Supplementary Materials: Solvent-Free Biginelli Reactions Catalyzed by Hierarchical Zeolite Utilizing a Ball Mill Technique: A Green Sustainable Process

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1. General Procedure for the Knoevenagel Adduct

MFI27_6 catalysts (0.35 g), were added to ethylacetoacetate **1a** (10 mmol) and benzadehyde derivative **2a** (10 mmol) in a mortar, the mixture was ground with a pestle at room temperature then placed in the 25 ml stainless steel gar equipped with two stainless steel balls. The gar was closed and milling was conducted at the frequancy 30 Hz. till the reaction complete at 10 min. The contents of the ball mill vessel were then dissolved in hot ethyl acetate and sonicated for 5 min. then remove the catalyst by filtration. The reaction product was separated as a solid after evaporation of ethyl acetate under reduced pressure to give pure compounds of ethyl 3-oxo-2-(4-(phenylsulfonyl)benzylidene)butanoate.

^{1}H NMR (DMSO-d_6): δ 1.23 (t, J = 6.9 Hz, 3H, CH_3 ester), 2.29 (s, 3H, CH_3), 4.36 (q, J = 6.9 Hz, 2H, CH_2 ester), 7.36–8.32 (m, 9H, ArH), 8.62 (s, 1H, CH).

2. Some NMR Spectra of the Novel Products

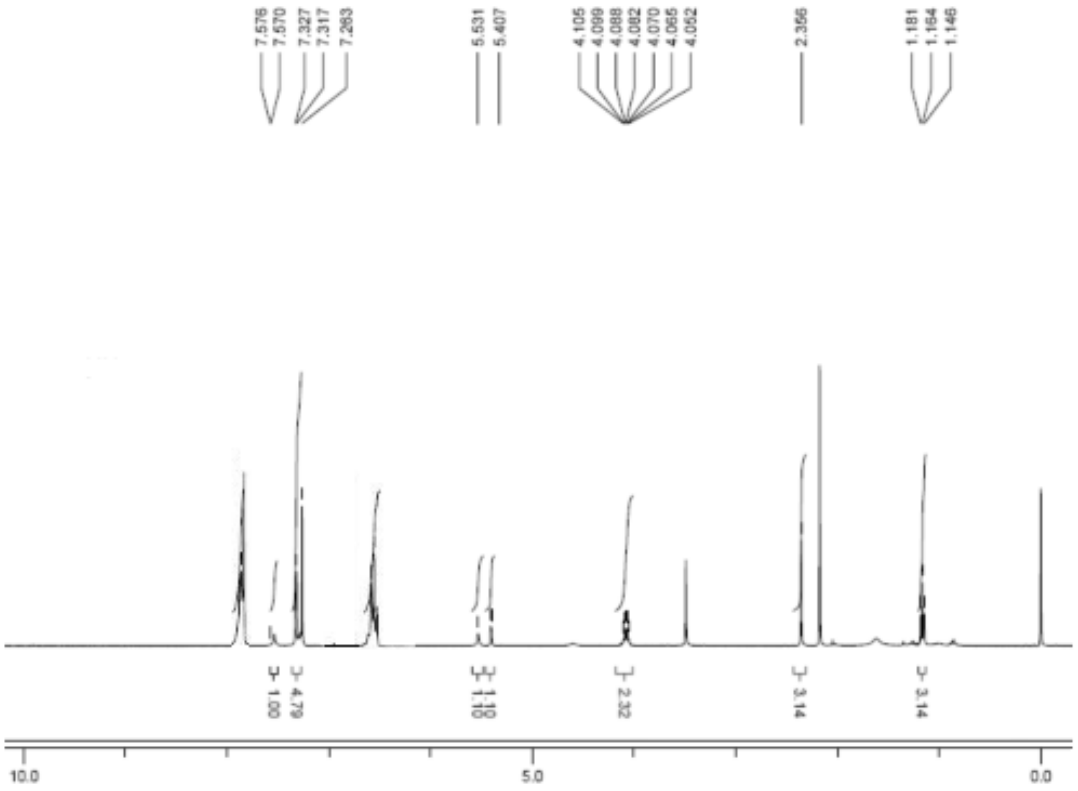

Figure S1. ^{1}H NMR of compound **4a**.

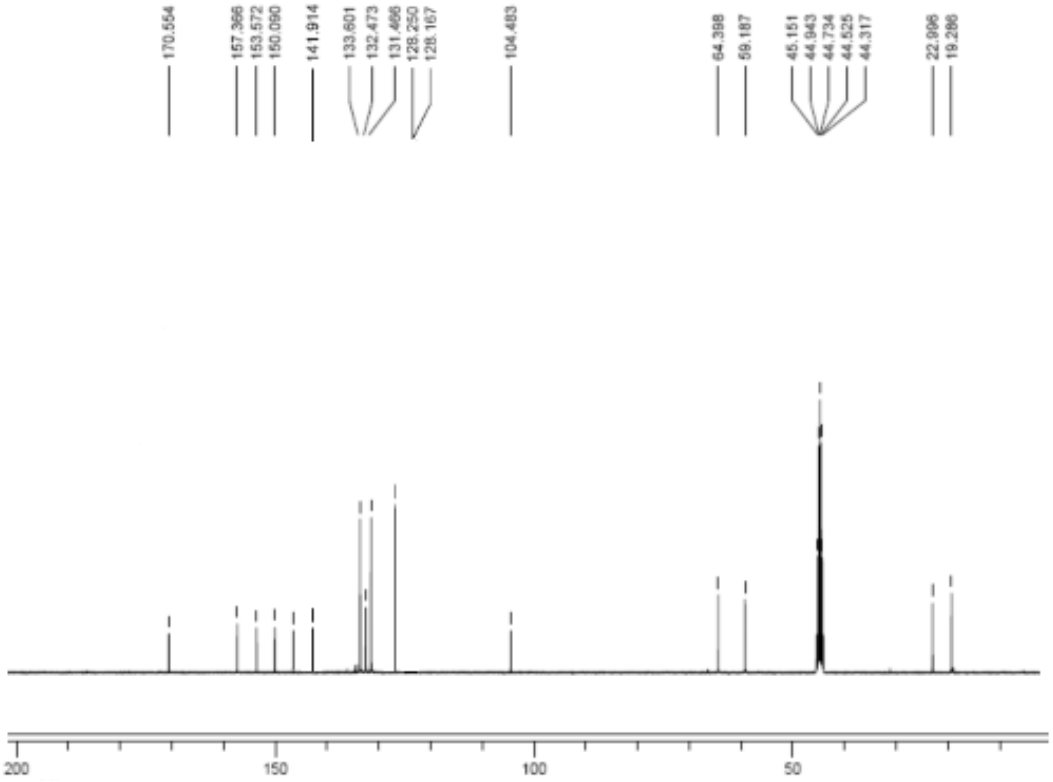

Figure S2. ^{13}C NMR of compound **4a**.

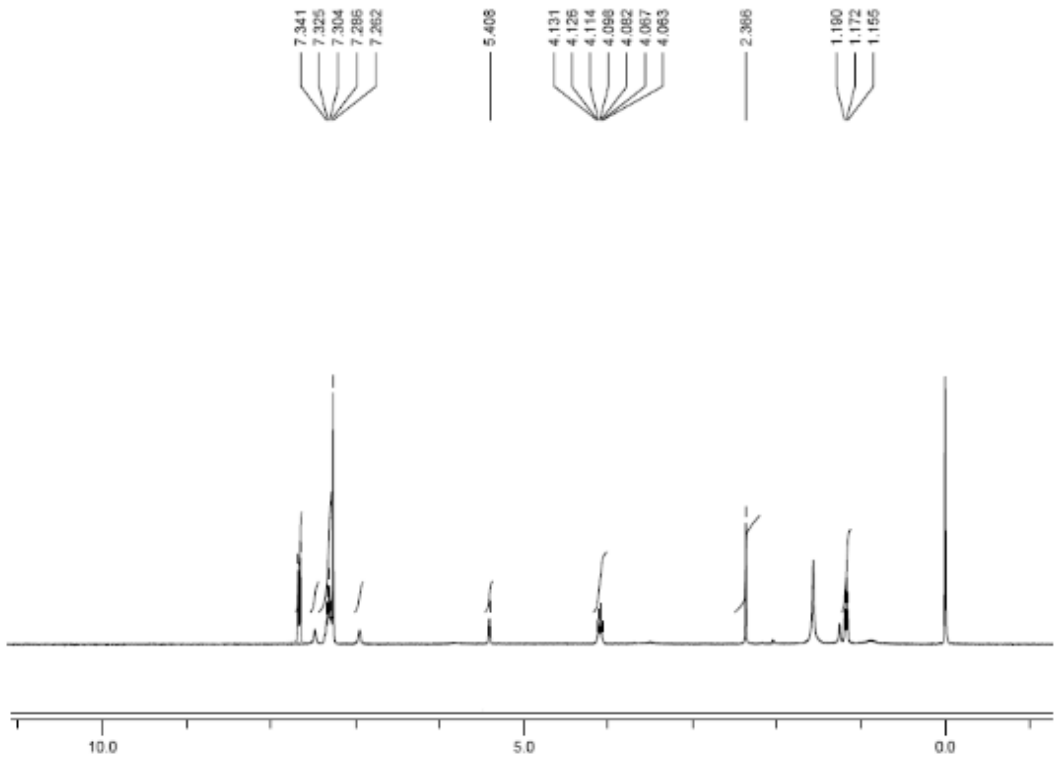

Figure S3. ^{1}H NMR of Compound **4b**.

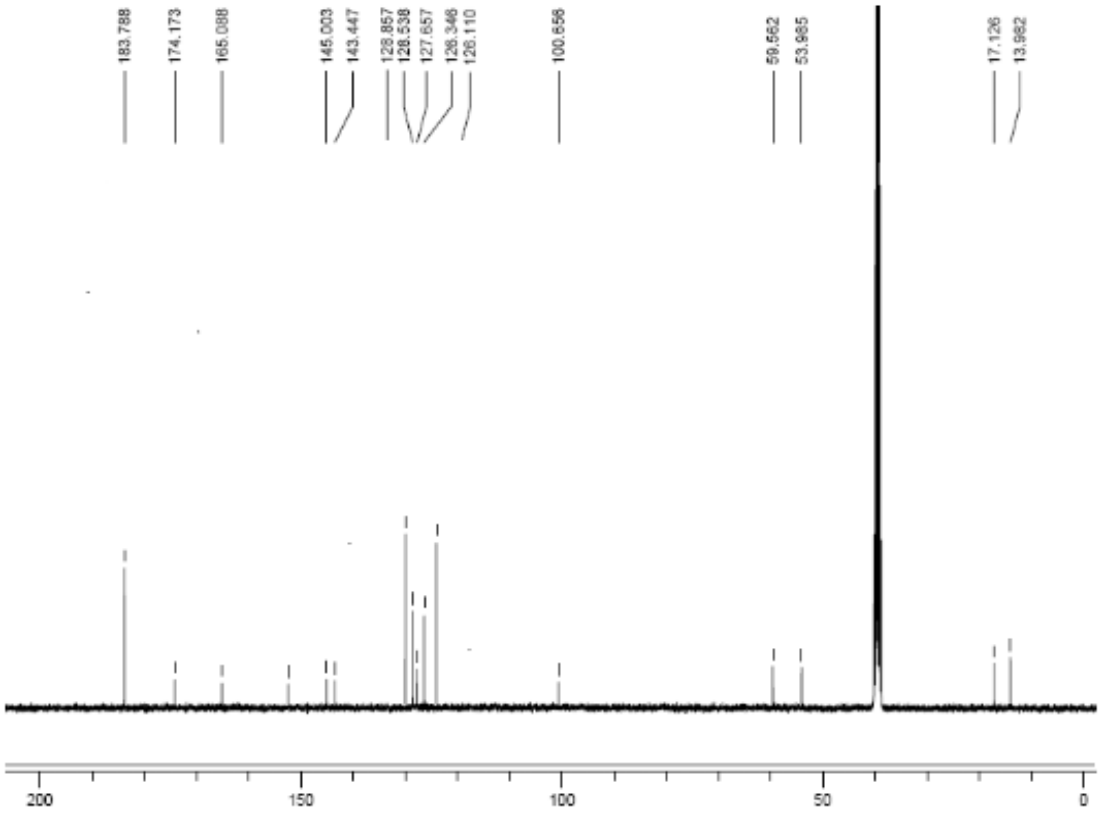

Figure S4. ^{13}C NMR of compound **4b**.

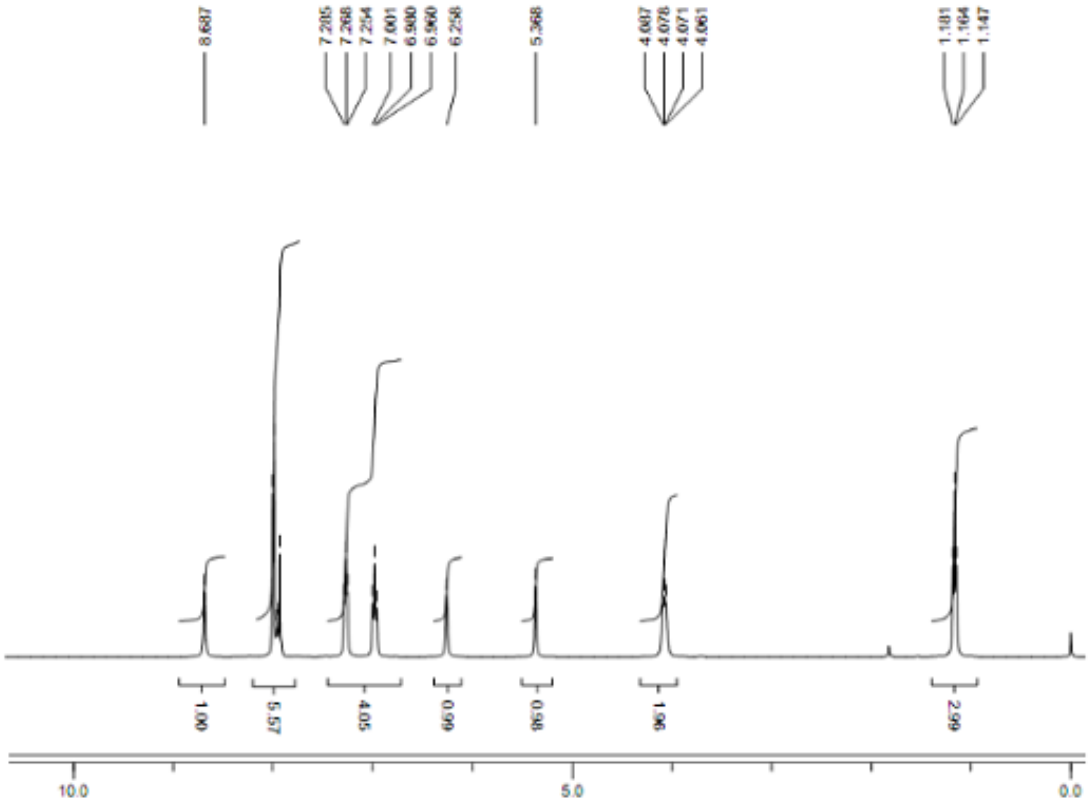

Figure S5. ^{1}H NMR of Compound **4e**.

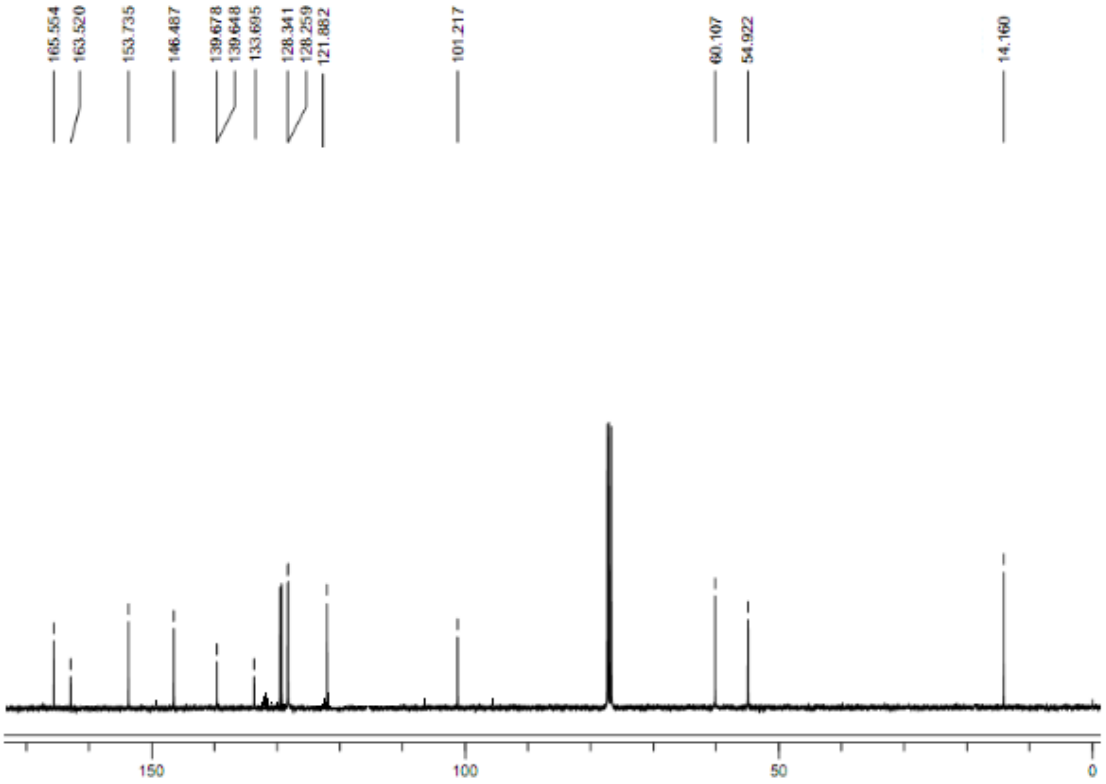

Figure S6. ^{13}C NMR of compound **4e**.

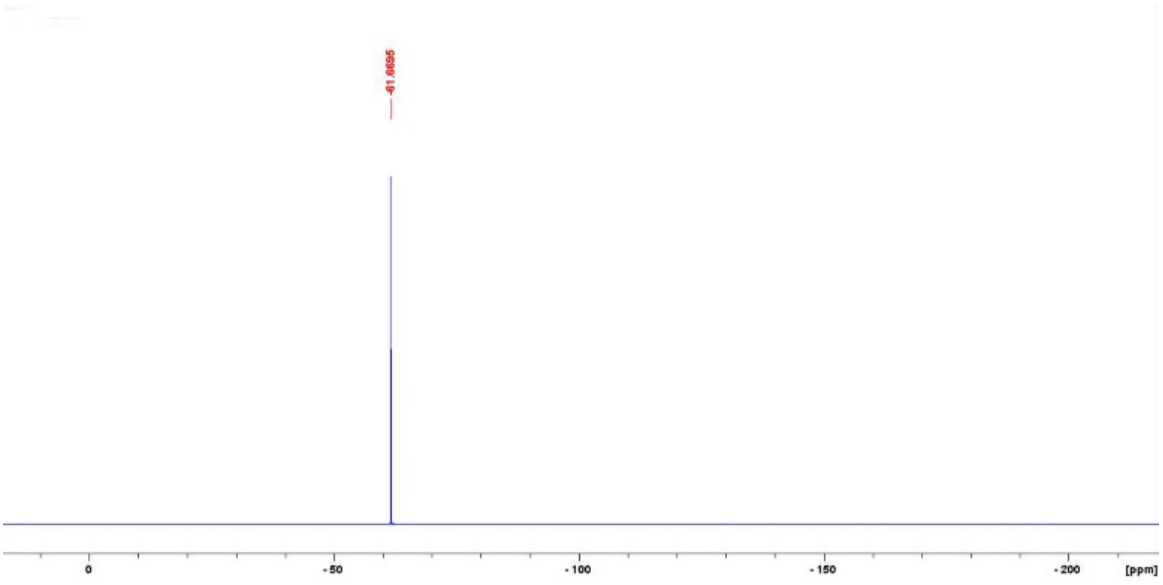

Figure S7. ^{19}F NMR of Compound **4e**.

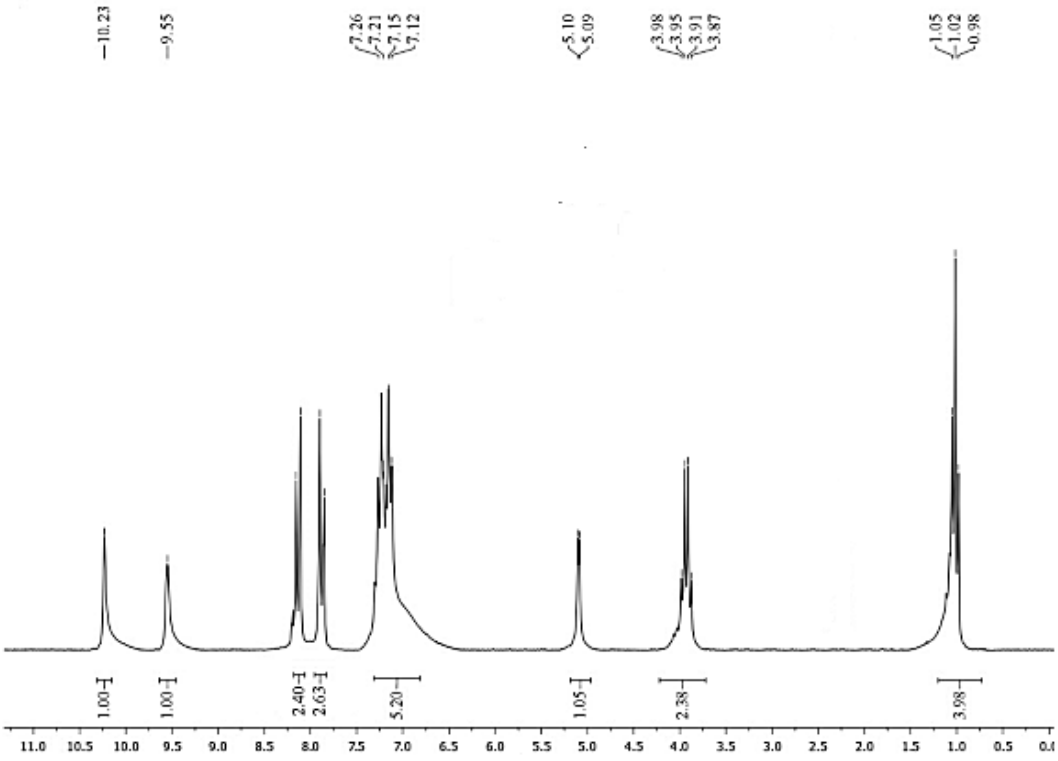

Figure S8. [1]H NMR of compound **4f**.

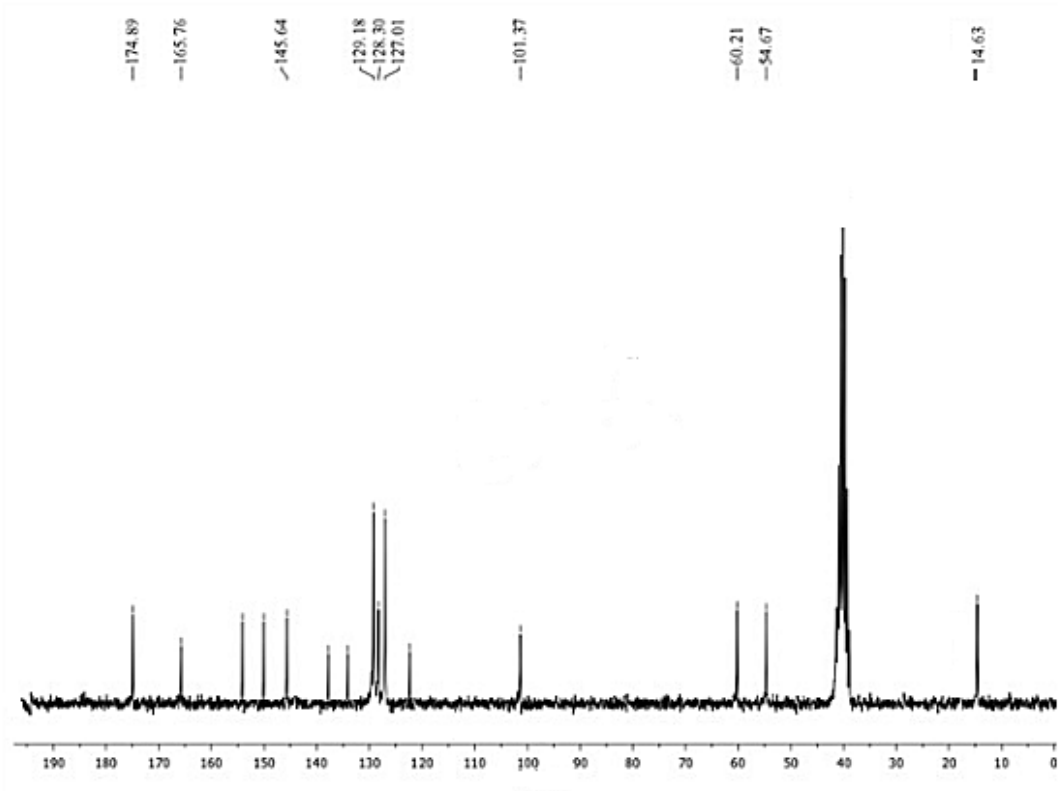

Figure S9. [13]C NMR of compound **4f**.

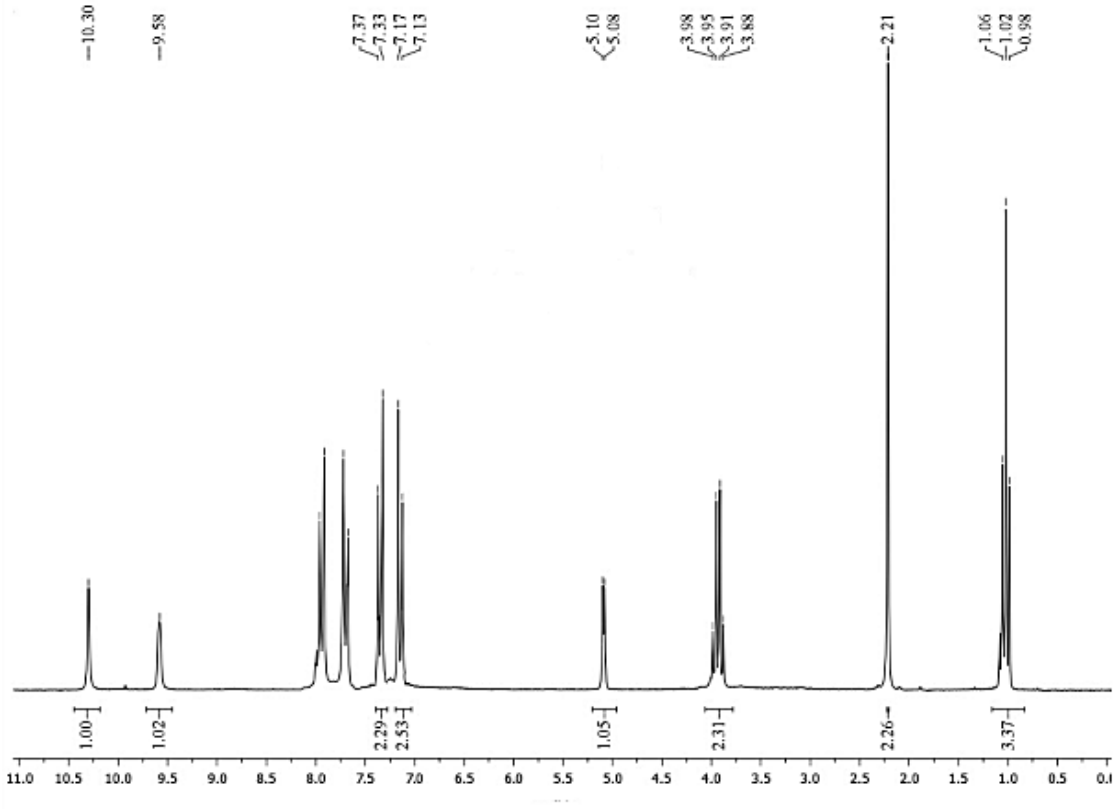

Figure S10. [1]H NMR of compound **4h**.

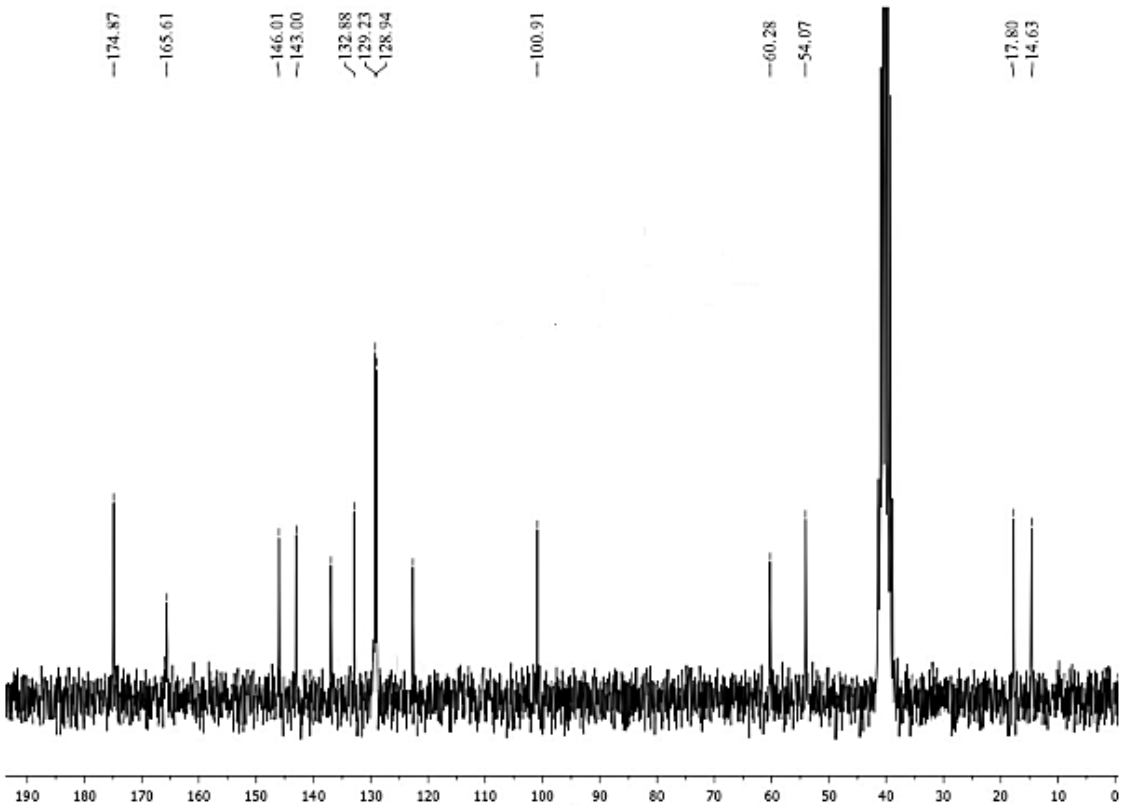

Figure S11. [13]C NMR of compound **4h**.

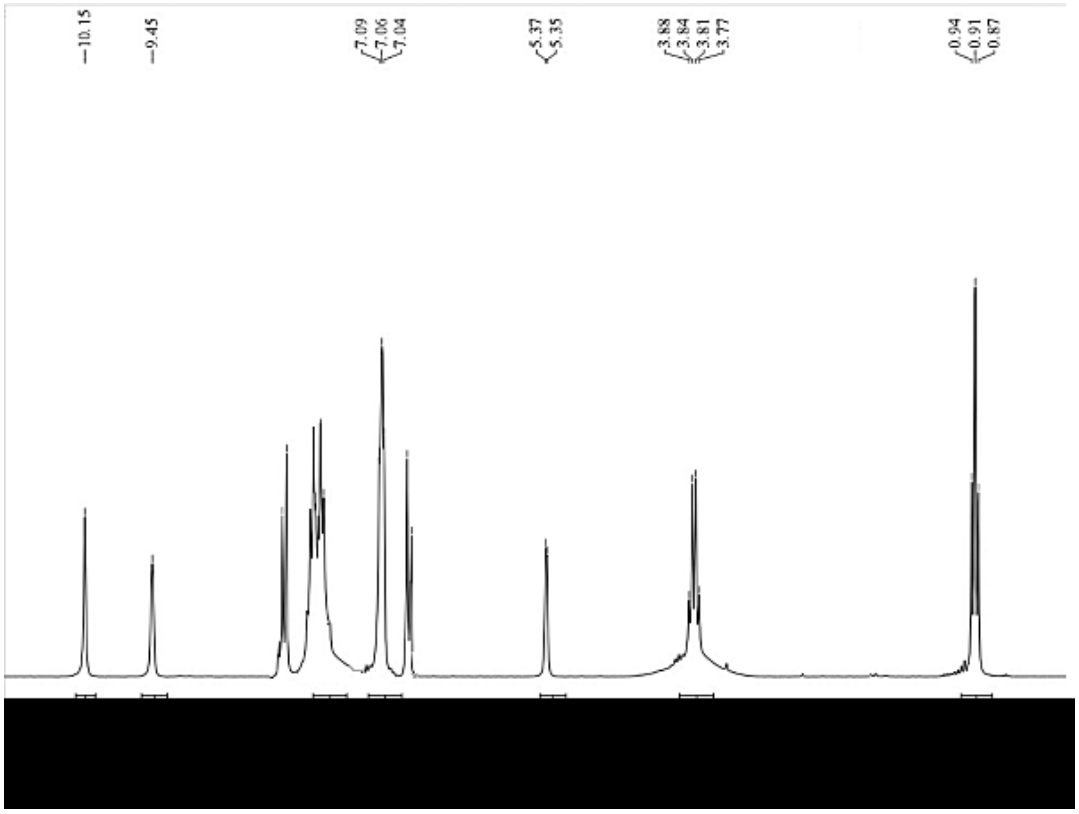

Figure S12. ^{1}H NMR of compound **4j**.

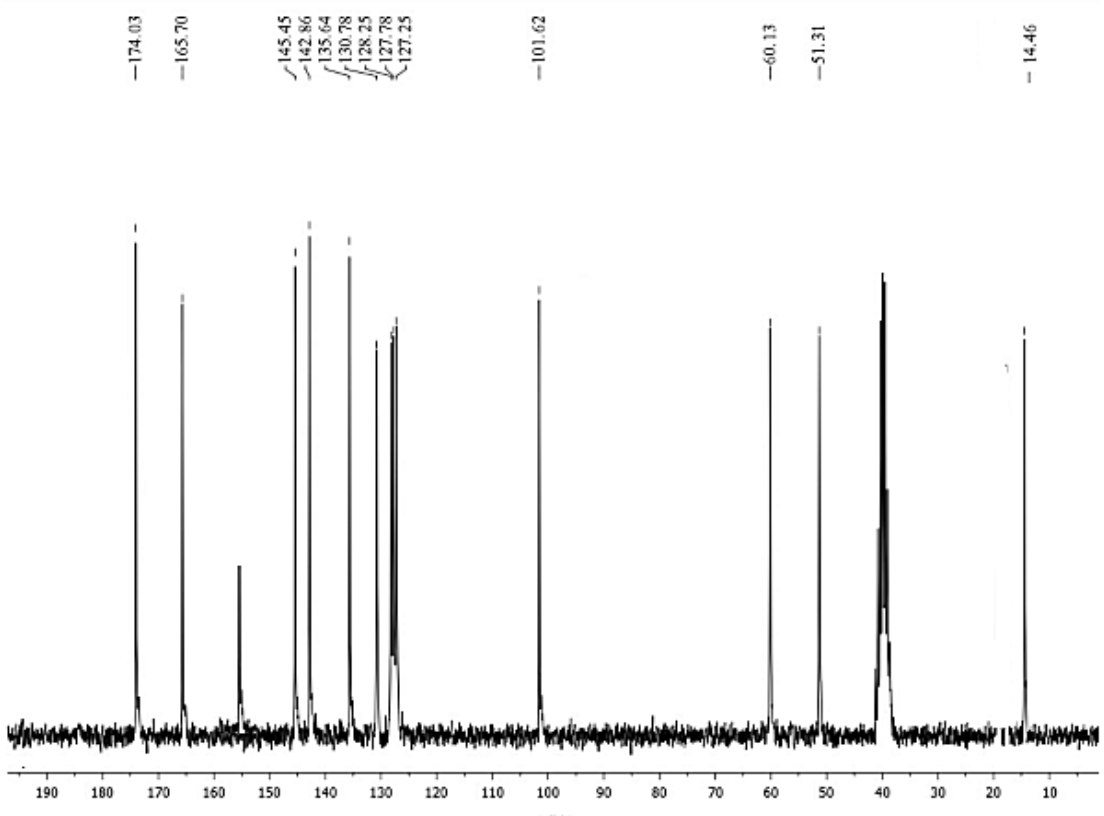

Figure S13. ^{13}C NMR of compound **4j**.

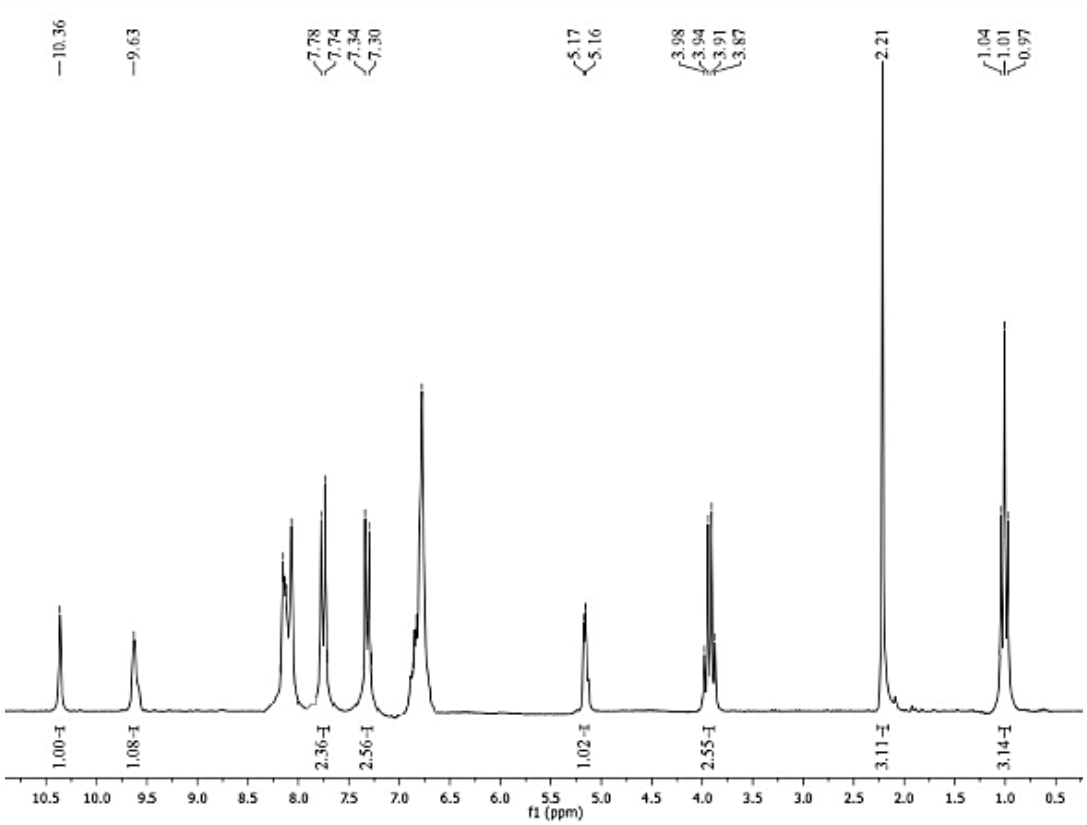

Figure S14. [1]H NMR of compound **4l**.

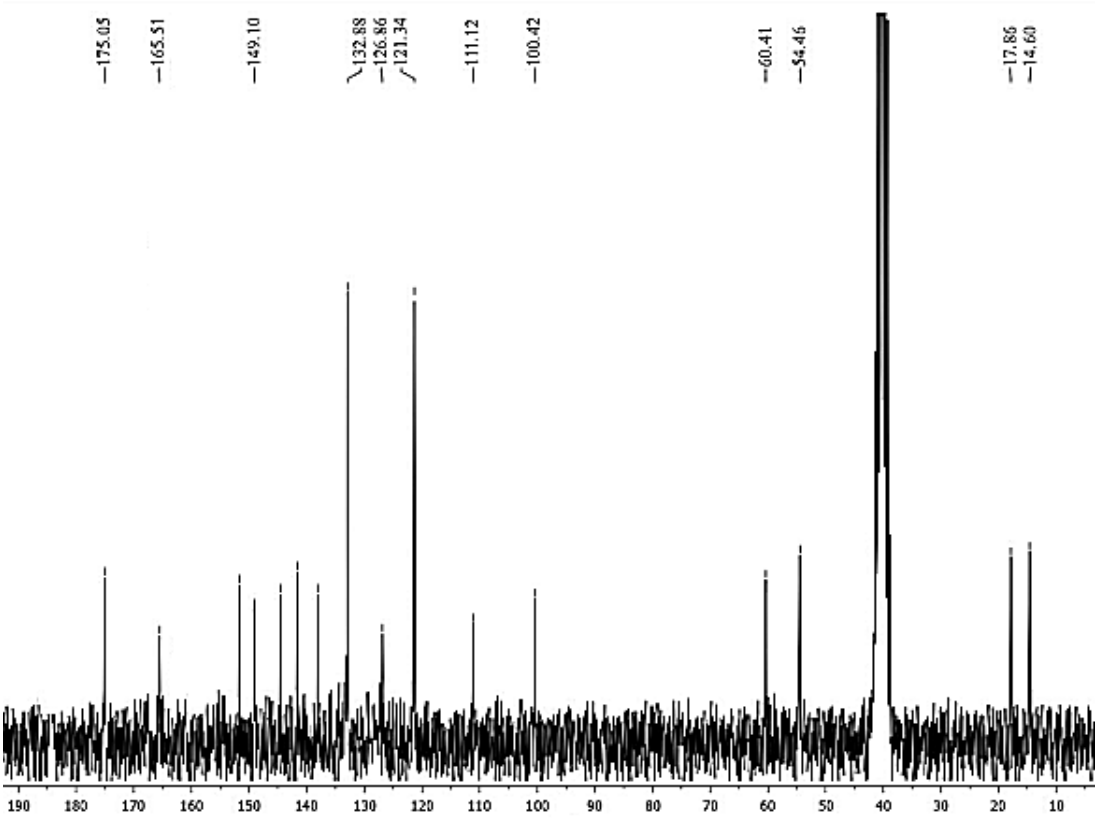

Figure S15. [13]C NMR of compound **4l**.