Electronic Supplementary Material (ESI) for Green Chemistry

L-Proline-catalysed sequential four-component "on water" protocol for the green synthesis of polyheterocyclic *ortho*quinones

Stephen Michael Rajesh,[a] Balasubramanian Devi Bala,[a] Subbu Perumal,[a,*] and J. Carlos Menéndez[b,*]

[a] Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625021, India. Tel./fax: +91-452-2459845; Email: subbu.perum@gmail.com

[b] Departamento de Química Orgánica y Farmacéutica, Facultad de Farmacia, Universidad Complutense, 28040 Madrid, Spain. Email: josecm@farm.ucm.es

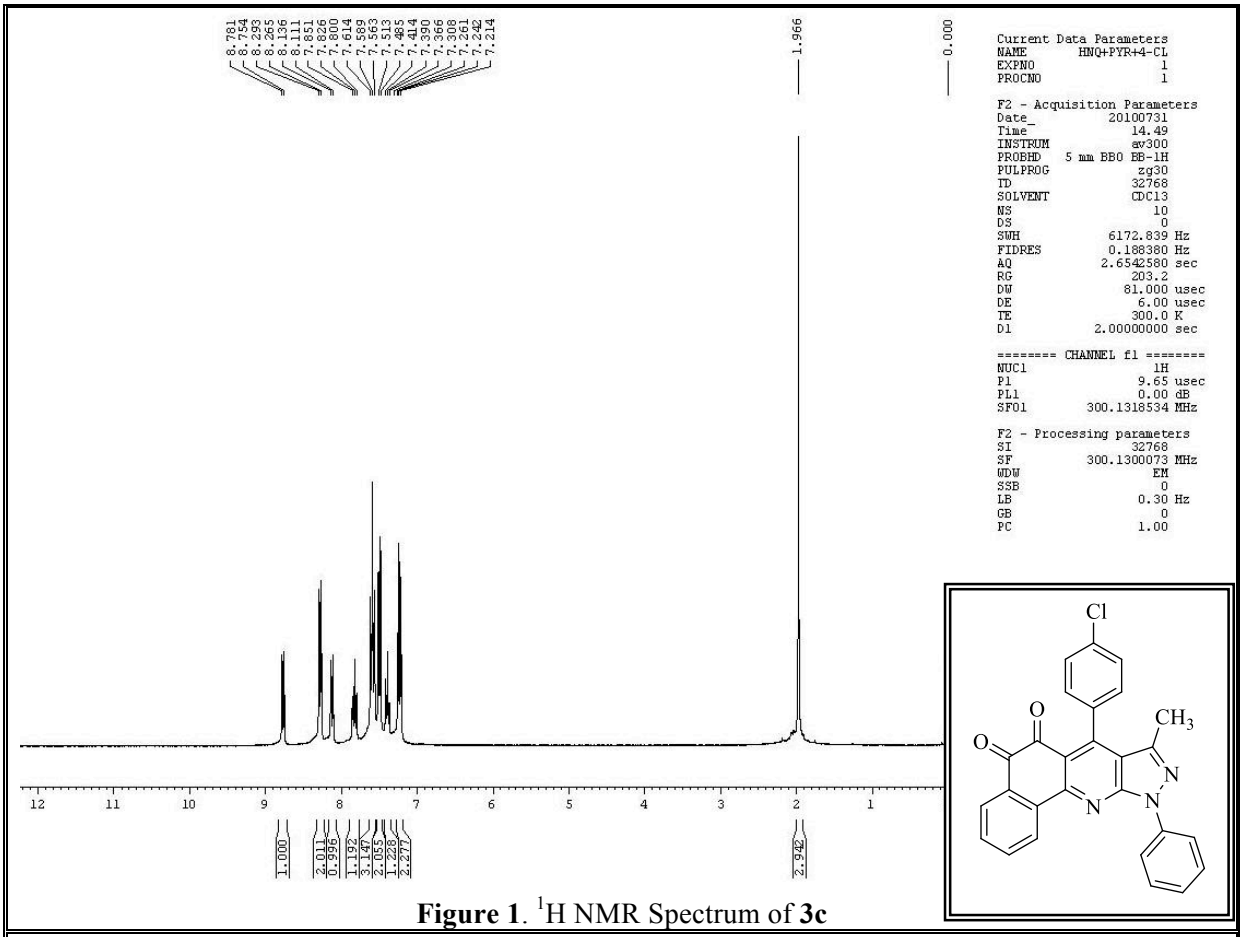

Figure 1. ^{1}H NMR Spectrum of **3c**

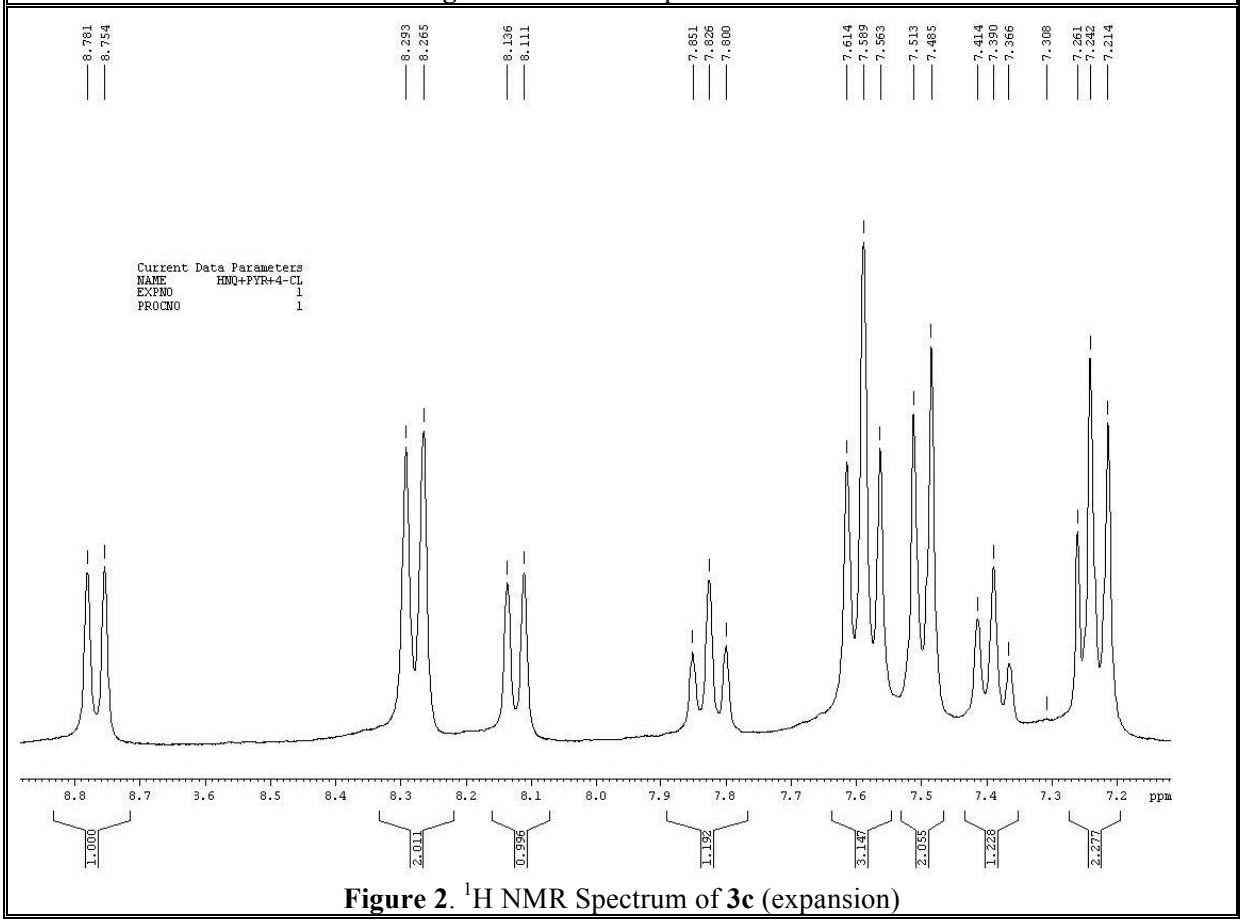

Figure 2. ^{1}H NMR Spectrum of **3c** (expansion)

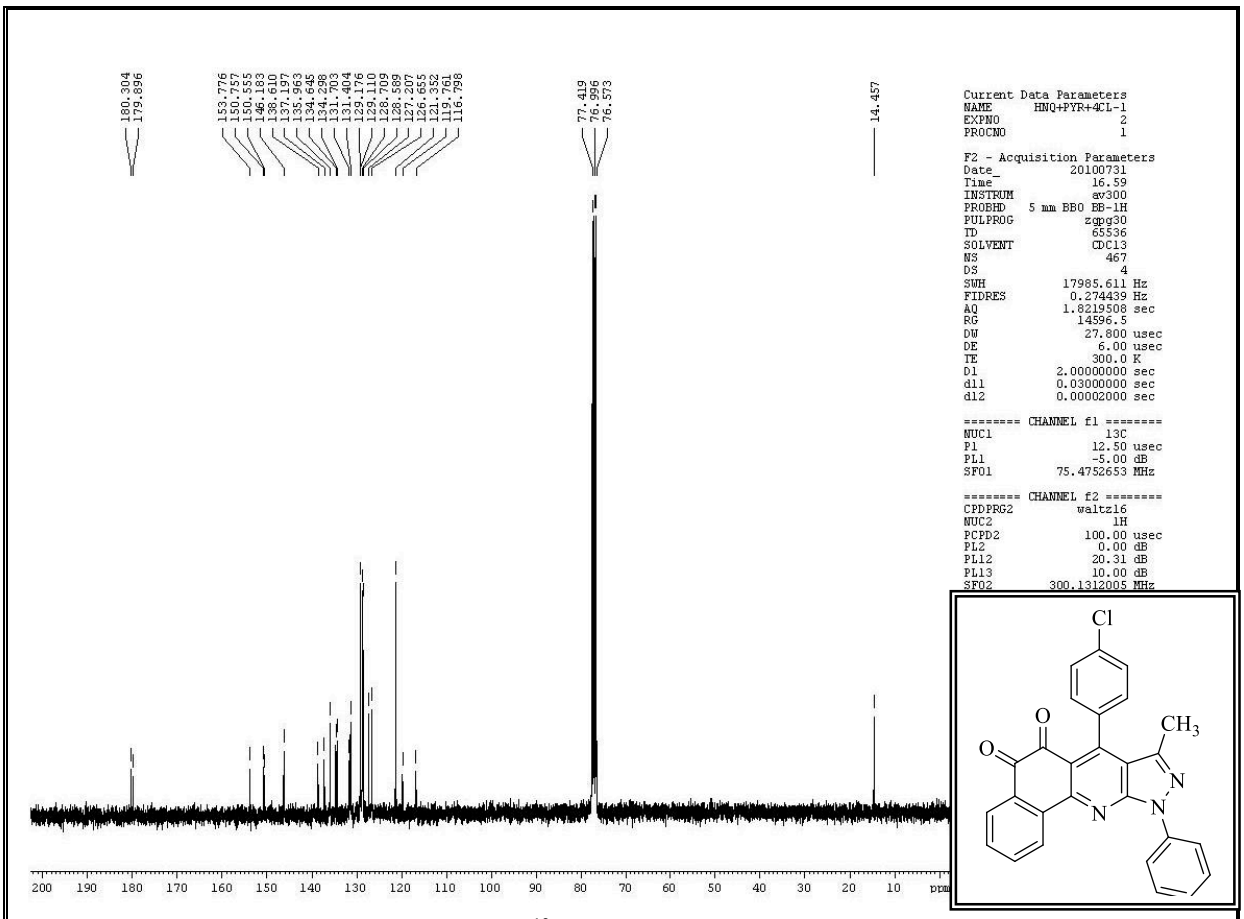

Figure 3. ^{13}C NMR Spectrum of **3c**

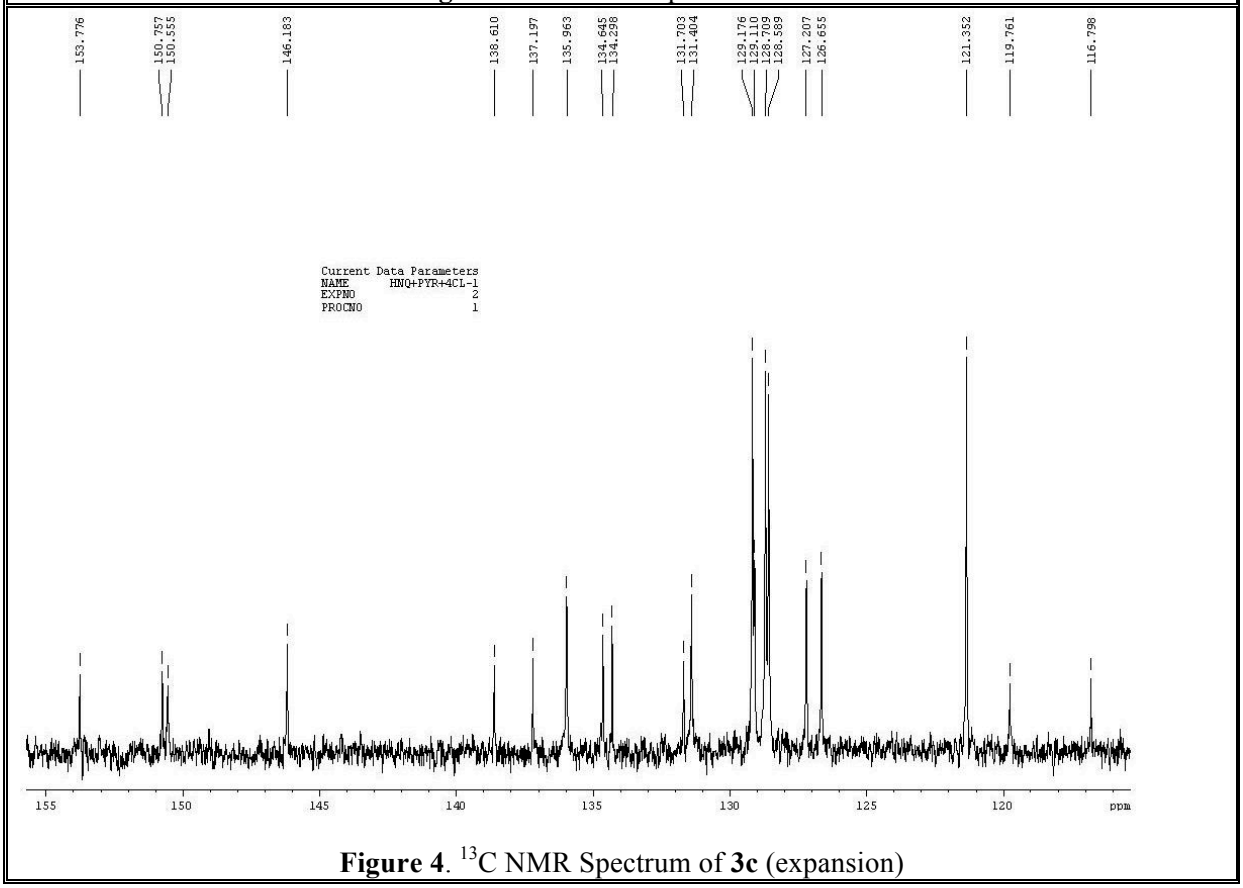

Figure 4. ^{13}C NMR Spectrum of **3c** (expansion)

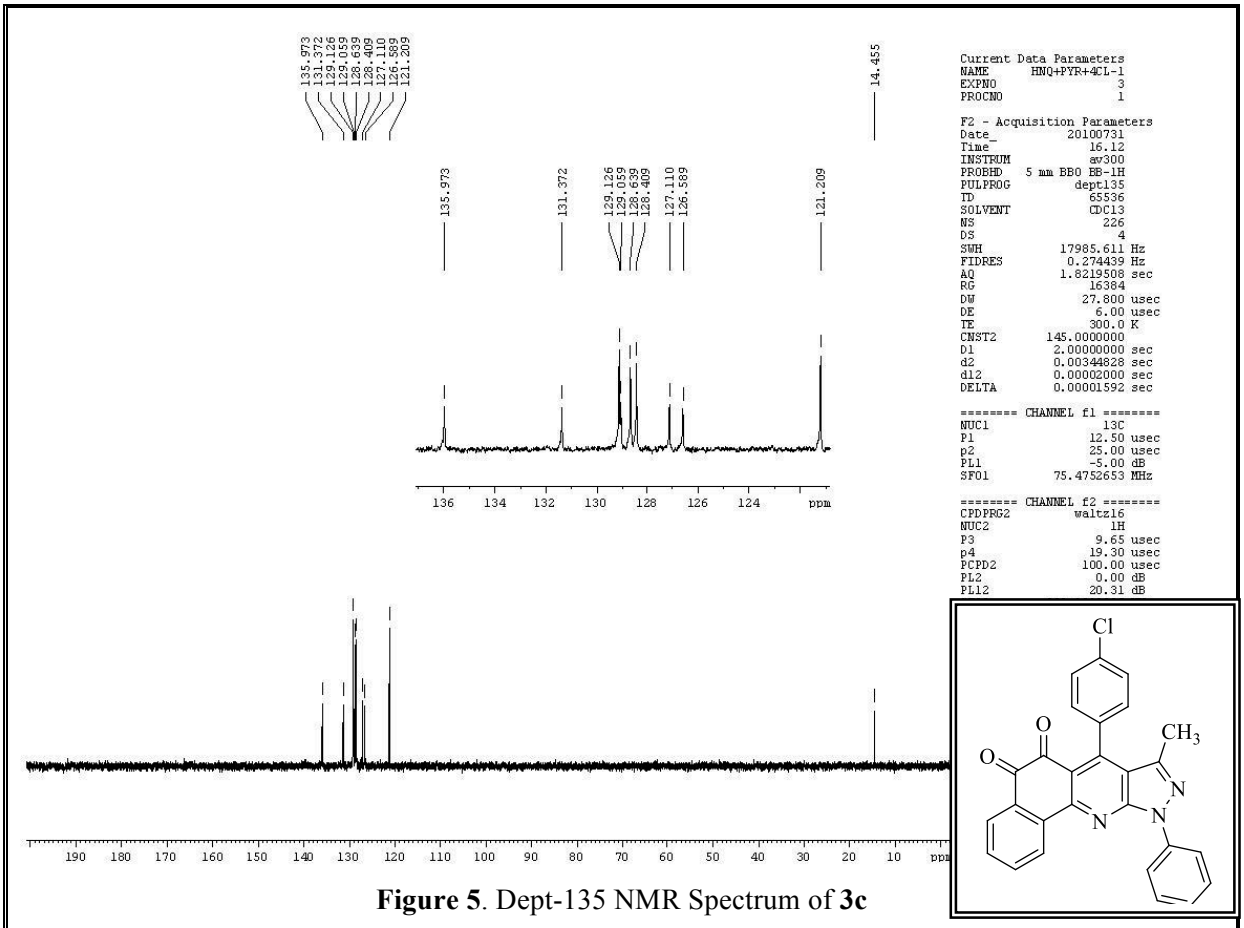

Figure 5. Dept-135 NMR Spectrum of **3c**

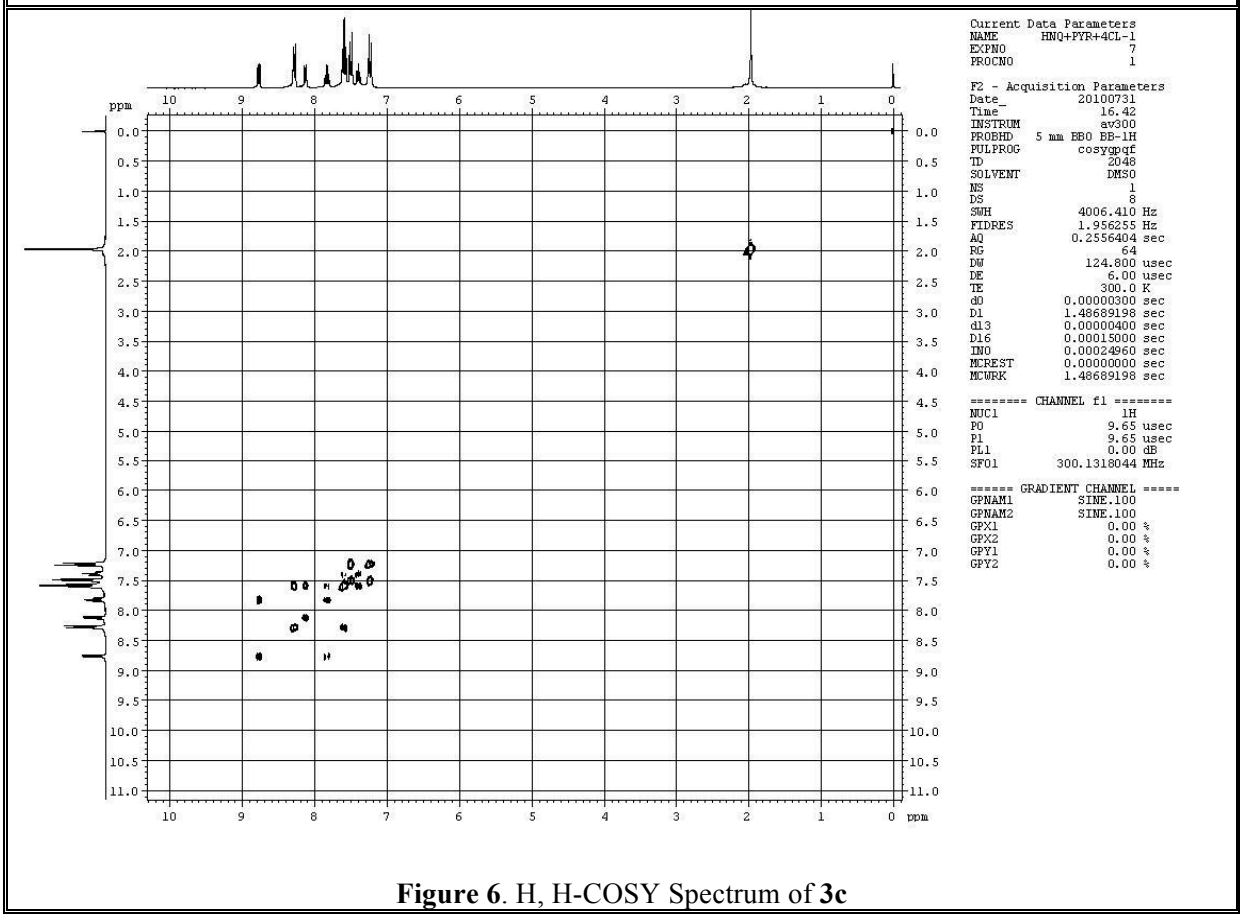

Figure 6. H, H-COSY Spectrum of **3c**

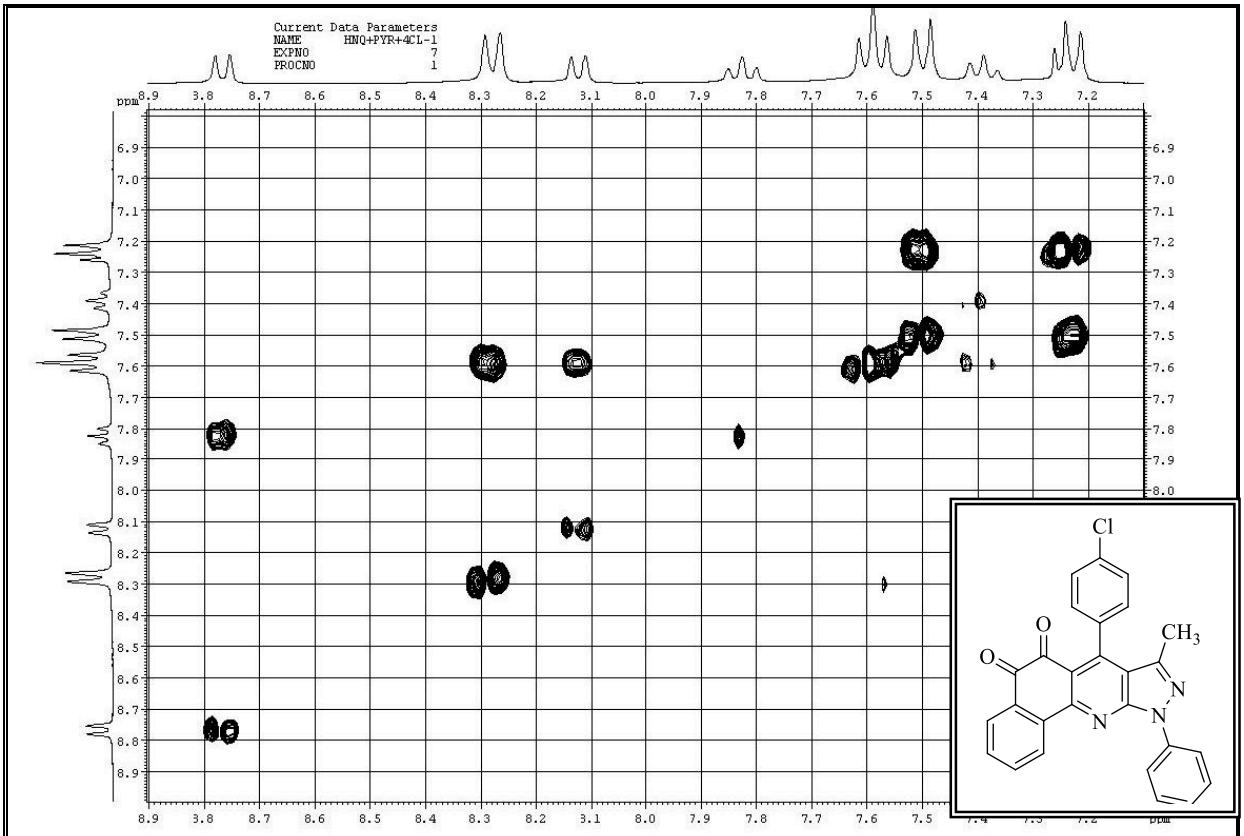

Figure 7. H, H-COSY Spectrum of **3c** (expansion)

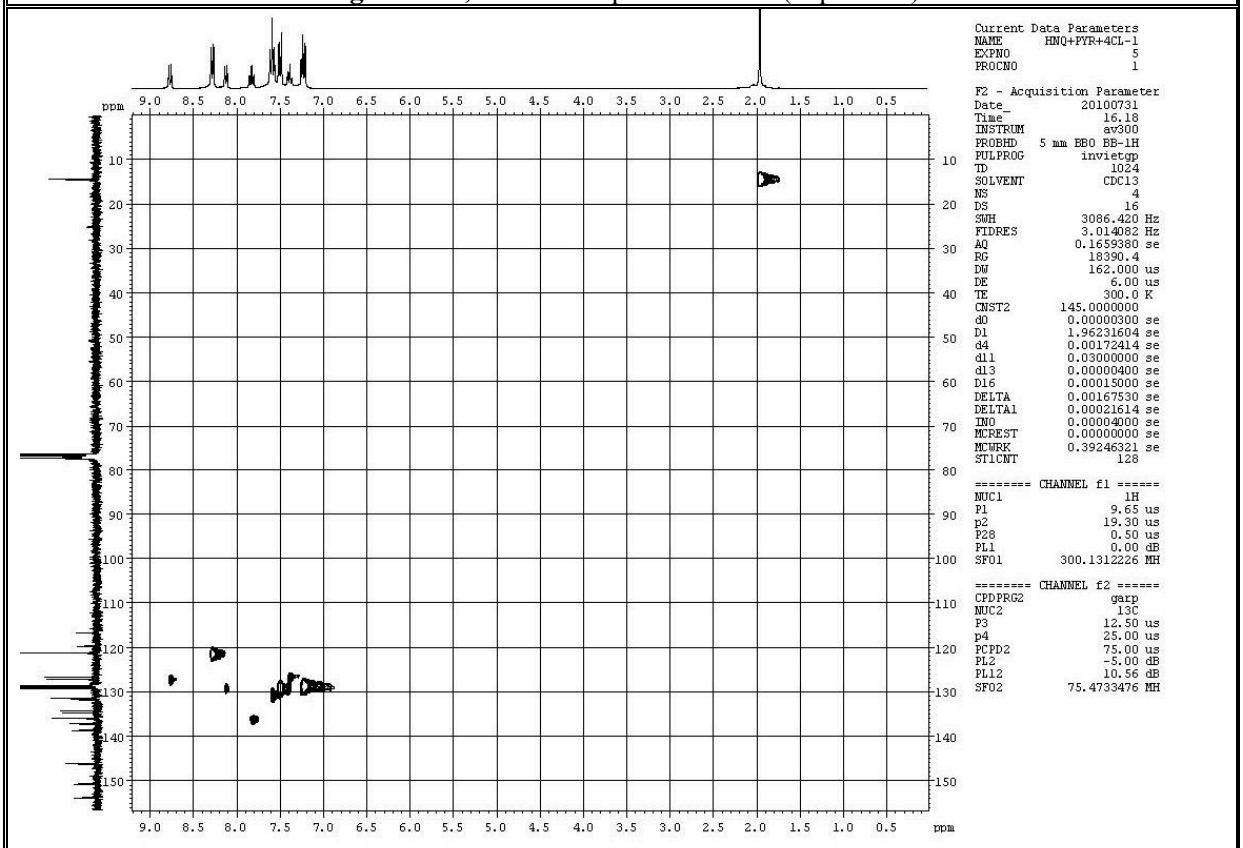

Figure 8. C, H-COSY Spectrum of **3c**

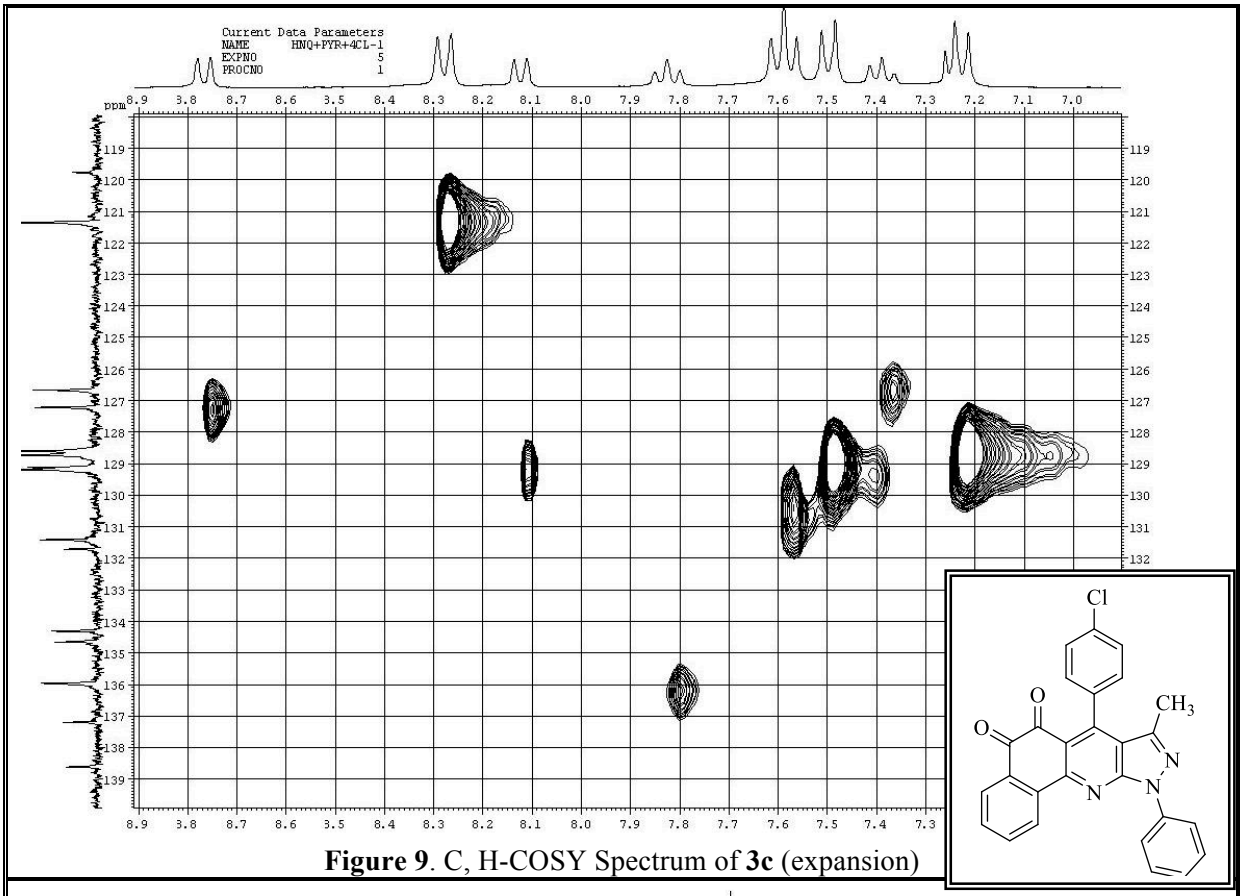

Figure 9. C, H-COSY Spectrum of **3c** (expansion)

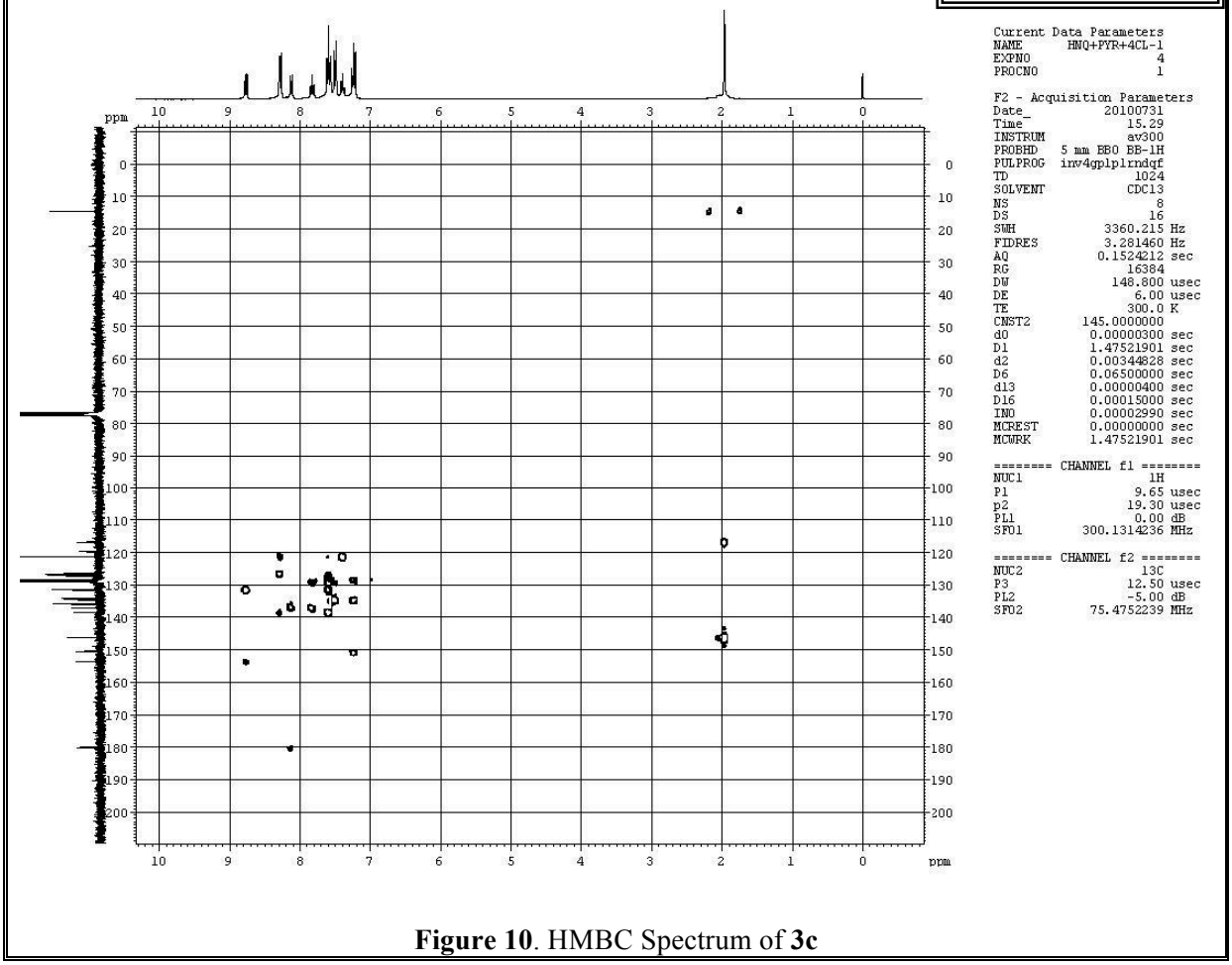

Figure 10. HMBC Spectrum of **3c**

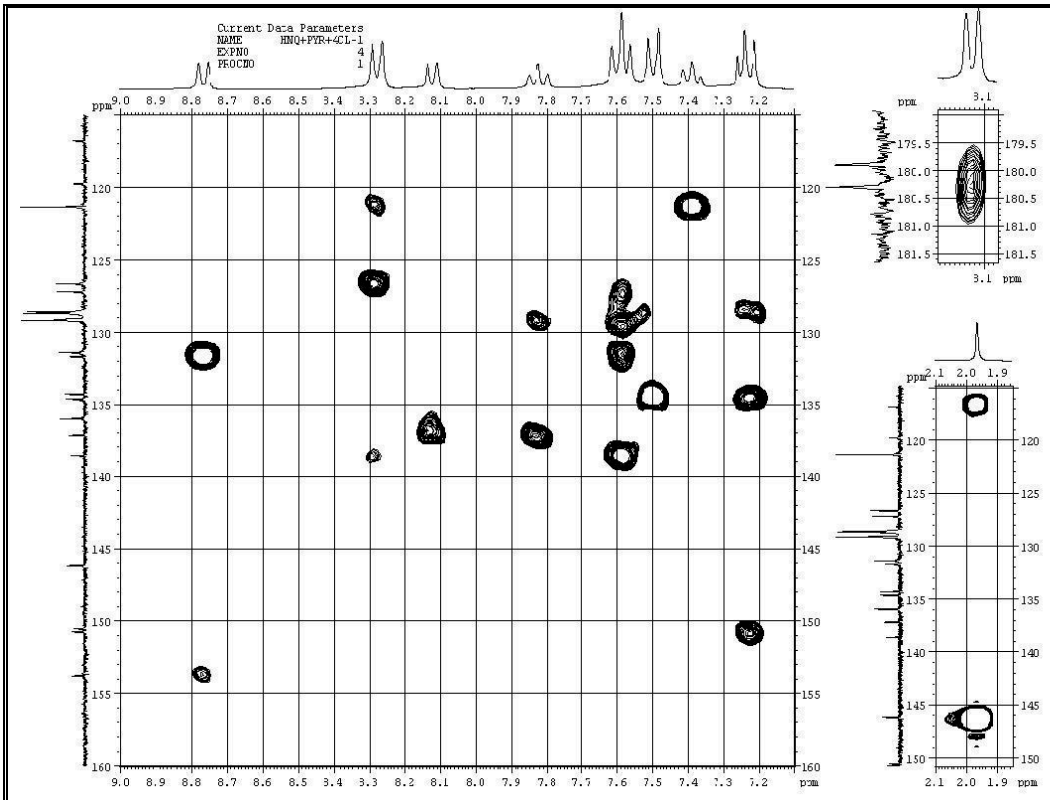

Figure 11. HMBC Spectrum of **3c** (expansion)

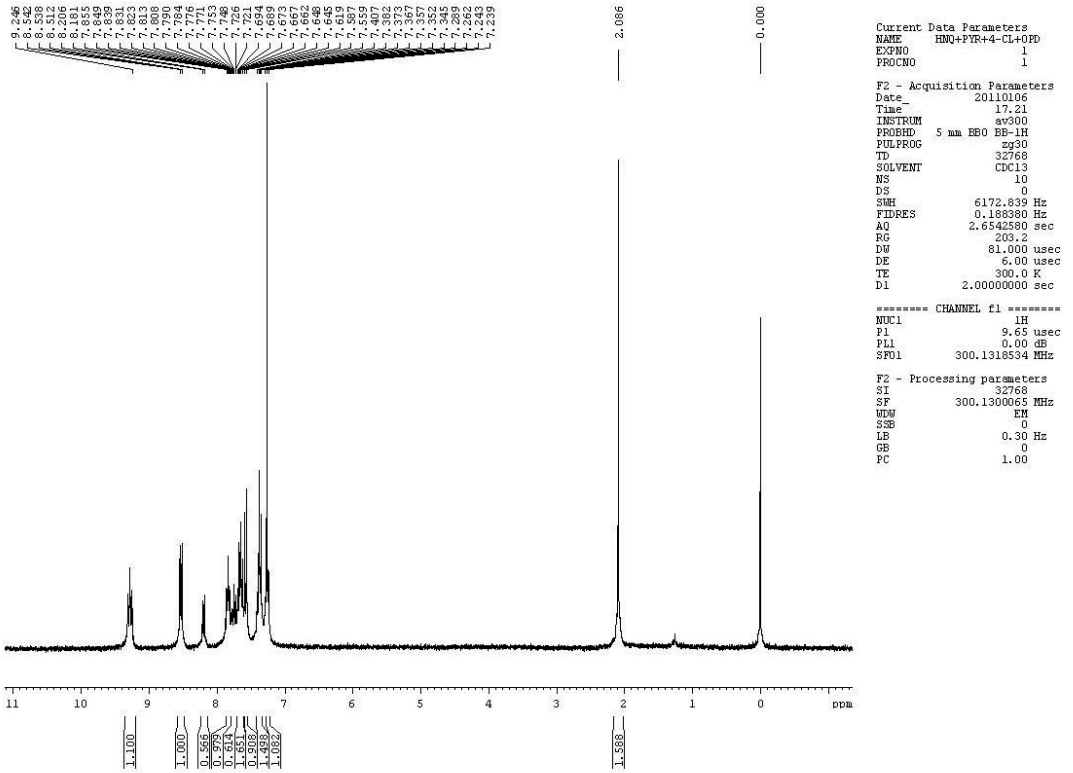

Figure 12. ^{1}H NMR Spectrum of **9**

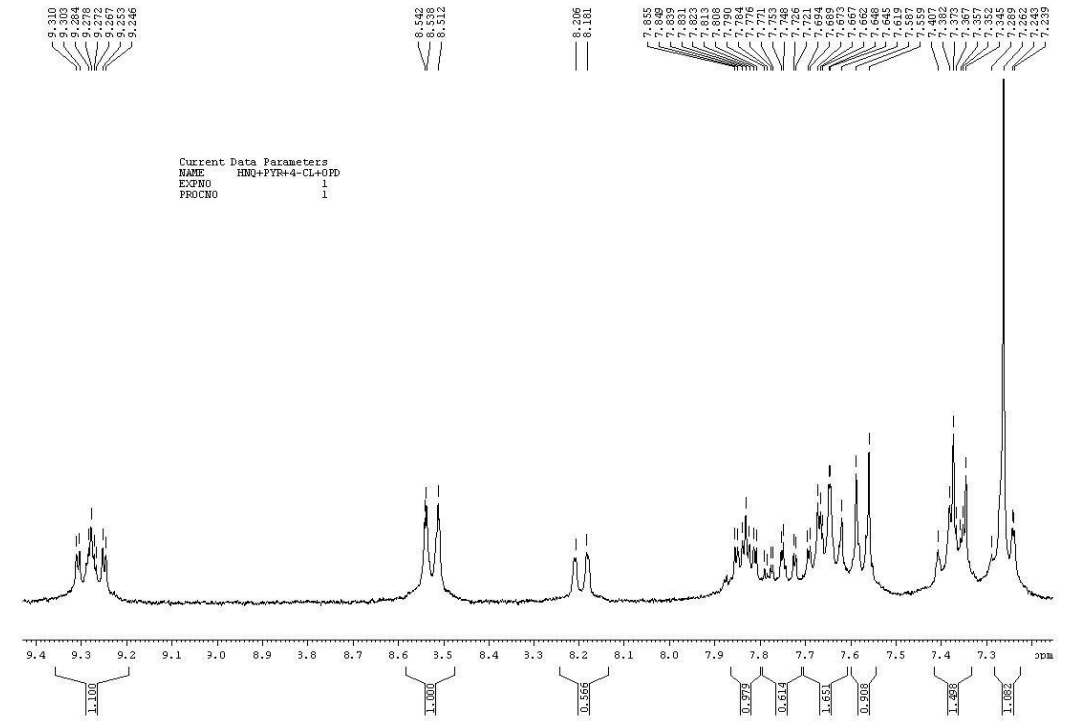

Figure 13. ^{1}H NMR Spectrum of **9** (expansion)

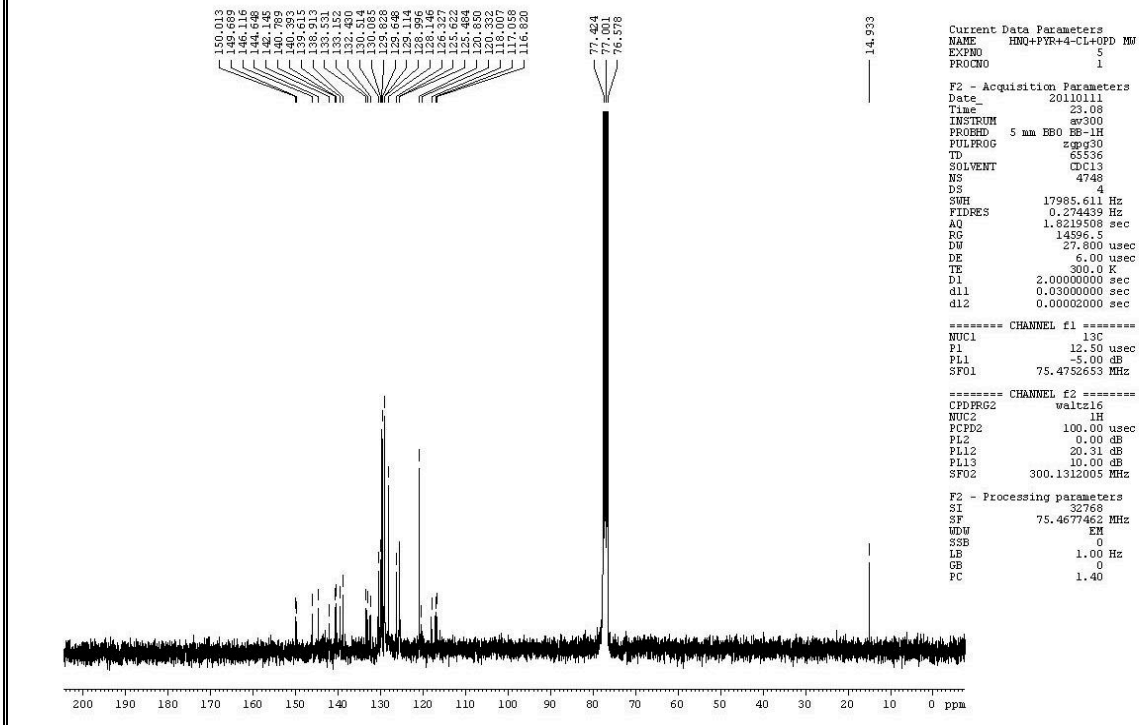

Figure 14. ^{13}C NMR Spectrum of **9**

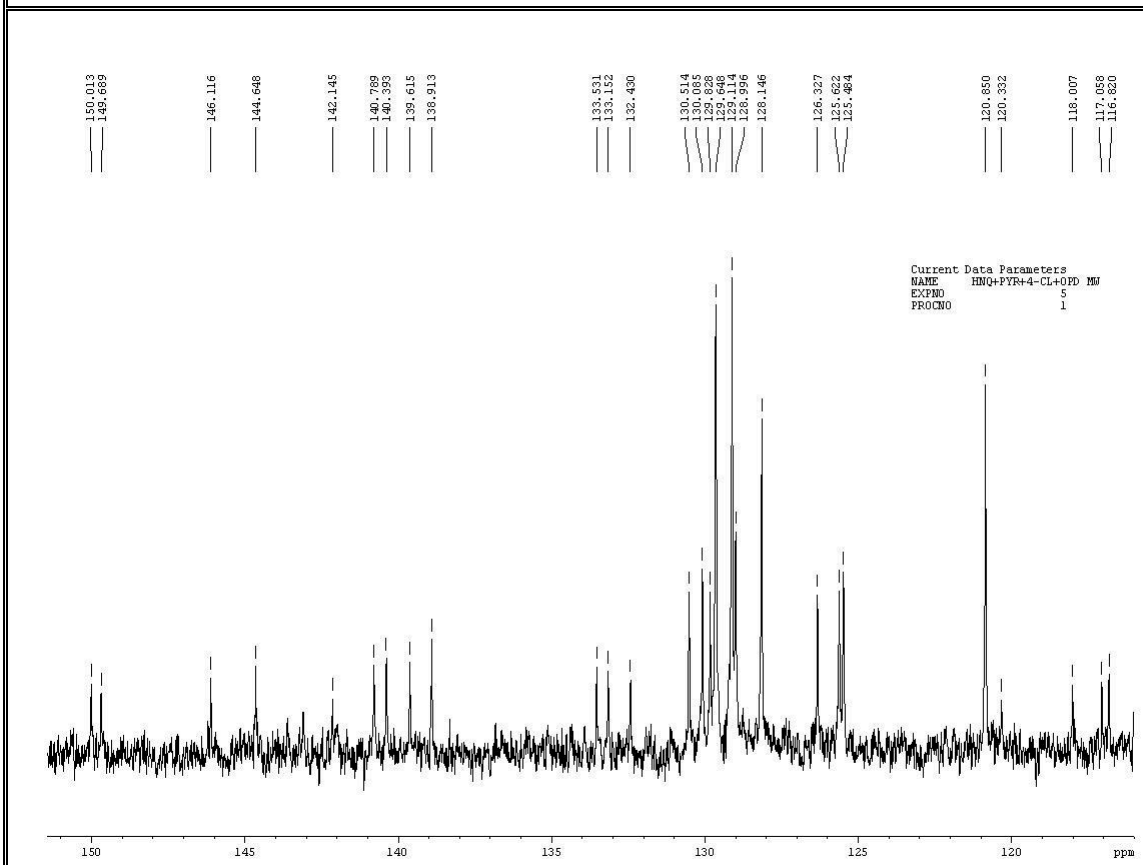

Figure 15. ^{13}C NMR Spectrum of **9** (expansion)

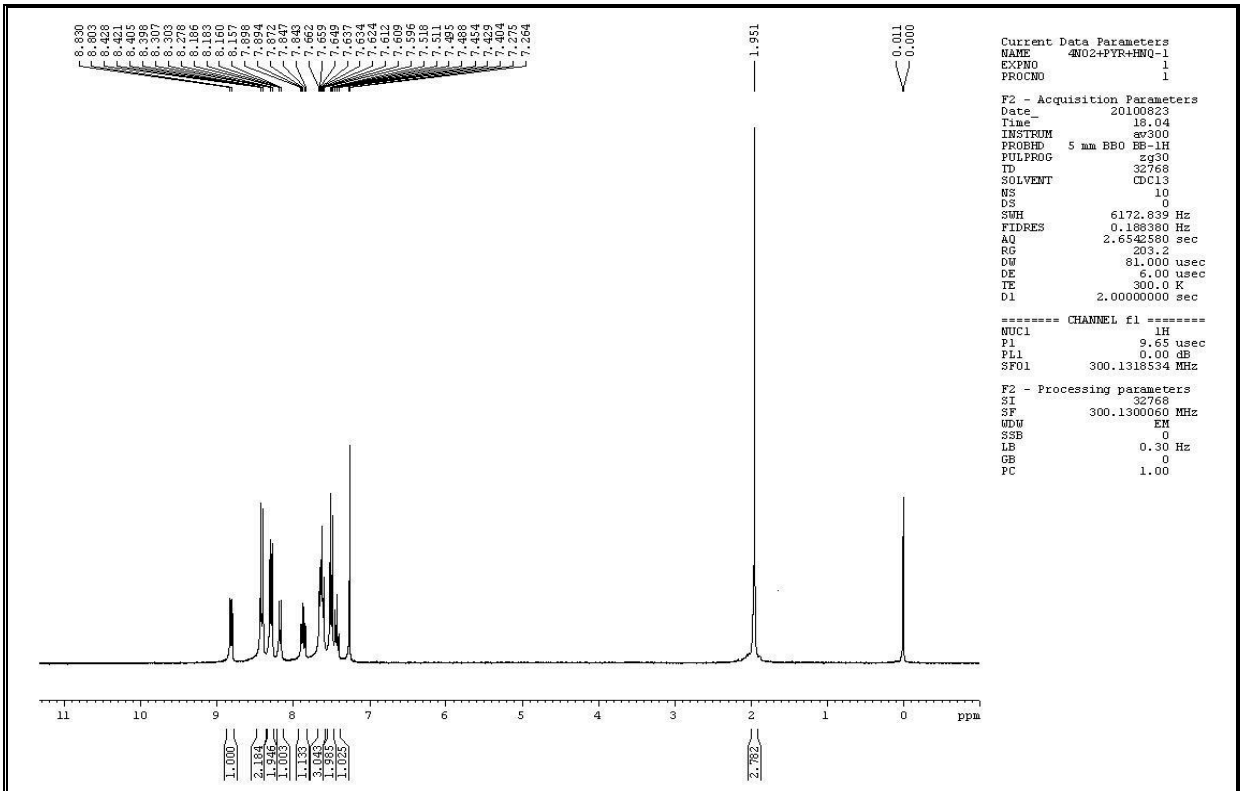

Figure 16. ^{1}H NMR Spectrum of 3**a**

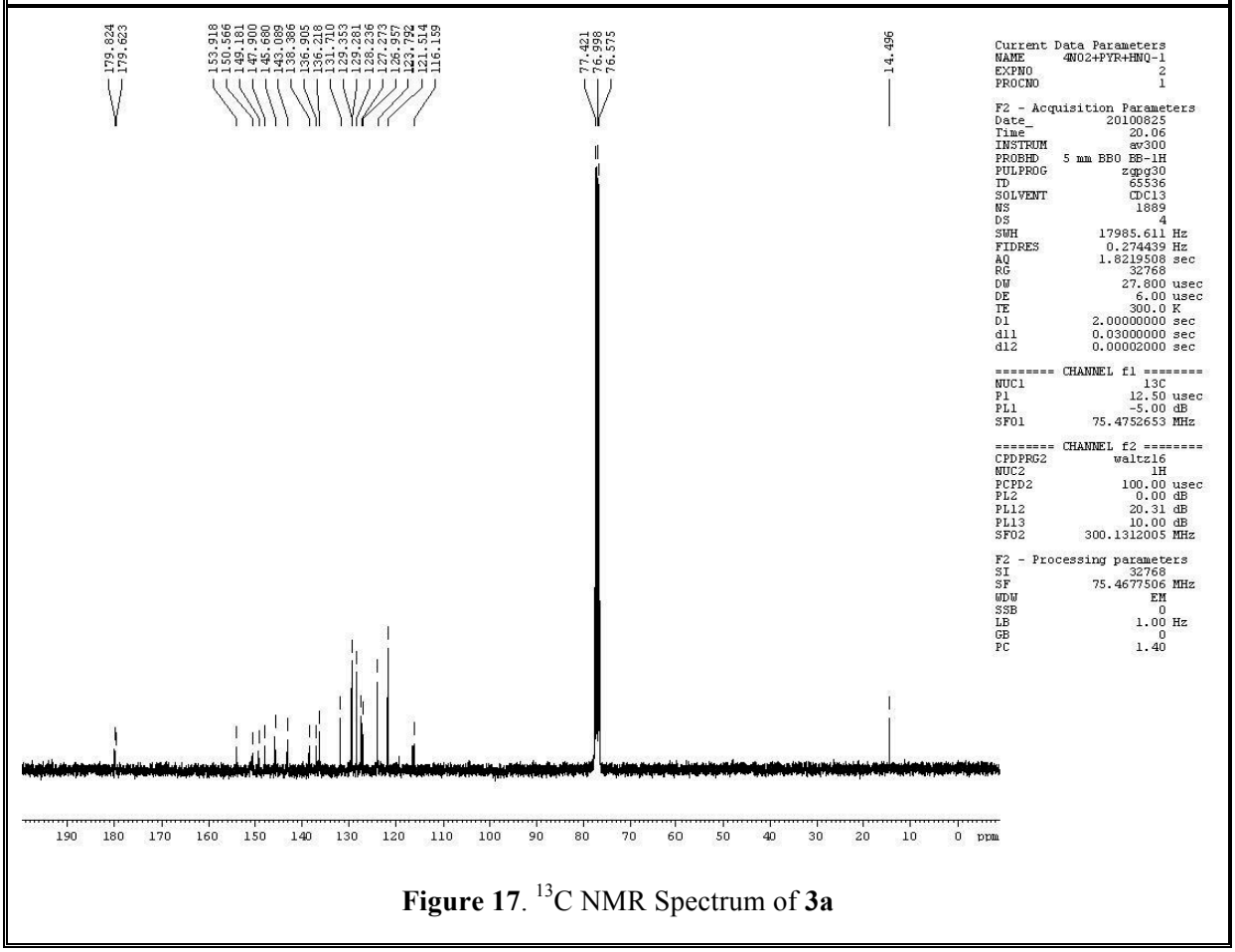

Figure 17. ^{13}C NMR Spectrum of **3a**

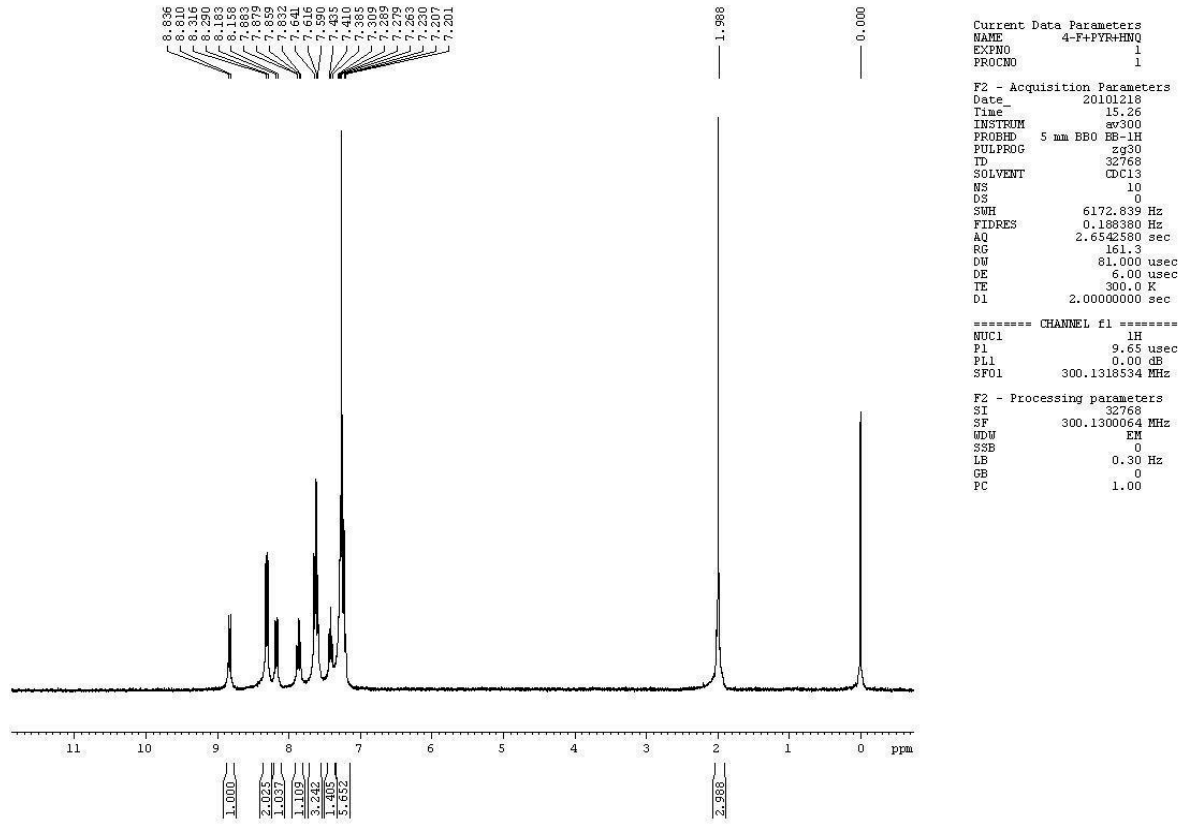

Figure 18. ^{1}H NMR Spectrum of **3b**

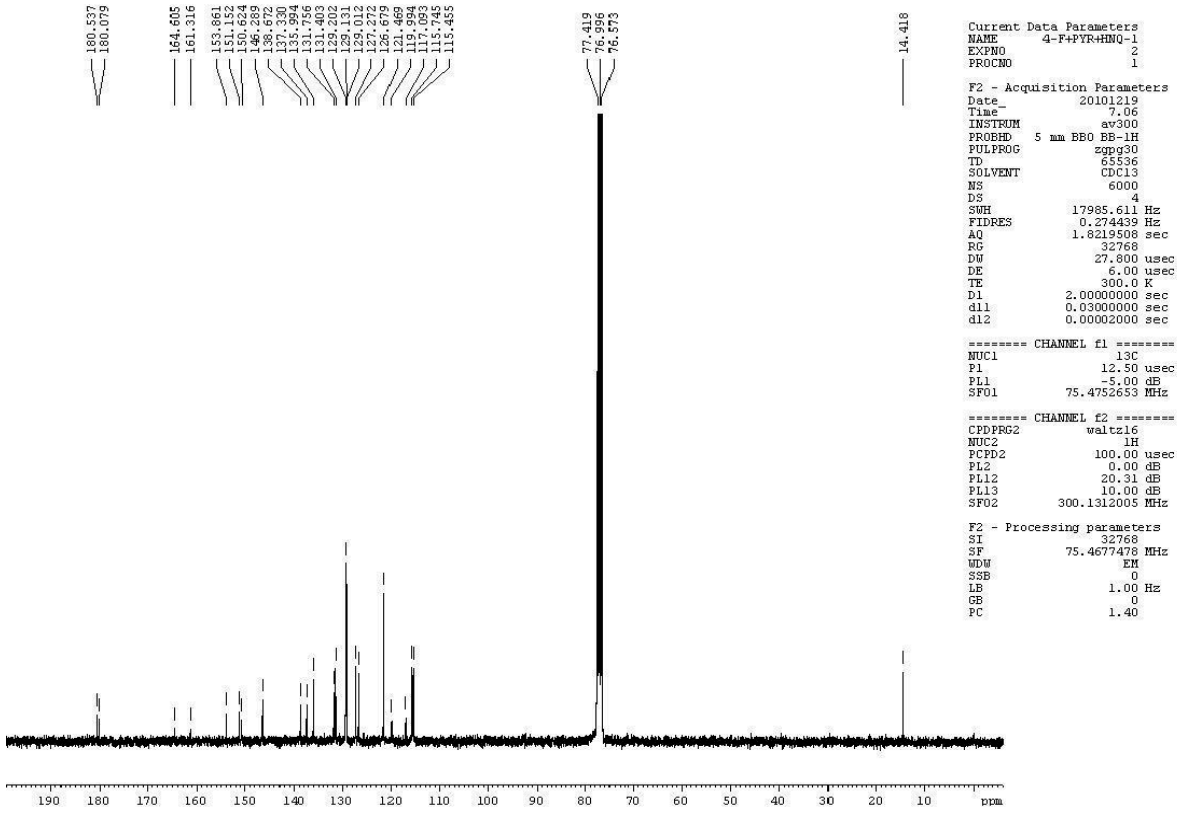

Figure 19. ^{13}C NMR Spectrum of **3b**

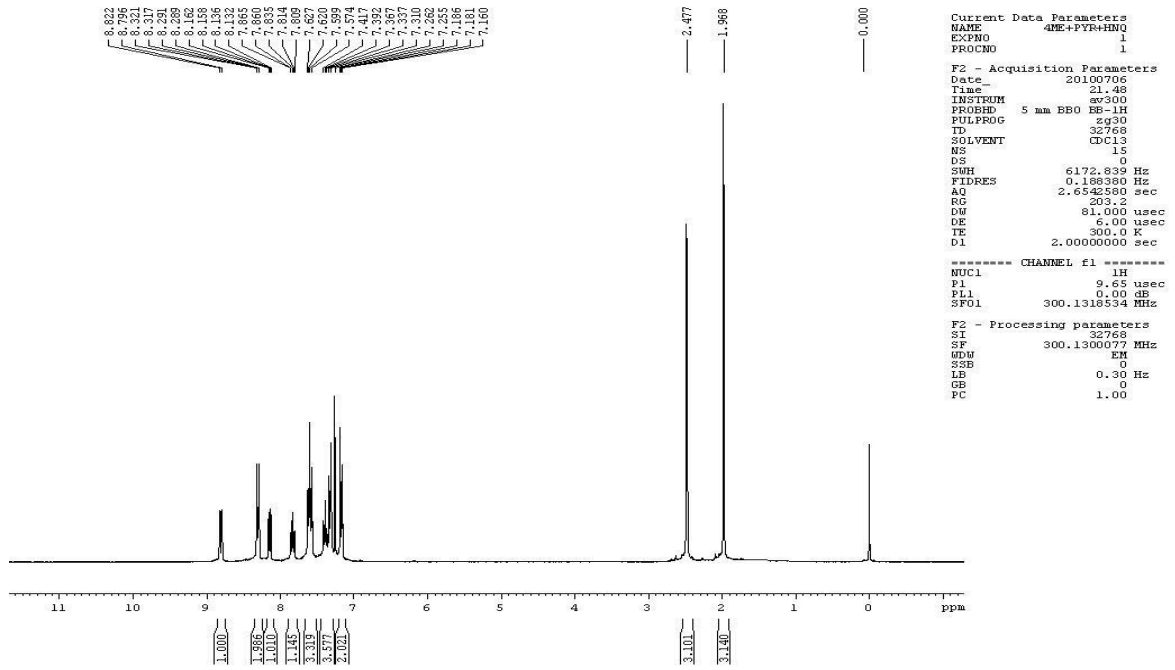

Figure 20. [1]H NMR Spectrum of **3d**

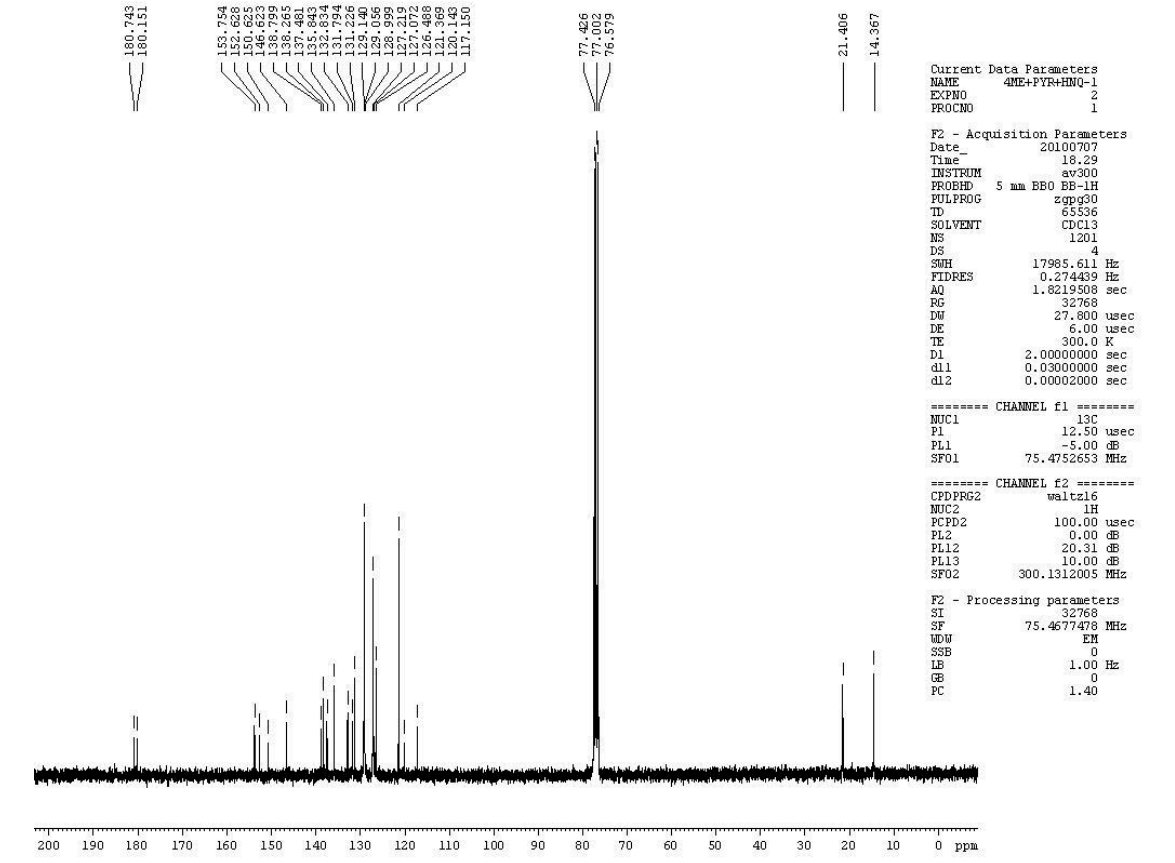

Figure 21. [13]C NMR Spectrum of **3d**

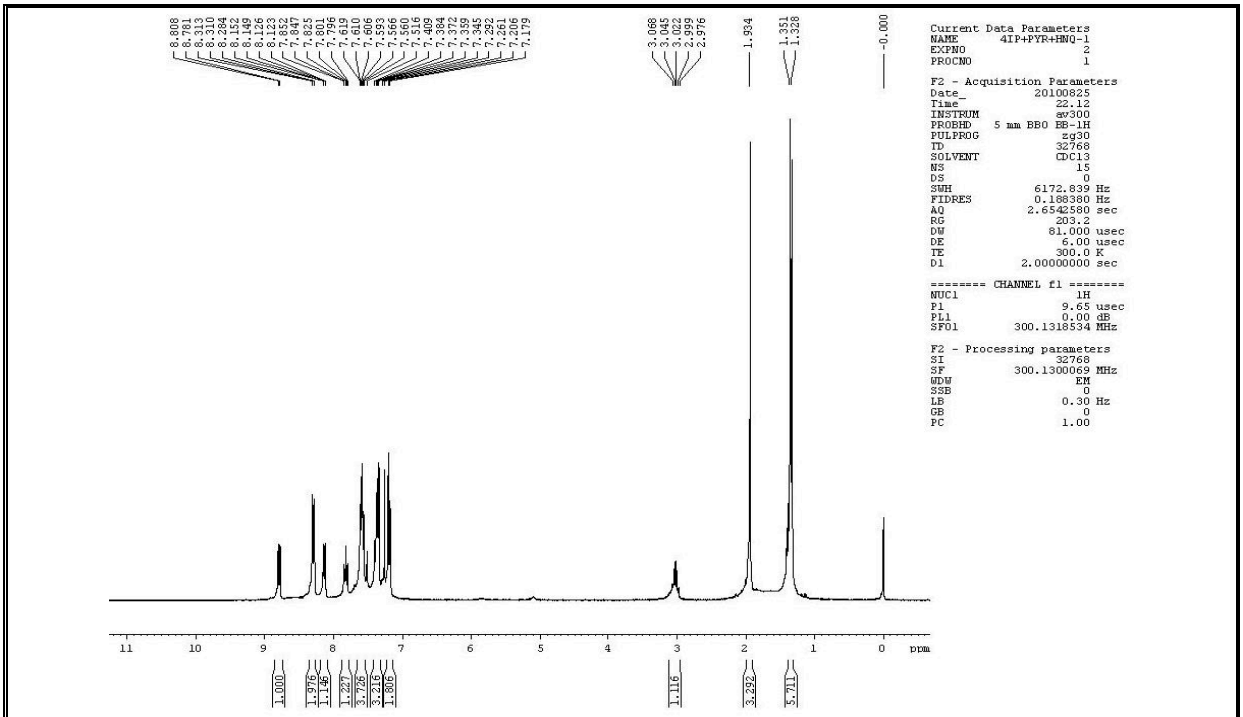

Figure 22. ^{1}H NMR Spectrum of **3e**

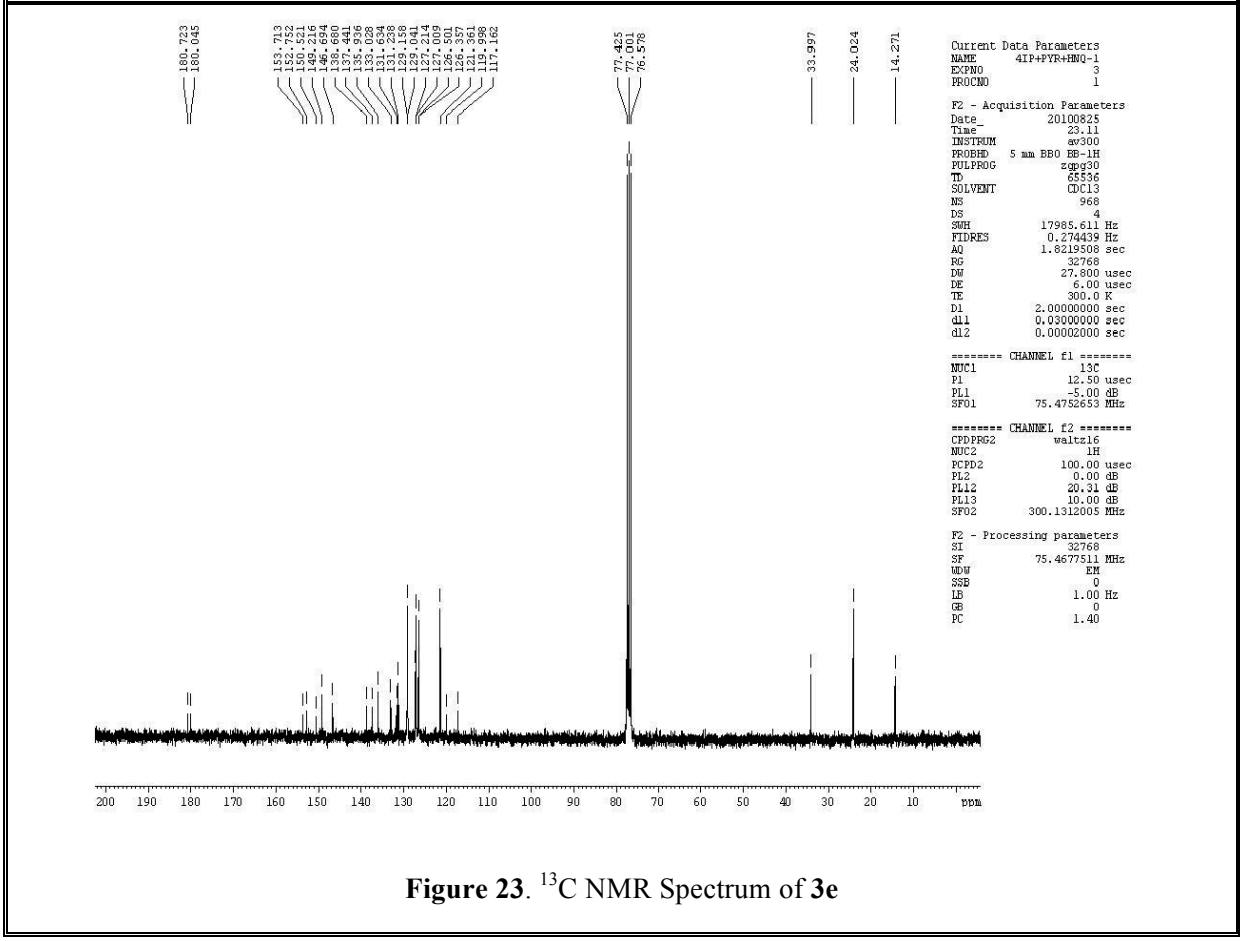

Figure 23. ^{13}C NMR Spectrum of **3e**

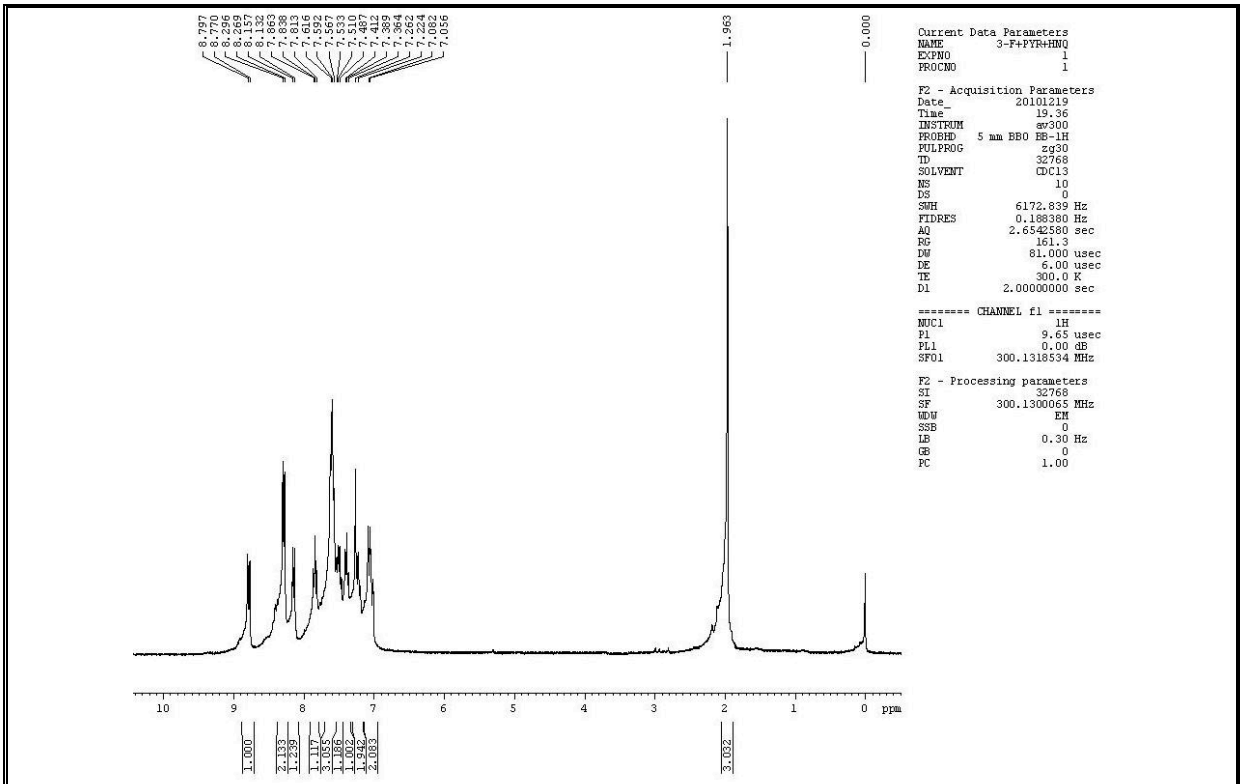

Figure 24. ^{1}H NMR Spectrum of **3f**

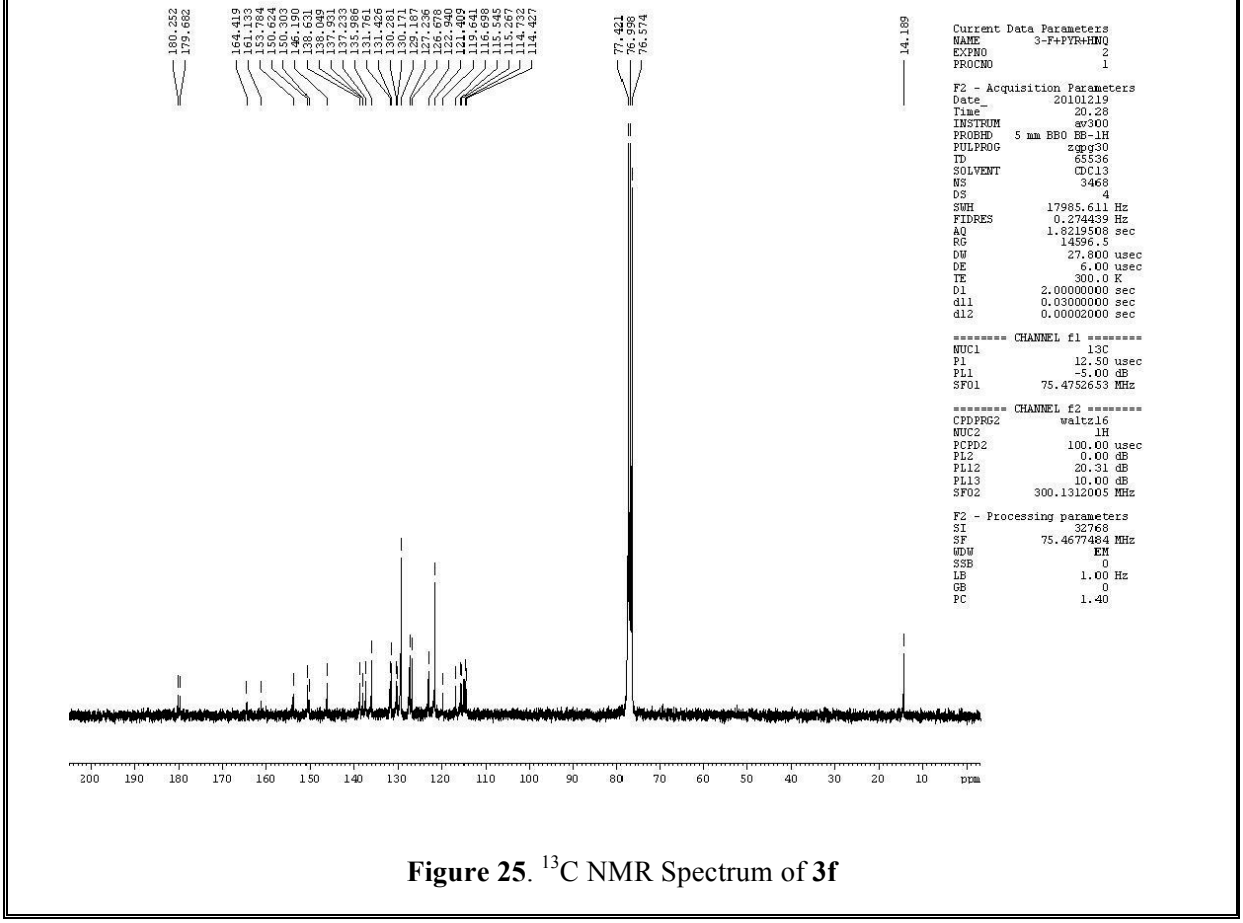

Figure 25. ^{13}C NMR Spectrum of **3f**

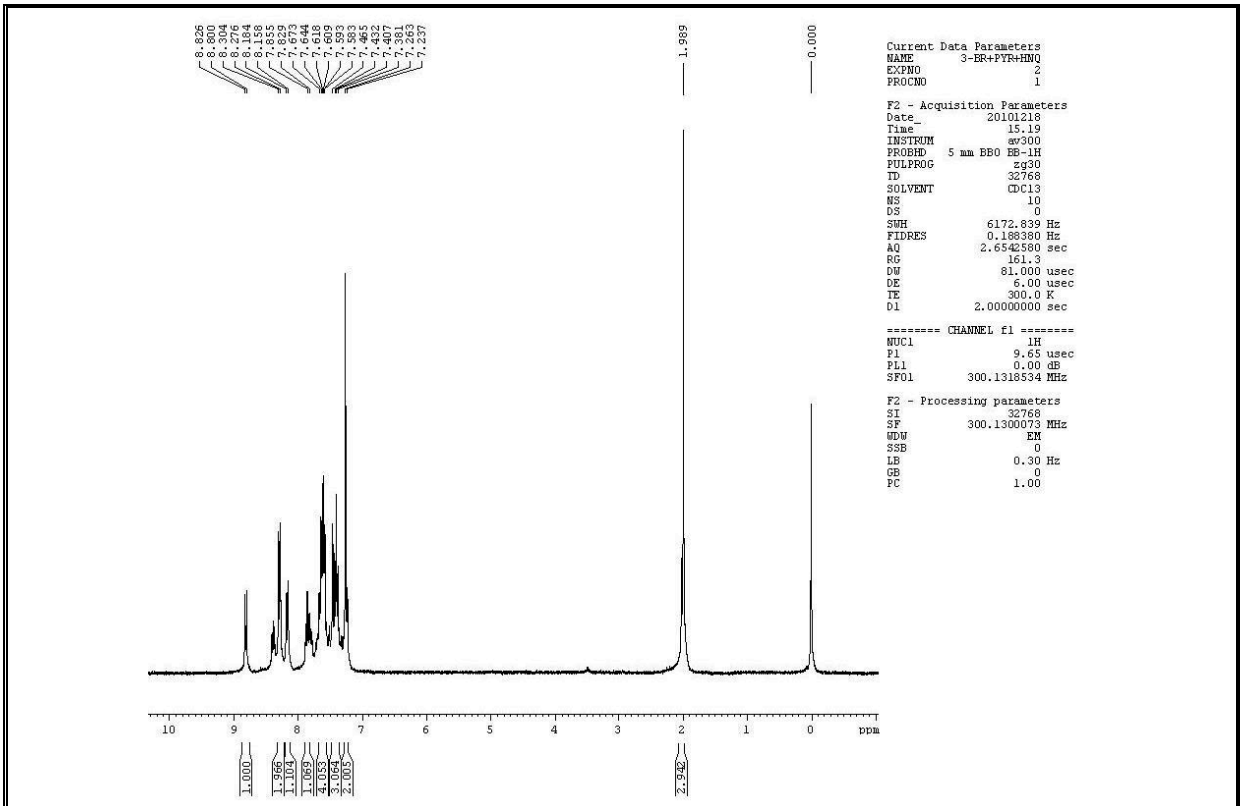

Figure 26. ^{1}H NMR Spectrum of **3g**

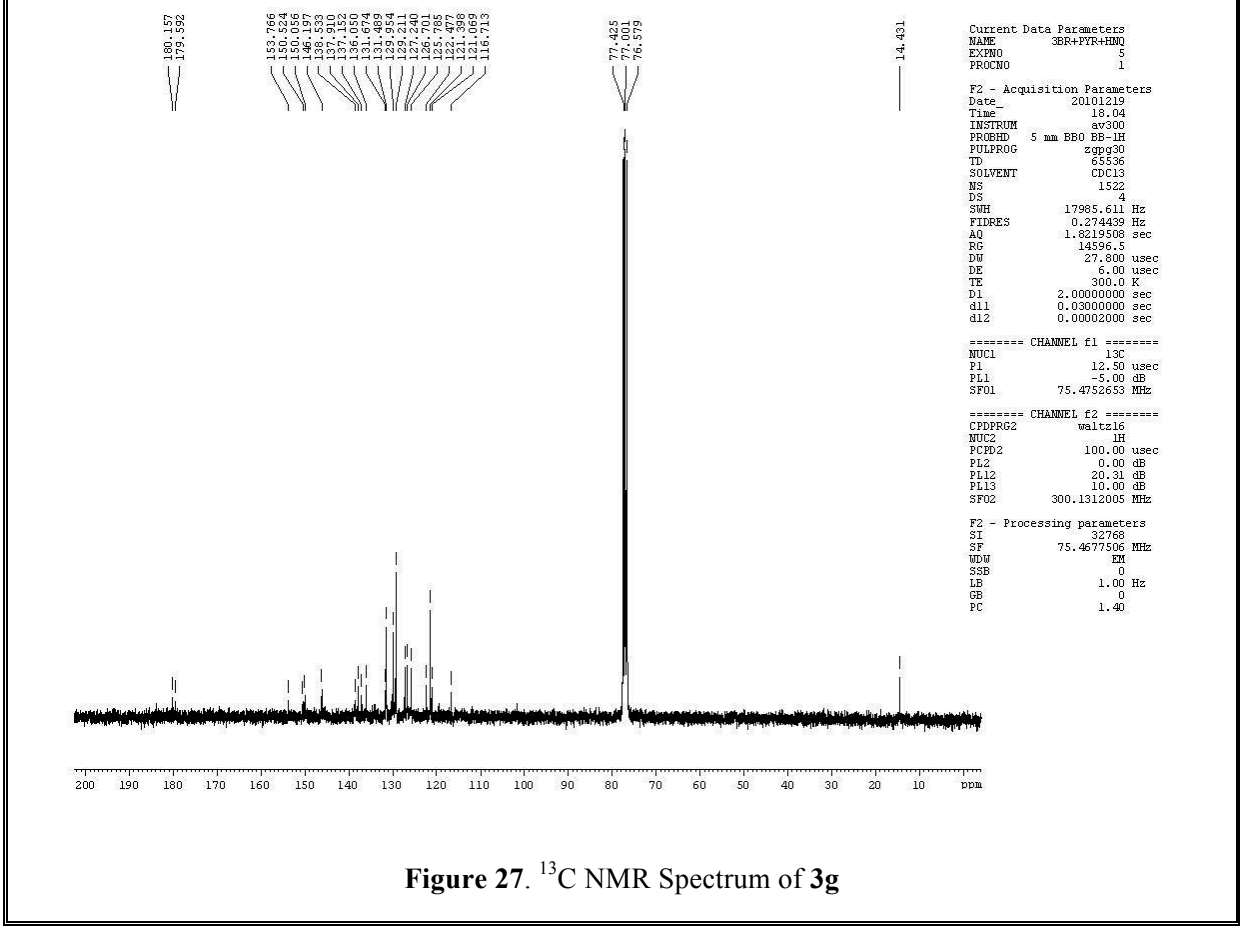

Figure 27. ^{13}C NMR Spectrum of **3g**

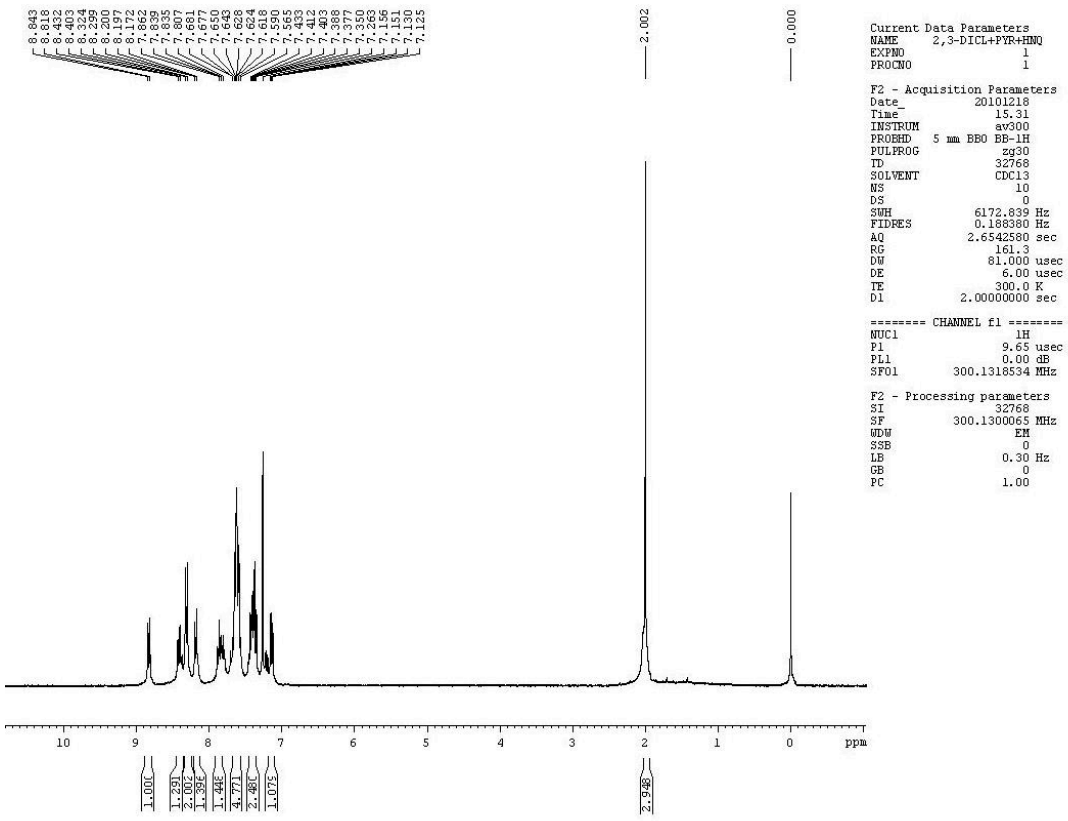

Figure 28. ^{1}H NMR Spectrum of **3h**

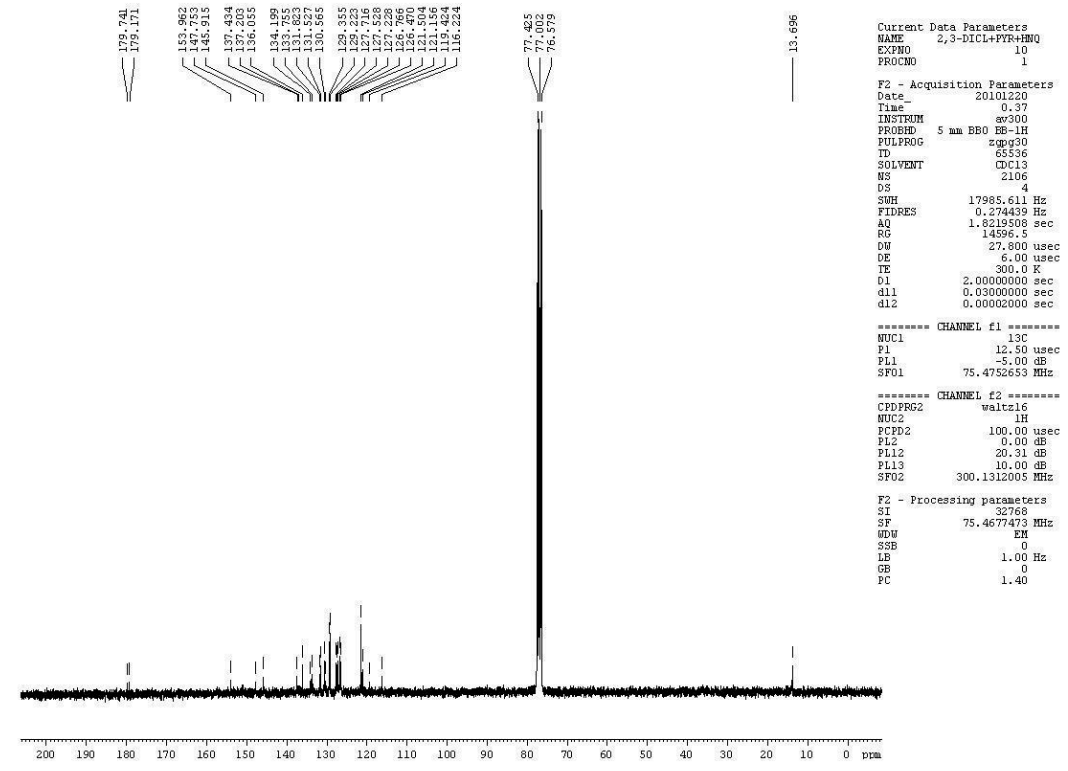

Figure 29. ^{13}C NMR Spectrum of **3h**

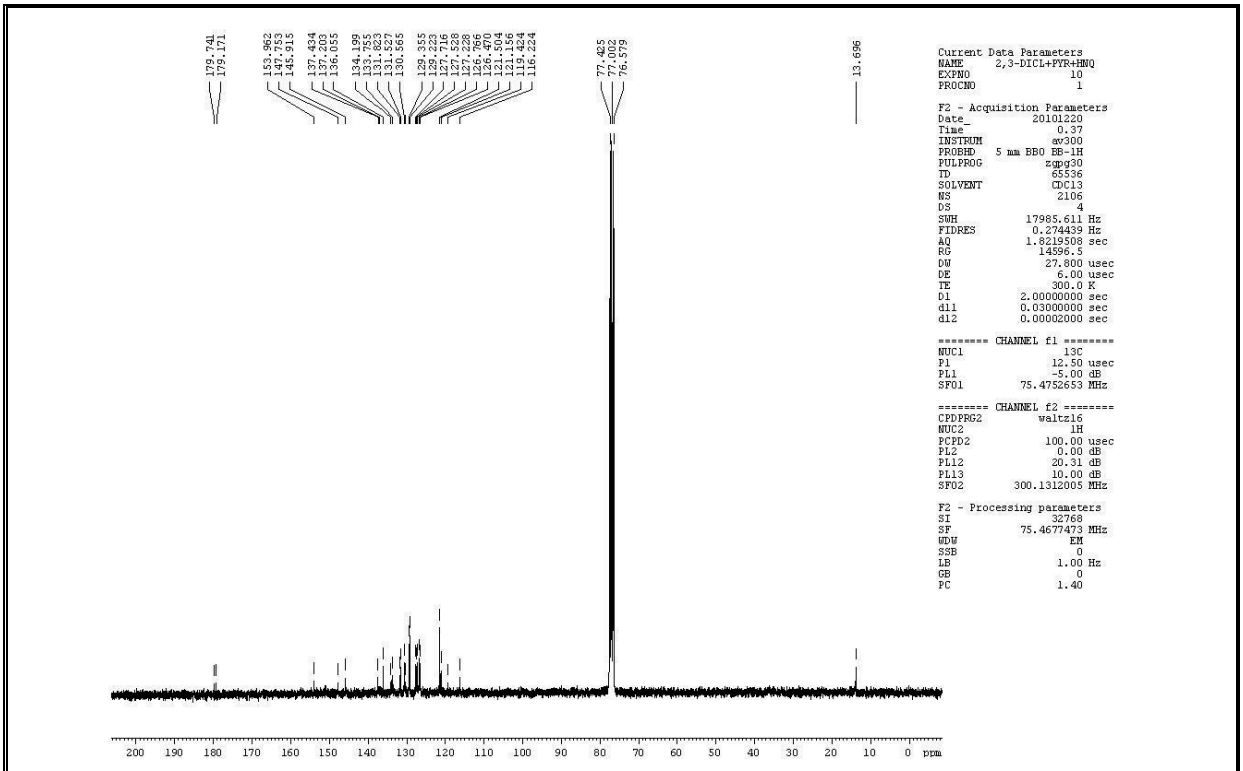

Figure 30. ^{1}H NMR Spectrum of **3i**

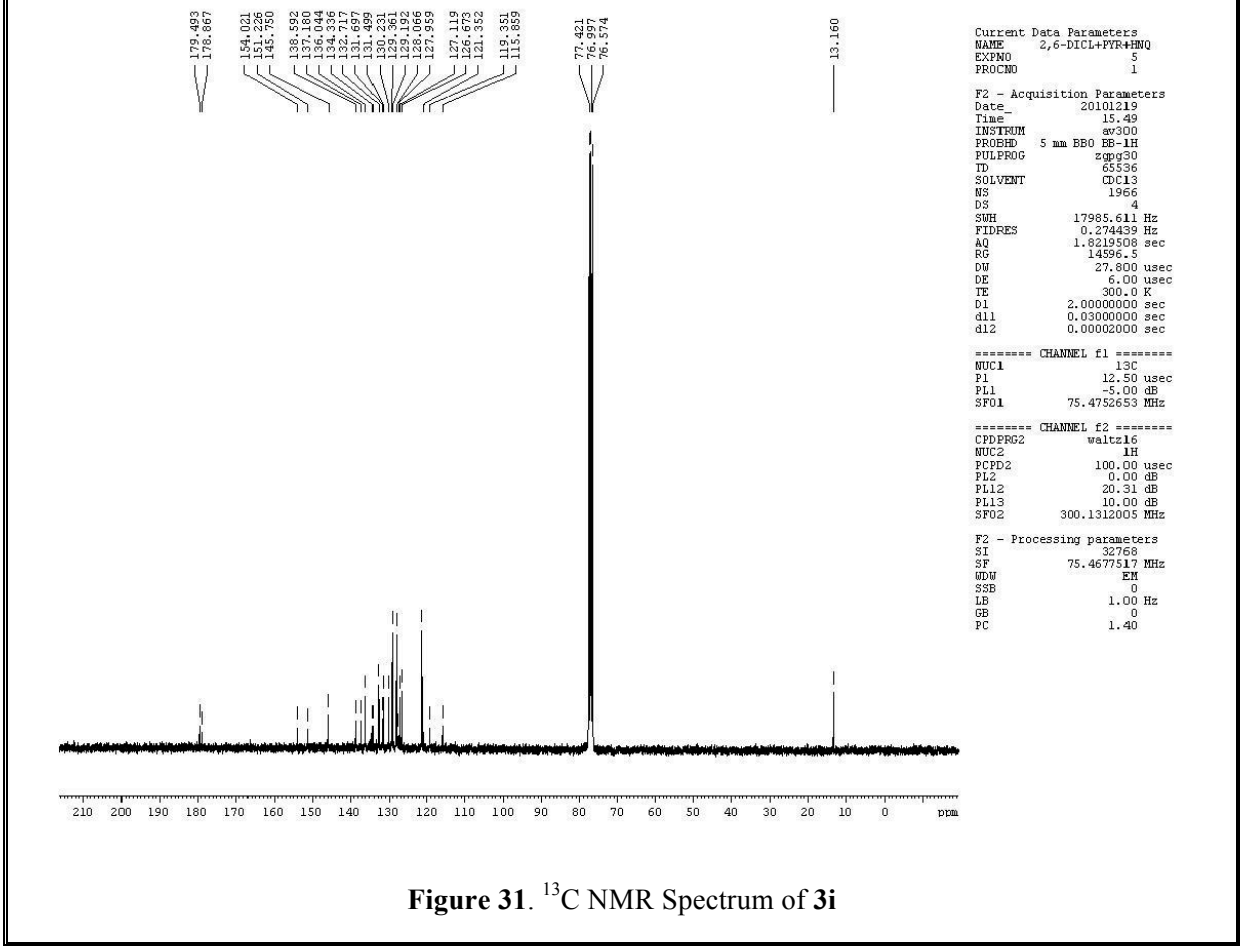

Figure 31. ^{13}C NMR Spectrum of **3i**

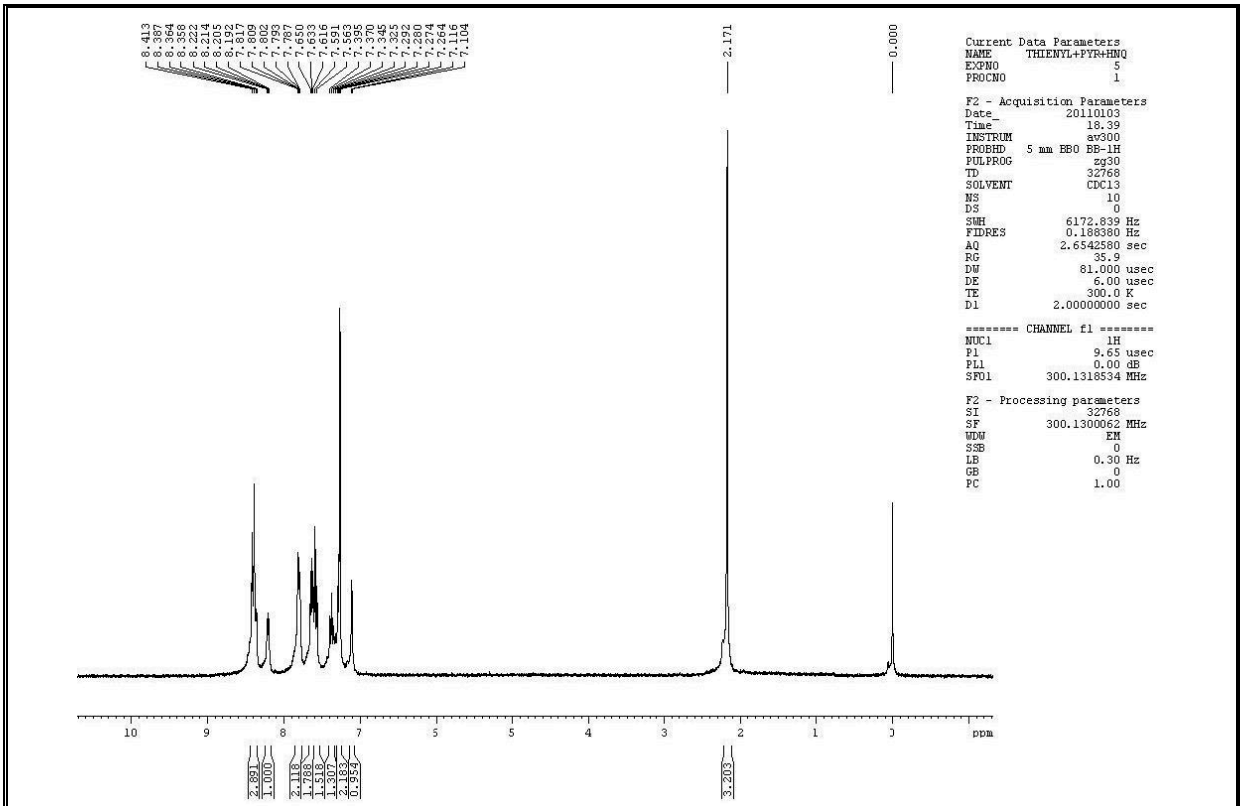

Figure 32. ^{1}H NMR Spectrum of **3j**

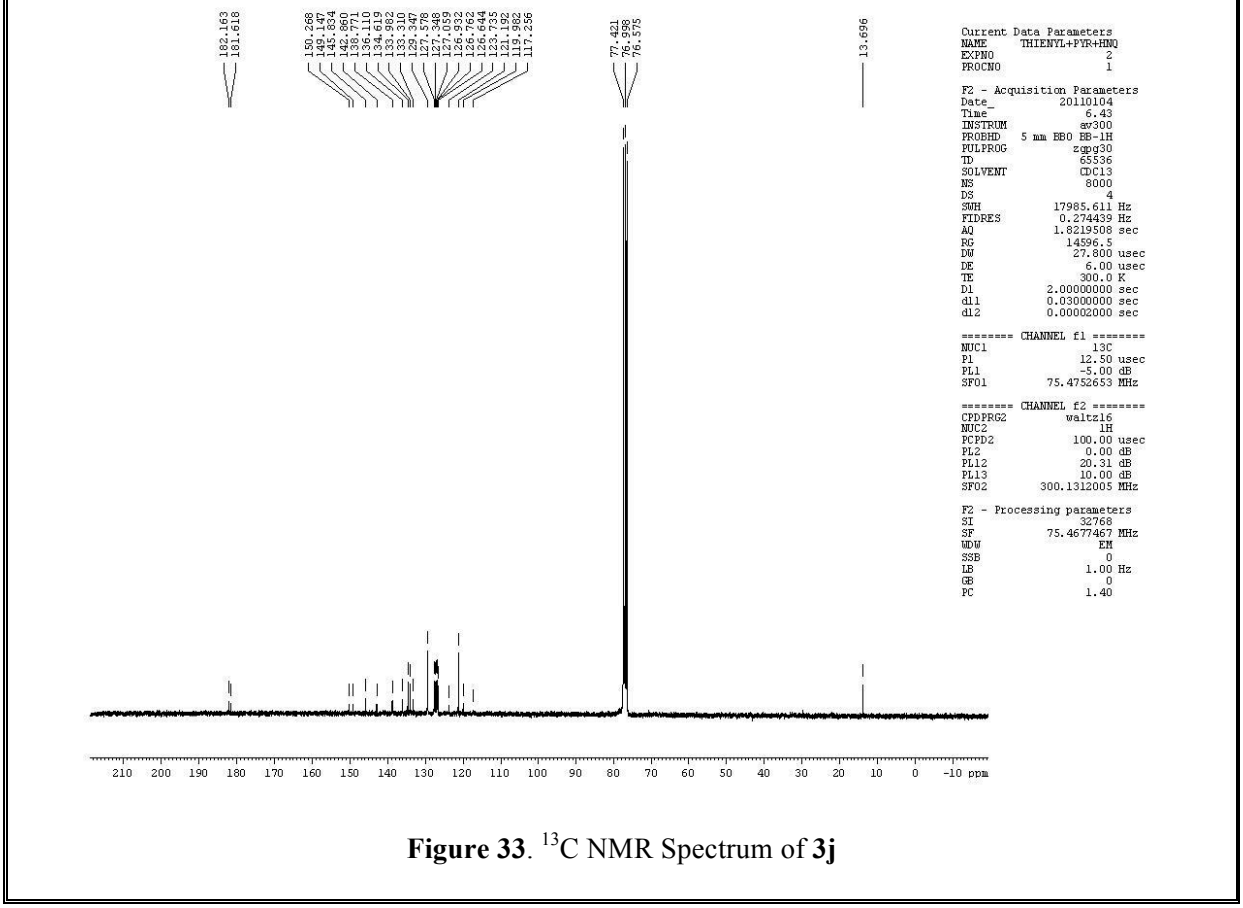

Figure 33. ^{13}C NMR Spectrum of **3j**

Characterization of compound 9

The structure of **9** was fully characterized by spectroscopic data (one and two-dimensional NMR and IR) and elemental analysis. The H-5 and H-8 occur as a multiplet at 9.25-9.31ppm, more downfield than expected of aromatic protons (Figure 34). This is explicable by the close proximity of these protons to the lone pairs of the neighbouring nitrogens and the consequent anisotropic and van de Waals deshielding. These hydrogens show H,H-COSY correlation with H-6 and H-7 at 7.81-7.87 ppm. The lack of any carbonyl signal and the presence of two imine carbon signals at 149.7 and 150.0 ppm in ^{13}C NMR spectrum of **9**, and the fact that **9** is formed by the reaction of one molecule of **3c** with one molecule of *o*-phenylenediamine clearly support the structure of **9,** which, in turn, further corroborates the structure of **3** and the regiochemistry of its formation.

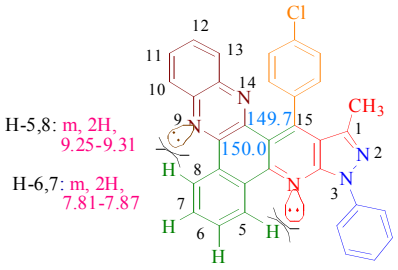

Figure 34. Characteristic ^{1}H and ^{13}C assignments of 9