Supplementary Material:

6,7-Dihydroxy-5,8-dimethoxy-2H-chromen-2-one

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Table of contents

*Synthesis of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol (**6**)*

Synthesized according to the described procedure [1]. A mixture of of 4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **4** (29.43 g, 140 mmol), SeO_2 (0.466 g, 4.2 mmol, 3 mol%) and 280 mL of t-BuOH were placed in a 500-mL round-bottom flask. Next, H_2O_2 (solution 37%, 23.2 mL, 280 mmol) was added at 50 °C. After 20 minutes the precipitate dissolves, a reddish solution is formed. The reaction mixture was stirred at 50 °C for 2.5 hours. After that, the reaction mixture was cooled in an ice-water bath, Na_2SO_3 (17.65 g, of 140 mmol) in 70 mL of water at 20-22 °C were added, forming an orange solution with a precipitate. Most of the t-BuOH was evaporated in vacuo and 200 mL of water and 100 mL of EtOAc was added. The organic layer was separated, the aqueous layer was extracted with ethyl acetate (2 × 100 and 2 × 50 mL). The organic phases were combined, washed with water (50 mL) and saturated NaCl solution (50 mL), dried, and evaporated in vacuo. To red-gray crystals of the intermediate formylphenol (30.79 g, 97% yield) 300 mL of methanol was added. Formed red solution with precipitate was cooled in an ice-water bath, then Et_3N (19.5 mL, 140 mmol) were added. The color of the mixture changed from red to purple, the mixture was stirred for 45 minutes at 20 °C. After stirring, the mixture was evaporated to dry and 100 mL of CH_2Cl_2 and 105 mL of 2M HCl solution (210 mmol) were added. The yellow aqueous layer was separated and extracted with CH_2Cl_2 (2 × 30 mL). The red organic layer was extracted with 2M NaOH solution (210 mmol, 105 mL). Black aqueous layer was washed with 30 mL CH_2Cl_2, combined organic layers extracted with water 30 mL Then, 22 mL of 11 M HCl solution (242 mmol) and 50 mL of CH_2Cl_2 were added to the alkaline aqueous layer, which turned red. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The organic phases were combined, dried, and evaporated in vacuo, 26.83 g 97% of brown crystalline residue was obtained. The product was purified by eluting through short 90 g SiO_2 column (CH_2Cl_2, R_f=0.46) to afford 24.09 g of **6**, yield 87%.

*4,7-Dimethoxybenzo[d][1,3]dioxol-5-ol (**6**):* colorless crystals (CH_2Cl_2); mp 84−86 °C (Lit. 84-85 °C (MeOH) [2]); ^{1}H NMR δ 8.94 (1H, br s, OH), 6.08 (1H, s, H-6), 5.87 (2H, s, OCH_2O), 3.72 (3H, s, OCH_3), 3.71 (3H, s, OCH_3); ^{13}C NMR δ 145.0 (C, C-5), 139.7 (C, C-7), 138.4 (C, C-3a), 128.2 (C, C-7a), 126.9 (C, C-4), 101.0 (C, C-2), 95.4 (CH, C-6), 60.1 (CH_3), 56.3 (CH_3).

*Synthesis of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde (**7**)*

Synthesized according to the modified literature method [2].

1. Preparation of the formylation mixture: A mixture of PCl_5 (32.7 g, 157 mmol), ethyl formate (12.96 g, 175 mmol) and 200 mL of CH_2Cl_2 were placed into a 500 mL round bottom flask. The reaction mixture was refluxed with a calcium chloride tube for 2 hours. A solution of dichloromethyl methyl ether (157 mmol) was obtained

2. Formylation: To a solution of **6** **(**19.82 g, 100 mmol) in 260 mL of CH_2Cl_2 placed in a 1000-mL round-bottom flask, $SnCl_4$ (104 g, 400 mmol) were added dropwise at 10 °C. At the start of the addition the temperature rose, the color of the solution turns yellow and yellow precipitate falls off. The reaction mass was stirred with cooling for 30 minutes, and then the formylation mixture prepared above was added dropwise at 5-10 °C, slow heating of the mixture was observed and precipitate dissolved. After the addition was completed, the red solution was stirred for 3 hours at 20 °C. After that, the solution was poured into 380 g of ice, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (6 × 50 mL). The organic phases were combined, dried, and evaporated in vacuo to yield 22.80 g (101%) of brown solid. The product was purified by recrystallization from 230 mL EtOH to give a 20.36 g of **7**, 90% yield.

*6-Hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde (**7**)**:*** yellow crystals (EtOH) ; mp 132–133 °C (Lit. 125-127 °C [2]); ^{1}H NMR δ 12.43 (1H, br s, OH), 9.95 (1H, s, CHO), 6.09 (2H, s, OCH_2O), 4.00 (3H, s, OCH_3), 3.79 (3H, s, OCH_3); ^{13}C NMR δ 192.5 (CHO), 153.6 (C, C-6), 148.2 (C, C-4), 139.1 (C, C-7a), 128.6 (C, C-3a), 126.3 (C, C-7), 107.1 (C, C-5), 102.7 (C, C-2), 60.4 (2 x CH_3).

*Synthesis of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one (sabandin) (**3**)*

Synthesized according to the optimized method [3].

A mixture of **7** (7.55 g, 33,4 mmol) and methyl (triphenylphosphoranylidene)acetate (13.41 g, 40.1 mmol) in N,N-diethylaniline (115 mL) were heated in a 250-mL round-bottom flask under argon at 190 °C for 45 min. Then, the red solution was cooled, N,N-diethylaniline was distilled off in vacuo (0.3 mbar), the residue was diluted with an aqueous solution of HCl (66 mL, 1 M) to acidic pH, extracted with CH_2Cl_2 (3 × 30 mL), solution was dried and evaporated in vacuo. Next, to the brown residue 22.82 g, solution of NaOH (13.36 g, 334 mmol) in CH_3OH (150 mL) and CH_2Cl_2 (100 mL) was added, and the suspension was stirred for 30 minutes at room temperature. Then the mixture was diluted with water (100 mL), the aqueous layer was separated, the organic phase was extracted with water (3 x 75 mL) Aqueous phases were combined, washed with CH_2Cl_2 (100 mL) and acidified with 35 mL 11 M HCl (385 mmol). The precipitate was filtered off, washed with water, and dried in a vacuum to obtain 7.56 g of **3**, 90% yield. An analytical sample was crystallized from MeOH.

*4,9-Dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one (sabandin) (**3**):* brownish crystals (MeOH); mp 146−147 °C (Lit. 131−133 °C [3], 143−145 °C [4]); ^{1}H NMR δ 7.94 (1H, d, *J* = 9.7 Hz, H-4), 6.26 (1H, d, *J* = 9.7 Hz, H-3), 6.13 (2H, s, OCH_2O), 3.99 (3H, s, OCH_3), 3.90 (3H, s, OCH_3); ^{13}C NMR δ 159.7 (C, C-6), 142.93 (C, C-9), 142.90 (C, C-4a), 139.1 (C, C-8), 133.2 (CH, C-3a), 132.9 (C, C-9a), 126.3 (C, C-4), 112.0 (C, C-7), 106.5 (CH, C-8a), 102.8 (C, C-2), 60.7 (CH_3), 60.3 (CH_3).

References

1. Asakawa, T.; Sagara, H.; Kanakogi, M.; Hiza, A.; Tsukaguchi, Y.; Ogawa, T.; Nakayama, M.; Ouchi, H.; Inai, M.; Kan, T. Practical Synthesis of Polymethylated Flavones: Nobiletin and Its Desmethyl Derivatives. *Org. Process Res. Dev.* **2019**, *23*, 595-602, doi:10.1021/acs.oprd.9b00091.
2. Tsyganov, D.V.; Chernysheva, N.B.; Salamandra, L.K.; Konyushkin, L.D.; Atamanenko, O.P.; Semenova, M.N.; Semenov, V.V. Synthesis of polyalkoxy-3-(4-methoxyphenyl)coumarins with antimitotic activity from plant allylpolyalkoxybenzenes. *Mendeleev Commun.* **2013**, *23*, 147-149, doi:10.1016/j.mencom.2013.05.009.
3. Maes, D.; Vervisch, S.; Debenedetti, S.; Davio, C.; Mangelinckx, S.; Giubellina, N.; De Kimpe, N. Synthesis and structural revision of naturally occurring ayapin derivatives. *Tetrahedron* **2005**, *61*, 2505-2511, doi:10.1016/j.tet.2004.12.061.
4. Murray, R.D. The naturally occurring coumarins. In *Fortschr. Chem. Org. Naturst.*, 2002/03/15 ed.; Herz, W., Falk, H., Kirby, G.W., Moore, R.E., Eds.; Springer-Verlag Wien, 2002; Volume 83, pp. 1-619.

Figure S1. ^{1}H NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

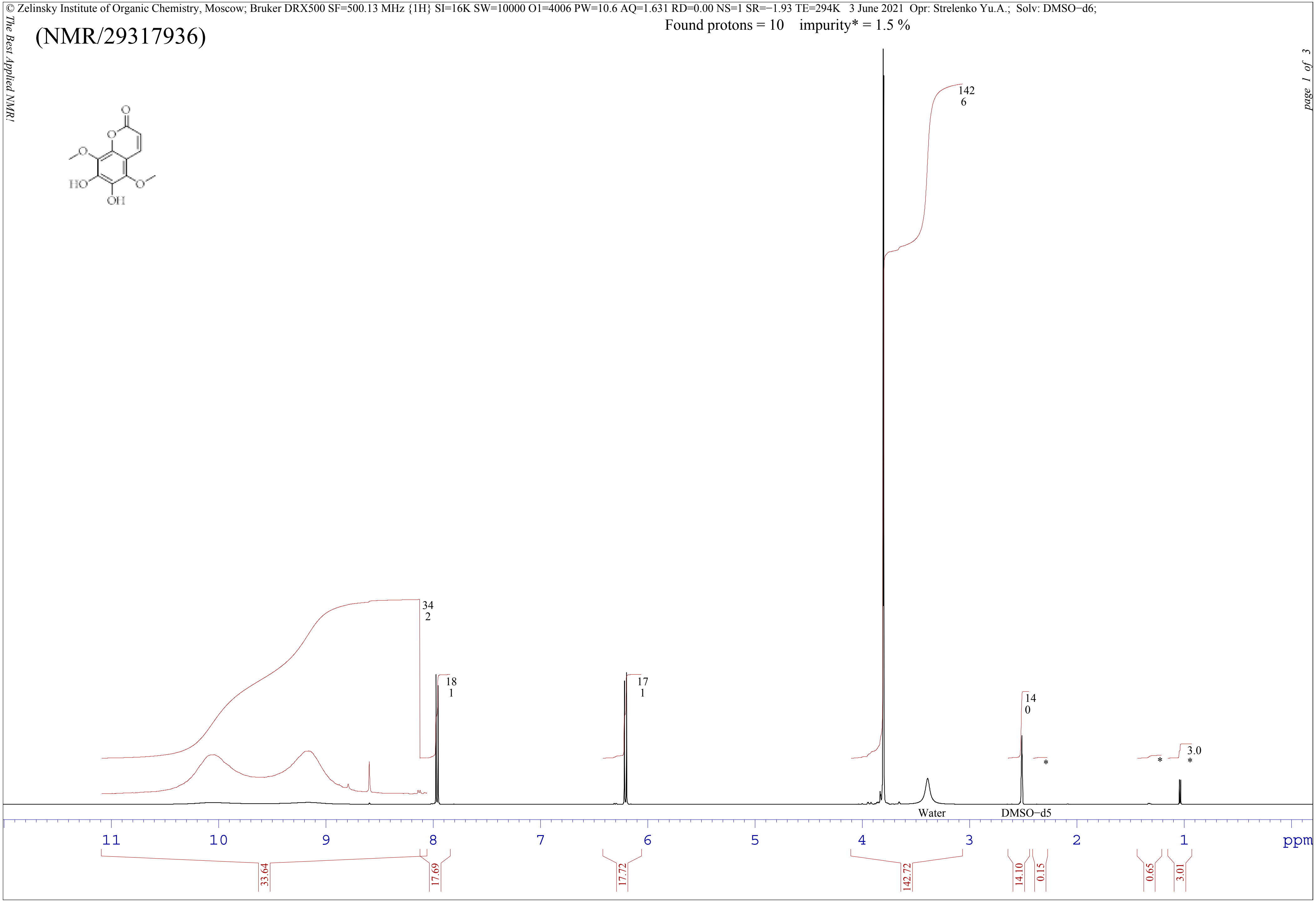


Figure S1. ^{1}H NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

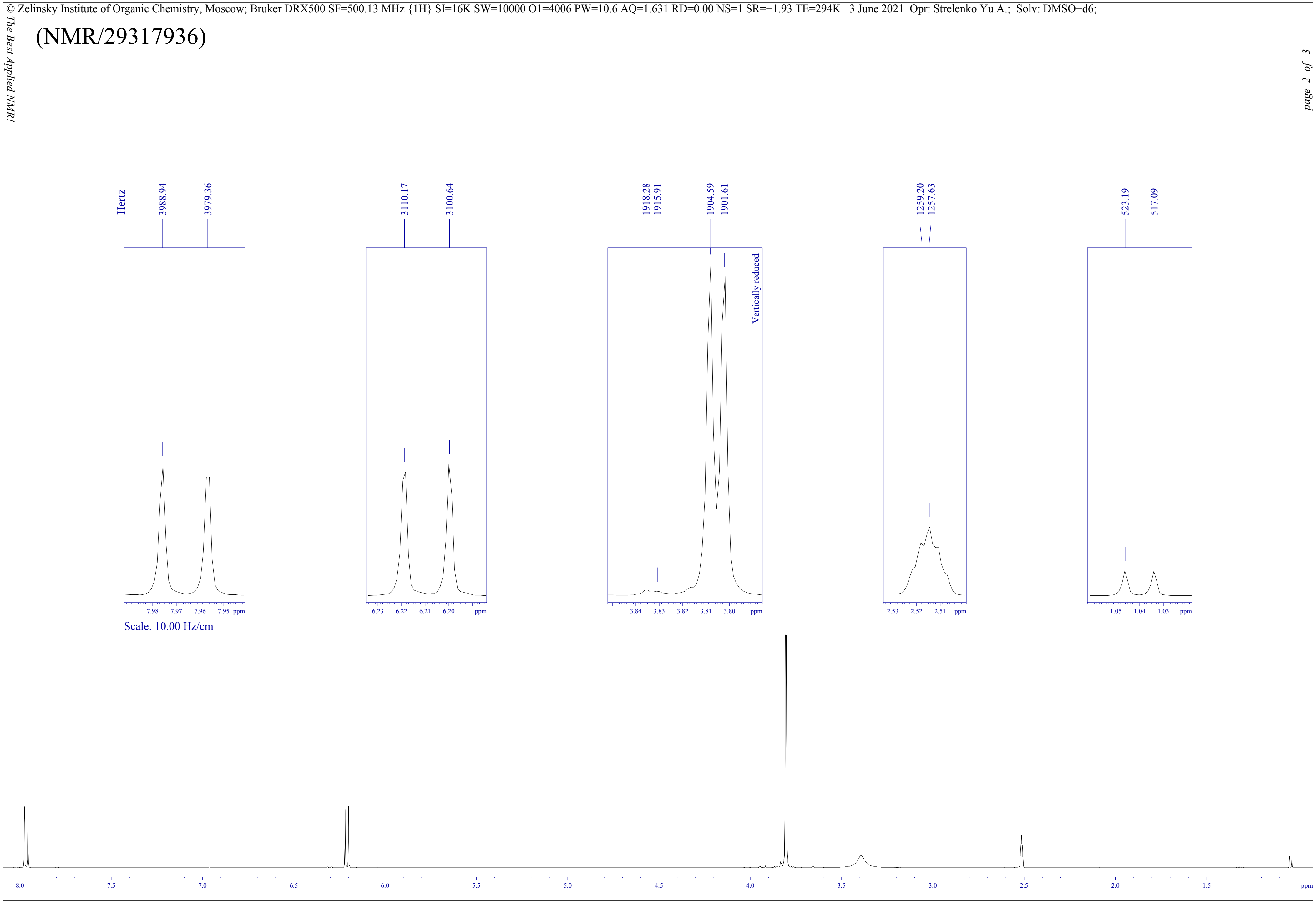
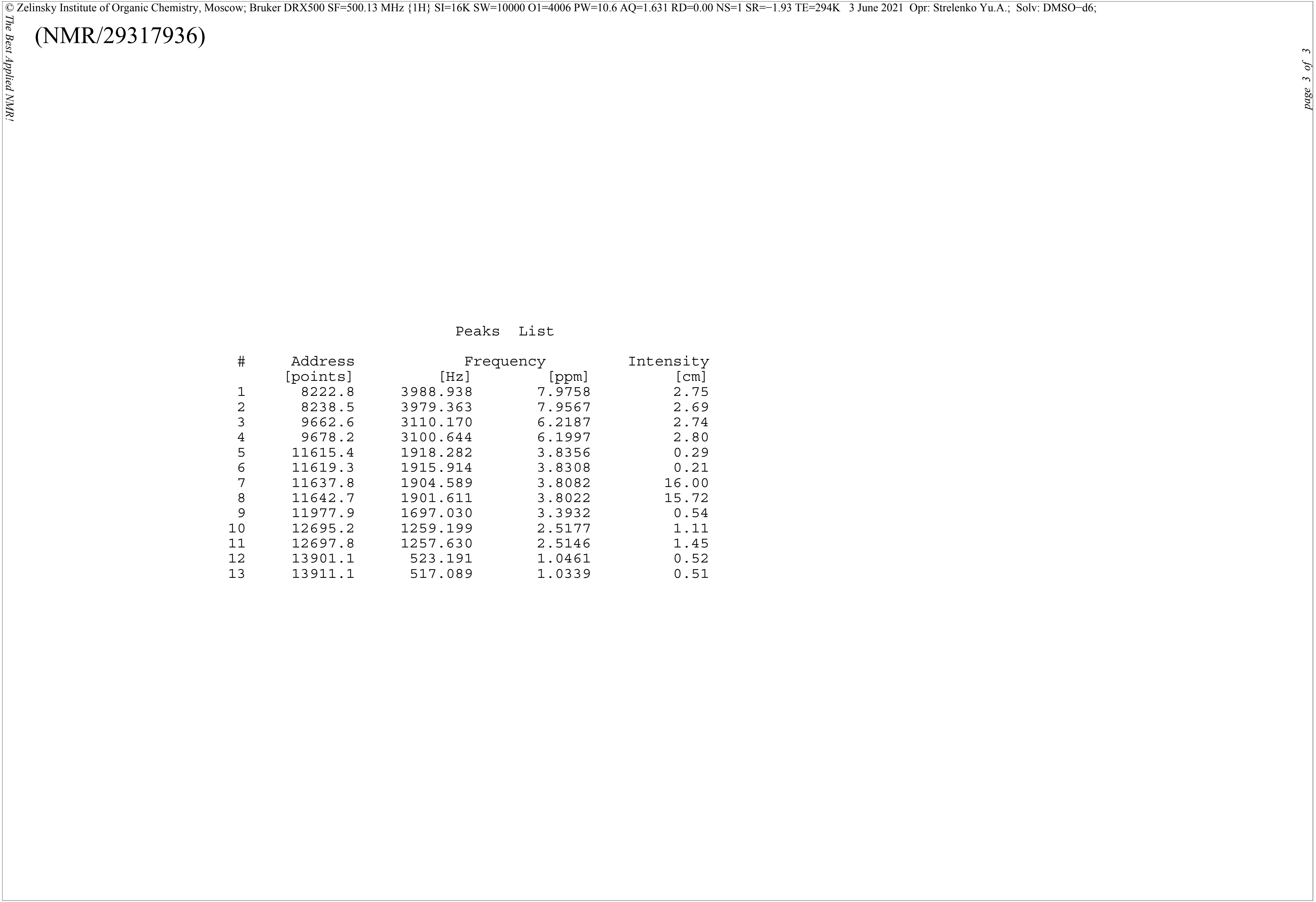


Figure S1. ^{1}H NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.



© Zelinsky Institute of Organic Chemistry, Moscow; Bruker DRX500 SF=500.13 MHz {1H} SI=16K SW=10000 O1=4006 PW=10.6 AQ=1.631 RD=0.00 NS=1 SR=−1.93 TE=294K 3 June 2021 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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(NMR/29317936)

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 4      9678.2      3100.644        6.1997        2.80
 5     11615.4      1918.282        3.8356        0.29
 6     11619.3      1915.914        3.8308        0.21
 7     11637.8      1904.589        3.8082       16.00
 8     11642.7      1901.611        3.8022       15.72
 9     11977.9      1697.030        3.3932        0.54
10     12695.2      1259.199        2.5177        1.11
11     12697.8      1257.630        2.5146        1.45
12     13901.1       523.191        1.0461        0.52
13     13911.1       517.089        1.0339        0.51
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Figure S2. ^{13}C NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

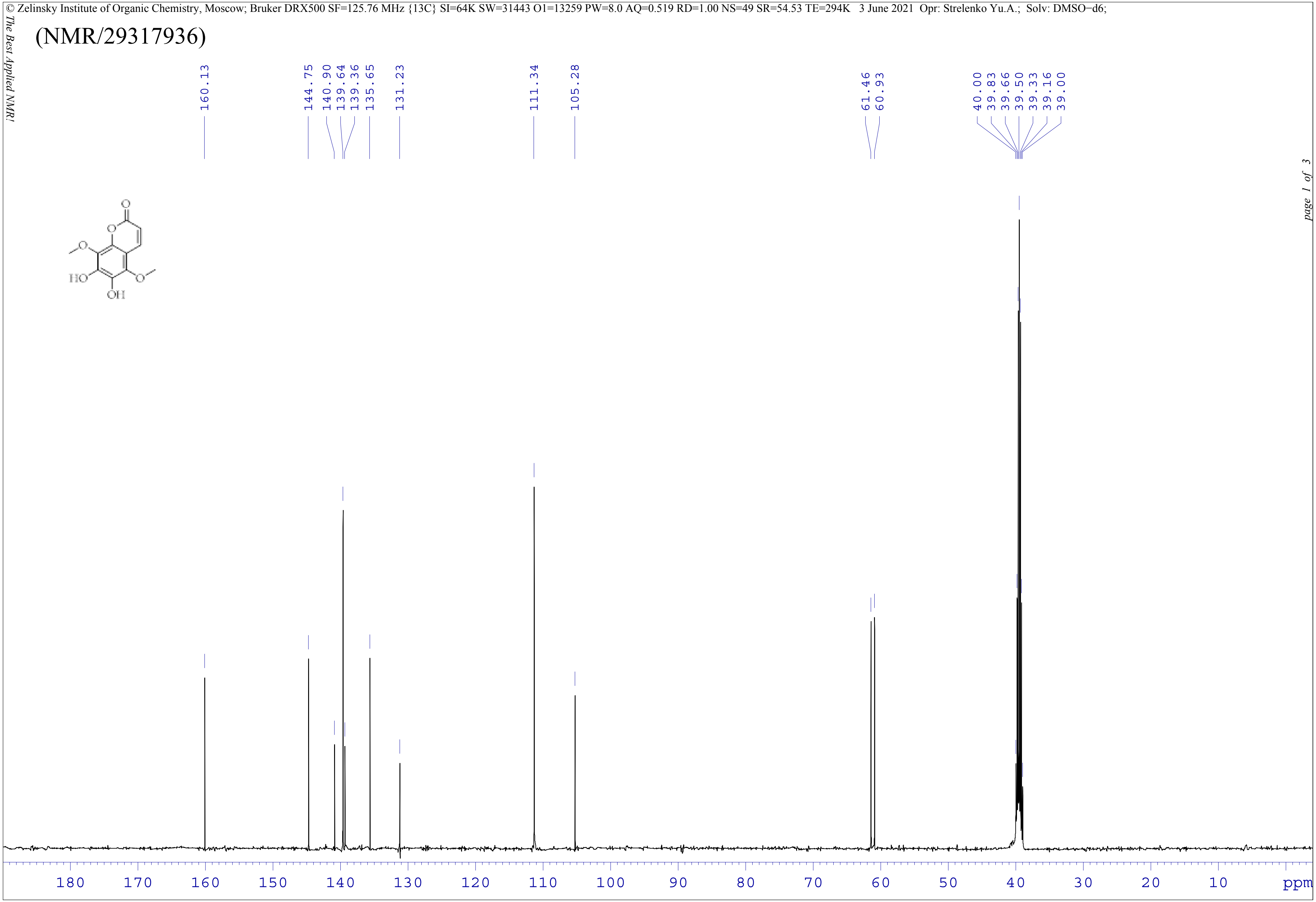

Figure S2. ^{13}C NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

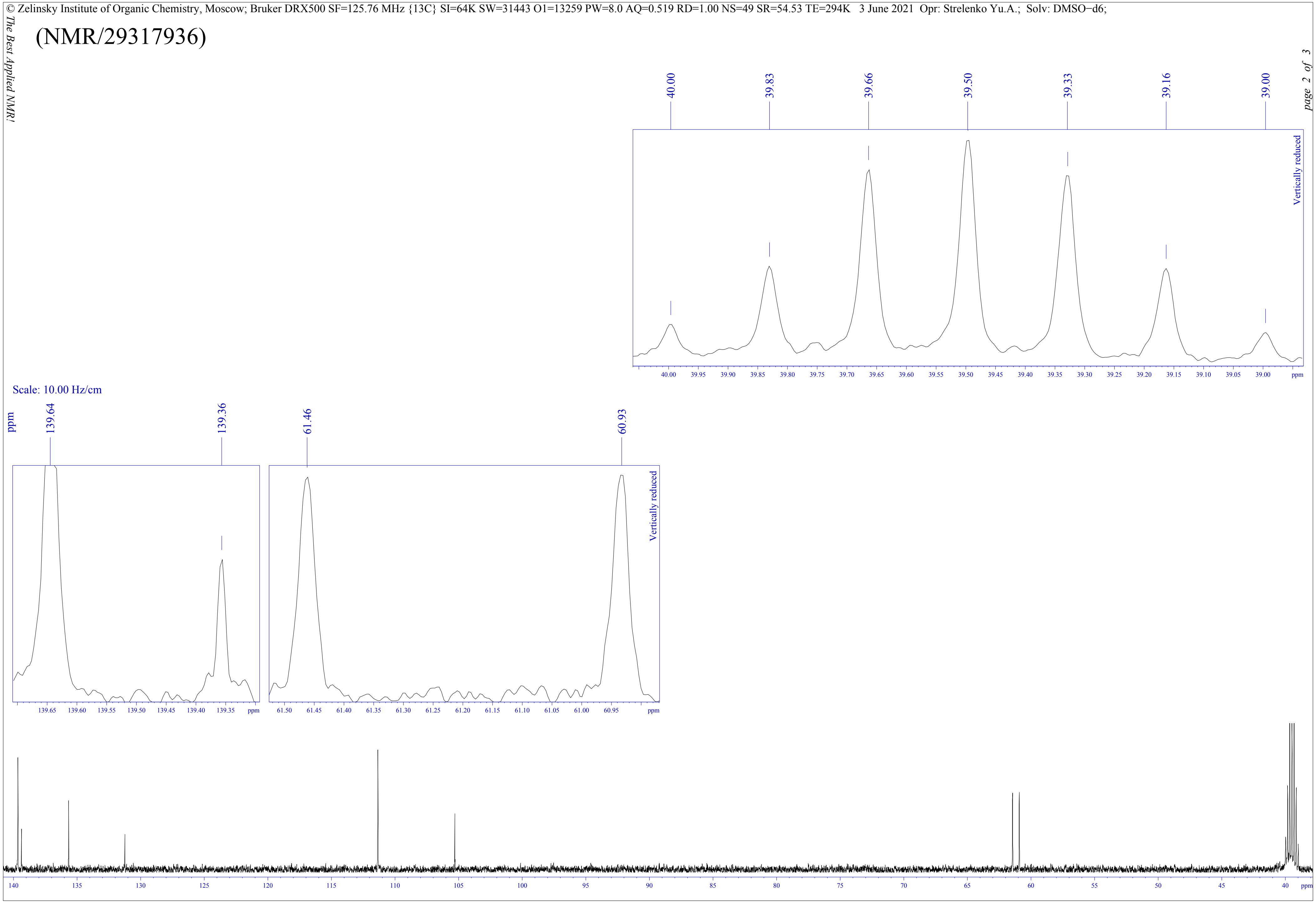

Figure S2. ^{13}C NMR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

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 5     23763.7    17525.182     139.3566          2.93
 6     24733.9    17059.613     135.6545          4.91
 7     25894.4    16502.768     131.2265          2.57
 8     31107.0    14001.595     111.3377          8.50
 9     32693.6    13240.282     105.2840          4.09
10     44178.7     7729.318      61.4619          5.46
11     44317.5     7662.729      60.9324          5.52
12     49804.5     5029.853      39.9963          2.34
13     49848.0     5008.961      39.8302          5.97
14     49891.7     4988.002      39.6636         12.08
15     49935.5     4966.978      39.4964         14.00
16     49979.5     4945.886      39.3286         11.77
17     50022.9     4925.054      39.1630          5.84
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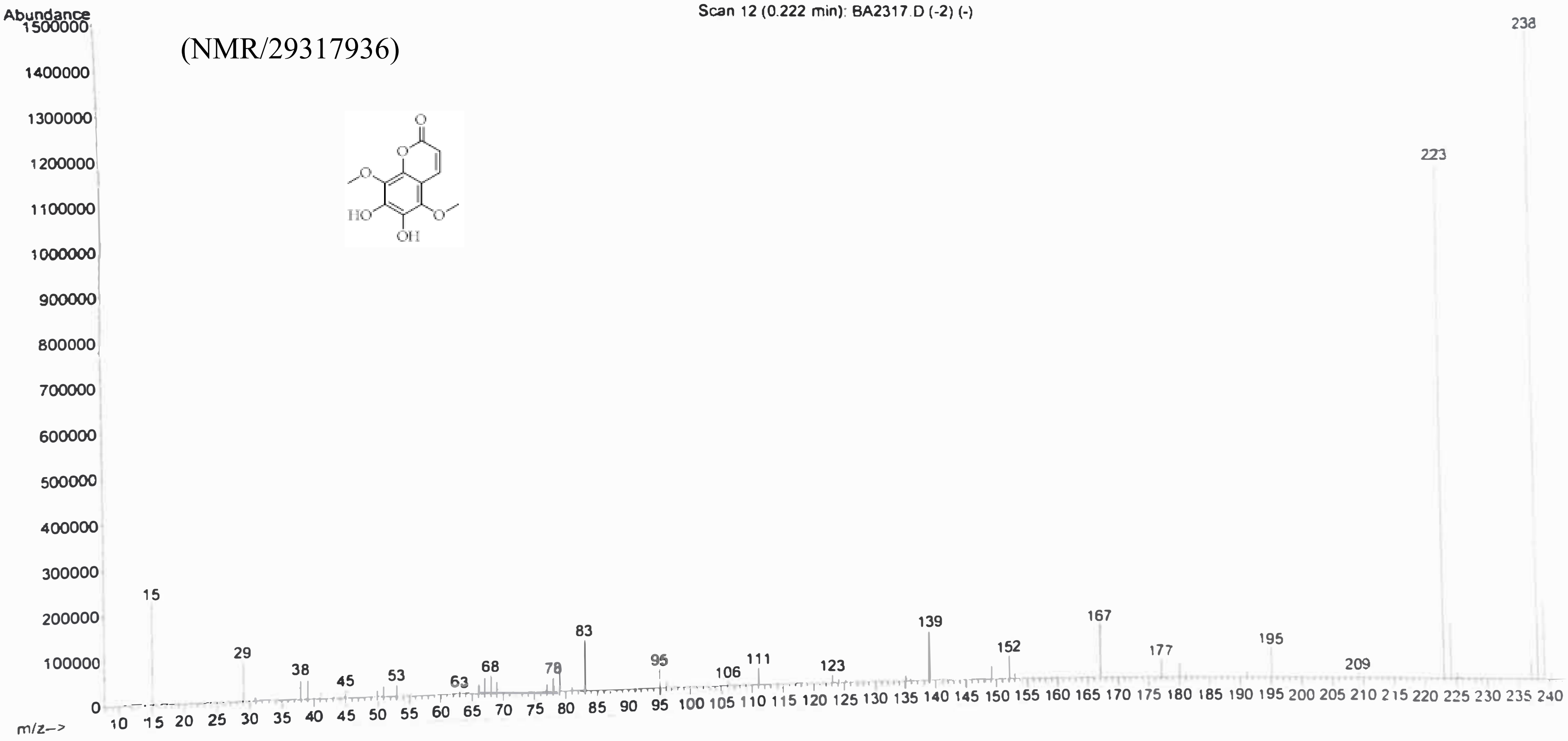

Figure S4. IR spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

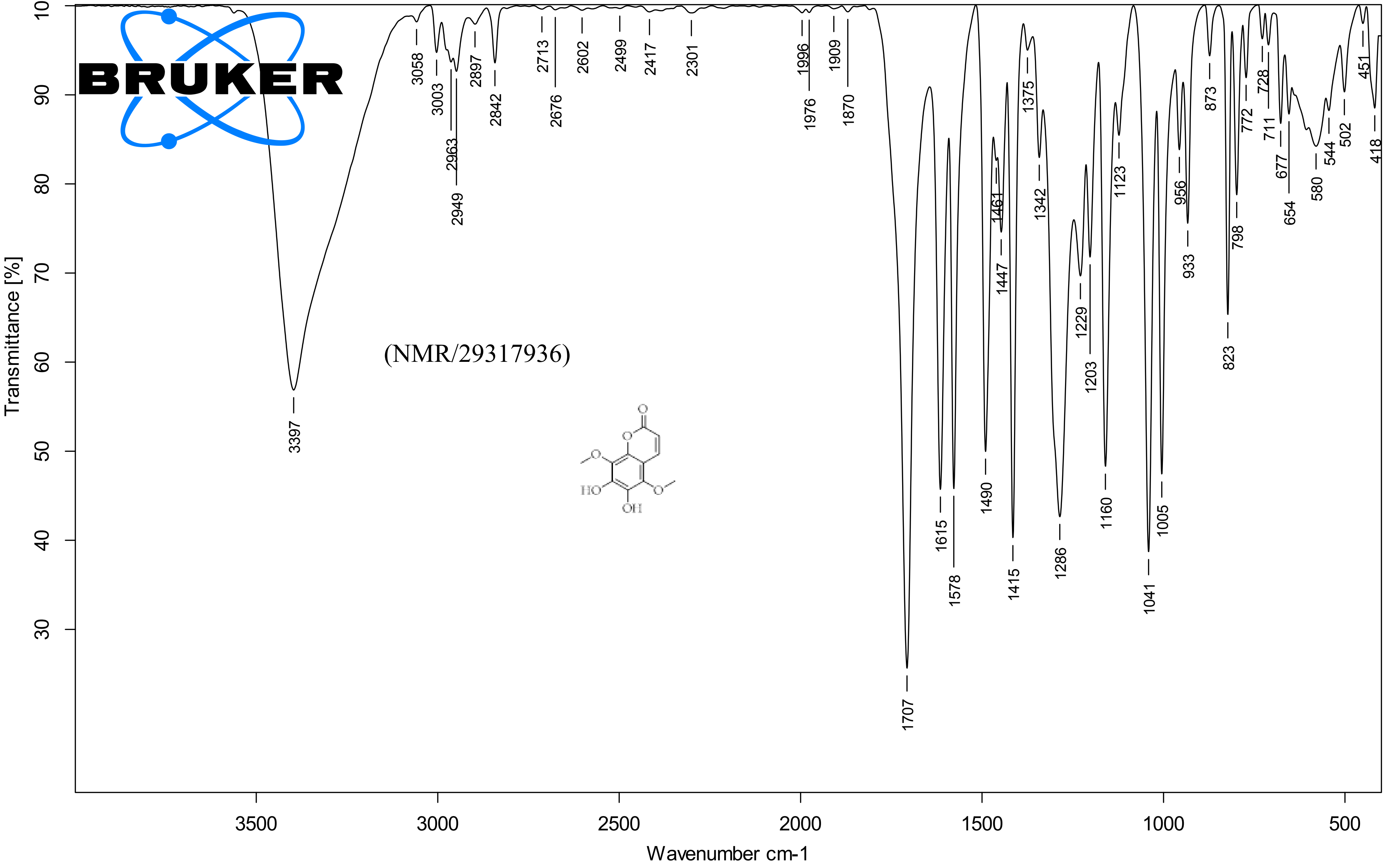

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Figure S5. HRMS spectrum of 6,7-dihydroxy-5,8-dimethoxy-2H-chromen-2-one **(2)**.

(NMR/29317936) Display Report

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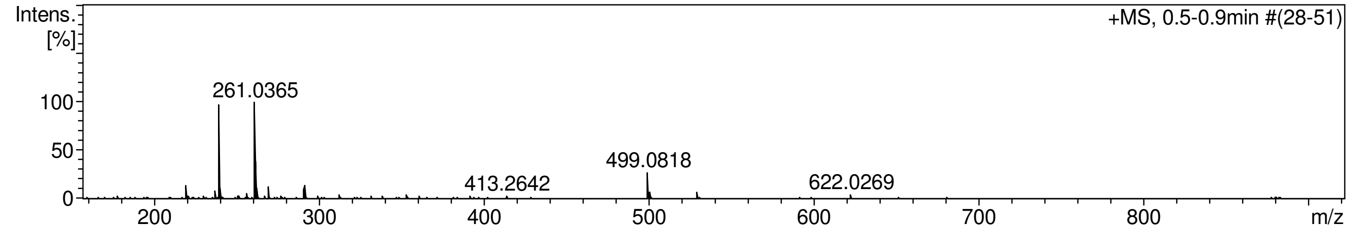


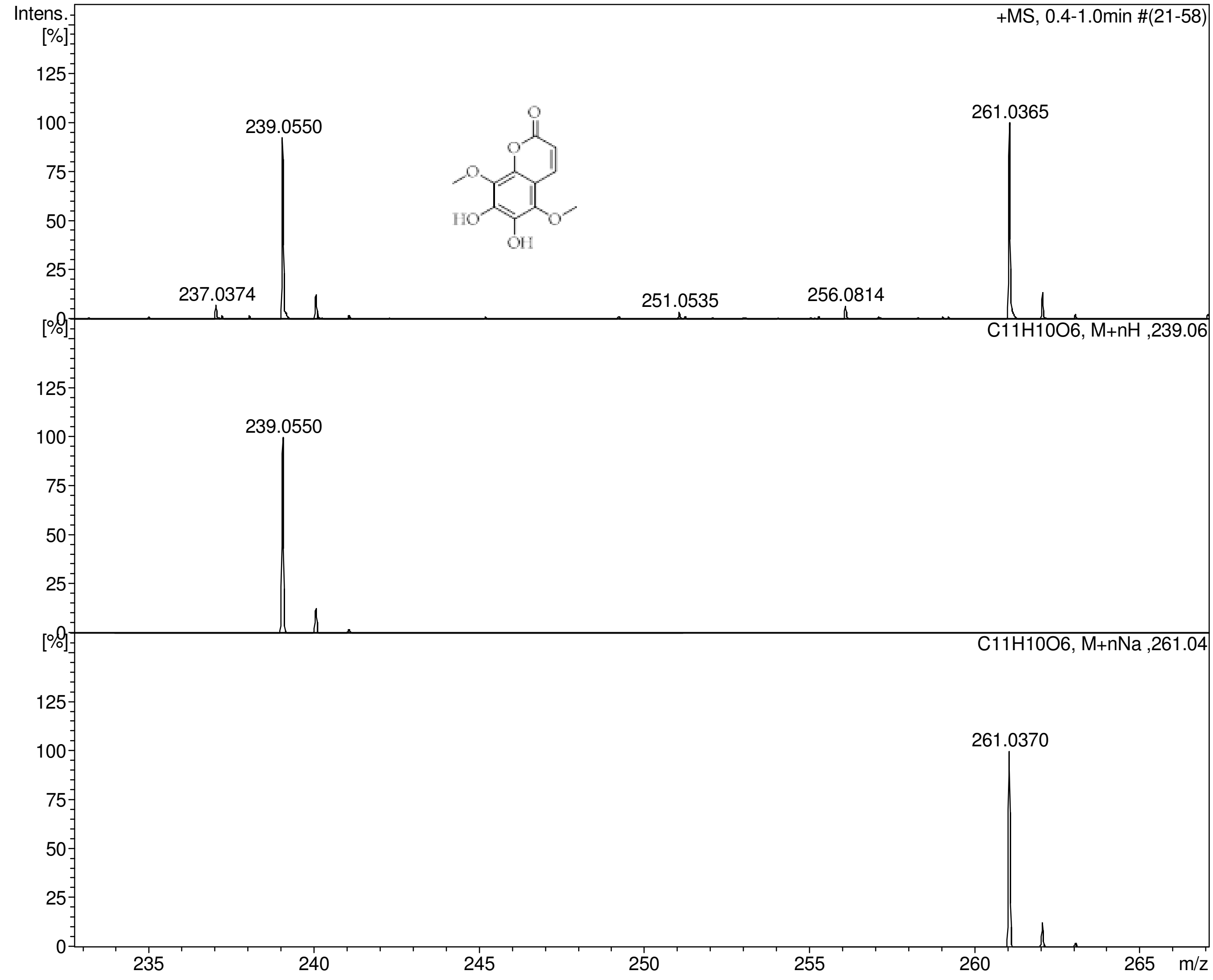


Figure S6. ^{1}H NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

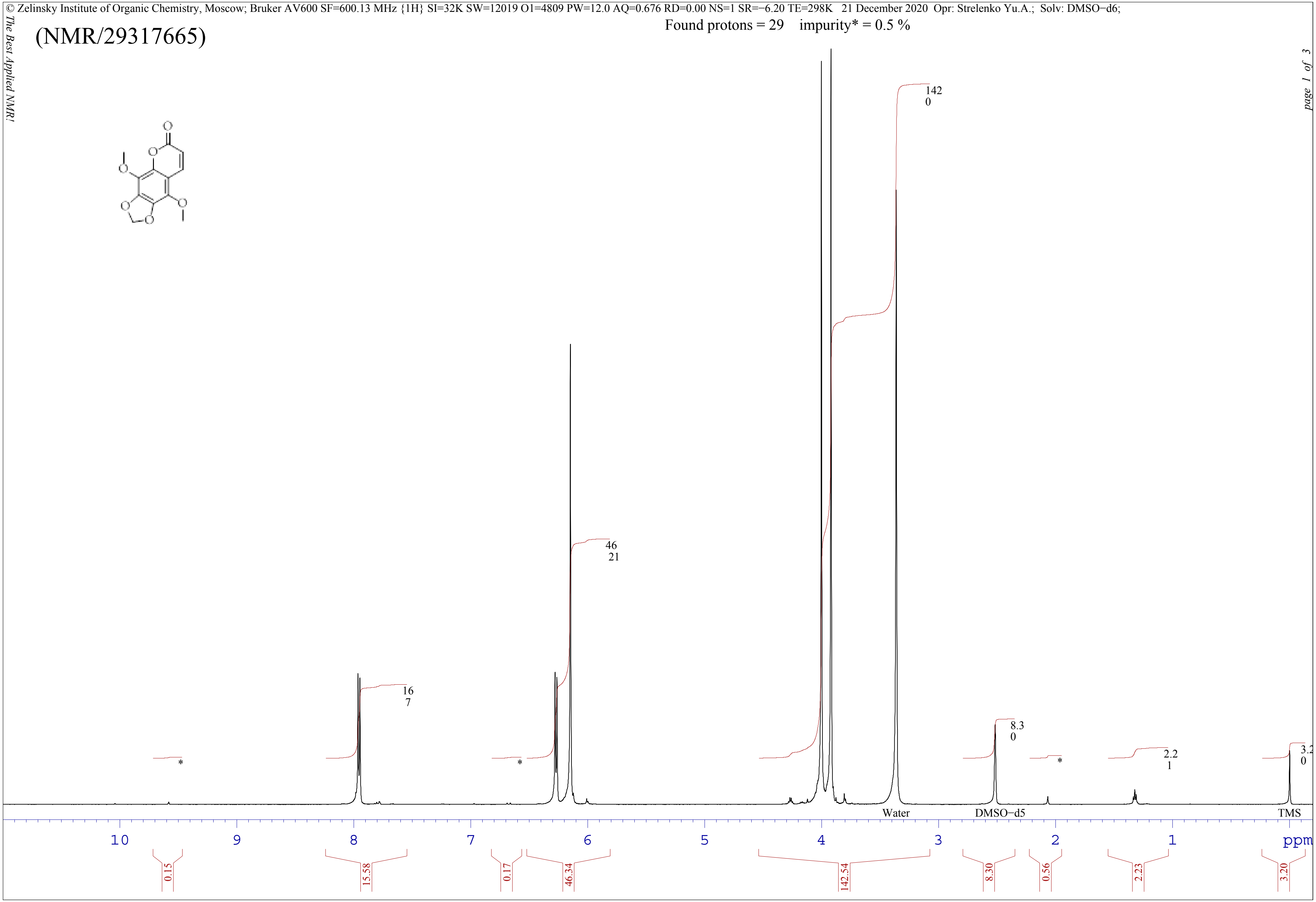


Figure S6. ^{1}H NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

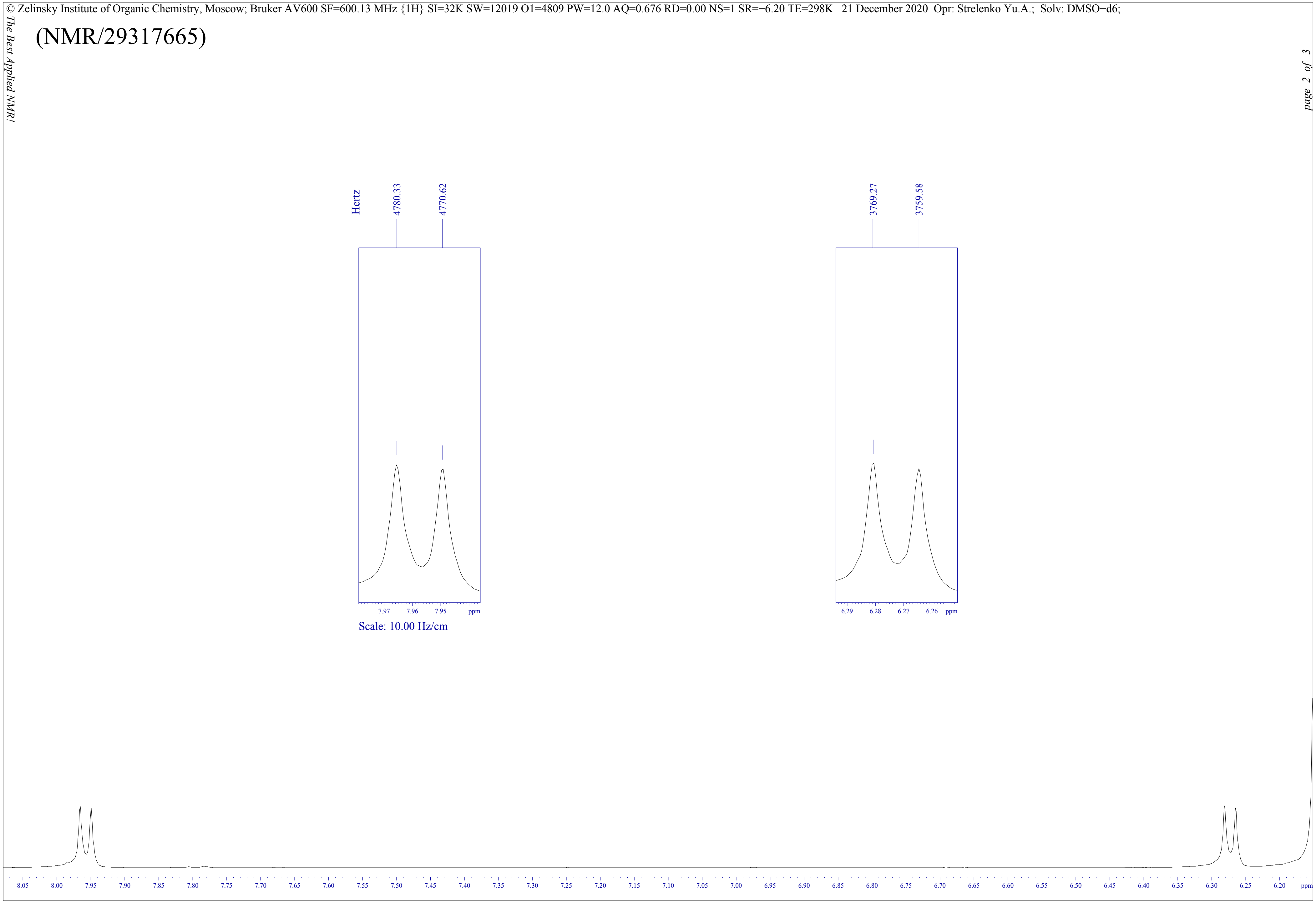
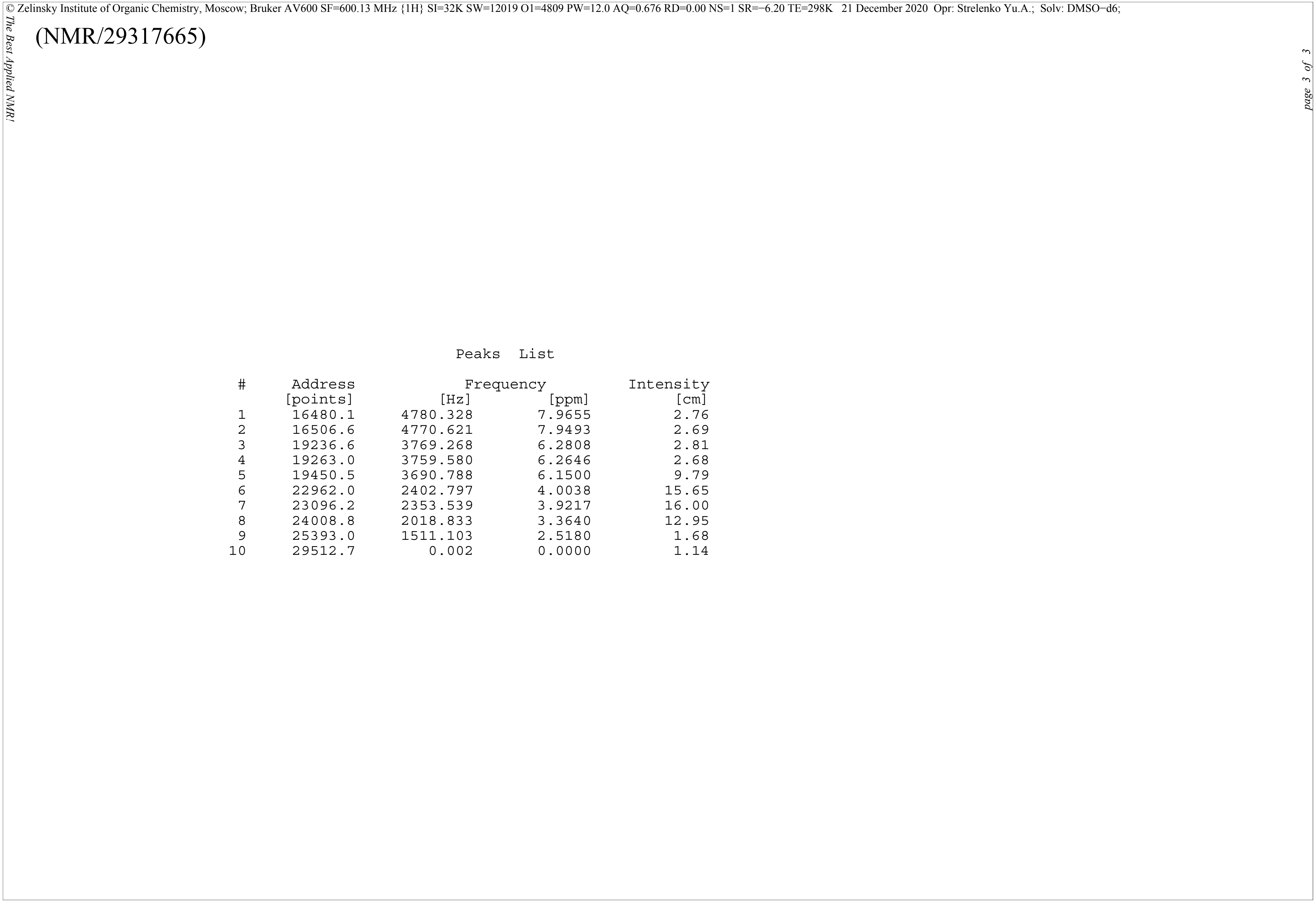


Figure S6. ^{1}H NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.



© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AV600 SF=600.13 MHz {1H} SI=32K SW=12019 O1=4809 PW=12.0 AQ=0.676 RD=0.00 NS=1 SR=−6.20 TE=298K 21 December 2020 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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(NMR/29317665)

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Figure S7. ^{13}C NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

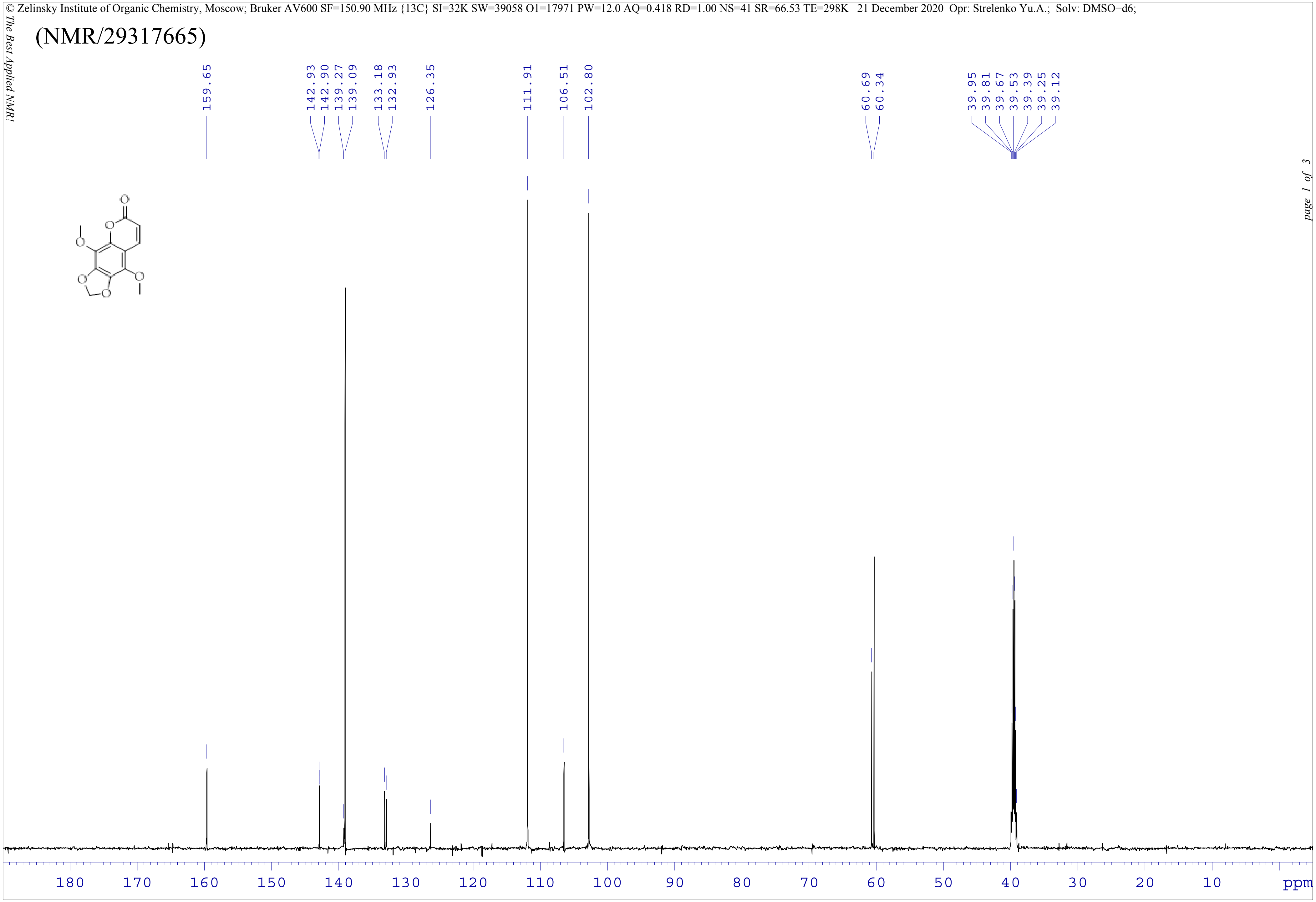

Figure S7. ^{13}C NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

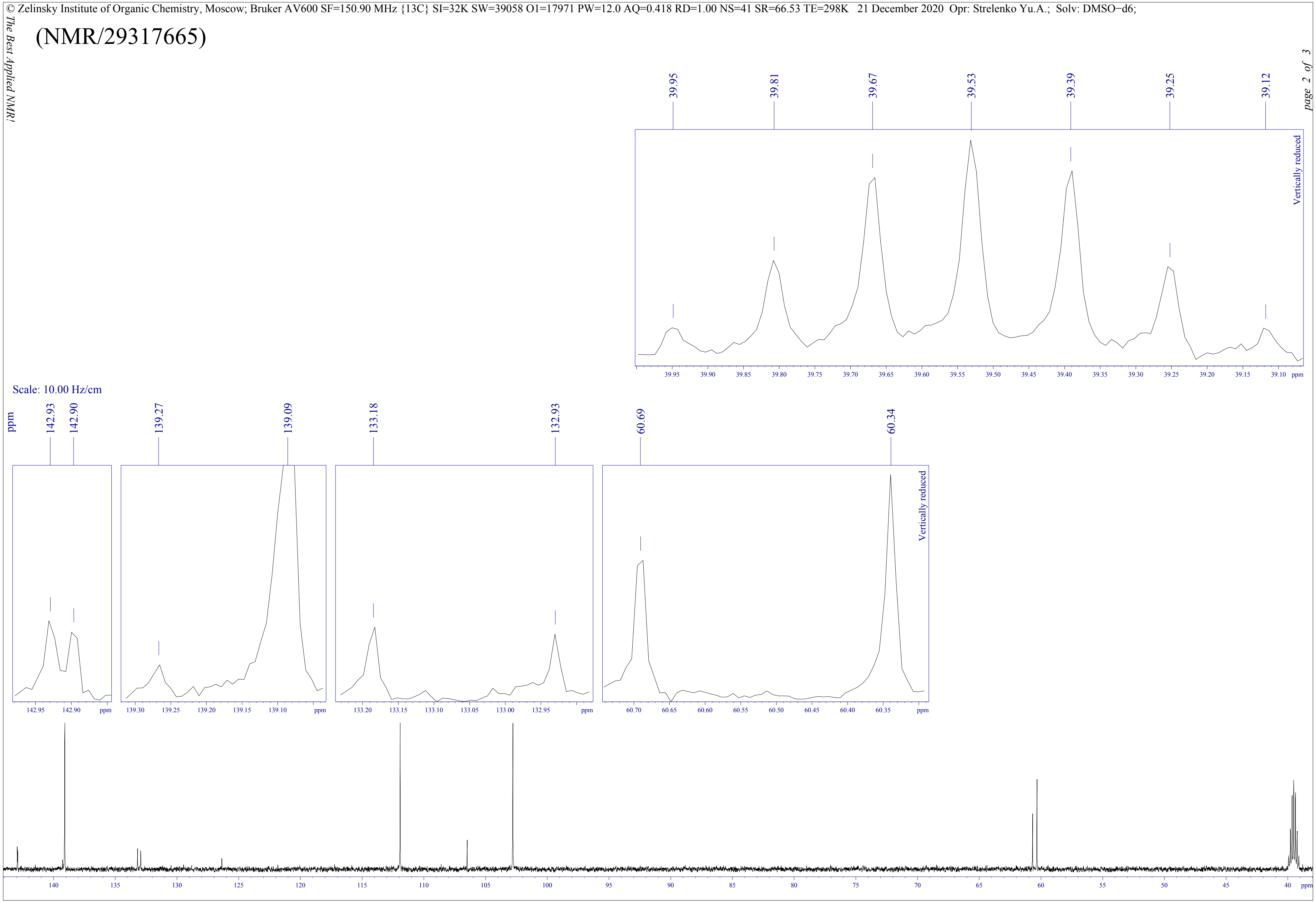

Figure S7. ^{13}C NMR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

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(NMR/29317665)

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  5      13796.8     20988.406      139.0855         12.28
  6      14543.8     20097.967      133.1848          1.51
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 17      26399.1      5965.265       39.5305          6.38
 18      26416.7      5944.259       39.3913          5.55
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 20      26451.4      5903.001       39.1179          0.99
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Figure S8. Mass spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

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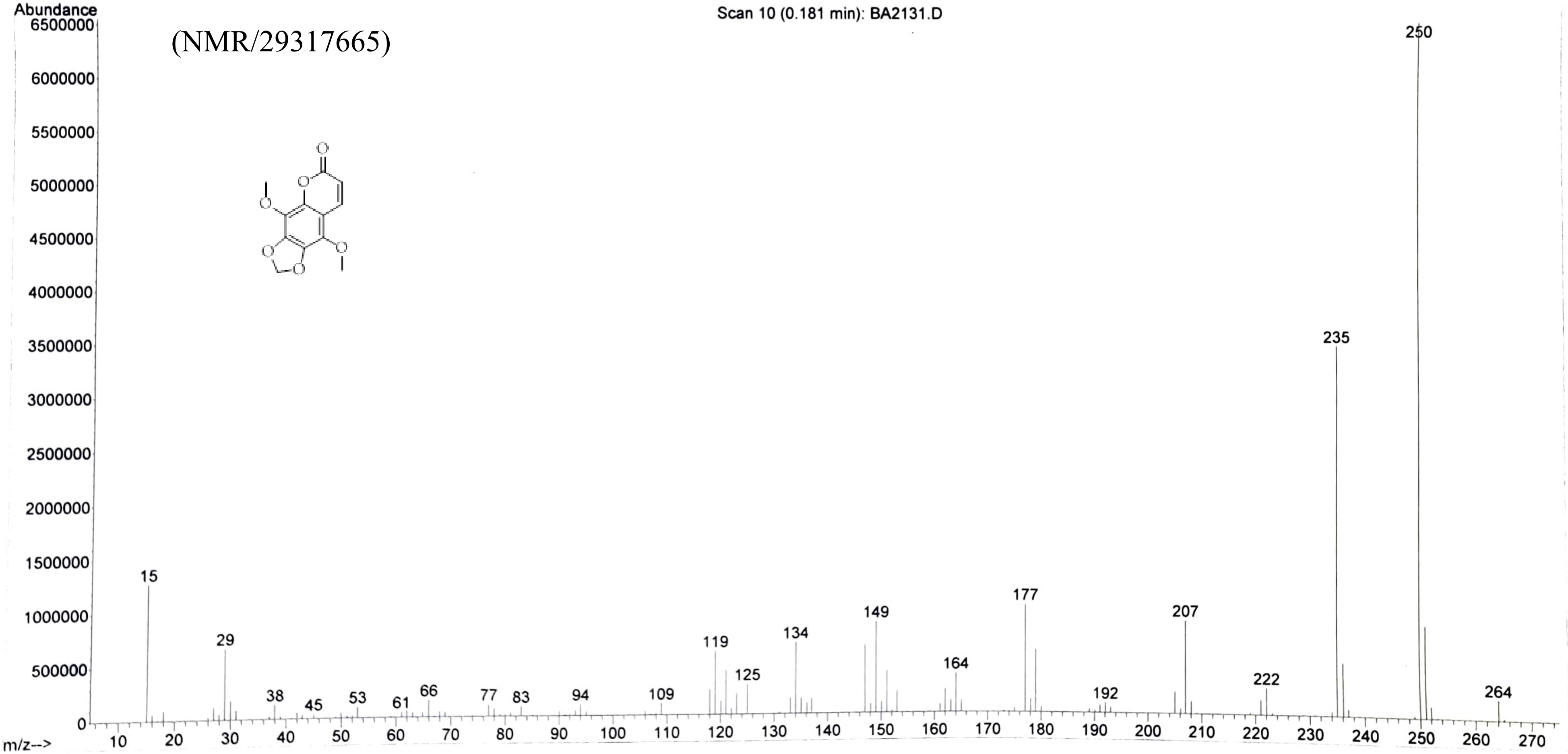
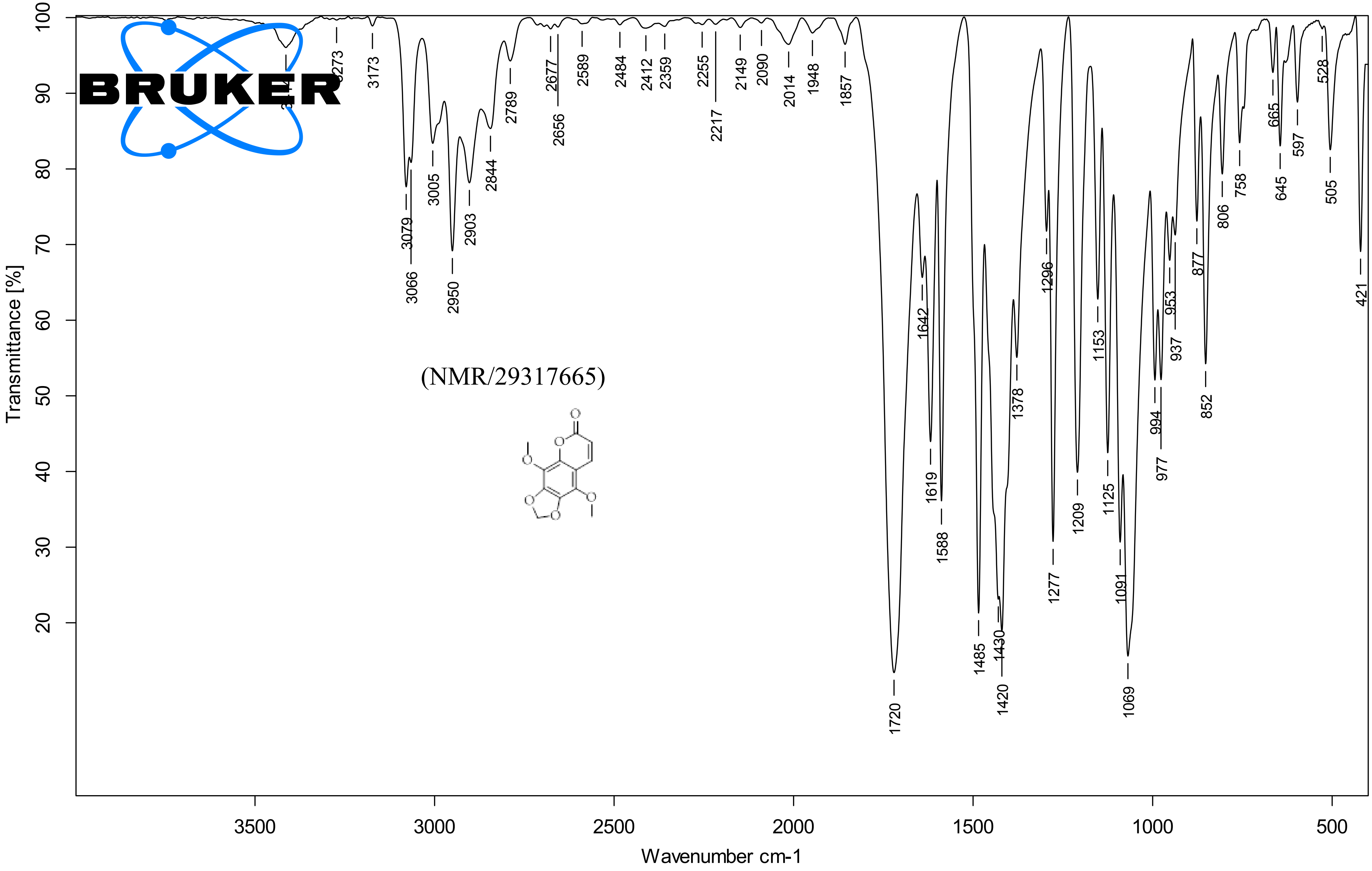


Figure S9. IR spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.



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09.06.2023

Figure S10. HRMS spectrum of 4,9-dimethoxy-6H-[1,3]dioxolo[4,5-g]chromen-6-one **(3)**.

(NMR/29317665) Display Report

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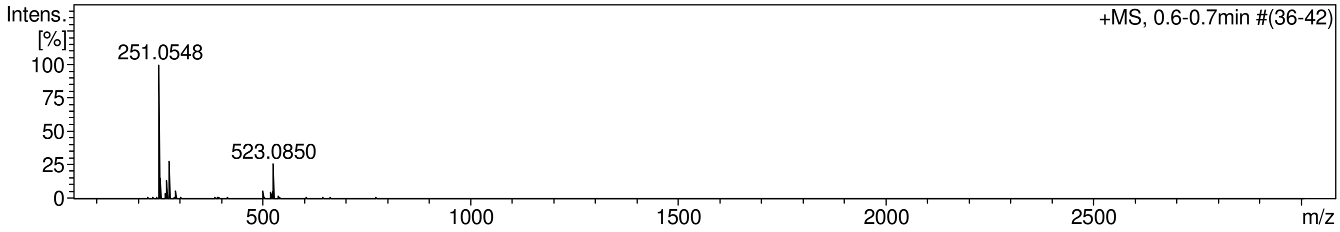

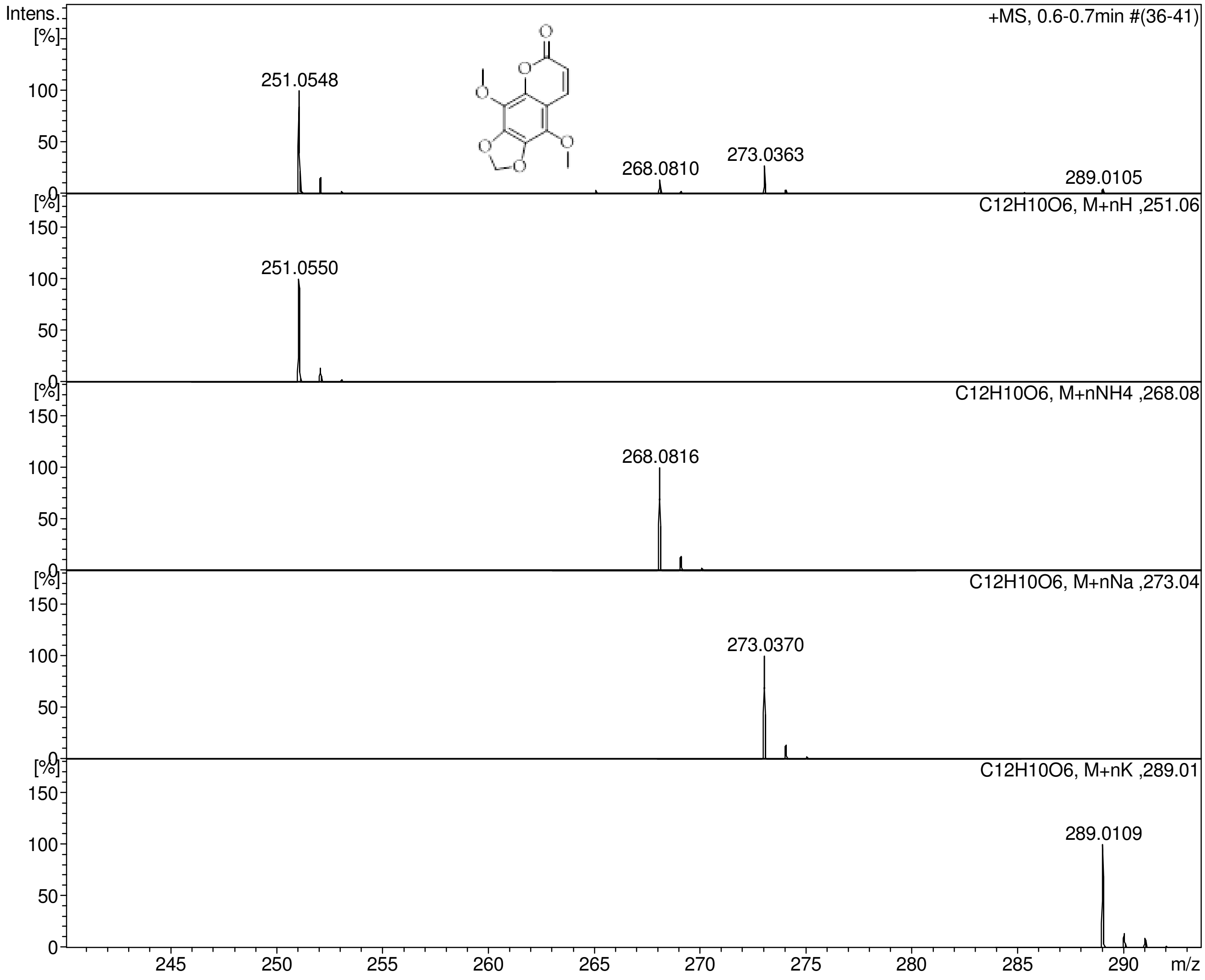

Figure S11. ^{1}H NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

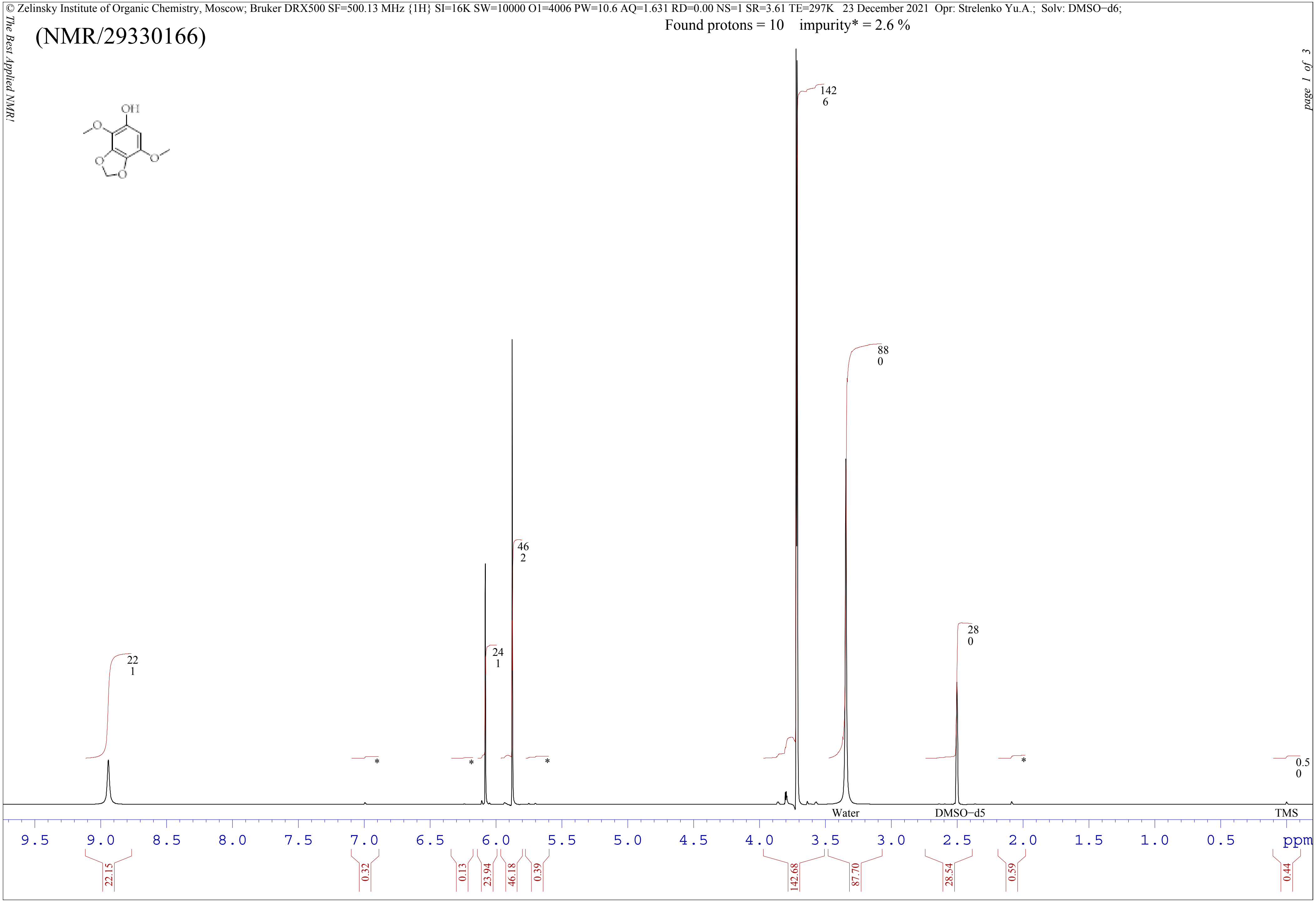

Figure S11. ^{1}H NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

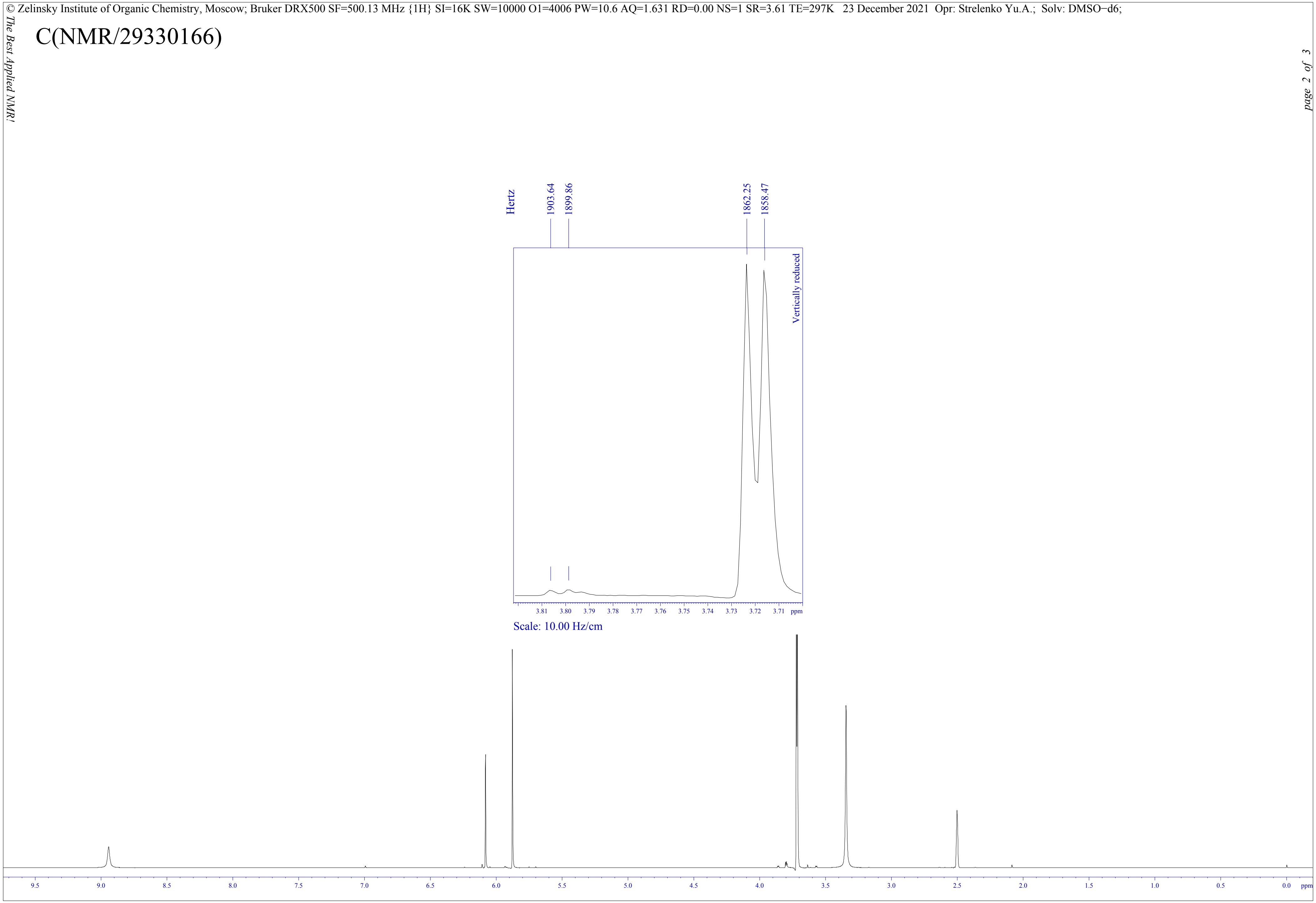

Figure S11. ^{1}H NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker DRX500 SF=500.13 MHz {1H} SI=16K SW=10000 O1=4006 PW=10.6 AQ=1.631 RD=0.00 NS=1 SR=3.61 TE=297K 23 December 2021 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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(NMR/29330166)

```
                          Peaks  List

#     Address           Frequency          Intensity
     [points]         [Hz]         [ppm]        [cm]
1      7421.6     4472.413        8.9425        0.94
2      9765.8     3041.657        6.0817        5.10
3      9933.5     2939.296        5.8771       10.17
4     11630.3     1903.636        3.8063        0.26
5     11636.5     1899.862        3.7987        0.28
6     11698.1     1862.249        3.7235       15.97
7     11704.3     1858.469        3.7160       16.00
8     12007.2     1673.619        3.3464        7.26
9     12697.4     1252.361        2.5041        2.60
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Figure S12. ^{13}C NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

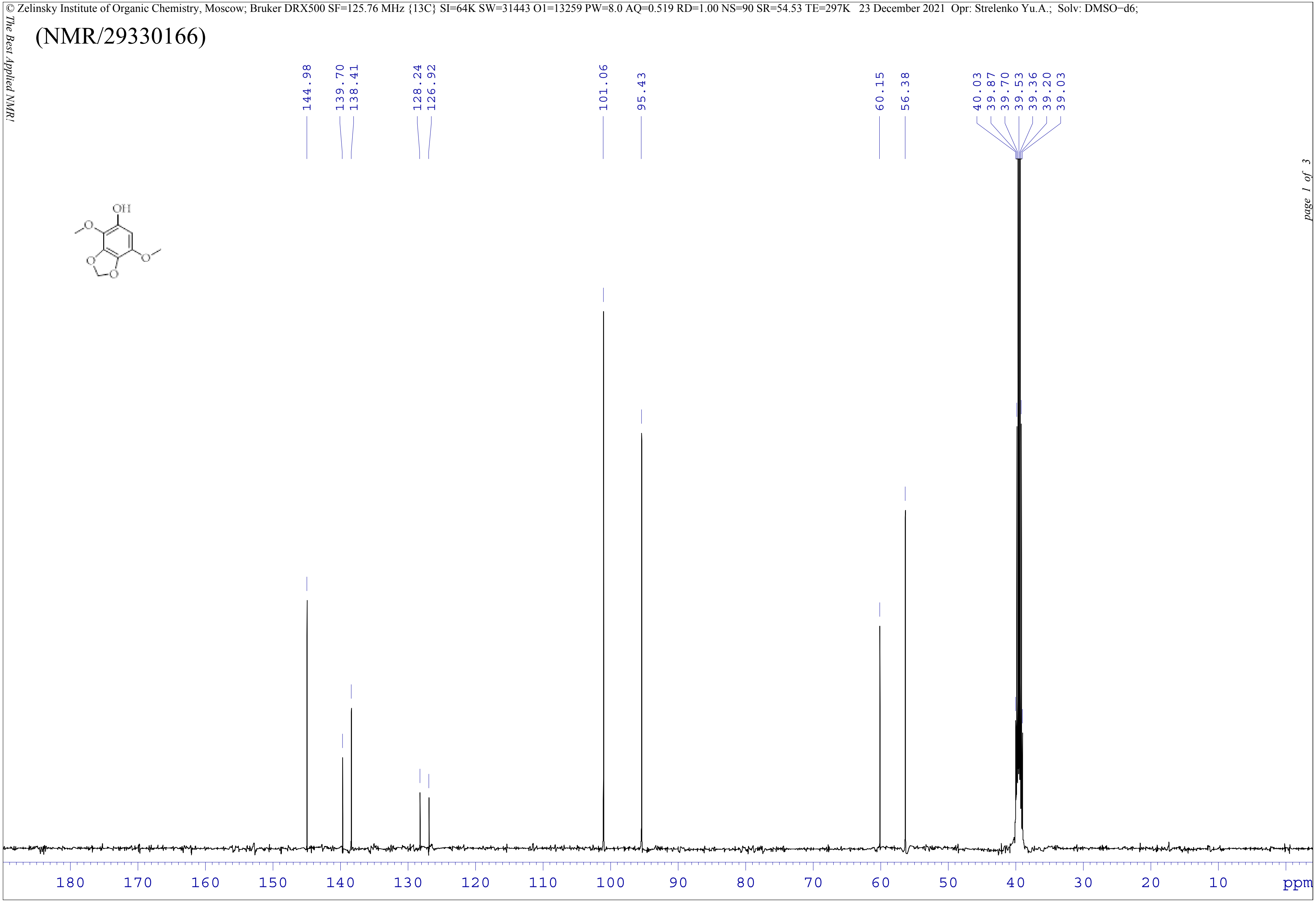

Figure S12. ^{13}C NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

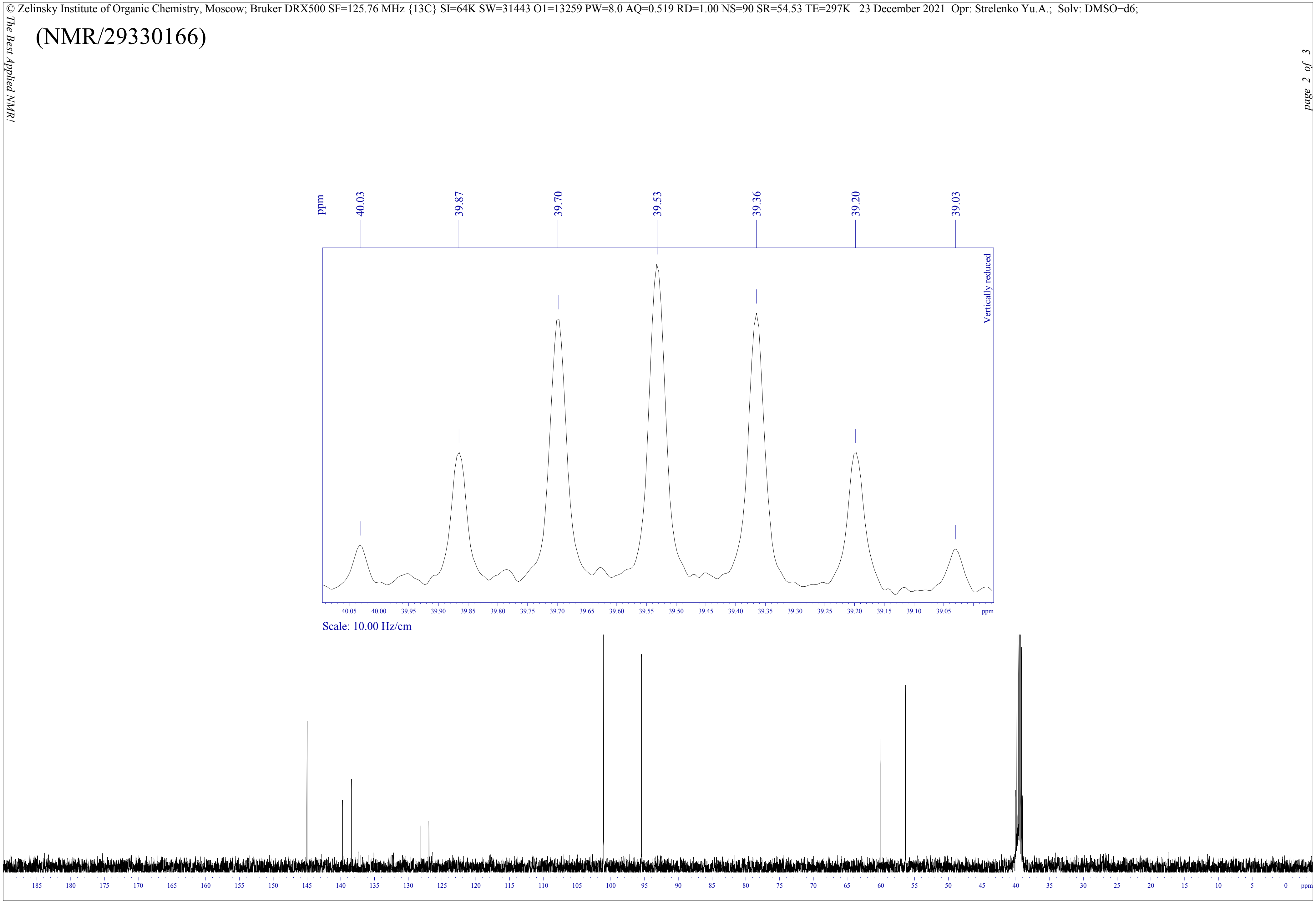

Figure S12. ^{13}C NMR spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker DRX500 SF=125.76 MHz {13C} SI=64K SW=31443 O1=13259 PW=8.0 AQ=0.519 RD=1.00 NS=90 SR=54.53 TE=297K 23 December 2021 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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                         Peaks  List

 #     Address            Frequency          Intensity
      [points]         [Hz]         [ppm]         [cm]
 1     22289.0    18232.764     144.9831          6.58
 2     23672.8    17568.809     139.7035          3.07
 3     24011.4    17406.305     138.4113          4.08
 4     26678.0    16126.793     128.2369          2.28
 5     27021.8    15961.798     126.9249          2.12
 6     33799.6    12709.579     101.0639         12.78
 7     35276.5    12000.894      95.4286          9.65
 8     44523.1     7564.057      60.1478          5.77
 9     45510.2     7090.404      56.3814          8.21
10     49795.3     5034.281      40.0315          3.51
11     49838.8     5013.381      39.8654          9.93
12     49882.6     4992.392      39.6985         19.32
13     49926.2     4971.446      39.5319         23.00
14     49970.0     4950.450      39.3649         19.56
15     50013.7     4929.483      39.1982          9.95
16     50057.8     4908.318      39.0299          3.25
```

Figure S13. Mass spectrum of 4,7-dimethoxybenzo[d][1,3]dioxol-5-ol **(6)**.

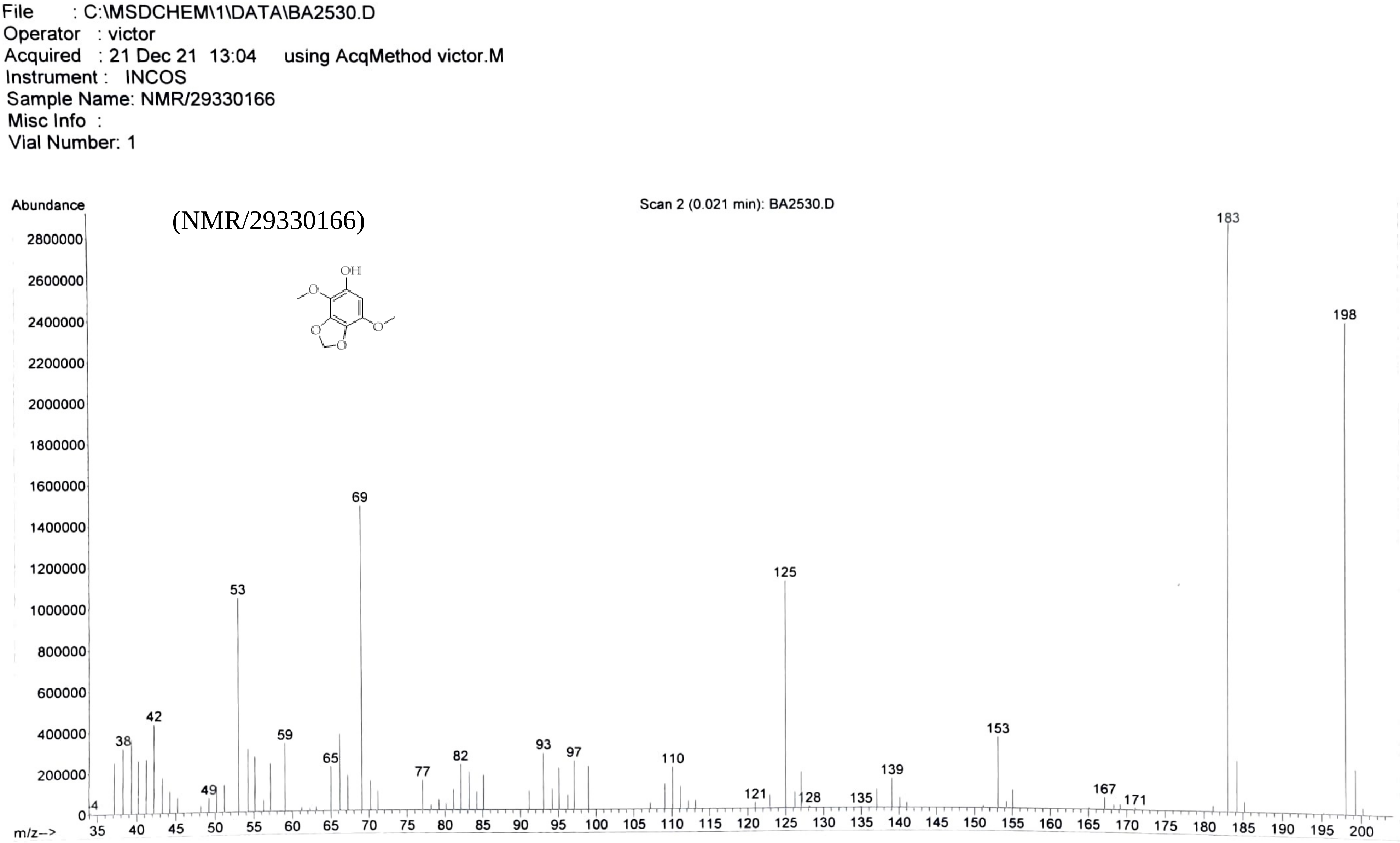

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Figure S14. ^{1}H NMR spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

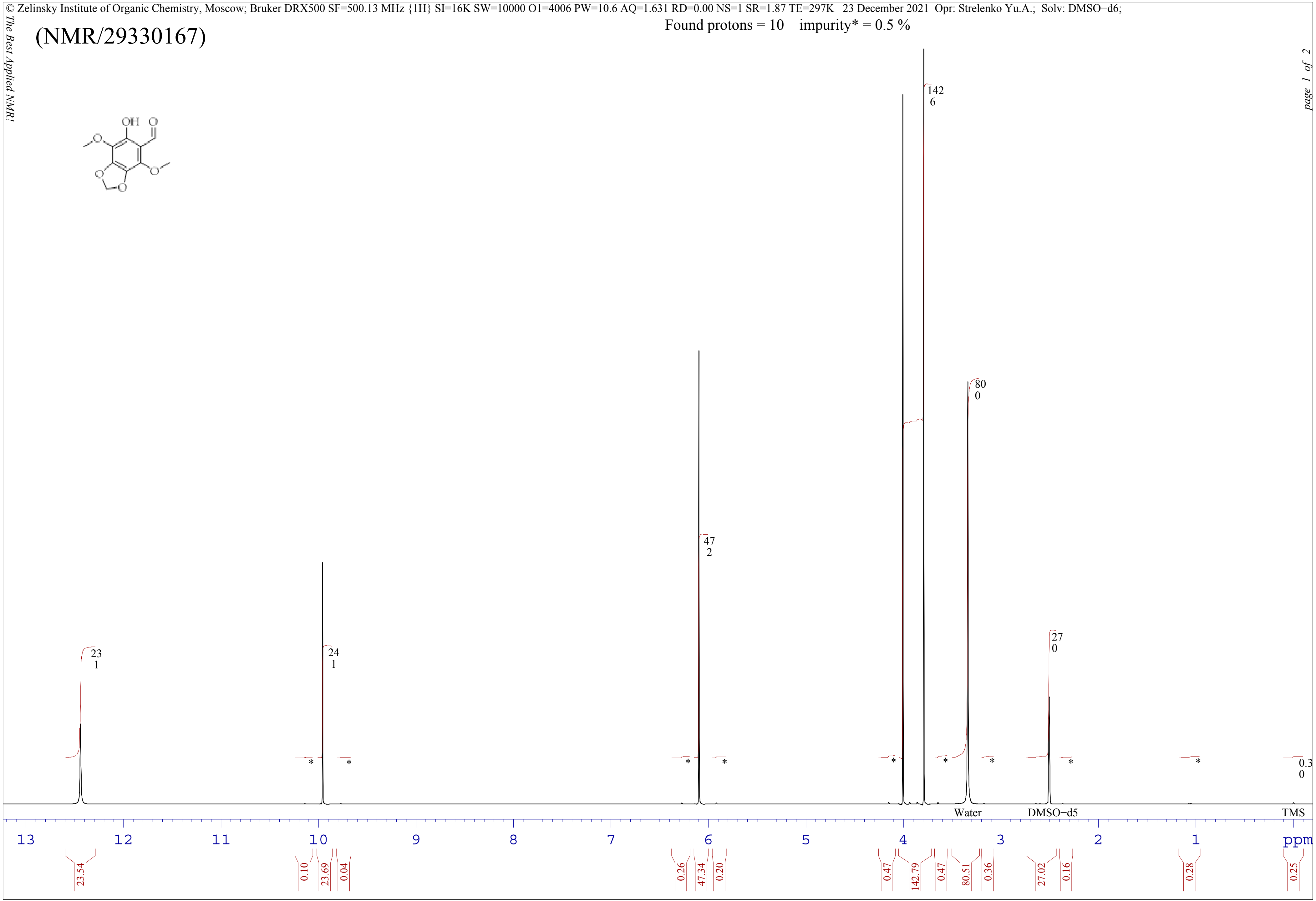

Figure S14. ^{1}H NMR spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker DRX500 SF=500.13 MHz {1H} SI=16K SW=10000 O1=4006 PW=10.6 AQ=1.631 RD=0.00 NS=1 SR=1.87 TE=297K 23 December 2021 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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```
                              Peaks  List

 #     Address             Frequency            Intensity
      [points]          [Hz]          [ppm]          [cm]
 1       4557.7     6222.117      12.4410          1.70
 2       6592.6     4980.132       9.9577          5.26
 3       9753.4     3050.934       6.1003          9.88
 4      11467.6     2004.708       4.0084         15.58
 5      11642.9     1897.668       3.7943         16.00
 6      12013.9     1671.272       3.3417          8.94
 7      12697.7     1253.902       2.5072          2.28
```

Figure S15. ^{13}C NMR spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

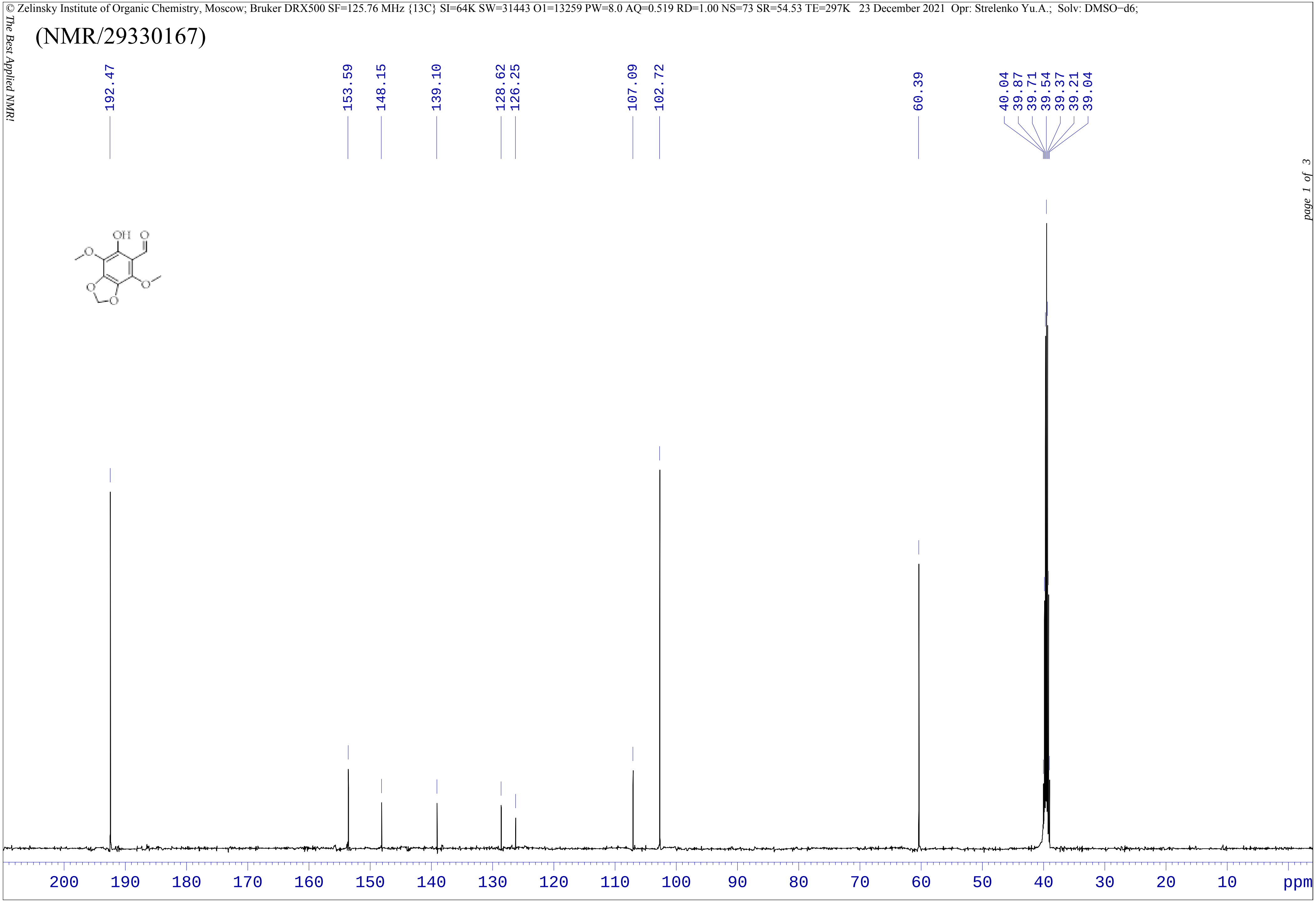

Figure S15. ^{13}C NMR spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

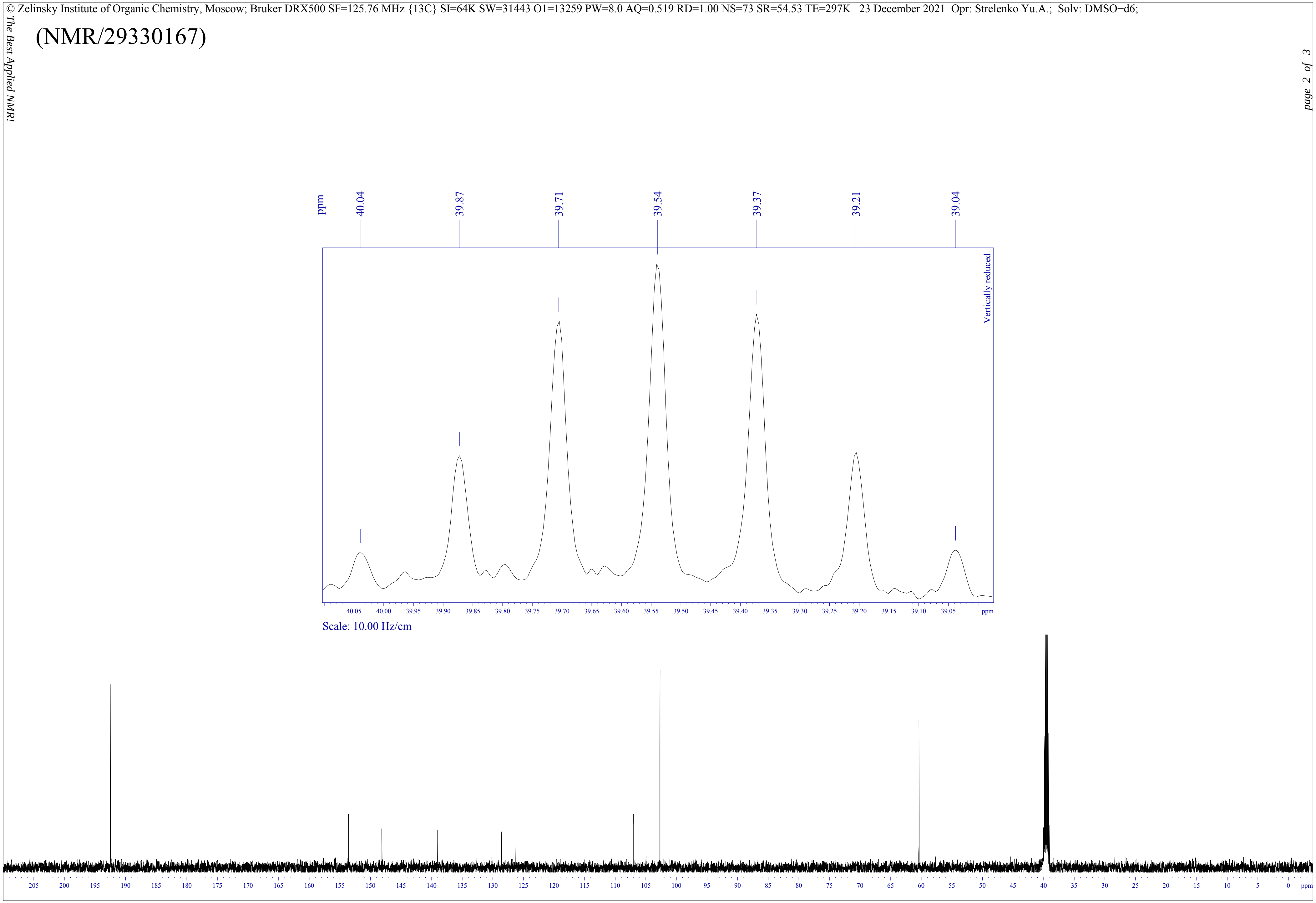

Figure S15. ^{13}C NMR spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

© Zelinsky Institute of Organic Chemistry, Moscow; Bruker DRX500 SF=125.76 MHz {13C} SI=64K SW=31443 O1=13259 PW=8.0 AQ=0.519 RD=1.00 NS=73 SR=54.53 TE=297K 23 December 2021 Opr: Strelenko Yu.A.; Solv: DMSO−d6;

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(NMR/29330167)

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                    Peaks  List

 #     Address          Frequency          Intensity
      [points]         [Hz]       [ppm]         [cm]
 1      9844.3    24204.211    192.4668         8.23
 2     20033.6    19314.982    153.5887         2.46
 3     21458.9    18631.117    148.1507         1.76
 4     23831.7    17492.516    139.0968         1.70
 5     26577.0    16175.236    128.6221         1.62
 6     27198.4    15877.059    126.2510         1.31
 7     32221.3    13466.914    107.0861         2.42
 8     33364.9    12918.153    102.7224         8.89
 9     44459.5     7594.566     60.3904         6.75
10     49793.2     5035.271     40.0394         1.82
11     49836.9     5014.294     39.8726         5.88
12     49880.7     4993.275     39.7055        11.58
13     49924.3     4972.363     39.5392        14.00
14     49968.1     4951.357     39.3722        11.84
15     50011.8     4930.387     39.2054         6.04
16     50055.7     4909.337     39.0380         1.92
```

Figure S16. Mass spectrum of 6-hydroxy-4,7-dimethoxybenzo[d][1,3]dioxole-5-carbaldehyde **(7)**.

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