

SUPPORTING INFORMATION

Intriguing Enigma of Nitrobenzofuroxan's 'Sphinx': Boulton–Katritzky rearrangement or unusual evidence of the *N*-1/*N*-3-oxide rearrangement?

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Content	Page
Figure S1. ¹ H NMR spectrum (399.9 MHz, CDCl ₃ , 25°C) of compounds 5a and 5'a .	S3
Figure S2. ¹³ C NMR spectrum (150.8 MHz, CDCl ₃ , 25°C) of compounds 5a and 5'a .	S4
Figure S3. ¹ H NMR spectrum (599.7 MHz, CDCl ₃ , 25°C) of compounds 5b and 5'b .	S5
Figure S4. ¹³ C NMR spectrum (150.8 MHz, CDCl ₃ , 25°C) of compounds 5b and 5'b .	S6
Figure S5. ESI-HRMS spectrum of compound 5b and 5'b .	S7
Figure S6. ¹ H NMR spectrum (400 MHz, CDCl ₃ , 25°C) of compounds 5c and 5'c .	S8
Figure S7. ¹³ C NMR spectrum (150.8 MHz, CDCl ₃ , 25°C) of compounds 5c and 5'c .	S9
Figure S8. ESI-HRMS spectrum of compound 5c and 5'c .	S10
Figure S9. ¹ H NMR spectrum (599.7 MHz, CD ₃ CN, 25°C) of compound 8a	S11
Figure S10. ¹³ C NMR spectrum (150.8 MHz, CD ₃ CN, 25°C) of compound 8a	S12
Figure S11. ESI-HRMS spectrum of compound 8a	S13
Figure S12. ¹ H NMR spectrum (300.0 MHz, CD ₃ CN, 25°C) of compound 8b	S14
Figure S13. ¹ H NMR spectrum (599.7 MHz, CDCl ₃ , 25°C) of compound 8b	S15
Figure S14. ¹³ C NMR spectrum (150.8 MHz, CDCl ₃ , 25°C) of compound 8b	S16
Figure S15. ESI-HRMS spectrum of compound 8b	S17
Figure S16. ¹ H NMR spectrum (599.7 MHz, CD ₃ CN, 25°C) of compound 8c	S18
Figure S17. ¹³ C NMR spectrum (150.8 MHz, CD ₃ CN, 25°C) of compound 8c	S19

Figure S18. ESI-HRMS spectrum of compound 8c	S20
Figure S19. ¹ H NMR spectrum (599.7 MHz, DMSO-d ₆ , 25°C) of intermediate Ma	S21
Figure S20. ¹³ C NMR spectrum (150.8 MHz, DMSO-d ₆ , 25°C) of intermediate Ma	S22
Figure S21. ESI-MS ⁻ spectrum of intermediate Ma	S23
Figure S22. ¹ H NMR spectrum (300.0 MHz, DMSO-d ₆ , 25°C) of intermediate Mb	S24
Figure S23. ¹³ C NMR spectrum (75.4 MHz, DMSO-d ₆ , 25°C) of intermediate Mb	S25
Figure S24. ESI-MS ⁻ spectrum of intermediate Mb	S26
Figure S25. ¹ H NMR spectrum (399.9 MHz, DMSO-d ₆ , 25°C) of intermediate Mc	S27
Figure S26. ¹³ C NMR spectrum (100.6 MHz, DMSO-d ₆ , 25°C) of intermediate Mc	S28
Figure S27. ESI-MS ⁻ spectrum of intermediate Mc	S29
Figure S28. ¹ H NMR spectrum in Acetone-d ₆ of compounds 5c and 5'c .	S30
Figure S29. ¹ H NMR spectrum in C ₆ D ₆ of compounds 5c and 5'c	S31
Figure S30. ¹ H NMR spectrum in CD ₃ CN of compounds 5c and 5'c	S32
Figure S31. ¹ H NMR spectrum in CD ₃ OD of compounds 5c and 5'c	S33
Figure S32. ¹ H NMR spectrum in THF-d ₈ of compounds 5c and 5'c	S34
Computational details	S35
Table S1. Cartesian coordinate of the N3-oxide tautomer (A)	S35
Table S2. Cartesian coordinate of the N1-oxide tautomer (A')	S36
Variable temperature NMR experimental details	S38

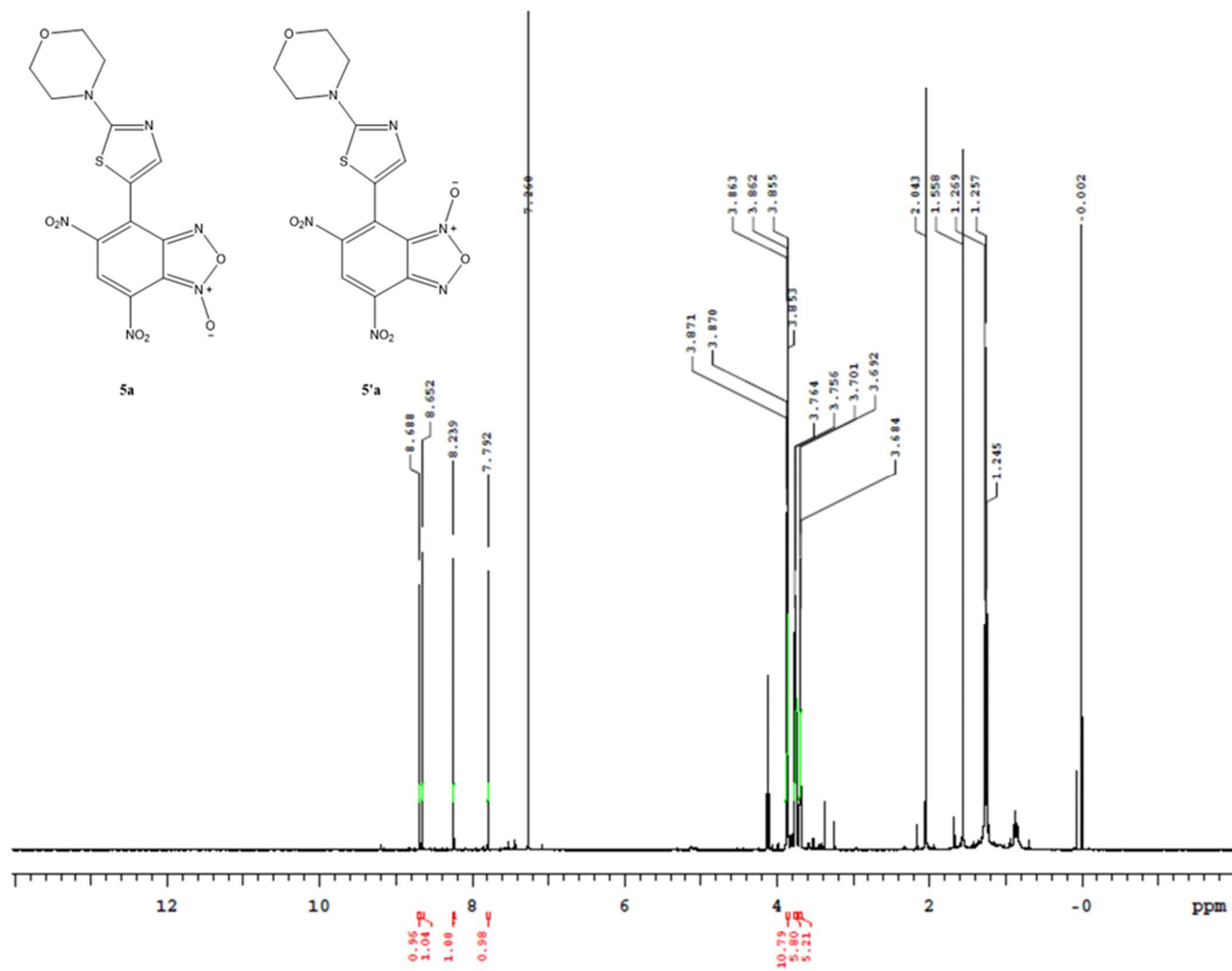


Figure S1. ^1H NMR spectrum (399.9 MHz, CDCl_3 , 25°C) of compounds **5a** and **5'a**.

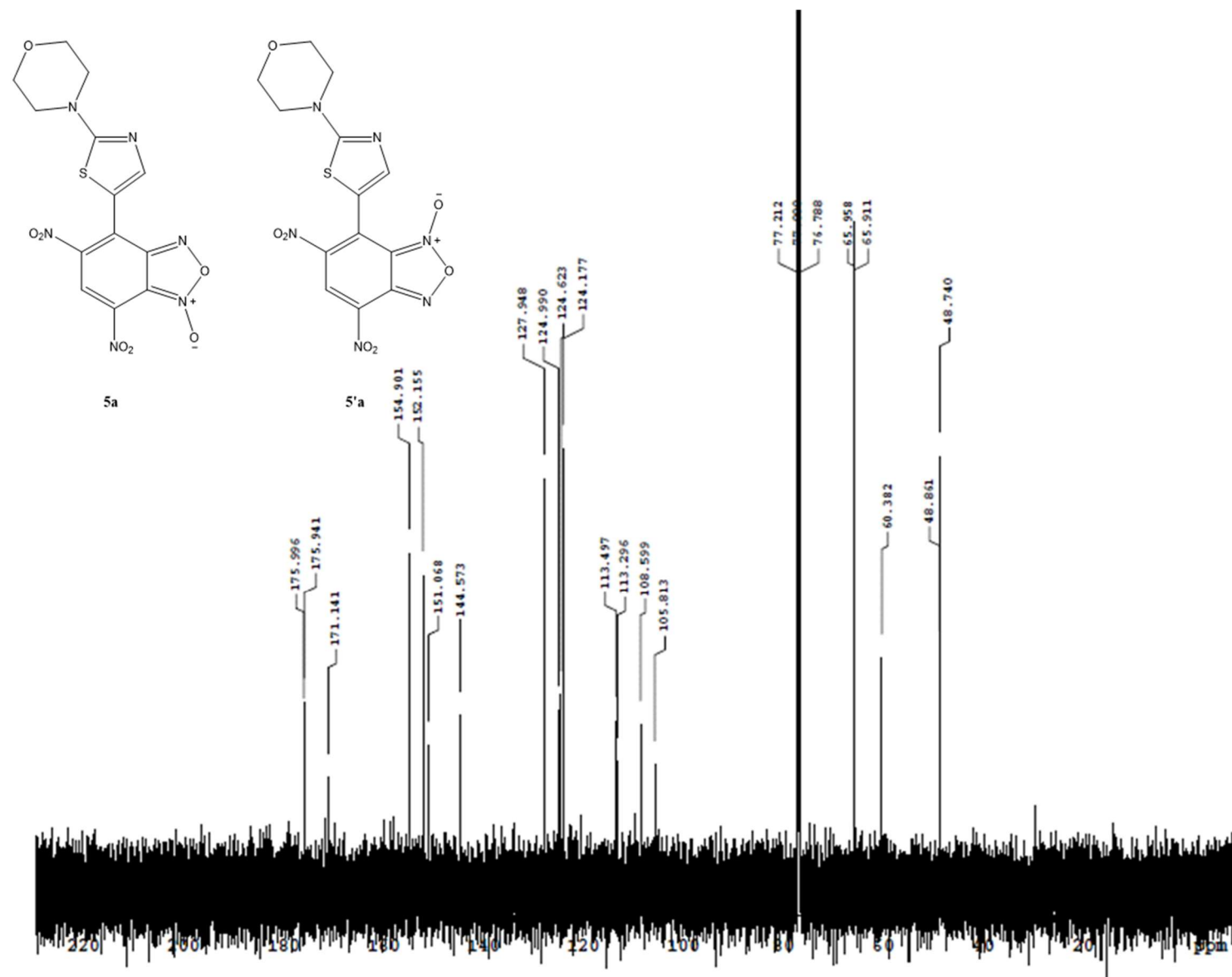


Figure S2. ¹³C NMR spectrum (150.8 MHz, CDCl₃, 25°C) of compounds **5a** and **5'a**.

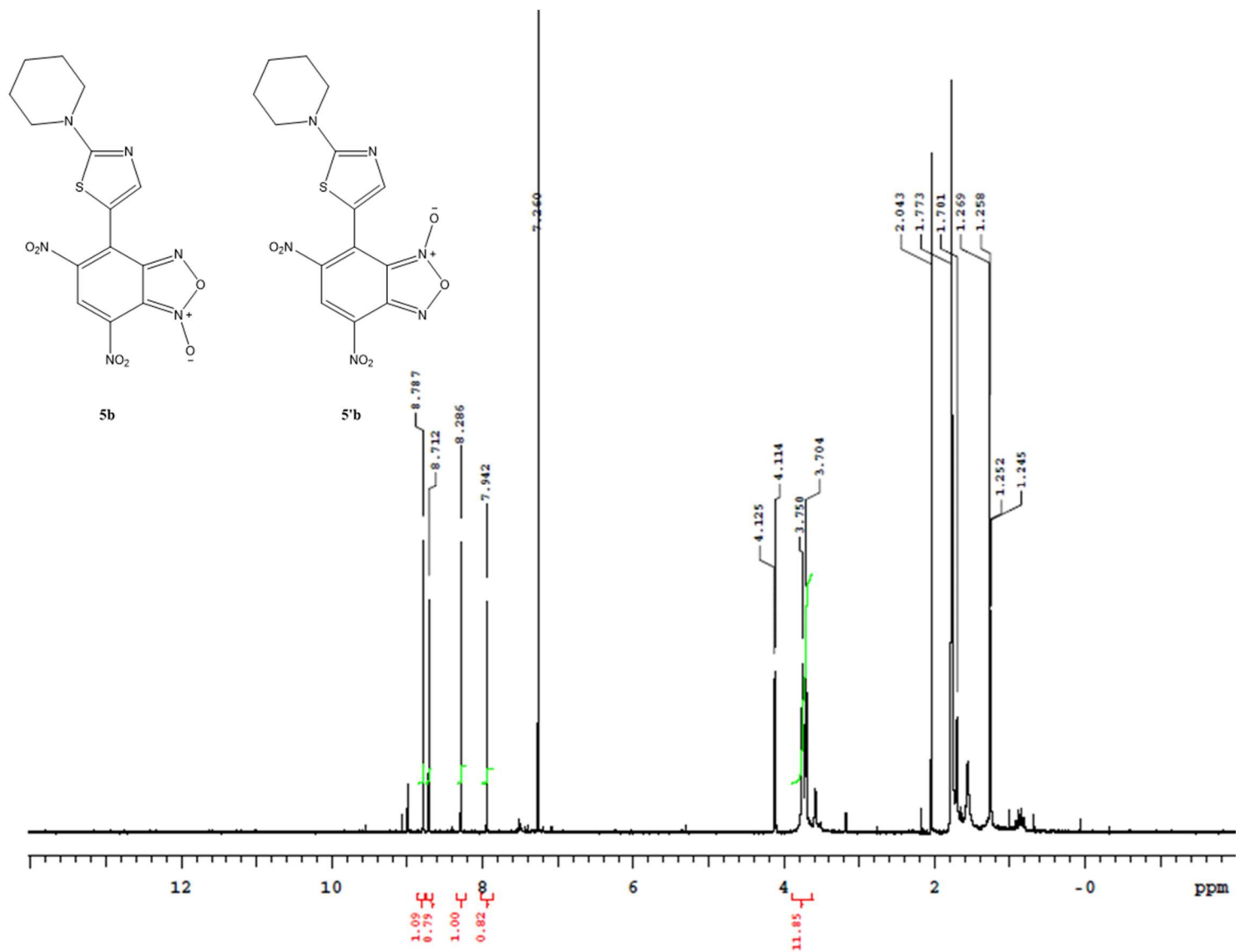


Figure S3. ¹H NMR spectrum (599.7 MHz, CDCl₃, 25°C) of compounds **5b** and **5'b**.

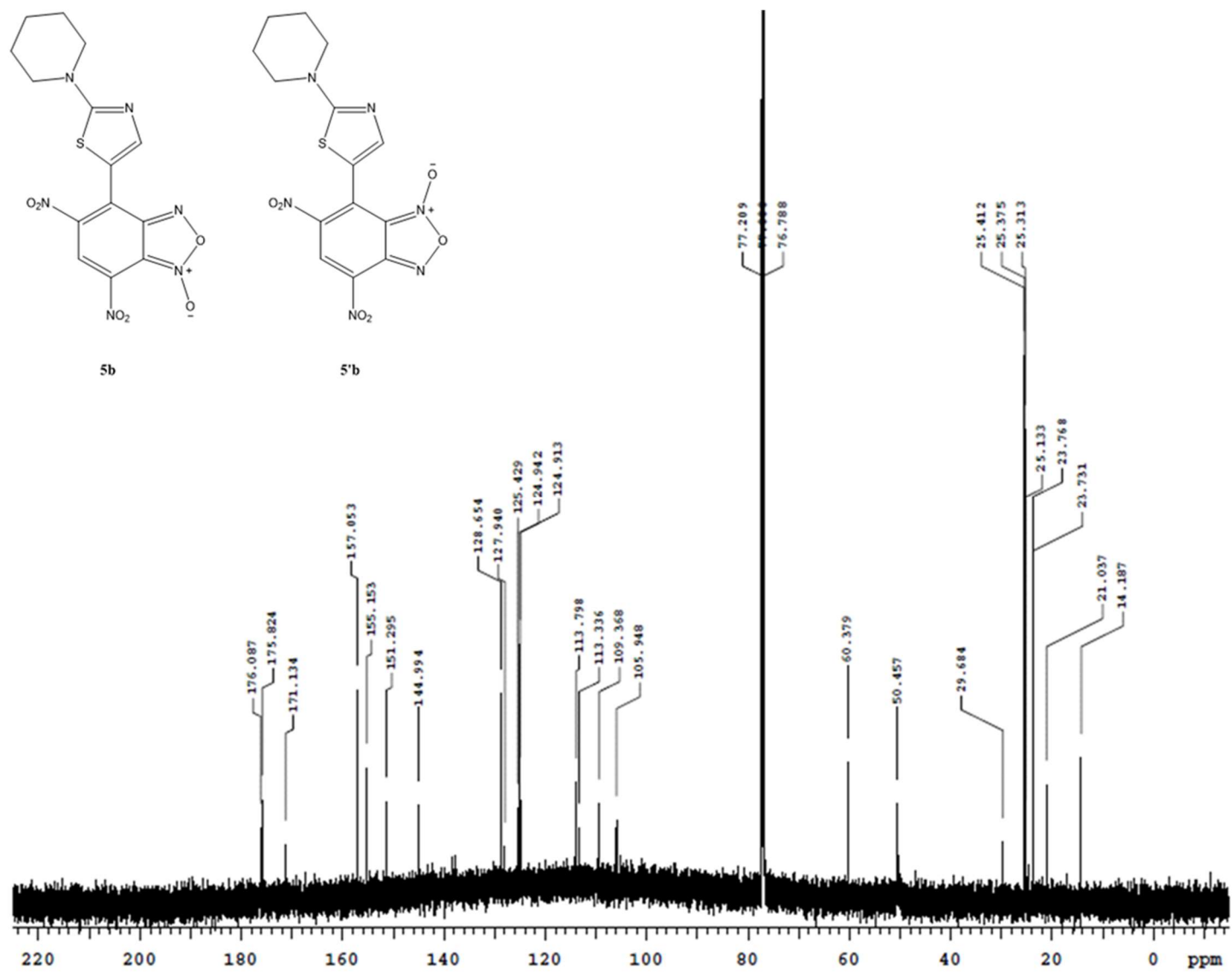


Figure S4. ^{13}C NMR spectrum (150.8 MHz, CDCl_3 , 25°C) of compounds **5b** and **5'b**.

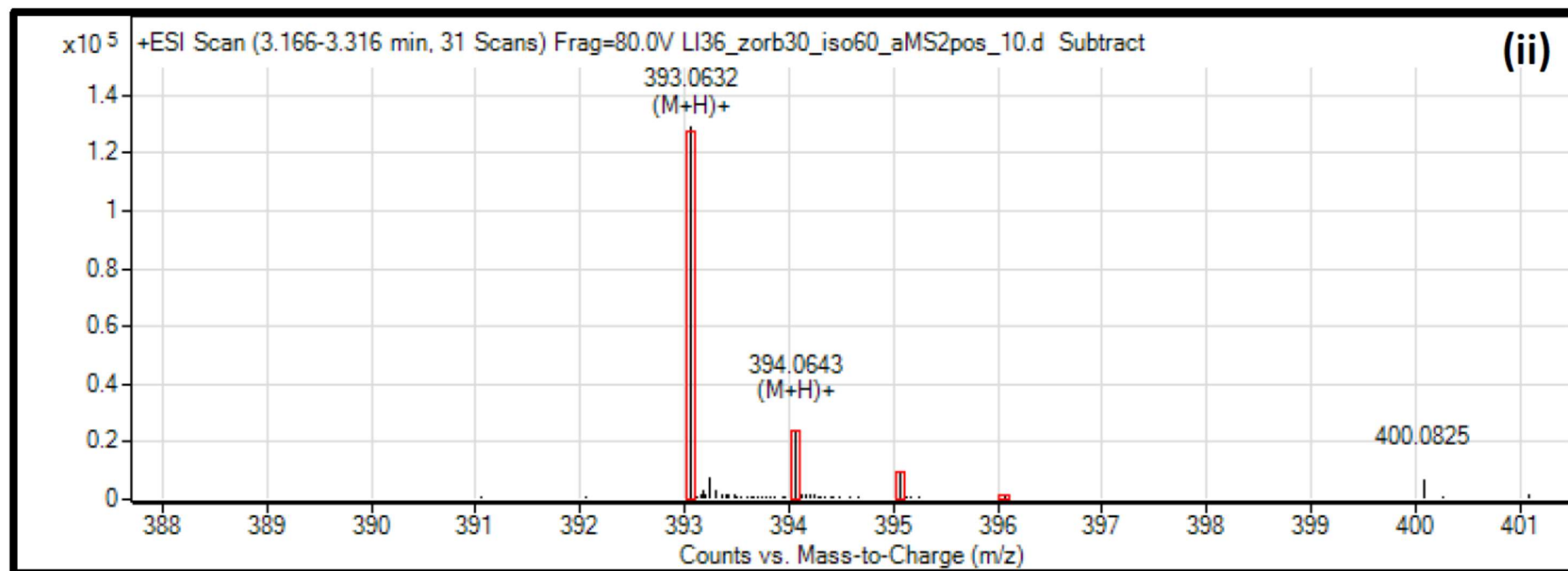


Figure S5. ESI-HRMS spectrum of compound **5b** and **5'b**.

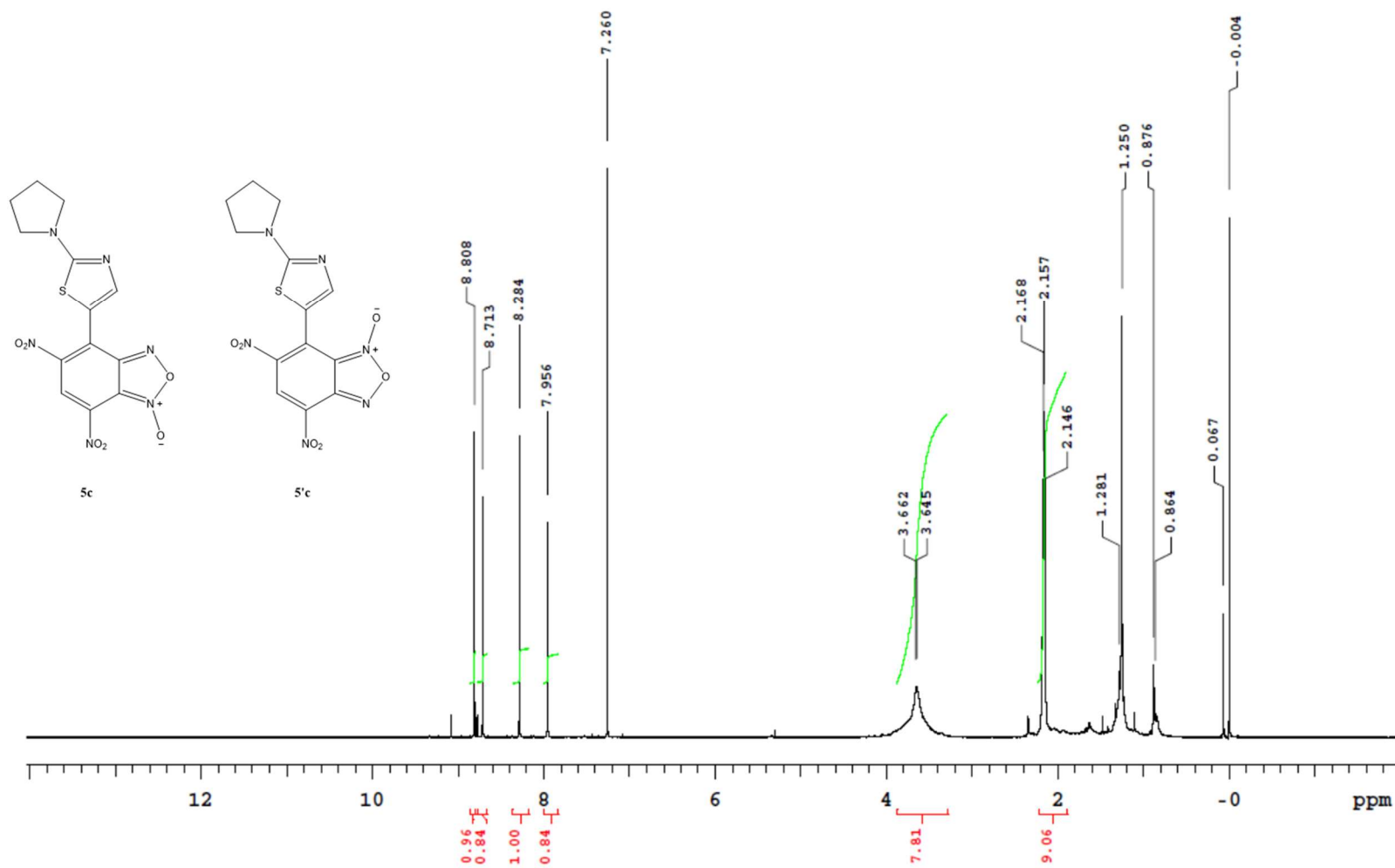


Figure S6. ^1H NMR spectrum (400 MHz, CDCl_3 , 25°C) of compounds **5c** and **5'c**.

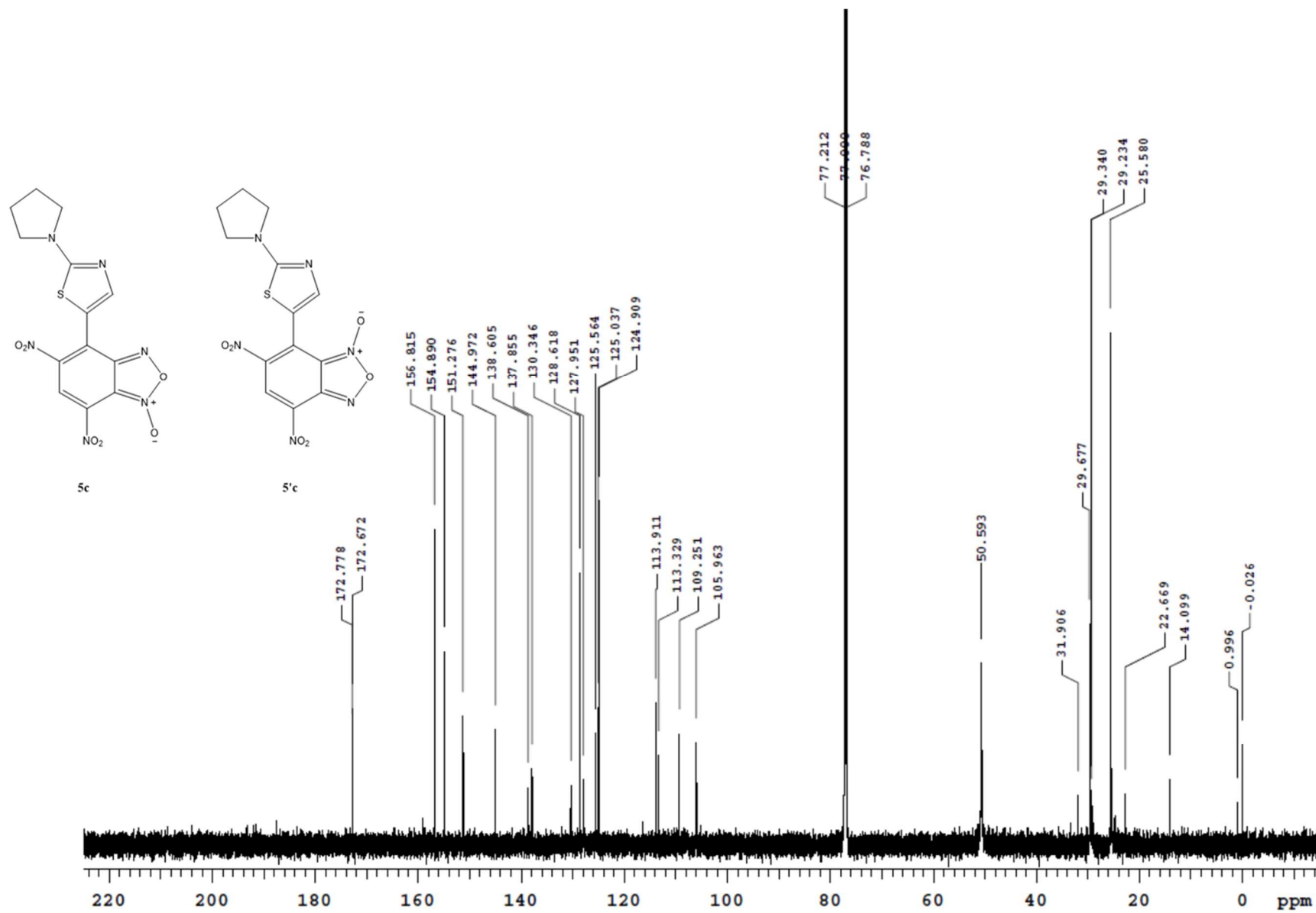


Figure S7. ^{13}C NMR spectrum (150.8 MHz, CDCl_3 , 25°C) of compounds **5c** and **5'c**.

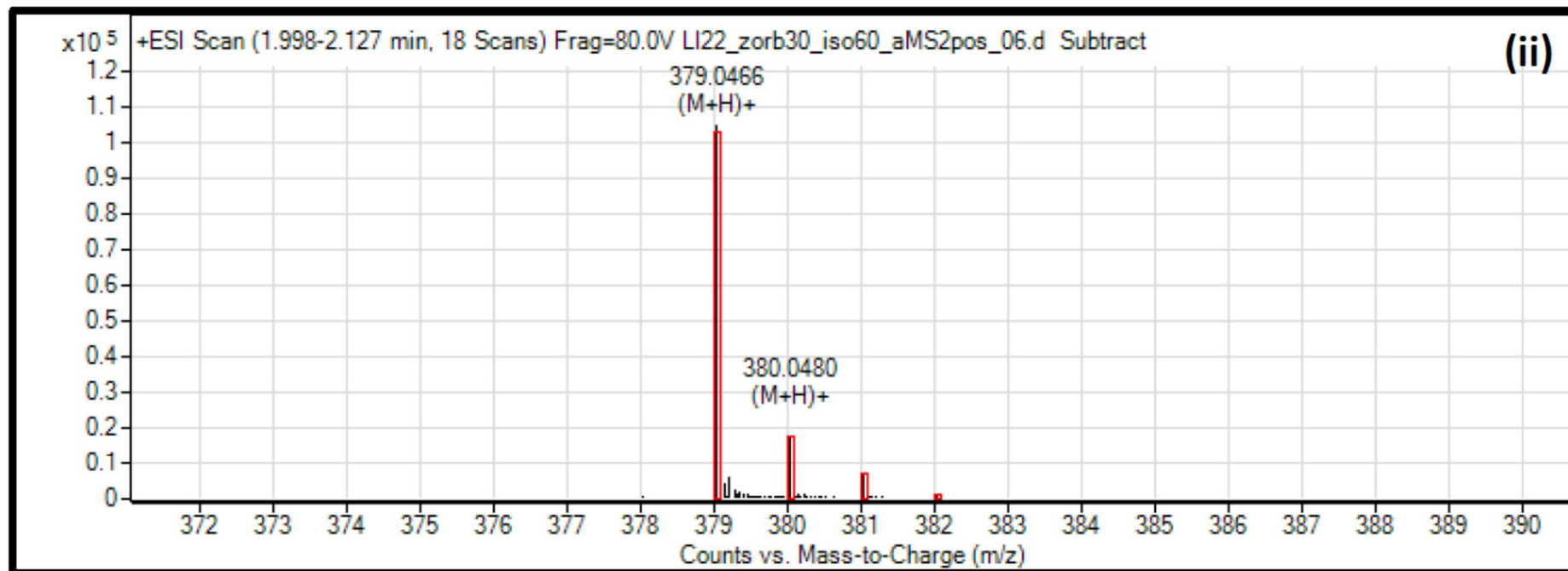


Figure S8. ESI-HRMS spectrum of compound **5c** and **5'c**.

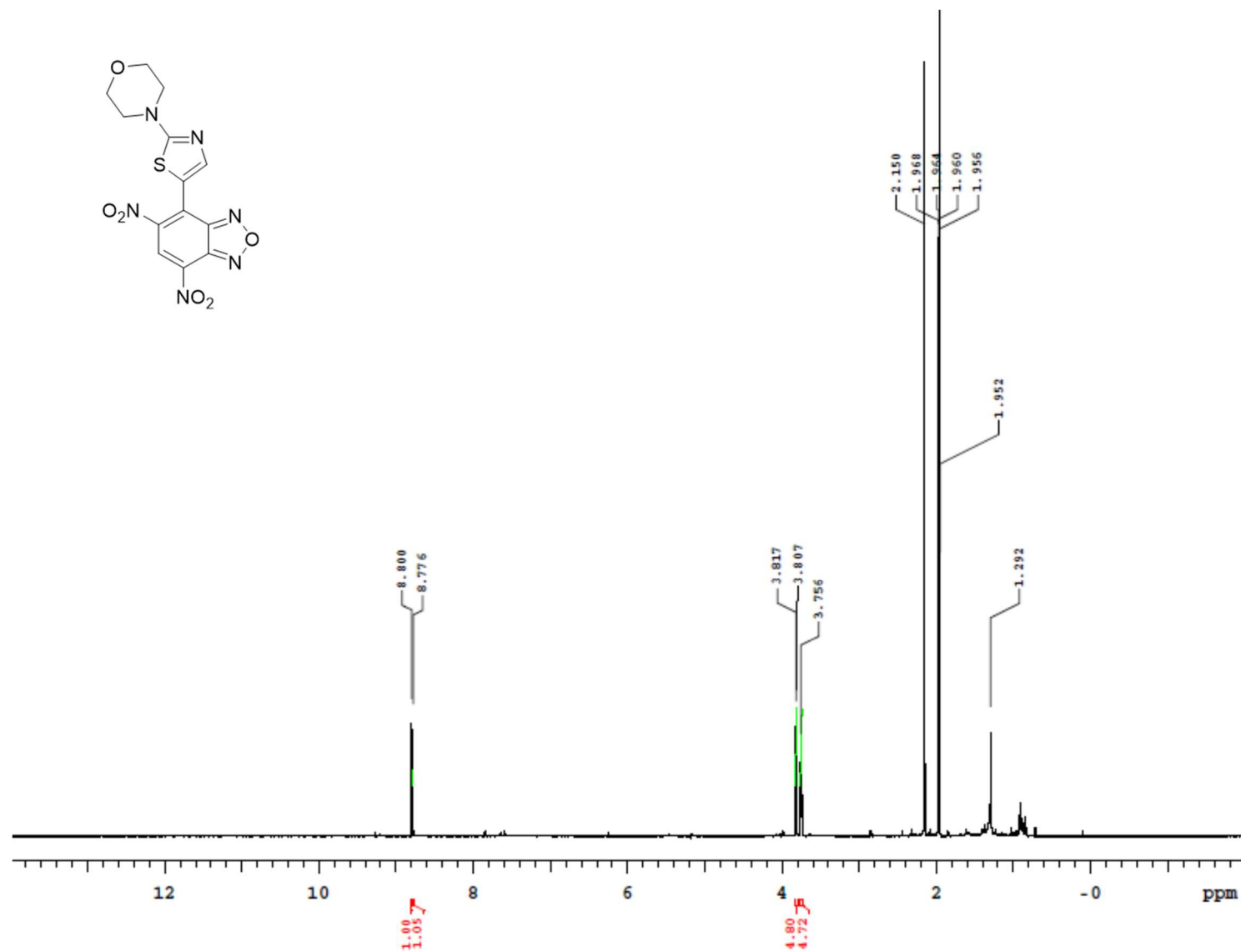


Figure S9. ¹H NMR spectrum (599.7 MHz, CD₃CN, 25°C) of compound **8a**.

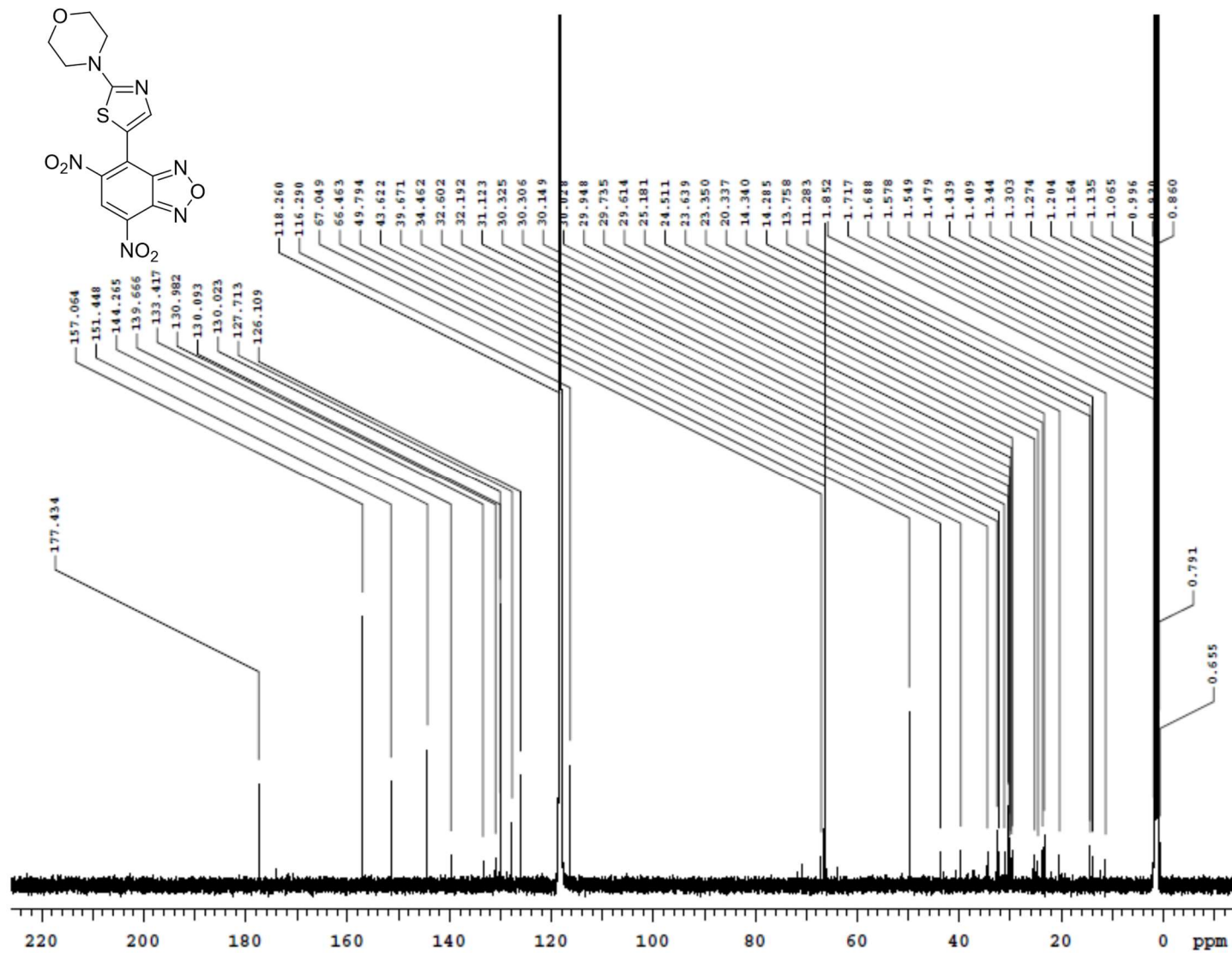


Figure S10. ¹³C NMR spectrum (150.8 MHz, CD₃CN, 25°C) of compound 8a.

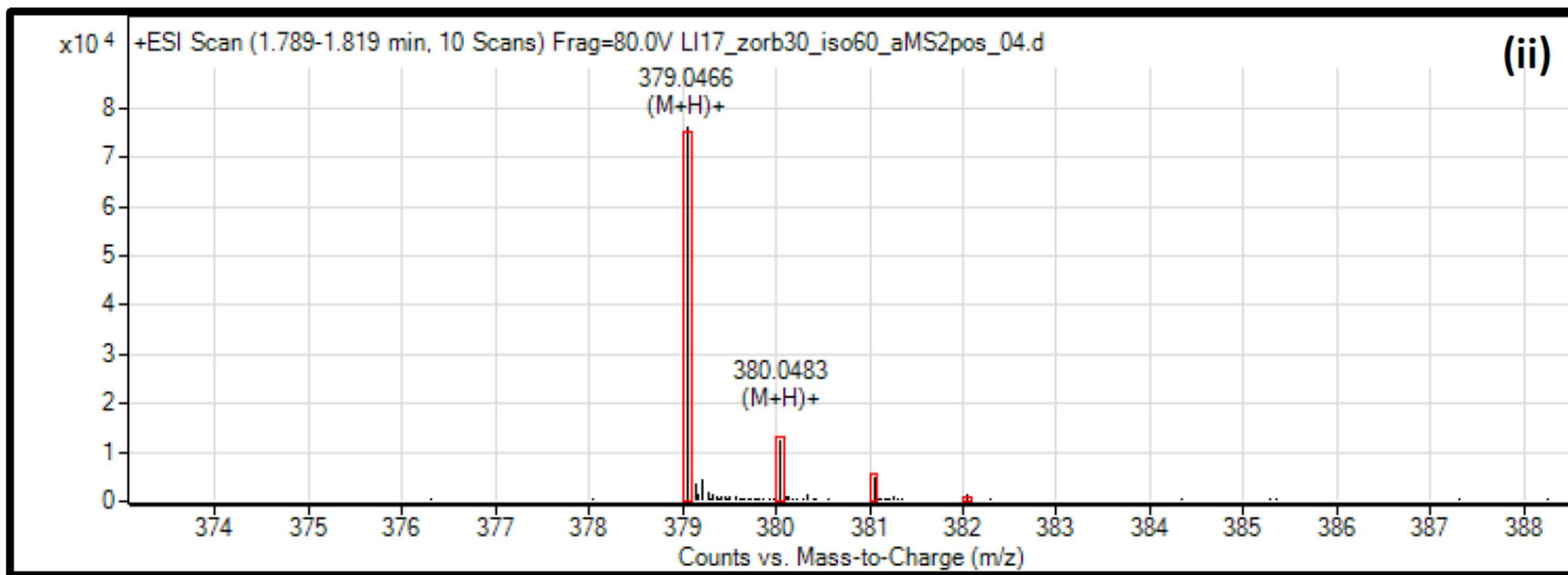


Figure S11. ESI-HRMS spectrum of compound **8a**.

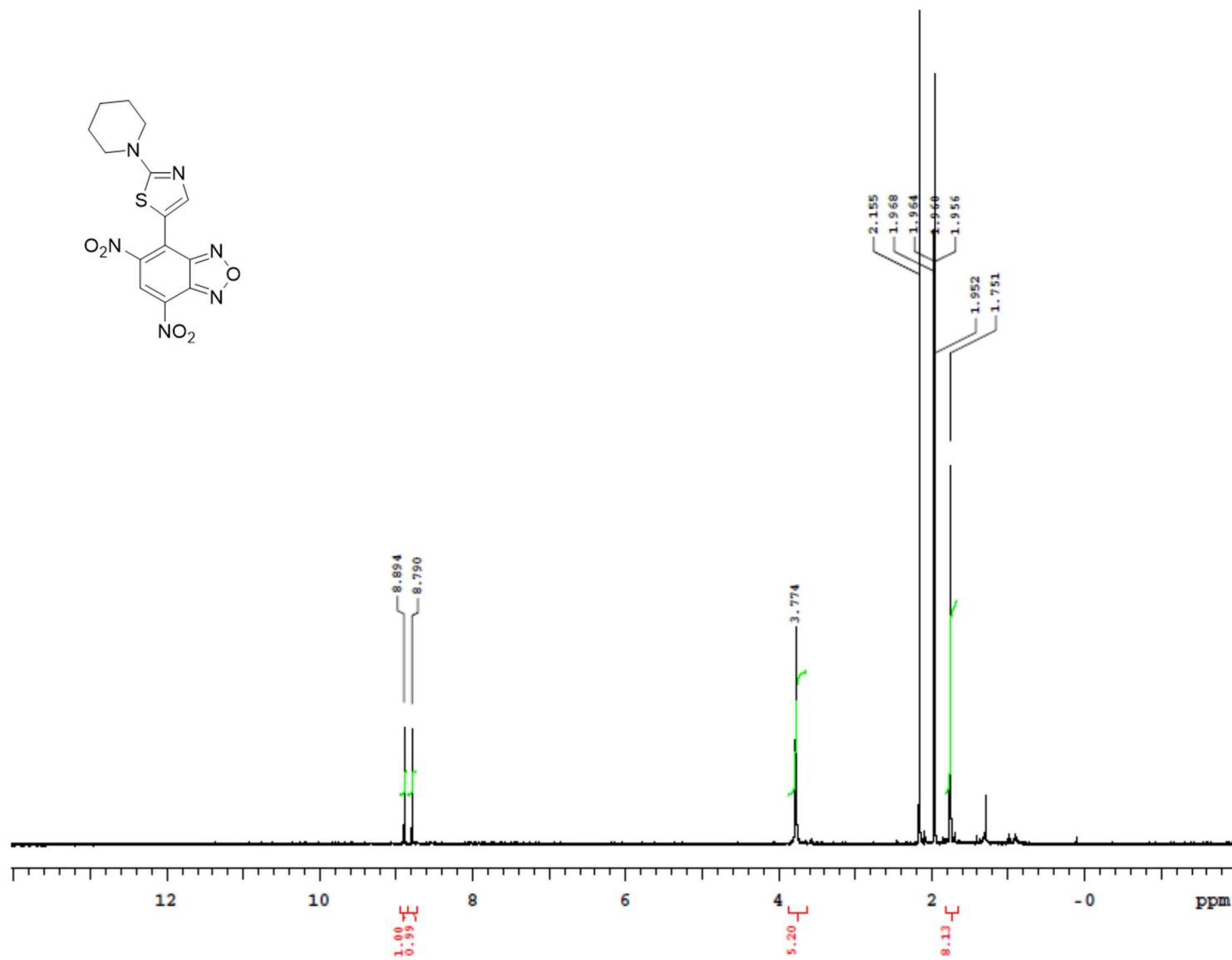


Figure S12. ^1H NMR spectrum (300.0 MHz, CD_3CN , 25°C) of compound **8b**.

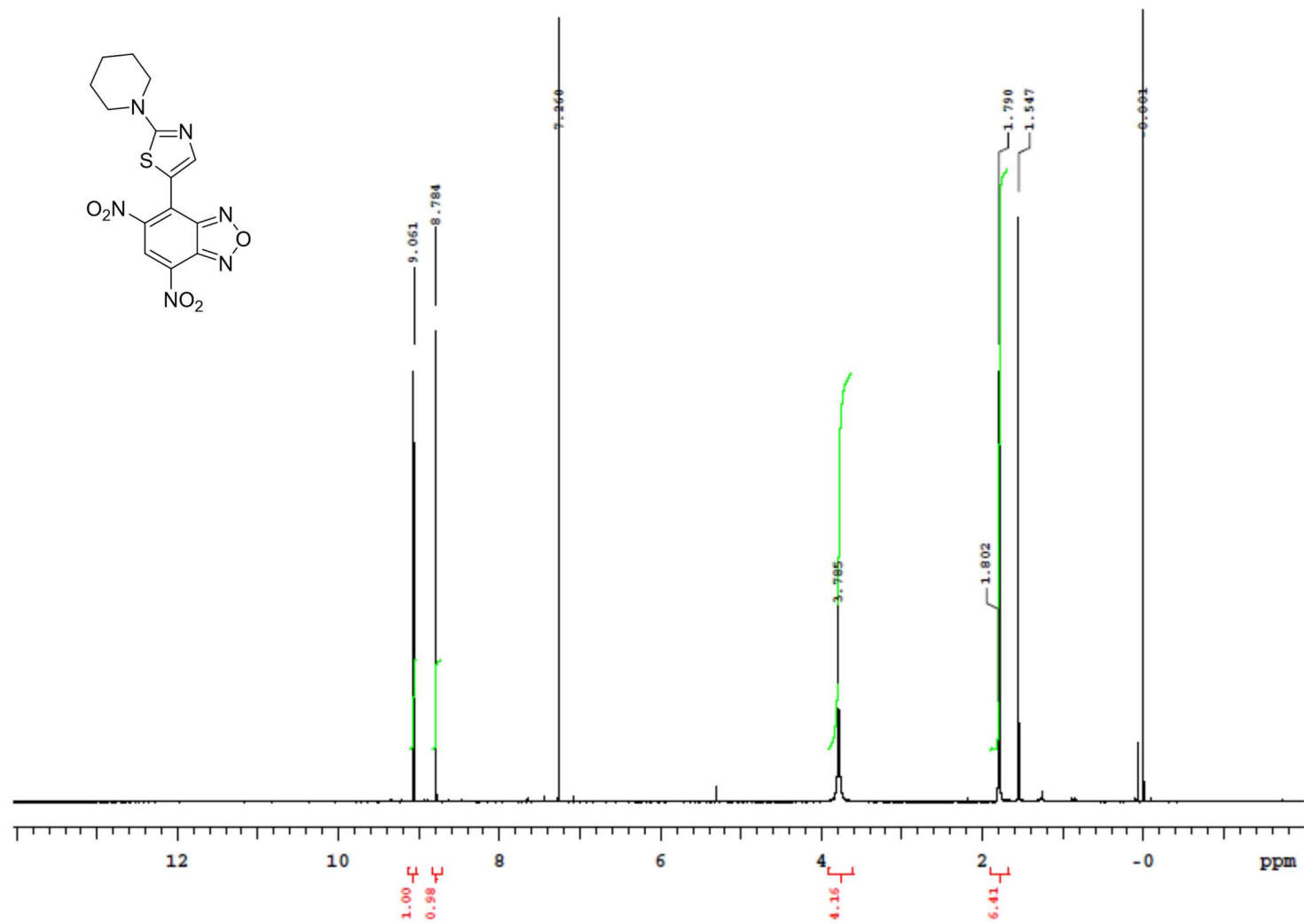


Figure S13. ^1H NMR spectrum (599.7 MHz, CDCl_3 , 25°C) of compound **8b**.

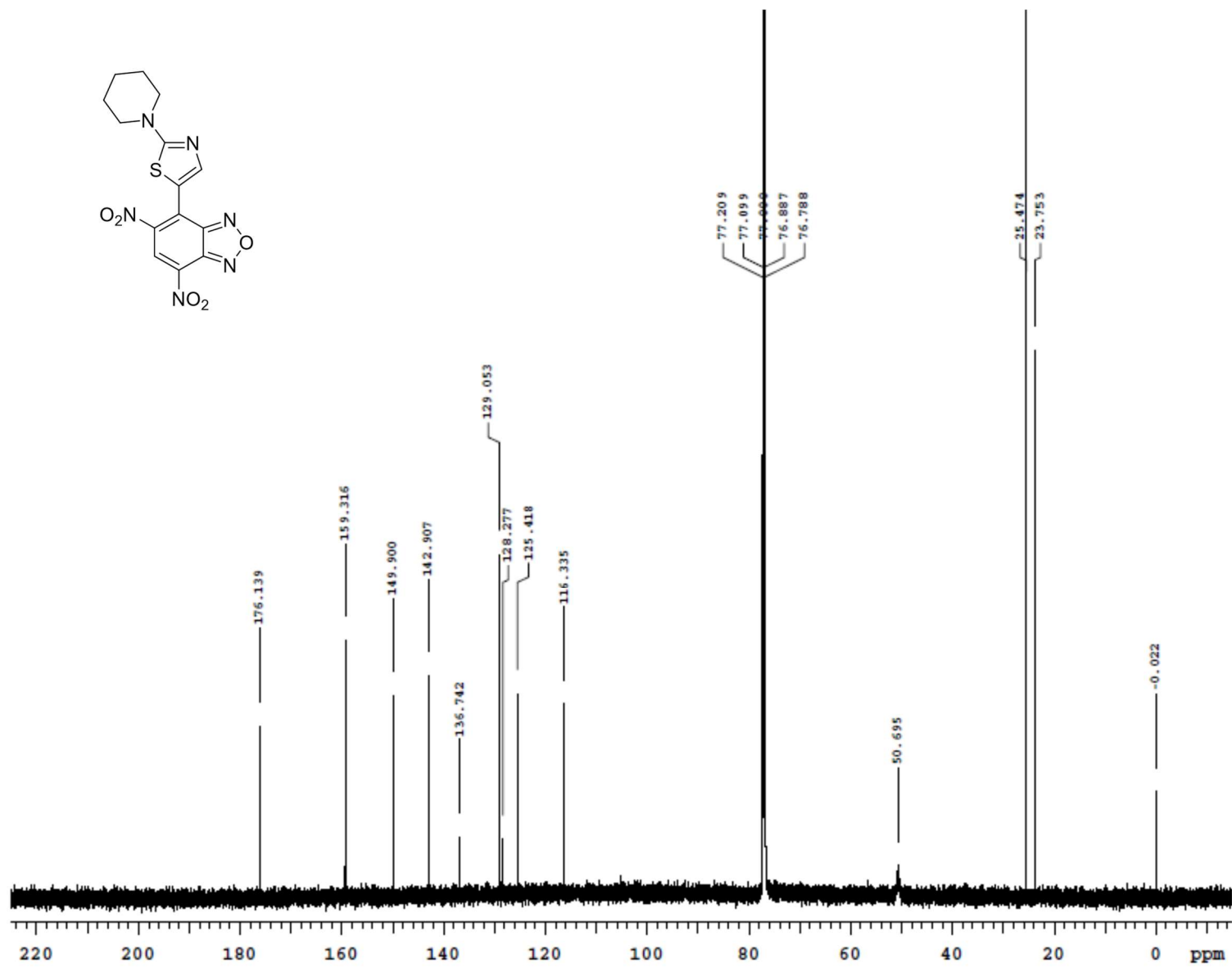


Figure S14. ¹³C NMR spectrum (150.8 MHz, CDCl₃, 25°C) of compound **8b**.

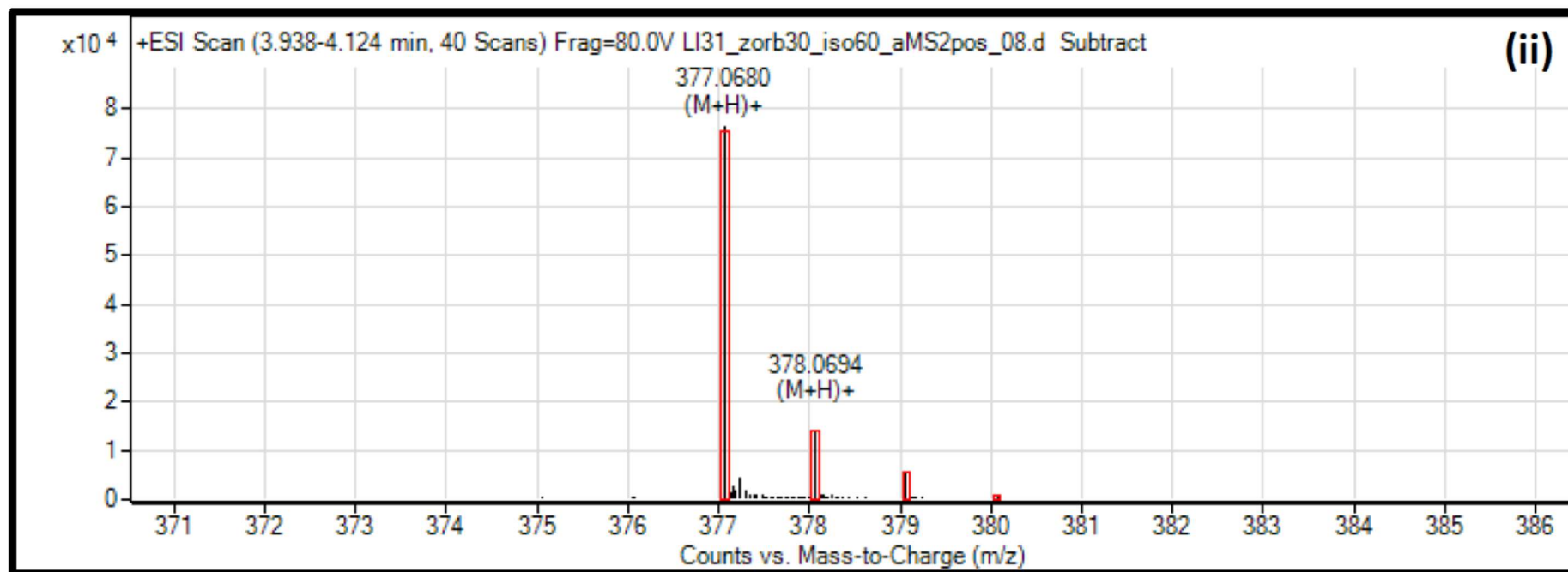


Figure S15. ESI-HRMS spectrum of compound **8b**.

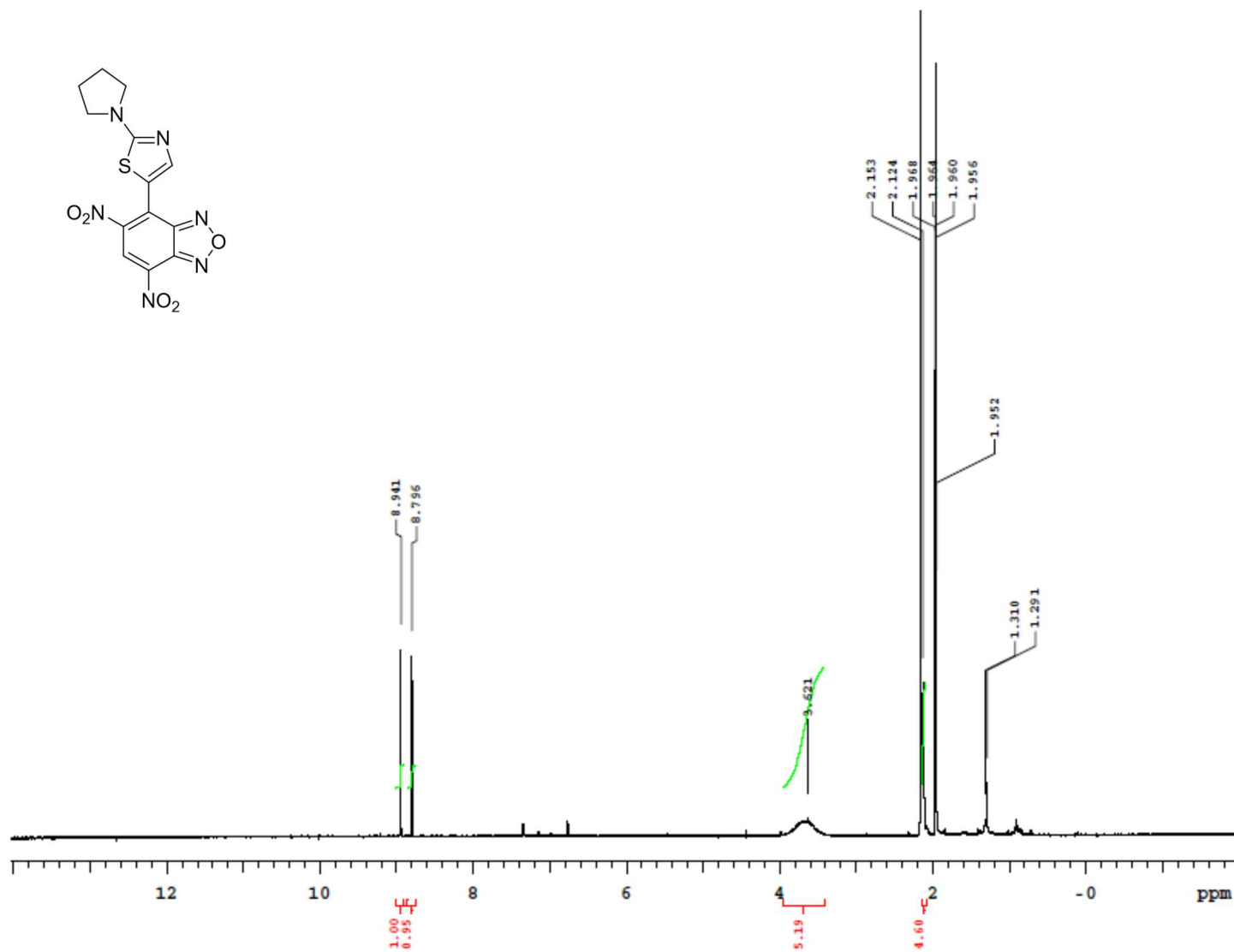


Figure S16. ¹H NMR spectrum (599.7 MHz, CD₃CN, 25°C) of compound **8c**.

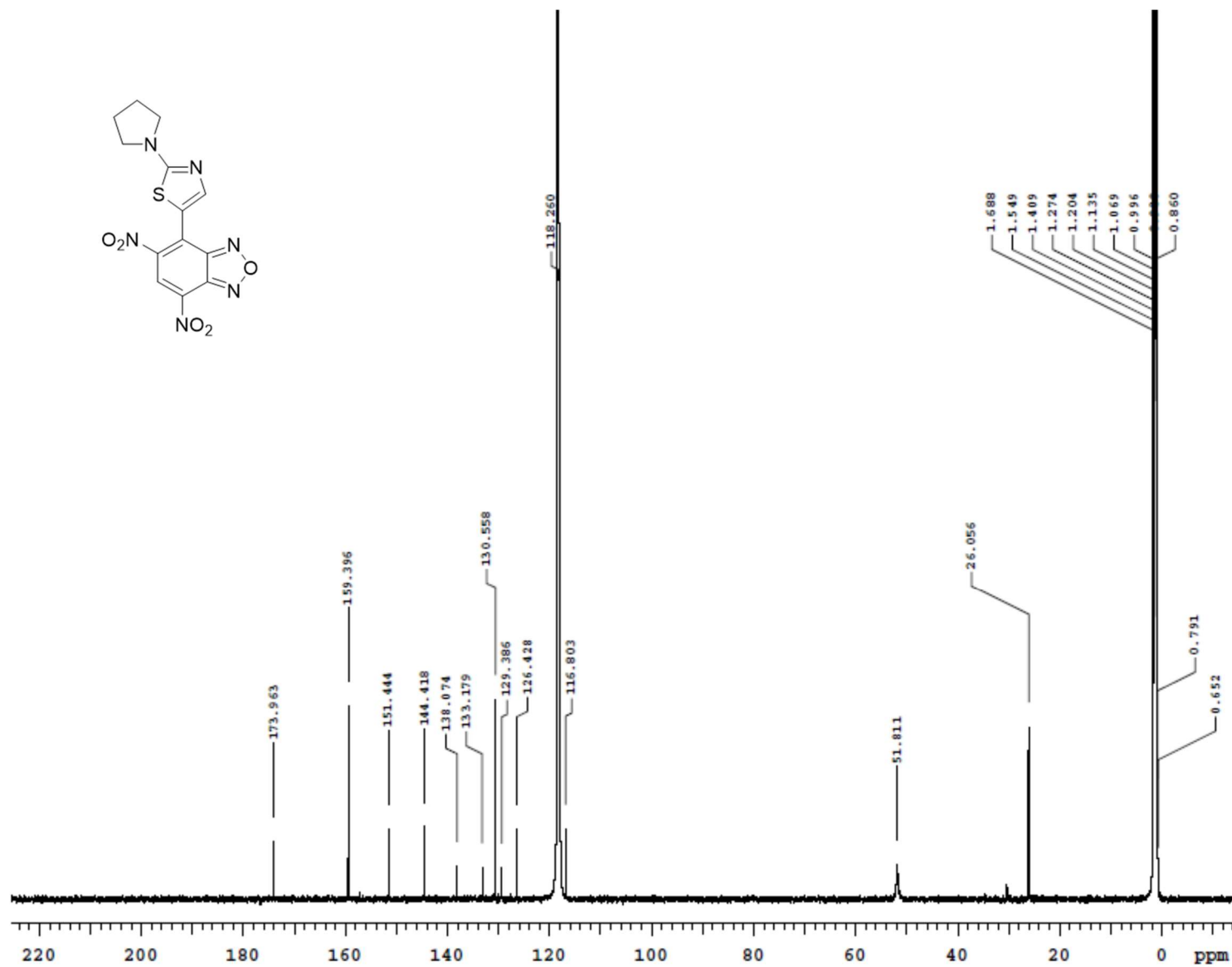


Figure S17. ¹³C NMR spectrum (150.8 MHz, CD₃CN, 25°C) of compound **8c**.

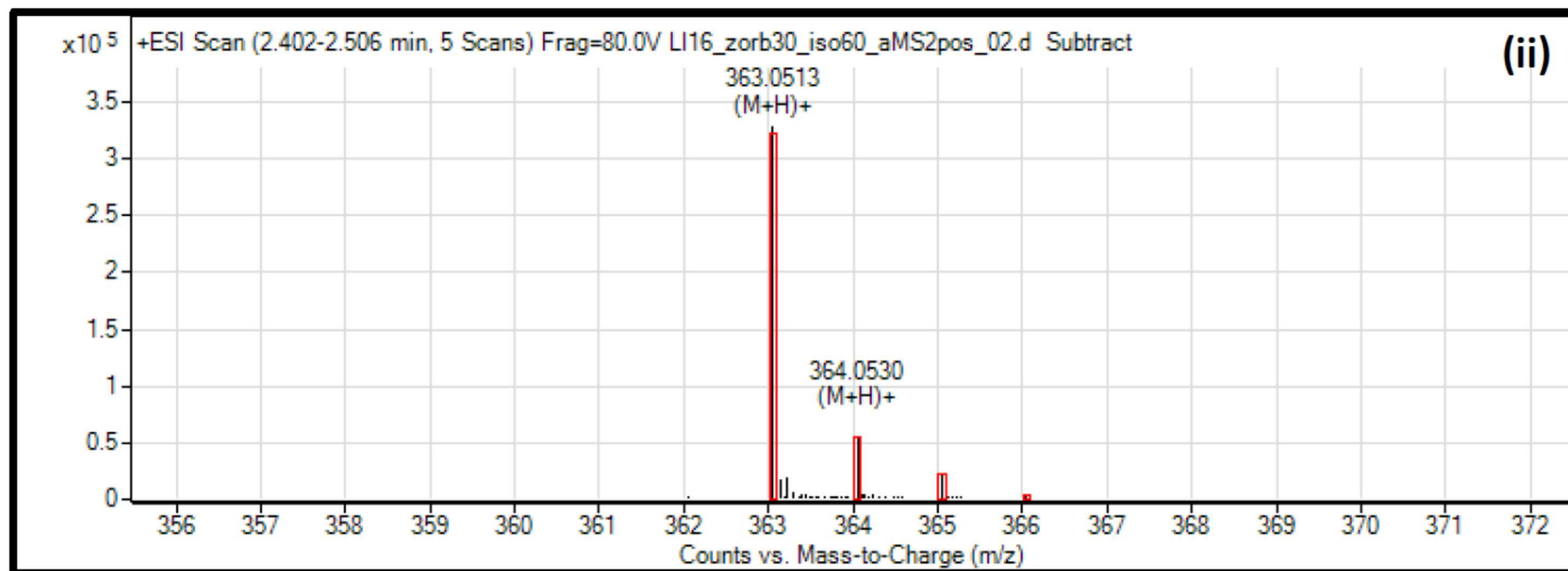


Figure S18. ESI-HRMS spectrum of compound **8c**.

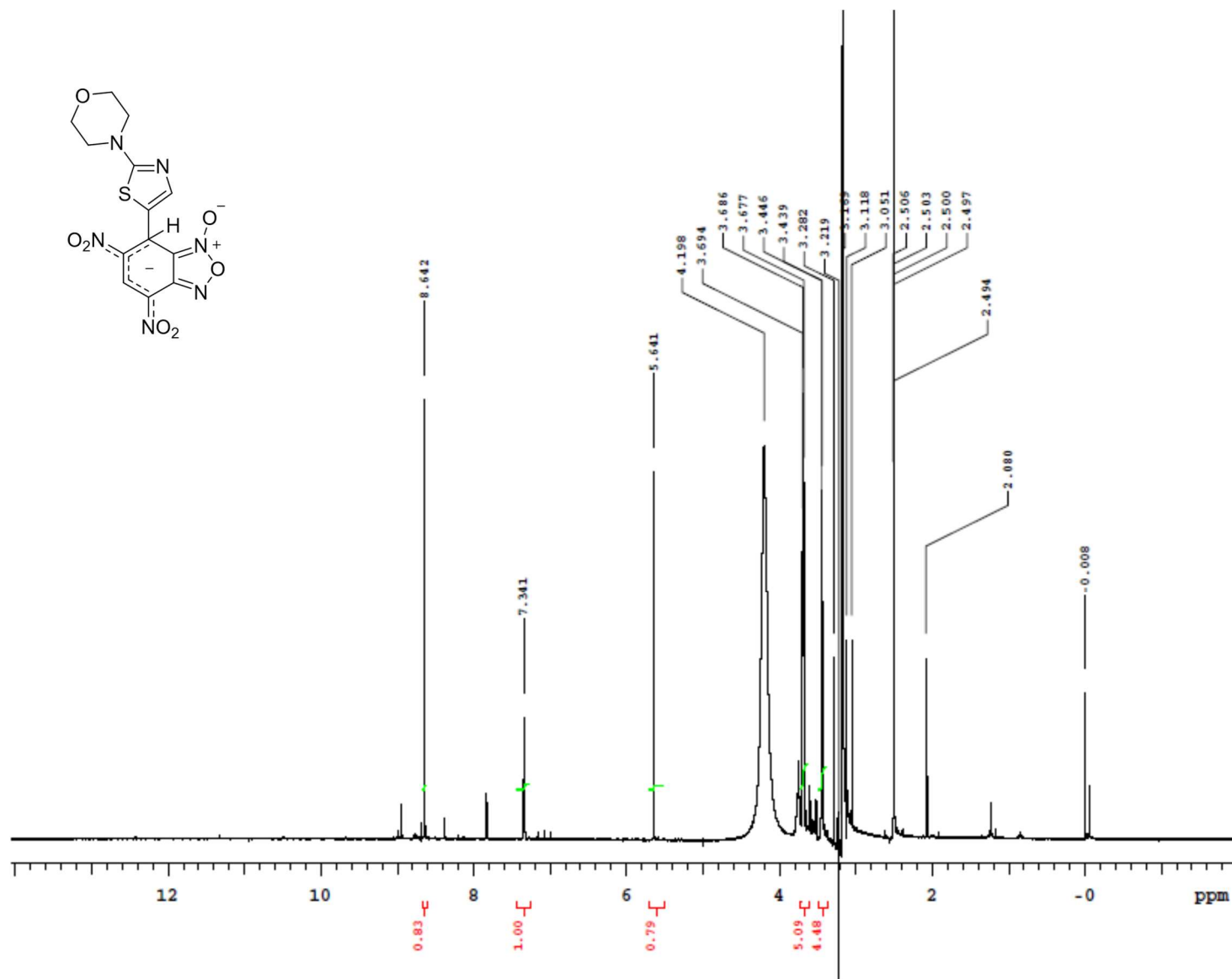


Figure S19. ¹H NMR spectrum (599.7 MHz, DMSO-d₆, 25°C) of compound **Ma**.

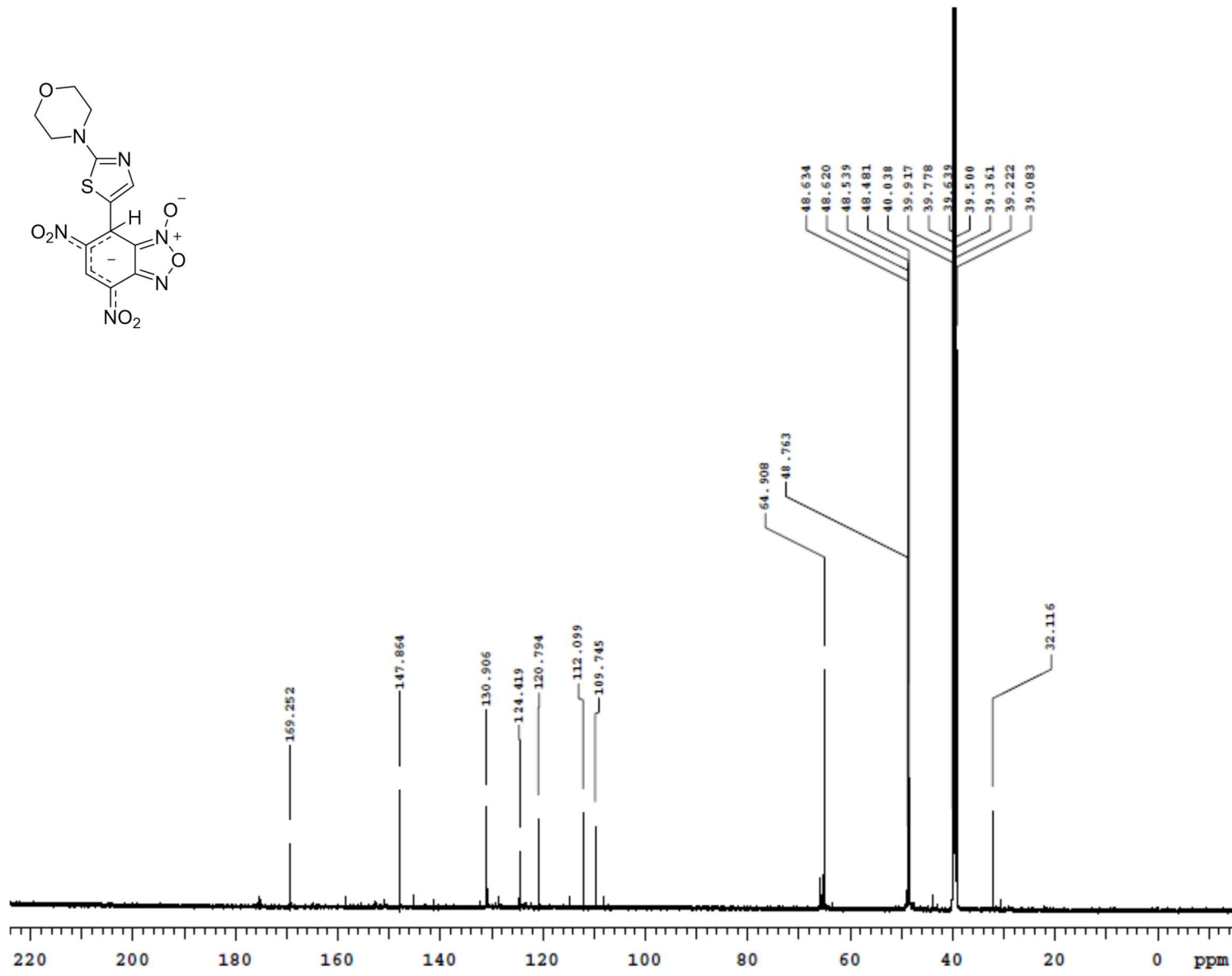


Figure S20. ¹³C NMR spectrum (150.8 MHz, DMSO-d₆, 25°C) of compound **Ma**.

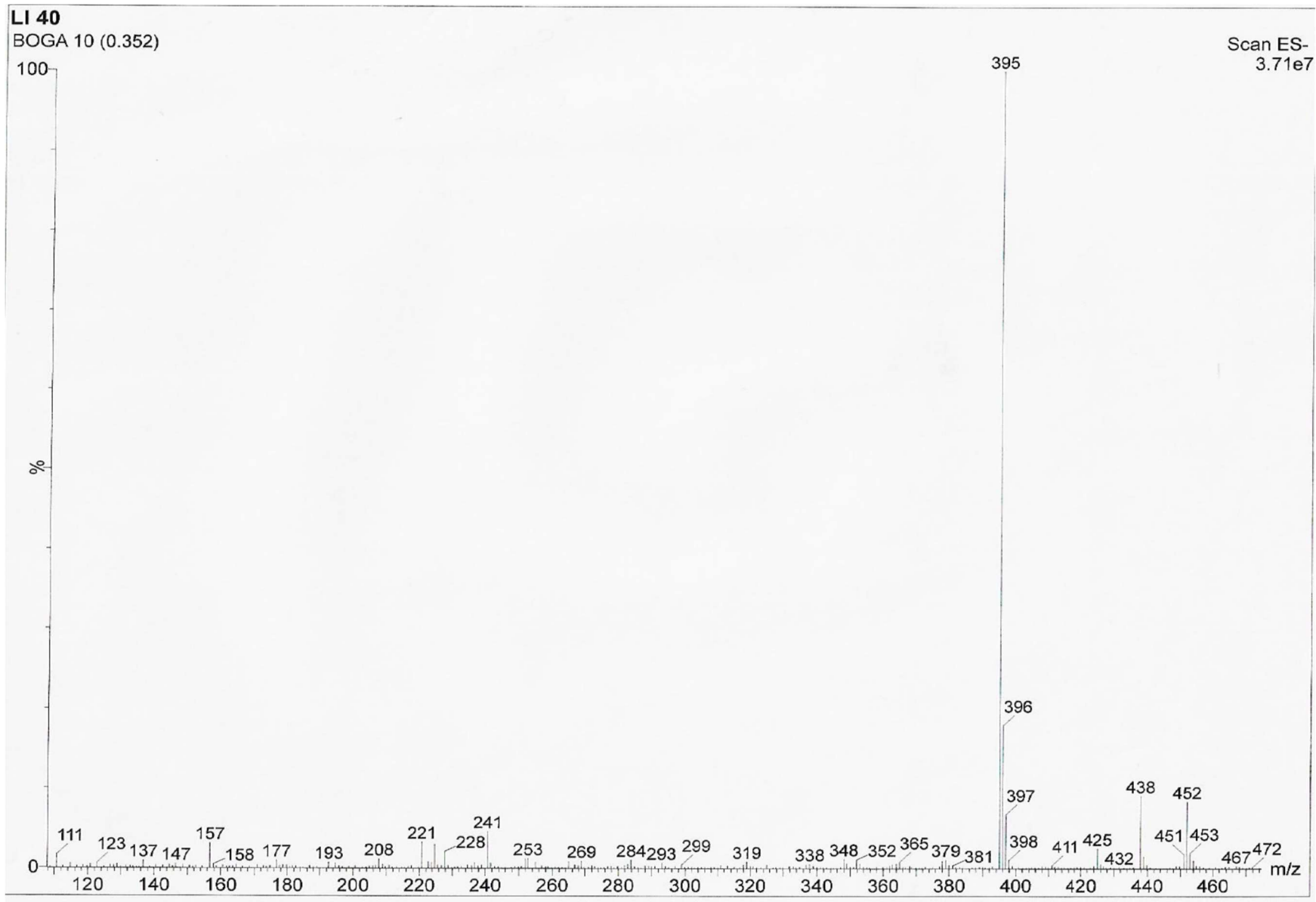


Figure S21. ESI-MS⁻ spectrum of compound Ma.

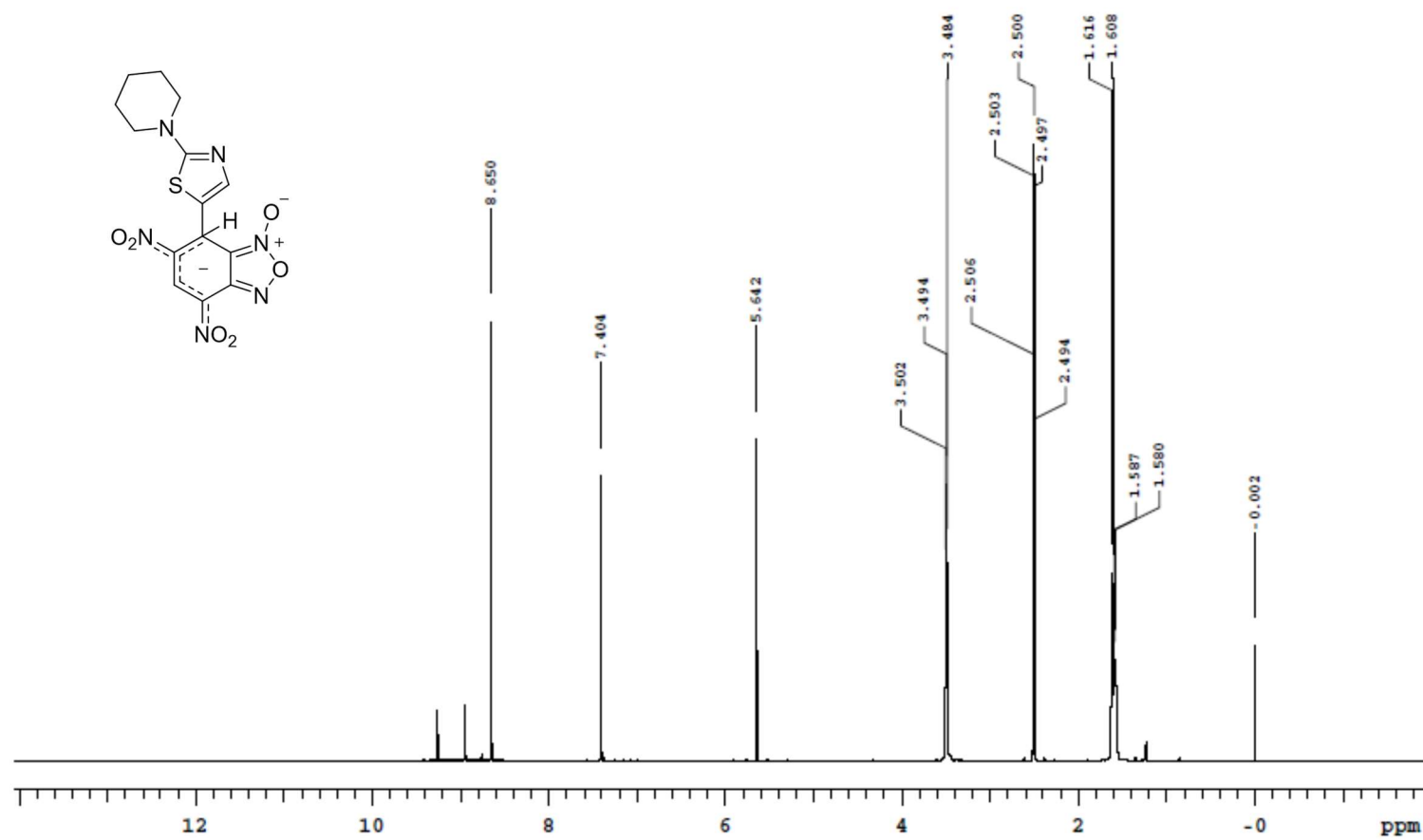


Figure S22. ¹H NMR spectrum (300.0 MHz, DMSO-d₆, 25°C) of compound **Mb**.

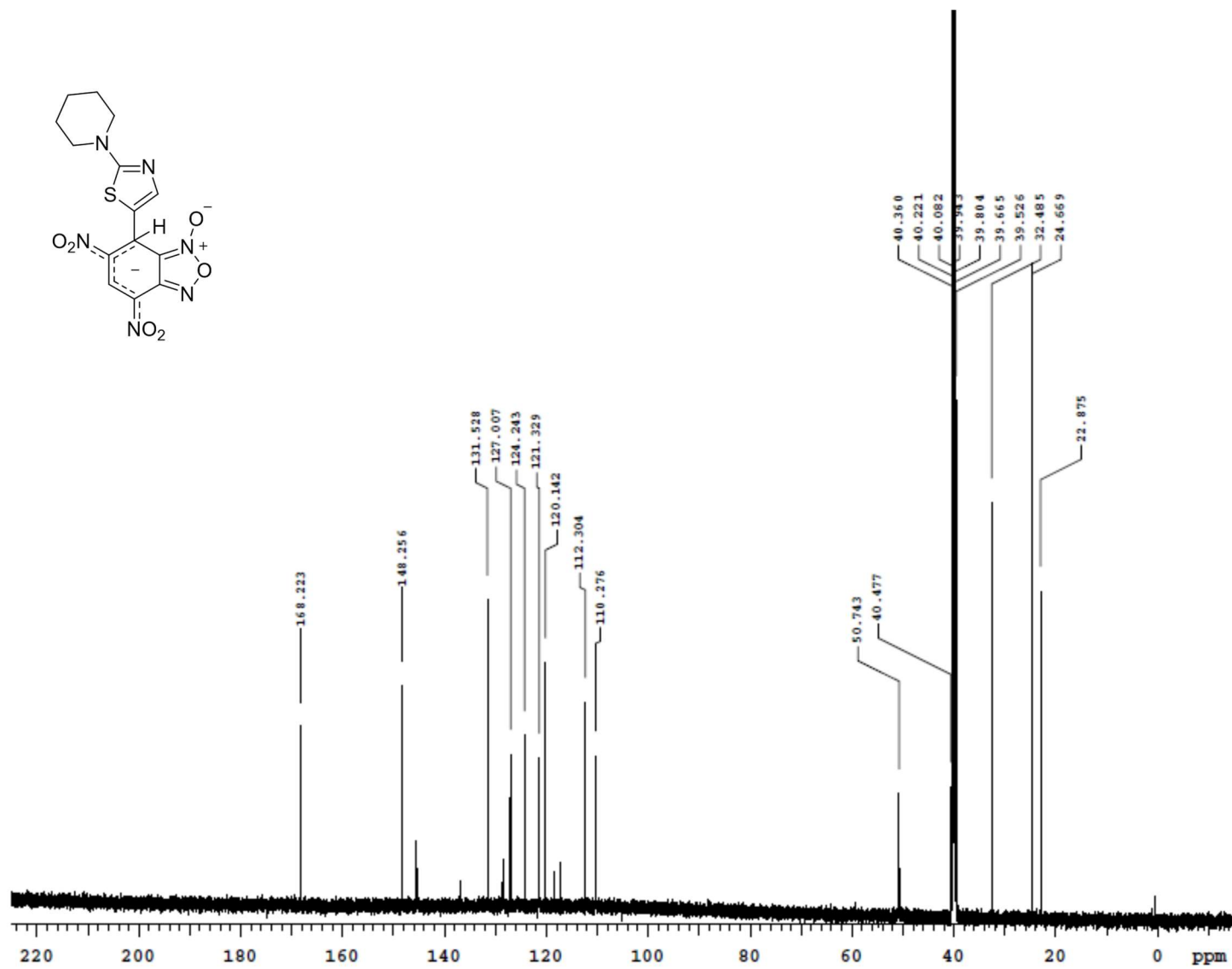


Figure S23. ¹³C NMR spectrum (75.4 MHz, DMSO-d₆, 25°C) of compound Mb.

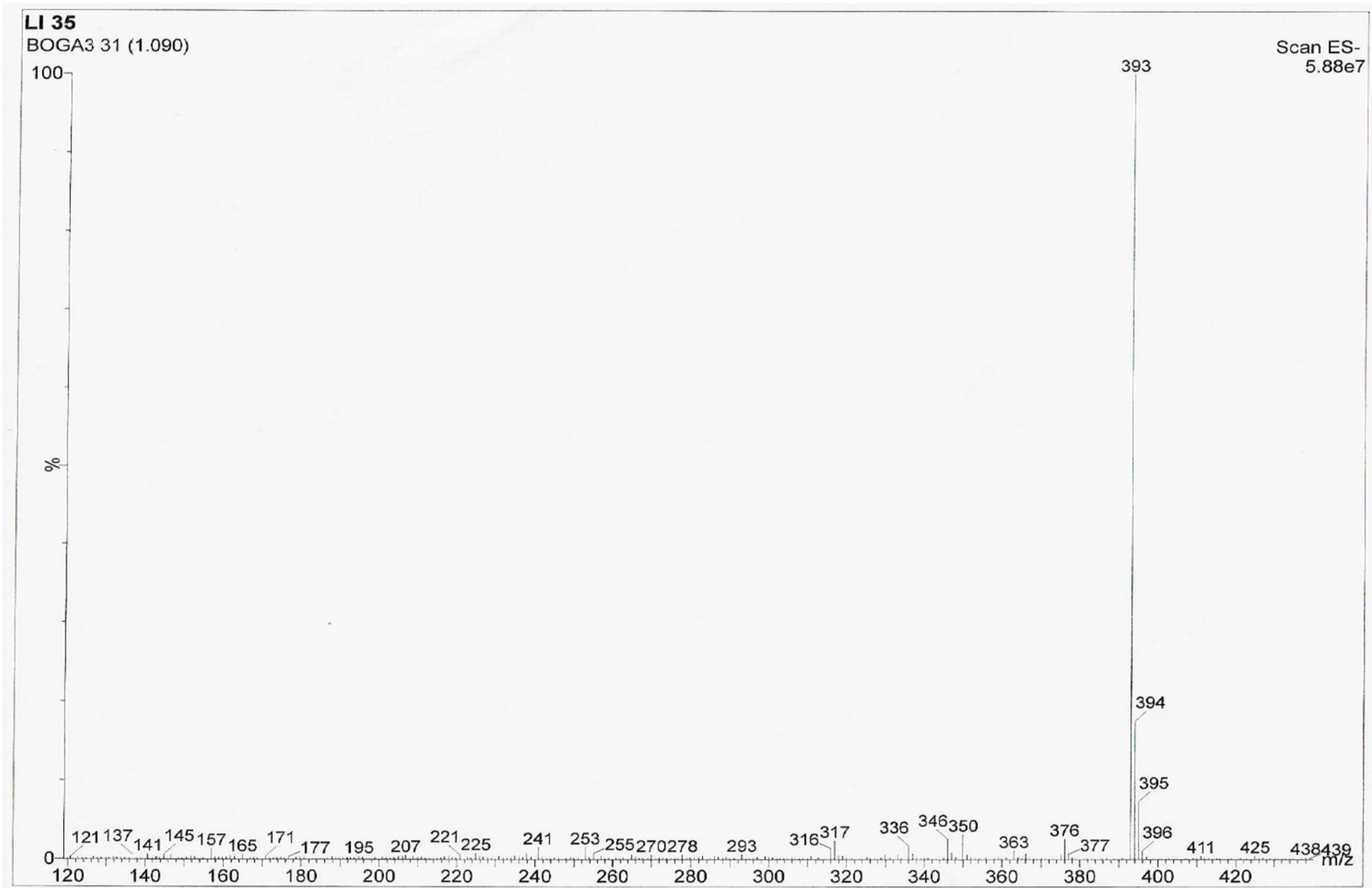


Figure S24. ESI-MS⁻ spectrum of compound **Mb**.

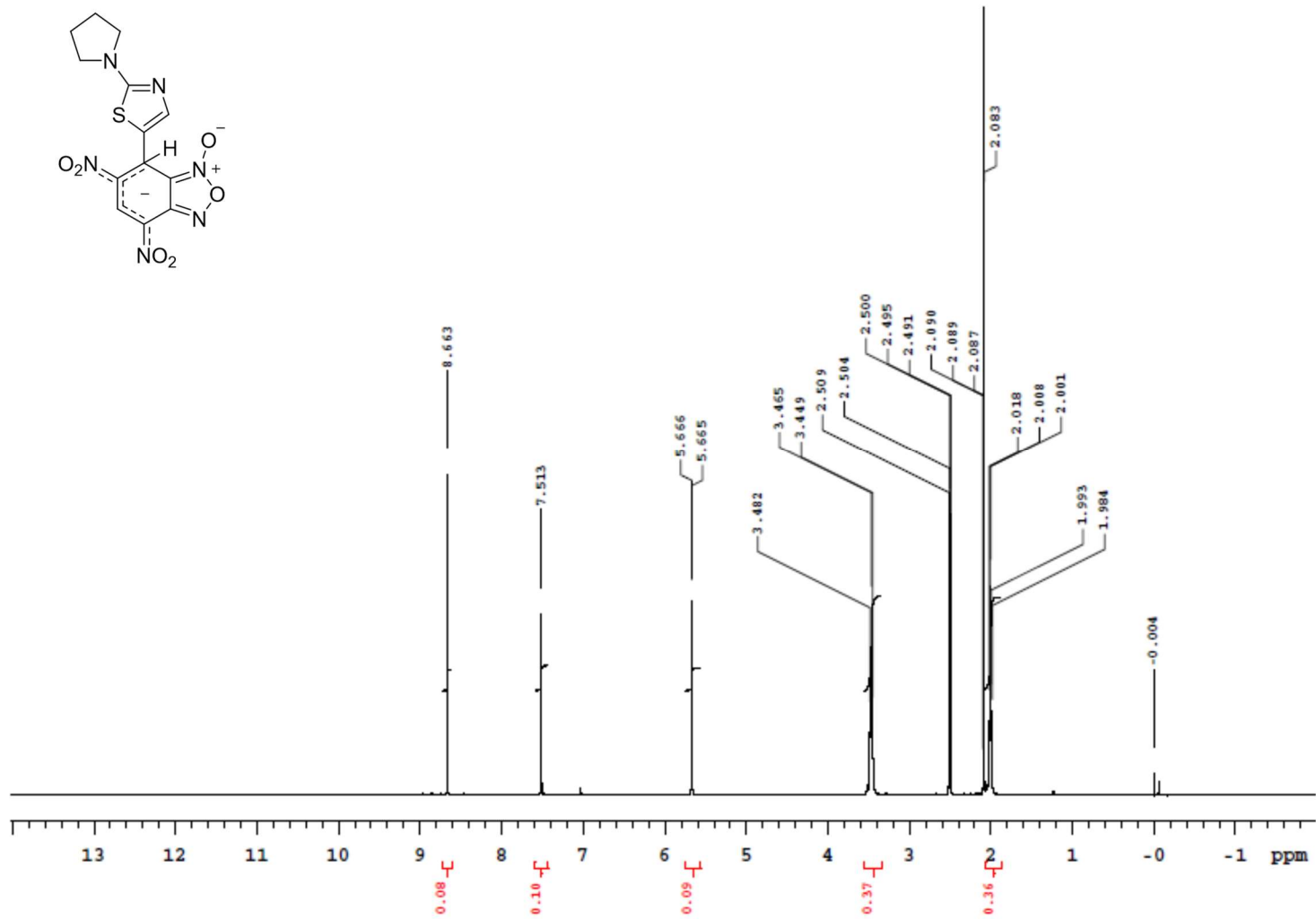


Figure S25. ¹H NMR spectrum (399.9 MHz, DMSO-d₆, 25°C) of compound **Mc**

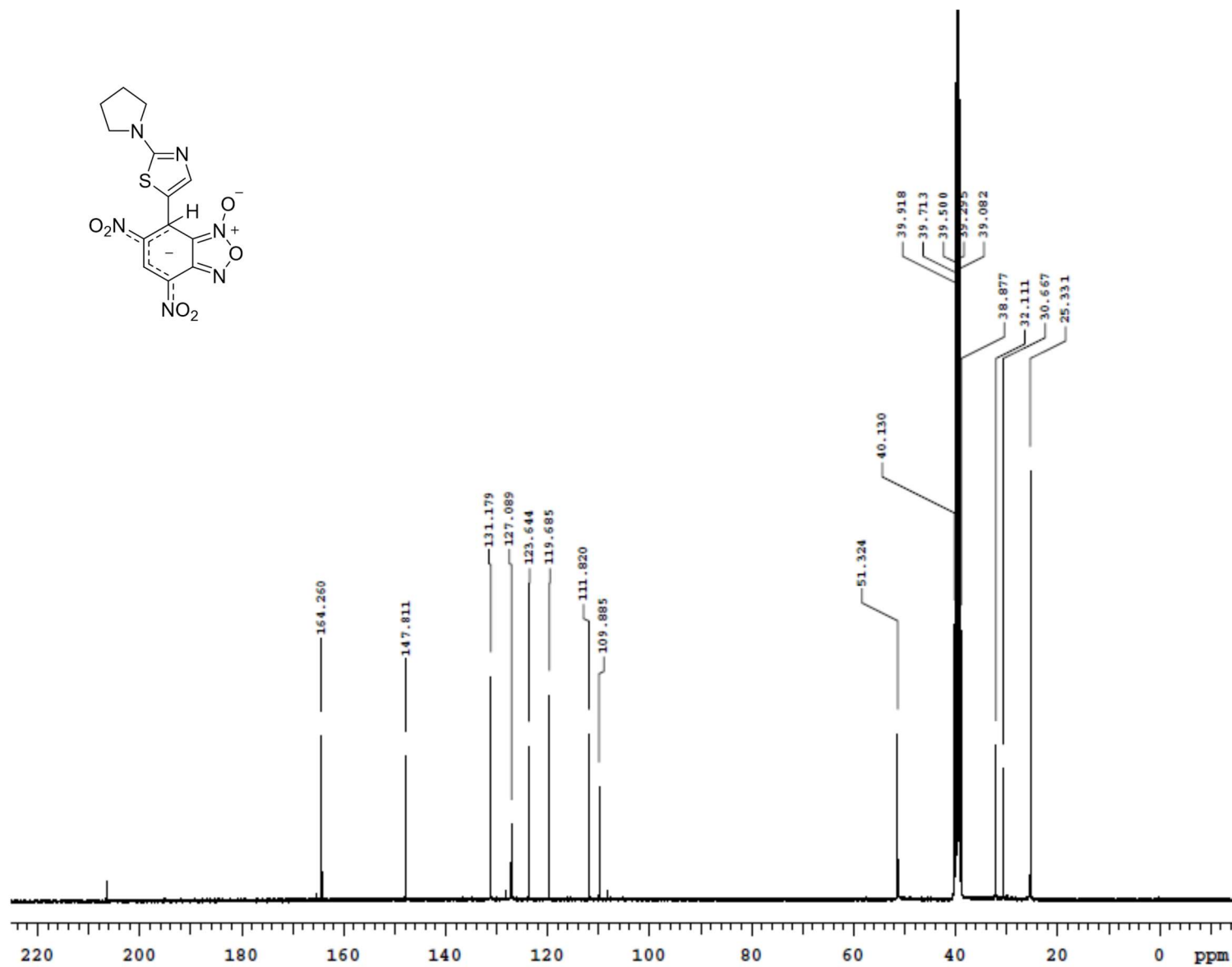


Figure S26. ¹³C NMR spectrum (100.6 MHz, DMSO-d₆, 25°C) of compound **Mc**

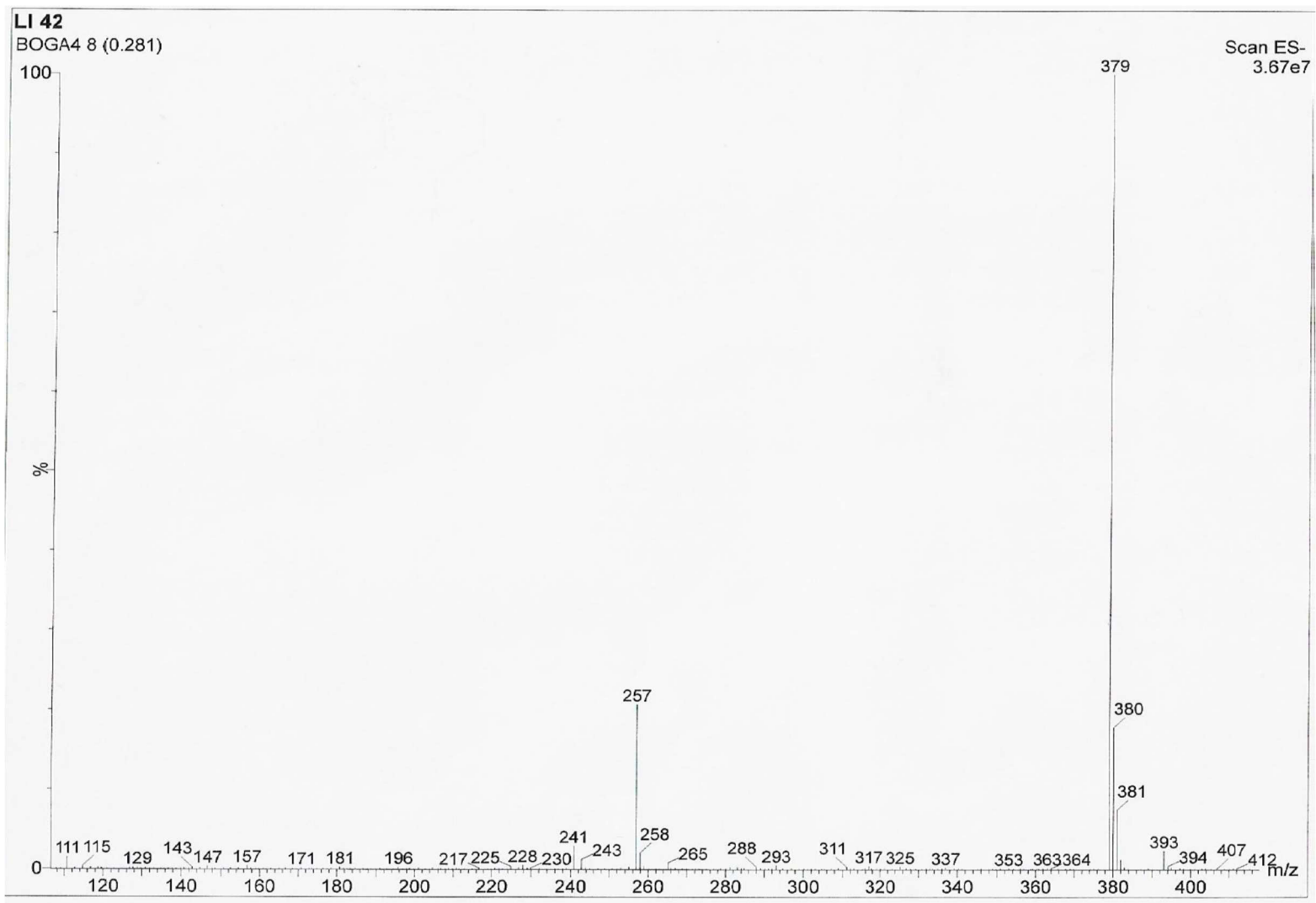


Figure S27. ESI-MS⁻ spectrum of compound Mc

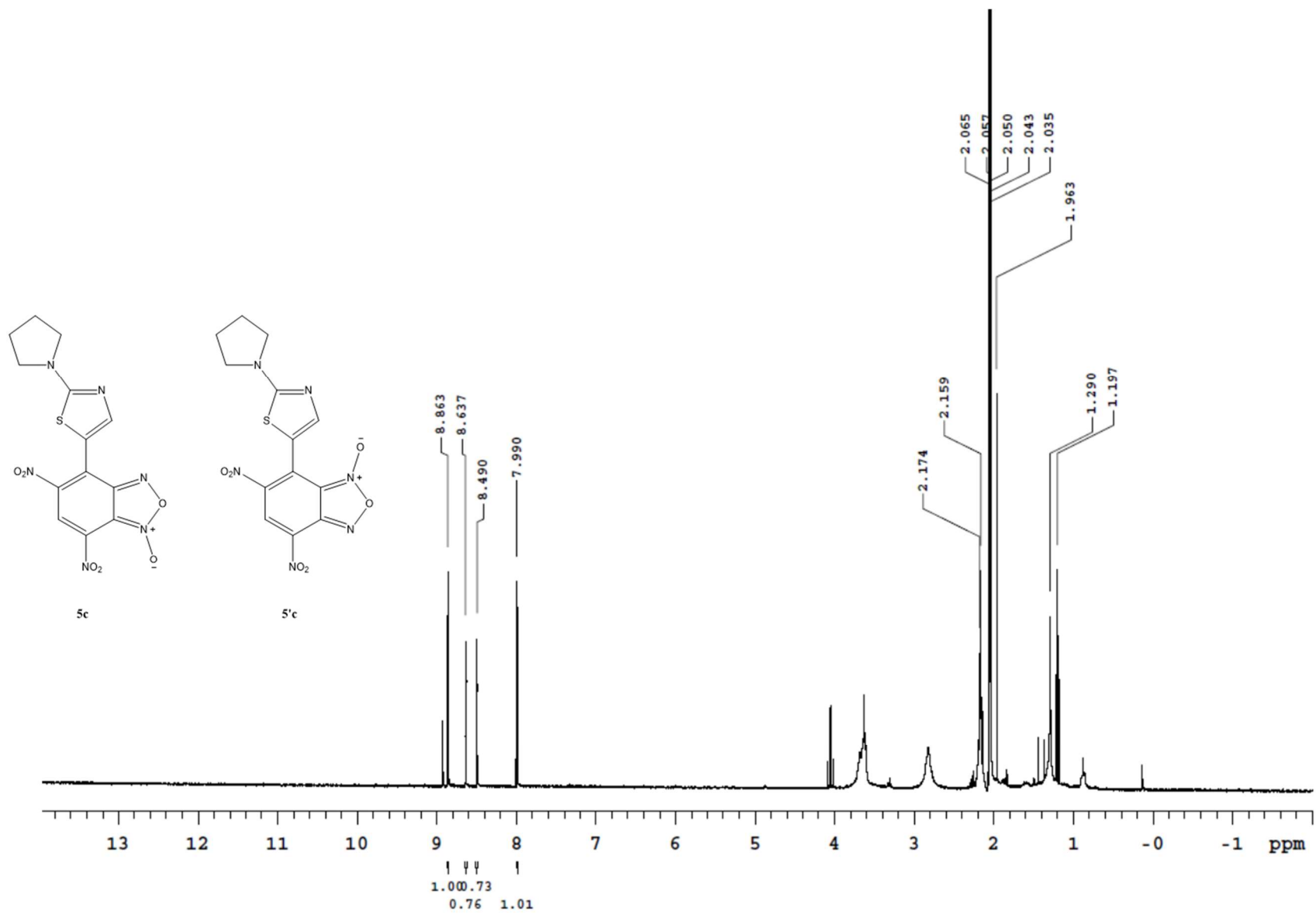


Figure S28. ^1H NMR spectrum in Acetone- d_6 of compounds **5c** and **5'c**.

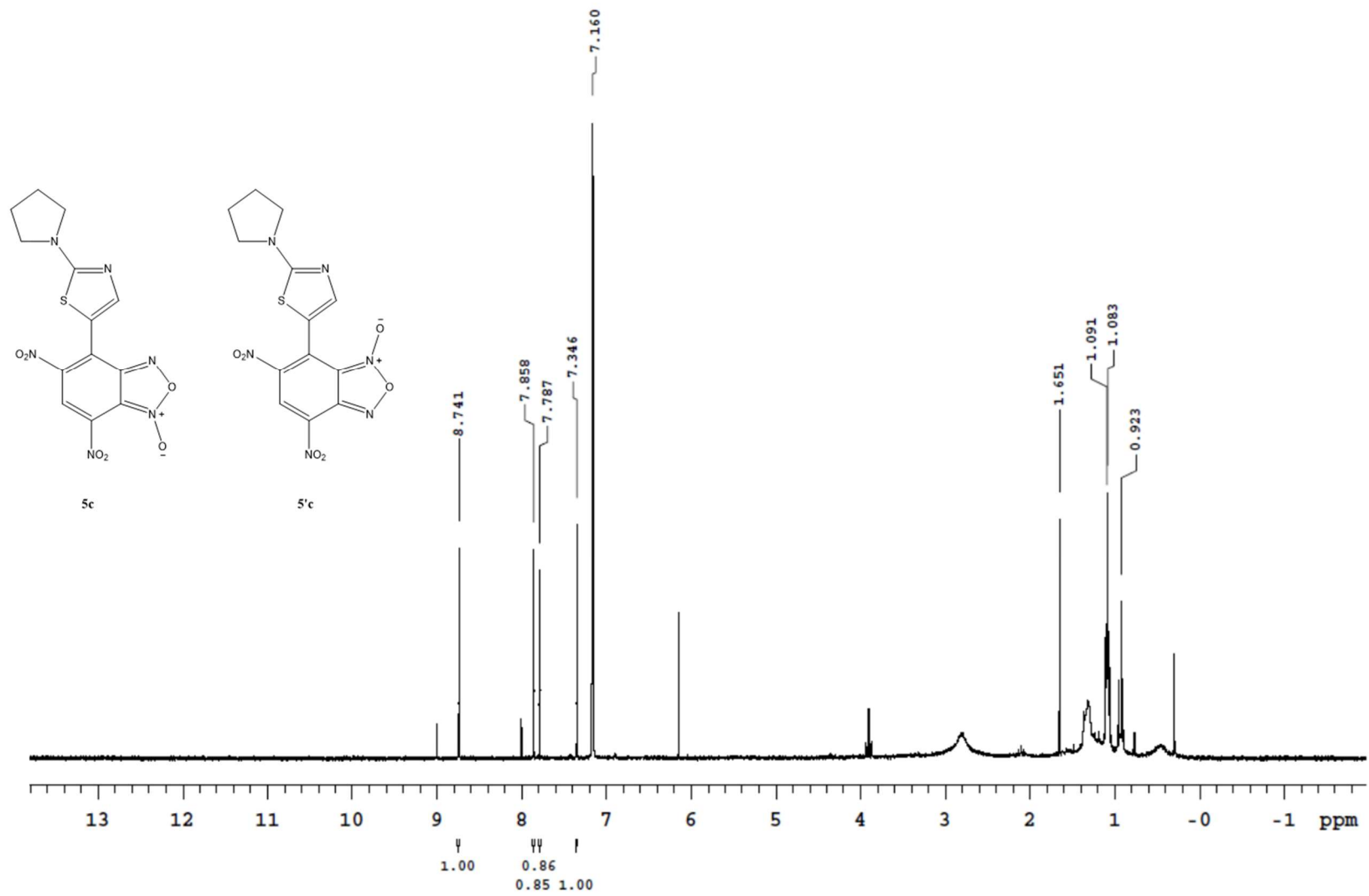


Figure S29. ¹H NMR spectrum in C₆D₆ of compounds 5c and 5'c.

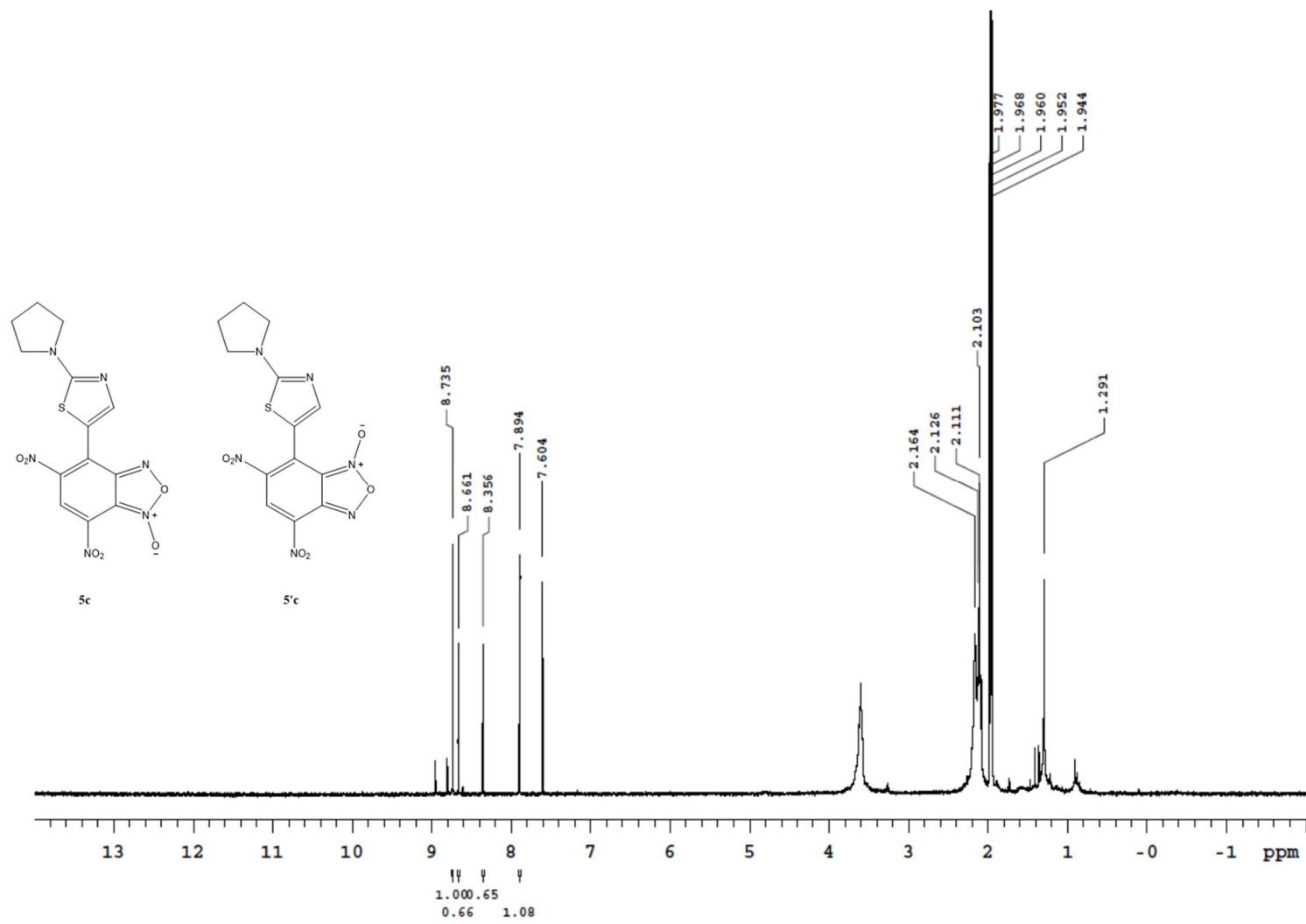


Figure S30. ^1H NMR spectrum in CD_3CN of compounds **5c** and **5'c**.

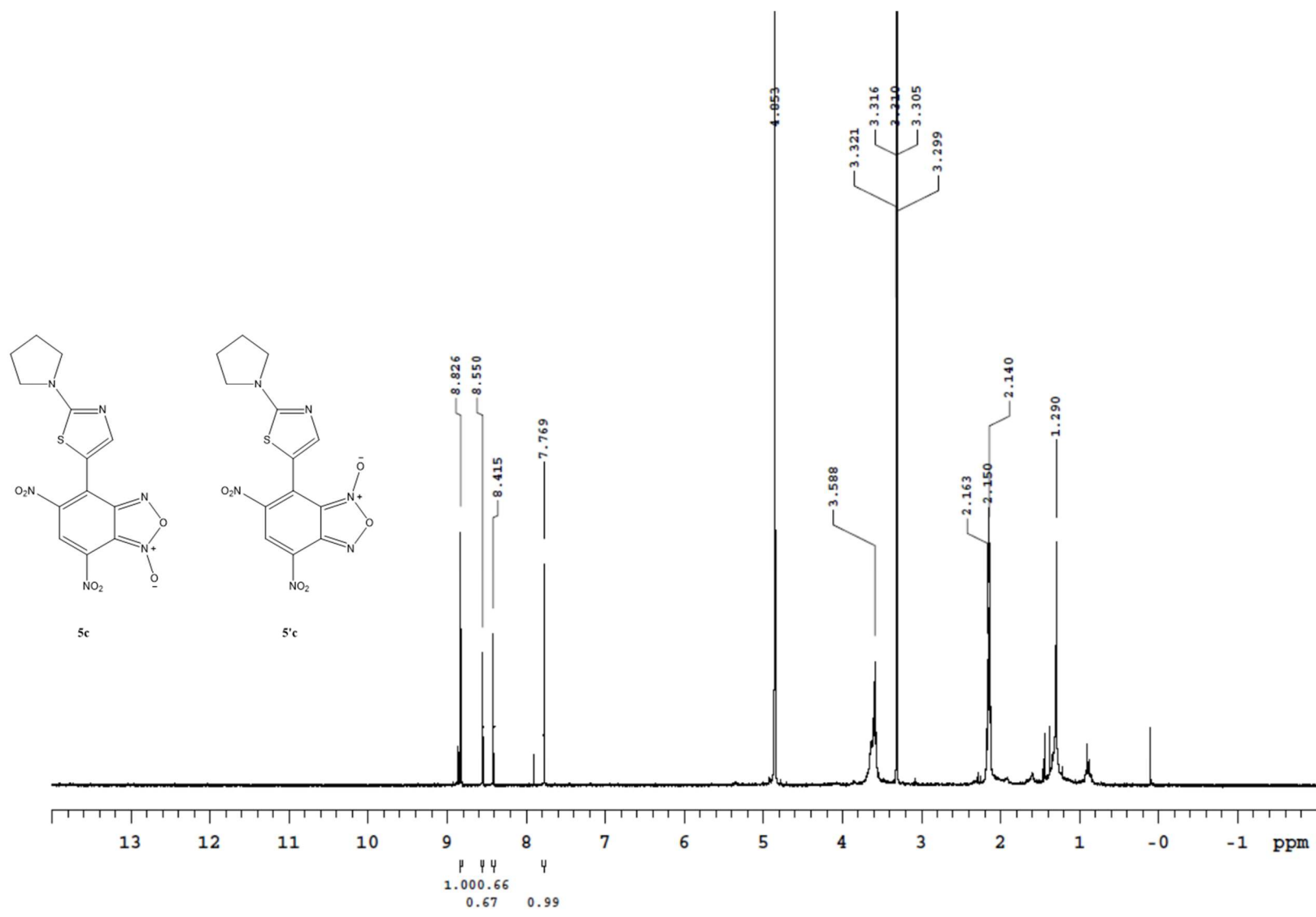


Figure S31. ¹H NMR spectrum in CD₃OD of compounds **5c** and **5'c**.

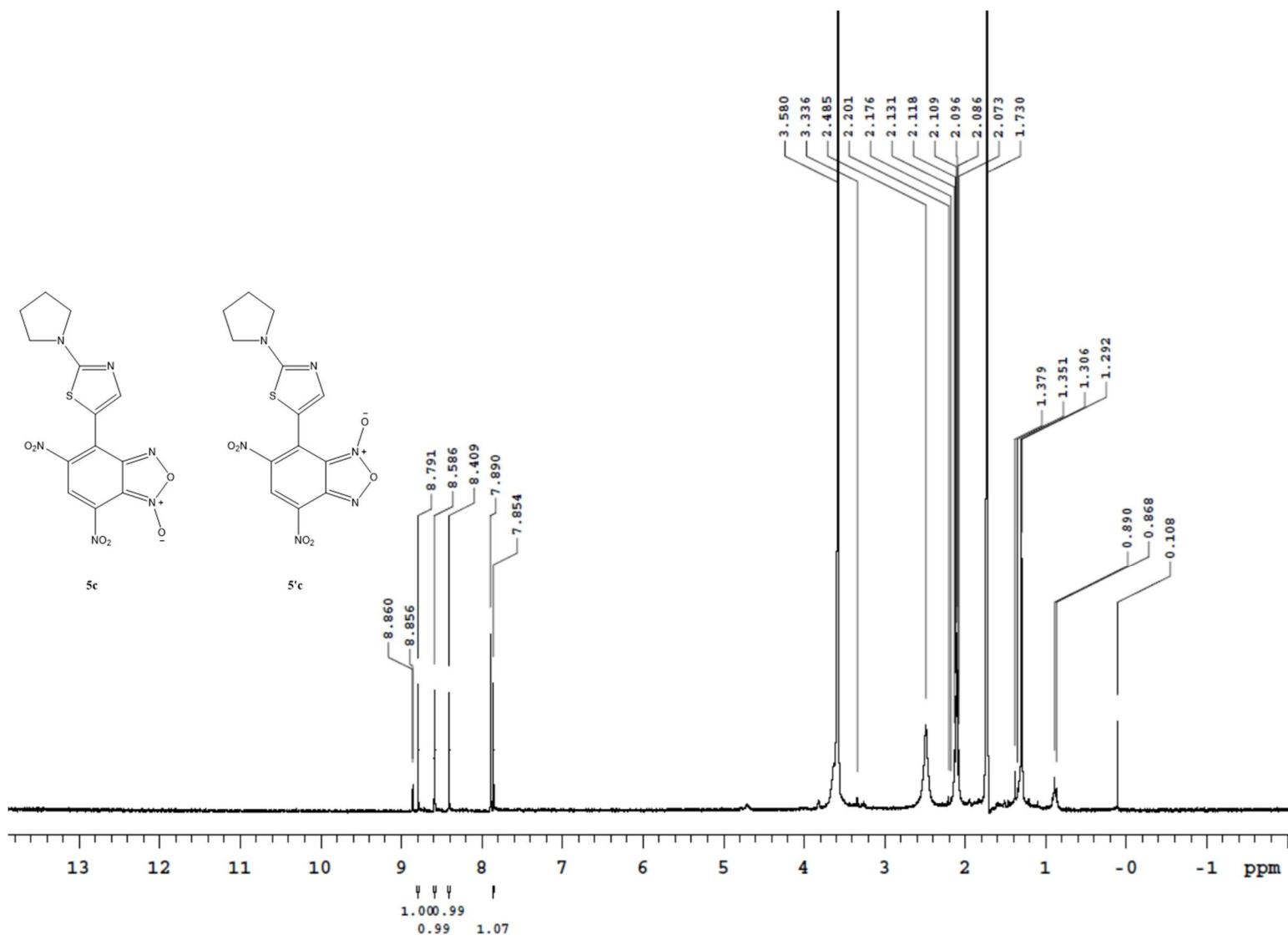


Figure S32. ^1H NMR spectrum in THF-d_8 of compounds **5c** and **5'c**.

Computational details.

All the computations reported herein were performed with Gaussian 09.¹ The geometry of the various critical points was fully optimized with the gradient method available in Gaussian 09 at the DFT level using the nonlocal hybrid Becke's three-parameter exchange functional denoted as B3LYP² and the 6-311++G(2d,p) basis set.³ A computation of the harmonic vibrational frequencies was carried out to confirm the nature of each critical point. The GIAO (gauge-invariant atomic orbital approach)⁴ was used to compute ¹³C NMR shielding constants, which were converted to chemical shifts by subtracting them from the shielding constant value of TMS computed at the same level of theory. Following an accurate and efficient procedure,⁵ developed for performing ¹³C NMR chemical shift calculations employing density functional theory with the gauge invariant atomic orbitals (DFT-GIAO), the ¹³C NMR shielding constants are calculated by single point calculation on the optimized geometry using the cc-pVDZ basis set for B3LYP. The effects of solvation were evaluated implicitly using the conductor-like polarizable continuum model (CPCM) for chloroform (CDCl₃). An empirically derived systematic error correction terms was used to correct the carbon shift alpha to sulfur in aminothiazole.⁵

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- 3 M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, 1984, **80**, 3265-3269.
- 4 K. Wolinski, J. F. Hilton and P. Pulay *J. Am. Chem. Soc.*, 1990, **112**, 8251-8260.
- 5 D. Xin, C. A. Sader, O. Chaudhary, P.-J. Jones, K. Wagner, C. S. Tautermann, Z. Yang, C. A. Busacca, R. A. Saraceno, K. R. Fandrick, N. C. Gonnella, K. Horspool, G. Hansen and C. H. Senanayake, *J. Org. Chem.*, 2017, **82**, 5135-5145.

Table S1. Cartesian coordinate of the N3-oxide tautomer (A)

scf done: -1679.491031

C	-0.085135	0.280931	0.312241
C	0.094379	-0.074084	1.669852
C	1.324040	-0.263506	2.219888
C	2.446105	-0.021186	1.384111
C	2.270324	0.287572	0.000502
C	0.951342	0.353858	-0.637363

H	-0.784012	-0.229394	2.279012
N	1.429866	-0.798088	3.568163
N	-1.480944	0.537005	-0.033350
O	-1.707558	1.465341	-0.810753
O	-2.346845	-0.143216	0.503440
O	2.417085	-1.480855	3.812047
O	0.512876	-0.562002	4.348651
N	3.747110	0.125335	1.666007
N	3.422367	0.576415	-0.562626
O	4.374843	0.475248	0.391245
O	4.446050	0.070213	2.650119
C	0.865170	0.392608	-2.059311
C	1.919237	0.136419	-2.945172
N	1.659553	0.072955	-4.252778
C	0.361744	0.272088	-4.477739
S	-0.604081	0.574602	-3.043042
H	2.931836	-0.028290	-2.613372
N	-0.170973	0.260784	-5.695393
C	-1.594283	0.484751	-5.979046
C	-1.637186	0.612623	-7.506050
C	-0.453731	-0.247695	-7.974664
C	0.620610	0.003490	-6.913071
H	-2.183158	-0.368171	-5.623824
H	-1.952275	1.380162	-5.465705
H	-1.485919	1.655065	-7.796022
H	-2.593171	0.287780	-7.915332
H	-0.108407	0.012828	-8.974769
H	-0.732732	-1.304210	-7.981046
H	1.232383	0.880200	-7.145189
H	1.292251	-0.838148	-6.751437

Table S2. Cartesian coordinate of the N1-oxide tautomer (A')

scf done: -1679.490665

C	-0.115974	0.164255	0.328670
C	0.134558	-0.220308	1.661370

C	1.388867	-0.322596	2.183340
C	2.487122	0.057249	1.351083
C	2.209468	0.376153	-0.020210
C	0.899006	0.332884	-0.640702
H	-0.711378	-0.451438	2.292730
N	1.565288	-0.744721	3.559319
N	-1.525296	0.312520	0.006234
O	-1.827198	1.191875	-0.804833
O	-2.337349	-0.398585	0.585381
O	2.716973	-0.873303	3.957883
O	0.556070	-0.951123	4.230482
N	3.746182	0.272302	1.656123
N	3.359921	0.861780	-0.523303
O	4.330325	0.760640	0.518910
O	3.712425	1.358953	-1.578082
C	0.793522	0.318997	-2.061516
C	1.785232	-0.187295	-2.906360
N	1.536742	-0.270933	-4.212029
C	0.314569	0.194266	-4.478533
S	-0.605332	0.720379	-3.078661
H	2.733919	-0.557172	-2.548137
N	-0.179654	0.251590	-5.710935
C	-1.516069	0.761762	-6.043201
C	-1.499318	0.834043	-7.574468
C	-0.517030	-0.275993	-7.978222
C	0.564358	-0.214531	-6.896106
H	-2.280934	0.068681	-5.675216
H	-1.685236	1.732959	-5.572512
H	-1.122680	1.807894	-7.895765
H	-2.493877	0.703339	-7.999529
H	-0.104053	-0.135510	-8.976731
H	-1.014268	-1.248781	-7.954814
H	1.351665	0.504322	-7.141233
H	1.039986	-1.171336	-6.686498

Variable temperature NMR reactions between 1–3 and DNBF (10): experimental details

DNBF (**10**, 4.86×10^{-5} mol) was dissolved in CD_3COCD_3 (0.5 mL) and introduced in a NMR spectroscopy tube that was inserted in the NMR probe. When the probe temperature reached -93 °C, an equimolar amount of **3a**, (or **3b**, **3c**) dissolved in acetone- d_6 , and kept at -93 °C, was added in the NMR tube. Immediately after the mixing, beside the signals of starting reagents, new signals appeared in the ^1H NMR spectrum. They were compatible with those of the σ -anionic intermediate **Ma** (or **Mb**, **Mc**). The system was monitored with time and the spectra were recorded at different temperatures until 25 °C. On gradually raising the temperature, the intensity of signals of **Ma–Mc** increased whereas those of reagents gradually decreased until to disappear (at 25 °C and 0 °C for **Mb** and **Mc**, respectively; traces of signals of reagents were present in spectrum at 25 °C in case **a**). When the tube was extracted from the NMR probe, a red solid appeared on the bottom. It was collected, dissolved in DMSO-d_6 and analyzed by ^1H NMR, ^{13}C NMR and g -HSQC experiments. The solid was stable enough to be analyzed also through ESI mass spectrometry (negative ion mode). Its physico-chemical data agreed with those of **Ma** (or **Mb**, **Mc**). The names of **Ma-c** have been created from ChemDraw Professional 17.1 version by drawing the canonical resonance form bearing the negative charge of the Meisenheimer moiety situated on the nitro group in para position with respect to the new bond formed, in assigning the name, we did not consider the proton as counter-ion. In main text are reported first the spectra recorded in acetone- d_6 at low temperature then the data collected after isolation of **Ma-Mc**.