

Supporting Information

A new method for the synthesis of diamantane by hydroisomerization of binor-S on treatment with sulfuric acid

Rishat I. Aminov†, Ravil I. Khusnutdinov

*Institute of Petrochemistry and Catalysis, Russian Academy of Sciences
pr. Oktyabrya 141, Ufa, Russia, 450075.*

†Correspondence should be addressed: e-mail: rishaminov@gmail.com.

Experimental

General procedures and materials

^1H and ^{13}C NMR spectra were measured on a Bruker Avance-III 400 Ascend instrument (400 MHz for ^1H and 100 MHz for ^{13}C in CDCl_3). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30 m \times 0.25 mm, helium as the carrier gas, temperature programming from 40 to 300°C at 8 °C/min, evaporation temperature of 280°C, ion source temperature of 200°C, and ionization energy of 70 eV). The elemental composition of the samples was determined on a Carlo Erba 1106 elemental analyzer. The course of the reaction and the purity of the products were monitored by gas liquid chromatography on a Shimadzu GC-9A, GC-2014 instrument [2 m \times 3 mm column, SE-30 silicone (5%) on Chromaton N-AW-HMDS as the stationary phase, temperature programming from 50 to 270°C at 8 °C/min, helium as the carrier gas (47 mL/min)].

The sonication was carried out with an ultrasound generator IL10-0.63 (INLAB LTD) for 180 min at a frequency of 22 kHz with a submerged of 15 mm diameter titanium horn, with output power 150 W. The reactions were carried out in a 100 \times 35 mm glass reactor equipped with a jacket to maintain the required temperature (20°C).

Preparation of diamantane.

Heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}. 0^{11,13}]tetradecane **2** (0.368 g, 2 mmol) and the solvent were charged into a glass reactor (V=100 mL). Then concentrated (98%) sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H_2SO_4 was added, the reaction mixture was stirred at 20°C for 15 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic phase was separated and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate : cyclohexane mixture.

Diamantane 1. White crystals, yield 65%, mp 244–245°C; ^1H NMR (400 MHz, CDCl_3): δ =1.72–1.80 (m, 20H). ^{13}C NMR (100 MHz, CDCl_3): δ =25.95 (C,⁴C⁹), 37.64 (C,³ C,⁵ C,⁸ C,¹⁰ C,¹³ C¹⁴), 38.37 (C,¹ C,² C,⁶ C,⁷ C,¹¹ C¹²). MS (EI, 70 eV): m/z (%)=188 [M]⁺ (100), 189 (15), 187 (18), 159 (10), 145 (8), 131 (23), 130 (18), 117 (12), 105 (13), 93 (12), 92 (11), 91(28), 77 (15), 67 (8). Calcd for $\text{C}_{14}\text{H}_{20}$: C, 88.29; H, 11.71; found C, 88.75; H, 11.25.

Preparation of endo-endo-pentacyclo[7.3.1.1^{5,8}.0.0^{3,7}]tetradecane (tetrahydrobinor-S).

Heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}. 0^{11,13}]tetradecane **2** (0.368 g, 2 mmol) was charged into a glass reactor (V=100 mL) and dissolved in cyclohexane (10 mL). Then 75-80%

sulfuric acid (1.96 g, 20 mmol) was added in portions with vigorous stirring. When the whole amount of H₂SO₄ was added, the reaction mixture was stirred at 20°C for 7 h. After completion of the reaction, 10% NaOH was added to the reaction mixture, the organic part was separated and filtered through a silica gel layer (with petroleum ether as the eluent). The solvent was distilled off and the residue was recrystallized from a 1:1 ethyl acetate : cyclohexane mixture.

Tetrahydrobinor-S 3c. White crystals, 68% yield, mp 104-106°C; ¹H NMR (400 MHz, CDCl₃): δ=0.95–0.98 (m, 4H), 1.38 (s, 8H), 1.66–1.71 (m, 4H), 1.99–2.01 (m, 2H), 2.12–2.16 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ=33.42 (C⁶, C⁹, C¹³, C¹⁴), 35.63 (C¹, C², C⁷, C⁸), 37.82 (C⁵, C¹⁰), 38.27 (C³, C¹²), 40.47 (C⁴, C¹¹). MS (EI, 70 eV): m/z (%)=188 [M]⁺ (100), 187 (35), 159 (24), 145 (23), 131 (38), 117 (25), 105 (39), 91 (82), 79 (57), 67 (29), 41 (47). Calcd for C₁₄H₂₀: C, 89.29; H, 10.71; found C, 89.14; H, 10.86.

Preparation of hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene and hexacyclo[6.6.0.0.2,6.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene

Heptacyclo[8.4.0.0^{2,12}.0^{3,8}.0^{4,6}.0^{5,9}.0^{11,13}]tetradecane **2** (0.368 g, 2 mmol) was charged into a glass reactor (V=100 mL) and dissolved in cyclohexane, then [Et₃NH]⁺[HSO₄]⁻ (1.99 g, 10 mmol) was added, and the reaction mixture was stirred at 40°C for 8 h. Then the reactor was cooled down to room temperature, and the reaction mixture was extracted with petroleum ether and filtered through a silica gel layer (with petroleum ether as the eluent).

Hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradecene-5 4a and hexacyclo[6.6.0.0.2,6.0^{5,14}.0^{7,12}.0^{9,13}]tetradecene-3 **4b (45:55)**

Colorless oil, 78% yield; **4a**: ¹H NMR (400 MHz, CDCl₃): δ = 1.04 (d, J = 7.2 Hz, 2H), 1.41 (d, J = 7.6 Hz, 2H), 1.95 (s, 2H), 2.09 (d, J = 7.2 Hz, 4H), 2.21 (d, J = 7.2 Hz, 2H) 2.56 (s, 2H), 5.87 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ=26.27 (C¹¹, C¹²), 34.62 (C¹⁰, C¹³), 36.34 (C¹, C¹⁴), 37.27 (C², C³), 40.68 (C⁴, C⁷), 44.68 (C⁸), 52.88 (C⁹), 134.82 (C⁵, C⁶). MS(EI, 70 eV): m/z (%)=184 [M]⁺ (44), 169 (14), 155 (16), 142 (34), 117 (100), 115 (37), 105 (22), 91 (73), 80 (38), 65 (17), 41 (21). **4b**: ¹H NMR (400 MHz, CDCl₃): δ = 1.19–1.24 (m, 1H), 1.31–1.36 (m, 1H), 1.48 (s, 1H), 1.56–1.59 (m, 2H), 1.71 (t, J = 6 Hz, 1H) 2.03–2.06 (m, 3H), 2.15–2.17 (m, 2H), 2.22 (s, 1H), 2.52 (s, 2H), 2.59 (s, 1H), 5.96–5.98 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ=24.08 (C¹⁰), 27.16 (C¹¹), 40.52 (C¹), 40.93 (C¹²), 42.30 (C¹⁴), 45.66 (C⁹), 47.38 (C²), 47.94 (C¹³), 48.61 (C⁷), 50.20 (C⁸), 54.09 (C⁵), 60.05 (C⁶), 133.69 (C⁴), 133.75 (C³). MS (EI, 70 eV): m/z (%)=184 [M]⁺ (40), 169 (21), 155 (45), 141 (45), 129 (51), 117 (100), 115 (53), 91 (88), 78 (43), 65 (21), 41 (20).

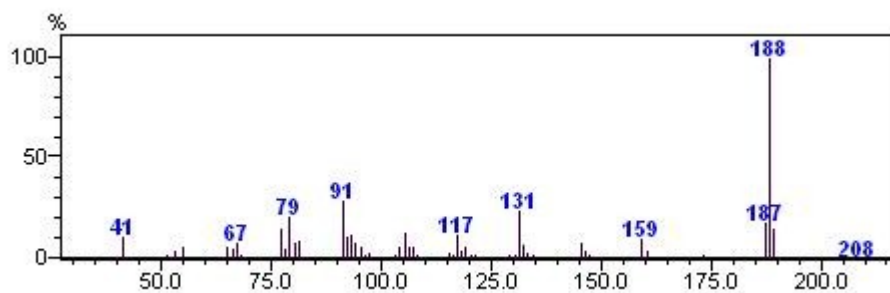


Figure S1. Mass spectrum of diamantane **1**

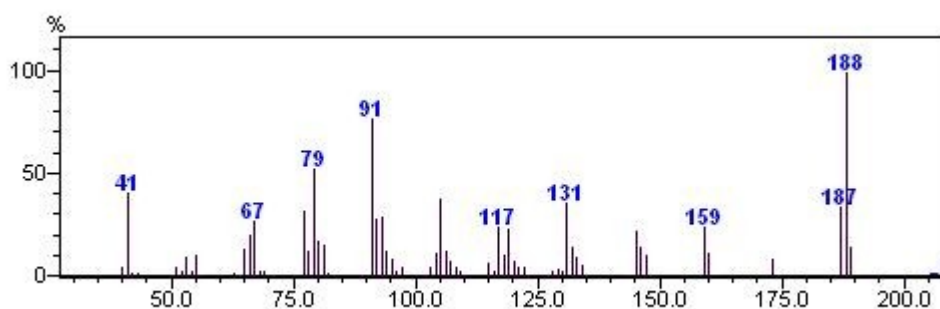


Figure S2. Mass spectrum of tetrahydrobinor-S **3c**

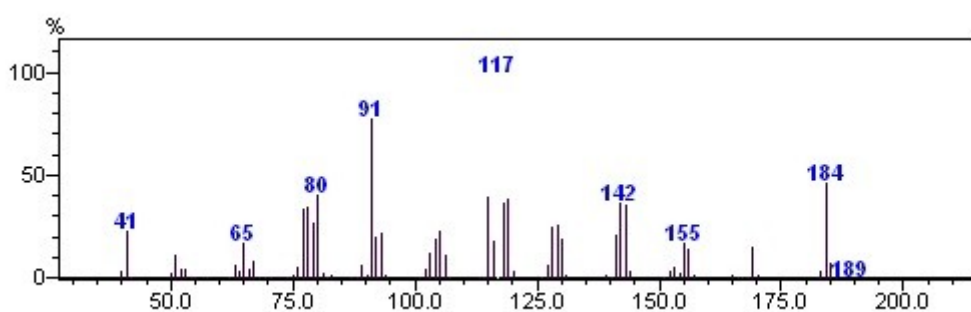


Figure S3. Mass spectrum of hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene **4a**

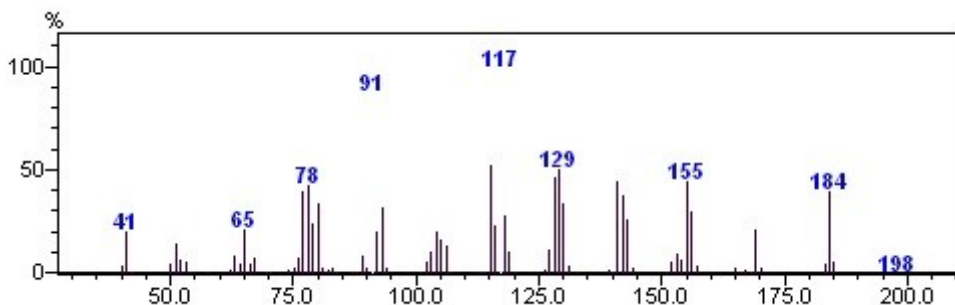


Figure S4. Mass spectrum of hexacyclo[6.6.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene **4b**

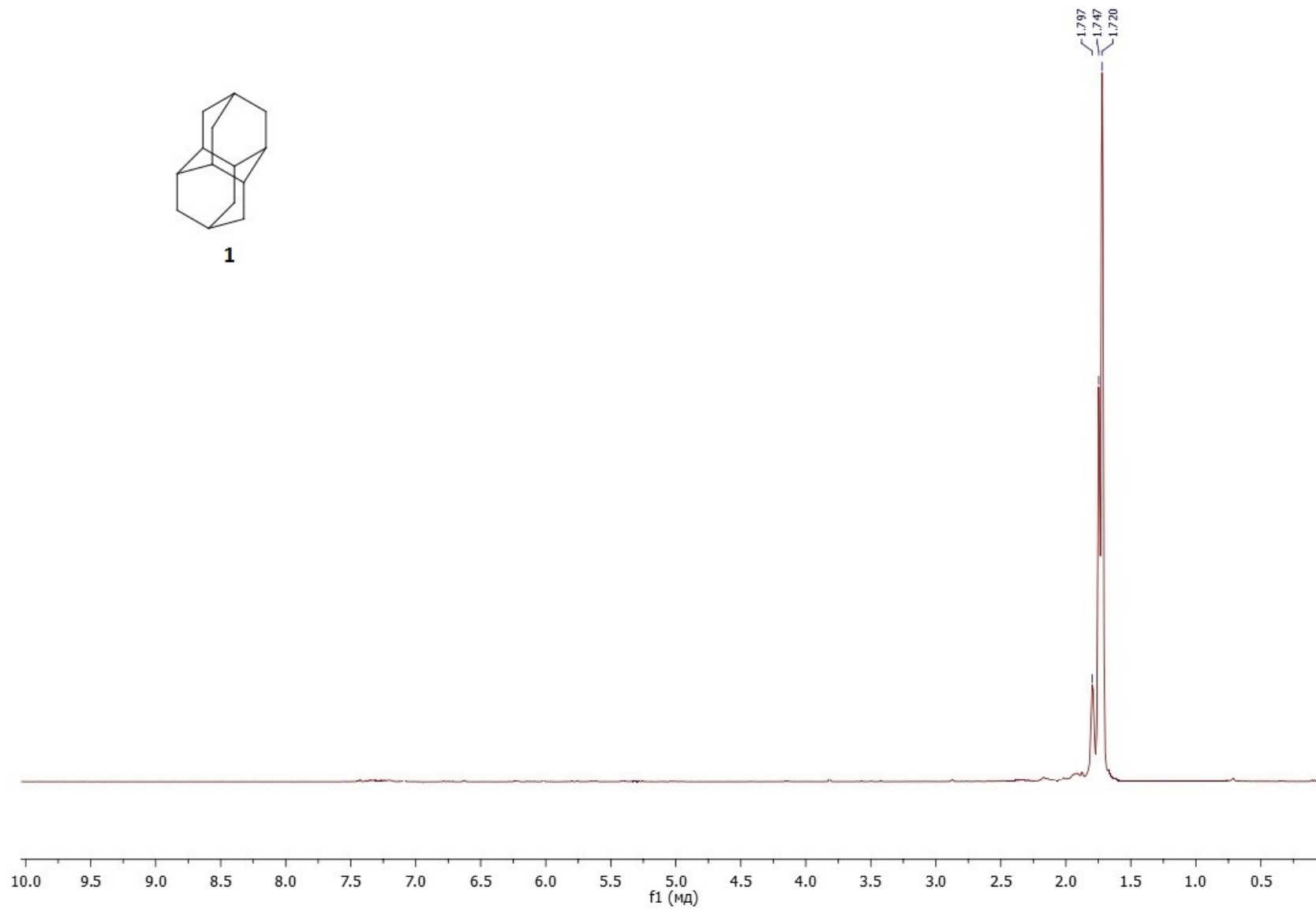
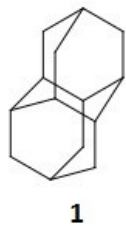


Figure S5. ^1H NMR spectrum of diamantane **1** in CDCl_3

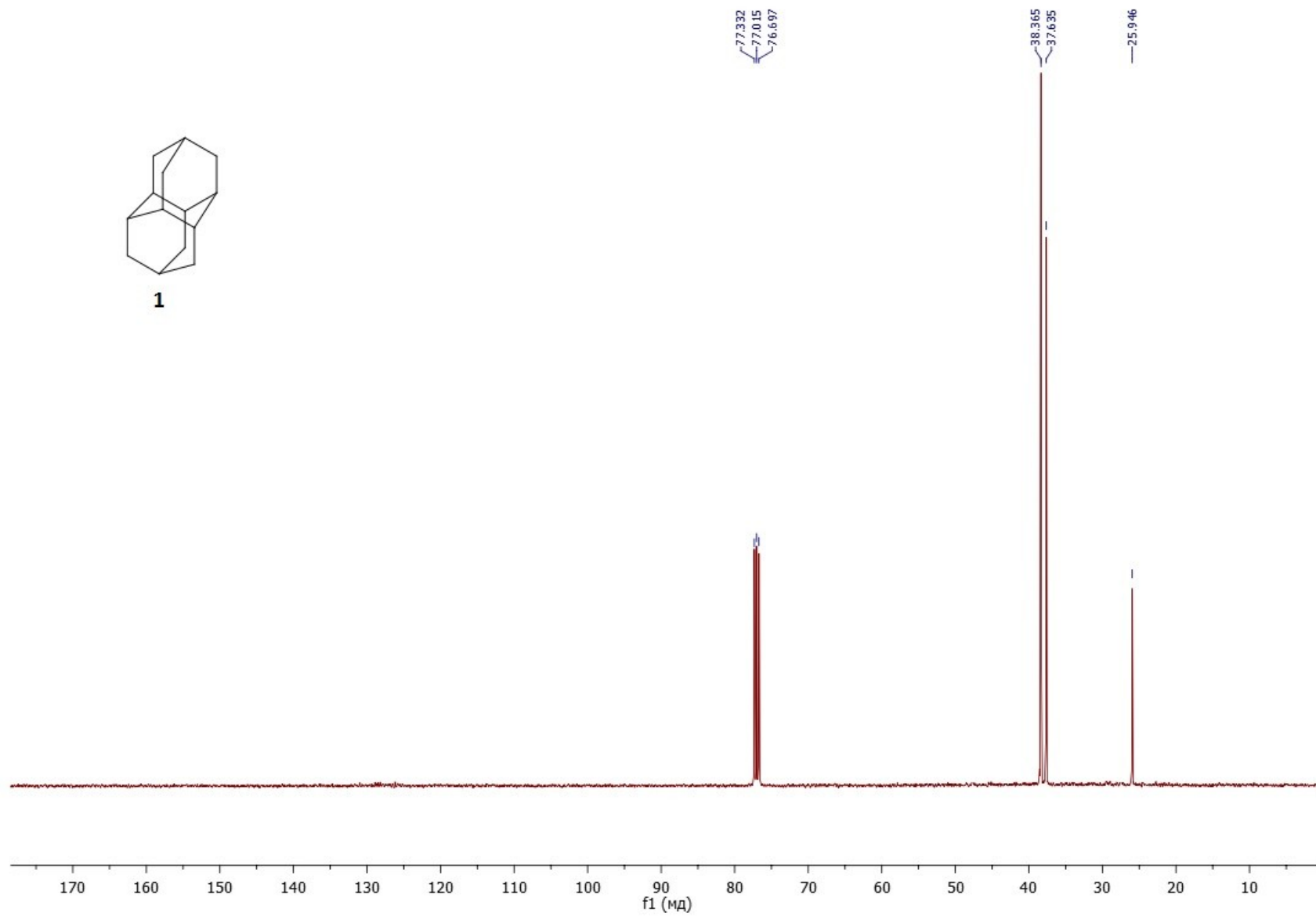


Figure S6. ¹³C NMR spectrum of diamantane **1** in CDCl₃

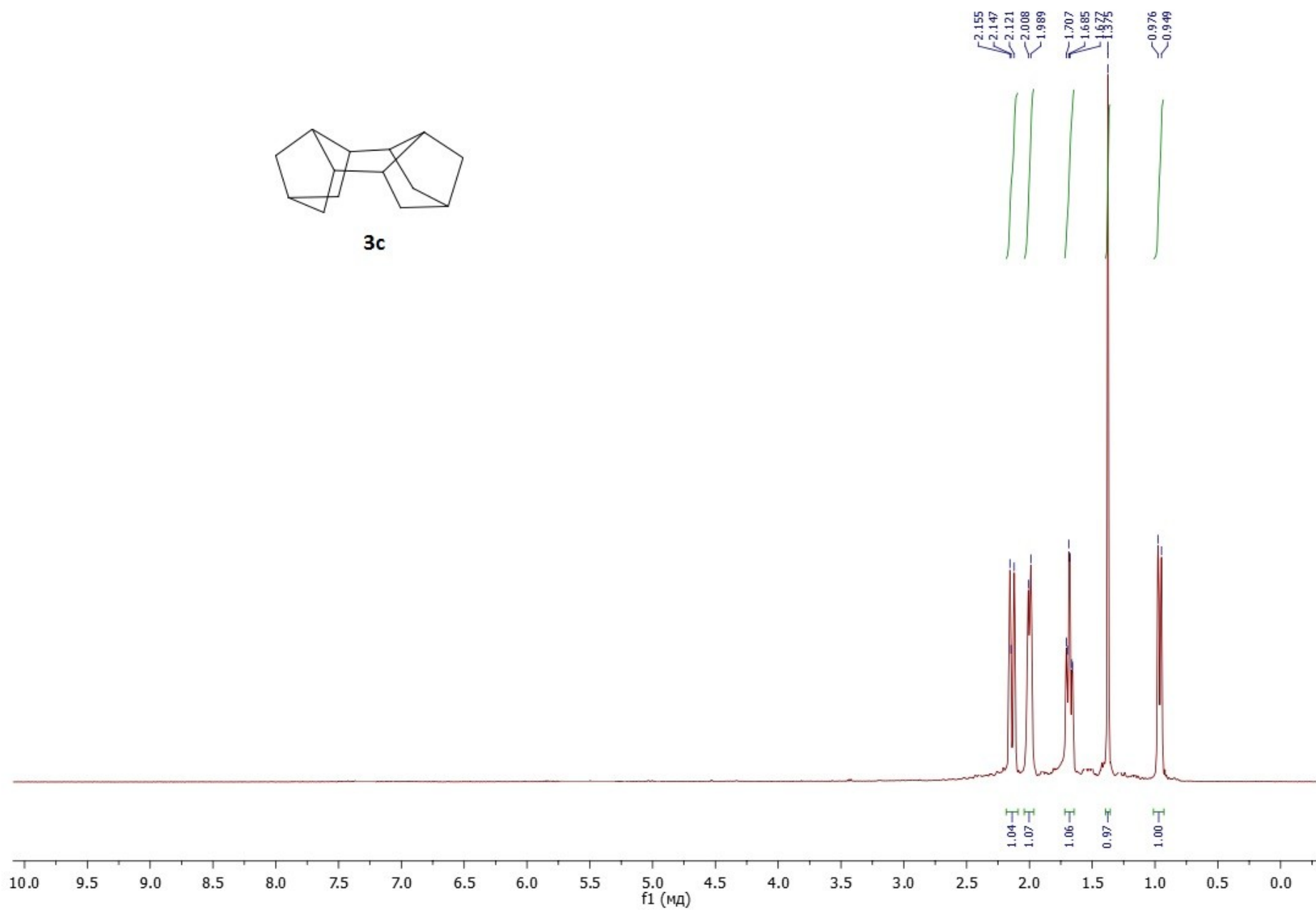


Figure S7. ¹H NMR spectrum of tetrahydrobinor-S **3c** in CDCl₃

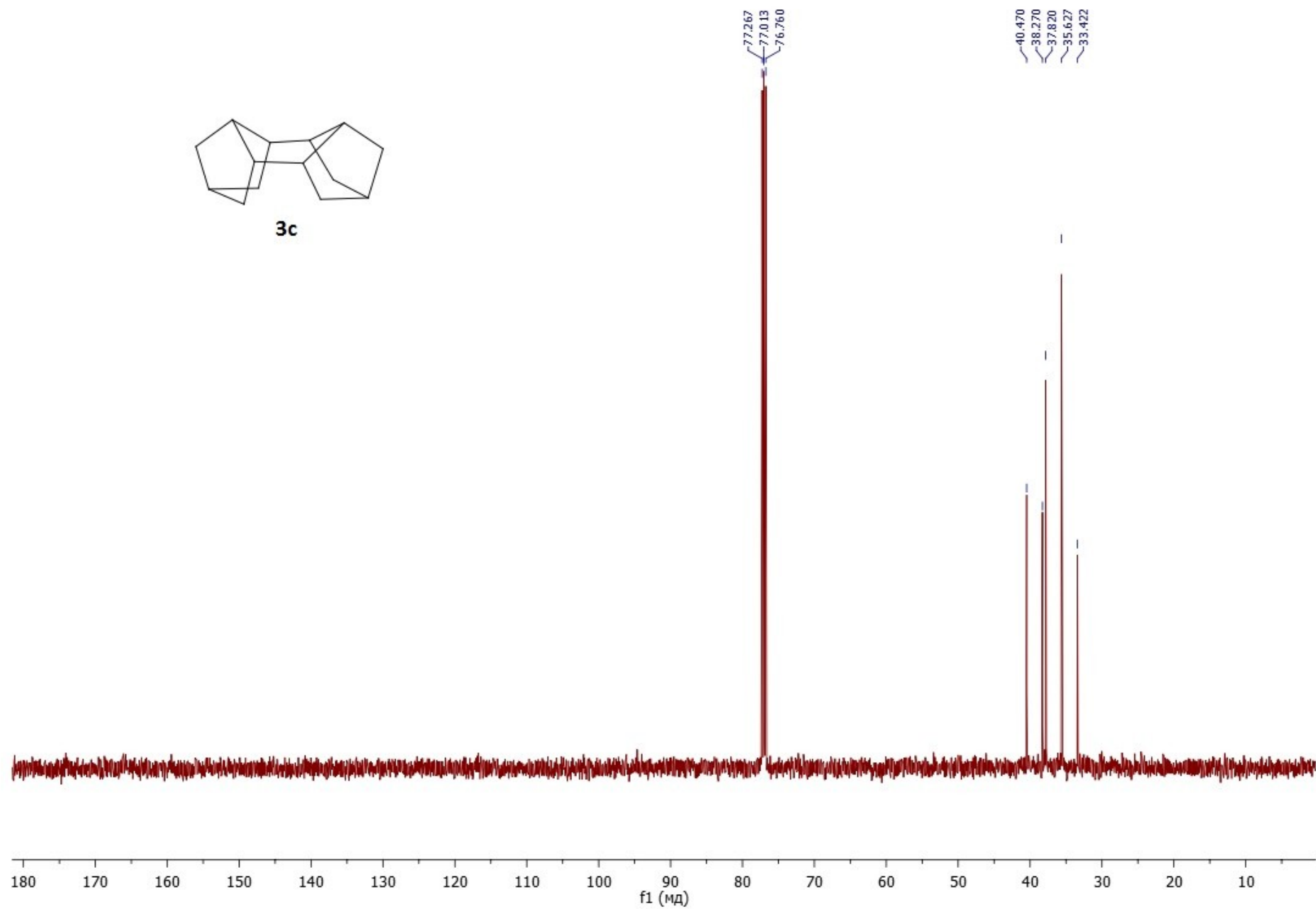


Figure S8. ^{13}C NMR spectrum of tetrahydrobinor-S **3c** in CDCl_3

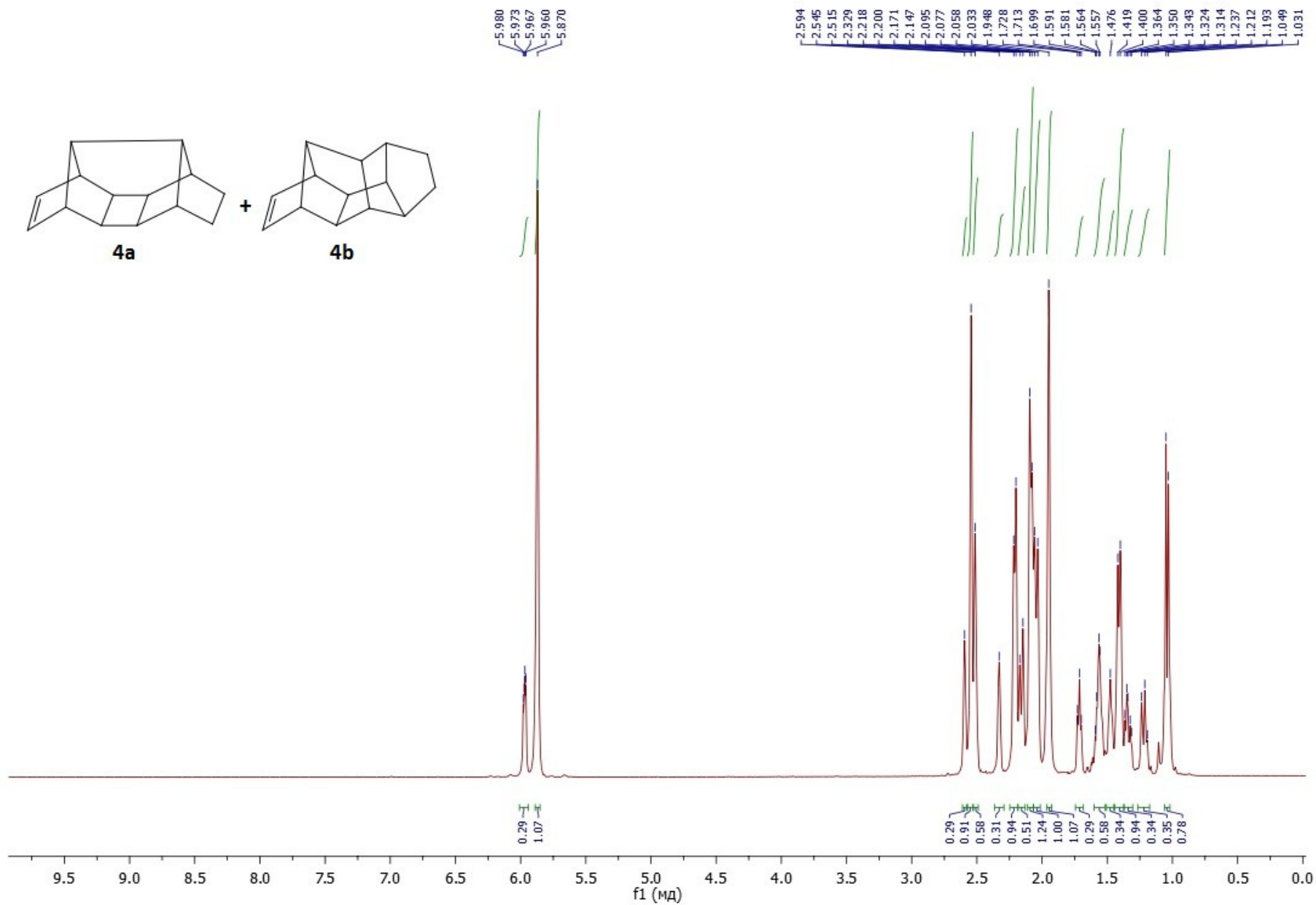


Figure S9. ¹H NMR spectrum of mixture hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene **4a** and hexacyclo[6.6.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene **4b** in CDCl₃

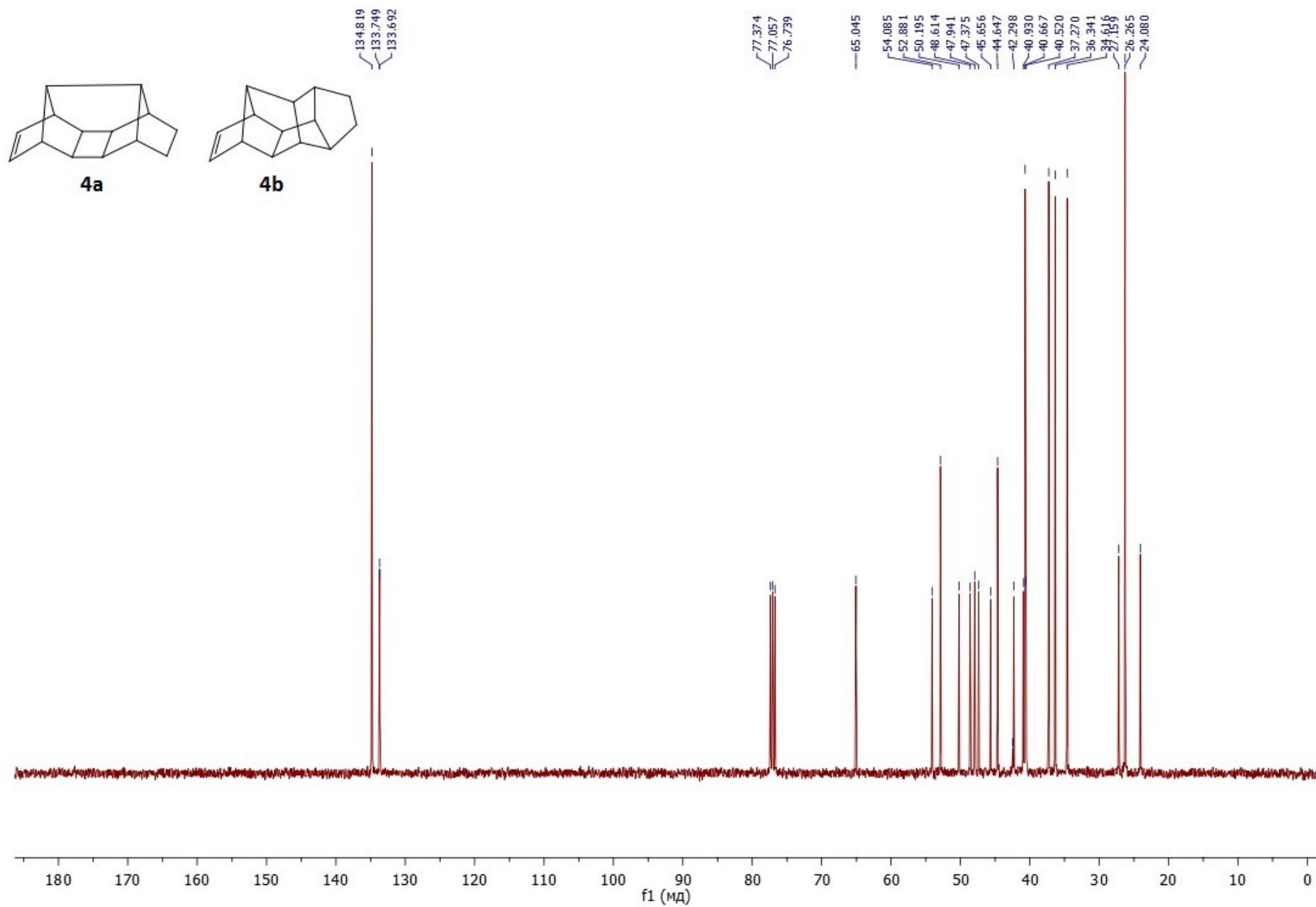


Figure S10. ^{13}C NMR spectrum of mixture hexacyclo[8.4.0.0^{2,7}.0^{3,14}.0^{4,8}.0^{9,13}]tetradec-5-ene **4a** and hexacyclo[6.6.0.0^{2,6}.0^{5,14}.0^{7,12}.0^{9,13}]tetradec-3-ene **4b** in CDCl_3