

Synthesis, Structure and Electrochemical Properties of Acetamide- and Caprolactam-Containing Silicon Catecholates

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Supramolecular organization in crystals of 1–8

The similar packing motif is observed for compounds **1** and **2** (Figure 1s and 2S) where noncoordinated 4-methyl catecholate ligand form N-H...O and O-H...O bonded chains. The crystal structure of **7** does not contain non-coordinated ligand, however, anions and N[cyc]₂⁺ cations are also assembled into N-H...O bonded chains (Figure 3S). Unlike to **1**, **2** and **7** in crystal of **4** cations and anions formed H-bonded dimers and supramolecular structure is maintained owing to weak Br... π and H...Br interactions (Figure 4S). The presence of nitro group in **6** caused the change of dimer structure as compared to **4**. In this case, the centrosymmetrical tetramers assembled by four N-H...O bonds with oxygen atoms of nitrogroup and 3-nitro catecholate ligands are formed (Figure 5S).

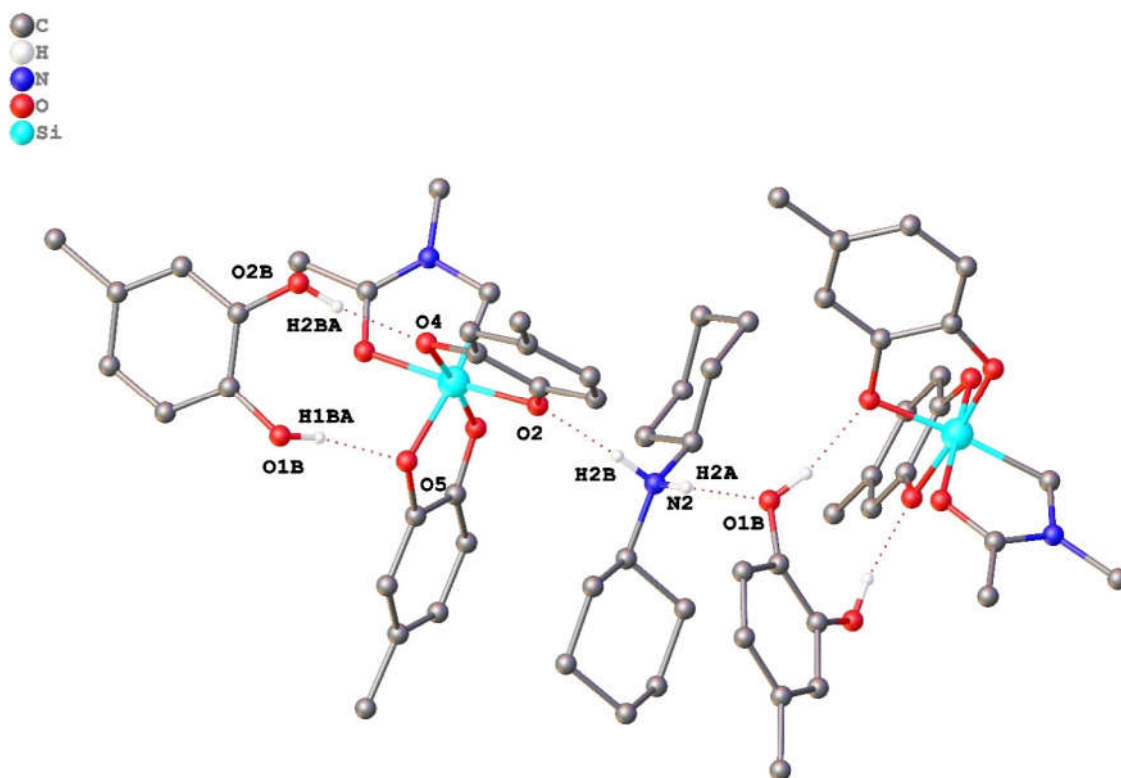


Figure S1. H-bonded chains in crystal structure of 1.

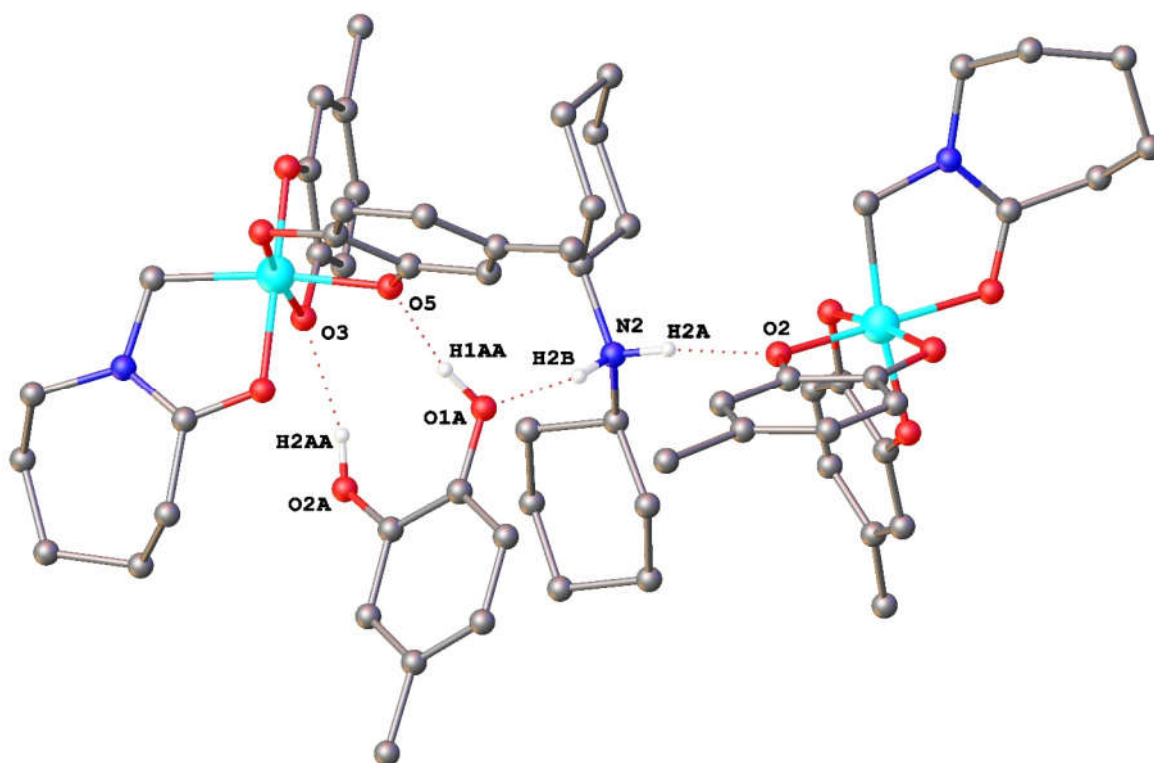


Figure S2. H-bonded chain in crystal structure of 2.

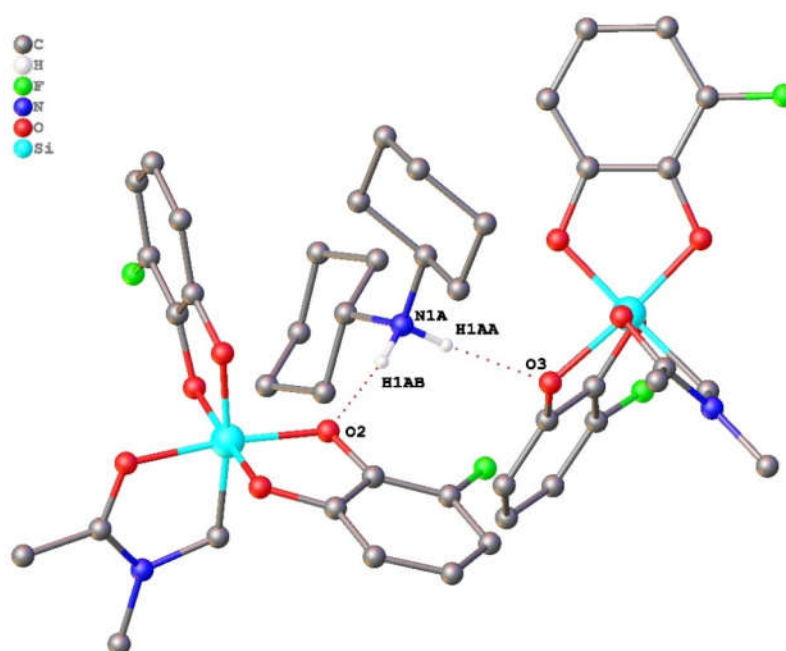


Figure S3. Cation-anion H-bonded chain in crystal structure of 7.

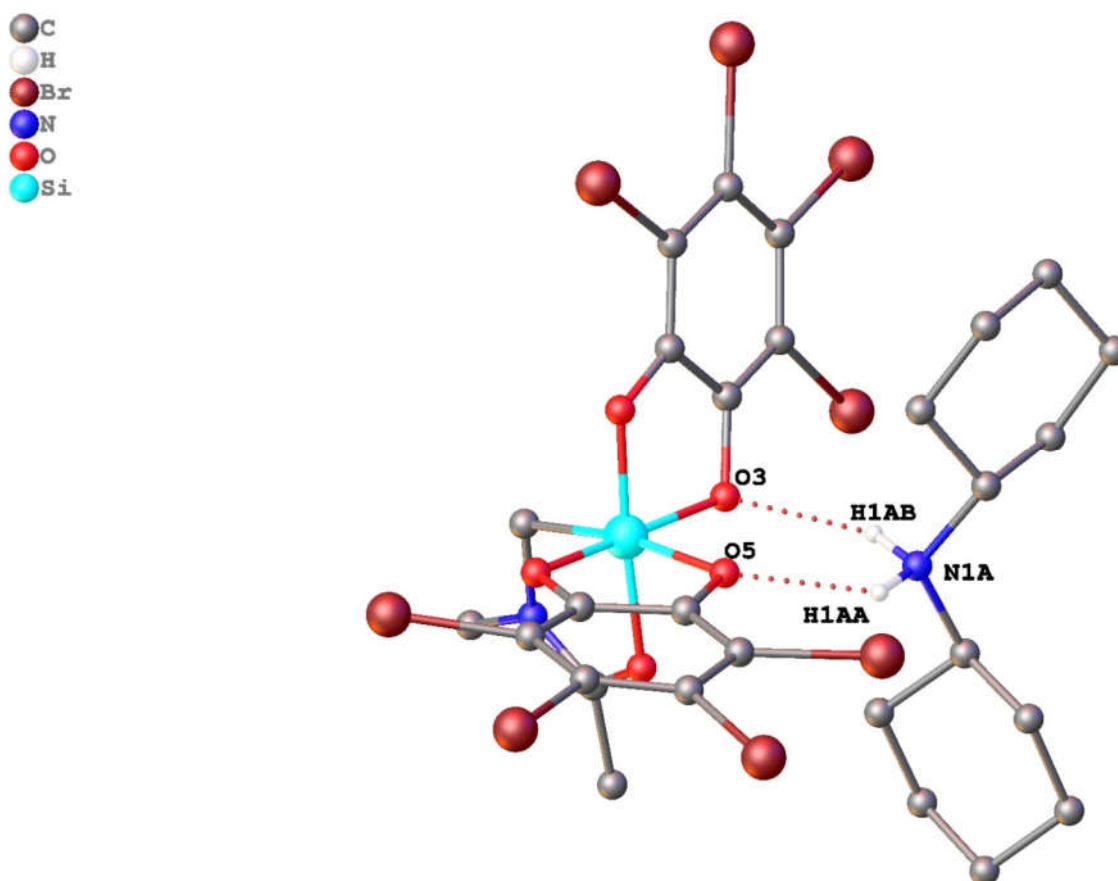


Figure S4. Cation-anion pair in crystal of 4.

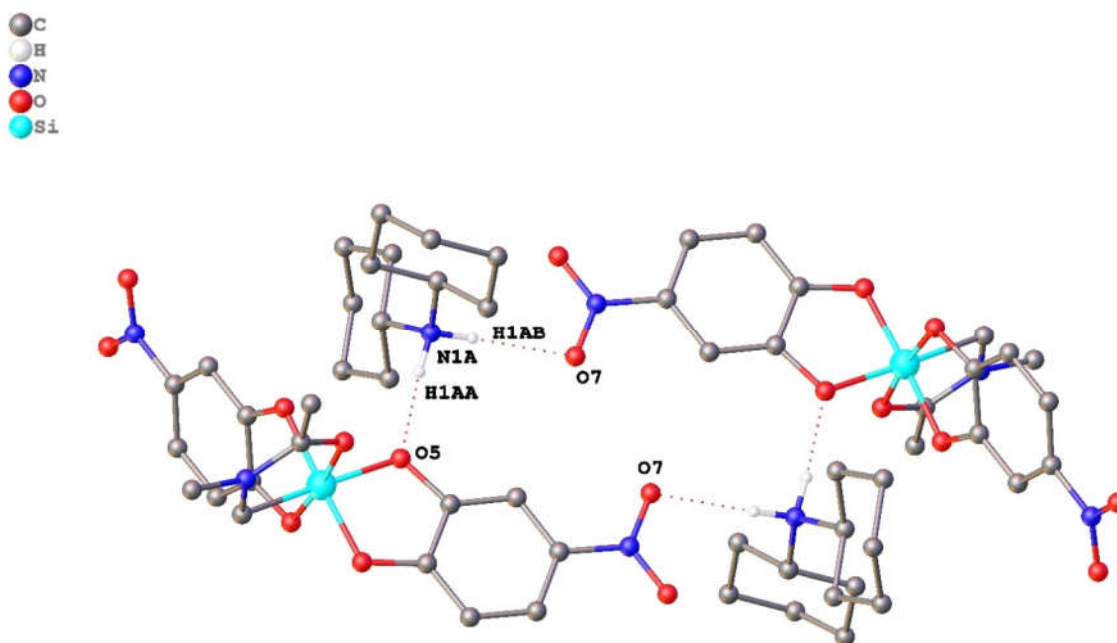


Figure S5. Cation-anion tetramer in crystal of 6.

In **3a** and **3b** Br...Br and stacking interactions between 2,3,4,5-tetrabromocatechol ligands play crucial role in their crystal packing. Indeed, Br...Br and stacking interactions between anions and potassium cations in **6** and **7** construct 2D sieve structure (Figures 6S and 7S). The N[cyc]₂⁺ cations and solvent molecules are located in inner cells of this sieve network. The structures **3a** and **3b** have almost the same composition, the only difference is the nature of solvate molecules. The first structure contains two solvated acetonitrile molecules while in **3b** one of acetonitrile is replaced by water. This replacement noticeably changes the nature of H-bonds. In **3a** cations and anions form dimers via N-H...O and N-H...Br bonds (Figure 8S). At the same time, in **3b** solvated water molecule serves as spacer between cation and anion forming two O-H...O bonds with oxygen atoms of 2,3,4,5-tetrabromocatechol ligand (Figure 9S). In turn, water molecules cations and anions assembled into infinite chains.

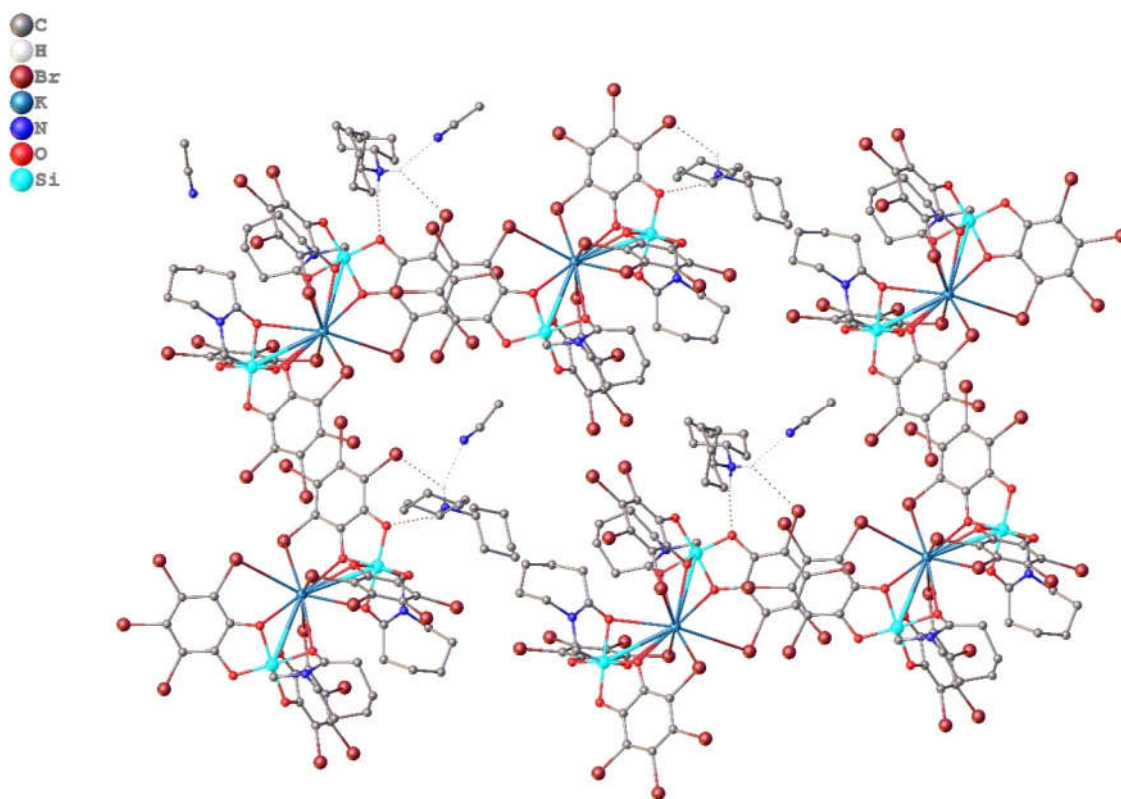


Figure S6. The sieve structure in crystal of 3a.

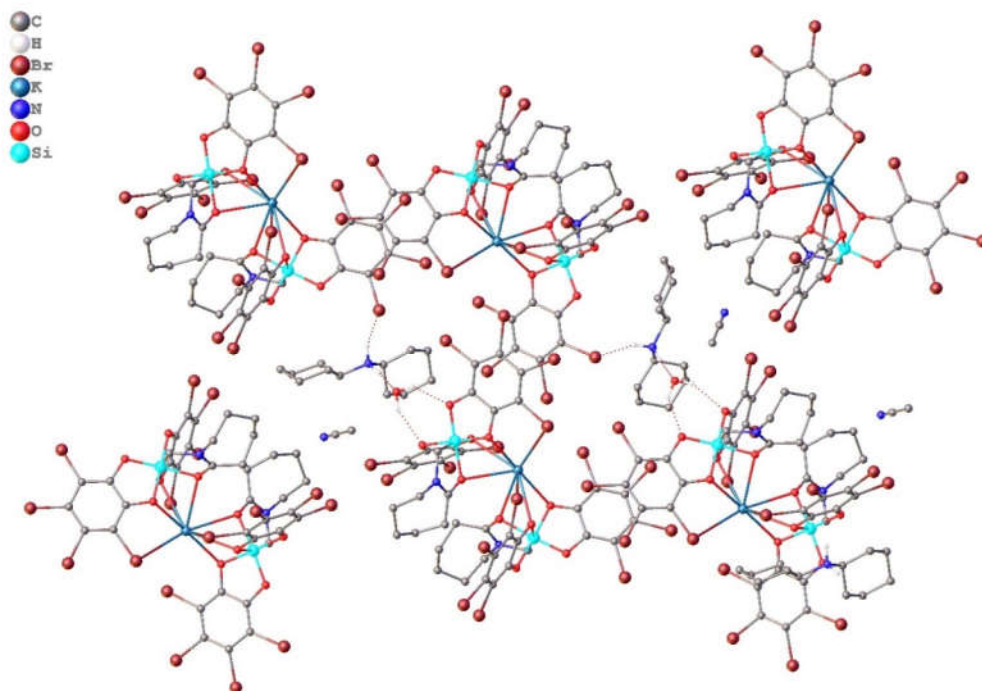


Figure S7. The sieve structure in crystal of 3b.

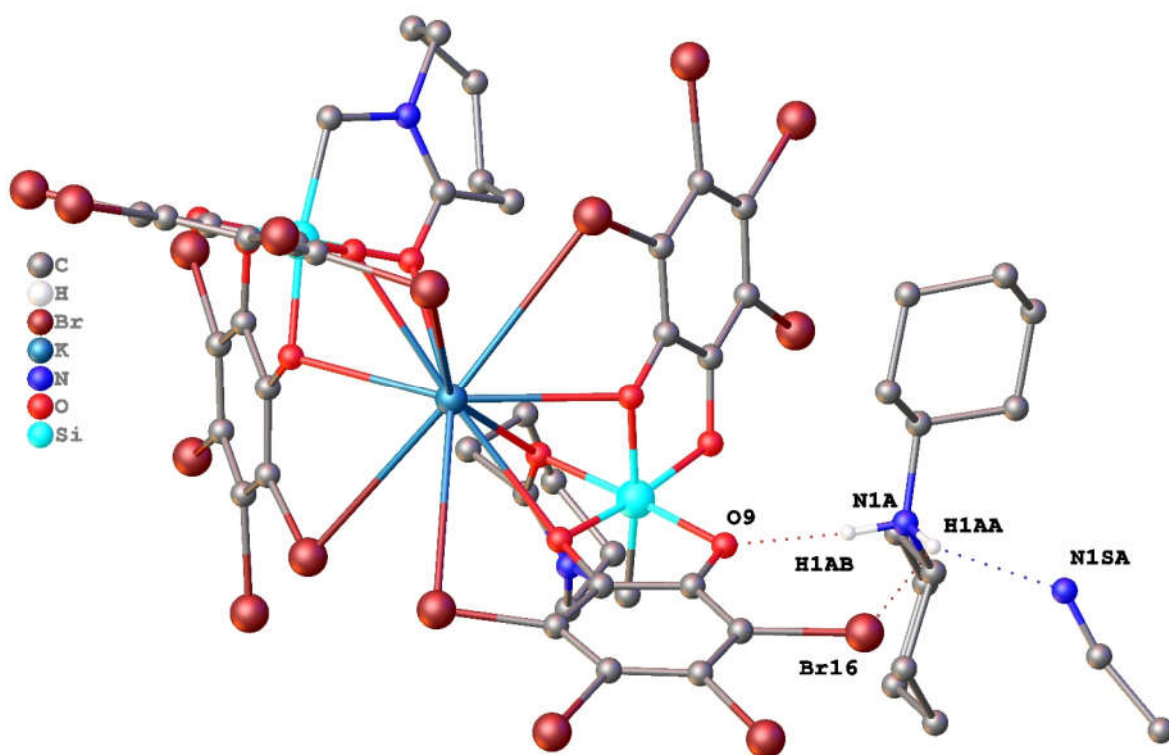


Figure S8. H-bonded chain in crystal of 3a.

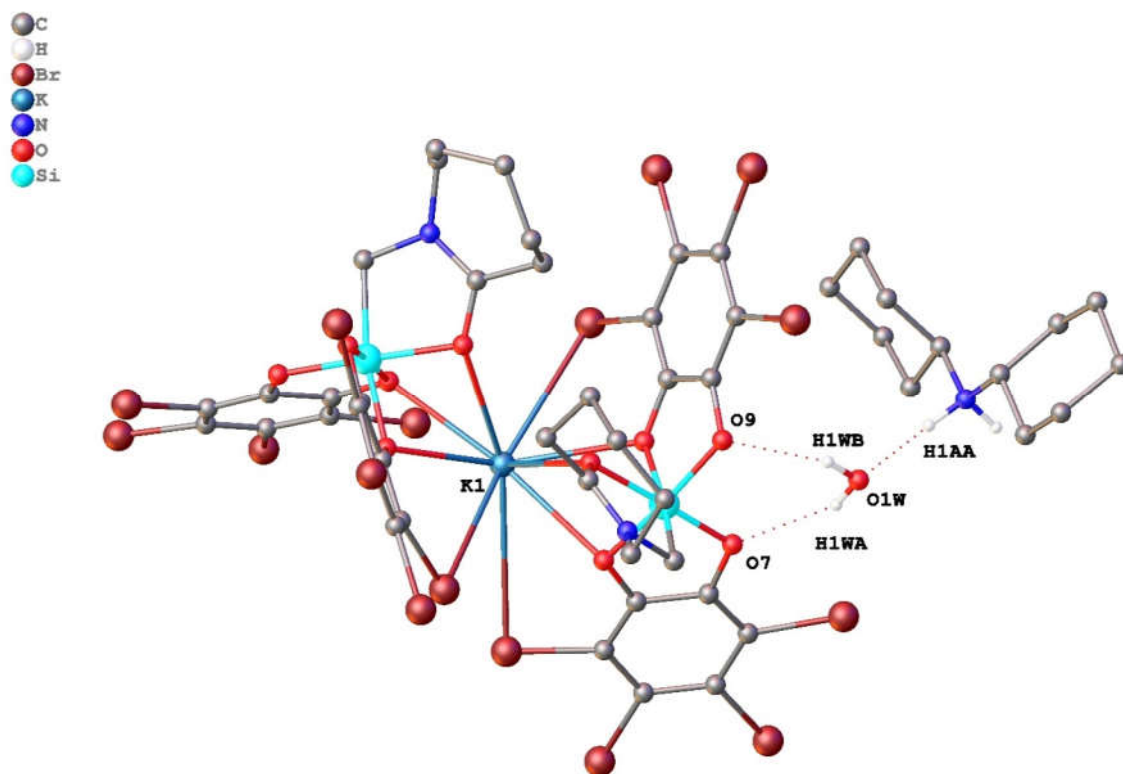


Figure S9. H-bonded chain in crystal of 3b.

Compound **5** is crystallized with two water molecules. Cations, anions and water molecules in crystal packing of **5** form chains via O-H...O and N-H...O bonds. In turn, these dimers are assembled into 3D network via N-H...O bond between one of water molecule and cyanogroup of substituted catecholate ligand.

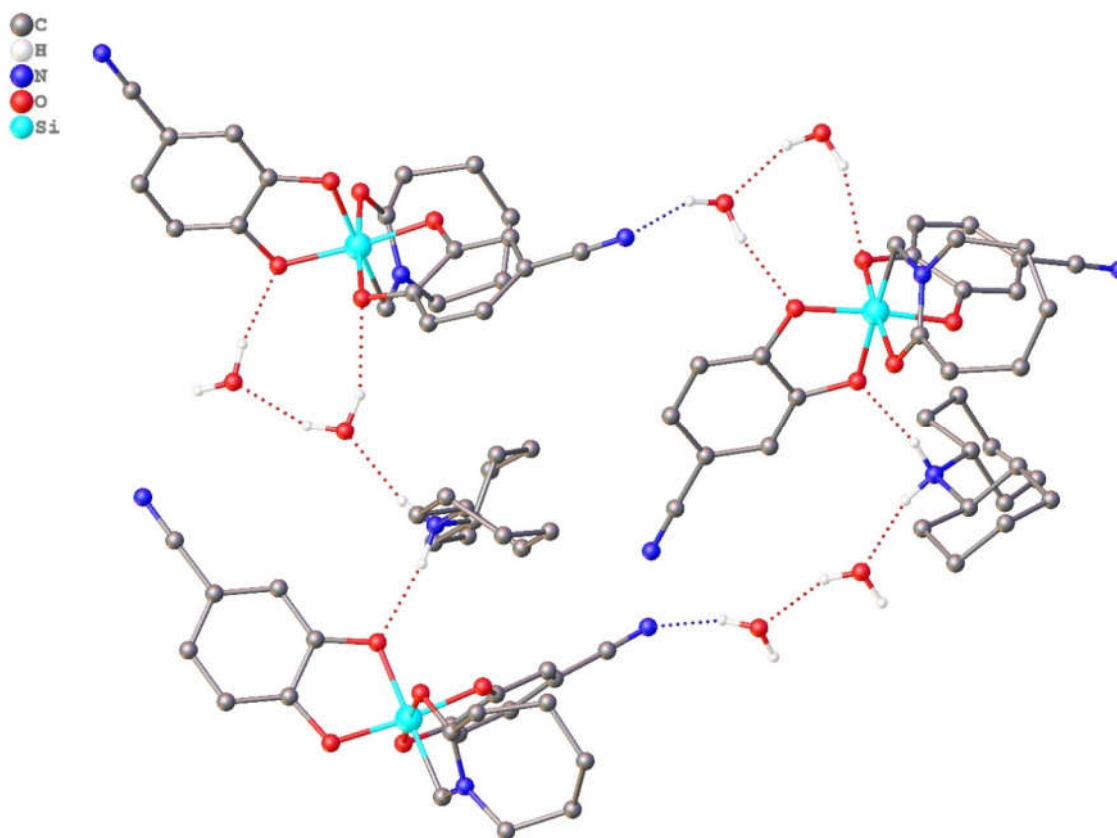


Figure S10. H-bonded cycle formed by cations and anion with inclusion of solvated water molecules in crystal of **5**.

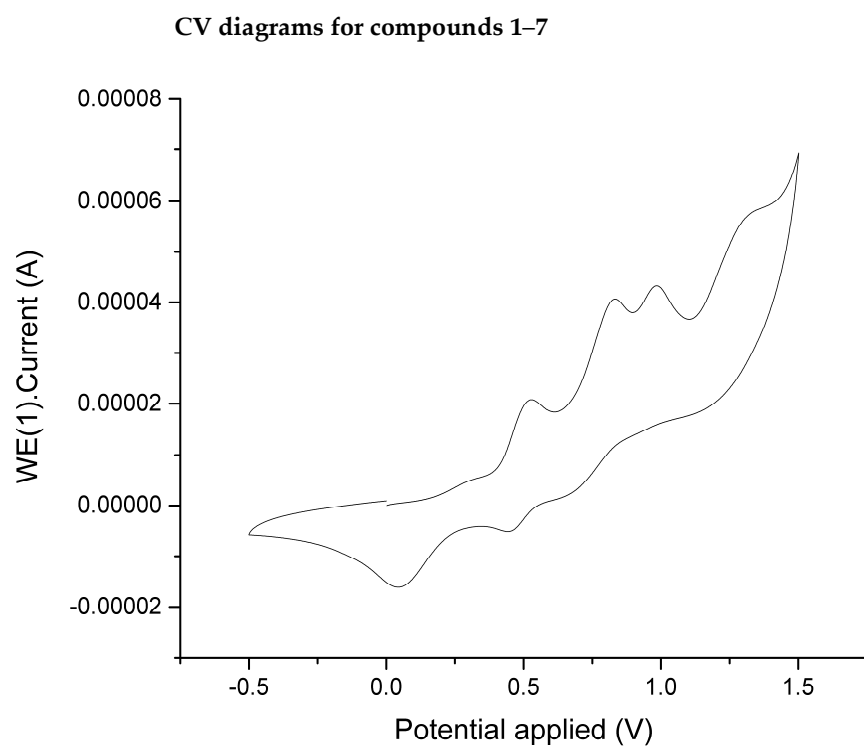


Figure S11. CV diagram of 2.

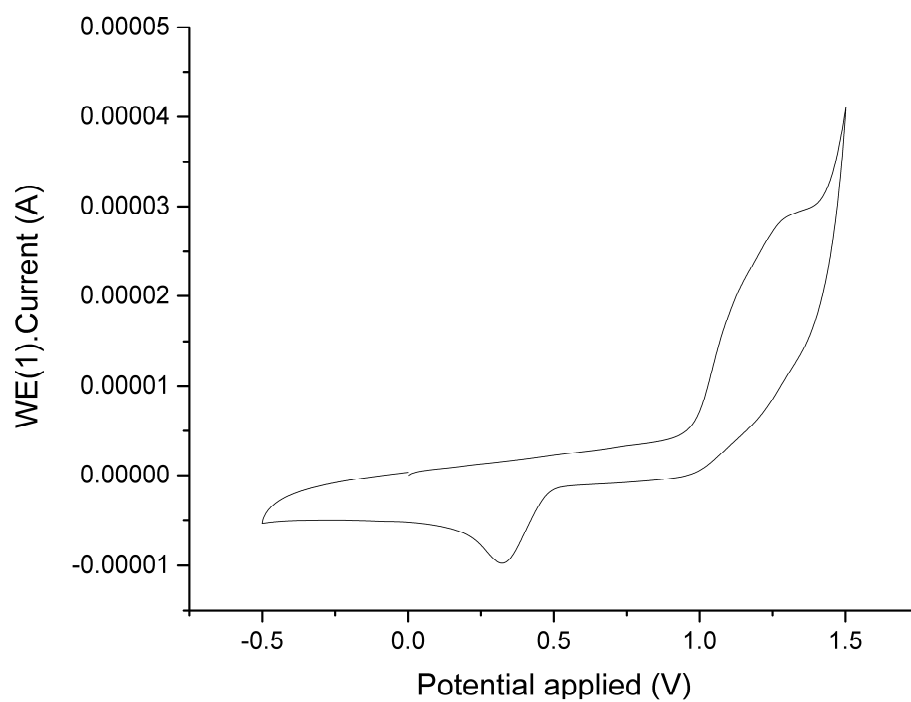


Figure S12. CV plot of 3a.

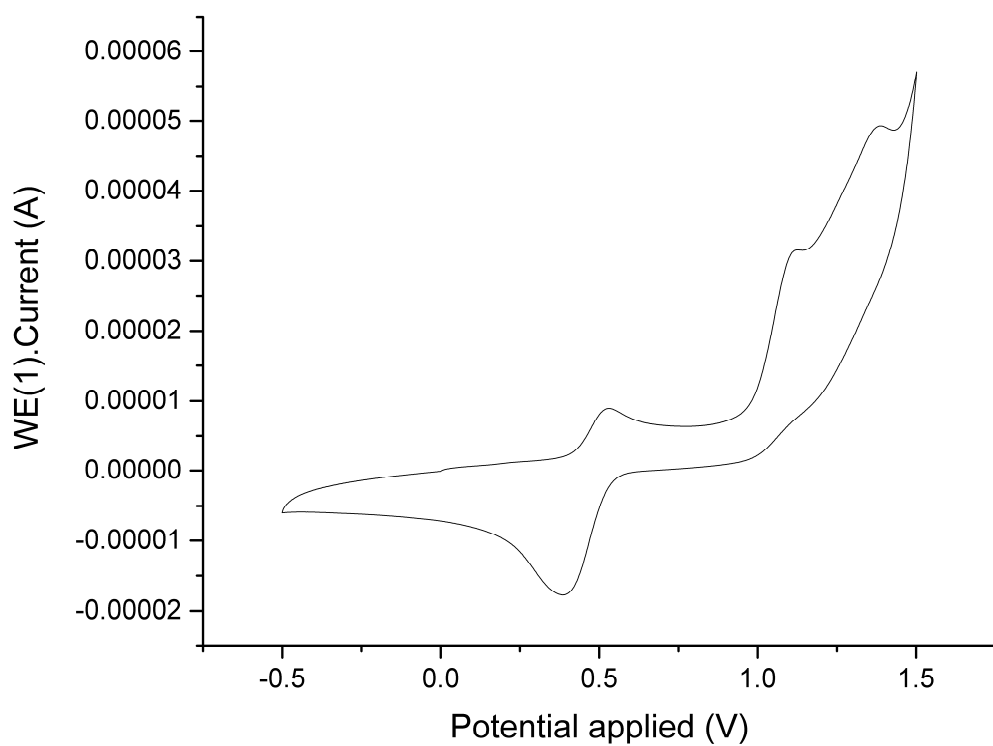


Figure S13. CV plot of 4.

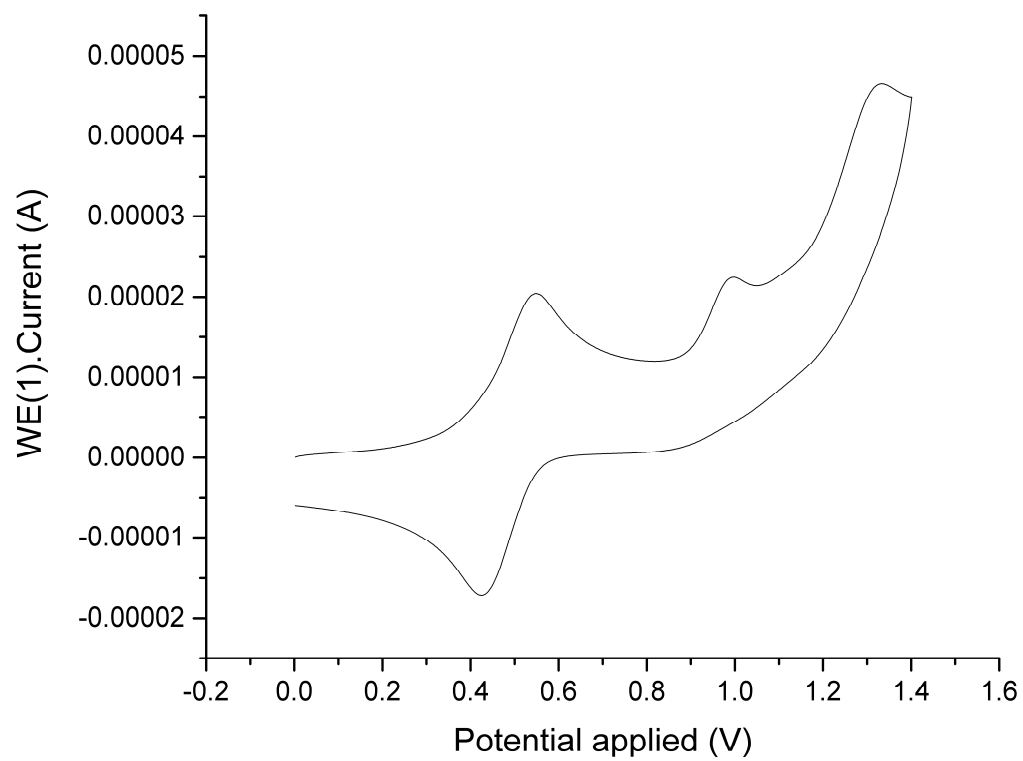


Figure S14. CV plot of 5.

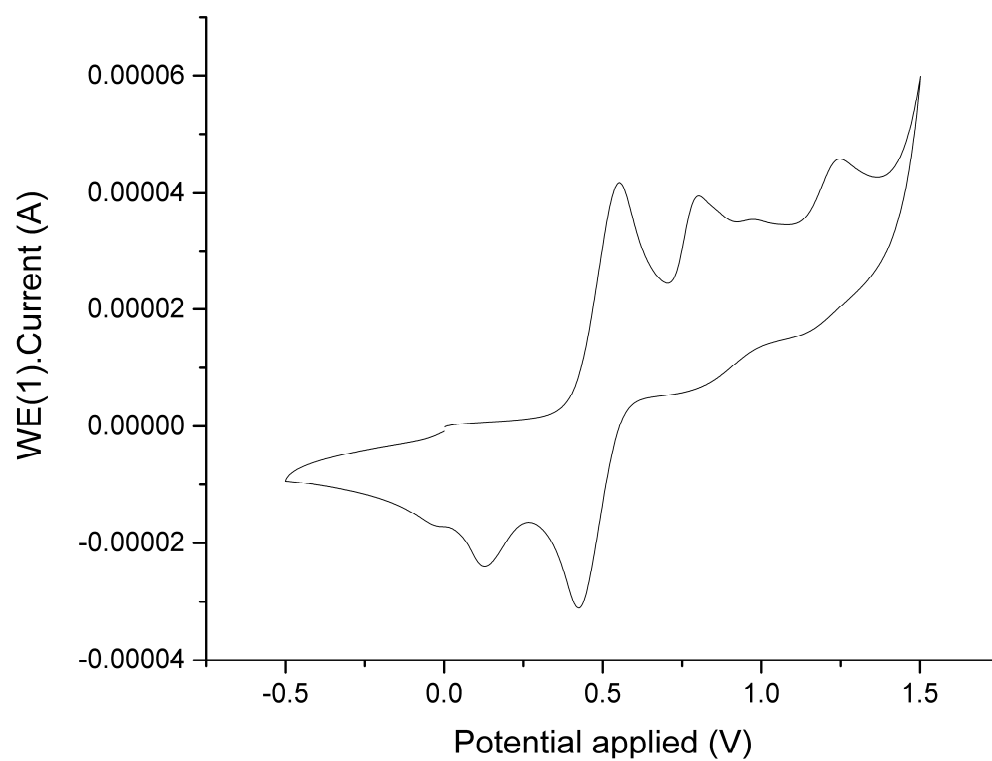
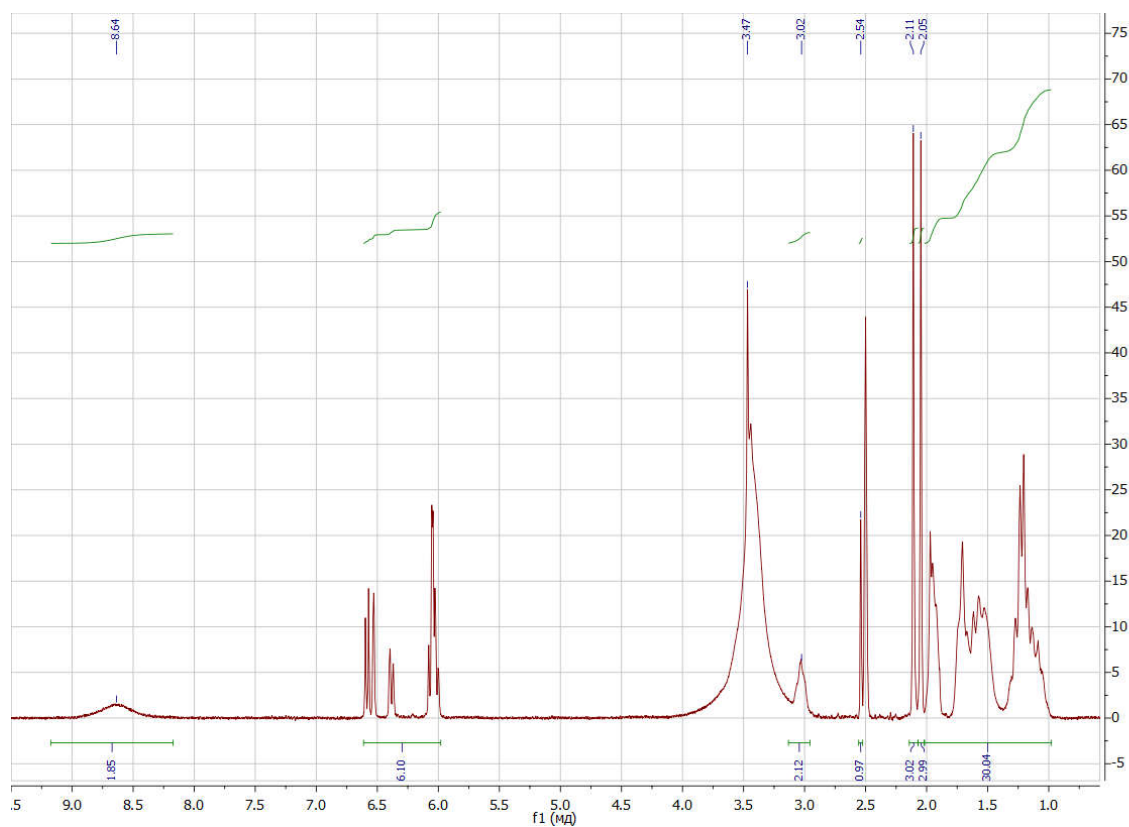
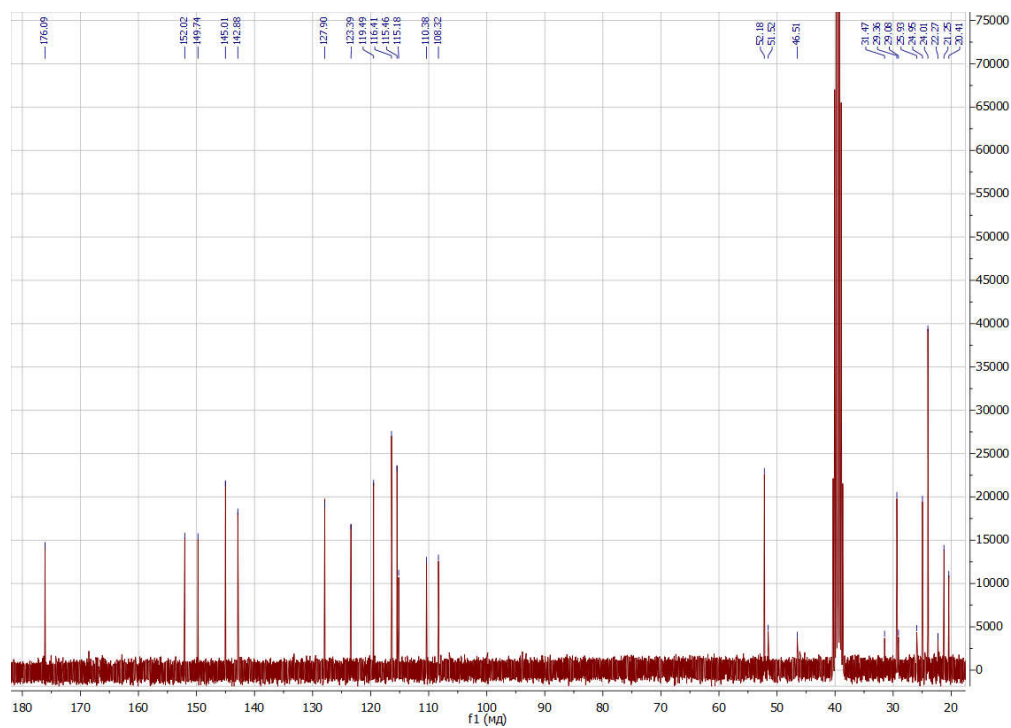
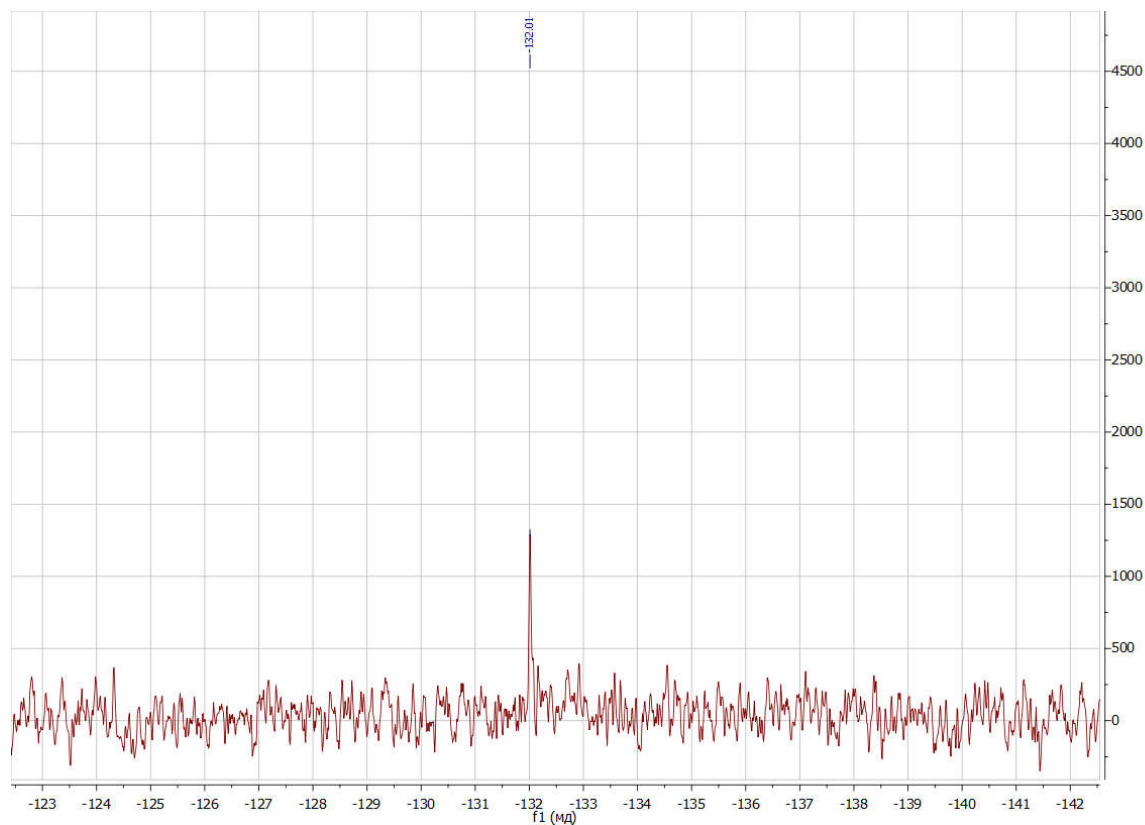
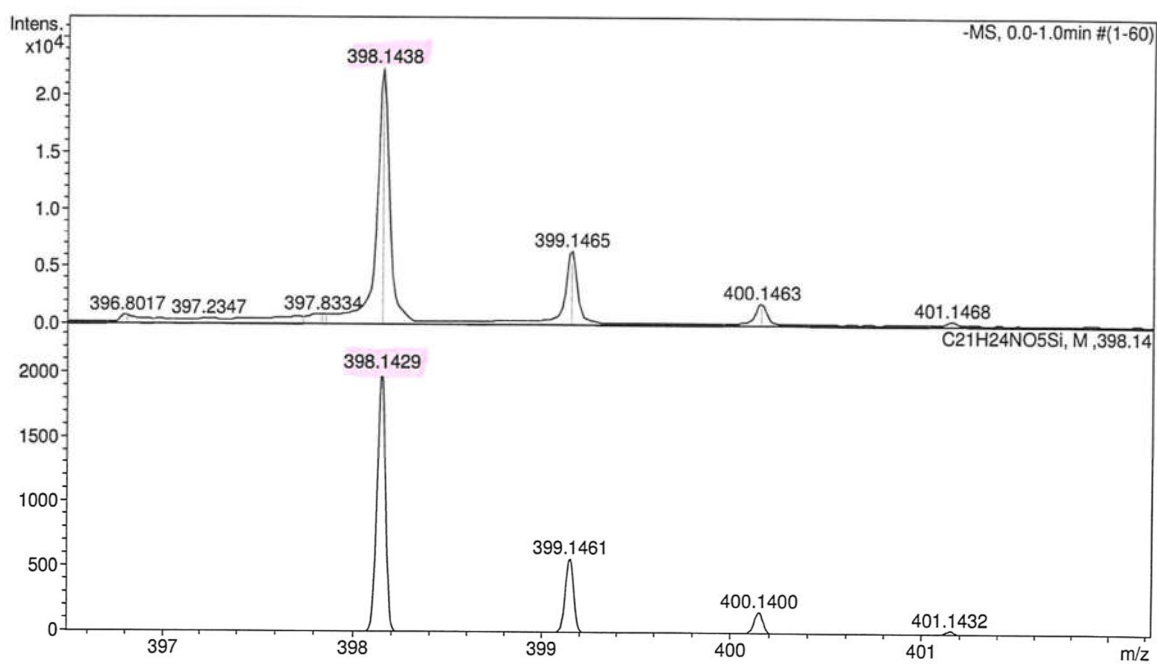


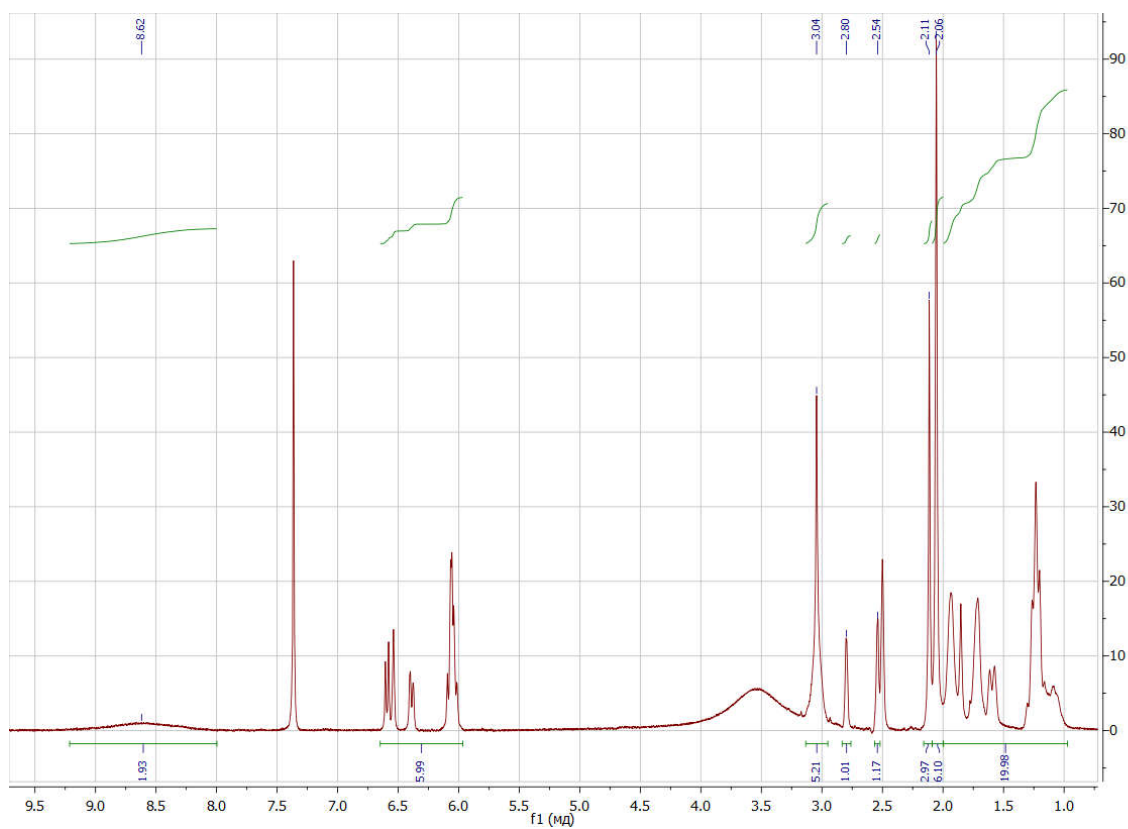
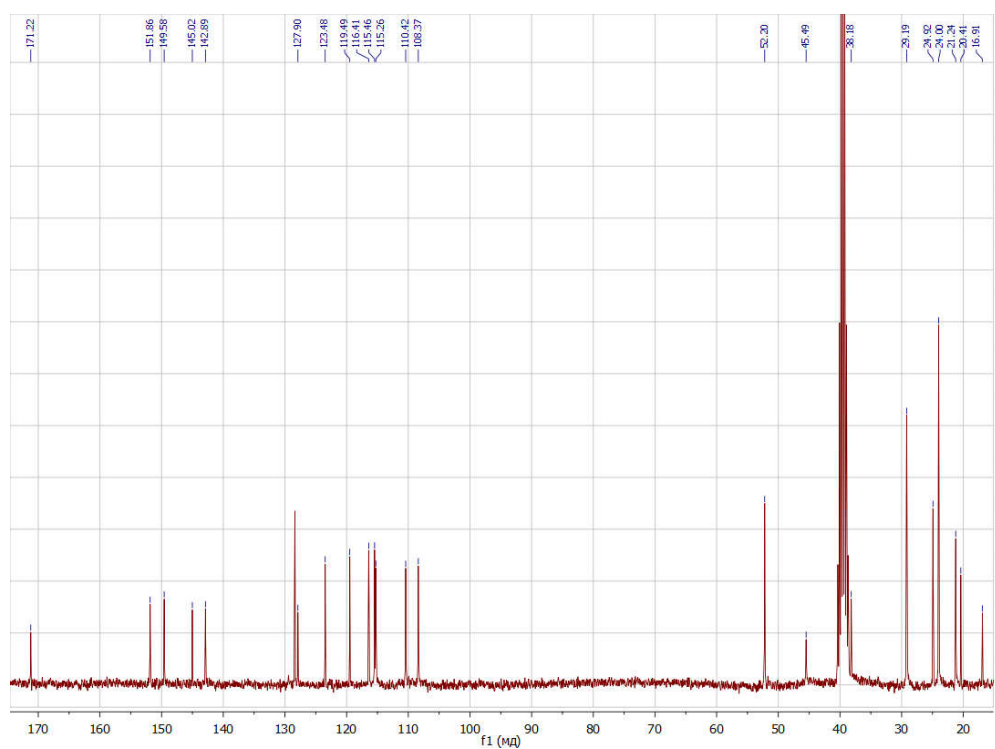
Figure S15. CV plot of 7.

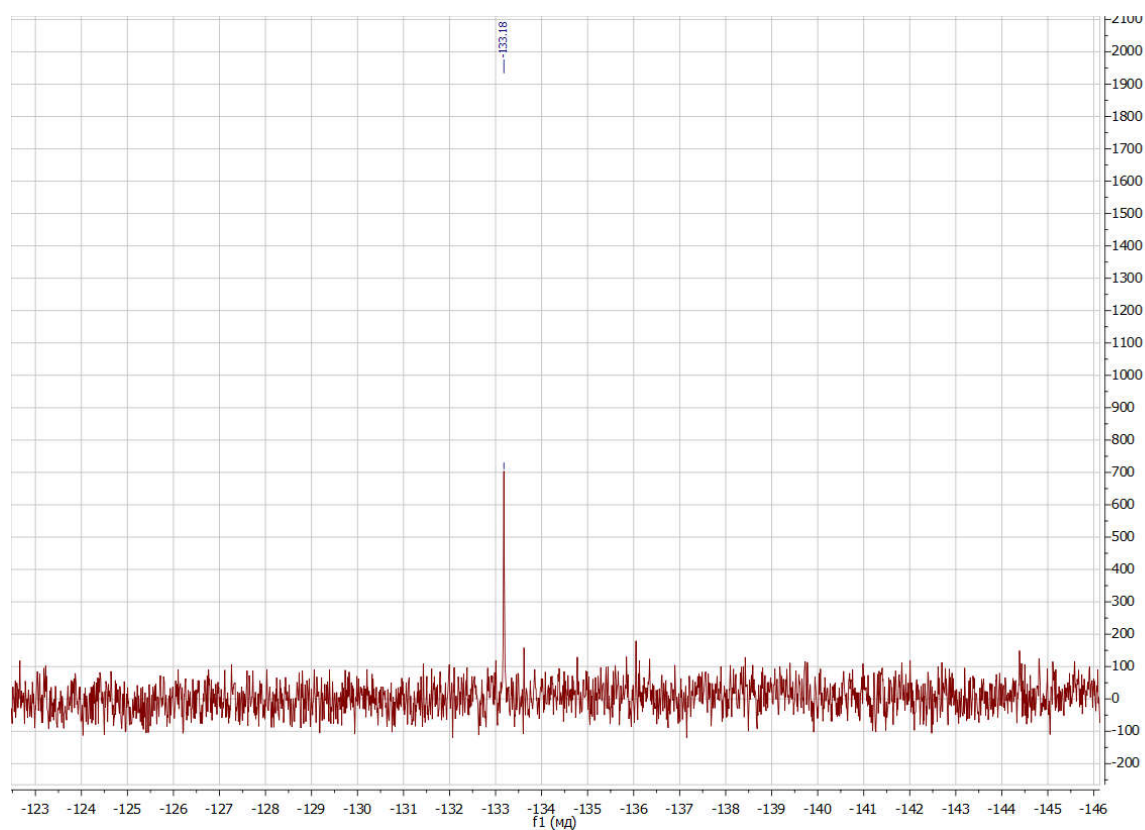
^1H , ^{13}C , ^{29}Si NMR and HRMS spectra ^1H NMR spectrum of compound 1. ^{13}C NMR spectrum of compound 1.

^{29}Si NMR spectrum of compound 1.

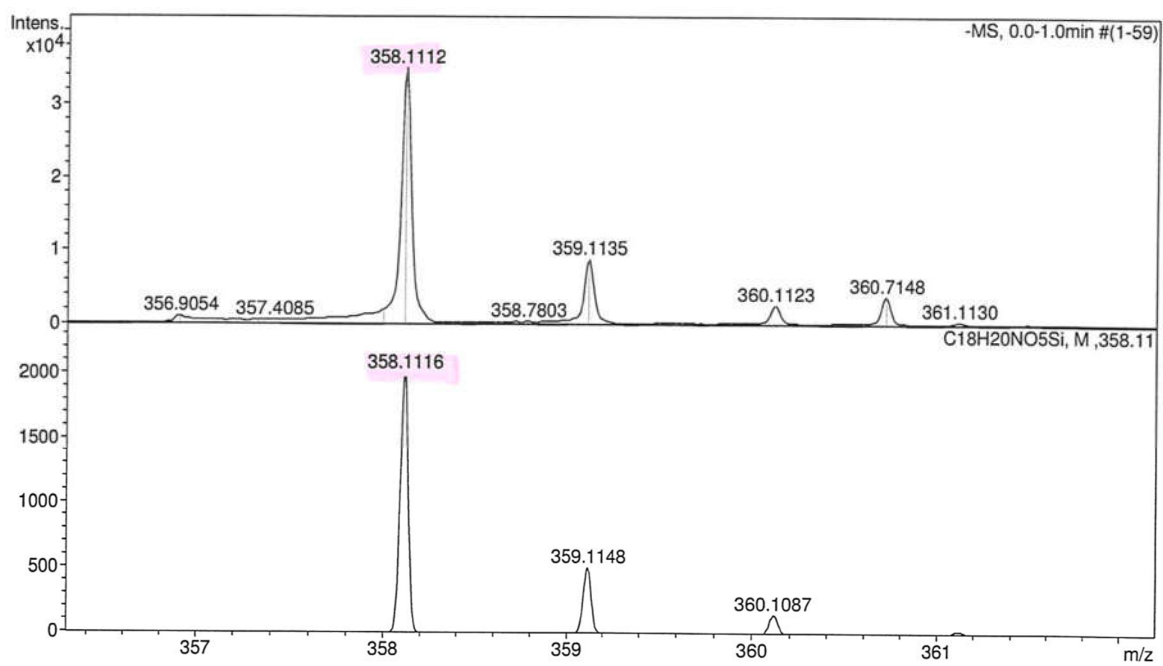
HRMS spectrum of compound 1.

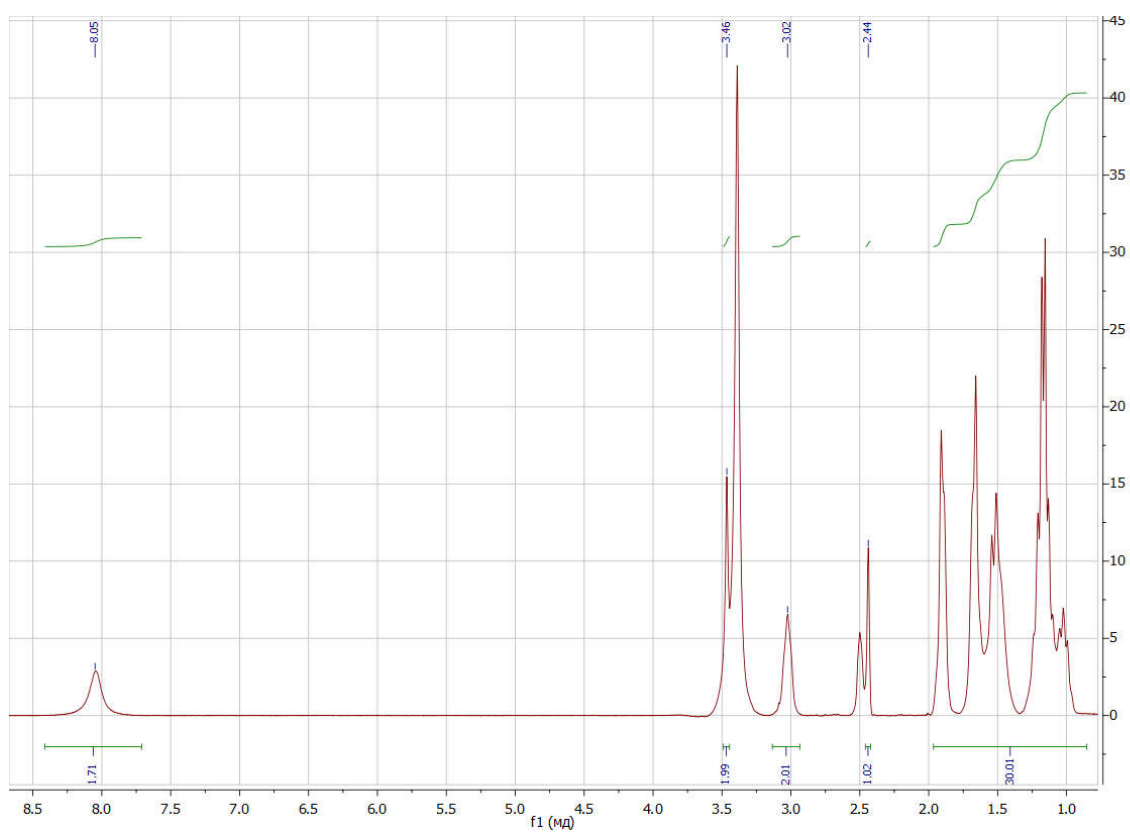
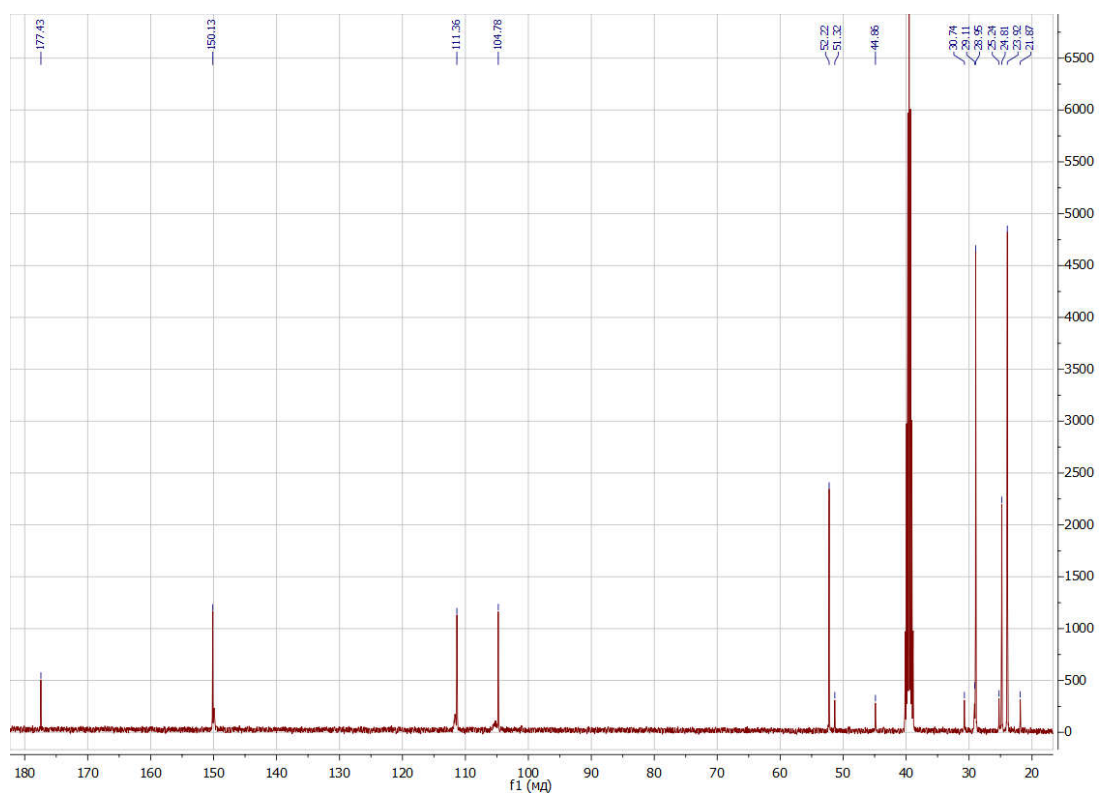


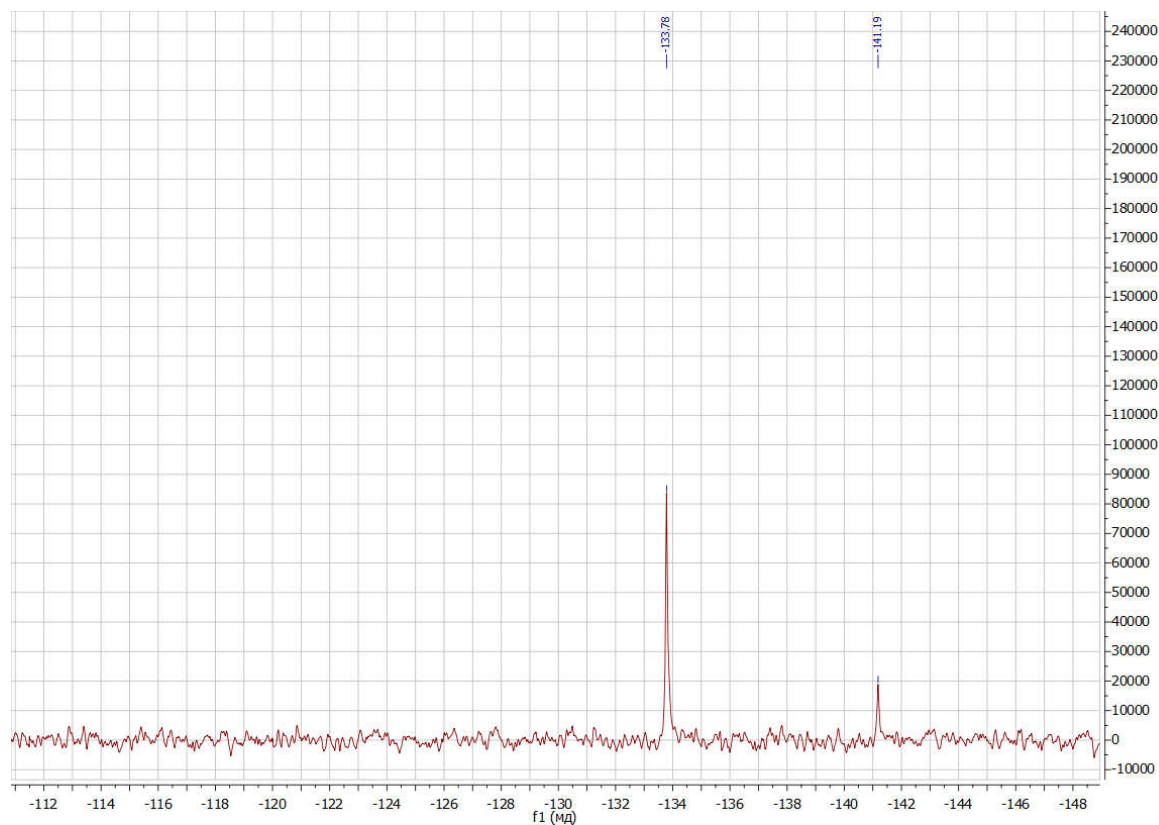
¹H NMR spectrum of compound 2.¹³C NMR spectrum of compound 2.

^{29}Si NMR spectrum of compound 2.

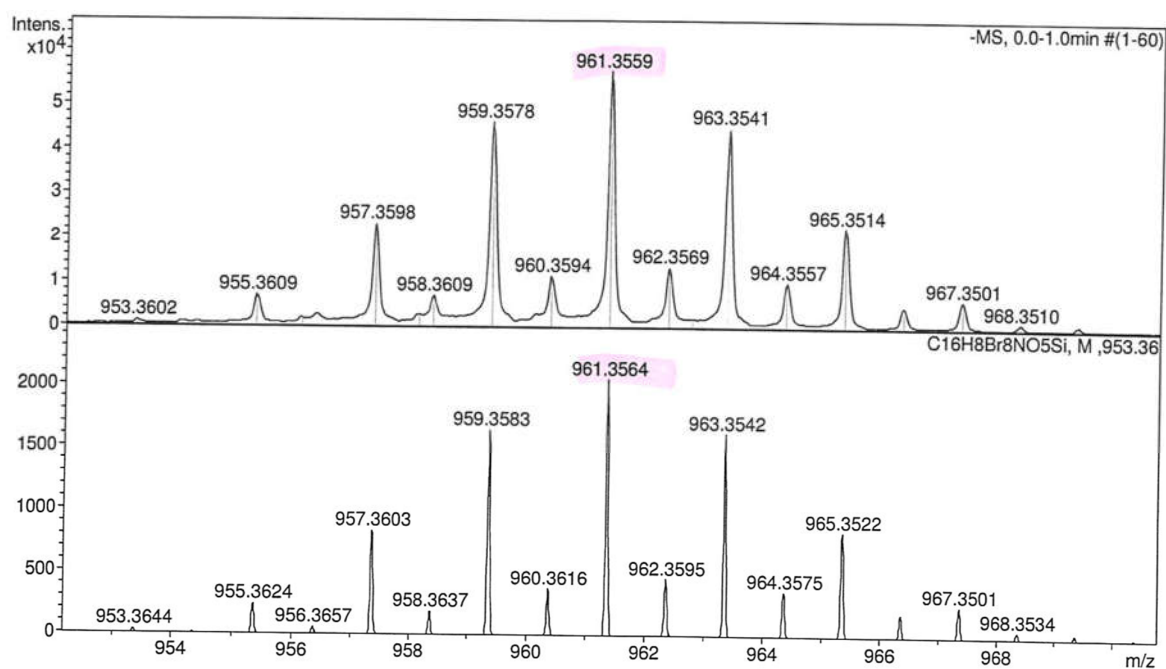
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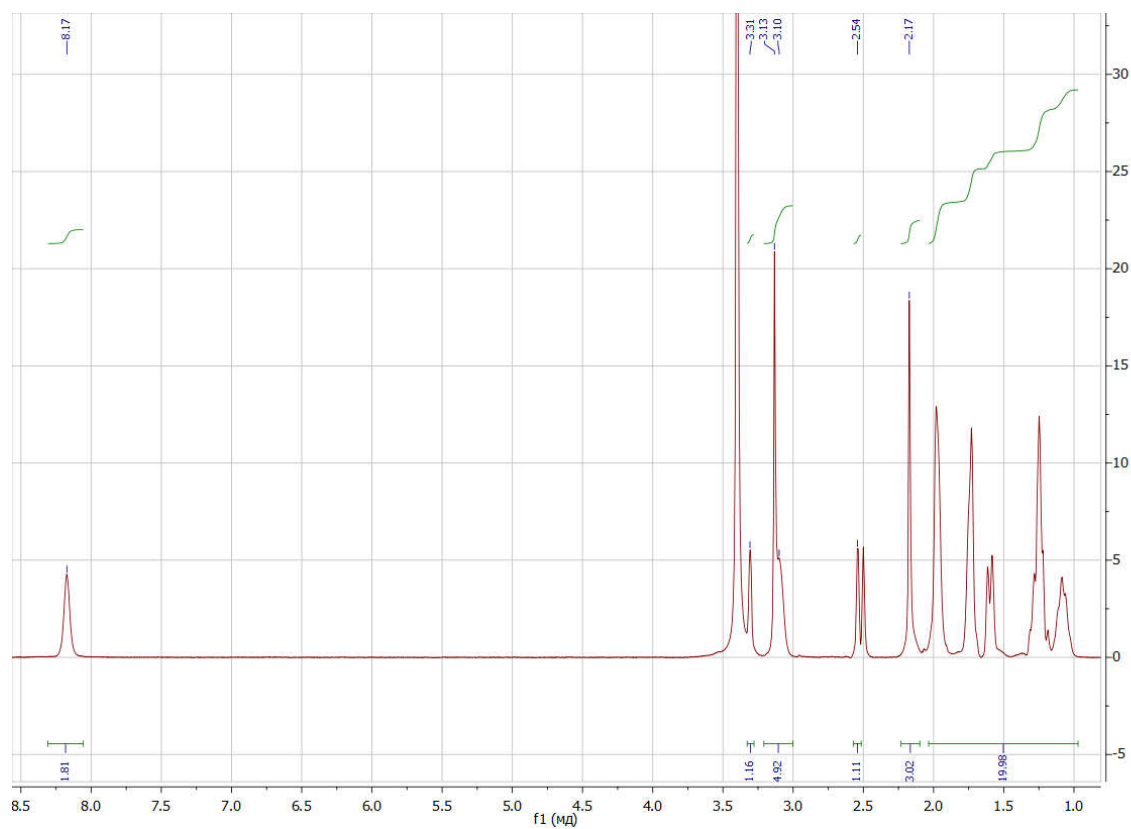
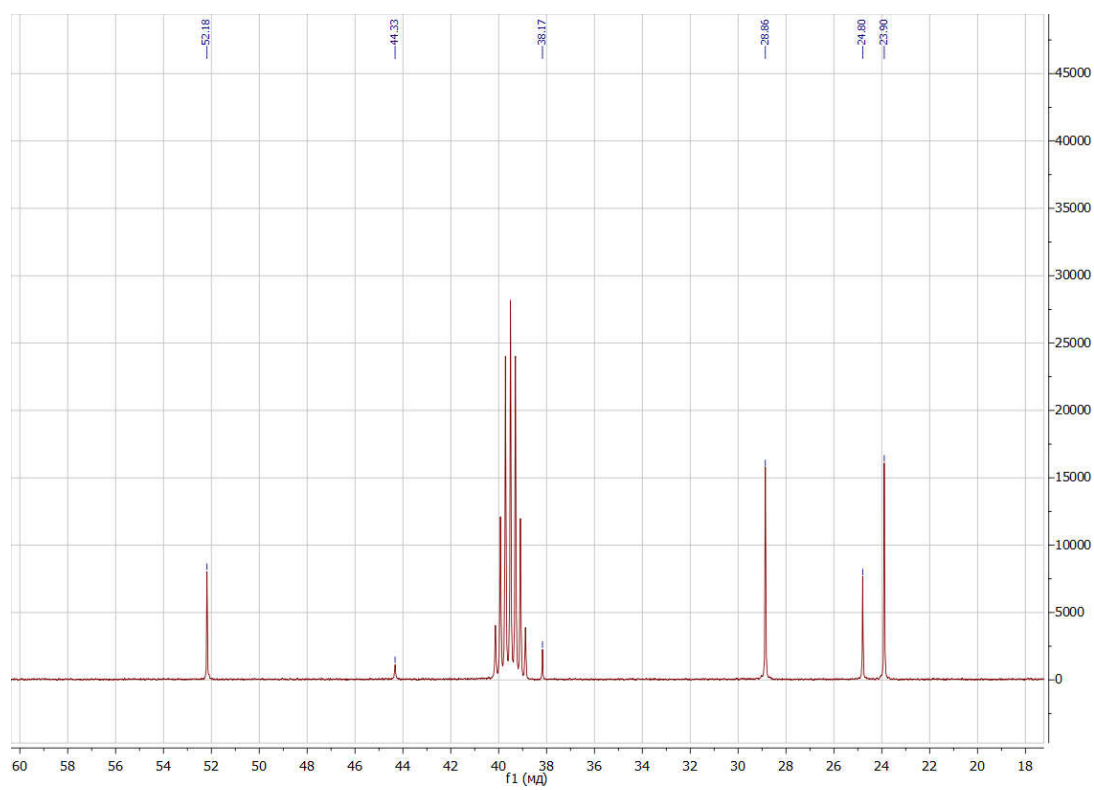


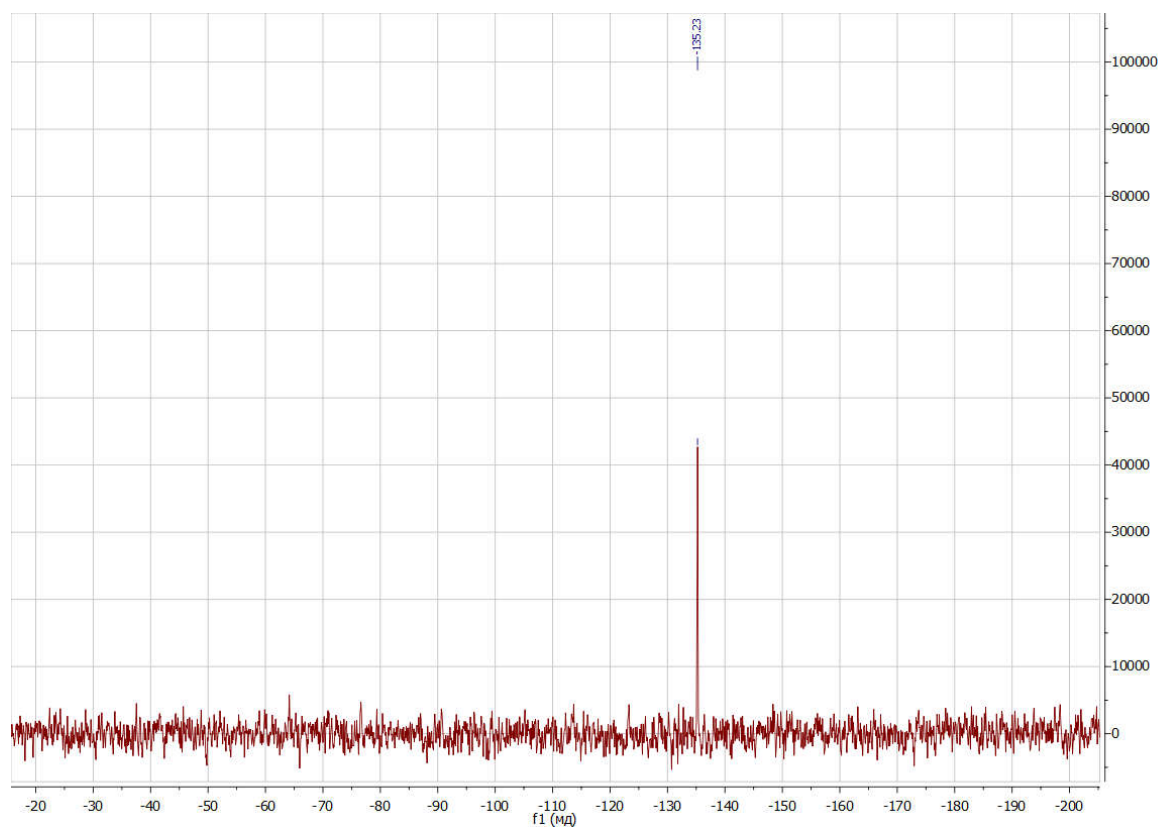
¹H NMR spectrum of compound 3.¹³C NMR spectrum of compound 3.

^{29}Si NMR spectrum of compound 3.

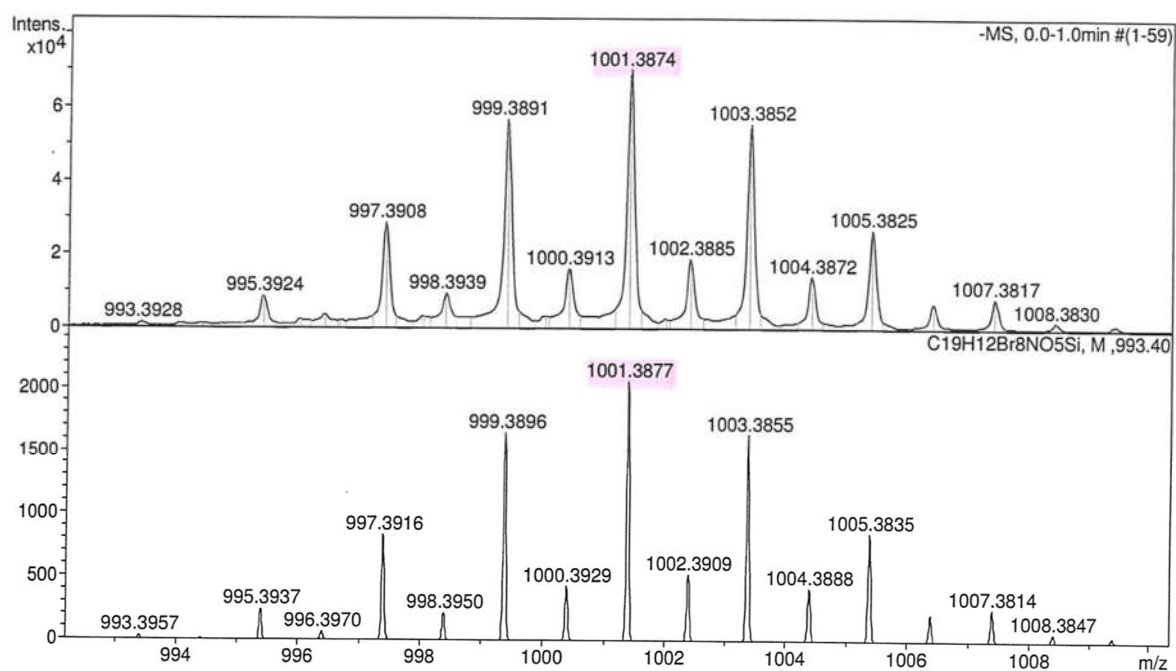
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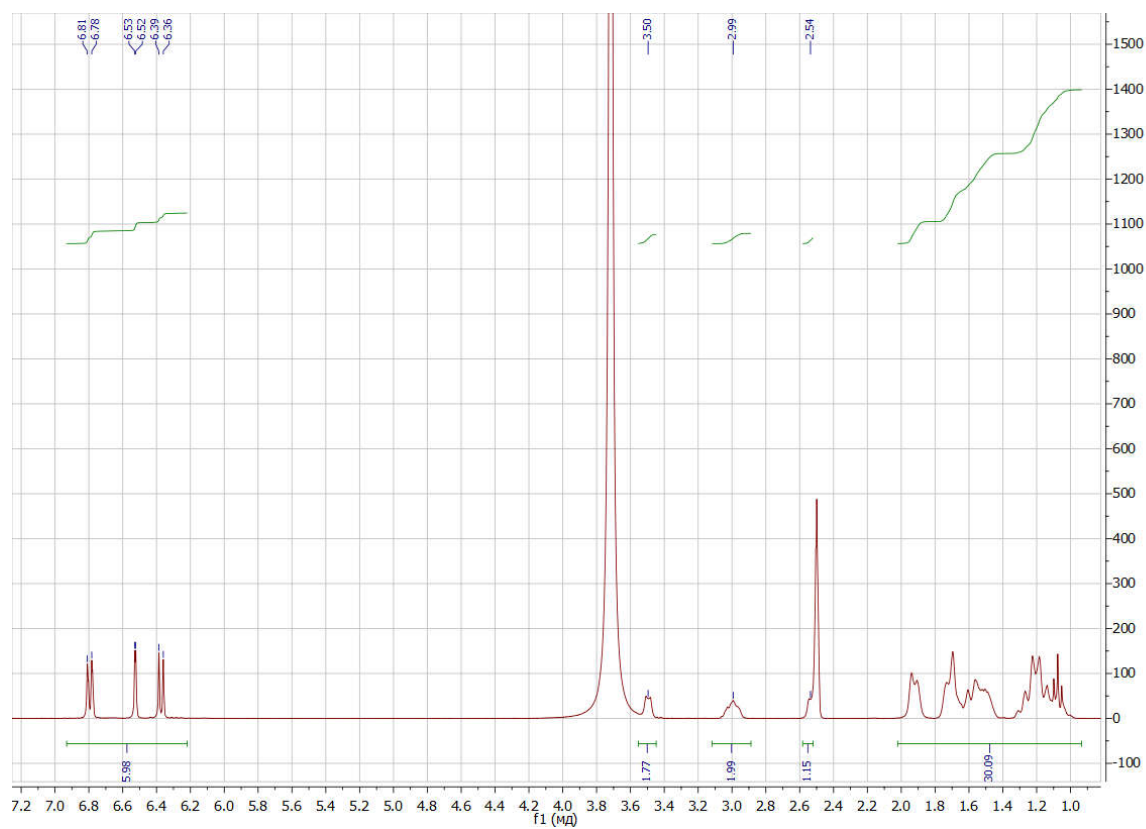
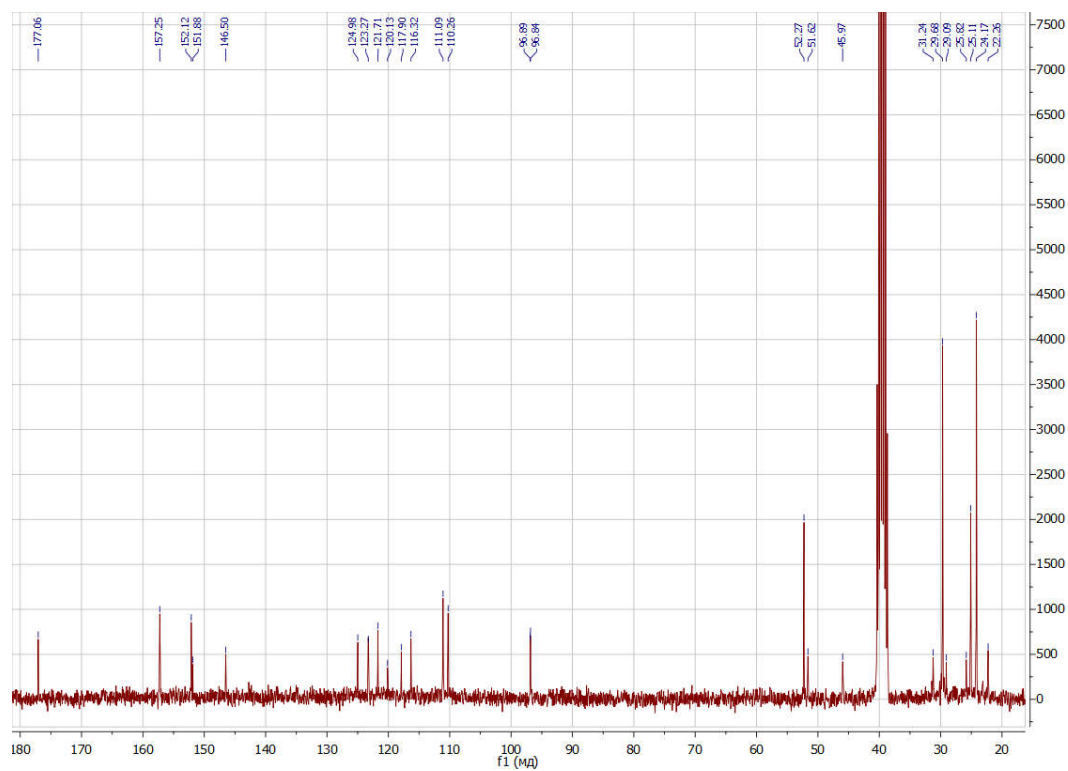


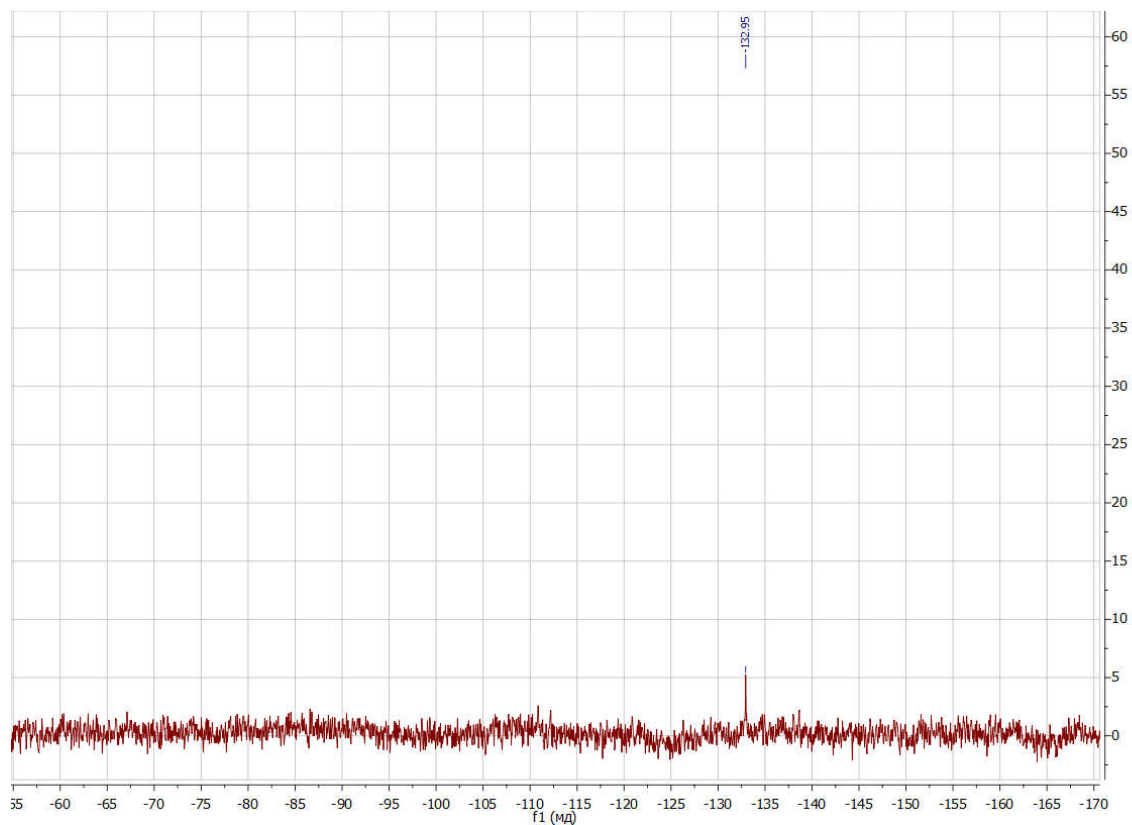
¹H NMR spectrum of compound 4.¹³C NMR spectrum of compound 4.

^{29}Si NMR spectrum of compound 4.

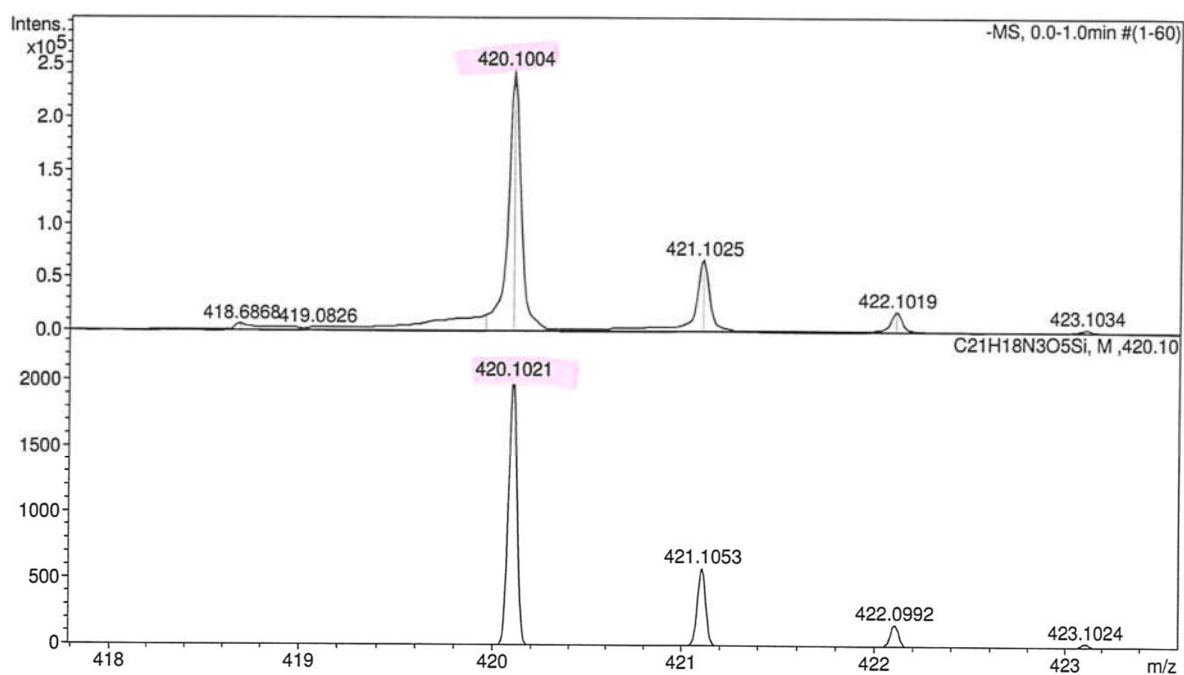
HRMS spectra of compound 4.

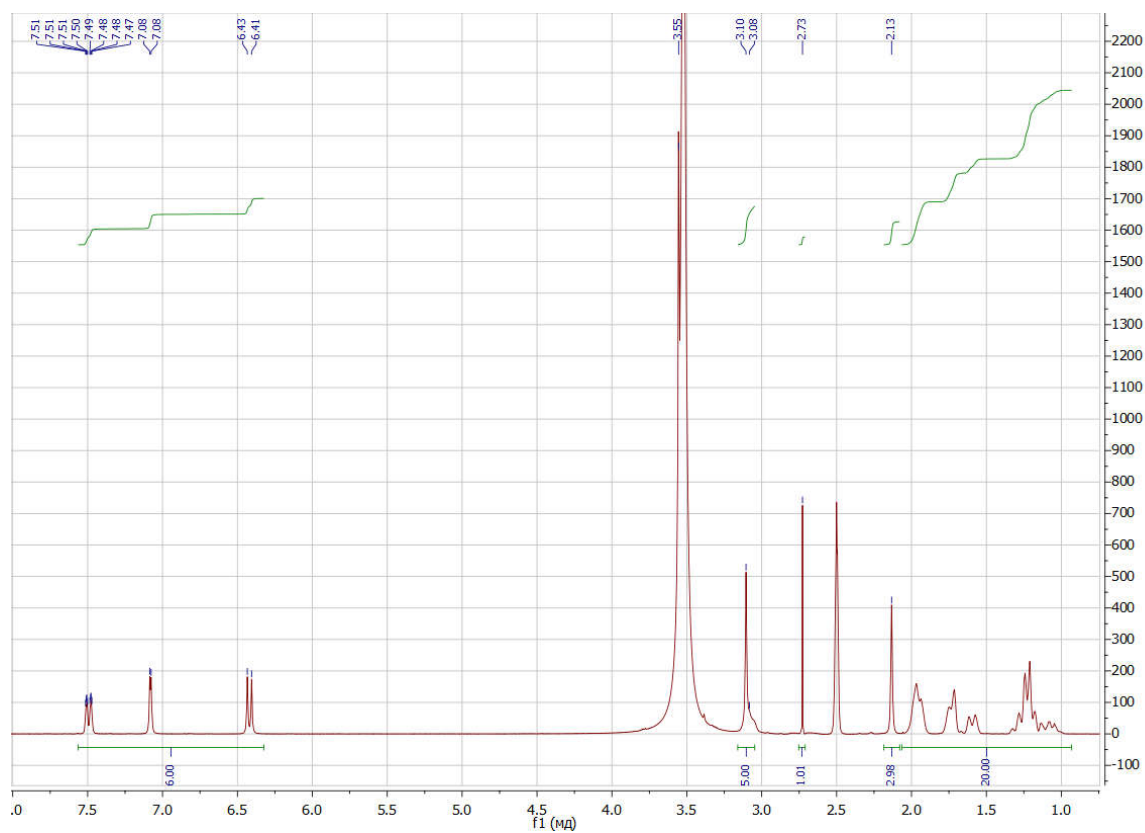
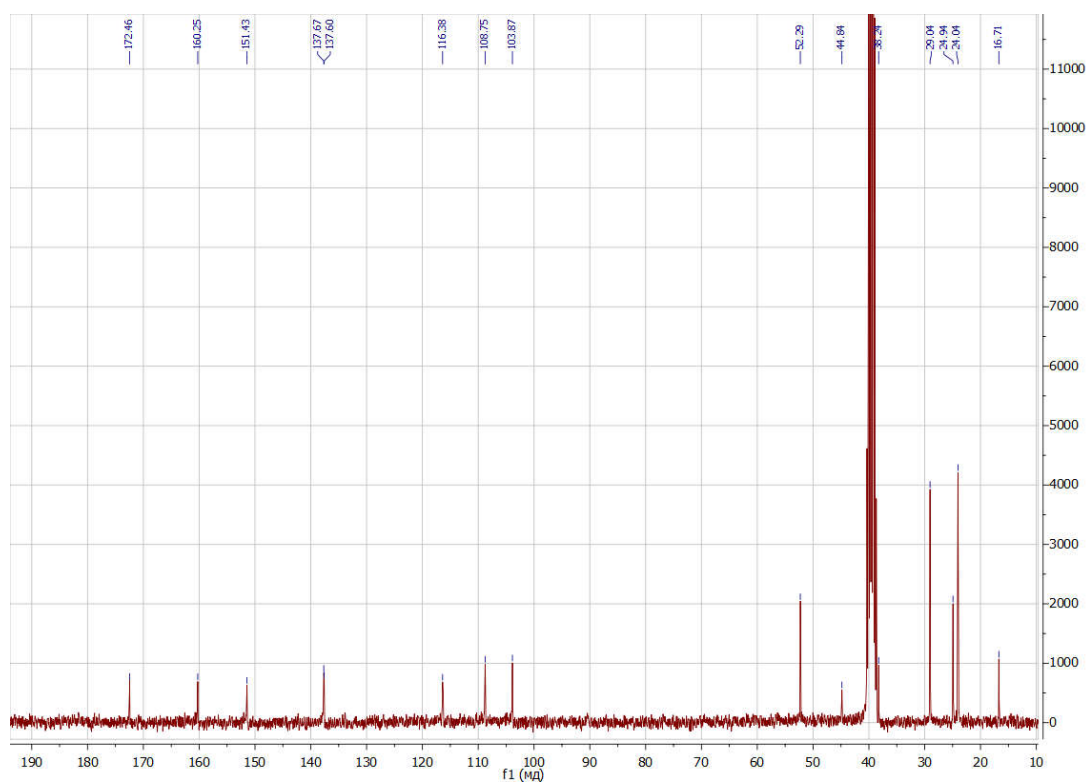


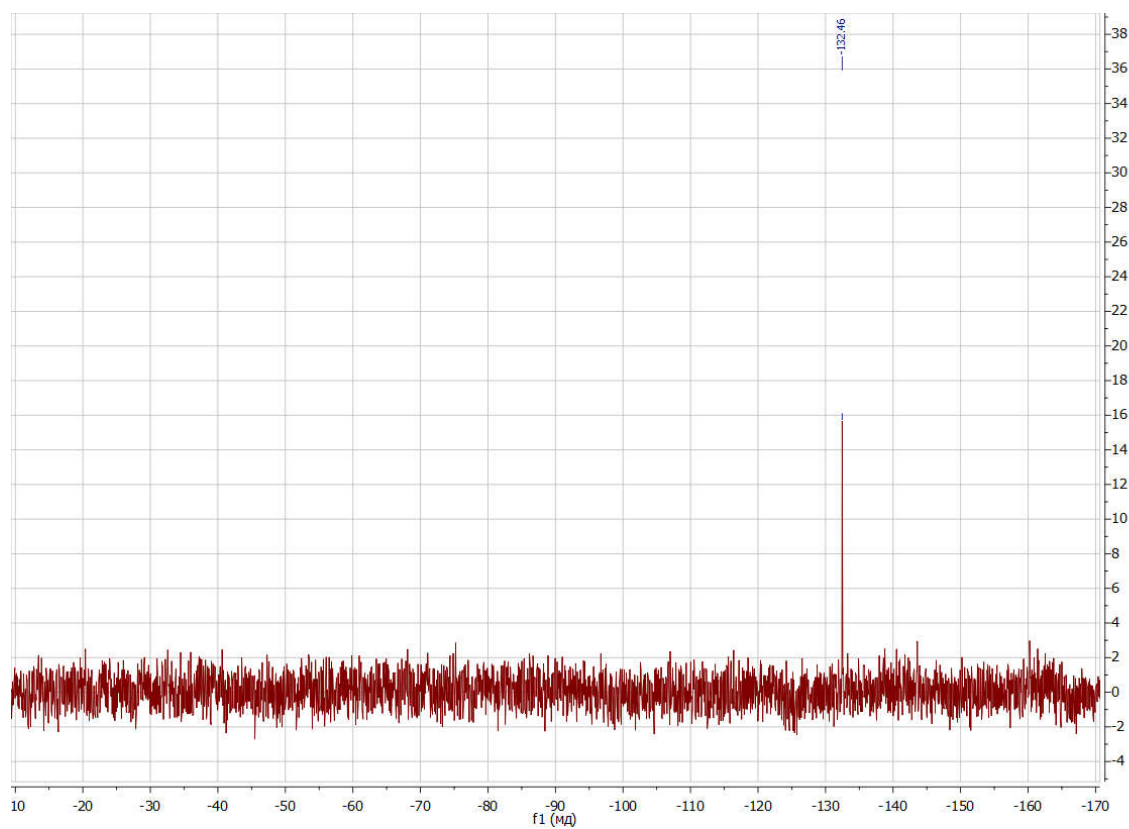
¹H NMR spectrum of compound 5.¹³C NMR spectrum of compound 5.

^{29}Si NMR spectra of compound 5.

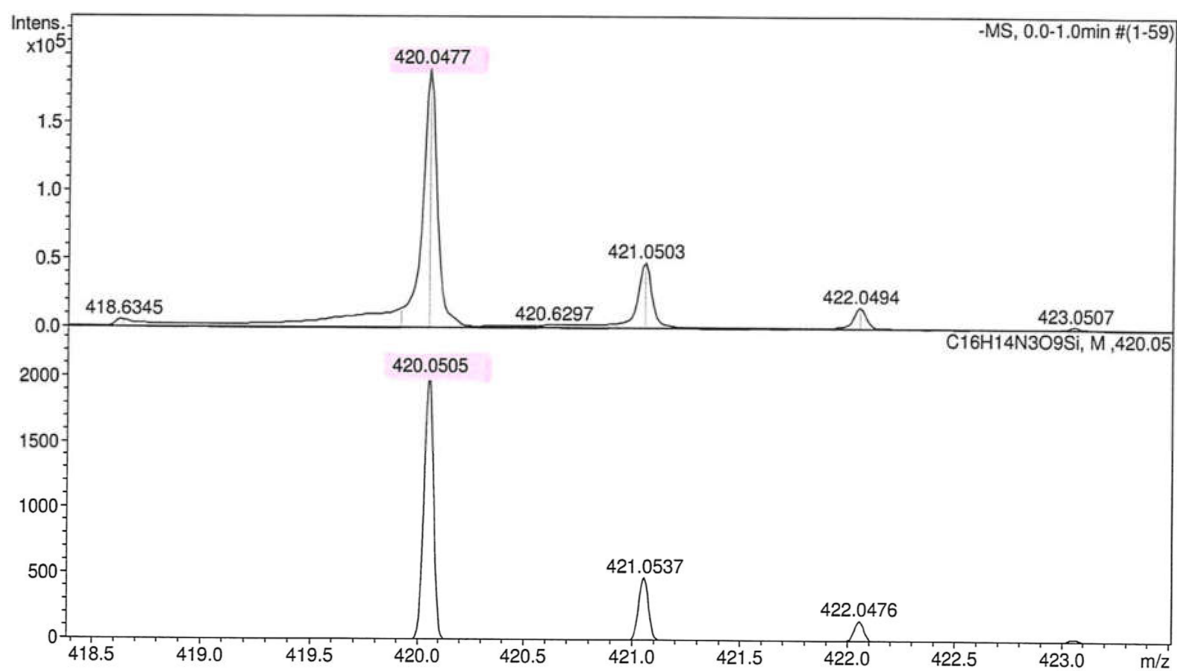
HRMS spectrum of compound 5.

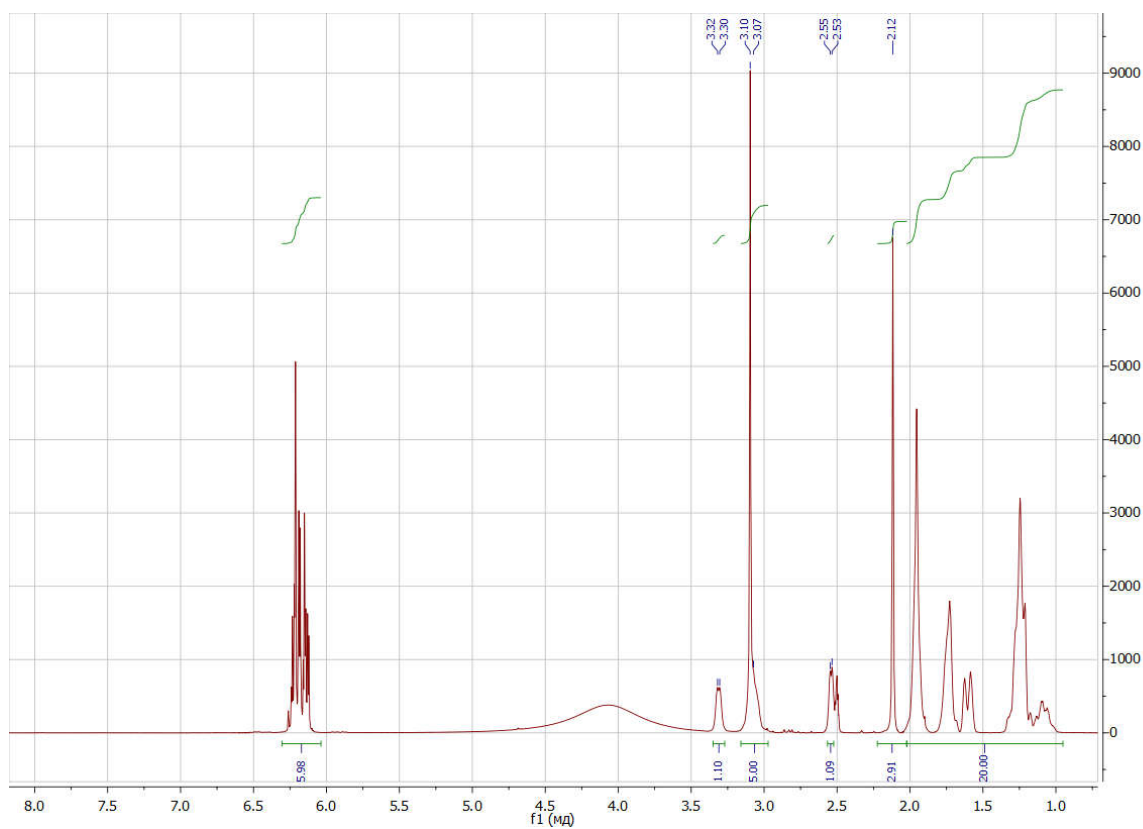
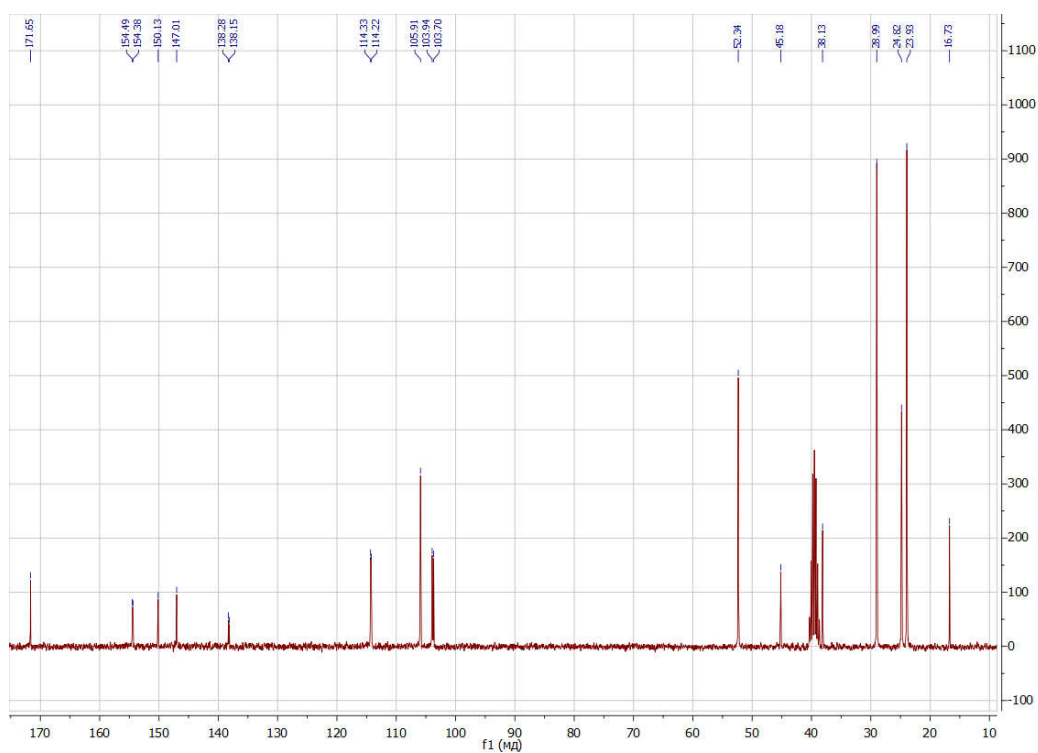


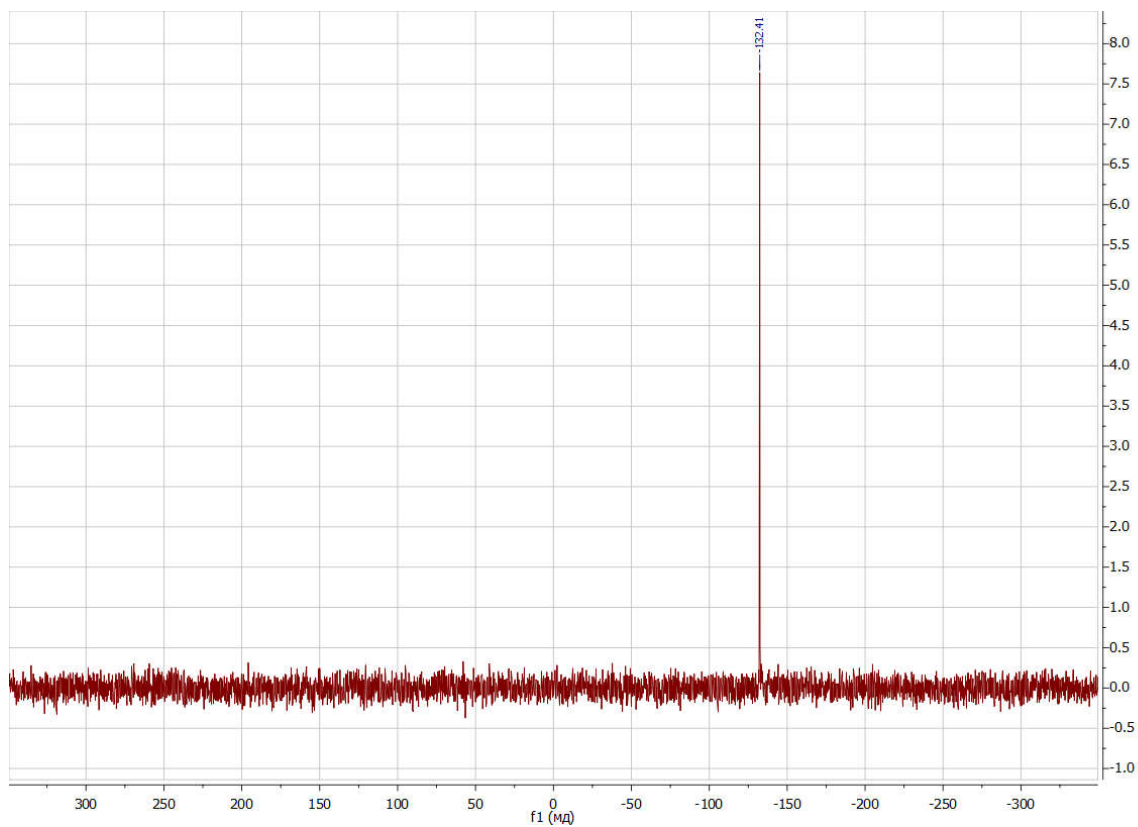
¹H NMR spectrum of compound 6.¹³C NMR spectrum of compound 6.

^{29}Si NMR spectra of compound 6.

HRMS spectrum of compound 6.



¹H NMR spectrum of compound 7.¹³C NMR spectrum of compound 7.

^{29}Si NMR spectrum of compound 7.

HRMS spectrum of compound 7.

