

Supplementary information

Efficient Synthesis of Symmetrically Substituted Pyridines and Substituted Alkene through Green and Heterogeneous Catalysis with Zinc Phosphate

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Materials and reagents

To ensure the accuracy of the reaction, all of the reaction processes were carried out in dried glassware at a temperature of 130°C.

The reagents used in this study were obtained from commercial sources such as Sigma-Aldrich, Ried-de-haen, and Fluka. These reagents were used without any prior purification, as they were of sufficiently high purity for the experiment.

The commercial grade purity of the aldehydes used in the experiment is $\geq 97\%$, while that of the acetophenone derivatives is $\geq 98\%$. The purity of ammonium acetate and malononitrile used in the experiment is 99% for both.

Thin-layer chromatography (TLC) analysis was performed on pre-coated glass plates of Silica Gel 60 F254 (0.25 mm, Merck), and a UVGL-25 compact UV lamp (4 W/254 nm) was used for UV light detection.

Melting points of the synthesized compounds were determined using a Kofler bench (MP-2D melting apparatus) with a temperature range of 0-260°C.

¹H NMR and ¹³C NMR spectra were recorded using a Bruker Avance 300 NMR spectrometer with a proton frequency of 300 MHz and a carbon frequency of 75 MHz. Chemical shifts are reported in ppm.

General procedure for Knoevenagel condensation

In a clean and oven-dried 10 ml beaker fitted with a magnetic stirrer, a mixture of 1 mmol of aromatic aldehyde, and 1 mmol of the active methylene compound was added to a mass of the

catalyst support prepared using ethanol as solvent. After adding all the components to the beaker, the reaction mixture is stirred at room temperature for 12 minutes. The progress of the reaction is monitored using TLC.

Once the reaction is complete, 5 ml of dichloromethane is added sequentially to the reaction mixture. After the addition of dichloromethane, the reaction mixture separates into two distinct phases. These phases are separated using a separatory funnel. The aqueous phase is then washed three times with dichloromethane. This helps to remove any remaining organic material from the aqueous phase. The organic phase is then dried using anhydrous Na_2SO_4 and filtered to remove any remaining drying agent. The solvent is then removed under a vacuum, leaving behind a solid residue. Finally, the solid obtained is filtered and recrystallized from ethanol to obtain the desired product in its pure crystalline form.

The synthesized products (**3a-i**) were characterized by their melting temperatures and by ^1H and ^{13}C NMR spectroscopy and then compared both spectral data and melting points with those reported in the literature.

Identification of synthetic products

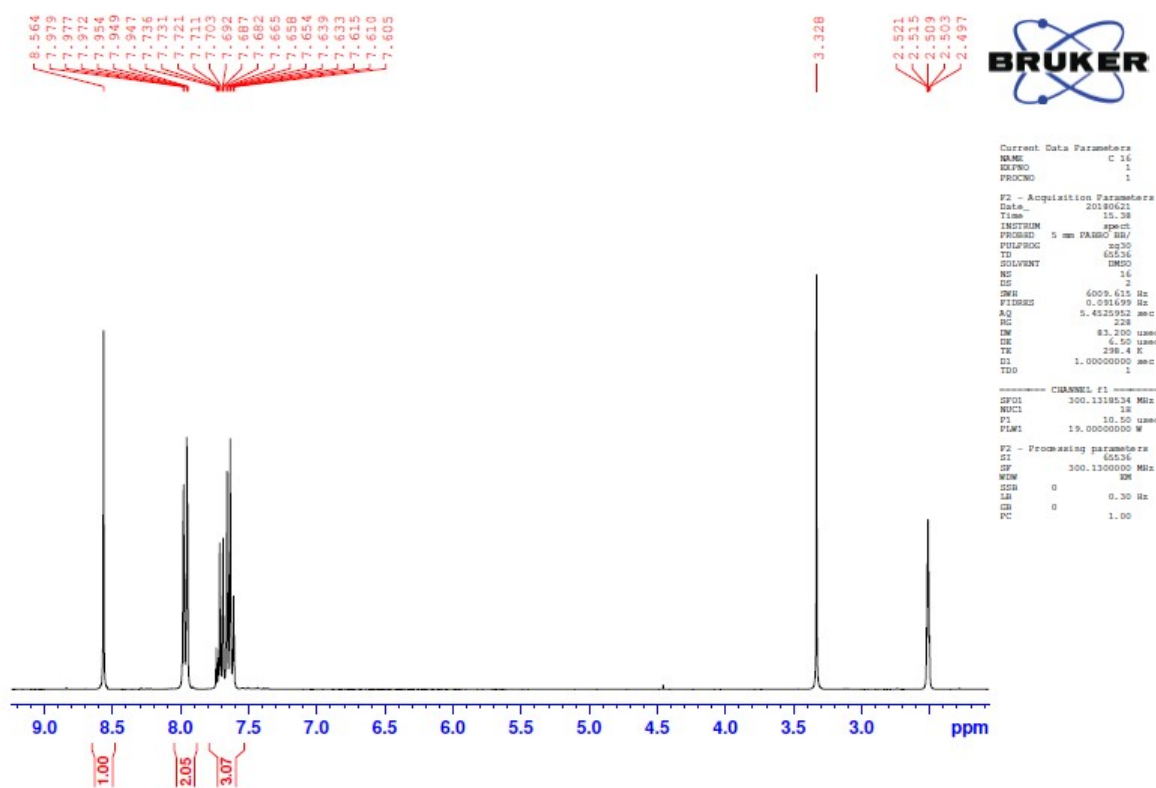


Figure S1. ^1H NMR spectrum of 2-benzylidenemalononitrile (**3a**)

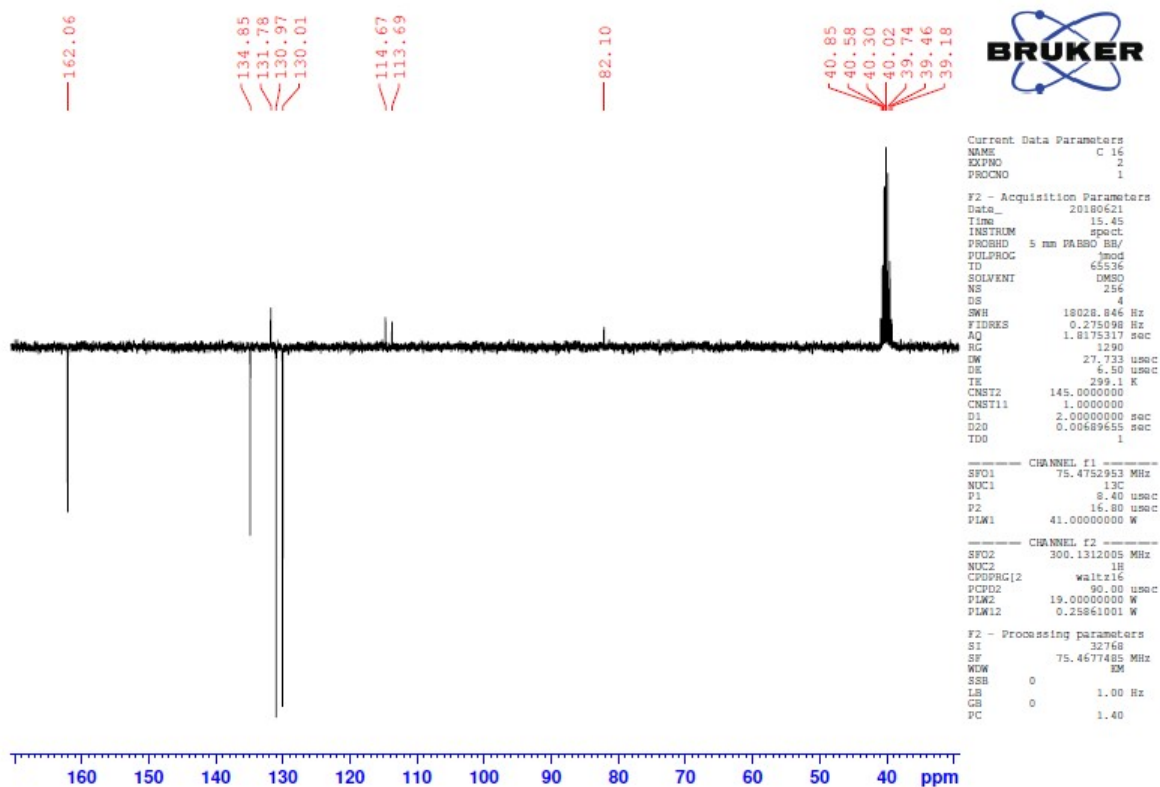


Figure S2. ¹³C NMR spectrum of 2-benzylidenemalononitrile (**3a**)

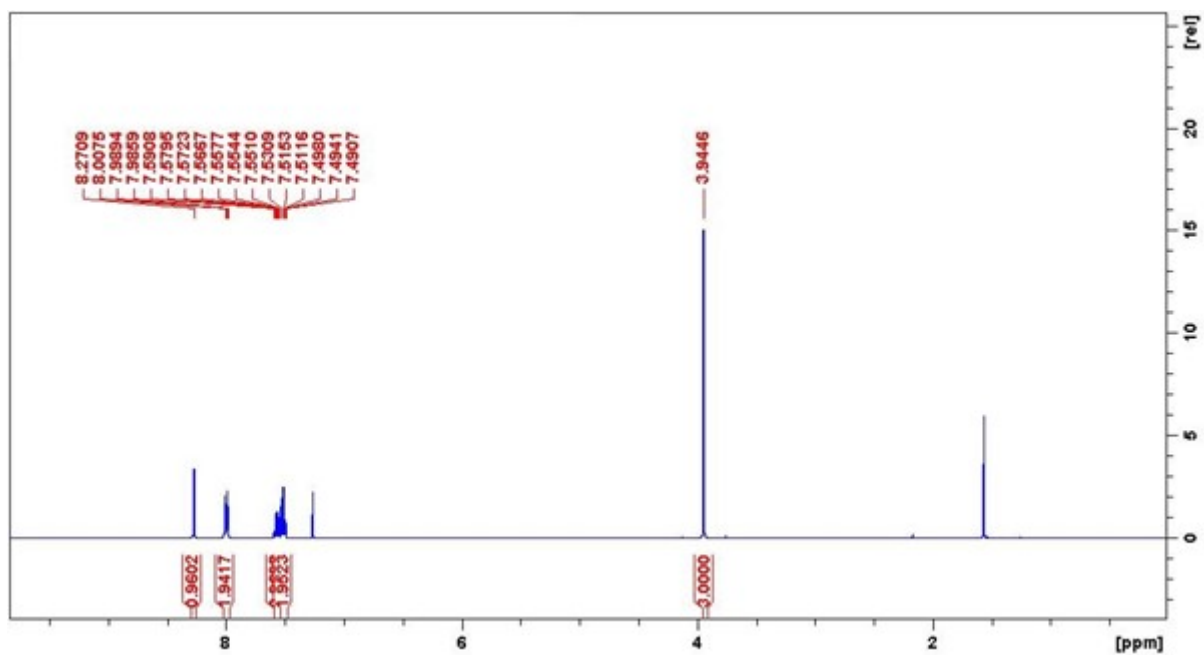


Figure S3. ¹H NMR spectrum of Methyl-2-cyano-3-phenylacrylate (**3b**)

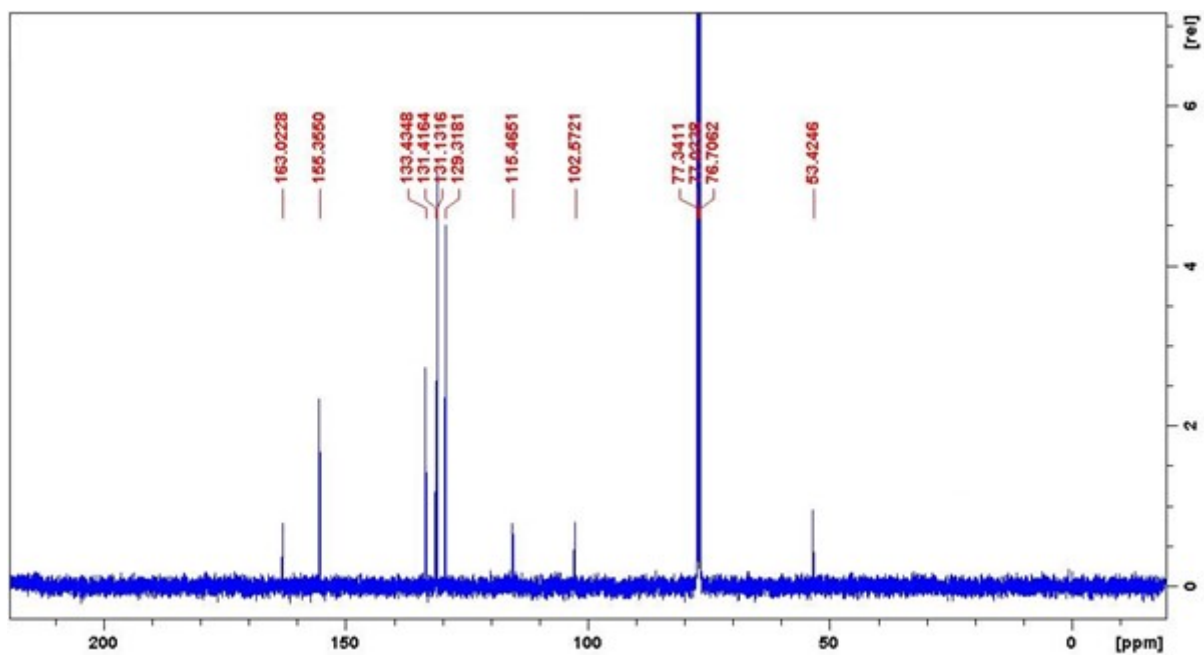


Figure S4. ^{13}C NMR spectrum of Methyl -2-cyano-3-phenylacrylate (**3b**)

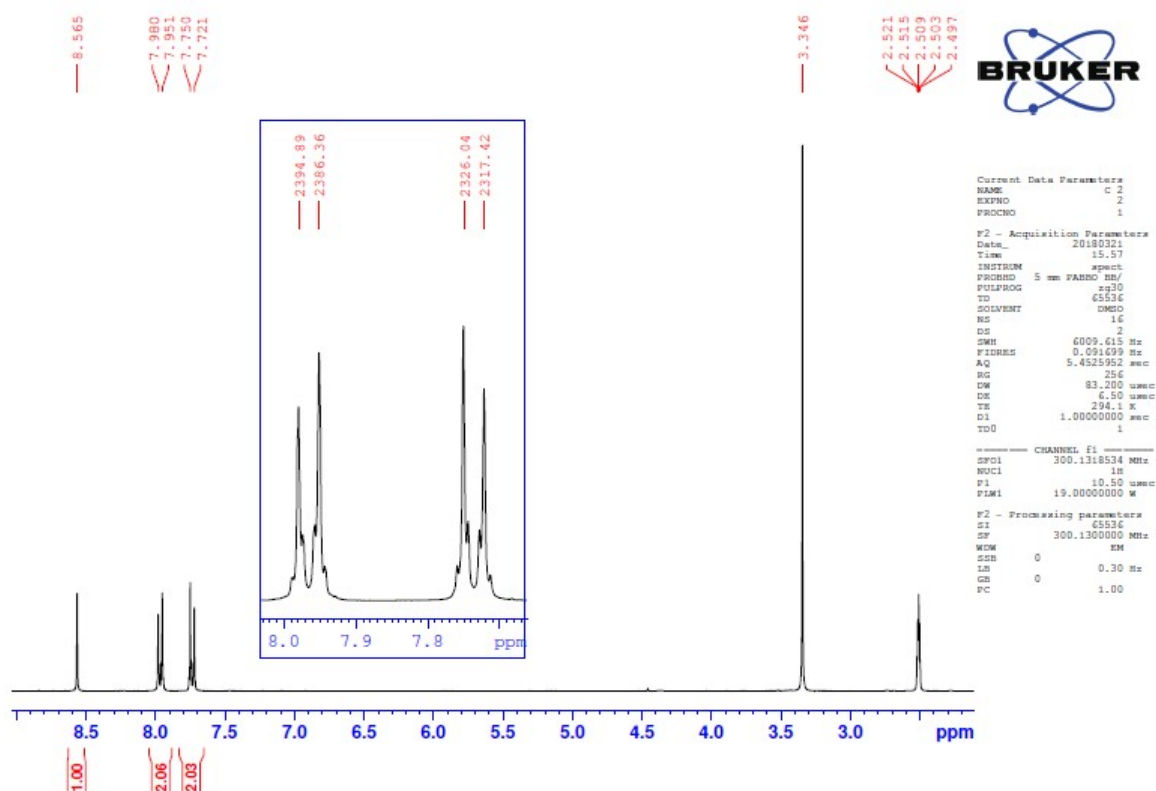


Figure S5. ^1H NMR spectrum of 2-(4-chlorobenzylidene) malononitrile (**3c**)

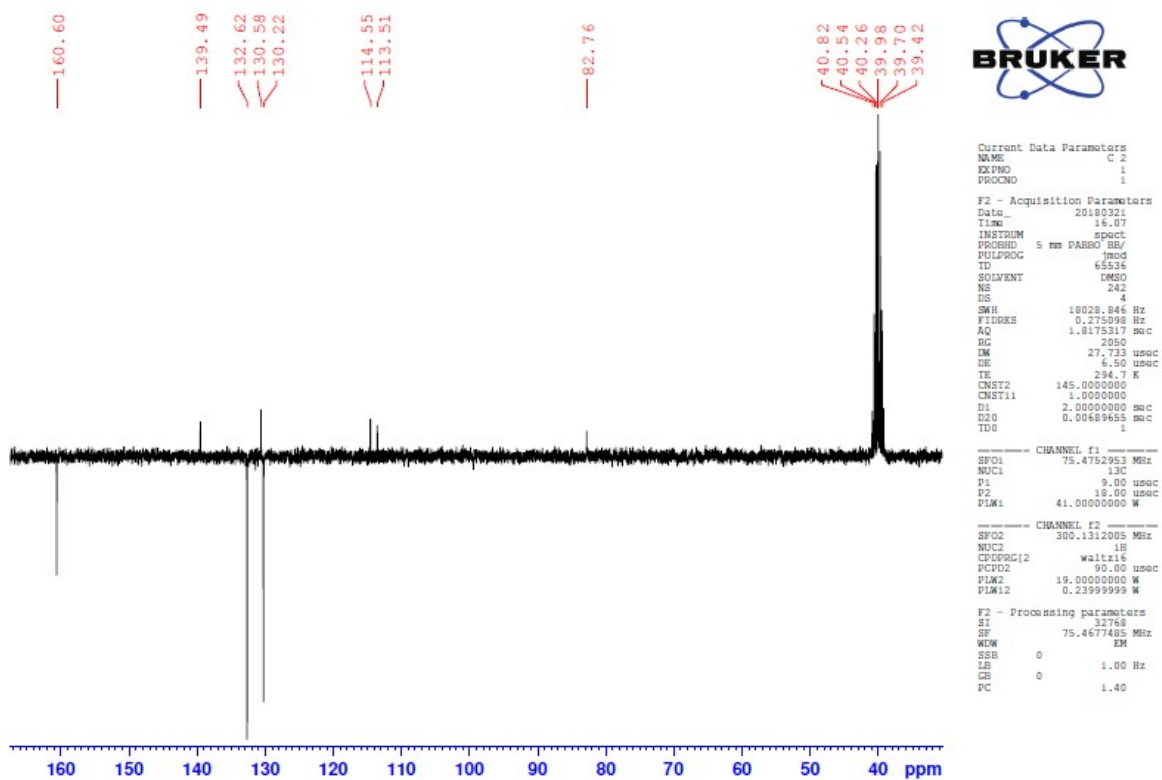


Figure S6. ^{13}C NMR spectrum of 2-(4-chlorobenzylidene) malononitrile (**3c**)

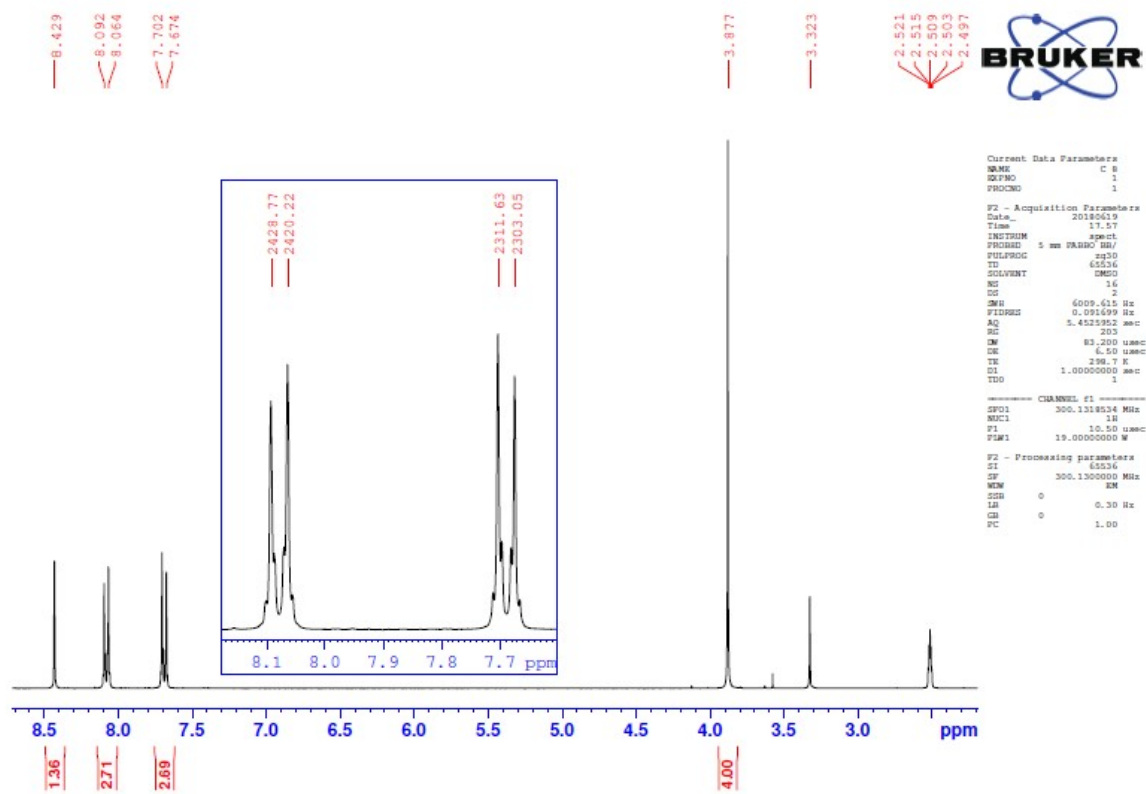


Figure S7. ^1H NMR spectrum of Methyl-3-(4-chlorophenyl)-2-cyanoacrylate (**3d**)

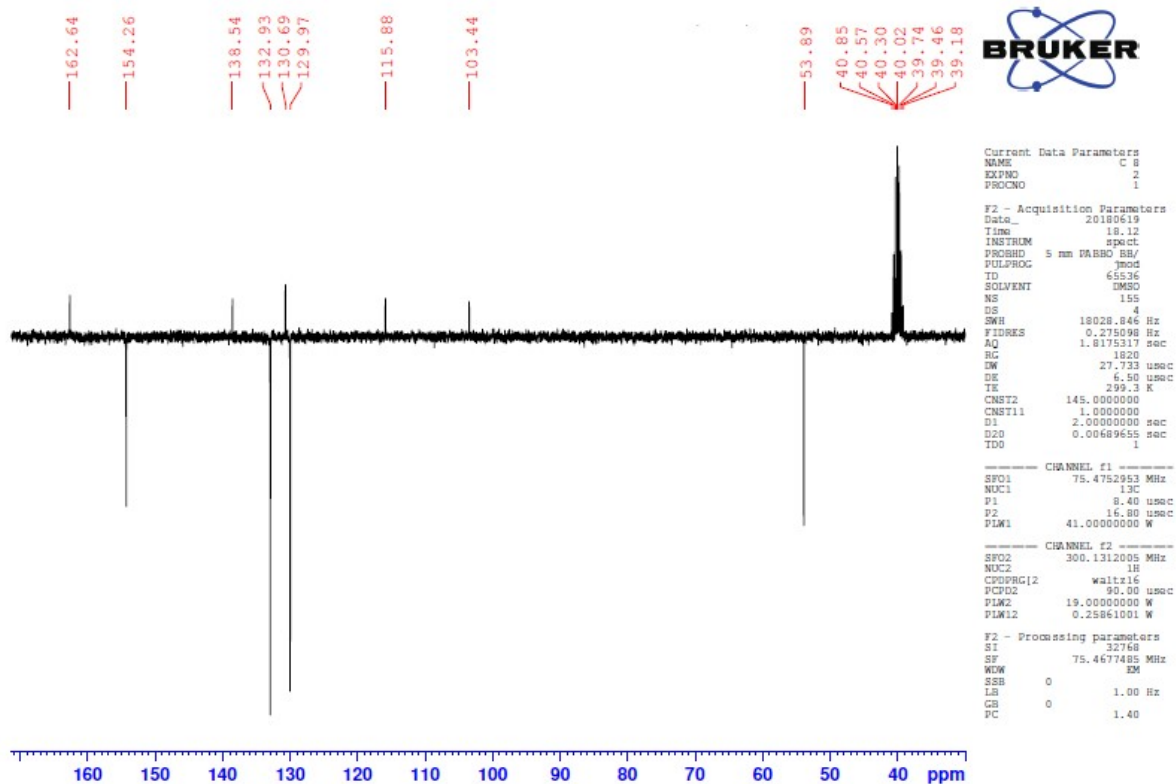


Figure S8. ^{13}C NMR spectrum of Methyl-3-(4-chlorophenyl)-2-cyanoacrylate (**3d**)

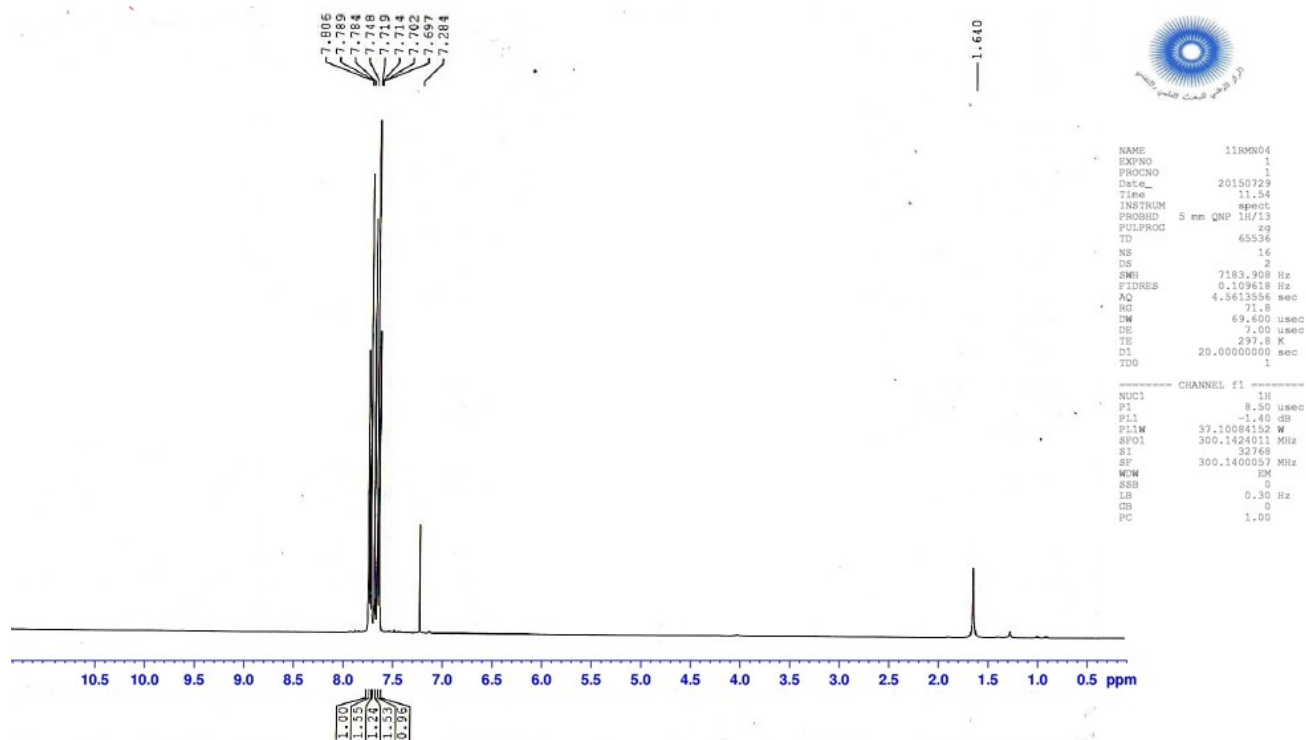


Figure S9. ^1H NMR spectrum of 2-(4-bromobenzylidene) malononitrile (**3e**)

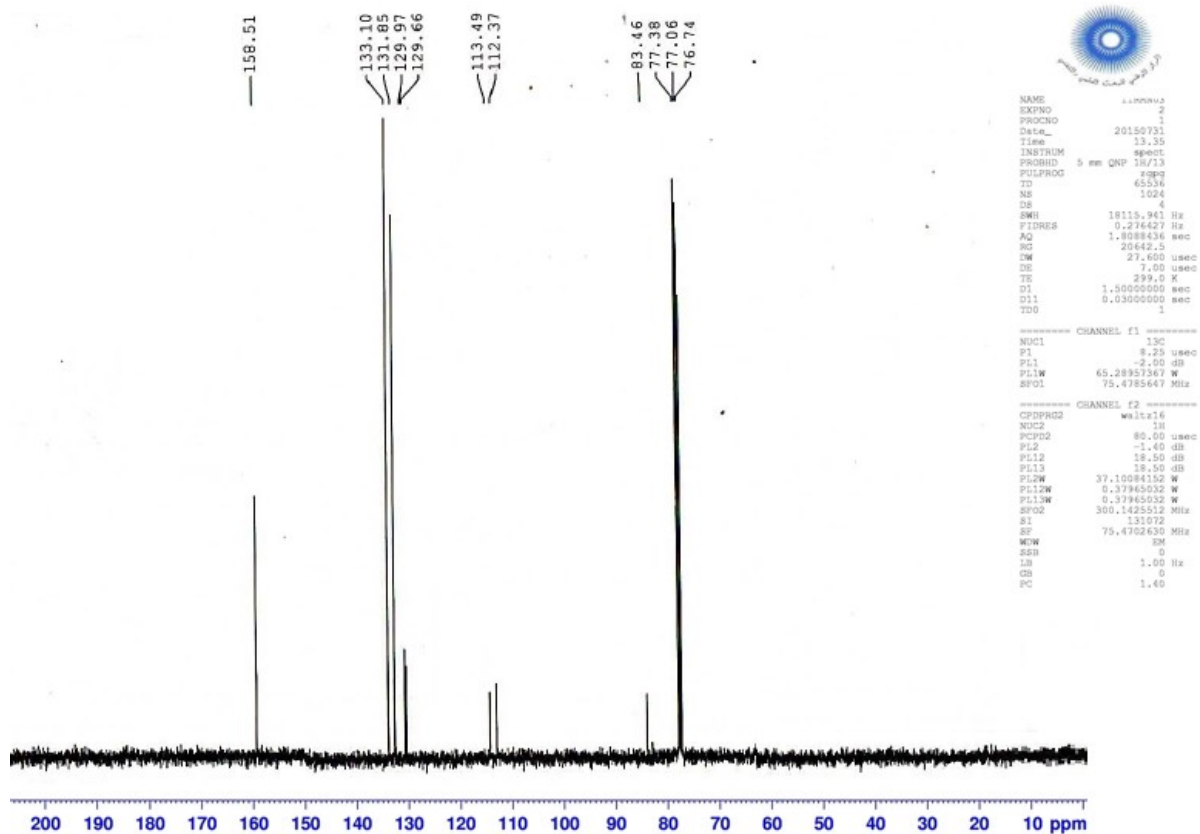


Figure S10. ^{13}C NMR spectrum of 2-(4-bromobenzylidene) malononitrile (**3e**)

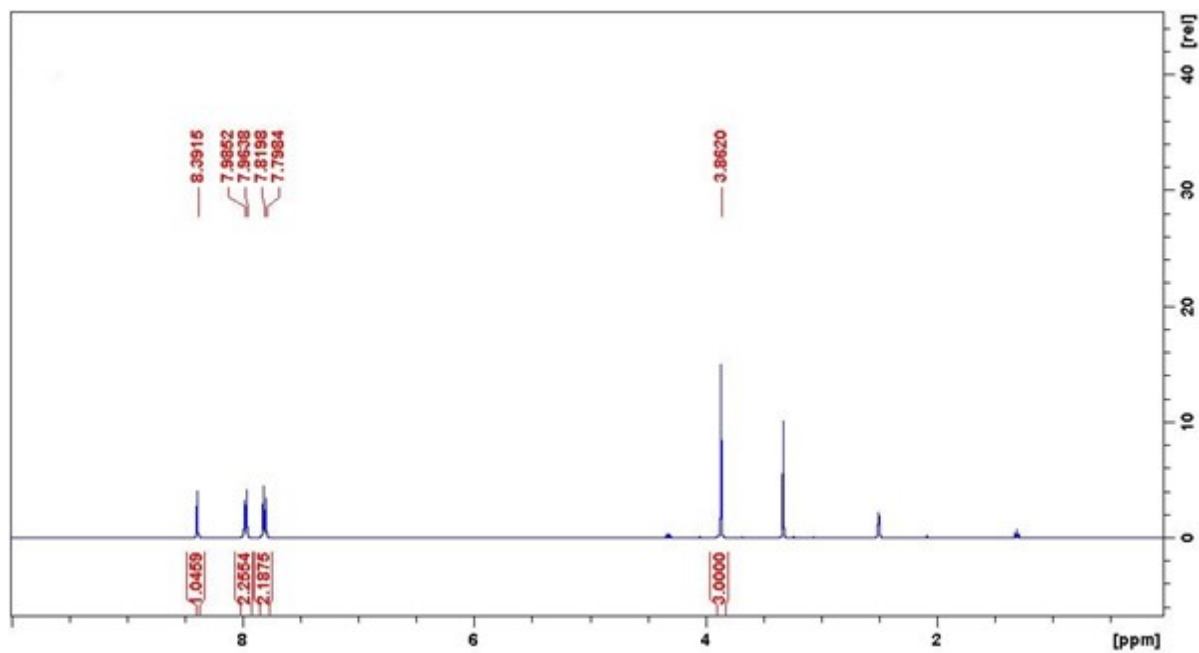


Figure S11. ^1H NMR spectrum of Methyl-3-(4-bromophenyl)-2 cyanoacrylate (**3f**)

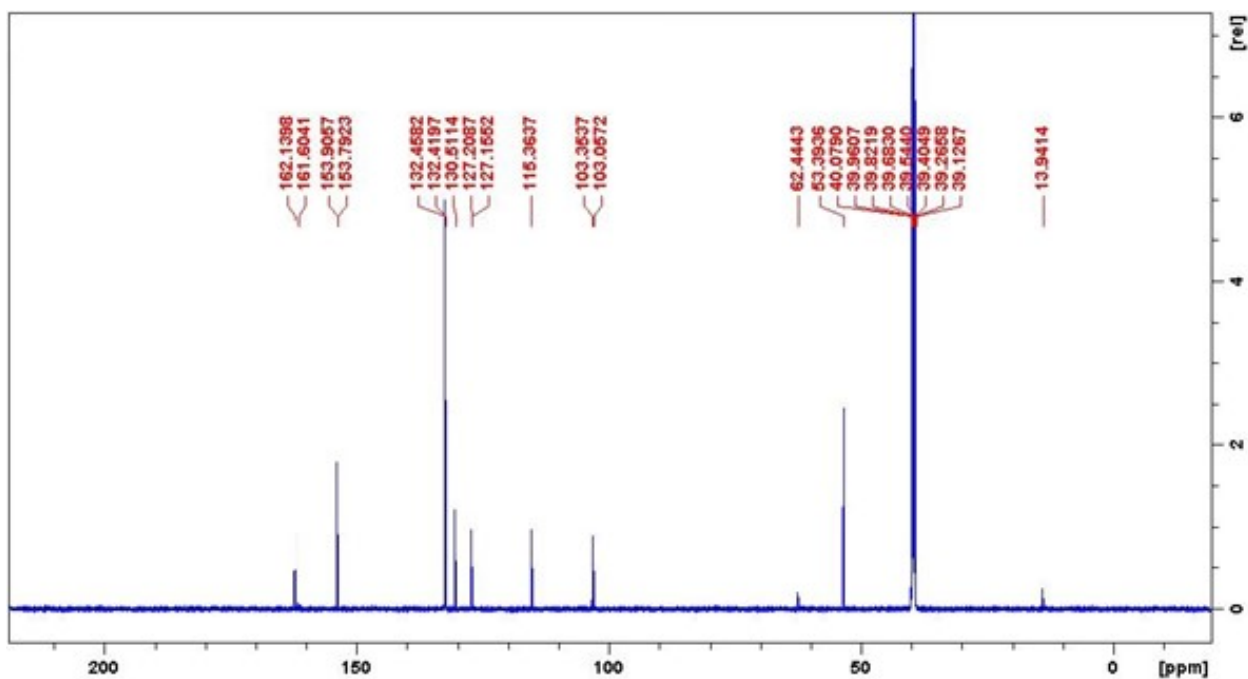


Figure S12. ^{13}C NMR spectrum of Methyl-3-(4-bromophenyl)-2 cyanoacrylate (**3f**)

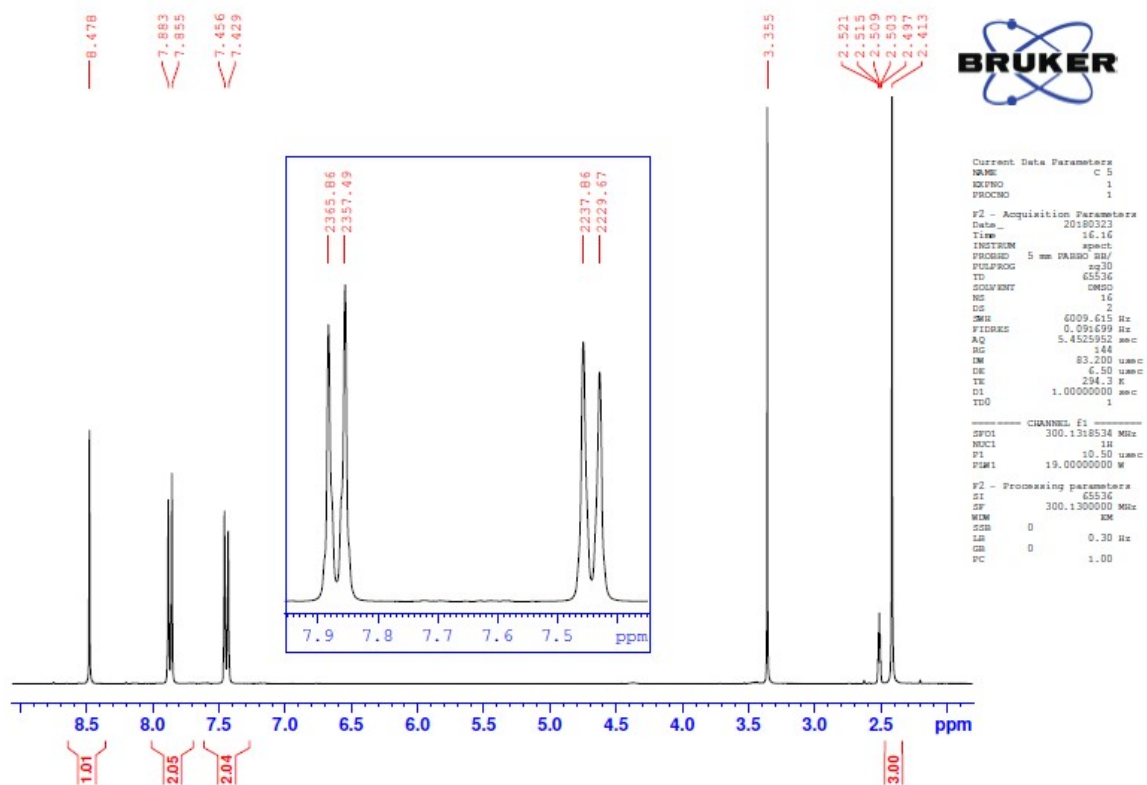


Figure S13. ^1H NMR spectrum of 2-(4-methylbenzylidene) malononitrile (**3g**)

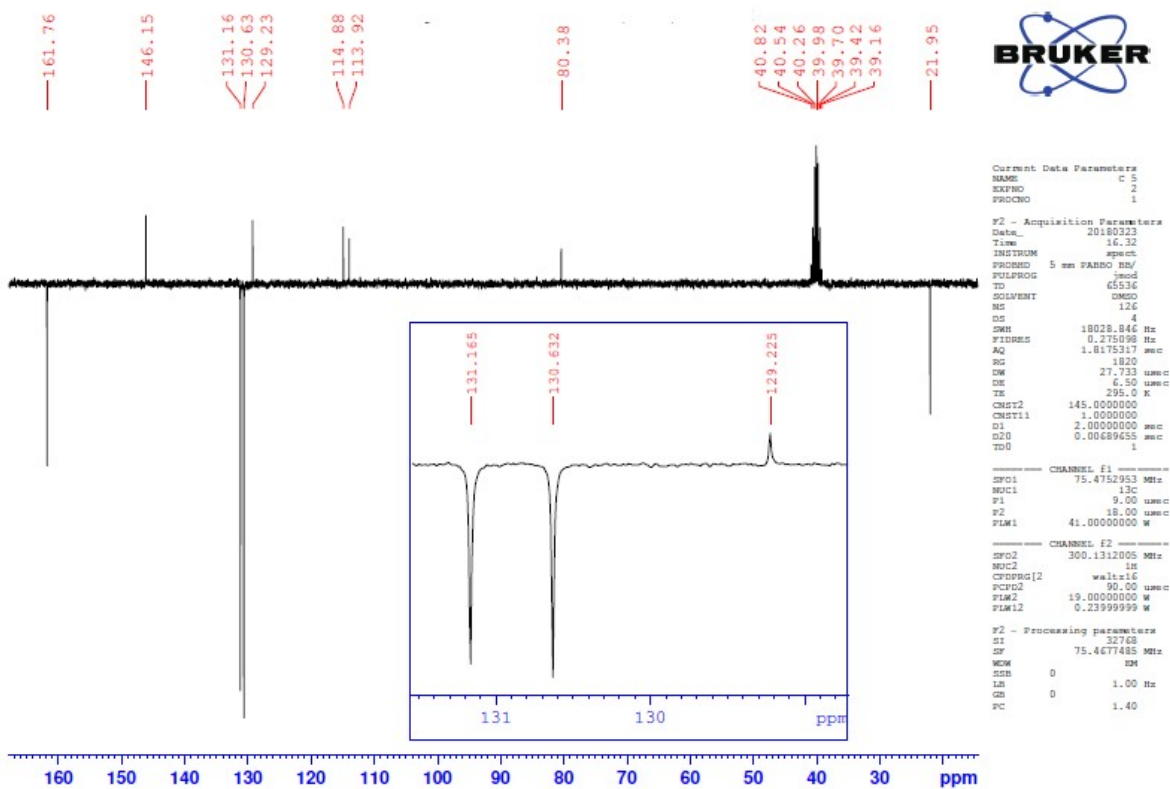


Figure S14. ¹³C NMR spectrum of 2-(4-methylbenzylidene) malononitrile (**3g**)

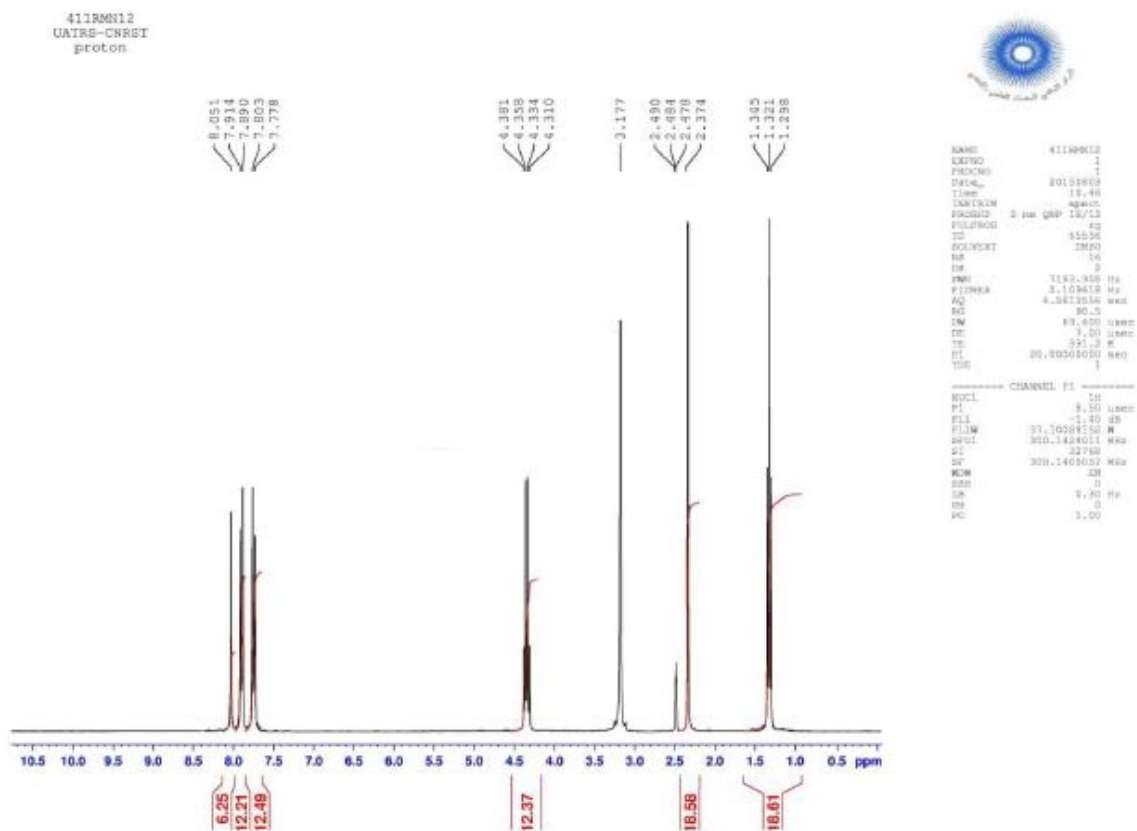


Figure S15. ¹H NMR spectrum of ethyl-2-cyano-3-*p*-tolylacrylate (**3h**)

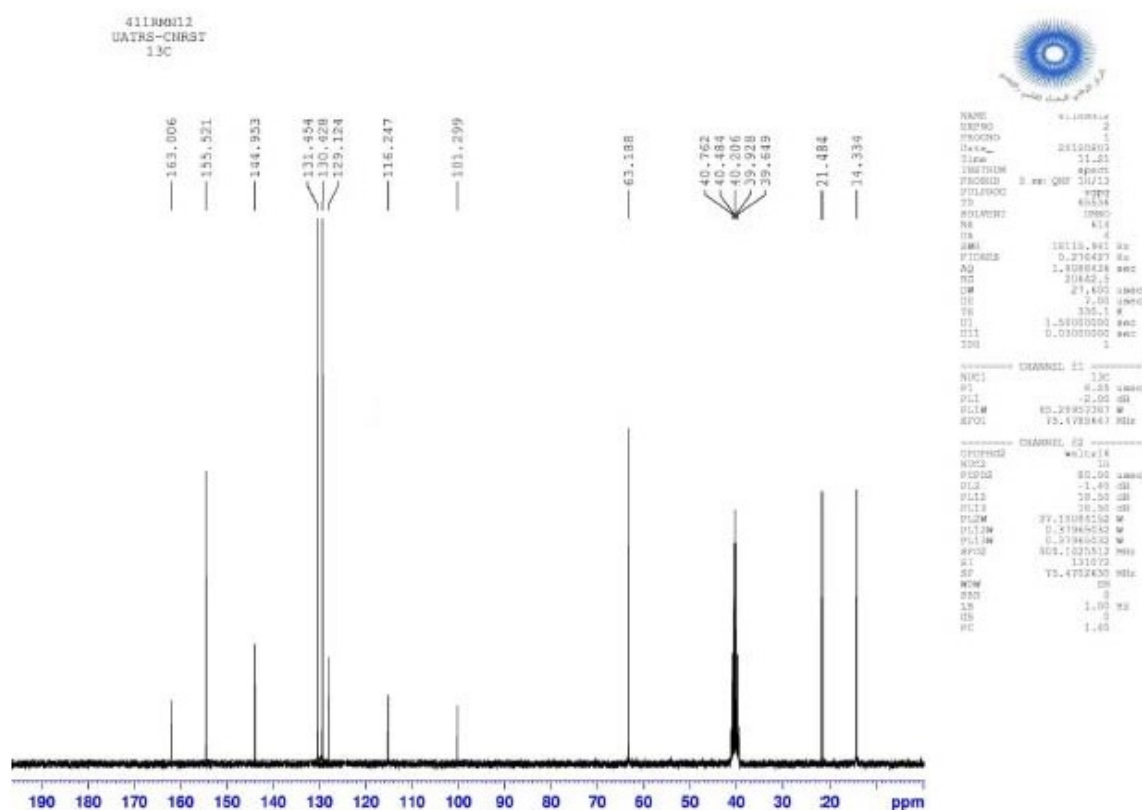


Figure S16. ¹³C NMR spectrum of ethyl-2-cyano-3-*p*-tolylacrylate (**3h**)

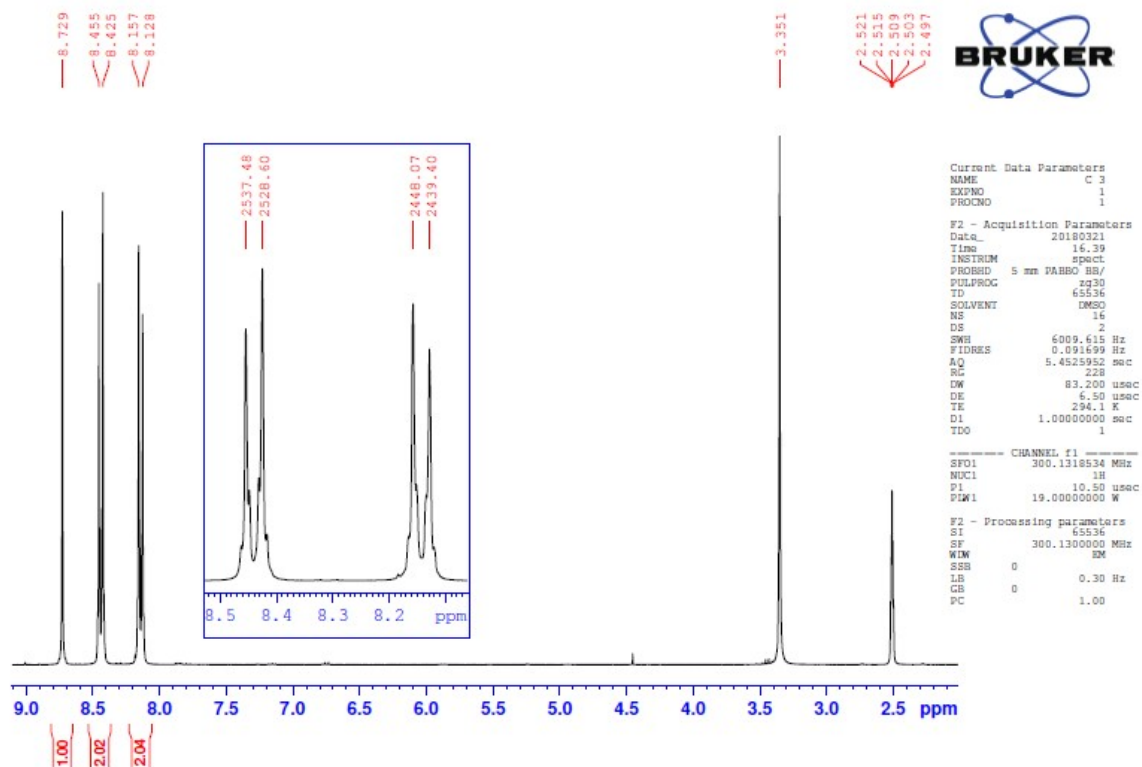


Figure S17. ¹H NMR spectrum of 2-(4-nitrobenzylidene) malononitrile (**3i**)

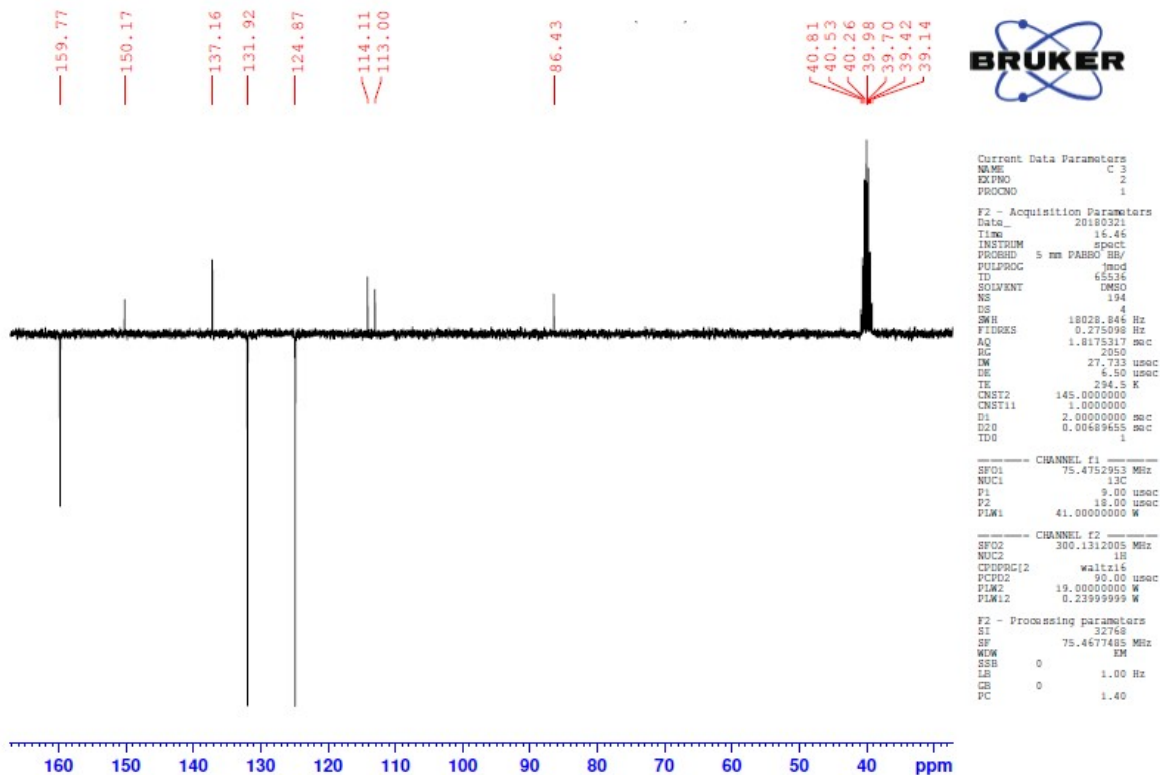


Figure S18. ¹³C NMR spectrum of 2-(4-nitrobenzylidene) malononitrile (**3i**)

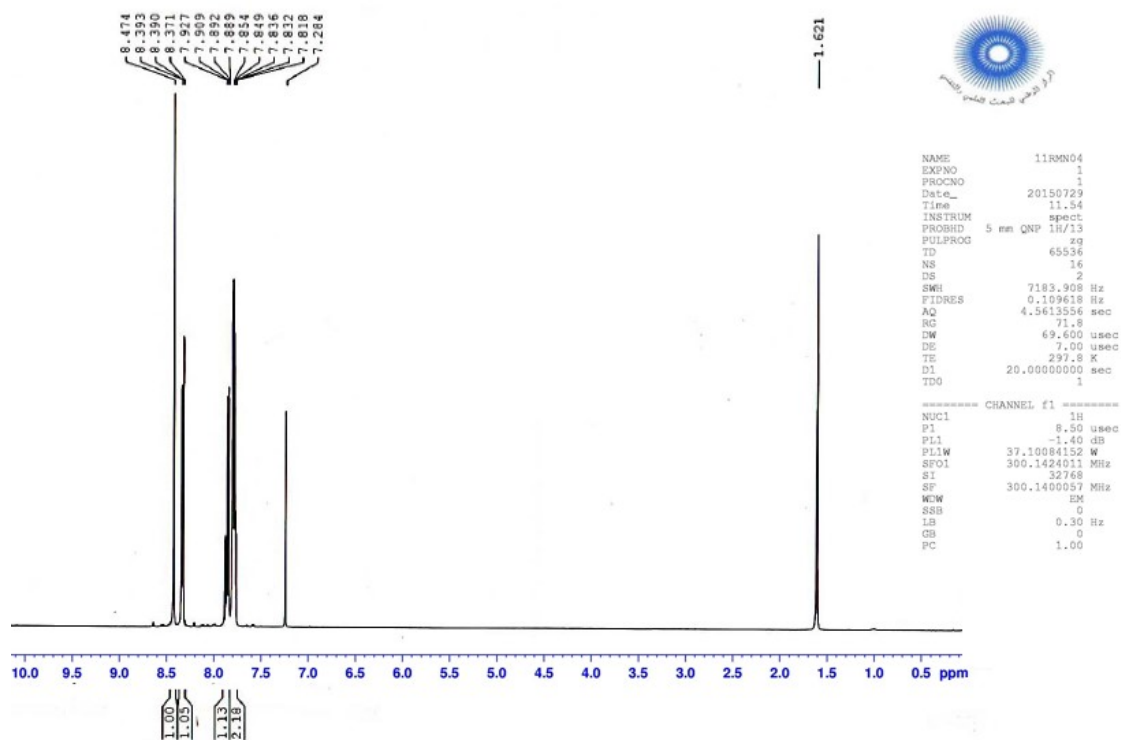


Figure S19. ¹H NMR spectrum of 2-(2-nitrobenzylidene) malononitrile (**3j**)

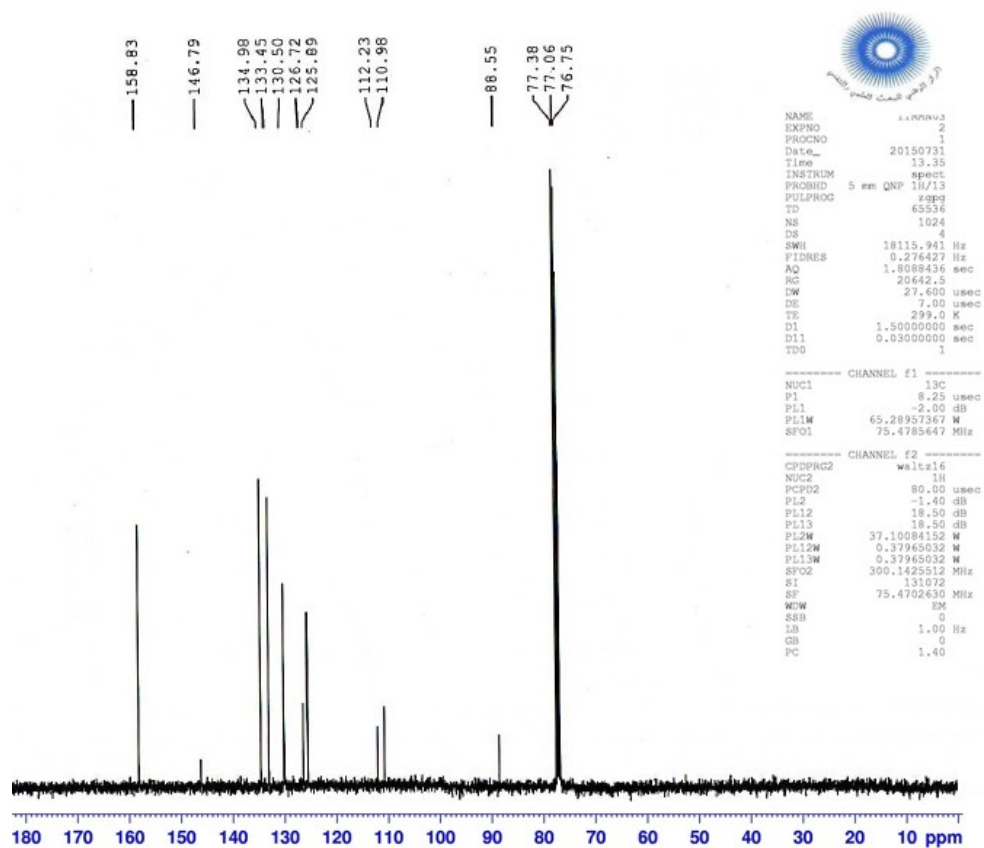


Figure S20. ¹³C NMR spectrum of 2-(2-nitrobenzylidene) malononitrile (**3j**)

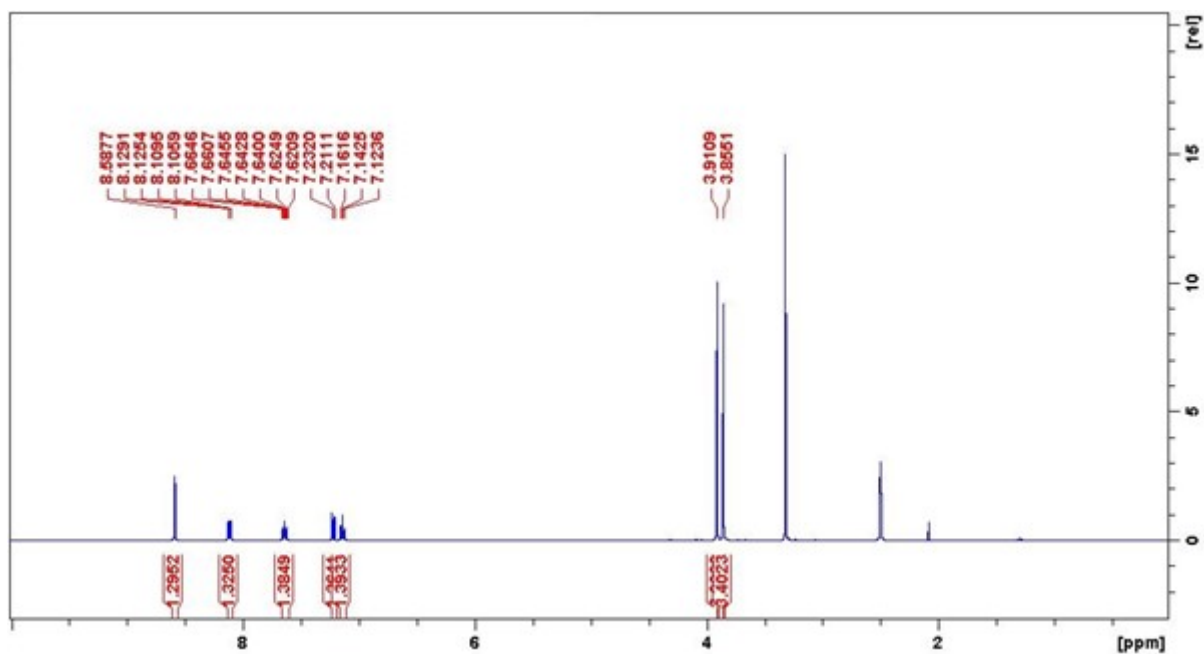


Figure S21. ¹H NMR spectrum of Methyl-3-(2-methoxyphenyl)-2 cyanoacrylate (**3k**)

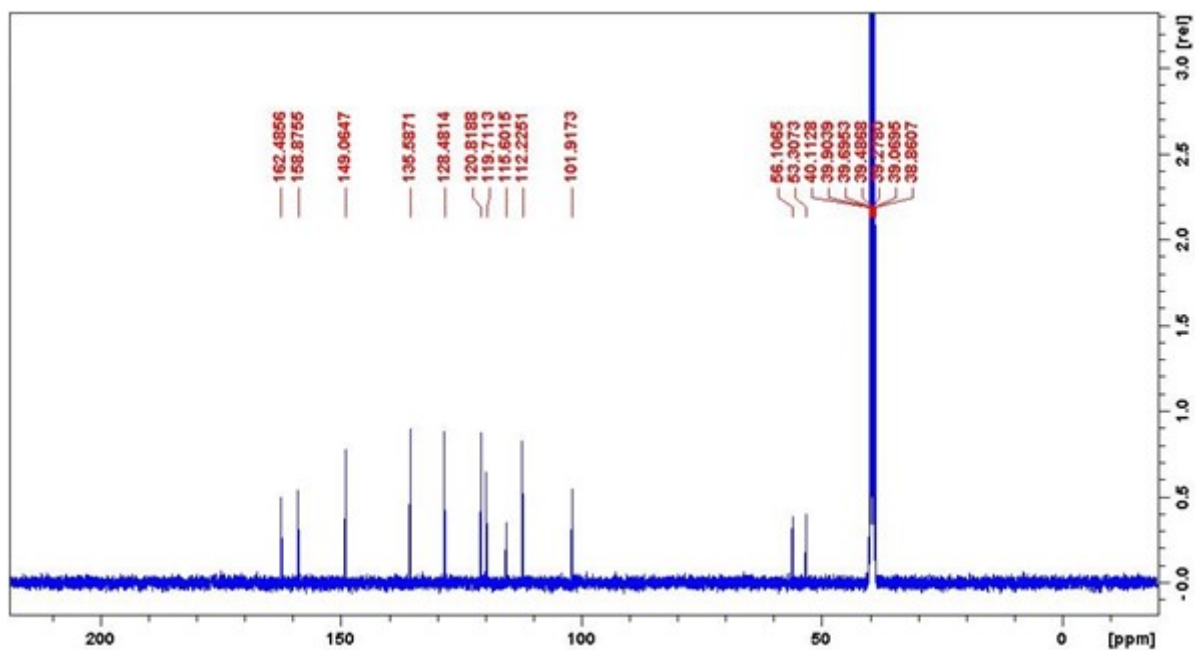


Figure S22. ^{13}C NMR spectrum of Methyl-3-(2-methoxyphenyl)-2 cyanoacrylate (**3k**)

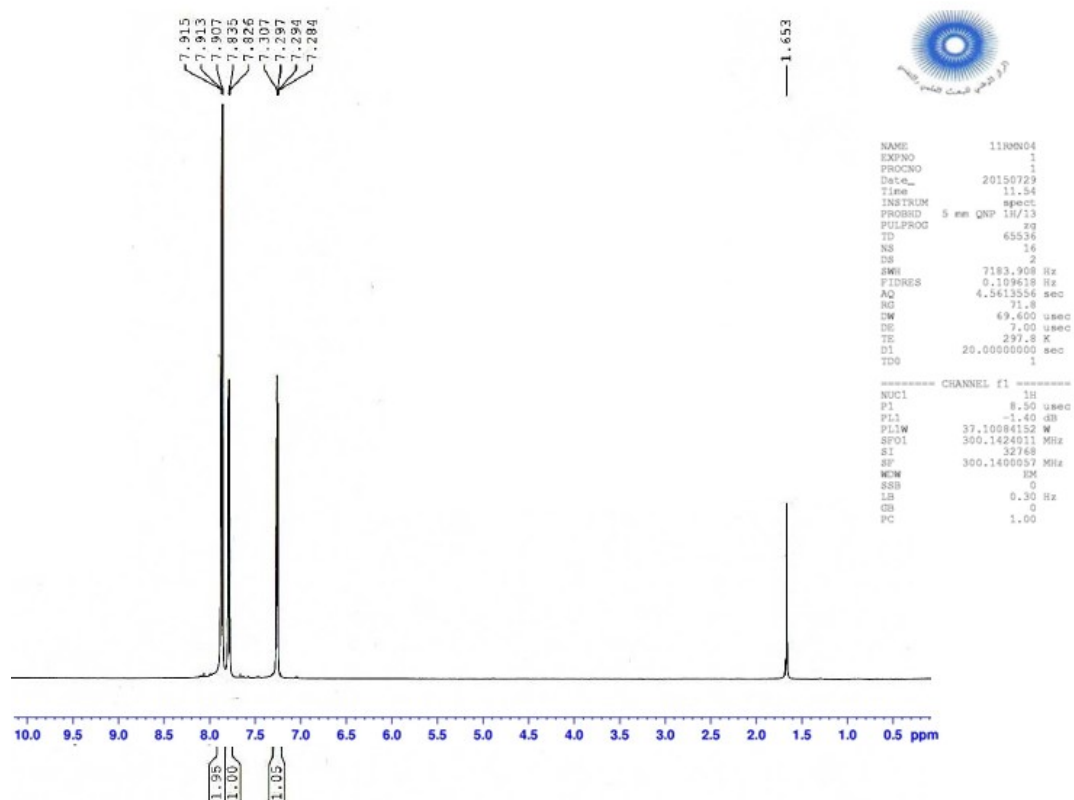


Figure S23. ^1H NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile (**3l**)

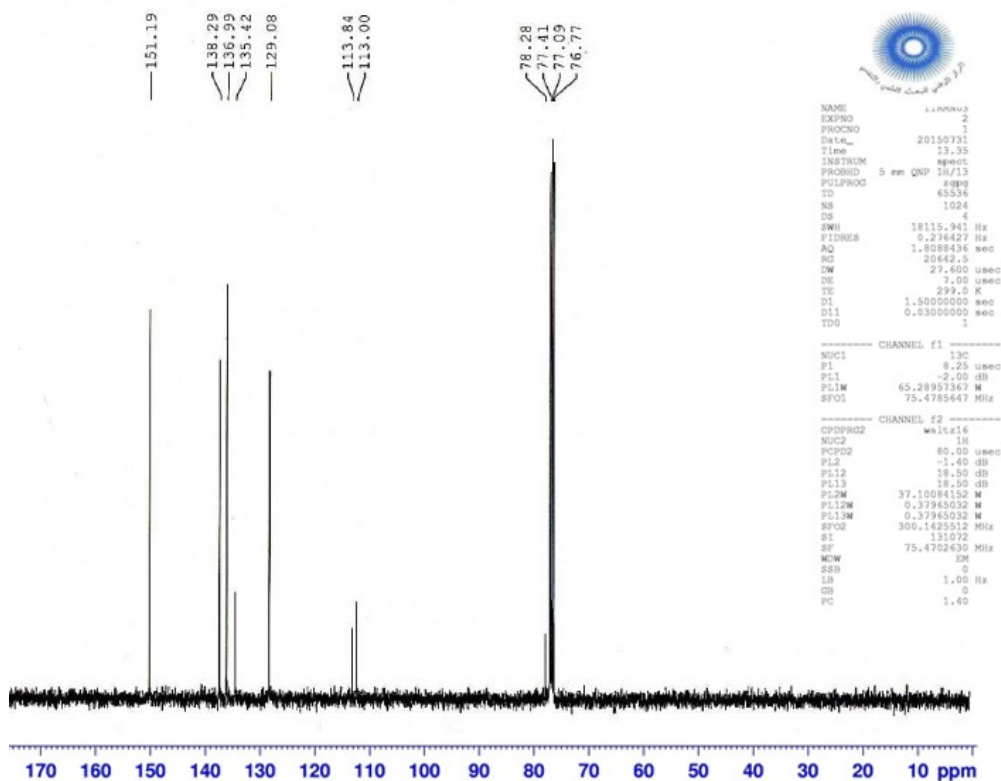


Figure S24. ¹³C NMR spectrum of 2-(thiophen-2-ylmethylene)malononitrile (**31**)

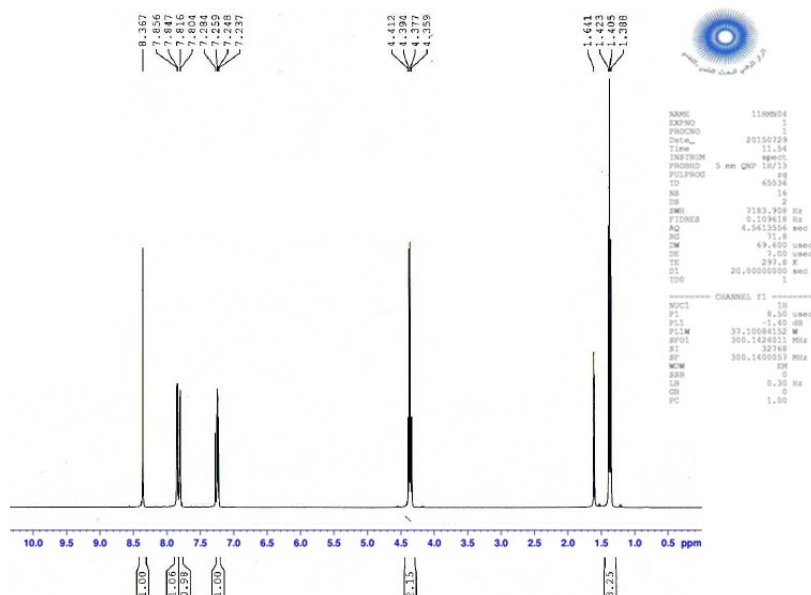


Figure S25. ¹H NMR spectrum of Ethyl 2-cyano-3-(thiophen-2-yl)acrylate (**3m**)

General procedure for the synthesis of 2,4,6-triaryl pyridine derivatives

The synthesis of 2,4,6-triaryl pyridine derivatives involves the condensation between acetophenone derivatives (2 mmol), aromatic aldehydes (1 mmol), ammonium acetate (0.8

mmol), and a small quantity of $Zn_3(PO_4)_2 \cdot 4H_2O$ (7 mg or 0.14 mol%). The mixture is stirred at reflux using a solvent mixture of ethanol and water in a 4:1 ratio, which is optimal. The reaction progress is monitored using TLC until completion. Afterward, the reaction mixture is filtered to remove the catalyst, and the filtrate is cooled in an ice bath, causing the formation of a crude 2,4,6-triaryl pyridine product. The desired compounds are obtained in their crystalline form through recrystallization using an ethanol solution.

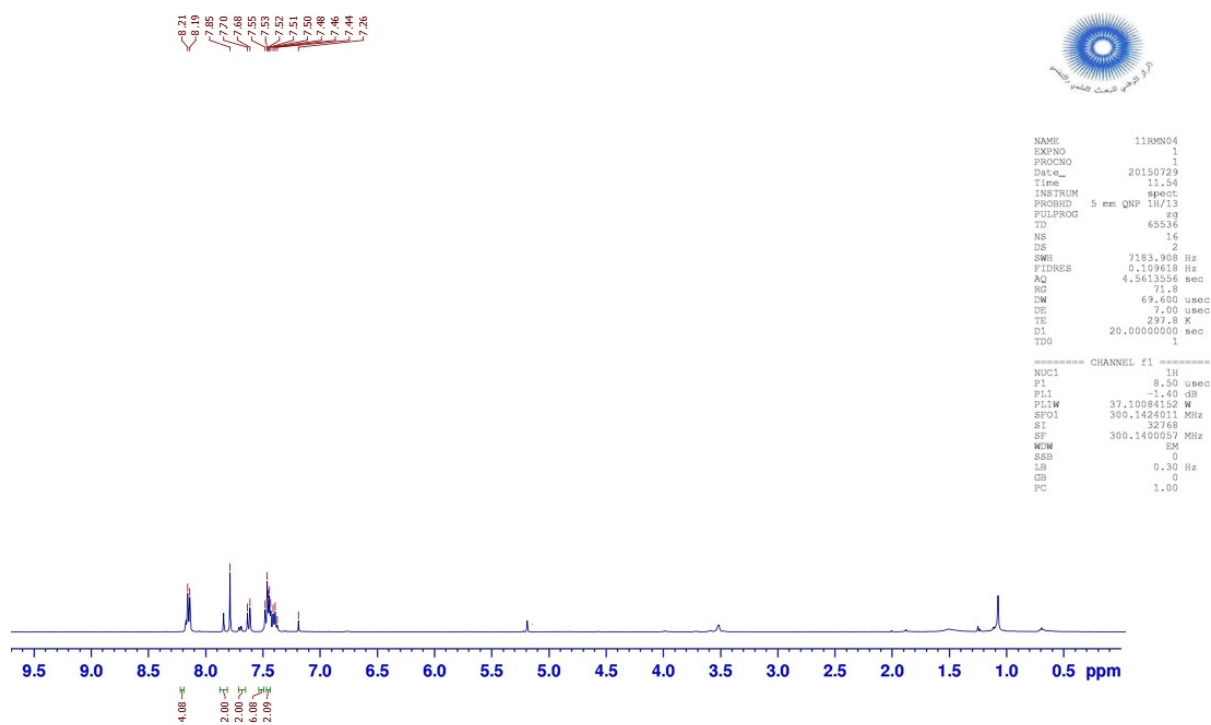


Figure S26. 1H NMR spectrum of 4-(4-chlorophenyl)-2,6-diphenylpyridine (**5a**).

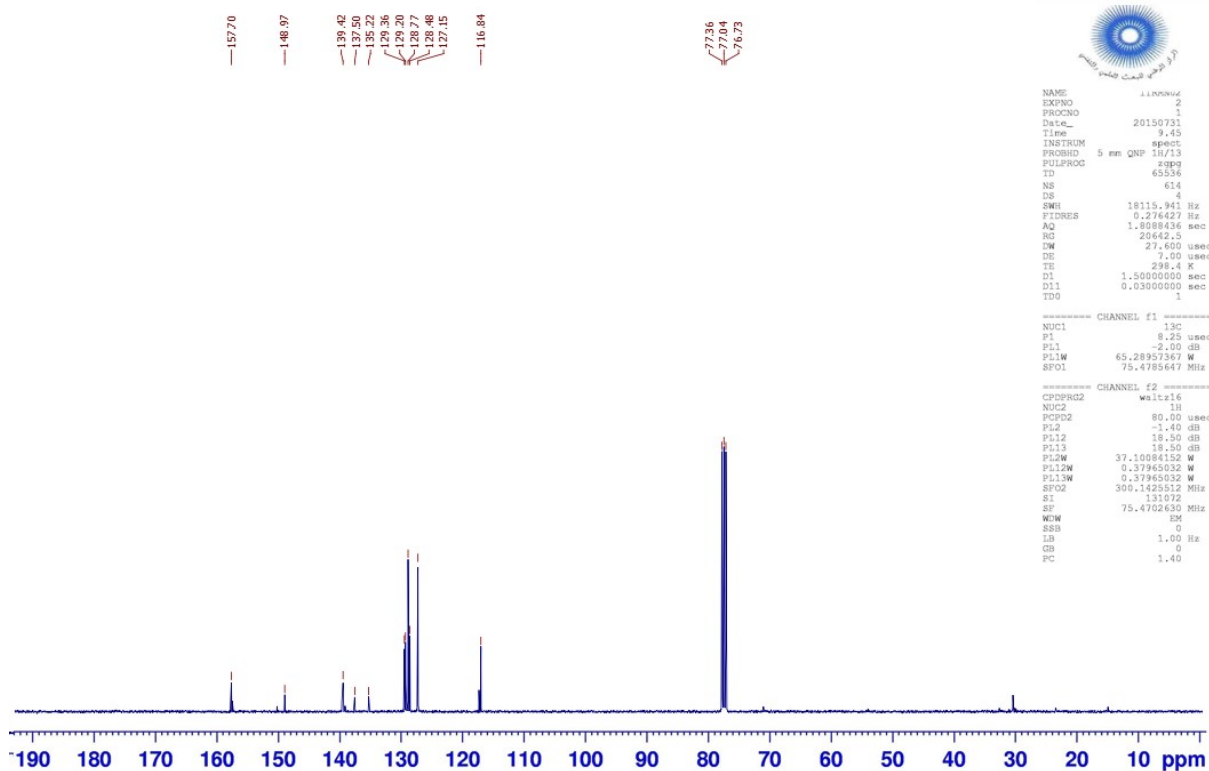


Figure S27. ^{13}C NMR spectrum of 4-(4-chlorophenyl)-2,6-diphenylpyridine (**5a**)

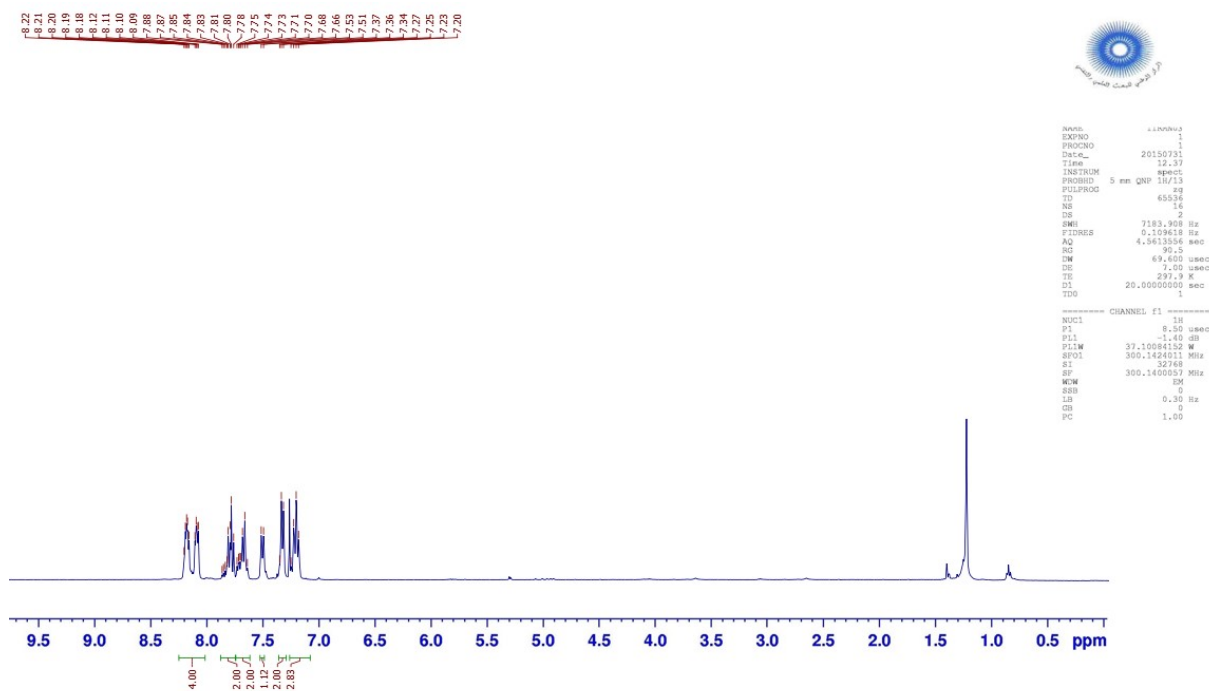


Figure S28. ^1H NMR spectrum of 2,4,6-tri(4-chlorophenyl)pyridine (**5b**).

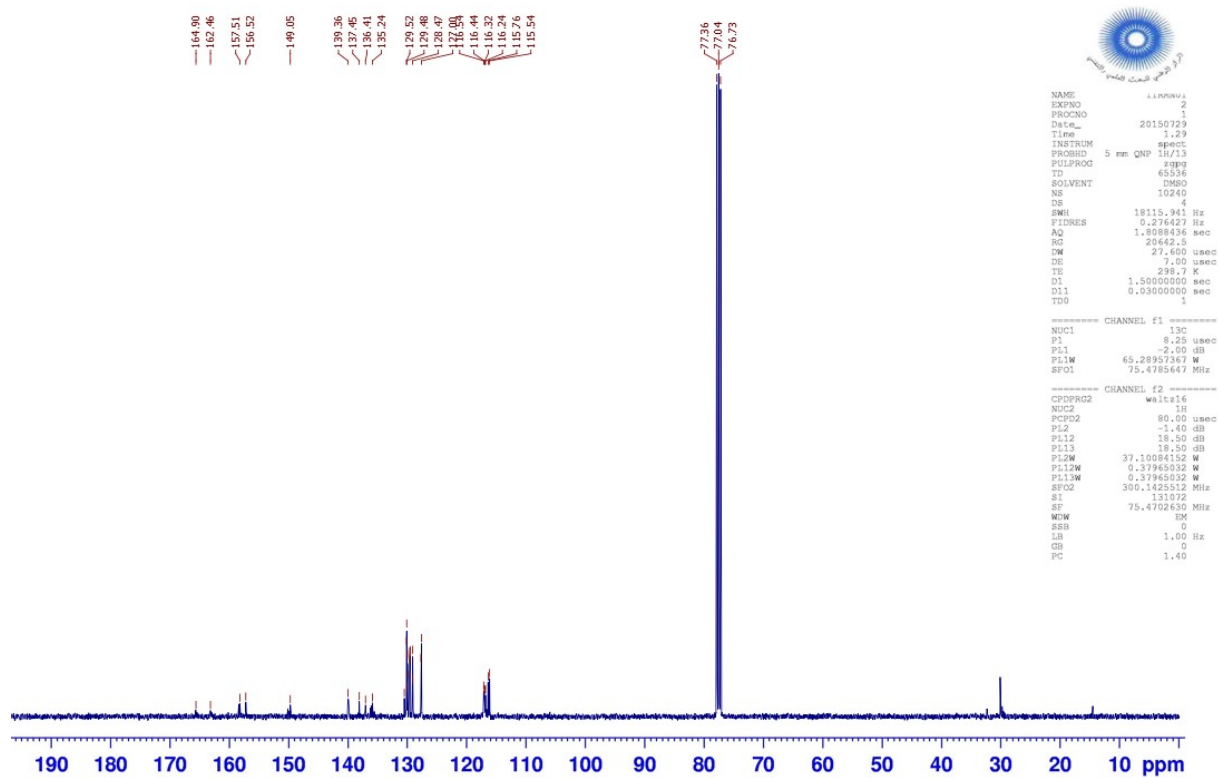


Figure S29. ^{13}C NMR spectrum of 2,4,6-tri(4-chlorophenyl)pyridine (**5b**).

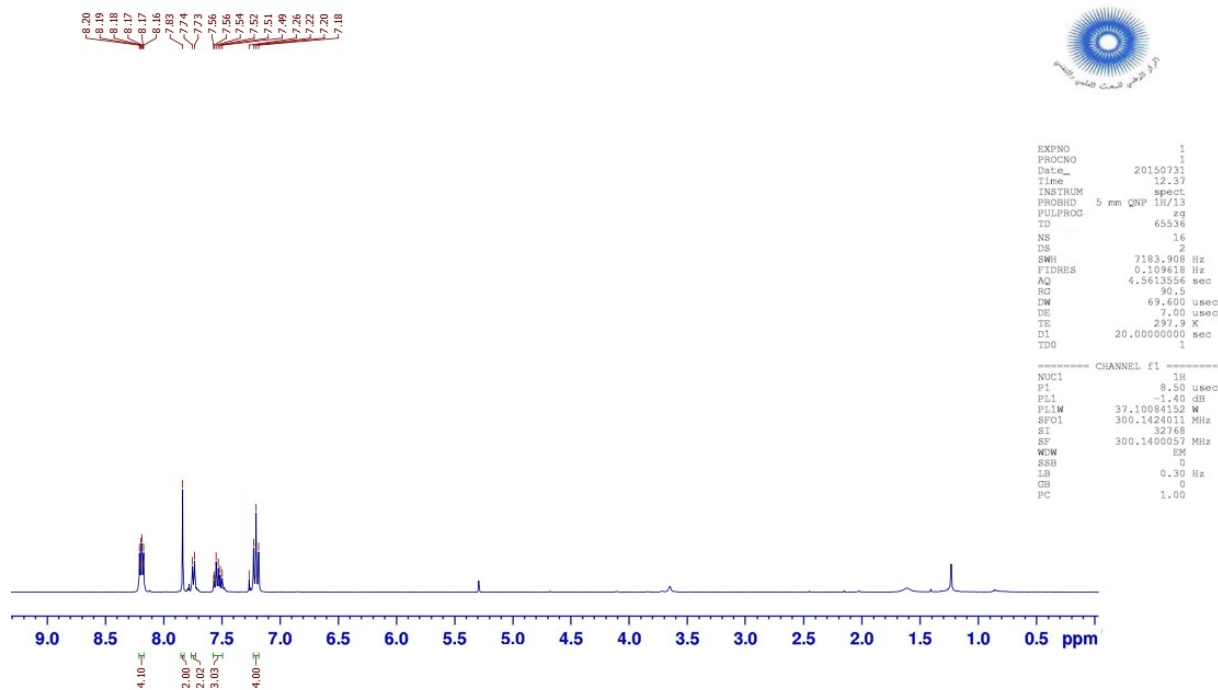


Figure S30. ^1H NMR spectrum of 4-(4-chlorophenyl)-2,6-bis(*p*-nitrophenyl)pyridine (**5d**).

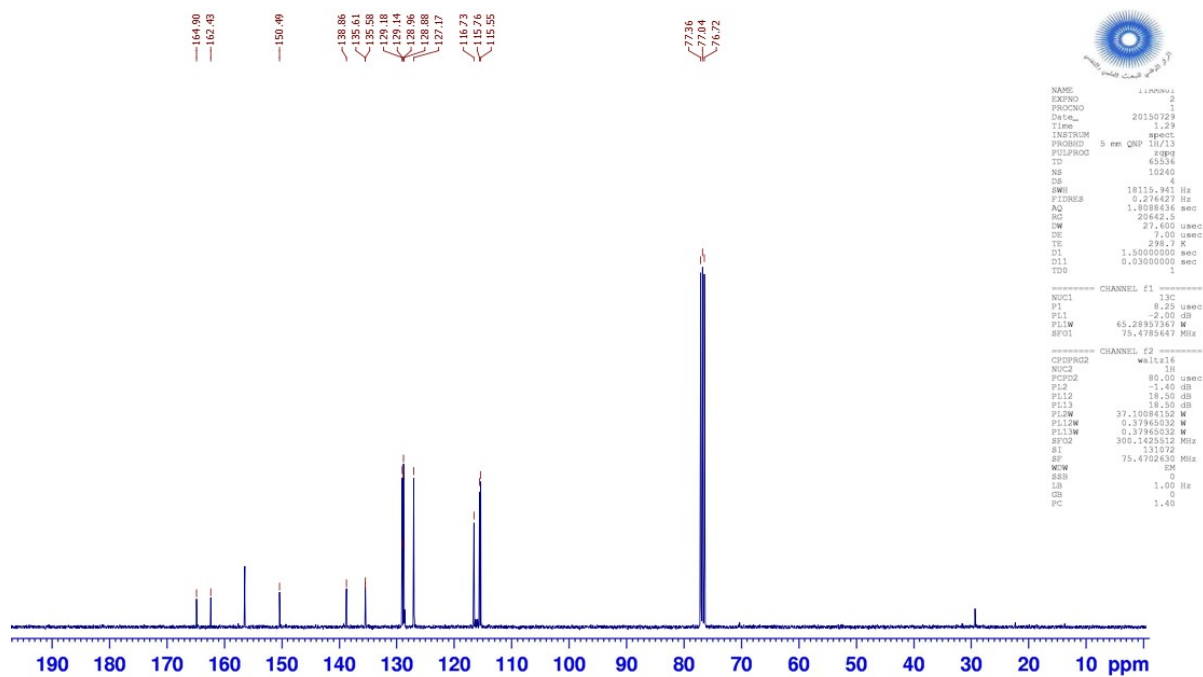


Figure S31. ^{13}C NMR spectrum of 4-(4-chlorophenyl)-2,6-bis(*p*-nitrophenyl)pyridine (**5d**).

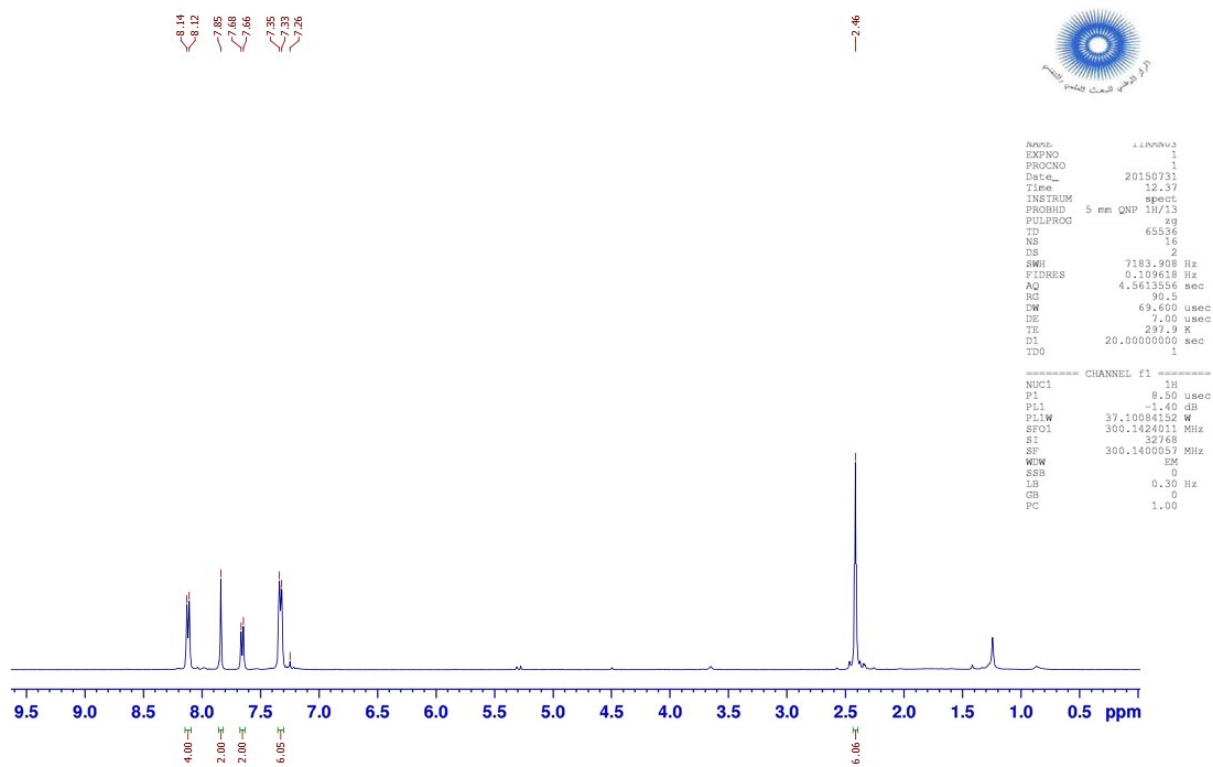


Figure S32. ^1H NMR spectrum of 4-(4-chlorophenyl) 2,6-ditolylypyridine (**5f**).

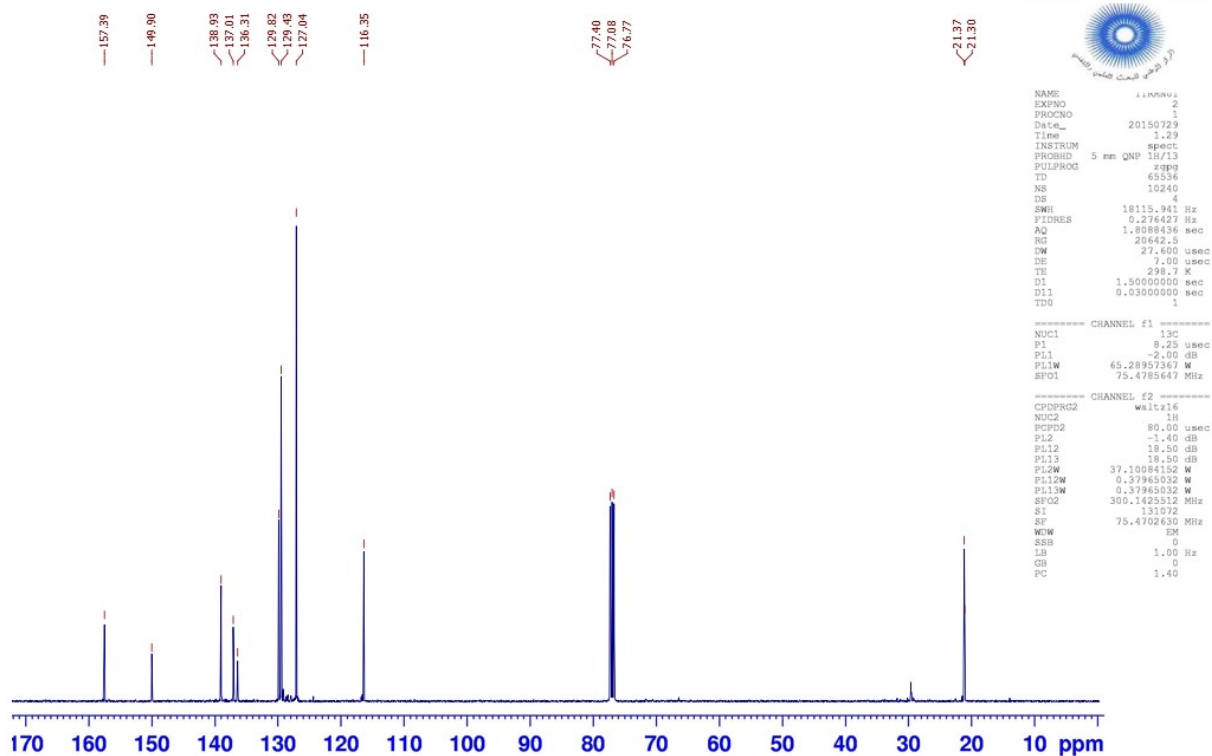


Figure S33. ¹³C NMR spectrum of 4-(4-chlorophenyl) 2,6-ditolylypyridine (**5f**).

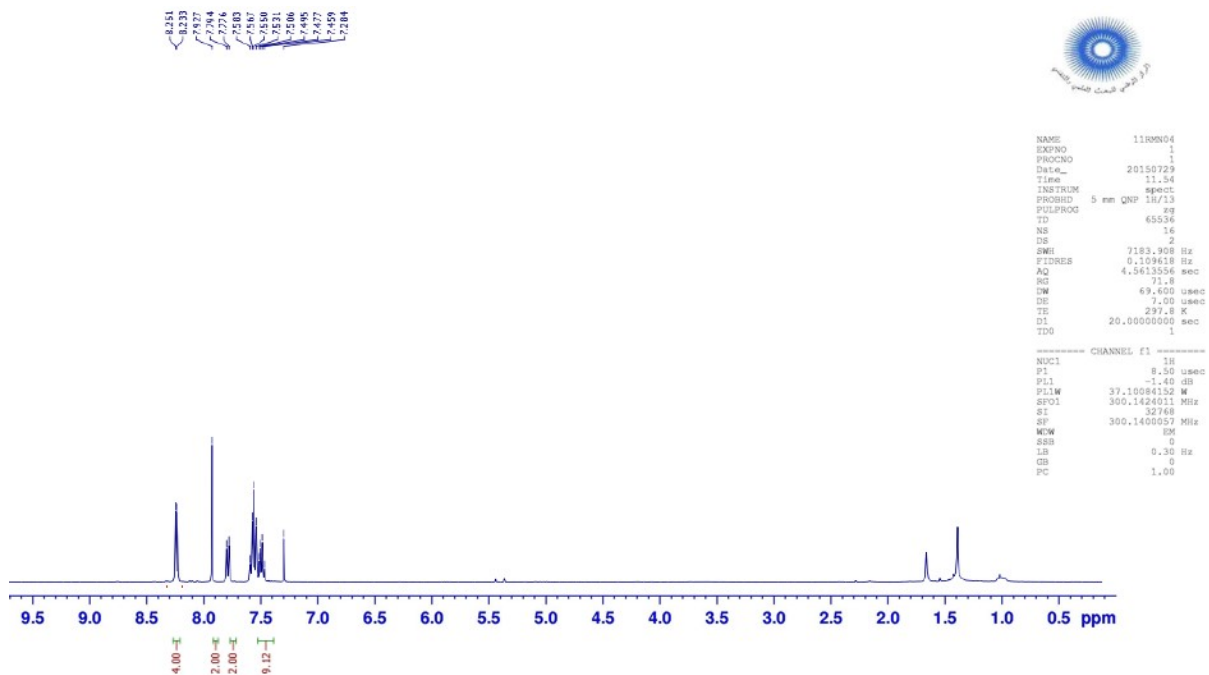


Figure S34. ¹H NMR spectrum of 2,4,6-triphenylpyridine (**5g**).

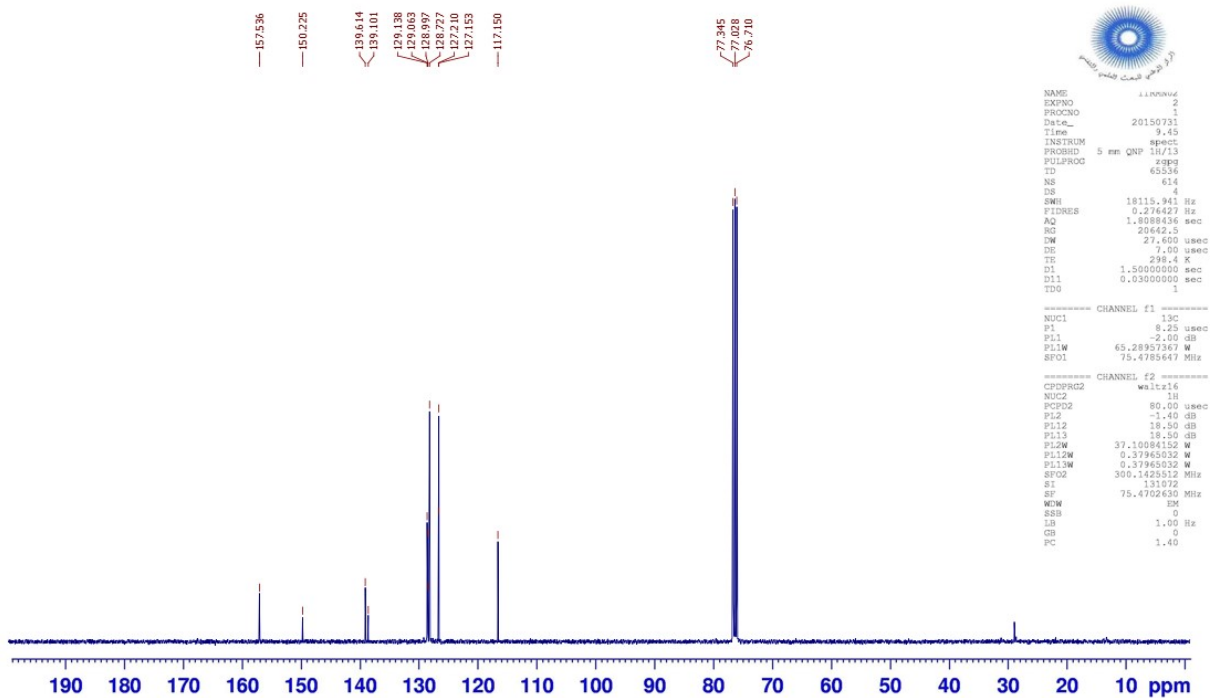


Figure S35. ¹³C NMR spectrum of 2,4,6-triphenylpyridine (**5g**)

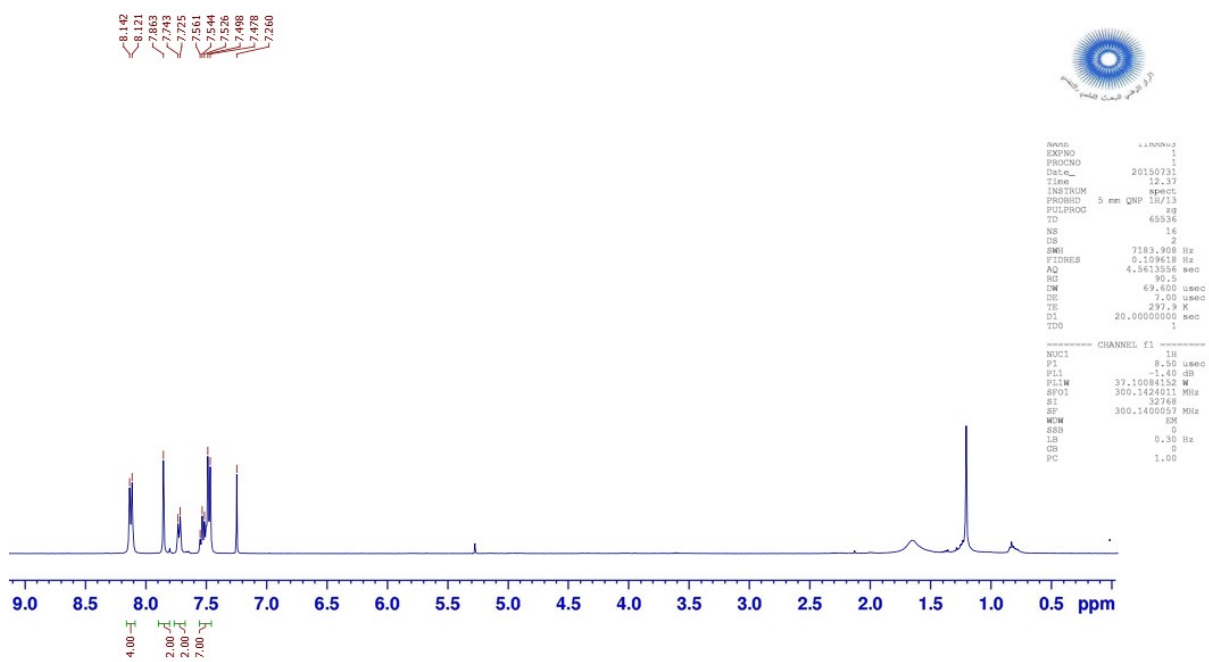


Figure S36. ¹H NMR spectrum of 2,6-di(4-chlorophenyl)-4-phenylpyridine (**5h**)

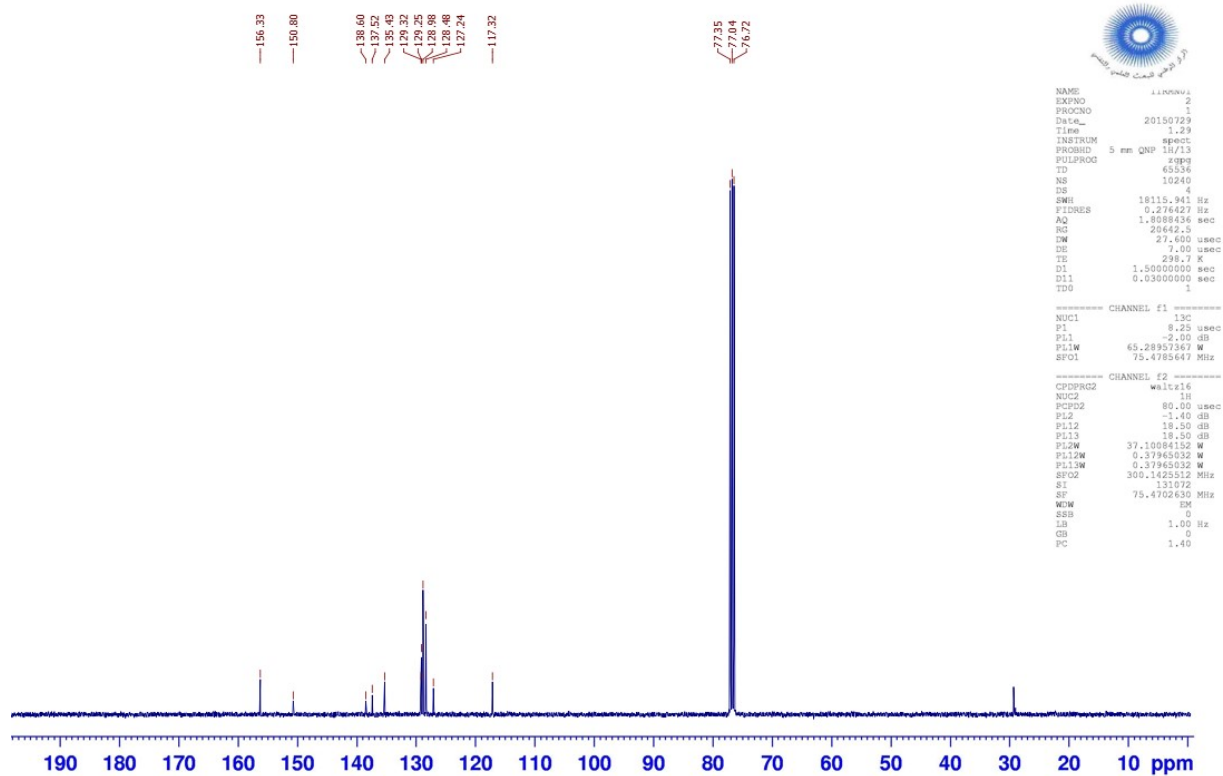


Figure S37. ¹³C NMR spectrum of 2,6-di(4-chlorophenyl)-4-phenylpyridine (**5h**)

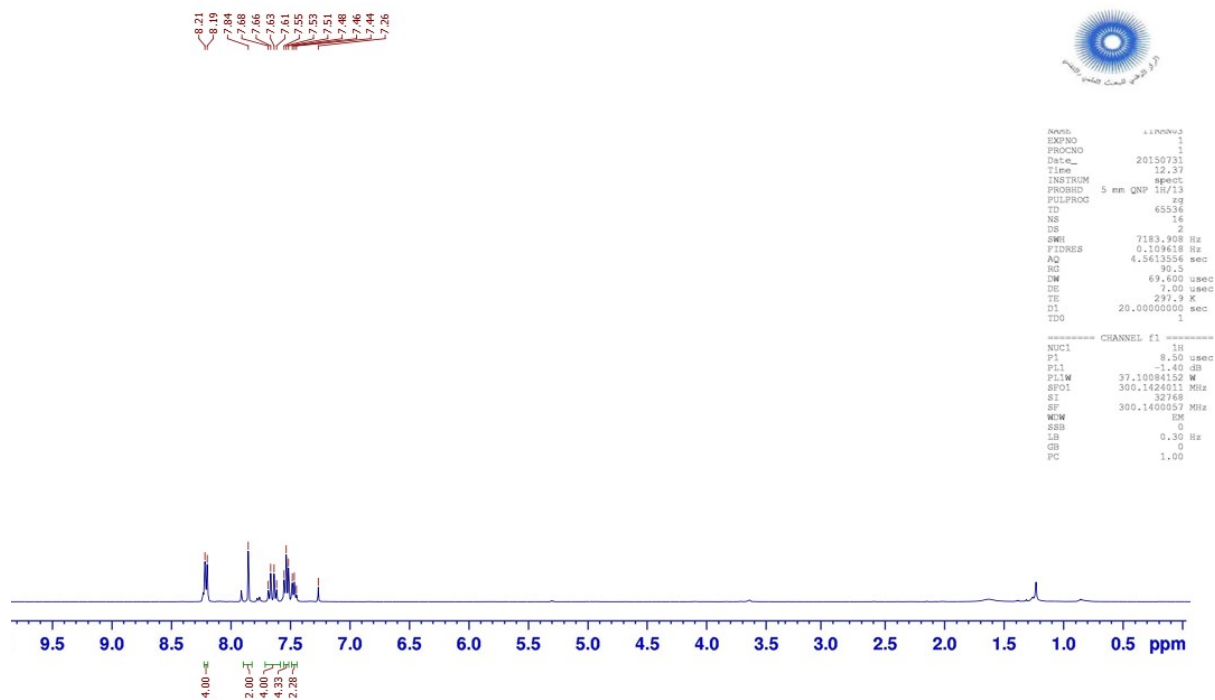


Figure S38. ¹H NMR spectrum of 4-(4-nitrophenyl)-2,6-diphenylpyridine (**5k**)

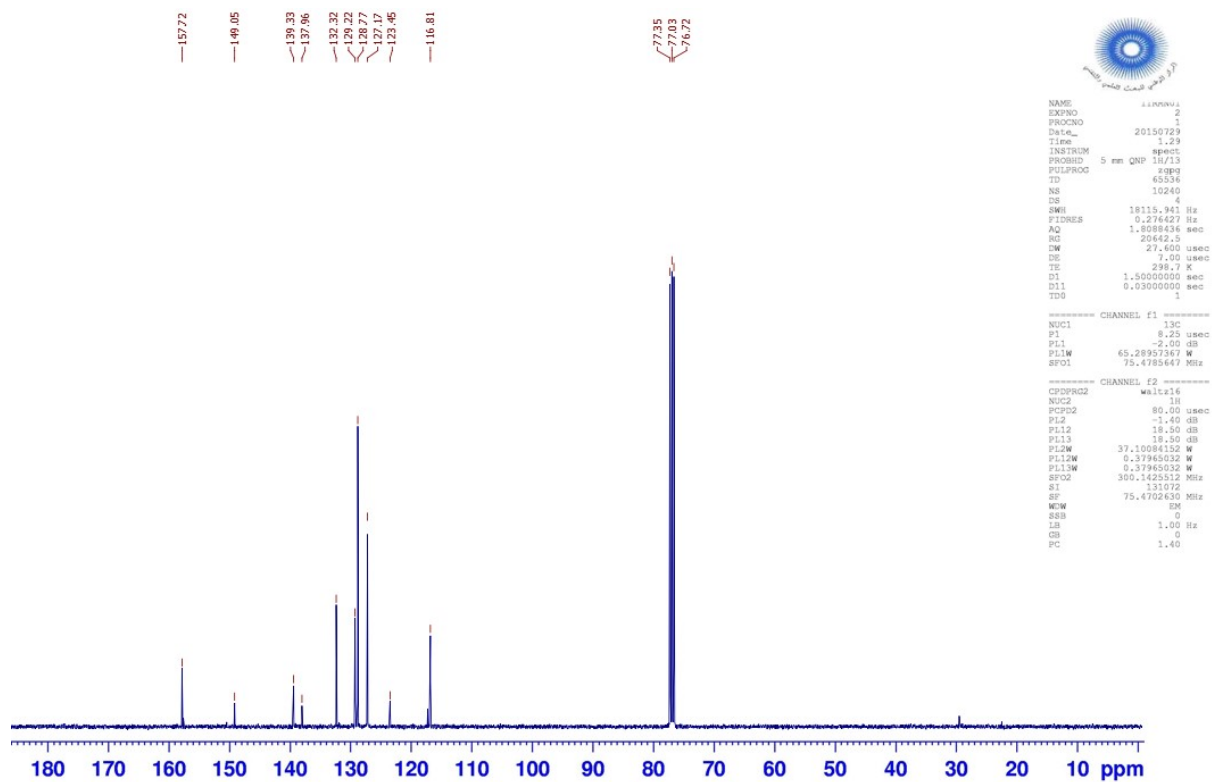


Figure S39. ^{13}C NMR spectrum of 4-(4-nitrophenyl)-2,6-diphenylpyridine (**5k**)