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Synthesis of diamantane by skeletal isomerization of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane induced by ionic liquids

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Contents

Experimental sections

General procedures and materials. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-II 400 Ascend instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C in $CDCl_3$). Mass spectra were run on a Shimadzu GCMS-QP2010Plus mass spectrometer (SPB-5 capillary column, 30m×0.25 mm, helium as the carrier gas, temperature programming from 40 to 300 °C at 8 K min^{-1}, evaporation temperature of 280 °C, ion source temperature of 200ºC, 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 × 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 K min^{-1}, helium as the carrier gas (47 ml min^{-1})].

Norbornadiene, dimethyl fumarate (Merck), hexane, tetrahydrofuran (Component-reagent), aluminum(III), iron(III), manganese(II), nickel(II), zinc(II), tin(II) and copper(II) chlorides, Pd/C (10%) (Acros), trimethyl- and triethylamine hydrochlorides, 1-ethyl-3-methyl- and 1-ethyl-3-buthylimidazolium chlorides (Aldrich) were commercial reagents.

(1-2:5-6-η-Cycloocta-1,5-diene)(1-6-η-cycloocta-1,3,5-triene)ruthenium was prepared as described [**S1**].

Pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene **5** was prepared as described [**S2**]. Colorless solid, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (dt, *J* = 8 Hz, 2H), 1.79 (dt, 2H, *J* = 8.0 Hz), 2.60 (qt, 1H, *J* = 8.0 Hz), 2.89–2.95 (m, 1H), 3.08–3.09 (m, 2H), 3.34–3.38 (m, 4H), 5.37 (d, 2H, *J* = 4 Hz), 5.55 (dd, 2H, *J* = 4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.84 (C^{7,9}), 48.20 (C^8), 52.25 (C^{6,10}), 55.49 (C^1), 56.68 (C^{3,13}), 58.08 (C^{2,14}), 130.01 (C^{5,11}), 134.57 (C^{4,12}). MS (EI, 70 eV): m/z (%) 184 [M]$^+$ (100). Anal. Calcd. C, 91.25 H, 8.75. Found C, 90.99 H, 9.01.

Preparation of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradecane 4. A glass reactor was charged with the Pd/C catalyst (0.05 g) and hydrocarbon **5** (0.5 g) dissolved in hexane (15 ml). Hydrogenation of norbornadiene dimer was carried out at room temperature (1 atm H_2). After completion of the reaction, the reaction mixture was filtered through a silica gel layer (elution with hexane). Colorless solid, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.07–1.14 (m, 3H), 1.18–1.35 (m, 11H), 1.49–1.54 (m, 2H), 1.55–1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 30.42 (C^{4,12}), 34.59 (C^{5,11}), 41.52 (C^{7,9}), 44.46 (C^{6,10}), 45.55 (C^8), 51.15 (C^{3,13}), 60.30 (C^1), 60.77 (C^{2,14}). MS (EI, 70 eV): m/z (%) 188 [M]$^+$ (100). Anal. Calcd. C, 89.29 H, 10.71. Found C, 89.85 H, 10.15.

Preparation of the ionic liquids. The ionic liquids were prepared by direct reactions of metal halides with Me_3N-HCl, Et_3N-HCl, EMIM-Cl, or BMIM$^-$Cl. A glass reactor (*V* = 100 ml) was charged under argon with Me_3N-HCl, Et_3N-HCl, EMIM-Cl, or BMIM$^-$Cl (1 equiv.) and metal chloride (Al^{III}, Fe^{III}, Mn^{II}, Ni^{II}, Zn^{II}, Sn^{II}, Cu^{II}, 3 equiv.). The reaction was carried out with continuous stirring at 70-80 °C for 3-5 h. In the case of reactions involving $CuCl_2$ (0.05 mmol) was added to the prepared ionic liquid, and the mixture was stirred for additional 1 h at room temperature.

Synthesis of diamantane 1. Hydrocarbon **4** (1 mmol) and pre-synthesized ionic liquid (3 mmol) were charged into a glass reactor (*V* = 100 ml) under argon. The reaction was conducted with continuous stirring at 50 °C for 6 h. Then the reactor was cooled to room temperature, and the reaction mixture was extracted with petroleum ether and filtered through a silica gel layer (elution with petroleum ether). Diamantane **1** was separated from the starting hydrocarbon **4** by multiple recrystallization. Colorless crystals, yield 85%, mp 244–245 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.72–1.80 (m, 20H).^{13}C NMR (100 MHz, $CDCl_3$): δ=25.93 (C,^{4}C^9), 37.62 (C,^{3} C,^{5} C,^{8} C,^{10} C,^{13} C^{14}), 38.36 (C,^{1} C,^{2} C,^{6} C,^{7} C,^{11} C^{12}). 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 $C_{14}H_{20}$: C, 88.29; H, 11.71; found C, 88.75; H, 11.25

References

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S2. P. Pertici, G. Vitulli, M. Paci and L. Porri, *J. Chem. Soc., Dalton Trans.*, 1980, 1961.

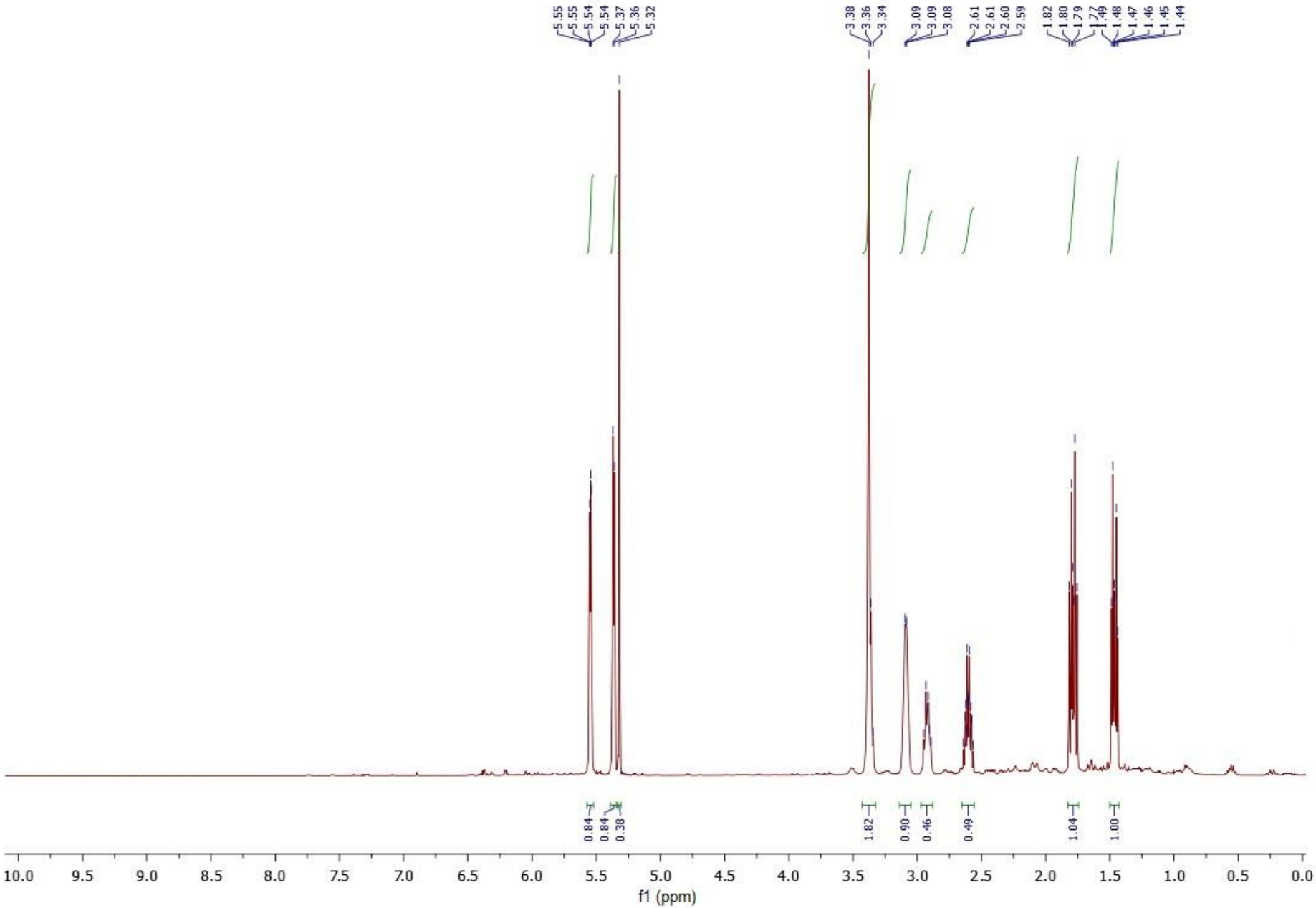

Figure S1. ^{1}H NMR spectrum of pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene **5** in $CDCl_3$

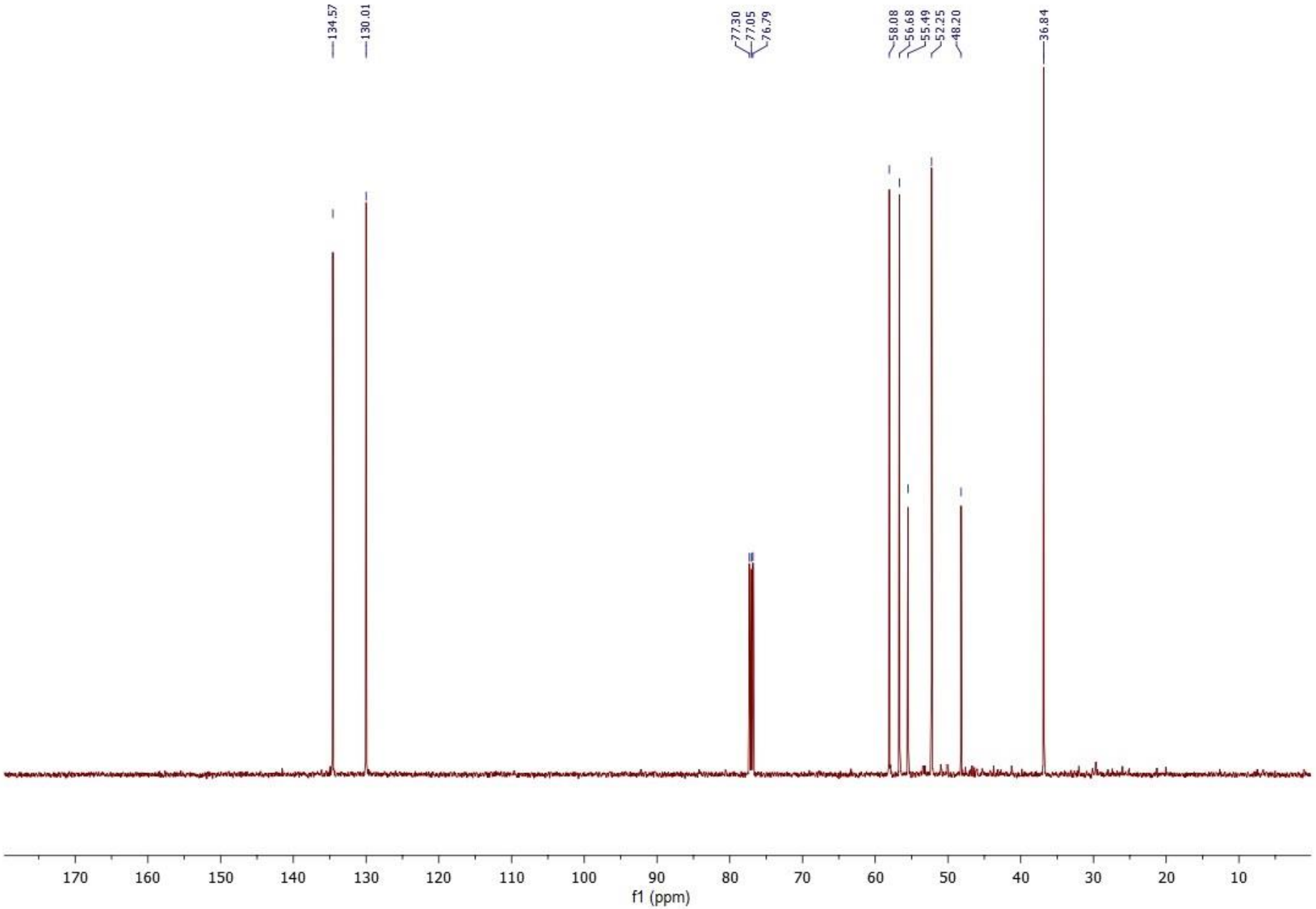

Figure S2. ^{13}C NMR spectrum of pentacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{10,14}]tetradeca-4,11-diene **5** in $CDCl_3$

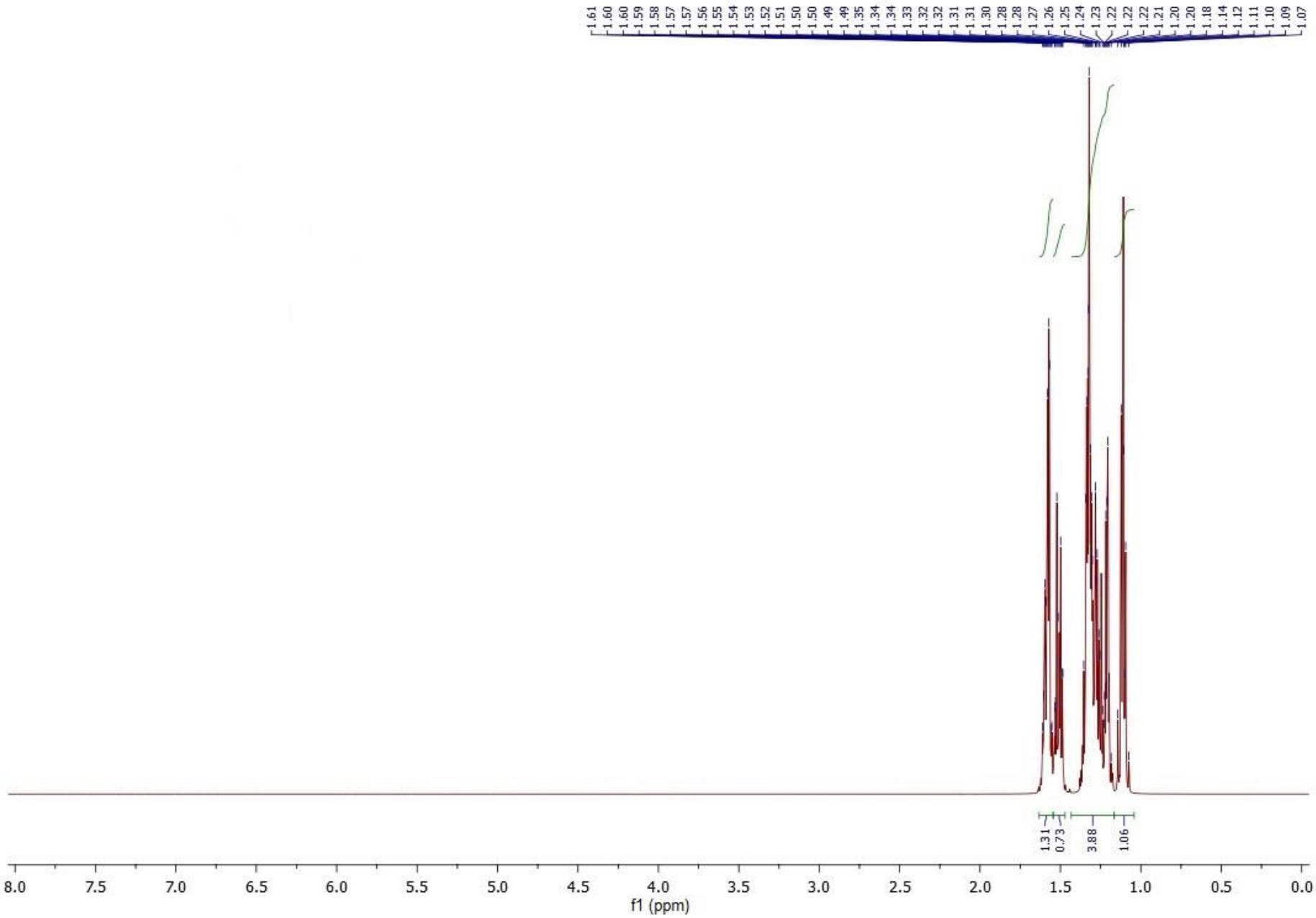

Figure S3. ^{1}H NMR spectrum of pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradecane **4** in $CDCl_3$

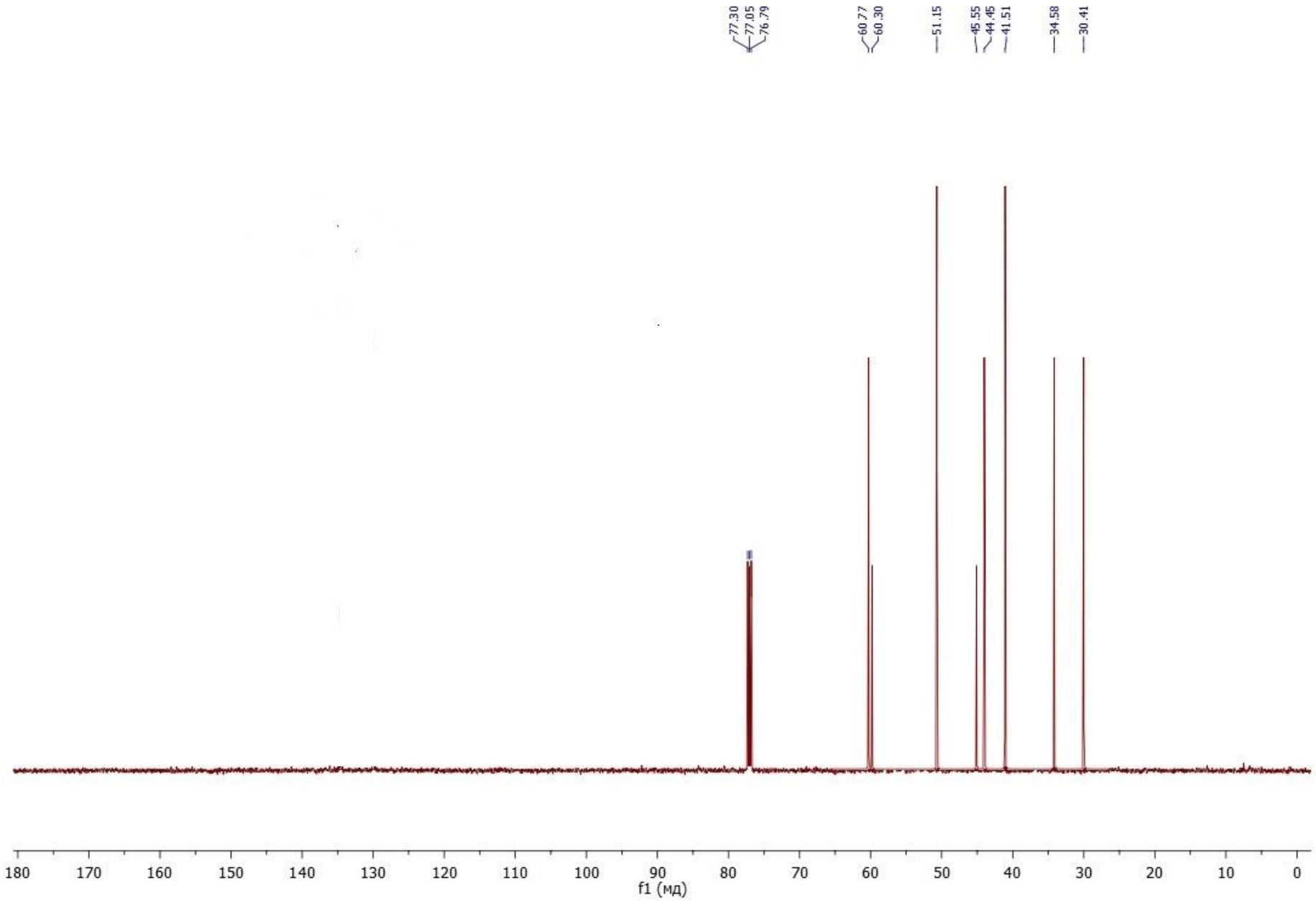

Figure S4. ^{13}C NMR spectrum of pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradecane **4** in $CDCl_3$

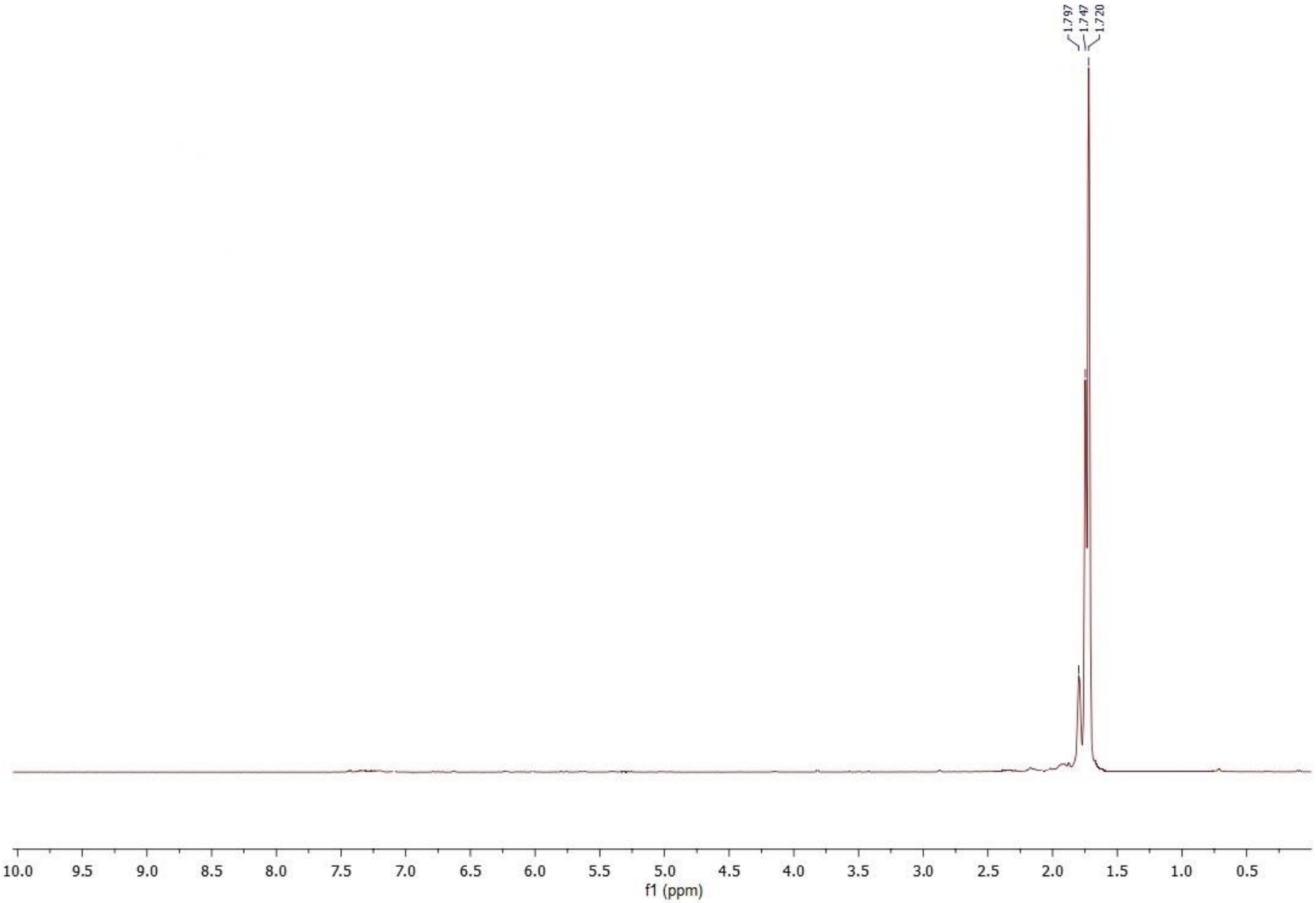

Figure S5. ^{1}H NMR spectrum of diamantane **1** in $CDCl_3$

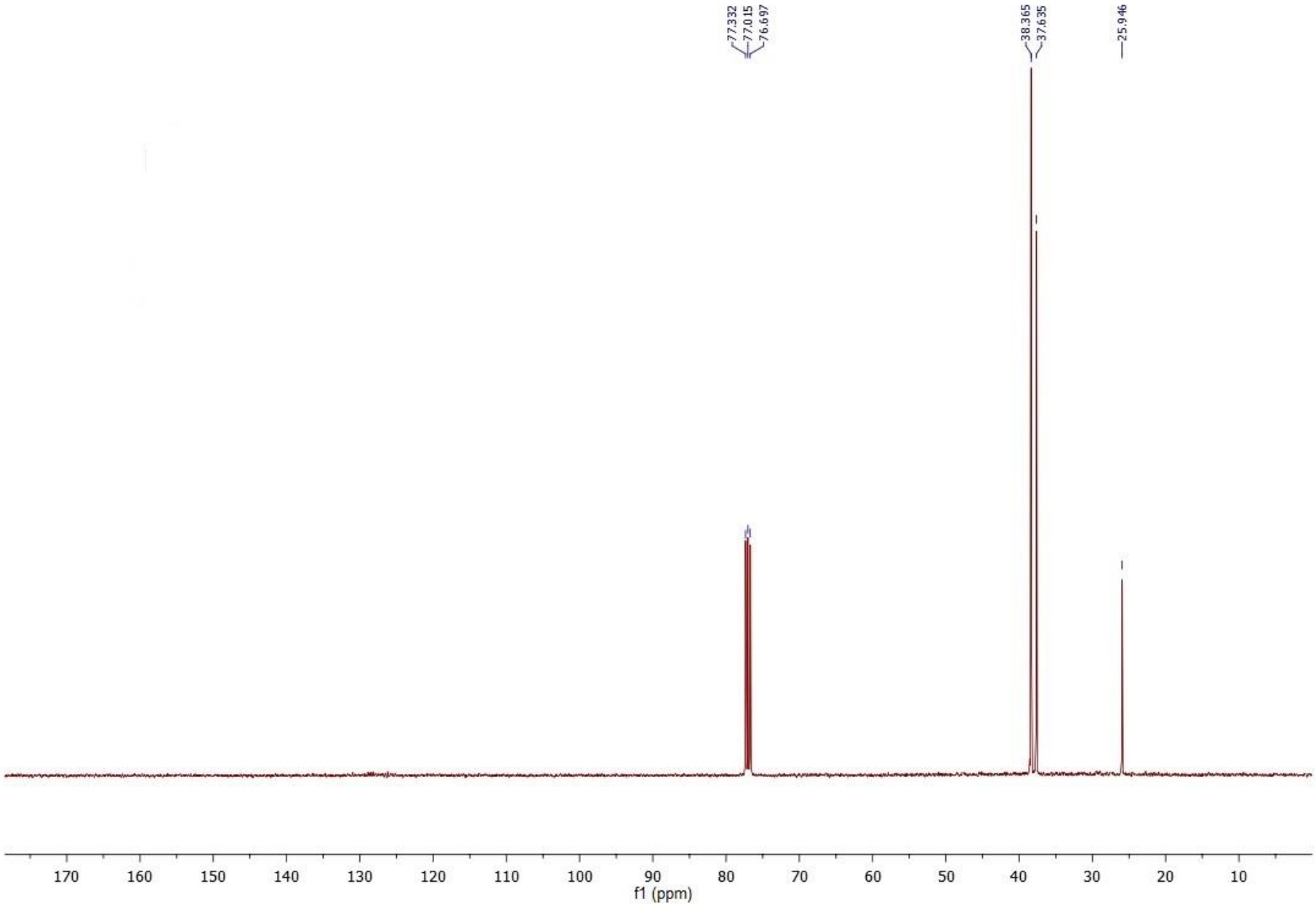

Figure S6. ^{13}C NMR spectrum of diamantane **1** in $CDCl_3$