Catalytic olefin hydrosilylation with an original bis(iminophosphorane)phosphine NPN Co^{II} complex

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X-ray data

The crystal structures were solved using Shelxt39 or olex40 and refined using Shelxl-97 or Shelxl-2014.39 ORTEP drawings were made using ORTEP III41 for Windows or Mercury.

Table S1 : Crystallographic Data for **L** and **1**

	L	**1**
Formula	$C_{48}H_{47}N_2P_3$	$C_{48}H_{47}Br_{0.26}Cl_{0.74}CoF_6N_2P_4$
Mw	744.78	995.58
Space group	P-1	$P2_1/n$
V (Å^3)	1978.23(16)	4475.0(5)
a (Å)	10.9376(5)	10.1288(6)
b (Å)	12.5643(6)	31.464(2)
c (Å)	14.6202(7)	14.1400(8)
α (deg)	90.478(4)	90
β (deg)	90.470(4)	96.761(4)
γ (deg)	100.039(4)	90
Z	2	4
d (g.cm^{-3})	1.250	1.478
F(000)	788.0	2047.0
$2\theta_{max}$	58.43	50.054
Rflns measd	21360	19855
Unique data	9385	7815
R_{int}	0.0317	0.0398
wR2 (all data/ I>2 σ)	0.1003 / 0.1033	0.0795/ 0.0850
R1 (all data/ I>2 σ)	0.0400 / 0.0555	0.0399 / 0.0739
GoF	0.981	0.932
CCDC number	2477583	2477584

Synthesis

All air and moisture sensitive reactions were performed under inert atmosphere using a vacuum line, inert Schlenk techniques (N_2) and a glove box (Ar, <0.1 ppm H_2O, <0.1 ppm O_2) with oven-dried glassware unless other notified. Reagents were used as received from commercially available suppliers without further purification unless otherwise noticed. The aminophosphonium $PPh_3N^iPr.HBr$ was synthesised as previously described.[1] CH_2Cl_2, pentane, ether and toluene were taken from solvent purification system (MBraun-SPS). THF was distilled and degassed using freeze-pump technique. NMR spectra were recorded on a Bruker AC-300 SY spectrometer at 300 MHz for ^1H, 120 MHz for ^{31}P and 75 MHz for ^{13}C. Solvent peaks were used as internal references for ^1H and ^{13}C chemical shifts (ppm). $^{31}P\{^1H\}$ NMR spectra are relative to an 85% H_3PO_4 external reference. Unless otherwise mentioned, NMR spectra were recorded at 300 K. Structural assignments were made with additional information from COSY, HSQC, and HMBC experiments. The spectra were analysed with Topspin software. The following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet. The labelling for the proligand and complexes is given in Scheme 2.
High-resolution mass spectrometry experiments were performed on a Tims-TOF mass spectrometer (Bruker, France equipped with atmospheric pressure chemical ionisation (APCI) source in positive mode. Capillary and end plate voltages were set at 4.2 kV and 0.5 kV for experiments, Corona for APCI was set at 4000 nA. Nitrogen was used as the nebuliser and drying gas at 3 bar and 2 L min^{-1}, respectively, with a drying temperature of 250 °C. APCI heater was set at 300°C. Tuning mix (Agilent, France) was used for calibration. The elemental compositions of all ions were determined with the instrument software Data Analysis, the precision of mass measurement was less than 5 ppm. Elemental analyses were carried out by the elemental analysis service of the Laboratoire de Chimie de Coordination (Toulouse) using a PerkinElmer 2400 series II analyser. X-ray crystallography data were collected at 150 K on a Bruker Kappa APEX II diffractometer using a Mo-κ (λ = 0.71069 Å) X-ray source and a graphite monochromator.

Preparation of LLi_2BrCl: A ^nBuLi solution in pentane (8.0 mmol, 5.0 mL, 1.6M) was added onto a cooled suspension (-78°C) of $PPh_3N^iPr.HBr$ (1.60 g, 4.0 mmol) in THF (50 mL). The white suspension turned into a yellow solution upon warming to room temperature. Stirring was pursued 30 minutes. Then, the yellow solution was cooled to -78°C and a solution of dichlorophenylphosphine (2.0 mmol, 358.0 mg in 2mL THF) was added dropwise. After warming the solution to room temperature, stirring was pursued for 2h. Afterwards, the volatiles were evaporated under vacuum. The solid was washed with of Et_2O (3x15 mL) and pentane (2x10 mL), the supernatants were separated by centrifugation. The product **LLi_2BrCl** was then isolated after drying under vacuum as a white solid (993.1 mg, 1.36 mmol, 73%).^{31}P NMR (121.5 MHZ, 296K, THF-d_8): δ = -0.4 (s) and -15.1 (s). ^1H NMR (300 MHz, THF-d_8): δ = 7.18-7.78 (m, 25H), 6.89-7.03 (m, 8H), 3.49-7.21 (m, 2H, CH_{iPr}), 0.79 (bs, 12H, CH_3).^{13}C NMR (75.0 MHz, THF-d_8): δ = 143.6 (d, $J_{P,C}$= 14.5 Hz, C),136.4 (d, $J_{P,C}$= 19.5 Hz, C),133.8 (d, $J_{P,C}$= 9.0 Hz, C),133.6 (d, $J_{P,C}$= 9.0 Hz, C),133.4 (s, CH),133.2 (s, CH),132.5 (d, $J_{P,C}$= 14.0 Hz, CH), 132.4 (d, $J_{P,C}$= 10.0 Hz, CH), 130.0 (s, CH),129.6 (s, CH),127.6 (d, $J_{P,C}$= 11.0 Hz, CH), 127.4 (d, $J_{P,C}$= 10.5 Hz, CH), 127.0 (d, $J_{P,C}$= 8.0 Hz, CH), 126.5 (s, CH), 45.6 (s, CH_{iPr}), 28.2 (s, $CH_{3\text{-}iPr}$). HRMS ($APCI^+$): [**L+**H]$^+$ = $[C_{48}H_{48}N_2P_3]^+$ exp. m/z 745.3025; calc. m/z 745.3025.

Preparation of 1: A suspension of **LLi_2BrCl** (829.6 mg, 1.0 mmol) and $CoCl_2$ (129.8 mg, 1.0 mmol) in THF (15 mL) was stirred at room temperature for 18h. The grey suspension turned to a green one. The solid was separated and washed with Et_2O (2x10 mL). The complex was then extracted into CH_2Cl_2 (50 mL), the solid was discarded, the solution was concentrated (15 mL remaining) and stirred for 3 days with an excess of KPF_6 (920.3 mg, 5.0 mmol). The salts were removed by filtration, the volatiles evaporated under vacuum and **1** was isolated (743.5 mg, 0.74 mmol, 74%). The X-ray diffraction data indicate a partial exchange of Co-Cl (Cl : Br 0.75 : 0.25). This was further confirmed by HR-MS where both the chloride and bromide containing complexes were observed. ^{31}P NMR (121.5 MHZ, 296K, CD_2Cl_2,): δ = -145.1 (sept, $J_{P,F}$= 719.0 Hz, PF_6). ^{19}F NMR

(376.5 MHZ, CD_2Cl_2,): δ = -73.5 (d, $J_{P,F}$= 719.0 Hz, PF_6). ^1H NMR (CD_2Cl_2, 300 MHz) : δ = 32.8 (s , 2H, CH), 15.32-14.8 (m, 12H), 13.0 (s , 4H, CH), 9.0 (s , 4H, CH), 7.8 (s , 4H, CH), -0.8 (s , 3H, CH), -12.2 (s , 2H, CH), -22.4-(-20.6) (m, 16H). Evans method (C = 6.3 mM; CD_2Cl_2): 4.31 μ_B, S = 3/2. HR-MS (APCI$^+$): $[C_{48}H_{47}ClCoN_2P_3]^+$ exp *m/z* 838.1969; calc *m/z* 838.1967, $[C_{48}H_{47}BrCoN_2P_3]^+$ exp *m/z* 882.1455; calc *m/z* 882.1462. Elemental analysis for $C_{48}H_{47}N_2CoP_4F_6Cl_{0.75}Br_{0.25}$: calc (%) C 57.90; H 4.72, N 2.81 found (%) C 57.50; H 4.38, N 2.66.

NMR Data for the ligand and complex

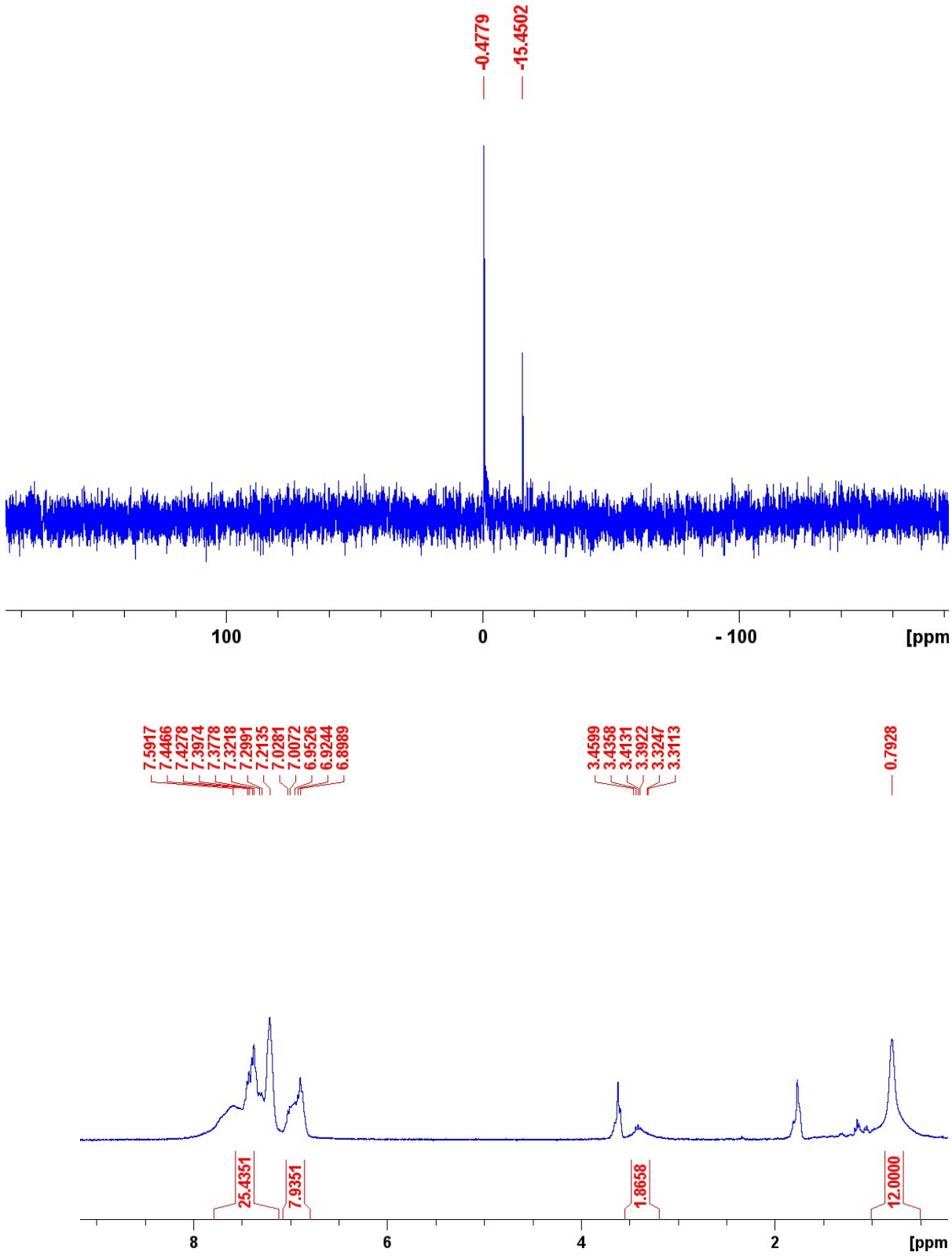


Figure S1: $^{31}P\{^{1}H\}$ NMR spectrum of **LLi_2BrCl** ($THF\text{-}d_8$, 121.5 MHz)

Figure S2: ^{1}H NMR spectrum of **LLi_2BrCl** ($THF\text{-}d_8$, 300 MHz)

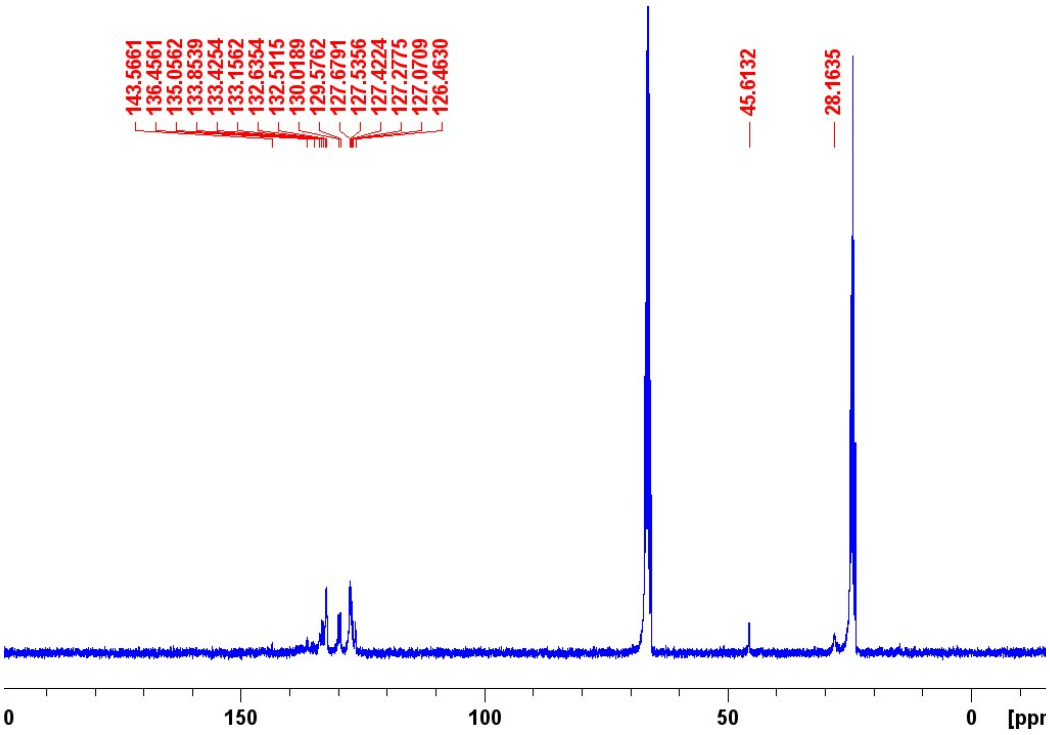


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum of **LLi_2BrCl** ($THF\text{-}d_8$, 75.0 MHz)

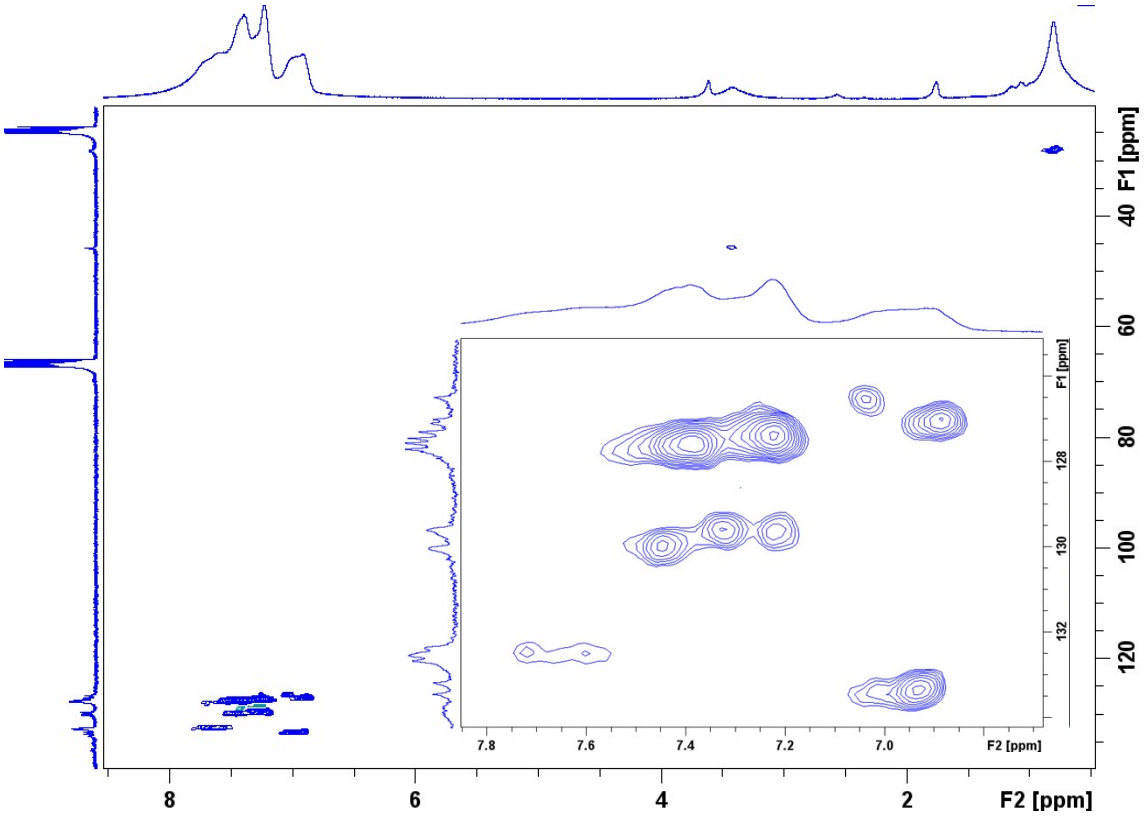


Figure S4: HSQC NMR spectrum of **LLi_2BrCl** ($THF\text{-}d_8$)

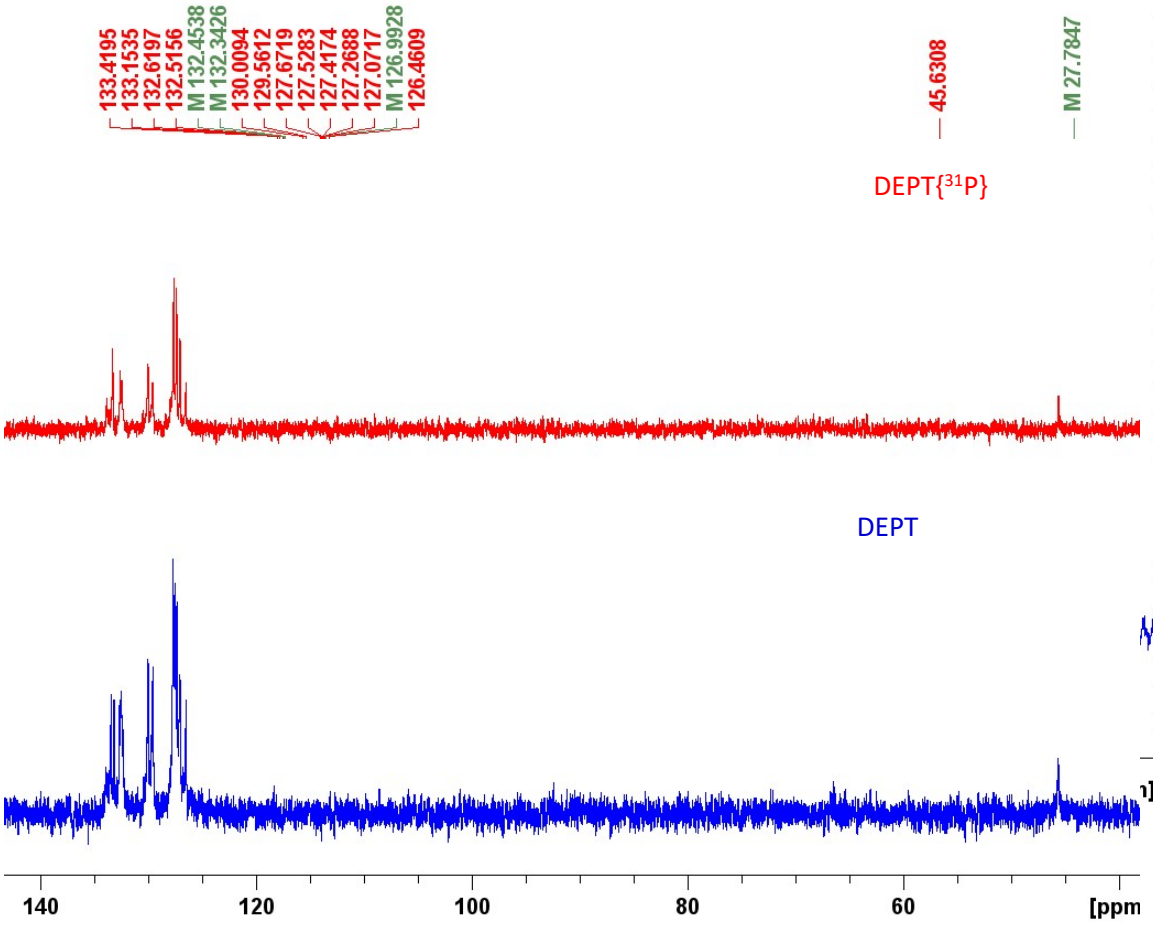


Figure S5: ^{13}C-DEPT DEPT NMR spectrum of **LLi$_2$BrCl** (THF-d$_8$, 75.0 MHz)

Figure S6: Superimposition of ^{13}C{^{31}P}-DEPT NMR (red) and ^{13}C-DEPT (blue) NMR spectra of **LLi$_2$BrCl** (THF-d$_8$, 75.0 MHz)

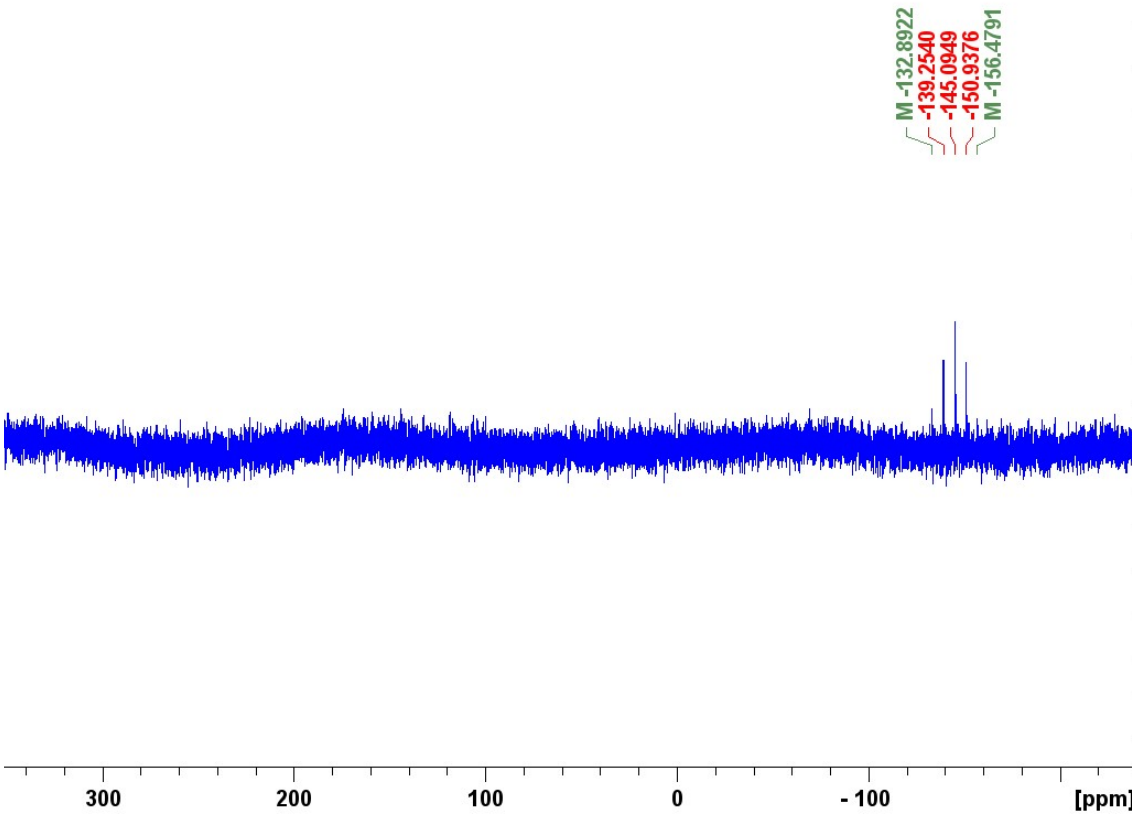
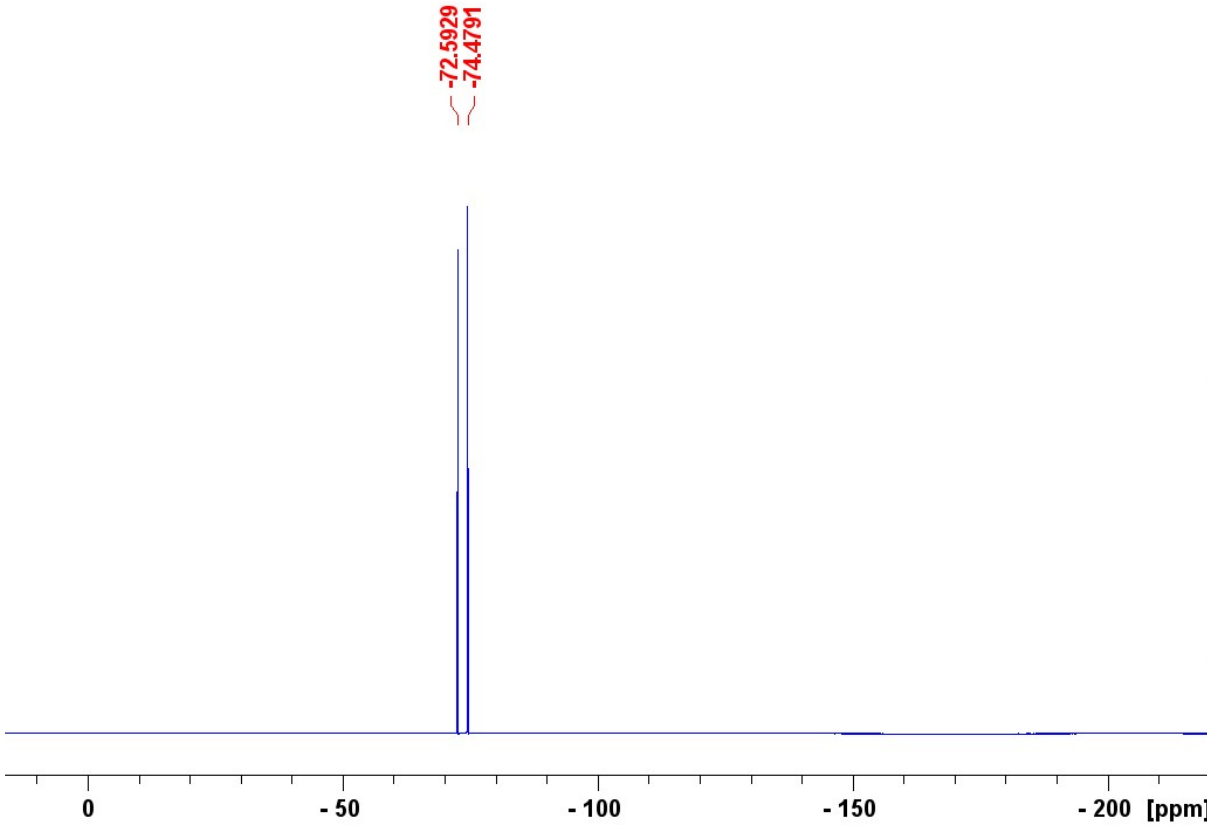


Figure S7: $^{31}P\{^{1}H\}$ NMR spectrum of **1** (CD_2Cl_2, 121.5 MHz)

Figure S8: ^{19}F NMR spectrum of **1** (CD_2Cl_2, 376.5 MHz)



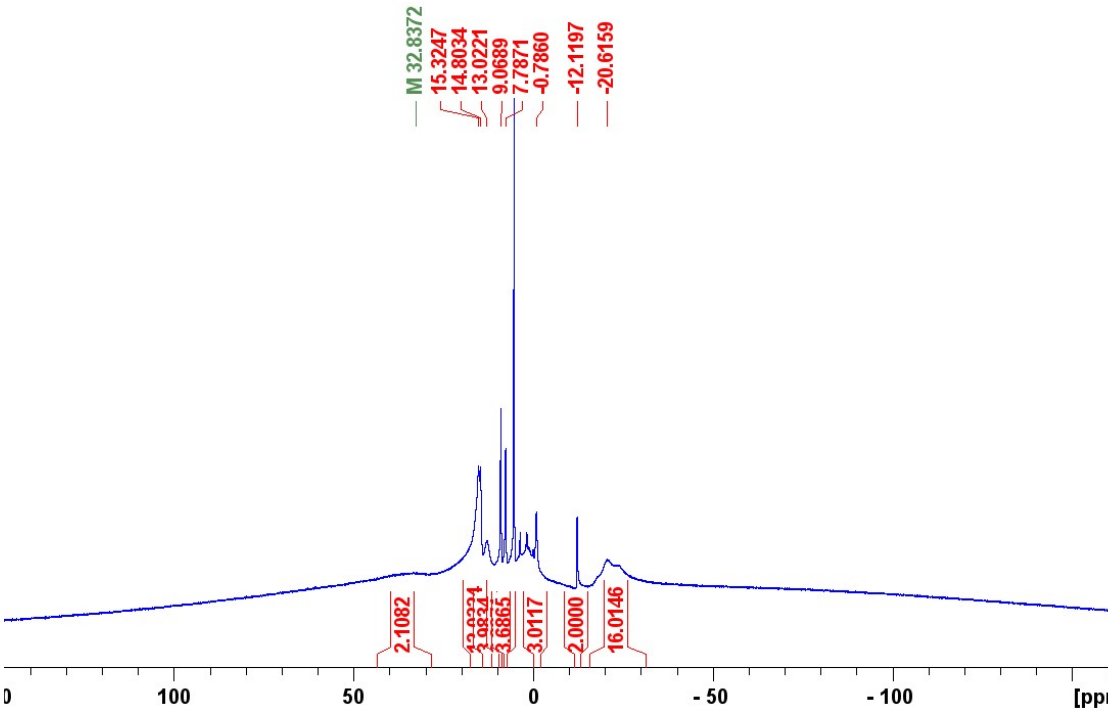
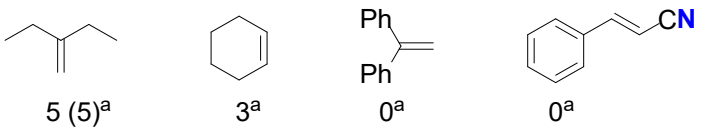


Figure S9: ^{1}H NMR spectrum of **1** (CD_2Cl_2, 300.0 MHz)

Catalysis

General procedure for the hydrosilylation of olefins

In the glovebox, trimethoxybenzene (11.8 mg, 0.07 mmol) and **1** (14.8 mg, 0.015 mmol, 1.5 mol%) were introduced in a 10 mL vial. Then, Ph_2SiH_2 (0.19 mL, 1 mmol, 1 equiv.) and the alkene (1 mmol, 1 equiv.) were added. Finally, THF was added to reach a volume of 0.5 mL (2 M concentration), then NaOMe (1.7 mg, 0.03, 1 mol%) was introduced and the vial was capped. After stirring 60°C for the request time, an aliquot of 20 µL was taken, quenched with 1 mL of distilled water and extracted with 2.5 mL of Et_2O then dried on $MgSO_4$. The solvent from the aliquot was evaporated on the rotary evaporator (10 min, 50 mbar, 40°C) and analysed by NMR in $CDCl_3$. The rest of the mixture was put on the rotary evaporator (30 min, 50 mbar, 40°C) and then the crude product was purified by flash chromatography and the silylether was isolated.



5 (5)[a] 3[a] 0[a] 0[a]

Scheme S1: Reluctant substrates for reactions conducted in THF at 60°C for 24 h using 3% (a) or 5% (b) mol% of catalyst **1**. NMR conversion and NMR yield indicated into brackets using trimethoxybenzene as internal reference.

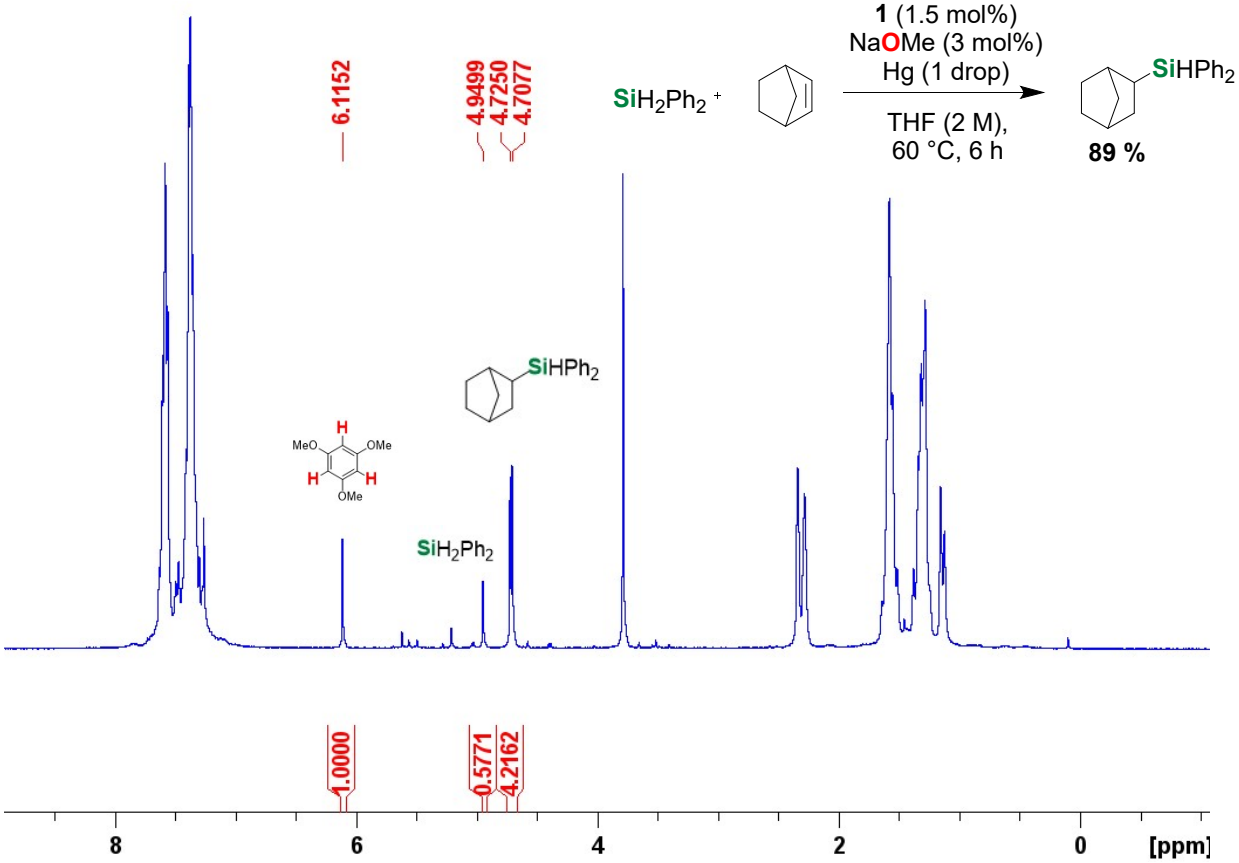
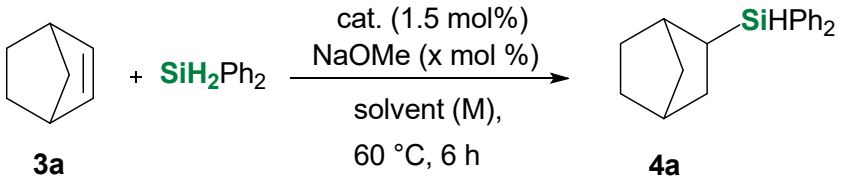


Figure S10: Catalytic hydrosilylation of norbornene in presence of a mercury drop and the corresponding ^{1}H NMR spectrum ($CDCl_3$, 300MHz)

Table S2: *Additional optimisation and control experiments*[a]



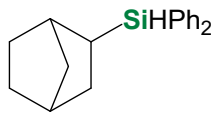
3a **4a**

Entry	Cat.	Solvent (x M)	x	Conv (%)[b]	Yield (%)[c]
1	1	MeCN (2)	3	38	38
2	1	THF (3)	1.5	94	94
3	1	THF (3)	7.5	100	99
4	1	THF (3)	0	15	14
5[d]	-	THF (3)	0	0	0
6[d]	-	THF (3)	3	9	8
7	$CoCl_2$	THF (3)	3	14	14

[a] Reaction conducted with norbornene (1 mmol) in presence of **1** (1.5 mol%), trimethoxybenzene (0.07 mmol) as reference, silane (1 mmol) and additive for 6 h at 60°C. [b] Determined by NMR by using the integration of the singlet at 4.92 ppm for SiH_2Ph_2 relative to the CH aromatic resonances of the reference at 6.10 ppm; [c] Determined by NMR by using the integration of the doublet at 4.72 ppm for $C_6H_{11}SiHPh_2$ relative to the CH aromatic resonances of the reference at 6.10 ppm.

NMR data of the catalysis products

2-(Diphenylsilyl)bicyclo[2.2.1]heptane **3a** (CAS 1125607-48-8)

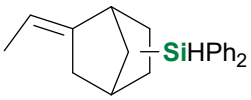


Column chromatography (pentane/Et_2O gradient from 100/0 to 95/5). **3a** was obtained as a colourless oil (213.6 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.52-7.64 (m, 4H, CH_{Ar}), 7.30-7.44 (m, 6H, CH_{Ar}), 4.70 (d, $J_{H,H}$= 5.0 Hz, 1H, SiH), 2.24-2.35 (m, 2H, CH), 1.53-1.61 (m, 4H, CH_2), 1.22-1.38 (m, 4H, CH_2), 1.10-1.13 (m, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): 135.5 (s, CH_{Ar}), 134.4 (s, C_{Ar}), 129.5 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 38.5 (s, CH), 37.5 (s, CH_2), 37.3 (s, CH), 33.9 (s, CH_2), 33.6 (s, CH_2), 29.3 (s, CH_2), 25.7 (s, CH). These data agree with the literature.[2]

3a,4,5,6,7,7a-Hexahydro-5-(diphenylsilyl)-4,7-methano-1H-indene and 3a,4,5,6,7,7a-Hexahydro-6-(diphenylsilyl)-4,7-methano-1H-indene **3b**

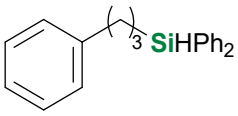
Column chromatography (pentane/Et_2O gradient from 100/0 to 95/5). **3b** was obtained as a mixture of regioisomers in proportion 3:2 (186.1 mg, 59%). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.52-7.64 (m, 4H, CH_{Ar}), 7.30-7.44 (m, 6H, CH_{Ar}), 5.50-5.82 (m, 2H, CH_{alkene}), 4.72 (d, $J_{H,H}$= 5.0 Hz, 0.6H, SiH), 4.68 (d, $J_{H,H}$= 5.0 Hz, 0.4H, SiH), 2.96-3.20 (m, 1H, CH), 2.52-2.64 (m, 1H, CH), 2.16-2.40 (m, 4H, CH/CH_2), 1.34-1.74 (m, 5H, CH/CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 135.5 (s, CH_{Ar}), 135.4 (s, CH_{Ar}), 135.1 (s, C_{Ar}), 135.0 (s, C_{Ar}), 134.5 (s, CH_{Alkene}), 132.9 (s, CH_{Alkene}), 132.2 (s, CH_{Alkene}), 132.1 (s, CH_{Alkene}), 130.5 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 127.8 (s, CH_{Ar}), 55.6 (s, CH), 53.0 (s, CH), 44.4 (s, CH), 43.1 (s, CH), 42.4 (s, CH), 41.8 (s, CH), 41.5 (s, CH), 40.6 (s, CH_2), 40.2 (s, CH), 40.1 (s, CH_2), 32.4 (s, CH_2), 32.1 (s, CH_2), 29.1 (s, CH_2), 26.1 (s, CH_2), 19.9 (s, CH), 16.6 (s, CH). Elemental analysis for $C_{22}H_{24}Si$: calc (%) C 83.48; H 7.64 found (%) C 83.15; H 7.85.

2-(Diphenylsilyl)-5-ethylidene-bicyclo[2.2.1]heptane and 2-(Diphenylsilyl)-6-ethylidenebicyclo[2.2.1] heptane **3c**



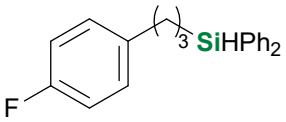
Column chromatography (pentane/Et_2O gradient from 100/0 to 95/5). **3c** was obtained as a mixture of regioisomers in proportion 9:1 (231.4 mg, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.52-7.64 (m, 4H, CH_{Ar}), 7.30-7.44 (m, 6H, CH_{Ar}), 5.10-5.34 (m, 1H), 4.95 (d, $J_{H,H}$= 5.0 Hz, 0.1H, SiH), 4.73 (d, $J_{H,H}$= 5.0 Hz, 0.9H, SiH), 2.66-2.70 (m, 1H), 2.34-2.50 (m, 1H), 2.08-2.24 (m, 1H), 1.83-2.00 (m, 1H), 1.47-1.74 (m, 6H), 0.86-1.40 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): 148.6 (s, C_{Ar}), 146.2 (s, C_{Ar}), 135.8 (s, CH_{Ar}), 135.5 (s, CH_{Ar}), 135.4 (s, CH_{Ar}), 134.8 (s, C_{Alkene}), 134.3 (s, C_{Alkene}), 129.5 (s, CH_{Ar}), 128.0 (s, CH_{Alkene}), 127.9 (s, CH_{Alkene}), 112.1 (s, CH_{Ar}), 109.2 (s, CH_{Ar}), 46.8 (s, CH), 46.2 (s, CH), 39.7 (s, CH_2), 38.7 (s, CH), 38.5 (s, CH_2), 38.2 (s, CH_2), 37.3 (s, CH), 35.0 (s, CH_2), 33.8 (s, CH_2), 32.3 (s, CH_2), 26.0 (s, CH), 25.2 (s, CH), 14.3 (s, CH_3), 13.8 (s, CH_3). HRMS (APCI$^+$): $[C_{21}H_{25}Si]^+$ exp. m/z 305.1708; calc. m/z 305.1720.

1-[3-(Diphenylsilyl)propyl]-benzene **3f** (CAS 18737-67-2)



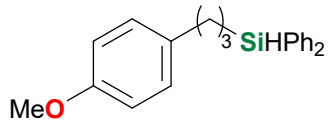
Column chromatography (pentane). **3f** was obtained as a colourless oil (291.0 mg, 93%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.52-7.62 (m, 4H, CH_{Ar}), 7.34-7.42 (m, 6H, CH_{Ar}), 7.10-7.22 (m, 5H, CH_{Ar}), 4.87 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 2.68 (t, $J_{H,H}$= 7.5 Hz, 2H, CH_2), 1.72-1.86 (m, 2H, CH_2), 1.14-1.24 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): 142.2 (s, C_{Ar}), 135.2 (s, CH_{Ar}), 134.4 (s, C_{Ar}), 129.6 (s, CH_{Ar}), 128.6 (s, CH_{Ar}), 128.3 (s, CH_{Ar}), 128.1 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 39.3 (s, CH_2), 26.4 (s, CH_2), 11.9 (s, CH_2). These data agree with the literature.[3]

1-[3-(Diphenylsilyl)propyl]-4-fluorobenzene **3g**



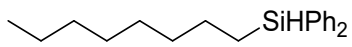
Column chromatography (pentane). **3g** was obtained as a colourless oil (290.1 mg, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.50-7.62 (m, 4H, CH_{Ar}), 7.34-7.42 (m, 6H, CH_{Ar}), 6.90-7.10 (m, 4H, CH_{Ar}), 4.86 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 2.64 (t, $J_{H,H}$=7.5 Hz, 2H, CH_2), 1.70-1.84 (m, 2H, CH_2), 1.12-1.22 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): 161.3 (d, $J_{F,C}$= 243.0 Hz, C_{Ar}), 137.8 (d, $J_{F,C}$= 3.5 Hz, C_{Ar}), 135.2 (s, CH_{Ar}), 134.3 (s, C_{Ar}), 129.9 (d, $J_{F,C}$= 7.5 Hz, CH_{Ar}), 129.7 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 115.0 (d, $J_{F,C}$= 21.0 Hz, CH_{Ar}), 38.4 (s, CH_2), 26.4 (s, CH_2), 11.7 (s, CH_2). ^{19}F ($CDCl_3$, 369.5 MHz): -117.8 (sept, $J_{F,H}$= 4.0 Hz). HRMS (APCI$^+$): $[C_{21}H_{20}SiF]^+$ exp. *m/z* 319.1308; calc. *m/z* 319.1313.

1-[3-(Diphenylsilyl)propyl]-4-methoxybenzene **3h** (CAS 2260749-21-9)



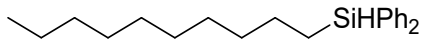
Column chromatography (pentane/EtOAc gradient from 100/0 to 85/15). **3h** was obtained as a colourless oil (308.4 mg, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.50-7.56 (m, 4H, CH_{Ar}), 7.32-7.42 (m, 6H, CH_{Ar}), 7.04 (d, $J_{H,H}$= 8.5 Hz, 2H, CH_{Ar}), 6.81 (d, $J_{H,H}$= 8.5 Hz, 2H, CH_{Ar}), 4.86 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 3.78 (s, 3H, OCH_3), 2.62 (t, $J_{H,H}$=7.5 Hz, 2H, CH_2), 1.70-1.82 (m, 2H, CH_2), 1.12-1.22 (m, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): 157.7 (s, C_{Ar}), 135.8 (s, C_{Ar}), 135.1 (s, CH_{Ar}), 134.4 (s, C_{Ar}), 129.5 (s, CH_{Ar}), 129.4 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 113.7 (s, CH_{Ar}), 55.2 (s, CH_3), 38.3 (s, CH_2), 26.5 (s, CH_2), 11.7 (s, CH_2). These data agree with the literature.[4]

Octyldiphenylsilane **3i** (CAS 136795-58-9)



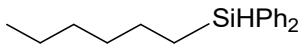
Column chromatography (pentane/ diethyl ether: gradient from 100/0 to 95/5). **3i** was obtained as a colourless oil (273 mg, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.54-7.57 (m, 4H, CH_{Ar}), 7.33-7.39 (m, 6H, CH_{Ar}), 4.84 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 1.10-1.48 (m, 14H, CH_2), 0.86 (t, $J_{H,H}$= 6.5 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): 135.1 (s, CH_{Ar}), 134.7 (s, C_{Ar}), 129.4 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 33.2 (s, CH_2), 31.9 (s, CH_2), 29.2 (s, CH_2), 29.1 (s, CH_2), 24.4 (s, CH_2), 22.6 (s, CH_2), 14.1 (s, CH_3), 12.1 (s, CH_2). These data agree with the literature.[2]

Decyldiphenylsilane **3j** (CAS 18754-81-9)



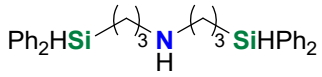
Column chromatography (pentane/ diethyl ether gradient from 100/0 to 95/5). **3j** was obtained as a pale yellowish oil (293 mg, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.54-7.57 (m, 4H, CH_{Ar}), 7.33-7.40 (m, 6H, CH_{Ar}), 4.84 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 1.50-1.56 (m, 2H, CH_2), 1.40-1.44 (m, 2H, CH_2), 1.14-1.46 (m, 12H, CH_2), 1.19-1.25 (m, 2H, CH_2), 0.86 (t, $J_{H,H}$= 6.5 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): 135.1 (s, CH_{Ar}), 134.7 (s, C_{Ar}), 129.4 (s, CH_{Ar}), 127.9 (s, CH_{Ar}), 33.2 (s, CH_2), 31.9 (s, CH_2), 29.6 (s, CH_2), 29.5 (s, CH_2), 29.3 (s, CH_2), 29.2 (s, CH_2), 24.4 (s, CH_2), 22.7 (s, CH_2), 14.1 (s, CH_3), 12.1 (s, CH_2). These data agree with the literature.[5]

(Diphenyl)(hexylsilane) **3k** (CAS 21654-93-3)



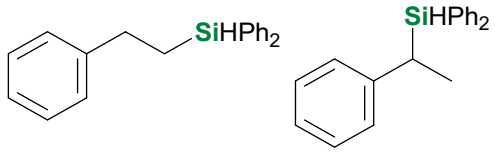
Column chromatography (pentane 100%). **3k** was obtained as a colourless oil (236 mg, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.45-7.48 (m, 4H, CH_{Ar}), 7.24-7.31 (m, 6H, CH_{Ar}), 4.78 (t, $J_{H,H}$= 3.5 Hz, 1H, SiH), 1.33-1.41 (m, 2H, CH_2), 1.25-1.31 (m, 2H, CH_2), 1.14-1.19 (m, 4H, CH_2), 1.03-1.08 (m, 2H, CH_2), 0.85 (t, $J_{H,H}$= 6.5Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz): 135.2 (s, CH_{Ar}), 134.8 (s, C_{Ar}), 129.5 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 32.9 (s, CH_2), 31.5 (s, CH_2), 24.4 (s, CH_2), 22.6 (s, CH_2), 14.1 (s, CH_3), 12.2 (s, CH_2). These data agree with the literature.[6]

N,N-di-[2-(Diphenylsilyl)propyl]amine **3l**



Column chromatography (pentane/EtOAc gradient from 100/0 to 30/70 with 12 drops of Et_3N). **3l** was obtained as a brown liquid (305.0 mg, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.52-7.58 (m, 8H, CH_{Ar}), 7.30-7.46 (m, 12H, CH_{Ar}), 4.85 (t, J_{HH}= 3.5 Hz, 2H, SiH), 2.58 (t, 4H, CH_2), 1.54-1.66 (m, 4H, CH_2), 1.08-1.14 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 135.1 (s, CH_{Ar}), 134.4 (s, C_{Ar}), 134.1 (s, C_{Ar}), 129.5 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 127.7 (s, CH_{Ar}), 126.2 (s, CH_{Ar}), 52.6 (s, CH_2), 25.0 (s, CH_2), 9.8 (s, CH_2). HRMS (APCI$^+$): $[C_{30}H_{36}Si_2N]^+$ exp. *m/z* 466.2361 calc. *m/z* 466.2380.

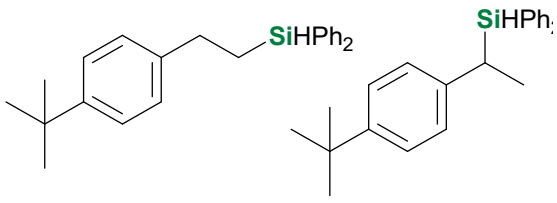
1-[2-(Diphenylsilyl)ethyl]-4-chlorobenzene **3o** (CAS 2044062-15-3) and 1-[1-(Diphenylsilyl)ethyl]-4-chlorobenzene **3o'** (CAS 375843-07-5)



19 : 1

Column chromatography (pentane/Et_2O gradient from 100/0 to 95/5). **3o/o'** was obtained as a mixture of regioisomers in proportion 30:1 (228.5 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.52-7.62 (m, 4H, CH_{Ar}), 7.34-7.42 (m, 6H, CH_{Ar}), 7.18-7.30 (m, 5H, CH_{Ar}), 4.91 (t, $J_{H,H}$= 3.5 Hz, 0.97H, SiH), 4.85 (d, $J_{H,H}$= 3.5 Hz, 0.03H, SiH), 2.75-2.85 (m, 2H), 1.52-1.56 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): 144.4 (s, C_{Ar}), 135.3 (s, CH_{Ar}), 134.2 (s, C_{Ar}), 129.8 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 125.8 (s, CH_{Ar}), 30.5 (s, CH_2), 14.3 (s, CH_2) (the minor regioisomer was not observed in ^{13}C NMR spectrum). These data agree with the literature.[3]

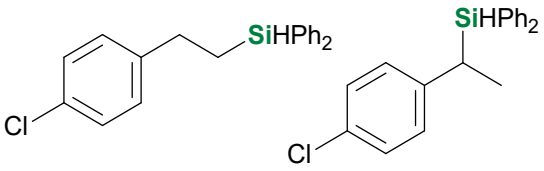
1-[2-(Diphenylsilyl)ethyl]-4-tertbutylbenzene **3p** (CAS 2054335-48-5) and 1-[1-(Diphenylsilyl)ethyl]-4-tertbutylbenzene **3p'** (CAS 2244062-21-1)



21 : 1

Column chromatography (pentane). **3p/p'** was obtained as a mixture of regioisomers in proportion 21:1 (304.1 mg, 88%). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.58-7.62 (m, 4H, CH_{Ar}), 7.39-7.44 (m, 6H, CH_{Ar}), 7.28-7.33 (m, 2H, CH_{Ar}), 7.14-7.16 (m, 2H, CH_{Ar}), 4.93 (t, $J_{H,H}$= 3.5 Hz, 0.95H, SiH), 4.85 (d, $J_{H,H}$=3.5 Hz, 0.05H, SiH), 2.74-2.81 (m, 2H), 1.53-1.57 (m, 2H), 1.33 (s, 9H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): 148.8 (s, C_{Ar}),141.2 (s, C_{Ar}), 135.1 (s, CH_{Ar}), 134.2 (s, C_{Ar}), 129.6 (s, CH_{Ar}), 128.0 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 125.2 (s, CH_{Ar}), 34.3 (s, C), 31.4 (s, CH_3), 29.8 (s, CH_2), 14.1 (s, CH_2) (the minor regioisomer was not observed in ^{13}C NMR spectrum). These data agree with the literature.[3]

1-[2-(Diphenylsilyl)ethyl]-4-chlorobenzene **2q** (CAS 2044062-15-3) and 1-[1-(Diphen-ylsilyl)ethyl]-4-chlorobenzene **2q'** (CAS 375843-07-5)



20 : 1

Column chromatography (pentane/Et_2O gradient from 100/0 to 95/5). **3q/q'** was obtained as a mixture of regioisomers in proportion 20:1 (265.1 mg, 81%). ^1H NMR ($CDCl_3$, 400 MHz): 7.34-7.62 (m, 10H, CH_{Ar}), 7.06-7.24 (m, 4H, CH_{Ar}), 4.88 (t, $J_{H,H}$=3.5 Hz, 0.94H, SiH), 4.81 (d, $J_{H,H}$=3.5 Hz, 0.06H, SiH), 2.68-2.78 (m, 2H), 1.44-1.54 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): 142.8 (s, C_{Ar}), 135.2 (s, CH_{Ar}), 133.9 (s, C_{Ar}), 131.5 (s, C_{Ar}), 129.8 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 128.5 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 30.0 (s, CH), 26.6 (s, CH_3), 16.5 (s, CH_2), 14.3 (s, CH_2). The attribution is similar to that previously depicted in the literature.[3]

NMR spectra of the catalysis products

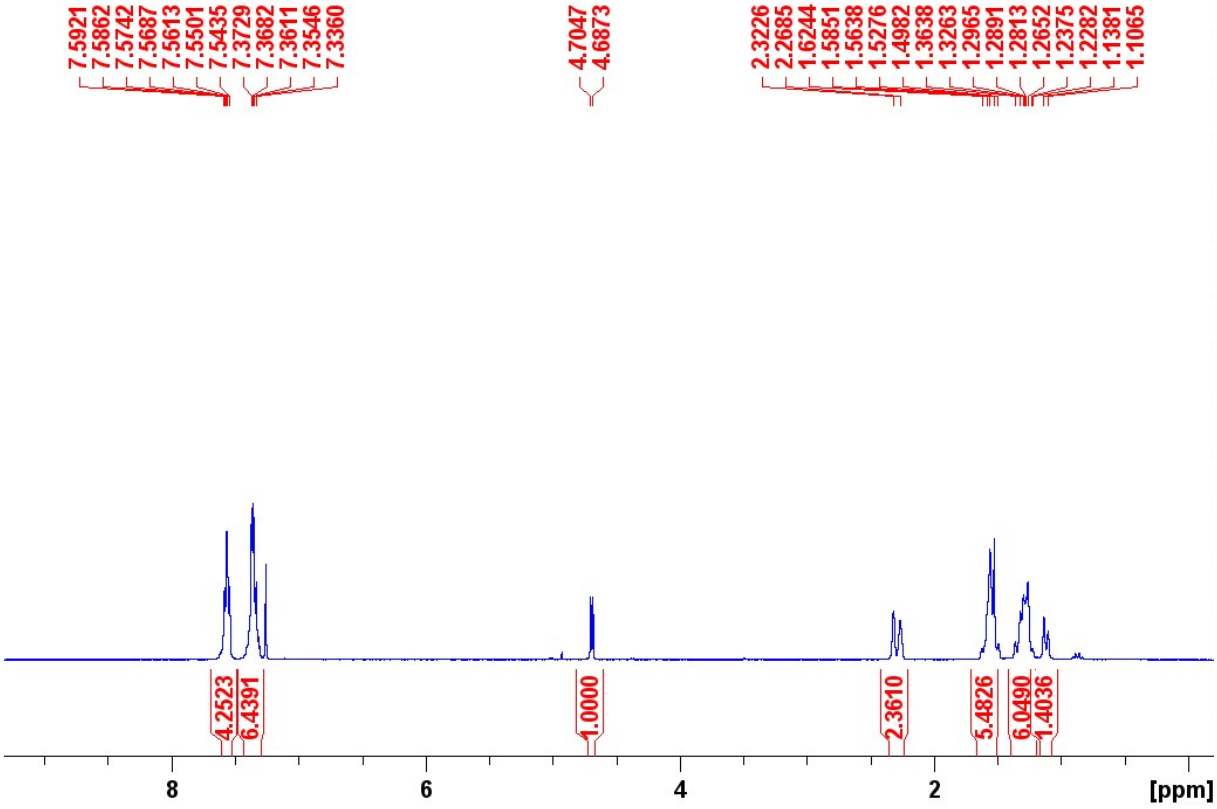


Figure S11: ^{1}H NMR spectrum of **3a** ($CDCl_3$, 400.0 MHz)

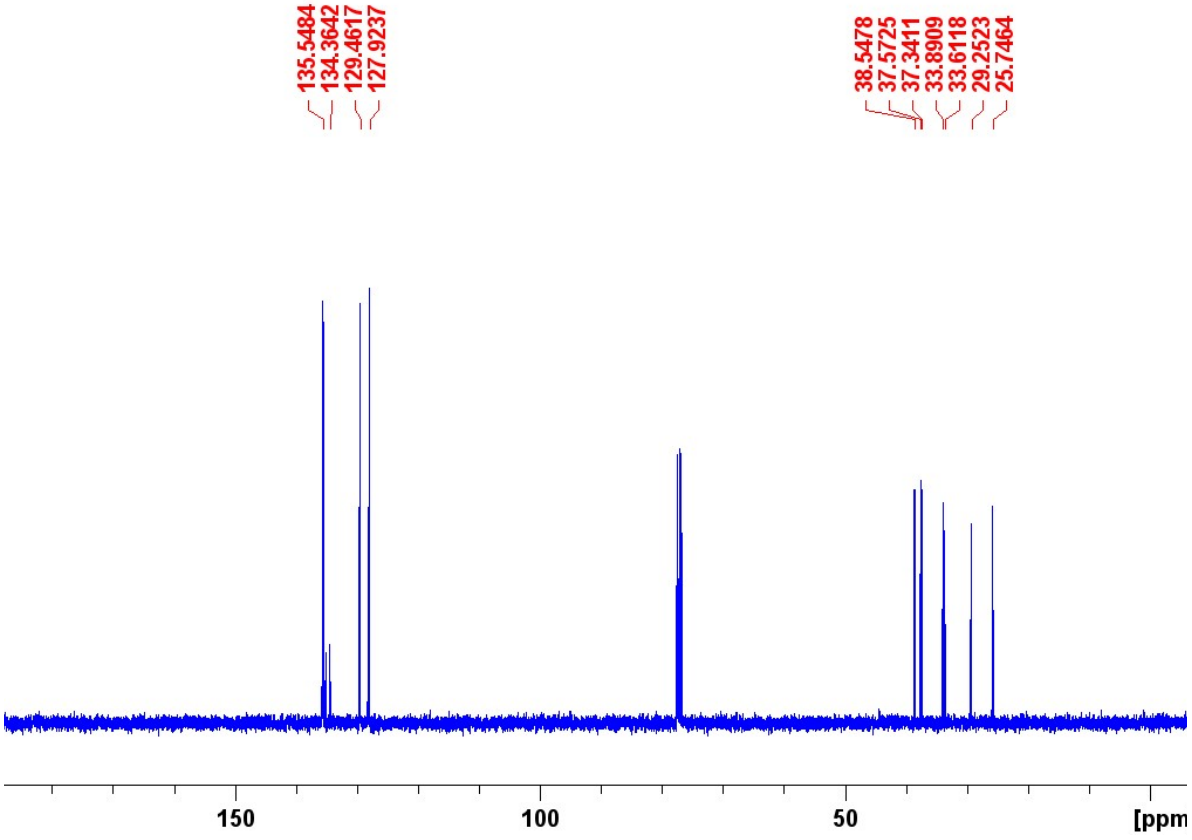
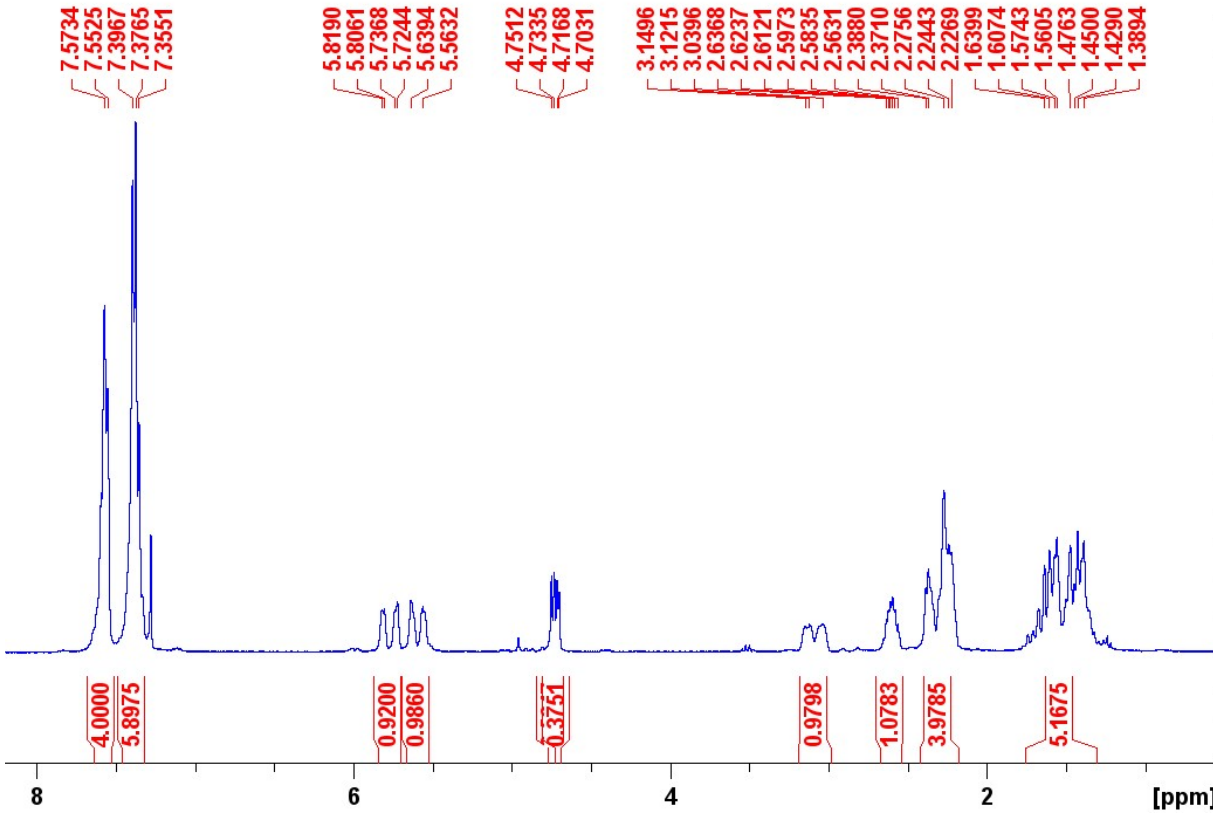


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of **3a** ($CDCl_3$, 100.6 MHz)



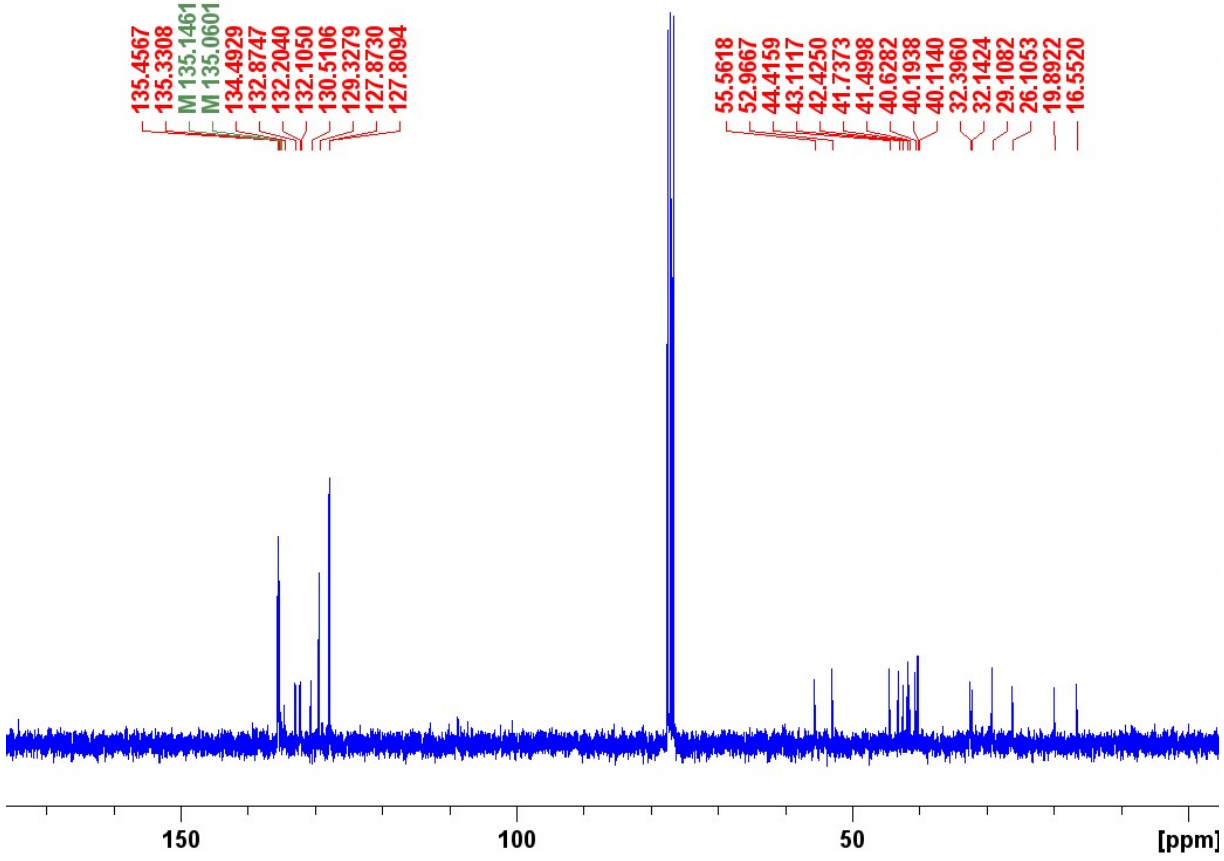


Figure S13: ^{1}H NMR spectrum of **3b** ($CDCl_3$, 300.0 MHz)

Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **3b** ($CDCl_3$, 75.0 MHz)

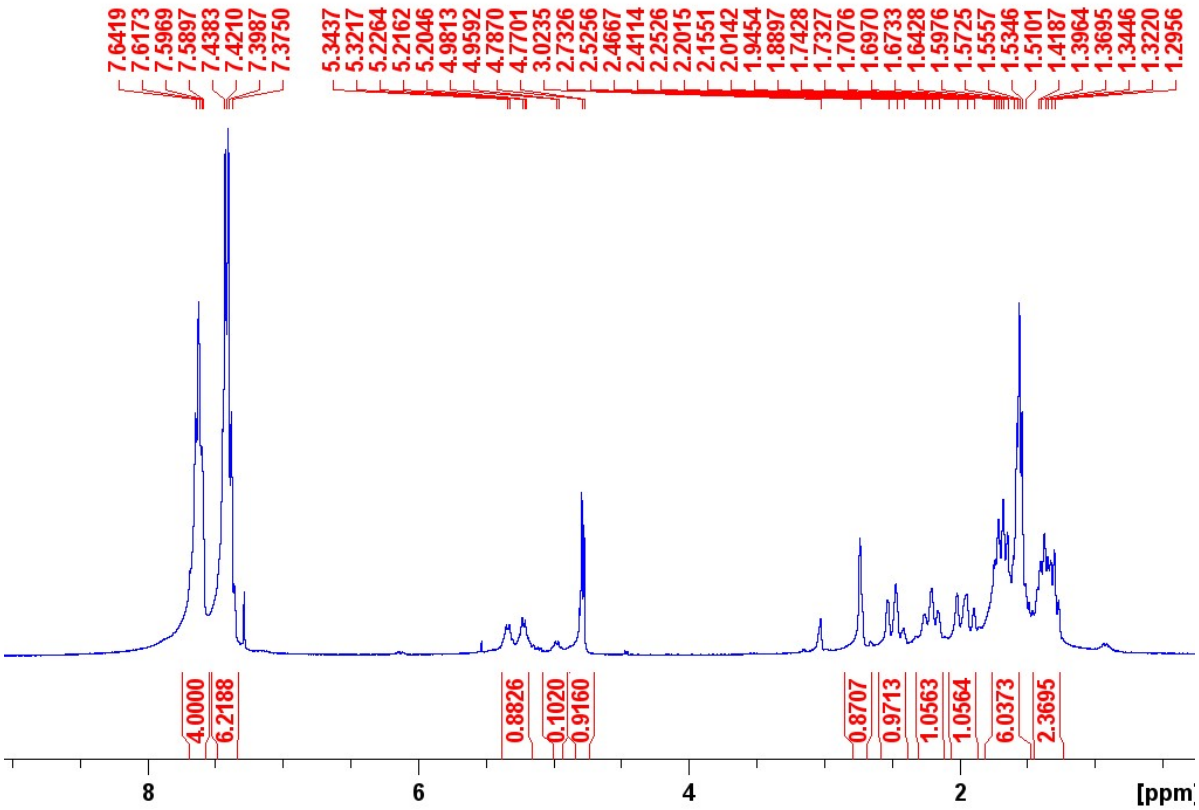


Figure S15: ^{1}H NMR spectrum of **3c** ($CDCl_3$, 300.0 MHz)

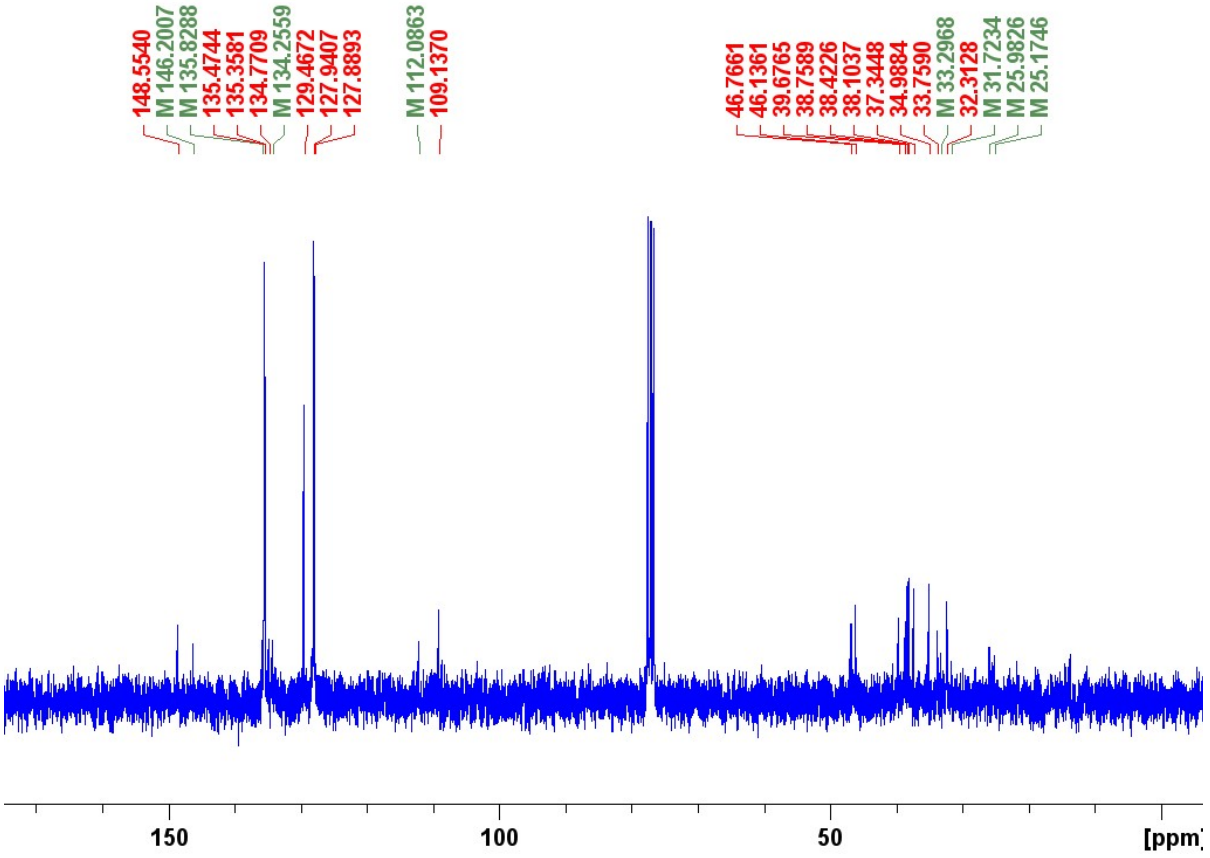
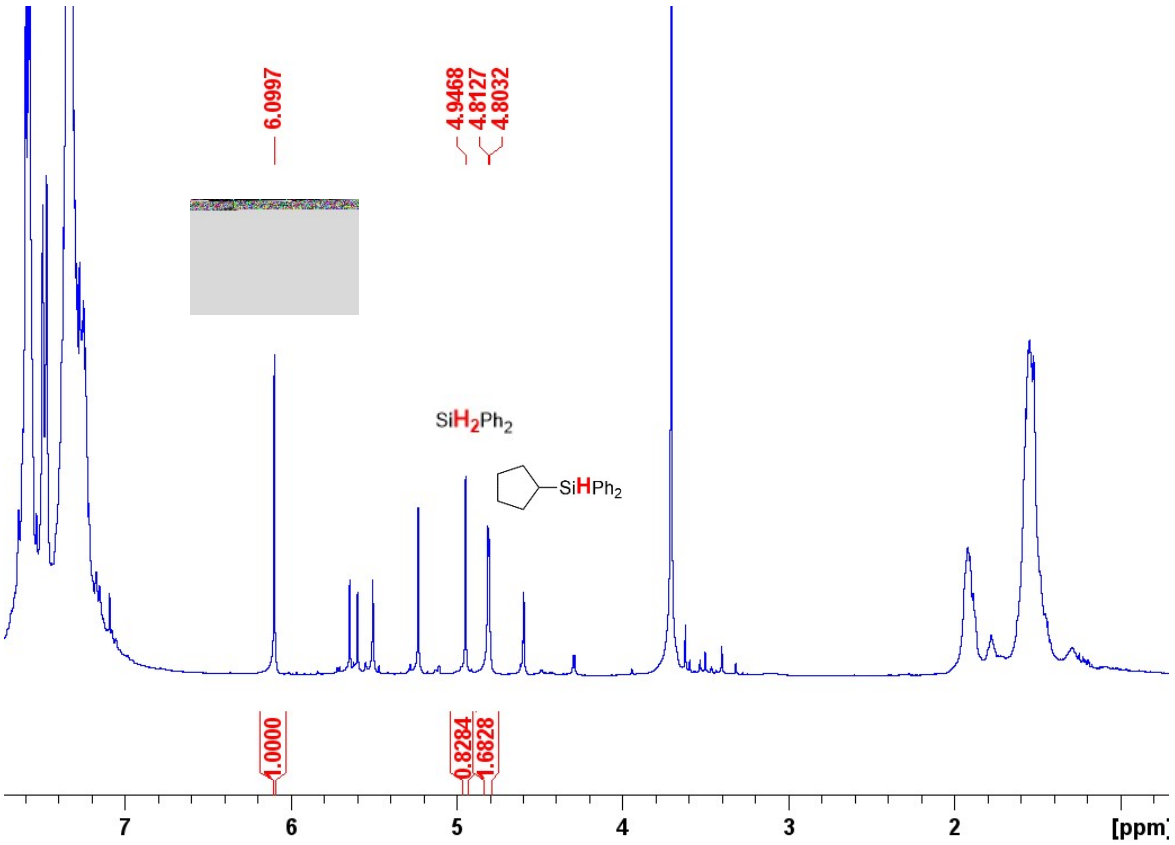


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of **3c** ($CDCl_3$, 75.0 MHz)



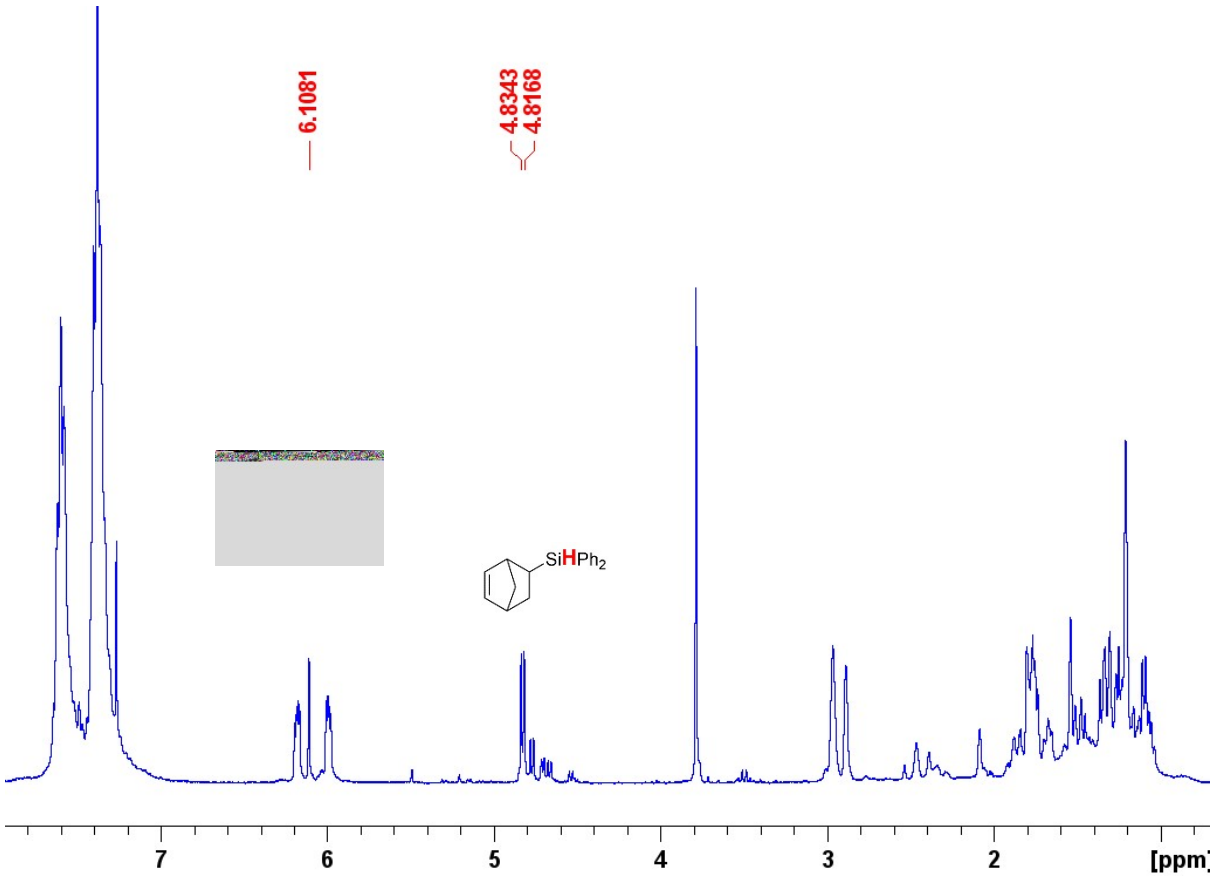
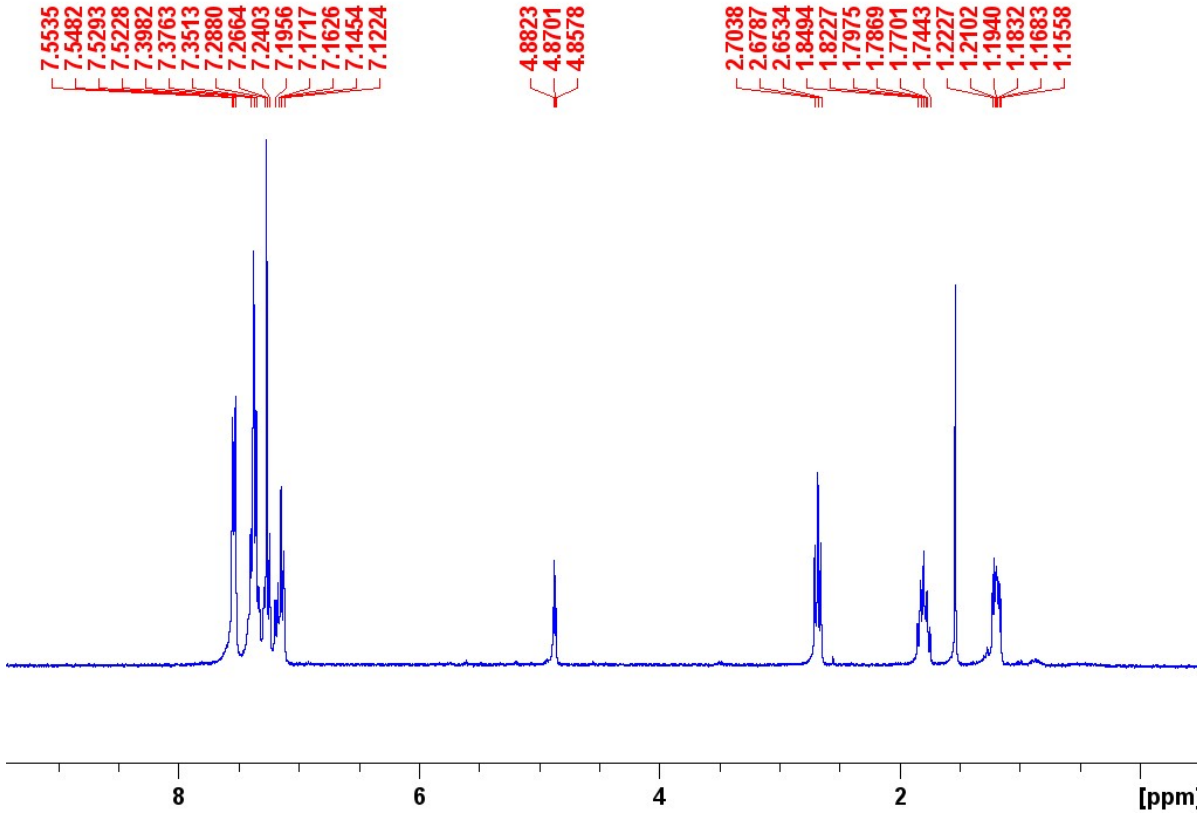


Figure S17: ^{1}H NMR spectrum of crude reaction mixture containing **3d** ($CDCl_3$, 300.0 MHz)

Figure S18: ^{1}H NMR spectrum of crude reaction mixture containing **3e** ($CDCl_3$, 300.0 MHz)



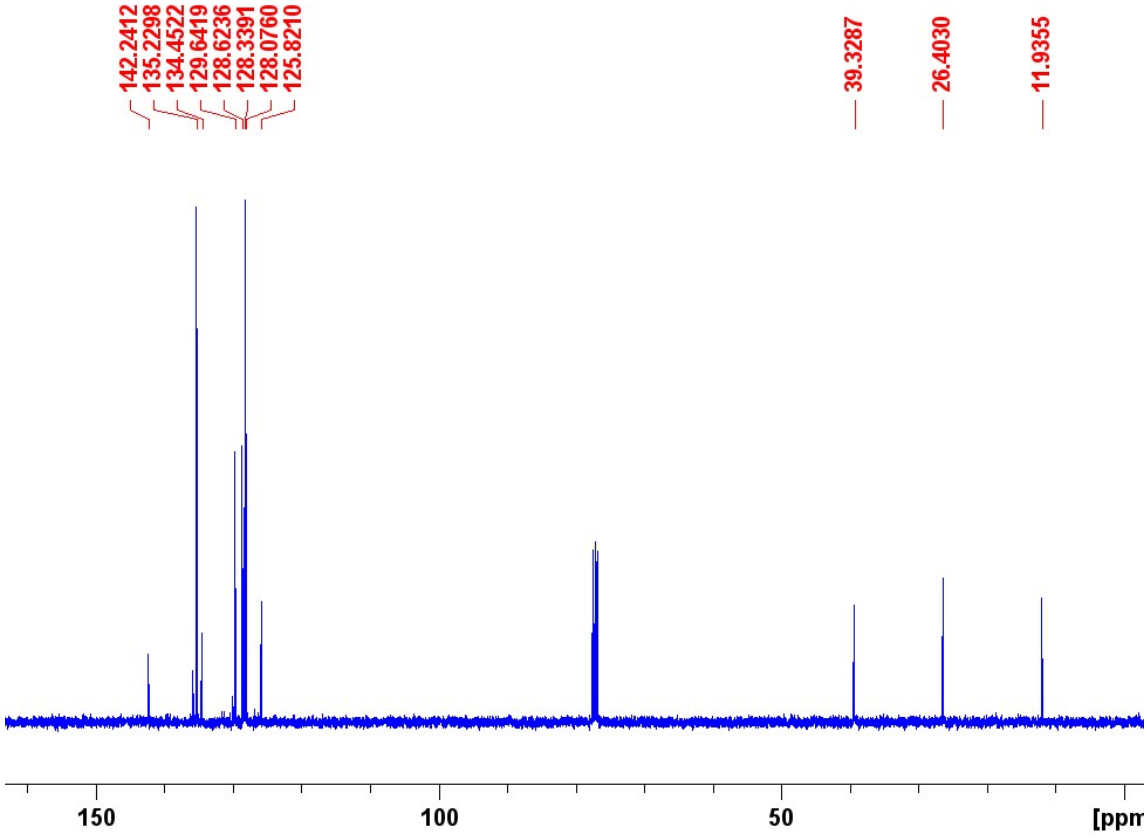


Figure S19: ^{1}H NMR spectrum of **3f** ($CDCl_3$, 400.0 MHz)

Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum of **3f** ($CDCl_3$, 100.6 MHz)

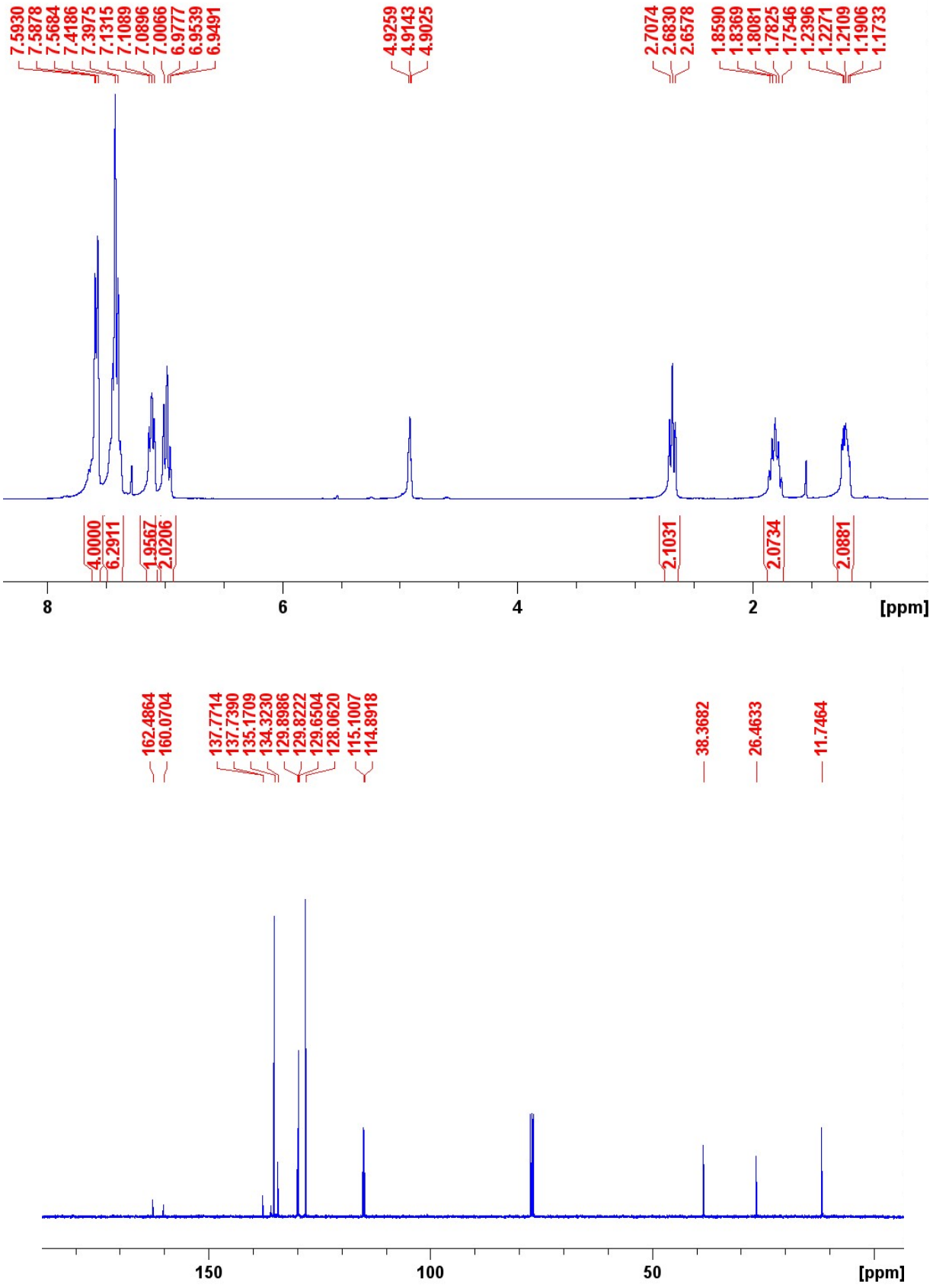


Figure S21: ^{1}H NMR spectrum of **3g** ($CDCl_3$, 400.0 MHz)

Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum of **3g** ($CDCl_3$, 100.6 MHz)

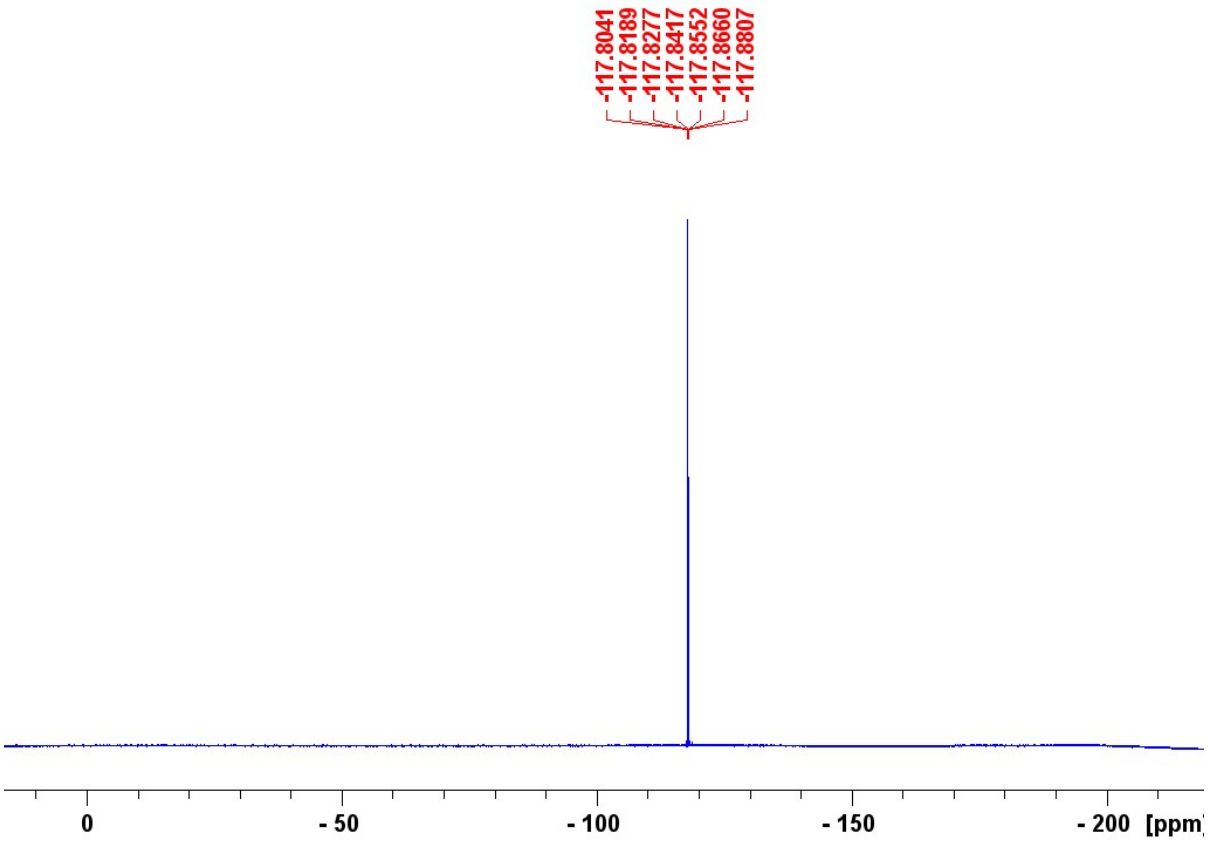


Figure S23: ^{19}F NMR spectrum of **3g** ($CDCl_3$, 376.5 MHz)

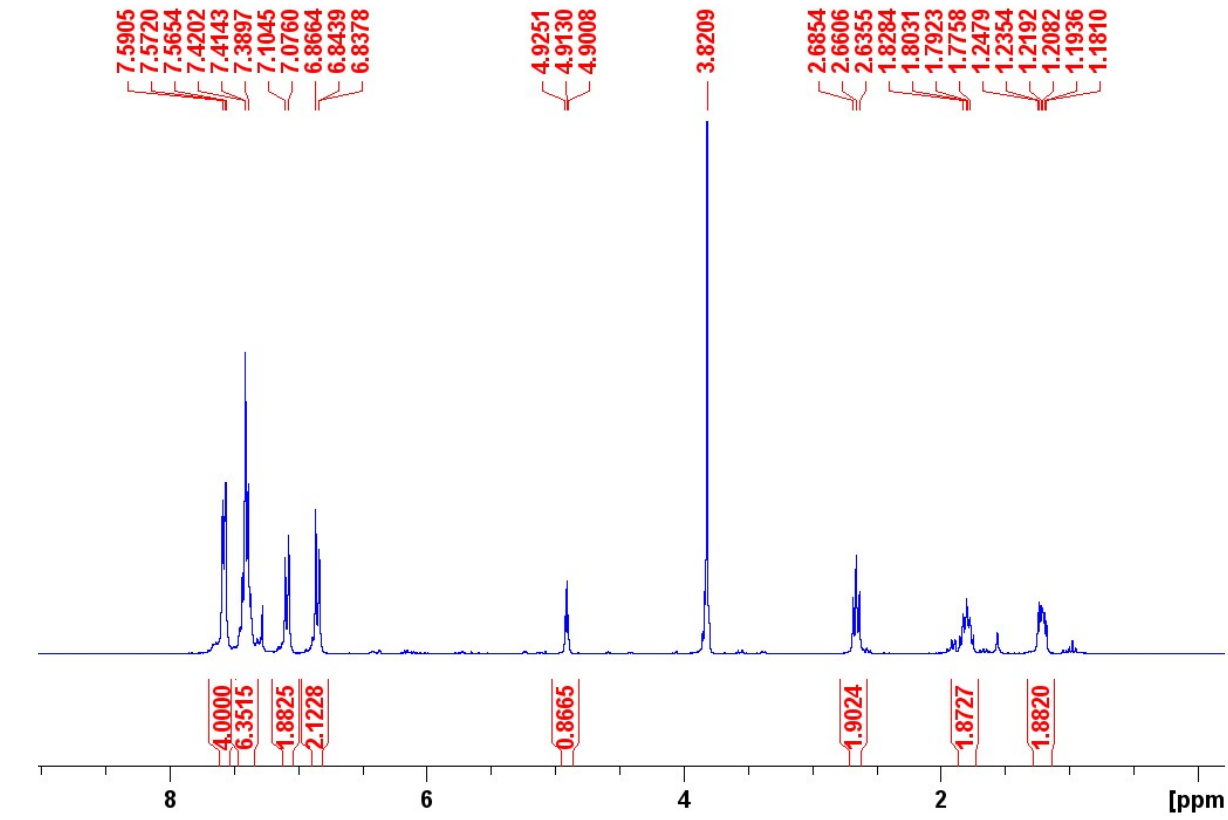


Figure S24: ^{1}H NMR spectrum of **3h** ($CDCl_3$, 300.0 MHz)

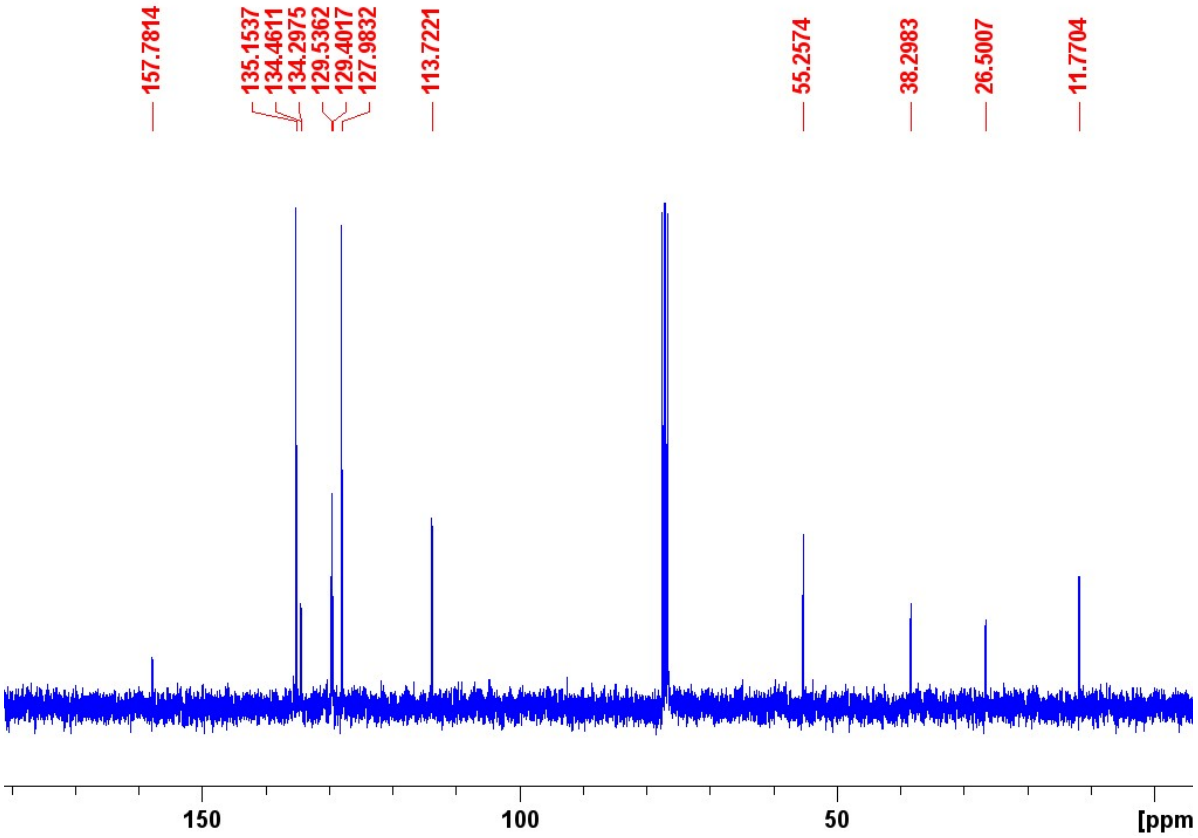


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of **3h** ($CDCl_3$, 75.0 MHz)

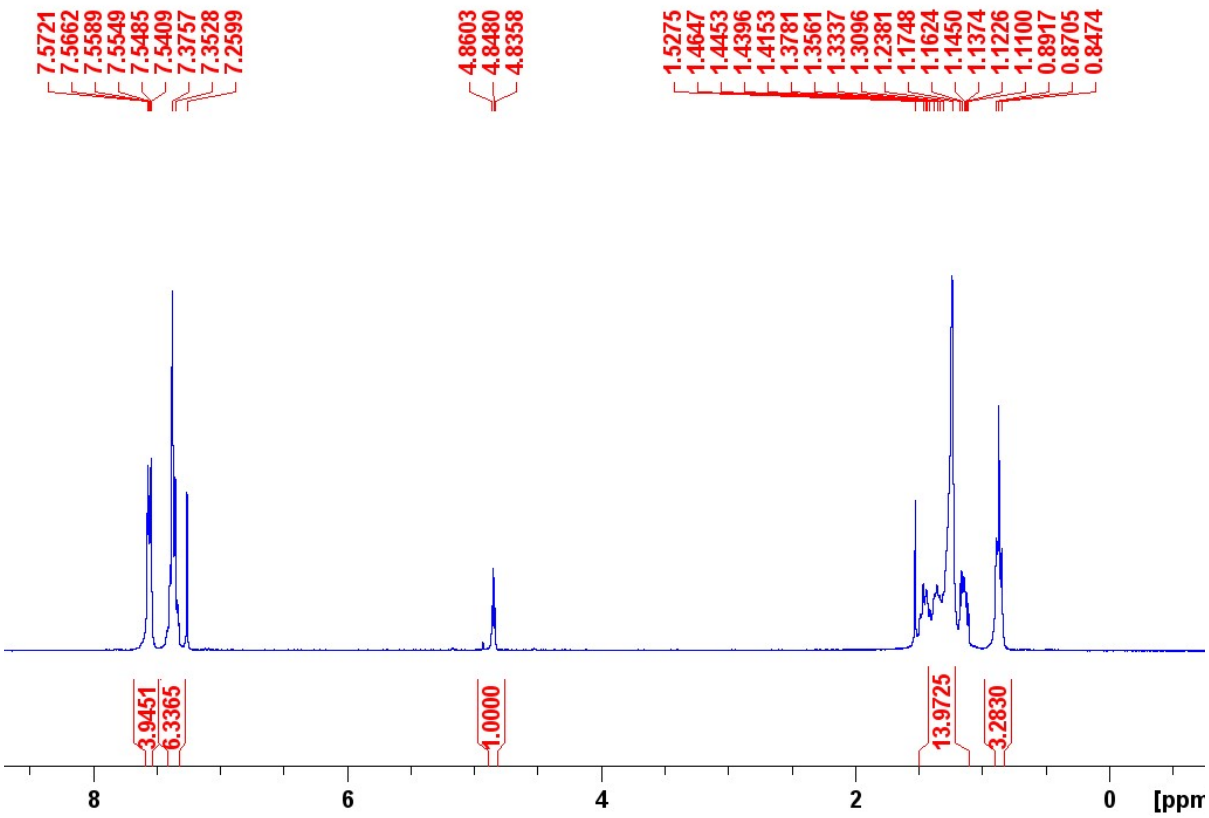


Figure S26: ^{1}H NMR spectrum of **3i** ($CDCl_3$, 400.0 MHz)

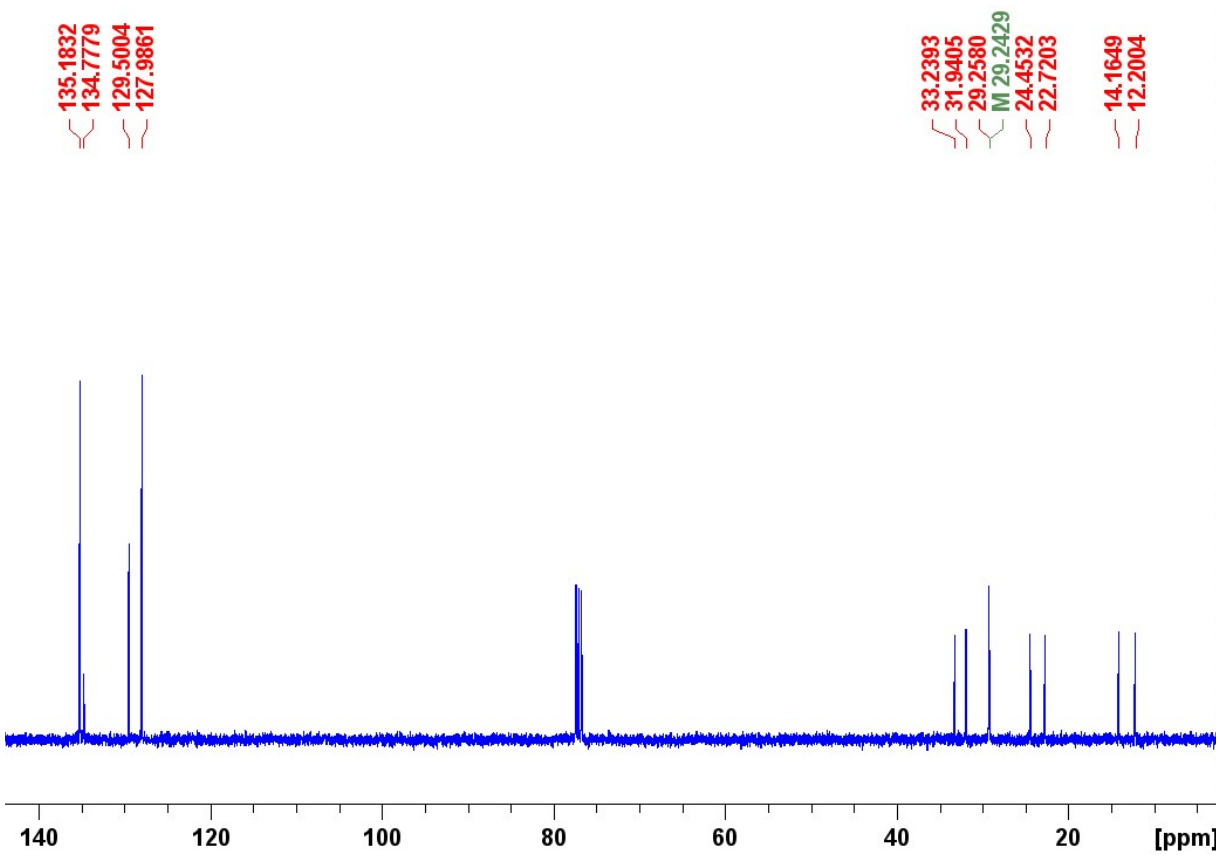


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of **3i** ($CDCl_3$, 100.6 MHz)

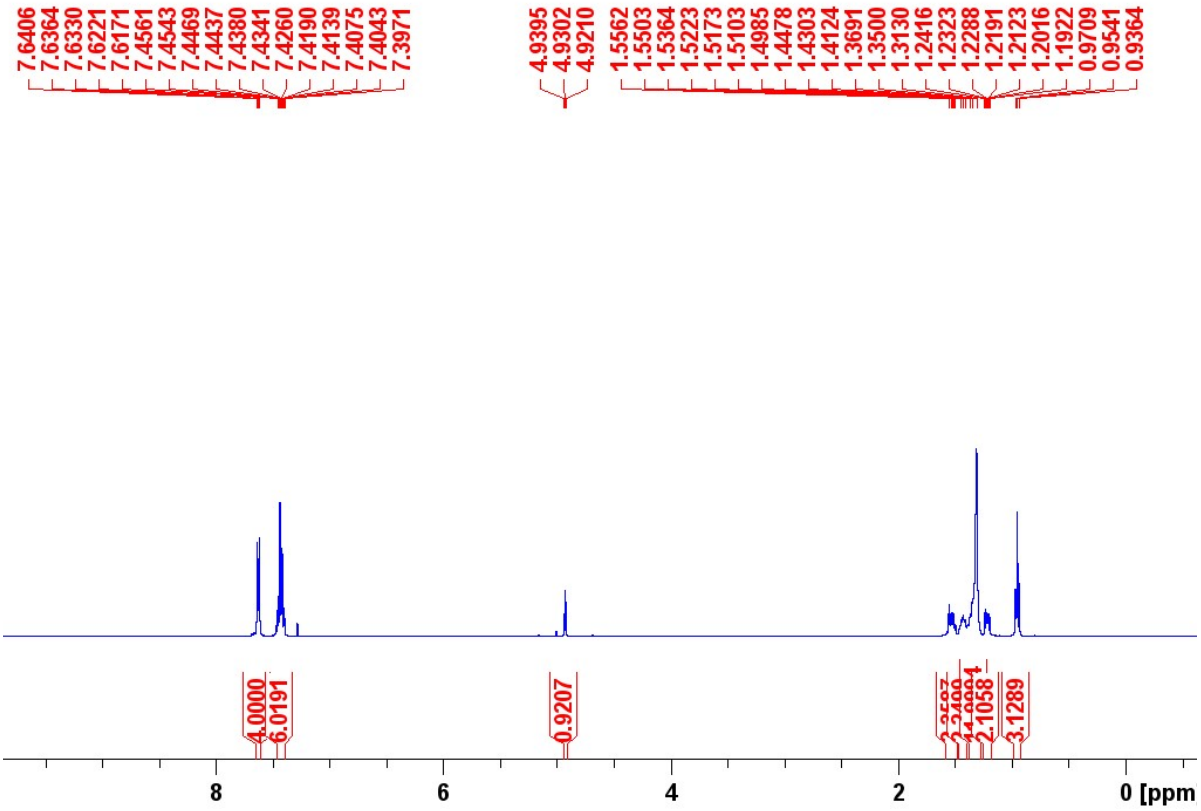


Figure S28: ^{1}H NMR spectrum of **3j** ($CDCl_3$, 400.0 MHz)

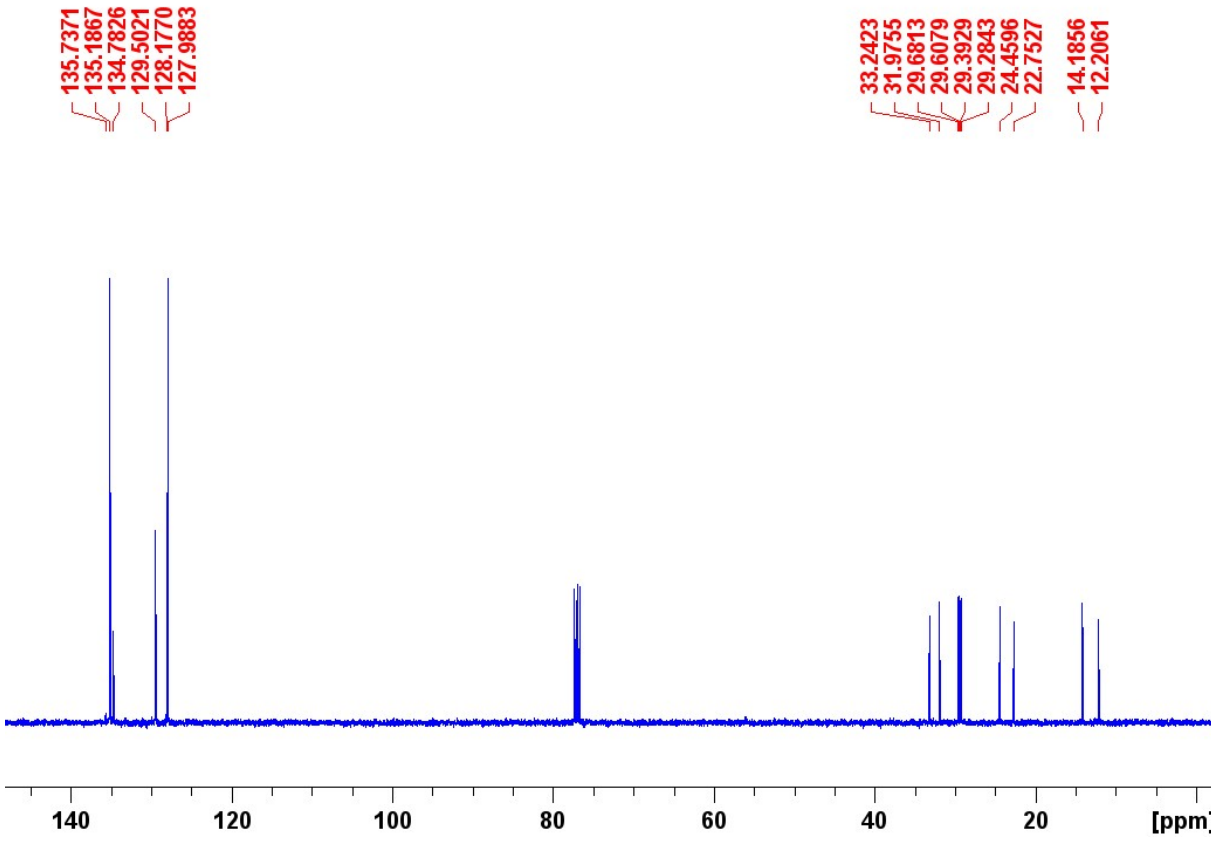


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum of **3j** ($CDCl_3$, 100.6 MHz)

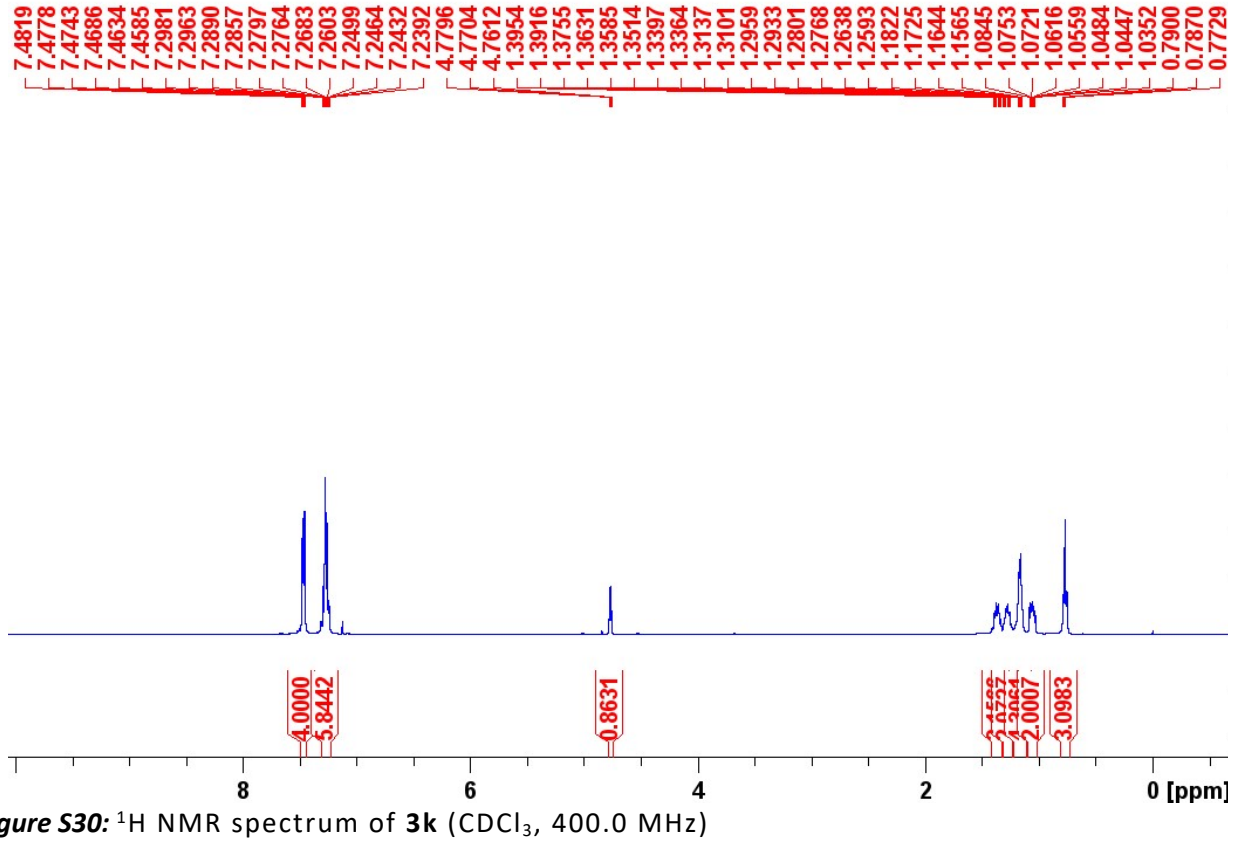


Figure S30: ^{1}H NMR spectrum of **3k** ($CDCl_3$, 400.0 MHz)

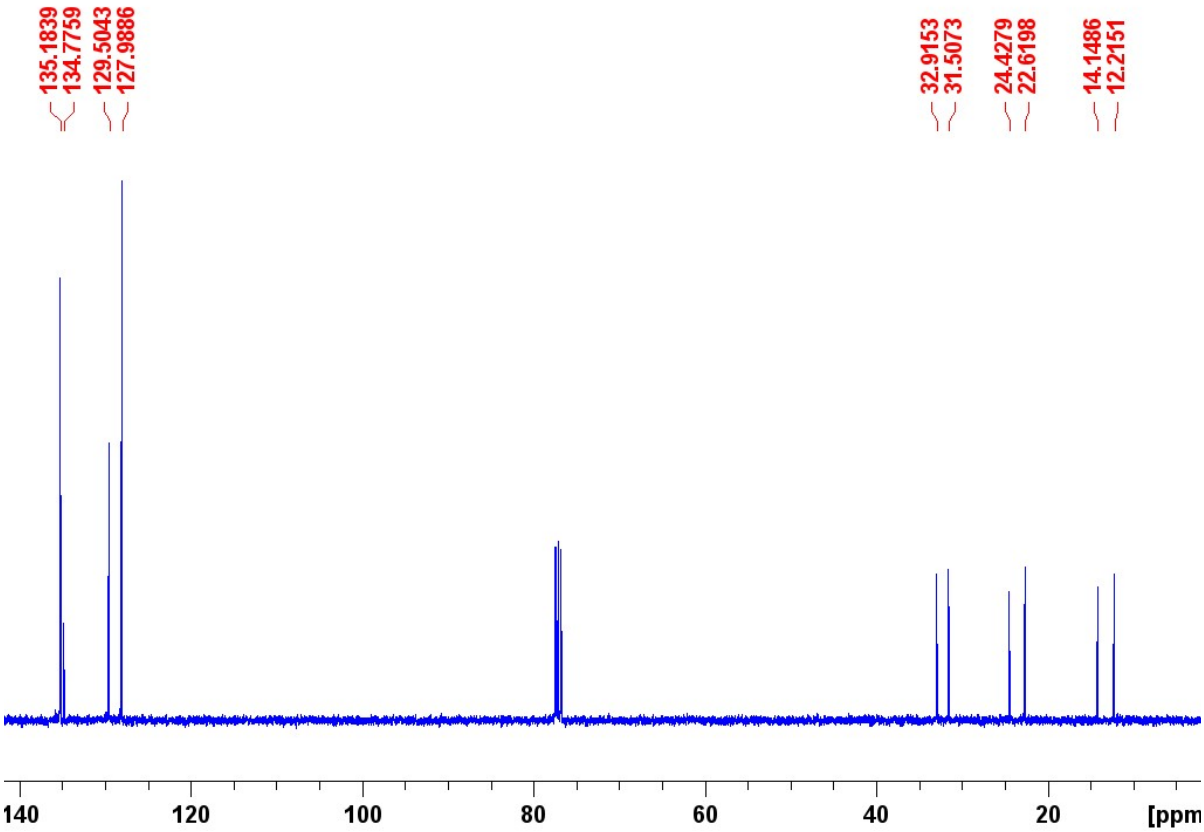


Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of **3k** ($CDCl_3$, 100.6 MHz)

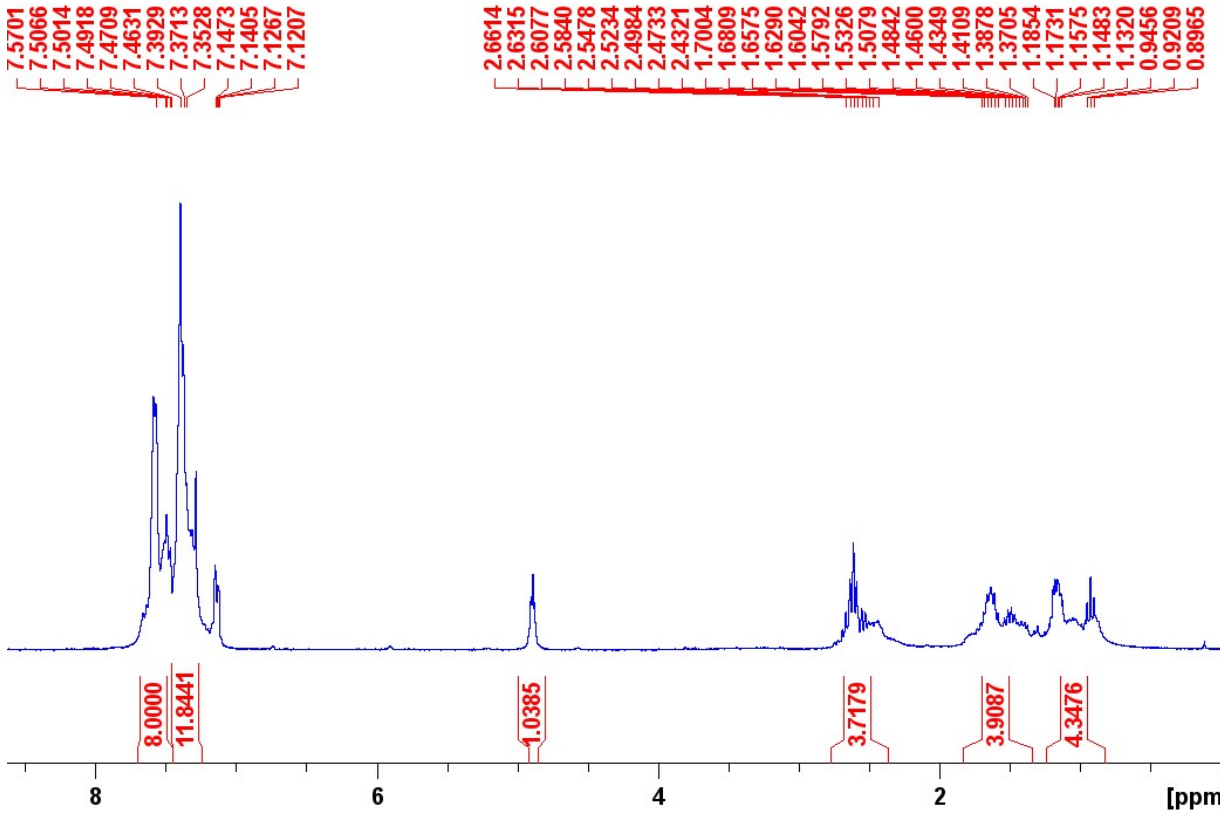


Figure S32: ^{1}H NMR spectrum of **3l** ($CDCl_3$, 300.0 MHz)

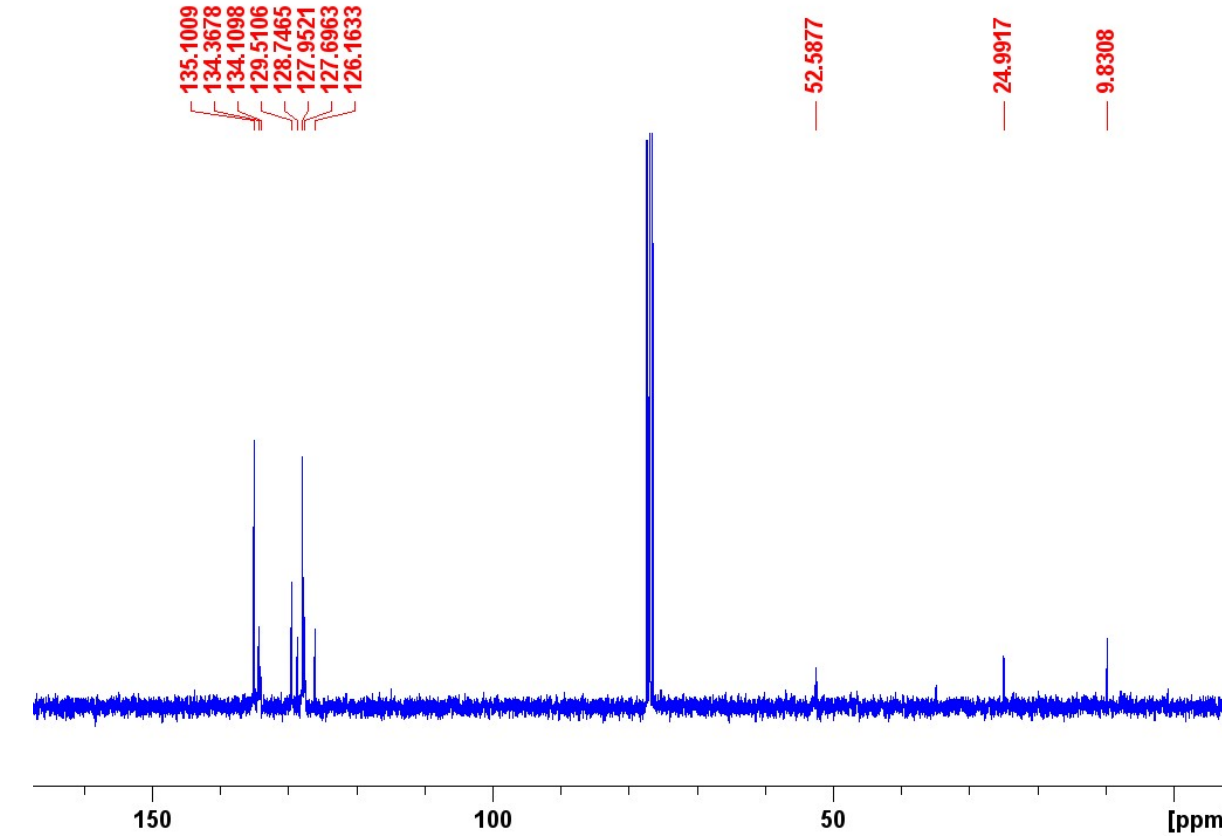


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum of **3l** ($CDCl_3$, 75.0 MHz)

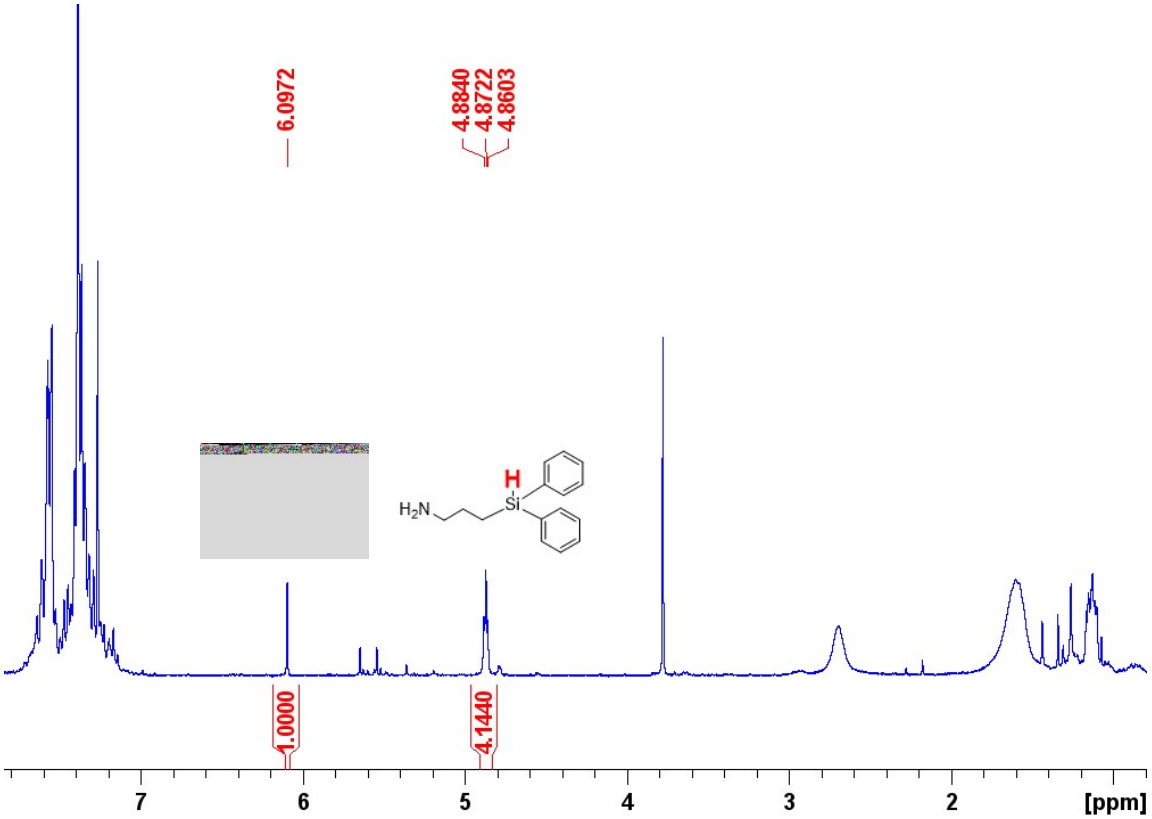


Figure S34: ^{1}H NMR spectrum of crude reaction mixture containing **3m** ($CDCl_3$, 300.0 MHz)

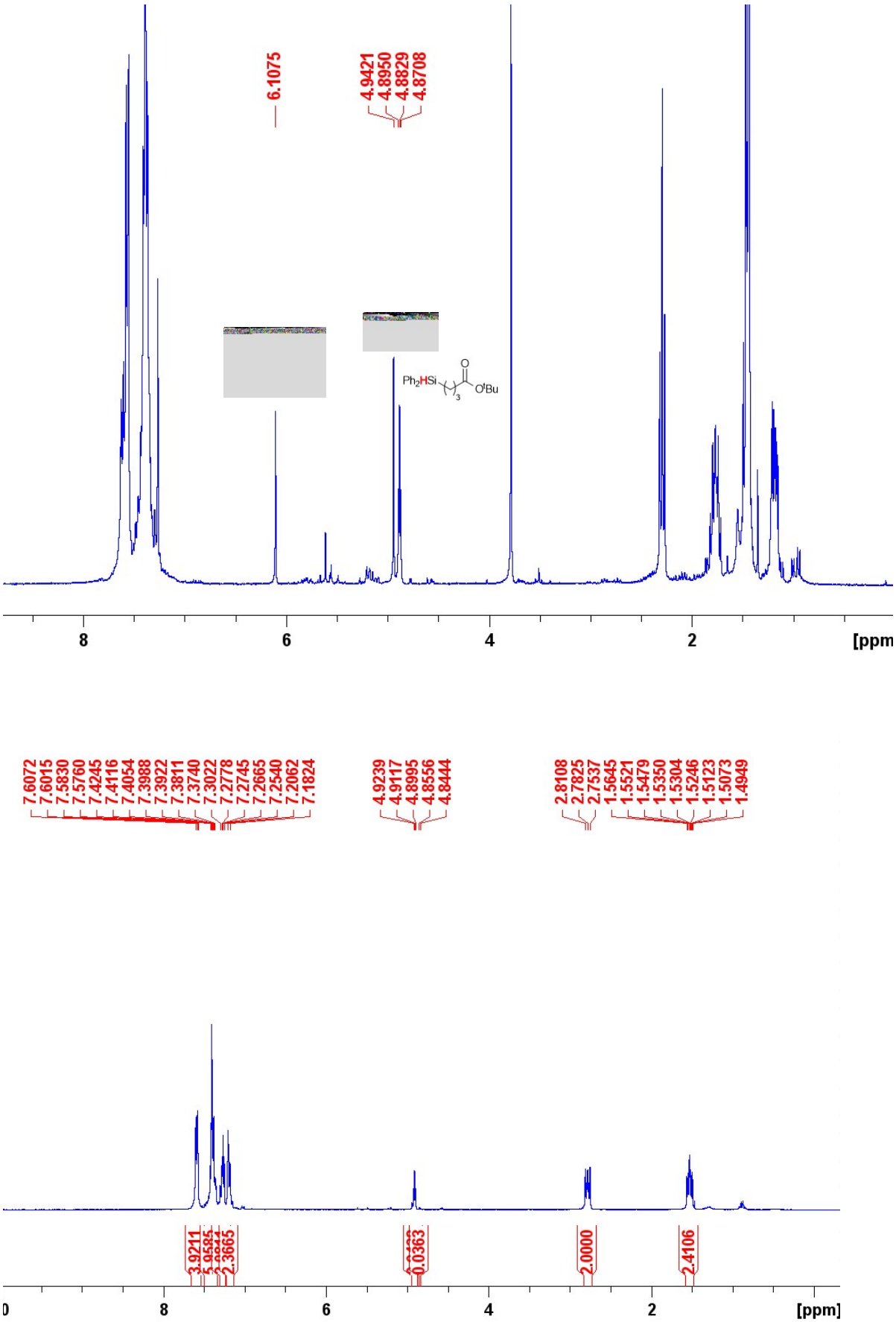


Figure S35: ^{1}H NMR spectrum of crude reaction mixture containing **3n** ($CDCl_3$, 300.0 MHz)

Figure S36: ^{1}H NMR spectrum of **3o/o'** ($CDCl_3$, 400.0 MHz)

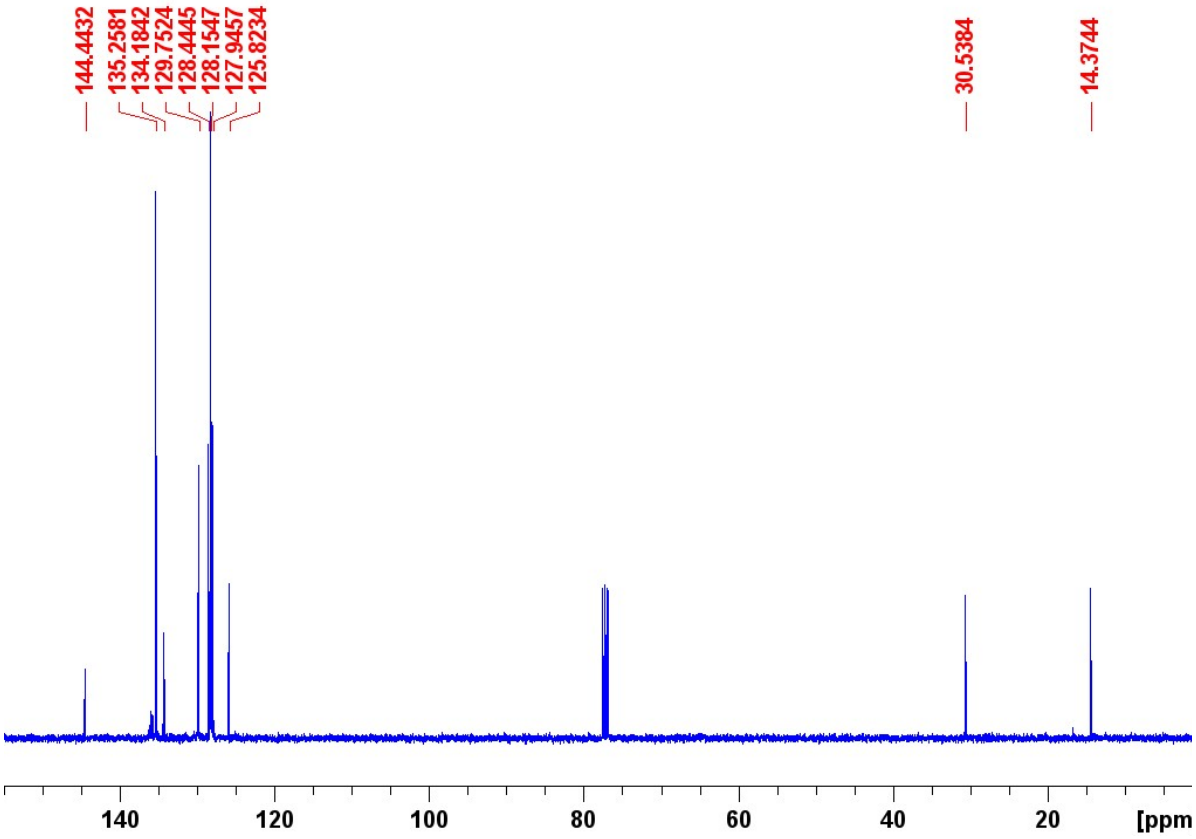


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **3o/o'** ($CDCl_3$, 100.6 MHz)

Figure S38: ^{1}H NMR spectrum of **3p/p'** ($CDCl_3$, 300.0 MHz)

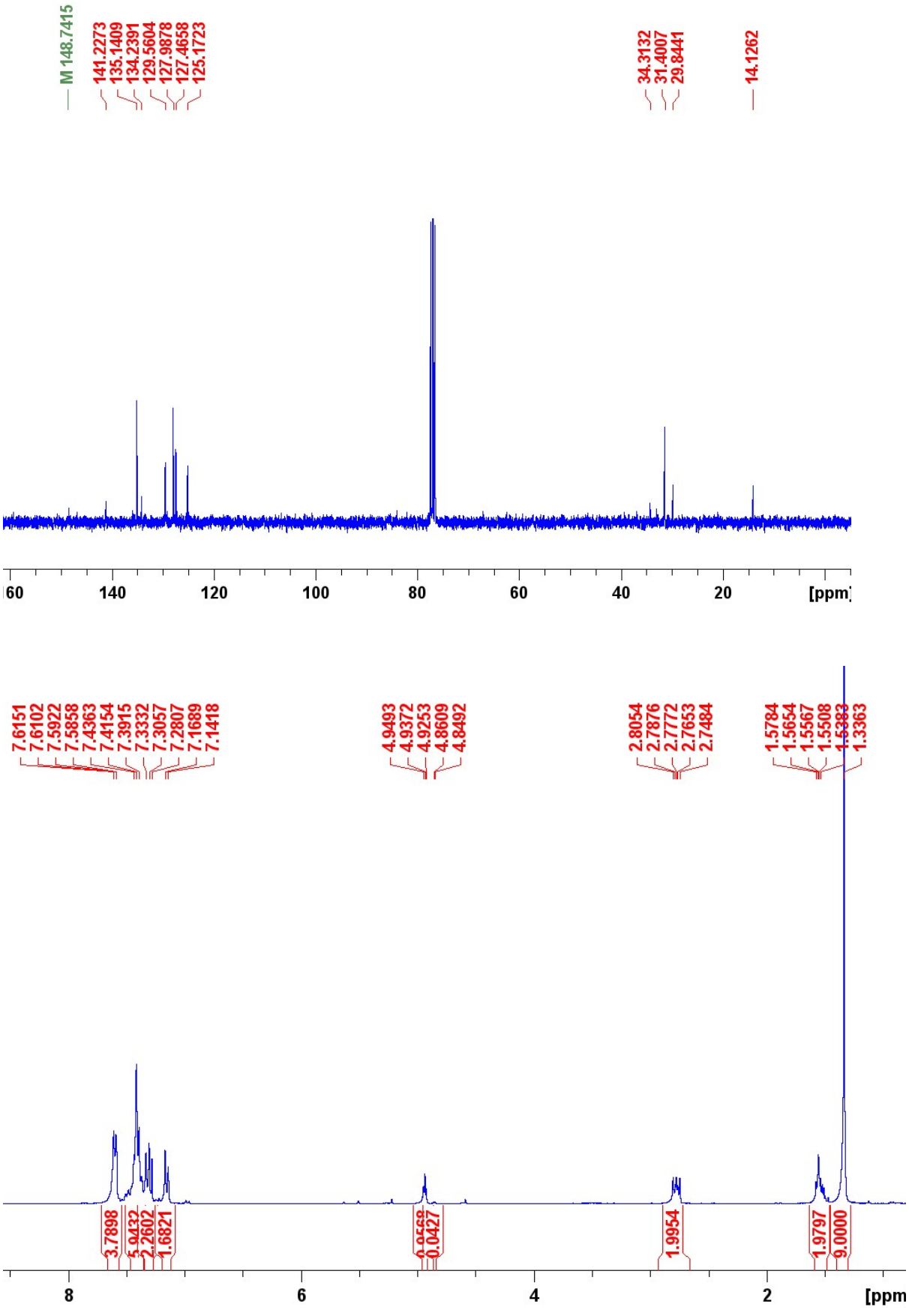


Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of **3p/p'** ($CDCl_3$, 75.0 MHz)

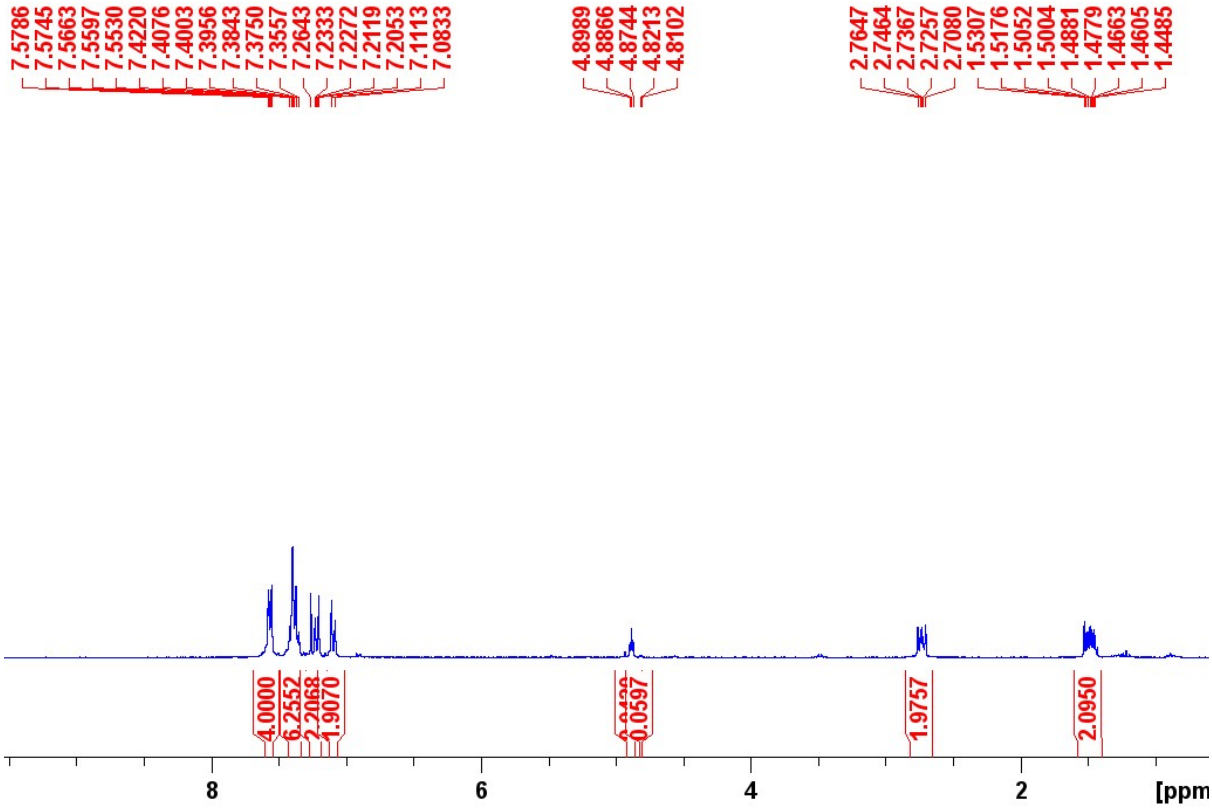


Figure S40: ^{1}H NMR spectrum of **3q/q'** ($CDCl_3$, 400.0 MHz)

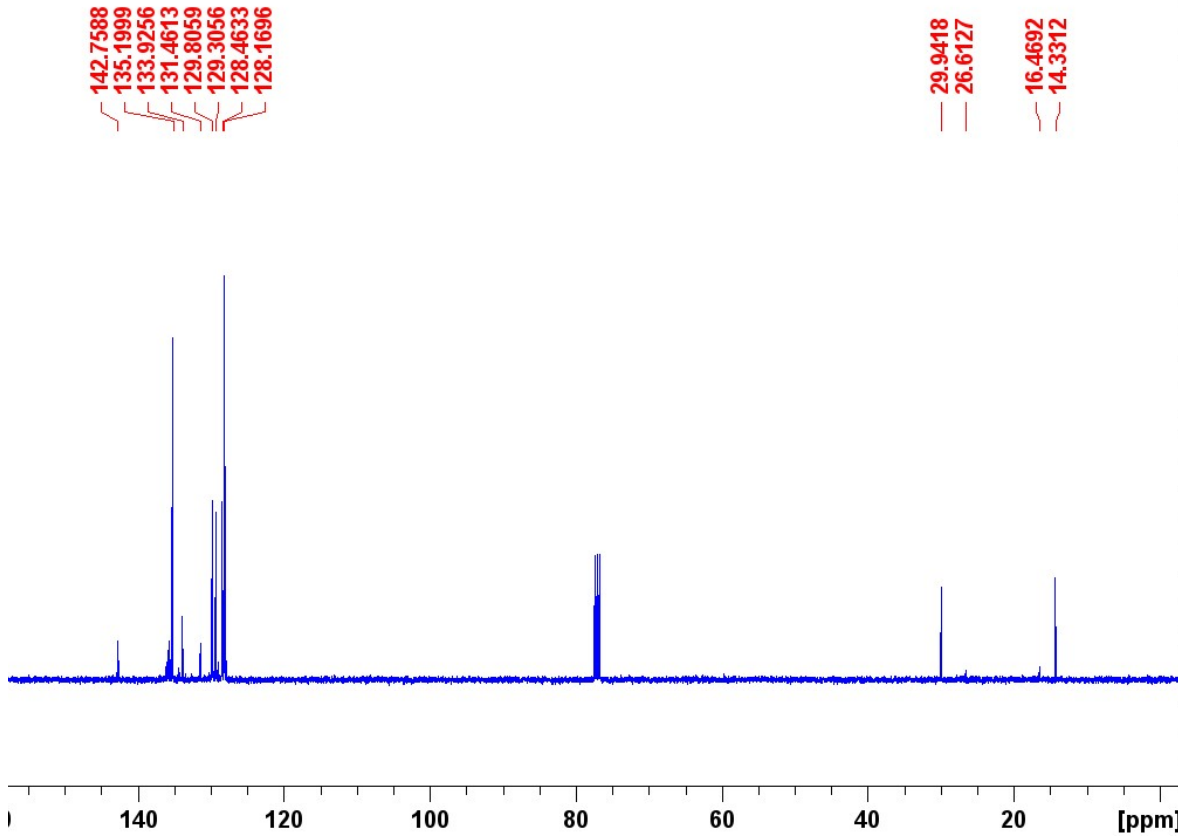


Figure S41: ^{13}C{^{1}H} NMR spectrum of **3o/o'** ($CDCl_3$, 100.6 MHz)

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