

Supplementary Information

Cu(II)-Catalyzed Domino Reaction of 2*H*-Azirines with Diazotetramic and Diazotetronic Acids. Synthesis of 2-Substituted 2*H*-1,2,3-Triazoles

Nikolai V. Rostovskii,^a Mikhail S. Novikov,^{a,*} Alexander F. Khlebnikov,^a Sergei M. Korneev,^a
Dmitry S. Yufit^b

^a Department of Chemistry, Saint-Petersburg State University, Universitetskii pr. 26, 198504 St. Petersburg, Russia

^b Department of Chemistry, Durham University, Durham, South Rd., DH1 3LE, UK.

* Corresponding author. Fax: +7 812-428-6939; Tel: +7 812-428-4021; E-mail: m.s.novikov@chem.spbu.ru

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General experimental details

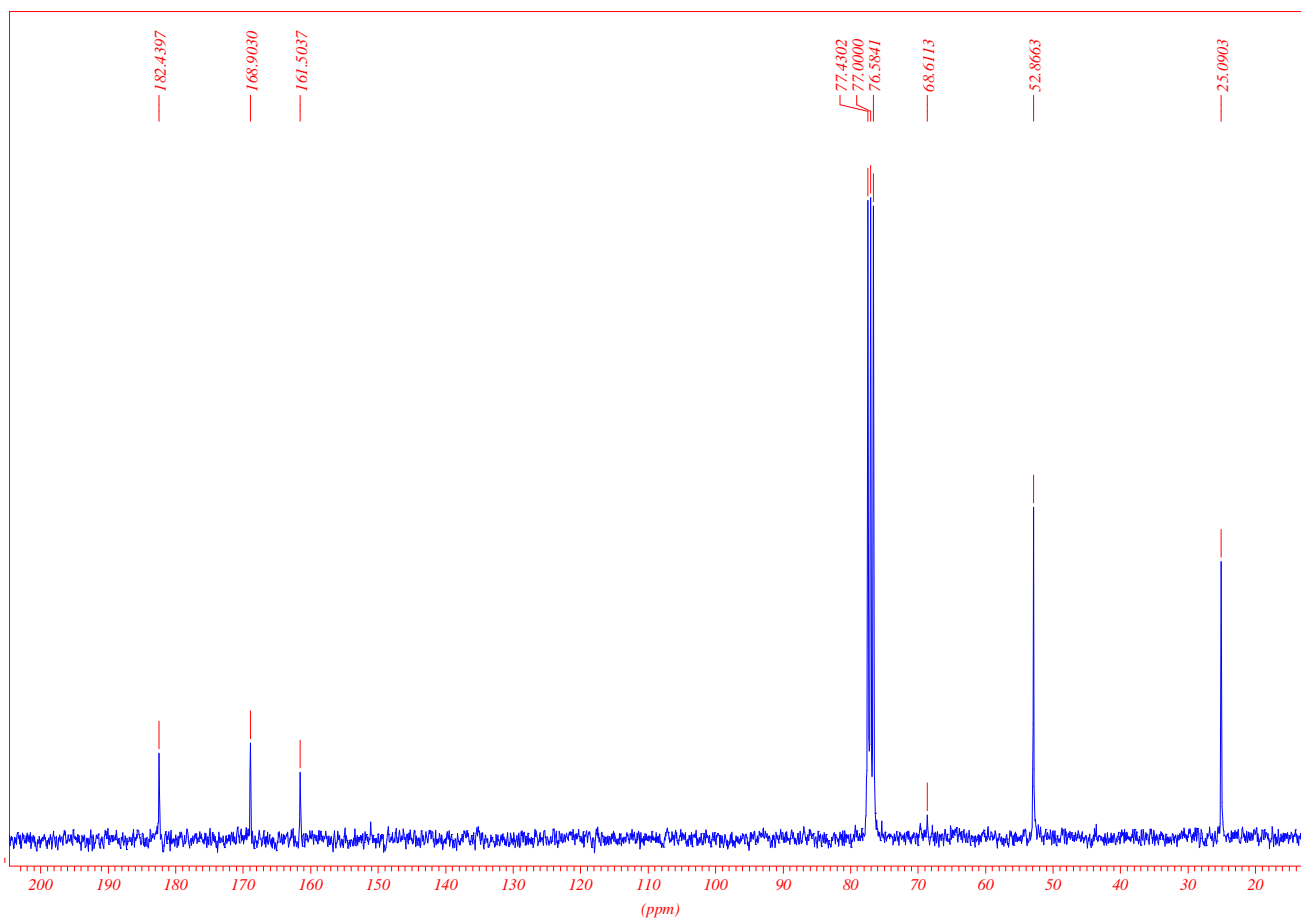
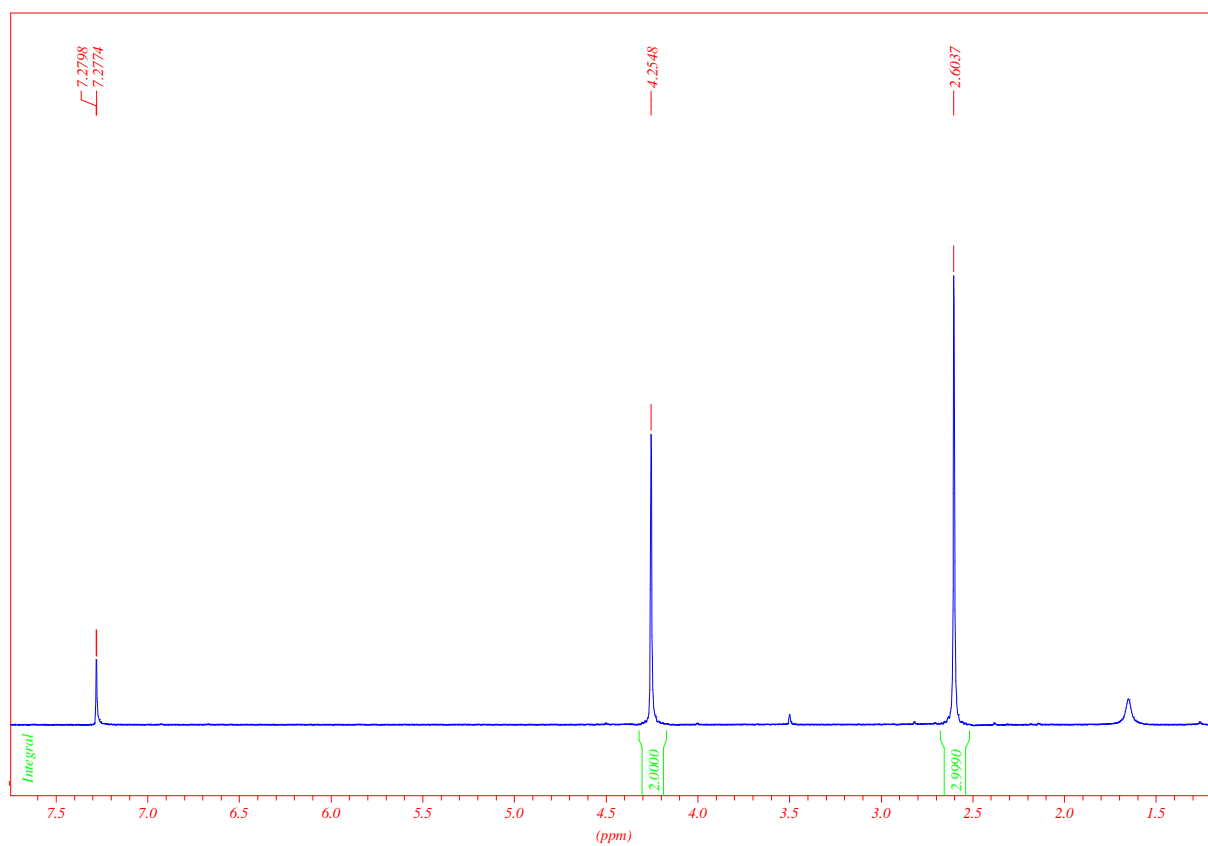
Melting points were determined on a hot stage microscope and are uncorrected. ^1H (300 MHz), ^{13}C (75 MHz) NMR spectra were measured in CDCl_3 or DMSO-d_6 on a Bruker DPX 300 spectrometer and ^1H (400 MHz), ^{13}C (100 MHz) NMR spectra were measured in CDCl_3 or DMSO-d_6 on a Bruker Avance-400 spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Electrospray ionization mass spectra were measured on a Bruker micrOTOF mass spectrometer. Elemental analysis was performed on a Hewlett-Packard 185B CHN-analyser. IR spectra were recorded on a Bruker TENSOR 27 spectrometer for tablets in KBr. Thin-layer chromatography (TLC) was conducted on aluminium sheets precoated with SiO_2 ALUGRAM SIL G/UV₂₅₄. Methyl 2,4-dioxopyrrolidine-3-carboxylate was synthesized according to the published procedure.¹

Synthesis of 3-diazopyrrolidine-2,4-dione (1a)

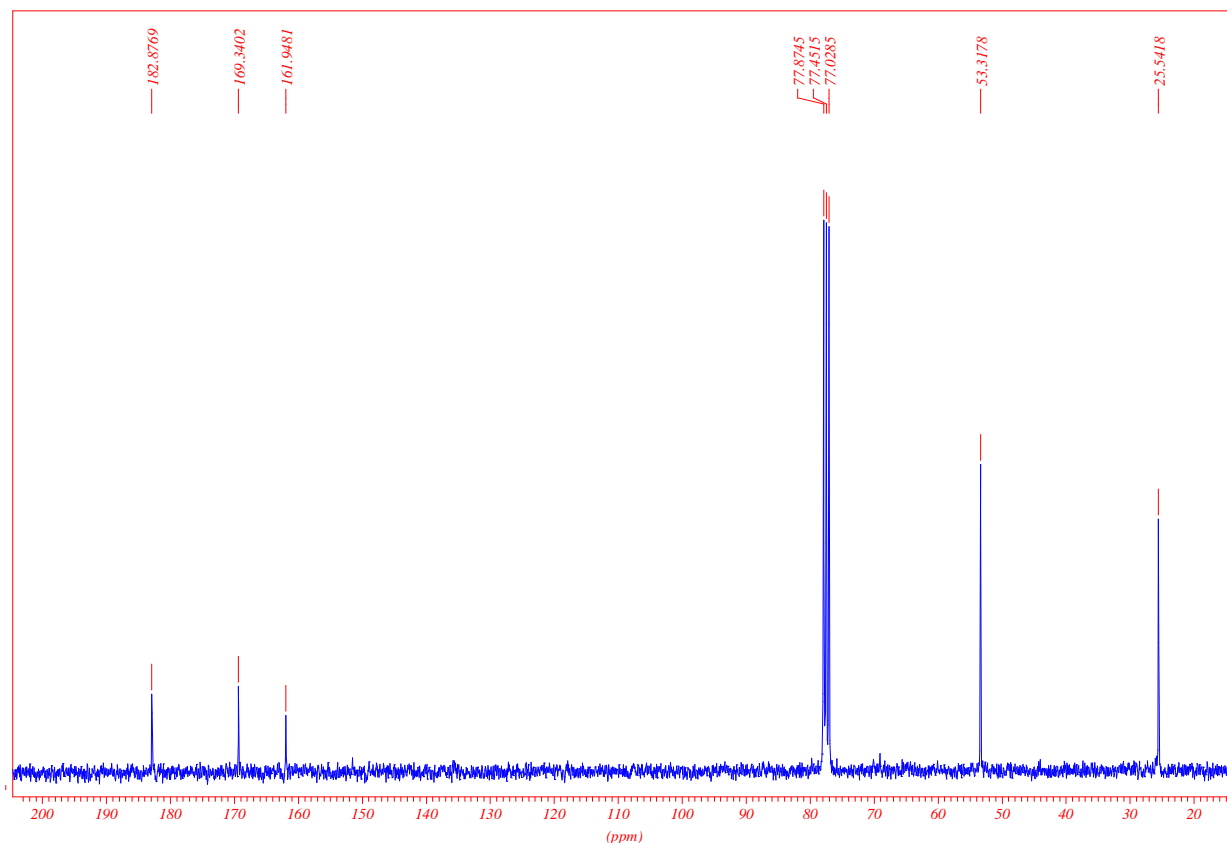
To a solution, obtained after heating under reflux of a suspension of methyl 2,4-dioxopyrrolidine-3-carboxylate (3.25 g, 20.7 mmol) in anhydrous acetonitrile (1.6 L) for 2 h, a solution of 4-acetamidobenzenesulfonyl azide (5.46 g, 27.7 mmol) in anhydrous acetonitrile (100 mL) and a solution of triethylamine (2.5 g, 24.8 mmol) in anhydrous acetonitrile (50 mL) were added at 0 °C under stirring. The mixture was stirred at 0 °C for 15 min and then at rt for 4 h. The solvent was removed under vacuum, and the orange solid was subjected to sublimation (150–160 °C/0.1–0.5 torr) for 1.5 h to give 1.47 g (57%) of 3-diazopyrrolidine-2,4-dione as a light yellow solid. δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 3.96 (2 H, s, CH_2), 5.92 (1 H, br. s, NH).

Synthesis of 1-acetyl-3-diazopyrrolidine-2,4-dione (1b)

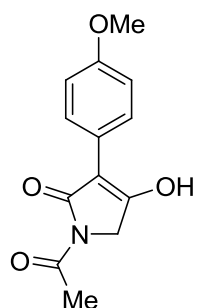
To a solution of 3-diazopyrrolidine-2,4-dione (623 mg, 5 mmol) and acetic anhydride (815 mg, 8 mmol) in anhydrous dichloromethane (20 mL) a solution of 4-(*N,N*-dimethylamino)pyridine (305 mg, 2.5 mmol) in anhydrous dichloromethane (3 mL) was added dropwise at rt in 5 min. The mixture was stirred at rt for additional 2 h, washed with 0.5 N HCl solution (2×20 mL) and dried with MgSO_4 . The removal of volatile components under vacuum and washing of the obtained solid with Et_2O gave 575 mg (69%) of 1-acetyl-3-diazopyrrolidine-2,4-dione as a beige solid. Recrystallization of the solid from Et_2O produces colorless prisms. Mp 115–116 °C. Found C, 43.34; H, 2.81; N, 25.15. $\text{C}_6\text{H}_5\text{N}_3\text{O}_3$ requires C, 43.12; H, 3.02; N 25.14. ν_{max} (KBr)/ cm^{-1} 2939, 2152 (C=N), 1691 (C=O). δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 2.60 (s, 3 H, CH_3), 4.25 (s, 2 H, CH_2). δ_{C} (75 MHz; CDCl_3 ; Me_4Si) 25.1 (CH_3), 52.9 (CH_2), 68.6 (C=N), 161.5 (C=O), 168.9 (C=O), 182.4 (C=O).



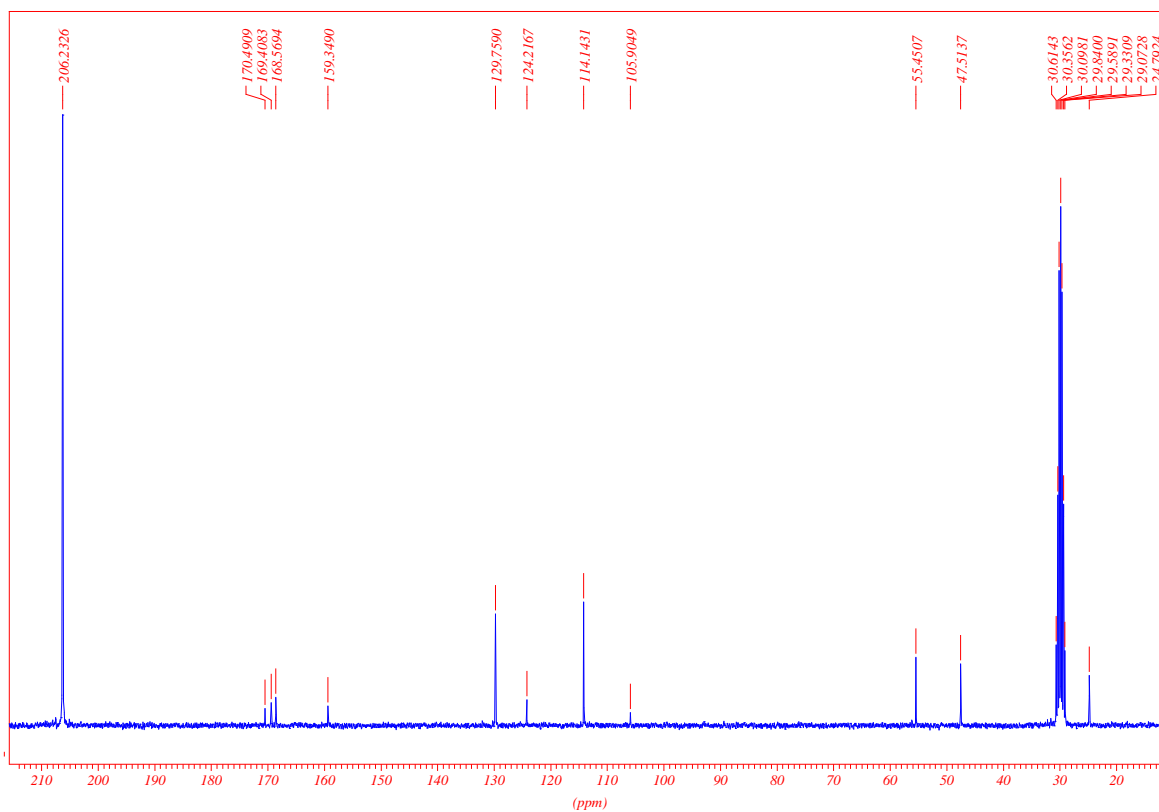
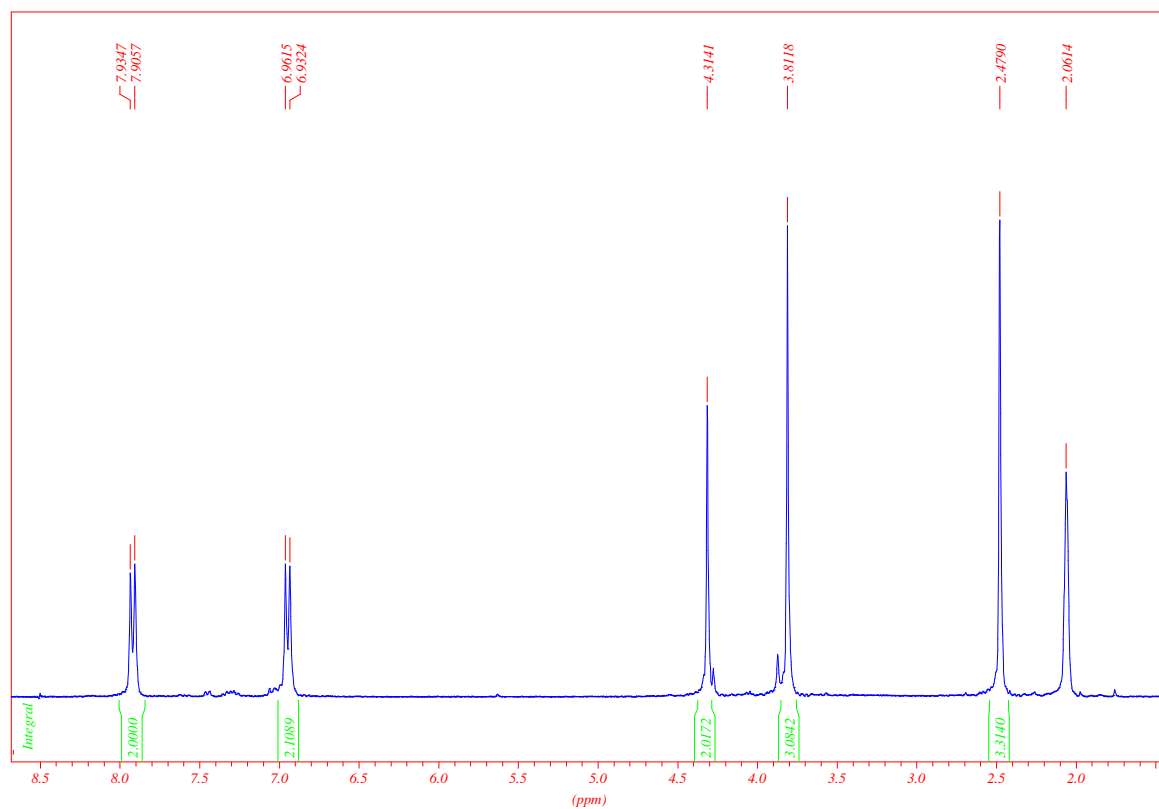
tert-Butyl 3-diazo-2,4-dioxopyrrolidine-1-carboxylate (1c) was prepared according to published procedure in 52% yield.² δ_{H} (300 MHz; CDCl_3 ; Me_4Si) 1.53 (9 H, s, CH_3), 4.16 (2 H, s, CH_2). δ_{C} (75 MHz; CDCl_3 ; Me_4Si) 27.9 (CH_3), 53.7 (CH_2), 68.5 ($\text{C}=\text{N}$), 84.2 ($\text{C}-(\text{CH}_3)_3$), 148.3 ($\text{C}=\text{O}$), 160.0 ($\text{C}=\text{O}$), 182.7 ($\text{C}=\text{O}$).



Synthesis of 1-acetyl-4-hydroxy-3-(4-methoxyphenyl)-1H-pyrrole-2(5H)-one (11)



A solution of 1-acetyl-3-diazopyrrolidine-2,4-dione (116 mg, 0.69 mmol) and $\text{Rh}_2(\text{OAc})_4$ (3 mg, 0.01 mmol) in anisole (14 mL) was heated at 120 °C under stirring for 30 min. Anisole was removed under vacuum and crystallization of the residue from Et_2O gave 140 mg (82%) of 1-acetyl-4-hydroxy-3-(4-methoxyphenyl)-1H-pyrrole-2(5H)-one **11** as a beige solid. Mp 153–203 °C (dec.). ν_{max} (KBr)/ cm^{-1} 2993, 2938, 2630, 1734 ($\text{C}=\text{O}$), 1605 ($\text{C}=\text{O}$), 1516, 1398, 1356, 1312, 1292, 1250, 1185, 1157, 1034, 984, 847. δ_{H} (300 MHz; acetone- d_6 ; Me_4Si) 2.48 (3 H, s, CH_3), 3.81 (3 H, s, CH_3), 4.31 (2 H, s, CH_2), 6.95 (2 H, d, J 8.7 Hz, ArH), 7.92 (2 H, d, J 8.7 Hz, ArH). δ_{C} (75 MHz; acetone- d_6 ; Me_4Si) 24.8 (CH_3), 47.5 (CH_2), 55.5 (CH_3), 105.9, 114.1, 124.2, 129.8, 159.3, 168.6, 169.4, 170.5. HRMS (ESI) [$\text{M} + \text{Na}^+$] calcd. for $\text{C}_{13}\text{H}_{13}\text{NO}_4\text{Na}$ 270.0737, found 270.0741.



^1H and ^{13}C NMR spectra of compounds 3, 4, 6, 7 and 12

(3*aRS*,6*aRS*)-6*a*-Hydroxy-2-(4-methylphenyl)-3*a*-[4-(4-methylphenyl)-2*H*-1,2,3-triazol-2-yl]-3*a*,5,6,6*a*-tetrahydropyrrolo[3,4-*b*]pyrrole-4(3*H*)-one (3*a*).

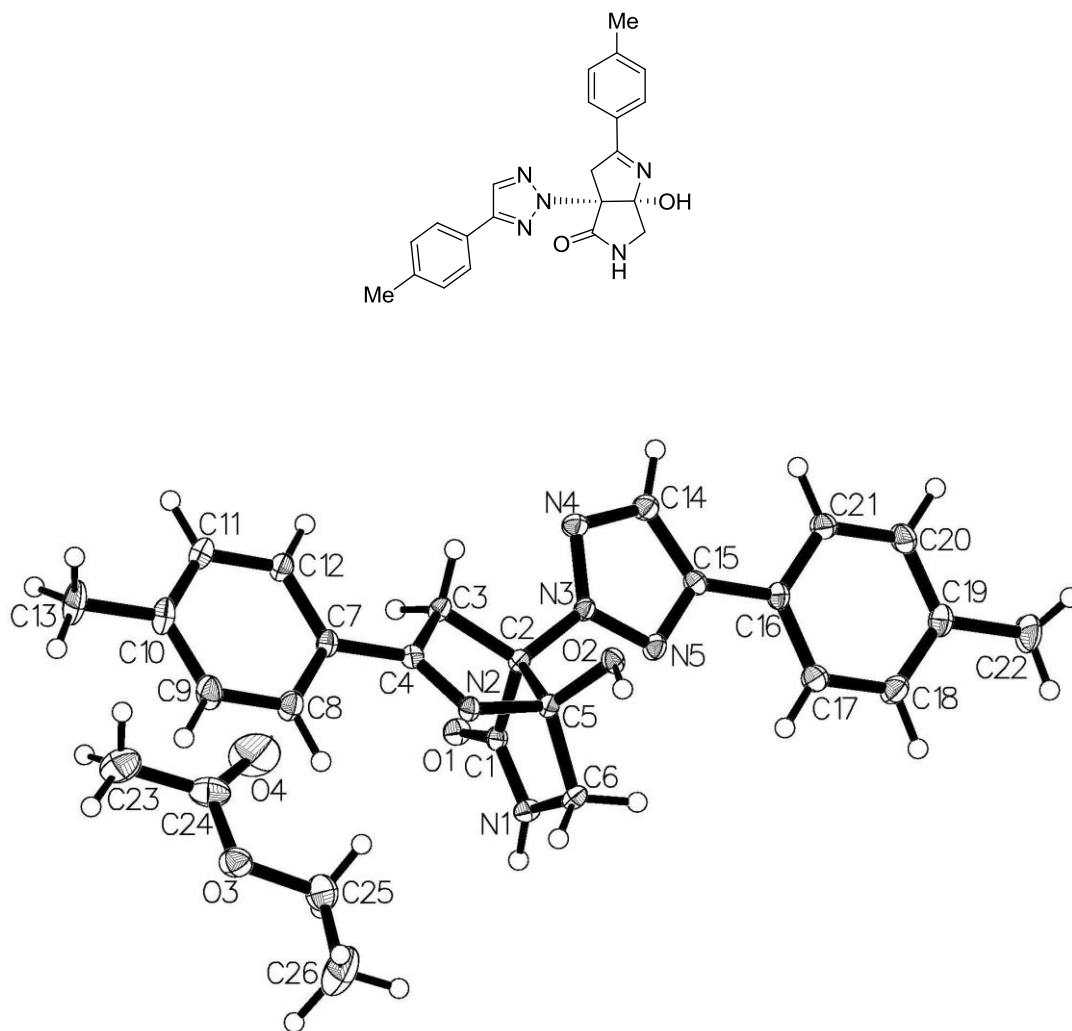
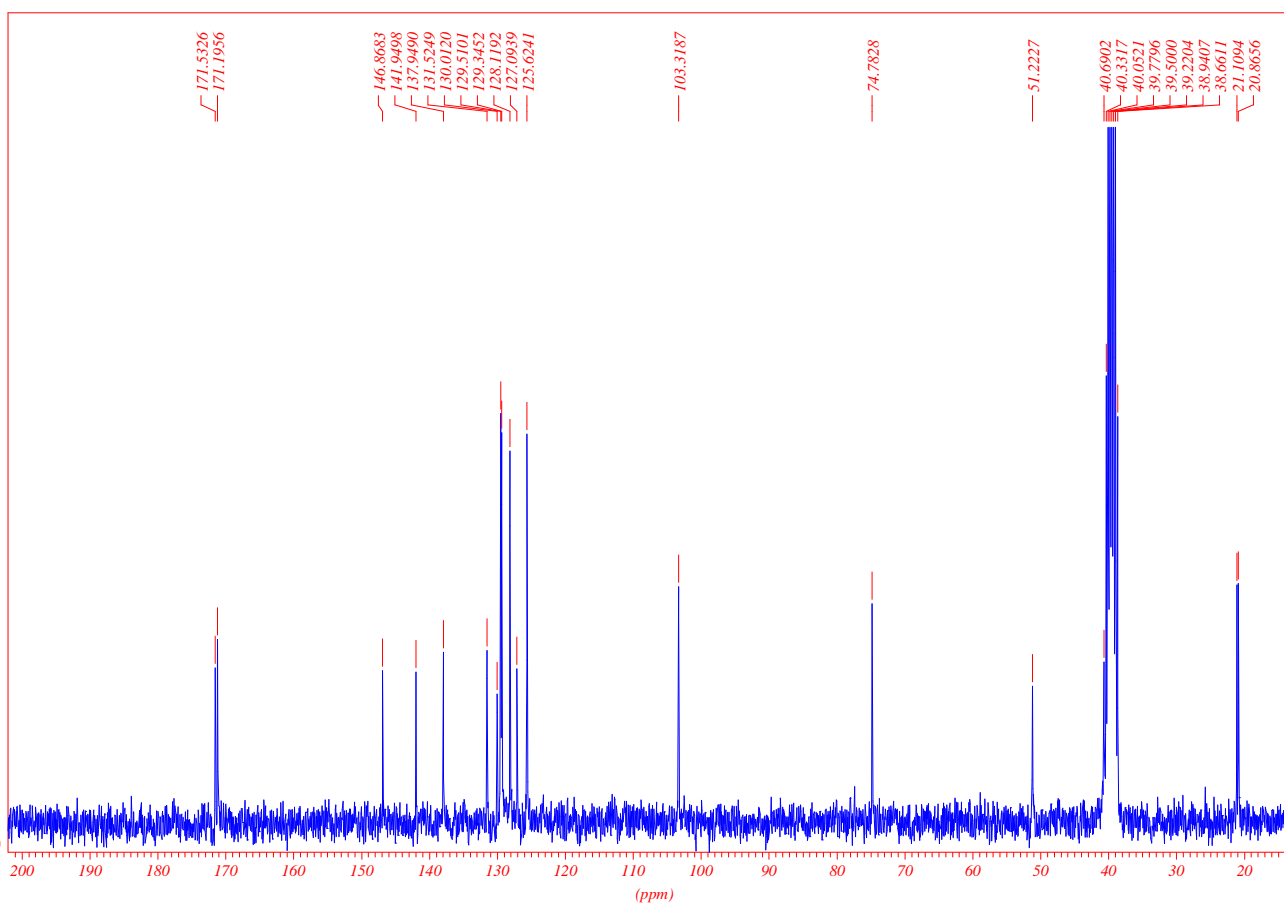
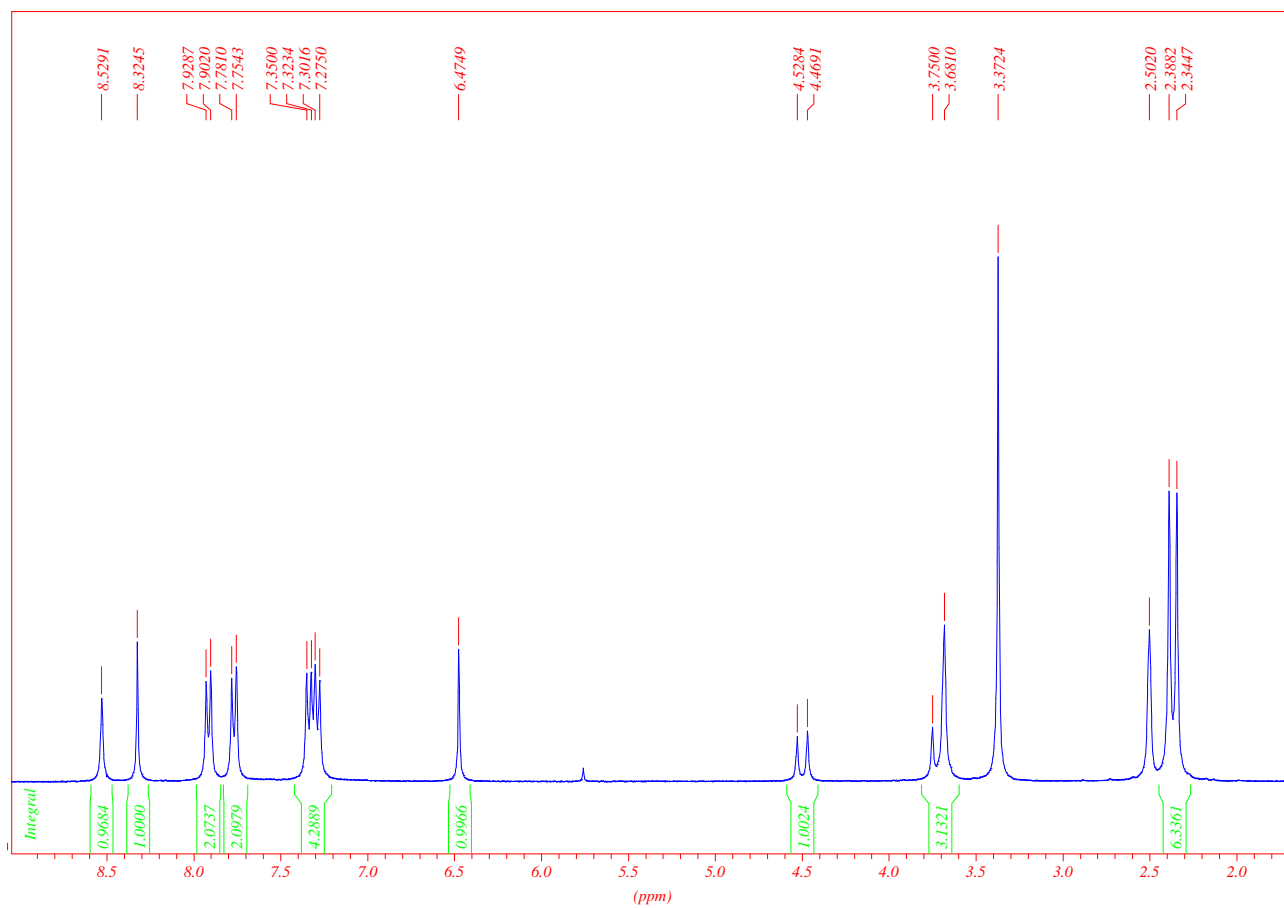
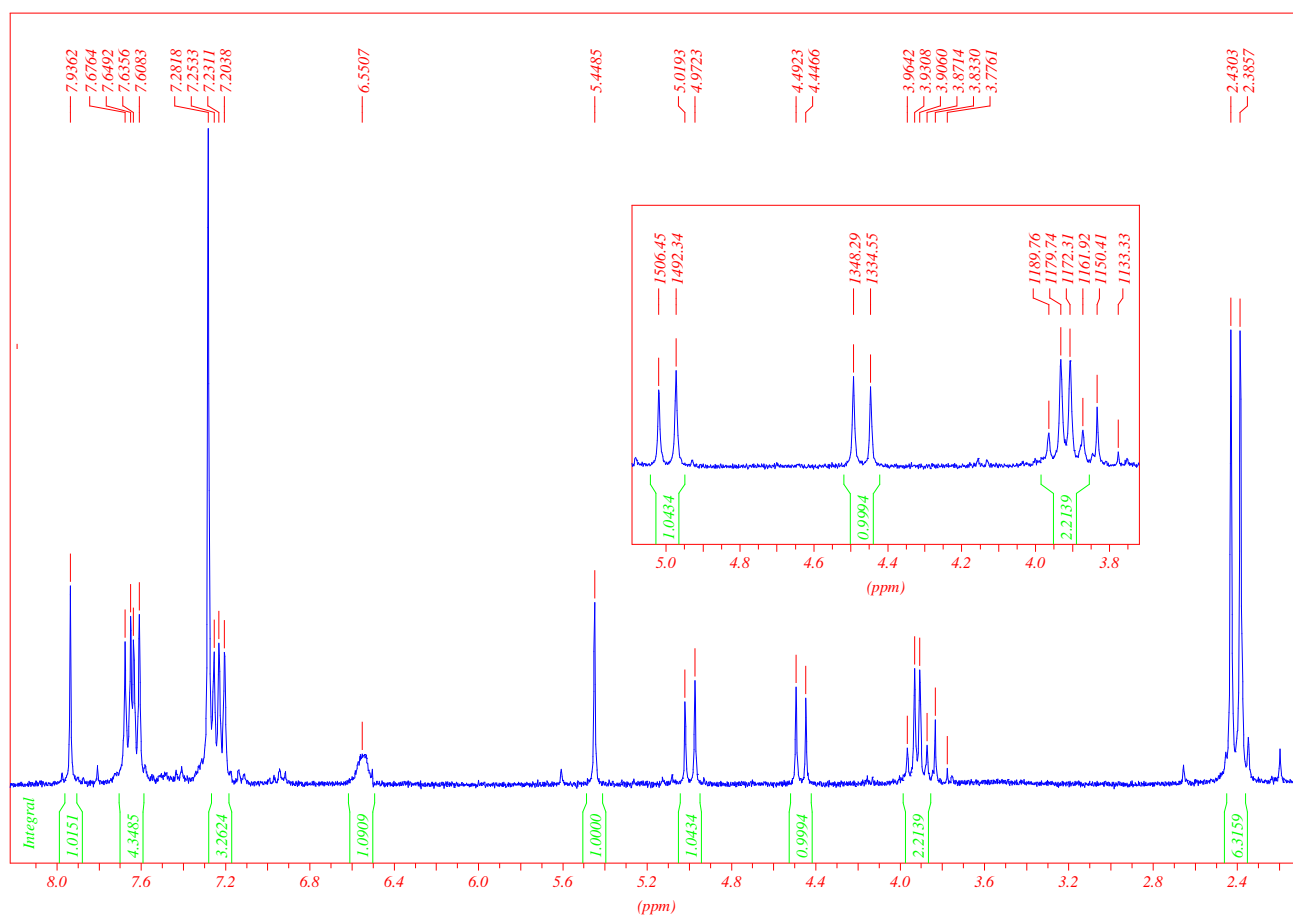
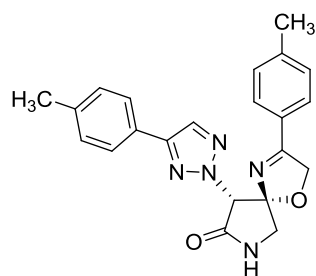
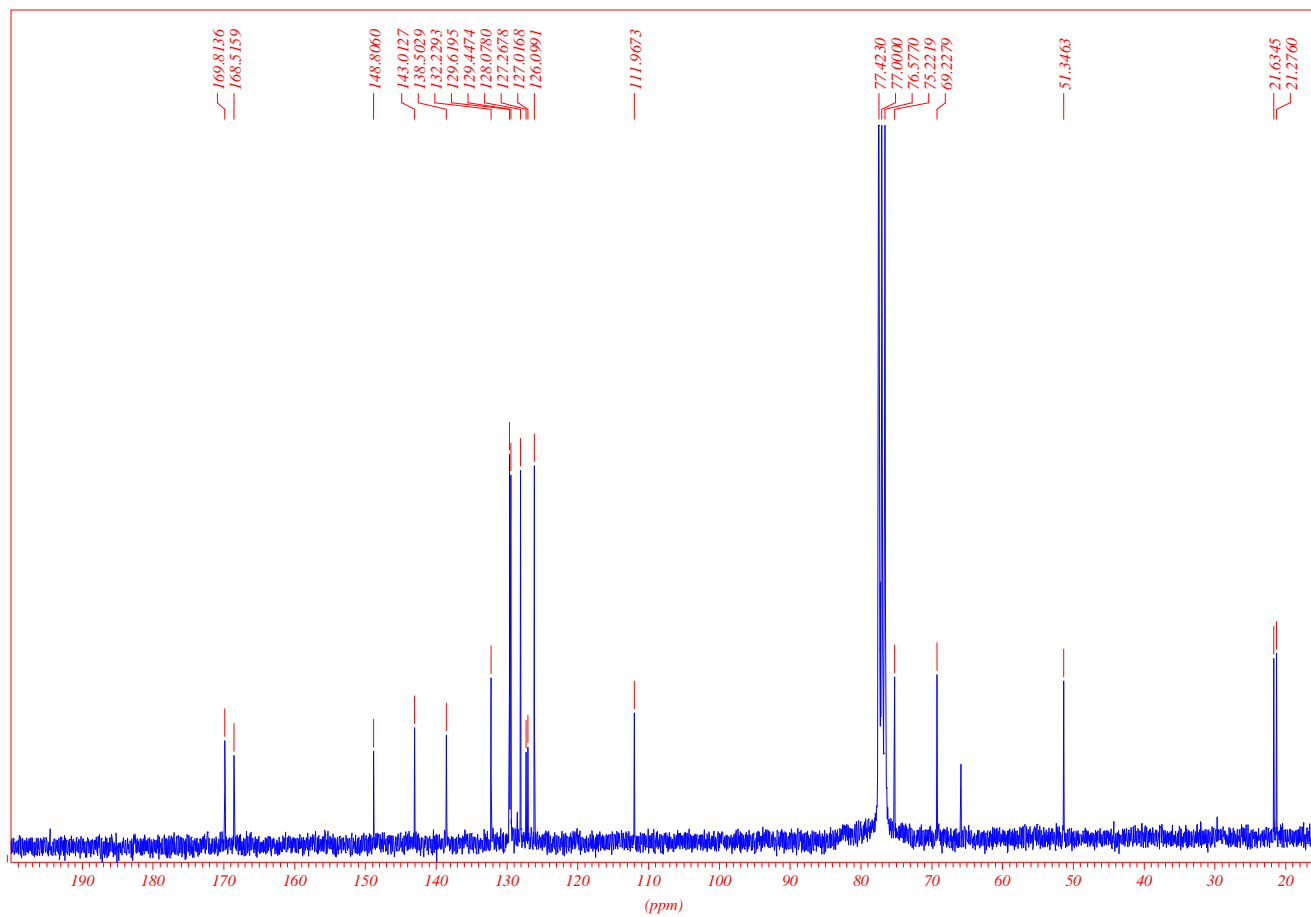


Fig. 1 X-ray structure of the solvate **3a**·EtOAc.

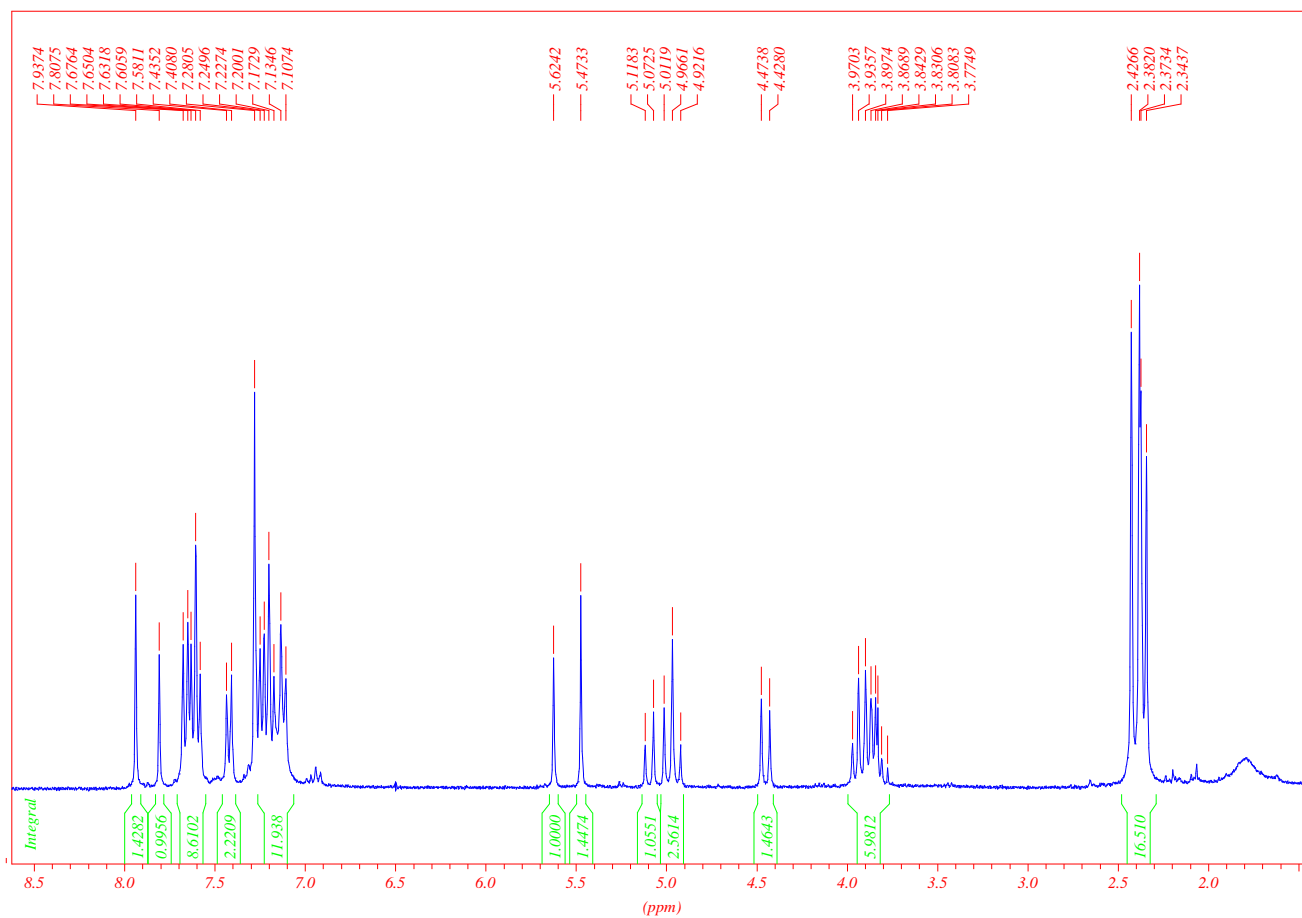


(5*RS*,9*RS*)-3-(4-Methylphenyl)-9-[4-(4-methylphenyl)-2*H*-1,2,3-triazol-2-yl]-1-oxa-4,7-diazaspiro[4.4]non-3-en-8-one (4a)





3-(4-Methylphenyl)-9-[4-(4-methylphenyl)-2*H*-1,2,3-triazol-2-yl]-1-oxa-4,7-diazaspiro[4.4]non-3-en-8-one (4a) (diastereomeric mixture)



(3a*RS*,6a*RS*)-5-Acetyl-6a-hydroxy-2-(4-methylphenyl)-3a-[4-(4-methylphenyl)-2*H*-1,2,3-triazol-2-yl]-3a,5,6,6a-tetrahydropyrrolo[3.4-*b*]pyrrol-4(3*H*)-one (3b)

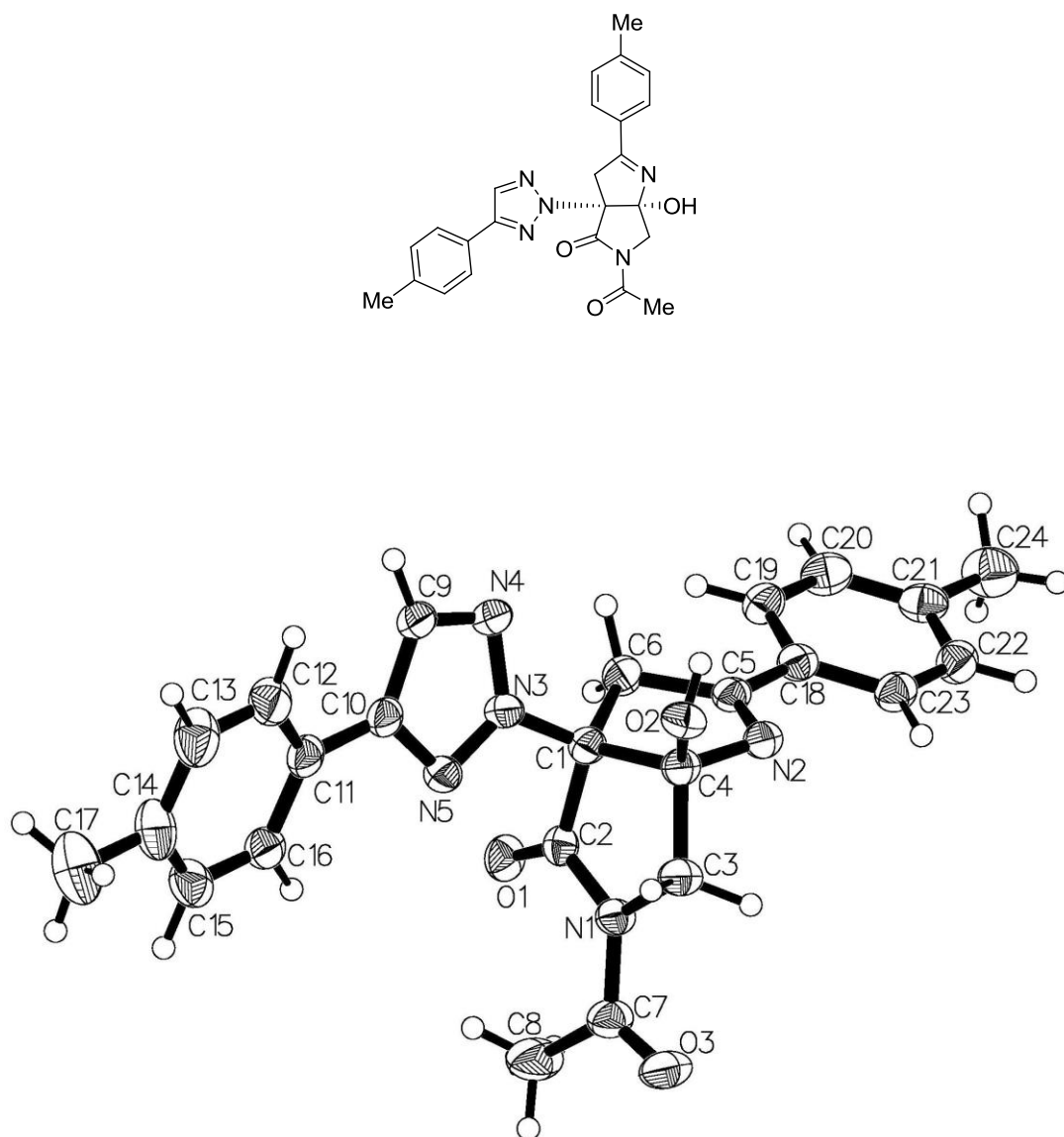
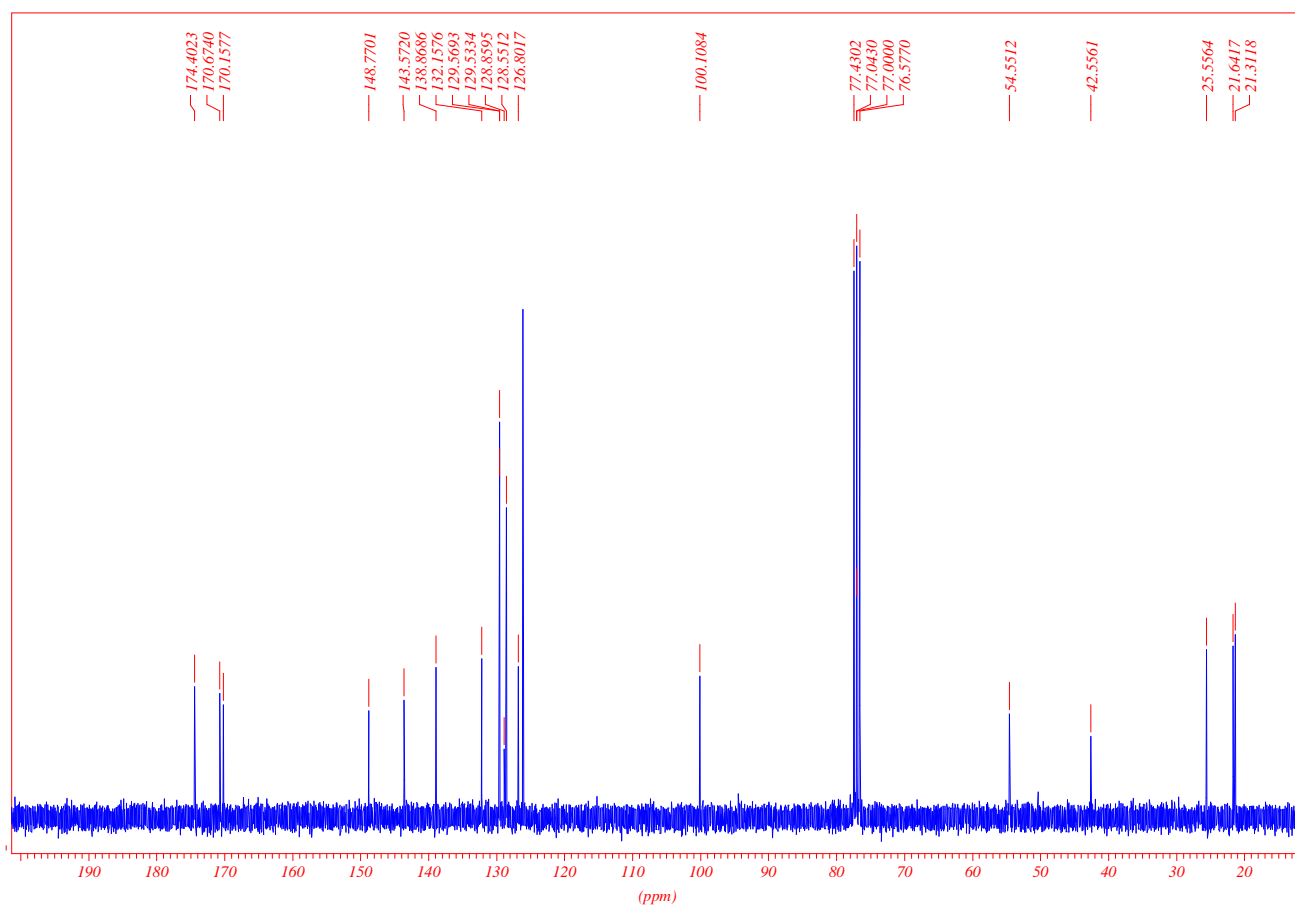
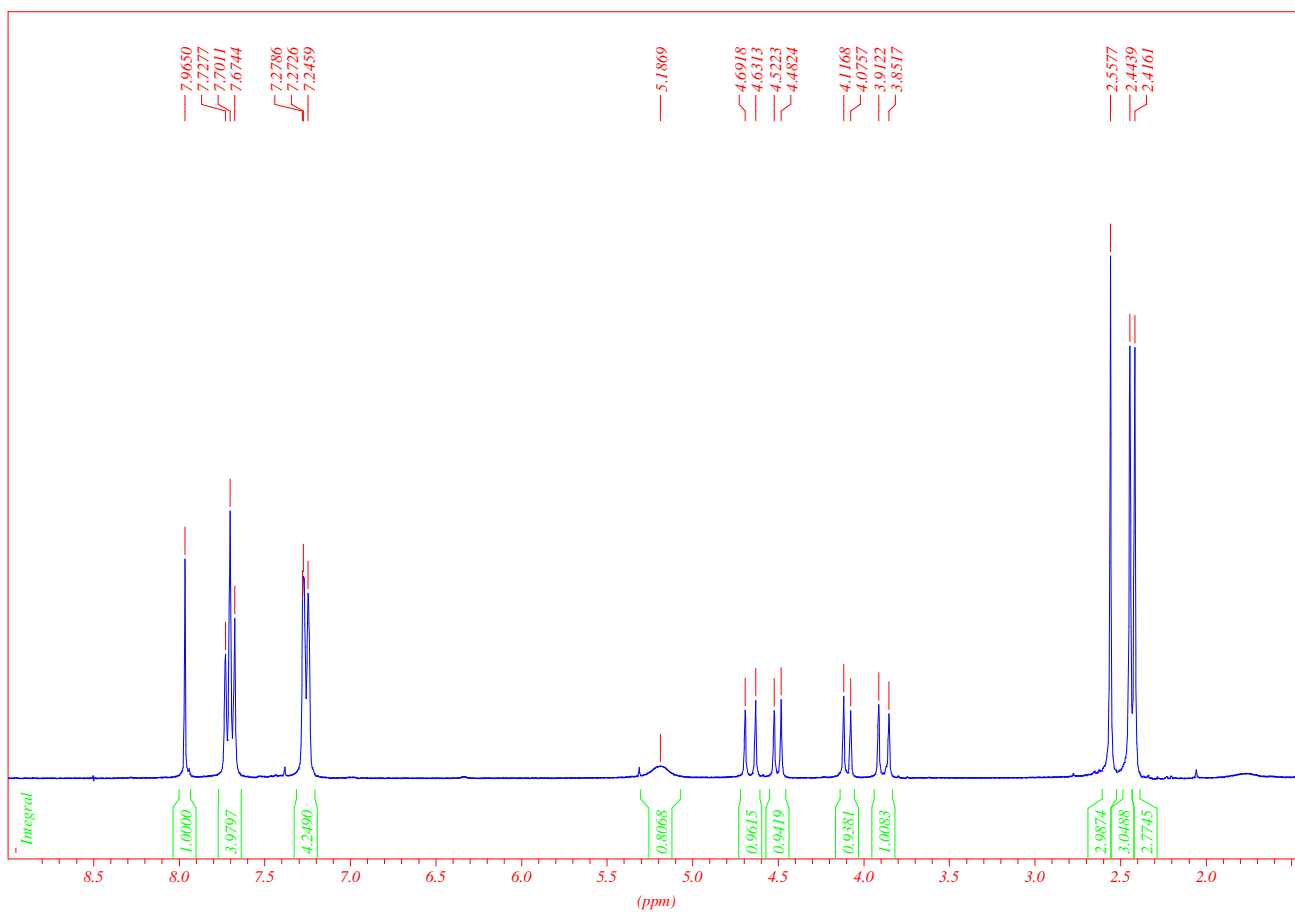
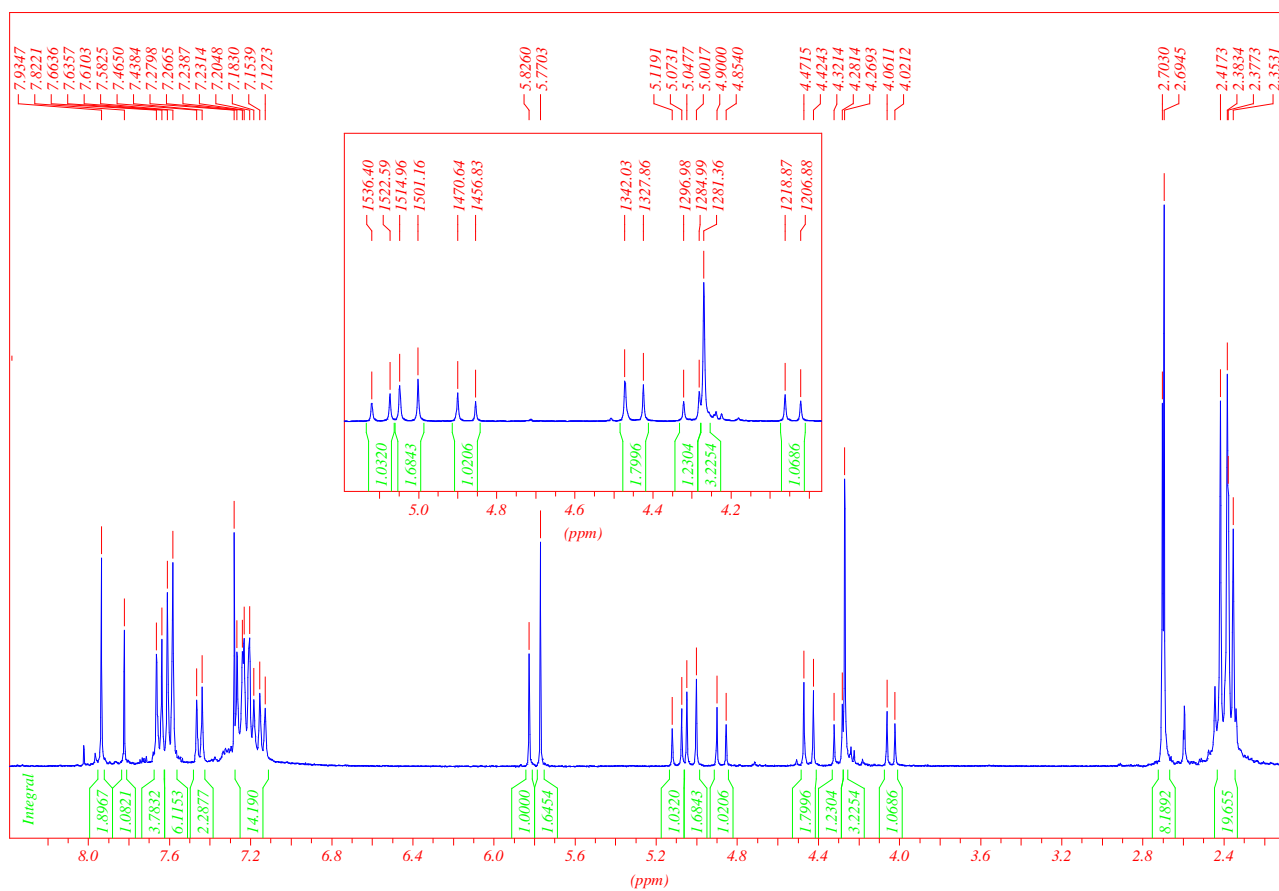
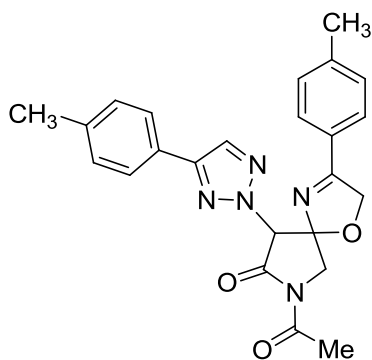
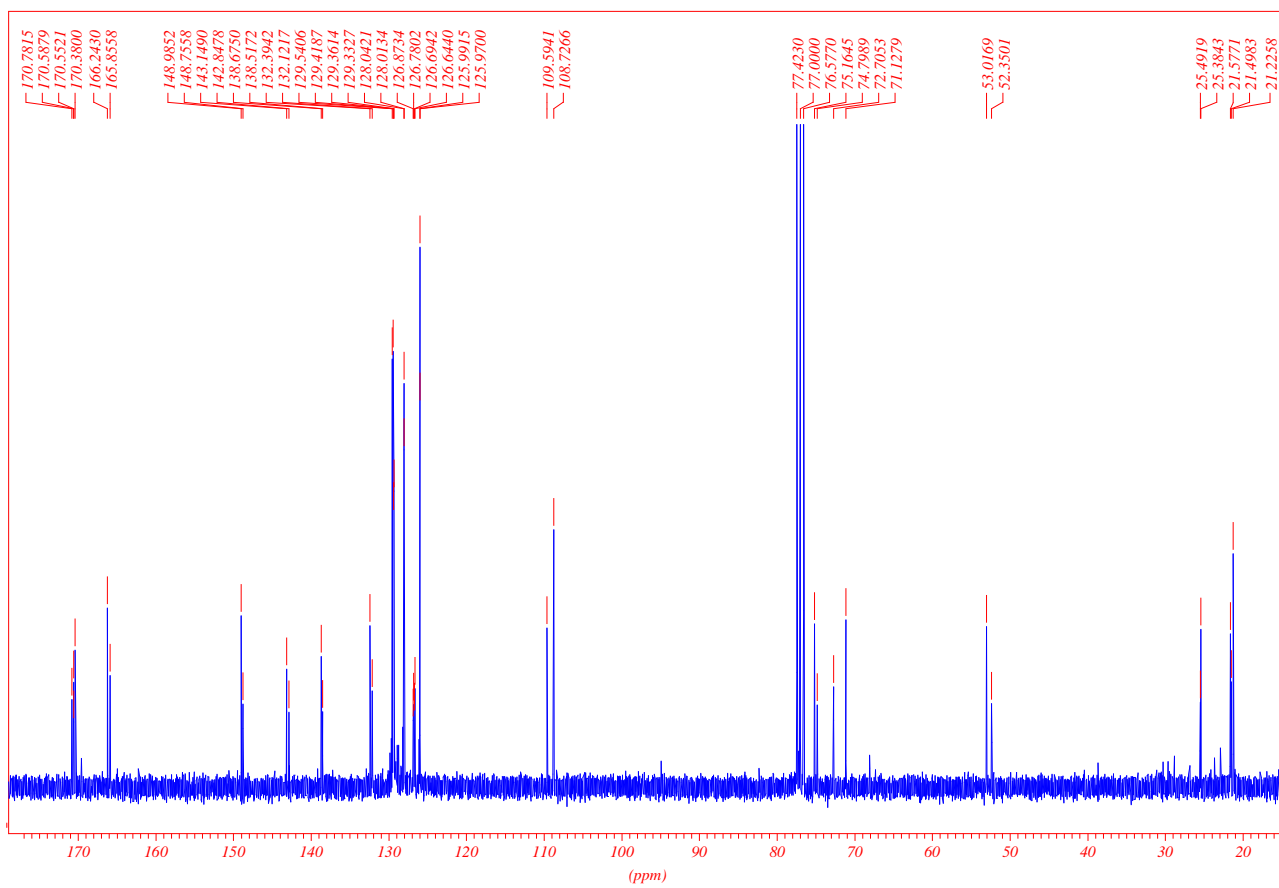


Fig. 2 X-ray structure of compound **3b**.

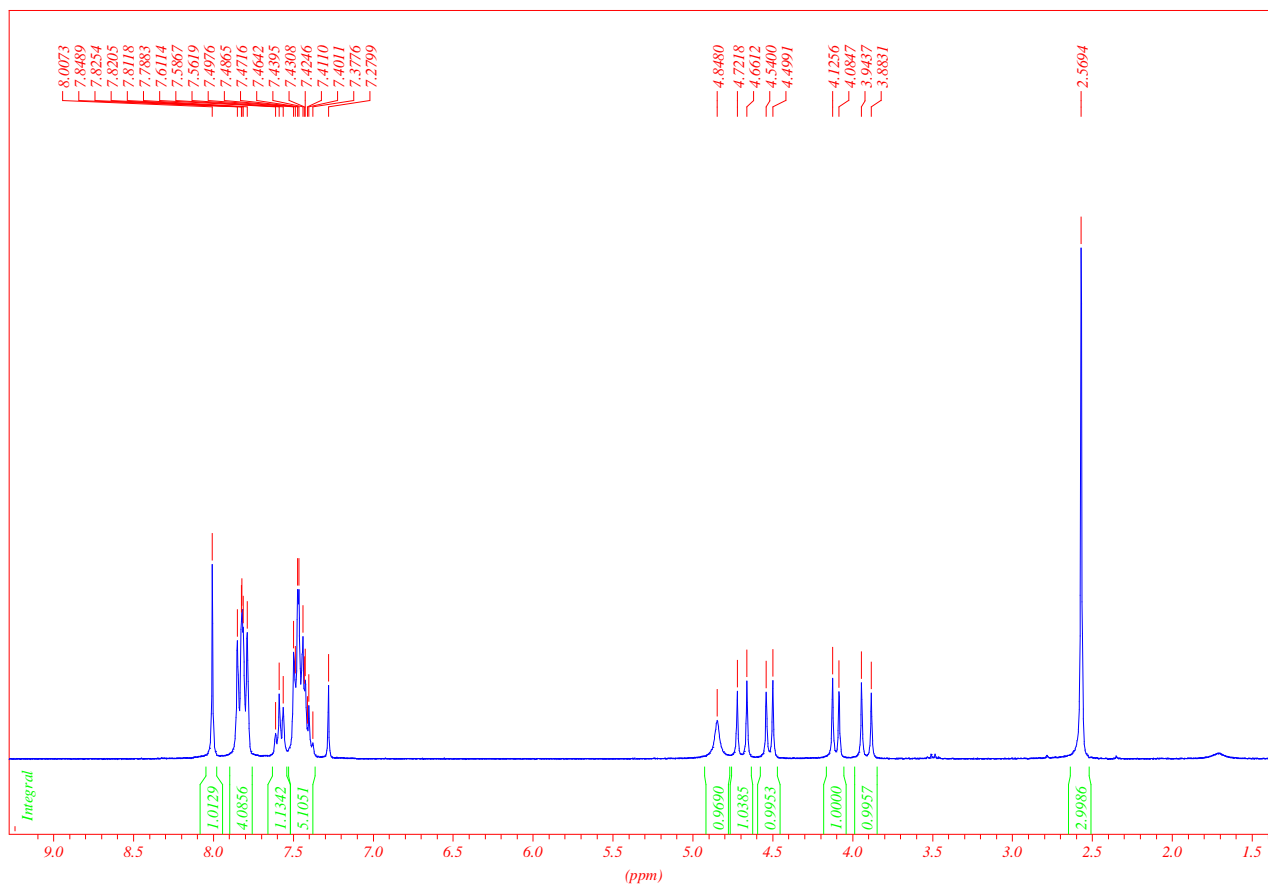
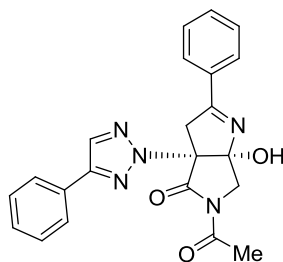


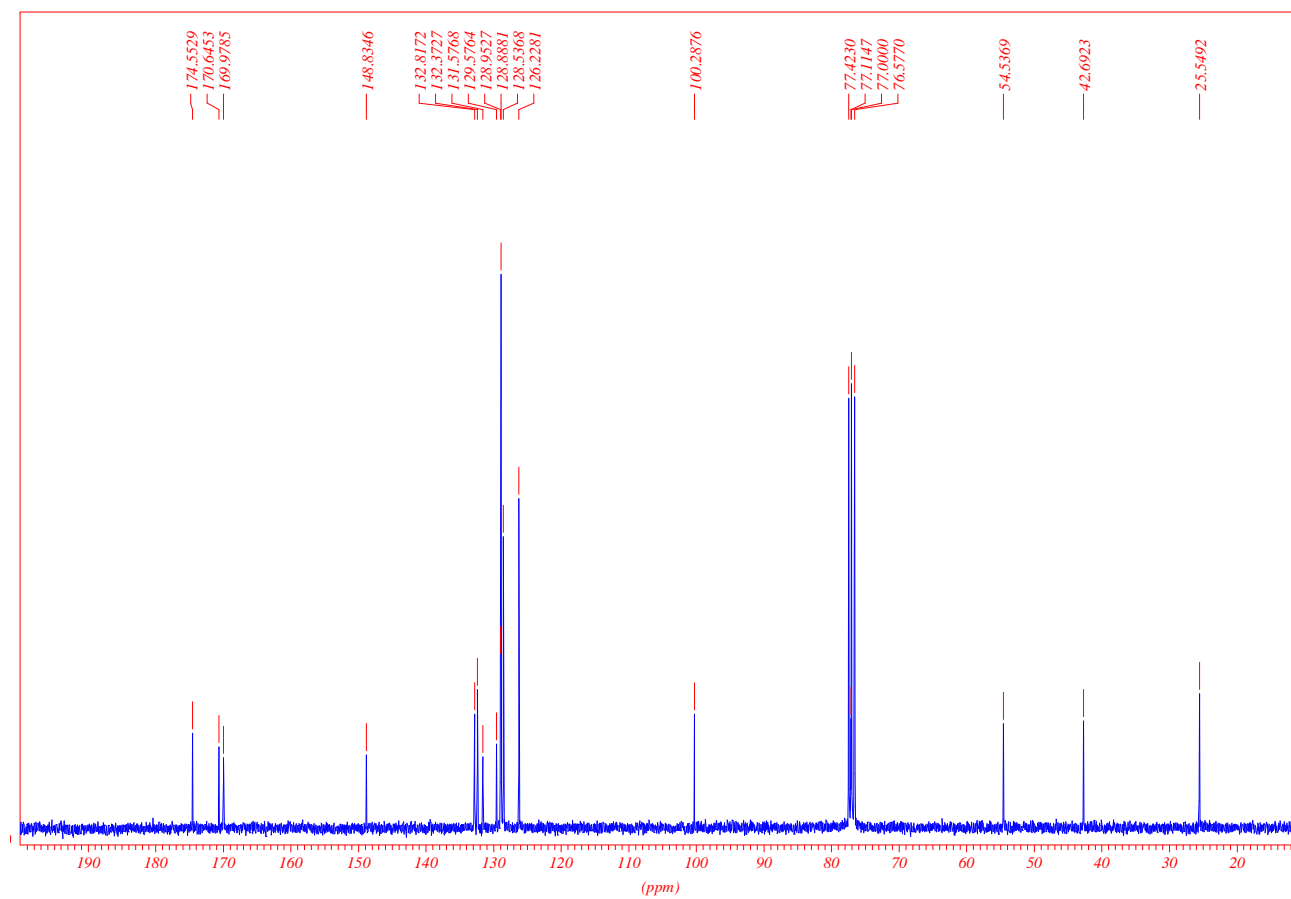
7-Acetyl-3-(4-methylphenyl)-9-[4-(4-methylphenyl)-2H-1,2,3-triazol-2-yl]-1-oxa-4,7-diazaspiro[4.4]non-3-en-8-one (4b)



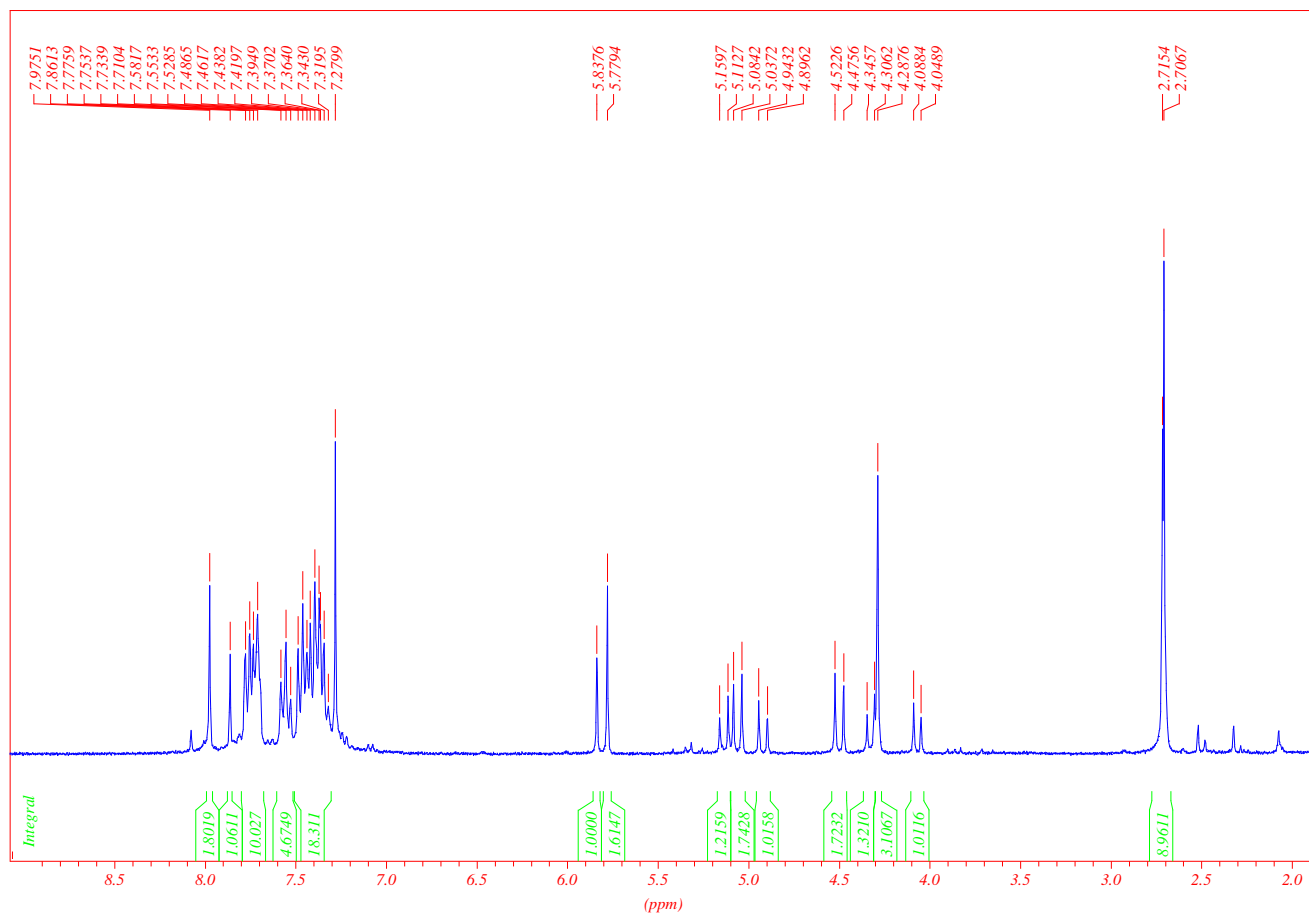
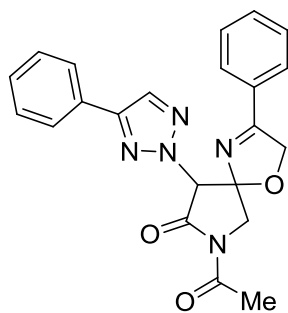


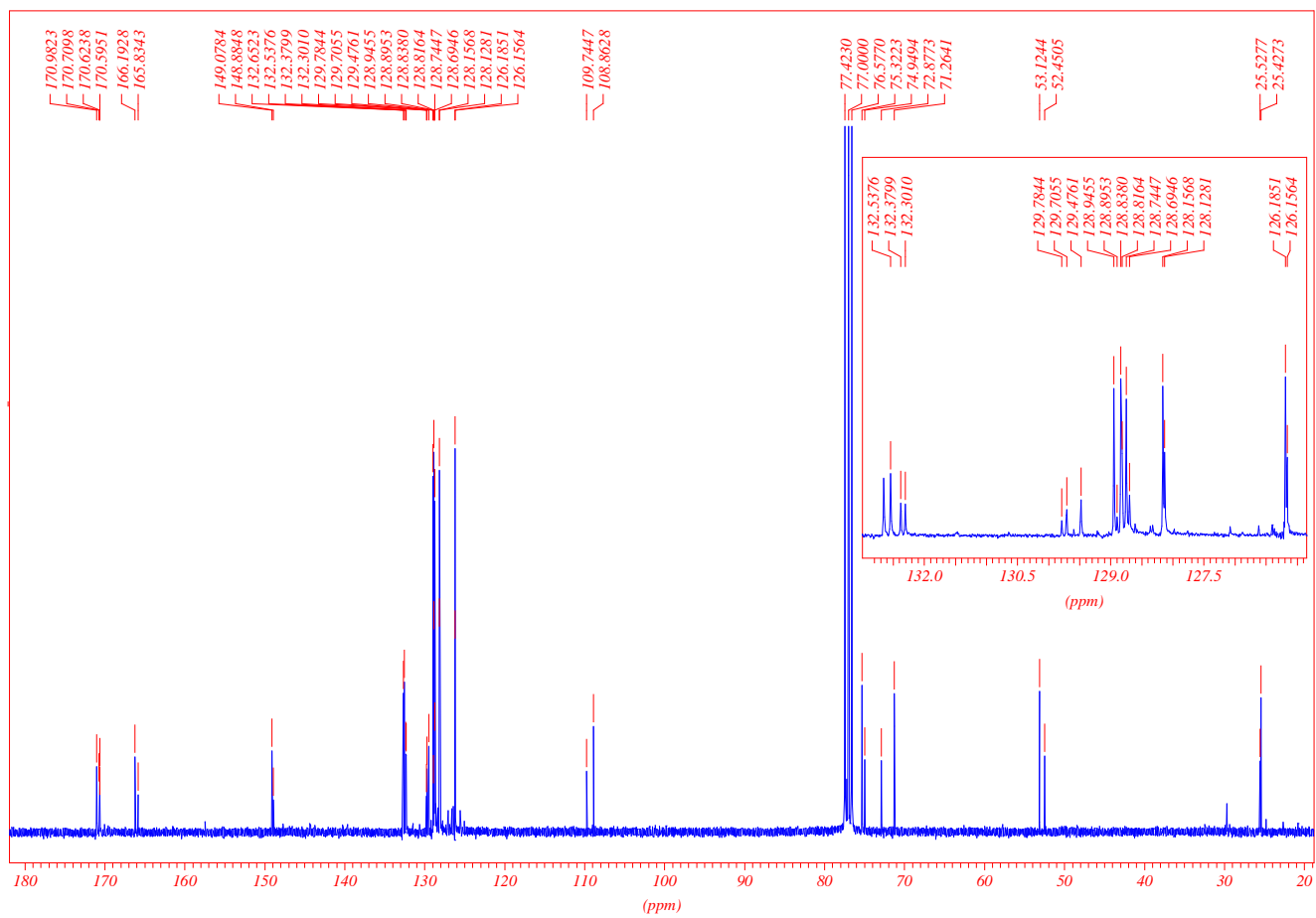
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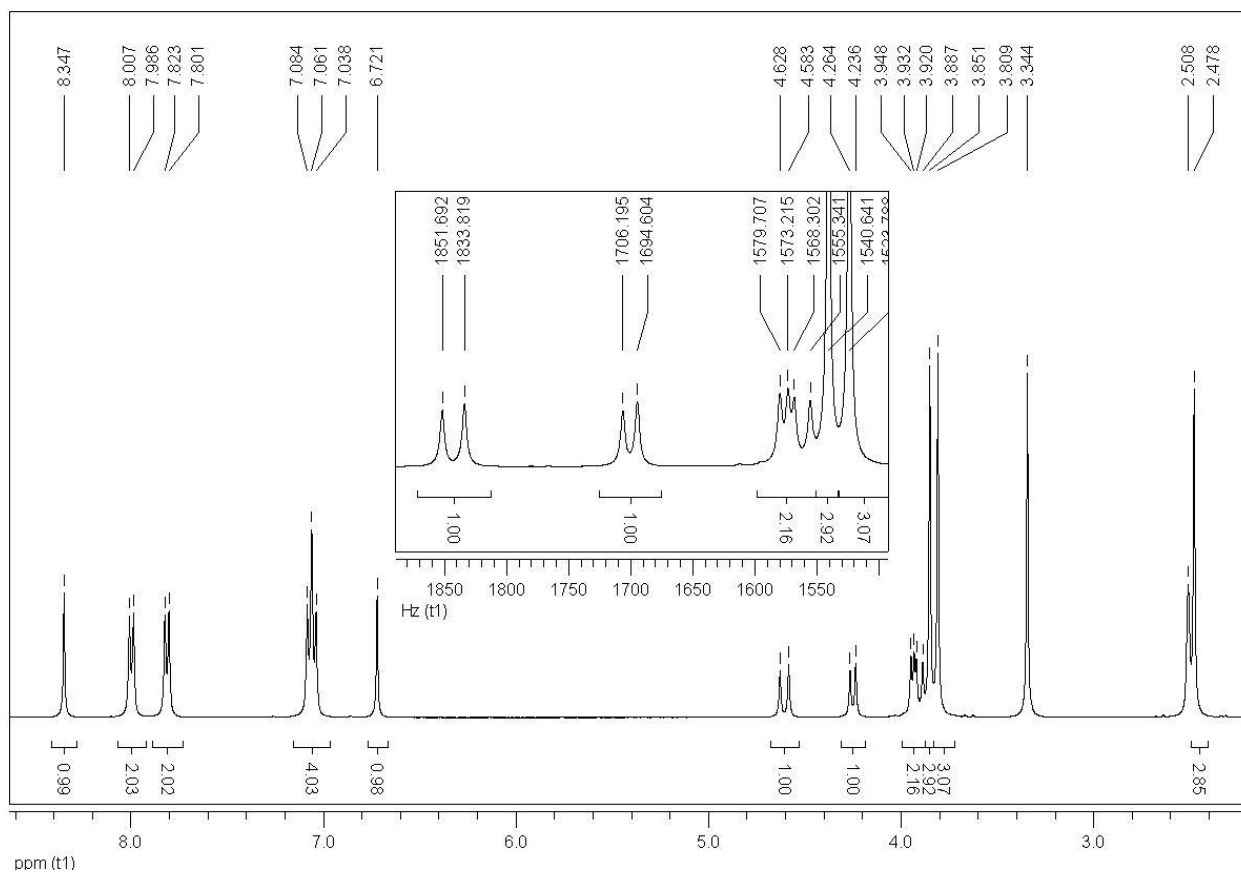
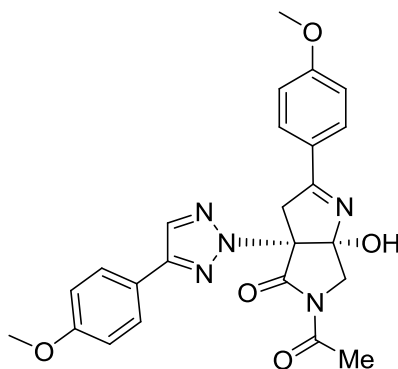


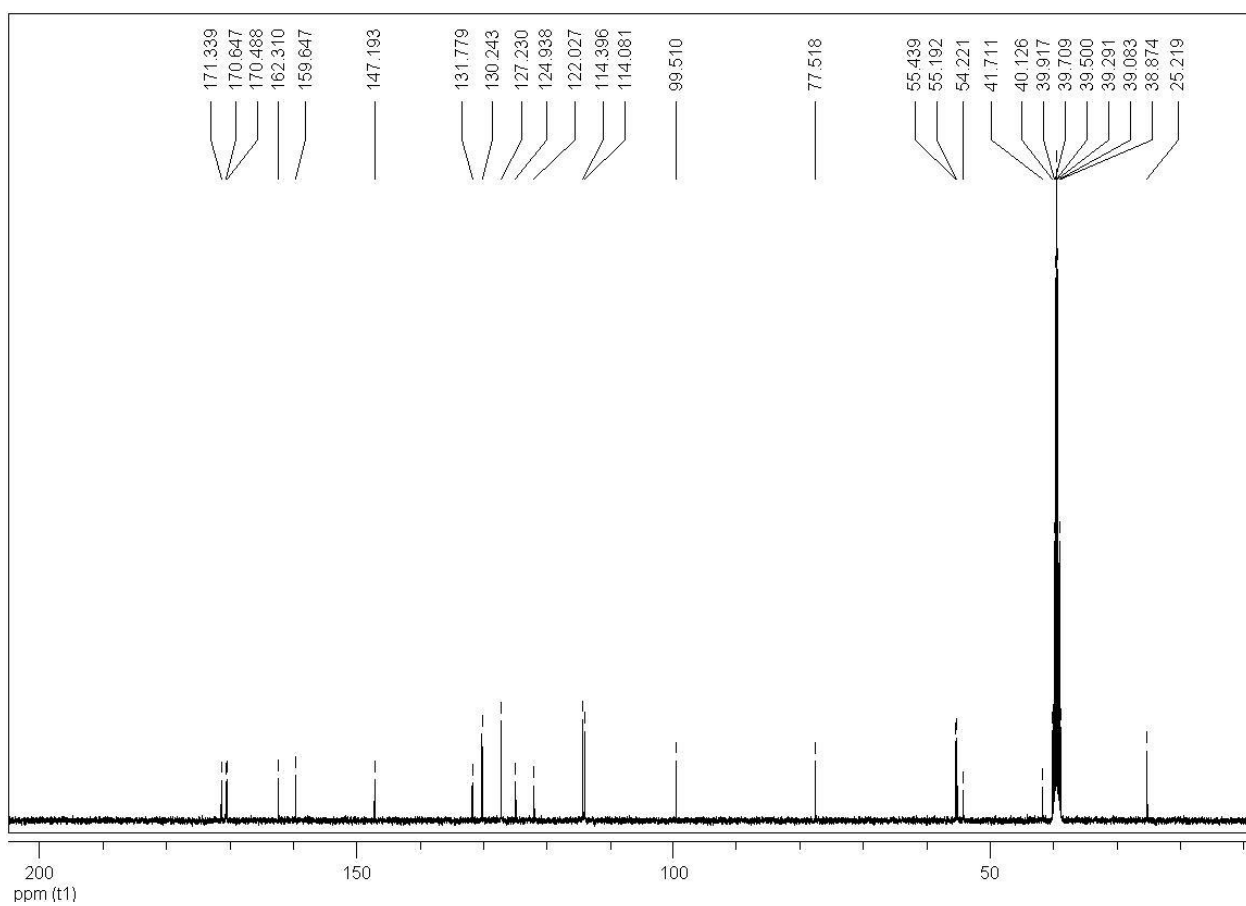
7-Acetyl-3-phenyl-9-[4-phenyl-2*H*-1,2,3-triazol-2-yl]-1-oxa-4,7-diazaspiro[4.4]non-3-en-8-one (4c)

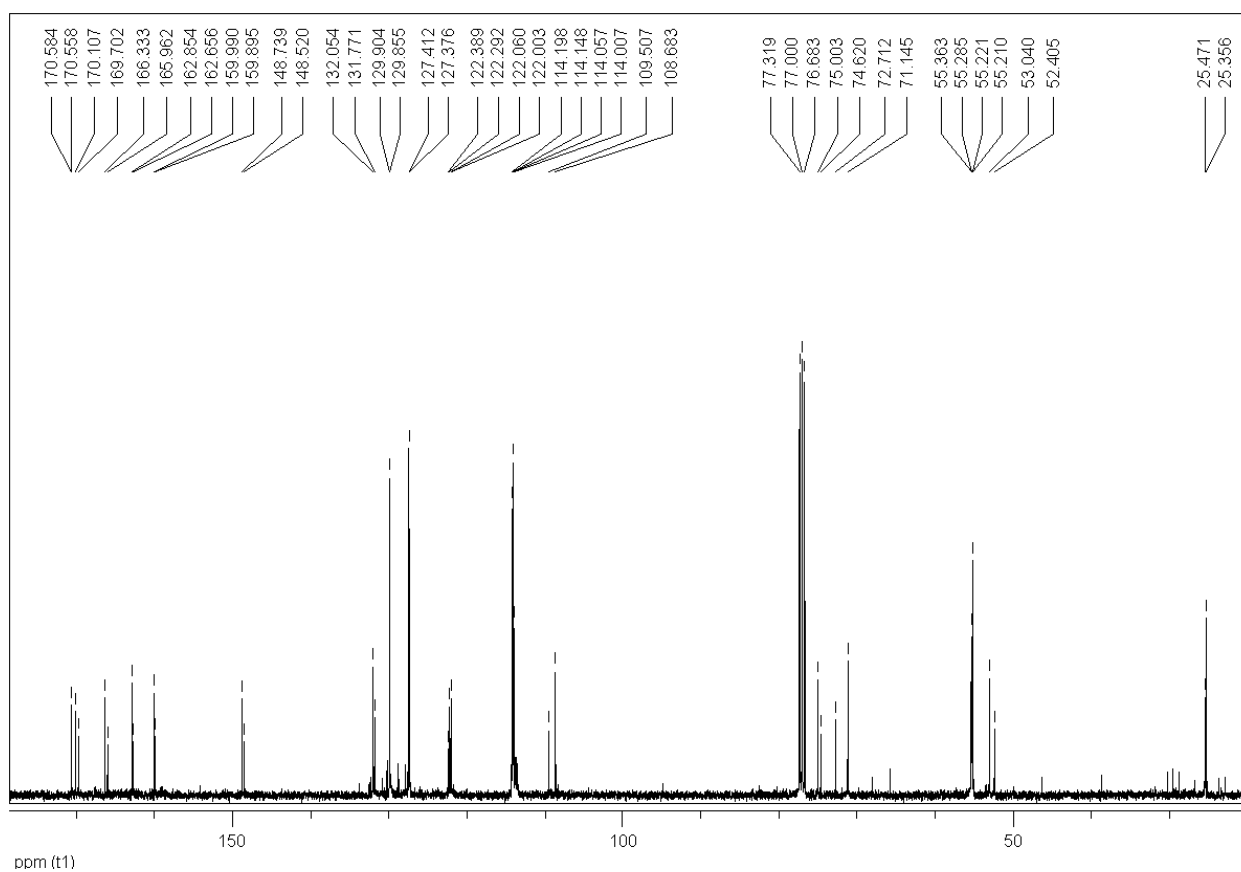




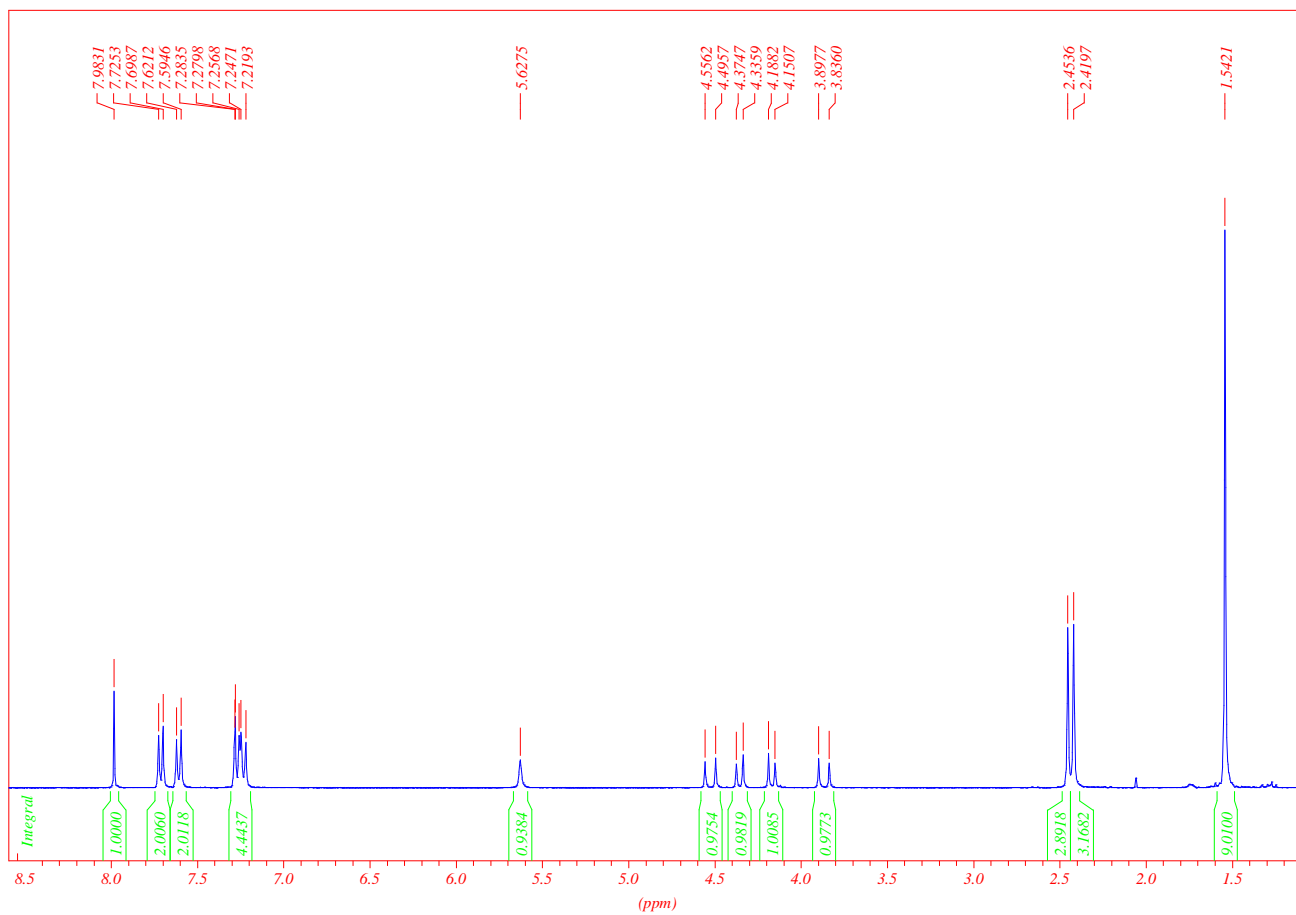
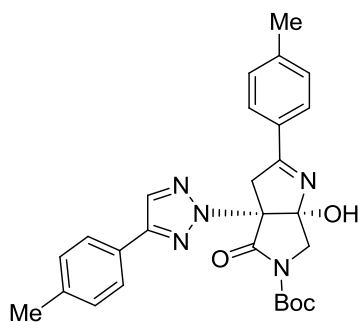
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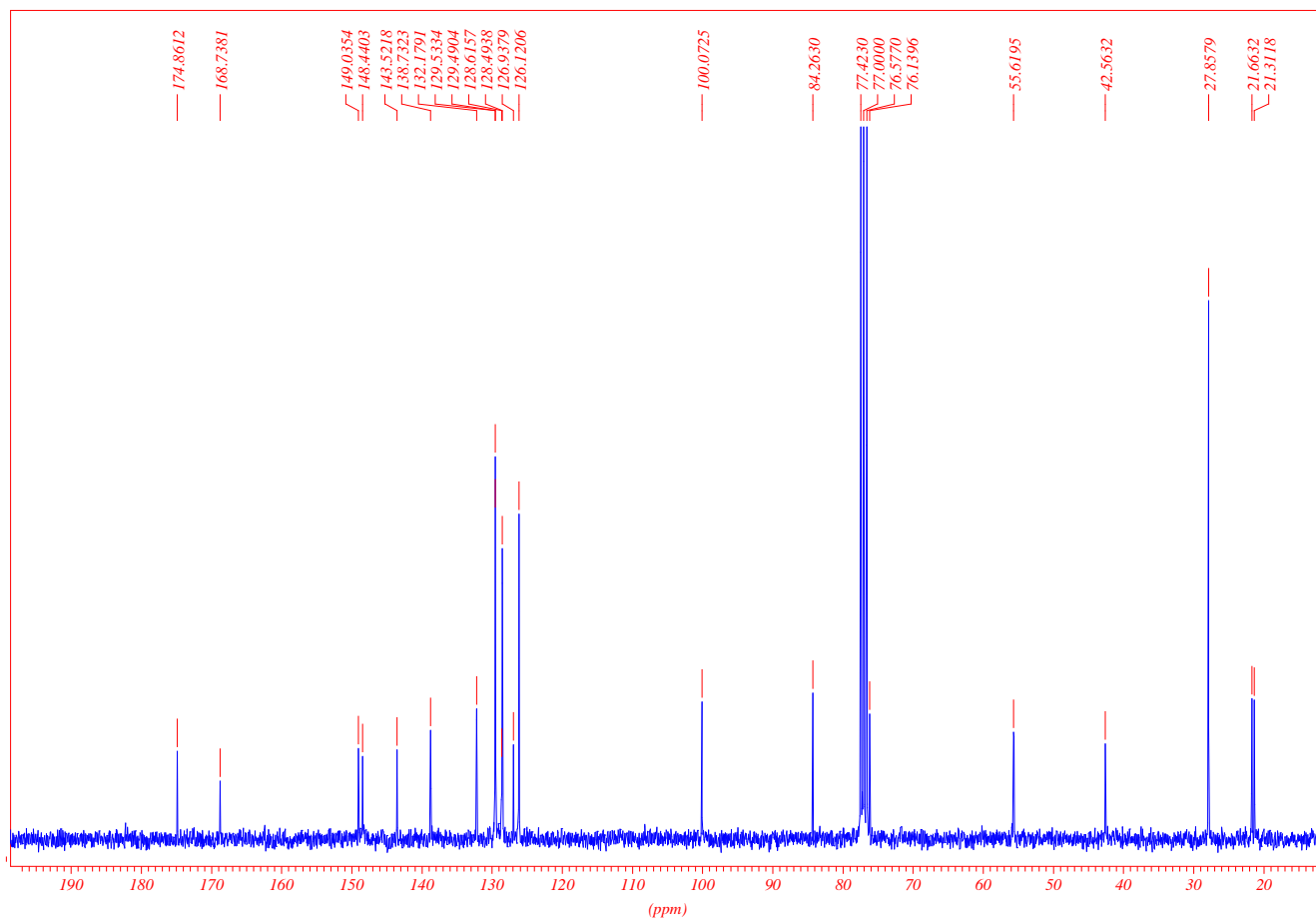




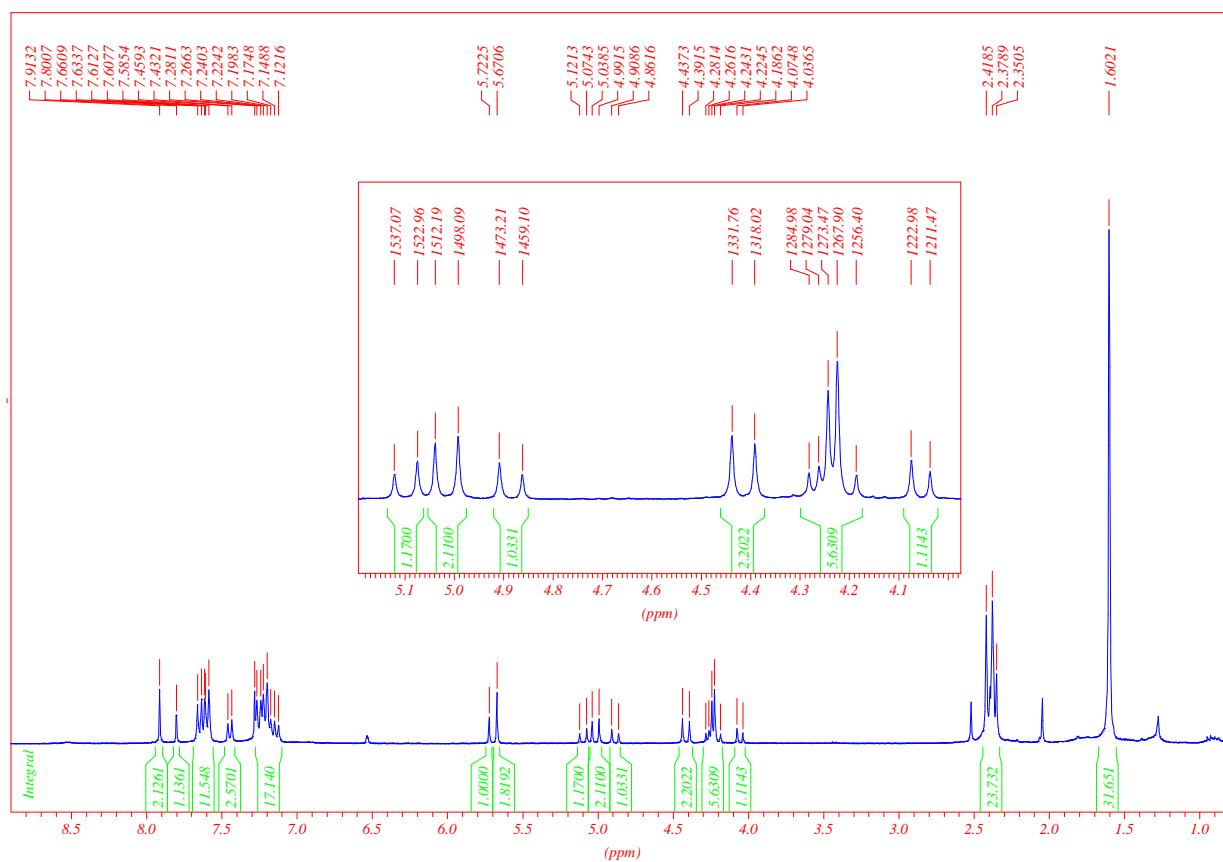
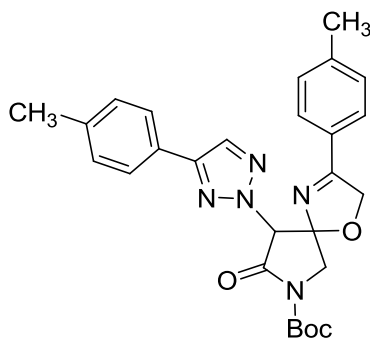


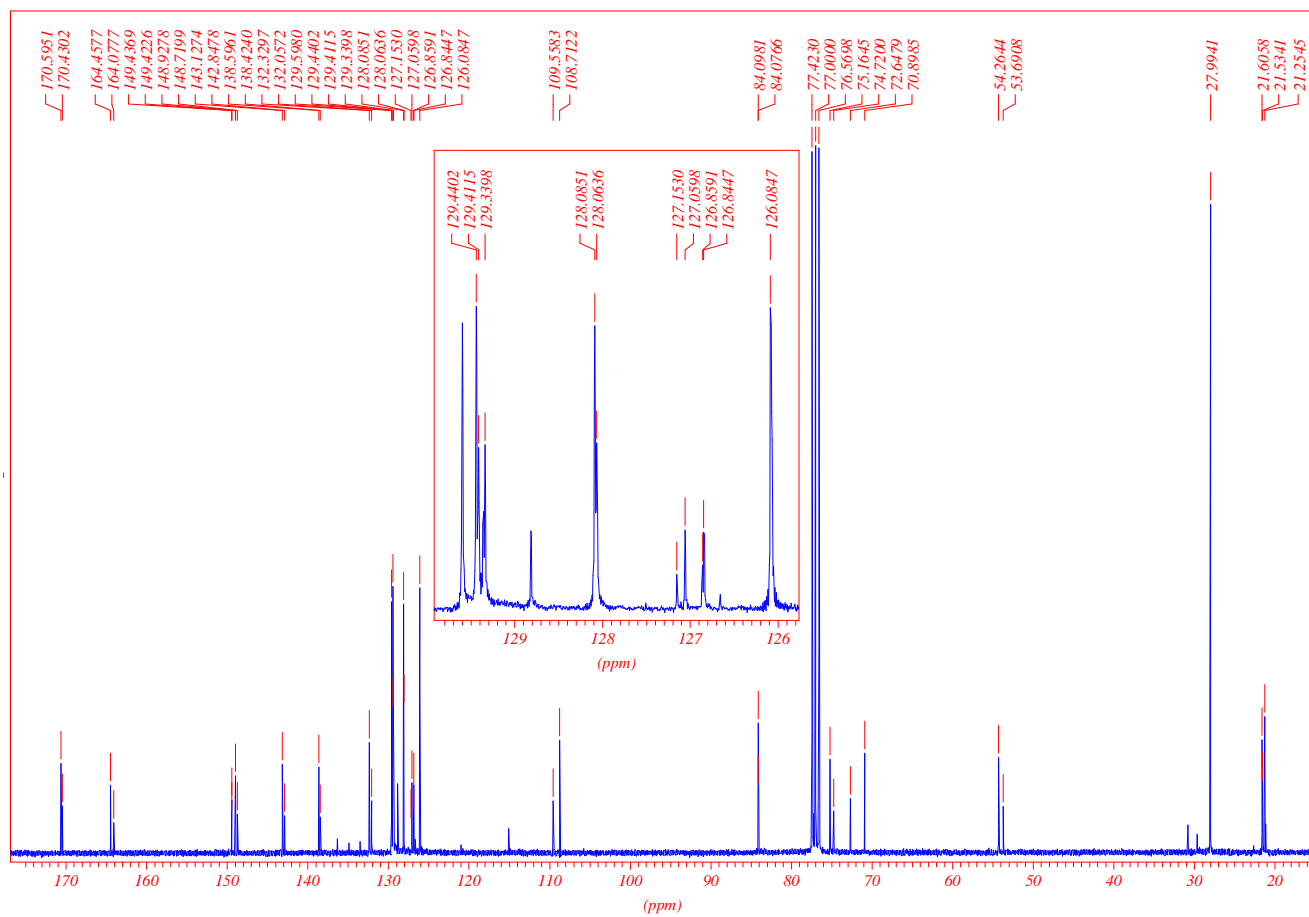
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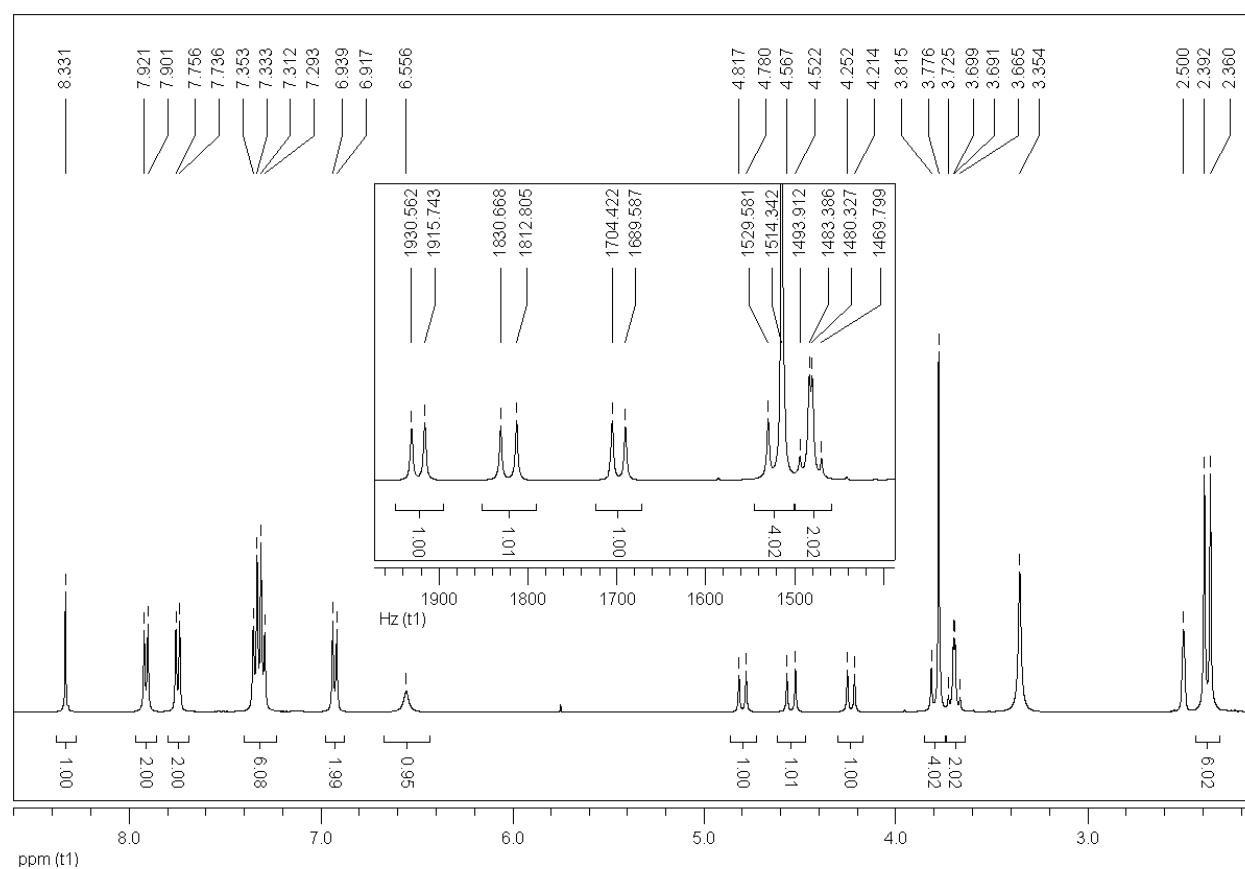
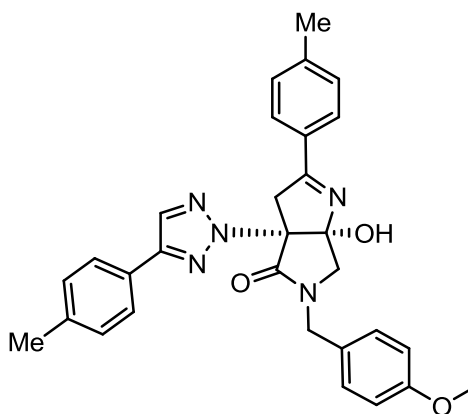


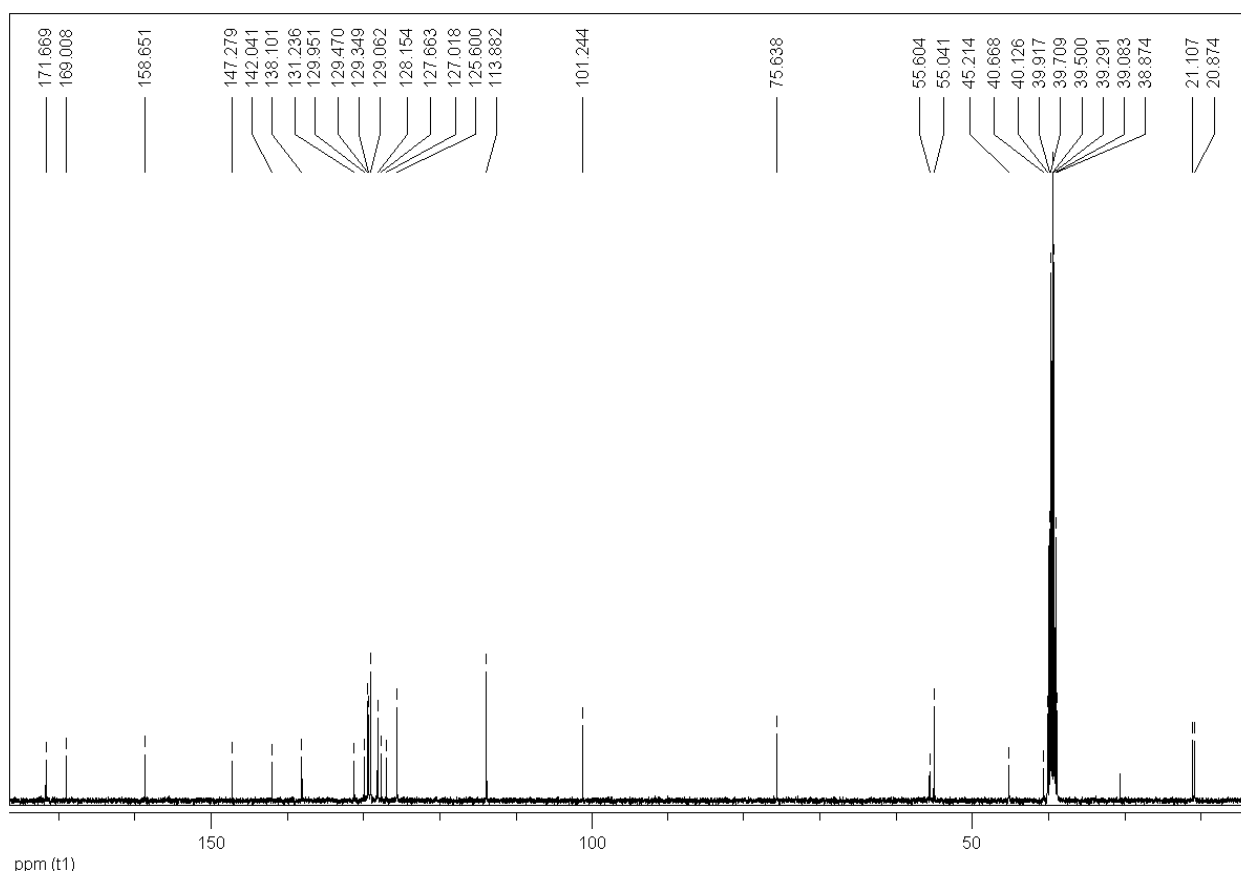
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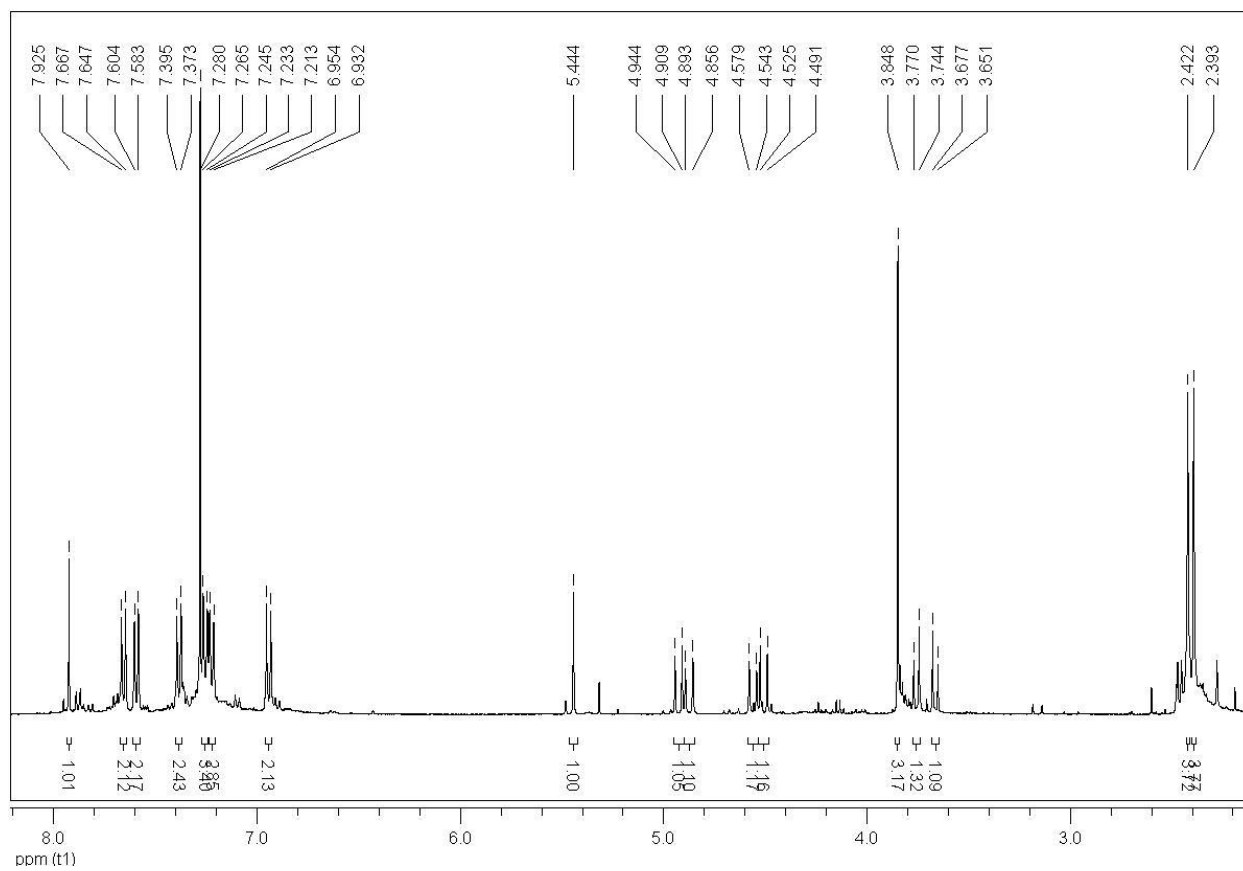
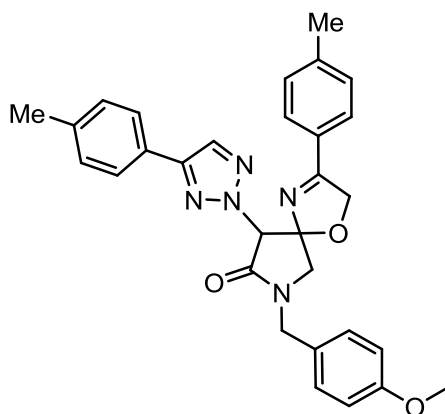


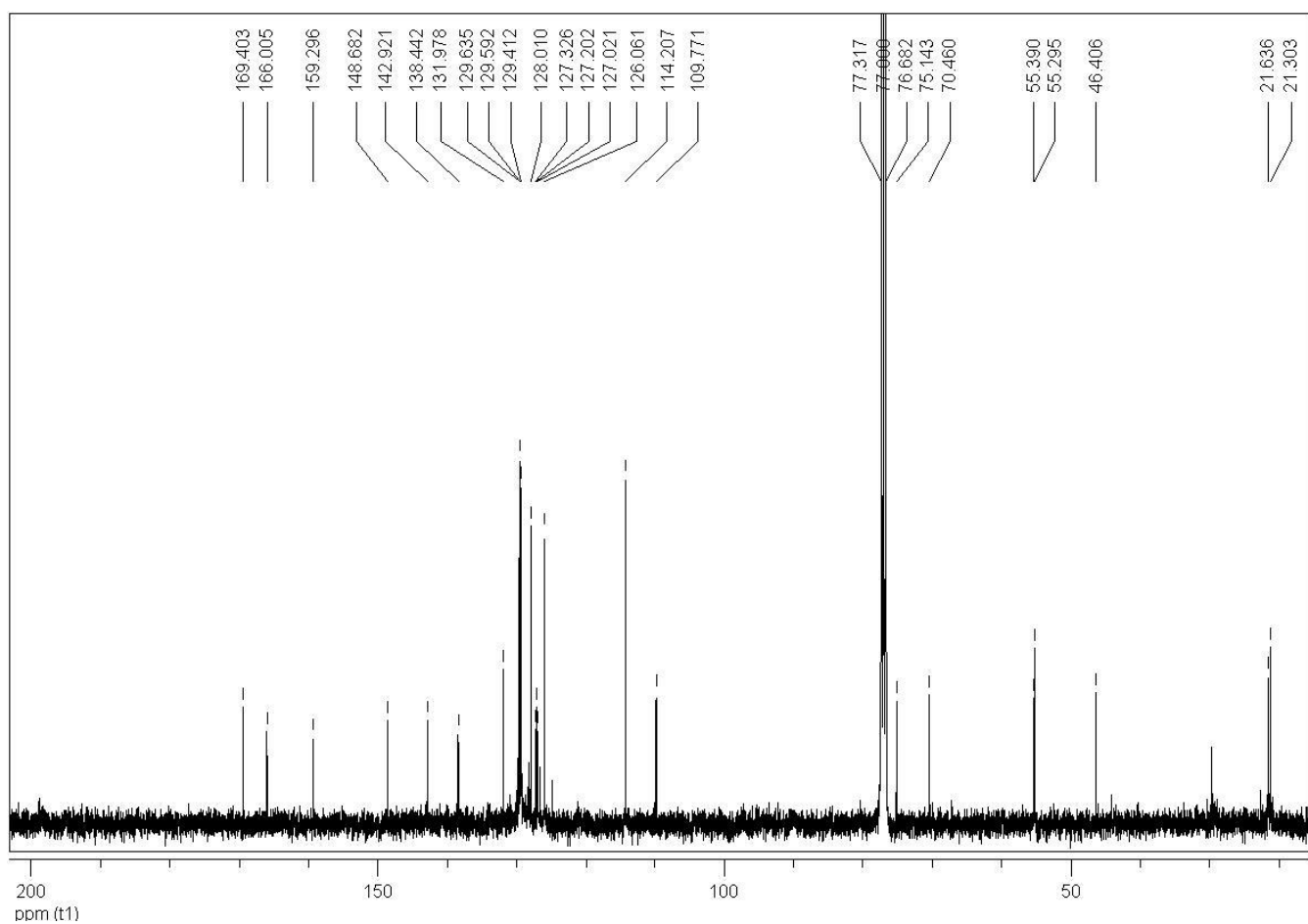
(3a*RS*,6a*RS*)-6a-Hydroxy-5-(4-methoxybenzyl)-2-(4-methylphenyl)-3a-[4-(4-methylphenyl)-2*H*-1,2,3-triazol-2-yl]-3a,5,6,6a-tetrahydropyrrolo[3,4-*b*]pyrrol-4(3*H*)-one (3f)





7-(4-Methoxybenzyl)-3-(4-methylphenyl)-9-[(4-methylphenyl)-2H-1,2,3-triazol-2-yl]-1-oxa-4,7-diazaspiro[4.4]non-3-en-8-one (4f)





(3*aRS*,6*aSR*)-6*a*-Hydroxy-2-(4-methylphenyl)-3*a*-[4-(4-methylphenyl)-1,2,3-triazol-2-yl]-6,6-dihydro-3*H*-furo[3,4-*b*]pyrrol-4(3*aH*)-one (6*a*)

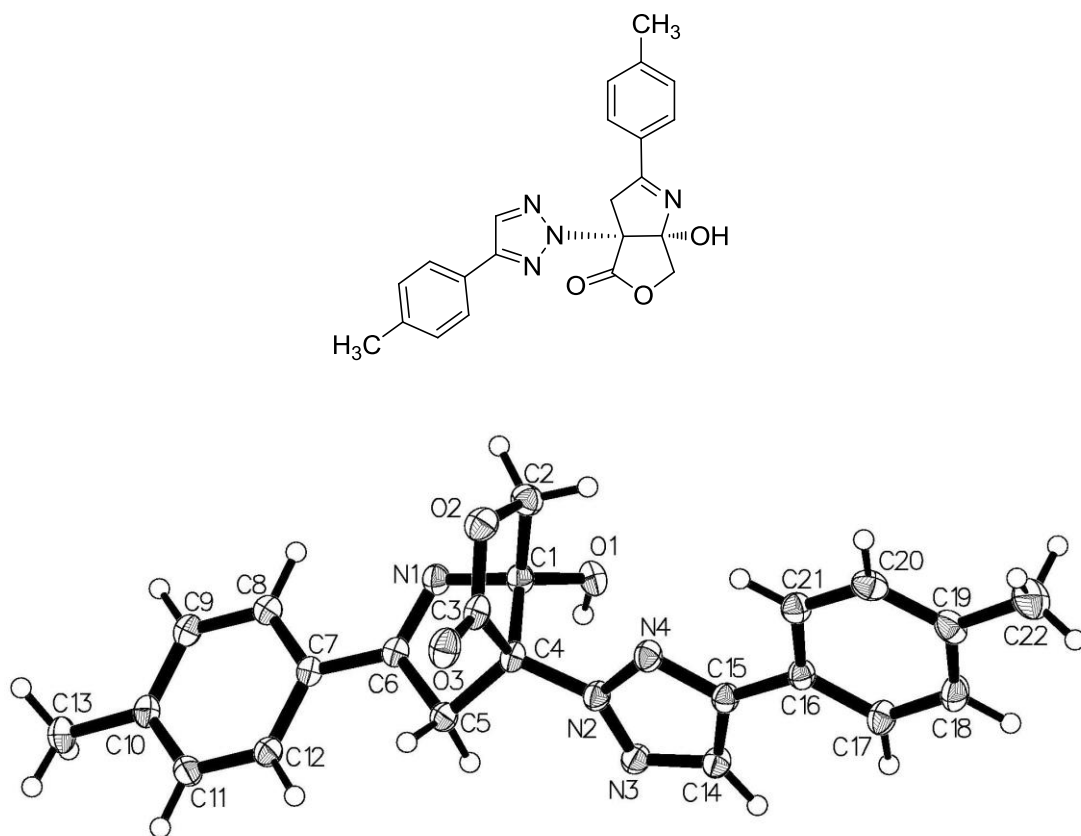
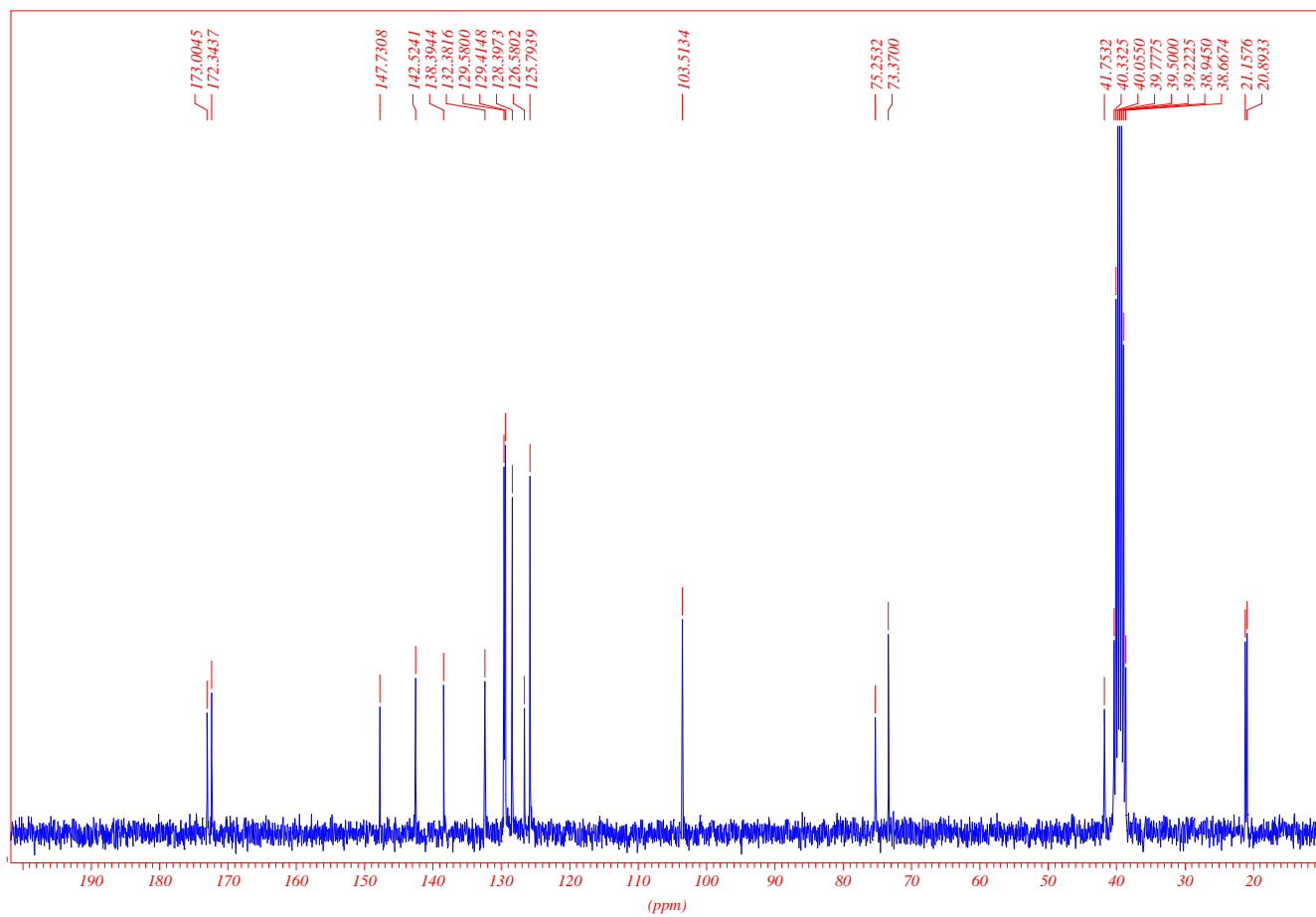
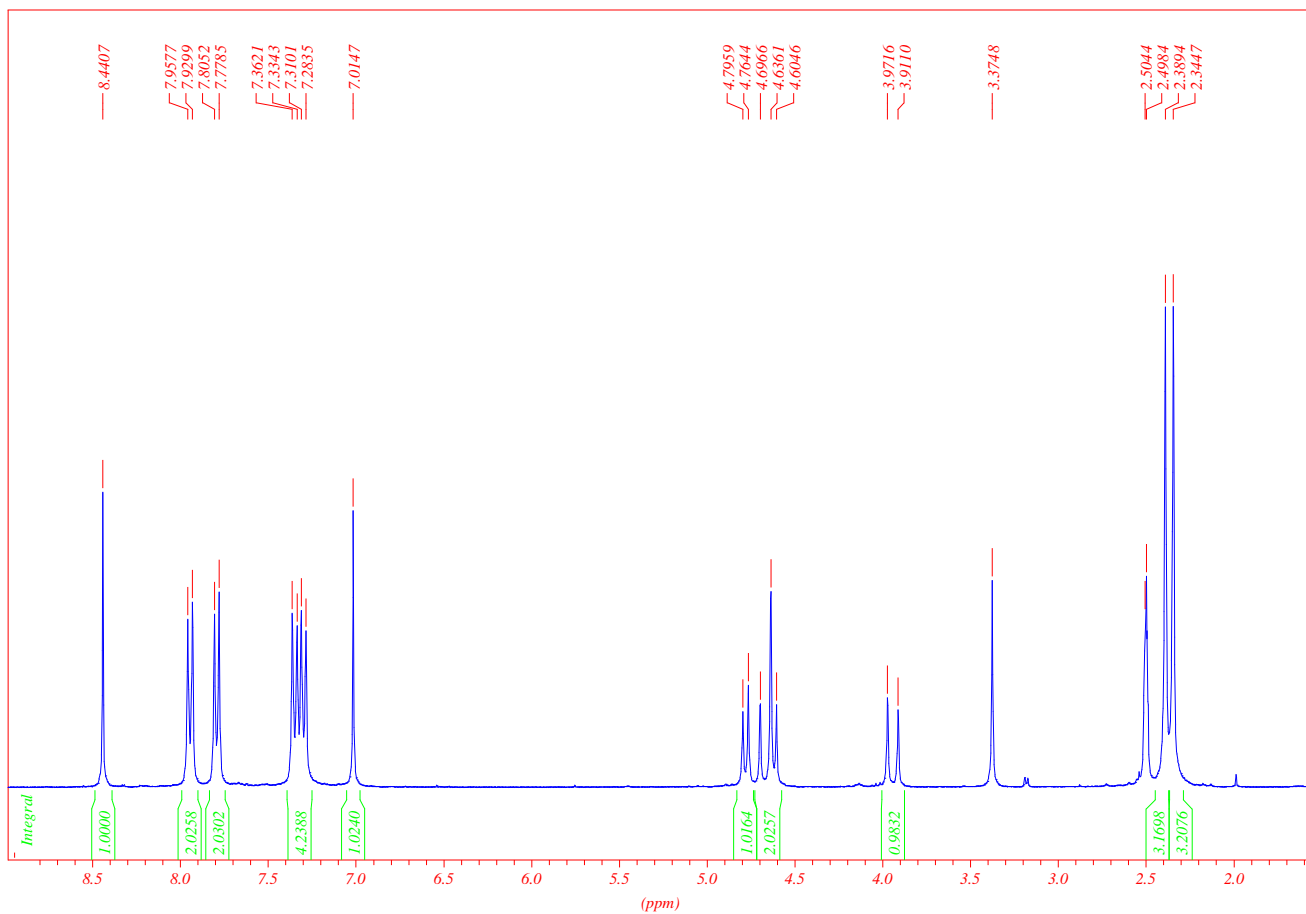


Fig. 3 X-ray structure of compound **6a**.



(5*RS*,9*SR*)-3-(4-Methylphenyl)-9-[4-(4-methylphenyl)-1,2,3-triazol-2-yl]-1,7-dioxo-4-azaspiro[4.4]non-3-en-8-one ((5*RS*,9*SR*)-7a)

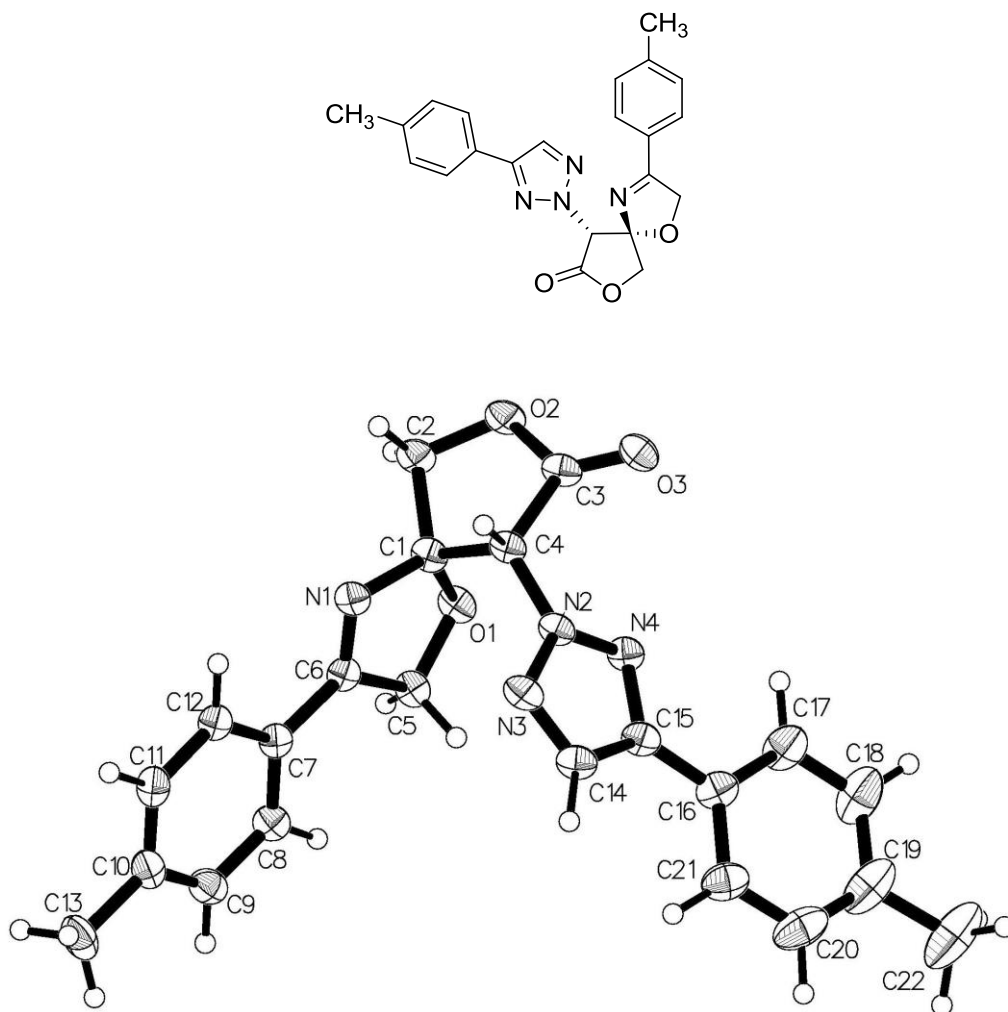
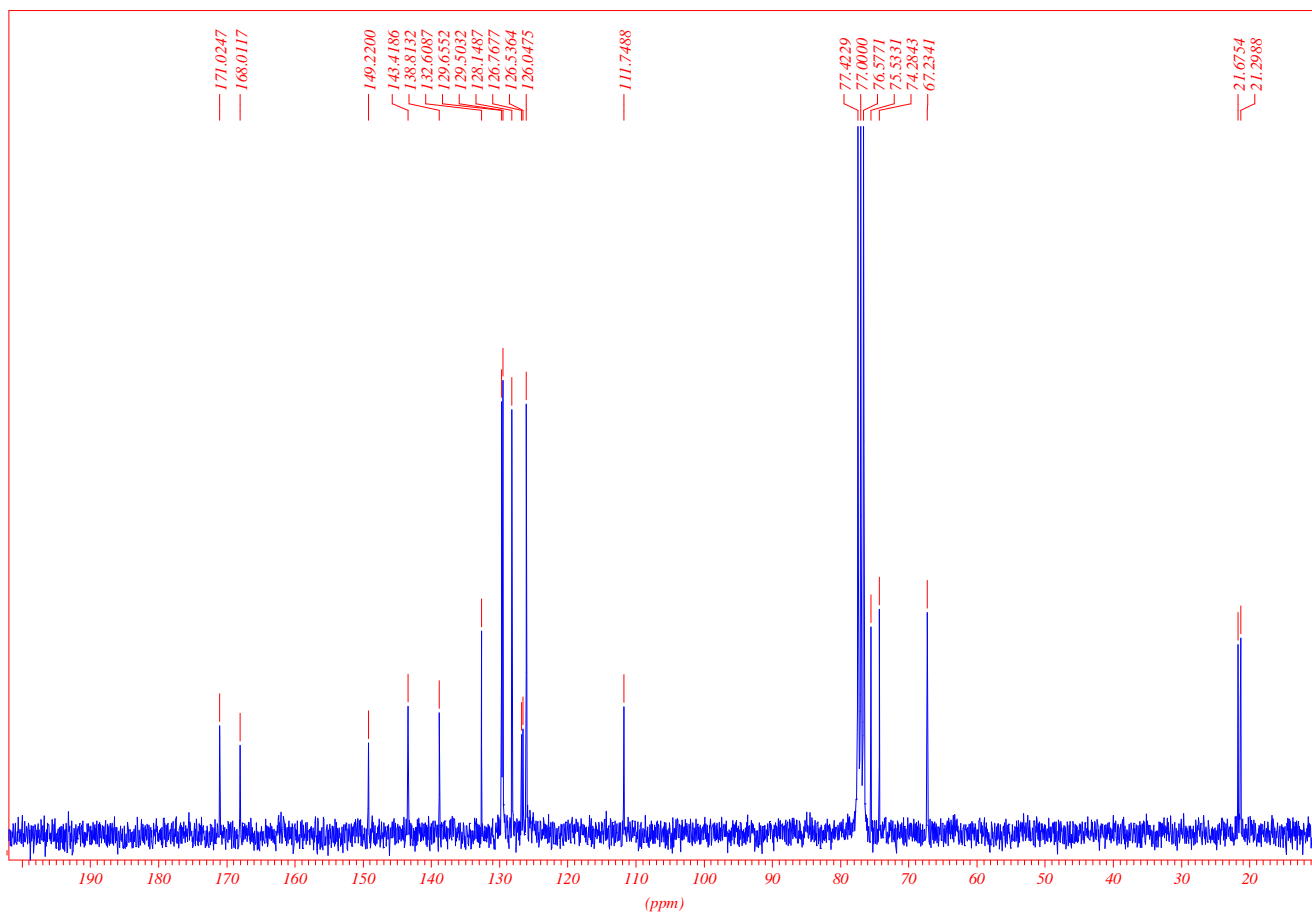
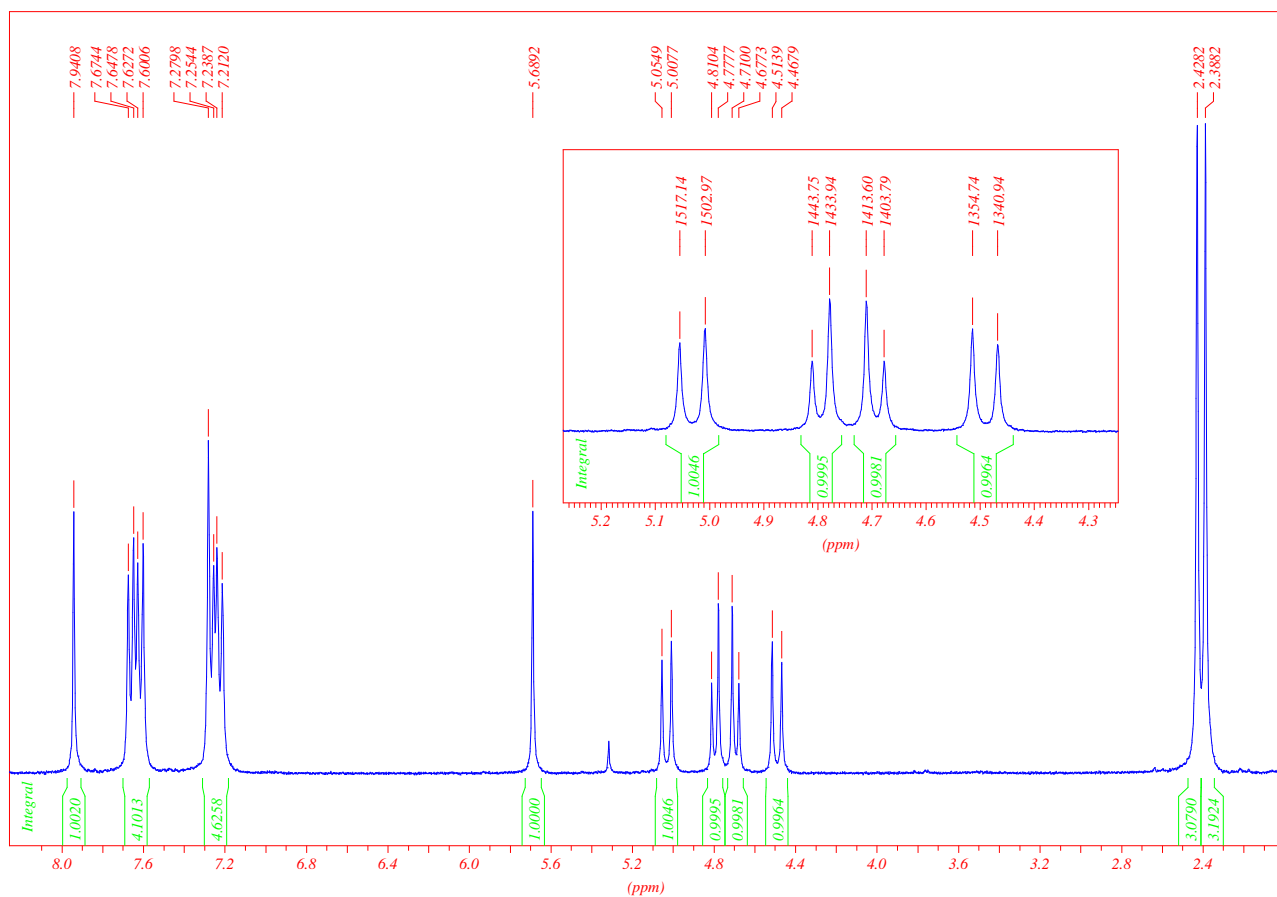
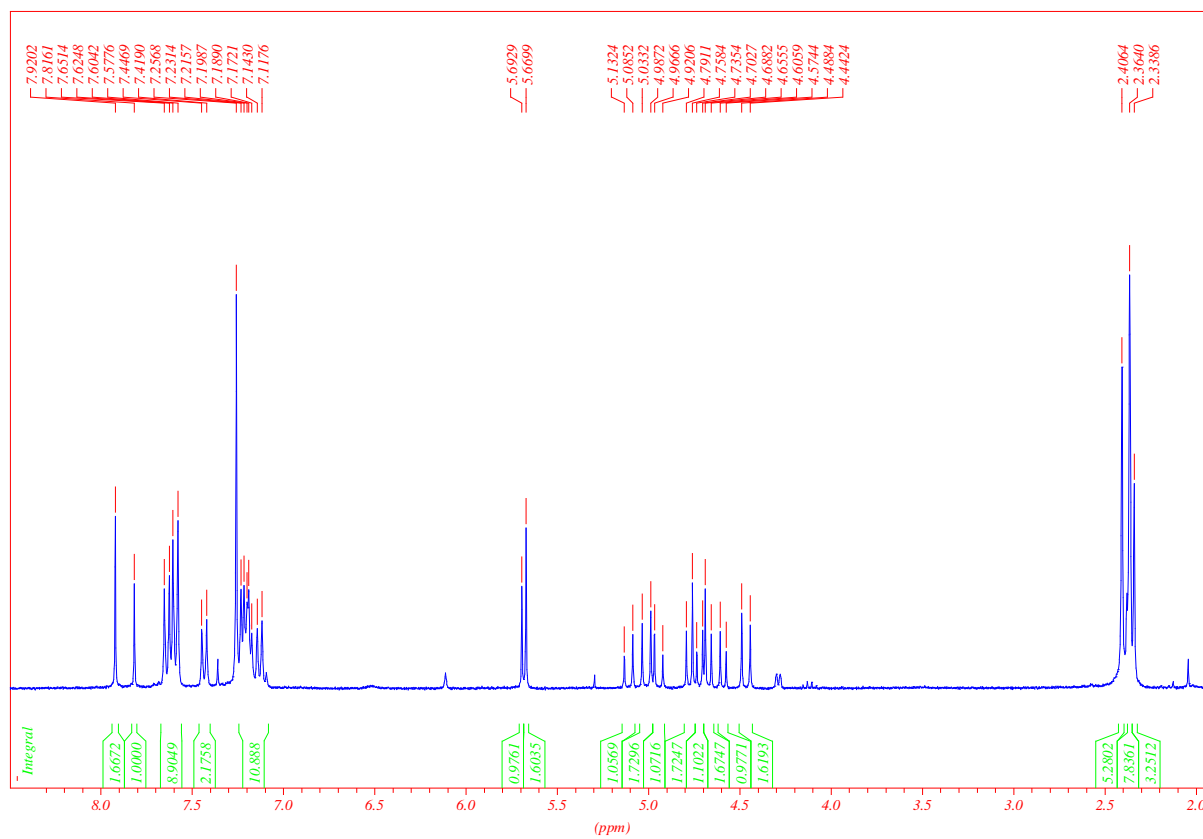


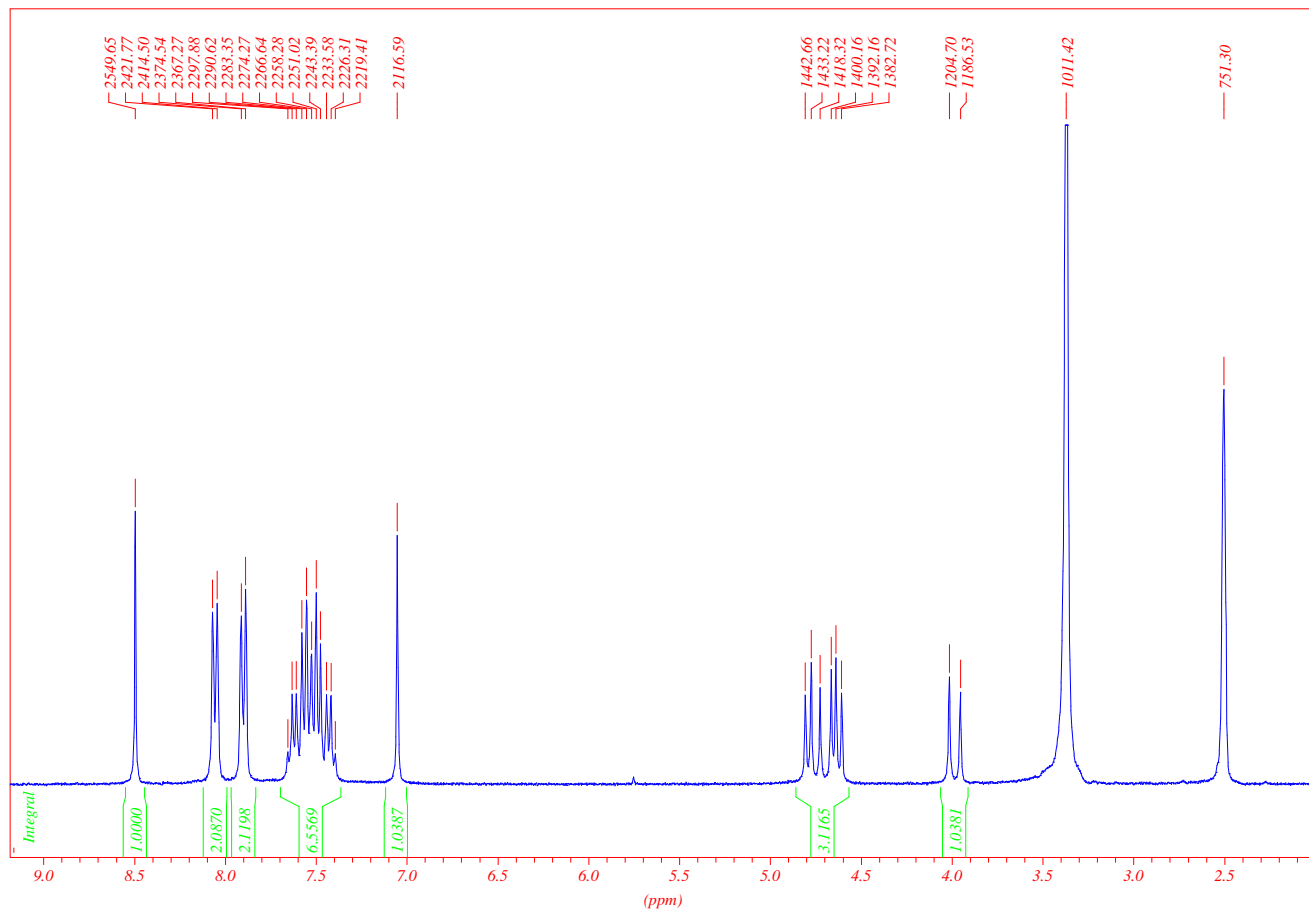
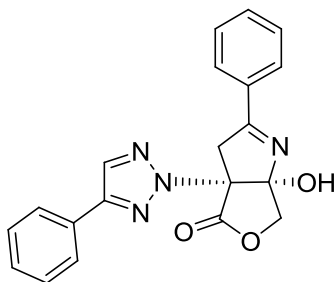
Fig. 4 X-ray structure of compound (5*RS*,9*SR*)-7a.

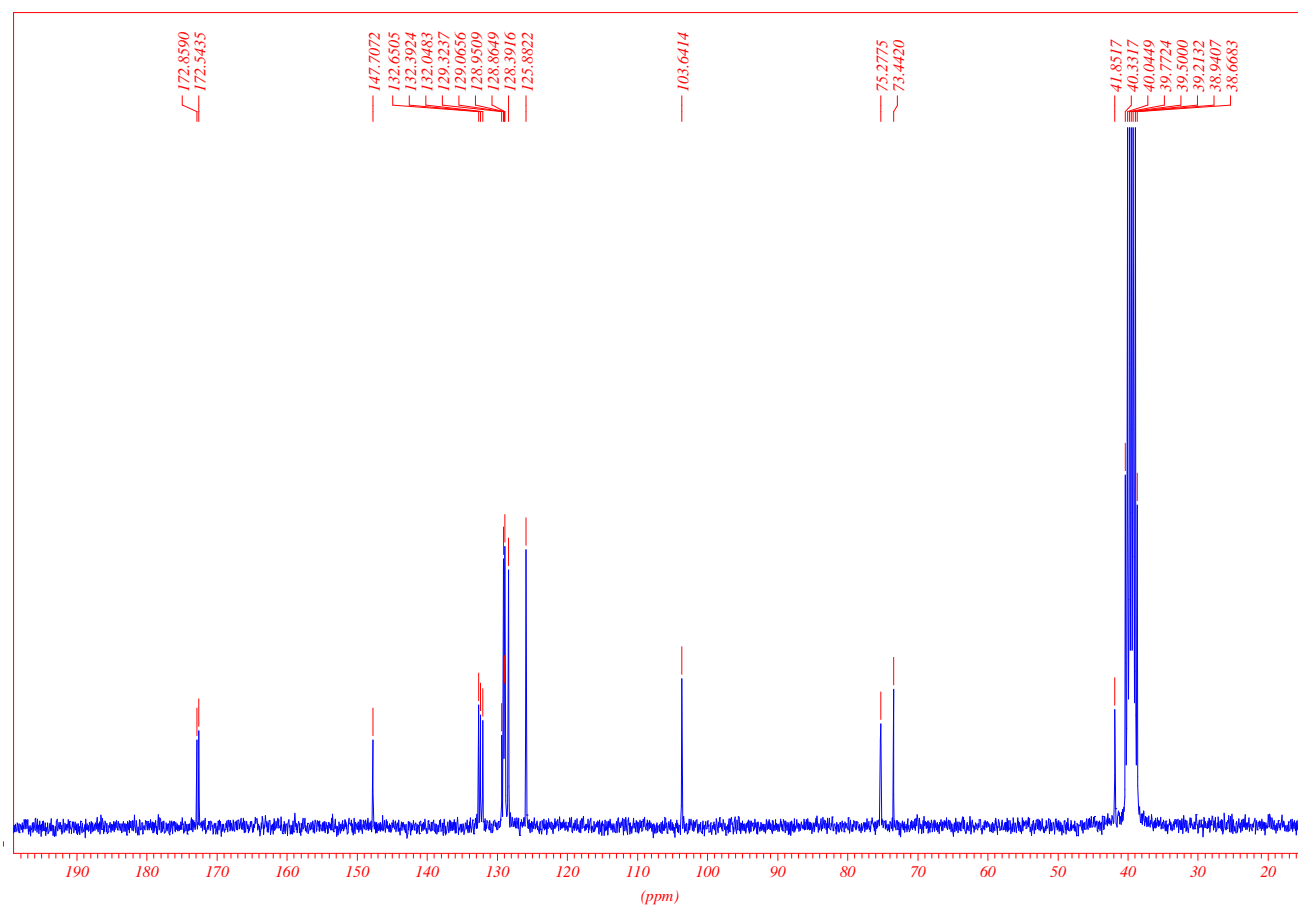


3-(4-Methylphenyl)-9-[4-(4-methylphenyl)-1,2,3-triazol-2-yl]-1,7-dioxo-4-azaspiro[4.4]non-3-en-8-one (7a) (diastereomeric mixture)

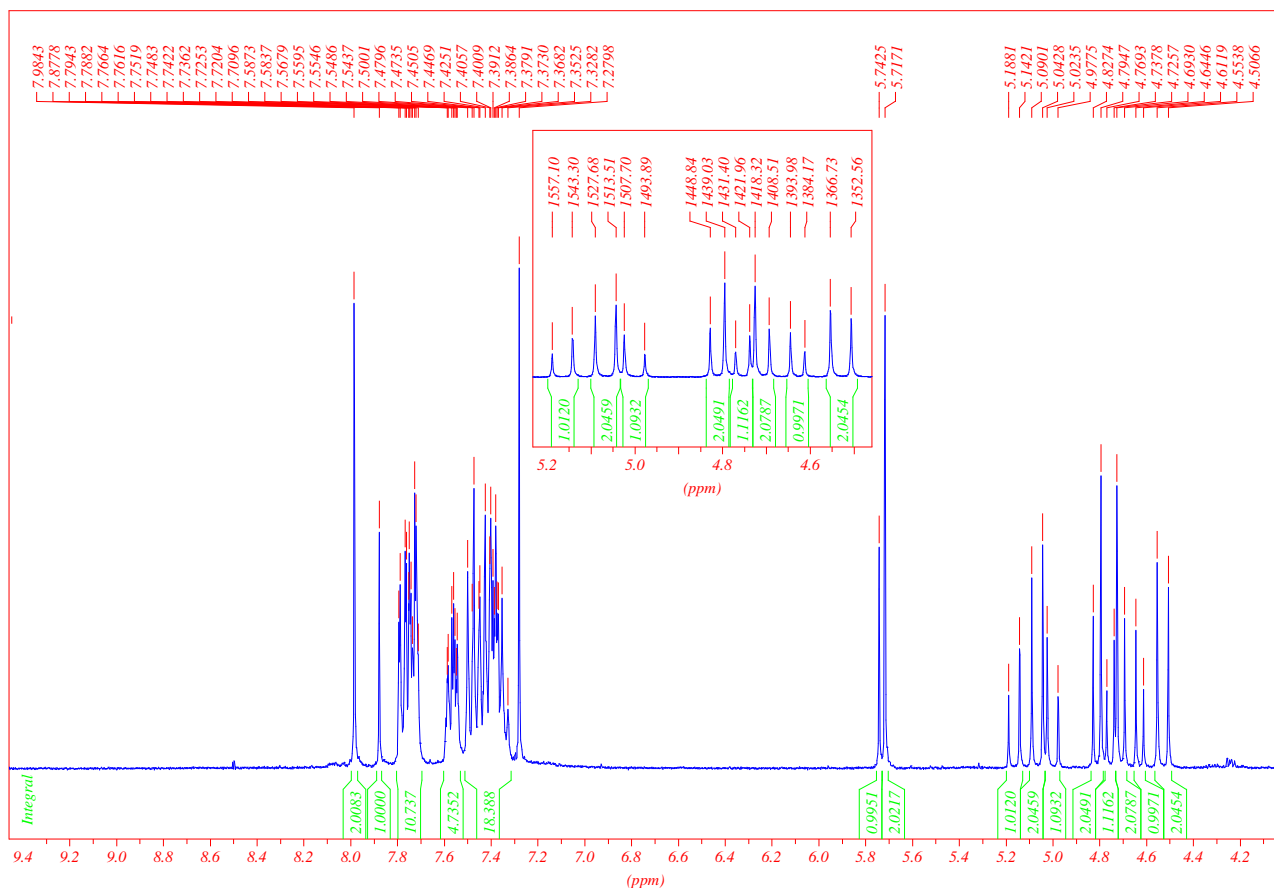
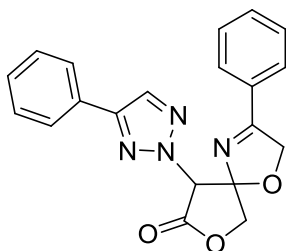


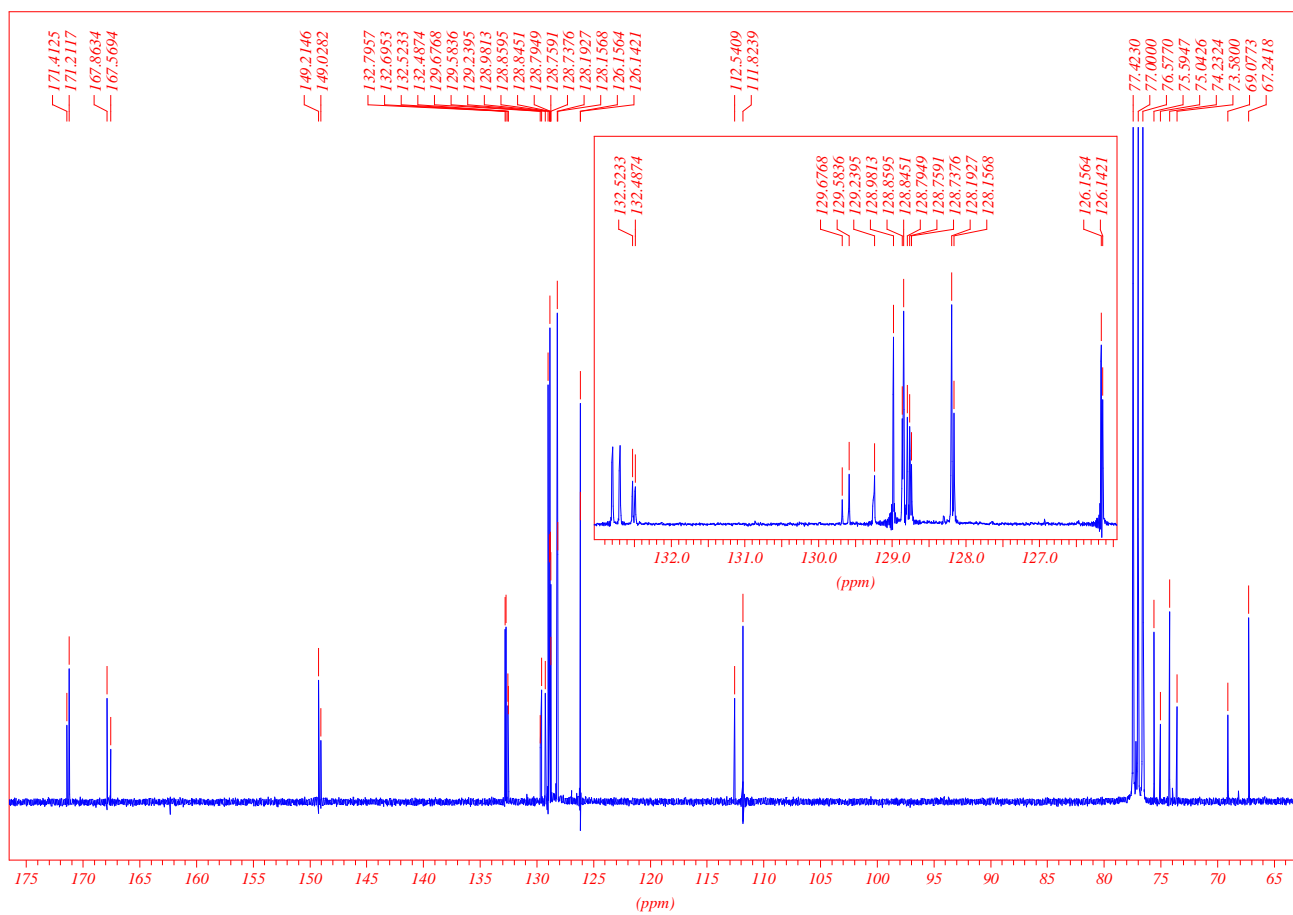
(3*aRS*,6*aSR*)-6*a*-Hydroxy-2-phenyl-3*a*-(4-phenyl-1,2,3-triazol-2-yl)-6,6*a*-dihydro-3*H*-furo[3,4-*b*]pyrrol-4(3*aH*)-one (6*b*)



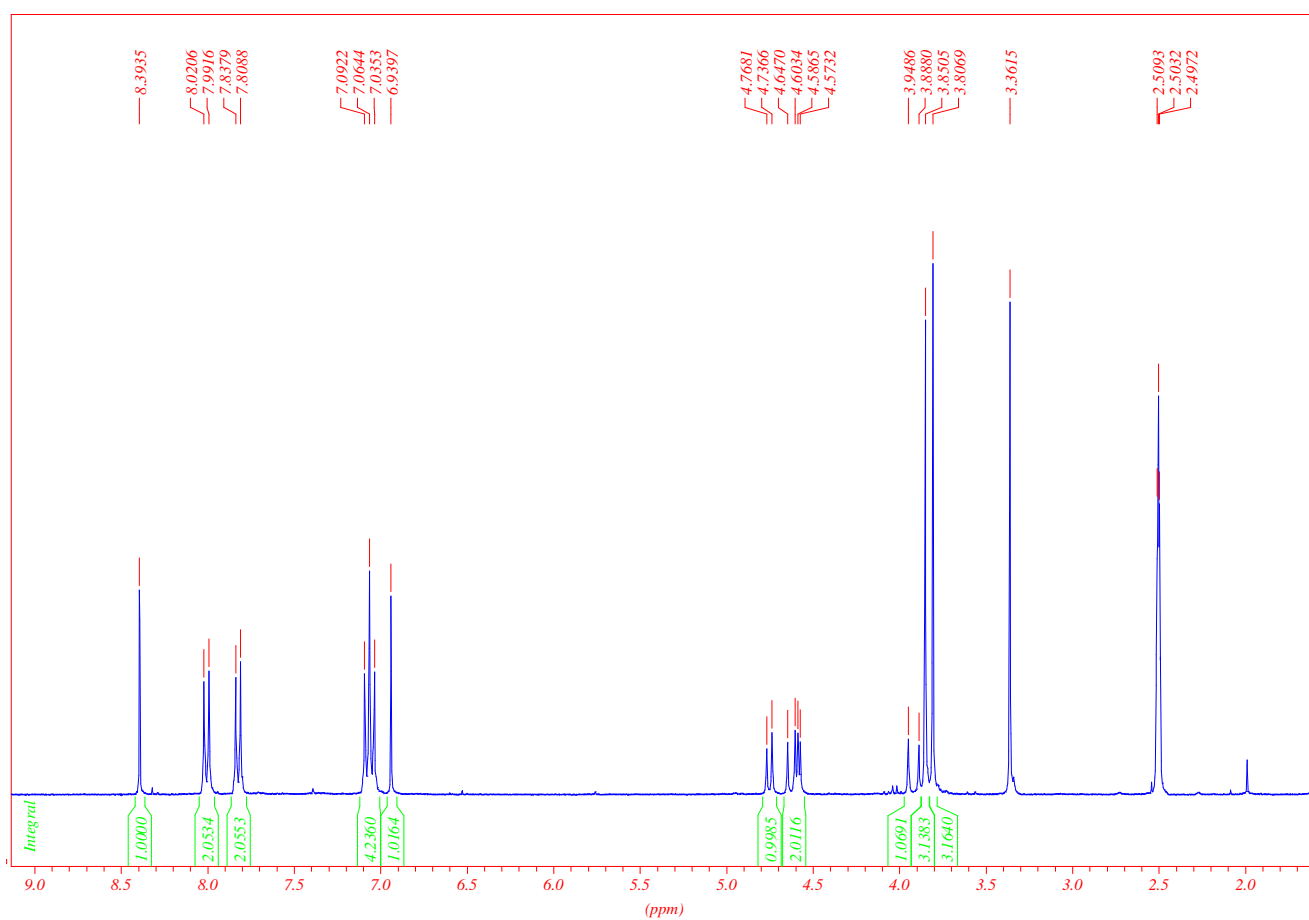
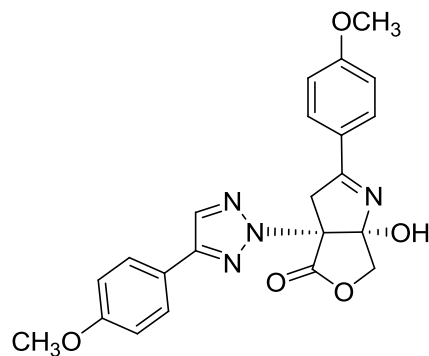


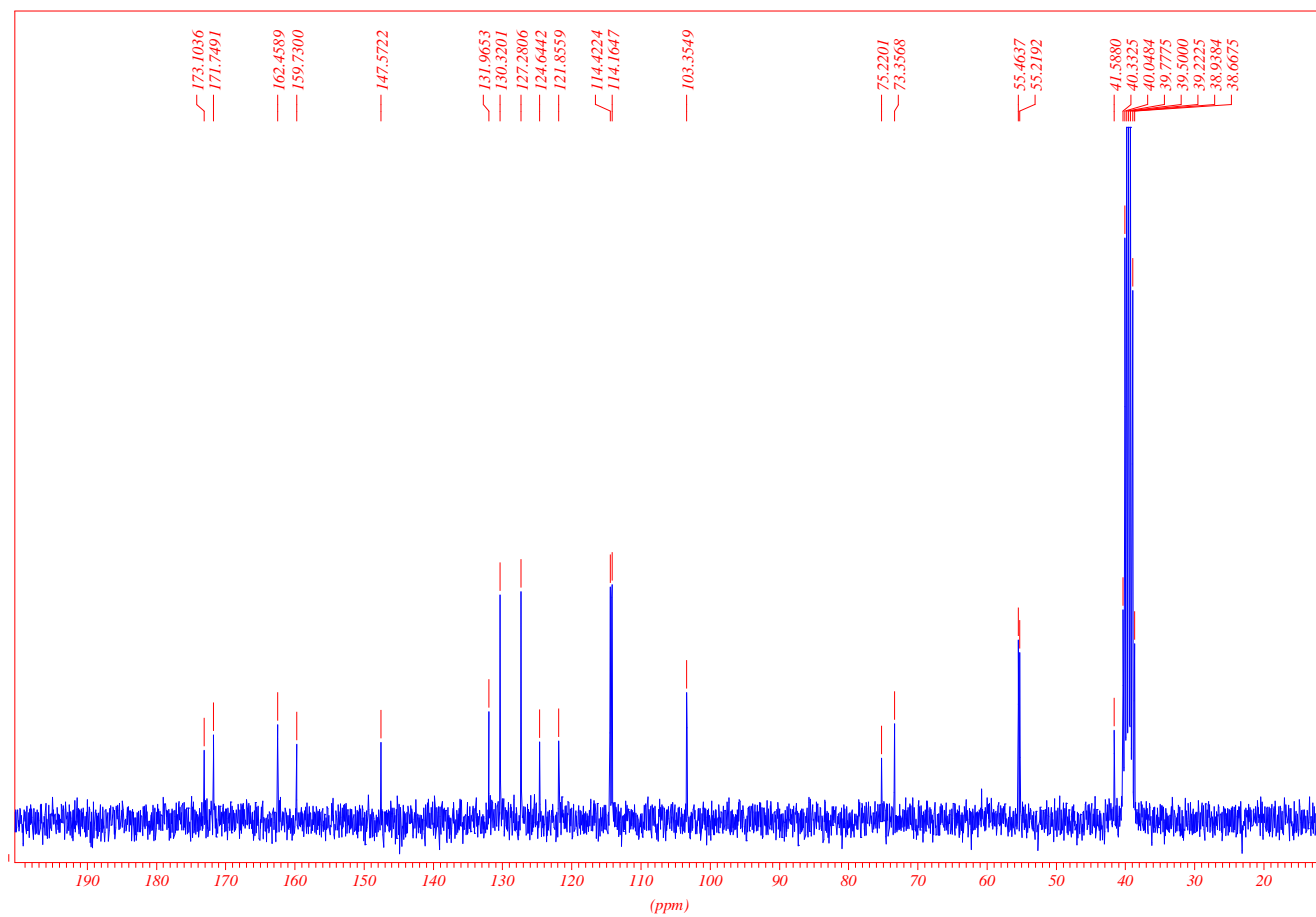
3-Phenyl-9-(4-phenyl-1,2,3-triazol-2-yl)-1,7-dioxo-4-aza-spiro[4.4]non-3-en-8-one (7b)



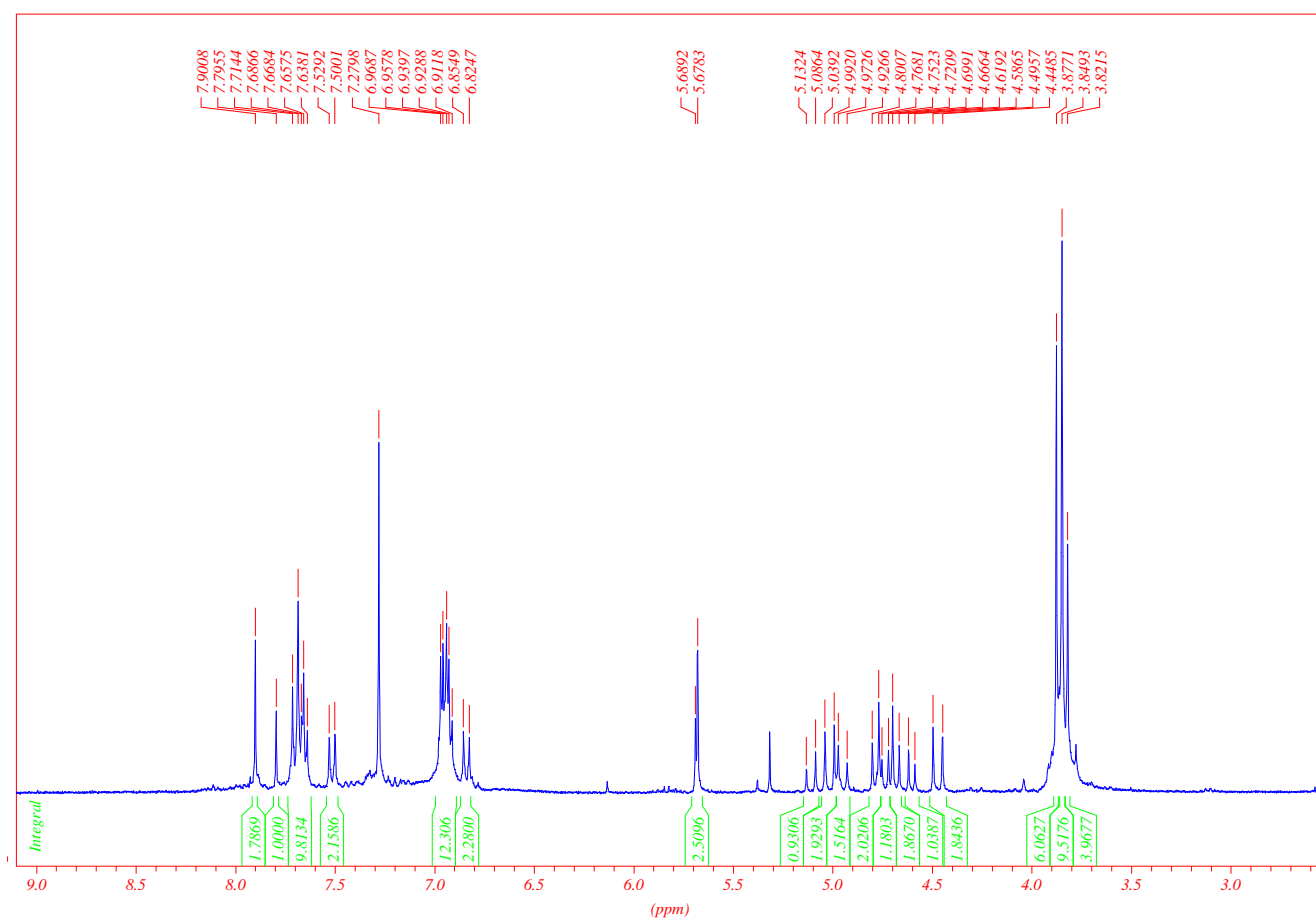
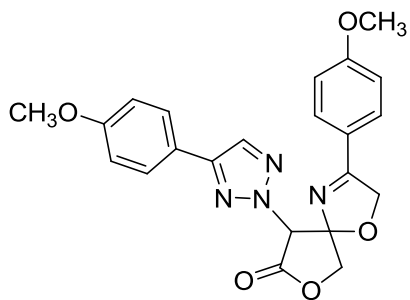


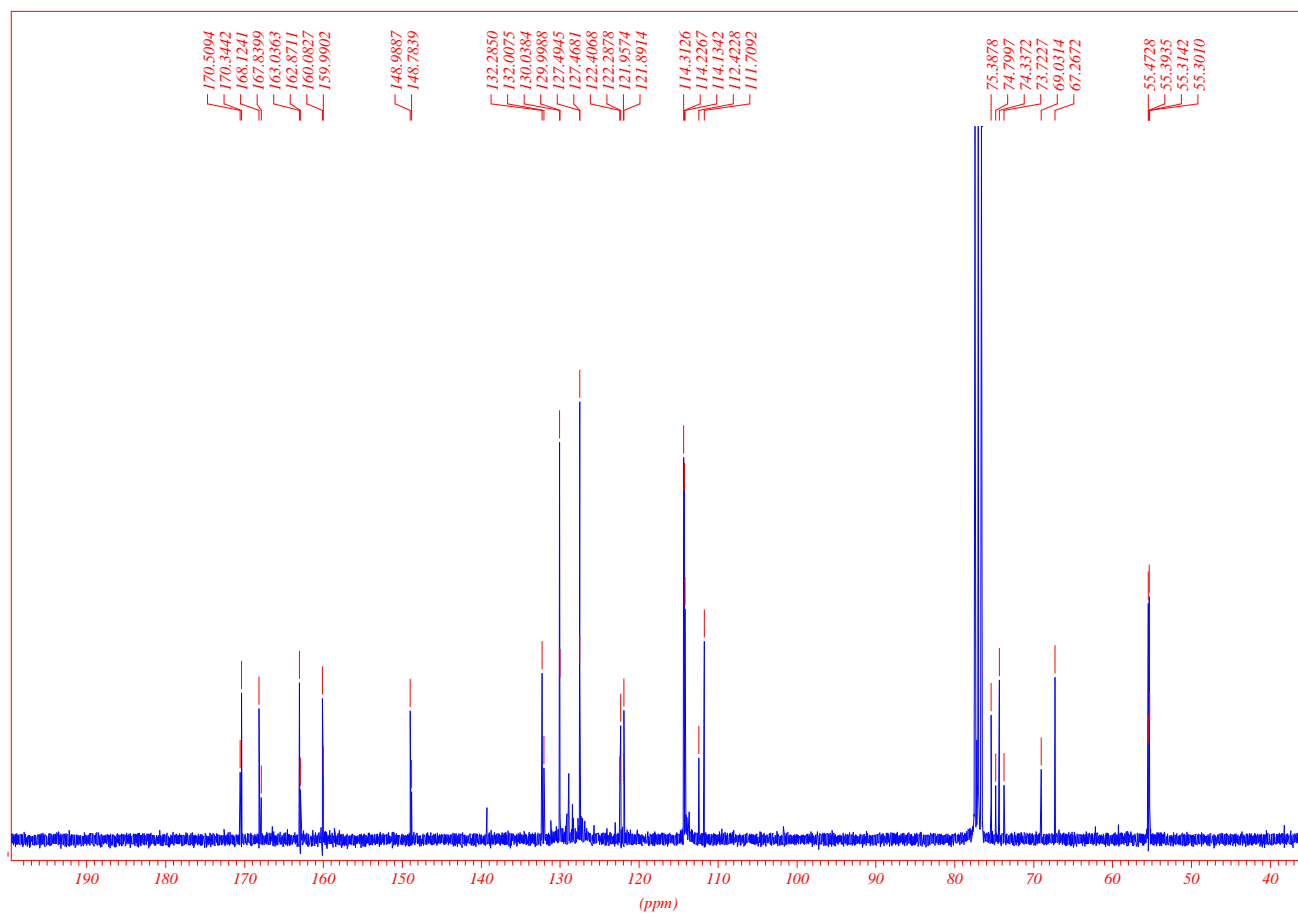
(3a*RS*,6a*SR*)-6a-Hydroxy-2-(4-methoxyphenyl)-3a-[4-(4-methoxyphenyl)-1,2,3-triazol-2-yl]-6,6a-dihydro-3*H*-furo[3,4-*b*]pyrrol-4(3a*H*)-one (6c)



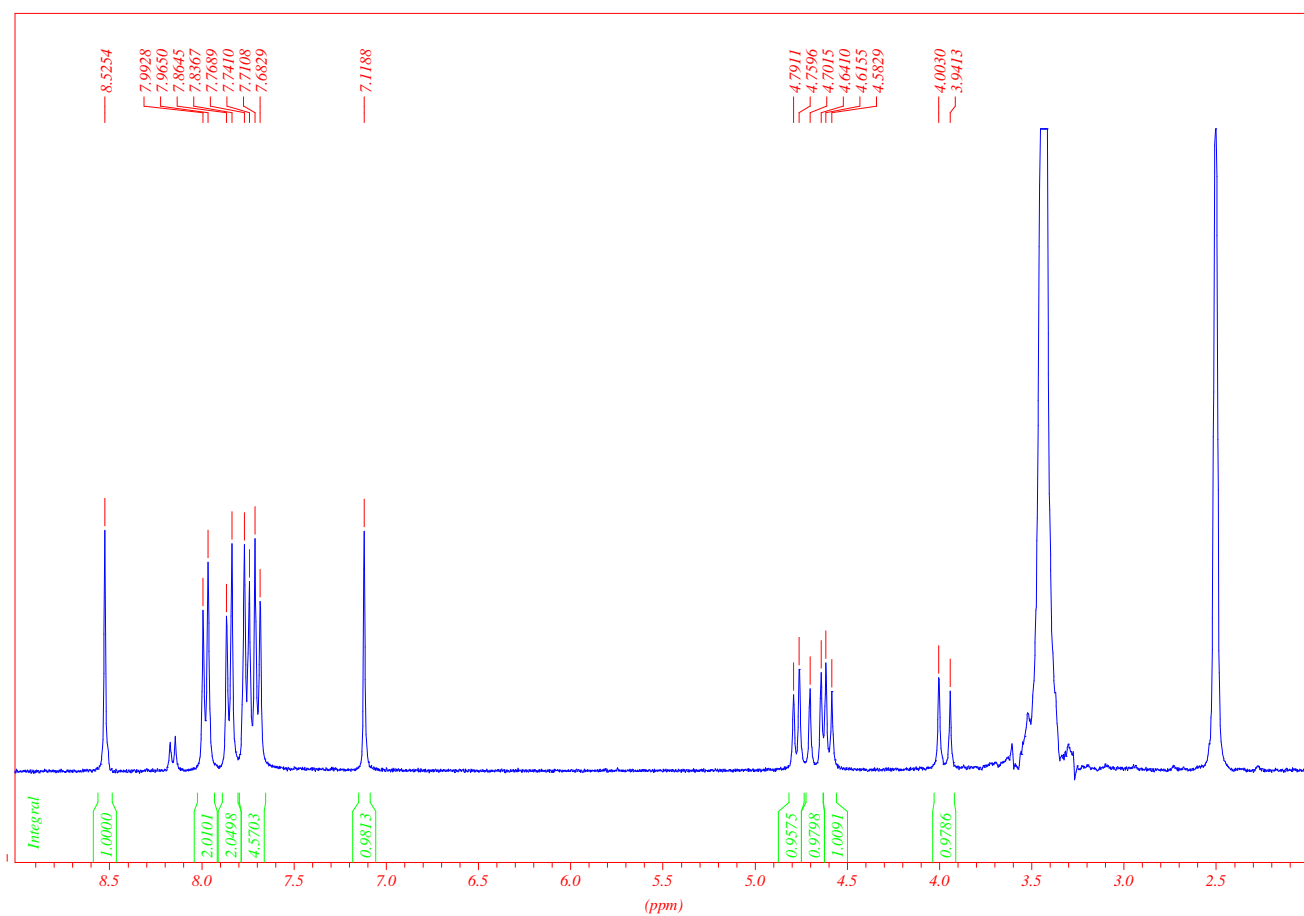
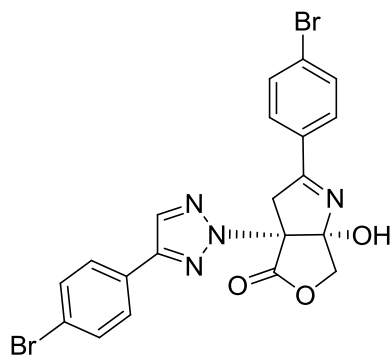


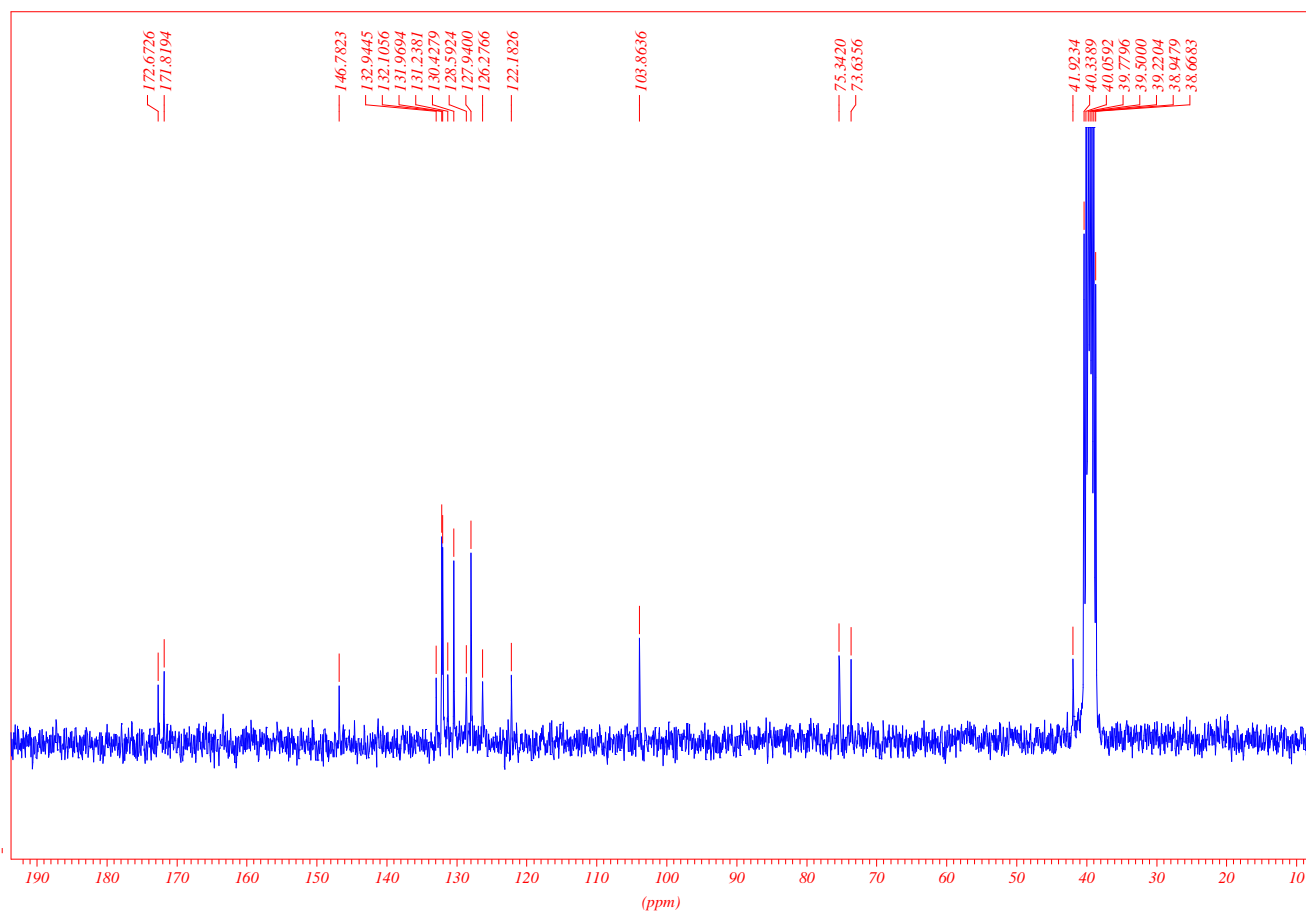
3-(4-Methoxyphenyl)-9-[(4-methoxyphenyl)-1,2,3-triazol-2-yl]-1,7-dioxaspiro[4.4]non-3-en-8-one (7c)



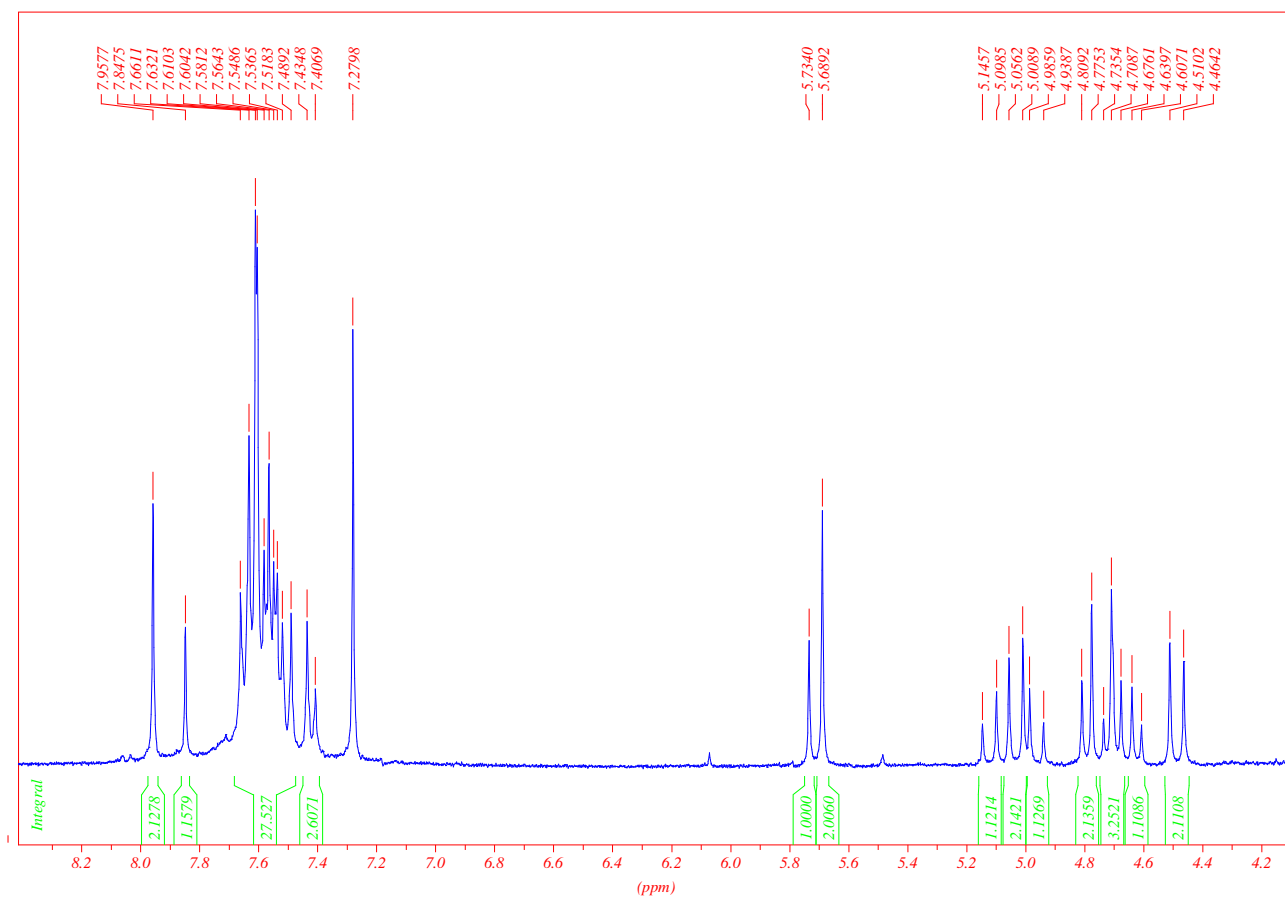
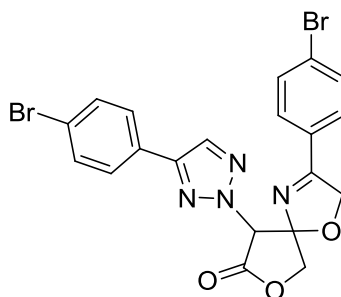


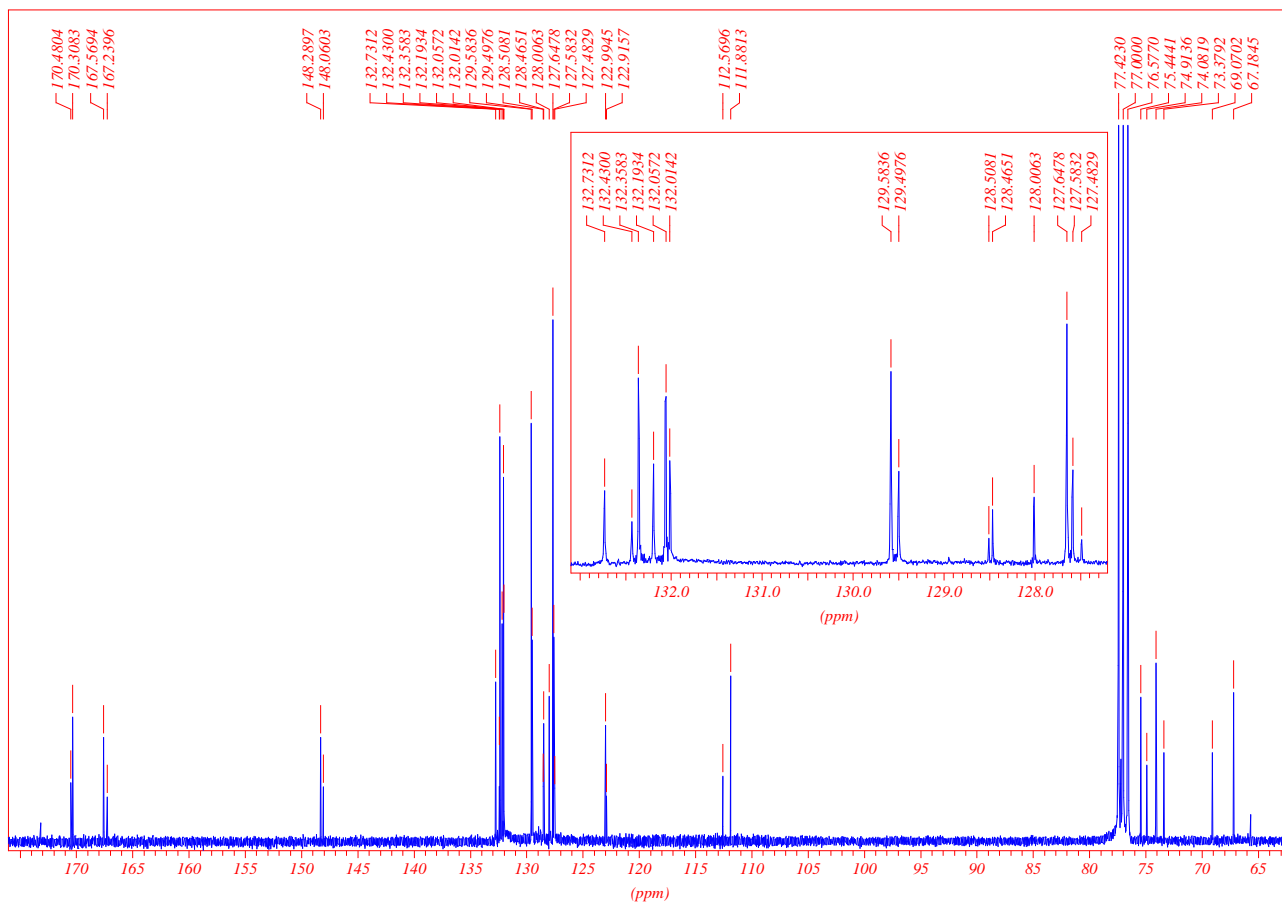
(3a*RS*,6a*SR*)-2-(4-Bromophenyl)-3a-[4-(4-bromophenyl)-1,2,3-triazole-2-yl]-6a-hydroxy--6,6a-dihydro-3*H*-furo[3,4-*b*]pyrrol-4(3a*H*)-one (6d)



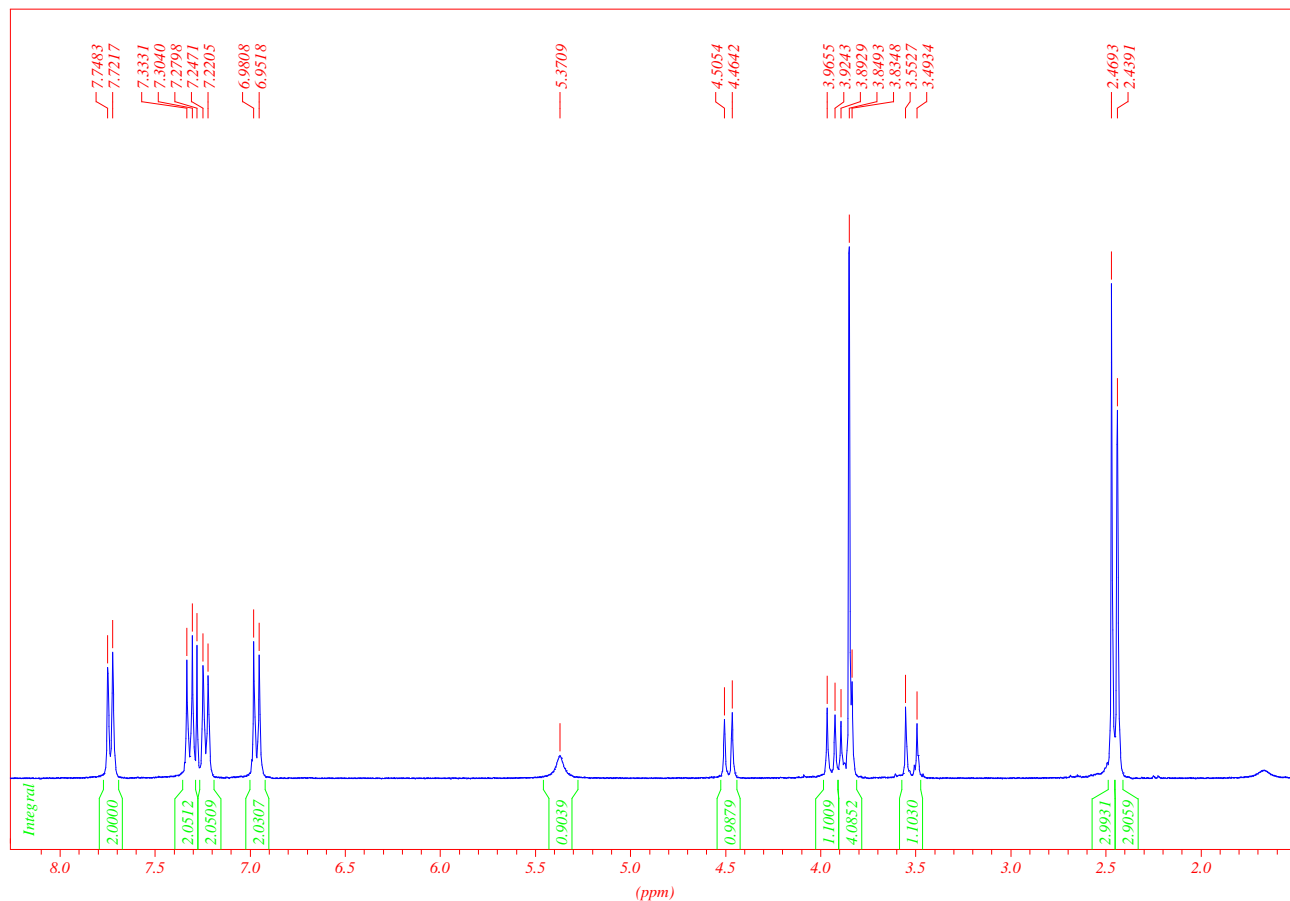
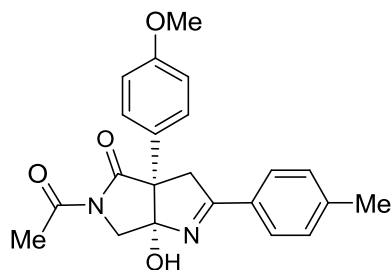


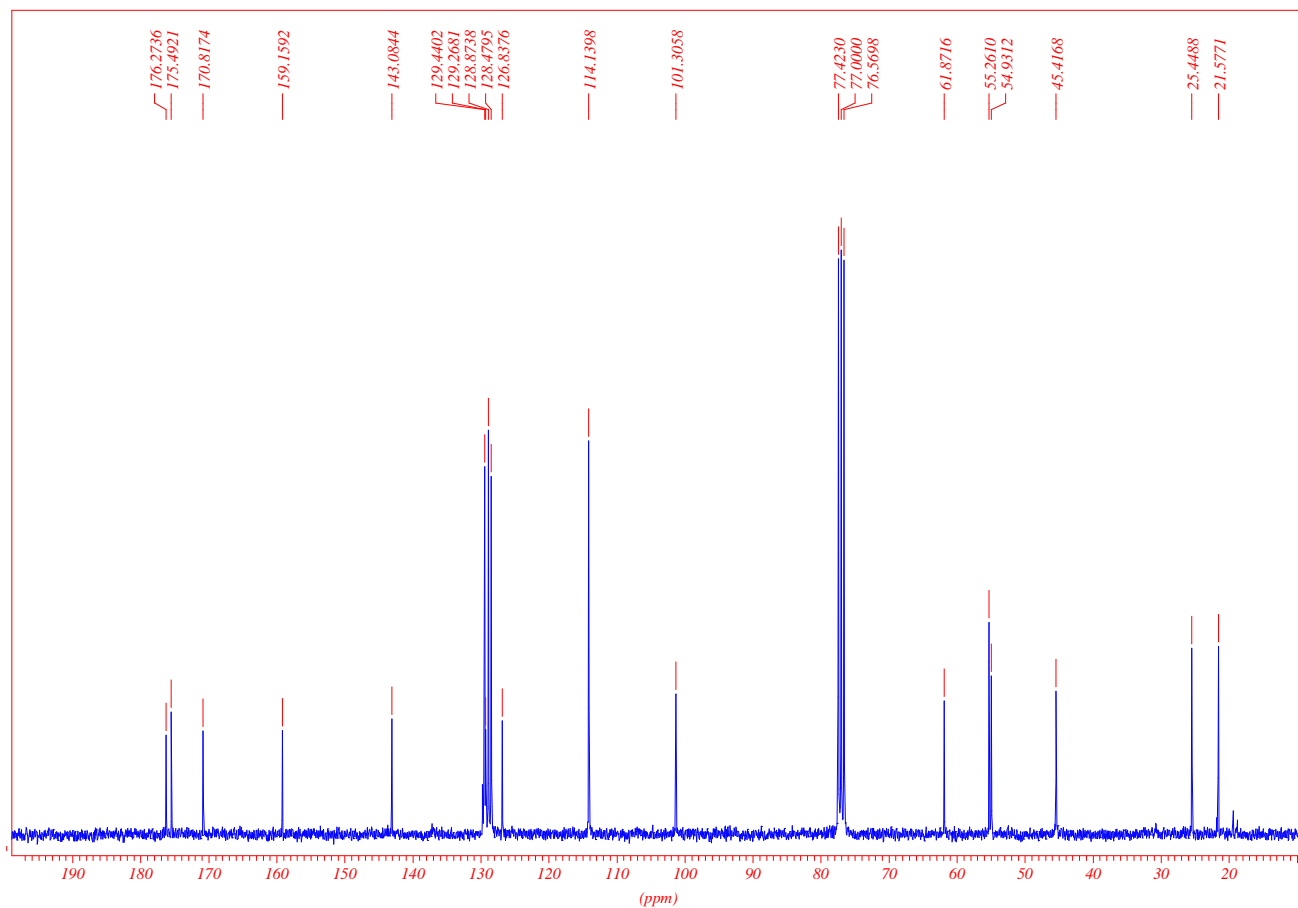
**3-(4-Bromophenyl)-9-[(4-bromophenyl)-1,2,3-triazol-2-yl]-1,7-dioxo-4-azaspiro[4.4]non-3-en-8-one
(7d)**





(3*aRS*,6*aSR*)-5-Acetyl-6*a*-hydroxy-2-(4-methylphenyl)-3*a*-(4-methoxyphenyl)-3,5,6,6*a*-tetrahydropyrrolo[3,4-*b*]pyrrol-4(3*H*)-one (12)





References

- 1 G. Lowe, H.W. Yeung, *J. Chem. Soc., Perkin Trans. 1* 1973, 2907–2910.
- 2 H.-D. Stachel, K. Zeitler, S. Dick, *Liebigs Ann.* 1996, 103–107.