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Diimidazo[4,5-*b*:4′,5′-*e*]pyridine: synthesis and nucleophilic aromatic substitution reaction

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X-ray experiments. X-ray diffraction experiments were performed: for **5** on a Bruker Smart Apex II diffractometer, and for **7a,b** on a Bruker Apex DUO diffractometer, both operating with MoKα radiation (λ = 0.71072 Å). Frames were integrated using the Bruker SAINT software package[S1] by a narrow-frame algorithm. A semiempirical absorption correction was applied with the SADABS[S2] program using the intensity data of the equivalent reflections. The structures were solved by direct methods with SHELXT program[S3] and refined by the full-matrix least-squares technique against F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms with SHELXL[S4] program. Hydrogen atoms connected to carbon atoms were placed in calculated positions and refined in the riding model with and Uiso(H)= 1.2Ueq(C). The structure **5** is pseudo-centrosymmetric, but there is no inversion center according to systematic absence violations. The structure **7a** contains a solvent/solvents, heavily disordered along channel-like voids. Possible solvents used in crystallization are: ethanol and water. The contribution of the solvent from the diffraction was removed with SQUEEZE method[S5]. The remaining formic acid solvate molecule in **7b** was found from difference Fourier synthesis and is disordered by two positions. The structure **7b** contains one acetic acid molecule in anionic form as well as two neutral acetic acid molecules. It was found that in the structure **7b** two different orientation of the pseudo-centrosymmetric dication overlaps and lie on the crystallographic inversion center (**Figure S4**). Hydrogen atoms connected to heteroatoms were found from difference Fourier synthesis in all cases and refined either in isotropic approximation or in the riding model. Detailed crystallographic information is given in **Table S1.**

References

[S1] SAINT (version 8.34A), Bruker AXS, Madison, Wisconsin, USA, 2014.
[S2] SADABS (version 2008/1), Bruker AXS, Madison, Wisconsin, USA, 2008.
[S3] G.M. Sheldrick, *Acta Crystallogr*., 2015, **A71**, 3.
[S4] G.M. Sheldrick, *Acta Crystallogr*., 2015, **C71**, 3.
[S5] A. L. Spek, *Acta Crystallogr*., 2015, **C71**, 9.

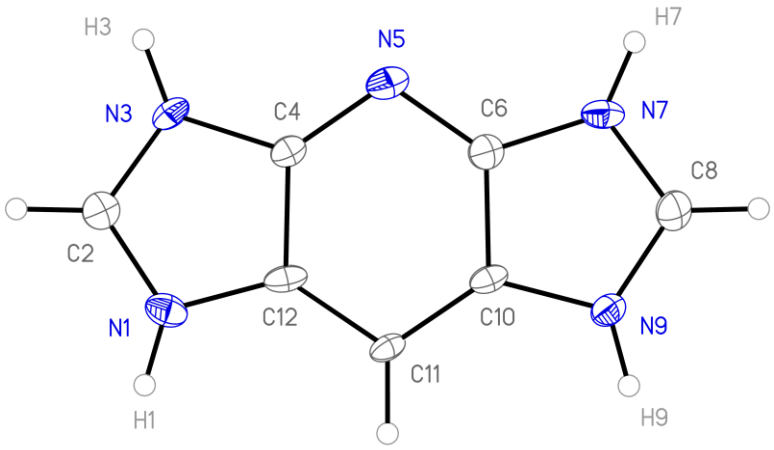
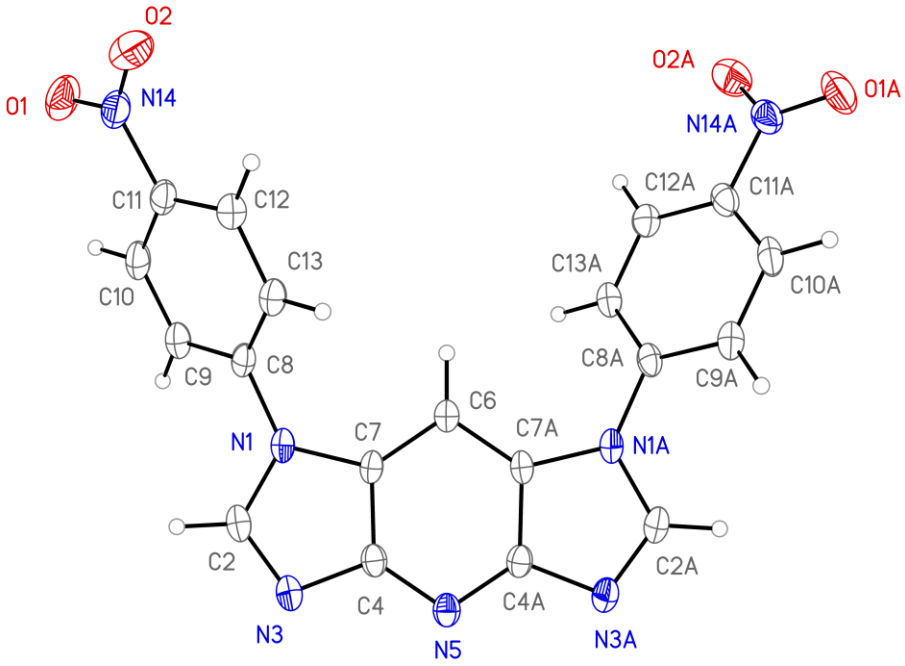


Figure S1. General view of the dication of DIP·2HCl (**5**) in thermal ellipsoid representation (p=50%). Chloride anions are omitted for clarity. Important bond lengths are: N1-C2 1.327(5), N1-C12 1.376(5), N3-C2 1.329(6), N3-C4 1.383(4), N5-C4 1.341(5), N5-C6 1.342(5), N7-C8 1.333(5), N7-C6 1.375(5), N9-C8 1.326(6), N9-C10 1.380(4), C4-C12 1.413(5), C6-C10 1.412(5), C10-C11 1.363(5), C11-C12 1.373(4) Å.



Firure S2. General view of the molecule 7**a** in thermal ellipsoid representation (p=50%). Solvate formic acid molecules are omitted for clarity. Important bond lengths are N1-C2 1.3627(15), N1-C7 1.3920(13), N1-C8 1.4222(15), N3-C2 1.3068(15), N3-C4 1.3887(14), N5-C4 1.3314(13), C4-C7 1.4126(16), C6-C7 1.3779(14) Å.

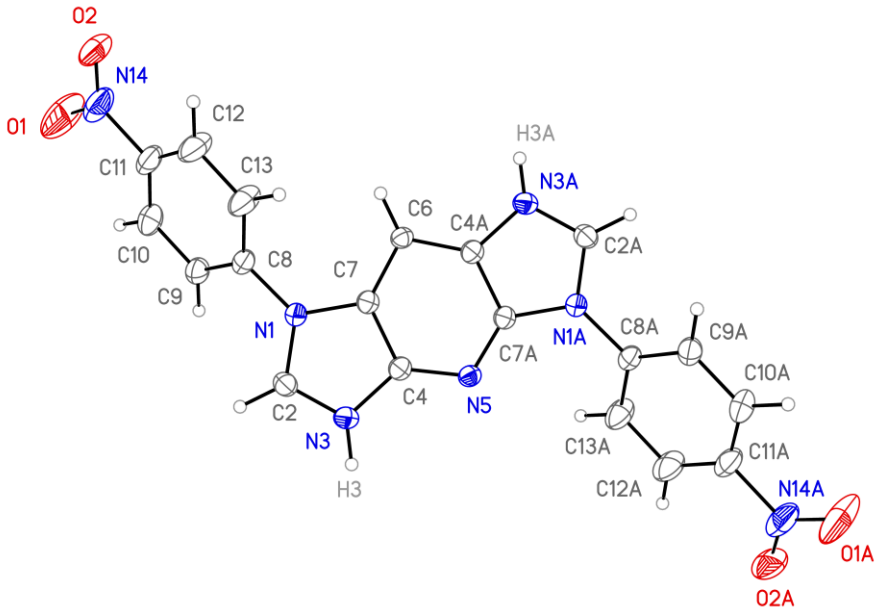


Figure S3. General view of the cation of 7**b** in thermal ellipsoid representation (p=50%). Only one part of the overlapping pseudo-centrosymmetric hereocycles is shown. The trifluoroacetate anions and trifluoroacetic acid solvate molecules are omitted for clarity. Important bond lengths are N1-C2 1.3332(18), N1-C7 1.3855(17), N1-C8 1.4273(17), N3-C2 1.3166(18), N3-C4 1.3795(18), N5-C4 1.33(2), C4-C7 1.4007(18).

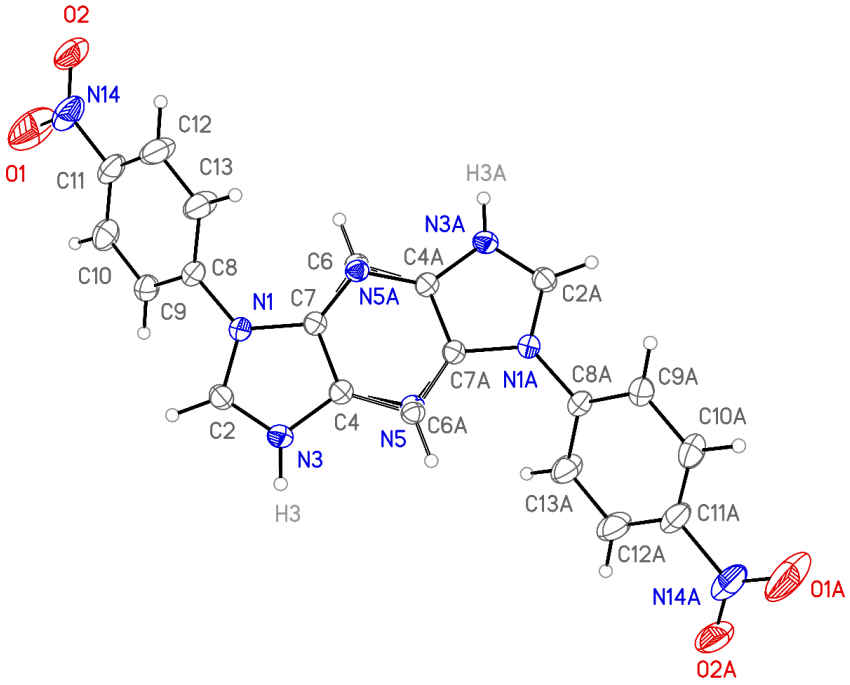


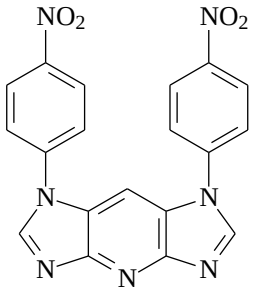
Figure S4. General view of the cation of 7**b** in thermal ellipsoid representation (p=50%). The overlap of the pseudo-centrosymmetric hereocycles in crystal is shown. The trifluoroacetate anions and trifluoroacetic acid solvate molecules are omitted for clarity. Important bond lengths are N1-C2 1.3332(18), N1-C7 1.3855(17), N1-C8 1.4273(17), N3-C2 1.3166(18), N3-C4 1.3795(18), N5-C4 1.33(2), C4-C7 1.4007(18).

Table S1. Crystal data and structure refinement parameters.

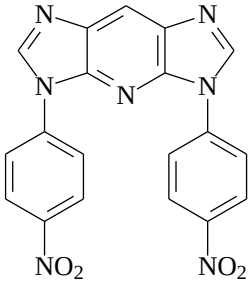
	5 (HCl salt)	**7a** (cis-1)	**7b** (trans)
CCDC	1868391	1868389	1868390
Empirical formula	$C_7H_7Cl_2N_5$	$C_{21}H_{15}N_7O_8$*	$C_{31}H_{17}F_{18}N_7O_{16}$
Molecular weight	232.08	493.40*	1085.52
T, K	120	120	120
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$C2/c$	$P2_1/n$
Z / Z'	2 / 1	4 / 0.5	2 / 0.5
a, Å	4.7530(6)	22.399(3)	10.0092(3)
b, Å	10.9303(14)	14.2557(16)	13.7495(4)
c, Å	8.6048(11)	7.1186(8)	15.3130(5)
β, °	95.439(3)	99.297(2)	94.4884(16)
V, Å^3	445.02(10)	2243.2(4)	2100.93(11)
d_{calc}, g cm^{-3}	1.732	1.461*	1.716
μ, cm^{-1}	6.92	1.16*	1.86
$2\theta_{max}$, °	60	60	60
Reflections collected /independent	5757 / 2571	13139 / 3419	74142 / 6125
Observed reflections [I>2σ(I)]	2301	2547	5034
Number of refined parameters	129	192	431
R_1	0.0342	0.0424	0.0532
wR_2	0.0819	0.1190	0.1371
GOF	1.030	1.054	1.007
Residual density, eÅ^{-3} (d_{max}/d_{min})	0.375/-0.305	0.299/-0.197	0.637/-0.598

*Some values for **7a** do not include the contribution from the solvent that was removed by SQUEEZE (see above).

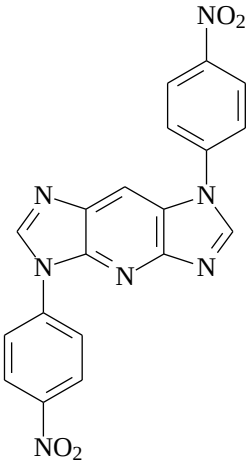
NMR data



'cis-1' (7a)

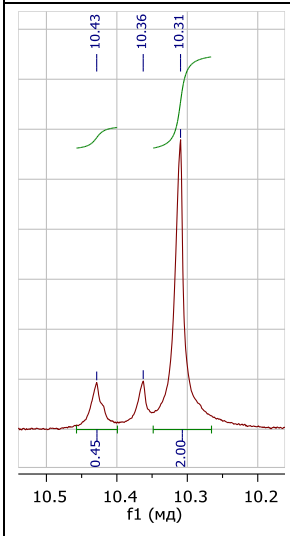
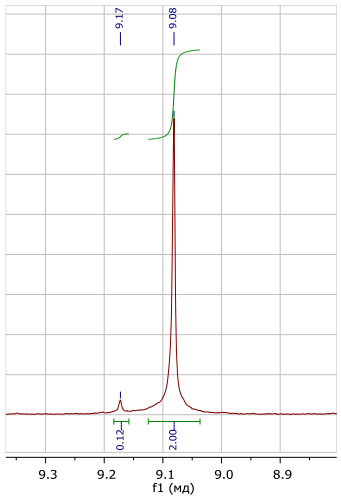
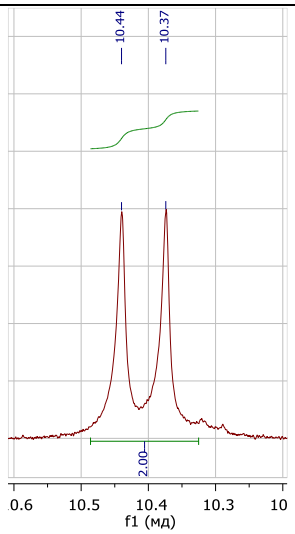
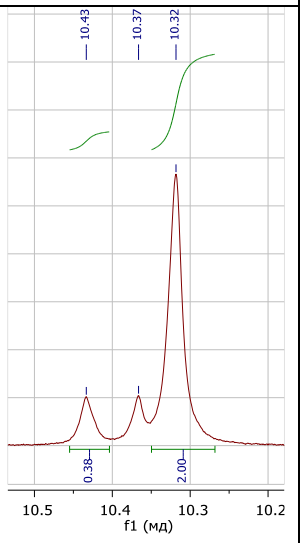


'cis-2'

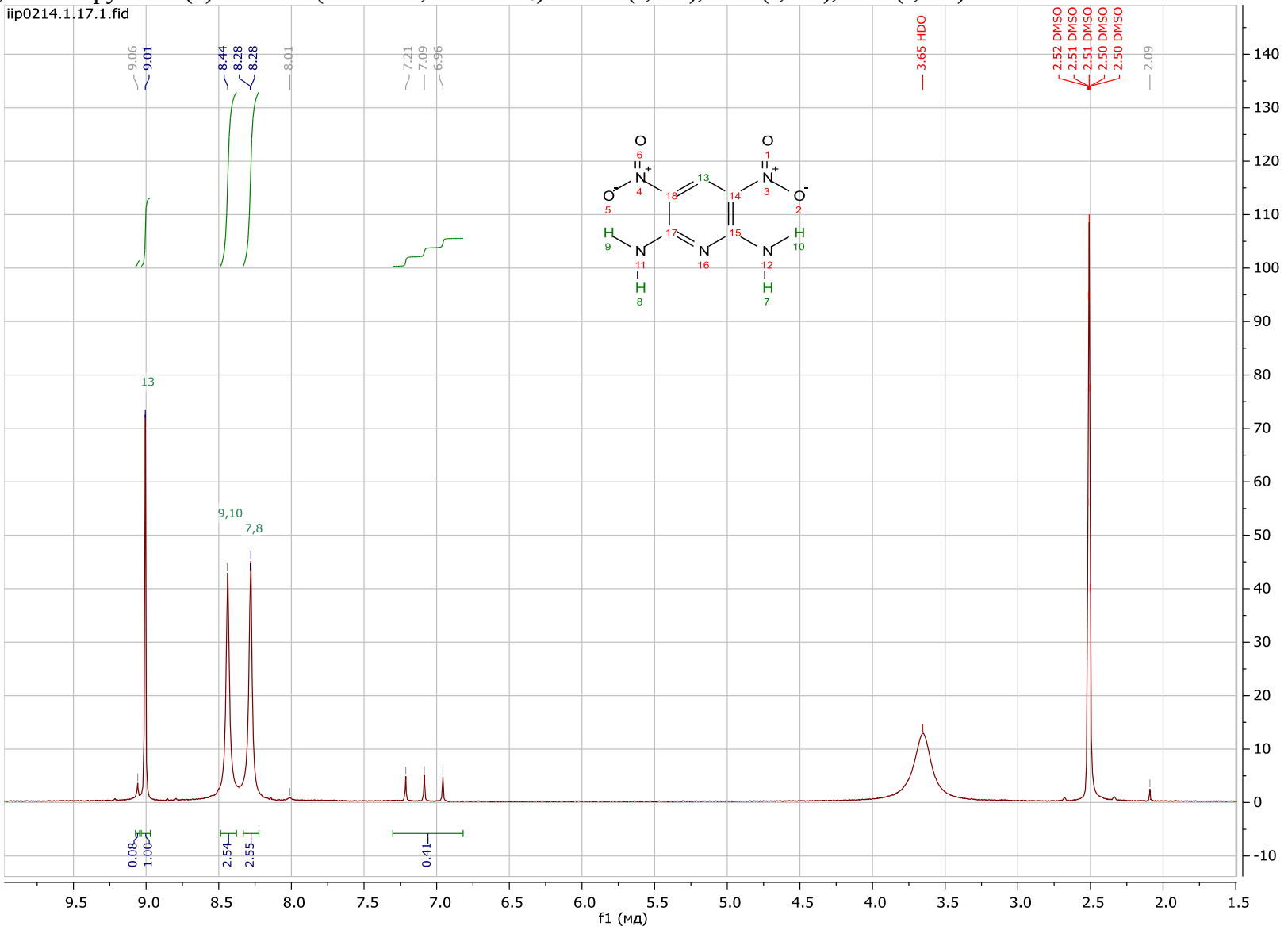


'trans' (7b)

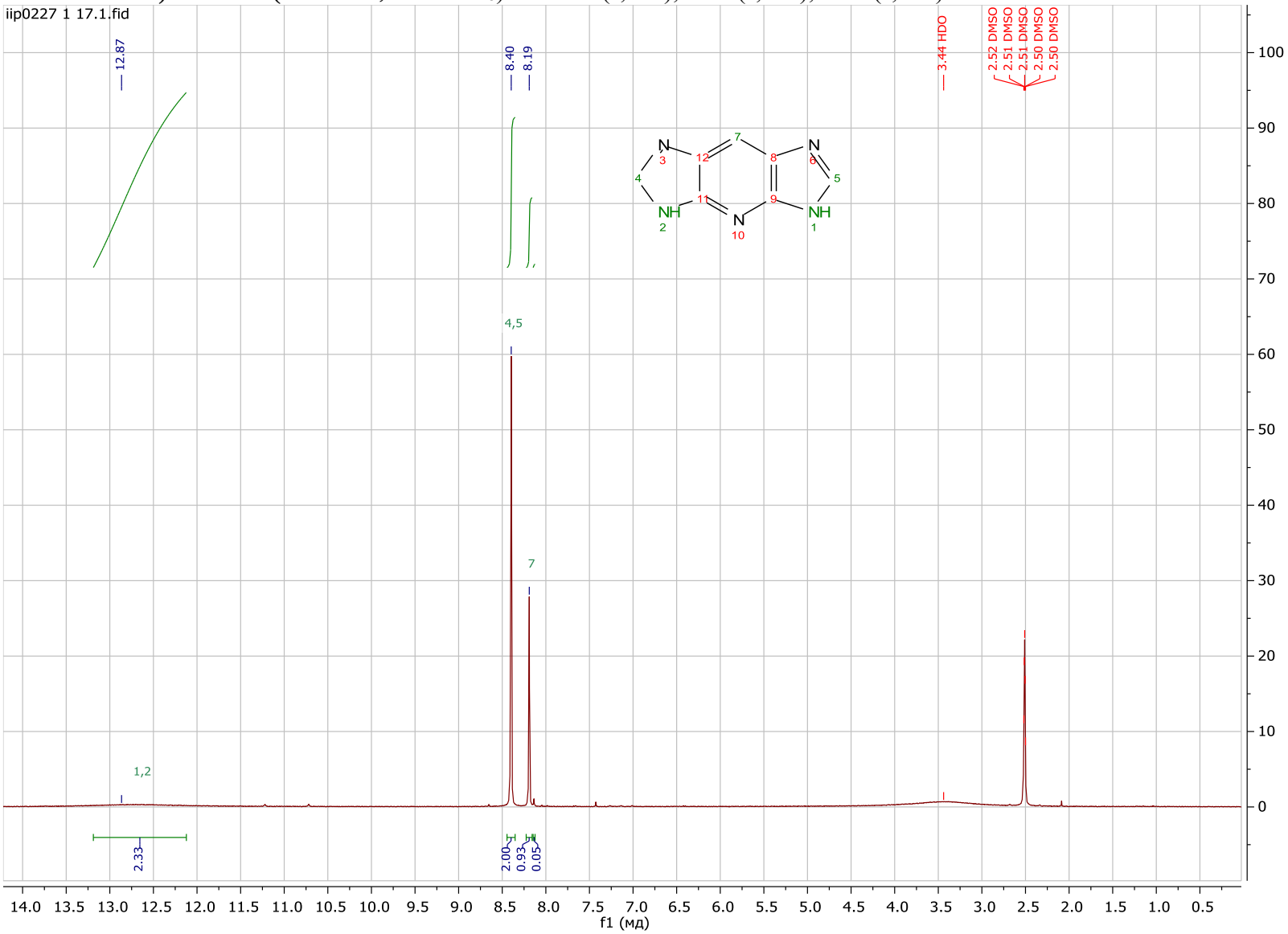
^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer. Chemical shifts δ were determined using residual proton signals of the deuterated solvent as an internal reference. The most characteristic signals were referred to the protons of the CH moieties in imidazole rings (**Table S2**), for the 'cis-1' product they appeared as a single peak, and for the 'trans' product – as two separate peaks. The ratio of the isomer products was close to 7:3 ('cis-1':'trans') in both cases. The minor peak in the spectrum of isolated 'cis-1' isomer can belong to 'cis-2'-product, 2,5-bis(4-nitrophenyl)-2,5-dihydrodiimidazo[4,5-*b*:4′,5′-*e*]pyridine.

DIP*2HCl model reaction products (CF_3COOD) (69% **7a**, 31% **7b**)	Isolated 'cis-1'- product **7a** (DMSO-d_6)	Isolated 'trans'-product **7b** (CF_3COOD)	DIP*2H_2O model reaction products (CF_3COOD) (73% **7a**, 27% **7b**)
			

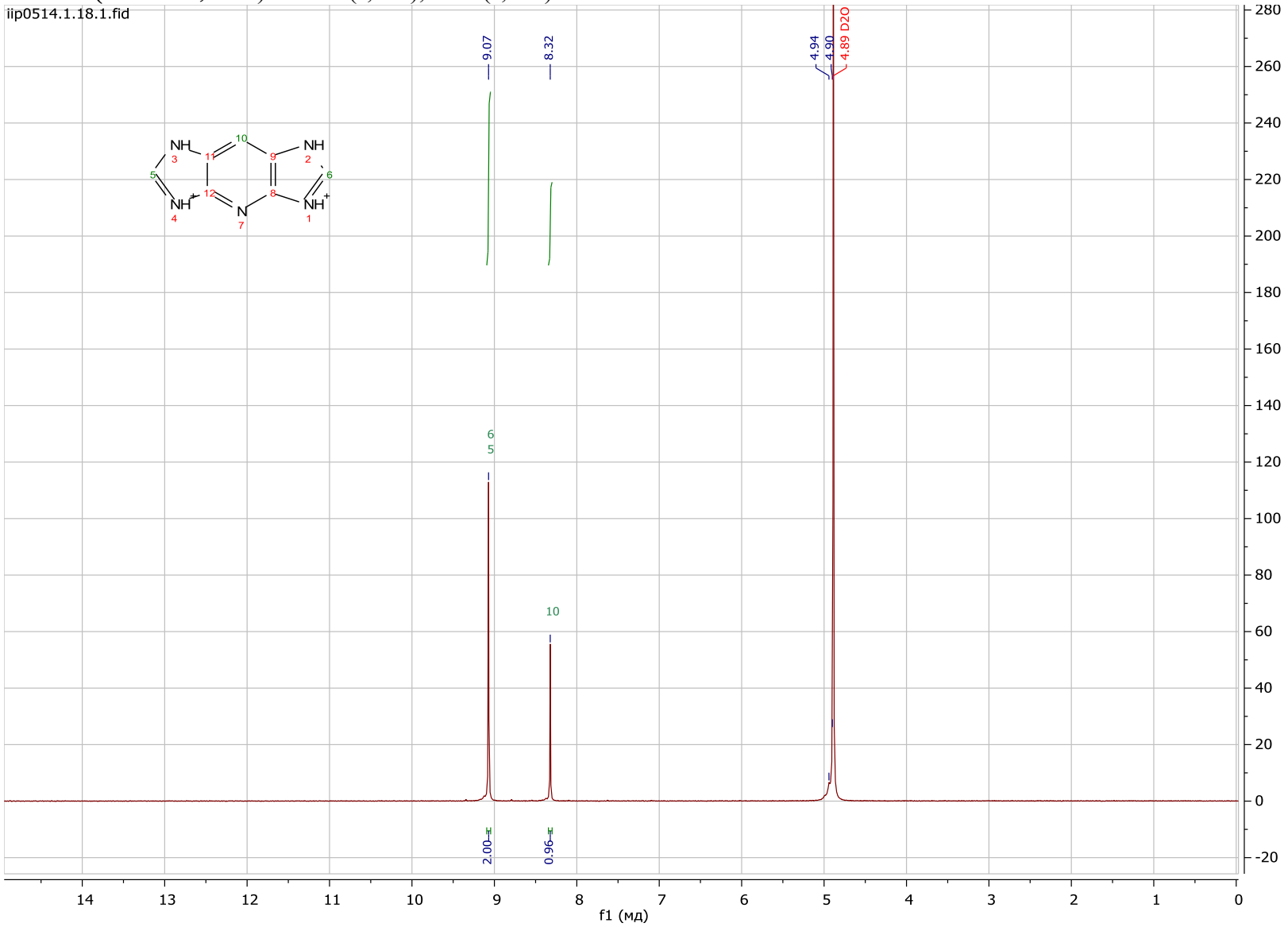
1,5 Diamino-2,4-dinitropyridine (**3**) ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.01 (s, 1H), 8.44 (s, 3H), 8.28 (s, 3H).



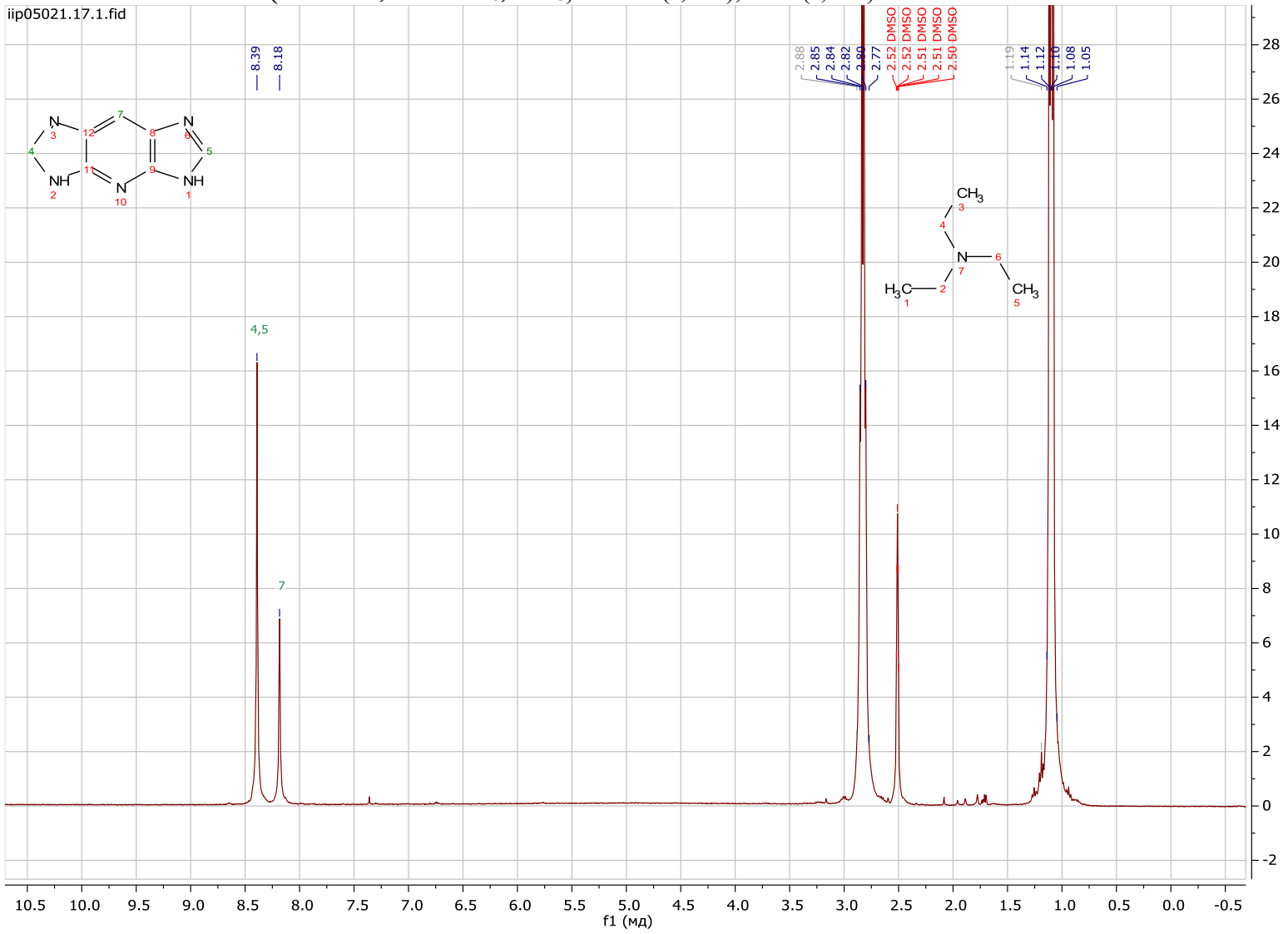
DIP·H_2O (**5**) (neutralized form) ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.87 (s, 2H), 8.40 (s, 2H), 8.19 (s, 1H).



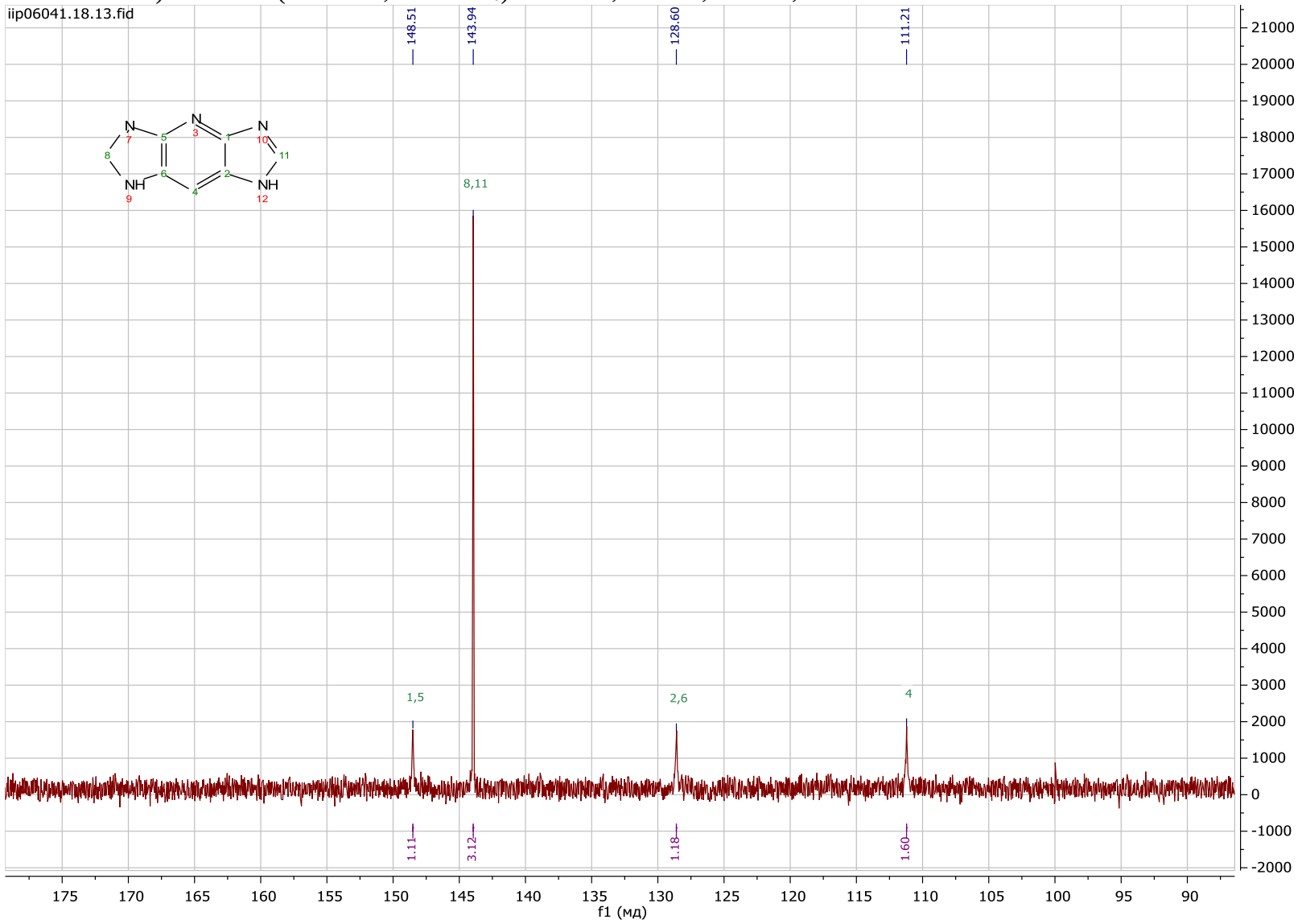
DIP·2HCl (**5**) ^{1}H NMR (400 MHz, D_2O) δ: 9.07 (s, 2H), 8.32 (s, 1H)



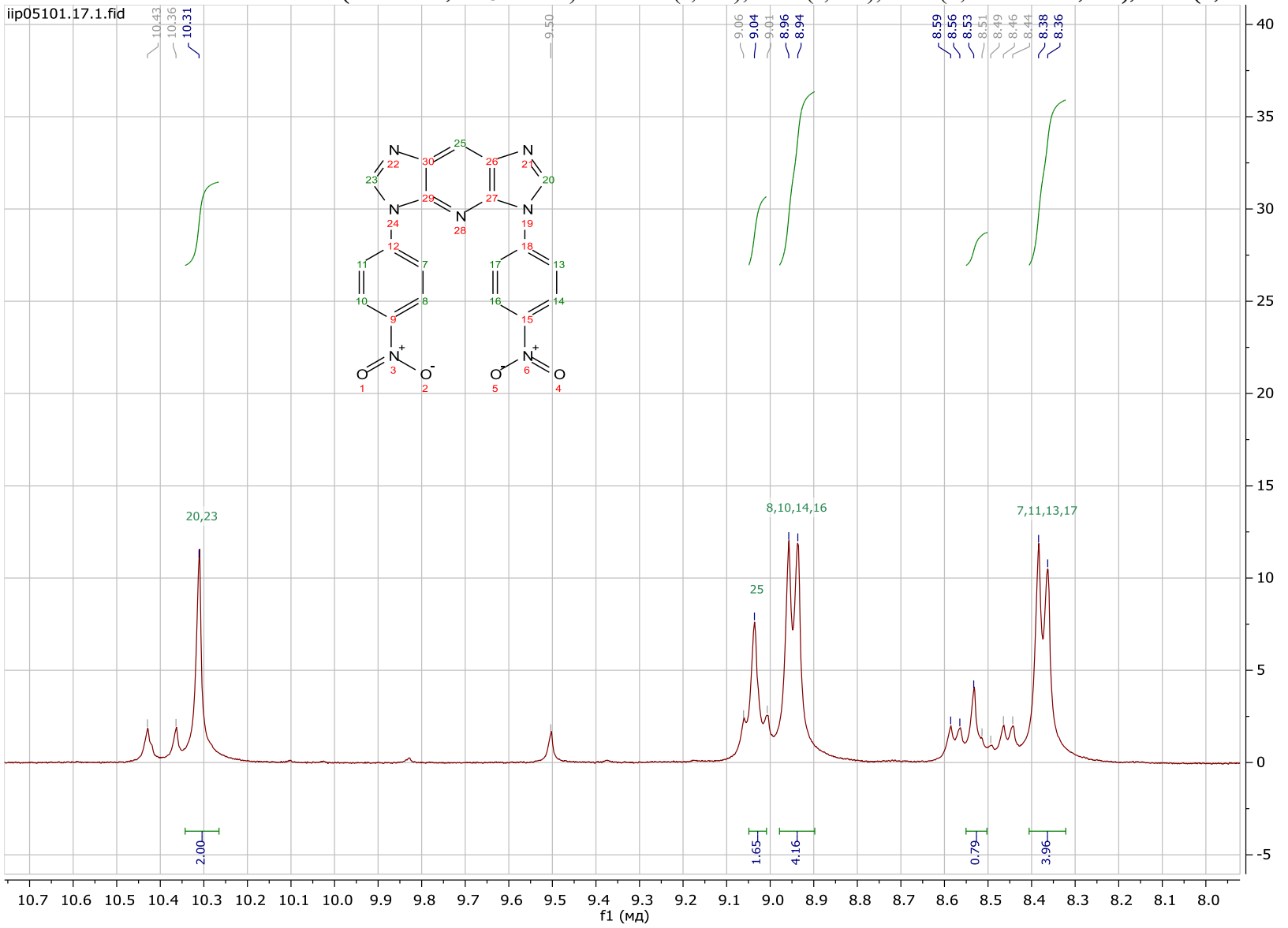
DIP·2HCl (**5**) neutralized *in situ* ^{1}H NMR (400 MHz, DMSO-d_6, NEt_3) δ: 8.39 (s, 2H), 8.18 (s, 1H).



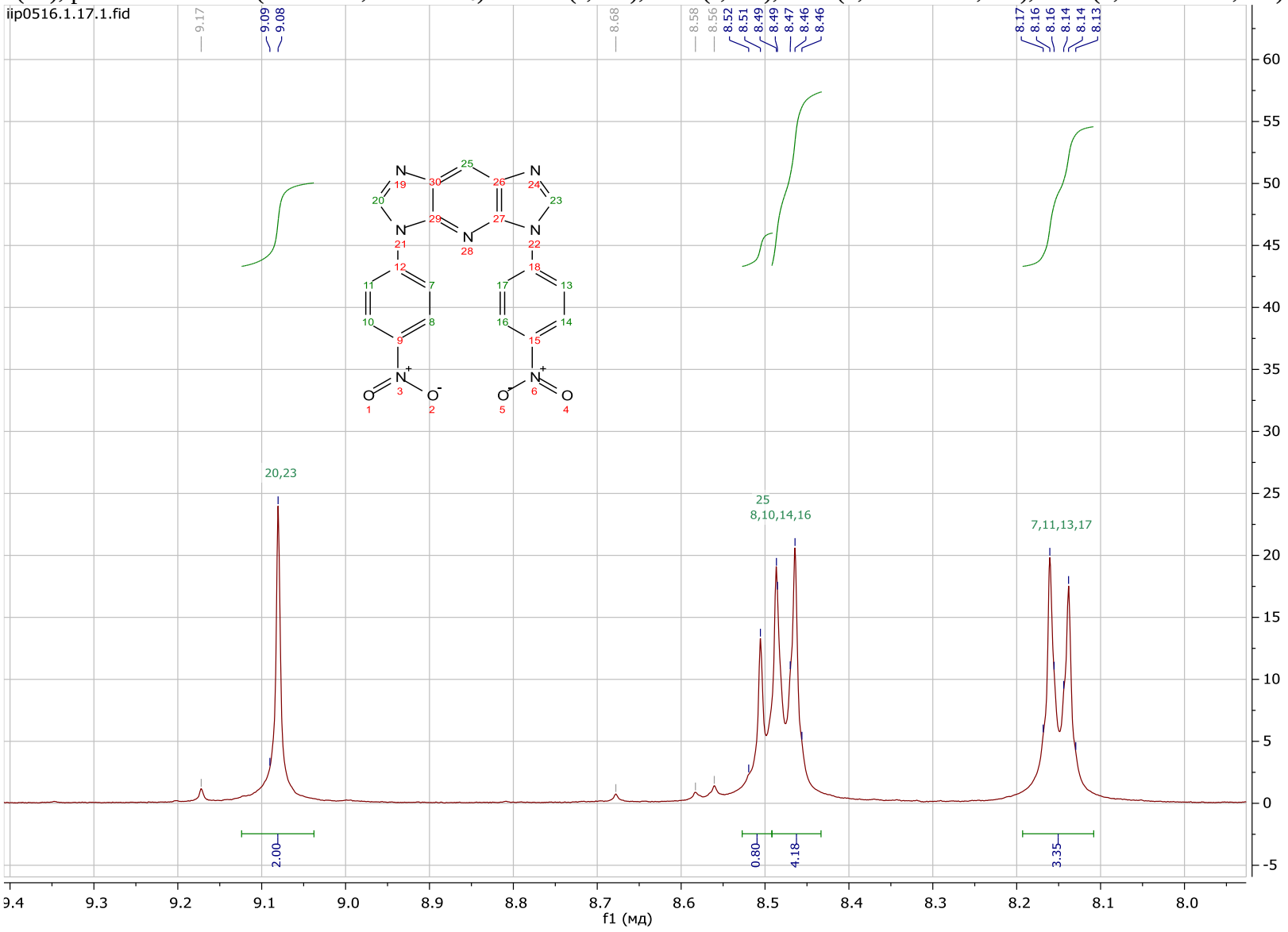
DIP·H_2O (**5**) (neutralized form) ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.51 , 143.94 , 128.60 , 111.21 .



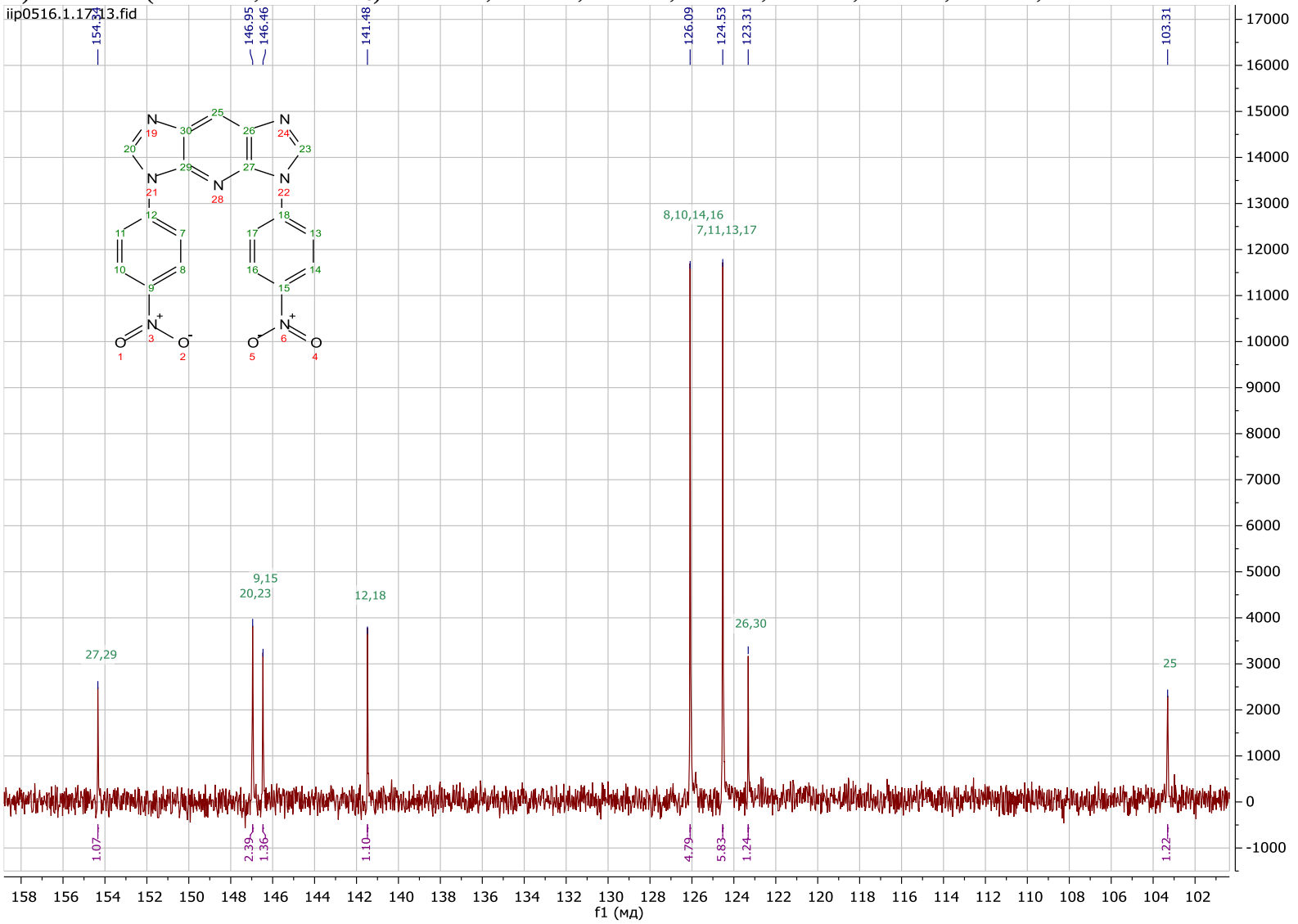
‘Cis-1’ product **7a** in mixture with **7b** ^{1}H NMR (400 MHz, CF_3COOD) δ: 10.31 (s, 2H), 9.04 (s, 1H), 8.95 (d, *J* = 8.4 Hz, 4H), 8.37 (d, *J* = 8.4 Hz, 4H).



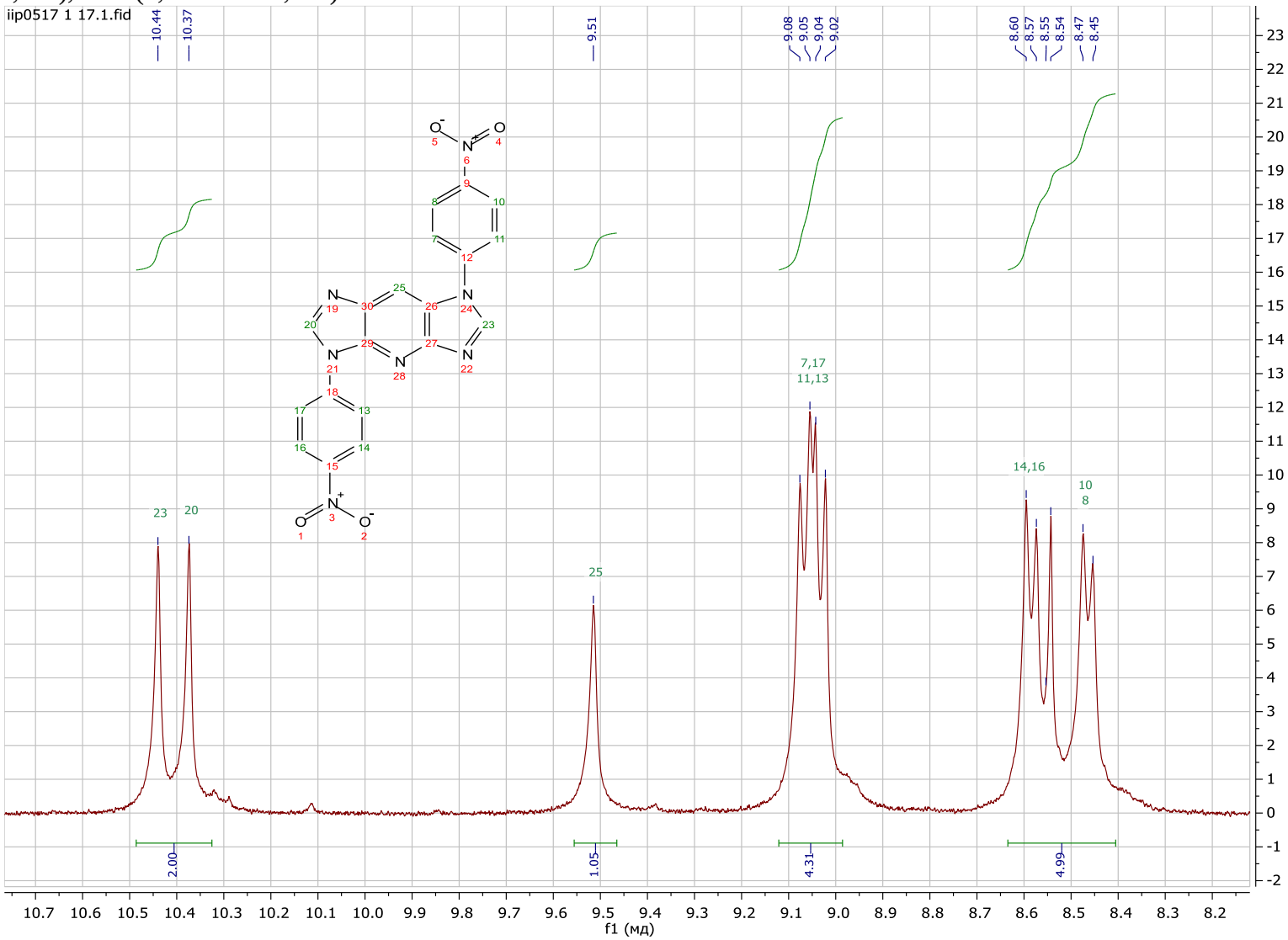
‘Cis-1’ product (**7a**), purified ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 9.09 (s, 2H), 8.52 (s, 1H), 8.47 (d, *J* = 8.9 Hz, 4H), 8.15 (d, *J* = 8.9 Hz, 4H).



‘Cis-1’ product (**7a**) ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.34 , 146.95 , 146.46 , 141.48 , 126.09 , 124.53 , 123.31 , 103.31 .



‘Trans’ product (**7b**) ^{1}H NMR (400 MHz, CF_3COOD) δ: 10,44 (s, 1H), 10,37 (s, 1H), 9,51 (s, 1H), 9.07 (d, *J* = 8.7 Hz, 2H), 9.03 (d, *J* = 8.4 Hz, 2H), 8.59 (d, *J* = 8.7 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 2H).



‘Trans’ product (**7b**) ^{13}C NMR (101 MHz, CF_3COOD) δ 153.13 , 152.52 , 148.95 , 148.66 , 146.52 , 146.39 , 140.48 , 139.98 , 130.02 , 129.85 , 129.45 , 129.29 , 128.37 , 127.88 .