 60%, was that determined for industrial pine lignin from 2D NMR studies (see VI.c.2. 2D NMR spectra).

Considering that a lignin sample has a polymerization degree $N = 2$ (or contains 2 mono aromatic units), the maximum theoretical yield in monoaromatic, *eg* $\tau(N)_S$ (*S* for softwood), is $\tau(N = 2)_S = 0.6$. In a longer polymer, the condition for having mono-aromatic derivatives requires to have two consecutive cleavable linkages on an aromatic unit.

Thus, for an infinite chain $N = \infty$, $\tau(N = \infty)_S = 0.6^2 \times 100 = 36$ %. (36 % corresponding to the asymptote of the curve $\tau(N)_S = f(N)$.

For a finite lignin polymer involving N monolignols, 2 aromatic units are located in the chain-ends while (N–2) aromatic units are surrounded with either cleavable or non-cleavable linkages. 60 % of the chain-ends can thus yield a mono-aromatic product, while 36 % of the remaining (N–2) monolignols can afford mono-aromatics. The maximum theoretical yield in mono aromatic compounds can be expressed as below for softwood lignin:

$$\boxed{\tau(N)_S = \frac{(\mathrm{N}-2)\ \mathrm{x}\ 0.6^2+2\ \mathrm{x}\ 0.6}{\mathrm{N}} \times\ 100}$$

Considering that softwood lignin involves a single mono-aromatic unit, the degree of polymerization (DP) of each lignin source has been evaluated (DP = $\frac{Mn}{Mw}$, where M_n = molar mass of the polymer and M_w = molar mass of the constituting monolignol). As mentioned above, the DP for a lignin polymer is DP = 5. Since the values of τ(*N*) are quite similar (τ(*N*) = 0.44 to 0.48) for N varying between 4 to 6, an average value of τ(*N*) = 5 was taken regardless of the softwood lignin source.

$$\tau(4) = 48\ \% \qquad \tau(5) = 46\ \% \qquad \tau(6) = 44\ \%$$

$$<\tau(5\pm1)> = 46\ \%$$

Using the molar mass of the theoretical general formulas of lignin oligomers[7] ($(196.2)_N$ g/mol) for softwood, the maximum theoretical yield R(X) (in wt%) of a mono-aromatic product X versus the initial mass of lignin would be:

$$\boxed{\mathrm{R}(X) = \frac{\mathrm{m\ (theor\ in\ silylated\ compound)}}{\mathrm{m(lignin)}} \times\ 100 = \frac{\tau(\mathrm{N})_S\ \mathrm{x\ Mw(X)}}{\mathrm{Mw(monolignol)}} \times\ 100}$$

For the synthesis of **10G** from industrial pine:

$$R(\mathbf{10G}) = \frac{0.46\ \mathrm{x}\ 510.98}{196.2} \times\ 100 = 119.8\ wt\%\ /\ wood\ lignin\ weight$$

The wt% maximum theoretical yields R(**10G**) have been calculated for all the lignin samples of this study by taking into account their respective percentages of cleavable linkages P determined by HSQC NMR (P is approximated to the percentage of β-O-4 linkages in lignin).

The results are summarized up in table 8.

Table 8: Calculation of the wt% maximum theoretical yield R(X) for the softwood lignins with β-O-4 expressed as percentage per 100 aromatics.

Lignin	P (% of cleavable linkages) β-O-4 per 100 aromatics	τ(5) (N = 5)	Theoretical yield R(**10G**)
Industrial Pine	35 (60 %)[a]	21 % (46 %)[b]	55 wt% (120 wt%)
Norway Spruce	30 (50 %)[a]	17 % (35 %)	45 wt% (91 wt%)
Lebanese Cedar	39 (60 %)[a]	25 % (46 %)	64 wt% (120 wt%)
Pacific Red Cedar	20 (20 %)[a]	10 % (10 %)	27 wt% (27 wt%)

[a]The values within parentheses represent the percentage of linkage based on the total linkages (β-O-4′ + β-β′ + β-5′ + β-1′ = 100) [b]The values in parentheses represent the calculation of the theoretical yield based on the relative percentage of β-O-4 in lignin (β-O-4′ + β-β′ + β-5′ + β-1′ = 100)

VII.c.2) Theoretical yield for hardwood lignins

This statistical reasoning on the theoretical yield in monomeric aromatics products as well as determination of the efficiency are based on a fine description (SEC, elementary analyses and HSQC NMR data) of the hardwood lignin preparation and lie on the following assumptions:

- The degree of lignin polymerization is known to be very low when obtained by the Formacell organosolv process (Cf. section VI.a and VI.b); hardwood lignin is thus considered as a linear polymer containing both **G** and **S** ($((MeO)_3PhC(O)CH_2CH_2OH)$) units (DP = 4, M_w(**S**) = 226.2 g/mol, M_w(**G**) = 196.2 g/mol).
- The S/G ratio varies from each essence of hardwood lignin. Classically, the S/G ratio is between 1/1 to 4/1.[11] In this study, the mean S/G ratio in hardwood lignins is approximated to 7/3 based on HSQC NMR integration (the S/G ratio are in the range 65/35 to 75/25).
- Hardwood lignins contain 60-62% of β-O-4 and 3-11% of α-O-4 linkages.[8] The percentages of cleavable bonds in hardwood lignins strongly depend on the wood sources. In the following demonstration, the percentage of C-O cleavable linkages, *eg* P = 70%, was determined for lignin from 2D HSQC NMR studies (see VI.c.2. 2D NMR spectra)

Considering that a lignin sample has a polymerization degree $N = 2$, the maximum theoretical yield $\tau(N)_H$ (H for hardwood) is $\tau(N = 2)_H = 70\%$. In a longer polymer, the condition for having mono-aromatic derivatives requires to have two consecutives cleavable linkages on an aromatic unit.

Thus, for an infinite chain $N = \infty$, $\tau(N = \infty)_H = 0.7^2 \times 100\ \% = 49\ \%$. (49 % corresponding to the asymptote of the curve $\tau(N)_H = f(N)_H$.)

For a finite lignin polymer involving with N monolignols, 2 aromatic units are located in the chain-ends while (N–2) aromatic units are surrounded with either cleavable or non-cleavable linkages. 70 % of the chain-ends can thus yield a mono-aromatic product, while $P^2 = (0.7)^2 =$ 49 % of the remaining (N–2) monolignols can afford mono-aromatics. The theoretical yield $\tau(N)_H$ in mono aromatic compounds can be expressed as below for a hardwood lignin:

$$\boxed{\tau(N)_H = \frac{(\mathrm{N}-2)\ \mathrm{x}\ 0.7^2 + 2\ \mathrm{x}\ 0.7}{\mathrm{N}} \times\ 100}$$

Considering that lignin involves 30 % of mono-aromatic units **G** and 70 % of mono-aromatic units **S**, the degree of polymerization (DP) of each lignin source has been evaluated (DP = $\frac{Mn}{0.3 \times \mathrm{Mw}(\text{monolignol } \mathbf{G}) + 0.7 \times \mathrm{Mw}(\text{monolignol } \mathbf{S})}$), where M_n = mean molecular weight of the polymer (determined by SEC measurement) and M_w = molar mass of the considered monolignol). As mentioned above, the DP for a hardwood Formacell lignin polymer is DP = 4.[7]

$$\tau(4)_H = 60\ \%$$

Using the molar mass of the theoretical general formulas of lignin oligomers[7a] (theoretical general formulas: $(G_{0.3}\text{-}S_{0.7})_N$, Mw = N x [0.3 x 196.2 + 0.7 x 226.2] g/mol) the wt% maximum theoretical yield R(X) in a mono-aromatic product X/lignin weight would be:

$$\mathrm{R}(X) = \frac{\mathrm{m\ (theor\ in\ silylated\ compound\ X)}}{\mathrm{m(lignin)}}$$

$$= \frac{\tau(\mathrm{N})_H \times \mathrm{y} \times \mathrm{Mw(X)}}{0.3 \times \mathrm{Mw}(\text{monolignol } \mathbf{G}) + 0.7 \times \mathrm{Mw}(\text{monolignol } \mathbf{S})} \times 100$$

where y is the rate (in %) of the considered monoaromatic unit in lignin.

For the synthesis of **10G** and **10S** from hardwood:

$$R(\mathbf{10}\boldsymbol{G}) = \frac{0.6 \times 0.3 \times 510.98}{(0.3 \times 196.2) + (0.7 \times 226.2)} \times 100 = 42{,}3\ wt\%\ /\ wood\ lignin\ weight$$

$$R(\mathbf{10}\boldsymbol{S}) = \frac{0.6 \times 0.7 \times 640.23}{(0.3 \times 196.2) + (0.7 \times 226.2)} \times 100 = 123.8\ wt\%\ /\ wood\ lignin\ weight$$

Table 9: Calculation of the wt% maximum theoretical yield R(X) for the hardwood lignins with β-O-4 expressed as percentage per 100 aromatics.

Lignin	P (% of cleavable linkages)	τ(4) (N = 4)	Theoretical yield R(**10G**)
Evergreen Oak	48.1 [a] (70 %)[b]	36 % [a] (60 %) [b]	25 / 74 wt% [a] (42 / 124 wt%) [b]
Black Poplar	47.2 (70 %)	34 % (60 %)	24 / 70 wt% (42 / 124 wt%)
Hybrid Plane	42.5 (70 %)	30 % (60 %)	21 / 61 wt% (42 / 124 wt%)
Common Beech	43.7 (70 %)	32 % (60 %)	23 / 66 wt% (42 / 124 wt%)

[a] Values obtained from approach 1; [b] The values in parentheses obtained from approach 2 (see VI.c.3)

VII.d) Efficiency of lignin depolymerization

The efficiency of lignin depolymerization (E) is defined as being the ratio of the experimental mass yield ($R(X)_{exp} = \frac{\text{wt of product X}}{\text{wt of lignin}}$) of a mono-aromatic product X over the theoretic mass yield $R(X)_{theo}$ in mono-aromatic X .

$$\boxed{E = \frac{\mathrm{R(X)exp}}{\mathrm{R(X)}theo} \times 100}$$

In the case of hardwood, the efficiency is the sum of the efficiencies of **10G** and **10S** weighted by their occurrences in native lignin which are 0.3 and 0.7, respectively:

$$\boxed{E = 0.3 \times \frac{\mathrm{R}(\mathbf{10G})\mathrm{exp}}{\mathrm{R}(\mathbf{10G})theo} + 0.7 \times \frac{\mathrm{R}(\mathbf{10S})\mathrm{exp}}{\mathrm{R}(\mathbf{10S})theo}}$$

The above formula is obtained as followed:

n = molar number (mol)

n(lignol) x $\tau(\mathrm{N})_H$ = theoretical number of lignol (maximum available)

n(lignol) = m(lignin)/average M_w (monolignol)

M_w (x) = molar weight (g.mol^{-1}) of compound X

G and **S** = monolignol units

m(X)= weight in compound X(g)

The molar efficiency is:

$$E = \frac{n(\mathbf{10G})exp + n(\mathbf{10S})exp}{n(lignol) \times \tau(N)}$$

$$E = \frac{m(\mathbf{10G})exp/Mw(\mathbf{10G})}{\tau(N) \times m(lignin)/Mw(lignol)} + \frac{m(\mathbf{10S})exp/Mw(\mathbf{10S})}{\tau(N) \times m(lignol)/Mw(lignol)}$$

$$E = \frac{m(\mathbf{10}\boldsymbol{G})exp \times Mw(lignol)}{\tau(N) \times m(lignin) \times Mw(\mathbf{10}\boldsymbol{G})} + \frac{m(\mathbf{10}\boldsymbol{S})exp \times Mw(lignol)}{\tau(N) \times m(lignin) \times Mw(\mathbf{10}\boldsymbol{S})}$$

As we know:

$$\mathrm{R}(\mathbf{10G})\mathrm{exp} = \frac{m(\mathbf{10}\boldsymbol{G})exp}{m(lignin)} \qquad and \qquad \mathrm{R}(\mathbf{10S})\mathrm{exp} = \frac{m(\mathbf{10}\boldsymbol{S})exp}{m(lignin)}$$

So, the efficiency can be expressed,

$$E = R(\mathbf{10}\boldsymbol{G})exp \times \frac{Mw(lignin)}{\tau(N) \times Mw(\mathbf{10}\boldsymbol{G})} + R(\mathbf{10}\boldsymbol{S})exp \times \frac{Mw(lignin)}{\tau(N) \times Mw(\mathbf{10}\boldsymbol{S})}$$

$$E = R(\mathbf{10}\boldsymbol{G})exp \times \frac{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})}{\tau(N) \times M(\mathbf{10}\boldsymbol{G})} + R(\mathbf{10}\boldsymbol{S})exp \times \frac{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})}{\tau(N) \times M(\mathbf{10}\boldsymbol{S})}$$

And we know:

$$\mathrm{R}(\mathbf{10G}) = \frac{\tau(N) \times 0.3 \times M(\mathbf{10}\boldsymbol{G})}{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})} \qquad and \qquad \mathrm{R}(\mathbf{10S}) = \frac{\tau(N) \times 0.7 \times M(\mathbf{10}\boldsymbol{S})}{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})}$$

$$\frac{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})}{\tau(N) \times M(\mathbf{10}\boldsymbol{G})} = \frac{0.3}{\mathrm{R}(\mathbf{10G})} \qquad and \qquad \frac{0.3 \times \mathrm{Mw}(\mathbf{G}) + 0.7 \times \mathrm{Mw}(\mathbf{S})}{\tau(N) \times M(\mathbf{10}\boldsymbol{S})} = \frac{0.7}{\mathrm{R}(\mathbf{10}\boldsymbol{S})}$$

Then, the formula is:

$$\boxed{E = 0.3 \times \frac{\mathrm{R}(\mathbf{10G})\mathrm{exp}}{\mathrm{R}(\mathbf{10G})theo} + 0.7 \times \frac{\mathrm{R}(\mathbf{10S})\mathrm{exp}}{\mathrm{R}(\mathbf{10S})theo}}$$

Table 10: Experimental results and efficiency calculations for depolymerization of lignins

Species	Product	**wt% of silylated product/lignin weight**	
		R(10G) Experimental (wt%)	**R(10G)** Theoretical (wt%)
Softwood			
Industrial pine	**10G**	120	55 (120)[a]
Norway spruce	**10G**	81	45 (91)
Lebanese cedar	**10G**	69	64 (120)
Pacific cedar	**10G**	11	27 (27)
Hardwood			
Evergreen oak	**10G / 10S**	32 / 130	25 / 74 (42 / 124)[b]
Hydrid plane	**10G / 10S**	36 / 94	24 / 70 (42 / 124)
Common beech	**10G / 10S**	42 / 83	21 / 61 (42 / 124)
Black poplar	**10G / 10S**	20 / 80	23 / 66 (42 / 124)

[a] The values in parentheses represent calculations based on the relative percentage of β-O-4 in lignin (β-O-4′ + β-β′ + β-5′ + β-1′ = 100)

VII.e) Global efficiency extraction of lignin monomers from wood

Considering that the maximum theoretical yield of extracted lignin by the Formacell process is 25 wt% of the initial weight of wood [7a] (Weight of lignin on the initial weight of wood (%wt)), thus the efficiency of the extraction of industrial pine lignin is 8/25 = 32%. (8 wt% of lignin have been extracted from the wood see Table 11).

Considering that the yields of purification and hydrolysis of compounds **10G** are respectively 70 % and 84 %, then the global efficiency is evaluated to 18.8%.

The same approach is applied for evergreen oak lignin.

Table 11: Results and global efficiency calculations from wood

Species	Product	**wt% lignin extracted by the Formacell process/wood weight**			**wt% of silylated product/lignin weight**		
		Experimental (wt%)	**Theoretical** (wt%)	**Efficiency** (%)	**Experimental** (wt%)	**Theoretical** (wt%)	**Efficiency** (%)
Industrial pine	**10G**	8	25	32	120	120	100
Evergreen Oak	**10G/10S**	10	25	40	32 / 130	42 / 124	96

Species	Product	**wt% of silylated product after purification/lignin weight**			**wt% hydrolyzed product/lignin weight**		
		Experimental (wt%)	**Theoretical** (wt%)	**Efficiency** (%)	**Experimental** (wt%)	**Theoretical** (wt%)	**Efficiency** (%)
Industrial pine	**10G**	96	120	80	26.5	32	84
Evergreen oak	**10G/ 10S**	112	130	86	30	32	94

Species	Product	**Global Efficiency** (%)
Industrial Pine	**10G**	21.5 (0.84 x 0.8 x 1 x 0.32)
Evergreen Oak	**10G/10S**	31.0 (0.94 x 0.86 x 0.96 x 0.40)

VII.f) Discussions

VII.f.1) Efficiencies based on β-O-4 content per 100 aromatics

Table 12: Calculations of Efficiencies based on β-O-4 linkages per 100 aromatics

Column	1	**2**	**3**	**4**
Lignin source	β-O-4' content (per 100 aromatics)	Yield **10G/10S** (%)	Theoretical yield (%)	Eff(b)
			Based on β-O-4 content in lignin per 100 aromatics	
Industrial Pine	35.1	46 %	21 %	> 100 %
Norway Spruce	20.2	31 %	17 %	> 100 %
Lebanese Cedar	38.9	27 %	25 %	> 100 %
Pacific Red Cedar	21	4 %	10 %	42 %
Evergreen Oak	48.1	58 %	36 %	> 100 %
Hybrid Plane	42.5	47 %	30 %	> 100 %
Common Beech	43.7	46 %	32 %	> 100 %
Black Poplar	47.2	36 %	34 %	> 100 %

The proportion of β-O-4 in lignin was first estimated with respect to the quantity of aromatics moieties. In agreement with the literature, hardwood lignin contains a higher proportion of β-O-4 linkages (42.5 to 48.1 per 100 aromatics) than softwood lignin (20.2 to 35.1 per 100 aromatics). Such values led to low theoretical maximum yield (10-36 %, Table 12, column 3) and consequently outliers of efficiencies (>100 %, Table 12, Column 4). These outliers could be caused by the underestimation of cleavable interunit linkages of lignin because β-O-4 linkages are the sole linkages observable The uncertainty of the integration of HSQC NMR spectra could also contribute to these excessive values because of the different T2 relaxation rate and the $^{1}J_{CH}$ spin coupling of the distinct nucleus (*e.g.* the aromatic C-H and aliphatic C-H bond).

VII.f.2) Efficiencies based on the relative proportion of β-O-4 linkages

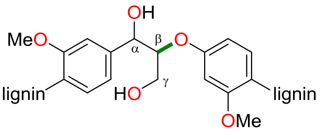
Table 13: Calculations of Efficiencies based on the relative proportion of β-O-4 linkages

Column	**1**	**2**	**3**	**4**
Lignin source	β-O-4’ content	Yield **10G/10S** (%)	Theoretical yield (%)	Eff(b)
			Based on relative abundance of β-O-4 in lignin side chains	
Industrial Pine	63 %	46 %	46 %	100 %
Norway Spruce	46 %	31 %	35 %	89 %
Lebanese Cedar	59 %	27 %	46 %	58 %
Pacific Red Cedar	20 %	4 %	10 %	42 %
Evergreen Oak	70 %	58 %	60 %	96 %
Hybrid Plane	65 %	47 %	60 %	79 %
Common Beech	65 %	46 %	60 %	77 %
Black Poplar	76 %	36 %	60 %	60 %

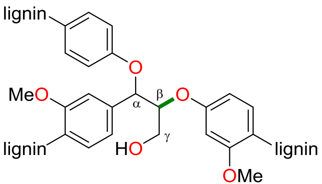
In this study, we focused on the main linkages present in lignins.[8a,10-12] As spirodienone and dibenzodioxocin linkages are not observed or not sufficiently resolved in the 2D HSQC NMR spectra, we only considered β-O-4, resinol and phenylcoumaran structures which represent 70-90 % of the linkages in lignin.[13] The undetected linkages in HSQC NMR are those of non-cleavable linkages (C-C bonds: 4-O-5’, 5-5, etc.) and also of cleavable linkages (C-O bonds: α-O-4, dibenzodioxocin, …).

As all of the undetected linkages are minor in lignin, the percentage of cleavable linkages in lignin (*i.e.* aryl-O-alkyl bonds) is approximated to the percentage of β-O-4 linkages determined by semi quantitative HSQC NMR method.’[14,15]

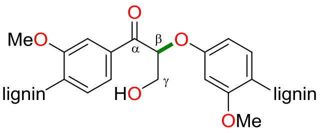
These calculations do not take into account of the carbohydrates content in lignin neither the carbohydrates-lignin complexes (LCC). Yet, LCC should affect the efficiencies since the yield of monoaromatic products is over-estimated. Interestingly, correlations between a decrease in efficiencies and the lignin-carbohydrates complexes (LCC) have been observed. For instance, HSQC NMR experiments reveal higher contents of carbohydrates in hybrid plane lignin than in evergreen oak lignin. This results in lower efficiencies for the former lignin depolymerization than those of the latter.



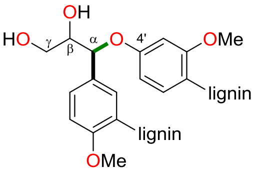
β–O–4'
β aryl ethers
Clivable



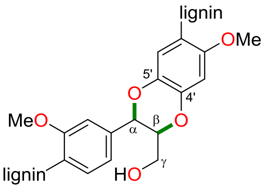
β–O–4'/α–O–4'
α,β diaryl ethers
Clivable



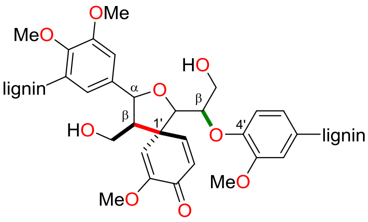
β–O–4'
α–Keto–β aryl ethers
Clivable



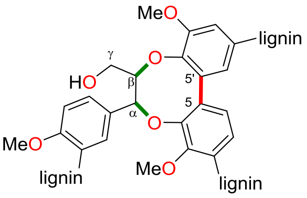
α-O-4
α aryl ether
Clivable



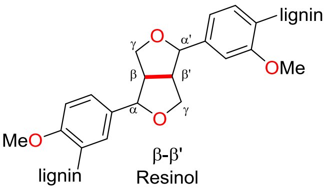
β-O-4'/α-O-5'
Benzodioxane
Clivable



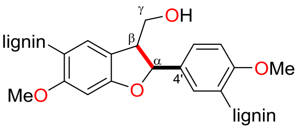
β-1'/β-O-4'
Spirodienone
Non-Clivable
and Clivable



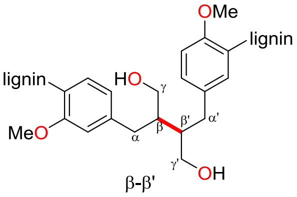
5-5'/β-O-4'/α-O-4'
Dibenzodioxocin
Non-Clivable
and Clivable



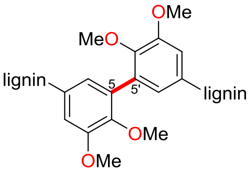
β-β'
Resinol
Non-Clivable



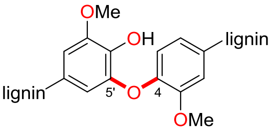
β-β'/α-O-4'
Phenylcoumaran
Non-Clivable



β-β'
Non-Clivable



5-5'
Diphenyl
Non-Clivable

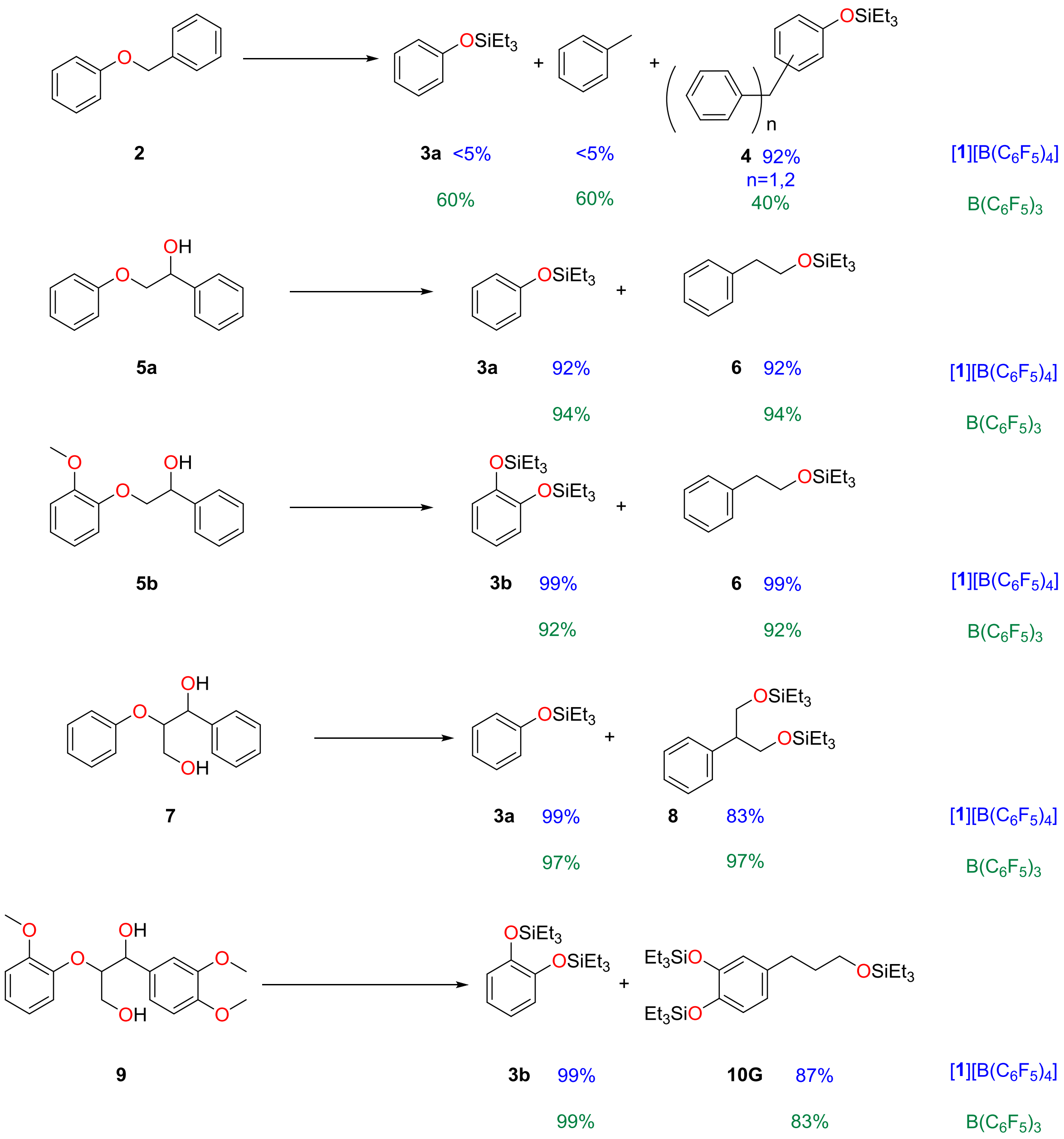


4-O-5'
Biphenyl ether
Non-Clivable

VIII) Hydrosilylating depolymerization of lignin: comparison of the two catalysts $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$]

VIII.a) Comparison between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$] on lignin models

Scheme 7: Comparison between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$] on lignin models



VIII.b) Comparison between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$] on wood lignins

Comparison of yield and efficiency between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$]

Table 14: Comparison of yield and efficiency between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$]

Species	Product	[**1**][$B(C_6F_5)_4$]		**$B(C_6F_5)_3$***	
		Experimental (wt%)	**Efficiency** (%)	**Experimental** (wt%)	**Efficiency** (%)
		Softwood		**Softwood**	
Industrial pine	**10G**	120	100	52	43
Norway spruce	**10G**	81	89	34	37
Lebanese cedar	**10G**	69	84	42	46
		Hardwood		**Hardwood**	
Evergreen oak	**10G / 10S**	32 / 130	96	12 / 111	71
Hydrid plane	**10G / 10S**	36 / 94	73	14 / 50	38
Common beech	**10G / 10S**	42 / 83	75	8 / 54	36
Black poplar	**10G / 10S**	20 / 80	57	16 / 126	82

* Values obtained from data reported in reference 7a

Calculation of TONs and TOFs of $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$]

The catalytic activity and properties of $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$ are compared for evaluating their respective optimal conditions in the depolymerization of lignin with hydrosilanes. $B(C_6F_5)_3$ performs best in the presence of Et_3SiH in CH_2Cl_2 at room temperature while [**1**][$B(C_6F_5)_4$] depolymerizes lignin at higher temperature (70°C) with Et_3SiH in C_6H_5Cl. This allows an evaluation of the TONs and TOFs and a quantification of the robustness and efficiency of the catalytic systems. In fact, a strict comparison would need operating systems within similar conditions. We have thus considered the two catalysts within the same conditions of depolymerization for industrial pine lignin (catalytic loading, temperature, solvent, etc.).

In our study, catalytic loadings, turn over numbers (TONs), and turn-over frequencies (TOFs) were calculated as described below:

Catalytic loadings were evaluated by considering the exact number of aromatic units in the lignin sample to provide the most realistic TONs and TOFs. It has been previously reported that lignin is an aromatic oligomers involving:[7a]

- For industrial pine lignin (softwood) : an average number of 5 aromatic units **G** with a mean molecular weight of $1099 g/mol^{-1}$.
- For evergreen oak lignin (hardwood) : an average number of 4 aromatic units with a mean molecular weight of $835\ g/mol^{-1}$.

Catalytic loadings were evaluated considering the number of aromatic units in lignin while TONs and TOFs require a calculation based on the products *i.e.* the aromatic groups extracted from the depolymerization of lignin.

For industrial pine lignin, considering its average molecular weight ($M_n = 1099\ g.mol^{-1}$) and its polymerization degree of 5, the catalytic loading in [**1**][$B(C_6F_5)_4$] corresponds to 1.6 mol% with respect to the molar quantity of aromatic units.

For example: For 110 mg of softwood lignin (0.1 mmol), 0.5 mmol of **G** aromatic units (Mw = 196.2 g.mol^{-1}) can be theoretically extracted. So 10 wt% of [**1**][$B(C_6F_5)_4$] corresponds with *ca* 1.6 mol% (M_w = 1351 g.mol^{-1}). With the same method, we can deduce that 15 wt% of $B(C_6F_5)_3$ (M_w = 511.98 g.mol^{-1}) corresponds with *ca* 6.4 mol% ((0.110 x 0.15)/(511.98 x 5)). For industrial pine lignin, for which a depolymerization efficiency of 100 % is obtained, the yield of depolymerization is maximum, and for 110 mg (0.1 mmol) lignin (theoretical molar yield τ(5) = 46 %) is equal to 0.46 x 0.1 x 5 = 0.23 mmol in **G** lignol derivative. This later values (0.23 mmol) with a catalyst charge in [**1**][$B(C_6F_5)_4$] (10 wt%, 0.00814 mmol) gives a TON of 28.4. With catalyst $B(C_6F_5)_3$ (15wt%, 0.0323mmol) which led to an efficiency of 43%, 0.11 mmol (0.46 x 0.43 x 0.5) of **G** units is obtained giving a TON of 3.1.

$$\text{TON}([\mathbf{1}][B(C_6F_5)_4]) = \frac{0.23}{0.0081} = 28.4$$

$$\text{TON}(B(C_6F_5)_3) = \frac{0.1}{0.0323} = 3.1$$

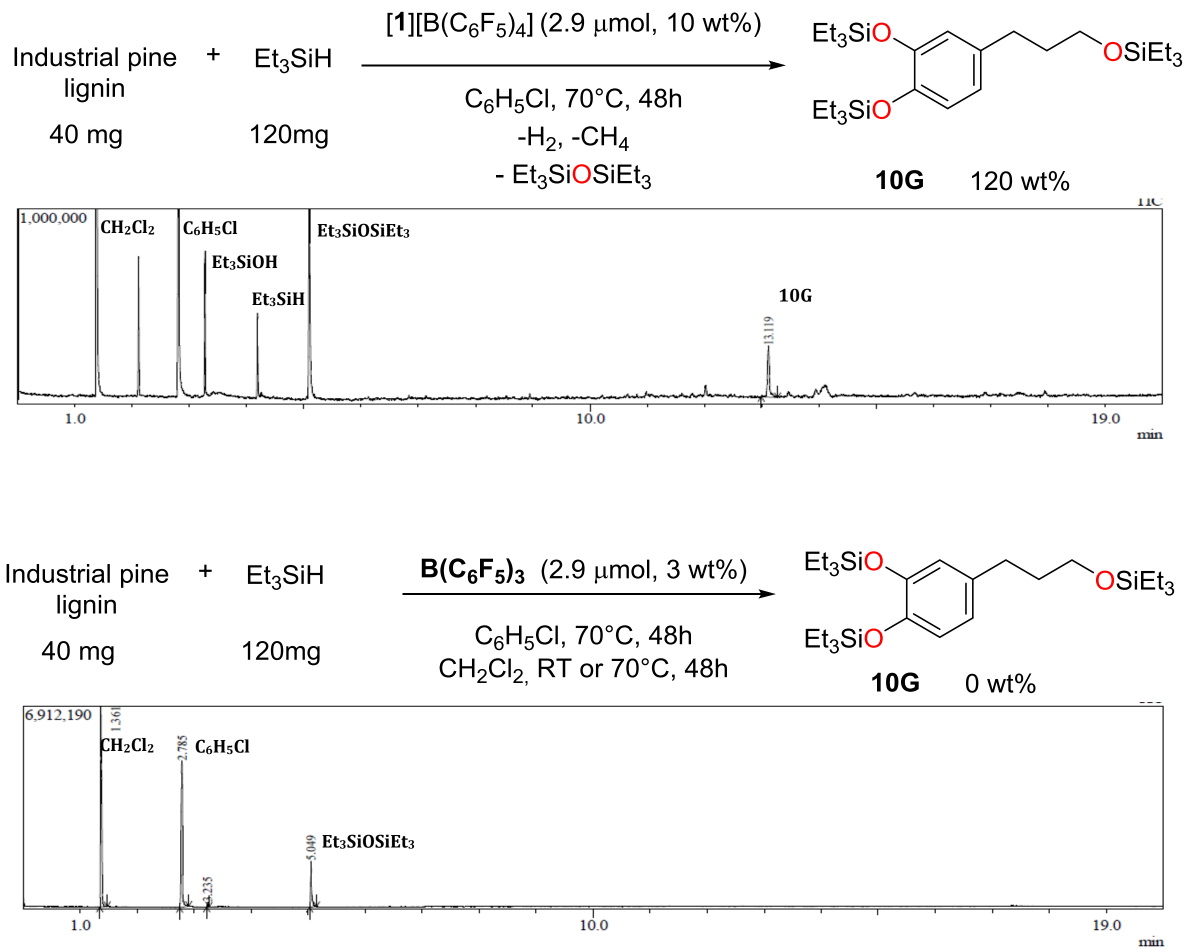
Wood Lignin	**Catalyst loading (mol%)**		**TONs (end of the reaction)**		**TOFs (h^{-1}) (end of the reaction)**	
	[**1**][$B(C_6F_5)_4$]	**$B(C_6F_5)_3$**	[**1**][$B(C_6F_5)_4$]	**$B(C_6F_5)_3$**	[**1**][$B(C_6F_5)_4$]	**$B(C_6F_5)_3$**
Industrial Pine	1.4	5.3	28	3.1	0.9	1.0
Evergreen Oak	3.1	8.3	18	4.4	0.64	1.5

Comparison of the catalytic activity of $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$ within similar conditions

For a proper comparison of the stabilities and activities of the two $B(C_6F_5)_3$/hydrosilane and **[1]**[$B(C_6F_5)_4$/hydrosilane systems, we carried out catalytic experiments under the optimal conditions, *e.g.* 70°C in chlorobenzene (scheme 8).

In an NMR tube equipped with a J. Young valve under inert atmosphere, Et_3SiH (120 mg, 1.1 mmol, 300 wt% from lignin) was added to 40 mg of lignin (~0.04 mmol lignin (M_n= 980 g/mole, $N_{aromatic}$ = 5), ~0.2 mmol of aromatic units) and [**1**][$B(C_6F_5)_4$] (4.0 mg, 2.9 µmol, 10 wt%) in C_6H_5Cl (3 ml). The mixture was stirred at room temperature until complete dissolution of the starting materials and the end of the gas release. After 20 min, all the solid were dissolved and the initial red-orange solution turned brown. The clear solution was then heated at 70°C for 48 h with stirring. Yields in mono aromatic(s) were determined by GC-MS analysis.

Scheme 8: Comparison between $B(C_6F_5)_3$ and [**1**][$B(C_6F_5)_4$] in similar conditions



IX) NMR Spectra

Figure14: ^{1}H NMR spectra of the triethyl(phenoxy)silane **3a** in CD$_2$Cl$_2$

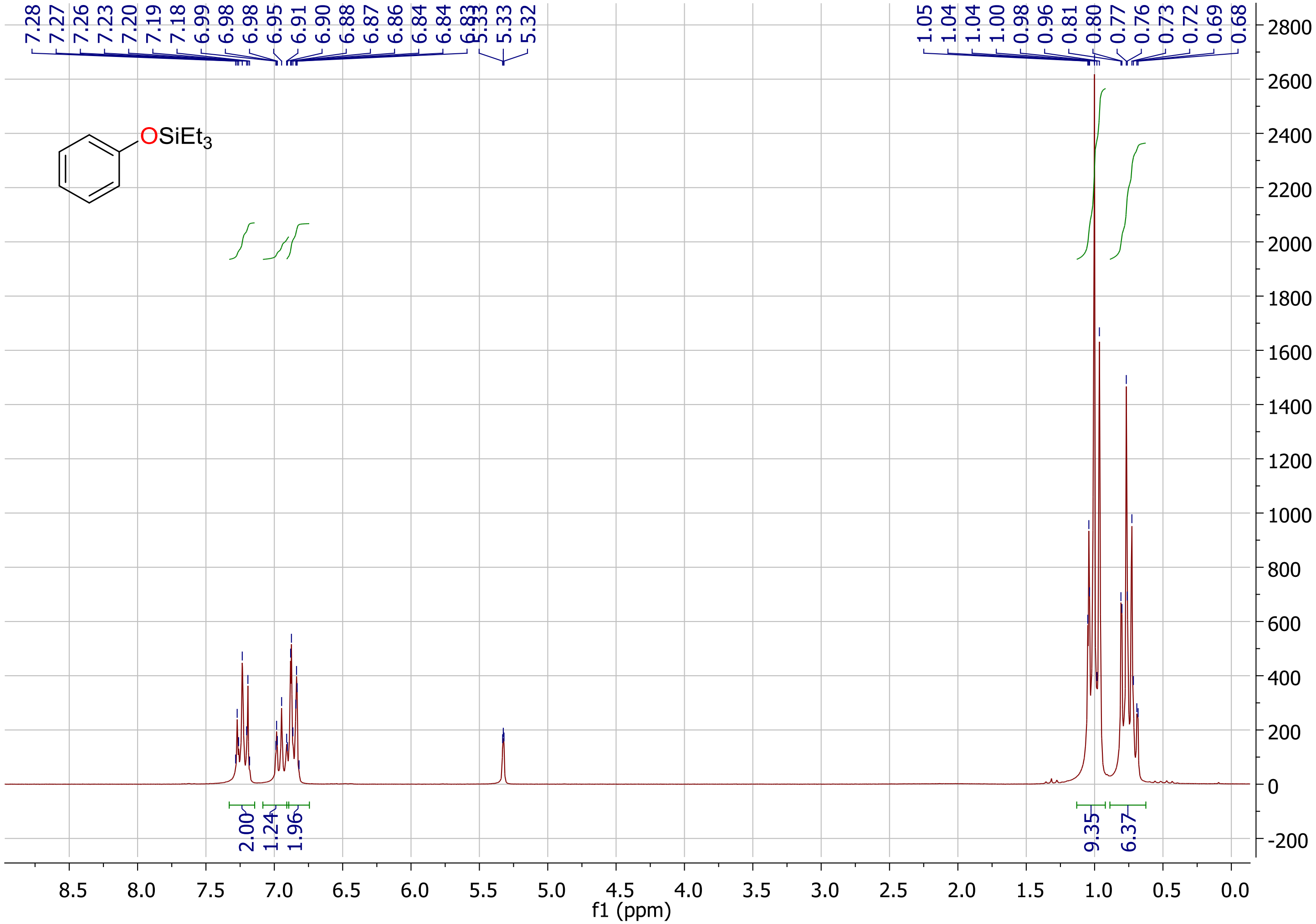


Figure 15: ^{13}C NMR spectra of the triethyl(phenoxy)silane **3a** in CD_2Cl_2

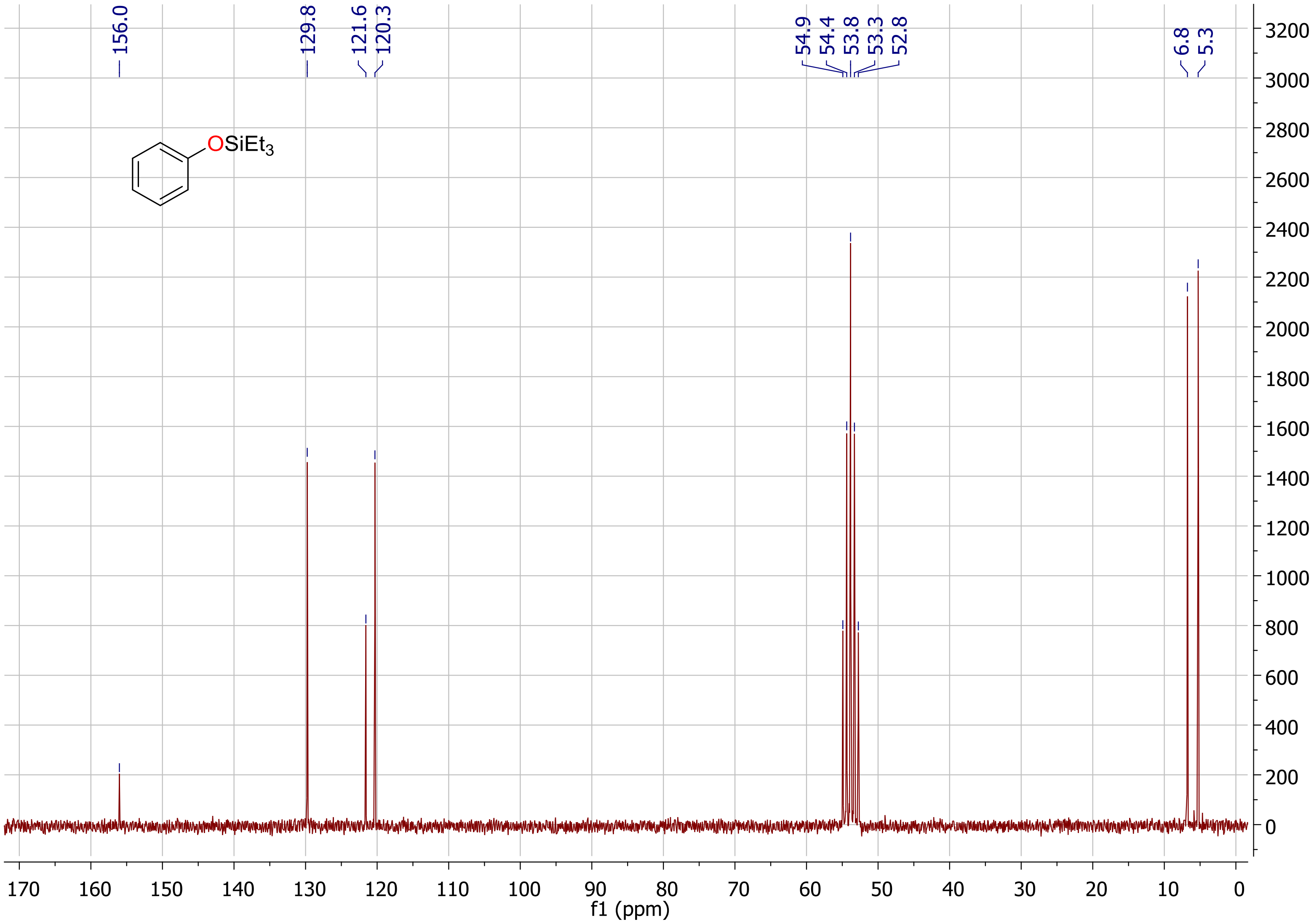


Figure 16: ^{1}H NMR spectra of the 1,2-bis((triethylsilyl)oxy)benzene **3b** in CD_2Cl_2

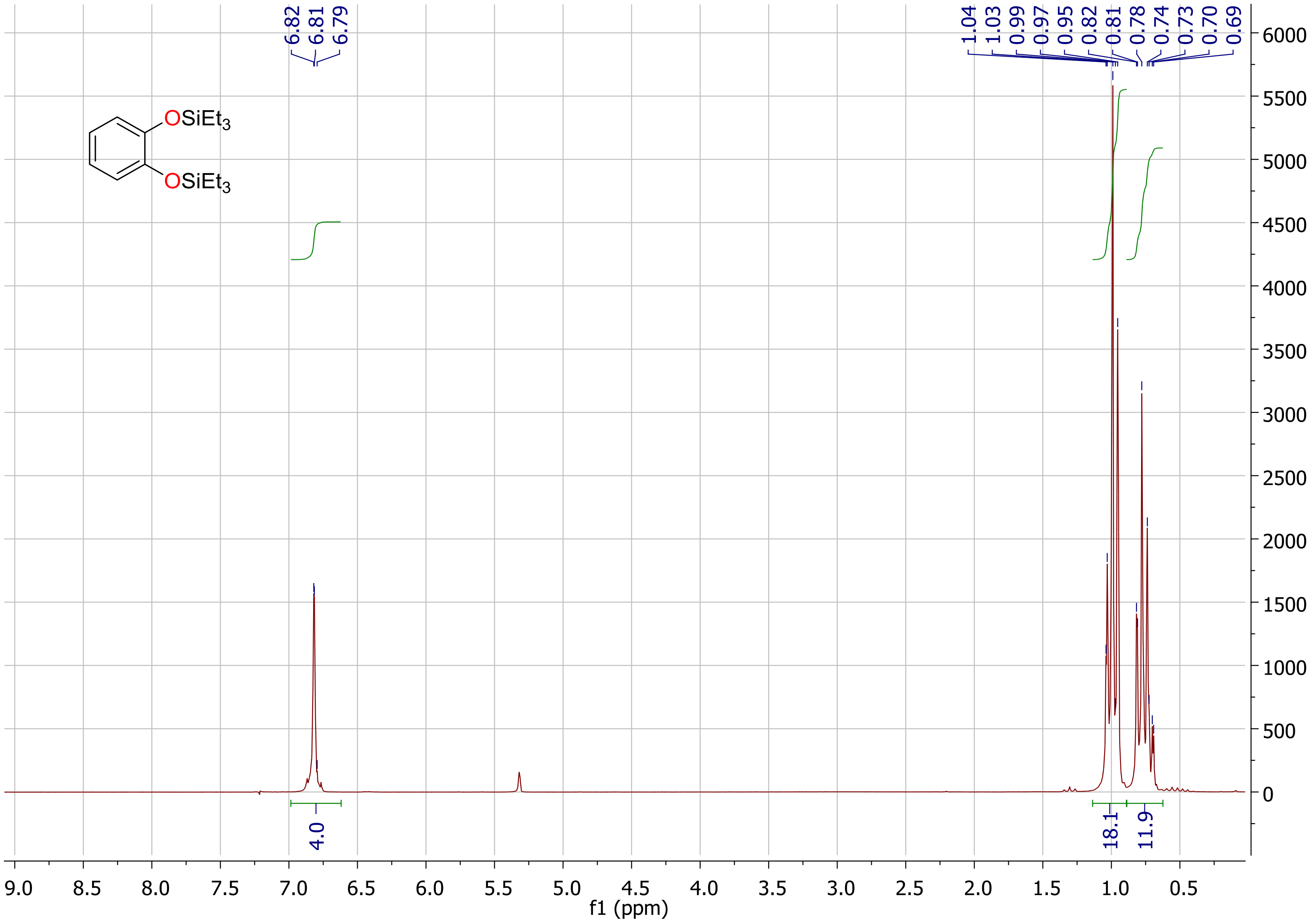


Figure 18: ^{13}C NMR spectra of the 1,2-bis((triethylsilyl)oxy)benzene **3b** in CD_2Cl_2

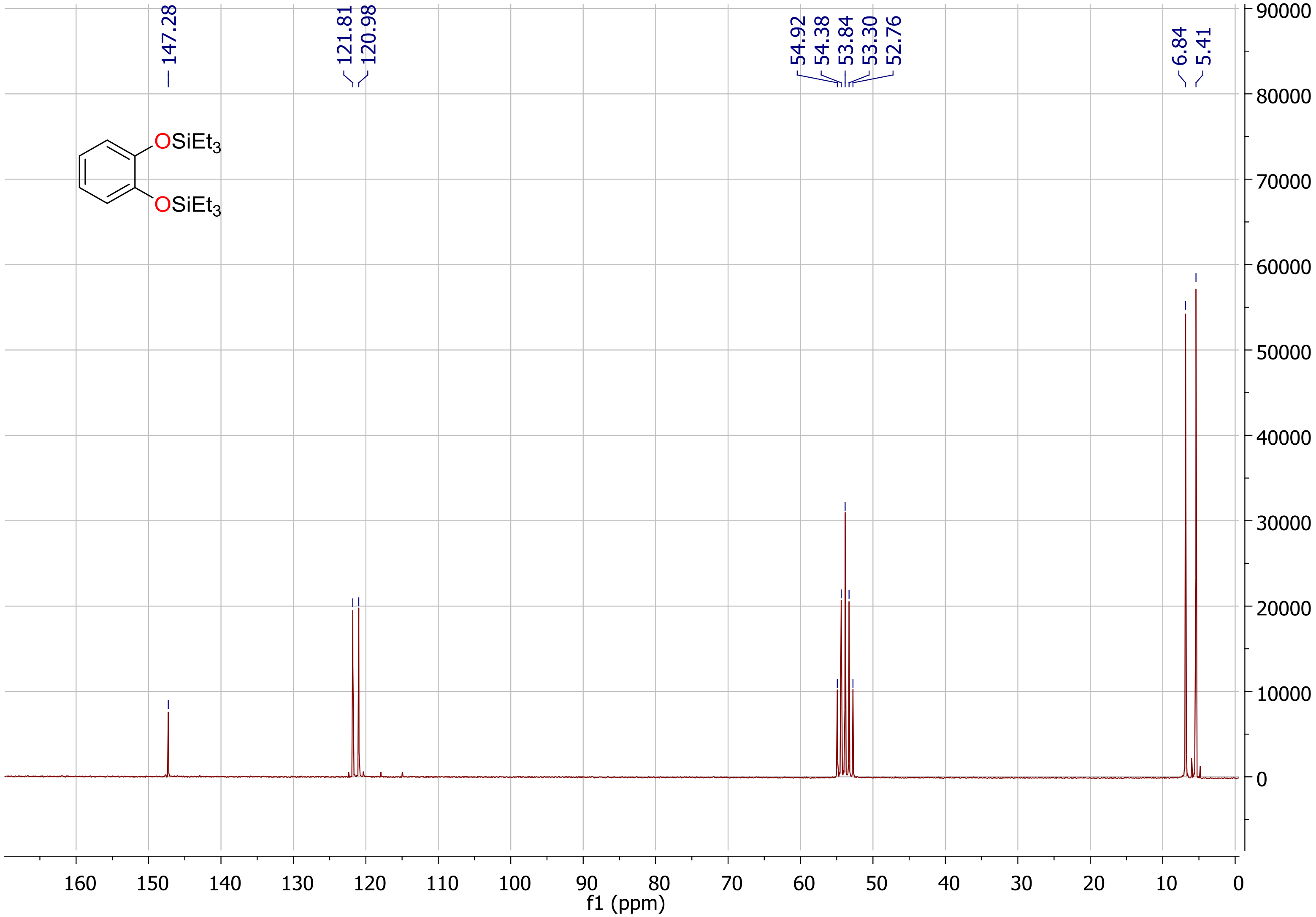


Figure 19: ^{1}H NMR spectra of the (4-benzylphenoxy)triethylsilane *p*-**4** in CD_2Cl_2

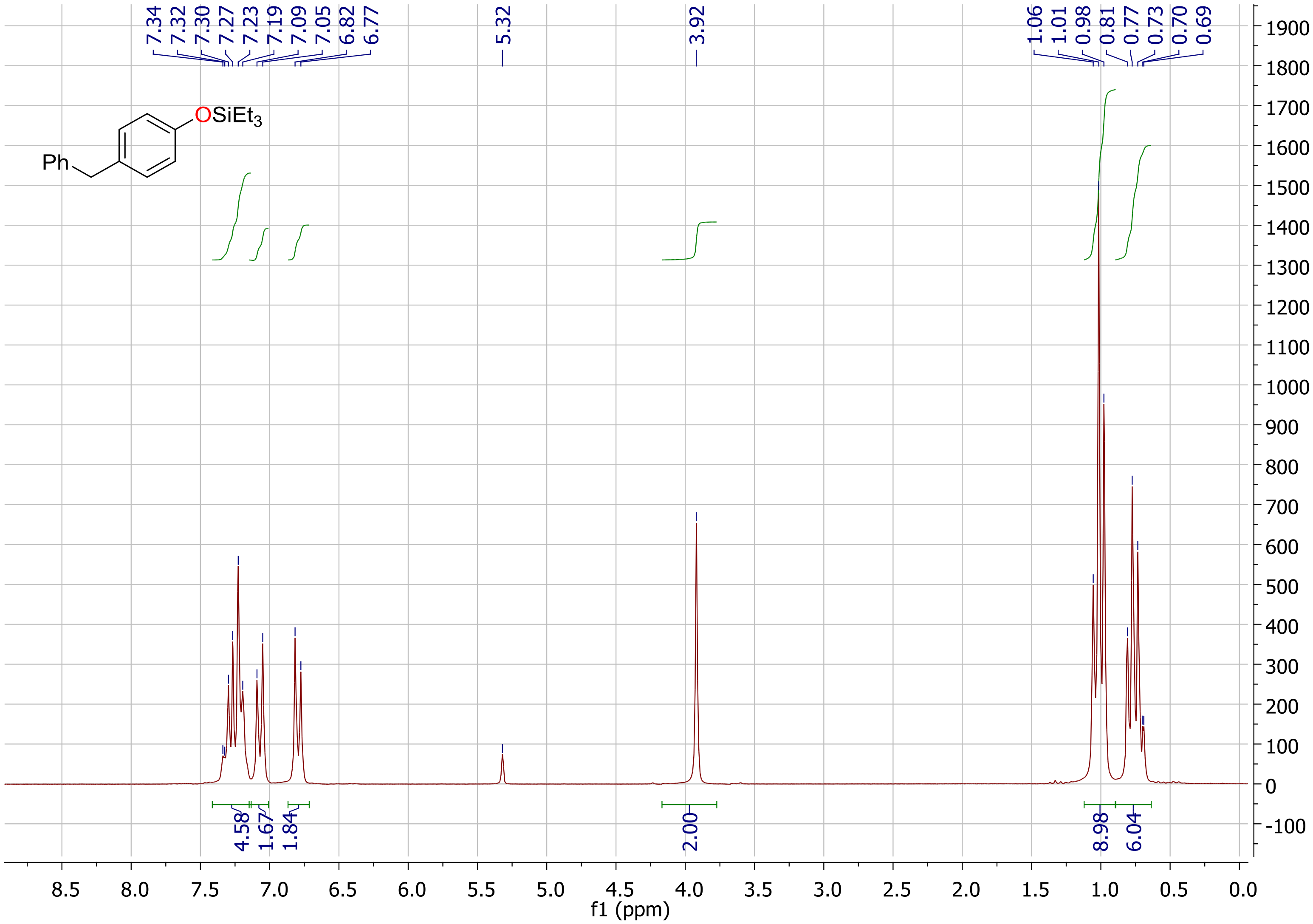


Figure 20: ^{13}C NMR spectra of the (4-benzylphenoxy)triethylsilane *p*-**4** in CD_2Cl_2

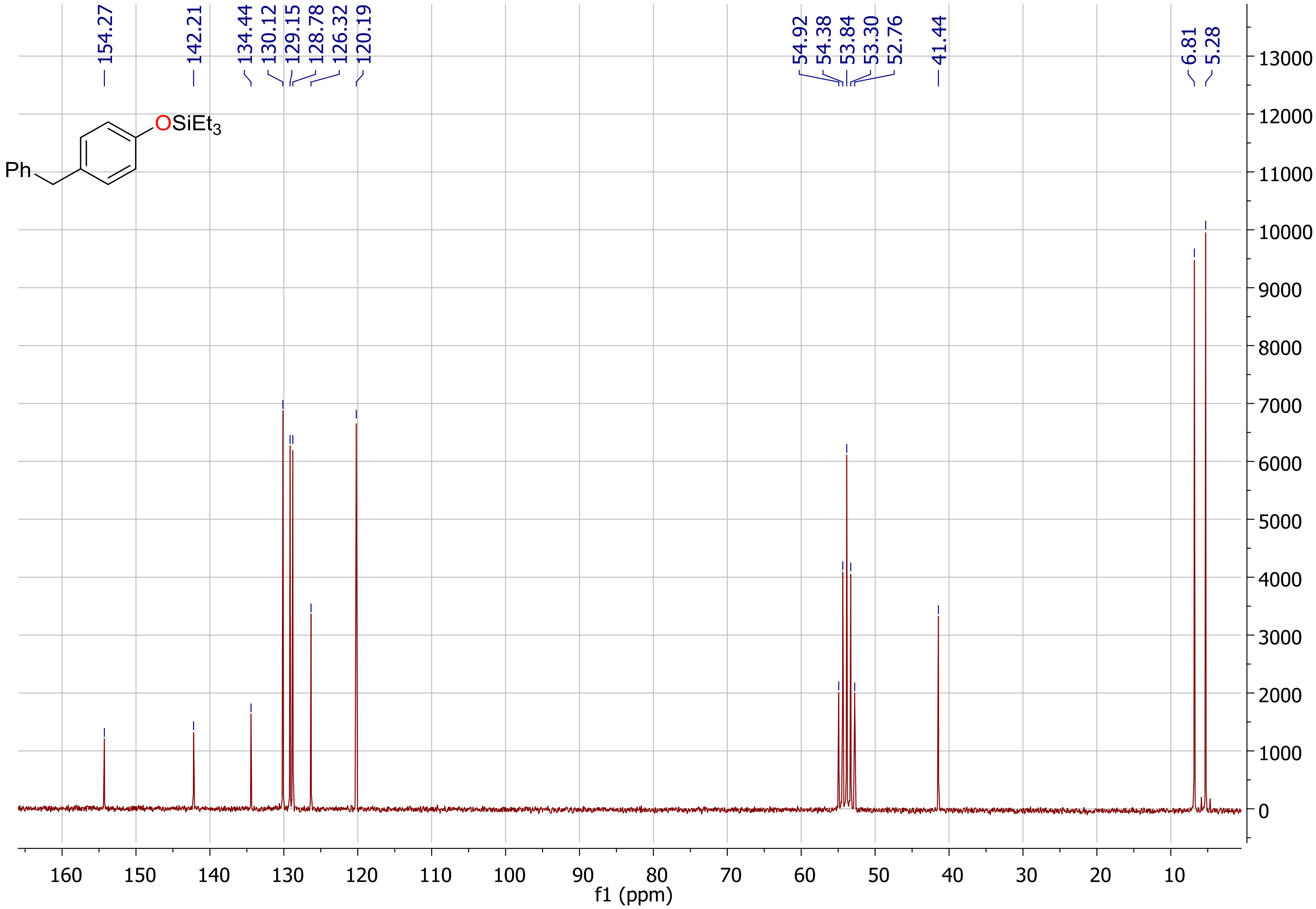


Figure 21: ^{1}H NMR spectra of the (2-benzylphenoxy)triethylsilane *o*-**4** in CD_2Cl_2

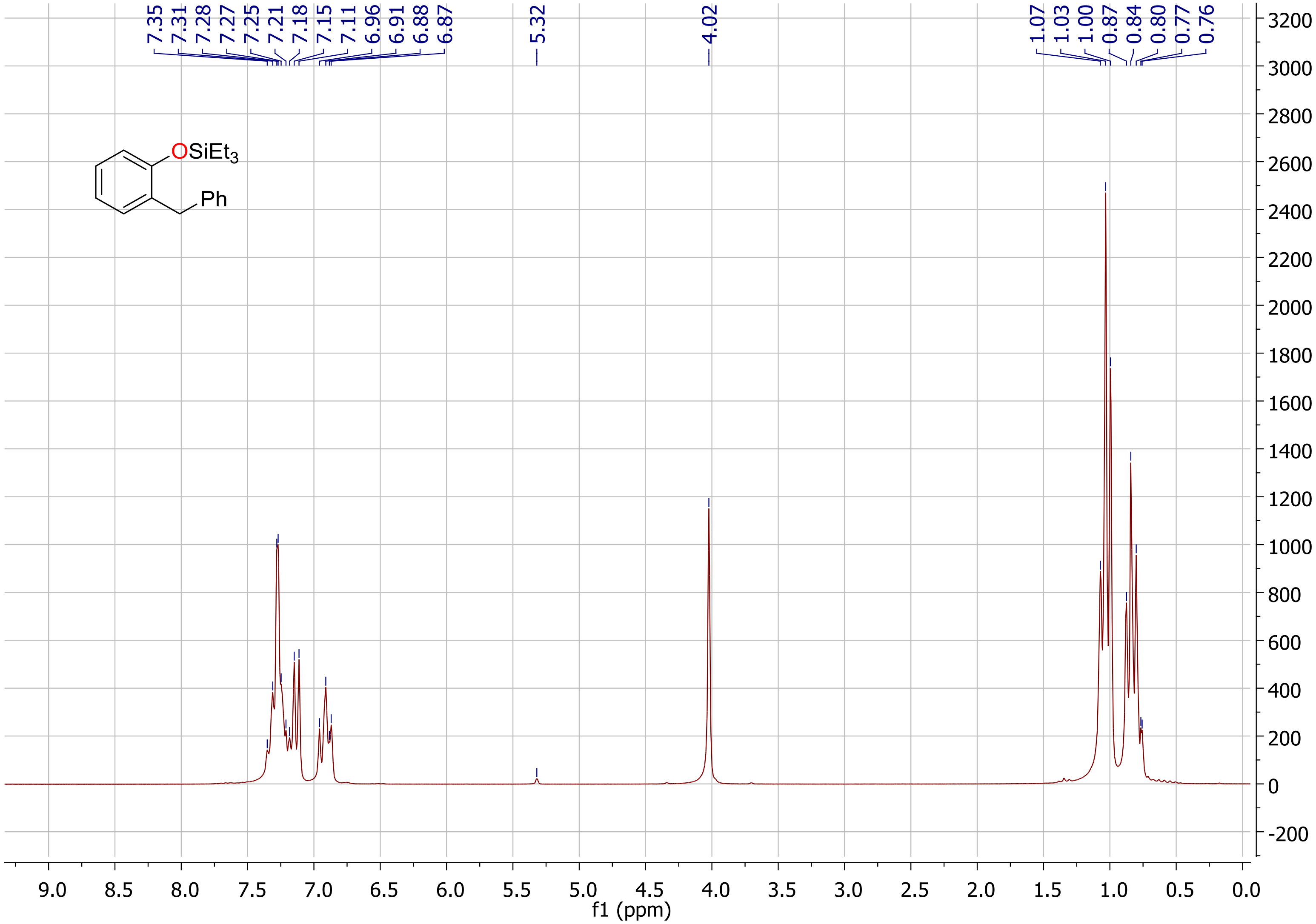
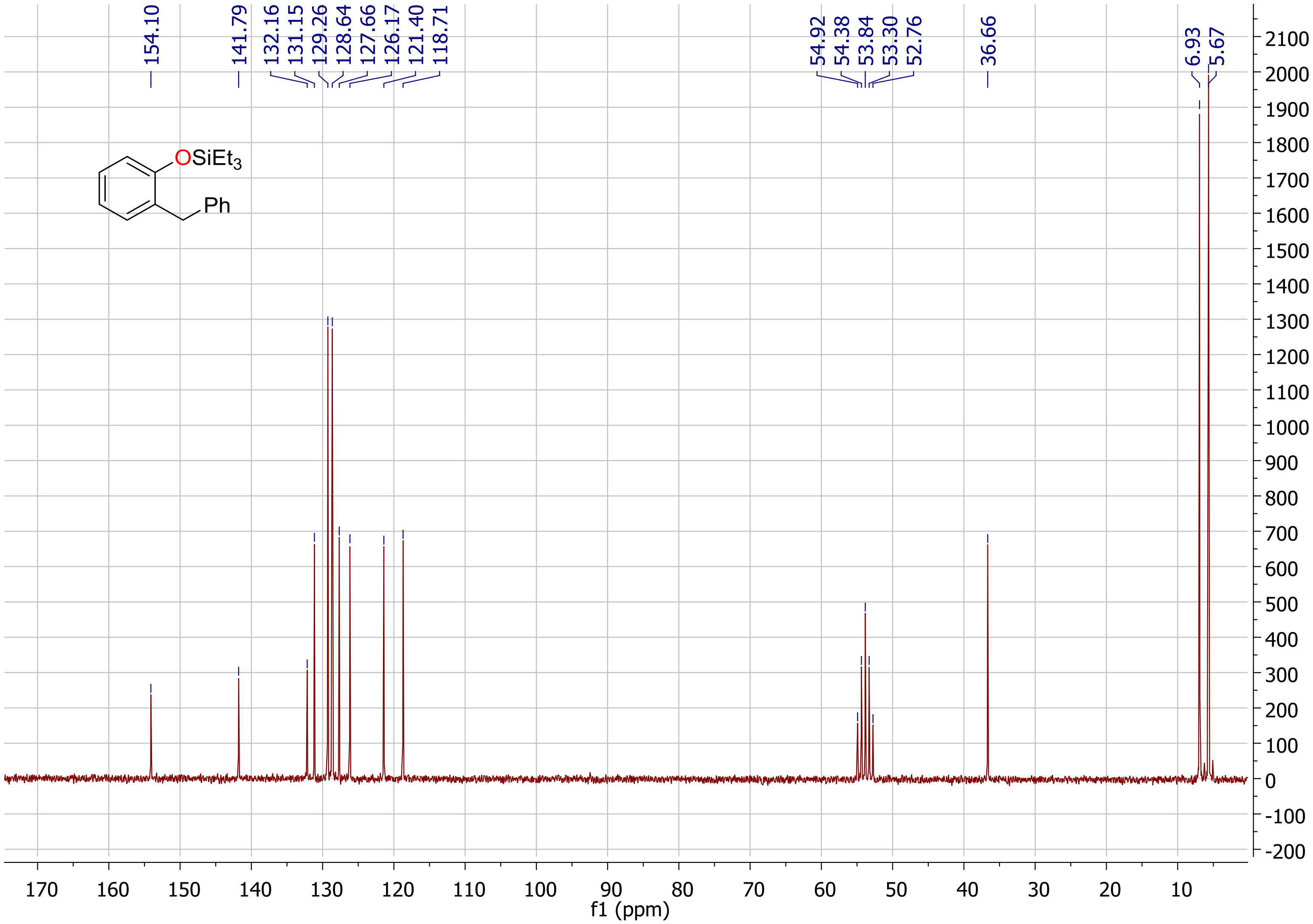
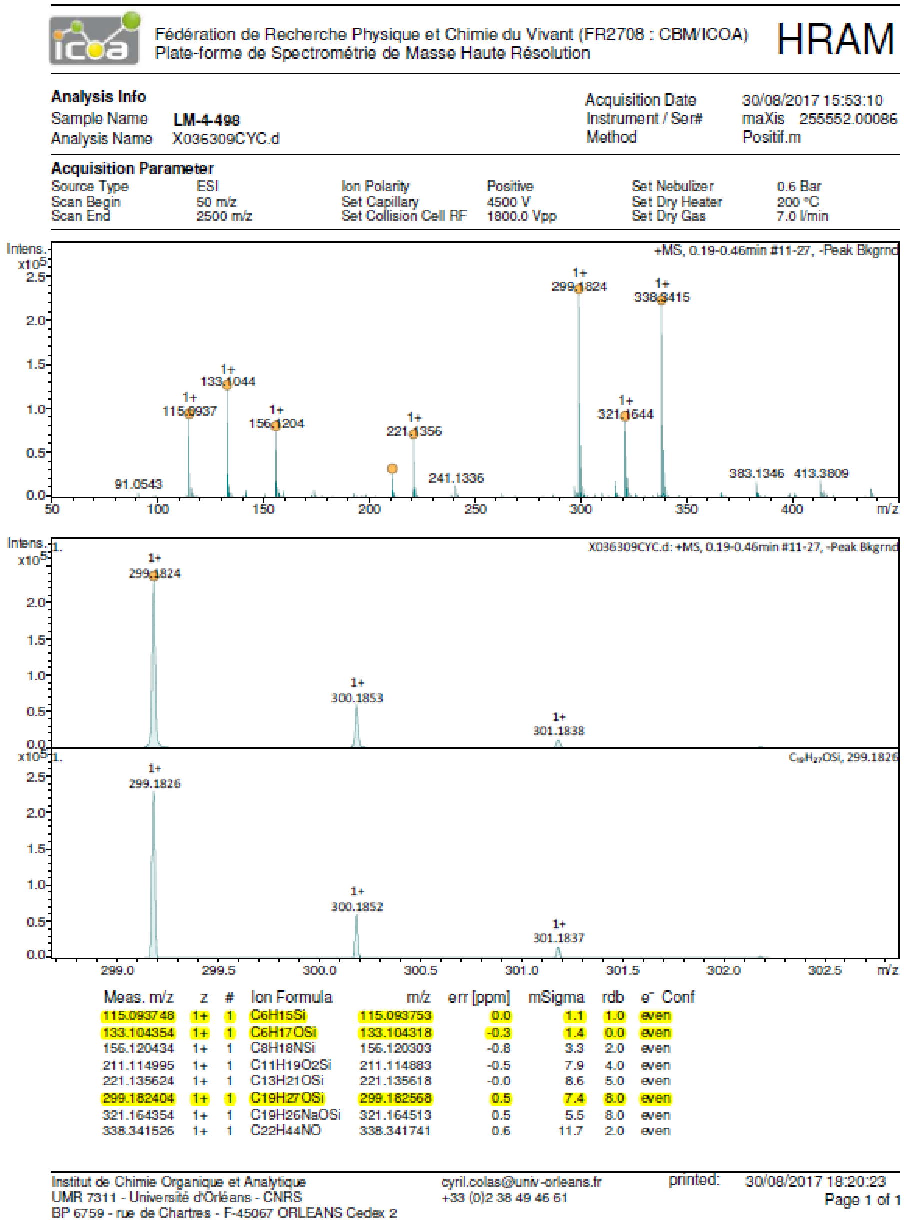


Figure 22: ^{13}C NMR spectra of the (2-benzylphenoxy)triethylsilane *o*-**4** in CD_2Cl_2





Fédération de Recherche Physique et Chimie du Vivant (FR2708 : CBM/ICOA)
Plate-forme de Spectrométrie de Masse Haute Résolution

HRAM

Analysis Info

Sample Name	**LM-4-498**	Acquisition Date	30/08/2017 15:53:10
Analysis Name	X036309CYC.d	Instrument / Ser#	maXis 255552.00086
		Method	Positif.m

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan End	2500 m/z	Set Collision Cell RF	1800.0 Vpp	Set Dry Gas	7.0 l/min

Meas. m/z	z	#	Ion Formula	m/z	err [ppm]	mSigma	rdb	e⁻ Conf
115.093748	1+	1	$C_6H_{15}Si$	115.093753	0.0	1.1	1.0	even
133.104354	1+	1	$C_6H_{17}OSi$	133.104318	-0.3	1.4	0.0	even
156.120434	1+	1	$C_8H_{18}NSi$	156.120303	-0.8	3.3	2.0	even
211.114995	1+	1	$C_{11}H_{19}O_2Si$	211.114883	-0.5	7.9	4.0	even
221.135624	1+	1	$C_{13}H_{21}OSi$	221.135618	-0.0	8.6	5.0	even
299.182404	1+	1	$C_{19}H_{27}OSi$	299.182568	0.5	7.4	8.0	even
321.164354	1+	1	$C_{19}H_{26}NaOSi$	321.164513	0.5	5.5	8.0	even
338.341526	1+	1	$C_{22}H_{44}NO$	338.341741	0.6	11.7	2.0	even

Institut de Chimie Organique et Analytique
UMR 7311 - Université d'Orléans - CNRS
BP 6759 - rue de Chartres - F-45067 ORLEANS Cedex 2

cyril.colas@univ-orleans.fr
+33 (0)2 38 49 46 61

printed: 30/08/2017 18:20:23
Page 1 of 1

Fragmentation:

m/z = 133 : $Et_3SiOH_2^+$
m/z = 115 : Et_3Si^+

m/z = 338 : contaminant = erucamide

Figure 23: ^{1}H NMR spectra of the triethyl(phenylethoxy)silane **6** in CD_2Cl_2

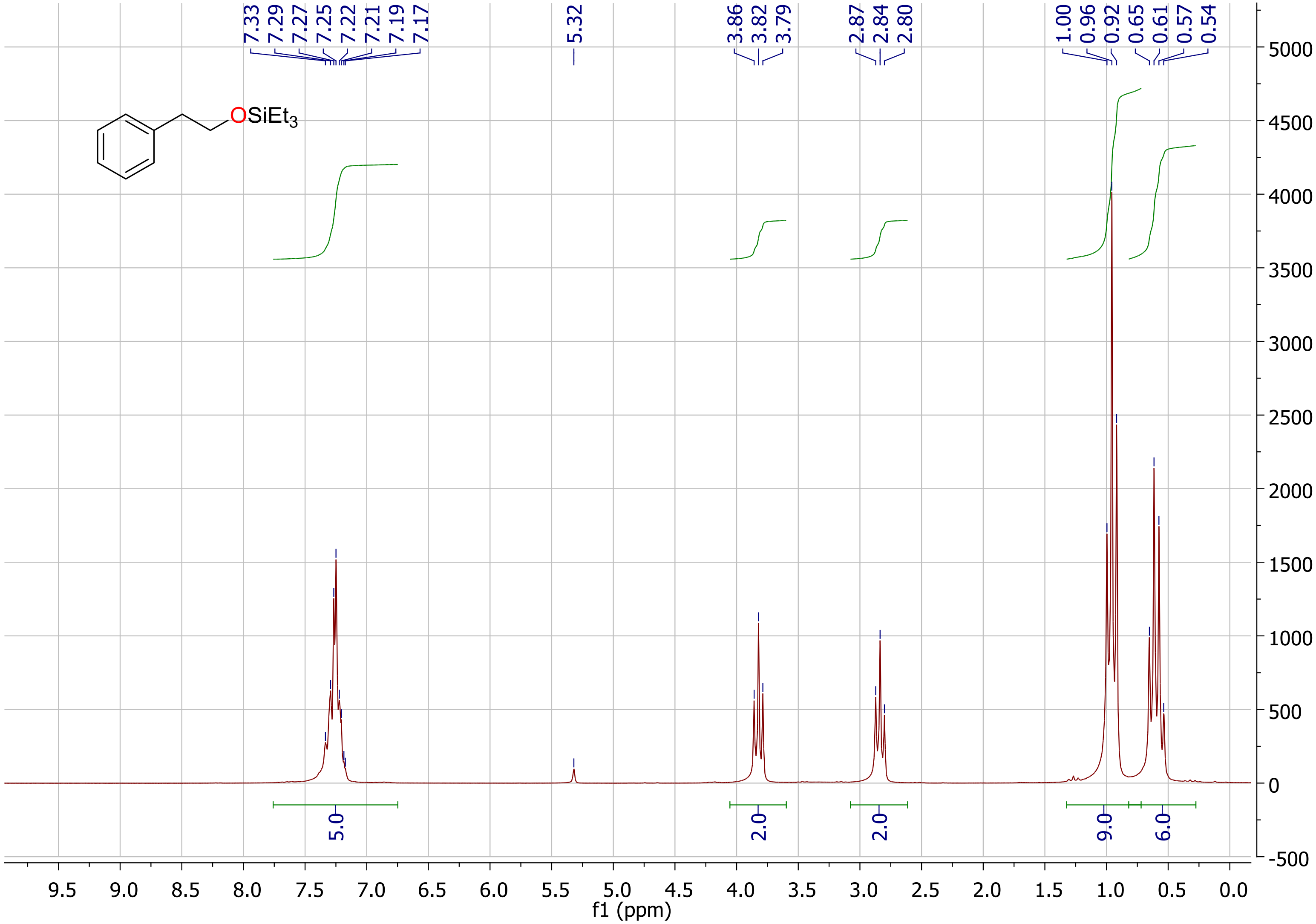


Figure 24: ^{13}C NMR spectra of the triethyl(phenylethoxy)silane **6** in CD_2Cl_2

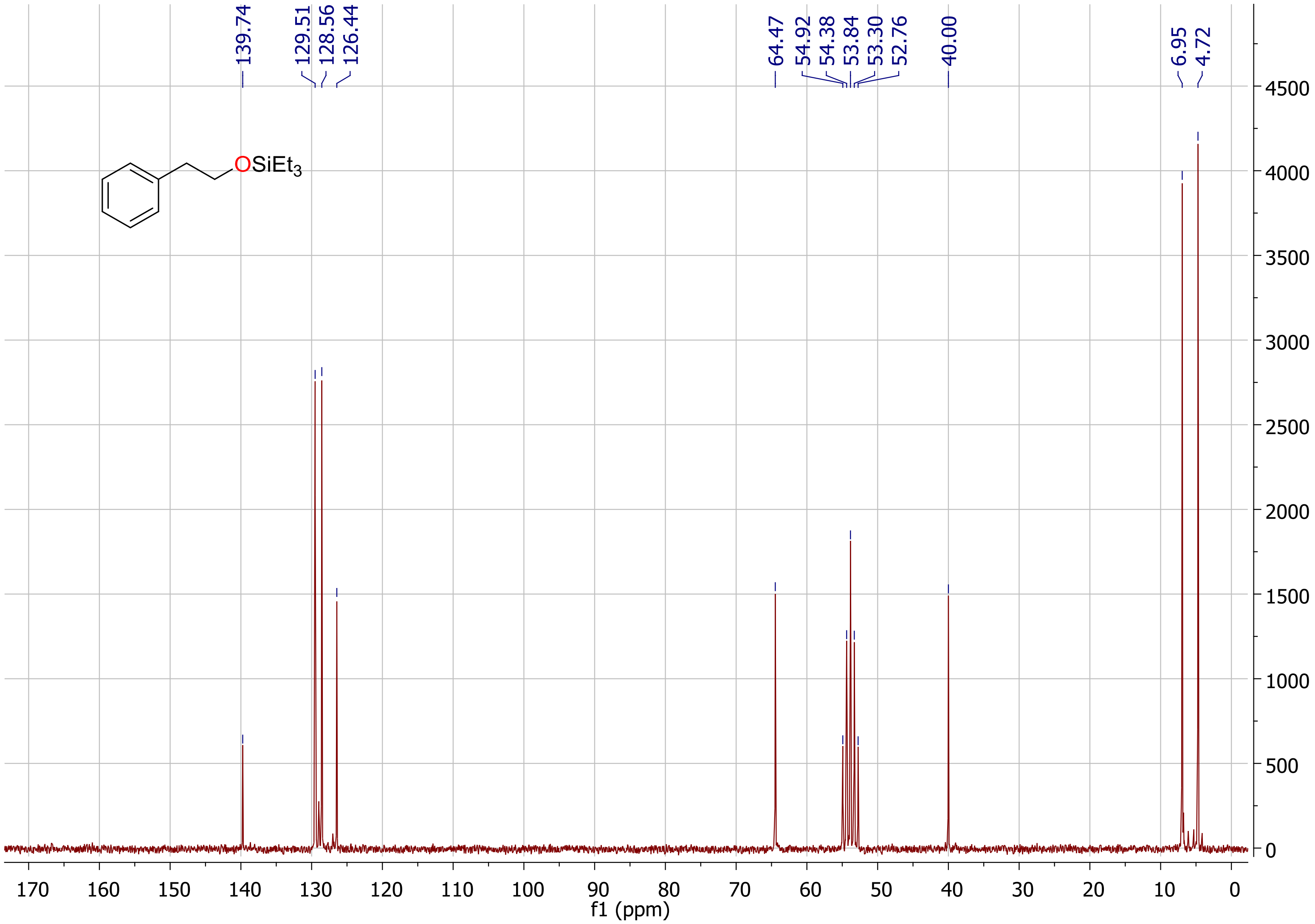


Figure 25: ^{1}H NMR spectra of the compound **10G** in CD_2Cl_2

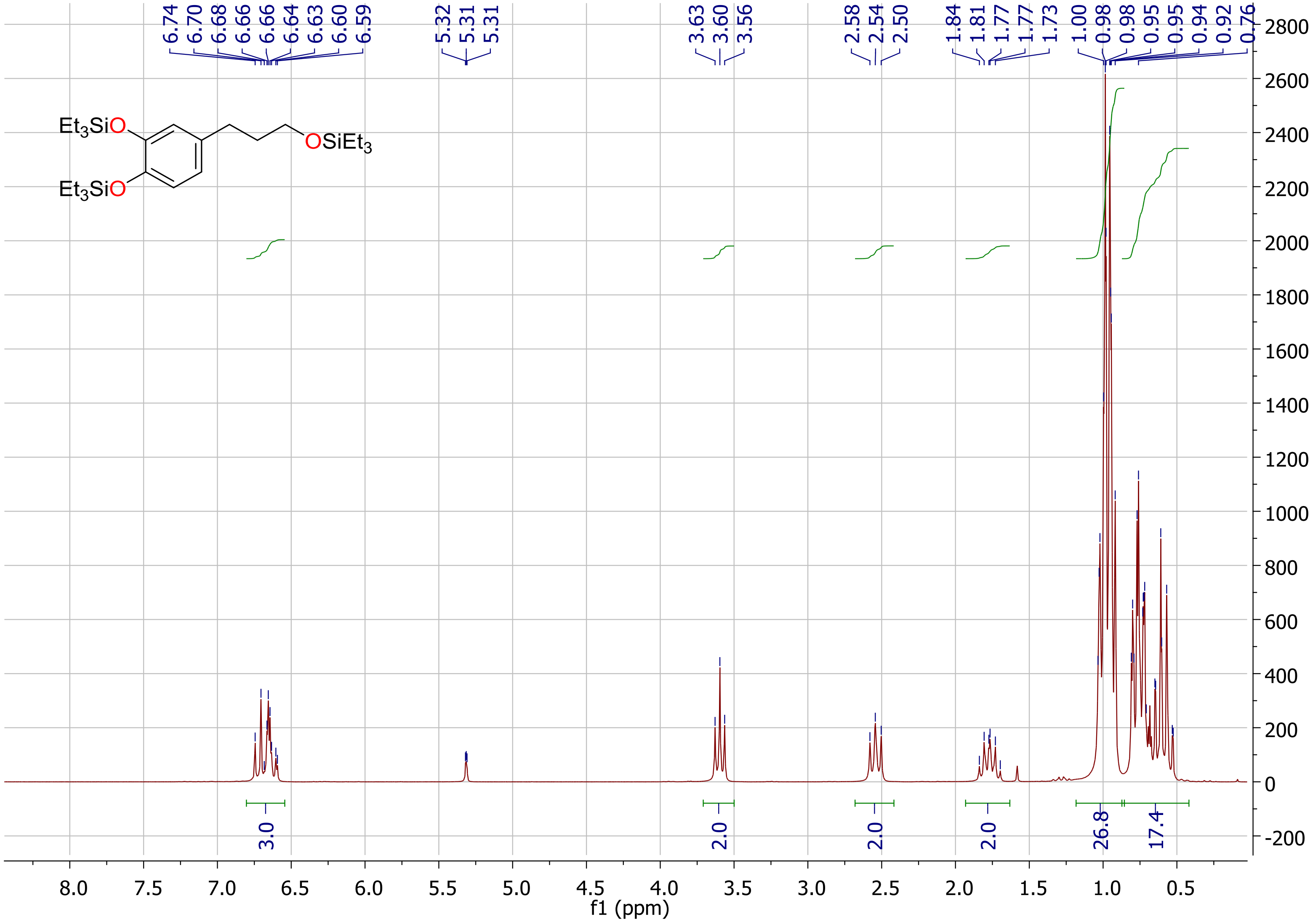


Figure 26: ^{13}C NMR spectra of the compound **10G** in CD_2Cl_2

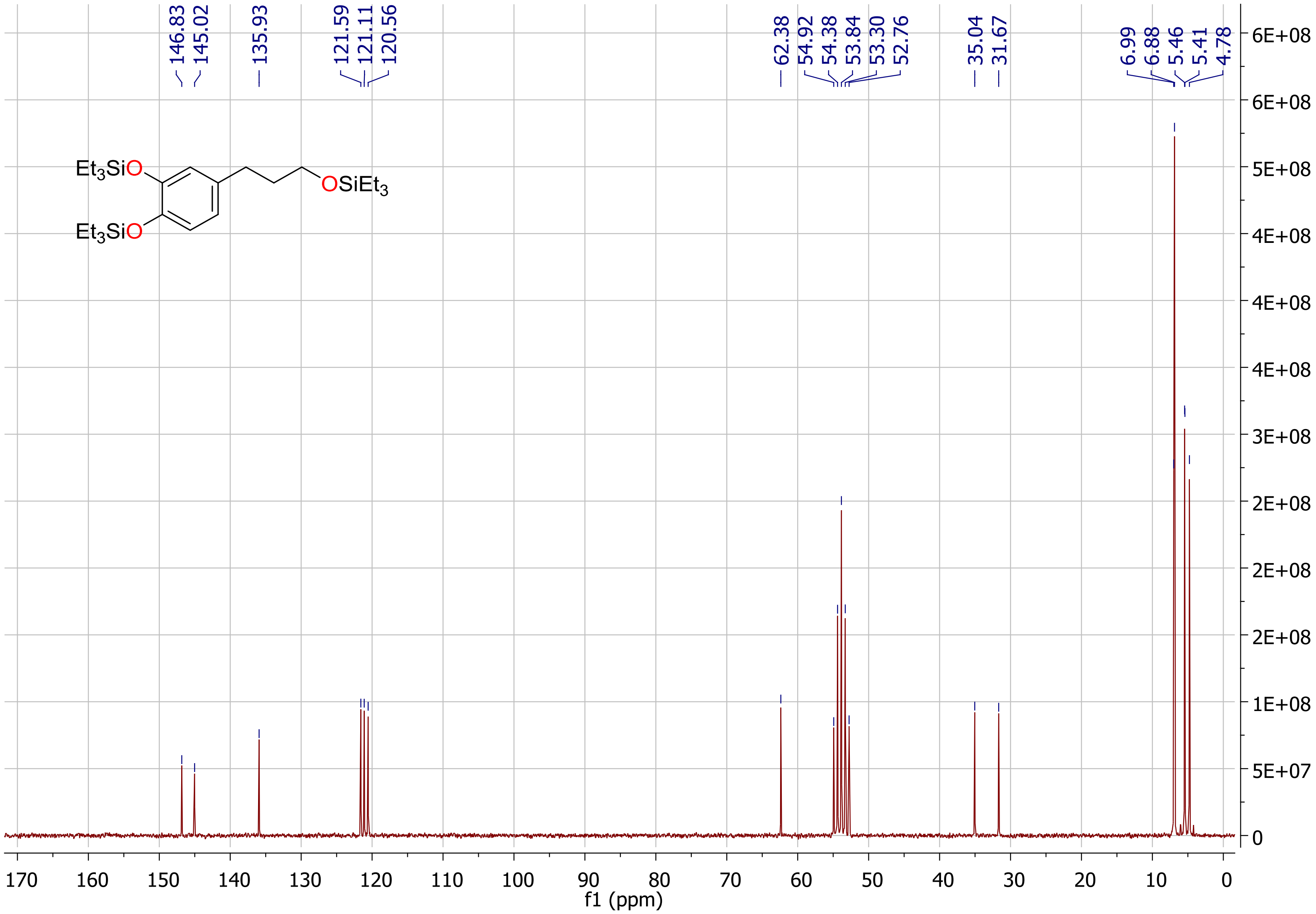


Figure 27: ^{1}H NMR spectra of the compound **10S** in CD_2Cl_2

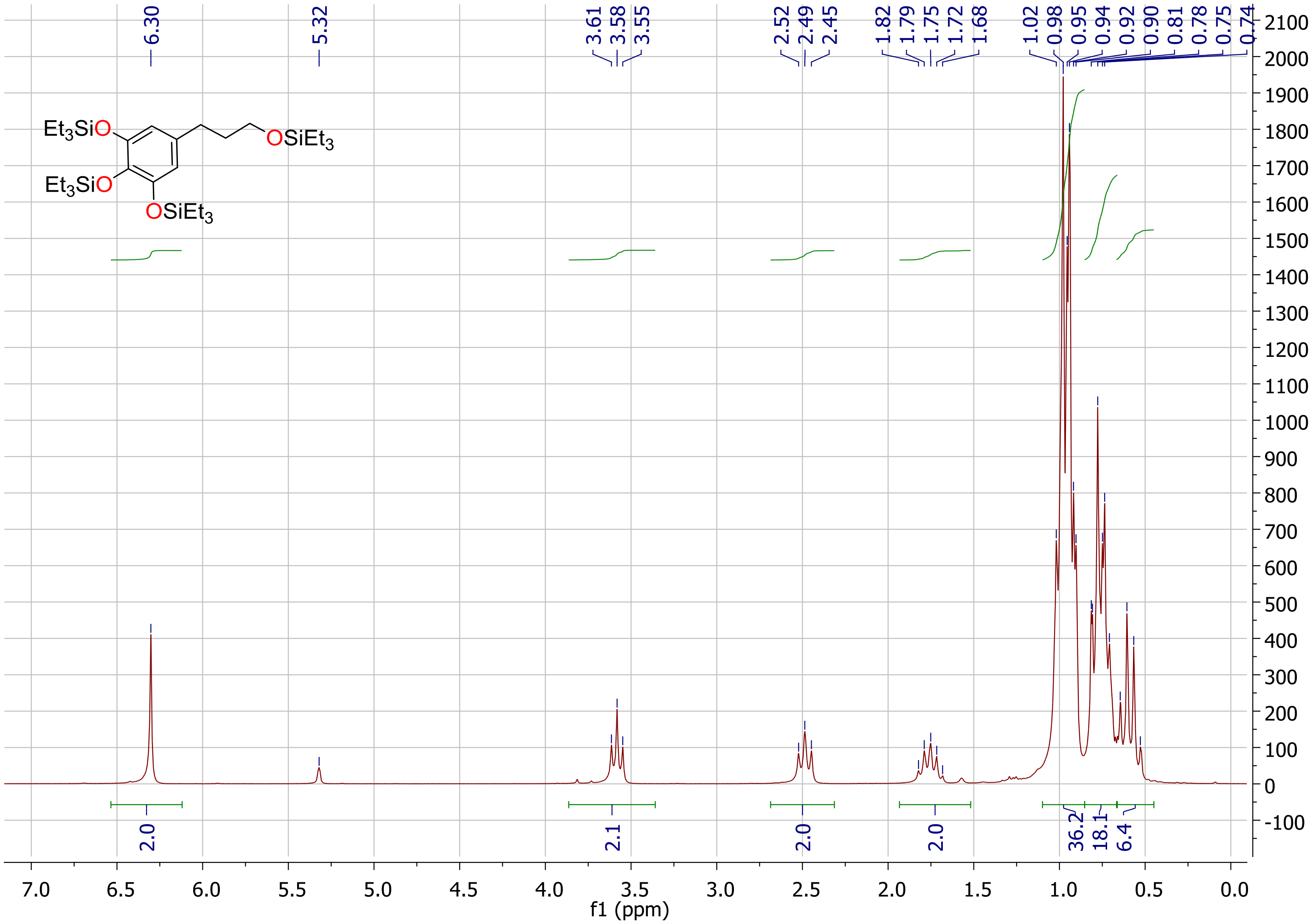


Figure 28: ^{13}C NMR spectra of the compound **10S** in CD_2Cl_2

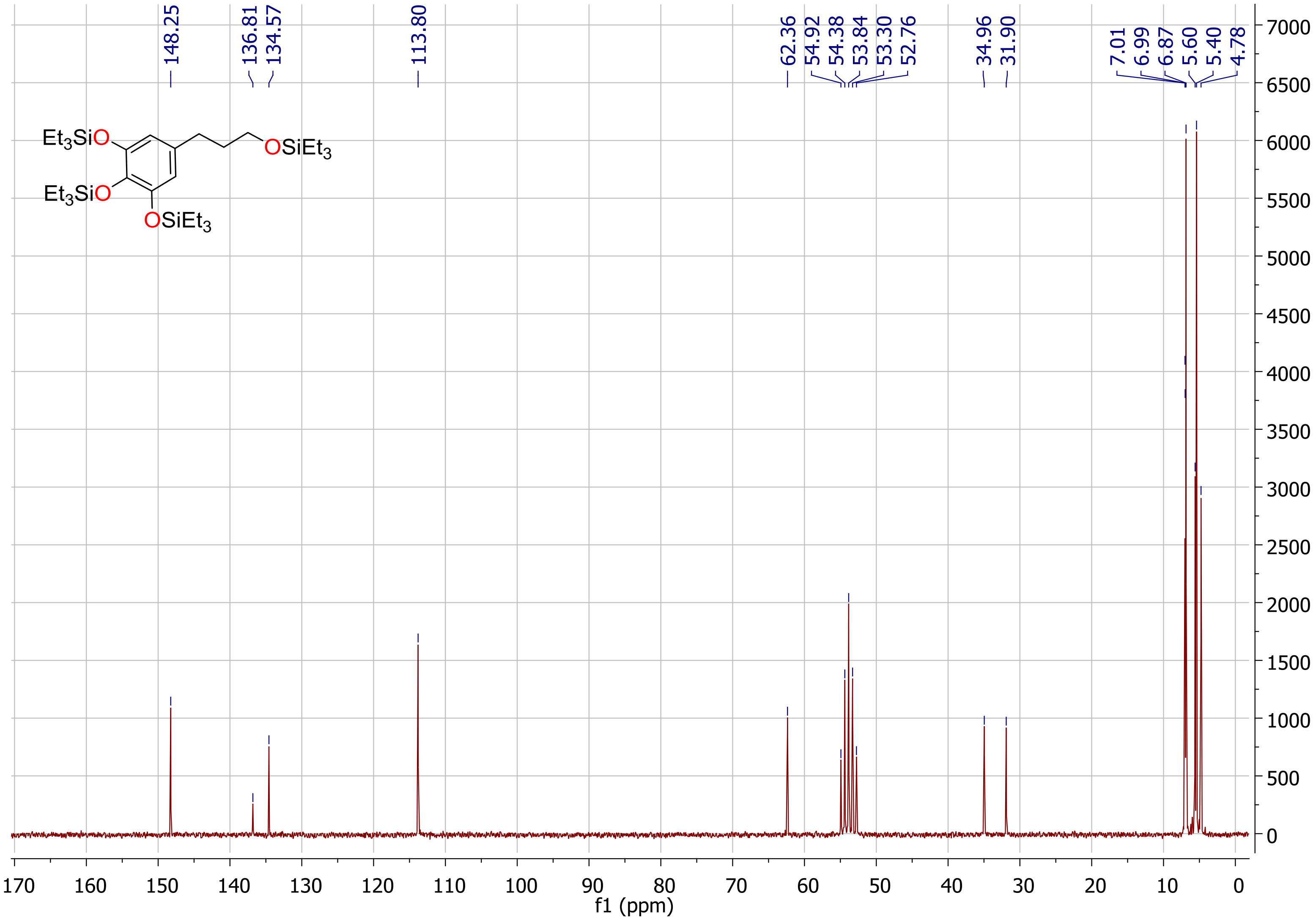


Figure 29: ^{1}H NMR spectra of the compound **11S** in CD_2Cl_2

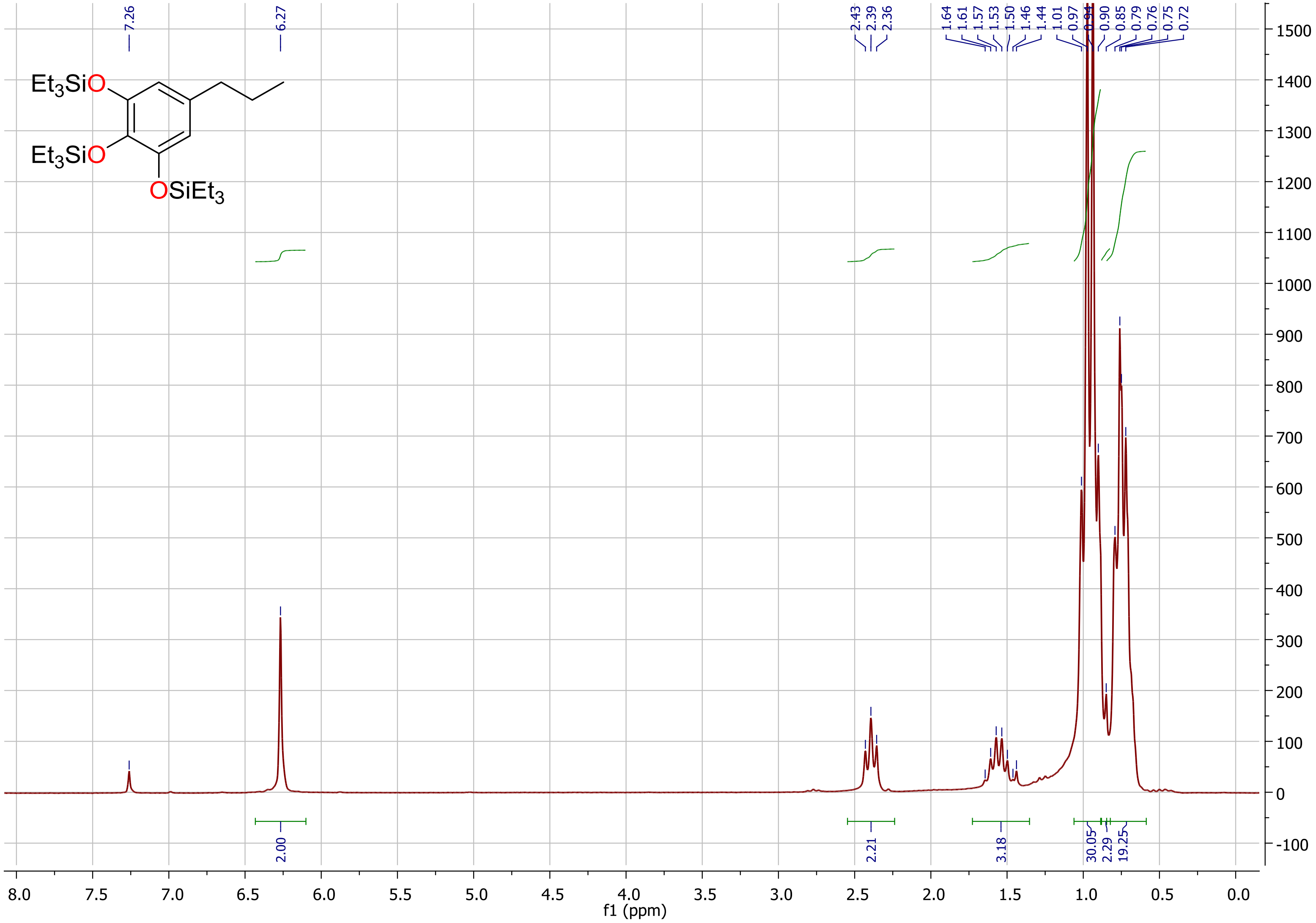
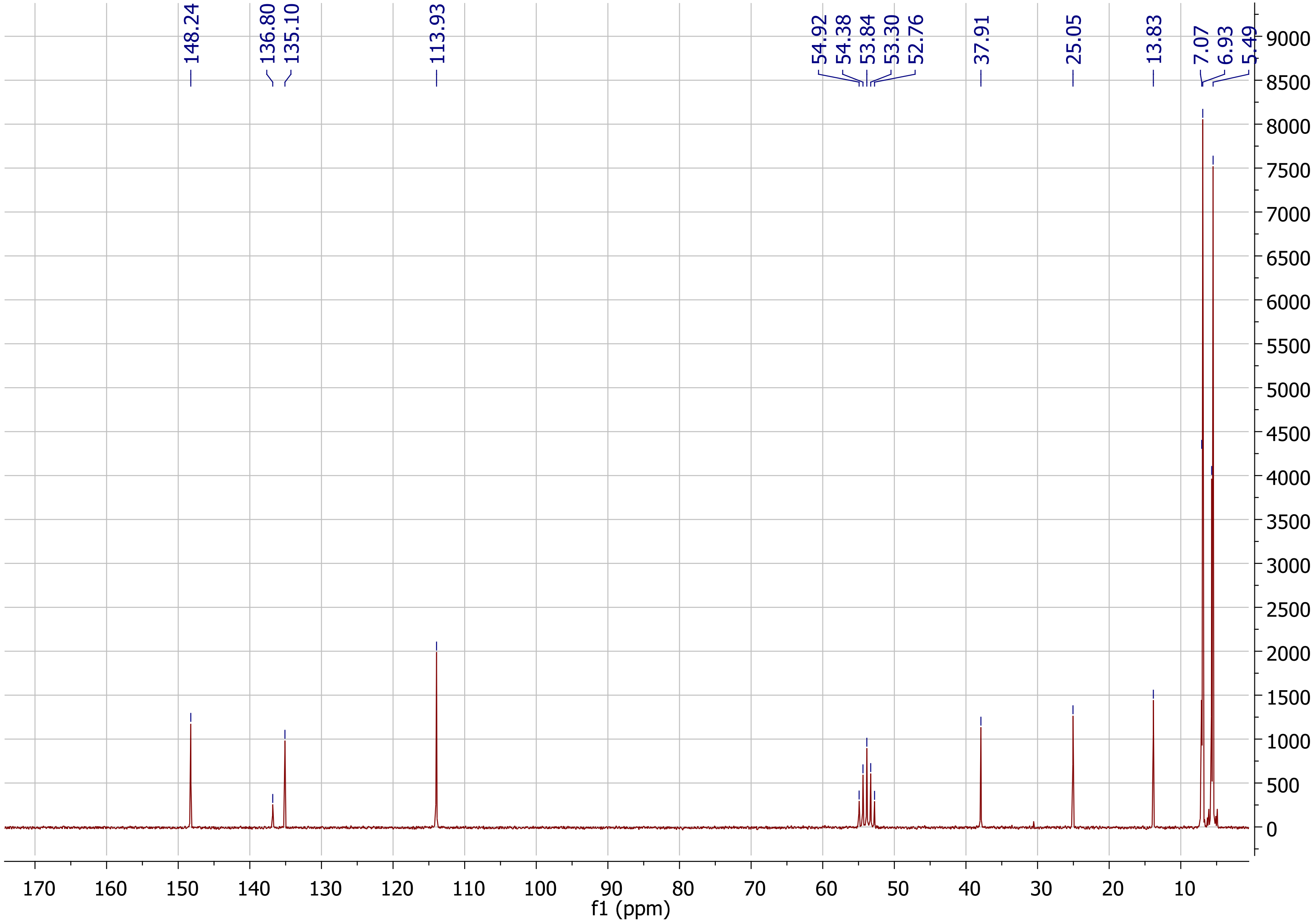


Figure 30: ^{13}C NMR spectra of the compound **11S** in CD_2Cl_2

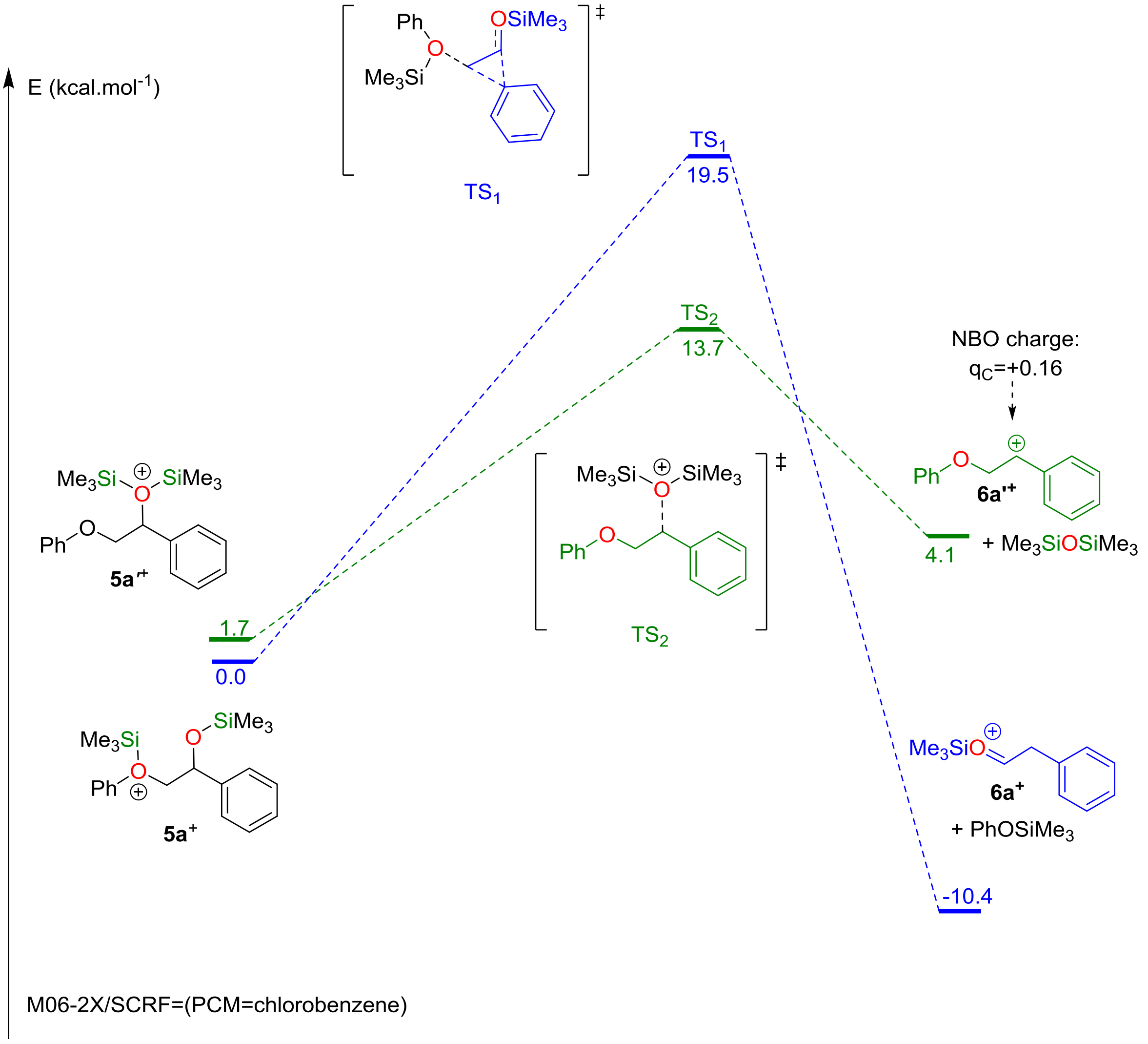


X) Mechanistic investigations from DFT calculations

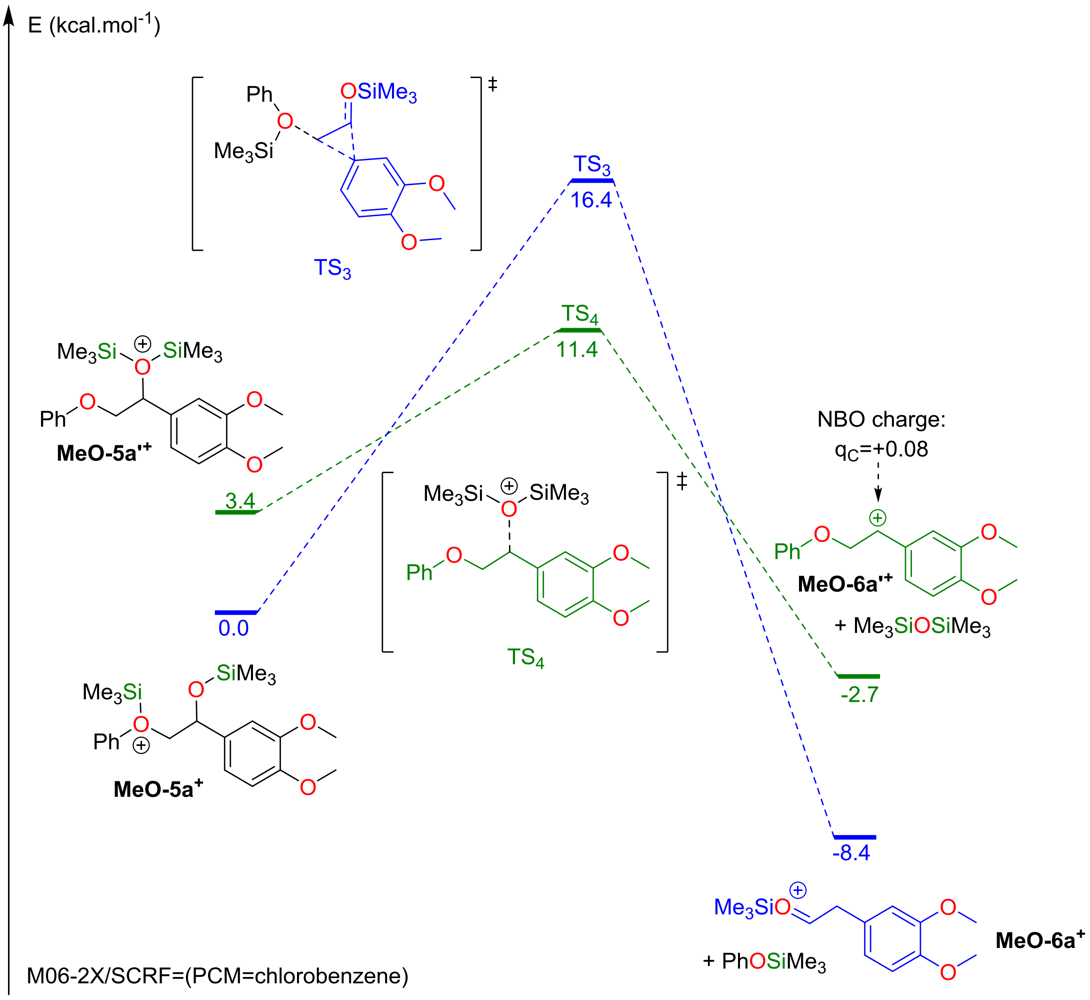
The M06-2X functional was used to optimize the equilibrium molecular structure of the model compounds (obtained by replacing $SiEt_3$ groups with $SiMe_3$)[16]. The 6-31+G* basis set was used for carbon, hydrogen, oxygen and silicon. All geometries were fully optimized without any symmetry constrains. Harmonic vibrational analyses were performed to characterize the structures as minima or transition states. Free energies were calculated within the harmonic approximation for vibrational frequencies. All calculations were fully optimized with solvents effects (PCM = chlorobenzene). All calculations were carried out using the Gaussian09 suite of codes[17] and NBO6.[18]

Computed pathways

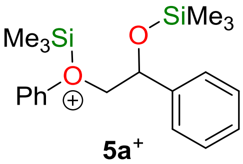
Scheme 9: Computed pathways for the conversion of **5a**$^+$ and **5a'**$^{•+}$ to **6a**$^+$ and **6a'**$^{•+}$



Scheme 10: Computed pathways for the conversion of **MeO-5a$^+$** and **MeO-5a'$^+$** to **MeO-6a$^+$**, **MeO-6a'$^+$**



Computed structures

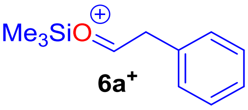


5a$^+$

	X	Y	Z		X	Y	Z
C	-3.065935000000	2.536483000000	-0.544154000000	Si	1.658221000000	2.069243000000	1.010968000000
C	-2.286657000000	1.524557000000	0.011847000000	C	1.799368000000	1.306585000000	2.720184000000
C	-2.202514000000	0.325289000000	-0.673726000000	H	0.819175000000	0.992427000000	3.099568000000
C	-2.843515000000	0.081151000000	-1.877523000000	H	2.465153000000	0.435453000000	2.722848000000
C	-3.613688000000	1.108609000000	-2.423316000000	H	2.212381000000	2.035780000000	3.426318000000
C	-3.726363000000	2.328330000000	-1.756824000000	C	3.355434000000	2.367256000000	0.276830000000
H	-3.151869000000	3.489087000000	-0.031460000000	H	3.871127000000	3.156882000000	0.836110000000
H	-1.748731000000	1.652387000000	0.945006000000	H	3.975191000000	1.464469000000	0.311912000000
H	-2.740999000000	-0.878363000000	-2.376810000000	H	3.281827000000	2.686571000000	-0.768782000000
H	-4.125630000000	0.949782000000	-3.366481000000	C	0.631325000000	3.632724000000	1.011055000000
H	-4.329816000000	3.122197000000	-2.184924000000	H	1.215819000000	4.477901000000	1.391133000000
C	-0.136223000000	-1.047605000000	-0.701015000000	H	0.305033000000	3.877761000000	-0.005858000000
H	-0.177730000000	-0.658137000000	-1.720087000000	H	-0.259364000000	3.532986000000	1.640809000000
H	-0.052807000000	-2.135754000000	-0.721002000000	O	-1.442408000000	-0.730631000000	-0.083058000000
C	0.974035000000	-0.398339000000	0.103215000000	Si	-2.322825000000	-1.977059000000	0.946482000000
H	0.897884000000	-0.751529000000	1.142915000000	C	-3.611544000000	-0.973909000000	1.820452000000
C	2.310528000000	-0.839859000000	-0.460874000000	H	-4.348687000000	-0.558343000000	1.126710000000
C	2.744436000000	-0.357756000000	-1.700149000000	H	-4.139436000000	-1.633744000000	2.519346000000
C	3.114909000000	-1.727282000000	0.255336000000	H	-3.168279000000	-0.157629000000	2.399195000000
C	3.974129000000	-0.761092000000	-2.214107000000	C	-2.984858000000	-3.185404000000	-0.297542000000
H	2.131019000000	0.354285000000	-2.247967000000	H	-3.418977000000	-4.042034000000	0.230583000000
C	4.347624000000	-2.130741000000	-0.258366000000	H	-3.776444000000	-2.731142000000	-0.901834000000
H	2.783213000000	-2.096115000000	1.223924000000	H	-2.206006000000	-3.568193000000	-0.965147000000
C	4.777486000000	-1.647536000000	-1.493369000000	C	-0.975152000000	-2.627019000000	2.045774000000
H	4.311363000000	-0.378980000000	-3.172867000000	H	-0.566184000000	-1.839568000000	2.687263000000
H	4.972866000000	-2.813491000000	0.308792000000	H	-1.416185000000	-3.389227000000	2.699086000000
H	5.738628000000	-1.956710000000	-1.892893000000	H	-0.156799000000	-3.105157000000	1.498183000000
O	0.768754000000	0.991746000000	0.043024000000				

Sum of electronic and zero-point Energies= -1509.216612 Hartree
Sum of electronic and thermal Energies= -1509.187975 Hartree
Sum of electronic and thermal Enthalpies= -1509.187031 Hartree
Sum of electronic and thermal Free Energies= -1509.275589 Hartree

Lowest Frequency: 27.2769 cm^{-1}



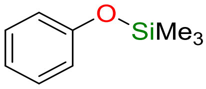
6a⁺

	X	Y	Z
C	3.228566000000	1.542227000000	-0.011655000000
C	1.976663000000	0.967594000000	-0.223472000000
C	1.838800000000	-0.423070000000	-0.248204000000
C	2.956301000000	-1.235650000000	-0.046805000000
C	4.207355000000	-0.658996000000	0.165717000000
C	4.344387000000	0.729013000000	0.183539000000
H	3.330915000000	2.622723000000	-0.000572000000
H	1.109730000000	1.605304000000	-0.380814000000
H	2.852625000000	-2.317398000000	-0.066295000000
H	5.074831000000	-1.294844000000	0.312912000000
H	5.319991000000	1.176282000000	0.346259000000
C	0.459892000000	-1.033979000000	-0.450972000000
H	-0.095714000000	-0.550758000000	-1.258033000000
H	0.553624000000	-2.104489000000	-0.685343000000
C	-0.257797000000	-0.947994000000	0.841440000000
H	0.250008000000	-1.311169000000	1.740543000000

	X	Y	Z
O	-1.391503000000	-0.471363000000	1.026064000000
Si	-2.700089000000	0.191724000000	-0.075270000000
C	-3.060991000000	-1.218207000000	-1.228474000000
H	-2.248586000000	-1.410943000000	-1.935402000000
H	-3.271374000000	-2.136857000000	-0.671498000000
H	-3.955269000000	-0.973288000000	-1.812934000000
C	-4.012447000000	0.535967000000	1.181699000000
H	-3.662845000000	1.262241000000	1.922076000000
H	-4.897486000000	0.952600000000	0.688973000000
H	-4.311149000000	-0.379066000000	1.701887000000
C	-1.954170000000	1.711863000000	-0.838738000000
H	-1.495676000000	2.350938000000	-0.077046000000
H	-1.218000000000	1.495027000000	-1.618039000000
H	-2.761694000000	2.287849000000	-1.305861000000

Sum of electronic and zero-point Energies=	-793.462310 Hartree
Sum of electronic and thermal Energies=	-793.446659 Hartree
Sum of electronic and thermal Enthalpies=	-793.445714 Hartree
Sum of electronic and thermal Free Energies=	-793.506290 Hartree

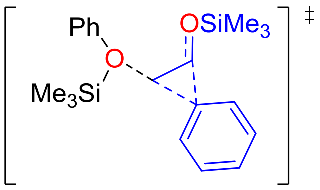
Lowest Frequency: 18.8467 cm^{-1}



	X	Y	Z
C	2.803449000000	-1.205554000000	0.067682000000
C	1.475294000000	-1.210432000000	-0.355690000000
C	0.810157000000	0.000000000000	-0.566922000000
C	1.475294000000	1.210432000000	-0.355691000000
C	2.803449000000	1.205554000000	0.067681000000
C	3.472825000000	0.000000000000	0.282651000000
H	3.315954000000	-2.149725000000	0.228434000000
H	0.944205000000	-2.141754000000	-0.531312000000
H	0.944205000000	2.141754000000	-0.531314000000
H	3.315954000000	2.149726000000	0.228432000000
H	4.507633000000	0.000000000000	0.610829000000
O	-0.485182000000	0.000000000000	-1.007628000000
Si	-1.790700000000	0.000000000000	0.077778000000
C	-1.696720000000	1.537552000000	1.145830000000
C	-1.696720000000	1.537552000000	1.145830000000
H	-0.783547000000	1.548316000000	1.751391000000
H	-1.712520000000	2.446948000000	0.535148000000
H	-2.552380000000	1.574636000000	1.830236000000
C	-1.696720000000	-1.537551000000	1.145831000000
H	-2.552380000000	-1.574634000000	1.830238000000
H	-1.712520000000	-2.446948000000	0.535150000000
H	-0.783547000000	-1.548315000000	1.751392000000
C	-3.301606000000	0.000000000000	-1.019237000000
H	-3.317876000000	-0.886934000000	-1.661343000000
H	-4.216565000000	0.000000000000	-0.416626000000
H	-3.317876000000	0.886933000000	-1.661343000000

Sum of electronic and zero-point Energies=	-715.745165 Hartree
Sum of electronic and thermal Energies=	-715.731973 Hartree
Sum of electronic and thermal Enthalpies=	-715.731028 Hartree
Sum of electronic and thermal Free Energies=	-715.785996 Hartree

Lowest Frequency: 10.459 cm^{-1}

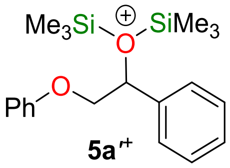


TS$_1$

	X	Y	Z		X	Y	Z
C	-2.243953000000	-0.586775000000	1.453929000000	Si	-2.205281000000	1.254400000000	-1.458373000000
C	-2.921166000000	-1.301353000000	2.442285000000	O	-1.697413000000	-0.293106000000	-0.869283000000
C	-3.739308000000	-2.376805000000	2.097082000000	C	3.552483000000	1.328283000000	1.487502000000
C	-3.881626000000	-2.740089000000	0.756747000000	H	3.569887000000	0.270736000000	1.776852000000
C	-3.209644000000	-2.033566000000	-0.239098000000	H	4.152854000000	1.441687000000	0.578198000000
C	-2.395793000000	-0.959072000000	0.117975000000	H	4.040649000000	1.898260000000	2.286364000000
H	-2.808222000000	-1.013344000000	3.483121000000	C	1.748754000000	3.677180000000	0.532598000000
H	-4.264449000000	-2.929377000000	2.869572000000	H	0.718337000000	4.001875000000	0.352928000000
H	-4.517710000000	-3.576294000000	0.483383000000	H	2.211176000000	4.390533000000	1.223398000000
H	-3.307657000000	-2.297634000000	-1.288159000000	H	2.292529000000	3.724658000000	-0.416900000000
C	0.304859000000	-1.008769000000	-0.965607000000	C	0.802849000000	1.772403000000	2.809213000000
H	-0.072252000000	-2.020694000000	-0.873431000000	H	1.279162000000	2.339113000000	3.617734000000
H	0.400735000000	-0.574213000000	-1.954465000000	H	-0.214241000000	2.161405000000	2.688355000000
C	0.925850000000	-0.352597000000	0.146906000000	H	0.736200000000	0.730098000000	3.142951000000
H	0.626425000000	-0.718105000000	1.134423000000	C	-2.185682000000	2.473630000000	-0.043567000000
C	2.150034000000	-1.200646000000	-0.365021000000	H	-2.957481000000	2.255164000000	0.701859000000
C	2.411446000000	-2.459119000000	0.204114000000	H	-1.207912000000	2.469170000000	0.449706000000
C	3.034468000000	-0.639783000000	-1.300431000000	H	-2.365455000000	3.485121000000	-0.426707000000
C	3.573587000000	-3.134929000000	-0.136167000000	C	-0.936851000000	1.670427000000	-2.760394000000
H	1.712139000000	-2.888112000000	0.918041000000	H	0.052430000000	1.819729000000	-2.313116000000
C	4.194850000000	-1.325600000000	-1.637679000000	H	-0.870709000000	0.891616000000	-3.528507000000
H	2.816487000000	0.335869000000	-1.727768000000	H	-1.220798000000	2.602909000000	-3.261294000000
C	4.462712000000	-2.566217000000	-1.054606000000	C	-3.924598000000	1.011755000000	-2.143391000000
H	3.790961000000	-4.099402000000	0.310145000000	H	-4.613823000000	0.669959000000	-1.363032000000
H	4.891096000000	-0.896557000000	-2.350251000000	H	-4.310923000000	1.956999000000	-2.540740000000
H	5.371791000000	-3.097795000000	-1.318330000000	H	-3.929739000000	0.274125000000	-2.952958000000
O	1.052205000000	1.006042000000	0.024676000000	H	-1.609739000000	0.258402000000	1.708340000000
Si	1.807445000000	1.955632000000	1.239287000000				

Sum of electronic and zero-point Energies= -1509.185847 Hartree
Sum of electronic and thermal Energies= -1509.156852 Hartree
Sum of electronic and thermal Enthalpies= -1509.155908 Hartree
Sum of electronic and thermal Free Energies= -1509.244688 Hartree

Lowest Frequencies: -460.5262 cm^{-1}
28.3989 cm^{-1}
36.7053 cm^{-1}

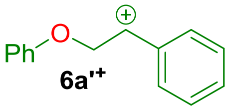


5a$^{\cdot+}$

	X	Y	Z
C	-4.895931000000	-1.989810000000	-0.169415000000
C	-3.521400000000	-1.771680000000	-0.034745000000
C	-3.078572000000	-0.556659000000	0.486898000000
C	-3.990763000000	0.428824000000	0.873263000000
C	-5.353274000000	0.195462000000	0.731978000000
C	-5.814133000000	-1.015892000000	0.208186000000
H	-5.240837000000	-2.936397000000	-0.574320000000
H	-2.826600000000	-2.548222000000	-0.335053000000
H	-3.616991000000	1.361631000000	1.283844000000
H	-6.059374000000	0.962327000000	1.035991000000
H	-6.878748000000	-1.195919000000	0.100269000000
O	-1.751494000000	-0.236544000000	0.649048000000
C	-0.794486000000	-1.214574000000	0.311241000000
H	-0.861288000000	-1.503769000000	-0.742354000000
H	-0.918231000000	-2.120170000000	0.919973000000
C	0.567476000000	-0.647968000000	0.656412000000
H	0.593159000000	-0.512456000000	1.738521000000
C	1.680219000000	-1.556893000000	0.200636000000
C	2.103408000000	-1.562253000000	-1.131456000000
C	2.268647000000	-2.431347000000	1.116349000000
C	3.113270000000	-2.428039000000	-1.541605000000
H	1.663593000000	-0.875506000000	-1.850641000000
C	3.275254000000	-3.303920000000	0.704159000000
H	1.942049000000	-2.431473000000	2.154173000000
C	3.700982000000	-3.299443000000	-0.623213000000
H	3.443772000000	-2.419908000000	-2.575472000000
H	3.729095000000	-3.980146000000	1.421573000000
H	4.490716000000	-3.972056000000	-0.943069000000
Si	2.135208000000	1.638541000000	0.889272000000
Si	-0.214978000000	1.530652000000	-1.218453000000
O	0.760199000000	0.718121000000	0.100014000000
C	1.092260000000	2.319511000000	-2.296087000000
H	0.545845000000	2.877153000000	-3.067541000000
H	1.777728000000	3.020738000000	-1.818107000000
H	1.682746000000	1.554312000000	-2.812209000000
C	-1.356148000000	2.719507000000	-0.348814000000
H	-2.358558000000	2.631514000000	-0.782742000000
H	-1.432177000000	2.480436000000	0.715824000000
H	-1.025259000000	3.756489000000	-0.456065000000
C	-1.109824000000	0.330818000000	-2.329460000000
H	-1.386421000000	0.939165000000	-3.201426000000
H	-0.489874000000	-0.488212000000	-2.705172000000
H	-2.035340000000	-0.069719000000	-1.909088000000
C	1.578728000000	3.412740000000	1.016760000000
H	2.396412000000	3.944180000000	1.520590000000
H	1.383463000000	3.933653000000	0.078093000000
H	0.695082000000	3.496071000000	1.657510000000
C	3.659799000000	1.332986000000	-0.131371000000
H	4.437508000000	2.028775000000	0.207021000000
H	4.027518000000	0.313574000000	0.024655000000
H	3.514207000000	1.487254000000	-1.203244000000
C	2.316102000000	0.958488000000	2.614033000000
H	2.698165000000	-0.065674000000	2.647082000000
H	3.058582000000	1.596965000000	3.109686000000
H	1.392904000000	1.023363000000	3.198884000000

Sum of electronic and zero-point Energies=	-1509.217110 Hartree
Sum of electronic and thermal Energies=	-1509.189523 Hartree
Sum of electronic and thermal Enthalpies=	-1509.188579 Hartree
Sum of electronic and thermal Free Energies=	-1509.273454 Hartree

Lowest Frequency: 31.6699 cm^{-1}

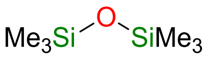


6a'$^{+}$

	X	Y	Z		X	Y	Z
C	4.312650000000	0.388660000000	1.208583000000	H	0.155276000000	0.526250000000	0.886210000000
C	3.041956000000	-0.185562000000	1.214239000000	C	-1.170137000000	-0.867029000000	0.000081000000
C	2.422353000000	-0.465196000000	-0.000037000000	H	-1.084214000000	-1.954505000000	0.000004000000
C	3.041886000000	-0.185348000000	-1.214297000000	C	-2.433905000000	-0.302813000000	0.000047000000
C	4.312581000000	0.388872000000	-1.208614000000	C	-2.631131000000	1.114694000000	0.000129000000
C	4.947287000000	0.677708000000	-0.000008000000	C	-3.566108000000	-1.175976000000	-0.000096000000
H	4.808027000000	0.604903000000	2.150112000000	C	-3.907917000000	1.623121000000	0.000115000000
H	2.534325000000	-0.427138000000	2.143647000000	H	-1.775345000000	1.782811000000	0.000228000000
H	2.534202000000	-0.426755000000	-2.143721000000	C	-4.841328000000	-0.650557000000	-0.000135000000
H	4.807909000000	0.605293000000	-2.150128000000	H	-3.405418000000	-2.250154000000	-0.000180000000
H	5.937756000000	1.121885000000	0.000010000000	C	-5.005563000000	0.740912000000	-0.000021000000
O	1.165431000000	-1.060561000000	-0.000061000000	H	-4.075816000000	2.693887000000	0.000204000000
C	0.111193000000	-0.130007000000	0.000071000000	H	-5.708070000000	-1.300990000000	-0.000252000000
H	0.155202000000	0.526419000000	-0.885943000000	H	-6.010192000000	1.153696000000	-0.000053000000

Sum of electronic and zero-point Energies=	-615.797271 Hartree
Sum of electronic and thermal Energies=	-615.784742 Hartree
Sum of electronic and thermal Enthalpies=	-615.783798 Hartree
Sum of electronic and thermal Free Energies=	-615.840179 Hartree

Lowest Frequency: 2.8862 cm^{-1}

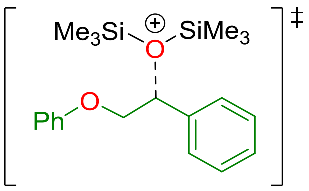


	X	Y	Z
Si	0.000000000000	1.544447000000	0.085816000000
C	-1.722276000000	1.964897000000	-0.532654000000
H	-2.467549000000	1.823866000000	0.258118000000
H	-1.769576000000	3.010718000000	-0.858670000000
H	-2.007511000000	1.335769000000	-1.383376000000
C	0.502156000000	2.705732000000	1.465858000000
H	-0.202261000000	2.643412000000	2.302725000000
H	1.499976000000	2.457137000000	1.843678000000
H	0.520547000000	3.743985000000	1.115412000000
C	1.222998000000	1.633519000000	-1.338686000000
H	2.235413000000	1.374750000000	-1.008184000000
H	0.945296000000	0.946962000000	-2.147783000000
H	1.253164000000	2.645676000000	-1.759122000000
O	0.000000000000	0.000000000000	0.717165000000

	X	Y	Z
Si	0.000000000000	-1.544447000000	0.085816000000
C	-0.502156000000	-2.705732000000	1.465858000000
H	-0.520547000000	-3.743985000000	1.115412000000
H	0.202261000000	-2.643412000000	2.302725000000
H	-1.499976000000	-2.457137000000	1.843678000000
C	1.722276000000	-1.964897000000	-0.532654000000
H	2.007511000000	-1.335769000000	-1.383376000000
H	2.467549000000	-1.823866000000	0.258118000000
H	1.769576000000	-3.010718000000	-0.858670000000
C	-1.222998000000	-1.633519000000	-1.338686000000
H	-2.235413000000	-1.374750000000	-1.008184000000
H	-0.945296000000	-0.946962000000	-2.147783000000
H	-1.253164000000	-2.645676000000	-1.759122000000

Sum of electronic and zero-point Energies= -615.797271 Hartree
Sum of electronic and thermal Energies= -615.784742 Hartree
Sum of electronic and thermal Enthalpies= -615.783798 Hartree
Sum of electronic and thermal Free Energies= -615.840179 Hartree

Lowest Frequency: 32.4296 cm^{-1}



TS$_2$

	X	Y	Z
C	5.074632000000	-0.536433000000	-0.566294000000
C	3.756792000000	-0.235167000000	-0.886411000000
C	2.729878000000	-1.064701000000	-0.428760000000
C	3.012718000000	-2.193993000000	0.337657000000
C	4.345383000000	-2.483758000000	0.648161000000
C	5.376460000000	-1.662795000000	0.205046000000
H	5.870474000000	0.110333000000	-0.922798000000
H	3.504271000000	0.630757000000	-1.491092000000
H	2.229210000000	-2.851615000000	0.698098000000
H	4.567244000000	-3.363283000000	1.244769000000
H	6.406789000000	-1.895861000000	0.452969000000
O	1.459402000000	-0.673104000000	-0.778882000000
C	0.394982000000	-1.503503000000	-0.409479000000
H	0.316929000000	-1.613363000000	0.682453000000
H	0.513424000000	-2.517181000000	-0.834850000000
C	-0.850118000000	-0.941195000000	-0.986118000000
H	-0.715320000000	-0.290060000000	-1.841697000000
C	-2.144114000000	-1.441927000000	-0.733814000000
C	-2.366198000000	-2.557975000000	0.110902000000
C	-3.240393000000	-0.821623000000	-1.382350000000
C	-3.648953000000	-3.038037000000	0.290307000000
H	-1.532961000000	-3.051685000000	0.602967000000
C	-4.525362000000	-1.289688000000	-1.172762000000
H	-3.063807000000	0.034773000000	-2.027432000000
C	-4.724358000000	-2.396944000000	-0.341027000000
H	-3.827201000000	-3.901379000000	0.921709000000
Si	-0.073675000000	2.320316000000	-0.912713000000
Si	-0.745214000000	1.068861000000	1.756126000000
O	-0.701198000000	1.043814000000	0.046501000000
C	-1.324886000000	2.750231000000	2.344158000000
H	-1.391808000000	2.721673000000	3.438701000000
H	-0.641802000000	3.563551000000	2.079787000000
H	-2.319781000000	2.991090000000	1.954267000000
C	0.966058000000	0.692820000000	2.430157000000
H	0.880203000000	0.296741000000	3.448973000000
H	1.511047000000	-0.043421000000	1.828436000000
H	1.583836000000	1.595134000000	2.476361000000
C	-1.977378000000	-0.213117000000	2.346087000000
H	-2.172588000000	-0.011825000000	3.406615000000
H	-2.933900000000	-0.149575000000	1.815106000000
H	-1.609211000000	-1.241393000000	2.281763000000
C	1.537855000000	2.896510000000	-0.153710000000
H	2.035919000000	3.590939000000	-0.840683000000
H	1.398859000000	3.418967000000	0.798693000000
H	2.209281000000	2.047430000000	0.017245000000
C	-1.355314000000	3.683165000000	-0.994925000000
H	-1.505520000000	4.196038000000	-0.041322000000
H	-1.037670000000	4.431105000000	-1.731336000000
H	-2.321028000000	3.282076000000	-1.323997000000
C	0.232477000000	1.731227000000	-2.666845000000
H	-0.684342000000	1.445762000000	-3.196462000000
H	0.649371000000	2.588157000000	-3.211230000000
H	0.958659000000	0.915703000000	-2.734430000000
H	-5.731248000000	-2.772482000000	-0.185170000000
H	-5.369491000000	-0.809845000000	-1.655027000000

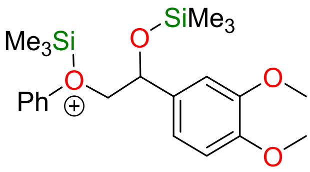
Sum of electronic and zero-point Energies= -1509.196003 Hartree

Sum of electronic and thermal Energies= -1509.167726 Hartree

Sum of electronic and thermal Enthalpies= -1509.166782 Hartree

Sum of electronic and thermal Free Energies= -1509.253686 Hartree

Lowest Frequencies: -148.4961 cm^{-1}
27.0383 cm^{-1}
37.3375 cm^{-1}

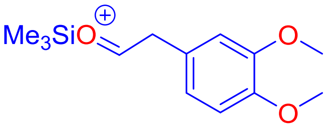


MeO-5a$^+$

	X	Y	Z		X	Y	Z
C	3.946138000000	2.268387000000	1.099699000000	H	-2.319364000000	3.576241000000	-1.900611000000
C	3.226730000000	1.336274000000	0.355224000000	H	-2.756543000000	1.946888000000	-1.349300000000
C	2.892388000000	0.140900000000	0.967650000000	H	-2.079874000000	3.119716000000	-0.203851000000
C	3.230292000000	-0.173522000000	2.274340000000	C	0.929768000000	3.599000000000	-1.547761000000
C	3.945051000000	0.774831000000	3.006814000000	H	0.547929000000	4.482637000000	-2.070865000000
C	4.302837000000	1.988310000000	2.420153000000	H	1.106429000000	3.875791000000	-0.502203000000
H	4.221006000000	3.216072000000	0.647558000000	H	1.892557000000	3.334877000000	-1.999241000000
H	2.915717000000	1.525822000000	-0.665868000000	O	2.180340000000	-0.829724000000	0.195841000000
H	2.937869000000	-1.124367000000	2.711316000000	Si	3.133482000000	-2.157410000000	-0.644843000000
H	4.219816000000	0.560026000000	4.034132000000	C	4.686044000000	-1.299875000000	-1.179364000000
H	4.859408000000	2.721430000000	2.994956000000	H	5.287129000000	-0.969141000000	-0.326998000000
C	0.742047000000	-1.002121000000	0.503786000000	H	5.285690000000	-2.012831000000	-1.757925000000
H	0.594315000000	-0.578633000000	1.498814000000	H	4.477262000000	-0.438961000000	-1.821590000000
H	0.548620000000	-2.076677000000	0.523197000000	C	3.369939000000	-3.443699000000	0.673510000000
C	-0.097201000000	-0.286750000000	-0.538439000000	H	3.800652000000	-4.342585000000	0.217717000000
H	0.124181000000	-0.721088000000	-1.524401000000	H	4.062538000000	-3.098517000000	1.447456000000
C	-1.557508000000	-0.526795000000	-0.219578000000	H	2.426681000000	-3.734202000000	1.147323000000
C	-2.149519000000	0.120904000000	0.872736000000	C	2.018861000000	-2.670477000000	-2.040250000000
C	-2.324536000000	-1.391518000000	-0.991001000000	H	1.864198000000	-1.855901000000	-2.755000000000
C	-3.481823000000	-0.090785000000	1.181107000000	H	2.516773000000	-3.488673000000	-2.574539000000
H	-1.583313000000	0.821154000000	1.483087000000	H	1.046091000000	-3.047041000000	-1.708409000000
C	-3.670064000000	-1.621608000000	-0.687724000000	O	-5.543642000000	-1.132369000000	0.789172000000
H	-1.880095000000	-1.894098000000	-1.847410000000	O	-4.034778000000	0.529711000000	2.267292000000
C	-4.258223000000	-0.977772000000	0.400756000000	C	-4.910604000000	1.607626000000	1.930949000000
H	-4.246599000000	-2.299999000000	-1.305784000000	H	-5.744725000000	1.252590000000	1.318788000000
O	0.272446000000	1.069663000000	-0.507468000000	H	-5.286625000000	2.004325000000	2.874175000000
Si	-0.291010000000	2.186199000000	-1.656701000000	H	-4.357196000000	2.387455000000	1.395119000000
C	-0.257151000000	1.350572000000	-3.335950000000	C	-6.355983000000	-2.030054000000	0.047468000000
H	0.730095000000	0.923009000000	-3.548796000000	H	-5.946207000000	-3.045248000000	0.082864000000
H	-1.003180000000	0.550553000000	-3.411573000000	H	-7.333462000000	-2.012120000000	0.527338000000
H	-0.479520000000	2.081000000000	-4.122449000000	H	-6.450225000000	-1.702732000000	-0.993640000000
C	-2.025414000000	2.755160000000	-1.235869000000				

Sum of electronic and zero-point Energies=	-1738.108854 Hartree
Sum of electronic and thermal Energies=	-1738.074783 Hartree
Sum of electronic and thermal Enthalpies=	-1738.073839 Hartree
Sum of electronic and thermal Free Energies=	-1738.176013 Hartree

Lowest Frequency: 9.6318 cm^{-1}



MeO-6a$^+$

	X	Y	Z		X	Y	Z
C	1.833712000000	1.395944000000	-0.301752000000	H	-5.404201000000	-0.867591000000	-1.669395000000
C	0.591171000000	0.785550000000	-0.482266000000	C	-5.190086000000	0.758610000000	1.259894000000
C	0.443783000000	-0.589540000000	-0.325265000000	H	-4.756179000000	1.505504000000	1.931766000000
C	1.556550000000	-1.360397000000	0.034068000000	H	-6.077305000000	1.197753000000	0.791339000000
C	2.794180000000	-0.766535000000	0.221973000000	H	-5.510401000000	-0.102743000000	1.853555000000
C	2.942937000000	0.630070000000	0.059525000000	C	-3.172854000000	1.680239000000	-0.925353000000
H	1.921780000000	2.467537000000	-0.436086000000	H	-2.569756000000	2.283731000000	-0.238982000000
H	-0.260434000000	1.400099000000	-0.761619000000	H	-2.556845000000	1.374745000000	-1.776288000000
H	1.481629000000	-2.436630000000	0.166894000000	H	-3.968053000000	2.327682000000	-1.313933000000
C	-0.926572000000	-1.232619000000	-0.491776000000	O	3.853926000000	-1.530787000000	0.613960000000
H	-1.495578000000	-0.789784000000	-1.312253000000	O	4.179302000000	1.119418000000	0.282274000000
H	-0.821313000000	-2.310396000000	-0.671156000000	C	4.835350000000	-1.745017000000	-0.404792000000
C	-1.597435000000	-1.053739000000	0.814492000000	H	5.245435000000	-0.793683000000	-0.754098000000
H	-1.093347000000	-1.431512000000	1.709253000000	H	5.623561000000	-2.343169000000	0.052227000000
O	-2.672025000000	-0.459104000000	1.021770000000	H	4.389876000000	-2.294470000000	-1.241518000000
Si	-3.976299000000	0.255278000000	-0.042264000000	C	4.377142000000	2.518971000000	0.134260000000
C	-4.514917000000	-1.170045000000	-1.104467000000	H	3.750961000000	3.076708000000	0.838550000000
H	-3.755240000000	-1.479974000000	-1.828069000000	H	5.427880000000	2.695411000000	0.358025000000
H	-4.790875000000	-2.033288000000	-0.490391000000	H	4.159212000000	2.835019000000	-0.891389000000

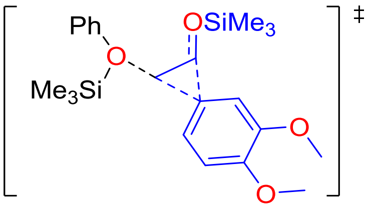
Sum of electronic and zero-point Energies= -1022.353648 Hartree

Sum of electronic and thermal Energies= -1022.332889 Hartree

Sum of electronic and thermal Enthalpies= -1022.331945 Hartree

Sum of electronic and thermal Free Energies= -1022.403486 Hartree

Lowest Frequency: 22.223 cm^{-1}



TS$_3$

	X	Y	Z		X	Y	Z
C	-2.906892000000	-1.077227000000	1.245050000000	C	-0.484306000000	4.145565000000	0.889539000000
C	-3.405870000000	-1.963073000000	2.199709000000	H	0.185852000000	4.389870000000	0.058127000000
C	-3.768240000000	-3.259364000000	1.833189000000	H	-1.514915000000	4.185178000000	0.520590000000
C	-3.630546000000	-3.672053000000	0.506851000000	H	-0.371101000000	4.920153000000	1.655549000000
C	-3.133920000000	-2.795195000000	-0.456062000000	C	-1.251503000000	1.952124000000	2.958377000000
C	-2.778627000000	-1.501906000000	-0.077001000000	H	-1.094236000000	2.589719000000	3.836376000000
H	-3.510415000000	-1.635899000000	3.229875000000	H	-2.300573000000	2.055050000000	2.658450000000
H	-4.157188000000	-3.946505000000	2.577734000000	H	-1.082566000000	0.915946000000	3.275585000000
H	-3.912508000000	-4.680011000000	0.218578000000	C	-3.788172000000	1.760626000000	-0.326527000000
H	-3.020868000000	-3.094327000000	-1.494108000000	H	-4.497061000000	1.259270000000	0.340551000000
C	-0.176402000000	-0.617941000000	-0.936348000000	H	-2.943562000000	2.127845000000	0.265628000000
H	-0.131738000000	-1.701385000000	-0.955212000000	H	-4.296058000000	2.628220000000	-0.764662000000
H	-0.159427000000	-0.082011000000	-1.877876000000	C	-2.008094000000	1.530430000000	-2.836569000000
C	0.095364000000	0.106975000000	0.280290000000	H	-1.205138000000	2.014139000000	-2.268606000000
H	-0.118377000000	-0.441809000000	1.204326000000	H	-1.570369000000	0.860261000000	-3.584657000000
C	1.569000000000	-0.132304000000	-0.151003000000	H	-2.551147000000	2.314643000000	-3.376529000000
C	2.300716000000	-1.223718000000	0.362009000000	C	-4.608699000000	-0.175253000000	-2.595541000000
C	2.201533000000	0.793838000000	-0.991731000000	H	-5.236785000000	-0.745048000000	-1.901777000000
C	3.635268000000	-1.371376000000	0.055227000000	H	-5.241139000000	0.579279000000	-3.076688000000
H	1.834139000000	-1.959775000000	1.012655000000	H	-4.244538000000	-0.859015000000	-3.369555000000
C	3.545426000000	0.655427000000	-1.307612000000	H	-2.622591000000	-0.062510000000	1.511503000000
H	1.639142000000	1.640598000000	-1.377171000000	O	4.327253000000	-2.447371000000	0.519692000000
C	4.273049000000	-0.428608000000	-0.798429000000	O	5.558617000000	-0.669846000000	-1.061491000000
H	4.019014000000	1.383008000000	-1.955205000000	C	5.268354000000	-2.144361000000	1.556165000000
O	-0.331073000000	1.415505000000	0.258922000000	H	4.741857000000	-1.751819000000	2.432855000000
Si	-0.082254000000	2.466306000000	1.588144000000	H	5.755218000000	-3.086174000000	1.807589000000
Si	-3.191248000000	0.644771000000	-1.699589000000	H	6.011469000000	-1.422974000000	1.206651000000
O	-2.247397000000	-0.649313000000	-1.026748000000	C	6.258763000000	0.222974000000	-1.925908000000
C	1.696284000000	2.312009000000	2.150956000000	H	6.287850000000	1.229032000000	-1.496810000000
H	1.936017000000	1.289188000000	2.465098000000	H	7.267707000000	-0.176952000000	-2.003206000000
H	2.397413000000	2.596603000000	1.358887000000	H	5.790757000000	0.244790000000	-2.914534000000
H	1.870789000000	2.971009000000	3.009435000000				

Sum of electronic and zero-point Energies= -1738.082123 Hartree

Sum of electronic and thermal Energies= -1738.047476 Hartree

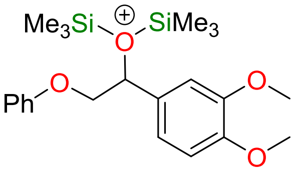
Sum of electronic and thermal Enthalpies= -1738.046532 Hartree

Sum of electronic and thermal Free Energies= -1738.149804 Hartree

Lowest Frequency: -510.9628 $\mathrm{cm^{-1}}$

13.7989 $\mathrm{cm^{-1}}$

25.5911 $\mathrm{cm^{-1}}$



MeO-5a$^{\cdot+}$

	X	Y	Z		X	Y	Z
C	4.556336000000	-3.432720000000	-0.185271000000	H	-0.582475000000	1.748955000000	2.870129000000
C	3.386778000000	-2.681109000000	-0.332922000000	C	2.969249000000	2.184858000000	0.902683000000
C	3.488930000000	-1.311901000000	-0.575914000000	H	3.808268000000	1.639529000000	1.349010000000
C	4.739820000000	-0.696405000000	-0.672300000000	H	3.095036000000	2.158779000000	-0.183721000000
C	5.892160000000	-1.458388000000	-0.522321000000	H	3.017136000000	3.224603000000	1.238644000000
C	5.807297000000	-2.831851000000	-0.276546000000	C	1.660025000000	-0.268323000000	2.269967000000
H	4.475391000000	-4.499131000000	0.002292000000	H	2.053703000000	0.031820000000	3.251429000000
H	2.423695000000	-3.173689000000	-0.258725000000	H	0.756149000000	-0.852995000000	2.464219000000
H	4.789542000000	0.369829000000	-0.869871000000	H	2.417742000000	-0.901295000000	1.801892000000
H	6.862490000000	-0.977568000000	-0.601647000000	C	0.687942000000	4.175312000000	-0.401159000000
H	6.709575000000	-3.423747000000	-0.161924000000	H	0.198697000000	5.055692000000	-0.837742000000
O	2.402176000000	-0.483551000000	-0.724050000000	H	0.884392000000	4.403152000000	0.647478000000
C	1.119206000000	-1.066022000000	-0.660765000000	H	1.643595000000	4.046586000000	-0.918954000000
H	0.939919000000	-1.546332000000	0.306864000000	C	-2.127779000000	2.810607000000	0.054968000000
H	0.983546000000	-1.820974000000	-1.446255000000	H	-2.533427000000	3.822330000000	-0.063768000000
C	0.114968000000	0.030956000000	-0.944911000000	H	-2.814598000000	2.109810000000	-0.431644000000
H	0.277129000000	0.356863000000	-1.973460000000	H	-2.106766000000	2.578323000000	1.122746000000
C	-1.305065000000	-0.420771000000	-0.746098000000	C	-0.571897000000	2.552041000000	-2.602715000000
C	-1.837751000000	-0.560570000000	0.542552000000	H	-1.280514000000	1.784116000000	-2.924311000000
C	-2.103454000000	-0.724570000000	-1.842995000000	H	-0.942524000000	3.512453000000	-2.982997000000
C	-3.146677000000	-0.968530000000	0.728950000000	H	0.400975000000	2.372127000000	-3.071671000000
H	-1.257373000000	-0.324463000000	1.431290000000	O	-3.660949000000	-1.021207000000	1.992003000000
C	-3.422907000000	-1.151491000000	-1.672006000000	O	-5.230099000000	-1.624250000000	-0.113685000000
H	-1.705848000000	-0.631280000000	-2.850624000000	C	-3.888815000000	-2.345373000000	2.483046000000
C	-3.960762000000	-1.263674000000	-0.389800000000	H	-4.577510000000	-2.888832000000	1.831000000000
H	-4.025028000000	-1.374103000000	-2.544928000000	H	-2.937167000000	-2.883373000000	2.559442000000
Si	-0.453918000000	2.744576000000	-0.754019000000	H	-4.328429000000	-2.231545000000	3.473775000000
Si	1.375811000000	1.361520000000	1.409155000000	C	-6.092717000000	-1.913774000000	-1.205842000000
O	0.381150000000	1.243279000000	-0.120396000000	H	-7.055958000000	-2.163546000000	-0.763913000000
C	0.282142000000	2.347176000000	2.561158000000	H	-6.200404000000	-1.040124000000	-1.857091000000
H	0.879619000000	2.539853000000	3.461540000000	H	-5.717613000000	-2.765981000000	-1.782350000000
H	-0.077851000000	3.311776000000	2.200429000000				

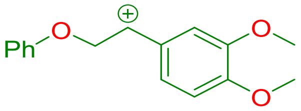
Sum of electronic and zero-point Energies= -1738.108662 Hartree

Sum of electronic and thermal Energies= -1738.075993 Hartree

Sum of electronic and thermal Enthalpies= -1738.075049 Hartree

Sum of electronic and thermal Free Energies= -1738.170594 Hartree

Lowest Frequency: 27.2052 cm^{-1}



MeO-6a$^{\bullet+}$

	X	Y	Z
C	-5.896054000000	0.374776000000	-1.112461000000
C	-4.623707000000	-0.193027000000	-1.172569000000
C	-3.933354000000	-0.433908000000	0.011930000000
C	-4.486839000000	-0.119600000000	1.249955000000
C	-5.759505000000	0.448014000000	1.299387000000
C	-6.463714000000	0.697091000000	0.120623000000
H	-6.444899000000	0.560651000000	-2.030621000000
H	-4.167867000000	-0.461133000000	-2.121455000000
H	-3.927357000000	-0.333543000000	2.156223000000
H	-6.202858000000	0.689199000000	2.260761000000
H	-7.455755000000	1.135639000000	0.164360000000
O	-2.679690000000	-1.026931000000	-0.042433000000
C	-1.620888000000	-0.094044000000	-0.090719000000
H	-1.630218000000	0.553753000000	0.799001000000
H	-1.716862000000	0.557426000000	-0.975581000000
C	-0.348548000000	-0.859193000000	-0.177512000000
H	-0.469803000000	-1.934864000000	-0.306603000000
C	0.919872000000	-0.345078000000	-0.128083000000
C	1.171254000000	1.061563000000	0.034689000000
C	2.043718000000	-1.236738000000	-0.255118000000
C	2.445231000000	1.549360000000	0.051224000000
H	0.338777000000	1.750321000000	0.142781000000
C	3.320635000000	-0.764391000000	-0.237349000000
H	1.878446000000	-2.303193000000	-0.380415000000
C	3.540841000000	0.650856000000	-0.093965000000
H	2.624716000000	2.610805000000	0.168482000000
O	4.382801000000	-1.582351000000	-0.427930000000
O	4.789103000000	1.022744000000	-0.114961000000
C	5.131706000000	-1.885167000000	0.759102000000
H	5.939445000000	-2.543387000000	0.442790000000
H	5.545989000000	-0.974557000000	1.199935000000
H	4.489482000000	-2.399624000000	1.480566000000
C	5.144835000000	2.412345000000	0.005388000000
H	4.809812000000	2.798229000000	0.970078000000
H	6.229674000000	2.431467000000	-0.054756000000
H	4.708673000000	2.977961000000	-0.820085000000

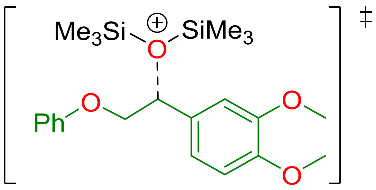
Sum of electronic and zero-point Energies= -844.703174 Hartree

Sum of electronic and thermal Energies= -844.685258 Hartree

Sum of electronic and thermal Enthalpies= -844.684313 Hartree

Sum of electronic and thermal Free Energies= -844.751570 Hartree

Lowest Frequency: 22.4212 cm^{-1}



TS$_4$

	X	Y	Z
C	5.712718000000	-1.446993000000	-1.052063000000
C	4.473971000000	-0.834722000000	-1.196286000000
C	3.337992000000	-1.440767000000	-0.652661000000
C	3.433602000000	-2.653731000000	0.027557000000
C	4.688378000000	-3.256330000000	0.162889000000
C	5.827202000000	-2.661755000000	-0.369703000000
H	6.593381000000	-0.974967000000	-1.476915000000
H	4.364463000000	0.105842000000	-1.728568000000
H	2.561797000000	-3.138479000000	0.453299000000
H	4.763099000000	-4.201135000000	0.692736000000
H	6.796029000000	-3.137525000000	-0.258603000000
O	2.164129000000	-0.750147000000	-0.828167000000
C	0.971603000000	-1.370240000000	-0.424806000000
H	0.961886000000	-1.574909000000	0.655421000000
H	0.834137000000	-2.330619000000	-0.950230000000
C	-0.156378000000	-0.481974000000	-0.822113000000
H	0.036857000000	0.133783000000	-1.691291000000
C	-1.507727000000	-0.739796000000	-0.508422000000
C	-1.910461000000	-1.851295000000	0.264294000000
C	-2.498505000000	0.138722000000	-1.020199000000
C	-3.245569000000	-2.082869000000	0.523478000000
H	-1.174926000000	-2.551917000000	0.649154000000
C	-3.827854000000	-0.057870000000	-0.741796000000
H	-2.211558000000	1.001515000000	-1.616522000000
C	-4.217416000000	-1.180326000000	0.048017000000
H	-3.537511000000	-2.946937000000	1.107003000000
Si	1.210135000000	2.438850000000	-0.678253000000
Si	0.547796000000	1.127355000000	1.969507000000
O	0.435977000000	1.204727000000	0.251745000000
C	0.322585000000	2.846515000000	2.676386000000
H	0.342488000000	2.759780000000	3.769889000000
H	1.116674000000	3.543611000000	2.392031000000
H	-0.642235000000	3.279968000000	2.392294000000
C	2.223202000000	0.430450000000	2.447284000000
H	2.146904000000	-0.066154000000	3.421920000000
H	2.601547000000	-0.301158000000	1.724824000000
H	2.975653000000	1.220700000000	2.535384000000
C	-0.825283000000	0.038465000000	2.624444000000
H	-0.873731000000	0.206933000000	3.707453000000
H	-1.803343000000	0.293890000000	2.203348000000
H	-0.648251000000	-1.031122000000	2.478150000000
C	2.952392000000	2.648118000000	-0.030093000000
H	3.515794000000	3.295413000000	-0.712526000000
H	2.990788000000	3.105523000000	0.963662000000
H	3.462029000000	1.679074000000	0.017776000000
C	0.180751000000	3.997118000000	-0.546960000000
H	0.237847000000	4.476358000000	0.433657000000
H	0.530913000000	4.719549000000	-1.293956000000
H	-0.872276000000	3.779979000000	-0.761802000000
C	1.266726000000	1.947953000000	-2.486549000000
H	0.274194000000	1.861627000000	-2.944291000000
H	1.781497000000	2.763670000000	-3.009540000000
H	1.831764000000	1.029429000000	-2.671318000000
O	-4.761427000000	0.837355000000	-1.159145000000
O	-5.516215000000	-1.287015000000	0.283993000000
C	-5.593573000000	0.381537000000	-2.233310000000
H	-6.163270000000	-0.502282000000	-1.935383000000
H	-6.273555000000	1.202892000000	-2.456182000000
H	-4.978808000000	0.158486000000	-3.111534000000
C	-5.996632000000	-2.364649000000	1.092461000000
H	-5.556415000000	-2.313226000000	2.091900000000
H	-7.073279000000	-2.222390000000	1.152360000000
H	-5.771688000000	-3.324782000000	0.620348000000

Sum of electronic and zero-point Energies= -1738.094177 Hartree

Sum of electronic and thermal Energies= -1738.060786 Hartree

Sum of electronic and thermal Enthalpies= -1738.059842 Hartree

Sum of electronic and thermal Free Energies= -1738.157916 Hartree

Lowest Frequencies: -271.7288 cm^{-1}

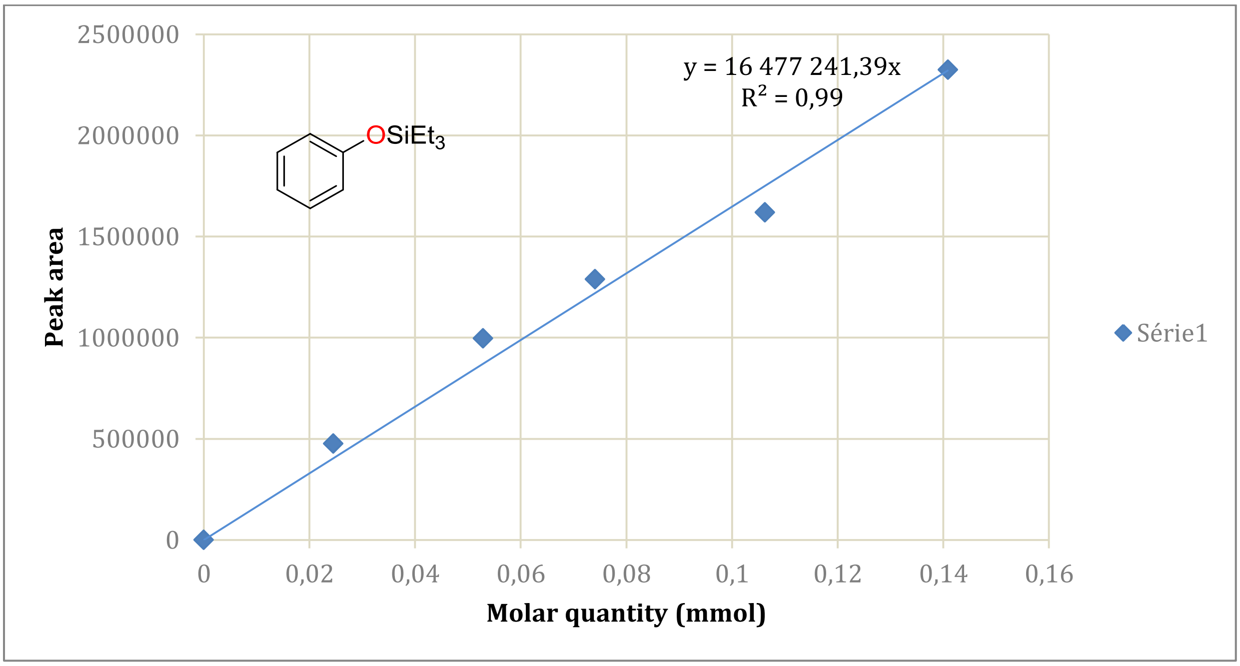
26.2879 cm^{-1}

32.7071 cm^{-1}

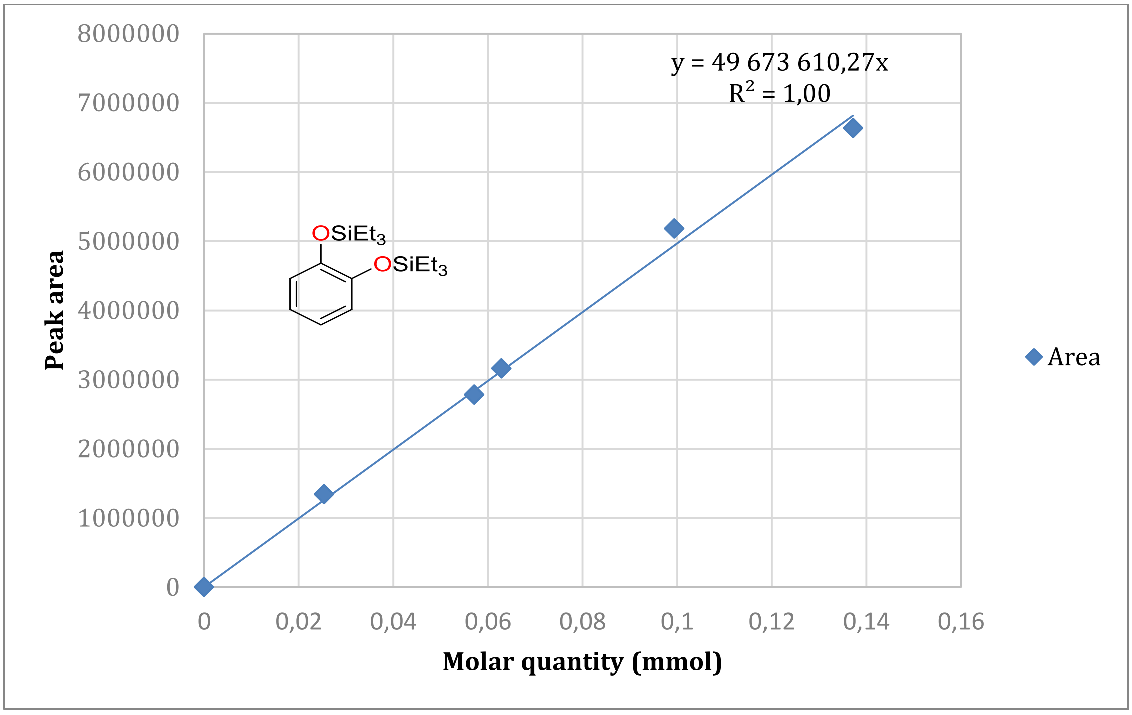
XI) GC-MS calibration curves

GC conditions for the analysis of all the samples: Injector temp.: 250 °C; Carrier gas: helium; Pressure: 120.0 kPa; Linear velocity: 51.9 cm/sec.; Oven temp.: 50 °C (hold 1 min.) to 200 °C at 40 °C/min, then to 280°C at 15 °C/min then 280°C (hold 20 min). Detector: MS (EI); Ion source temp.: 200 °C; Interface temp.: 250 °C; Detector voltage: 0.8 kV

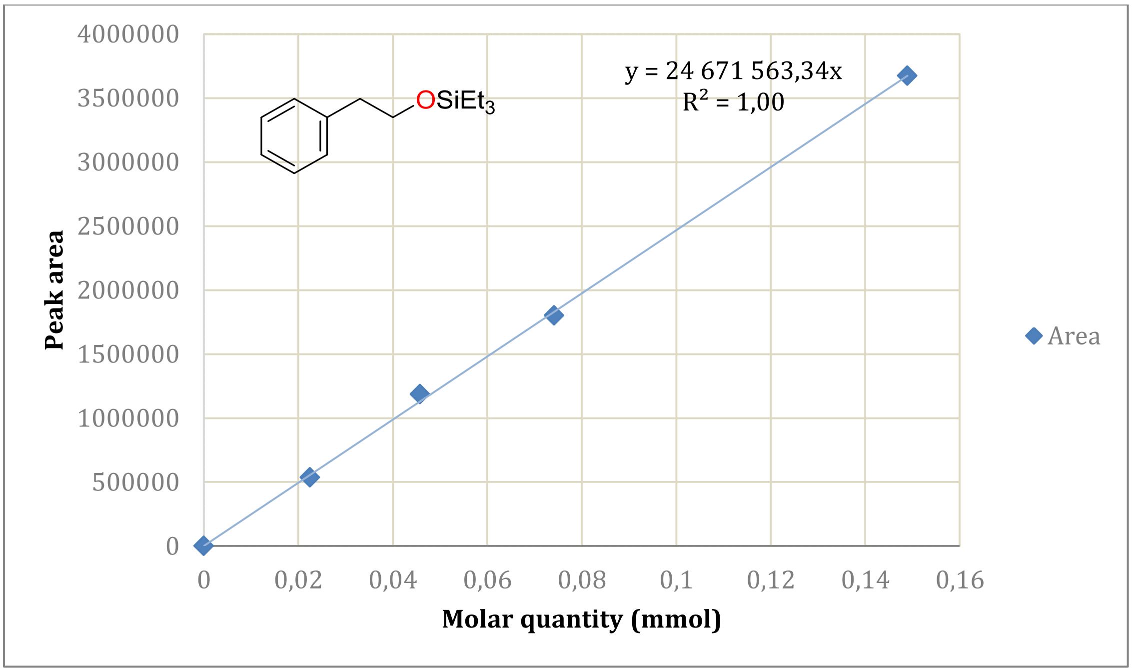
XI.a) Calibration curve of compound **3a**



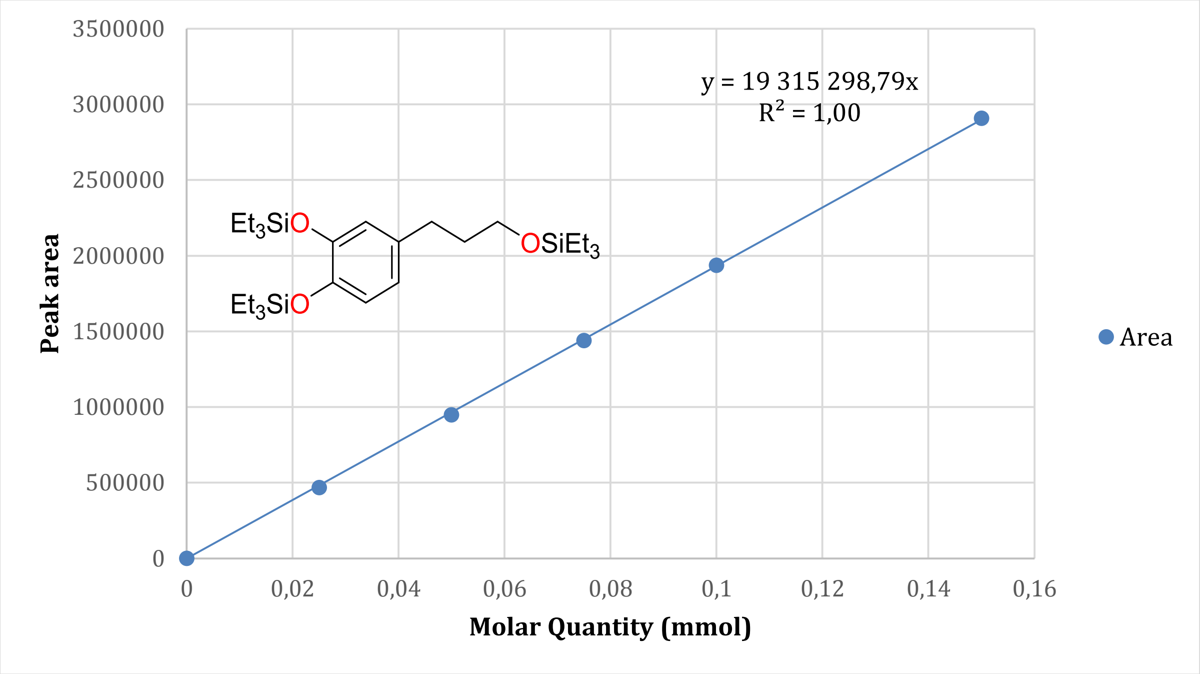
XI.b) Calibration curve of compound **3b**



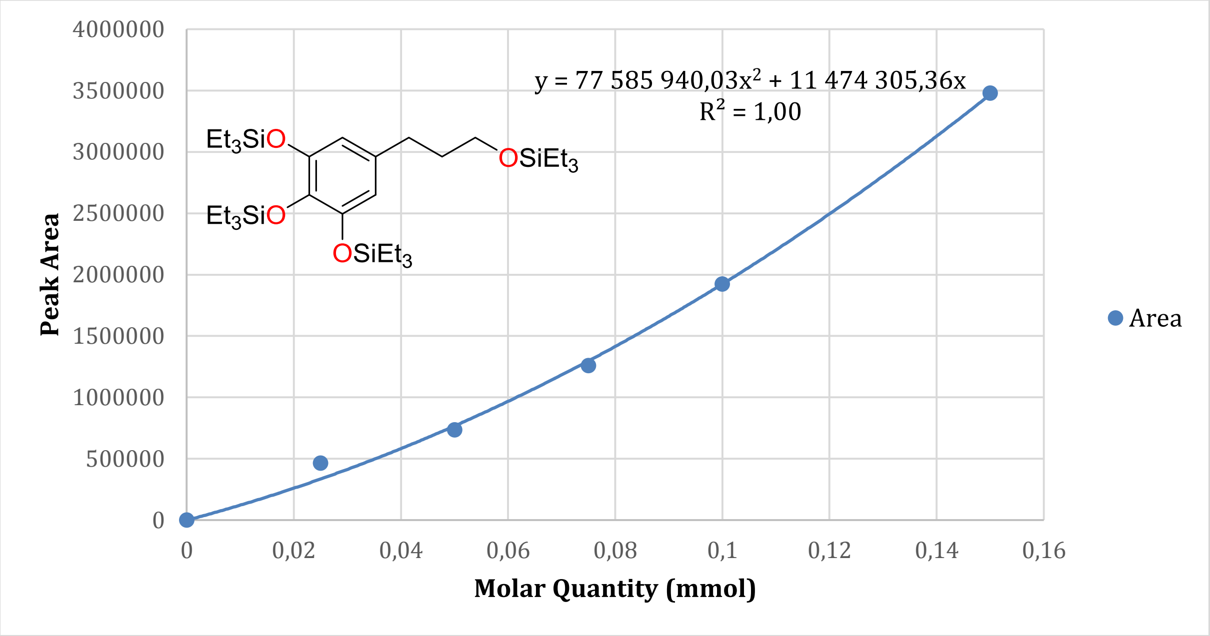
XI.c) Calibration curve of compound **6**



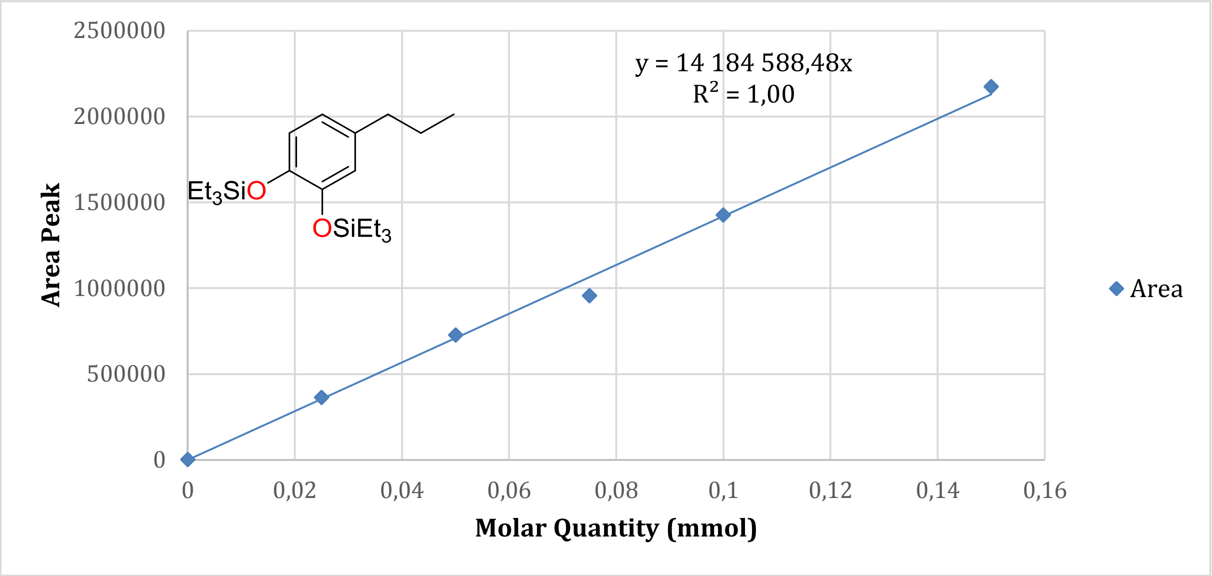
XI.d) Calibration curve of compound **10G**



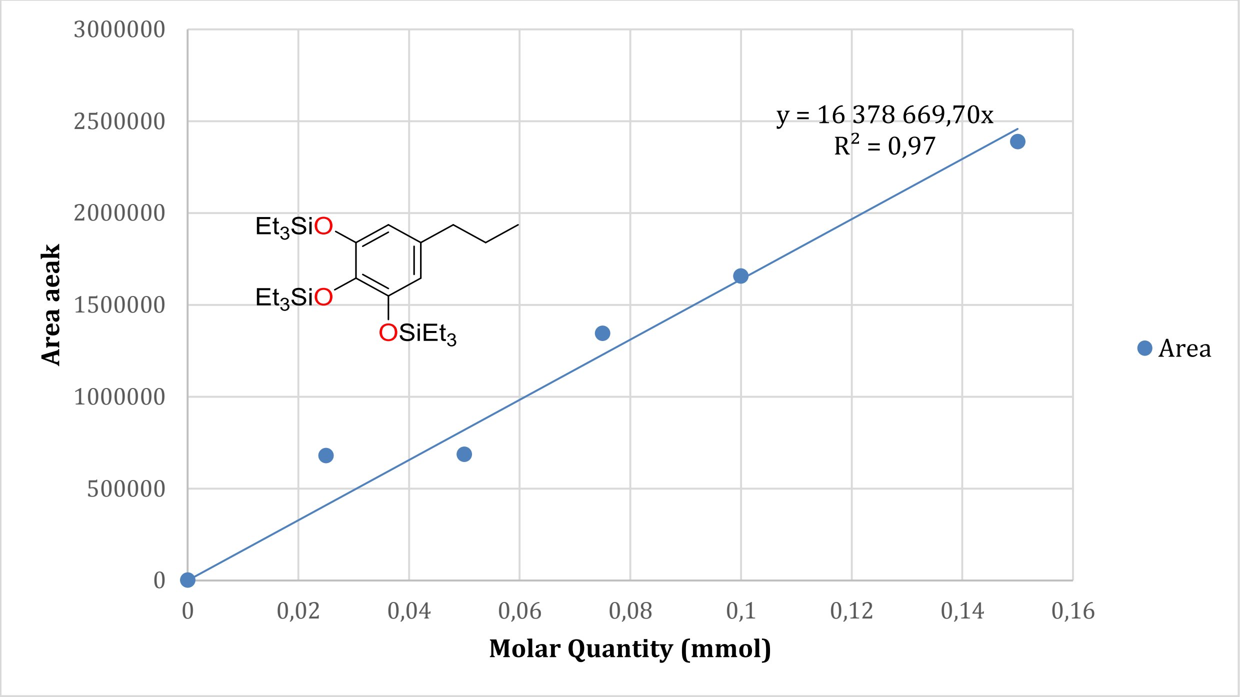
XI.e) Calibration curve of compound **10S**



XI.f) Calibration curve of compound **11G**



XI.g) Calibration curve of compound **11S**



XII) References

---

[1] J. Yang, M. Brookhart, *J. Am. Chem. Soc.*, **2007**, *129*, 12656.

[2] J. M. Nichols, L. M. Bishop, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc*. **2010**, *132*, 12554–12555.

[3] J. Buendia, J. Mottweiler, C. Bolm, *Chem. Eur. J.* **2011**, *17*, 13877–13882.

[4] H. Q. Lam, Y. Le Bigot, M. Delmas, G. Avignon, *Industrial Crops and Products*, **2001**, *14*, 139.

[5] I. Göttker-Schnetmann, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 9330.

[6] J. Yang, P.S. White, M. Brookhart, *J. Am. Chem. Soc.*, **2008**, *130*, 17509.

[7] (a) E. Feghali, G. Carrot, P. Thuéry, C. Genre, T. Cantat, *Energy Environ. Sci.*, **2015**, *8*, 2734. (b) E. Feghali and T. Cantat, *Chem. Commun.*, **2014**, *50*, 862-865.

[8] (a) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijnincx, B. M. Weckhuysen, *Angew.Chem. Int.Ed.* **2016**, *55*,8164. (b) J.Zakzeski, P.C. A. Bruijnincx, A. L. Jongerius, B. M. Weckhuysen *Chem. Rev*,. **2010**, *110*, 3552 (c) M. P. Pandey, C. S. Kim, *Chem. Eng. Technol*. **2011**, *34*, 29.

[9] (a) J. C. del Río, J. Rencoret, P. Prinsen, Á. T. Martínez, J. Ralph and A. Gutierrez, *J. Agric. Food Chem.* **2012**, *60*, *5922−5935* (b) J.-L. Wen, S.-L. Sun, B.-L. Xue and R.-C. Sun, *Materials*, **2013**, *6*, 359-391

[10] (a) Ralph, J.; Landucci, L. L. (2010) NMR of Lignins in Lignin and Lignans; Advances in Chemistry, eds. (b) Heitner, C.; Dimmel, D. R.; Schmidt, J. A. (CRC Press (Taylor & Francis Group), Boca Raton, FL), pp. 137-234 (c) Kim, H.; Ralph, *J. Org. Biomol. Chem*. **2010**, *8*, 576. (d) K. Cheng, H. Sorek, H. Zimmermann, D. E. Wemmer, and M. Pauly, *Anal. Chem.*, **2013**, *85*, 3213–3221

[11] (a) B.H. Davison, S.R Drescher, G.A. Tuskan, M.F Davis, N.P Nghiem, *Appl. Biochem. Biotechnol*. **2006**, *129*, 427. (b) M. Govender, T. Bush, A. Spark, S. K. Bose, R. C. Francis, *Bioresource Technology*, **2009**, *23*, 5834. (c) C.A. Nunes, C.F. Lima, L.C.A. Barosa, J.L. Colodette, A.F.G Gouveia, F.O. Silverio, *Bioresource Technology*, **2010**, 11, 4056. (d) S.K. Bose, R.C. Francis, M. Govender, T. Bush, A. Spark, *Bioresource Technology*, **2009**, *4*, 1628.

[12] (a) M. D. Kärkäs, B. S. Matsuura, T. M. Monos, G. Magallanes and C. R. J. Stephenson, *Org. Biomol. Chem.*, **2016**, *14*, 1853-1914. (b) J. C. del Río, J. Rencoret, G. Marques, J. Li, G. Gellerstedt, J. Jiménez-Barbero, Á. T. Martínez and A. Gutierrez, *J. Agric. Food Chem.*, **2009**, *57* ,10271–10281.

[13] Y.-C. Sun, M. Wang and R.-C. Sun, *ACS Sustainable Chem. Eng*. **2015**, *3*, 2443−2451

---

[14] P. Prinsen,. A. Narani, G. Rothenberg, *ChemSusChem* **2017**, *10*,1022 –1032

[15] (a) M. V. Galkin, S. Sawadjoon, V. Rohde, M. Dawange, J. S. M. Samec, *ChemCatChem* **2014**, *6*, 179 – 184 (b) J. M. W. Chan, S. Bauer, H. Sorek, S. Sreekumar, K. Wang, and F. D. Toste, *ACS Catal*. **2013**, *3*, 1369−1377 (c) A. Rahimi, A. Azarpira, H. Kim, J. Ralph, and S. S. Stahl, *J. Am. Chem. Soc*. **2013**, *135*, 6415−6418

[16] (a) Zhao, Y., Schultz, N. E. & Truhlar, D. G. *J. Chem. Theory Comput*., **2006**, *2*, 364-382; (b) Zhao, Y. & Truhlar, D. G. *Accounts Chem. Res*., **2008**, *41*, 157-167.

[17] Gaussian09, Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

[18] NBO 6.0. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold (Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2013); http://nbo6.chem.wisc.edu/