Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 509–511

Synthesis of diamantane from new polycyclic hydrocarbons C_{14} under the action of ionic liquids

Rishat I. Aminov

Contents

Experimental sections S2
General procedures and materials S2
General procedure for the preparation of unsaturated polycyclic hydrocarbons **3a**, **3b** and **6a**, **6b** S2
General procedure for the preparation of cyclopropane-containing hydrocarbons **2** and **5a**, **5b** S3
Preparation of ionic liquids S4
General procedure for the preparation of hydrocarbons **4** and **7** S4
Synthesis of diamantane S5
References S5
Mass spectrum of compounds **1-7** S6
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1** S9
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1** S10
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**, **3b** S11
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**, **3b** S12
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2** S13
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2** S14
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4** S15
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4** S16
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6a**, **6b** S17
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6a**, **6b** S18
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**a, **5b** S19
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5a**, **5b** S20
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7** S21
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7** S22

EXPERIMENTAL SECTION

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 $CDCl_3$) and Bruker Avance-III HD 500 Ascend instrument (500 MHz for ^{1}H and 125 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°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 [2m×3mm 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)].

Norbornadiene, dicyclopentadiene, 5-methylnorbornene (Merck), sulfuric acid (SigmaTec), cyclohexane (Component-reagent), aluminum chloride, Pd/C (10%) (Acros), triethylamine hydrochloride (Aldrich) commercial reagents.

General procedure for the preparation of unsaturated polycyclic hydrocarbons 3a, 3b and 6a, 6b.

Dicyclopentadiene (5.28 g, 0.04 mol)) and norbornadiene (7.37 g, 0.08 mol) or 5-methylnorbornene (8.65 g, 0.08 mol) were loaded into a steel autoclave (V = 17 ml). The autoclave was hermetically sealed and heated at 190 °C for 18–20 h with constant stirring. After completion of the reaction, the autoclave was cooled to room temperature. Pure samples of the obtained hydrocarbons **3a,b** and **6a,b** was obtained by distillation under vacuum.

exo-*endo*-**3a**, *endo*-*endo*-Tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-diene **3b**.[S1,S2] (70:30). Colorless oil, 69% yield; **3a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.99 (d, J = 12 Hz, 1H), 1.51 (d, J = 8 Hz, 2H), 1.63 (d, J = 8 Hz, 1H), 2.22 (s, 2H), 2.50 (s, 2H), 2.70 (s, 2H) 6.06 (s, 2H), 6.23 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.41 (C^{11}), 42.65 ($C^{3,6}$), 44.39 ($C^{1,8}$), 48.09 ($C^{2,7}$), 55.65 (C^{12}), 136.11 ($C^{4,5}$), 141.23 ($C^{9,10}$). MS (EI, 70 eV): m/z (%) 158 $[M]^+$ (2), 157 (5), 129 (12), 117 (21), 106 (63), 91 (20), 77 (100), 66 (15), 41 (9). **3b**:

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54-1.55 (m, 4H), 2.57-2.62 (m, 4H), 2.77 (m, 2H), 5.32–5.33 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.99 ($C^{11,12}$), 44.53 ($C^{1,3,6,8}$), 55.54 ($C^{2,7}$), 131.45 ($C^{4,5,9,10}$). MS (EI, 70 eV): m/z (%) 158 $[M]^+$ (2), 157 (4), 129 (17), 117 (28), 105 (32), 91 (100), 79 (68), 66 (13), 41 (9). $C_{12}H_{14}$.

exo-*exo*-**6a**, *endo*-*exo*-5-Methyl-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4-ene **6b** (55:45). Colorless oil, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.39–0.42 (m, 2H), 0.65 (d, J = 8 Hz, 3H), 0.72 (d, J = 8 Hz, 3H), 0.88 (d, J = 4 Hz, 1H), 0.97 (d, J = 8 Hz, 1H), 1.18–1.21 (m, 1H), 1.29–1.33 (m, 1H), 1.69–1-86 (m, 6H), 1.87–2.00 (m, 11H), 2.14–2.16 (m, 2H), 2.30–2.32 (m, 2H), 2.84 (t, J = 8 Hz, 1H), 5.94–5.96 (m, 1H), 6.01–6.03 (m, 1H). **6a**: ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.40 (CH_3), 30.28 (C^5), 36.09 (C^4), 39.63 (C^6), 40.64 (C^3), 40.85 ($C^{1,8}$), 44.73 (C^{12}), 46.50 (C^{11}), 47.86 (C^7), 49.06 (C^2), 135.16 (C^{10}), 135.43 (C^9). MS (EI, 70 eV): m/z (%) 174 $[M]^+$ (10), 159 (3), 132 (8), 117 (10), 91 (17), 66 (22), 41 (11). **6b**: ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.25 (CH_3), 36.12 (C^5), 38.58 (C^4), 38.88 (C^6), 40.85 (C^3), 41.88 ($C^{1,8}$), 46.64 (C^7), 46.67 (C^2), 47.05 (C^{11}), 49.61 (C^{12}), 135.64 (C^{10}), 136.19 (C^9). MS (EI, 70 eV): m/z (%) 174 $[M]^+$ (30), 148 (80), 133 (20), 119 (23), 106 (34), 91 (45), 81 (100), 66 (77), 53 (23), 41 (39). $C_{13}H_{18}$.

General procedure for the preparation of cyclopropane-containing hydrocarbons 2 and 5a, 5b.

At 0 °C under argon, a glass reactor (V=100 ml) was charged successively with dichloromethane (15 ml), hydrocarbons **3a**,**b** or **6a**,**b** (5 mmol), Et_3Al (30 mmol for **3** or 20 mmol for **6**) and CH_2I_2 (30 mmol for **3** or 20 mmol for **6**), and this was stirred at room temperature for 6-10 hours. After completion of the reaction, the mixture was cooled to -10°C and treated with 10% HCl solution. The aqueous layer was extracted with ethyl acetate (3×10 ml), the extract was combined with organic. The solvent was evaporated on a rotary evaporator. Individual compounds were isolated by distillation under reduced pressure.

exo,*endo*-Hexacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{10,12}]tetradecane **2**. Colorless oil, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05–0.13 (m, 2H), 0.58–0.69 (m, 6H), 0.74–0.77 (m, 2H), 1.04-1.07 (m, 1H), 1.84-1.88 (m, 3H), 2.22 (s, 2H) 2.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.30 (C^5), 4.40 (C^{11}) 13.62 ($C^{4,6}$), 18.17 ($C^{10,12}$), 22.48 (C^{14}), 29.58 (C^{13}), 35.89 ($C^{3,7}$), 39.39 ($C^{2,8}$), 52.52 ($C^{1,9}$). MS (EI, 70 eV): m/z (%) 186 $[M]^+$ (4), 157 (3), 129 (12), 117 (16), 106 (100), 91 (93), 78 (74), 66 (12), 41 (15) . Anal. Calcd. C, 90.26 H, 9.74. $C_{14}H_{18}$. Found C, 90.08 H, 9.92.

exo,exo-**5a**, *endo*-*exo*-4-Methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane **5b** (55:45). Colorless oil, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.02–0.06 (m, 2H), 0.37–0.39 (m, 1H), 0.53–0.54 (m, 2H), 0.57-0.61 (m, 2H), 0.77–0.80 (m, 4H), 0.92 (dd, 5H, *J* = 4 Hz), 1.01-1.08 (m, 4H), 1.27–1.39 (m, 4H), 1.56–1.63 (m, 3H), 1.79-1.87 (m, 3H), 2.00–2.10 (m, 3H), 2.20 (d, 2H, *J* = 12 Hz), 2.27 (d, 1H, *J* = 8 Hz), 2.34 (br.s, 4H). **5a**: ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.18 (C^{10}),12.92 (C^{11}), 13.30 (C^9), 21.61 (CH_3), 29.03 (C^4), 35.79 (C^5), 37.36 (C^{12}), 38.45 (C^{13}), 40.14 (C^6), 40.31 (C^2), 40.56 (C^1), 41.65 (C^8), 43.51 (C^3), 50.19 (C^7). MS (EI, 70 eV): m/z (%) 188 $[M]^+$ (4), 160 (3), 147 (10), 131 (11), 109 (22), 91 (46), 79 (75), 66 (82), 41 (17). **5b**: ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.34 (C^{10}), 13.17 (C^{11}), 13.49 (C^9), 16.97 (CH_3), 28.89 (C^4), 32.16 (C^5), 38.09 (C^{12}), 38.34 (C^{13}), 40.27 (C^6), 40.52 (C^2), 41.51 (C^1), 42.41 (C^8), 51.29 (C^3), 51.88 (C^7); MS (EI, 70 eV): m/z (%) 188 $[M]^+$ (38), 173 (25), 160 (36), 146 (61), 131 (68), 119 (54), 109 (66), 109 (78), 79 (12), 67 (60), 41 (30). $C_{14}H_{20}$.

Preparation of ionic liquids.

The ionic liquid was prepared by direct reactions of aluminum halide with triethylamine hydrochloride. A glass reactor (*V* = 100 ml) was charged under argon with Et_3N-HCl (1.7 g, 12 mmol) and $AlCl_3$ (3.3 g, 24 mmol). The reaction was conducted with continuous stirring at 80°C for 3 h. In experiments with palladium on coal, Pd/C (10%) 5 wt% was added to the prepared ionic liquid, and the mixture was stirred for an additional 3 h at room temperature.

General procedure for the preparation of hydrocarbons 4 and 7.

Hydrocarbons **2** or **5a**,**b** (2 mmol) was placed into a glass reactor (*V* = 100 ml) and dissolved in cyclohexane (20 ml). Then 98% sulfuric acid (20 mmol) was added in portions with vigorous stirring. After the whole amount of H_2SO_4 was added, the reaction mixture was stirred at 20°C for 7 h. After completion of the reaction, a 5% solution of NaOH was added to the reaction mixture, and the organic phase was separated and filtered through a silica gel layer (elution with petroleum ether). The solvent was distilled off.

Pentacyclo[5.3.1.1^{3,7}.0^{2,8}.0^{4,5}]tetradecane **4**. Colorless oil, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ. 0.04-0.17 (m, 2H), 0.89-0.91 (m, 6H), 1.29-1.33 (m, 1H), 1.46-1.68 (m, 5H), 1.83 (s, 2H), 2.33 (s, 2H), 2.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.34 (C^{5}), 14.13 (C^{11}), 18.97 (C^{4,6}), 28.62 (C^{10,12}), 43.48 (C^{13}), 44.24 (C^{14}), 46.61 (C^{1,9}), 47.72 (C^{3,7}), 48.19 (C^{2,8}). MS (EI, 70 eV): m/z (%) 188 [M]$^{+}$ (100), 173 (12), 159 (13), 146 (15), 131 (23), 117 (17), 106 (16), 91 (47), 79 (28), 66 (12), 41 (12). Anal. Calcd. C, 89.29 H, 10.71. $C_{14}H_{20}$. Found C, 88.94 H, 11.06.

exo,*exo*-4-Methyltetracyclo[6.3.1.1^{3,6}.0^{2,7}]tridecane **7**. Colorless oil, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ. 0.73-0.77 (m, 1H), 0.94 (s, CH_3), 1.24–1.32 (m, 3H), 1.37–1.42 (m, 2H), 1.45–1.58 (m, 8H), 1.62–1.75 (m, 3H), 1.87 (d, J = 12 Hz, 1H), 1.97-2.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.71 (CH_3), 24.37 (C^{9,11}), 24.93 (C^{10}), 26.44 (C^{4}), 28.53 (C^{5}), 28.95 (C^{13}), 29.16 (C^{12}), 30.59 (C^{6}), 34.44 (C^{2}), 35.62 (C^{1}), 36.18 (C^{8}), 41.52 (C^{3}), 42.37 (C^{7}). MS (EI, 70 eV): m/z (%) 190 [M]$^{+}$ (43), 161 (90), 133 (15), 119 (14), 115 (30), 91 (22), 81 (100), 67 (38), 41 (16). Anal. Calcd. C, 88.35 H, 11.65. $C_{14}H_{22}$. Found C, 88.01 H, 11.99.

Synthesis of diamantane 1.

Hydrocarbon **2**, **4**,**5a,b** or **7** (1 mmol) and pre-synthesized ionic liquid $[Et_3NH]^+[Al_2Cl_7]^-$ (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 mixture was extracted with petroleum ether and filtered through a silica gel layer (elution with petroleum ether). White crystals, yield 76-83%, 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), 187 (7), 159 (5), 131 (12), 117 (5), 106 (6), 91 (13), 79 (10), 67 (4), 41 (5). Anal. calcd. C, 88.29; H, 11.71. $C_{14}H_{20}$. Found C, 88.64; H, 11.36.

References

S1 A. P. Marchand and J. E. Rose, *J. Am. Chem. Soc*., 1968, **9**, 3724.

S2 V. E. U. Costa, M. E. S. Mollmann and V. B. Riatto, *Synth. Commun*., 1995, **25**, 2091.

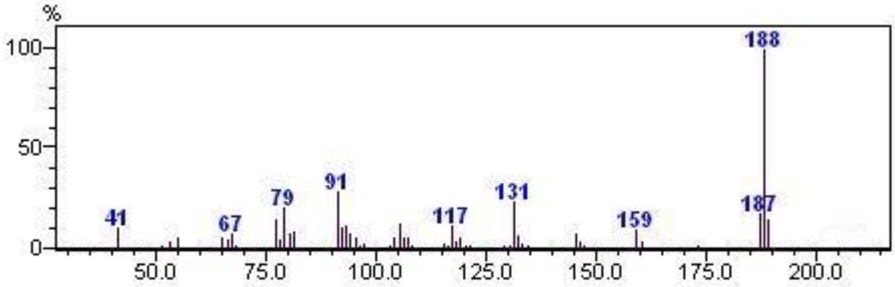

Figure S1. Mass spectrum of diamantane **1**

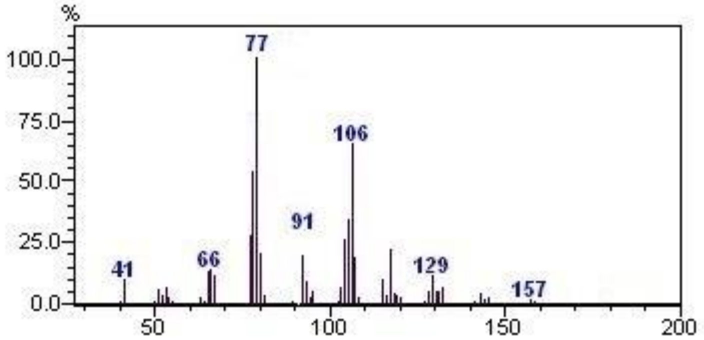

Figure S2. Mass spectrum of *exo,endo*-tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-diene **3a**

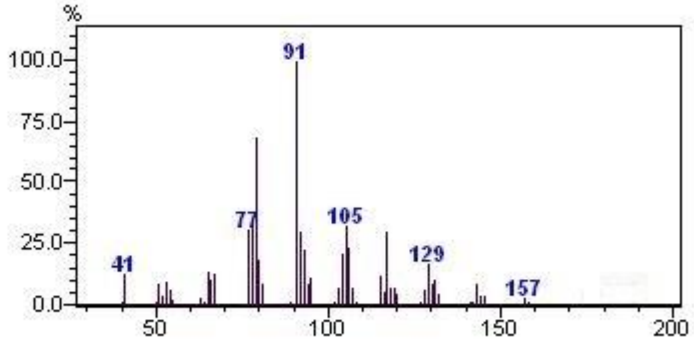

Figure S3. Mass spectrum of *endo,endo*-tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-diene **3b**

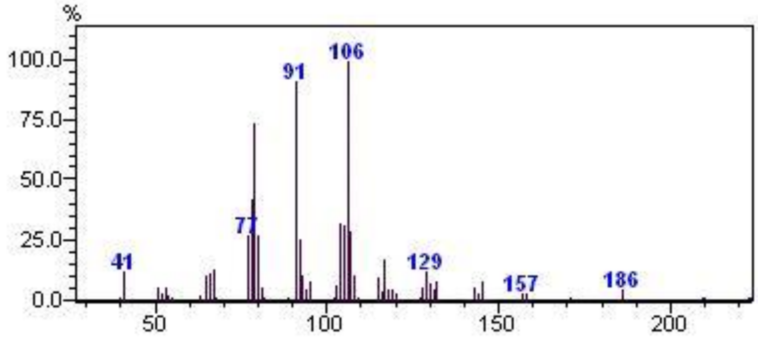

Figure S4. Mass spectrum of *exo,endo*-hexacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{10,12}]tetradecane **2**

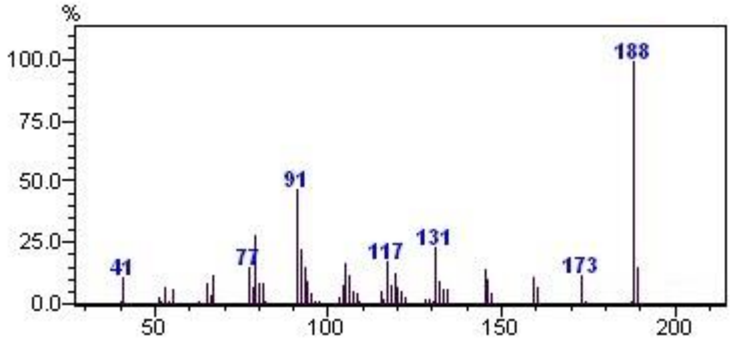

Figure S5. Mass spectrum of pentacyclo[5.3.1.1^{3,7}.0^{2,8}.0^{4,5}]tetradecane **4**

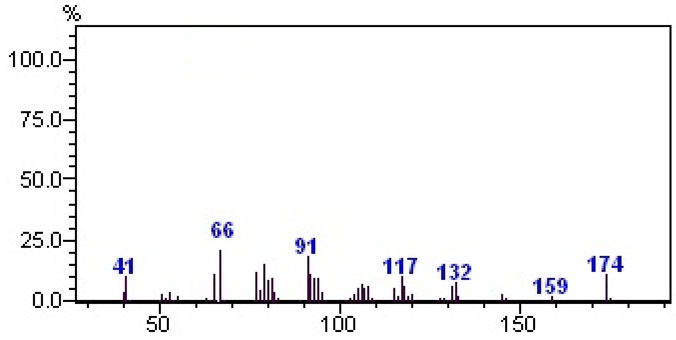

Figure S6. Mass spectrum of *exo,exo*-5-Methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4-ene **6a**

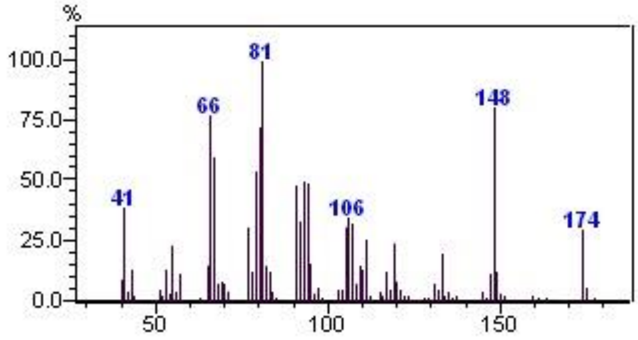

Figure S7. Mass spectrum of *endo,exo*-5-Methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4-ene **6b**

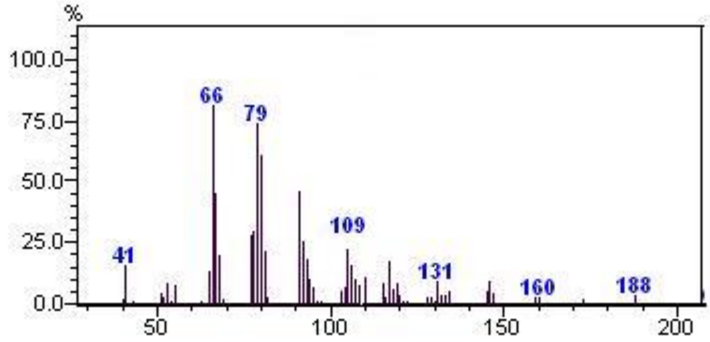

Figure S8. Mass spectrum of *exo,exo*-4-Methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane **5a**

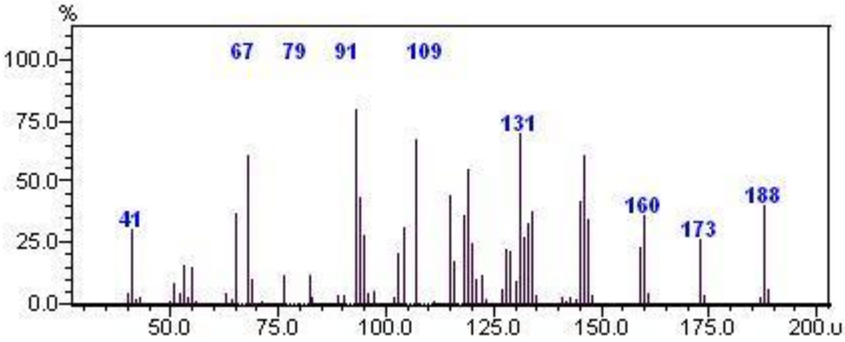

Figure S9. *endo*,*exo*-4-Methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane **5b**.

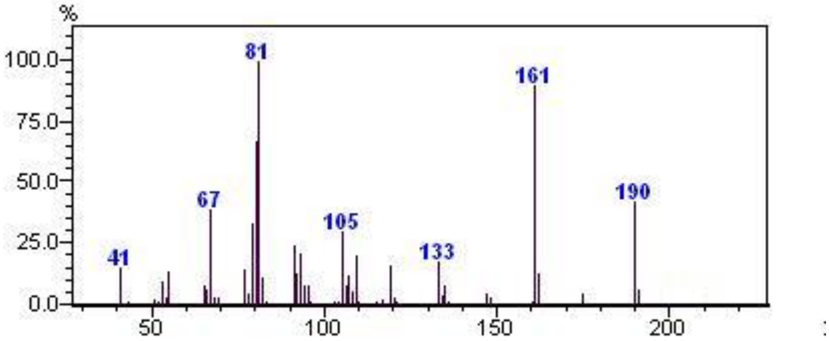

Figure S10. *exo*,*exo*-4-Methyltetracyclo[6.3.1.1^{3,6}.0^{2,7}]tridecane **7.**

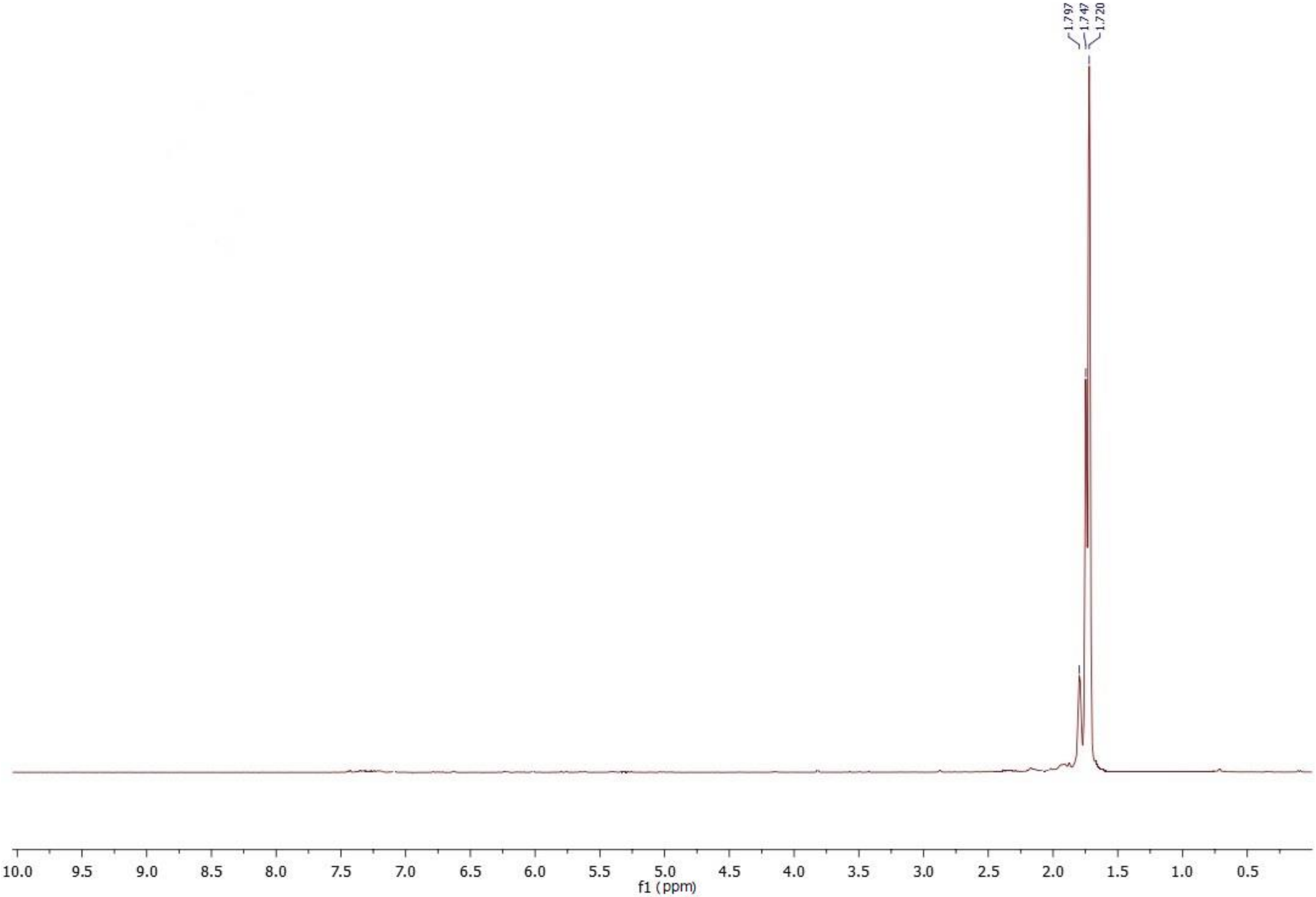

Figure S11. ^{1}H NMR spectrum of diamantane **1** in $CDCl_3$

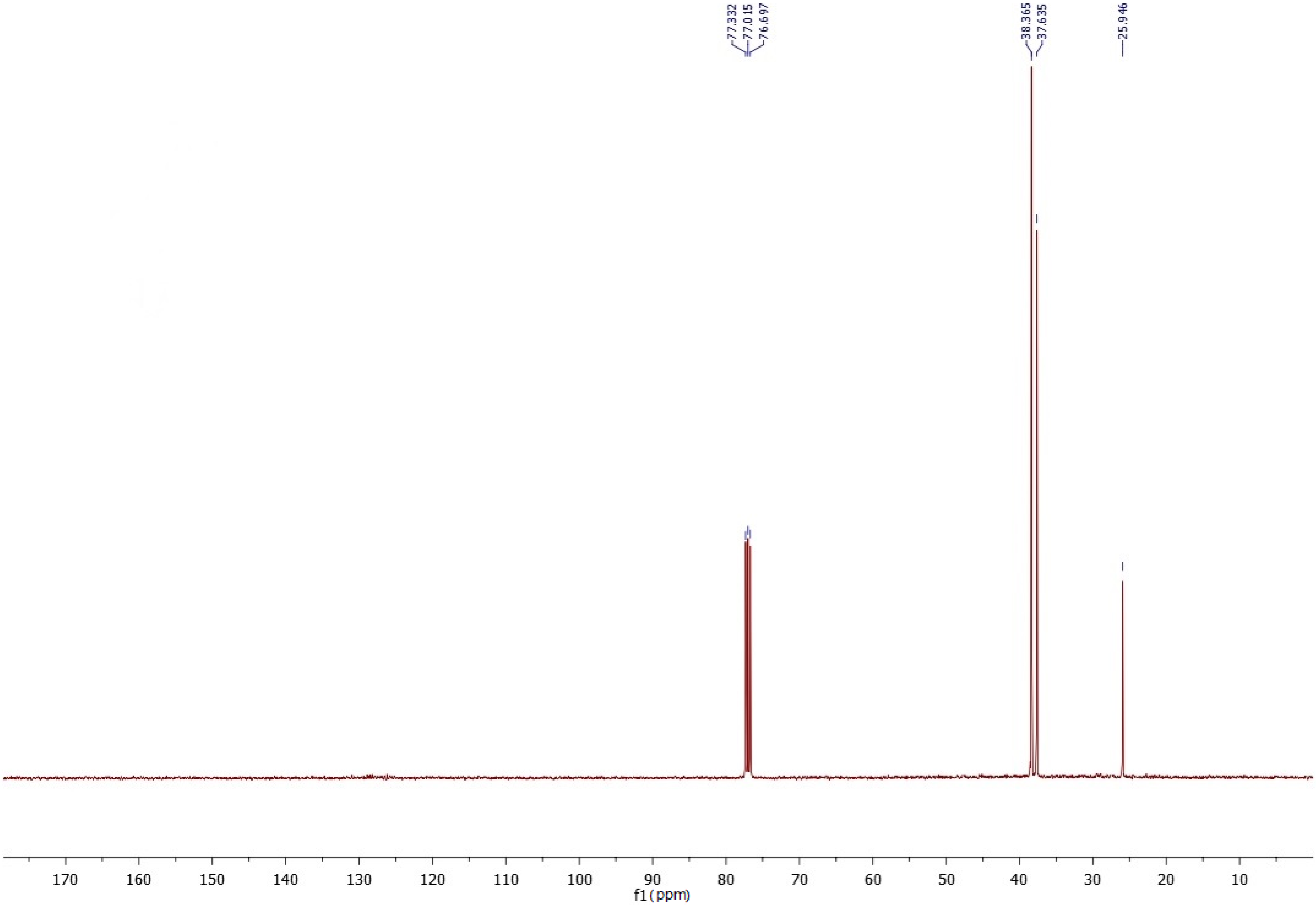

Figure S12. ^{13}C NMR spectrum of diamantane **1** in $CDCl_3$

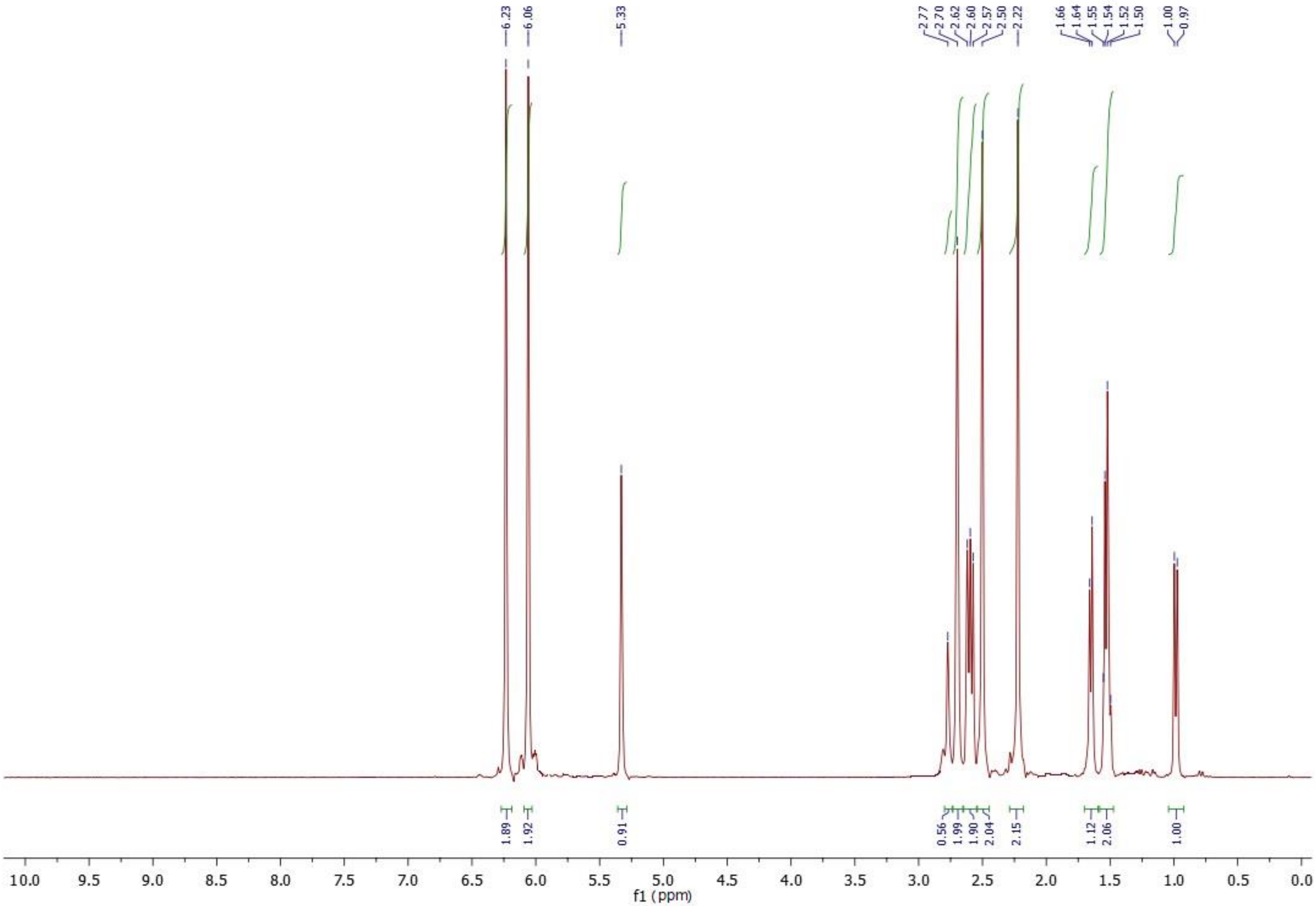

Figure S13. ^{1}H NMR spectrum of *exo,endo*-**3a**, *endo,endo*-tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-diene **3b** in $CDCl_3$

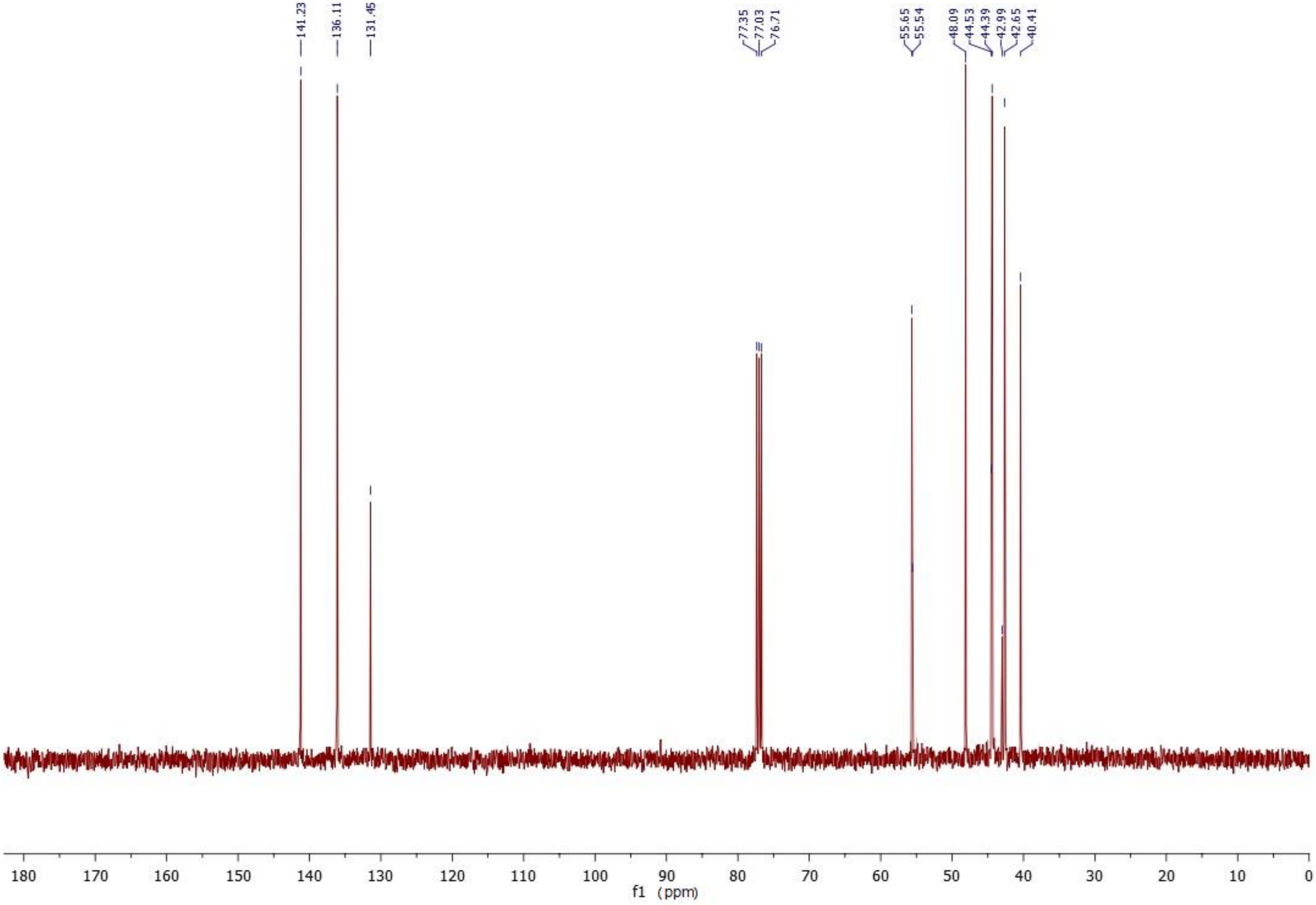

Figure S14. ^{13}C NMR spectrum of *exo,endo*-**3a**, *endo,endo*-tetracyclo[6.2.1.0^{2,7}.0^{3,6}]dodeca-4,9-diene **3b** in $CDCl_3$

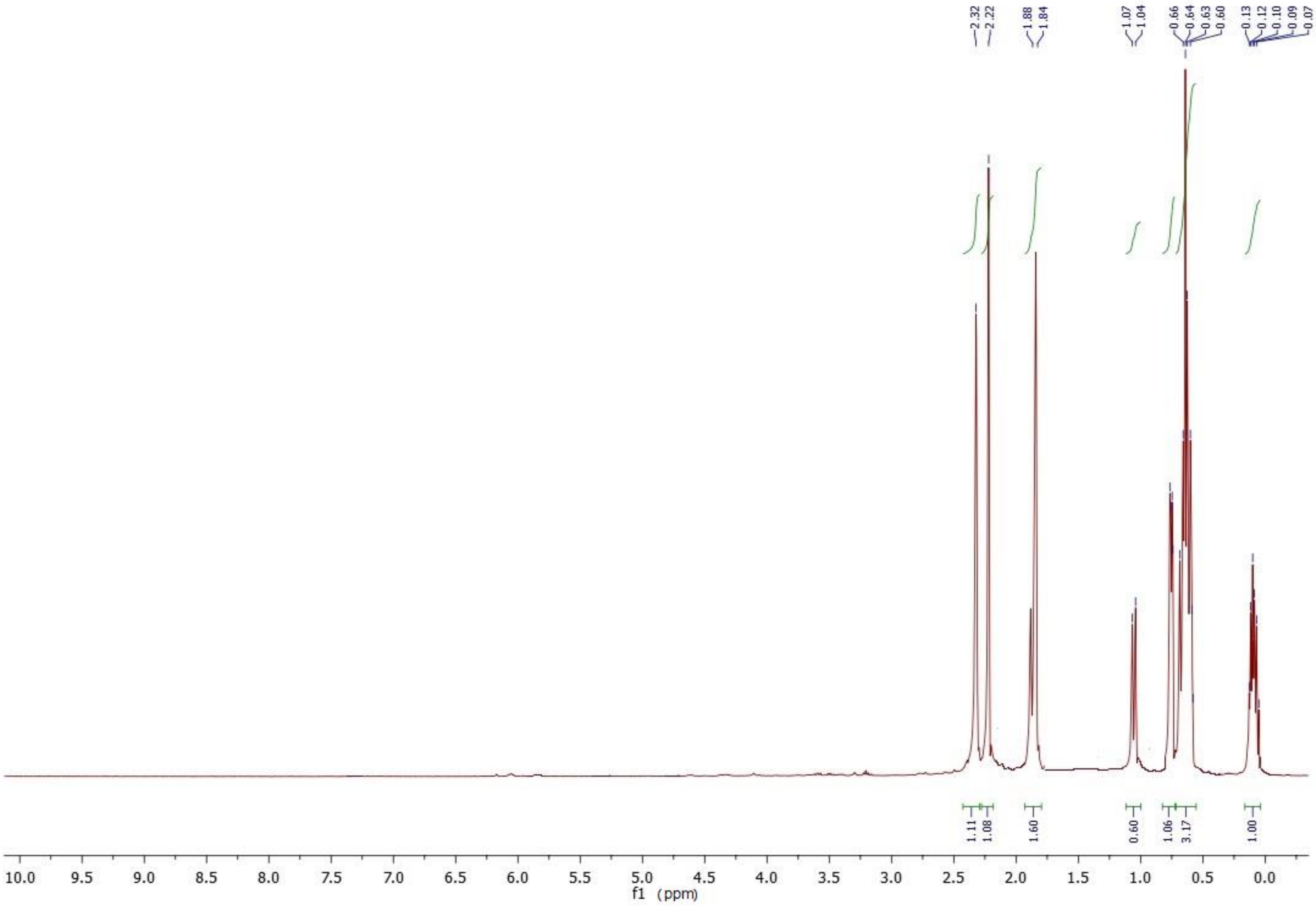

Figure S15. ^{1}H NMR spectrum of *exo,endo*-hexacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{10,12}]tetradecane **2** in CDCl$_3$

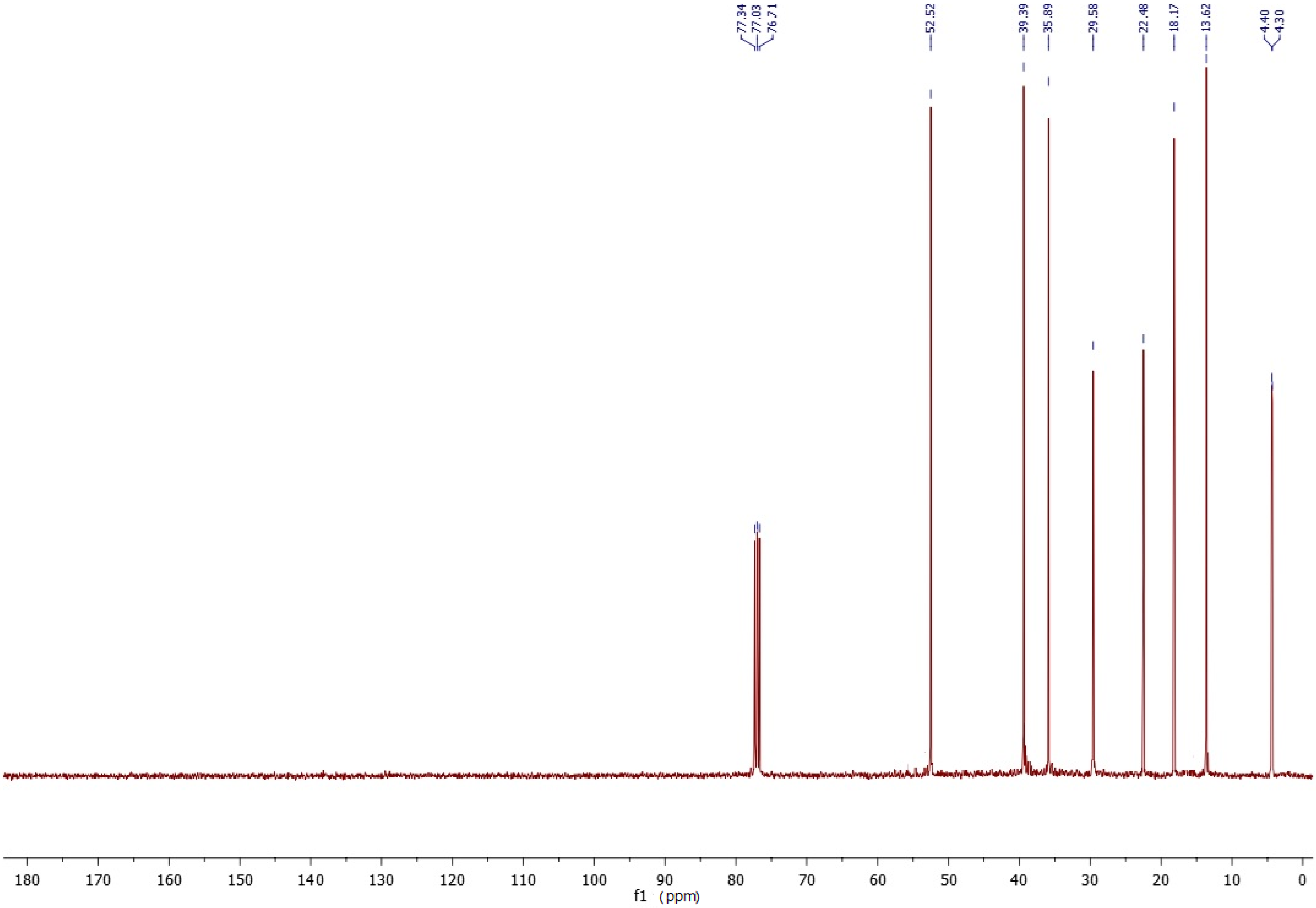

Figure S16. ^{13}C NMR spectrum of *exo*,*endo*-hexacyclo[7.3.1.1^{3,7}.0^{2,8}.0^{10,12}]tetradecane **2** in $CDCl_3$

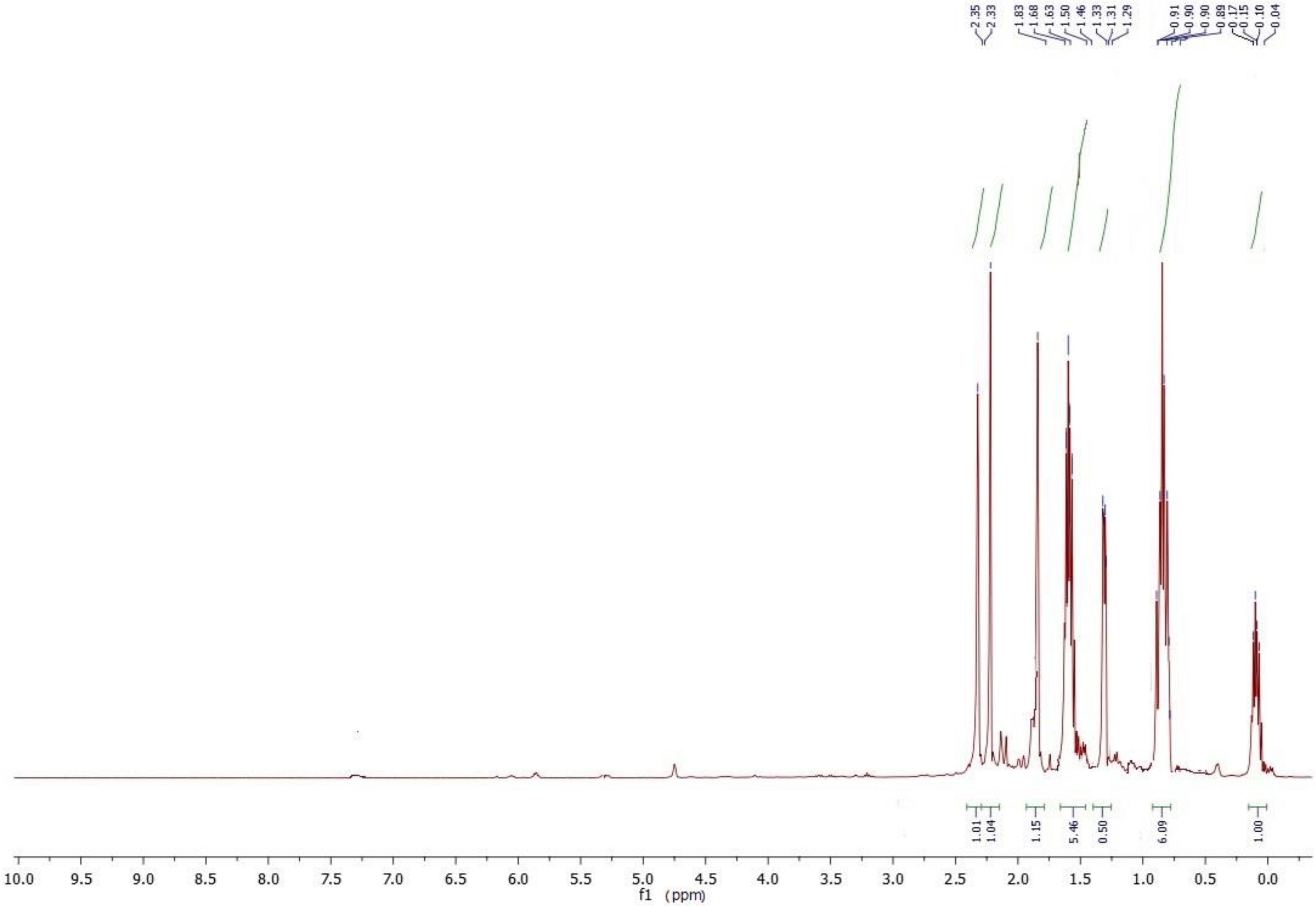

Figure S17. ^{1}H NMR spectrum of pentacyclo[5.3.1.1^{3,7}.0^{2,8}.0^{4,5}]tetradecane **4** in CDCl$_3$

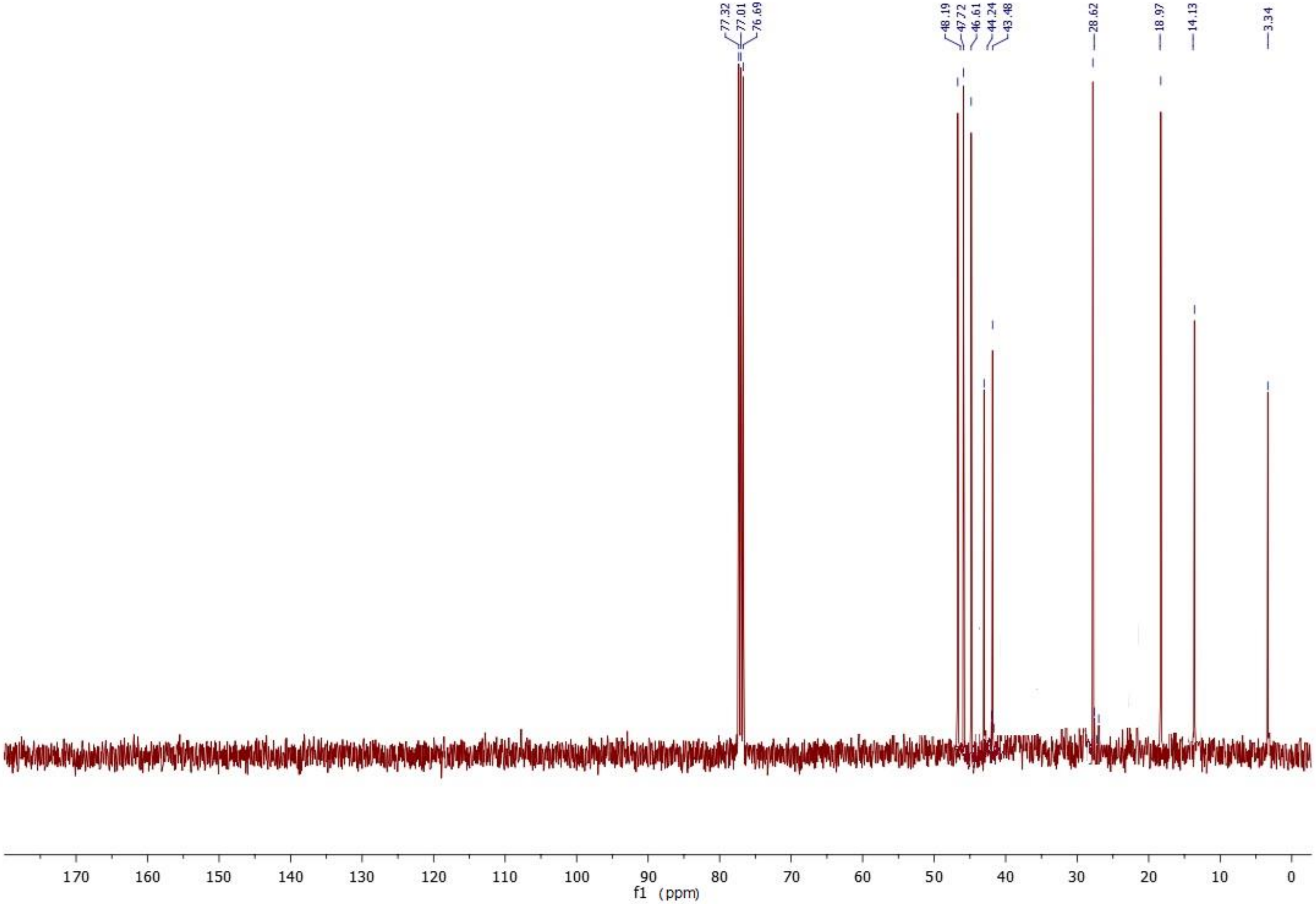

Figure S18. ^{13}C NMR spectrum of pentacyclo[5.3.1.1^{3,7}.0^{2,8}.0^{4,5}]tetradecane **4** in $CDCl_3$

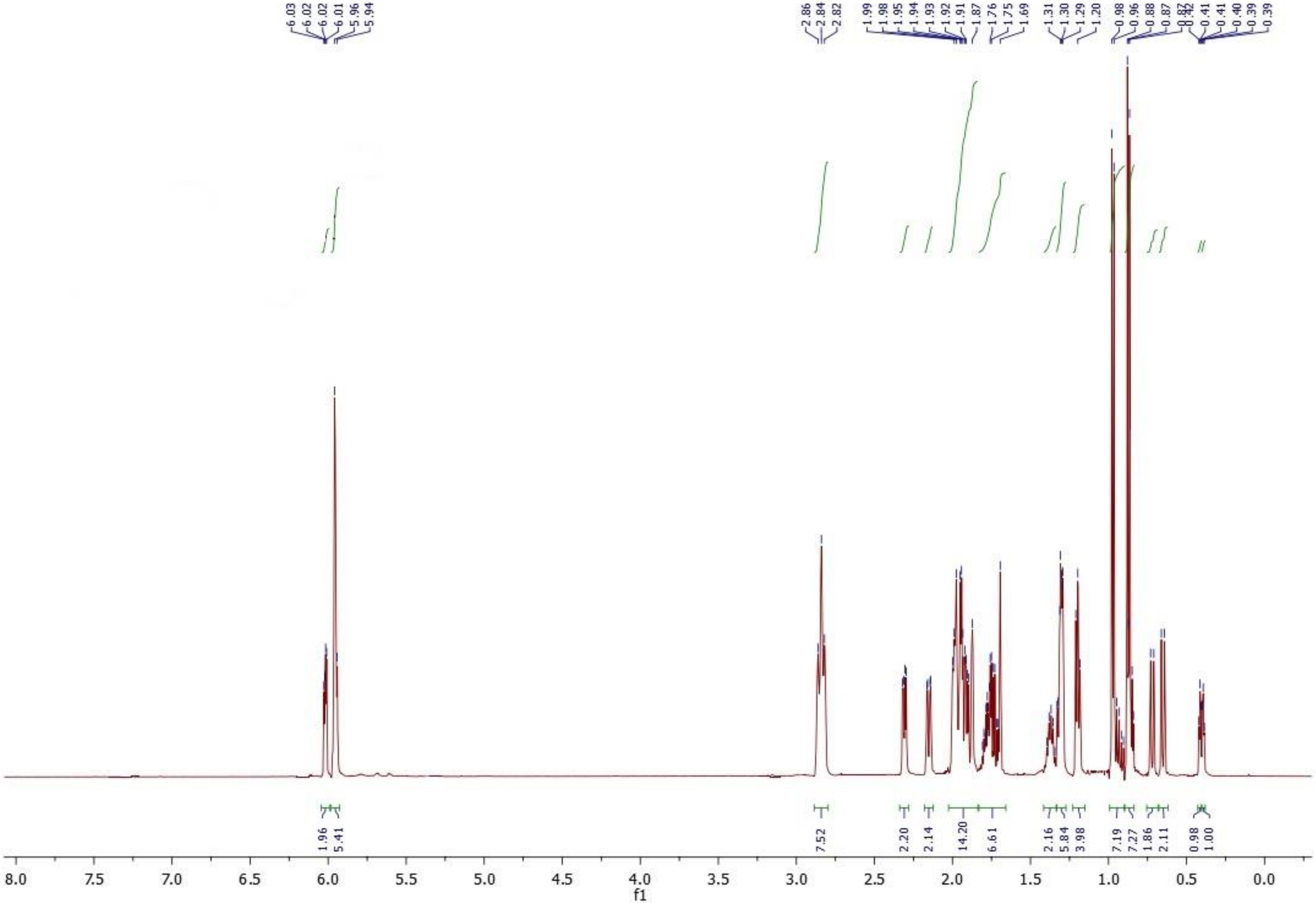

Figure S19. ^{1}H NMR spectrum of *exo,exo*-**6a** and *endo,exo*-5-methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4-ene **6b** in CDCl$_3$

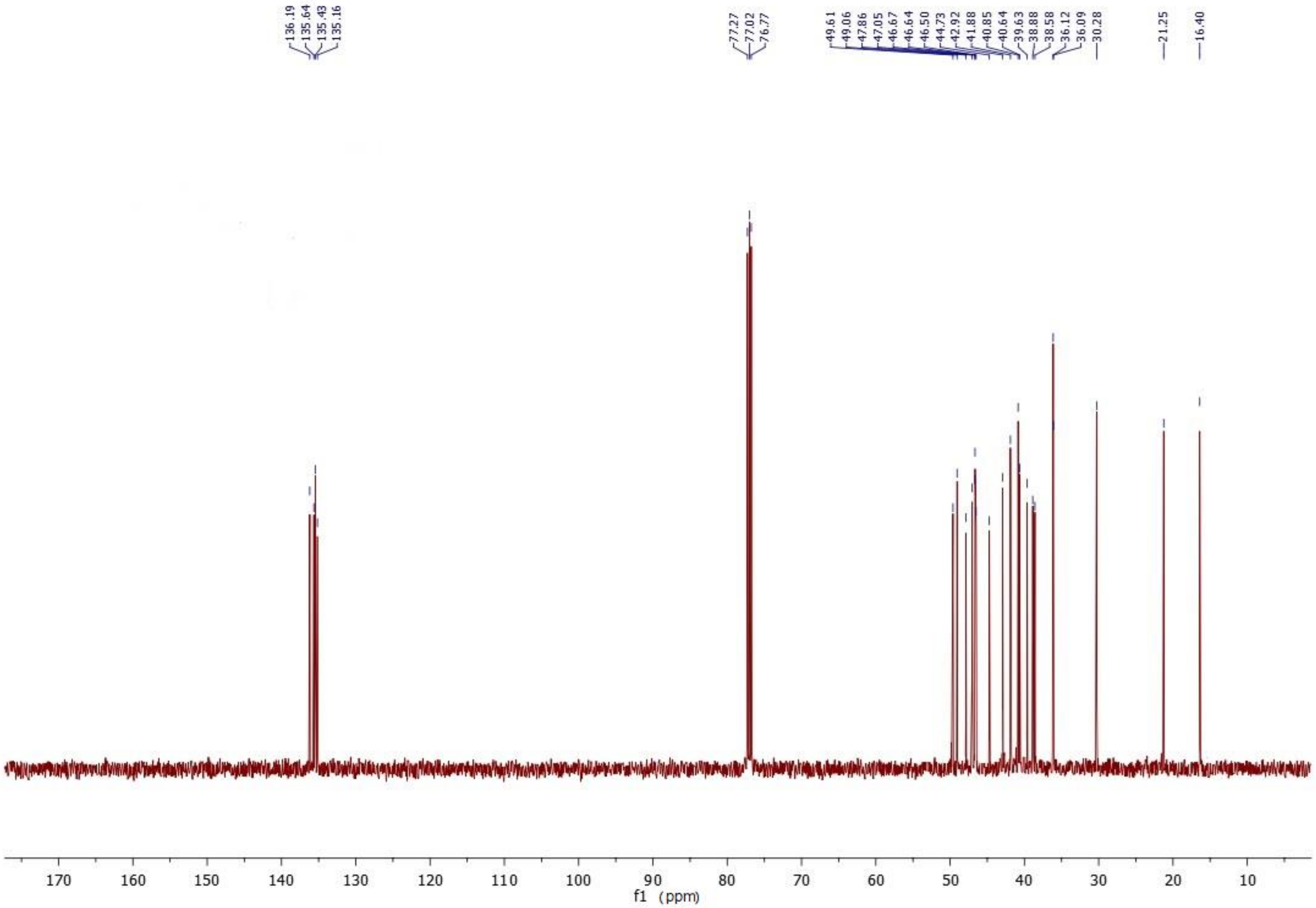

Figure S20. ^{13}C NMR spectrum of *exo,exo*-**6a** and *endo,exo*-5-methyltetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4-ene **6b** in $CDCl_3$

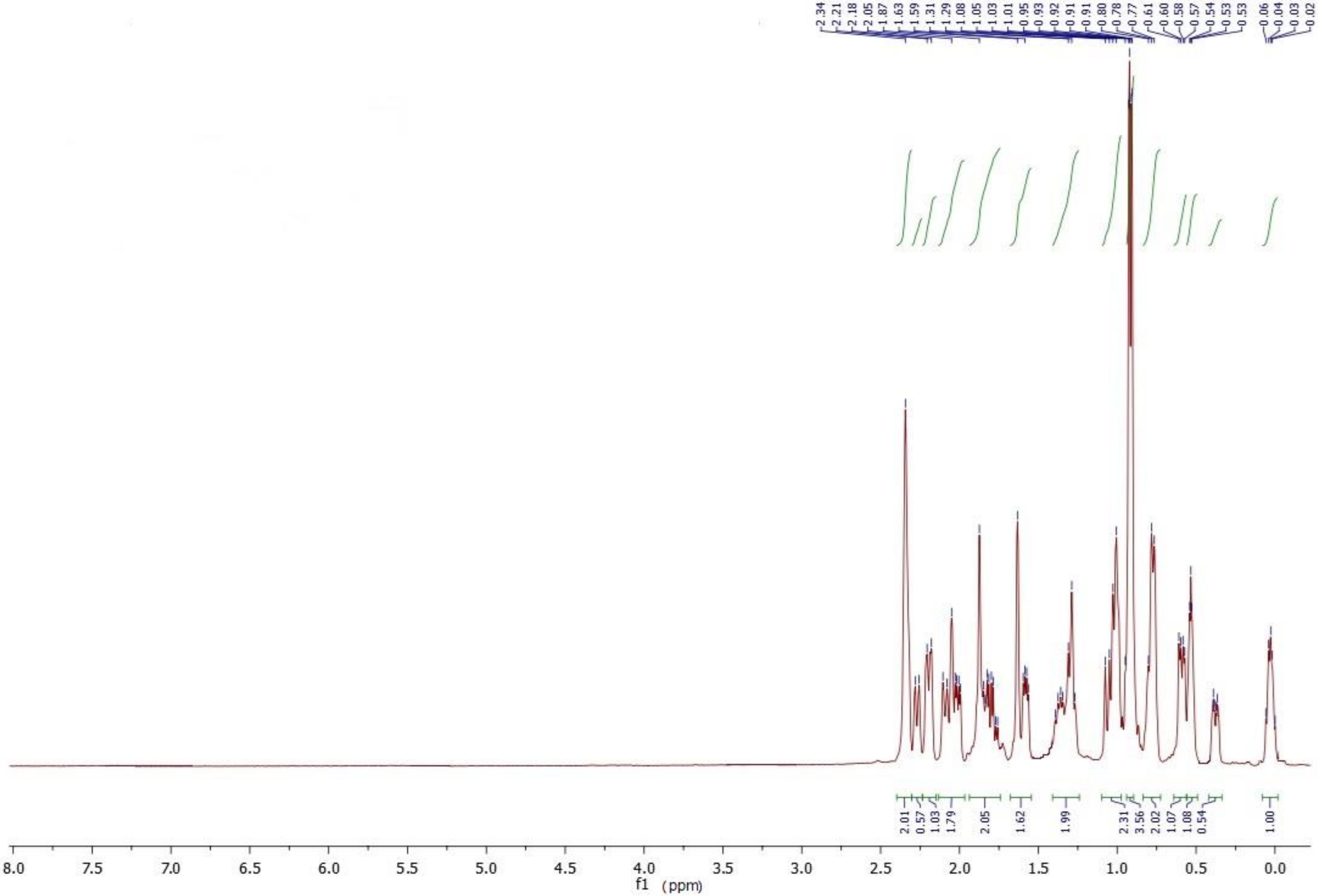

Figure S21. ^{1}H NMR spectrum of *exo,exo*-**5a** and *endo,exo*-4-methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane **5b** in CDCl$_3$

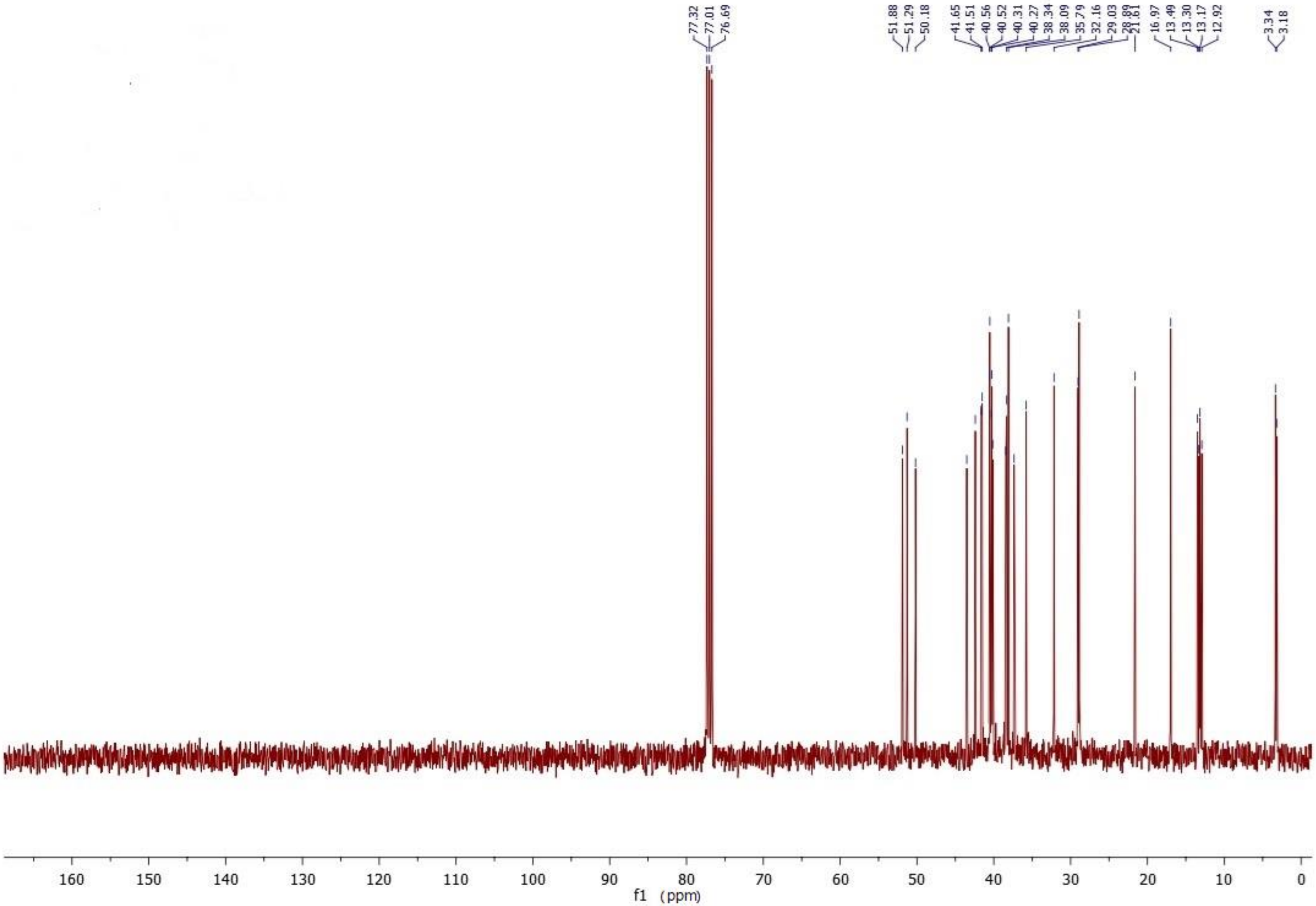

Figure S22. ^{13}C NMR spectrum of *exo,exo*-**5a** and *endo,exo*-4-methylpentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridecane **5b** in $CDCl_3$

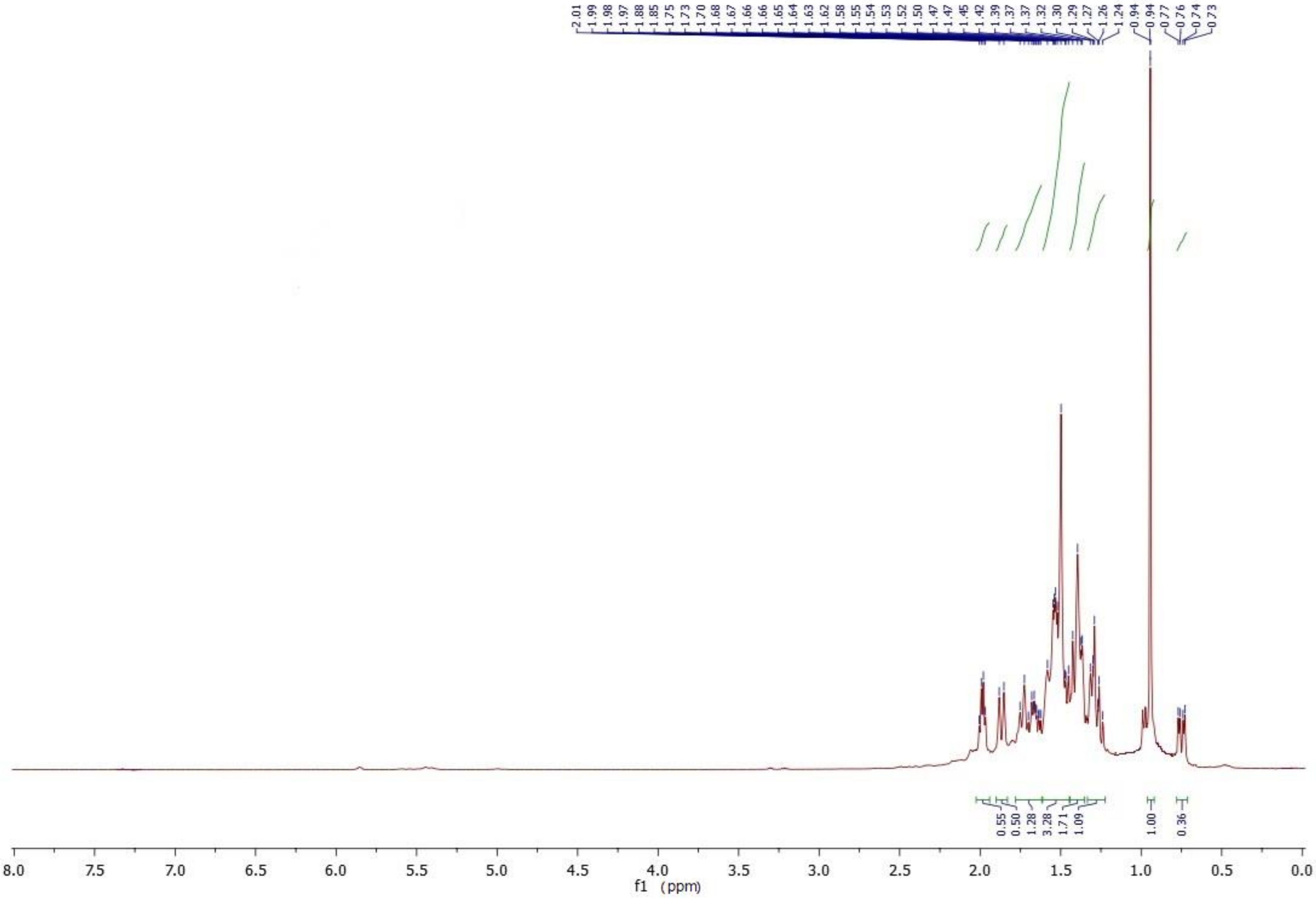

Figure S23. ^{1}H NMR spectrum of *exo*,*exo*-4-methyltetracyclo[6.3.1.1^{3,6}.0^{2,7}]tridecane **7** in $CDCl_3$

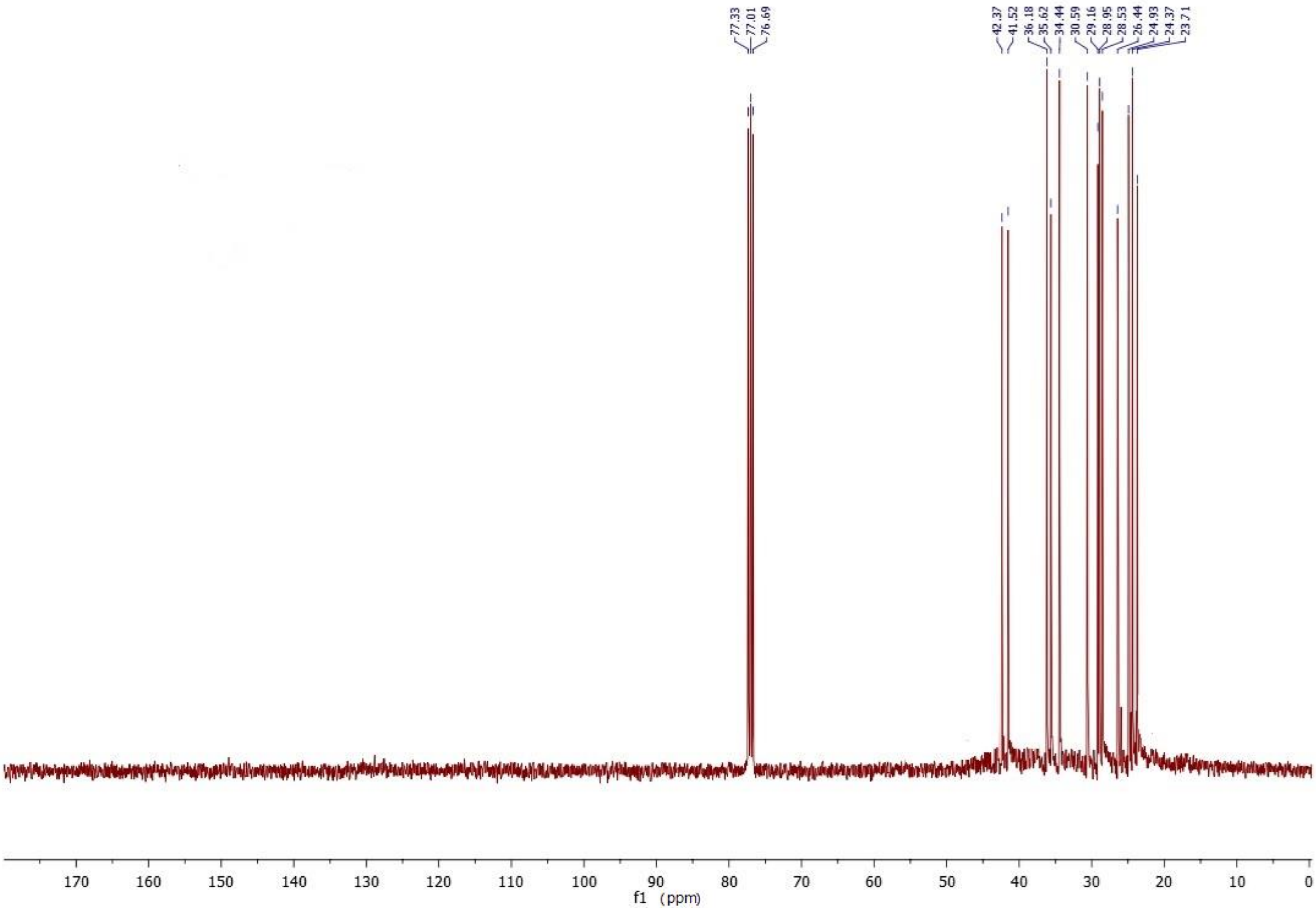

Figure S24. ^{13}C NMR spectrum of *exo,exo*-4-methyltetracyclo[6.3.1.1^{3,6}.0^{2,7}]tridecane **7** in CDCl$_3$