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Study of Spacer Effects in Metal-Free Organic Dyes for Visible-Light-Driven Dye-Sensitized Photocatalytic Hydrogen Production

Supplementary Information

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Reflectance Absorption spectra

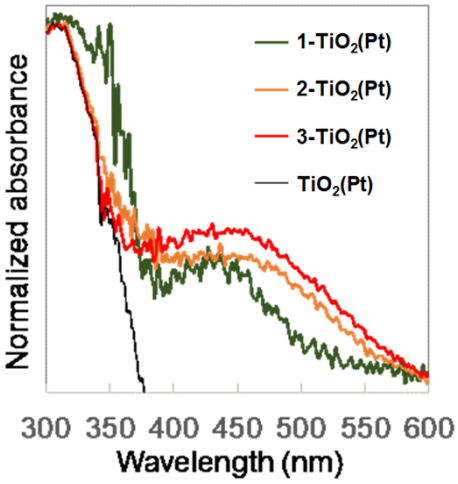

Fig. S1. Reflectance absorption spectra of before dye loading TiO_2-Pt particle (**TiO_2(Pt)**), and after dye loading TiO_2-Pt particles (**1-TiO_2(Pt), 2-TiO_2(Pt), 3-TiO_2(Pt)**).

Absorption spectra of dyes on TiO_2 film

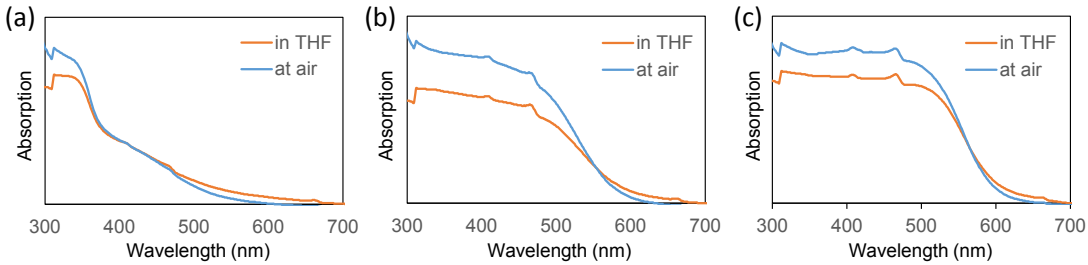

Fig. S2. Absorption spectra of dyes on TiO_2 film in THF and at air conditions. (a): **1@TiO_2**, (b): **2@TiO_2**, and (c): **3@TiO_2**.

Cyclic voltammograms

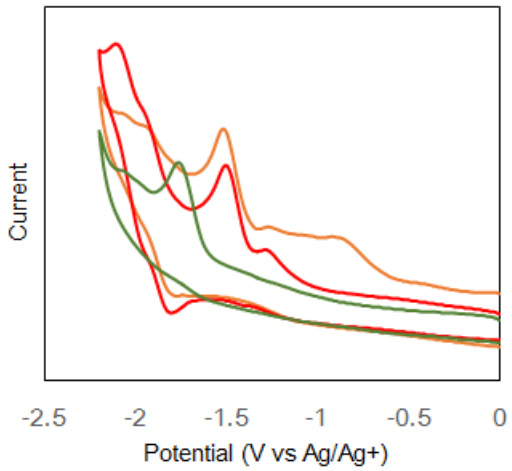

Fig. S3. Cyclic voltammograms of **1–3** in 0.1 M Bu_4NPF_6-containing THF solutions. The scan rate was 100 mV/s.

Water splitting at 420 nm

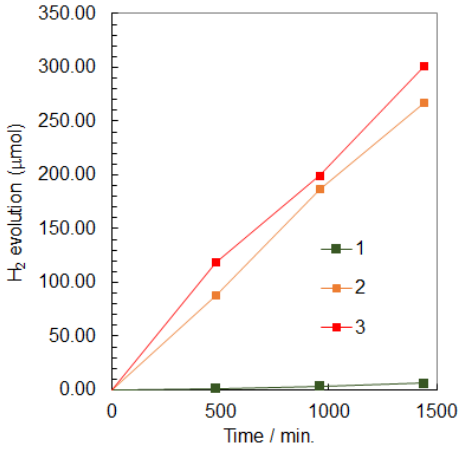

Fig. S4. Photocatalytic activities of dyes **1**–**3** in water splitting reactions at single wavelength of 420 nm (7.36 mW/cm^2). Reaction conditions: 10 vol% aqueous TEA (10 mL), 33.0 mg TiO_2/dye/Pt catalyst, pH = 7.0, the reaction surface area was 17.34 cm^2.

Table S1. The the quantum efficiency for hydrogen conversion of water with dyes **1**–**3** on TiO_2

Dyes	Reaction time (min.)[a]	Amount of H_2 (μmol)	Φ [b](%)
1	1440	6.37	0.03
2	1440	299.9	1.46
3	1440	301.1	1.65

[a] 420 nm (7.36 mW/cm^2) of single wavelength was used, the reaction surface area were 17.34 cm^2. [b] Estimated by eq. (1) in main text.

Time- Resolved Absorption Spectra

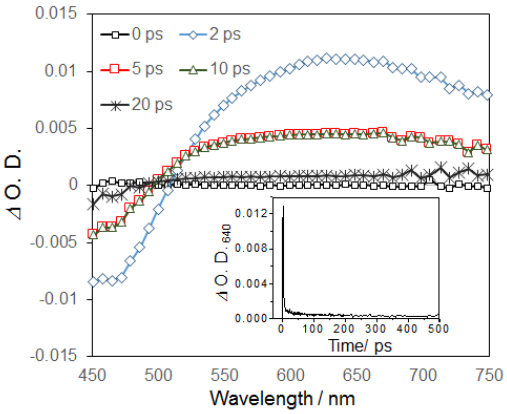

Fig S5. Time-resolved absorption spectra of dye **3** in acetonitrile solution.

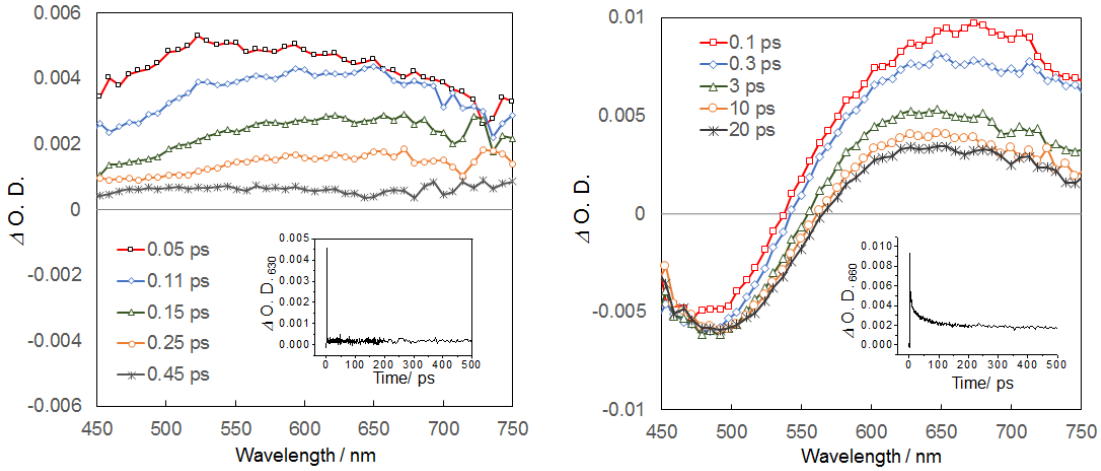

Fig. S6. Time-resolved absorption spectra of dye **1** on TiO_2 film (left) and dye **2** on TiO_2 film (right).

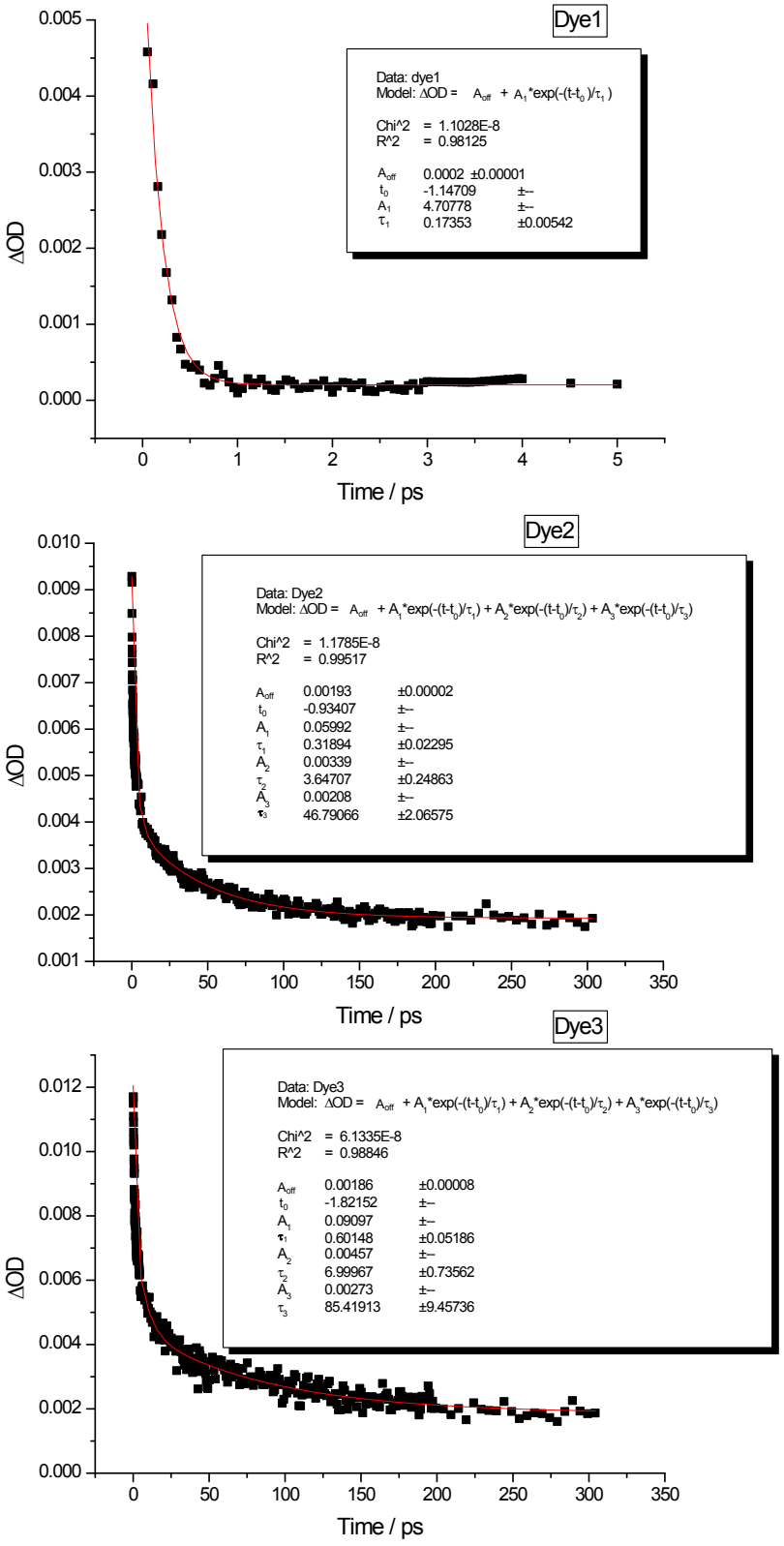

Fig. S7. Analysed results of curve fitting data for (top) dye **1** on TiO_2 film with single exponential decay fitting, (middle) dye **2** on TiO_2 film with triple exponential decay fitting, and dye **3** with on TiO_2 film with triple exponential decay fitting.

Computation Result

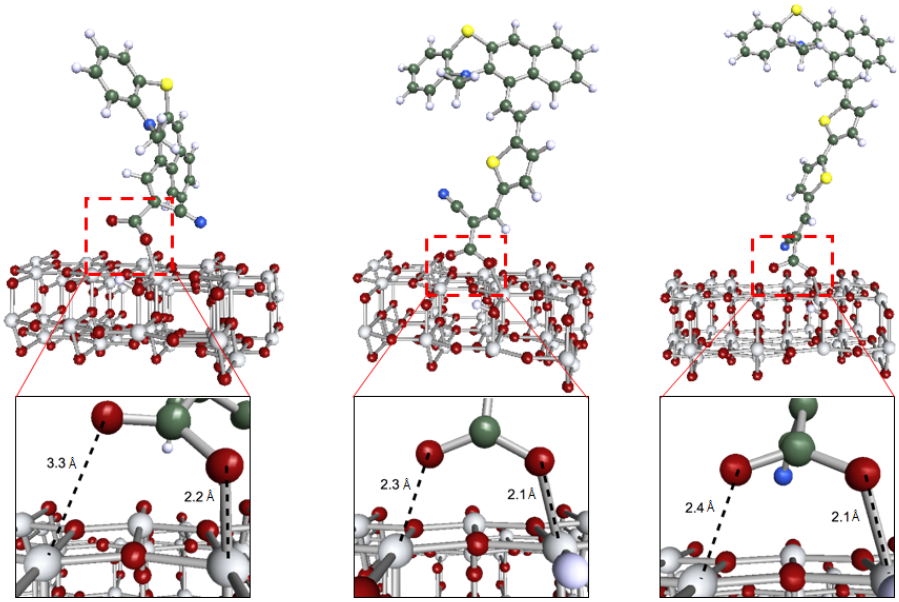

Fig. S8. DFT BP86/def-sv(p) optimized structures of dyes **1–3**@$(TiO_2)_{82}$. The extended parts indicated (a) monodentate with carboxylate type coordination structure of dye **1** on TiO2, (b) biadentate with carboxylate coordination type structure of dye **2** structure TiO_2, and (c) biadentate with carboxylate coordination type structure of dye **3** structure TiO_2.

^{1}H and ^{13}C NMR spectra

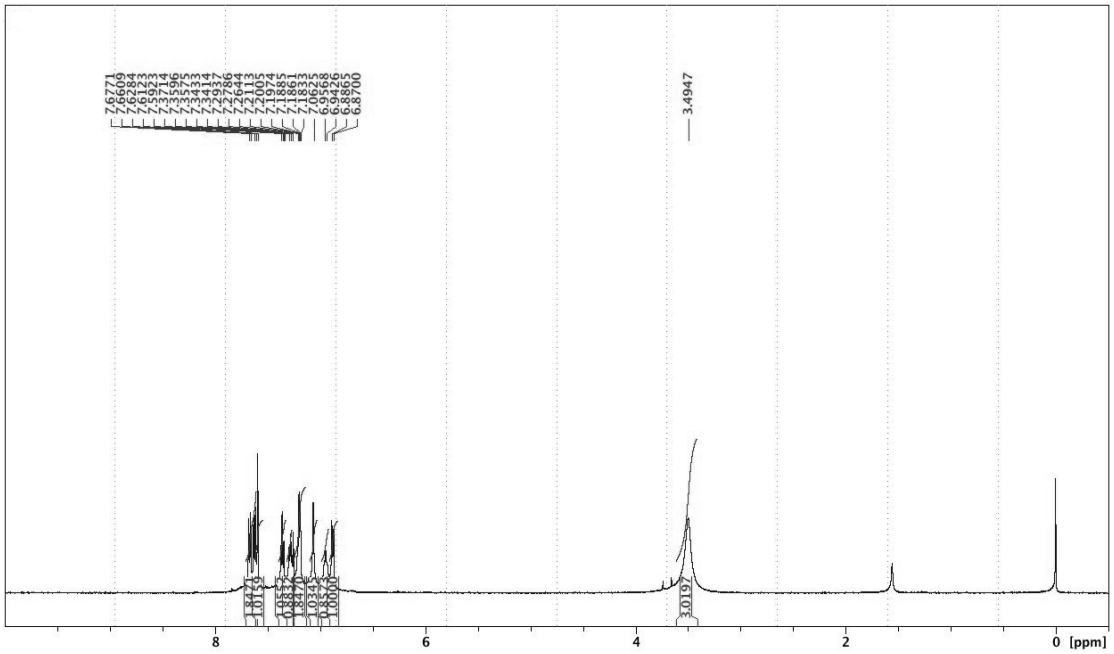

Figure S9. ^{1}H NMR of **5**

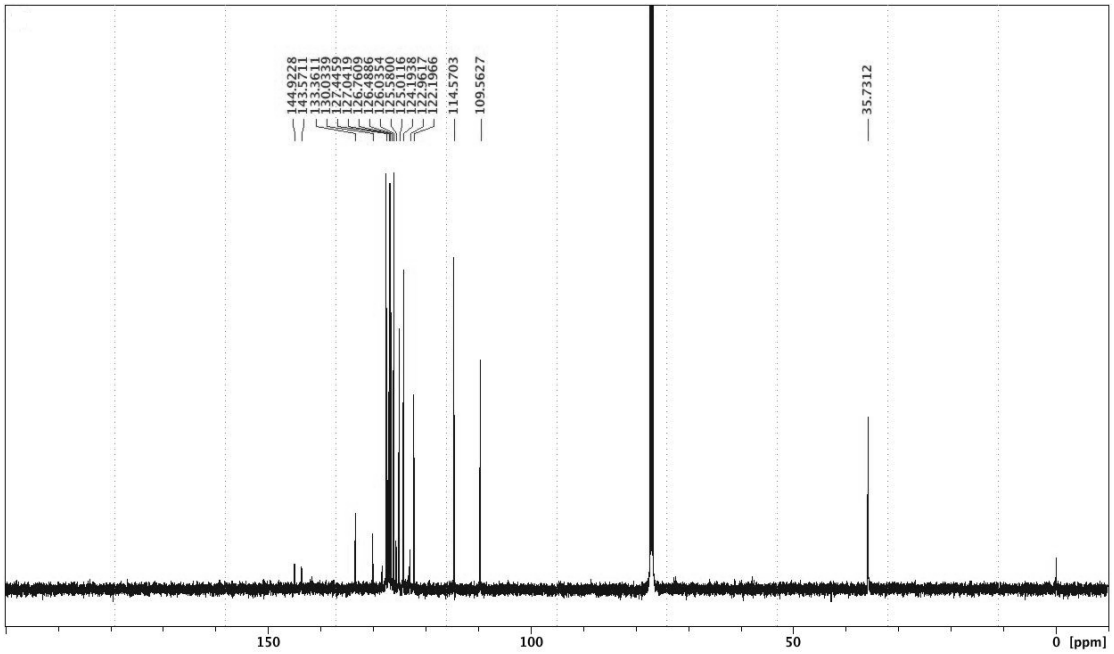

Figure S10. ^{13}C NMR of **5**

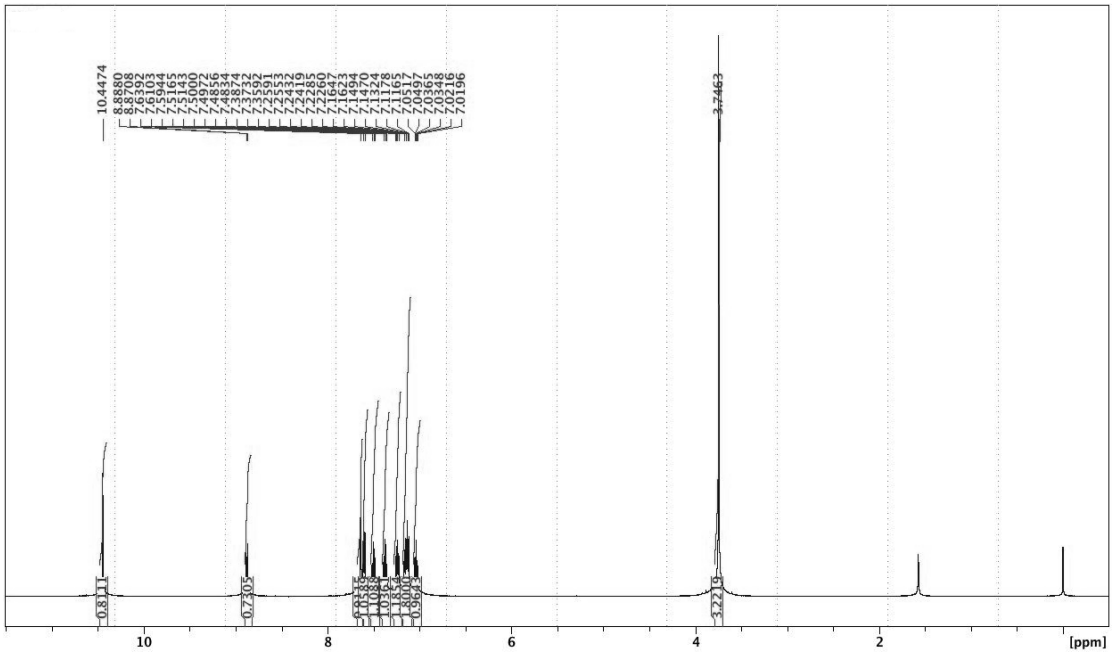

Figure S11. ^{1}H NMR of **6**

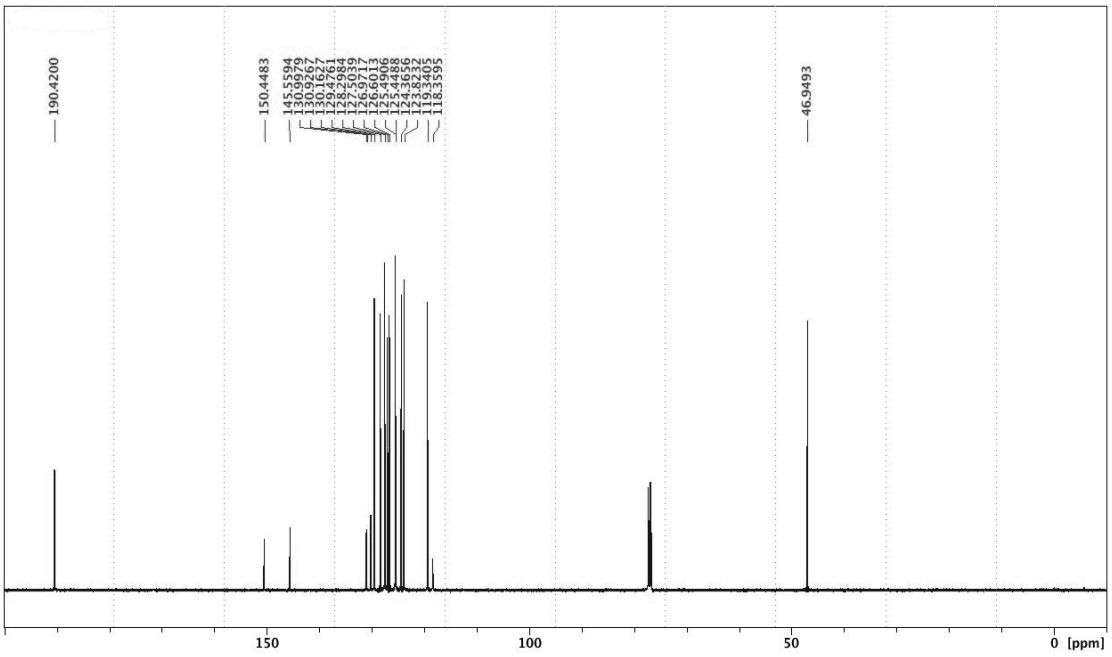

Figure S12. ^{13}C NMR of **6**

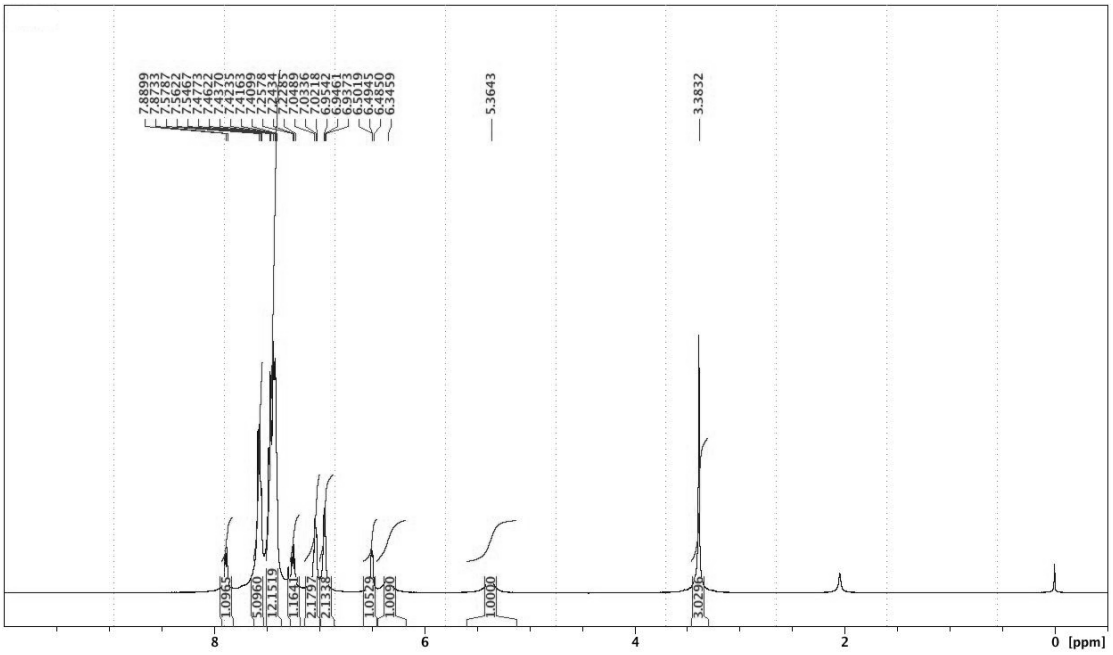

Figure S13. [1]H NMR of **8**

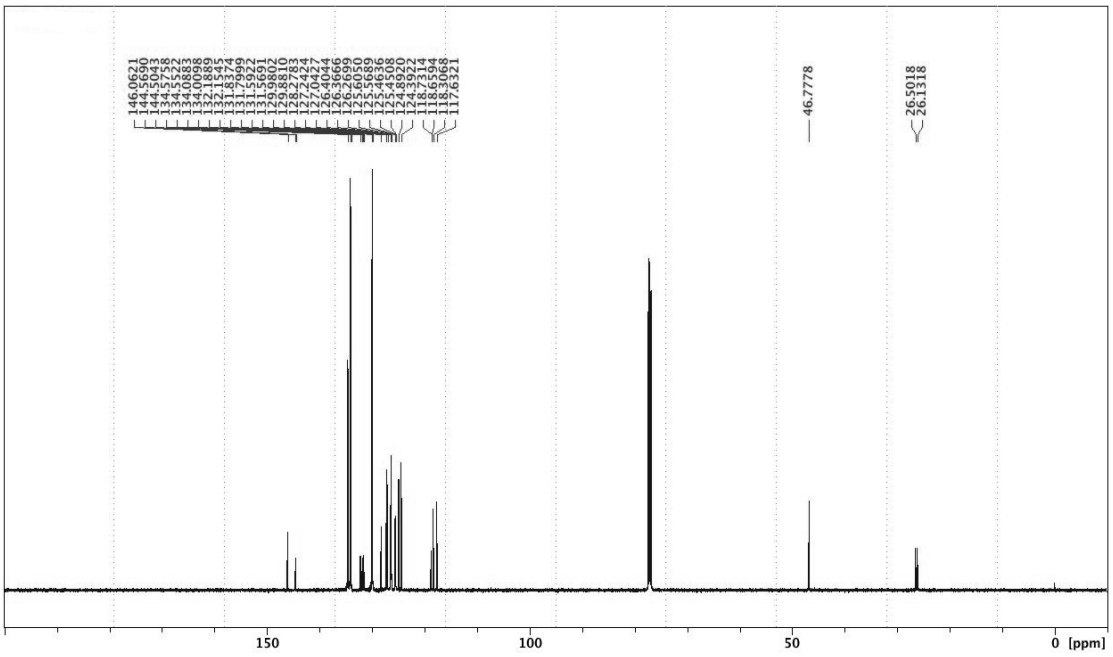

Figure S14. [13] C NMR of **8**

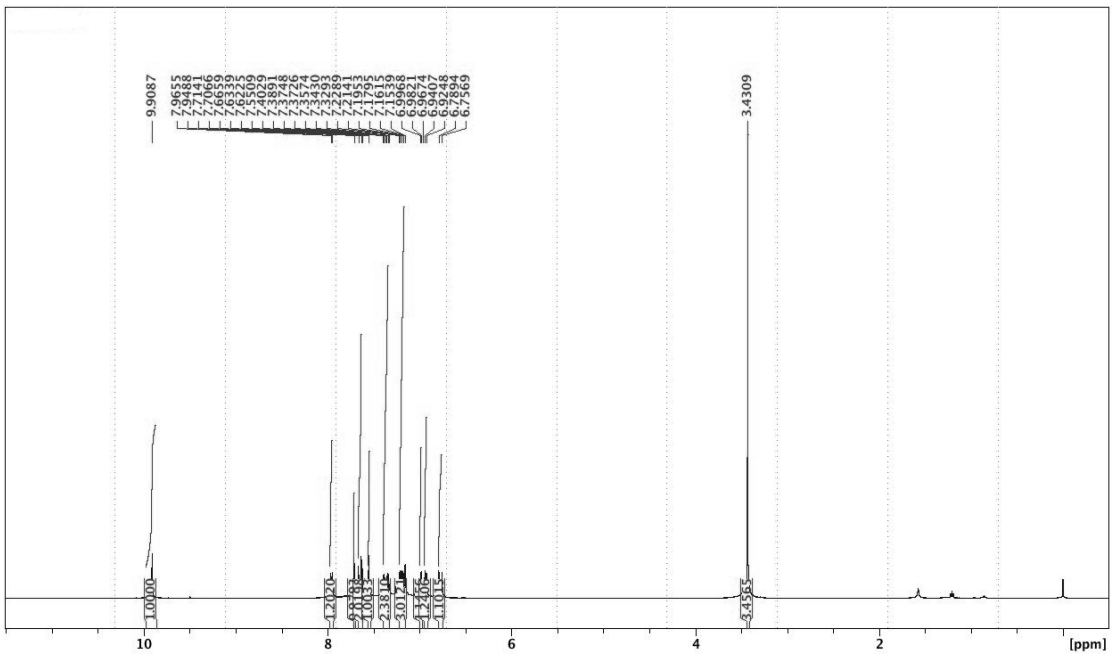

Figure S15. ^{1}H NMR of **9**

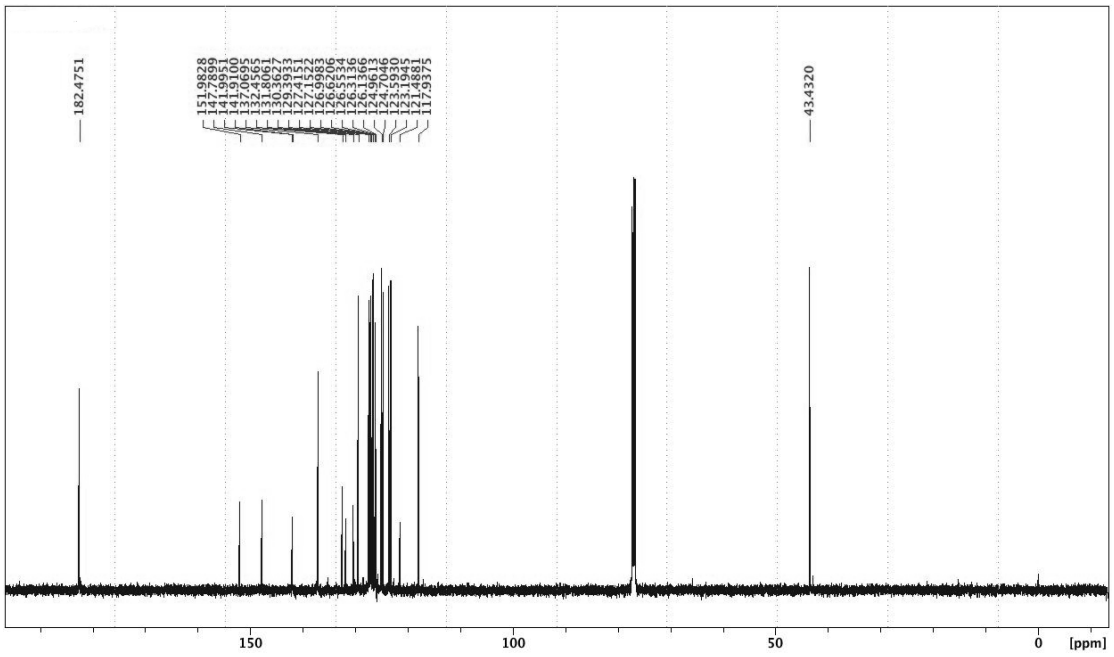

Figure S16. ^{13}C NMR of **9**

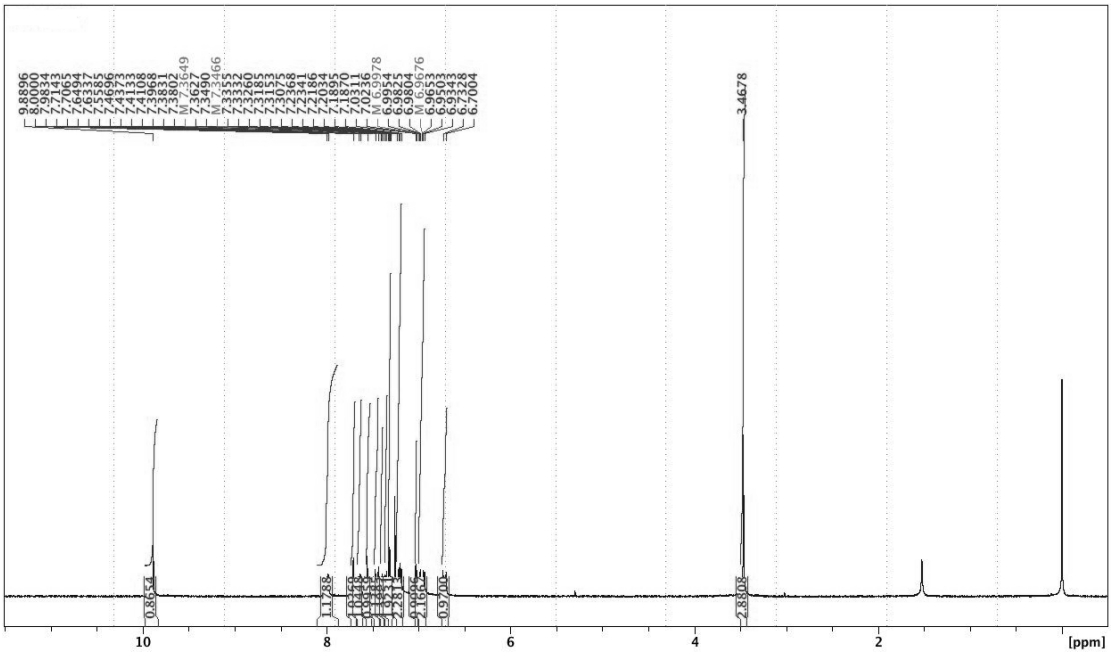

Figure S17. ^{1}H NMR of **10**

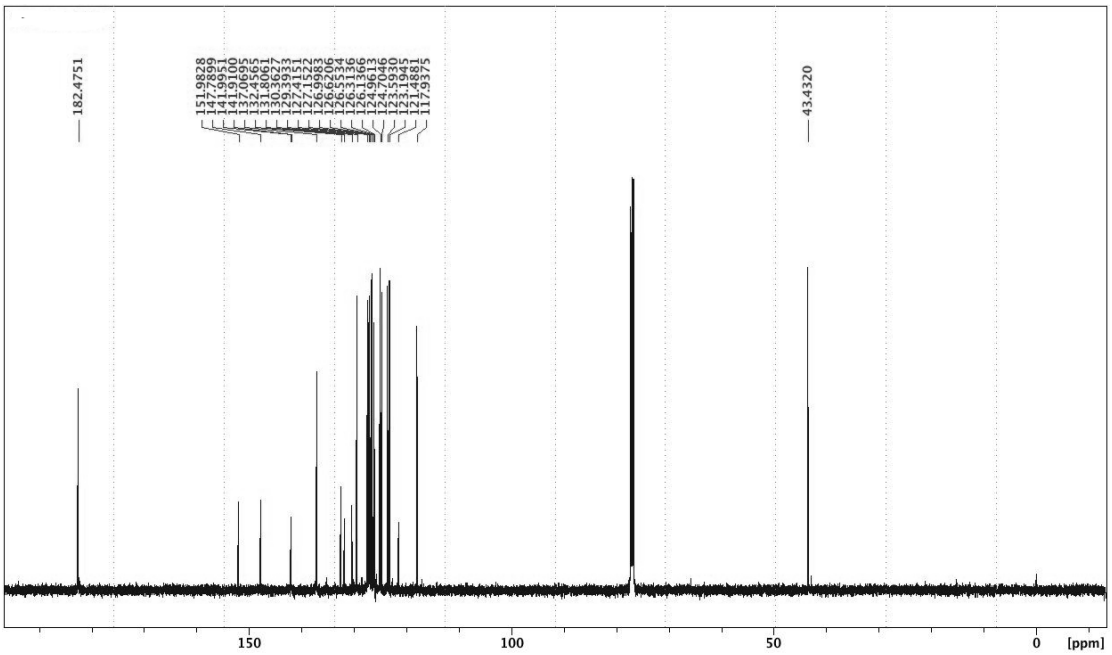

Figure S18. ^{13}C NMR of **10**

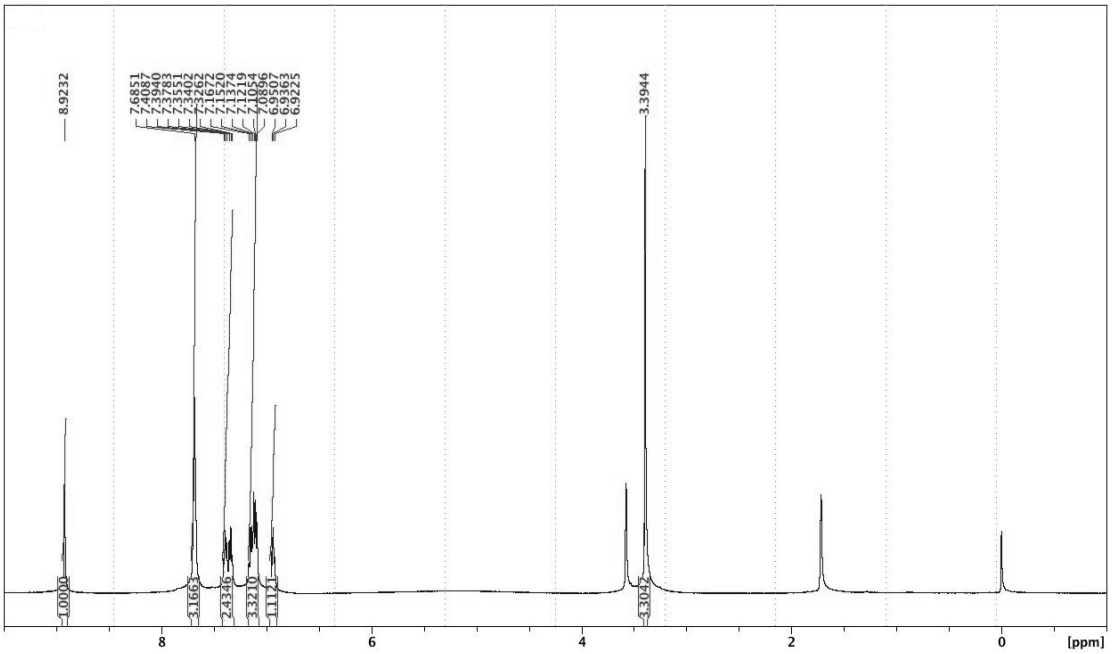

Figure S19. ^{1}H NMR of **1**

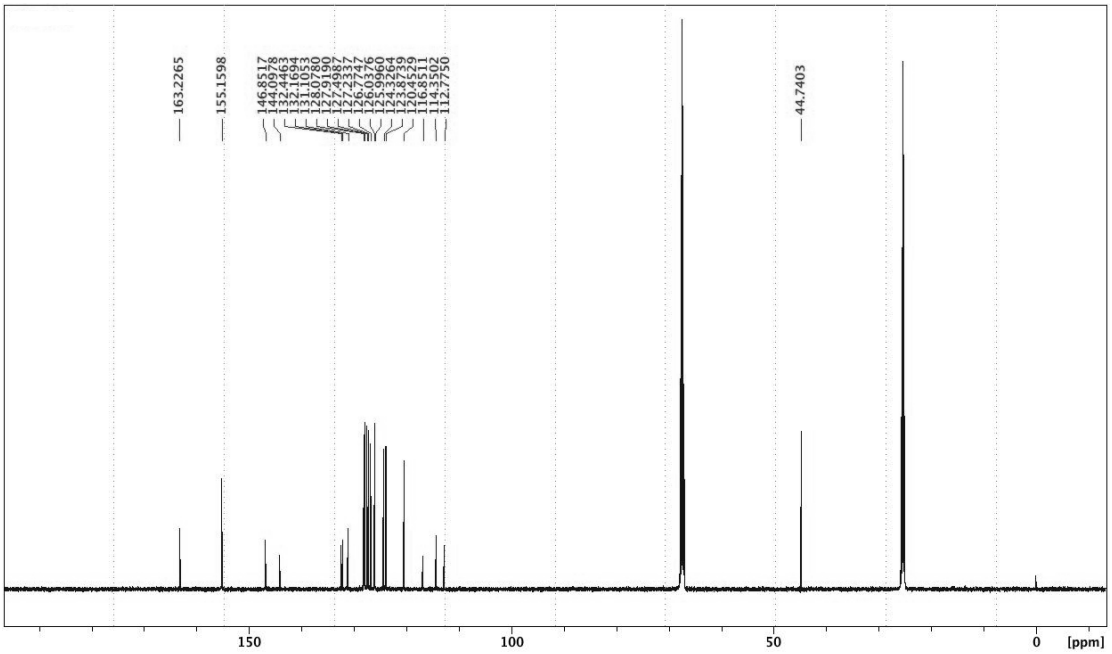

Figure S20. ^{13}C NMR of **1**

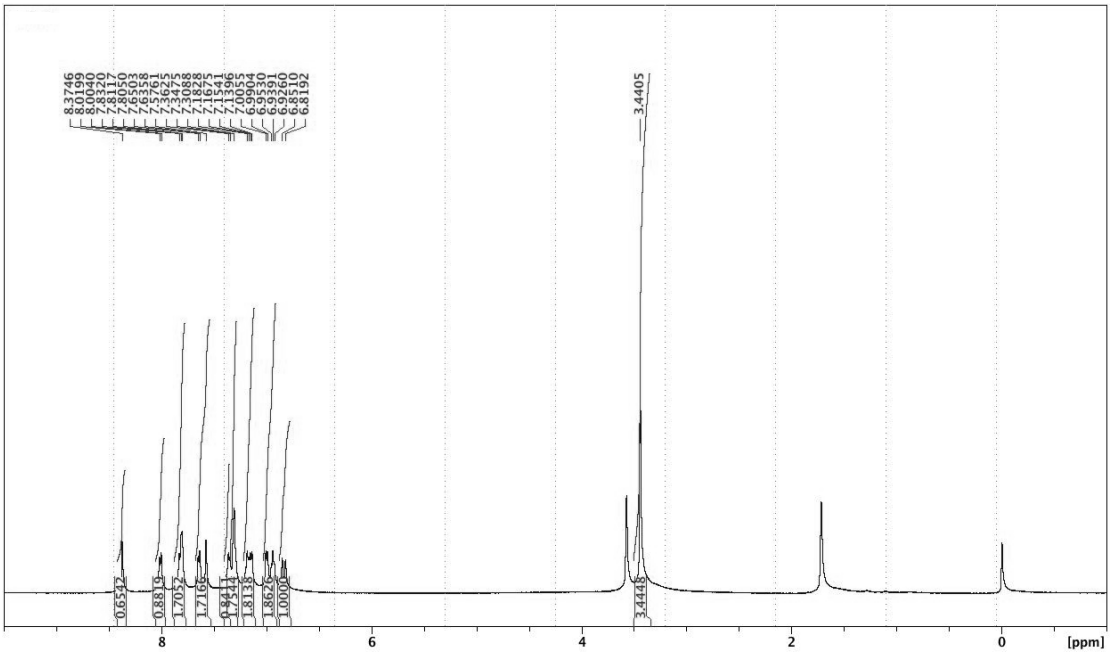

Figure S21. ^{1}H NMR of **2**

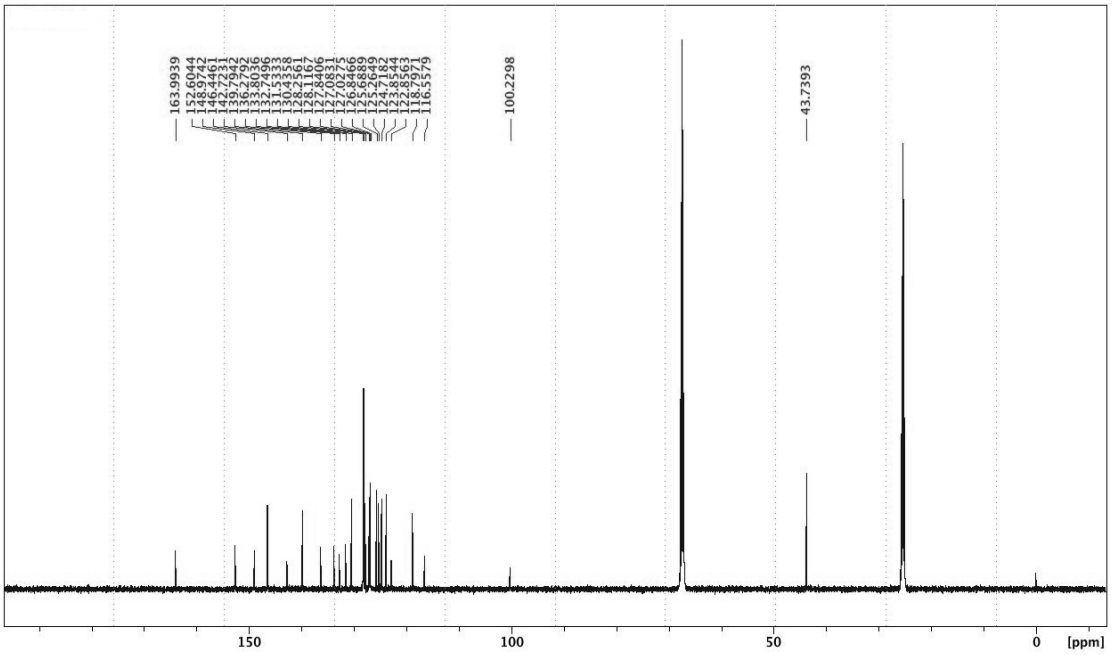

Figure S22. ^{13}C NMR of **2**

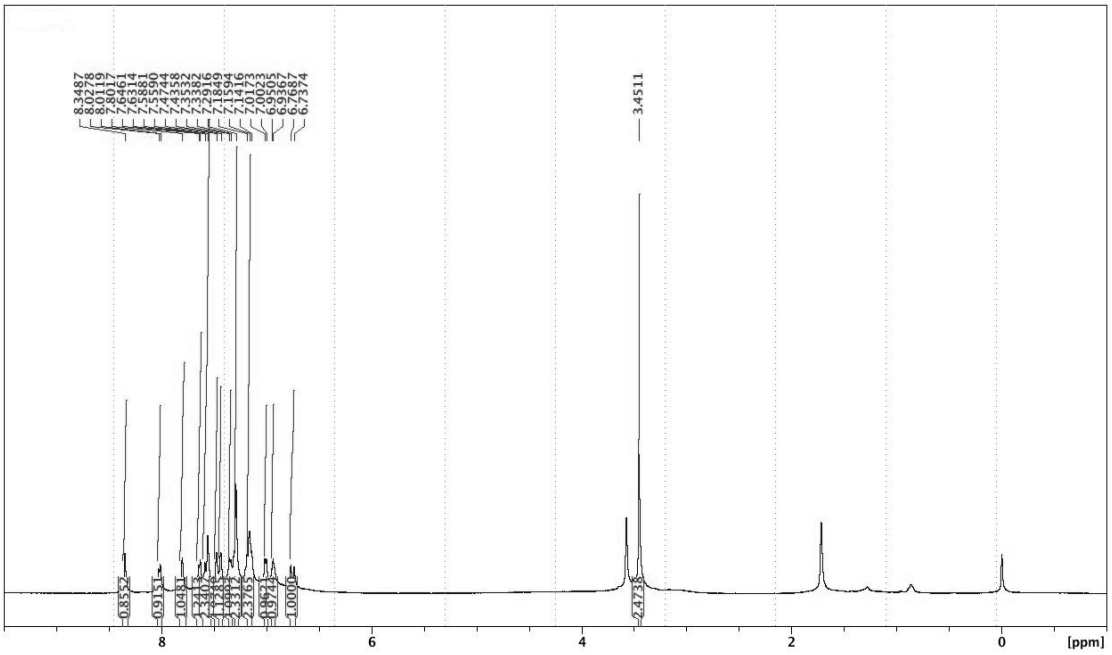

Figure S23. ^{1}H NMR of **3**

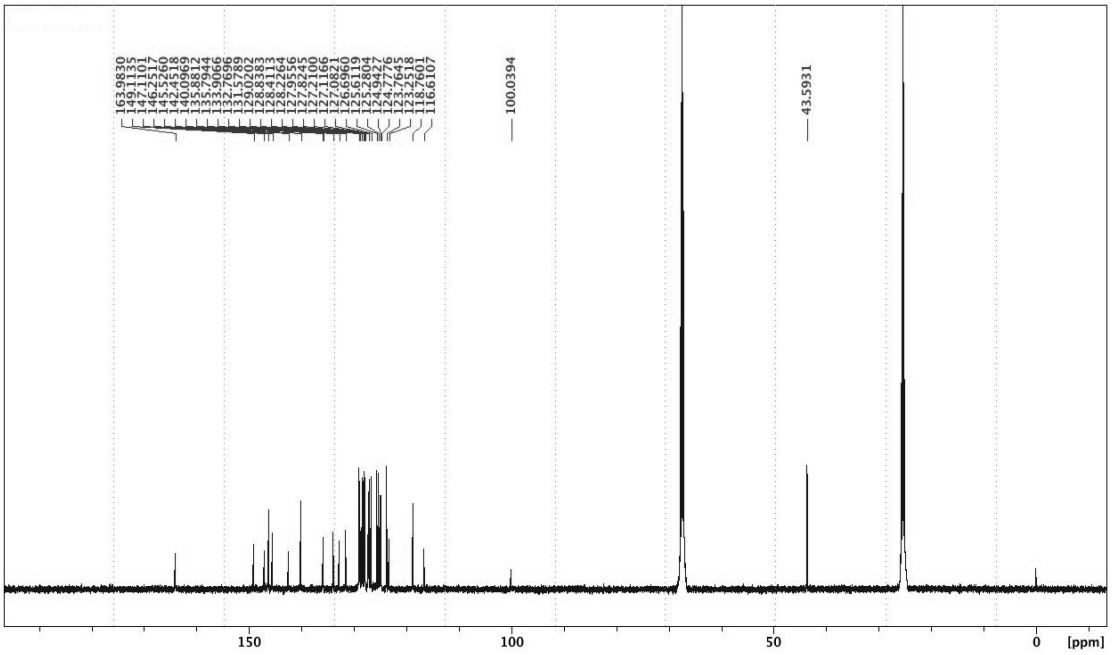

Figure S24. ^{13}C NMR of **3**