Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

For

Ruthenium-catalyzed dealkenative *N*-silylation of amines by substituted vinylsilanes

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1. General Considerations.

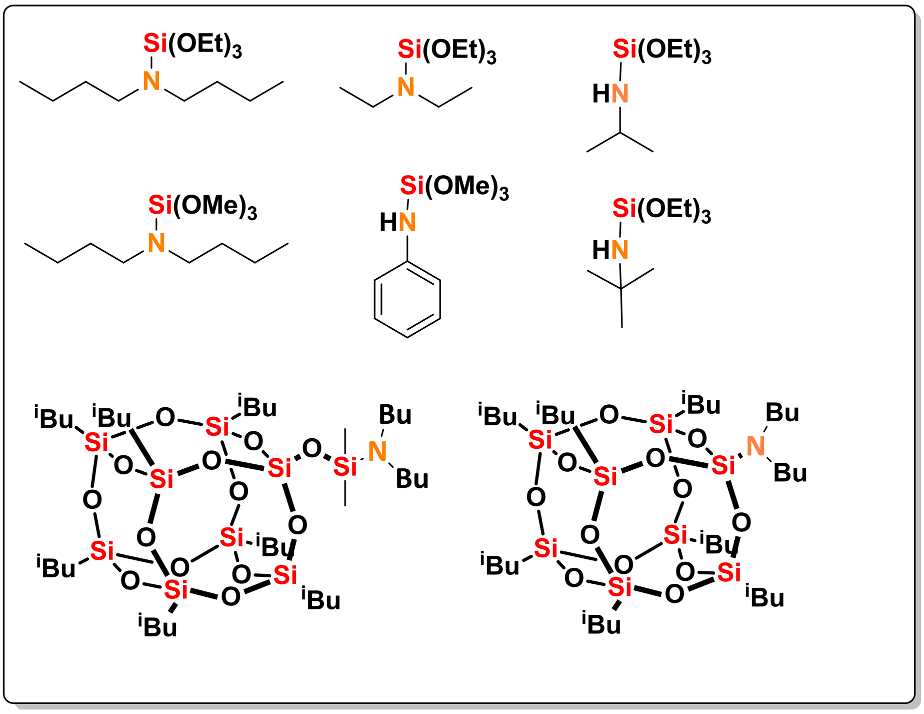
Reactions were carried out under ambient atmosphere unless otherwise noted. All air-sensitive compounds and reactions were performed under an inert atmosphere of nitrogen using rotaflow stopcock. All glassware was stored in an oven or flame-diered prior to use. Deutrated toluene was diered over NaK alloy. The reagents used for experiments were purchased from Sigma-Aldrich Co and fleshly distilled before use and stored under argon atmosphere. The synthesis of the starting 1-vinyl-3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.3,9.15,1517,13]-octasiloxane and 1-(vinyldimethyl)siloxy-(3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.3,9.15,1517,13]octasiloxane was based on literature procedure.[2,3] $[RuHCl(CO)(PCy_3)_2]$ was prepared according to a literature method.[1] Toluene were dried according to standard procedures and freshly distilled prior to use. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 MHz spectrometer using C_6D_6 or C_7D_8 as a solvent. GC analyses were performed on a Varian 3400CX with a Megabore column (30 m x 0.15 nm) and TCD. Mass spectra of the products were determined by GC-MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and a Finigan Mat 800 ion trap detector.

NMR measurements were performed on Bruker Avance III DRX 600, operating at frequencies of 600.200 MHz (^{1}H), 92.197 MHz (^{2}H) and 242.965 MHz (^{31}P). NMR spectra were recorded at 298 K. ^{1}H resonance was observed using signals of deuterated toluene (2.08 ppm) as internal standard. ^{2}H spectra were recorded using mixture of 10% deuterated and 90% of undeutrated form of toluene. Chemical shifts are reported in ppm, relative to deuterated toluene at 2.08 ppm (^{1}H and ^{2}H NMR). ^{31}P NMR spectra were refered to 85% H_3PO_4 at 0 ppm, the ^{31}P chemical shifts were uncorrected. Deuterium resonance was measured using ^{2}H lockswitch unit, with 1D sequence without decoupling. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

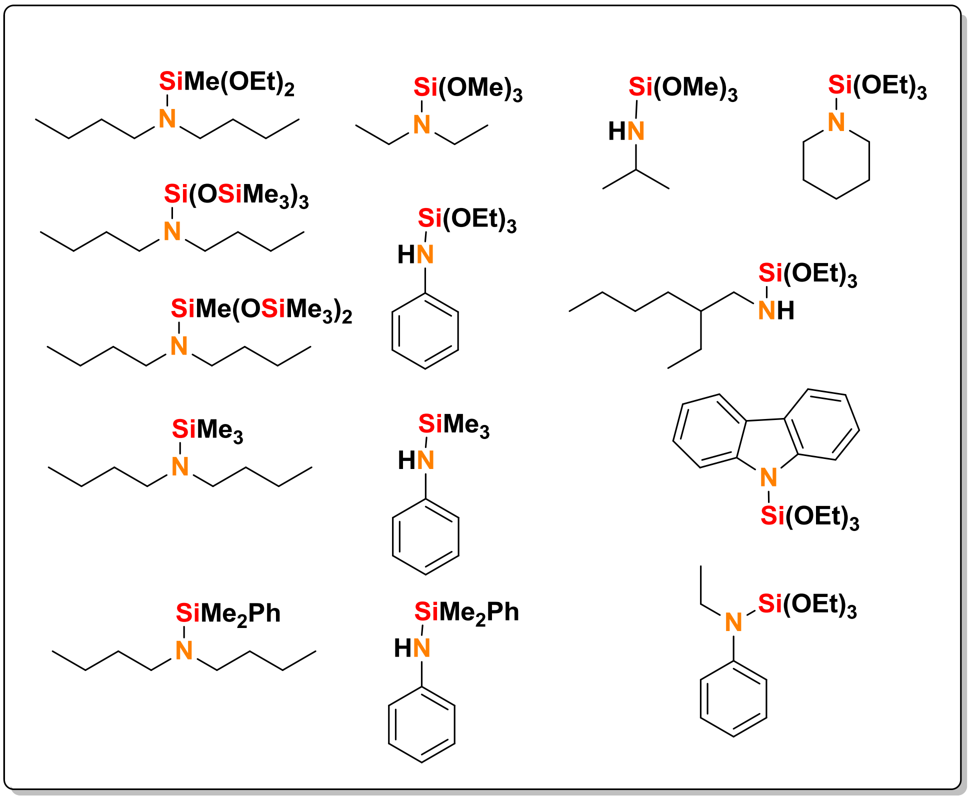
2. Experimental section

2.1 Preparation of Products

2.1.1 Obtained compounds-isolated



2.1.2 Obtained compounds-not isolated



2.2 A general procedure for *N*-silylation of amines with vinylsilanes

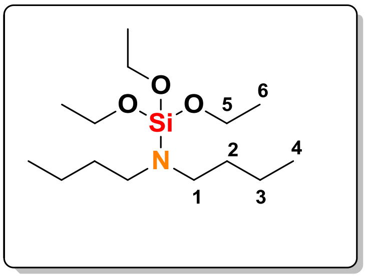
Reagents and solvent were dried and deoxygenated, the syntheses were carried out in a closed system under argon atmosphere. The ruthenium catalyst $[RuHCl(CO)(PCy_3)_2]$ (10 mg, 0.0138 mmol – entry entry 1-3, 6, 9-11 or 16.7 mg, 0.023 mmol - entry 4, 5, 7, 8, 12-21; see Table 1.) was dissolved in toluene (2 mL) and introduced into a Schlenk vessel equipped with rotaflo stopcock and magnetic stirring bar. Then in order: amine (0.46 mmol) and vinylsilane (0.46 mmol) for terminal vinylsilanes and styryltriethoxysilane or amine (0.92 mmol) and bis(silyl)ethene (0.46 mmol) were added. The reaction mixture was stirred and heated at 120°C and maintained at that temperature for 24 - 140 h (see Table 1). The progress of the reaction was monitored by GC and GCMS. The selected compounds were isolated by distillation.

2.3 A general procedure for stoichiometric reaction.

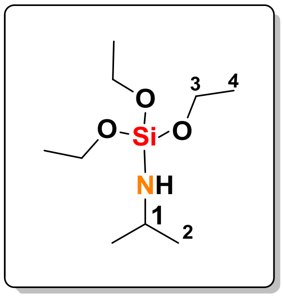
In an J. Young NMR tube 0.01 g (0.013 mmol) of $[RuHCl(CO)(PCy_3)_2]$ and 0.6 mL of toluene-d_8 were placed under argon. Next 0.102 g (1.37 mmol) of diethylamine-*N*-d and 0.247 g (0.688 mmol) of *(E)*-styryltriethoxysilane or 0.374 g (1,37 mmol) of triethoxy-[(*E*)-2-phenylethenyl]silane was added respectively and the reaction was monitored by ^{1}H NMR during heating at 120°C.

3. Analytical Data

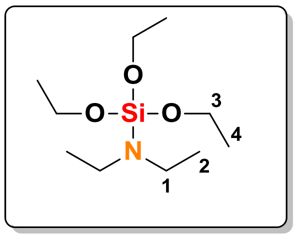
3.1 Spectroscopic data of selected products



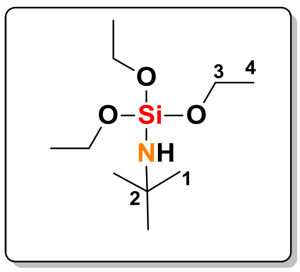
***N*-(triethoxysilyl)dibutylamine**. ^{1}H NMR (300 Mz, C_6D_6) δ (ppm): 0.97 (t, J_{HH} = 7.48 Hz, 6H, H_4), 1.23 (t, J_{HH} = 7.02 Hz, 9H, H_6), 1.35 (m, 4H, H_3), 1.55 (p, J_{HH} = 7.55 Hz, 4H, H_2), 2.95 (t, J_{HH} = 7.48 Hz, 4H, H_1), 3.85 (q, J_{HH} = 7.02 Hz, 6H, H_5). ^{13}C NMR (75 Mz, C_6D_6) δ (ppm): 14.36 (C_4), 18.57 (C_6), 20.68 (C_3), 32.61 (C_2), 45.94 (C_1), 58.79 (C_5). MS (EI): m/z (rel. intensity-%): 290.2$^{•+}$ (2), 248.2 (100), 204.3 (12), 162.2 (11), 119 (5), 63 (3).



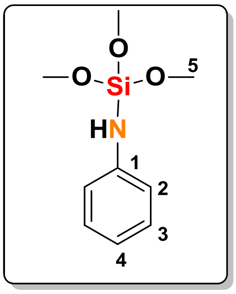
***N*-(triethoxysilyl)isopropylamine**.^{1}H NMR (300 Mz, C_6D_6) δ (ppm): 1.06 (d, J_{HH} = 6.34 Hz, 6H, H_2), 1.21 (t, J_{HH} = 6.99 Hz, 9H, H_4), 3.24 (m, 1H, H_1), 3.86 (q, J_{HH} = 6.99 Hz, 6H, H_3). ^{13}C NMR (75 Mz, C_6D_6) δ (ppm): 18.58 (C_4), 27.53 (C_2), 42.73 (C_1), 58.74 (C_3). MS (EI): m/z (rel. intensity-%): 222.3$^{\bullet+}$ (100), 206 (72), 176.10 (5), 162 (4), 119 (3).



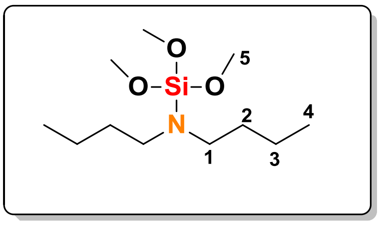
***N*-(triethoxysilyl)diethylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 1.05 (t, J_{HH} = 7.03 Hz, 6H, H_2), 1.18 (t, J_{HH} = 7.03 Hz, 9H, H_4), 2.37 (q, J_{HH} = 7.14 Hz, 1H, H_1), 2.92 (q, J_{HH} = 6.99 Hz, 3H, H_1), 3.8 (q, J_{HH} = 6.99 Hz, 6H, H_3). ^{13}C NMR (75 Mz, C_7D_8) δ (ppm): 18.52 (C_2), 21.42 (C_4), 33.25 (C_1), 58.64 (C_3). MS (EI): m/z (rel. intensity-%): 234.2$^{\bullet+}$ (8), 220.2 (100), 190.3 (5), 176.2 (39), 163.2 (10), 148.3 (3), 132.2 (5), 119.1 (11), 107.2 (3), 91.1 (3), 79.1 (5), 72.2 (3), 45.1 (3).



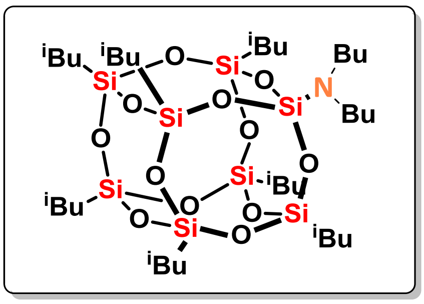
***N*-(triethoxysilyl)*tert*-butylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 0.81 (s, 12H: 9H from H_1 and 3H from $C_4H_{11}N$), 1.0 (t, J_{HH} = 7.02 Hz, 9H, H_4), 3.65 (q, J_{HH} = 7.02 Hz, 6H, H_3). ^{13}C NMR (75 Mz, C_7D_8) δ (ppm): 16.06 (C_1), 30.37 (C_4), 44.78 (C_2), 56.88 (C_3). MS (EI): m/z (rel. intensity-%): 226.3$^{\bullet+}$ (7), 220.5 (100), 176.3 (7), 119.3 (3).



***N*-(trimethoxysilyl)phenylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 3.43 (s, 9H, H_5), 6.32 - 6.34 (d, J_{HH} = 7.58 Hz 2H, H_2), 6.66 (t, J_{HH} = 7.34 Hz, 1H, H_4), 7.02 (t, J_{HH} = 7.34 Hz, 2H, H_3). ^{13}C NMR (75 Mz, C_7D_8) δ (ppm): 50.36 (C_5), 115.01 (C_2), 118.19 (C_4), 122.92 (C_3), 137.51 (C_1). MS (EI): m/z (rel. intensity-%): 213.2$^{\bullet+}$ (100), 195.2 (7), 181.2 (22), 151.2 (4), 121.7 (7), 106.1 (4), 91.2 (7), 59 (7), 45 (3).

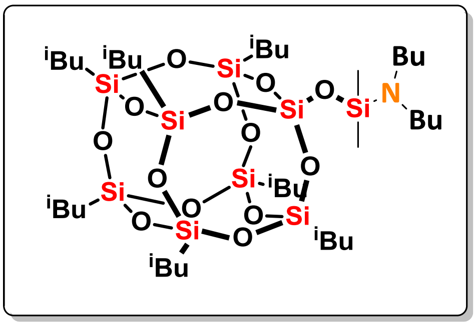


***N*-(trimethoxysilyl)dibutylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 0.91 (t, J_{HH} = 7.34 Hz, 6H, H_4), 1.28 (sextet, J_{HH} = 6 Hz, 4H, H_3), 1.48 (m, 4H, H_2), 2.33 (t, J_{HH} = 6.97 Hz, 3H, H_2), 2.86 (t, J_{HH} = 7.46 Hz, 1H, H_1), 3.48 (s, 9H, H_5). ^{13}C NMR (75 Mz, C_7D_8) δ (ppm): 13.81 (C_4), 20.15 (C_3), 32.11 (C_2), 50.15 (C_1), 53.92 (C_5). MS (EI): m/z (rel. intensity-%): 248.3$^{\bullet+}$ (36), 236.3 (3), 217 (6), 206.3 (100), 176.2 (6), 164.2 (88), 58.1 (12).



***N*-(3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.^{3,9}.1^{5,15}1^{7,13}]-octasiloxane)dibutylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 0.54 (d, J_{HH} = 6 Hz, 14H, H_3), 0.82

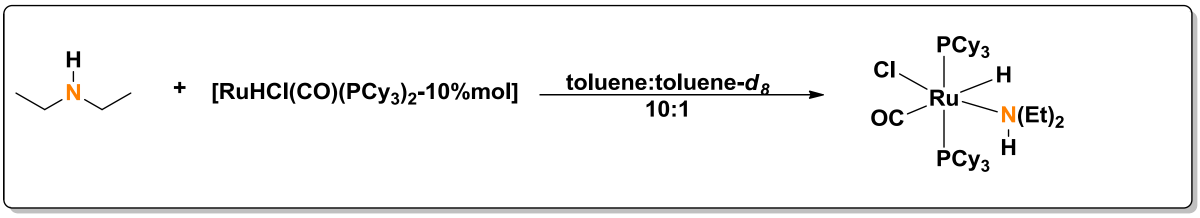
(t, J_{HH} = 6 Hz, 6H, H_4), 0.88 (d, J_{HH} = 6 Hz, 42H, H_1), 1.15 (m, 4H, H_5), 1.32 (m, 4H, H_6), 1.79 (m, 7H, H_2), 2.69 (t, J_{HH} = 6 Hz, 4H, H_7);



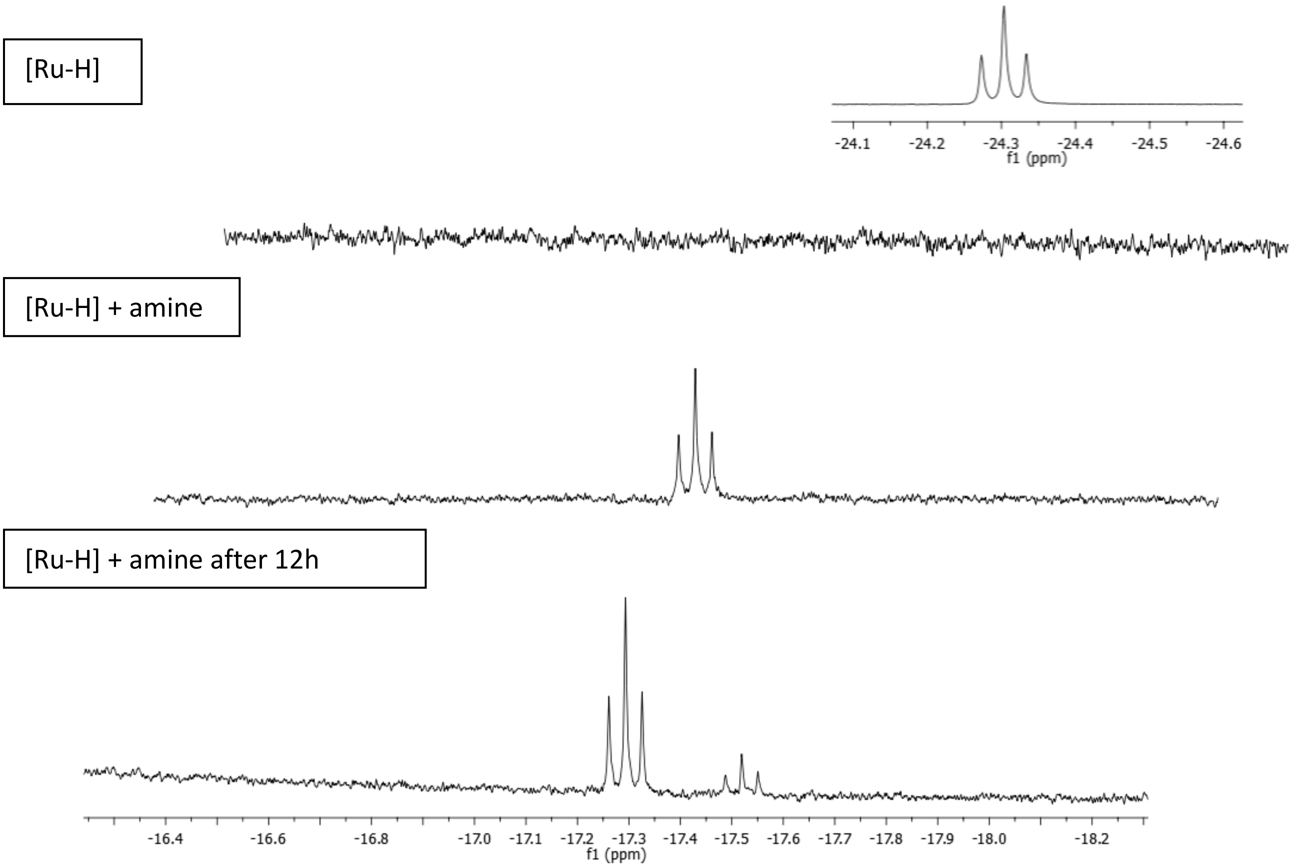
***N*-(1-dimethylsiloxy-(3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.^{3,9}.1^{5,15}1^{7,13}]octa-siloxane))dibutylamine**. ^{1}H NMR (300 Mz, C_7D_8) δ (ppm): 0.04 (s, 6H, H_4), 0.54 (d, J_{HH} = 6 Hz, 14H, H_3), 0.82 (t, J_{HH} = 6 Hz, 6H, H_5), 0.88 (d, J_{HH} = 6 Hz, 42H, H_1), 1.28 (m, 4H, H_6), 1.46 (m, 4H, H_7), 1.79 (m, 7H, H_2), 2.69 (t, J_{HH} = 6 Hz, 4H, H_8);

4. Test reactions proving stages of the reaction mechanism

4.1 The coordination of the amine to complex [Ru-H]

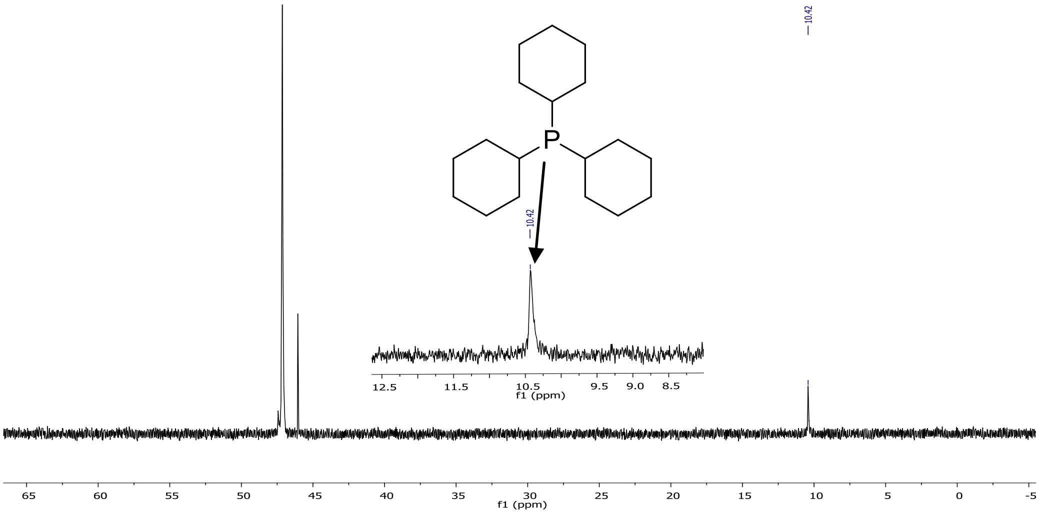


4.1.1 Spectra ^{1}H NMR after addition of amine to complex $[RuHCl(CO)(PCy_3)_2]$



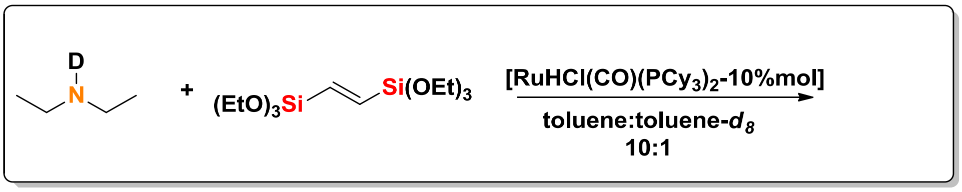
On this spectra we observed formation of new ruthenium-hydride peak at -17.29 ppm (t, J_{PH} = 19.07 Hz) after addition of amine to complex $[RuHCl(CO)(PCy_3)_2]$ at room temperature. After 12h we observed the formation of two triplets at -17.29 ppm (t, J_{PH} = 19.07 Hz) and -17.52 ppm (t, J_{PH} = 18.73 Hz). The peaks were assigned to isomeric ruthenium hydride complexes containing Et_2NH as a ligand.

4.1.2 Spectrum ^{31}P NMR after addition of *(E)*-1,2-bis(triethoxysilyl)ethene to complex 2

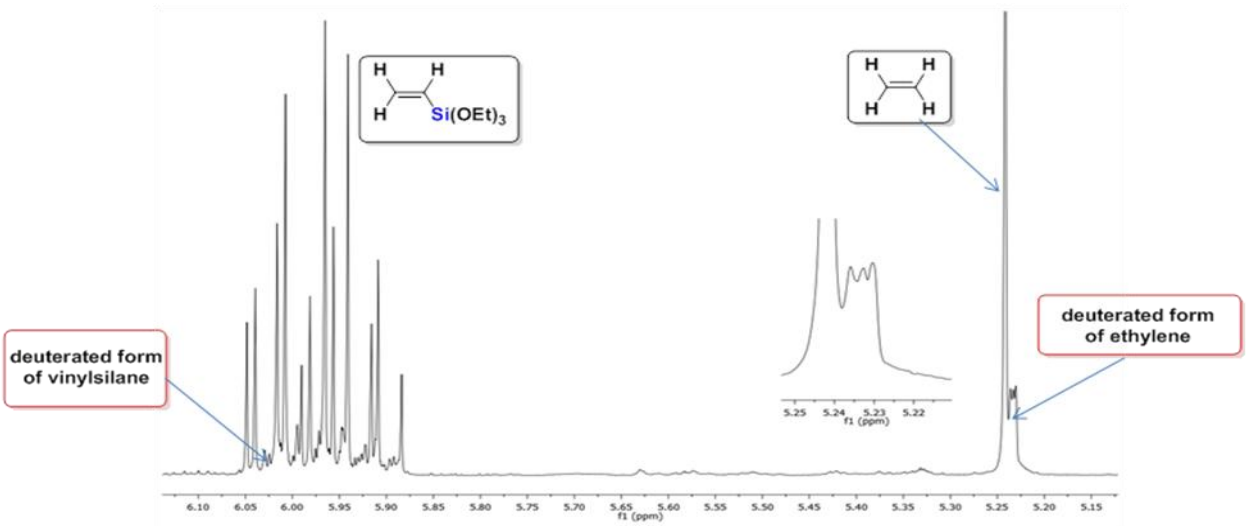


^{31}P NMR spectrum confirming dissociation of free PCy_3 from complex **2** after addition of bis(silyl)ethene and heating at 120^{o}C.

4.2 Reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine-*d*

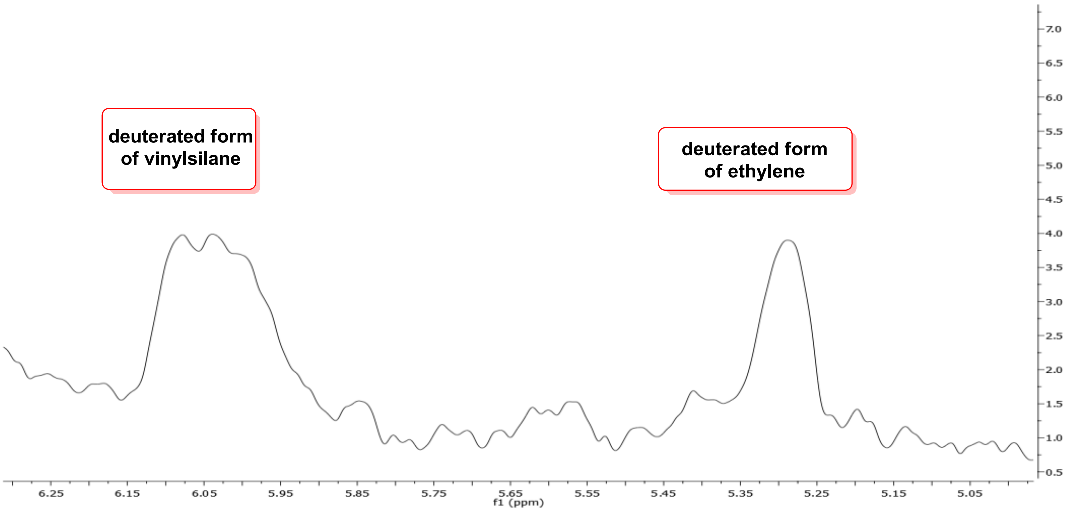


4.2.1 Spectrum ^{1}H NMR



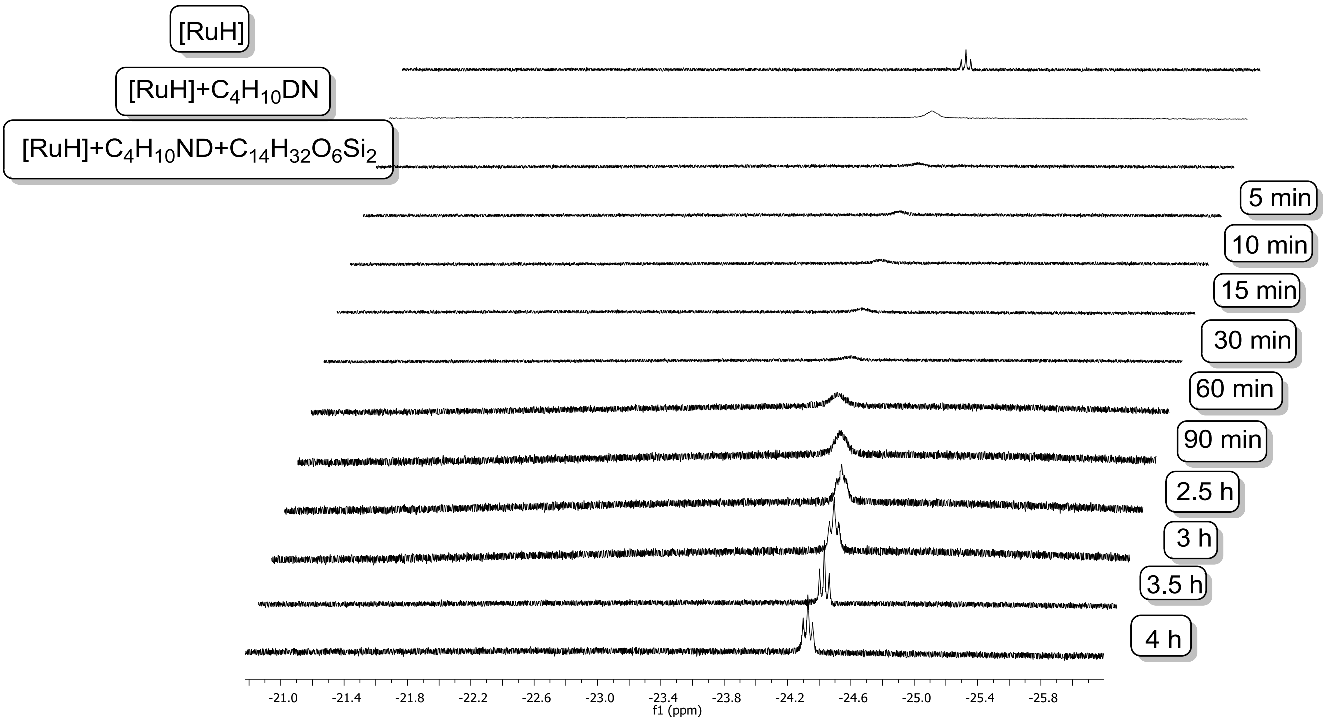
^{1}H NMR spectrum of ethylene and deuterated ethylene as well as vinylsilane and deuterated vinylsilane observed in the reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine-*d.*

4.2.2 Spectrum ^2H NMR



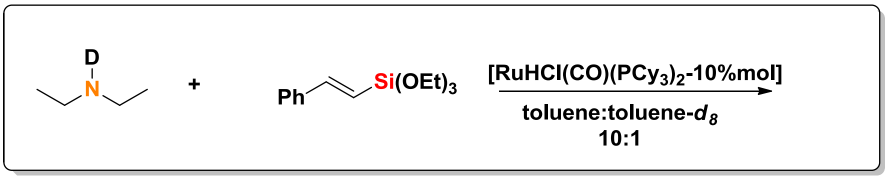
^2H NMR spectrum of deuterated ethylene and deuterated vinylsilane observed in the reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine-*d* (1D sequence without decoupling using 2H lockswitch unit).

4.2.3 Spectra ^1H NMR

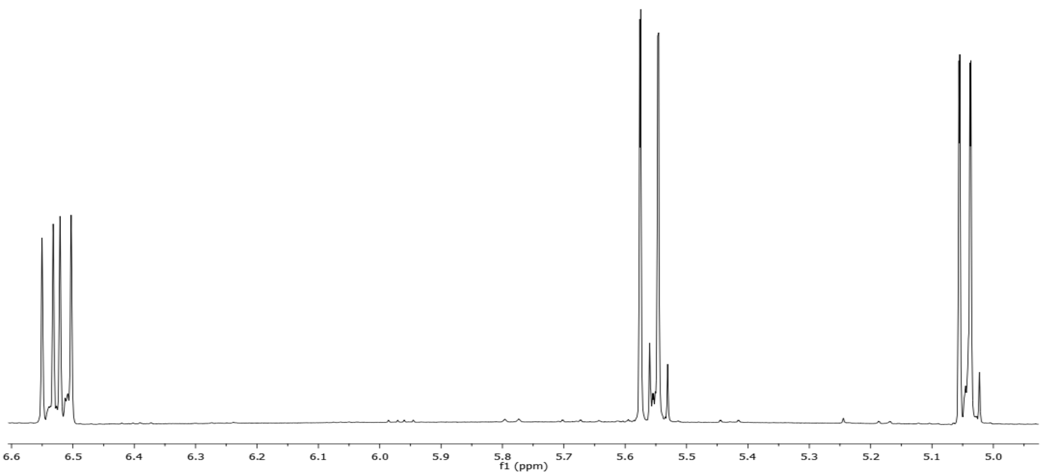


^1H NMR spectra of reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine-*d* in the presence of 10 mol% of **1** confirming the regeneration of ruthenium-hydride complex **1**.

4.3 Reaction between (*E*)-styryl(triethoxy)silane and diethylamine-*d*

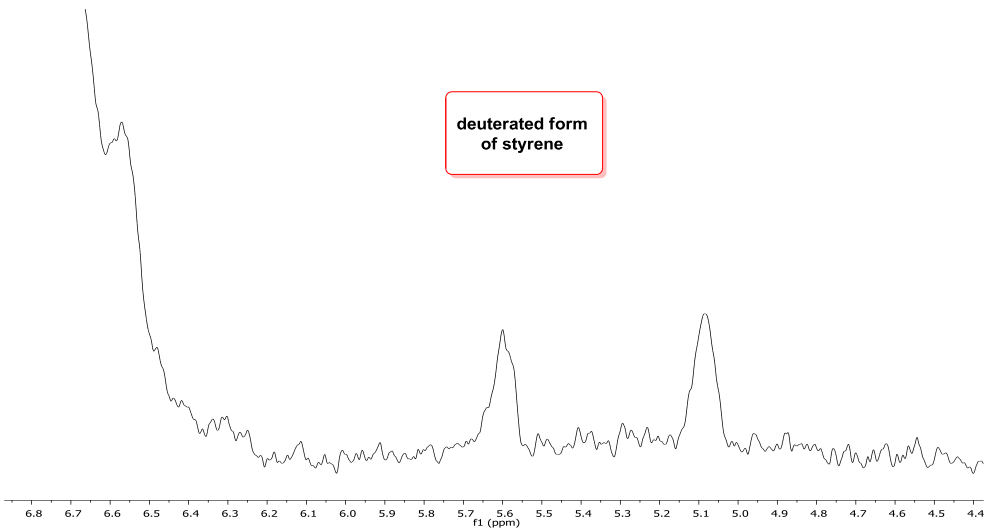


4.3.1 Spectrum ^{1}H NMR



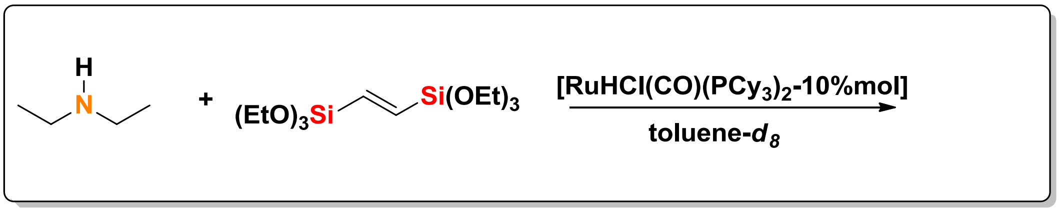
^{1}H NMR spectrum of styrene and deuterated styrene observed in the reaction between *(E)*-styryl(triethoxy)silane and diethylamine-*d*.

4.3.2 Spectrum ^{2}H NMR

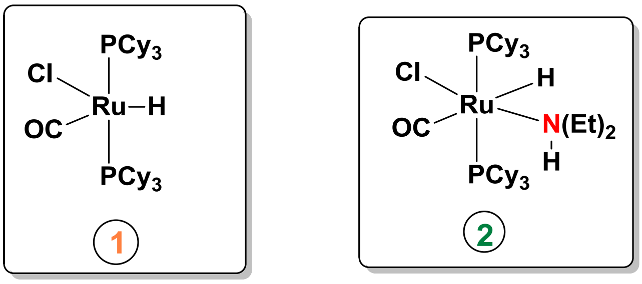


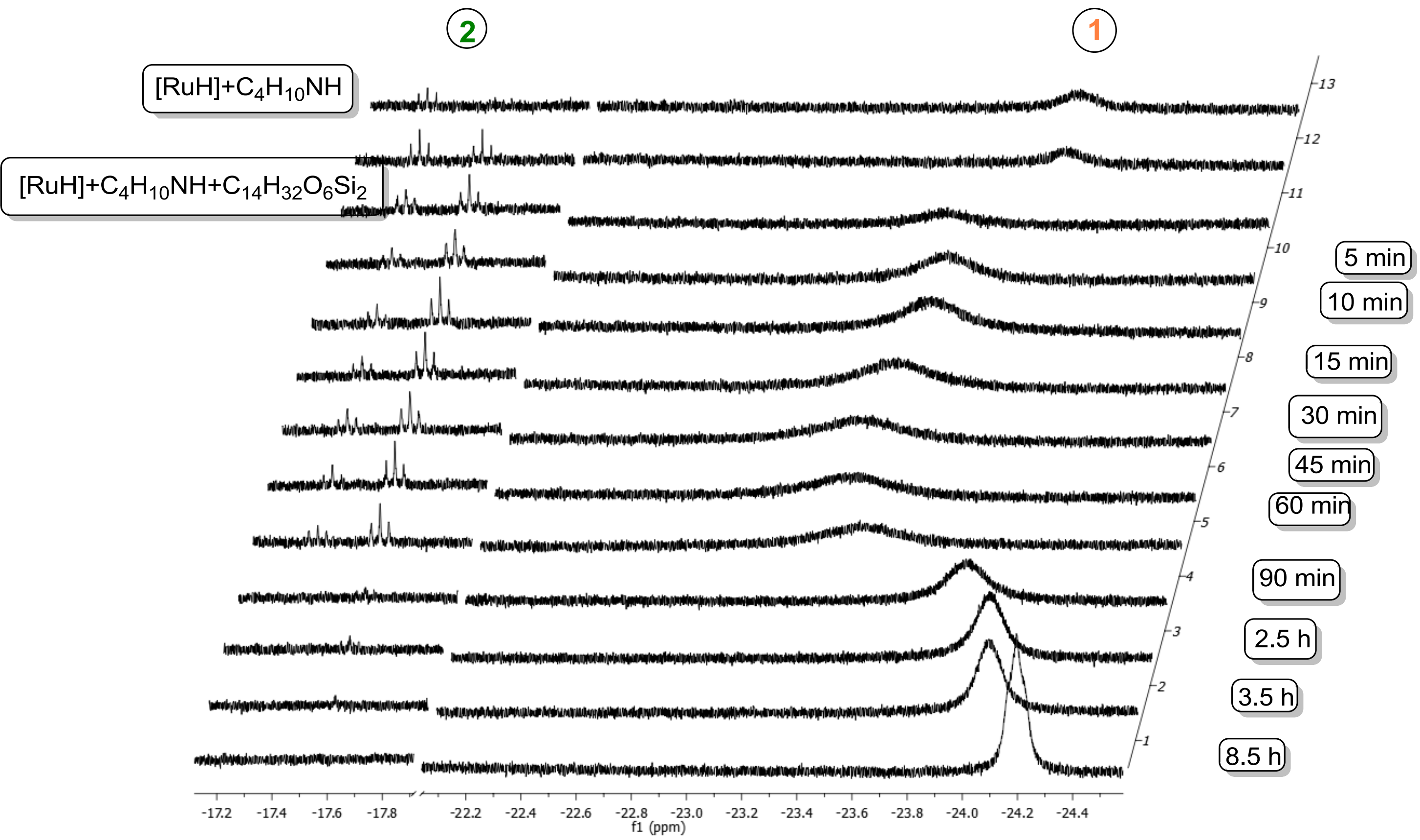
^{2}H NMR spectrum of deuterated styrene observed in the reaction between *(E)*-styryl (triethoxy)silane and diethylamine-*d.*

4.4 Reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine



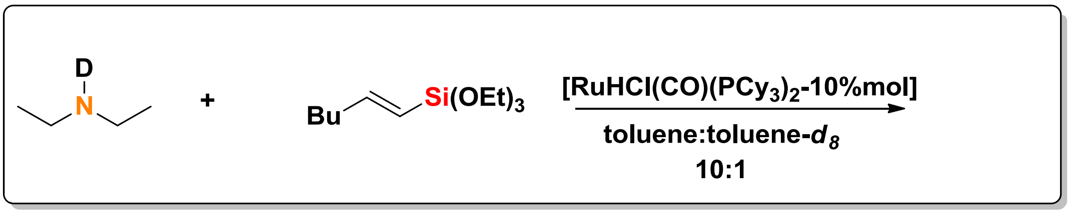
4.4.1 Spectra ^{1}H NMR



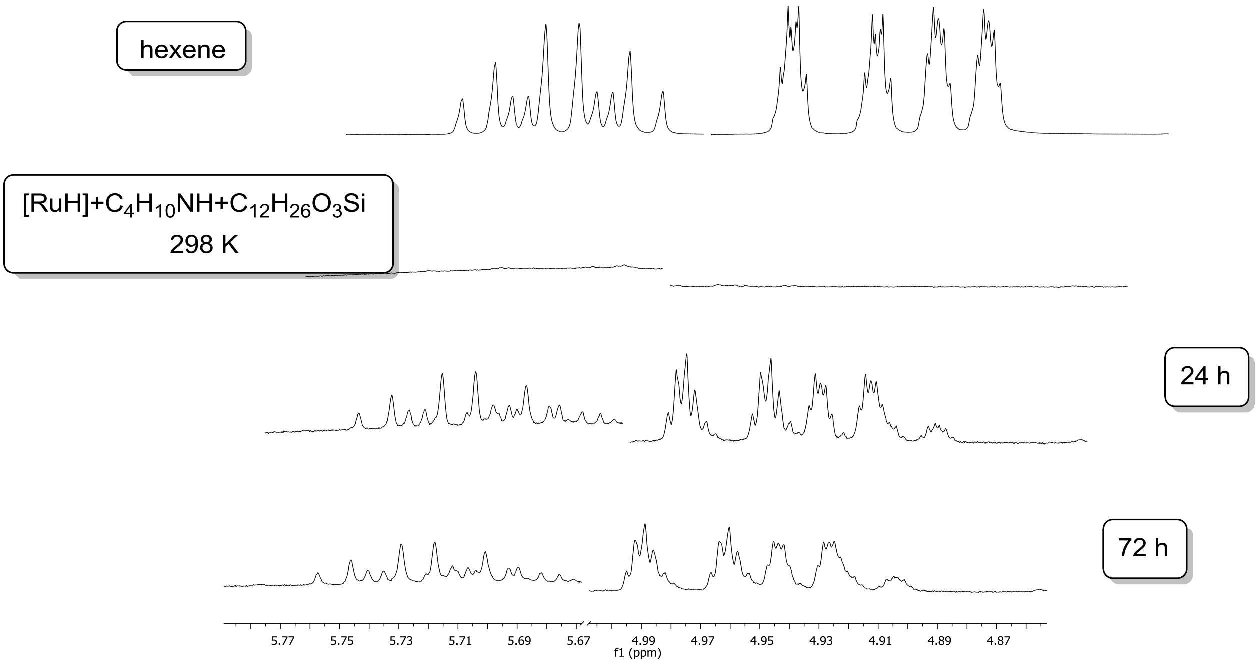


^{1}HNMR spectra of the reaction between *(E)*-1,2-bis(triethoxysilyl)ethene and diethylamine confirming the regeneration of ruthenium-hydride **1** and the formation of two new ruthenium-hydride complexes with coordinated amine.

4.5 Reaction between (*E*)-hexenyl(triethoxy)silane and diethylamine-*d*



4.5.1 Spectra ^{1}H NMR



^{1}H NMR spectra of pure hexene and hexene observed in the reaction between *(E)*-hexenyl(triethoxy)silane and diethylamine-*d.* This is evidence on the formation of olefin molecule.

5. References

[1] C. S. Yi, D. W. Lee, Y. Chen*, Organometallics,* **1999**, *18,* 2043.

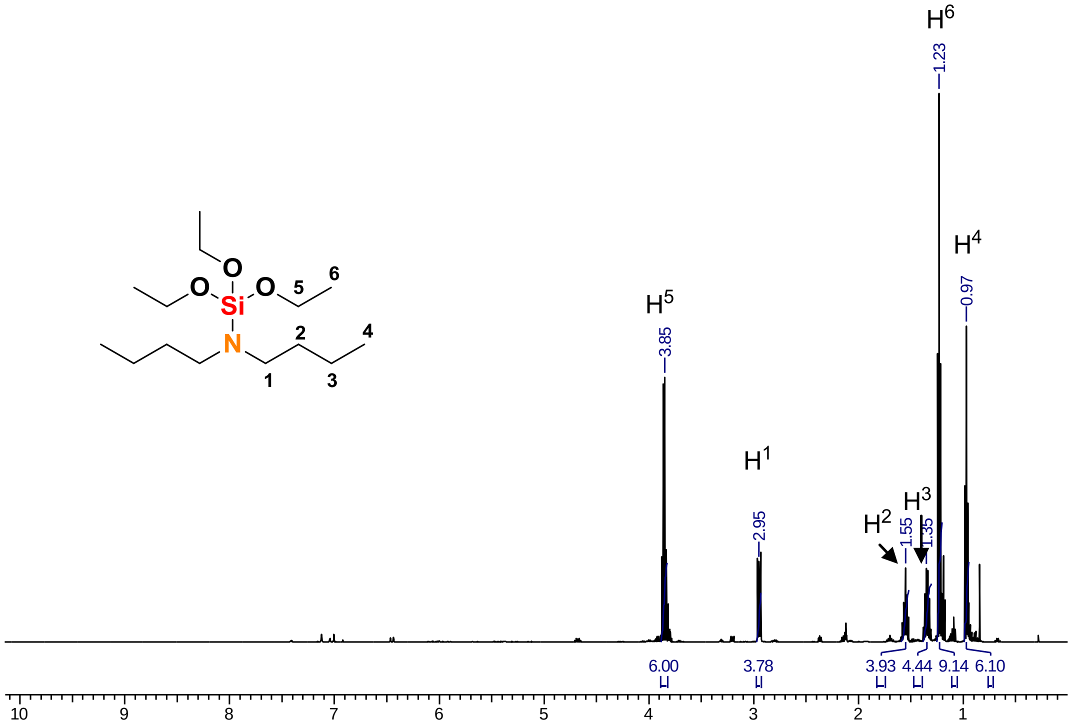
[2] P. Żak, C. Pietraszuk, B. Marciniec, G. Spólnik, W. Danikiewicz, *Adv. Synth. Catal*. **2009**, *351*, 2675 – 2682

[3] J. Waehner, B. Marciniec, P. Pawluć, *Eur. J. Inorg. Chem.* **2007**, 2975 - 2980

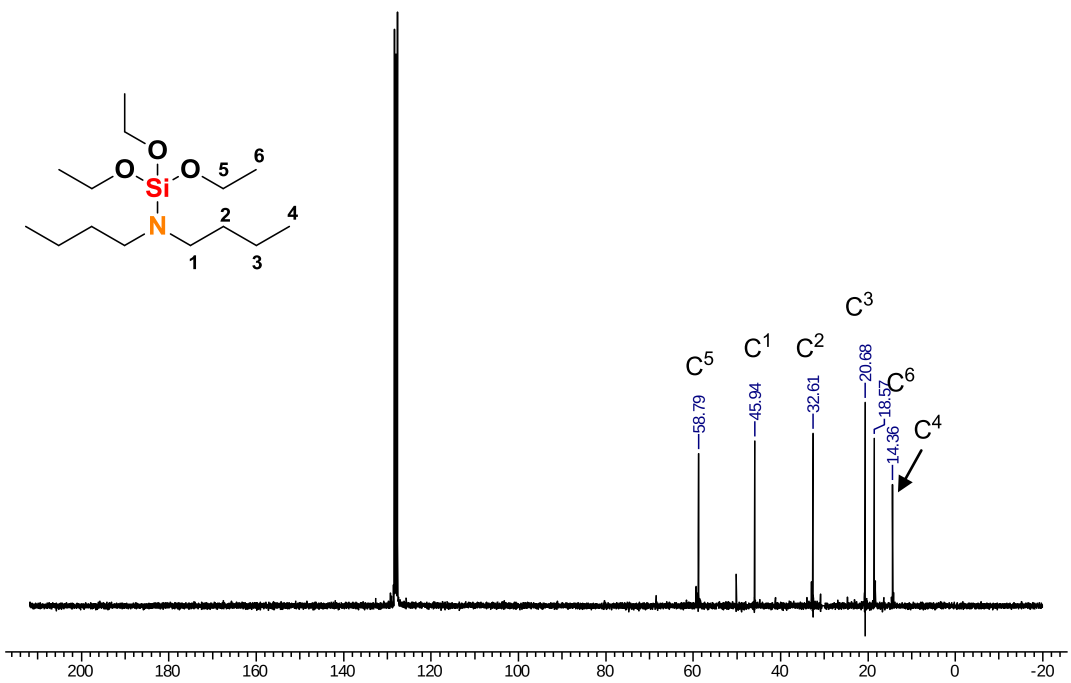
6. NMR Spectra for New Compounds

6.1 Spectra of *N*-(triethoxysilyl)dibutylamine

^{1}H NMR

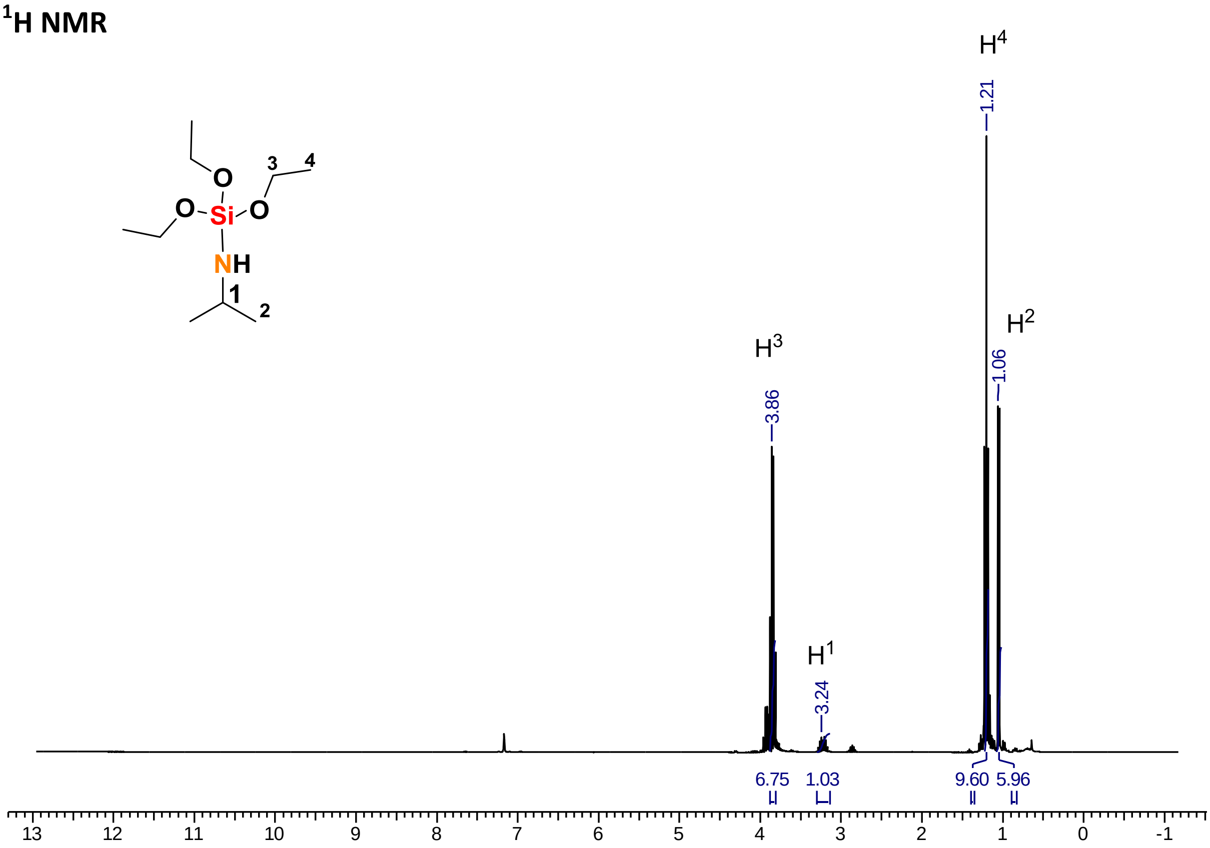


^{13}C NMR

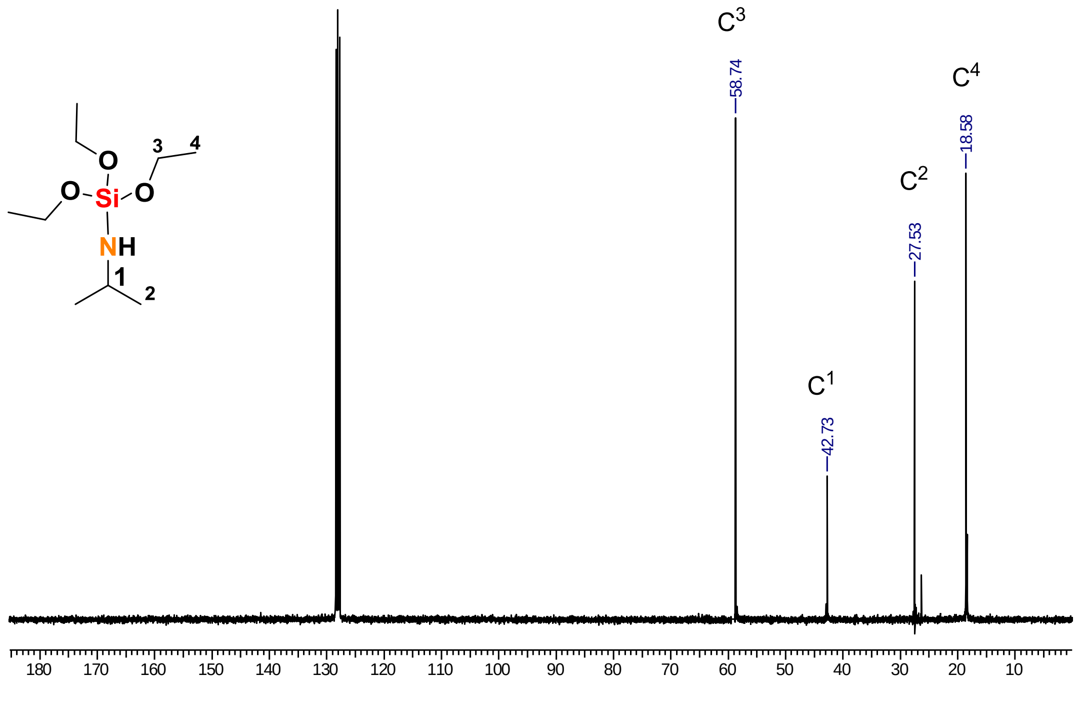


6.2 Spectra of *N*-(triethoxysilyl)isopropylamine

^{1}H NMR

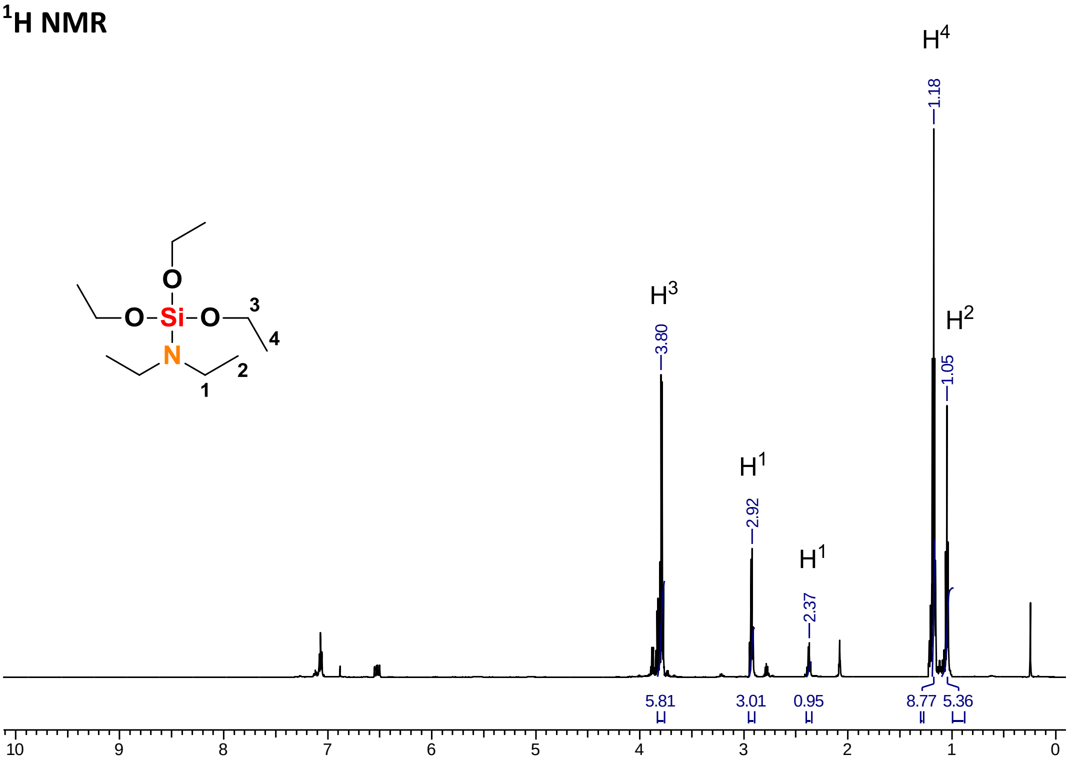


^{13}C NMR

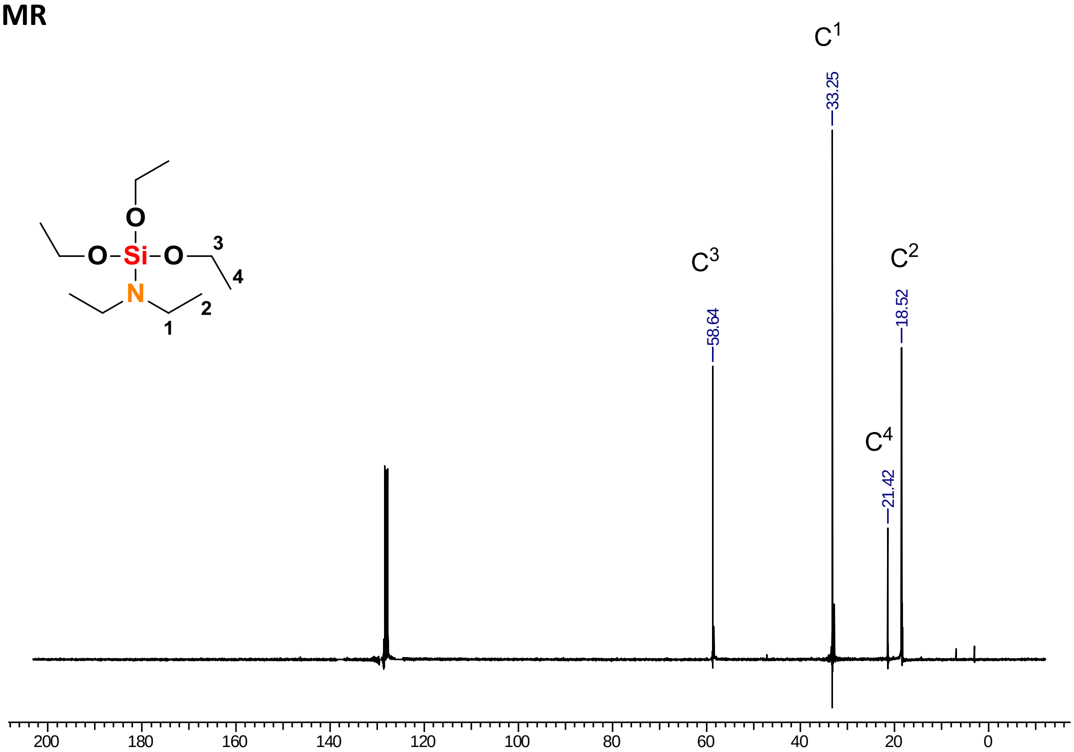


6.3 Spectra of *N*-(triethoxysilyl)diethylamine.

^{1}H NMR

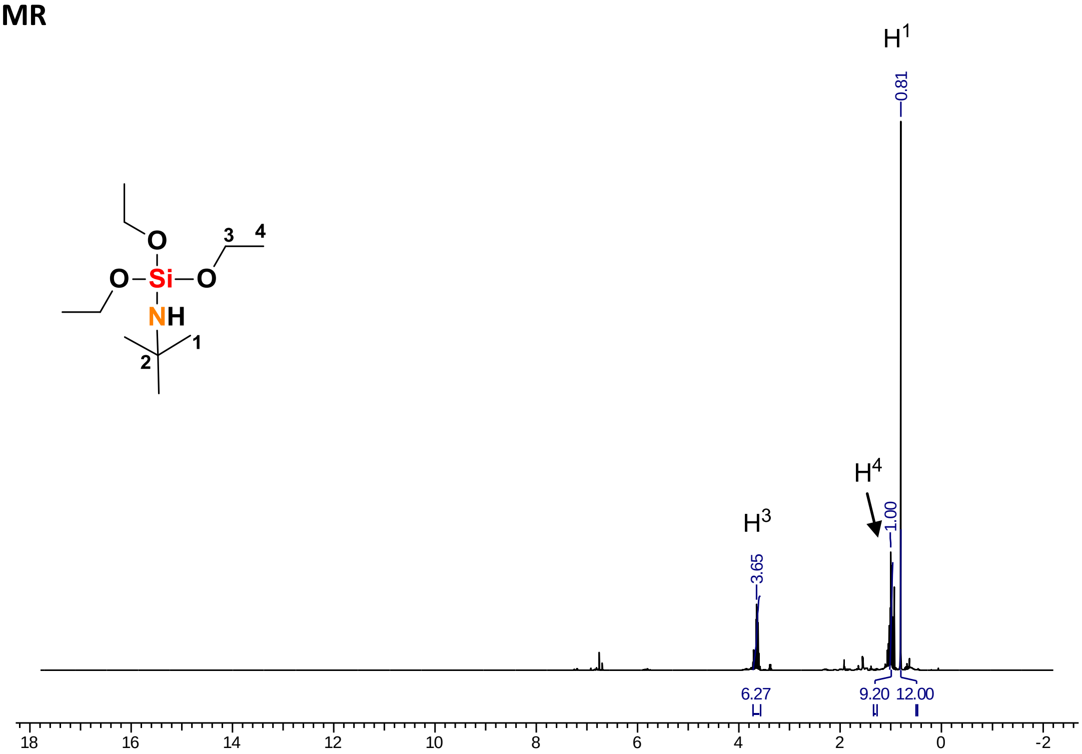


^{13}C NMR

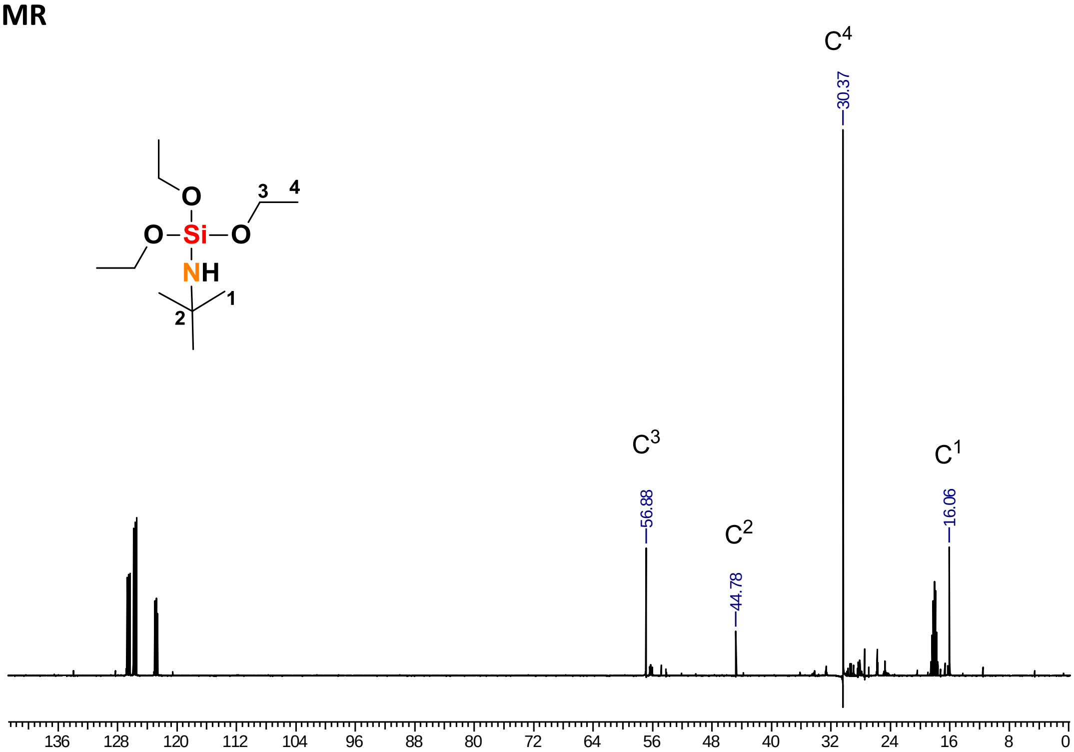


6.4 Spectra of *N*-(triethoxysilyl)*tert*-butylamine

^{1}H NMR

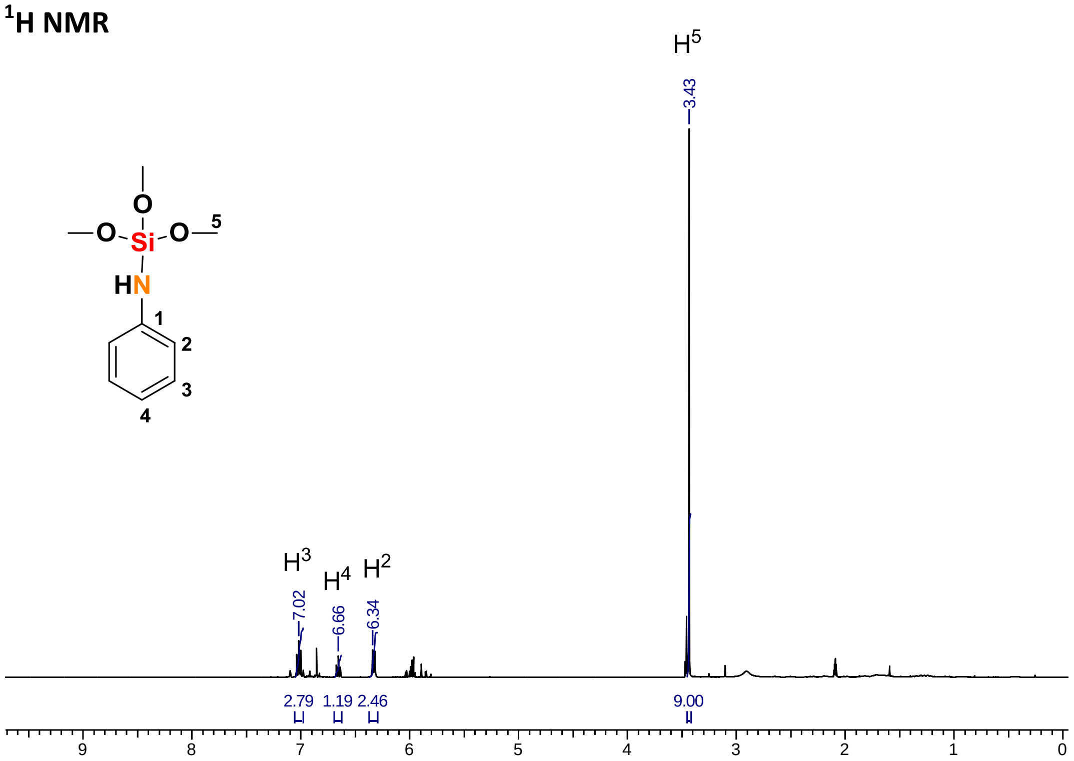


^{13}C NMR

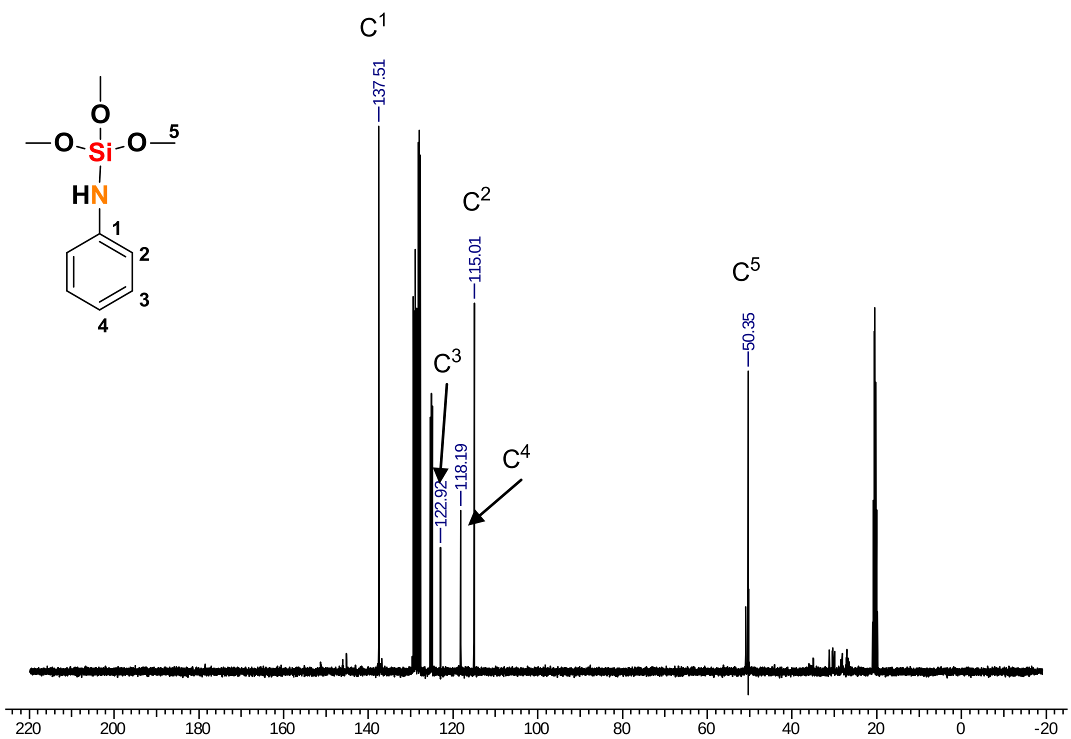


6.5 Spectra of *N*-(trimethoxysilyl)phenylamine.

^{1}H NMR

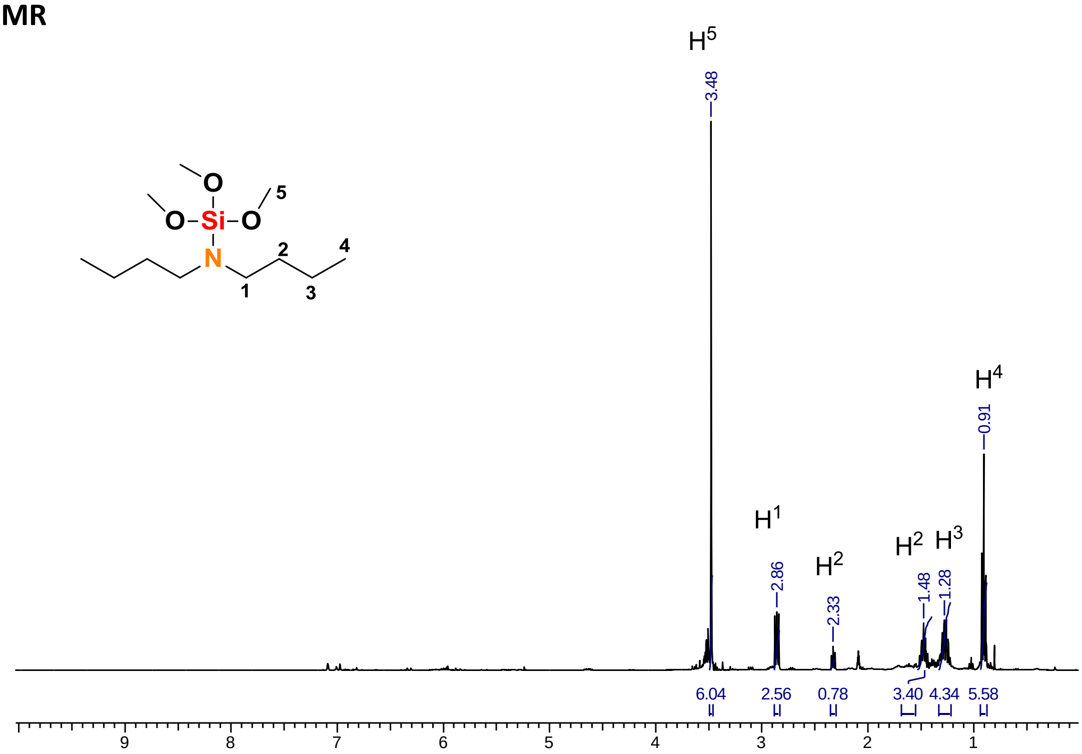


^{13}C NMR

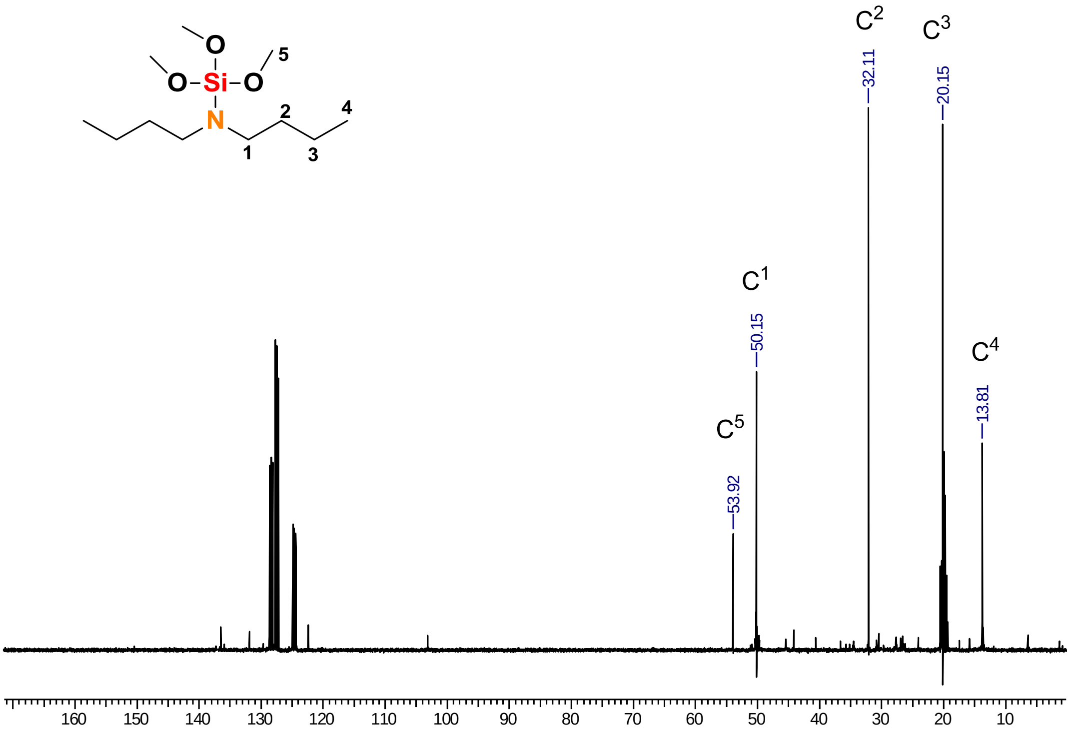


6.6 Spectra of *N*-(trimethoxysilyl)dibutylamine

^{1}H NMR

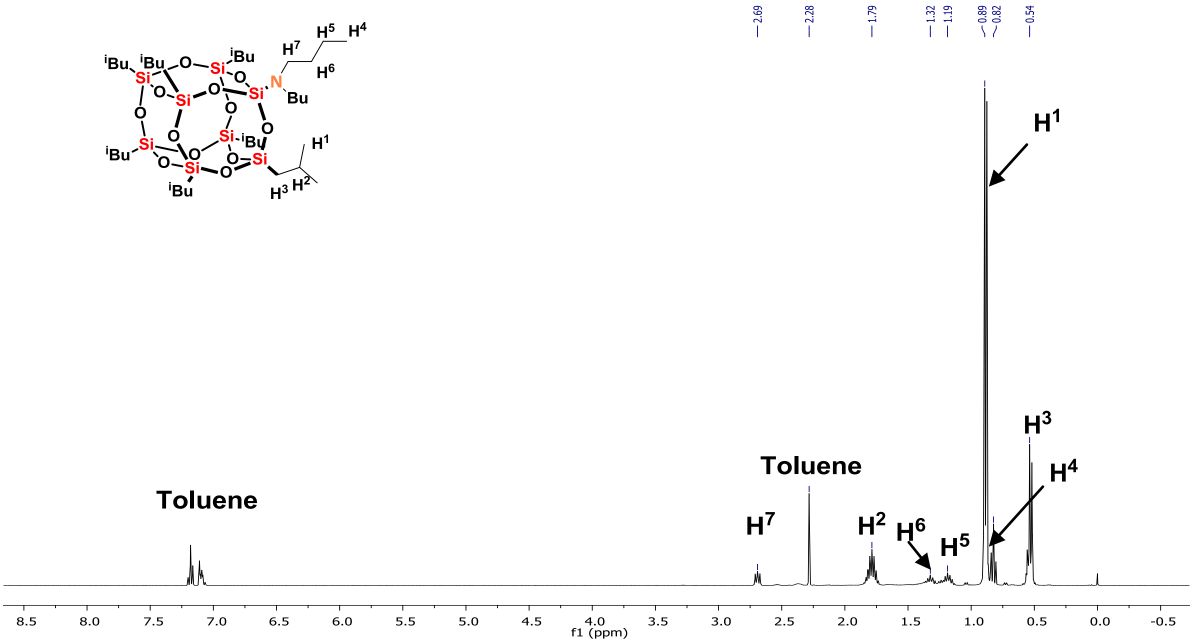


^{13}C NMR



6.7 Spectrum of *N*-(1-dimethylsiloxy-(3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.^{3,9}.1^{5,15} 1^{7,13}]octasiloxane))dibutylamine

^{1}H NMR



6.8 . Spectrum of *N*-(3,5,7,9,11,13,15-hepta(isobutyl)pentacyclo-[9.5.1.1.^{3,9}.1^{5,15}1^{7,13}] octa-siloxane)dibutylamine

^{1}H NMR