

Supplementary Material: TBD- or PS-TBD- Catalyzed One-Pot Synthesis of Cyanohydrin Carbonates and Cyanohydrin Acetates from Carbonyl Compounds

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Instrumentation and Chemicals (S1)
Experimental procedure S1
Copies of ¹H- and ¹³C-NMR Spectra of products S2

1. Instrumentation and Chemicals

IR spectra were recorded on a JUSCO FT/IR-430 spectrometer (JASCO Corporation, Tokyo, Japan). ¹H-NMR spectra were determined for solutions in CDCl₃ with Me₄Si as internal standard (CDCl₃: 7.24 ppm, Me₄Si: 0.00 ppm) on a Bruker Avance III instrument (Bruker Corporation, Billerica, MA, USA). ¹³C-NMR spectra were determined for solutions in CDCl₃ with Me₄Si as internal standard (CDCl₃: 77.00 ppm, Me₄Si: 0.00 ppm) on a Bruker Avance III instrument (Bruker Corporation). HRMS data were measured on a JEOL JMS-700 mass spectrometer (JEOL Ltd., Tokyo, Japan).

All reactions were performed under an argon atmosphere using oven-dried glassware. Flash column chromatography was performed using silica gel Wakogel C-200 (Wako Chemical, Osaka, Japan). Dehydrate DMF, THF, toluene and CH₃CN were purchased from Kanto Kagaku (Tokyo, Japan) as the “anhydrous” and stored over 4A molecular sieves under Ar. Other commercially available reagent was used as received without further purification.

2. General Procedure for TBD-Catalyzed Cyanation Reactions of Carbonyl Compounds with Methyl Cyanofornate

TBD was dried in vacuo before use. To a solution of TBD (0.05 mmol) in CH₃CN (1 mL) was added carbonyl compound (1.0 mmol) and methyl cyanofornate (1.25 mmol) at room temperature. After the reaction was complete (as determined by TLC), the reaction mixture was quenched with water. The resultant mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water and brine and dried with Na₂SO₄. After the filtration, the residue was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (EtOAc:hexane = 1:5 → 1:3) to give the corresponding product.

3. General Procedure for TBD-Catalyzed Cyanation Reactions of Aldehydes with Acetyl Cyanide

TBD was dried in vacuo before use. To a solution of TBD (0.10 mmol) in CH₃CN (1 mL) was added aldehyde (1.0 mmol) and acetyl cyanide (1.5 mmol) at room temperature. After the reaction was complete (as determined by TLC), the reaction mixture was quenched with water. The resultant mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with water and brine and dried with Na₂SO₄. After the filtration, the residue was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (EtOAc:hexane = 1:10 → 1:5) to give the corresponding product.

4. General Procedure for PS-TBD Catalyzed Cyanation Reactions of Carbonyl Compounds with Methyl Cyanofornate

To a solution of PS-TBD (0.10 mmol) in CH₃CN (1 mL) was added carbonyl compound (1.0 mmol) and methyl cyanofornate (1.25 mmol) at room temperature. After the reaction was complete (as determined by TLC), EtOAc (10 mL) was added to the mixture and PS-TBD was separated by filtration. The filtrate was washed with water and brine and dried with Na₂SO₄. After

the filtration, the residue was concentrated in vacuo. The crude product was purified by column chromatography on silica gel (EtOAc:hexane = 1:5 → 1:3) to give the corresponding product.

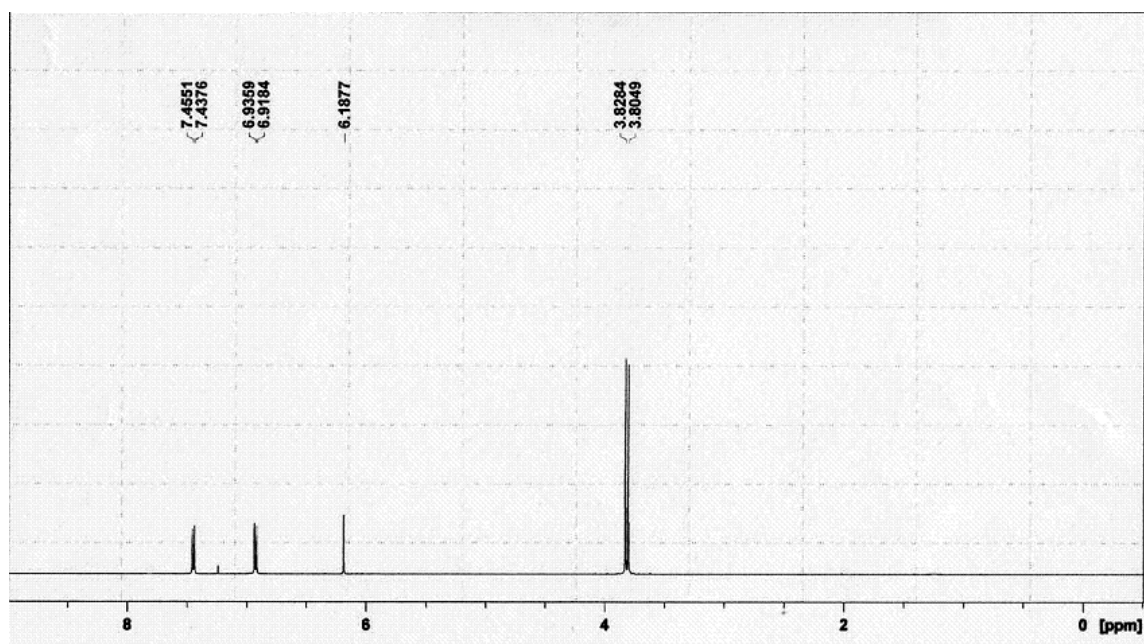


Figure S1. ¹H-NMR Spectrum of compound 2a.

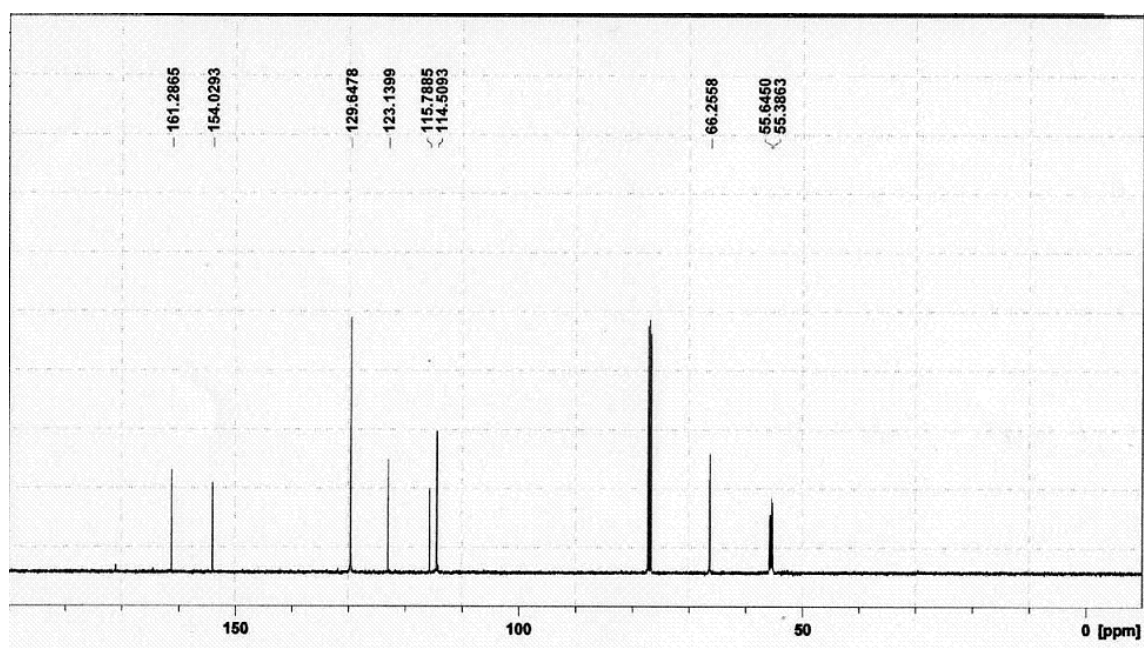
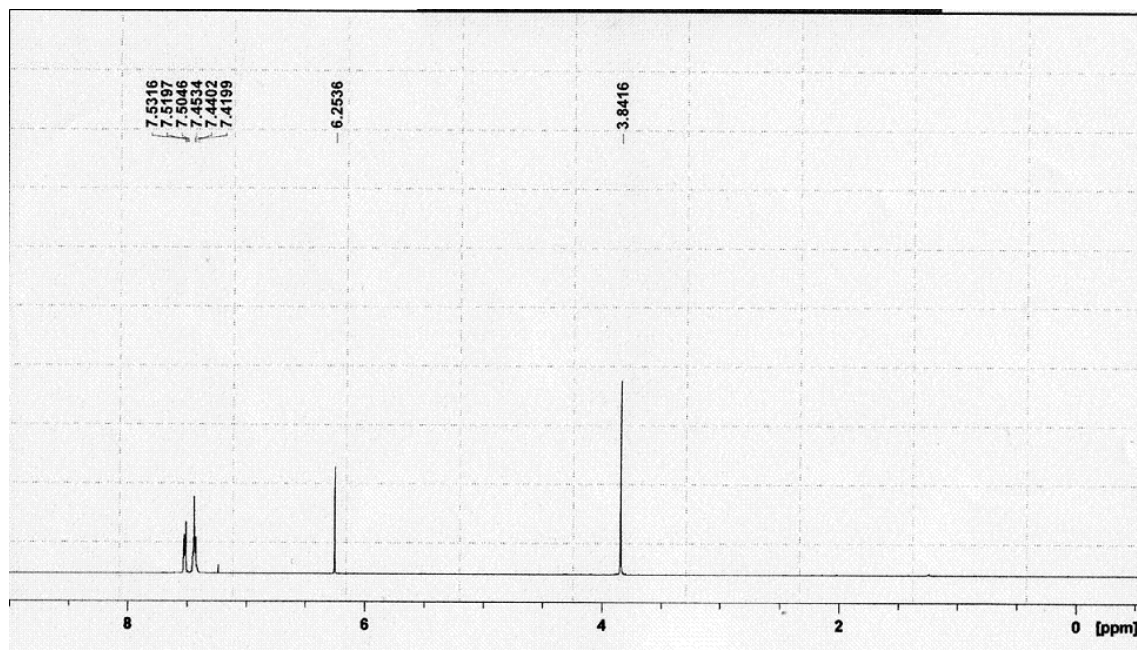
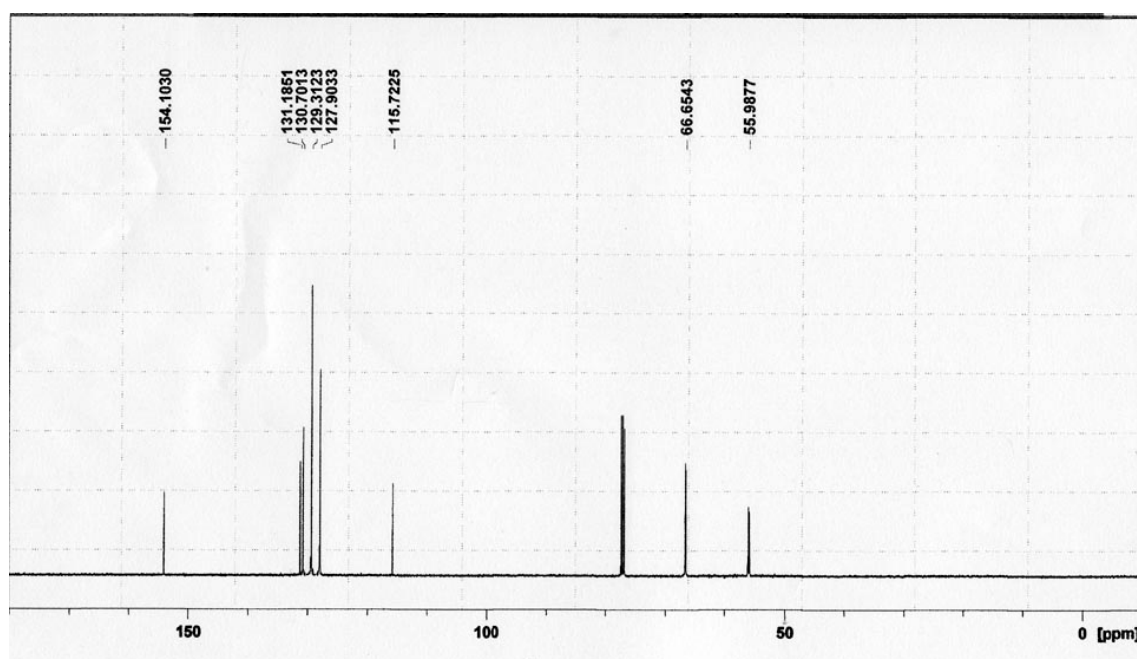
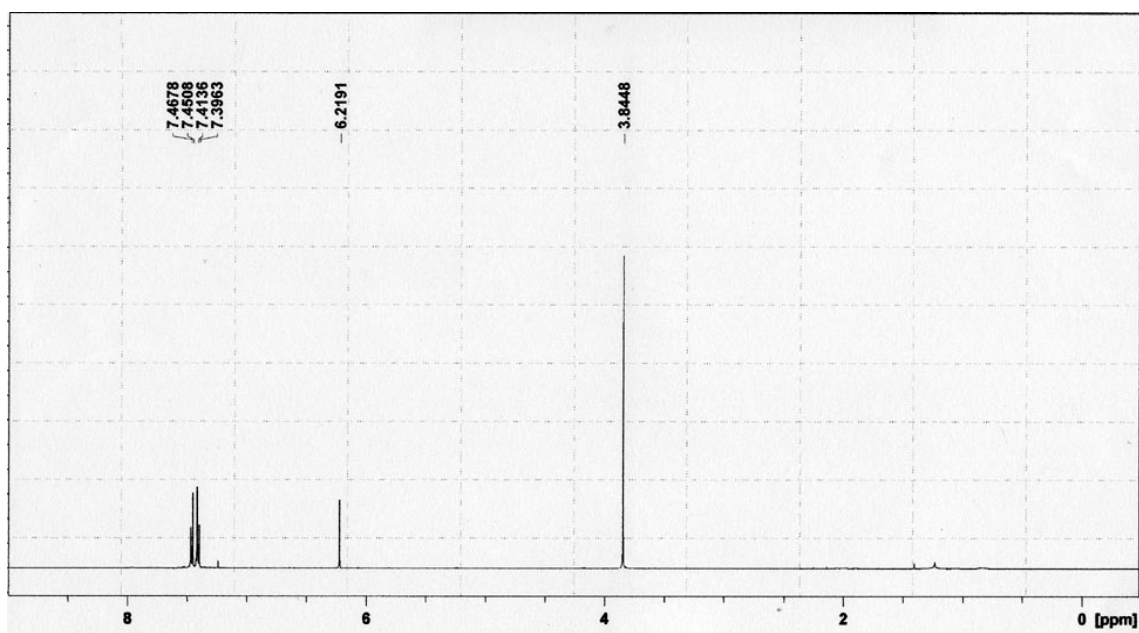
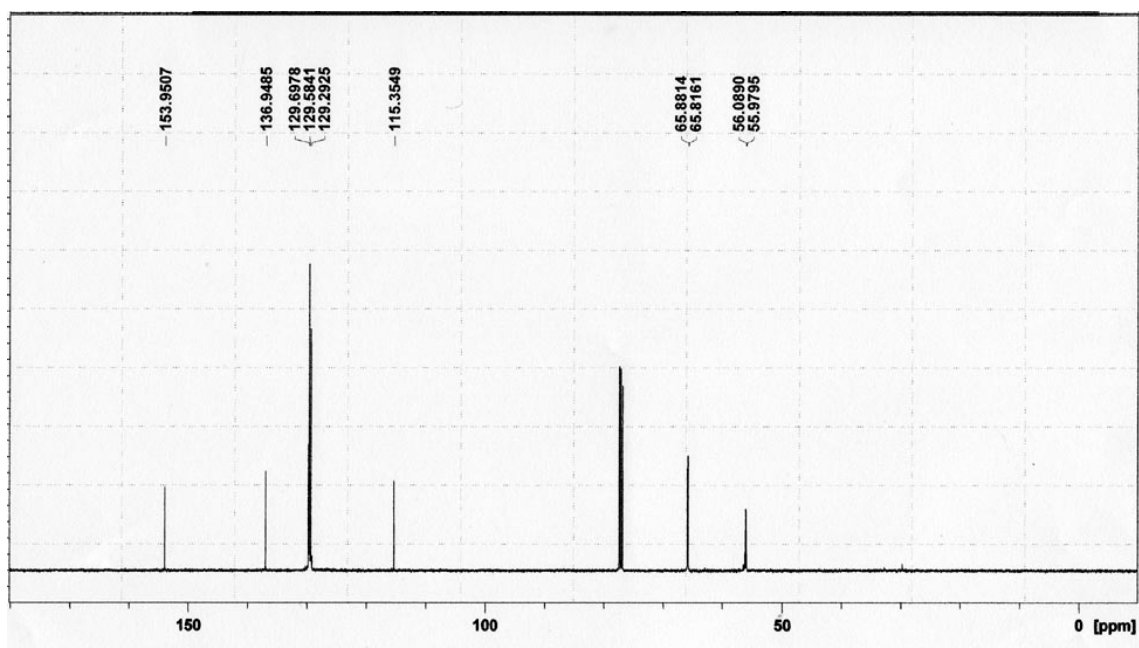
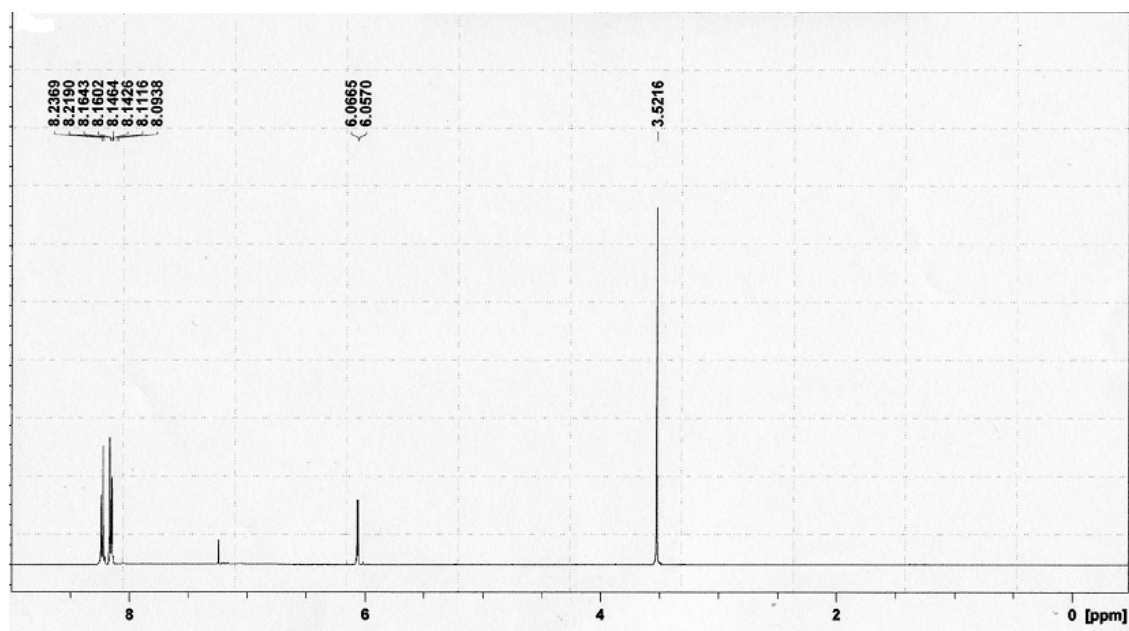
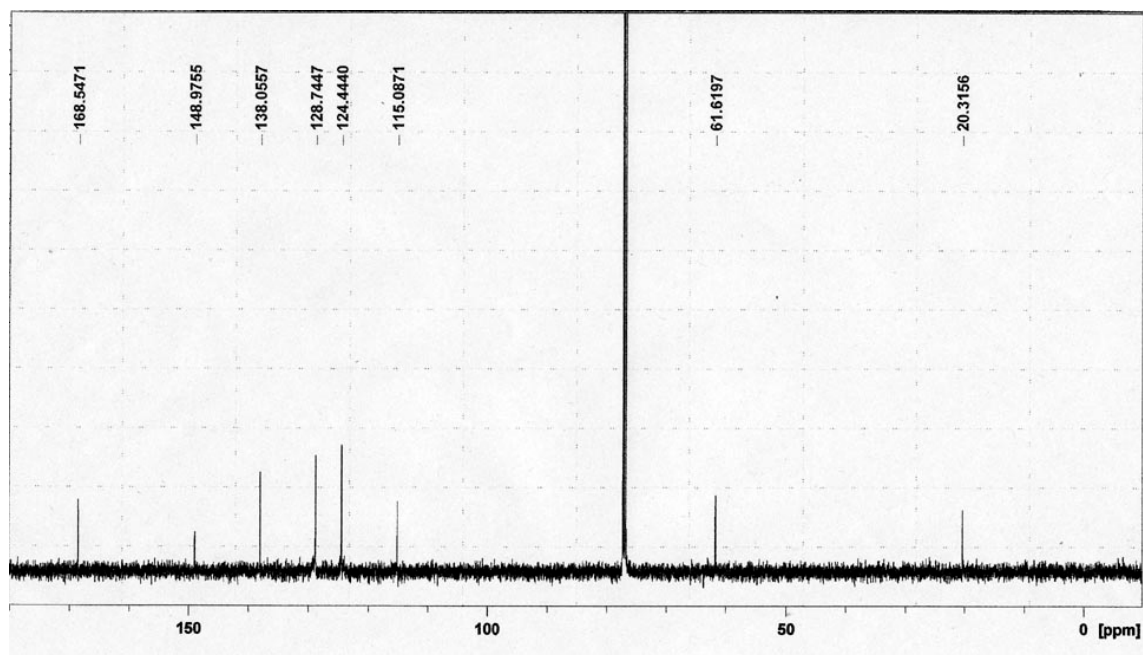
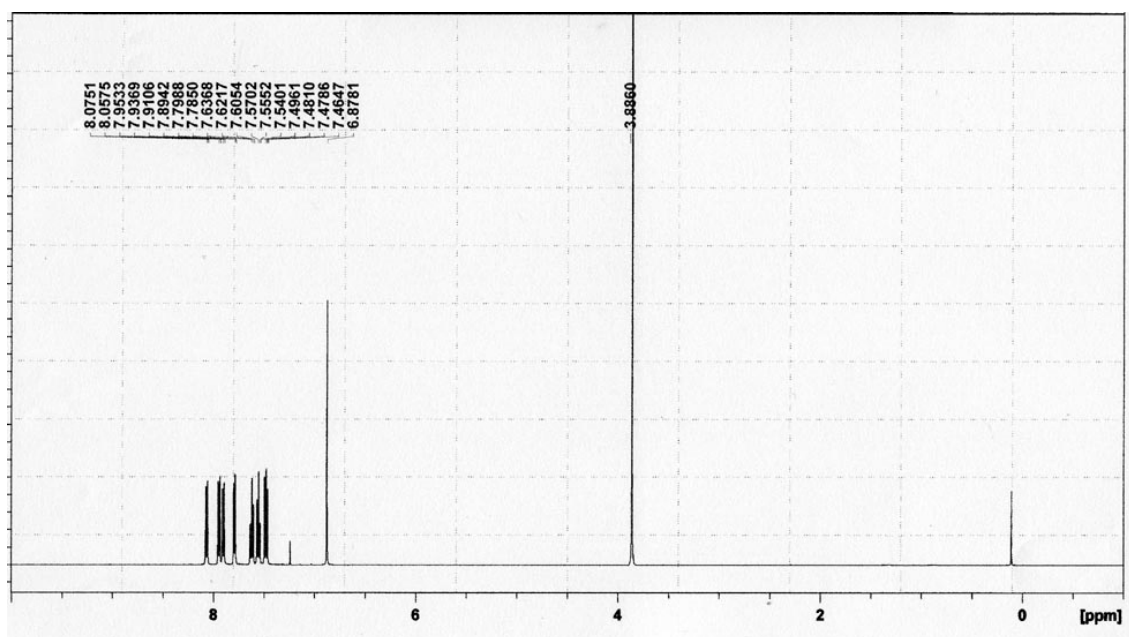
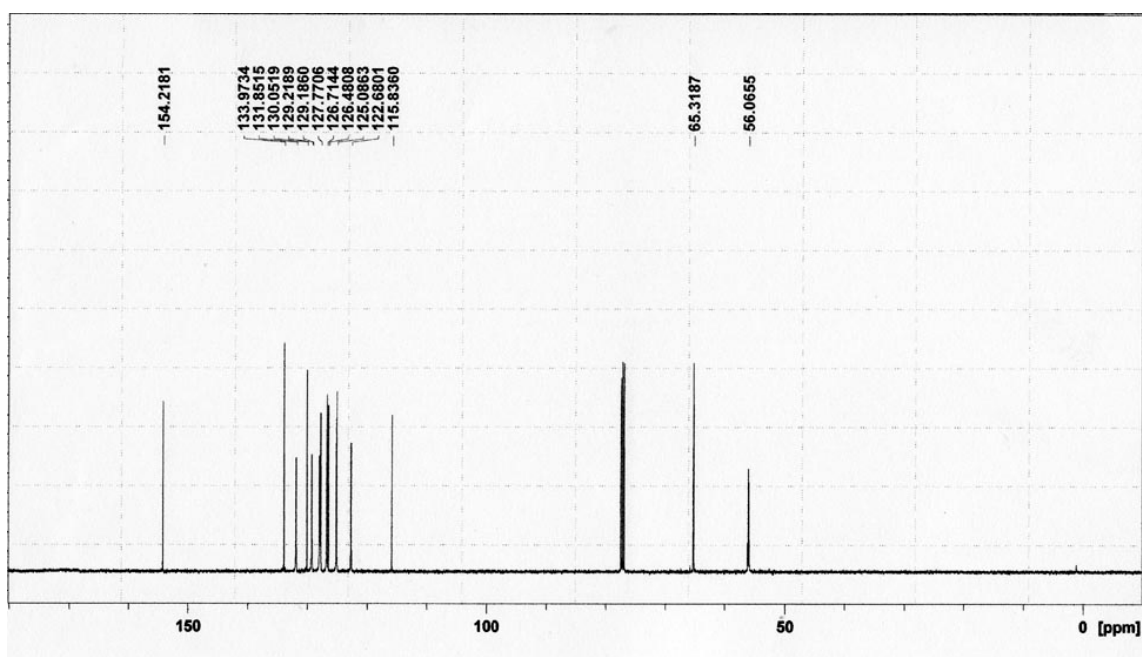


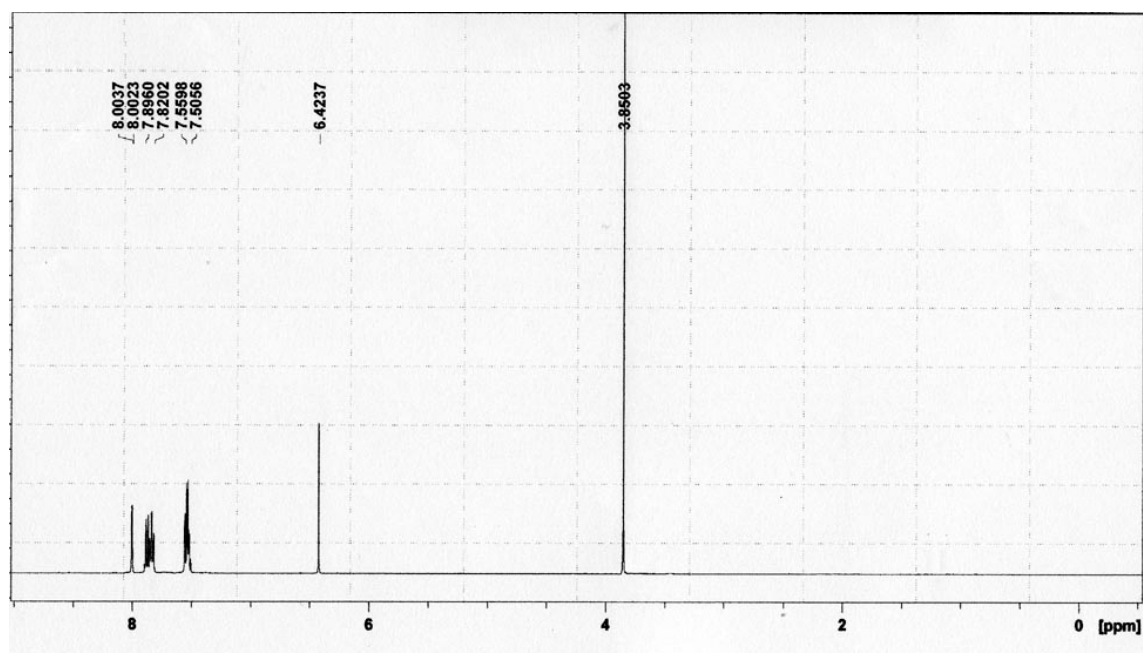
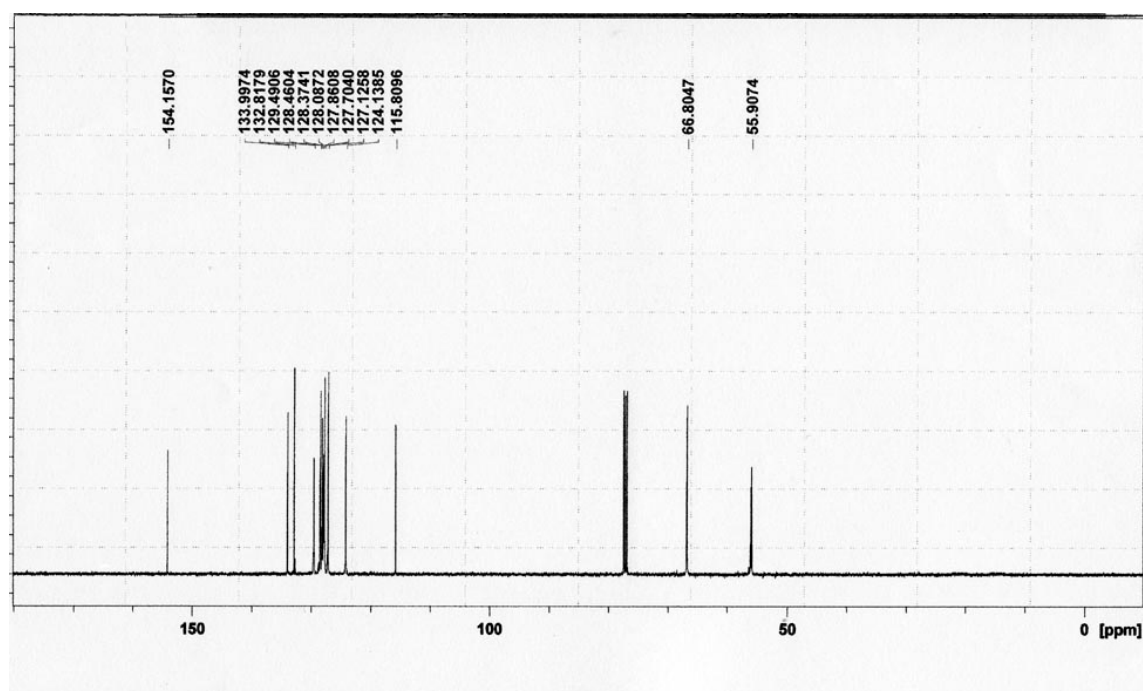
Figure S2. ¹³C-NMR Spectrum of compound 2a.

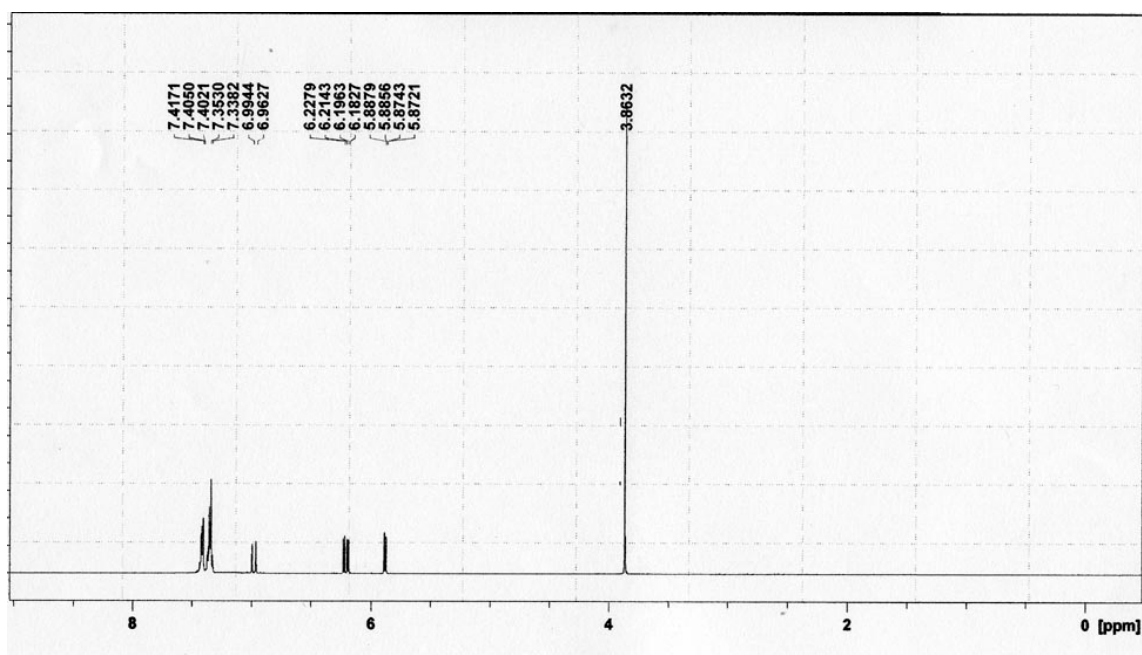
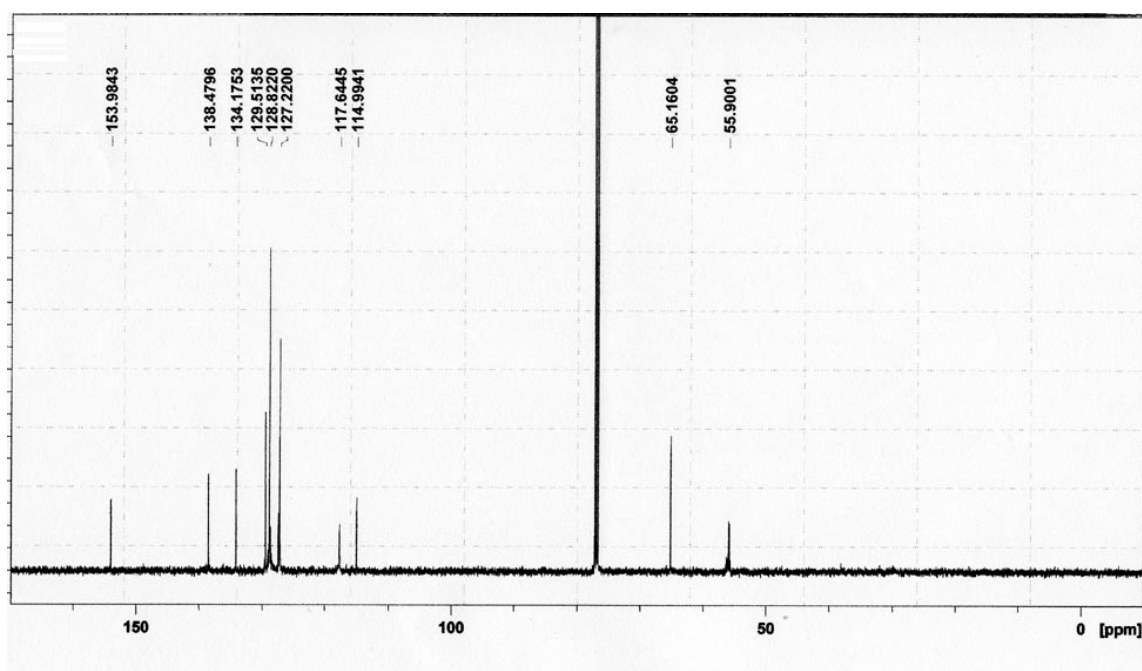
Figure S3. ¹H-NMR Spectrum of compound 2b.Figure S4. ¹³C-NMR Spectrum of compound 2b.

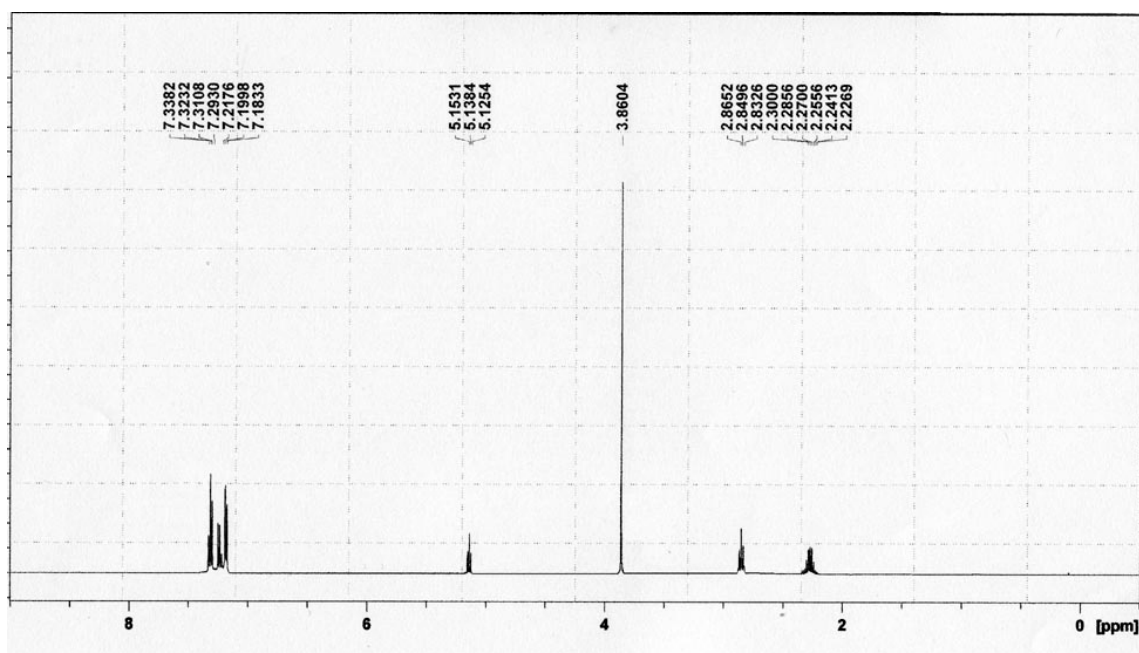
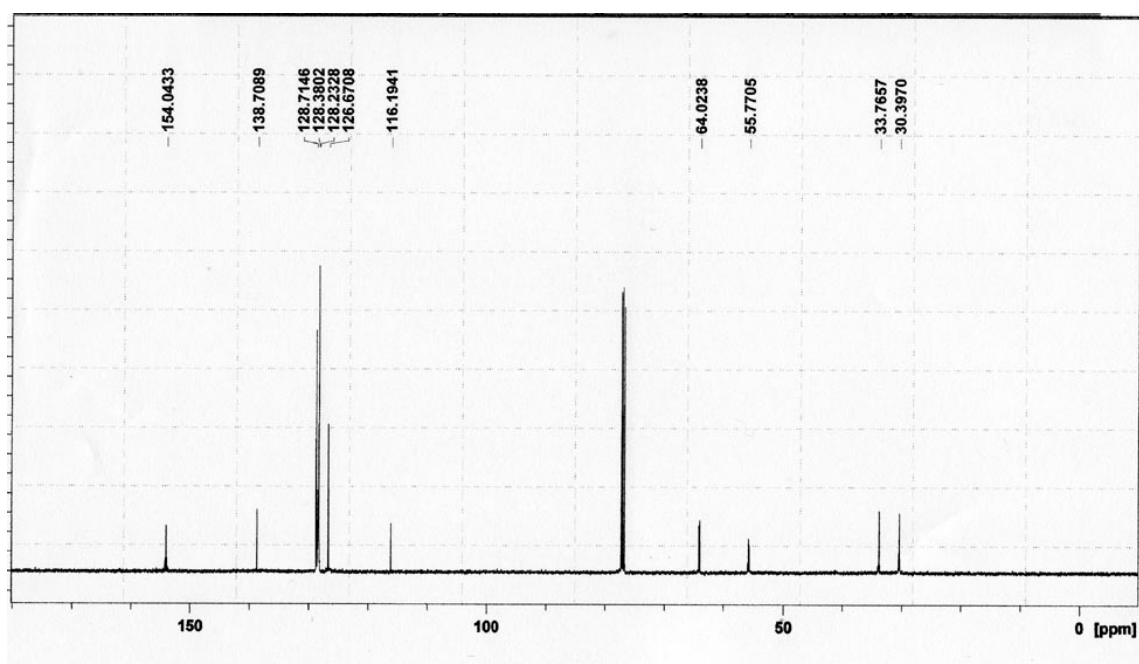
Figure S5. ¹H-NMR Spectrum of compound 2c.Figure S6. ¹³C-NMR Spectrum of compound 2c.

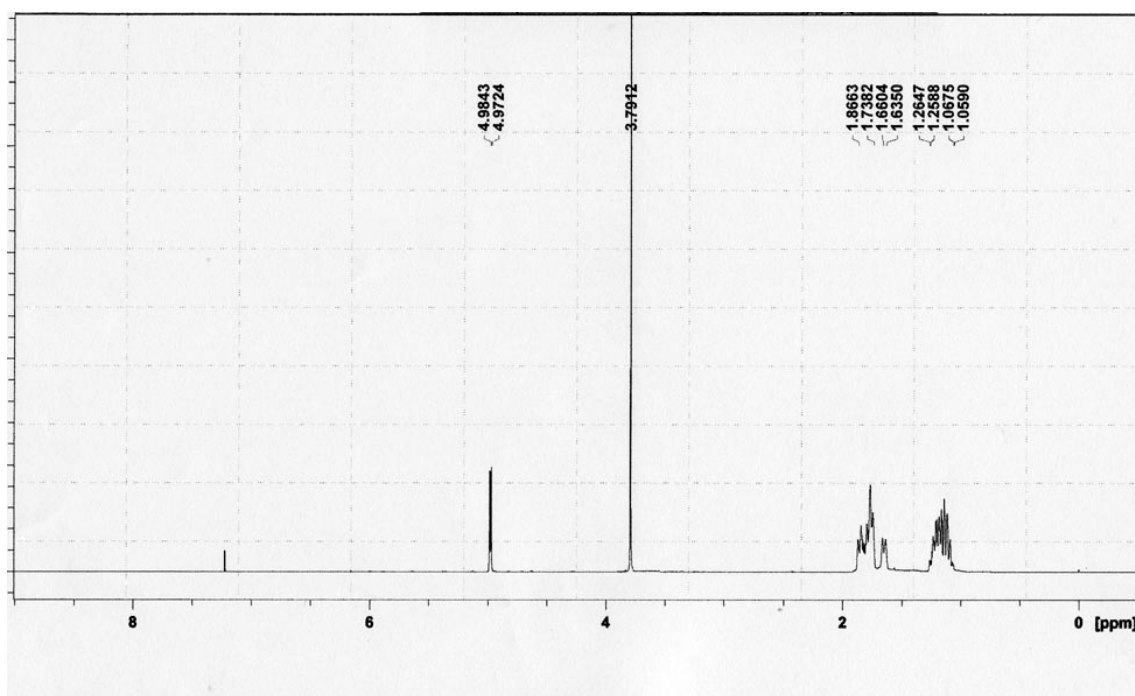
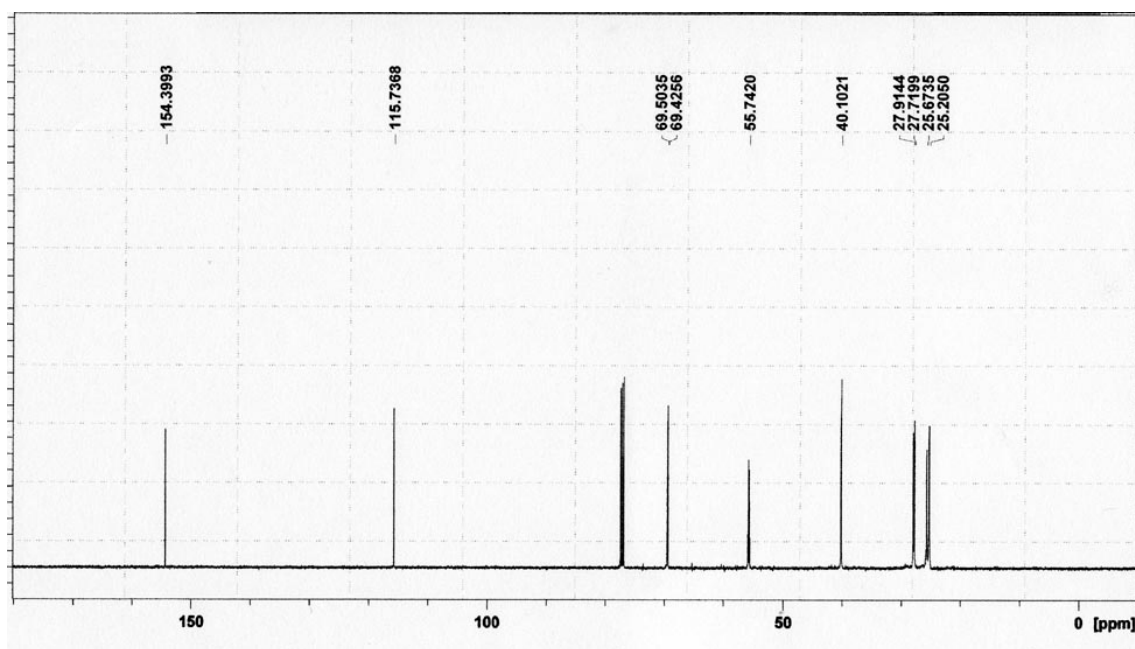
Figure S7. ¹H-NMR Spectrum of compound 2d.Figure S8. ¹³C-NMR Spectrum of compound 2d.

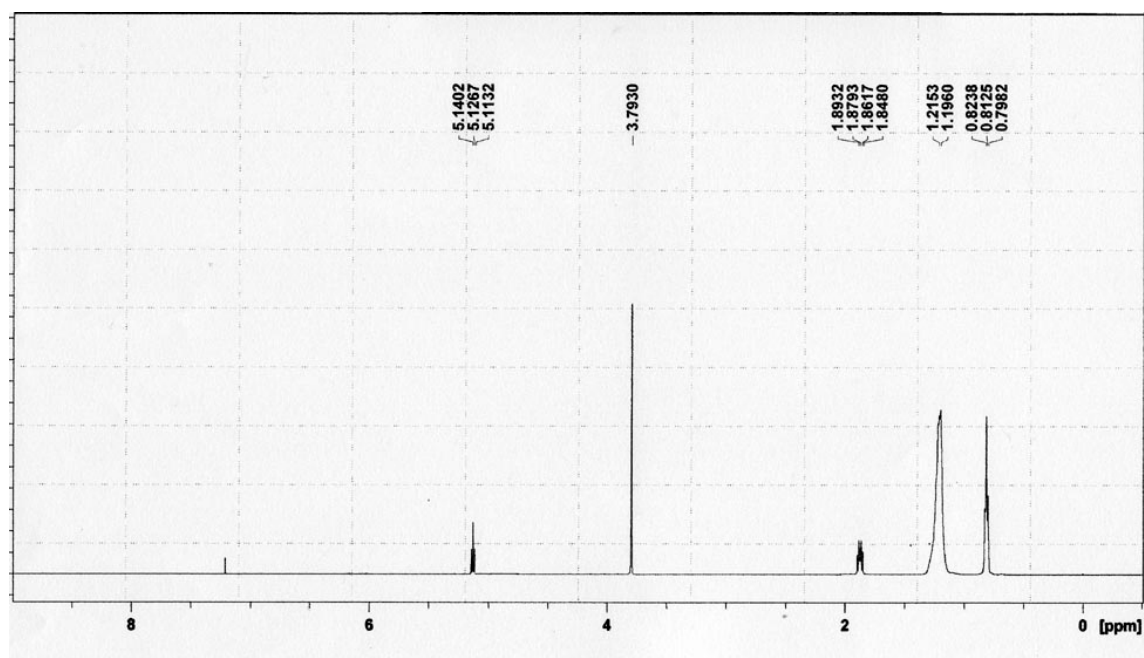
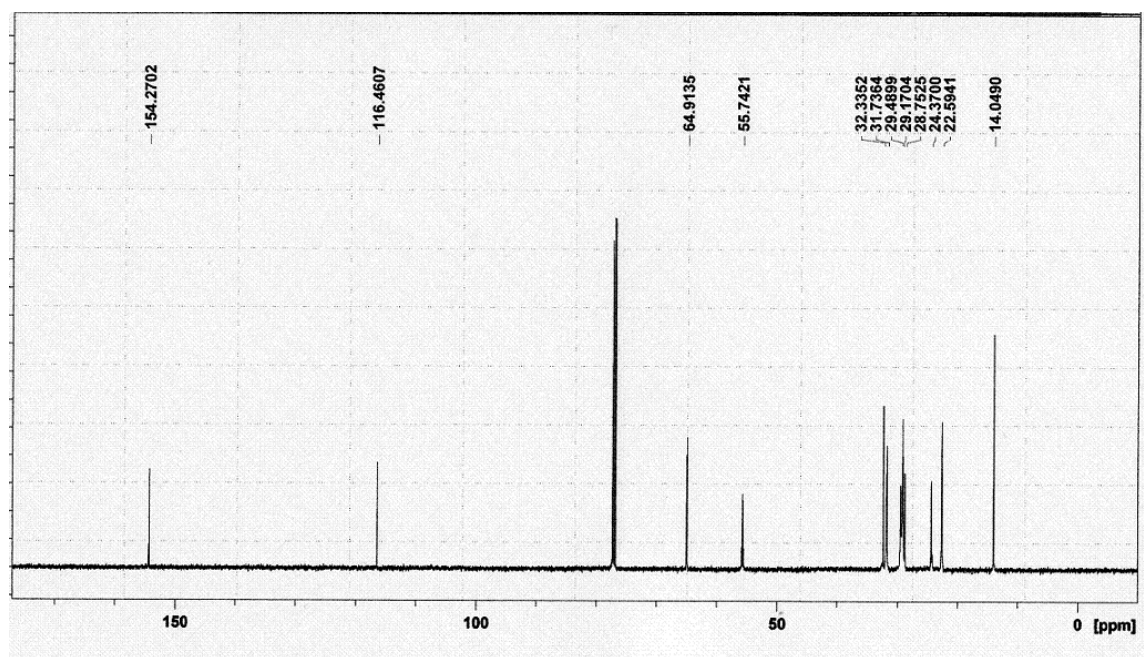
Figure S9. ¹H-NMR Spectrum of compound 2e.Figure S10. ¹³C-NMR Spectrum of compound 2e.

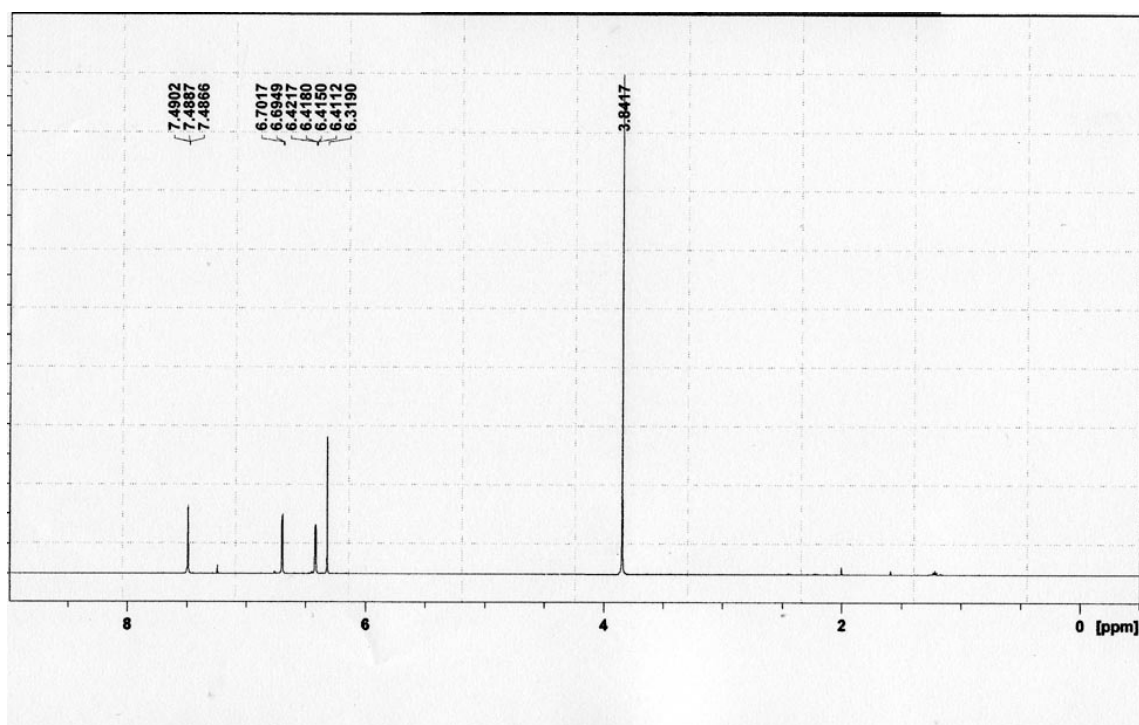
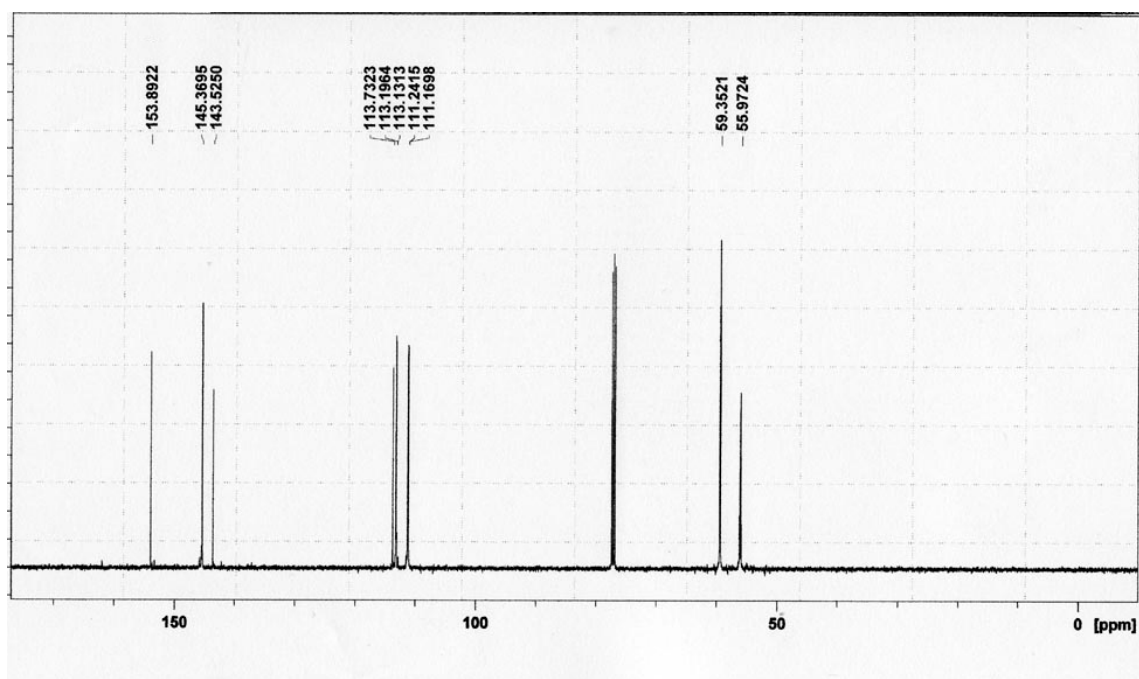
Figure S11. ¹H-NMR Spectrum of compound 2f.Figure S12. ¹³C-NMR Spectrum of compound 2f.

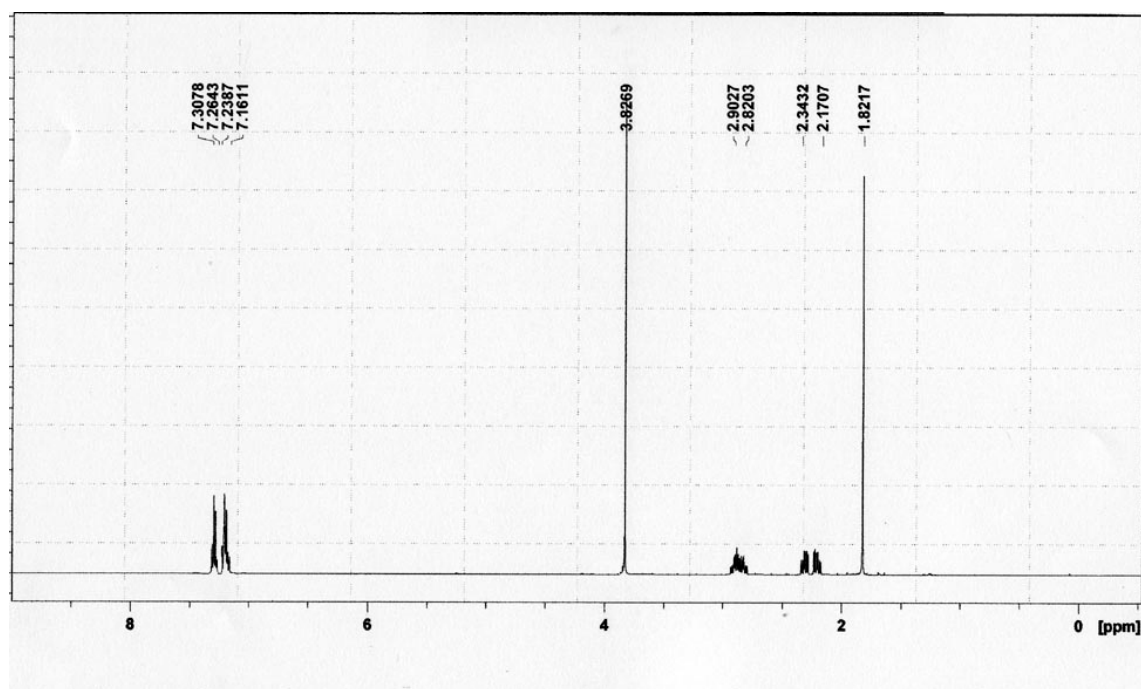
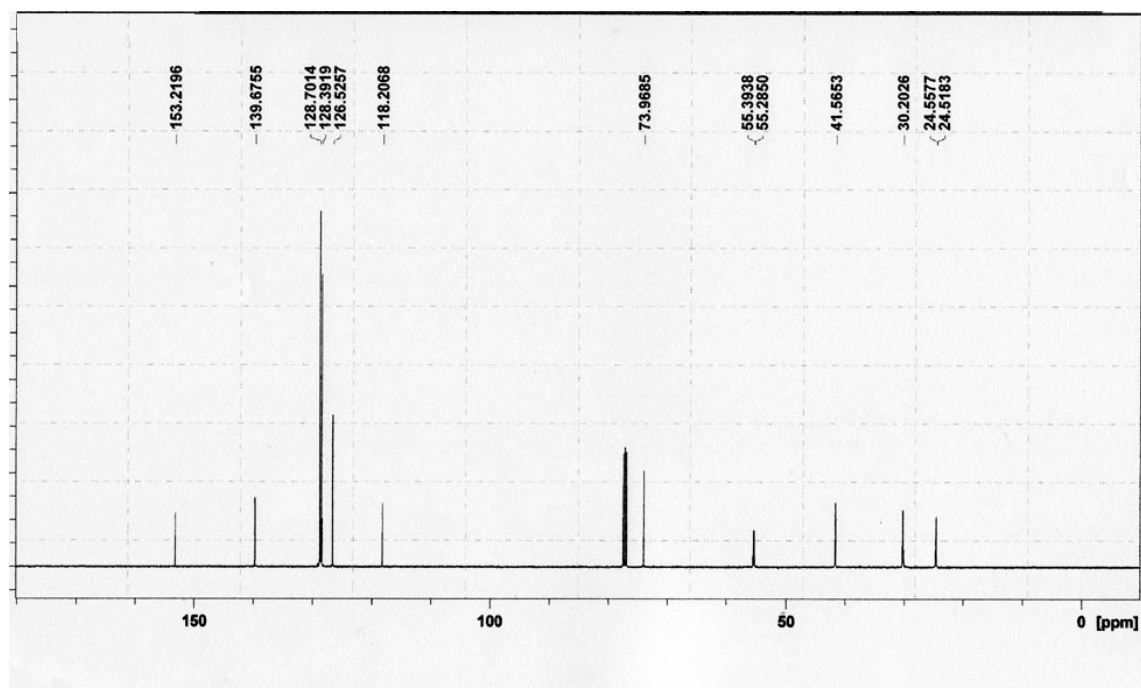
Figure S13. ¹H-NMR Spectrum of compound 2g.Figure S14. ¹³C-NMR Spectrum of compound 2g.

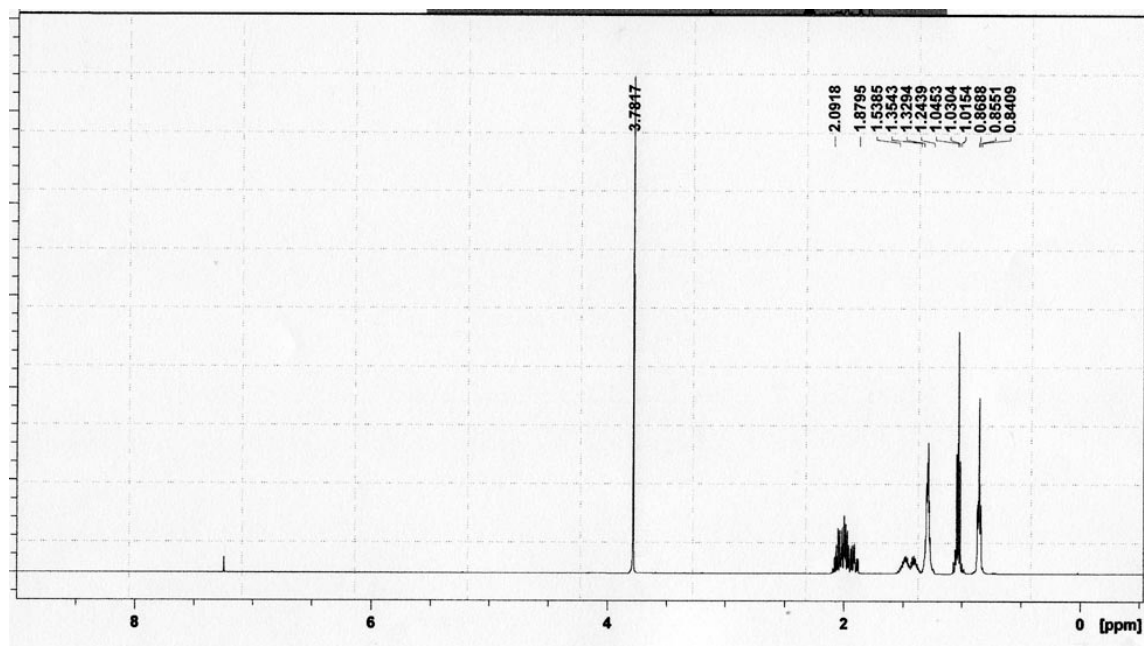
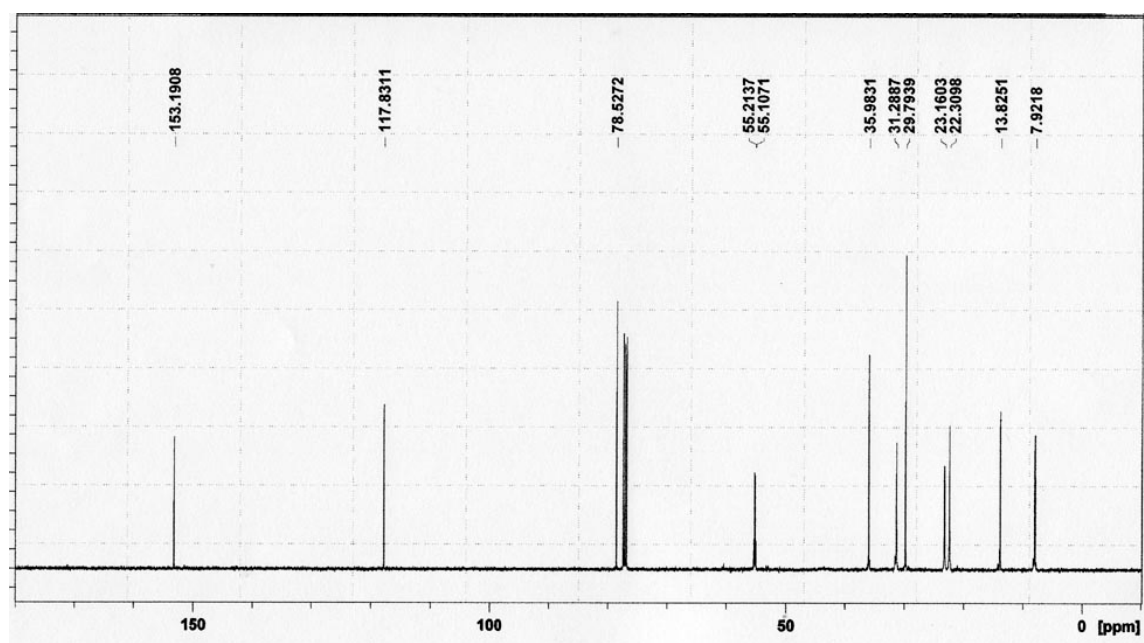
Figure S15. ¹H-NMR Spectrum of compound 2h.Figure S16. ¹³C-NMR Spectrum of compound 2h.

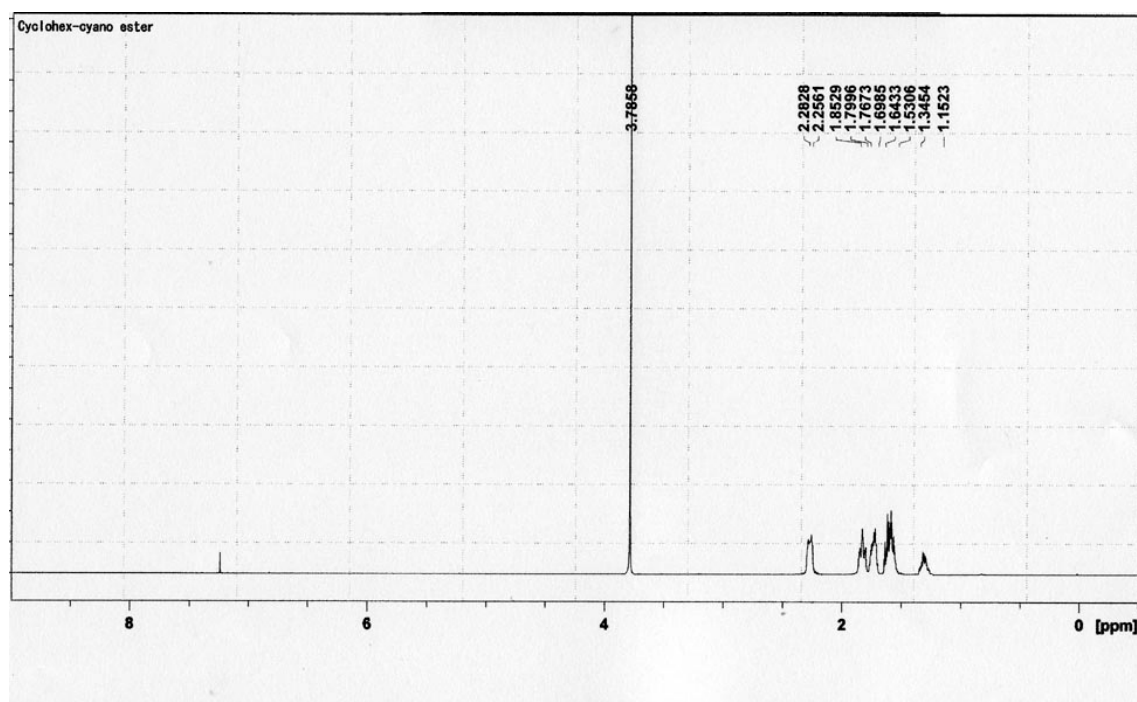
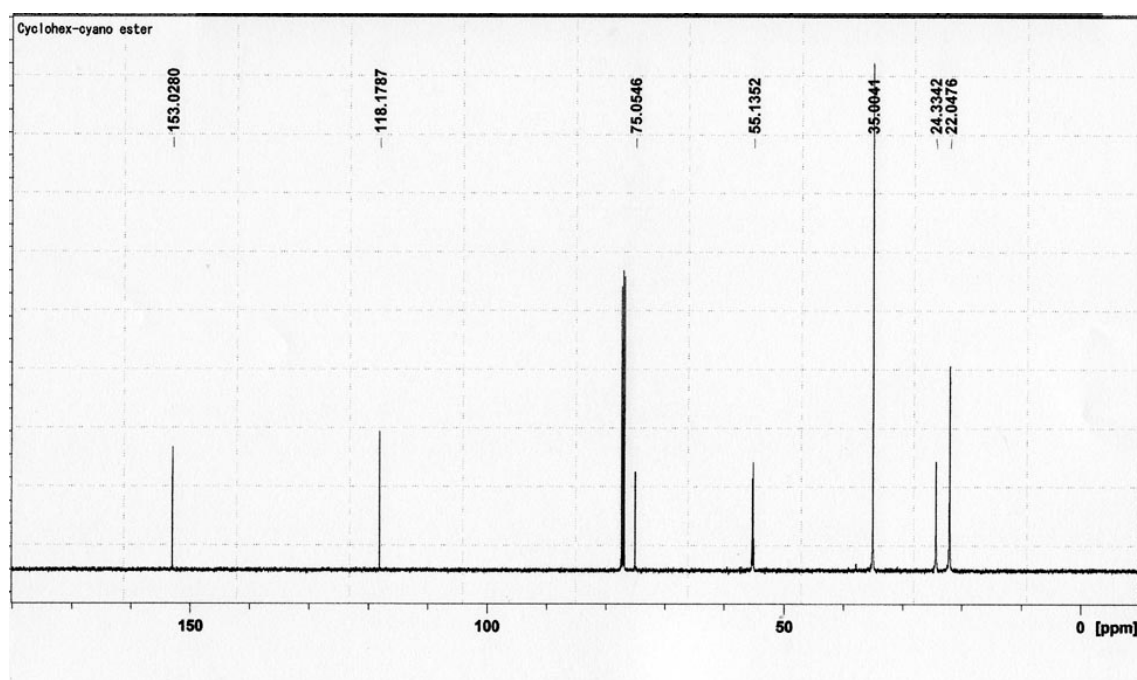
Figure S17. ¹H-NMR Spectrum of compound 2i.Figure S18. ¹³C-NMR Spectrum of compound 2i.

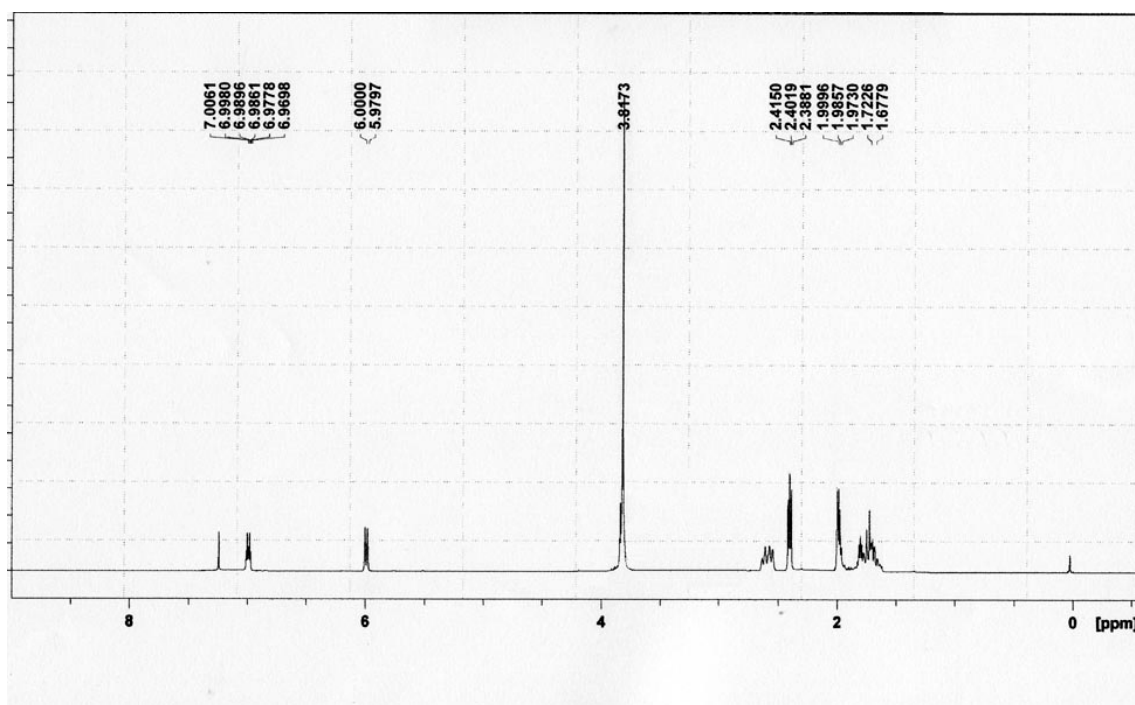
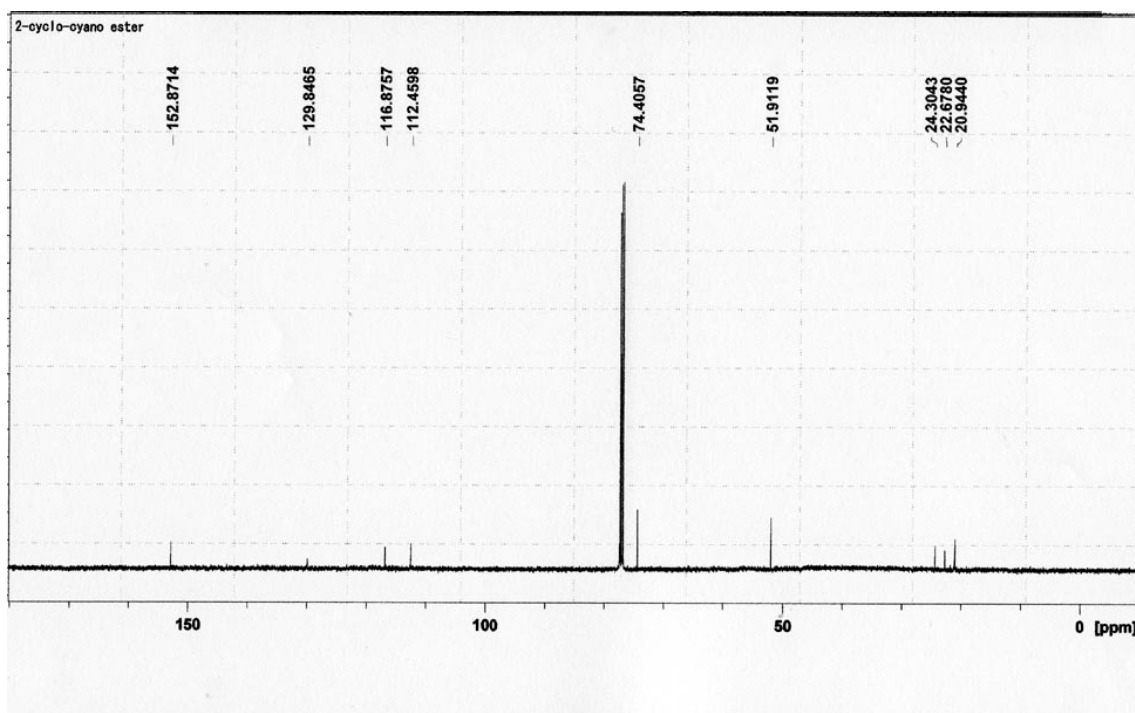
Figure S19. ¹H-NMR Spectrum of compound 2j.Figure S20. ¹³C-NMR Spectrum of compound 2j.

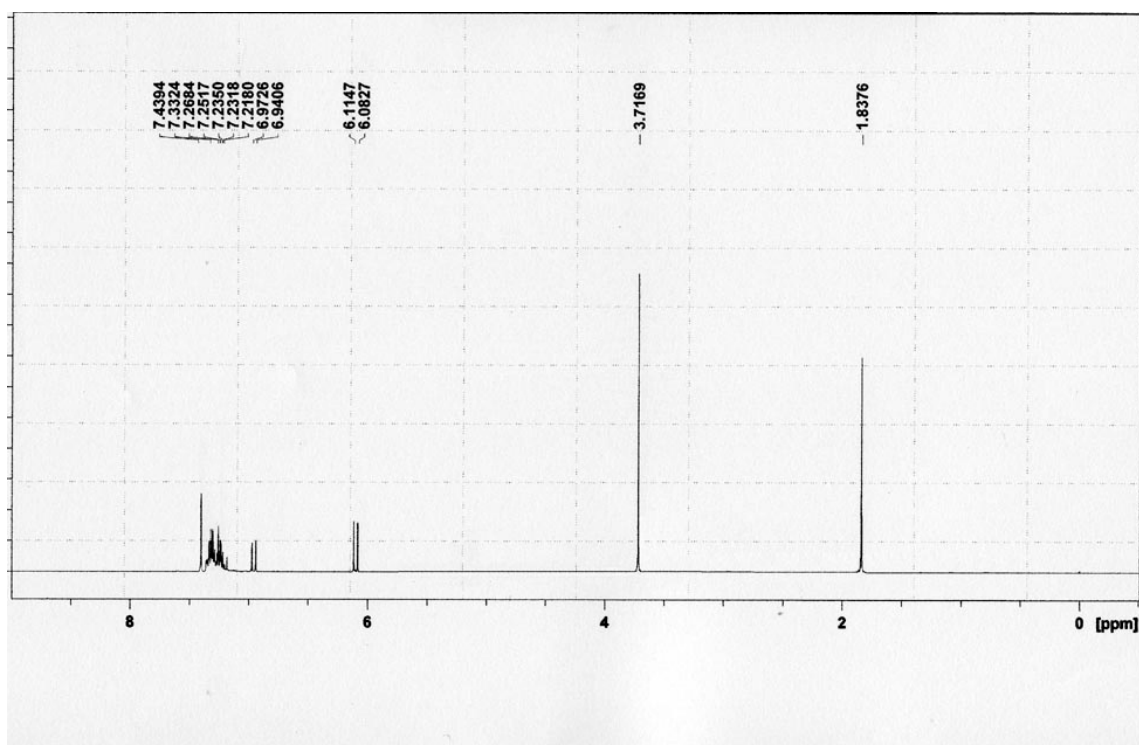
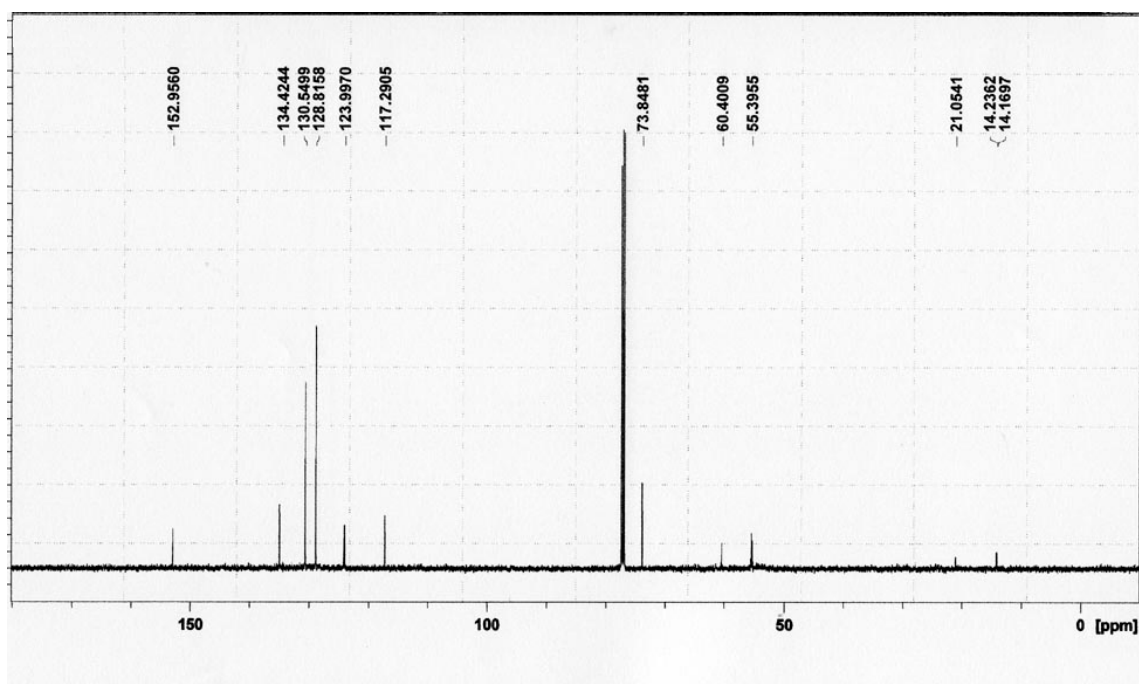
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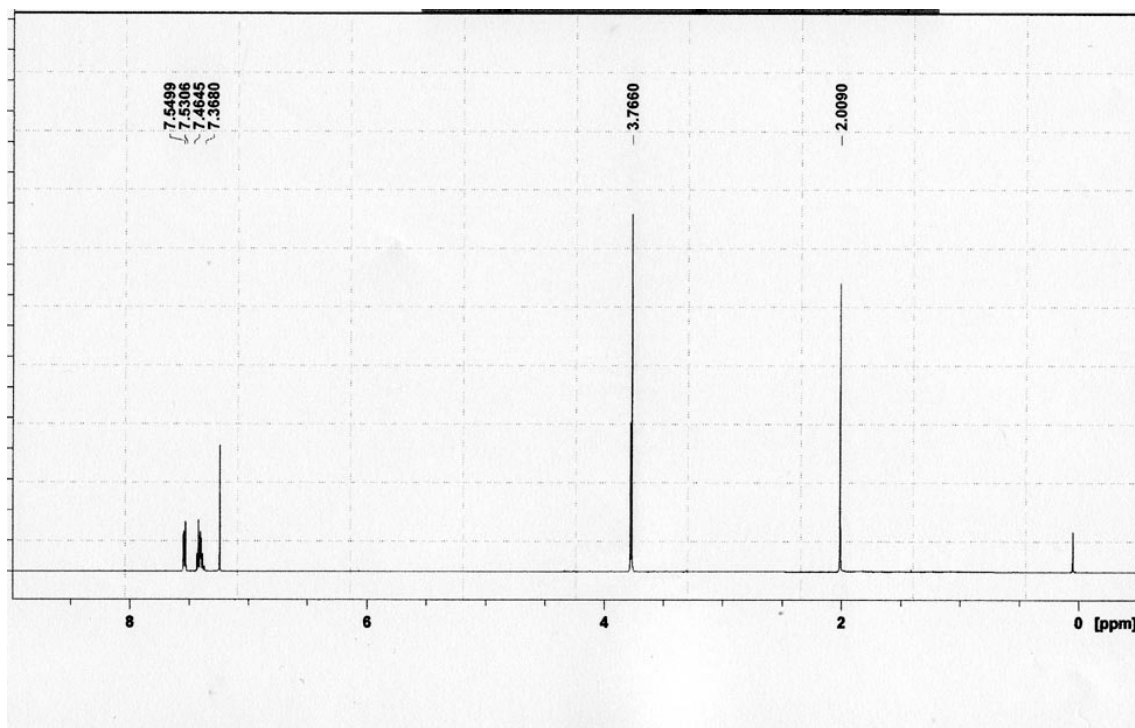
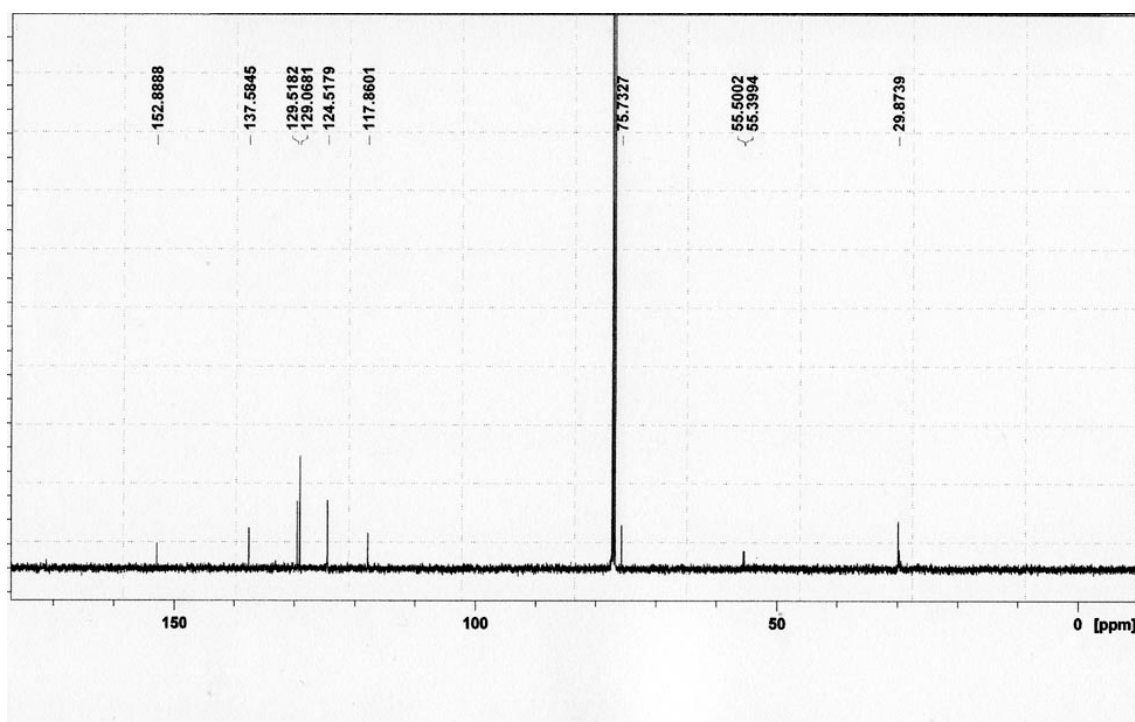
Figure S23. ¹H-NMR Spectrum of compound 4a.Figure S24. ¹³C-NMR Spectrum of compound 4a.

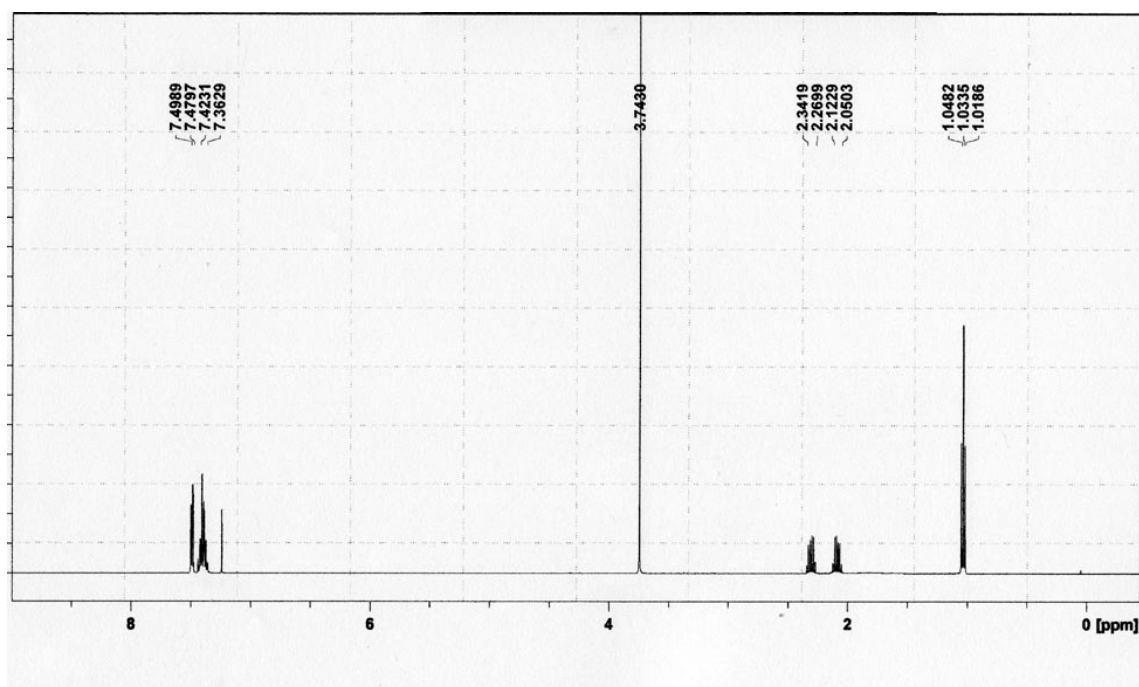
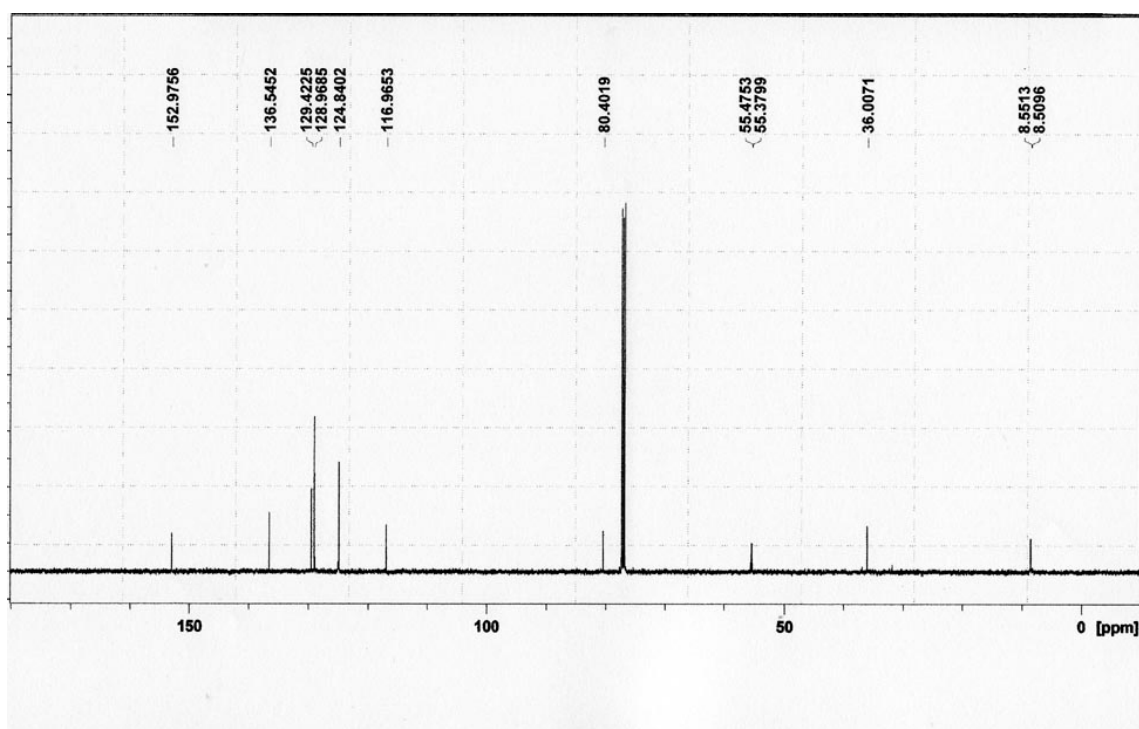
Figure S25. ¹H-NMR Spectrum of compound 4b.Figure S26. ¹³C-NMR Spectrum of compound 4b.

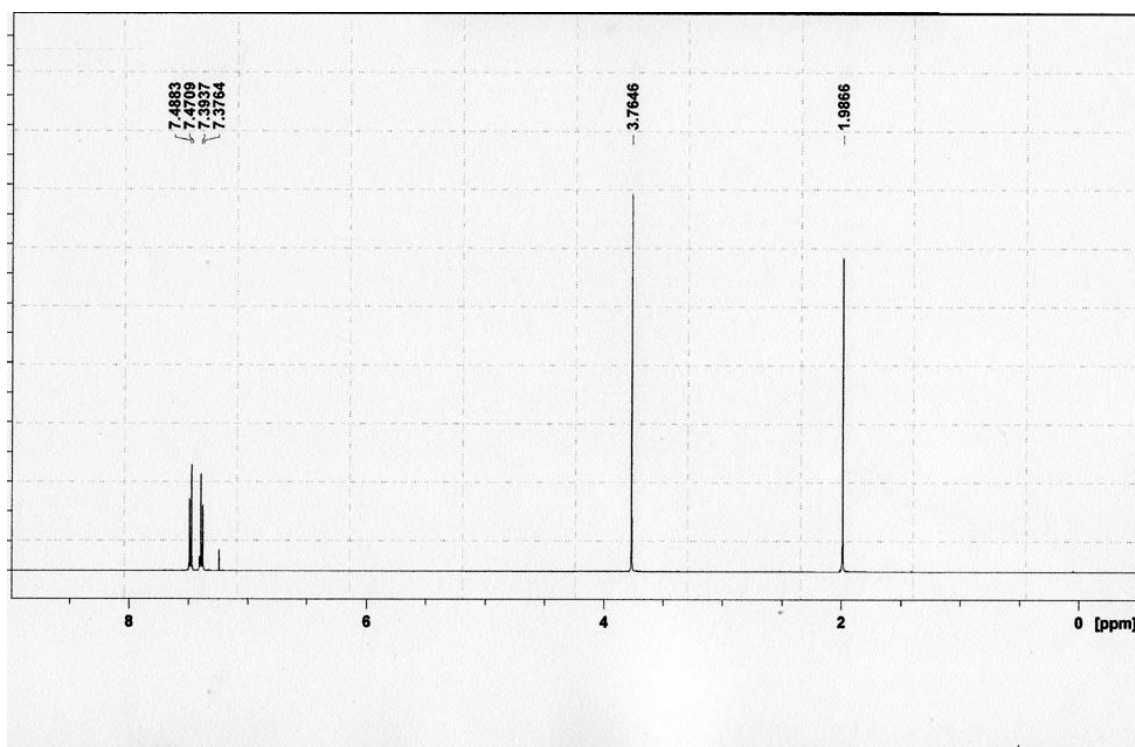
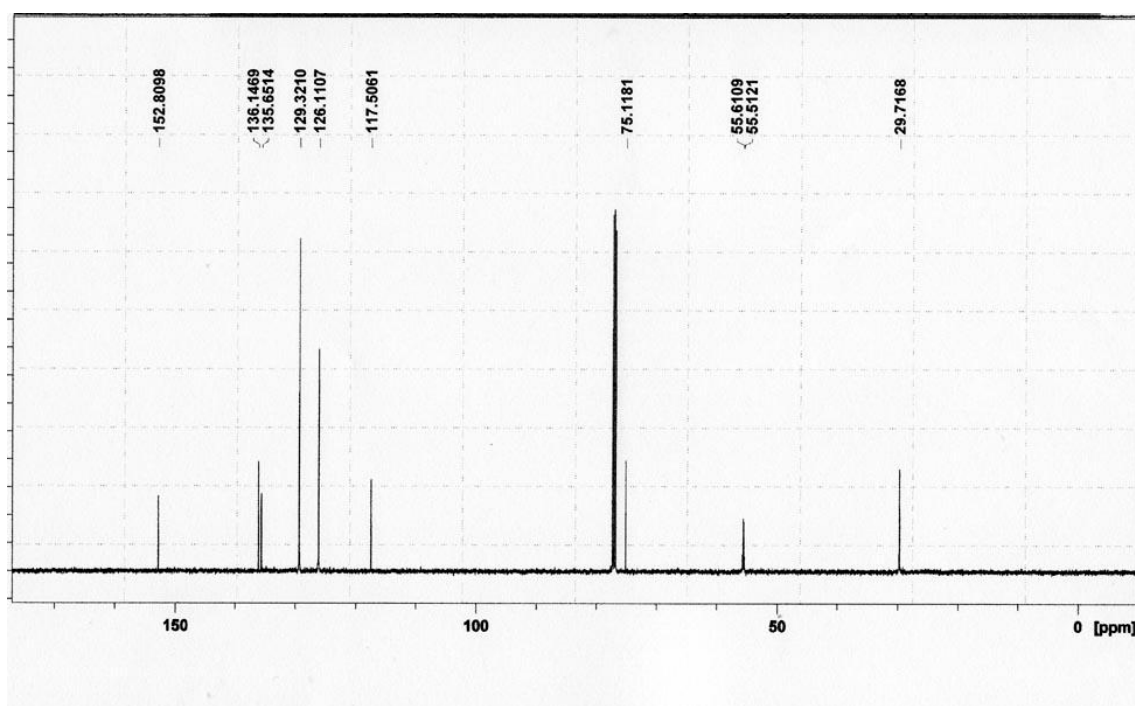
Figure S27. ¹H-NMR Spectrum of compound 4c.Figure S28. ¹³C-NMR Spectrum of compound 4c.

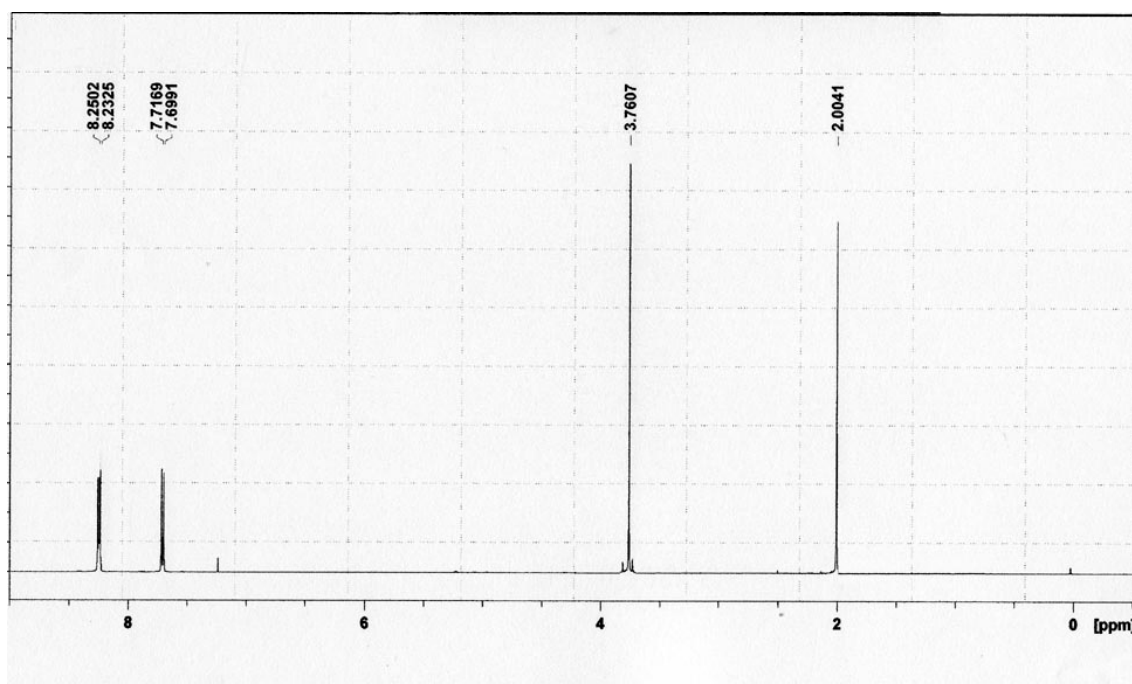
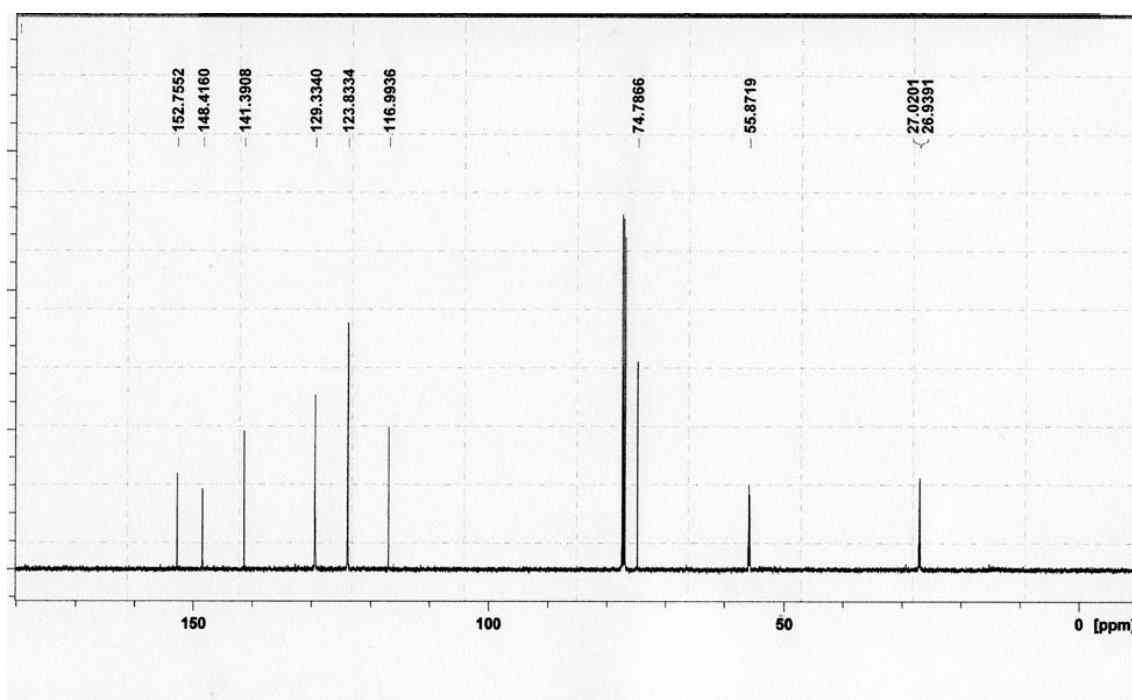
Figure S29. ¹H-NMR Spectrum of compound 4d.Figure S30. ¹³C-NMR Spectrum of compound 4d.

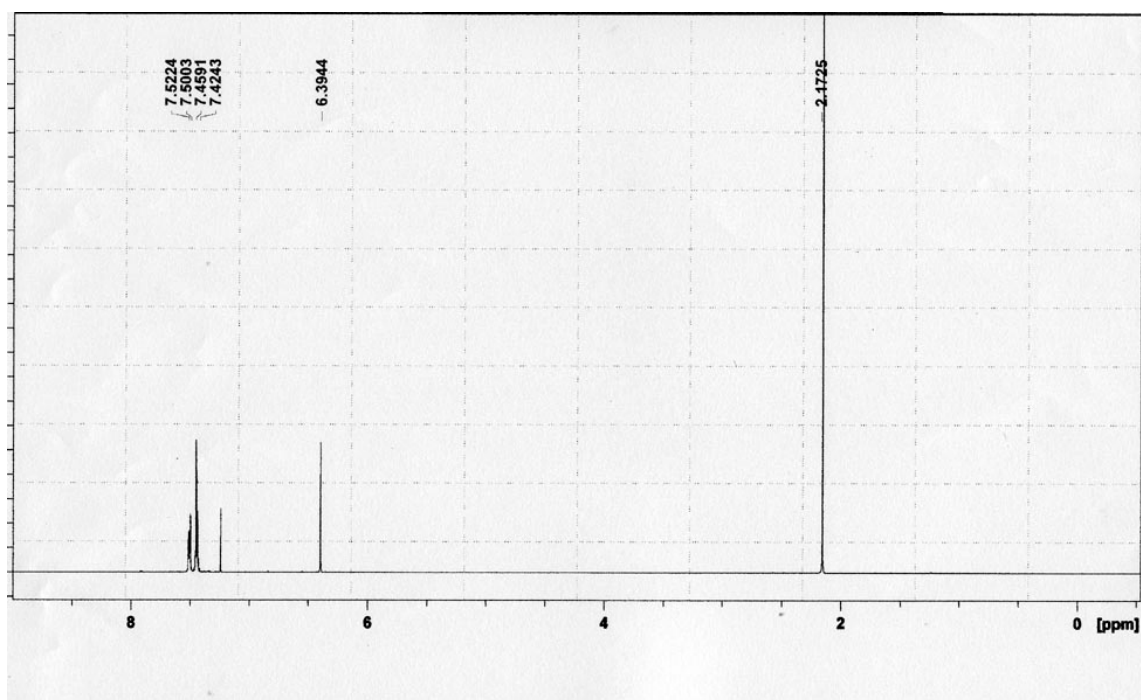
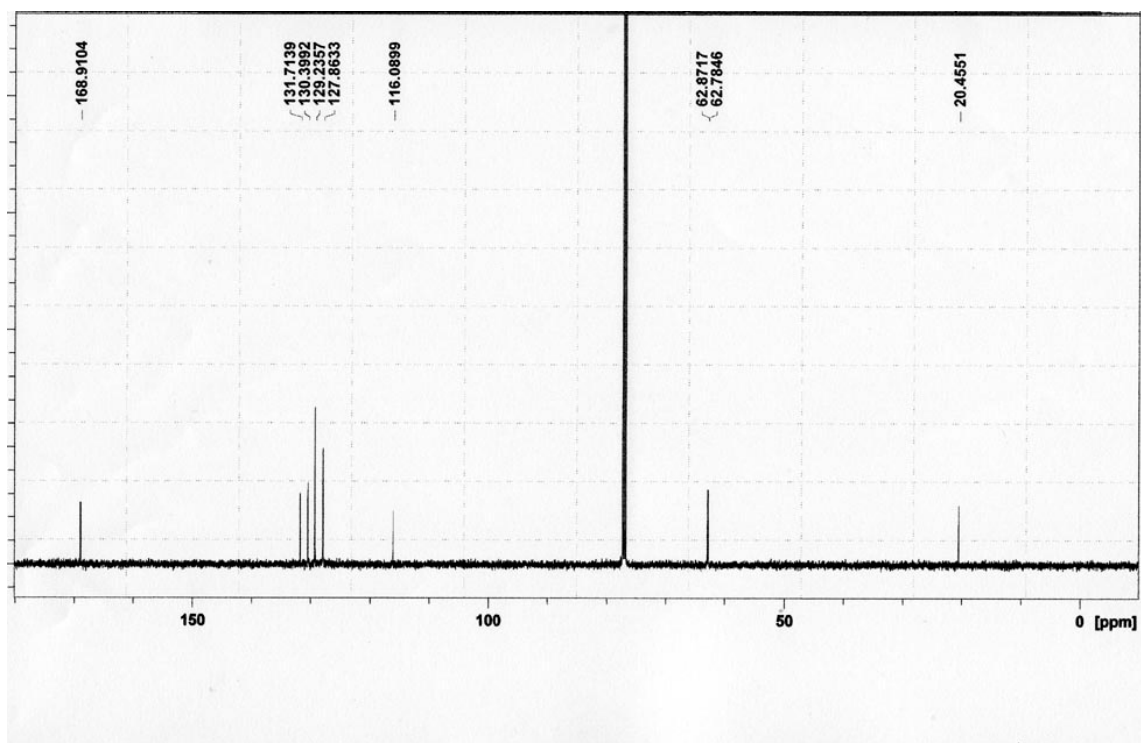
Figure S31. ¹H-NMR Spectrum of compound 4e.Figure S32. ¹³C-NMR Spectrum of compound 4e.

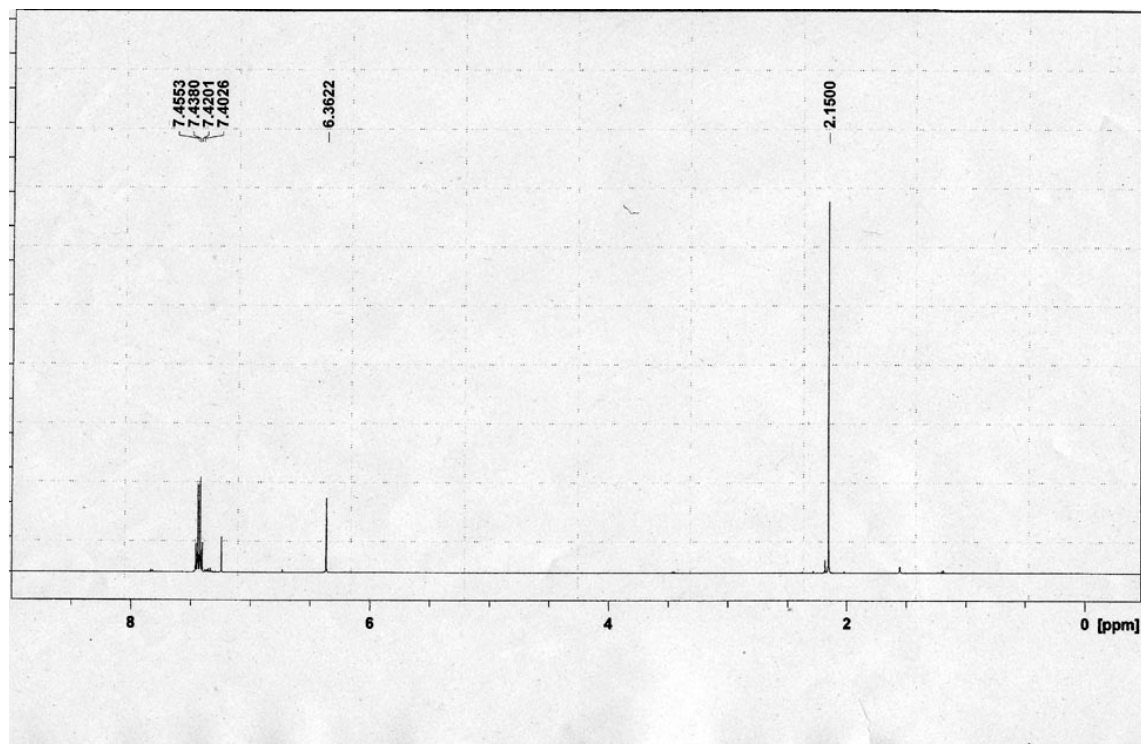
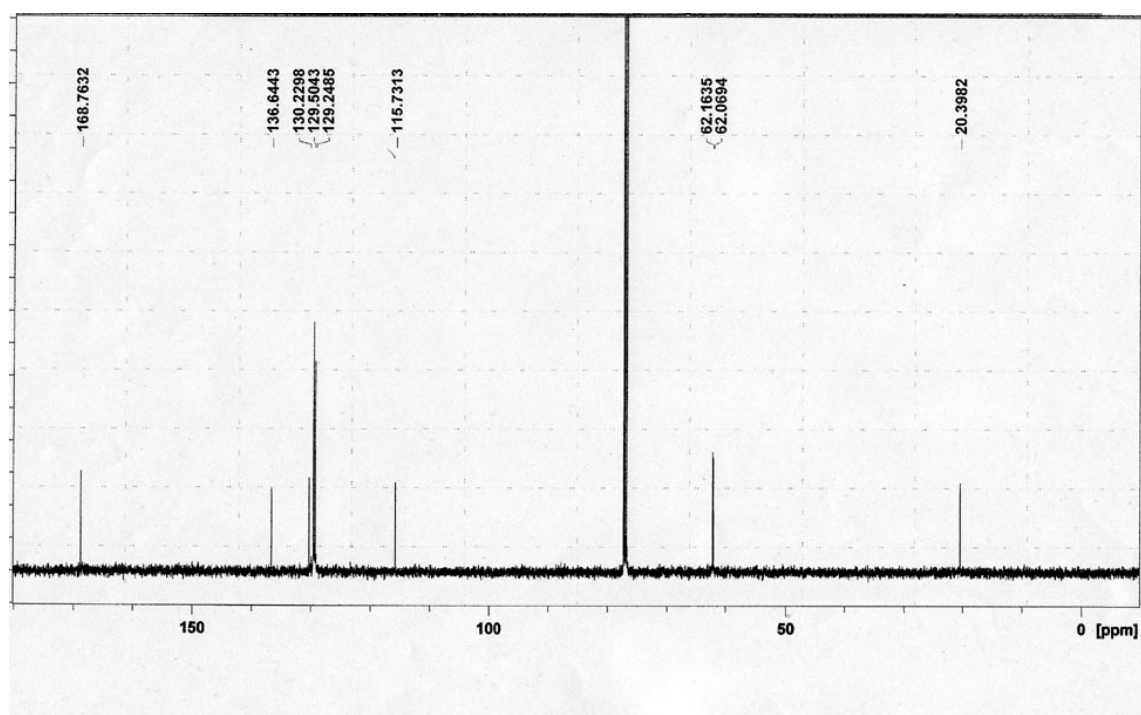
Figure S33. ¹H-NMR Spectrum of compound 4f.Figure S34. ¹³C-NMR Spectrum of compound 4f.

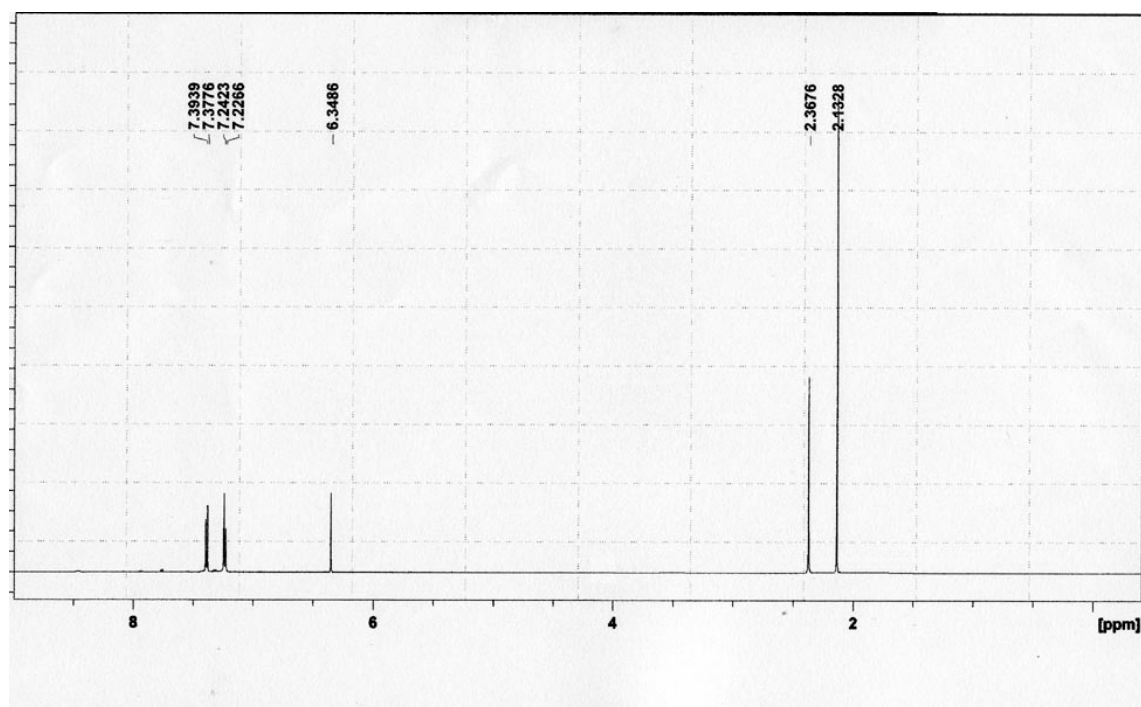
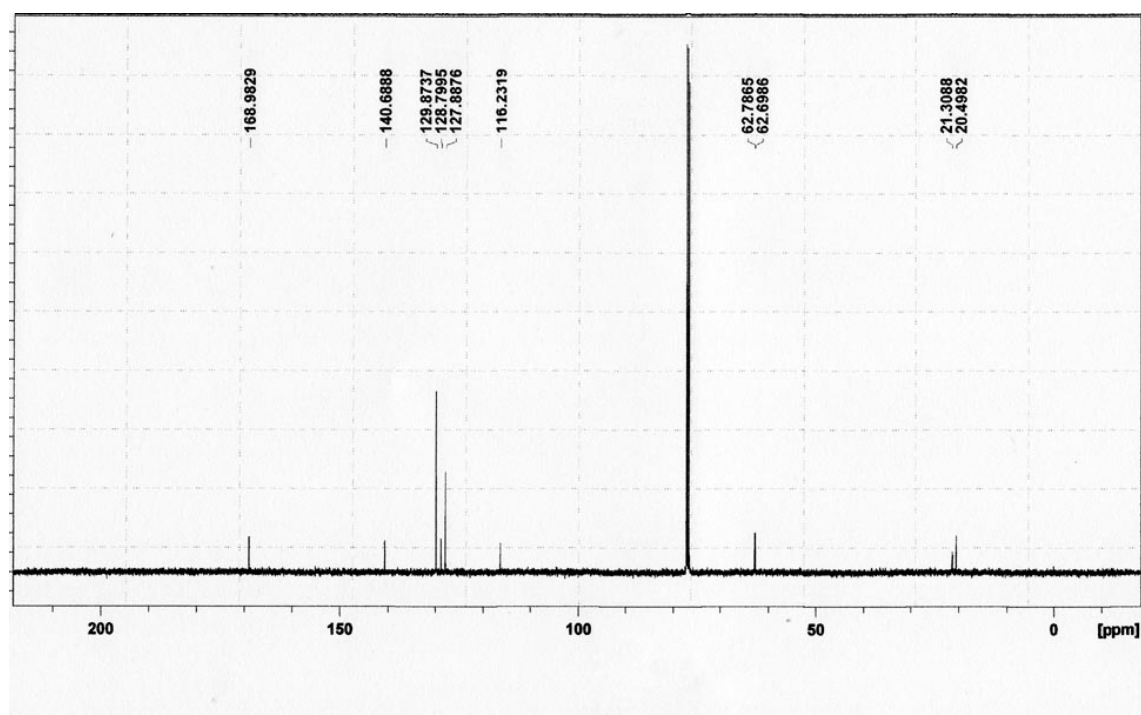
Figure S35. ¹H-NMR Spectrum of compound 4g.Figure S36. ¹³C-NMR Spectrum of compound 4g.

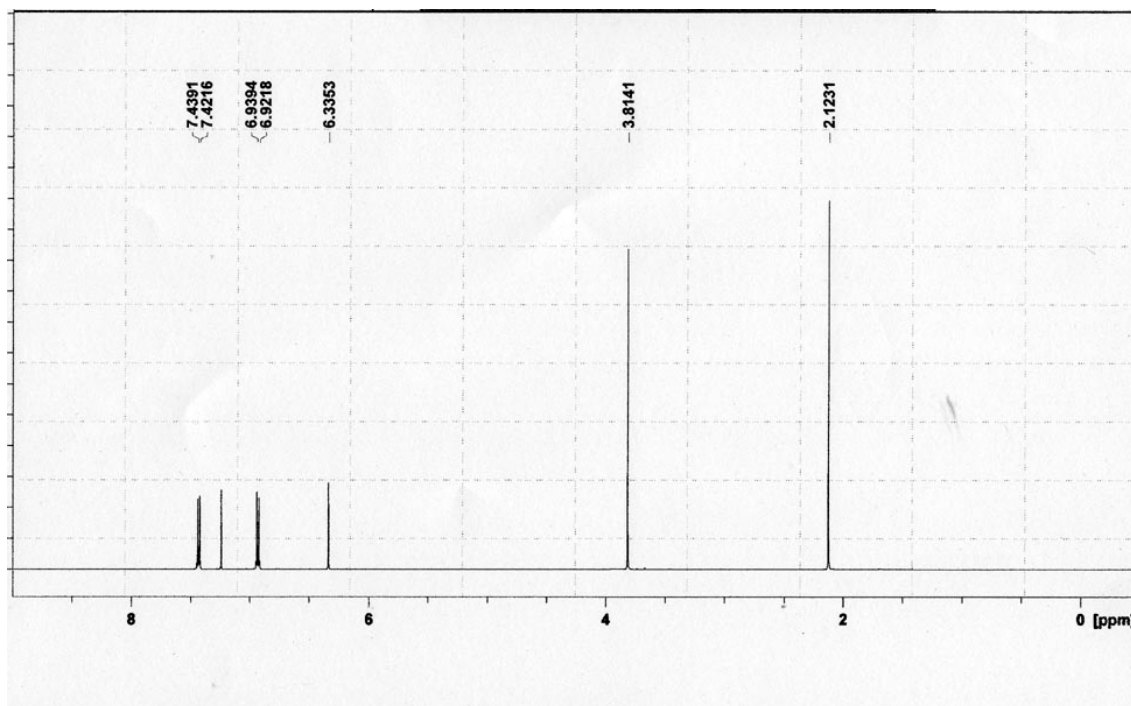
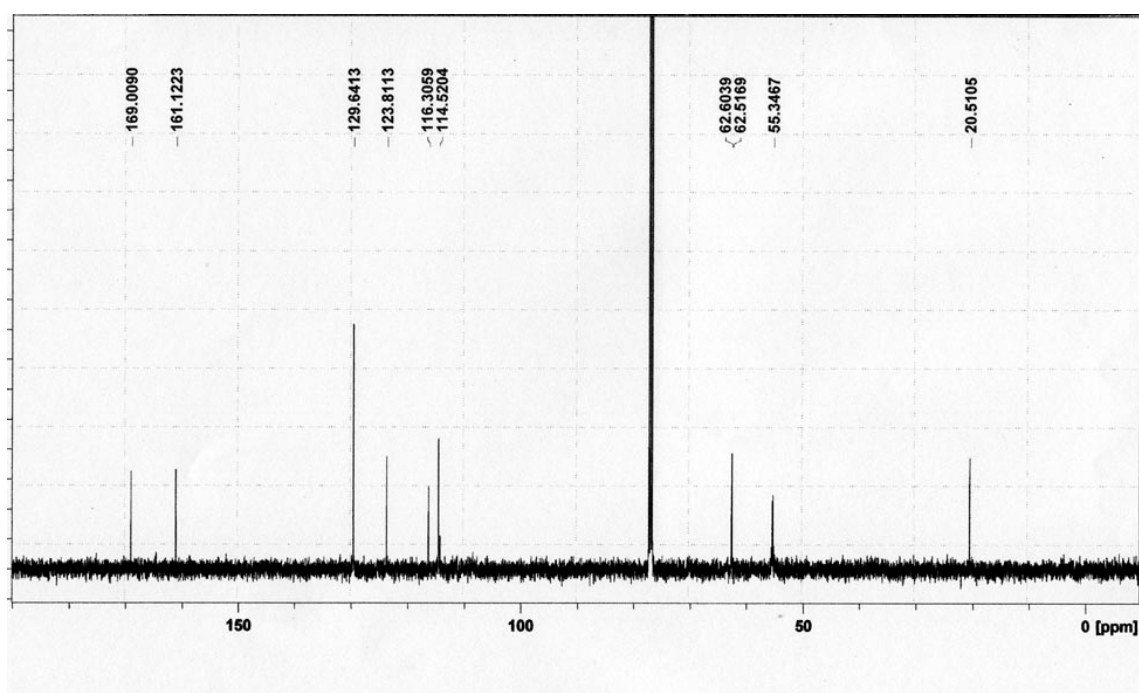
Figure S37. ¹H-NMR Spectrum of compound 4h.Figure S38. ¹³C-NMR Spectrum of compound 4h.

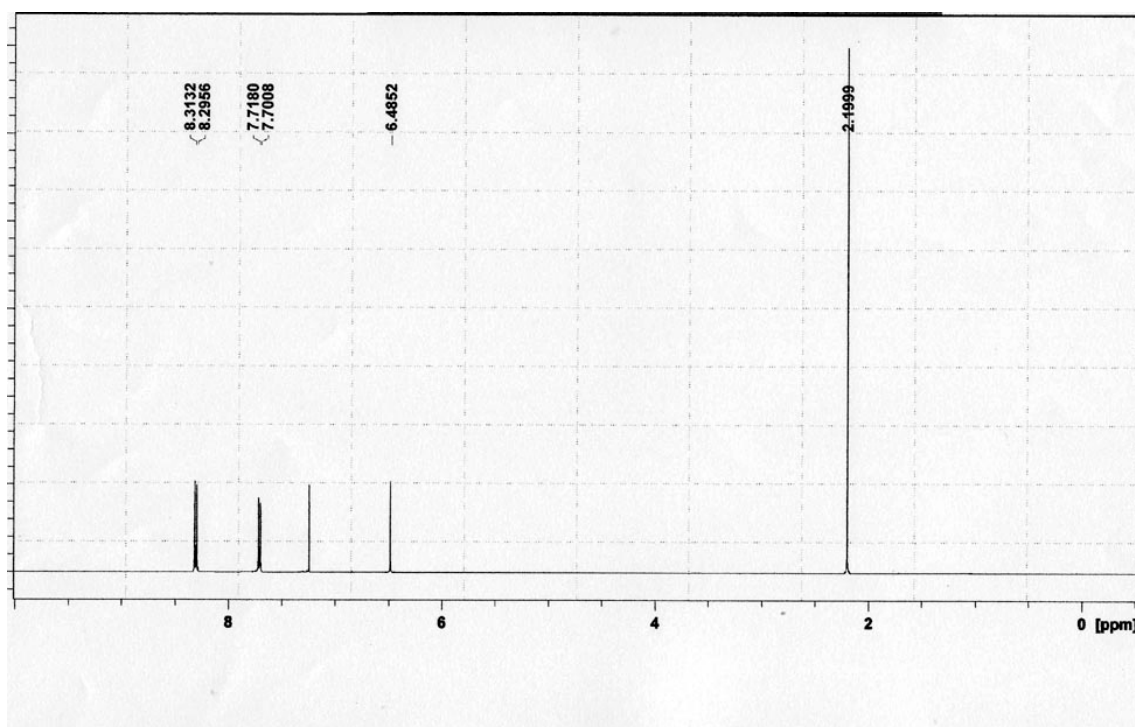
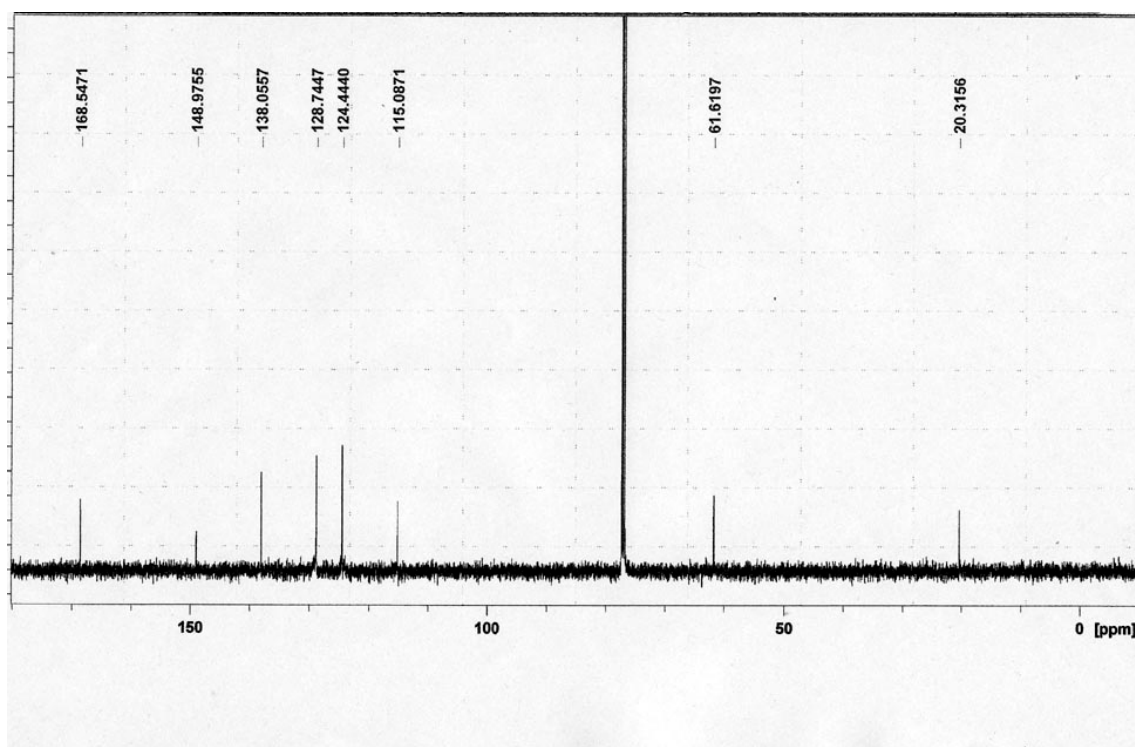
Figure S39. ¹H-NMR Spectrum of compound 4i.Figure S40. ¹³C-NMR Spectrum of compound 4i.

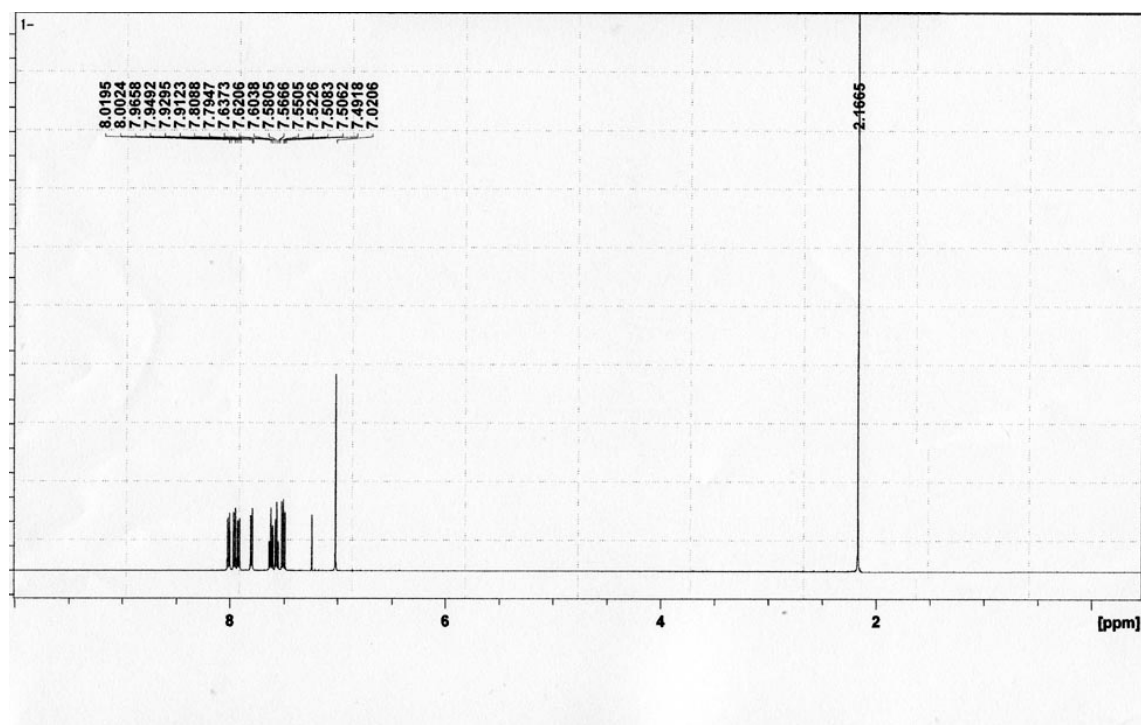
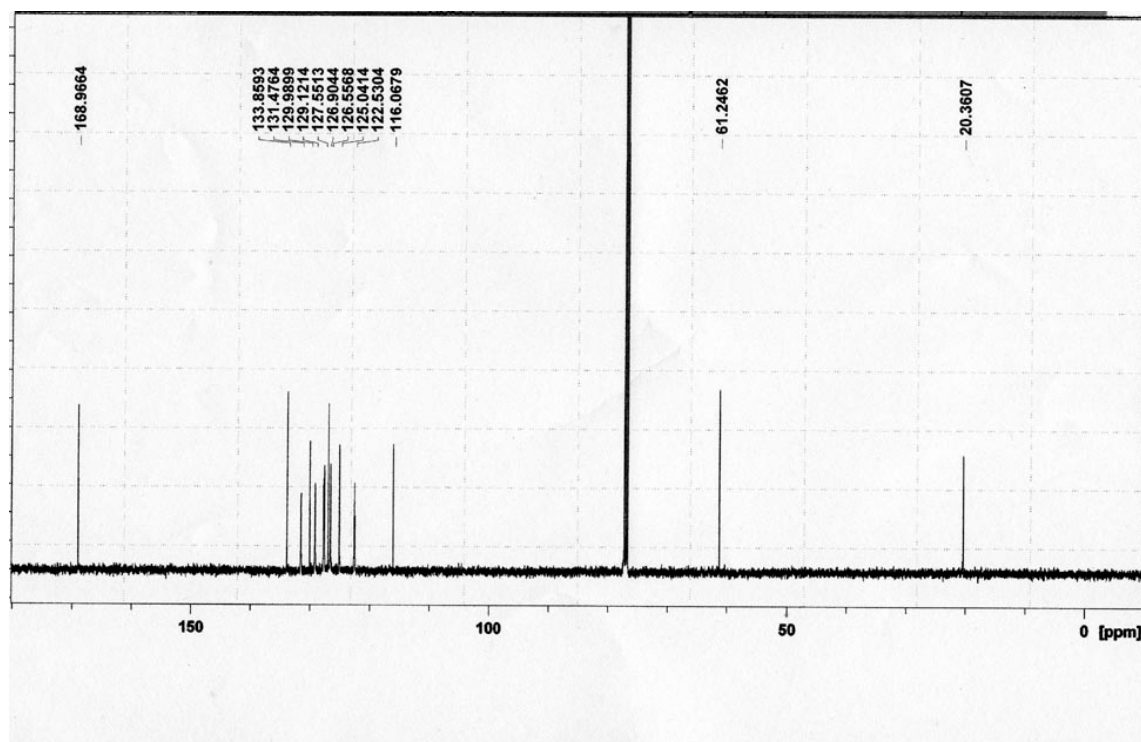
Figure S41. ¹H-NMR Spectrum of compound 5a.Figure S42. ¹³C-NMR Spectrum of compound 5a.

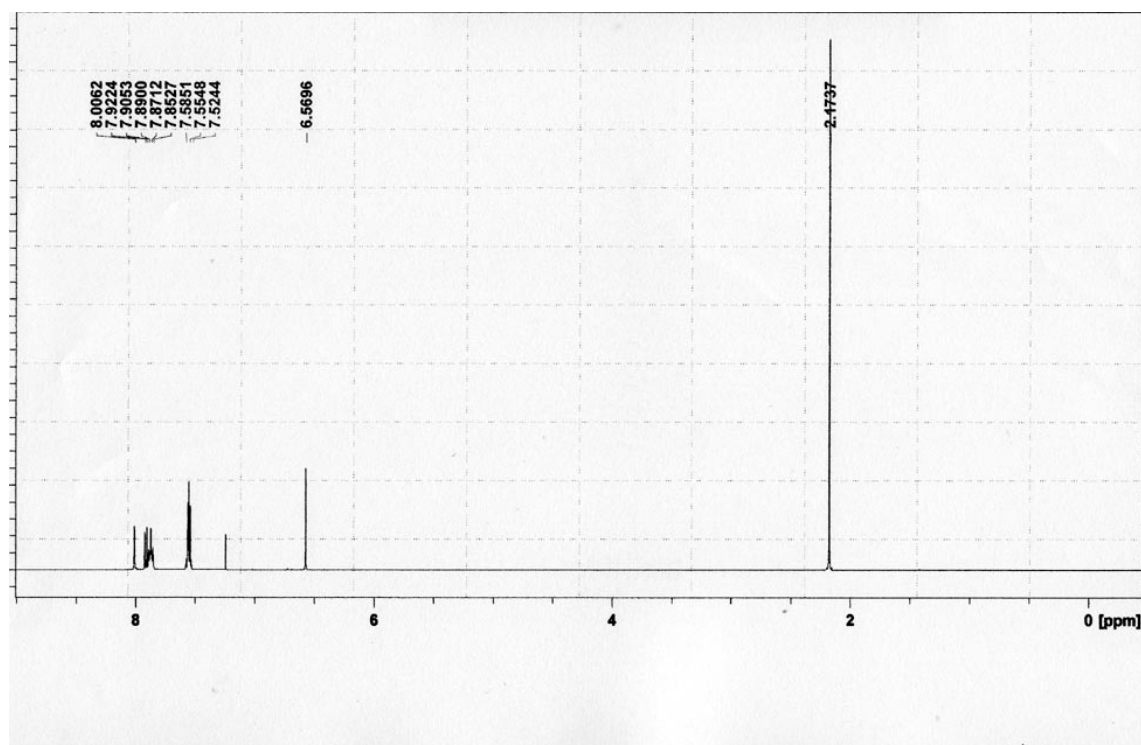
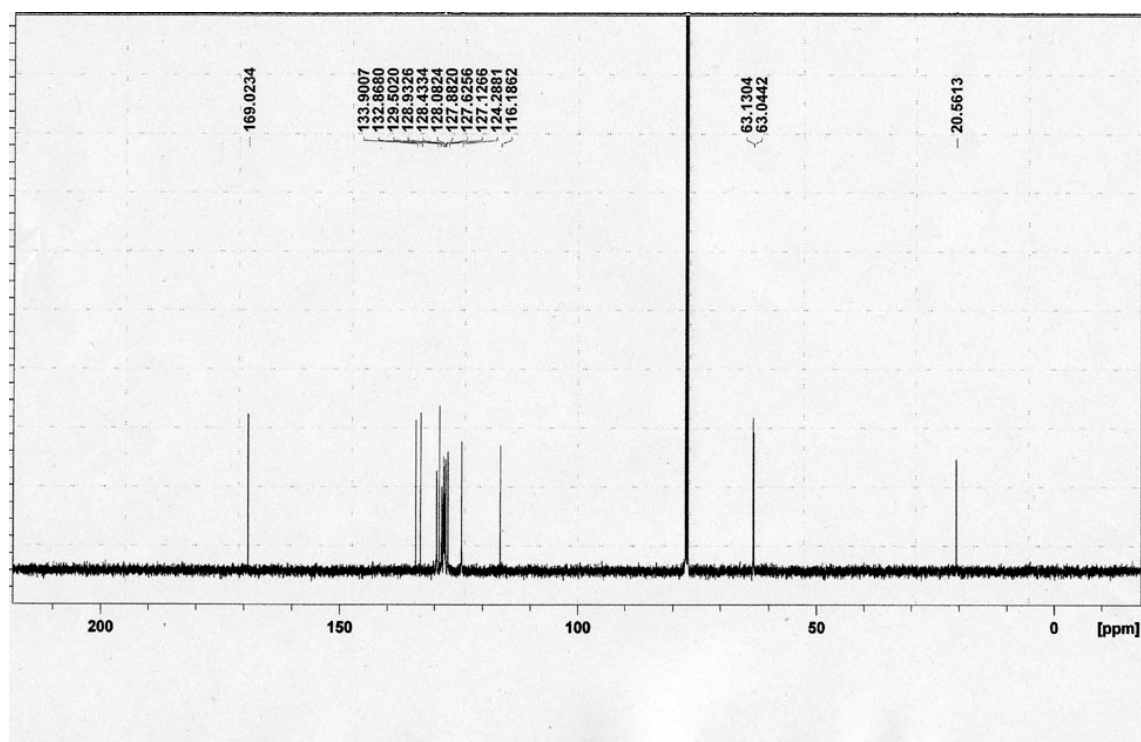
Figure S43. ¹H-NMR Spectrum of compound 5b.Figure S44. ¹³C-NMR Spectrum of compound 5b.

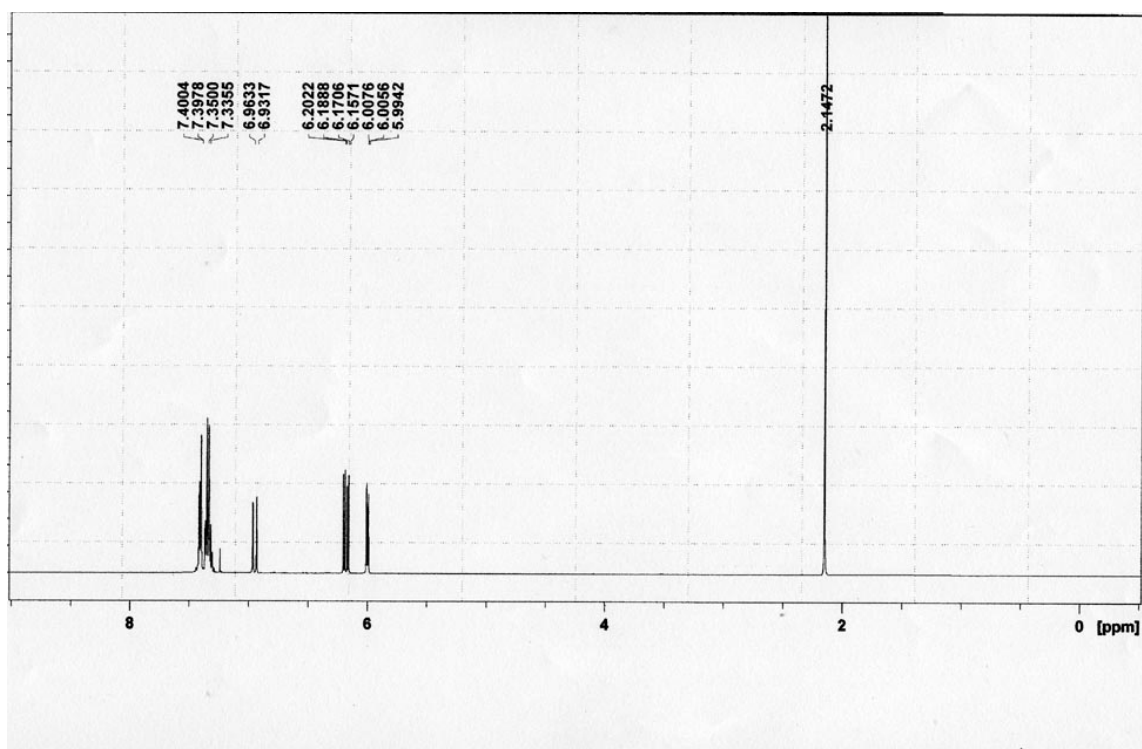
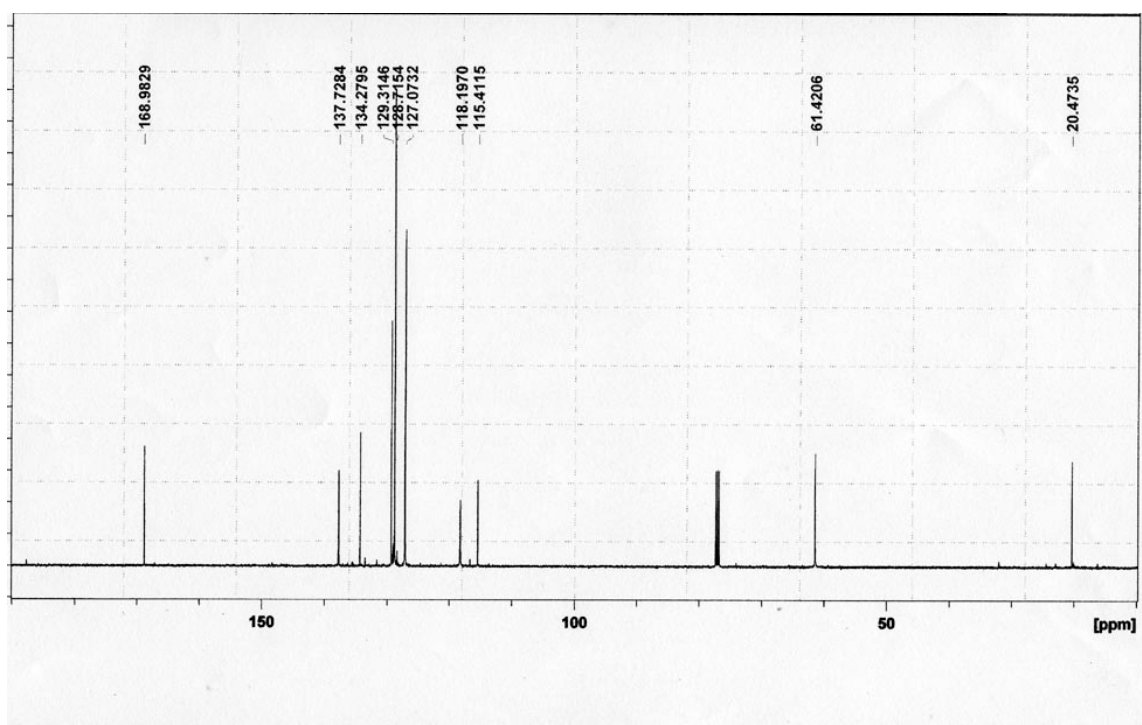
Figure S45. ¹H-NMR Spectrum of compound 5c.Figure S46. ¹³C-NMR Spectrum of compound 5c.

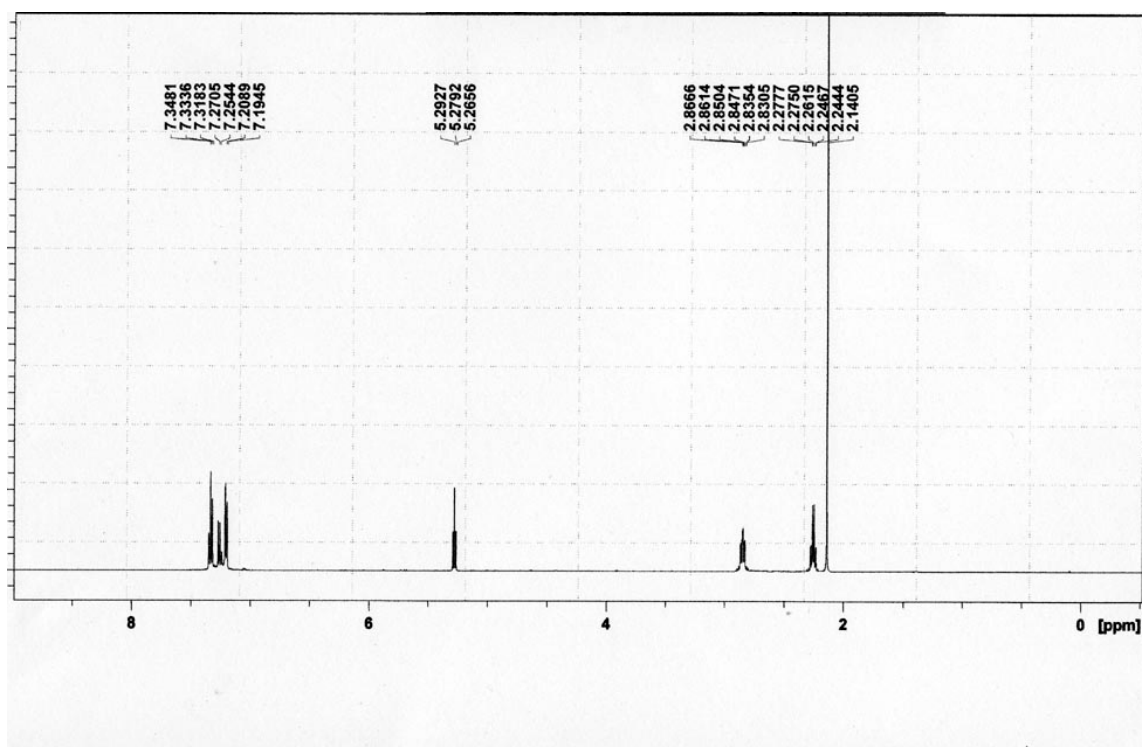
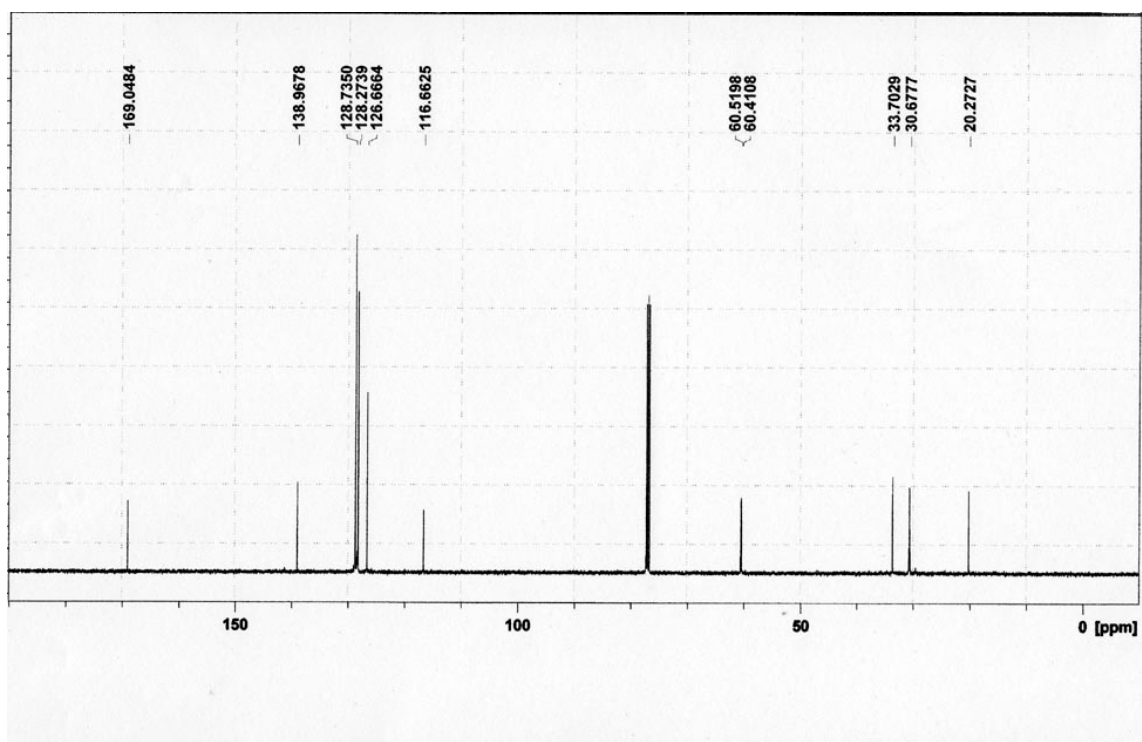
Figure S47. ¹H-NMR Spectrum of compound 5d.Figure S48. ¹³C-NMR Spectrum of compound 5d.

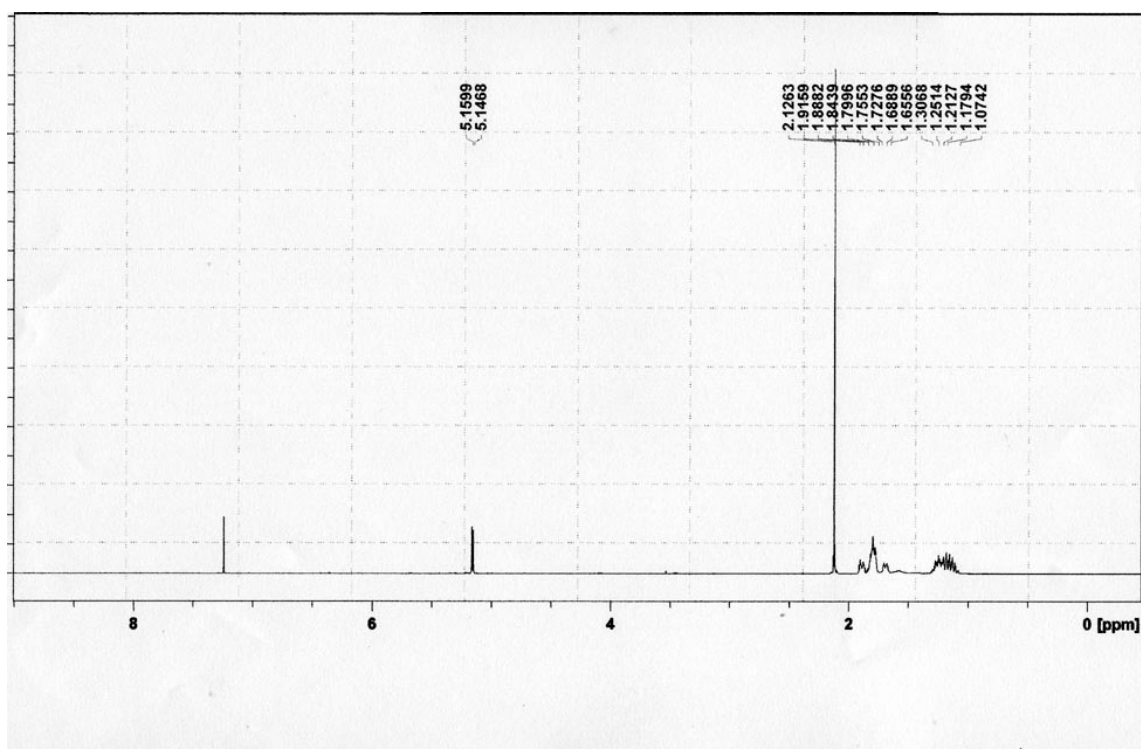
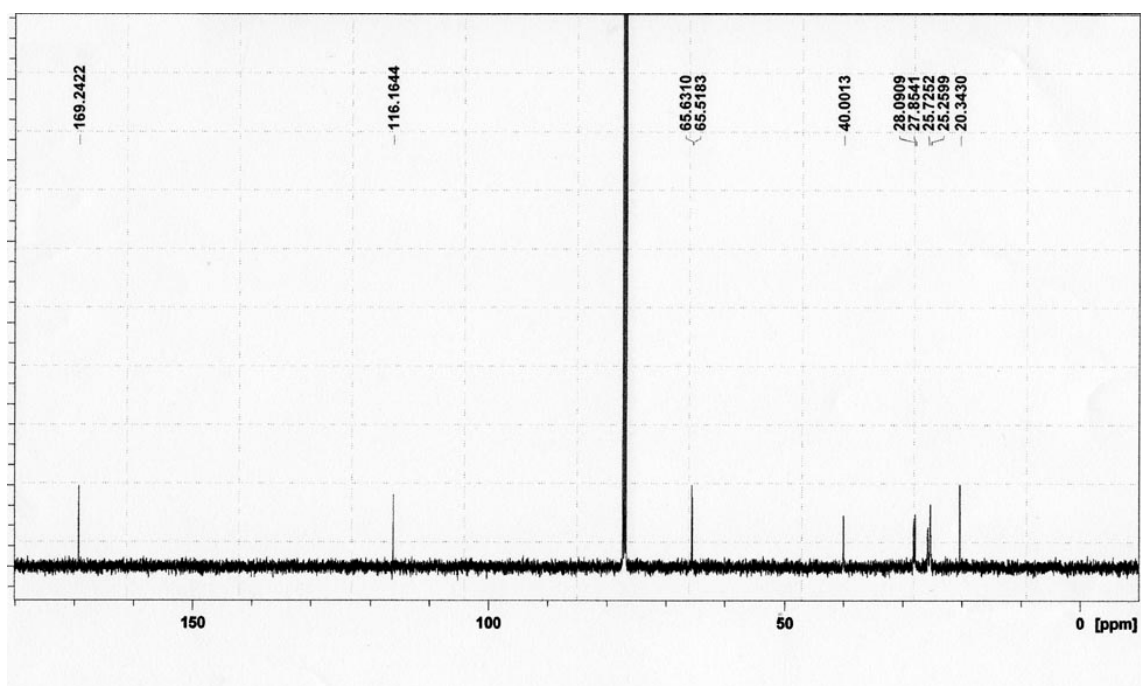
Figure S49. ¹H-NMR Spectrum of compound 5e.Figure S50. ¹³C-NMR Spectrum of compound 5e.

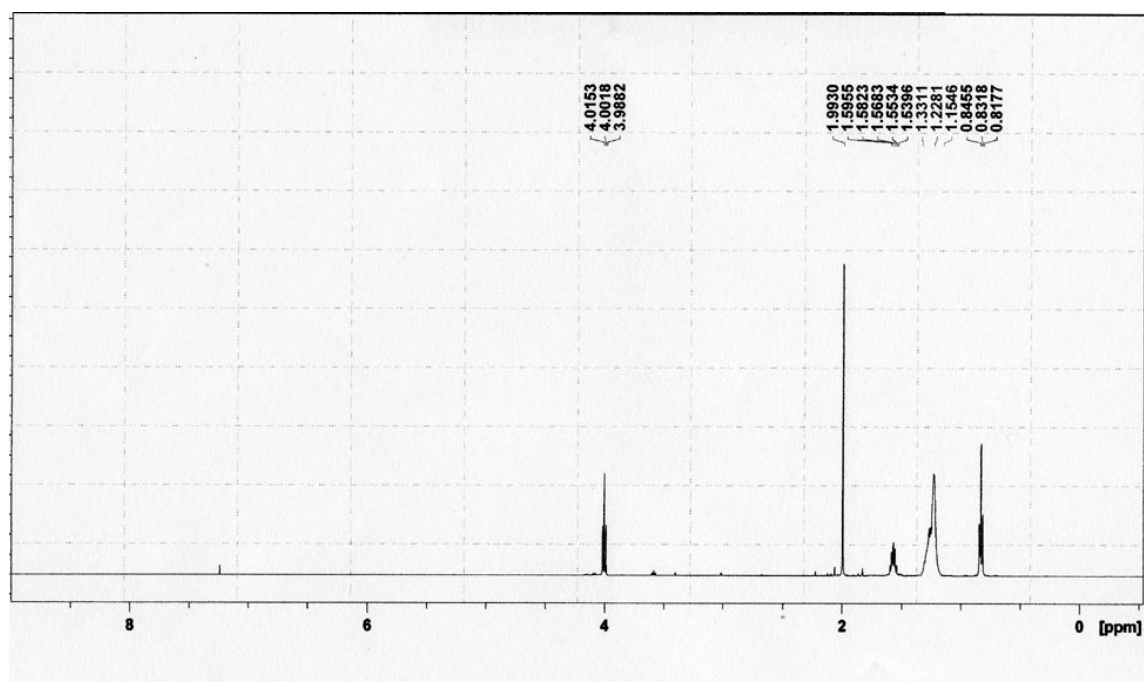
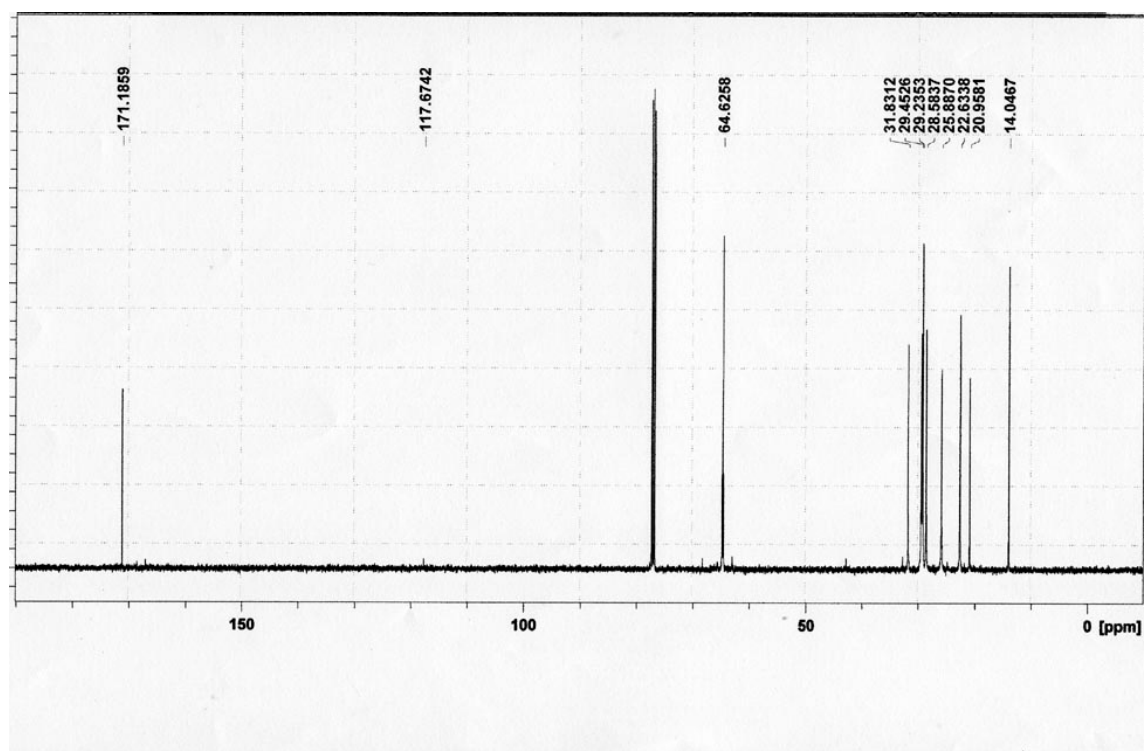
Figure S51. ¹H-NMR Spectrum of compound 5f.Figure S52. ¹³C-NMR Spectrum of compound 5f.

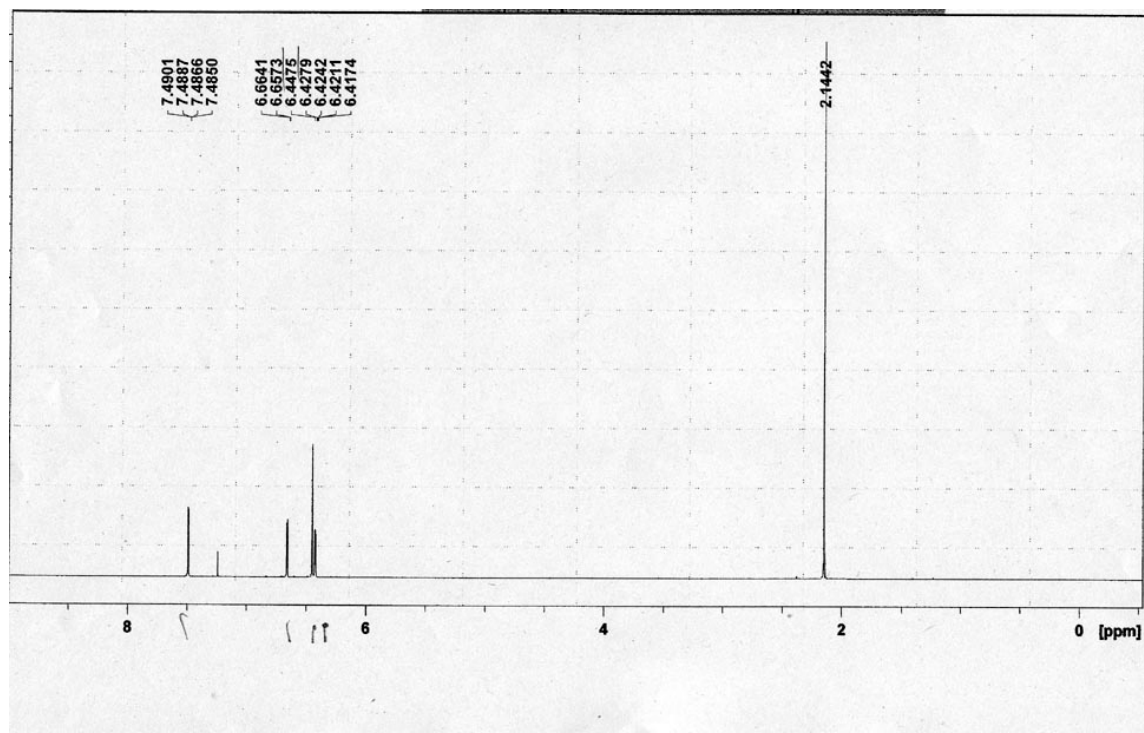
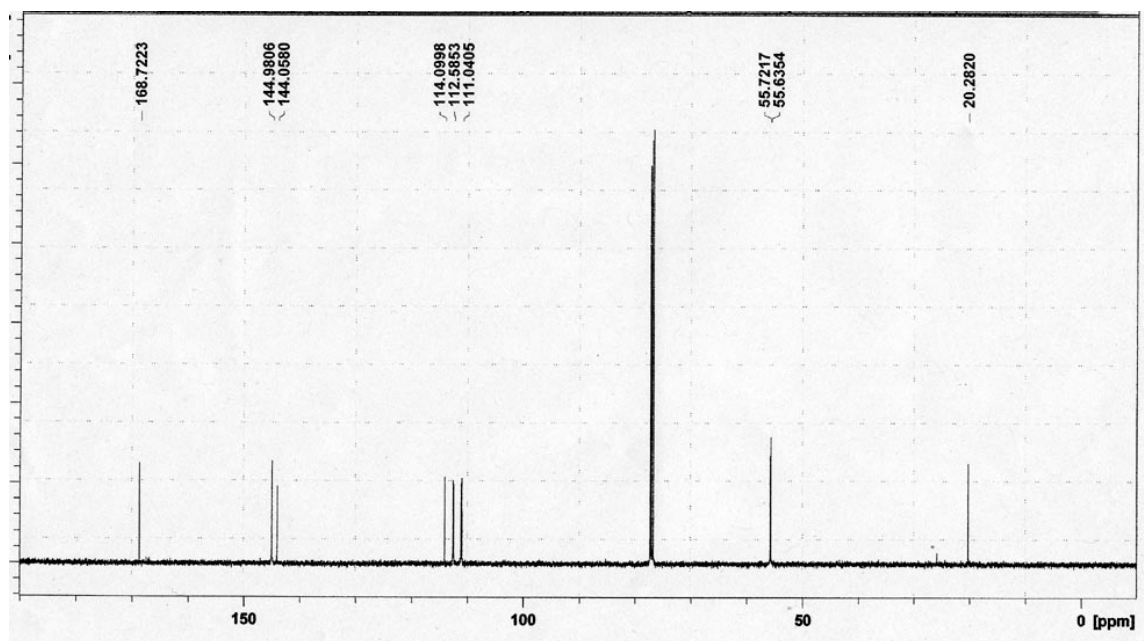
Figure S53. ¹H-NMR Spectrum of compound 5g.Figure S54. ¹³C-NMR Spectrum of compound 5g.

Figure S55. ¹H-NMR Spectrum of compound 5h.Figure S56. ¹³C-NMR Spectrum of compound 5h.

Figure S57. ¹H-NMR Spectrum of compound 5i.Figure S58. ¹³C-NMR Spectrum of compound 5i.

Figure S59. ¹H-NMR Spectrum of compound 5j.Figure S60 ¹³C-NMR Spectrum of compound 5j.

Figure S61. ¹H-NMR Spectrum of compound 5k.Figure S62. ¹³C-NMR Spectrum of compound 5k.

Figure S63. ¹H-NMR Spectrum of compound 51.Figure S64. ¹³C-NMR Spectrum of compound 51.