Supporting Information

Synthesis of D-(+)-camphor based N-acylhydrazones and their antiviral activity

Kseniya S. Kovaleva*[abc], Fedor I. Zubkov*[c], Nikolay I. Bormotov[d], Roman A. Novikov[e], Pavel V. Dorovatovskii[f], Victor N. Khrustalev[cf], Yuriy V. Gatilov[ab], Vladimir V. Zarubaev[g], Olga I. Yarovaya*[ab], Larisa N. Shishkina[d], Nariman F. Salakhutdinov[ab]

a) *Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Lavrentjev Ave. 9, 630090 Novosibirsk, Russian Federation. e-mail: ooo@nioch.nsc.ru*
b) *Novosibirsk State University, Pirogova St. 2, 630090 Novosibirsk, Russian Federation. e-mail: kseniya.kovaleva3103@yandex.ru*
c) *RUDN University, 6 Miklukho-Maklaya St., 117198 Moscow, Russian Federation; e-mail: fzubkov@sci.pfu.edu.ru*
d) *Department of prevention and treatment of especially dangerous infections, State Research Centre of Virology and Biotechnology VECTOR, Koltsovo, Novosibirsk Region, 630559, Russian Federation.*
e) *Engelhardt Institute of Molecular Biology, Russian Academy of Sciences, 32 Vavilov St., 119991 Moscow, Russian Federation.*
f) *National Research Center "Kurchatov Institute", 1 Acad. Kurchatov Sq., 123182 Moscow, Russian Federation.*
g) *Pasteur Institute of Epidemiology and Microbiology, 14 Mira str., 197101 St. Petersburg, Russia*

1. Experimental Section

1.1. Chemistry

Commercially available reagent grade chemicals used as received. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DRX-500 spectrometer (500 and 125 MHz, respectively) in $CDCl_3$, with residual solvent signals used as internal standards (7.24 ppm for ^{1}H nuclei, 76.9 ppm for ^{13}C nuclei). High-resolution mass spectra were recorded on a Thermo Scientific DFS instrument in full scan mode over the *m/z* range of 0–500, ionization by electron impact at 70 eV, and direct introduction of samples. The reaction products were separated by column chromatography (60-200 μm silica gel, Masherey-Nagel). GC-MS analysis was performed on an Agilent 7890 A gas chromatograph with an Agilent 5975C quadrupole mass spectrometer as detector, HP-5MS 30000×0.25 mm fused silica column, carrier gas – helium. The identification of compounds was performed by comparing the retention times with a series of authentic samples and comparing the complete experimentally obtained mass spectra with mass spectral database. The structures of the obtained compounds were established from ^{1}H and ^{13}C NMR spectra, two-dimensional homonuclear ^{1}H–^{1}H COSY and NOESY experiments, as well as two-dimensional heteronuclear ^{1}H–^{13}C HSQC and HMBC experiments. The atom numbering in the compounds is intended for the assignment of NMR signals and does not match the IUPAC nomenclature.

1.2. X-ray diffraction studies.

The single-crystal X-ray diffraction data for **13** and **16** were collected at the 'Belok' beamline of the Kurchatov Synchrotron Radiation Source (National Research Center 'Kurchatov Institute', Moscow, Russian Federation) using a Rayonix SX165 CCD detector at λ = 0.80246 Å. A total of 720 images for two different

orientations in the case of each crystal were collected using an oscillation range of 1.0° and φ scanning mode. The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite [1] and then scaled and corrected for absorption using the Scala program [2]. For details, see Table S1. The structures were determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. The independent parts of the unit cells of **13** and **16** contained two ethyl acetate solvate molecules. The hydrogen atoms of the amino groups were objectively localized in the difference-Fourier maps and refined isotropically with fixed displacement parameters [U_{iso}(H) = 1.2U_{eq}(N)]. The other hydrogen atoms in **13** and **16** were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite [3].

The X-ray diffraction data of **11** (Figure S1) were collected with a Bruker KAPPA APEX II CCD diffractometer with graphite monochromated Mo-*K*α radiation (0.71073 Å) at the Collective Chemical Service Center of SB RAS. Absorption corrections were applied with SADABS [4]. The structure was solved by the direct method. The positions and temperature factors for the non-hydrogen atoms were refined anisotropically by the full-matrix least-squares technique. The hydrogen atoms of the amine groups were localized in a difference Fourier map and refined isotropically; the other hydrogen atoms were refined in a riding model. All computations were done with the SHELX-97 program suite [3].

Crystallographic data for **11, 13**•½$CH_3COOC_2H_5$and **16**•½$CH_3COOC_2H_5$have been deposited with the Cambridge Crystallographic Data Center, CCDC 1873457 (**11**), CCDC 1860266 (**13**) and CCDC 1860267 (**16**).

[1] Battye, T. G. G.; Kontogiannis, L.; Johnson, O.; Powell, H. R.; Leslie, A. G. W. *ActaCryst*. **2011**, *D67*, 271-281.

[2] Evans, P. R. *ActaCryst*.**2006**, *D62*, 72-82.

[3] Sheldrick, G. M. *ActaCryst*.**2015**, *C71*, 3-8.

[4] G. M. Sheldrick, *SADABS, Program for Area Detector Adsorption Correction*, University of Gottingen, Germany, **1996**.

Table S1. Crystal data and structure refinements for compounds **11**, **13** and **16**.

Compound	**11**	**13**•½$CH_3CO_2C_2H_5$	**16**•½$CH_3CO_2C_2H_5$
Empirical formula	$C_{15}H_{20}N_2O_2$	$C_{48}H_{70}N_6O_{10}$	$C_{58}H_{74}N_6O_8$
Formula weight	260.33	891.10	983.23
Temperature, K	296(2)	100.0(2)	100.0(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a, Å	10.6401(9)	10.819(2)	10.949(2)
b, Å	13.1077(13)	14.713(3)	15.752(3)
c, Å	11.0890(11)	30.167(6)	31.273(6)
α, deg.	90	90	90
β, deg.	111.310(4)	96.24(3)	98.92(3)
γ, deg.	90	90	90
V, Å^3	1440.8(2)	4773.5(16)	5328.4(18)
Z	4	4	4
D_{calc}, g·cm^{-3}	1.200	1.240	1.226
Absorption coefficient, μ	0.080	0.113	0.106
F(000)	560	1920	2112
Crystal size, mm	0.025×0.21×0.28	0.20×0.25×0.30	0.15×0.40×0.40
Theta range for data collection	1.97 - 25.73	3.22 – 30.97	1.64 – 31.02
Index ranges	-12 < h < 12 -15 < k < 15 -13 < l < 13	-13 < h < 13 -18 < k < 18 -38 < l < 38	-13< h < 13 -20< k < 20 -40< l <40
Reflections collected	27666	51592	59231
Independent reflections, R_{int}	5454, 0.064	20491, 0.064	21802, 0.081
Reflections observed with $I > 2\sigma(I)$	3608	18394	16961
Absorption correction	semi-empirical	semi-empirical	semi-empirical
Data / restraints/ parameters	5454 / 1 / 349	20491 / 1 / 1186	21802 / 1/ 1314
Goodness-of-fit on F^2	1.008	1.042	1.012
R_1 [$I > 2\sigma(I)$]	0.047	0.061	0.075
wR_2 [all data]	0.122	0.157	0.178
Extinction coefficient	-	0.0219(13)	0.0078(5)
T_{min} / T_{max}	0.943 / 0.988	0.960 / 0.970	0.950 / 0.980

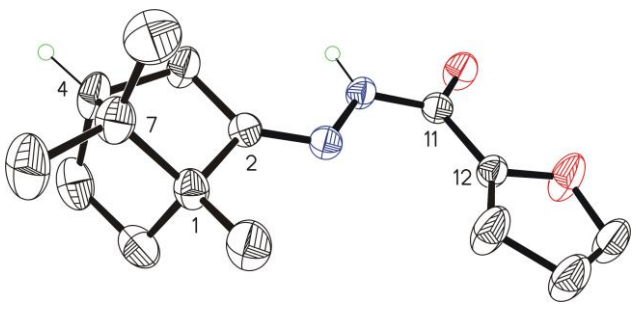
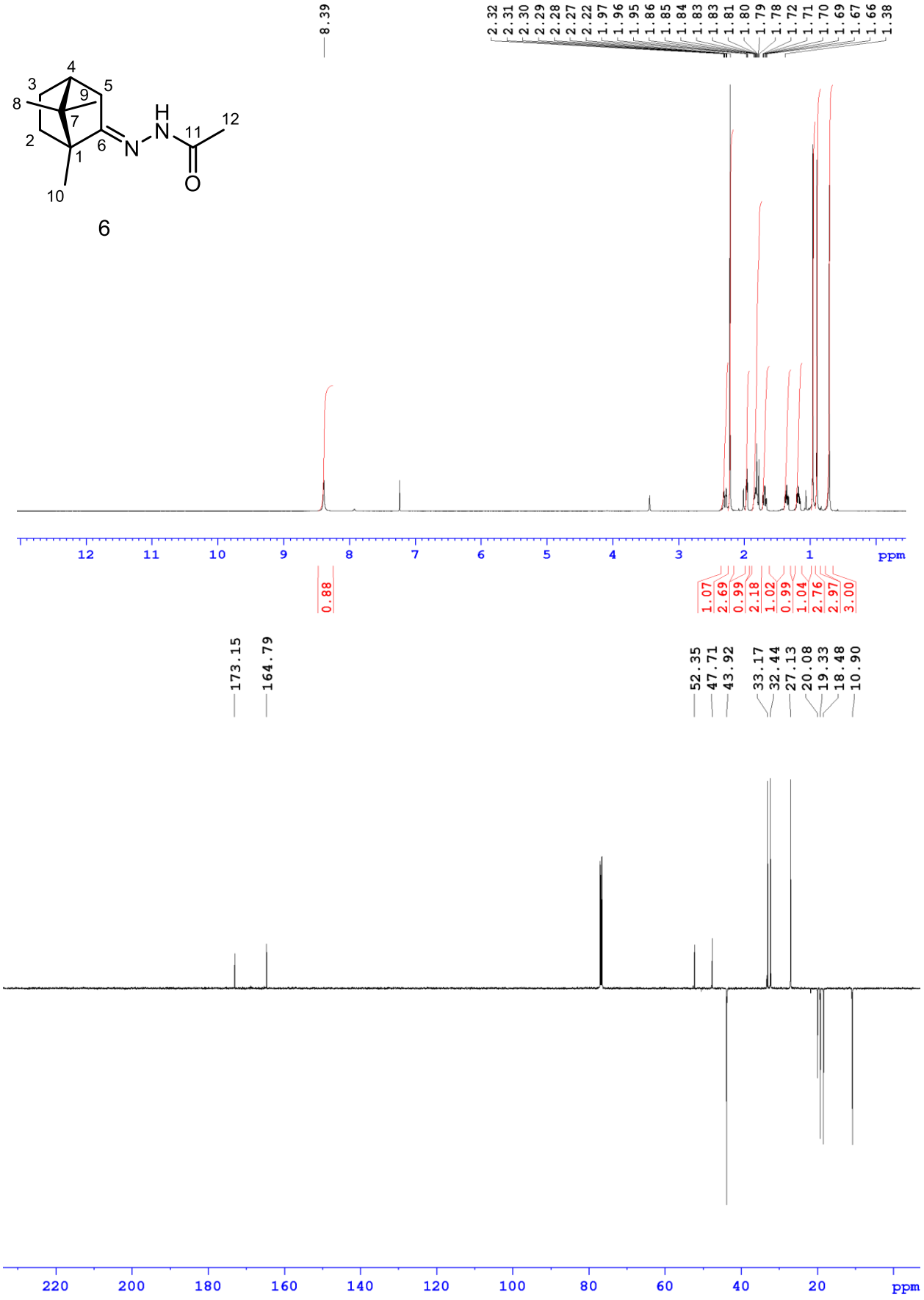


Figure S1. Molecular structure of **11**. Displacement ellipsoids are depicted at the 30% probability level. Only hydrogen atoms at the asymmetric center and at the amine group are presented.

2. Copies of the NMR Spectra for compounds 6-19.

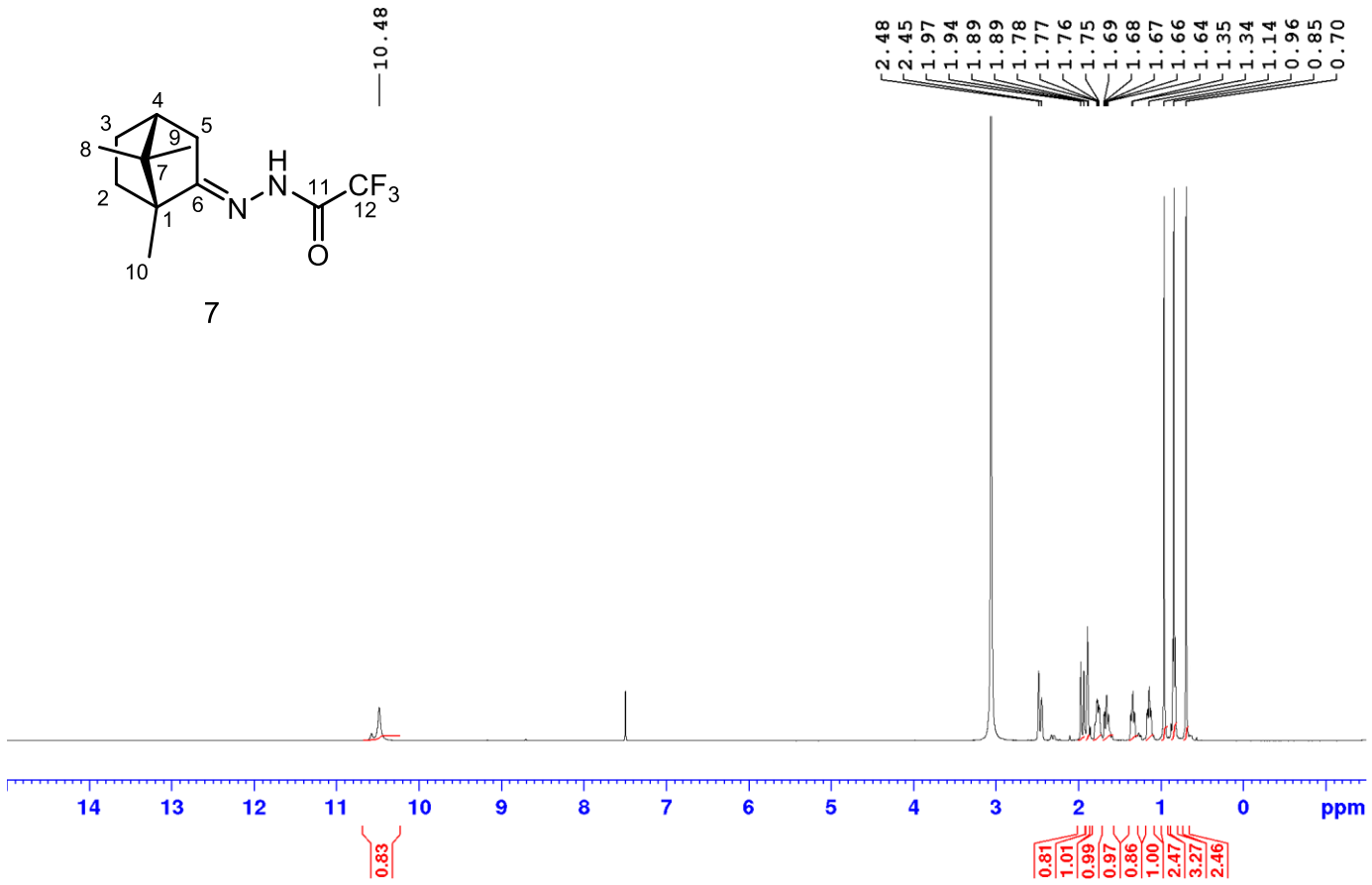
2.1. N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetohydrazide 6 ($CDCl_3$, 400.0 MHz)

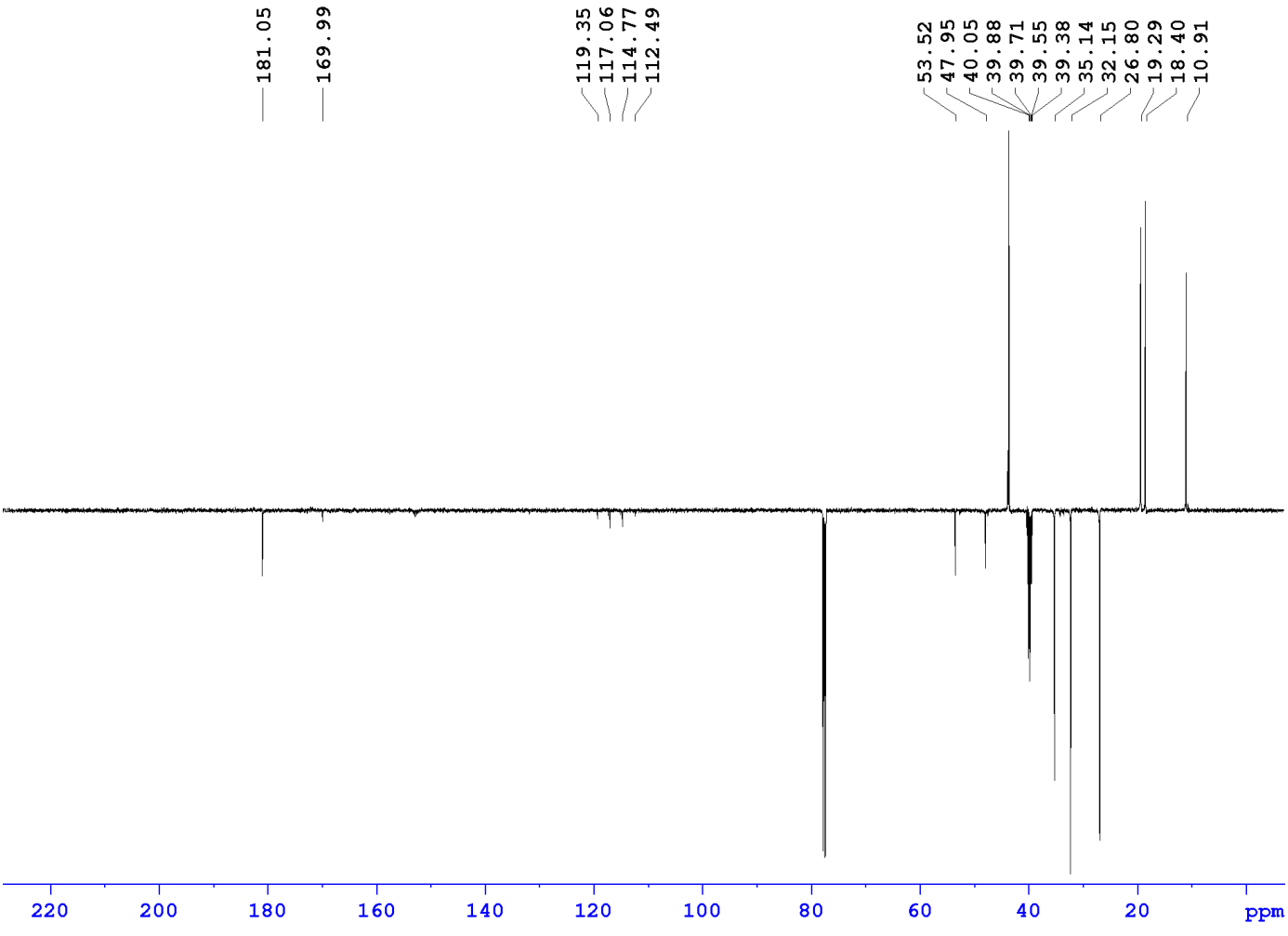
6



2.2. 2,2,2-trifluoro-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]acetohydrazide 7 ($CDCl_3$+DMSO-d6, 400.0 MHz)

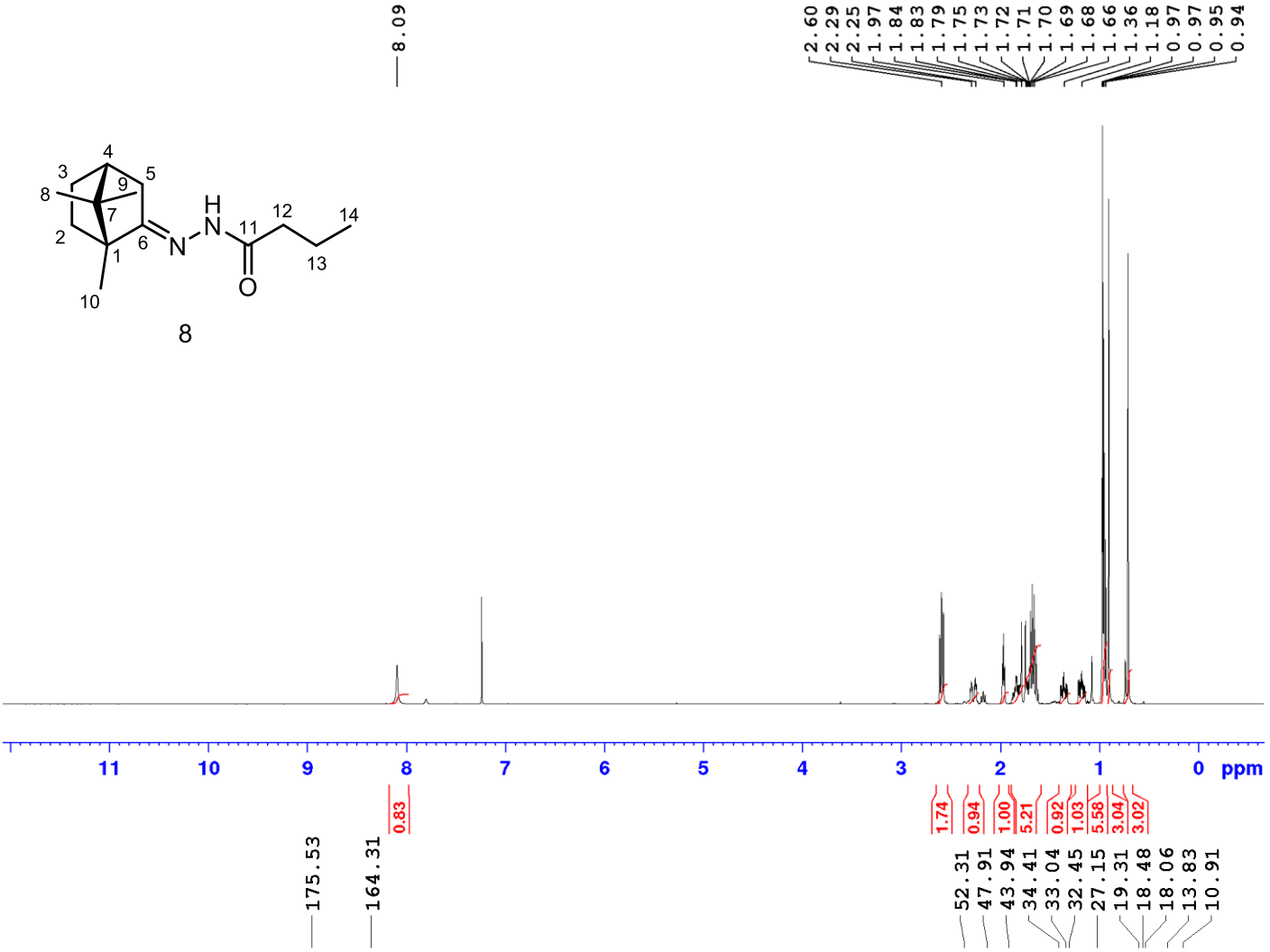
7

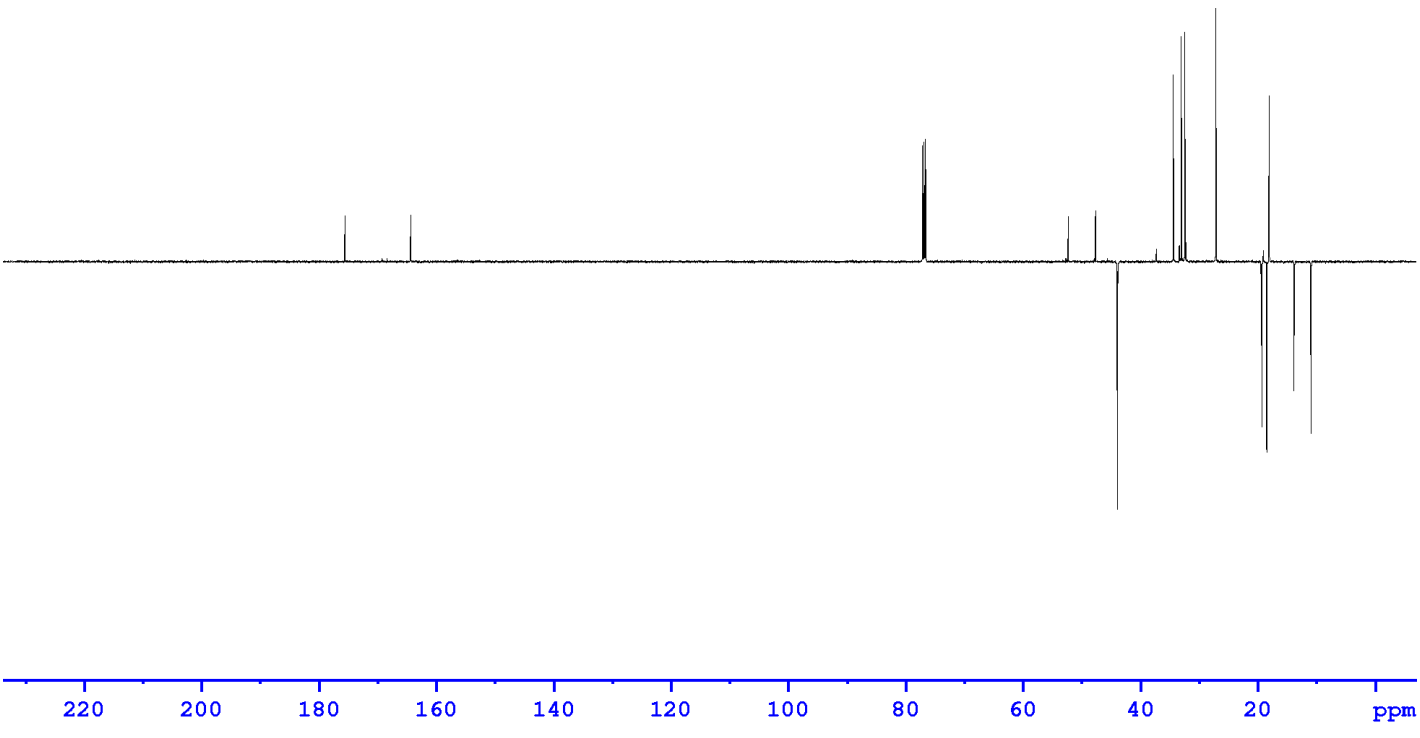




2.3. N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]butanohydrazide 8 ($CDCl_3$, 400.0 MHz)

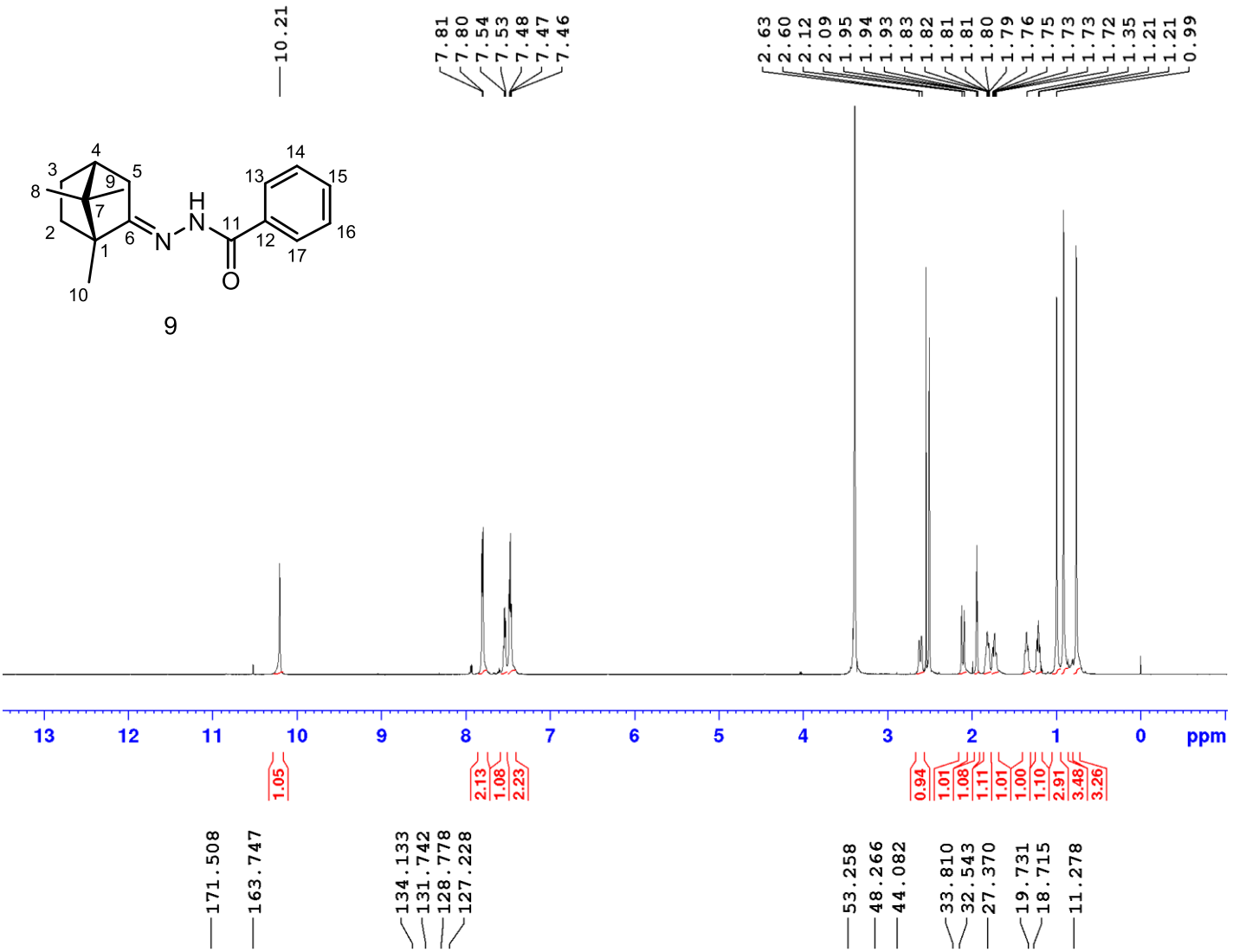
8

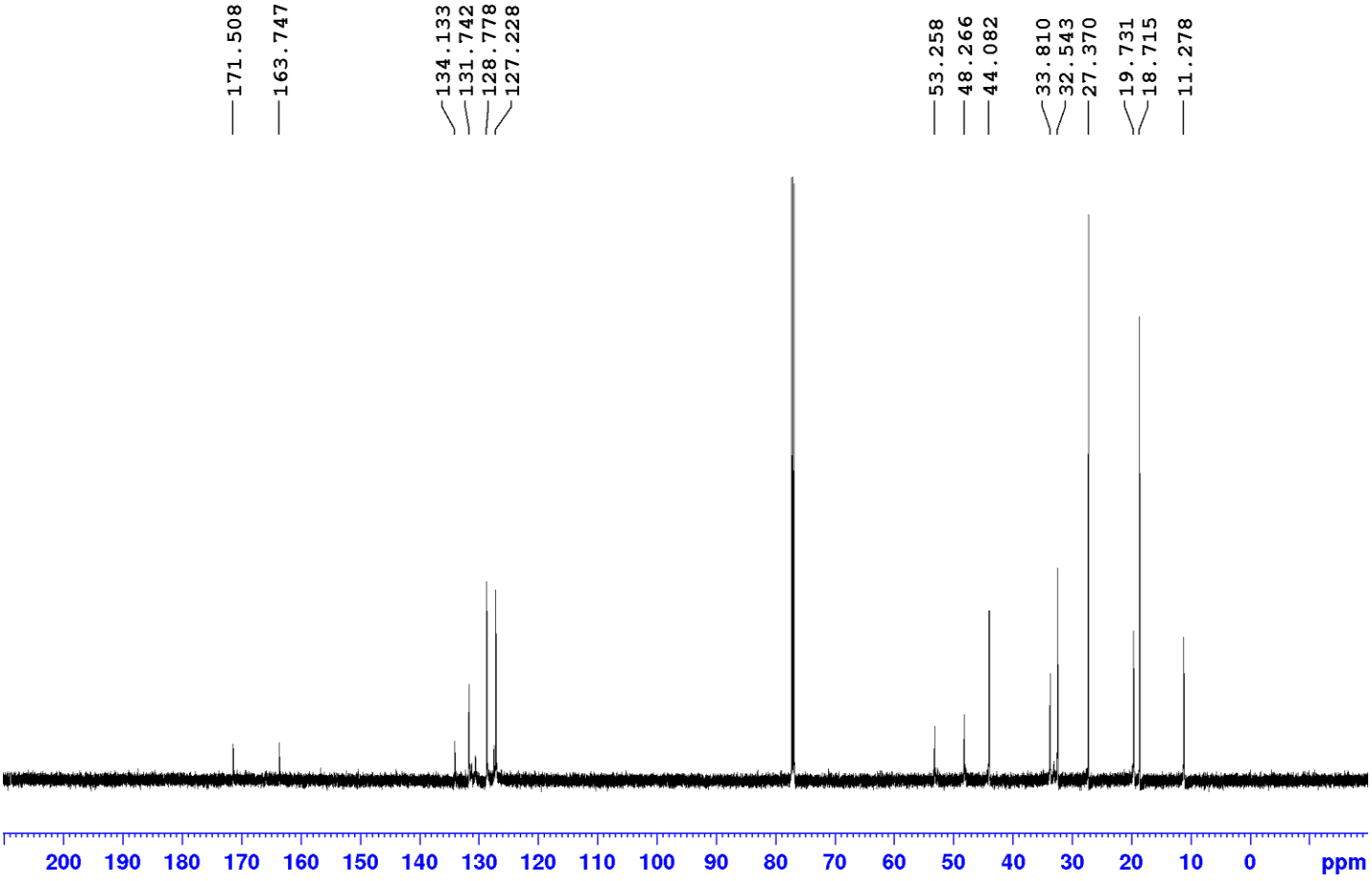




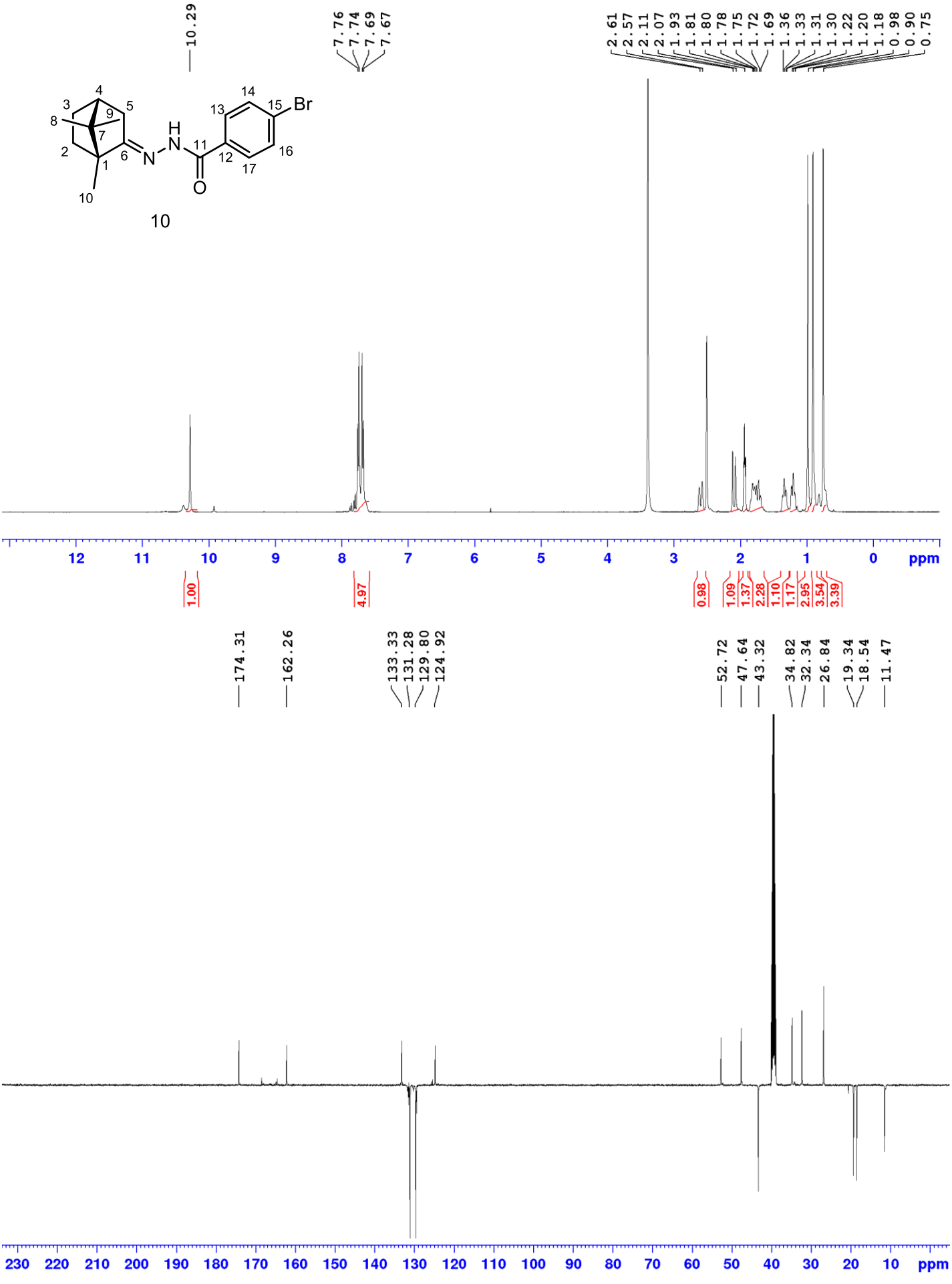
2.4. N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]benzohydrazide 9 (DMSO-d6, 400.0 MHz)

9

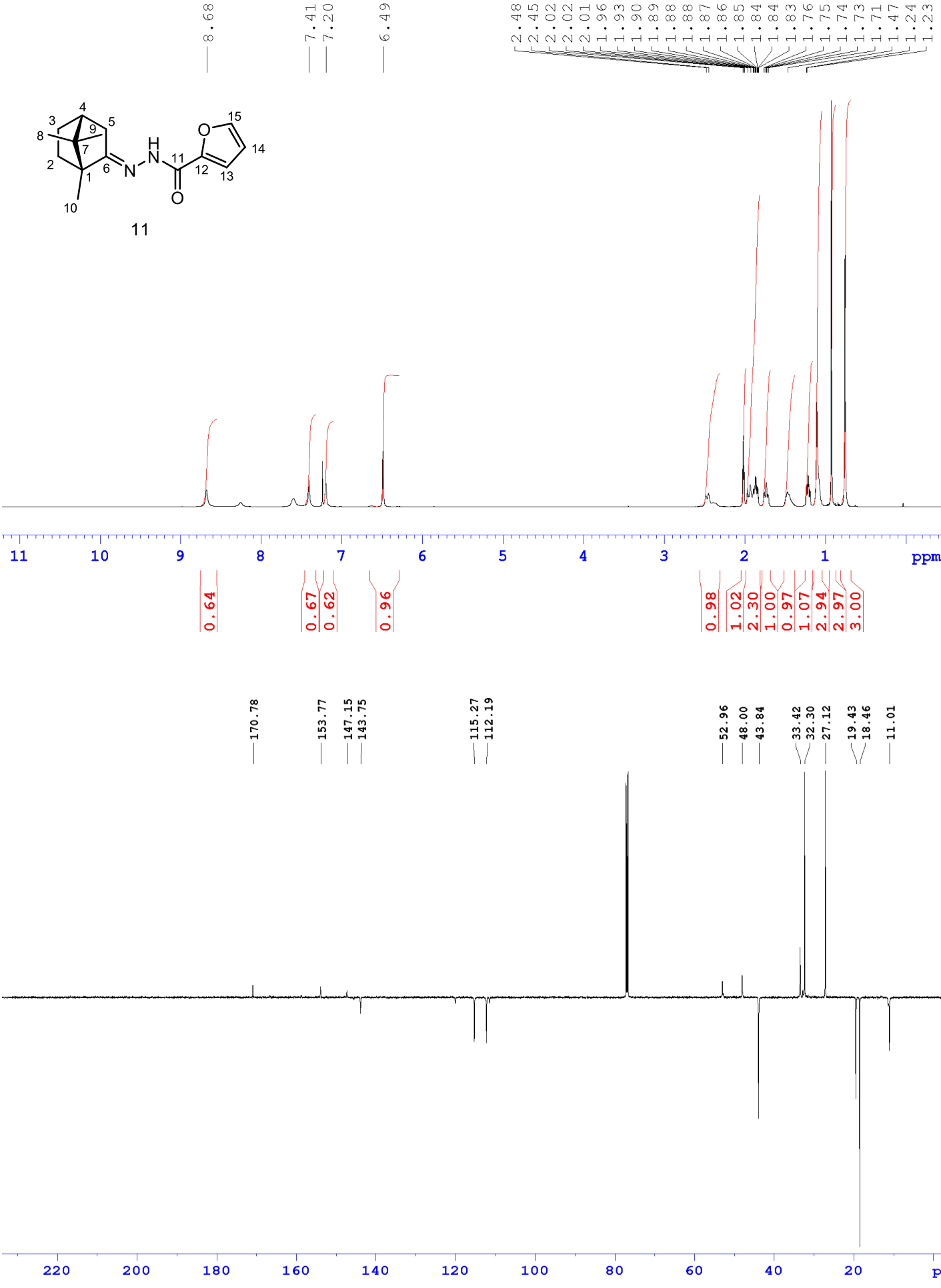




2.5. 4-bromo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]benzohydrazide 10 (DMSO-d6, 400.0 MHz)

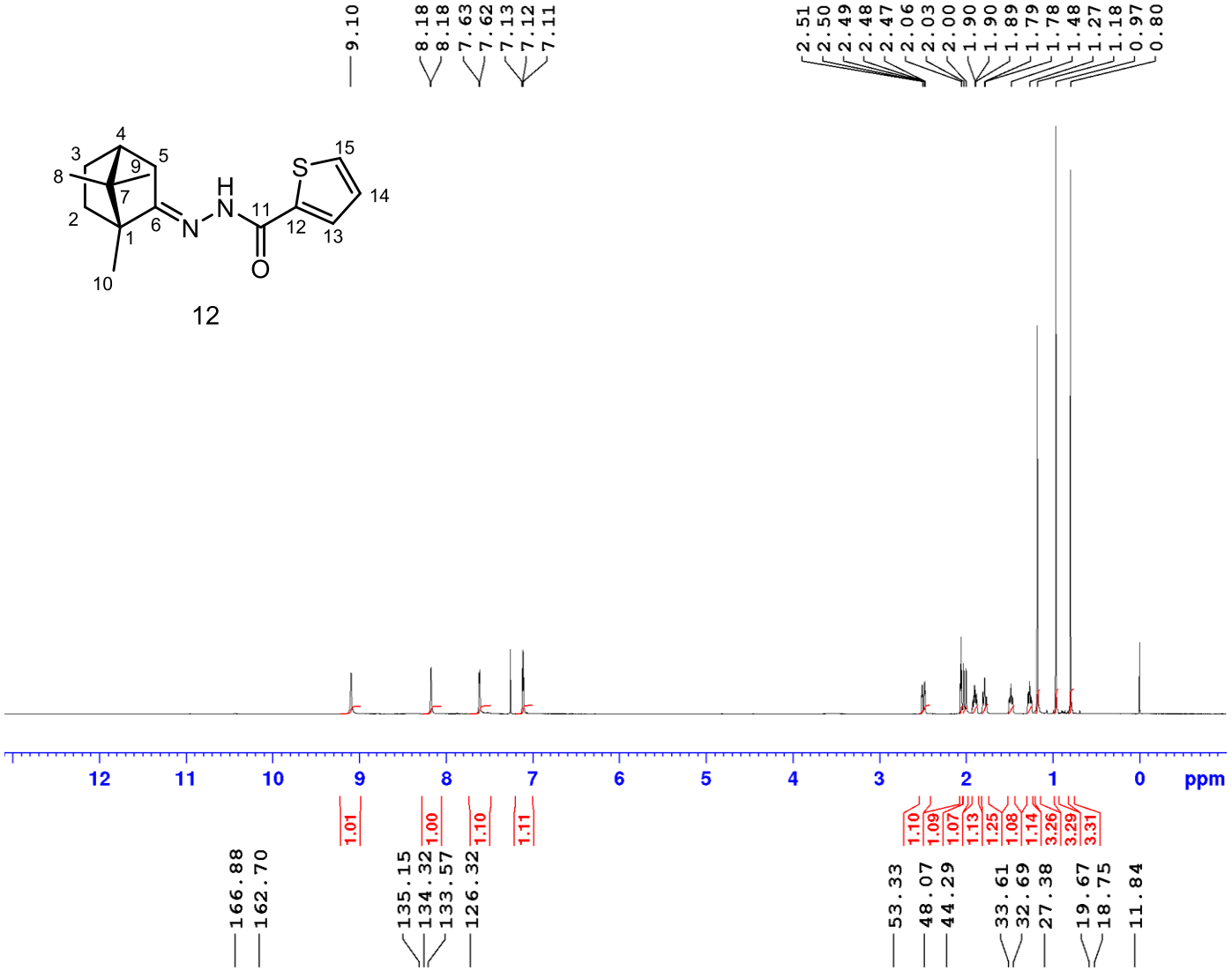


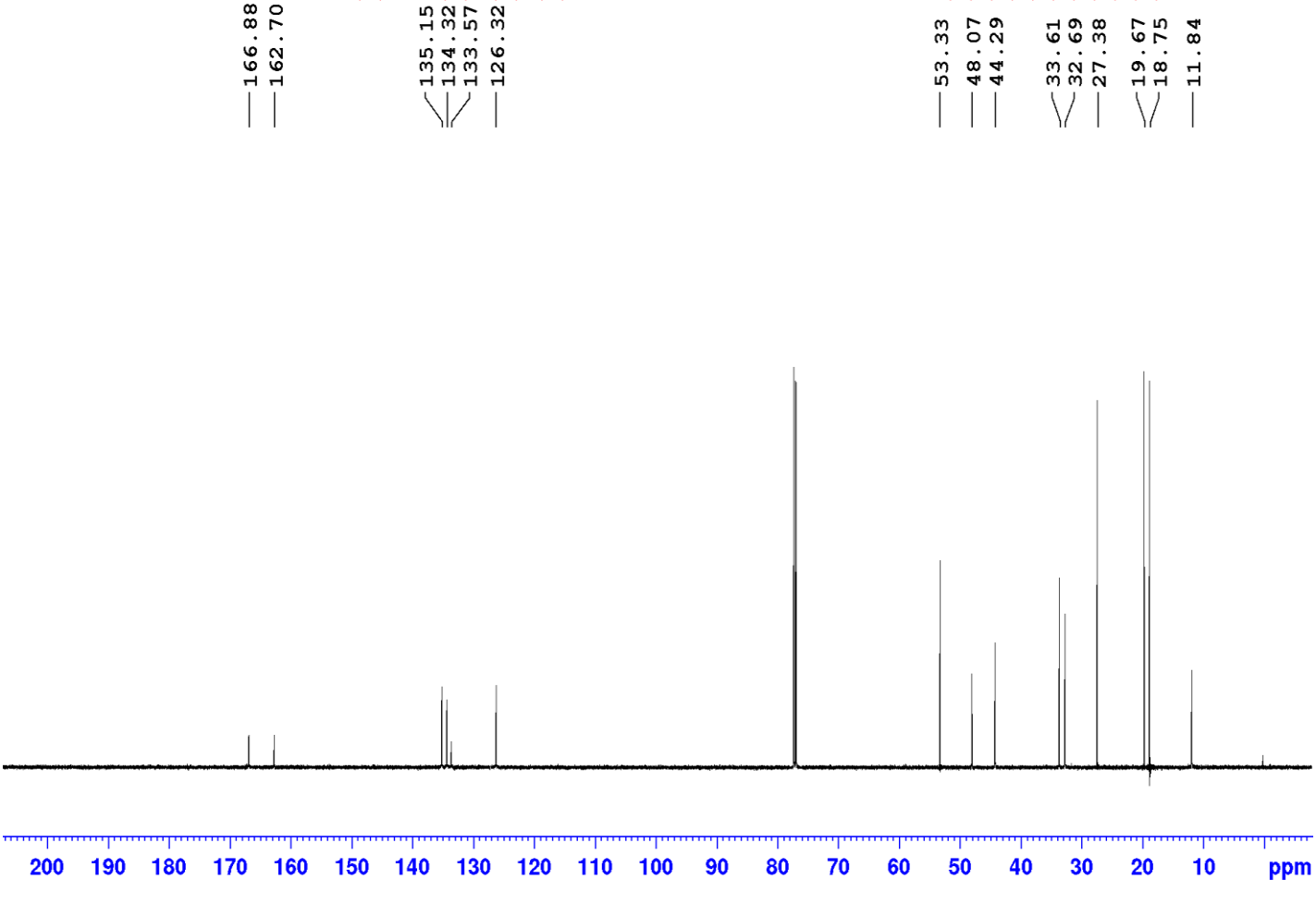
2.6. N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2-furohydrazide 11 ($CDCl_3$, 400.0 MHz)



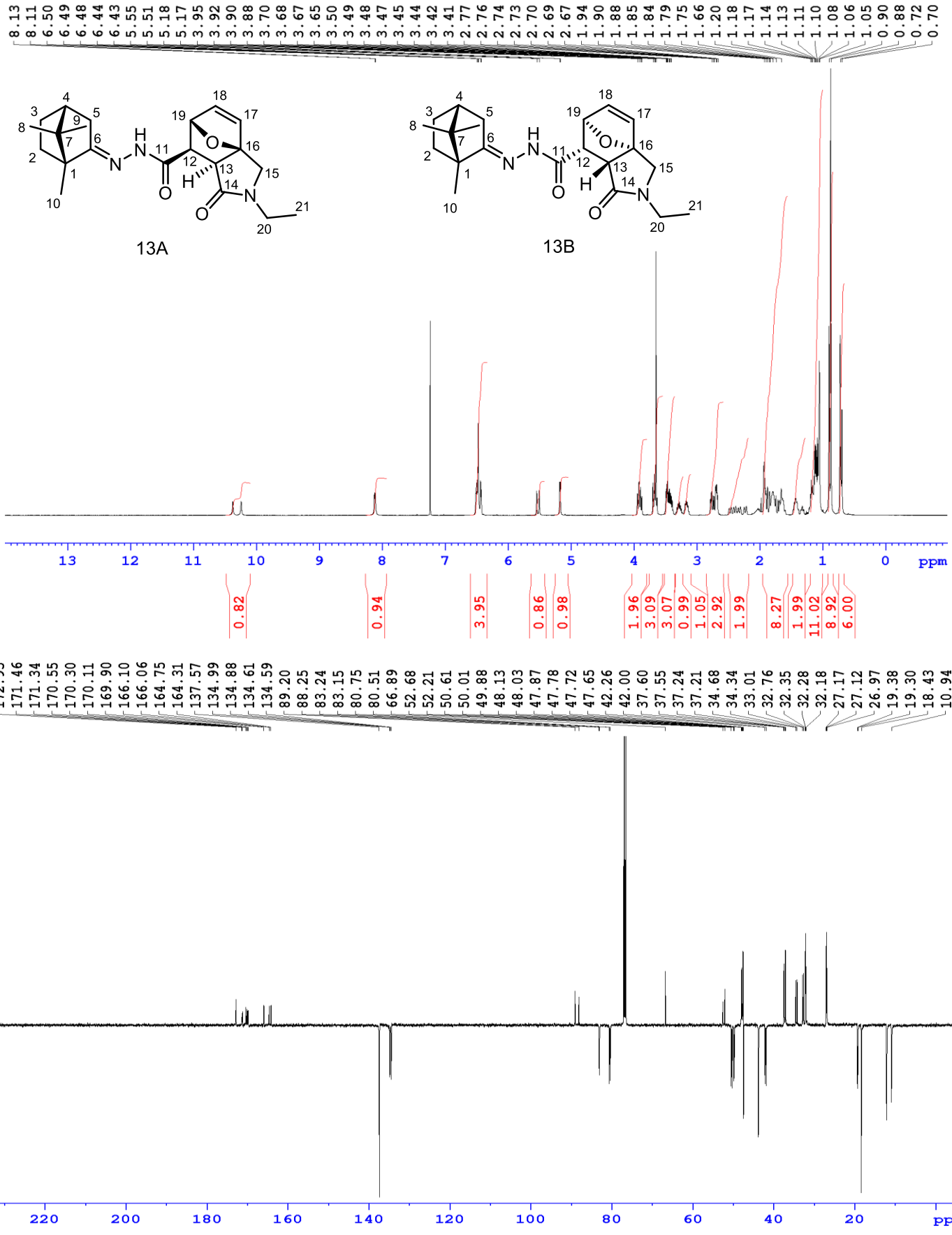
2.7. N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]thiophene-2-carbohydrazide 12 ($CDCl_3$, 400.0 MHz)

12

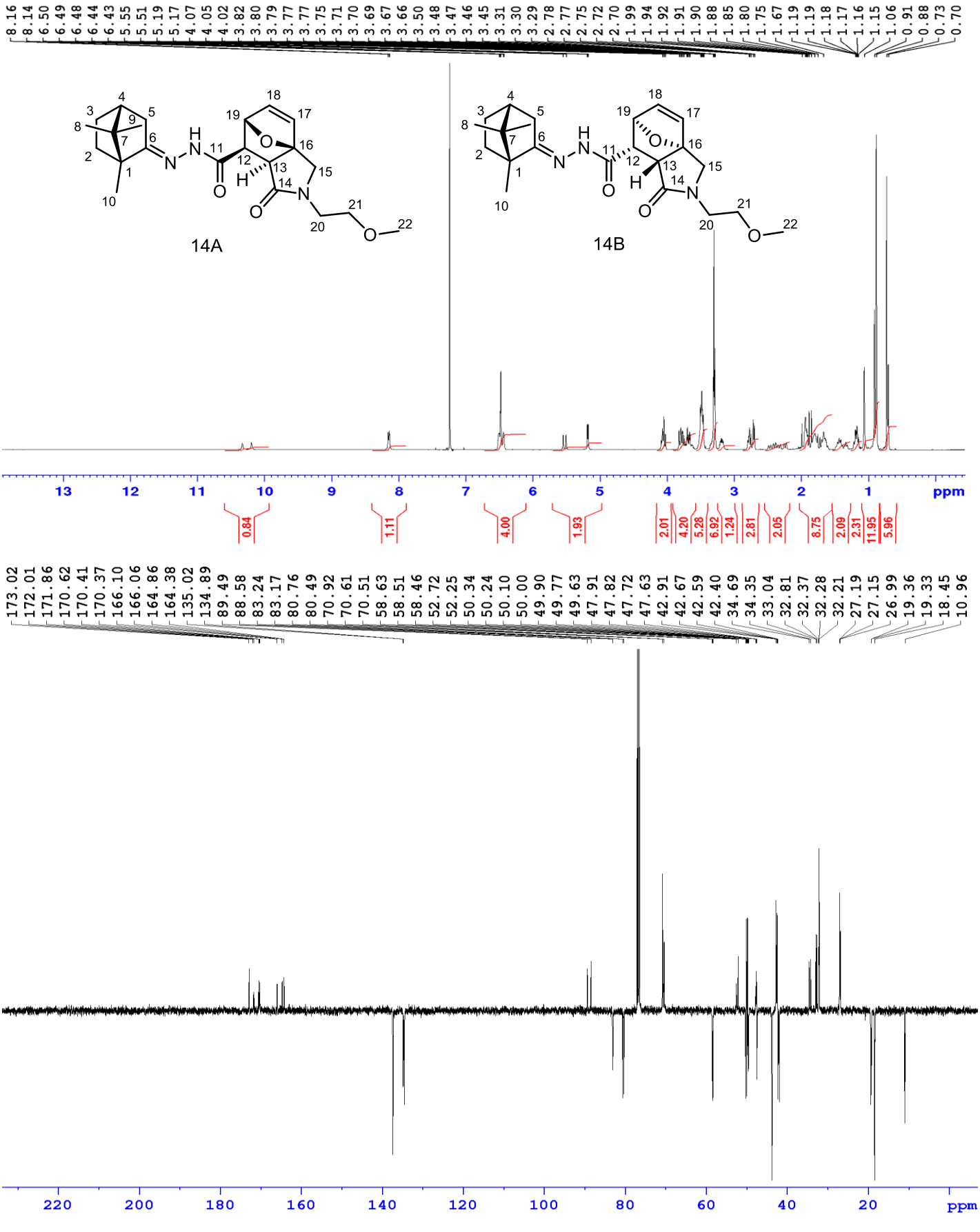




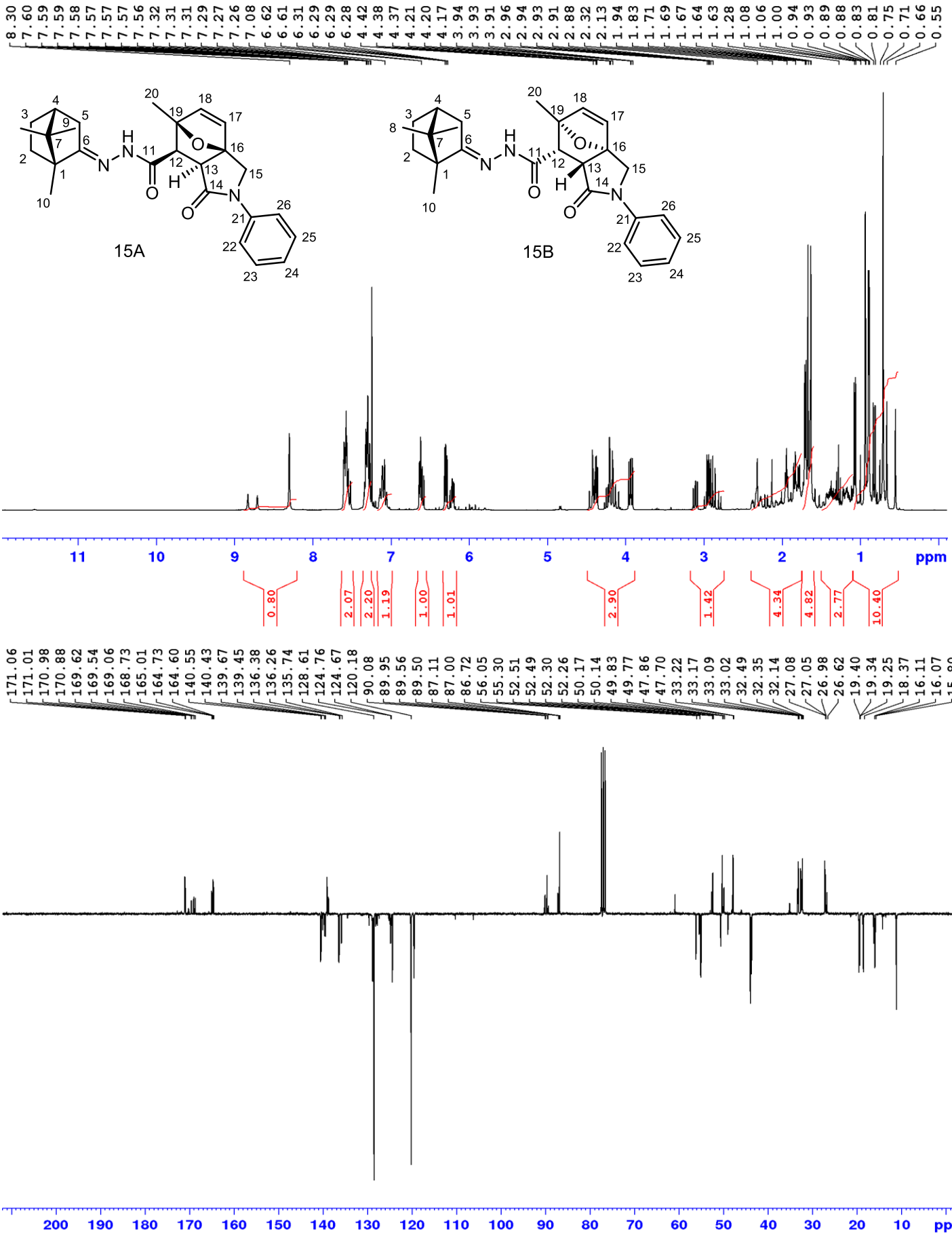
2.8. A mixture of (3aR,6S,7R,7aS)-2-ethyl-1-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (A) and (3aS,6R,7S,7aR)-2-ethyl-1-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (B) 13 ($CDCl_3$, 400.0 MHz)



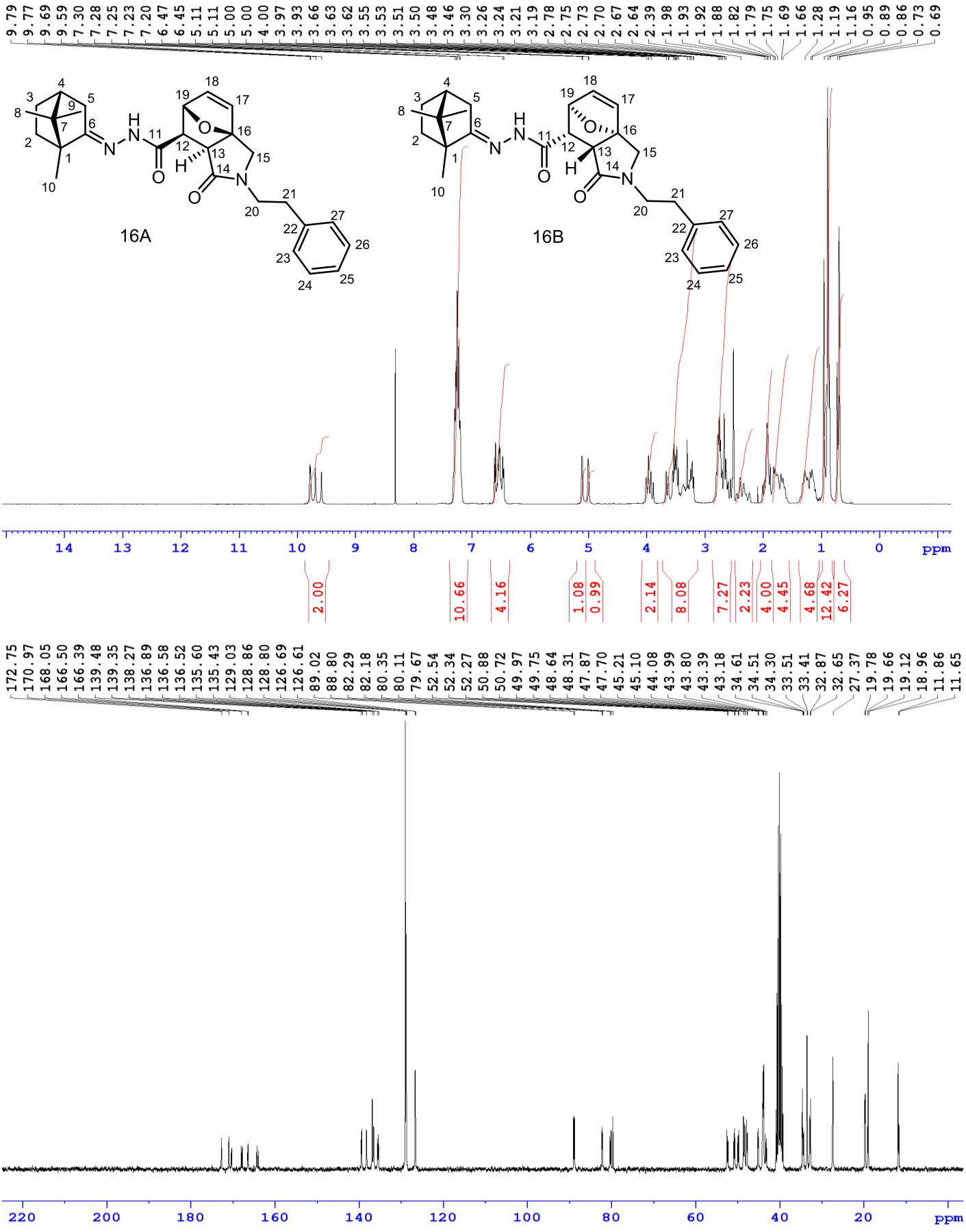
2.9. A mixture of (3aR,6S,7R,7aS)-2-(2-methoxyethyl)-1-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (A) and (3aS,6R,7S,7aR)-2-(2-methoxyethyl)-1-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (B) 14 ($CDCl_3$, 400.0 MHz)



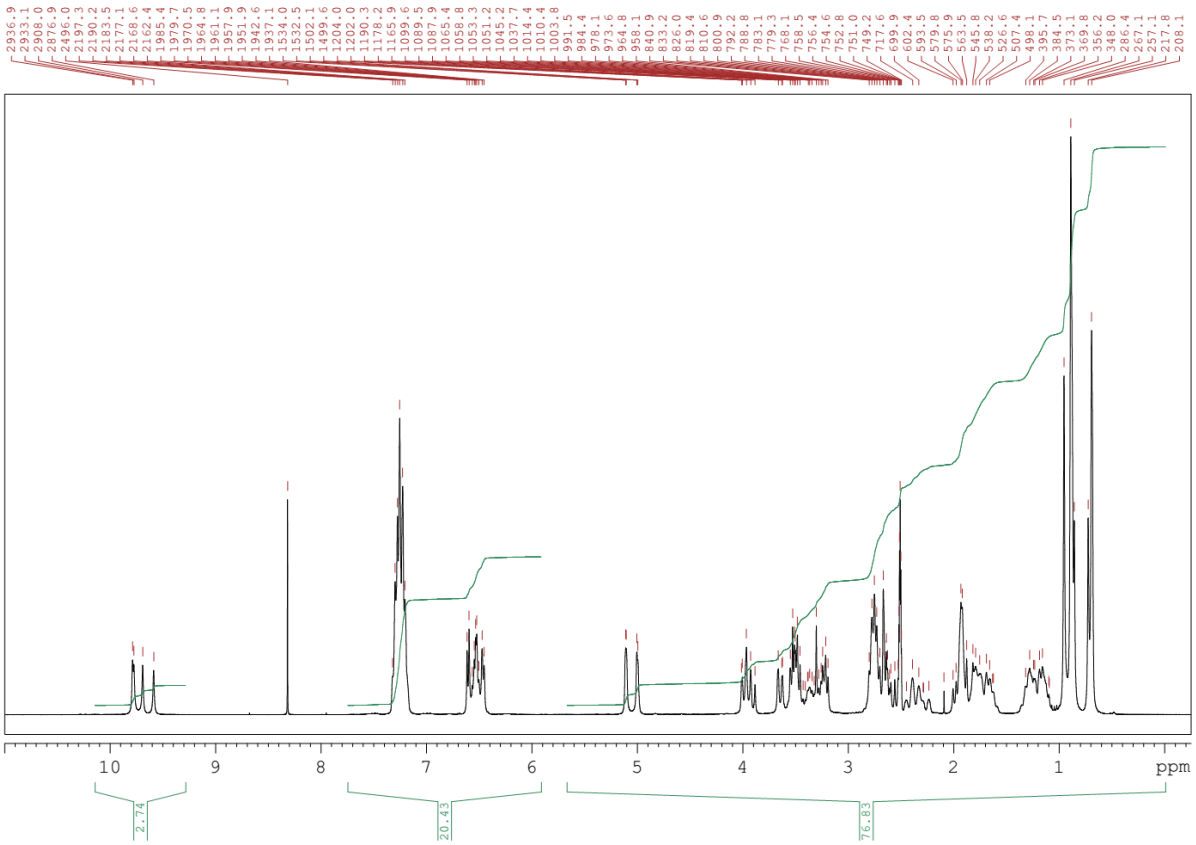
2.10. A mixture of (3aR,6S,7R,7aS)-6-methyl-1-oxo-2-phenyl-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (A) and (3aS,6R,7S,7aR)-6-methyl-1-oxo-2-phenyl-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (B) 15 ($CDCl_3$, 400.0 MHz)



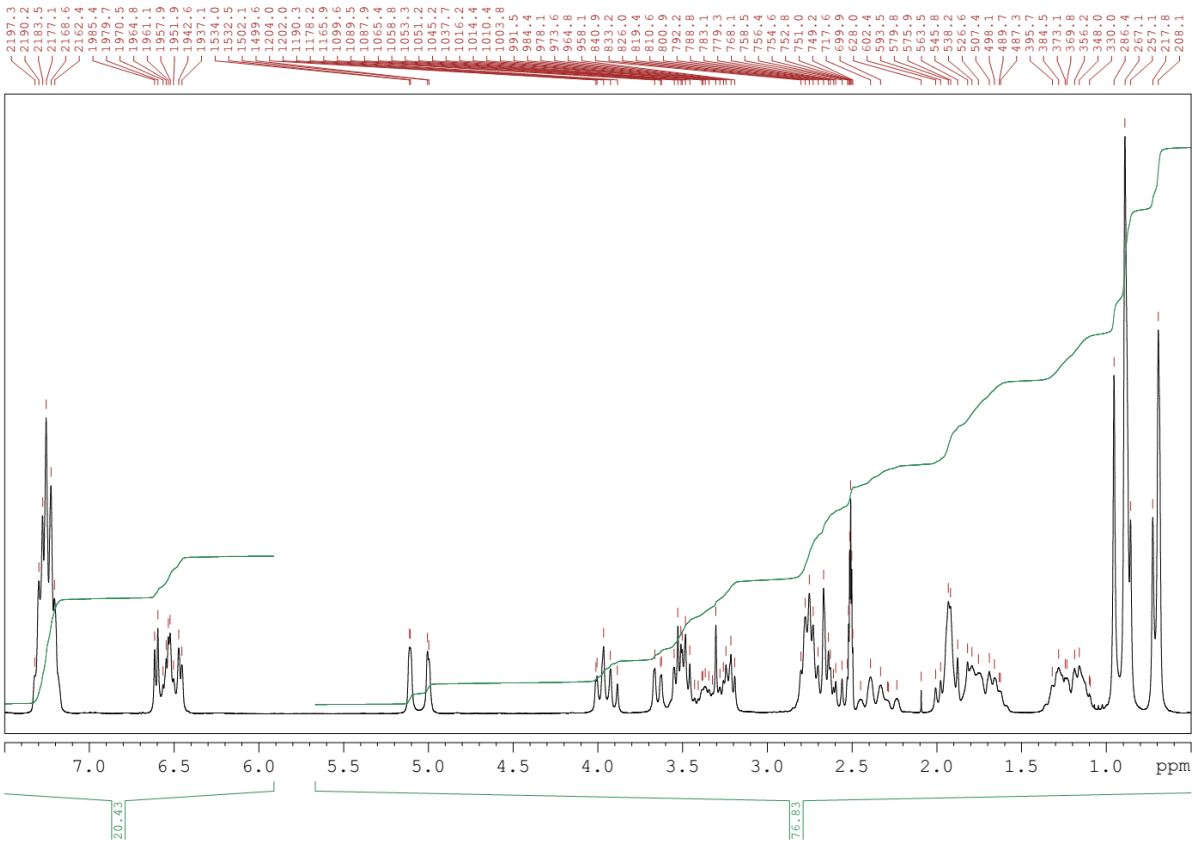
2.11. A mixture of (3aR,6S,7R,7aS)-1-oxo-2-(2-phenylethyl)-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (A) and (3aS,6R,7S,7aR)-1-oxo-2-(2-phenylethyl)-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (B) 16 (DMSO-d6, 400.0 MHz)



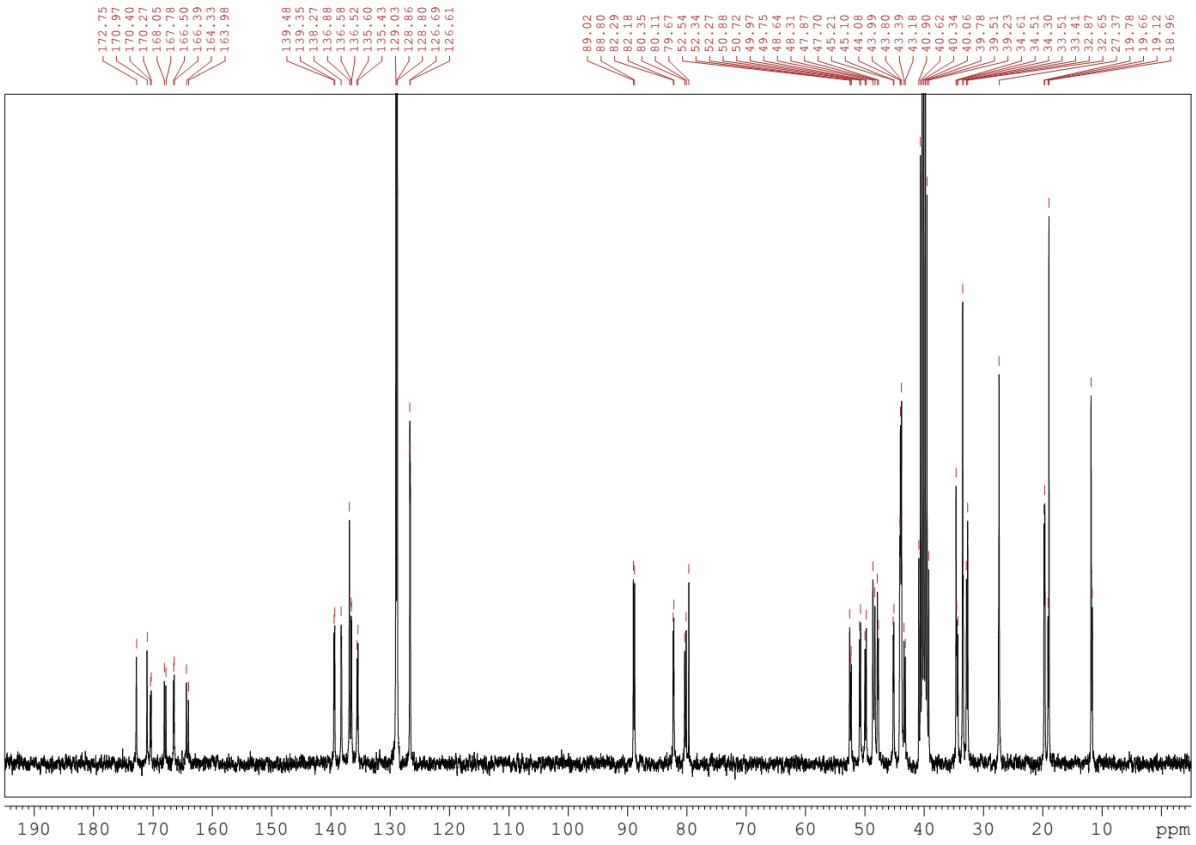
^{1}H NMR (DMSO-d_6, 300.1 MHz)



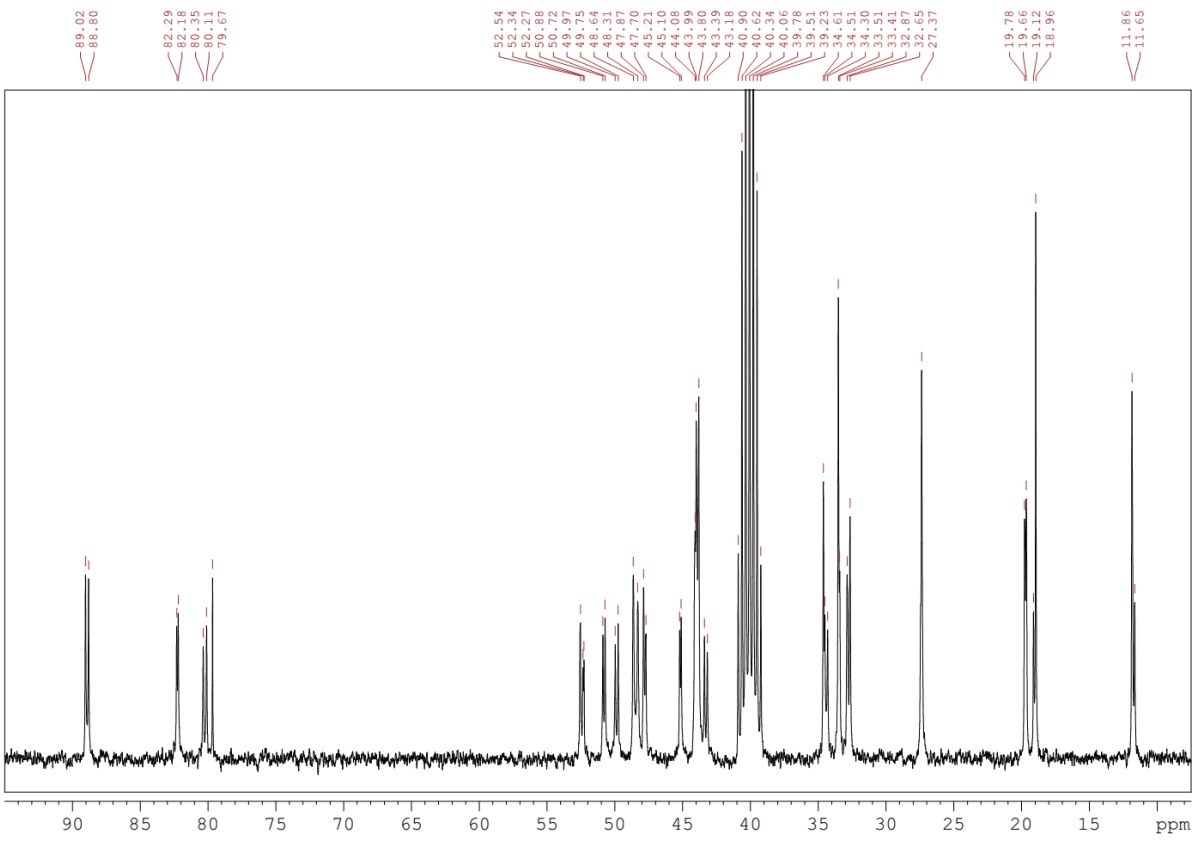
^{1}H NMR (DMSO-d_6, 300.1 MHz)



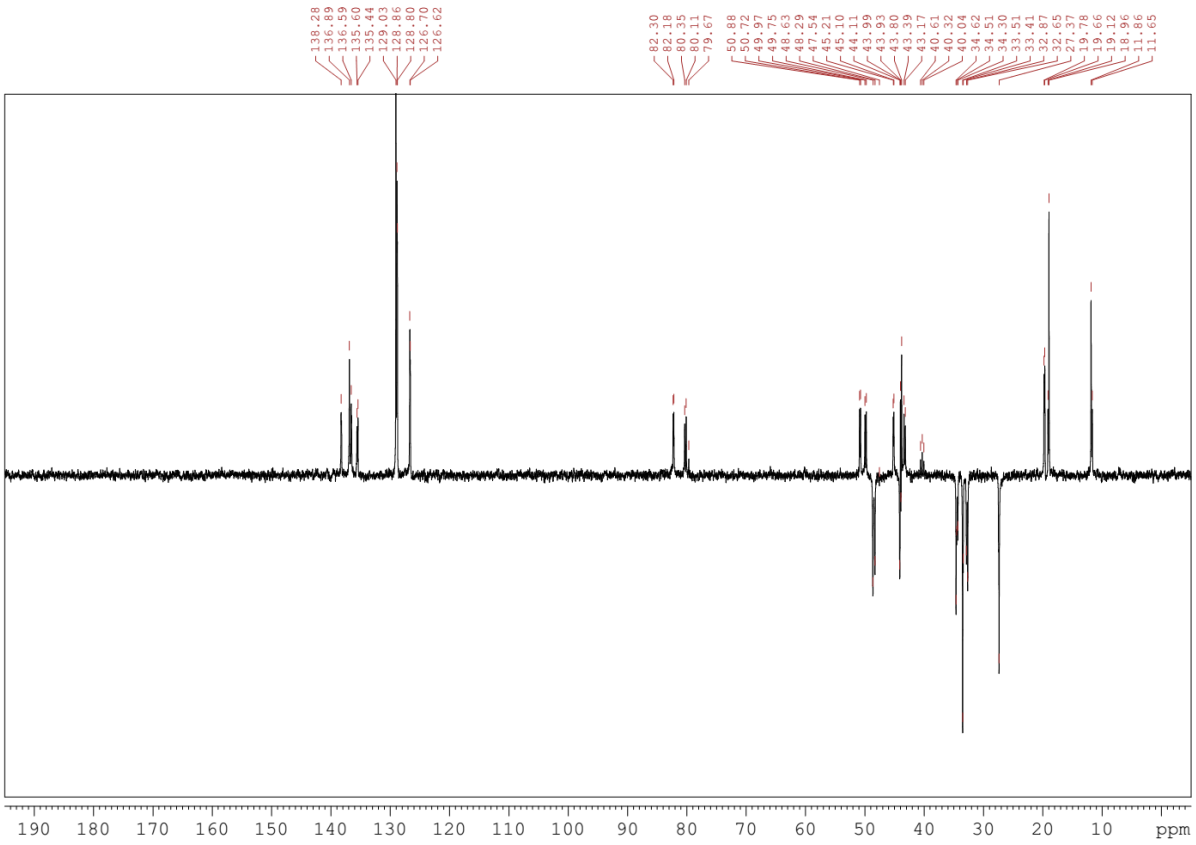
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



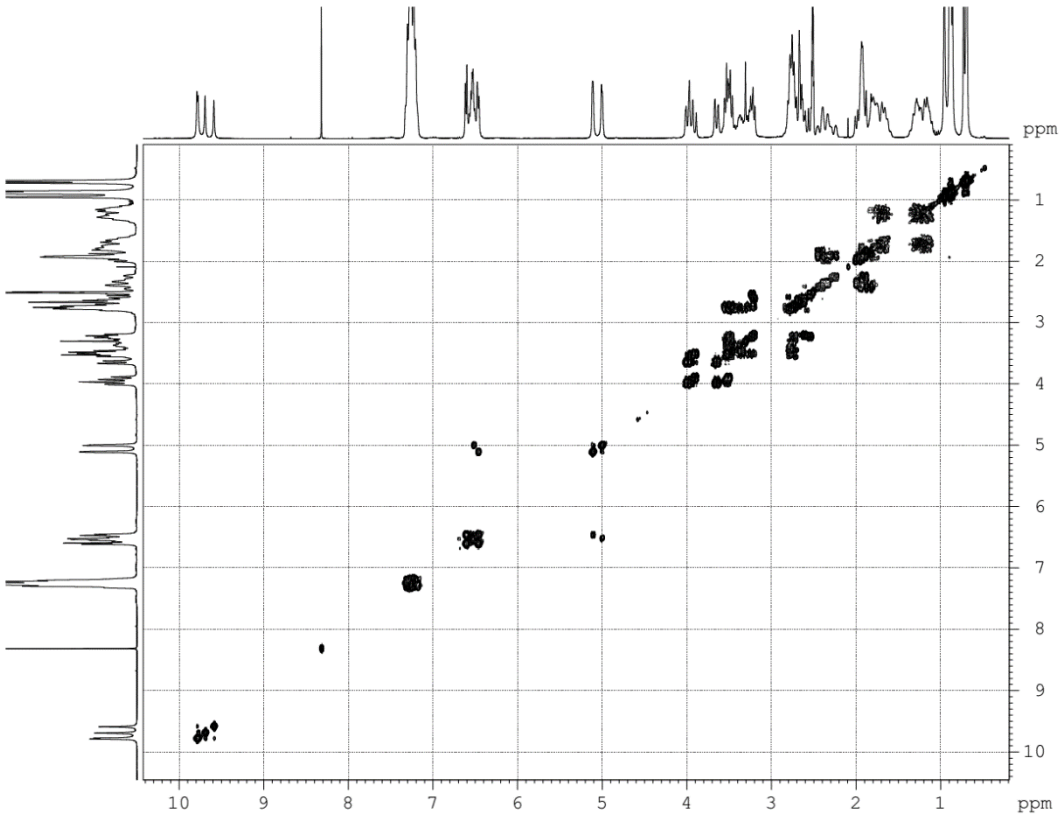
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



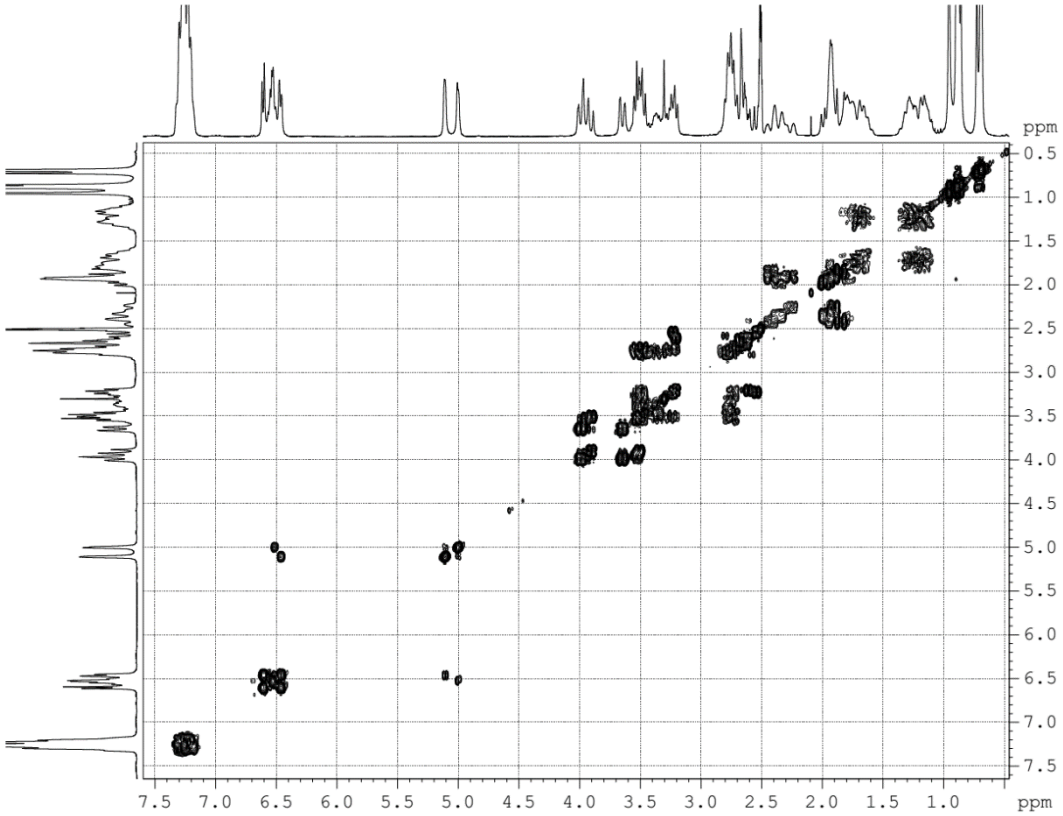
DEPT-135 NMR (DMSO-d_6, 75.5 MHz)



2D ^{1}H,^{1}H-COSY (DMSO-d_6, 300.1 MHz)



2D ^{1}H,^{1}H-COSY (DMSO-d_6, 300.1 MHz)



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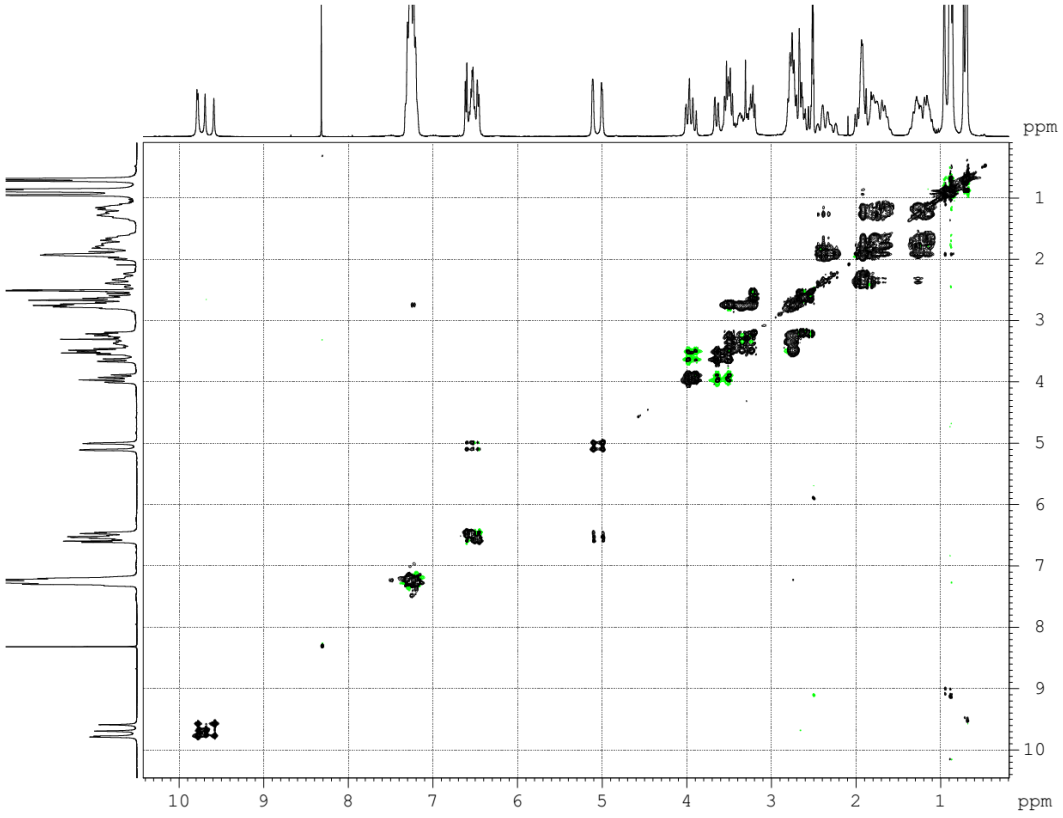
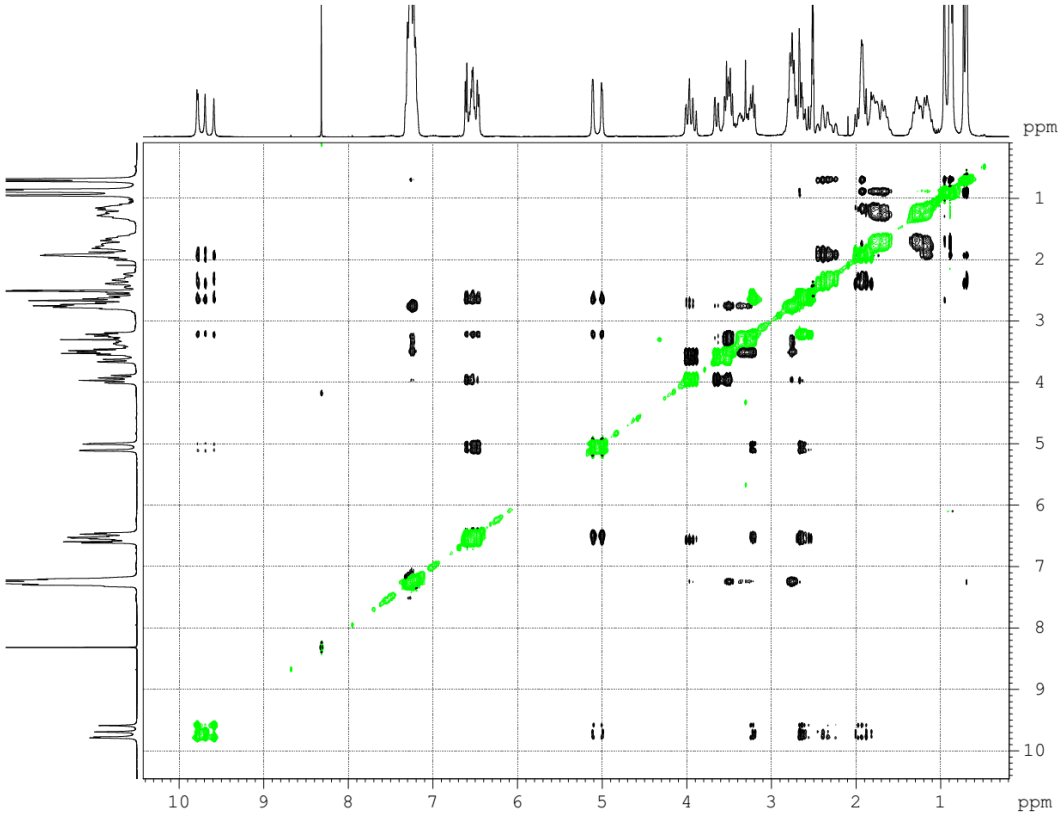


2D ^{1}H,^{1}H-NOESY (DMSO-d_6, 300.1 MHz)



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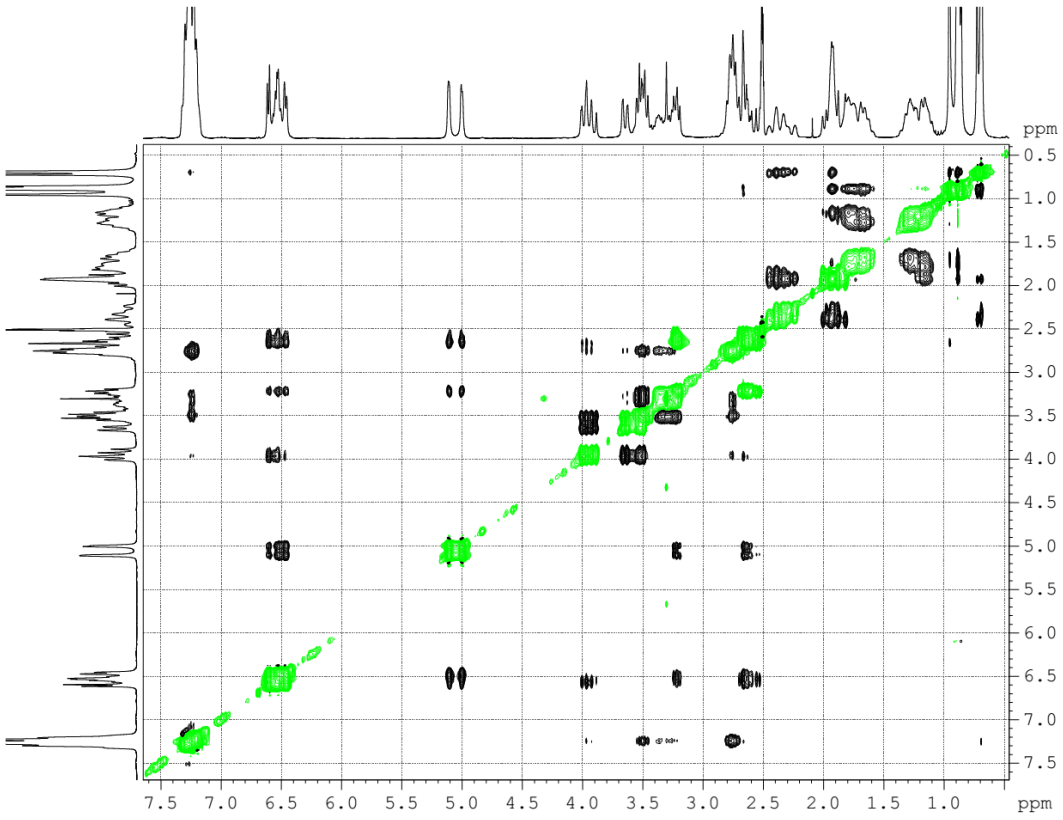

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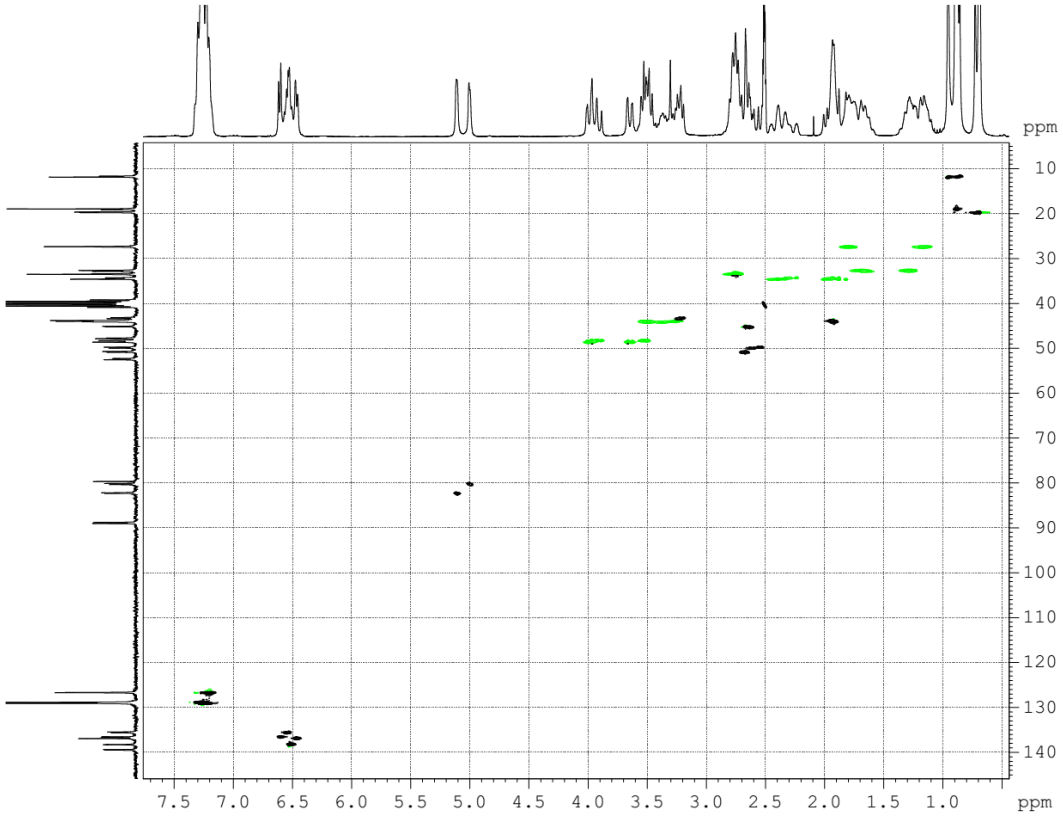
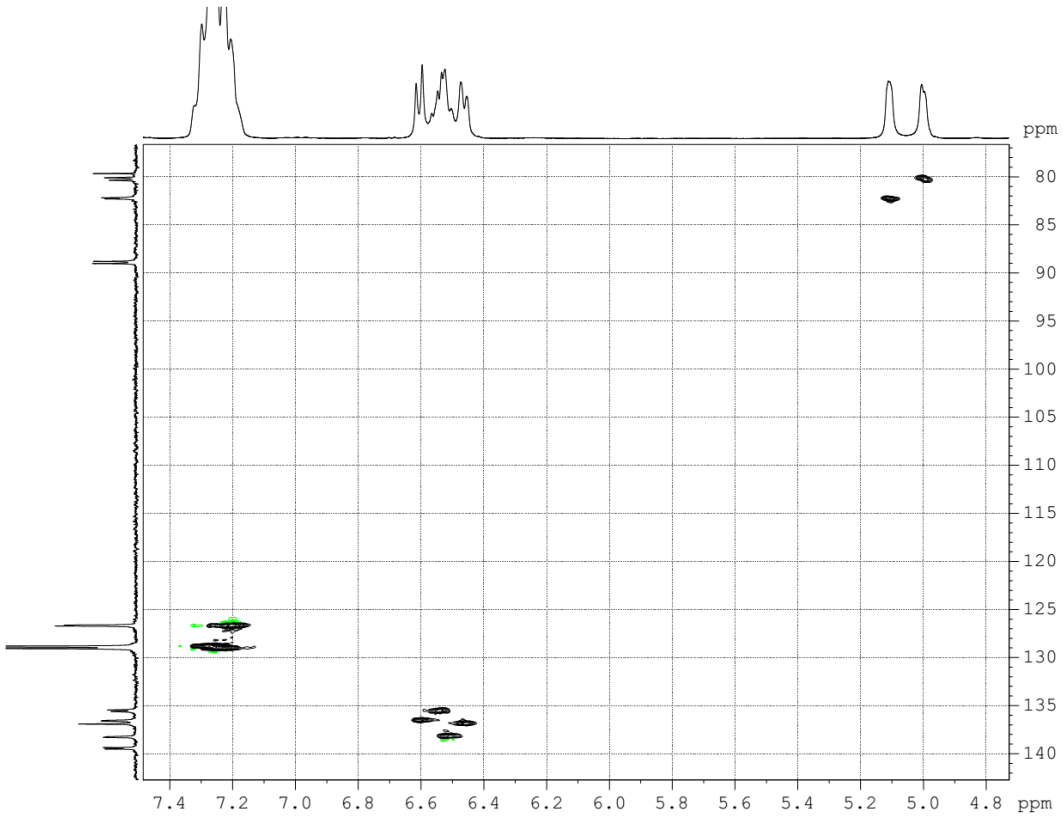
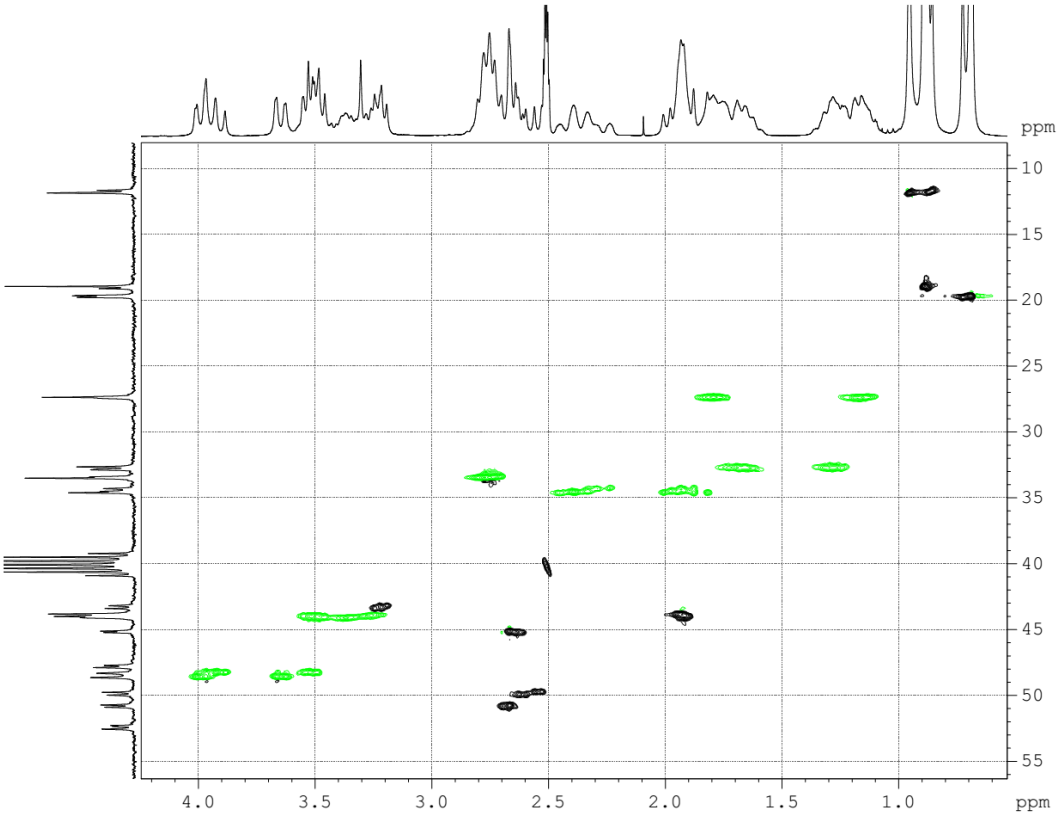


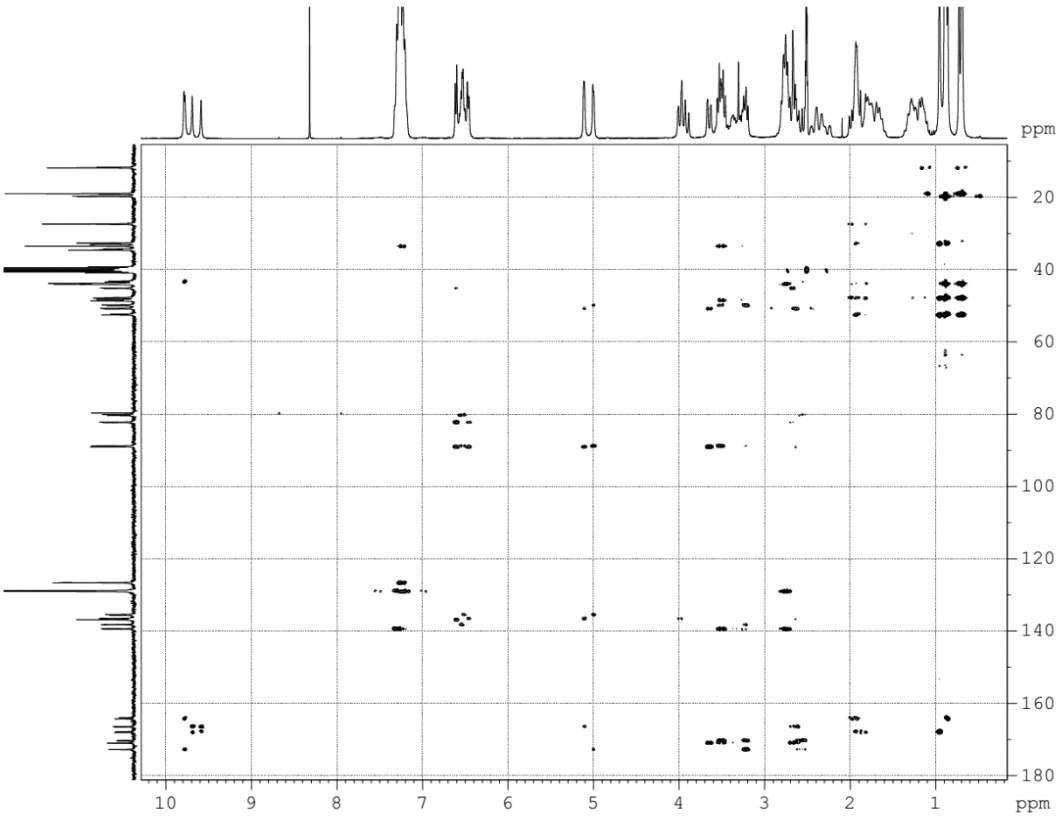
2D $^{1}H,^{13}C$-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



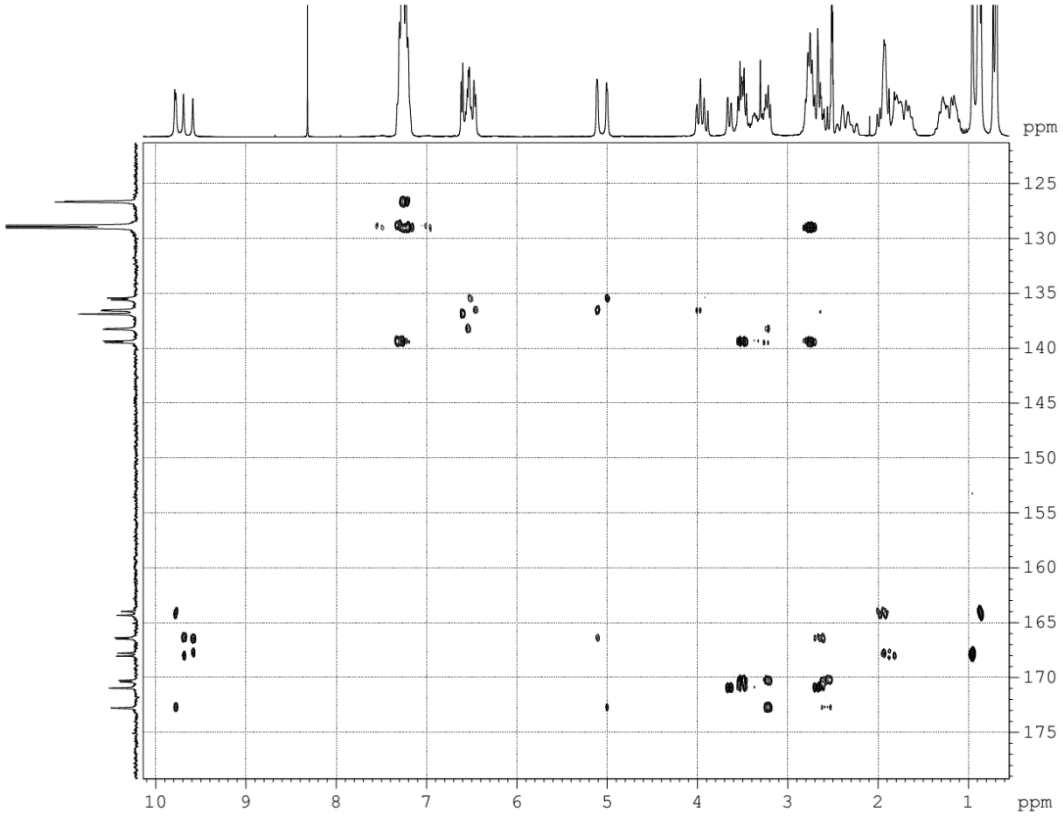
2D $^{1}H,^{13}C$-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



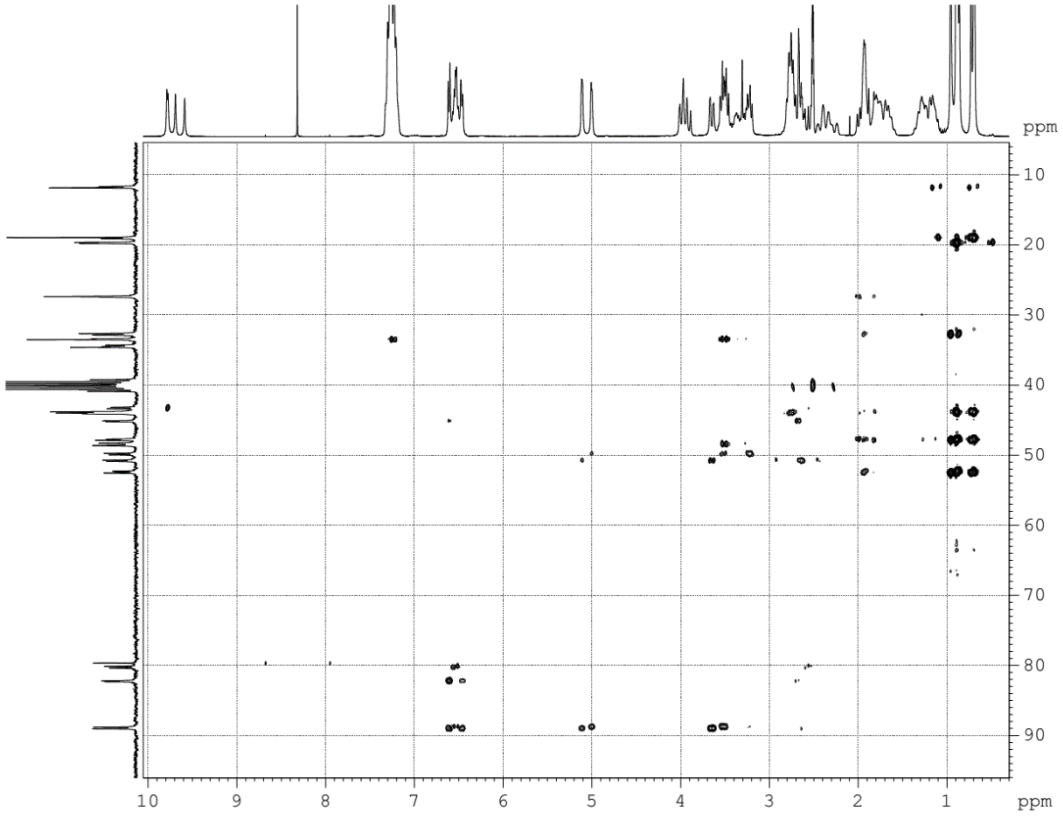
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



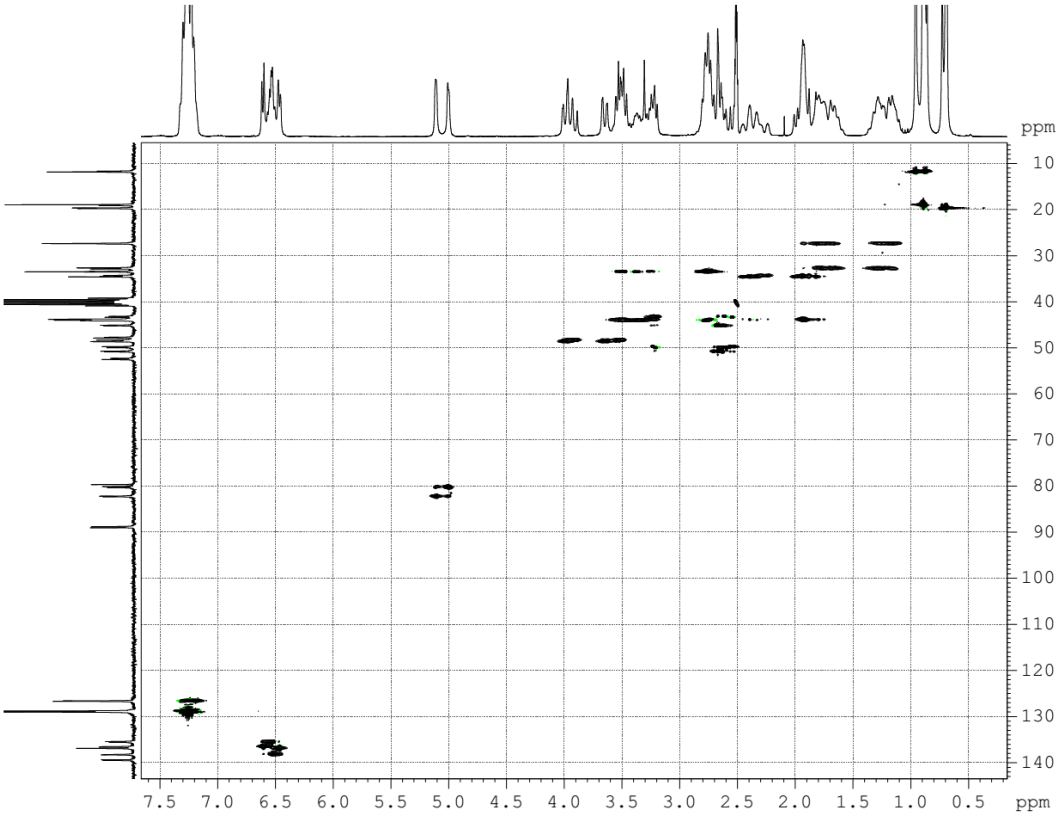
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



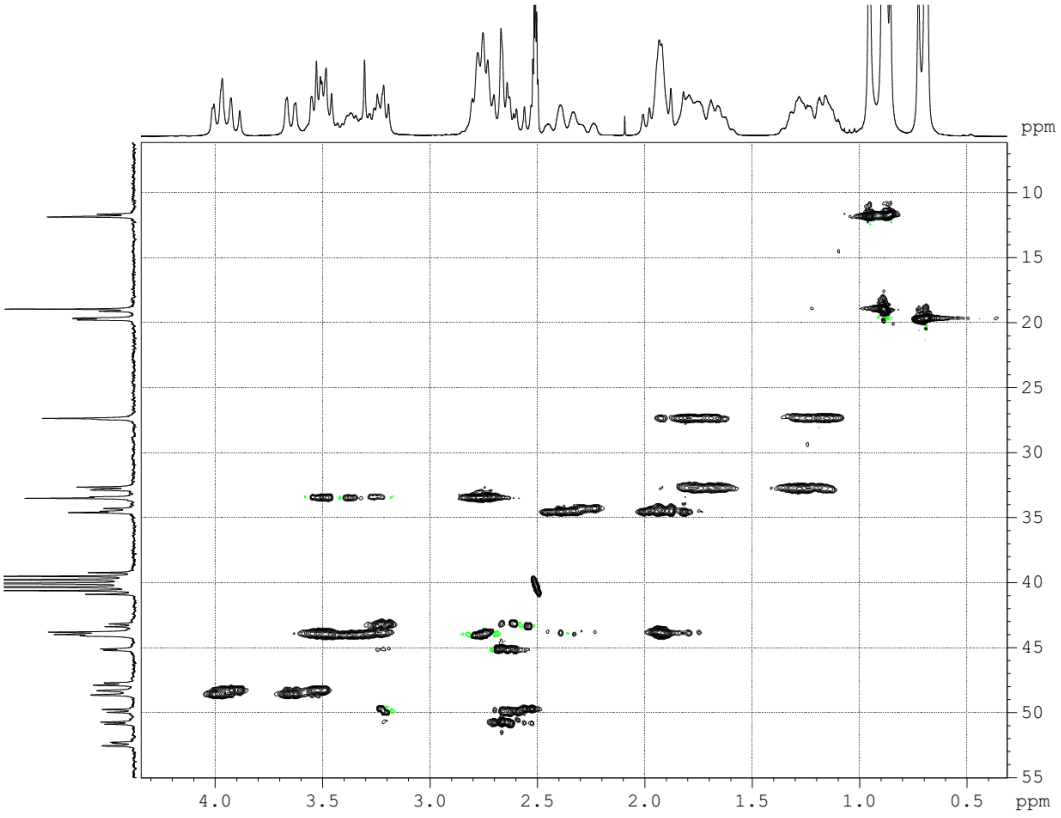
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



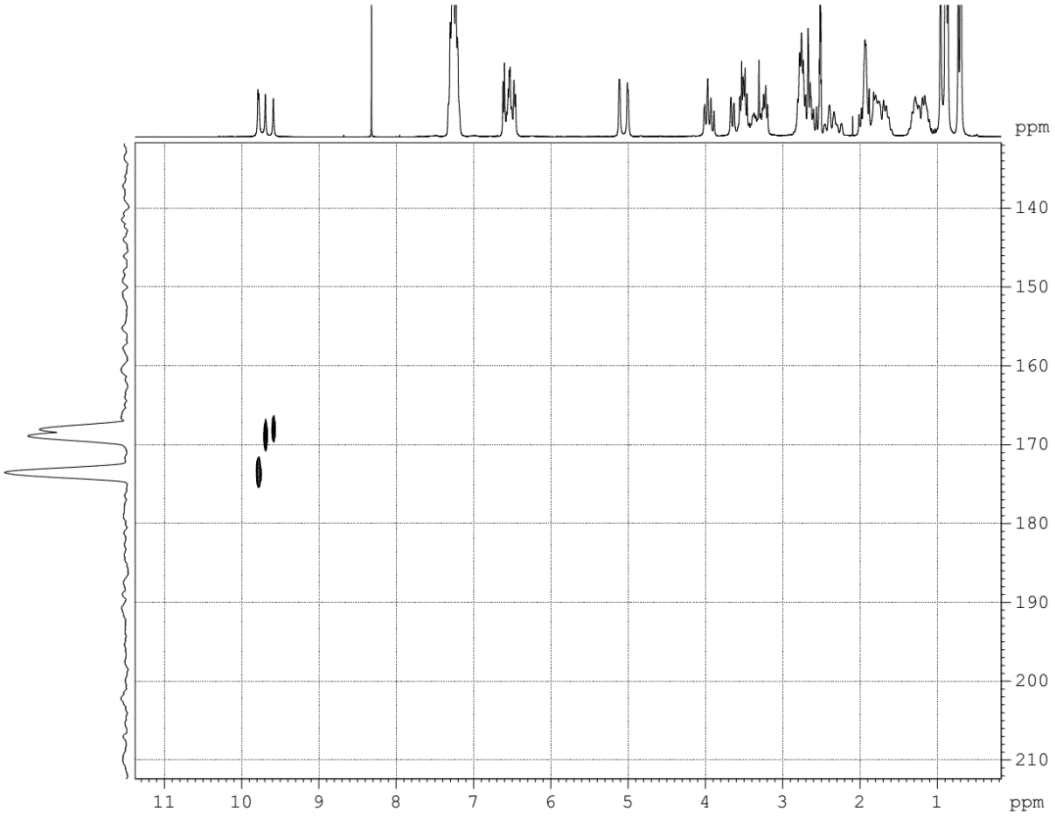
2D $^{1}H,^{13}C$-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



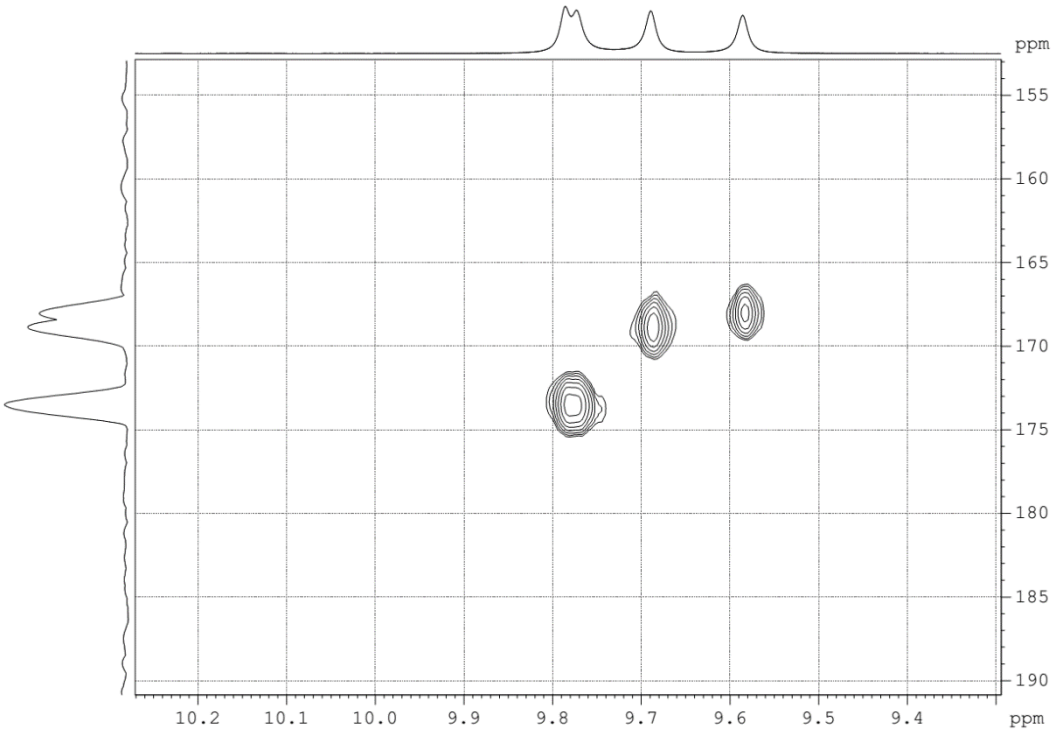
2D $^{1}H,^{13}C$-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



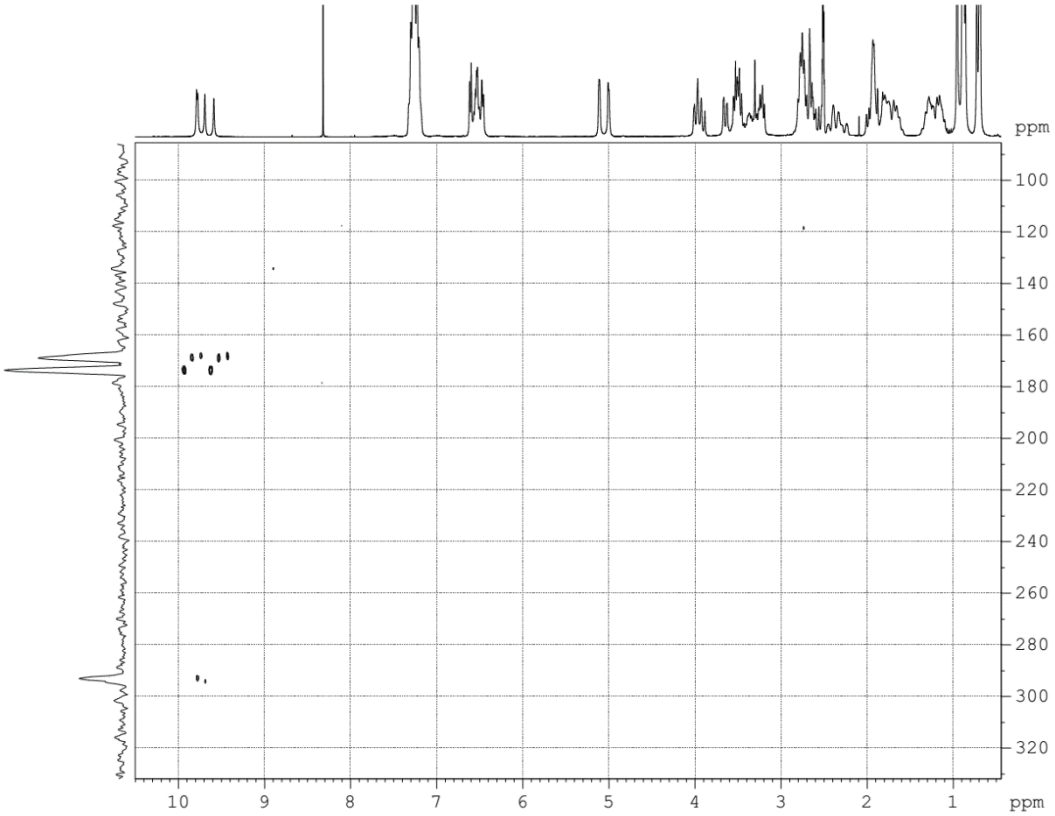
2D $^{1}H,^{15}N$-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)



2D $^{1}H,^{15}N$-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)



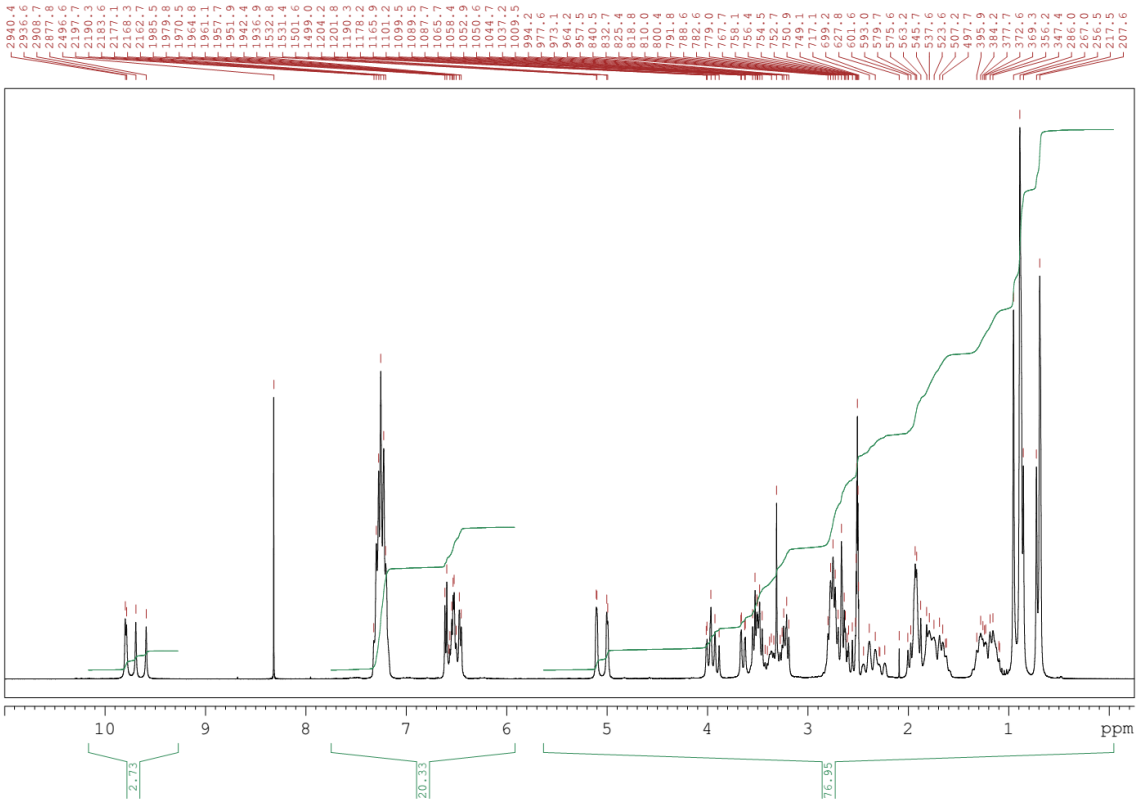
2D $^{1}H,^{15}N$-HMBC (DMSO-d_6, 300.1 & 30.4 MHz)



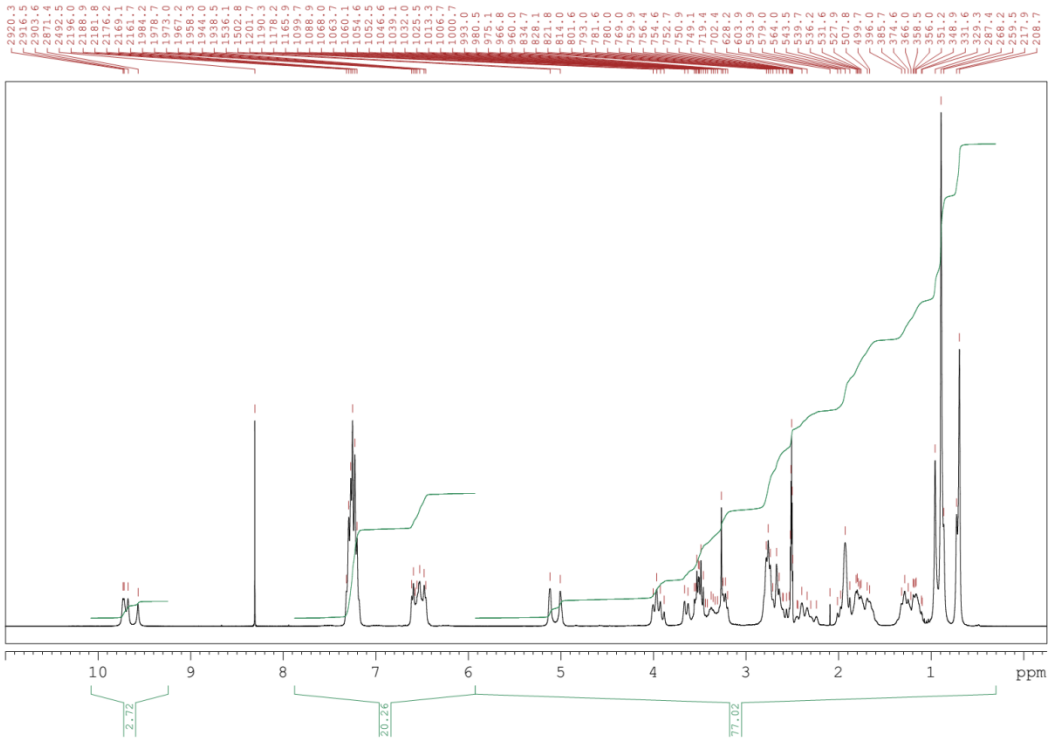
Dynamic NMR study for compound 16.

^{1}H NMR spectra were recorded on a 300 MHz spectrometer. Dynamic experiments were carried out in DMSO-d_6 solutions as a direct monitoring in an NMR tube with recording of spectra at different temperatures in the interval 30–110 °C with 10 °C step.

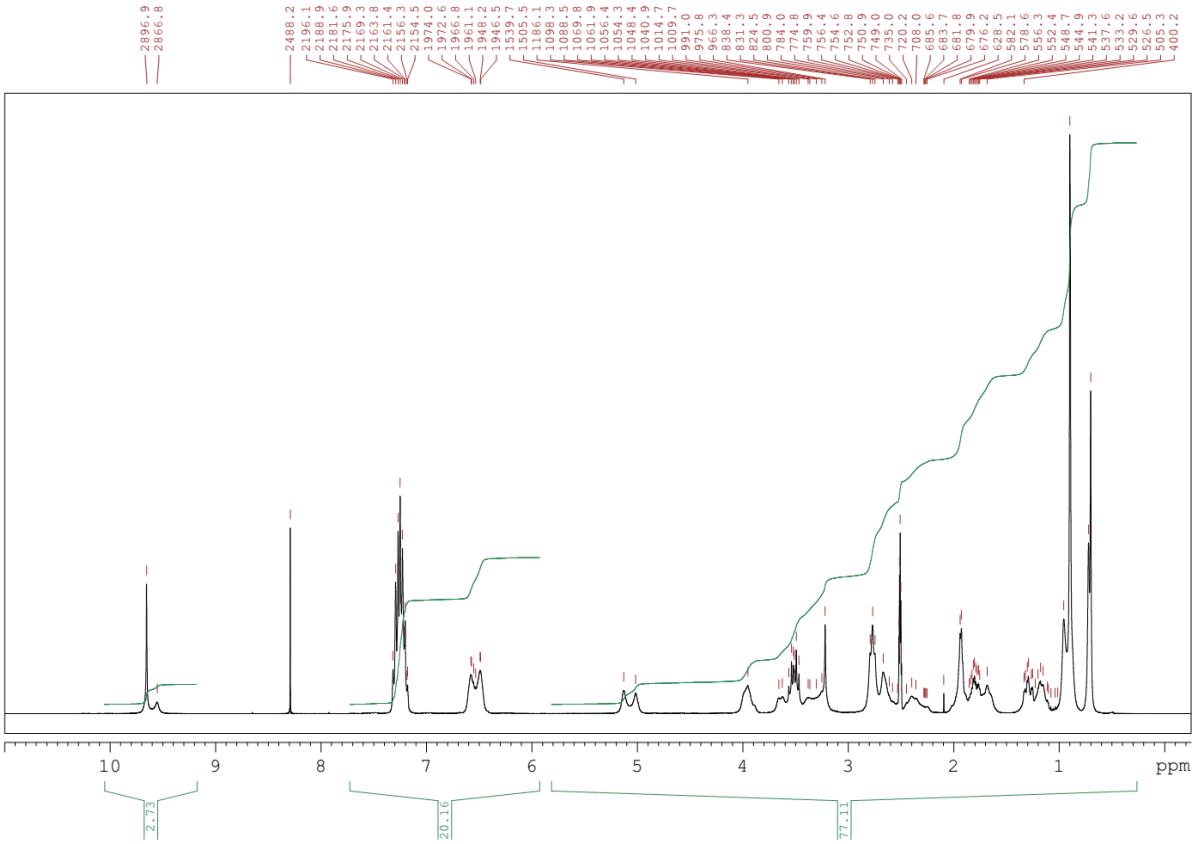
^{1}H NMR (DMSO-d_6, 300.1 MHz), +30 °C for comp 16



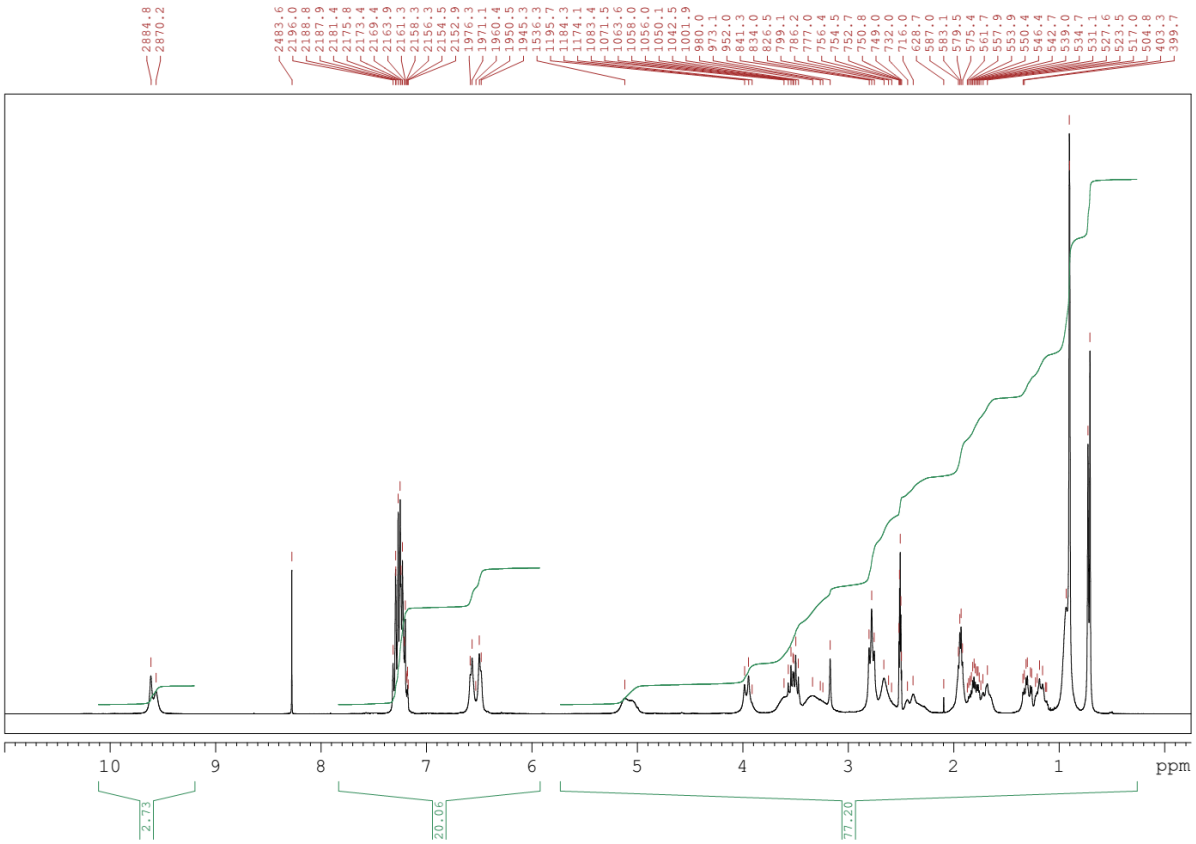
^{1}H NMR (DMSO-d_6, 300.1 MHz), +40 °C



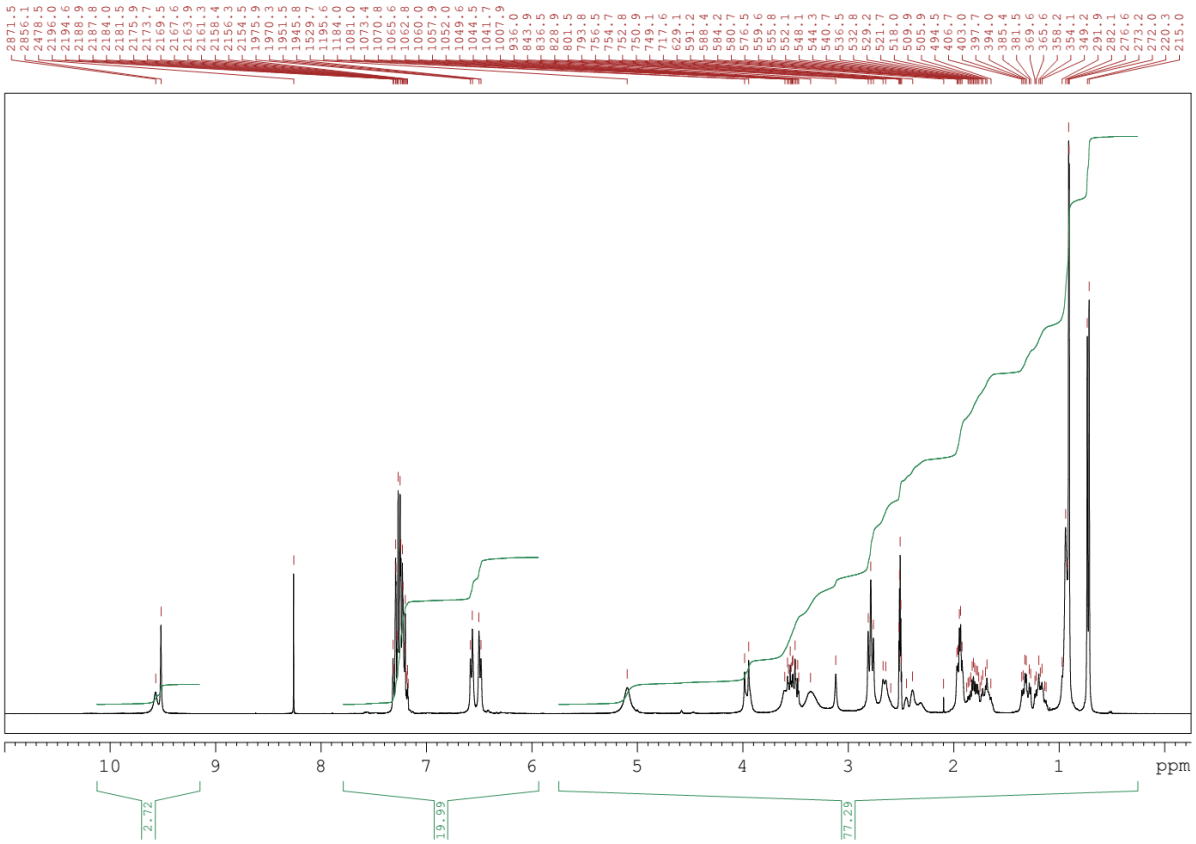
^{1}H NMR (DMSO-d_6, 300.1 MHz), +50 °C



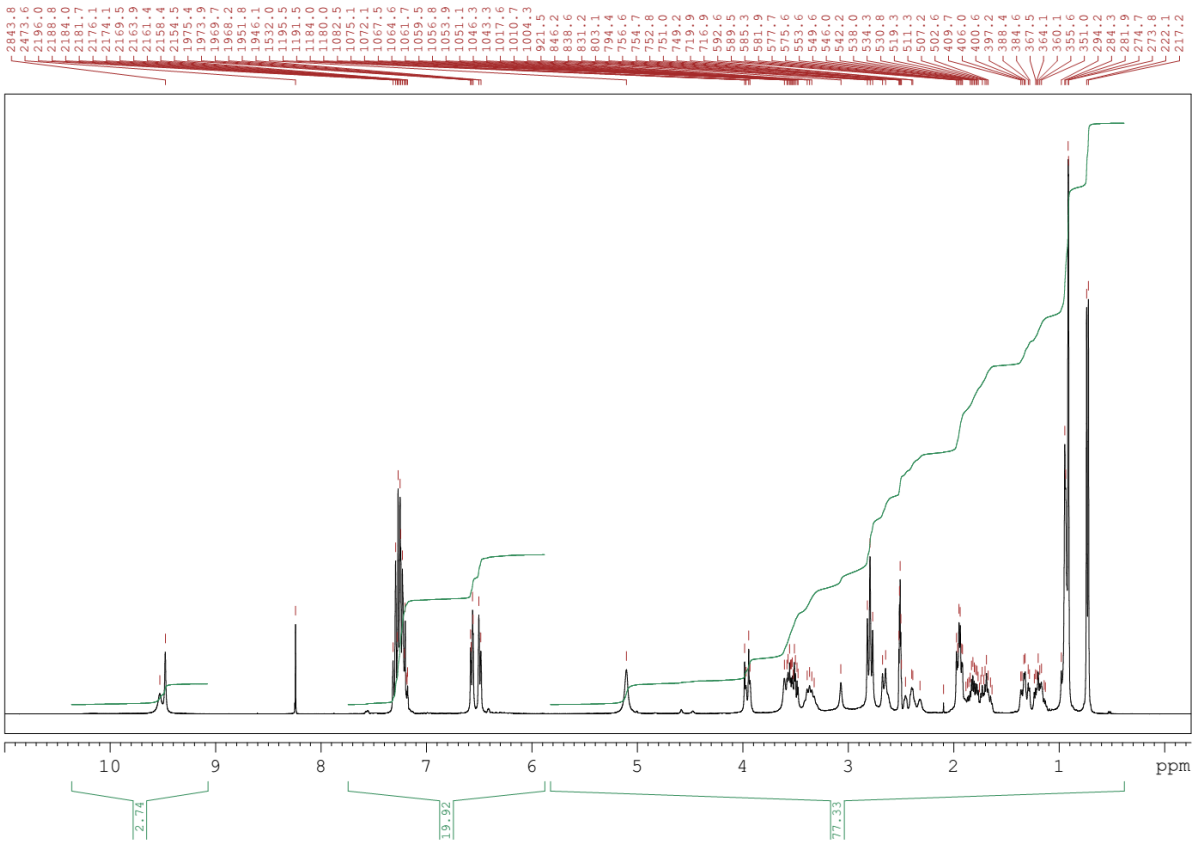
^{1}H NMR (DMSO-d_6, 300.1 MHz), +60 °C



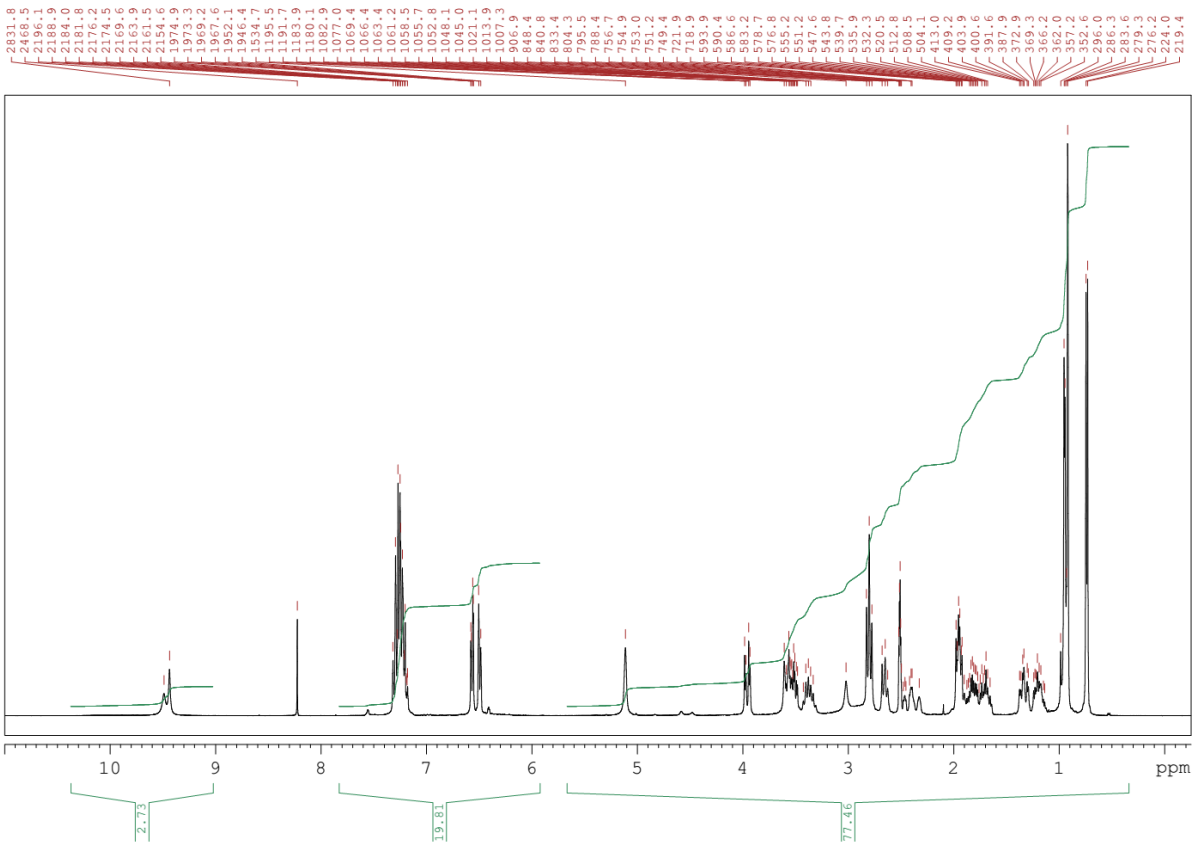
^{1}H NMR (DMSO-d_6, 300.1 MHz), +70 °C



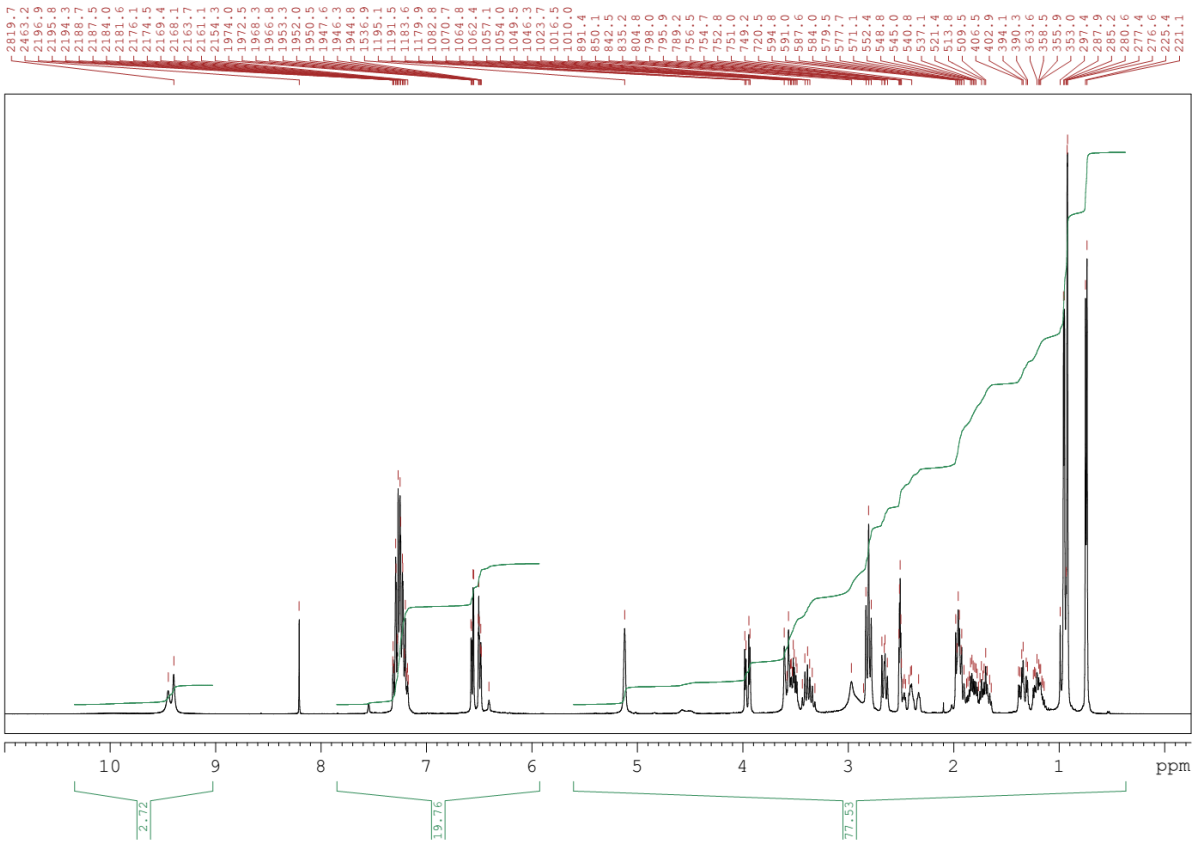
^{1}H NMR (DMSO-d_6, 300.1 MHz), +80 °C



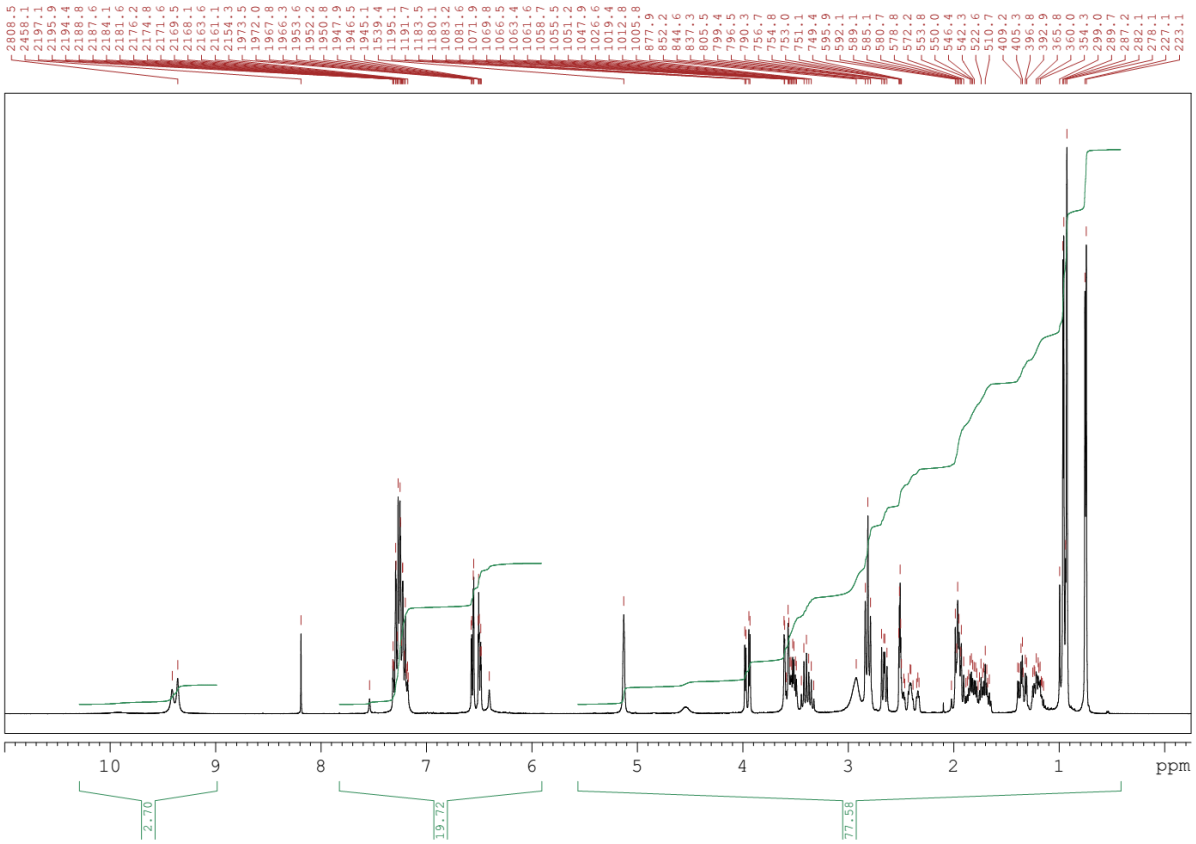
^{1}H NMR (DMSO-d_6, 300.1 MHz), +90 °C



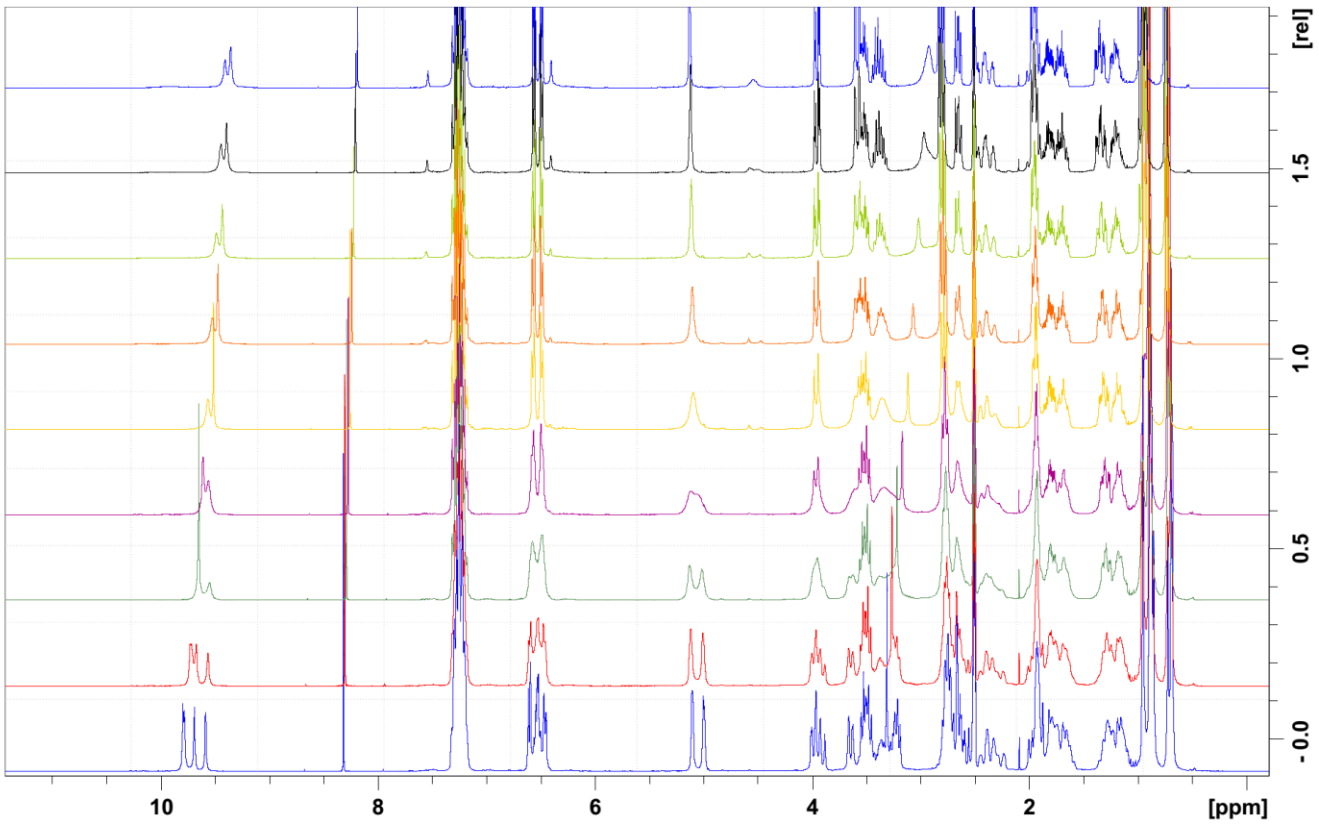
^{1}H NMR (DMSO-d_6, 300.1 MHz), +100 °C



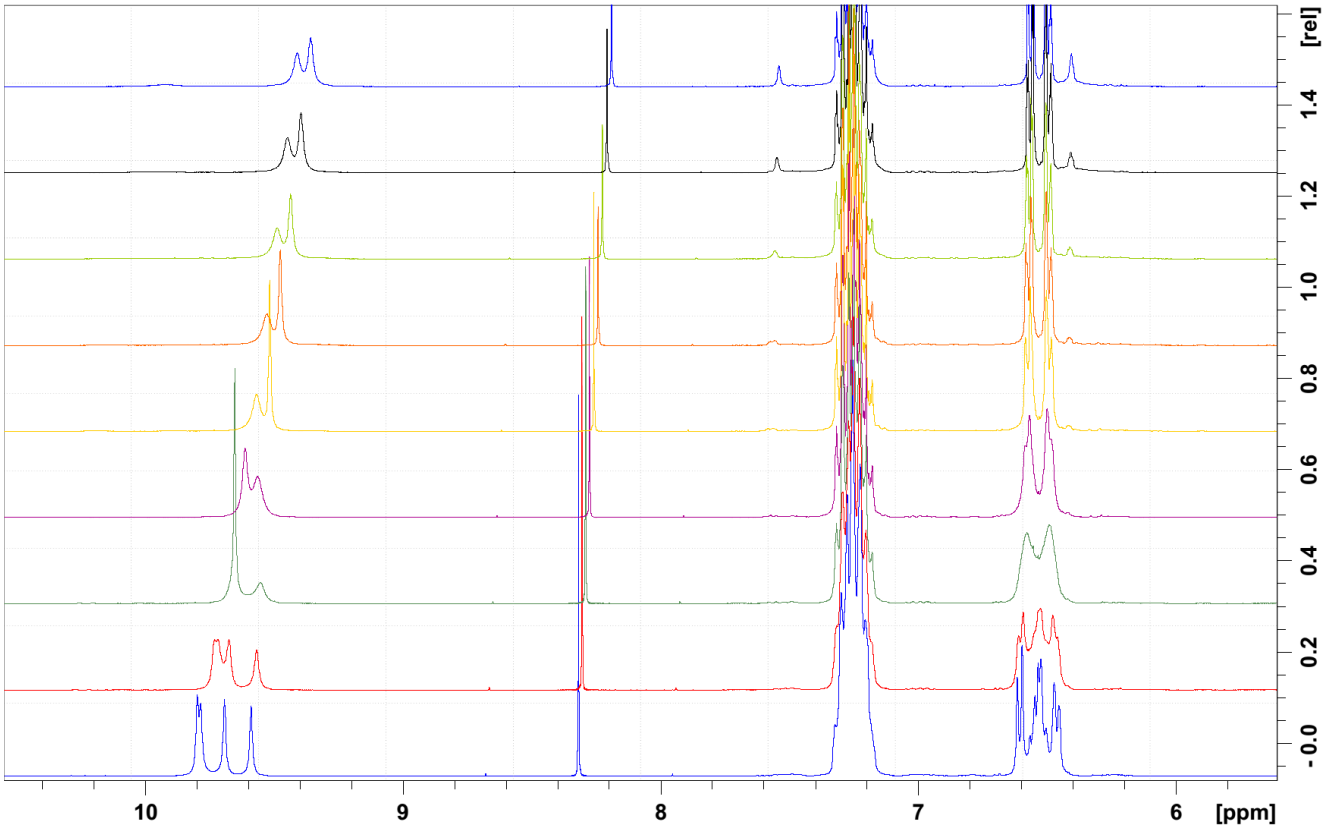
^{1}H NMR (DMSO-d_6, 300.1 MHz), +110 °C



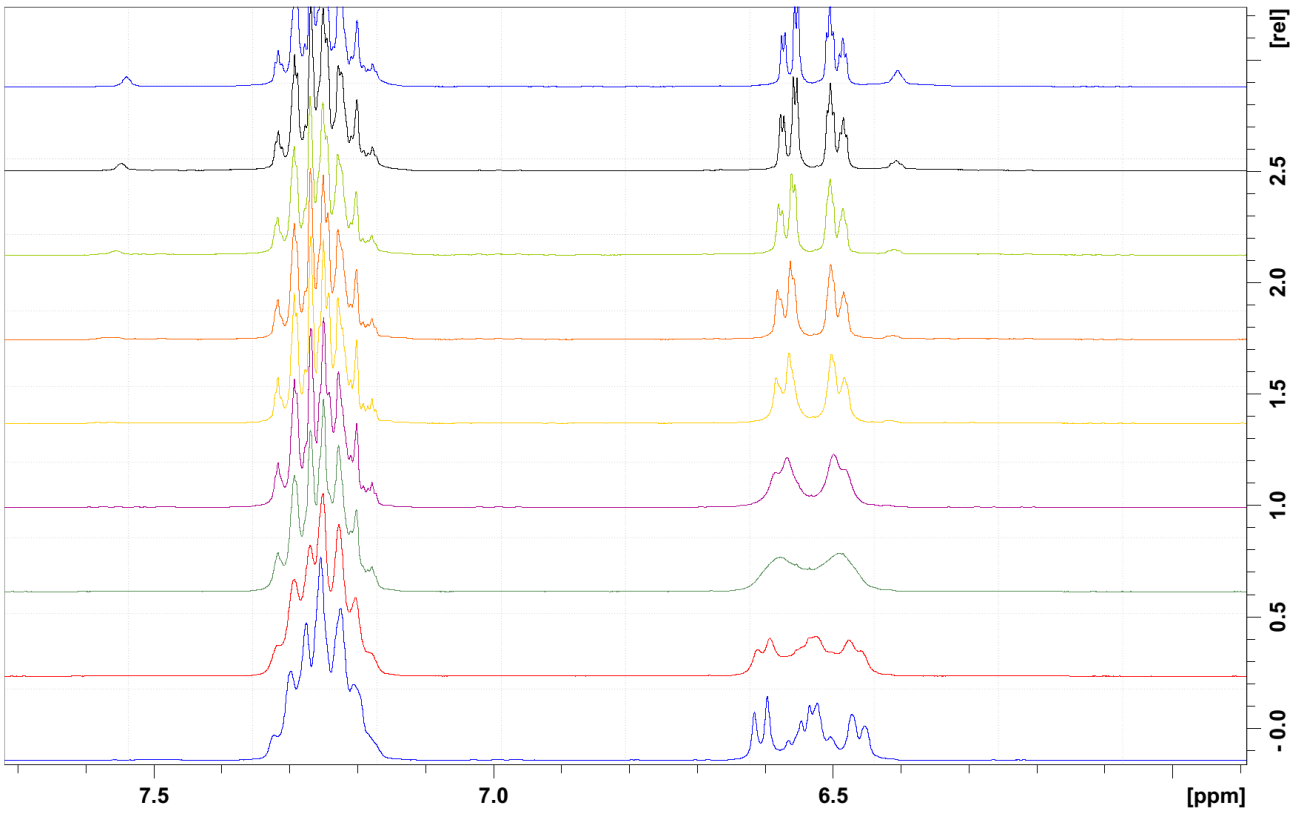
^{1}H NMR (DMSO-d_6, 300.1 MHz), different temp. {30 – 40 – 50 – 60 – 70 – 80 – 90 – 100 – 110 °C}



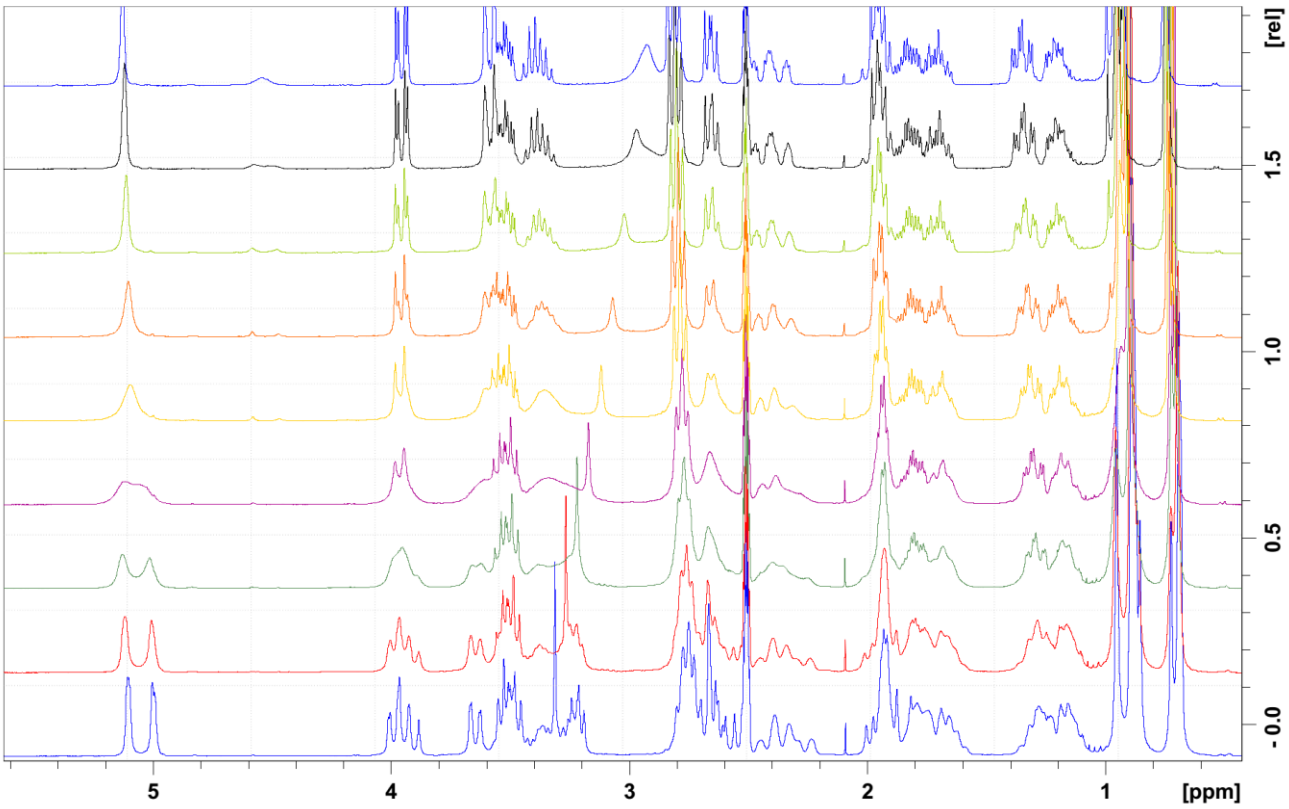
^{1}H NMR (DMSO-d_6, 300.1 MHz), different temp. {30 – 40 – 50 – 60 – 70 – 80 – 90 – 100 – 110 °C}



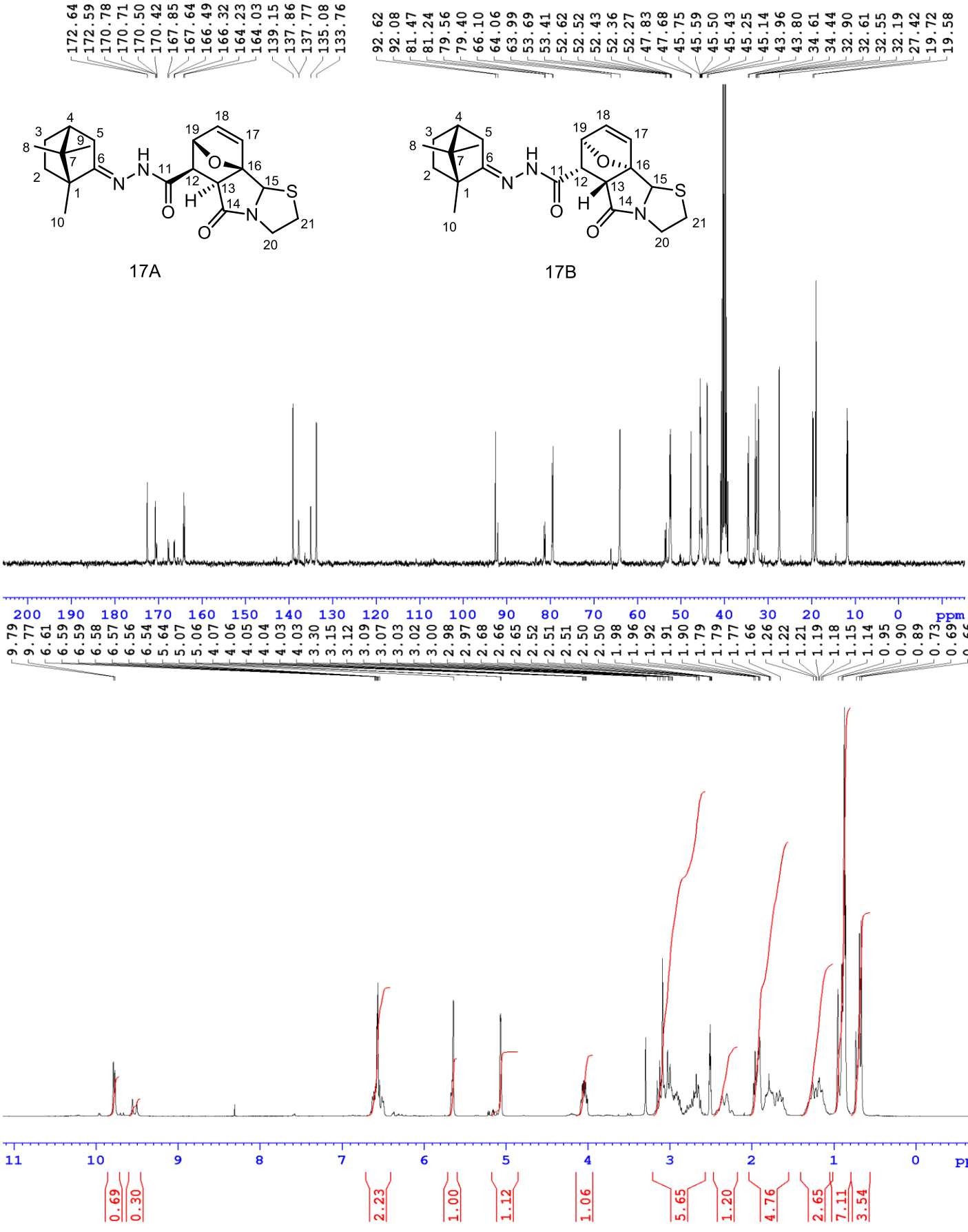
^{1}H NMR (DMSO-d_6, 300.1 MHz), different temp. {30 – 40 – 50 – 60 – 70 – 80 – 90 – 100 – 110 °C}



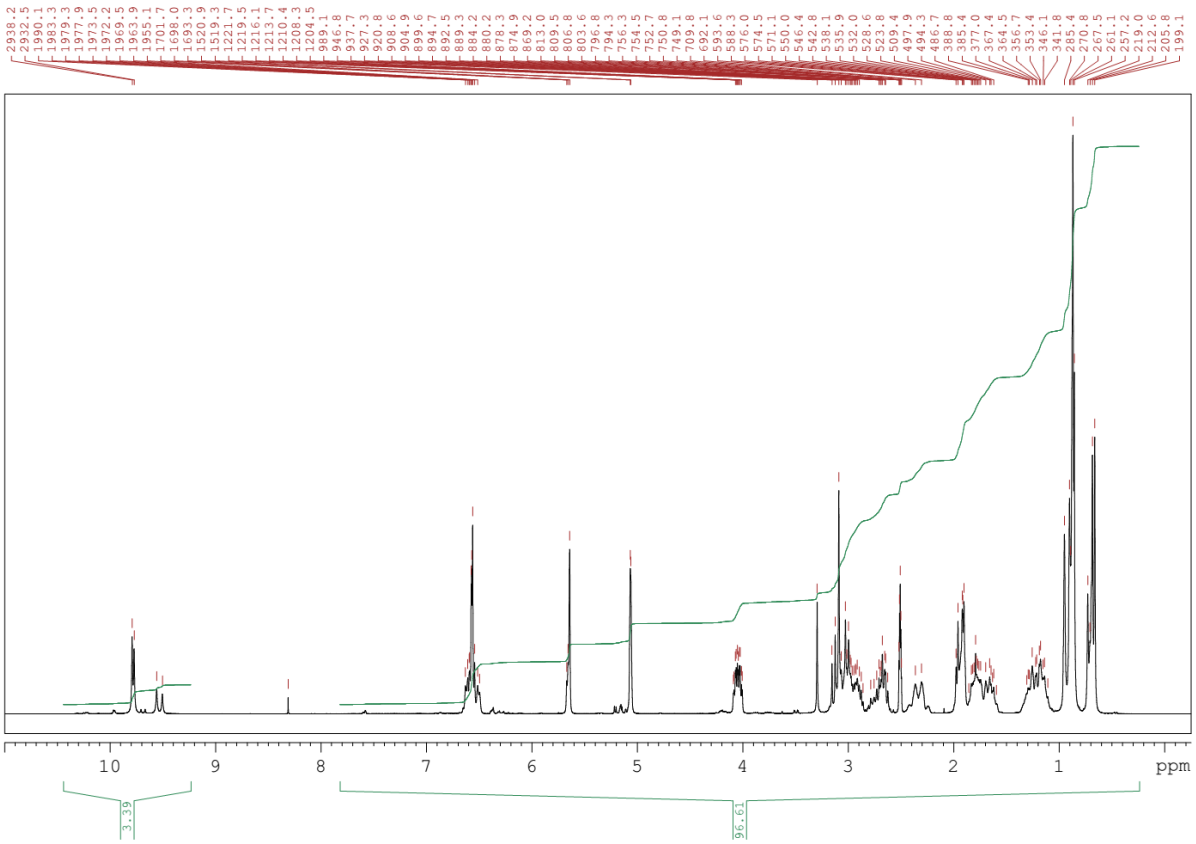
^{1}H NMR (DMSO-d_6, 300.1 MHz), different temp. {30 – 40 – 50 – 60 – 70 – 80 – 90 – 100 – 110 °C}



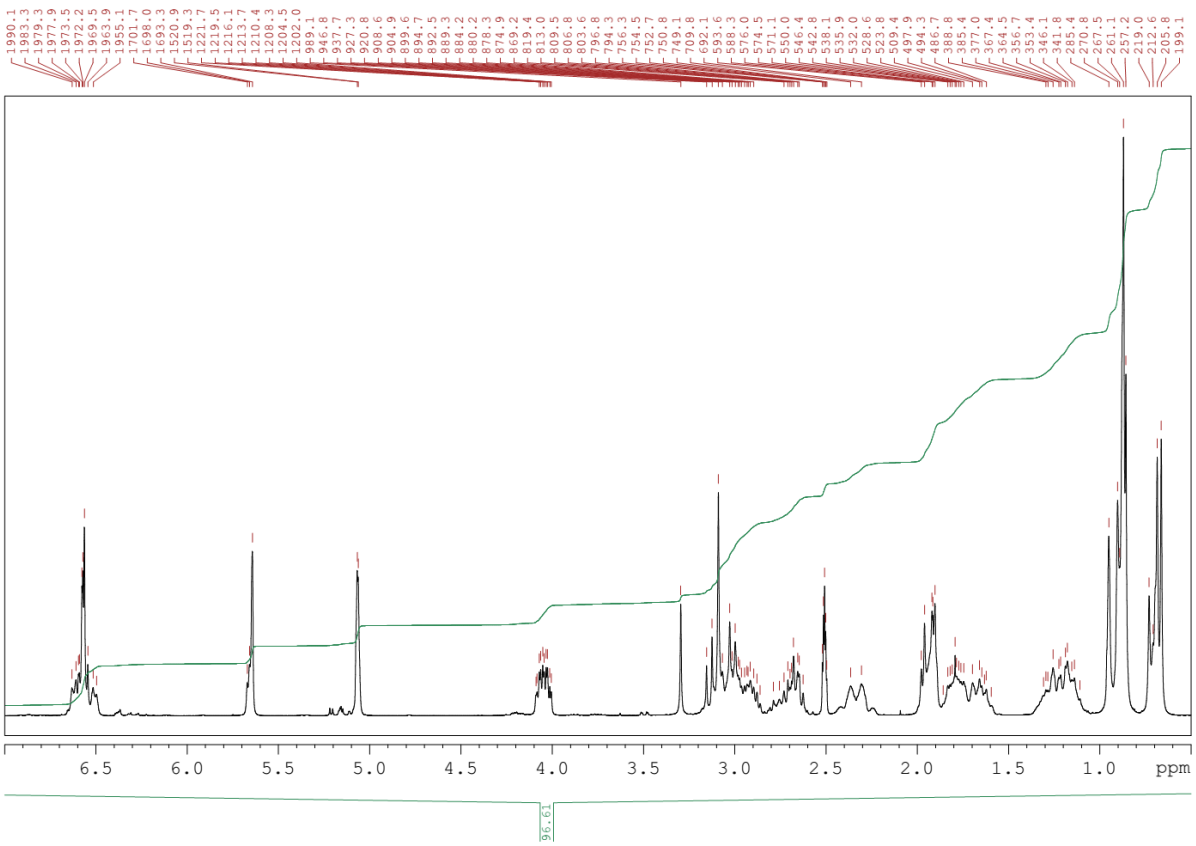
2.12. A mixture of (5aS,6R,7S,9aR)-5-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (A) and (5aR,6S,7R,9aS)-5-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (B) 17 (DMSO-d_6, 400.0 MHz)



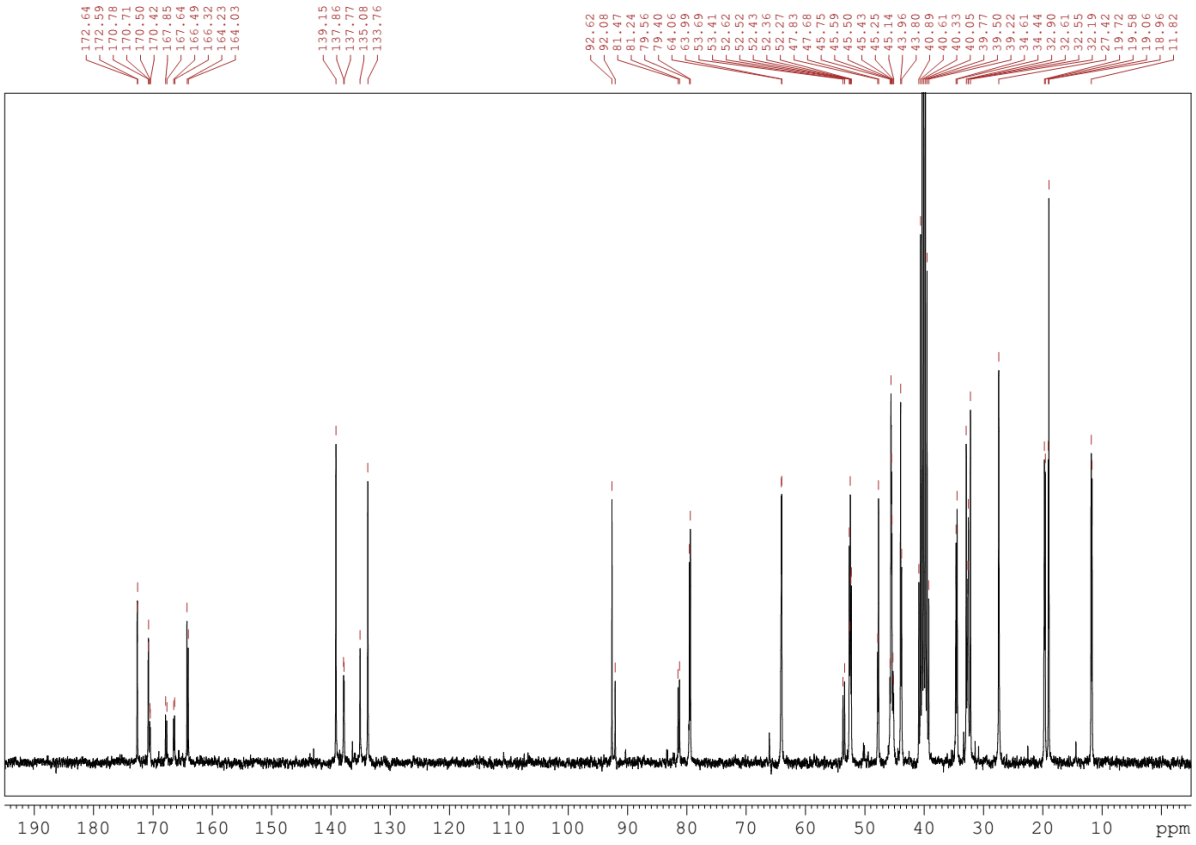
^{1}H NMR (DMSO-d_6, 300.1 MHz) for 17.



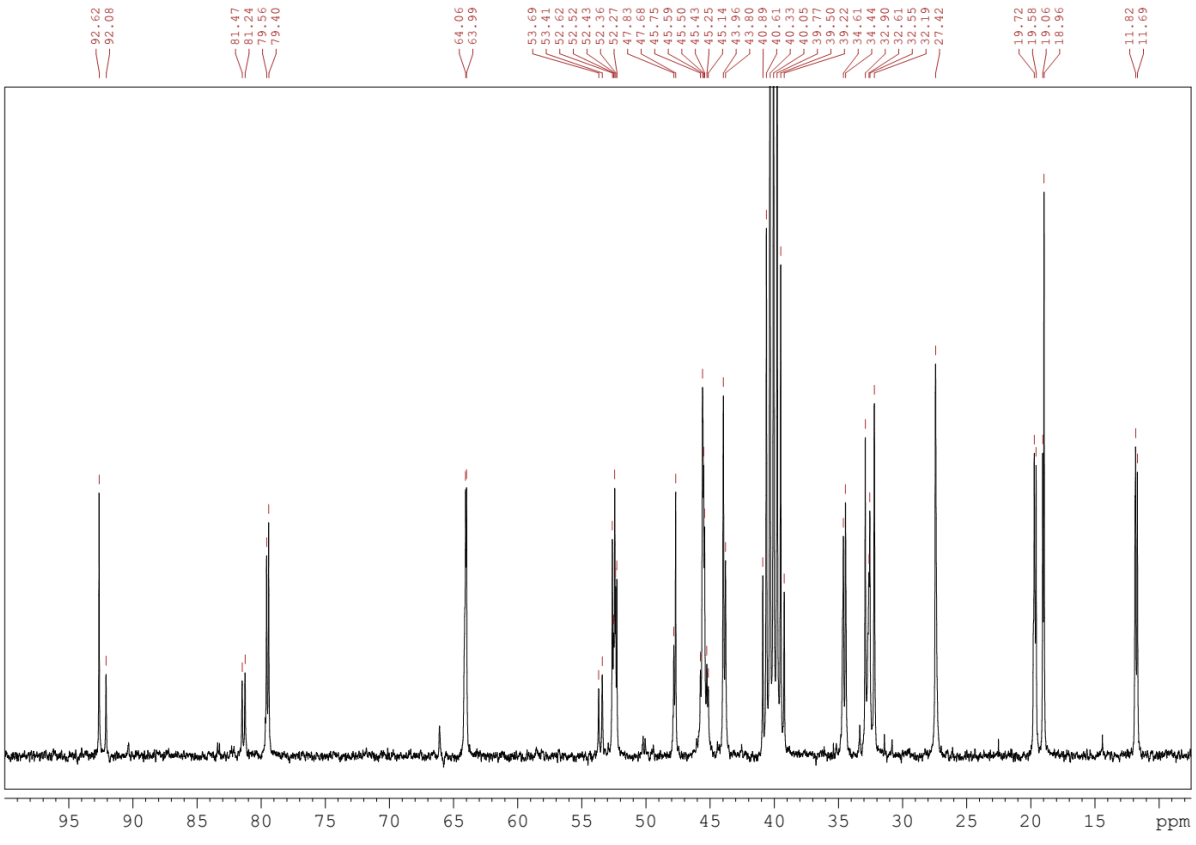
^{1}H NMR (DMSO-d_6, 300.1 MHz)



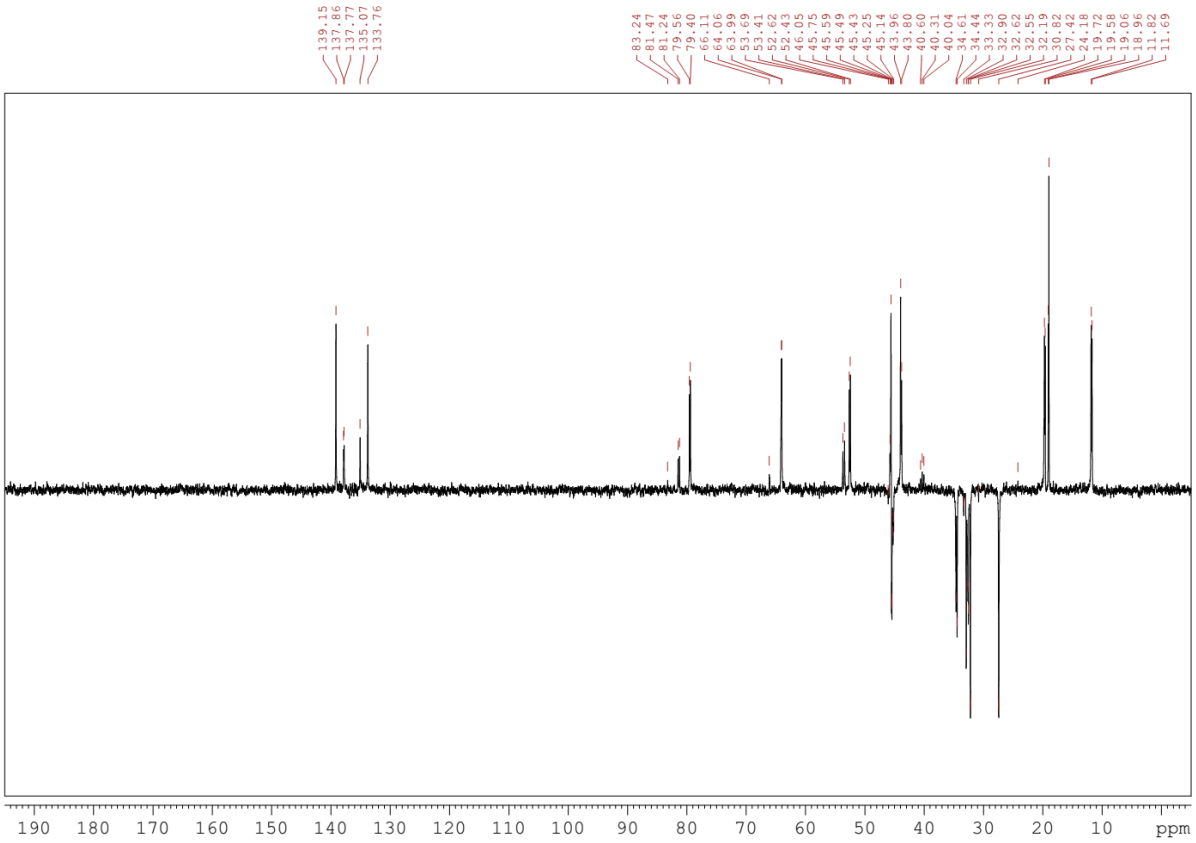
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



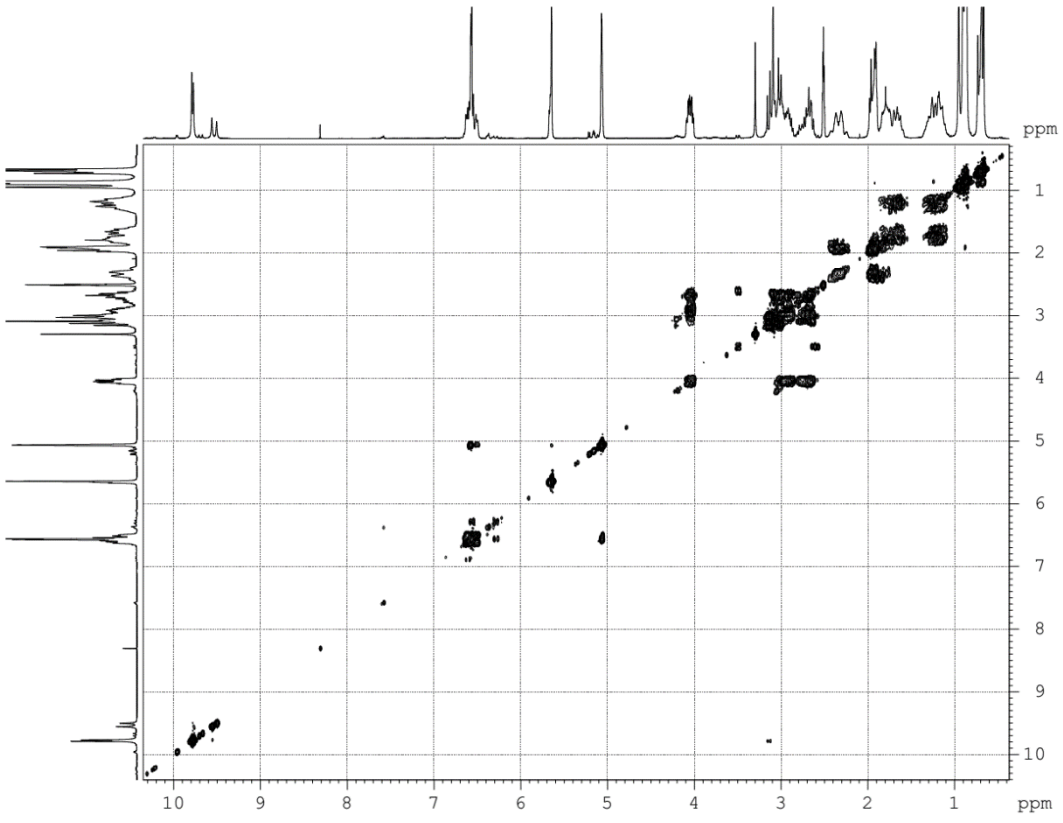
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



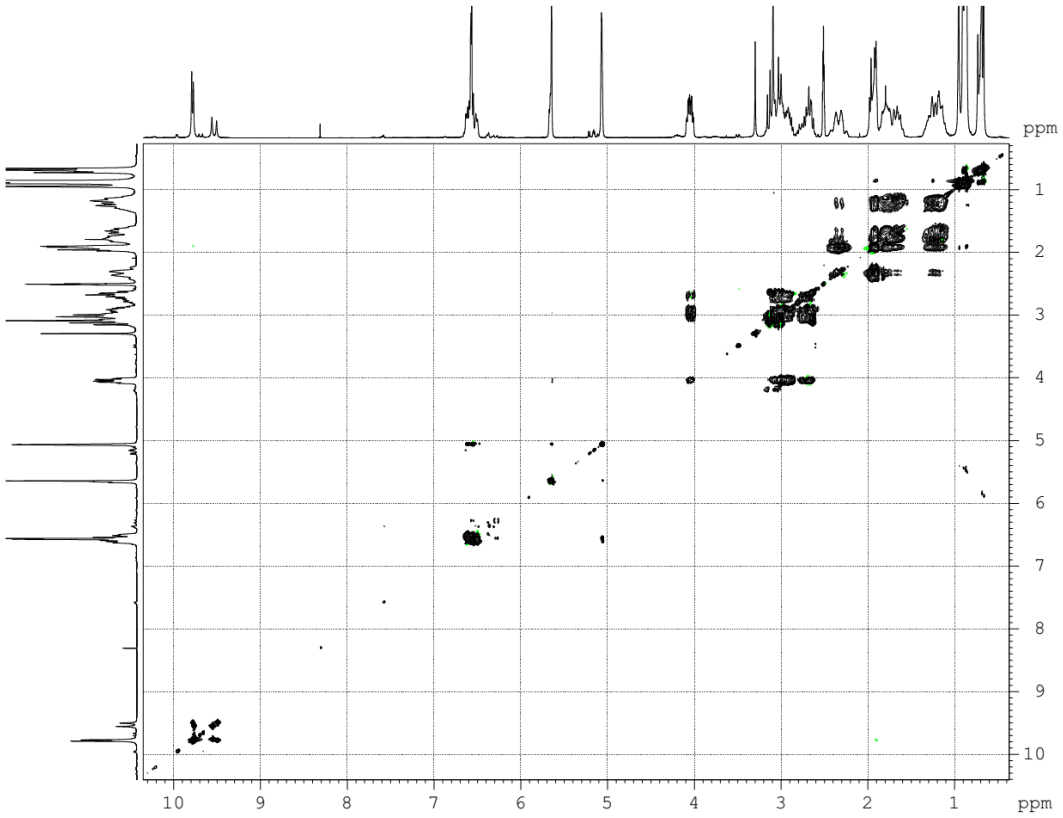
DEPT-135 NMR (DMSO-d_6, 75.5 MHz)



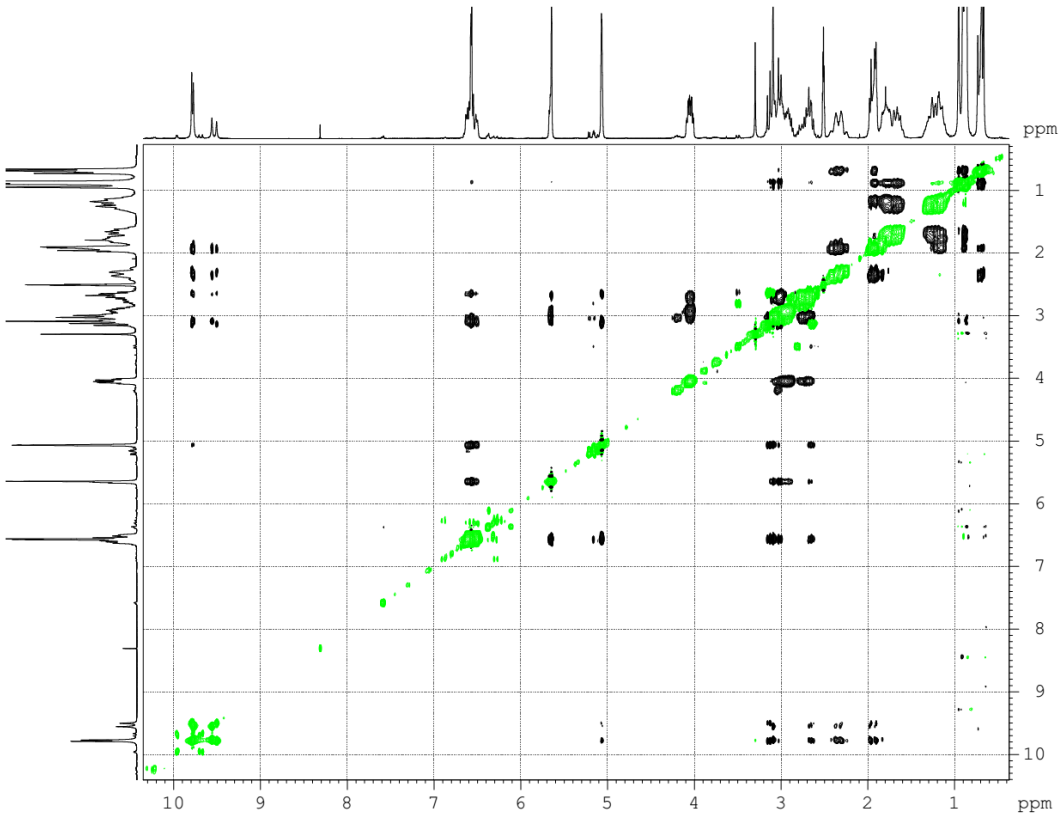
2D ^{1}H,^{1}H-COSY (DMSO-d_6, 300.1 MHz)



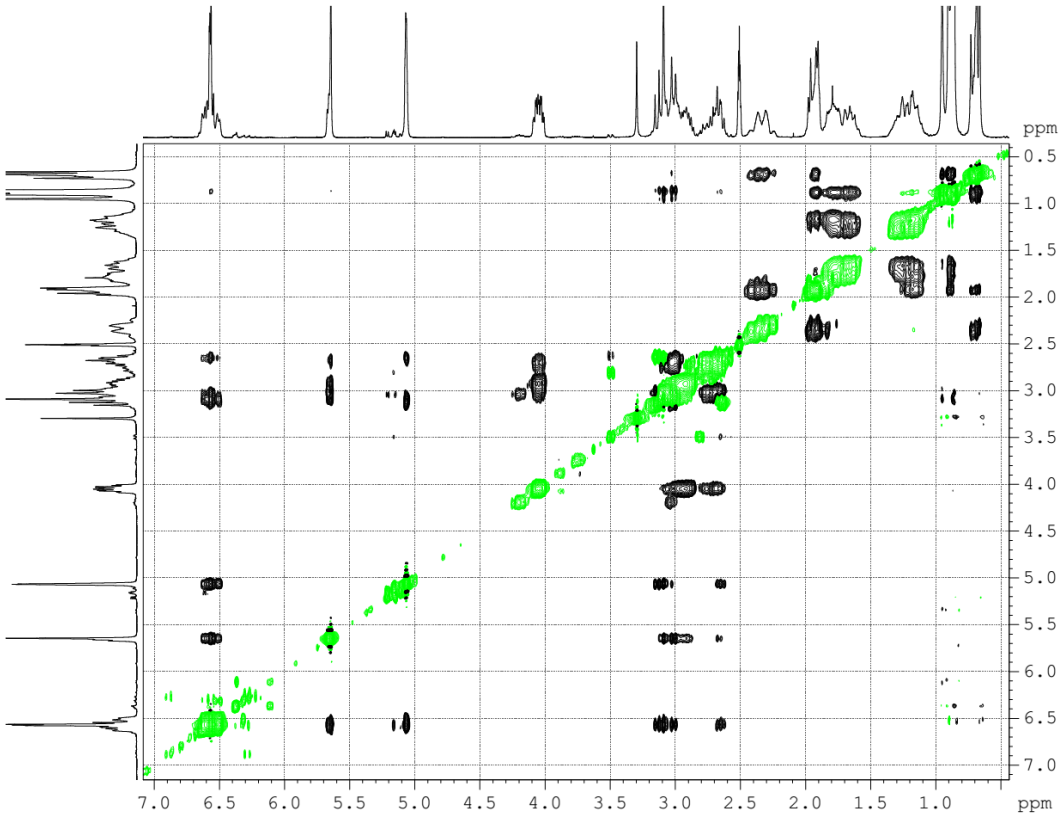
2D ^{1}H,^{1}H-TOCSY (DMSO-d_6, 300.1 MHz)



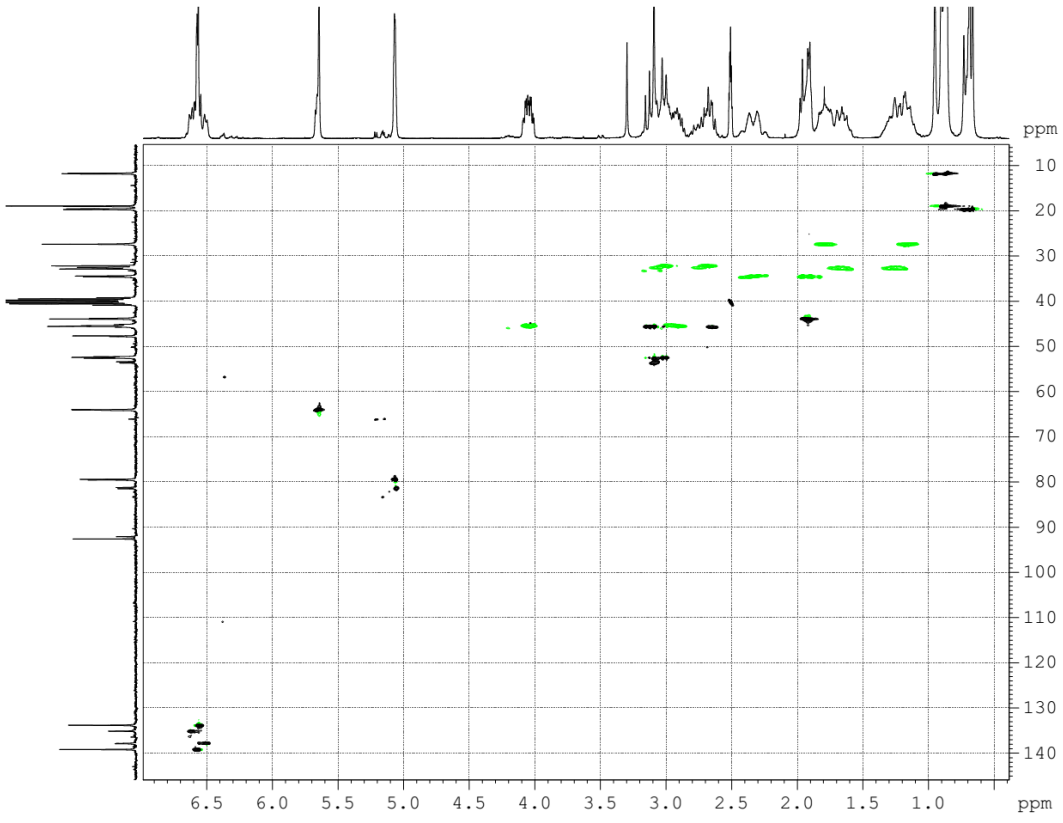
2D ^{1}H,^{1}H-NOESY (DMSO-d_6, 300.1 MHz)



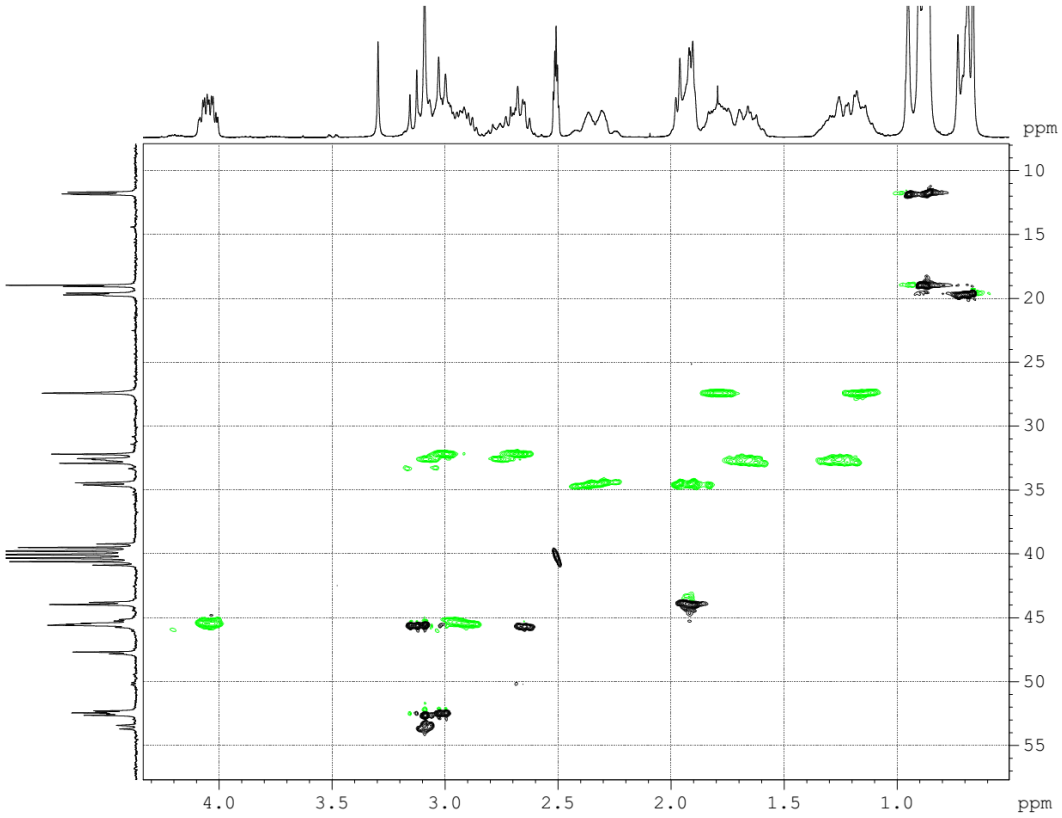
2D ^{1}H,^{1}H-NOESY (DMSO-d_6, 300.1 MHz)



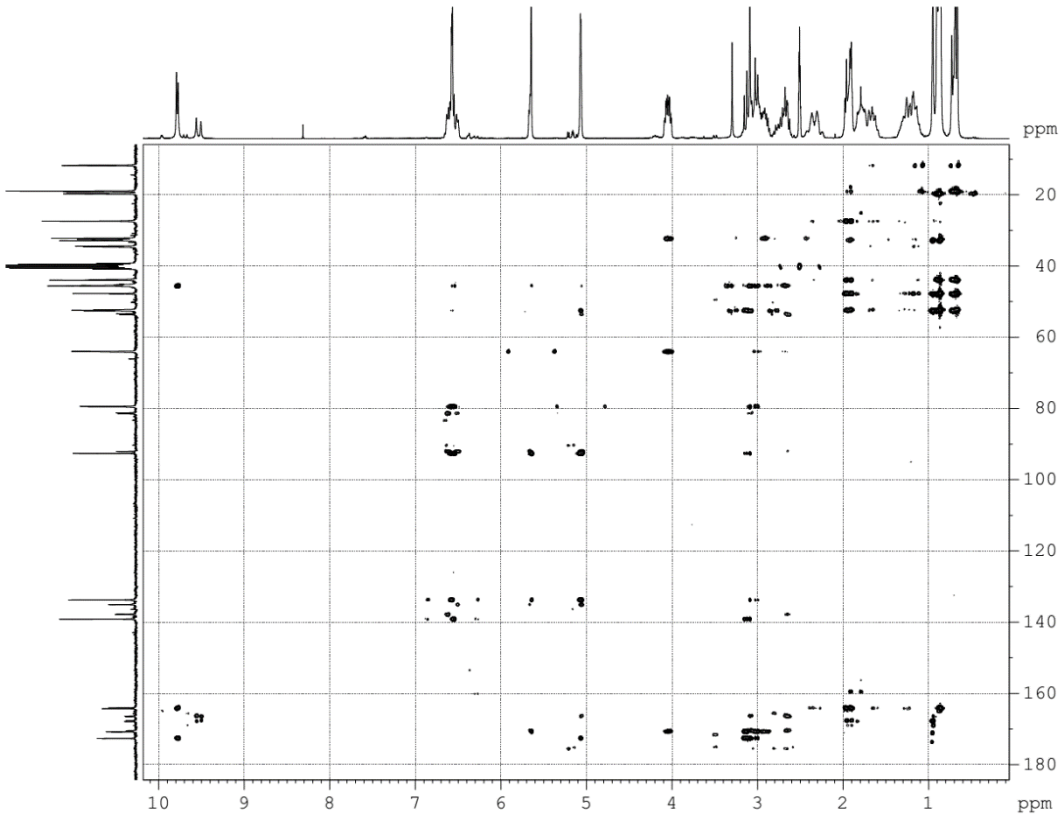
2D ^{1}H,^{13}C-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



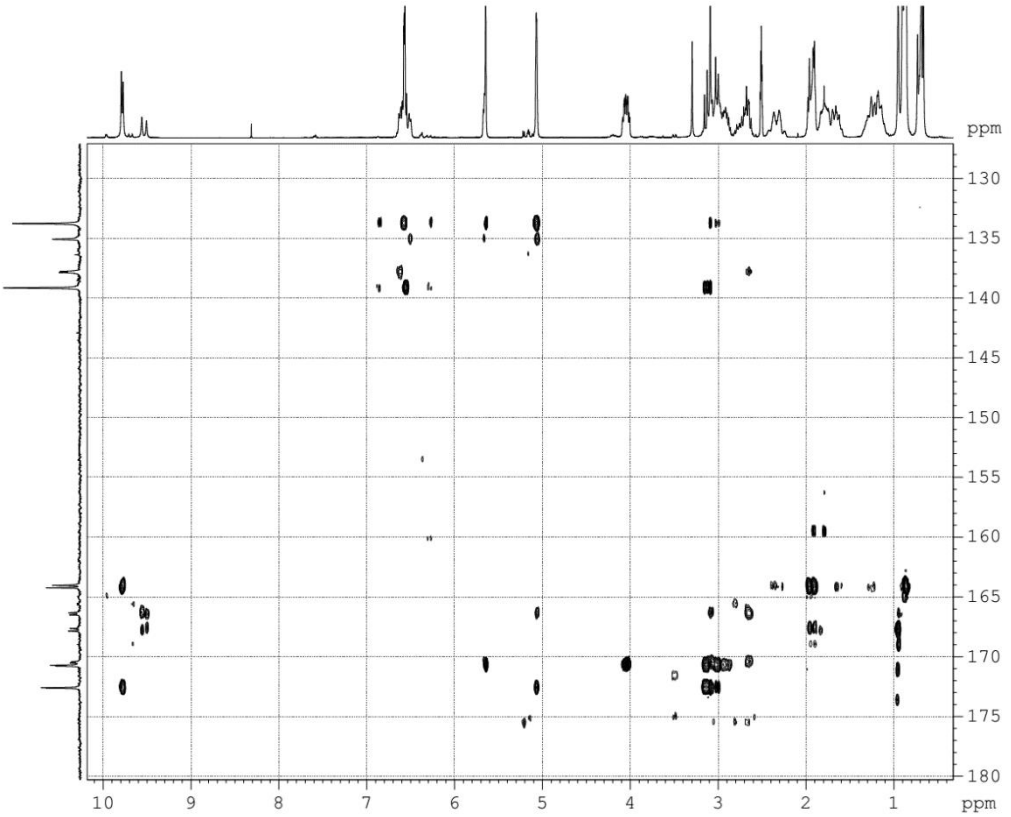
2D $^{1}H,^{13}C$-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



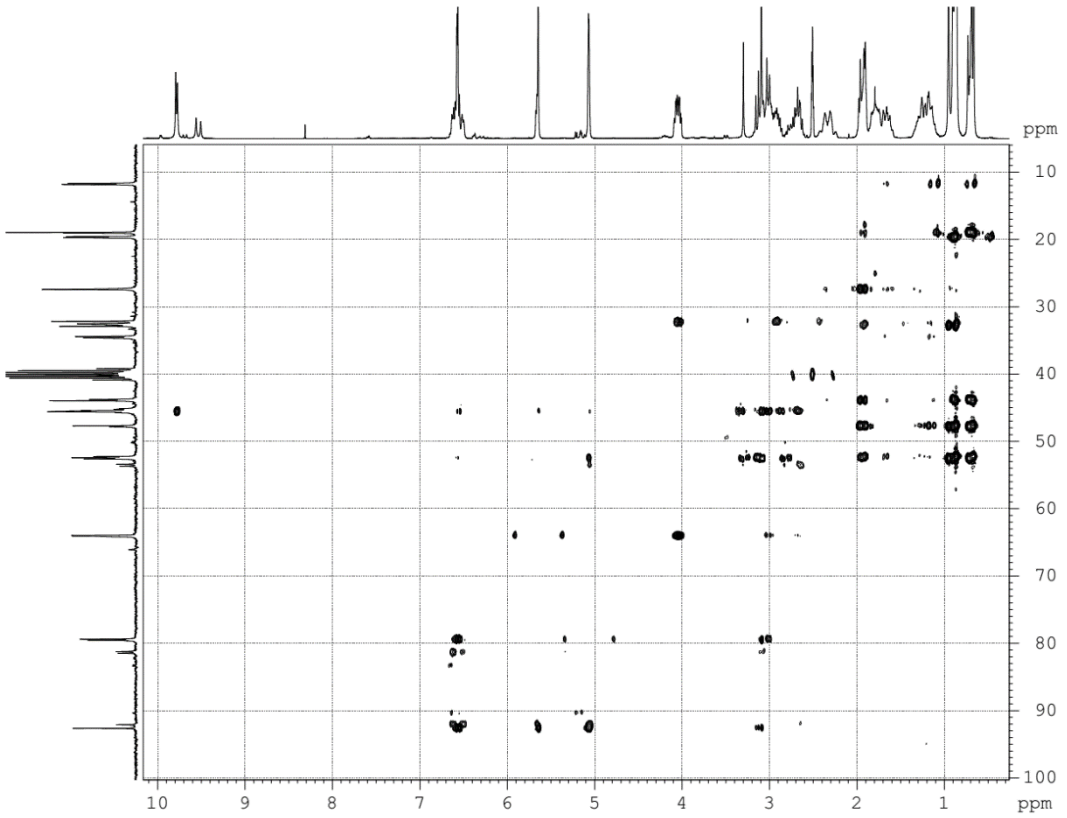
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



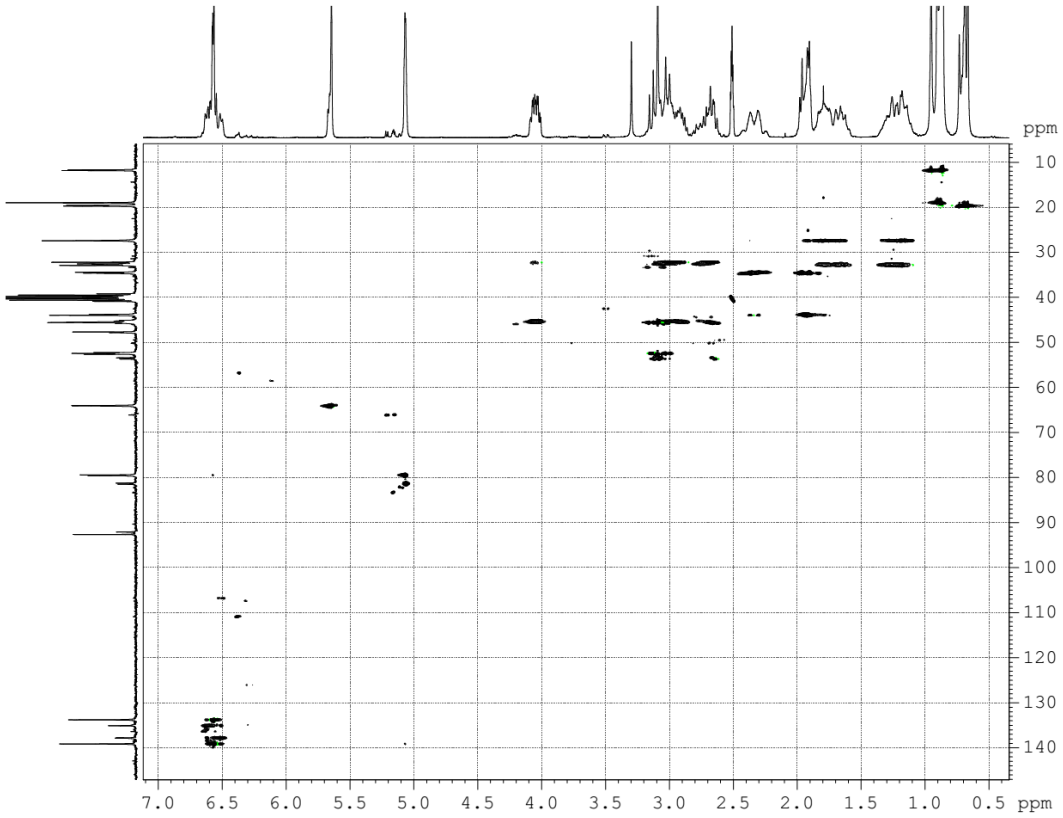
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



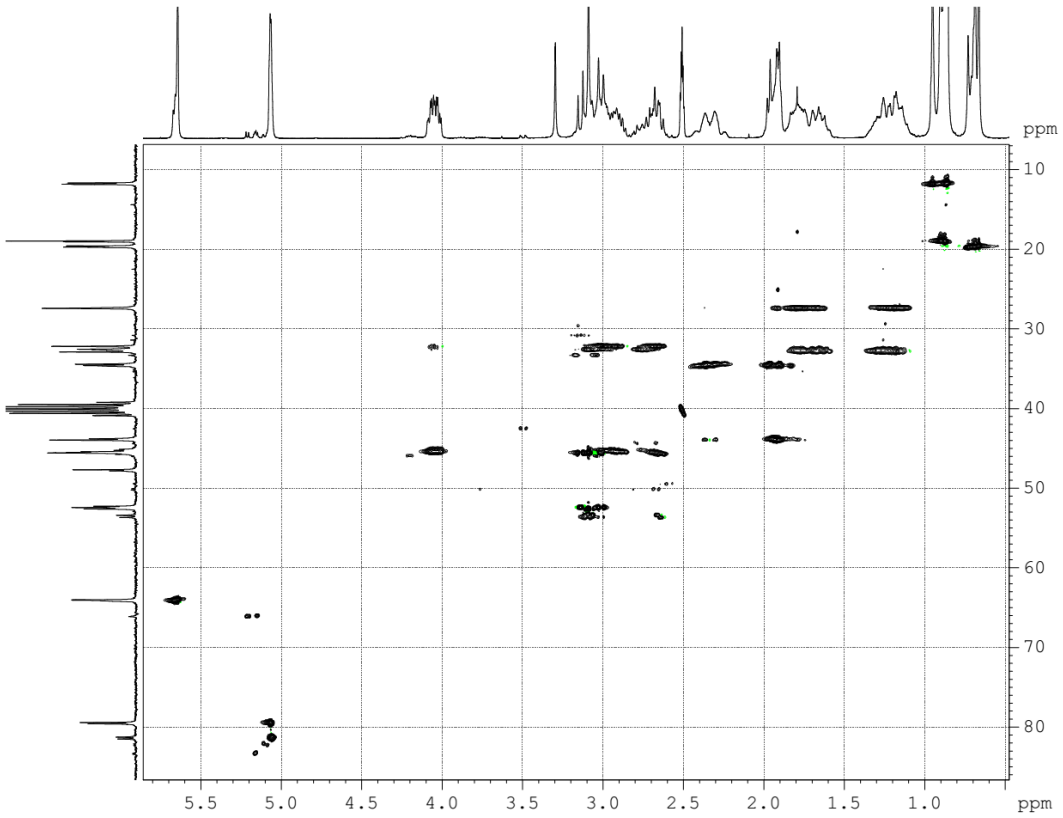
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



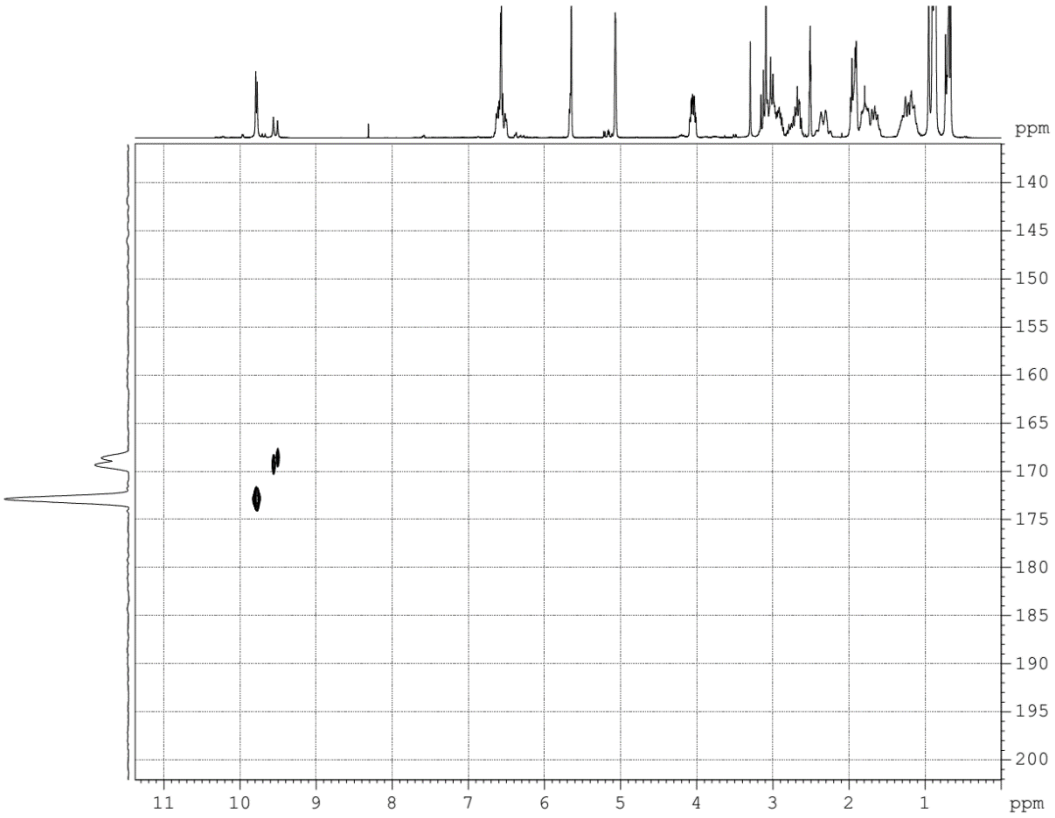
2D ^{1}H,^{13}C-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



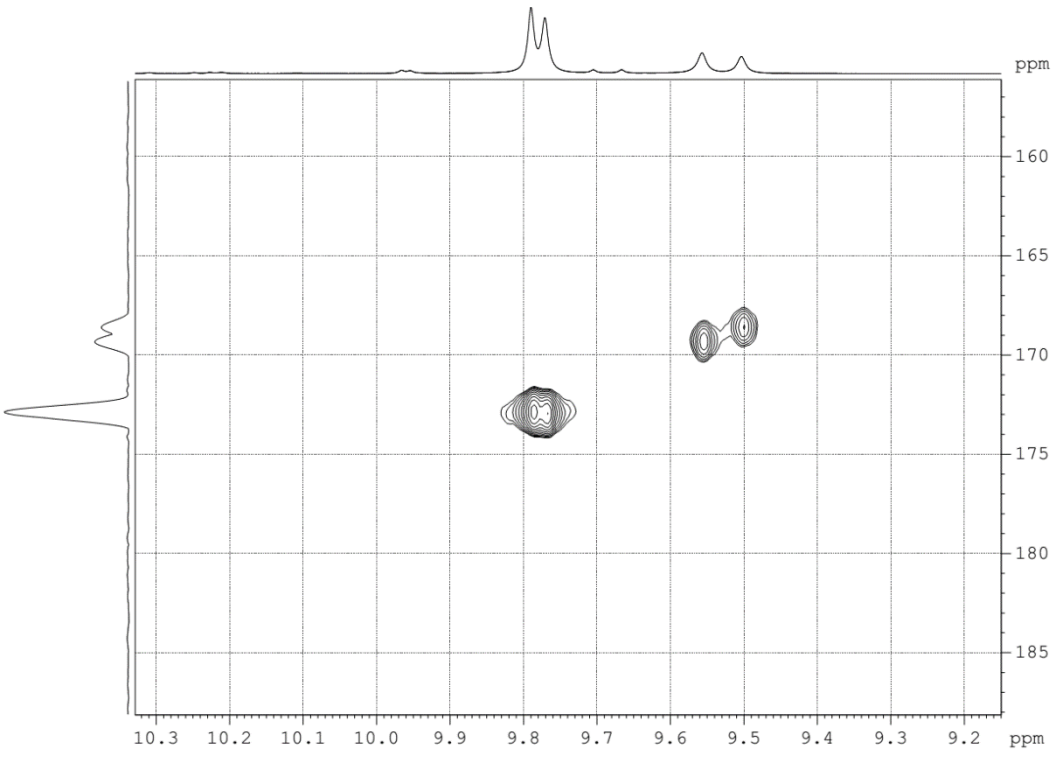
2D ^{1}H,^{13}C-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



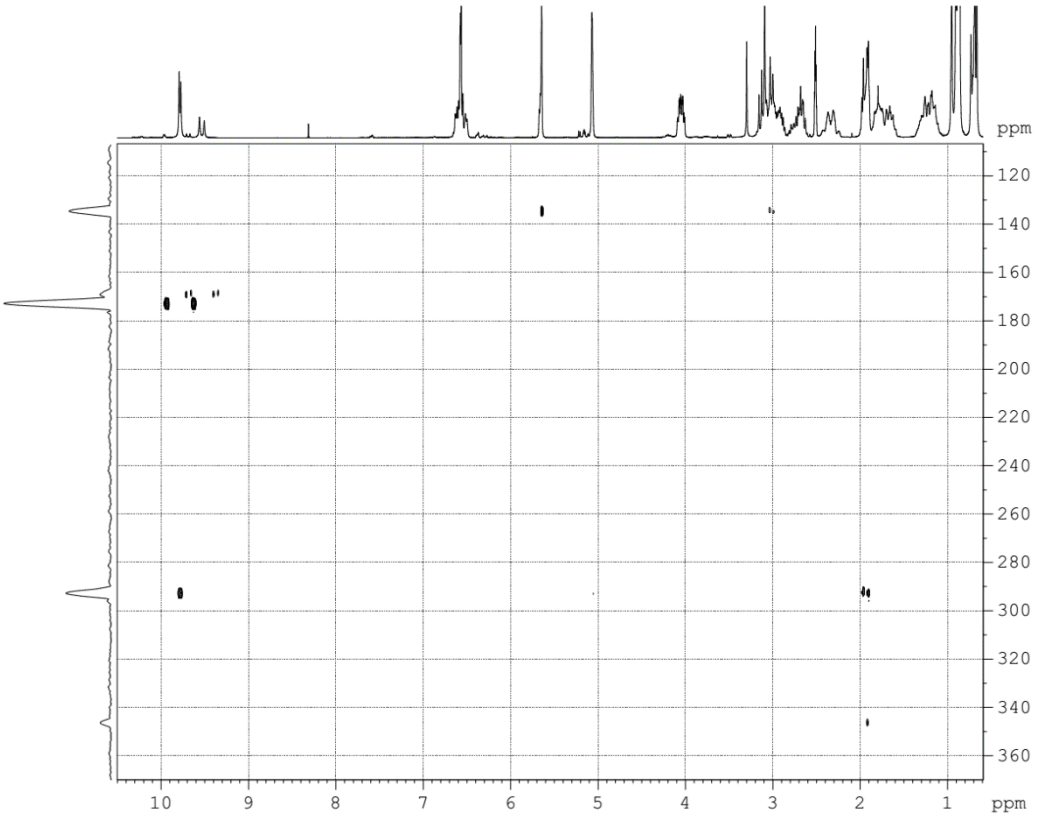
2D ^{1}H,^{15}N-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)



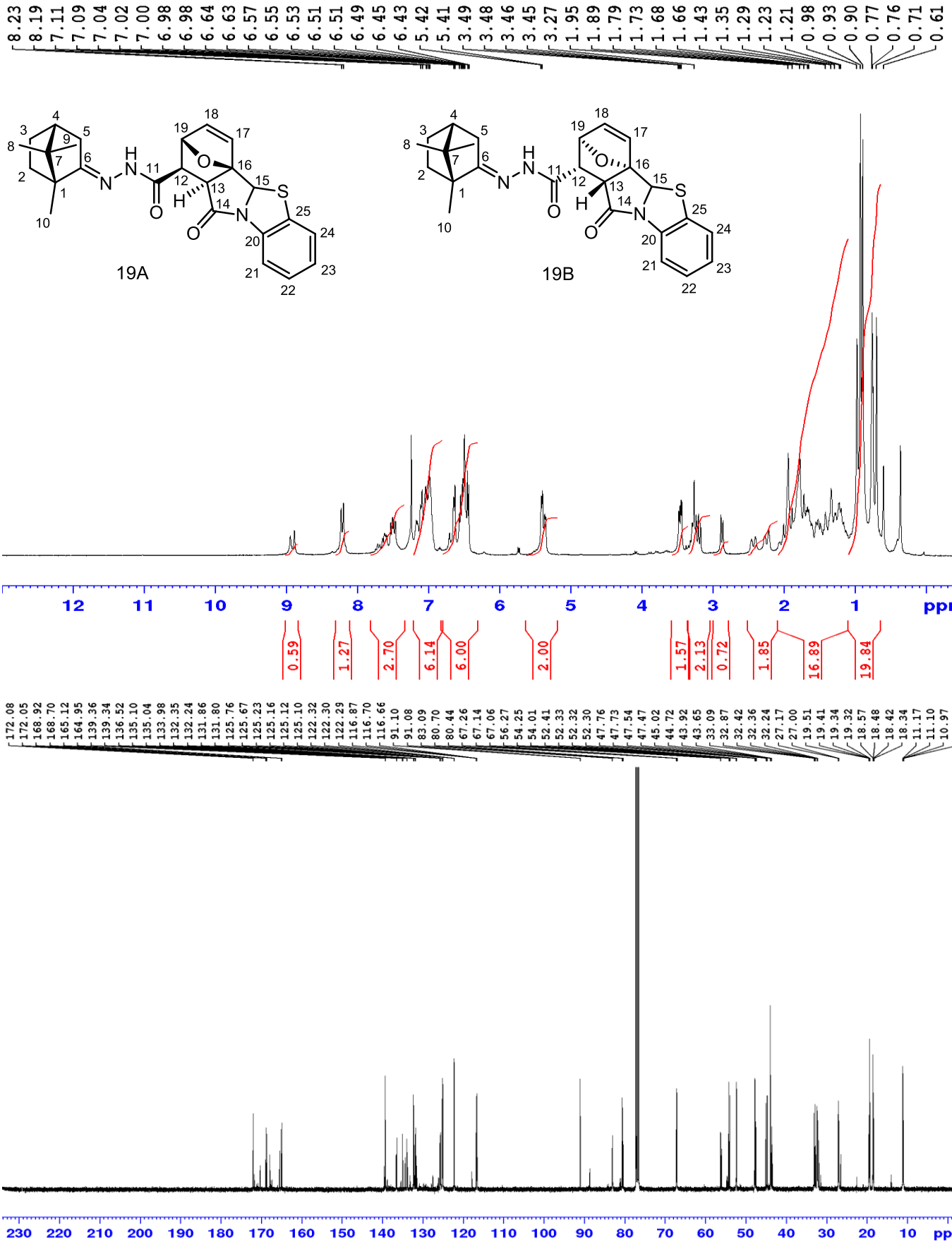
2D ^{1}H,^{15}N-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)



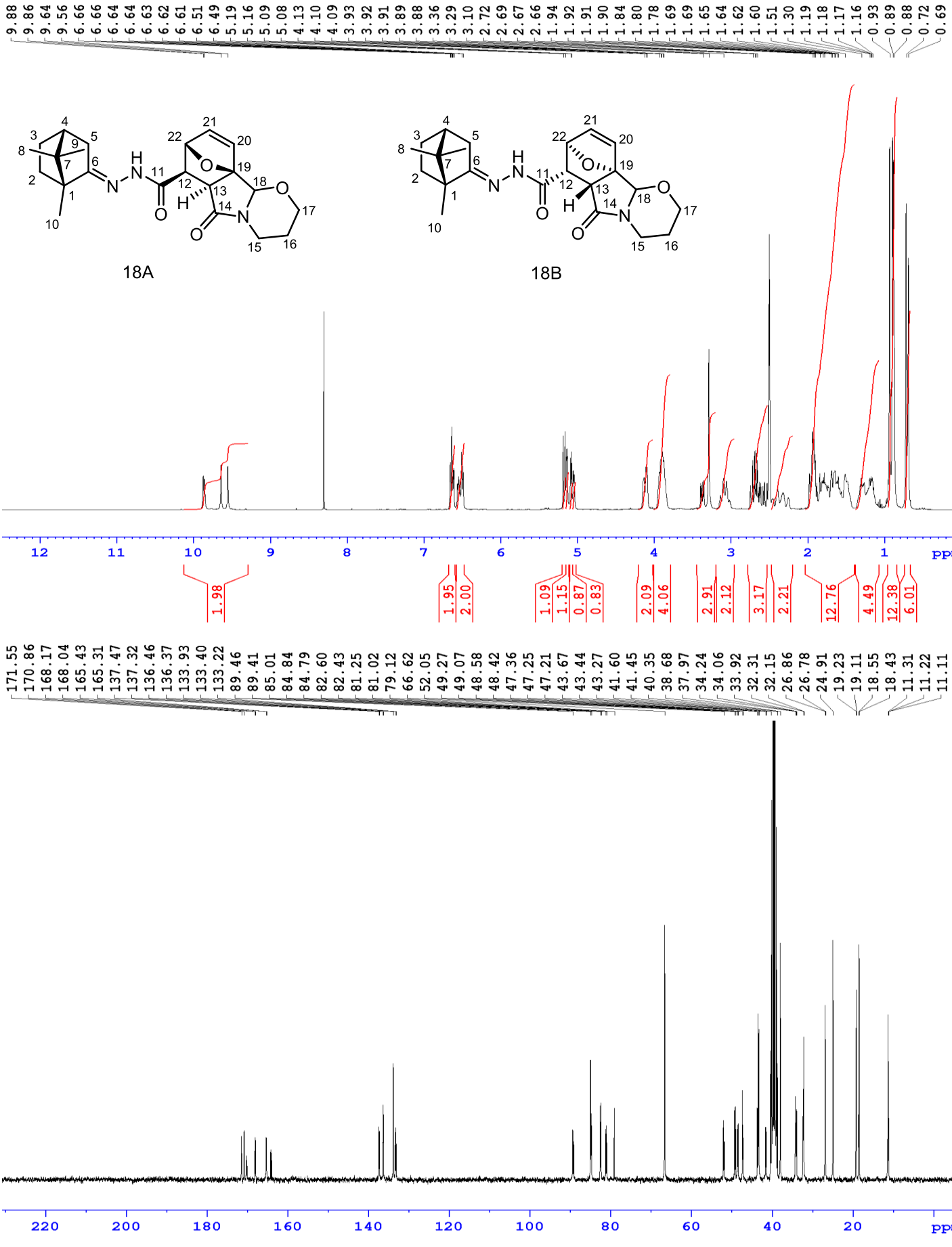
2D $^{1}H,^{15}N$-HMBC (DMSO-d_6, 300.1 & 30.4 MHz)



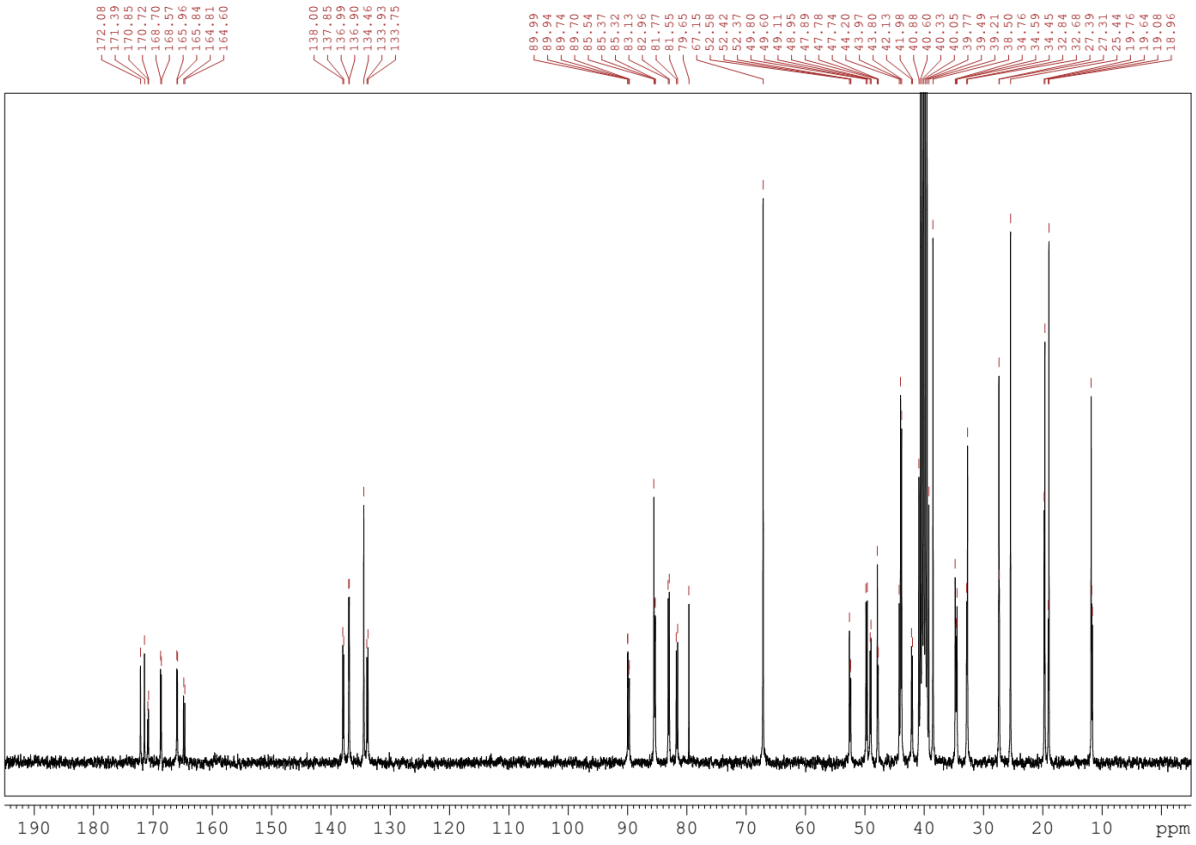
2.13. A mixture of diastereomers (1R,2S,4aR,11aS)-11-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (A) and (1S,2R,4aS,11aR)-11-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (B) 19 ($CDCl_3$, 400.0 MHz)



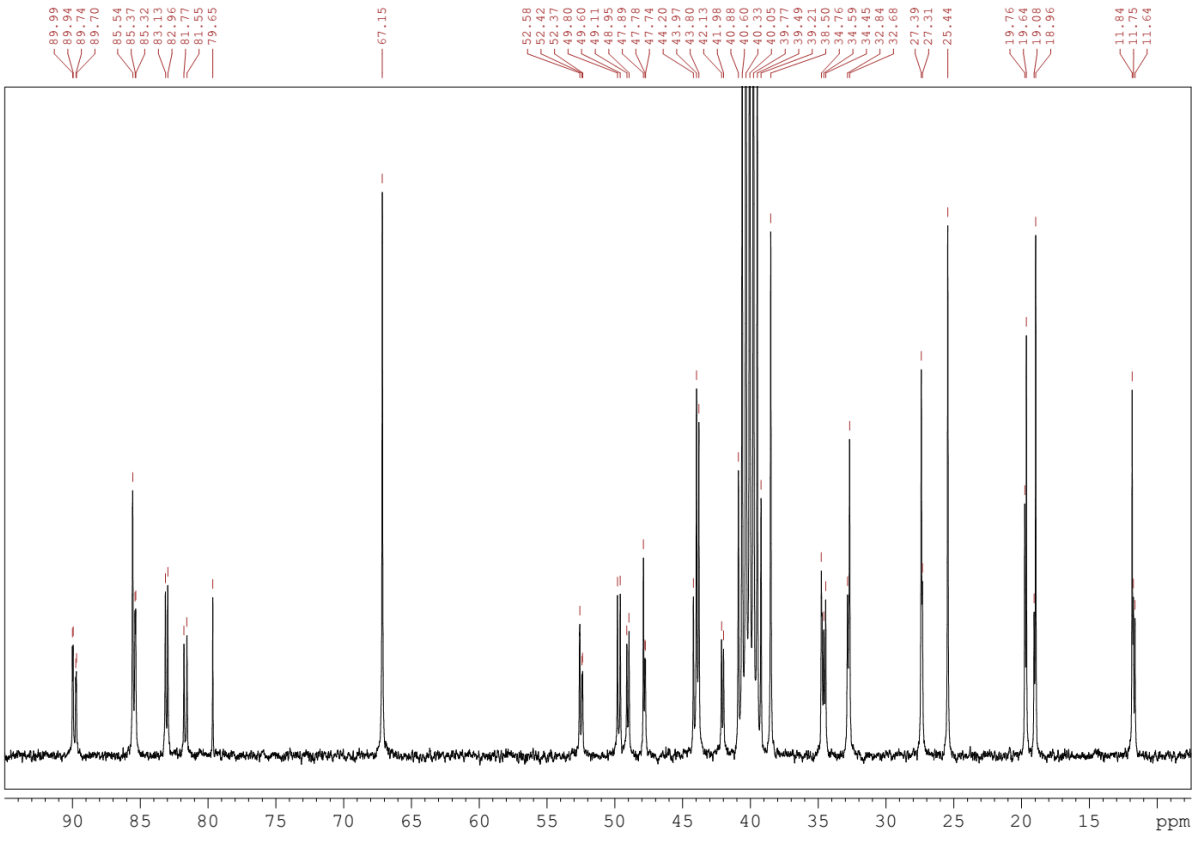
2.14. A mixture of diastereomers (6aS,7R,8S,10aR,10bR)-6-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (A) and (6aR,7S,8R,10aS,10bS)-6-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (B) 18 (DMSO-d_6, 300 & 75.5 MHz)



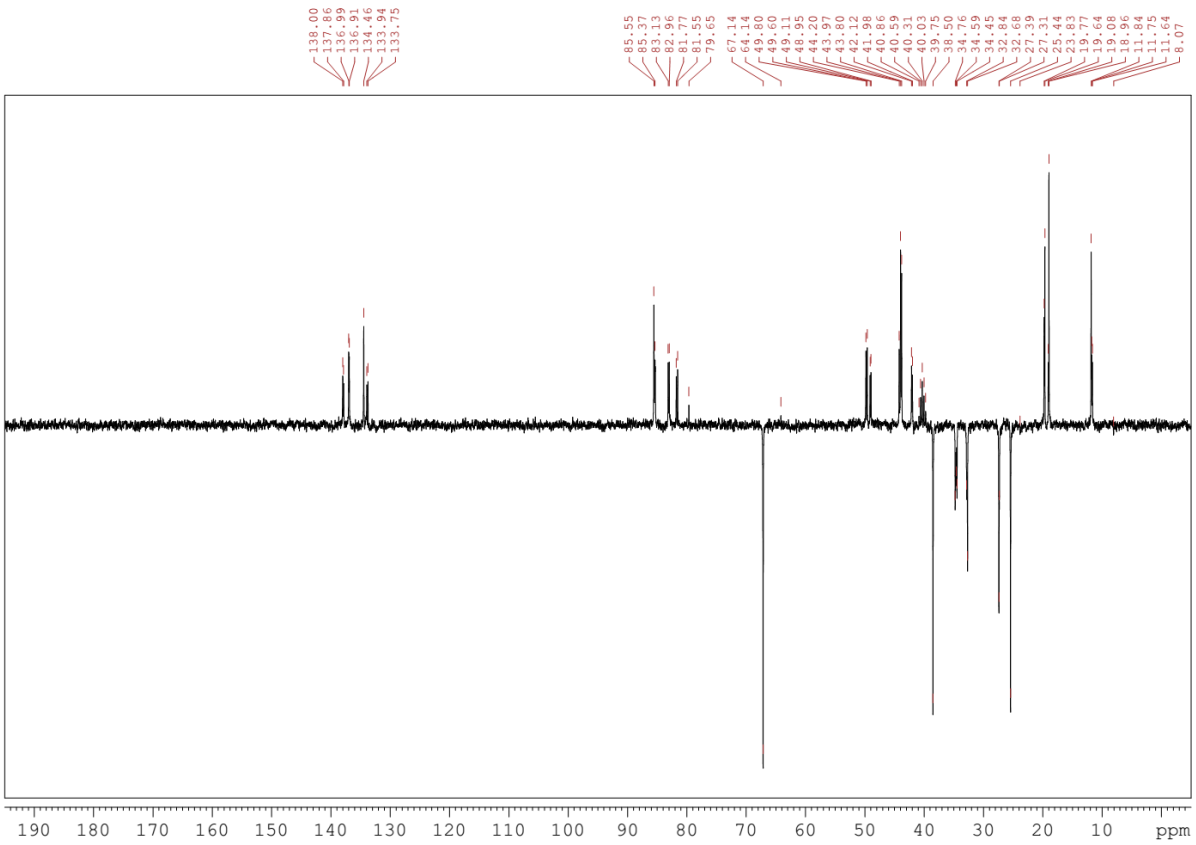
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



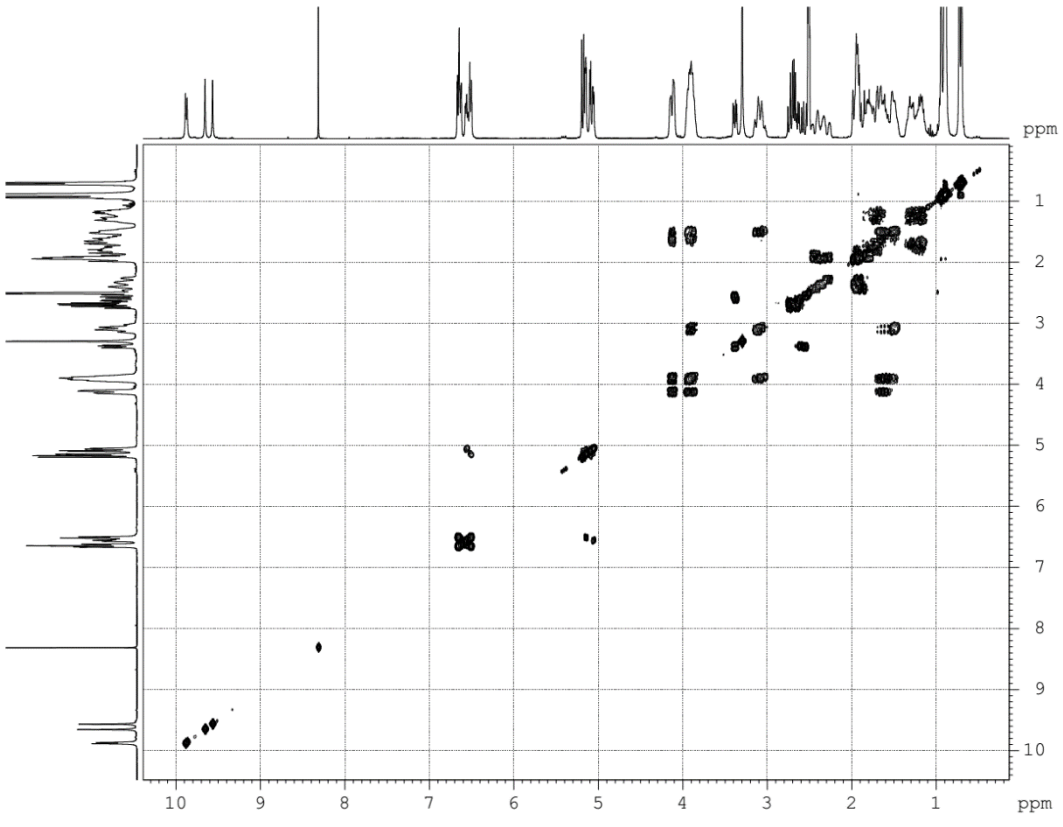
$^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 75.5 MHz)



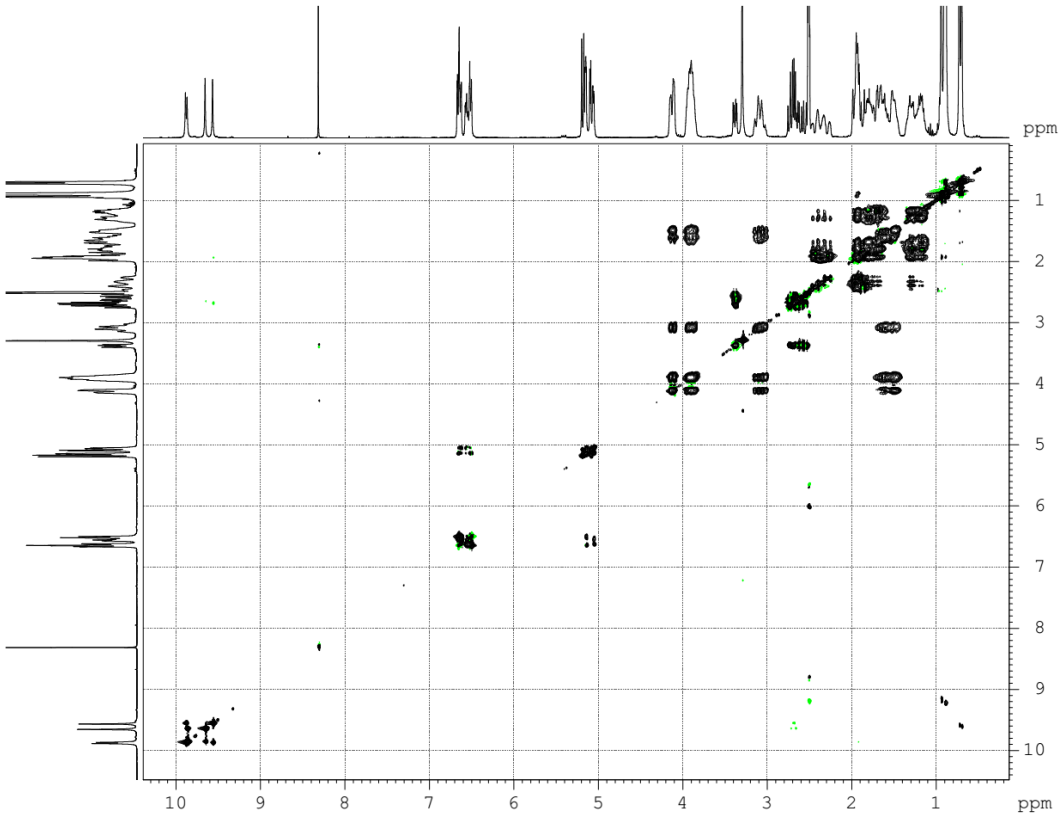
DEPT-135 NMR (DMSO-d_6, 75.5 MHz)



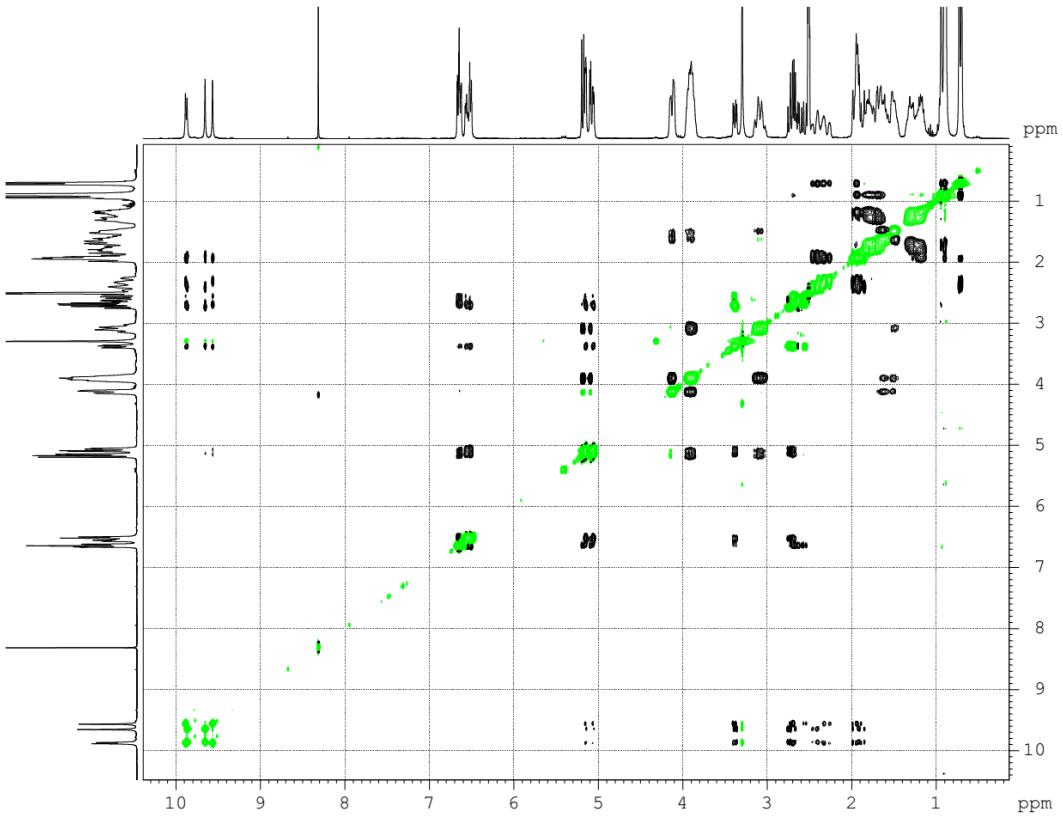
2D ^{1}H,^{1}H-COSY (DMSO-d_6, 300.1 MHz)



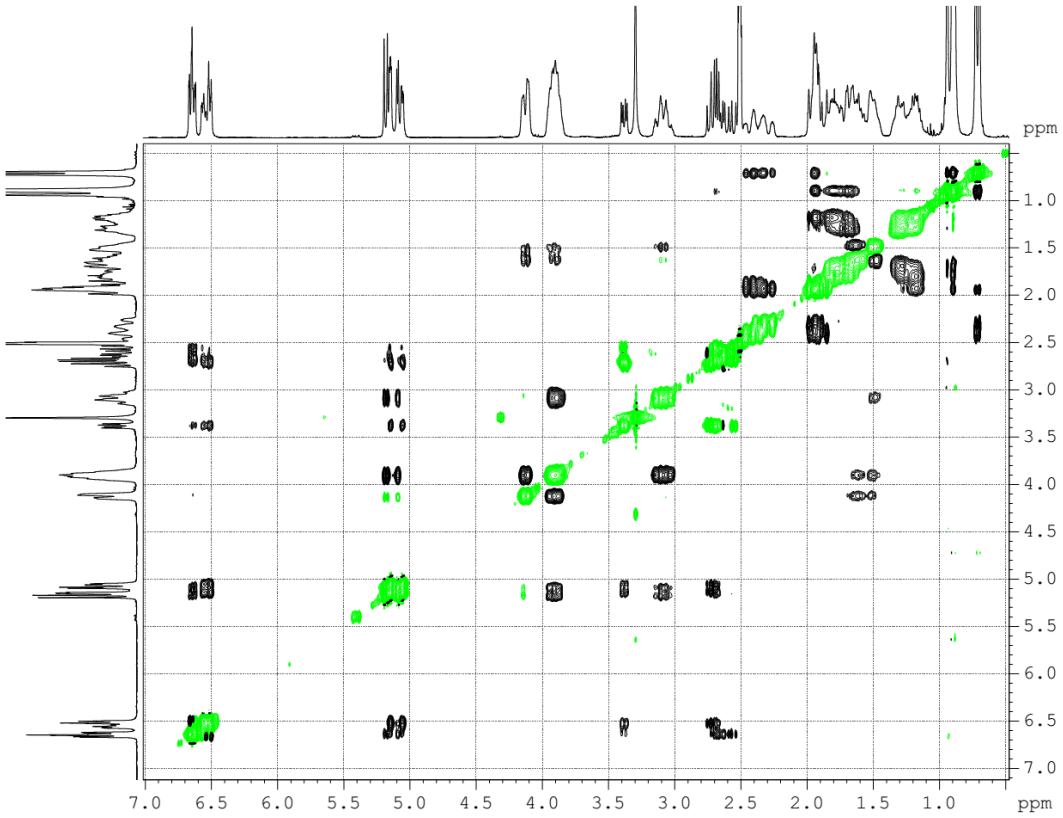
2D ^{1}H,^{1}H-TOCSY (DMSO-d_6, 300.1 MHz)



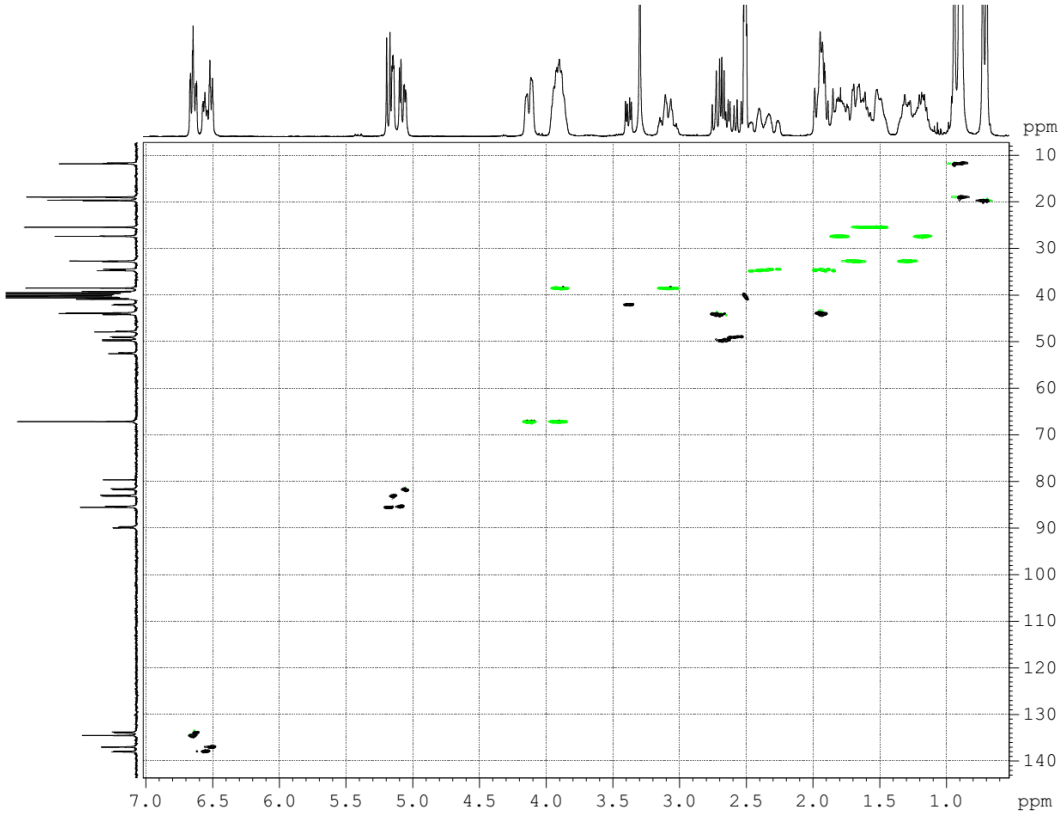
2D ^{1}H,^{1}H-NOESY (DMSO-d_6, 300.1 MHz)



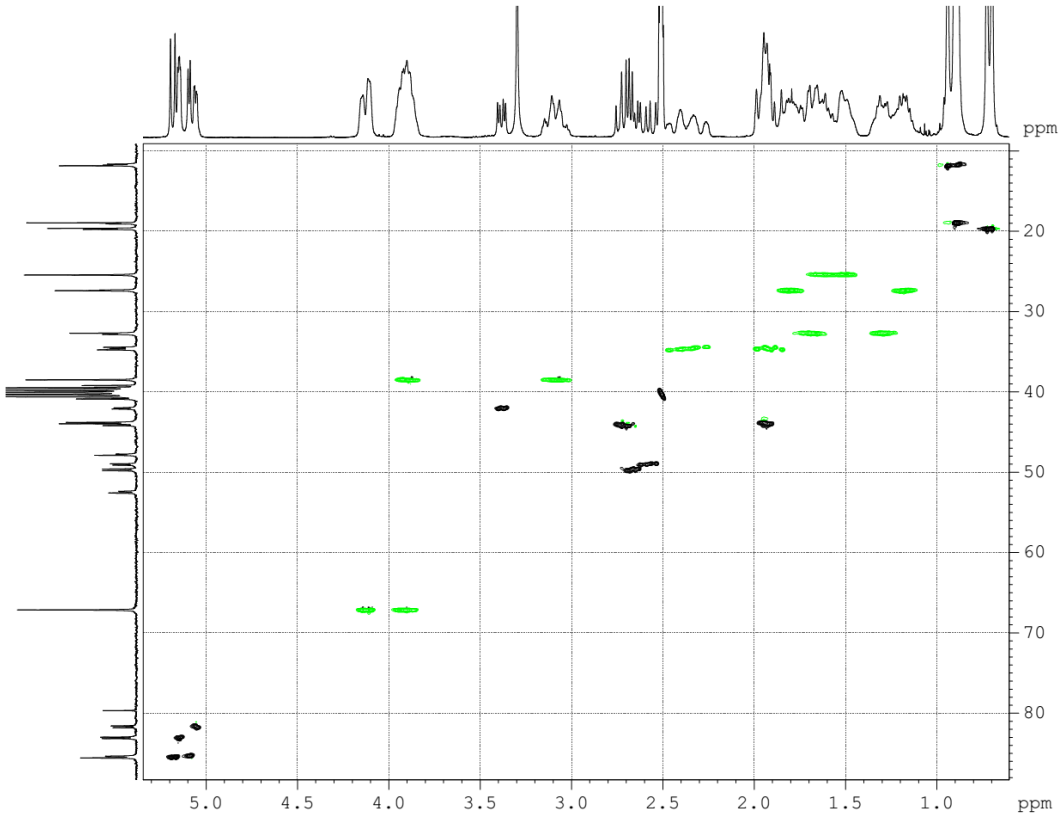
2D ^{1}H,^{1}H-NOESY (DMSO-d_6, 300.1 MHz)



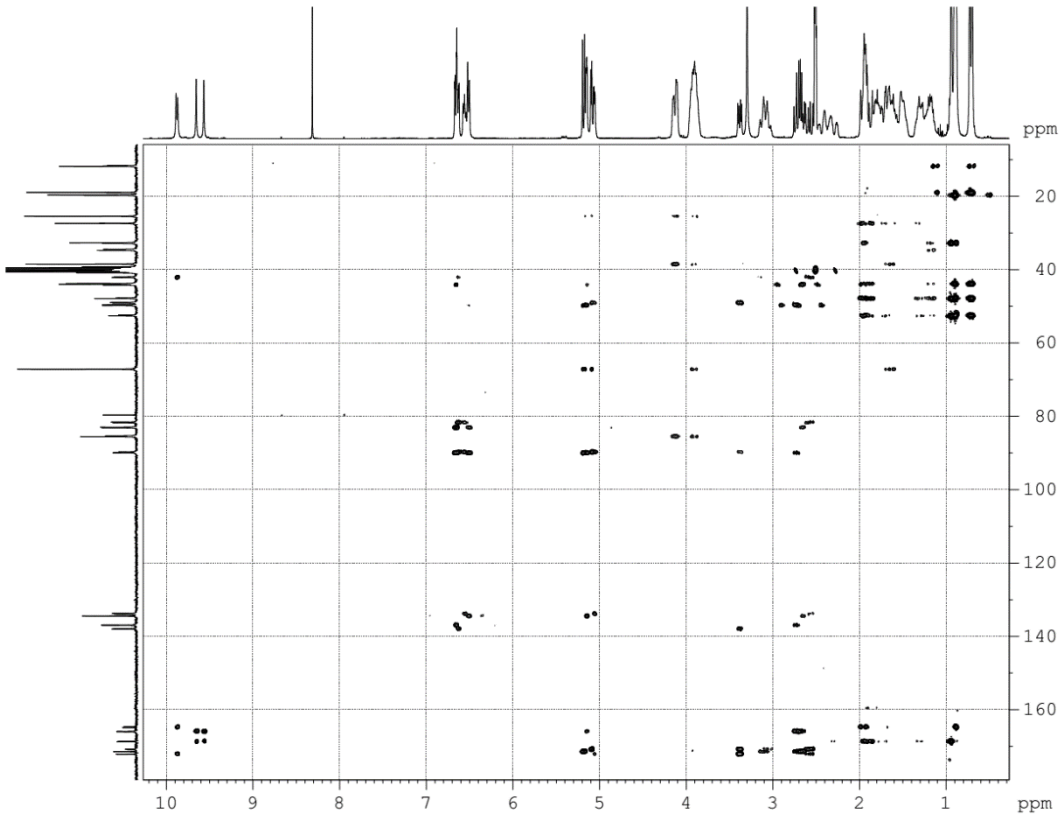
2D ^{1}H,^{13}C-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



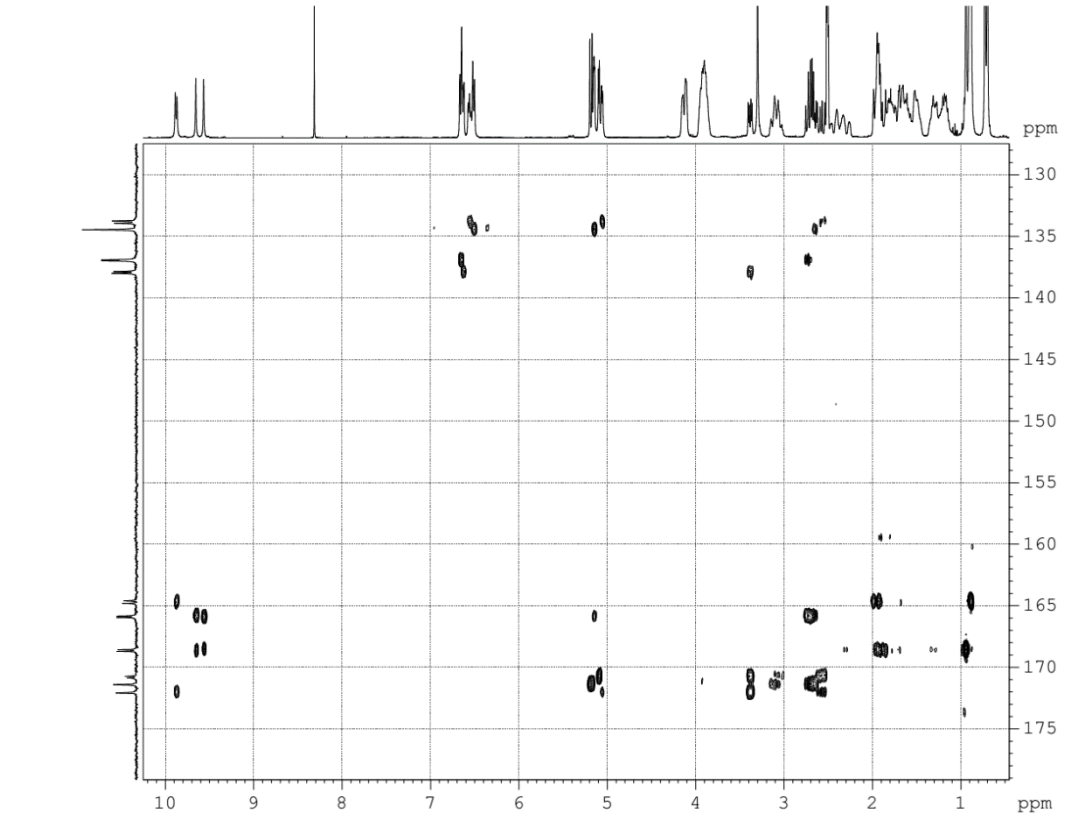
2D $^{1}H,^{13}C$-edited-HSQC (DMSO-d_6, 300.1 & 75.5 MHz)



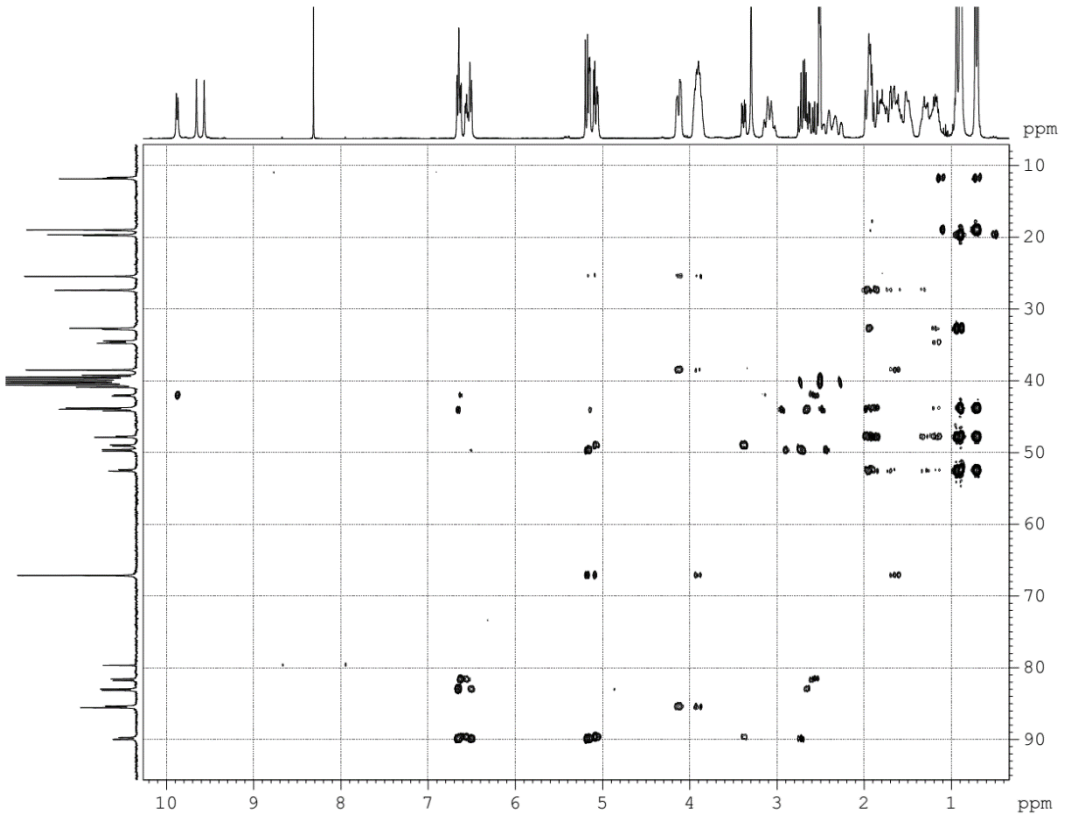
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



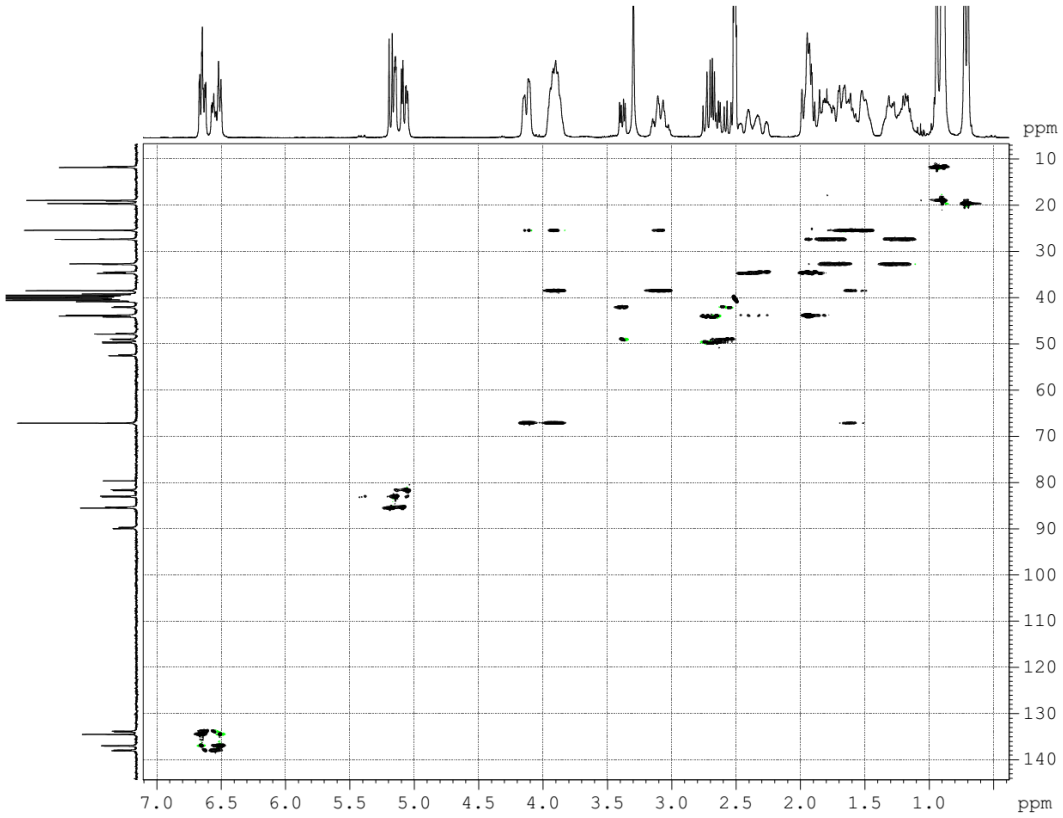
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



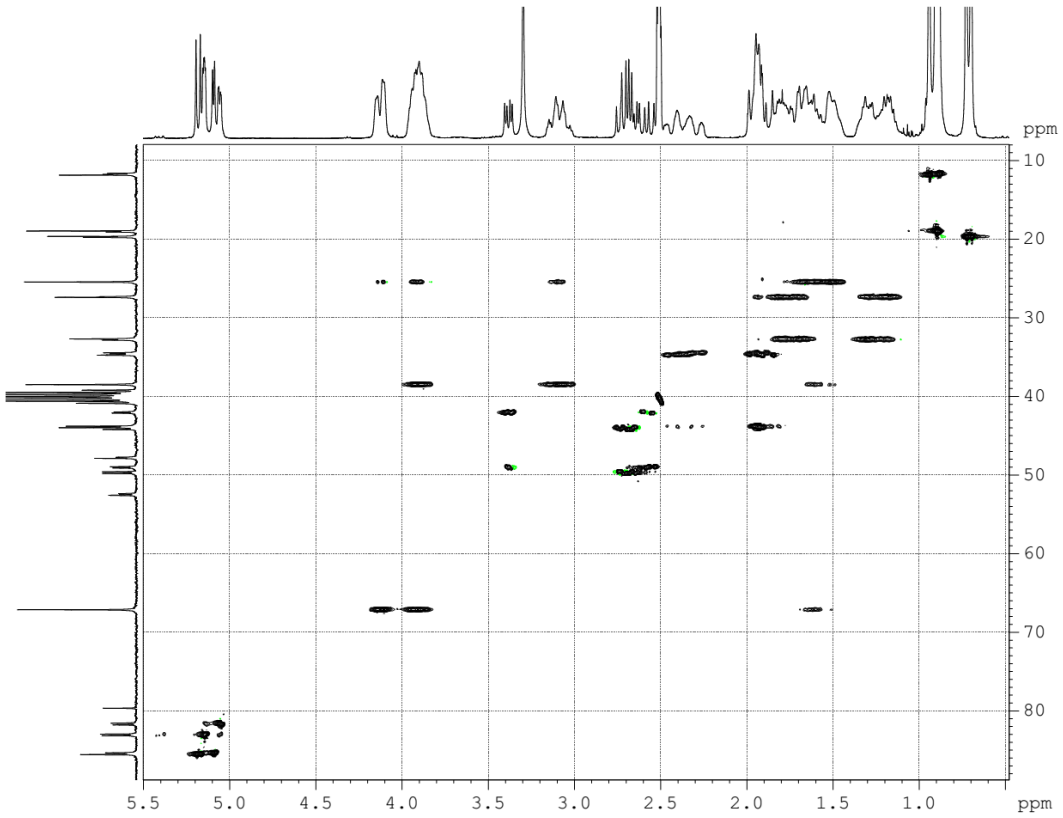
2D $^{1}H,^{13}C$-HMBC (DMSO-d_6, 300.1 & 75.5 MHz)



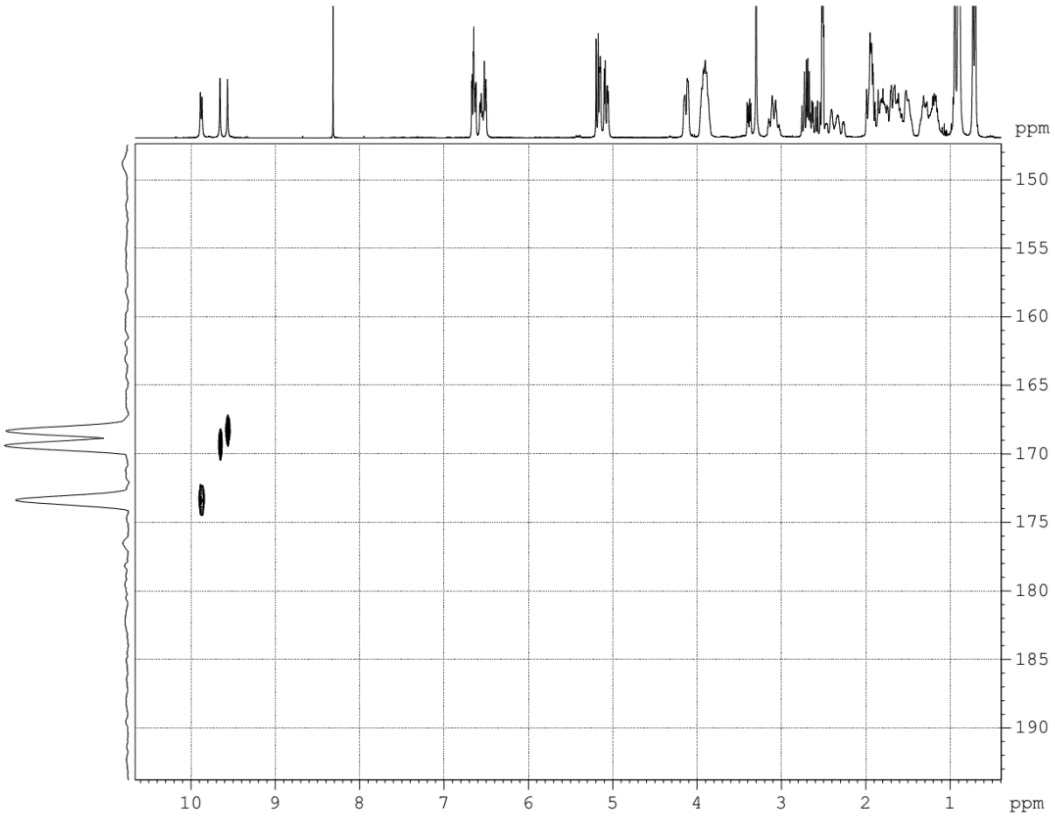
2D $^{1}H,^{13}C$-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



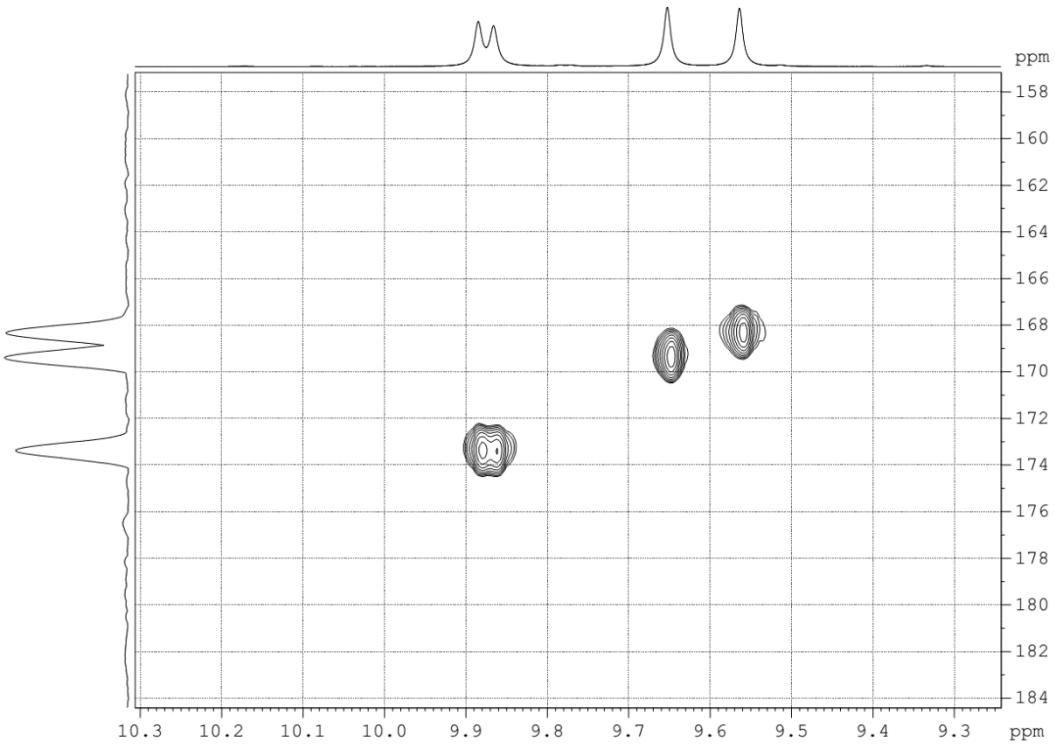
2D $^{1}H,^{13}C$-HSQC-COSY (DMSO-d_6, 300.1 & 75.5 MHz)



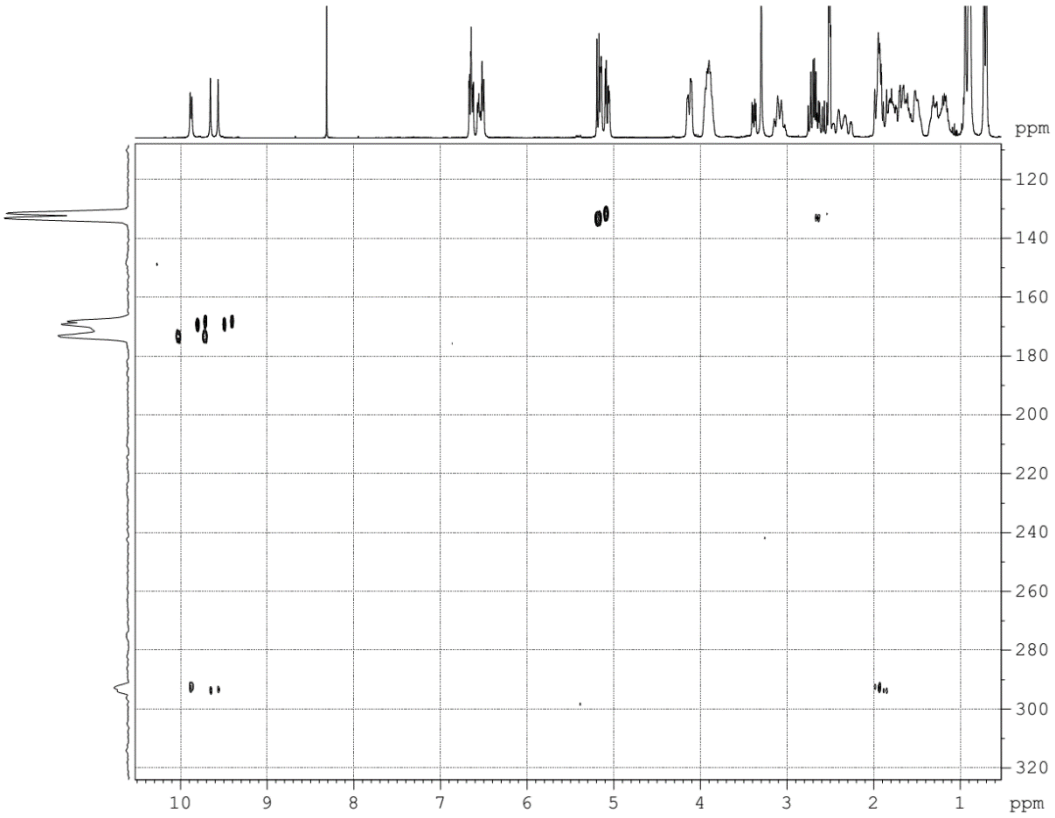
2D ^{1}H,^{15}N-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)



2D ^{1}H,^{15}N-HSQC (DMSO-d_6, 300.1 & 30.4 MHz)

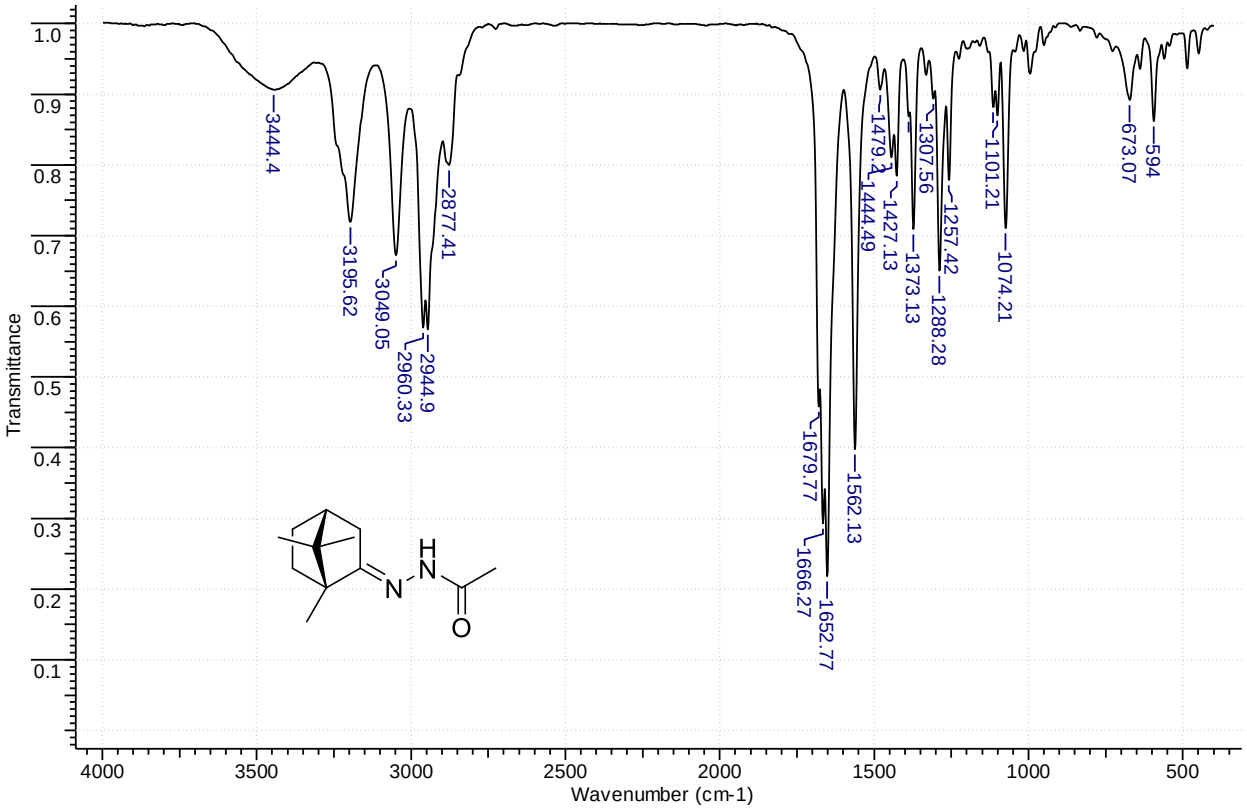


2D $^{1}H,^{15}N$-HMBC (DMSO-d_6, 300.1 & 30.4 MHz)

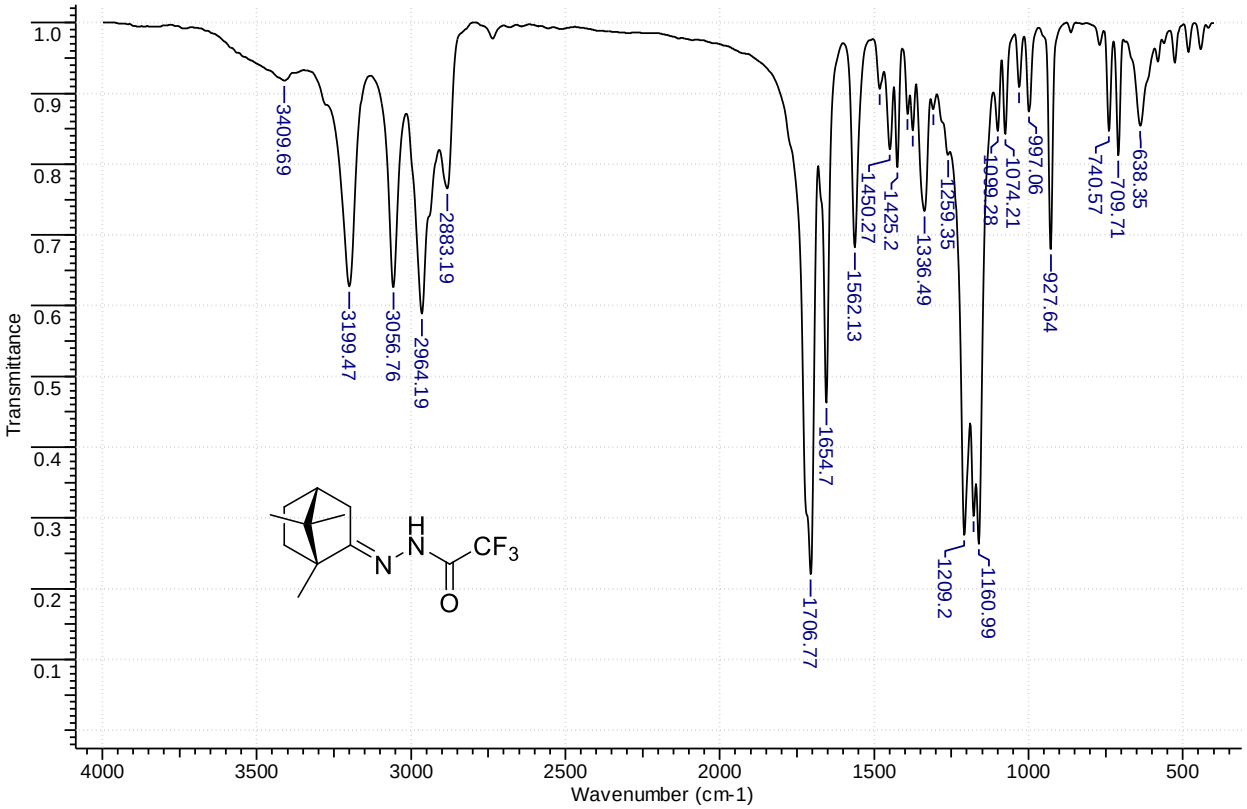


3. Copies of the IR Spectra for selected compounds

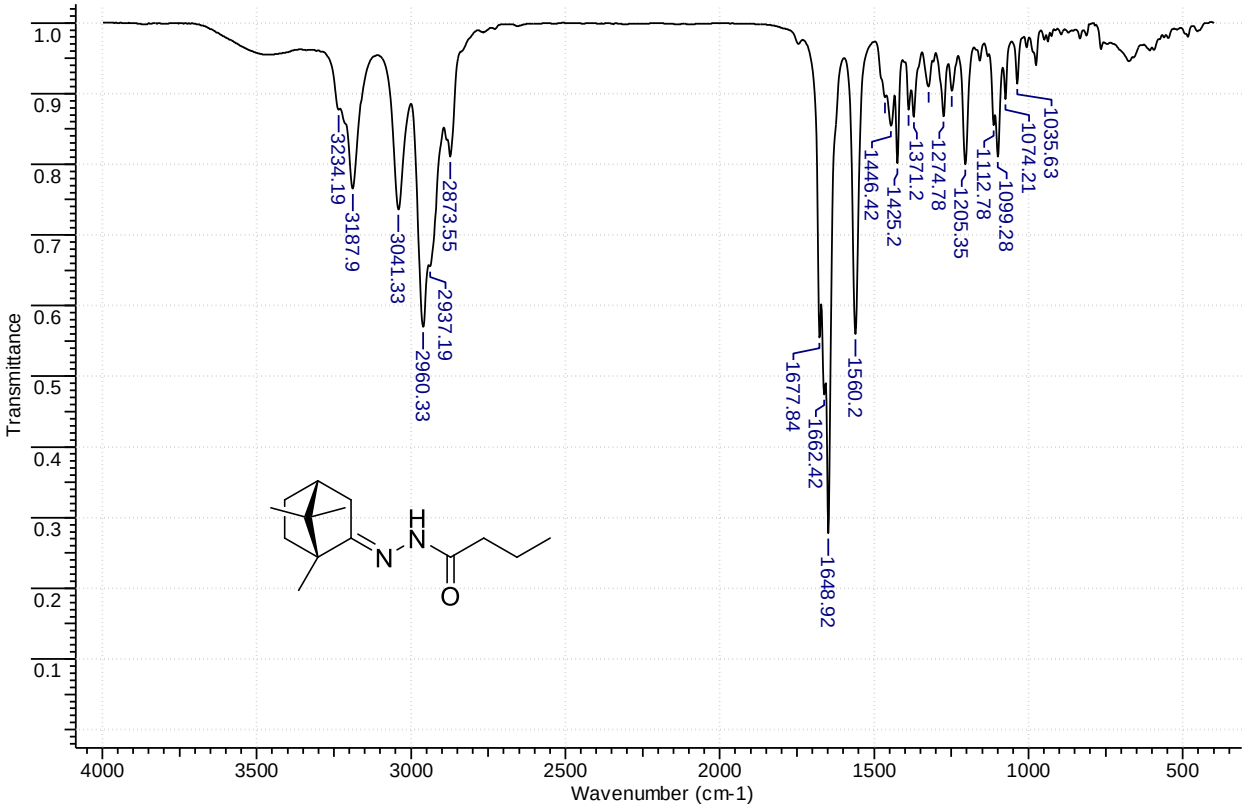
3.1. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)acetohydrazide (6)



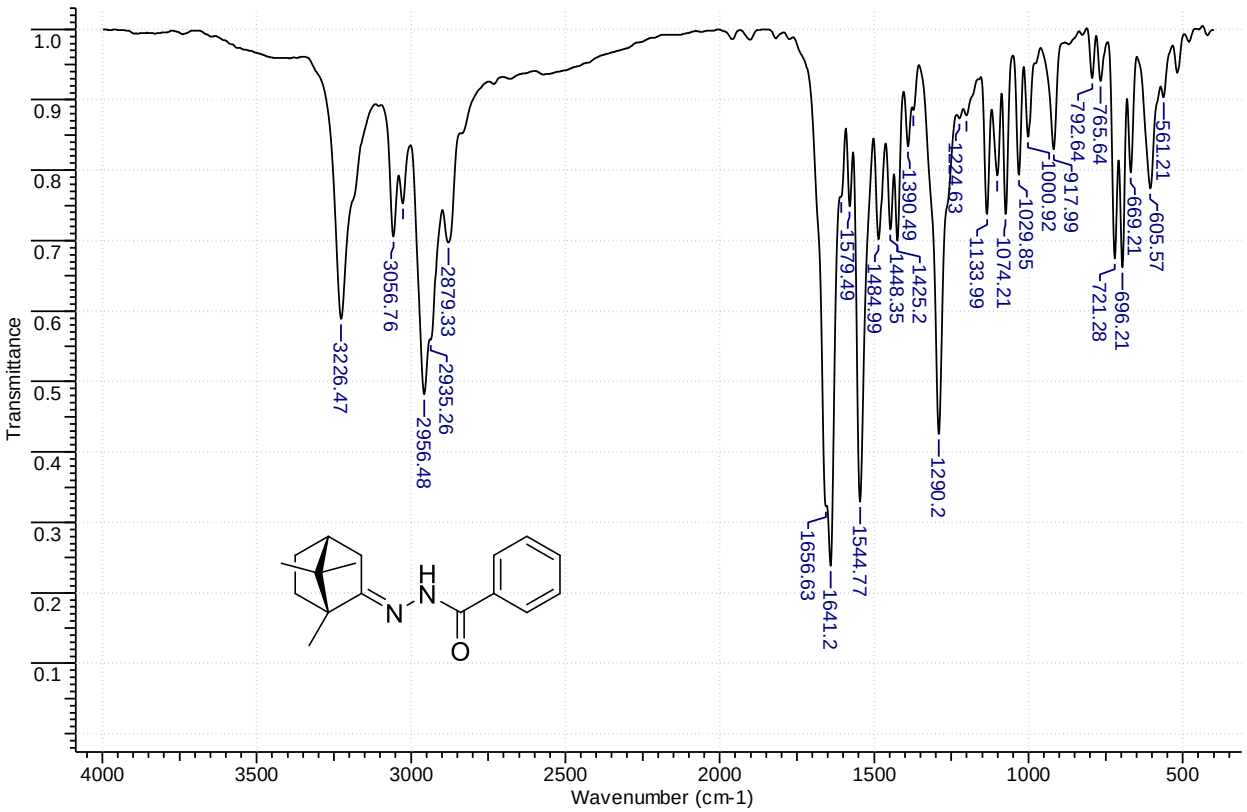
3.2. (E)-2,2,2-trifluoro-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)acetohydrazide (7)



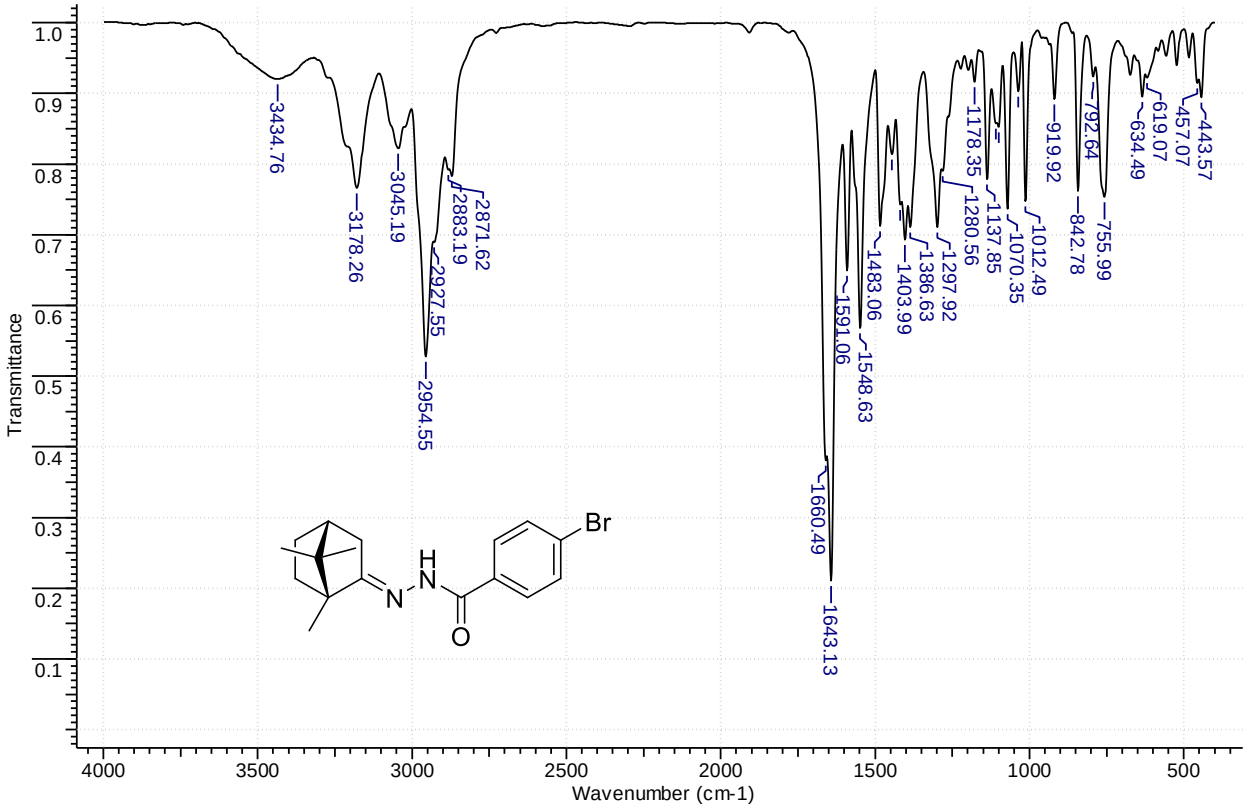
3.3 (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)butyrohydrazide (8)



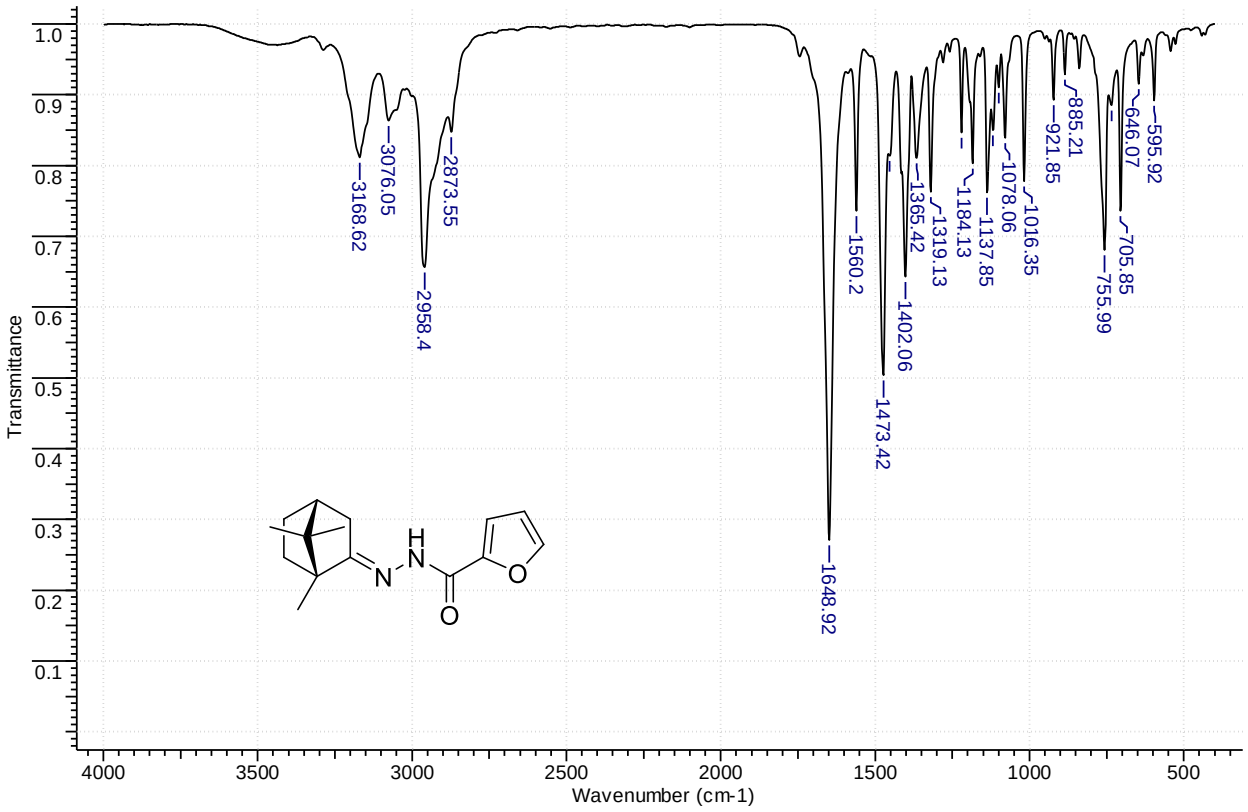
3.4 (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)benzohydrazide (9)



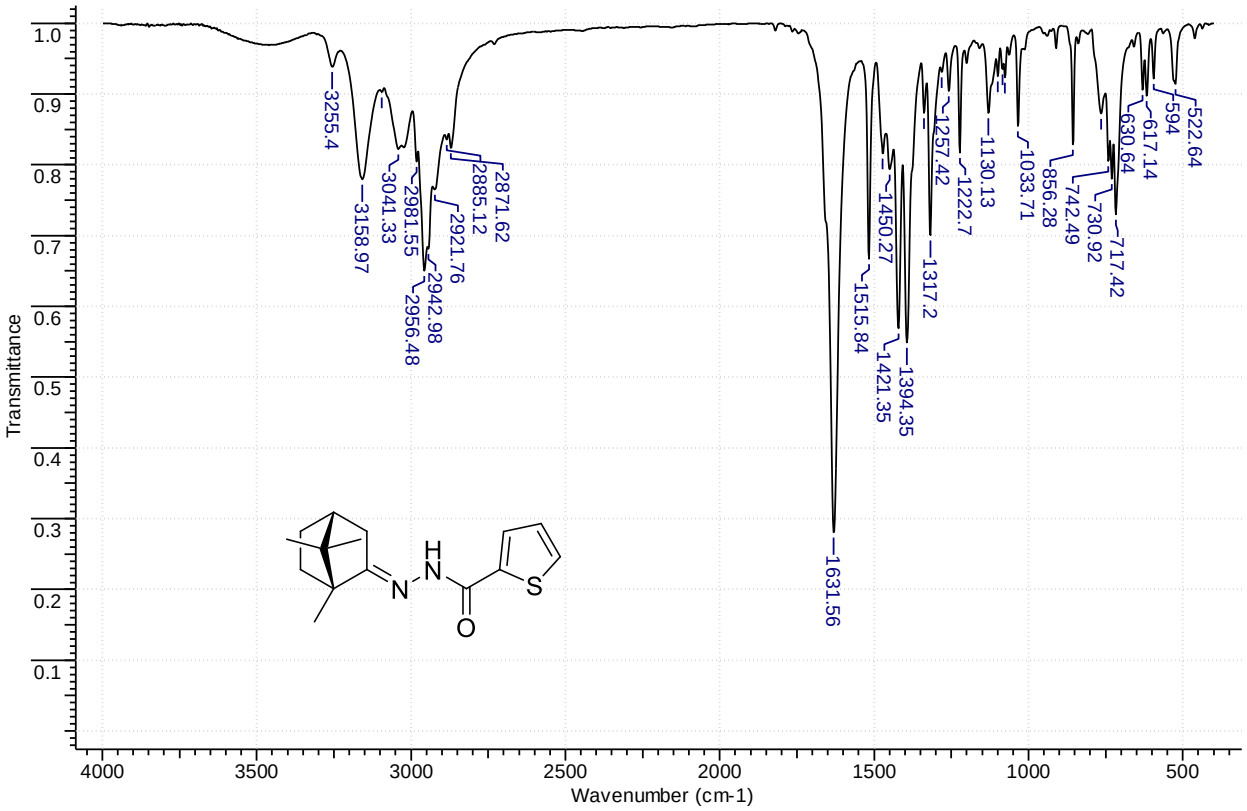
3.5 (E)-4-bromo-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)benzohydrazide (10)



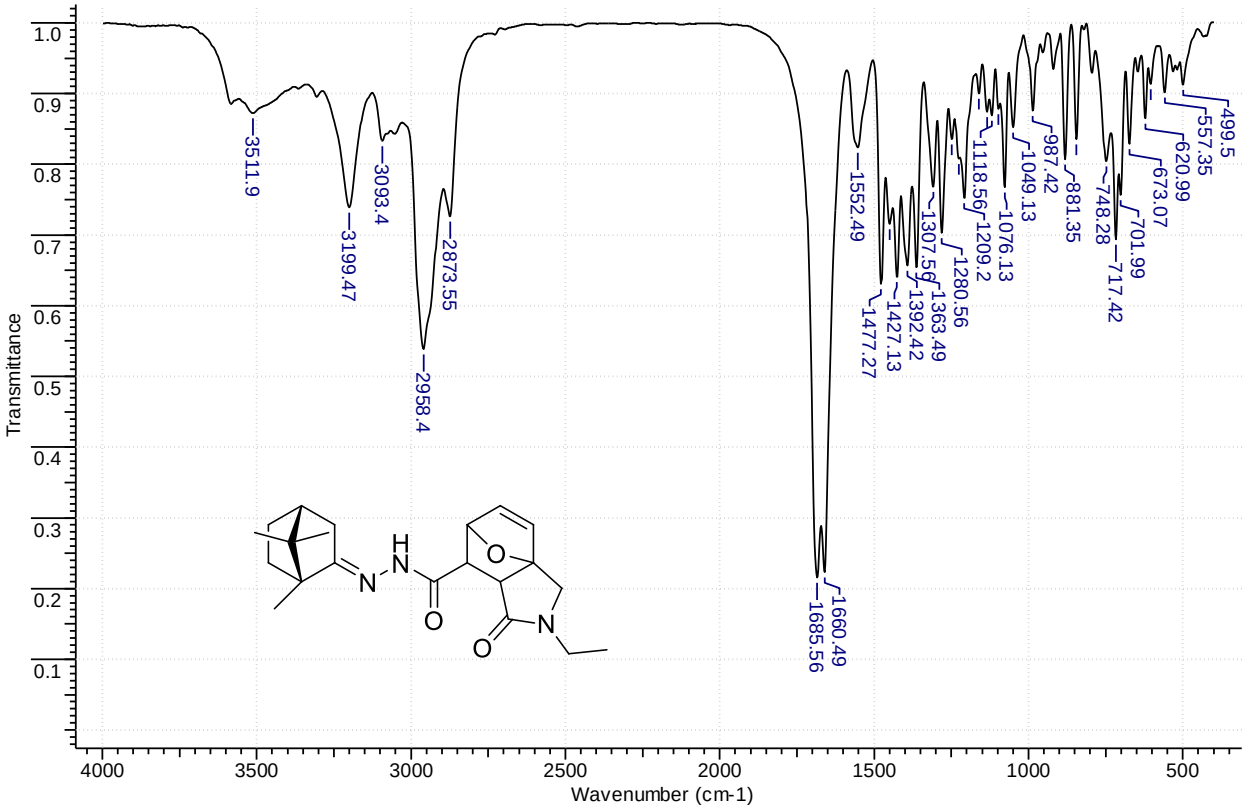
3.6 (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)furan-2-carbohydrazide (11)



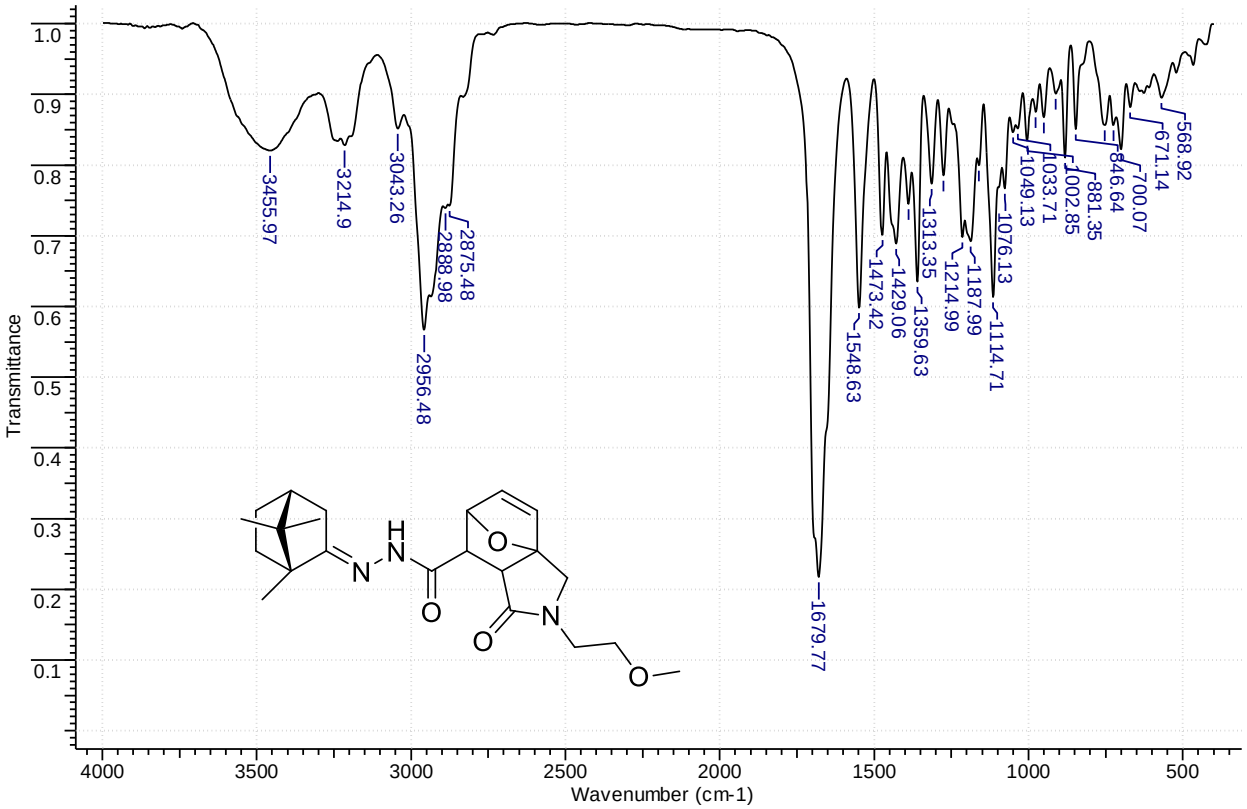
3.7. N'-[(1*R*,2*E*,4*R*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]thiophene-2-carbohydrazide (12)



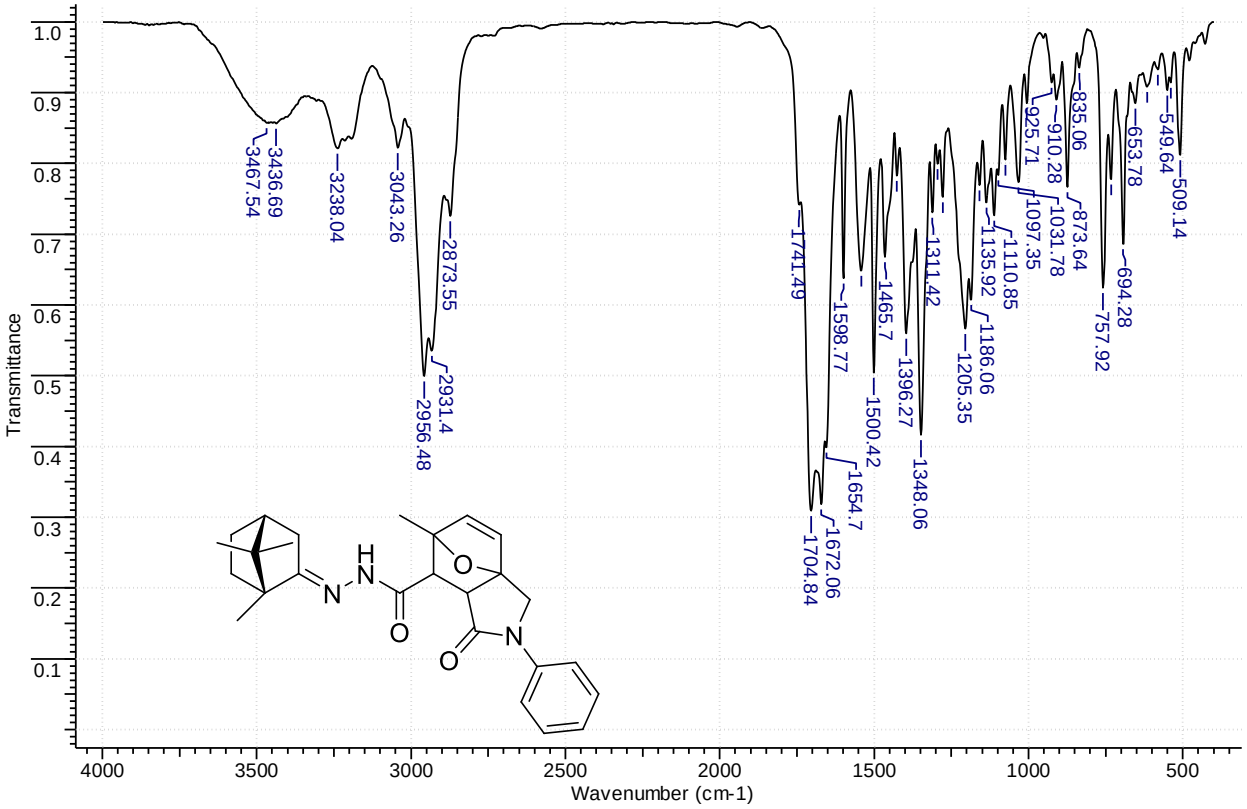
3.8 Mixture of (3a*R*,6*S*,7*R*,7a*S*)-2-ethyl-1-oxo-*N*'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-2-ethyl-1-oxo-*N*'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) 13



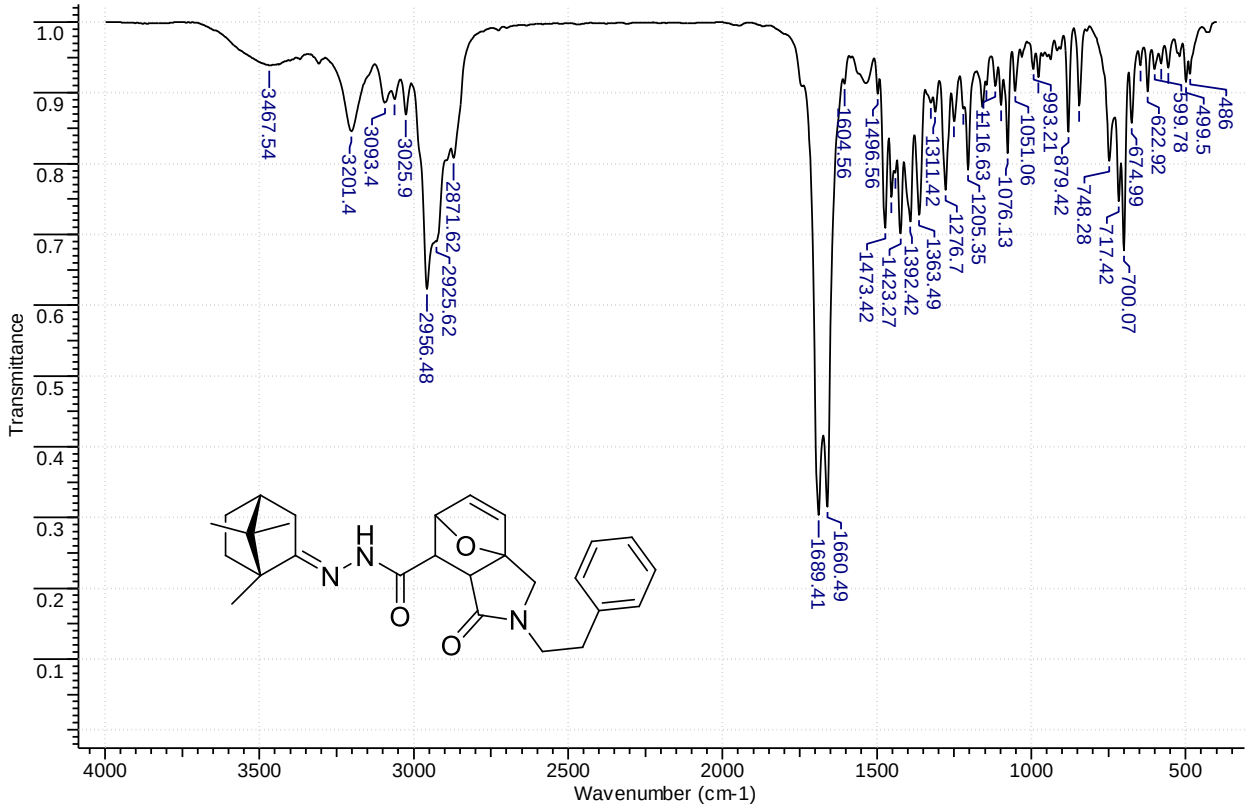
3.9. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-2-(2-methoxyethyl)-1-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-2-(2-methoxyethyl)-1-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (14)



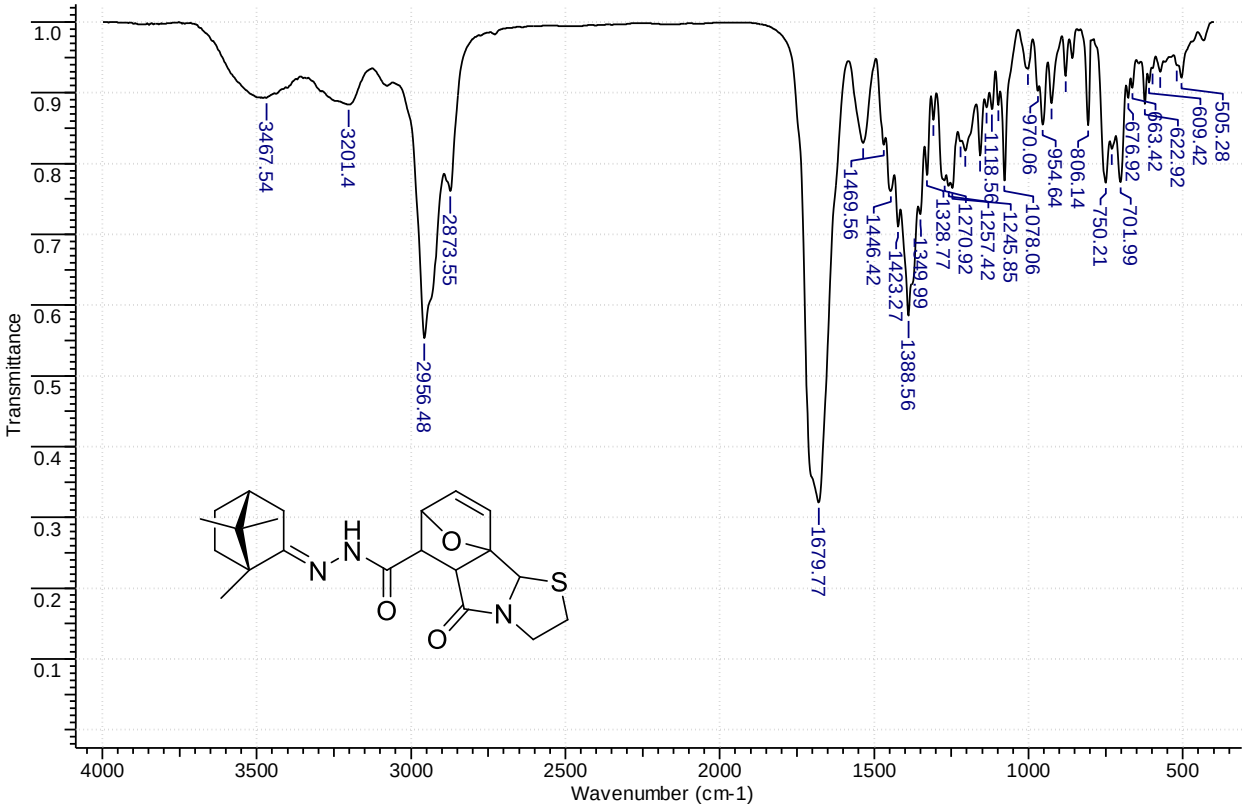
3.10. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-6-methyl-1-oxo-2-phenyl-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-6-methyl-1-oxo-2-phenyl-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (15)



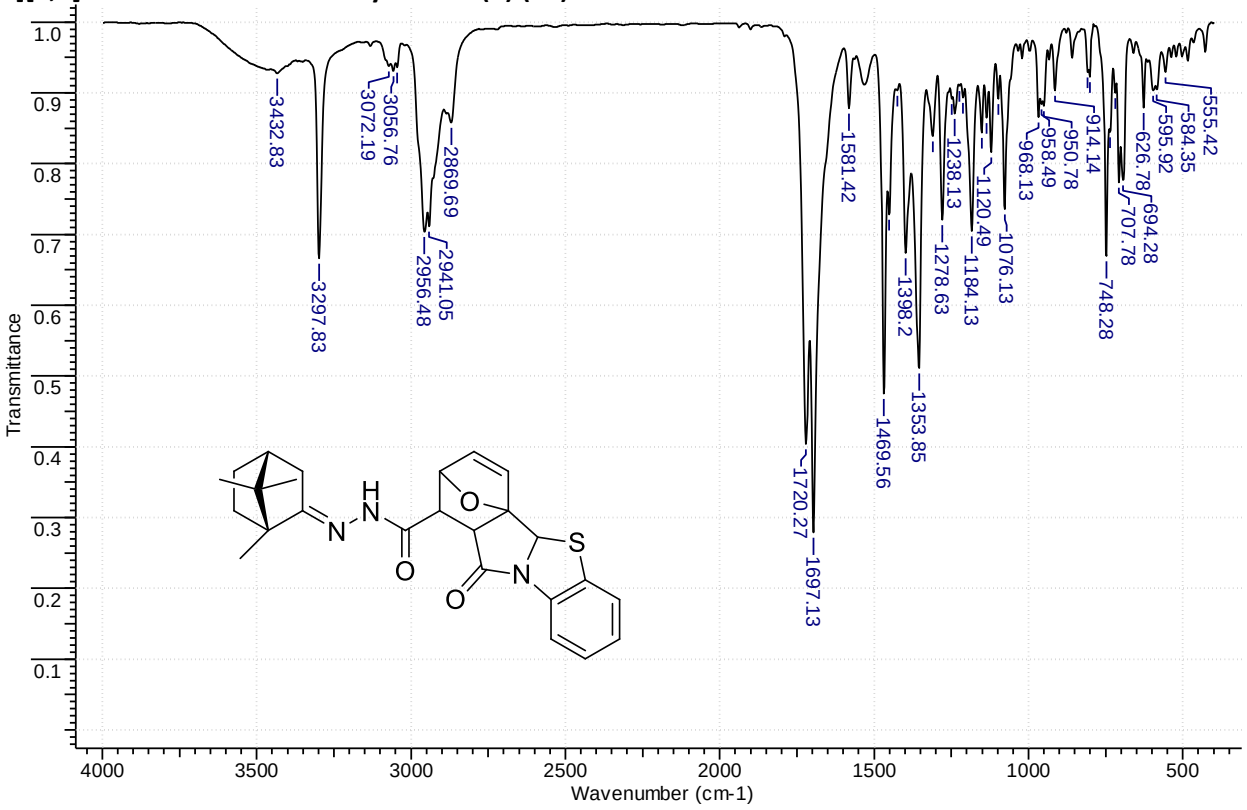
3.11. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-1-oxo-2-(2-phenylethyl)-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-1-oxo-2-(2-phenylethyl)-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (16)



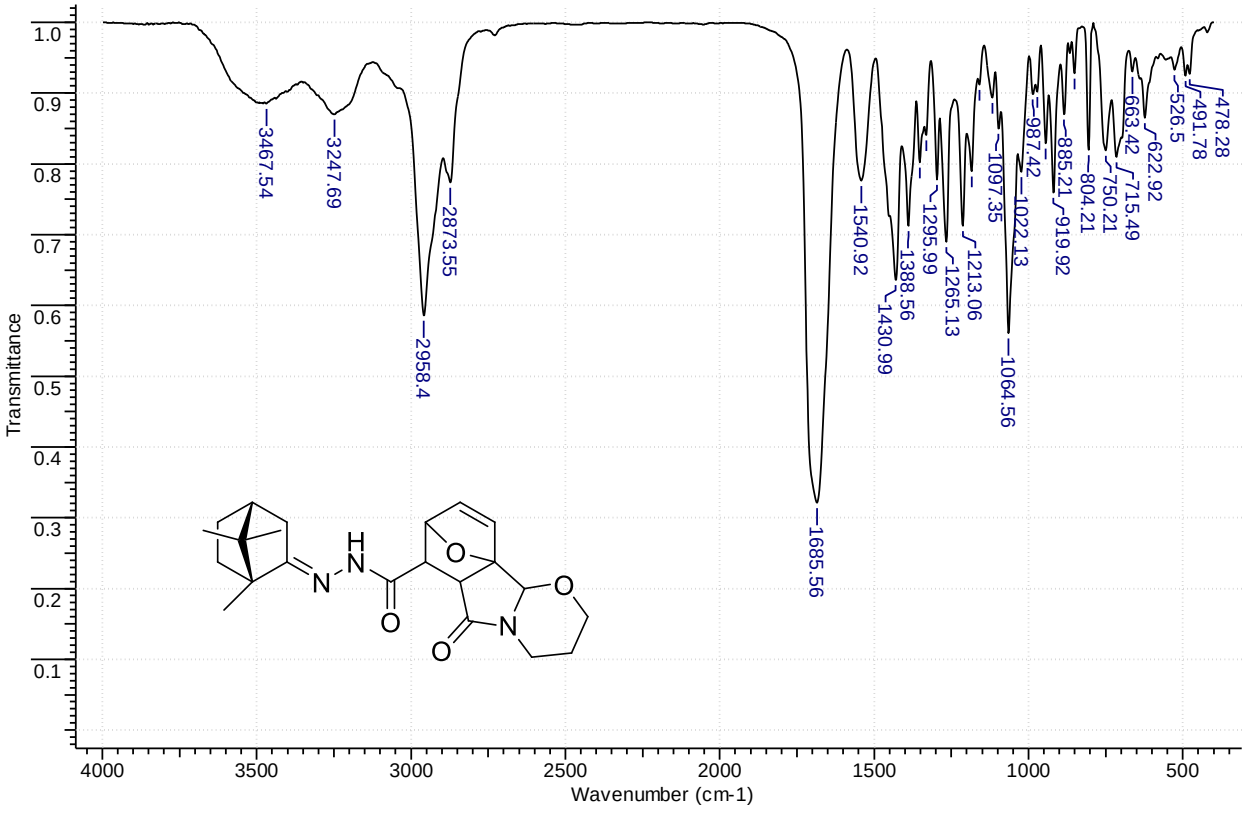
3.12. Mixture of (5a*S*,6*R*,7*S*,9a*R*)-5-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (a) and (5a*R*,6*S*,7*R*,9a*S*)-5-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (b) (17)



3.13. Mixture of (1*R*,2*S*,4a*R*,11a*S*)-11-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (a) and (1*S*,2*R*,4a*S*,11a*R*)-11-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (b) (19)

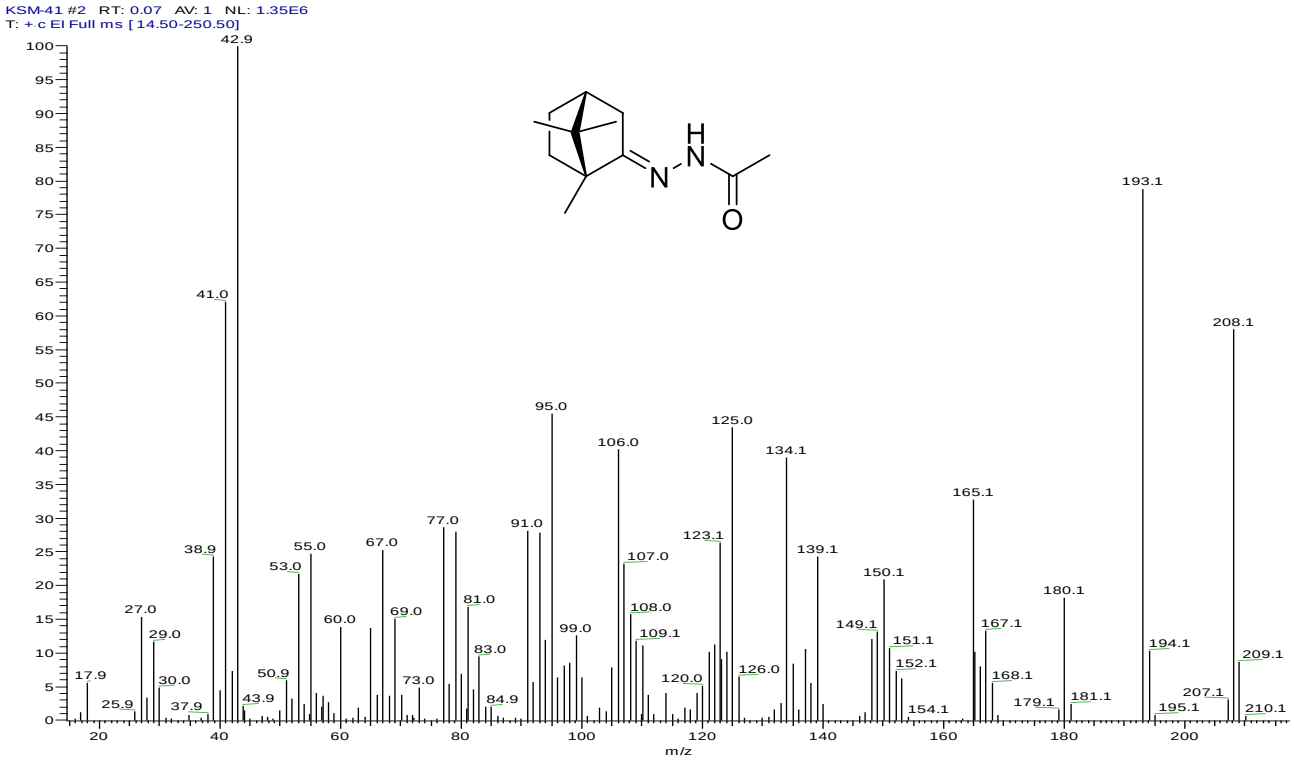


3.14. Mixture of (6a*S*,7*R*,8*S*,10a*R*,10b*R*)-6-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (a) and (6a*R*,7*S*,8*R*,10a*S*,10b*S*)-6-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (b) (18)

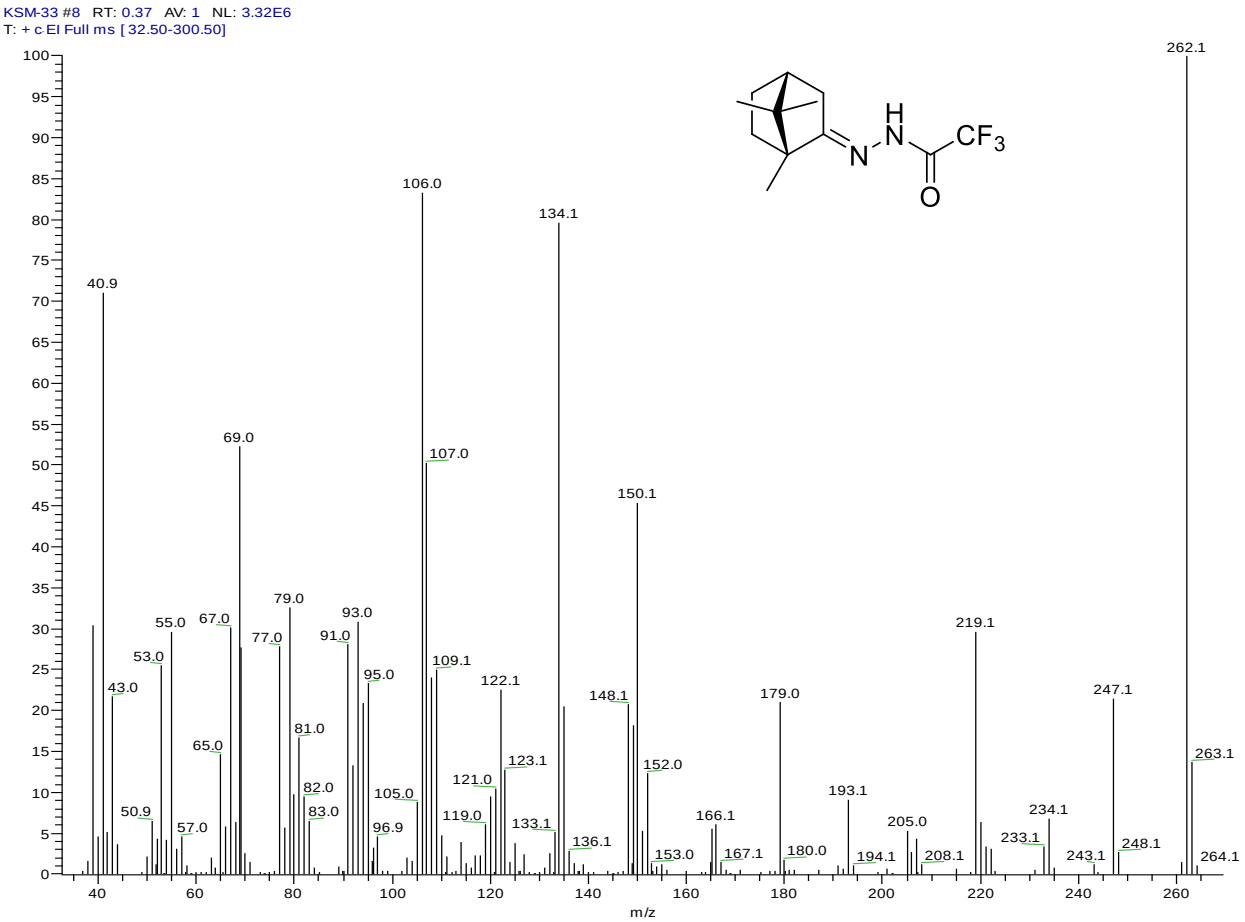


4. High Resolution Mass Spectra of Selected Compounds

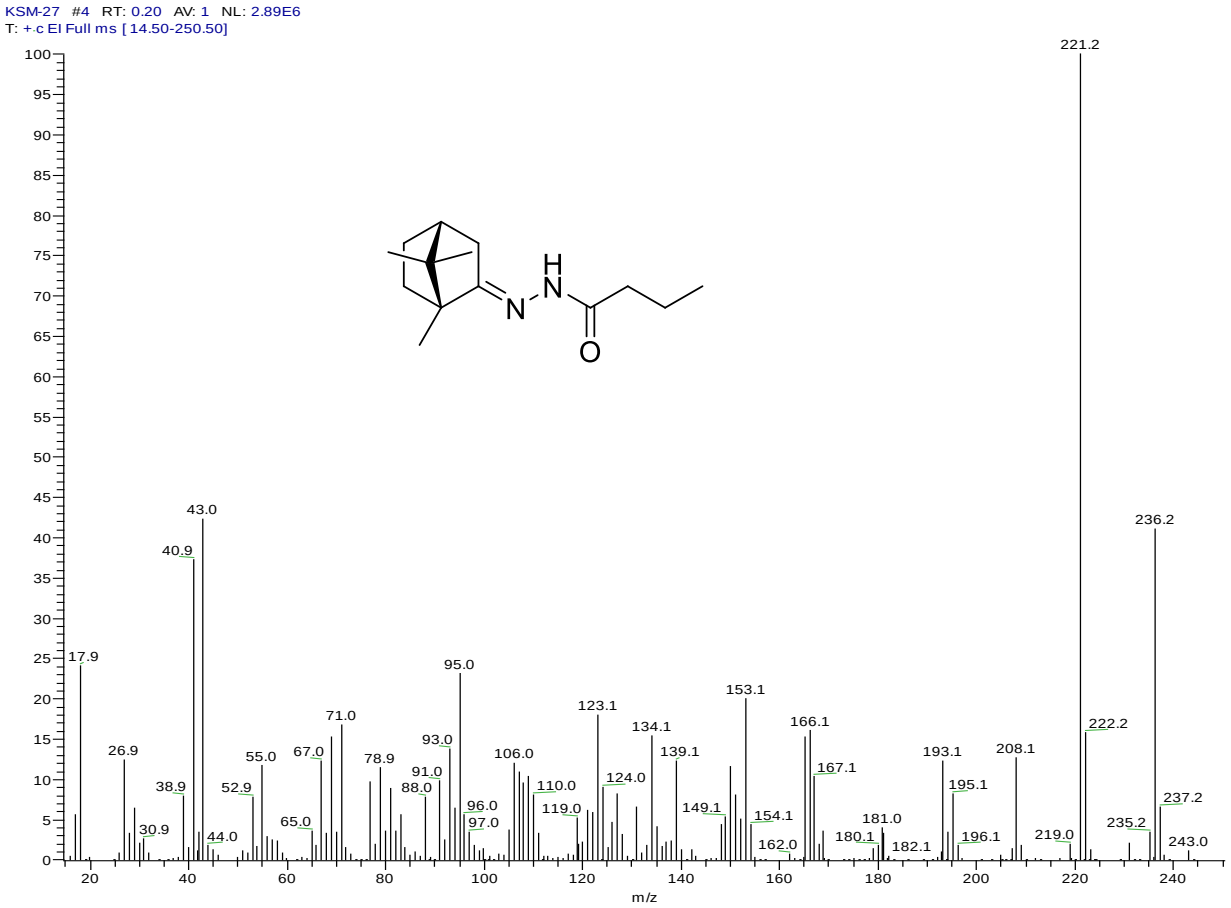
4.1. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)acetohydrazide (6)



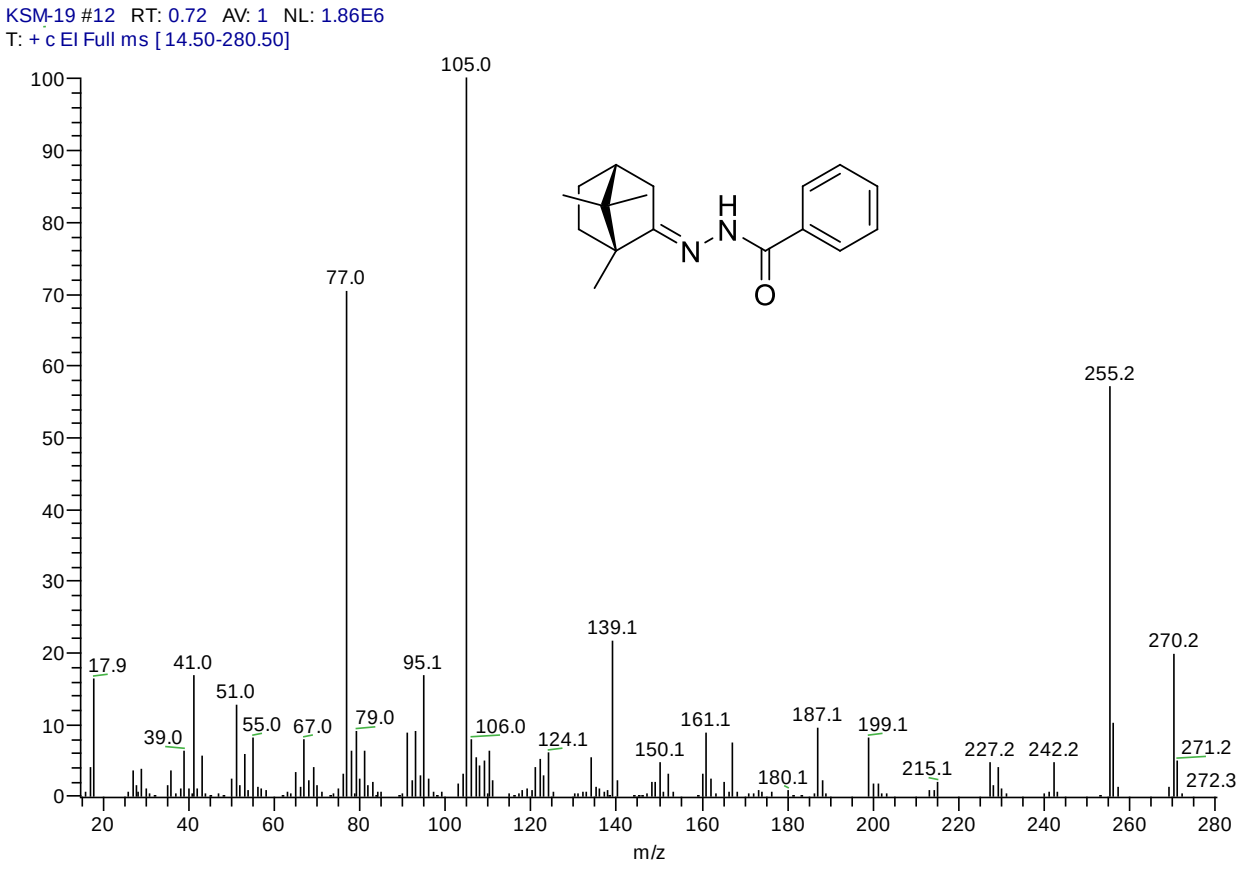
4.2. (E)-2,2,2-trifluoro-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)acetohydrazide (7)



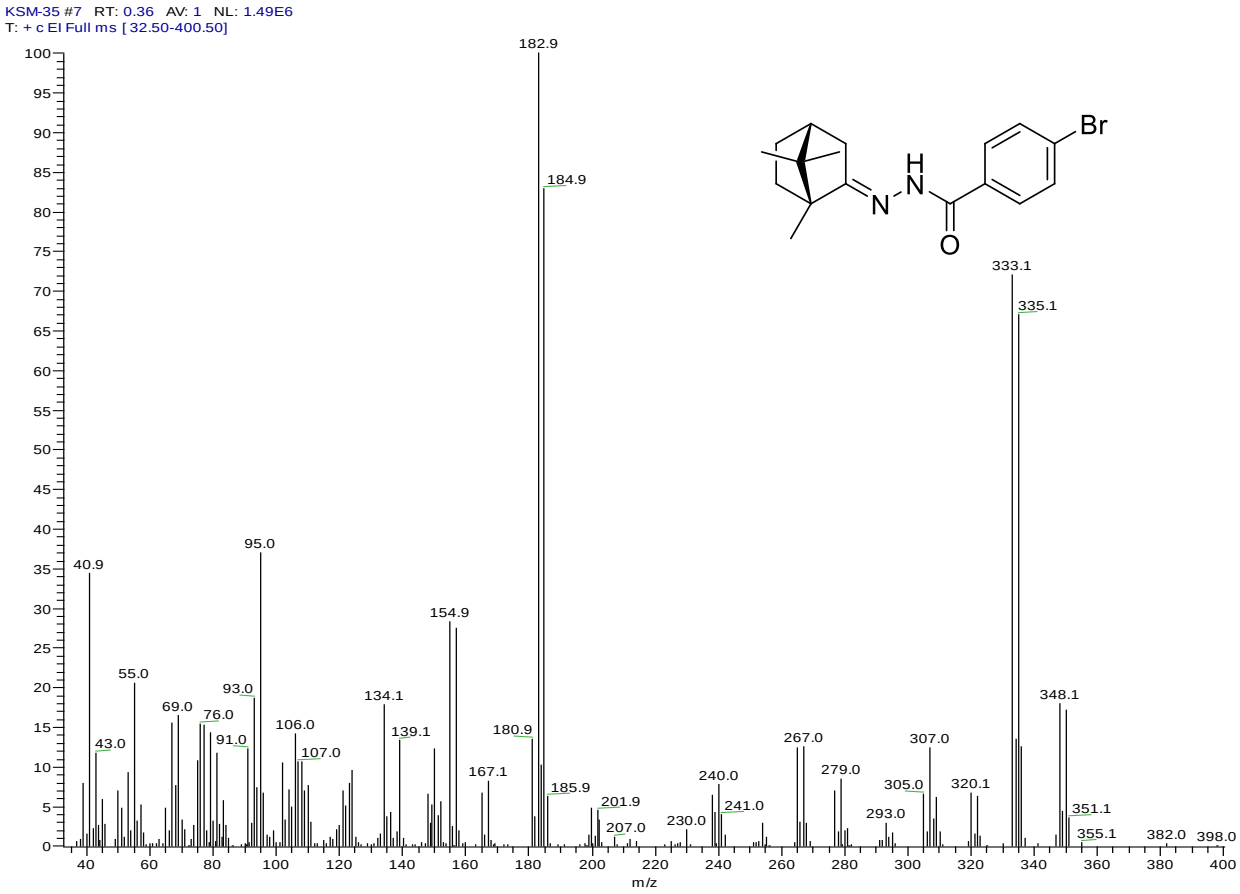
4.3. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)butyrohydrazide (8)



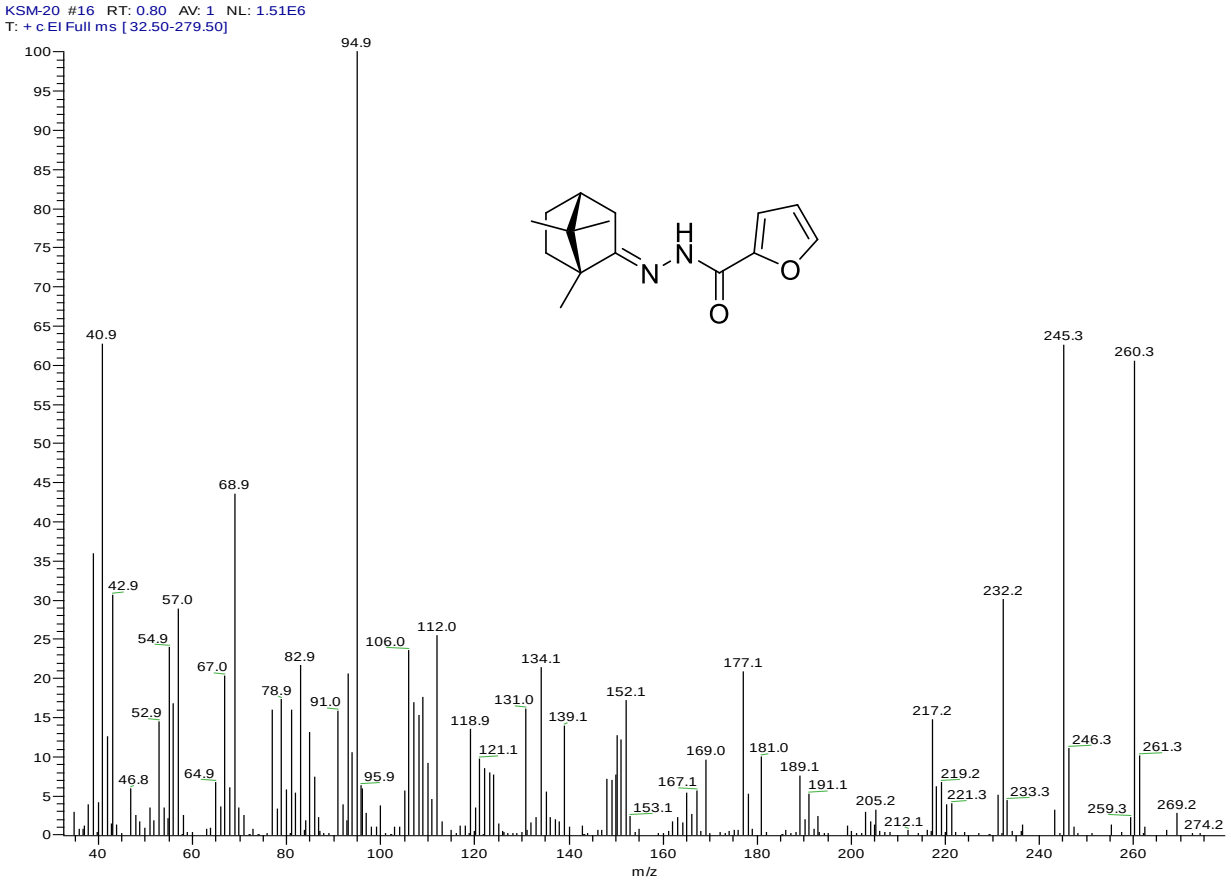
4.4. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)benzohydrazide (9)



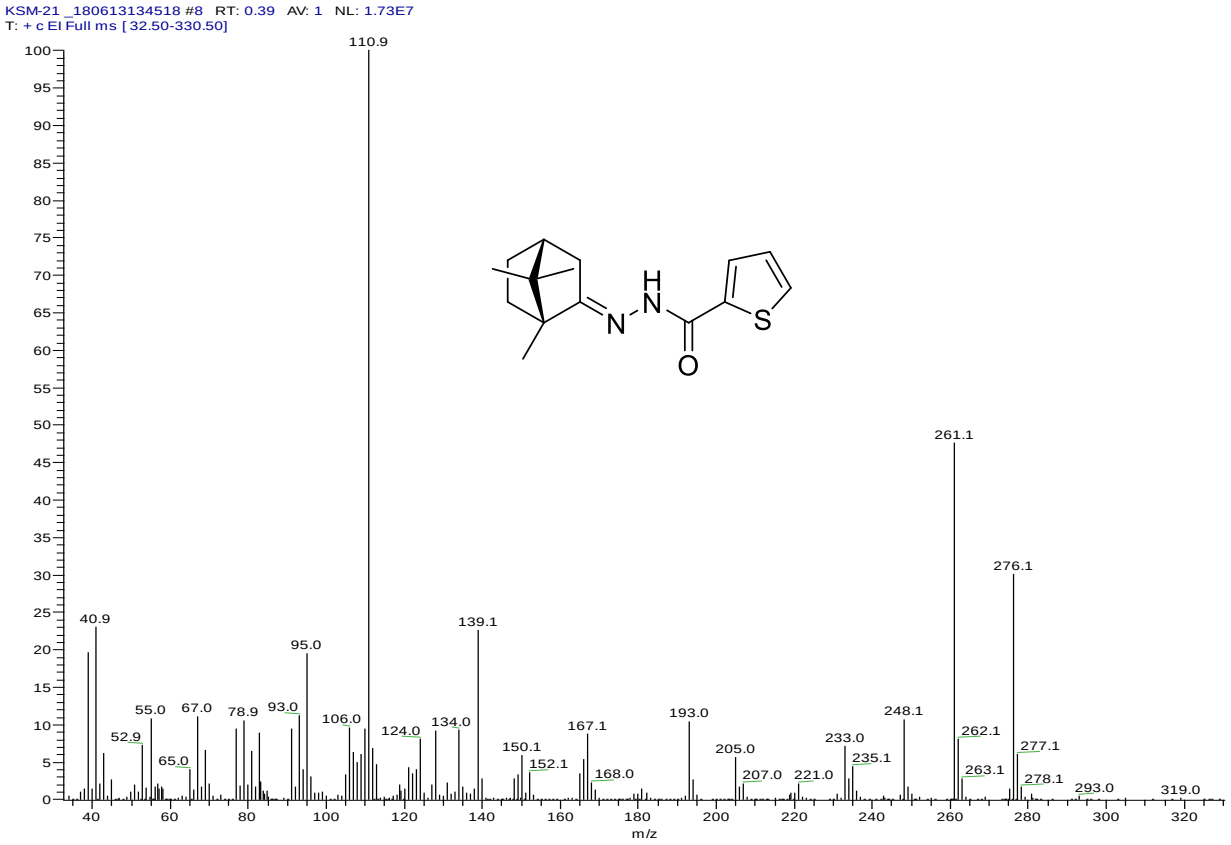
4.5. (E)-4-bromo-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)benzohydrazide (10)



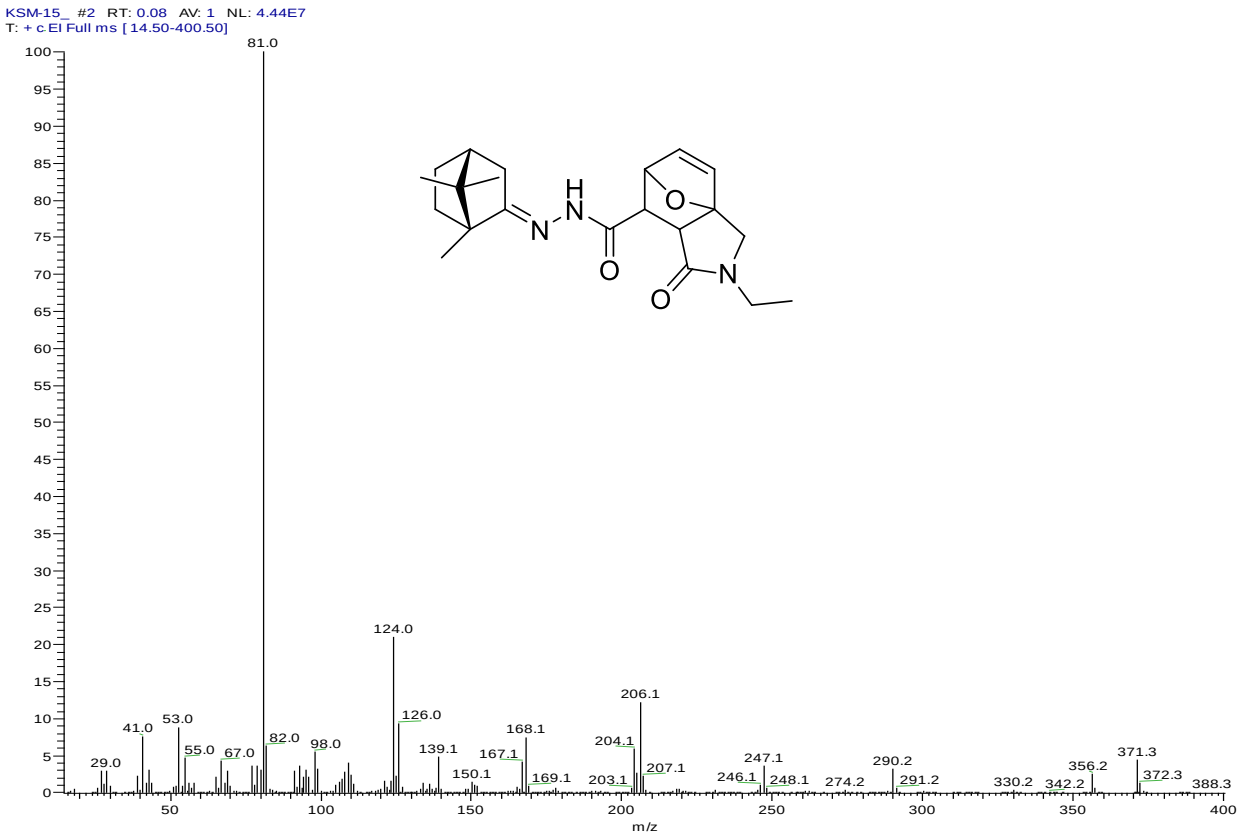
4.6. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)furan-2-carbohydrazide (11)



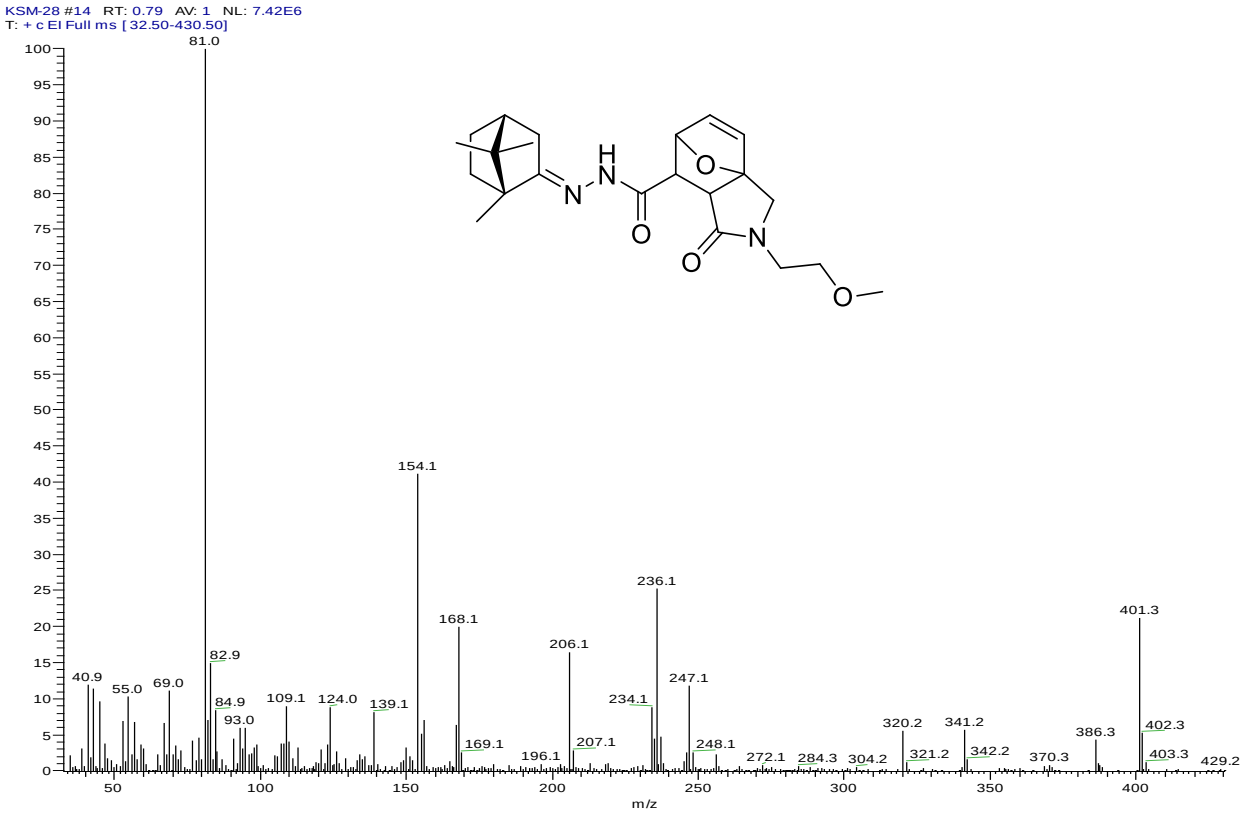
4.7. (E)-N'-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)thiophene-2-carbohydrazide (12)



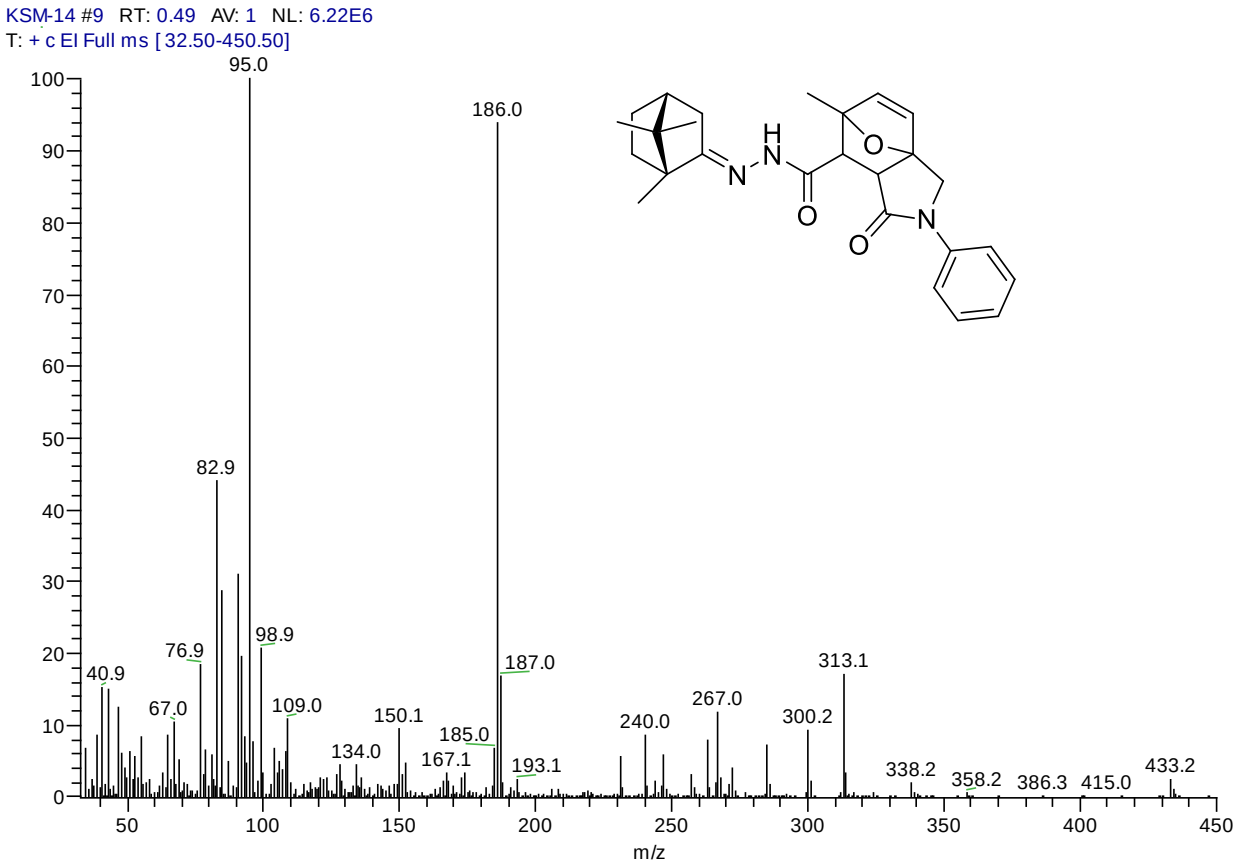
4.8. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-2-ethyl-1-oxo-*N*'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-2-ethyl-1-oxo-*N*'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (13)



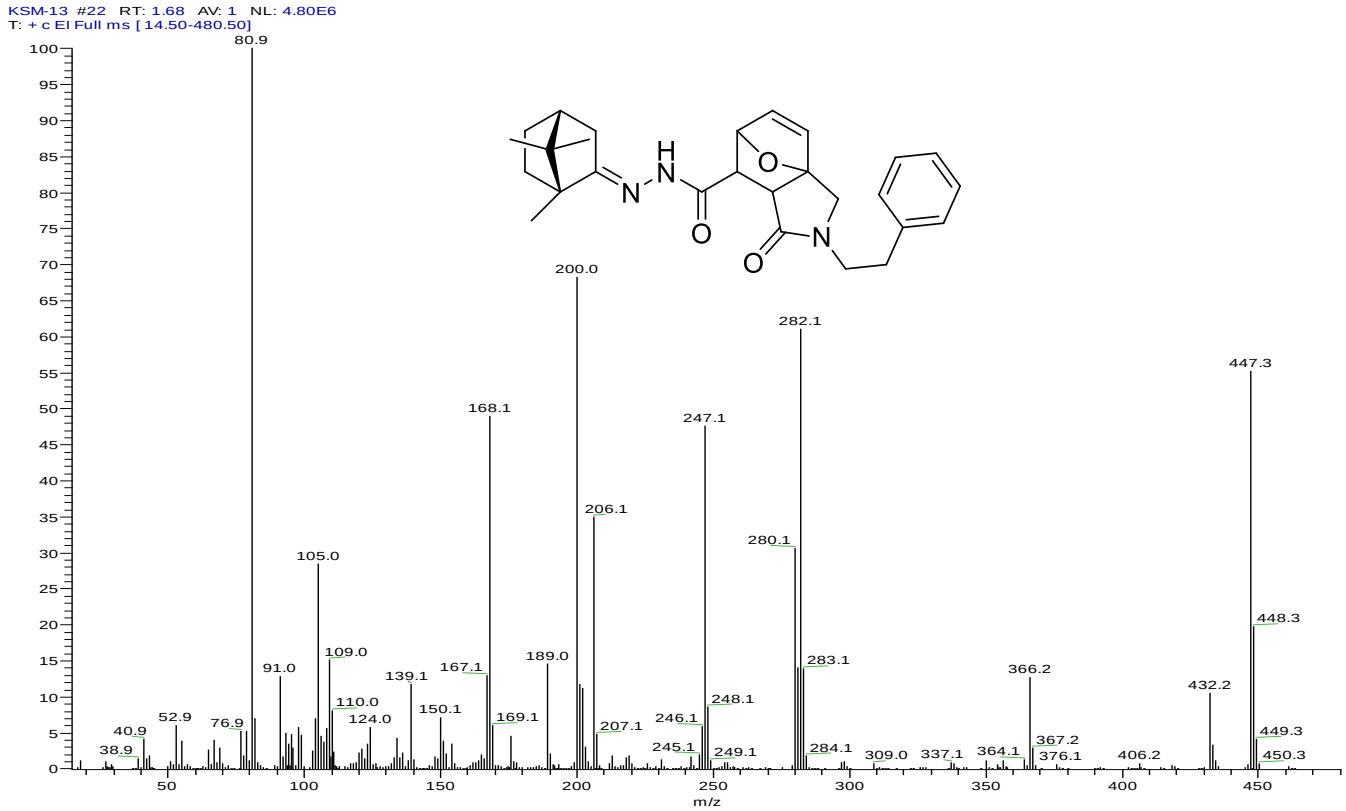
4.9. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-2-(2-methoxyethyl)-1-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-2-(2-methoxyethyl)-1-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (14)



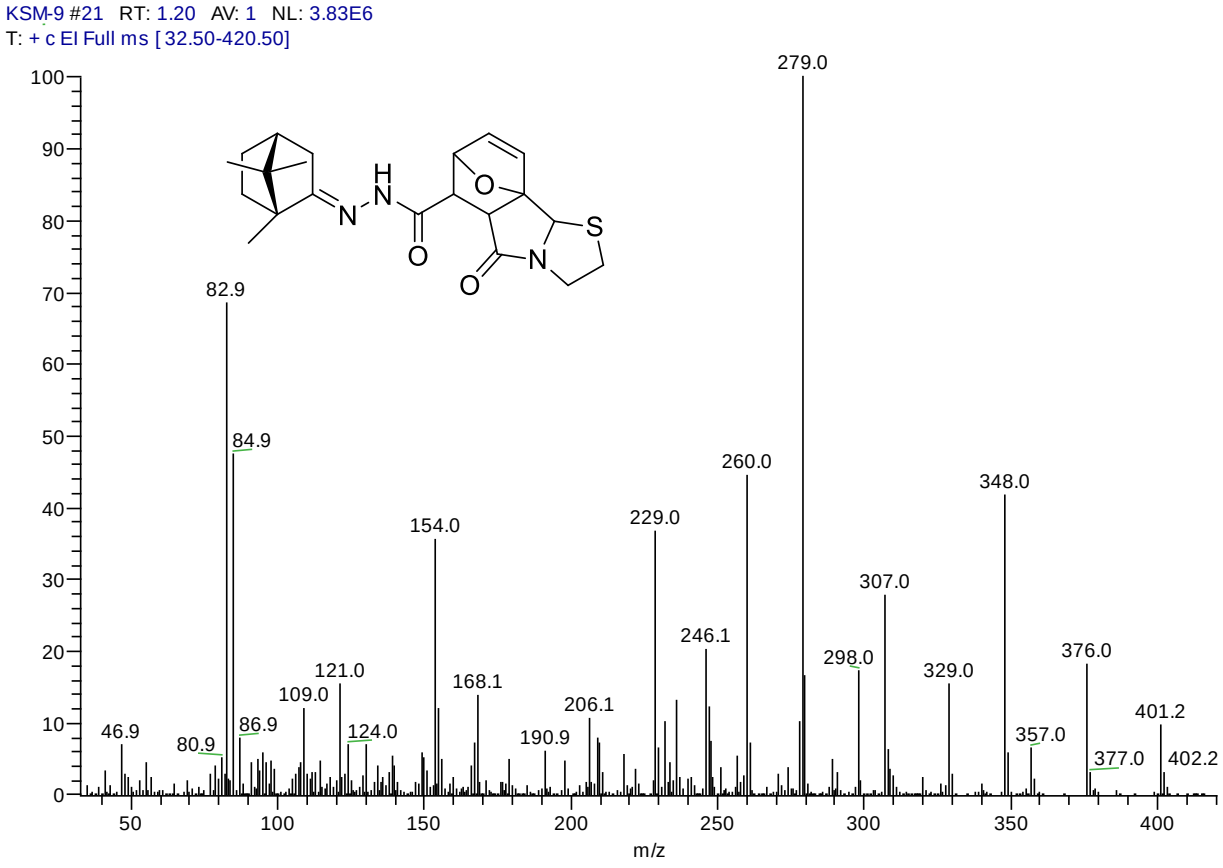
4.10. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-6-methyl-1-oxo-2-phenyl-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-6-methyl-1-oxo-2-phenyl-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (15)



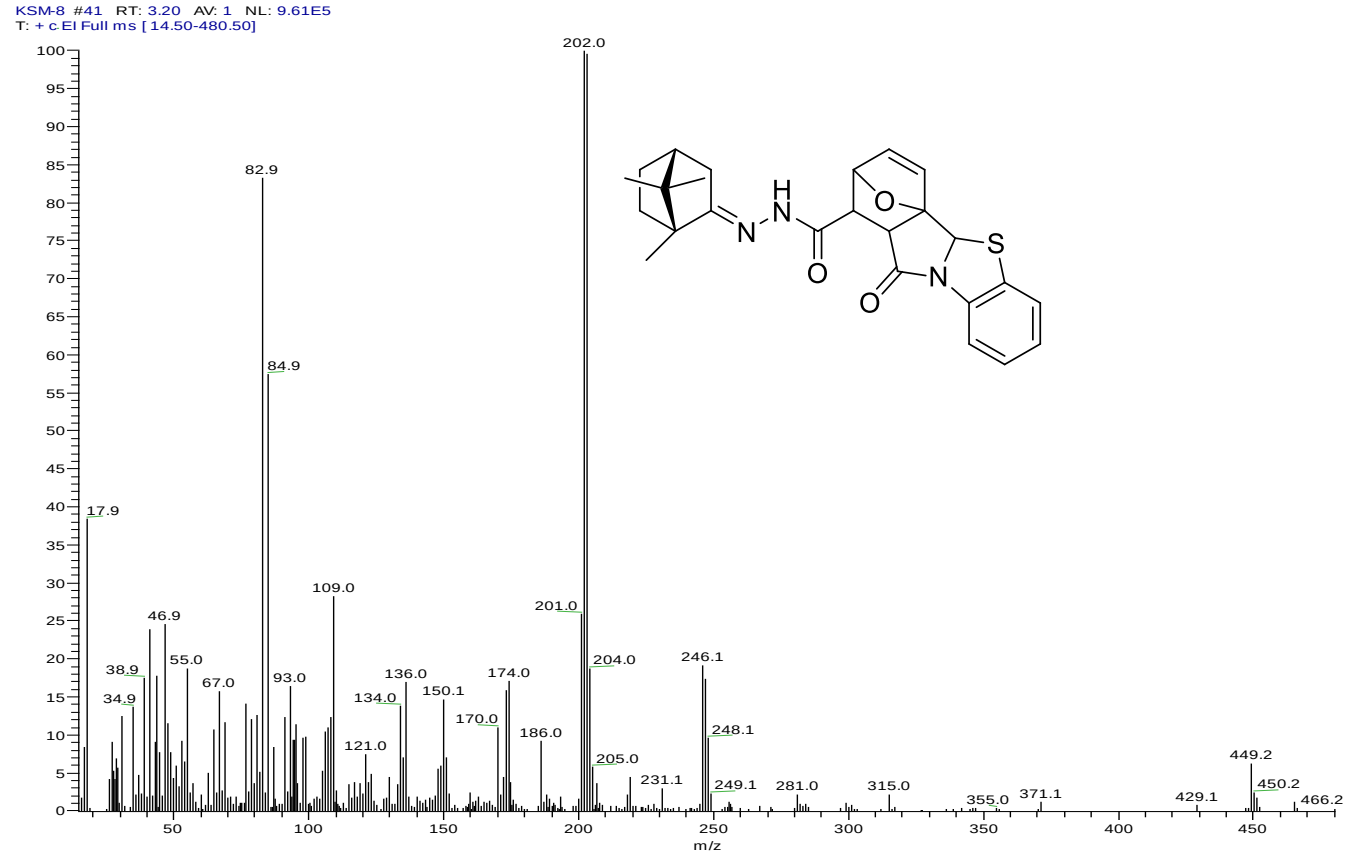
4.11. Mixture of (3a*R*,6*S*,7*R*,7a*S*)-1-oxo-2-(2-phenylethyl)-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (a) and (3a*S*,6*R*,7*S*,7a*R*)-1-oxo-2-(2-phenylethyl)-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,3,6,7,7a-hexahydro-3a,6-epoxyisoindole-7-carbohydrazide (b) (16)



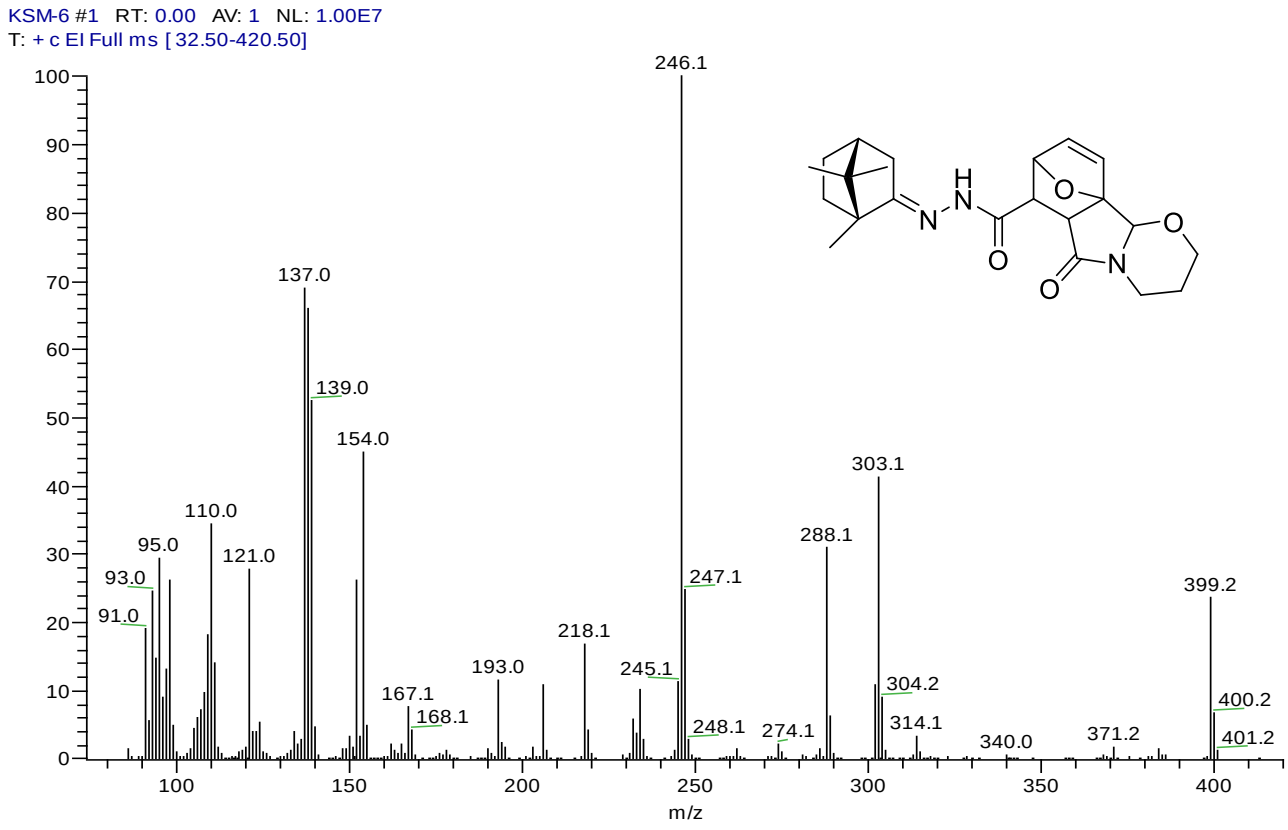
4.12. Mixture of (5a*S*,6*R*,7*S*,9a*R*)-5-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (a) and (5a*R*,6*S*,7*R*,9a*S*)-5-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-2,3,5,5a,6,7-hexahydro-7,9a-epoxy[1,3]thiazolo[2,3-a]isoindole-6-carbohydrazide (b) (17)



4.13. Mixture of (1*R*,2*S*,4a*R*,11a*S*)-11-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (a) and (1*S*,2*R*,4a*S*,11a*R*)-11-oxo-N'-[(1R,2E,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-1,2,11,11a-tetrahydro-2,4a-epoxyisoindolo[1,2-b][1,3]benzothiazole-1-carbohydrazide (b) (19)



4.14. Mixture of (6a*S*,7*R*,8*S*,10a*R*,10b*R*)-6-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (a) and (6a*R*,7*S*,8*R*,10a*S*,10b*S*)-6-oxo-N'-[(1*R*,2*E*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-ylidene]-3,4,6,6a,7,8-hexahydro-2H-8,10a-epoxy[1,3]oxazino[2,3-a]isoindole-7(10bH)-carbohydrazide (b) (18)



4.15. N'-[(1*S*,2*E*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]hept-2-ylidene]benzohydrazide (20)