

Supplementary Material for

A sulfonic acid polyvinyl pyridinium ionic liquid catalyzes the multi-component synthesis of spiro-indoline-3,5'-pyrano[2,3-*d*]-pyrimidines and -pyrazines

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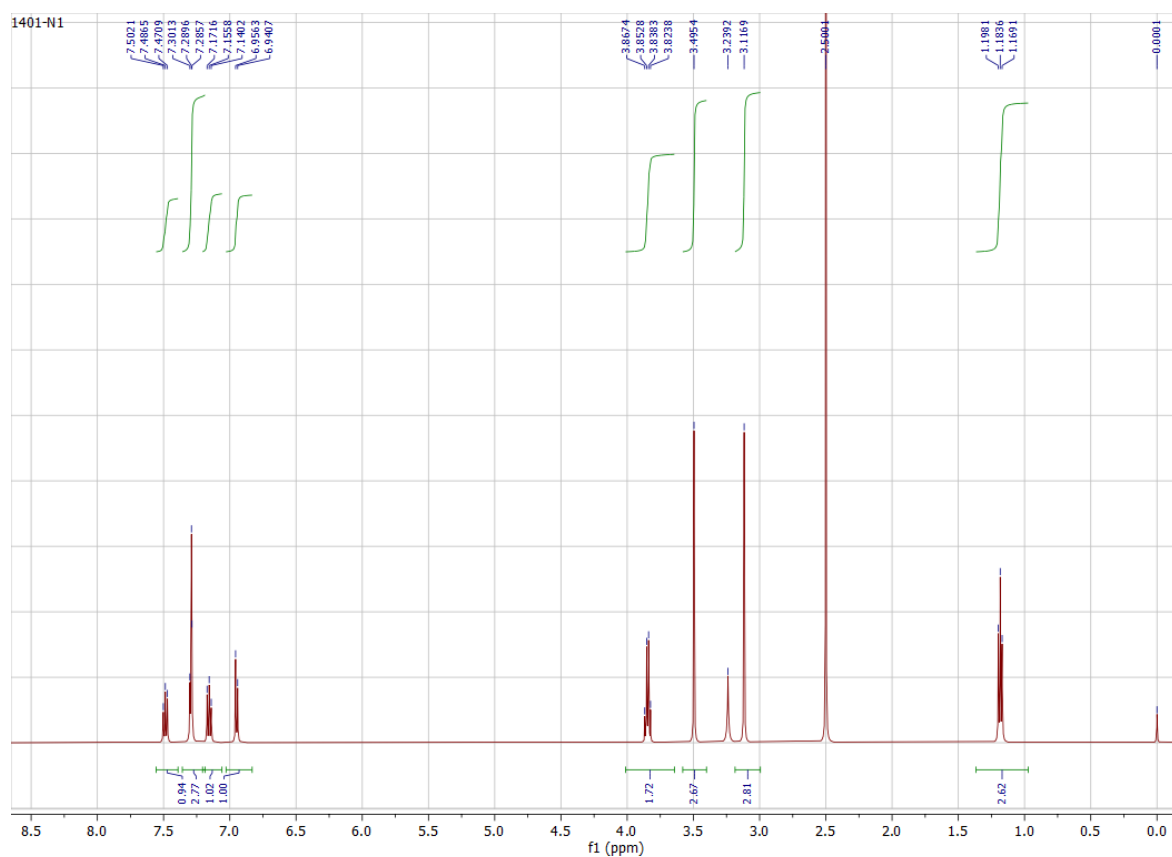


Figure S1. ¹H NMR spectrum of 7'-amino-1-ethyl-1',3'-dimethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**1c**) in DMSO-d₆.

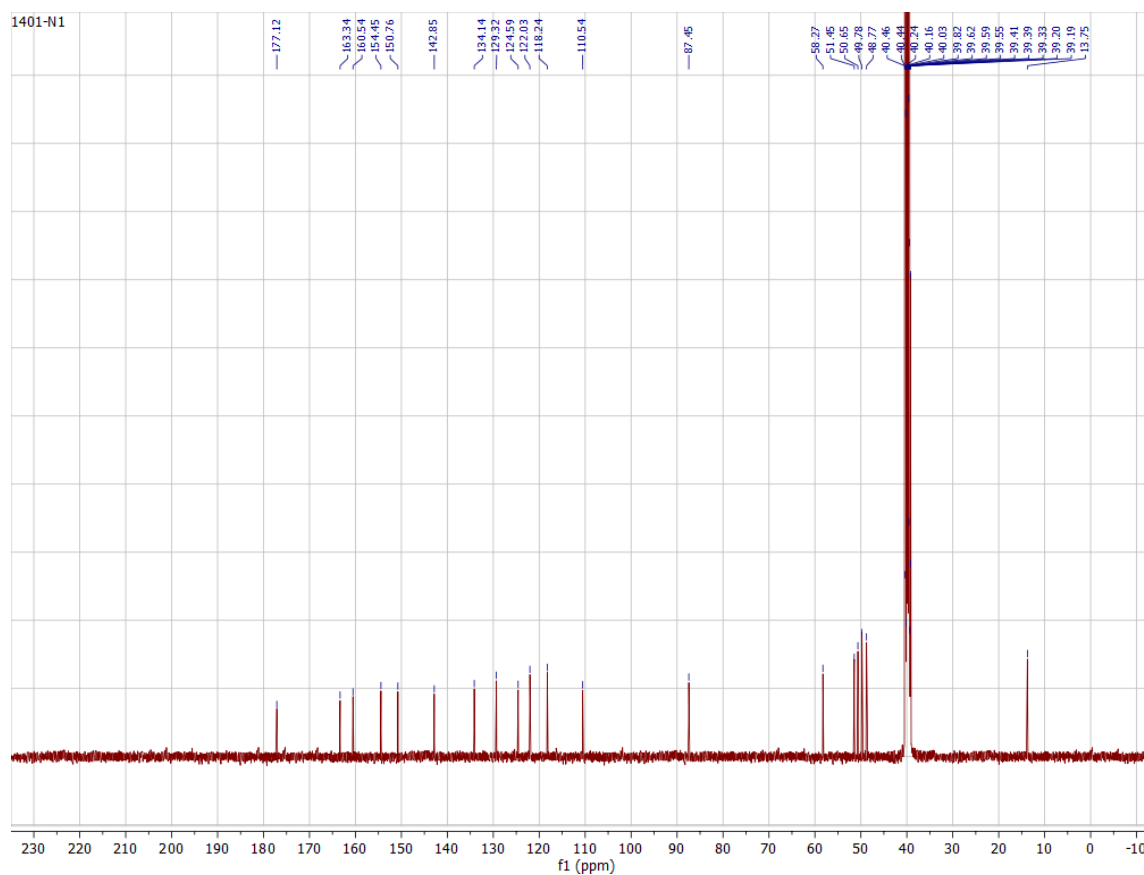


Figure S2. ¹³C NMR spectrum of 7'-amino-1-ethyl-1',3'-dimethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**1c**) in DMSO-d₆.

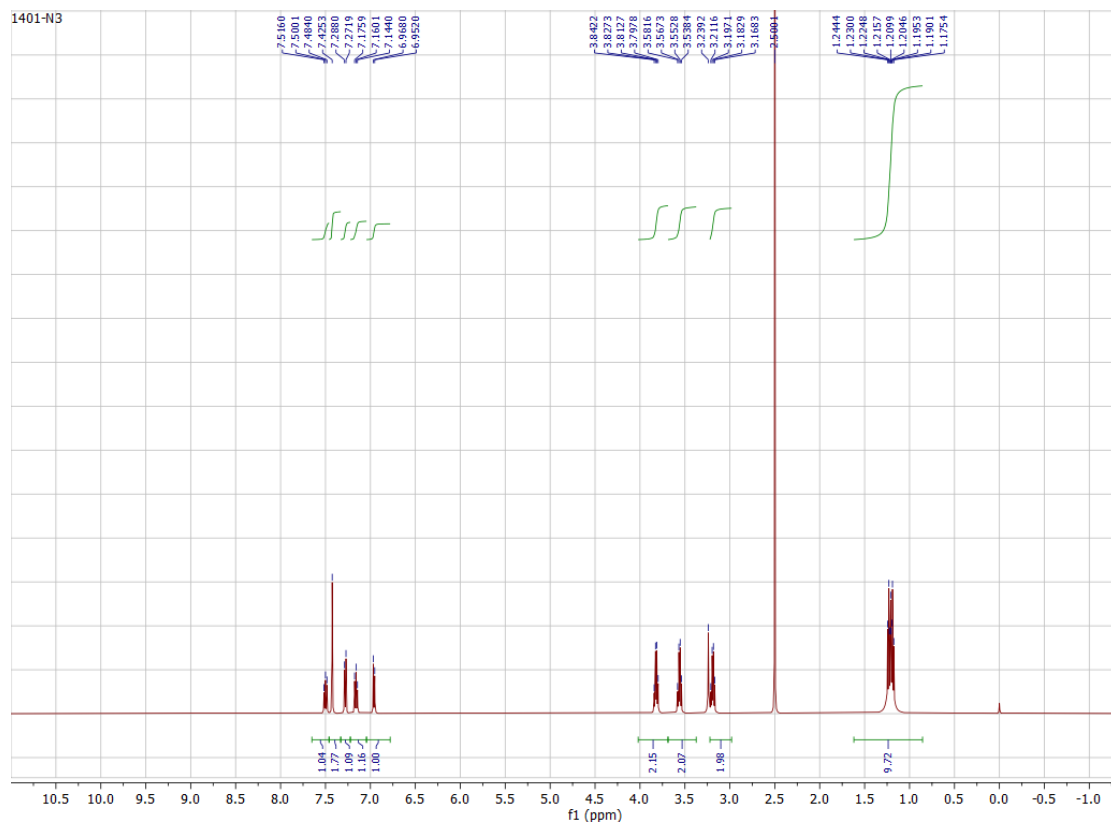


Figure S3. ^1H NMR spectrum of 7'-amino-1,1',3'-triethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**2c**) in $\text{DMSO-}d_6$.

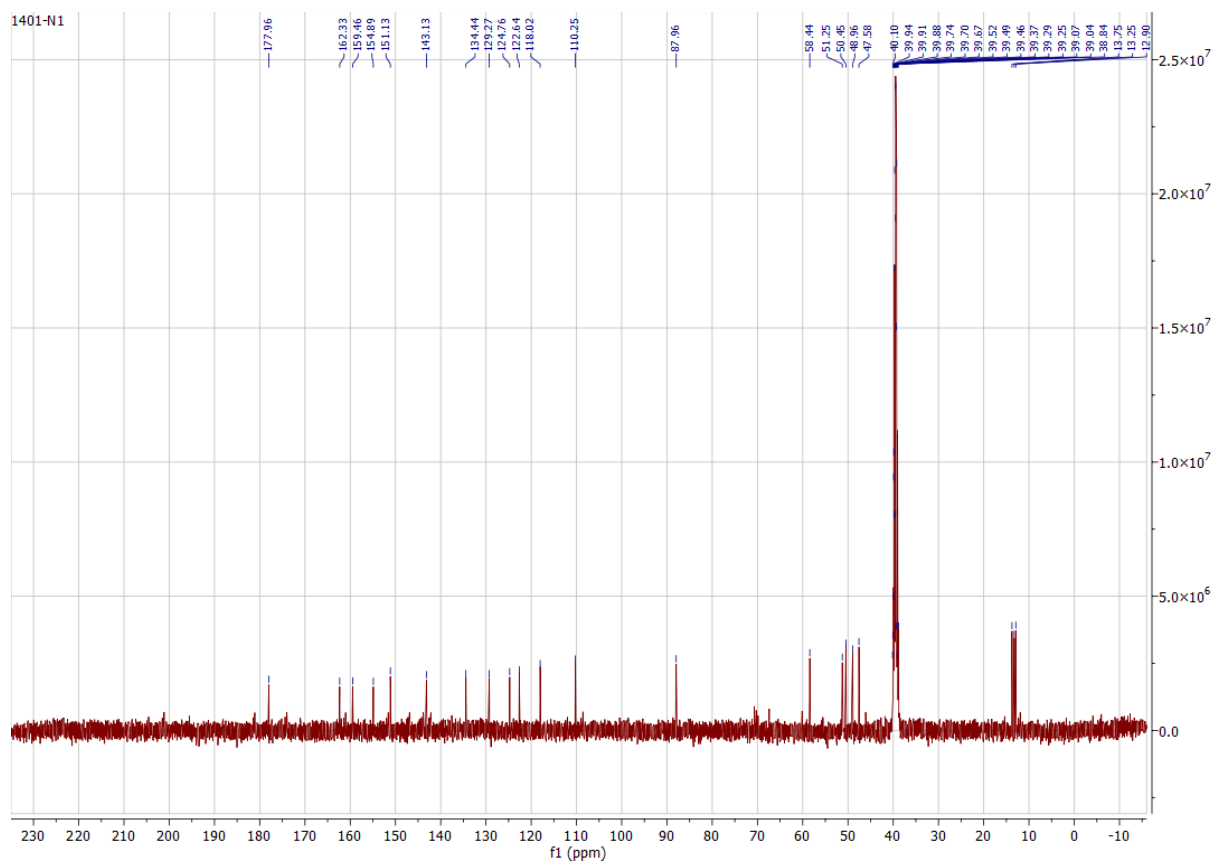


Figure S4. ^{13}C NMR spectrum of 7'-amino-1,1',3'-triethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**2c**) in $\text{DMSO-}d_6$.

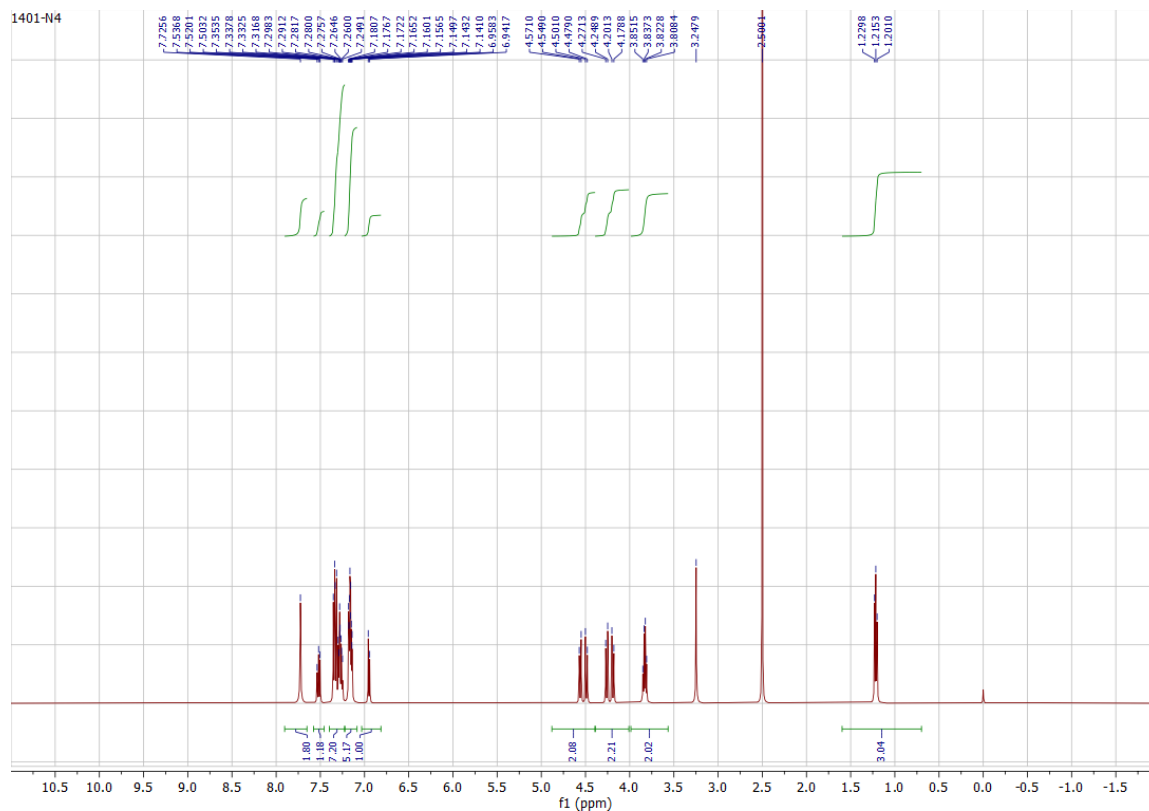


Figure S5. ^1H NMR spectrum of 7'-amino-1',3'-dibenzyl-1-ethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**3c**) in $\text{DMSO-}d_6$.

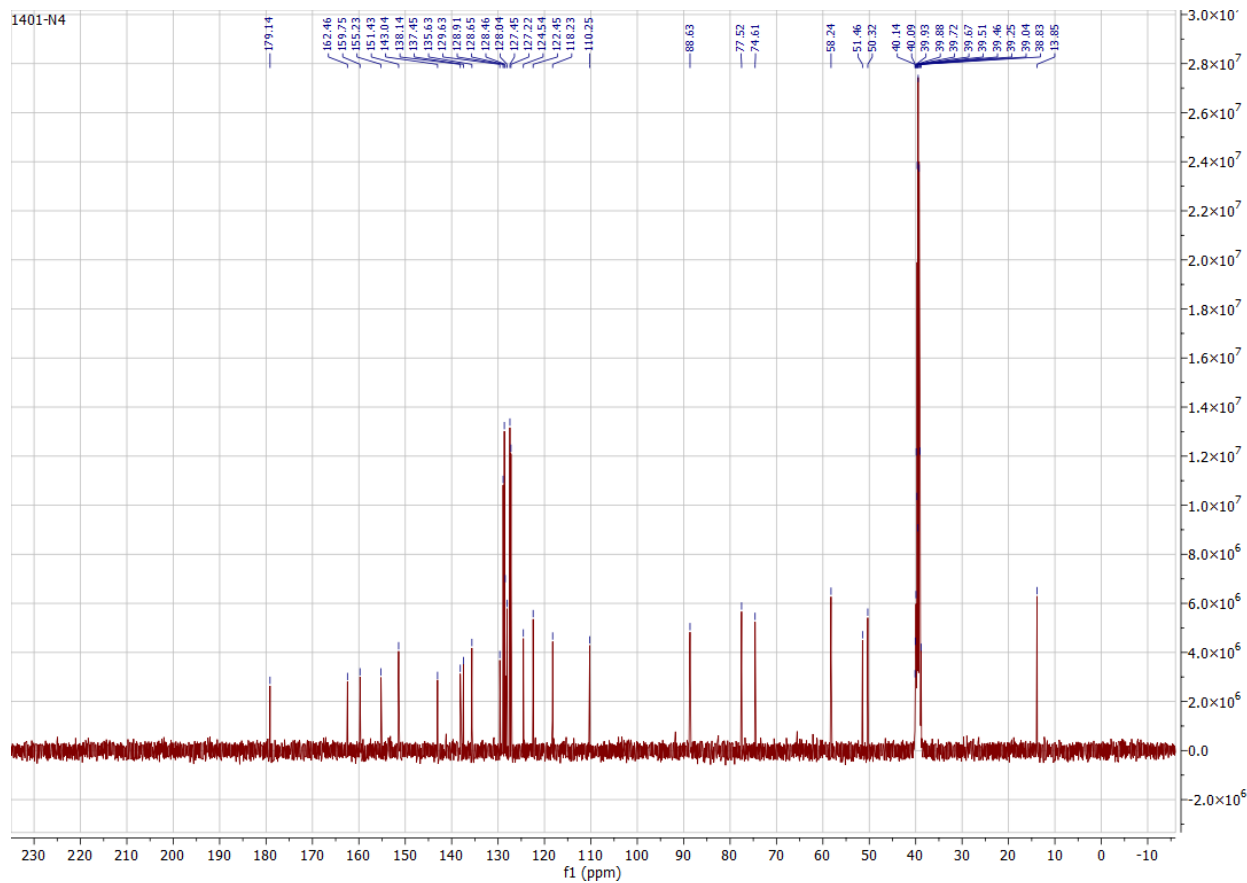


Figure S6. ^{13}C NMR spectrum of 7'-amino-1',3'-dibenzyl-1-ethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**3c**) in $\text{DMSO-}d_6$.

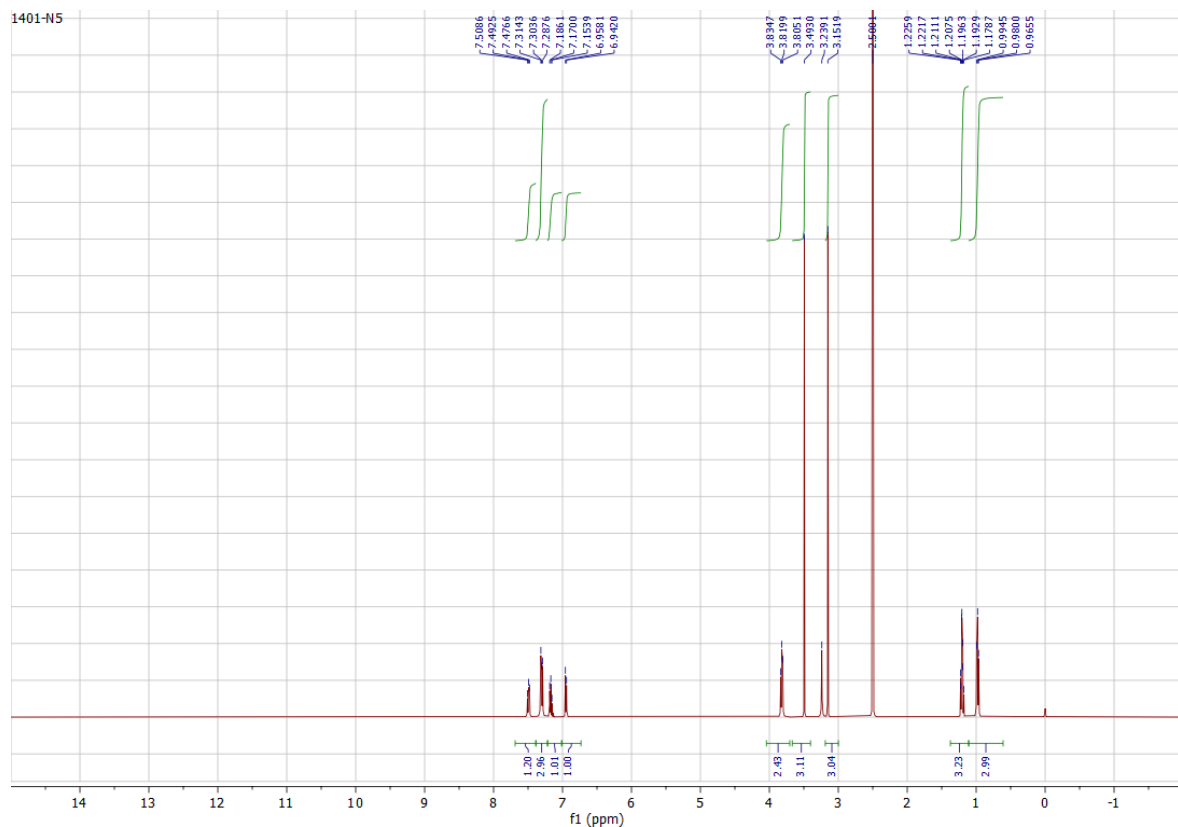


Figure S7. ¹H NMR spectrum of 7'-amino-1',3'-dimethyl-2,2',4'-trioxo-1-propyl-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**4c**) in DMSO-d₆.

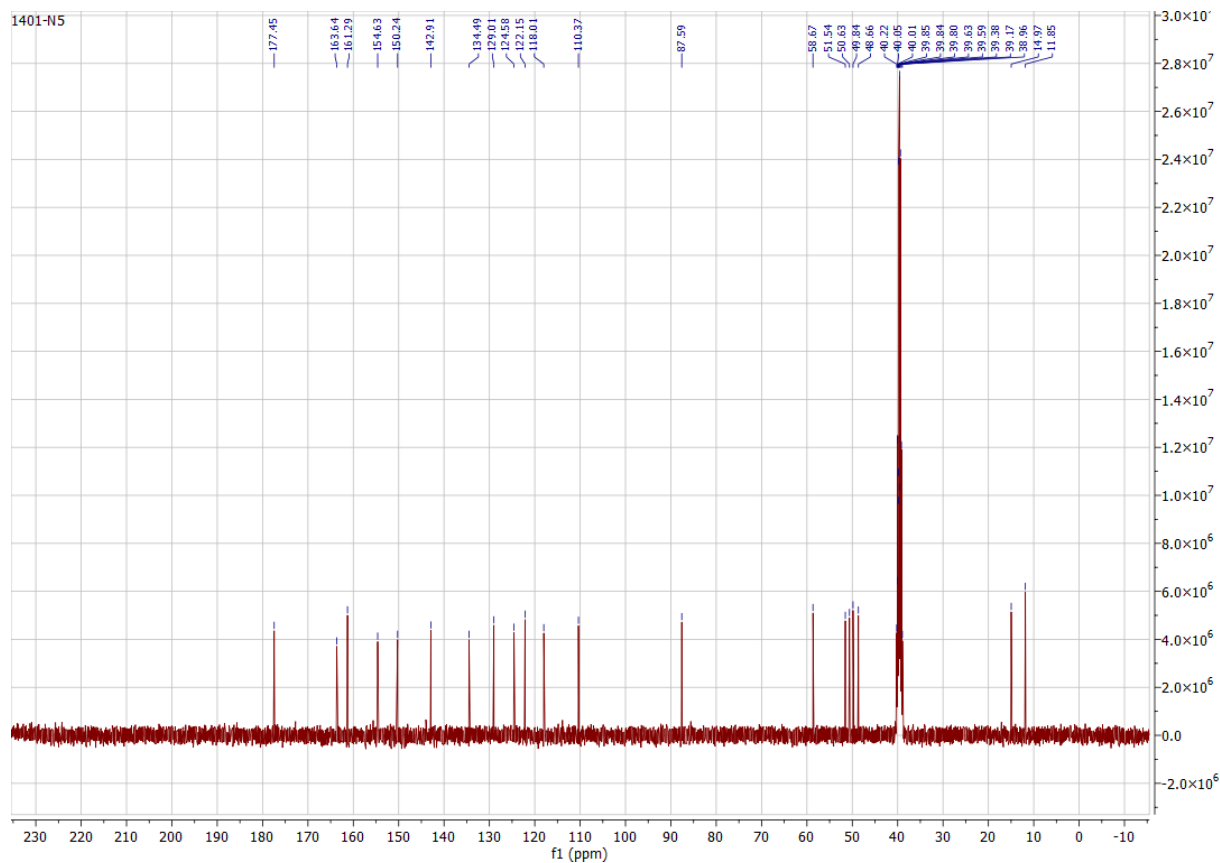


Figure S8. ¹³C NMR spectrum of 7'-amino-1',3'-dimethyl-2,2',4'-trioxo-1-propyl-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**4c**) in DMSO-d₆.

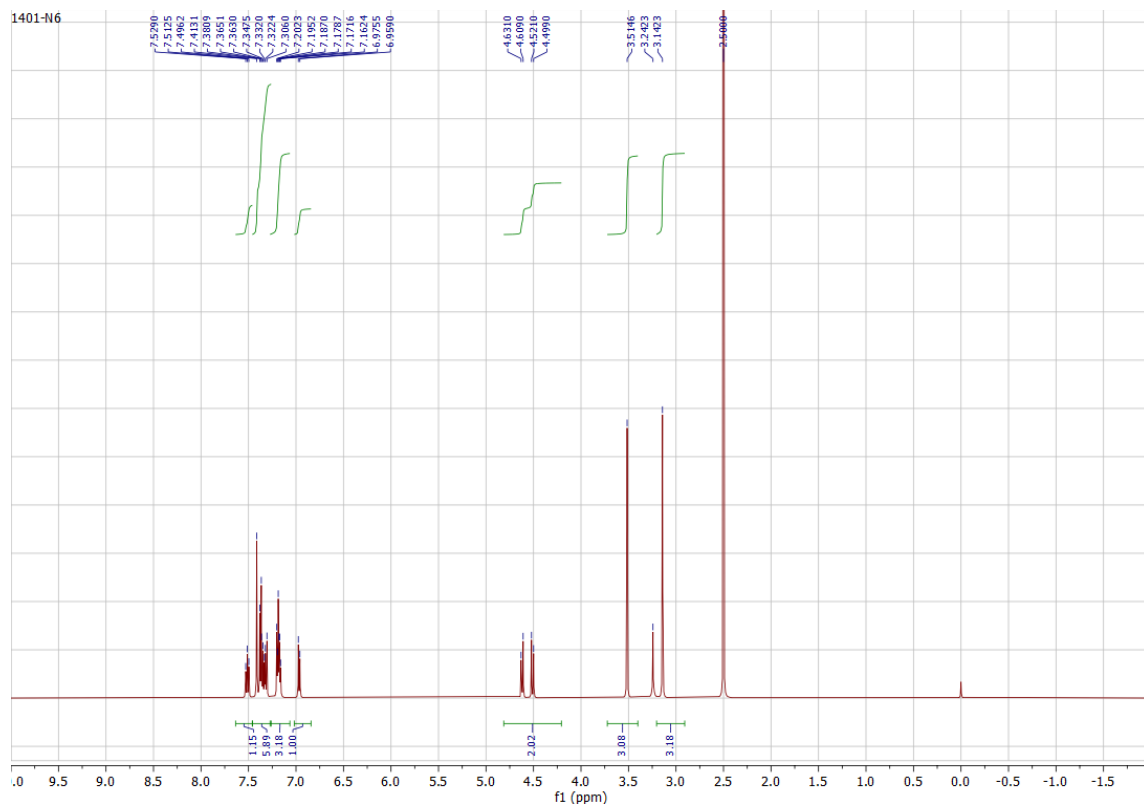


Figure S9. ^1H NMR spectrum of 7'-amino-1-benzyl-1',3'-dimethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**5c**) in $\text{DMSO-}d_6$.

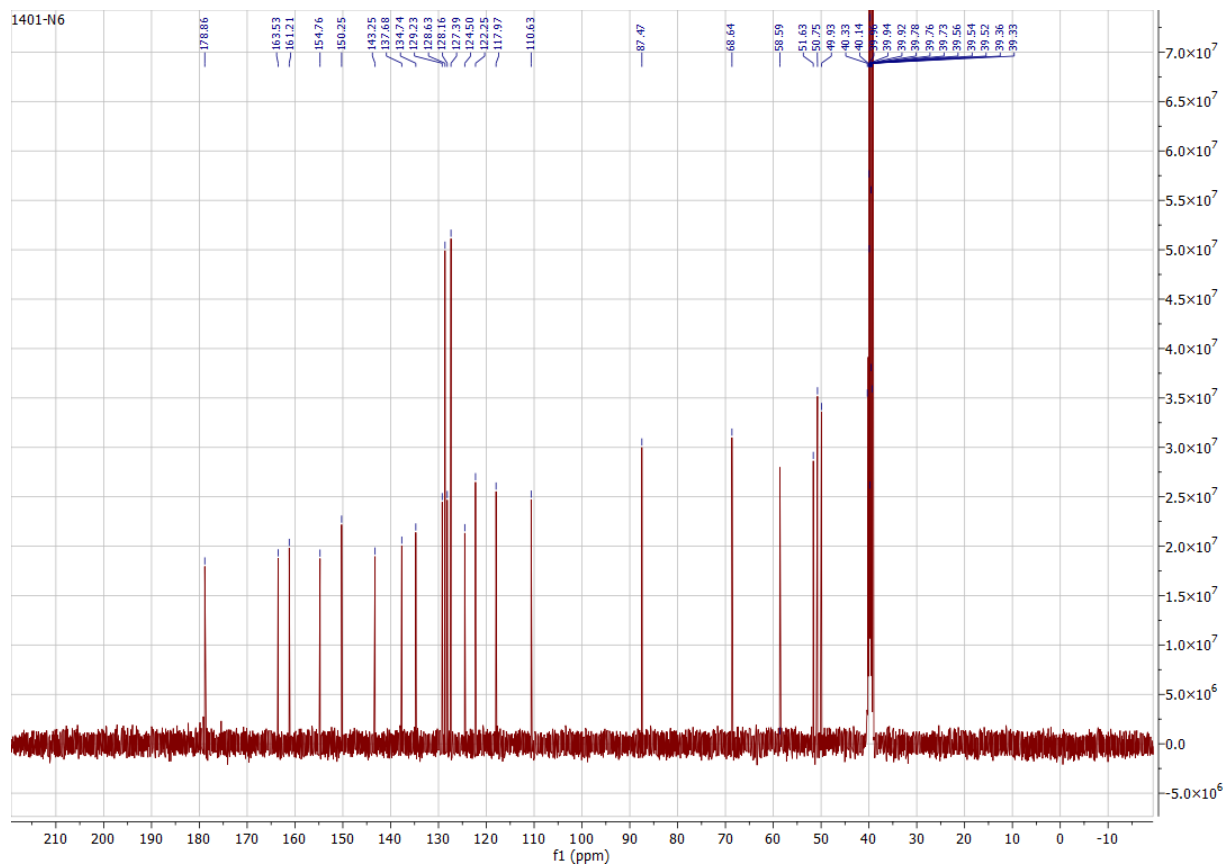


Figure S10. ^{13}C NMR spectrum of 7'-amino-1-benzyl-1',3'-dimethyl-2,2',4'-trioxo-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**5c**) in $\text{DMSO-}d_6$.

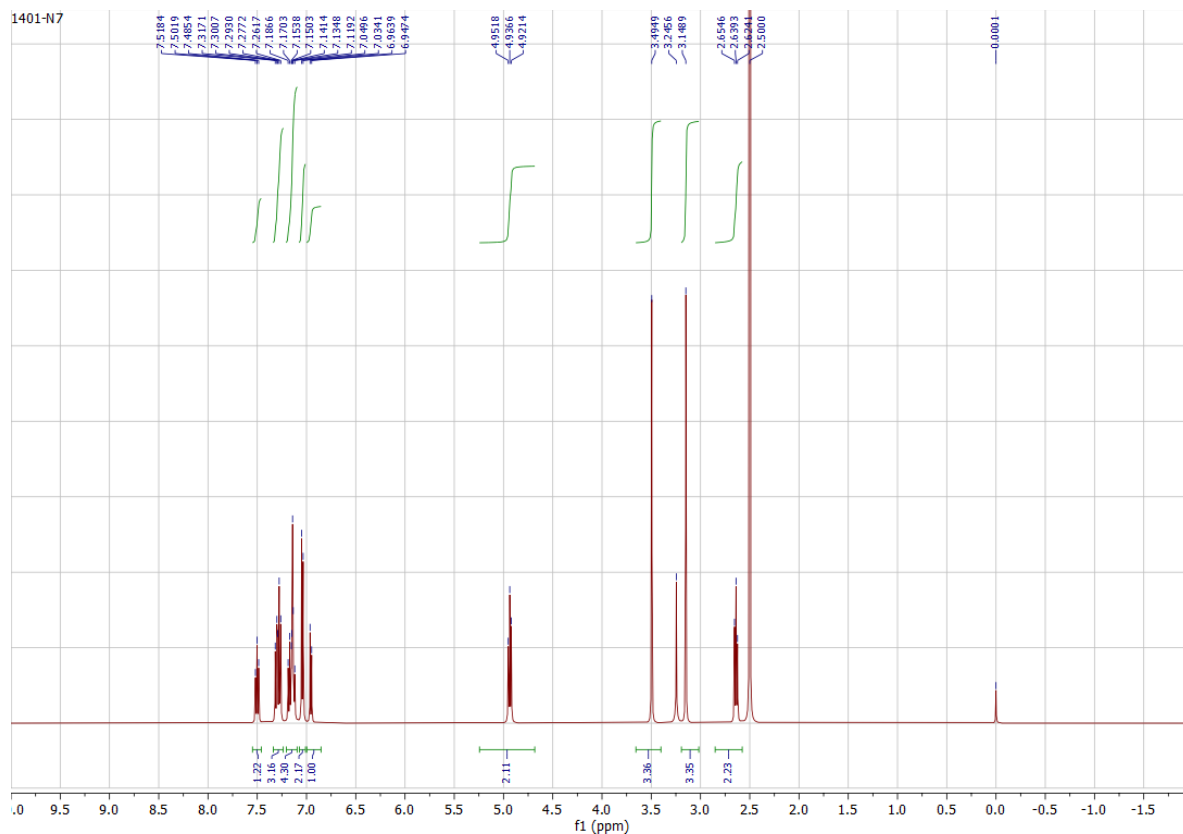


Figure S11. ¹H NMR spectrum of 7'-amino-1',3'-dimethyl-2,2',4'-trioxo-1-phenethyl-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**6c**) in DMSO-*d*₆.

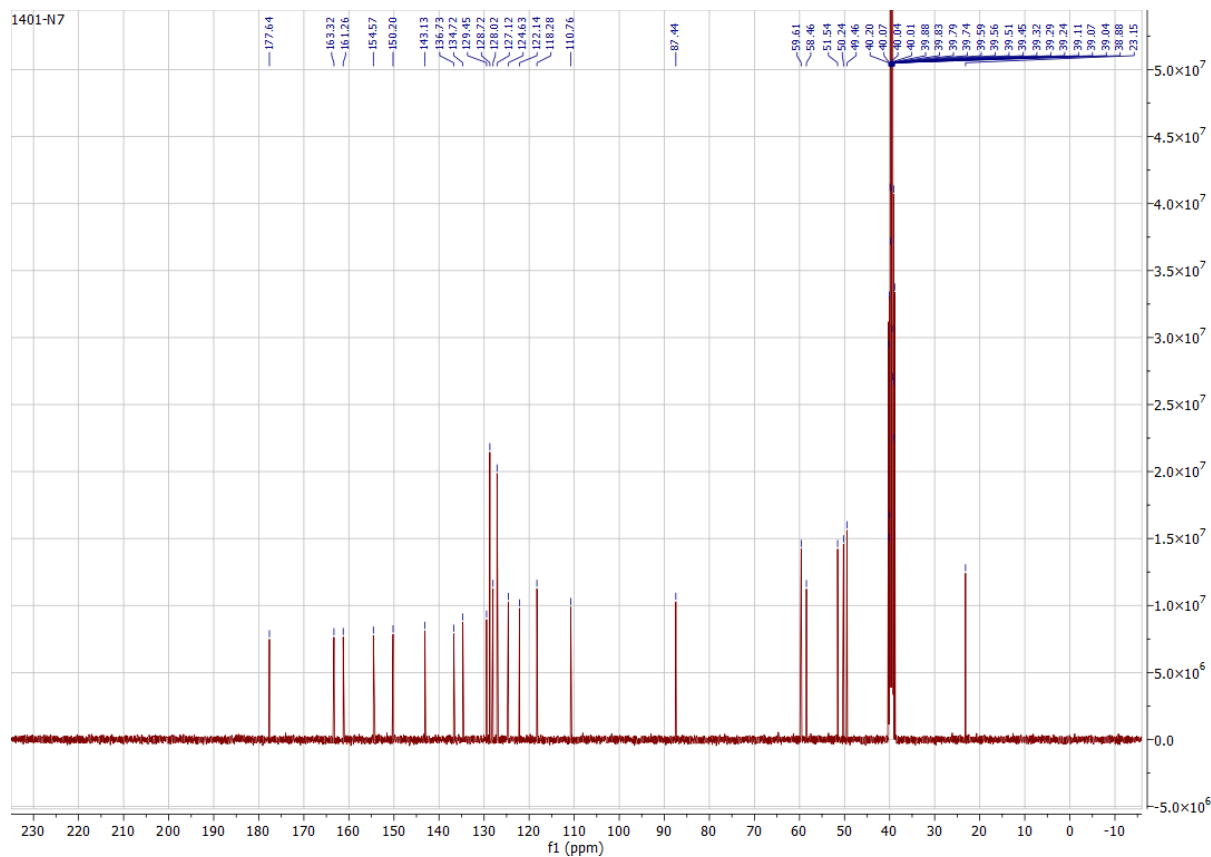


Figure S12. ¹³C NMR spectrum of 7'-amino-1',3'-dimethyl-2,2',4'-trioxo-1-phenethyl-1',2',3',4'-tetrahydrospiro[indoline-3,5'-pyrano[2,3-*d*]pyrimidine]-6'-carbonitrile (**6c**) in DMSO-*d*₆.

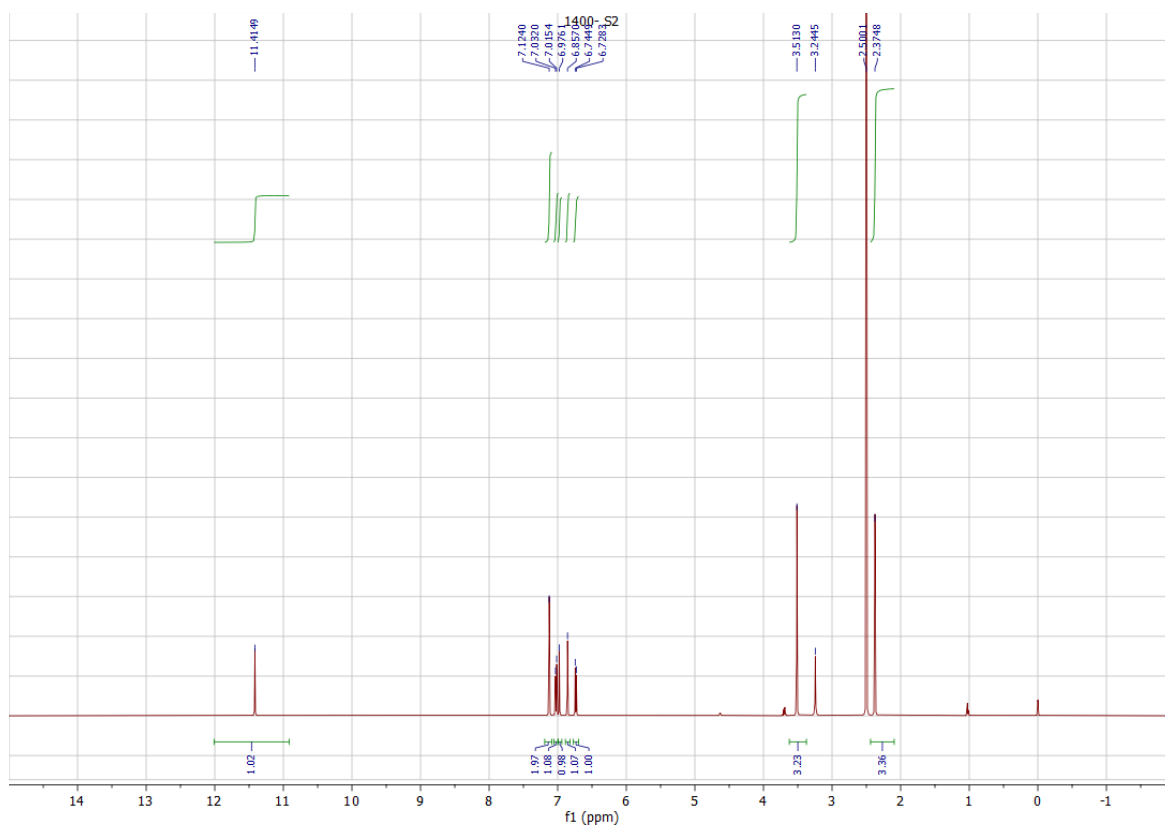


Figure S13. ¹H NMR spectrum of methyl 6'-amino-5'-cyano-5-methyl-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**1d**) in DMSO-*d*₆.

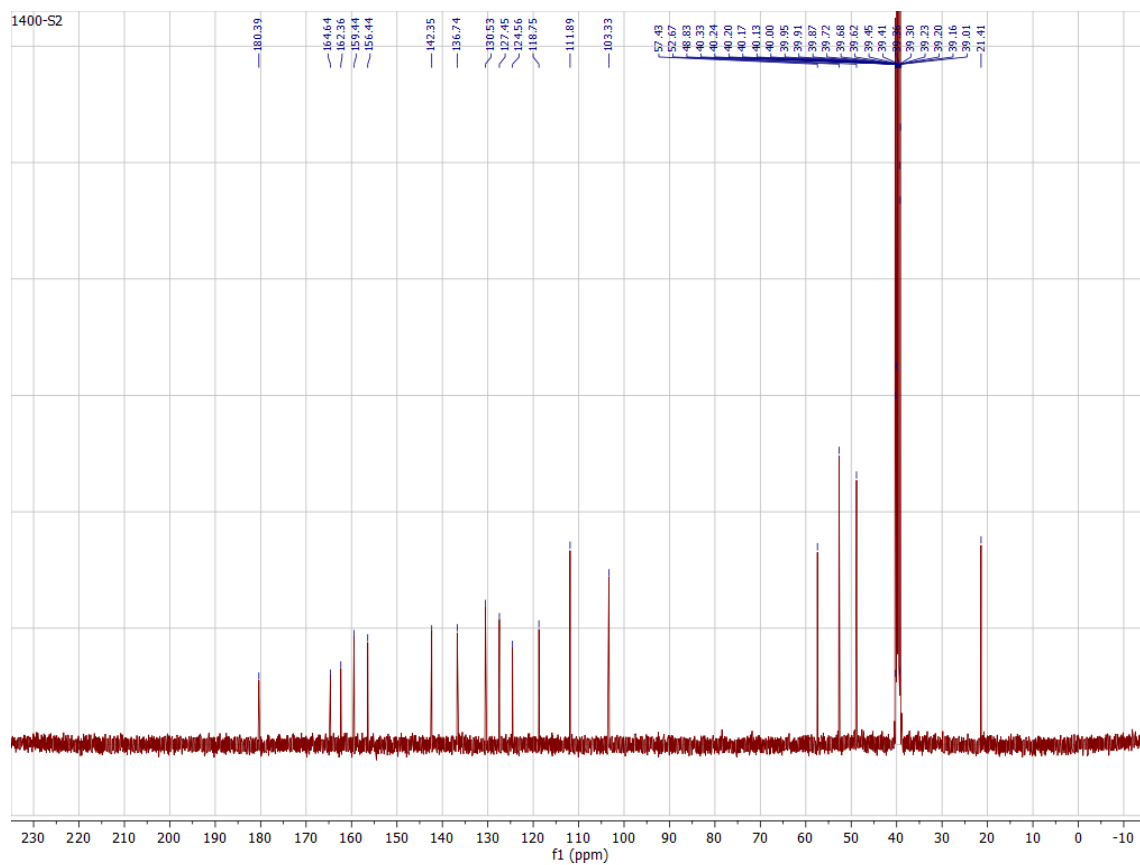


Figure S14. ¹³C NMR spectrum of methyl 6'-amino-5'-cyano-5-methyl-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**1d**) in DMSO-*d*₆.

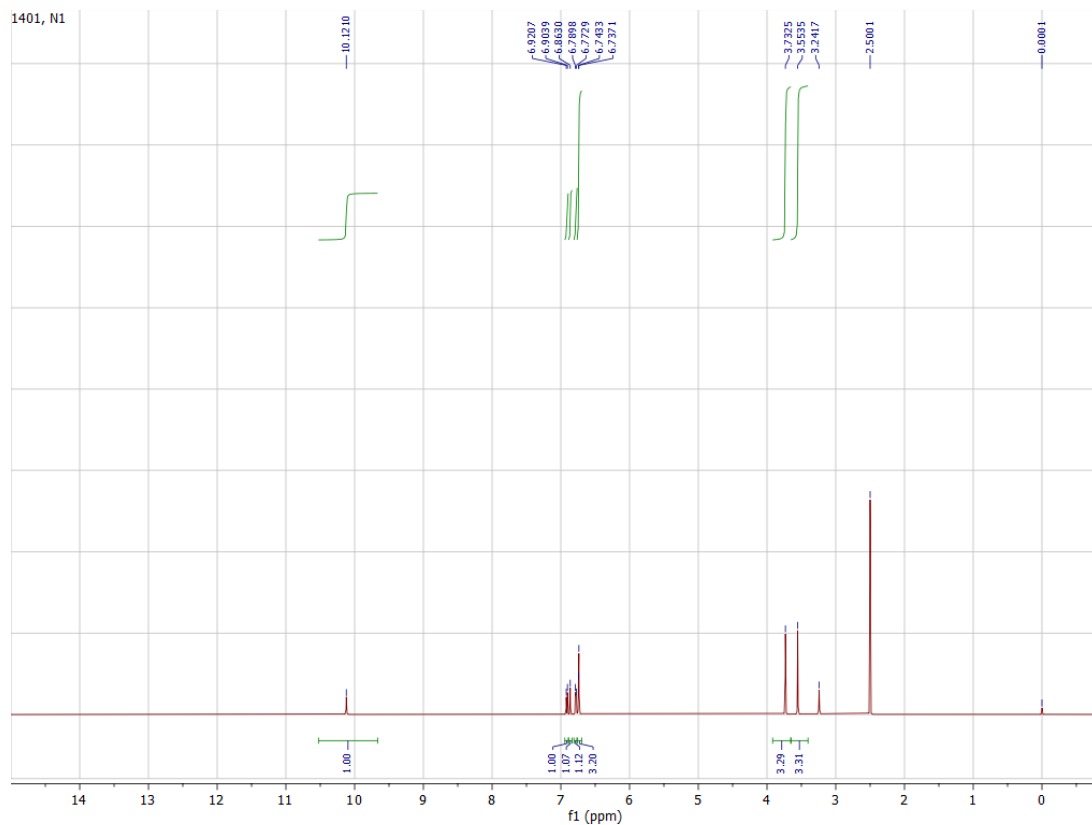


Figure S15. ¹H NMR spectrum of methyl 6'-amino-5'-cyano-5-methoxy-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**2d**) in DMSO-d₆.

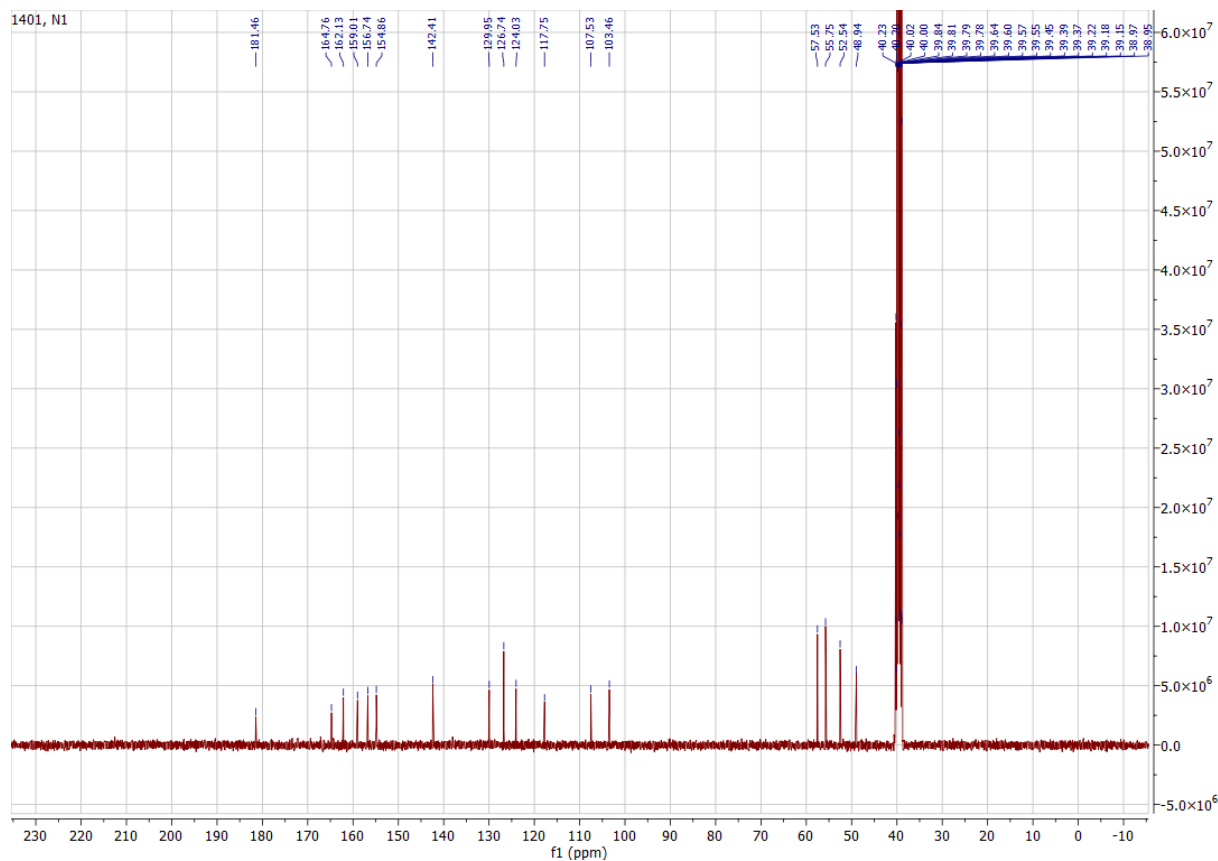


Figure S16. ¹³C NMR spectrum of methyl 6'-amino-5'-cyano-5-methoxy-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**2d**) in DMSO-d₆.

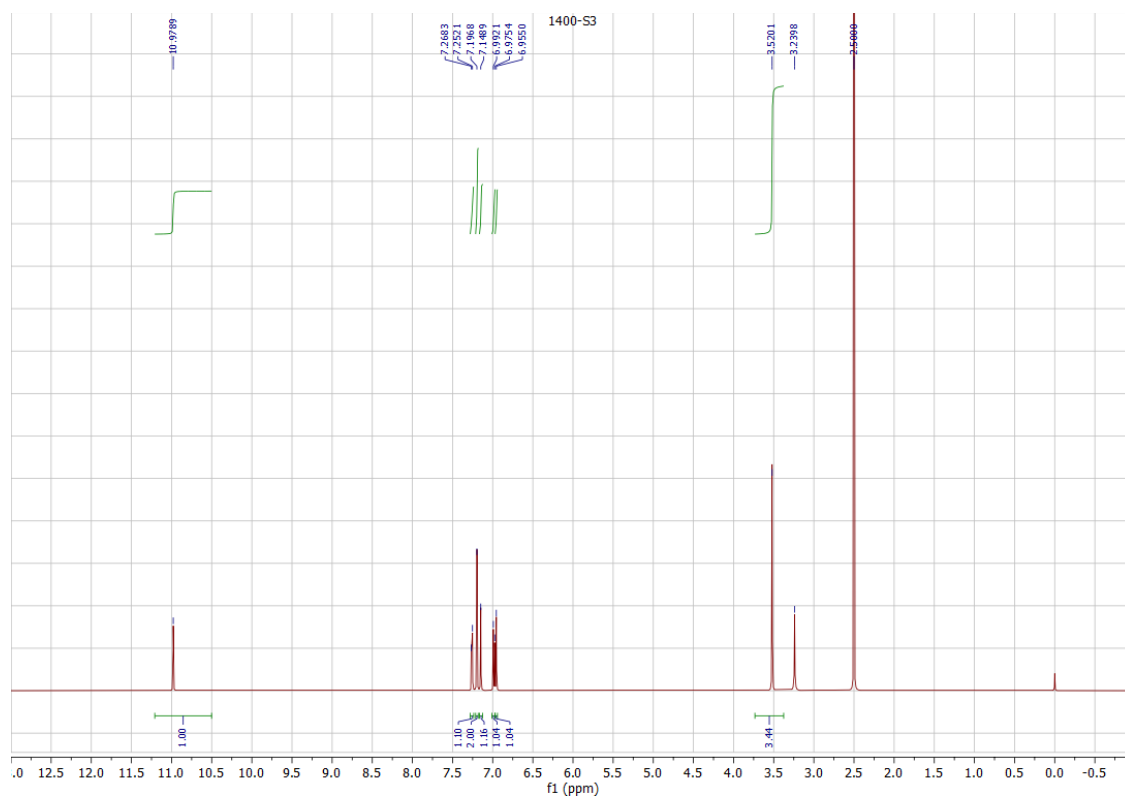


Figure S17. ¹H NMR spectrum of methyl 6'-amino-5-chloro-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**3d**) in DMSO-d₆.

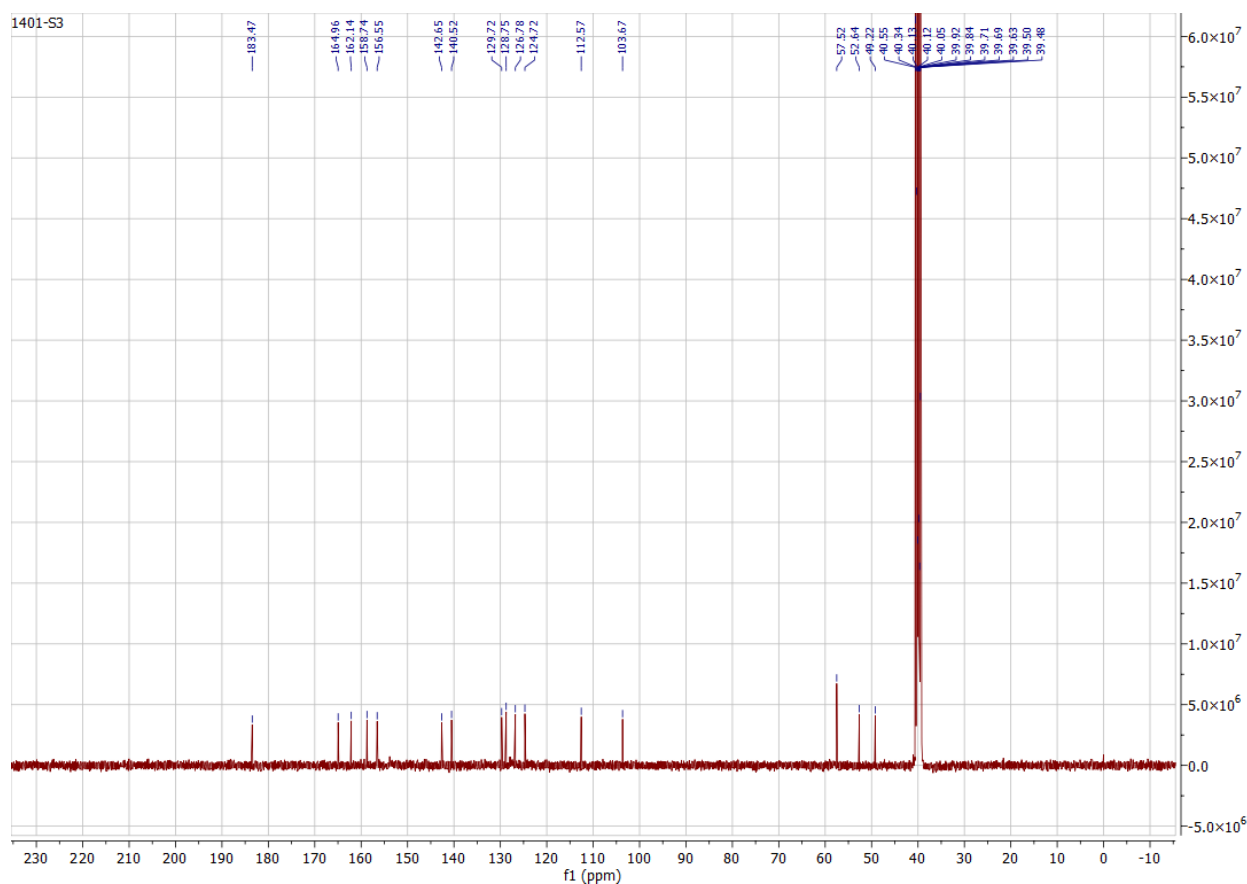


Figure S18. ¹³C NMR spectrum of methyl 6'-amino-5-chloro-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**3d**) in DMSO-d₆.

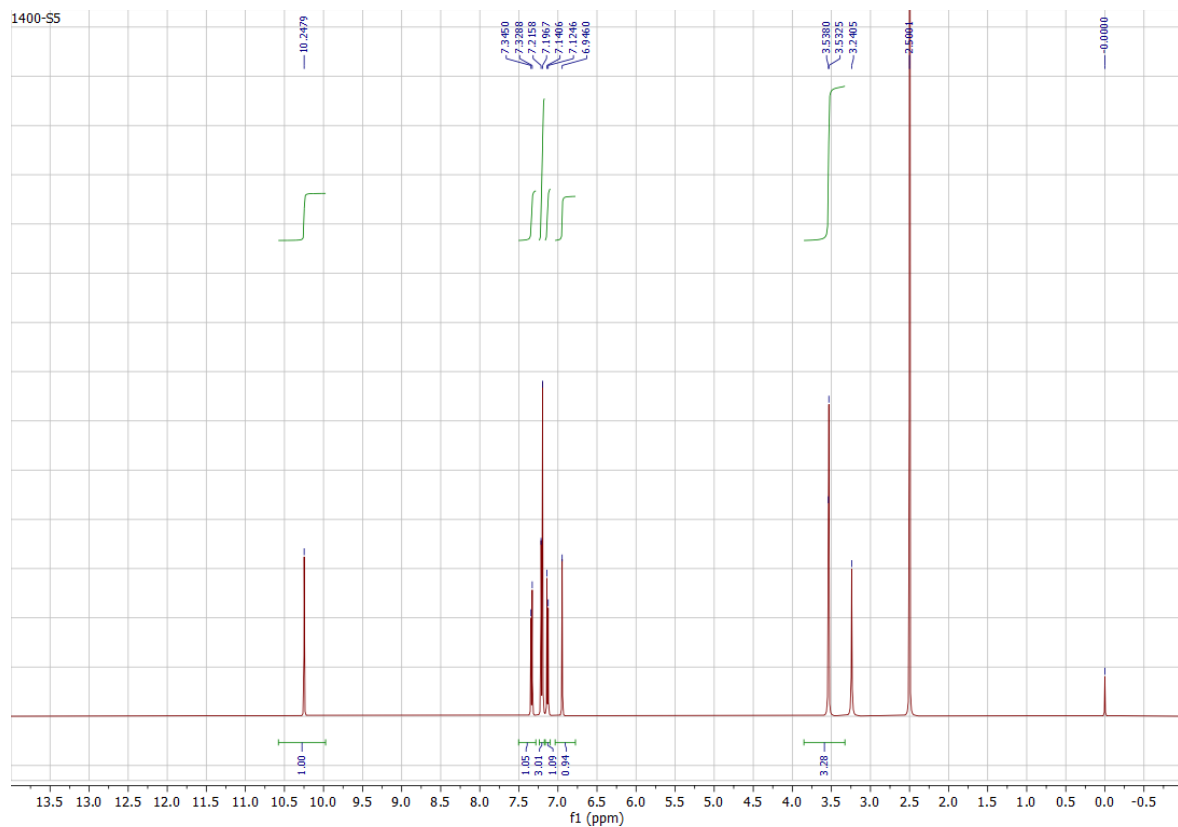


Figure S19. ¹H NMR spectrum of methyl 6'-amino-5-bromo-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**4d**) in DMSO-*d*₆.

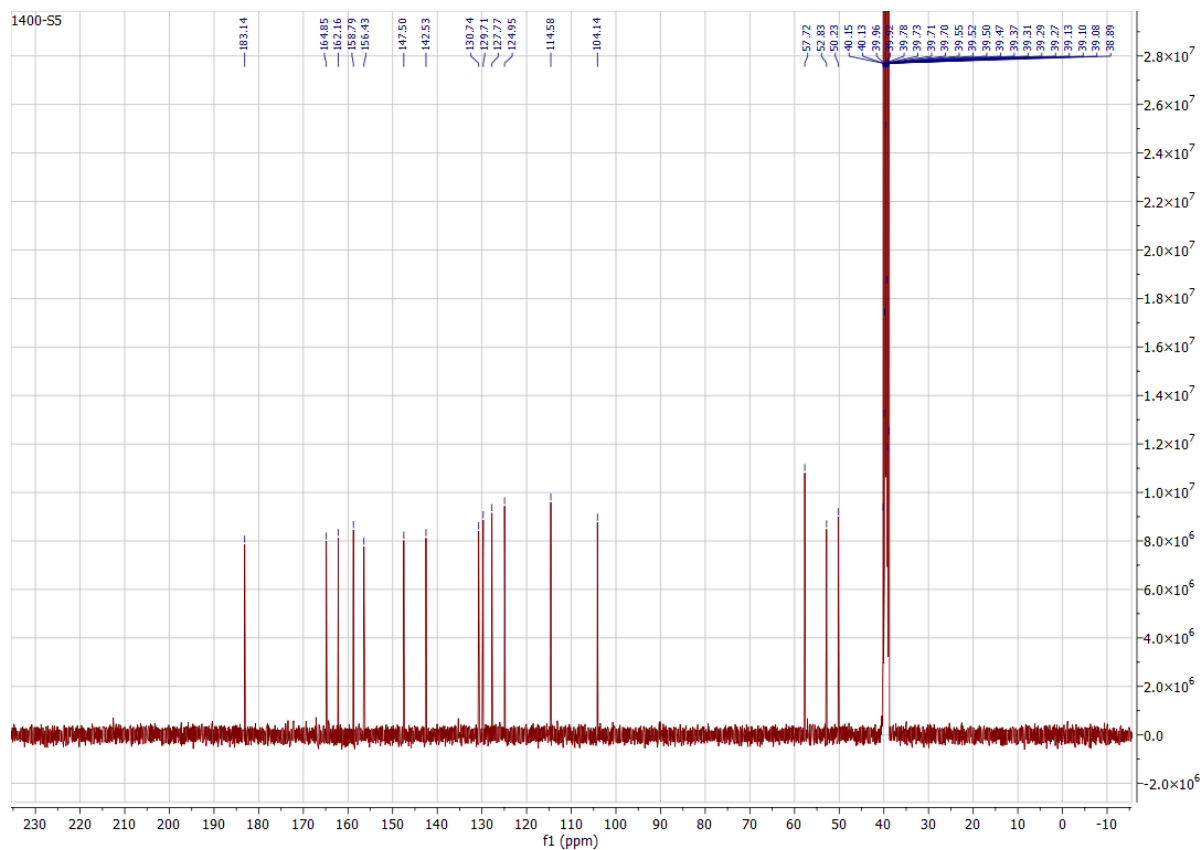


Figure S20. ¹³C NMR spectrum of methyl 6'-amino-5-bromo-5'-cyano-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**4d**) in DMSO-*d*₆.

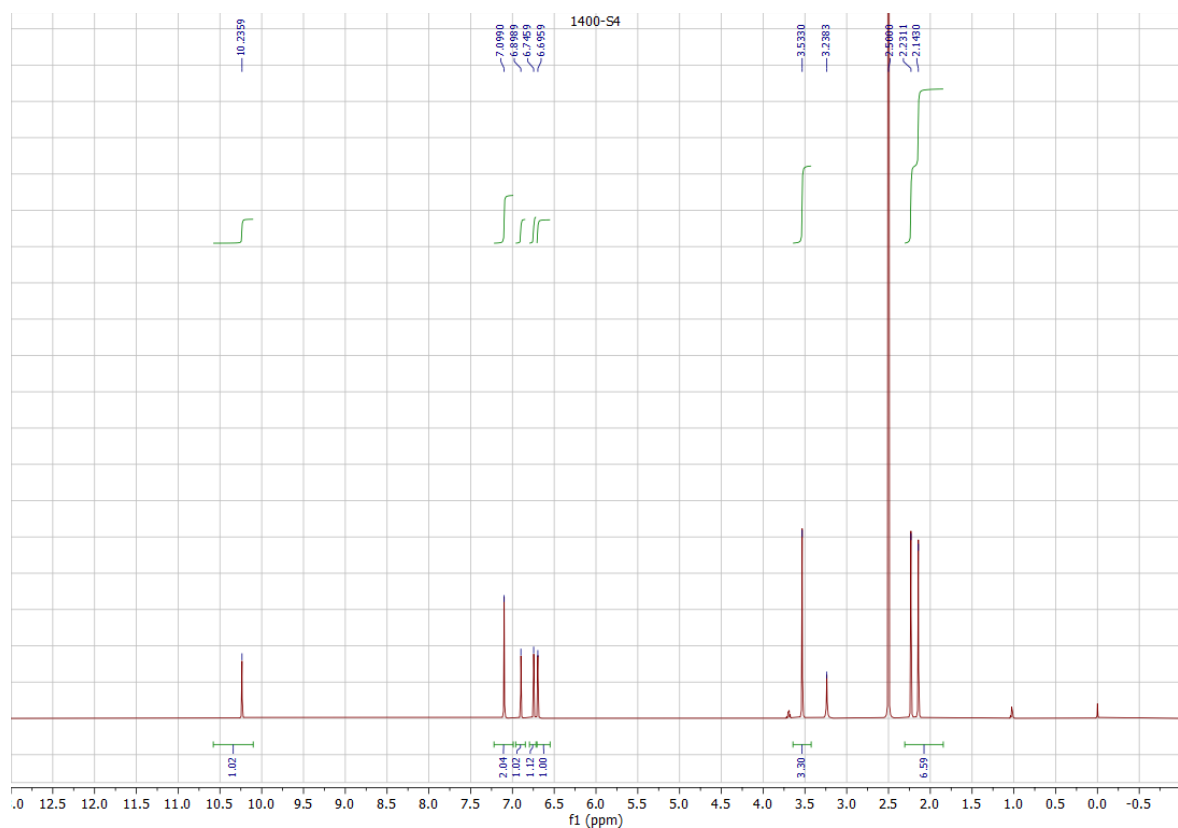


Figure S21. ¹H NMR spectrum of methyl 6'-amino-5'-cyano-5,7-dimethyl-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**5d**) in DMSO-*d*₆.

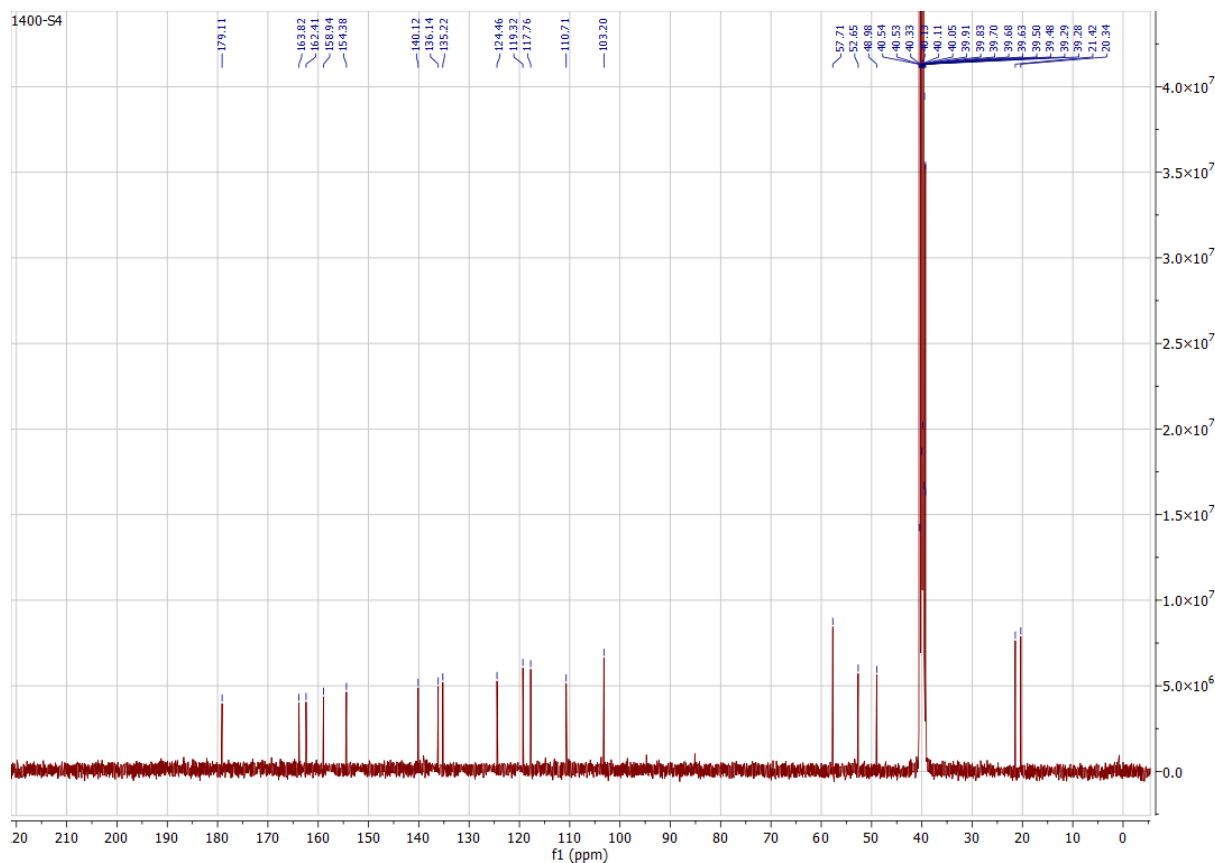


Figure S22. ¹³C NMR spectrum of methyl 6'-amino-5'-cyano-5,7-dimethyl-2-oxo-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**5d**) in DMSO-*d*₆.

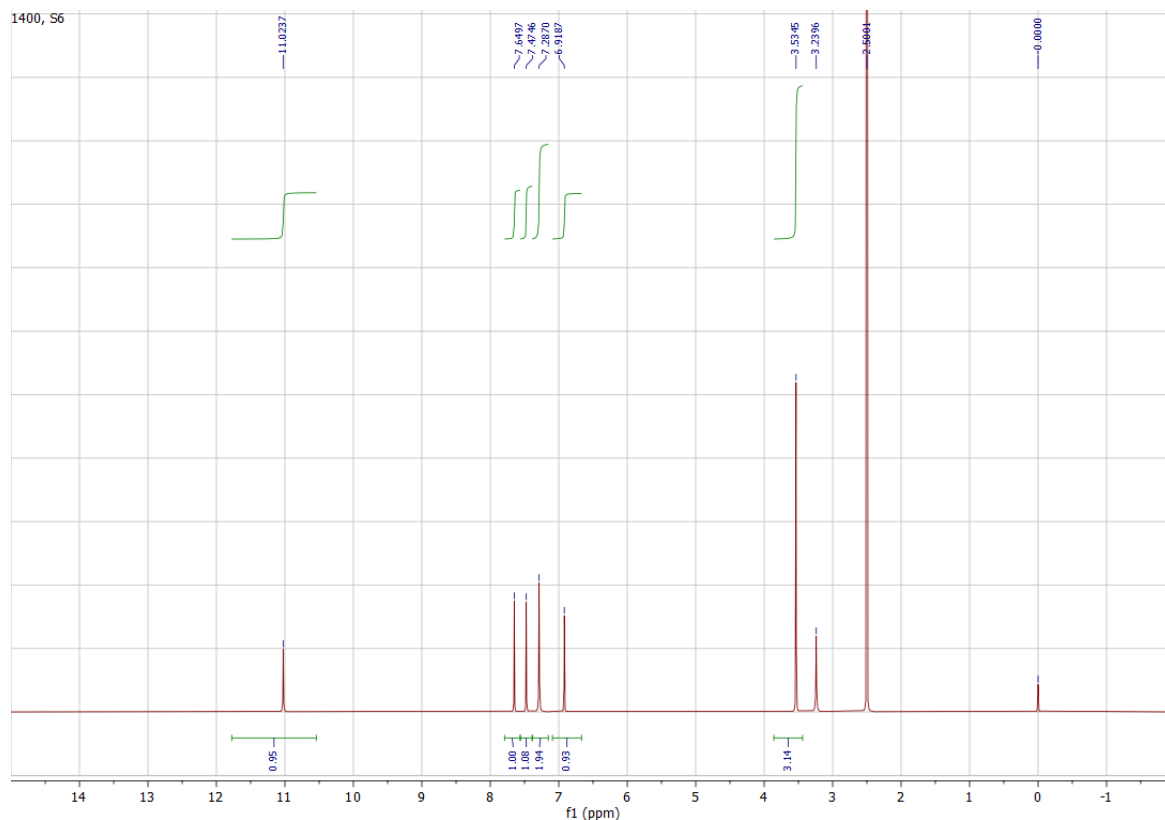


Figure S23. ¹H NMR spectrum of methyl 6'-amino-5,7-dibromo-5'-cyano-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**6d**) in DMSO-d₆.

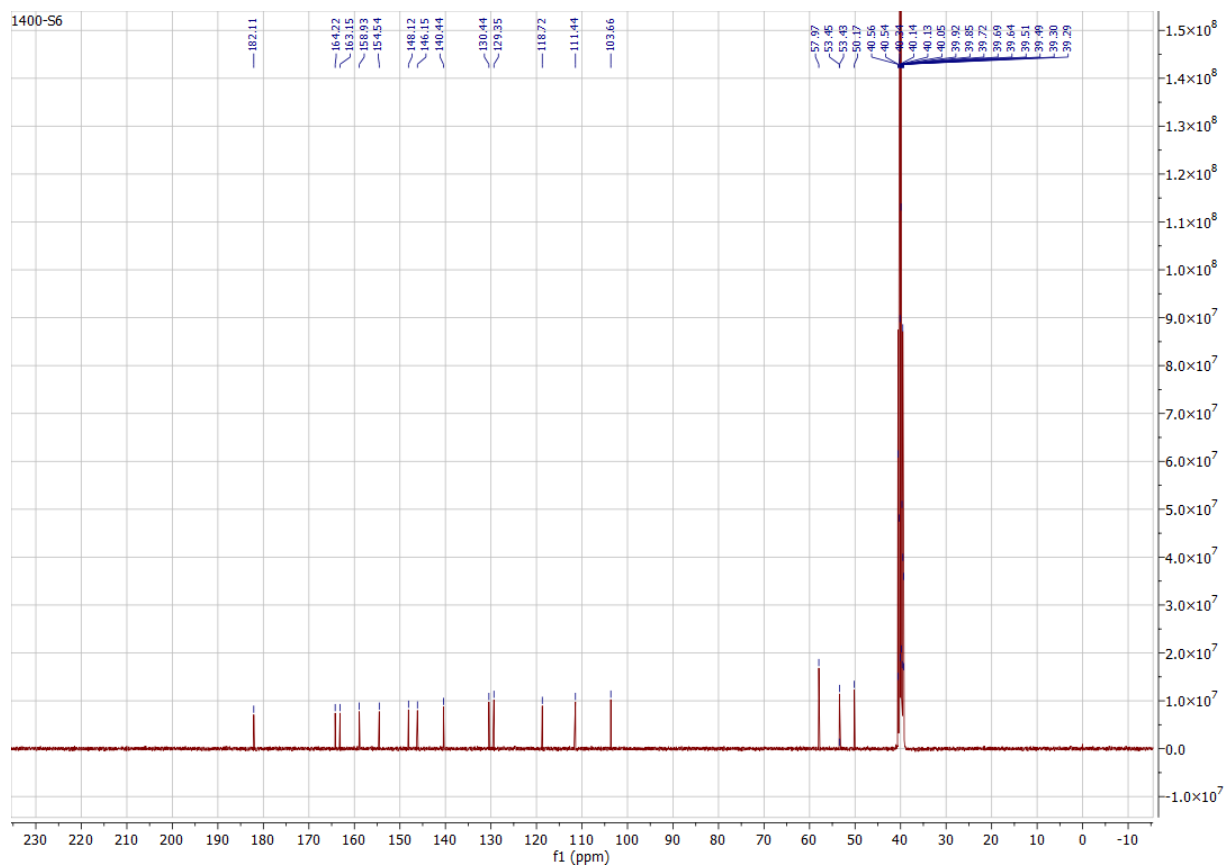


Figure S24. ¹³C NMR spectrum of methyl 6'-amino-5,7-dibromo-5'-cyano-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**6d**) in DMSO-d₆.

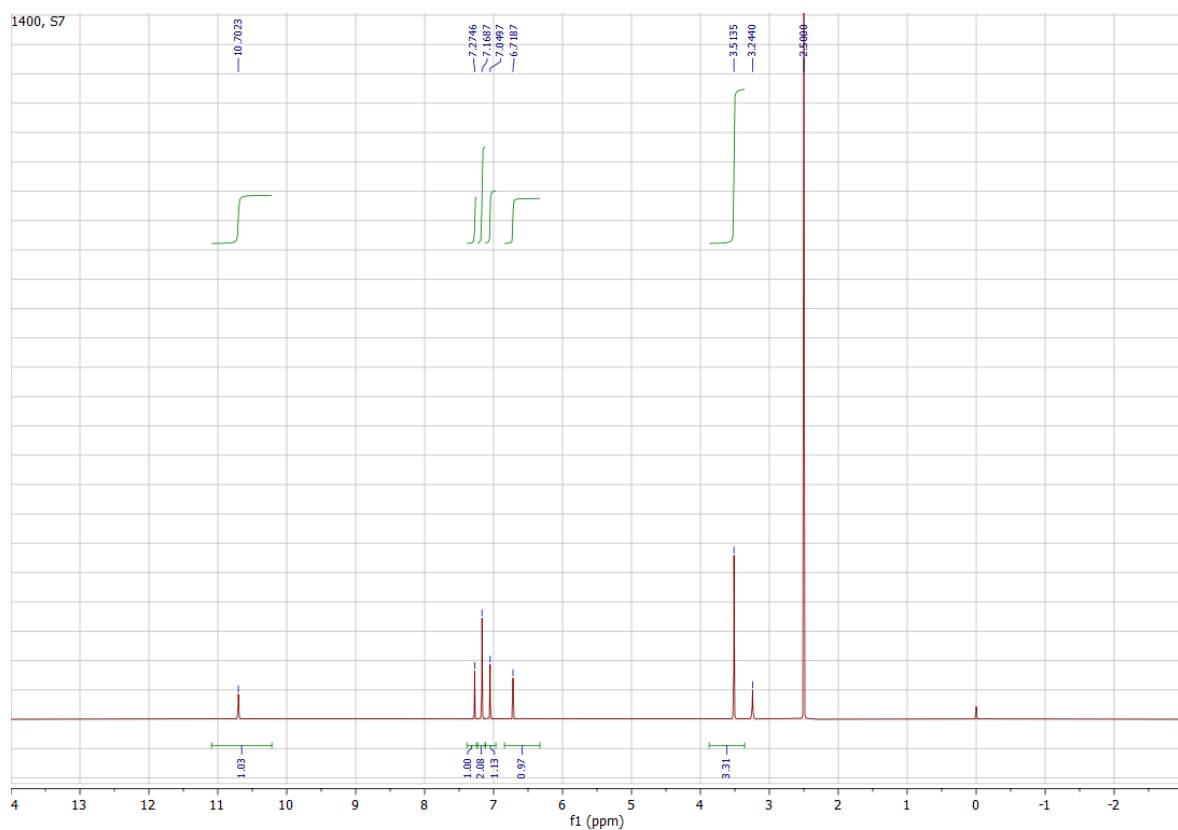


Figure S25. ¹H NMR spectrum of methyl 6'-amino-5,7-dichloro-5'-cyano-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**7d**) in DMSO-d₆.

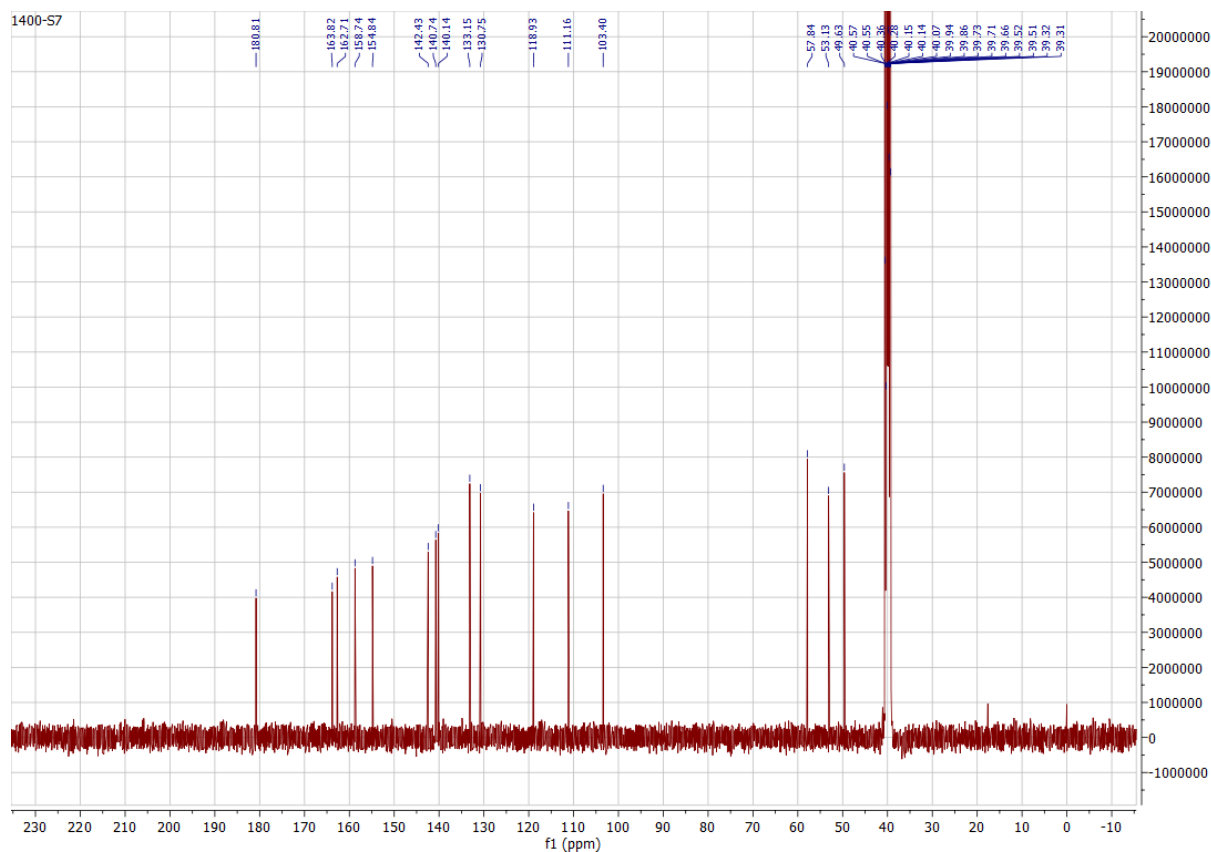


Figure S26. ¹³C NMR spectrum of methyl 6'-amino-5,7-dichloro-5'-cyano-2-oxo-2'H-spiro[indoline-3,4'-pyrano[2,3-c]pyrazole]-3'-carboxylate (**7d**) in DMSO-d₆.

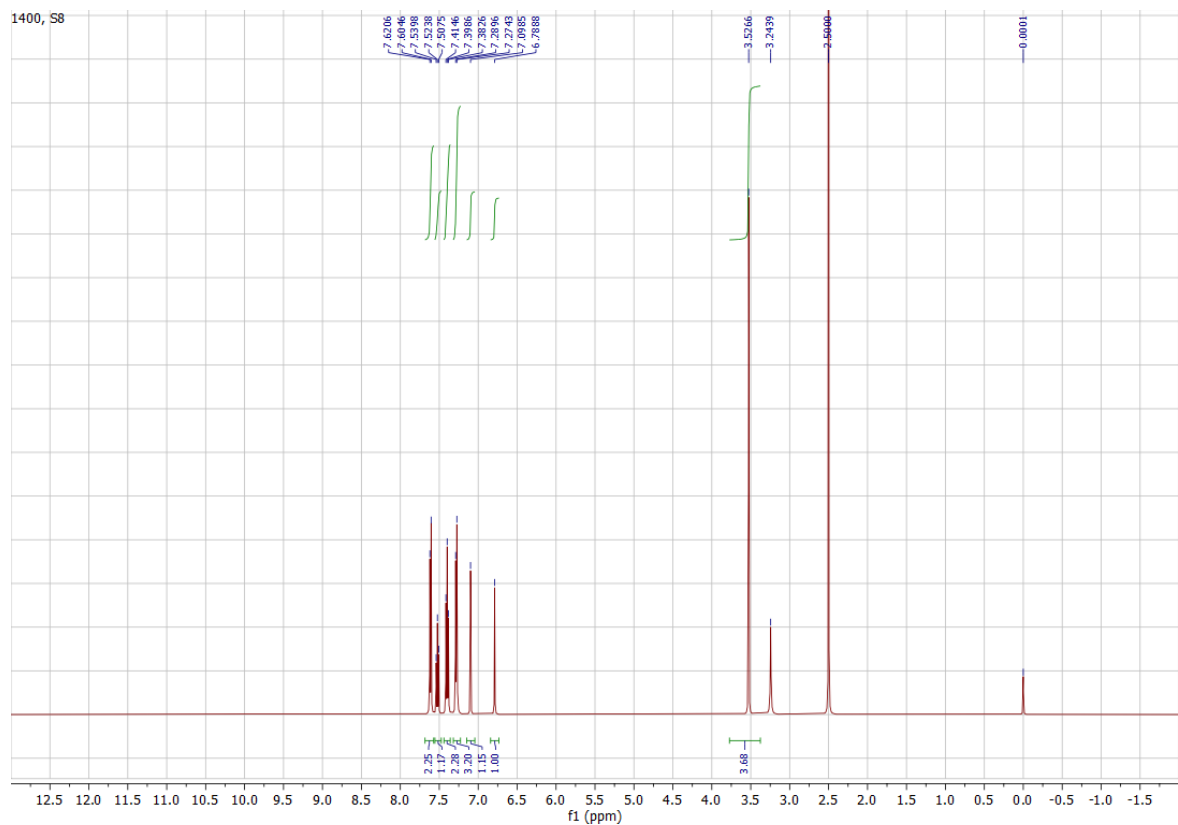


Figure S27. ¹H NMR spectrum of methyl 6'-amino-5,7-dichloro-5'-cyano-2-oxo-1-phenyl-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**8d**) in DMSO-d₆.

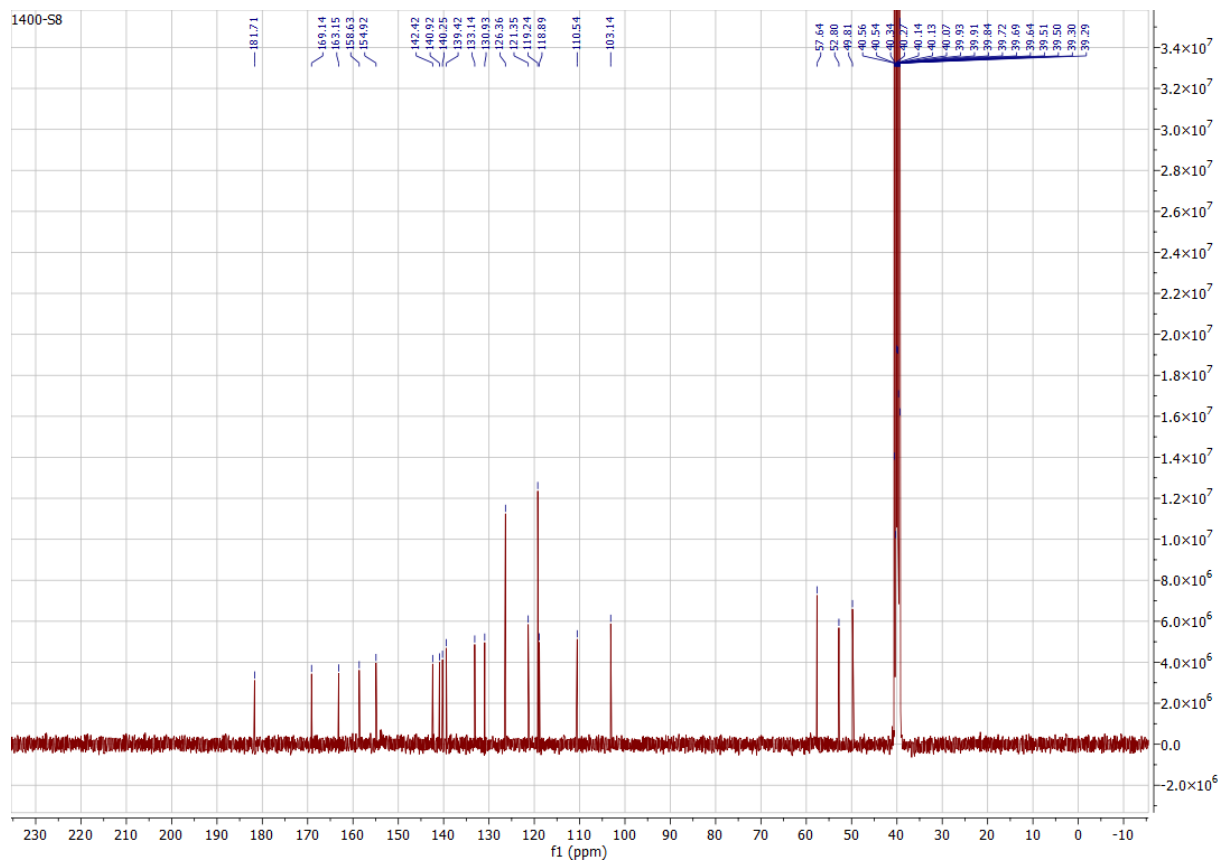


Figure S28. ¹³C NMR spectrum of methyl 6'-amino-5,7-dichloro-5'-cyano-2-oxo-1-phenyl-2'*H*-spiro[indoline-3,4'-pyrano[2,3-*c*]pyrazole]-3'-carboxylate (**8d**) in DMSO-d₆.