Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 570–571

The Suzuki modification of functional polydimethylsiloxanes

Fedor V. Drozdov, Georgii V. Cherkaev and Aziz M. Muzafarov

Contents

1. Experimental details.

Microwave syntheses were carried out in a CEM Discover Benchmate (USA) microwave reactor. Gel Permeation Chromatography (GPC) analysis was performed on a Shimadzu LC-10A series chromatograph (Japan) equipped with an RID-10A refractometer and SPD-M10A diode matrix detectors. For analytical separation, Phenomenex column (USA) with a size of 7.8 mm × 300 mm filled with the Phenogel sorbent with a pour size of 500 Å was used. ^{1}H NMR spectra were recorded using a Bruker WP-250 SY spectrometer with working frequency of 250.13 MHz. Residual protons of $CDCl_3$ (δ=7.25 ppm) were used as a reference. ^{1}H, ^{13}C, ^{29}Si NMR spectra and their nucleus correlations were recorded using a Bruker Avance II 300 spectrometer at 300, 75 and 60 MHz, respectively. High-resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 μl min^{-1}). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Organic chemicals (Sigma-Aldrich) with purity not less than 95% were used as purchased. The Karsted's catalyst and silicon-containing precursors were purchased from ABCR GMbH. Solvents such as THF, toluene, dioxane, hexane, ethanol were purified routinely and were freshly distilled prior to use.

*1,1,1,3,5,5,5-Heptamethyltrisiloxane **1*** was synthesized as described [1] in yield of 78% as a colourless dense liquid. B.p. 140-141 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.65 (s, 1H, Si<u>H</u>), 0.12 (s, 21H, SiC<u>H</u>$_3$)

*4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane **2**.* To a stirred solution of 4-bromo-styrene (4.1 g, 22.4 mmol) in dry THF (20 ml) at -78 °C under inert atmosphere, *n*-BuLi (9.0 ml of hexane solution, 22.4 mmol) was added dropwise. The mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.17 g, 22.4 mmol) was added dropwise, and the mixture stirred for 30 min at -78 °C. The reaction mixture was allowed to reach room temperature. The mixture was stirred overnight and then extracted with diethyl ether (2x50 ml). The organic phase was separated and washed with brine and then pure water twice. The solution was dried (Na_2SO_4) and evaporated to dryness. The product was obtained as yellowish liquid in a yield of 5.08 g (96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 (d, 2H, J=8.2 Hz, Ph), 7.40 (d, 2H, J=8.2 Hz, Ph), 6.66 (dd, 1H, J=10.6, 6.6 Hz, Vin-H), 5.77 (1H, d, J=17.7 Hz, Vin-H), 5.26 (1H, d, J=11.6 Hz, Vin-H), 1.34 (s, 12H, C<u>H</u>$_3$);

Anionic polymerization of hexamethylcyclotrisiloxane. Monofunctional polydimethylsiloxane **5** was synthesized as reported [2]. Mobile liquid. M_n=900, M_w=1060, PDI=1.16. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4,71 (m, 1H, Si-<u>H</u>), 3.52 (m, 3H, C<u>H</u>$_3$), 0.89 (m, 4H, C<u>H</u>$_2$), 0.55 (m, 2H, C<u>H</u>$_2$), 0.09 (s, 89H, C<u>H</u>$_3$)

Cationic polymerization of octamethylcyclotetrasiloxane. To a vigorously stirred mixture of octamethylcyclotetrasiloxane (49.83 g, 0.168 mol) and 1,1,2,2-tetramethyldisiloxane (0.27 g, 0.002 mol), two drops of trifluoromethanesulfonic acid were added. The mixture was heated at 60 °C for 12 h. After the reaction was completed, the temperature was raised to 120 °C, and cyclic byproducts were removed by vacuum distillation. Product **8** was obtained as dense colourless liquid. M_n=4900, M_w=7300, PDI=1.49. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.72 (m, 2H, Si-<u>H</u>), 0.09 (s, 391H, C<u>H</u>$_3$)

Hydrosilylation (general procedure). To a stirred 20% solution of siloxane **1,5** or **8** in dry dioxane in argon atmosphere and compound **2** (1 equiv. per each Si-H group), the Karsted's catalyst (0.1 vol. %) was added, and the mixture was heated at 50 °C for 6 h. After the reaction was complete, the mixture was passed through a thin layer of silica, and the solvent was evaporated. The products **3,6** or **9** were dried in vacuum.

The Suzuki reaction (general procedure). A mixture of silyloxy styryl borolane (1 equiv.), bromobenzene (2.5 equiv.), Na_2CO_3 (2 *M* aq., 5 equiv.) and toluene (10 ml) was purged with argon. Tetrakis(triphenylphosphine)palladium (5 mol. %) was added and purging with argon was continued for 10 min. The reaction vessel was sealed and irradiated in a microwave reactor (110 °C, 150 W) for 2-3 h. Then mixture was diluted with toluene. The organic phase was washed

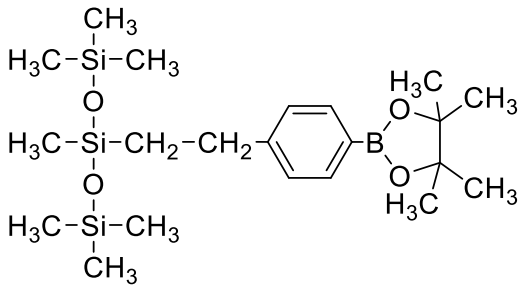
---

[1] R. R. Khairova, S. A. Milenin, G. V. Cherkaev, I. I. Stoikov and A. M. Muzafarov. *Russ. Chem. Bull., Int. Ed.*, 2016, **65**, 1285.

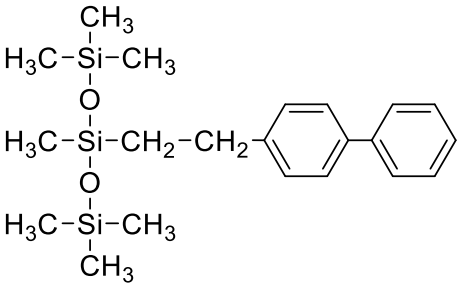
[2] C. L. Frye, R. M. Salinger, F. W. G. Fearson, J. M. Klosowski and T. Deyoun. *J. Org. Chem.*, 1970, **35**, 130.

with brine and water. The solution was dried (Na_2SO_4) and the solvent was evaporated. The products **4,7,10** were obtained as colourless liquids.

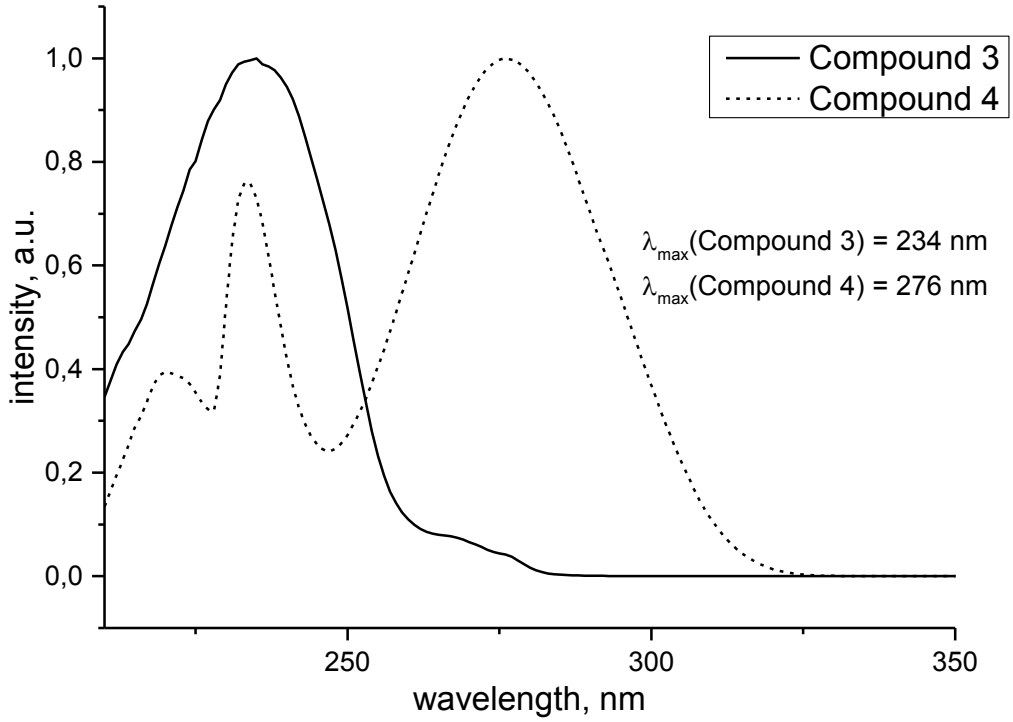
2. **Absorption spectra of sources (solid) and products (dashed)**

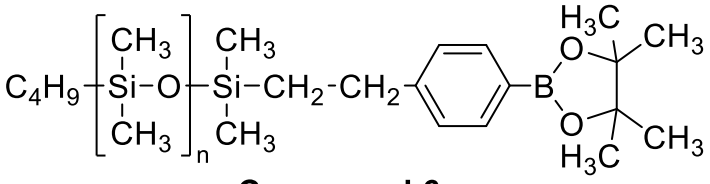


Compound 3
(mixture of regioisomers)



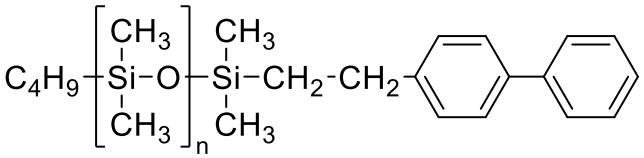
Compound 4
(mixture of regioisomers)





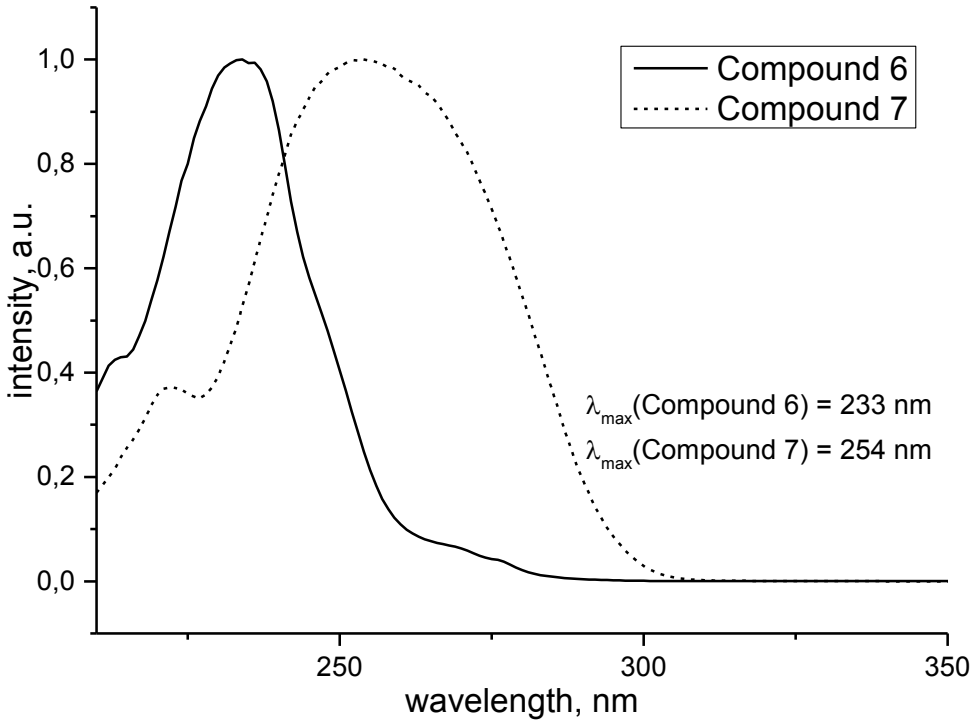
Compound 6

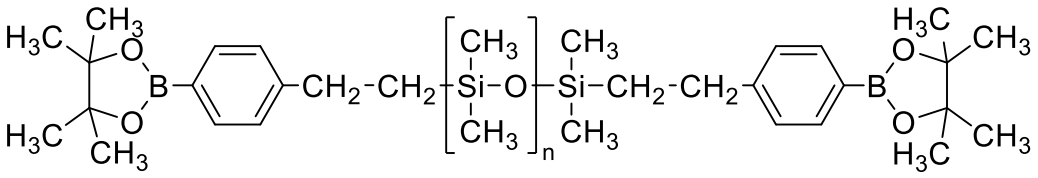
(mixture of regioisomers)



Compound 7

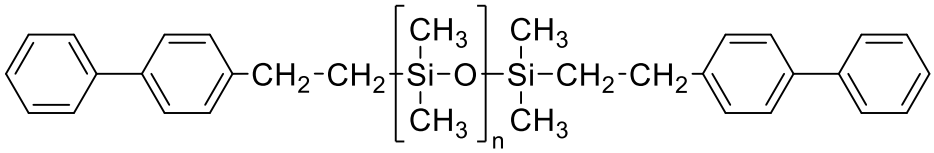
(mixture of regioisomers)





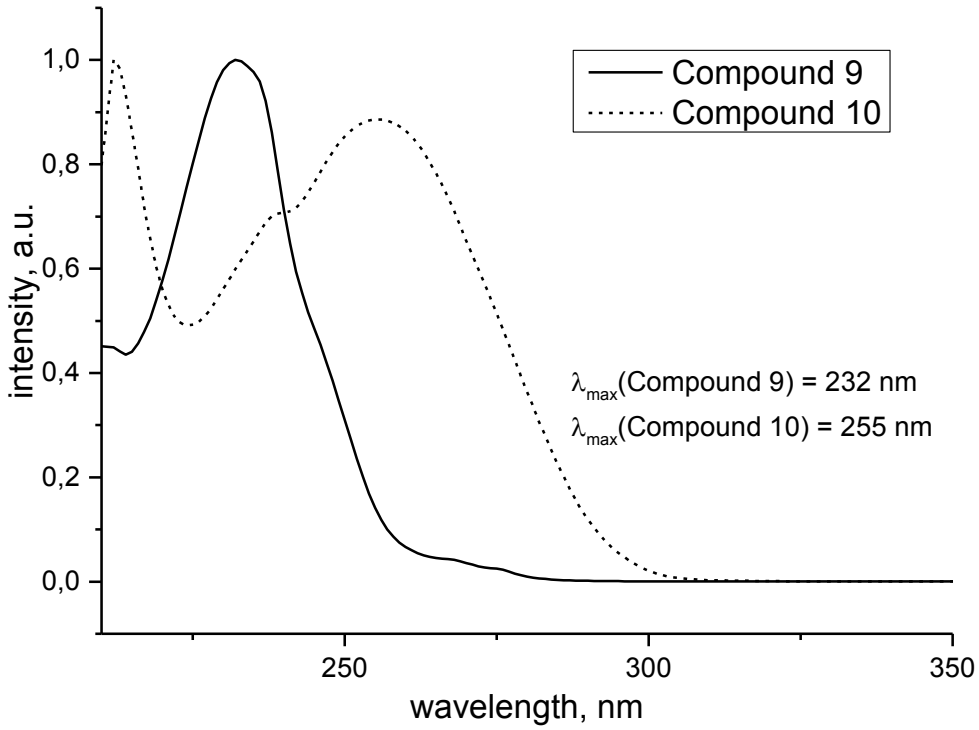
Compound 9

(mixture of regioisomers)



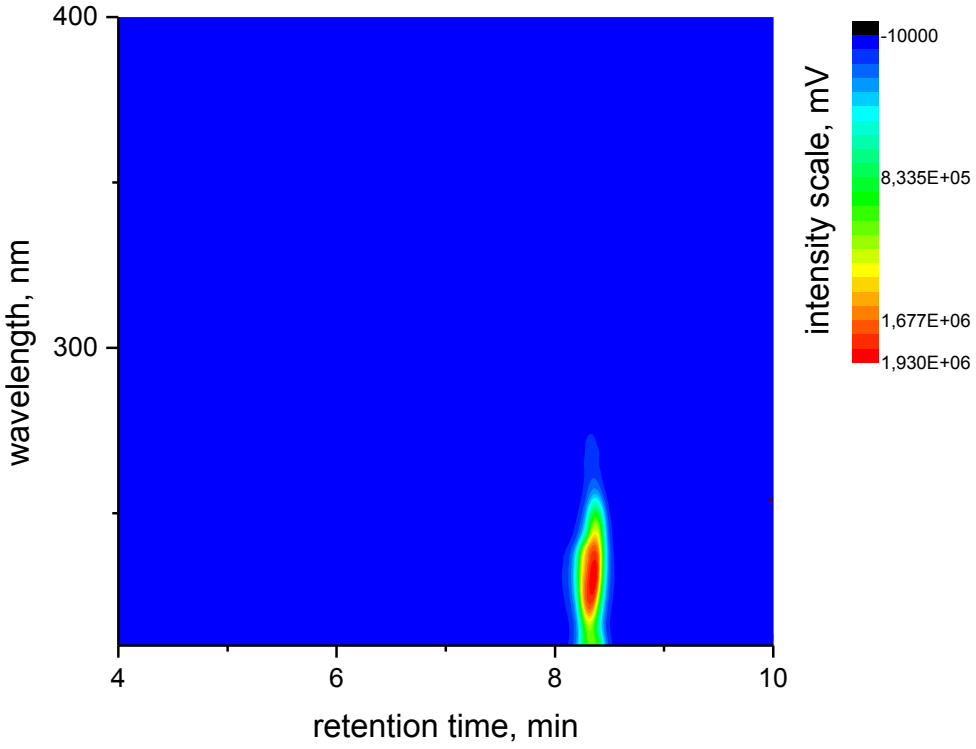
Compound 10

(mixture of regioisomers)

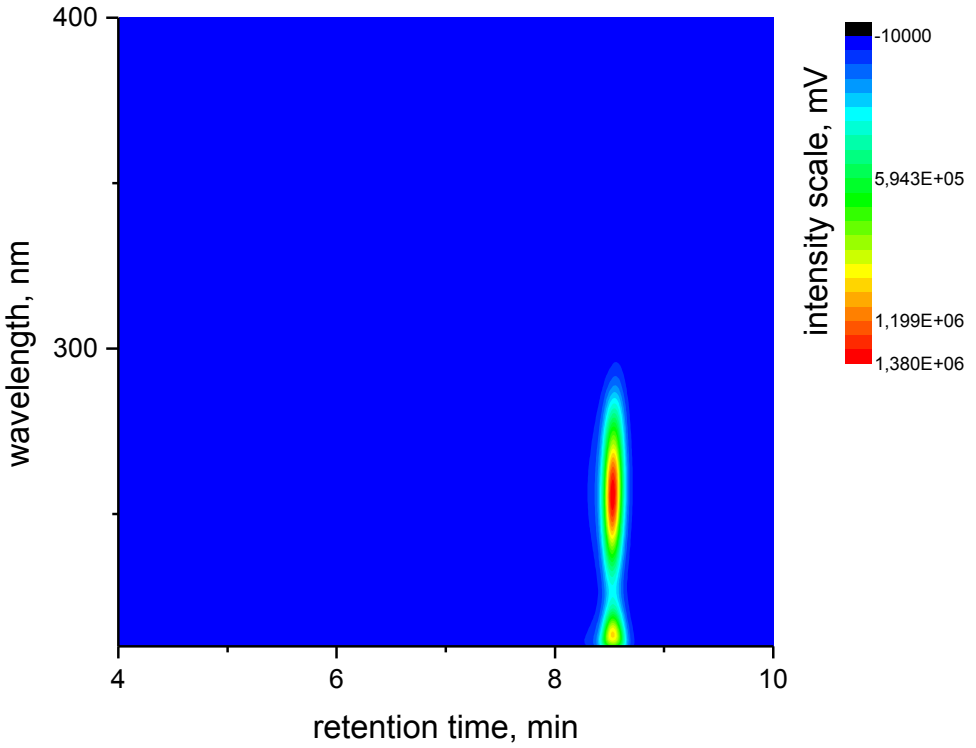


3. **3-D contours of the sources siloxy styryl borolanes and Suzuki reaction products**

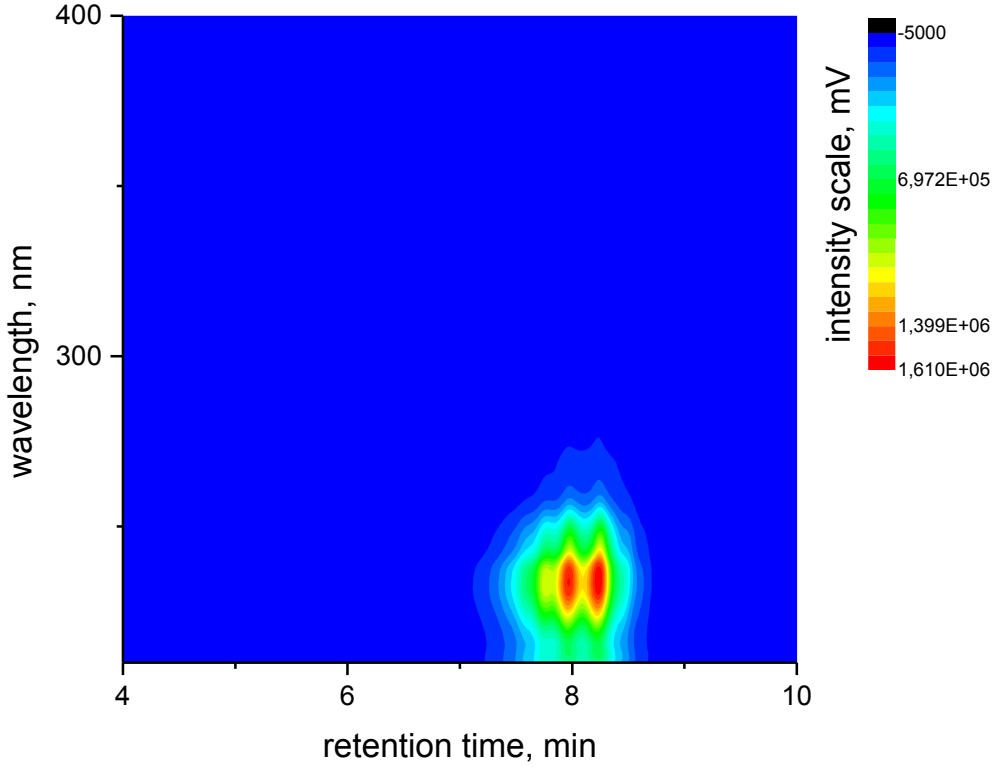
Compound 3



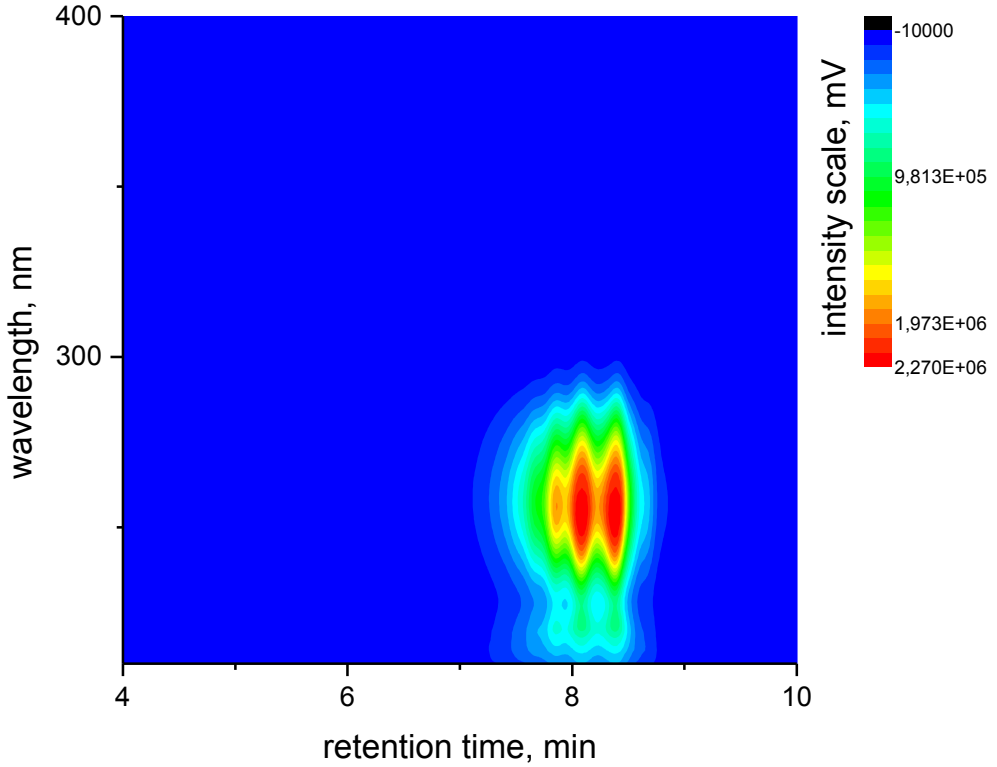
Compound 4



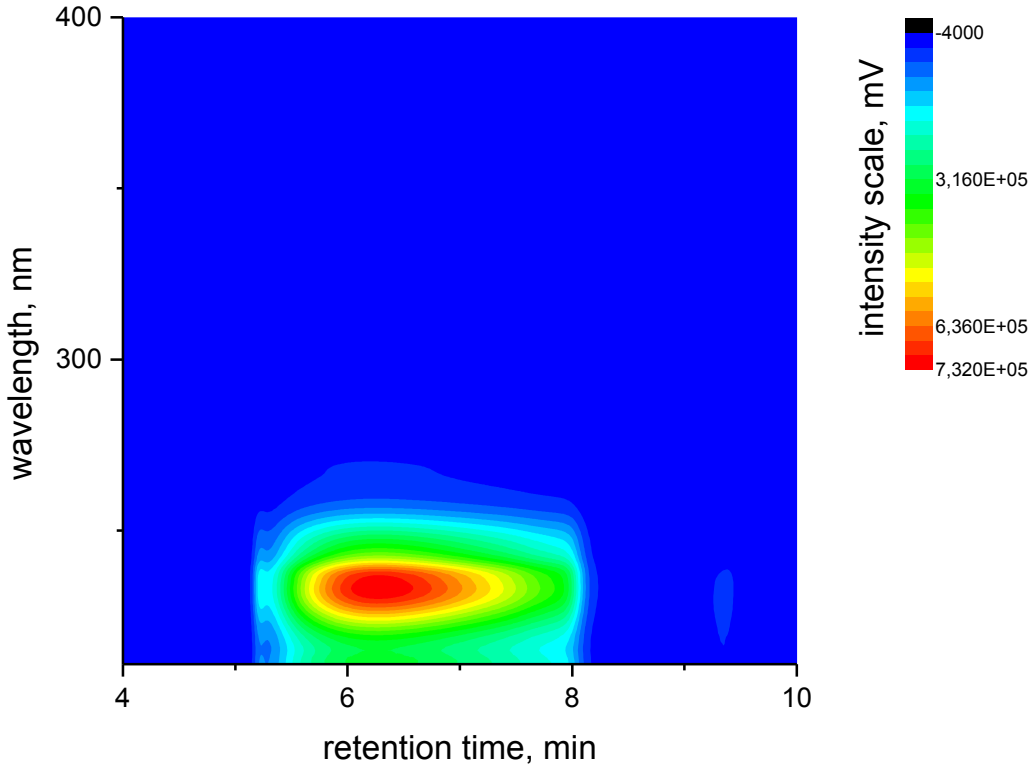
Compound 6



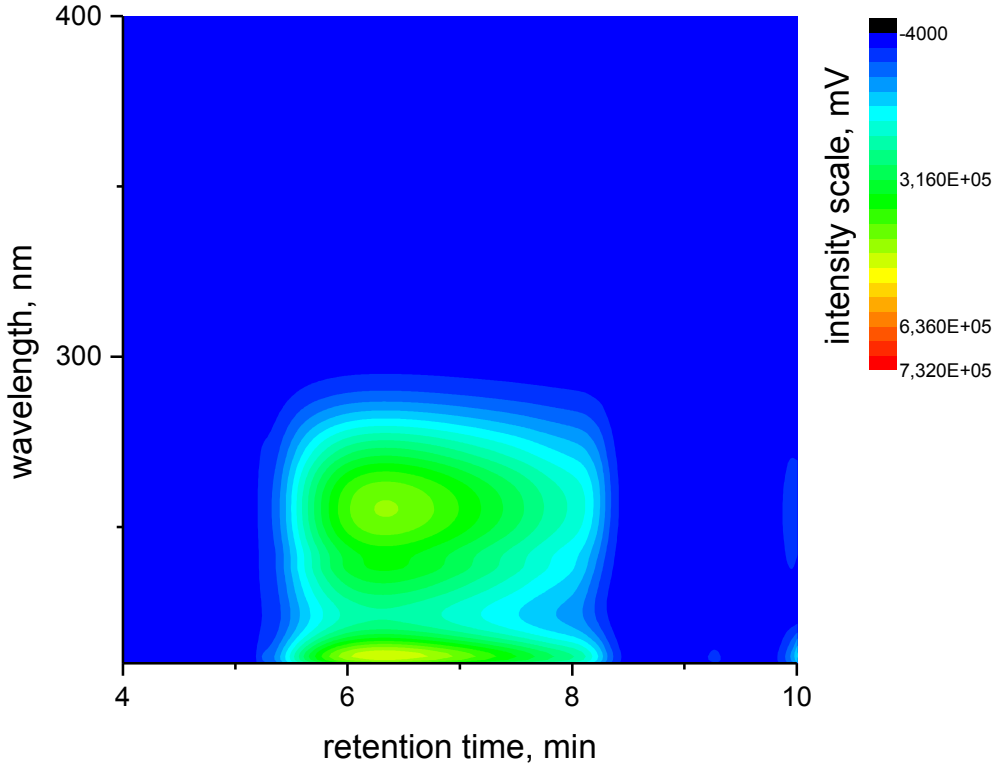
Compound 7



Compound 9



Compound 10



4. HRESIMS spectrum of Compound 3

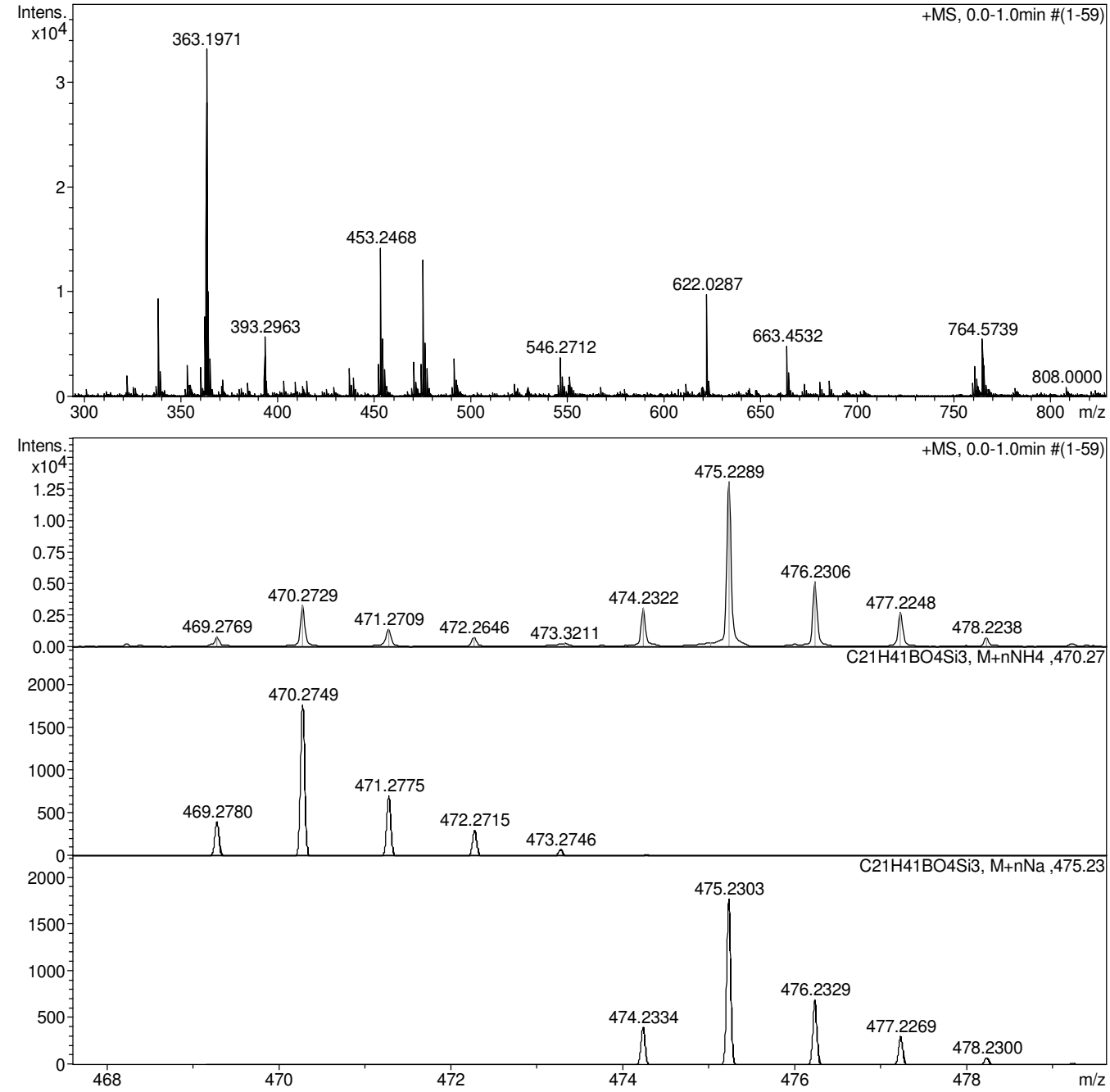
Display Report

Analysis Info

Analysis Name	D:\Data\Chizhov\Muzafarov\Drozdov\fd-591_&clb.d	Acquisition Date	20.01.2017 17:08:12
Method	tune_wide.m	Operator	BDAL@DE
Sample Name	/CHIZ FD-591	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100 %, dil. 2000, calibrant added		

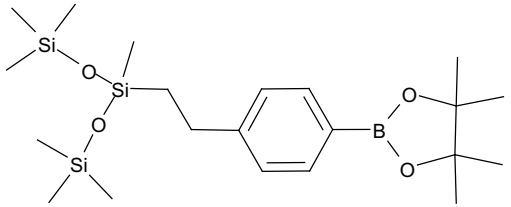
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

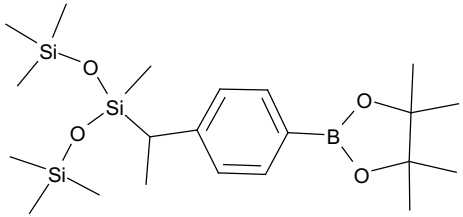


5. NMR spectrum of sources and products

FD591/1/fid | 1H NMR (300MHz) | Solvent: CDCl3

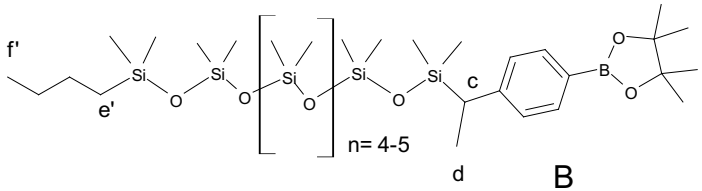


A
~70%

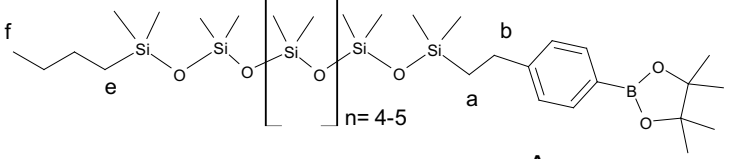


B
~30%

FD496/1/fid | 1H NMR (300MHz) | Solvent: CDCl3



B
~40%



A
~60%

f,f'

d

a

e,e'

b

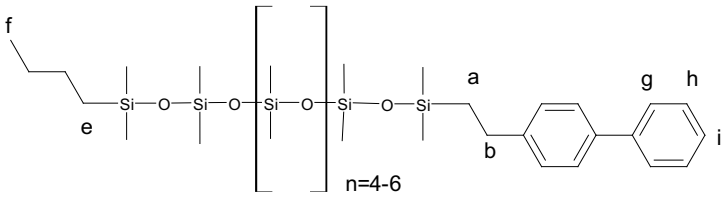
c

7.7 7.3 7.2 7.1 7.0 2.8 2.7 2.6 2.3 2.2 2.1 1.4 1.3 1.2 1.0 0.9 0.8 0.6 0.5
(ppm)

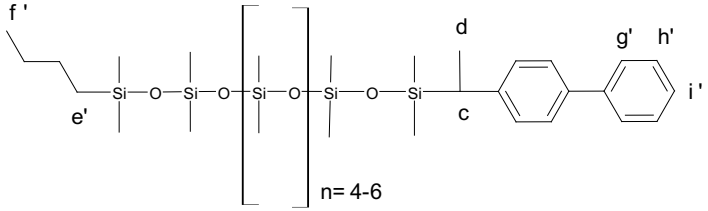
2.84 2.01 3.08 2.12 2.97 1.00 43.16 10.93 5.13 126.85

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
(ppm)

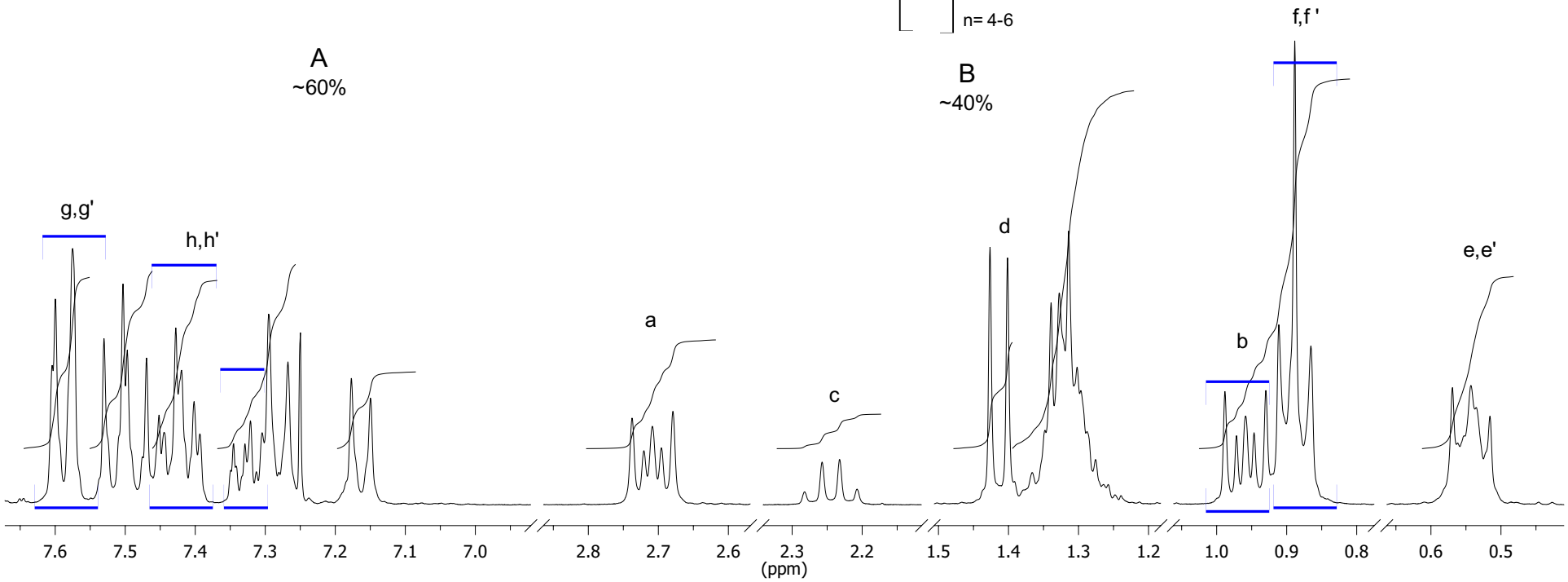
FD642/1/fid | 1H NMR (300MHz) | Solvent: CDCl3

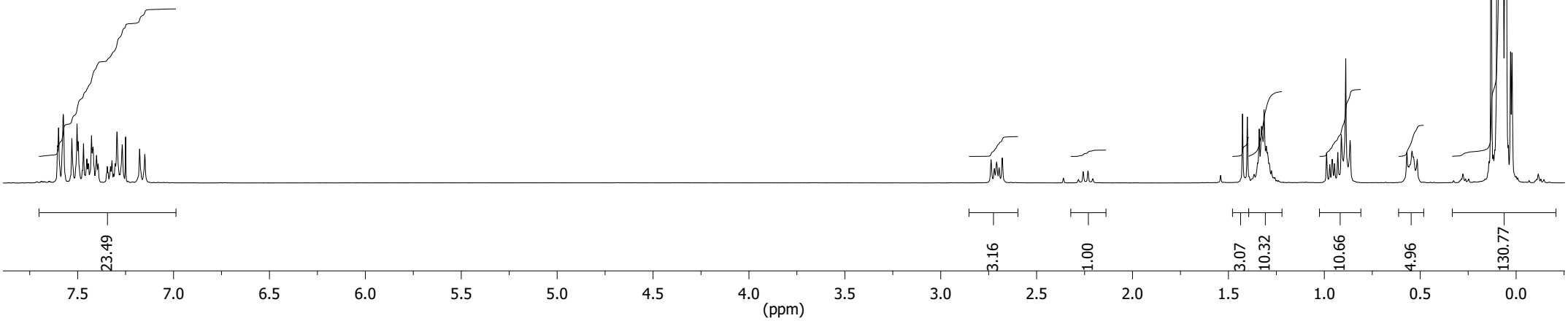


A
~60%

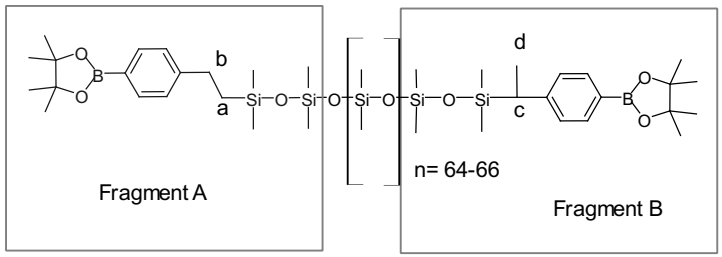


B
~40%

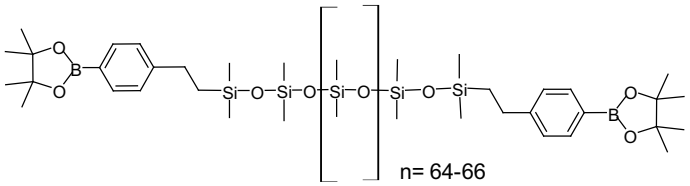




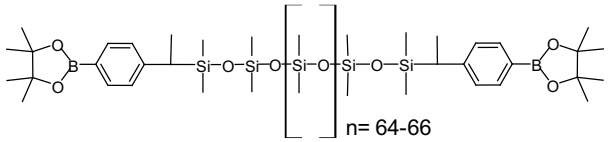
FD604.002/2/fid | 1H NMR (300MHz) | Solvent: CDCl3



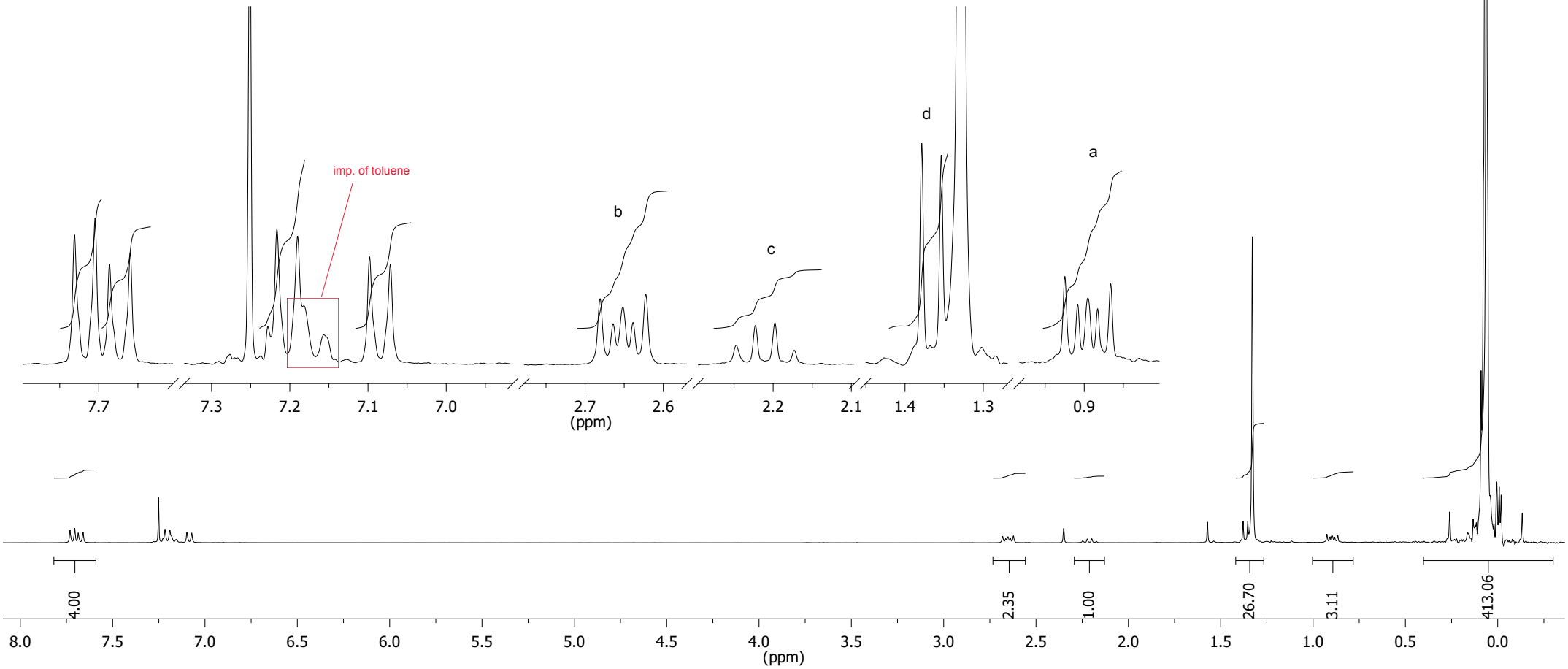
major structure



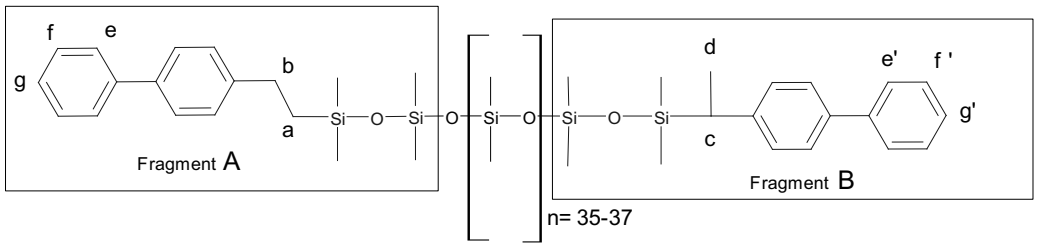
minor structure



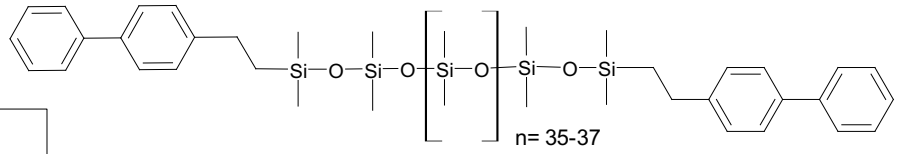
minor structure



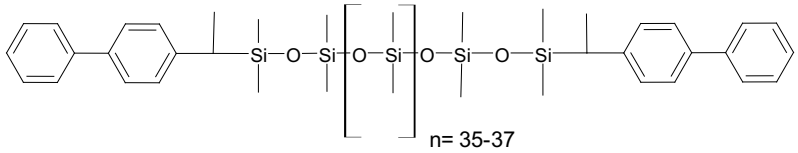
FD640/1/fid | 1H NMR (300MHz) | Solvent: CDCl3



major structure



minor structure



minor structure