

Electronic Supplementary Information

Photocatalytic ensemble **HP-T@ Au-Fe₃O₄**: Synergistic and balanced operation in Kumada and Heck coupling reactions.

Harpreet Kaur, Manoj Kumar*, Vandana Bhalla*

Department of Chemistry, UGC Sponsored Centre for Advanced Studies-II, Guru Nanak Dev University, Amritsar 143005, and Punjab, India

vanmanan@yahoo.co.in

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GENERAL EXPERIMENTAL SECTION

Materials and reagents: All the reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone as an indicator. UV-vis studies were performed in THF, distilled water and HEPES buffer (0.05 M) (pH = 7.05).

Instrumentation: UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25°C. The fluorescence spectra were recorded with a SHIMADZU- 5301 PC spectrofluorimeter. The TEM and HR-TEM images were recorded in HR-TEM-JEM 2100 microscope. The dynamic light scattering (DLS) data were recorded with MALVERN Instruments (Nano-ZS). ¹H and ¹³C NMR spectra were recorded on a BRUKER-AVANCE-II FT-NMR-AL 500 MHz and JEOL 400 MHz spectrophotometer using CDCl₃, as solvent and tetramethylsilane, SiMe₄ as internal standards. Data are reported as follows: chemical shifts in ppm, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet), coupling constants *J* (Hz), integration and interpretation. Silica gel 60 (60-120 mesh) was used for column chromatography.

Procedure for analyte sensing by derivative 2

A 5.58 mg portion of compound **2** was dissolved in 10.0 mL of dry THF to prepare a 10⁻³ M stock solution. This stock solution (15 μL) was further diluted with 1185 μL of double distilled water and 1800 μL of dry THF to prepare an experimental solution of derivative **2** (3.0 mL 5.0 μM) in Water/THF (4/6, v/v), pH 7.06, which was used for each UV-vis and fluorescence experiment. 10⁻¹ M to 10⁻³ M solutions of Au³⁺ and Fe³⁺ metal ions as their perchlorate/chloride salts were used. In titration experiments, each time a 3 ml solution of **2** was taken in a quartz cuvette to record the spectra.

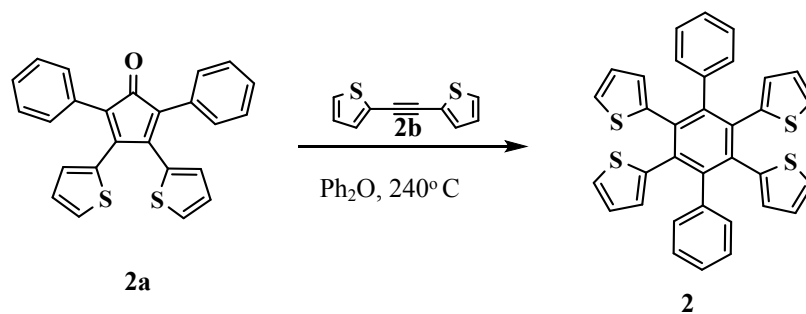
Synthesis of Supramolecular Ensemble HP-T@Au-Fe₃O₄ nanohybrid material

An aqueous solution of 38 μL of 10⁻³ M AuCl₃ and 30 μL of 10⁻³ M FeCl₃ was mixed into 3.0 mL of a 5.0 μM solution of compound **2** in an H₂O/THF (4/6, v/v)

mixture. The reaction mixture was stirred at room temperature, and the color of solution changed from colourless to reddish brown after 1h; thereafter formation of brown **HP-T@AuFe₃O₄** nanohybrid material.

Synthesis of Derivative 2.

A solution of [2,5-diphenyl-3,4-di(thiophen-2-yl)cyclopenta-2,4 dien-1-one] **2a** (0.2 g, 1.0 mmol) and [1,2-di(thiophen-2-yl)ethyne] **2b** (0.095 g, 1.0 mmol) were mixed in 2mL of diphenylether and refluxed for 24 h under an inert atmosphere (N₂). After the completion of reaction, the reaction mixture was cooled down to r.t. and methanol (10 mL) was then added to it. The reaction mixture was kept for stirring at r.t for 1h. After this, methanol layer was decanted off, and the insoluble dark oil was subjected to column chromatography using 10:90 EtOH/hexane as an eluent to give (0.210 g, 75%) of compound **2** as a white solid. ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 5 Hz, 4H), 7.71 (d, *J* = 5 Hz, 4H), 7.46 (d, *J* = 5 Hz, 2H), 7.37 (d, *J* = 5 Hz, 2H), 7.20 – 7.18 (m, 2H), 7.01-6.99 (m, 4H), 6.61-6.56 (m, 2H), 6.47 (d, *J* = 5 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 143.4, 141.2, 135.6, 130.5, 129.3, 126.9, 126.0, 125.7. The ESI-MS of C₃₄H₂₂S₄ showed a parent ion peak at *m/z* 559.6495 corresponding to [M + H]⁺. Elemental analysis: Found for C₃₄H₂₂S₄: C, 73.08; H, 3.97; S, 22.95. Anal. Calcd for C₃₄H₂₂S₄: 72.84; H, 3.66; S, 22.89.



Scheme S1. Synthesis of derivative **2**

General procedure for the photocatalytic Kumada cross coupling catalyzed by Supramolecular ensemble HP-T@AuFe₃O₄: Chlorobenzene **3a** (100 mg, 1 mmol) was dissolved in THF (2 mL) in the presence of HP-T@AuFe₃O₄ (200 uL) in a 10 mL RBF, then the Grignard reagent **4** (4 mmol) was slowly added dropwise. The solution was stirred for 20 min at RT under visible light irradiation. After the reaction was completed (TLC), The reaction mixture was diluted with water and ethyl acetate. The resultant organic layer was passed through anhydrous Na₂SO₄ and was concentrated under reduced pressure to acquire the crude sample. The target products (**5a-5h**) were purified by flash chromatography using hexane as an eluent. The desired products **5a-5h** were found in excellent to good yield and confirmed from their spectroscopic and analytical data.

General procedure for the photocatalytic Heck coupling catalyzed by Supramolecular ensemble HP-T@AuFe₃O₄: A mixture of aryl-halides (**3a**, 100 mg, 1 mmol), acrylate (Me/Et/n-Bu, 1.2 mmol) and K₂CO₃ (1 mmol) in the presence of HP-T@AuFe₃O₄ (200 uL) was stirred for 2h at 40 °C under visible light irradiation. The reaction progress was screened by TLC at different time intervals. After the completion of the reaction, the reaction mixture was treated with water and extracted with ethyl acetate and the resultant organic layer was dried over anhydrous Na₂SO₄ and was concentrated under reduced pressure to acquire the crude sample. The desired products (**8a-8g**) were purified by flash chromatography using hexane as an eluent. The desired products **8a-8g** were found in excellent to good yield and confirmed from their spectroscopic and analytical data.

Tables S1. Comparison of catalytic activity of HP-T@ Au-Fe₃O₄ nano hybrid material for preparation of biaryl derivatives through Kumada coupling over other catalytic system reported in literature.

S. No.	Publication	Catalyst used	Ar-X (X)	Solvent	Reaction condition	Photo catalysis	Temp. (°C)	Recyclability	Yield (%)	
									X-Cl	X-I
1.	Present Work	HP-T@Au Fe ₃ O ₄	Cl	H ₂ O/THF	Aerial atm.	Yes (Visible light)	RT	Yes	93	87
2.	Angew. Chem. Int. Ed. 2019, 58 , 13030-13034.	Fe(acac) ₃ and NHC	Cl	Dry THF	N ₂ atm	Yes (Blue LED)	RT	No	93-95	--
3.	Org. Lett. 2019, 21 , 50–55	Ni(xant)(o Tol)Cl	Cl	Dry THF/ (Toluene or NMP)	N ₂ atm	No	RT-60 °C	No	93	--
4.	Adv. Synth. Catal. 2019, 361 , 2329-2336.	Ni(dppe)Cl ₂	OTs	Dry THF	Ar atm.	No	23 °C	No	94	--
5.	ACS Appl. Nano Mater. 2018, 1 , 6950-6958.	Fe (II) NPs. (SAFe)	I/Br	Dry THF	Ar atm.	No	75 °C	Yes	13	96
6.	J. Am. Chem. Soc. 2018, 140 , 13628-13633.	Ni-Li-Olefin Complex	Cl/Br	MTBE	Ar atm.	No	-50 °C	No	60-70	--
7.	Organometallics 2017, 36 , 255-265.	[Ni(IMe)] ₂ (μ-Cl)(μ:η ¹ , η ² -C ₆ H ₅)	Cl	Dry THF	N ₂ atm	No	RT	No	85	--
8.	Chem Asian J. 2017 12 , 1234-1239.	Co(PMe ₃) ₃ (1-Si(Me) ₂ -2-(PPh ₂)C ₆ H ₄)	Cl	Toluene	N ₂ atm	No	80 °C	No	85	--
9.	Adv. Synth. Catal. 2016, 358 , 2449-2459.	Au supported Ni NPs	I	Dry THF	Ar atm.	No	75 °C	Yes	--	90

Tables S2. Comparison of catalytic activity of HP-T@ Au-Fe₃O₄ nanohybrid material for Heck coupling reaction over other catalytic system reported in literature.

S. No.	Publication	Catalyst used	Ar-X (X)	Base/Additive	Solvent	Photo catalysis	Reaction Temp. (°C)	Recyclability	Yield(%) / Time	
									X-Cl	X-I
1.	Present Work	HP-T@Au-Fe ₃ O ₄ NPs	Cl	K ₂ CO ₃	Neat	Yes	RT-40 °C	Yes	82/2 h	91/2 h
2.	Green Chem. 2019, 21 , 1718-1734.	Fe ₃ O ₄ @SiO ₂ @Im[Cl]Co(III)-melamine	Cl	Mn powder	EtOH	No	Reflux	Yes	82/3.6 h	91/1.3 h
3.	J. Am. Chem. Soc. 2019, 141 , 1928–1940	Pd@EVOH	I/Br	KOAc	Toluene or NMP	No	95 °C	Yes	--	91/24 h
4.	Org. Biomol. Chem., 2019, 17 , 8969–8976	Pd(II)–NHC complex	Br/Cl	K ₃ PO ₄ /TBAB	Water	No	110 °C	Yes	70/12 h	--
5.	Green Chem., 2018, 20 , 1506-1514	Pd-Ni NPs	I/Br/Cl	K ₂ CO ₃	H ₂ O/Et OH	No	(MW) 120 °C	Yes	82/10 min	88/10 min
6.	J. Am. Chem. Soc. 2018, 140 , 16929–16935	CuCl	Br	Cs ₂ CO ₃	DMSO/THF	No	60 °C	No	--	82/4 h
7.	ACS Sustainable Chem. Eng. 2018, 6 , 8223–8229	Au NPS	I/Br/Cl	K ₂ CO ₃	Water	Yes	RT	Yes	60/6 h	89/1 h
8.	Chemistry Select 2019, 4 , 6913 –6916	NiBr ₂ (PPh ₃) ₂	I/Br/Cl	TBAB Zn powder, BMIM.O Tf	DMA	No	120 °C	No	50/4 h	75/4 h
9.	Green Chem., 2017, 19 , 1353–1361	Co-MS@MNPs/CS	I/Br/Cl	K ₃ PO ₄	PEG	No	80 °C	Yes	71/1 h	88/1 h
10.	New J. Chem., 2017, 41 , 3172--3176	Pd ₂ (dba) ₃	Br	P(tBu) ₃ -HBF ₄	Toluene		95 °C		83	

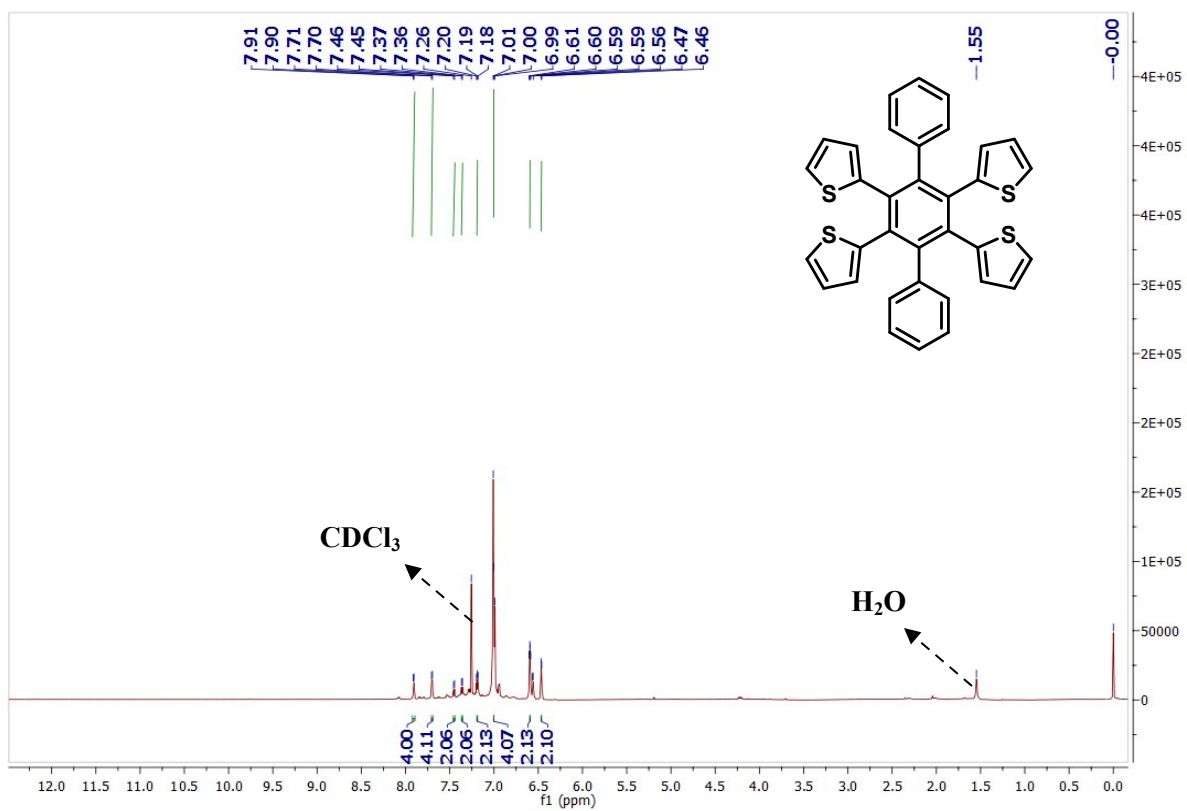


Fig. S1A ¹H NMR spectra (CDCl₃, 500 MHz, ppm) of derivative 2.

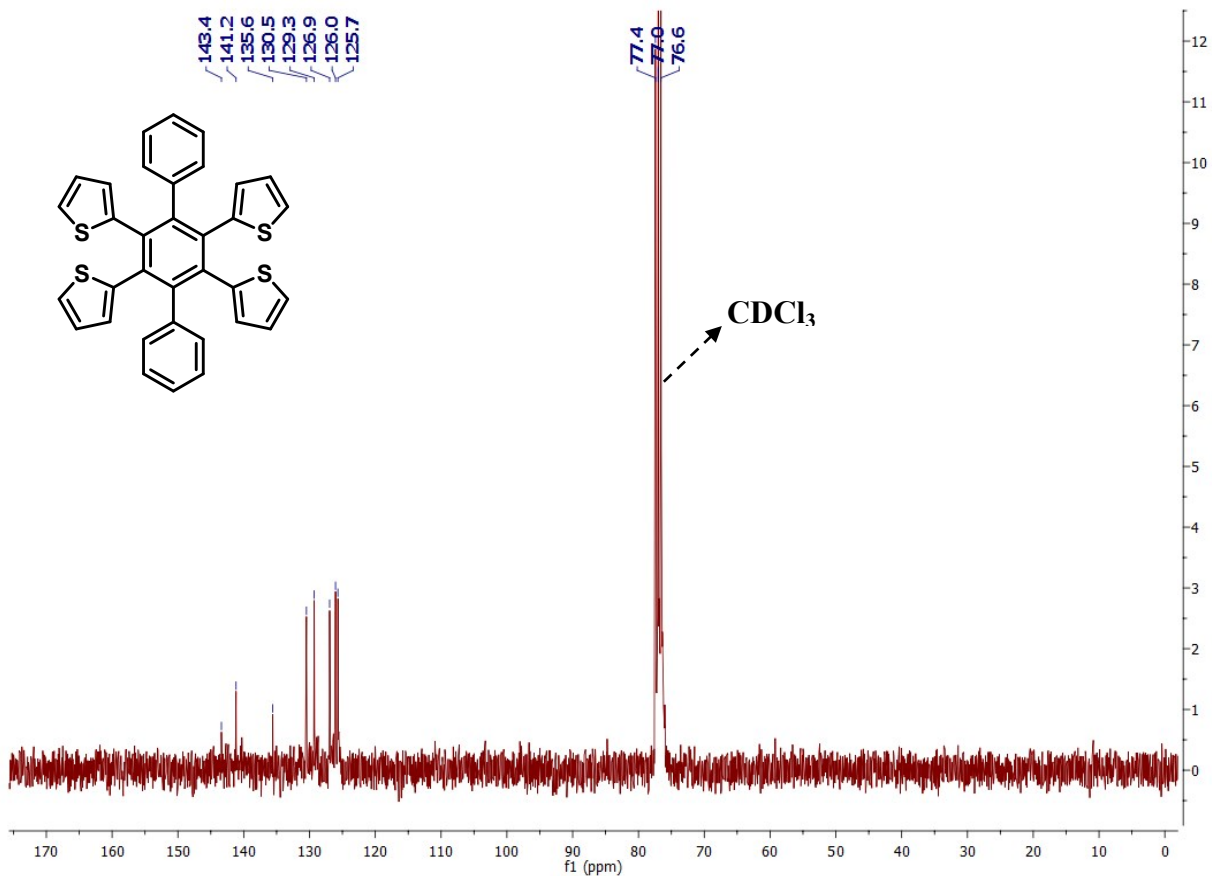


Fig. S1B ¹³C NMR spectra (CDCl₃, 75 MHz, ppm) of derivative 2.

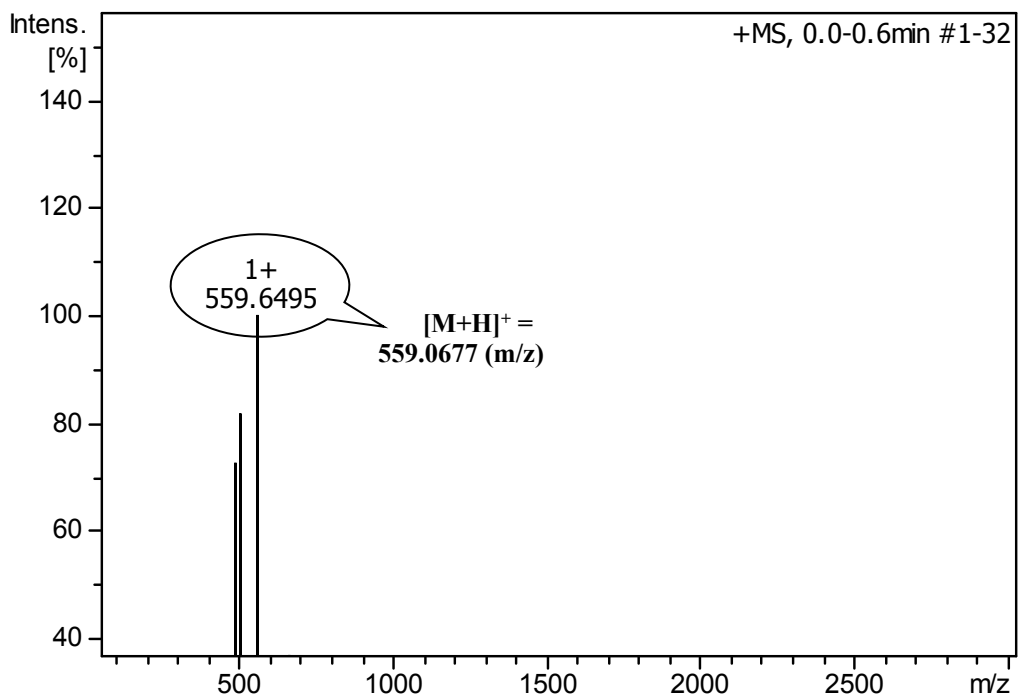


Fig. S1C ESI-MS spectrum of derivative **2**.

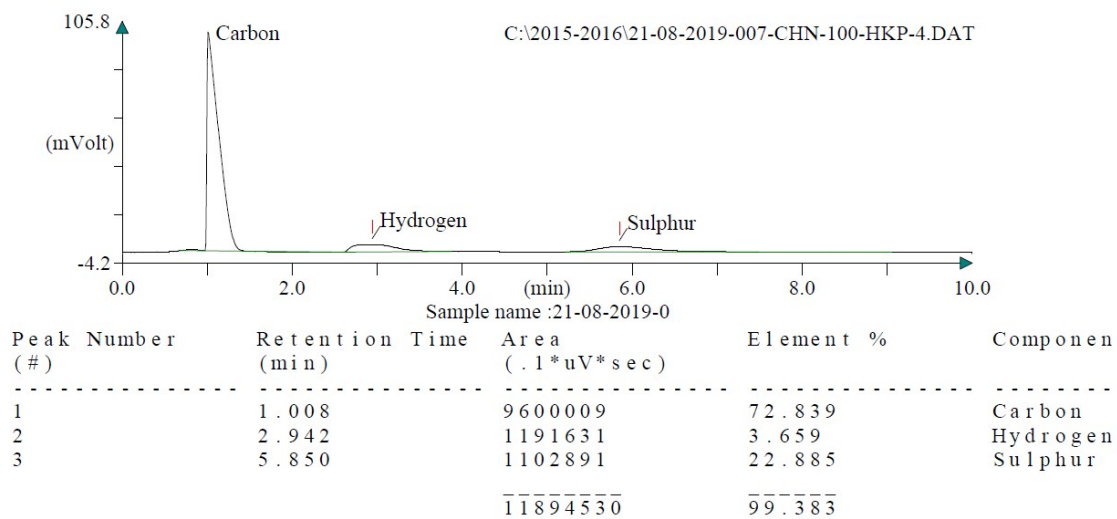


Fig. S1D Elemental Analysis of derivative **2**.

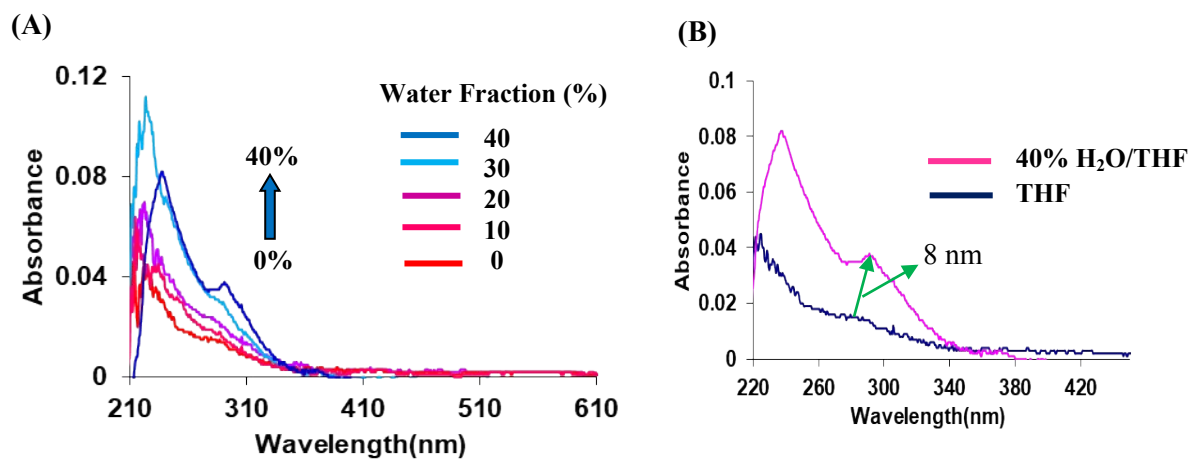


Fig. S2 UV-vis absorption spectra of derivative **2** ($5\mu\text{M}$) (A) showing variation in $\text{H}_2\text{O}/\text{THF}$ upto 40% water fraction indicating the AIEE behavior (B) showing bathochromic shift upon addition of water (40% water fraction) to THF solution of derivative **2**.

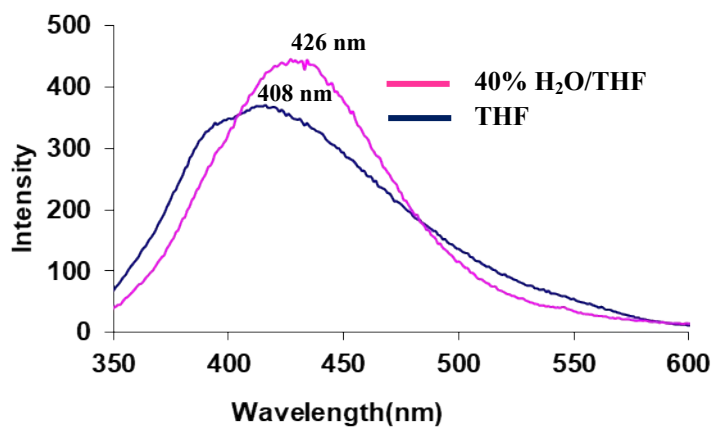


Fig. S3 Fluorescence spectra of derivative **2** ($5\mu\text{M}$) showing variation in $\text{H}_2\text{O}/\text{THF}$ upto 40% water fraction indicating the AIEE behaviour and showing bathochromic shift upon addition of water (40% water fraction) to THF solution of derivative **2**.

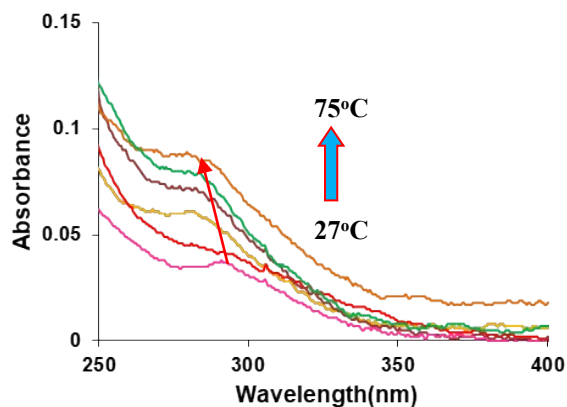


Fig. S4 UV-vis spectra of derivative **2** in H₂O/THF (4:6; v/v) mixture upon increasing temperature from room temperature to 75 °C, indicating the formation of *J*-aggregates.

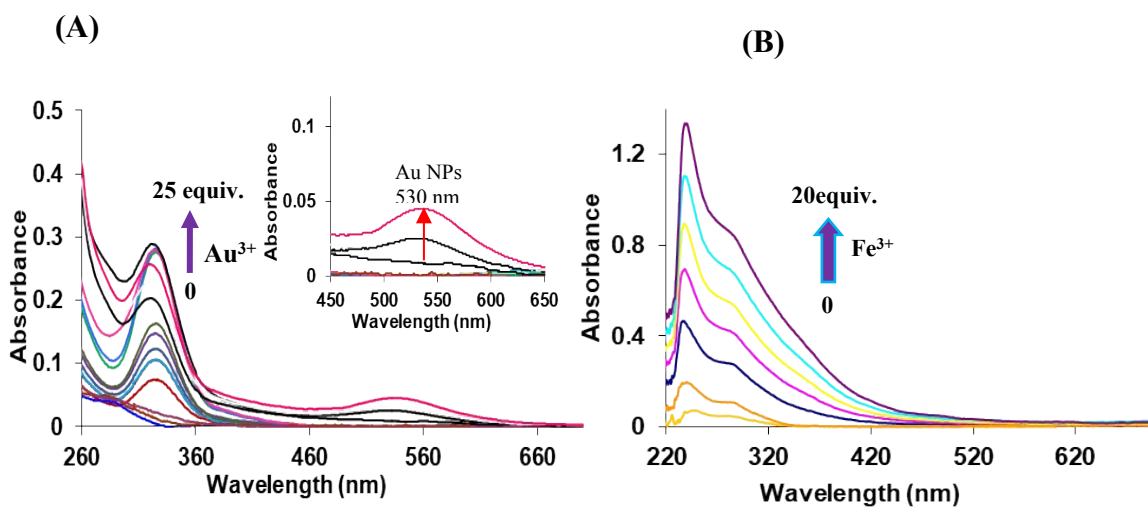


Fig. S5 UV-vis spectra of derivative **2** (5 μM) upon addition of (A) Au³⁺ ions (0-25 equiv.), indicate the formation of Au NPs. (B) Fe³⁺ ions (20 equiv.) indicate the interaction between Fe³⁺ ions and derivative **2**.

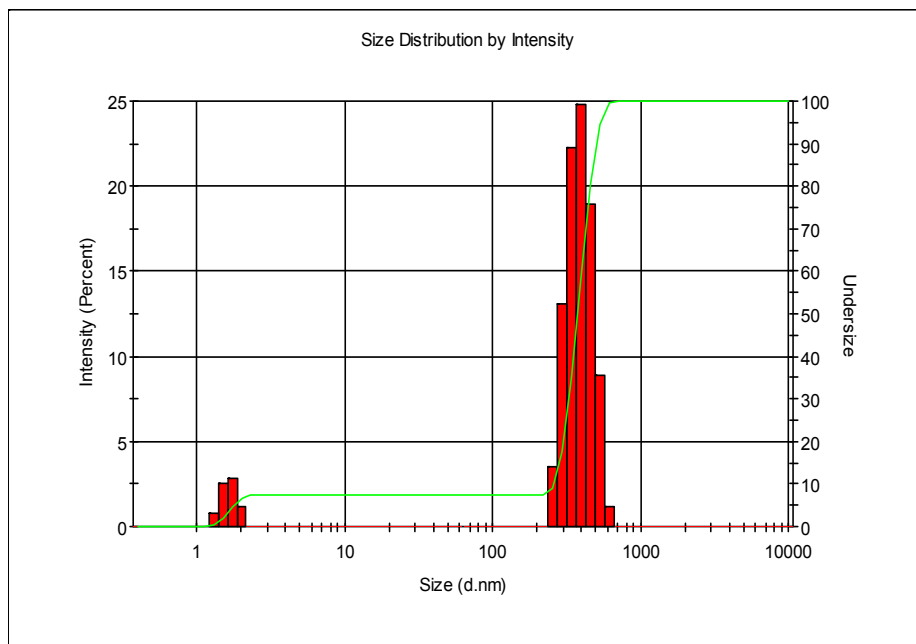


Fig. S6 DLS studies of **HP-T@Au-Fe₃O₄** nanohybrid material indicated the presence of particles having size in the range of 1.5-2.0 nm.

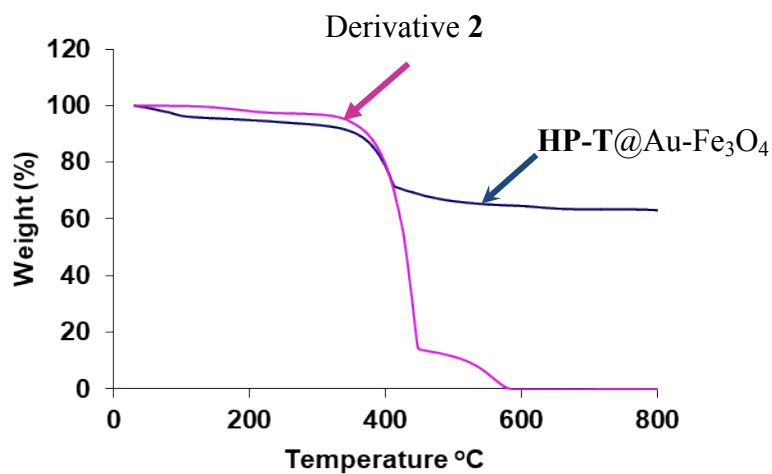


Fig. S7 Thermogravimetric analysis (TGA) of derivative **2** and supramolecular ensemble **HP-T@Au-Fe₃O₄**.

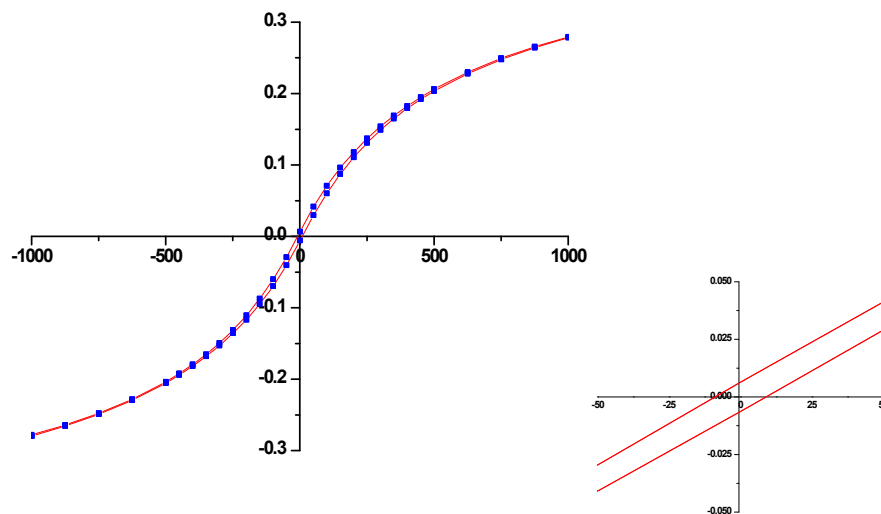


Fig. S8 Hysteresis loop of **HP-T@Au-Fe₃O₄** nanohybrid material at room temperature. Inset showing expanded curve.

Table S3. Showing the coercivity, magnetization values obtained from Hysteresis loop of polymer capsulated Au-Fe₃O₄ nanohybrid material at room temperature; 25°C.

Parameter	Value	Parameter definition
H _c (Oe)	8.760	Coercive Field: Field at which M/H changes sign
M _r (emu g ⁻¹)	0.339	Remanent Magnetization: M at H=0
M _s (emu g ⁻¹)	27.65	Saturation Magnetization: maximum M measured
S	0.0122	Squareness = M _r /M _s

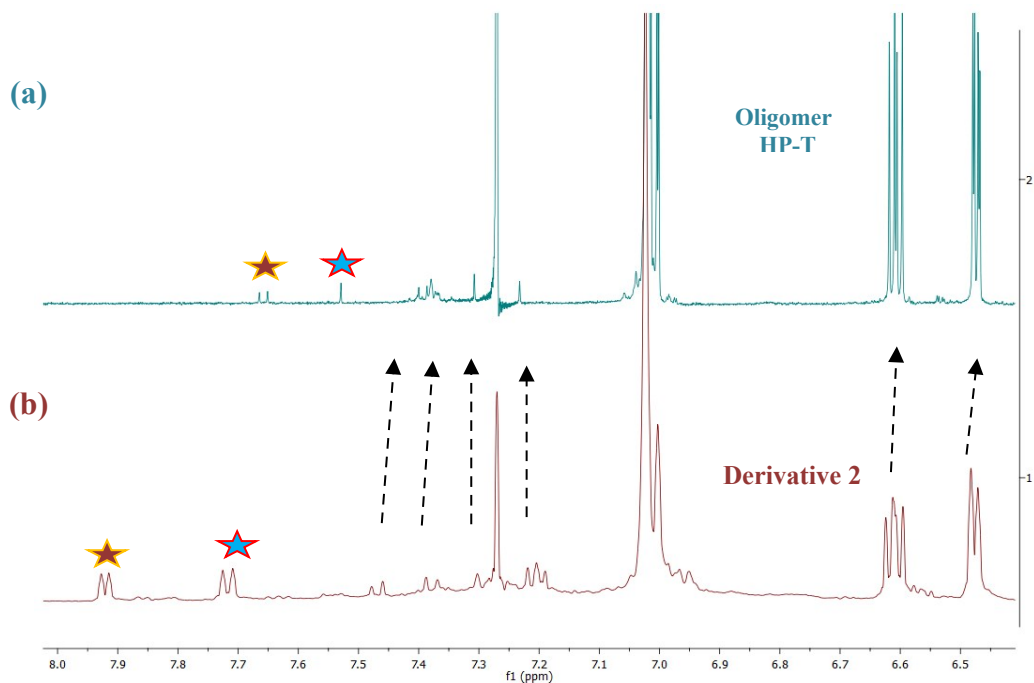


Fig. S9 Overlay ^1H NMR spectra of (a) **HP-T** after reaction of derivative **2** with AuCl_3 and FeCl_3 in CDCl_3 and (b) derivative **2**

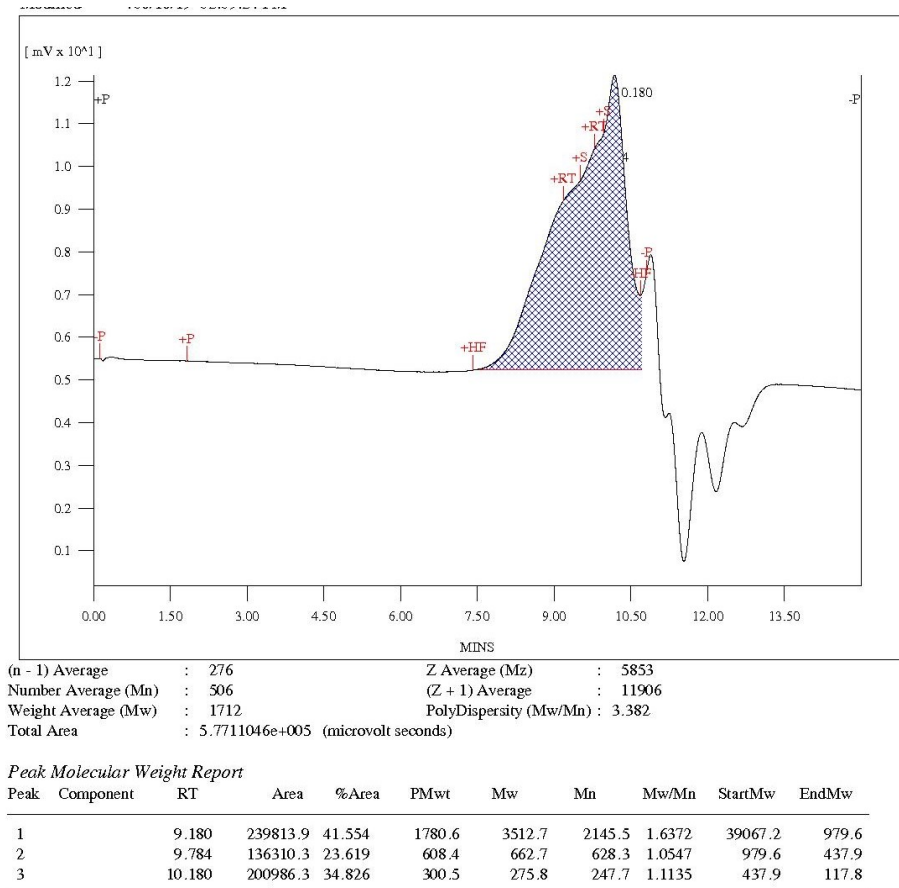


Fig. S10 GPC Chromatogram of oligomeric species **HP-T**.

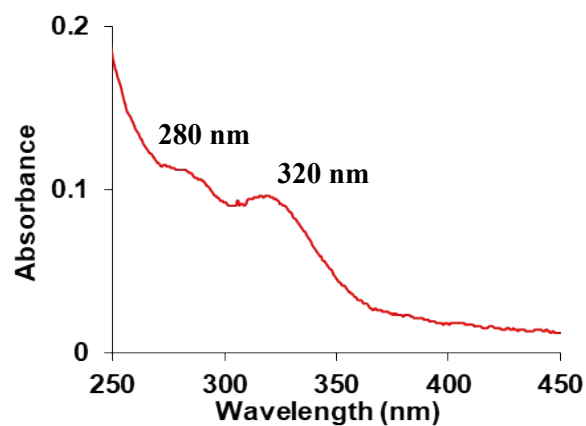


Fig. S11 UV-vis spectra of **HP-T** (5 μ M) in H_2O/THF (4:6, v/v) mixture.

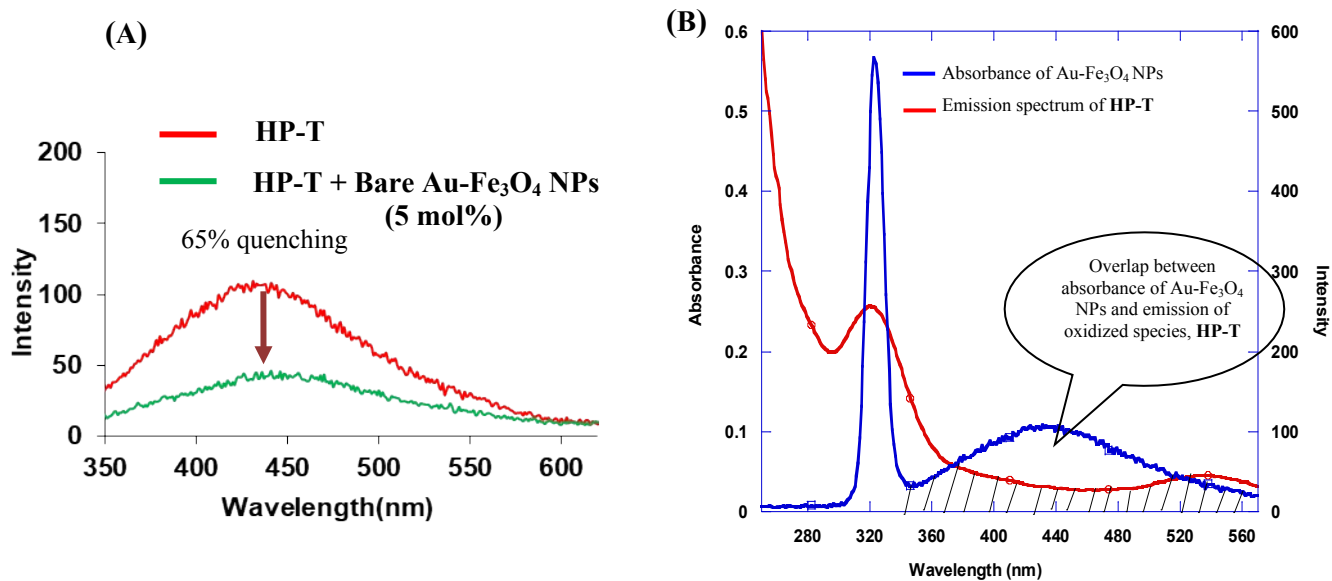


Fig. S12 (A) Fluorescence spectra of oxidized species, **HP-T**, in H_2O/THF (4:6) upon addition of bare $Au-Fe_3O_4$ nanoparticles, $\lambda_{ex}=290$ nm. (B) Spectral overlap of absorption spectrum of $Au-Fe_3O_4$ NPs and fluorescence spectrum of **HP-T** in H_2O/THF (4:6) mixture showing energy transfer from **HP-T** to $Au-Fe_3O_4$ NPs.

Table S4. Kumada coupling between aryl chloride (1 mmol), *p*-tolylmagnesium bromide (4 mmol) catalysed by **HP-T@ Au-Fe₃O₄** nanohybrid material in different solvents.

Entry	Solvent	Yield/Time
1.	H ₂ O/THF	93/20 min.
2.	Dioxane	93/20 min.
3.	Toluene	80/45 min.

Table S5. Kumada Coupling between chlorobenzene **3a** (1 mmol), *p*-tolylmagnesium bromide **4** (4 mmol) using various amount of catalytic system.

Entry	HP-T@AuFe ₃ O ₄ (mmol)	Time	Yield (%)	TON ^a	TOF (h ⁻¹) ^a
1.	6 mmol	15 min	94%	522.22	2088.88
2.	5 mmol	20 min	93%	620	1878.78
3.	4 mmol	30 min	89%	741.66	1483.33
4.	2 mmol	1 h	84%	1400	1400
5.	1 mmol	3 h	78%	2600	866.66
6.	0.5 mmol	6 h	72%	4800	800

a) w.r.t Au³⁺ ions (mmol) in **HP-T@ Au-Fe₃O₄** nanohybrid material

i) Calculations of turnover number (TON) and turnover frequencies (TOF) of the catalyst.

$$\text{TON} = \frac{\text{no. of moles of product formed}}{\text{Moles of catalyst used}} \times \% \text{ yield of the product}$$

$$\text{TOF} = \text{TON} / \text{time of reaction}$$

ii) To calculate moles of Au NPs and Fe₃O₄ NPs in **HP-T@** Au-Fe₃O₄ nanohybrid material (5 mmol).

$$0.005 \text{ M} = \frac{\text{given weight (X)}}{\text{Molecular weight of Au/Fe}_3\text{O}_4 \text{ NPs}}$$

1 mol of AuCl₃ used to form 1 mol of Au NPs in nanohybrid material

196.966 g of Au NPs required = 303.33 g of AuCl₃

$$(X) \text{ g of Au NPs required} = \frac{196.966}{303.33} \times (X) \text{ g of AuCl}_3$$

3 mol of FeCl₃ used to form 1 mol of Fe₃O₄ NPs in nanohybrid material

231.495 g of Fe₃O₄ NPs required = 3 x 162.20 g of FeCl₃

$$(X) \text{ g of Fe}_3\text{O}_4 \text{ NPs required} = \frac{3 \times 162.20}{231.495} \times (X) \text{ g of FeCl}_3$$

Table S6. ICP-MS studies of **HP-T@** Au-Fe₃O₄ nanohybrid material.

Sample	Au	Fe	Pd
	ppb	ppb	ppb
H2	3841.49	1071.72	ND

ND MEANS LESS THAN 1 PPT

Table S7. ICP-MS studies of whole reaction mixture (including **HP-T@** Au-Fe₃O₄ nanohybrid material, chlorobenzene and *p*-tolymagnesium bromide) and reaction mixture (including chlorobenzene and *p*-tolymagnesium bromide

Sample Code	Pd
	PPB
R-N	ND
R-Mx	ND

ND MEANS LESS THAN 1 PPT

[5a]¹. [4-methyl-1,1'-biphenyl]: (Colorless solid, 93% yield). ¹H NMR (500 MHz, CDCl₃, ppm) δ = 7.57 (d, J = 10 Hz, 2H), 7.49 (d, J = 10 Hz, 2H), 7.41 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.25 (d, J = 5 Hz, 2H), 2.39 (s, 3H).

[5b]². [4,4'-dimethyl-1,1'-biphenyl]: (Colorless solid, 90% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.47 (d, J = 8 Hz, 4H), 7.23 (d, J = 8 Hz, 4H), 2.38 (s, 6H).

[5c]¹. [4-methoxy-4'-methyl-1,1'-biphenyl]: (Colorless solid, 94% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.48 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 6.60 (d, J = 8 Hz, 2H), 3.69 (s, 3H), 2.31 (s, 3H).

[5d]³. [3,4'-dimethyl-1,1'-biphenyl]: (Colorless oil, 85% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.66 (dd, J = 8 Hz, 1H), 7.50 (dd, J = 8 Hz and 4 Hz, 2H), 7.44 (d, J = 8 Hz, 2H), 7.10 (d, J = 4 Hz, 2H), 6.95 (t, J = 8 Hz, 1H), 2.26 (s, 6H).

[5e]⁴. [2-(p-tolyl)thiophene]: (Colorless solid, 84% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 7.48-7.46 (m, 1H), 7.37-7.30 (m, 4H), 7.10-6.99 (m, 2H), 2.35 (s, 3H).

[5f]⁵. [2-(p-tolyl)naphthalene]: (Colorless oil, 87% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.01 (d, J = 8 Hz, 1H), 7.87-7.80 (m, 2H), 7.71 (t, J = 8 Hz, 2H), 7.60 (d, J = 8 Hz, 2H), 7.47-7.44 (m, 2H), 7.37-7.25 (m, 2H), 2.39 (s, 3H).

[5g]⁶. [4-methyl-4'-nitro-1,1'-biphenyl]: (Colorless solid, 70% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.23 (d, J = 8 Hz, 2H), 7.66 (d, J = 12 Hz, 2H), 7.57 (d, J = 8 Hz, 2H), 7.41 (d, J = 4 Hz, 2H), 2.62 (s, 3H).

[5h]. [2-cyclohexylnaphthalene]: (Colorless oil, 81% yield). ¹H NMR (400 MHz, CDCl₃, ppm) δ = 8.02 (d, J = 8 Hz, 1H), 7.88 (m, 4H), 7.73-7.60 (m, 2H), 7.48-7.44 (m, 2H), 7.37-7.26 (m, 2H), 1.30-1.26 (m, 5H), 0.87-0.83 (m, 6H).

[8a]. [methyl cinnamate]: (Colorless solid, 82% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.63$ (d, $J = 16$ Hz, 1H), 7.42-6.88 (m, 5H), 6.38 (d, $J = 16$ Hz, 1H), 3.71(s, 3H).

[8b]. [methyl (E)-3-(p-tolyl)acrylate]: (Colorless solid, 80% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.67$ (d, $J = 16$ Hz, 1H), 7.42 (d, $J = 8$ Hz, 2H), 7.19 (d, $J = 8$ Hz, 2H), 6.40 (d, $J = 16$ Hz, 1H), 3.80(s, 3H), 2.37(s, 3H).

[8c]. [methyl (E)-3-(4-methoxyphenyl)acrylate]: (White solid, 79% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.65$ (d, $J = 16$ Hz, 1H), 7.48 (d, $J = 8$ Hz, 2H), 6.91 (d, $J = 12$ Hz, 2H), 6.32 (d, $J = 16$ Hz, 1H), 3.84(s, 3H), 3.80(s, 3H).

[8d]. [methyl (E)-3-(m-tolyl)acrylate]: (Colorless solid, 75% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.67$ (d, $J = 16$ Hz, 1H), 7.33 (d, $J = 4$ Hz, 2H), 7.29-7.25 (m, 1H), 7.20 (d, $J = 4$ Hz, 1H), 6.43 (d, $J = 16$ Hz, 1H), 3.80(s, 3H), 2.37 (s, 3H).

[8e]. [methyl (E)-3-(2,6-dimethylphenyl)acrylate]: (Colorless solid, 72% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.83$ (d, $J = 16$ Hz, 1H), 7.08 (t, $J = 12$ Hz, 1H), 6.06 (d, $J = 16$ Hz, 1H), 3.79(s, 3H), 2.42 (s, 3H), 2.32 (s, 3H).

[8f]. [ethyl (E)-3-(4-nitrophenyl)acrylate]: (Yellow solid, 78% yield). ^1H NMR (500 MHz, CDCl_3 , ppm) $\delta = 8.37$ (d, $J = 8$ Hz, 1H), 8.25 (d, $J = 8$ Hz, 2H), 7.68 (d, $J = 4$ Hz, 2H), 6.57 (d, $J = 12$ Hz, 1H), 4.30 (q, $J = 7.5$ Hz, 2H), 1.36 (t, $J = 7.5$ Hz, 3H).

[8g]. [butyl (E)-3-(m-tolyl)acrylate]: (Colorless solid, 77% yield). ^1H NMR (400 MHz, CDCl_3 , ppm) $\delta = 7.64$ (d, $J = 16$ Hz, 1H), 7.30 (d, $J = 8$ Hz, 2H), 7.25-7.22 (m, 1H), 7.16 (d, $J = 8$ Hz, 1H), 6.42 (d, $J = 16$ Hz, 1H), 4.19 (t, $J = 6$ Hz, 2H), 2.34 (s, 3H), 1.71-1.64 (m, 2H), 1.47-1.40 (m, 2H), 0.95 (t, $J = 6$ Hz, 3H).

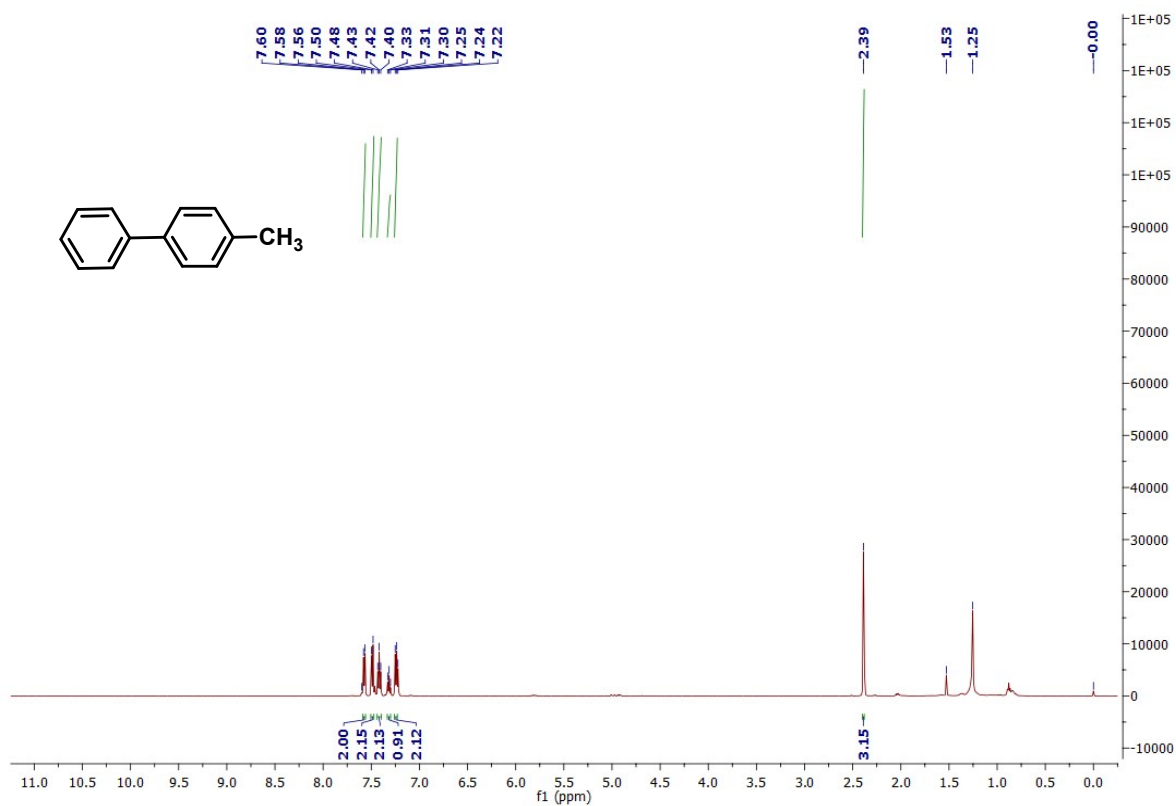


Fig. S15 $^1\text{H-NMR}$ spectra (CDCl_3 , 500MHz, ppm) of compound 5a.

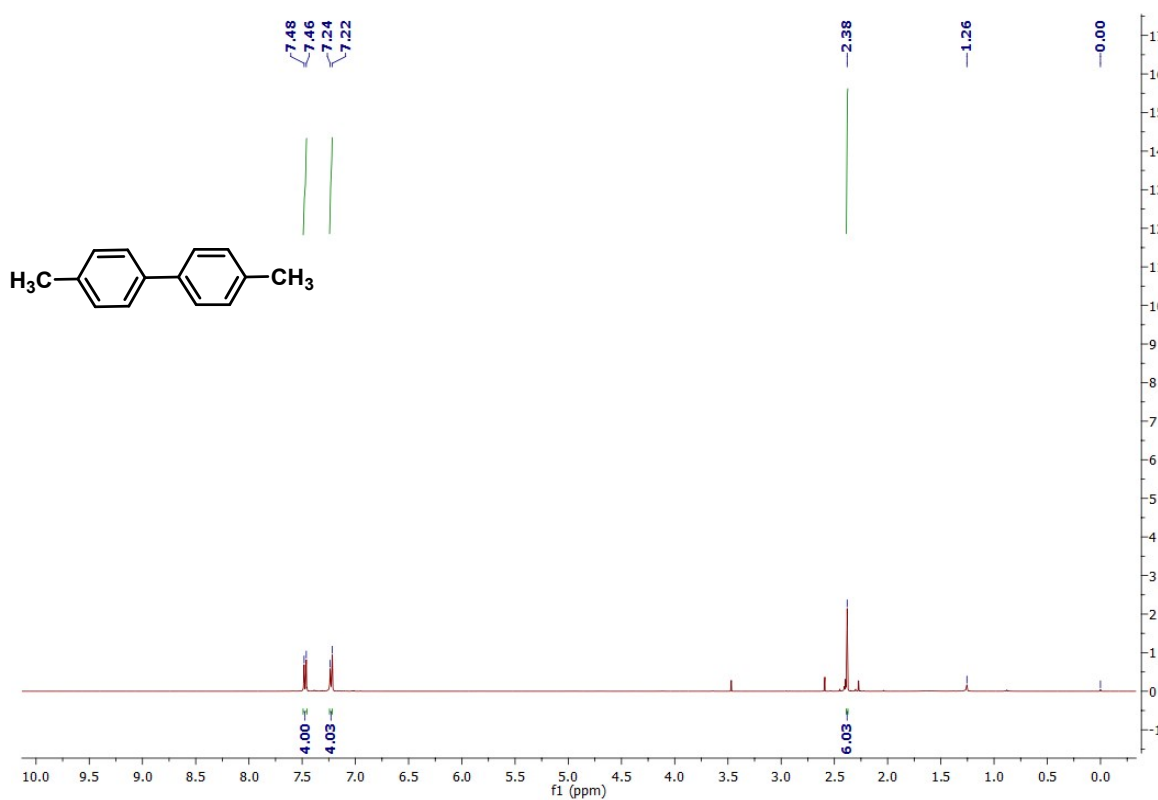


Fig. S16 $^1\text{H-NMR}$ spectra (CDCl_3 , 400MHz, ppm) of compound 5b.

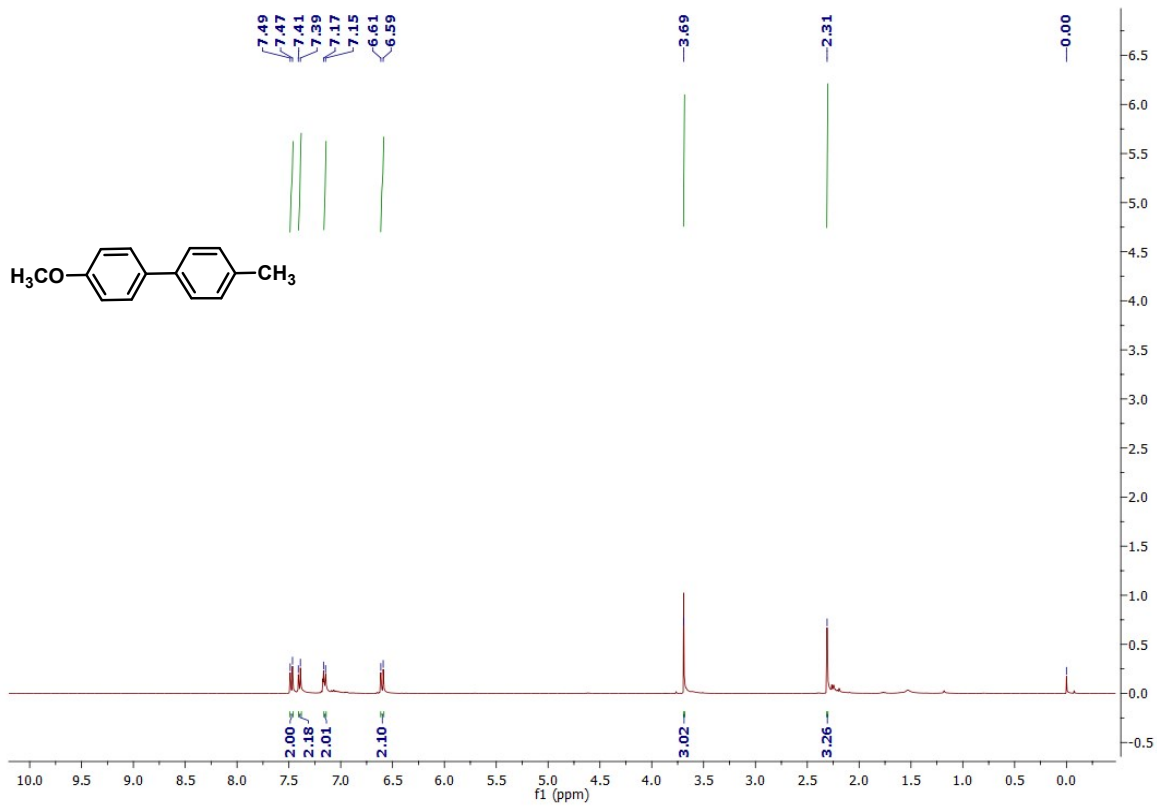


Fig. S17 $^1\text{H-NMR}$ spectra (CDCl_3 , 400MHz, ppm) of compound 5c.

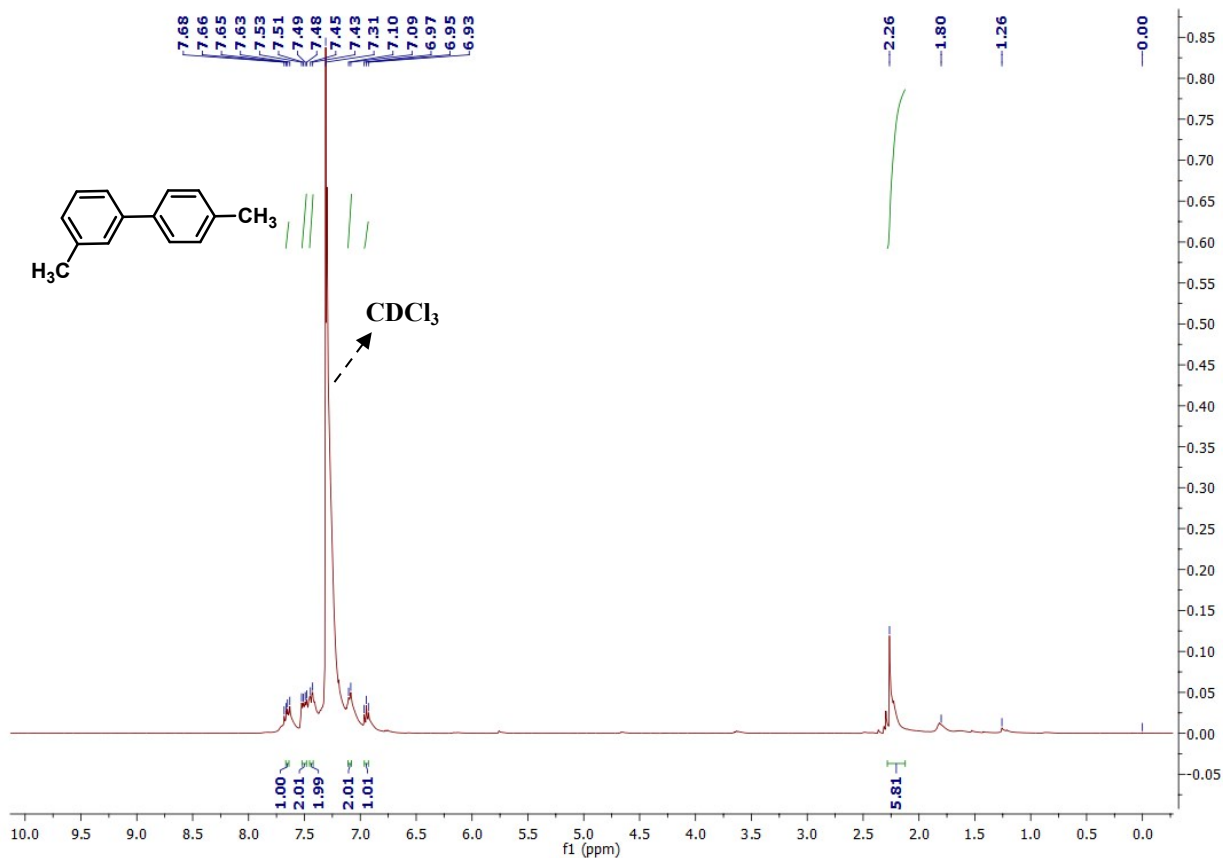


Fig. S18 $^1\text{H-NMR}$ spectra (CDCl_3 , 400MHz, ppm) of compound 5d.

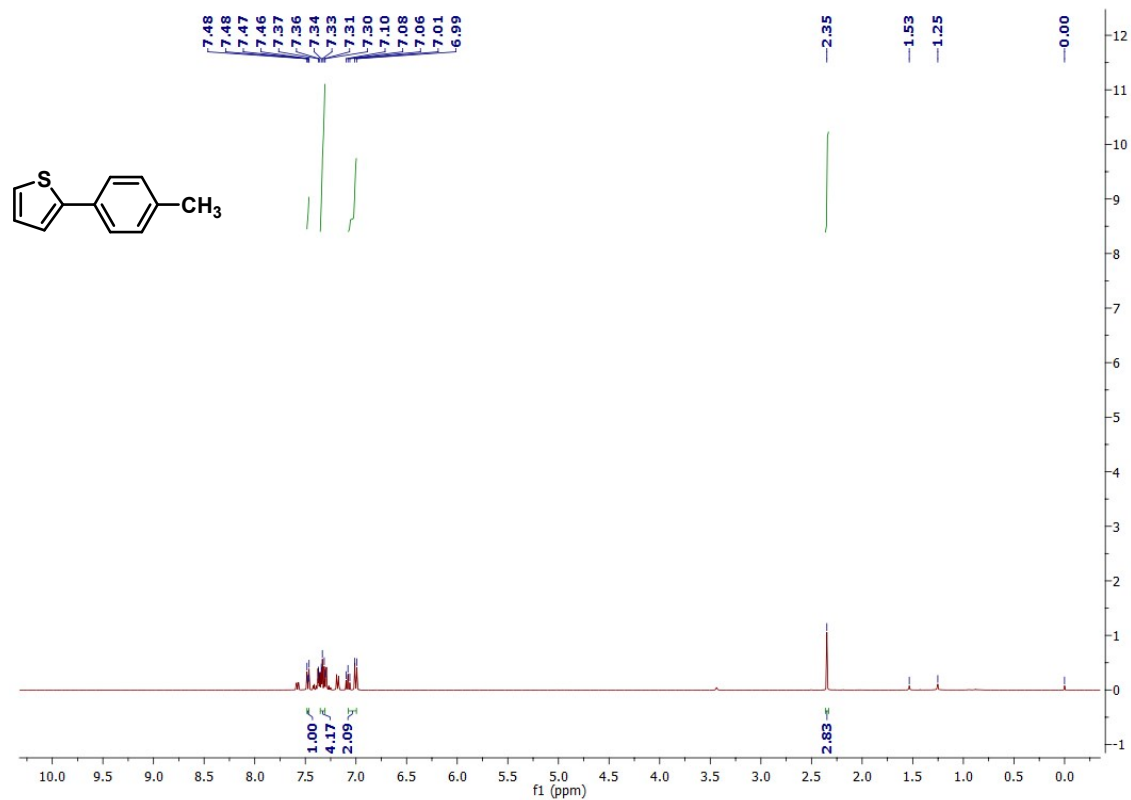


Fig. S19 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 5e.

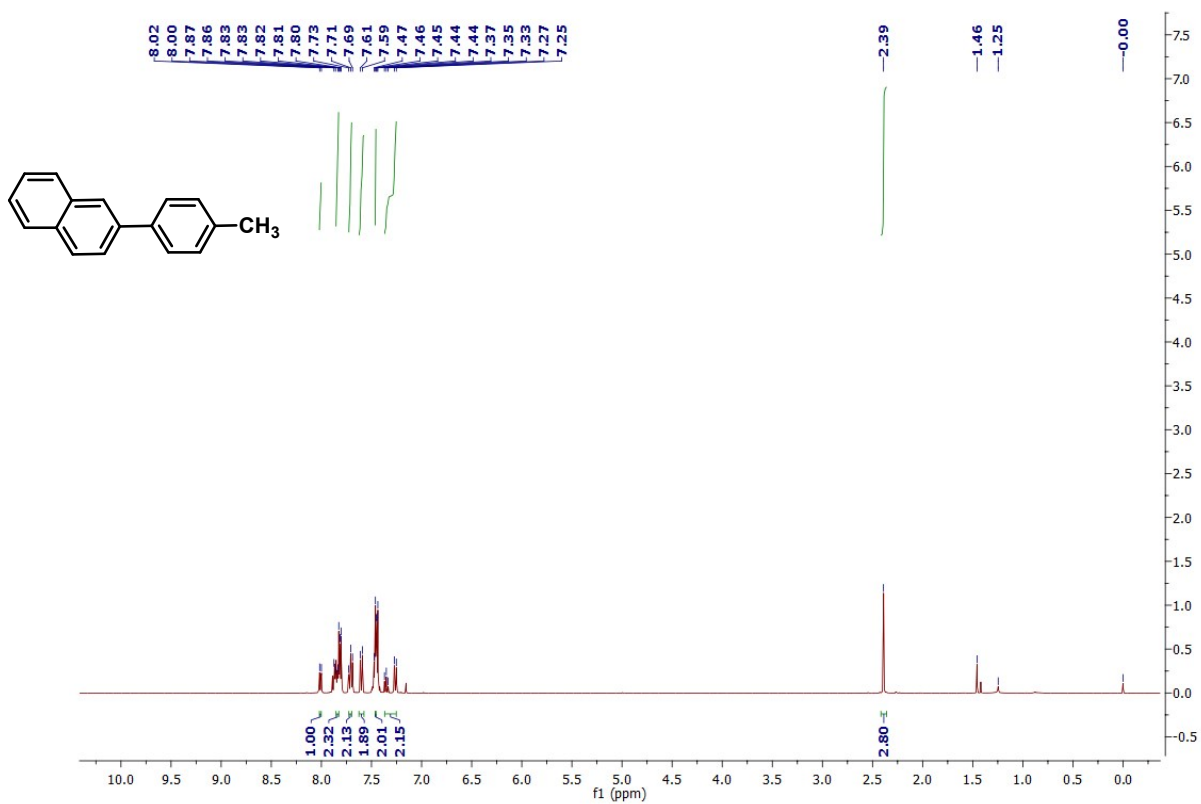


Fig. S20 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 5f.

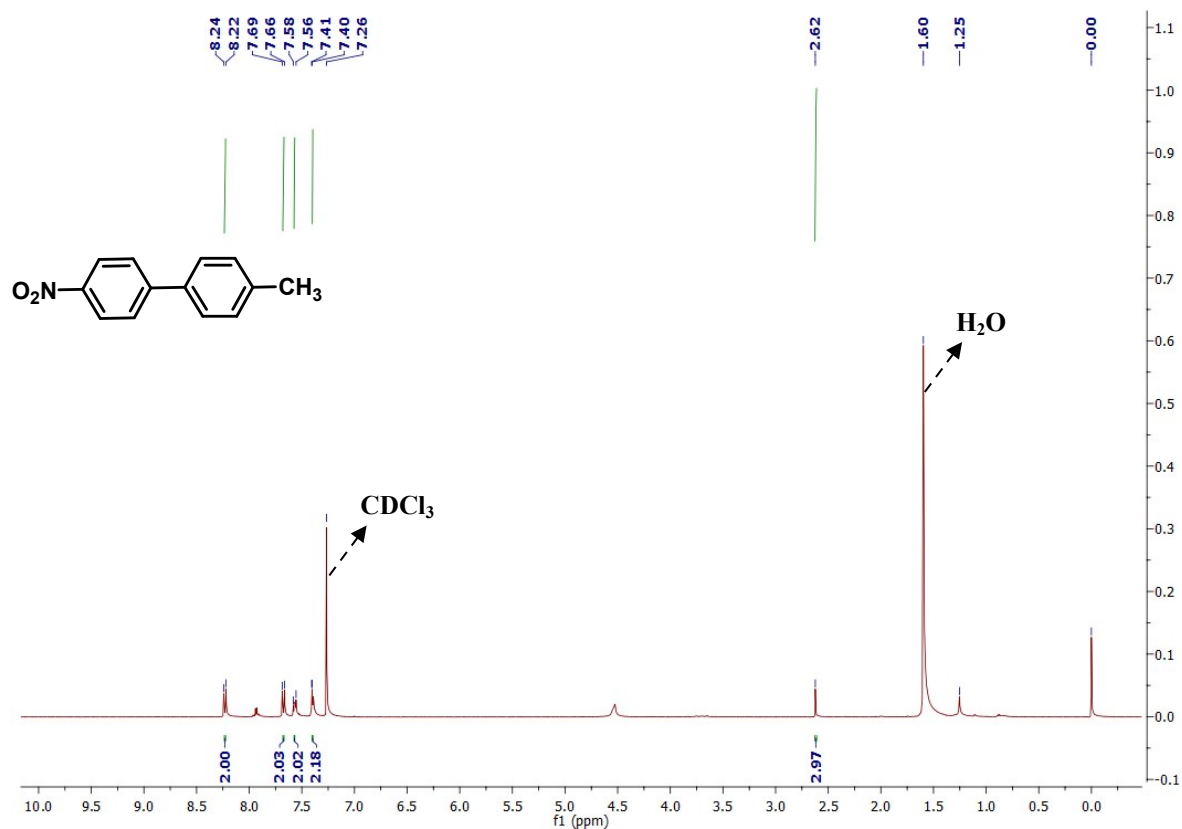


Fig. S21 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 5g.

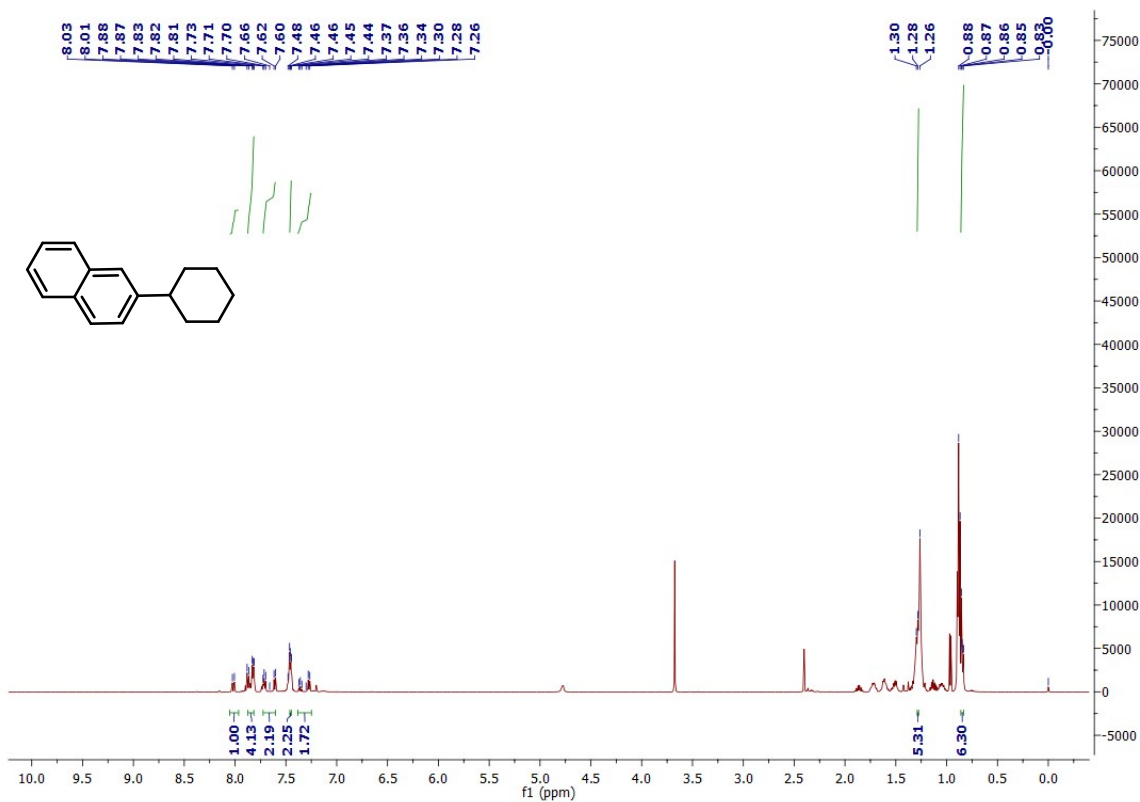


Fig. S22 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 5h.

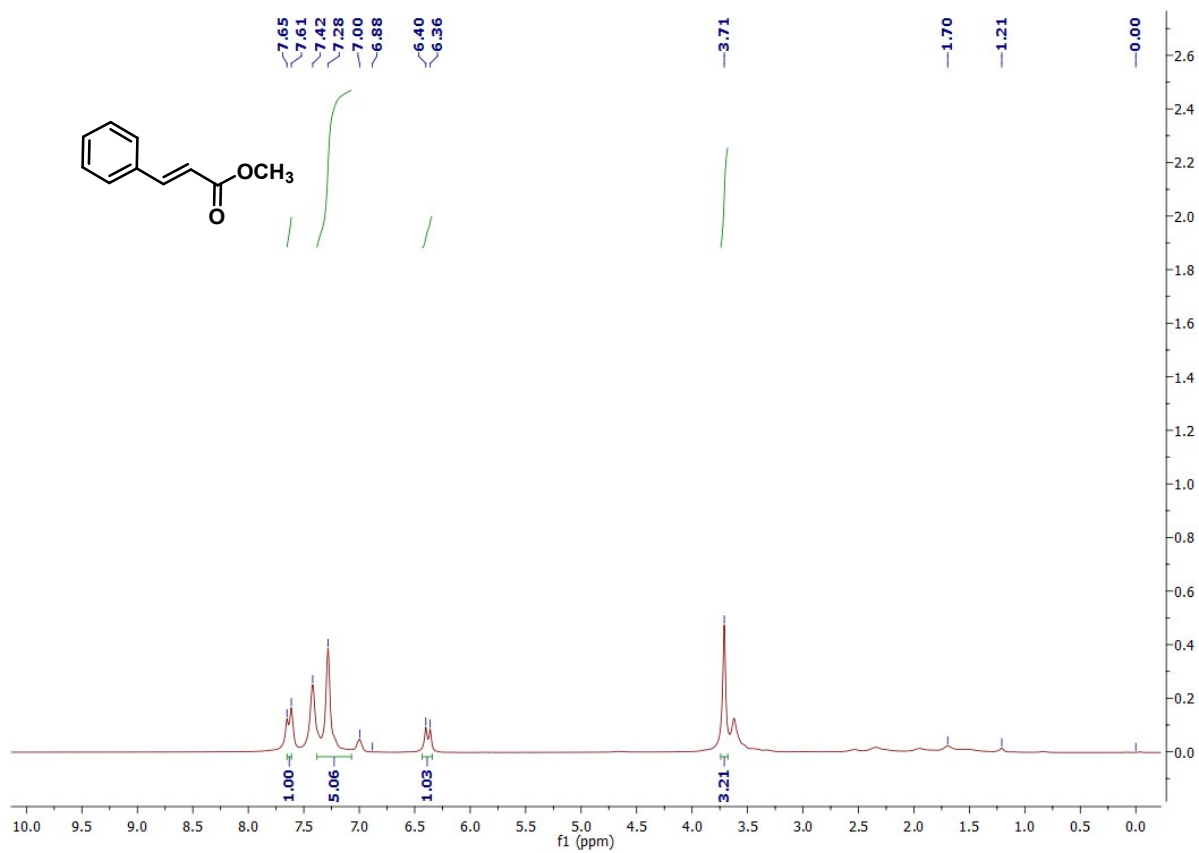


Fig. S23 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8a.

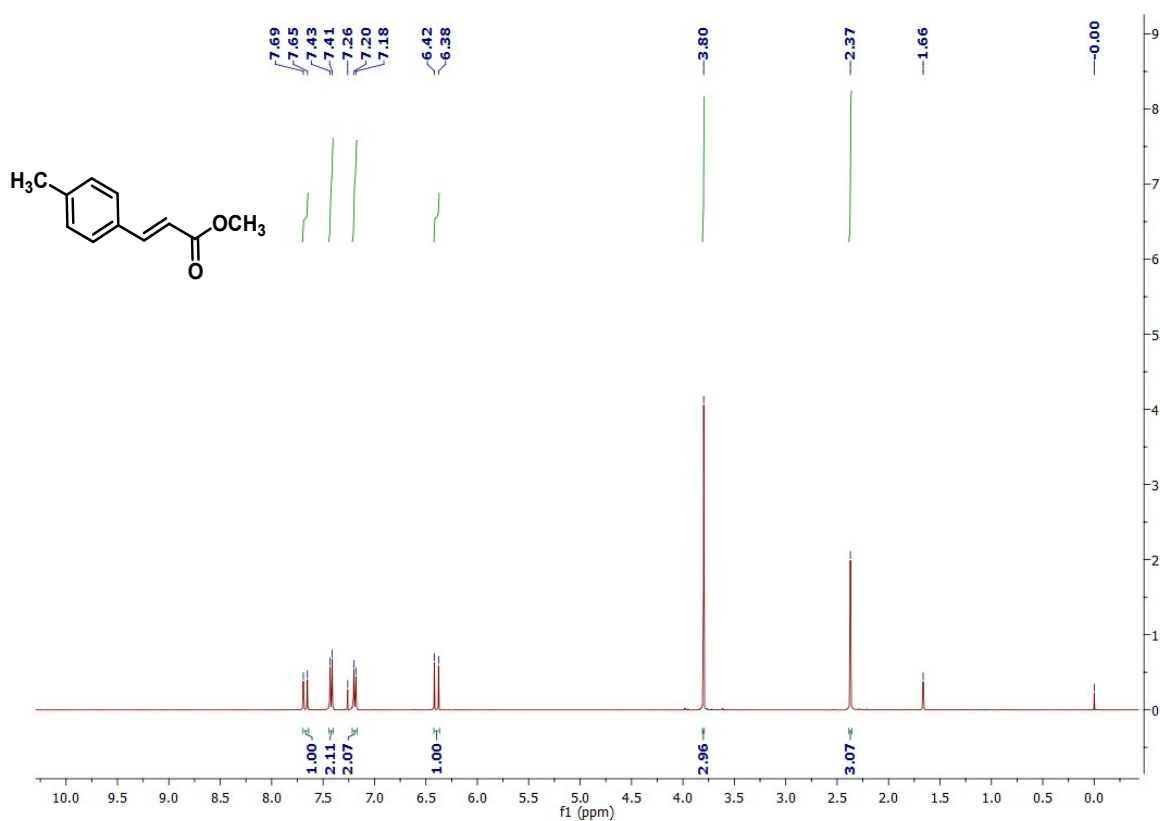


Fig. S24 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8b.

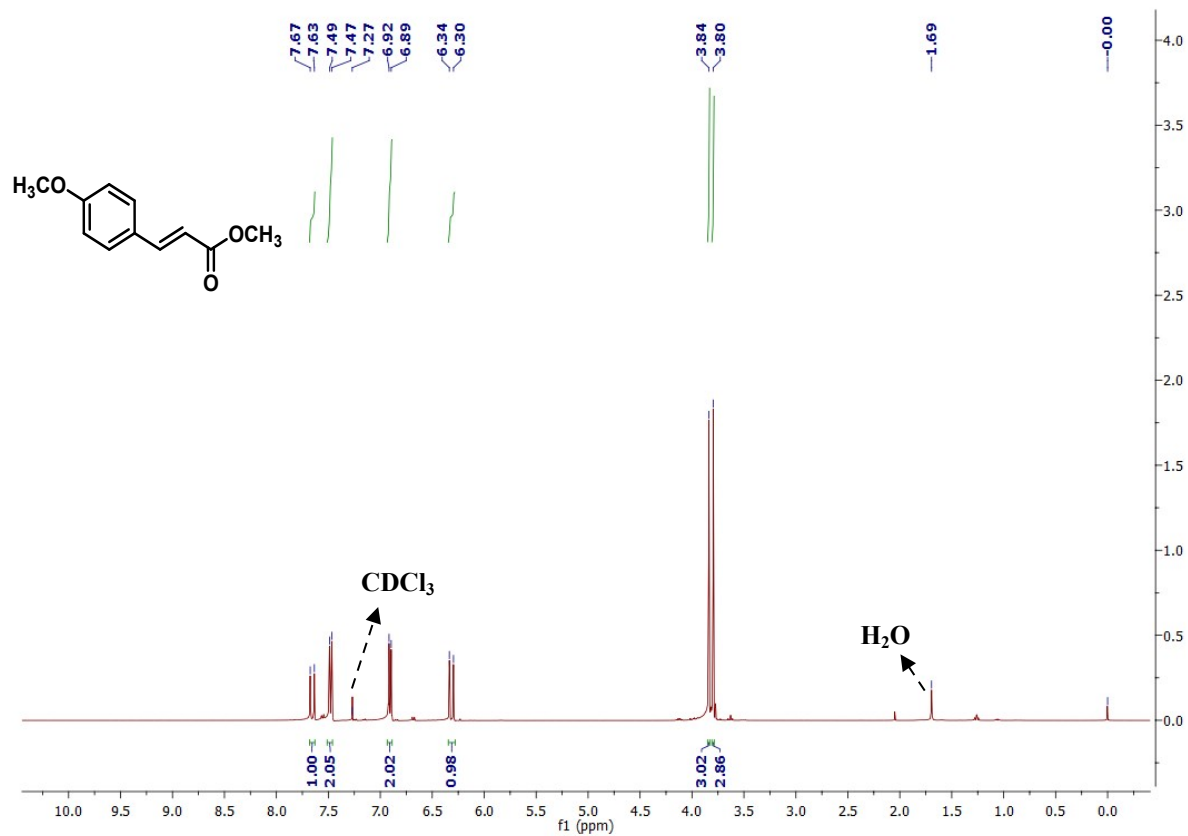


Fig. S25 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8c.

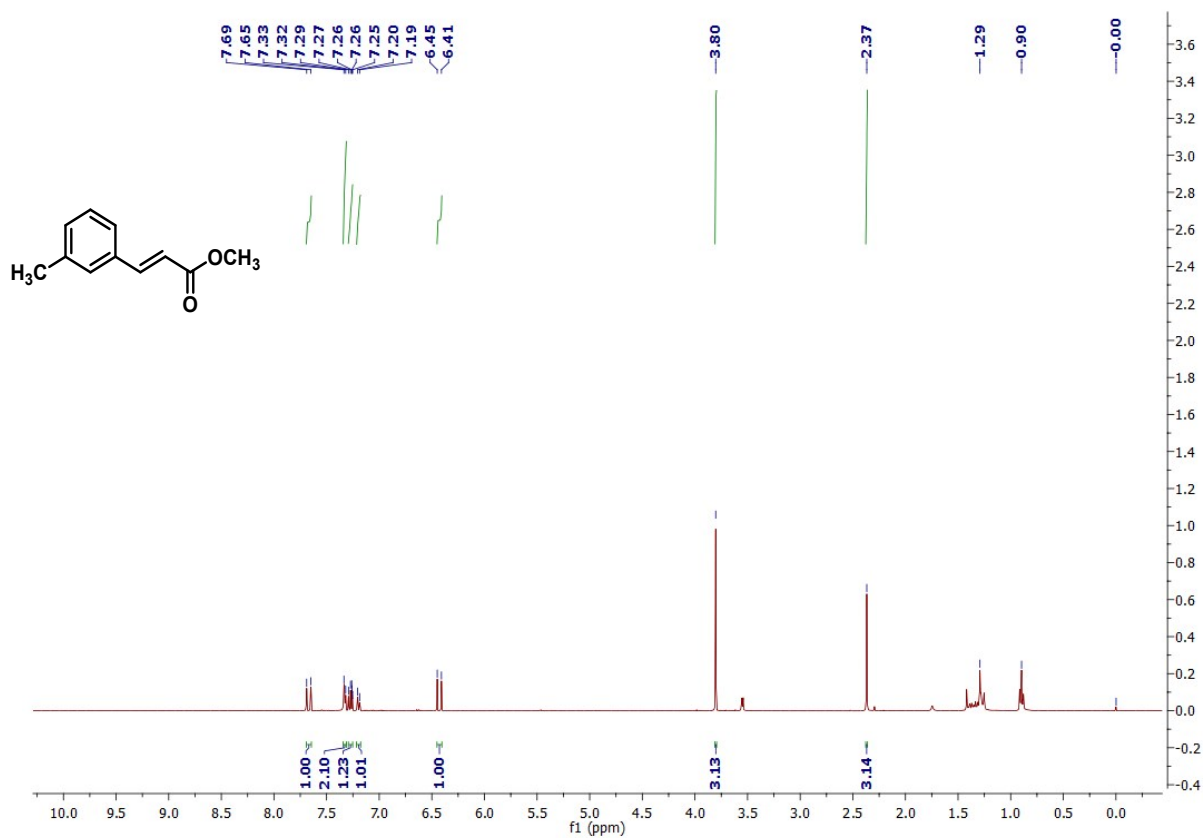


Fig. S26 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8d.

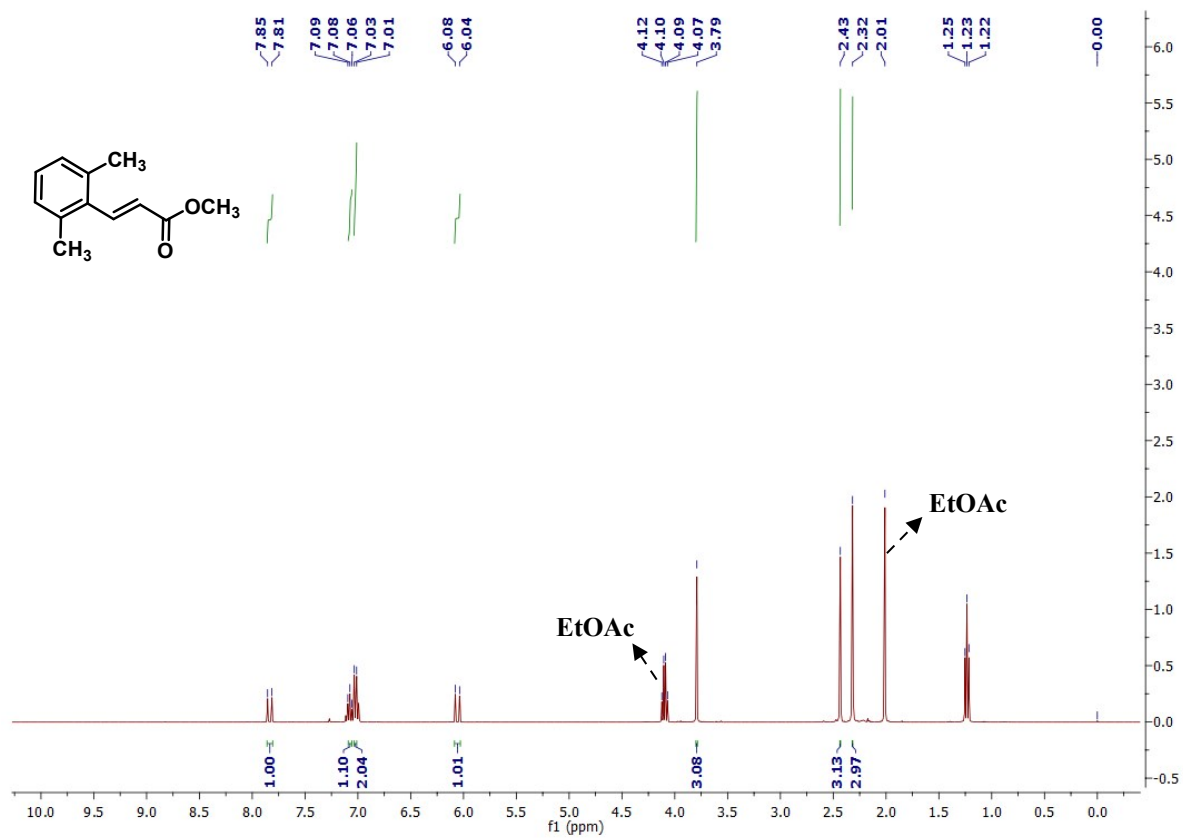


Fig. S27 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8e.

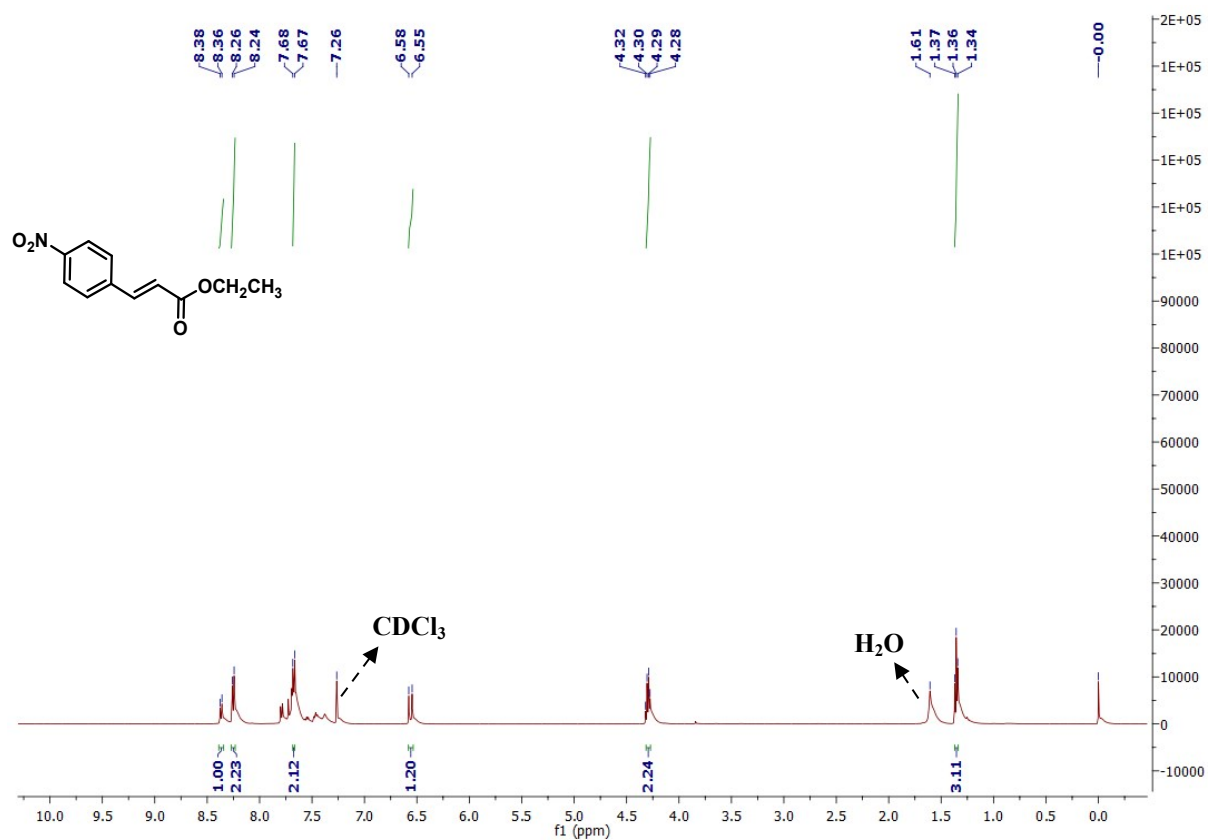


Fig. S28 ¹H-NMR spectra (CDCl₃, 500MHz, ppm) of compound 8f.

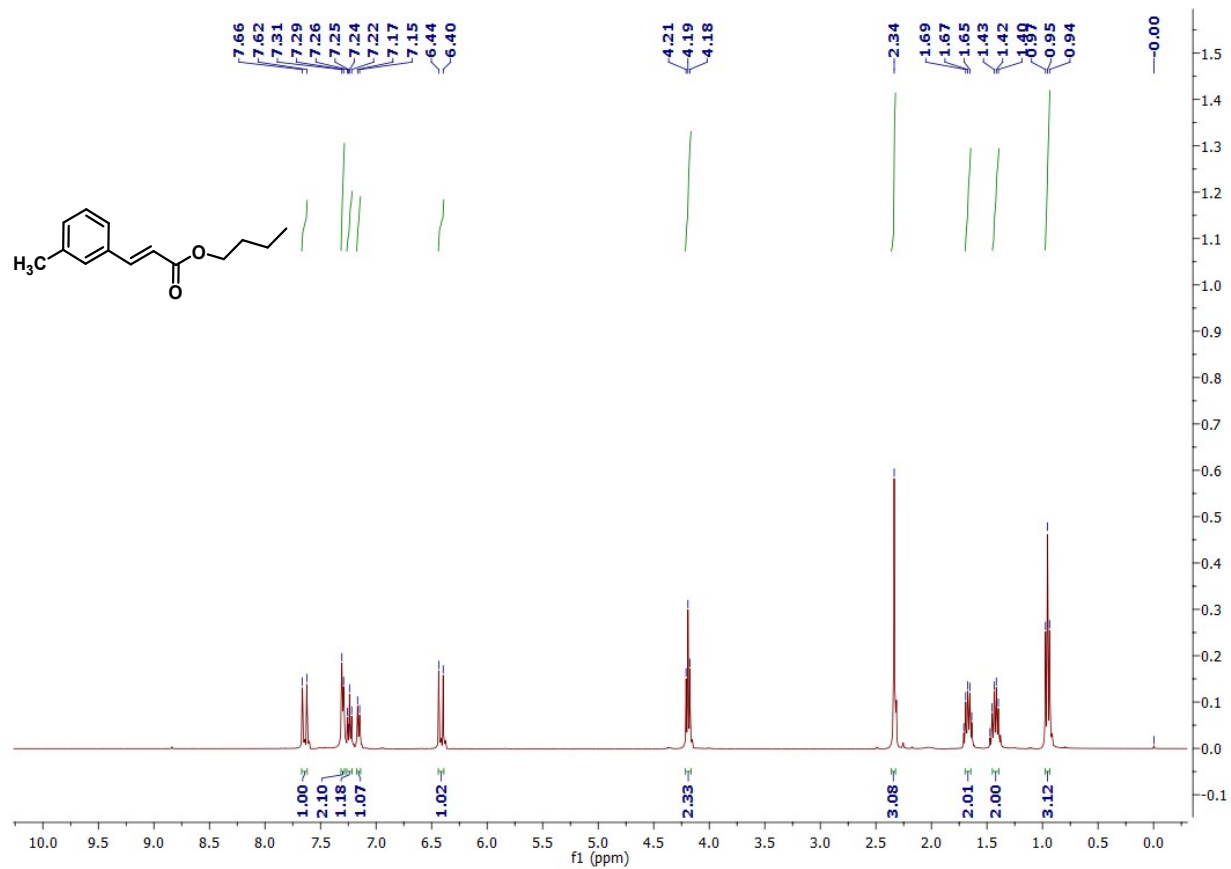


Fig. S29 ¹H-NMR spectra (CDCl₃, 400MHz, ppm) of compound 8g.

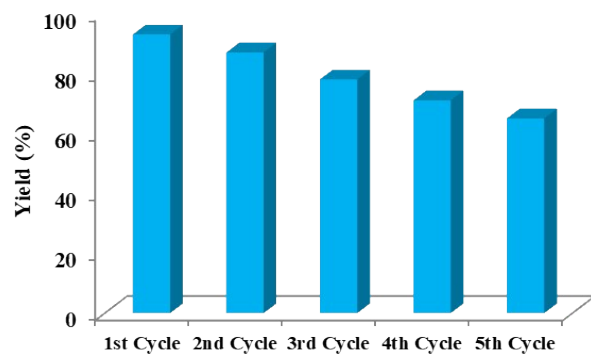


Fig. S30 Recyclability of **HP-T@Au-Fe₃O₄** catalytic system for Kumada coupling reaction.

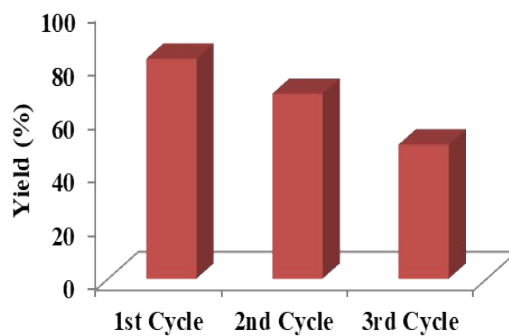


Fig. S31 Recyclability of **HP-T@Au-Fe₃O₄** catalytic system for Heck coupling reaction.

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