Electronic Supplementary Information for

Self-assembly of Iodoacetylenyl-substituted Nitronyl Nitroxides via Halogen Bonding

Matvey K. Shurikov,[a] Evgeny V. Tretyakov,*[b] Pavel V. Petunin,*[a] Darya E. Votkina,[a] Galina V. Romanenko,[c] Artem S. Bogomyakov,[c] Sergi Burguera,[d] Antonio Frontera,[d] Vadim Yu. Kukushkin,[e] Pavel S. Postnikov[a]

a M. K. Shurikov, Dr. P. V. Petunin, D. E. Votkina, Prof. Dr. P. S. Postnikov
Research School of Chemistry & Applied Biomedical Sciences
Tomsk Polytechnic University
Lenin Av. 30, Tomsk 634050, Russian Federation
E-mail: petuninpavel@tpu.ru

b Prof. Dr. E. V. Tretyakov
N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences
Leninsky Av. 47, Moscow 119991, Russian Federation
E-mail: tretyakov@ioc.ac.ru

c Prof. Dr. G. V. Romanenko, Dr. A. S. Bogomyakov
International Tomography Center, Siberian Branch of Russian Academy of Sciences
Institutskaya Str. 3a, Novosibirsk 630090, Russian Federation

d S. Burguera, Prof. Dr. A. Frontera
Departament de Química
Universitat de les Illes Balears
Crta de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain

e Prof. Dr. V. Yu. Kukushkin
Institute of Chemistry
Saint Petersburg State University
Universitetskaya Nab. 7/9, Saint Petersburg 199034, Russian Federation

Table of content

Section S1. A CSD search for self-assembled halogenated nitroxides

A search in the Cambridge Structural Database revealed a series of halogen-substituted nitroxides, whose XRD structures featuring C−Hal···O_{NO} short contacts. In 2-chloro-5-fluorophenyl-substituted benzimidazol-l-yl *N*,*N*'-dioxide (**I**), the assembly led to occurrence of centrosymmetric dimers exhibiting Cl···O XB (3.155 Å, Nc = 0.96) (**Figure 1**; see figure legend for the definition of Nc).[1]

Crystal structure analysis of different type of brominated nitroxides (**II**–**V**) reveled infinite 1D-chains halogen-bonded by C−Br···O_{NO} contacts (Nc < 1; **Figure 1**).[2–5] Notably, very short C−Br···O_{NO} contacts (2.809 Å; Σ_{vdW} = 3.37 Å) were found in crystals of hybrid phenoxyl-nitroxide radical (**II**).[5] A special case is the solid-sate structure of dibromo-derivative (**VI**), which is assembled by NCIs (3.034 Å) of a nitroxide O-atom with Br-atoms of different radicals; this assembly leads to occurrence of 2D-layered architectures.[6] Moreover, in crystals of dibrominated benzo-TTF bearing nitronyl nitroxide (**VII**), the molecules are arranged in a square-like manner by Br···S intermolecular contacts (approx. 3.6 Å) between one of the Br-atoms and a S-atom of the benzodithiole ring; each remaining Br forms a very short contact (2.901 Å) with the nitroxide O-atom from a neighboring molecule.[7]

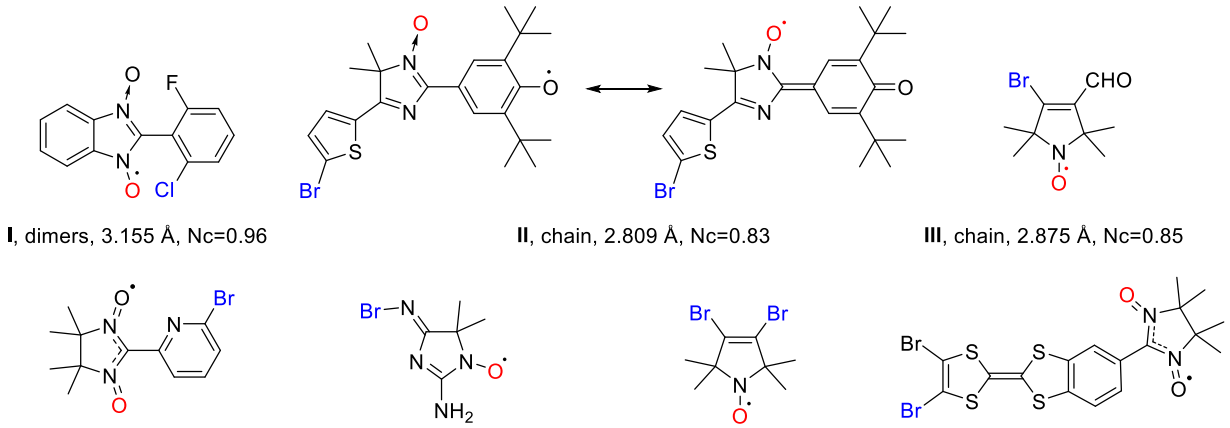

Figure S1. Halogen-substituted nitroxides **I**–**VII** of different types assembled by C−Hal···O_{NO} short contacts (interacted atoms are colored; motif of packing in crystals based on C−X···O_{NO} short contacts as well as X···O distances are indicated). The "normalized contact" Nc for interacted atoms i and j is defined as the ratio Dij/(rvdW,i + rvdW,j) wherein Dij is the experimentally determined distance between atoms i and j and rvdW,i and rvdW,j are Bondi[8] van der Waals radii of i and j.

In the crystal state, iodo-substituted nitroxides are prone to form XBs between nitroxide O-atoms and halogen sites to give, in most cases, 1D-chains, in which I···O_{NO} distances are considerably shorter than Σ_{vdW} (3.50 Å; **Figure 2**).[9–11] In crystals of triiodo-derivative **XI**, we observed short intermolecular contacts of two types, I···O_{NO} and I···O_{CO}, that assemble the structure in 2D-layers.[12] Finally, 2-chloro, 2-bromo, and 2-iodo nitronyl nitroxides **XIV**–**XVI** give isomorphous crystal structures consisting of chains linked by Hal···O_{NO} XB (**Figure 2**).[13–15]

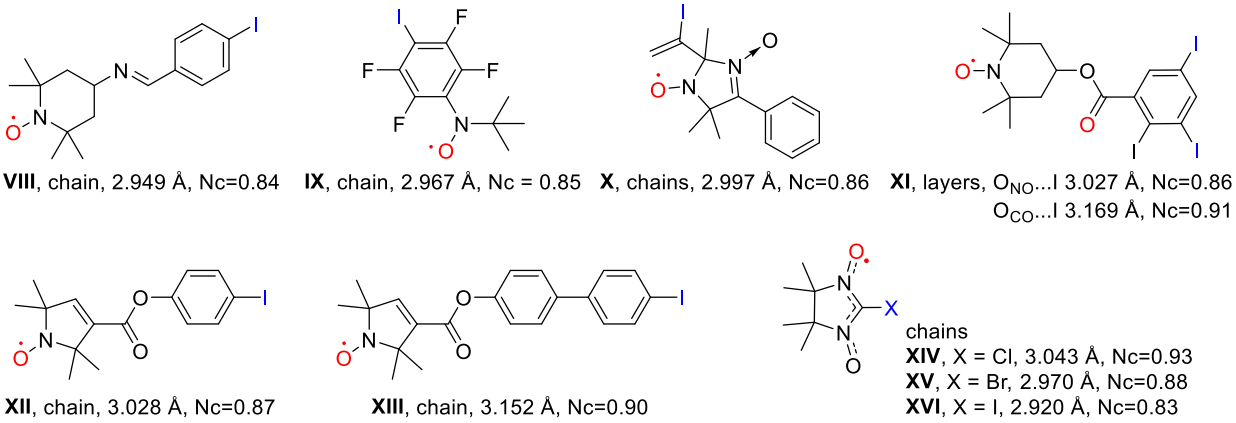

Figure S2. Iodo-substituted nitroxides **VIII**–**XVI** featuring I···O_{NO} short contacts (interacted atoms are colored; motif of packing of radicals in crystals based on C–X···O_{NO} short contacts; X···O distances are indicated).

References:

1 A. Zakrassov, V. Shteiman, Y. Sheynin, B. Tumanskii, M. Botoshansky, M. Kapon, A. Keren, M. Kaftory, T. E. Vos and J. S. Miller, *J. Mater. Chem.*, 2004, **14**, 1827–1837.

2 M. A. Hollas, S. J. Webb, S. L. Flitsch and A. J. Fielding, *Angew. Chemie - Int. Ed.*, 2017, **56**, 9449–9453.

3 F. M. Romero, R. Ziessel, A. De Cian, J. Fischer and P. Turek, *New J. Chem.*, 1996, **20**, 919–924.

4 E. V. Tretyakov, A. S. Bogomyakov, E. Y. Fursova, G. V. Romanenko, V. N. Ikorskii and V. I. Ovcharenko, *Russ. Chem. Bull.*, 2006, **55**, 457–463.

5 E. Zaytseva, D. Shiomi, Y. Ten, Y. V. Gatilov, A. Lomanovich, D. Stass, A. Bogomyakov, A. Yu, K. Sugisaki, K. Sato, T. Takui, E. Bagryanskaya and D. Mazhukin, *J. Phys. Chem. A*, 2020, **124**, 2416–2426.

6 J. M. White and R. Chowdury, *CCDC structrure No. 1960256 NOTWOL*, DOI:10.5517/ccdc.csd.cc23st2t.

7 H. Komatsu, M. M. Matsushita, S. Yamamura, Y. Sugawara, K. Suzuki and T. Sugawara, *J. Am. Chem. Soc.*, 2010, **132**, 4528–4529.

8 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.

9 F. Iwasaki, J. H. Yoshikawa, H. Yamamoto, E. Kan-nari, K. Takada, M. Yasui, T. Ishida and T. Nogami, *Acta Crystallogr. Sect. B Struct. Sci.*, 1999, **55**, 231–245.

10 L. V. Politanskaya, P. A. Fedyushin, T. V. Rybalova, A. S. Bogomyakov, N. B. Asanbaeva and E. V. Tretyakov, *Molecules*, 2020, **25**, 5427.

11 L. G. Kuz'mina and Y. T. Struchkov, *J. Struct. Chem.*, 1987, **27**, 760–766.

12 T. Hauenschild, J. Reichenwallner, V. Enkelmann and D. Hinderberger, *Chem. - A Eur. J.*, 2016, **22**, 12825–12838.

13 E. V Tretyakov and V. I. Ovcharenko, *Russ. Chem. Rev.*, 2009, **78**, 971–1012.

14 Y. Hosokoshi, M. Tamura, K. Nozawa, S. Suzuki, M. Kinoshita, H. Sawa and R. Kato, *Synth. Met.*, 1995, **71**, 1795–1796.

15 Z.-L. Liu, S. Ye and C. Du, *CCDC structrure No. 244384 TOLKOU01*, DOI:10.5517/cc869c3.

Section S2. Powder XRD data

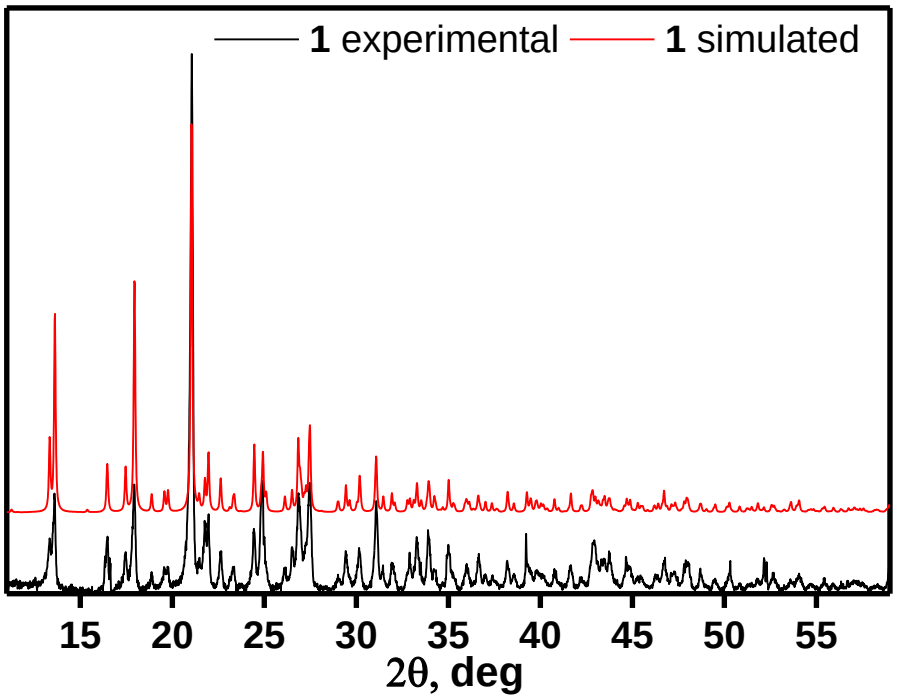

Figure S3. Experimental (black) and simulated (red) powder XRD pattern of nitroxide **1**.

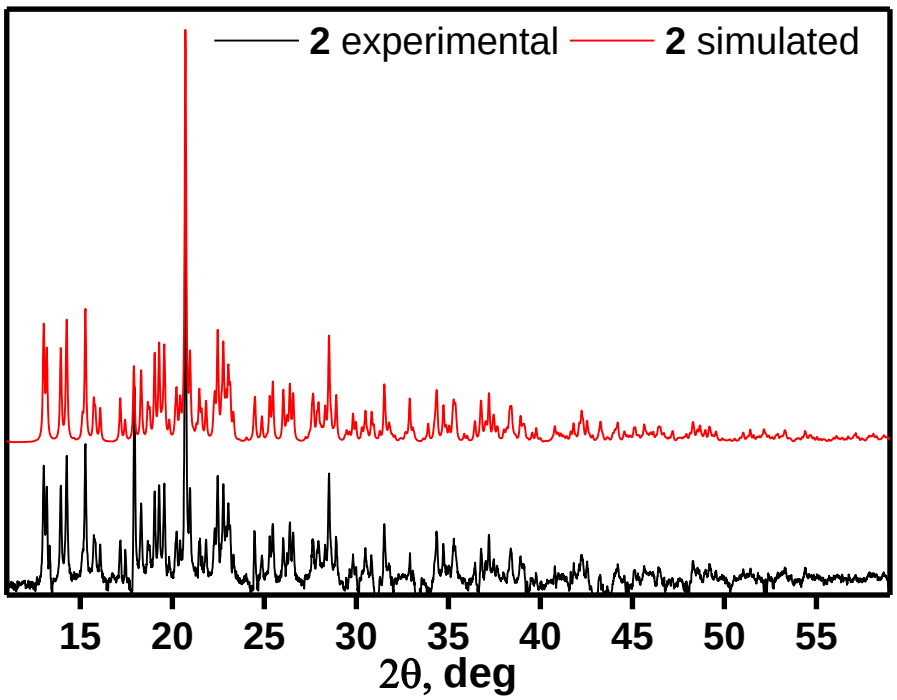

Figure S4. Experimental (black) and simulated (red) powder XRD pattern of nitroxide **2**.

Section S3. UV-Vis spectra

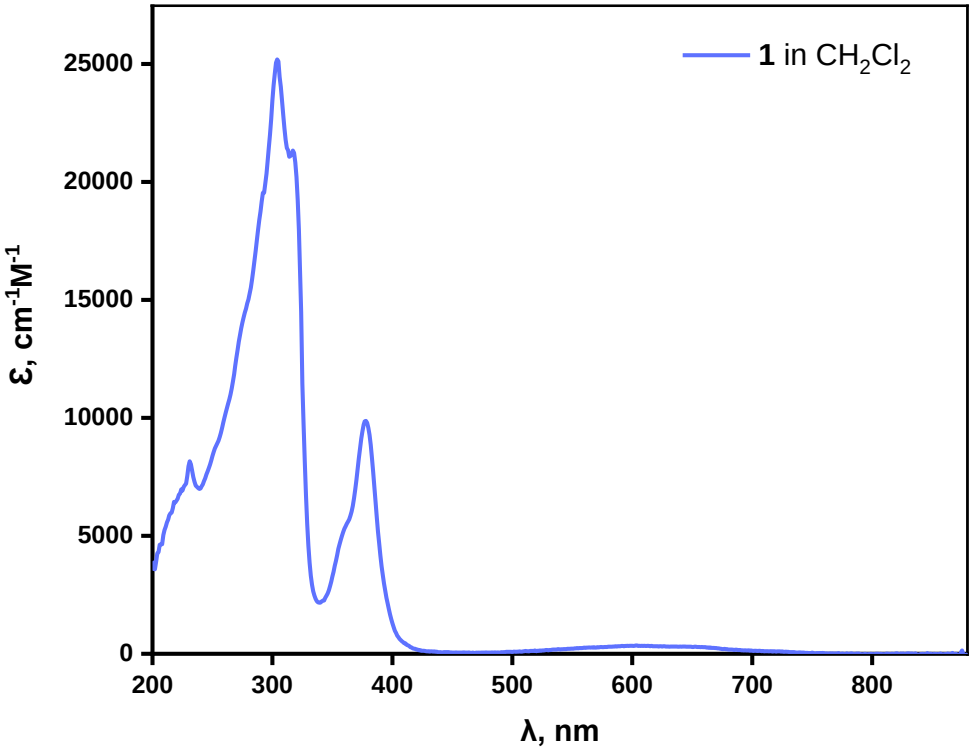

Figure S5. UV-Vis spectrum of **1** in CH_2Cl_2.

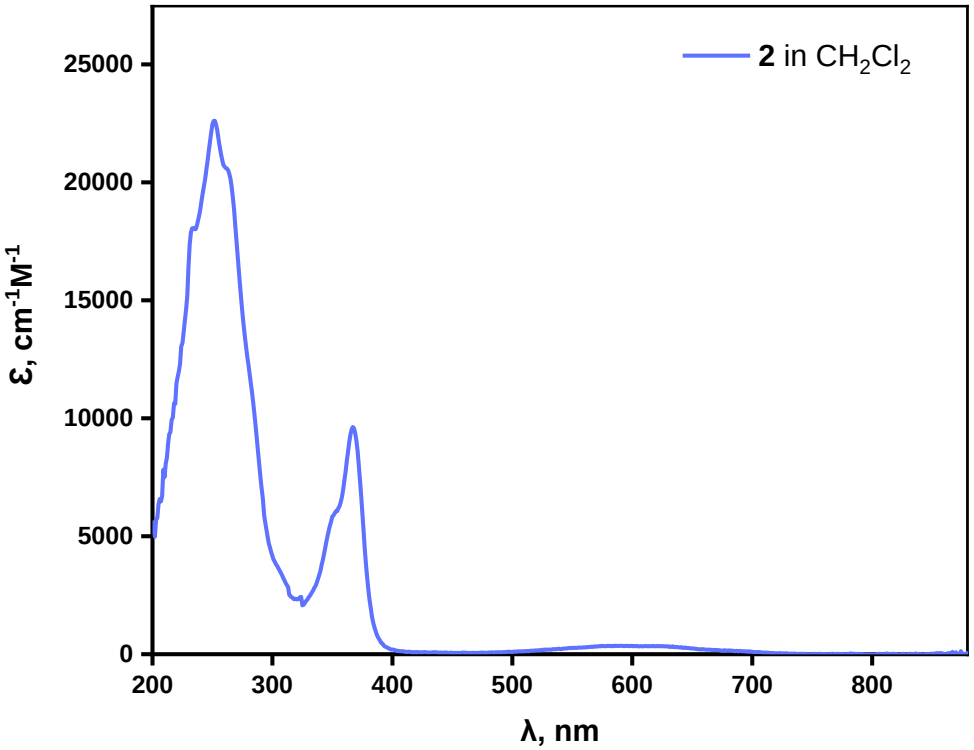

Figure S6. UV-Vis spectrum of **2** in CH_2Cl_2.

Section S4. CW EPR spectra

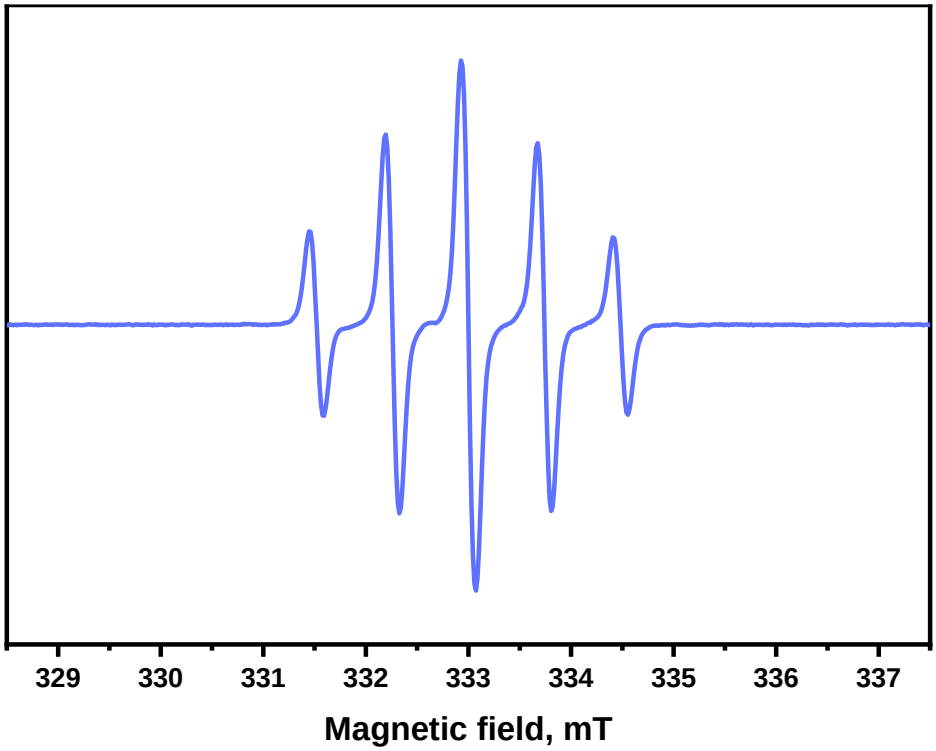

Figure 7. Experimental CW-ESR spectrum of **1** in deoxygenated toluene solution.

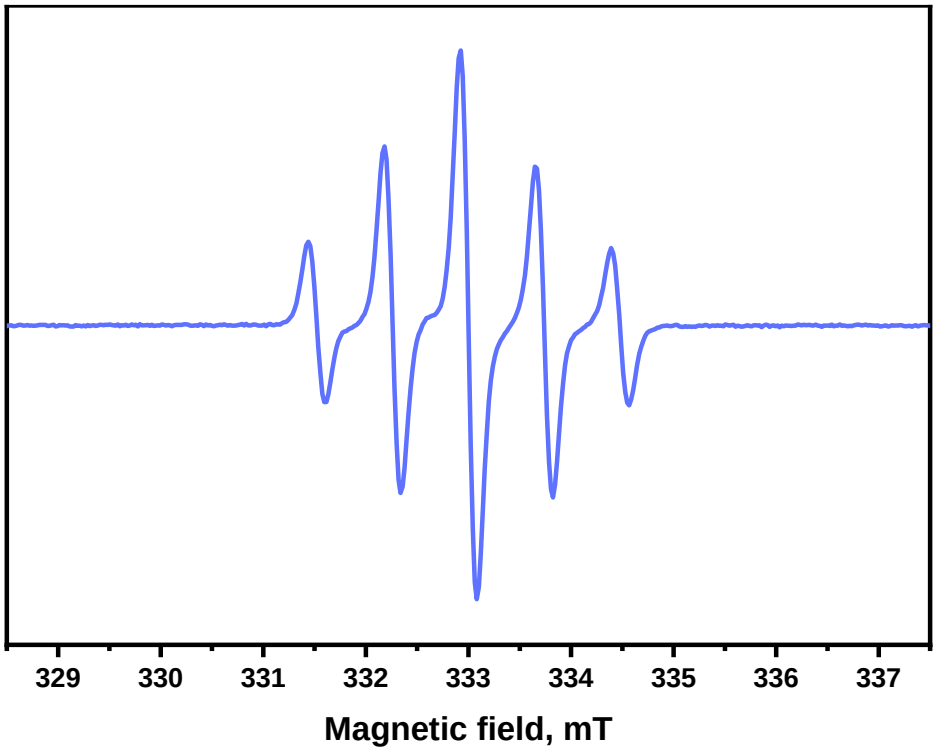

Figure S8. Experimental CW-ESR spectra of **2** in deoxygenated toluene solution.

Section S5. NMR spectra

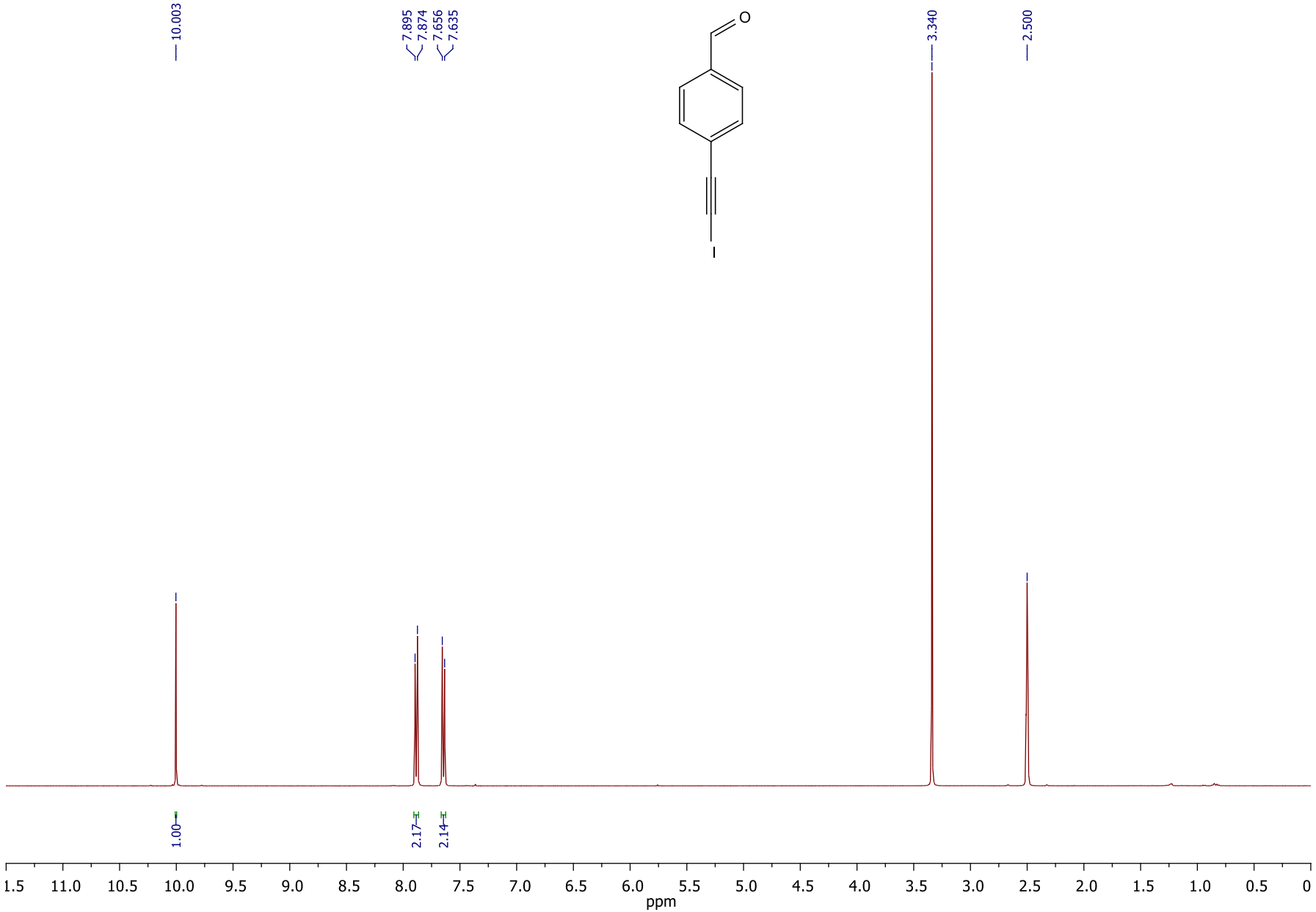

Figure S9. ^{1}H NMR spectrum (DMSO-d_6) of 4-(iodoethynyl)benzaldehyde (**7**).

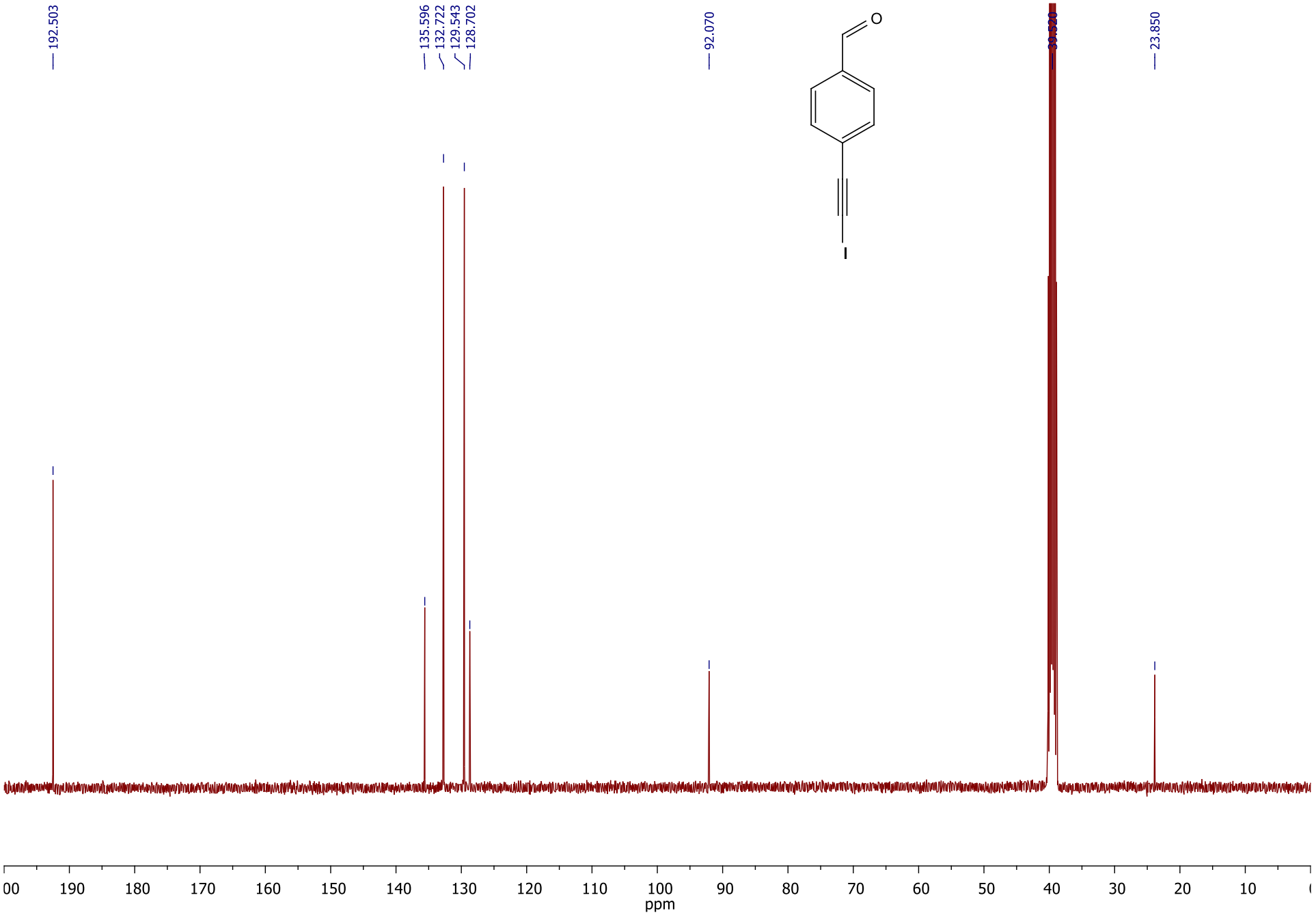

Figure S10. $^{13}C\{1H\}$ spectrum (DMSO-d_6) of 4-(iodoethynyl)benzaldehyde (**7**).

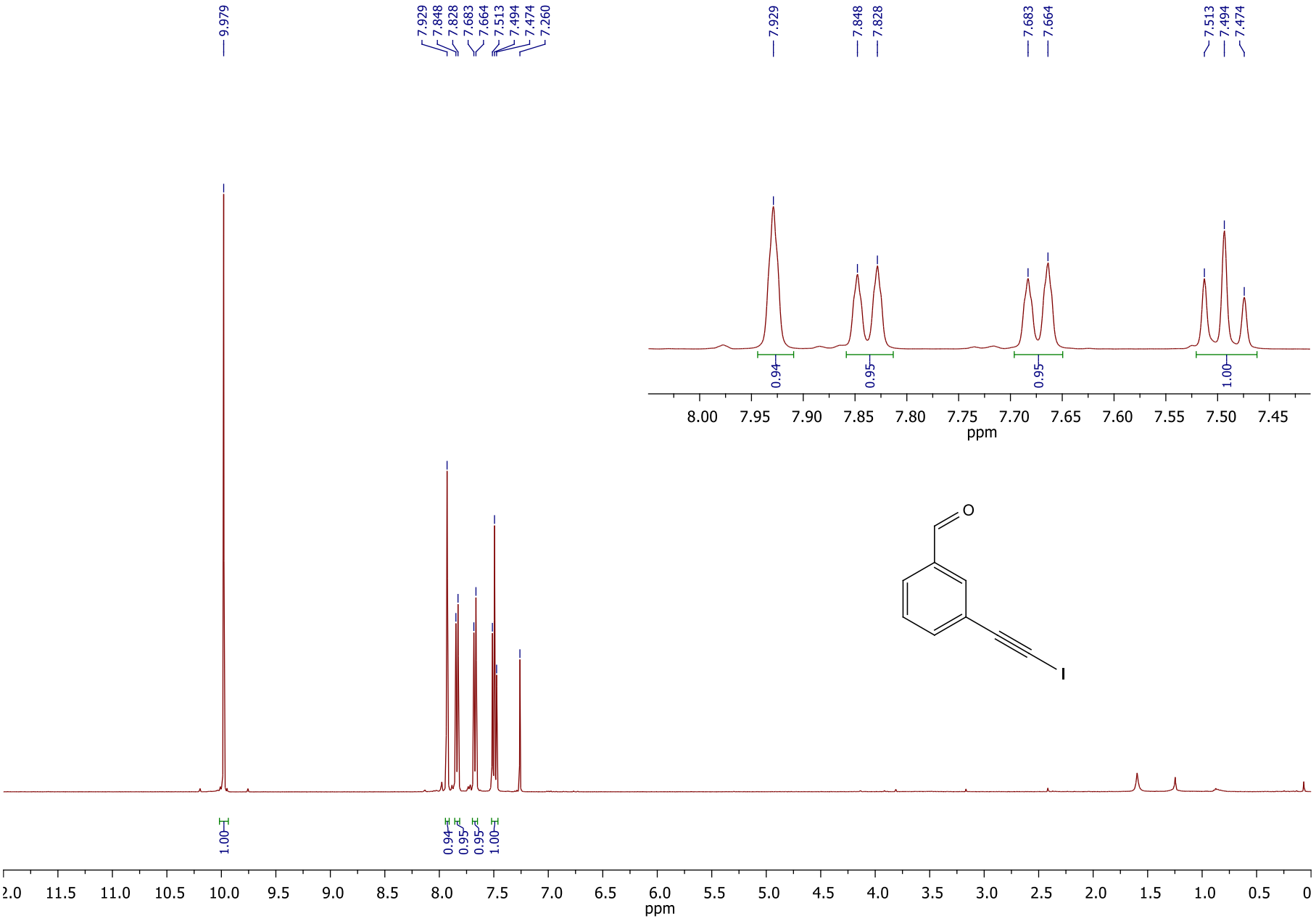

Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of 3-(iodoethynyl)benzaldehyde (**8**).

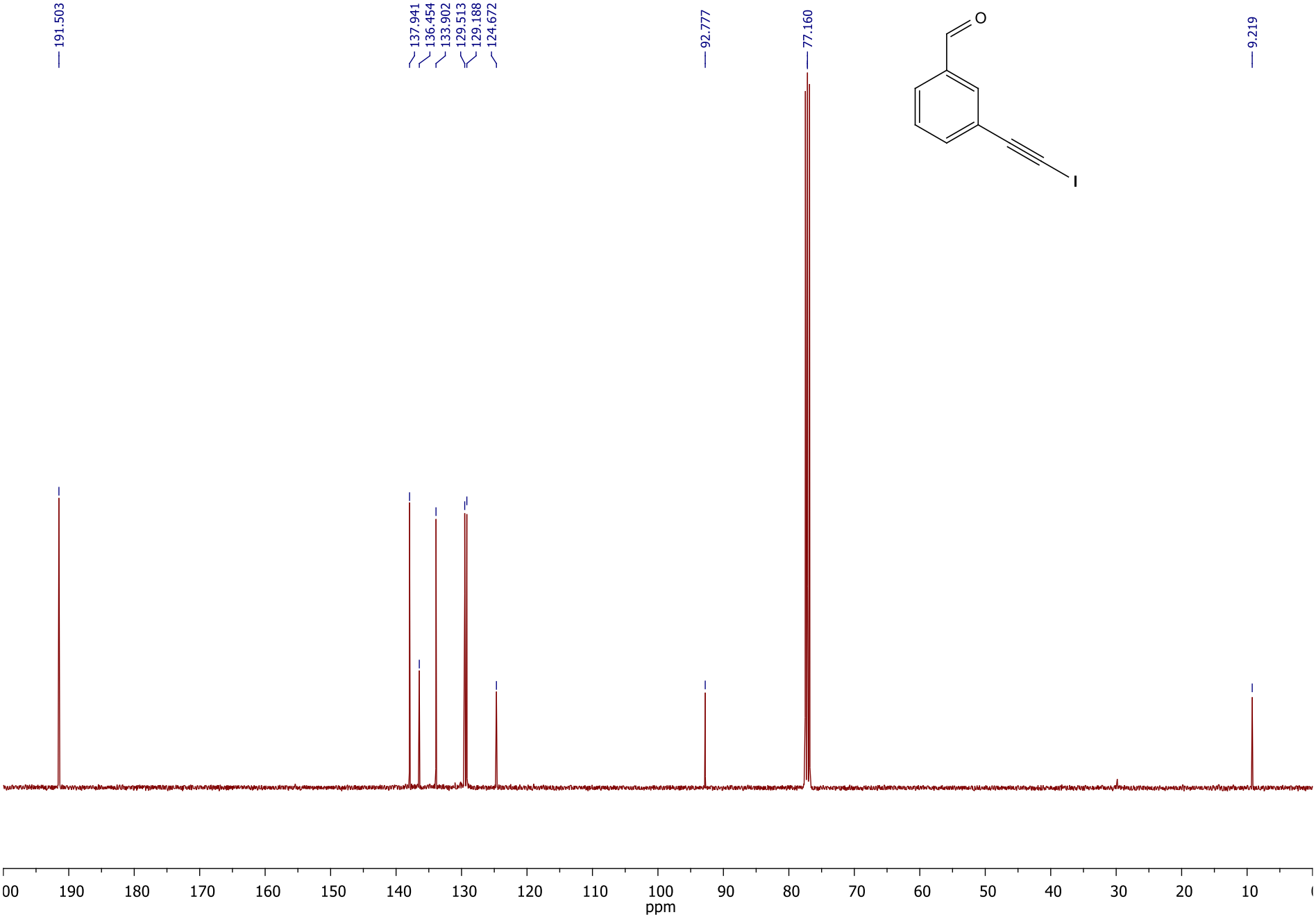

Figure S12. $^{13}C\{1H\}$ spectrum ($CDCl_3$) of 3-(iodoethynyl)benzaldehyde (**8**).

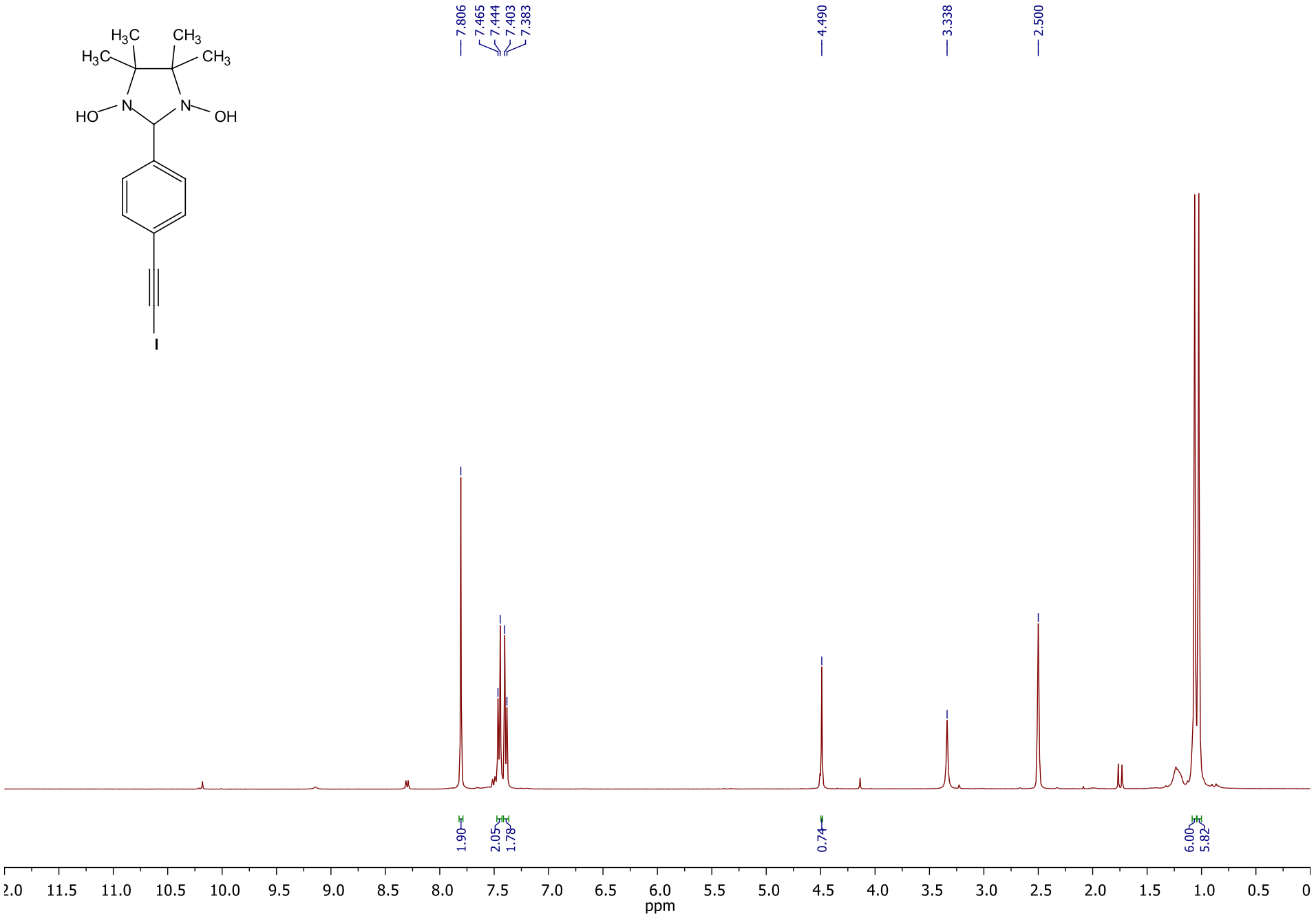

Figure S13. ^{1}H NMR spectrum (DMSO-d_6) of 2-(4-iodoethynyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (**9**).

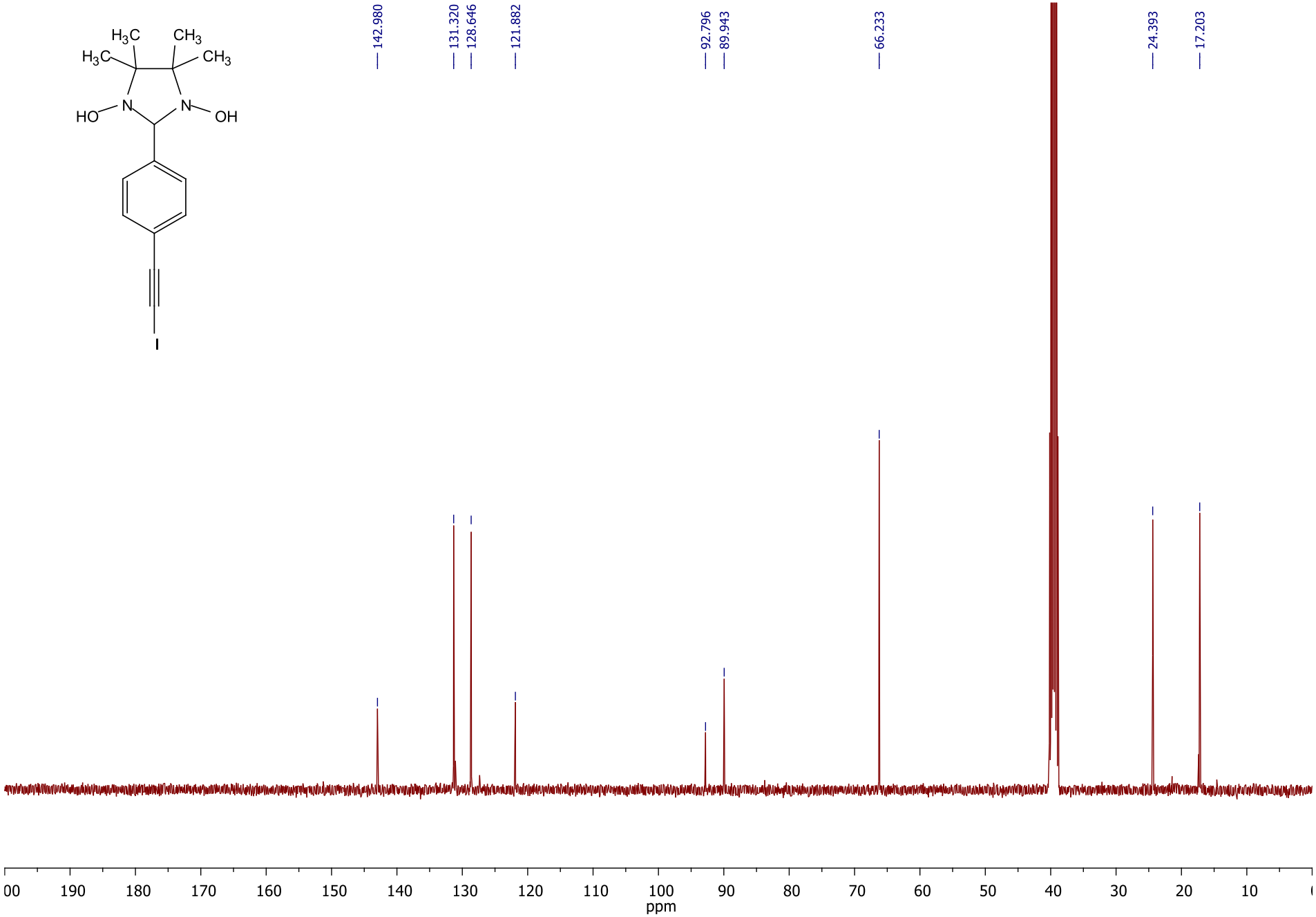

Figure S14. $^{13}C\{1H\}$ spectrum (DMSO-d_6) of 2-(4-iodoethynyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (**9**).

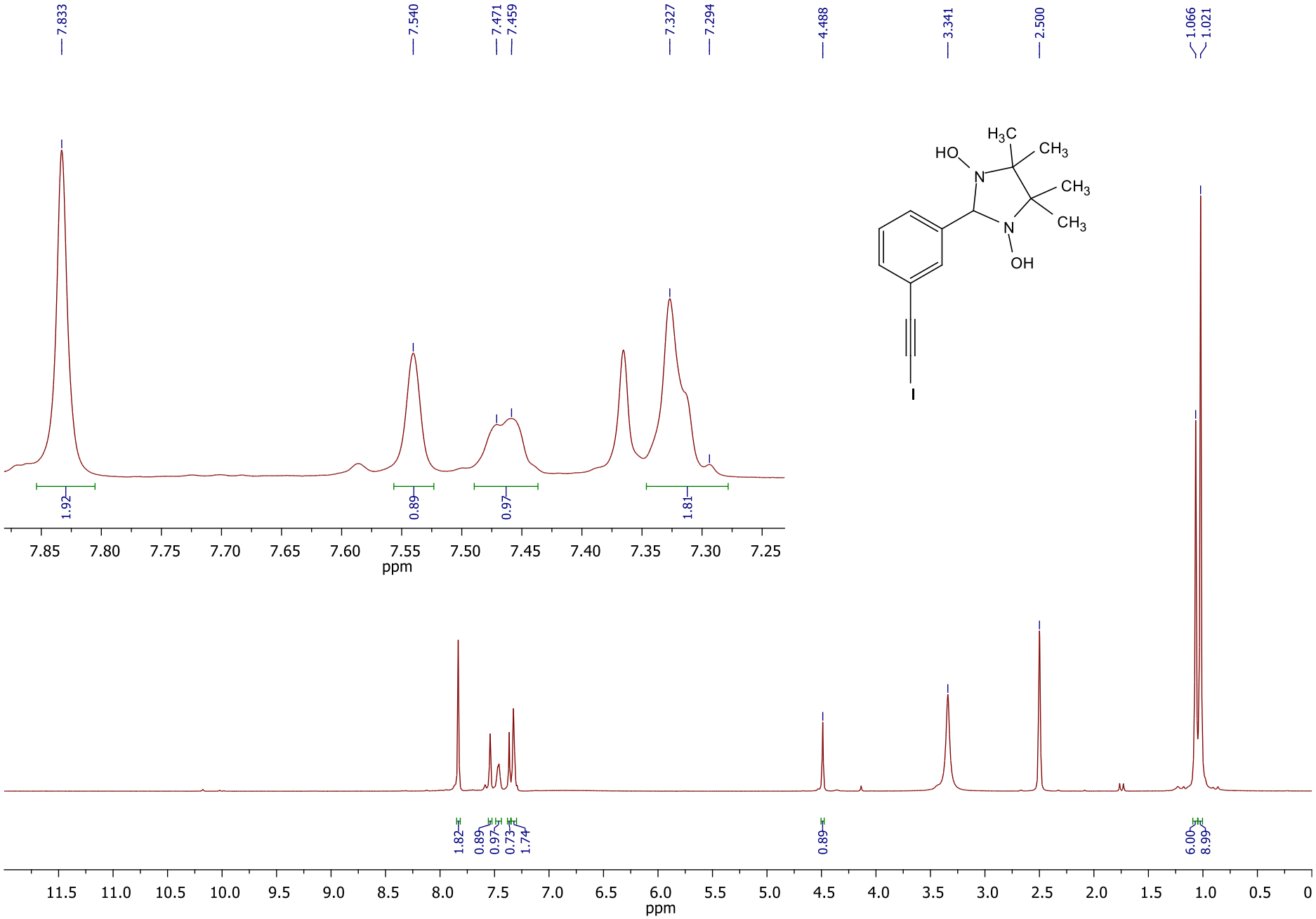

Figure S15. ^{1}H NMR spectrum (DMSO-d_6) of 2-(3-iodoethynyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (**10**).

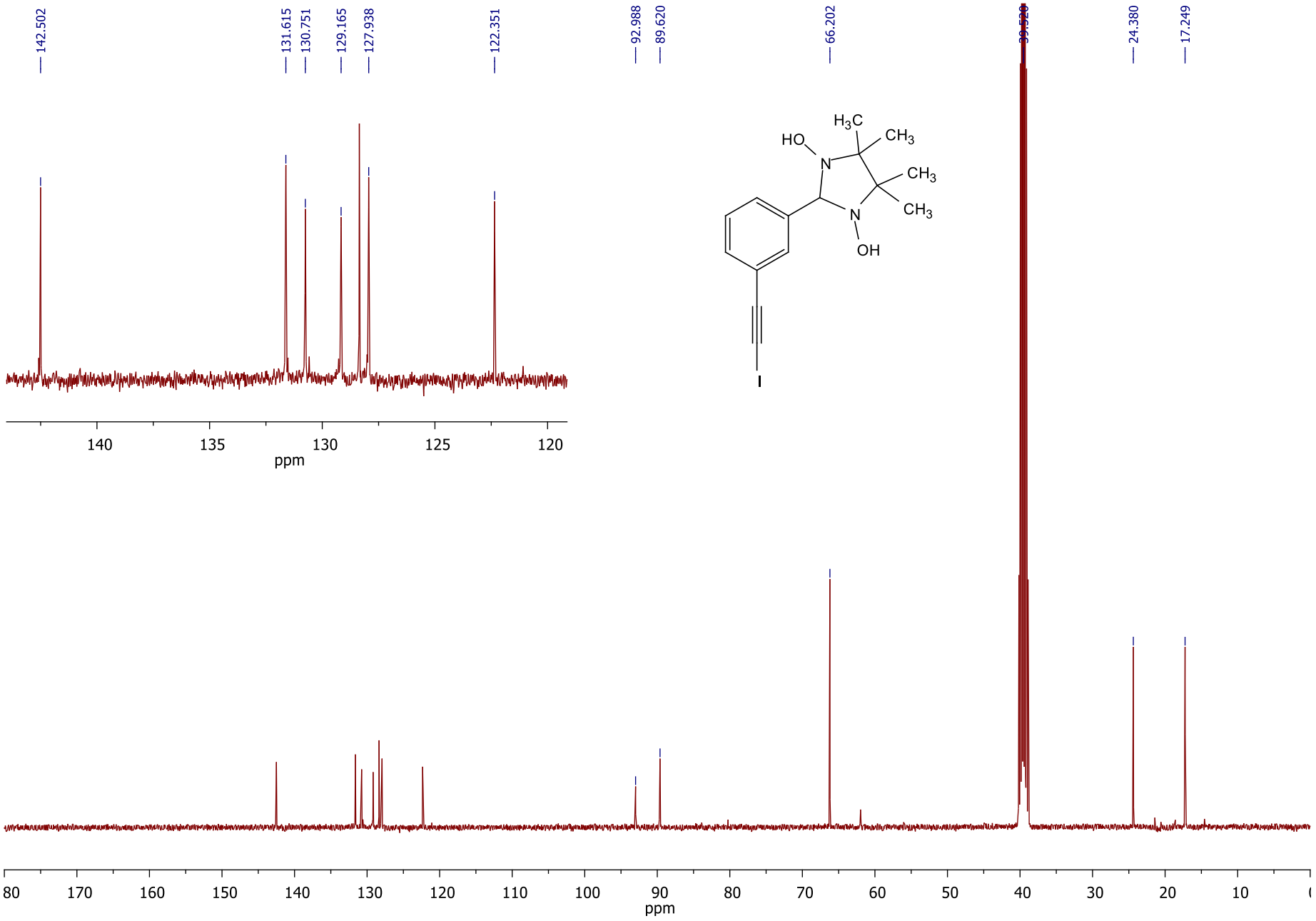

Figure S16. $^{13}C\{1H\}$ spectrum (DMSO-d_6) of 2-(3-iodoethynyl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (**10**).