

Supplementary Material

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1. Instrumentation and Chemicals

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). Preparative thin-layer chromatography was carried out on silica gel Wakogel B-5F (Wako Chemical). Dehydrate DMF, THF, toluene and CH₃CN were purchased from Wako Chemical. Other commercially available reagent was used as received without further purification. The aziridines were prepared according to literature procedure [66]. Yields refer to isolated compounds estimated to be >95% pure, as determined by ¹H-NMR spectroscopy. IR spectra were recorded on a JUSCO FT/IR-430 spectrometer (JASCO Corporation, Tokyo, Japan). ¹H- and ¹³C-NMR spectra were determined for solutions in CDCl₃ with Me₄Si as internal standard on a Bruker Avance III instrument (Bruker Corporation, Billerica, MA, USA). HRMS data were measured on a JEOL JMS-700 mass spectrometer (JEOL Ltd., Tokyo, Japan).

2. General Procedure for TBD-Catalyzed Ring-Opening of Aziridines with Acid Anhydride

To a solution of TBD (0.05 mmol) in DMF (1 mL) was added aziridine (1.0 mmol) and acid anhydride (1.25 mmol) at room temperature. After the reaction was complete (as determined by TLC), the reaction mixture was treated with saturated NH₄Cl and extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over Na₂SO₄, concentrated *in vacuo* and purified by column chromatography on silica gel (EtOAc:hexane = 1:3) to give the corresponding product.

3. General Procedure for PS-TBD Catalyzed Ring-Opening of Aziridines with Acid Anhydride

To a solution of PS-TBD (0.10 mmol) in DMF (1 mL) was added aziridine (1.0 mmol) and acid anhydride (1.25 mmol) at room temperature. After the reaction was complete (as determined by TLC), EtOAc (5 mL) was added to the mixture and PS-TBD was separated by filtration. The filtrate was washed with saturated NH₄Cl, dried over Na₂SO₄, concentrated *in vacuo* and purified by column chromatography on silica gel (EtOAc:hexane = 1:3) to give the corresponding product. The recovered catalyst is reusable after washing (acetone and water) and drying *in vacuo*.

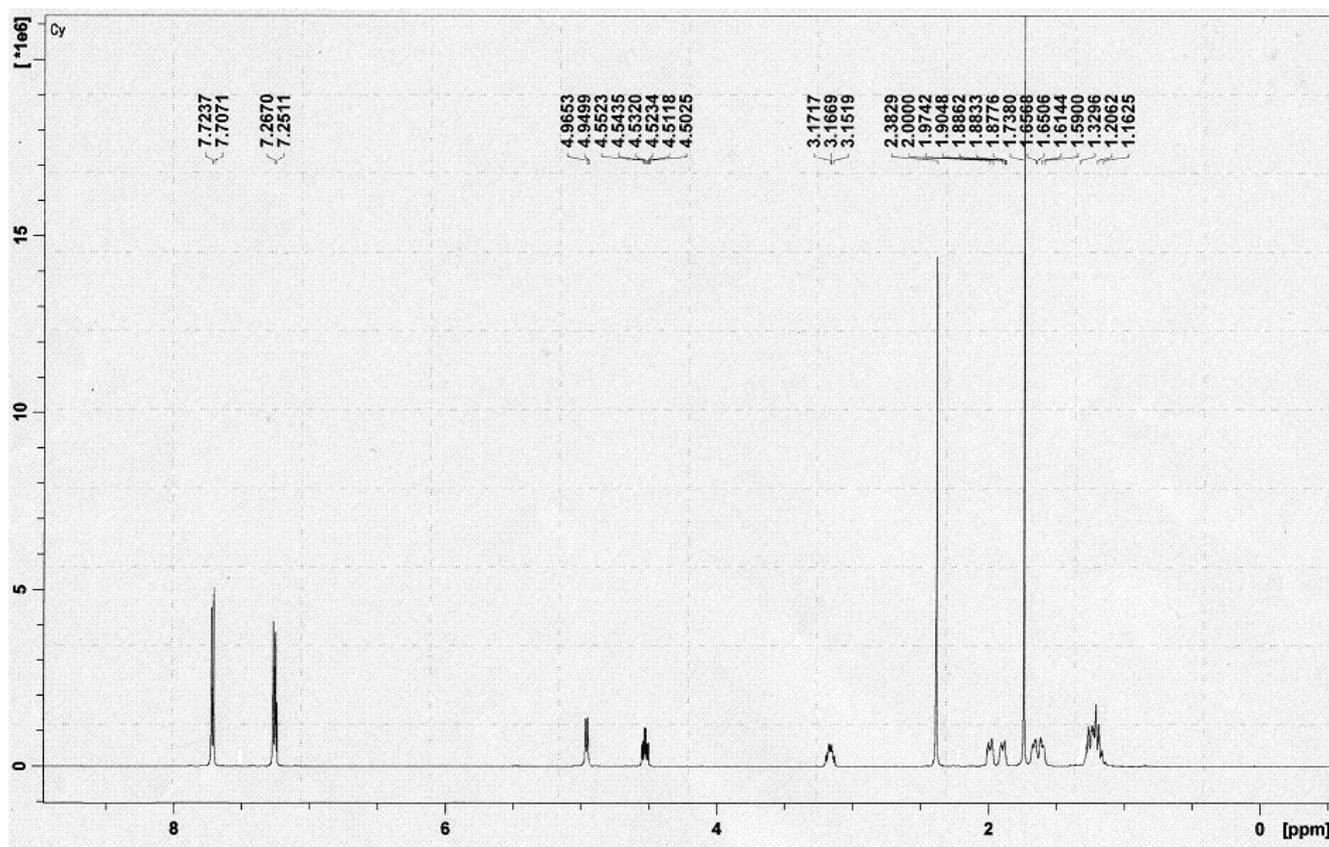


Figure S1. ¹H-NMR Spectrum of compound 2a.

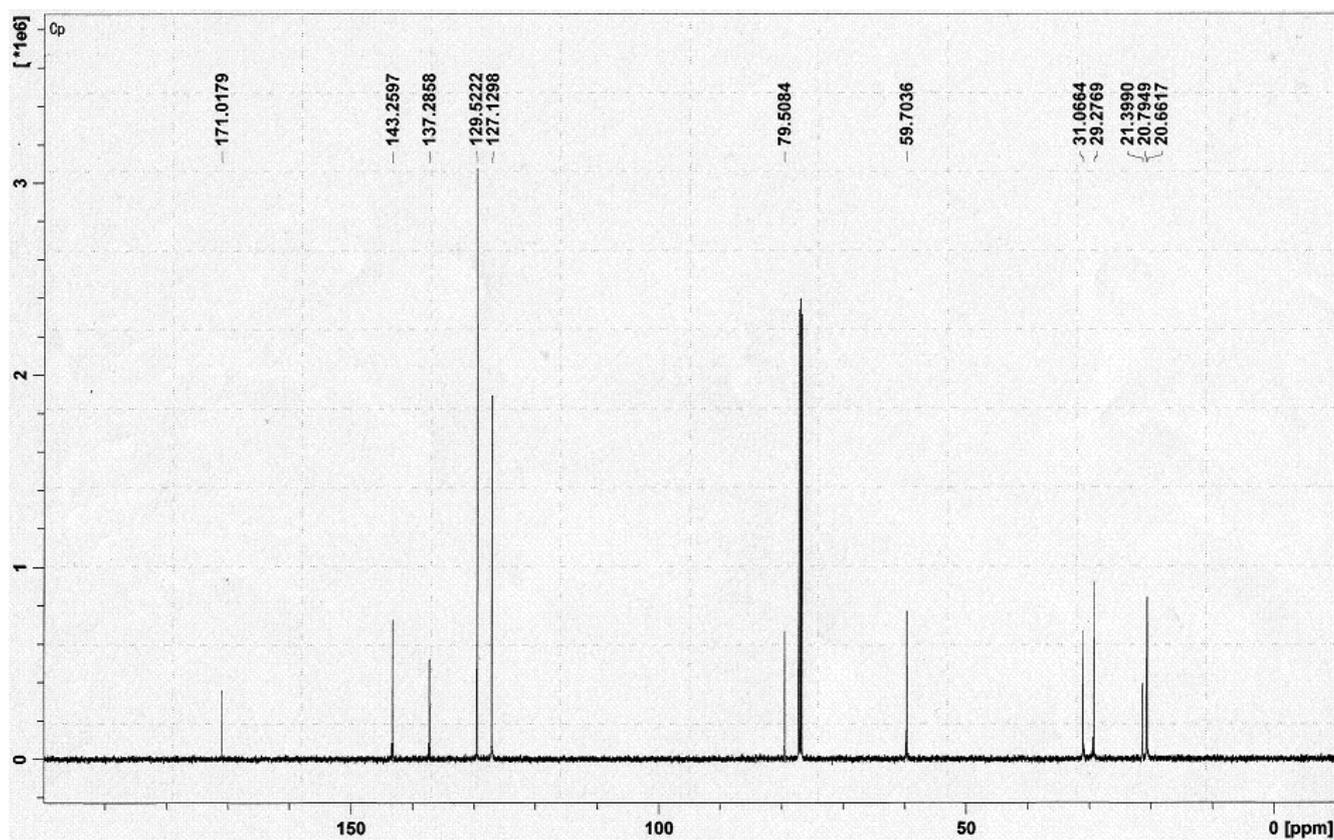


Figure S2. ¹³C-NMR Spectrum of compound 2a.

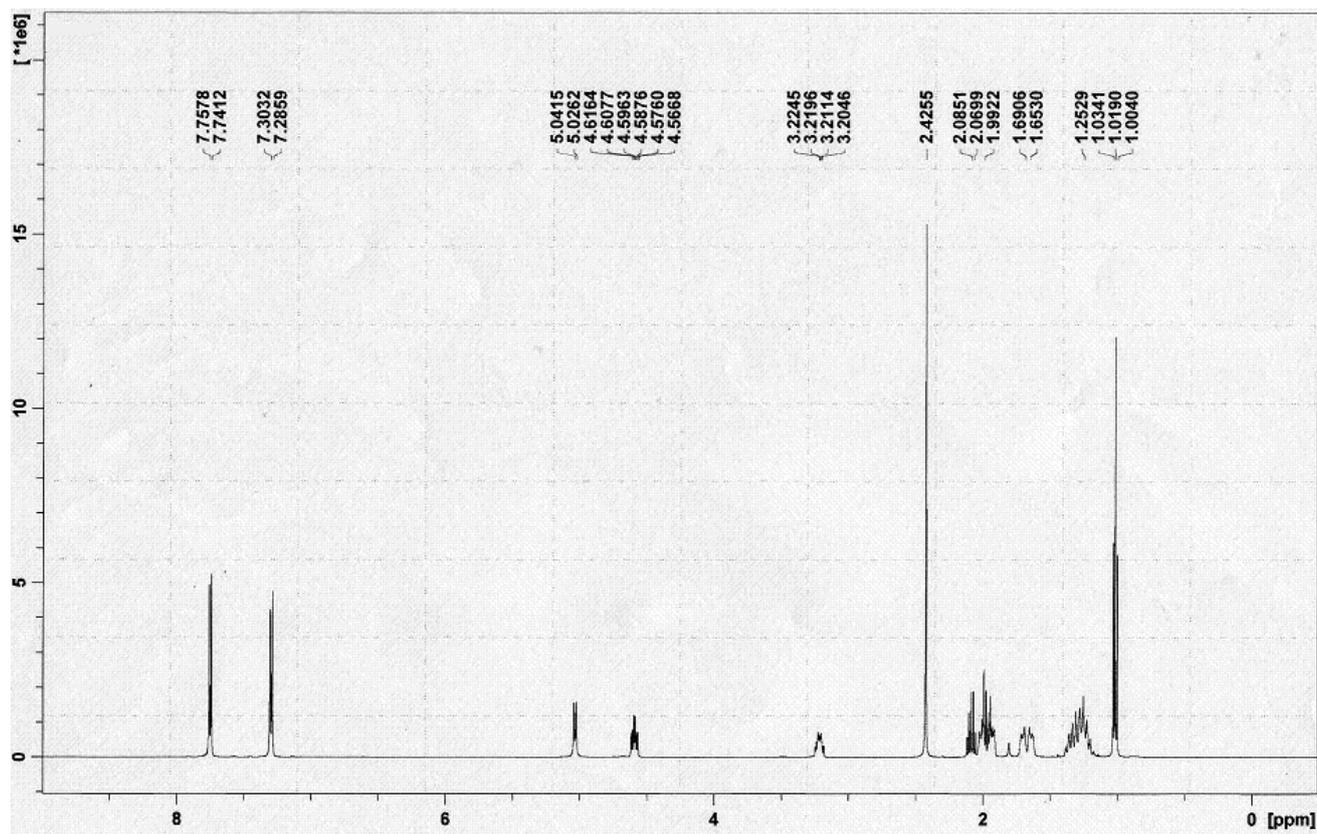


Figure S3. ¹H-NMR Spectrum of compound 2a'.

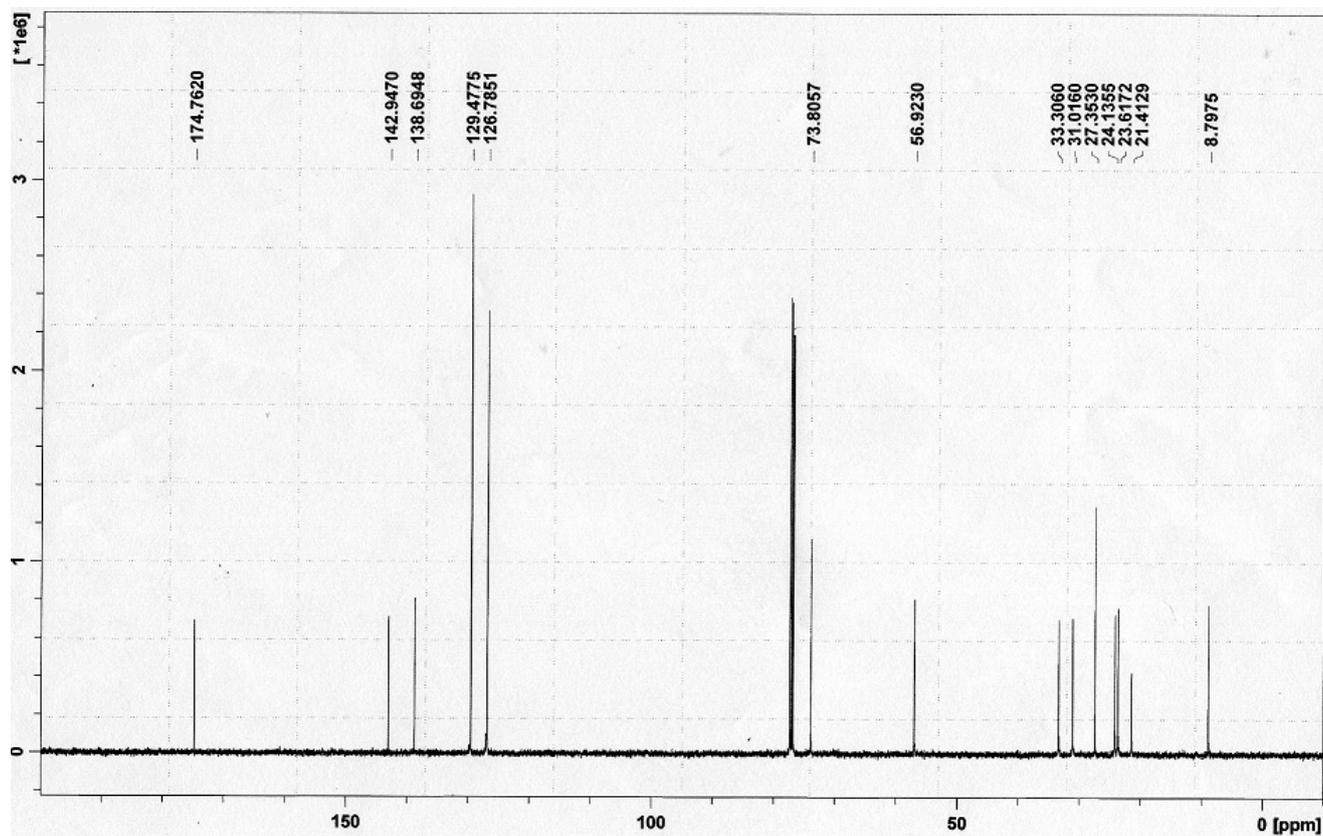


Figure S4. ¹³C-NMR Spectrum of compound 2a'.

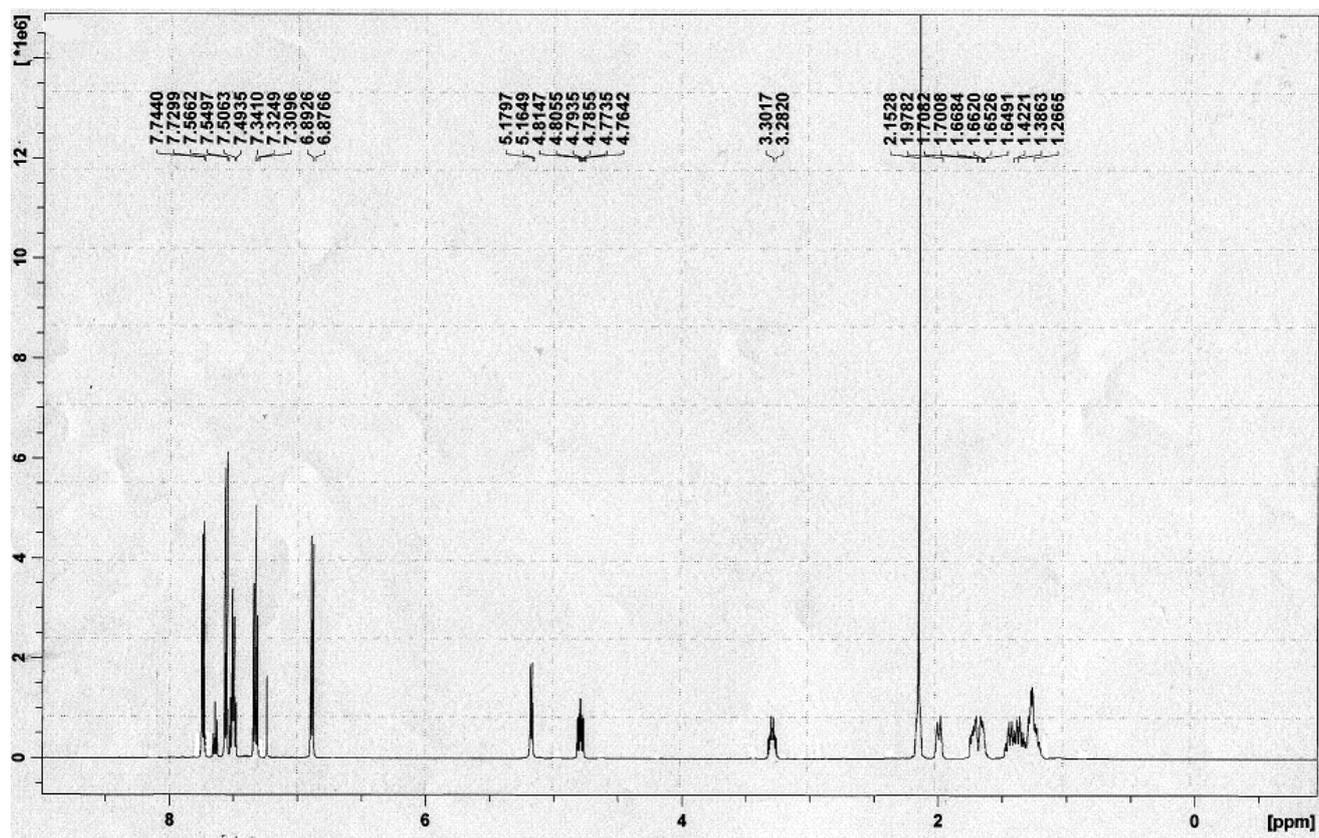


Figure S5. ¹H-NMR Spectrum of compound 2a''.

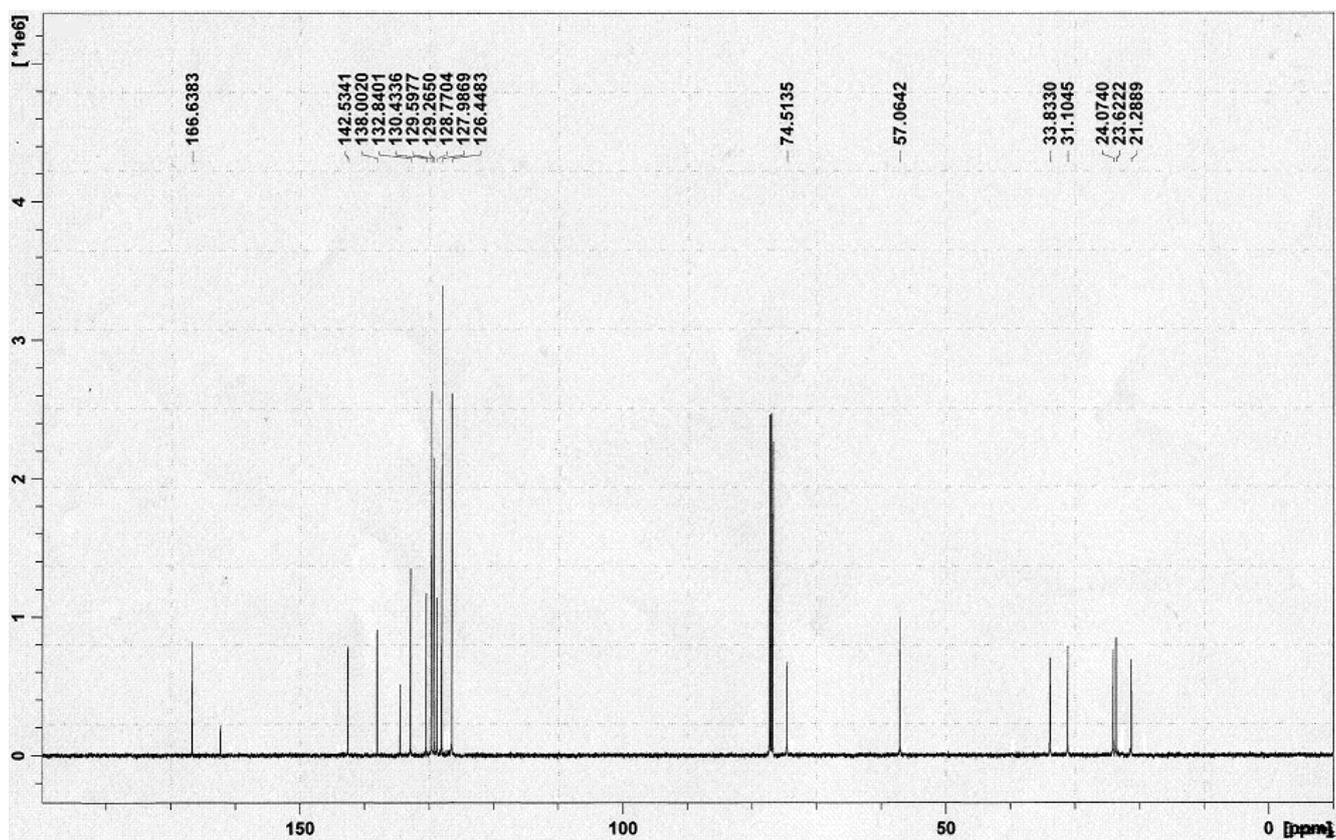


Figure S6. ¹³C-NMR Spectrum of compound 2a'.

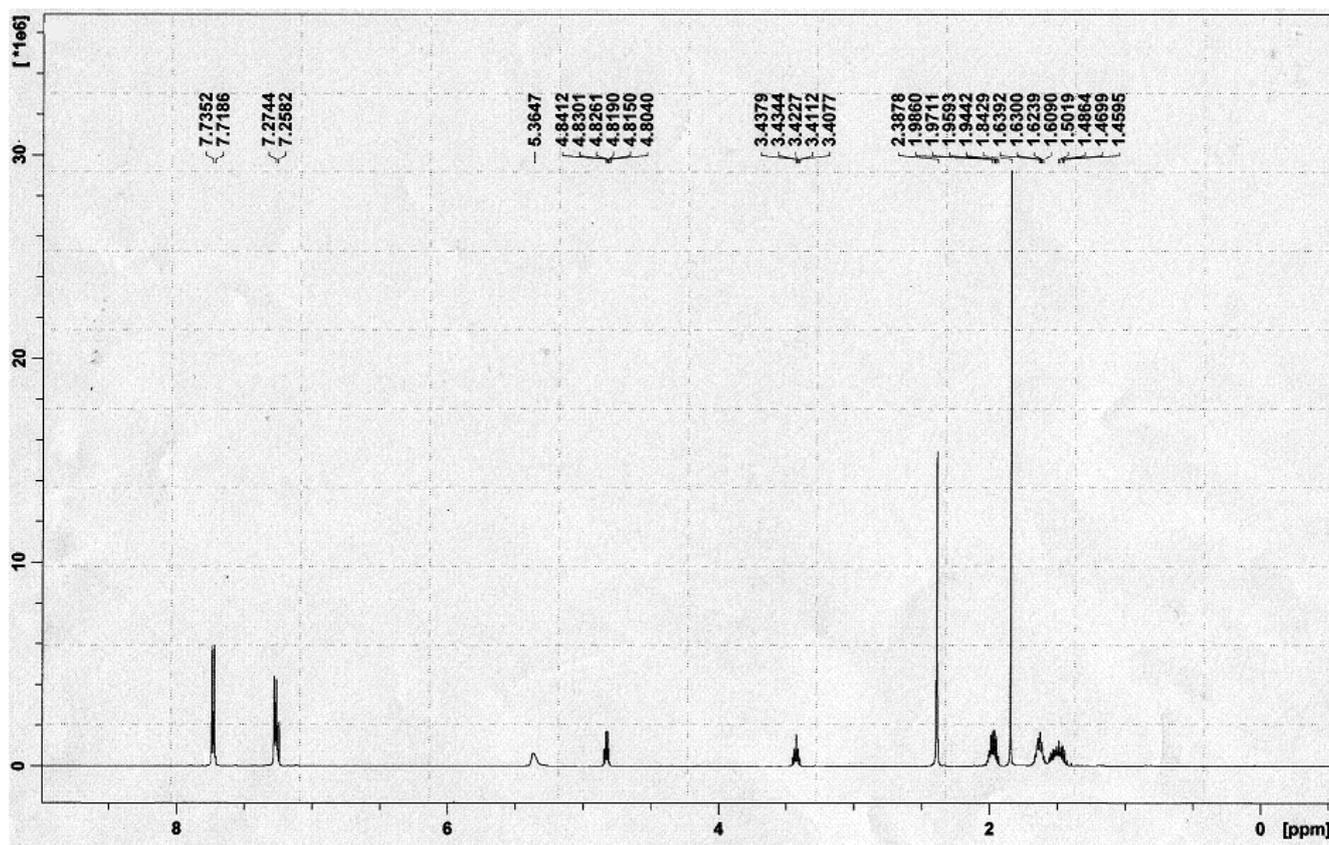


Figure S7. ¹H-NMR Spectrum of compound 2b.

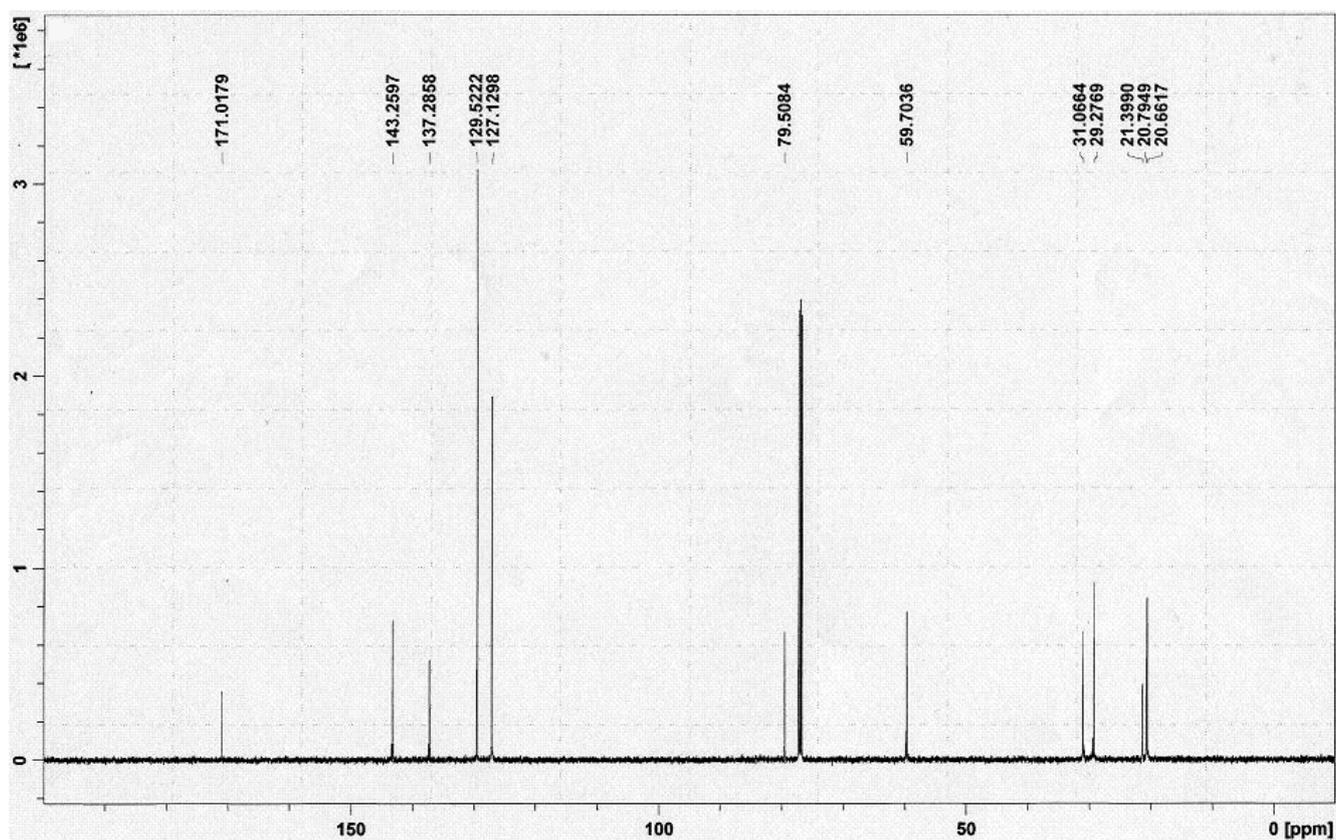
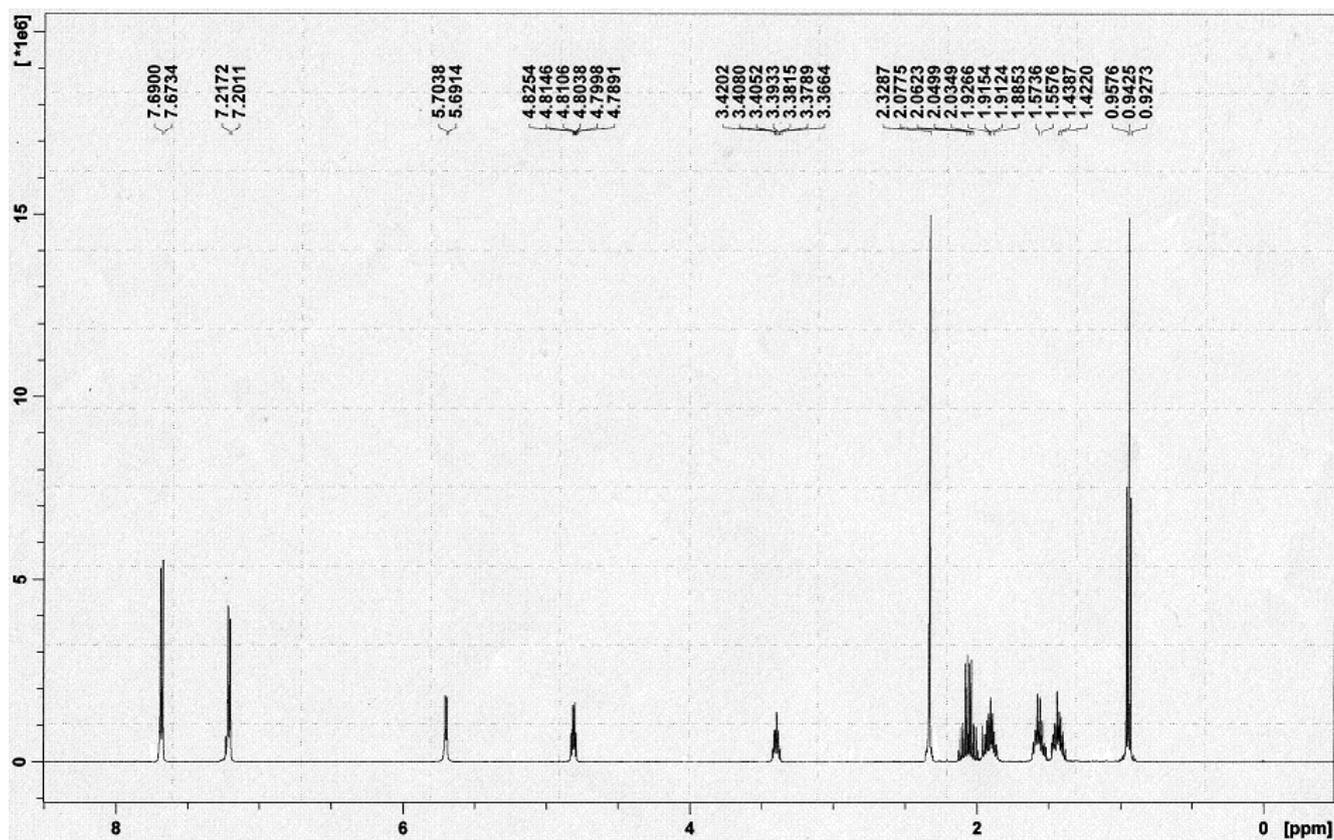
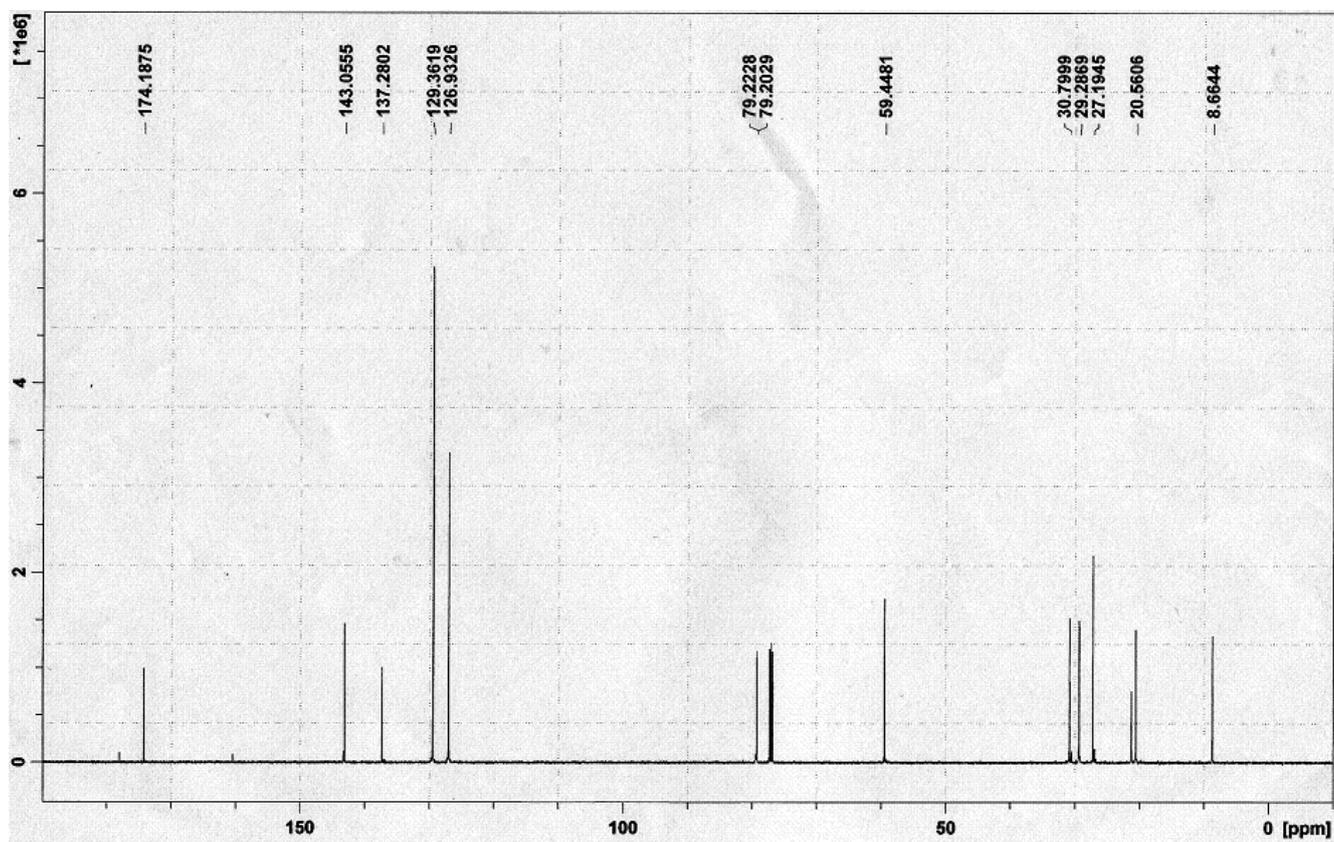


Figure S8. ¹³C-NMR Spectrum of compound 2b.

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

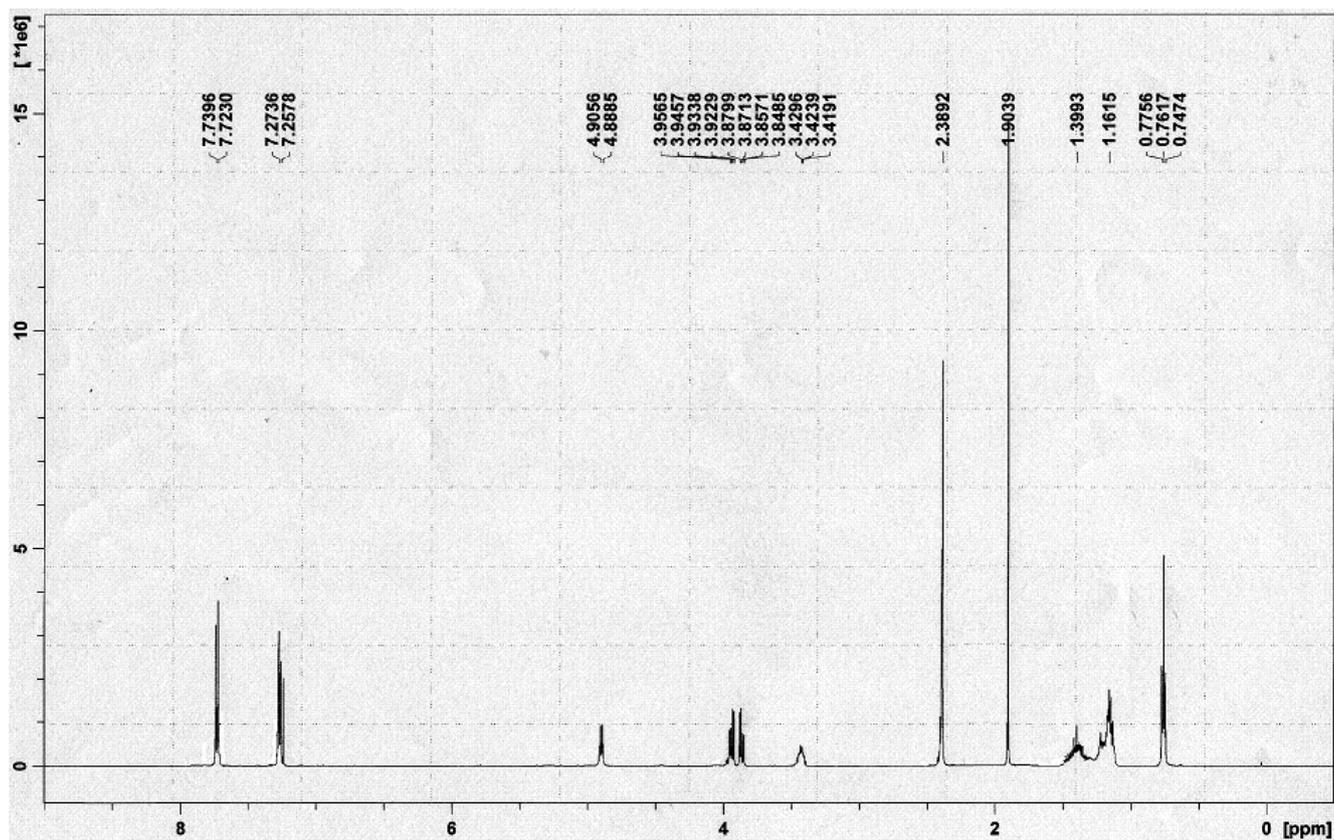


Figure S11. ¹H-NMR Spectrum of compound 2c.

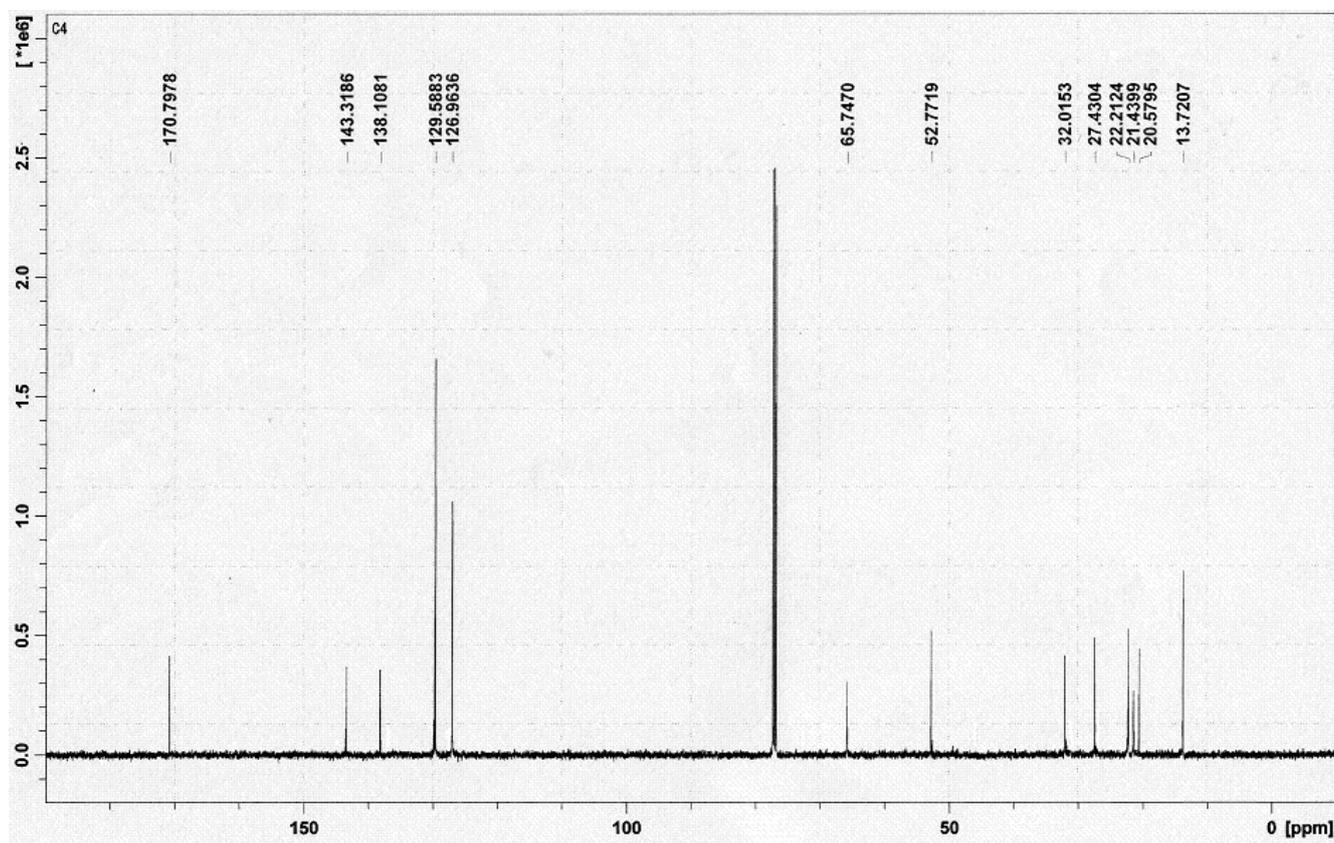
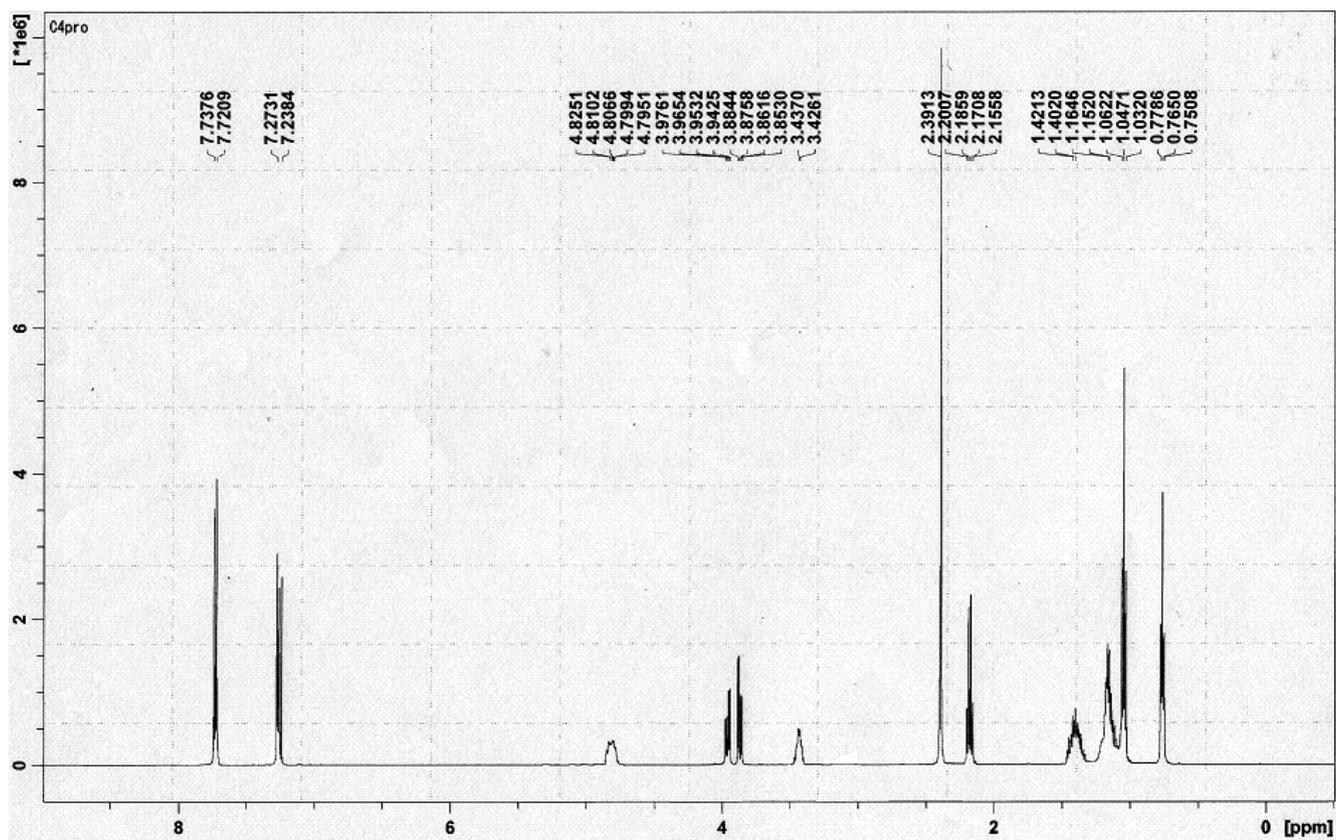
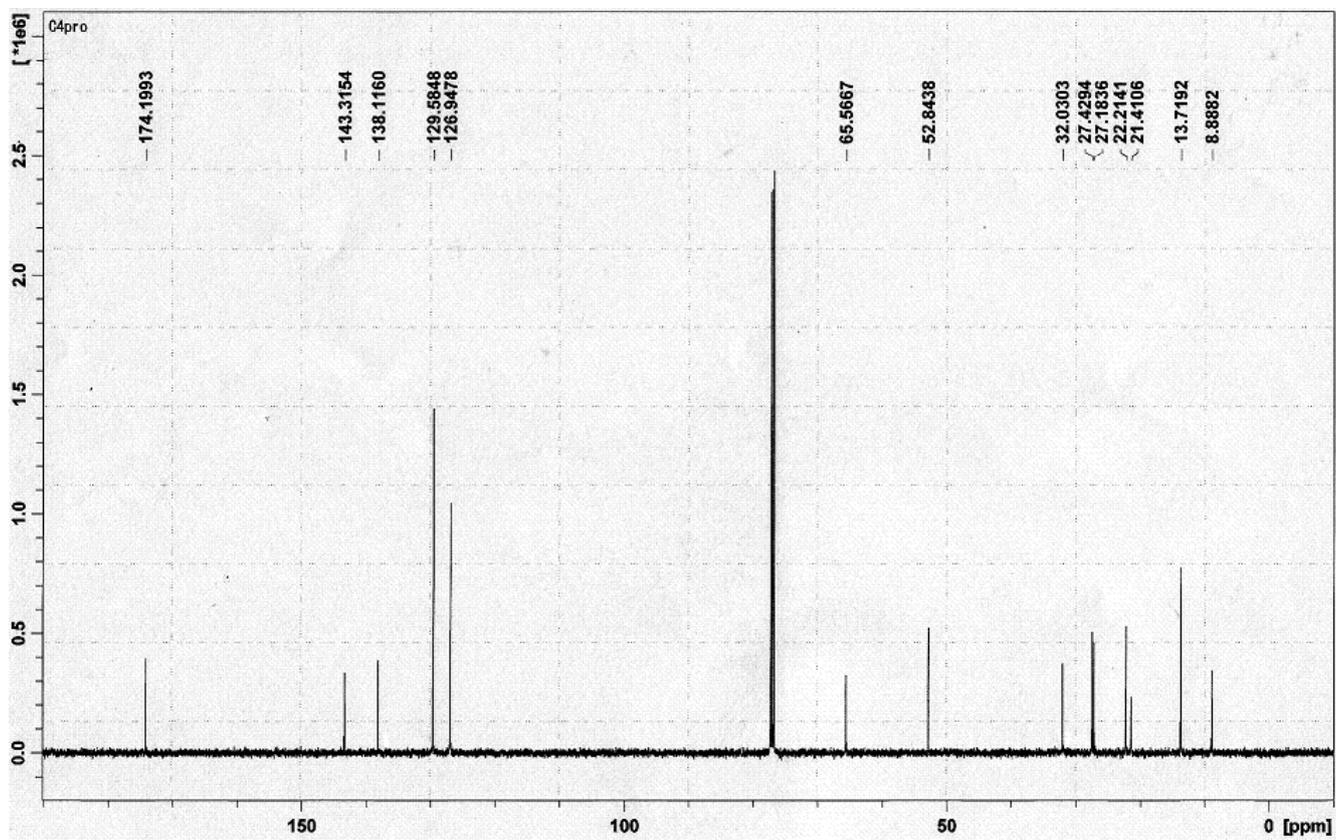


Figure S12. ¹³C-NMR Spectrum of compound 2c.

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

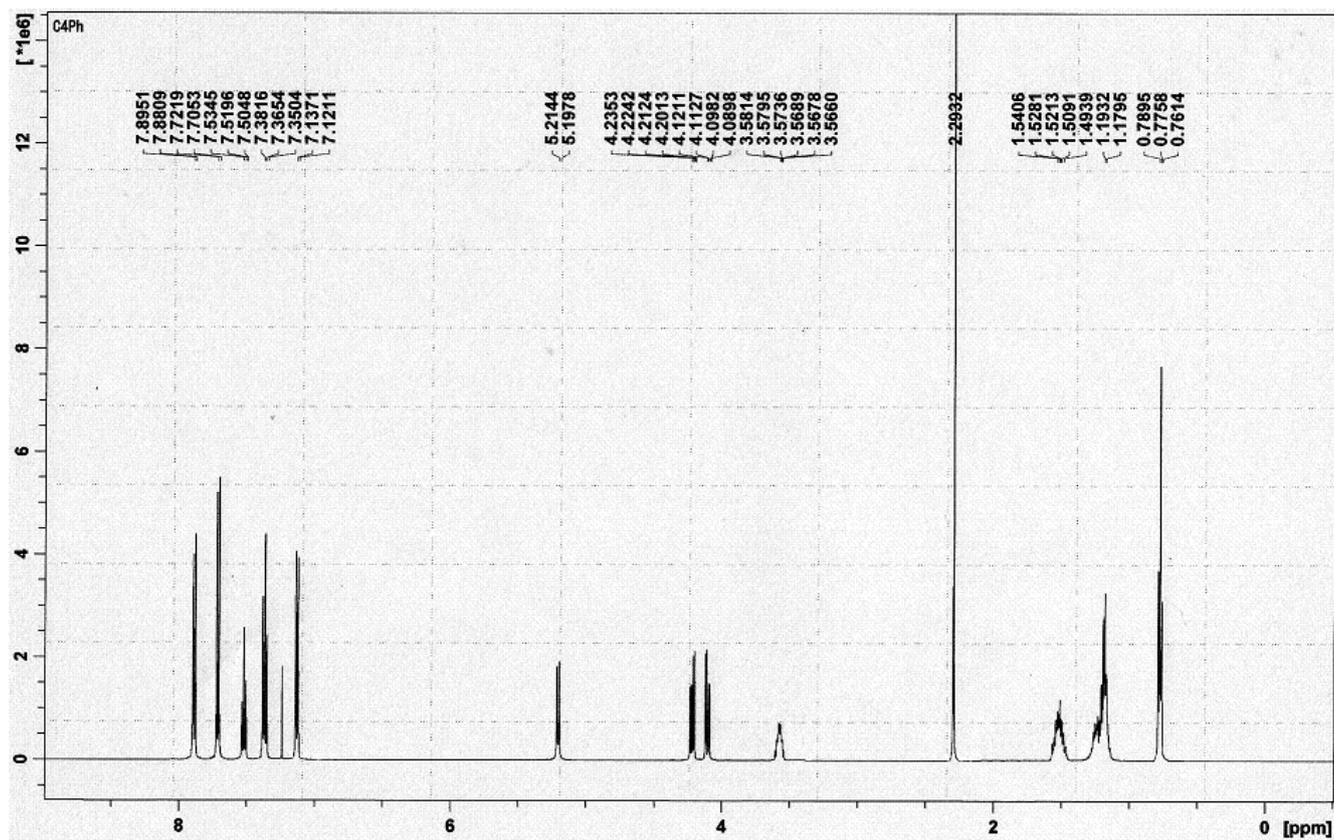


Figure S15. ¹H-NMR Spectrum of compound 2c''.

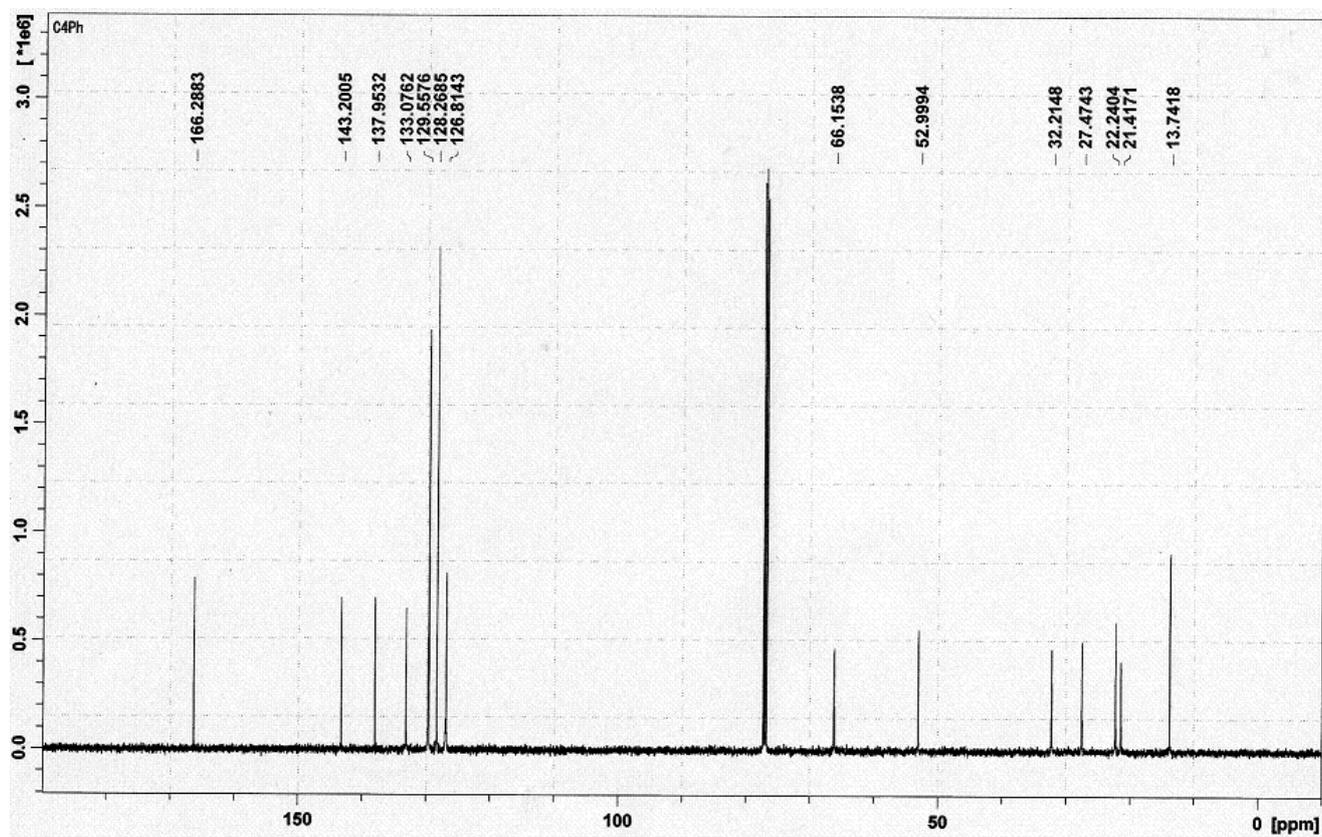
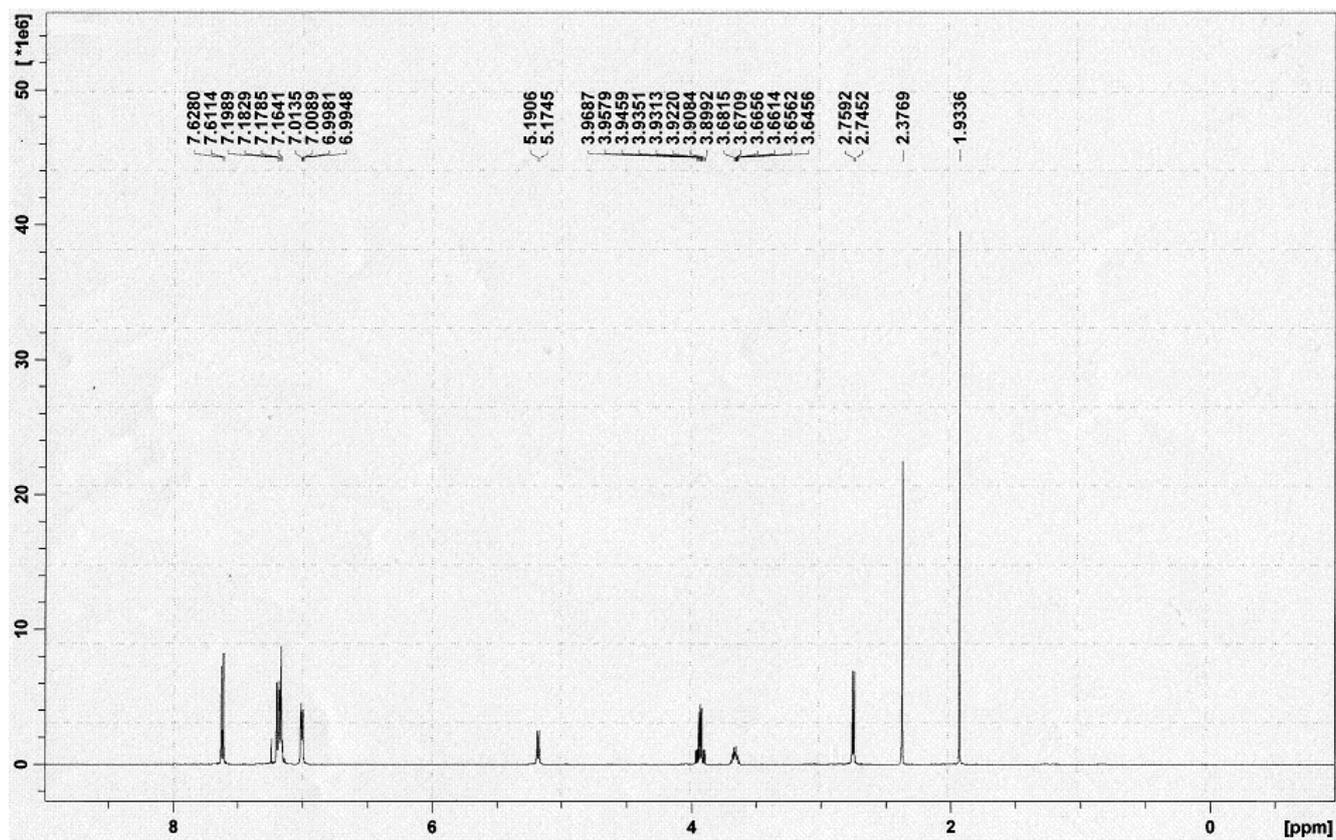
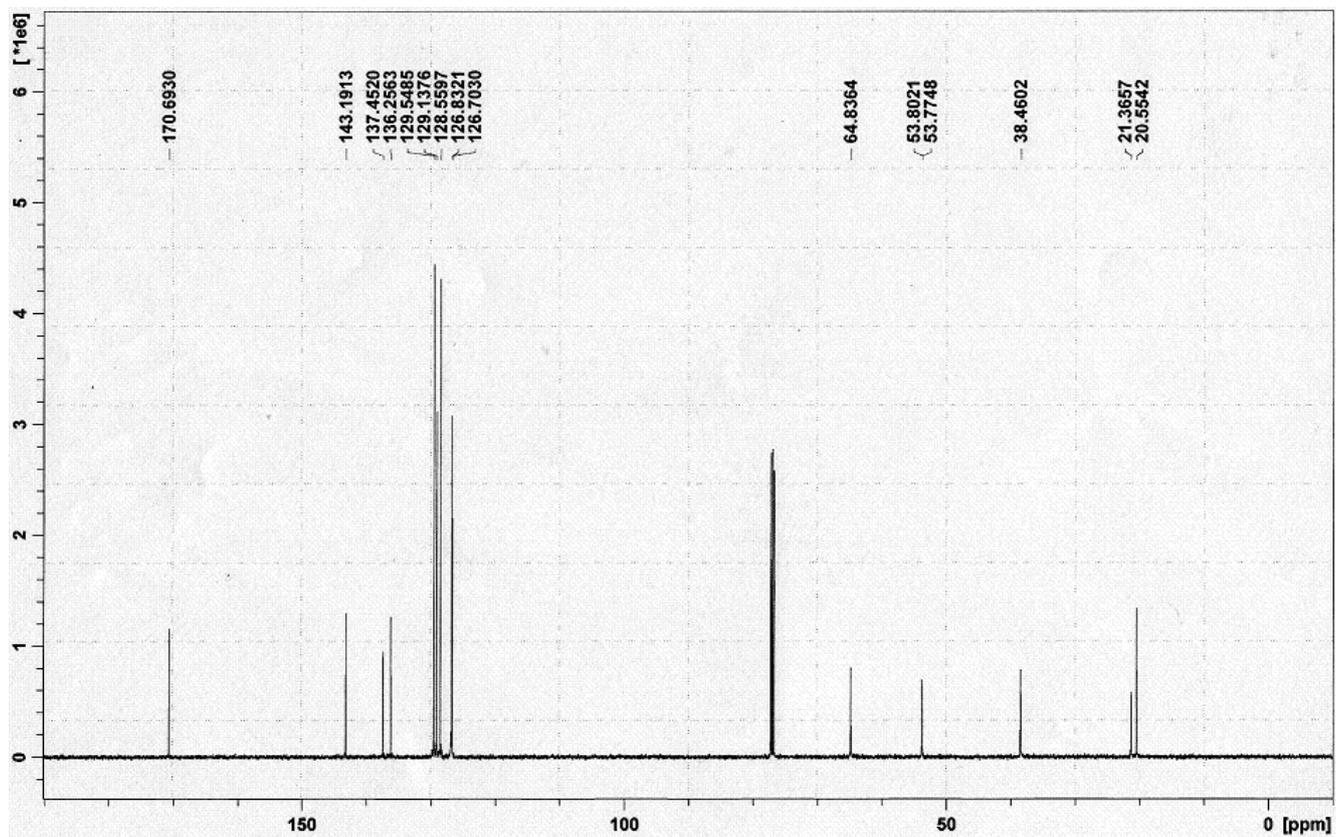
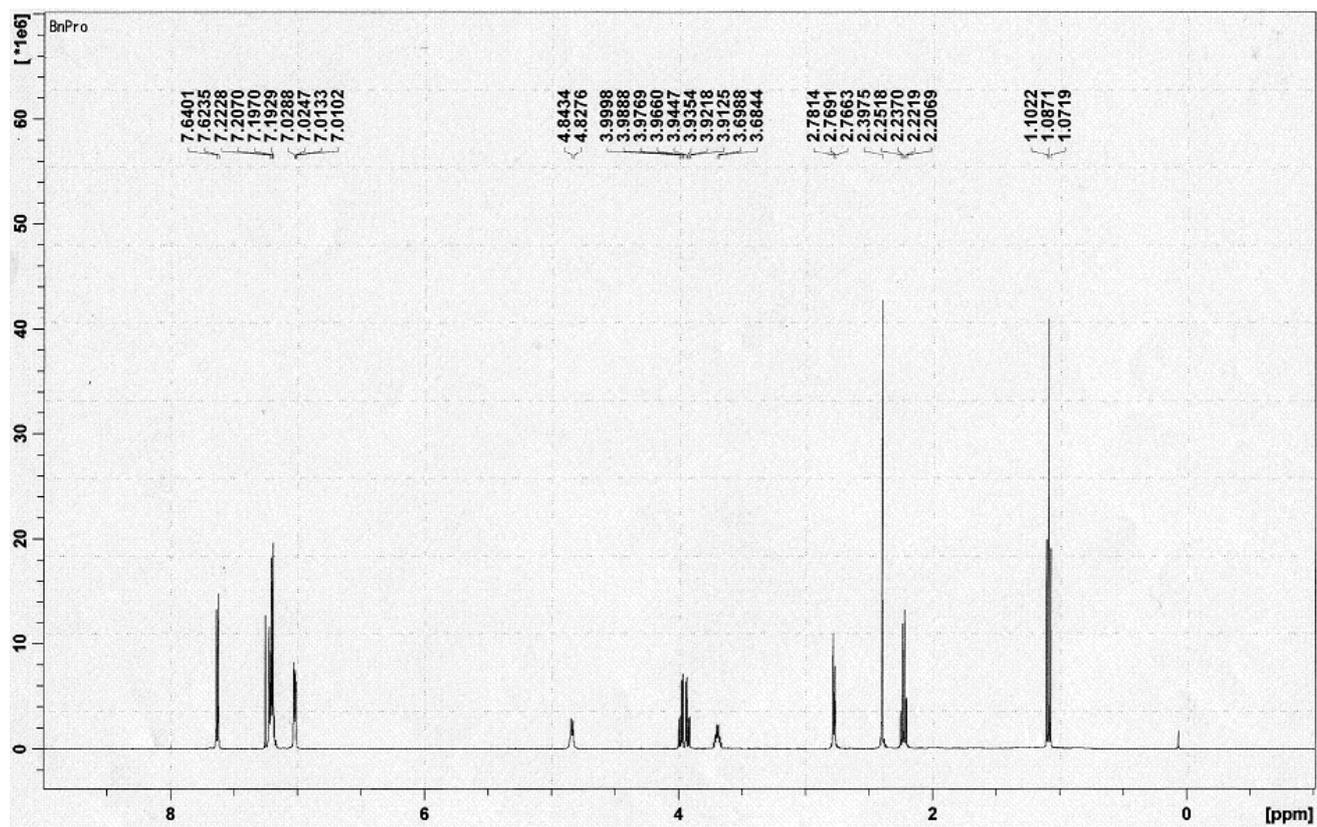
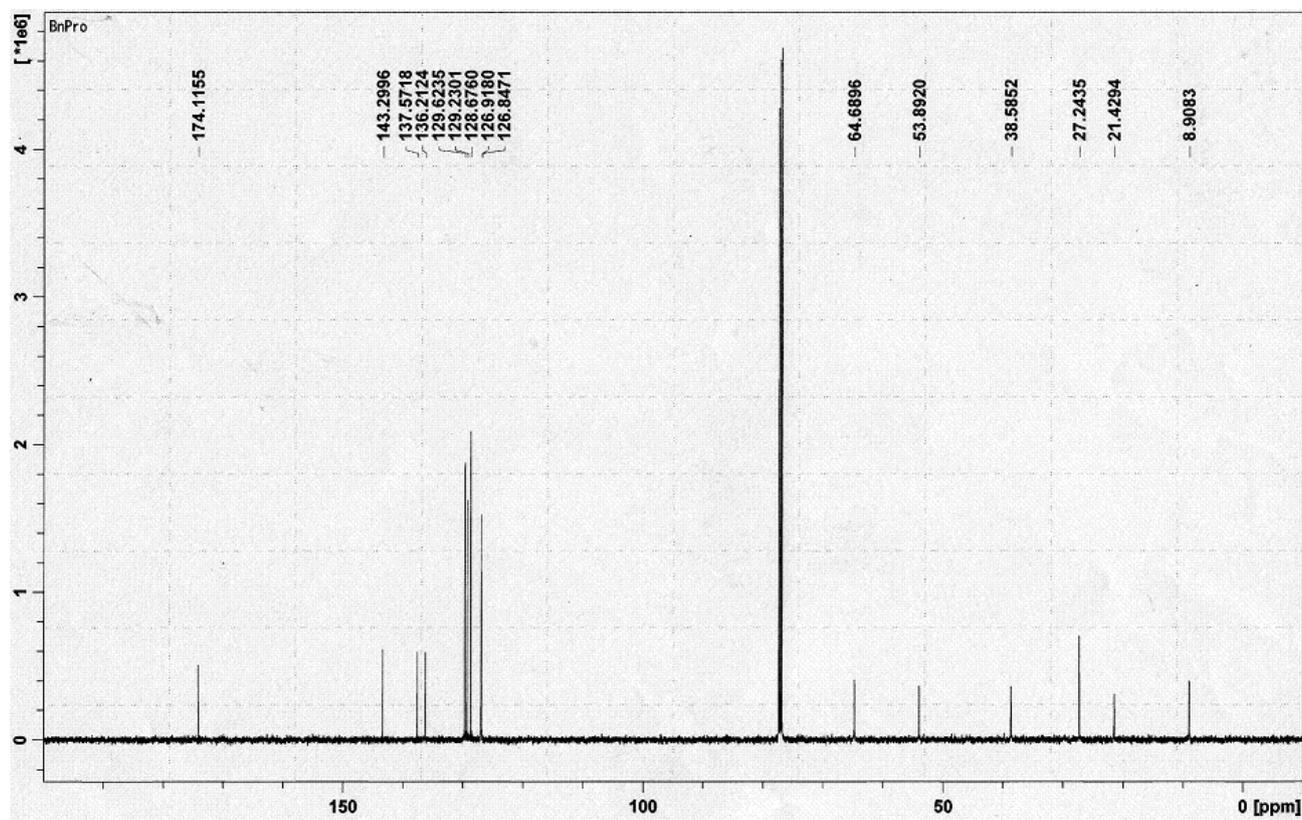


Figure S16. ¹³C-NMR Spectrum of compound 2c''.

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

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

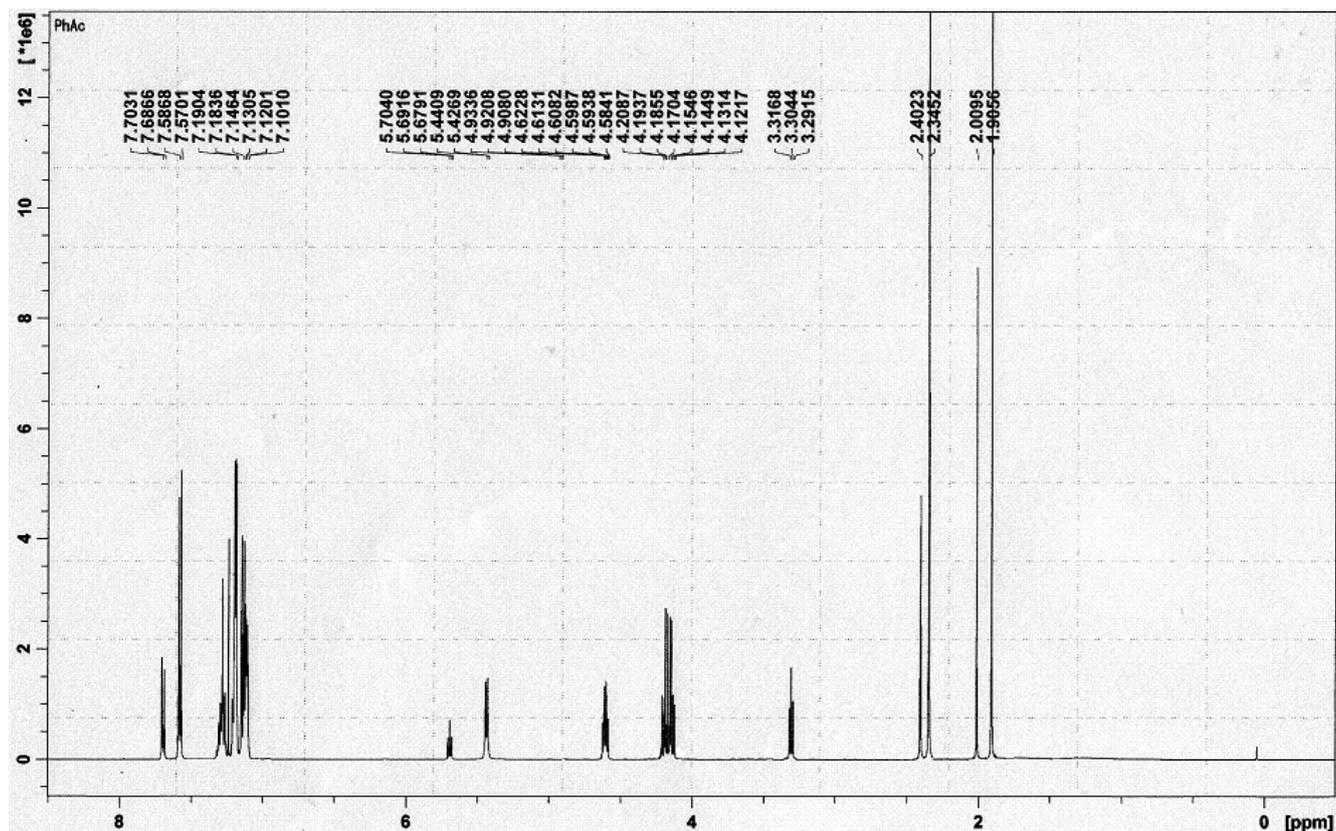


Figure S21. ^1H -NMR Spectrum of compound 2e.

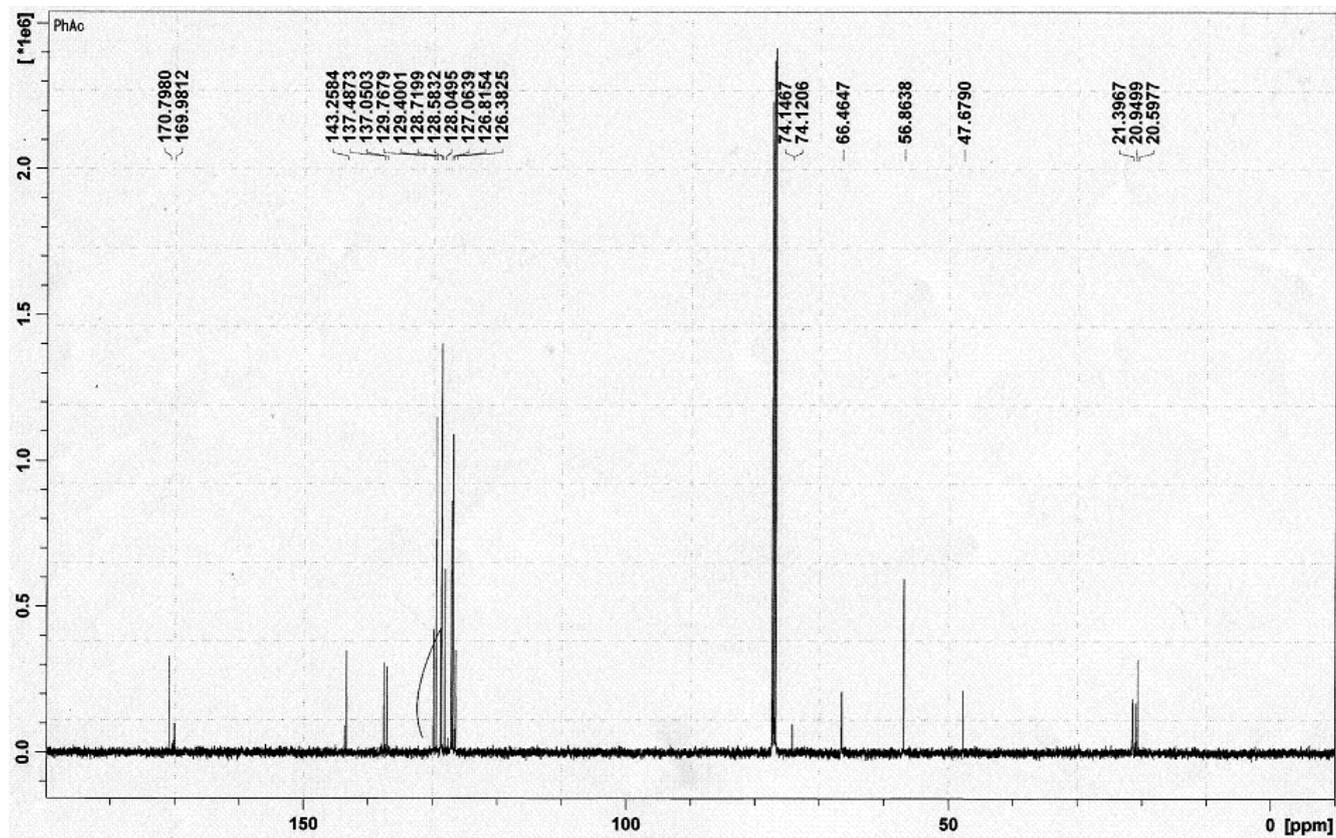
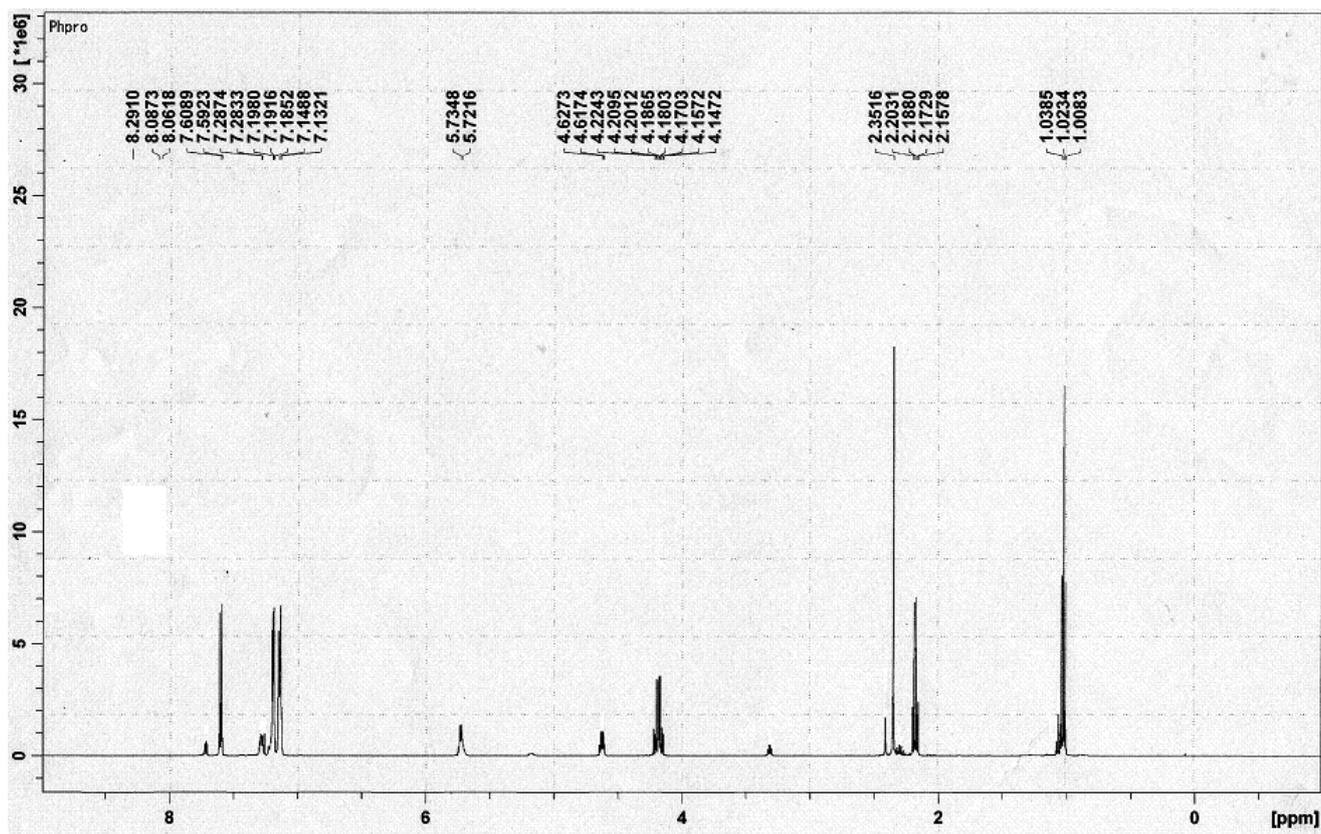
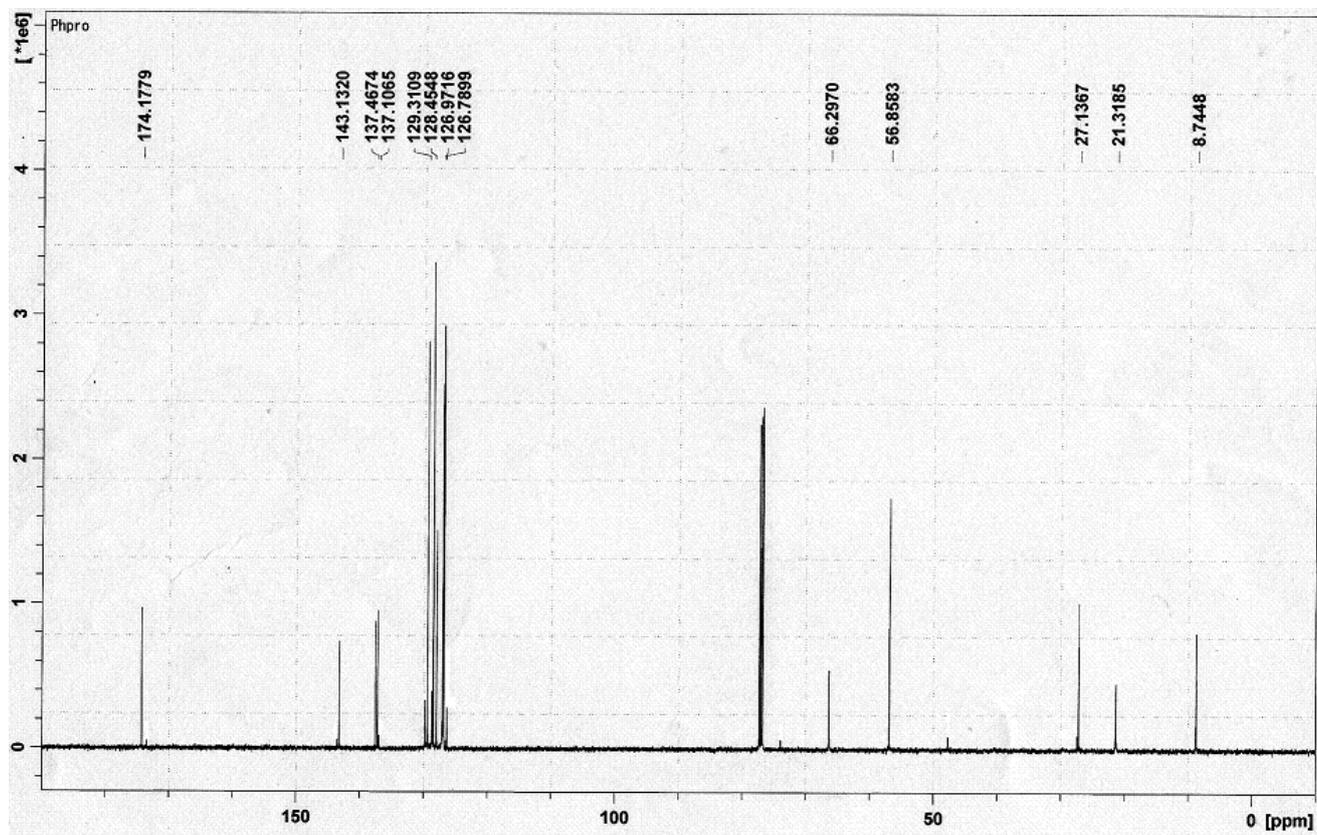


Figure S22. ^{13}C -NMR Spectrum of compound 2e.

Figure S23. $^1\text{H-NMR}$ Spectrum of compound $2e'$.Figure S24. $^{13}\text{C-NMR}$ Spectrum of compound $2e'$.

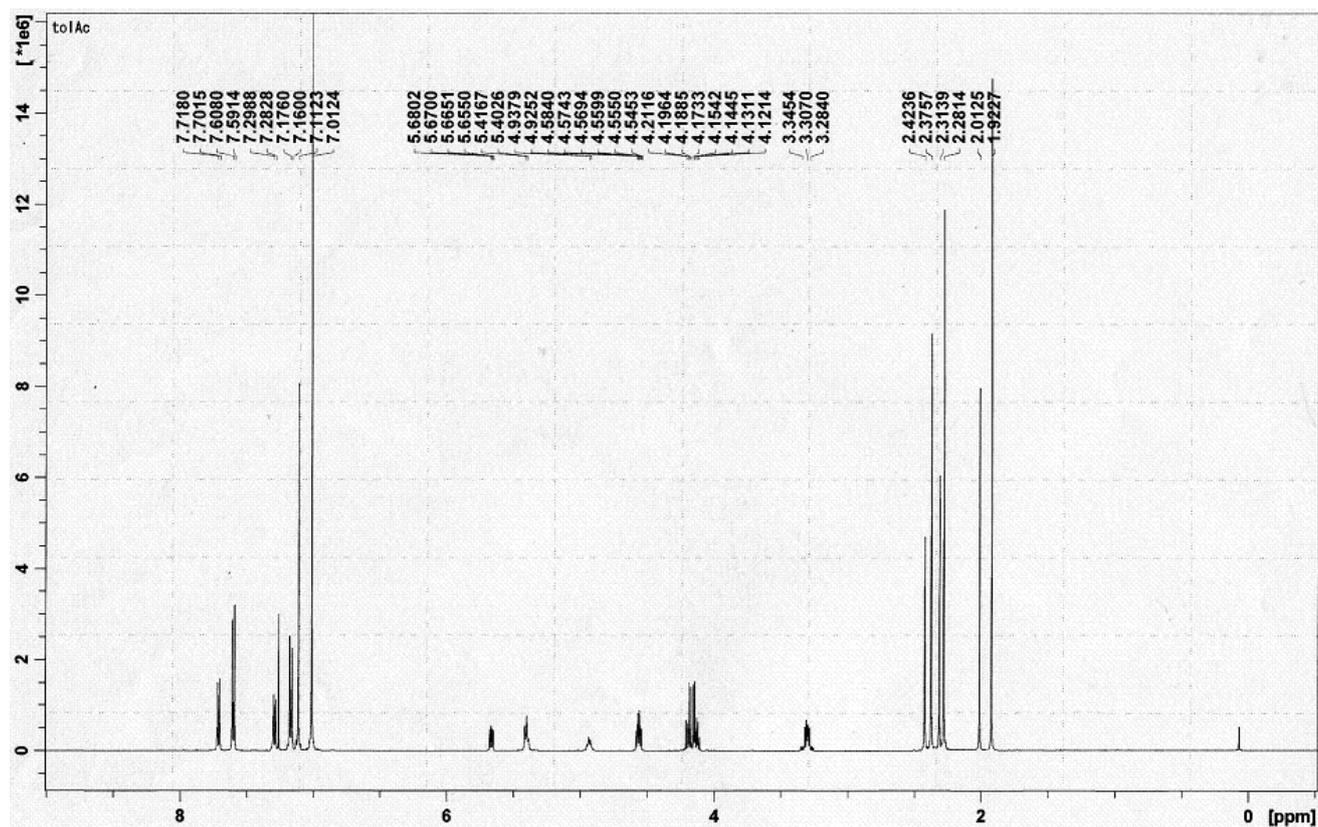


Figure S25. ¹H-NMR Spectrum of compound 2f.

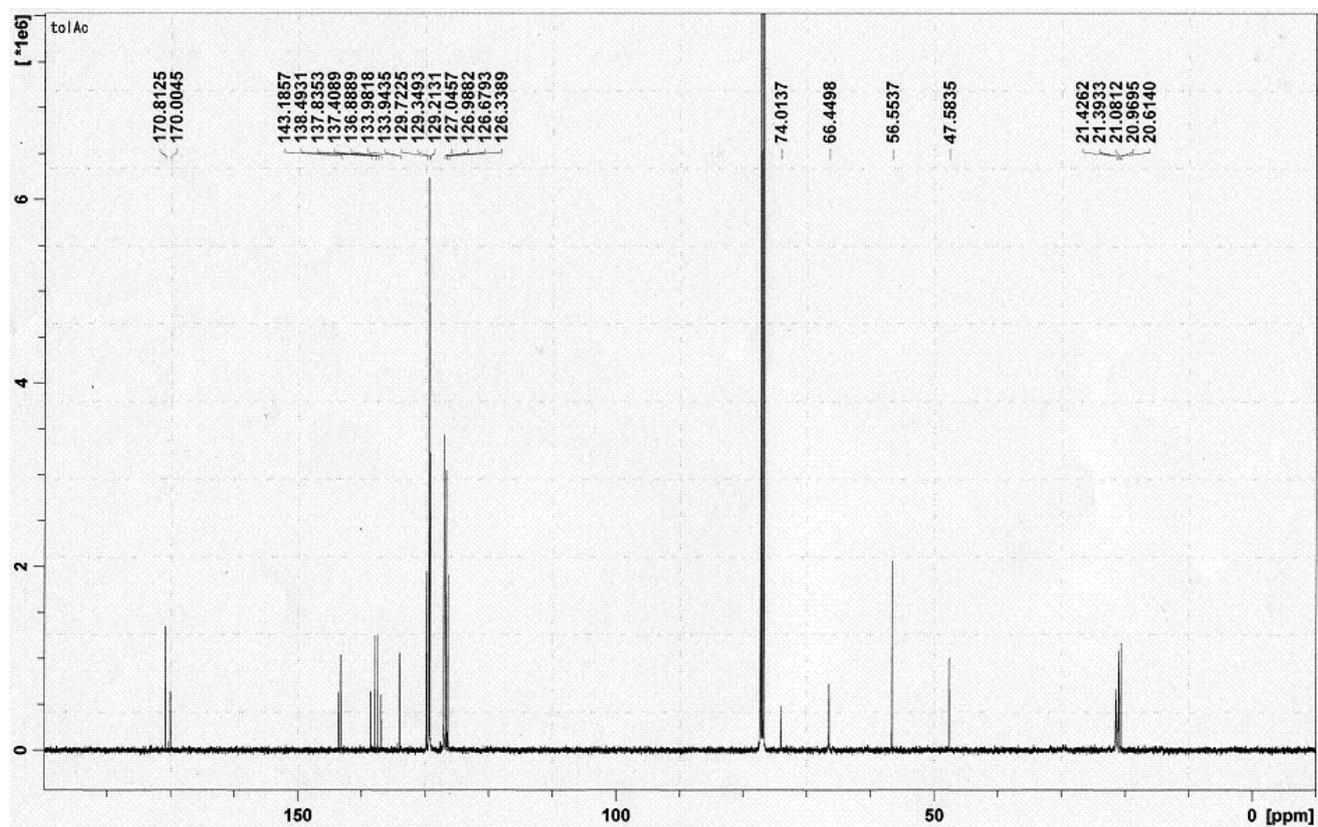


Figure S26. ¹³C-NMR Spectrum of compound 2f.

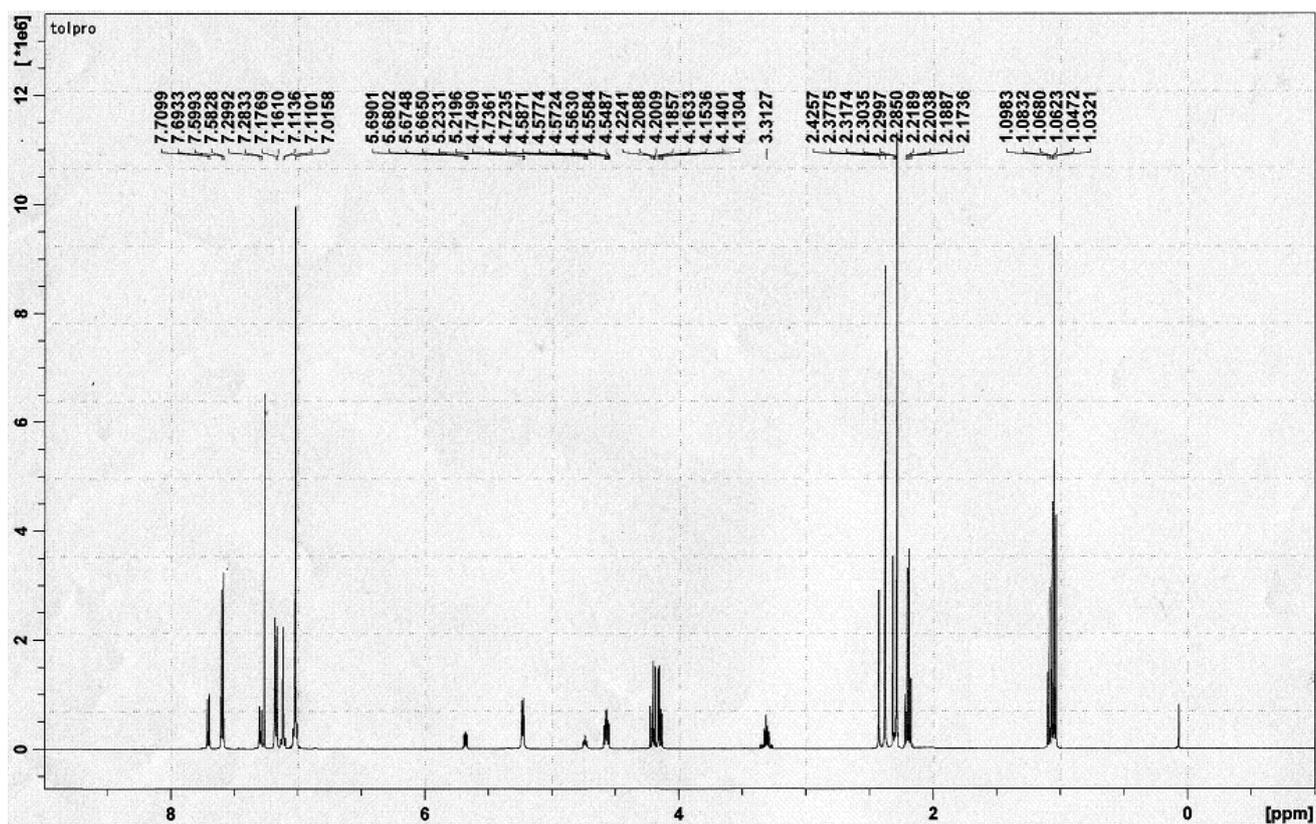


Figure S27. $^1\text{H-NMR}$ Spectrum of compound **2f'**.

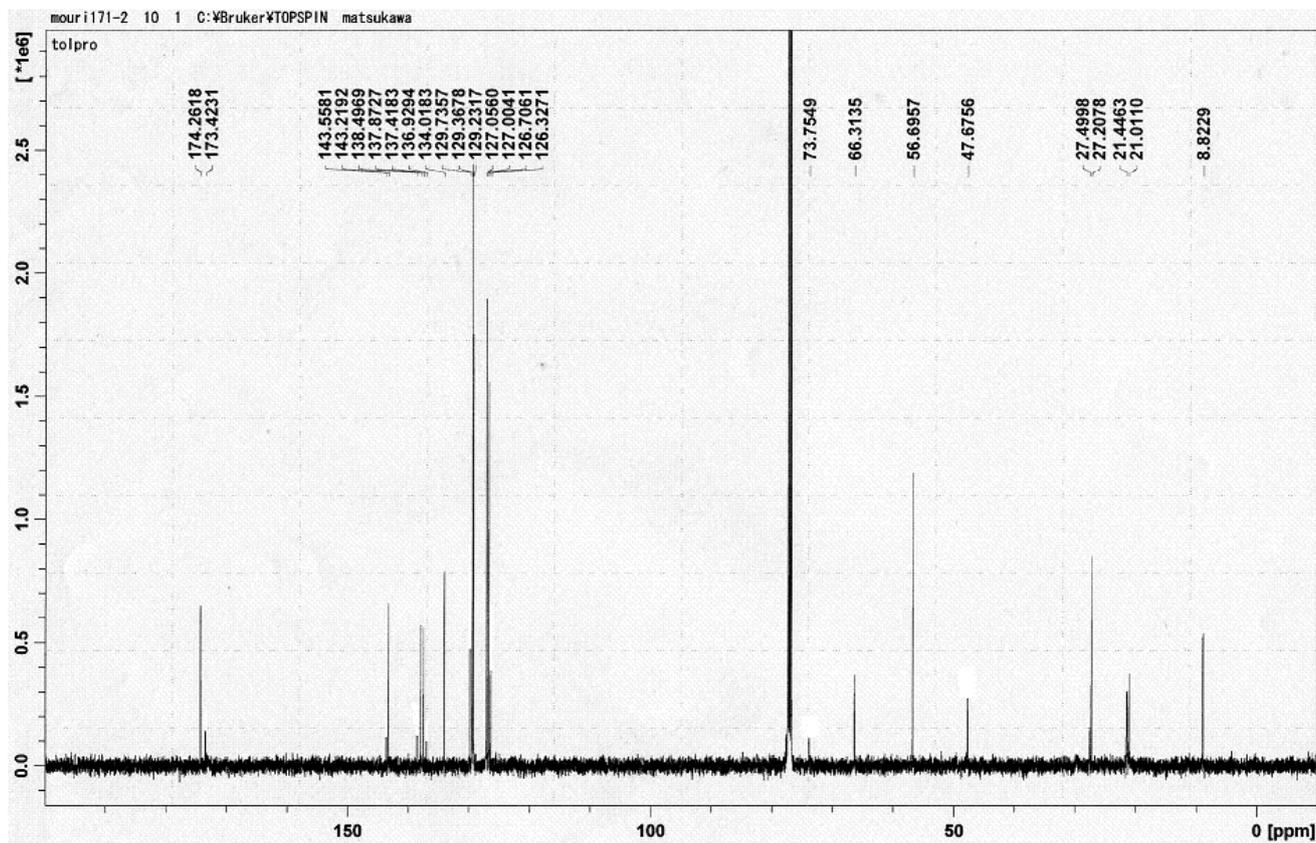


Figure S28. $^{13}\text{C-NMR}$ Spectrum of compound **2f'**.

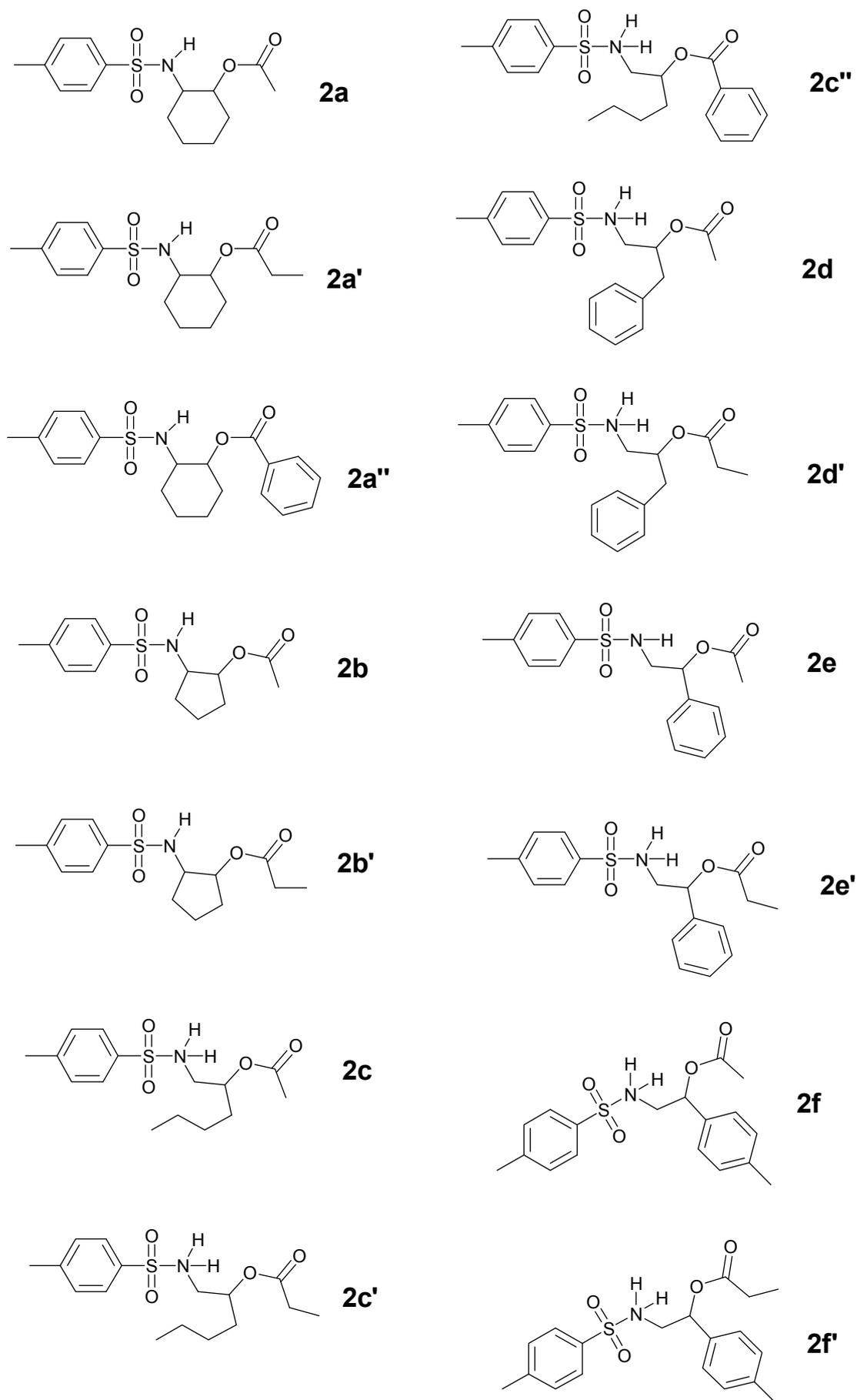


Figure S29. Structure of compounds **2a–2f**, **2a'–2f'**, **2a''**, and **2c''**.