Electron Supporting Information

Tetranuclear $Cu^{II}_2Dy^{III}_2$ Coordination Clusters as Suzuki (C–C) Coupling Reaction promoters

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1. Materials and Instrumentation

Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions using materials and solvents as received. NMR spectra were recorded on a Varian VNMRS solution-state spectrometer at 500 MHz at 30°C using residual isotopic solvent (DMSO, δ_H= 2.50 ppm) as internal reference. Chemical shifts are quoted in ppm. Coupling constants (J) are recorded in Hz. IR spectra of the samples were recorded over the range of 4000-650 cm^{-1} on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with an UATR polarization accessory. ESI-MS data were obtained on a VG Autospec Fissions instrument (EI at 70 eV). TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, UK) under nitrogen and at a scan rate of 10 °C/min.

2. Synthesis

The synthesis of ligand H_2L has been carried out according to the reported synthetic procedure.[1] The synthesis of 1NiDy, 1CoDy and 1CoY by us.[2,3] The synthesis of **1** is the following. H_2L (0.2mmol) and Et_3N (0.45mmol, 61µL) in MeCN (20 ml) was stirred for 5 minutes. $Cu(NO_3)_2.6H_2O$ (0.1mmol, 30mg) and $Dy(NO_3)_3.5H_2O$ (0.2mmol, 88mg) were added and the solution was stirred for a further 2h. The cloudy yellow solution was filtered and greenish crystals of **1** were collected after 3 days and dried overnight. 60% yield calculated via for Cu^{II}. CHN (expected) $[(Cu^{II}_2Dy^{III}_2(L)_4(NO_3)_2(CH_3CN)_2]$ $2(CH_3CN)$ C-45.08%; H-3.31%, N-8.21%. CHN (observed) C-44.15%; H-3.18%; N-6.98%. The observed CHN data corresponds to $[(Cu^{II}_2Dy^{III}_2(L)_4(NO_3)_2(CH_3CN)_2]$ $0.5(H_2O)$ C-44.15%; H-3.15%; N-6.87%, indicating partial replacement of CH_3CN by H_2O.

3. Crystallographic data

Data for **1** (ω- scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 173(2) K using Mo Kα radiation (λ = 0.71073 Å). CRYSALIS CCD and RED software was used respectively for data collection and processing. Reflection intensities were corrected for absorption by the multi-scan method. All crystal structures were then refined on Fo^2 by full-matrix least-squares refinements using SHELXL.[4] Geometric/crystallographic calculations were performed using PLATON,[5] Olex2,[6] and WINGX[7] packages; graphics were prepared with Crystal Maker.[8] Structure **1** have been given CCDC deposition number 1860013

Crystal Data for $C_{64}H_{56}Cu_2Dy_2N_{10}O_{18}$ (M =1705.26 g/mol): orthorhombic, space group Pbca (no. 61), a = 14.0995(4) Å, b = 16.9713(6) Å, c = 25.9304(8) Å, V = 6204.8(3) $Å^3$, Z = 4, T =

173 K, μ(CuKα) = 14.139 mm^{-1}, *Dcalc* = 1.825 g/cm^3, 18688 reflections measured (9.266° ≤ 2Θ ≤ 124.34°), 4867 unique (R_{int} = 0.0932, R_{sigma} = 0.0757) which were used in all calculations. The final R_1 was 0.0522 (I > 2σ(I)) and wR_2 was 0.1350 (all data).

4. Thermal Studies.

The thermal behavior of fresh crystals of **1** was studied up to 800ºC.

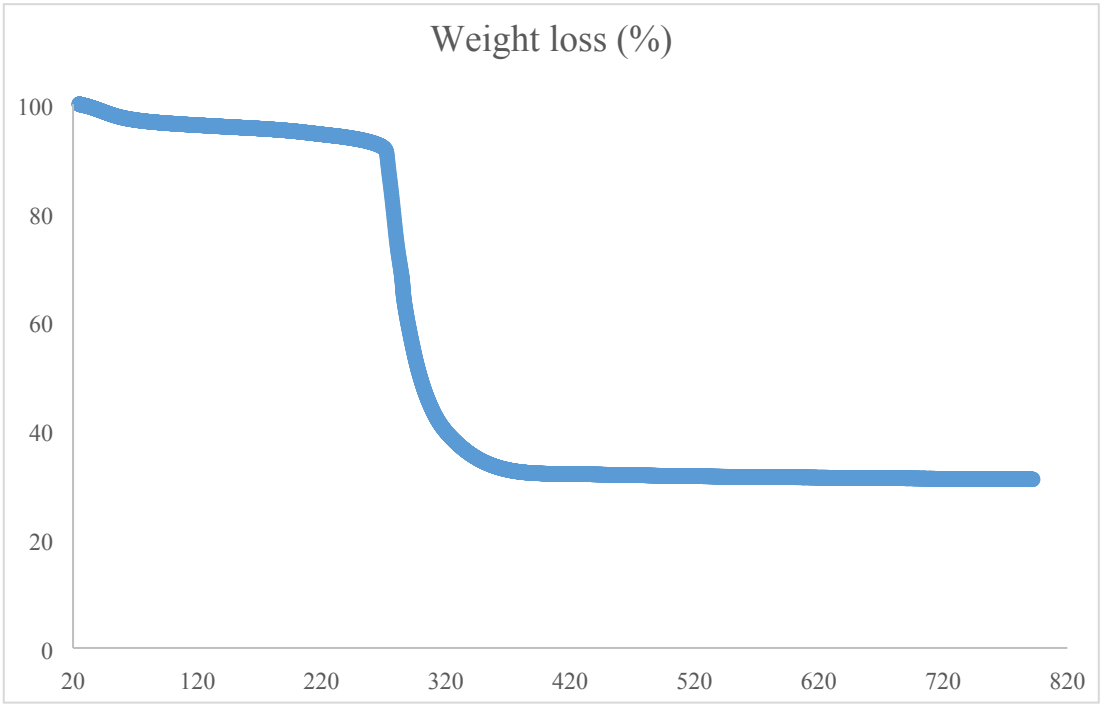


Figure S1. Thermal study of compound **1**. The framework collapses at 250ºC.

5. UV-Vis

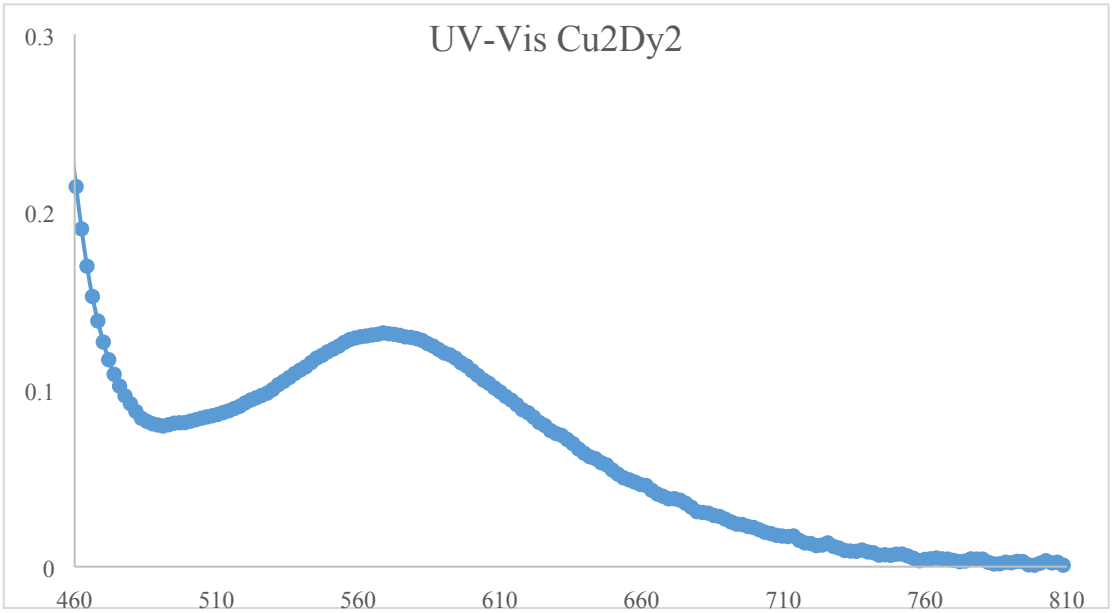


Figure S2. The UV-Vis graph of compound **1** in CH_3CN, certifying the presence of a Cu(II) centre in the solution.

6. Catalytic studies

General procedure for Suzuki coupling reaction

K_2CO_3 (690 mg, 5.0 mmol) was added to a 100 ml three-necked flask with a stirring bar and the flask was dried under vacuum and then filled with nitrogen, aryl halide (1.0 mmol), phenylboronic acid (1.1 mmol), and PPh_3 (2.0 mol%) in DME:water (1:1). Then 5.0 mol% of Cu_2Dy_2 was added under nitrogen atmosphere. The mixture was stirred at 80 °C for the indicated reaction time. The mixture was cooled and the precipitate was removed by filtration and the product was extracted from the filtrate with diethyl ether. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. After evaporation, the obtained residue was purified by silica-gel column chromatography to give the coupling product. The yield of the product was determined by ^1H NMR.

Effect of Base. Further, the effect of a base on the reaction performance was studied using different bases such as K_2CO_3, KOH, Na_2CO_3, NaOH, Et_3N, Cs_2CO_3 and KO^{t}Bu in a mixture of DME and water solvent (FigS2). It was investigated that the K_2CO_3 is the desirable base for the reaction with higher product yield for this reaction. In the absence of catalyst, coupling product was formed with very less yield (5.0 %) using K_2CO_3 base. The presence of base, as it is essential to activate boronic acid via enhancing the polarization of the organic ligand and thus facilitate transmetallation.

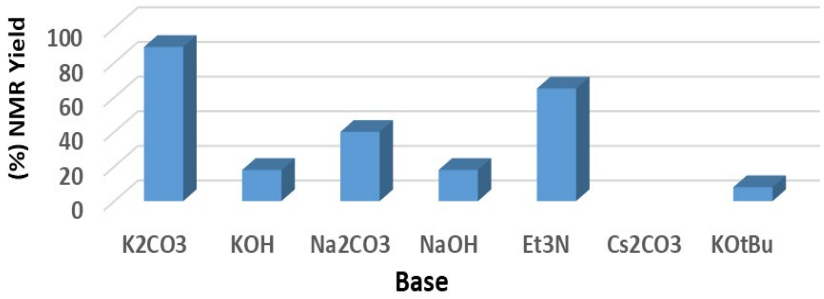


Figure S2. A summarizing table showing the effect of the base on the reaction performance.

Effect of Temperature: An investigation of the influence of the temperature on coupling between phenyl boronic acid and iodobenzene was also carried out with a range of temperature (0° C – 120° C). Control experiments showed that Cu_2Dy_2 can give good conversion to the coupled product at 80° C but no conversion obtained at a temperature lower than 40°C (Fig S3). A temperature of 80 °C was used as the best condition for the reaction model. At 100 and 120 °C, the catalyst gets degraded and afforded low yield.

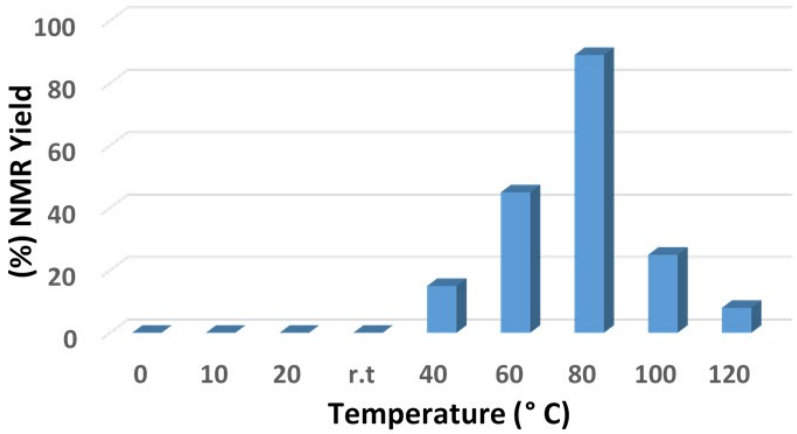
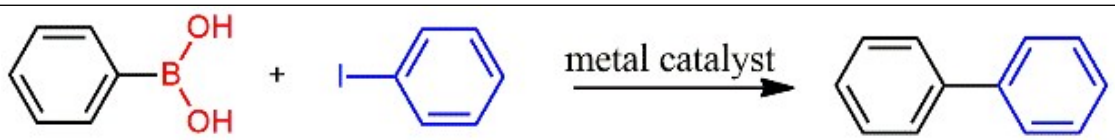


Figure S3. A summarizing table showing the effect of the temperature on the reaction performance.

Table S1. Metal salt screening influence of metal catalysts for C-C coupling reaction



Entry	Catalyst	(%) Yield[a]
1	$Cu(NO_3)_2$	33
2	$Cu(OAc)_2$	-
3	$CuCl_2$	31
4	CuI	40
5	$Dy(NO_3)_3$	-
6	$Cu(NO_3)_2$ / $Dy(NO_3)_3$	25
7	$Cu(NO_3)_2$ / $Dy(NO_3)_3$ / H_2L (1:1:2)	8
8	Cu_2Dy_2	89

Iodobenzene (1.0 mmol), phenylboronic acid (1.1mmol), PPh_3 (2.0 mmol), catalyst (5.0 mol %), K_2CO_3 (5.0 mmol) DME:water (1:1), 80 °C. [a]Isolated yield.

7. NMR Data

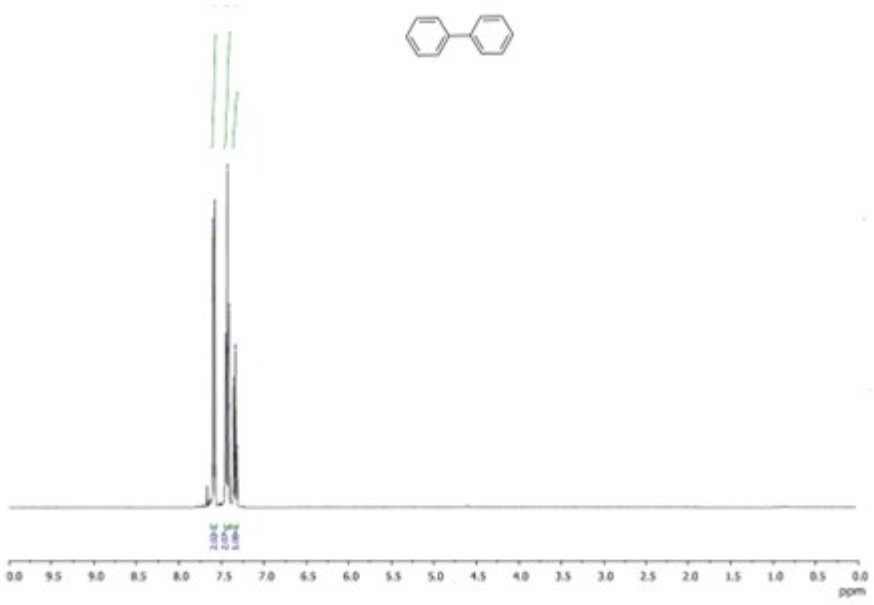


Figure S4. ^{1}H NMR data of compound **4aa**.

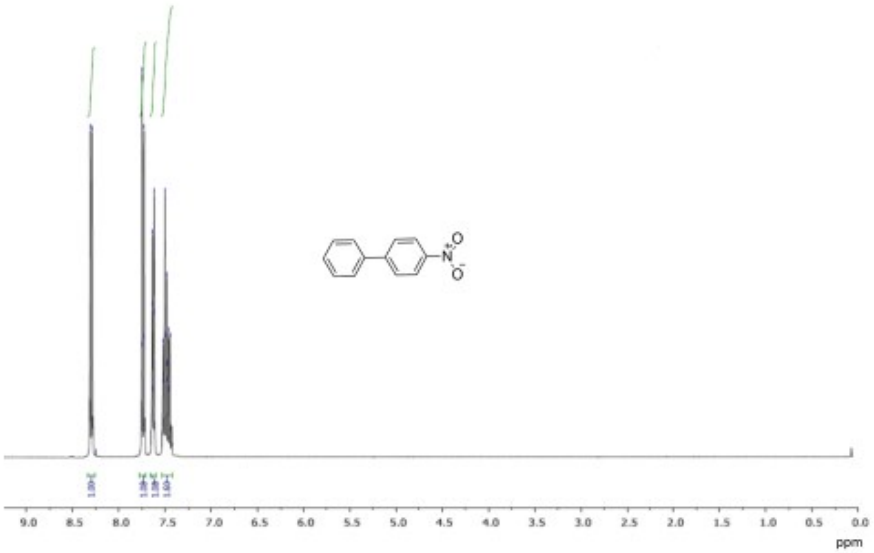


Figure S5. ^{1}H NMR data of compound **4ac**

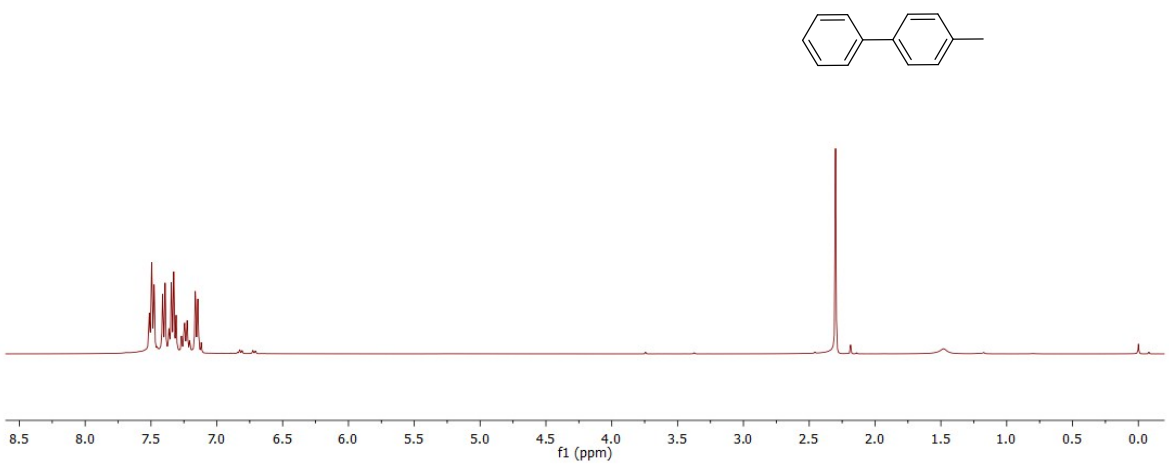


Figure S6. [1]H (upper) and [13]C (lower) NMR data of compound **4ad**.

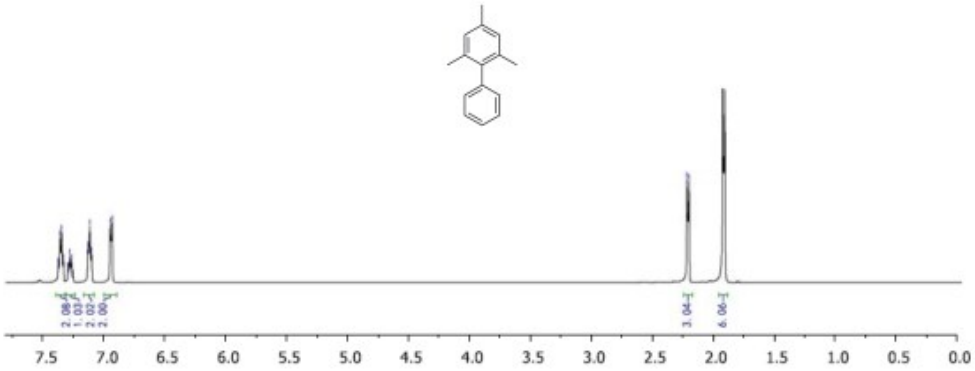


Figure S7. [1]H NMR data of compound **4ba**.

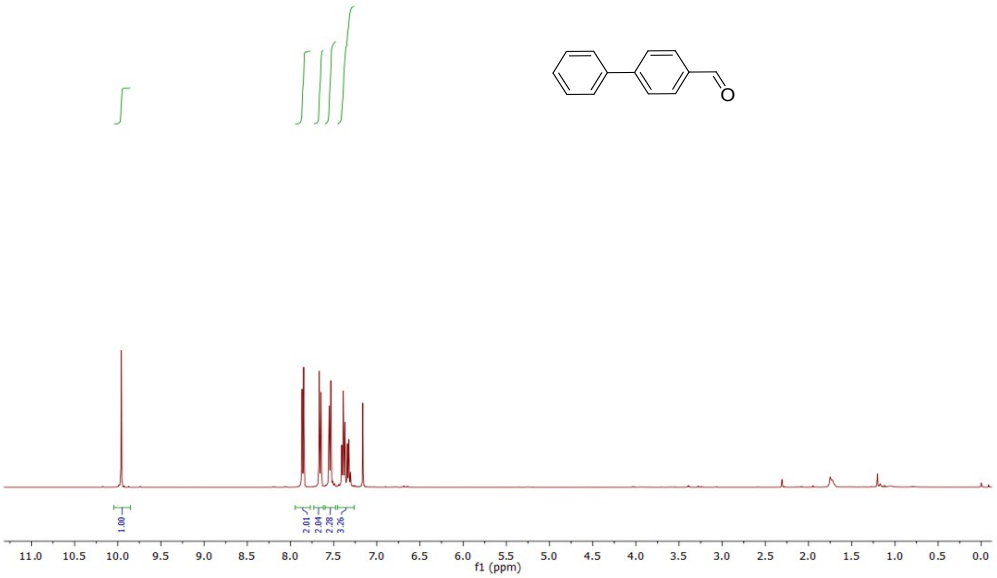


Figure S9. ^{1}H NMR data of compound **4da**

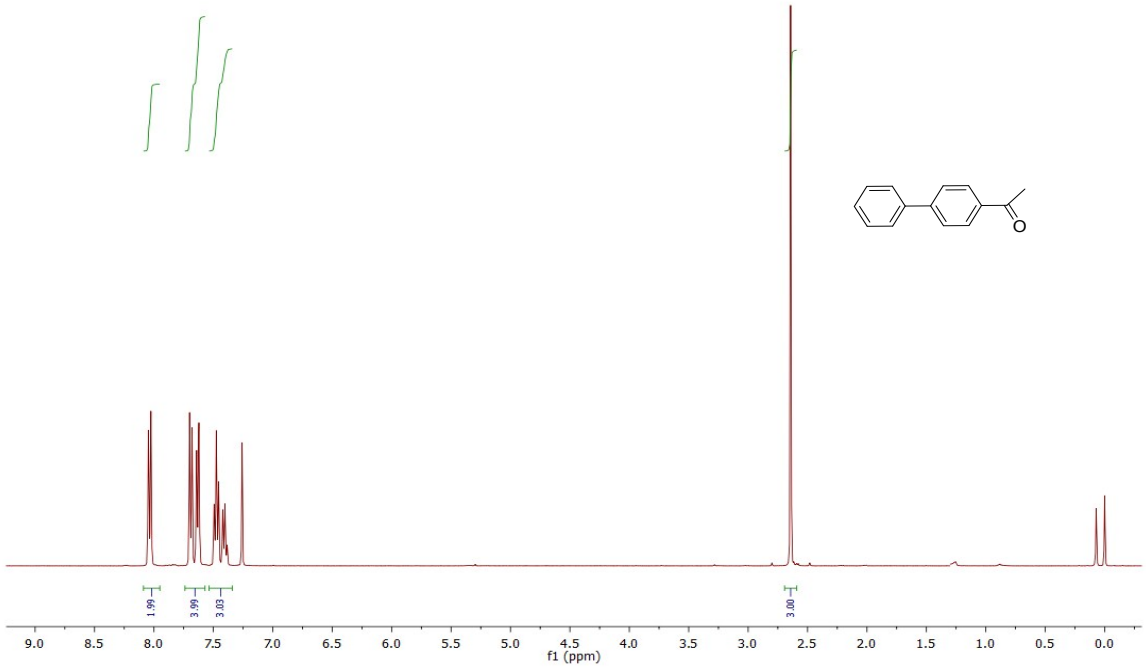


Figure S10. ^{1}H NMR data of compound **4db**

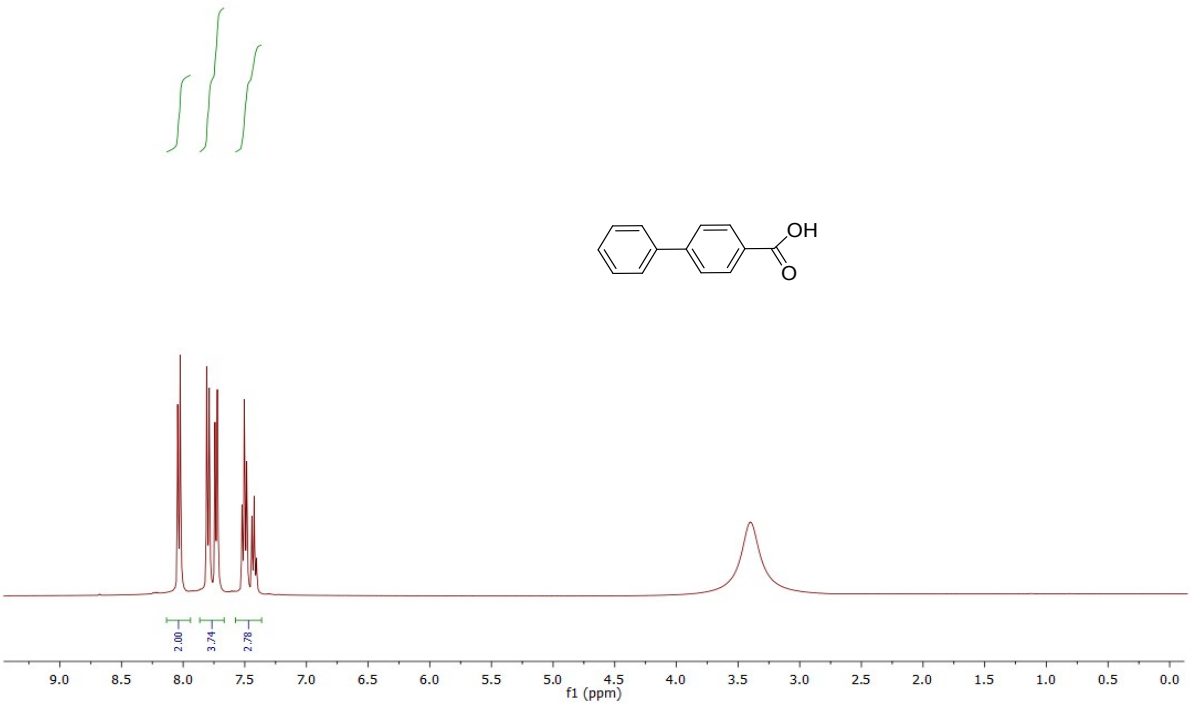


Figure S11. [1]H NMR data of compound **4dc**

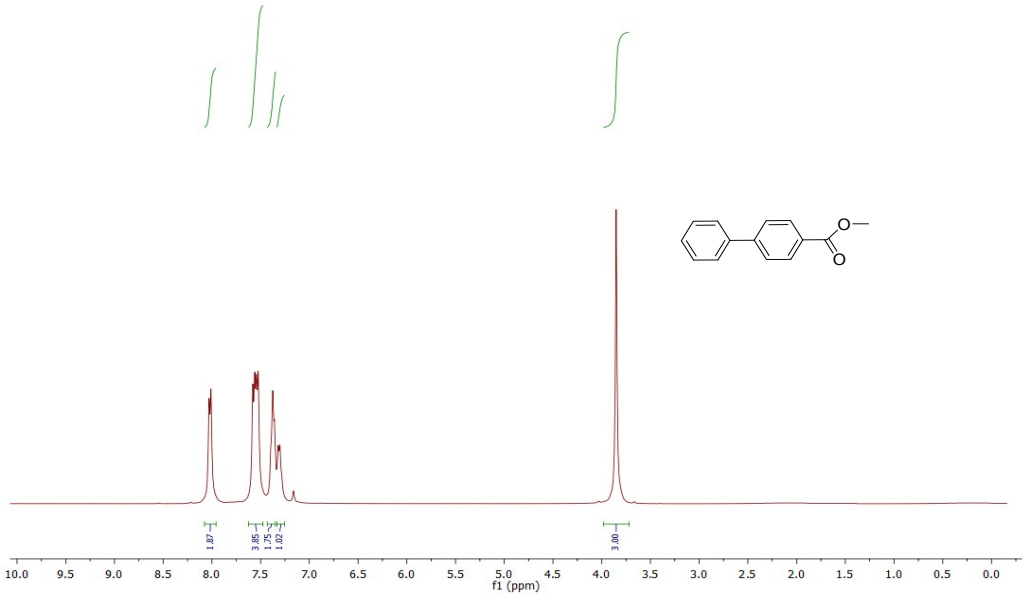


Figure S12. [1]H NMR data of compound **4dd**

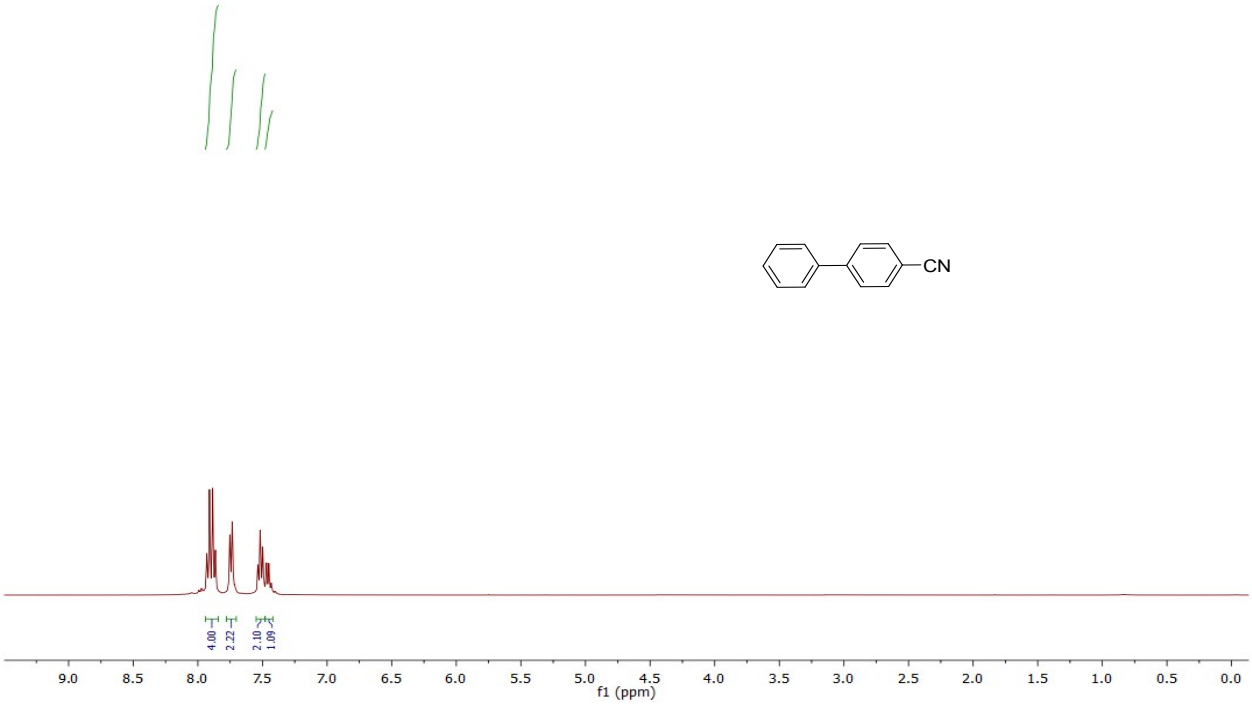


Figure S13. [1]H NMR data of compound **4ea**

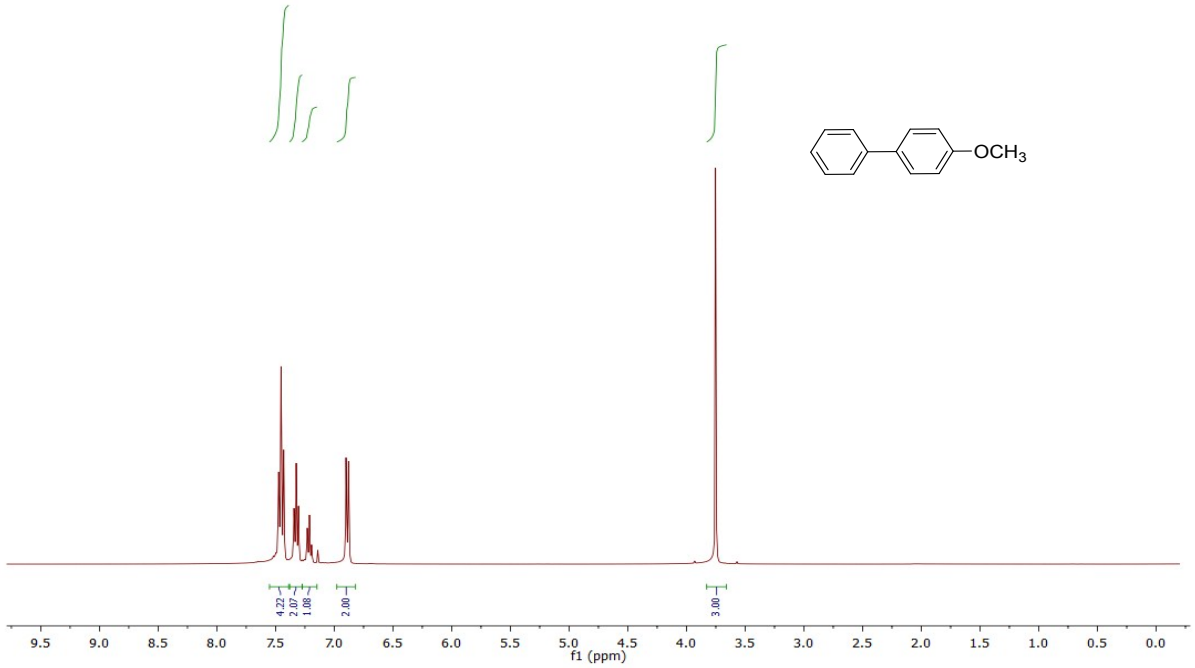


Figure S13. [1]H NMR data of compound **4fa**

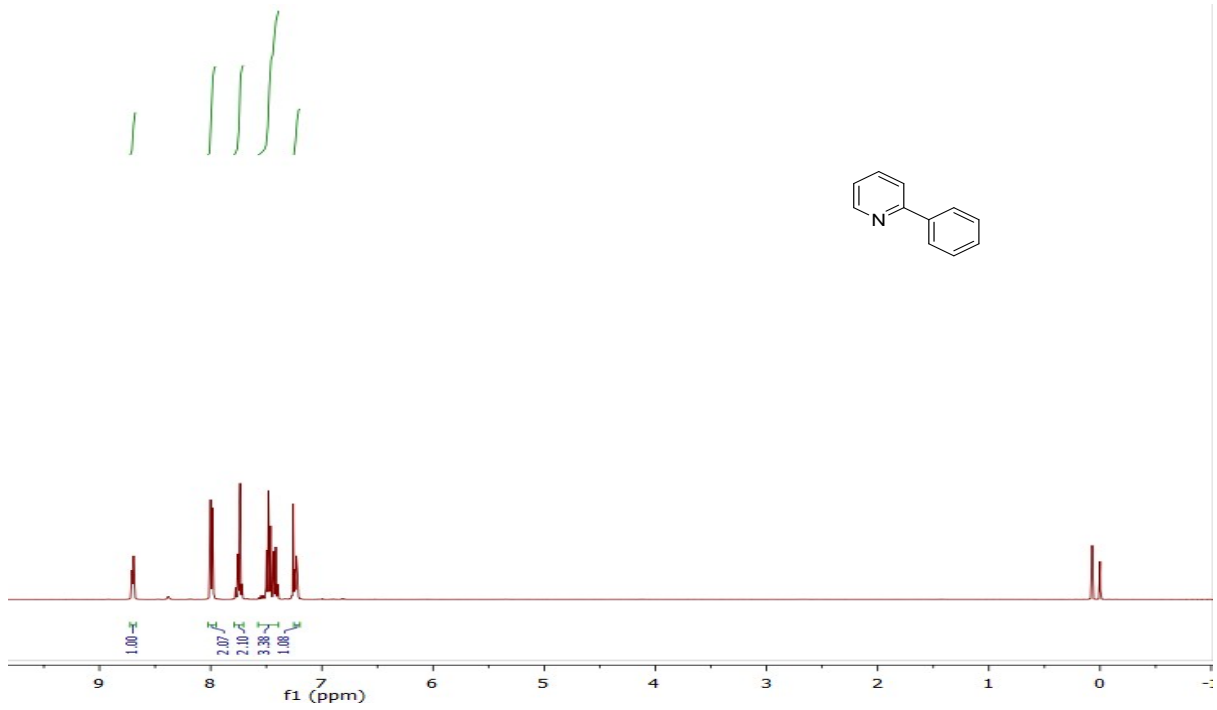


Figure S14. [1]H NMR data of compound **7aa**

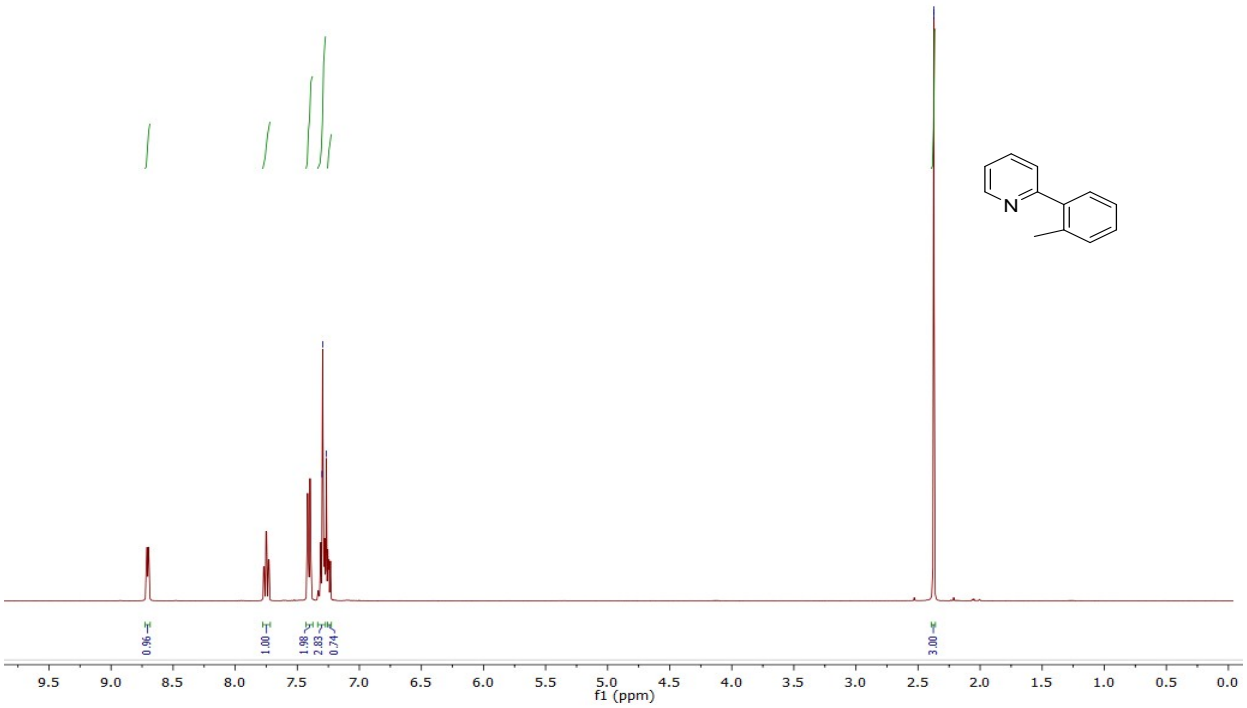


Figure S15. [1]H NMR data of compound **7ab**

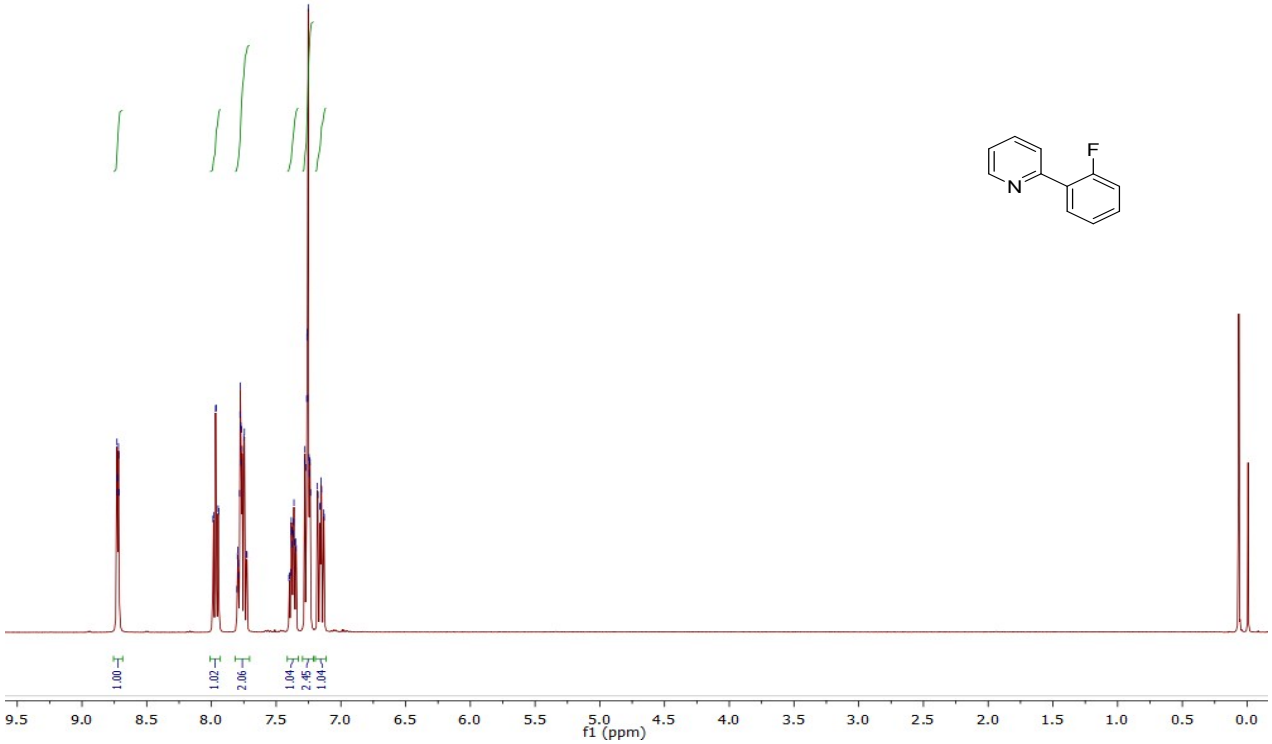


Figure S16. [1]H NMR data of compound **7ac**

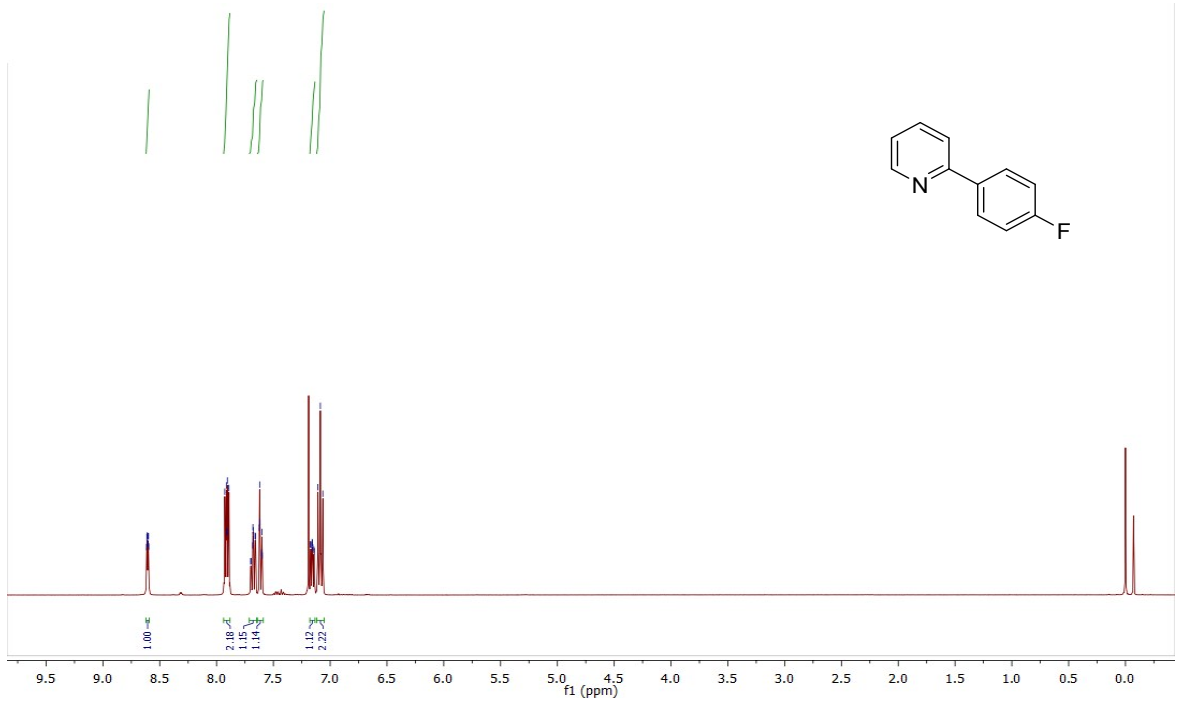


Figure S17. [1]H NMR data of compound **7ad**

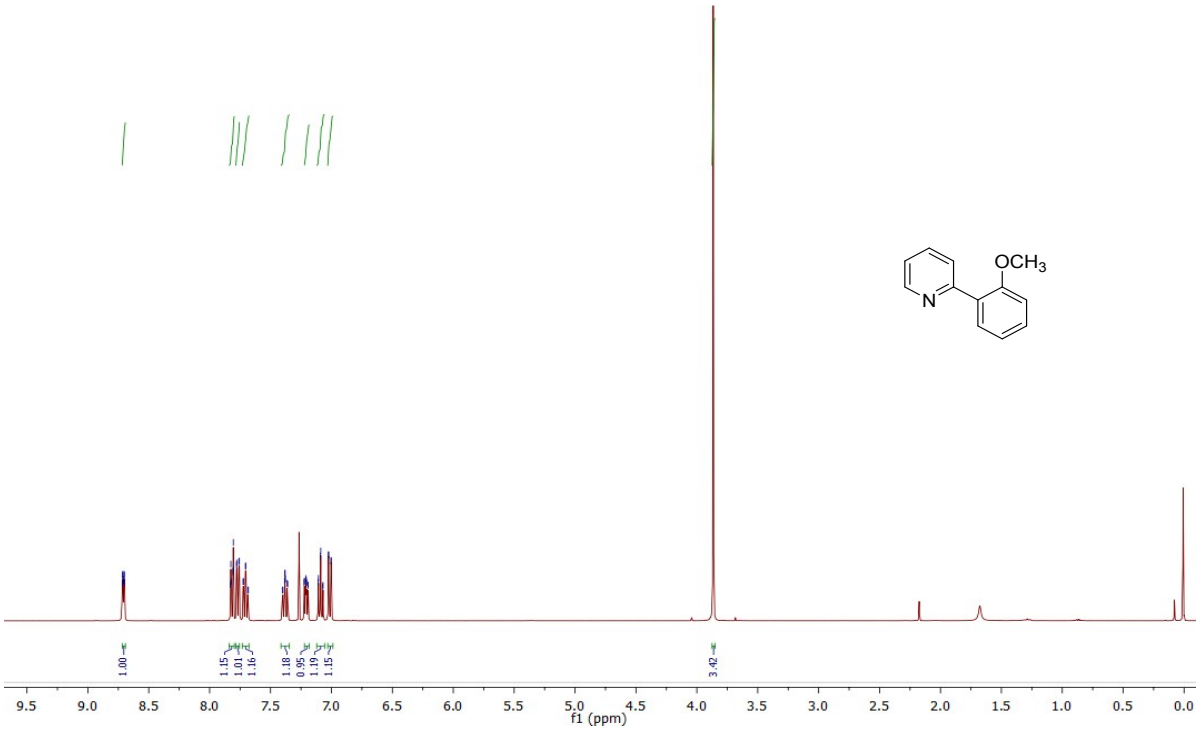


Figure S18. [1]H NMR data of compound **7ae**

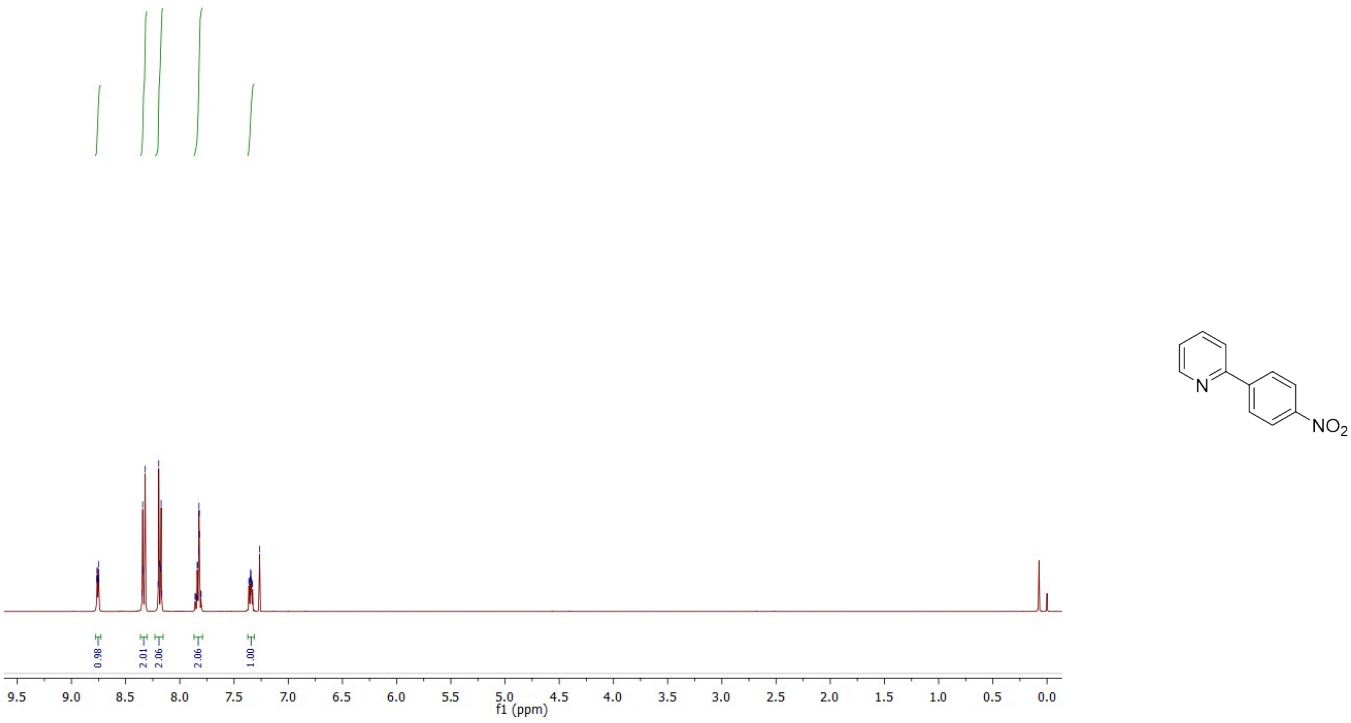


Figure S19. [1]H NMR data of compound **7af**

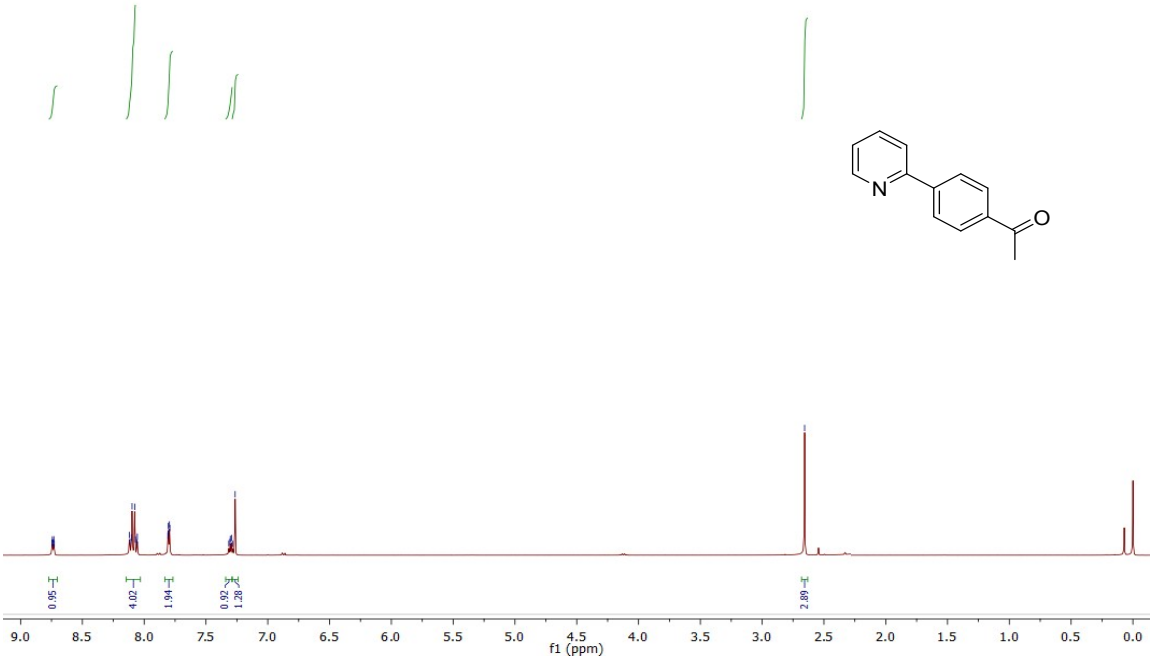


Figure S20. [1]H NMR data of compound **7ag**

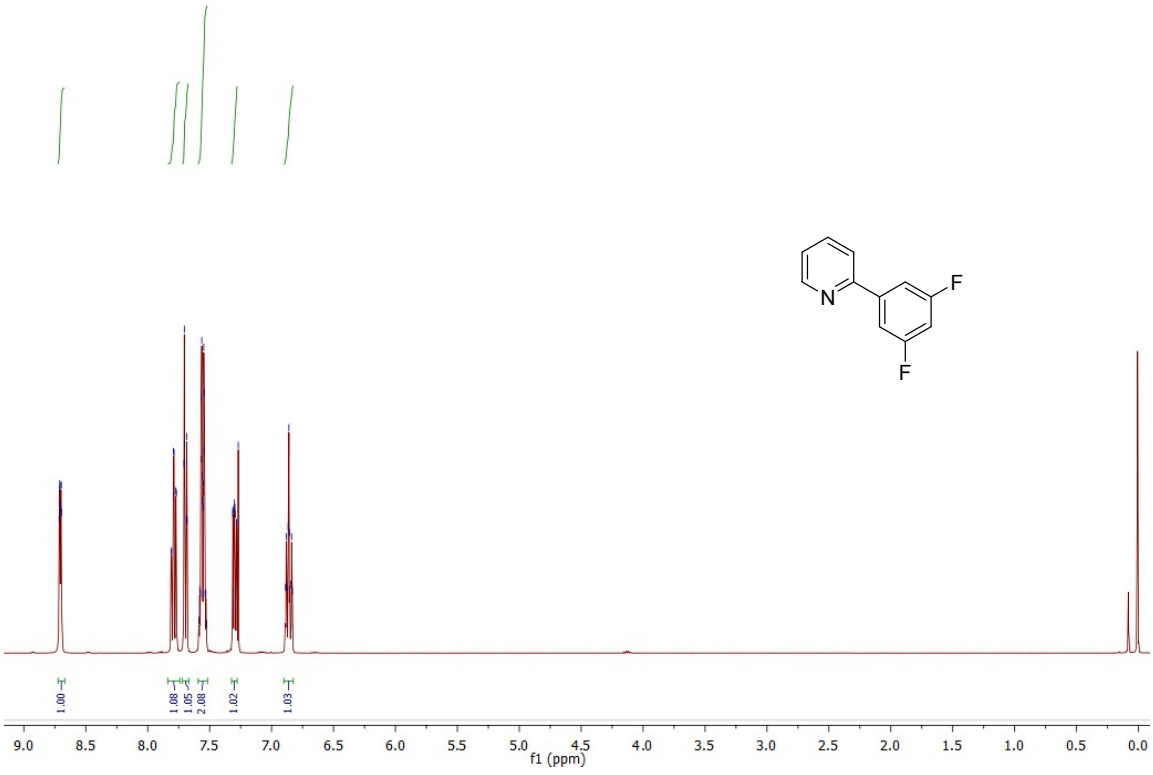


Figure S21. [1]H NMR data of compound **7ah**

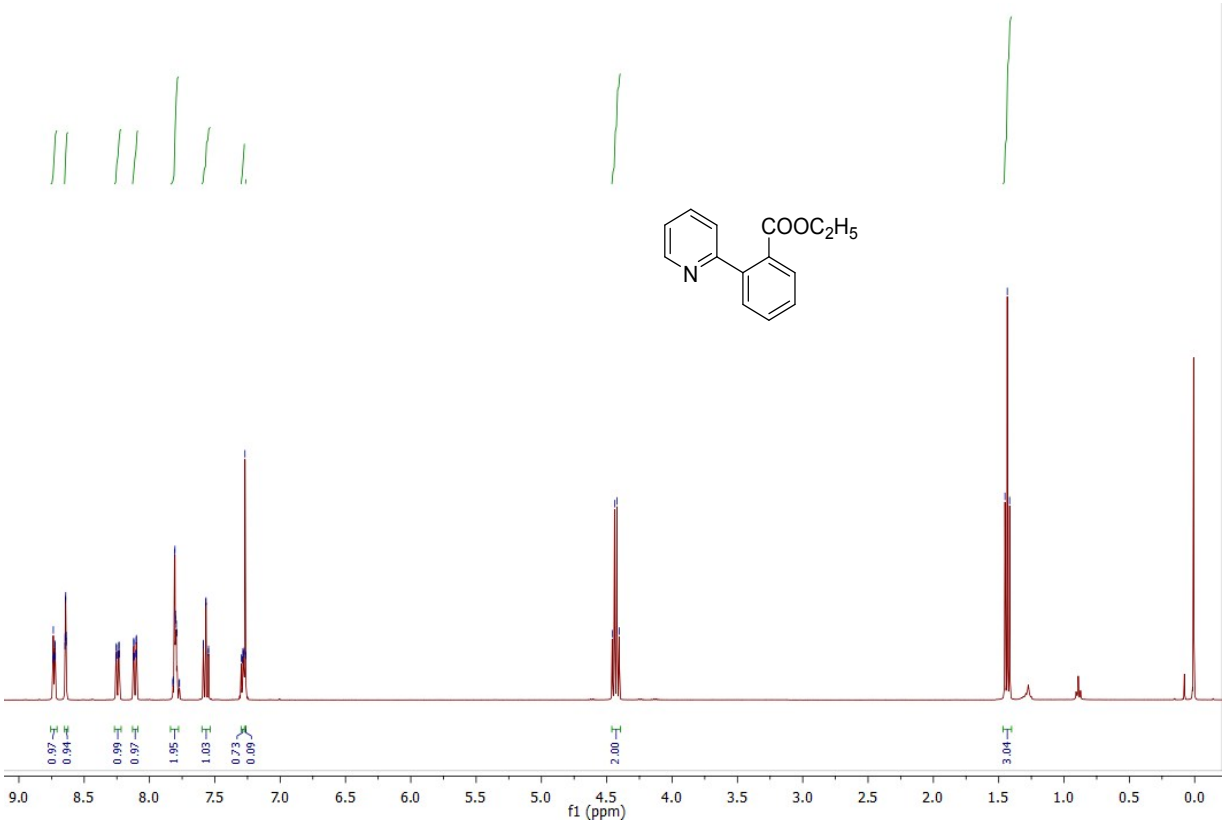


Figure S22. ^{1}H NMR data of compound **7ai**

8. References

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