Electronic supplementary information

SEARCH FOR NEW APPROACHES TO JANUS DENDRIMERS BASED ON NATURAL COMPOUNDS

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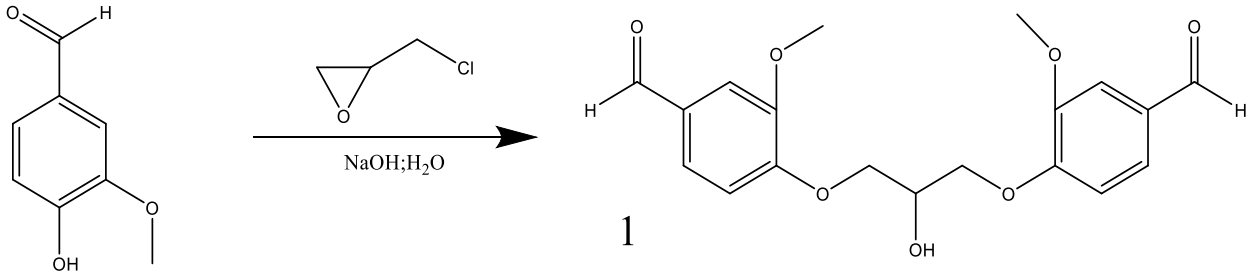
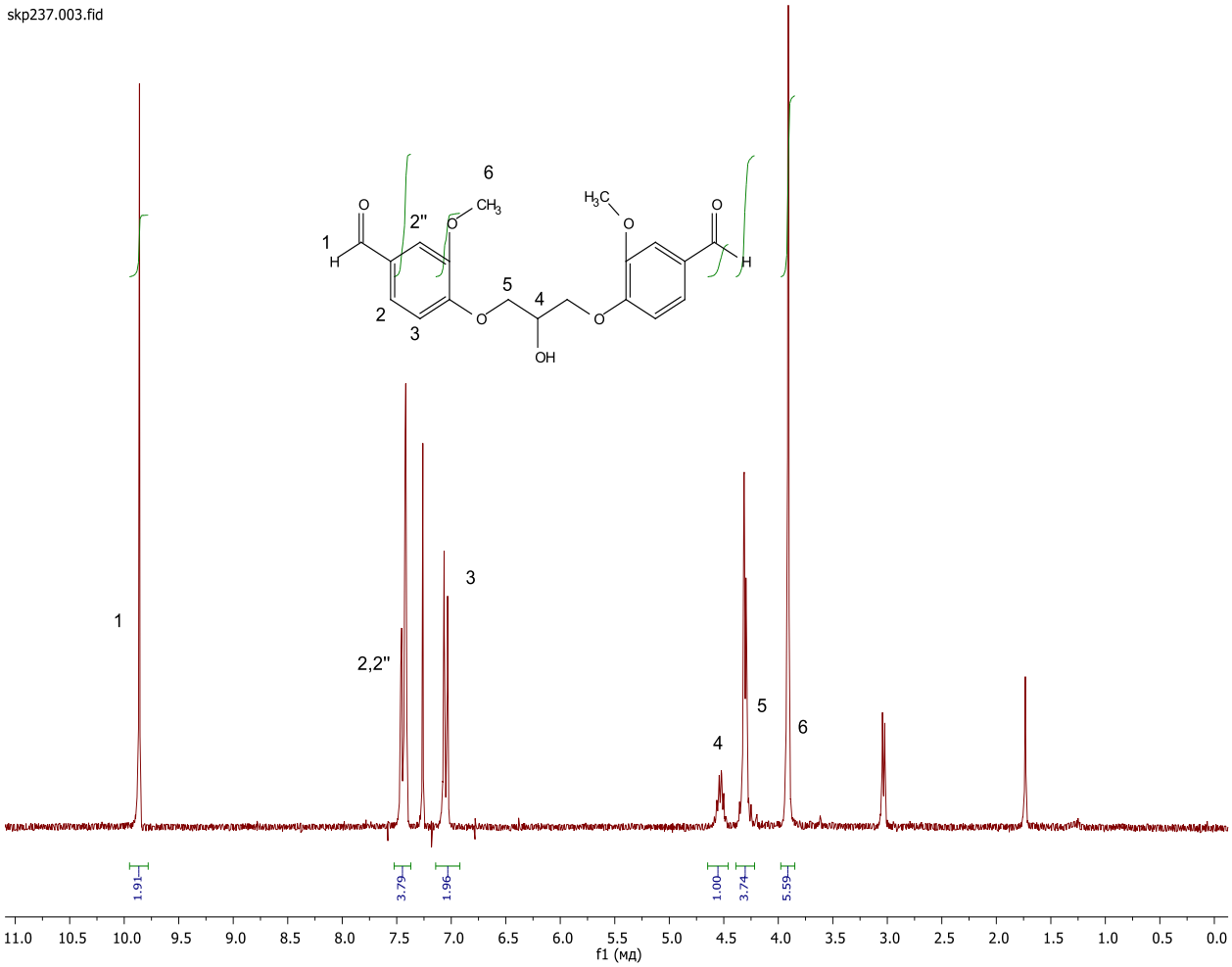
Synthesis of compound 1

A three-neck flask equipped with a thermometer, a dropping funnel, and a mechanical stirrer was charged with sodium hydroxide (26.5 g, 0.66 mol) and water (500 mL). Then vanillin (100 g, 0.66 mol) was added. Epichlorohydrin (25.33 mL, 0.33 mol) was added dropwise for 2 h, after which the reaction mixture was stirred at 60 °C for 6 h. The resulting precipitate was filtered off and washed with hot 40% aq. ethanol (500 mL) to give 47.2 g of the target product. Yield: 40%.

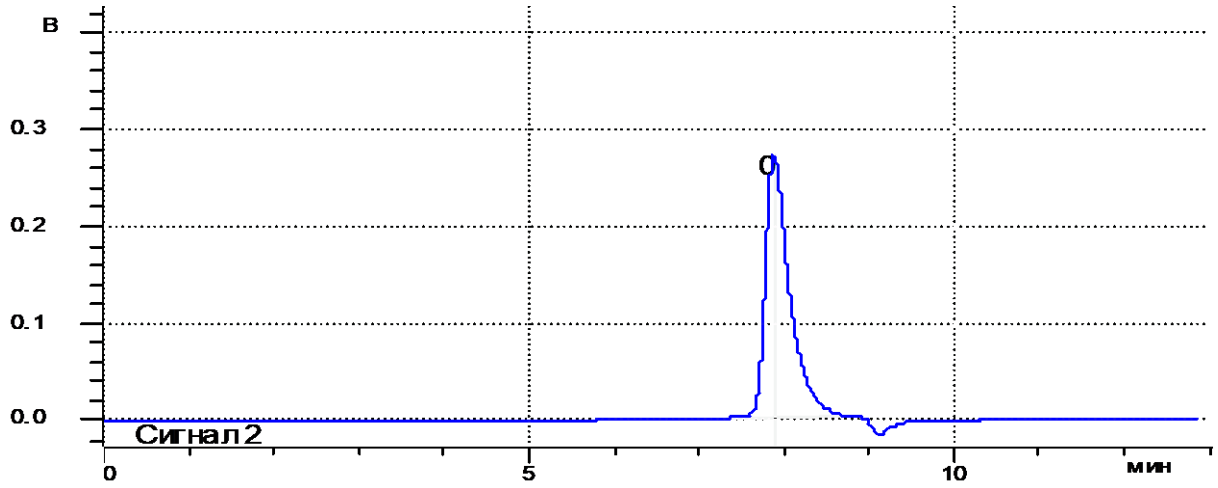


1

40%



^{1}H NMR spectrum of compound **1**

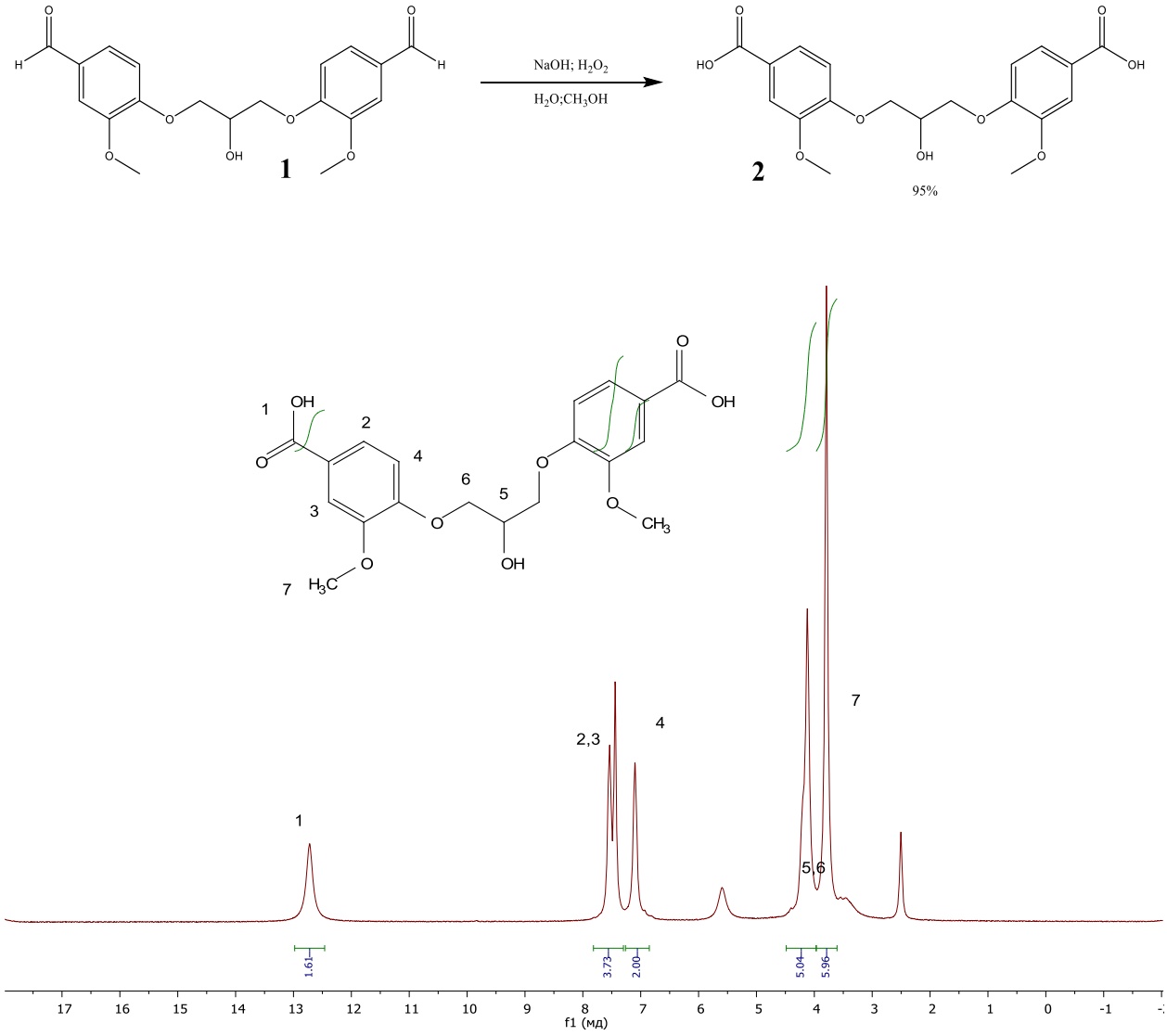


GPC curve of compound **1**

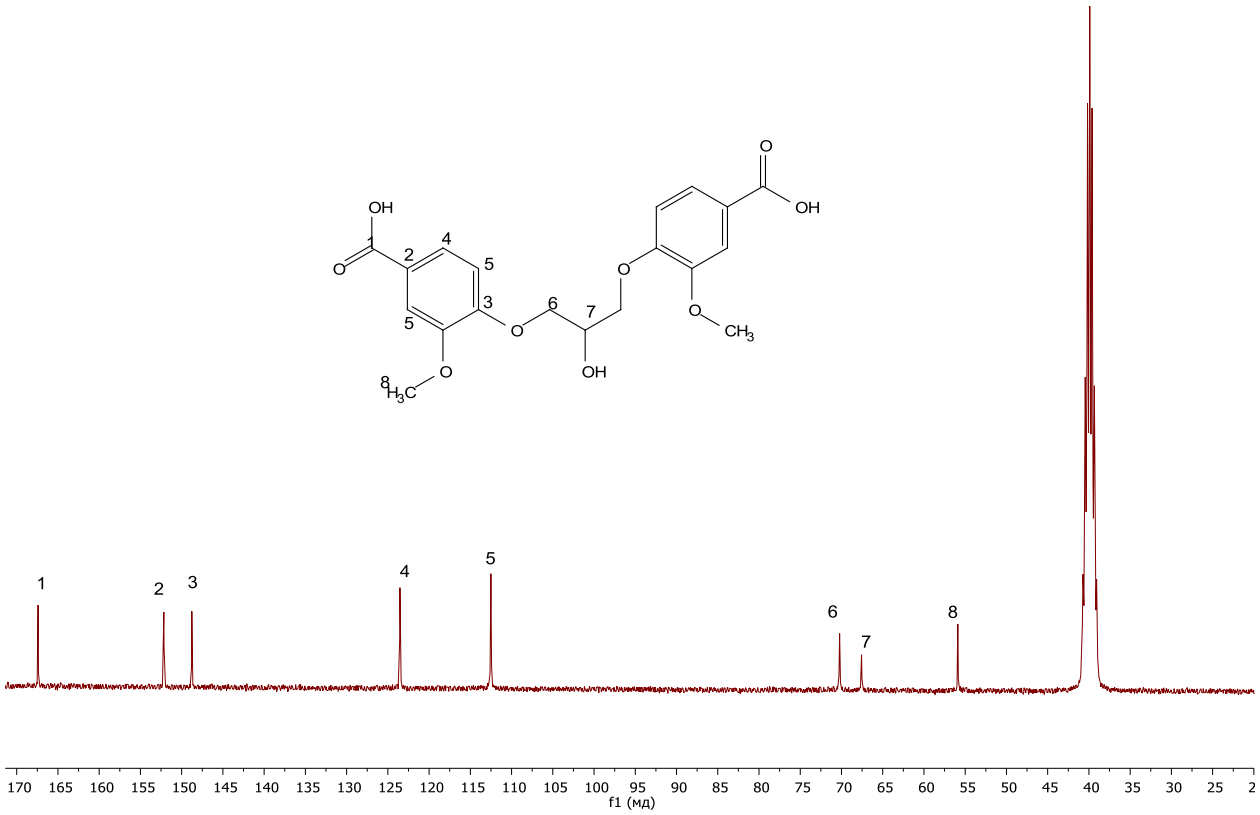
Synthesis of compound 2

A flask equipped with a mechanical stirrer and a thermometer was charged with compound **1** (40 g, 0.11 mol) and sodium hydroxide (35 g, 0.89 mol). Then methanol (380 mL) and water (40 mL) were added. The reaction mixture was cooled to 0 °C, then 30% aq. hydrogen peroxide (300 mL) was added dropwise under stirring for 3 h. After the addition of H_2O_2, the reaction mixture became transparent. It was acidified with 0.1 M aq. HCl. The resulting precipitate was filtered

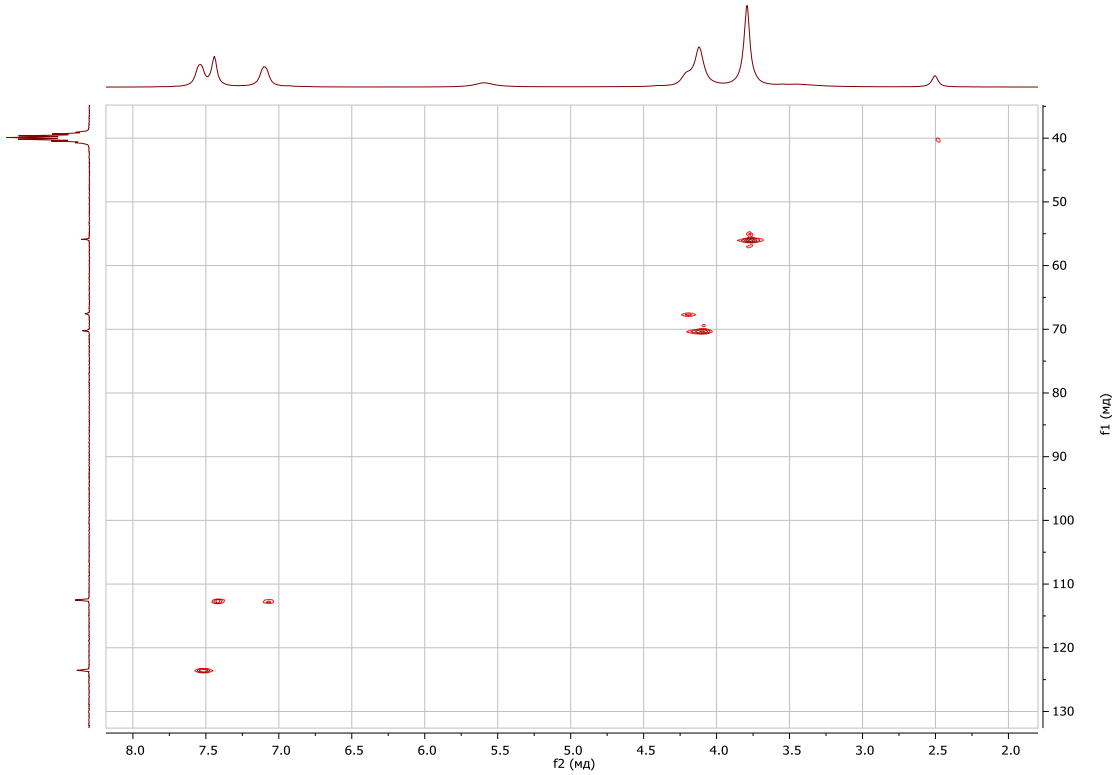
off and dried under vacuum upon heating for 8 h to give 41.38 g of compound **2**. Yield: 95%. The product purity was determined by TLC (eluent: benzene–methanol–acetic acid).



^{1}H NMR spectrum of compound **2**

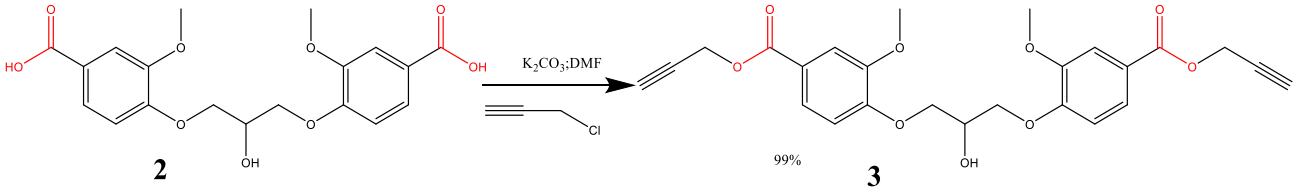


^{13}C NMR spectrum of compound **2**

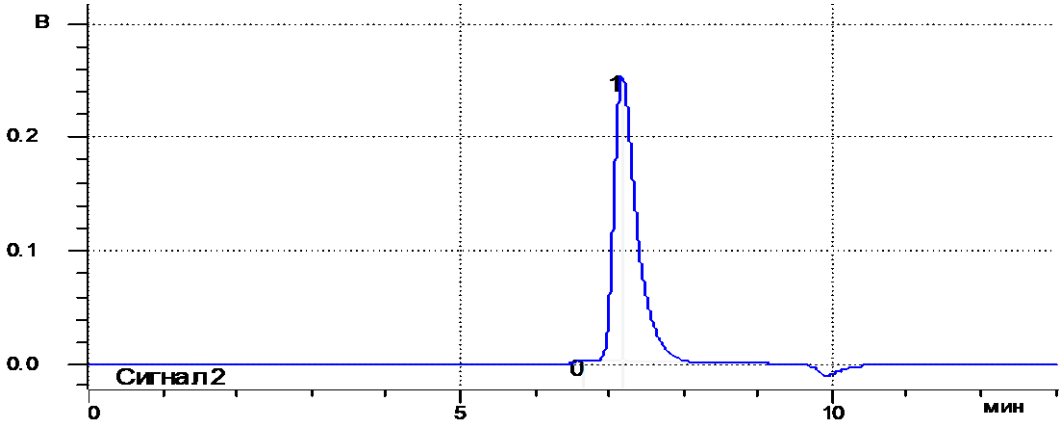


HSQC spectrum of compound **1**

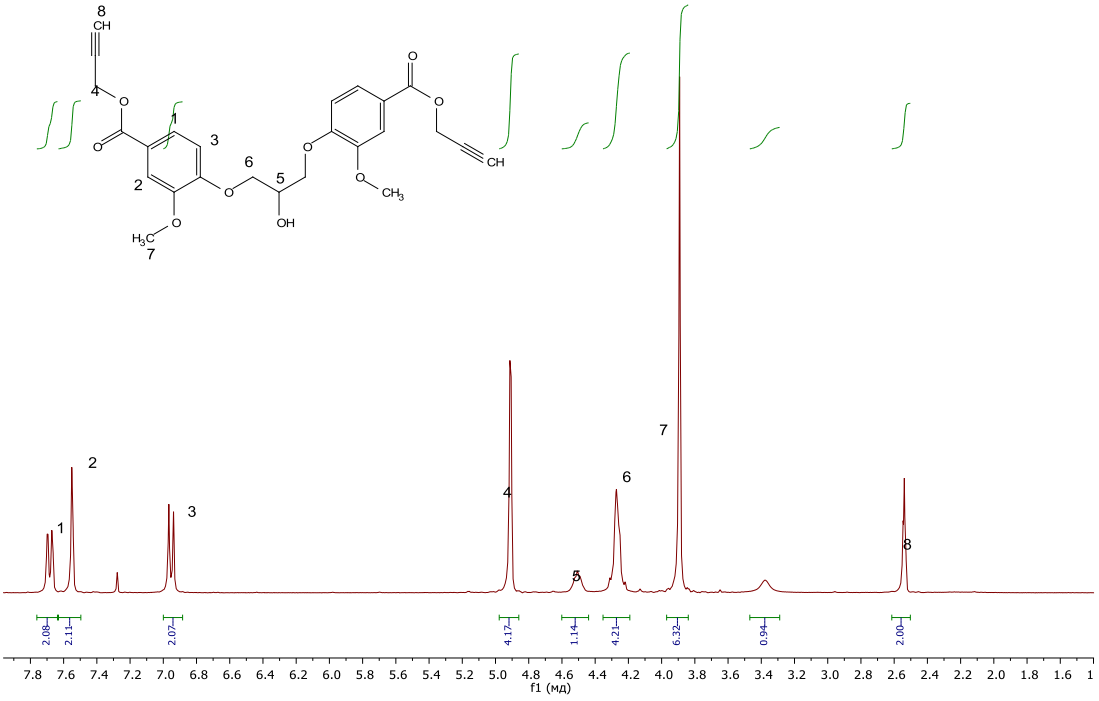
Synthesis of compound 3



Compound **2** (18 g, 0.046 mol) and calcined potassium carbonate (38 g) were placed in a flask. Then DMF (45 mL) was added. The reaction mixture was stirred at room temperature for 2 h. After addition of propargyl chloride (7.2 mL, 0.11 mol), the resulting mixture was stirred at room temperature overnight. Then 0.1 M HCl was added dropwise to the mixture obtained. The resulting precipitate was filtered off and dried under vacuum for 3 h.



GPC curve of compound **3**



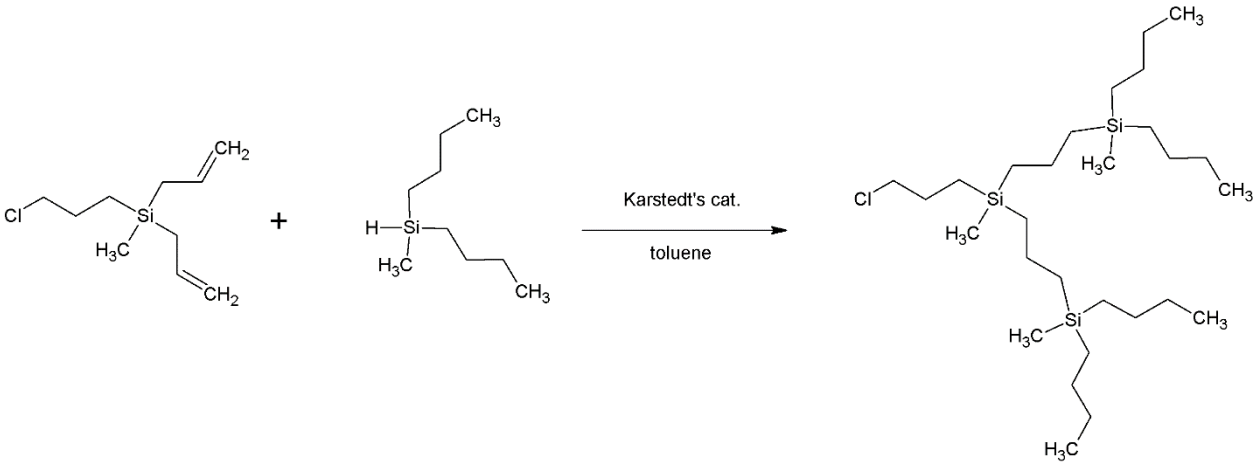
^{1}H NMR spectrum of compound **3**

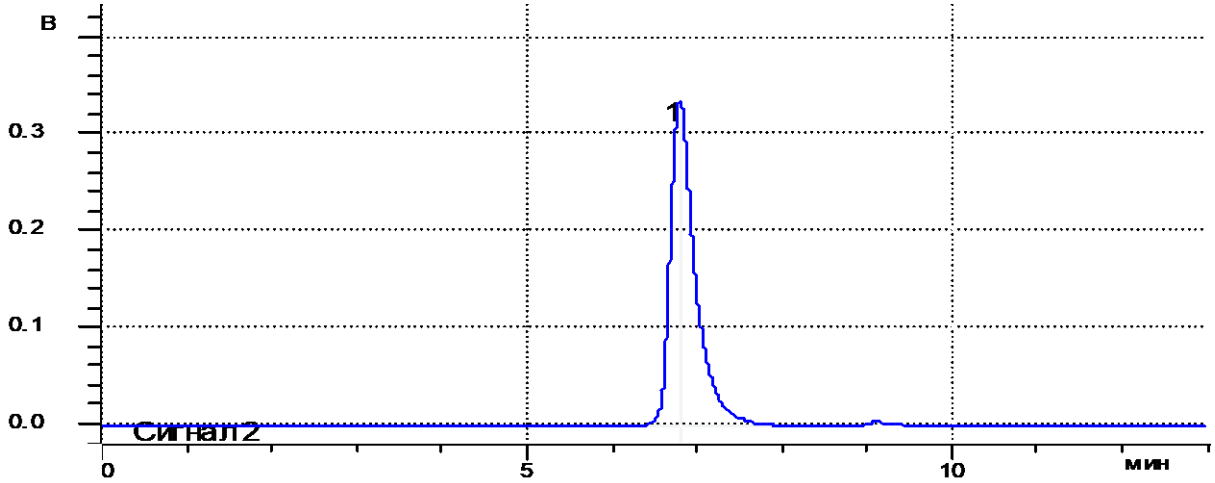
Synthesis of compound 4

Compound **4** was synthesized in 2 stages.

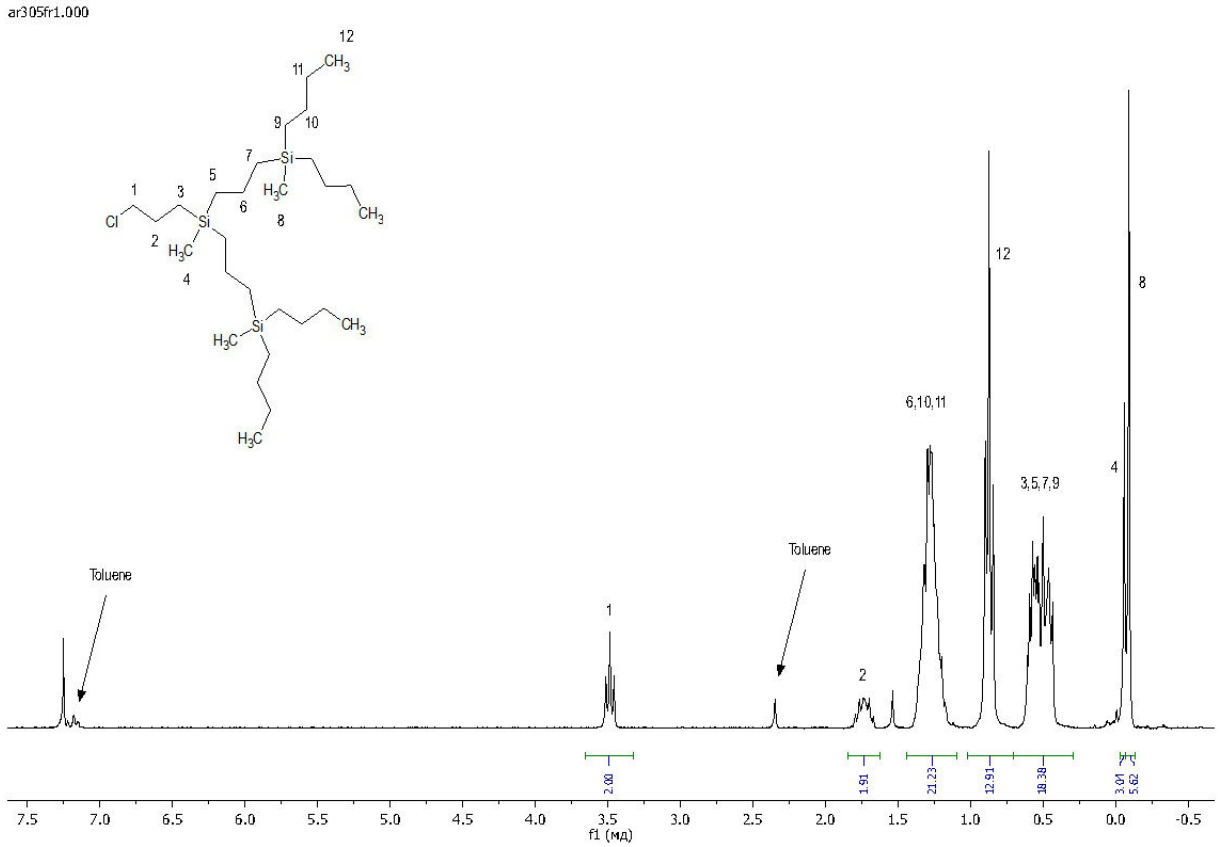
Compound 4.1.

Dibutylmethylsilane (1.87 g, 0.012 mol) and Karstedt's catalyst (15 μL) were added to a solution of 3-chloropropyldiallylmethylsilane (1 g, 0.0049 mol) in absolute toluene (15 mL). The resulting mixture was stirred at 60 °C for 5 h. The product yield was 95%.



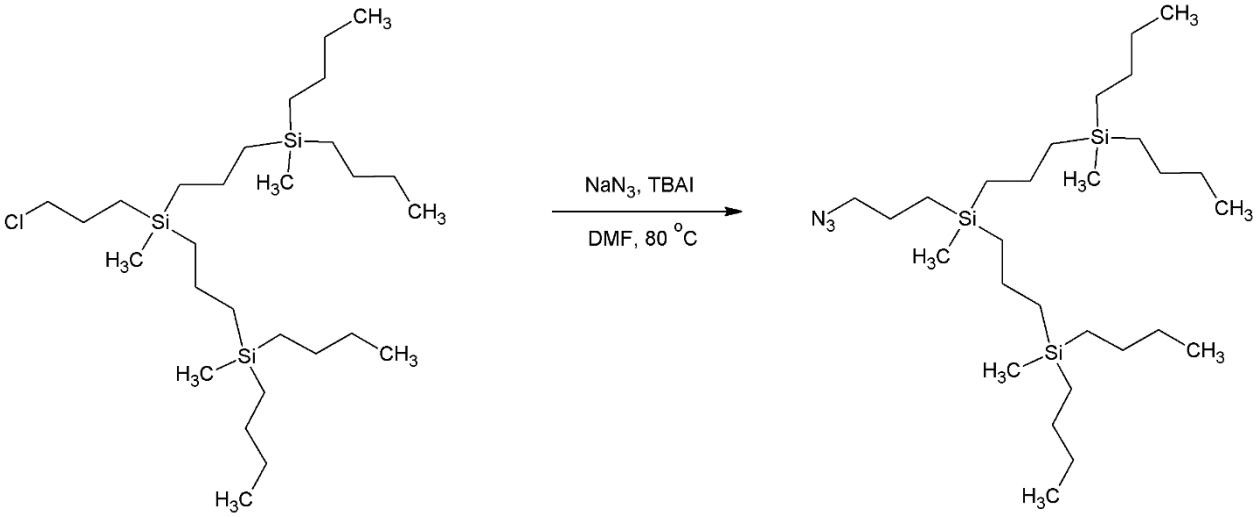


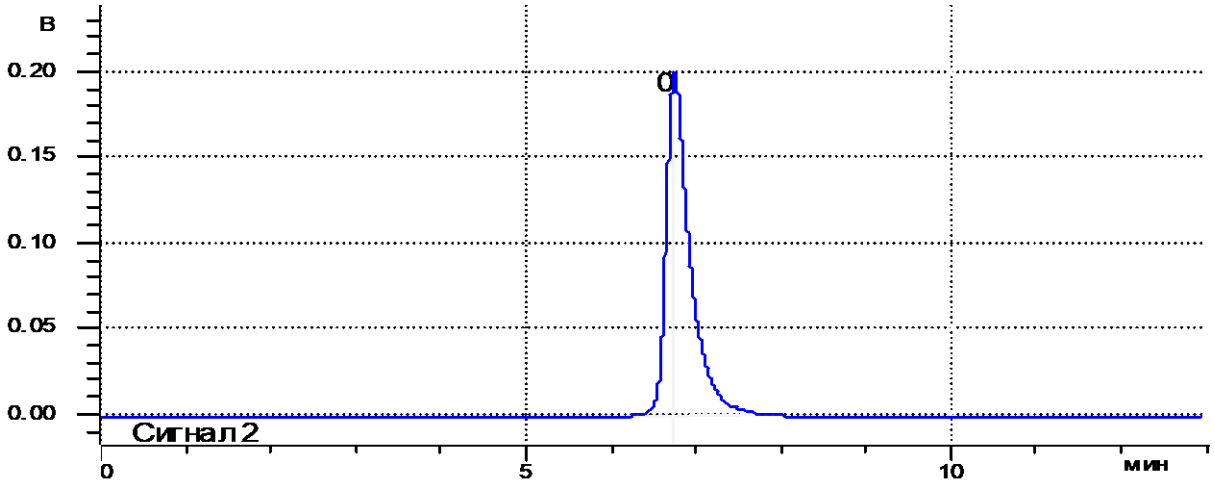
GPC curve of compound **4.1**



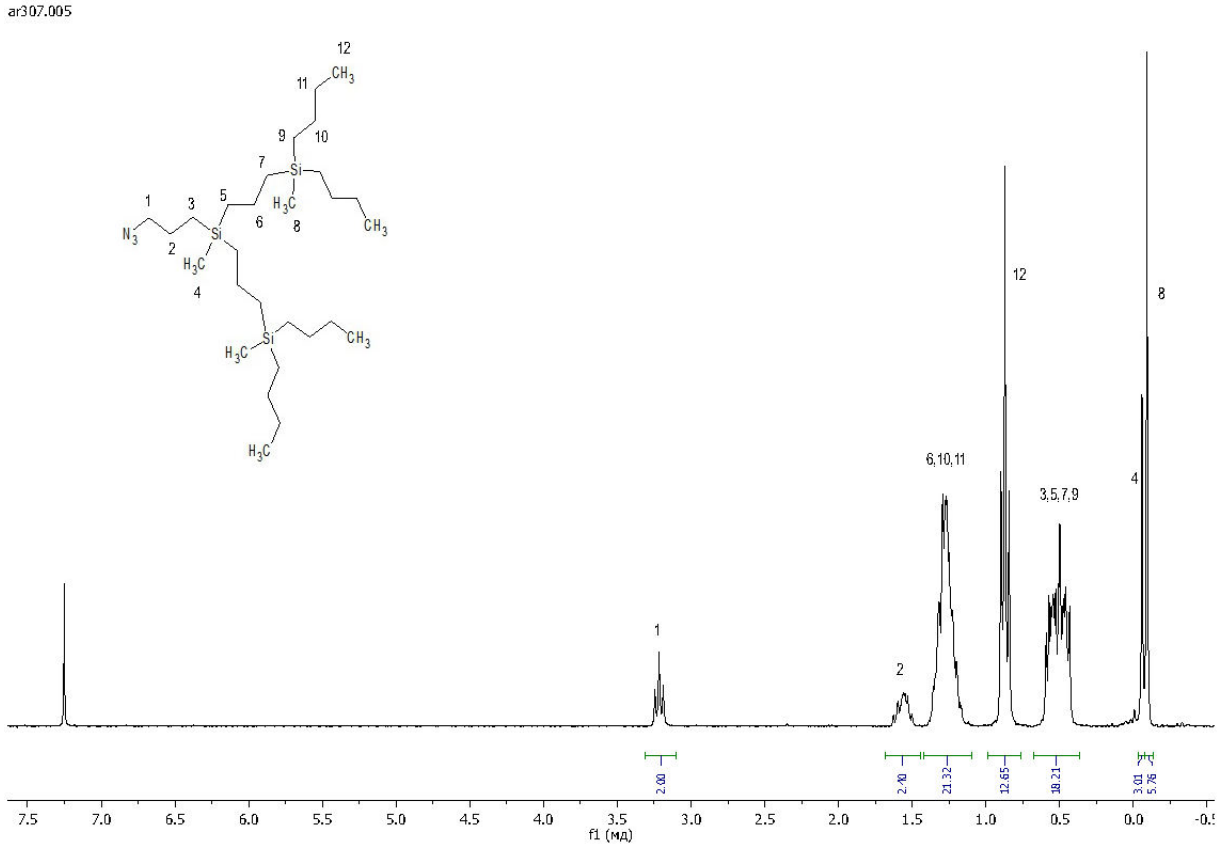
^{1}H NMR spectrum of compound **4.1**

Compound 4. A mixture of compound **4.1** (1 g, 0.0019 mol), sodium azide (0.19 g, 0.0029 mol), a catalytic amount of *tert*-butylammonium iodide, and absolute DMF (6 mL) was heated at 80 °C for 8 h. The reaction mixture was diluted with dichloromethane (60 mL). The resulting mixture was filtered, and the filtrate was evaporated and dried under vacuum. Yield: 95%.



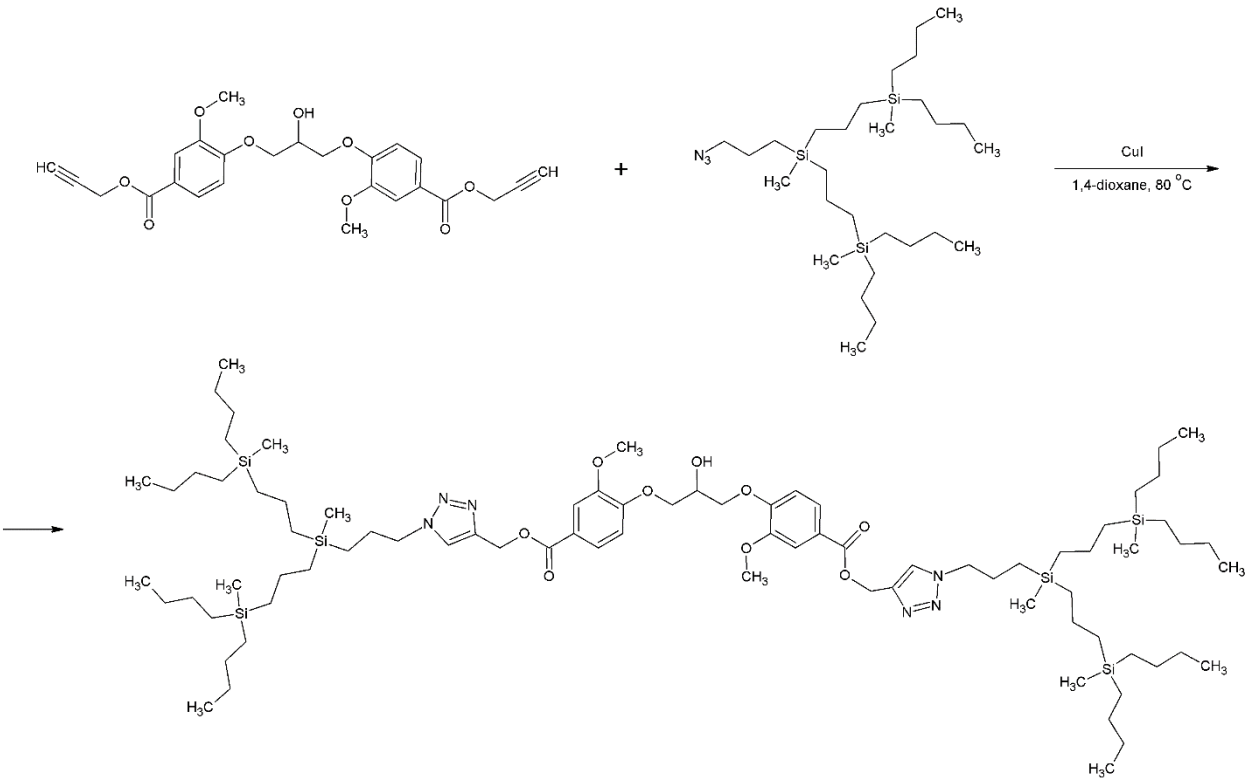


GPC curve of the azidopropyl hydrophobic monodendron

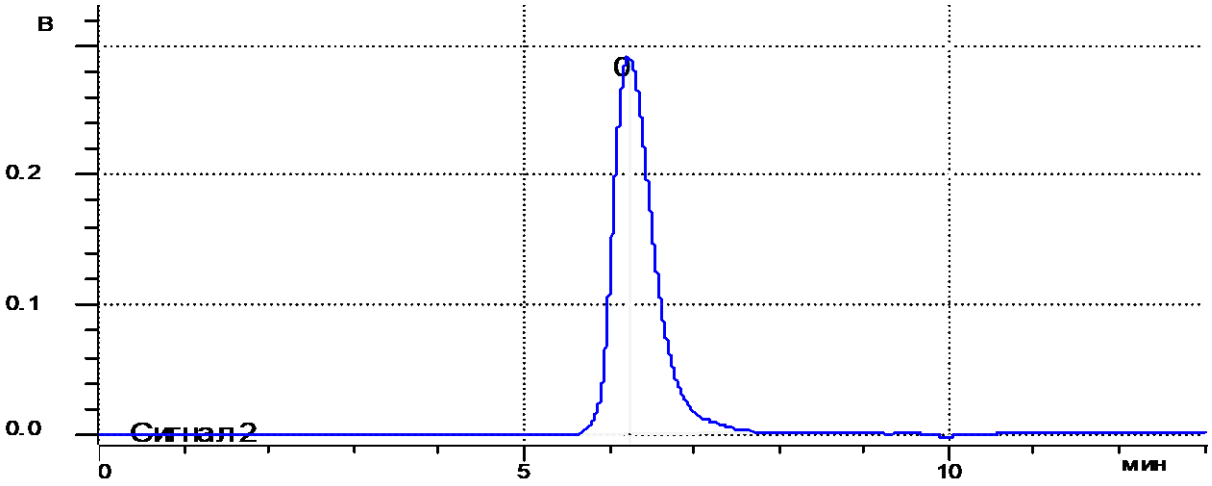


^{1}H NMR spectrum of of the azidopropyl hydrophobic monodendron

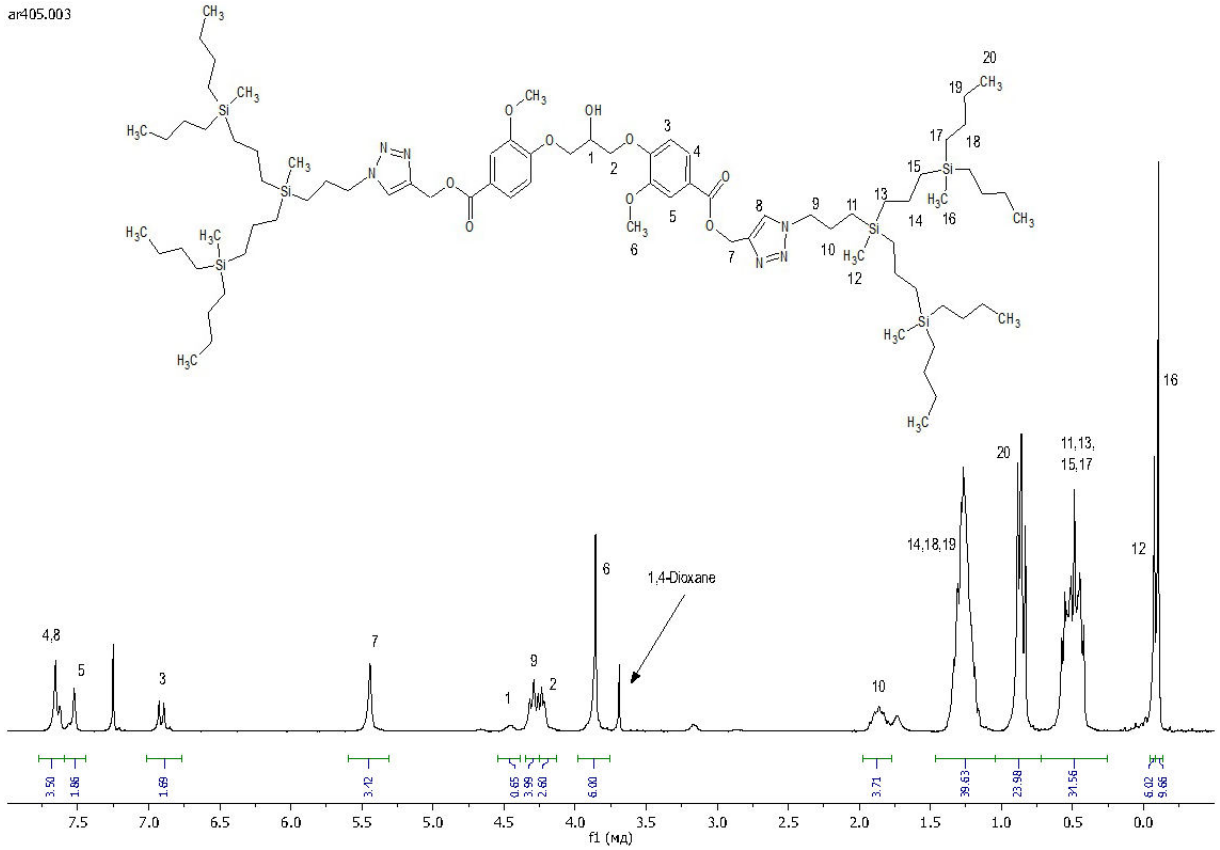
Compound 6. A stirred mixture of compound **4** (0.25 g, 0.48 mmol), compound **3** (0.1 g, 0.21 mmol), a catalytic amount of triethylamine and copper(I) iodide, and absolute 1,4-dioxane (2 mL) were heated at 80 °C for 8 h. The resulting mixture was evaporated to dryness to give the target product in quantitative yield.



Synthesis of Janus dendrimer **5**



GPC curve of Janus dendrimer **5**

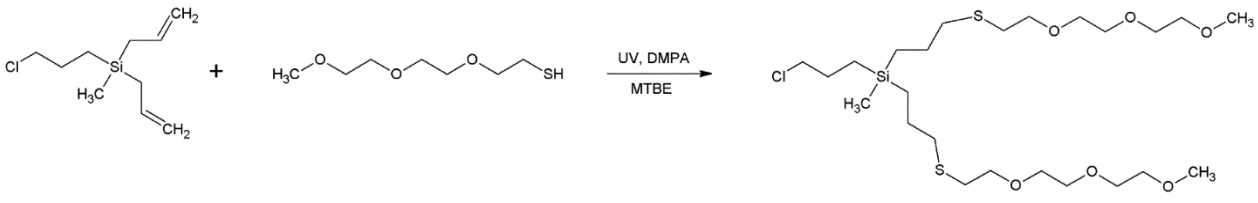


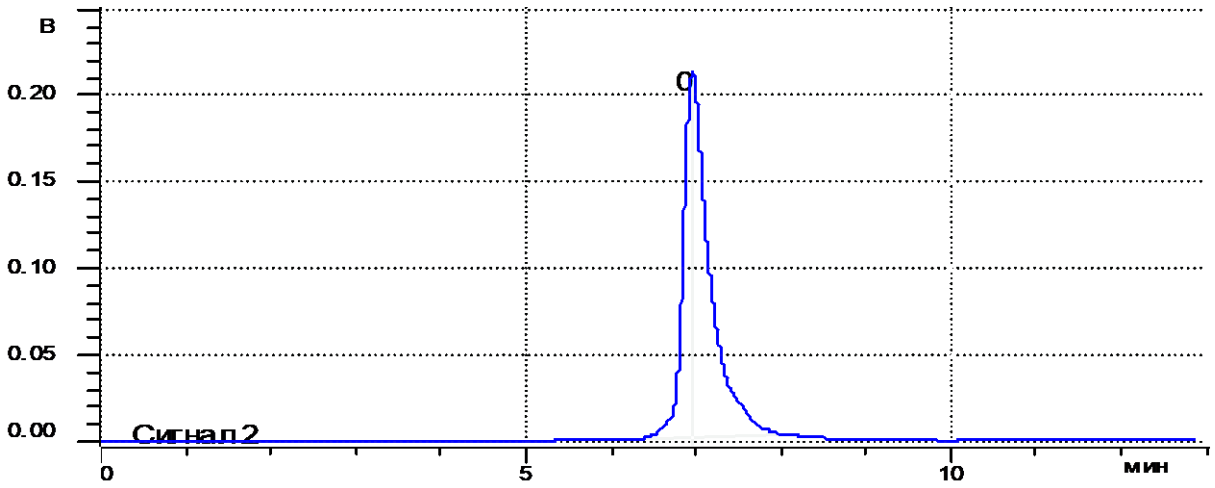
^{1}H NMR spectrum of Janus dendrimer **5**

Synthesis of compound 6

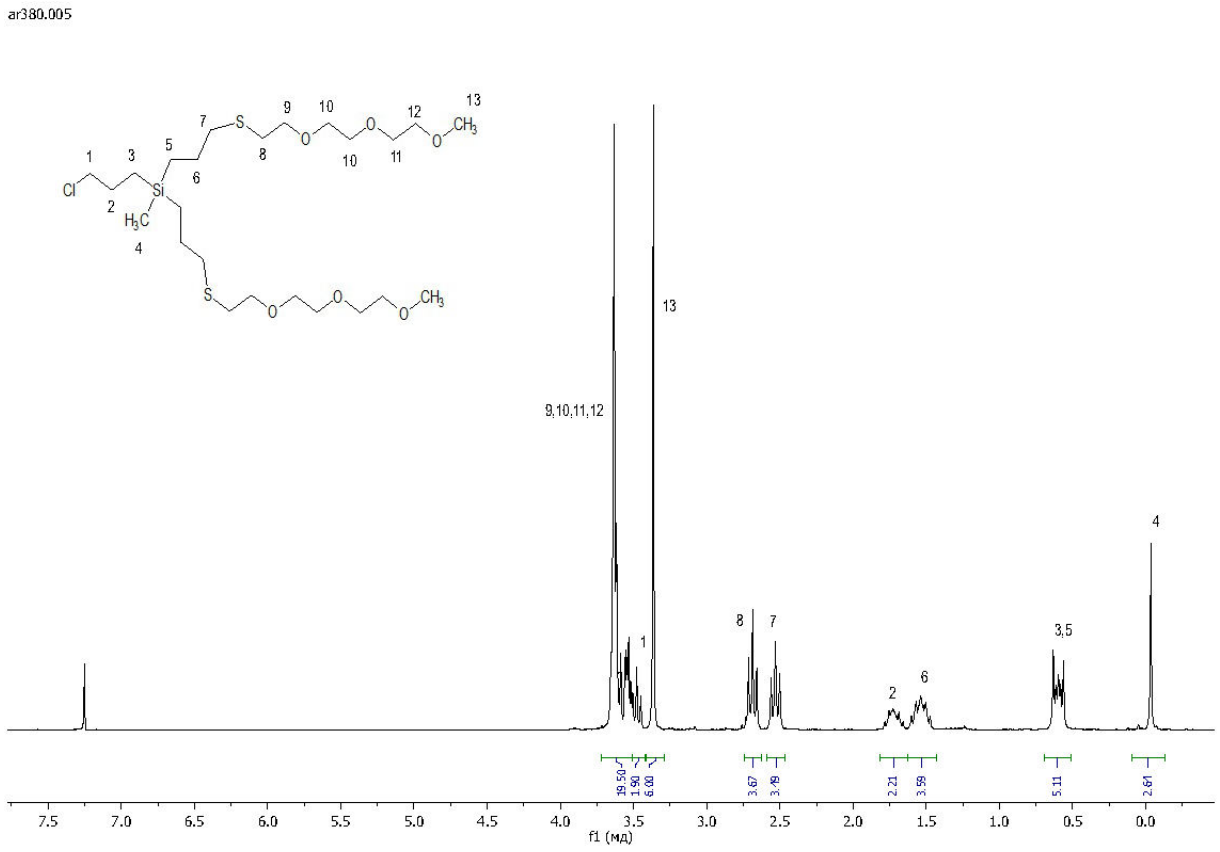
Compound **6** was prepared in 2 stages.

Compound 6.1. Mercapto-functionalized MTEG (2.13 g, 0.012 mol) and 2,2-dimethoxy-2-phenylacetophenone (13 mg, 0.049 mmol) were added to a solution of (chloropropyl)diallylmethylsilane (1 g, 0.0049 mol) in absolute MTBE (14 mL). The reaction mixture was stirred under UV irradiation (365 nm) for 6 h. The resulting mixture was evaporated on a rotary evaporator. The residue obtained was dried at 80 °C and 0.5 mbar to give the target product in quantitative yield.



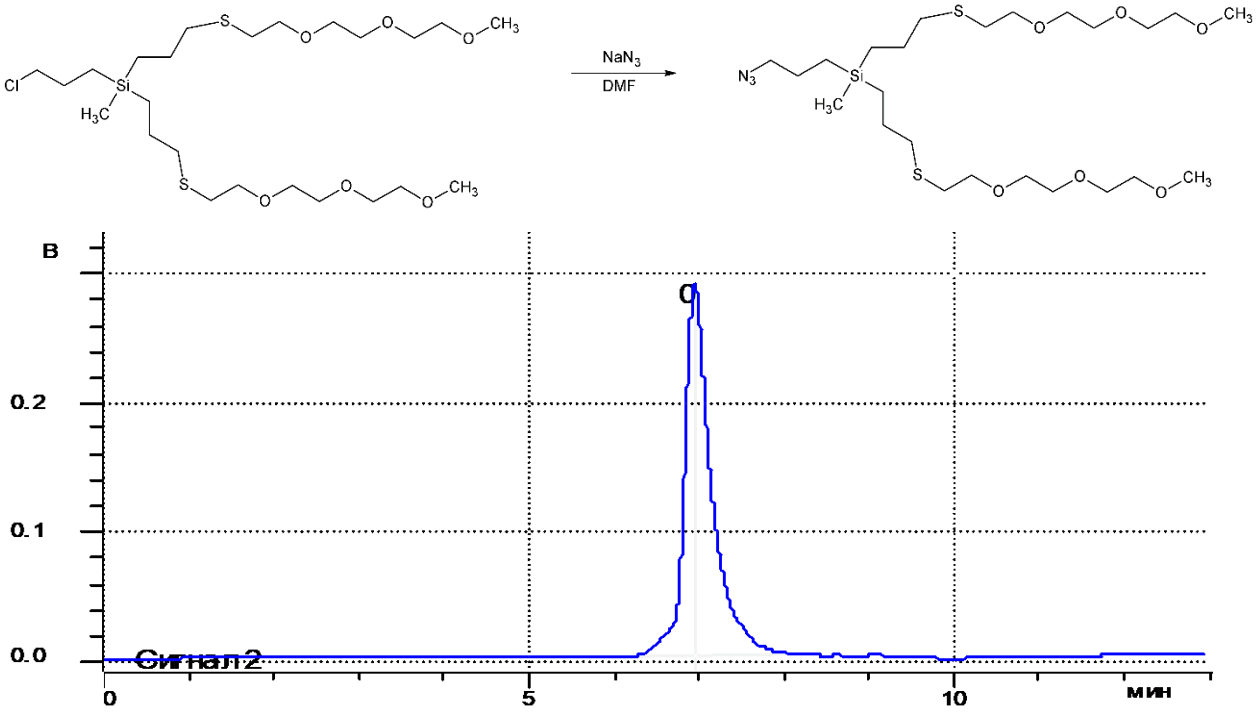


GPC curve of compound **6.1**

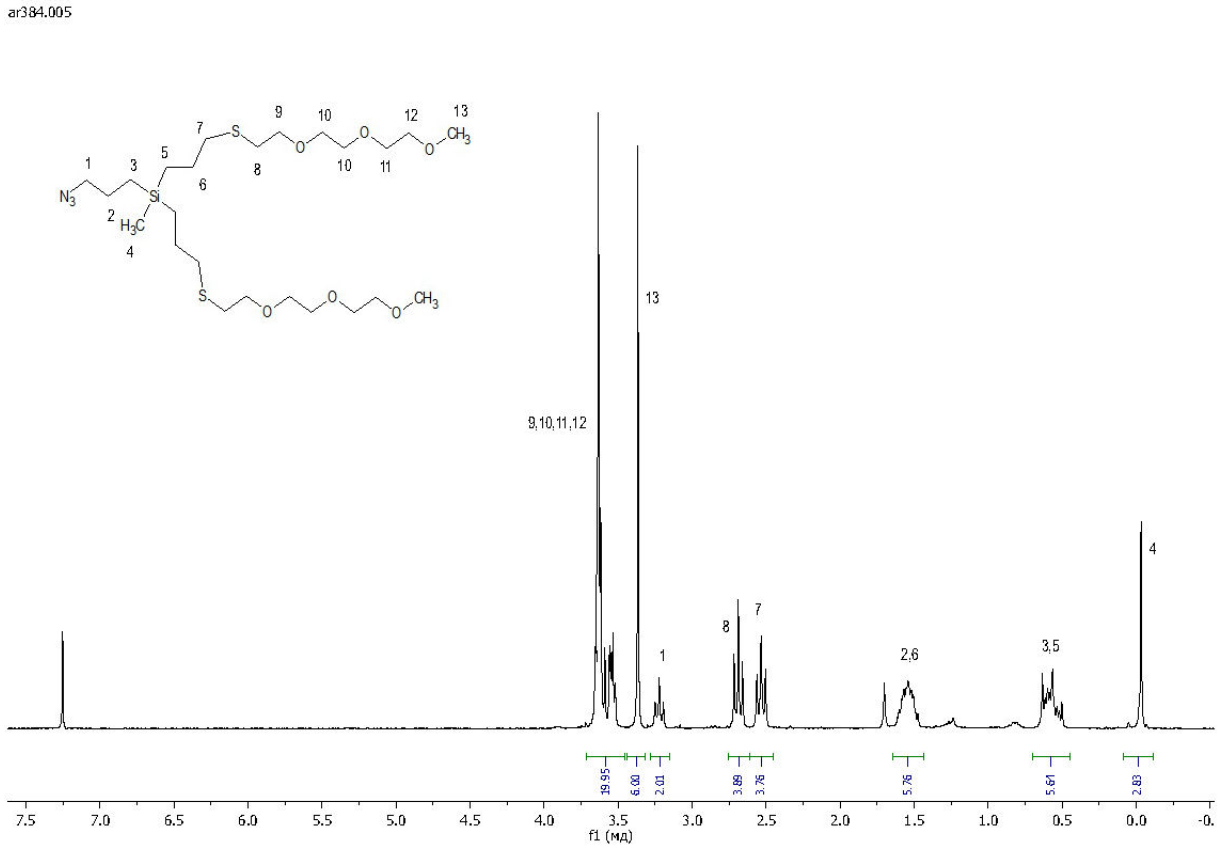


^{1}H NMR spectrum of the product of hydrothiolation of (3-chloropropyl)diallylmethylsilane and mercapto-functional MTEG

Compound 6. Sodium azide (0.35 g, 0.0053 mol) was added to a solution of compound **6.1** (2 g, 0.0035 mol) in absolute DMF (12 mL). The resulting mixture was stirred at 80 °C for 6 h. The target product was extracted with toluene. The organic layer was washed with water, dried over sodium sulfate, and evaporated and dried on an oil pump. The target product was obtained in 92% yield.



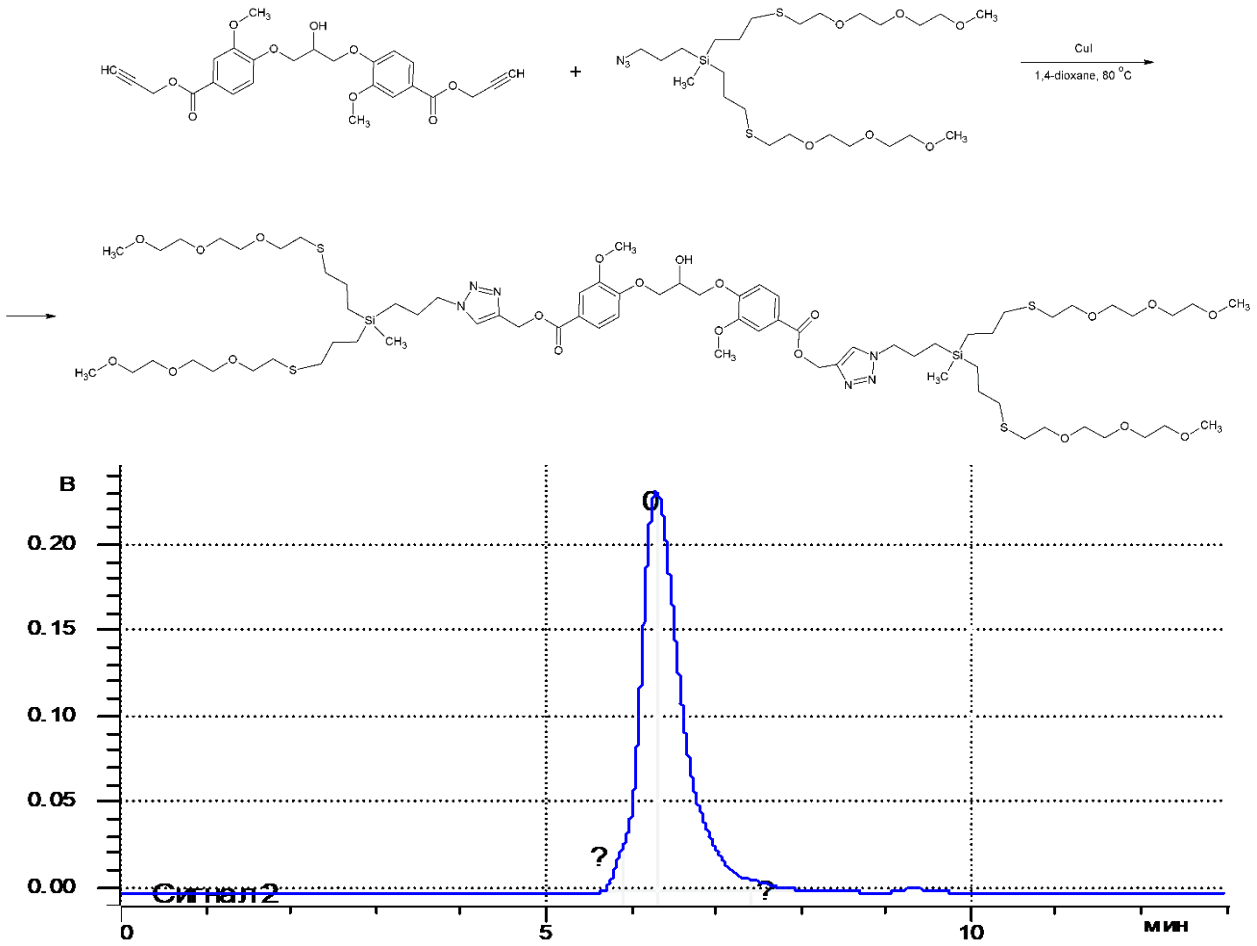
GPC curve of compound **6**



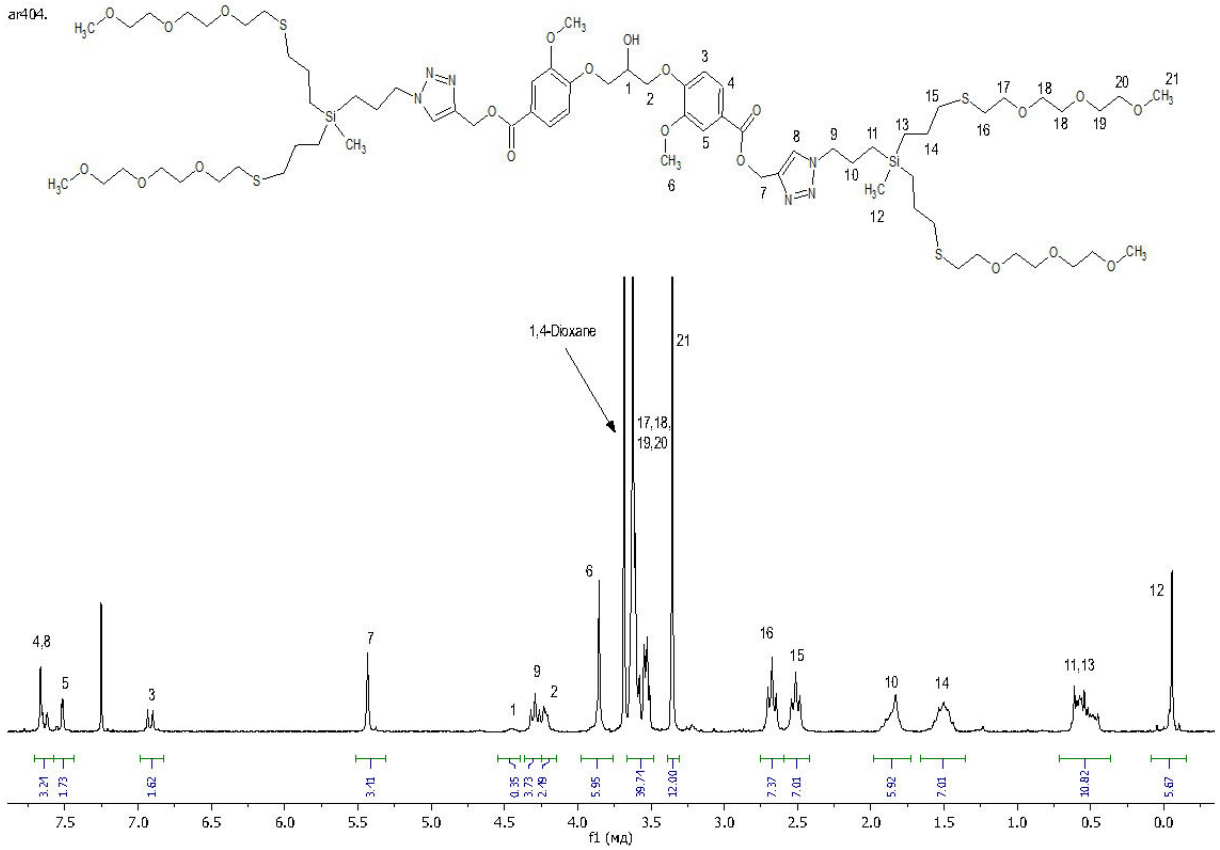
^{1}H NMR spectrum of compound **6**

Compound 5. Compound **3** (0.1 g, 0.21 mmol) was added to a solution of compound **4** (0.27 g, 0.47 mmol) in absolute 1,4-dioxane (2 mL). Then a catalytic amount of triethylamine and copper(I) iodide were added. The reaction mixture was stirred at 80 °C for 6 h. The resulting

mixture was evaporated on a rotary evaporator. The residue obtained was dried on an oil pump to give the target product in quantitative yield.



GPC curve of Janus dendrimer **5**



^{1}H NMR spectrum of Janus dendrimer **5**