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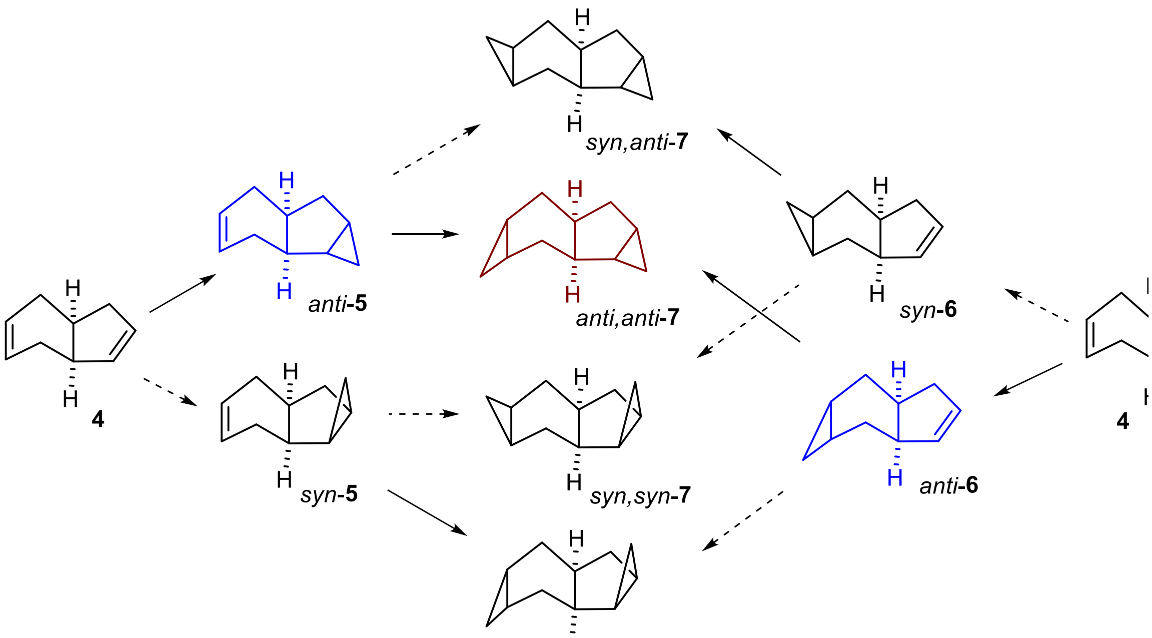
Pathways of Pd-catalyzed cyclopropanation of tetrahydroindene with diazomethane

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

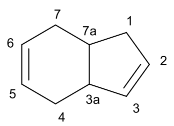


Scheme S1

Experimental Section

All commercial reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a «Bruker AV-600» (600 and 150 MHz, respectively) and «Bruker AVANCE II 300» (300 and 75 MHz, respectively) spectrometers in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. Assignments of ^1H and ^{13}C signals were made with the aid of 1D DEPT-135 and 2D COSY, NOESY, HSQC and HMBC spectra. GC/MS analysis was carried out on a Trace C Ultra chromatograph (Thermo Scientific) with a DSQ-II mass spectrometric detector using a capillary column with a non-polar phase TR-5MS with a length of 30 m and an inner diameter of 0.25 mm (film thickness of the stationary phase 0.25 μm). Analysis mode: isotherm 40 °C (3 min), heating to 250°C (20° / min) and final isotherm 250°C (20 min), carrier gas – helium, evaporator temperature 250°C, dosed sample volume ~ 0.1 μl.

3a,4,7,7a-Tetrahydro-1H-indene **4** was prepared as described [L. Crombie and K. M. Mistry, *J. Chem. Soc., Perkin Trans. 1,* 1991, 1981]. B.p. 110.4–110.8°C (180 Torr). ^1H NMR (600 MHz): δ 5.82–5.89 (m, 2H, H(5) and H(6)), 5.67–5.71 (m, 1H, H(2)), 5.61–5.64 (m, 1H, H(3)), 2.80–2.85 (m, 1H, H(3a)), 2.47–2.53 (m, 1H, H_a(1)), 2.39–2.46 (m, 1H, H(7a)), 2.22–2.29 (m, 1H, H_a(4)), 2.12–2.19 (m, 1H, H_a(7)), 1.97–2.03 (m, 1H, H_b(1)), 1.83–1.88 (m, 2H, H_b(4) and H_b(7)). ^{13}C NMR ($CDCl_3$, 150 MHz): 136.24 (C(3)), 129.81 (C(2)), 128.26 (C(5) and C(6)), 42.73 (C(3a)), 40.15 (C(1)), 34.95 (C(7a)), 28.49 (C(7)), 27.42 (C(4)). MS (*m/z*, %): 120 (52) $[M]^+$, 66 (100), 91 (16), 79 (19), 77 (15).

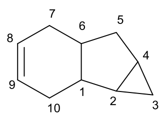


It should be noted that *N*-methyl-*N*-nitrosourea (MNU) obtained by the usual technique [F. Arndt, *Organic Syntheses. Collection*, 1943, **2**, 165] usually contains a significant amount of water (8–15%) while remaining quite loose. In addition, the yield of diazomethane from the decomposition of MNU with an alkali is not quantitative. In view of this, to correctly determine the yields of the resulting compounds, we focused on the amount of diazomethane generated, which averages 70–75% of the amount of MNU used. The yield of CH_2N_2 that we estimated was found to be approximately the same both from the results of titration of diazomethane dissolved in CH_2Cl_2 and from the ^1H NMR spectra of an aliquot of the solution in the presence of 1,4-dichlorobenzene as the internal standard. Thus, in the cyclopropanation *in situ*, no less than 1.3 equivalents of technical grade *N*-methyl-*N*-nitrosourea corresponds to the equimolar olefin/CH_2N_2 ratio.

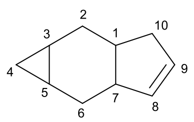
CAUTION: Diazomethane is highly explosive. Use a special glassware kit. Do not use ground glass joints or glassware with any signs of cracking. Use appropriate precautions.

General procedure for the cyclopropanation of the 3a,4,7,7a-tetrahydro-1H-indene **4**. Tetrahydroindene **4** (6.1 g, 50 mmol) in CH_2Cl_2 (20 ml) and then a small portion of *N*-methyl-*N*-nitrosourea (MNU, ~1.5 g) were added with stirring to a 50% KOH solution (32 g) at 15–18°C. After that a solution of $Pd(acac)_2$ (15.2 mg, 0.05 mmol) in CH_2Cl_2 (3 ml) was added. In this case, nitrogen evolution and weakening of the colour were observed. From this moment, NMU was added in small portions (~ 1.5 g. 10.0 g total) to obtain monoadducts **5,6**. In the synthesis of diadduct **7**, total amount of MNU was 19.5 g. These amounts of MNU correspond to the generation of about 1.5 or 2.9 equivalents of CH_2N_2. After the nitrogen evolution ceased, the main part of the organic layer was separated, the alkaline solution was extracted with hexane (2 × 10 ml), and the combined extracts were filtered through a short layer of alumina. The solvents were evaporated, and the residue was fractionated under reduced pressure. In the first case, when 1.5 equiv. diazomethane was used, a fraction with b.p. 93.6–95.4°C (40 Torr) was collected (3.55 g, 53%) containing monoadducts **5,6** in a ratio of ~ 3.2: 1. In the second case, when generating an excess of CH_2N_2, 6.65 g (~ 90%) of stereoisomeric tetracyclo[5.4.0.0^{3,5}.0^{8,10}]undecanes **7** were obtained in a ratio of ~8: 1: 1; colourless liquid, b.p. 112–118°C (40 Torr).

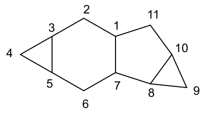
Tricyclo[4.4.0.0^{2,4}]dec-8-ene **5**. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.62–5.66 and 5.58–5.62 (both m, 2 × 1H, H(8) and H(9)), 2.14–2.30 (m, 2H, $H_aC(7)$ and $H_aC(10)$), 1.84–1.96 (m, 2H, $H_bC(7)$ and $H_bC(10)$), 1.61–1.79 (m, 3H, H(1), H(6) and $H_a(5)$), 1.44–1.51 (m, 1H, $H_b(5)$), 1.09–1.18 (m, 2H, H(2) and H(4)), 0.44–0.47 and 0.26–0.30 (both m, 2 × 1H, $H_2C(3)$). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 125.10 and 125.04 (C(8) and C(9)), 33.92 and 28.47 (C(1) and C(6)), 31.84 (C(5)), 28.44 and 25.08 (C(7) and C(10)), 23.73 and 14.02 (C(2) and C(4)), 6.33 (C(3)). MS (*m/z*, %): 134 (23) [M]$^+$, 91 (100), 119 (39), 106 (12), 105 (18), 93 (27), 92 (87), 80 (97), 79 (96), 78 (24), 77 (44).



Tricyclo[5.3.0.0^{3,5}]dec-8-ene **6**. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 5.58–5.61 (m, 1H, H(9), overlapped with the signal of isomer **5**), 5.48–5.51 (m, 1H, H(8)), 2.65–2.72 (m, 1H, H(7)), 2.57–2.63 (m, 1H, $H_a(10)$), 2.15–2.19 (m, 1H, H(1), overlapped with the signal of isomer **5**), 2.05–2.11 (m, 1H, $H_b(10)$), 1.61–1.79 (m, 4H, $H_2C(2)$ and $H_2C(6)$, overlapped with the signal of isomer **5**), 0.75–0.85 (m, 2H, H(3) and H(5)), 0.36–0.40 (m, 1H, *anti*-H(4)), 0.27–0.31 (m, 1H, *syn*-H(4), overlapped with the signal of isomer **5**). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 134.76 (C(8)), 128.51 (C(9)), 42.12 (C(7)), 40.60 (C(10)), 31.46 (C(1)), 28.25 and 26.34 (C(2) and C(6)), 7.86 and 7.47 (C(3) and C(5)), 6.52 (C(4)). MS (*m/z*, %): 134 (16) [M]$^+$, 66 (100), 119 (13), 92 (19), 91 (28), 80 (11), 79 (29), 77 (20), 67 (12), 65 (11), 39 (10).

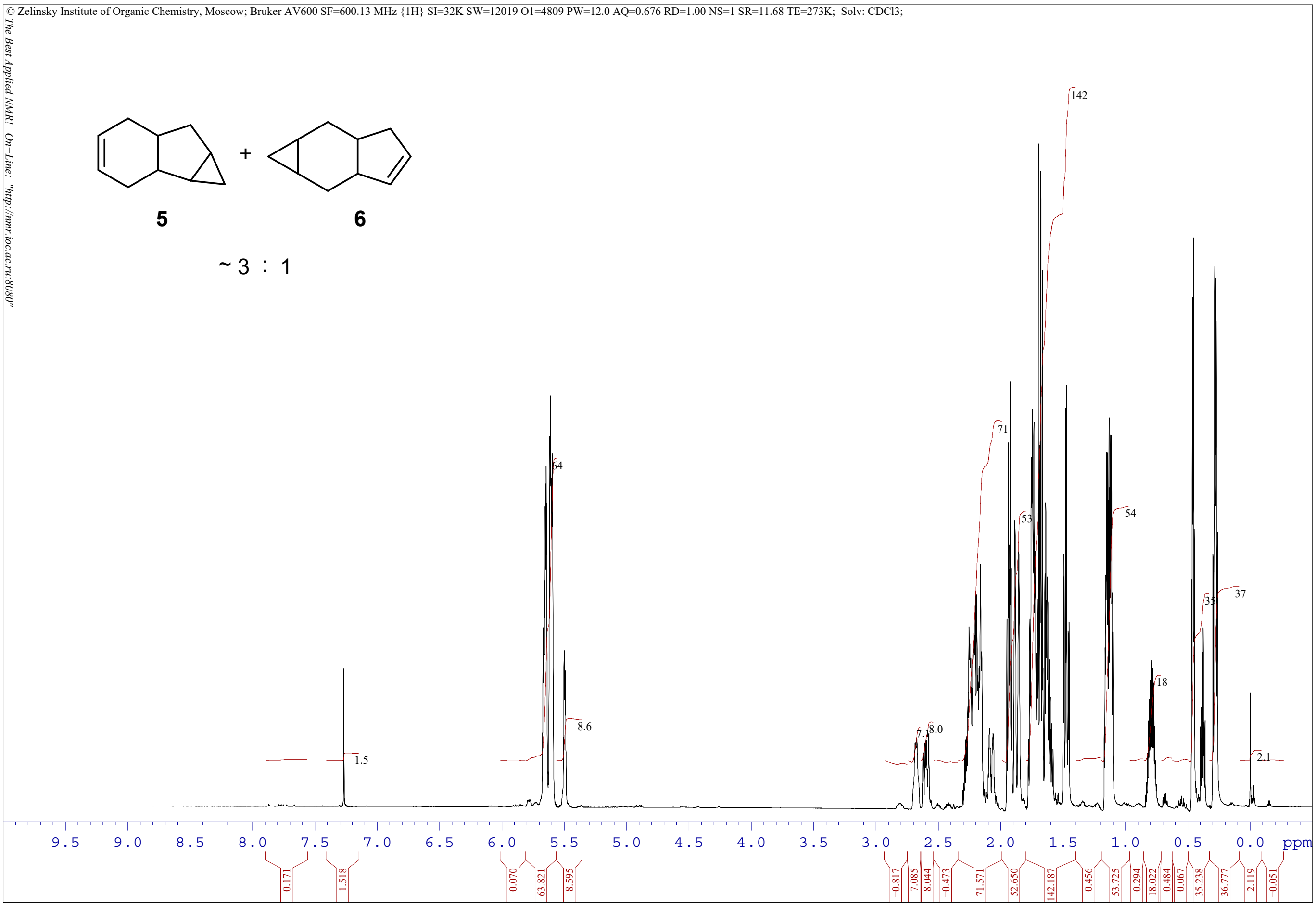


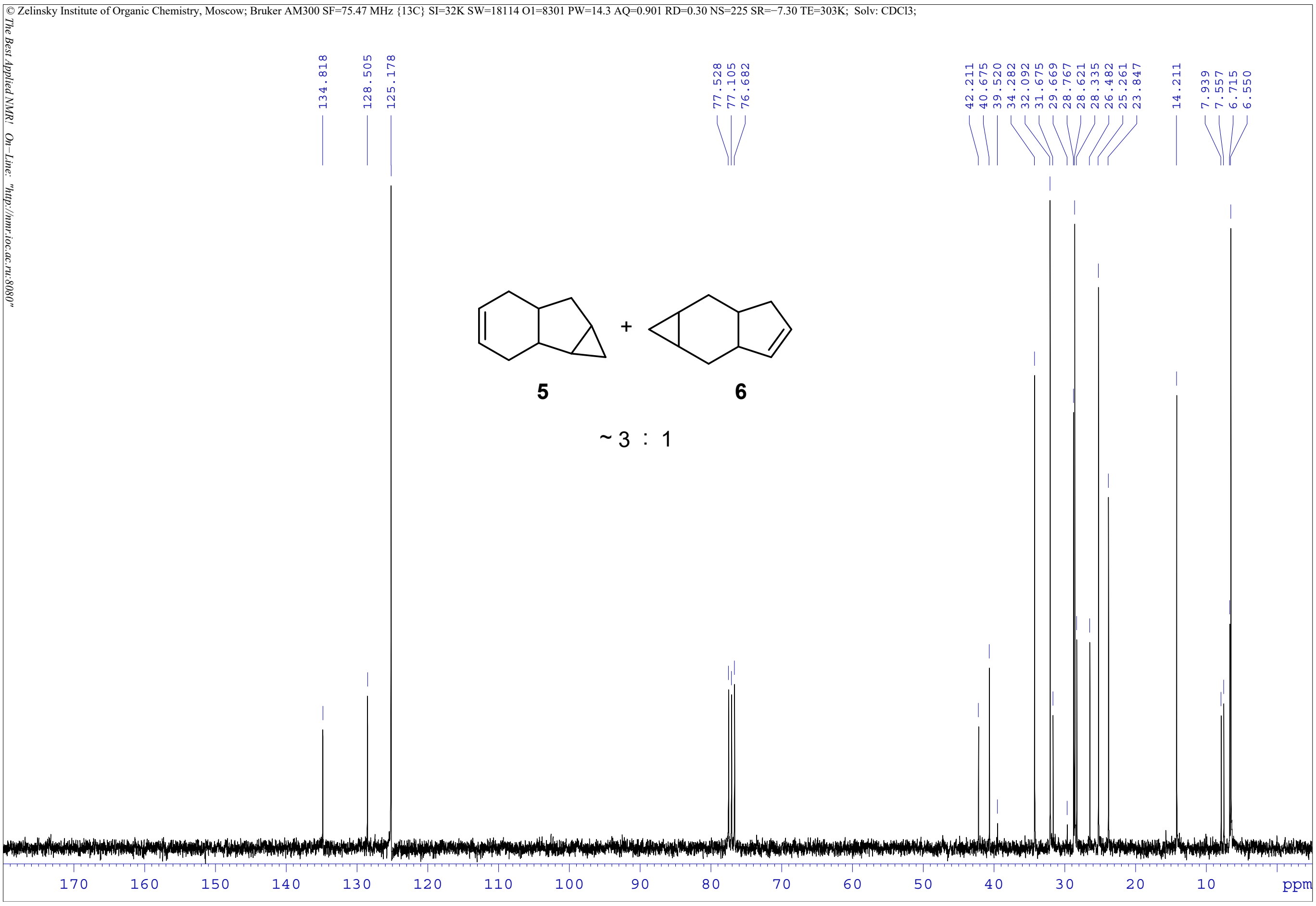
Tetracyclo[5.4.0.0^{3,5}.0^{8,10}]undecane (**7**). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.46–1.93 (m, 8H, H(1), H_2C(2), H_2C(6), H(7) and H_2C(11)), 1.08–1.17 and 0.98–1.05 (both m, 2 × 1H, H(8) and H(10)),

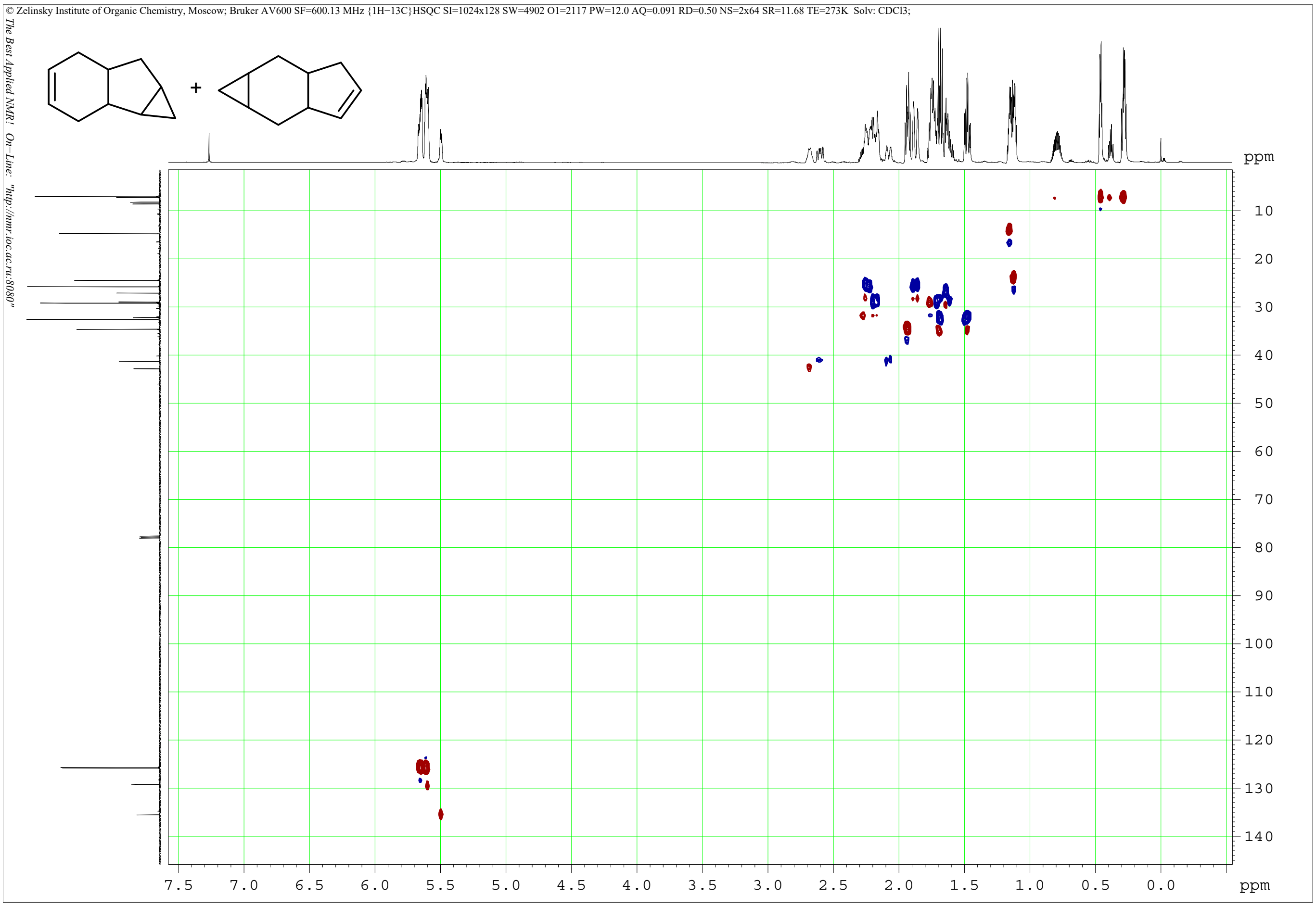


0.83–0.94 and 0.73–0.82 (both m, 2 × 1H, H(3) and H(5)), 0.33–0.40 and 0.14–0.20 (both m, 2 × 1H, H_2C(4)), 0.25–0.33 and 0.02–0.08 (both m, 2 × 1H, H_2C(9)). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 35.75 (C(11)), 34.88 and 29.06 (C(1) and C(7)), 26.27 and 25.49 (C(2) and C(6)), 22.48 and 15.44 (C(8) and C(10)), 9.75 and 7.99 (C(3) and C(5)), 8.14 (C(9)), 6.52 (C(4)). MS (*m/z*, %): 148 (4) $[M]^+$, 79 (100), 132 (30), 120 (16), 118 (27), 107 (24), 106 (28), 104 (34), 94 (12), 93 (21), 92 (37), 90 (75), 80 (54), 78 (15), 77 (33).

NMR spectral data for obtained compounds



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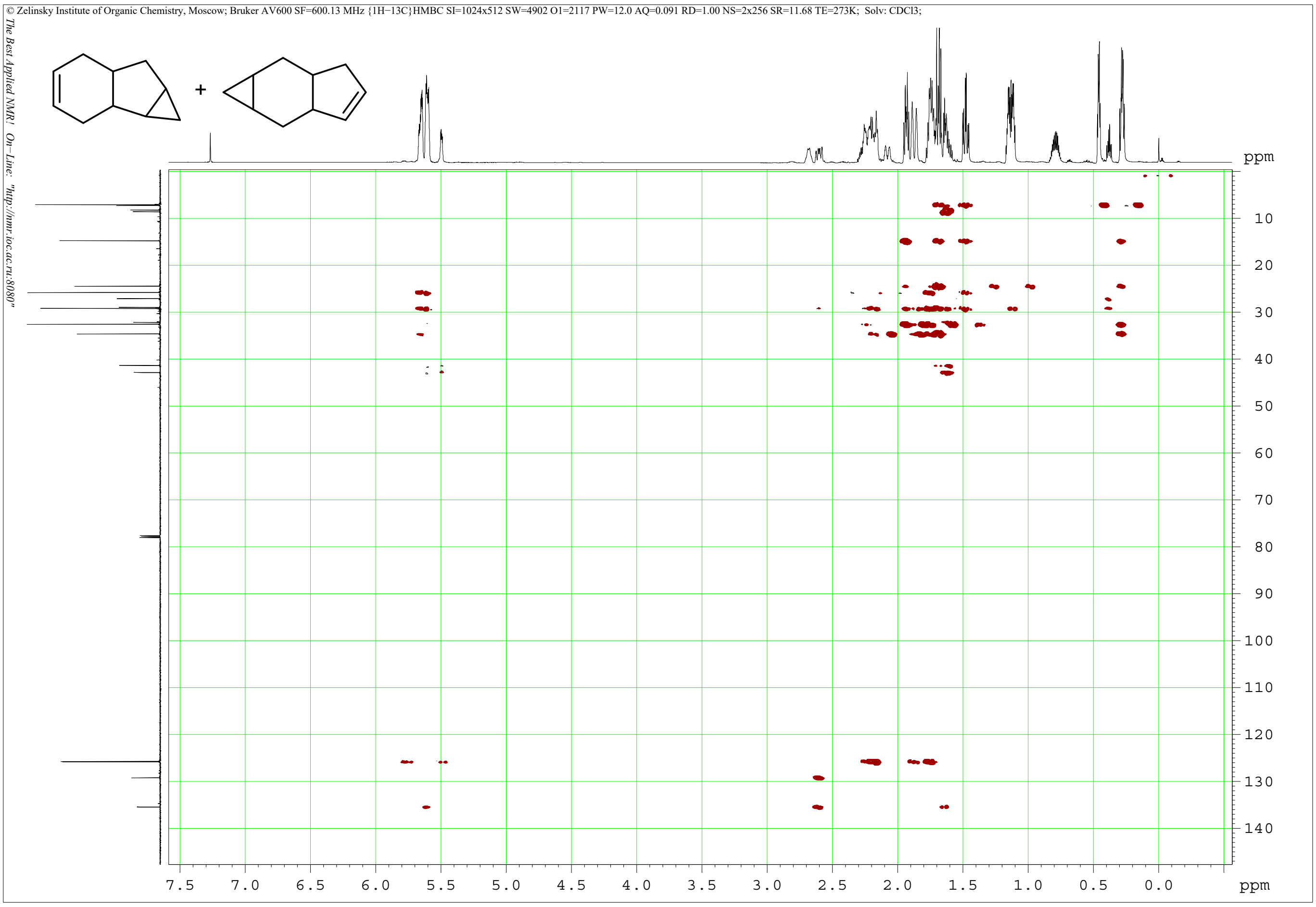
© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AV600 SF=600.13 MHz {1H−13C}HMBC SI=1024x512 SW=4902 O1=2117 PW=12.0 AQ=0.091 RD=1.00 NS=2x256 SR=11.68 TE=273K; Solv: CDCl3;
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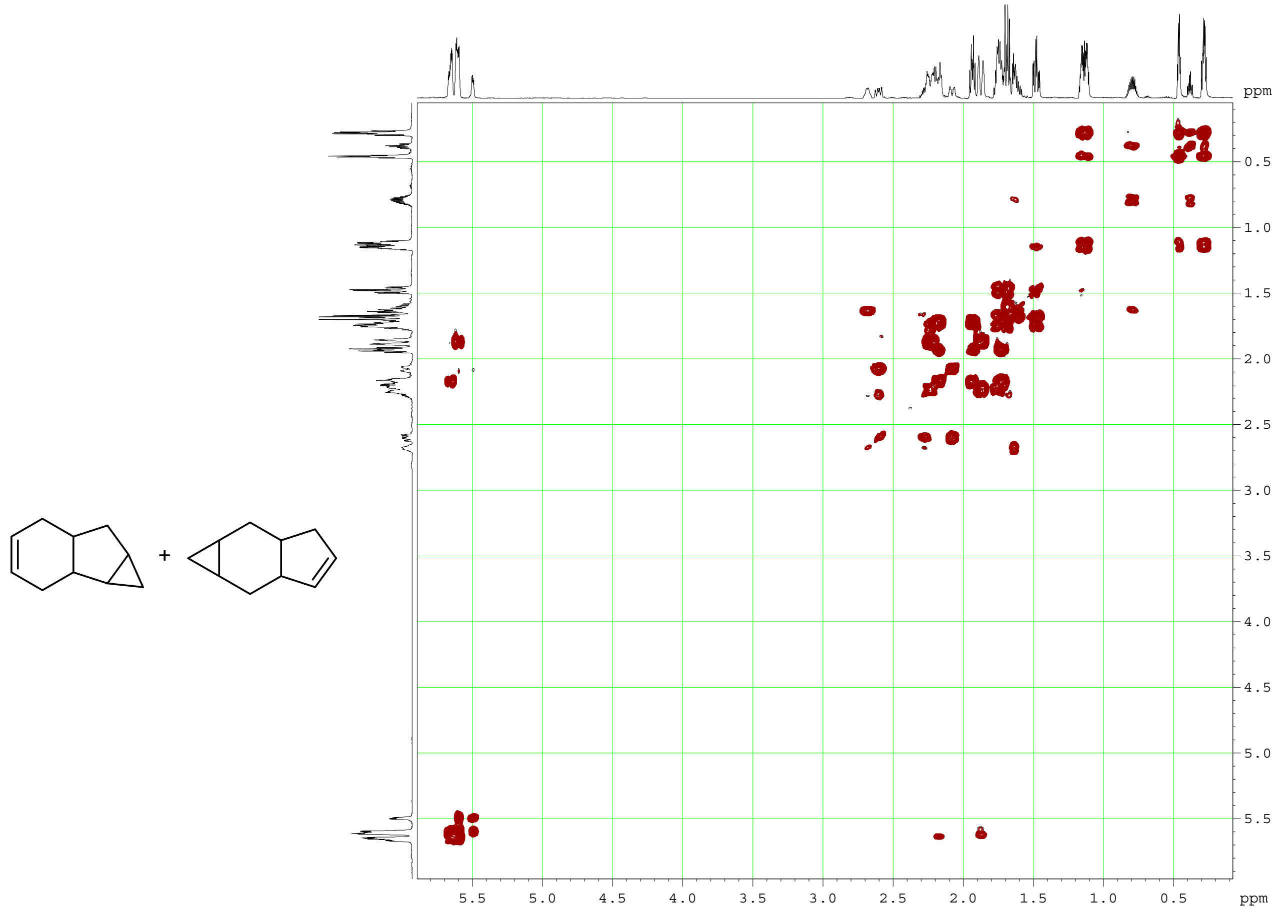
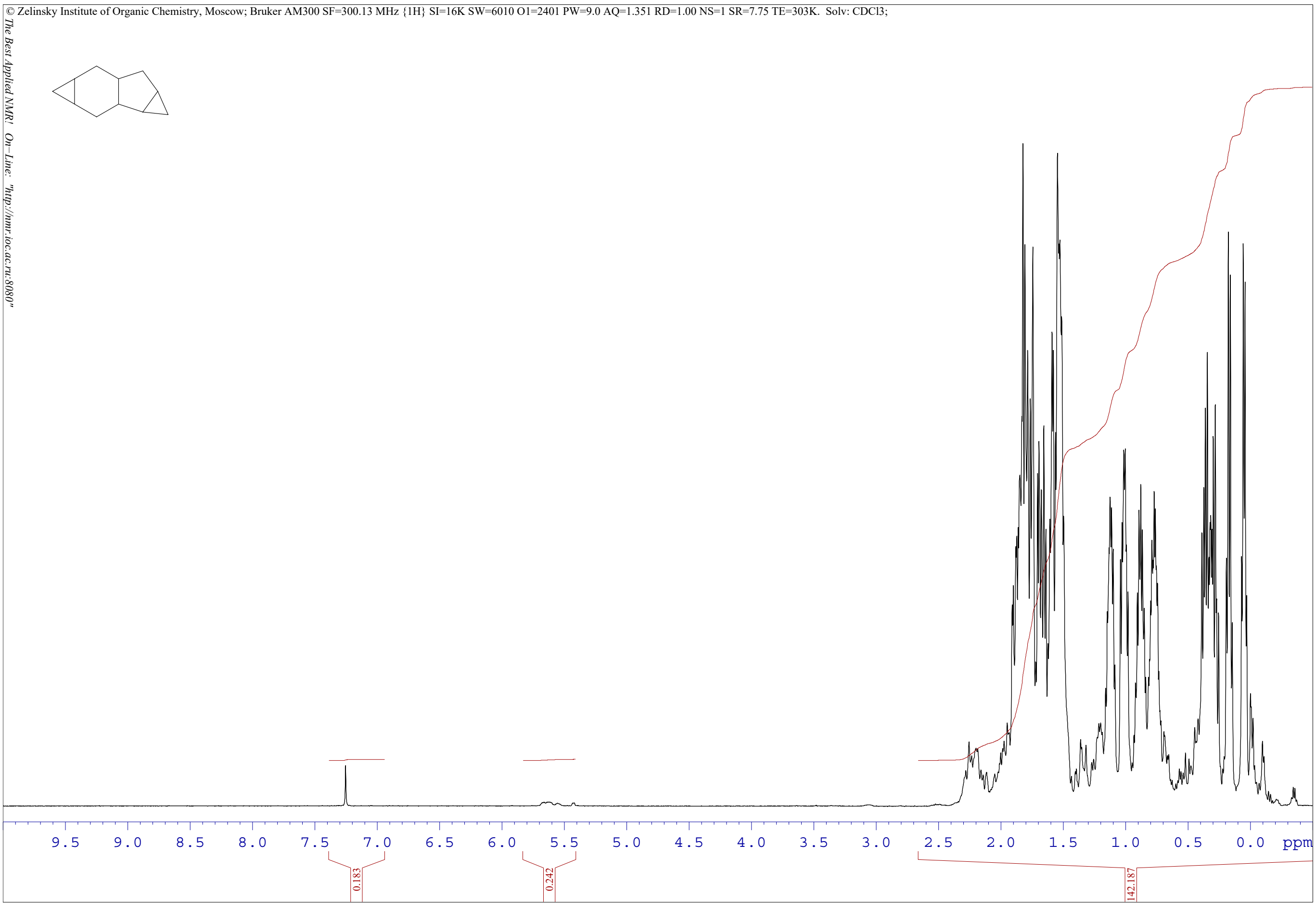
The Best Applied NMR!

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9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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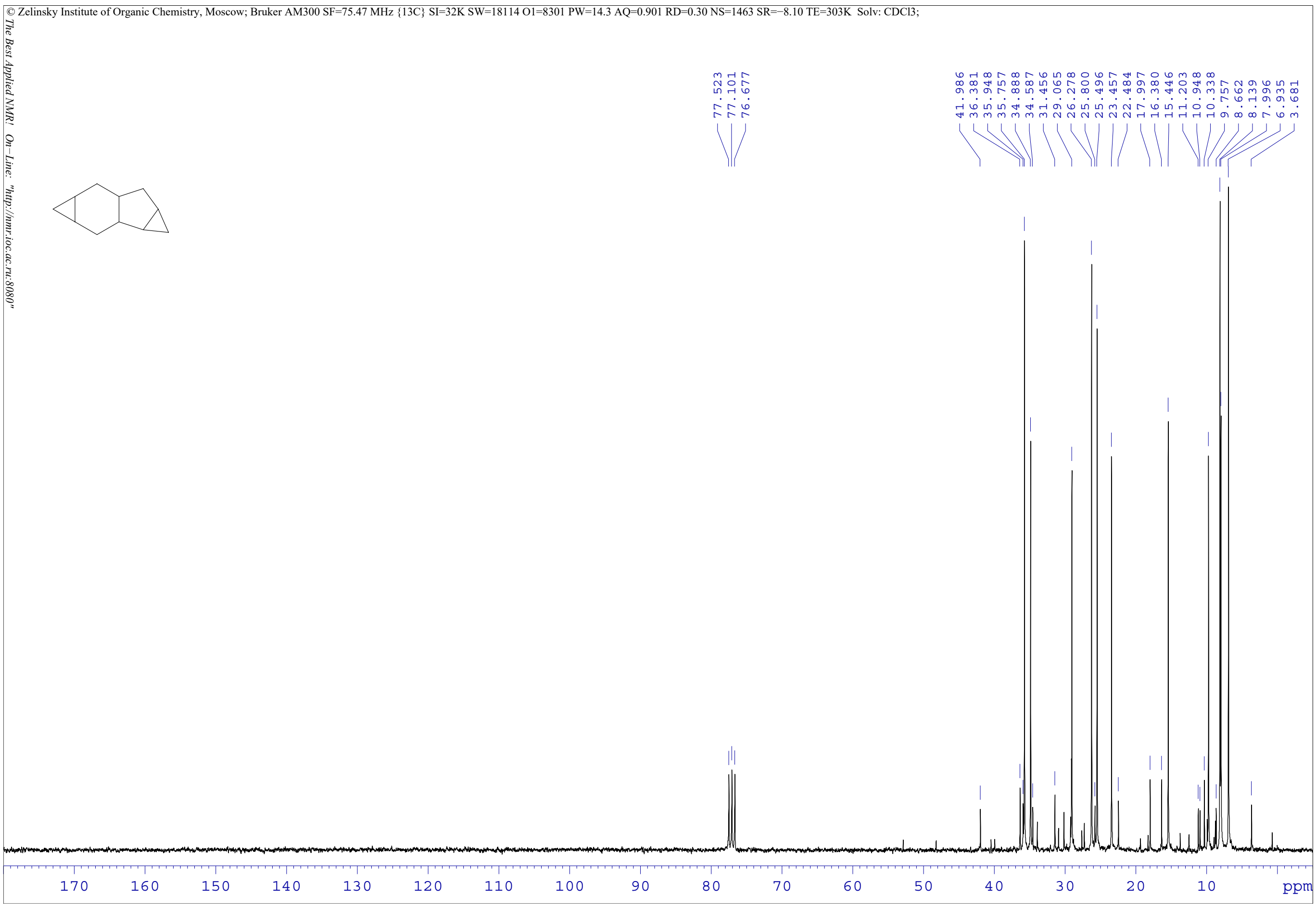
0.242
142.187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35.948
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34.888
34.587
31.456
29.065
26.278
25.800
25.496
23.457
22.484
17.997
16.380
15.446
11.203
10.948
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8.662
8.139
7.996
6.935
3.681
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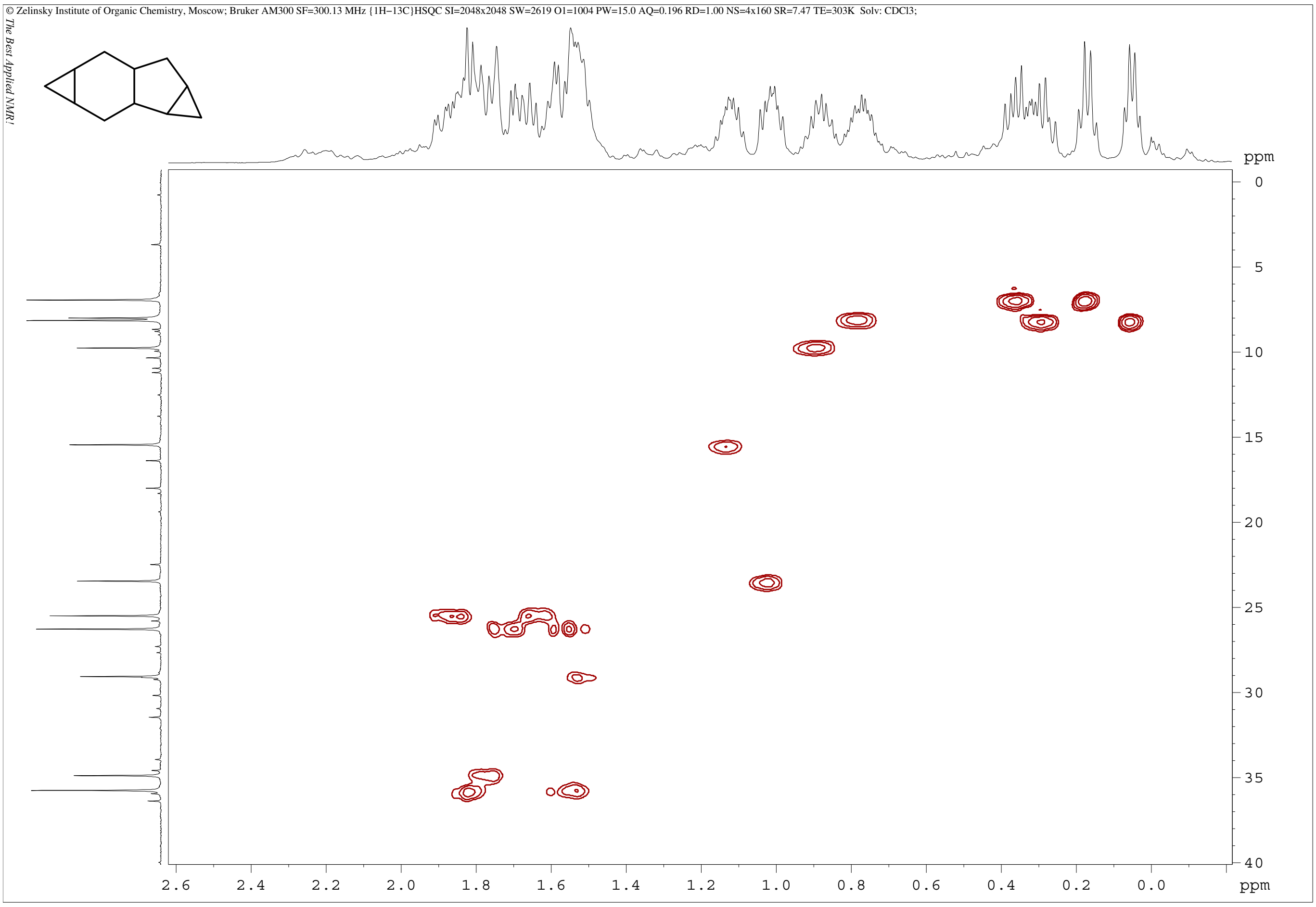
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15
20
25
30
35
40
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2.4
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1.0
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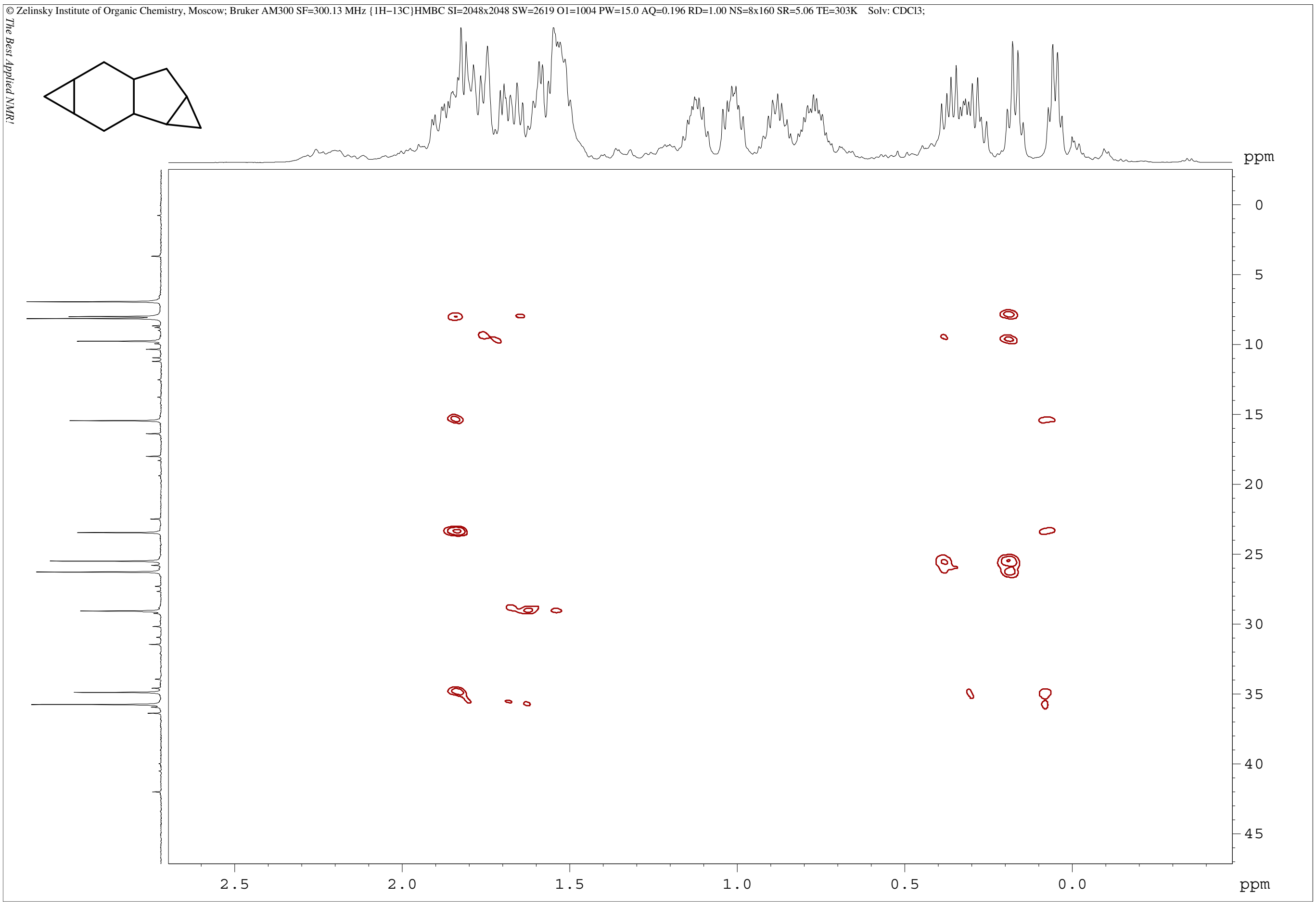
0.6
0.4
0.2
0.0
ppm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ppm
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10
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20
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30
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40
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1.0
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0.0
ppm

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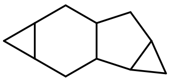

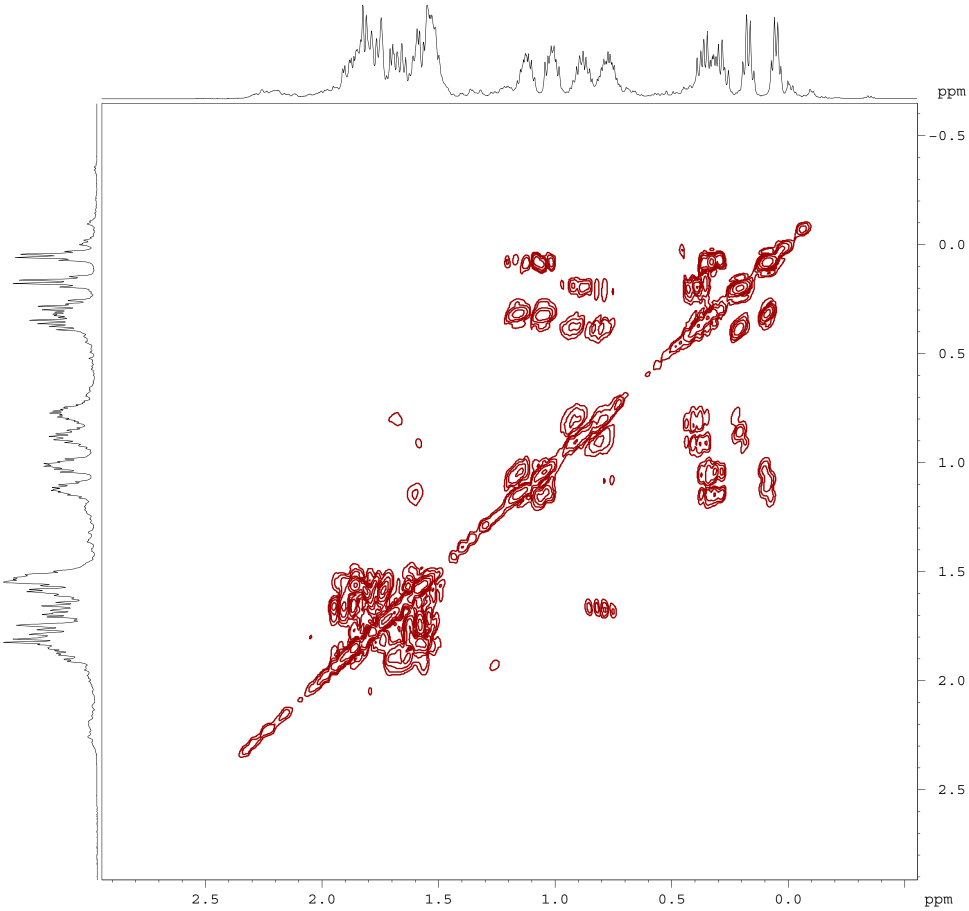

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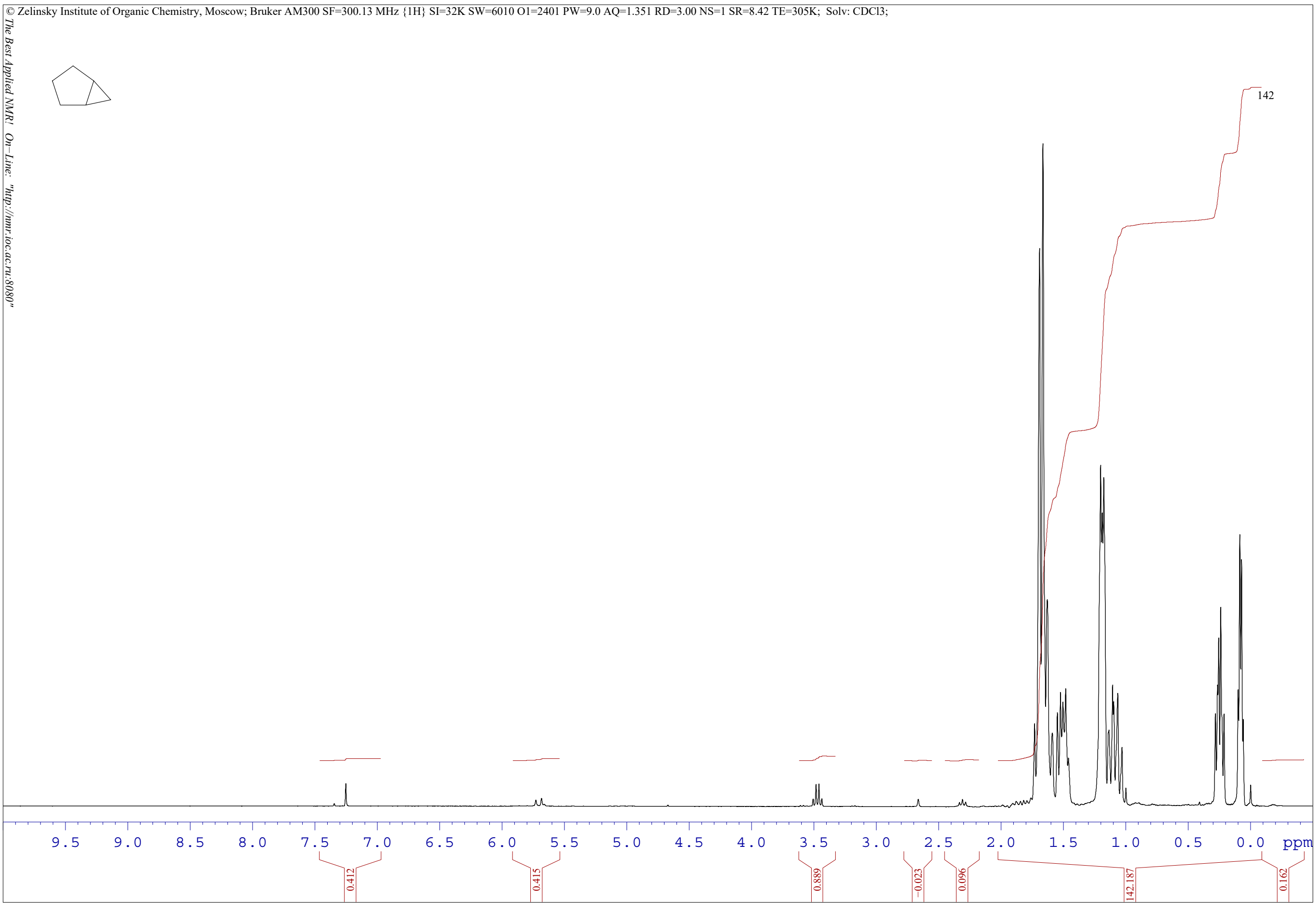

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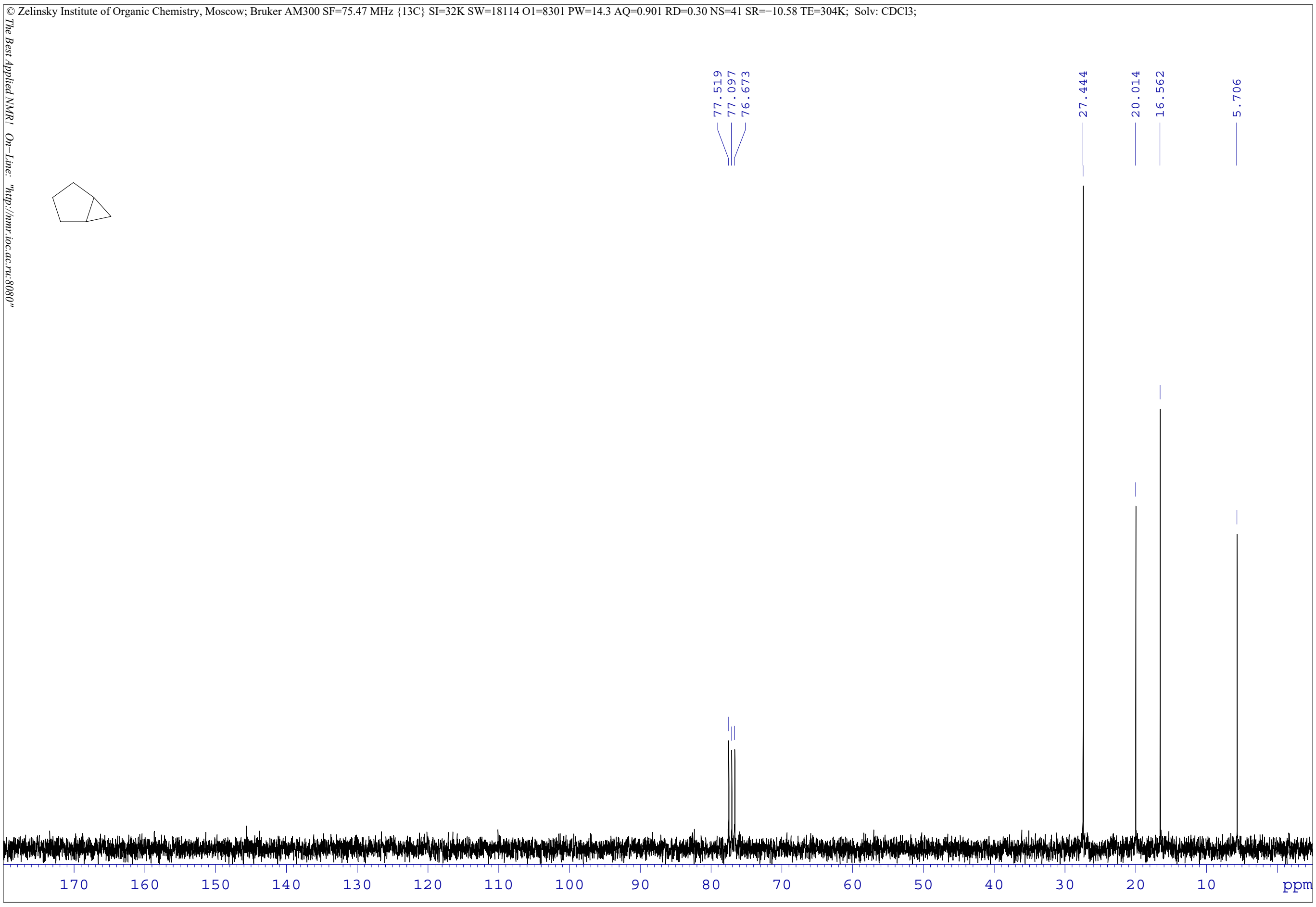

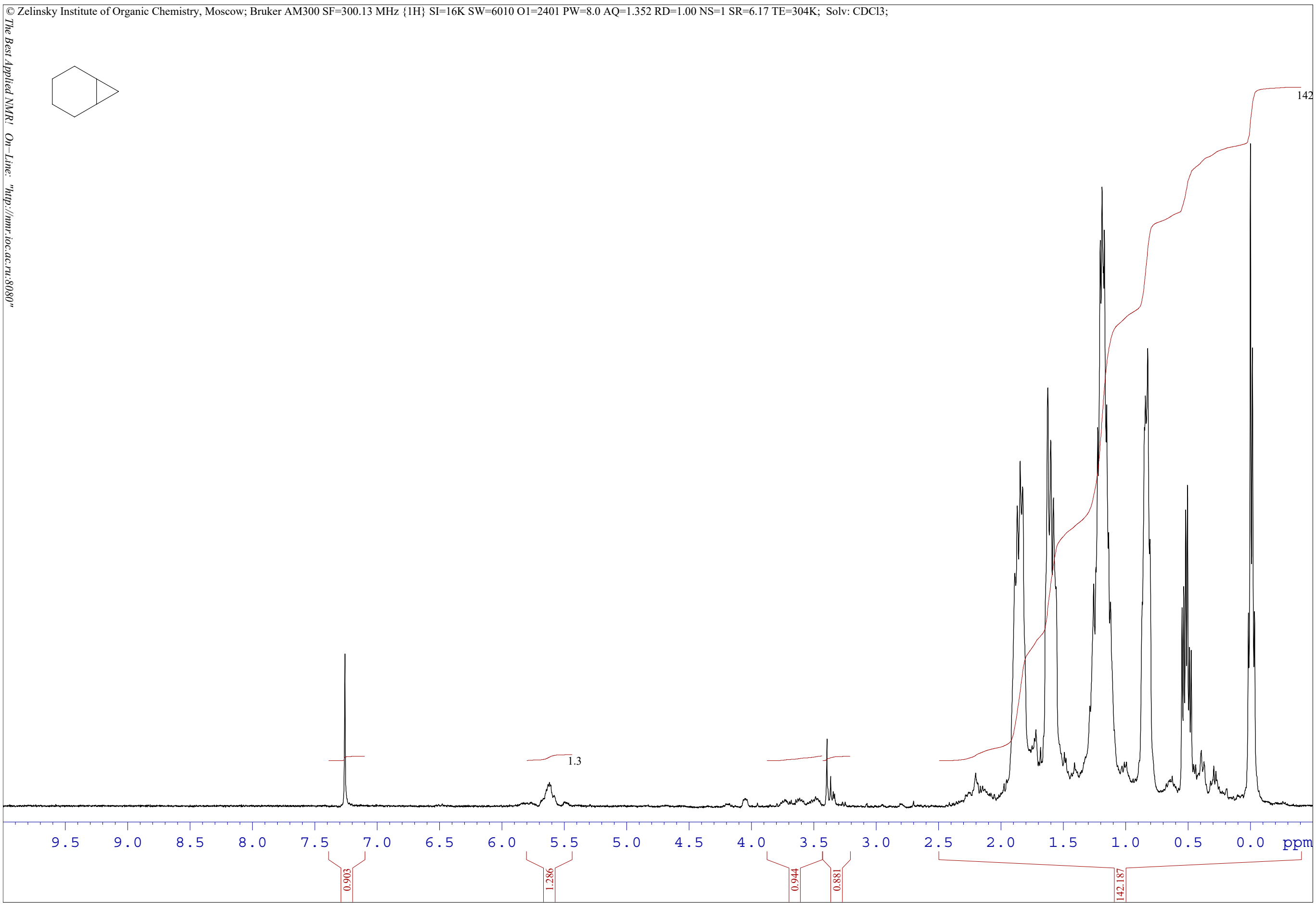
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142
1.3
0.903
1.286
0.944
0.881
142.187
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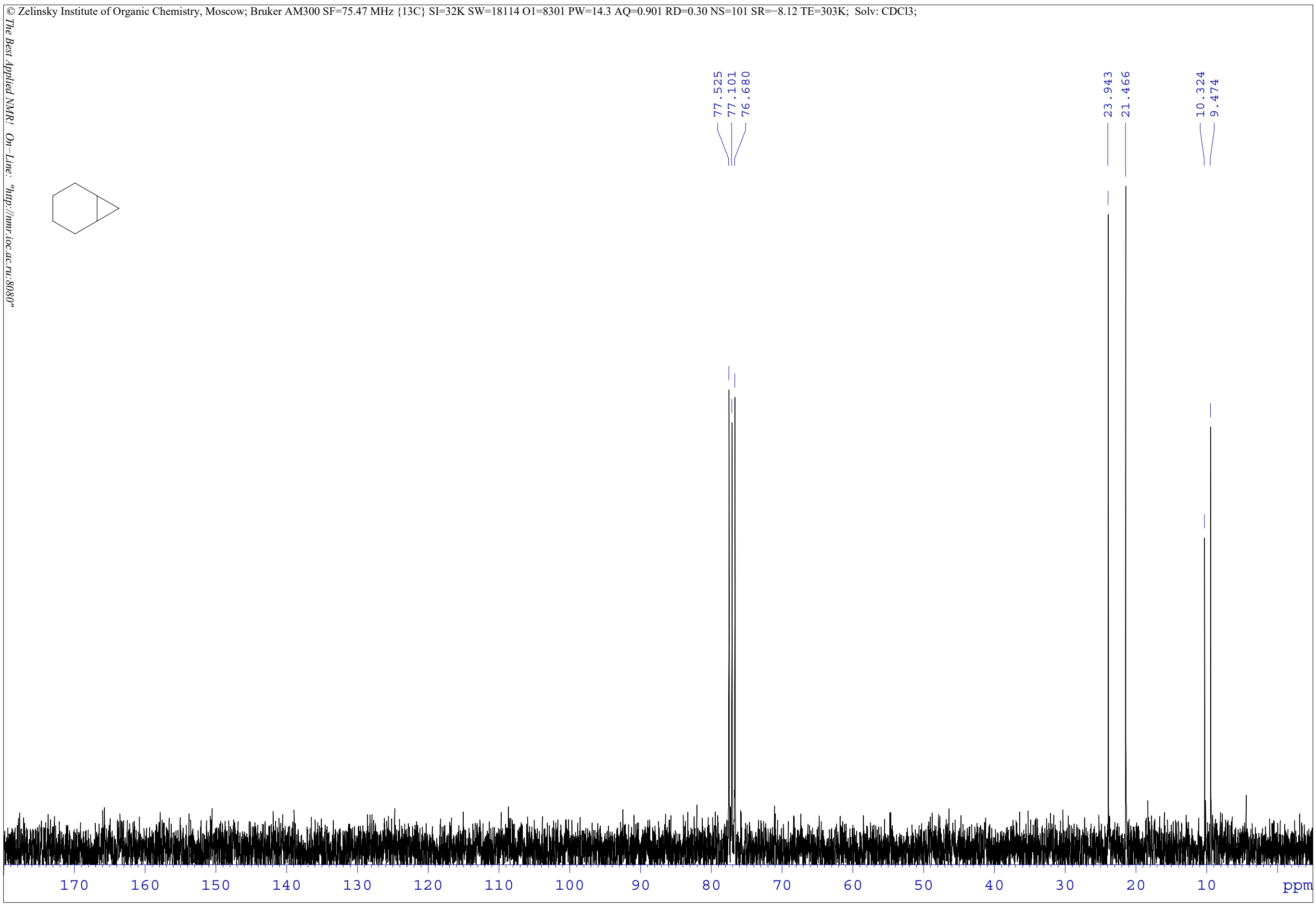
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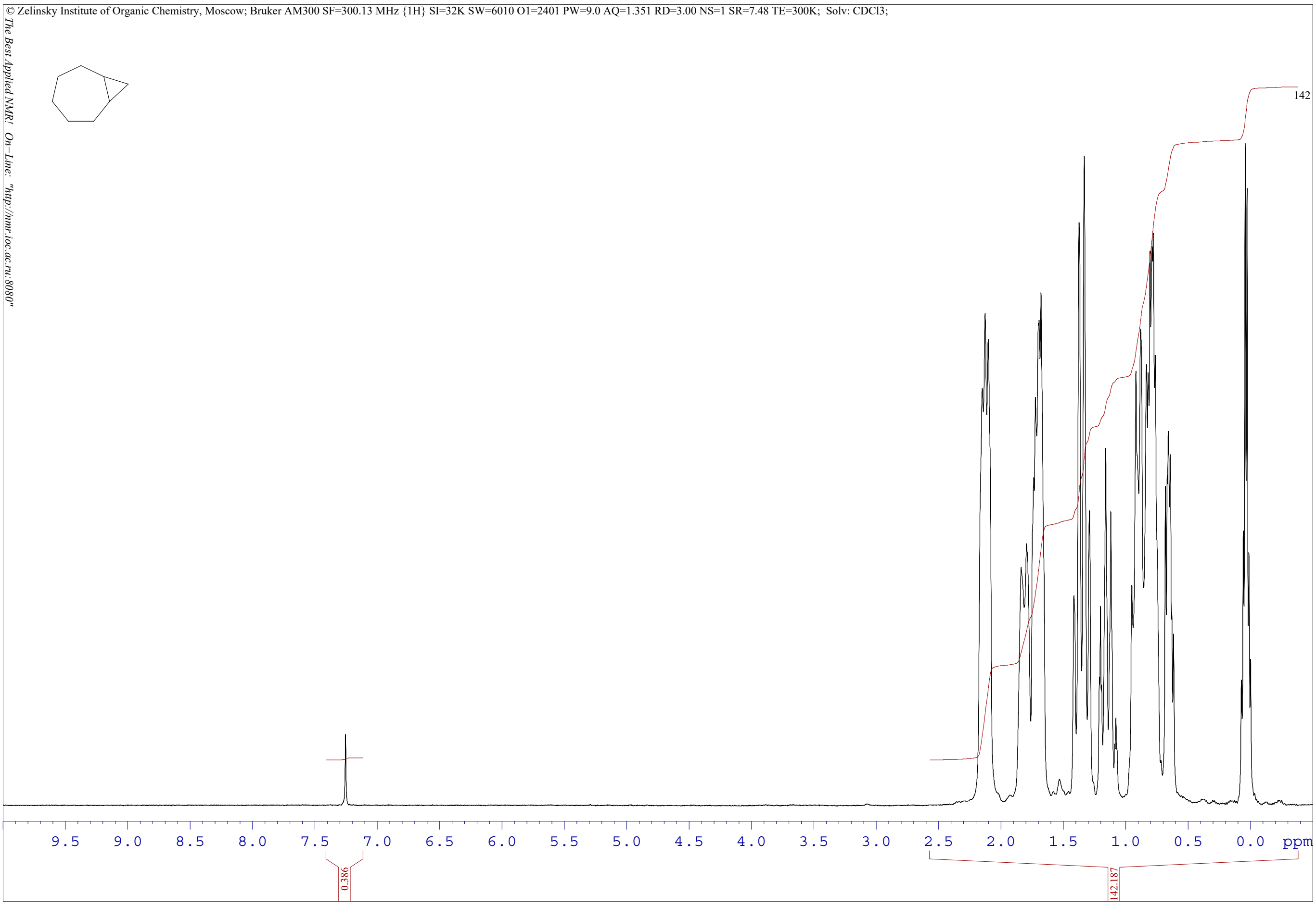
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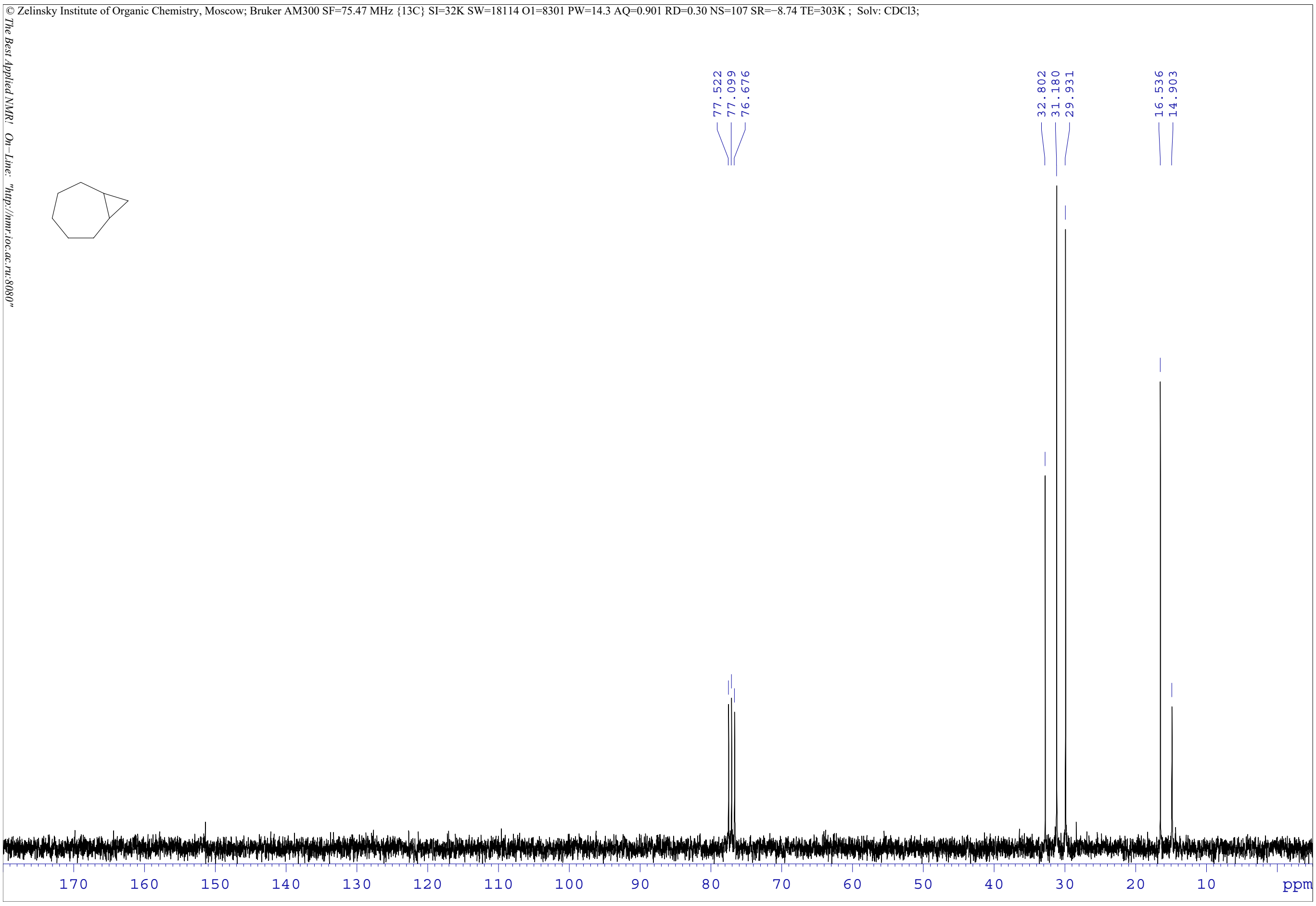
142
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.386
142.187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14.903
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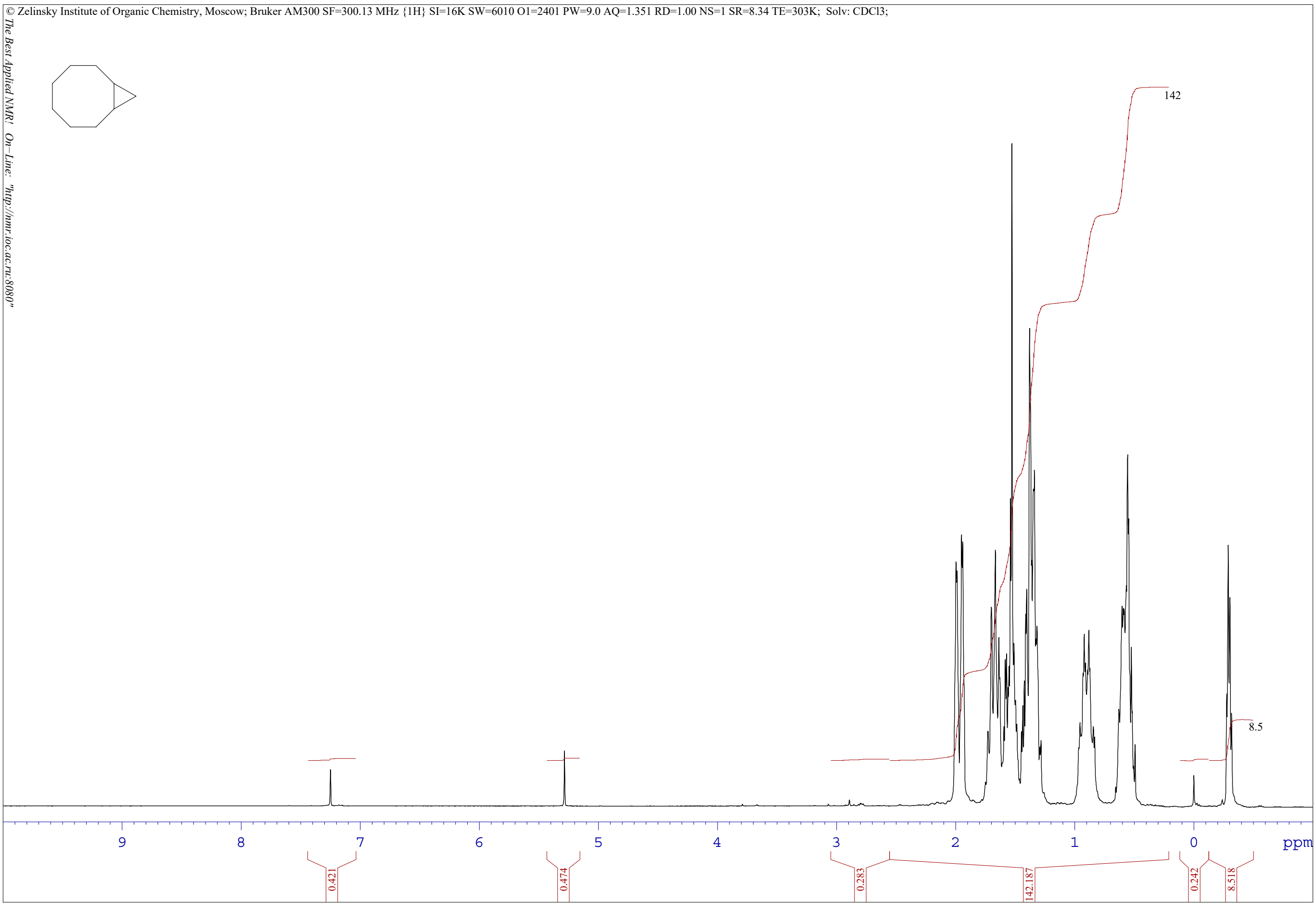
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142
8.5
9
8
7
6
5
4
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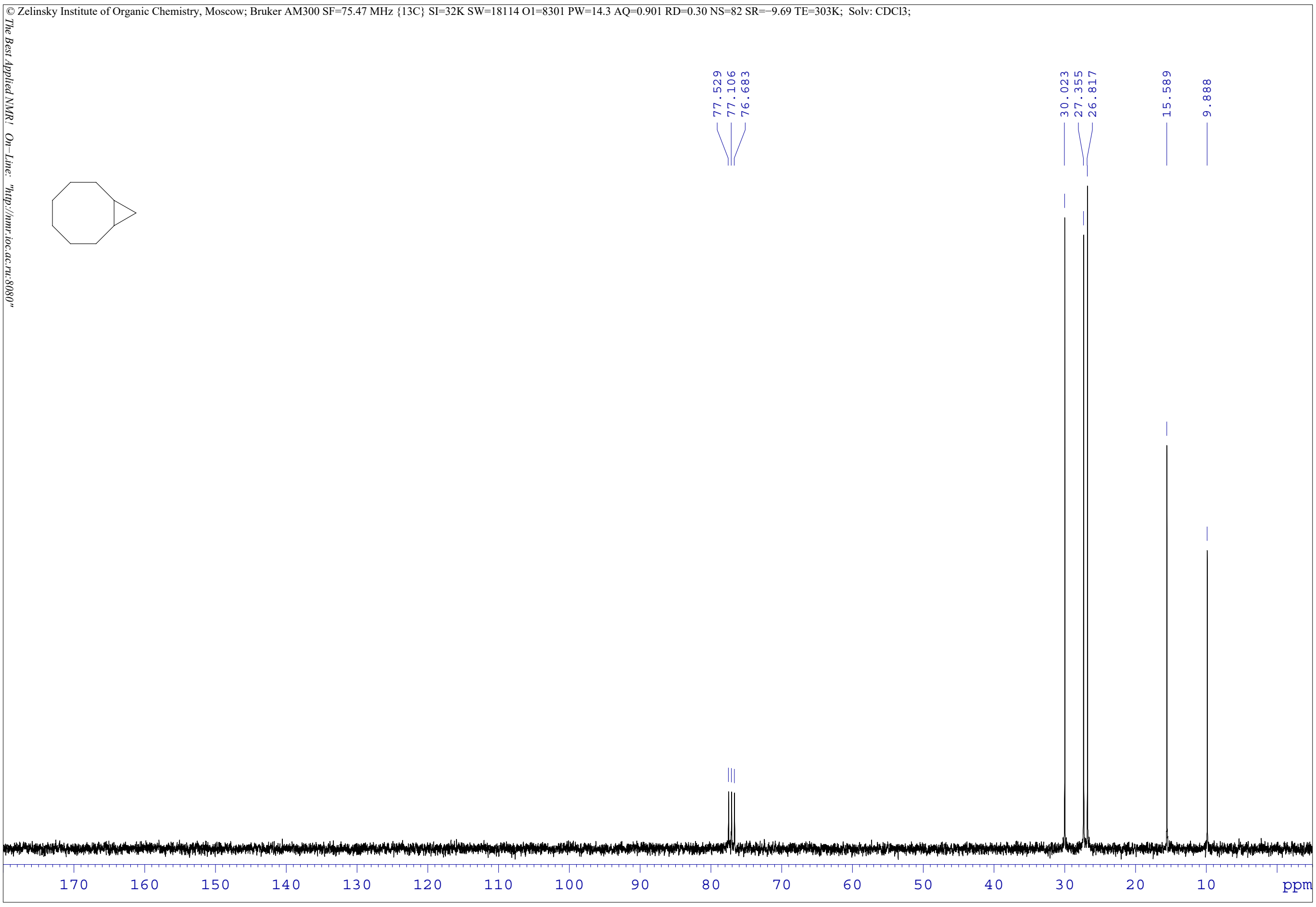
0.242
8.518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76.683
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40
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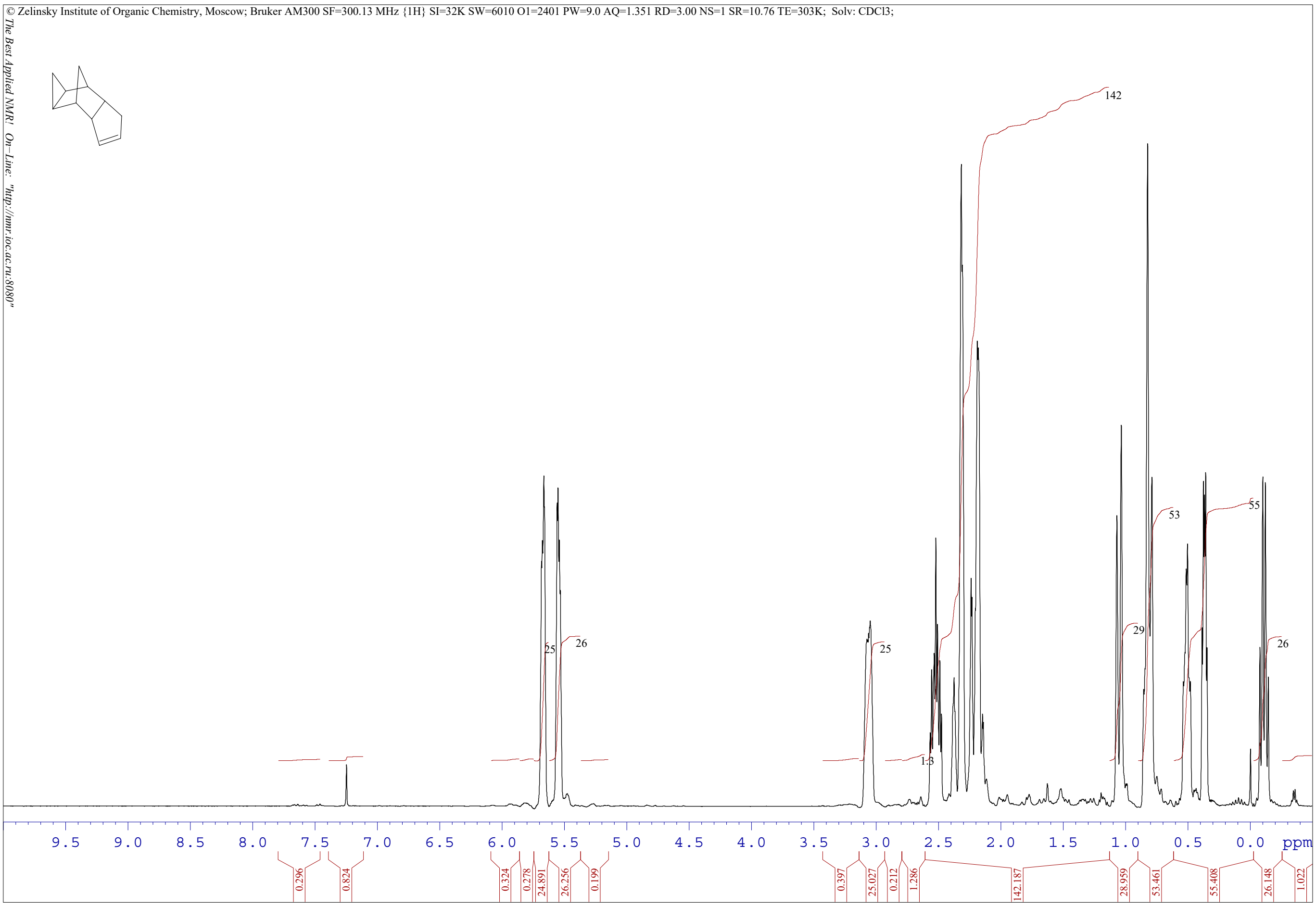
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142
53
55
25
26
25
29
26
1.3
0.296
0.824
0.324
0.278
24.891
26.256
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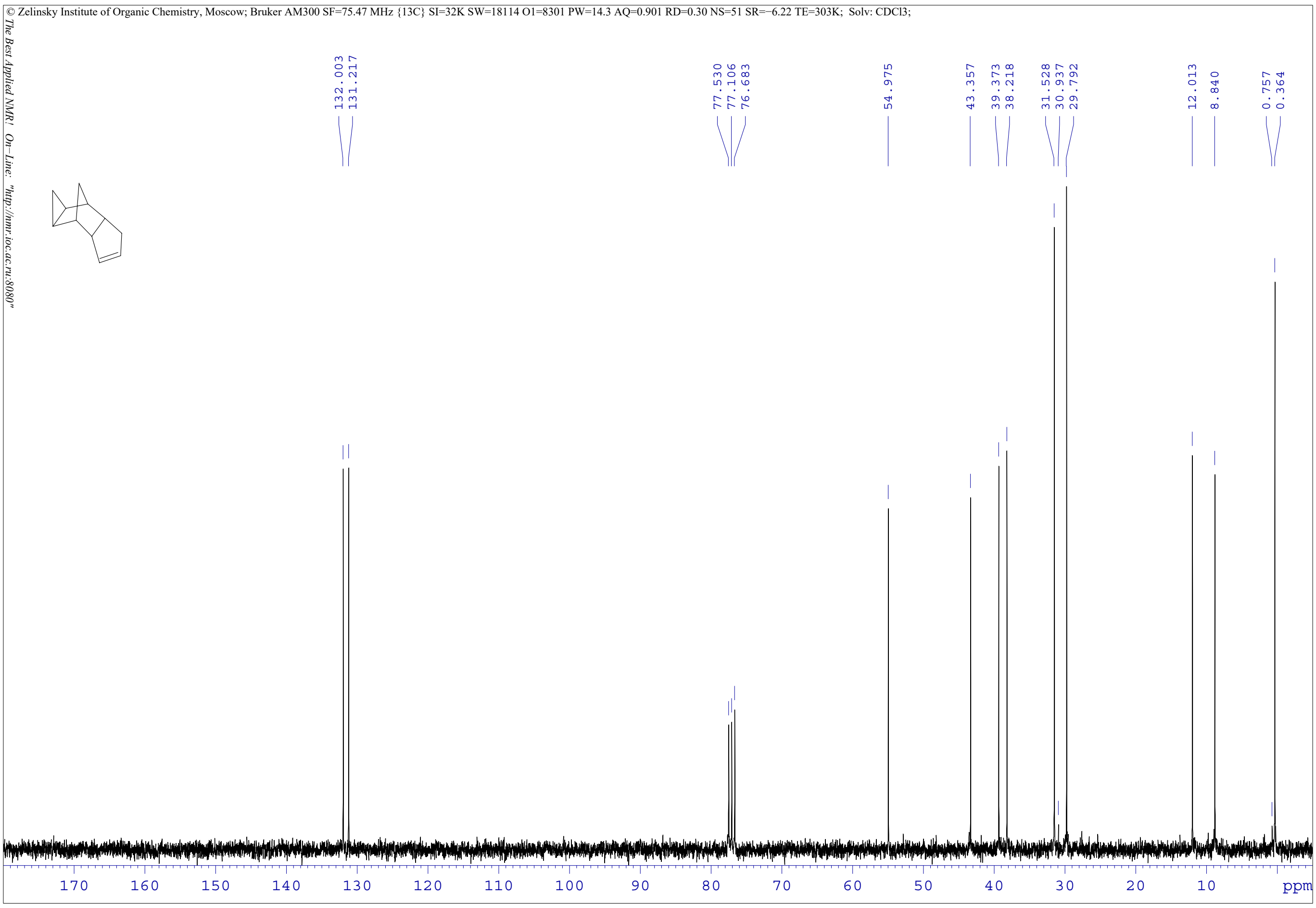
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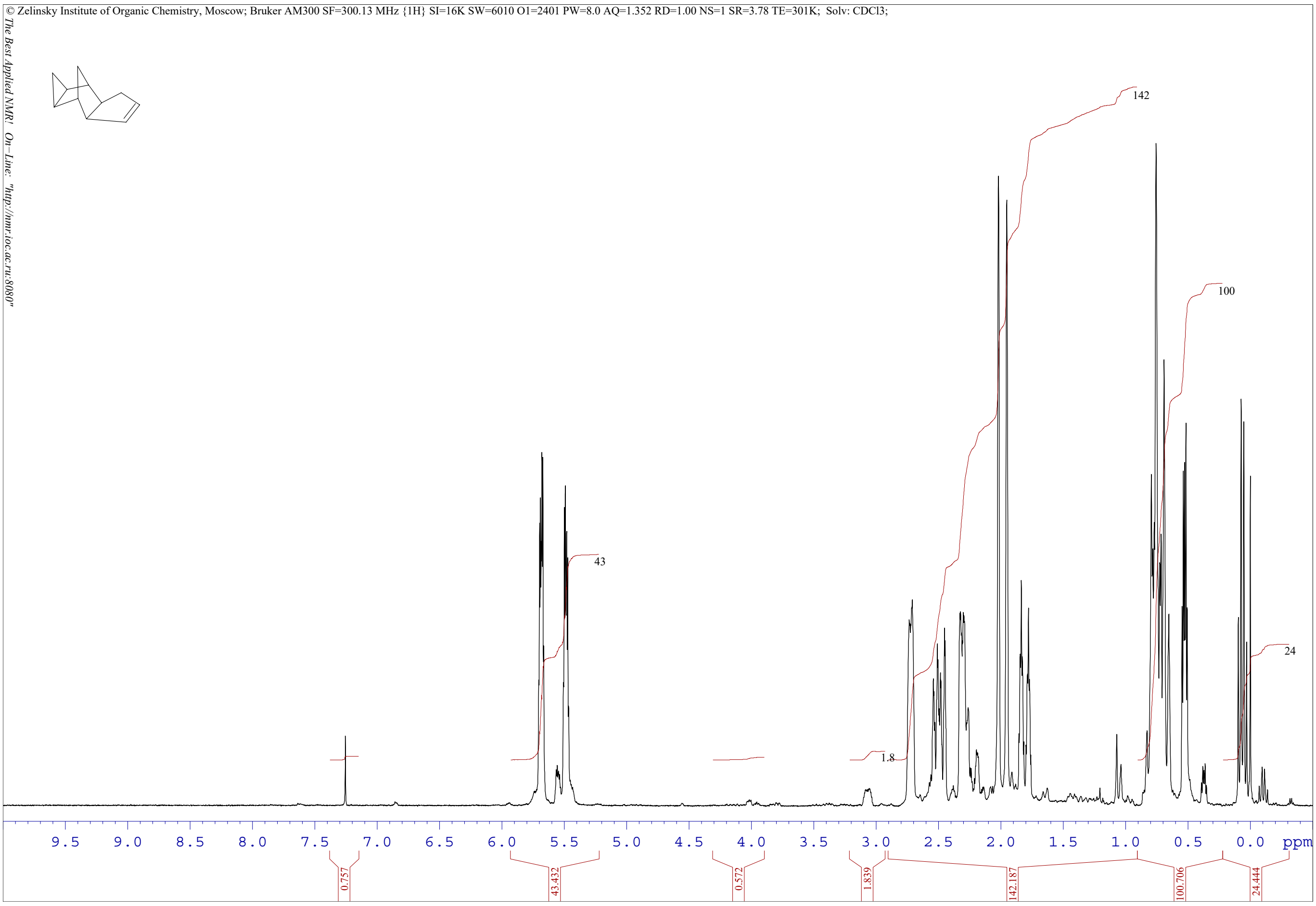
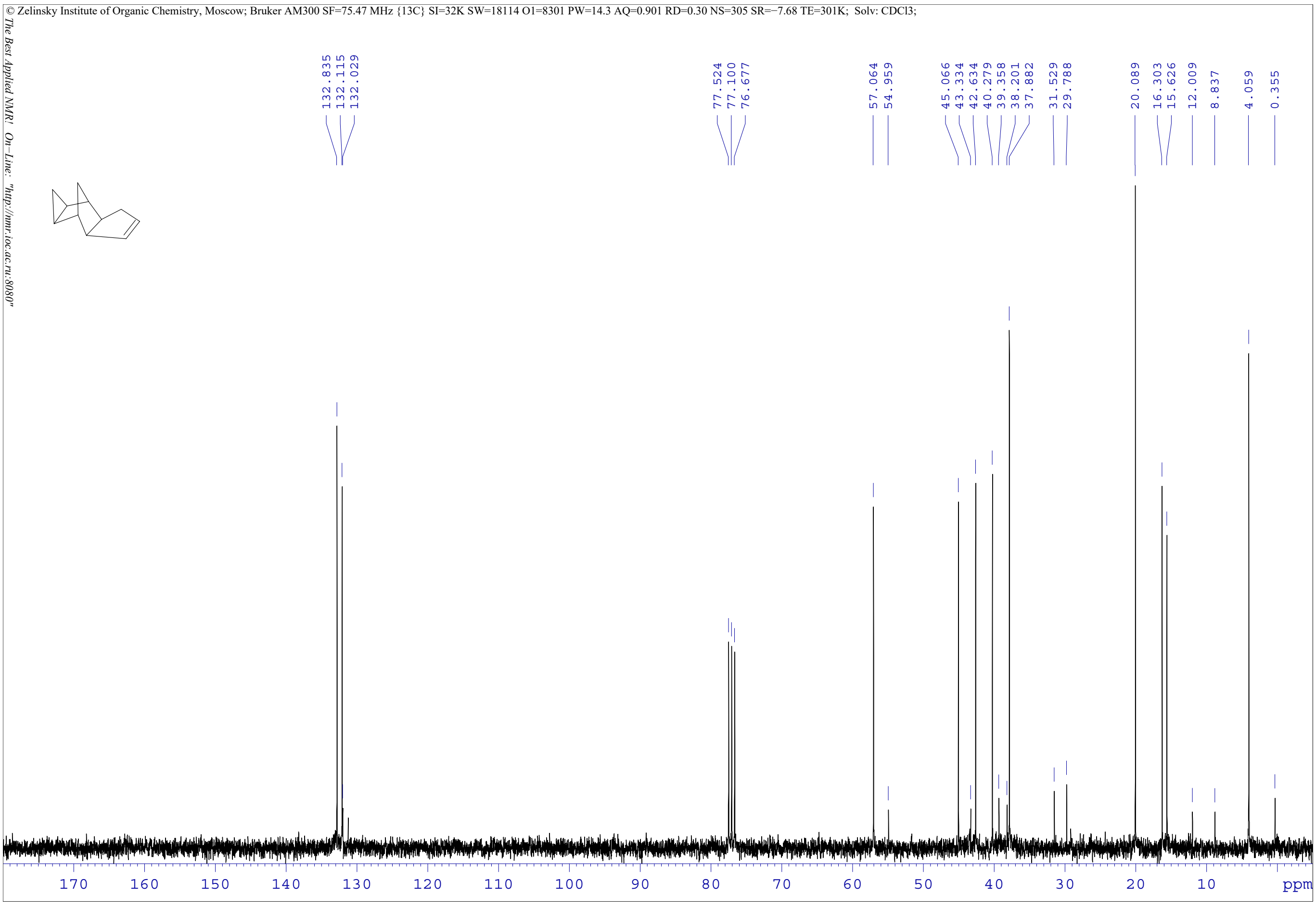
131.217
77.530
77.106
76.683
54.975
43.357
39.373
38.218
31.528
30.937
29.792
12.013
8.840
0.757
0.364
ppm

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=6010 O1=2401 PW=8.0 AQ=1.352 RD=1.00 NS=1 SR=3.78 TE=301K; Solv: CDCl3;

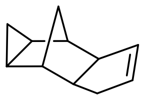


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=14.3 AQ=0.901 RD=0.30 NS=305 SR=−7.68 TE=301K; Solv: CDCl3;

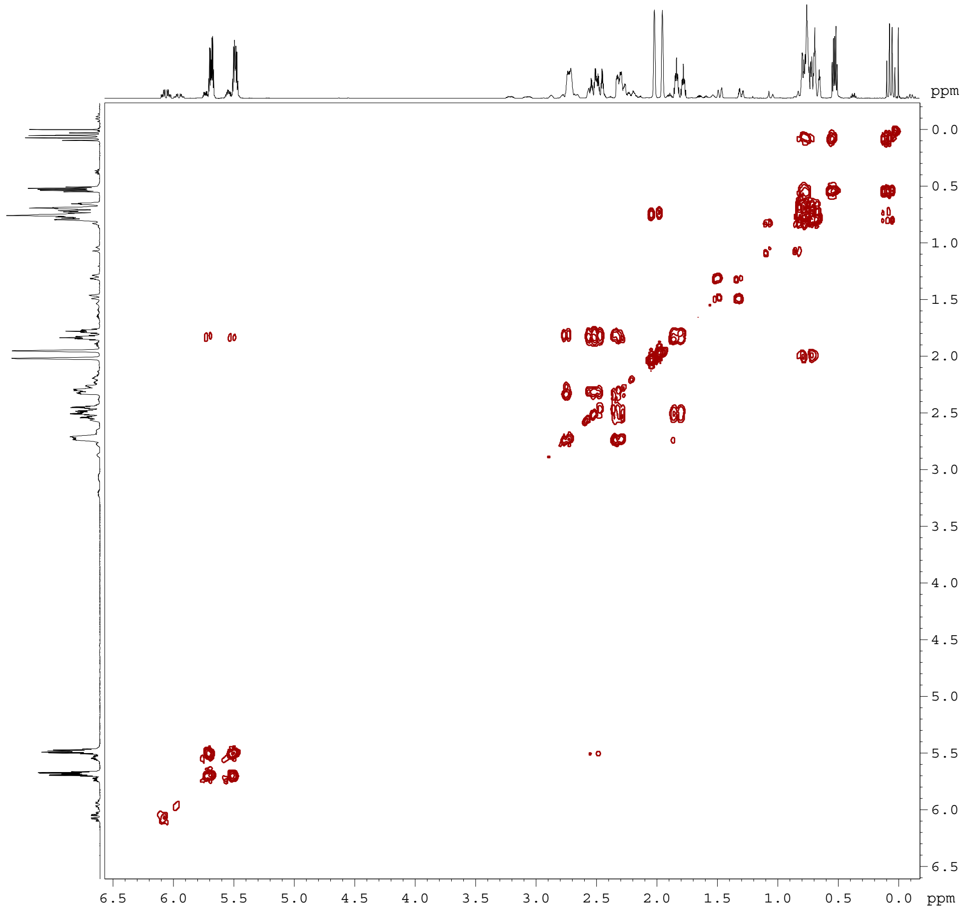


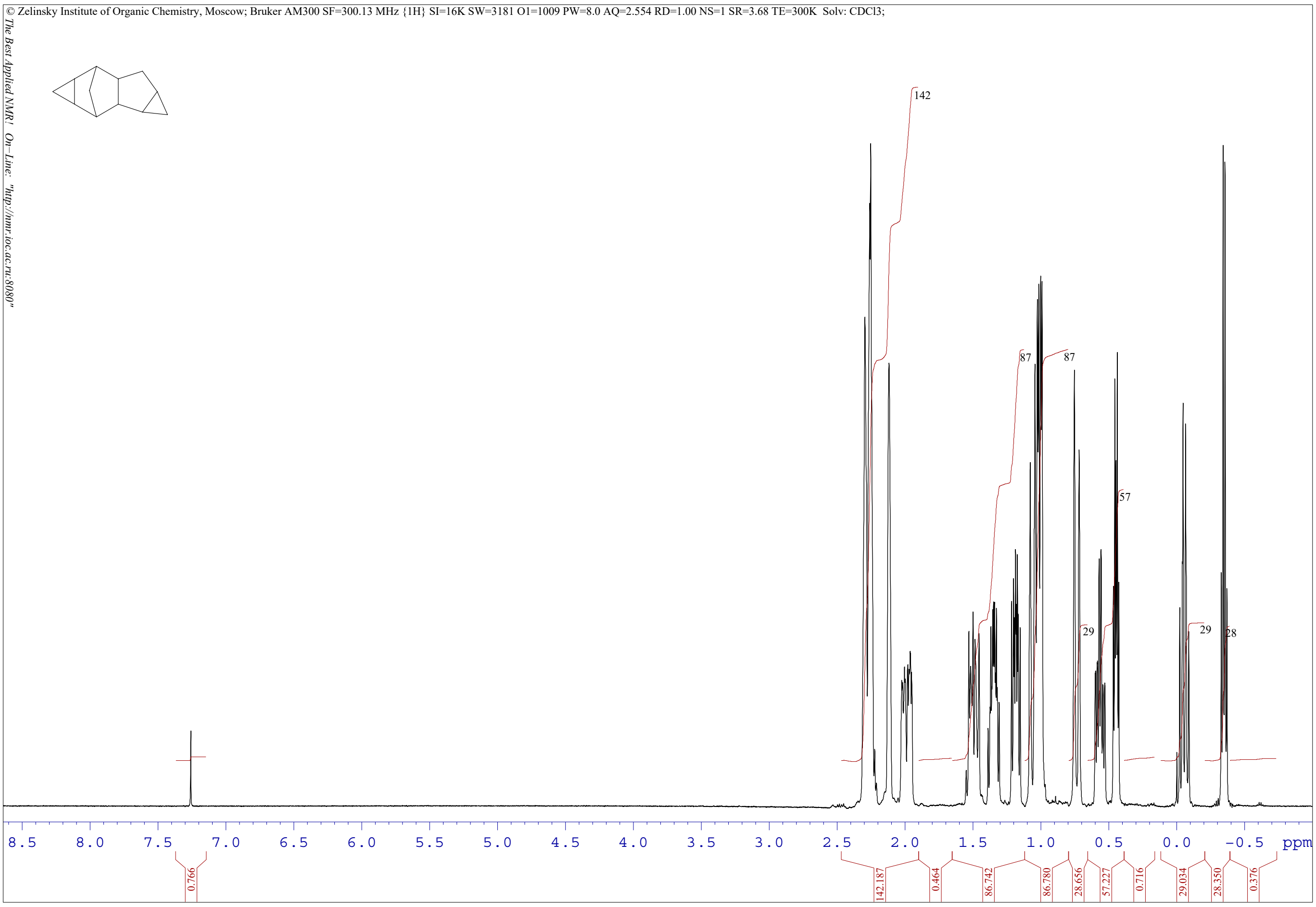
 Bruker AM300 SF=300.13 MHz {1H-1H}COSY SI=2048x2048 SW=2451 O1=1111 PW=8.0 AQ=0.209 RD=1.00 NS=1x128 SR=1.94 TE=304K; Solv: $CDCl_3$;

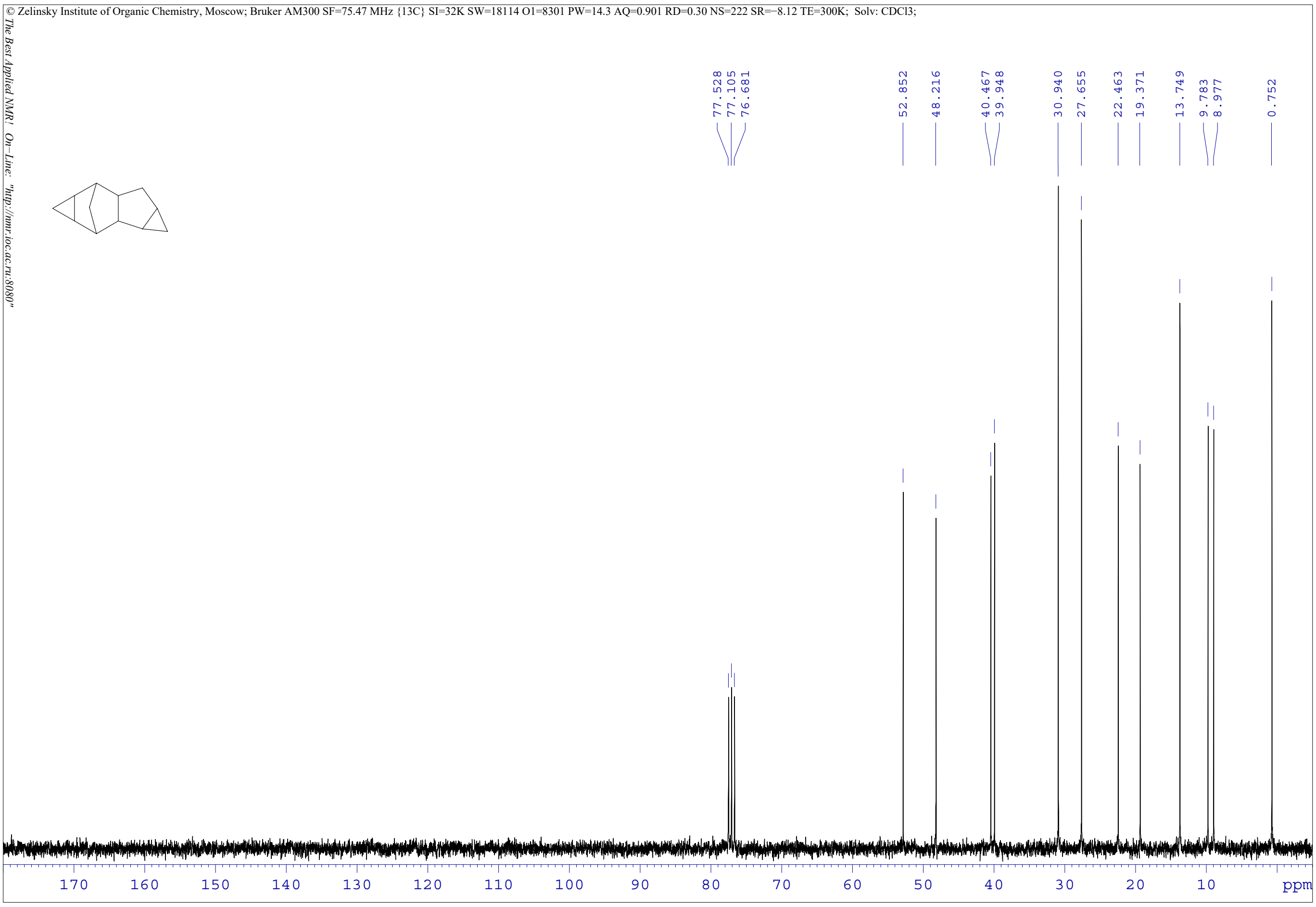
The Best Applied NMR!

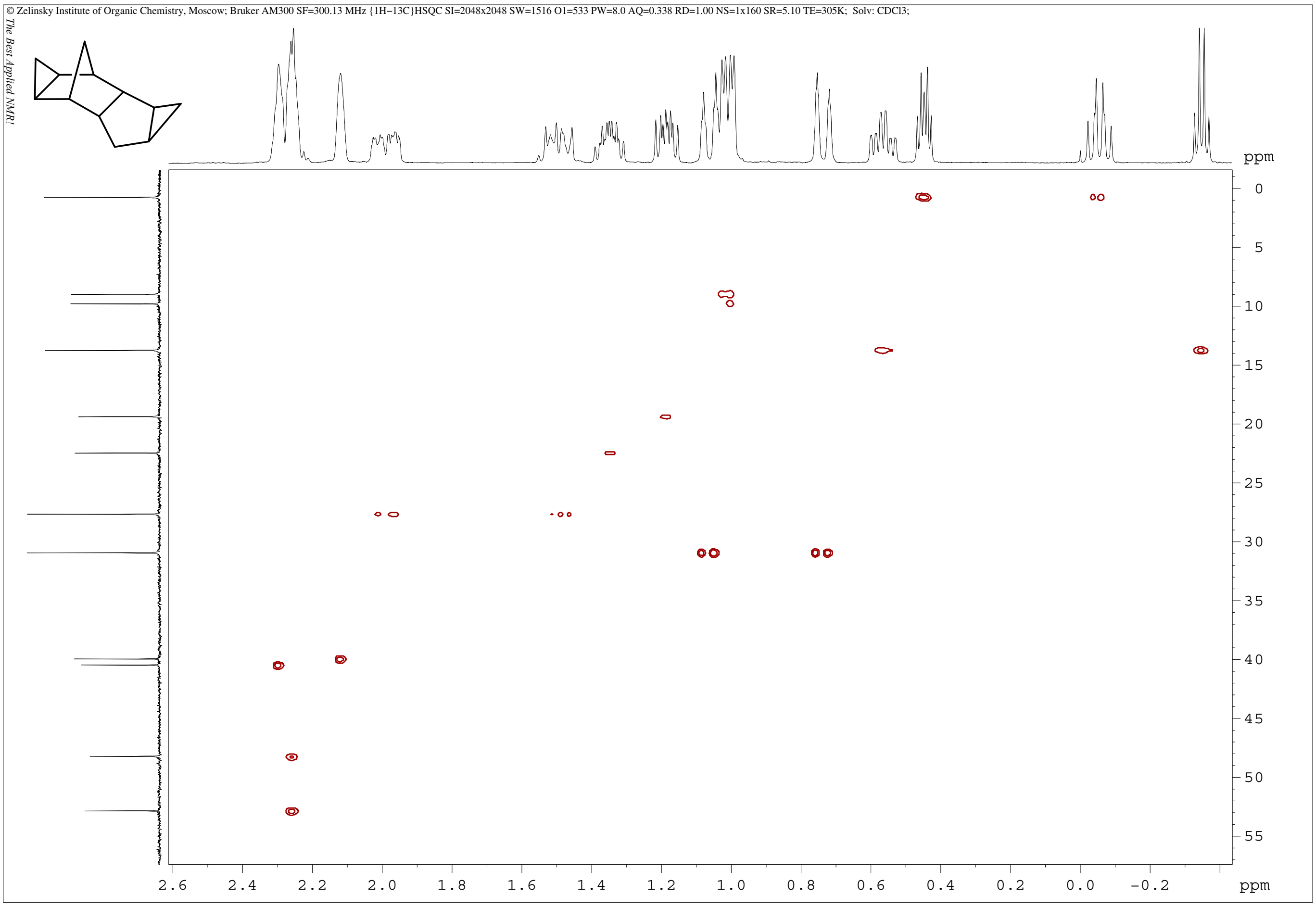


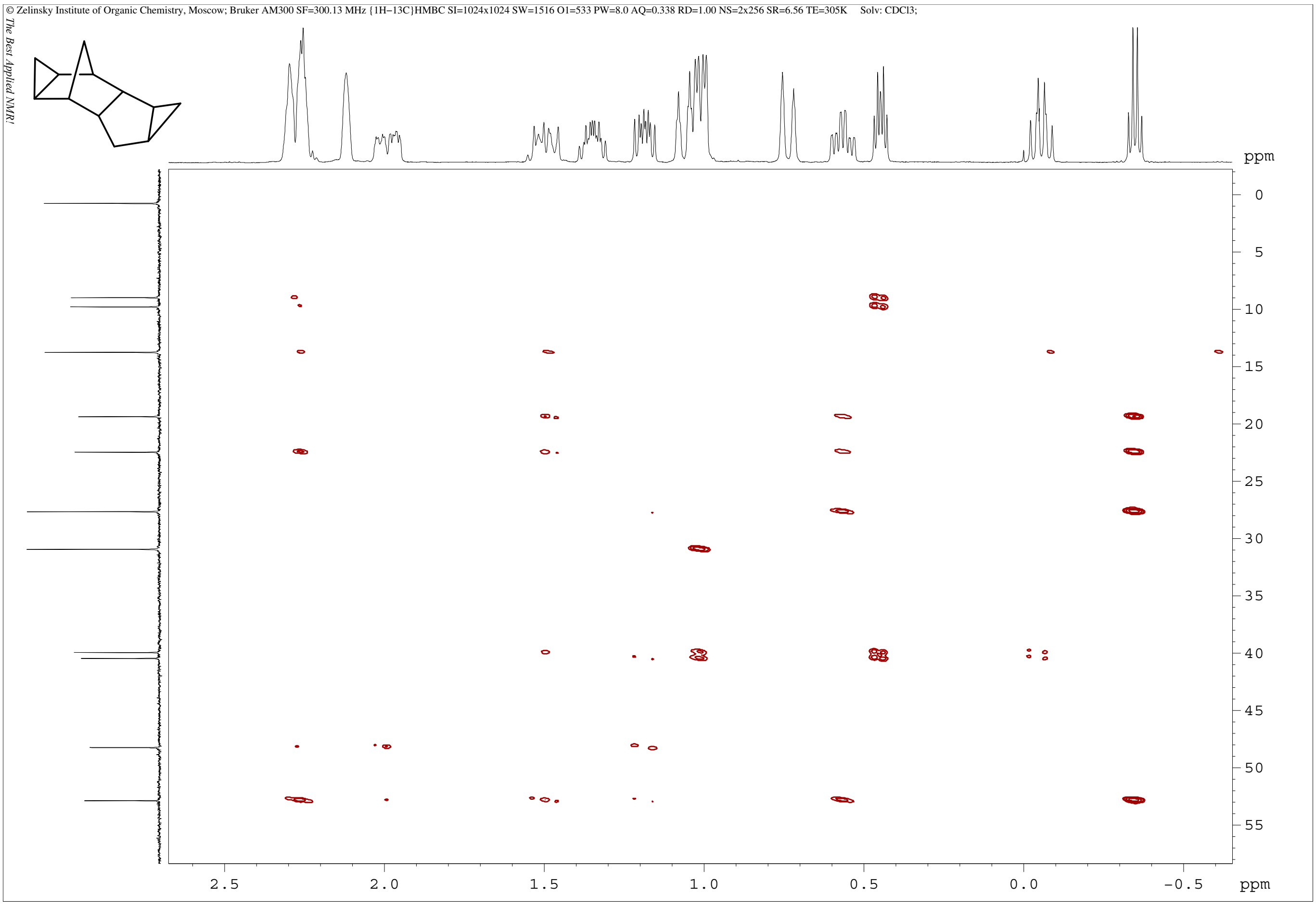
exo-



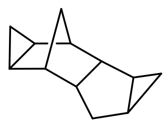

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H} SI=16K SW=3181 O1=1009 PW=8.0 AQ=2.554 RD=1.00 NS=1 SR=3.68 TE=300K Solv: CDCl3;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080"
142
87
87
57
29
29
28
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.766
142.187
0.464
86.742
86.780
28.656
57.227
0.716
29.034
28.350
0.376

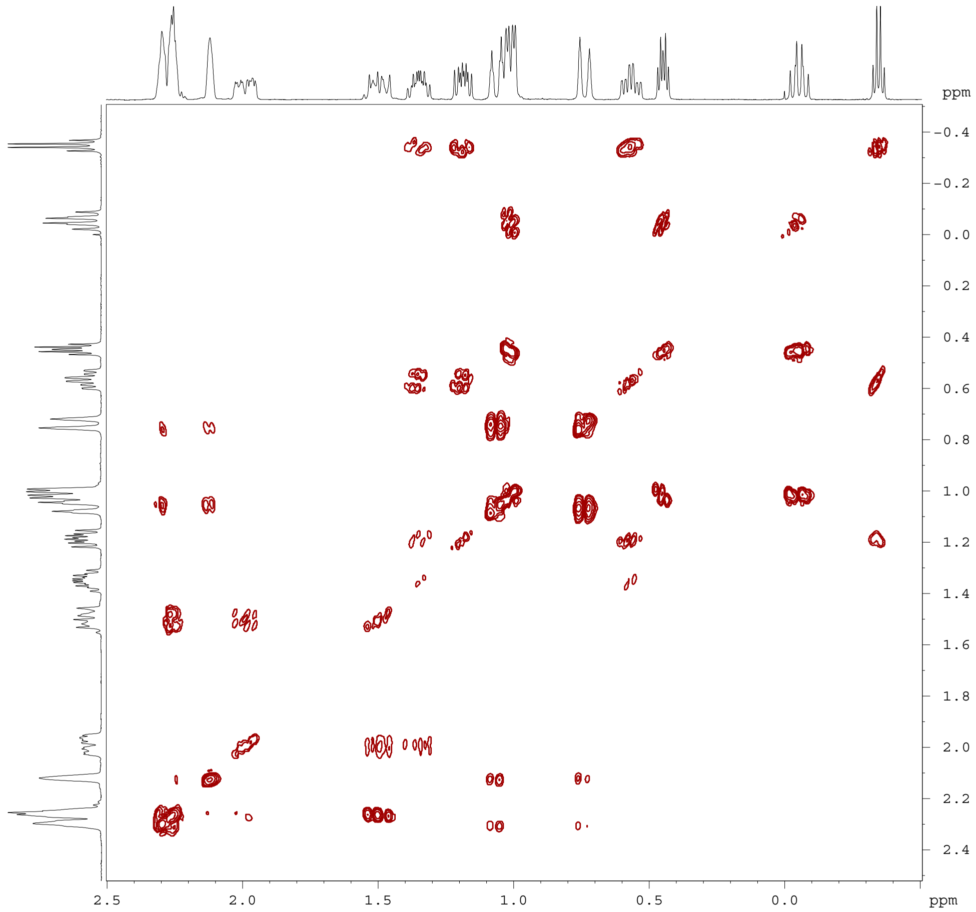

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=75.47 MHz {13C} SI=32K SW=18114 O1=8301 PW=14.3 AQ=0.901 RD=0.30 NS=222 SR=-8.12 TE=300K; Solv: CDCl3;
The Best Applied NMR! On-Line: "http://nmr.ioc.ac.ru:8080"
77.528
77.105
76.681
52.852
48.216
40.467
39.948
30.940
27.655
22.463
19.371
13.749
9.783
8.977
0.752
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H−13C}HSQC SI=2048x2048 SW=1516 O1=533 PW=8.0 AQ=0.338 RD=1.00 NS=1x160 SR=5.10 TE=305K; Solv: CDCl3;
The Best Applied NMR!
ppm
ppm

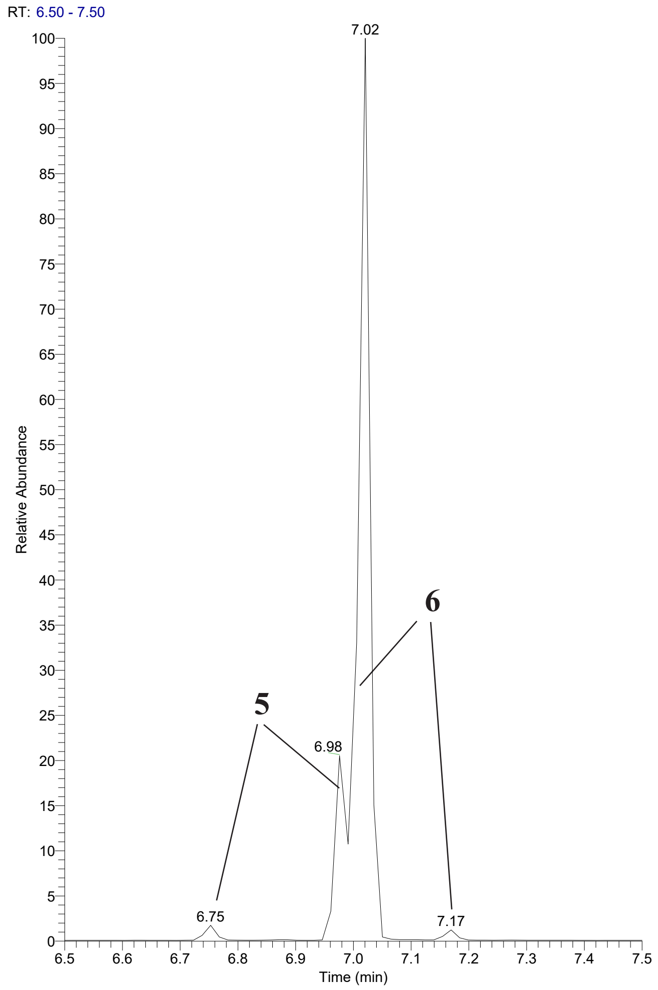

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H−13C}HMBC SI=1024x1024 SW=1516 O1=533 PW=8.0 AQ=0.338 RD=1.00 NS=2x256 SR=6.56 TE=305K Solv: CDCl3;
The Best Applied NMR!
ppm
ppm

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz {1H−1H}COSY SI=2048x2048 SW=1516 O1=533 PW=15.0 AQ=0.338 RD=1.00 NS=2x128 SR=7.42 TE=300K; Solv: $CDCl_3$;

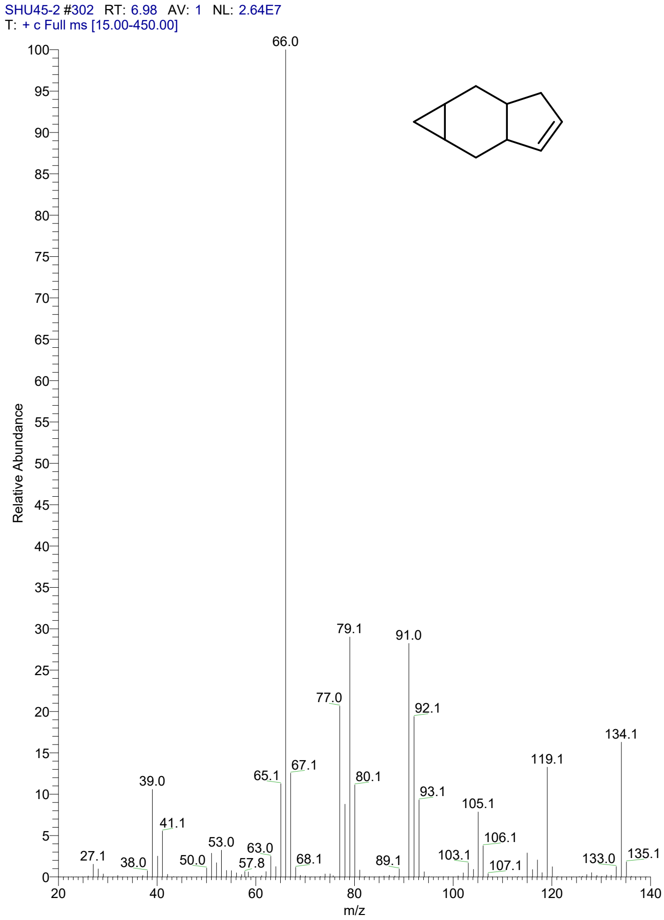


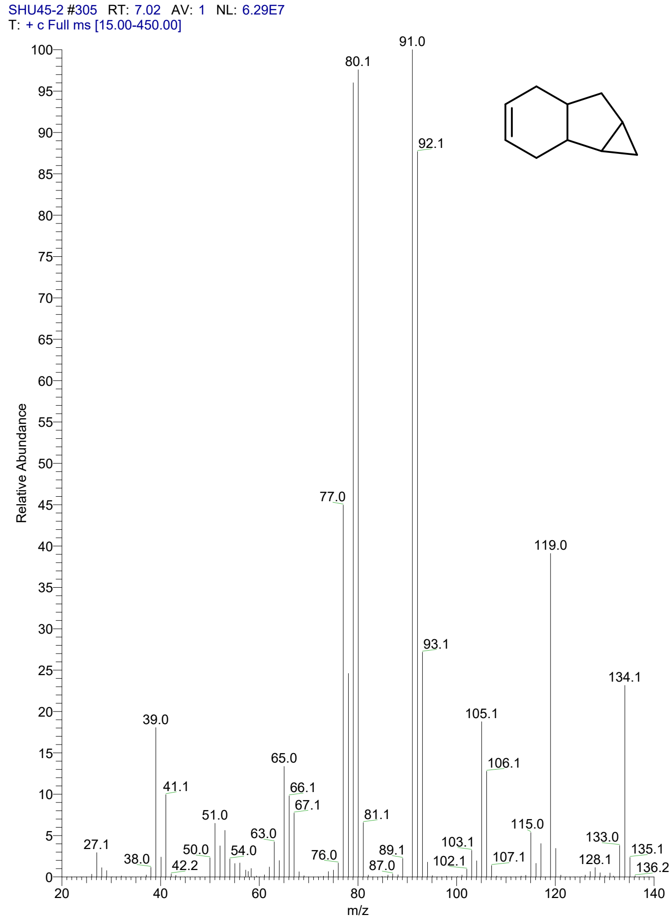


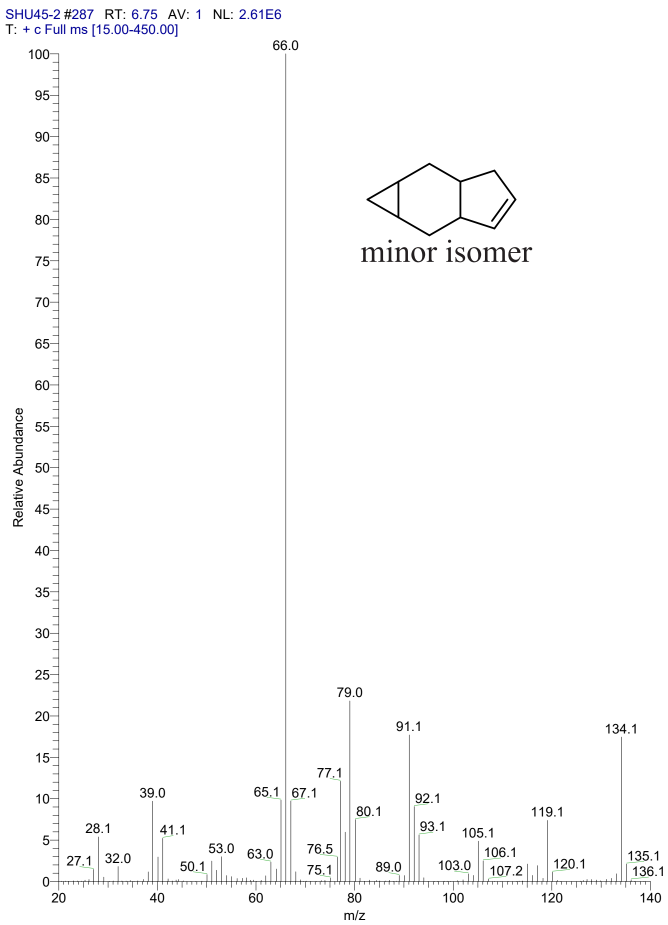
Chromatogram of reaction mixture of 5 and 6

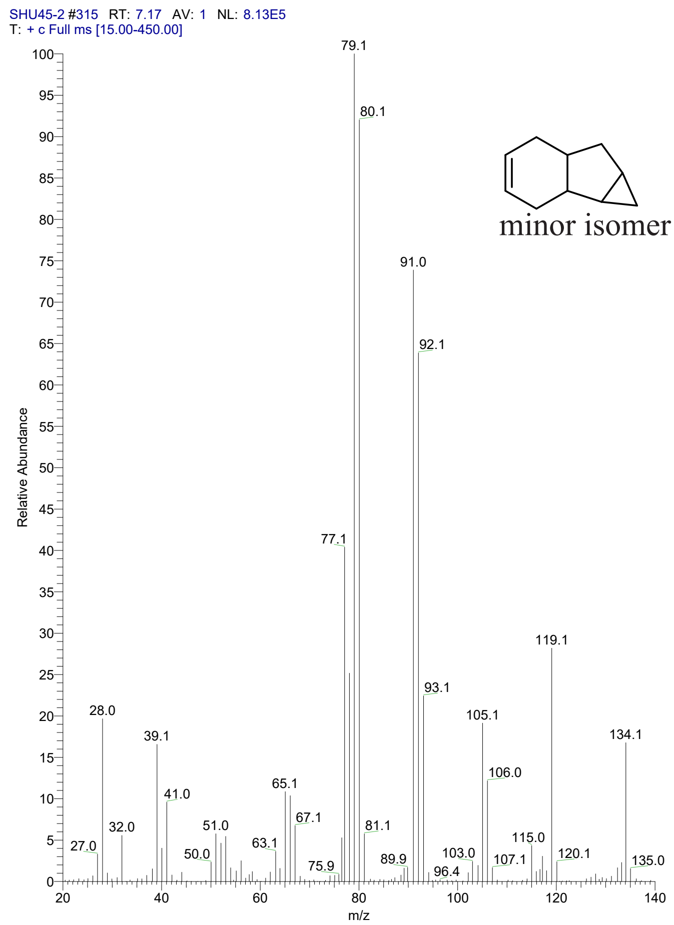


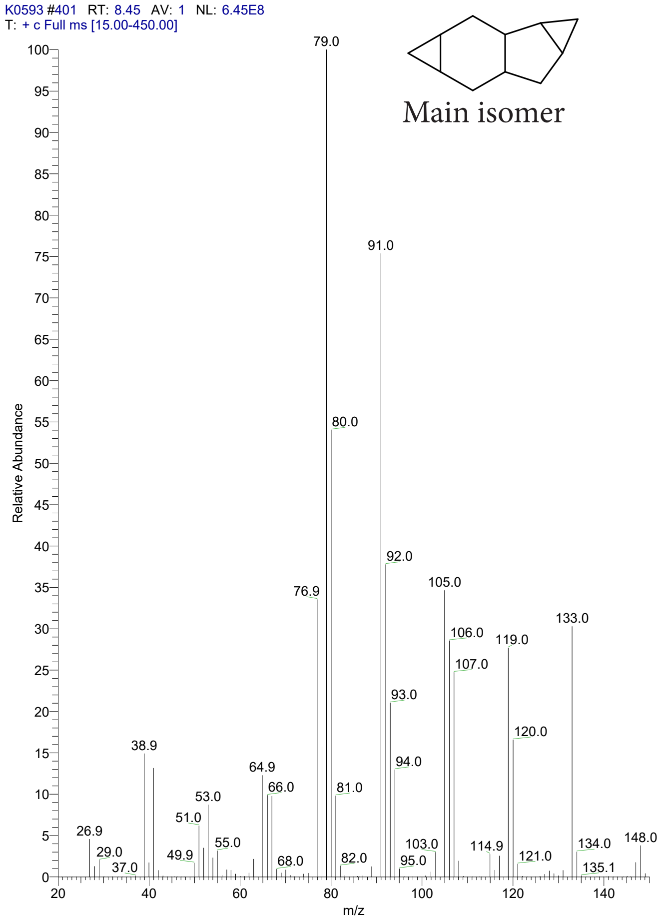
Mass spectra

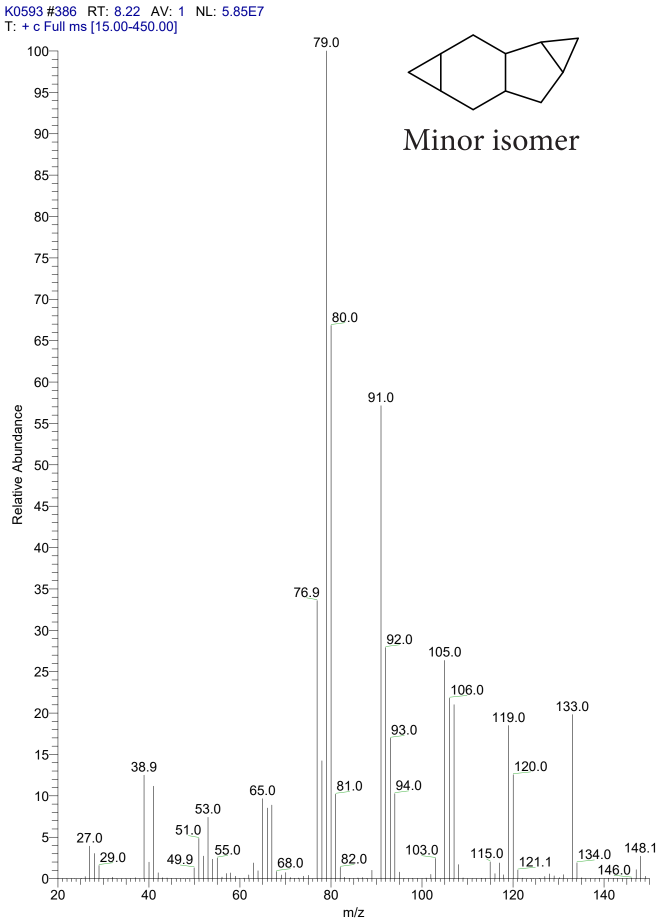


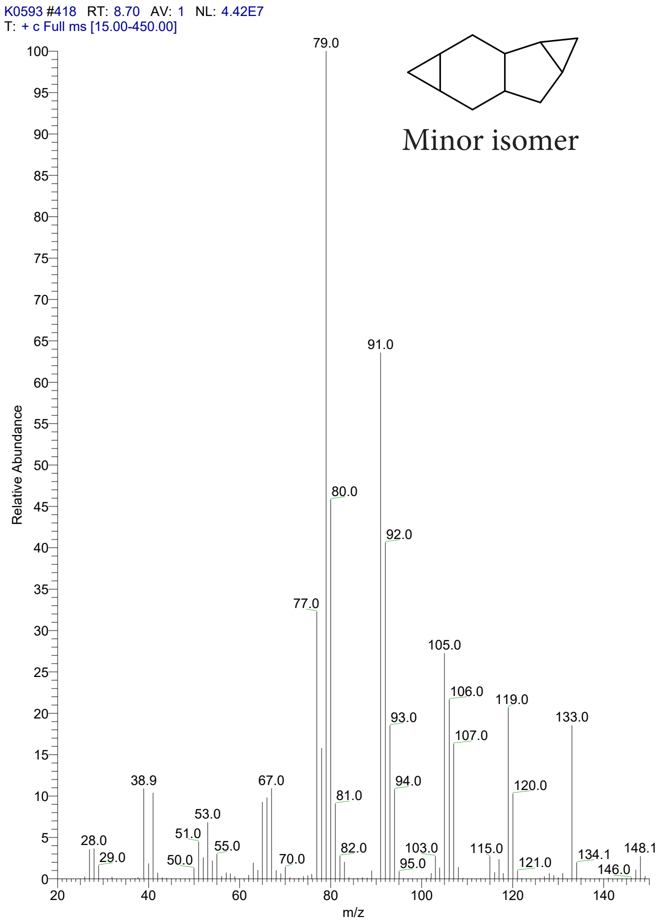







K0593 #401 RT: 8.45 AV: 1 NL: 6.45E8
T: + c Full ms [15.00-450.00]
Main isomer
Relative Abundance
m/z
79.0
91.0
80.0
92.0
76.9
105.0
133.0
106.0
119.0
107.0
93.0
120.0
38.9
94.0
64.9
66.0
81.0
53.0
51.0
26.9
55.0
148.0
103.0
134.0
114.9
29.0
49.9
82.0
121.0
37.0
68.0
95.0
135.1


K0593 #386 RT: 8.22 AV: 1 NL: 5.85E7
T: + c Full ms [15.00-450.00]
Minor isomer
Relative Abundance
m/z
79.0
80.0
91.0
76.9
92.0
105.0
106.0
133.0
119.0
93.0
38.9
120.0
81.0
94.0
65.0
53.0
51.0
27.0
55.0
148.1
29.0
49.9
68.0
82.0
103.0
115.0
134.0
121.1
146.0


K0593 #418 RT: 8.70 AV: 1 NL: 4.42E7
T: + c Full ms [15.00-450.00]
Minor isomer
Relative Abundance
m/z
79.0
91.0
80.0
92.0
77.0
105.0
106.0
119.0
93.0
133.0
107.0
38.9
67.0
81.0
94.0
120.0
53.0
51.0
28.0
55.0
148.1
29.0
50.0
70.0
82.0
103.0
95.0
115.0
134.1
121.0
146.0