Supporting Information

EVALUATION OF 4,4'-DIAMINODIPHENYLMETHANE AS A PLATFORM FOR PROTON, pH, AND METAL ION RESPONSIVE FLUORESCENT PROBE.

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1. General Information

Chemicals and reagents were commercially available and used without further purification, except for 2-formyl pyridine, which was purified by alumina and silica gel. ^{1}H, and ^{13}C NMR spectra were measured on a Bruker Advance III 400 spectrometer. Chemical shifts were reported in part per million (ppm) relative to TMS (0.00 ppm for ^{1}H and ^{13}C). The coupling constants (*J*) were given in hertz (Hz). MALDI-TOF mass was performed on Bruker autoflex speed. Elemental analysis was carried out with JSL JM11. Absorption spectra were recorded on a PerkinElmer Lambda 35. Fluorescence spectra were measured on a JASCO FP-750.

Relative quantum yields of **1** were estimated from eq. 1 using anthracene as a standard (in EtOH, 27%, λ_{ex} = 340 nm).

$$\Phi^{i} = \frac{F^{i} f_{s} n_{i}^{2}}{F^{s} f_{i} n_{s}^{2}} \Phi^{s}$$

where Φ^{i} and Φ^{s} are the quantum yields of the sample and the standard, respectively. F^{i} and F^{s} are the area of the fluorescence spectra of the sample and the standard, respectively.

2. Proton responsiveness

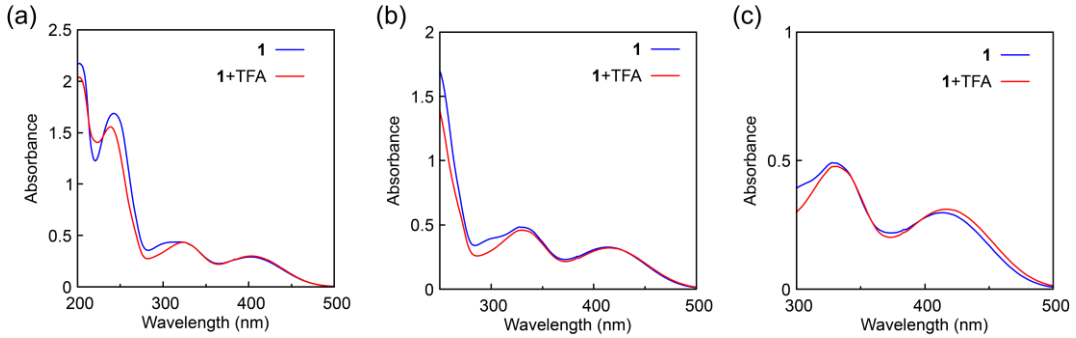

Figure S1. Absorption spectra of **1** (50 μM) in (a) CH_3CN, (b) CH_2Cl_2, and (c) toluene.

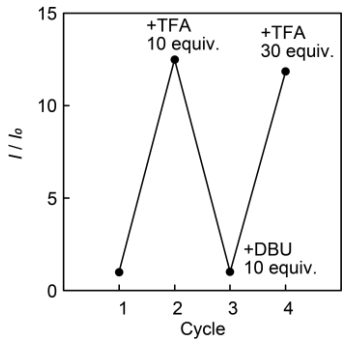

Figure S2. The reversible change of the fluorescent behavior of **1** (50 μM) by using TFA and DBU in CH_3CN and CH_3OH (1:1 v/v) (λ_{ex} = 400 nm).

Table S1. Relative quantum yield of **1** using anthracene in EtOH as a reference (27%, λ_{ex} = 340 nm).

	Φ / %
CH_3CN	< 0.01
CH_3CN + TFA	0.03
CH_2Cl_2	< 0.01
CH_2Cl_2 + TFA	0.05
Toluene	< 0.01
Toluene +TFA	0.10

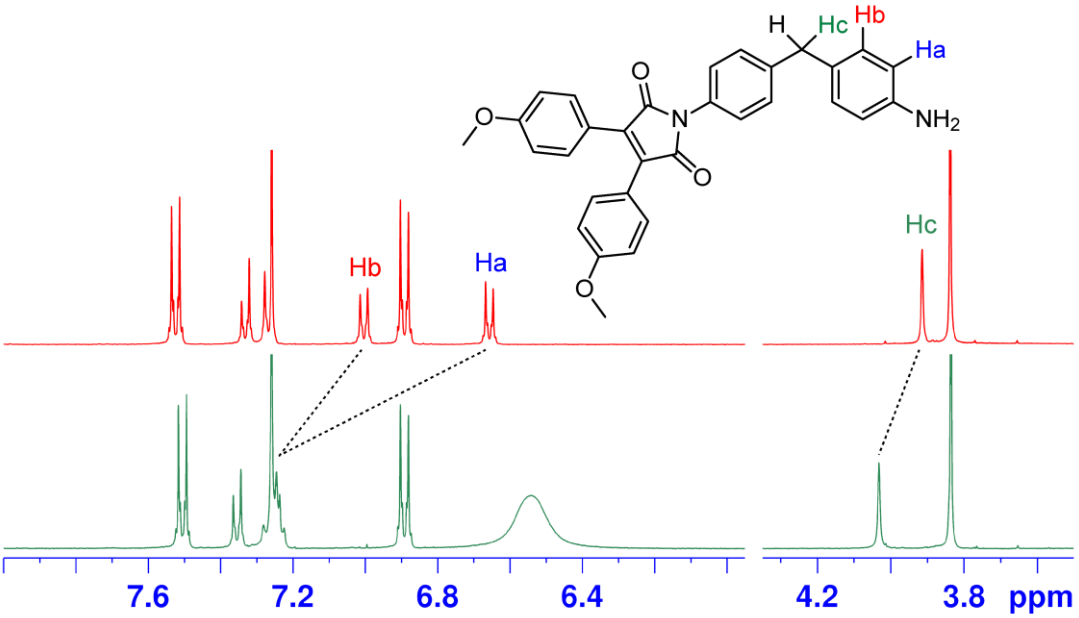

Figure S3. The partial ^{1}H NMR spectra of **1** in $CDCl_3$ before (top) and after (bottom) the addition of TFA.

4. Metal sensing

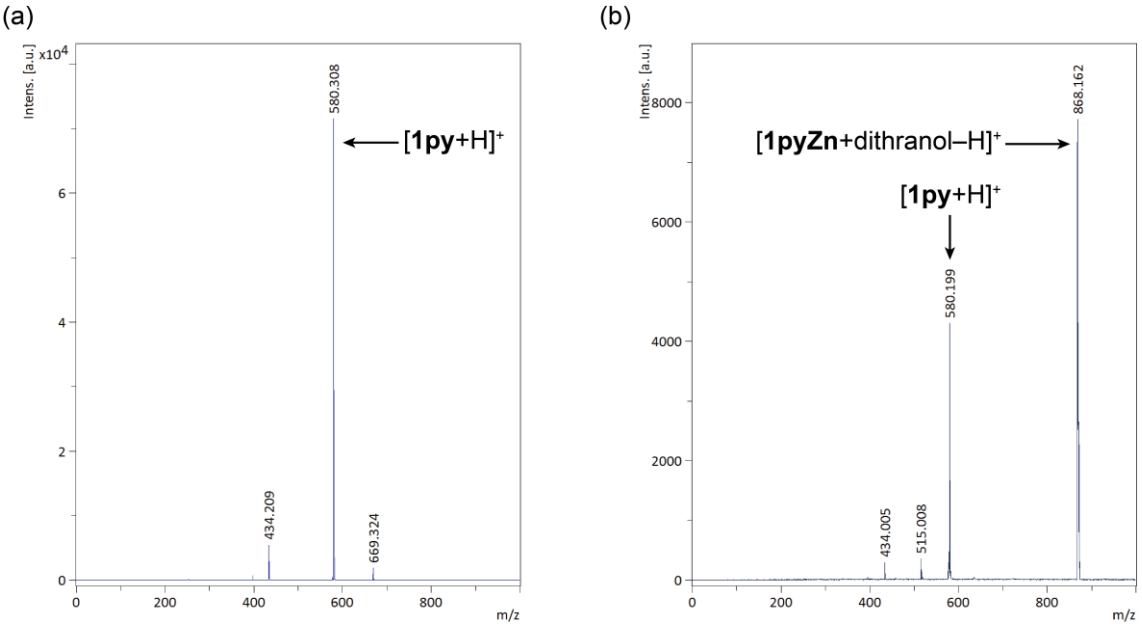

Figure S4. MALDI-TOF MS of (a) **1py** and (b) **1pyZn**. Dithranol was used as a matrix.

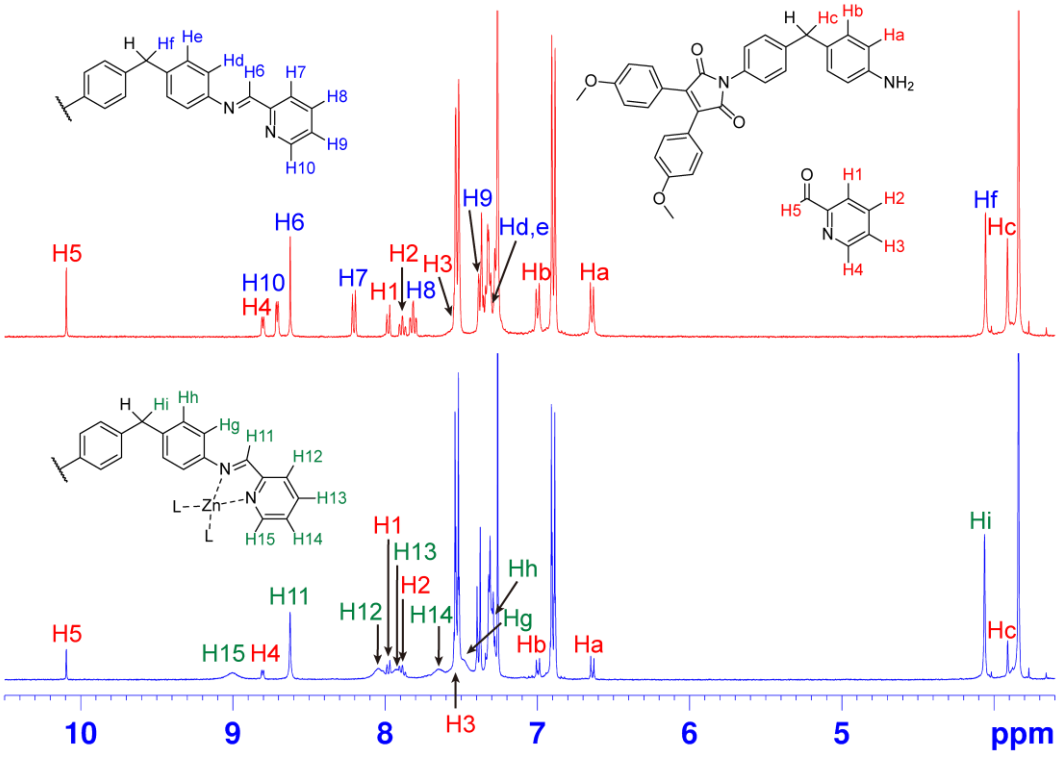

Figure S5. The partial ^{1}H NMR spectra of the mixture of **1** and **1py** (top) and the mixture of **1** and **1pyZn** (bottom) in $CDCl_3$.

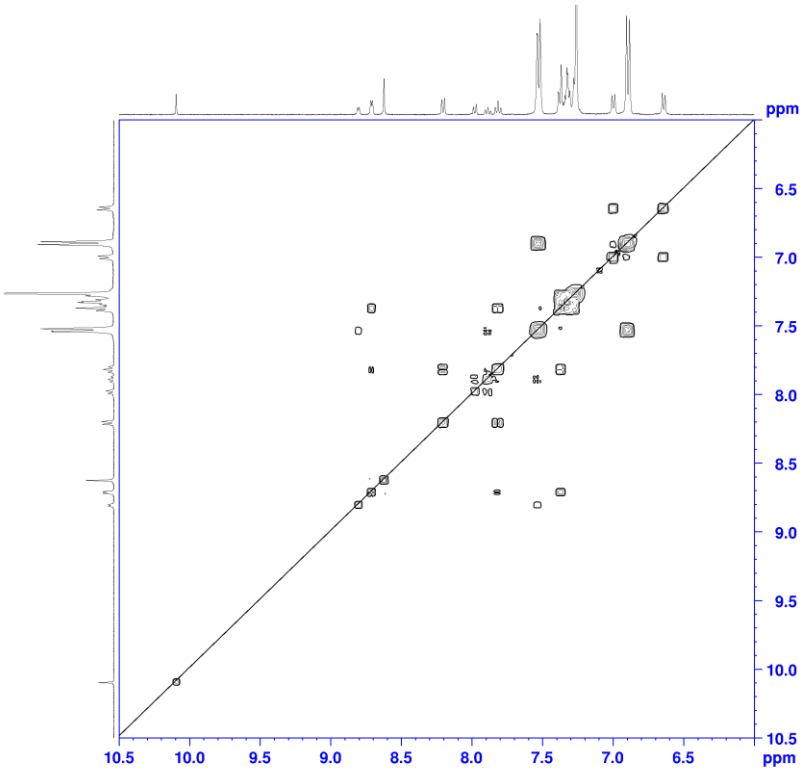

Figure S6. The partial ^{1}H-^{1}H cosy spectrum of **1py** in $CDCl_3$.

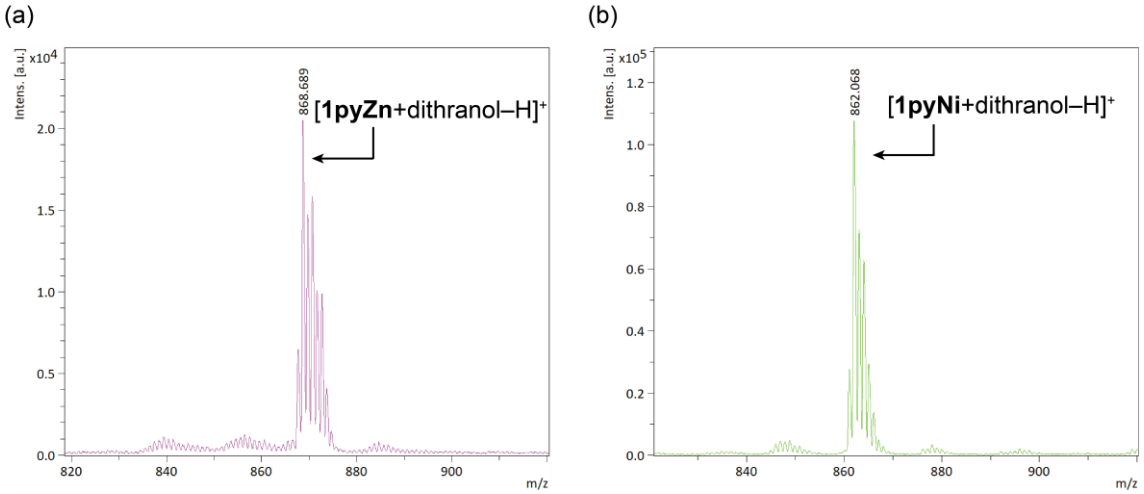

Figure S7. MALDI-TOF MS of (a) **1pyZn** and (b) **1pyNi** after fluorescence measurement. Dithranol was used as a matrix.

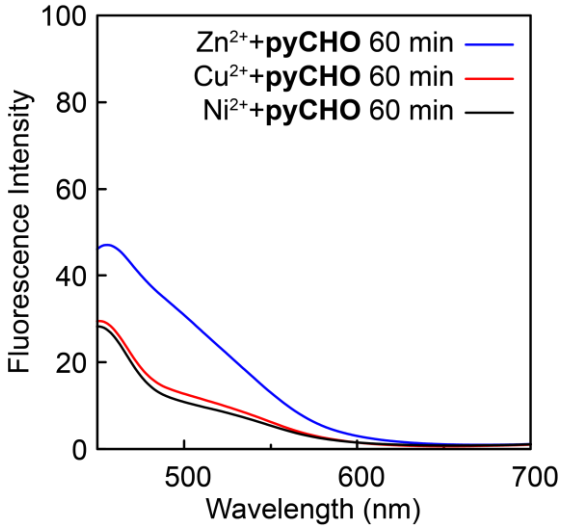

Figure S8. Fluorescence spectra of **pyCHO** and $Zn(OAc)_2•2H_2O$ (blue), $Cu(OAc)_2•H_2O$ (red), and $Ni(OAc)_2•4H_2O$ (black) in MeCN and MeOH (1:1 v/v) after mixing for 1 hour.

4. NMR spectra

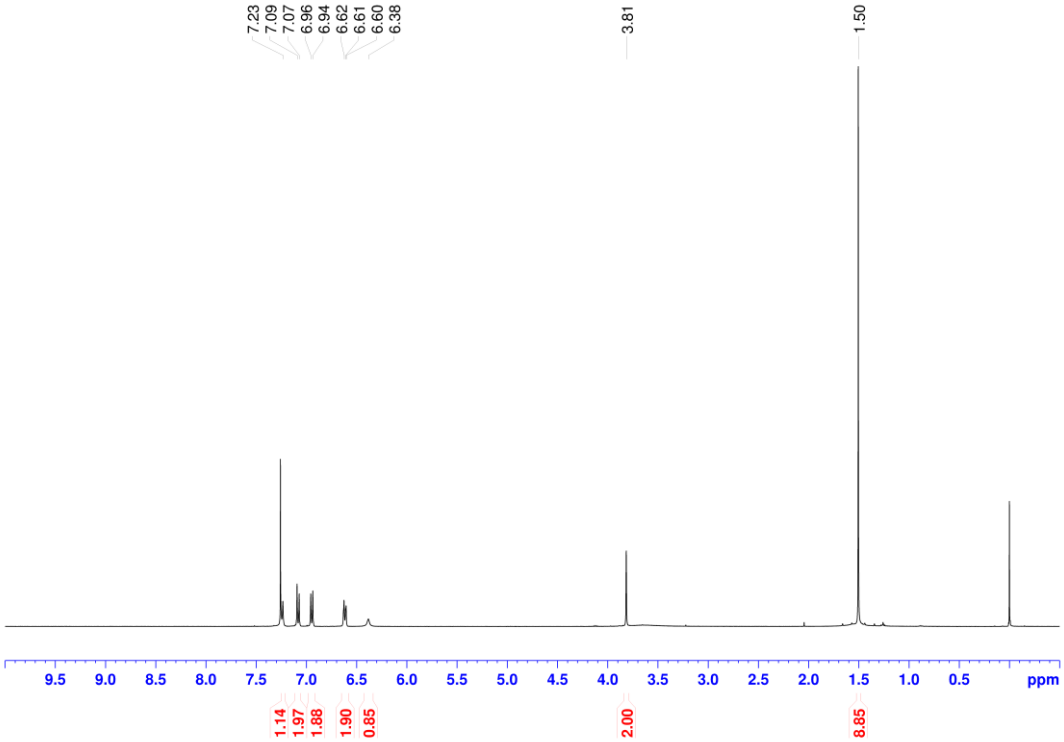

Figure S9. ^{1}H NMR spectra of **2** in $CDCl_3$.

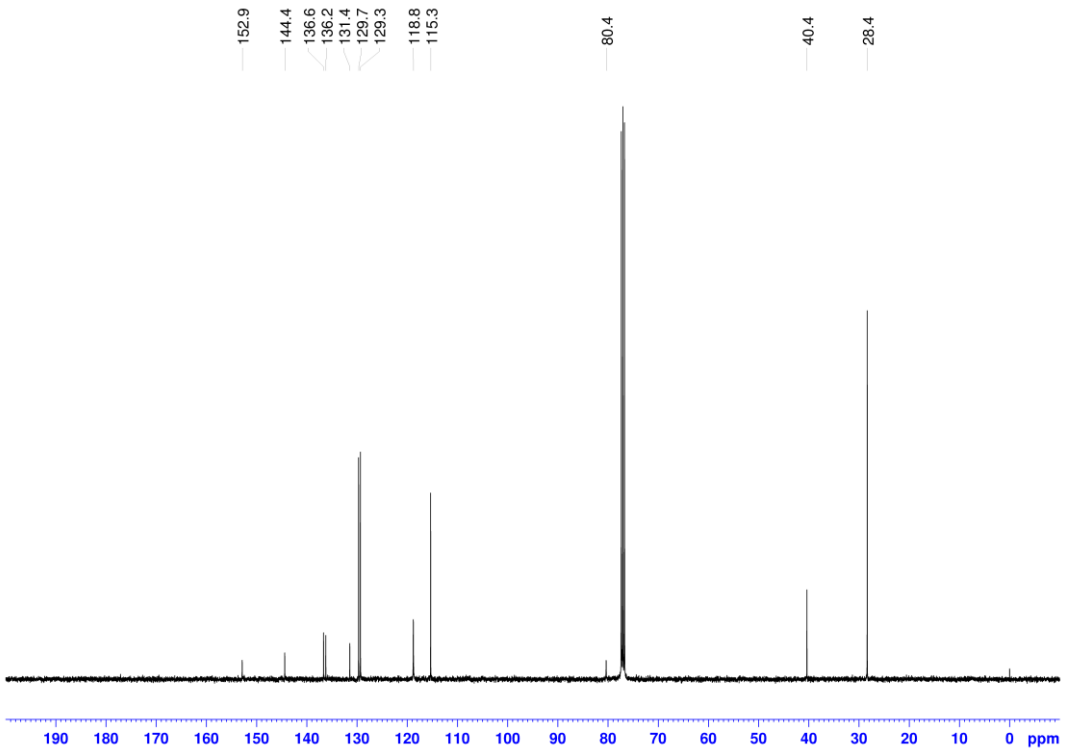

Figure S10. ^{13}C NMR spectra of **2** in $CDCl_3$.

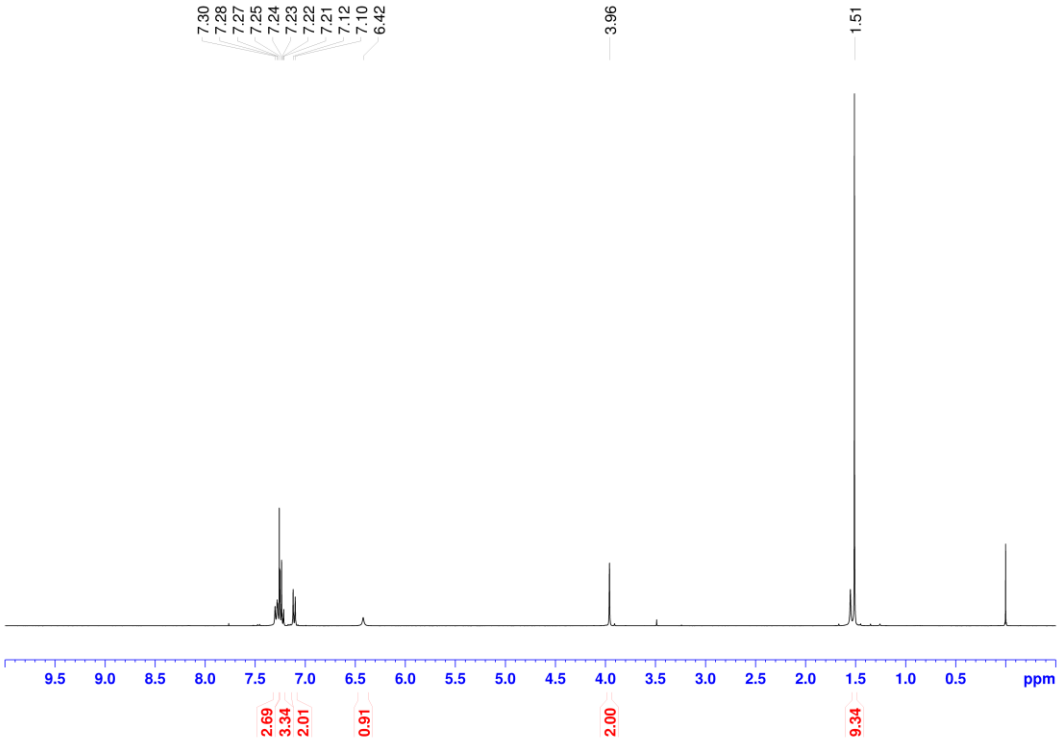

Figure S11. ^{1}H NMR spectra of **3** in $CDCl_3$.

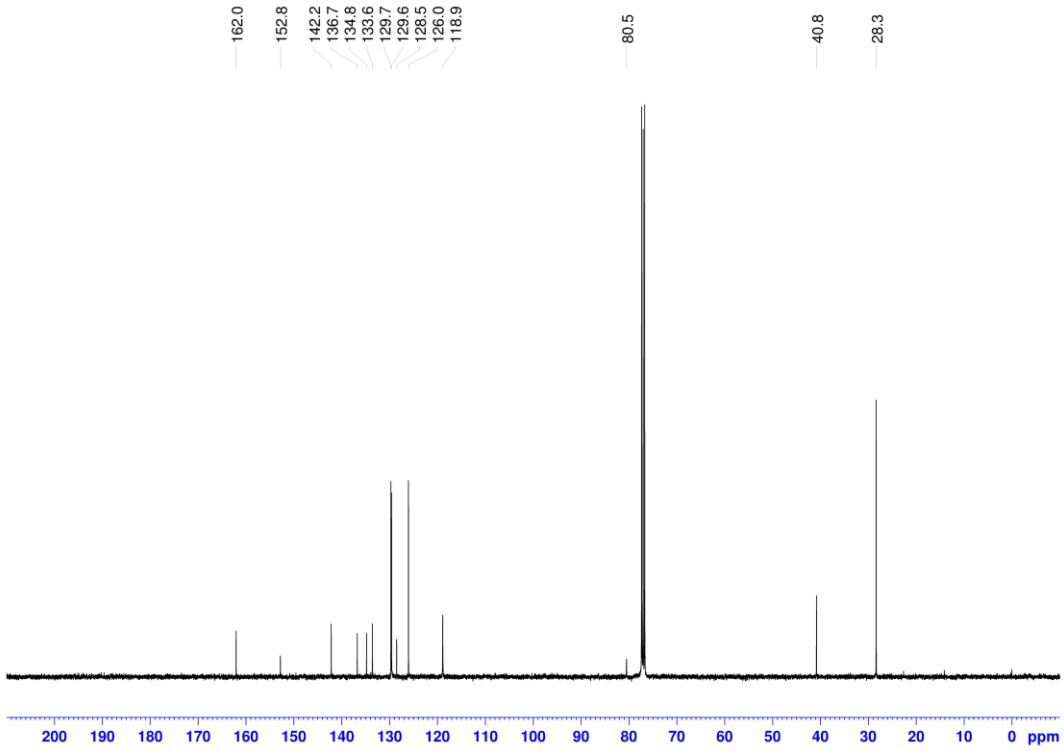

Figure S12. ^{13}C NMR spectra of **3** in $CDCl_3$.

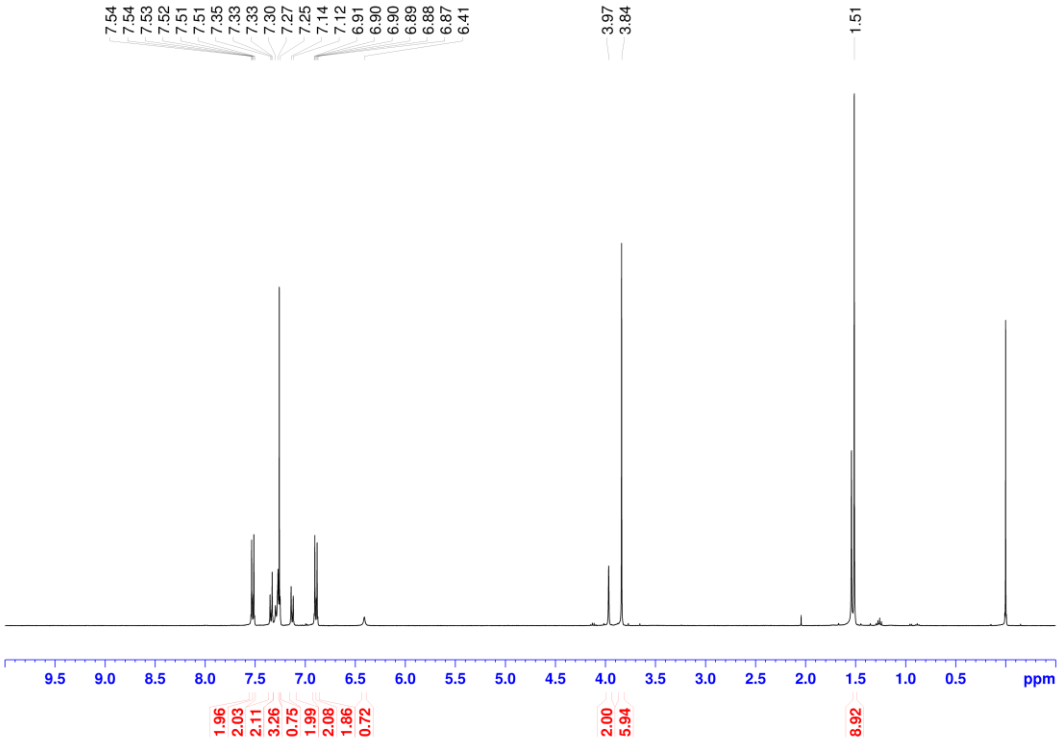

Figure S13. ^{1}H NMR spectra of **4** in $CDCl_3$.

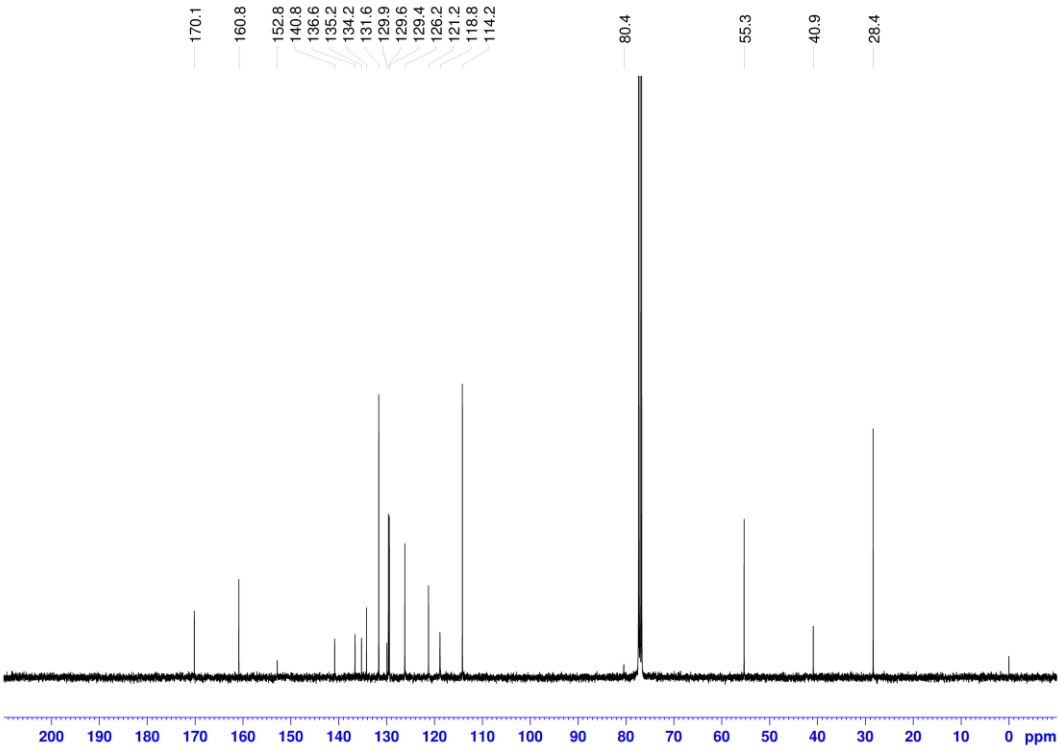

Figure S14. ^{13}C NMR spectra of **4** in $CDCl_3$.

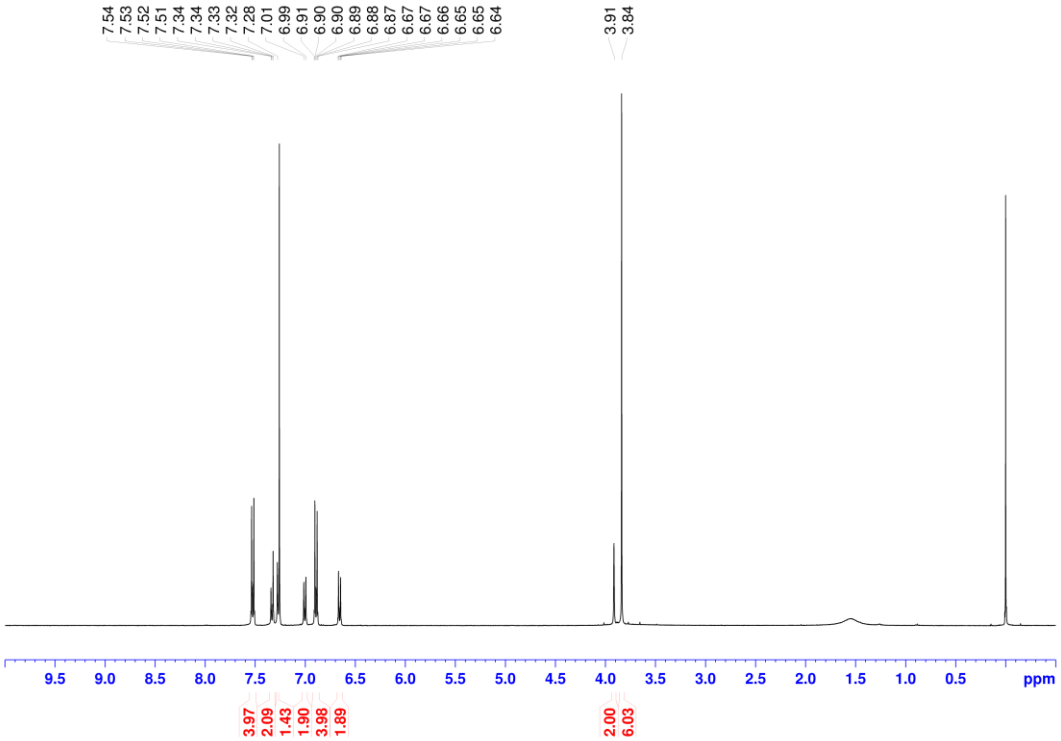

Figure S15. ^{1}H NMR spectra of **1** in $CDCl_3$.

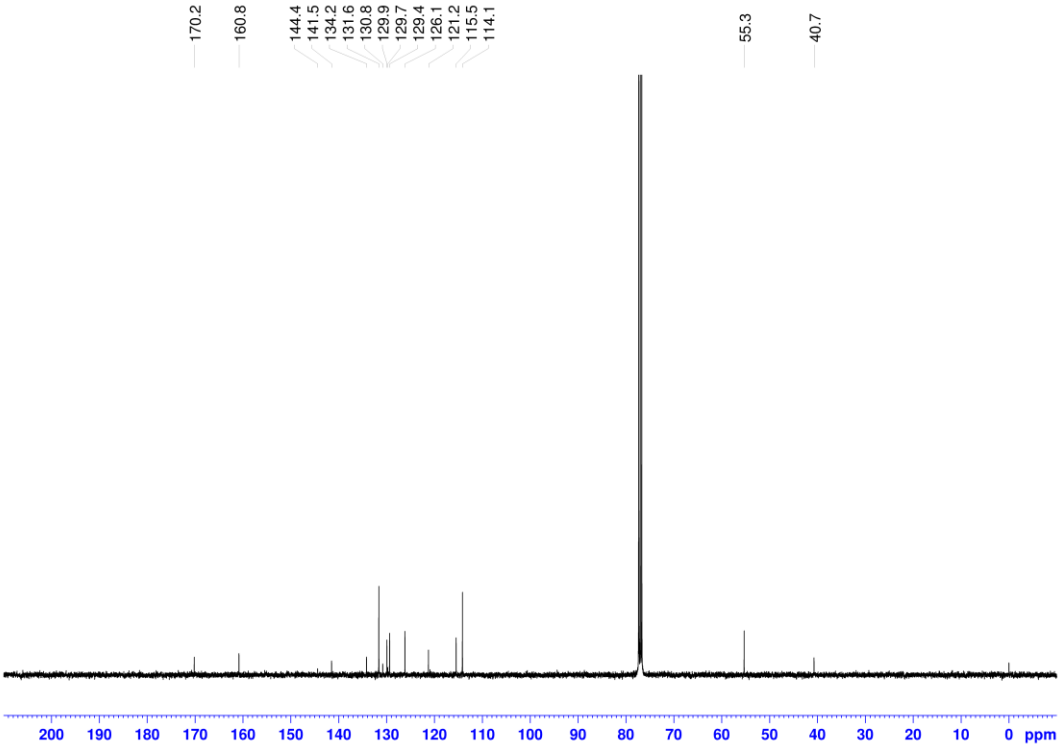

Figure S16. ^{13}C NMR spectra of **1** in $CDCl_3$.