

## Supplementary Material

### An Efficient One-pot, Four-component Synthesis of Pyrazolo[3,4-*b*]pyridines Catalyzed by Tetrapropylammonium Bromide (TPAB) in Water

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4-Benzoyl-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (5a)

Fig. S1. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound 5a.

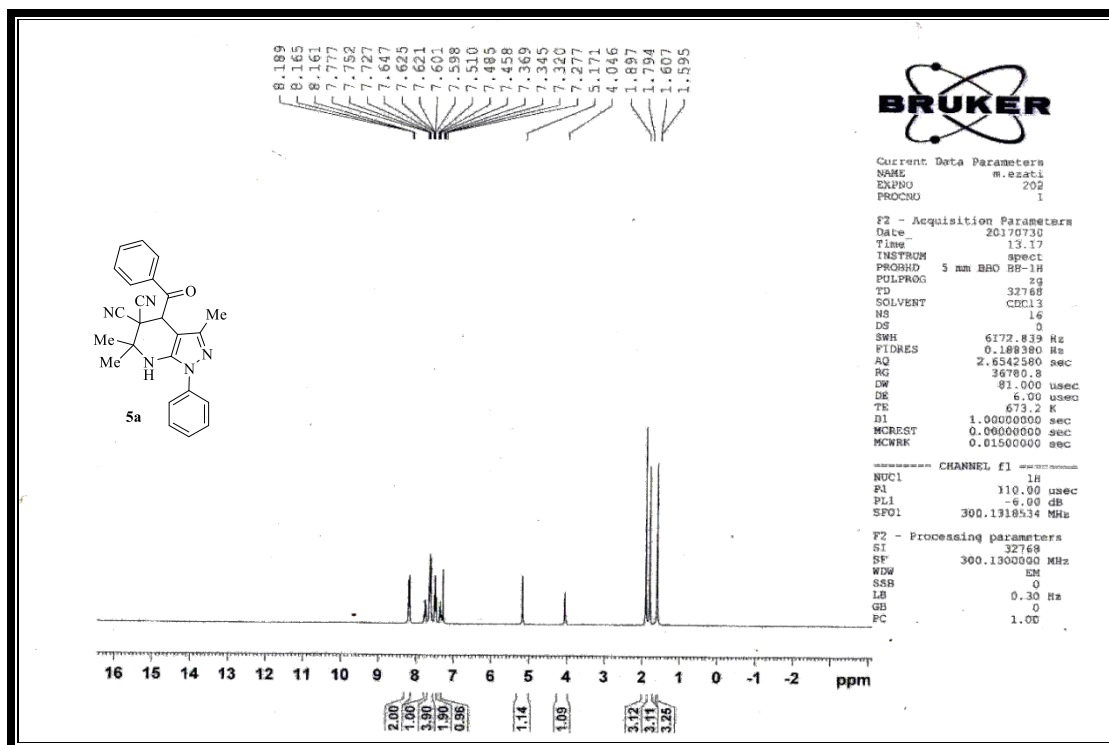


Fig. S2. <sup>13</sup>C NMR spectrum (75.5 MHz, CDCl<sub>3</sub>) of compound 5a.

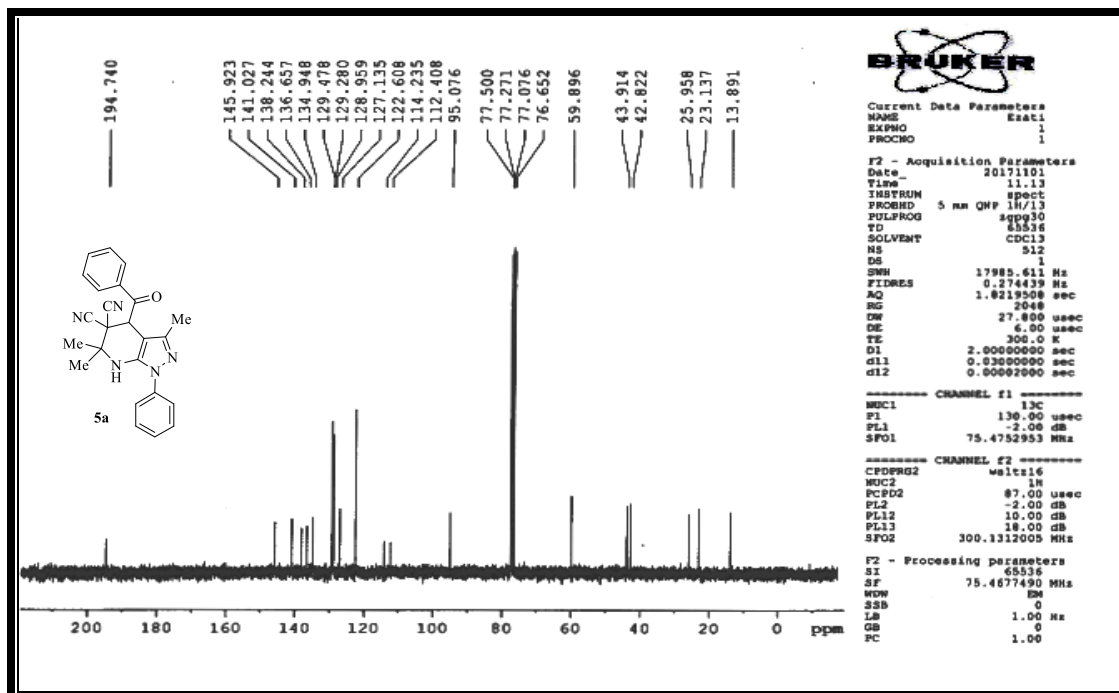


Fig. S3. IR spectrum (KBr) of compound 5a.

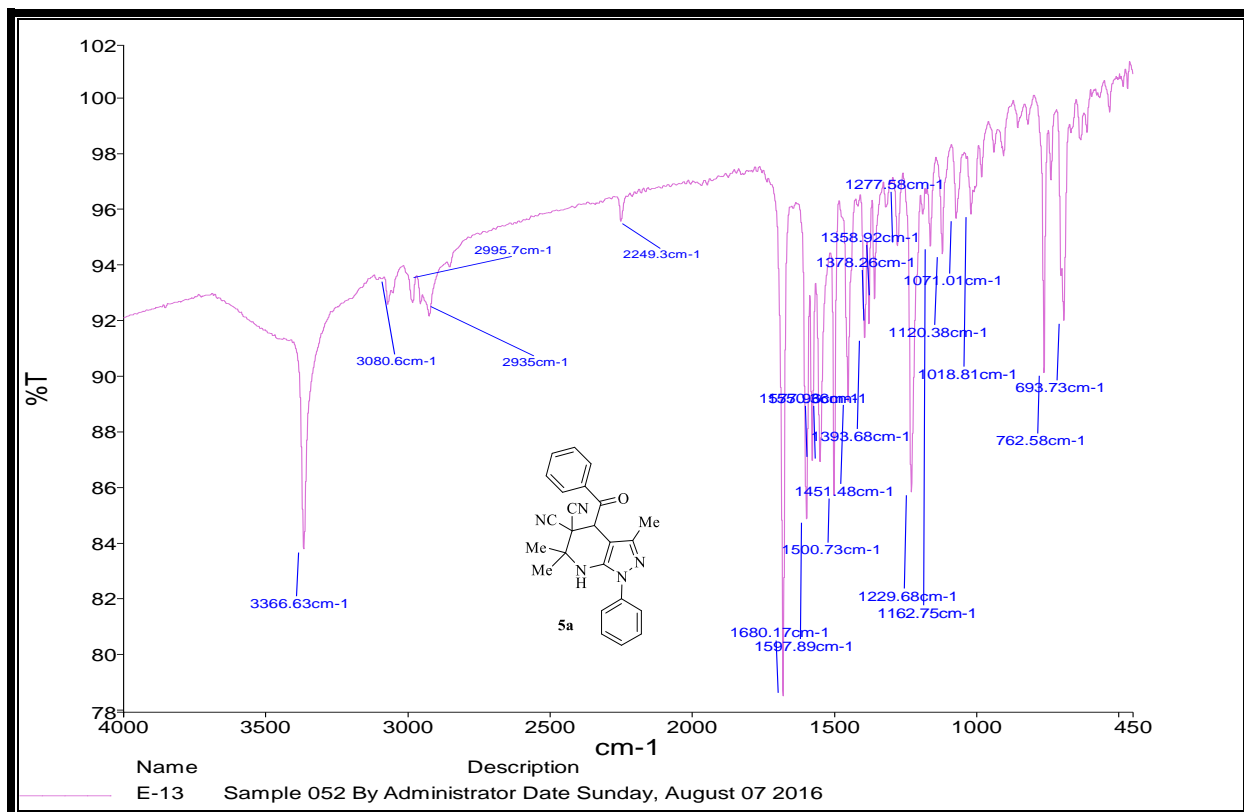
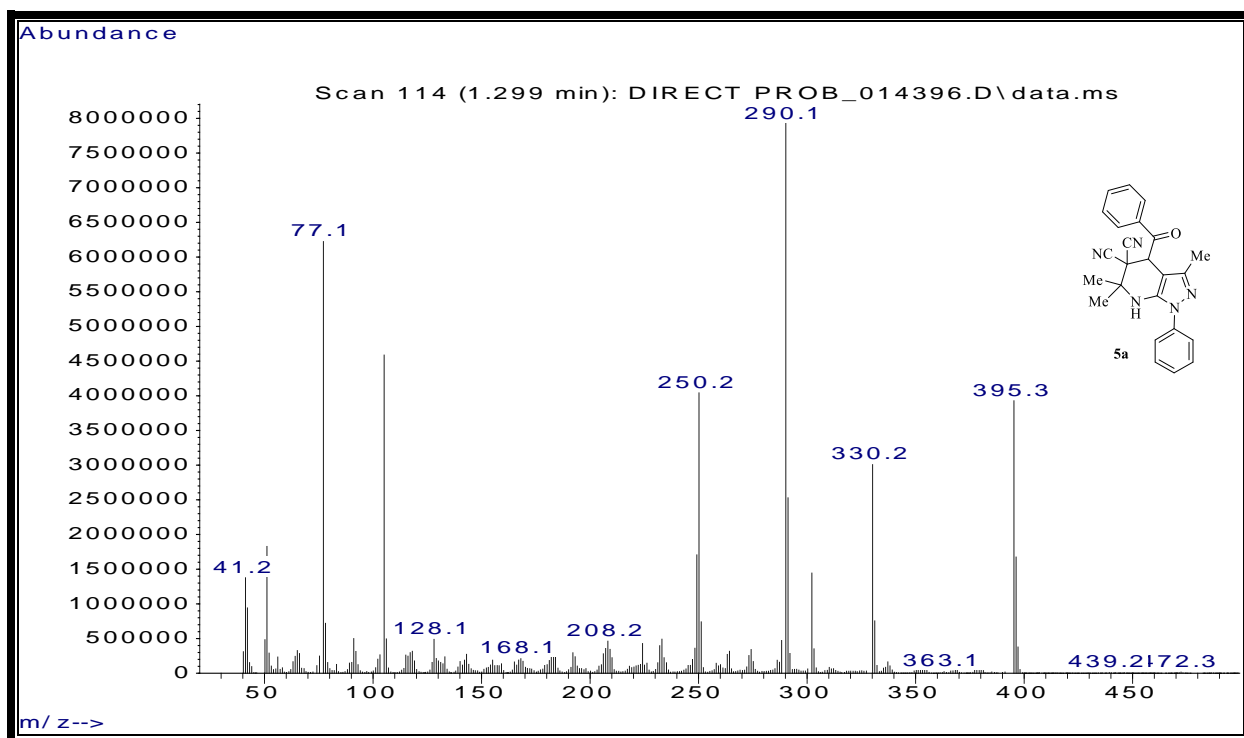


Fig. S4. Mass spectrum of compound 5a.



4-(4-Chlorobenzoyl)-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (**5b**)

Fig. S5. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound **5b**.

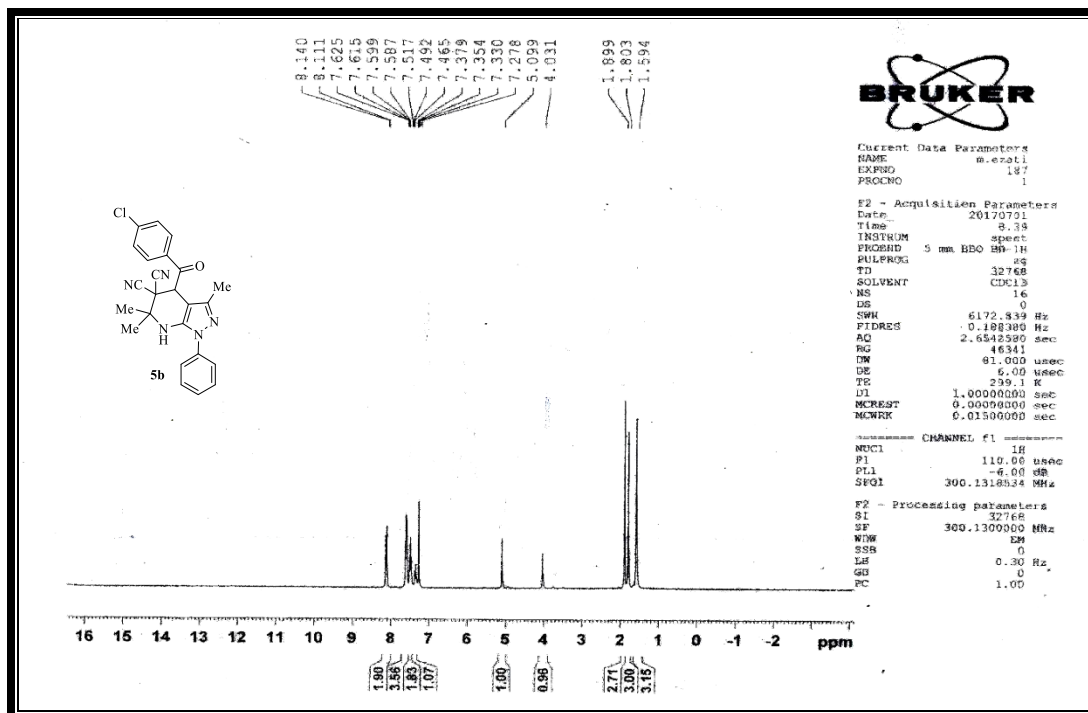


Fig. S6. <sup>13</sup>C NMR spectrum (75.5 MHz, DMSO-*d*<sub>6</sub>) of compound **5b**.

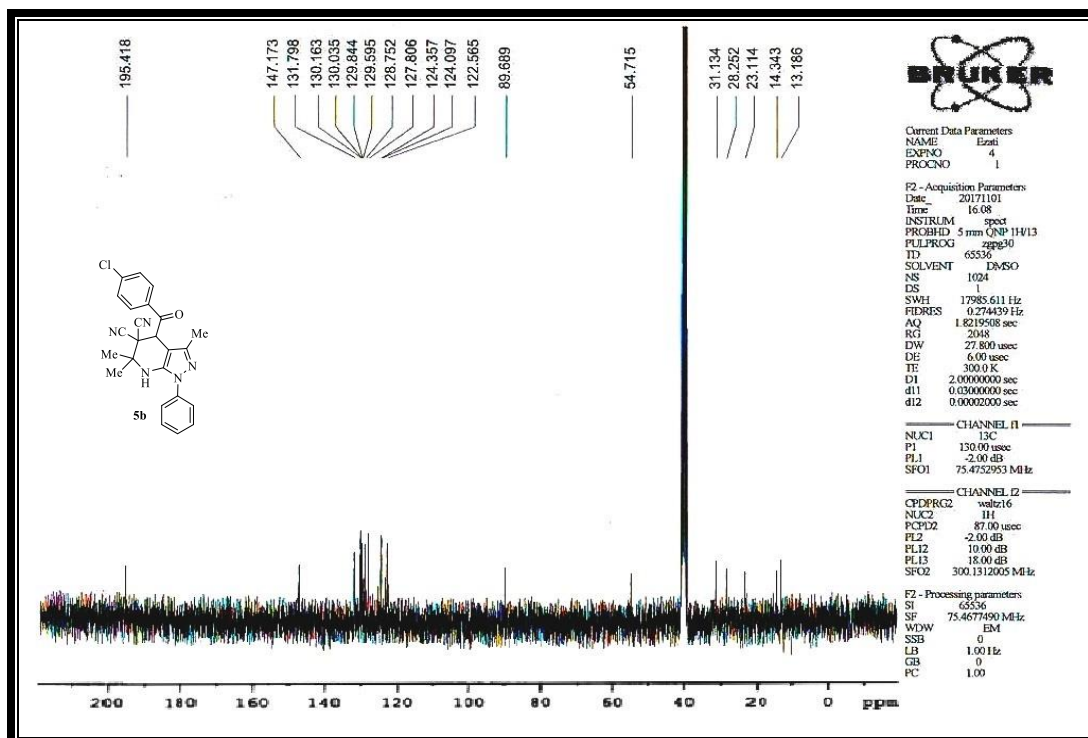


Fig. S7. IR spectrum (KBr) of compound 5b.

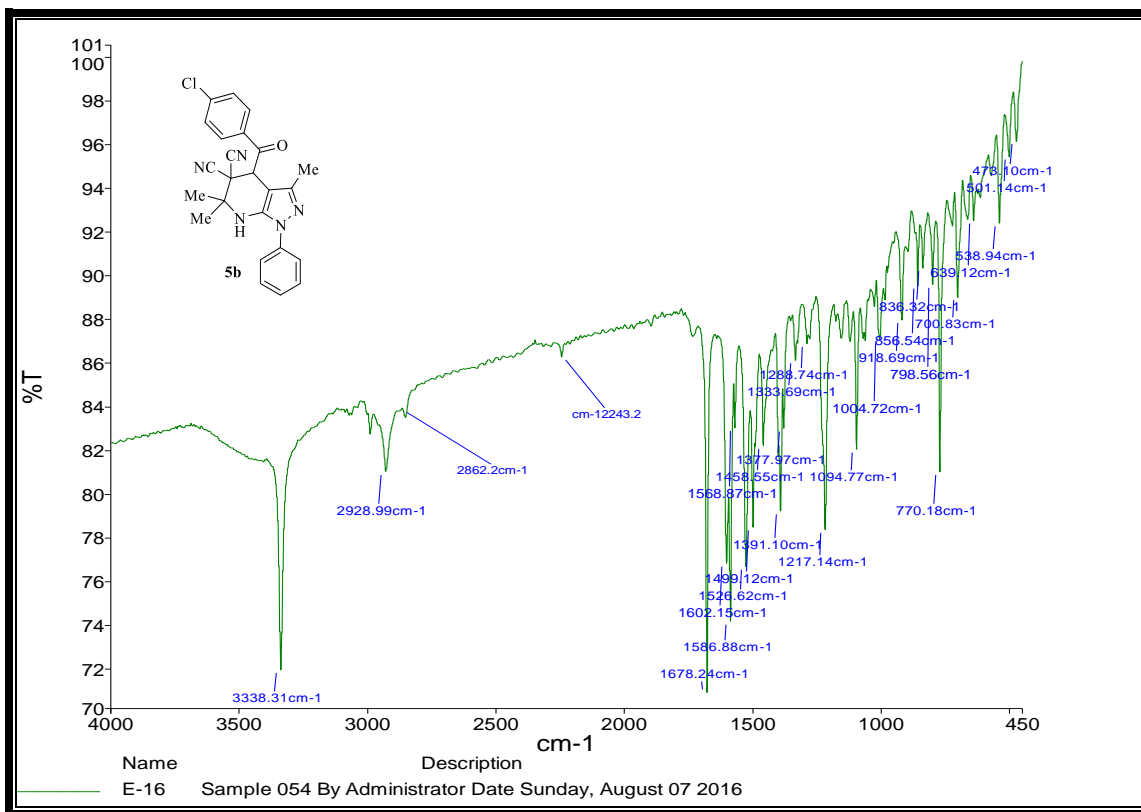
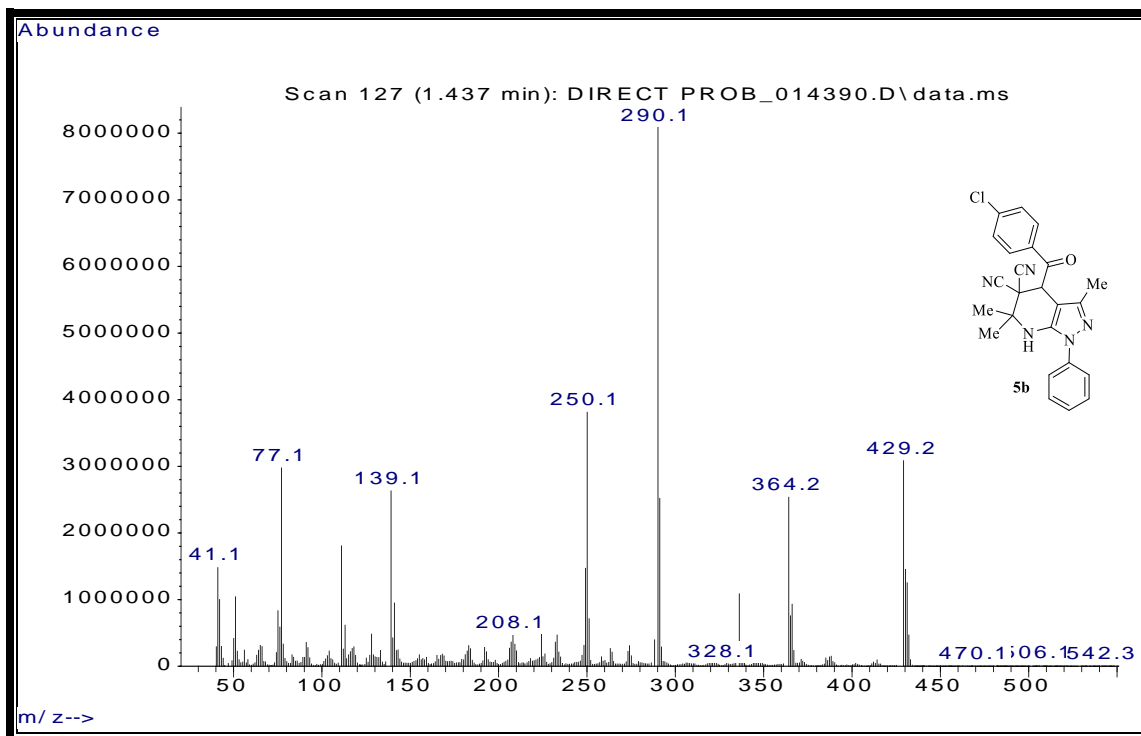


Fig. S8. Mass spectrum of compound 5b.



4-(4-Fluorobenzoyl)-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (**5c**)

Fig. S9. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound **5c**

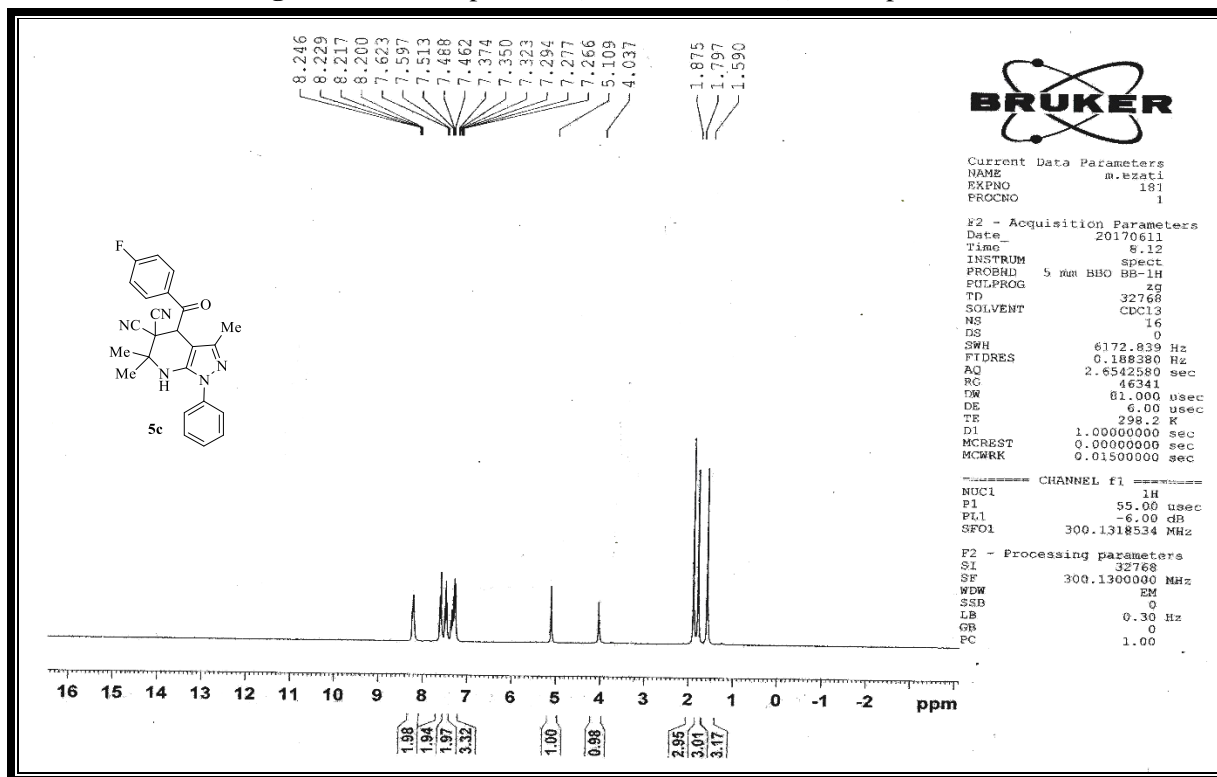


Fig. S10. <sup>13</sup>C NMR spectrum (75.5 MHz, CDCl<sub>3</sub>) of compound **5c**.

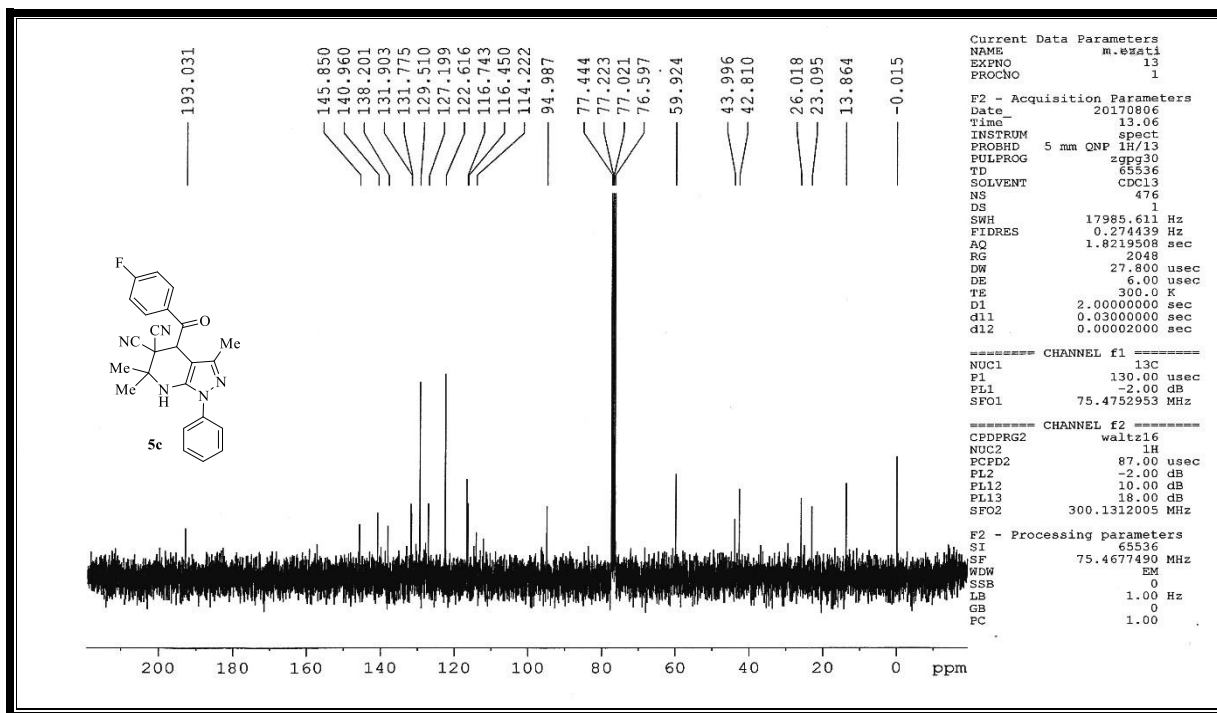


Fig. S11. IR spectrum (KBr) of compound 5c.

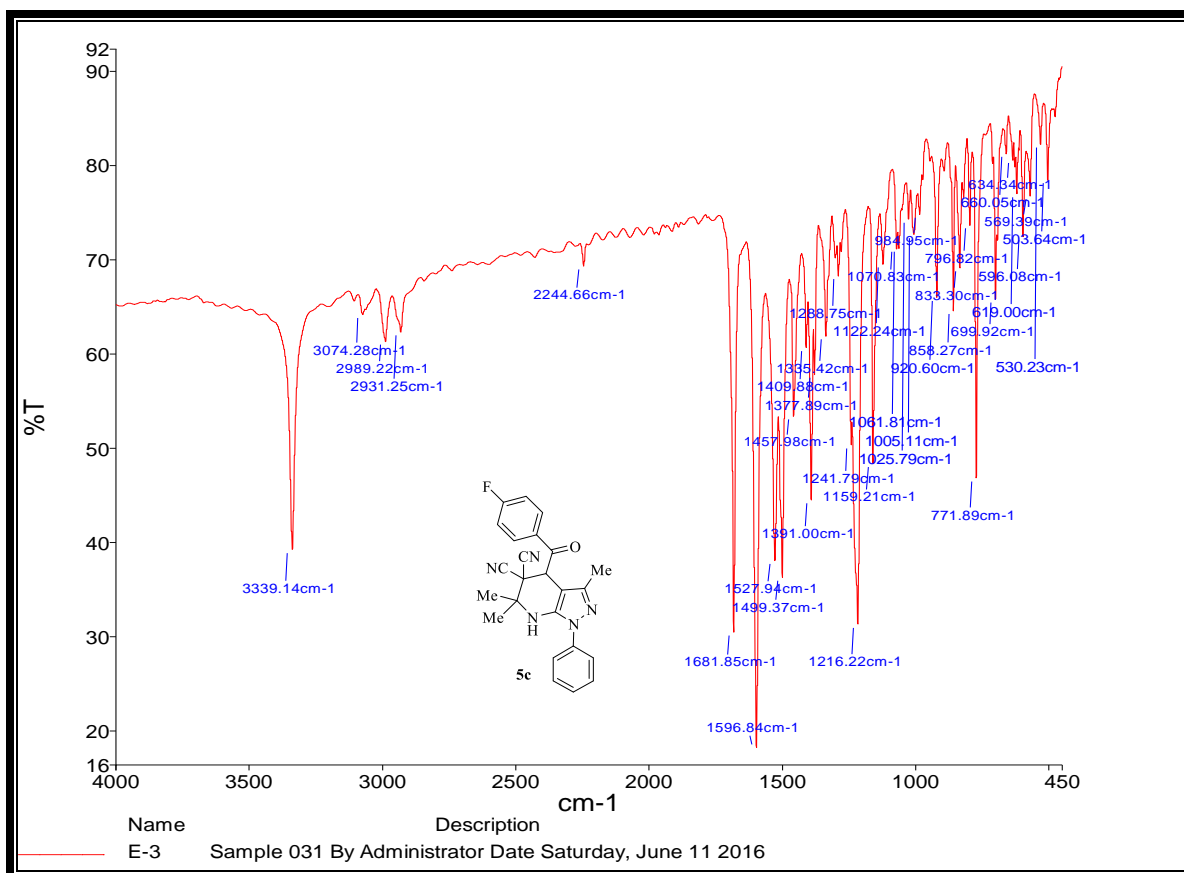
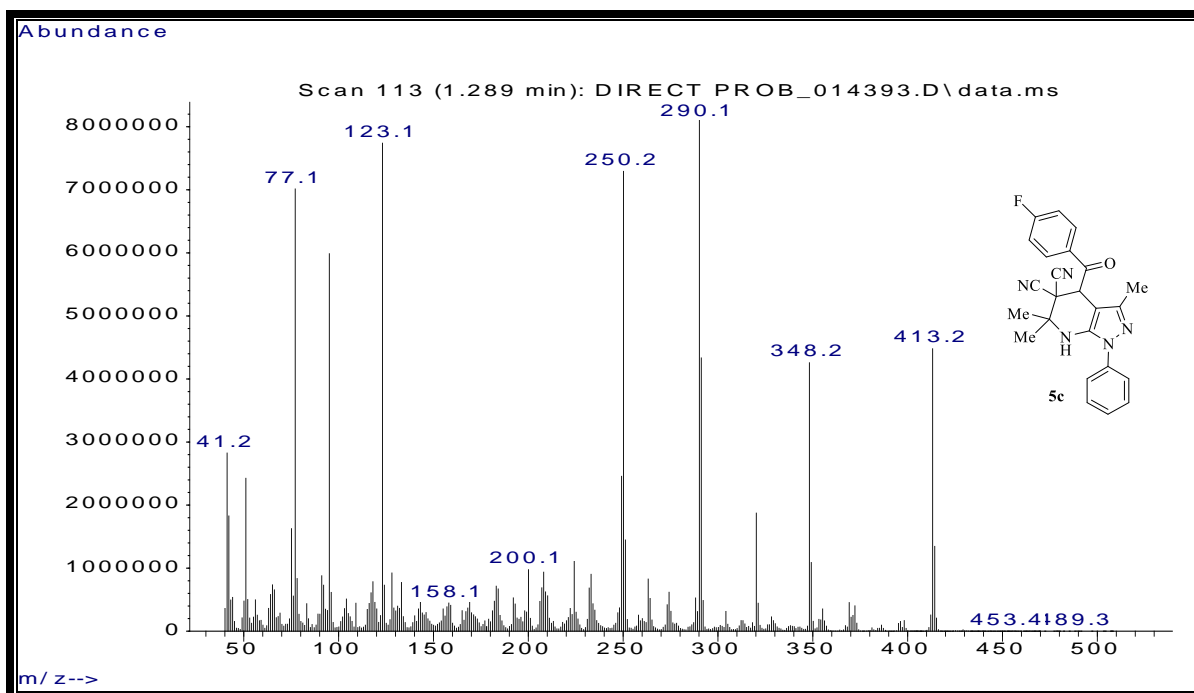


Fig. S12. Mass spectrum of compound 5c.





3,6,6-Trimethyl-4-(4-methylbenzoyl)-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (5d)

Fig. S13. <sup>1</sup>H NMR spectrum (300 MHz, DMSO-*d*<sub>6</sub>) of compound 5d.

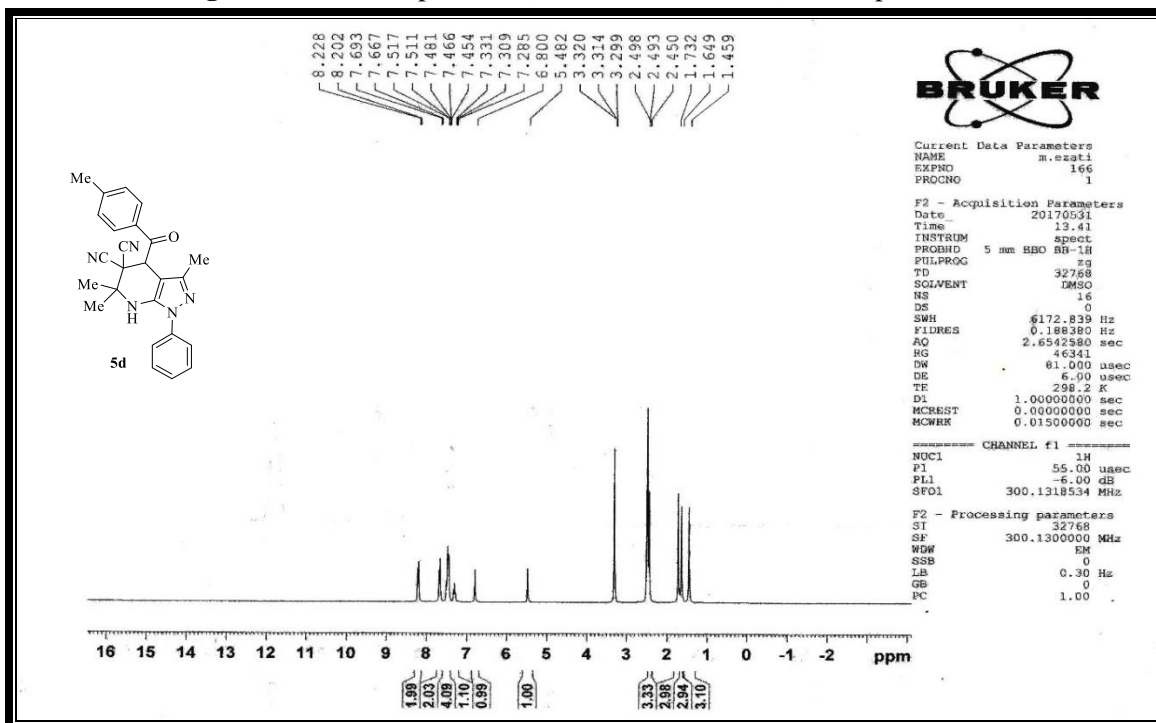
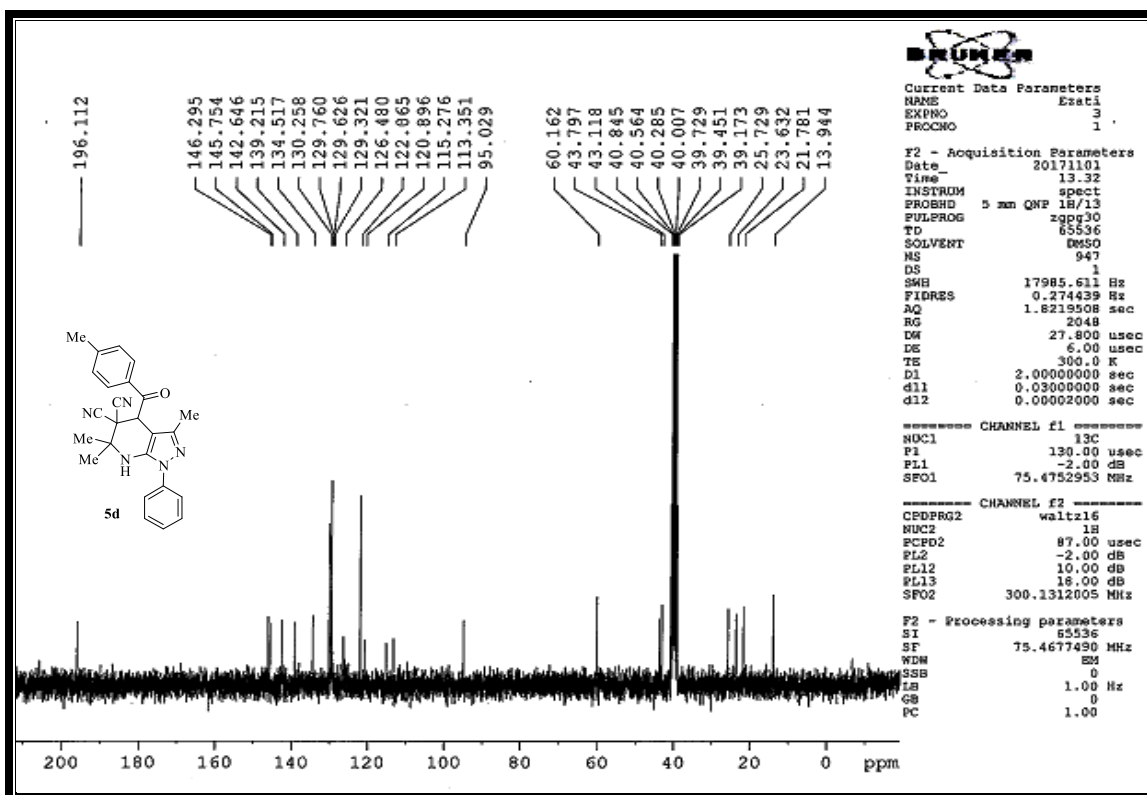
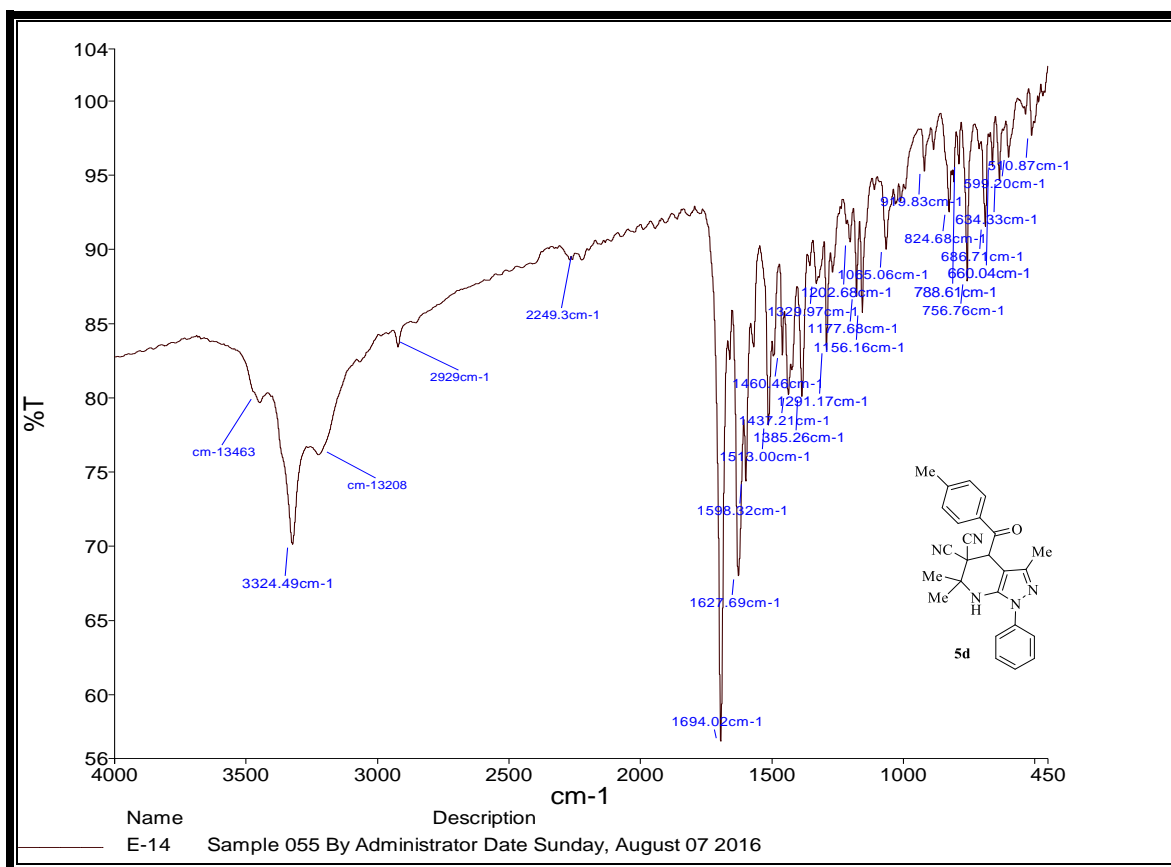


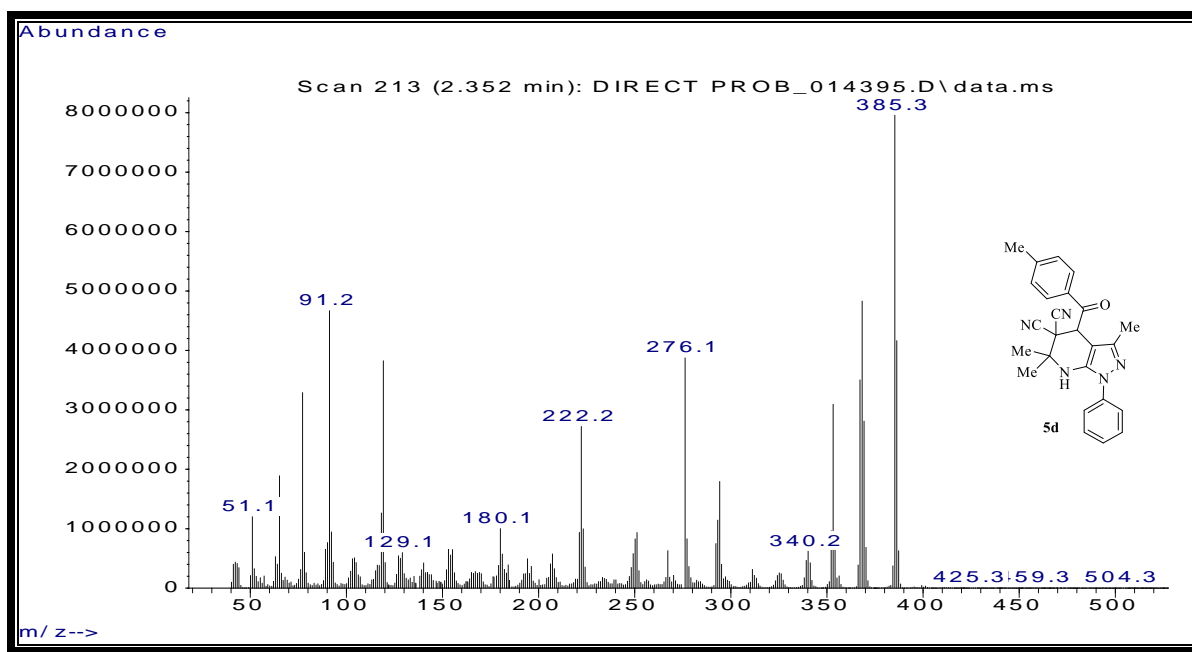
Fig. S14. <sup>13</sup>C NMR spectrum (75.5 MHz, DMSO-*d*<sub>6</sub>) of compound 5d.



**Fig. S15.** IR spectrum (KBr) of compound **5d**.

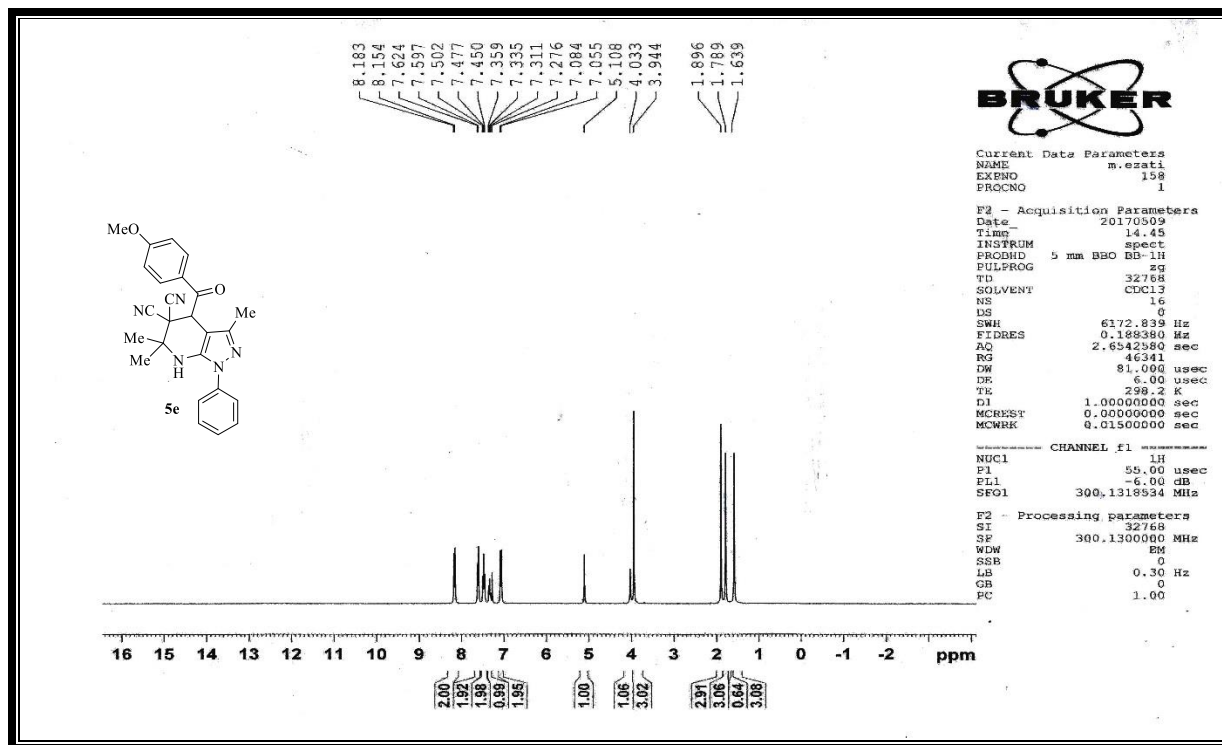


**Fig. S16.** Mass spectrum of compound **5d**.



**4-(4-Methoxybenzoyl)-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (5e)**

**Fig. S17.**  $^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of compound **5e**.



**Fig. S18.**  $^{13}\text{C}$  NMR spectrum (75.5 MHz,  $\text{DMSO}-d_6$ ) of compound **5e**.

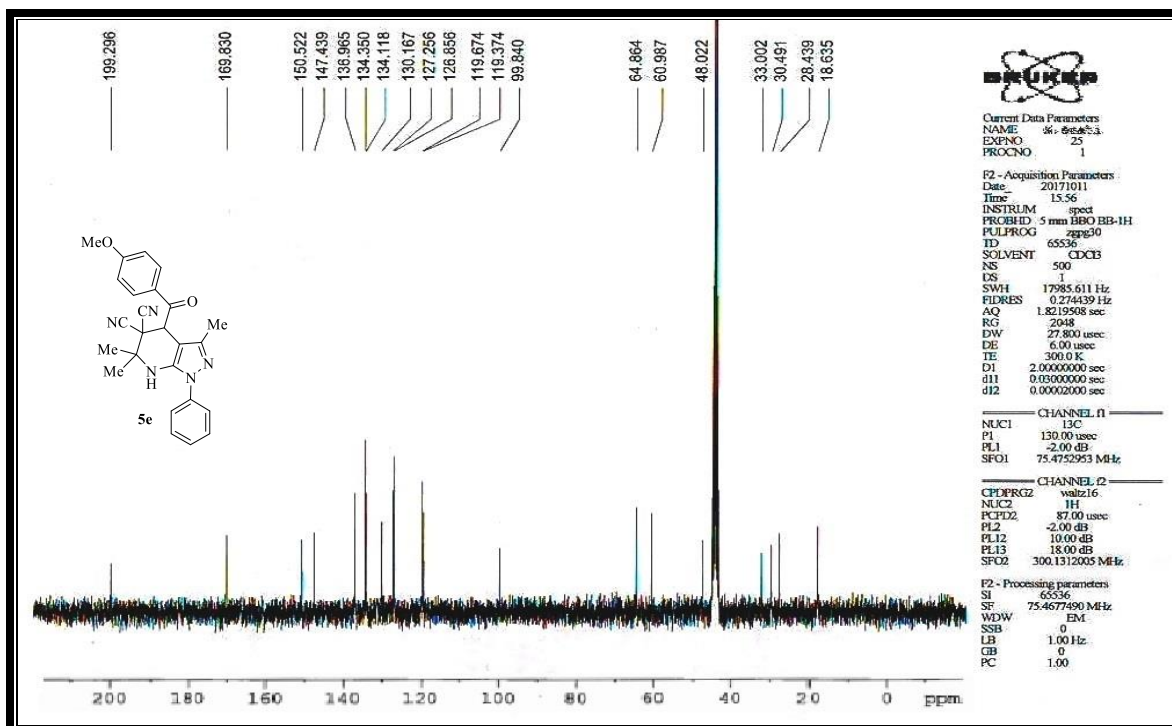


Fig. S19. IR spectrum (KBr) of compound 5e.

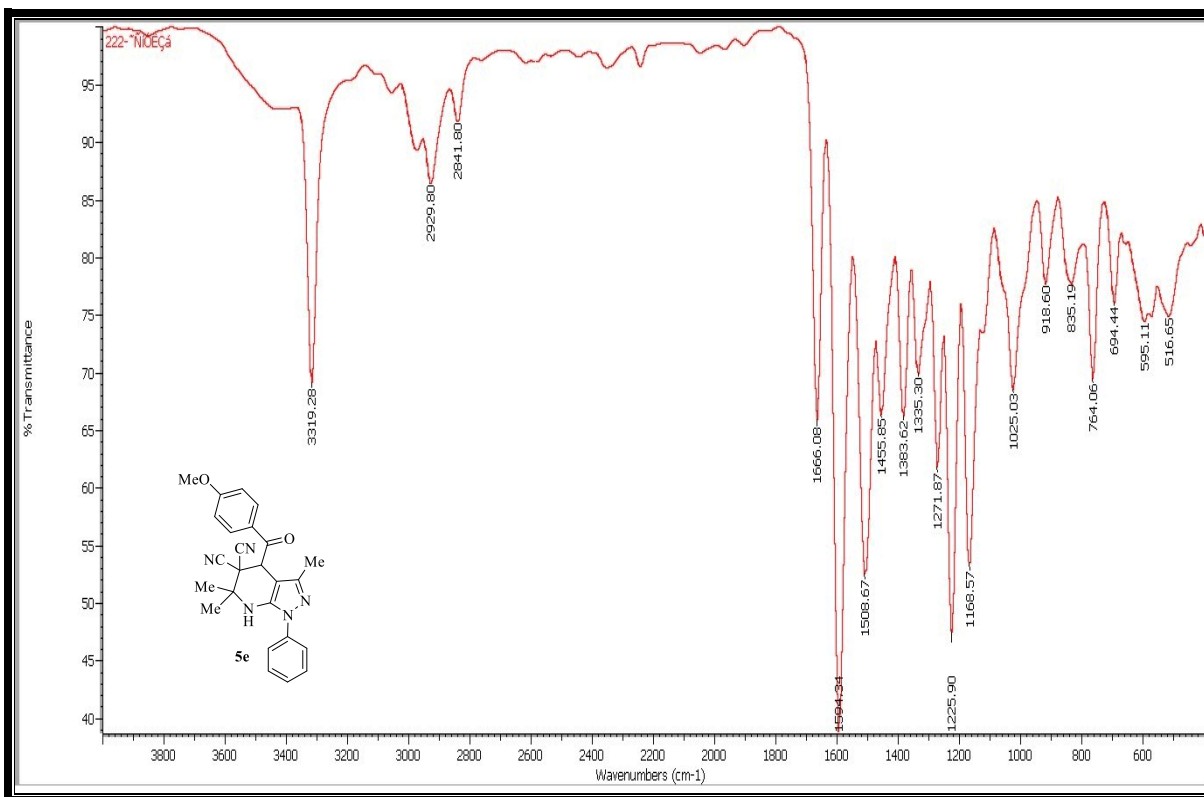
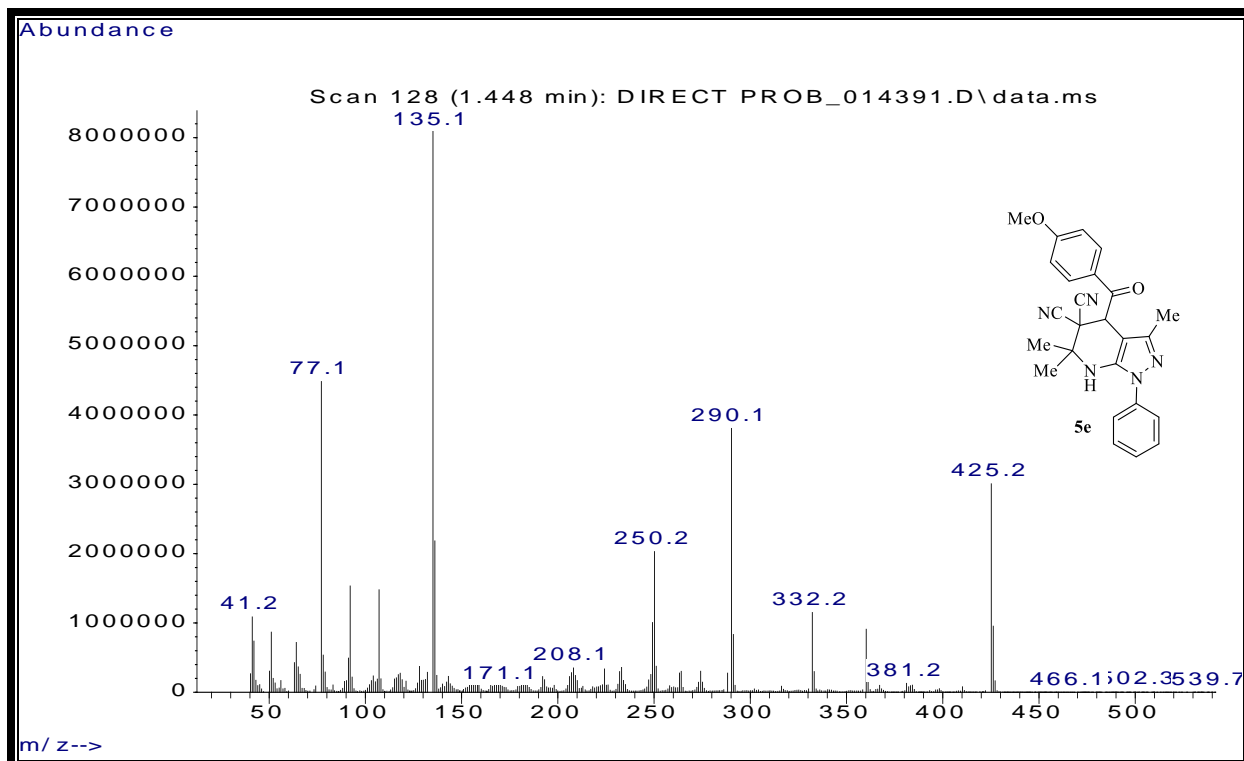


Fig. S20. Mass spectrum of compound 5e.



4-(3,4-Dimethoxybenzoyl)-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (5f)

Fig. S21. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound 5f.

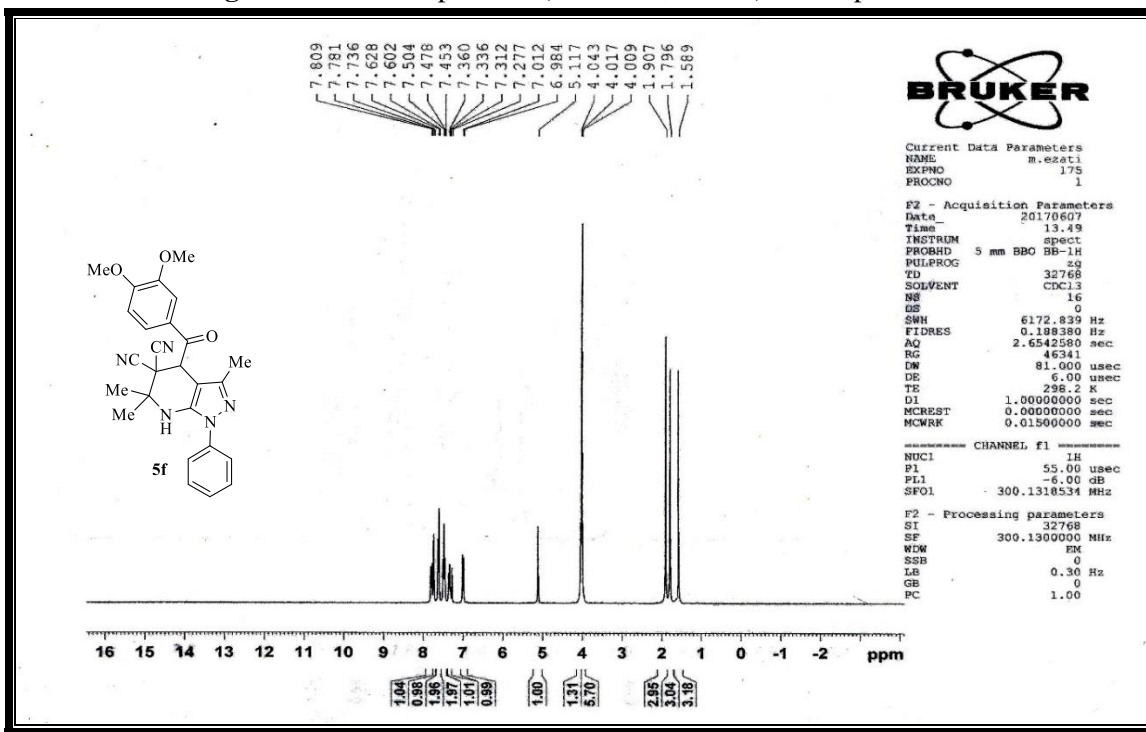


Fig. S22. <sup>13</sup>C NMR spectrum (75.5 MHz, CDCl<sub>3</sub>) of compound 5f.

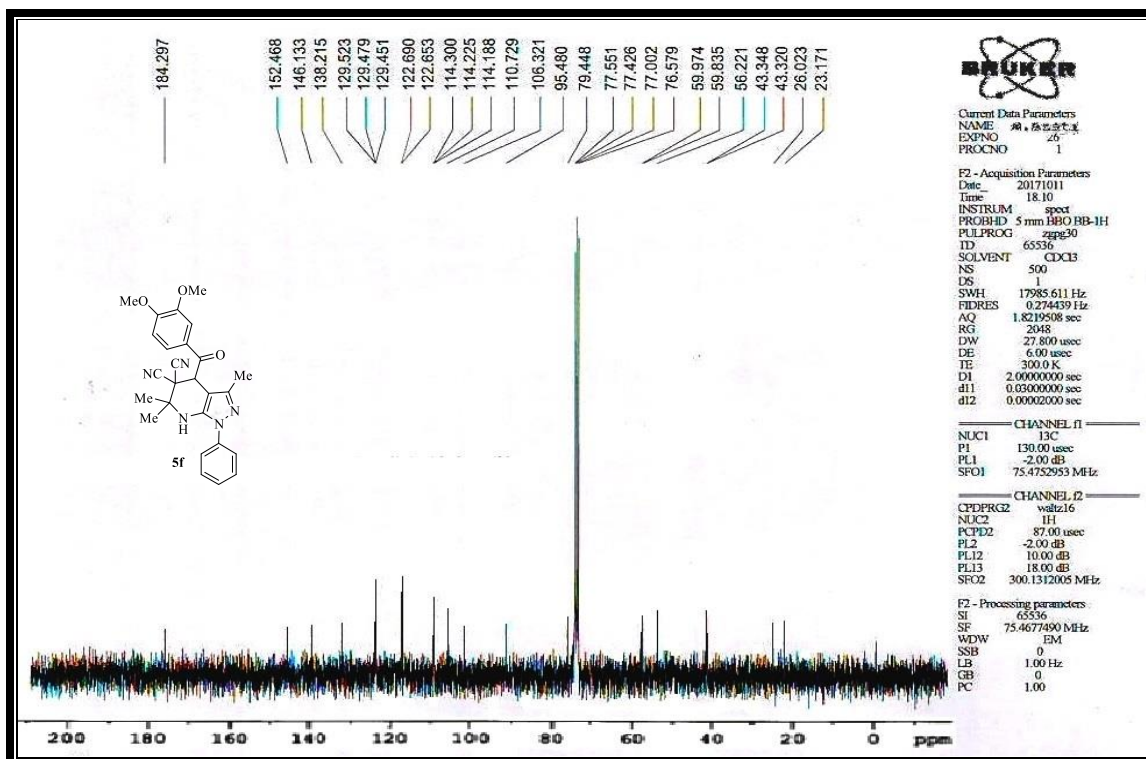


Fig. S23. IR spectrum (KBr) of compound 5f.

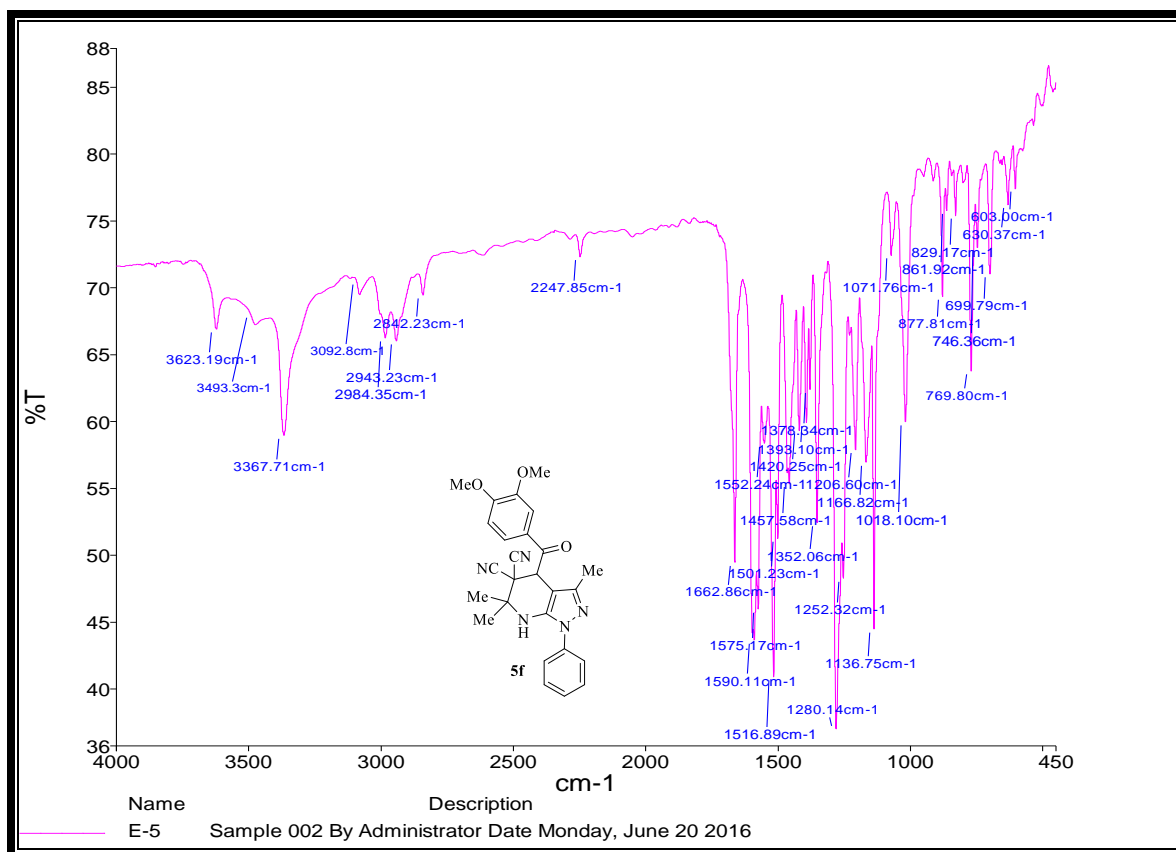
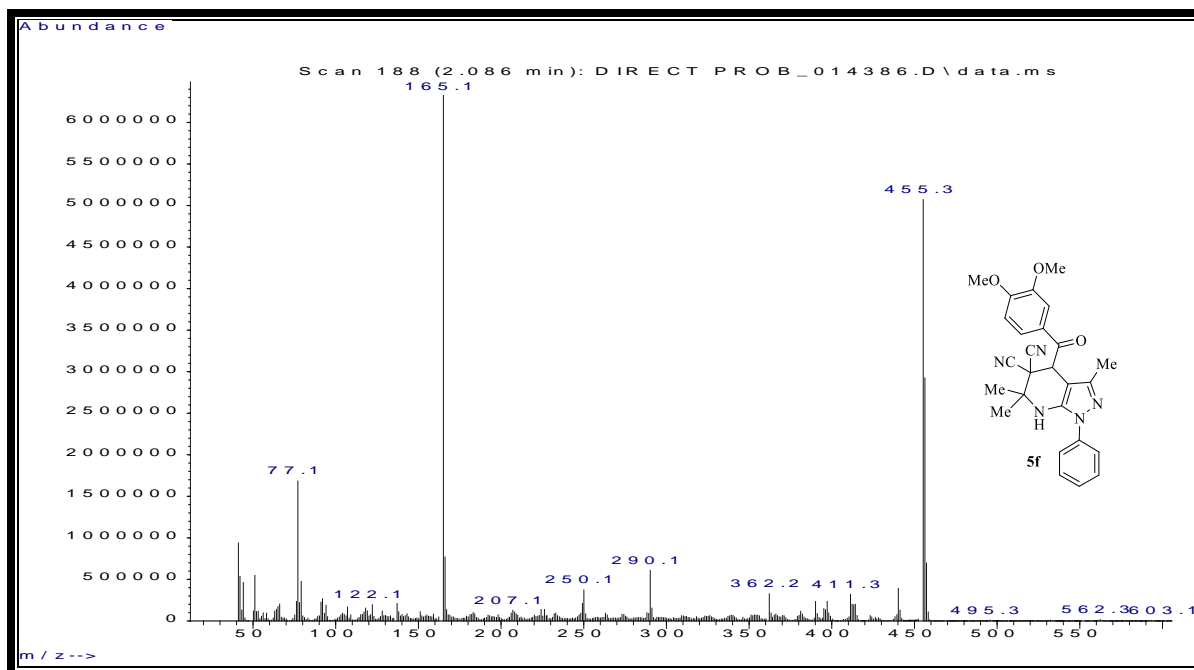


Fig. S24. Mass spectrum of compound 5f.



4-(4-Hydroxy-3-methoxybenzoyl)-3,6,6-trimethyl-1-phenyl-1,4,6,7-tetrahydro-5H-pyrazolo[3,4-b]pyridine-5,5-dicarbonitrile (5g)

Fig. S25. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound 5g.

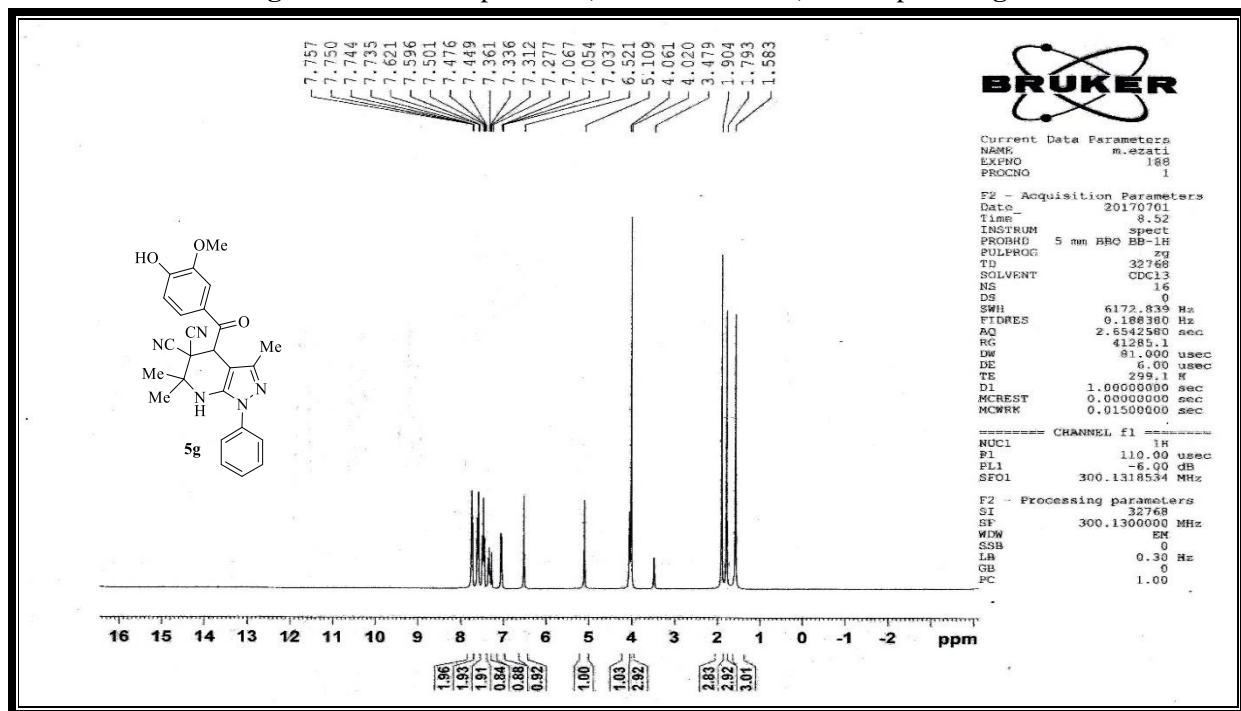


Fig. S26. <sup>13</sup>C NMR spectrum (75.5 MHz, CDCl<sub>3</sub>) of compound 5g.

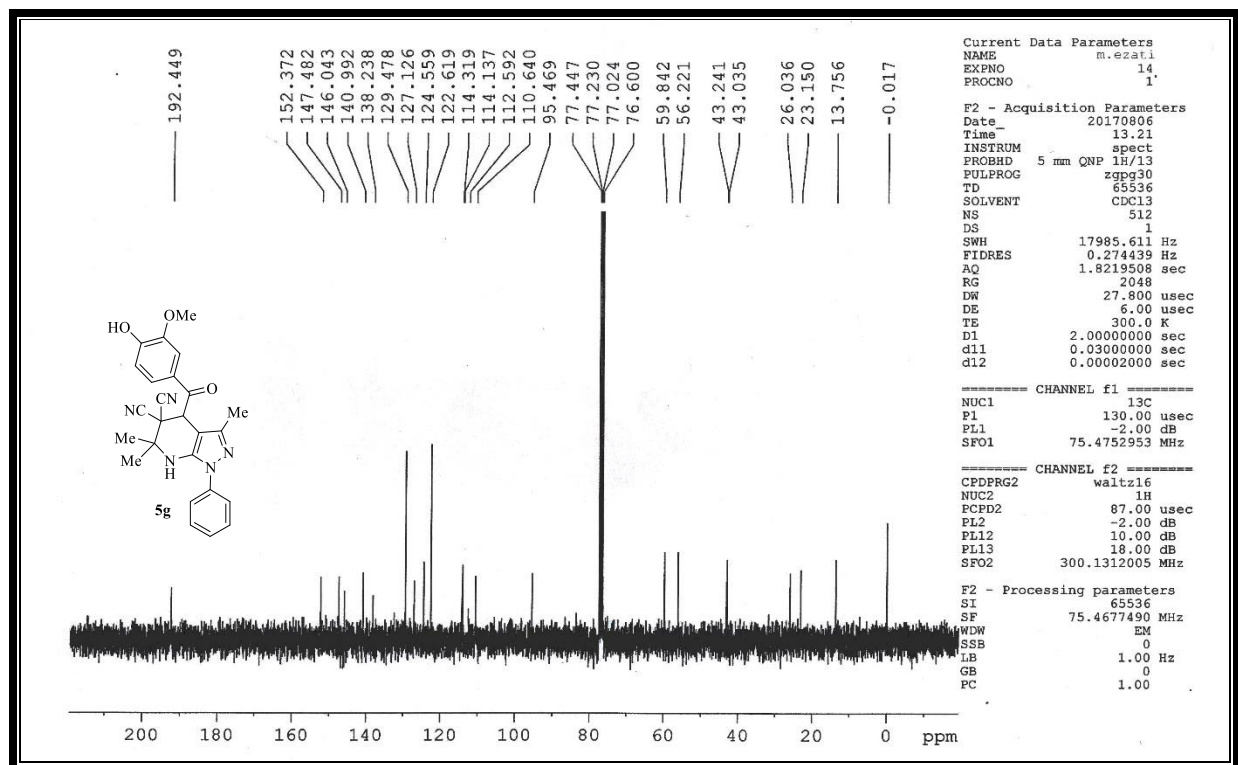


Fig. S27. IR spectrum (KBr) of compound 5g.

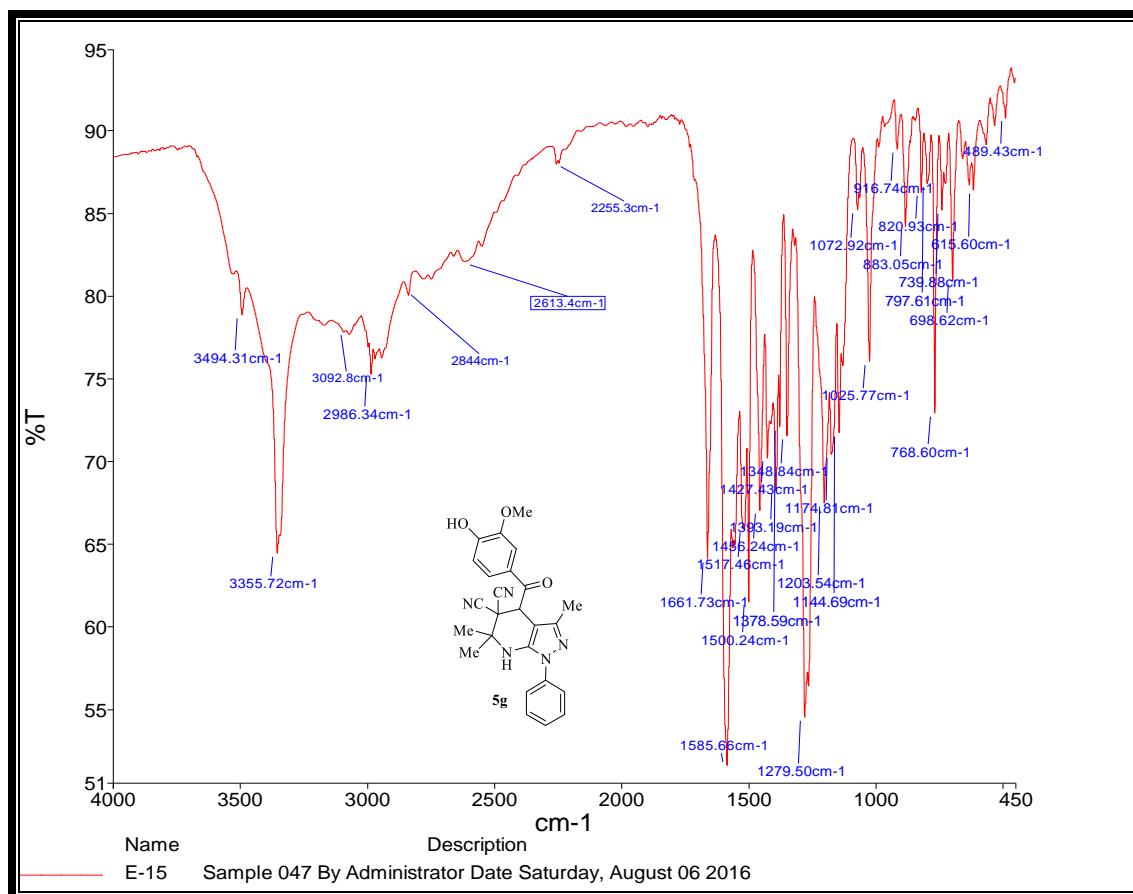
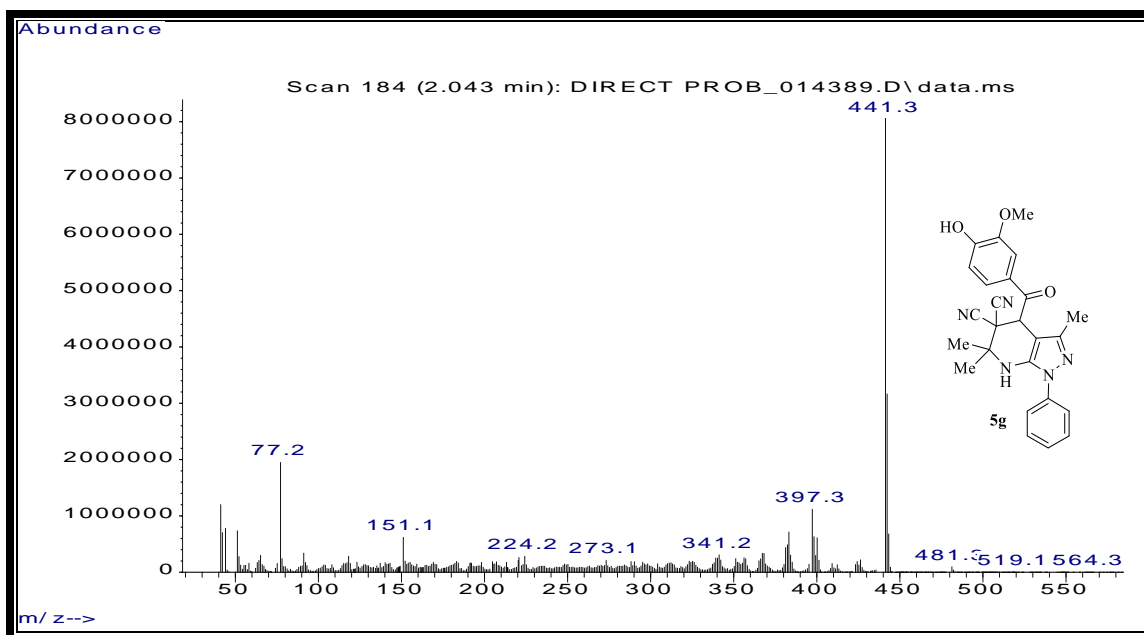


Fig. S28. Mass spectrum of compound 5g.





1-(5-Amino-3-methyl-1-phenyl-1H-pyrazol-4-yl)-2-(4-nitrophenyl)ethane-1,2-dione (6).

Fig. S29. <sup>1</sup>H NMR spectrum (300 MHz, CDCl<sub>3</sub>) of compound 6.

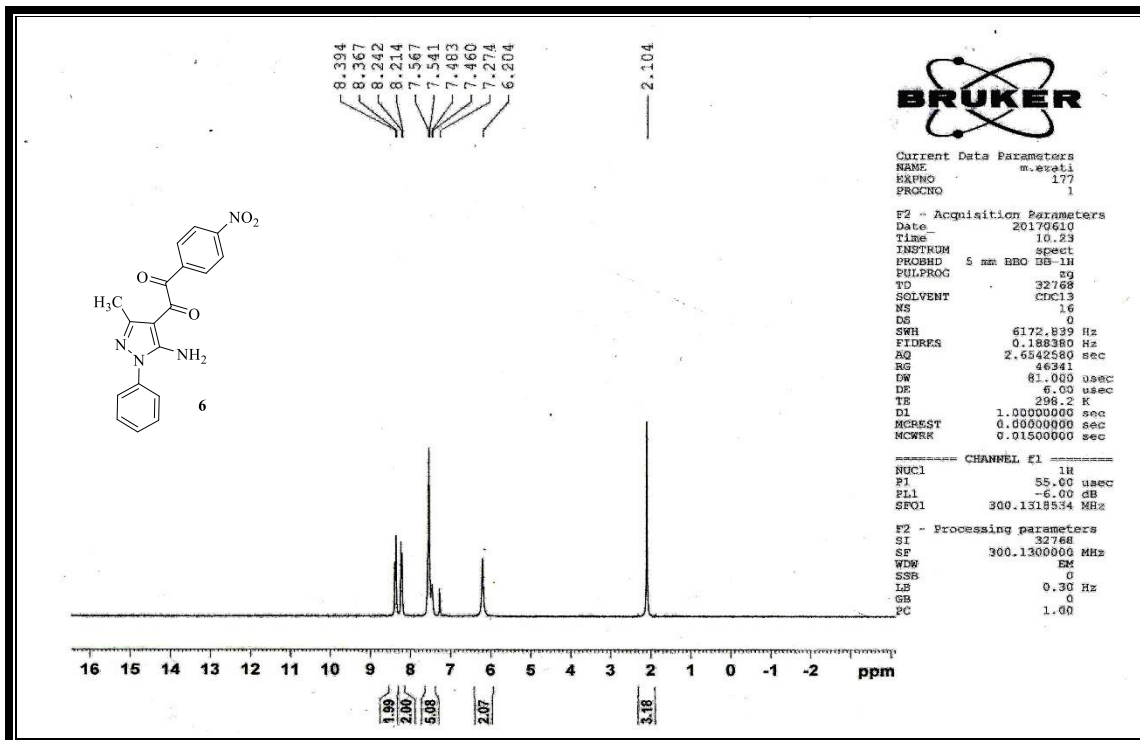


Fig. S30. <sup>13</sup>C NMR spectrum (75.5 MHz, DMSO-*d*<sub>6</sub>) of compound 6.

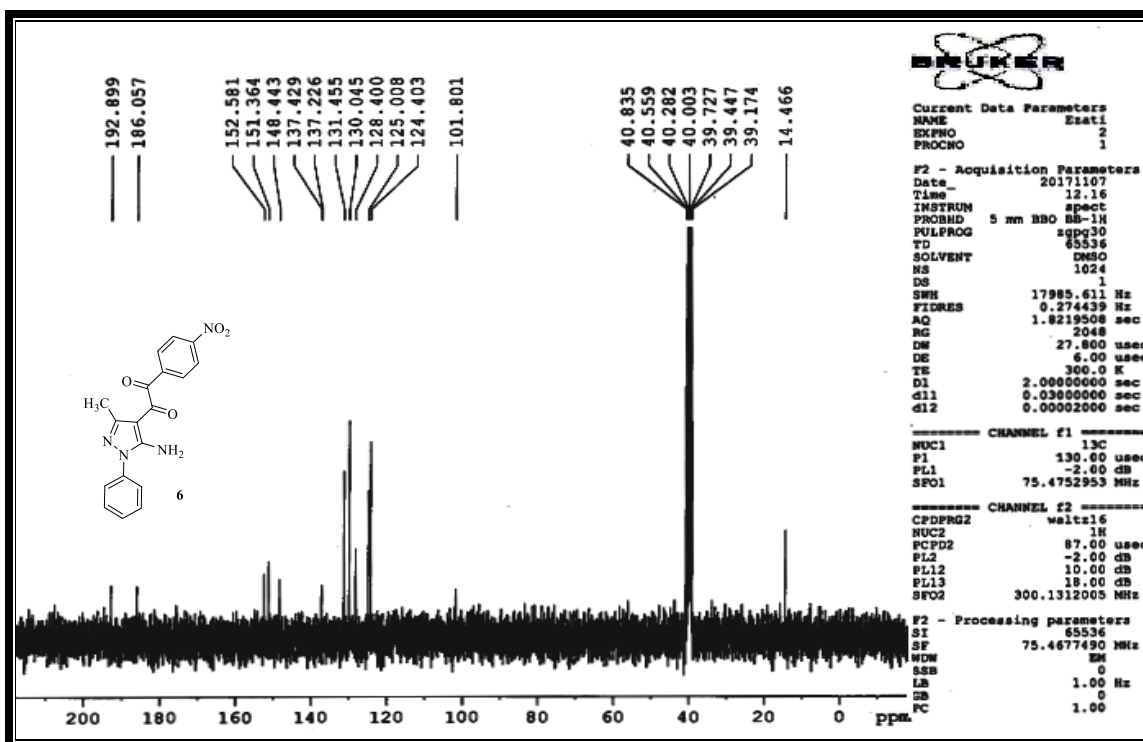


Fig. S31. IR spectrum (KBr) of compound 6.

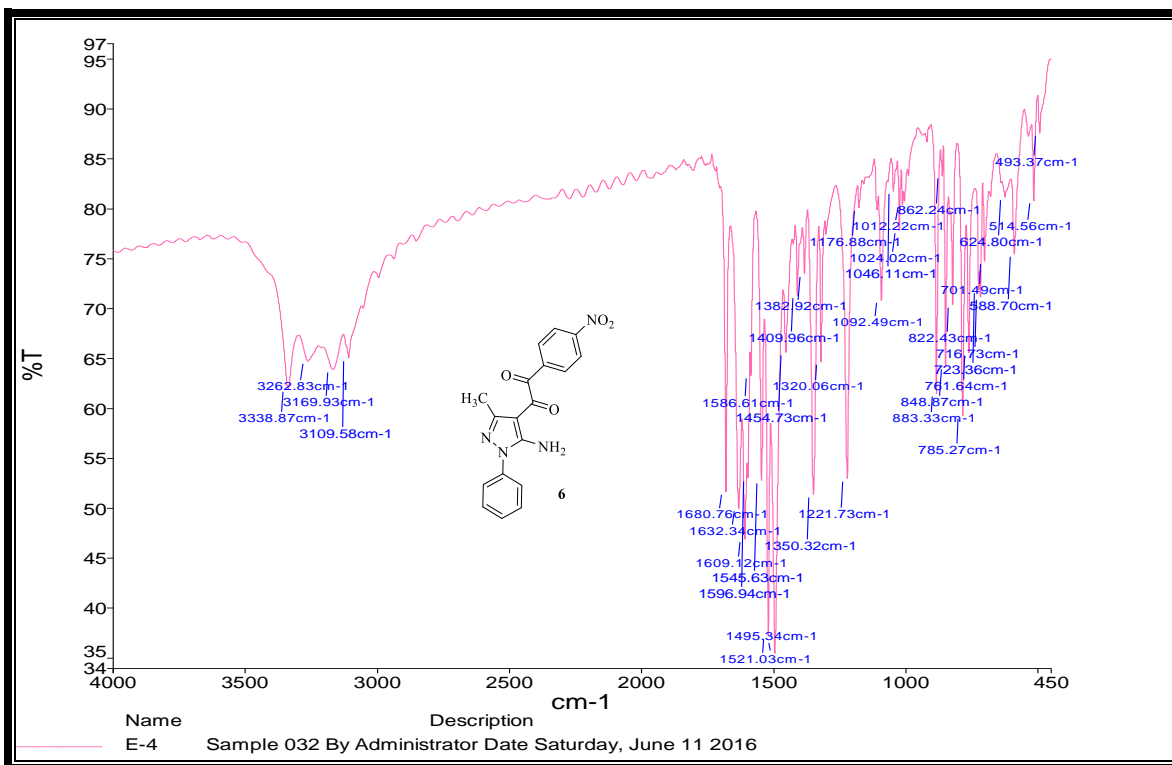


Fig. S32. Mass spectrum of compound 6.

