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New all-*cis*-tetra(*p*-tolyl)cyclotetrasiloxanetetraol and its functionalization

Yuliya S. Vysochinskaya, Anton A. Anisimov, Sergey A. Milenin, Alexander A. Korlyukov, Fedor M. Dolgushin, Elena G. Kononova, Alexander S. Peregudov, Mikhail I. Buzin, Olga I. Shchegolikhina and Aziz M. Muzafarov

CONTENTS

1. Experimental

1.1. General Considerations

Solvents were prepared according to earlier [1] described procedures. All solvents were purified before use. n-Butanol was distilled. Toluene was distilled from calcium hydride under argon. Sodium hydroxide, pyridine, chlorodimethylvinylsilane, chlorodimethylsilane, chlorotrimethylsilane, HCl were purchased from Aldrich. *p*-Tolyltriethoxysilane was synthesized by earlier described method [2].

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 F2.

1.2. Synthesis

1.2.1. Synthesis of compound **1**

A solution of sodium *cis*-tetratolylcyclotetrasiloxanolate **2** (10.85 g; 8.31 mmol) in a toluene/ethanol (70:4 ml) mixture was added dropwise to the solution of water (200 ml) and concentrated hydrochloric acid (10.3 ml) at 0°C. After 2-3 min of stirring, the organic layer was separated and added to water (490 ml) under vigorous stirring. The resulting white crystalline product was filtered, washed with water until neutral reaction to Cl^- ion, and dried in vacuum over $CaCl_2$ at room temperature for a few days. Yield: 4.04 g (81%).

CHN: Calc. (%) for, $C_{28}H_{32}O_8Si_4$. MM 608.89, C, 55.23; H, 5.30; Si, 18.45, Found: (%) C, 55.38; H, 5.25; Si, 18.22.

^{1}H NMR (600 MHz, $(CD_3)_2O$, ppm): δ 7.36 (d, 8 H, J = 6 Hz); 7.26 (t, 4 H, J = 12 Hz); 7.18 (t, 8 H, J = 18 Hz); 6.25 (s, 4 H, OH).

^{13}C NMR(150 MHz, $(CD_3)_2O$, ppm): δ 20.67, 128.13, 130.02, 134.17, 139.59.

^{29}Si NMR (150 MHz, $(CD_3)_2O$, ppm), δ: –69.9.

IR (cm^{-1}): 3256, 3072, 2912-2851, 1609, 132, 1102, 927-897

HRMS (ESI) m/z calc. for $C_{28}H_{32}O_8Si_4$ $[(M+Na)^+]$: 631.88, found 631.11.

1.2.2. Synthesis of compound **3a**

Compound **1** (0.38 g, 0.62 mmol) was added to a solution of toluene (4 ml), $ClSi(CH=CH_2)Me_2$ (0.45 g, 3.74 mmol), and pyridine (0.30 g, 3.74 mmol). The reaction mixture was stirred for 1 h. The precipitate was filtered off, the toluene filtrate was washed with water until the absence of chloride ions in washings and dried over sodium sulfate. Toluene was removed in vacuum to afford 0.37 g (63%) of a white wax-like product.

CHN: Calc. (%) for, $C_{44}H_{64}O_8Si_8$. MM 945.66, C, 55.93; H, 6.78; Si, 23.73, Found: (%) C, 55.72; H, 6.84; Si, 23.48.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.24 (d, 24H), 2.29 (s, 12H), 5.77-6.21 (m, 12H), 6.92 (d, 8H), 7.21 (d, 8H).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 0.36, 21.54, 128.08, 129.54, 132.13, 134.13, 138.87, 139.40.

^{29}Si NMR (119 MHz, $CDCl_3$, ppm): δ -79.10, -1.48.

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

HRMS (ESI) m/z calc. for $C_{44}H_{64}O_8Si_8$ $[(M+NH_4)^+]$: 963.70, found 962.31, $[(M+Na)^+]$: 968.65, found 967.27

1.2.3. Synthesis of compound **3b**

Analogously to the synthesis of **3a**, 0.96 g (70%) of the product were obtained from **1** (1 g, 1.64 mmol) and $(Me)_2HSiCl$ (0.93g, 9.85 mmol) in the presence of pyridine (0.78 g, 9.85 mmol) in toluene (10 ml).

CHN: Calc. (%) for; MM 841.51; $C_{36}H_{56}O_8Si_8$ C, 51.43; H, 6.67; Si, 26.67. Found: C, 51.39; H, 6.83; Si, 26.55.

^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 0.32 (d, 24H), 2.33 (s, 12H), 4.1 (spt, 4H), 7.01 (d, 8H), 7.30 (d, 8H).

^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 0.68, 21.61, 128.33, 129.16, 134.09, 139.77.

^{29}Si NMR (119 MHz, $CDCl_3$, ppm): δ -77.96, -4.

IR (cm^{-1}): 3072-3016, 2921, 2136, 1606, 1255, 1127, 1048.

HRMS (ESI) m/z calc. for $C_{36}H_{56}O_8Si_8$ $[(M+NH_4)^+]$: 859.55, found 858.25, $[(M+Na)^+]$: 864.50, found 863.29.

2. Crystallographic Studies

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX DUO diffractometer equipped with Oxford cryosystems Cobra (T = 120 K). The structures were solved by direct methods and refined in full matrix anisotropic approximation against F2. In the structure of **1**, hydrogen atoms of hydroxyl groups were located from difference Fourier maps, the rest hydrogen atoms in structures of **1** and **3a** were placed geometrically and included in the structure factors calculations in the riding motion approximation. In the structure of **1**, analysis of difference Fourier maps revealed the presence of electron density maxima, but their nature was not properly identified (most probably they correspond to symmetrically disordered solvate toluene molecule). Consequently, their contribution to diffraction intensities was excluded using SQUEEZE procedure [3]. The structure solution and refinement were performed with the OLEX2 (for structure **1**) and SHELXL (for structure **3a**) program packages [4, 5]. Crystallographic data and refinement details for structures **1** and **3a** are presented in Table S2. CIFs have been deposited at the Cambridge Crystallographic Database Centre and may be obtained from http://www.ccdc.cam.ac.uk by citing reference numbers CCDC 1589864 and 1589865 for compounds **1** and **3a** respectively.

In the crystal structure of **1**, these hydrophobic coated (by the tolyl groups) H-bonded chains are packed in pseudo-hexagonal arrays in an absent of specific intermolecular interactions between chains (Fig. S1, a).

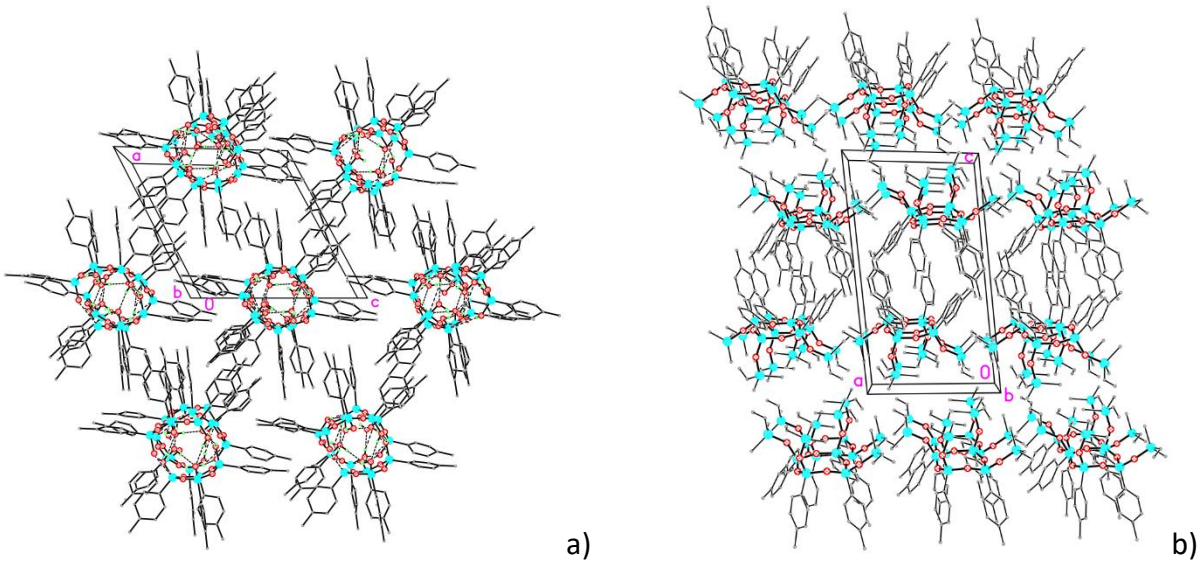

Figure S1. Packing diagram of tubelike chains in crystal of **1** (a) and layered structure in crystal of **3a** (b). Color code: Si cyan, O red, C gray, H open green circle.

In the crystal structure of **3a**, no specific intermolecular interactions (at most, very weak C-H…π contacts and no stacking of the aryl groups) are detected. The crystal packing is dominated by the segregation of cyclotetrasiloxane molecules in layers (Fig. S1, b).

Each layer is separated from its neighbors by facing the aryl and $SiMe_2Vin$ groups of the molecules in coincidence with crystal packing of analogous cyclotetrasiloxanes, *all-cis*-[(*p*-BrC_6H_4)Si(O)$OSiMe_3$]$_4$ and *all-cis*-[(*p*-IC_6H_4)Si(O)$OSiMe_2Vin$]$_4$.

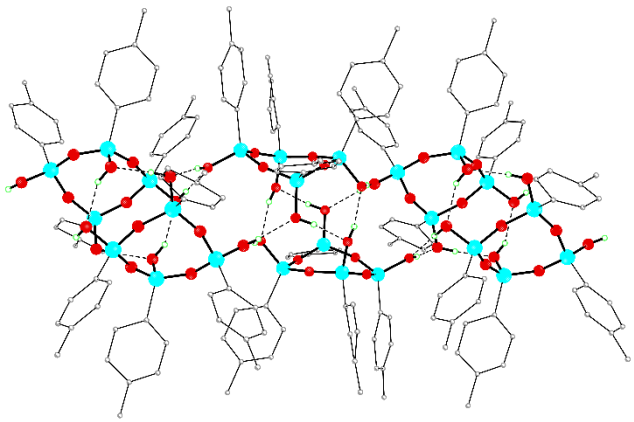

Figure S2. Fragment of H-bonded 1D chain

Table S1. Geometrical parameters (interval and average values) of cyclic tetrasiloxanes **1** and **3a**

Compound	**1**	**3a**
Si-O(endocyclic), Å	1.593(3)-1.620(2) <1.612>	1.603(3)-1.613(3) <1.609>
Si-O(exocyclic), Å	1.601(3)-1.633(3) <1.623>	1.591(3)-1.611(3) <1.602>
Si-C(Tol), Å	1.834(3)-1.847(4) <1.840>	1.835(4)-1.842(4) <1.838>
O-Si(terminal), Å	--------	1.627(3)-1.638(3) <1.633>
O-Si-O(endocyclic), deg.	108.3(1)-111.7(1) <110.2>	107.8(1)-110.8(1) <109.3>
Si-O-Si(endocyclic), deg.	149.3(2)-164.5(2) <155.9>	142.5(2)-163.5(2) <154.2>
Si-O-Si(exocyclic), deg.	--------	140.6(2)-146.9(2) <143.8>

Table S2. Crystal data, collection data and structure refinement parameters for compounds **1** and **3a**

Compound	**1**	**3a**
Formula	$C_{28}H_{32}O_8Si_4$	$C_{44}H_{64}O_8Si_8$
molecular wt	608.89	945.67
crystal size (mm)	0.35×0.03×0.03	0.55×0.24×0.14
crystal syst	triclinic	triclinic
space group	*P*-1	*P*-1
a (Å)	15.5244(3)	11.332(3)
b (Å)	15.9252(3)	11.930(3)
c (Å)	15.9405(3)	20.029(5)
α (deg)	103.1449(11)	80.694(4)
β (deg)	113.4462(12)	81.979(4)
γ (deg)	101.8319(13)	76.573(4)
V (Å^3)	3322.62(11)	2584.3(12)
Z	4	2
d_{calcd} (g·cm^{-3})	1.217	1.215
Wavelength	Cu Kα	Mo Kα
linear absorption μ (cm^{-1})	20.29	2.54
T_{min}/T_{max}	0.549/0.754	0.785/0.965
θ_{max} (deg)	71.7	27.0

no. of unique reflns (R_{int})	12426 (0.0642)	11277 (0.0599)
no. of obsd reflns ($I>2\sigma(I)$)	10181	7862
no. of params	748	553
R_1 (on F for obsd reflns)[a]	0.0677	0.0671
wR_2 (on F^2 for all reflns)[b]	0.1830	0.1829
GOOF	1.061	1.111

[a] $R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

3. NMR, IR and Mass Spectra

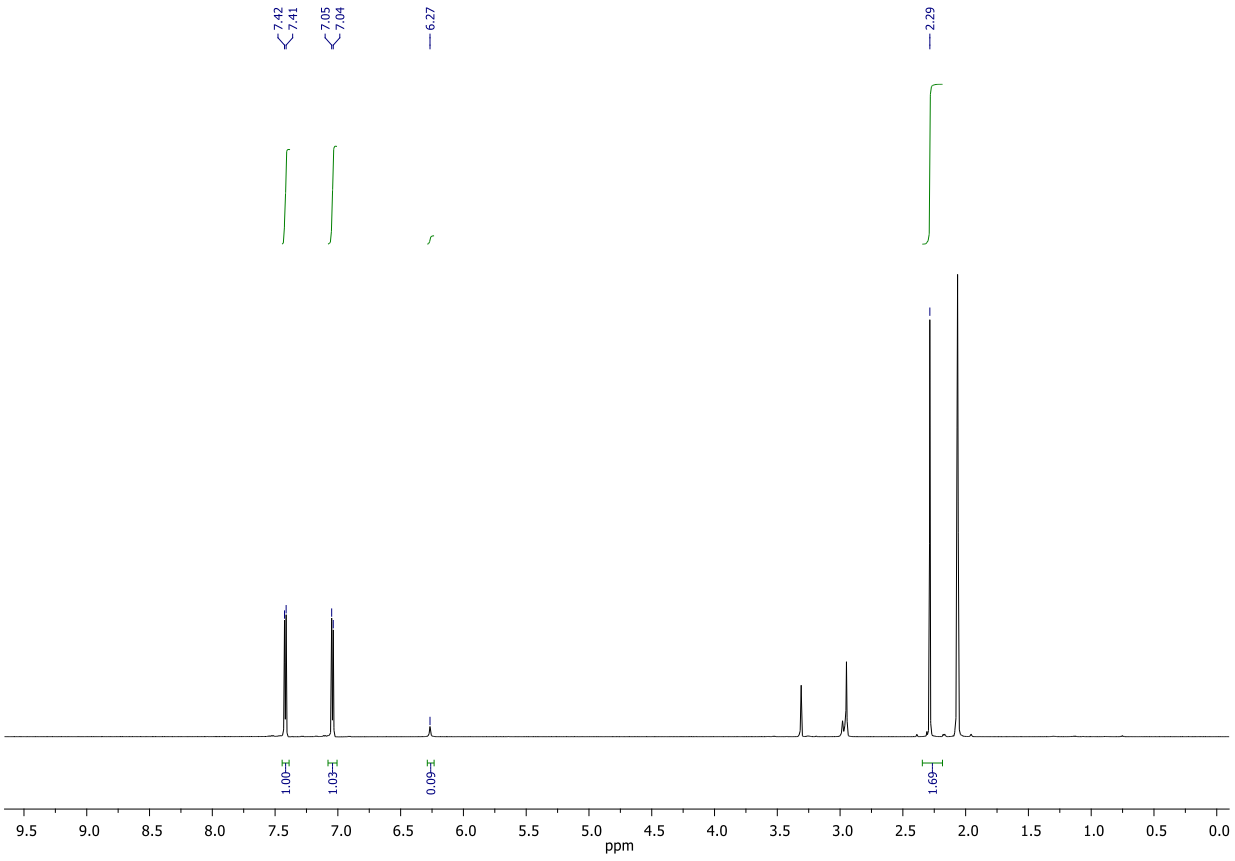

Figure S3. ^{1}H NMR-spectrum of compound **1**

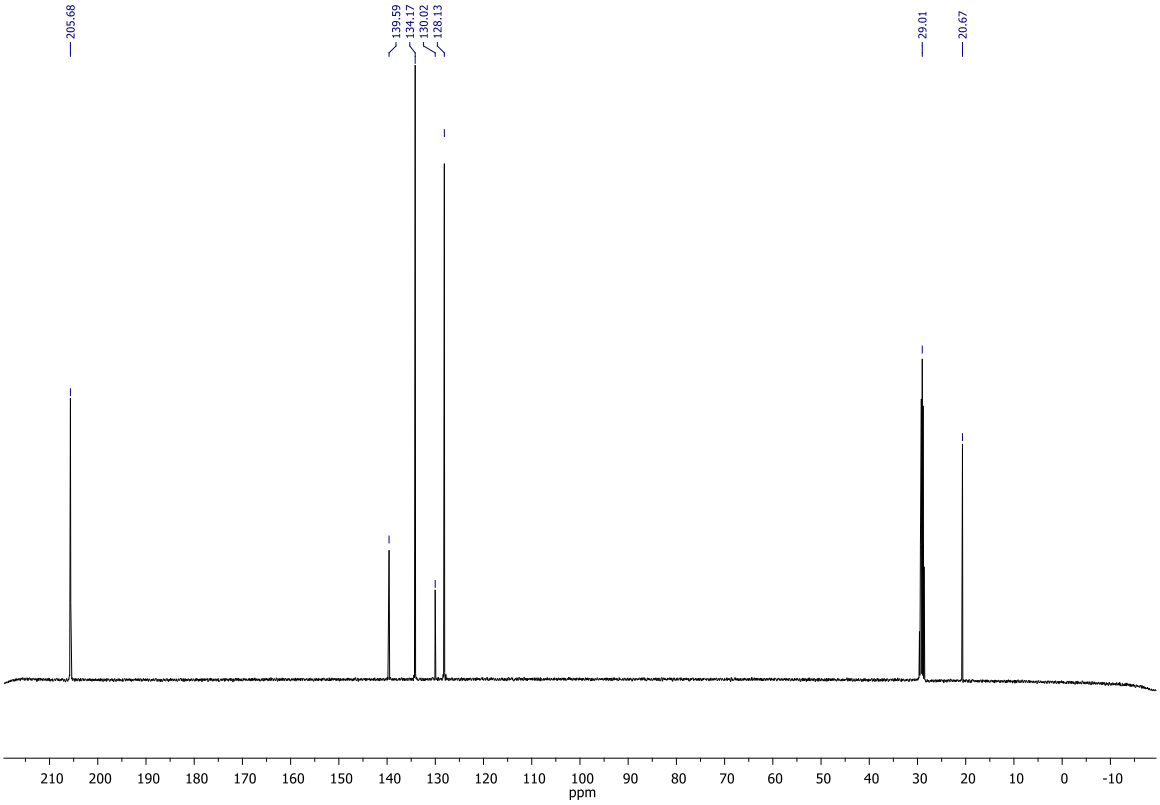

Figure S4. ^{13}C NMR-spectrum of compound **1**

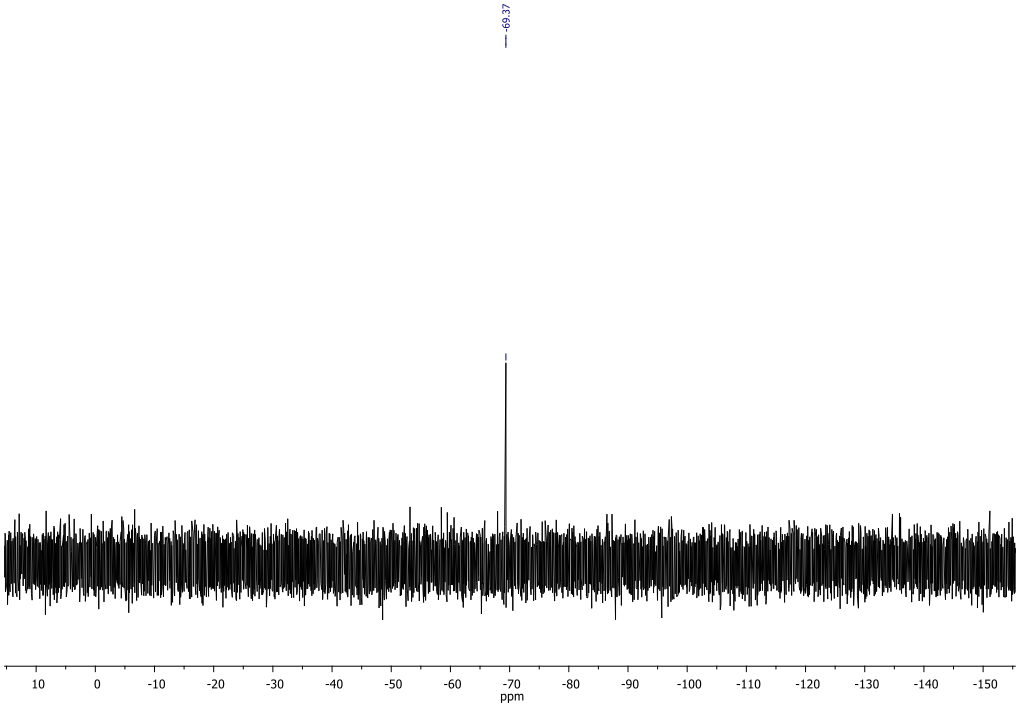

Figure S5. ^{29}Si NMR-spectrum of compound **1**

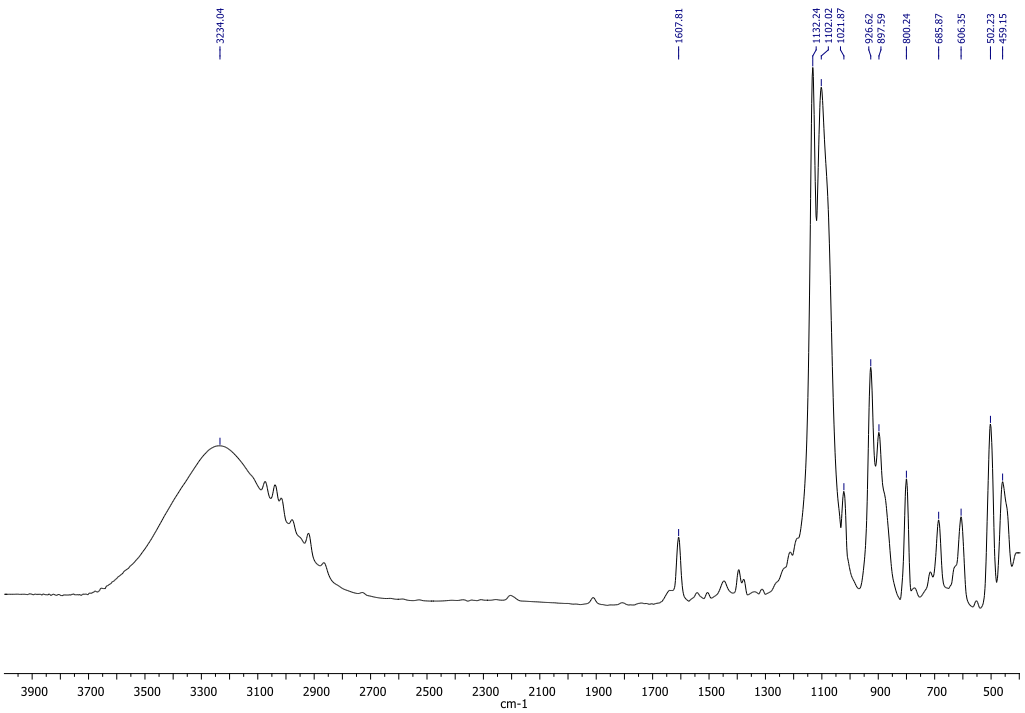

Figure S6. IR- spectrum of compound **1**

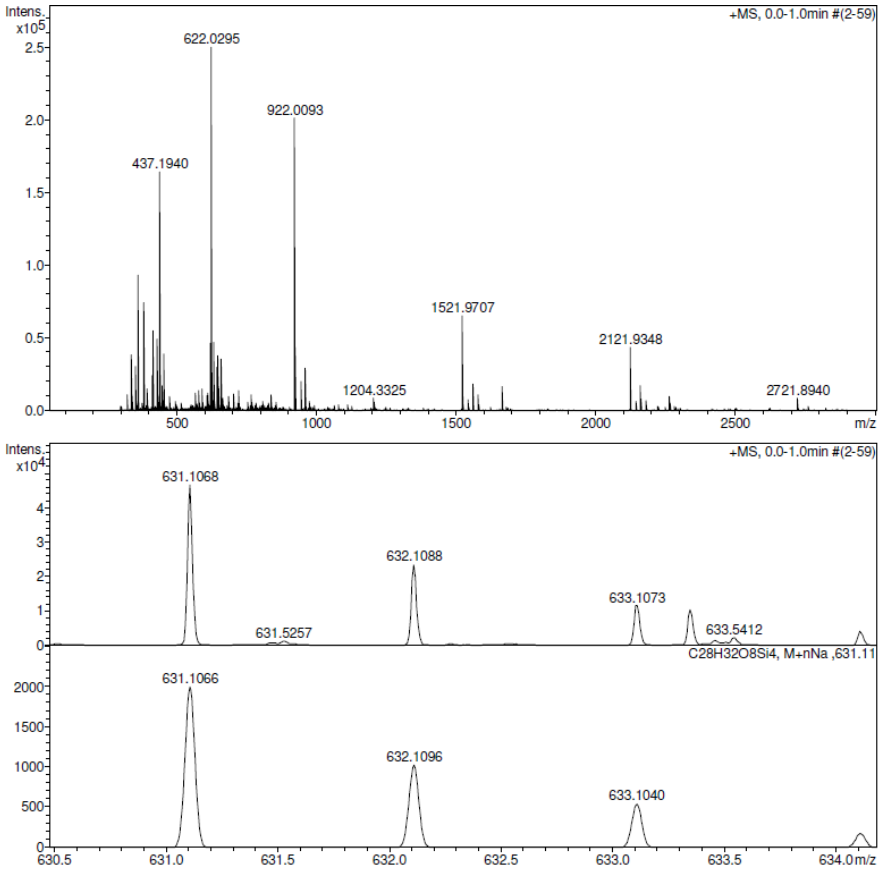

Figure S7. Mass- spectrum of compound **1**

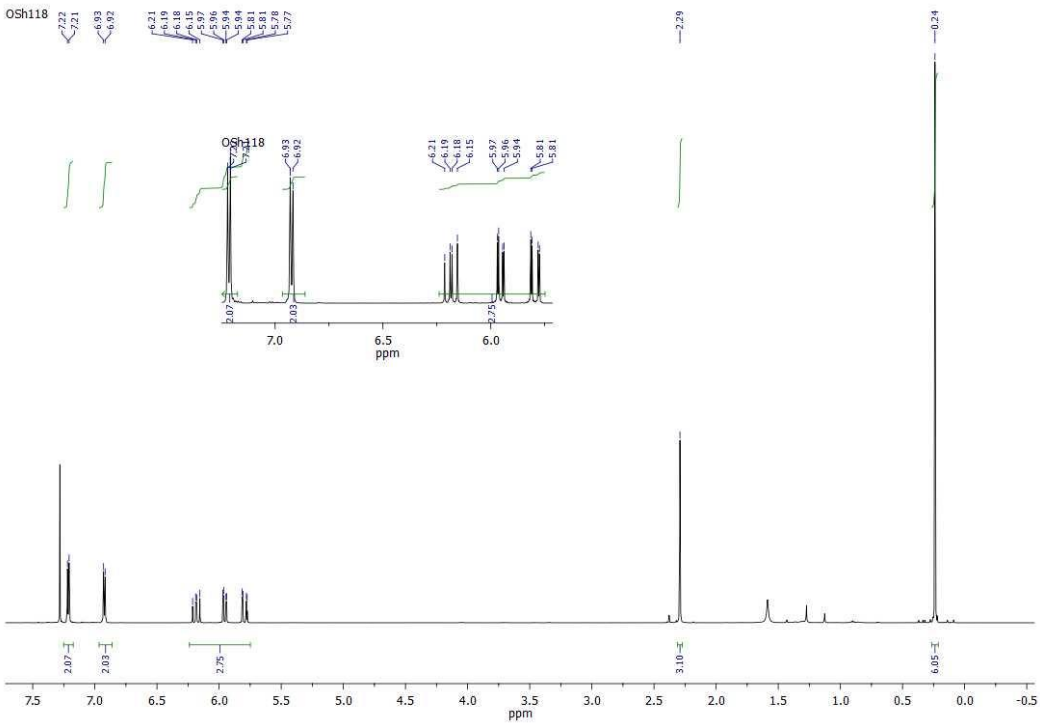

Figure S8. ^{1}H NMR-spectrum of compound **3a**

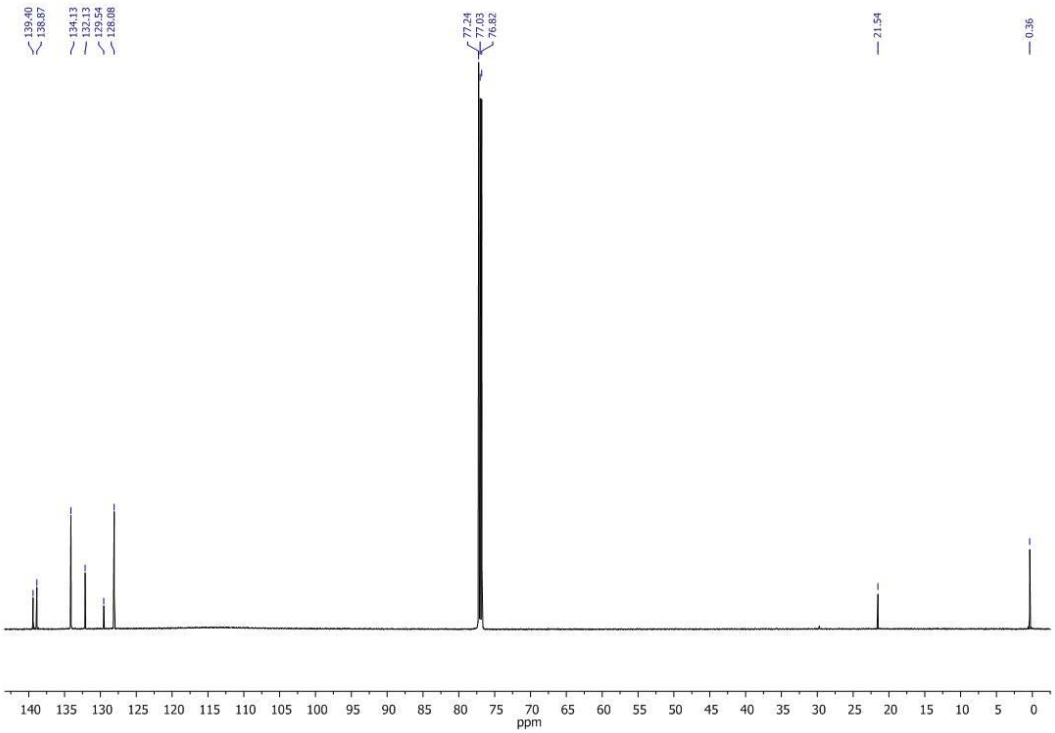

Figure S9. ^{13}C NMR-spectrum of compound **3a**

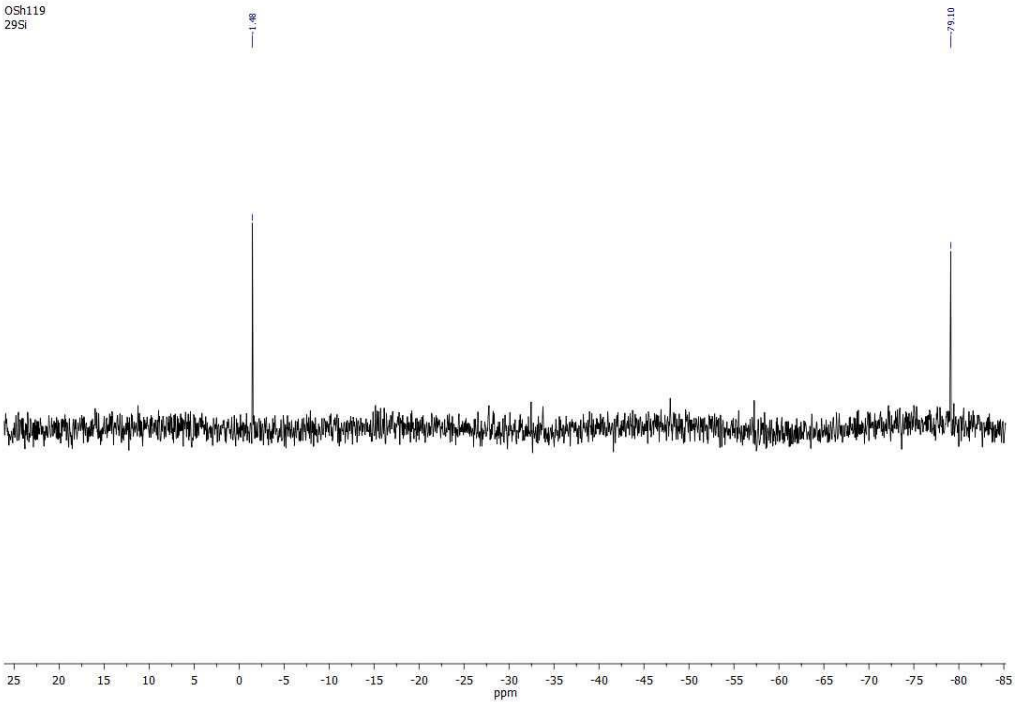

Figure S10. ^{29}Si NMR-spectrum of compound **3a**

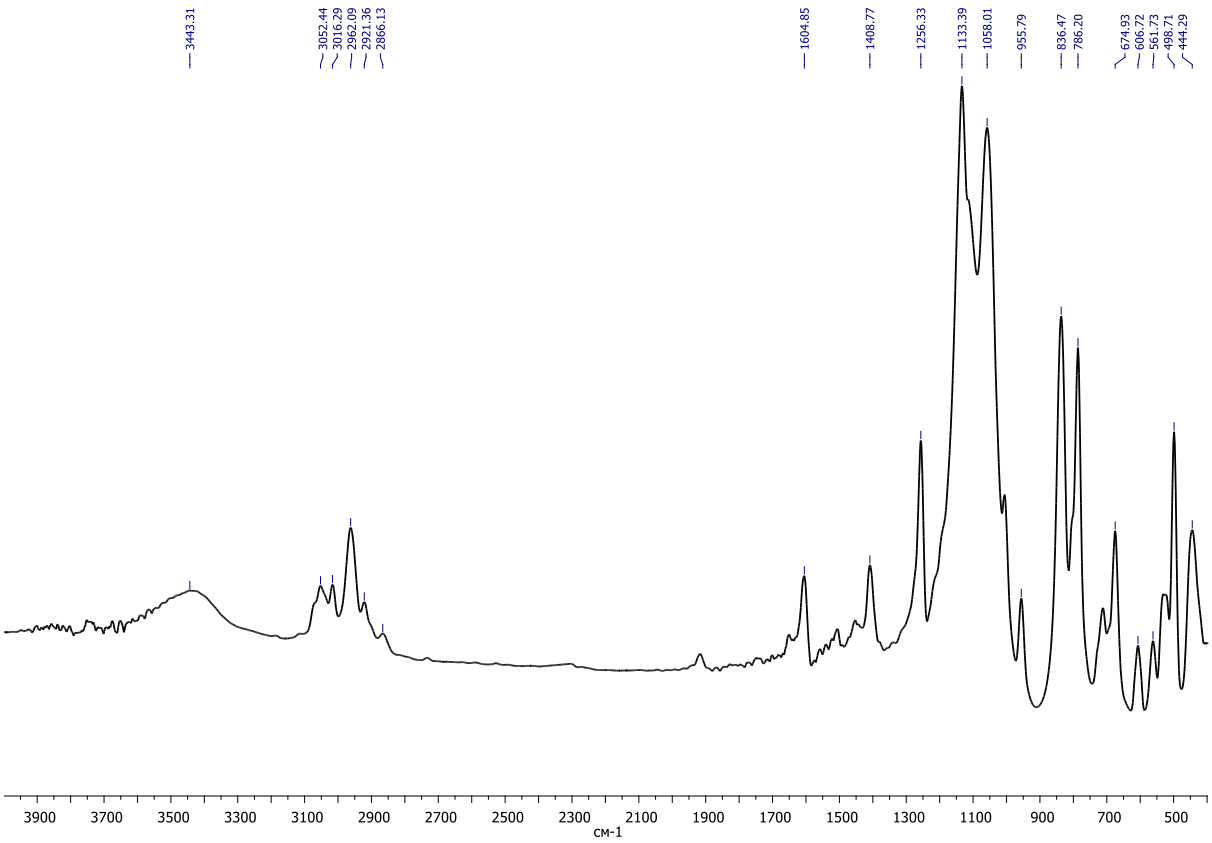

Figure S11. IR- spectrum of compound **3a**

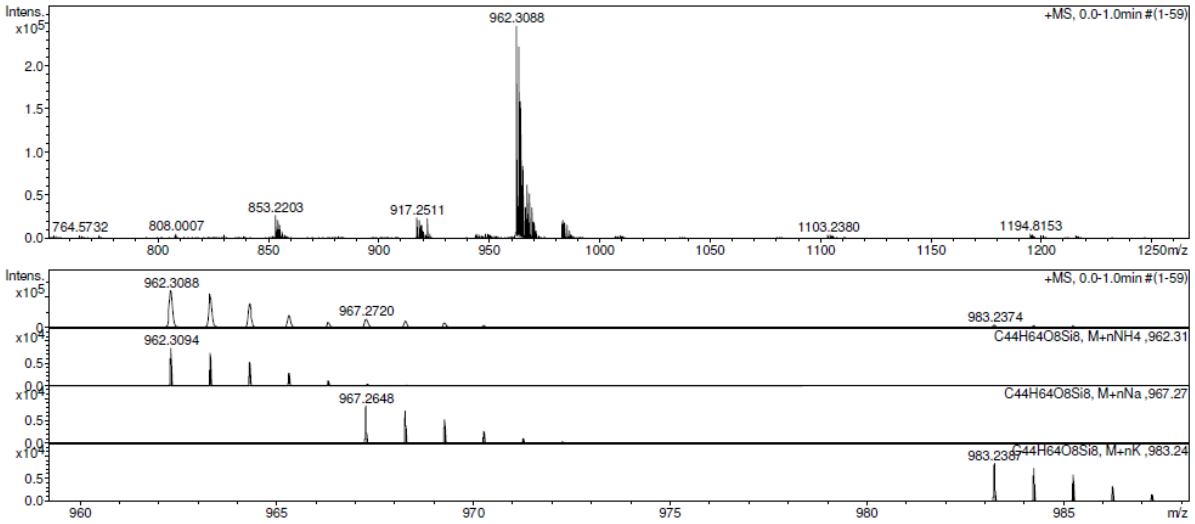

Figure S12. Mass- spectrum of compound **3a**

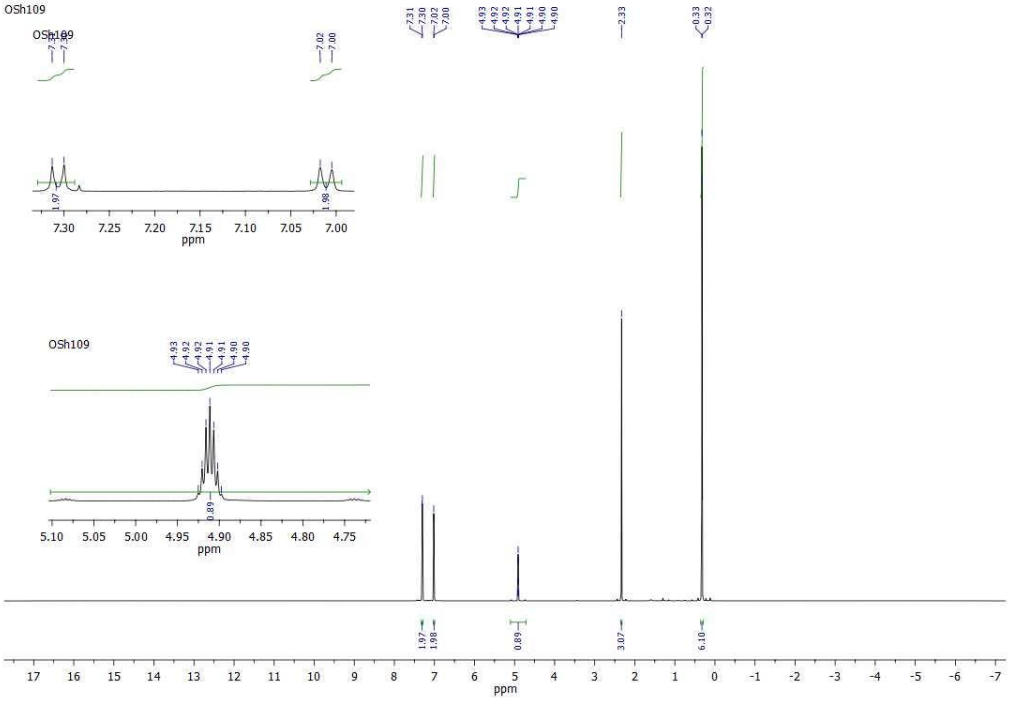

Figure S13.[1]H NMR-spectrum of compound **3b**

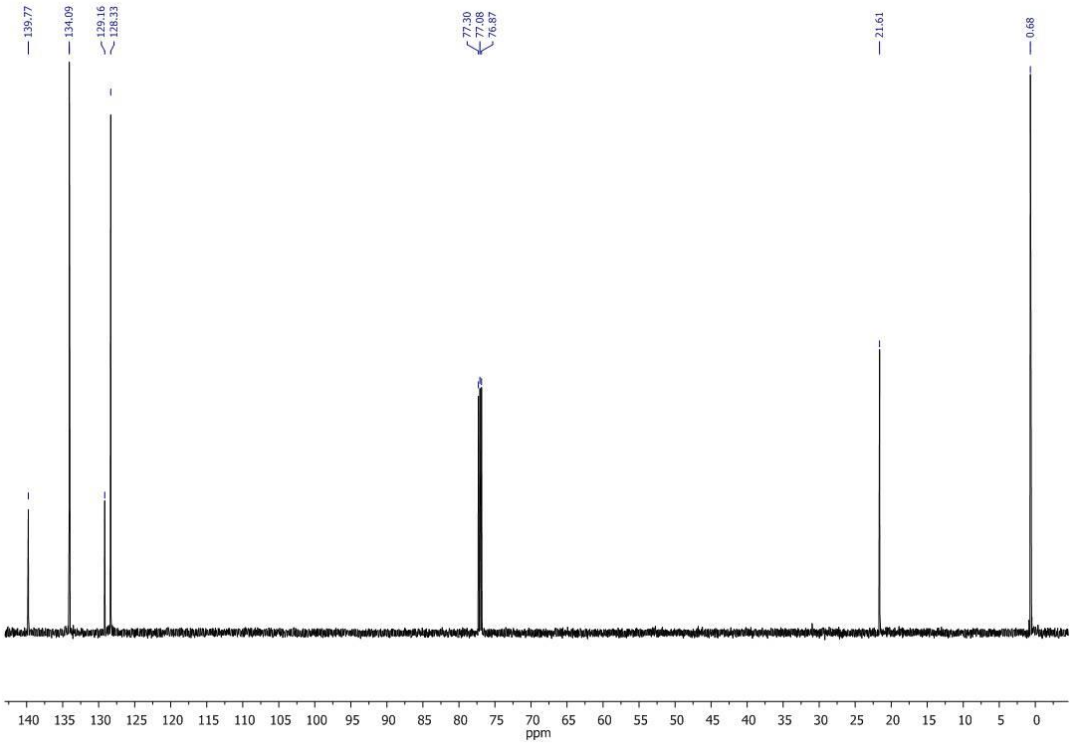

Figure S14. ^{13}C NMR-spectrum of compound **3b**

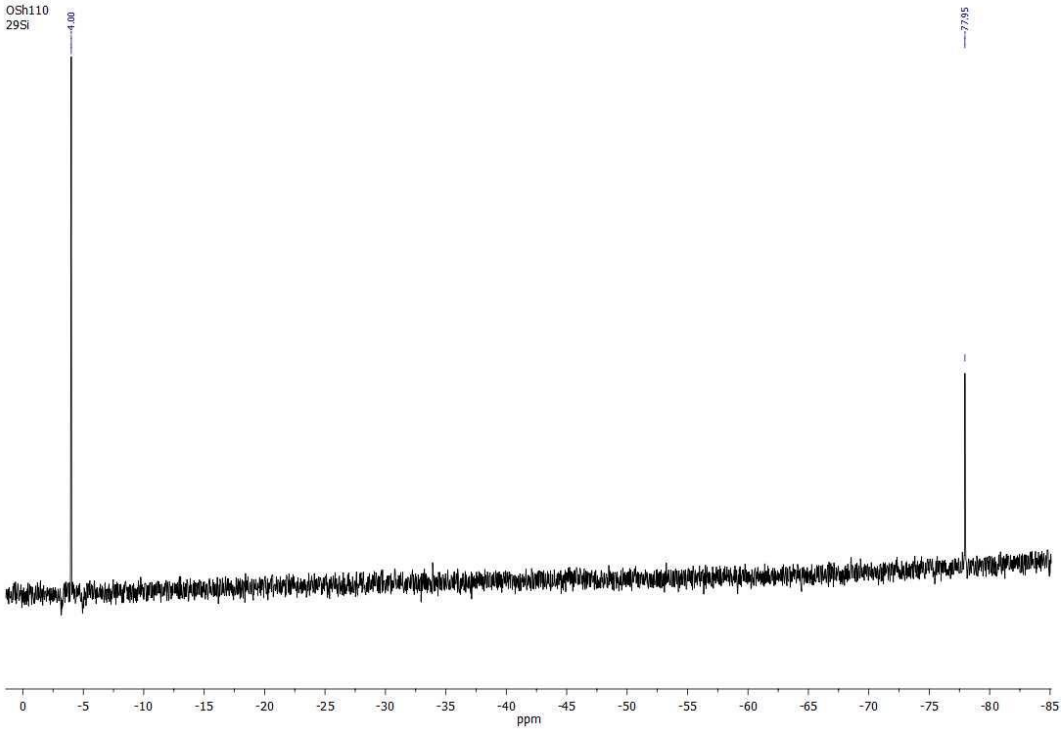

Figure S15. ^{29}Si NMR-spectrum of compound **3b**

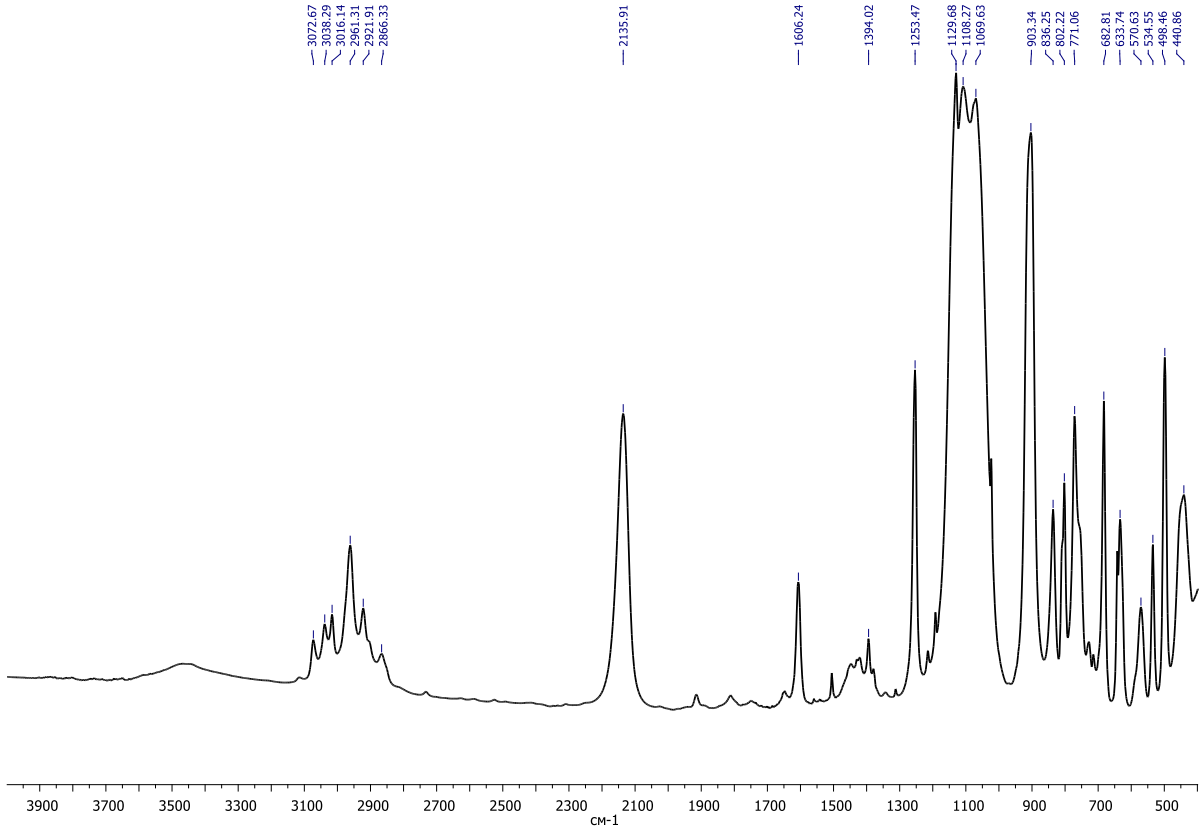

Figure S16. IR- spectrum of compound **3b**

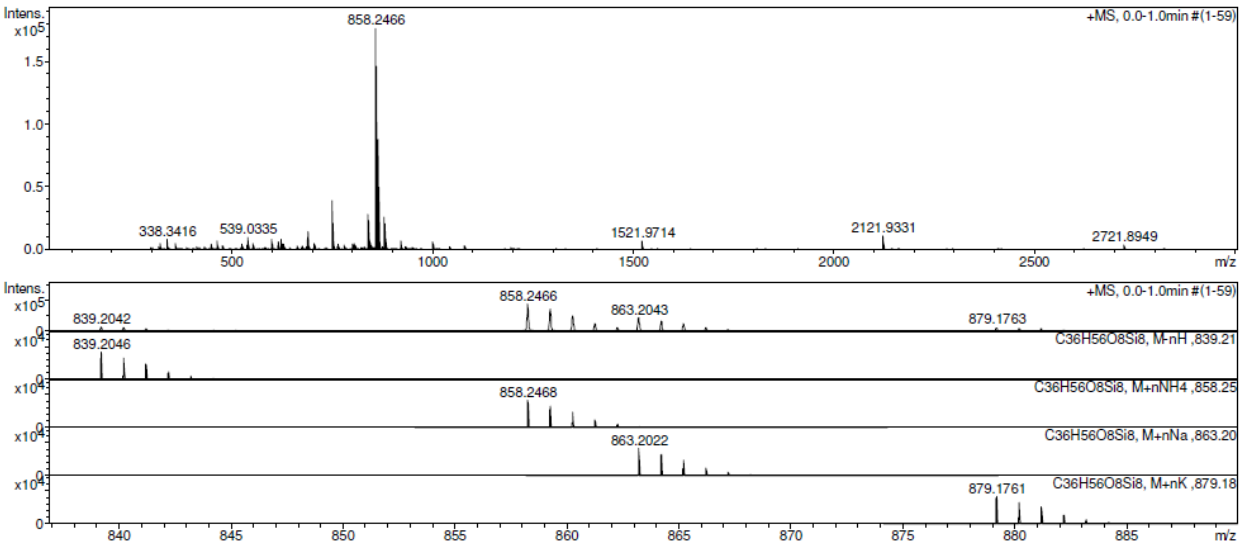

Figure S17. Mass- spectrum of compound **3b**

4. Polarized optical microscopy

The polarized optical microscopy results for compound **3a** well agree with the DSC data and can be are assigned to mesophases of a plastic-crystalline type, where the molecules form, as in usual crystals, a crystal lattice with long-range order, but also possess a rotational degree of freedom [6].

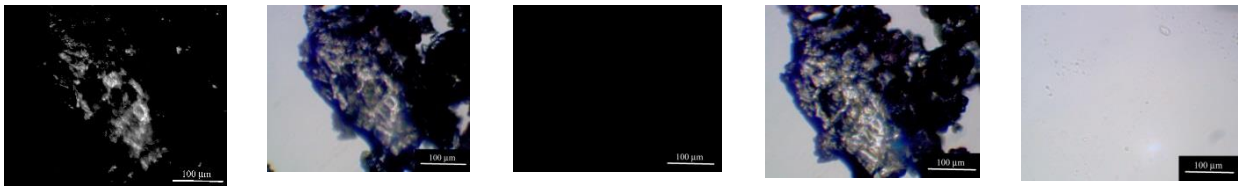

Figure S18. Microphotographs of compound **3a** in crossed (a,c) and parallel (b,d,e) nicols at temperatures 25°C (a,b), 80°C (c,d) and 125°C (e).

5. References

1. A. J. Gordon and R. A. Ford, *The Chemist's Companion*, Wiley-*Interscience*, New York, 1972.
2. A. S. Manoso, C. Ahn, A. Soheili, C. J. Handy, R. Correia, W. M. Seganish and P. De Shong, *J. Org. Chem*., 2004, **69**, 8305.
3. A. L. Spek, *Acta Crystallogr*., 2015, **C71**, 9-18
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. *Appl. Cryst.*, 2009, **42**, 339-341.
5. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3-8.
6. J. Timmermans, *J. Phys. Chem. Solids*, 1961, **18**, 1.