Biocompatible Silicomolybdic Acid Promoted One-Pot Expeditious Synthesis of 1,2,3-*NH*-Triazoles

Danish Ansari, Manoj K. Jaiswal, Mangal S. Yadav, Vinay K. Pandey, Mayank Singh, and Vinod K. Tiwari*

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, UP-221005, INDIA

*E-mail: tiwari_chem@yahoo.co.in, vinod.tiwari@bhu.ac.in

Contents:

1. General Information:

All the reagents and chemicals were of pure analytical grade and until unless mentioned used directly as such. Thin layer chromatography (TLC) was performed on 60 F-254 silica gel, which was per-coated on aluminum plates and seen by UV light (λ max = 254 nm). Column chromatography was performed using silica gel (100-200 mesh and 200-400 mesh) for the purification of the developed 4-Aryl-*NH*-1,2,3-triazoles.Solvents were condensed under low pressure at ≤ 55°C. The ^{1}H, and $^{13}C\{^{1}H\}$NMR spectra were recorded at 500 MHz and 125 MHz, respectively. All NMR spectra were recorded at 25°C and reported in δ ppm, indicated with respect to a deuterated solvent at Jeol delta NMR spectrometer. The chemical shifts of internal TMS are presented in ppm downfield in the ^{1}H NMR spectra and J values are described as: 's' (singlet), 'd' (doublet), "dd' (double doublet), t' (triplet), and 'm' (multiplet) and residual protic solvent of DMSO-$D_6$and $CDCl_3$ (^{1}H NMR, 2.49 & 7.26 ppm; ^{13}C NMR, 39.50& 77.0 ppm) respectively. SCIEX X500r Q-TOF, High-Resolution mass spectrometry was used to capture mass spectra (HRMS).

2. ^{1}H NMR and ^{13}C NMR spectra of 1,2,3-*NH*-Triazole (**2a-l**)

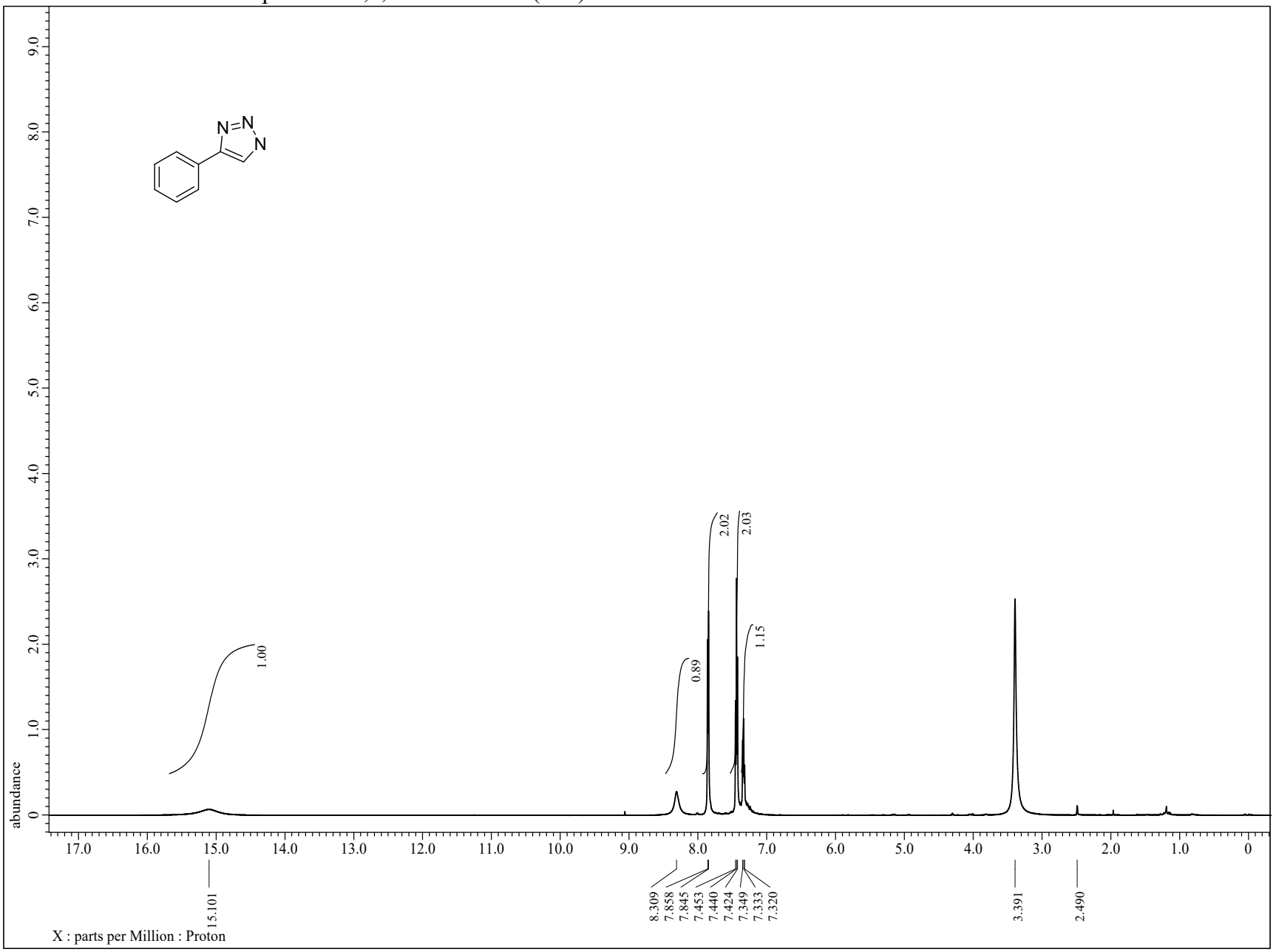

Figure S1: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2a**[1]

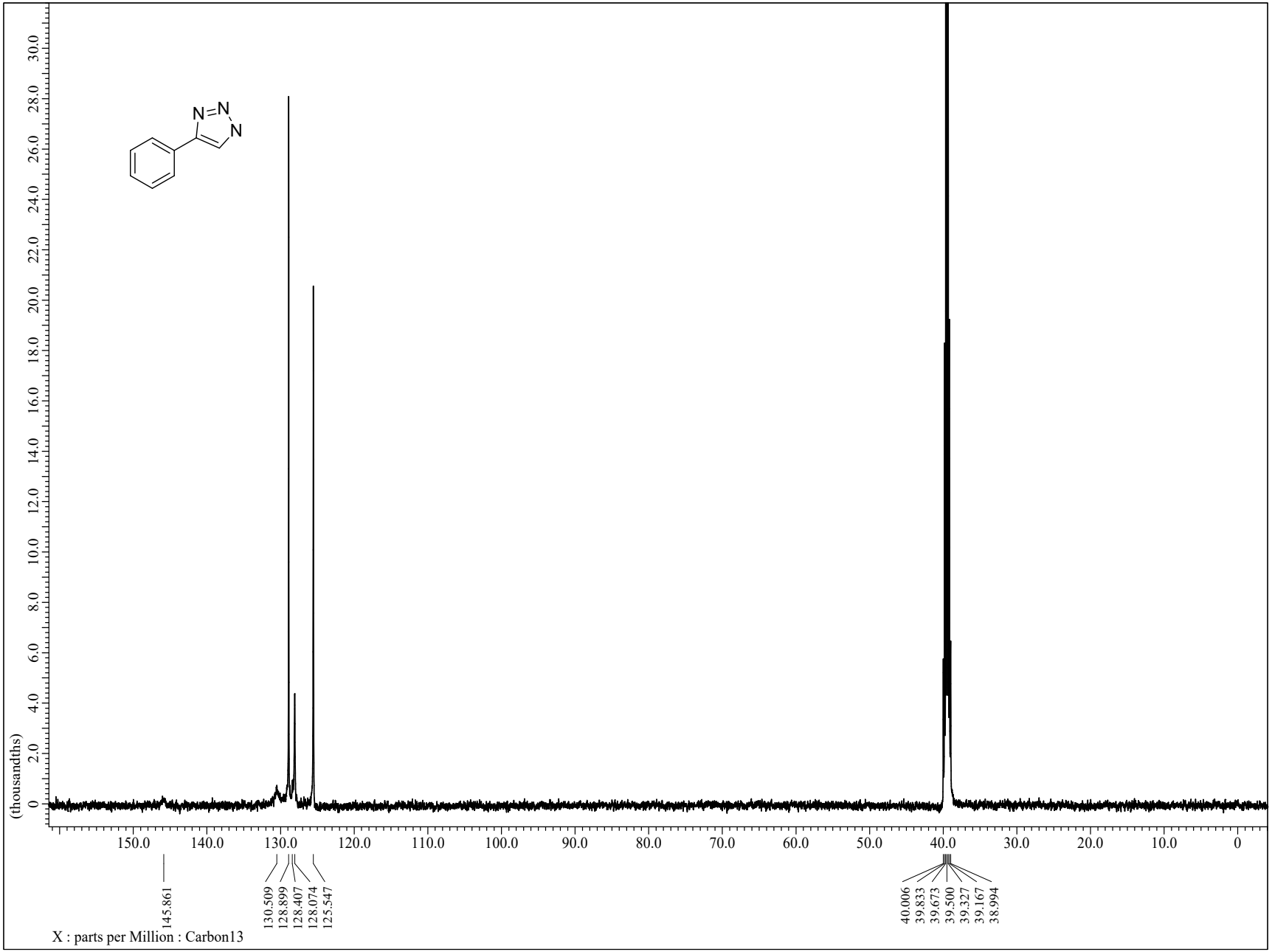

Figure S2: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2a**

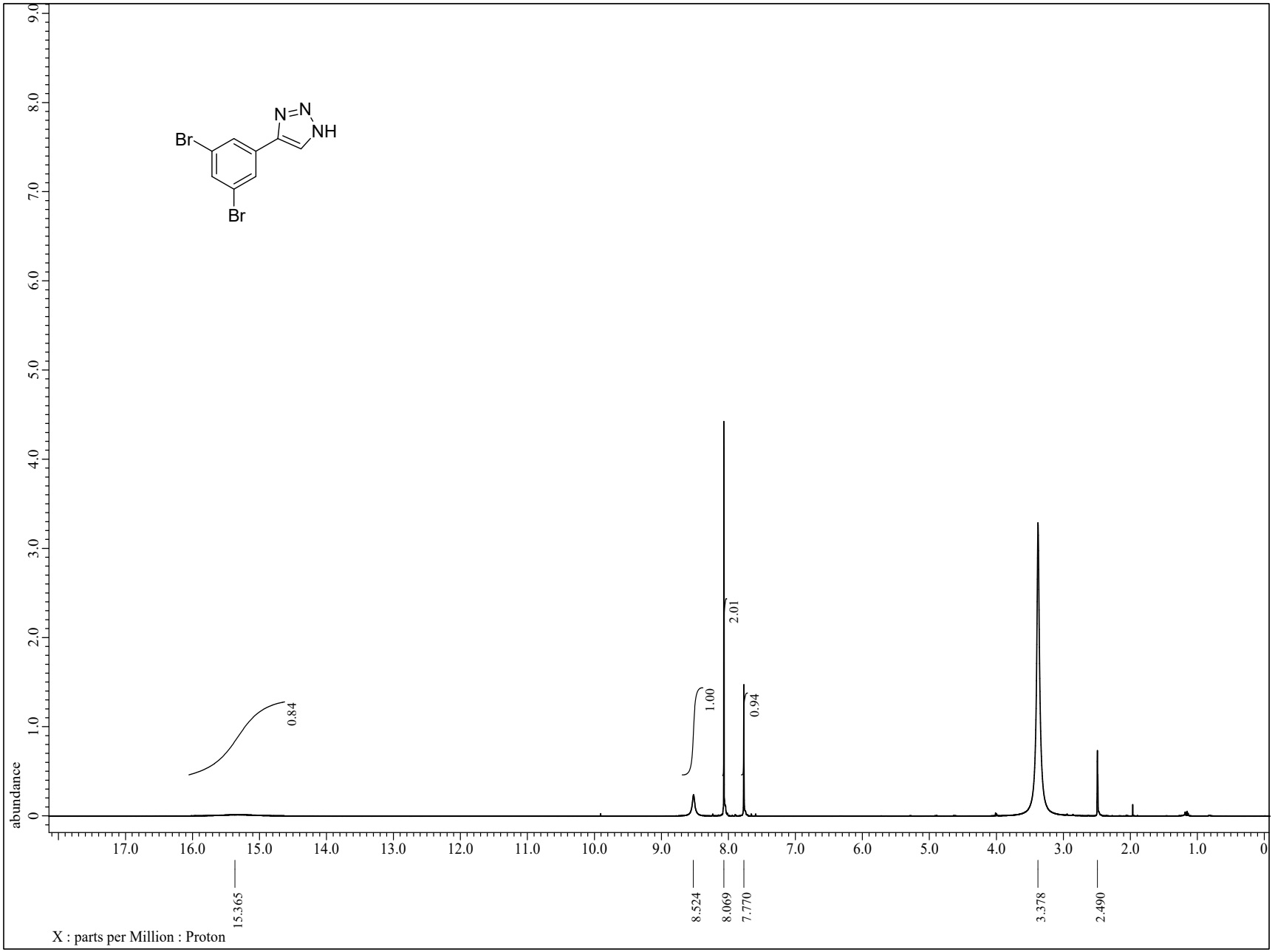

Figure S3: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2b**

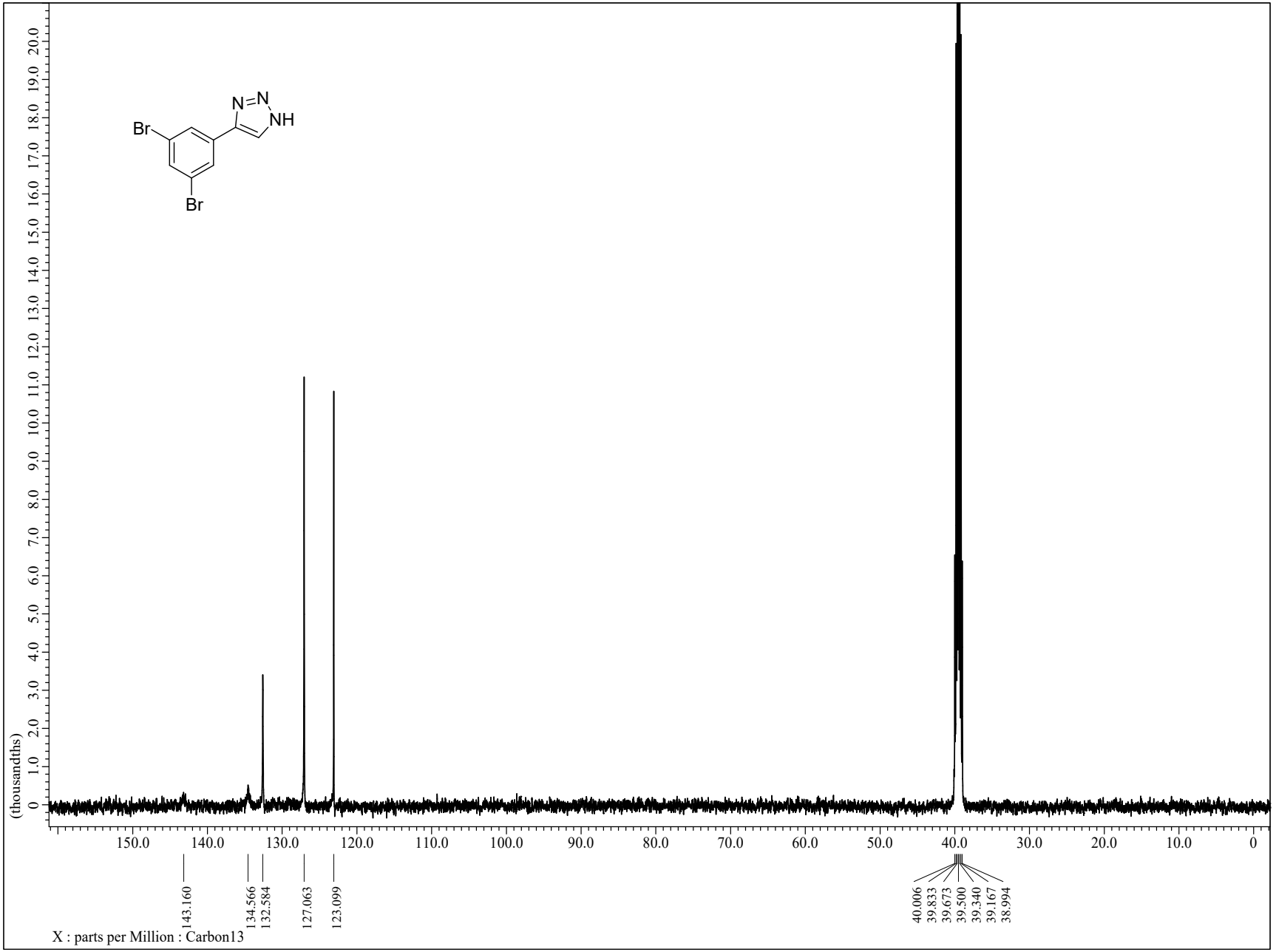

Figure S4: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2b**

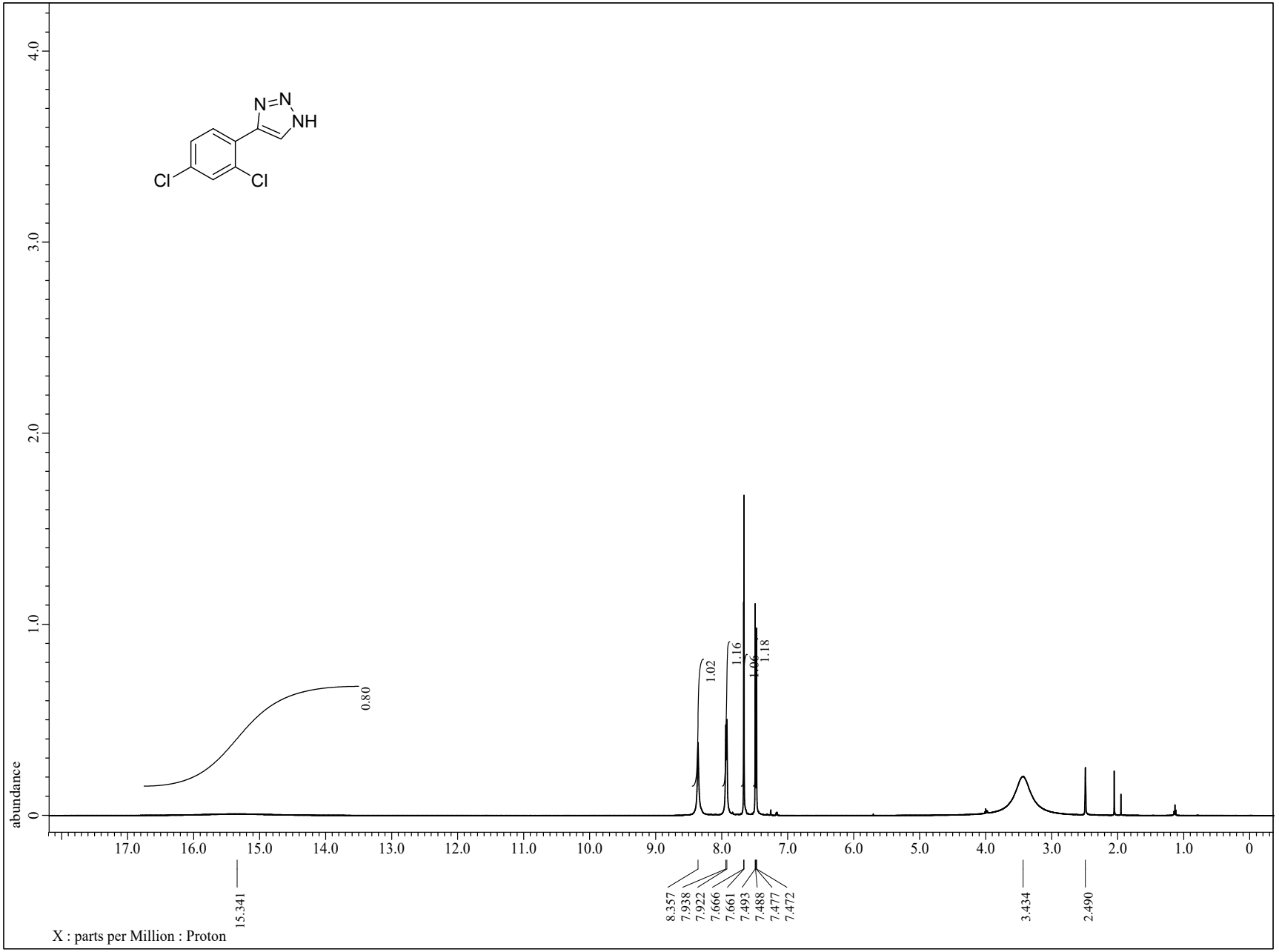

Figure S5: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2c**

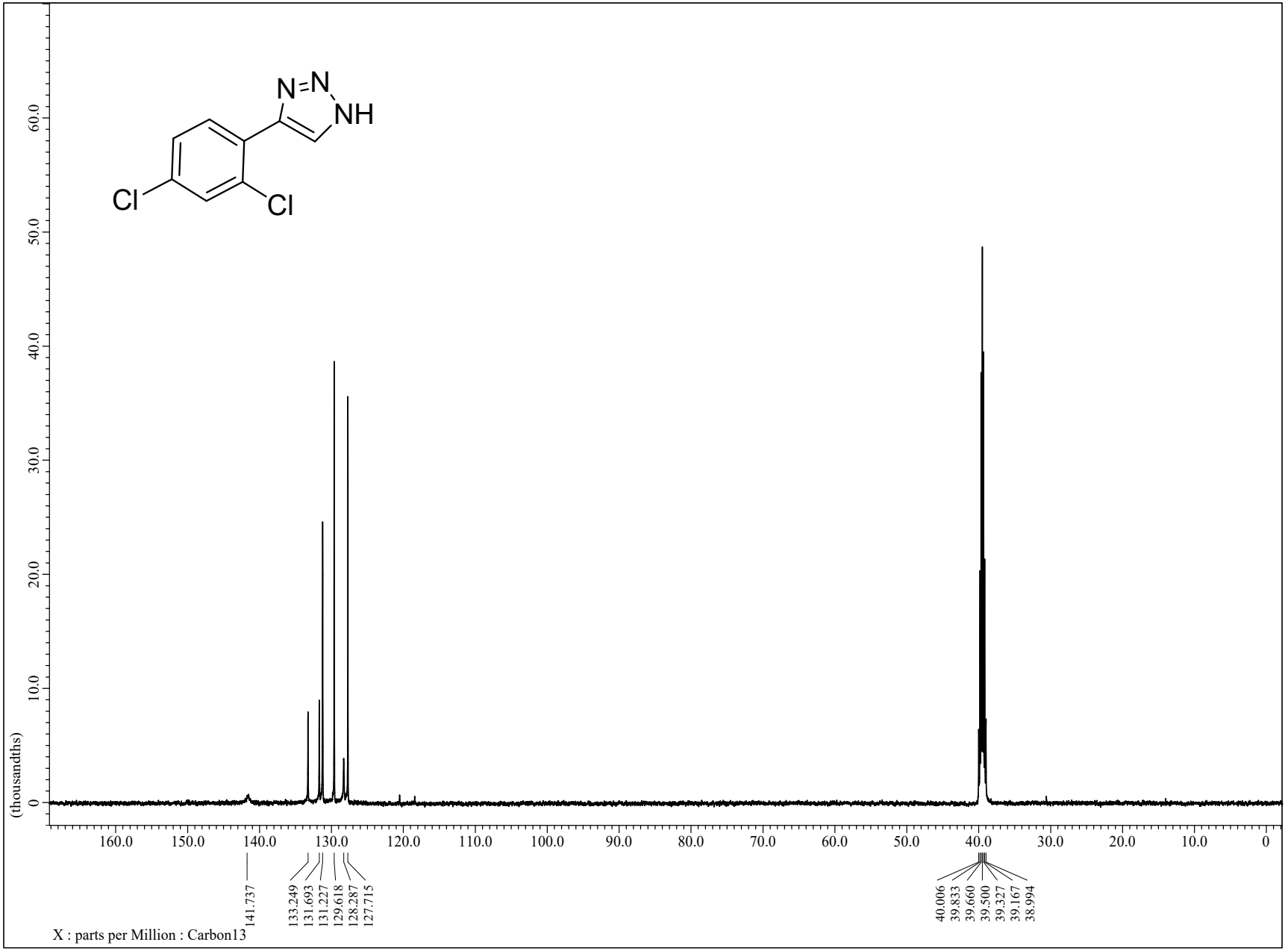

Figure S6: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2c**

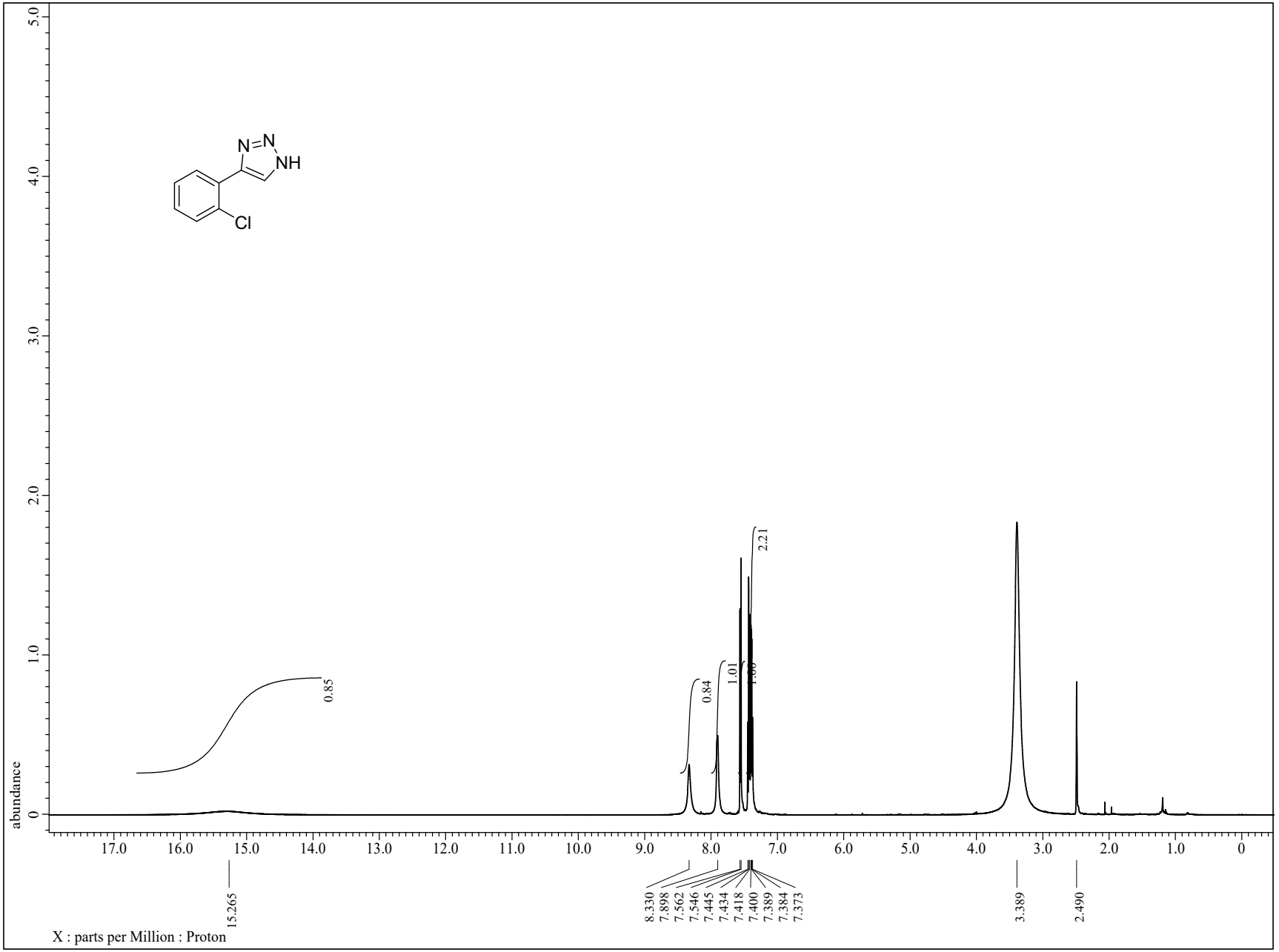

Figure S7: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2d**

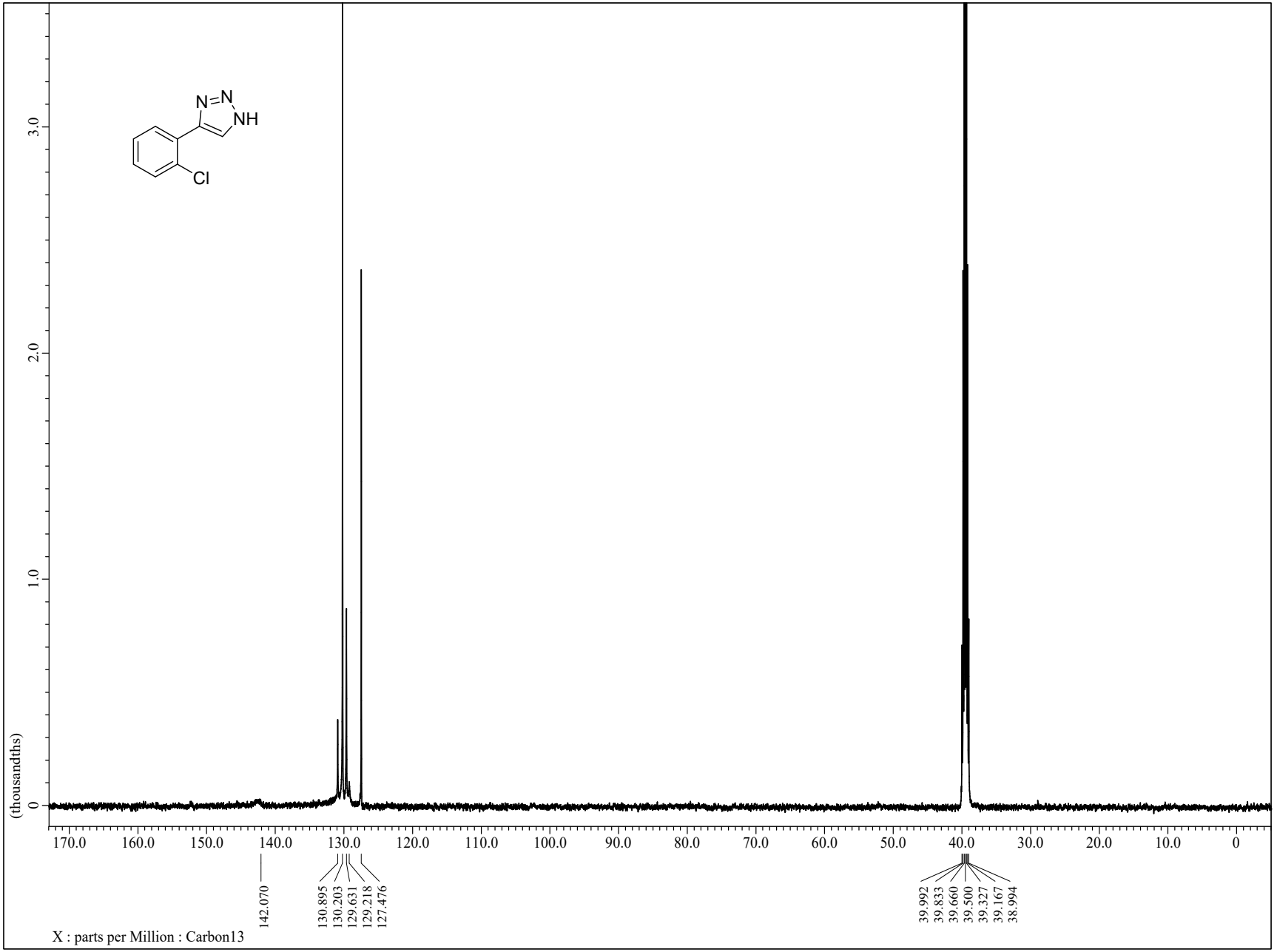

Figure S8: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2d**

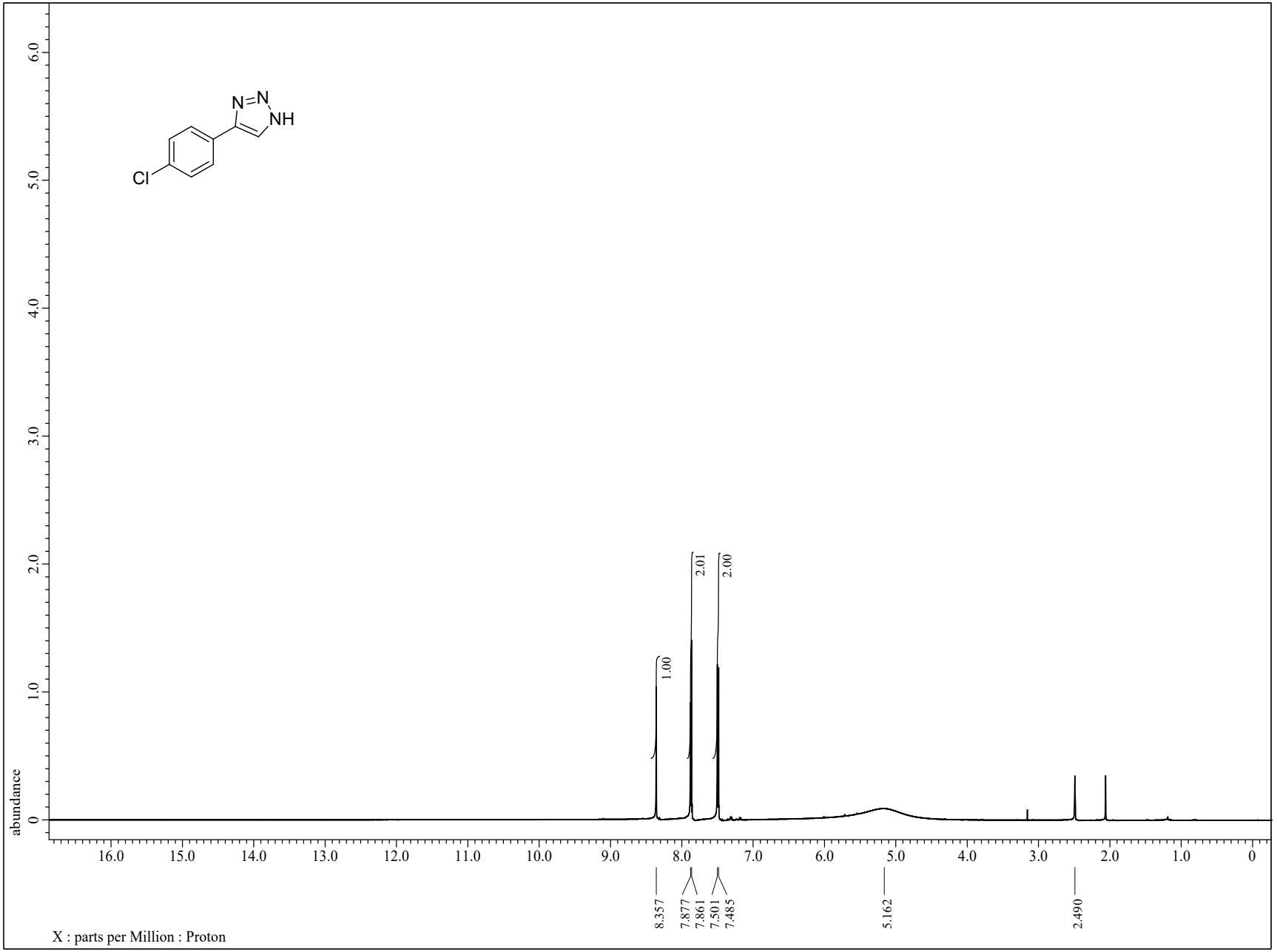

Figure S9: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2e**

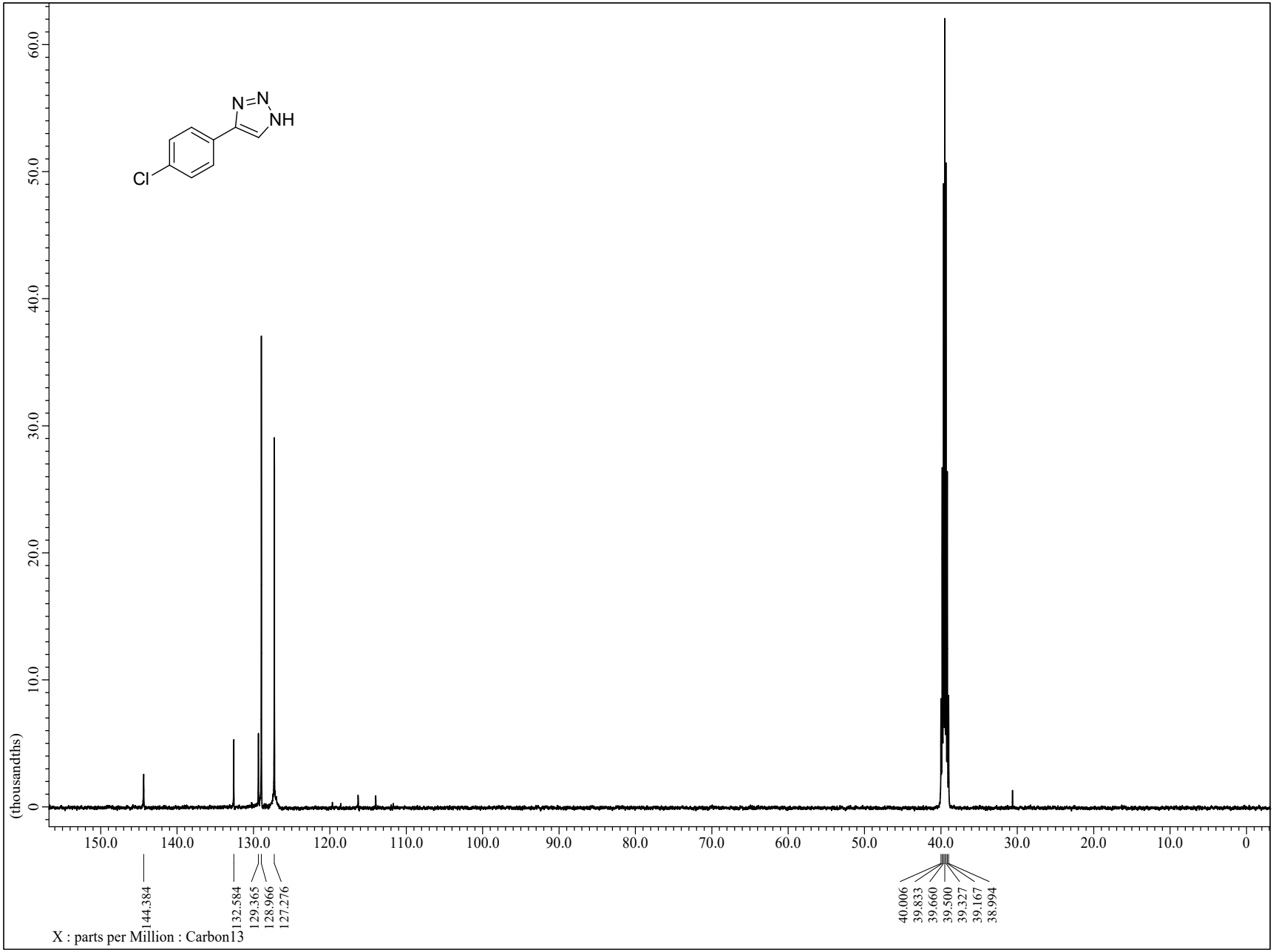

Figure S10: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2e**

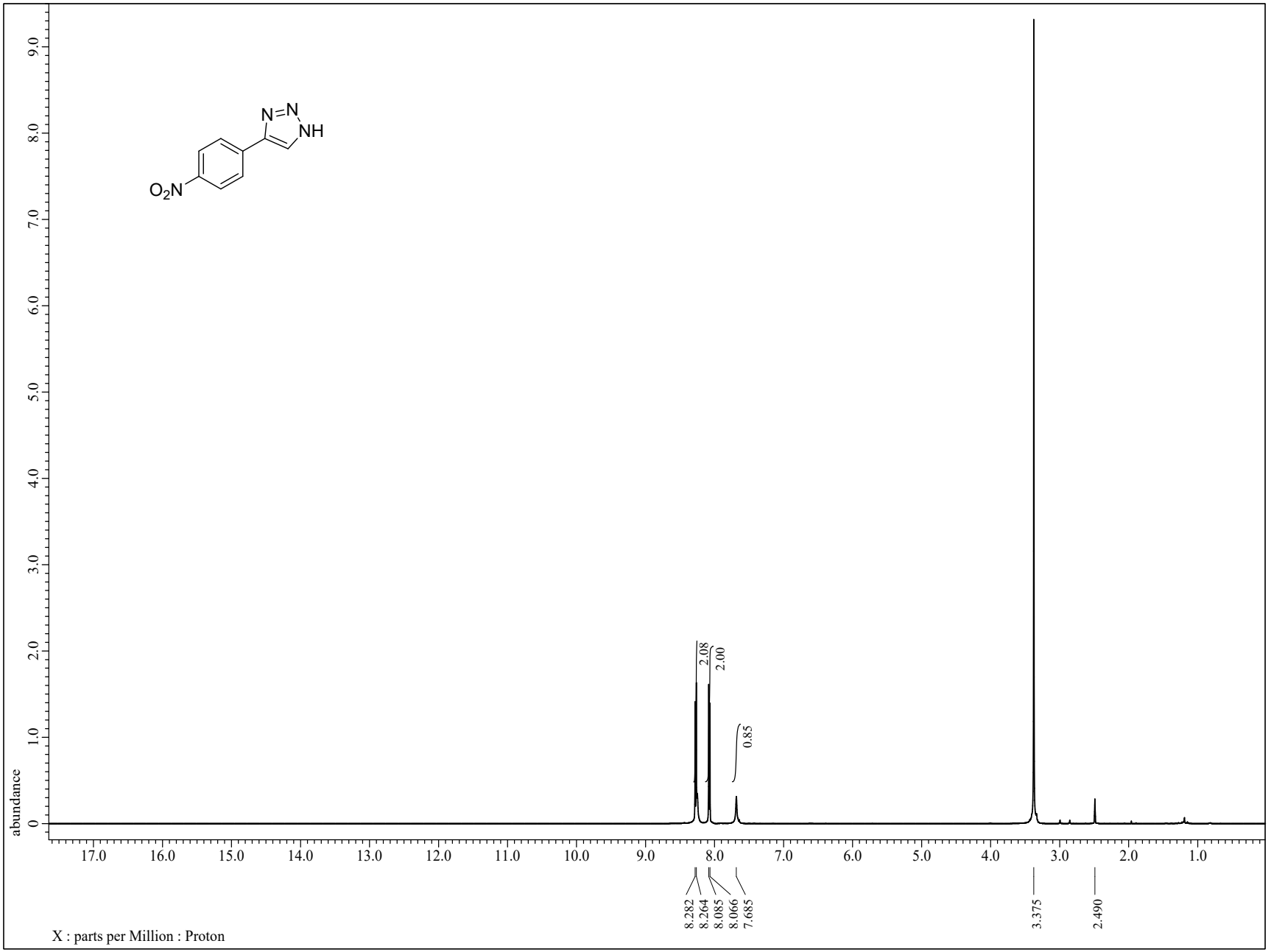

Figure S11: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2f**

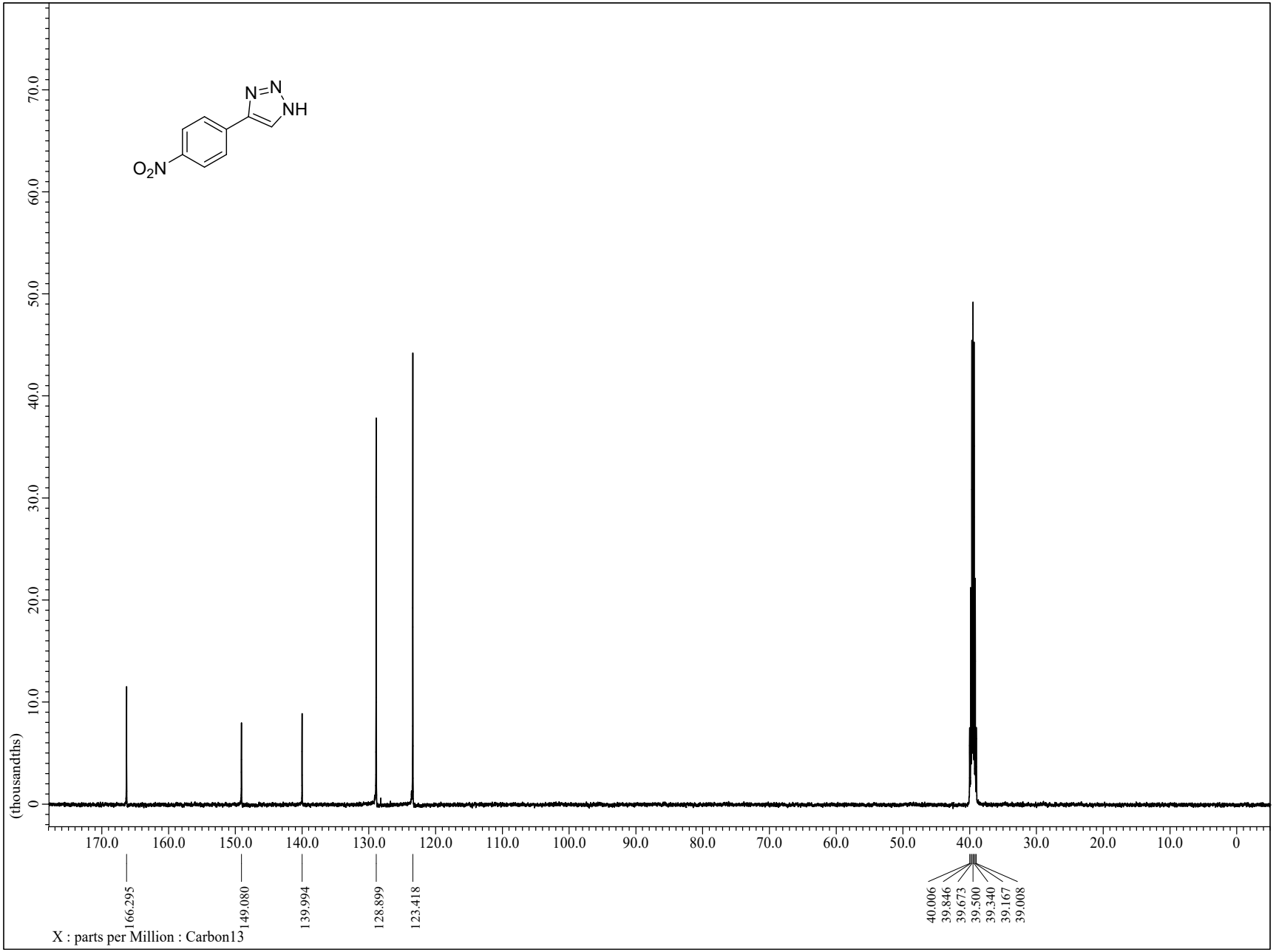

Figure S12: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2f**[1]

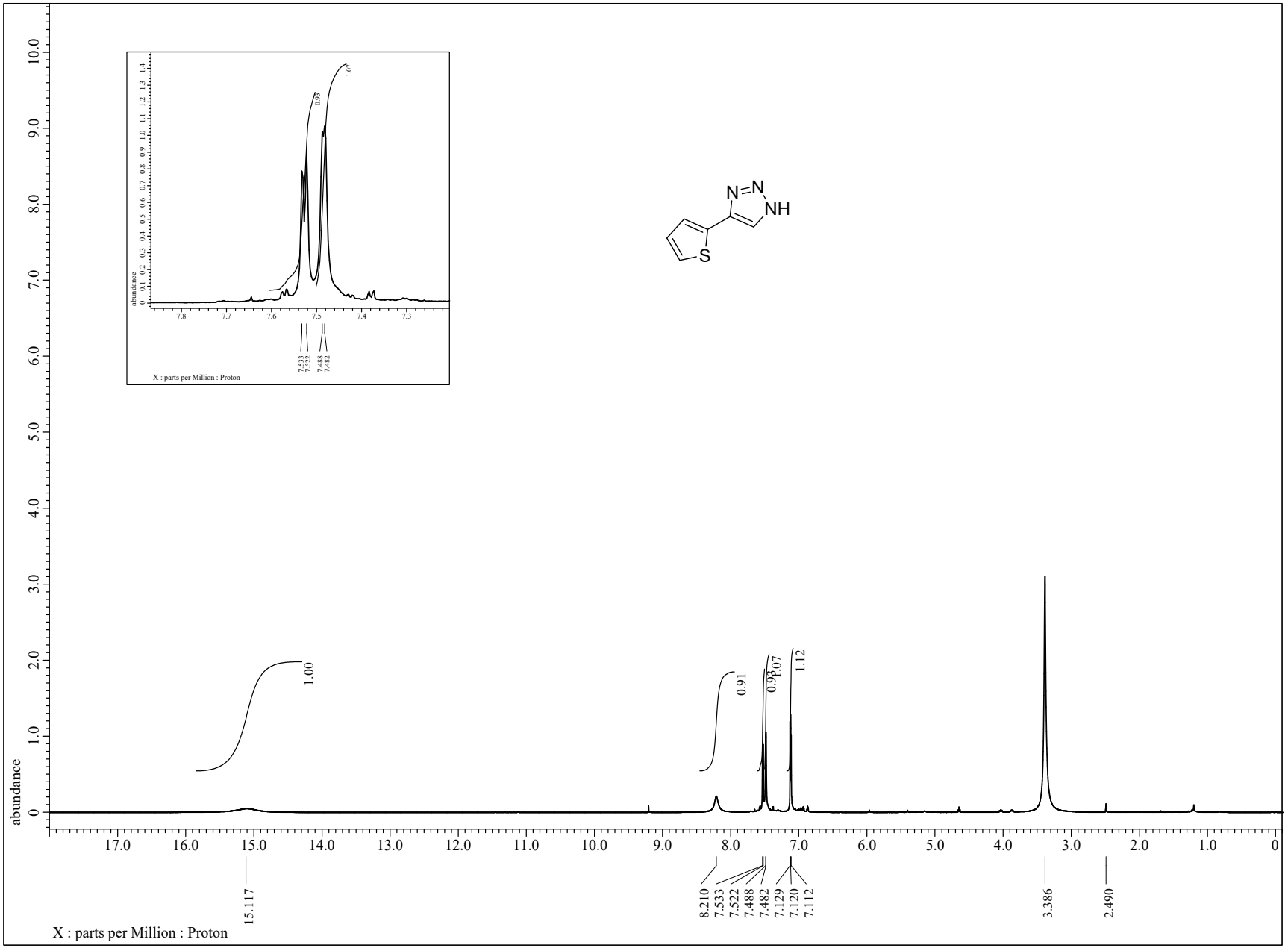

Figure S13: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2g**

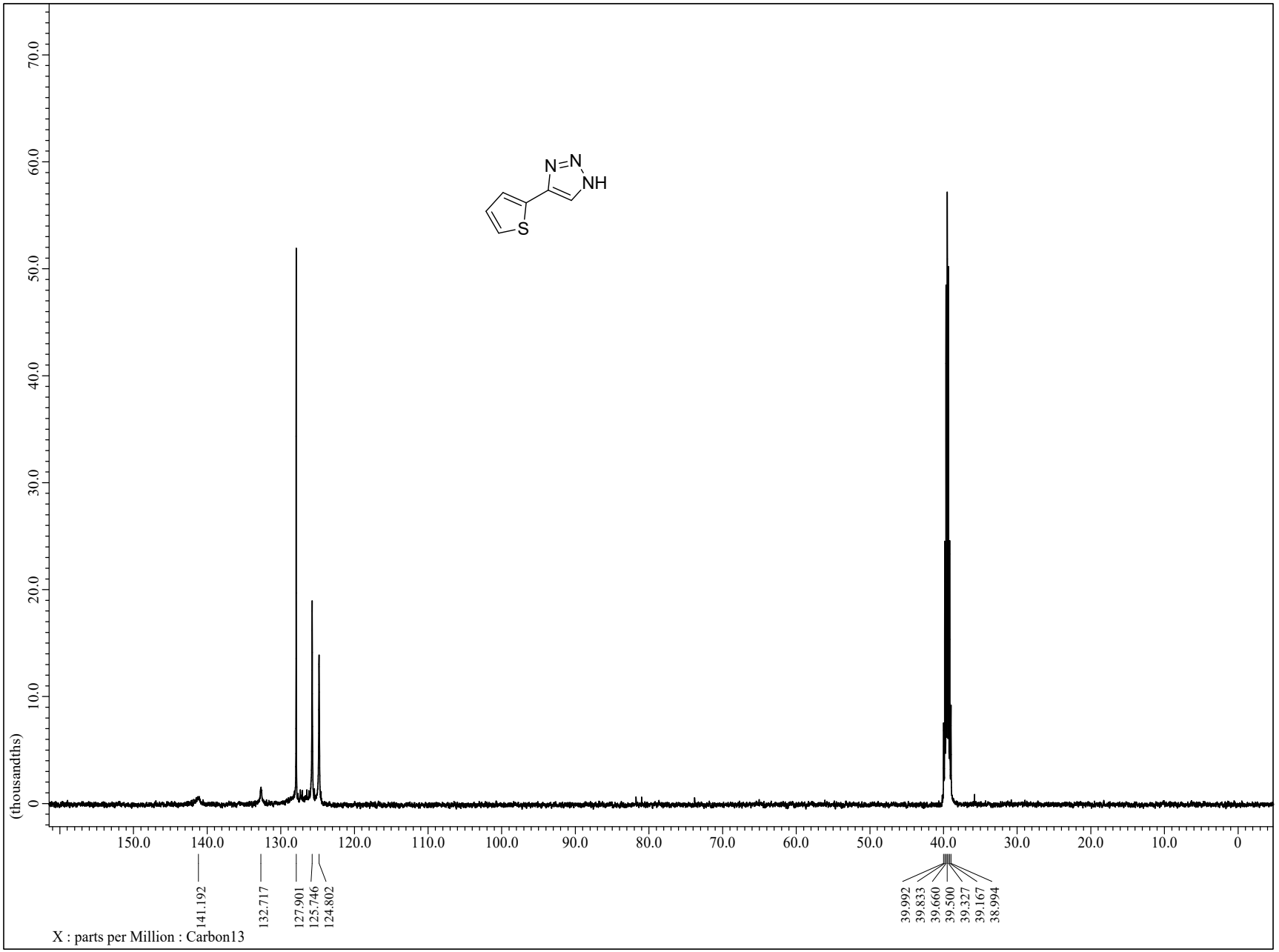

Figure S14: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2g**

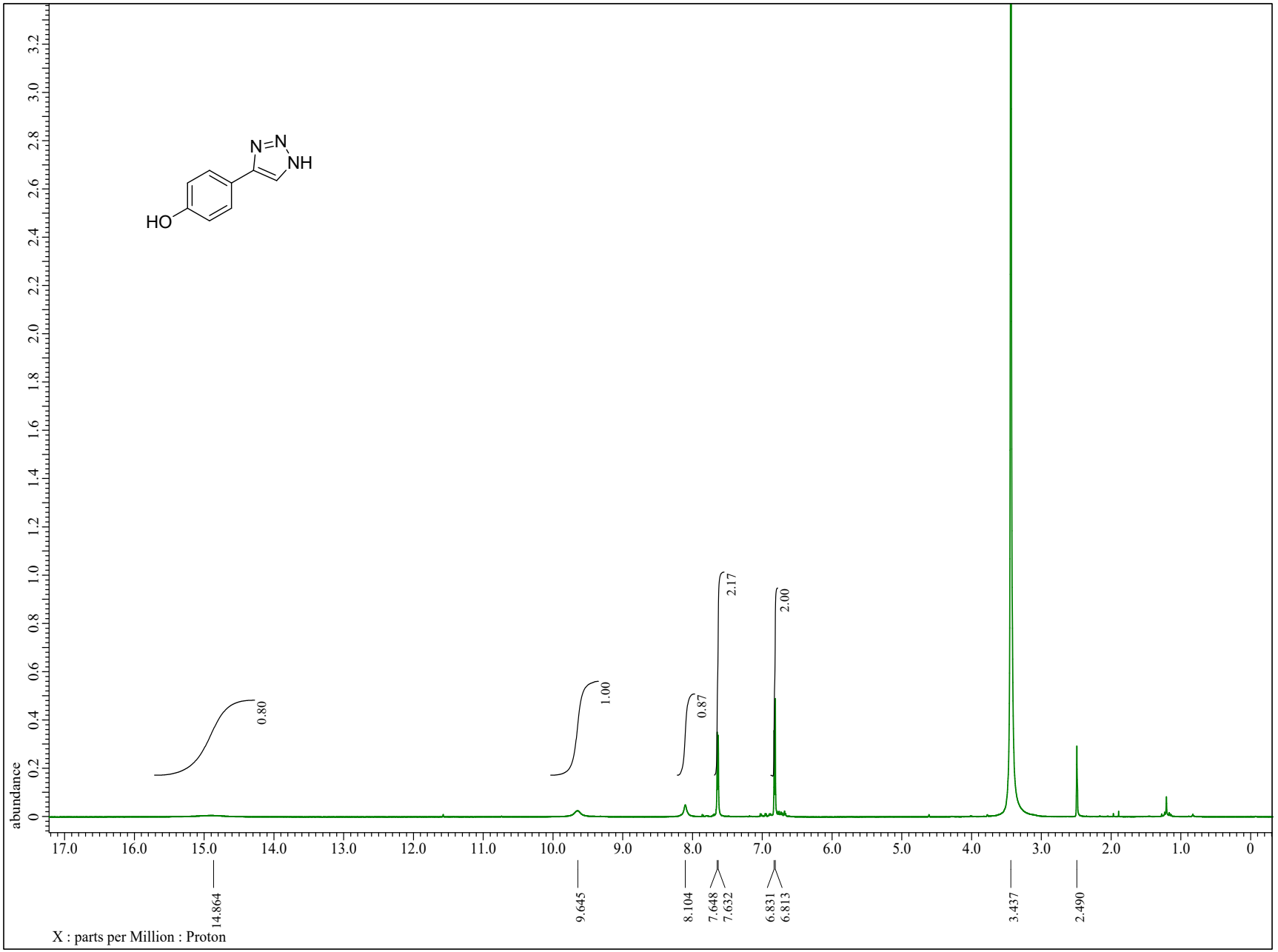

Figure S15: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2h**

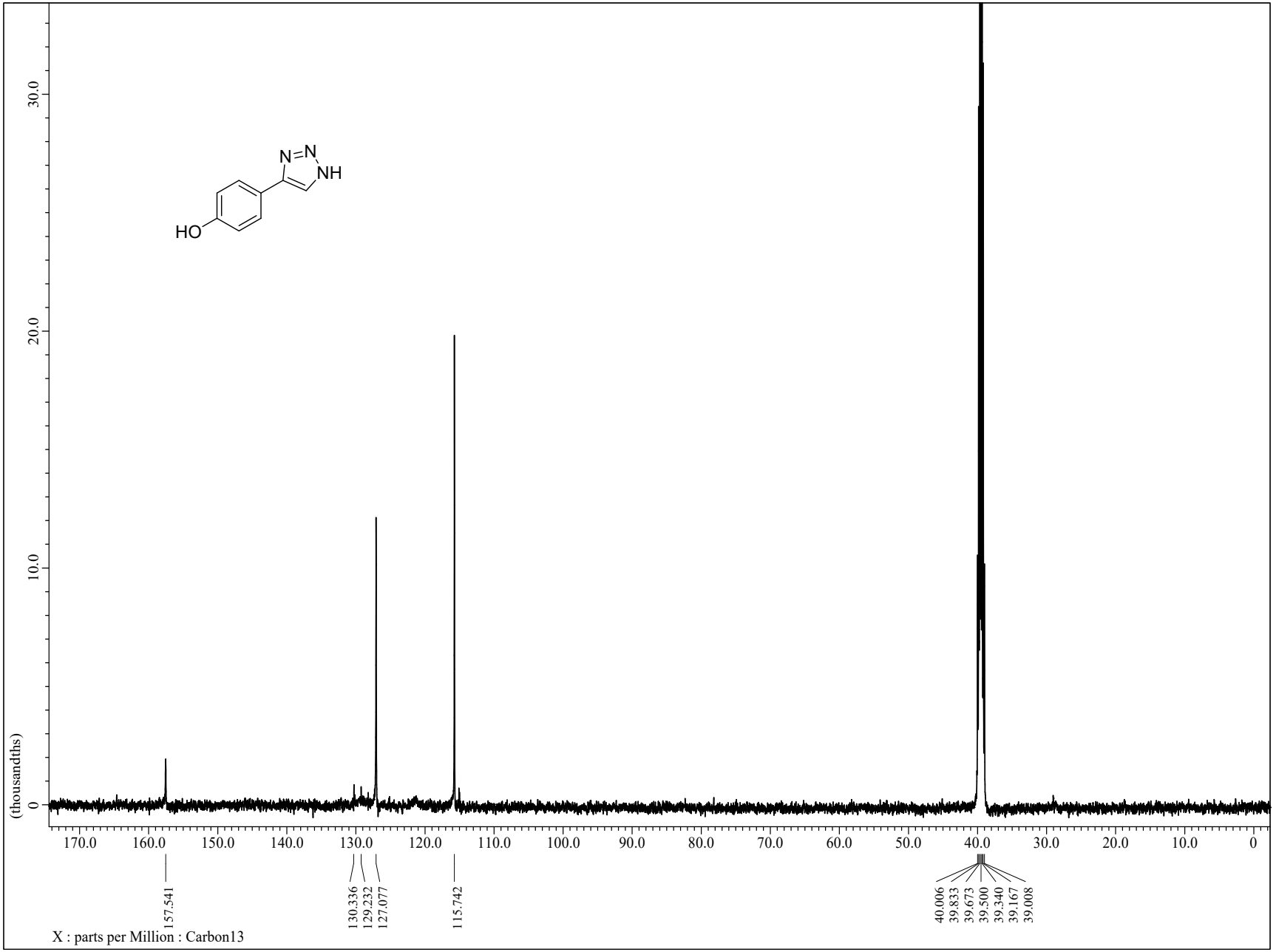

Figure S16: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2h**

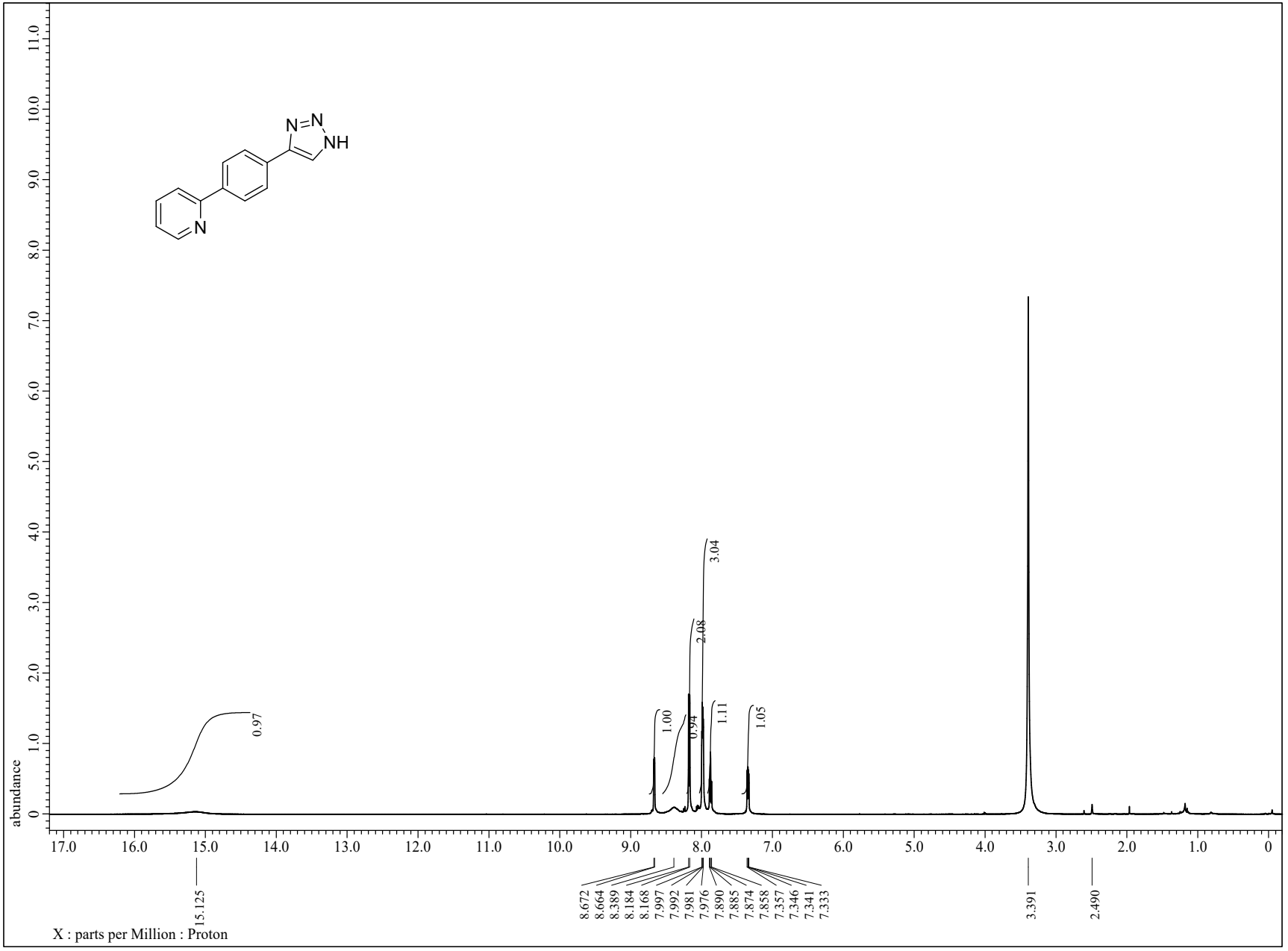

Figure S17: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2i**

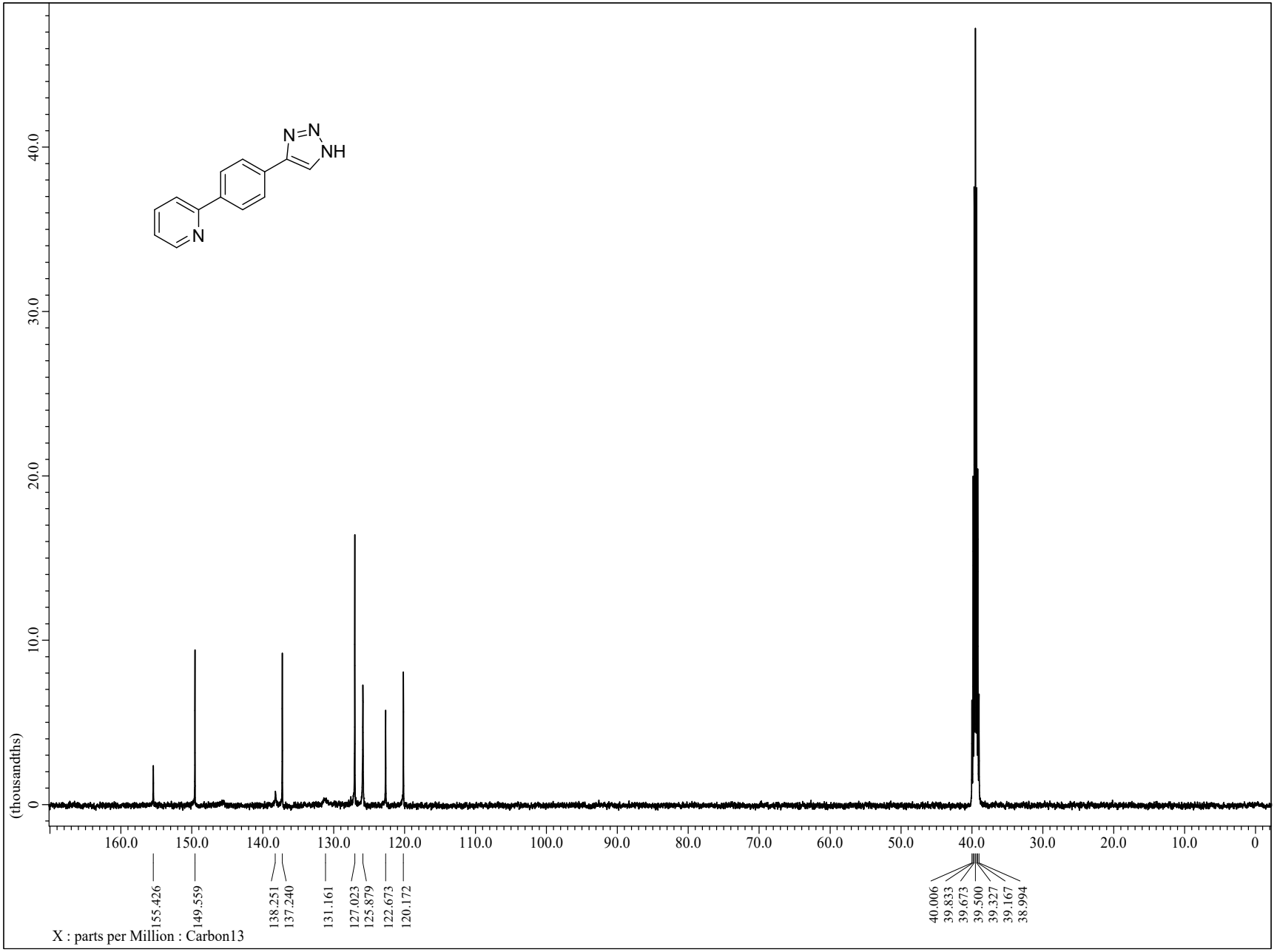

Figure S18: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2i**

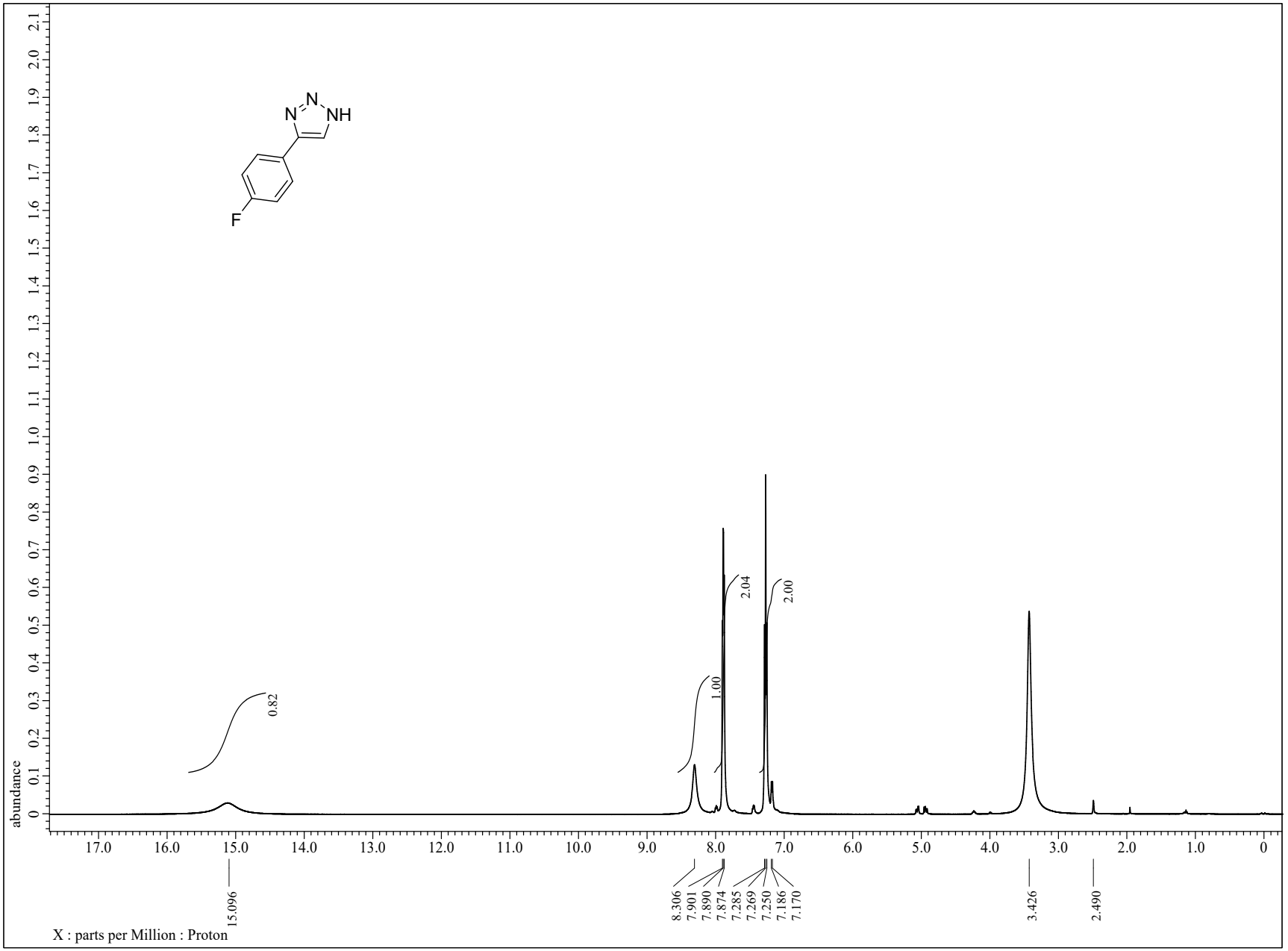

Figure S19: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2j**

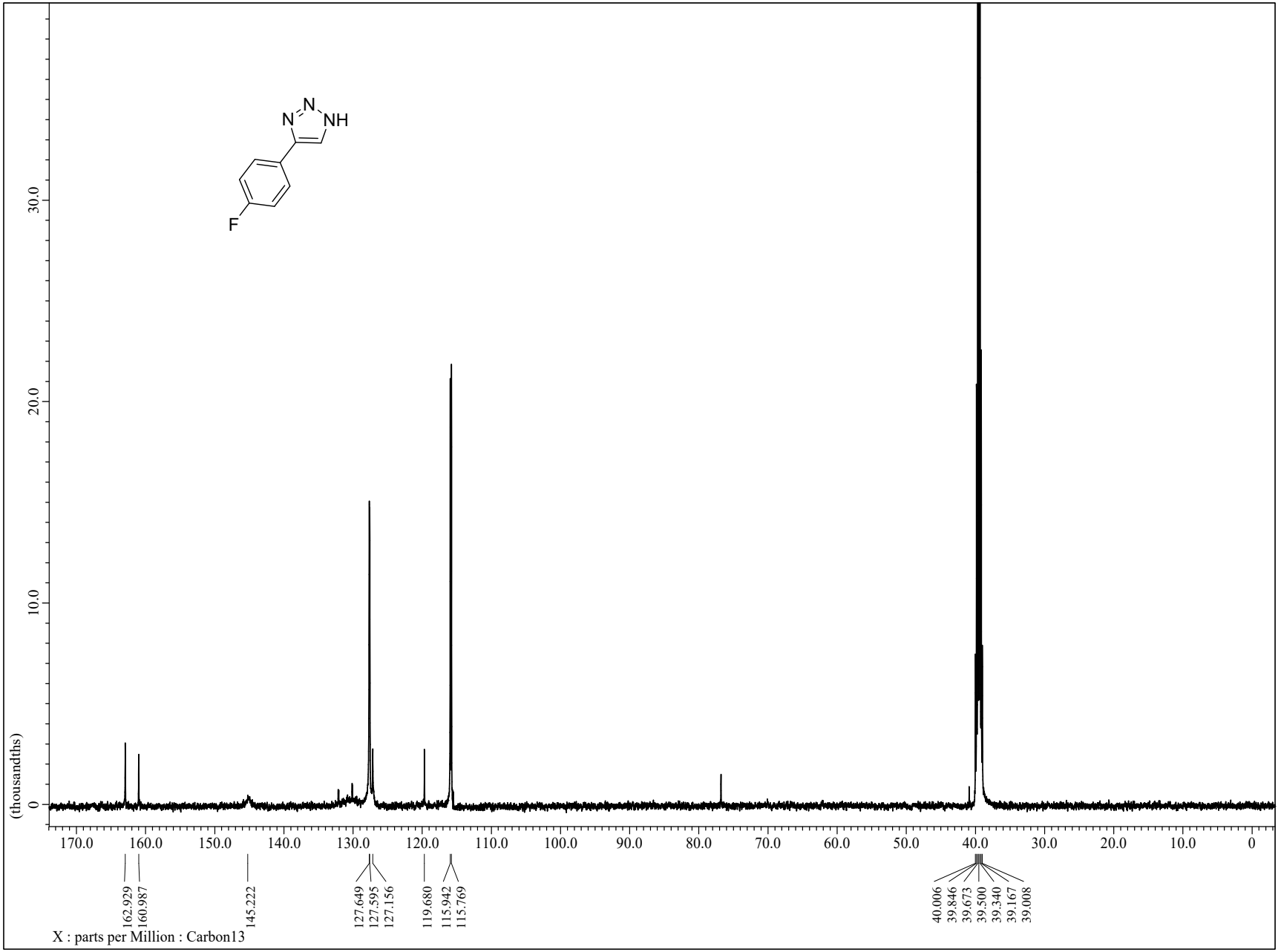

Figure S20: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2j**

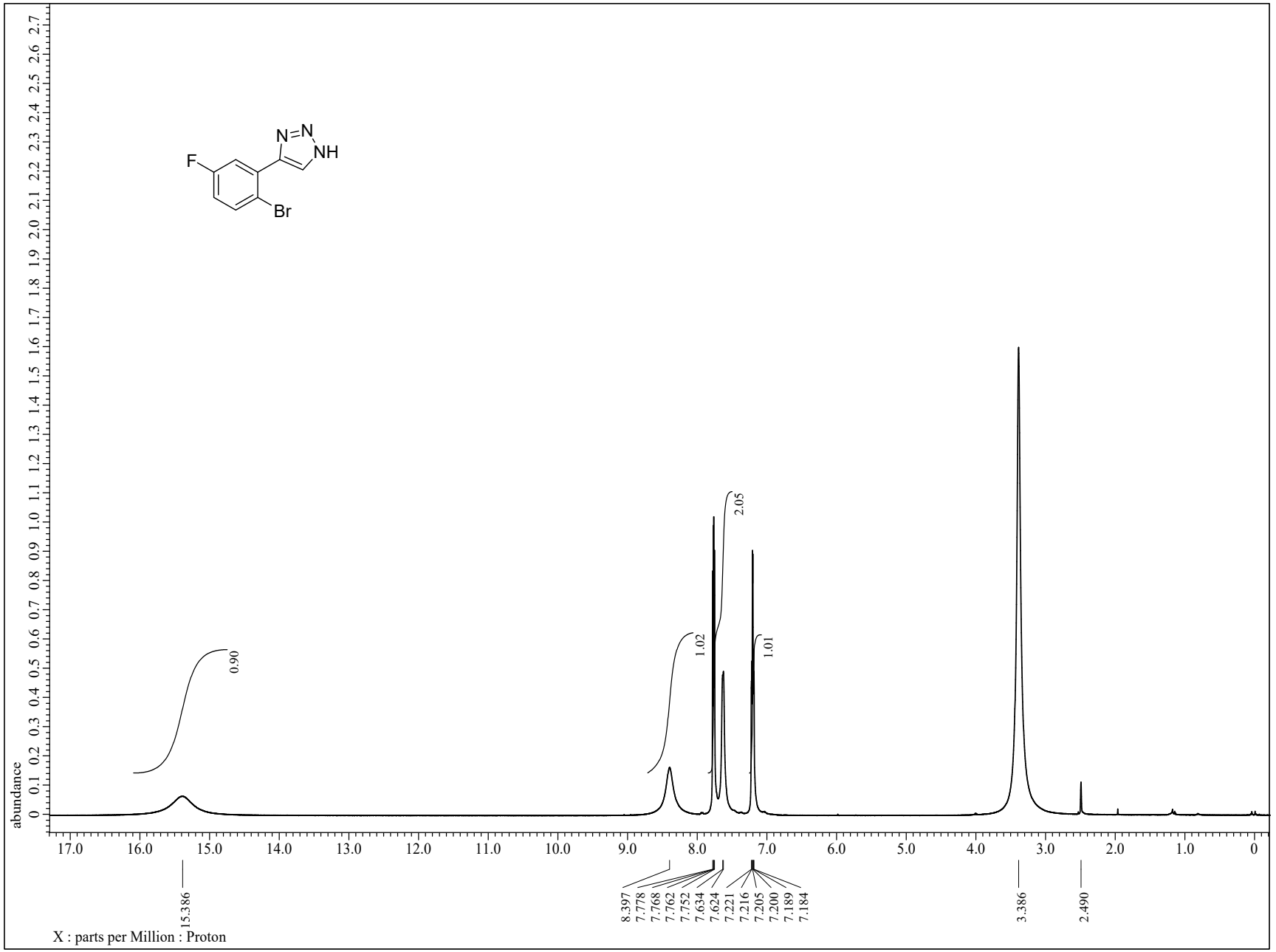

Figure S21: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2k**

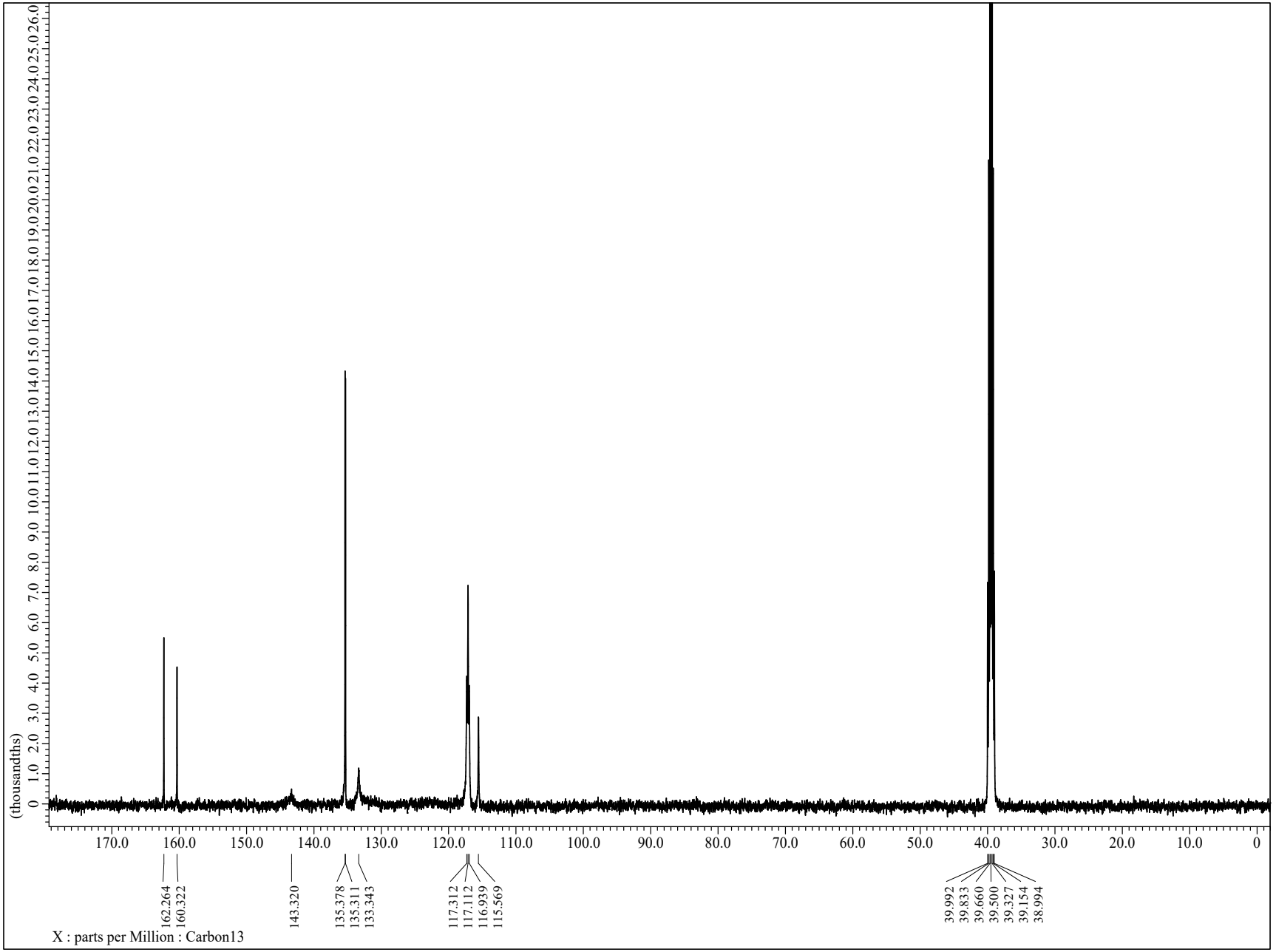

Figure S22: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2k**

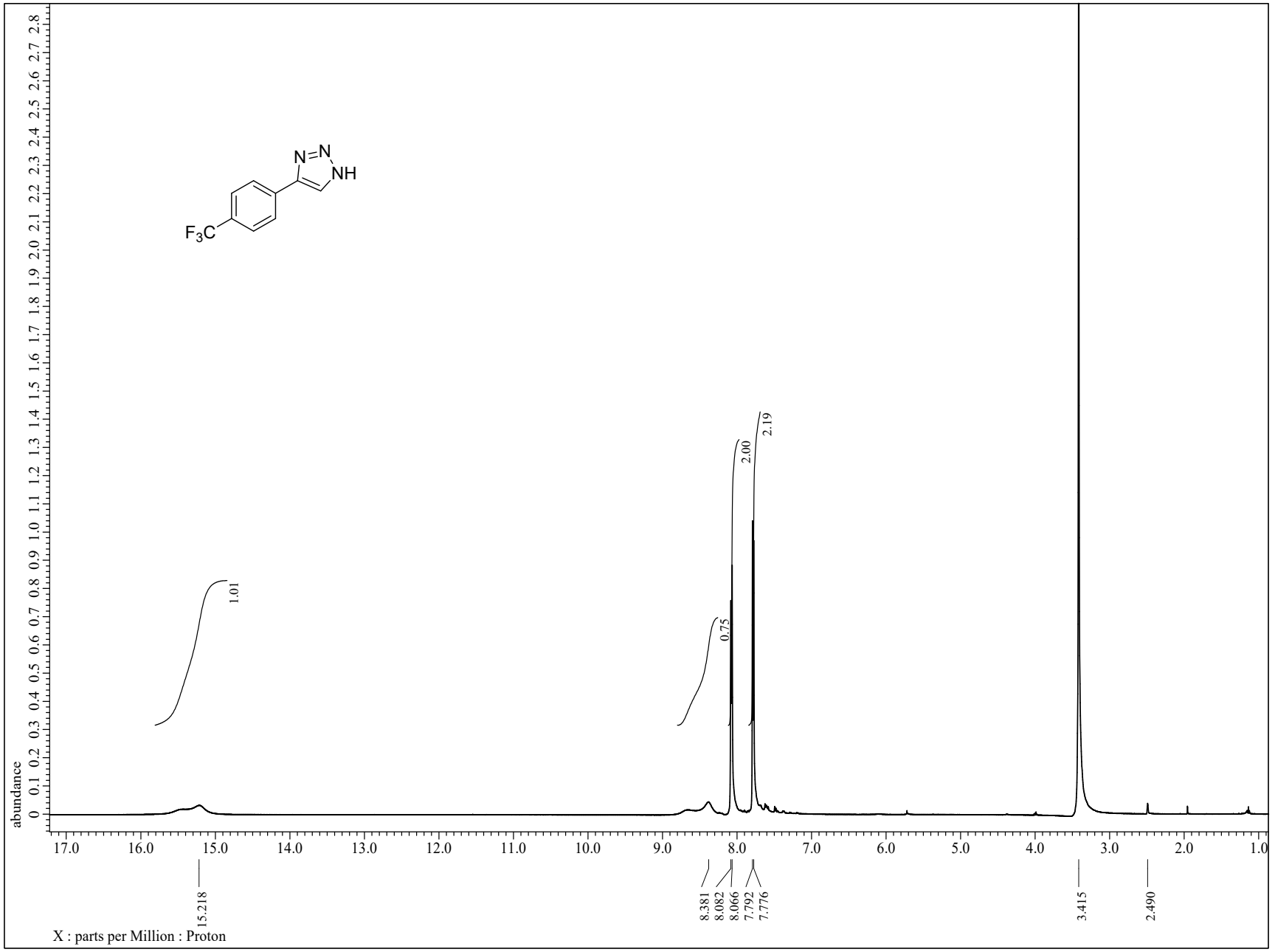

Figure S23: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2l**

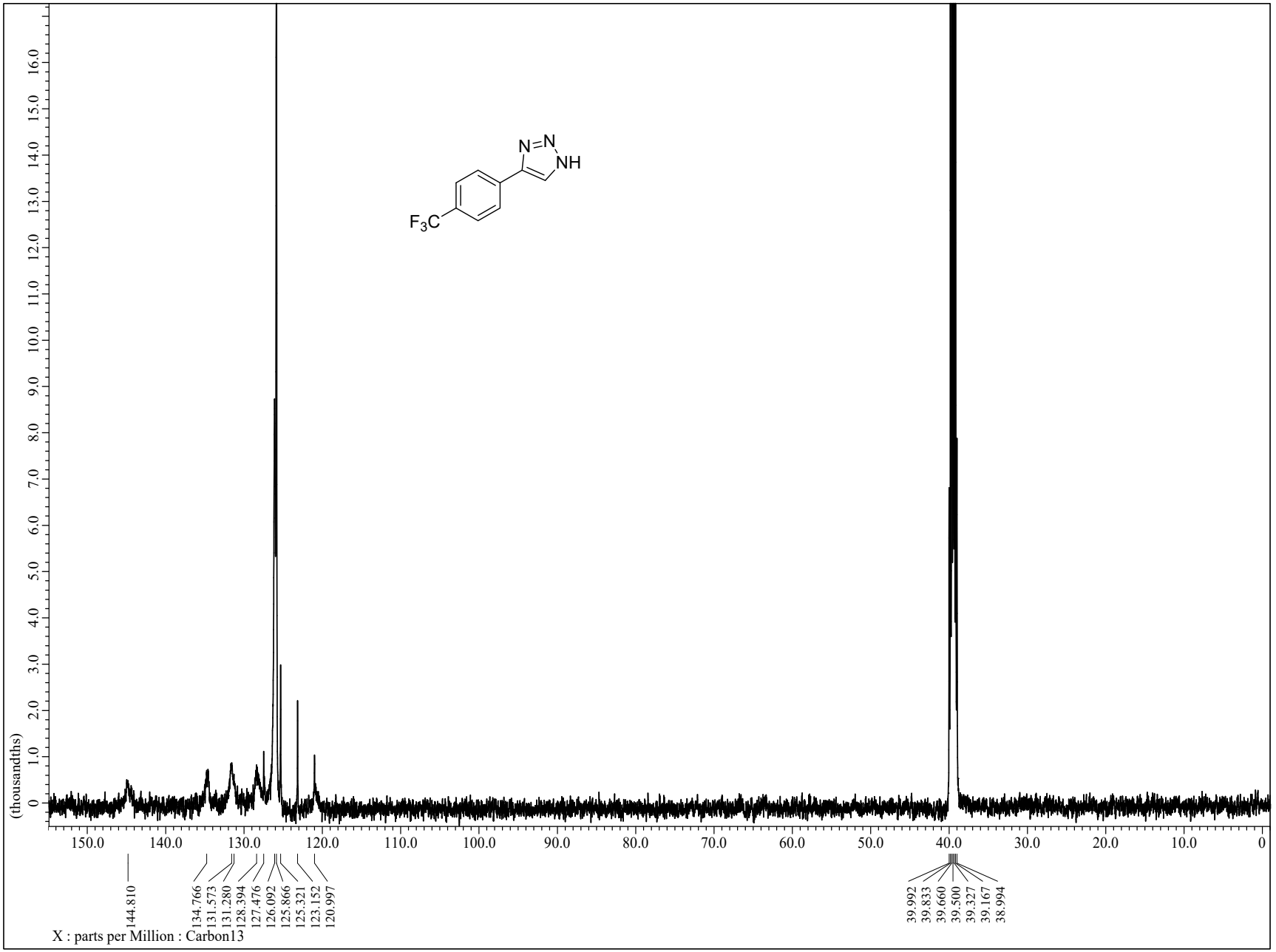

Figure S24: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2l**

3. ^{1}H and ^{13}C NMR spectra of 4,5-disubstituted-*NH*-1,2,3-triazoles(**2m-af**)

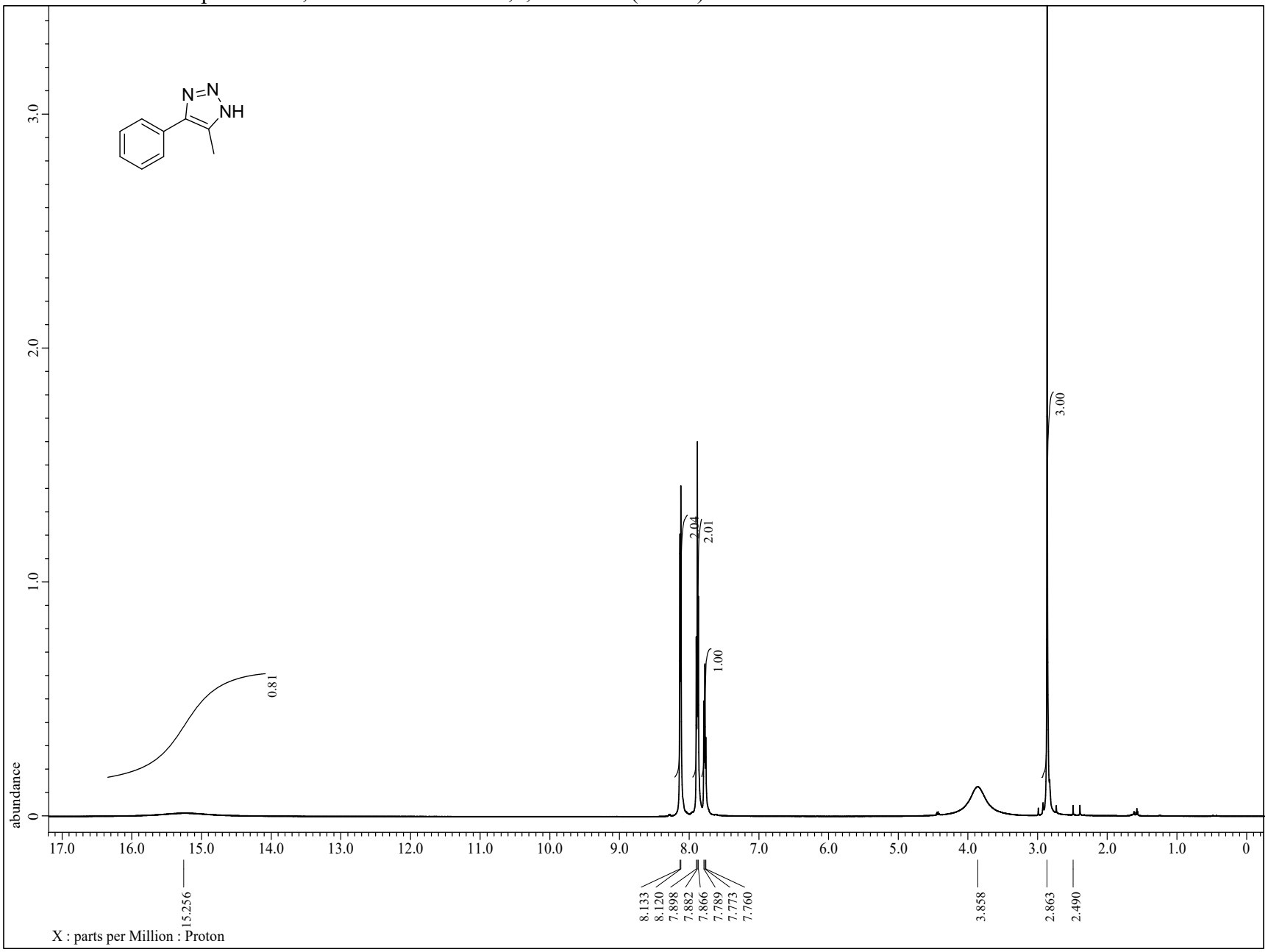

Figure S25: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2m**

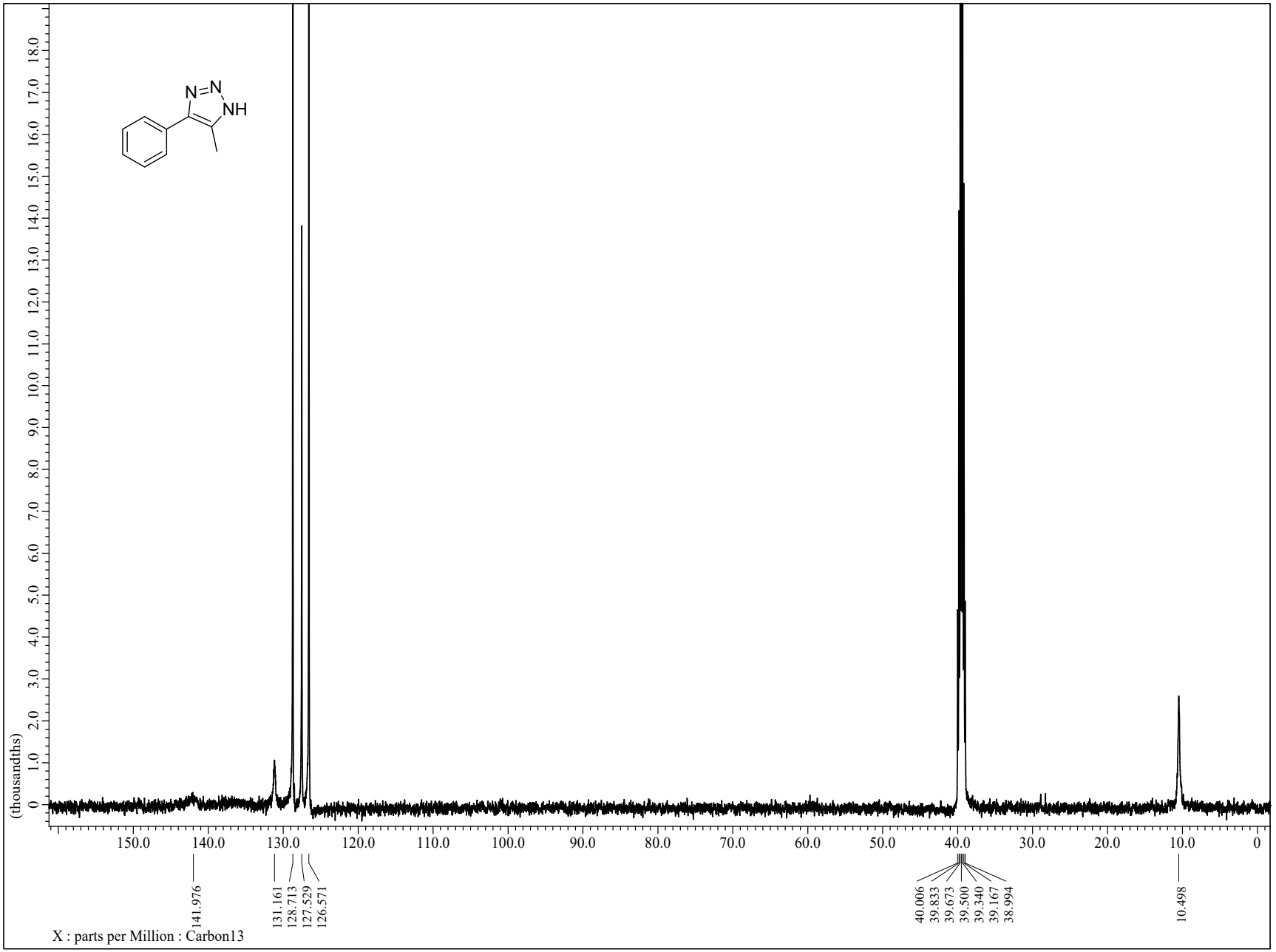

Figure S26: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2m**[2]

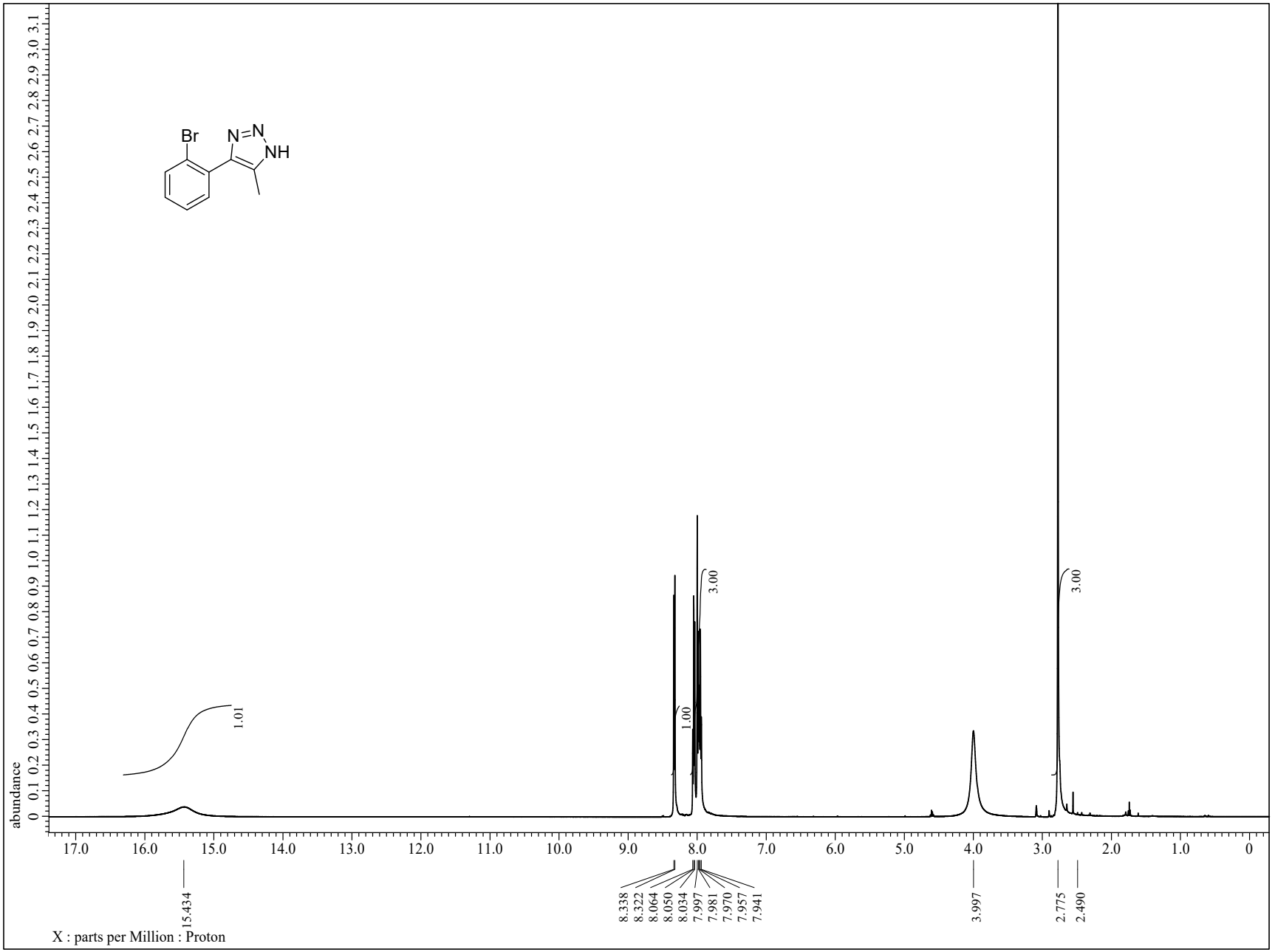

Figure S27: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2n**

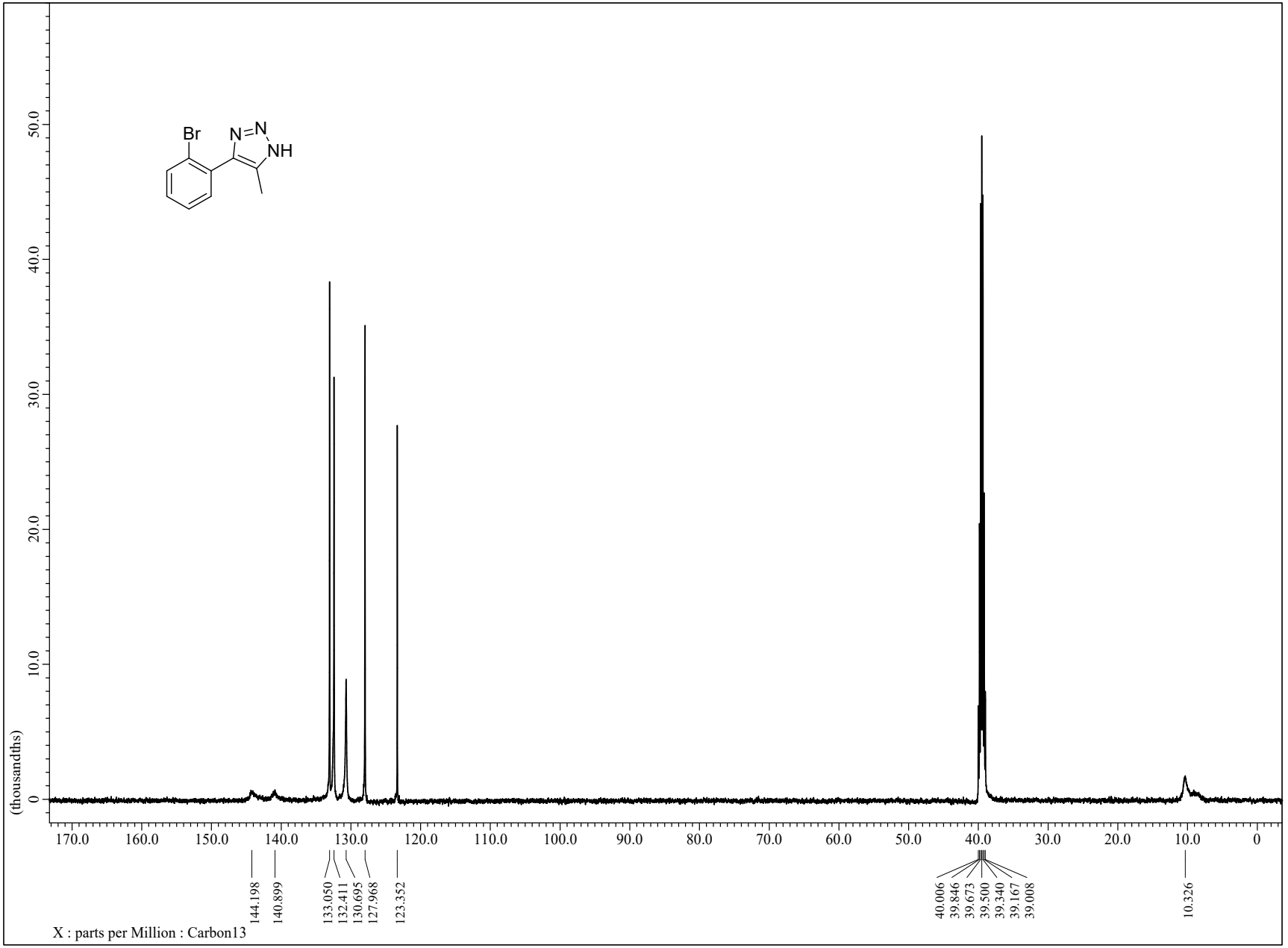

Figure S28: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2n**

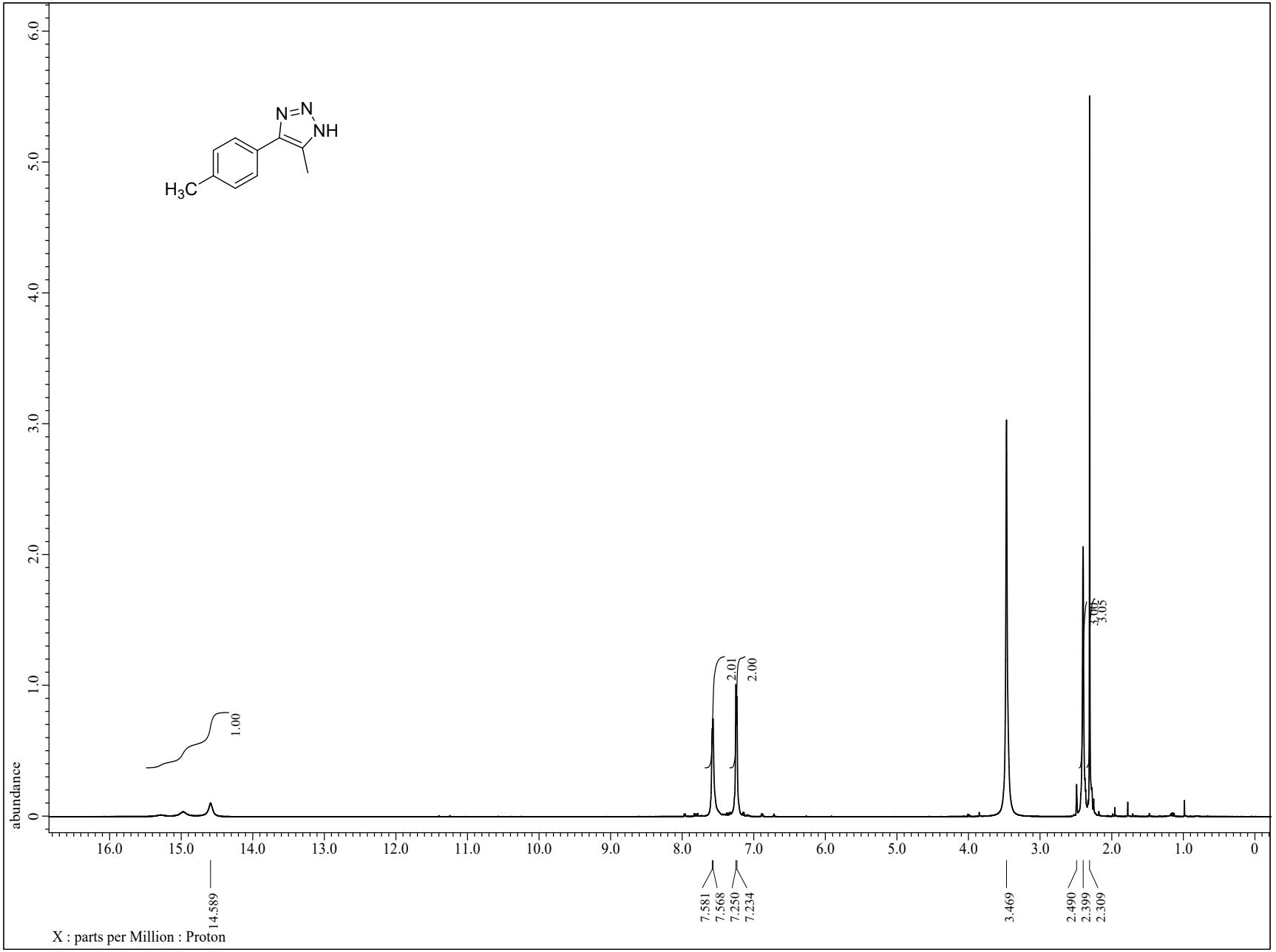

Figure S29: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2o**

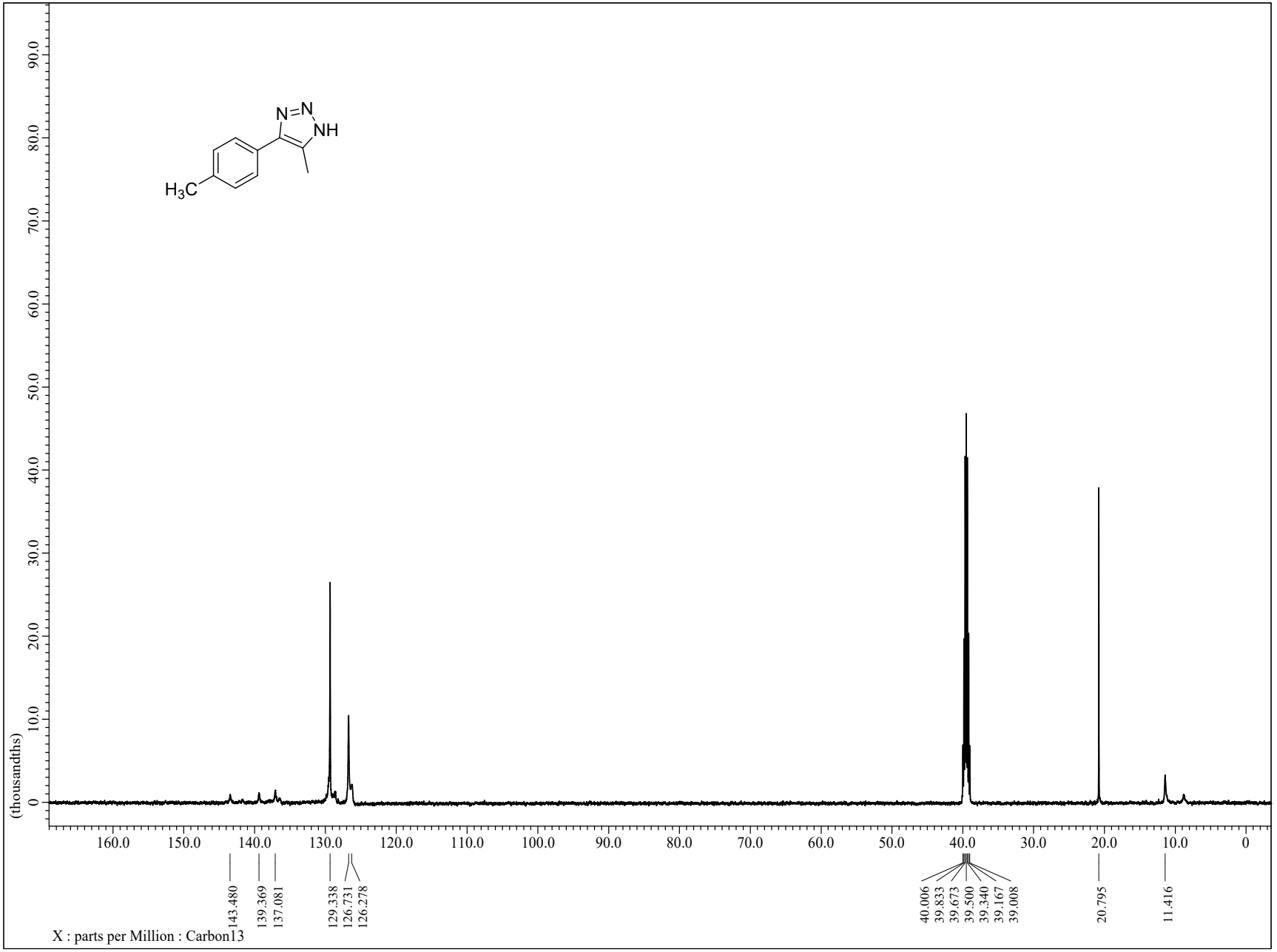

Figure S30: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2o**

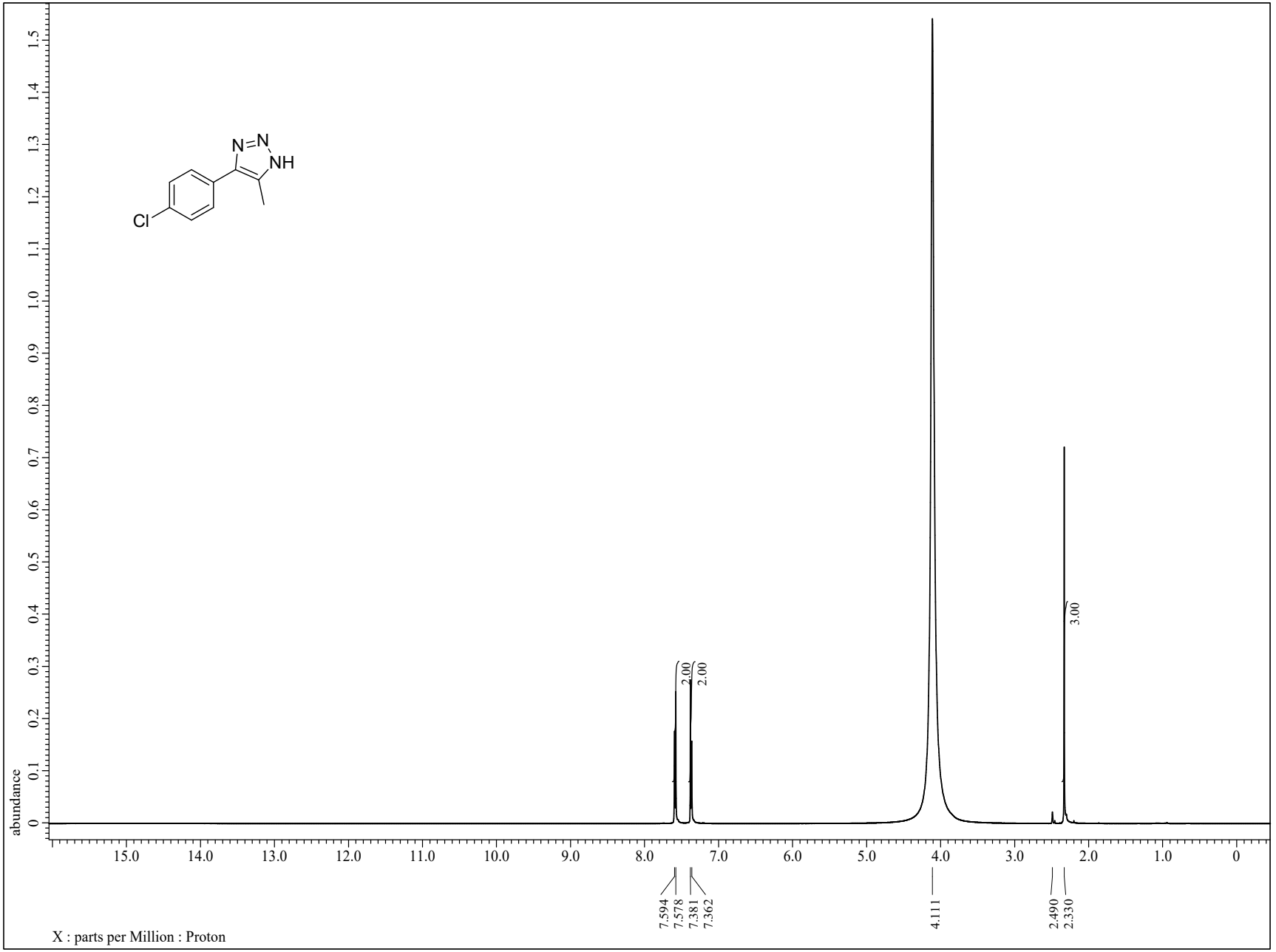

Figure S31: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2p**

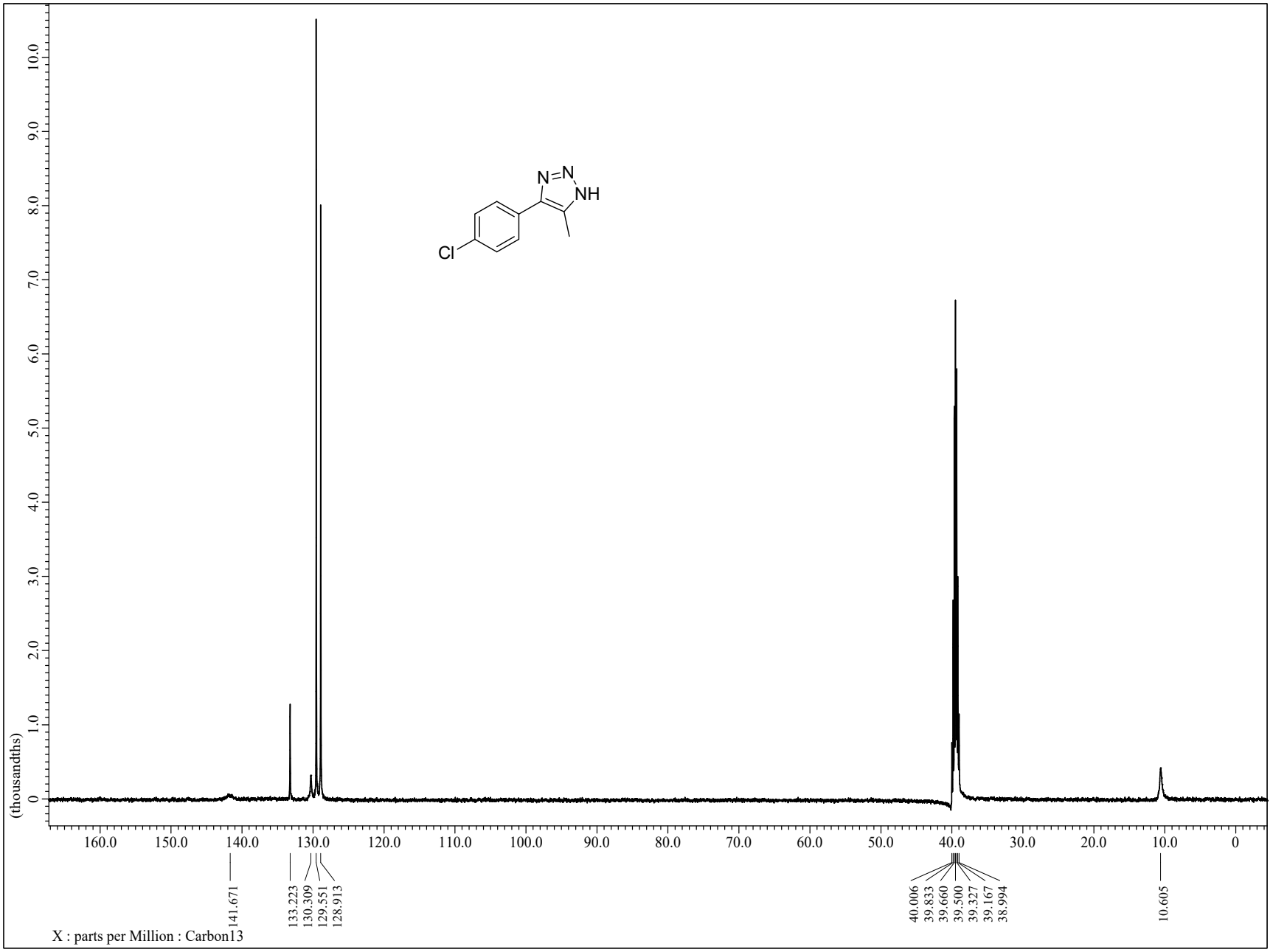

Figure S32: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2p**

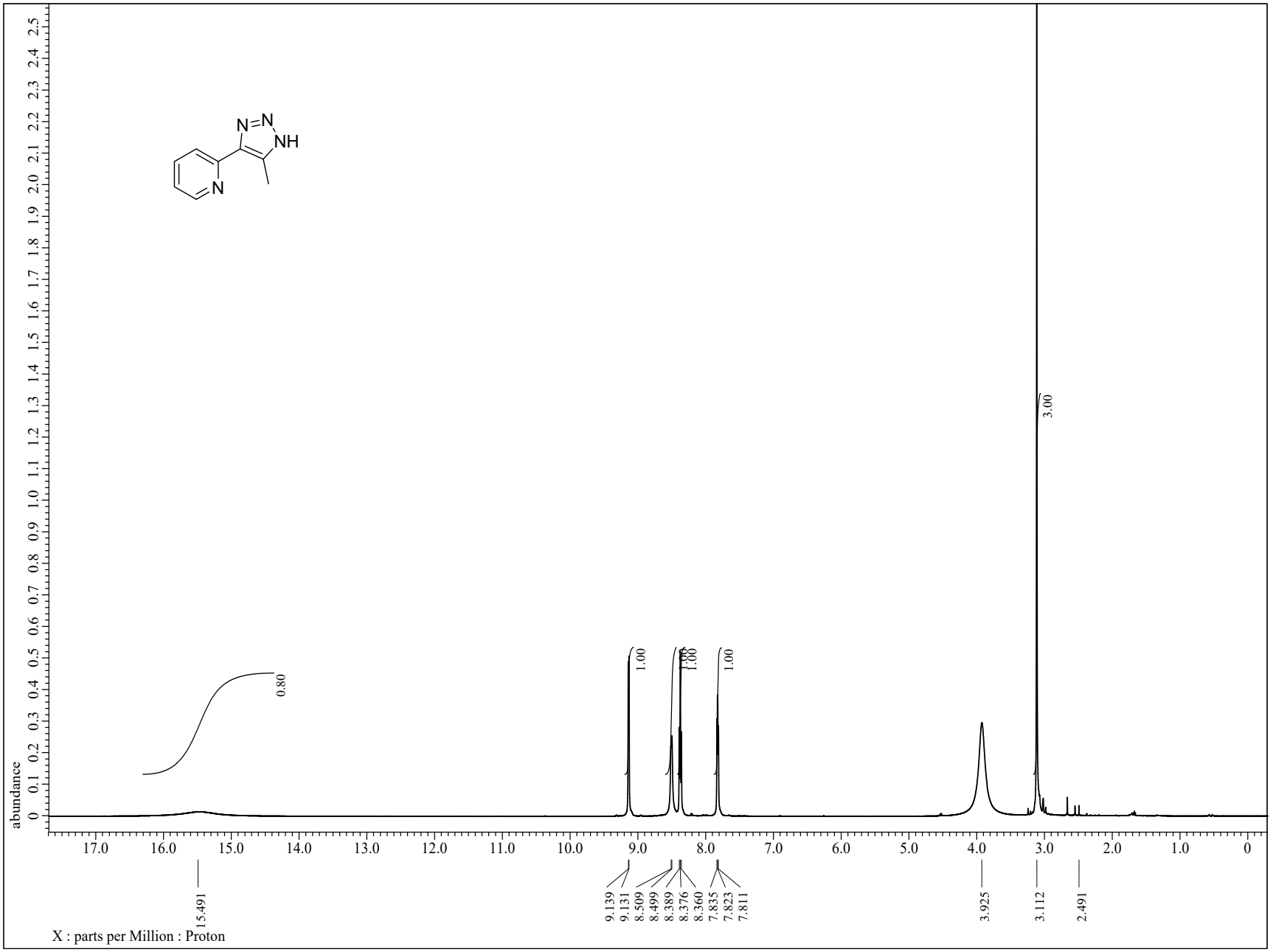

Figure S33: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2q**

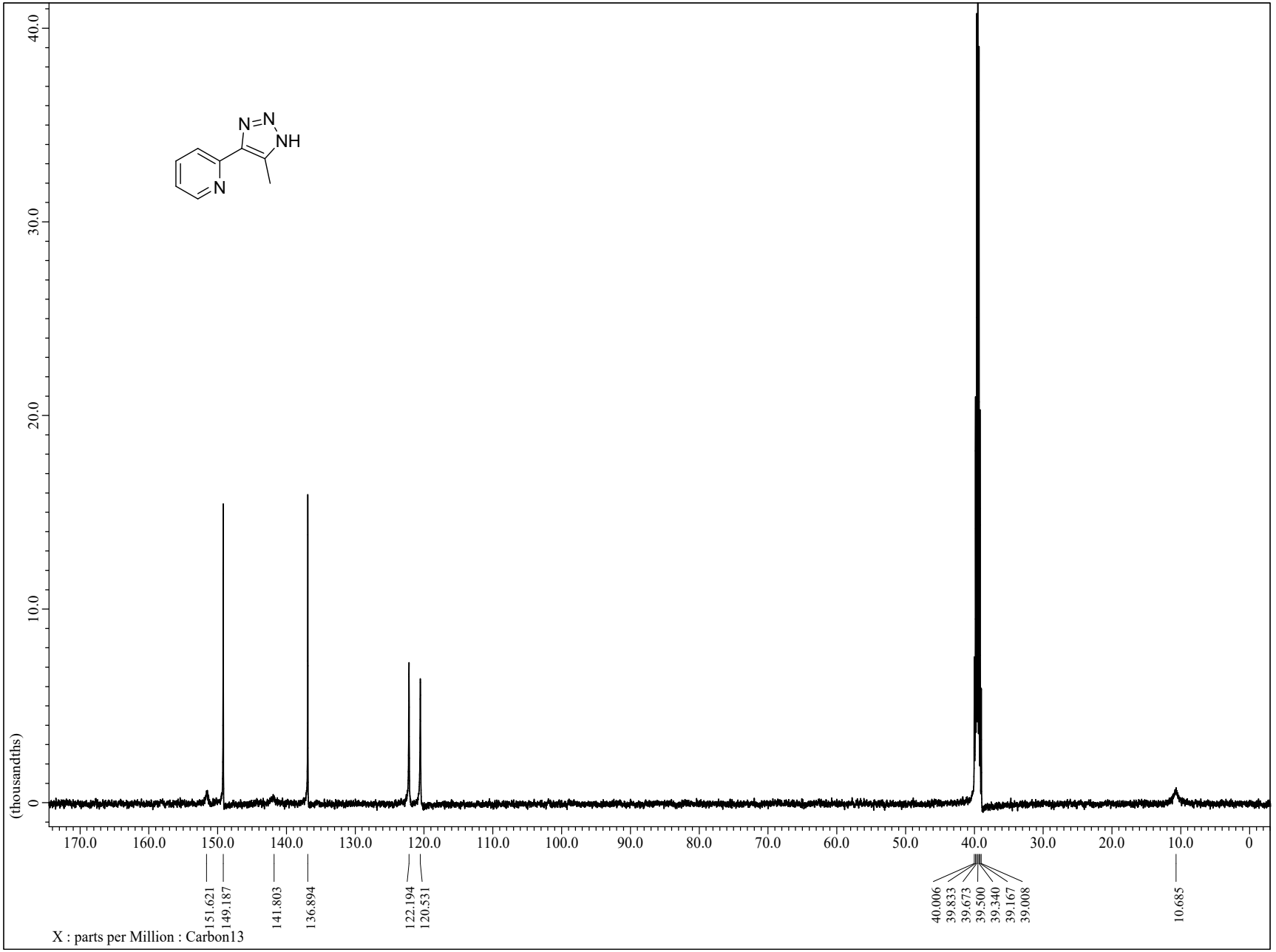

Figure S34: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2q**

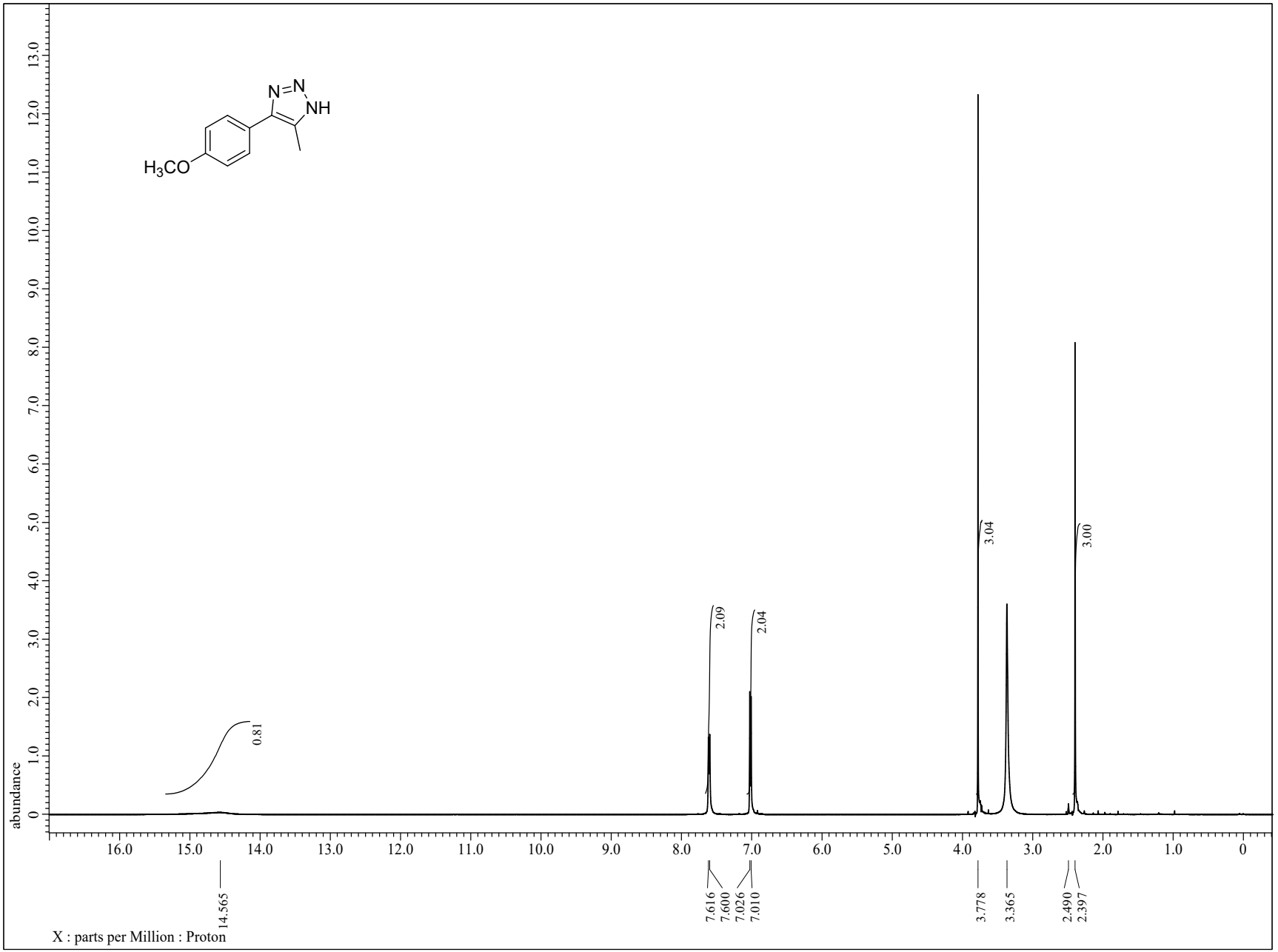

Figure S35: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2r**[2]

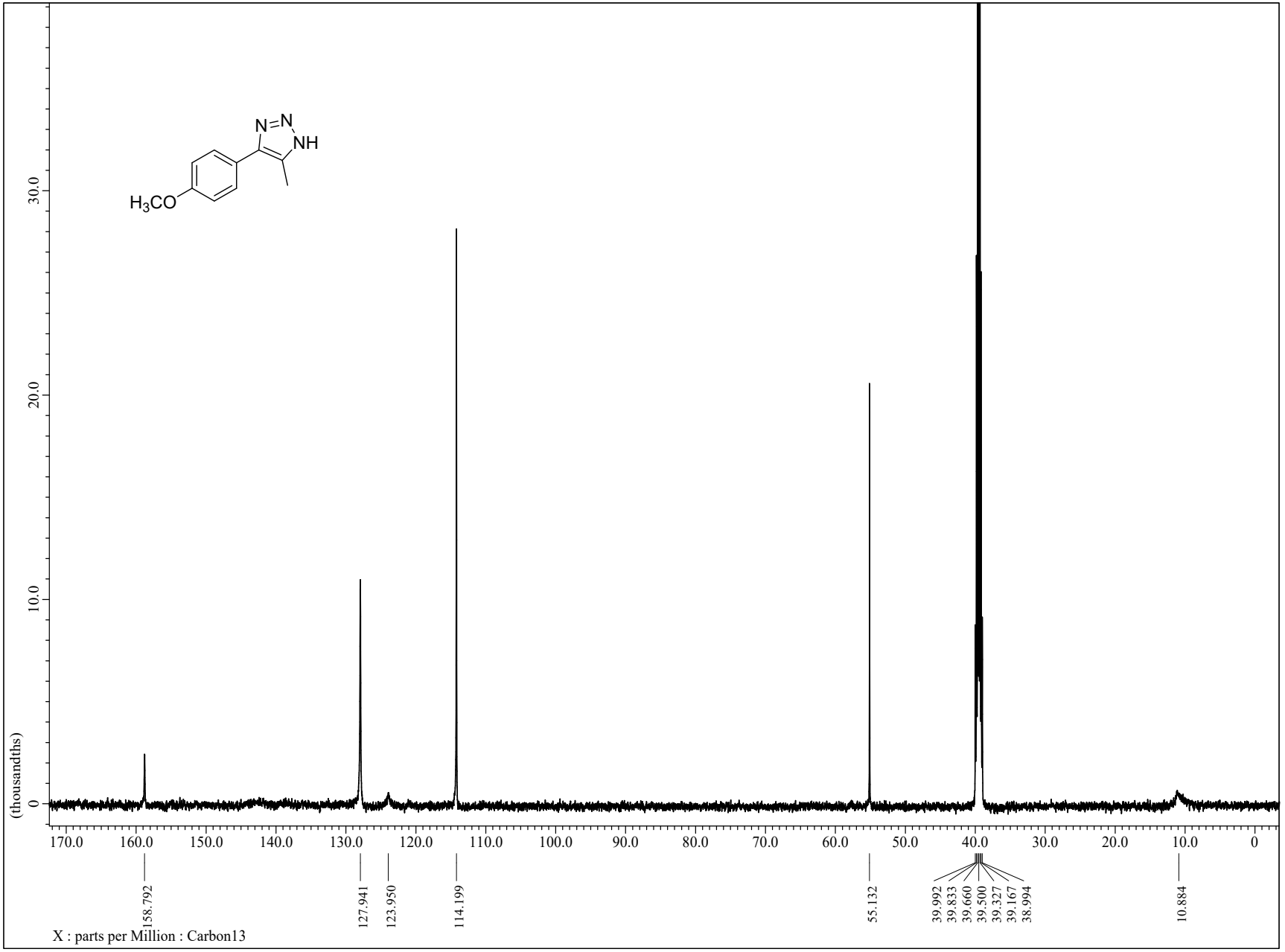

Figure S36: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2r**

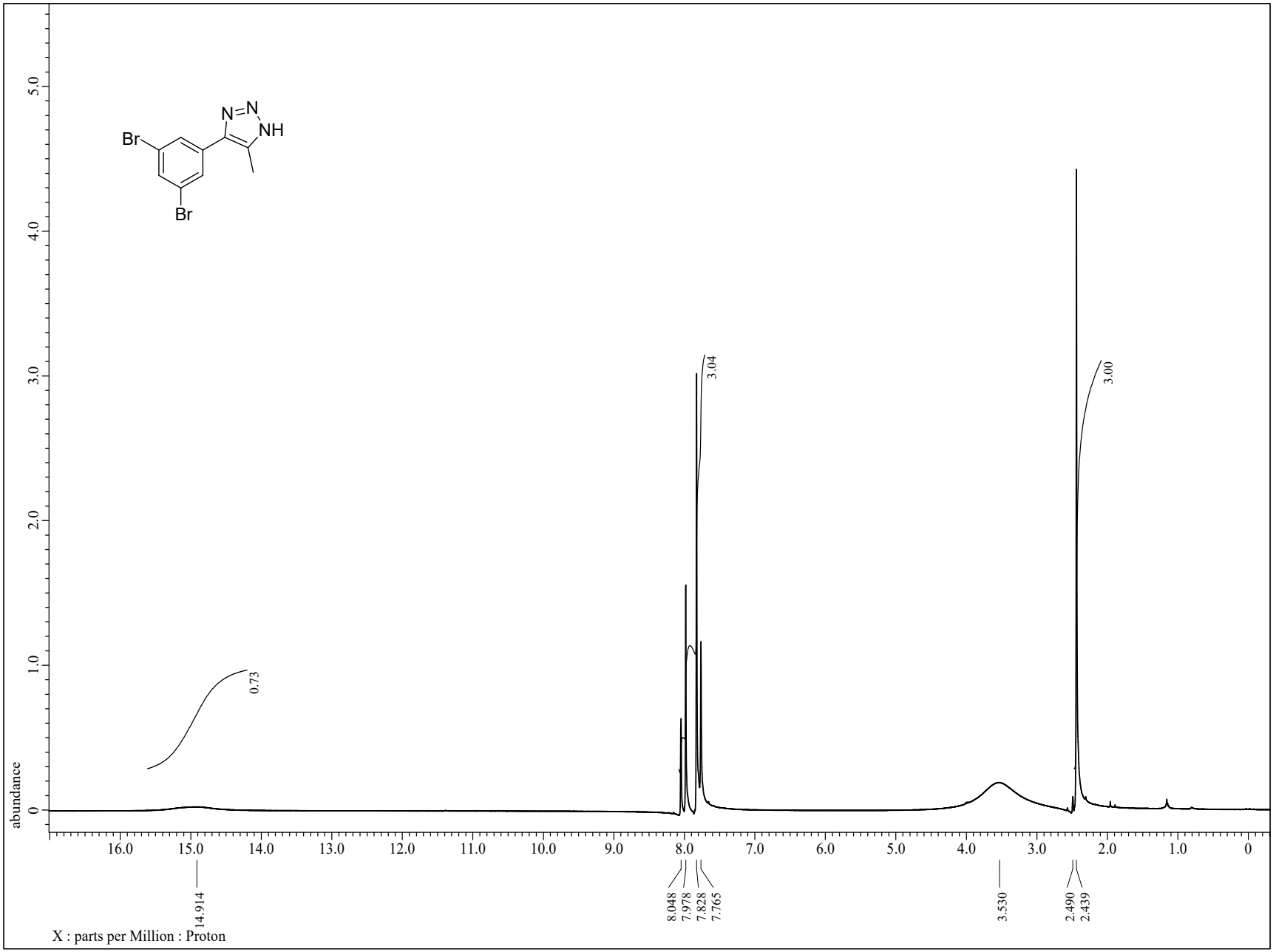

Figure S37: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2s**

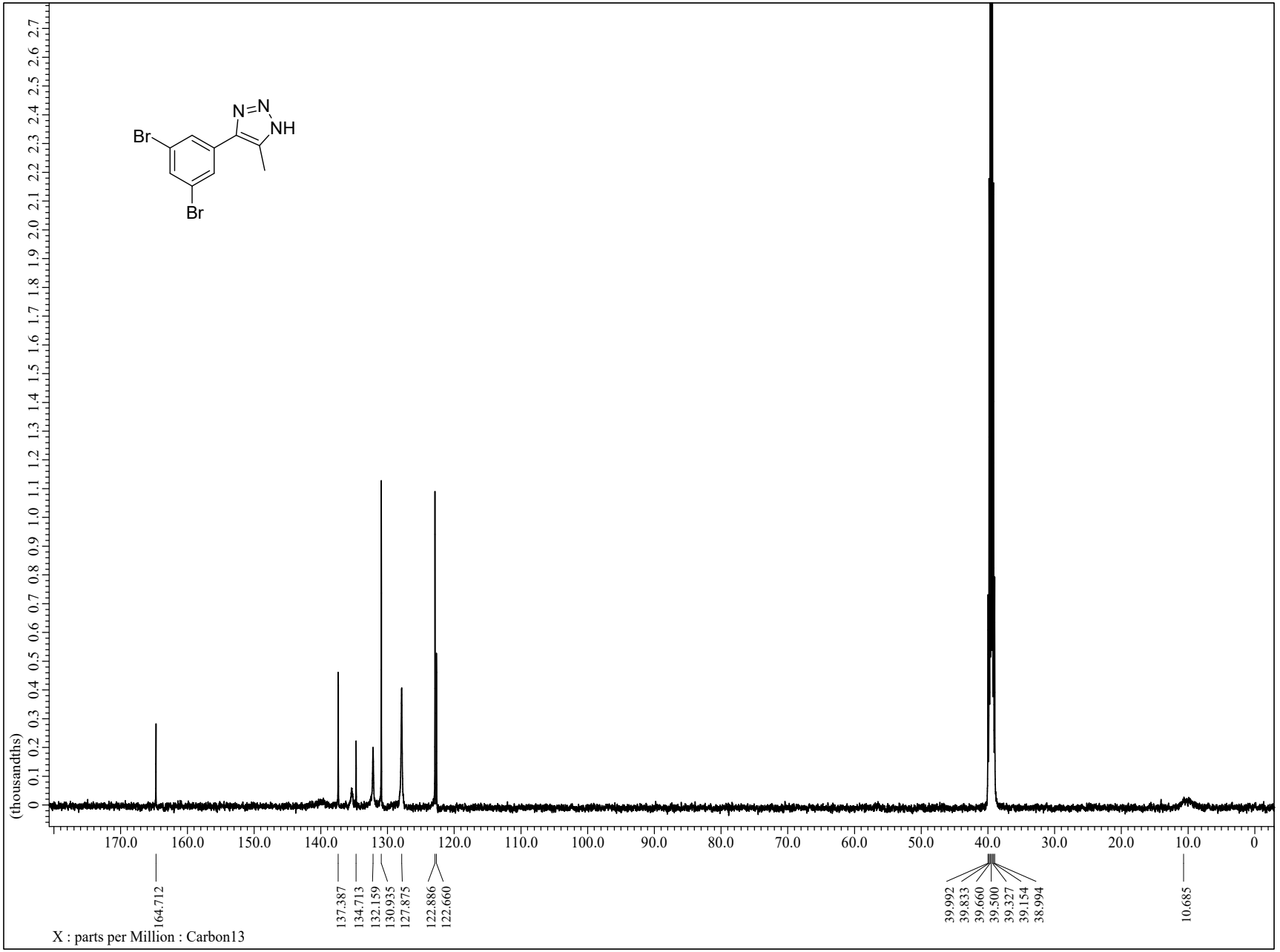

Figure S38: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2s**

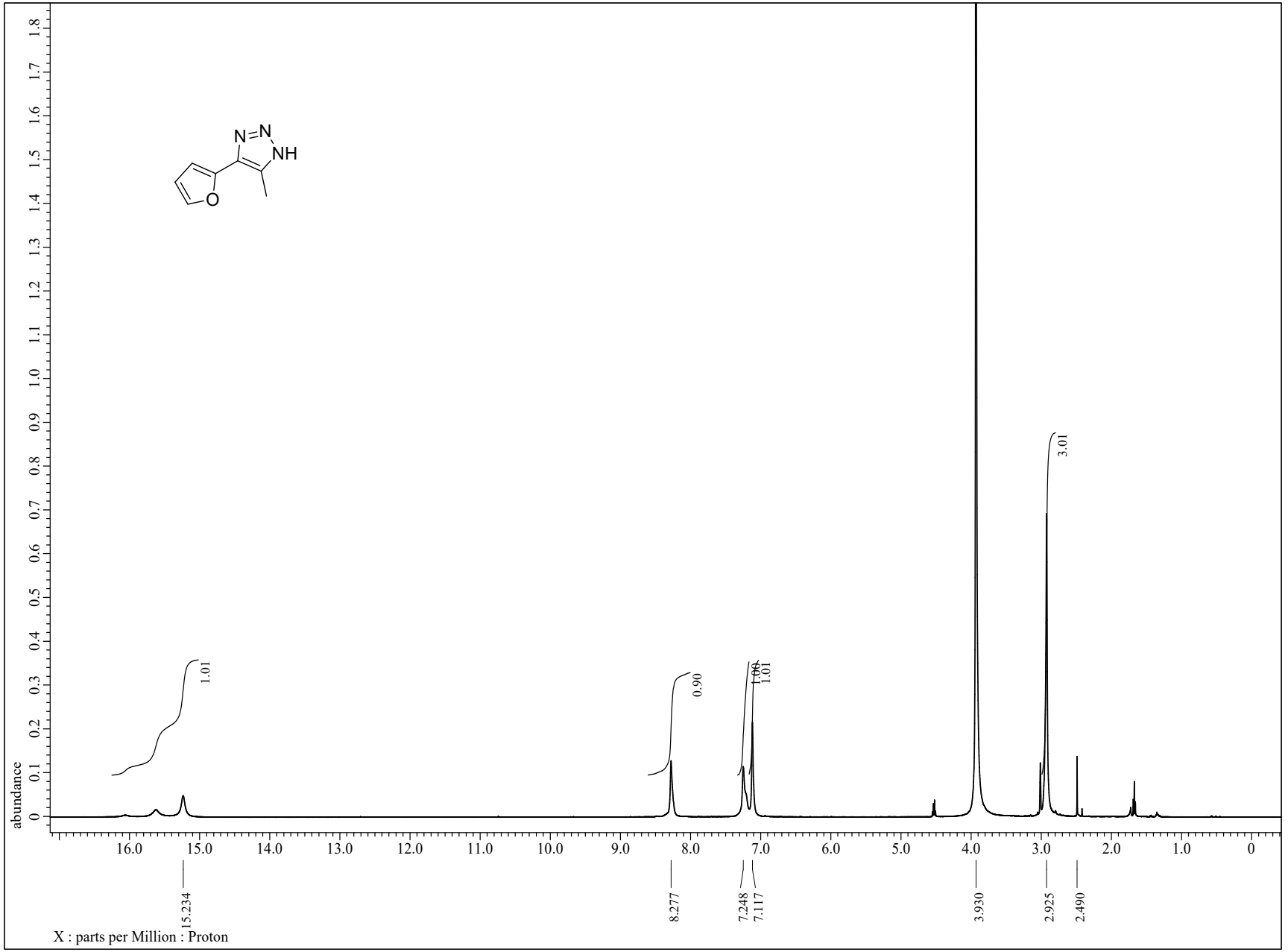

Figure S39: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2t**

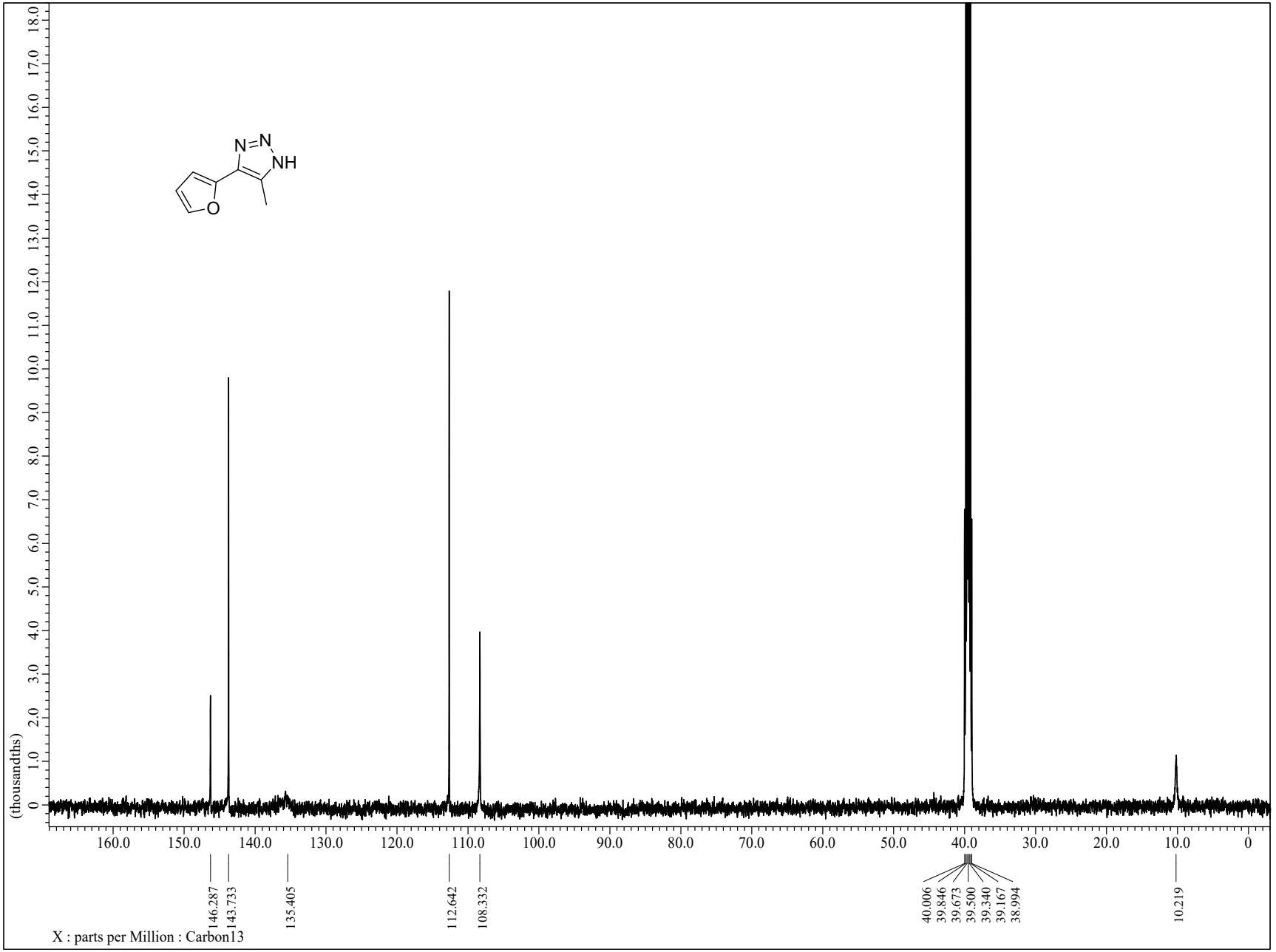

Figure S40: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2t**

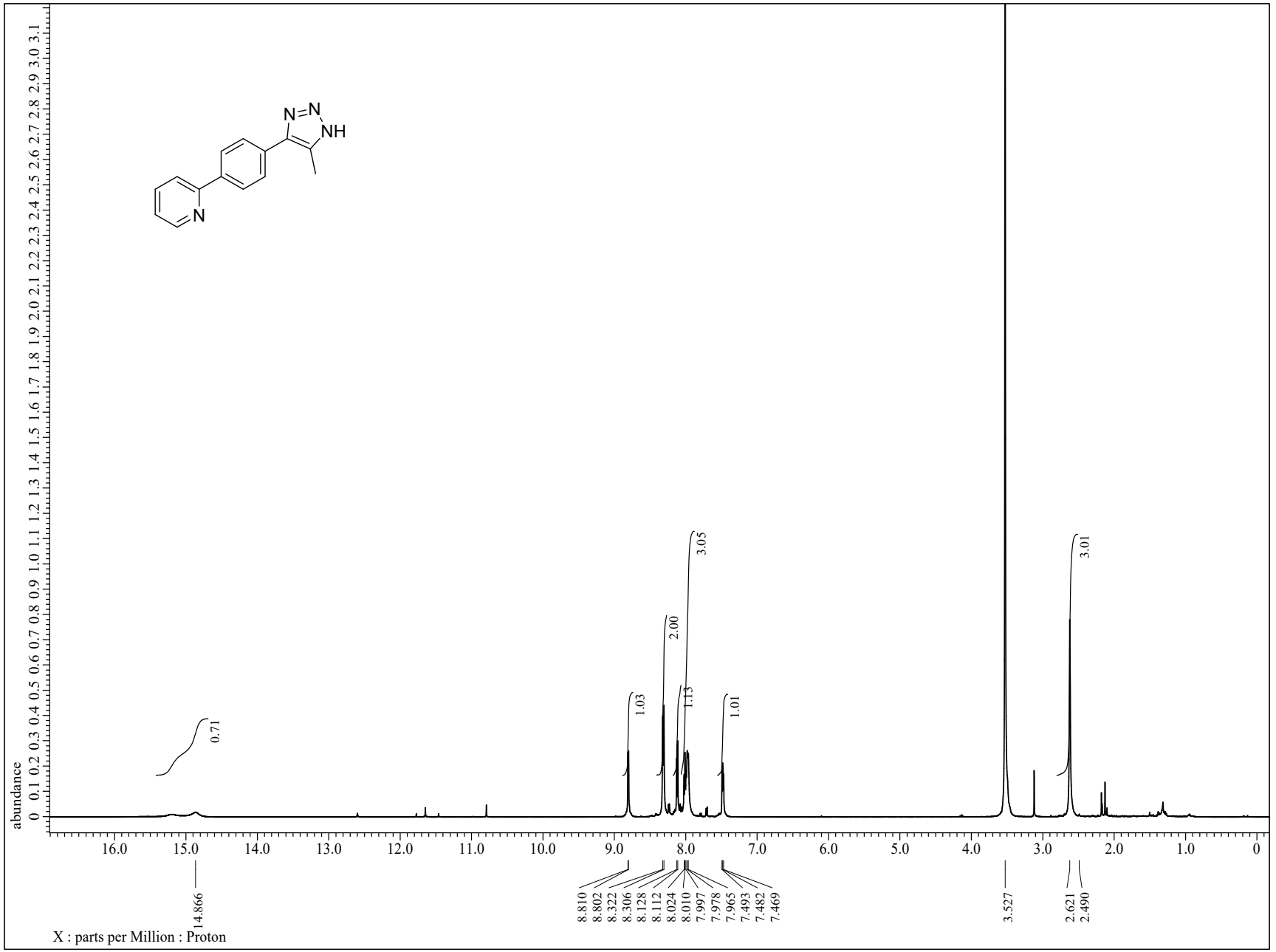

Figure S41: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2u**

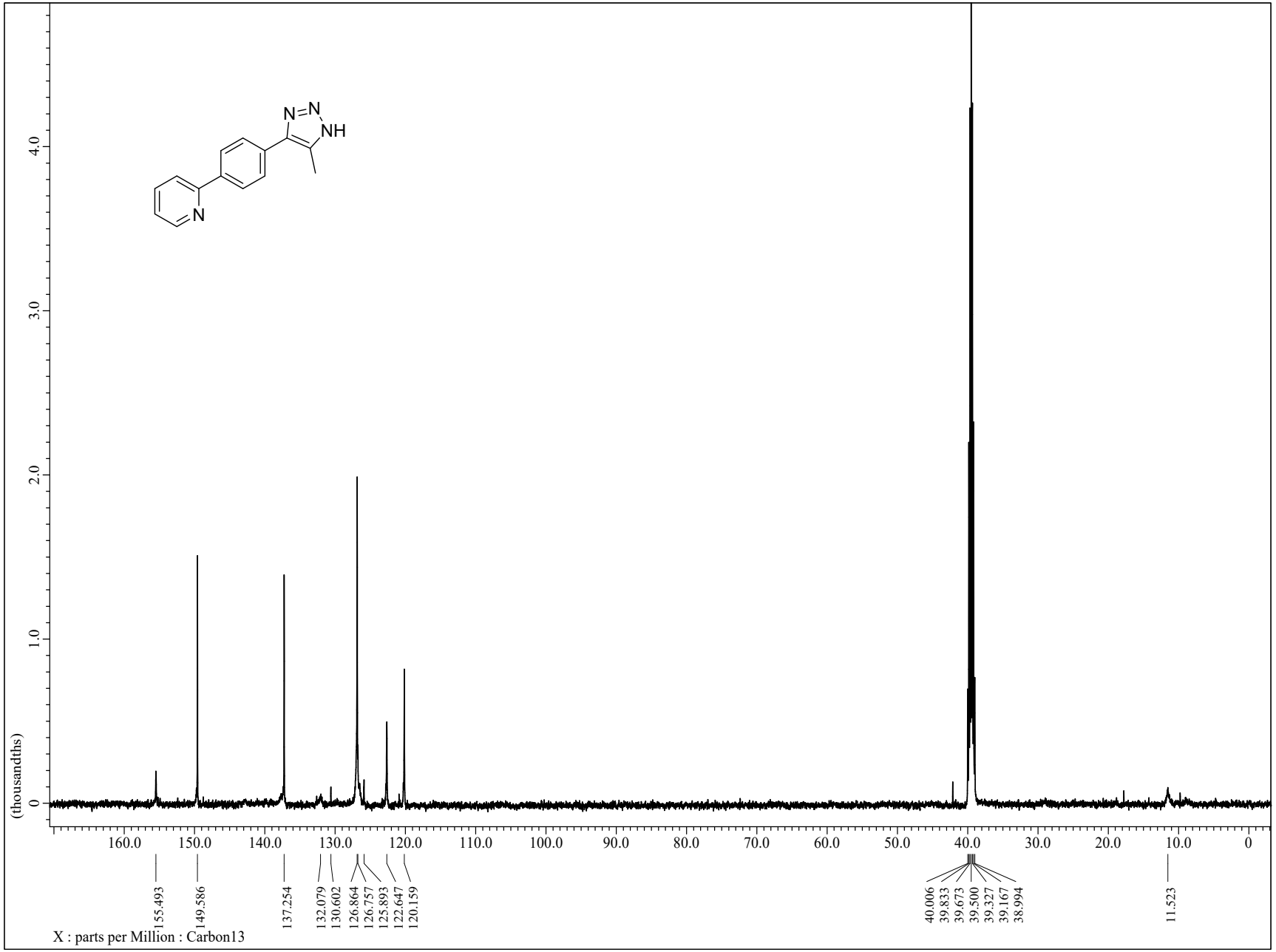

Figure S42: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2u**

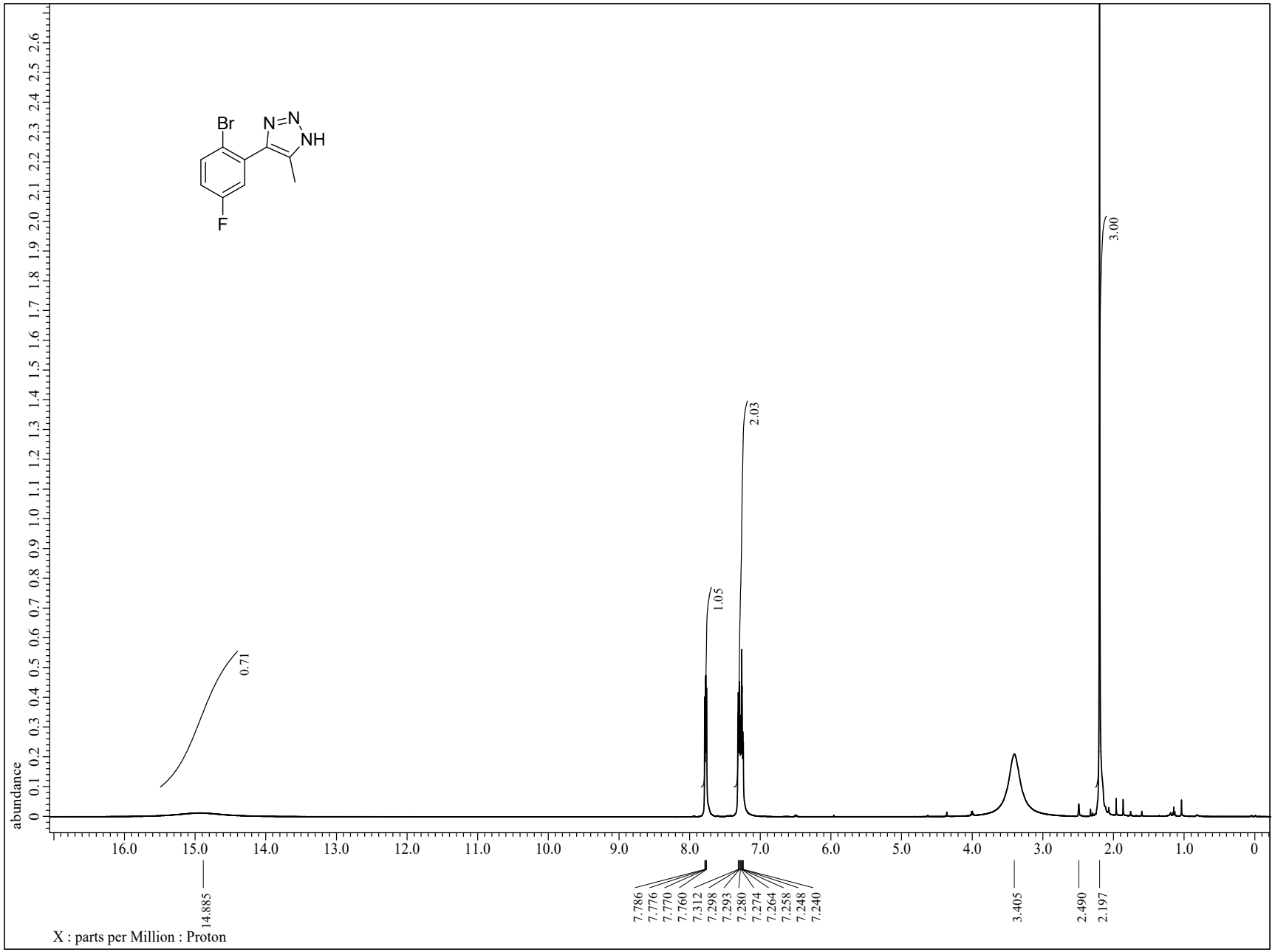

Figure S43: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2v**

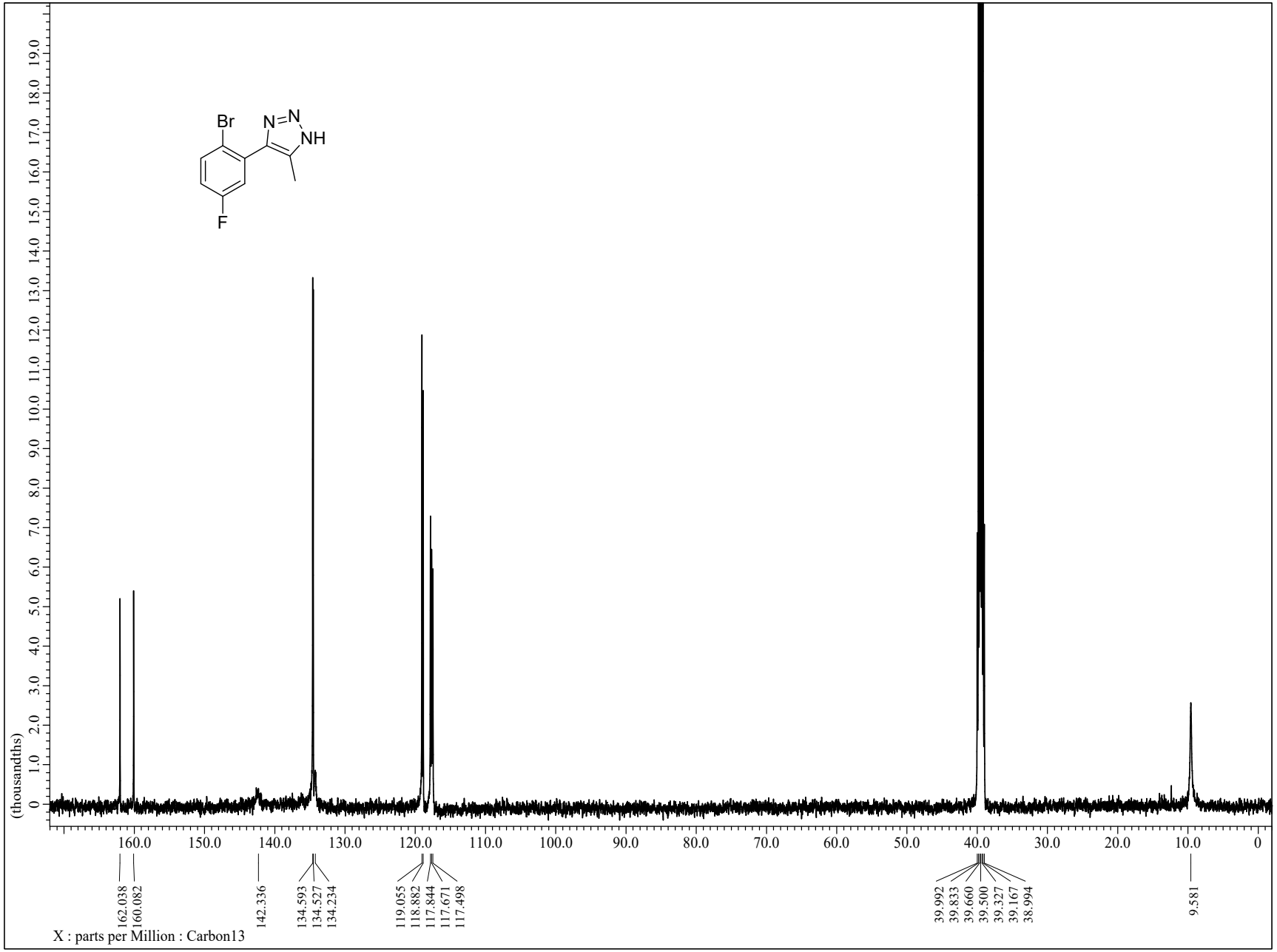

Figure S44: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2v**

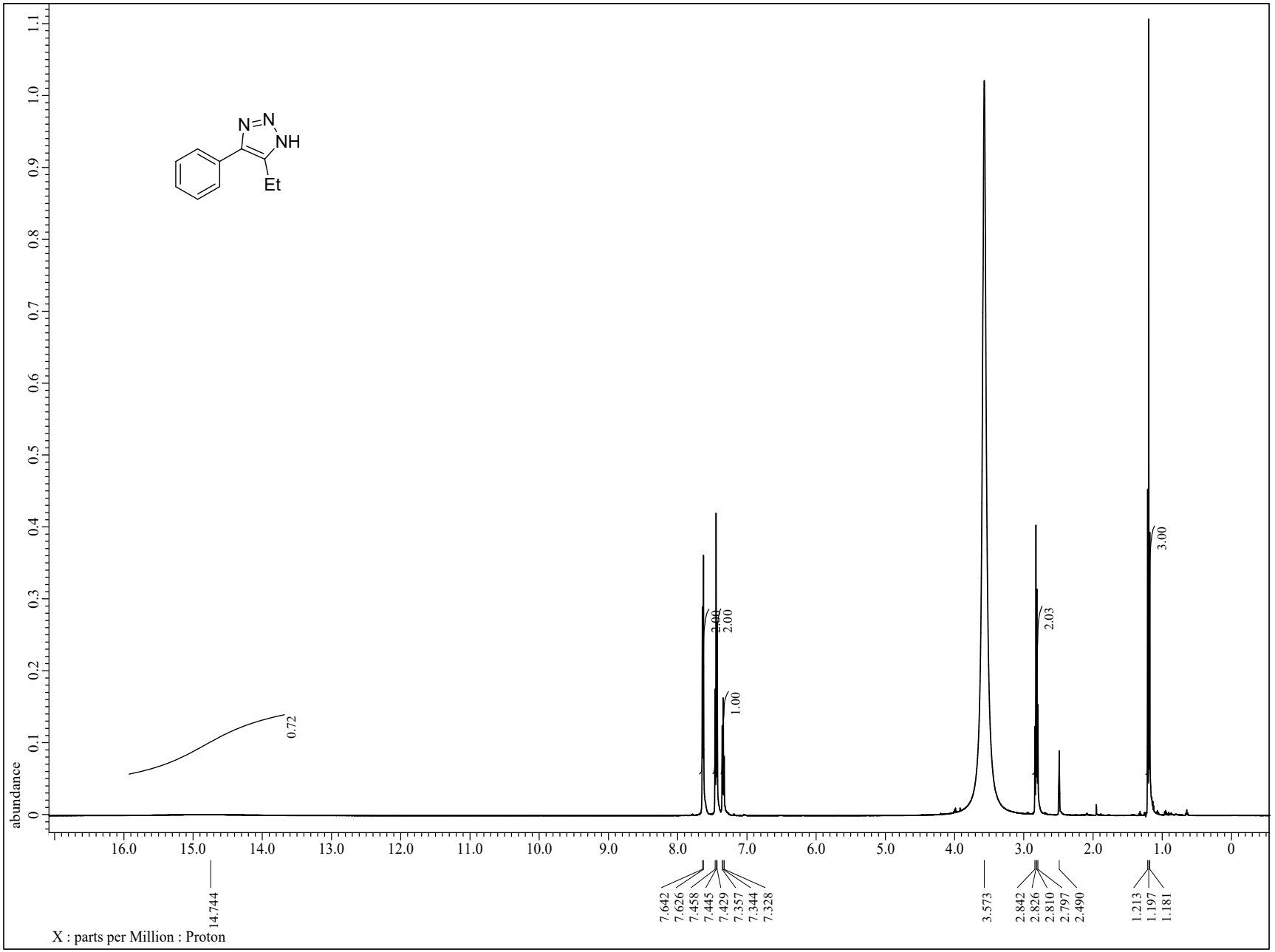

Figure S45: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2w**

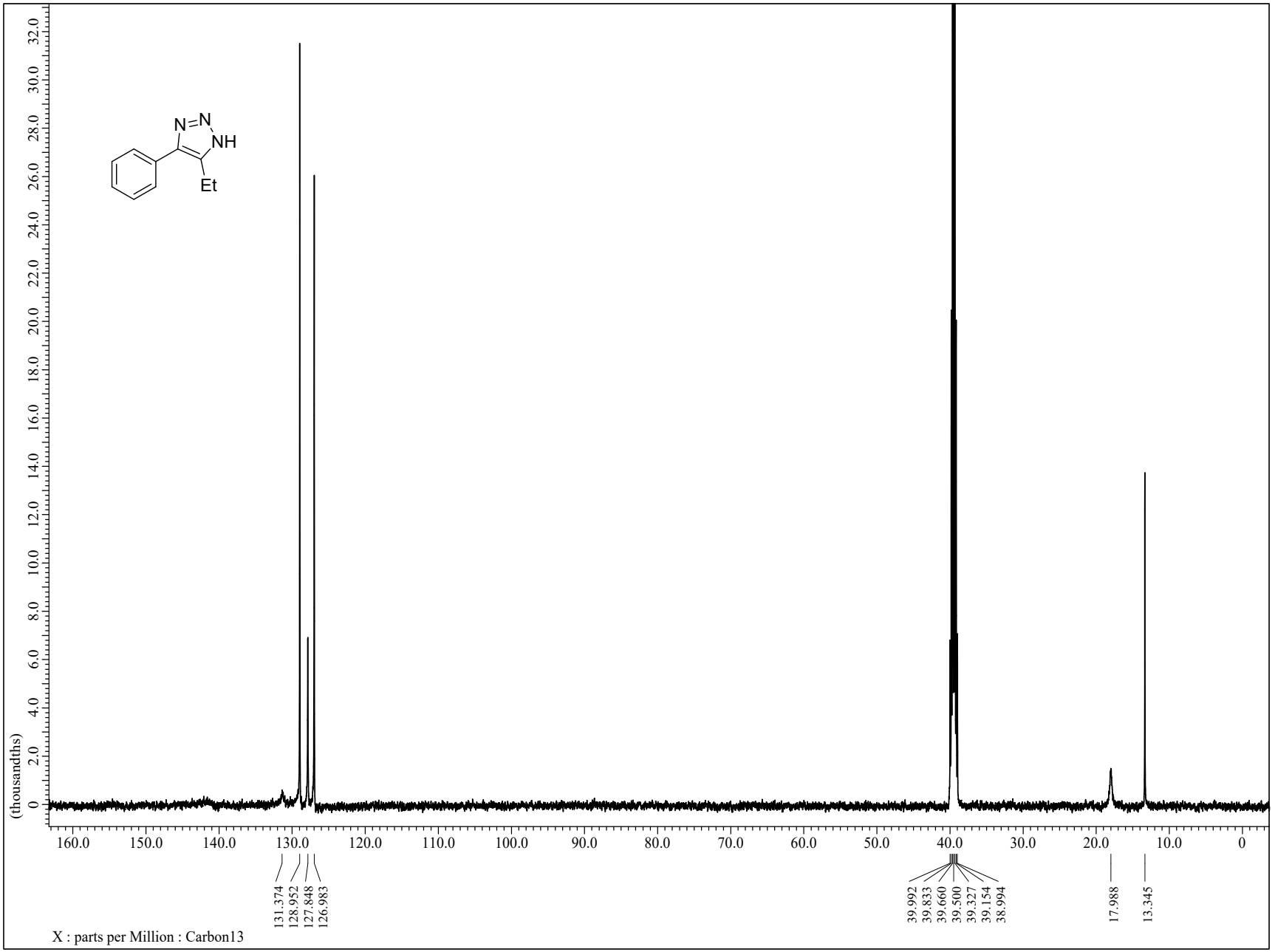

Figure S46: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2w**

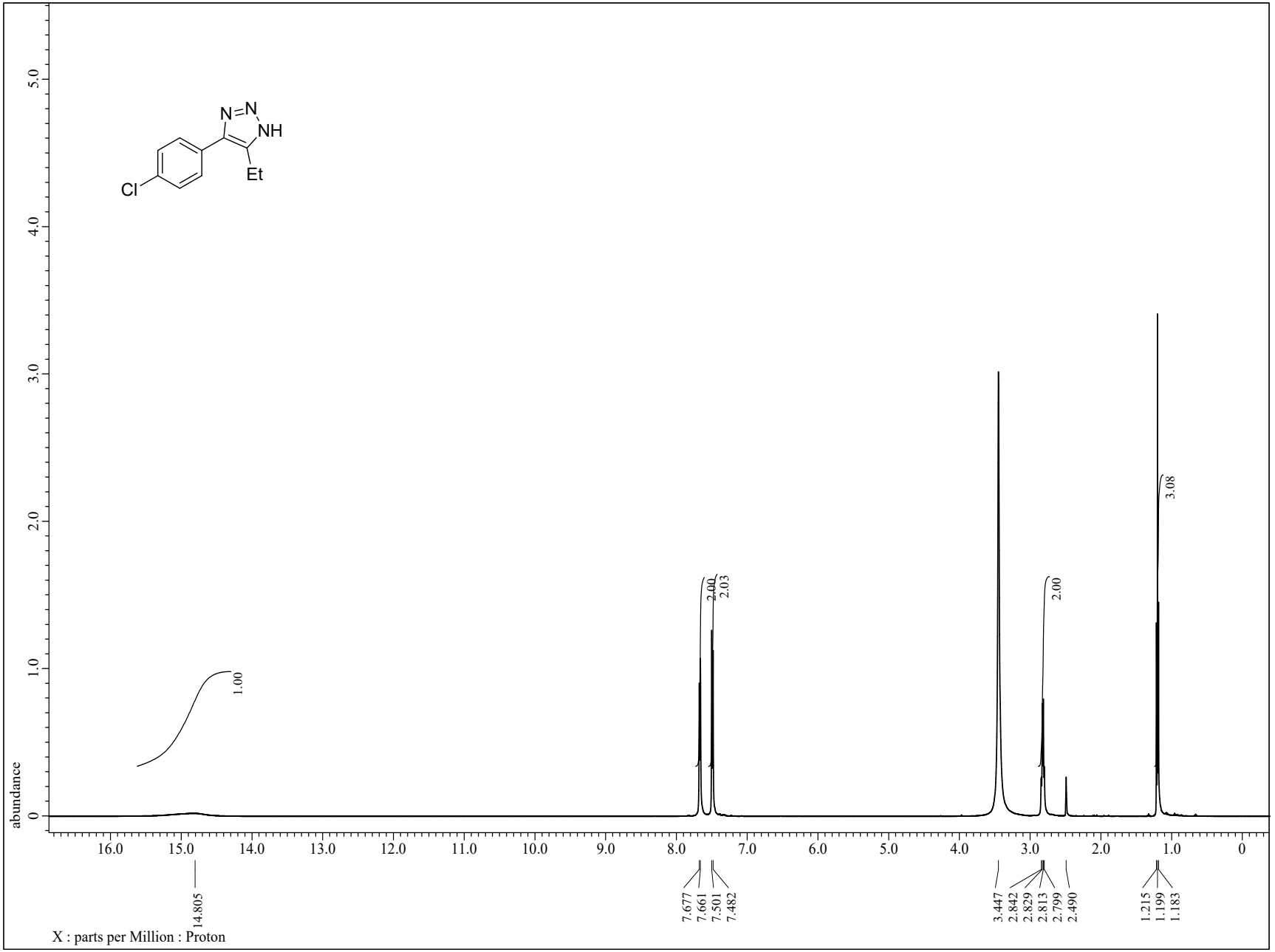

Figure S47: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2x**

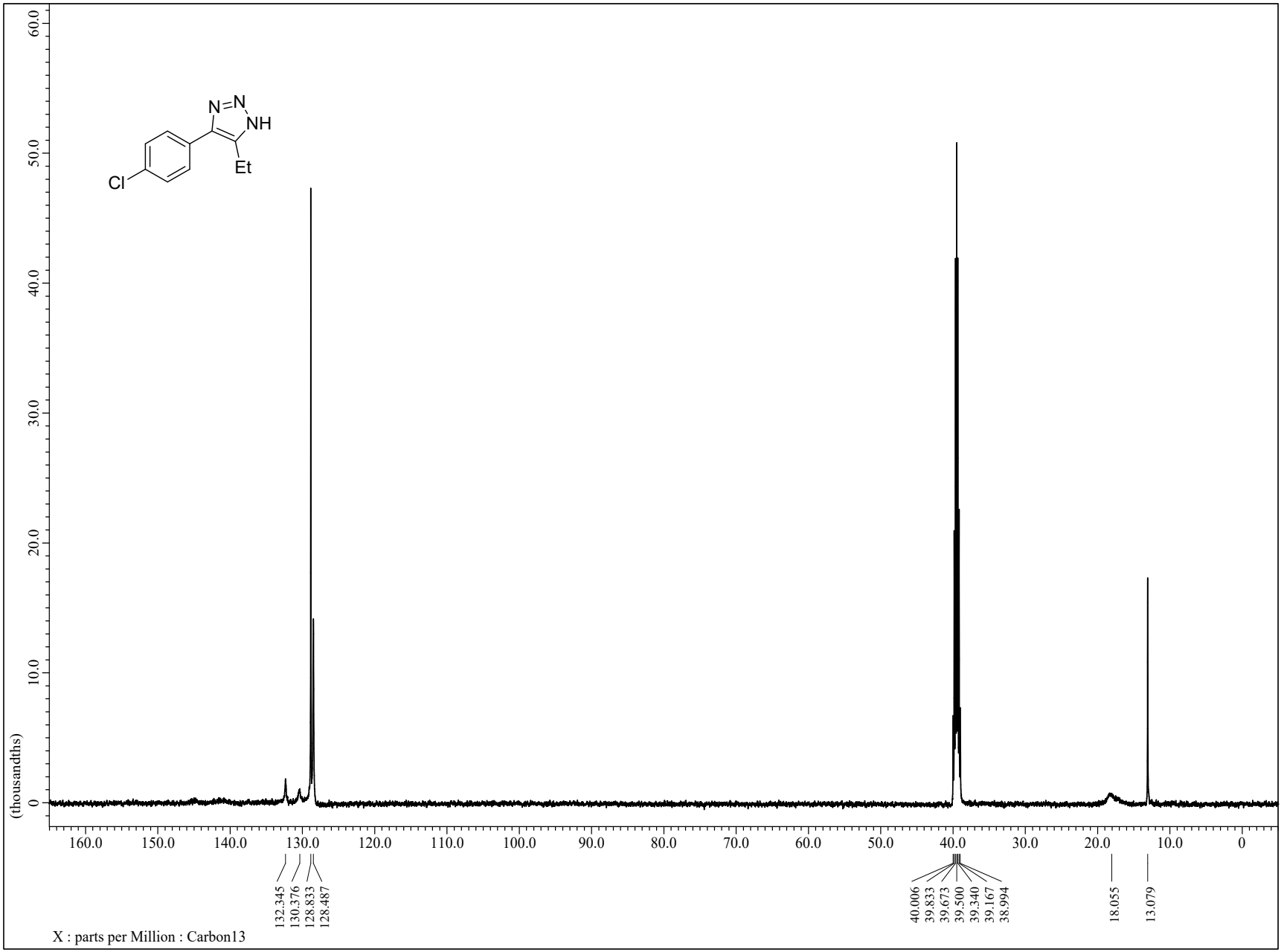

Figure S48: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2x**

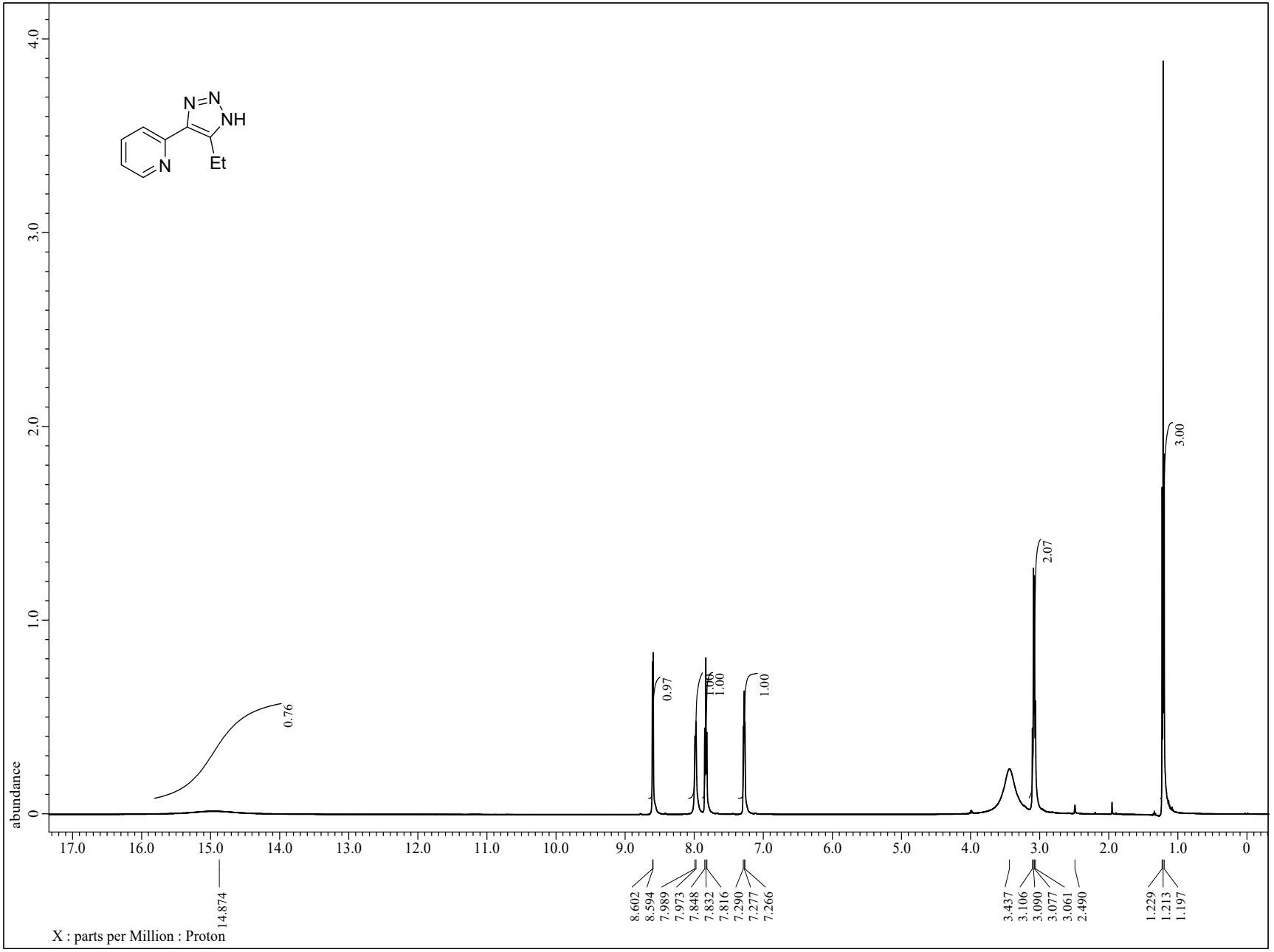

Figure S49: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2y**

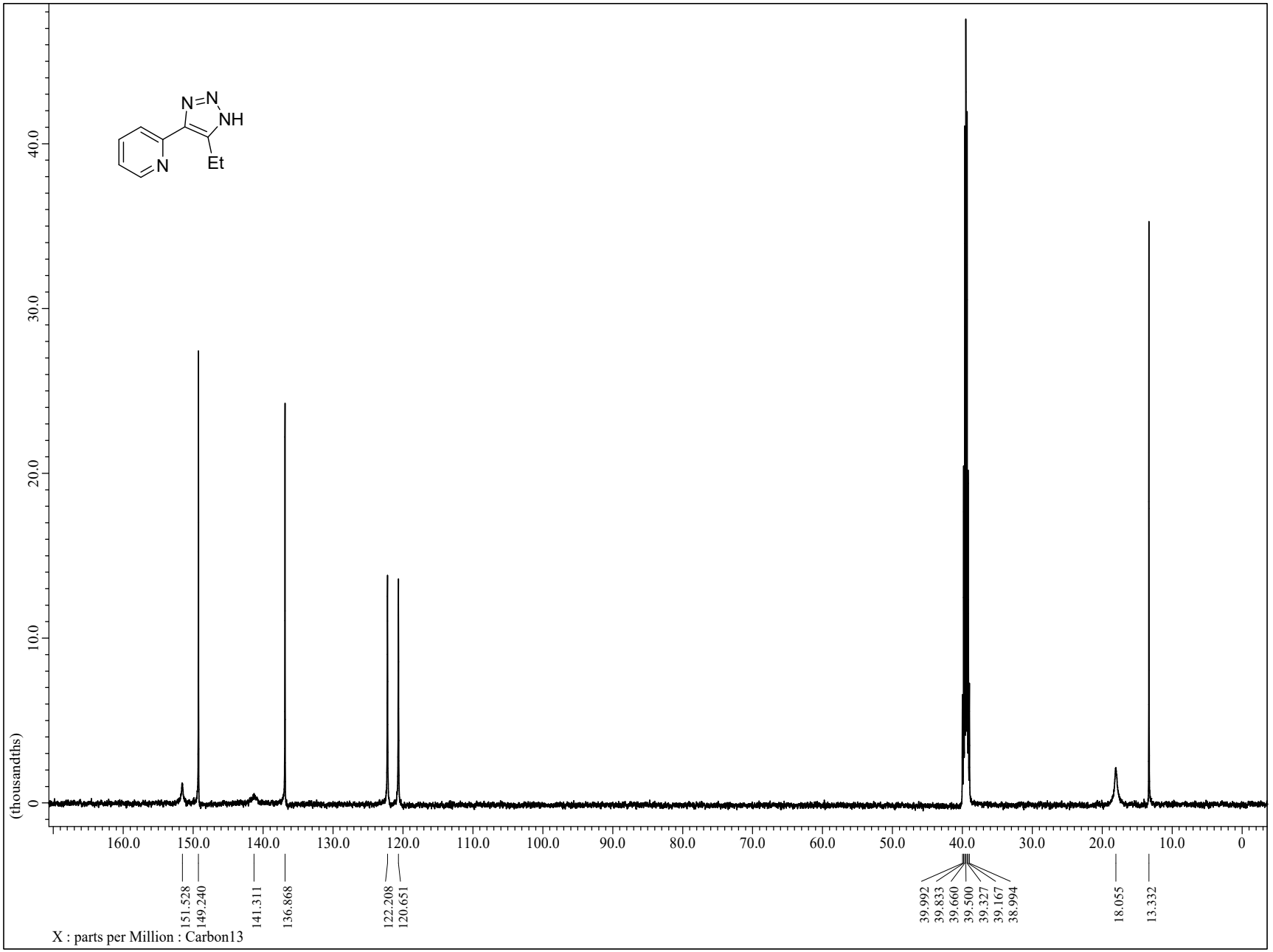

Figure S50: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2y**

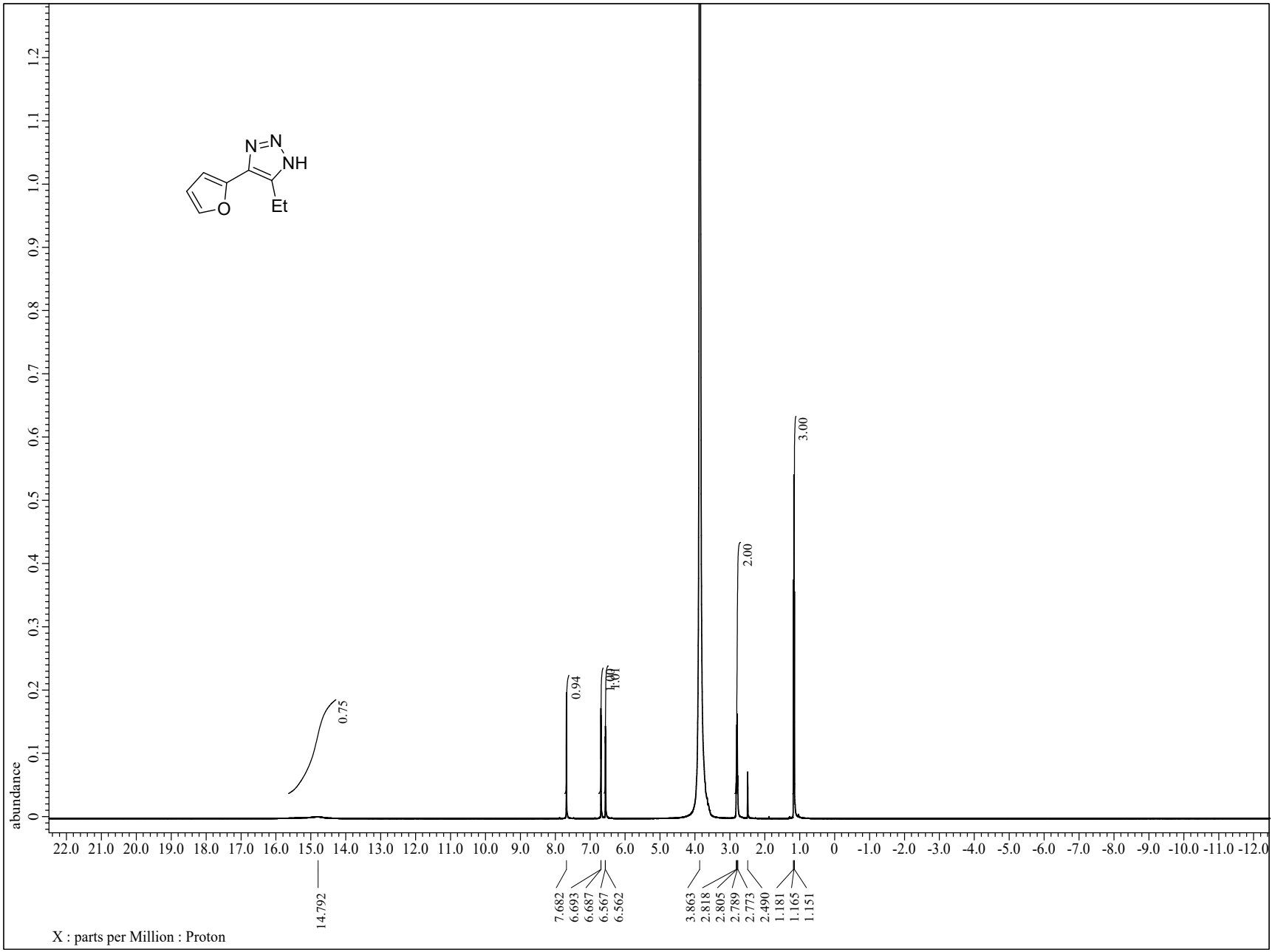

Figure S51: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2z**

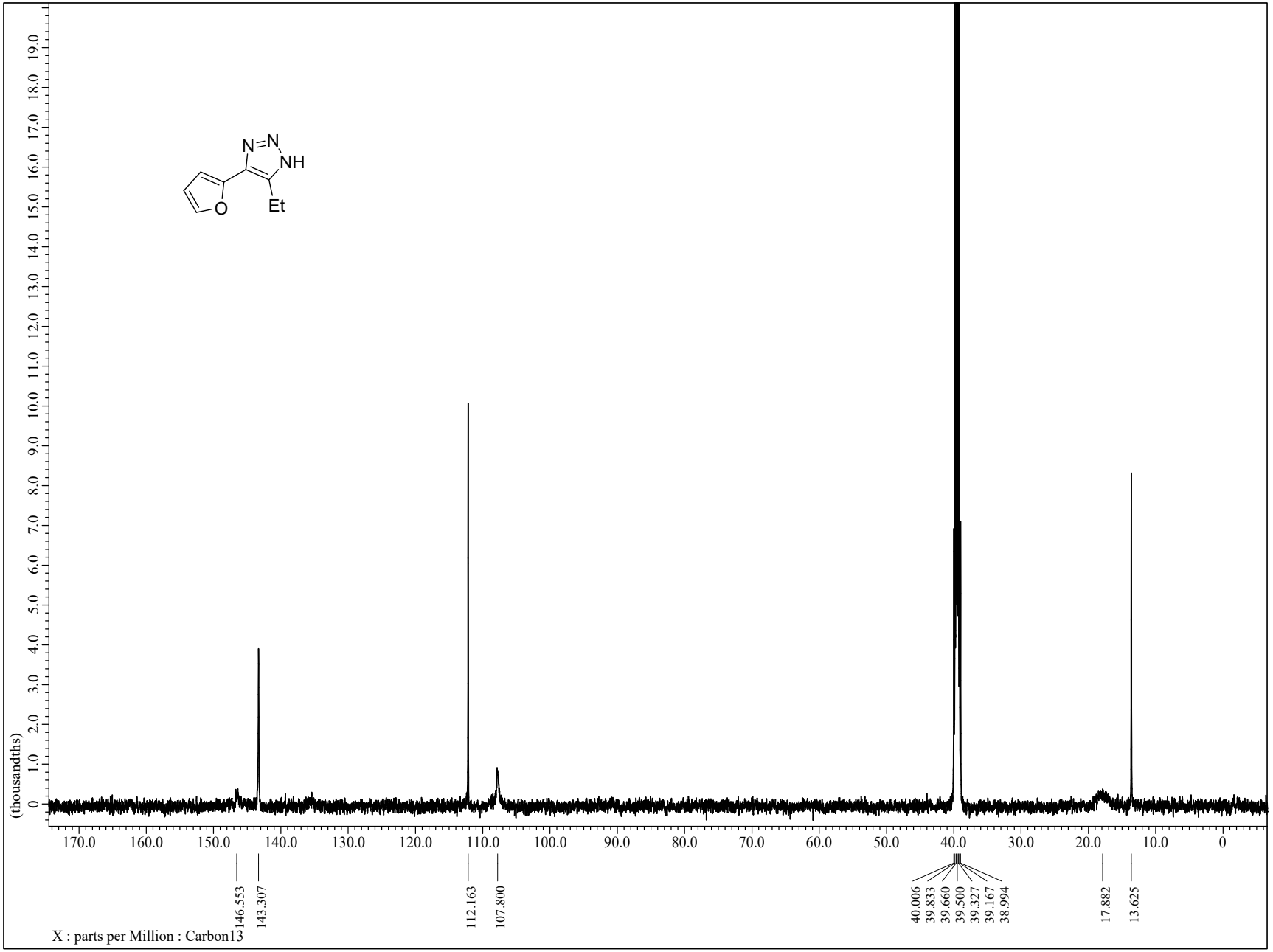

Figure S52: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2z**

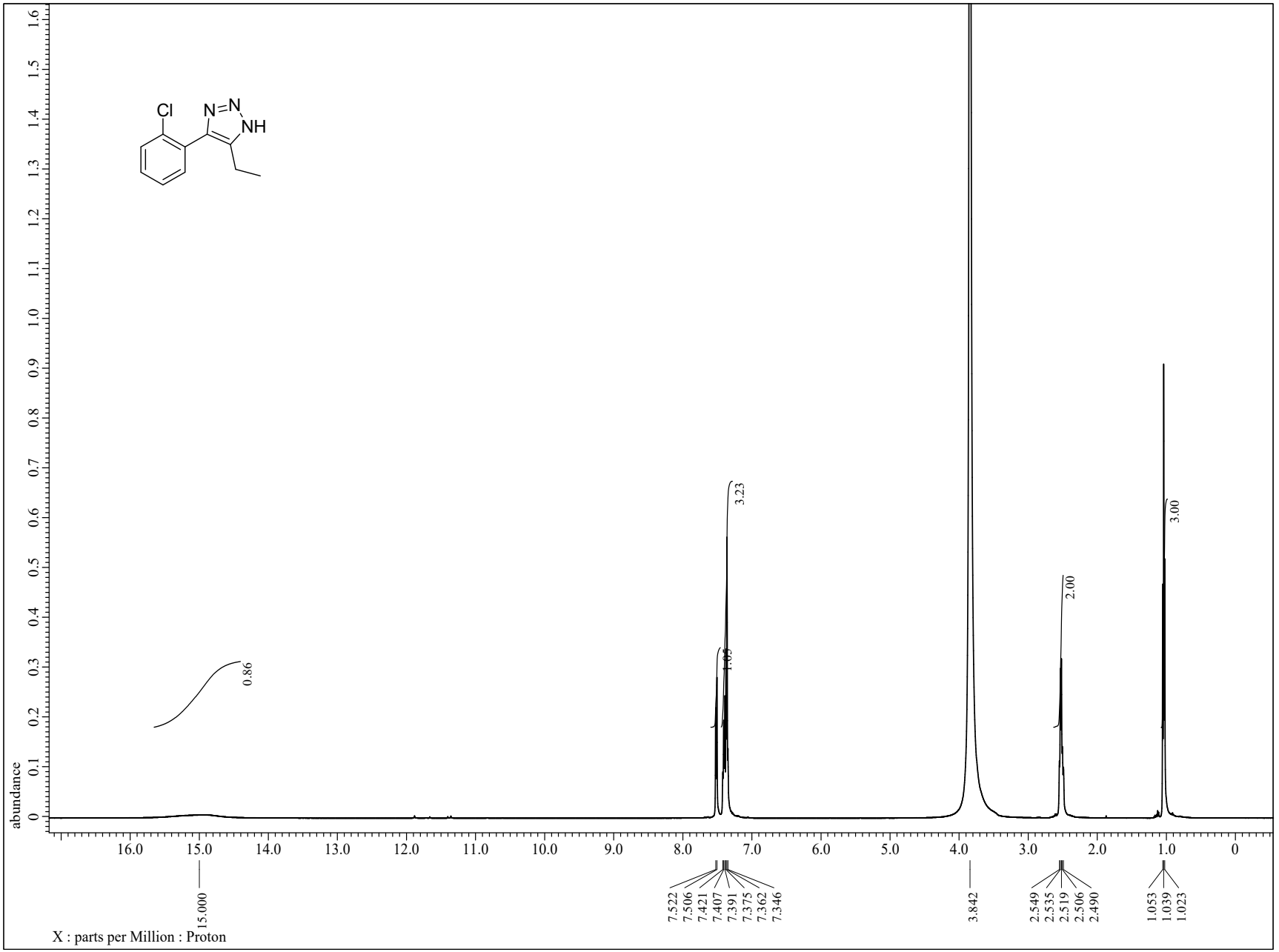

Figure S53: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2aa**

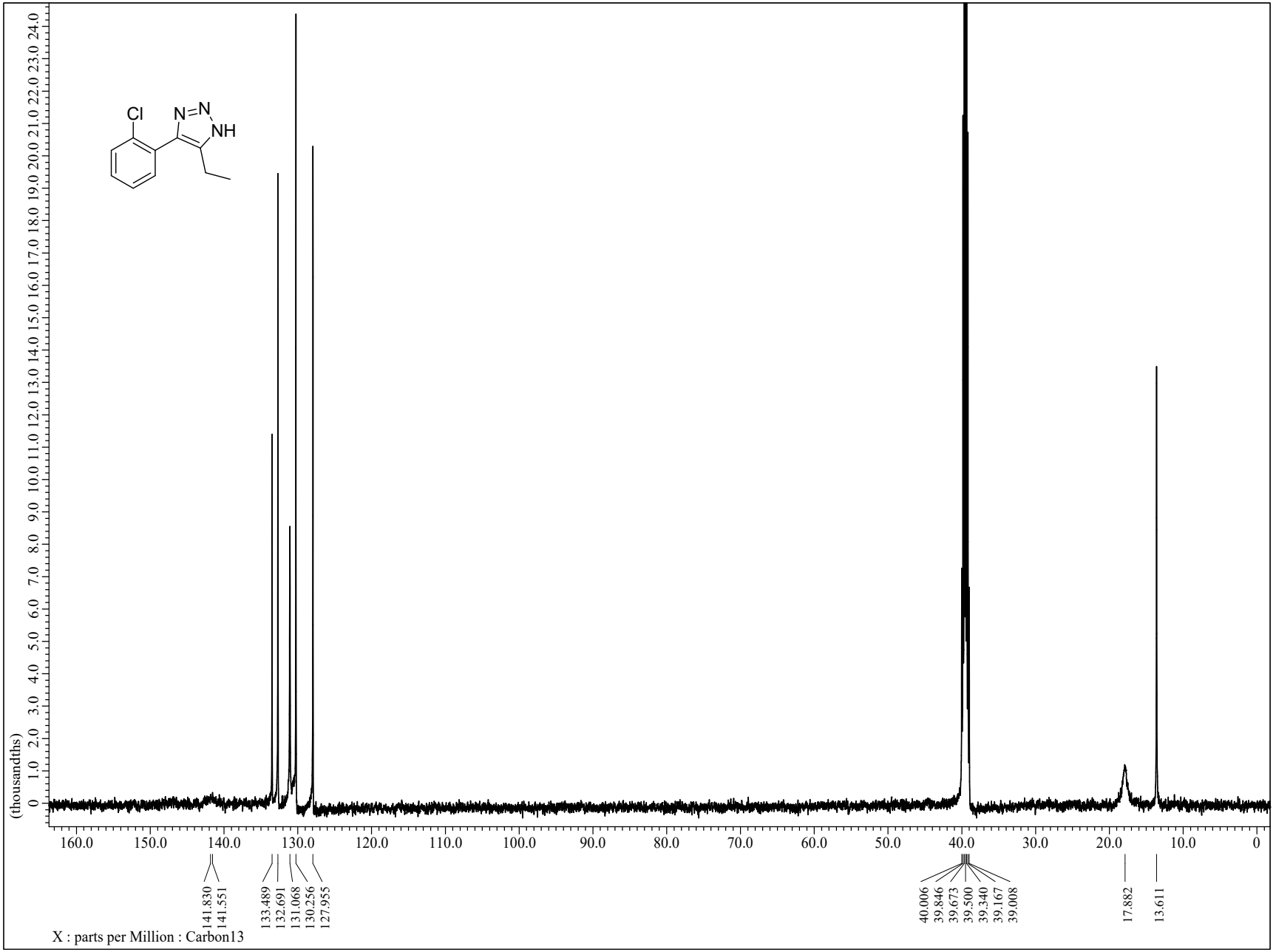

Figure S54: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2aa**

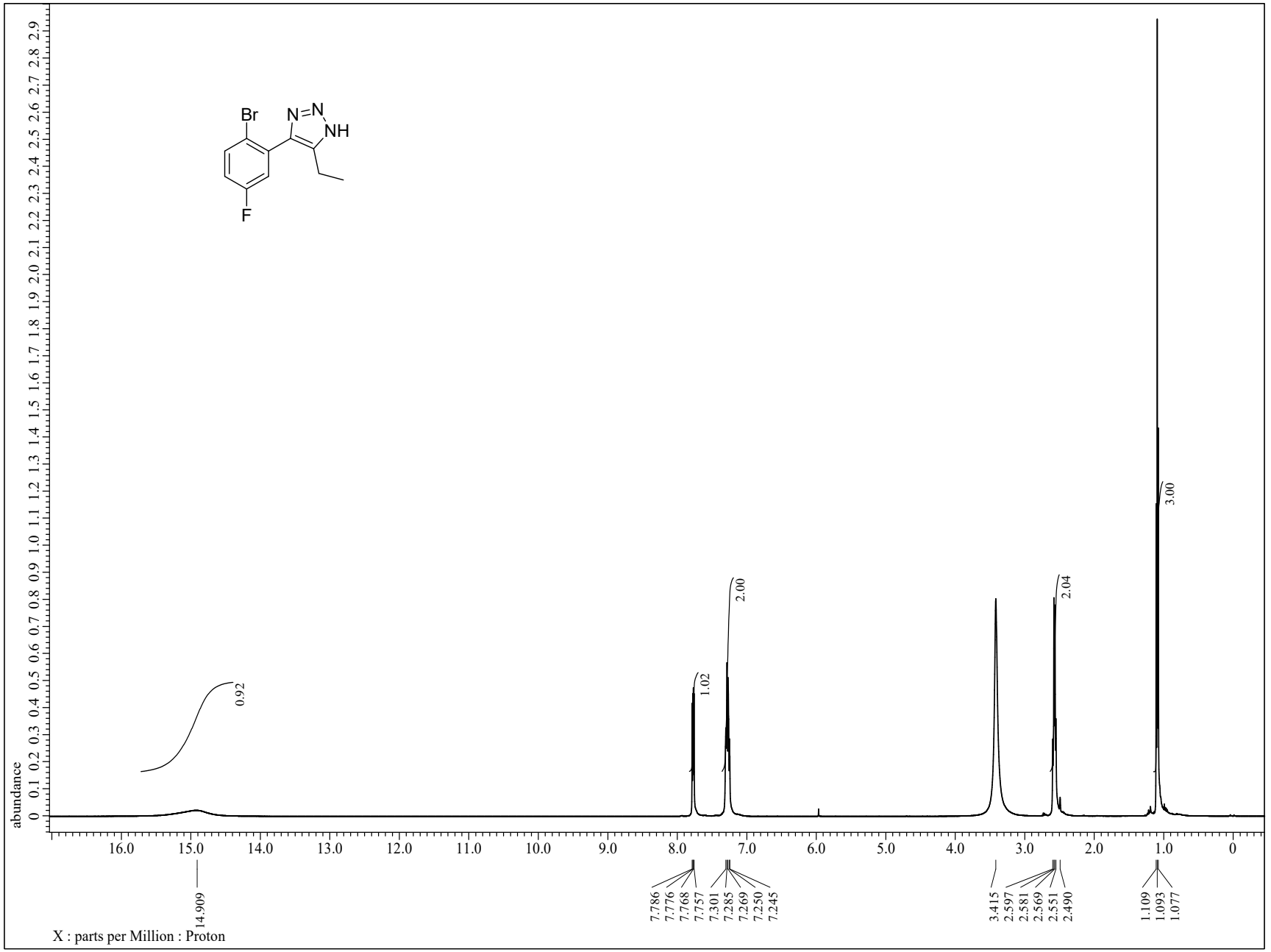

Figure S55: ^{1}H NMR (500 MHz, DMSO-d_6) of compound **2ab**

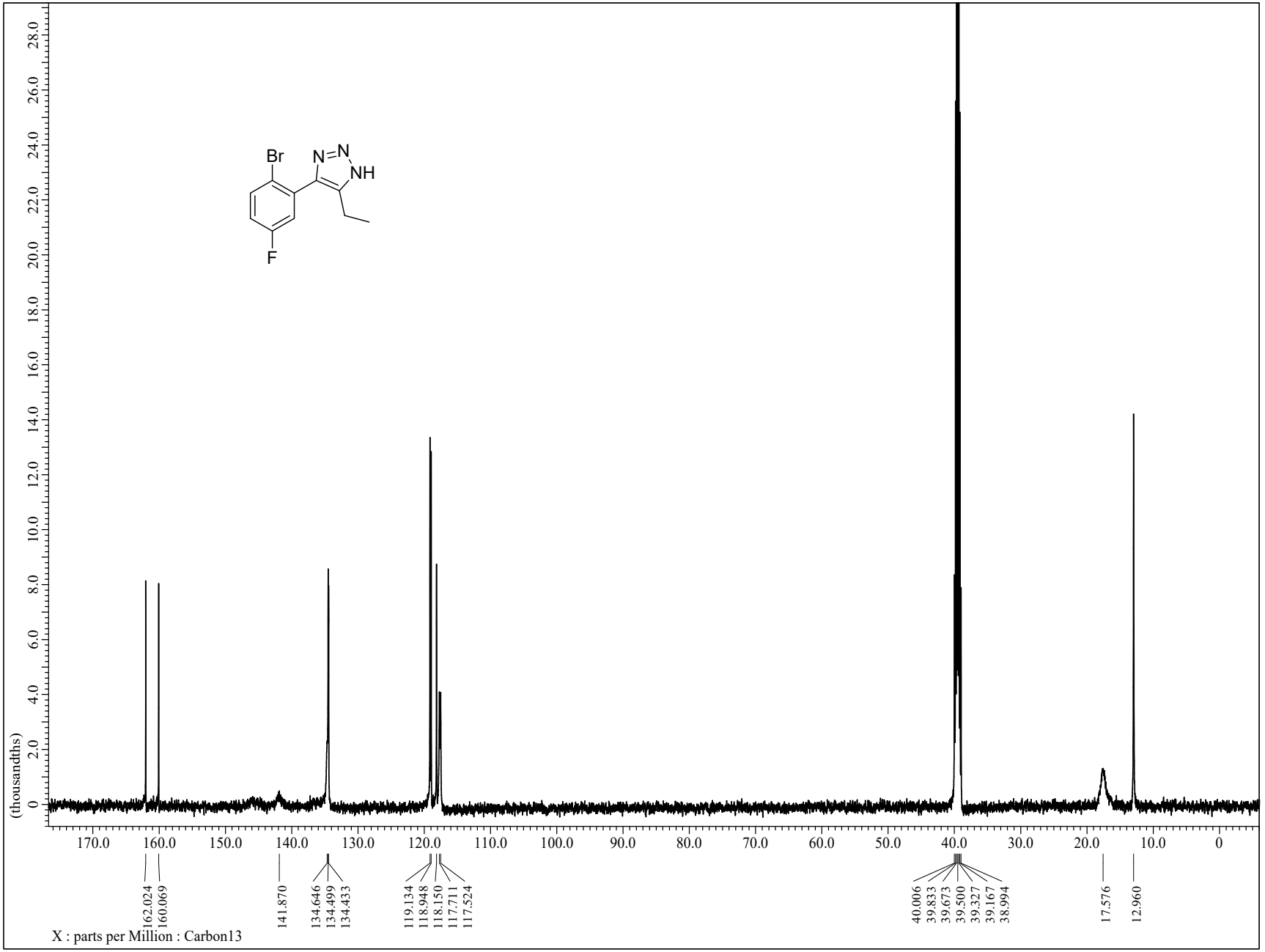

Figure S56: ^{13}C NMR (125 MHz, DMSO-d_6) of compound **2ab**

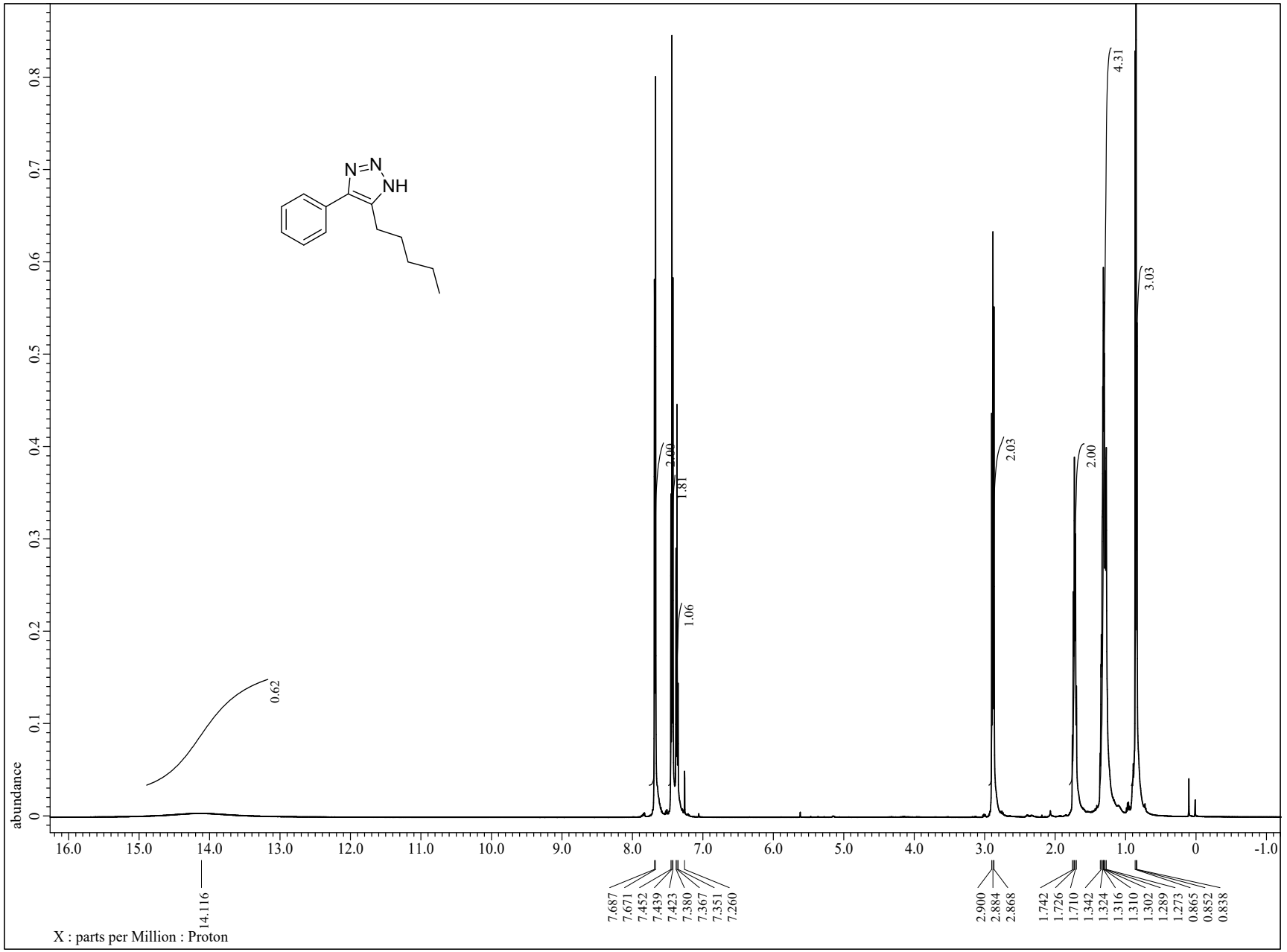

Figure S57: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2ac**

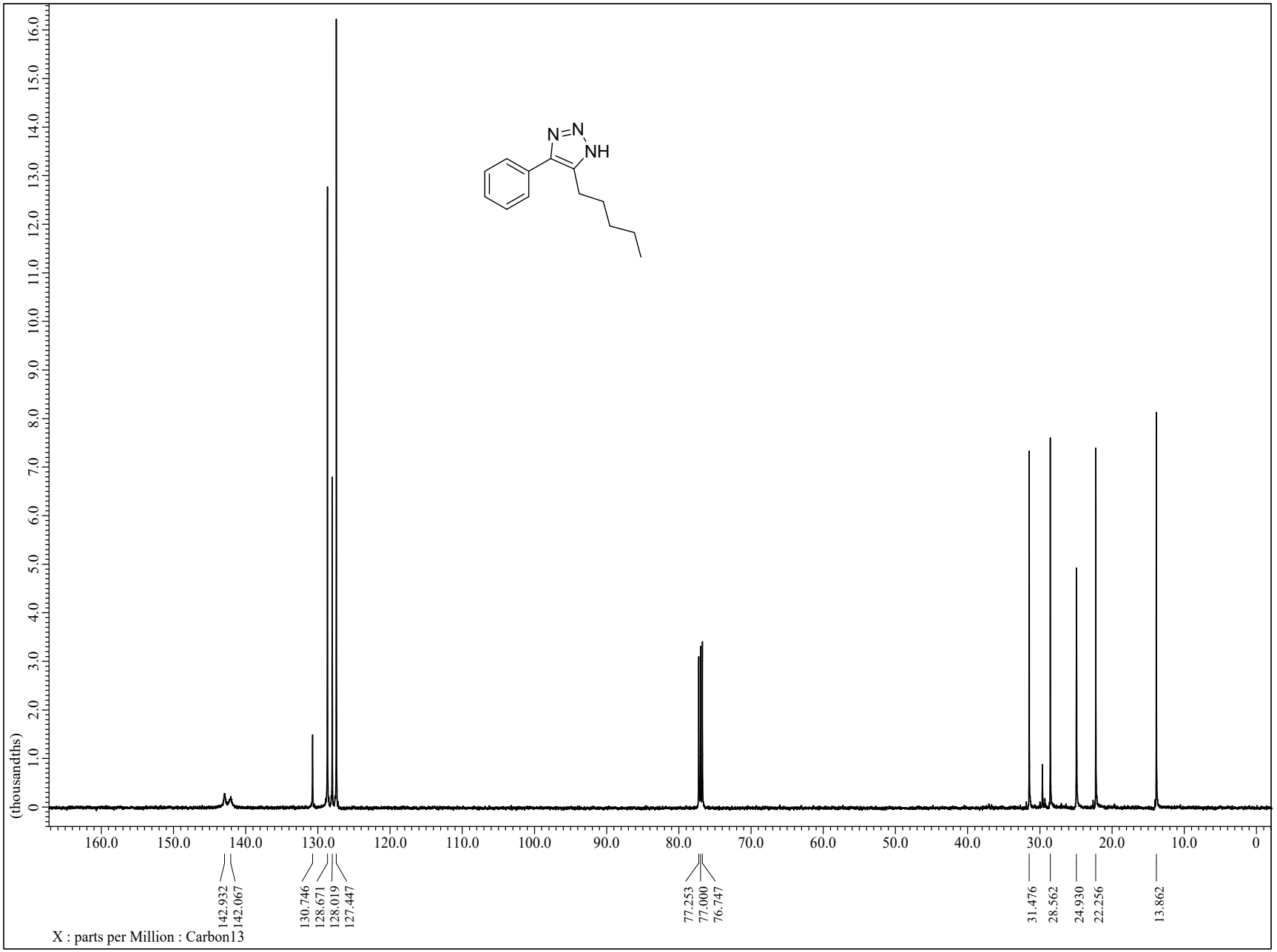

Figure S58: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2ac**

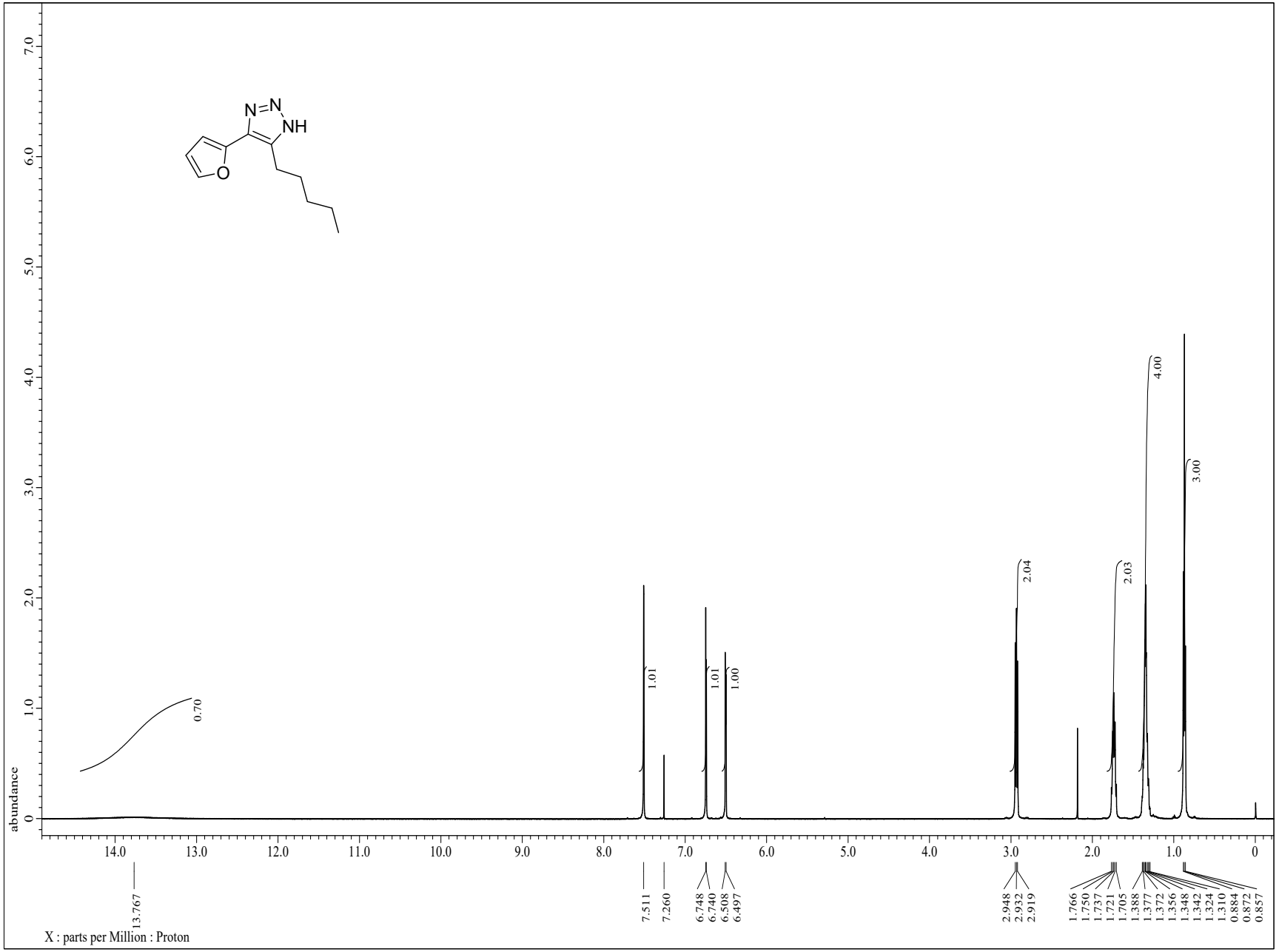

Figure S59: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2ad**

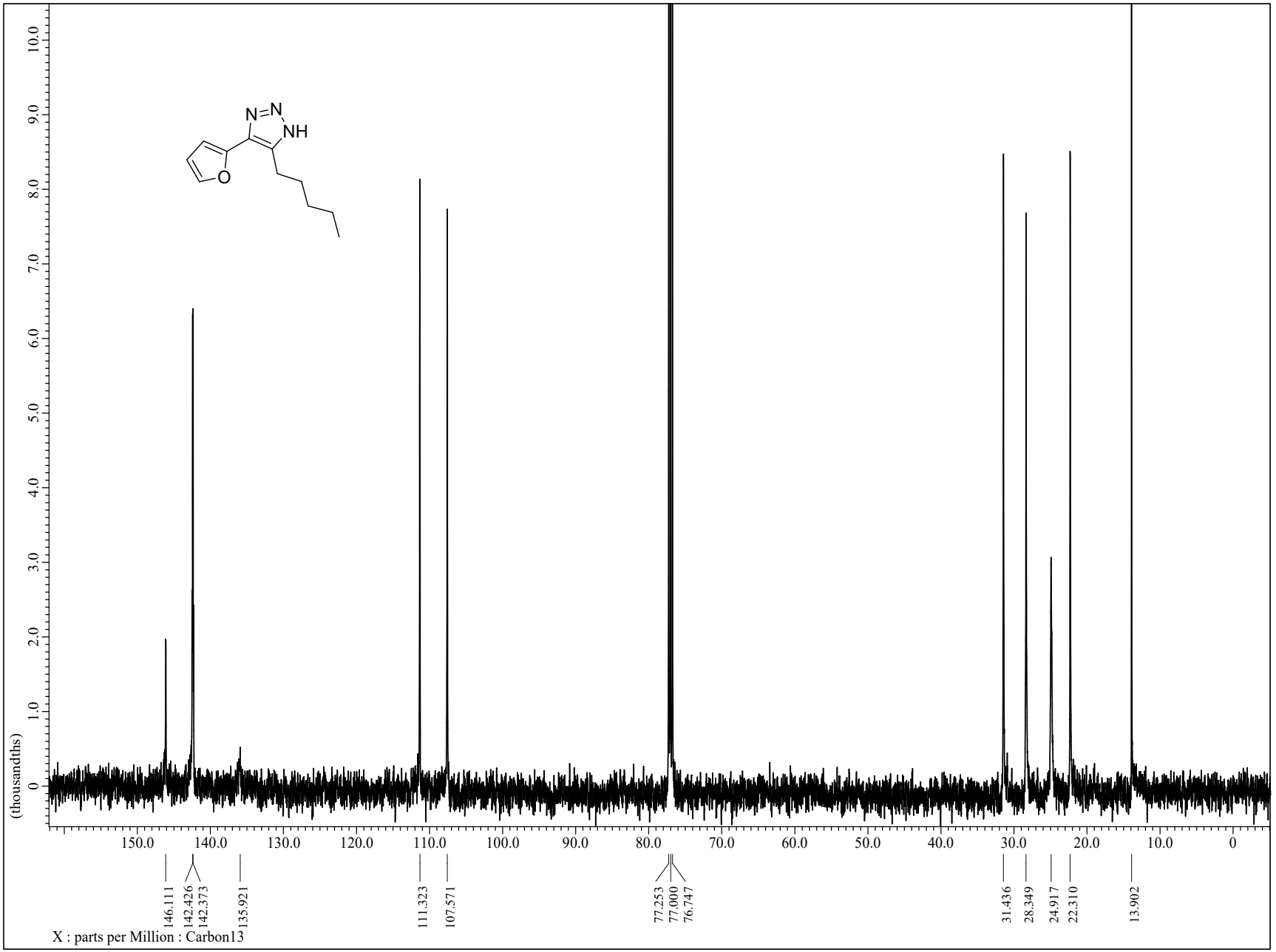

Figure S60: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2ad**

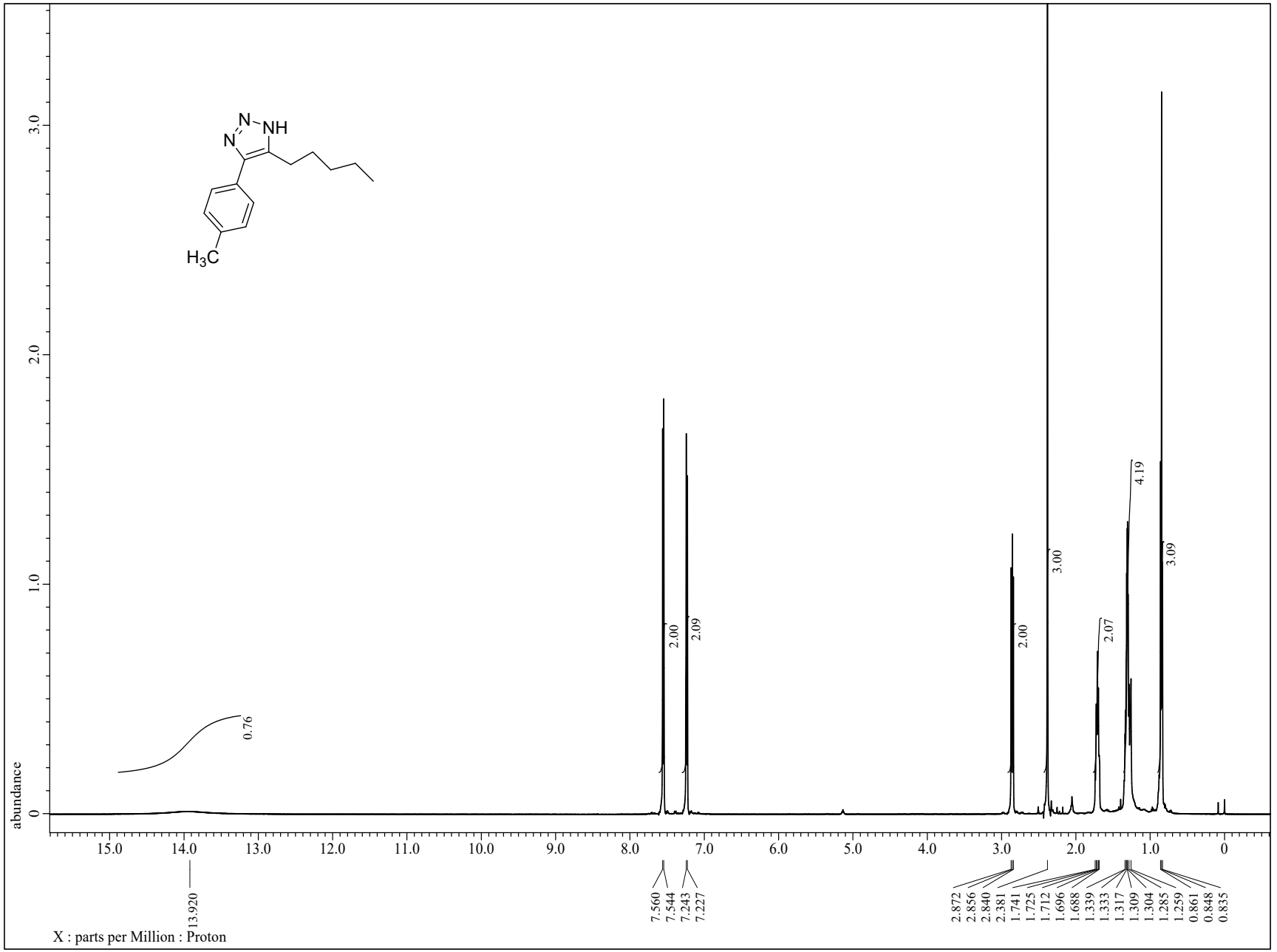

Figure S61: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2ae**

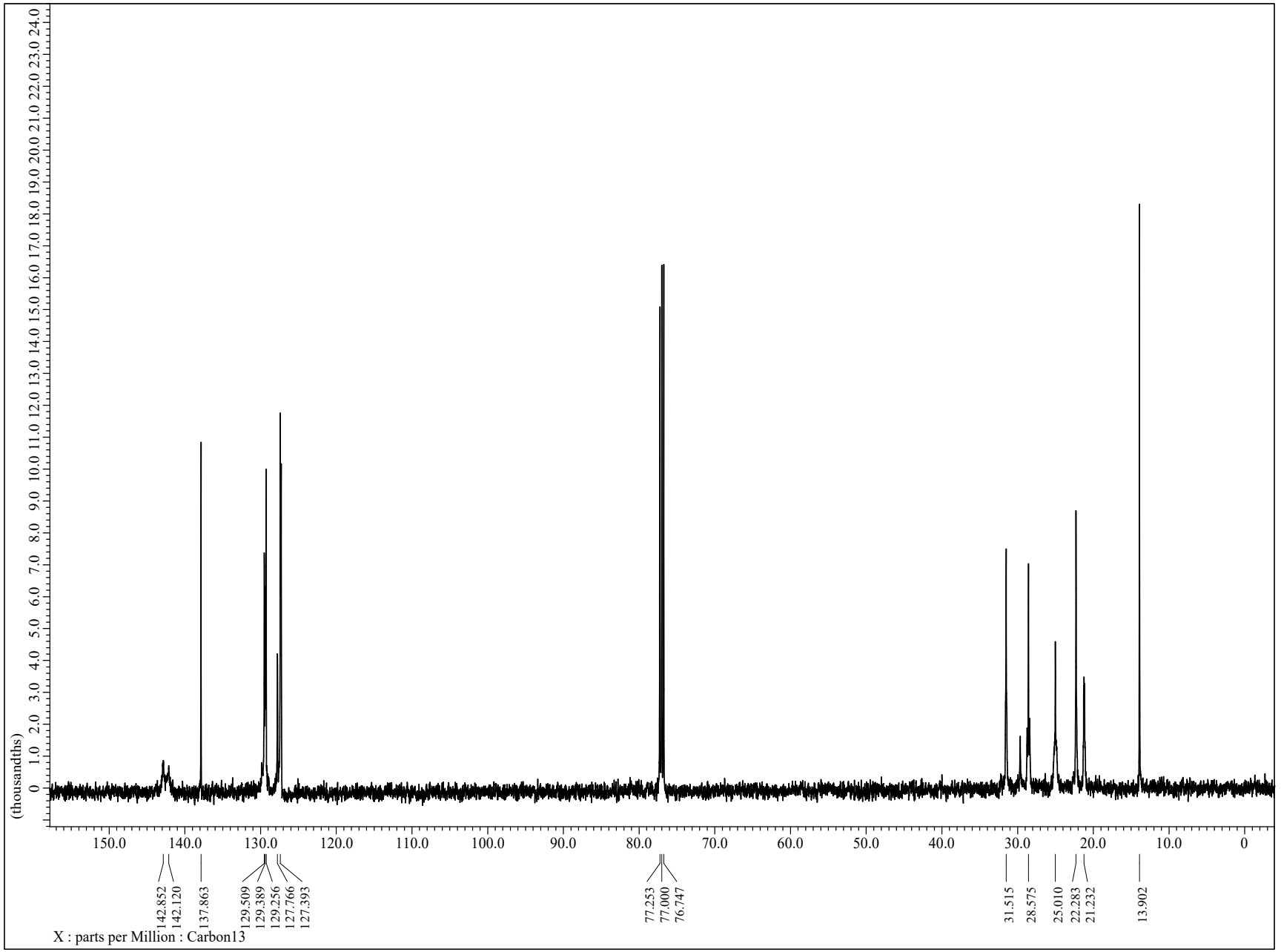

Figure S62: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2ae**

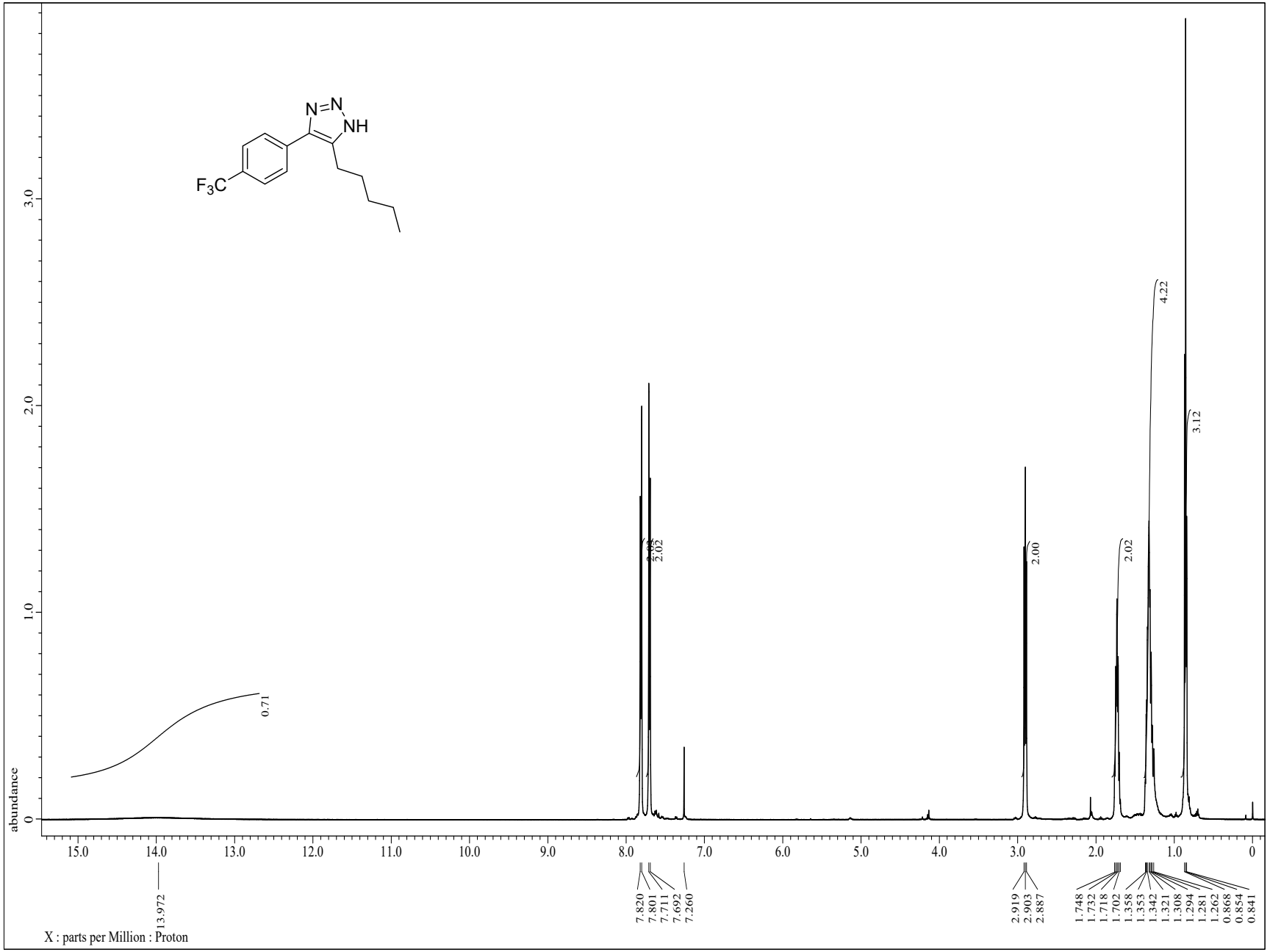

Figure S63: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2af**

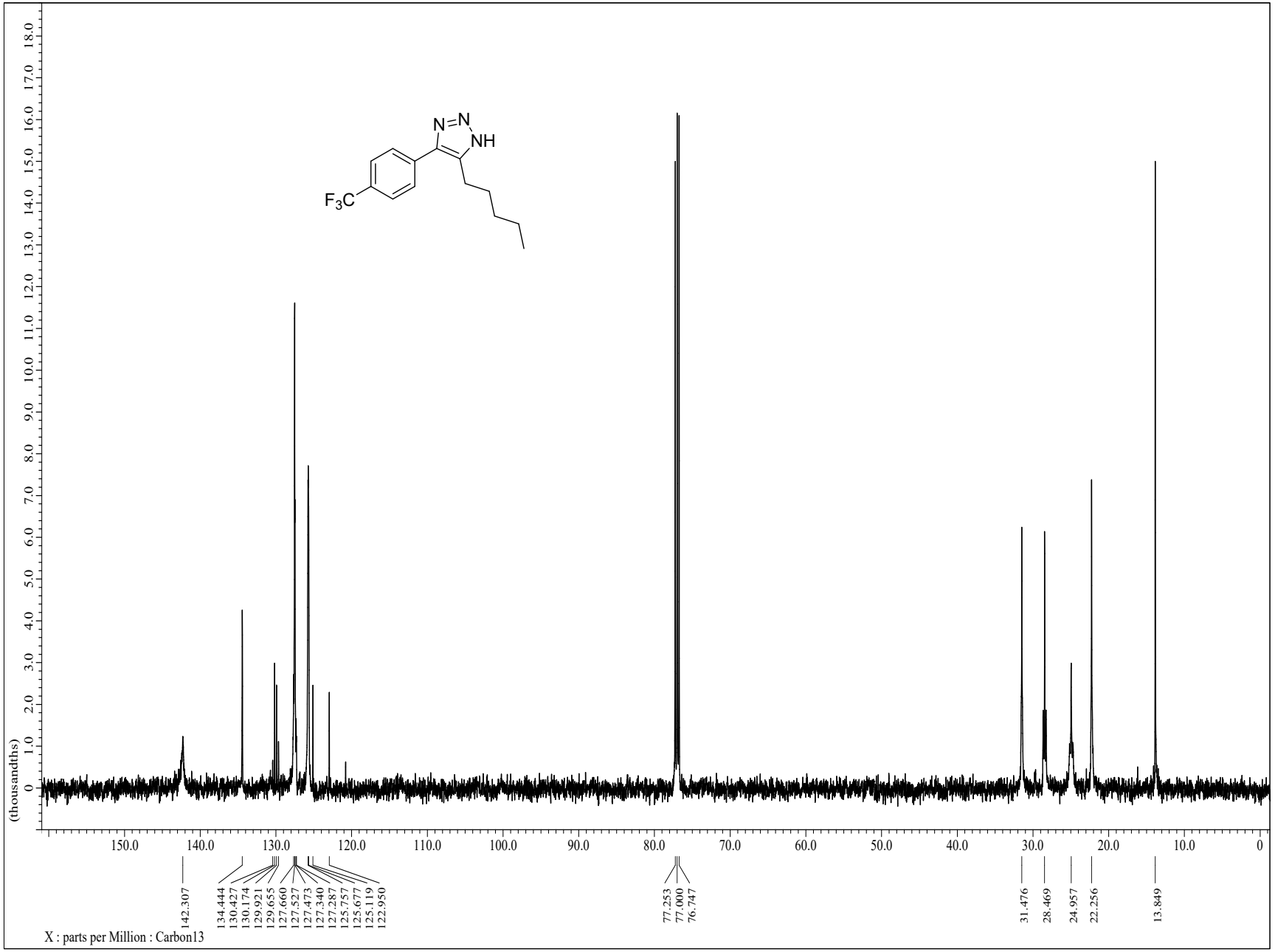

Figure S64: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **2af**

4. ^{1}H and ^{13}C NMR spectra of 5-Functionalized 4-aryl–*NH*–1,2,3-triazoles (**4a-c**)

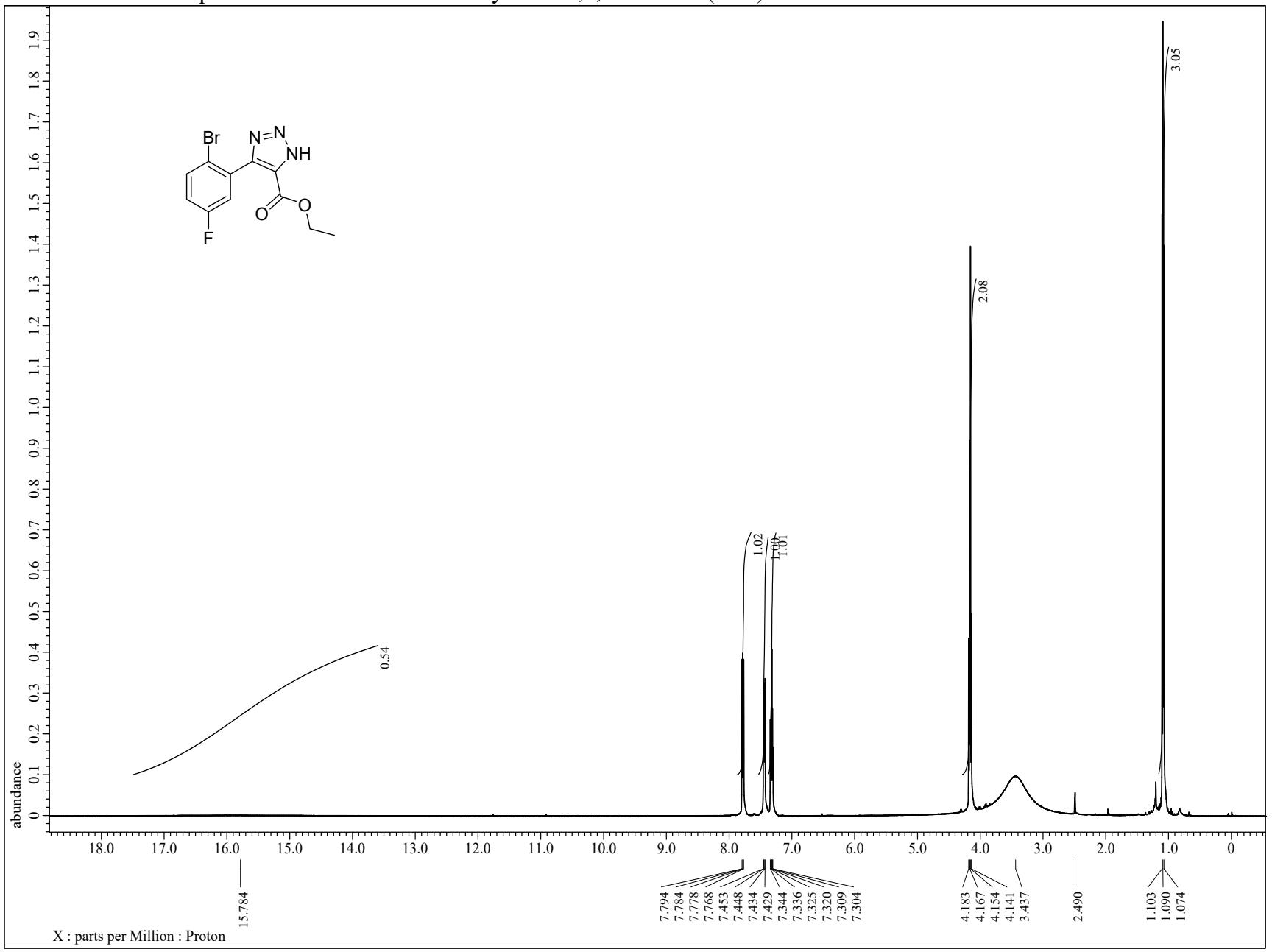

Figure S65: ^{1}H NMR (500 MHz, DMSO-D_6) of compound **4a**

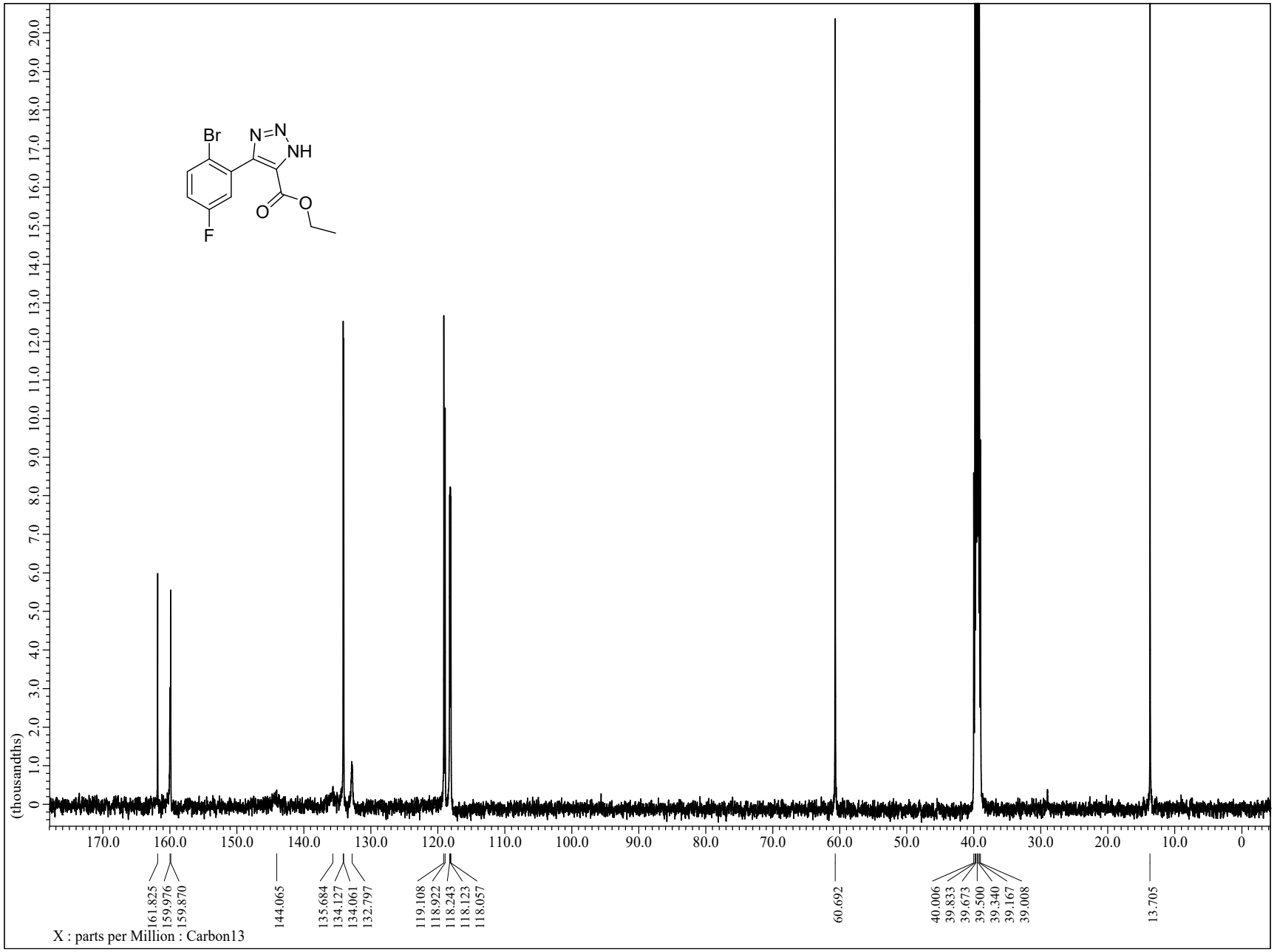

Figure S66: ^{13}C NMR (125 MHz, DMSO-D_6) of compound **4a**

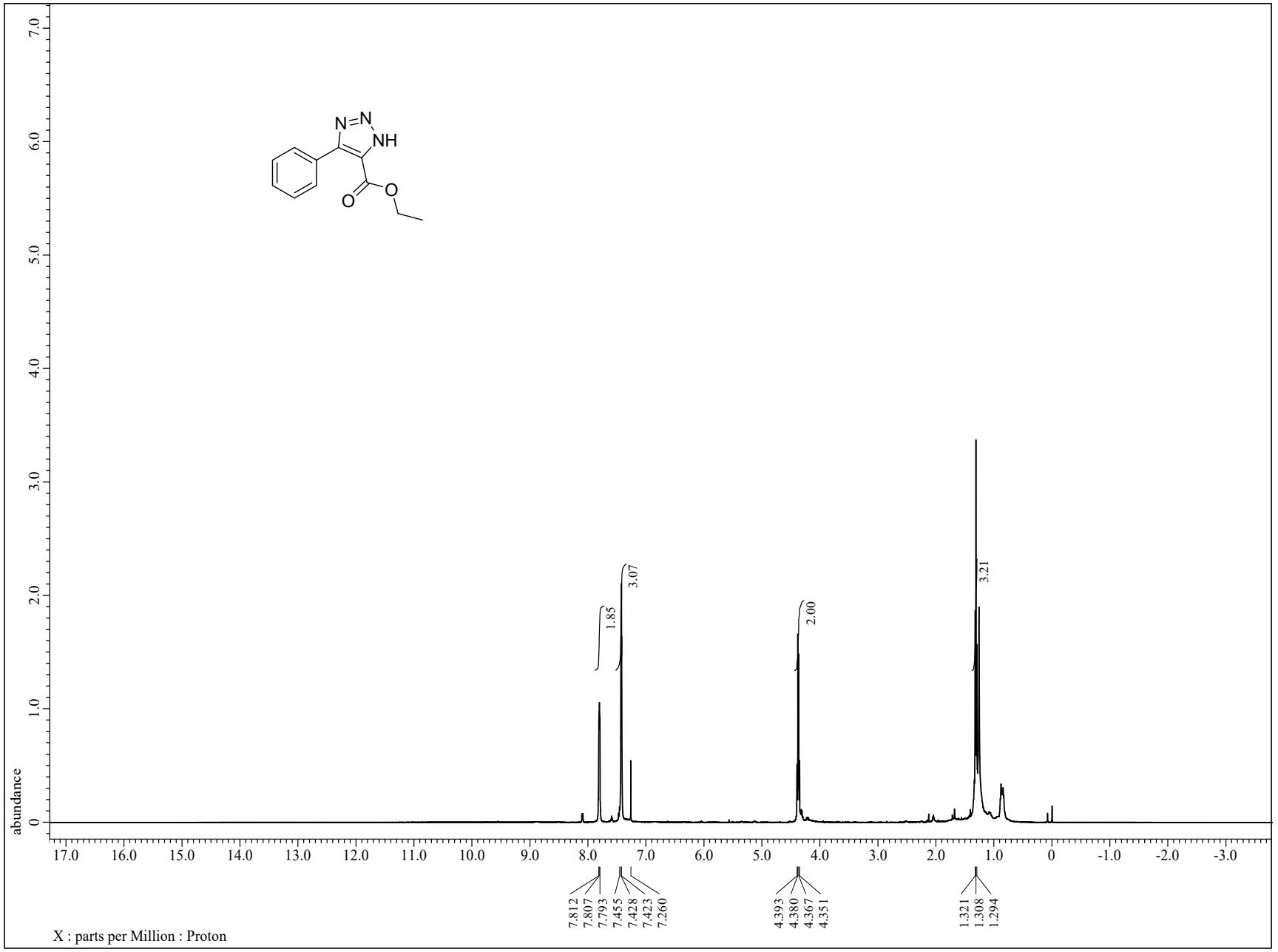

Figure S67: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **4b**

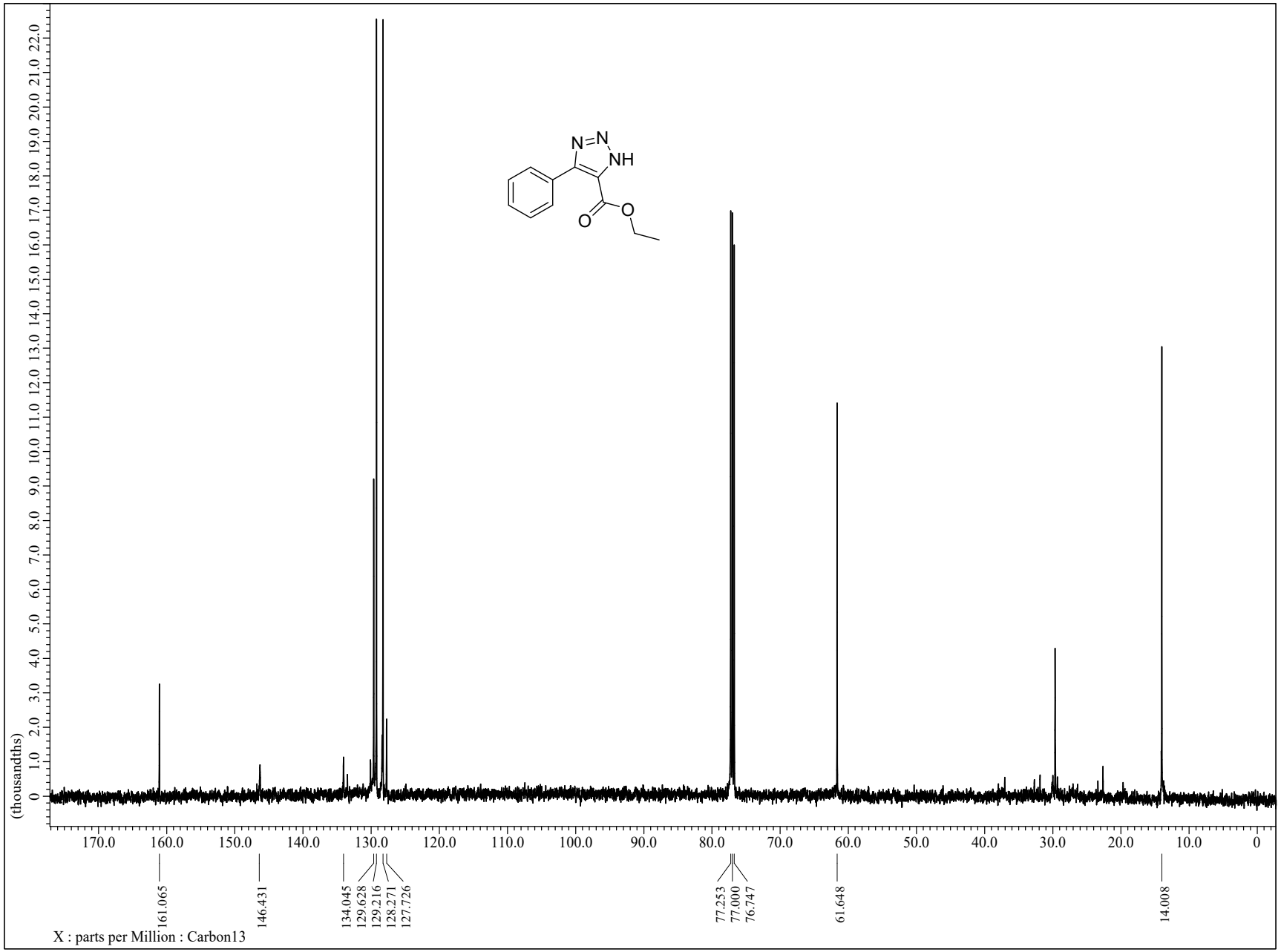

Figure S68: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **4b**

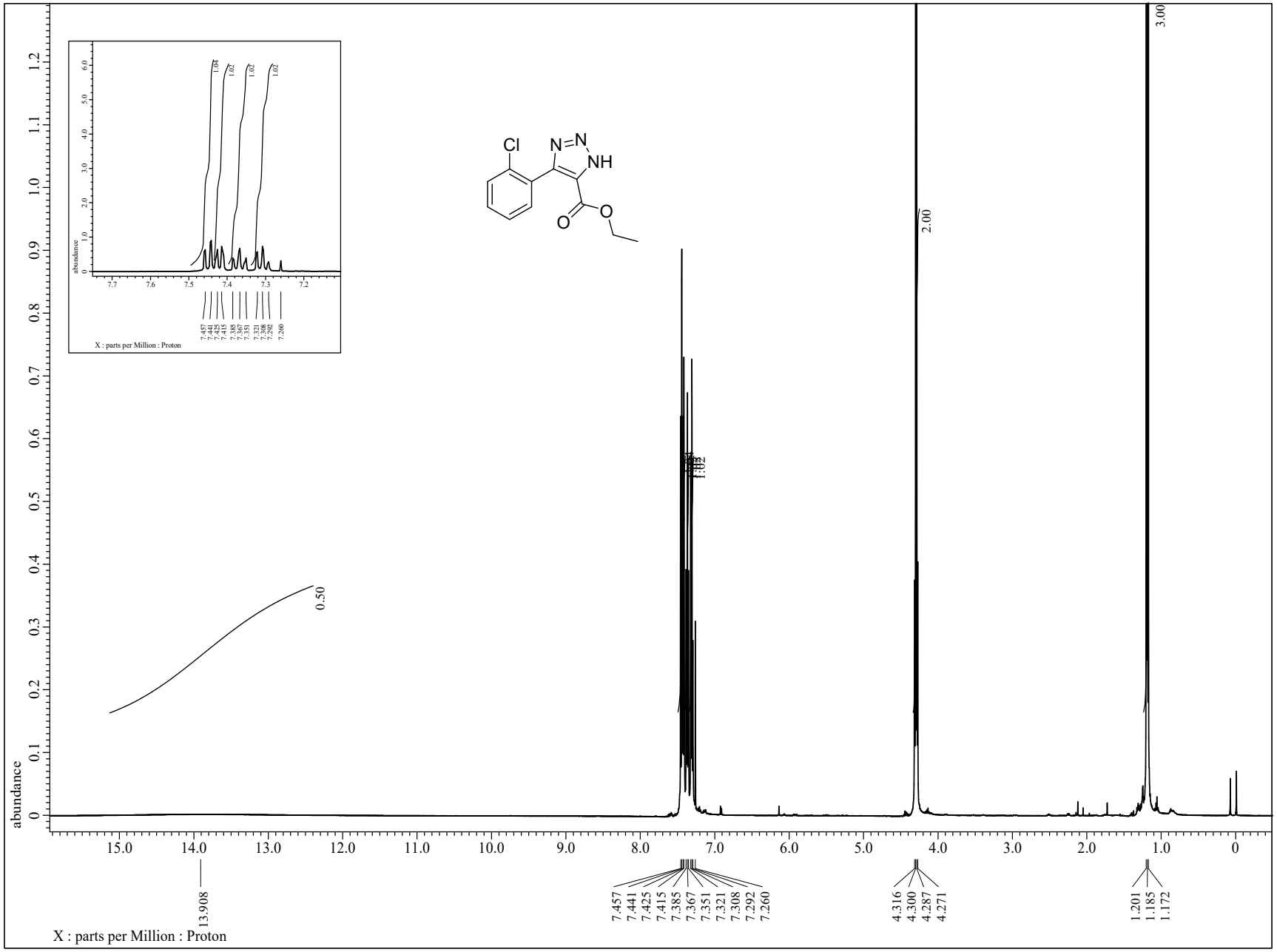

Figure S69: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **4c**

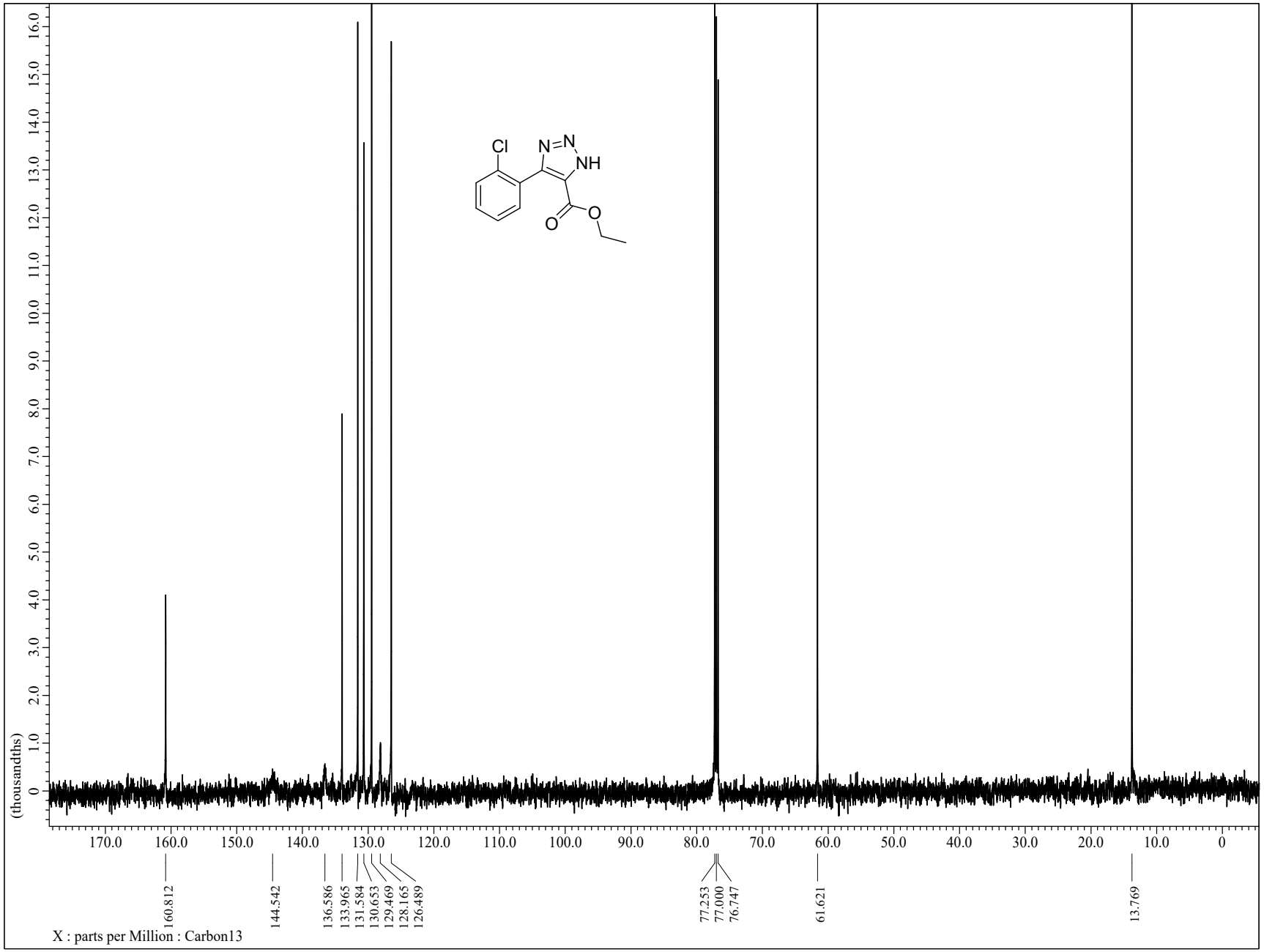

Figure S70: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **4c**

5. ^{1}H and ^{13}C NMR spectra of 4-(2-(1H-1,2,3-triazol-4-yl)phenyl)-1-benzyl-1*H*-1,2,3-triazole **6**

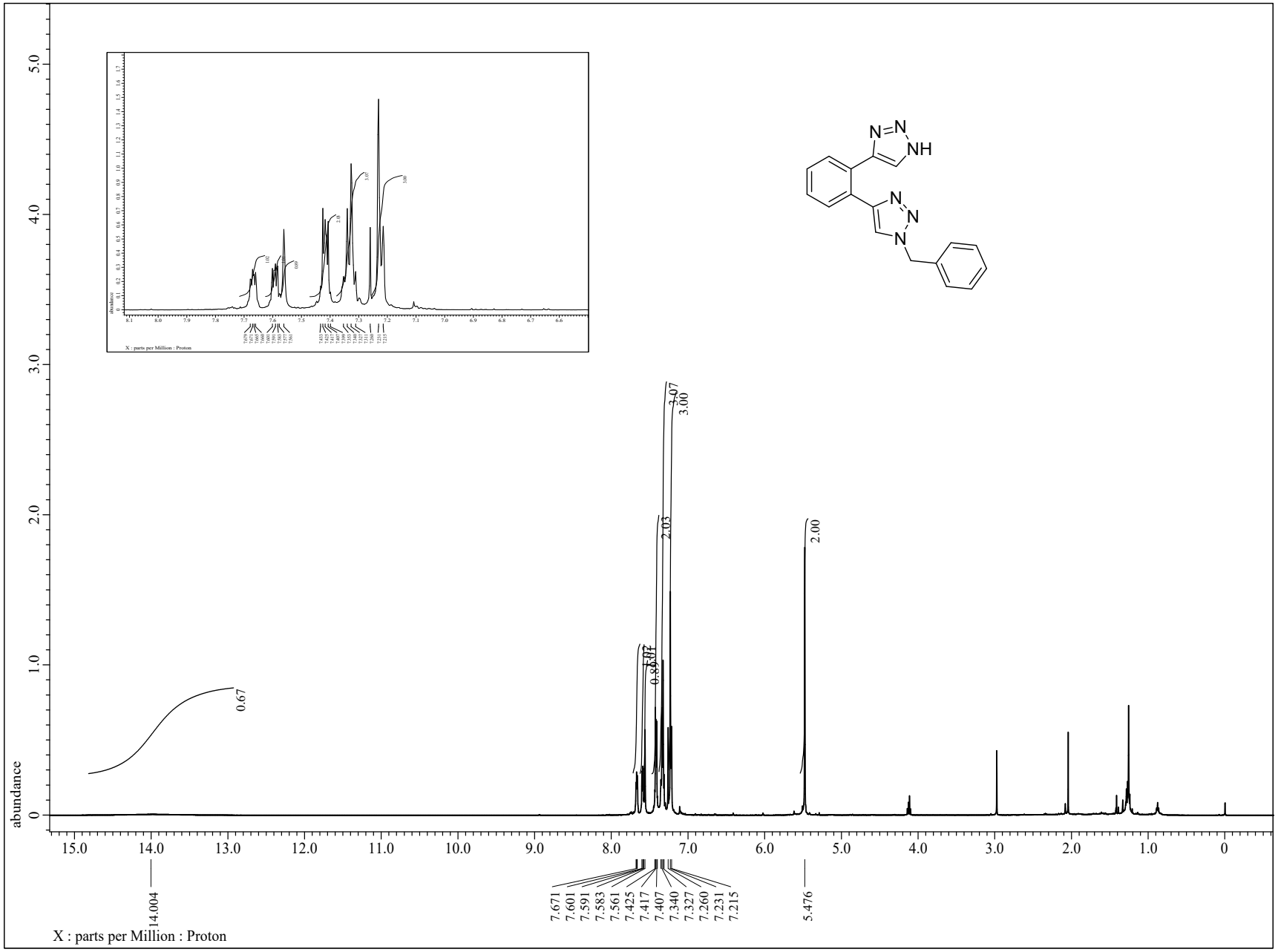

Figure S71: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**

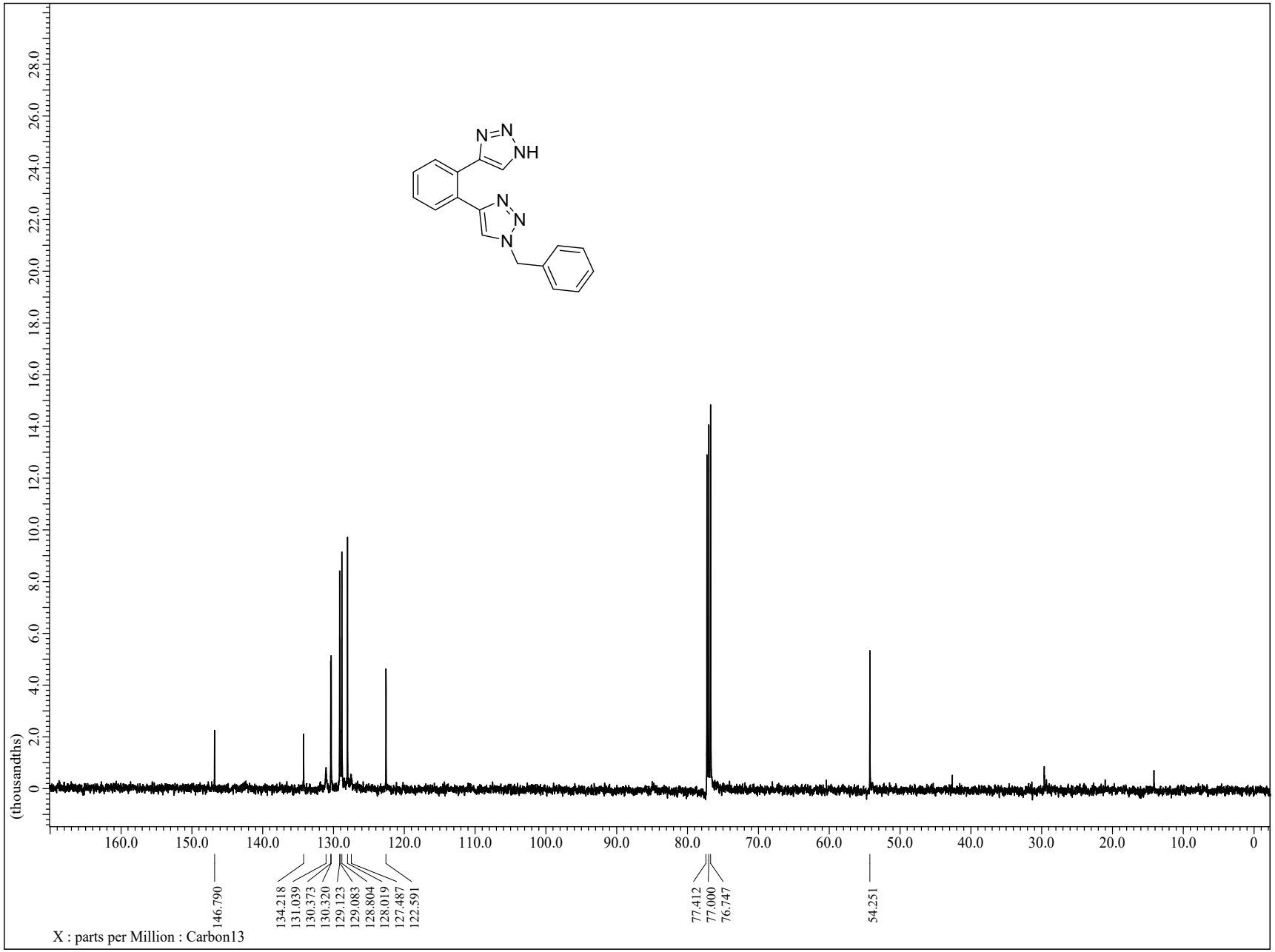

Figure S72: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **6**

6. ^{1}H and ^{13}C NMR spectra of 4-glycosyl-*NH*-1,2,3-triazoles (**8, 9, 11, 13**)

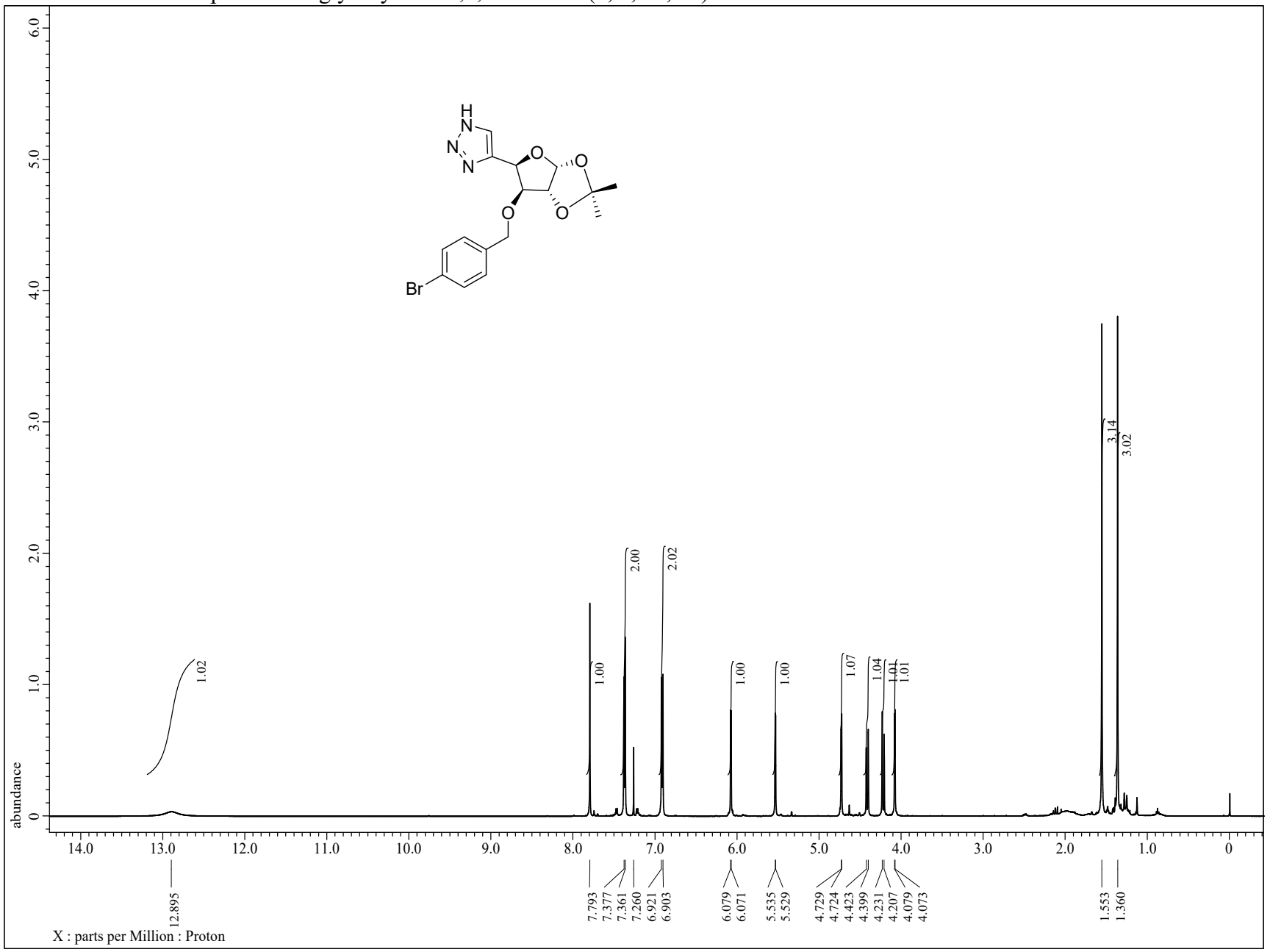

Figure S73: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**

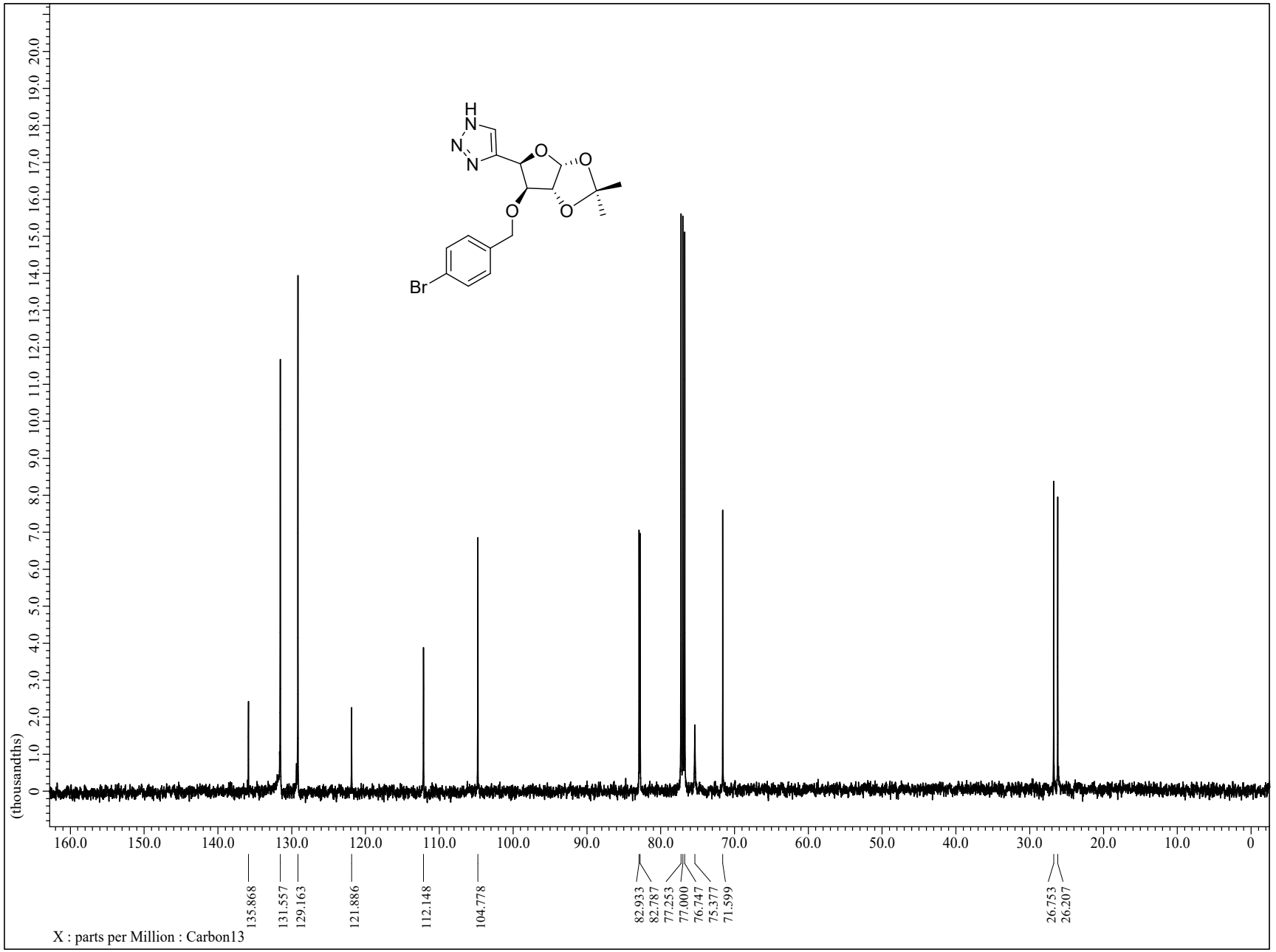

Figure S74: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **8**

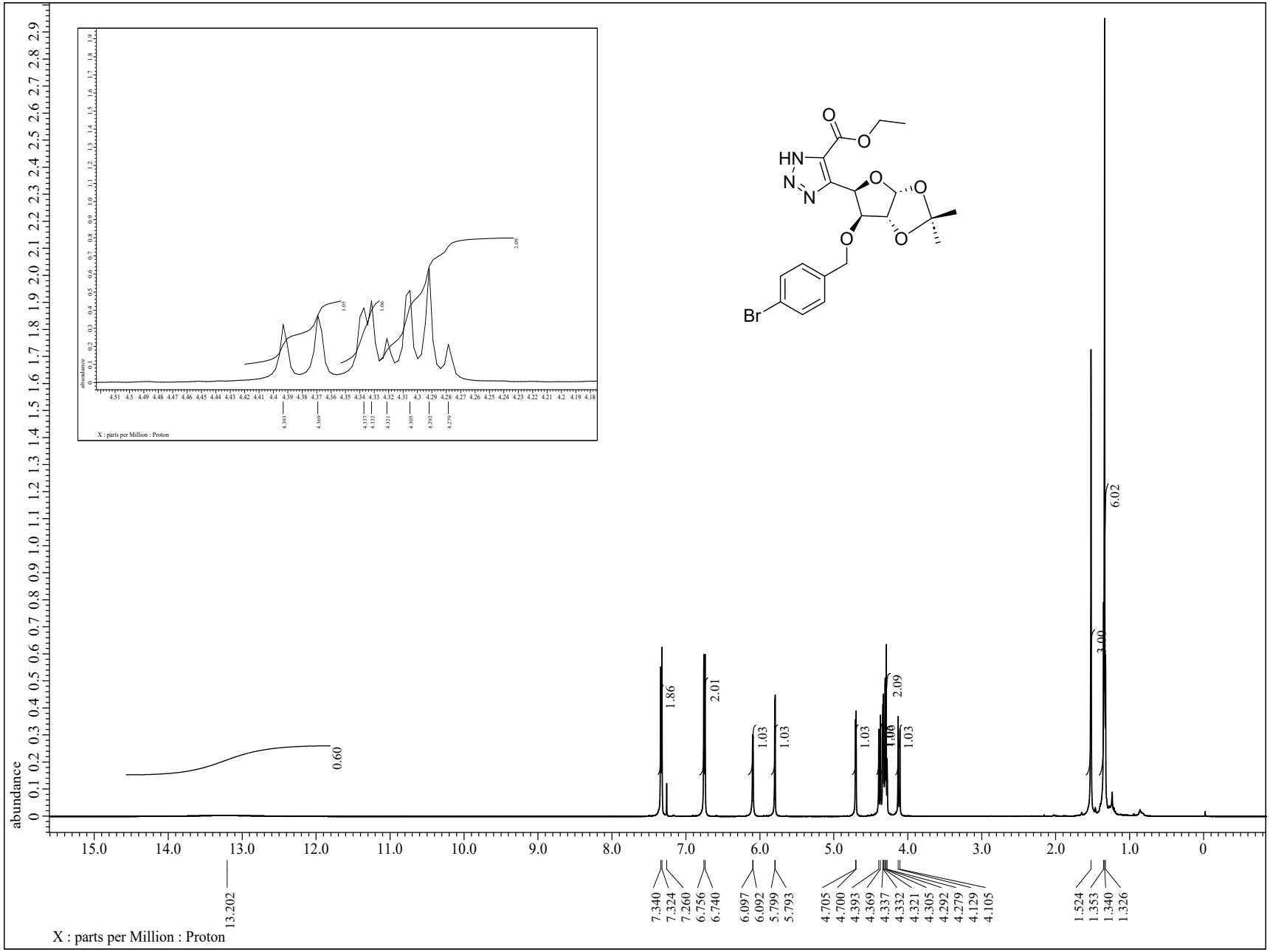

Figure S75: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **9**

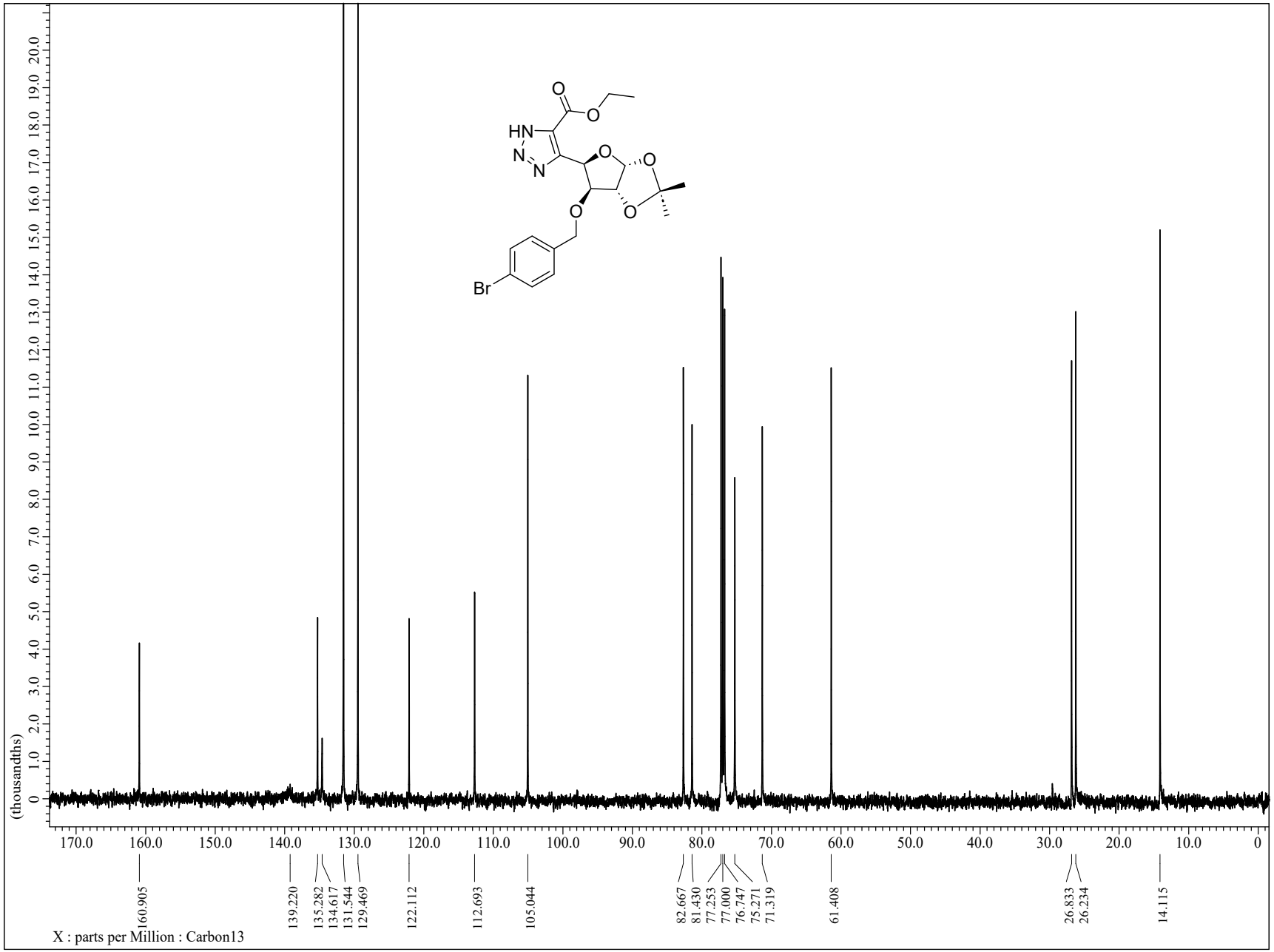

Figure S76: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **9**

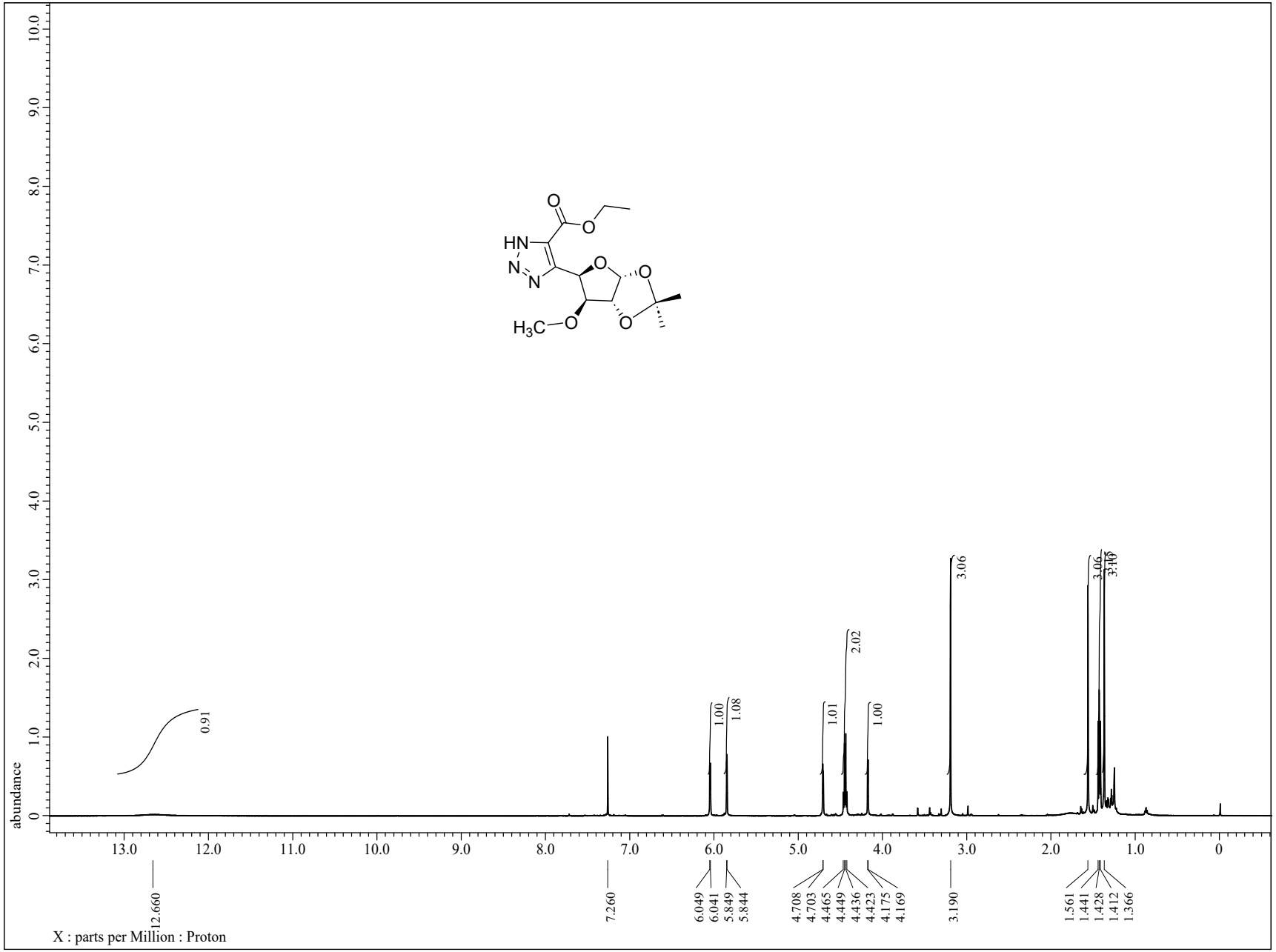

Figure S77: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**

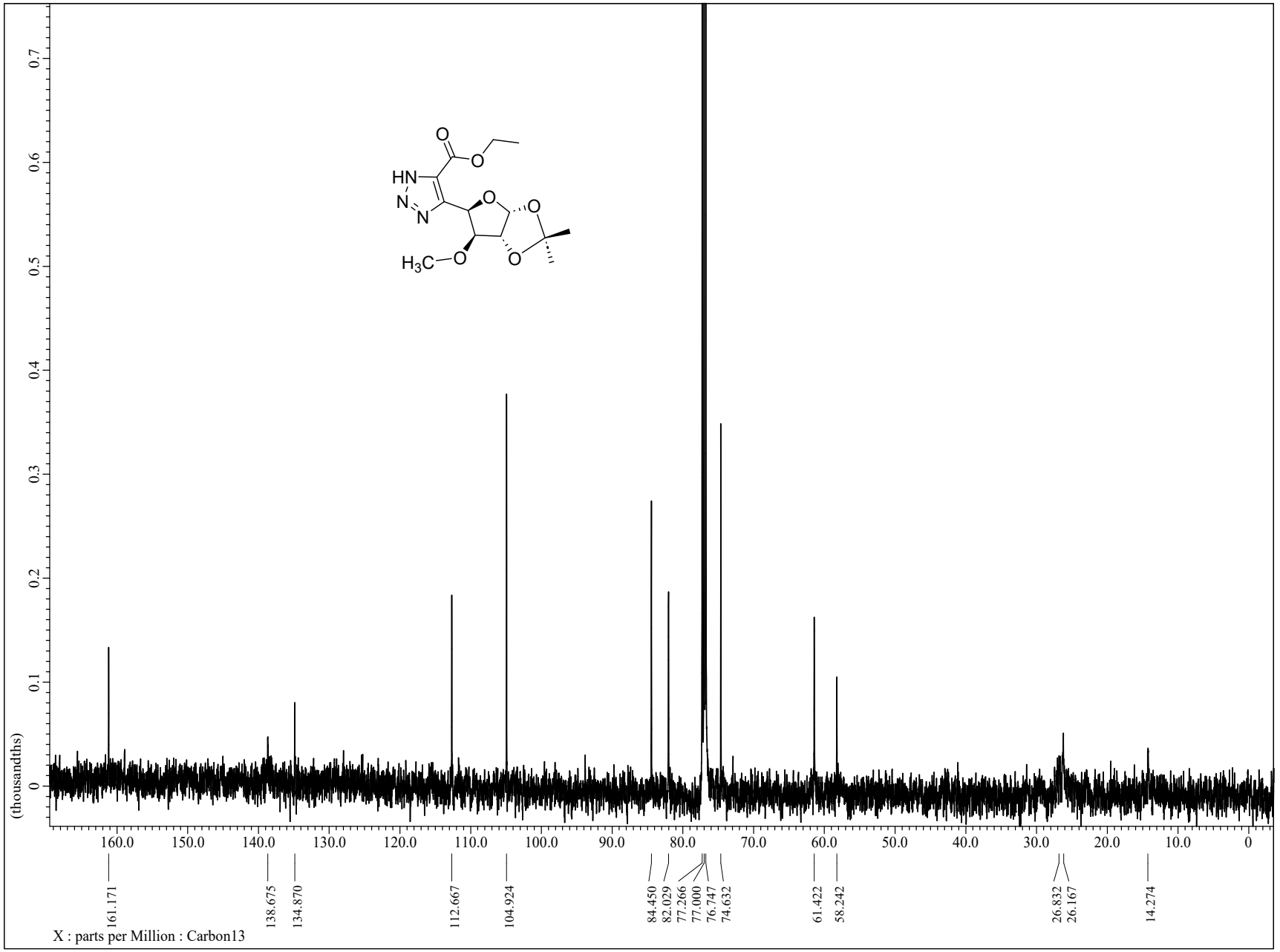

Figure S78: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **11**

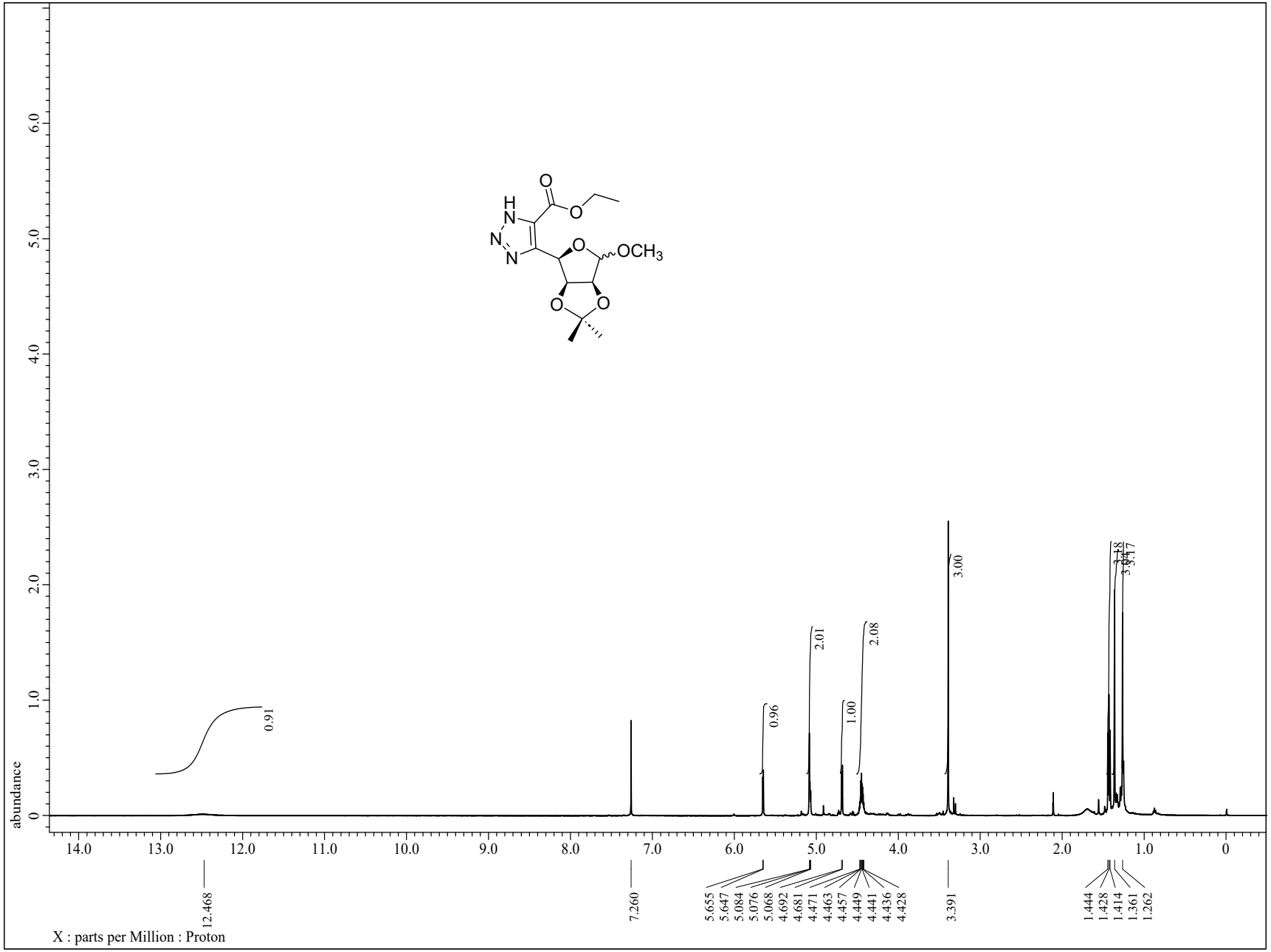

Figure S79: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **13**

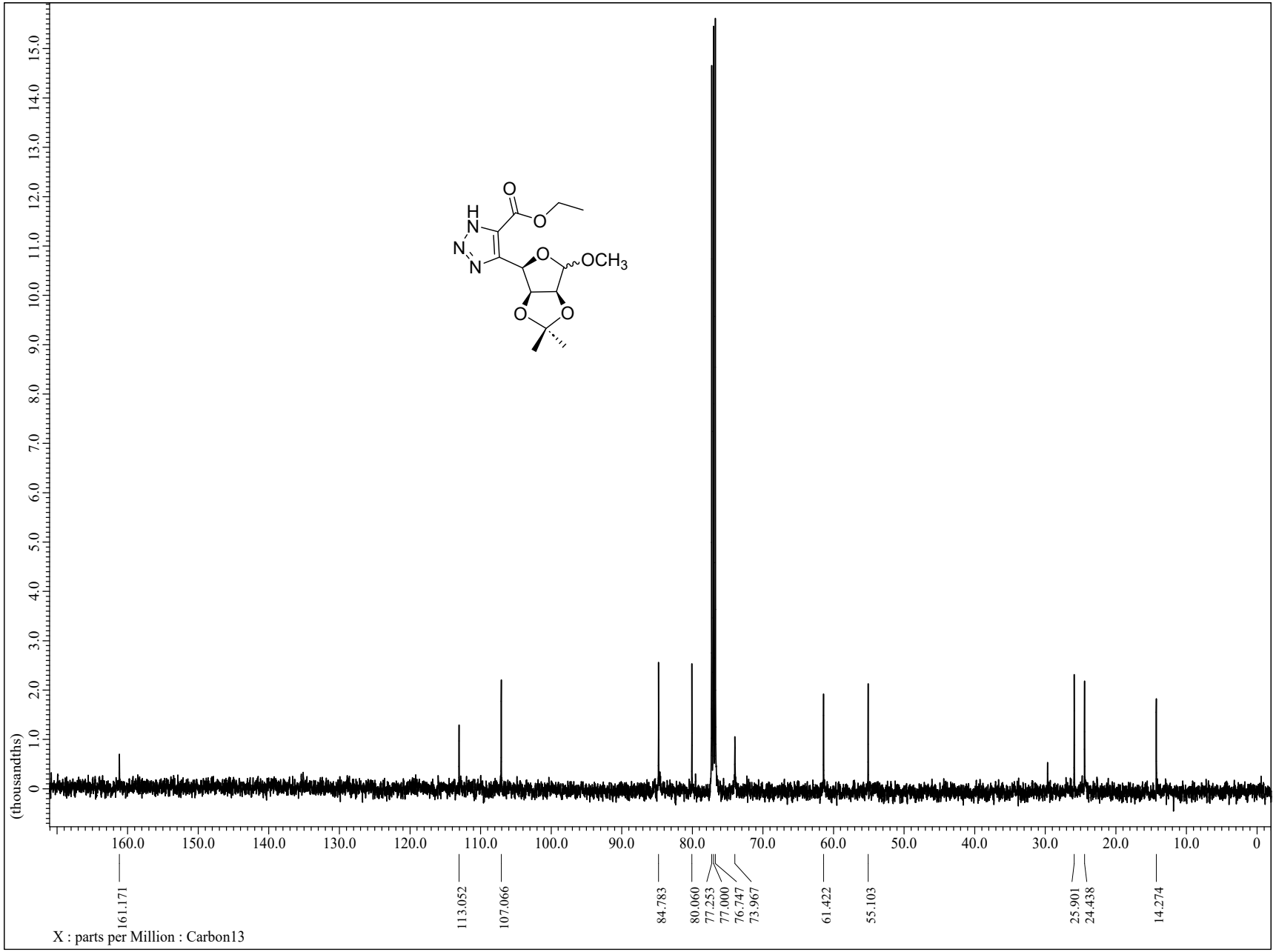

Figure S80: ^{13}C NMR (125 MHz, $CDCl_3$) of compound **13**

6. ^{19}F NMR Spectra of compound**s 2j**, **2k, 2l, 2v**, **2ab, 2af, 4a**

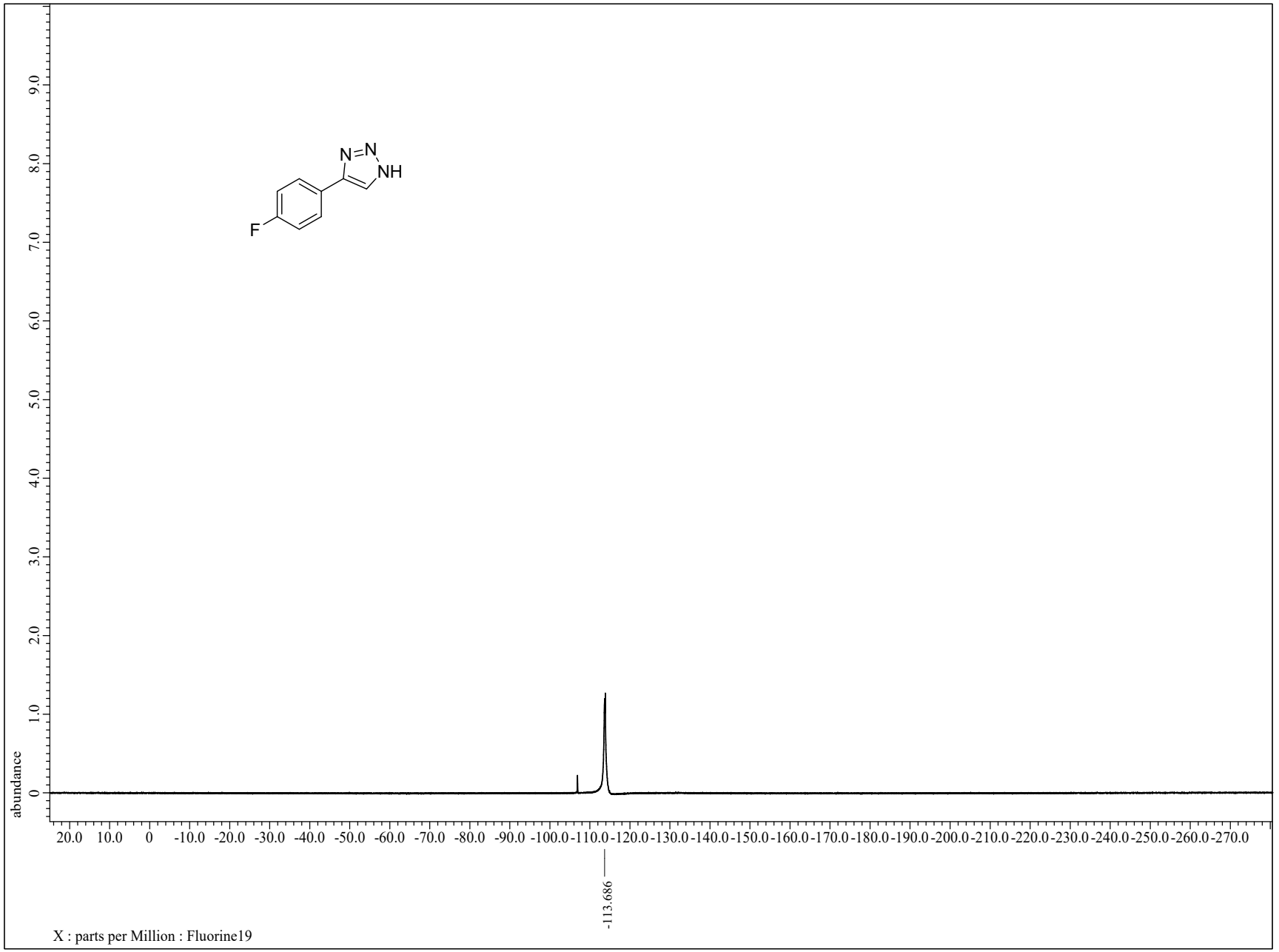

Figure S81: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2j**

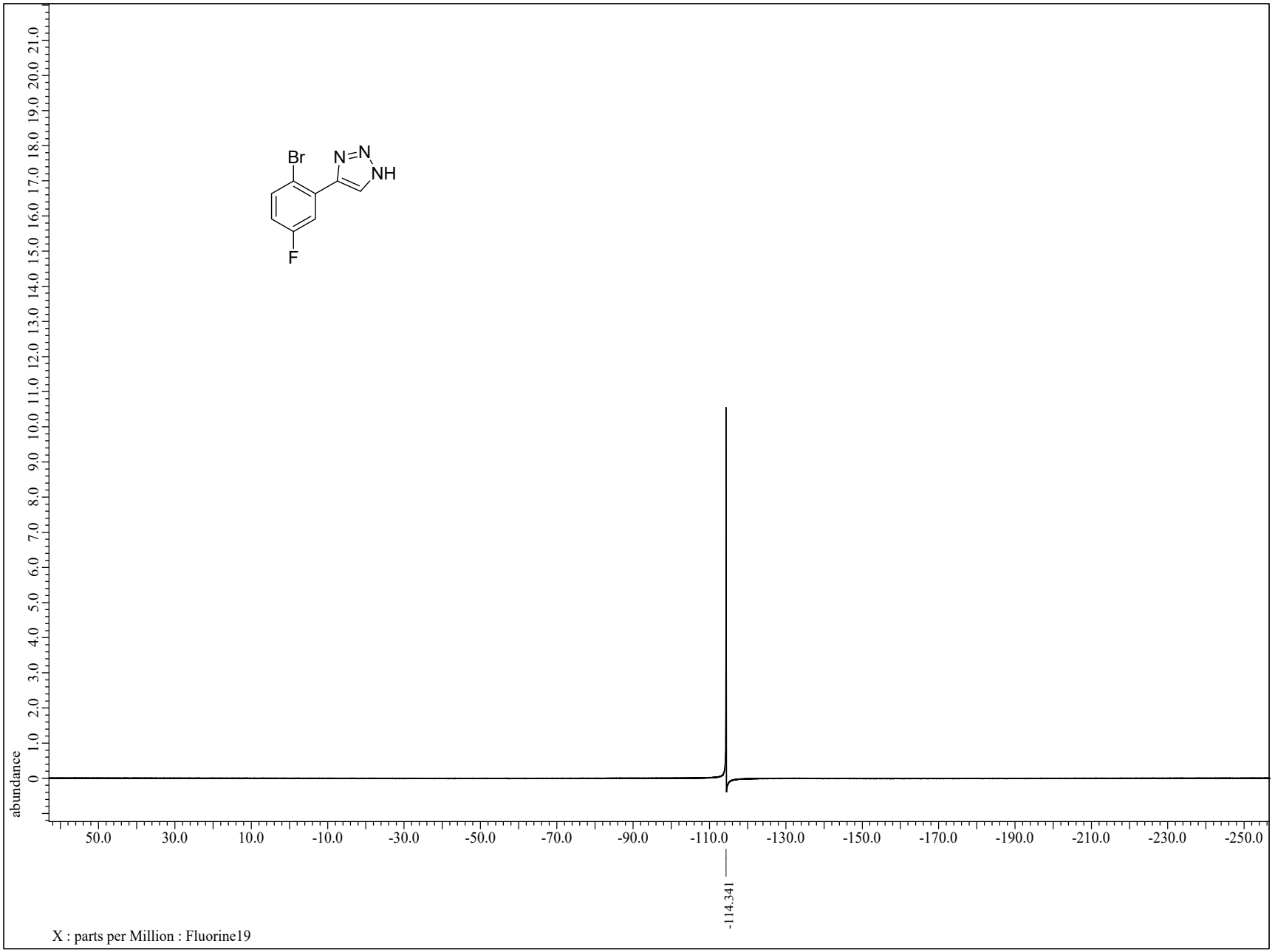

Figure S82: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2k**

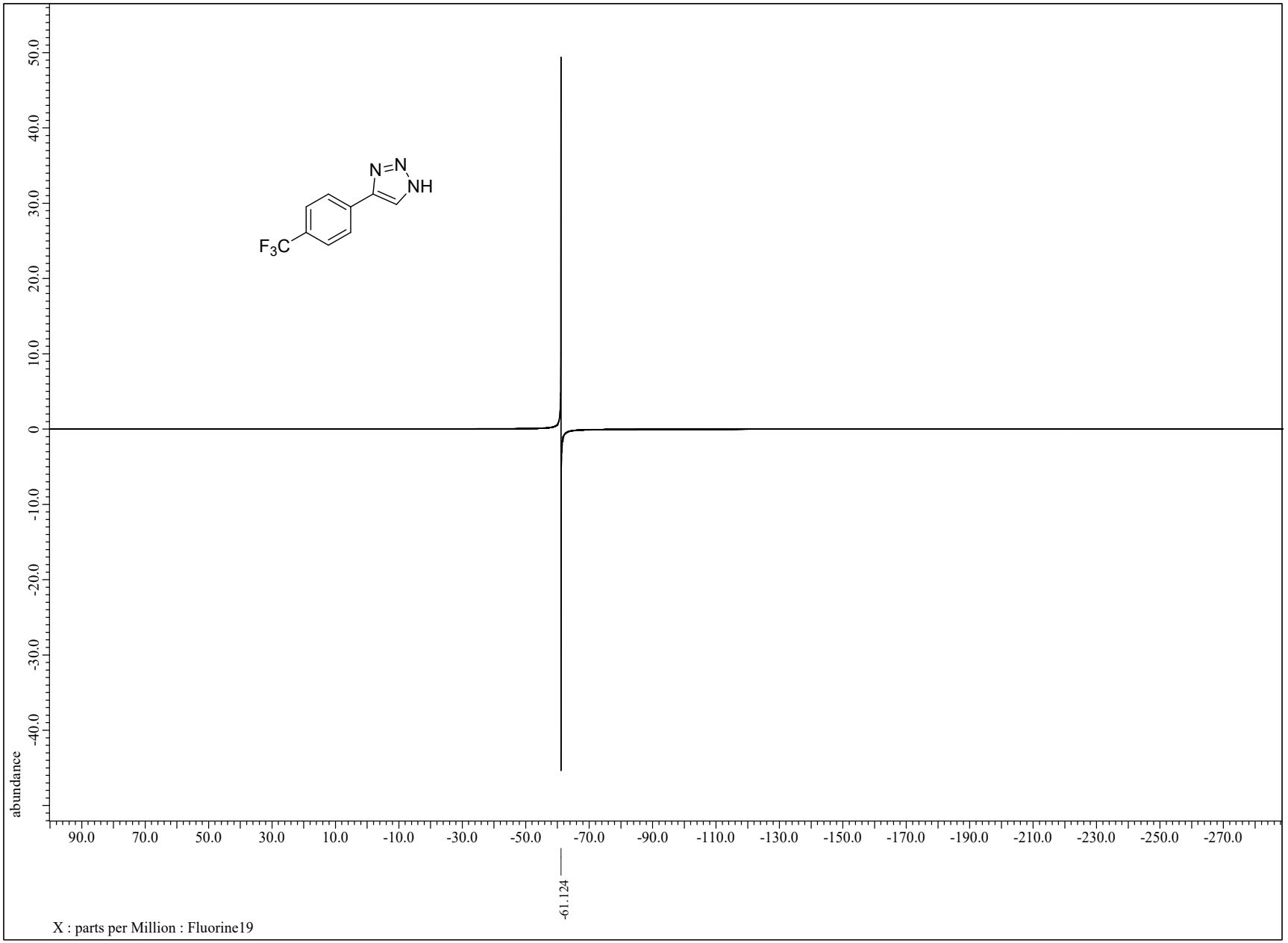

Figure S83: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2l**

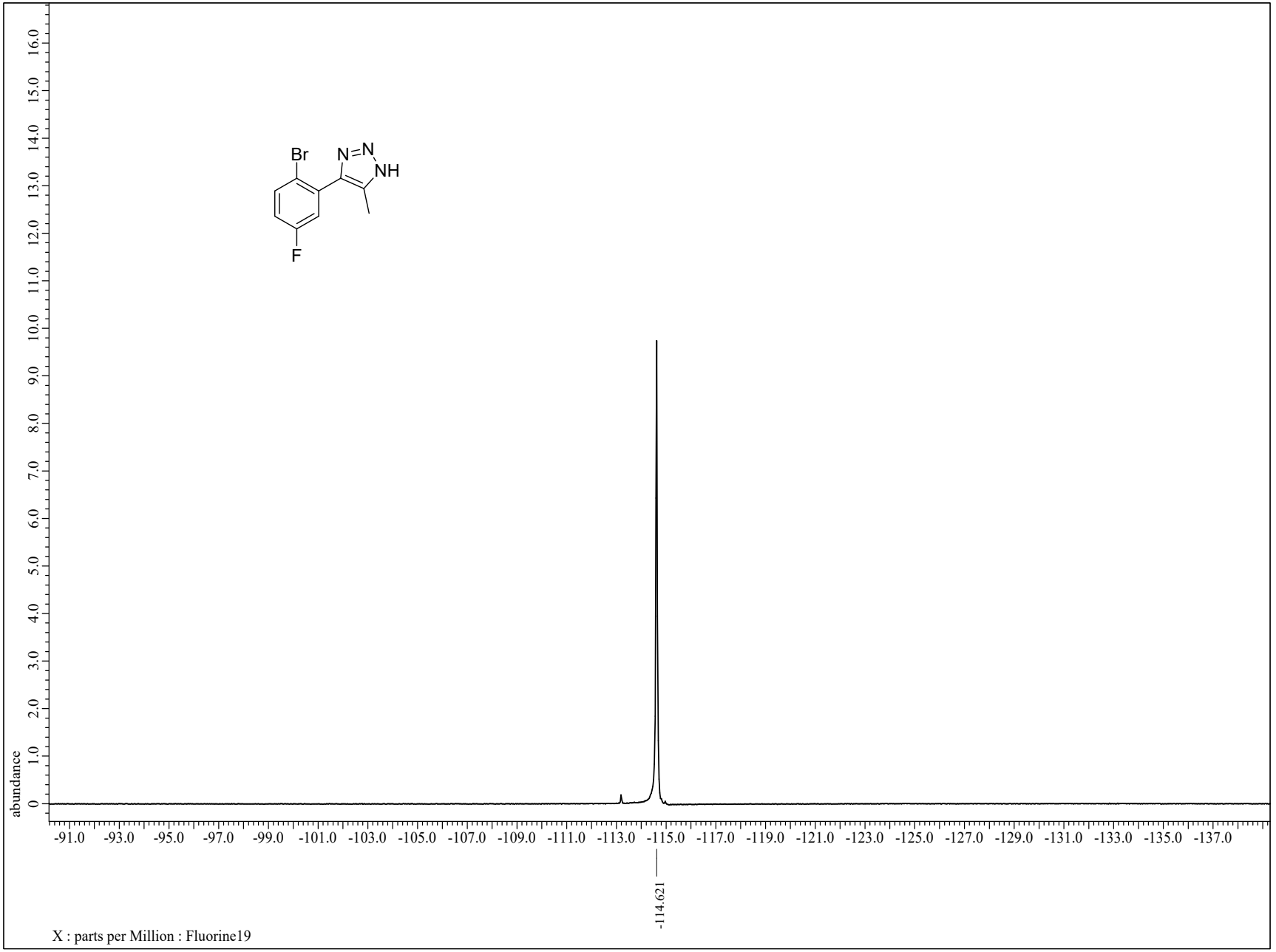

Figure S84: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2v**

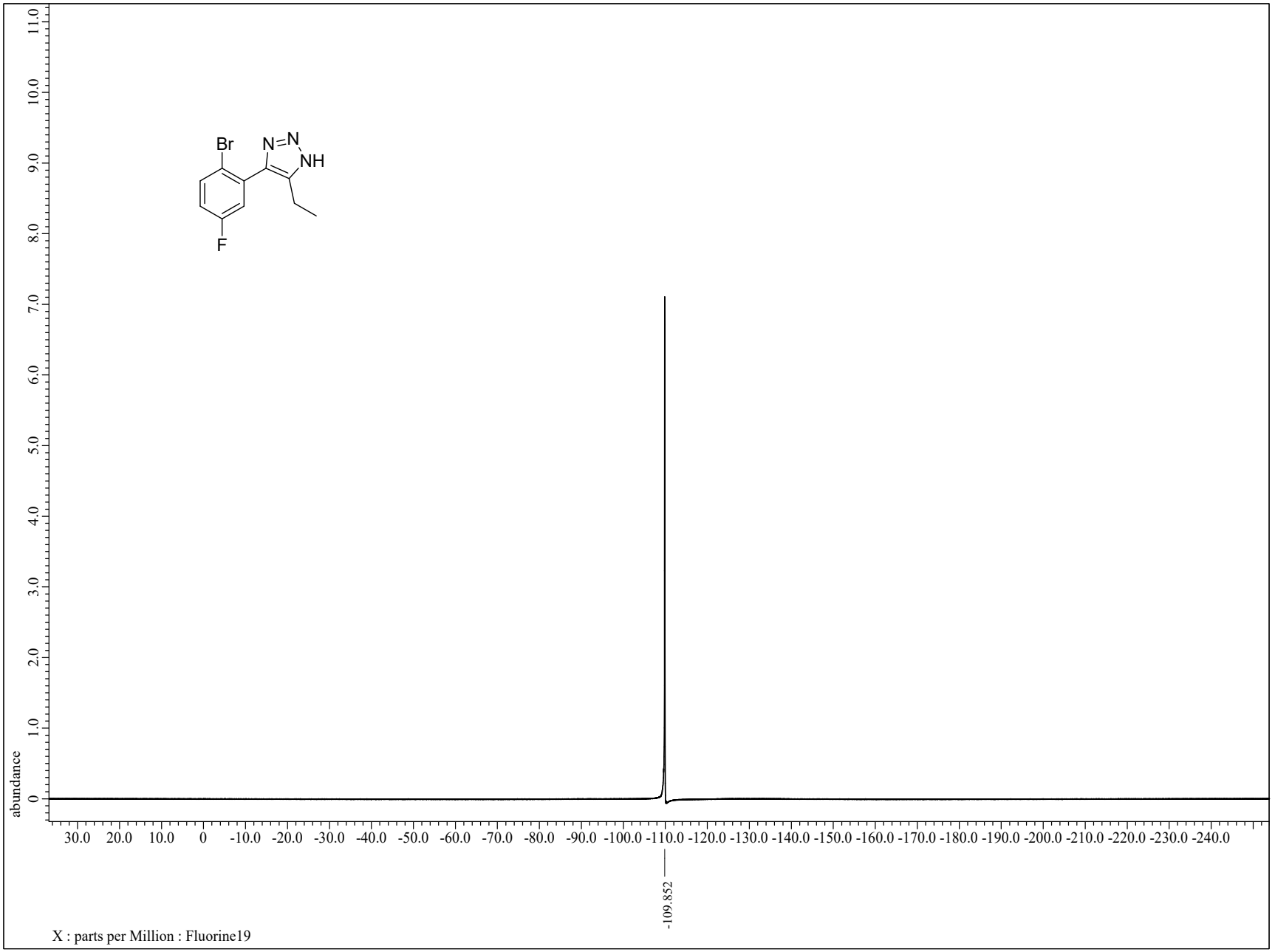

Figure S85: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2ab**

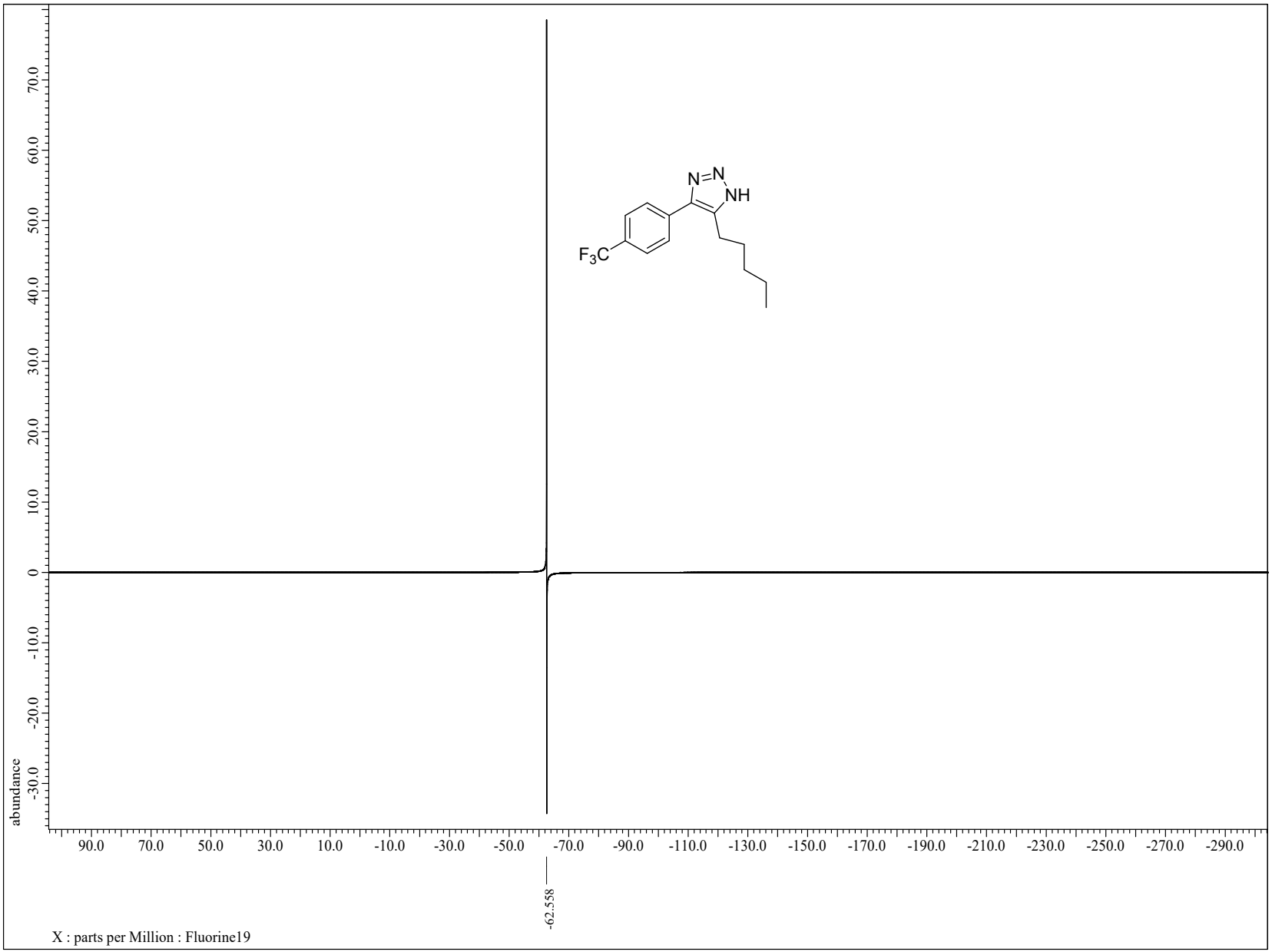

Figure S86: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **2af**

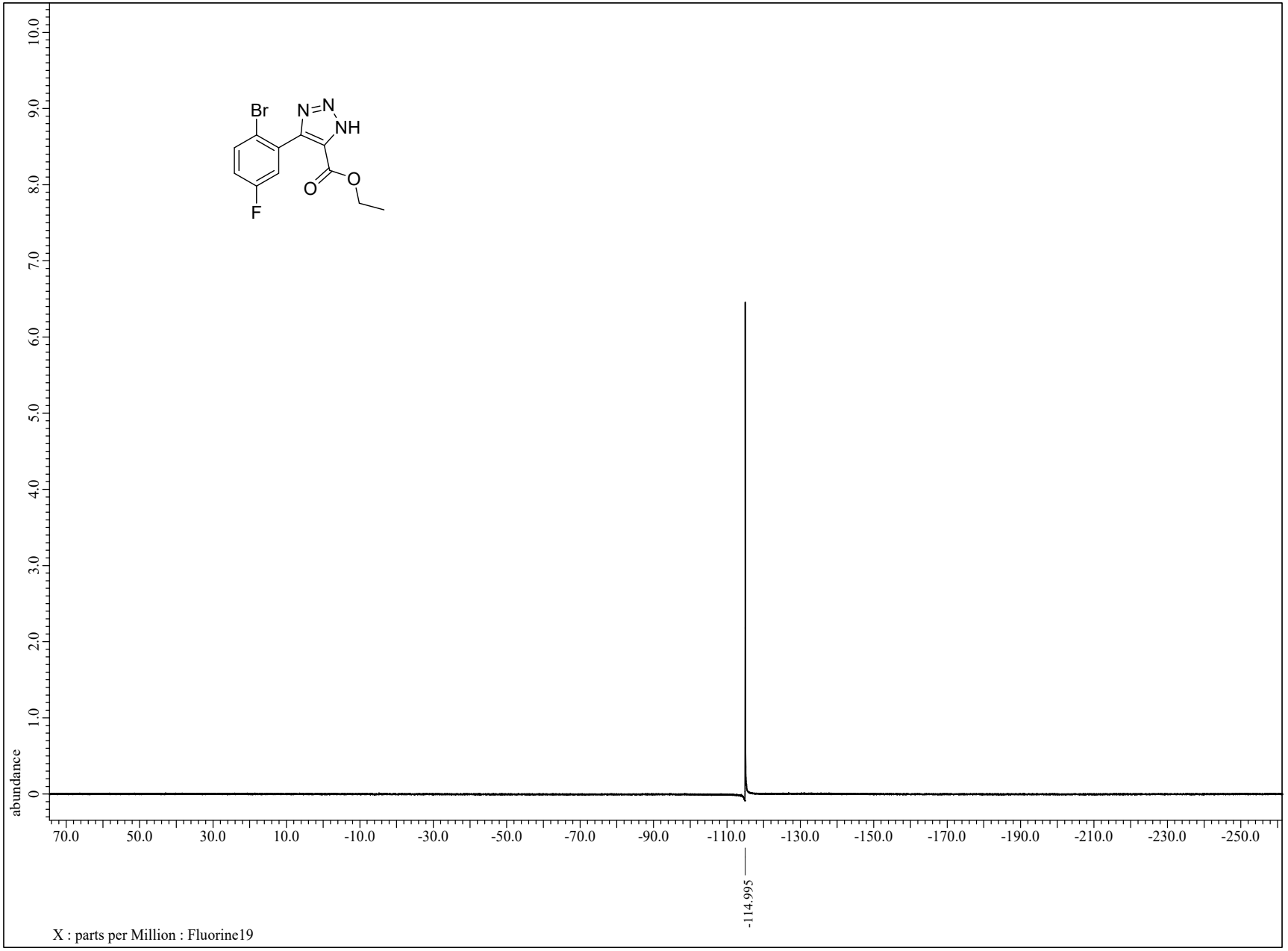

Figure S87: ^{19}F NMR (470 MHz, DMSO-d_6) of compound **4a**

8. HRMS of developed compounds **2h,2i, 2k, 2l, 2q, 2s, 2u, 2v, 2z, 2ab, 2ac, 2ad, 2ae, 2af, 4a, 4b, 4c, 6**, **8, 9, 11, 13.**.

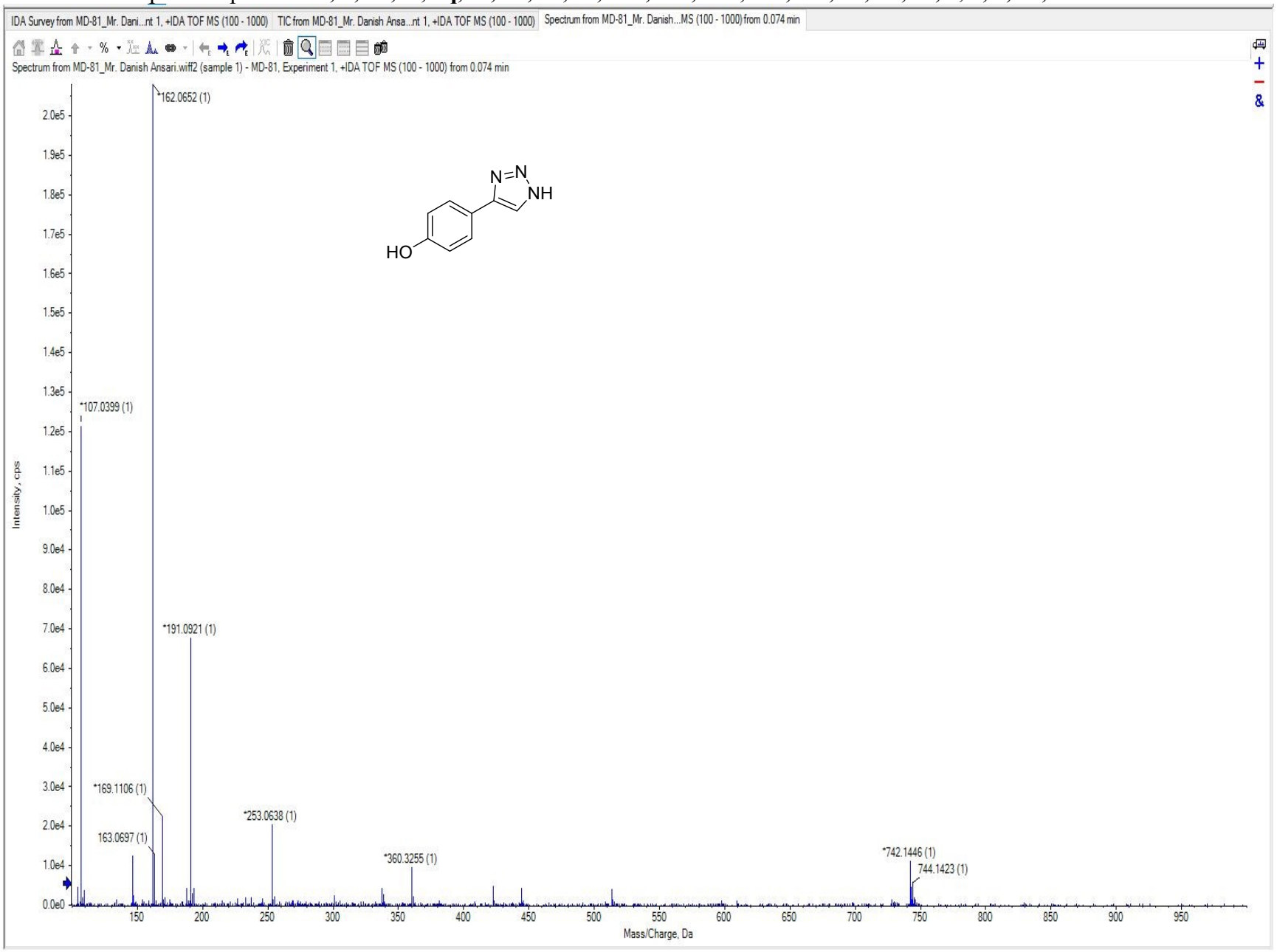

Figure S88: HRMS spectra of compound **2h**

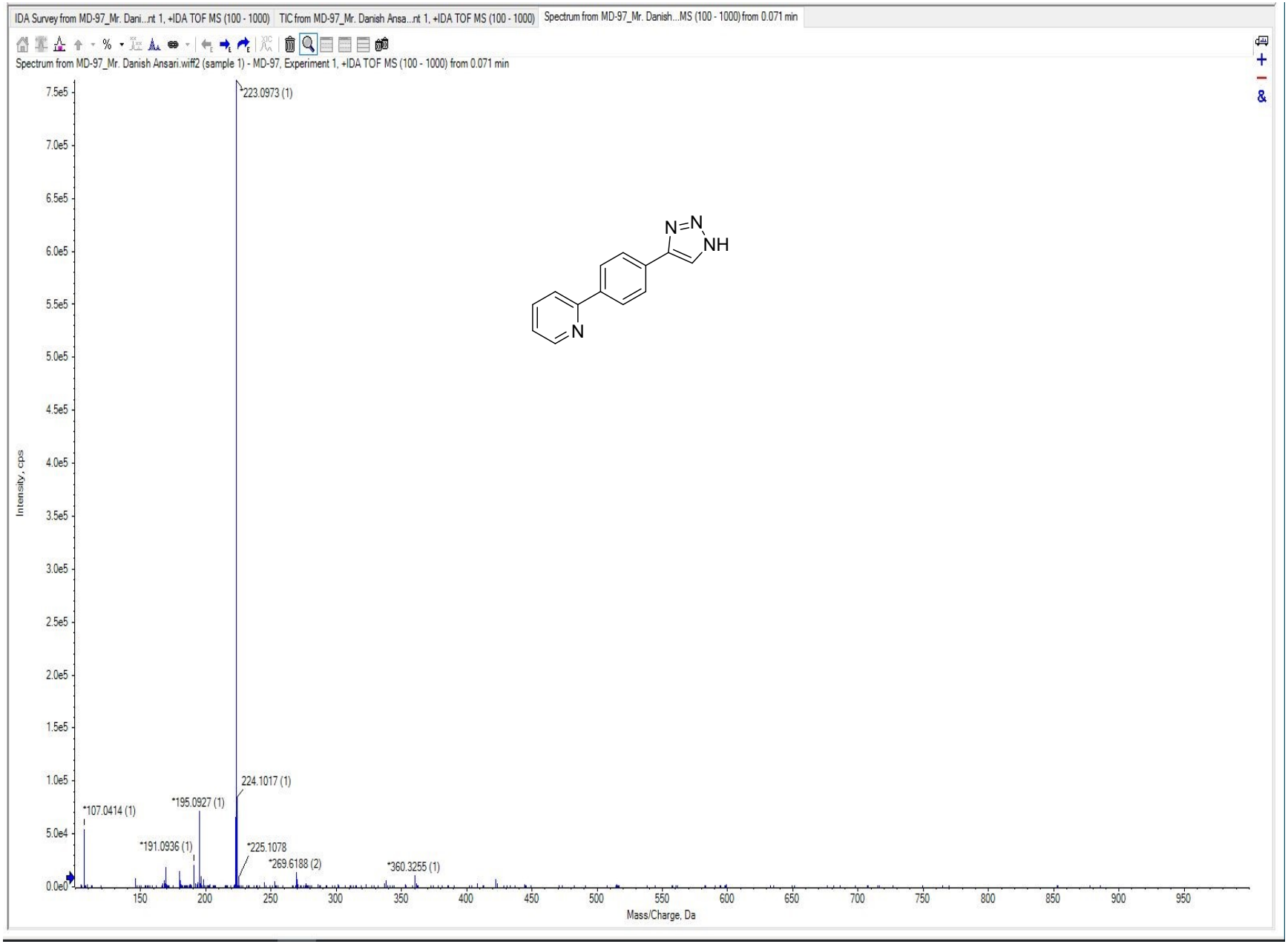

Figure S89: HRMS spectra of compound **2i**

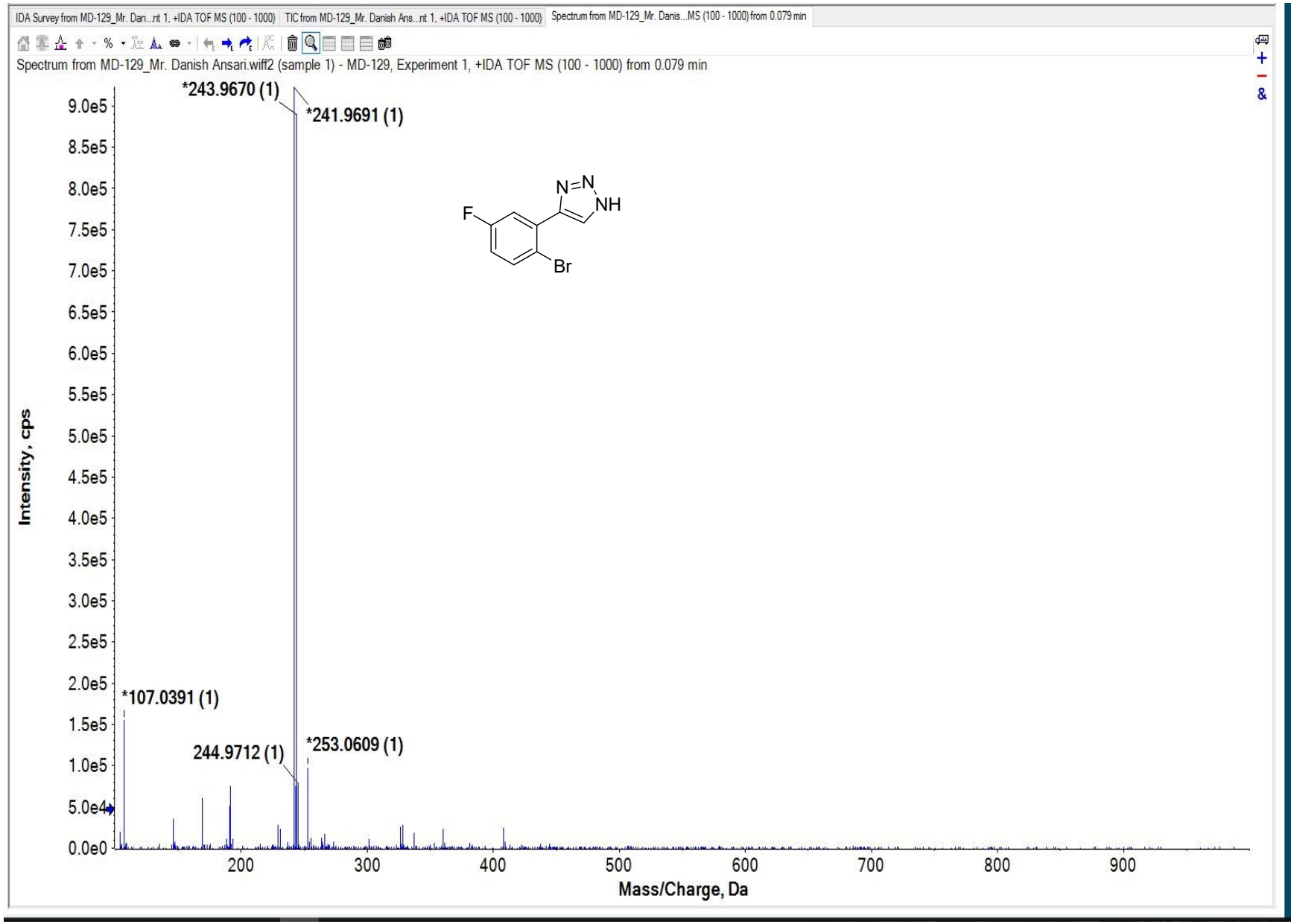

Figure S90: HRMS spectra of compound **2k**

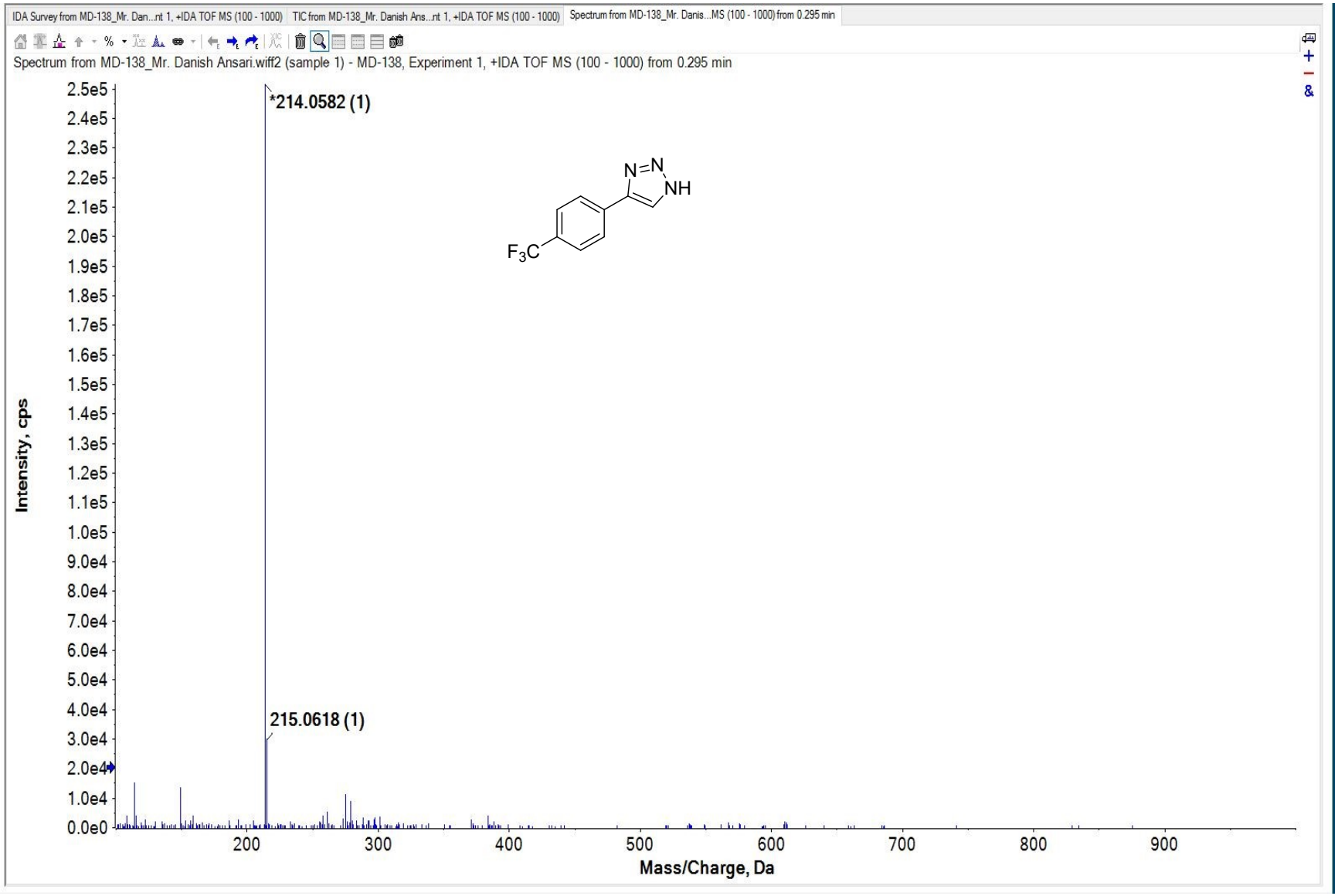

Figure S91: HRMS Spectra of compound **2l**

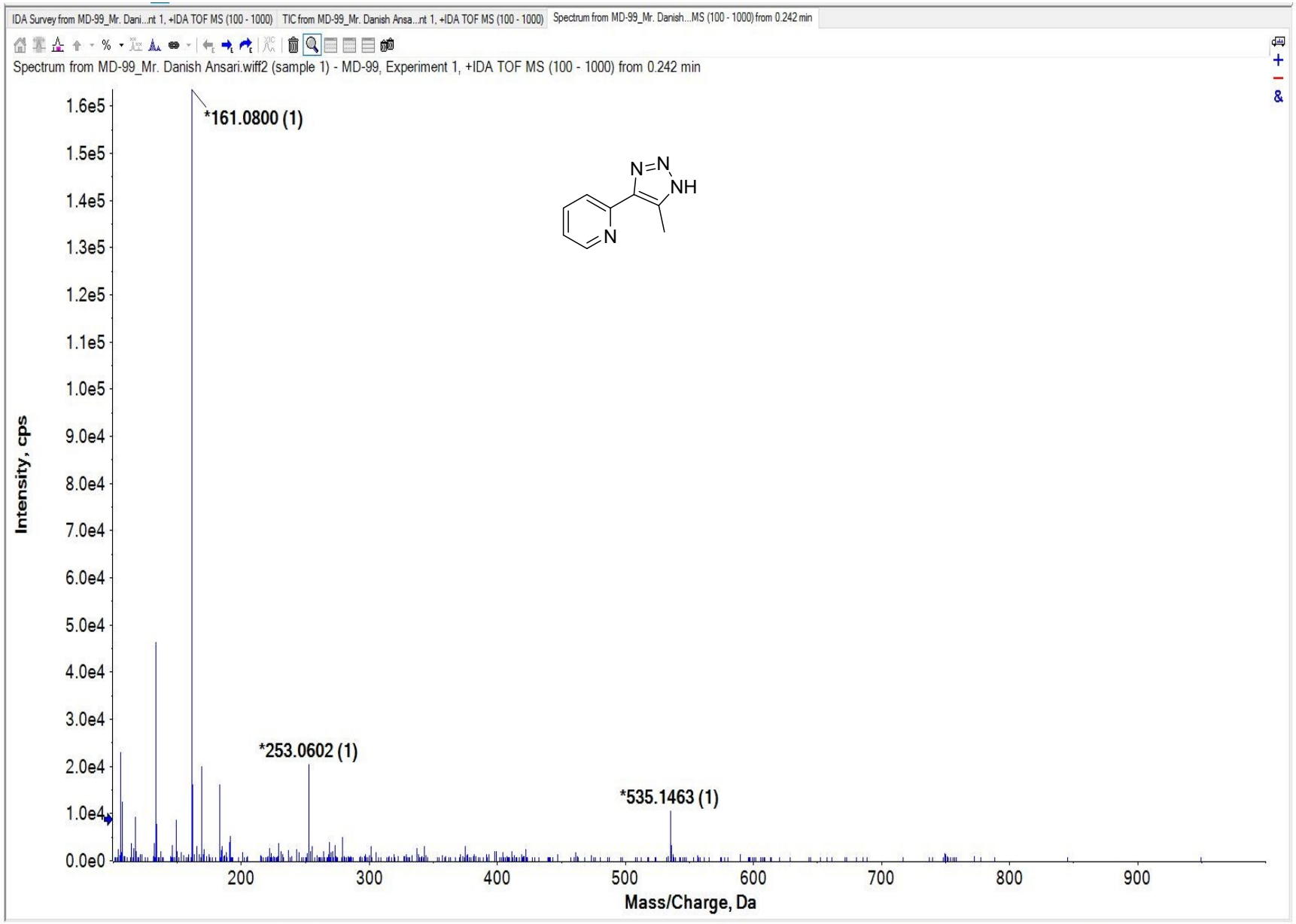

Figure S92: HRMS Spectra of compound **2q**

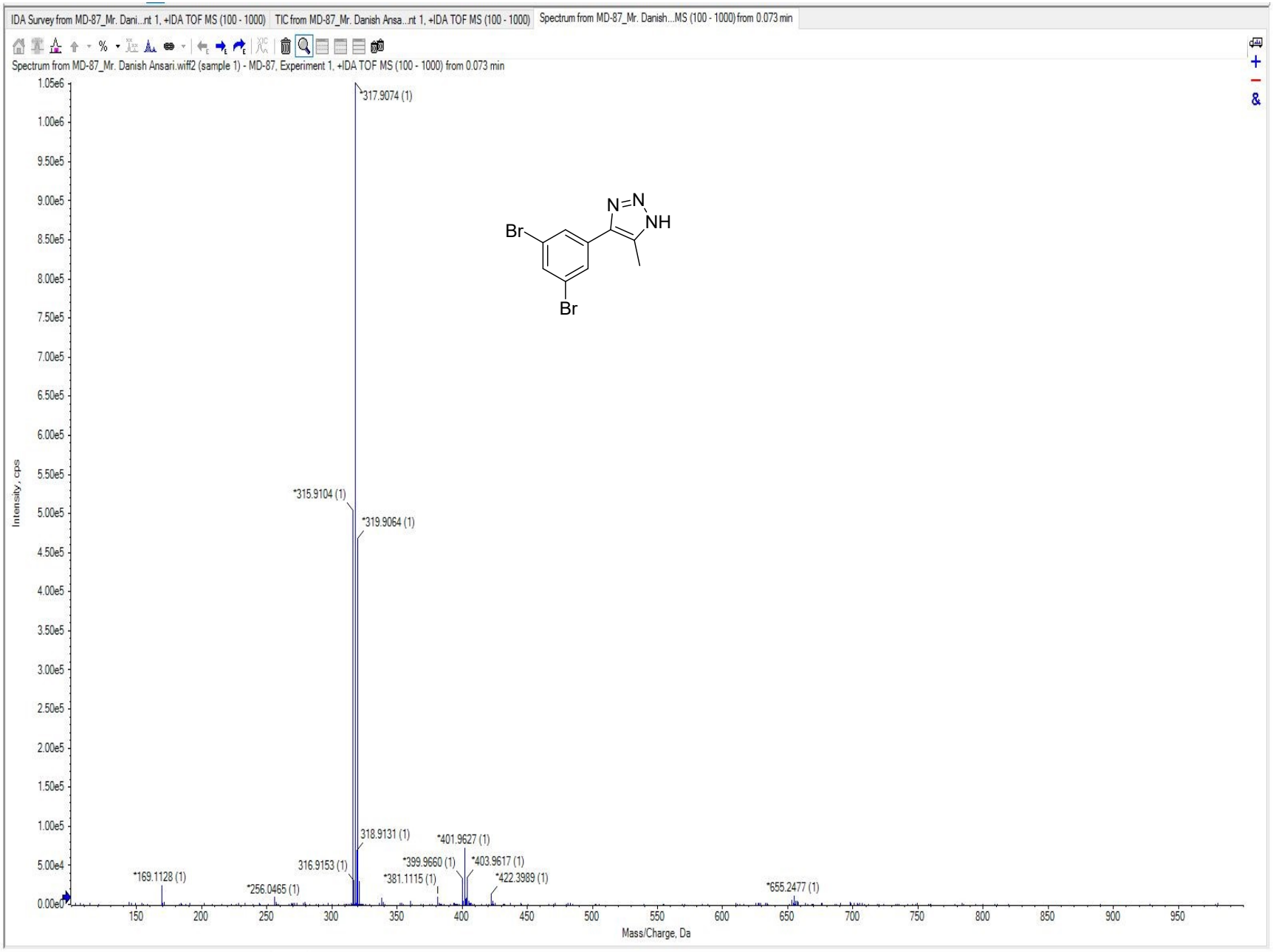

Figure S93: HRMS Spectra of compound **2s**

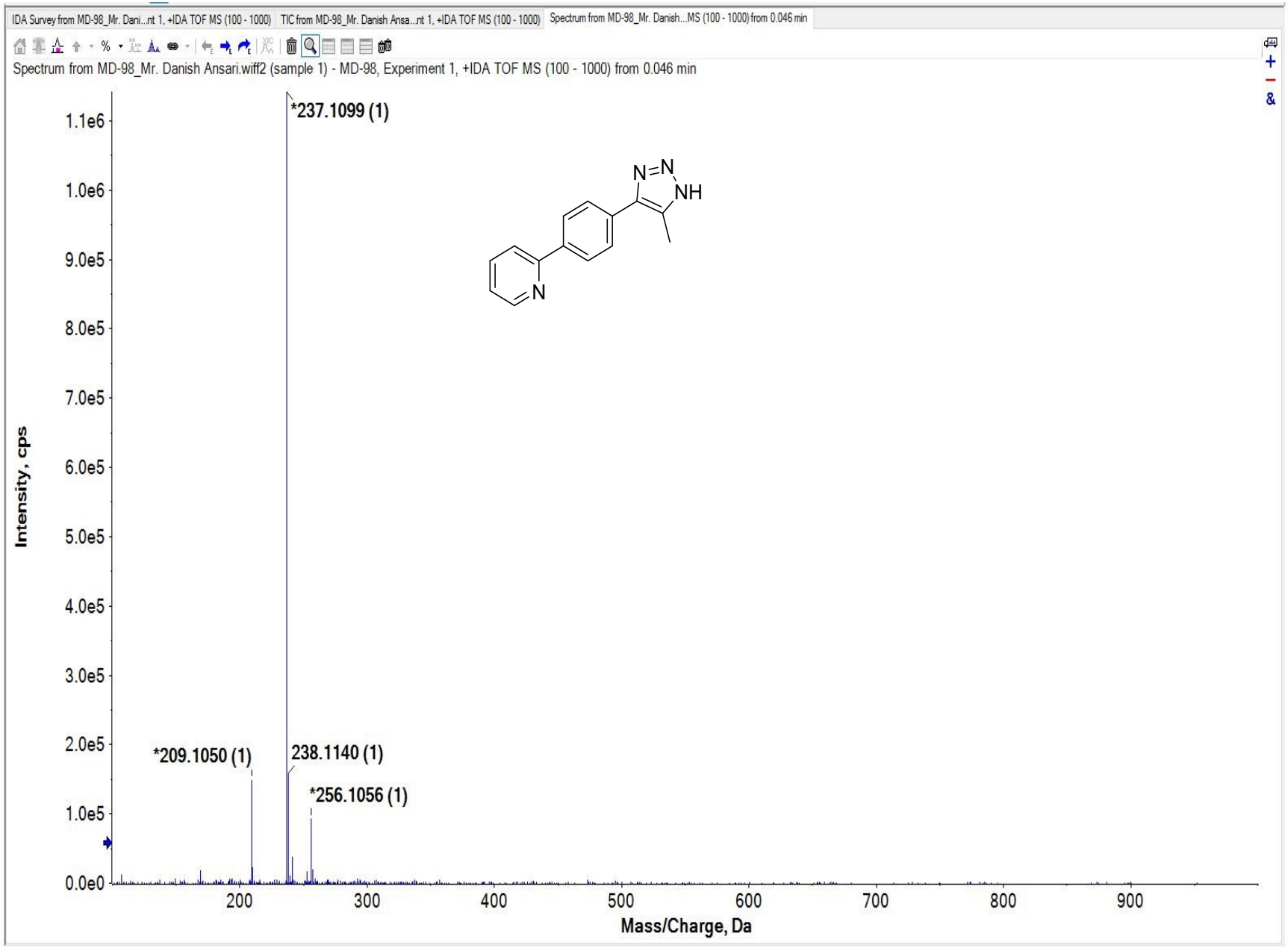

Figure S94:HRMS Spectra of compound **2u**

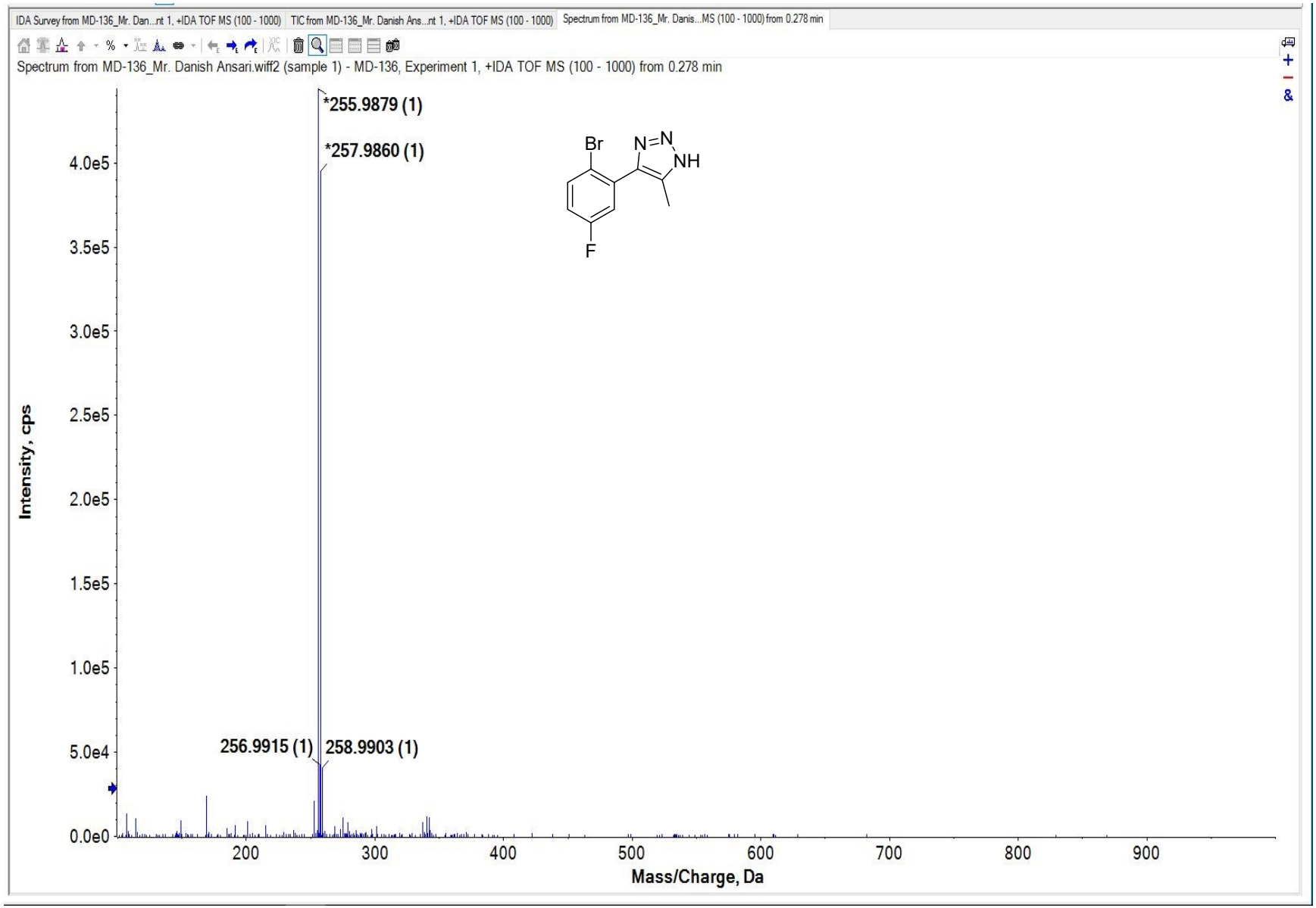

Figure S95:HRMS Spectra of compound **2v**

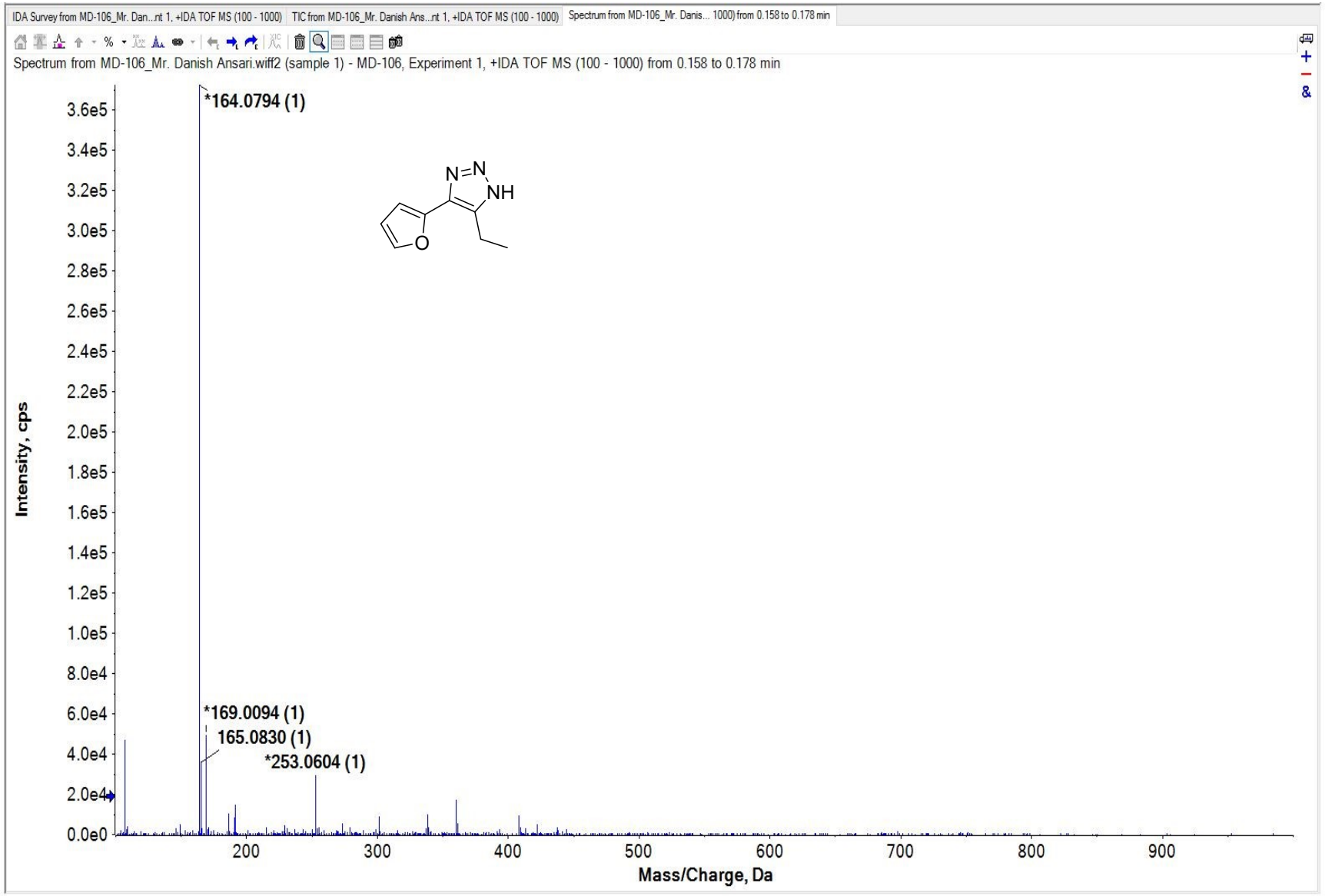

Figure S96: HRMS Spectra of compound **2z**

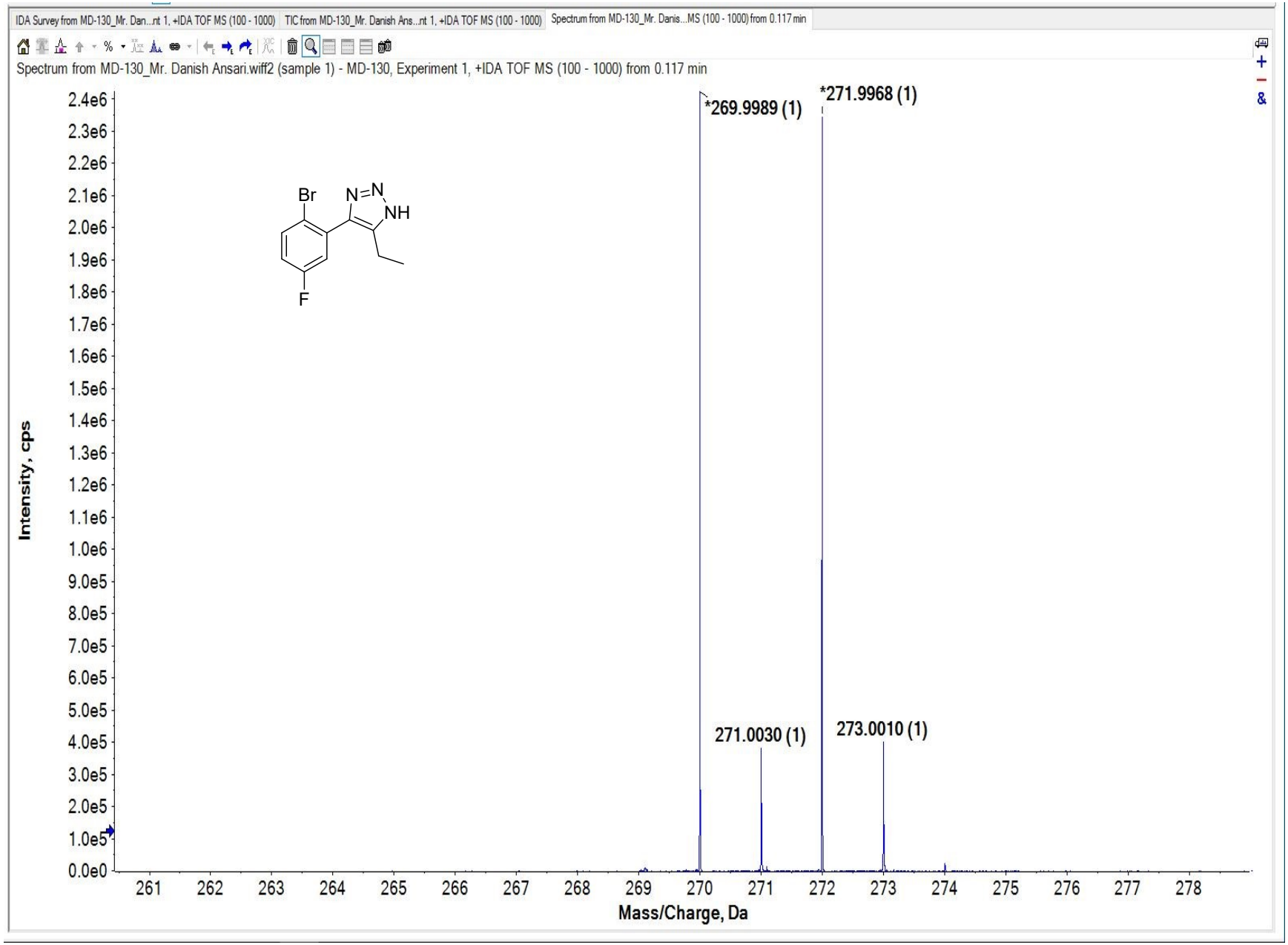

Figure S97: HRMS Spectra of compound **2ab**

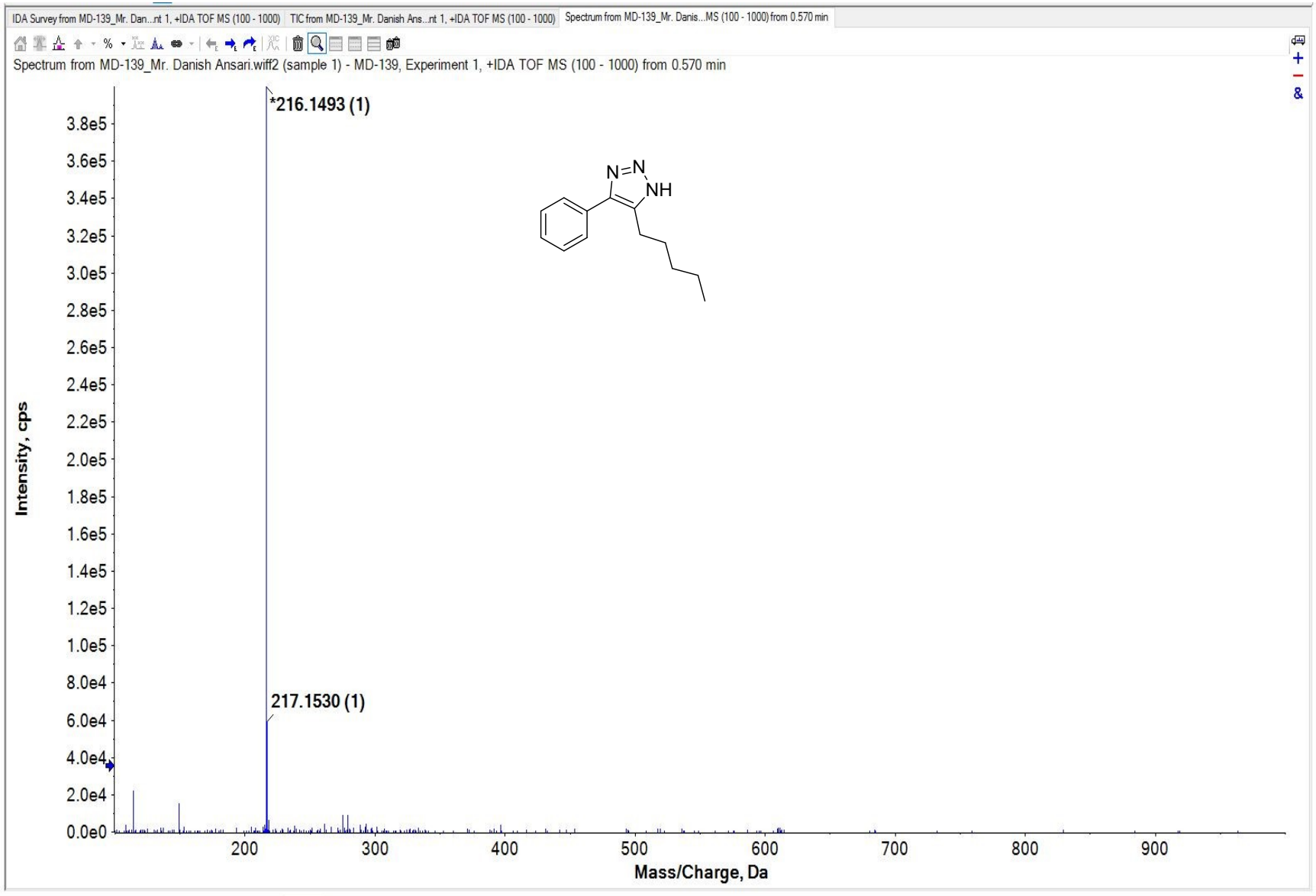

Figure S98: HRMS Spectra of compound **2ac**

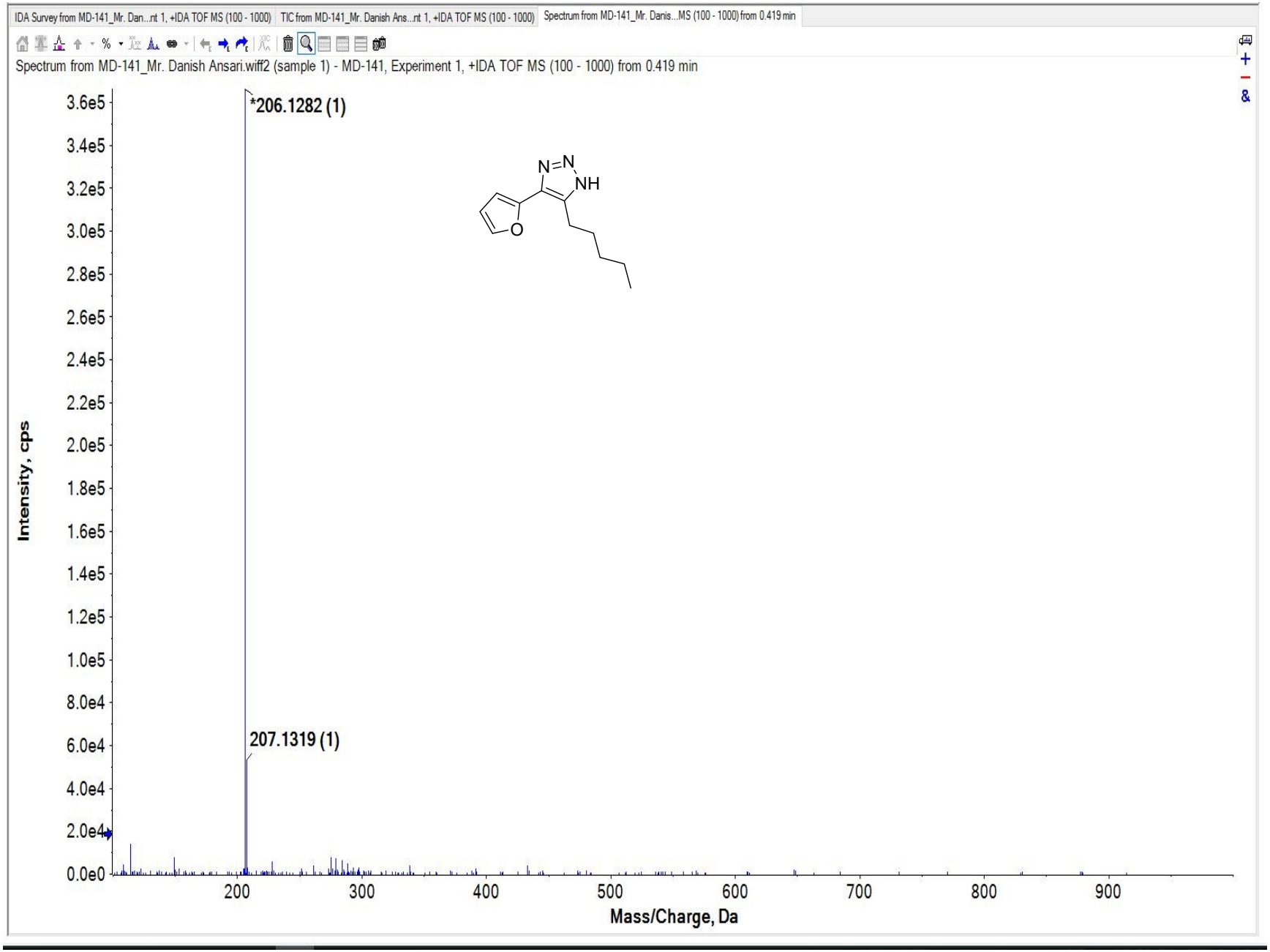

Figure S99: HRMS Spectra of compound **2ad**

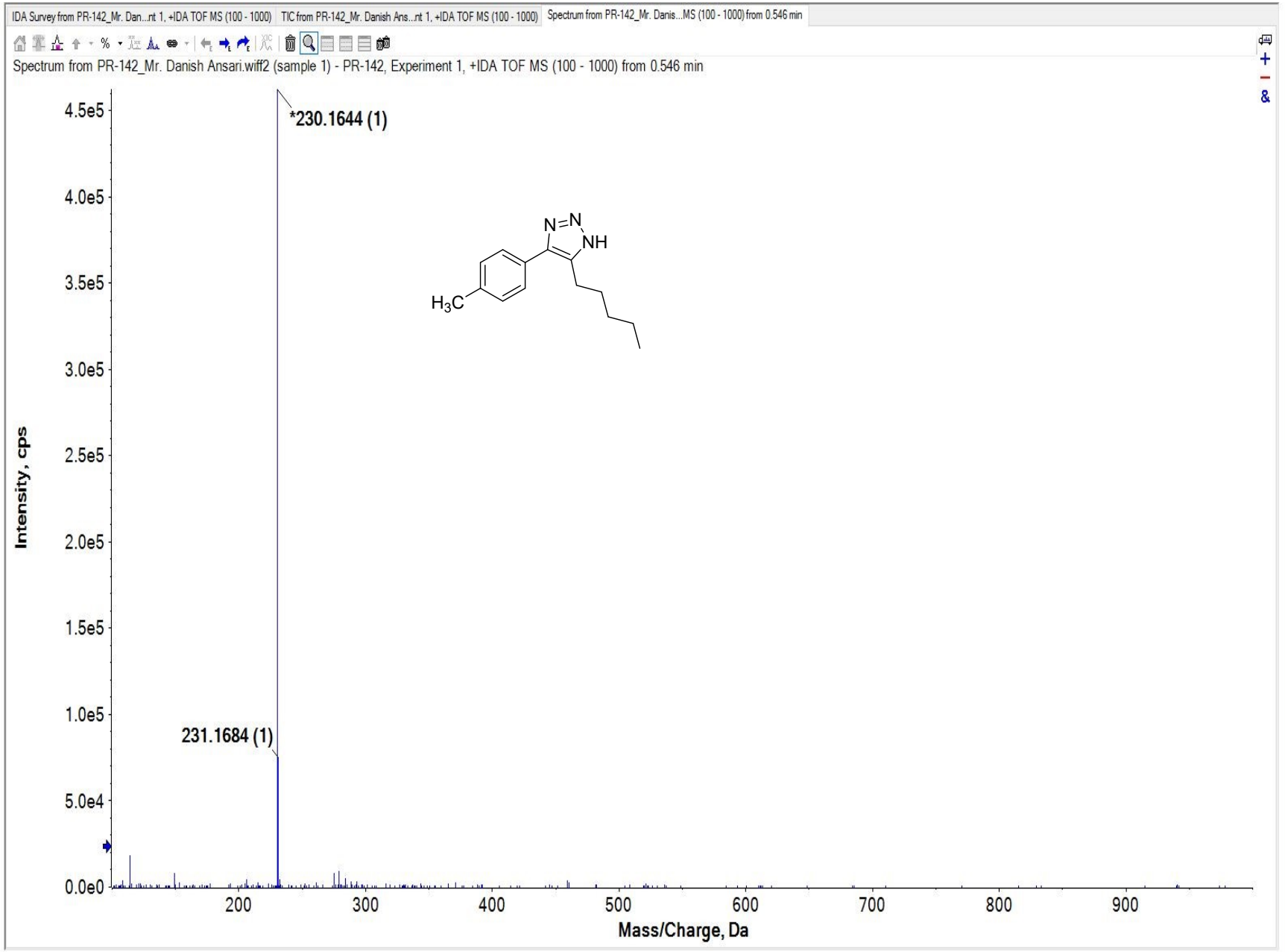

Figure S100: HRMS Spectra of compound **2ae**

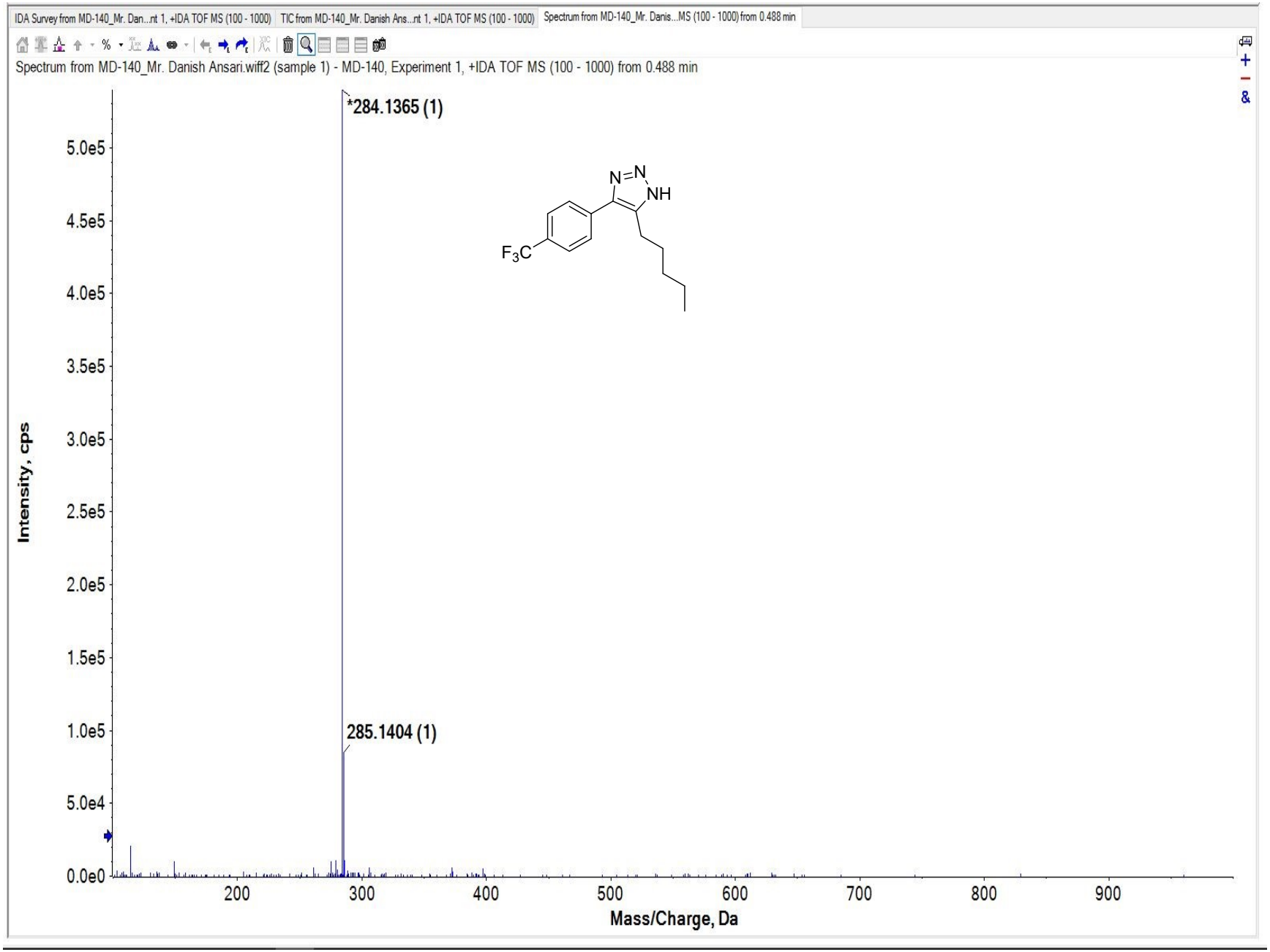

Figure S101: HRMS Spectra of compound **2af**

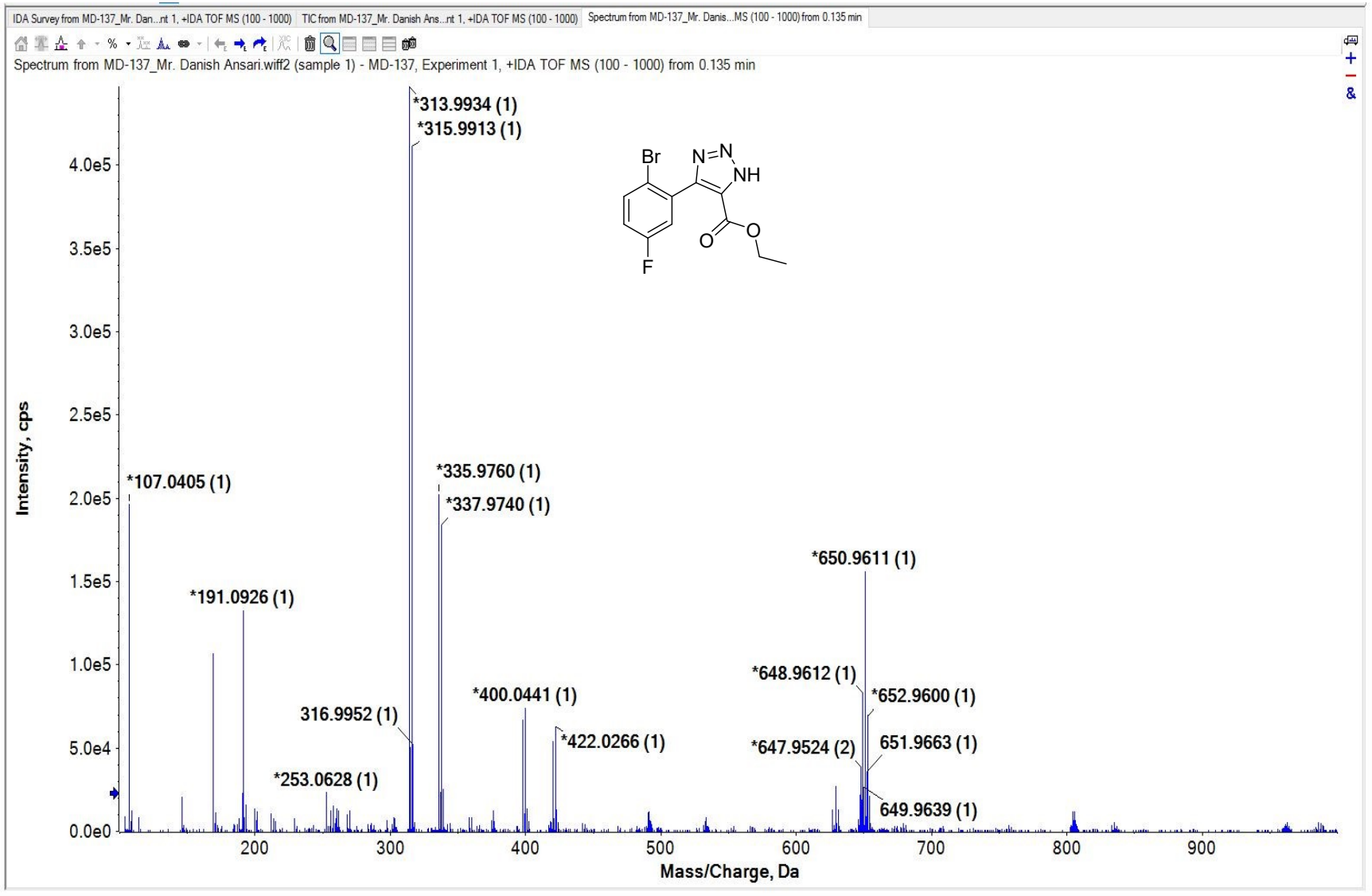

Figure S102: HRMS Spectra of compound **4a**

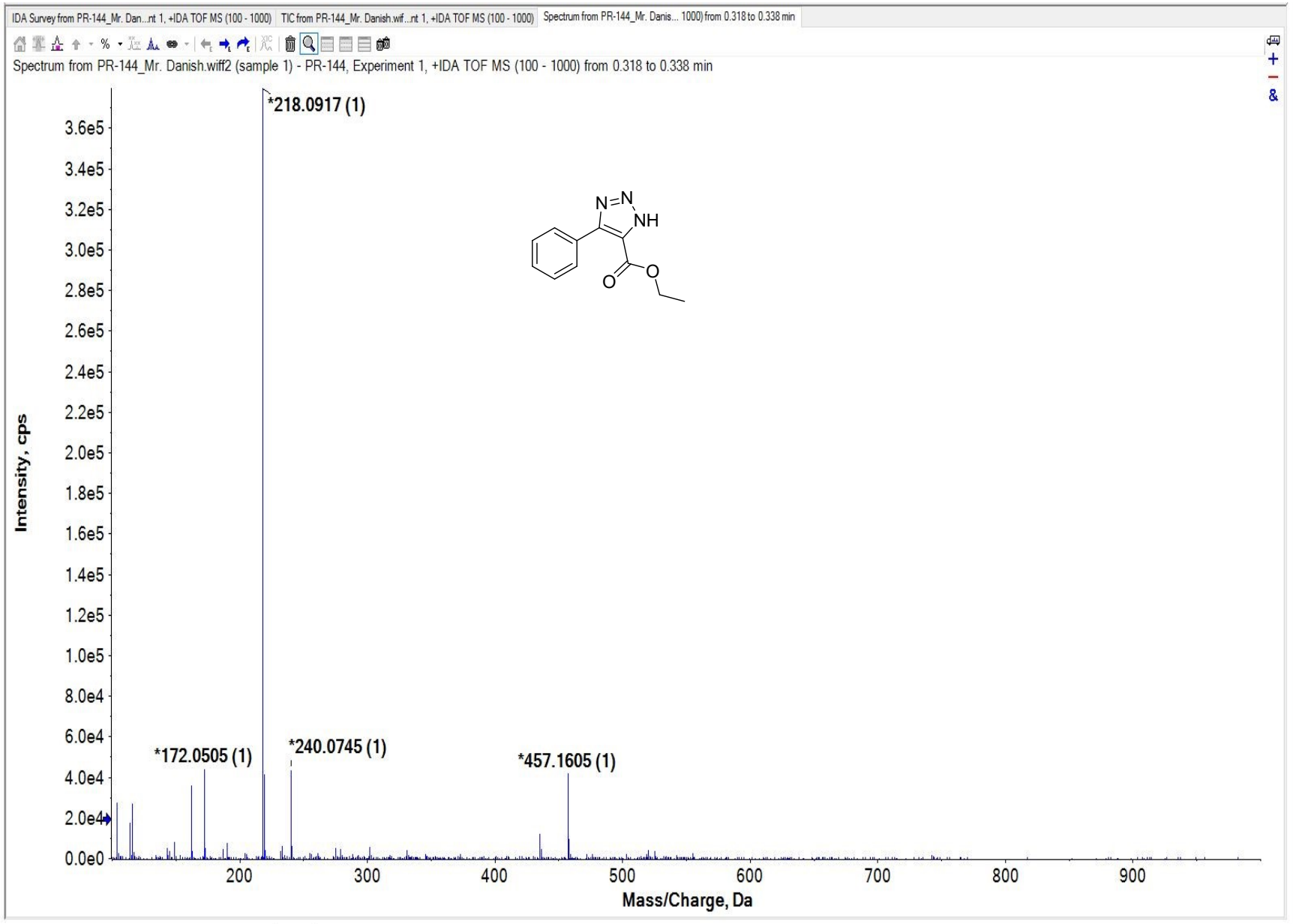

Figure S103: HRMS Spectra of compound **4b**

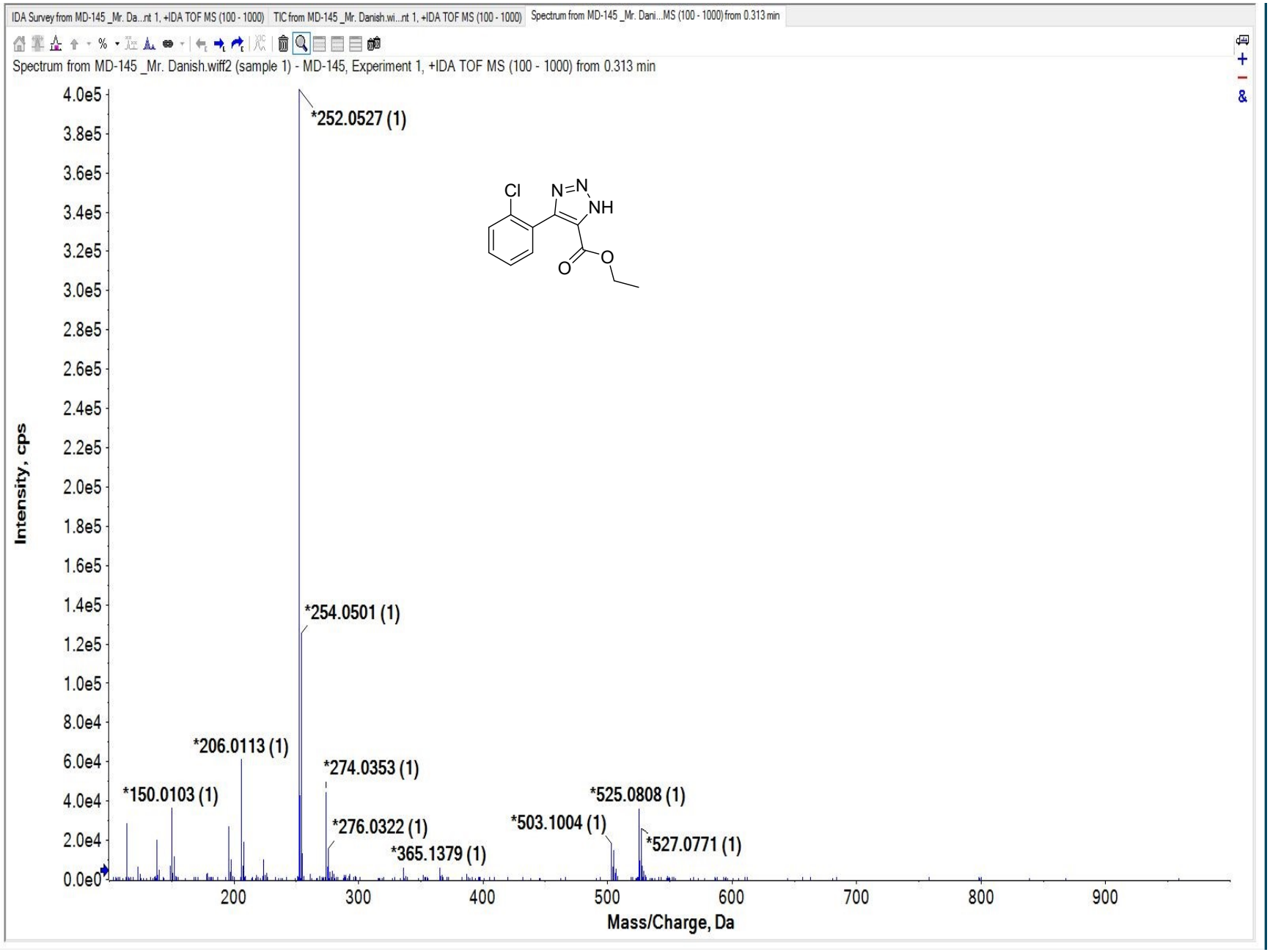

Figure S104: HRMS Spectra of compound **4c**

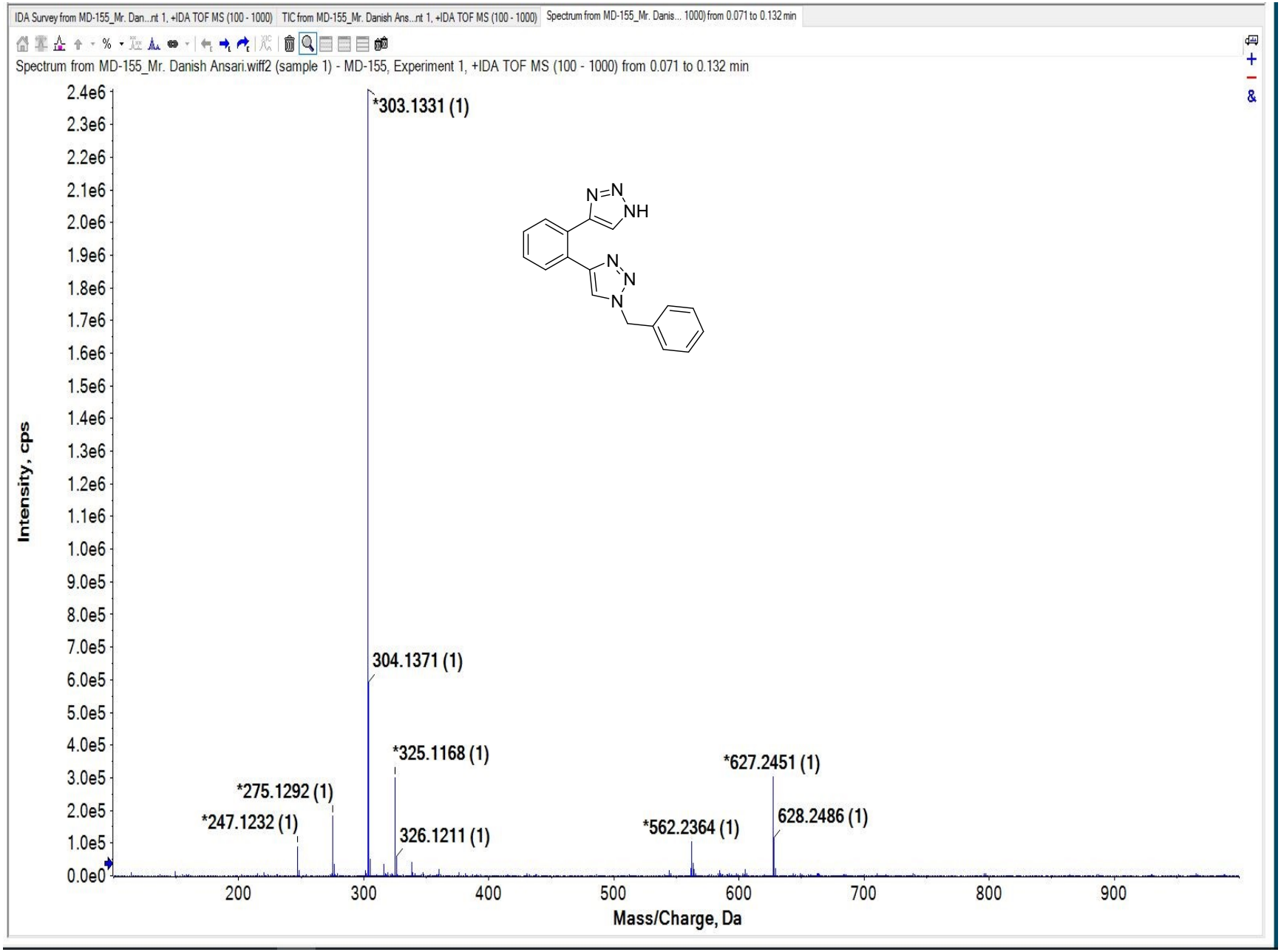

Figure S105: HRMS Spectra of compound **6**

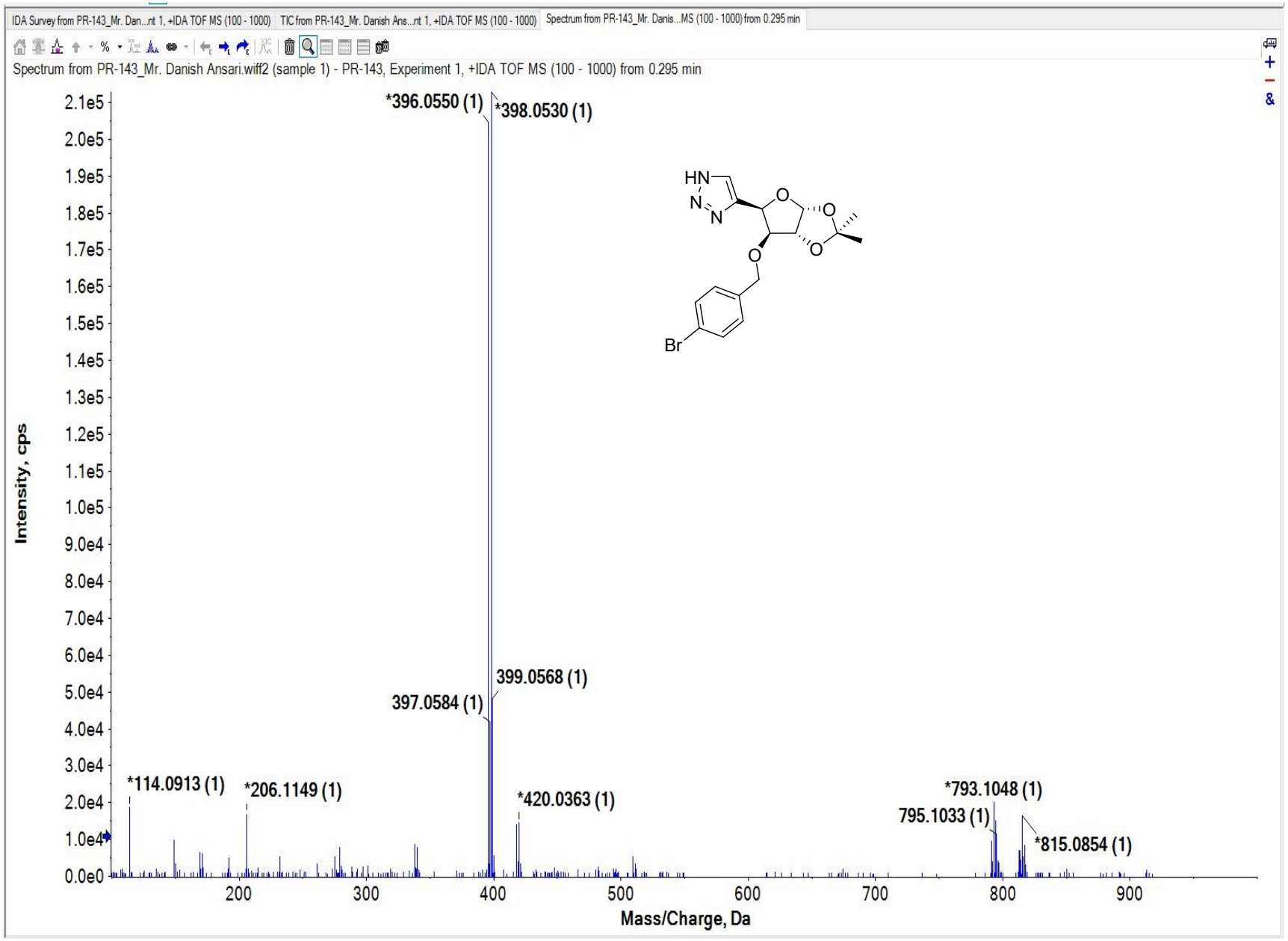

Figure S106: HRMS Spectra of compound **8**

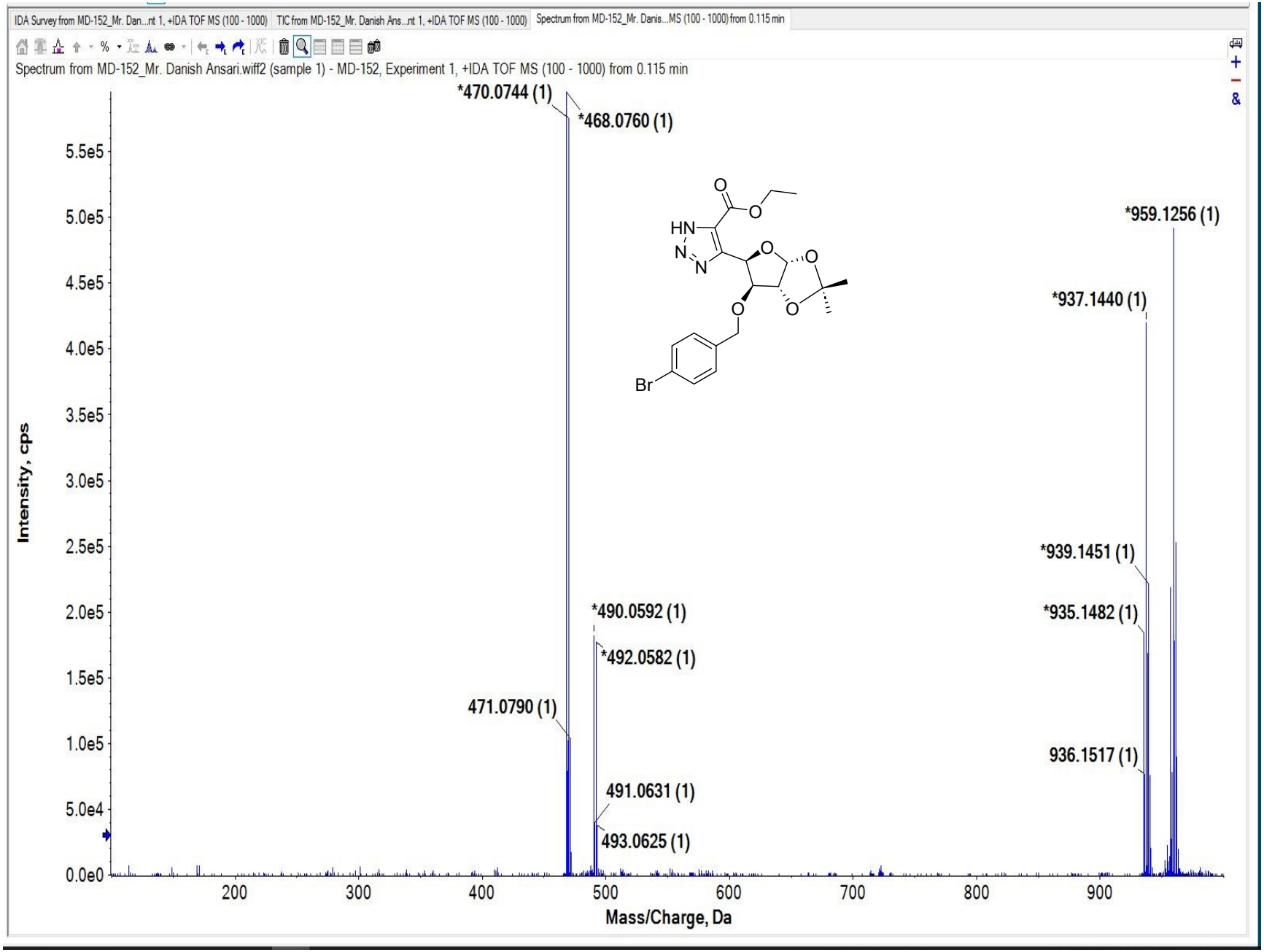

Figure S107: HRMS Spectra of compound **9**

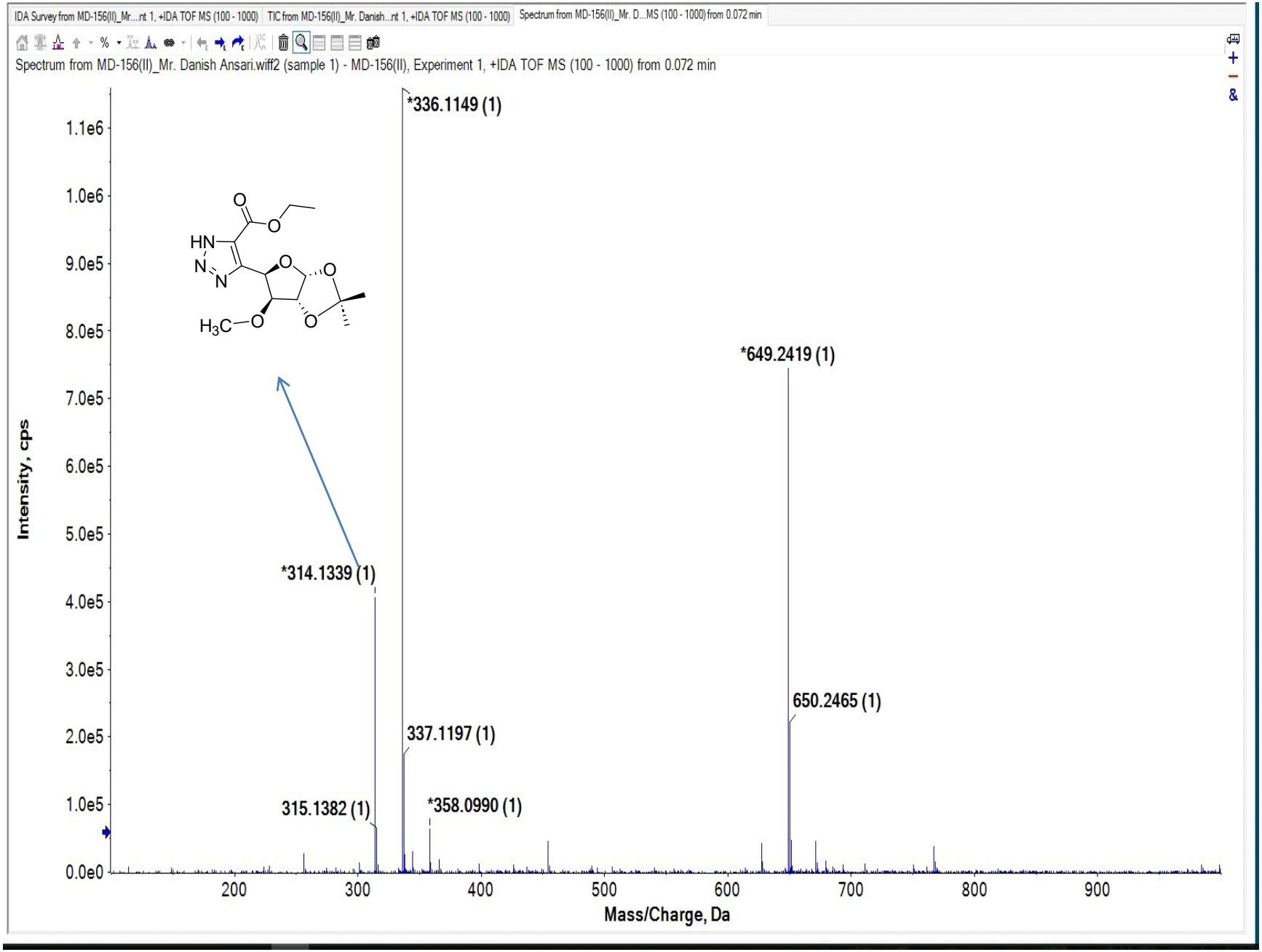

Figure S108: HRMS Spectra of compound **11**

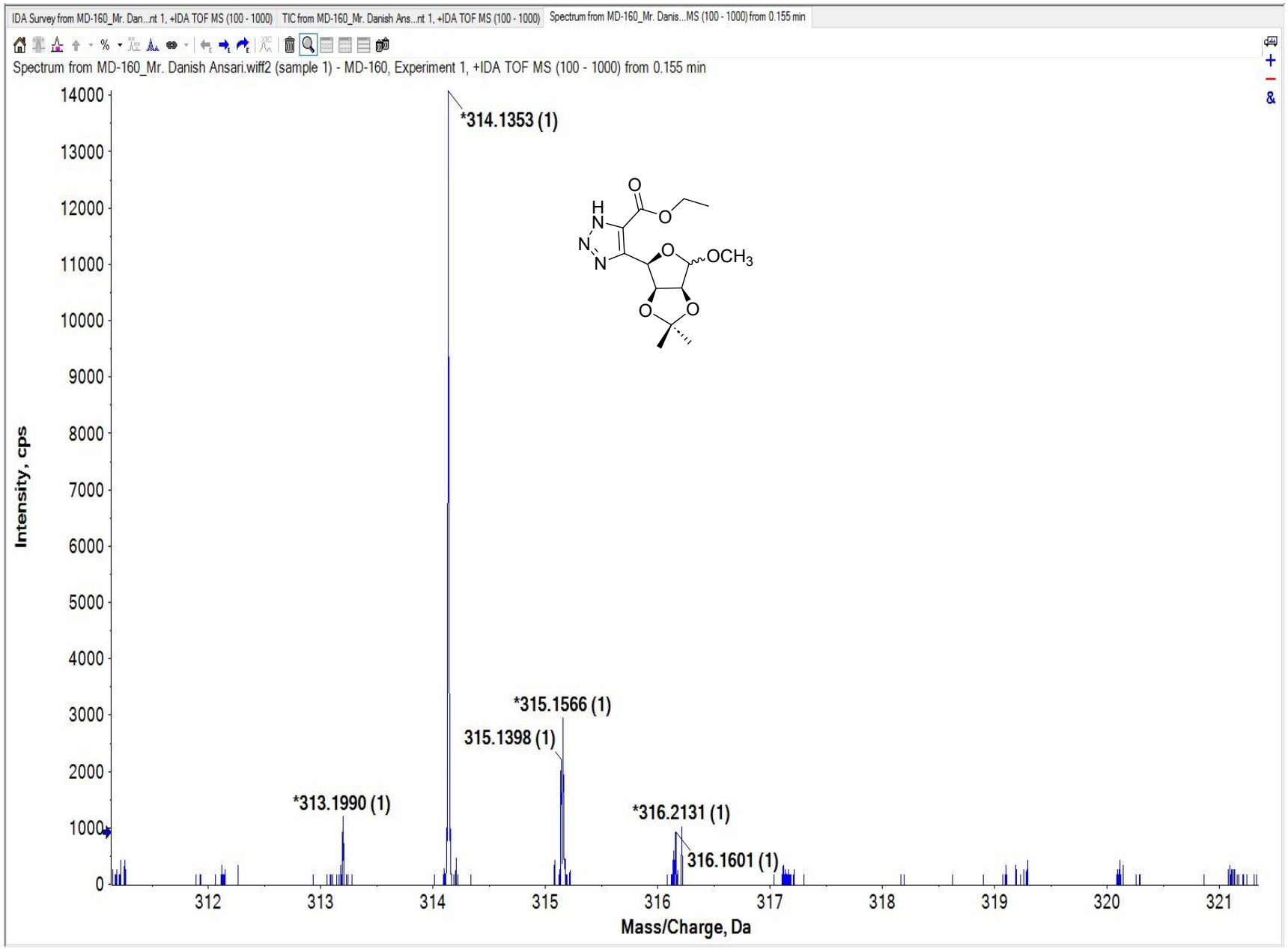

Figure S109: HRMS Spectra of compound **13**

9. HRMS ofIndermediate A and B in mechanism.

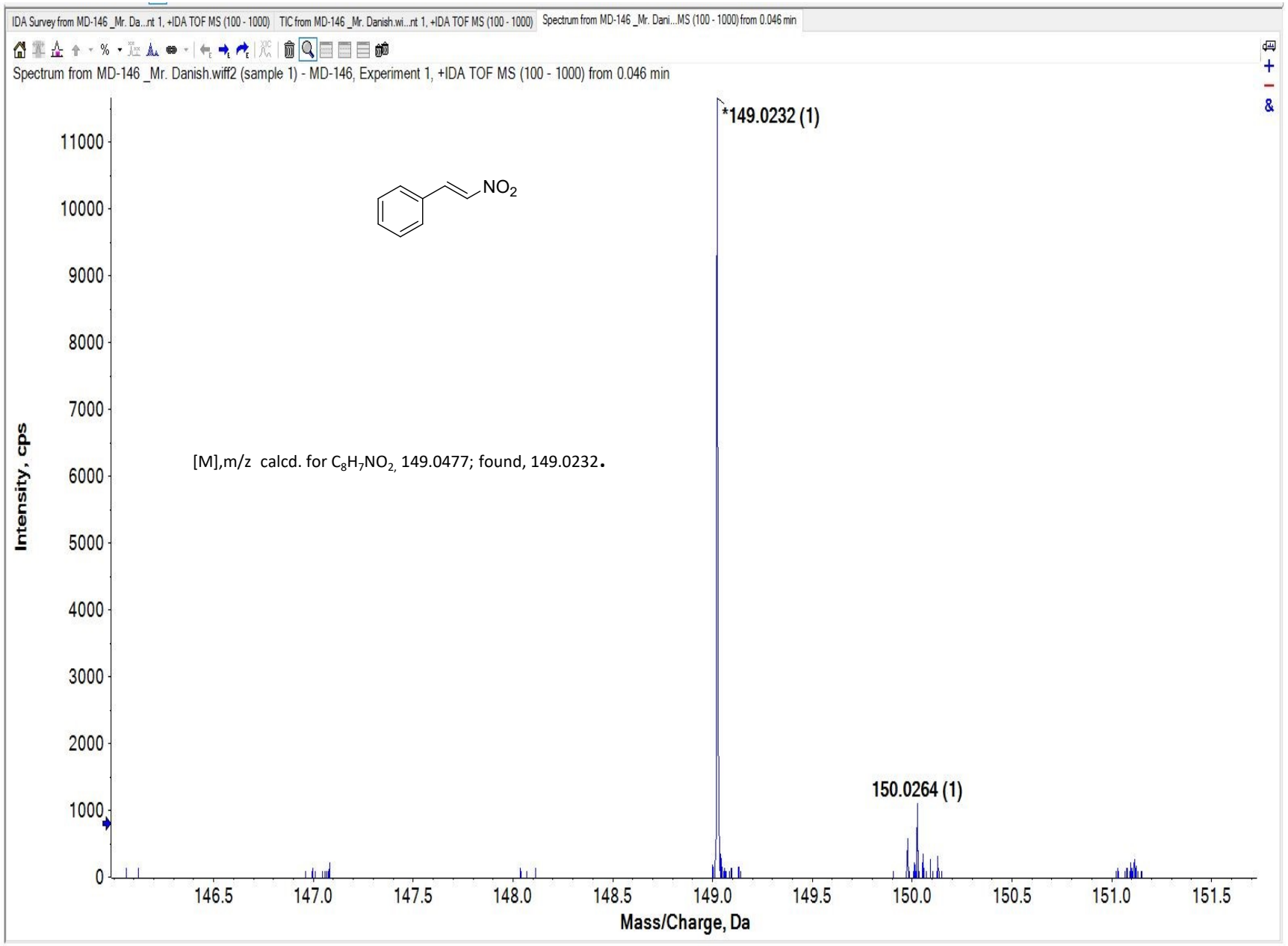

Figure S110: HRMS Spectra of Intermediate A

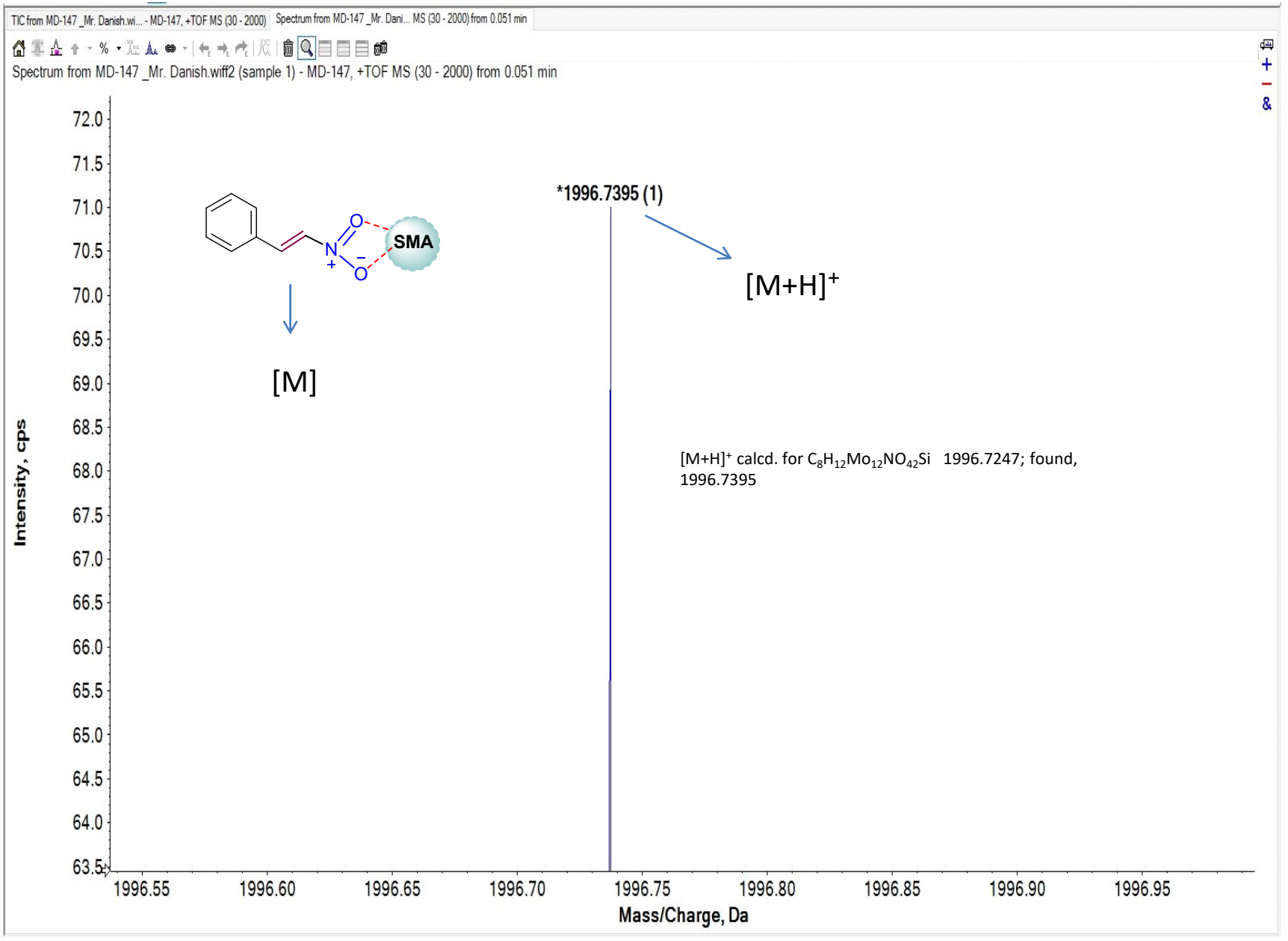

Figure S111: HRMS Spectra of Intermediate B

10. Single Crystal X-Ray Data Collection and Refinement:[4]

Data of compounds **2y**was collected on Rigaku Oxford diffraction (XtaLAB Synergy-i) using graphite monochromatedCu*K*α radiation (λ = 1.54184 Å). The structures were solved using the direct method as the compound containsfluorine and then refined on *F*2 using the full matrix least-squares technique with the SHELX-2019 set of software using the OLEX-2 program package. All non-hydrogen atoms were refined anisotropically in respect to electron density and hydrogen atoms were treated as riding atoms using SHELX default parameters. The process has been validated through the IUCR site (International Union of Crystallography) and no A-level or B-level error was found, validating the solved crystal. The ORTEP diagram of the crystal **2y** is given in **Figure S99**. Further information on the crystal structure (excluding structure factors) has been given in **Table 1,** and also deposited in the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers **2393742**. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via the internet.[3]

Procedure for crystallization of compound2y

For crystallization of compound **2y**, the compound was taken in a 3 mL vial and dissolved in ethyl acetate (2 mL), added hexane (2 mL) to it. The solution was kept in the dark at room temperature. After fifteen days, the plate-shaped white color single crystal seemed.Isolated in its initial stage of growth and washed with *n*-pentane numerous times before analysis.

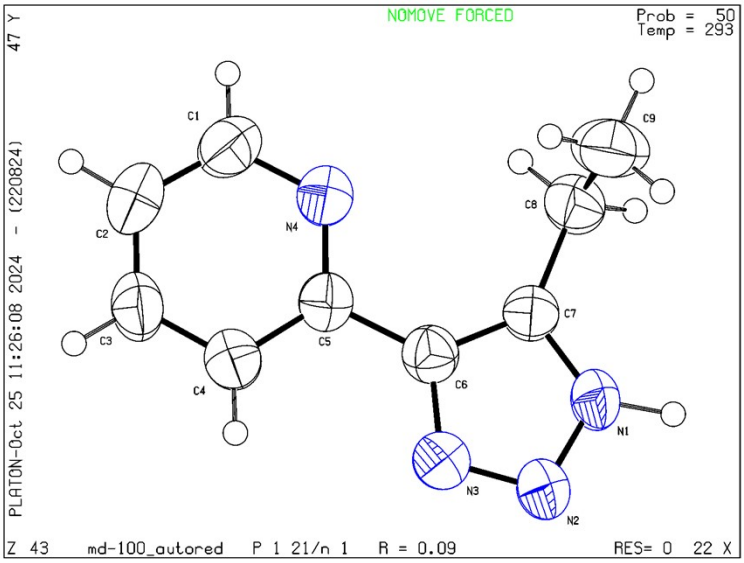

Figure S99: ORTEP diagram of compound **2y**

Table S1. Crystal data and structure refinement for **2y**

Identification code	MD-100
CCDC	**2393742**
Empirical formula	$C_9H_{10}N_4$
Dcalc./ g cm-3	1.303
μ/mm-1	0.679
Formula Weight	174.21
T/K	293(2)
Crystal System	monoclinic
Space Group	*P*21/*n*
a/Å	4.98700(10)
b/Å	9.0189(2)
c/Å	19.7788(4)
α/°	90
β/°	93.055(2)

γ/°	90
V/Å3	888.33(3)
Z	4
θmin/°	4.477
θmax/°	68.073
Measured Refl's.	11682
Indep'tRefl's	1599
Rint	0.0480
GooF	1.118
wR2 (all data)	0.2598
wR2	0.2560
R1 (all data)	0.0959
R1	0.0896
Dcalc./ g cm-3	1.303
μ/mm-1	0.679

11. Reference

[1] a) D. Jankovic, M. Virant, M. Gazvoda, *J. Org. Chem*. **2022**, *87*, 4018-4028. (b) T. Jin, S. Kamijo, Y. Yamamoto, *Eur. J. Org. Chem*. **2004**, 3789-3791. (c) J. D. Kim, T. Palani, M. R. Kumar, S. Lee, H. C. J. Choi, *Mater. Chem*. **2012**, *22*, 20665-20670.

[2] A. Garg, D. Sarma, A. A. Ali. *Curr. Res. Green Sustain. Chem*. **2020**, *3*, 100013.

[3] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.,***2009**,*42*, 339-341.