SUPPORTING INFORMATION

Synthesis and Structure of New Polyhedral Ni,Na- and Cu, Na-metallasiloxanes with Tolyl Substituent at the Silicon Atom

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1. Experimental

1.1 General Considerations

Solvents were prepared according to earlier [2] described procedures. All solvents were purified before use. n-Butanol was distilled. Toluene was distilled from calcium hydride under argone. NaOH, Pyridine, $CuCl_2$, $Ni(NH_3)_6Cl_2$ were purchased from Aldrich;
p-Tolyltriethoxysilane was synthesized by earlier described method [1].
NMR spectra were recorded on a Bruker Avance™ 600 spectrometer (Germany) operating at 600.22, 150.93 and 119.26 MHz for ^{1}H, ^{13}C and ^{29}Si respectively. The chemical shifts for ^{1}H and ^{13}C were indirectly referenced TMS via the solvent signals. The chemical shifts for ^{29}Si were measured with TMS as an external standard.
IR spectra were obtained using an IR spectrometer with a Fourier transformer Bruker "Tensor 37" (Germany). The samples were prepared by pressing KBr pellets.

High-resolution mass spectra (HRMS) were measured using a Bruker micrOTOF II instrument with electrospray ionization (ESI) (Germany).

X-ray measurements were carried out with Bruker Smart APEX DUO difractometer (Germany). The structures were solved by direct methods and refined in full matrix anisotropic approximation againt F^2.

1.2 Synthesis of 1

$TolSi(OEt)_3$ (4 g, 15.7 mmol), NaOH (0.87g, 22 mmol), and H_2O (0.29 g, 15.7 mmol) were added to 50 mL of n-BuOH under vigorous stirring. The reaction mixture was stirred at reflux temperature within 40 min. Then $Ni(NH_3)_6Cl_2$ (1.60 g, 6.92 mmol) was added to the reaction mixture which was refluxed for another 40 min, and the hot solution was filtered to remove NaCl. Filtrate was evaporated and a residue was dissolved under reflux in rectified ethanol. Yellow-green crystals precipitated from the solution into an hour. After separation they were dried in a vacuum at 70°C. The yield of the product **1** was 2.25g (66%).

CHN: Calc. (%) for:
$\{(Na^+)_2[C_7H_7Si(O)O^-]_6(Na^+)_4(Ni^{2+})_4(m\mu_3\text{-}OH^-)_2[C_7H_7Si(O)O^-]_6\}\cdot(C_2H_5OH)_5(H_2O)_{10}$; Mol. mass: 2631.80; $C_{94}H_{136}Si_{12}Ni_4Na_6O_{41}$: C, 43.12; H, 5.23; Si, 12.88; Na, 5.23; Ni, 8.96. Found: C, 43.61; H, 4.46; Si, 13.04; Na, 5.8; Ni, 7.8.

1.3 Synthesis of 2

Compound **1** (1.9 g, 0.72 mmol) was added under vigorous stirring to a mixture of Me_3SiCl (3.44 g, 4.03 mL, 31.7 mmol) and pyridine (1.82 g, 1.85 mL, 23 mmol) in 30 mL of toluene. The mixture was stirred for 2 h at room temperature and then filtered. The filtrate was washed with distilled water to pH 7. After the solvent was distilled off, the product was dried at 50°C under 1 mBar and recrystallized from rectified ethanol. The yield of the product **2** was 1.38g (71%).

CHN: Calc. (%) for $[CH_3C_6H_4Si(O)OSi(CH_3)_3]_6$, $C_{60}H_{96}Si_{12}O_{12}$. MM: 1346.42, C,53.52; H,7.19; Si 25.03, Found: (%)C, 53.60; H, 7.31; Si, 24.89.

^{1}H NMR (600.22 MHz, $CDCl_3$, ppm) 7.07 (d, J=7.5 Hz, 12H, $C_6\mathbf{H}_4$), 6.74 (d, J=7.5 Hz, 12H, $C_6\mathbf{H}_4$) 2.25 (s, 18H, $C_6H_4\text{-}C\mathbf{H}_3$), 0.17 (s, 54H, $OSi(C\mathbf{H}_3)_3$.

^{13}C NMR (150.93 MHz $CDCl_3$, ppm) 138.6 ($CH_3\text{-}\mathbf{C}_6H_4\text{-}$), 134.2 ($CH_3\text{-}\mathbf{C}_6H_4\text{-}$) 130.4 ($\text{-Si-}\mathbf{C}_6H_4\text{-}$), 127.8, ($CH_3\text{-}\mathbf{C}_6H_4\text{-}$), 21.5 ($\mathbf{C}H_3\text{-}C_6H_4\text{-}$), 2.1 ($OSi\text{-}(\mathbf{C}H_3)_3$).

^{29}Si NMR (119.26 MHz $CDCl_3$, ppm) 9.1 ($Si\text{-}O\text{-}\mathbf{Si}(CH_3)_3$), -81.2 ($\mathbf{Si}\text{-}O\text{-}Si$)

IR (cm^{-1}): 3072-3016, 2921, 1606, 1255, 1127, 1048.

HRMS (ESI) *m/z* calc. for $C_{60}H_{96}Si_{12}O_{12}$ $[(M+NH_4)^+]$: 1362.45, found 1362.45, $[(M+Na)^+]$: 1367.40, found 1367.40.

1.4 Synthesis of 3

A mixture of n-BuOH (50 mL), $TolSi(OEt)_3$ (5.25g, 21mmol), NaOH (0.84 g, 21 mmol) and water (0.38 mL, 21 mmol) was stirred under reflux for 1 h. Then a solution of anhydrous $CuCl_2$ in n-BuOH (0.93 g, 6.92 mmol) was added dropwise to the reaction mixture. After completion, the reaction mixture was refluxed for an additional 30 min. The hot solution was filtered to remove NaCl. The filtrate was evaporated and a residue dissolved under reflux in rectified ethanol. Precipitated blue crystals were filtered and dried at reduced pressure (70°C under 1 mBar). The yield of the product **3** was 3.09 g (76%).

CHN: Calc. (%) for $\{[C_7H_7Si(O)O^-]_{12}(Na^+)_4(Cu^{2+})_4\}\cdot(C_2H_5OH)_1(H_2O)_7$; Mol. mass: 2332.90; $C_{86}H_{104}Cu_4Na_4O_{32}Si_{12}$: C, 44.28; H, 4.49; Si, 14.45; Na, 3.94; Cu, 10.90. Found: C, 44.42; H, 4.19; Si, 14.52; Na, 4.23; Cu, 10.70.

1.5 Synthesis of 4

Similar to the synthesis of **2** from Me_3SiCl (2.51 g, 2.94 mL, 23.1 mmol), pyridine (1.09 g, 1.11 mL, 13.8 mmol), compound **3** (1.8 g, 0.77 mmol) and toluene (50 mL). Yield: 1.45 g (70%).

CHN: Calc. (%) for $[CH_3C_6H_4Si(O)OSi(CH_3)_3]_{12}$, $C_{120}H_{192}Si_{24}O_{24}$. MM: 2692.86, C, 53.26; H, 7.38; Si, 24.70, Found: (%) C, 51.54; H, 7.17; Si, 24.96.

^{1}H NMR (600.22 MHz, $CDCl_3$, ppm) 7.39 (d, J=7.8 Hz, 18H, $C_6\mathbf{H}_4$), 7.22 (d, J=7.9 Hz, 6H, $C_6\mathbf{H}_4$), 6.93 (d, J=7.5 Hz, 18H, $C_6\mathbf{H}_4$), 6.85 (d, J=7.6 Hz, 6H, $C_6\mathbf{H}_4$), 2.34 (s, 24H, C_6H_4-$C\mathbf{H}_3$), 2.27 (s, 12H, C_6H_4-$C\mathbf{H}_3$), -0.08 (s, 36H, $OSi(C\mathbf{H}_3)_3$, -0.27 (s, 72H, $OSi(C\mathbf{H}_3)_3$.

^{13}C NMR (150.93 MHz $CDCl_3$, ppm) 138.54 (-$\mathbf{C}_6H_4$-), 138.50 (-$\mathbf{C}_6H_4$-), 134.73 (CH_3-$\mathbf{C}_6H_4$-), 134.67 (-$\mathbf{C}_6H_4$-), 130.95 (-$\mathbf{C}_6H_4$-), 130.88 (-$\mathbf{C}_6H_4$-), 127.89 (-$\mathbf{C}_6H_4$-), 127.86 (-$\mathbf{C}_6H_4$-), 21.61 ($\mathbf{C}H_3$-C_6H_4-), 21.49 ($\mathbf{C}H_3$-C_6H_4-), 1.95 (OSi-($\mathbf{C}H_3)_3$), 1.54 (OSi-($\mathbf{C}H_3)_3$).

^{29}Si NMR (119.26 MHz $CDCl_3$, ppm) 9.2 (Si-O-**Si**$(CH_3)_3$), 7.9 (Si-O-**Si**$(CH_3)_3$), -80.9 (**Si**-O-Si), -81.1 (**Si**-O-Si).

IR (cm^{-1}): 3074-3019, 2959-2865, 1608, 1255, 1133, 1050.

HRMS (ESI) *m/z* calc. for $C_{120}H_{192}Si_{24}O_{24}$ $[(M+NH_4)^+]$: 2706.86, found 2706.86, $[(M+Na)^+]$: 919.27, found 919.27, $[(M+K)^+]$: 2711.82, found 2711.86.

2. Crystallographic Studies

The datasets for **1-3** was collected with Bruker APEX DUO diffractometer. The structure was solved by direct method and refined in anisotropic approximation. Sodium atoms in **1** and **3** were disordered over two positions that caused subsequent disorder of coordinated ethanol molecules. Hydrogen atoms were calculated from geometrical point of view and then they were refined with restraints applied for their displacement parameters and C-H (O-H) bond length. One molecule of ethanol in **1** were strongly disordered over crystallographic centre of inversion. The contribution of this molecule to integral intensities was excluded from dataset using SQUEEZE procedure (implemented in PLATON [3] software).

Unfortunately, it was impossible to collect the reflection intensities for single crystal of **4** using the laboratory equipment (even in the case of microfocus copper tube). The quality of all collected datasets was unsatisfactory due to strong disorder of some methyl trimethylsilyl groups and solvated hexane molecules (as consequence the intensity of diffraction was very weak with almost absent high-angle reflections). To overcome the limitation of laboratory equipment we used protein station of Kurchatov Centre for Synchrotron radiation. The results were much better than that obtained with laboratory diffractometer. We succeeded to localize all non-hydrogen atoms and refine their positions. The position of hydrogen atoms were calculated from geometrical point of view and refined with restraints applied for C-H bonds and equivalent displacement parameters. All calculations were carried out using SHELX program suite [4] and OLEX2 program [5].

Crystallographic data for **1-4** was submitted to CSD (CCDC numbers) and can be obtained free of charge using web request form http://www.ccdc.cam.ac.uk/request.

Table 1 Crystalographic data for the structures **1-4**.

	1	**2**	**3**	**4**
Brutto formula	$C_{112}H_{170}Na_6Ni_4O_{42}Si_{12}$	$C_{60}H_{96}O_{12}Si_{12}$	$C_{100}H_{128.5}Cu_4Na_4O_{32}Si_{12}$	$C_{129}H_{210}O_{24}Si_{24}$
Formula weight	2898.33	1346.44	2525.72	2819.12
Diffractometer	Bruker APEX DUO, λ [CuKα = 1.5418 Å]	Bruker APEX DUO, λ [CuKα = 1.5418 Å]	Bruker APEX DUO, λ [CuKα = 1.5418 Å]	Syncrotron, λ = 0.987 Å
T, K	120	120	120	120
Space group	P-1	P-1	C2/c	P-1
Z	1	2	4	2

a, Å	14.7272(4)	12.9190(6)	24.6412(9)	18.511(4)
b, Å	15.6359(4)	13.6750(6)	19.7915(7)	19.755(4)
c, Å	16.9320(5)	23.8149(11)	27.4630(10)	26.771(5)
α/°	113.9140(10)	76.2710(11)	90	71.01(3)
β/°	96.9800(10)	77.6651(11)	113.730(2)	88.51(3)
γ/°	95.989(2)	74.0613(10)	90	62.94(3)
V, Å^3	3486.80(17)	3880.0(3)	12260.9(8)	8156(4)
ρ_{calc}, g/cm^3	1.380	1.152	1.368	1.148
μ, cm^{-1}	24.23	2.51	26.39	6.5
F(000)	1524	1440	5250	3024
$2q_{max}$, °	135	52	135	72
Reflections collected	43724	52519	49439	135390
Independent reflections	11712	23917	10296	22936
Reflections with I>2s(I)	10453	12234	7632	17715
Parameters	787	776	690	1642
R_1 [for refl. with I>2s(I)]	0.0714	0.0771	0.0858	0.0519
wR_2 [all reflections]	0.2096	0.1851	0.2687	0.1644
GOF	1.052	1.011	1.047	1.136
Residula electron density, e Å^{-3} (ρ_{min}/ρ_{max})	3.028/-1.551	0.988/-0.515	1.486/-0.628	0.540/-0.547

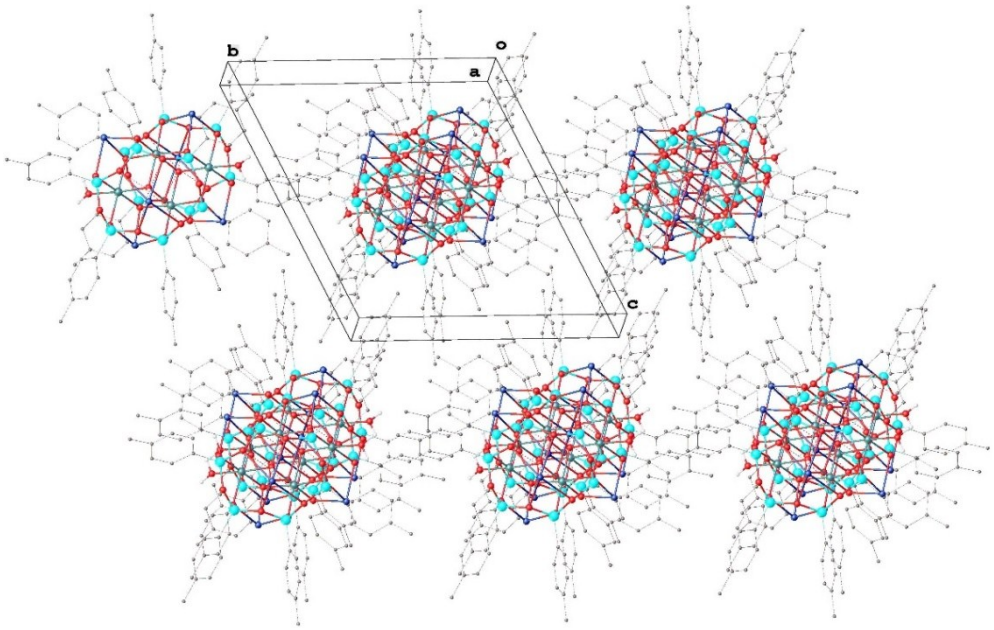

Figure 1. Crystal packing of **1**

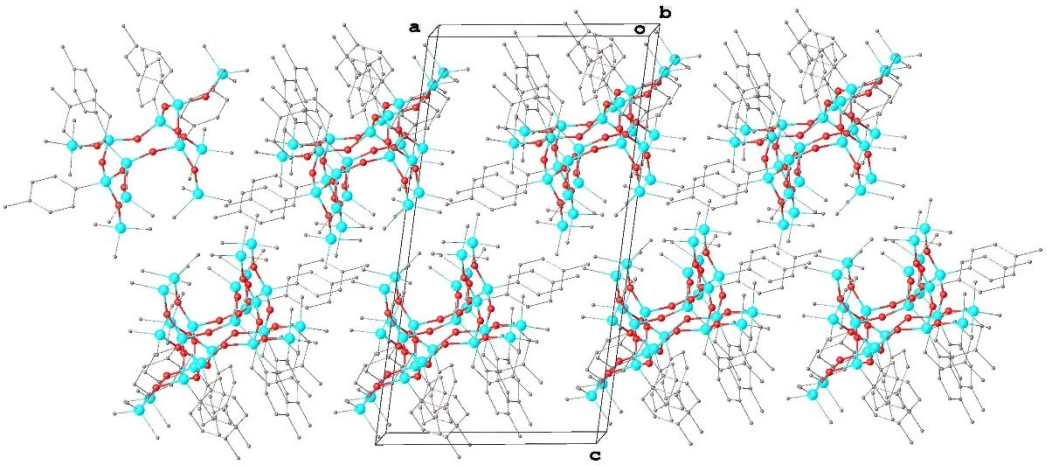

Figure 2. Crystal packing of **2**

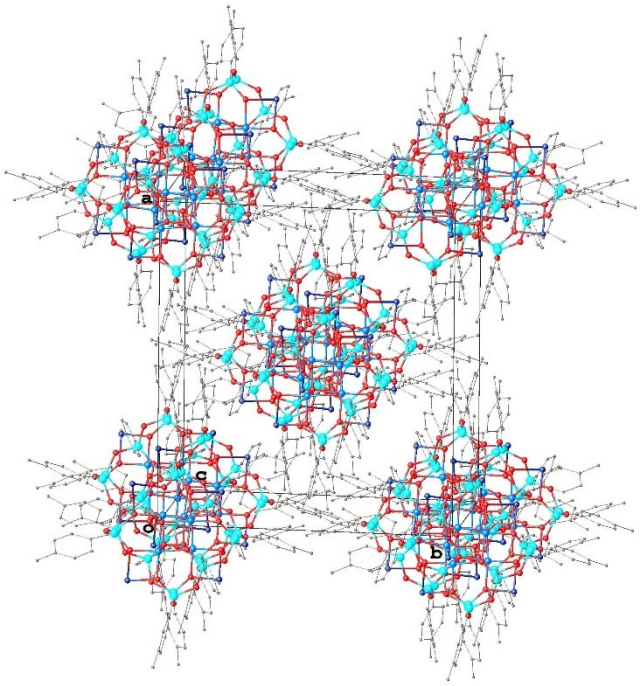

Figure 3. Crystal packing of **3**

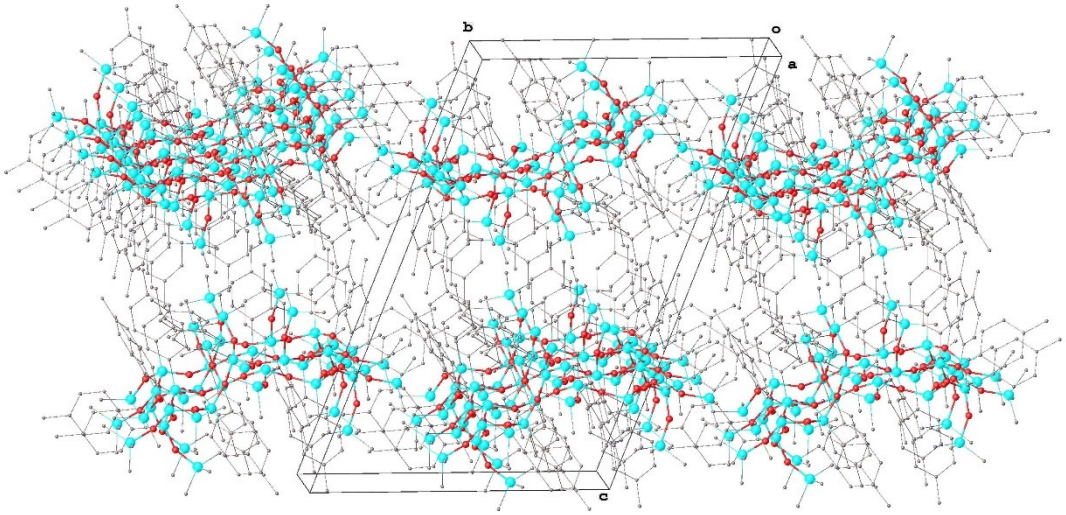

Figure 4. Crystal packing of **4**

3. NMR and Mass Spectra for 2 and 4

3.1 Compound 2

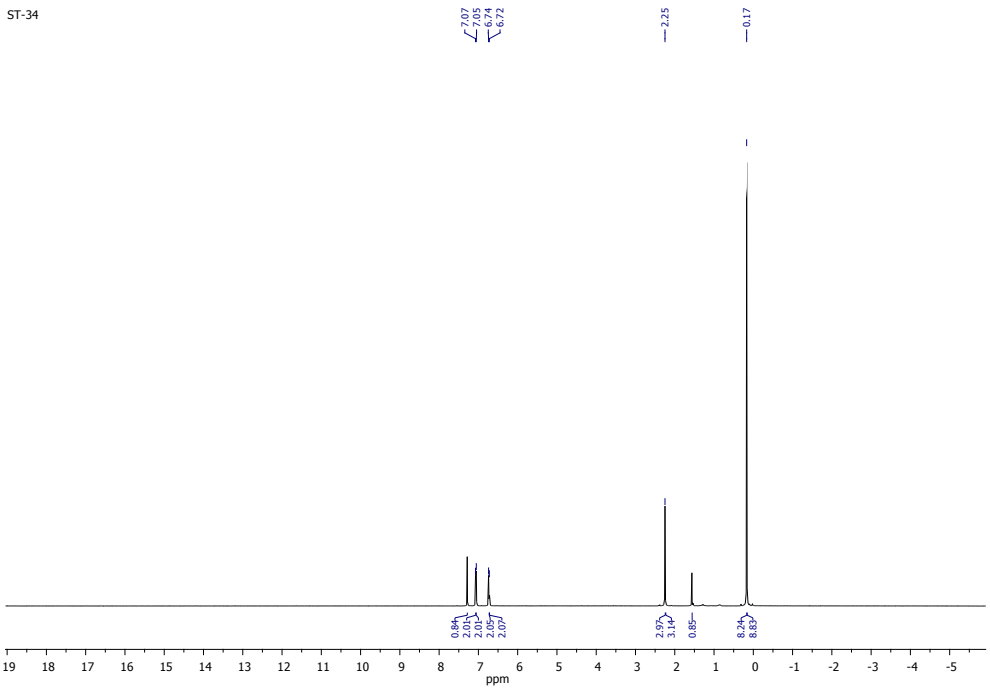

Figure 5. ^{1}H NMR (600.22 MHz, $CDCl_3$) of **2**

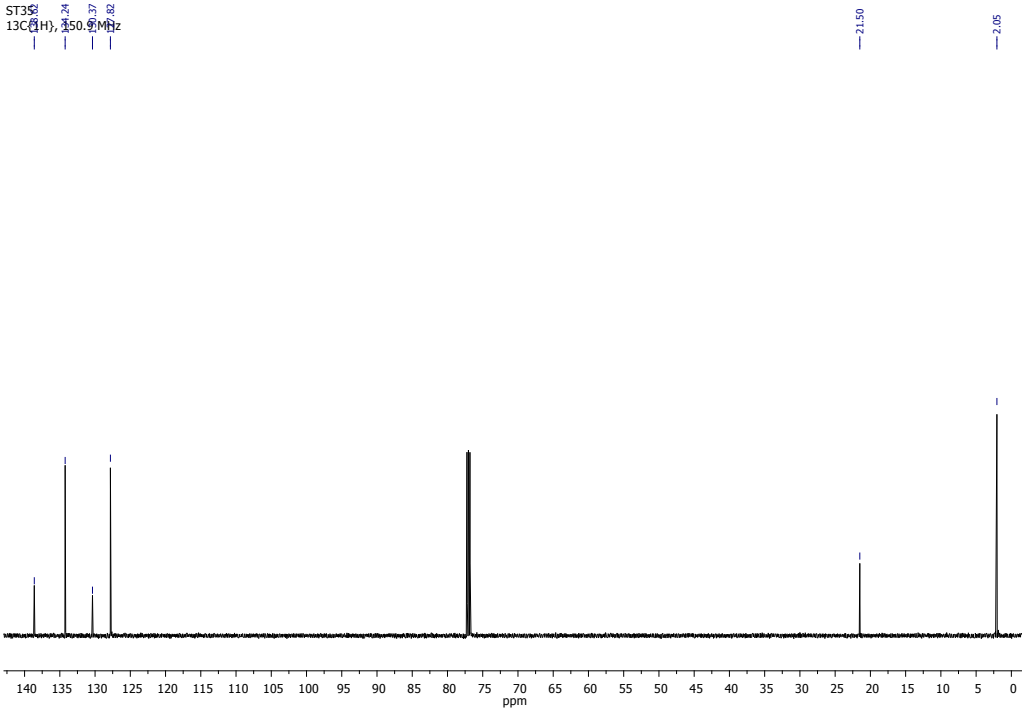

Figure 6. ^{13}C NMR (150.93 MHz, $CDCl_3$) of **2**

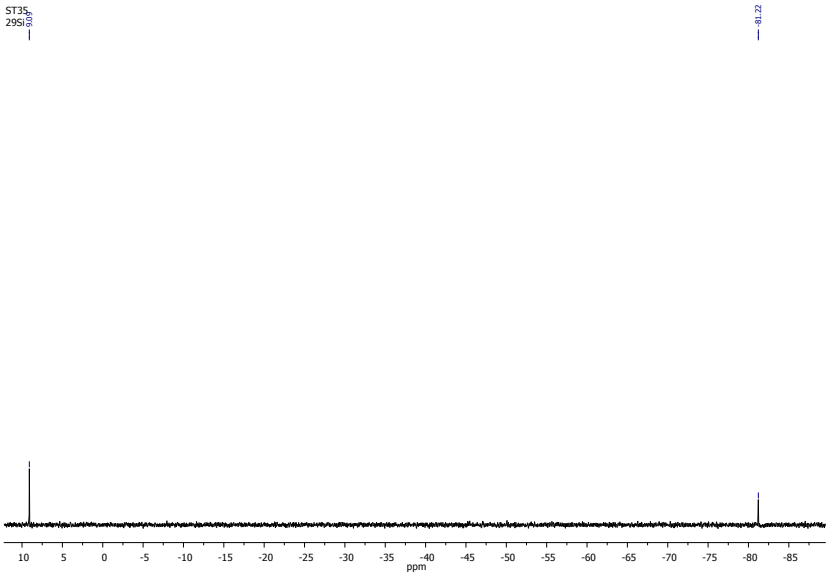

Figure 7. ^{29}Si NMR (119.26 MHz, $CDCl_3$) of **2**

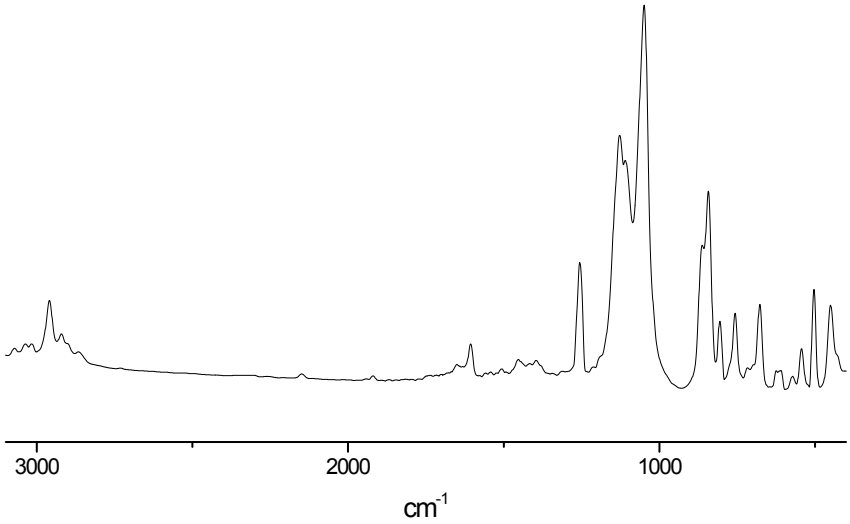

Figure 8. IR (cm^{-1}) of **2**

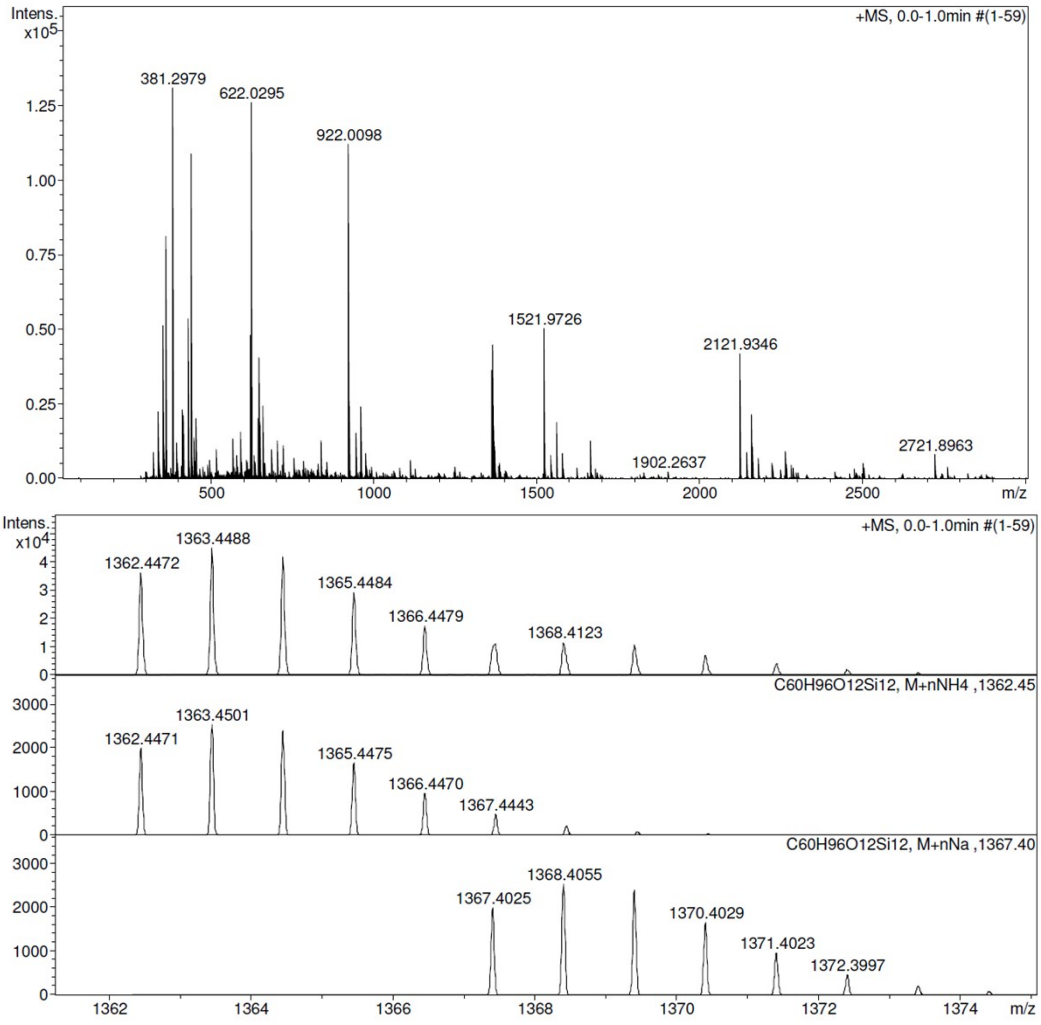

Figure 9. HRMS (ESI) of **3**

3.1 Compound 4

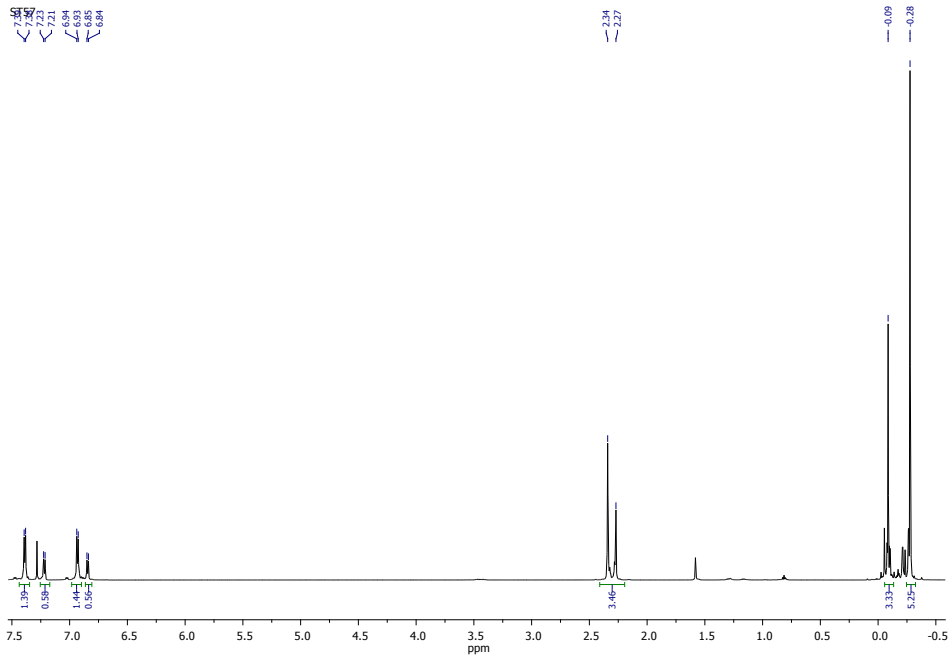

Figure 10. ^{1}H NMR (600.22 MHz, $CDCl_3$) of **4**

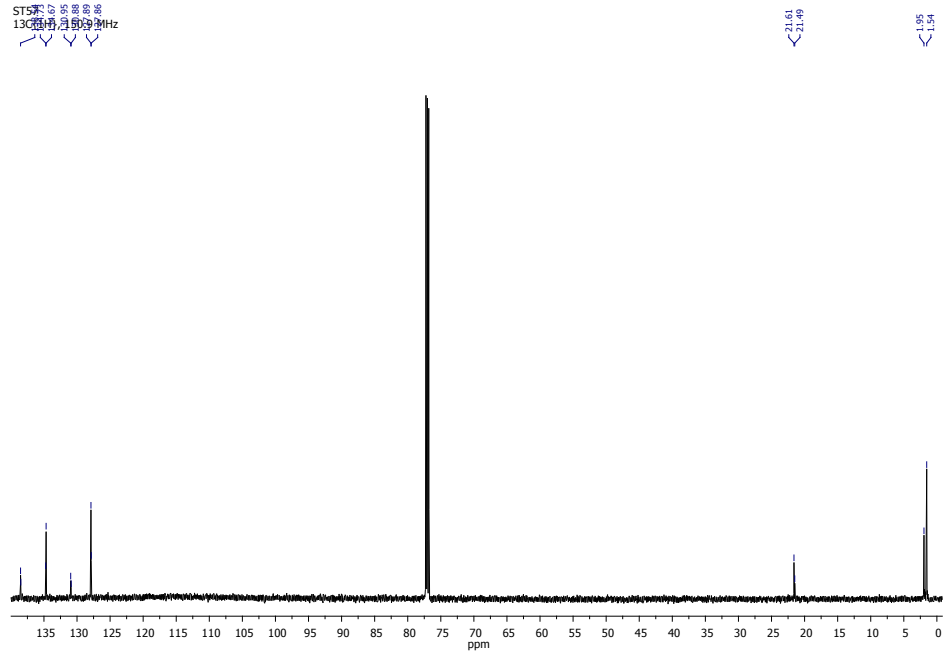

Figure 11. ^{13}C NMR (150.93 MHz, $CDCl_3$) of **4**

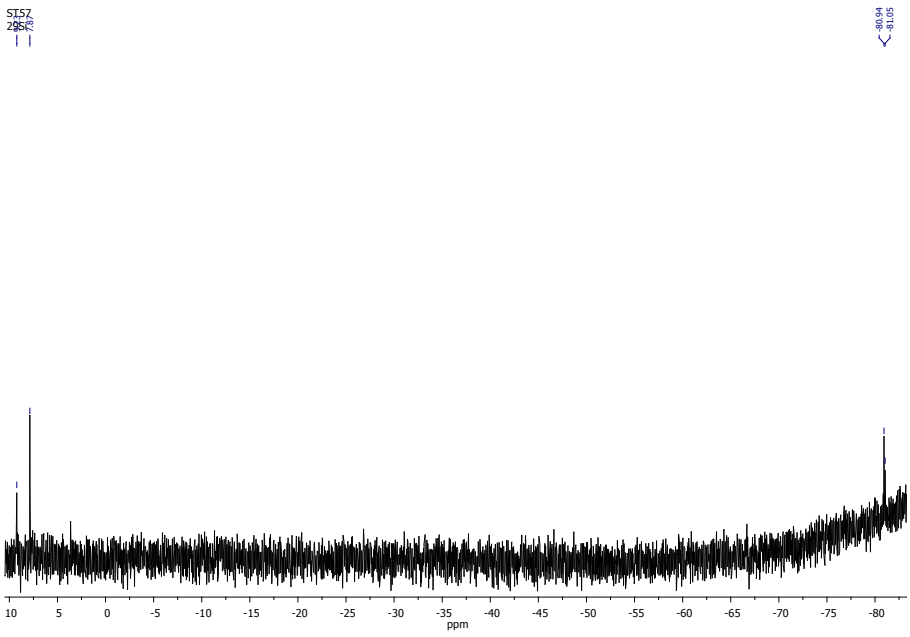

Figure 12. ^{29}Si NMR (119.26 MHz, $CDCl_3$) of **4**

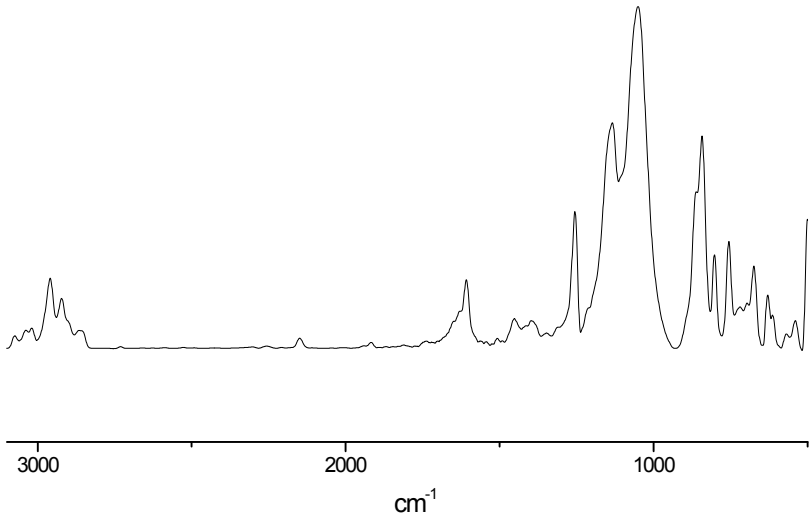

Figure 13. IR (cm−1) of **4**

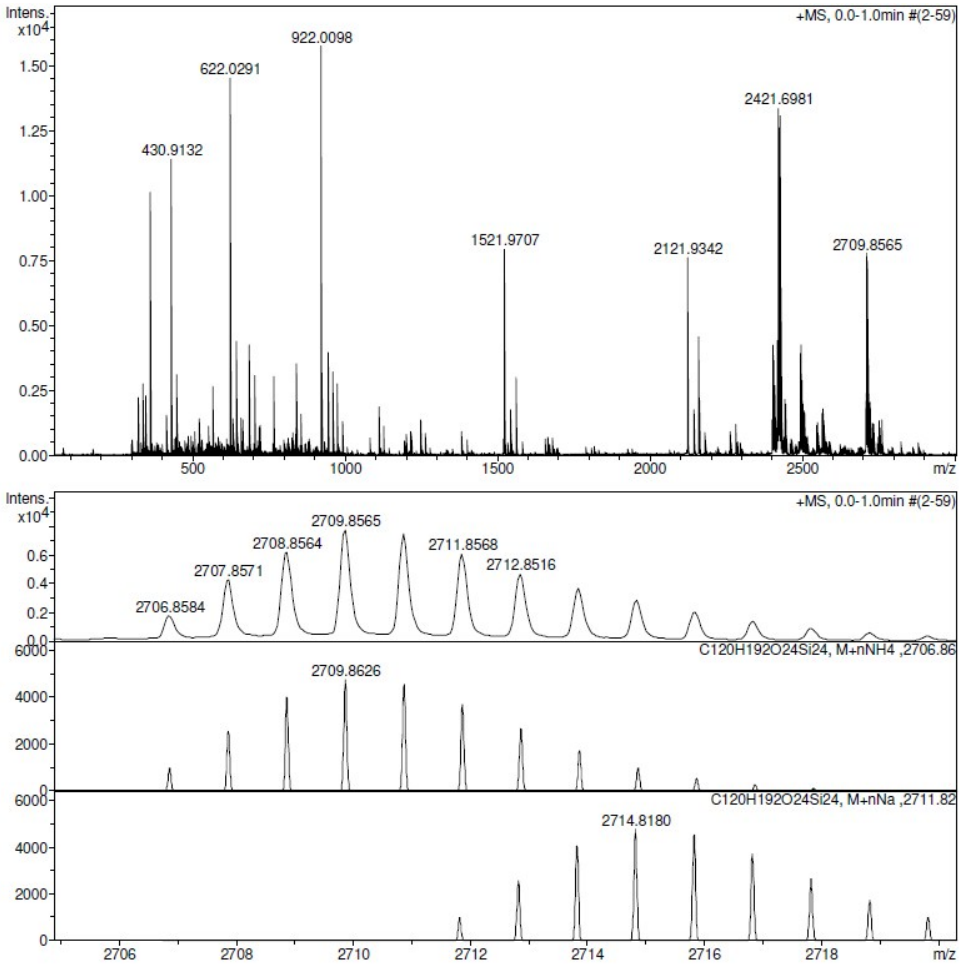

Figure 14. HRMS (ESI) of **4**

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