Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 512–514

Catalytic cyclopropanation of hexa-1,3,5-triene with diazomethane as a simple synthesis of high-energy tercyclopropane

Evgeny V. Shulishov, Olga A. Pantyukh, Leonid G. Menchikov and Yury V. Tomilov

Table of contents

1. Characterization

Analytical methods. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were recorded on a Bruker AV-600 NMR spectrometer. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Bruker AV-300 NMR spectrometer. All spectra were recorded at 300 K in $CDCl_3$ solution using tetramethylsilane (TMS) as internal standard. Chemical shifts δ are reported in parts per million (ppm) relative to TMS and coupling constants are expressed in Hertz (Hz).

GC/MS analysis was performed on a Trace GC Ultra chromatograph (Thermo Scientific) coupled to a DSQ-II mass spectrometer detector fitted with a non-polar TR-5MS capillary column (30 m × 0.25 mm; 0.25 μm film thickness). The oven temperature was programmed from 40°C (held for 3 min) to 280°C at 20°C min^{-1} and held at the final temperature for 20 min. Helium carrier gas flow was 2.0 ml min^{-1}. The injector temperature was 280°C, and the injection size 0.1 μl. MS were taken at 70 eV with a mass range of *m*/*z* 20-450.

The calorific values of tercyclopropane were measured with the use of the IKA C200 calorimeter according to the ASTM D4809. The mean standard deviation in the gross calorific values determination amounted to 60 kJ·kg^{-1}. The density of tercyclopropane were measured using a vibration densitometer VIP-2MR according to the ASTM D4052 (measurement precision within ± 0.1 kg m^{-3}). The freezing point of tercyclopropane were measured with the using of ‘Lintel Kristall-20E’ (‘BashNefteKhimavtomatika’, Russia) according to the ASTM D2386 method.

2. Cyclopropanation of hexa-1,3,5-triene with diazomethane generated *in situ*

General Information. Commercial hexa-1,3,5-triene **5** (isomer ratio *E*/*Z*=7:1) was distilled before use. All other commercial reagents were used without further purification.

Cyclopropanation of hexa-1,3,5-triene 5 with diazomethane generated *in situ* (method[1]). A solution of KOH in water (130 g, about 50%) was placed in a flask without thin sections, cooled to 12°C, and a solution of hexa-1,3,5-triene (6.5 g, 0.079 mol) in CH_2Cl_2 (20 ml) was added. With stirring, loose *N*-methyl-*N*-nitrosourea (about 0.3-0.5 g) was added until a yellow color appeared, and then a solution of catalyst (Pd(acac)$_2$ or (PhCN)$_2$PdCl$_2$, 0.2 mmol) in CH_2Cl_2 (10 ml) was added. In this case, there is a release of nitrogen and the weakening of the yellow color. From this point on, a total of 15.0 g (0.14 mol) of *N*-methyl-*N*-nitrosourea was added in portions of 1 g with stirring at 18–20°C. After that reaction mixture was additionally stirred for 15–20 min, organic layer was separated and filtered through a small layer of alumina. Then solvent was evaporated and the residue was fractionated under reduced pressure. With catalyst Pd(acac)$_2$, yield of tercyclopropane **2** 8.7 g (90%, *E*/*Z*=7:1), colorless liquid, b.p. 151–152 °C, d_4^{20} 0.860 g ml^{-1}.

Note. The cyclopropanation reaction with diazomethane generated *in situ* consists of two steps. In the first step, the active form of the catalyst is formed by reacting of Pd(acac)$_2$ with diazomethane. At this step, it is important to maintain a temperature of 12–16°C. The second step is the cyclopropanation reaction of hexa-1,3,5-triene **5**. It is important to add *N*-methyl-*N*-nitrosourea at such a rate that diazomethane does not accumulate (control by yellow color). It is most convenient and safe to carry out the reaction at a temperature of 18–20°C, but not higher than 25°C, at which an irreversible loss of catalyst activity occurs. When the temperature drops to +5°C, the

---

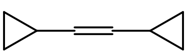
[1] Nefedov O. M., Tomilov Yu. V., Kostitsyn A. B., Dzhemilev U. M., Dokitchev V. A. Cyclopropanation of Unsaturated Compounds with Diazomethane Generated in situ: A New Efficient and Practical Route to Cyclopropane Derivatives. *Mendeleev Commun*. 1992; 2(1): 13-5. https://doi.org/10.1070/MC1992v002n01ABEH000099.

generation of diazomethane stops, and the reaction mixture becomes very thick and difficult to be stirred.

The use of an excess of diazomethane makes it possible to carry out exhaustive cyclopropanation of all intermediate products with the selective formation of tercyclopropane **2**. The reaction is not accompanied by any side processes. All intermediate products of this reaction can be isolated by controlling the amount of diazomethane introduced into the reaction.

1,2-Dicyclopropylethene 3. Aqueous KOH solution (45–50%, 20 ml) and dichloromethane (20 ml) are placed in a flask equipped with a stirrer, micropowder addition funnel and a coiled condenser. Then hexa-1,3,5-triene **5** (8.10 g, 0.1 mol), *N*-methyl-*N*-nitrosourea (1.5–2.0 g) and Pd(acac)$_2$ (0.24 g, 0.8 mmol) were successively added to the reaction mixture at 15–18 °C. In this case, the release of nitrogen should be observed. After that, the addition of *N*-methyl-*N*-nitrosourea (30–34 g) was continued in small portions, making sure that the condensate from the reflux condenser was not colored yellow. At the end of the reaction the organic layer is separated, the resulting solution is filtered through Al_2O_3 at about 5 °C, the sorbent is washed with dichloromethane (2 ml), then the solvent is removed and the product is isolated by fractional distillation. Yield of 1,2-dicyclopropylethene **3** is 8.53 g (88%, *E*/*Z*=7:1), colorless liquid, b.p. 138–140 °C. Physical and spectroscopic data were consistent with the literature data. [2]

1,2-Dicyclopropylethene 3



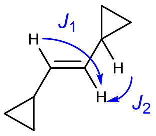
E-**3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.27-0.34 and 0.60-0.68 (two 4H m, cyclo-CH_2), 1.32 (m, 2H, cyclo-CH), 5.06 (m, 2H, H_1, J = 15.25, J = 8.5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.70 (C=C) 13.56 (cyclo-CH), 6.48 (cyclo-CH_2). Mass spectrum, *m/z* (*I*, %): 108 (35) $[M]^+$, 79 (94), 77 (100).

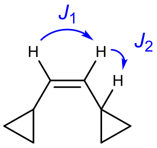
---

[2] Ahmar M, Knoke M, de Meijere A, Cazes B. Pauson-Khand Carbonylative Cocyclizations of Acetylenes with Cyclopropylallenes. *Synthesis* 2007;2007(03):442-6. https://doi.org/10.1055/s-2007-965882.

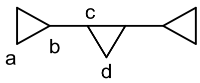
Z-**3**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.30-0.37 and 0.71-0.79 two 4H m, cyclo-CH_2), 1.70 (m, 2H, cyclo-CH), 4.70 (m, 2H, H_1, *J* = *J* = 10.0). ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.36 (C=C) 9.99 (cyclo-CH), 7.05 (cyclo-CH_2).

The ratio of *E*/*Z* isomers of 1,2-dicyclopropylethene **3** was established based on the analysis of spin-spin coupling constants (SSCC) in NMR spectra. The ^{1}H NMR spectrum of the main isomer contains two SSCCs, $^3J_1$ = 15.25 and $^3J_2$ = 8.5 Hz, which corresponds to the *E*-isomer. For the minor *Z*-isomer, $^3J_1$ = $^3J_2$ = 10.0 Hz. The isomer ratio is *E*:*Z* = 7.5 : 1.0.





1,1′:2′,1′′-Tercyclopropane 2.



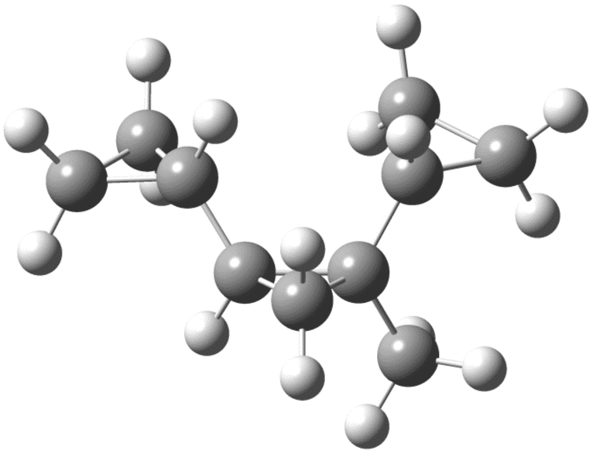
E-**2** (the main component of the mixture). ^{1}H NMR (600 MHz, $CDCl_3$): δ -0.04-0.03 and 0.27-0.34 (two 4H m, C_aH_2), 0.11 (ex. t, 2H, *J* = 6.9, C_dH_2), 0.54 (m, 2H, C_bH), 0.75 (m, 2H, C_cH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.59 ($2C_b$), 12.21 ($2C_c$), 7.98 (C_d), 3.07 and 2.91 ($4C_a$). Mass spectrum, *m/z* (*I*, %): 122 (1) $[M]^+$, 81 (50), 79 (100).

Z-**2** (minor component of the mixture). ^{1}H NMR (600 MHz, $CDCl_3$): δ -0.07 (ex.q., 1H, *J* = 5.2, C_dH), 0.14-0.21 (two m, 1H + 1H, C_aH), 0.37-0.45 (two m, 1H + 1H, C_aH + C_dH), 0.51 (m, 1H, C_aH), 0.57 (m, 2H, C_bH), 0.71 (m, 2H, C_cH). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.78 ($2C_b$), 9.65 ($2C_c$), 8.40 (C_d), 4.85 и 4.48 ($4C_a$). Mass spectrum, *m/z* (*I*, %): 122 (1) $[M]^+$, 81 (49), 79 (100).

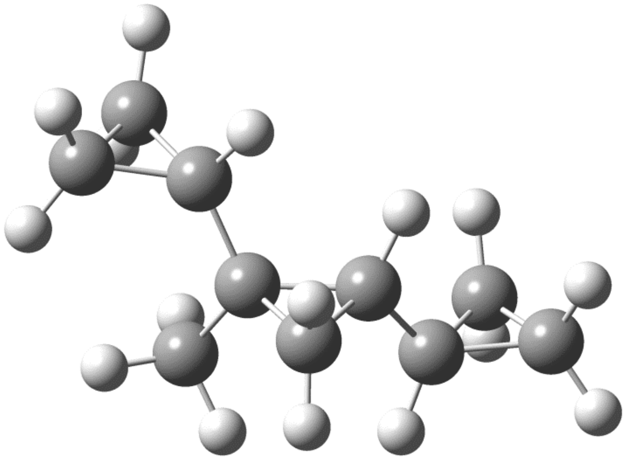
The isomer ratio of tercyclopropane **2** was determined from the data of ^{1}H and 2D ^{1}H-^{13}C HMBC NMR spectra (*E*:*Z* ~ 7 : 1).

3. Computational Details

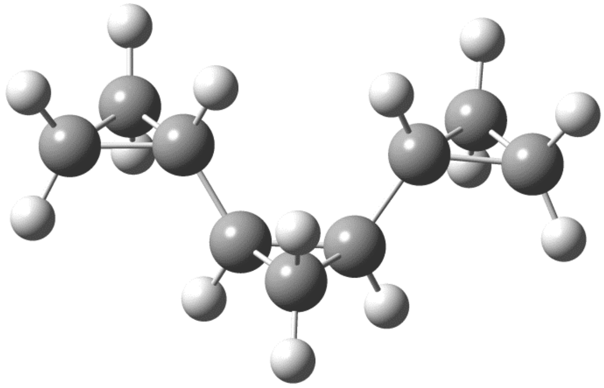
All calculations were performed using the Gaussian 09 program package.[3] All structures was optimized by a DFT/B3LYP method using 6-31G(d,p) basis set.



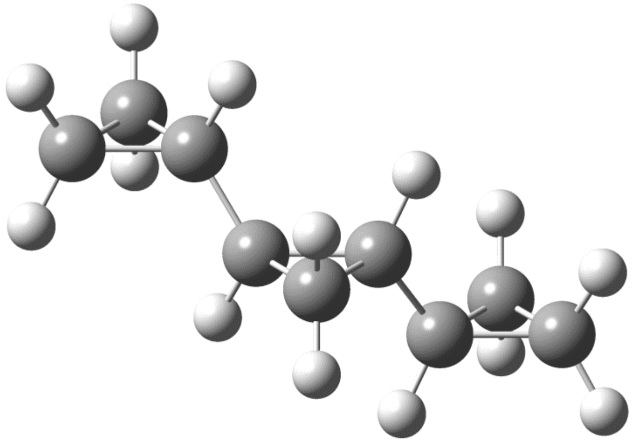
Z-**1**



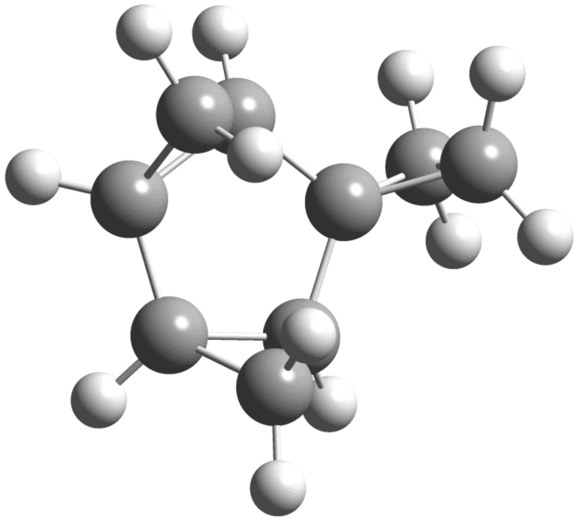
E-**1**



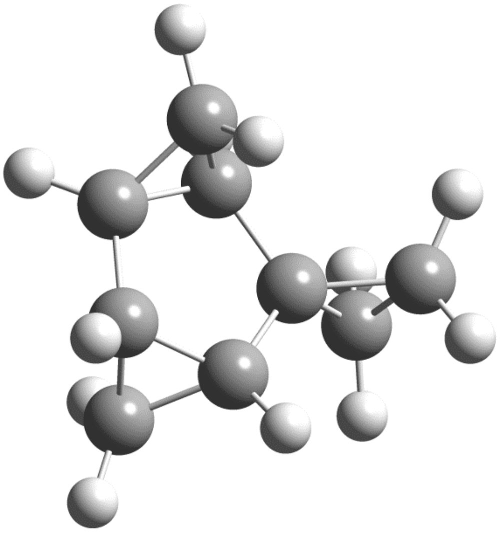
Z-**2**



E-**2**



Z-**7**



E-**7**

---

[3] Frisch M. J., Trucks G. W., Schlegel H. B., Scuseria G.E., Robb M.A., Cheeseman J. R. *et al*. Gaussian 09, Revision D.01. Gaussian Inc, Wallingford, CT 2013.

Table S1. Calculation data (in a.u.) of structures **1**, **2**, **7** in gas phase (273.15 K) of the optimized geometries (B3LYP/6-31+G(d,p)).

Compound	Total Energy	Enthalpies*	Gibbs Free energy*
Z-**1**	-390.62721272	-390.380956	-390.428710
E-**1**	-390.62742189	-390.381177	-390.429254
Z-**2**	-351.31054746	-351.093691	-351.138672
E-**2**	-351.31243043	-351.095851	-351.141176
Z-**7**	-350.09557597	-349.901860	-349.941399
E-**7**	-350.10486592	-349.911078	-349.950669

* with ZPE correction

Coordinates of *E*-1.

C	0.76367634	0.35343351	-0.51410463
C	-0.60552094	0.45216094	0.14714208
C	0.04426665	1.68379317	-0.45770932
C	-1.75167996	-0.14479898	-0.63961405
C	2.03807339	0.11265009	0.24043919
C	-2.53177707	-1.35582458	-0.18385402
C	-3.20093327	-0.00156142	-0.23518125
C	2.68366418	-1.25440999	0.22689136
C	3.32858884	-0.10914189	-0.51554144
H	0.75466855	-0.13706199	-1.48771280
C	-0.70098659	0.36824733	1.66118609
H	0.43297447	2.43564479	0.22494783
H	-0.36918201	2.09502901	-1.37476555
H	-1.58279416	-0.09660601	-1.71450279
H	2.13648790	0.67014976	1.16862172
H	-2.80507529	-2.10067427	-0.92545518
H	-2.31565774	-1.77069509	0.79566303
H	-3.43256608	0.48188294	0.70894261
H	-3.93269149	0.18811182	-1.01495083
H	3.15669282	-1.61451458	1.13568829
H	2.20162499	-2.03209948	-0.35909800
H	3.28273296	-0.11630287	-1.60114602
H	4.24344836	0.31774971	-0.11532980
H	-1.63094079	0.81739464	2.02660221
H	0.12070057	0.90345546	2.14261509
H	-0.66465249	-0.66875301	2.01195608

Coordinates of *E*-2.

C	0.68010999	0.45391741	-0.33128246
C	-0.68011019	0.45391790	0.33128242
C	0.00000022	1.76429825	-0.00000032
C	-1.90205991	0.01305203	-0.41670698
C	1.90205951	0.01305134	0.41670717
C	-2.57474770	-1.29799666	-0.08388677
C	-3.25501362	0.00713699	0.25592466
C	2.57474806	-1.29799672	0.08388609
C	3.25501357	0.00713754	-0.25592379
H	0.68442093	0.17925920	-1.38611815
H	-0.68442126	0.17926019	1.38611824
H	0.40494181	2.35595398	0.81665107
H	-0.40494108	2.35595378	-0.81665201
H	-1.89953549	0.29036189	-1.47006105
H	1.89953443	0.29036021	1.47006149
H	-2.97836775	-1.89568116	-0.89580467
H	-2.16104074	-1.88318104	0.73277250
H	-3.29955564	0.29984740	1.30135491
H	-4.12440235	0.30388504	-0.32332198
H	2.97836796	-1.89568181	0.89580364
H	2.16104180	-1.88318054	-0.73277395
H	3.29955599	0.29984894	-1.30135374
H	4.12440186	0.30388546	0.32332358

Coordinates of *Z*-1.

C	-0.83072336	0.79338978	0.05731424
C	0.69177578	0.71684844	0.01734277
C	-0.05791863	1.58657584	-0.97483442
C	1.33373834	-0.54167803	-0.52199137
C	-1.73524808	-0.33724753	-0.33421175
C	2.82634451	-0.78330713	-0.49735347
C	1.91219417	-1.61458808	0.37146350
C	-2.49324525	-1.10552167	0.72326870
C	-3.23365521	-0.17705499	-0.20914926
C	1.43259239	1.43961333	1.13088732
H	-1.22723414	1.37708188	0.88848352
H	0.00066374	2.66702770	-0.87195113
H	-0.10756297	1.24583502	-2.00627686
H	0.84216119	-0.92169165	-1.41414720
H	-1.40231454	-0.92074736	-1.18882603
H	3.28221892	-1.24856663	-1.36635979
H	3.46413319	-0.05630378	-0.00502515
H	1.93618855	-1.43597133	1.44221175
H	1.73937964	-2.65285441	0.10422668
H	-2.61914257	-2.17666461	0.59667069
H	-2.37026829	-0.79426232	1.75700945
H	-3.60916955	0.75845742	0.19649252
H	-3.86710601	-0.61110719	-0.97710082
H	2.40630181	1.81114188	0.79282482
H	0.85658400	2.30371434	1.47569104
H	1.60003910	0.79273137	1.99965903

Coordinates of *Z*-2.

C	-0.75929201	0.77111613	0.46382614
C	0.75929236	0.77111659	0.46382608
C	-0.00000019	1.91796802	-0.16718144
C	1.57097732	-0.17453728	-0.37041874
C	-1.57097668	-0.17453830	-0.37041828
C	3.07958066	-0.15755300	-0.27831671
C	2.30244065	-1.32725423	0.27671048
C	-2.30244186	-1.32725357	0.27671184
C	-3.07958013	-0.15755251	-0.27831817
H	-1.21605256	0.98677712	1.42936773
H	1.21605299	0.98677764	1.42936760
H	-0.00000053	2.88697691	0.32363642
H	-0.00000017	1.97459334	-1.25323576
H	1.16819118	-0.37034720	-1.36152935
H	-1.16818940	-0.37035022	-1.36152802
H	3.65651201	-0.30312265	-1.18678513
H	3.53413858	0.53178759	0.42802854
H	2.23412837	-1.42469613	1.35673103
H	2.34592849	-2.27571996	-0.25027703
H	-2.34592990	-2.27572009	-0.25027423
H	-2.23413105	-1.42469384	1.35673263
H	-3.53413831	0.53178960	0.42802542
H	-3.65651048	-0.30312310	-1.18678708

Coordinates of *E*-7.

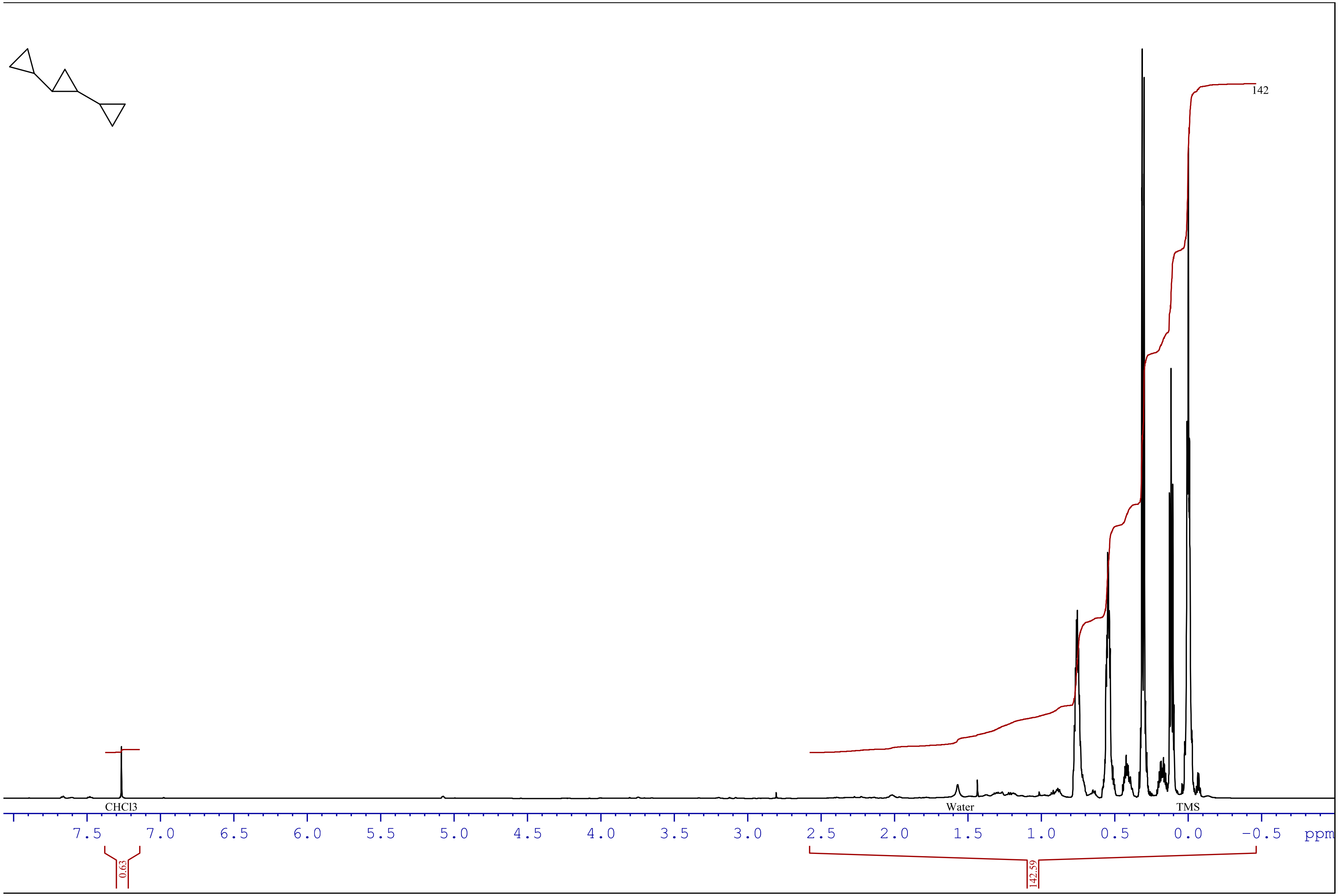
C	0.76367634	0.35343351	-0.51410463
C	-0.60552094	0.45216094	0.14714208
C	0.04426665	1.68379317	-0.45770932
C	-1.75167996	-0.14479898	-0.63961405
C	2.03807339	0.11265009	0.24043919
C	-2.53177707	-1.35582458	-0.18385402
C	-3.20093327	-0.00156142	-0.23518125
C	2.68366418	-1.25440999	0.22689136
C	3.32858884	-0.10914189	-0.51554144
H	0.75466855	-0.13706199	-1.48771280
C	-0.70098659	0.36824733	1.66118609
H	0.43297447	2.43564479	0.22494783
H	-0.36918201	2.09502901	-1.37476555
H	-1.58279416	-0.09660601	-1.71450279
H	2.13648790	0.67014976	1.16862172
H	-2.80507529	-2.10067427	-0.92545518
H	-2.31565774	-1.77069509	0.79566303
H	-3.43256608	0.48188294	0.70894261
H	-3.93269149	0.18811182	-1.01495083
H	3.15669282	-1.61451458	1.13568829
H	2.20162499	-2.03209948	-0.35909800
H	3.28273296	-0.11630287	-1.60114602
H	4.24344836	0.31774971	-0.11532980
H	-1.63094079	0.81739464	2.02660221
H	0.12070057	0.90345546	2.14261509
H	-0.66465249	-0.66875301	2.01195608

Coordinates of *Z*-7.

C	-0.83072336	0.79338978	0.05731424
C	0.69177578	0.71684844	0.01734277
C	-0.05791863	1.58657584	-0.97483442
C	1.33373834	-0.54167803	-0.52199137
C	-1.73524808	-0.33724753	-0.33421175
C	2.82634451	-0.78330713	-0.49735347
C	1.91219417	-1.61458808	0.37146350
C	-2.49324525	-1.10552167	0.72326870
C	-3.23365521	-0.17705499	-0.20914926
C	1.43259239	1.43961333	1.13088732
H	-1.22723414	1.37708188	0.88848352
H	0.00066374	2.66702770	-0.87195113
H	-0.10756297	1.24583502	-2.00627686
H	0.84216119	-0.92169165	-1.41414720
H	-1.40231454	-0.92074736	-1.18882603
H	3.28221892	-1.24856663	-1.36635979
H	3.46413319	-0.05630378	-0.00502515
H	1.93618855	-1.43597133	1.44221175
H	1.73937964	-2.65285441	0.10422668
H	-2.61914257	-2.17666461	0.59667069
H	-2.37026829	-0.79426232	1.75700945
H	-3.60916955	0.75845742	0.19649252
H	-3.86710601	-0.61110719	-0.97710082
H	2.40630181	1.81114188	0.79282482
H	0.85658400	2.30371434	1.47569104
H	1.60003910	0.79273137	1.99965903

4. NMR spectra

Bruker AV-600 NMR spectrometer



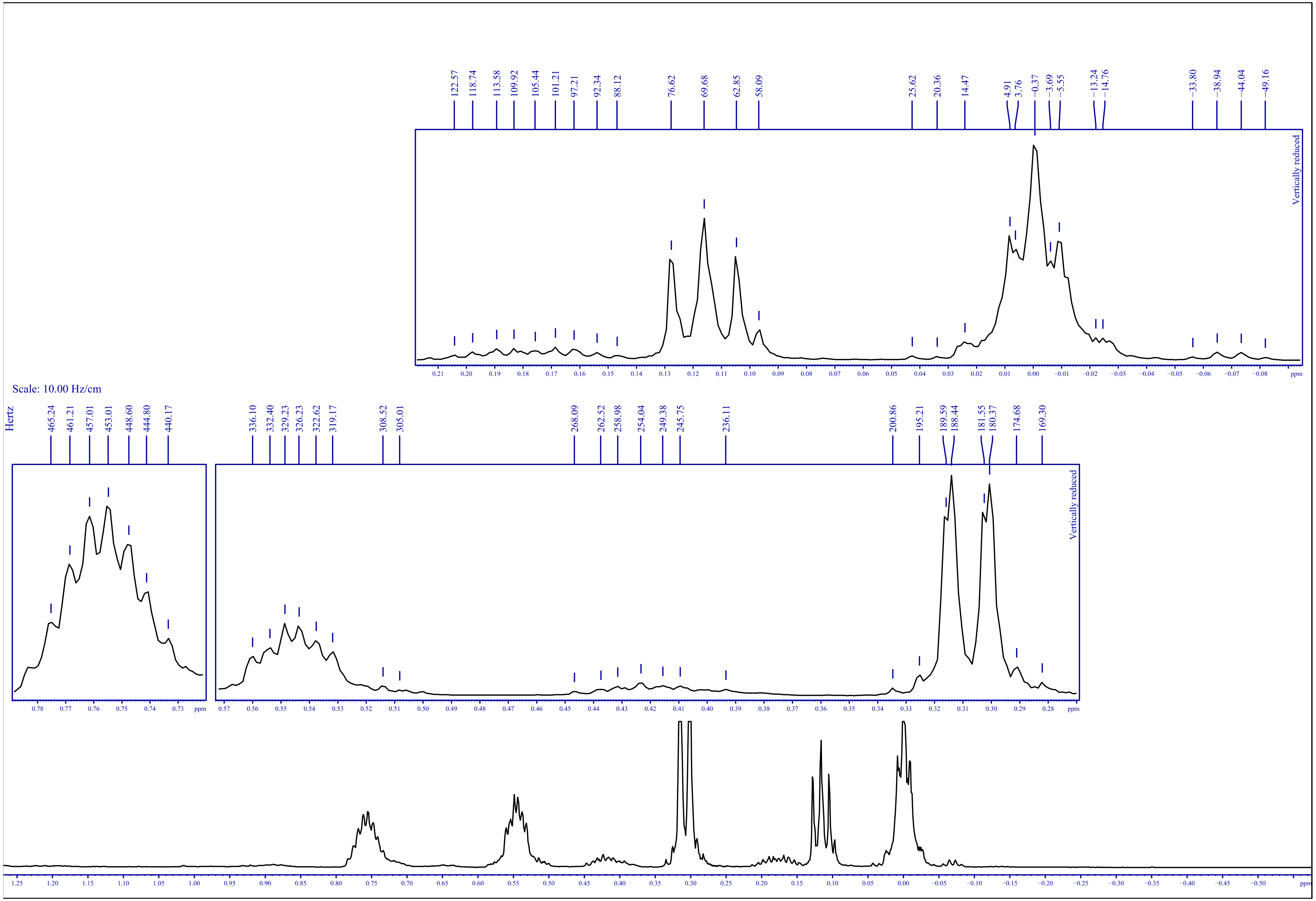


Figure S01: ^{1}H NMR (600 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**.

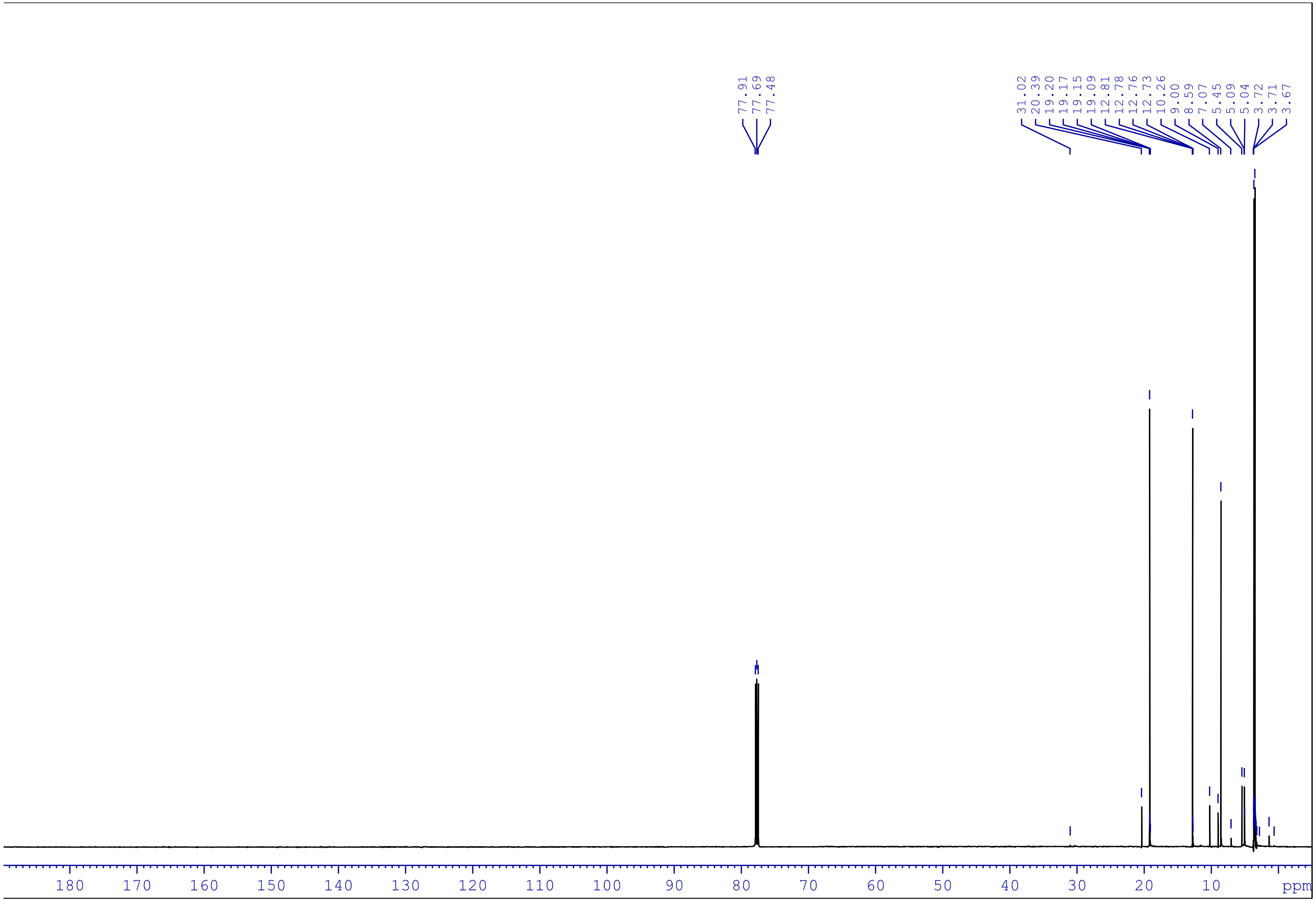


Figure S02: ^{13}C NMR (150 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**

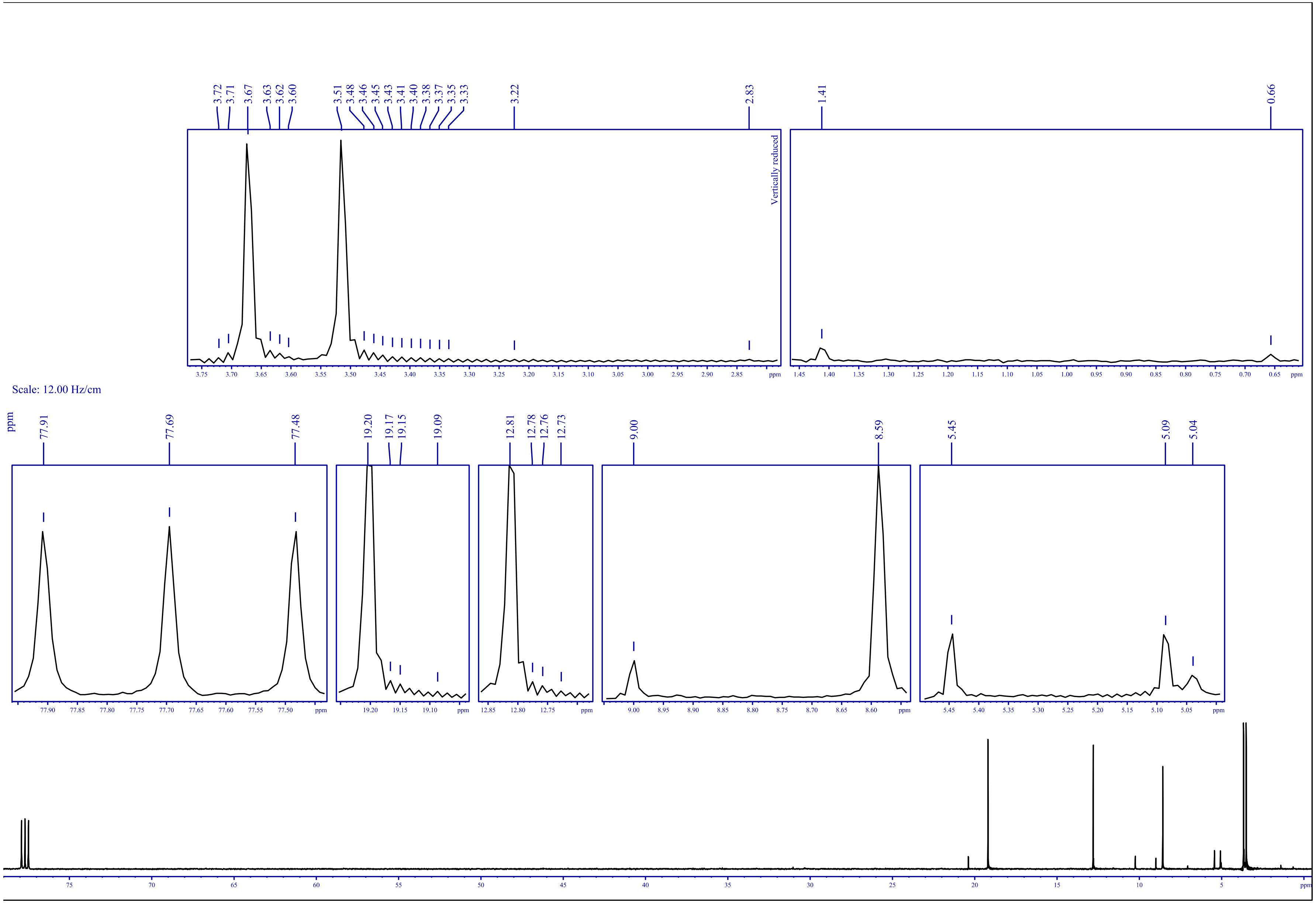


Figure S02: ^{13}C NMR (150 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**

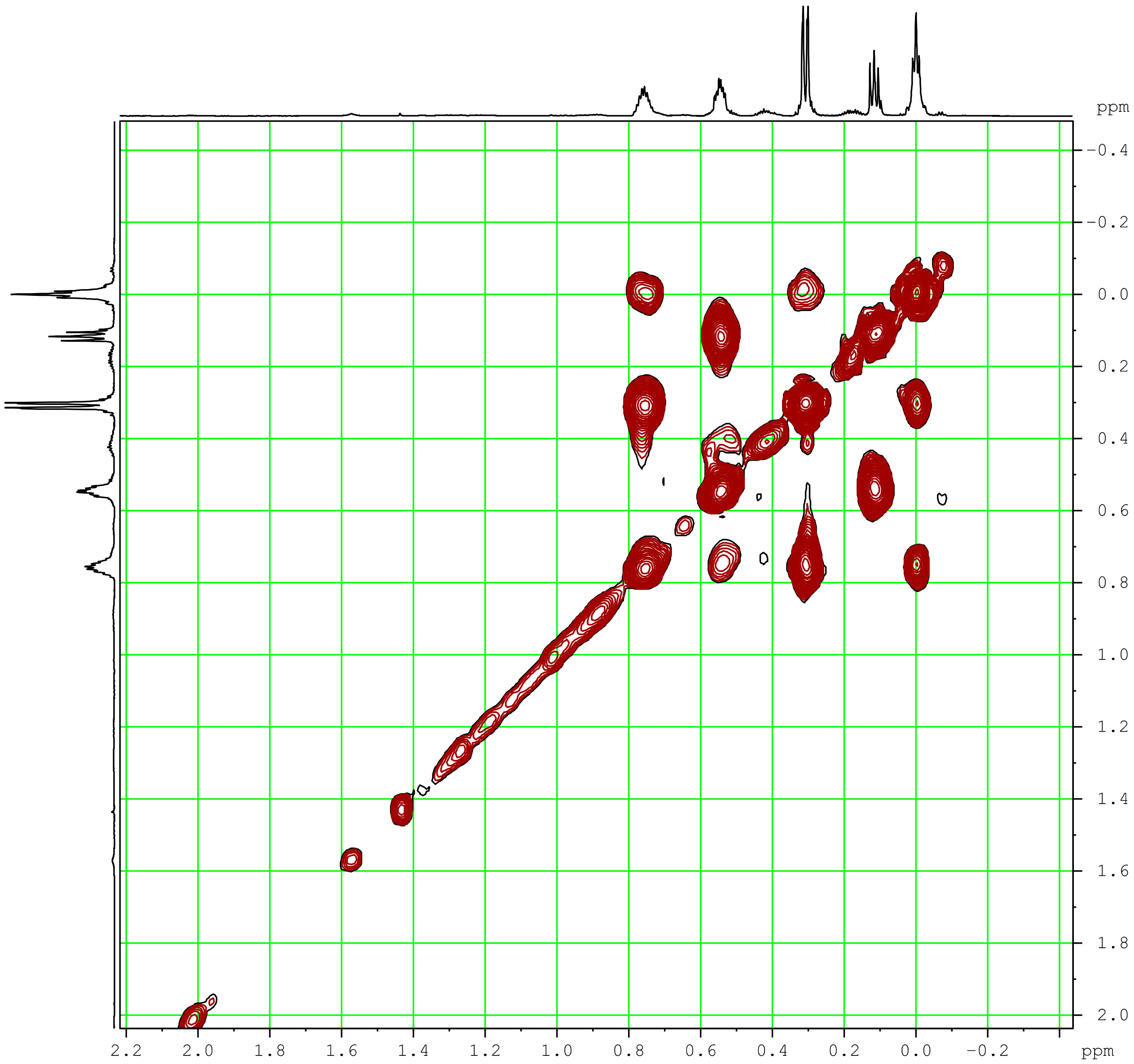


Figure S03: 2D ^1H-^1H COSY NMR (600 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**.

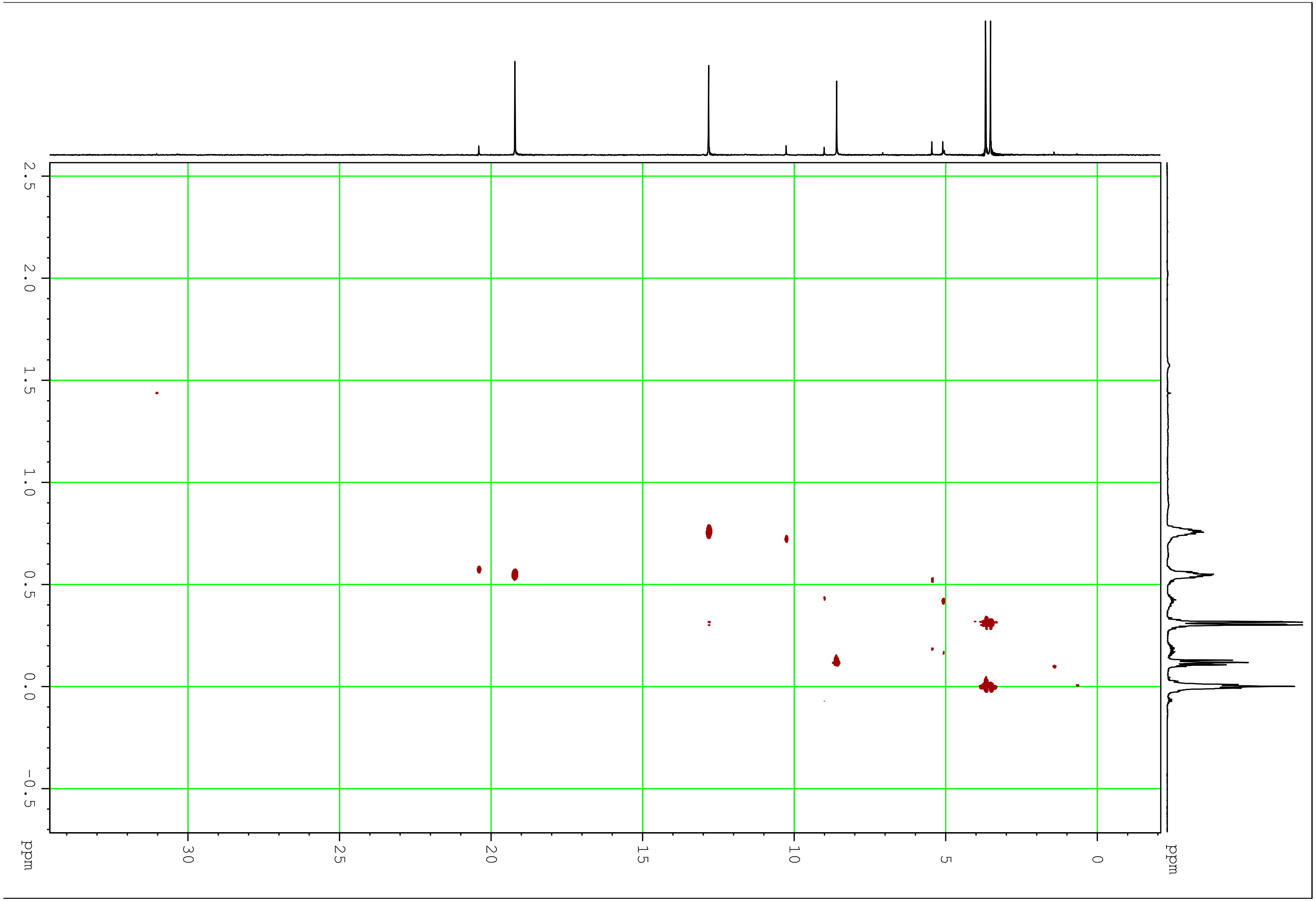


Figure S04: 2D ^{1}H-^{13}C HSQC NMR (600 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**

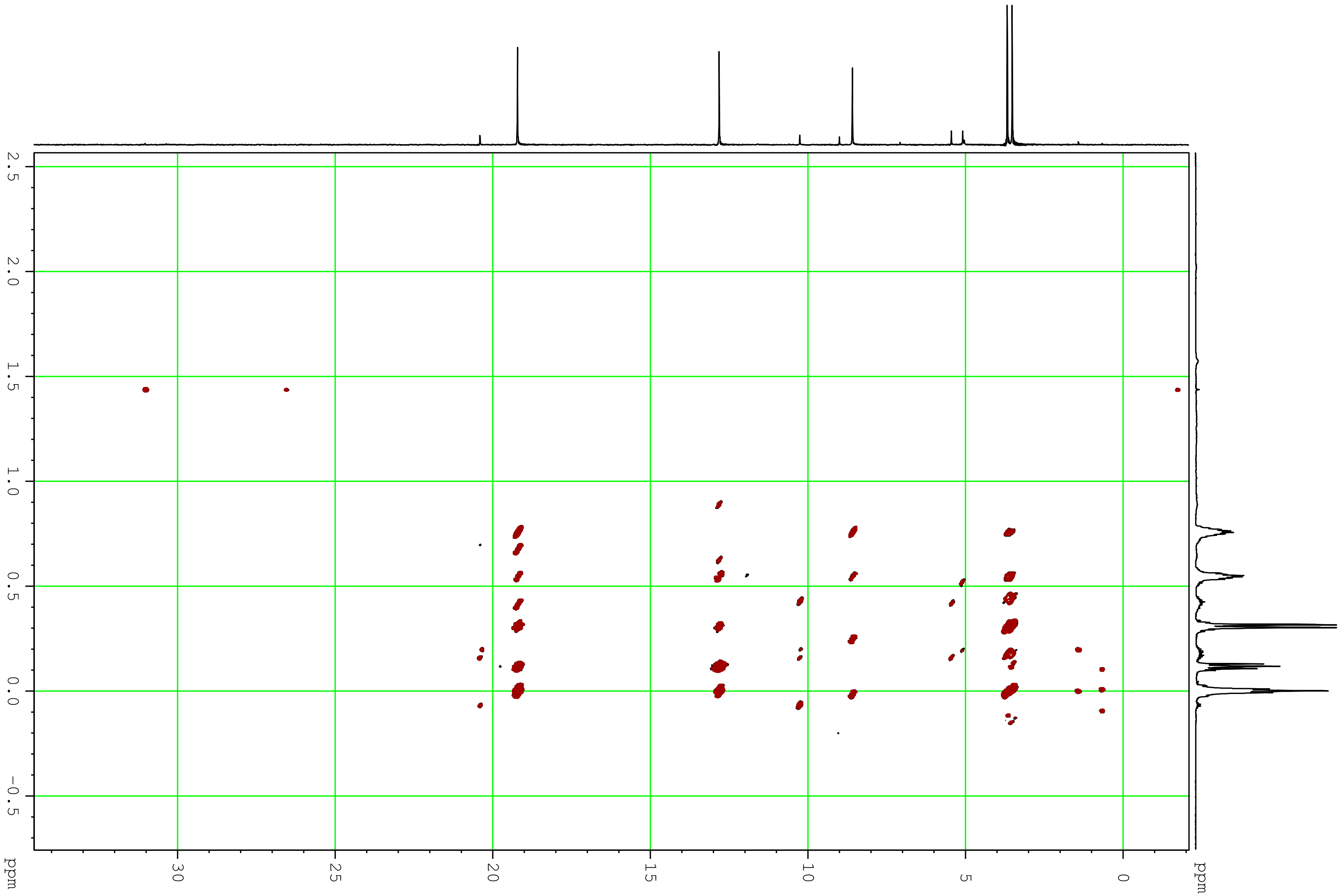


Figure S05: 2D ^{1}H-^{13}C HMBC NMR (600MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**.

Bruker AV-300 NMR spectrometer

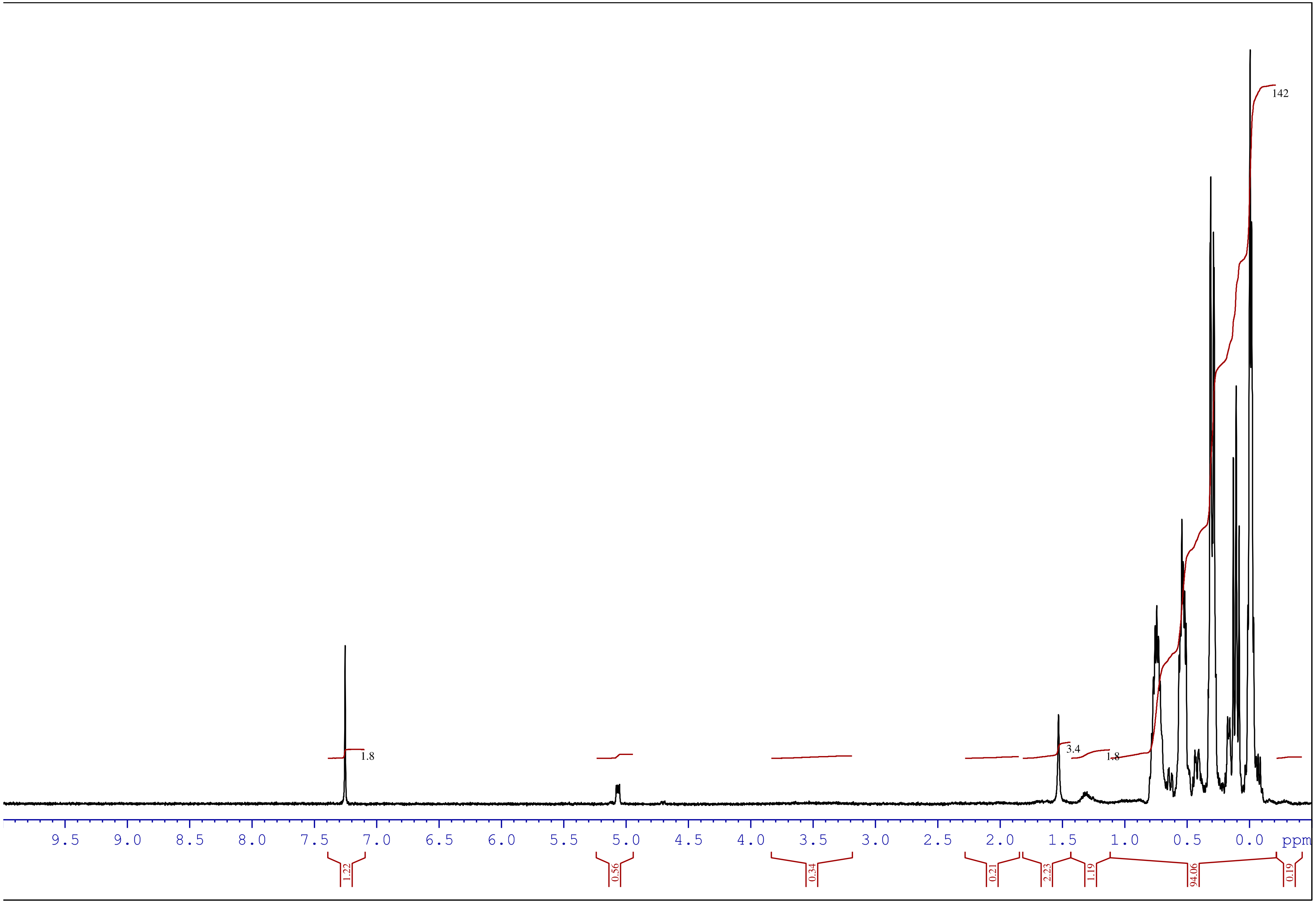


Figure S06: ^{1}H NMR (300 MHz) spectrum of 1,1′:2′,1″-tercyclopropane **2**.

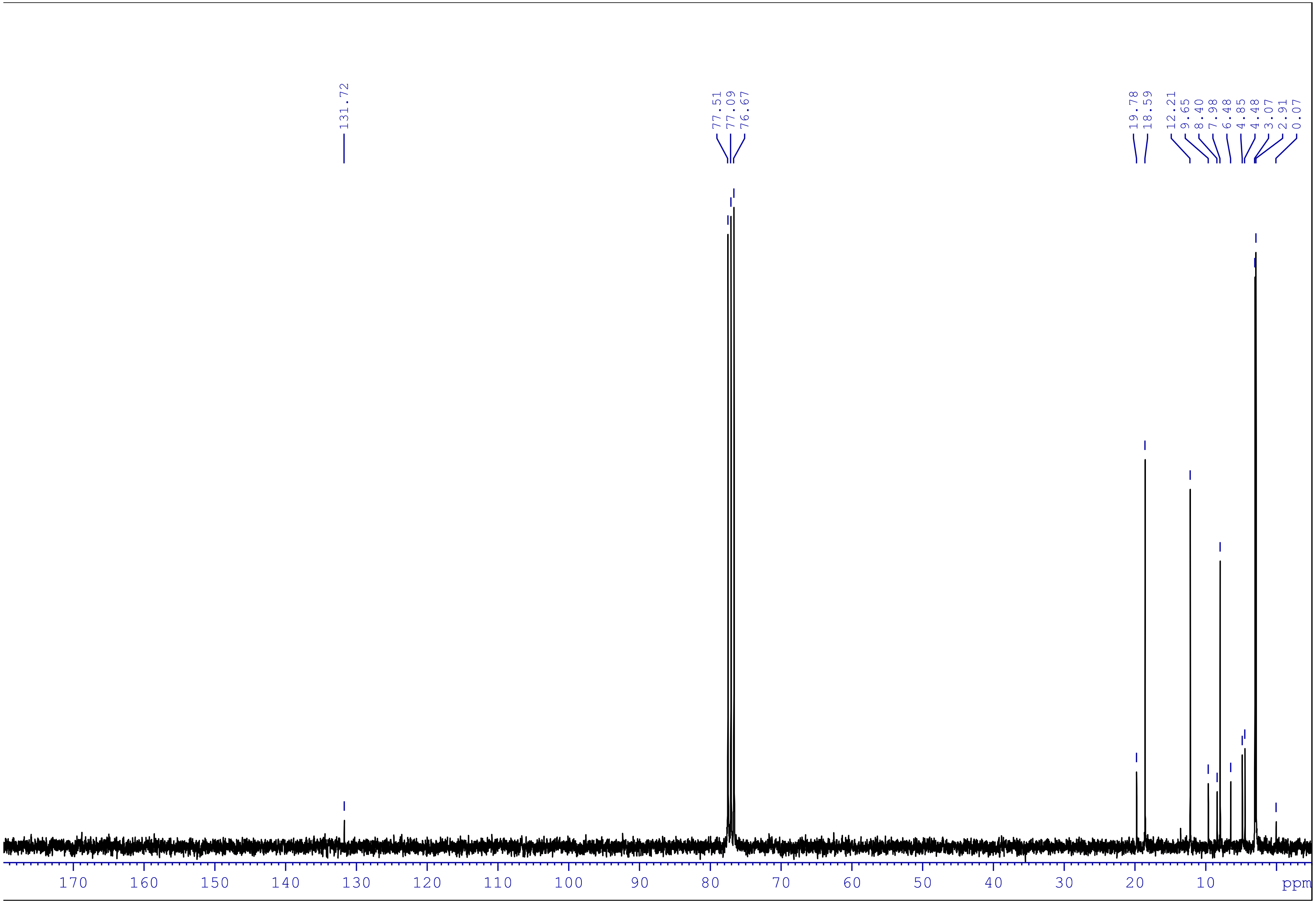


Figure S07: ^{13}C NMR (75 MHz) spectrum of 1,1´:2´,1″-tercyclopropane **2**.

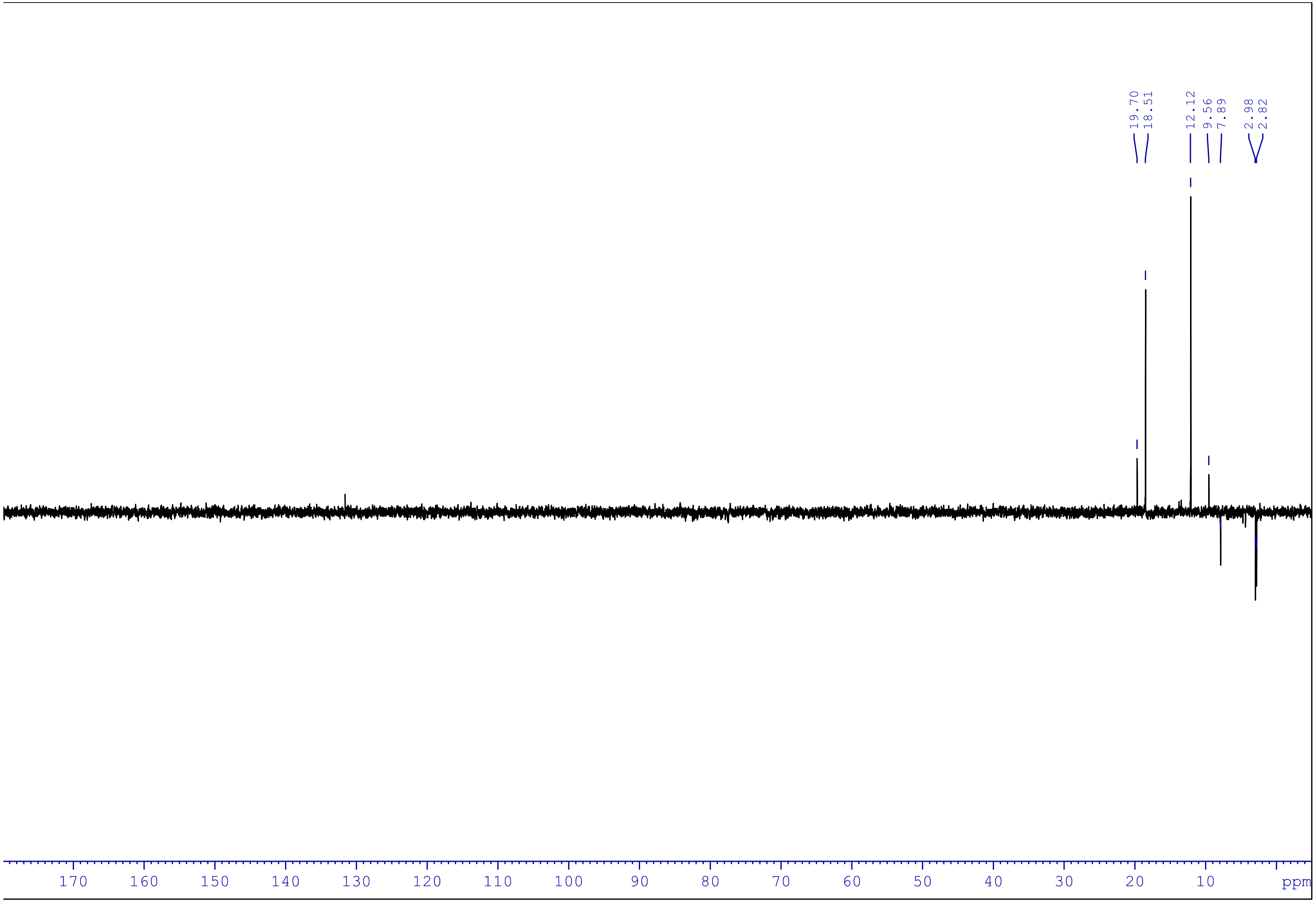


Figure S08: ^{13}C DEPT135 NMR spectrum of 1,1´:2´,1″-tercyclopropane **2**.

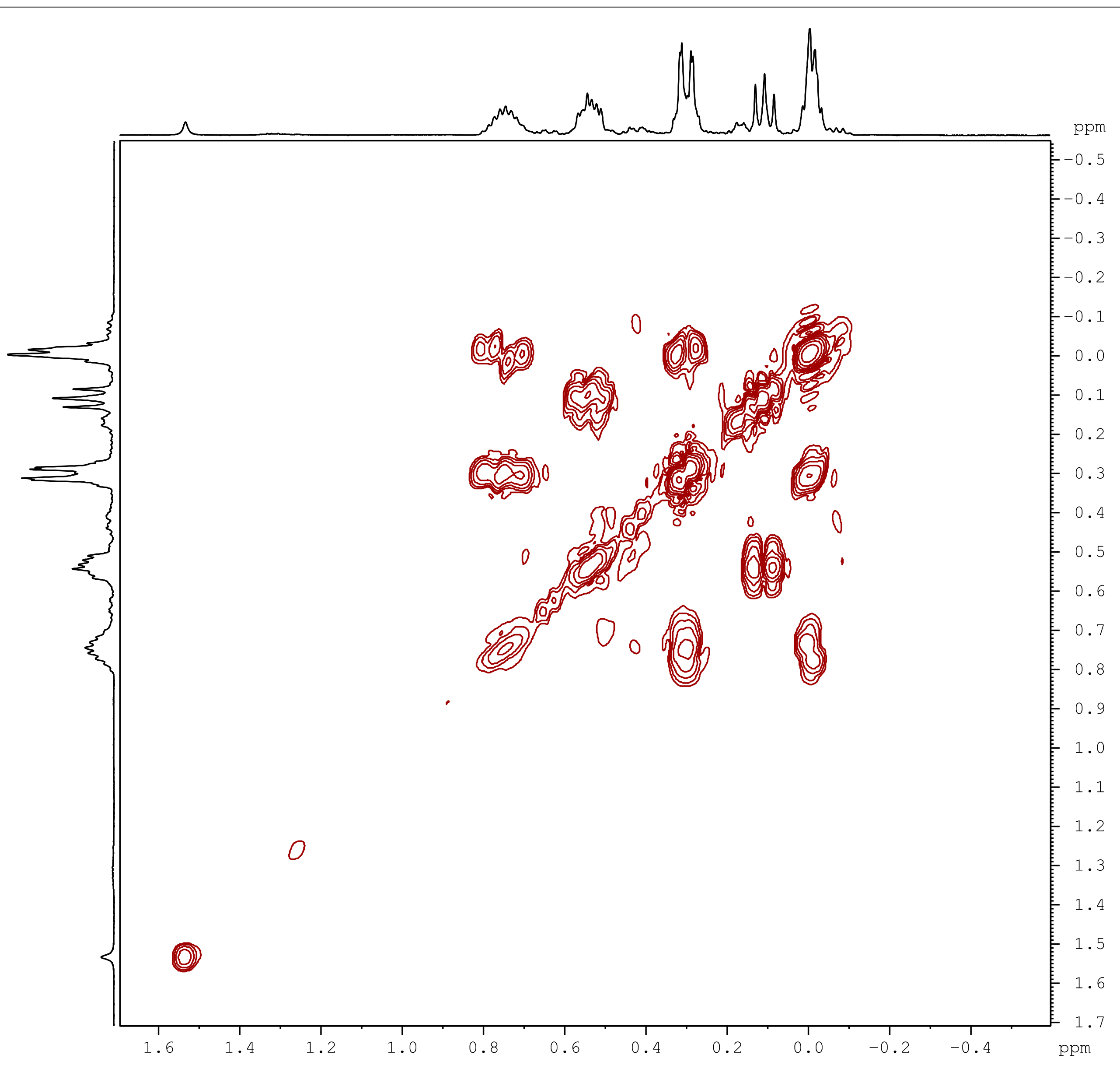


Figure S09: 2D ^{1}H-^{1}H COSY NMR spectrum of 1,1′:2′,1″-tercyclopropane **2**.

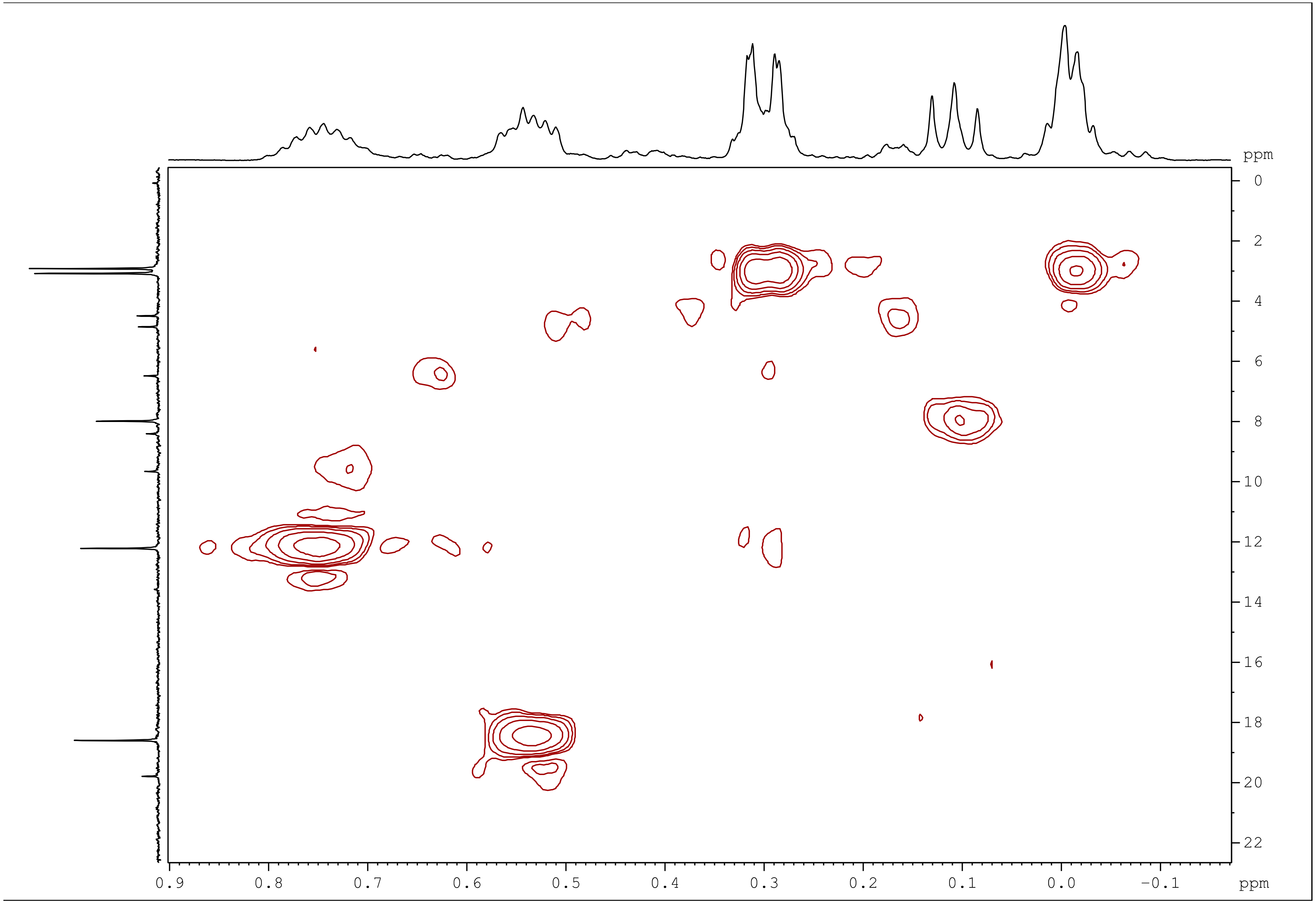


Figure S10: 2D ^{1}H-^{13}C HSQC NMR spectrum of 1,1′:2′,1″-tercyclopropane **2**.

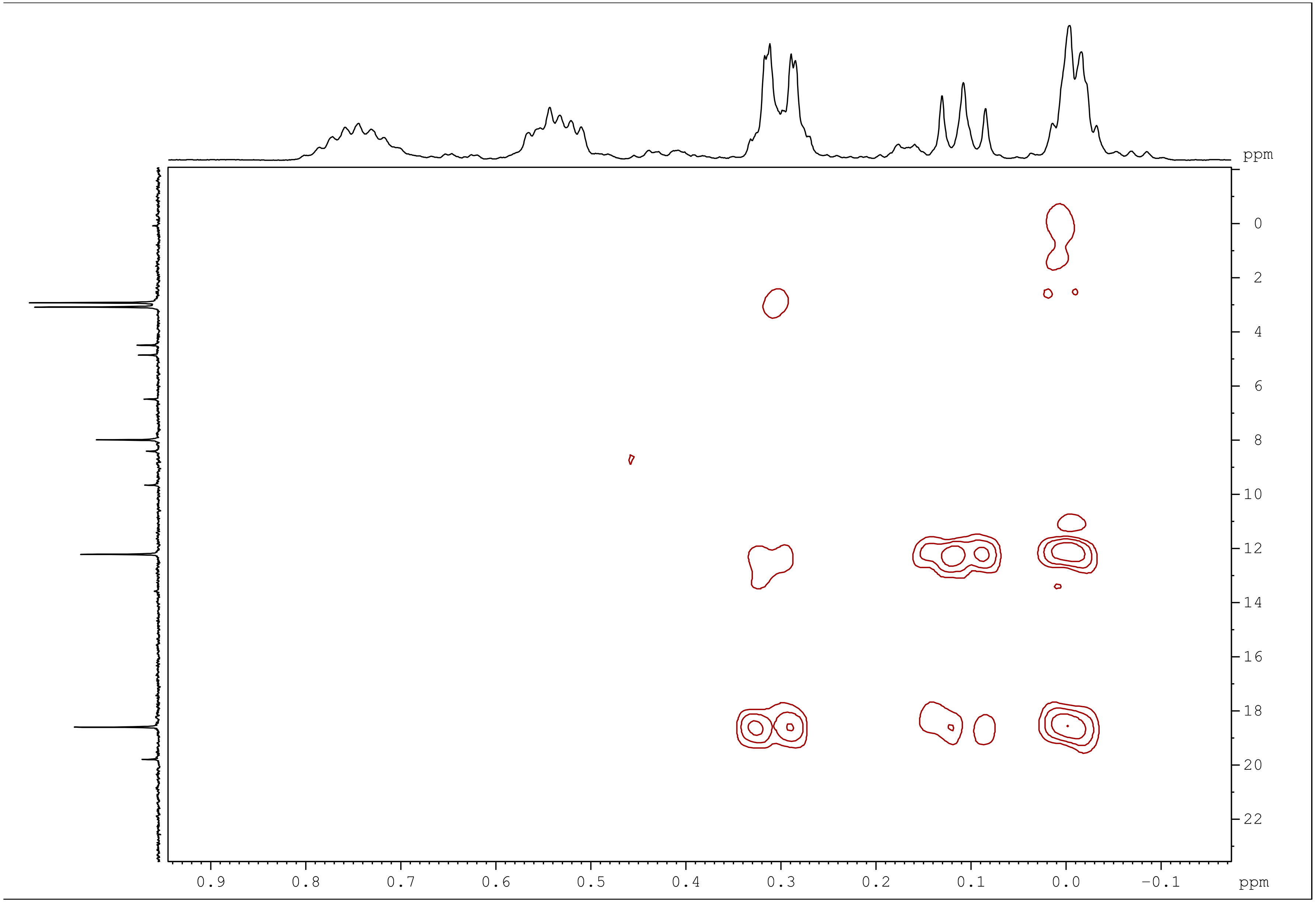


Figure S11: 2D ^{1}H-^{13}C HMBC NMR spectrum of 1,1′:2′,1″-tercyclopropane **2**.

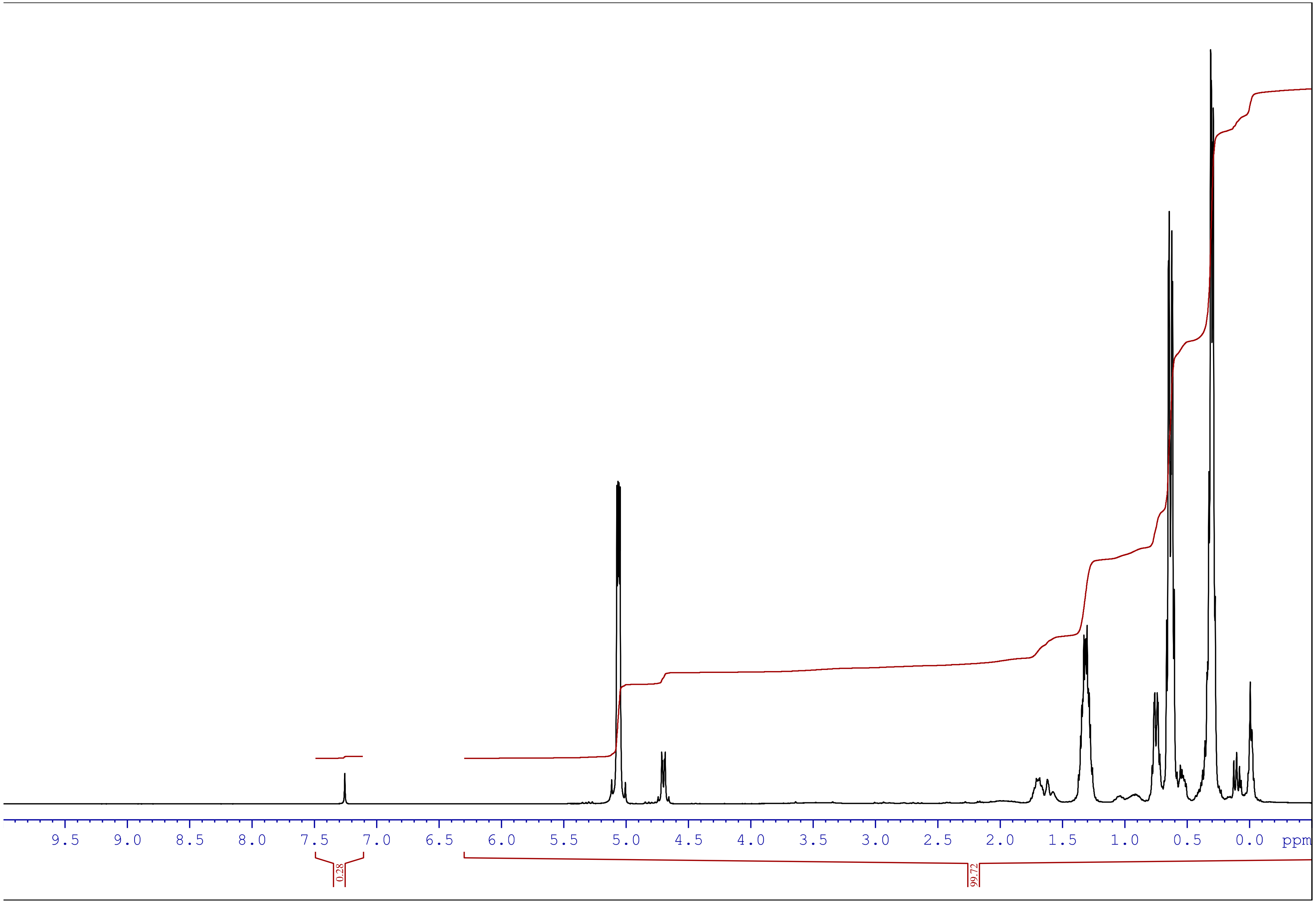


Figure S12: ^{1}H NMR spectrum of 1,2-dicyclopropylethene **3**.

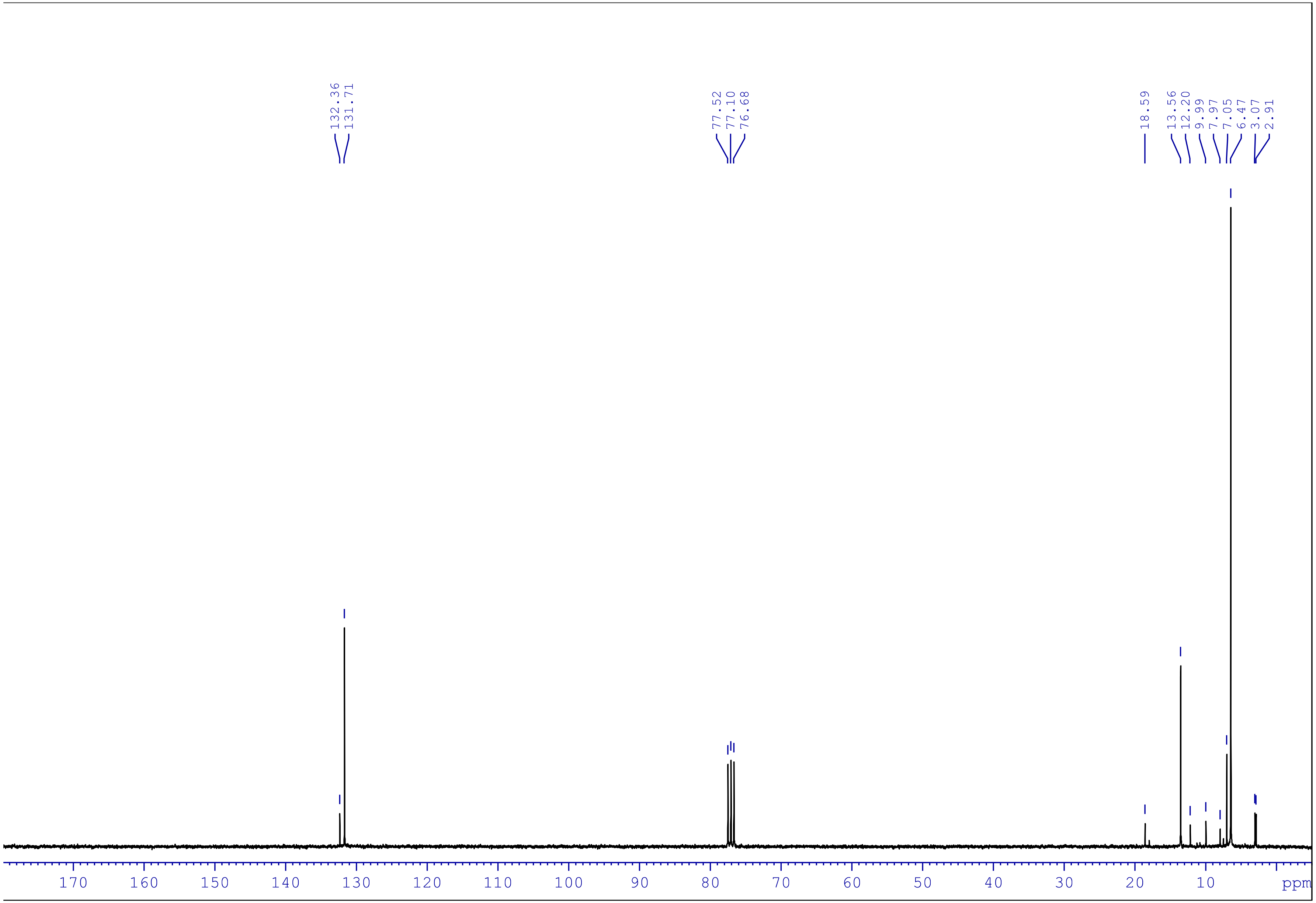


Figure S12: ^{1}H NMR spectrum of 1,2-dicyclopropylethene **3**.

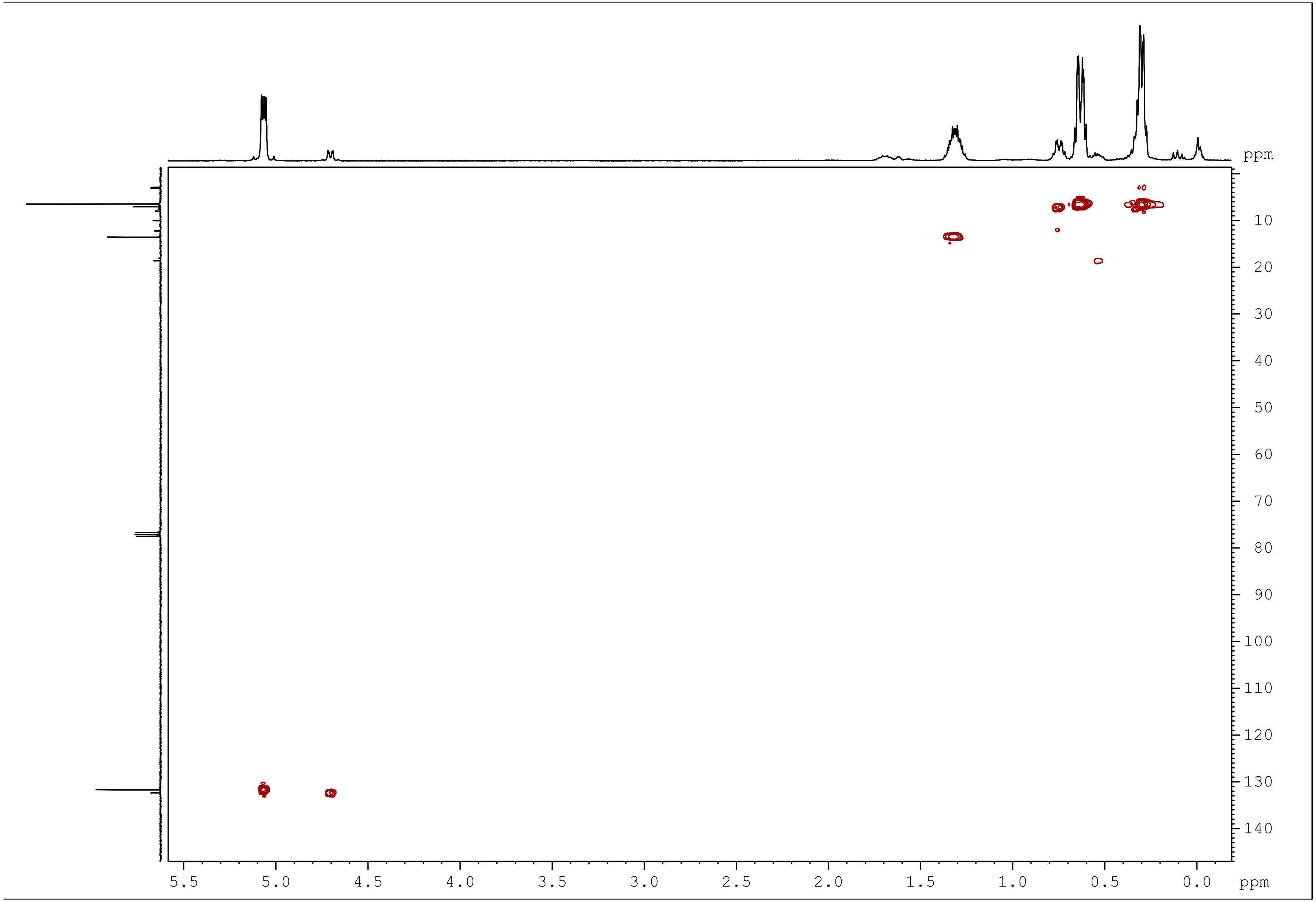


Figure S14: 2D ^{1}H-^{13}C HSQC NMR spectrum of 1,2-dicyclopropylethene **3**.

4. Mass spectra

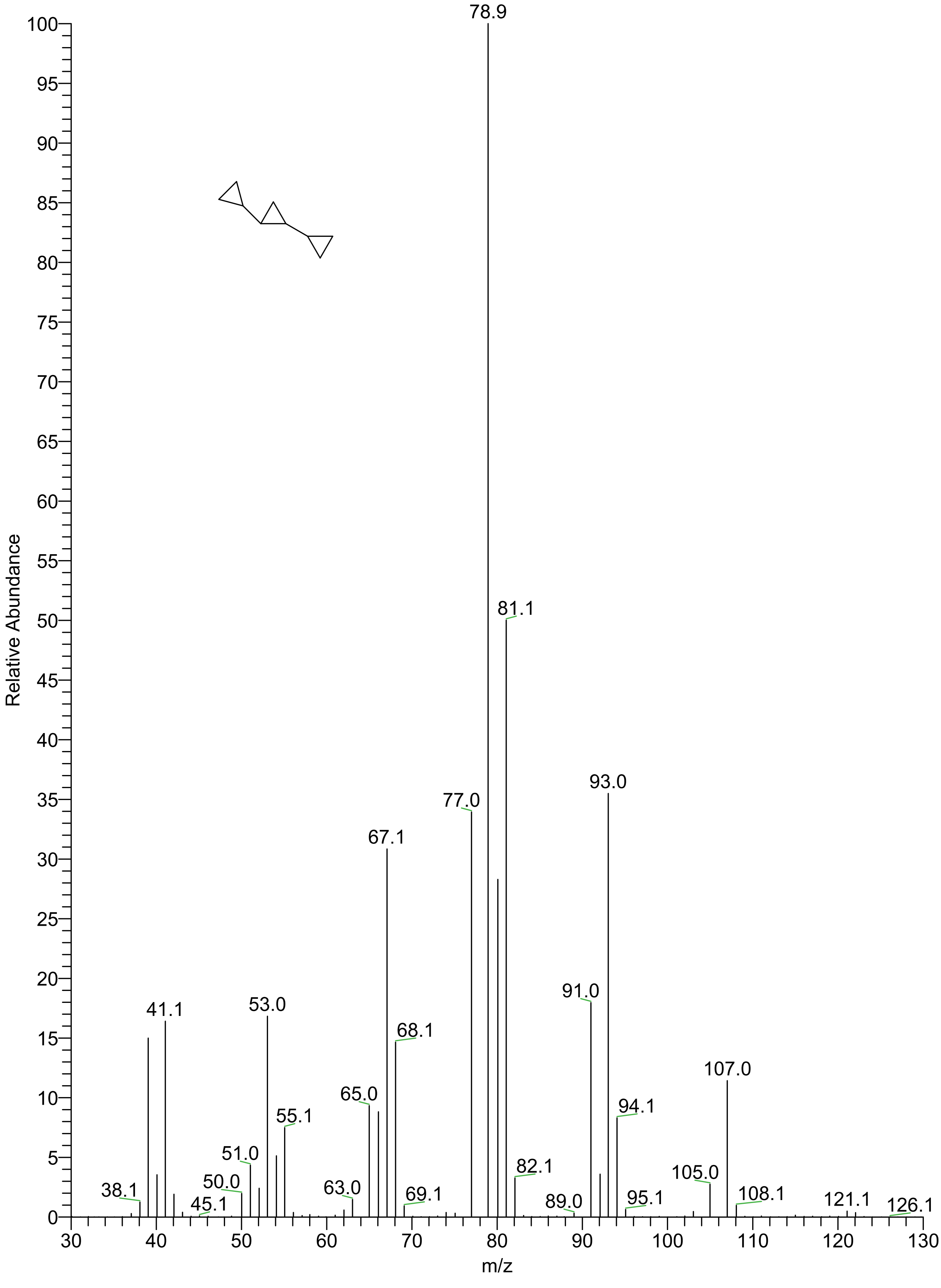


Figure S15: Mass-spectra of *E*-1,1′:2′,1″-tercyclopropane **2**.

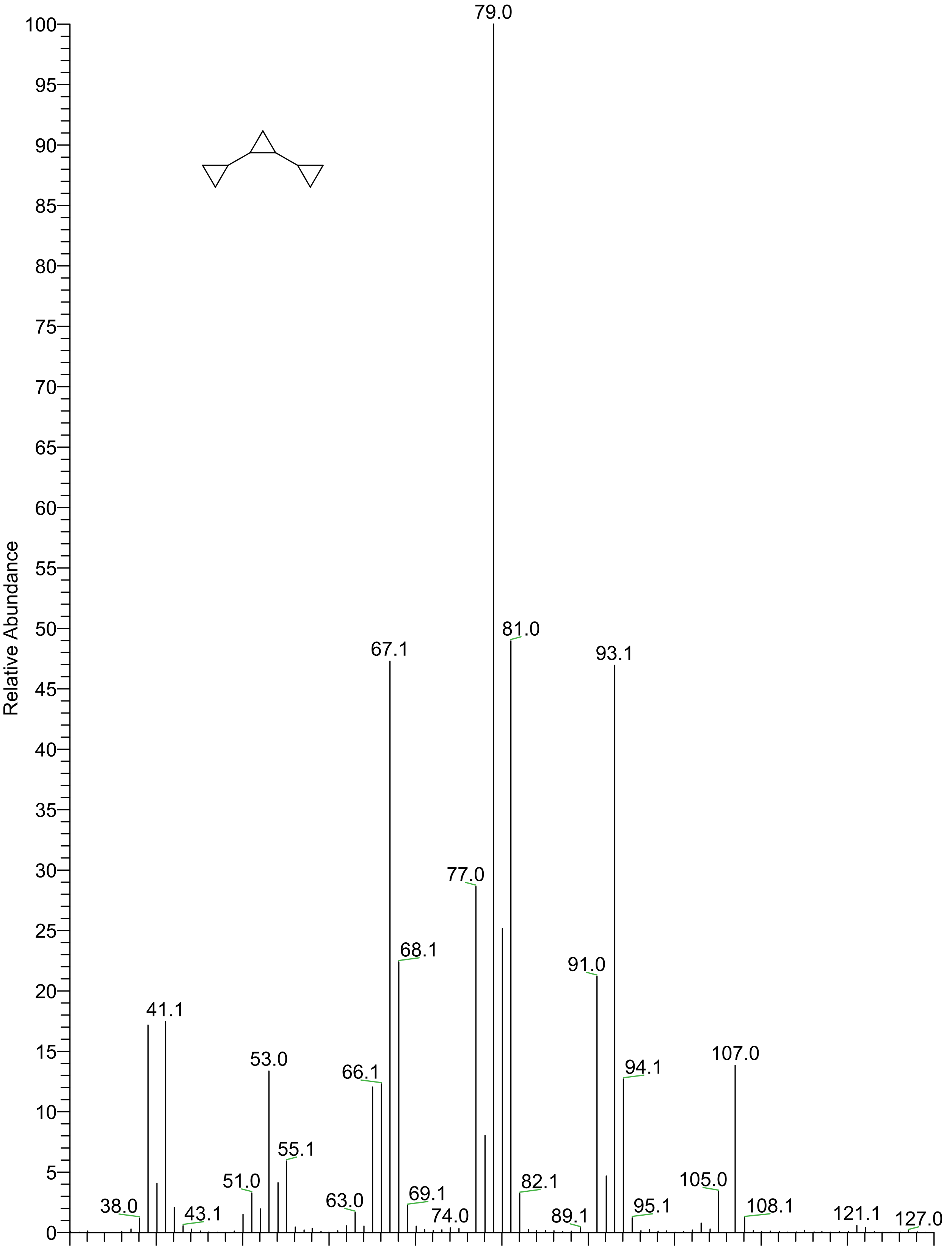


Figure S16: Mass-spectra of *Z*-1,1′:2′,1″-tercyclopropane **2**.

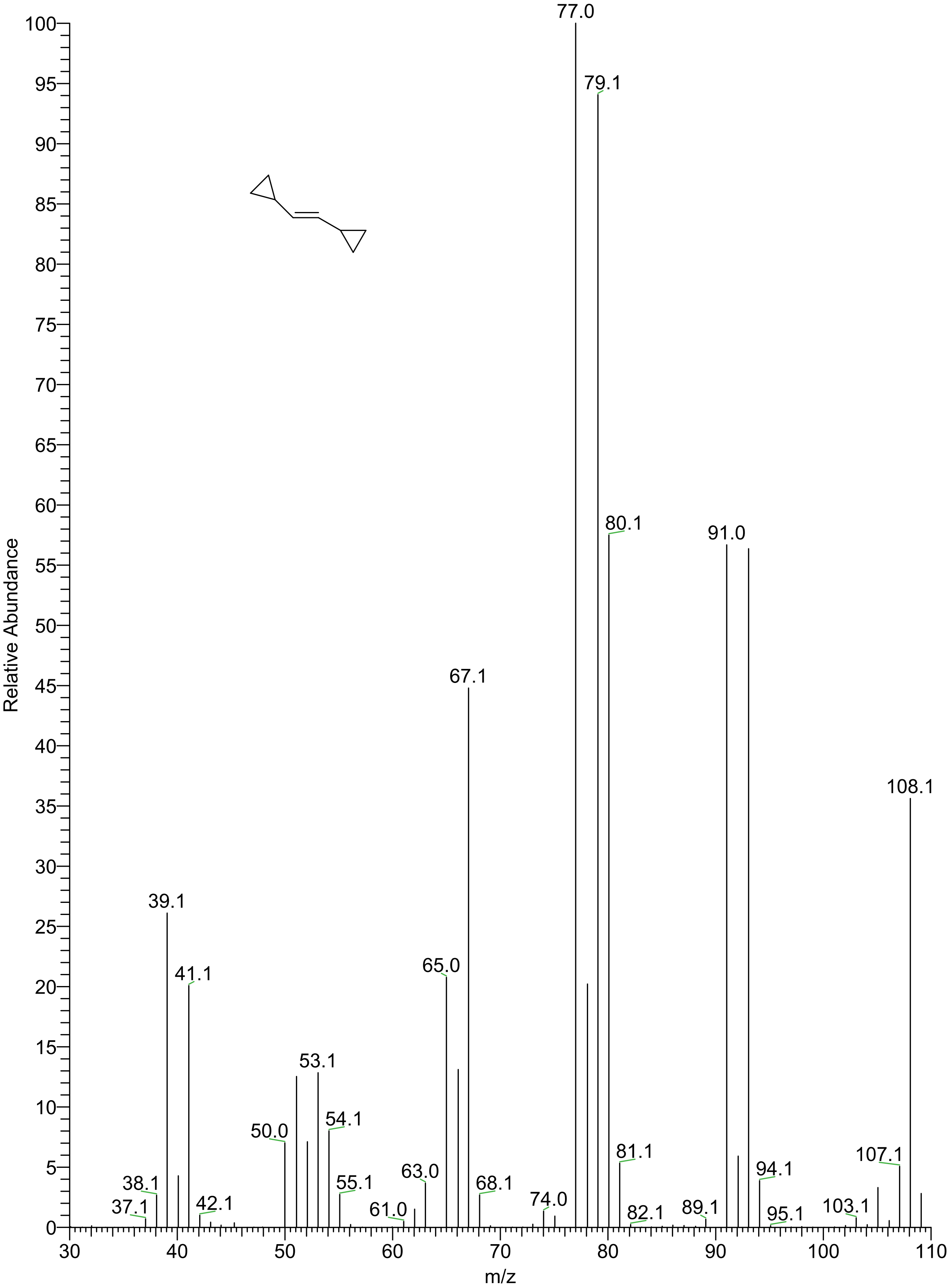


Figure S17: Mass-spectra of a mixture of *E/Z*-isomers of 1,2-dicyclopropylethene **3**.