

Electronic Supporting Information for

**Synthesis of Polyoxometalate-Loaded MOF (POM@MOF) for Heterogeneous Catalysis
and Enhanced Dye Adsorption**

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S1 Materials

All the commercially available solvents and reagents used in this research were of analytical grade and were utilized without further purification. The chemicals employed included Benzene-1,2,4,5-tetracarboxylic acid (H₄BTA), Indium-(III) nitrate hydrate (In(NO₃)₃·H₂O), sodium molybdate dihydrate (Na₂MoO₄·2H₂O), tetrabutylammonium bromide, dimethylformamide (DMF), methanol (MeOH), ethyl acetate (EA), petroleum ether, *tert*-Butyl Hydroperoxide (TBHP), benzaldehyde, various amines, 2,5-hexadione, methylene blue (MB), NaOH, HCl, HNO₃, and rhodamine B (RHB). These chemicals were sourced from Sigma Aldrich (India), Finar, TCI, and Spectrochem.

S2 Characterization Methods

Nuclear Magnetic Resonance (NMR) Spectroscopy

- **Instrumentation:** ECS 400 MHz NMR spectrometer (JEOL).
- **Solvents and Standard:** Deuterated dimethyl sulfoxide (DMSO-d₆) and deuterated chloroform (CDCl₃) were used as solvents. Tetramethylsilane (TMS) served as the external standard.
- **Chemical Shifts:** Reported in parts per million (ppm).

Fourier Transform Infrared (FT-IR) Spectroscopy

- **Instrumentation:** SHIMADZU IR Affinity-1.
- **Data Collection:** 45 scans were performed at a resolution of 4 cm⁻¹.

Powder X-ray Diffraction (XRD)

- **Instrumentation:** Panalytical X'Pert Pro X-ray Diffractometer.
- **Data Analysis:** Conducted using the Reflex module of Materials Studio V6.0 software.

Thermogravimetric Analysis (TGA)

- **Instrumentation:** Thermogravimetric Differential Thermal Analyzer (TGA-DTA) TA Module Q 600.
- **Conditions:** Analyses were performed under nitrogen gas flow (20 ml/min, purge and protective). Samples were heated from room temperature (RT) to 800°C at a rate of 10°C per minute.

Surface Area and Porosimetry (BET Analysis)

- **Instrumentation:** Nova Touch LX₂ gas sorption analyzer from Quantachrome.

- **Sample Preparation:** 20-100 mg of sample.
- **Analysis Conditions:** Nitrogen adsorption isotherms were measured at 77 K in a liquid nitrogen bath, with exposures to ultrahigh-purity N₂ up to approximately 1 atm.

Field Emission Scanning Electron Microscopy (FE-SEM)

- **Instrumentation:** Nova Nano FE-SEM 450 (FEI).
- **Sample Preparation:** Samples were sputter-coated with platinum for 100 seconds before observation.

X-ray Photoelectron Spectroscopy (XPS)

- **Instrumentation:** ThermoScientific NEXA Surface Analyzer.
- **Sample Preparation:** 10 mg of solid sample was used for analysis.

These techniques collectively provide comprehensive structural, thermal, and surface characterization of the materials studied.

S3 Experimental Section

S3.1 Synthesis of tetrabutylammonium octamolybdate(VI) [(*n*-C₄H₉)₄N]₄[Mo₈O₆]

Tetrabutylammonium octamolybdate is synthesised using reported method, In a 50-mL Erlenmeyer flask, a solution of 5.00 g (20.7 mmol) of commercially available sodium molybdate dihydrate (Na₂MoO₄·2H₂O) in 12 mL of water is acidified by adding 5.17 mL of 6.0 N aqueous HCl (31.0 mmol) with vigorous stirring. This acidification is performed over 1 to 2 minutes at room temperature. Next, a solution of 3.34 g (10.4 mmol) of commercially available tetrabutylammonium bromide is added to the flask, also with vigorous stirring. Immediate formation of a white precipitate is observed. The mixture is stirred for 10 minutes, and then the precipitate is collected on a medium-porosity filter using suction. The collected precipitate is washed sequentially with 20 mL of water, 20 mL of ethanol, 20 mL of acetone, and 20 mL of diethyl ether. The resulting crude product weighs 4.78 g. The crude product is dissolved in 35 mL of acetonitrile and stored at -10 °C for 24 hours. Clear, colourless, block-shaped crystals form during this time. These crystals are collected by suction filtration and dried under vacuum (0.1 torr) for 12 hours. The crystals lose their transparency upon drying. The yield of the final product is 3.58 g (1.66 mmol), which corresponds to 64% of the theoretical yield based on molybdenum.

S3.2 Synthesis of MIL-117 in RBF

To synthesize MIL-117 in RBF, 1,2,4,5-benzenetetracarboxylic acid (0.050 g, 0.2 mmol) was dissolved in 10 mL of N, N-dimethylformamide (DMF). A solution of indium (III) nitrate (0.601 g, 2 mmol) in 5 mL of distilled water was then added to the reaction mixture using a dropping funnel over the course of 2 hours. The reaction mixture was stirred and heated in an oil bath at 100 °C for 24 hours. After the completion of the reaction, the resulting white microcrystals were cooled to room temperature, filtered, and washed with DMF and deionized water. Finally, the product was dried under high vacuum conditions at 80°C for 24 hours.

S3.3 Impregnation Method Used for Synthesis of Mo₈O₂₆@MIL-117

The Mo₈O₂₆@MIL-117 composite was also prepared using the following impregnation method: 0.1 g of MIL-117 was dispersed in 10 mL of ethanol and subjected to ultrasonic irradiation to create a uniform dispersion. Separately, a specific amount of [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆] equivalent to 1 mmol was dissolved in 5 mL of acetonitrile. The prepared [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆] solution was then steadily added to the former dispersion of MIL-117, and the mixture was stirred for 24 hours at room temperature. The resulting mixture was filtered and rinsed multiple times with acetonitrile, followed by deionized water, and then dried at 80°C for 12 hours.

S3.4 Synthesis of Mo₈O₂₆@MIL-117 (1 mmol and 2 mmol)

In a two-neck round-bottom flask (RBF), a mixture containing [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆] (1.0 mmol) and 1,2,4,5-benzenetetracarboxylic acid (0.050 g, 0.2 mmol) was dissolved in 10 mL of N,N-dimethylformamide (DMF). A solution of indium (III) nitrate (0.601 g, 2 mmol) in 5 mL of distilled water was added to the reaction mixture using a dropping funnel over the course of 2 hours. The reaction mixture was stirred and heated in an oil bath at 100 °C for 24 hours (**Figure 1**). The product, containing either 1 mmol or 2 mmol of [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆], depending on the initial loading, was obtained. To prepare a product with 2 mmol of [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆], start with 2 mmol of [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆]. After the completion of the reaction, the resulting white microcrystals were cooled to room temperature, filtered, and washed with DMF and acetonitrile to remove any remaining [(*n*-C₄H₉)₄N]₄[Mo₈O₂₆]. Finally, the product was dried under high vacuum conditions for 24 hours.

S3.5 General Method for Catalytic Oxidative C-N Bond Formations

In this experiment, an oven-dried screw cap reaction tube was employed. Inside the reaction tube, a magnetic stir bar was placed to ensure efficient mixing. The tube was then charged with amine (0.5 mmol), Benzaldehyde (2.5 mmol), $\text{Mo}_8\text{O}_{26}@MIL-117$ (10 mg, 2 mmol Mo loading), TBHP (2 mmol), and acetonitrile (2 mL) under air atmosphere. To initiate the reaction, the screw cap was securely closed, and the reaction tube was subjected to vigorous stirring. To maintain optimal conditions, a preheated oil bath was utilized, maintaining a constant temperature of 85 °C for 1 hour. Upon completion, the mixture was diluted with EtOAc (25 mL) and filtered with a celite pad. Then, the EtOAc layer was concentrated using a rotary evaporator followed by column chromatography using silica (100–200 mesh size) and petroleum ether/ethyl acetate as the eluent.

S3.6 General Method for Catalytic Paal Knorr Pyrrole Synthesis

In this experiment, an oven-dried screw cap reaction tube equipped with a magnetic stir bar was used to ensure efficient mixing. Inside the tube, 10 mg of $\text{Mo}_8\text{O}_{26}@MIL-117$ (containing 2 mmol of Mo) was combined with 2,5-hexadione (1 mmol) and an amine (1 mmol). The mixture was stirred at room temperature under solvent-free conditions. After 15 minutes, for the reaction to reach completion, boiling ethanol (5 mL) was added. The catalyst was then separated from the mixture by filtration. The final pure product was obtained by recrystallization from n-hexane.

S3.7 Recovering and Reusability of the Catalyst from Oxidative C-N Bond Formation

In this procedure, a mixture comprising amine (0.5 mmol), benzaldehyde (2.5 mmol), $\text{Mo}_8\text{O}_{26}@MIL-117$ (10 mg, containing 2 mmol Mo), TBHP (2 mmol), and acetonitrile (2 mL) was prepared under an air atmosphere. The reaction was initiated by securely closing the screw cap on the reaction tube and vigorously stirring the mixture. The reaction tube was then placed in a preheated oil bath set at a constant temperature of 85°C and maintained for 1 hour to ensure optimal reaction conditions. Following the reaction, the catalyst was recovered by thoroughly washing it with ethanol (10 mL) and deionized water (10 mL). The cleaned catalyst was subsequently dried under vacuum at 100°C and was reused in subsequent experiments.

S3.8 Hot Filtration Test for Oxidative C-N Bond Formation

Five separate reaction tubes were prepared, with each tube containing the following components: aniline (0.5 mmol), benzaldehyde (2.5 mmol), Mo₈O₂₆@MIL-117 catalyst (10 mg, containing 2 mmol Mo), TBHP (2 mmol), and acetonitrile (2 mL), all under ambient air conditions. Then, all reactions were initiated at 85°C. After 30 minutes, each tube was filtered. Tube 1 underwent post-synthesis work-up, followed by purification using flash column chromatography to determine the isolated yield. After removing the catalyst, the four reaction tubes were restarted. At time intervals of 45, 60, 75, 90, and 100 minutes, each tube was processed separately using purification by flash column chromatography to determine the isolated yield.

S3.9 Preparation of Dye Adsorbates

A dye stock solution with a 1000 ppm concentration was diluted to produce solutions with concentrations between 10 ppm and 100 ppm. For all of the dye solutions, a neutral pH has been maintained.

S3.10 Adsorption Tests

The concentrations of MB and RHB dyes were determined using a UV-*vis* spectrometer at wavelengths of, 664 nm, and 553 nm, respectively. To study the influence of initial dye concentration, 10 mg of the adsorbent was added to 10 mL of MB solution with concentrations ranging from 10 PPM to 100 PPM. The experiments were conducted in 30 mL culture tubes, stirred at 300 rpm at room temperature for a specified duration. Afterward, the adsorbent was separated using a centrifuge, and the equilibrium concentration was determined by UV-*vis* analysis. The removal percentage (**R%**) and equilibrium adsorption capacity (*q_e*, mg/g) were calculated using the following equations:

$$R\% = \frac{(C_0 - C_E)100}{C_0}$$

In these equations, *C_E* (mg/L) represents the equilibrium concentration of the dye pollutant, and *C₀* (mg/L) denotes the initial concentration.

S3.11 pH Study

For the pH study, the same batch adsorption method was employed, with all parameters identical to those used in the batch adsorption study (**Section 3.10**). However, the pH of the

solution was varied from 2 to 12 to assess the effect of pH on MB adsorption, while maintaining constant initial MB concentration, adsorbent dosage, stirring speed, and temperature.

S3.12 Salt Study

For the salt study, 80 ppm solutions of different salts were prepared, with all other parameters remaining consistent with those outlined in the adsorption study (**Section 3.10**). This approach aimed to evaluate the impact of various salts on the adsorption of MB onto Mo₈O₂₆@MIL-117, while maintaining constant MB concentration, adsorbent dosage, stirring speed, and temperature.

S3.13 Solvent Study

Different solvents were utilized in the study, including methanol, ethanol, DMF, DMSO, acetone, xylene, and toluene. These solvents were selected to evaluate their effects on the adsorption efficiency of MB onto Mo₈O₂₆@MIL-117, providing insights into the role of solvent polarity and interactions in the adsorption process. The adsorption experiments were conducted under controlled conditions, maintaining constant parameters such as initial MB concentration, adsorbent dosage, stirring speed, and temperature for consistent comparative analysis (**Section 3.10**).

S3.14 Adsorption kinetics

For the adsorption studies of MB onto Mo₈O₂₆@MIL-117, 10 mL solutions containing an initial MB concentration of 80 ppm and 10 mg of the Mo₈O₂₆@MIL-117 composite were prepared. The solutions were stirred at 150 rpm at room temperature. The adsorption time was varied until equilibrium was reached. The amount of MB adsorbed at any time was determined using the following equation (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q_t (mg/g) is the amount of MB adsorbed at time t , C_0 and C_t (mg/L) represent the initial and time-dependent MB concentrations, respectively, V (L) is the volume of the solution, and m (g) is the mass of Mo₈O₂₆@MIL-117 used.

S3.15 Pseudo-first-order kinetics

The equation for the pseudo-first-order kinetic model is given by:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (2)$$

Where, q_e = Amount of dye adsorbed at equilibrium (mg/g), q_t = Amount of dye adsorbed at time t (mg/g), k_1 = The pseudo-first-order rate constant (min^{-1})

S3.16 Pseudo-second-order kinetics

The equation for the pseudo-second-order kinetic model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (3)$$

where, q_e = Amount of dye adsorbed at equilibrium (mg/g), q_t = Amount of dye adsorbed at time t (mg/g), k_2 = The pseudo-second-order rate constant (g/mg min)

S3.17 Dye Removal Thermodynamics

The thermodynamic investigation of MB adsorption onto $\text{Mo}_8\text{O}_{26}@MIL-117$ was performed at different temperatures (303–333 K) using a warm water bath and a Corning stirrer for consistent sample mixing. The thermodynamic parameters evaluated include the free energy change (ΔG°), standard enthalpy change (ΔH°), and entropy change (ΔS°), which were determined using the following equations:

$$\Delta G^\circ = -RT \ln k \quad (4)$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

where k is the distribution coefficient, R is the thermodynamic gas constant (-8.314 J/mol K), and T is the temperature (K).

S3.18 Regeneration and Reusability of $\text{Mo}_8\text{O}_{26}@MIL-117$

After the MB molecules were removed from the solution, the $\text{Mo}_8\text{O}_{26}@MIL-117$ exhausted. To release the absorbed dyes, the composite underwent a washing process using a diluted NaOH solution with a concentration of 5 ppm (20 mL). This regeneration process aimed to recover the adsorbed dyes from the composite. After the adsorbent regeneration, the MB solution (80 ppm, 10 mL), previously described, was reused for another adsorption cycle. The concentration of the dyes in the resulting filtrate was measured by recording the UV-*vis* spectra, as previously mentioned.

S3.19 Stability Test

The $\text{Mo}_8\text{O}_{26}@MIL-117$ was stirred in solutions of 0.1 N HCl, 0.1 N NaOH, and 1.0 M NaCl for 72 H to examine the composite's stability in diverse conditions. To evaluate the $\text{Mo}_8\text{O}_{26}@MIL-117$ stability in aqueous environments, immersion in pure water was also done for 72 H. The degradation of MIL-117 and detachment of $\text{Mo}_8\text{O}_{26}^{4-}$ from the $\text{Mo}_8\text{O}_{26}@MIL-117$ was quantified by measuring the concentration of Indium metal ions in the supernatant using ICP-OES. This test serves as an indicator of the $\text{Mo}_8\text{O}_{26}@MIL-117$ stability under various immersion environments.

S4 Figures

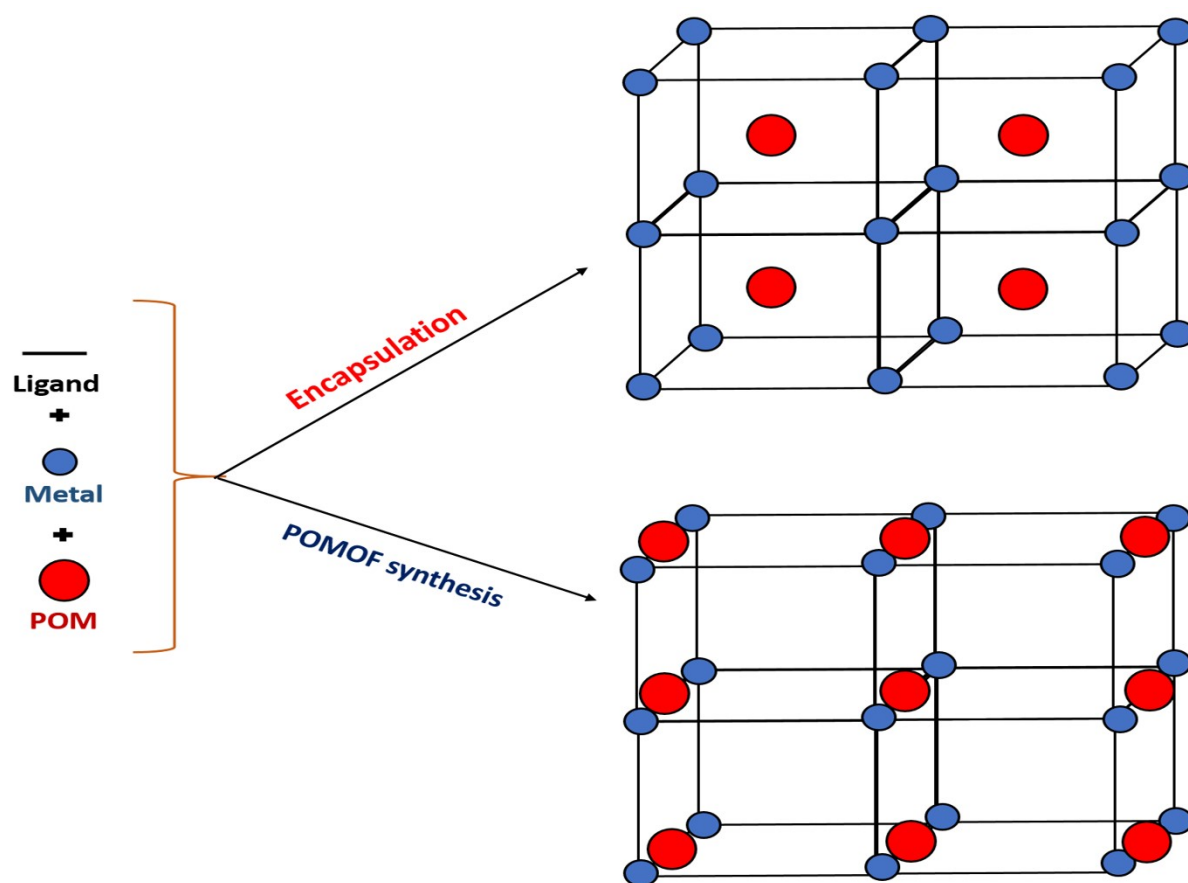


Figure S1: Synthetic approaches for the integration of POMs with MOFs.

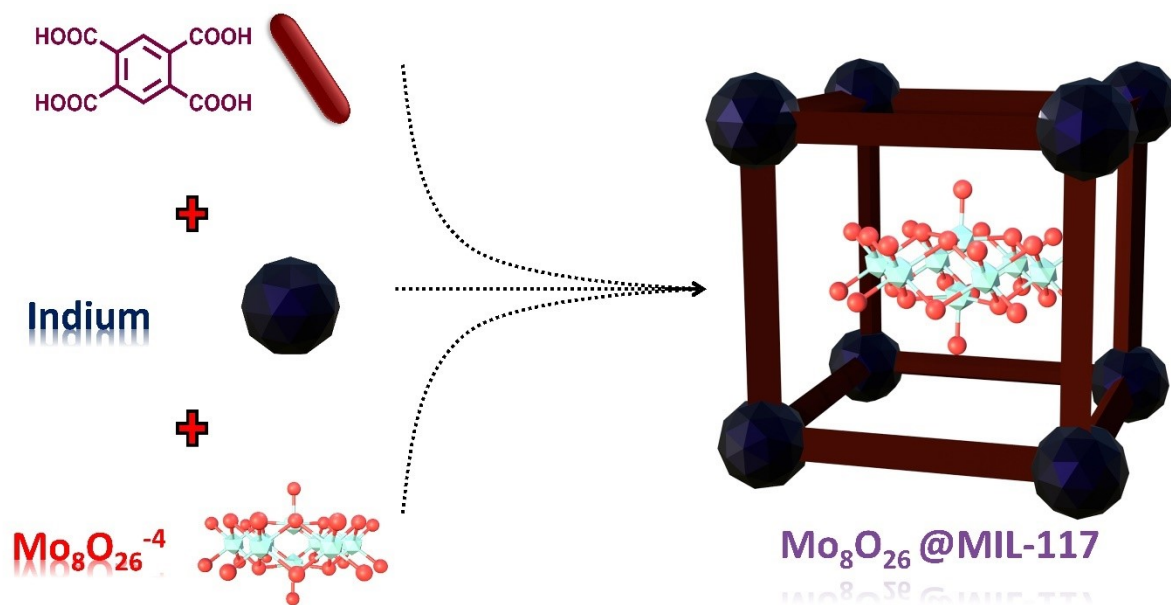


Figure S2: Synthetic strategy for preparing $\text{Mo}_8\text{O}_{26} @ \text{MIL-117}$ catalyst.

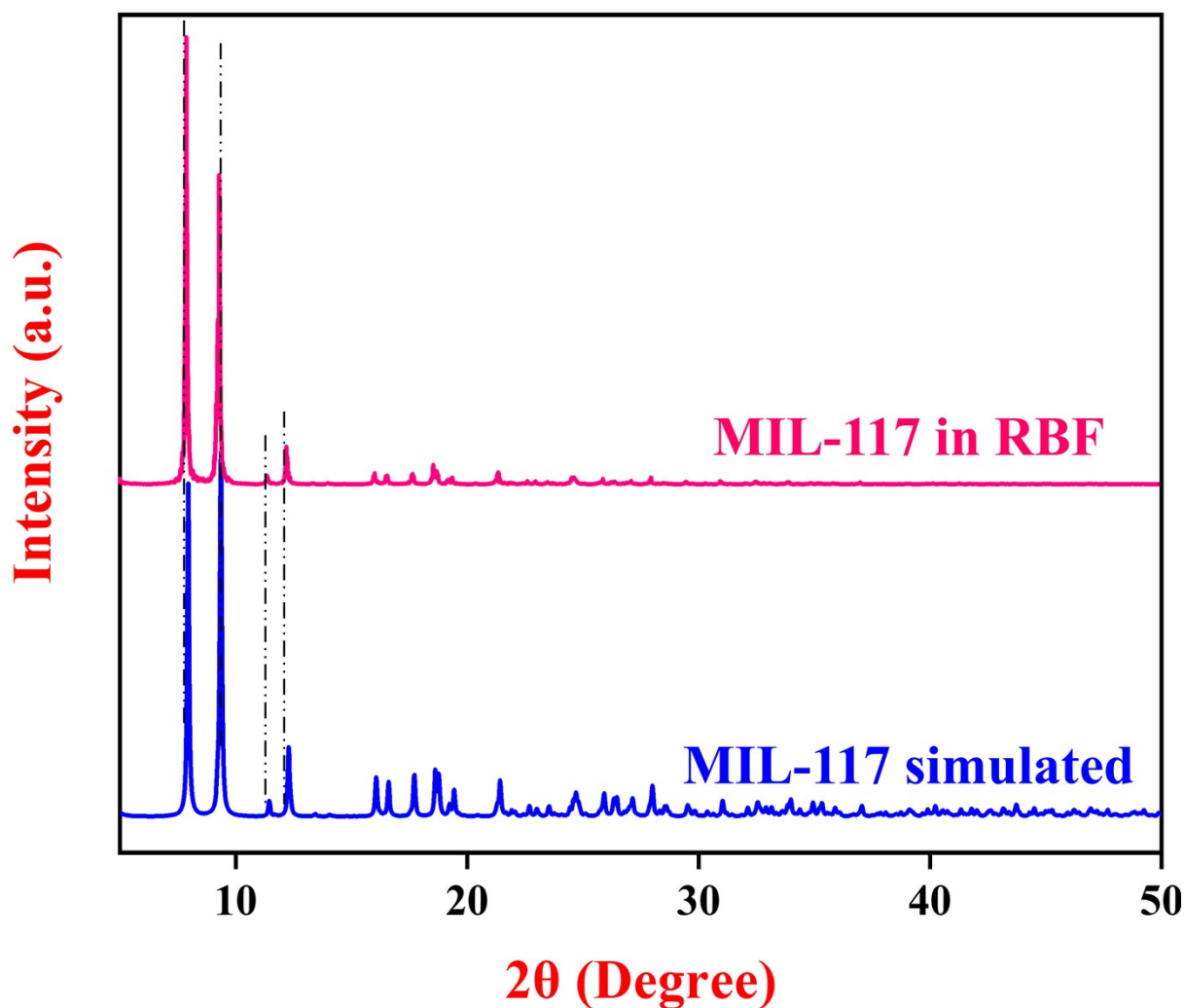


Figure S3: Comparison of the PXR D data of MIL-117 synthesized in RBF with the simulated pattern.

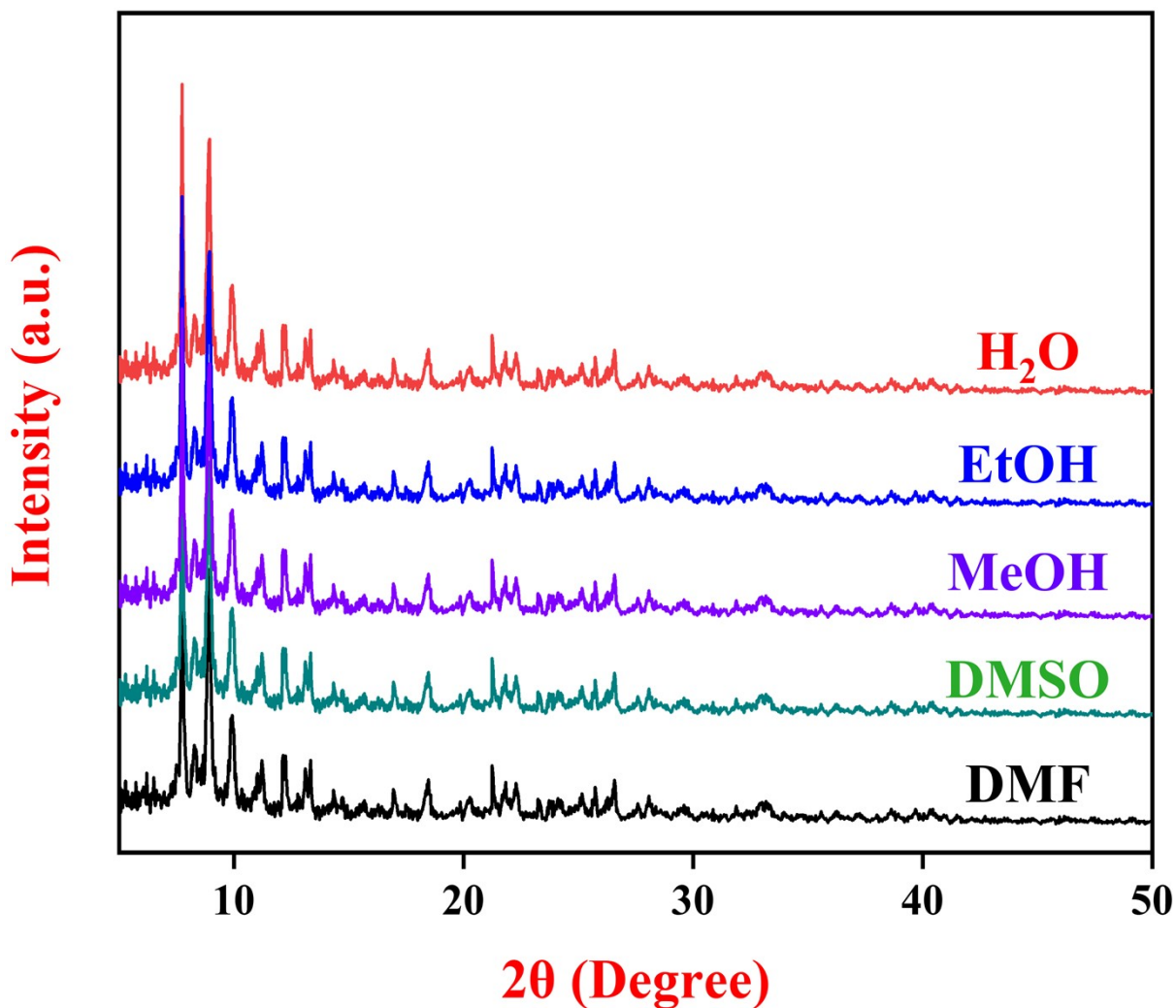


Figure S4: PXRD data of $\text{Mo}_8\text{O}_{26}@MIL-117$ after soaking in various solvents.

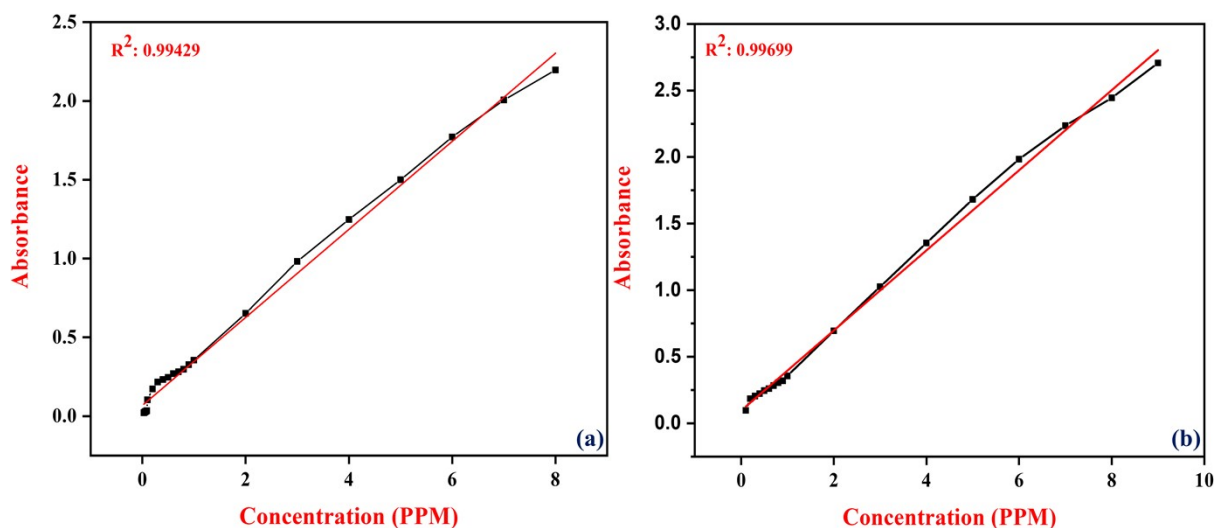


Figure S5: Calibration curve for MB, and RHB to determine unknown concentrations.

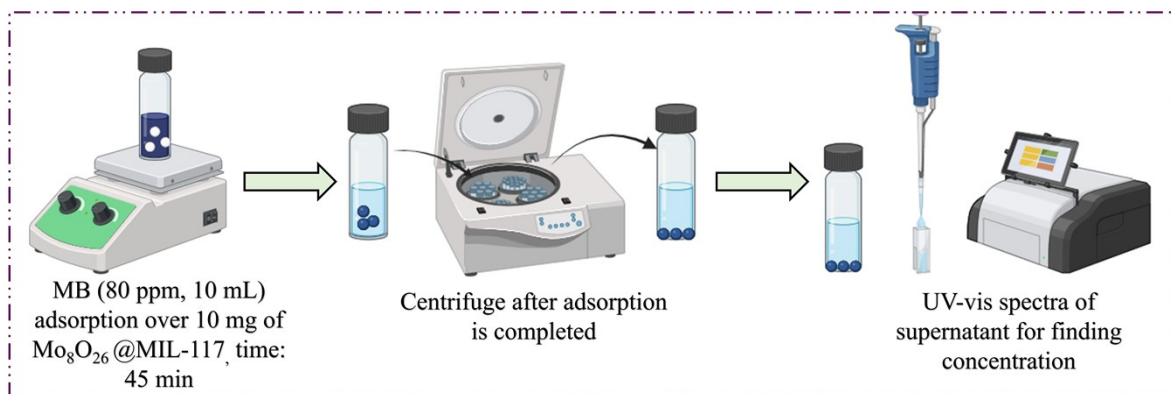


Figure S6: General dye removal procedure using $\text{Mo}_8\text{O}_{26}@MIL-117$.

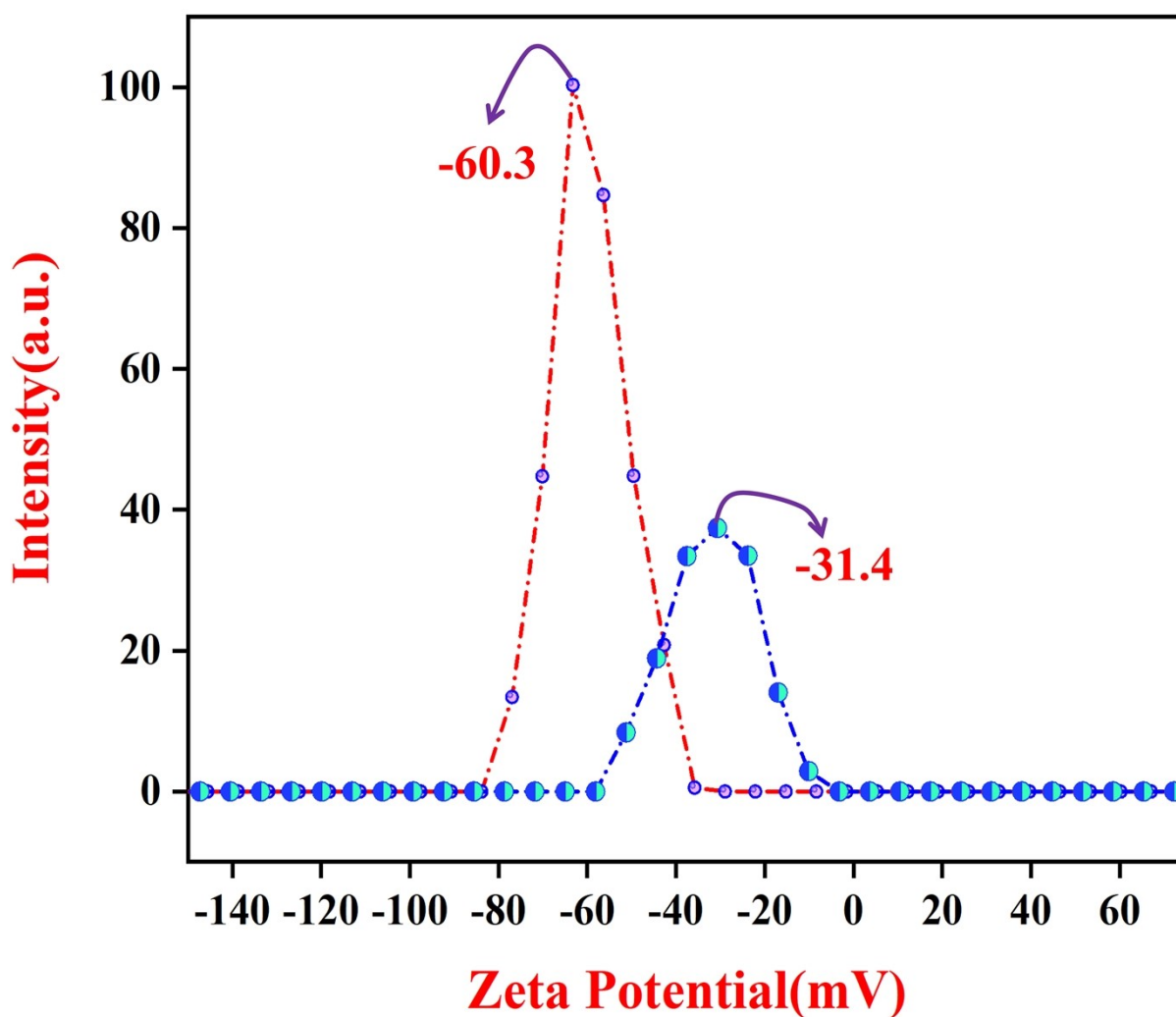


Figure S7: Zeta potential of $\text{Mo}_8\text{O}_{26}@MIL-117$ (1 mmol (blue line) and 2 mmol (red line)) with different $\text{Mo}_8\text{O}_{26}^{4-}$ loadings.

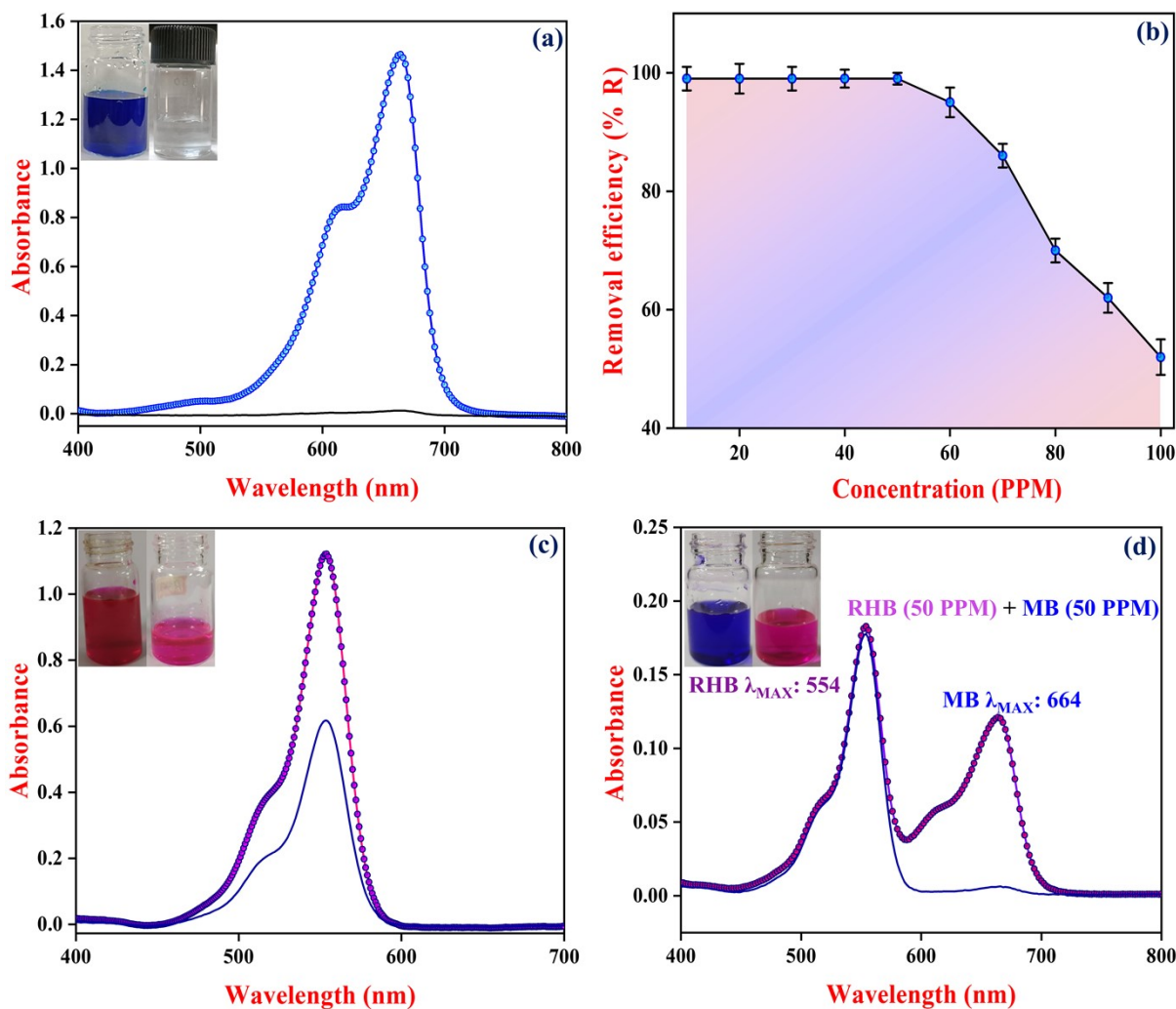


Figure S8: (a) Before and after Uv-vis spectra of MB (50 ppm, 10 mL) removal using MIL-117. (b) MIL-117 removal efficiency over 10 to 100 ppm MB solution. (c) Before and after Uv-vis spectra of RHB (50 ppm, 10 mL) removal using MIL-117. (d) Selective dye removal in MB (50 ppm) and RHB (50 ppm) mixture using MIL-117.

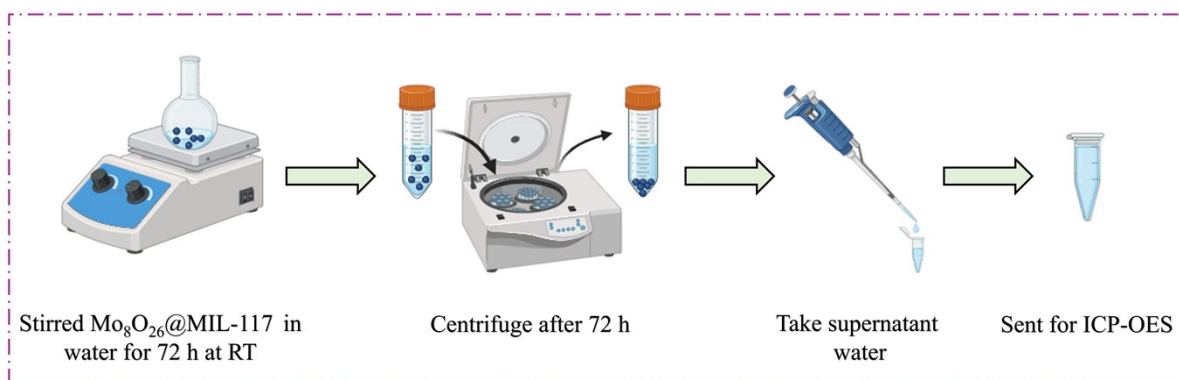


Figure S9: $\text{Mo}_8\text{O}_{26}@MIL-117$ water stability procedure.

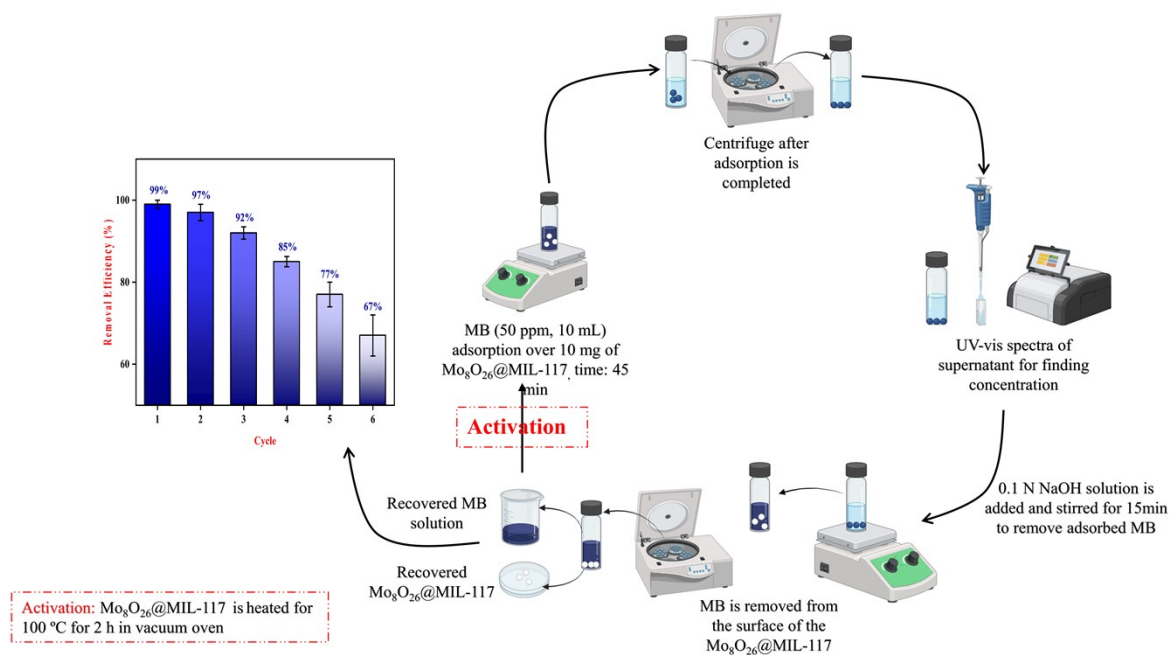


Figure S10: General reusability and reactivation procedure for $\text{Mo}_8\text{O}_{26}@MIL-117$ for MB adsorption.

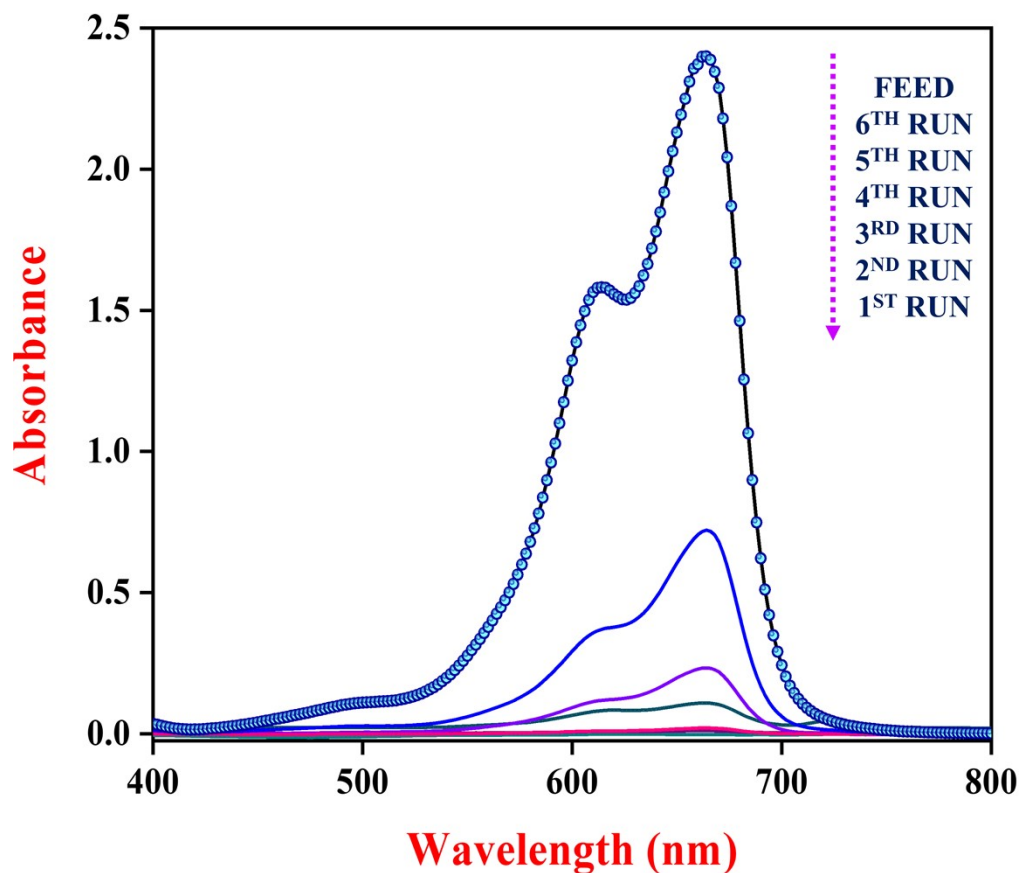


Figure S11: UV-vis spectra of MB (50 ppm) after five consecutive cycles of adsorption and desorption.

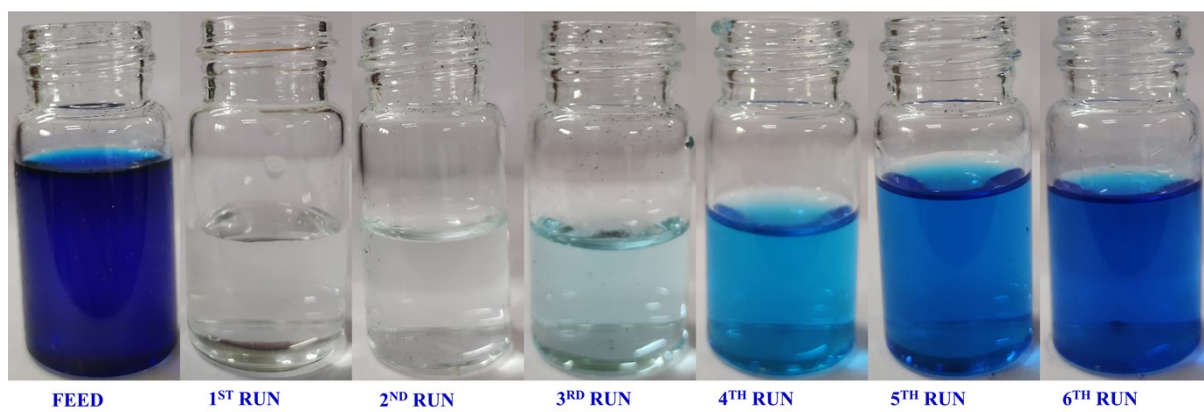


Figure S12: Supernatant solutions acquired after all runs.

S5 Tables

Table S1: ICP-OES results of $\text{Mo}_8\text{O}_{26}@MIL-117$ synthesised via different strategy.

Catalyst	Method	% Mo
$\text{Mo}_8\text{O}_{26}@MIL-117$	Direct Sonication	0.005
$\text{Mo}_8\text{O}_{26}@MIL-117$ (1 mmol)	In-situ addition	1.8%
$\text{Mo}_8\text{O}_{26}@MIL-117$ (2 mmol)		4.4%

S4.1 Screening Reactions for Oxidative C-N Cond Formation

Table S2: Catalyst Screening^[a]

Entry	Catalyst	Catalyst Loading [weight]	Yield ^[b] [%]
1	A	10 mg	54
2	A	15 mg	56
3	B	10 mg	74
4	B	15 mg	73
5	MIL-117	10 mg	7
6	MIL-117	15 mg	13
7	$[(n\text{-C}_4\text{H}_9)_4\text{N}]_4[\text{Mo}_8\text{O}_{26}]$	10 mg	28
8	$[(n\text{-C}_6\text{H}_9)_4\text{N}]_4[\text{Mo}_8\text{O}_{26}]$	15 mg	39
9	$\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$	10 mg	<5

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), TBHP (1.0 equvi.), CH_3CN (03 mL), 75 °C, and 1 h.

^[b] Isolated yield

A: $\text{Mo}_8\text{O}_{26}@MIL-117$ (1 mmol Mo loading), **B:** $\text{Mo}_8\text{O}_{26}@MIL-117$ (2 mmol Mo loading)

Table S3: Temperature Screening ^[a]

Entry	Temperature [°C]	Yield [%] ^[b]
1	RT	7
2	45	27
3	60	58
4	75	74
5	85	84
6	90	83
7	100	64
8	120	62

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), TBHP (1.0 equvi.), **B** (10 mg), CH_3CN (03 mL), and 1 h.

^[b] Isolated yield

Table S4: Solvent Screening^[a]

Entry	Solvent	Yield ^[b] [%]
1	Methanol	56
2	Ethanol	58
3	DMF	24
4	DMSO	27
5	Acetonitrile	84
6	Dichloromethane	36

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), TBHP (1.0 equvi.), **B** (10 mg), Solvent (03 mL), 85 °C and 1 h.

^[b] Isolated yield

Table S5: Time Screening^[a]

Entry	Time [min]	Yield ^[b] [%]
1	15	54
2	30	60
3	45	69
4	60	84
5	85	83

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), TBHP (1.0 equvi.), **B** (10 mg), Solvent (03 mL), 85 °C and 1 h.

^[b] Isolated yield

Table S6: Oxidant screening Screening^[a]

Entry	Oxidant (1.0 Equivalent)	Yield ^[b] [%]
1	TBHP	84
2	DTBP	54
3	K ₂ S ₂ O ₈	0
4	(NH ₄) ₂ S ₂ O ₈	0
5	DCP	51
6	BZ ₂ O ₂	74
7	H ₂ O ₂	0
8	O ₂	0

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), **B** (10 mg), Solvent (03 mL), 85 °C and 1h.

^[b] Isolated yield

Table S7: Oxidant Loading Screening^[a]

Entry	Oxidant (Equivalent)	Yield ^[b] [%]
1	0.5	74
2	1.0	84
3	2.0	92
4	2.5	85

^[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), **B** (10 mg), Solvent (02 mL), 85 °C and 1 h.

^[b] Isolated yield

Table S8: Substrate Ratio Screening^[a]

Entry	Amine (Equivalent)	Aldehyde (Equivalent)	Yield ^[b] [%]
1	1.0	1.0	78
2	1.0	2.0	92
3	1.0	3.0	94
4	1.0	4.0	94
5	1.0	5.0	95
6	1.5	5.0	95
7	2.0	5.0	94

^[a]Reaction conditions: **B** (10 mg), TBHP (2.0 mmol) Solvent (02 mL), 85 °C and 1 h.

^[b] Isolated yield

S4.2 Screening Reactions for Pall Knorr Pyrrole Synthesis

Table S9: Catalyst Screening^[a]

Entry	Catalyst	Catalyst Loading [weight]	Yield ^[b] [%]
1	A	10 mg	78
2	A	15 mg	84
3	B	10 mg	94
4	B	15 mg	93
5	MIL-117	10 mg	17
6	MIL-117	15 mg	24
7	[(<i>n</i> -C ₄ H ₉) ₄ N] ₄ [Mo ₈ O ₂₆]	10 mg	56
8	[(<i>n</i> -C ₄ H ₉) ₄ N] ₄ [Mo ₈ O ₂₆]	15 mg	58

9	In(NO ₃) ₃ · xH ₂ O	10 mg	11
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^[a]Reaction conditions: **19** (1 mmol), **20** (1 mmol), Solvent Free, Room Temperature, and 20 min

^[b] Isolated yield

A: Mo₈O₂₆@MIL-117 (1 mmol Mo loading), **B:** Mo₈O₂₆@MIL-117 (2 mmol Mo loading)

Table S10: Solvent Screening^[a]

Entry	Solvent	Yield ^[b] [%]
1	Methanol	56
2	Ethanol	58
3	Acetonitrile	65
4	Dichloromethane	56
5	Solvent Free	94

^[a]Reaction conditions: **19** (1 mmol), **20** (1 mmol), **B** (10 mg), and Room Temperature, and 20 min

^[b] Isolated yield

Table S11: Time Screening^[a]

Entry	Time [min]	Yield ^[b] [%]
1	5	54
2	10	80
3	15	94
4	20	94

^[a]Reaction Conditions: **19** (1 mmol), **20** (1 mmol), **B** (10 mg), Solvent Free, and Room Temperature

^[b] Isolated yield

Table S12: Substrate Ratio Screening^[a]

Entry	Aniline (equivalent)	2,5-hexadione (Equivalent)	Yield ^[b] [%]
1	1.0	0.5	88
2	1.0	1.0	94
3	1.0	1.5	94
4	1.0	2.0	94
5	1.5	1.0	93
6	2.0	1.0	93

7	2.0	1.0	94
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^[a]Reaction Conditions: **B** (10 mg), Solvent Free, and Room Temperature

^[b]Isolated yield

Table S13: ICP-OES result after C-N bond coupling reaction filtration

Sample	Medium	% of Indium	% of Molybdenum
Mo ₈ O ₂₆ @MIL-117	Ethanol	0	0

Table S14: Kinetic parameters for methylene blue adsorption onto the Mo₈O₂₆@MIL-117 composite.

Dye	Pseudo-First order			Pseudo-Second order		
	k ₁ (1/min)	q _e (cal.)	R ²	k ₂ (g/mg min)	q _e (cal.)	R ²
MB	4.5 × 10 ⁻³	85.6453	0.8425	3.44 × 10 ⁻³	80.6754	0.9992

Experimental conditions: MB concentration = 80 ppm; Adsorbent amount = 10 mg; Volume: 10 mL

Table S15: The thermodynamic parameters for the adsorption of MB onto the Mo₈O₂₆@MIL-117 composite.

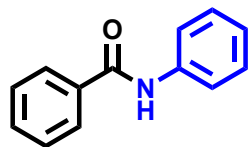
Dye	Temp. (K)	Δ G° (kJ/mol)	Δ H° (kJ/mol)	Δ S° (J/mol K)
MB	303	-9.54	23.94	110.46
	313	-10.61		
	322	-11.71		
	333	-12.82		

Experimental conditions: MB concentration = 80 ppm; Adsorbent amount = 10 mg; Volume: 10 mL

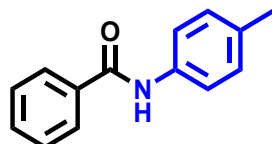
Table S16: ICP-OES result after immersing Mo₈O₂₆@MIL-117 in to water

Sample	Medium	Time	% of Indium	% of Molybdenum
Mo ₈ O ₂₆ @MIL-117	Water	72 h	0	0

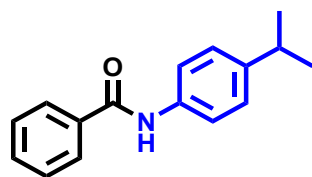
S6 Characterization Data of Synthesized Compounds



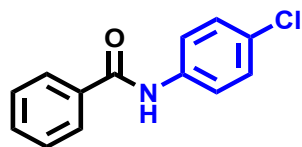
N-phenylbenzamide (Scheme 1, Entry 3): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). ¹H NMR (400 MHz, DMSO) δ 10.26 (s, 1H), 8.00 – 7.96 (m, 2H), 7.83 – 7.78 (m, 2H), 7.63 – 7.51 (m, 3H), 7.36 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 139.09, 134.04, 132.49, 129.98, 129.01, 127.11, 125.87, 119.15, 114.94.



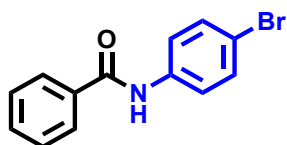
N-(p-tolyl)benzamide (Scheme 1, Entry 4): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.86 – 7.81 (m, 2H), 7.53 – 7.48 (m, 3H), 7.46 – 7.40 (m, 2H), 7.16 – 7.11 (m, 2H), 2.32 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.69, 135.40, 135.12, 134.25, 131.73, 129.59, 128.76, 127.02, 120.36, 120.33, 20.92.



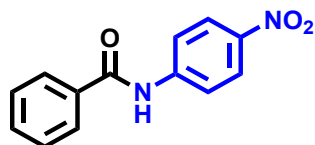
N-(4-isopropylphenyl)benzamide (Scheme 1, Entry 5): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.87 – 7.81 (m, 2H), 7.60 – 7.48 (m, 3H), 7.48 – 7.40 (m, 2H), 7.24 – 7.17 (m, 2H), 2.89 (hept, *J* = 6.9 Hz, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 165.75, 145.34, 135.63, 135.13, 131.72, 131.66, 128.74, 128.68, 127.04, 126.98, 126.92, 120.46, 120.40, 33.65, 33.59, 24.04, 23.98.



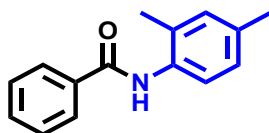
N-(4-chlorophenyl)benzamide (Scheme 1, Entry 6): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). $^1\text{H NMR}$ (400 MHz, DMSO) δ 10.40 (s, 1H), 8.04 – 7.94 (m, 2H), 7.94 – 7.80 (m, 2H), 7.68 – 7.51 (m, 3H), 7.51 – 7.40 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, DMSO) δ 166.13, 138.63, 135.19, 132.16, 128.98, 128.88, 128.15, 127.75, 122.32.



N-(4-bromophenyl)benzamide (Scheme 1, Entry 7): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 – 7.84 (m, 2H), 7.79 (s, 1H), 7.59 – 7.53 (m, 3H), 7.53 – 7.46 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.75, 135.22, 135.09, 133.13, 131.74, 131.25, 129.77, 128.79, 127.41, 127.08, 123.56.

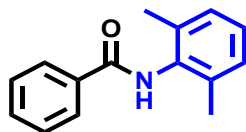


N-(4-nitrophenyl)benzamide (Scheme 1, Entry 8): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.50 (t, J = 2.2 Hz, 1H), 8.16 – 8.08 (m, 2H), 8.00 (ddd, J = 8.2, 2.2, 0.9 Hz, 1H), 7.97 – 7.81 (m, 2H), 7.64 – 7.56 (m, 1H), 7.56 – 7.44 (m, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 139.09, 134.04, 132.49, 129.98, 129.01, 127.11, 125.87, 119.15, 114.94.

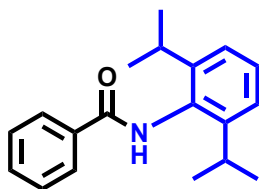


N-(2,4-dimethylphenyl)benzamide (Scheme 1, Entry 9): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (dd, J = 7.3, 1.7 Hz, 2H), 7.71 (d, J = 8.2 Hz, 1H), 7.66 (s, 1H), 7.55 – 7.44 (m, 3H), 7.04 (d, J = 6.4 Hz, 2H), 2.29 (d, J = 13.8 Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3)

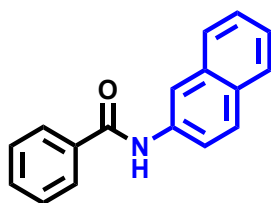
δ 165.75, 135.22, 135.09, 133.13, 131.74, 131.25, 129.77, 128.79, 127.41, 127.08, 123.56, 77.37, 77.05, 76.73, 20.92, 17.80.



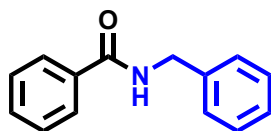
N-(2,6-dimethylphenyl)benzamide (Scheme 1, Entry 10): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.95 – 7.81 (m, 2H), 7.62 (s, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.17 – 7.01 (m, 3H), 2.23 (s, 7H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 166.01, 135.65, 134.49, 133.97, 131.78, 128.74, 128.28, 127.43, 127.28, 18.47.



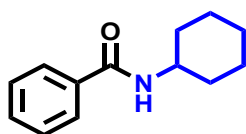
N-(2,6-diisopropylphenyl)benzamide (Scheme 1, Entry 11): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.92 – 7.88 (m, 2H), 7.58 – 7.53 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 (s, 1H), 7.34 (dd, J = 8.3, 7.1 Hz, 1H), 7.22 (d, J = 7.6 Hz, 2H), 3.14 (hept, J = 6.8 Hz, 2H), 1.21 (d, J = 6.9 Hz, 12H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 167.00, 146.44, 134.61, 131.78, 131.21, 128.82, 128.52, 127.21, 123.58, 28.93, 23.67.



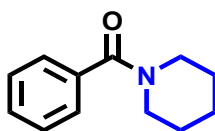
N-(naphthalen-2-yl)benzamide (Scheme 1, Entry 12): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, R_f = 0.5). **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 8.31 (s, 1H), 7.99 – 7.89 (m, 3H), 7.89 – 7.82 (m, 2H), 7.74 – 7.67 (m, 1H), 7.57 – 7.51 (m, 1H), 7.51 – 7.39 (m, 5H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 166.45, 134.79, 134.19, 132.47, 131.93, 128.82, 128.79, 127.70, 127.28, 126.39, 126.21, 126.06, 125.75, 121.57, 120.97.



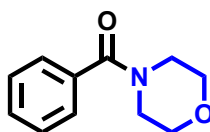
N-benzylbenzamide (Scheme 1, Entry 13): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, Rf = 0.5). ¹H NMR (500 MHz, CHLOROFORM-D) δ 7.81 – 7.76 (m, 2H), 7.52 – 7.44 (m, 1H), 7.43 – 7.35 (m, 2H), 7.34 – 7.31 (m, 4H), 6.75 (t, J = 5.6 Hz, 1H), 4.60 (d, J = 5.7 Hz, 2H). ¹³C NMR (126 MHz, CHLOROFORM-D) δ 167.58, 138.36, 134.44, 131.65, 128.86, 128.68, 127.98, 127.67, 127.14, 44.16.



N-cyclohexylbenzamide (Scheme 1, Entry 14): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, Rf = 0.5). ¹H NMR (400 MHz, CHLOROFORM-D) δ 7.73 – 7.65 (m, 2H), 7.47 – 7.39 (m, 1H), 7.36 (dd, J = 8.1, 6.7 Hz, 2H), 5.97 (d, J = 8.0 Hz, 1H), 3.97 – 3.87 (m, 1H), 1.97 (dd, J = 12.6, 3.9 Hz, 2H), 1.70 (dt, J = 13.4, 3.9 Hz, 2H), 1.60 (dt, J = 12.8, 3.8 Hz, 1H), 1.44 – 1.29 (m, 2H), 1.18 (qd, J = 12.1, 3.8 Hz, 4H). ¹³C NMR (126 MHz, CHLOROFORM-D) δ 166.76, 135.16, 131.34, 128.60, 126.95, 48.78, 33.31, 29.81, 25.65, 25.04.

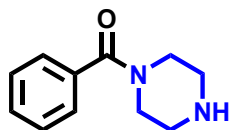


Phenyl(piperidin-1-yl)methanone (Scheme 2, Entry 15): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, Rf = 0.5). ¹H NMR (500 MHz, Chloroform-d) δ 7.54 – 7.49 (m, 2H), 7.49 – 7.41 (m, 3H), 3.51 – 3.44 (m, 4H), 1.69 – 1.62 (m, 6H). ¹³C NMR (101 MHz, Chloroform-d) δ 170.28, 136.51, 129.32, 128.37, 126.76, 24.57.

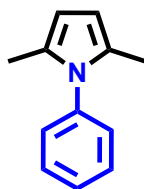


Morpholino(phenyl)methanone (Scheme 2, Entry 16): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, Rf = 0.5). ¹H NMR (500

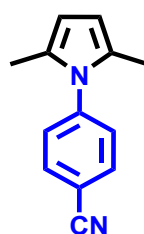
MHz, Chloroform-*d*) δ 7.54 – 7.39 (m, 5H), 3.65 (td, $J = 7.0, 0.9$ Hz, 4H), 3.55 (td, $J = 7.1, 1.0$ Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.40, 135.34, 129.86, 128.55, 127.08, 66.87.



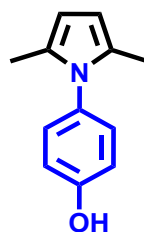
Phenyl(piperazin-1-yl)methanone (Scheme 2, Entry 17): Isolated by flash column chromatography (eluent ethyl acetate/petroleum ether (v/v) = 1:5, $R_f = 0.5$). ^1H NMR (500 MHz, Chloroform-*d*) δ 7.52 – 7.48 (m, 2H), 7.48 – 7.42 (m, 3H), 3.60 (t, $J = 7.1$ Hz, 2H), 3.53 (t, $J = 7.1$ Hz, 2H), 2.83 (td, $J = 7.1, 5.4$ Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.37, 135.88, 129.57, 128.45, 126.95.



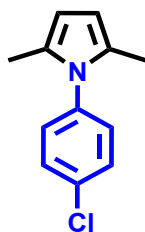
2,5-dimethyl-1-phenyl-1H-pyrrole (Scheme 3, Entry 19): ^1H NMR (400 MHz, CDCl_3) δ 7.48 – 7.43 (m, 2H), 7.41 – 7.36 (m, 1H), 7.23 – 7.19 (m, 2H), 5.90 (s, 2H), 2.03 (s, 7H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 137.59, 133.63, 129.60, 129.43, 128.85, 106.10, 13.09.



4-(2,5-dimethyl-1H-pyrrol-1-yl)benzonitrile (Scheme 3, Entry 20): ^1H NMR (500 MHz, CHLOROFORM-*D*) δ 7.80 – 7.75 (m, 2H), 7.36 – 7.31 (m, 2H), 5.94 (s, 2H), 2.05 (s, 6H). ^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 143.16, 133.24, 129.05, 128.65, 118.37, 111.53, 107.21, 13.22.



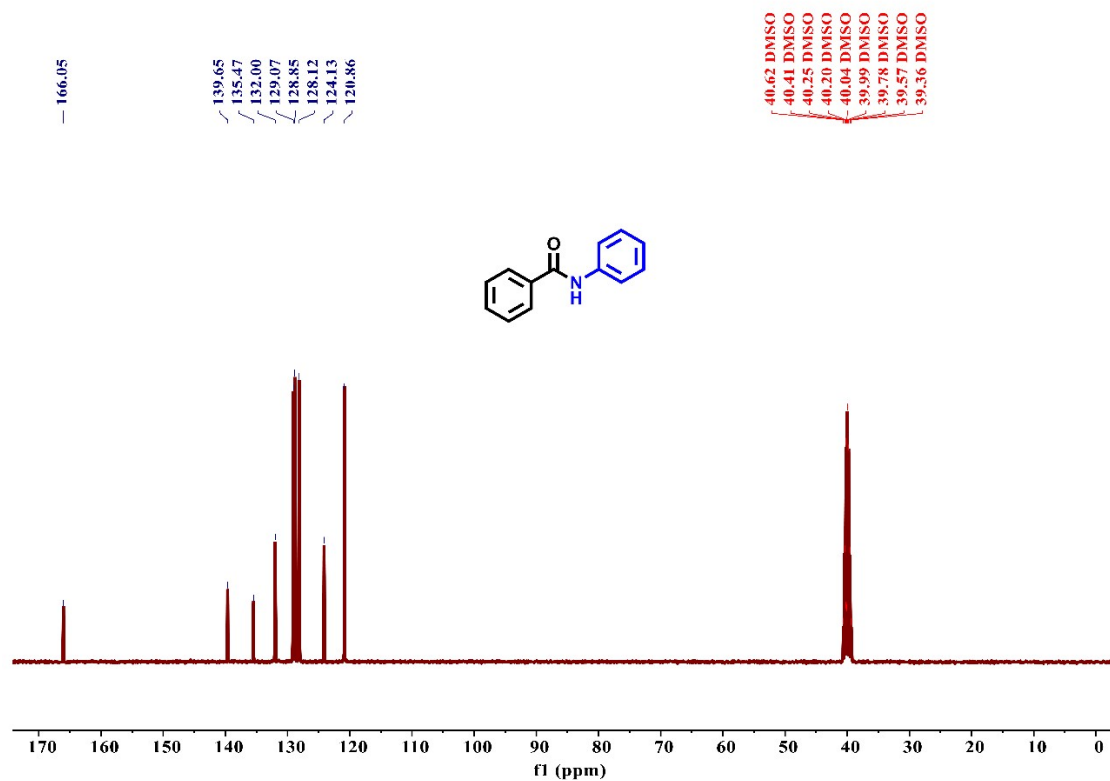
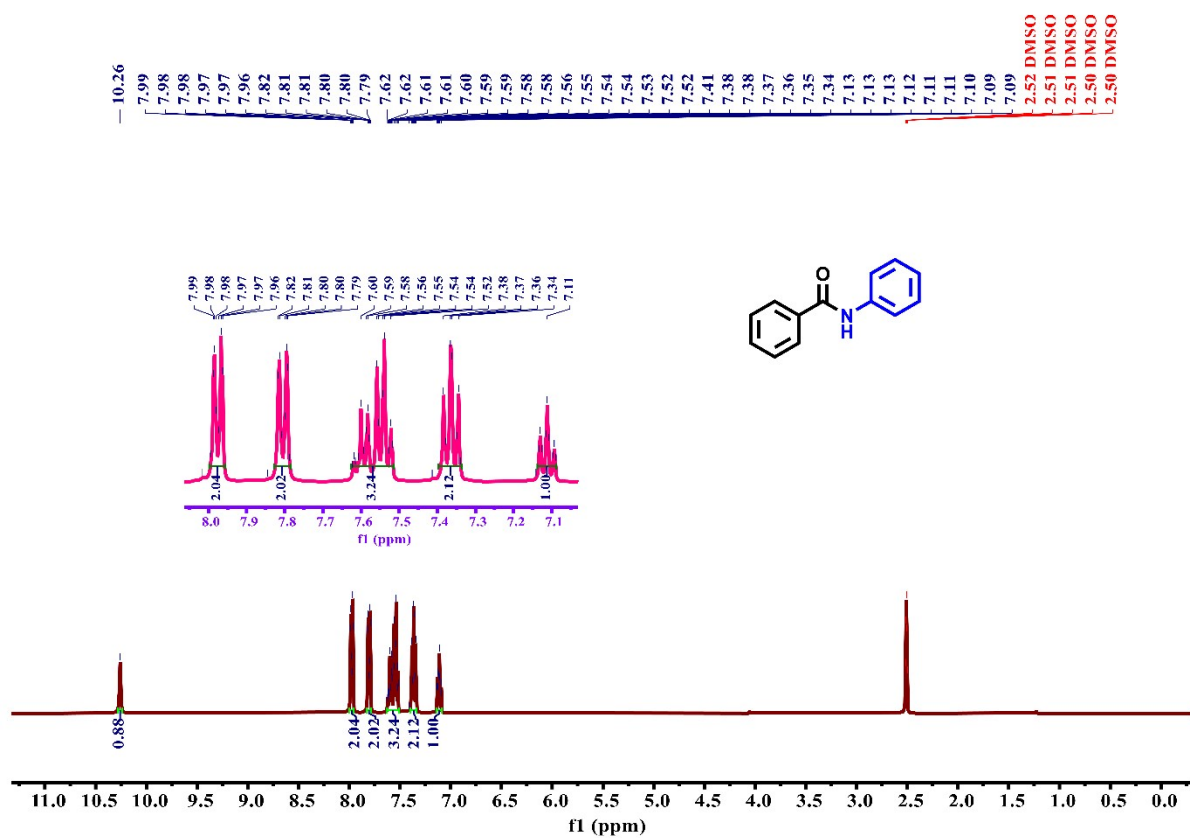
4-(2,5-dimethyl-1H-pyrrol-1-yl)phenol (Scheme 3, Entry 21): $^1\text{H NMR}$ (500 MHz, CHLOROFORM-*D*) δ 7.09 – 7.05 (m, 2H), 6.90 – 6.86 (m, 2H), 5.88 (s, 2H), 4.95 (s, 1H), 2.00 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CHLOROFORM-*D*) δ 154.99, 131.99, 129.55, 129.19, 115.83, 105.34, 13.07.



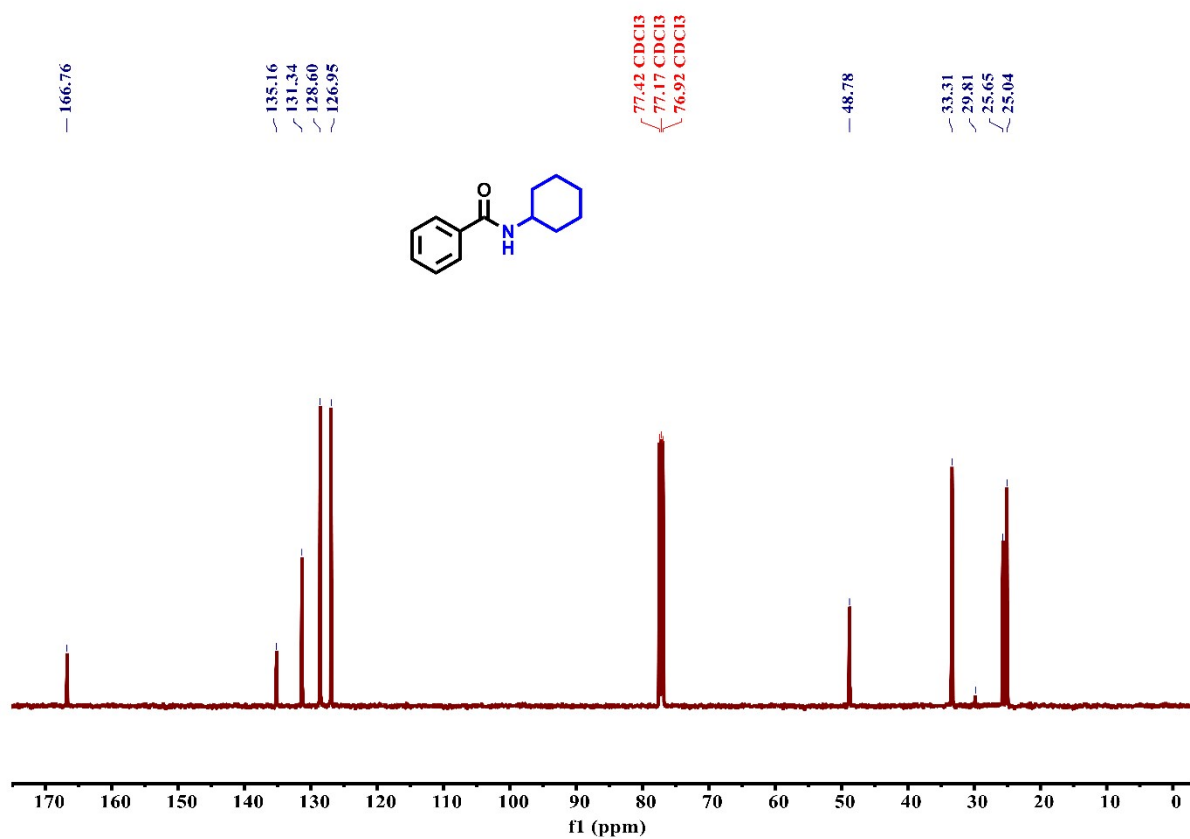
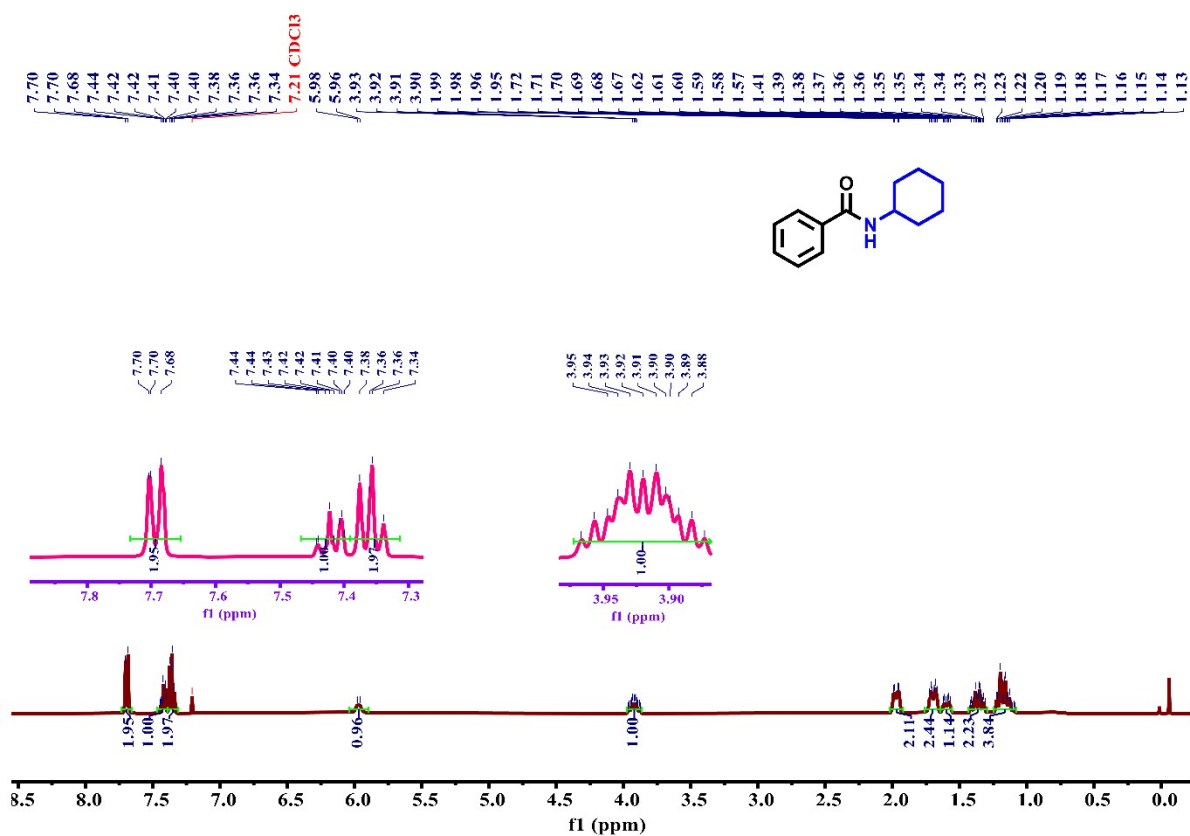
1-(4-chlorophenyl)-2,5-dimethyl-1H-pyrrole (Scheme 3, Entry 22): $^1\text{H NMR}$ (500 MHz, CHLOROFORM-*D*) δ 7.45 – 7.41 (m, 2H), 7.17 – 7.13 (m, 2H), 5.90 (s, 2H), 2.02 (s, 4H). $^{13}\text{C NMR}$ (126 MHz, CHLOROFORM-*D*) δ 137.59, 133.63, 129.60, 129.43, 128.85, 106.10, 13.09.

S7 NMR Spectra of Products

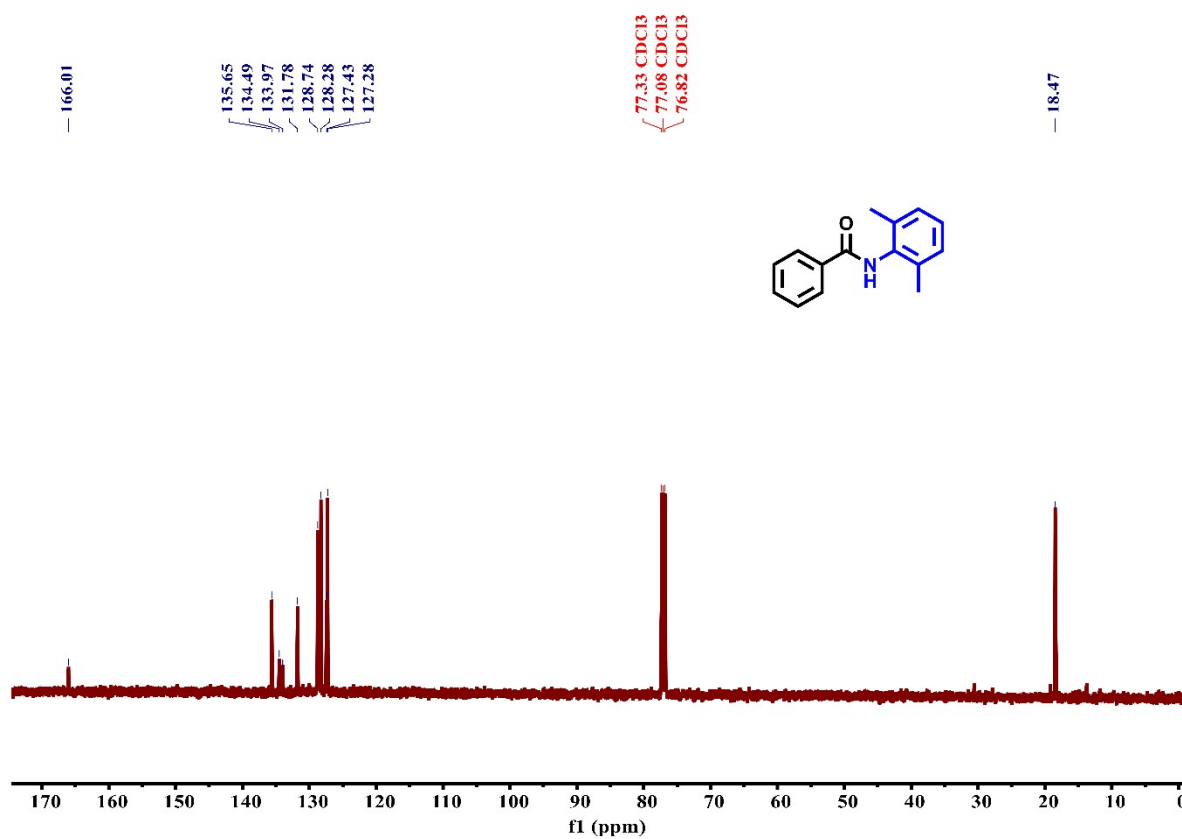
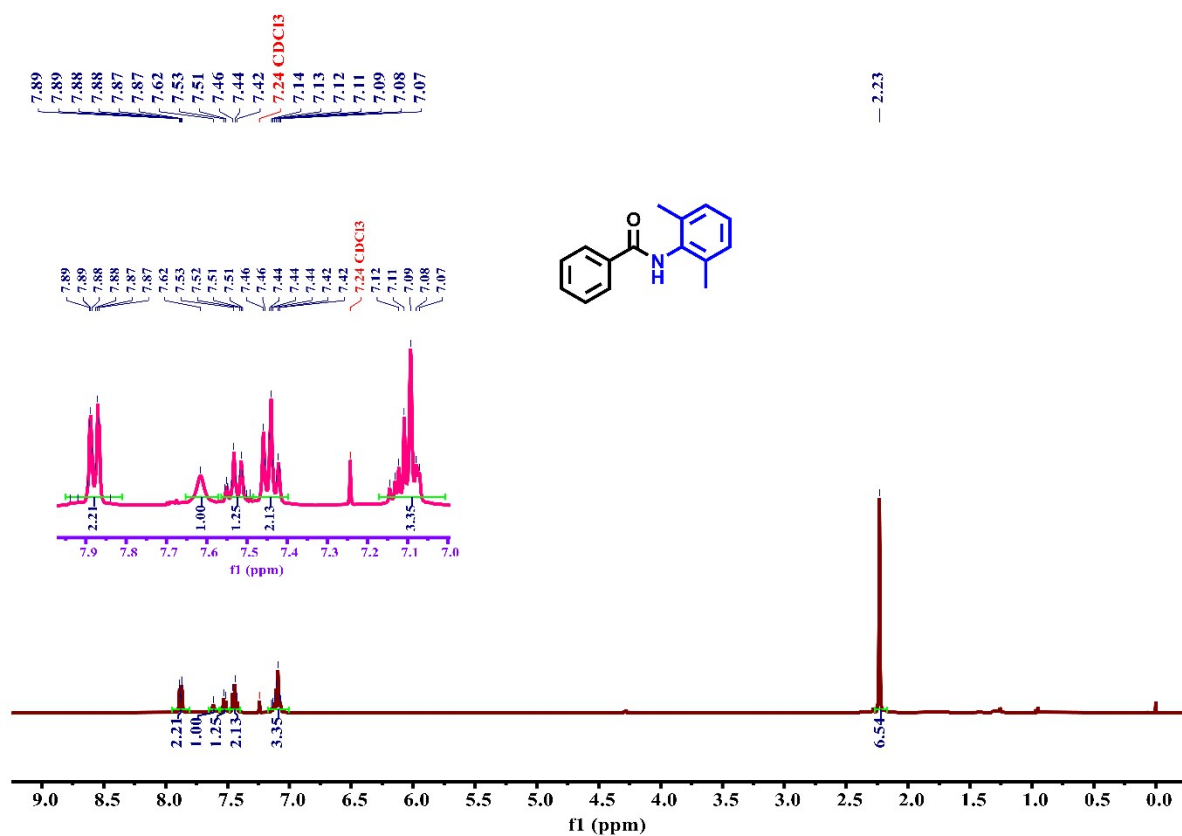
Scheme 1, entry 3



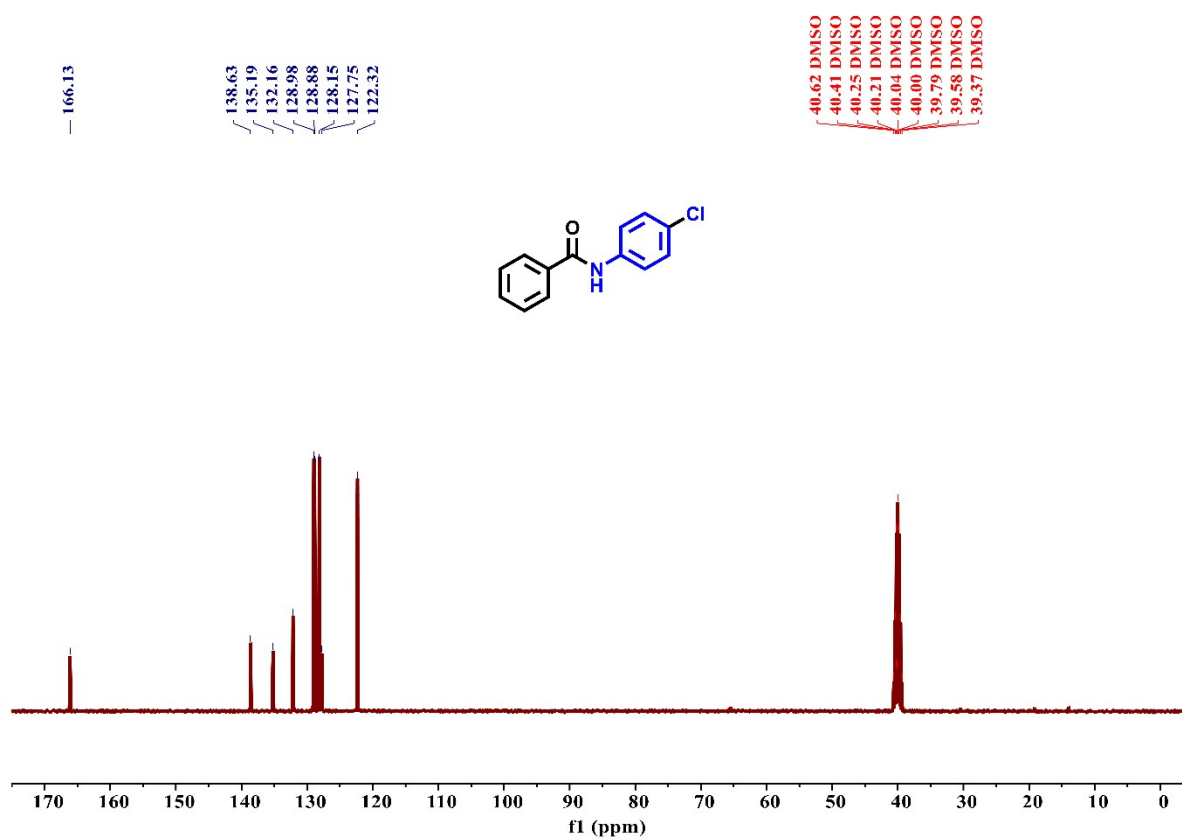
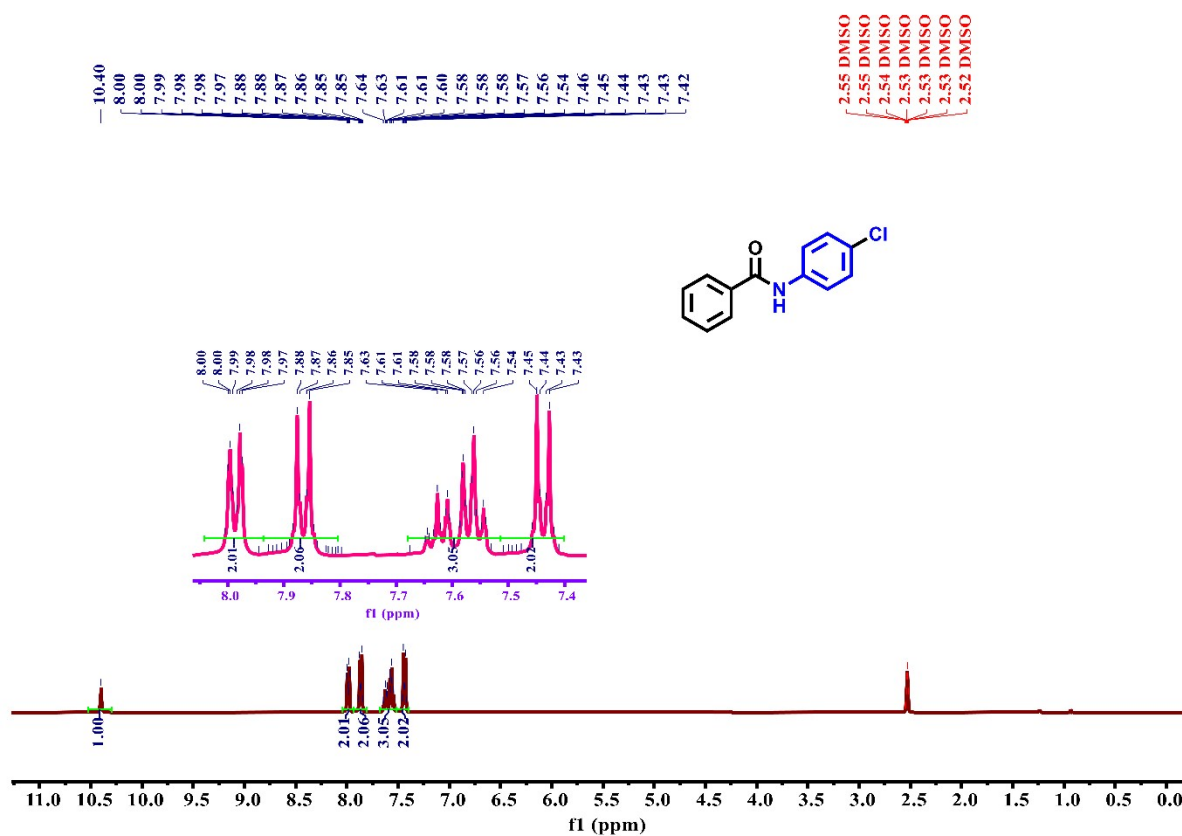
Scheme 1, Entry 4



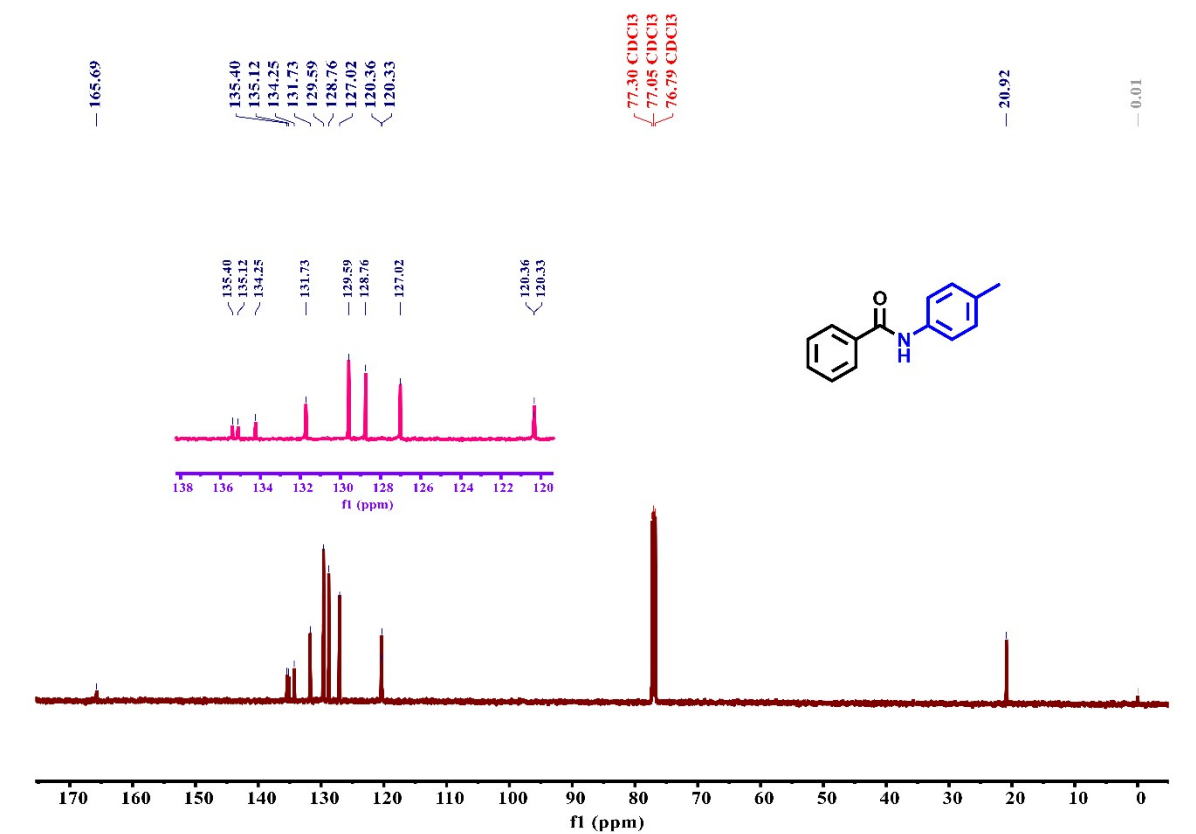
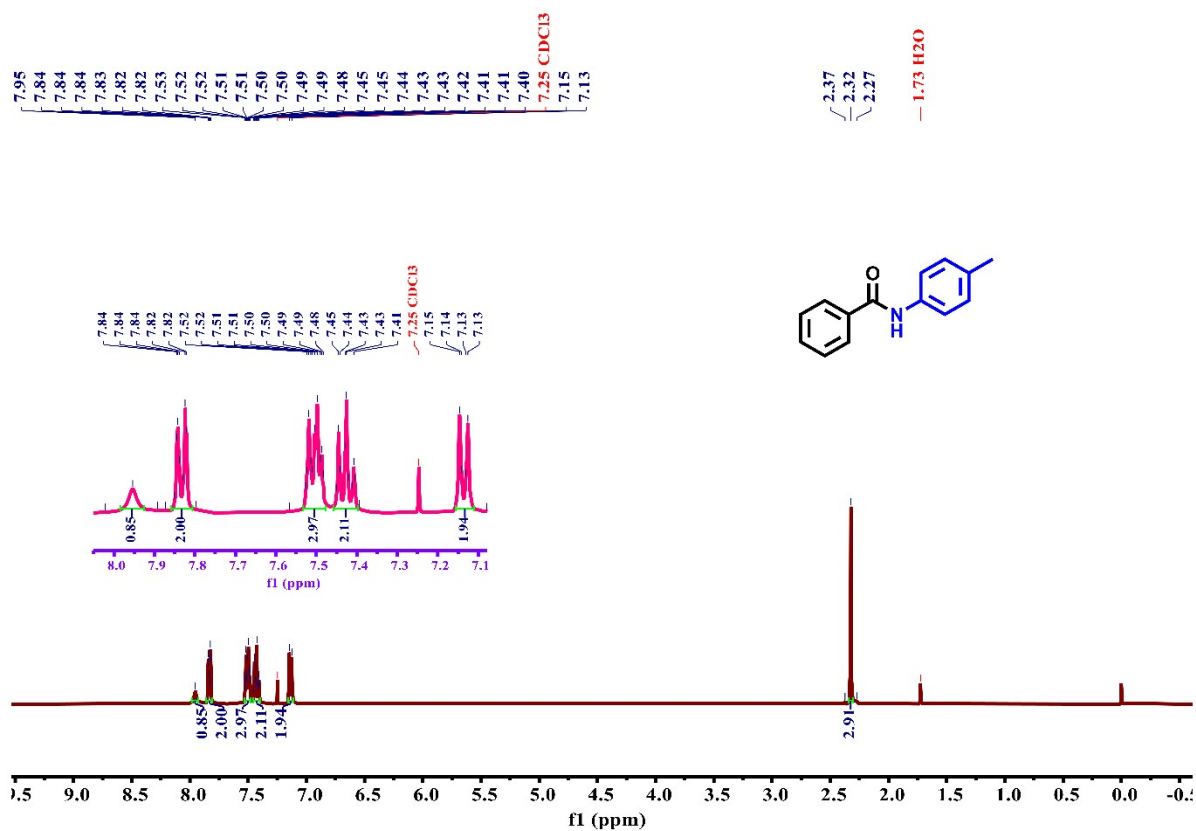
Scheme 1, Entry 5



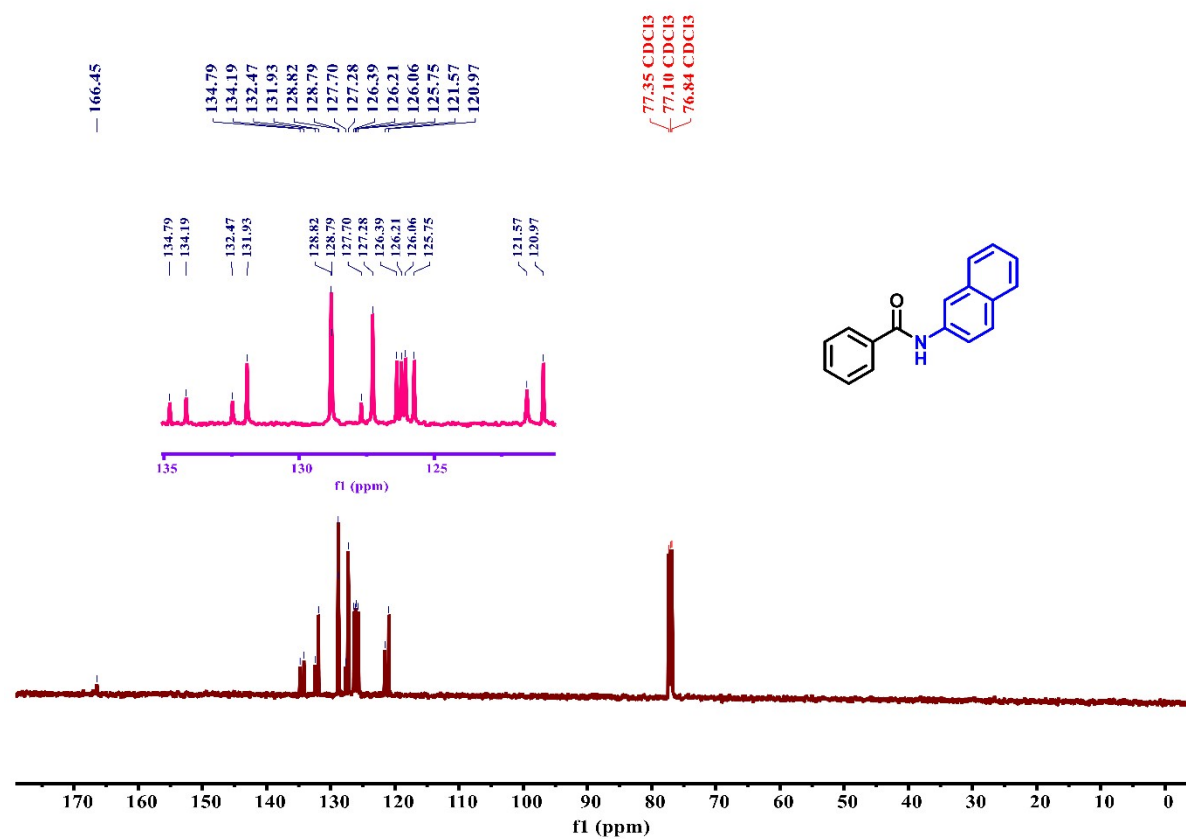
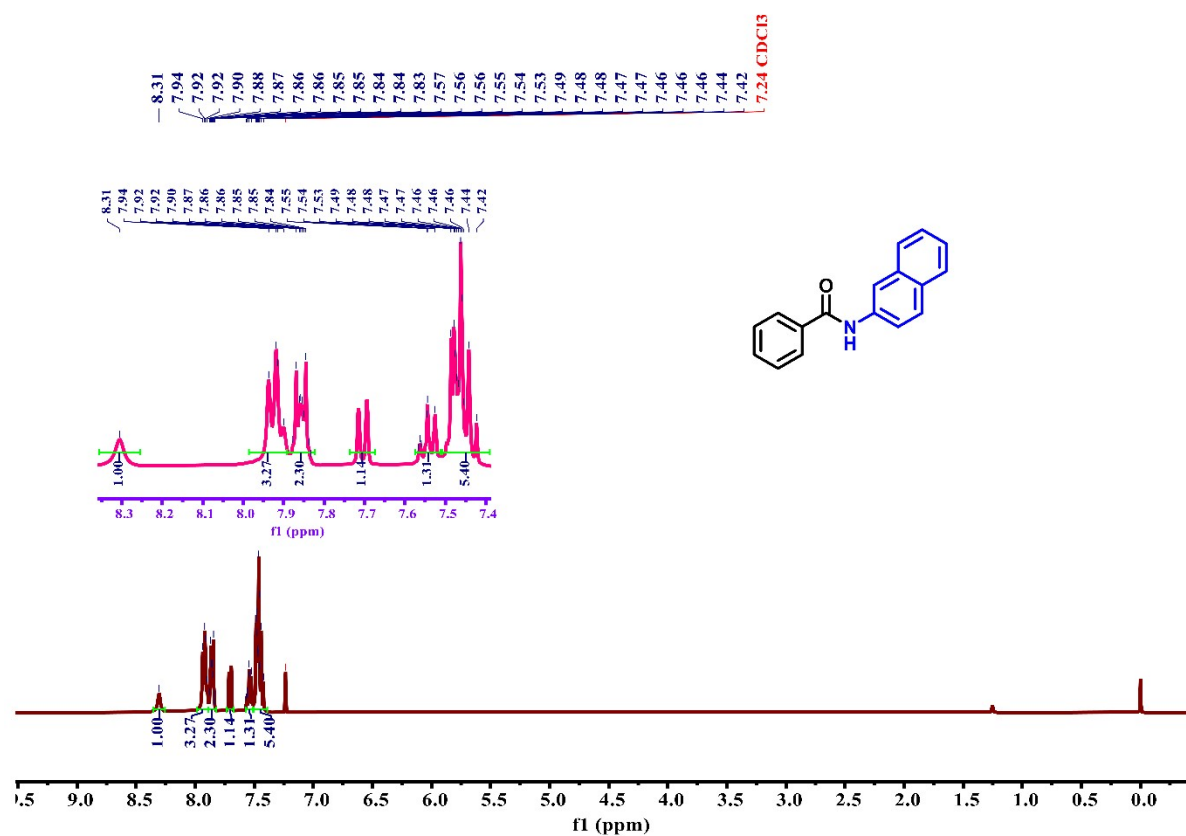
Scheme 1, Entry 6



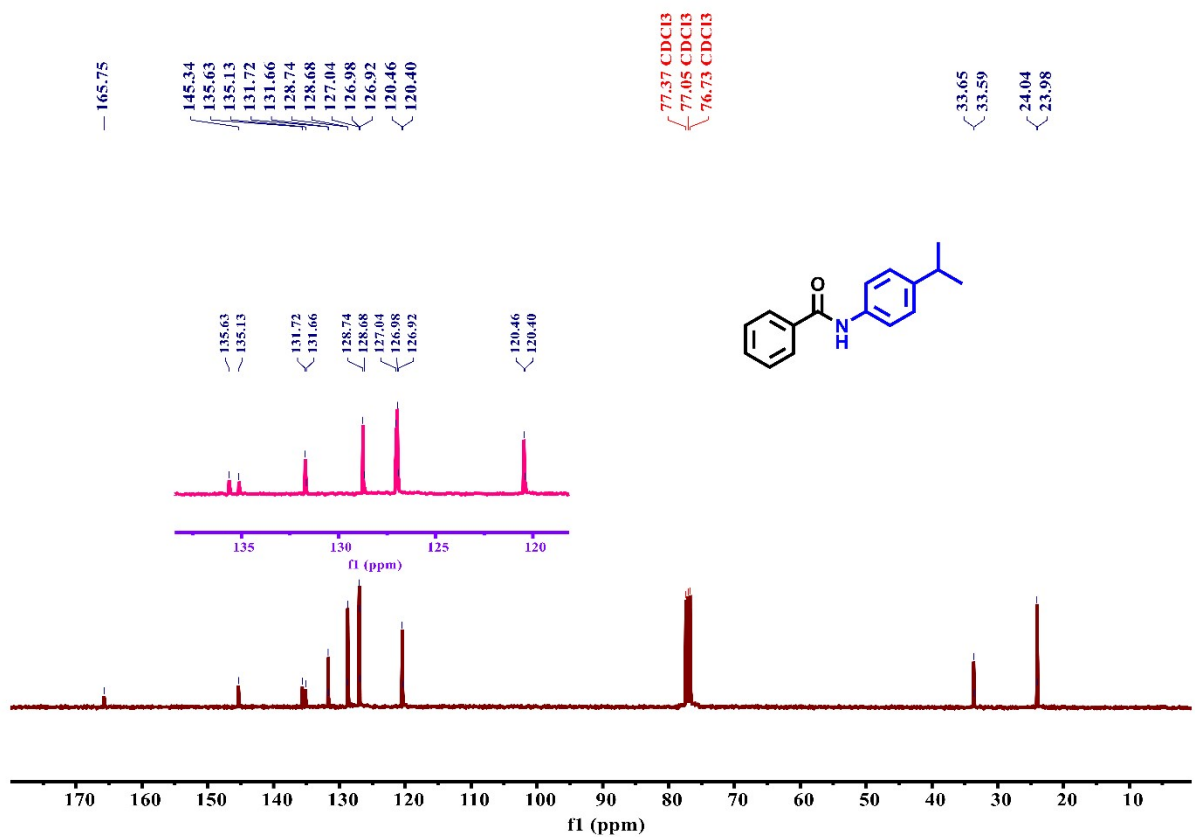
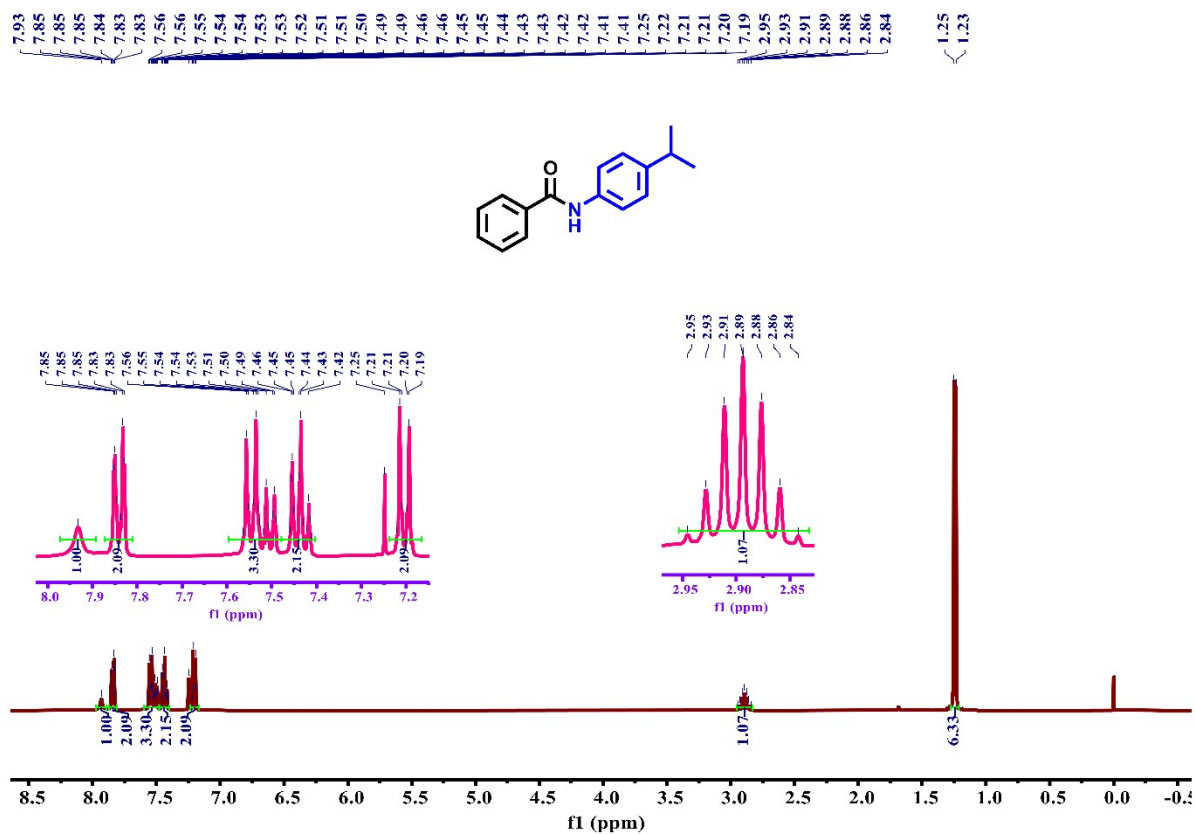
Scheme 1, Entry 7



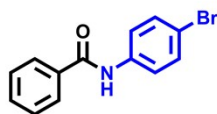
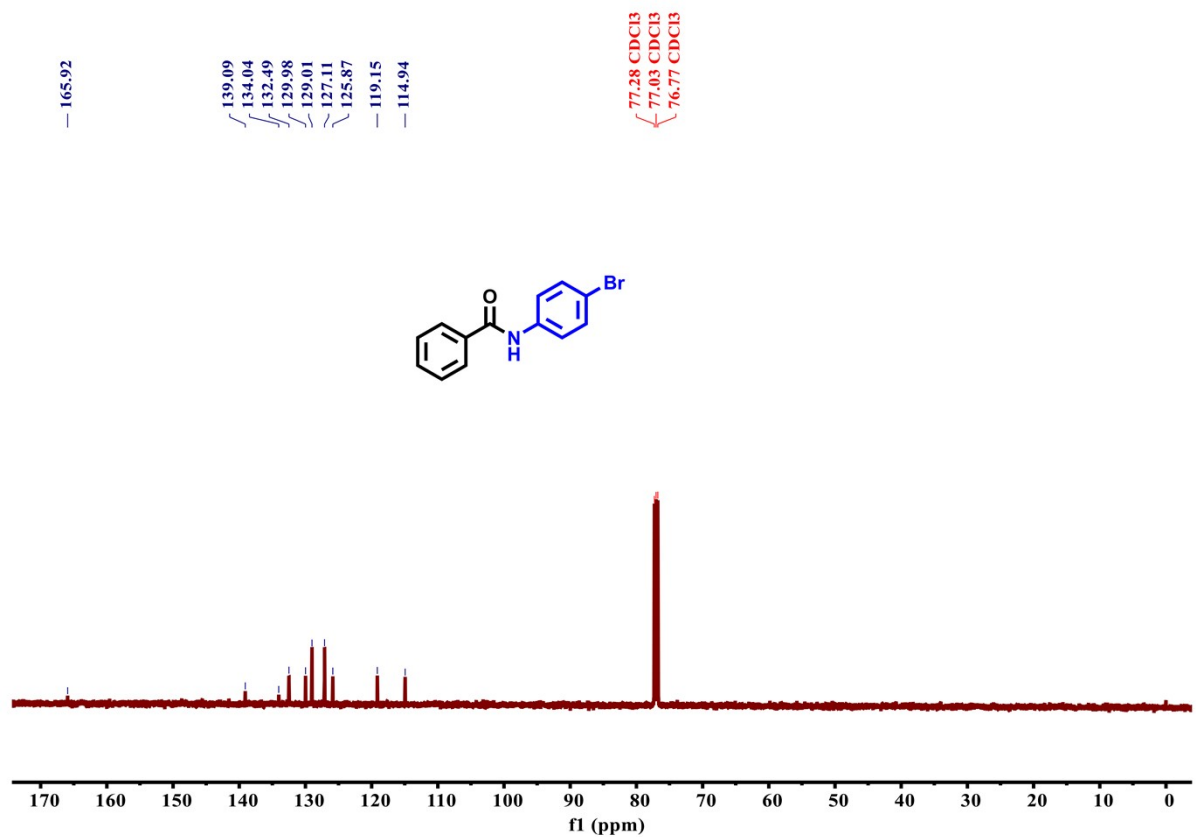
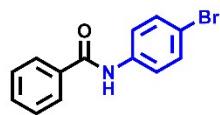
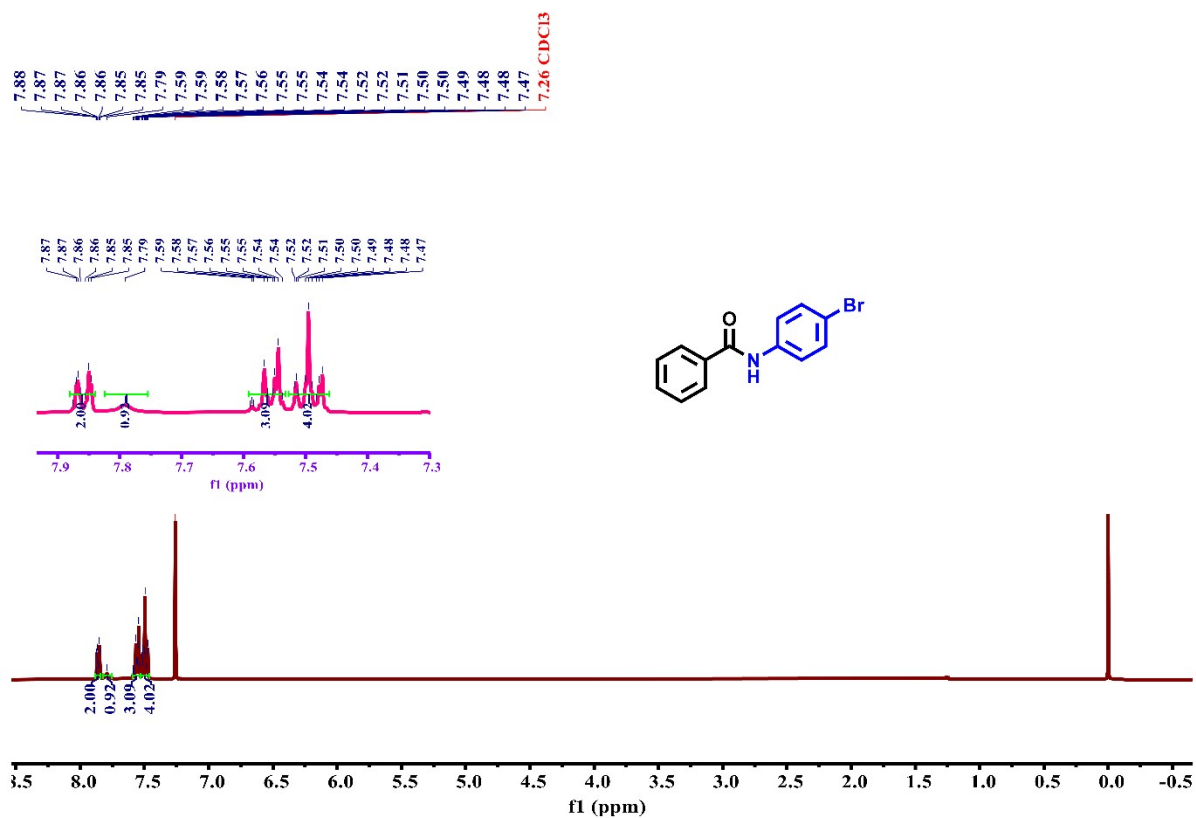
Scheme 1, Entry 8



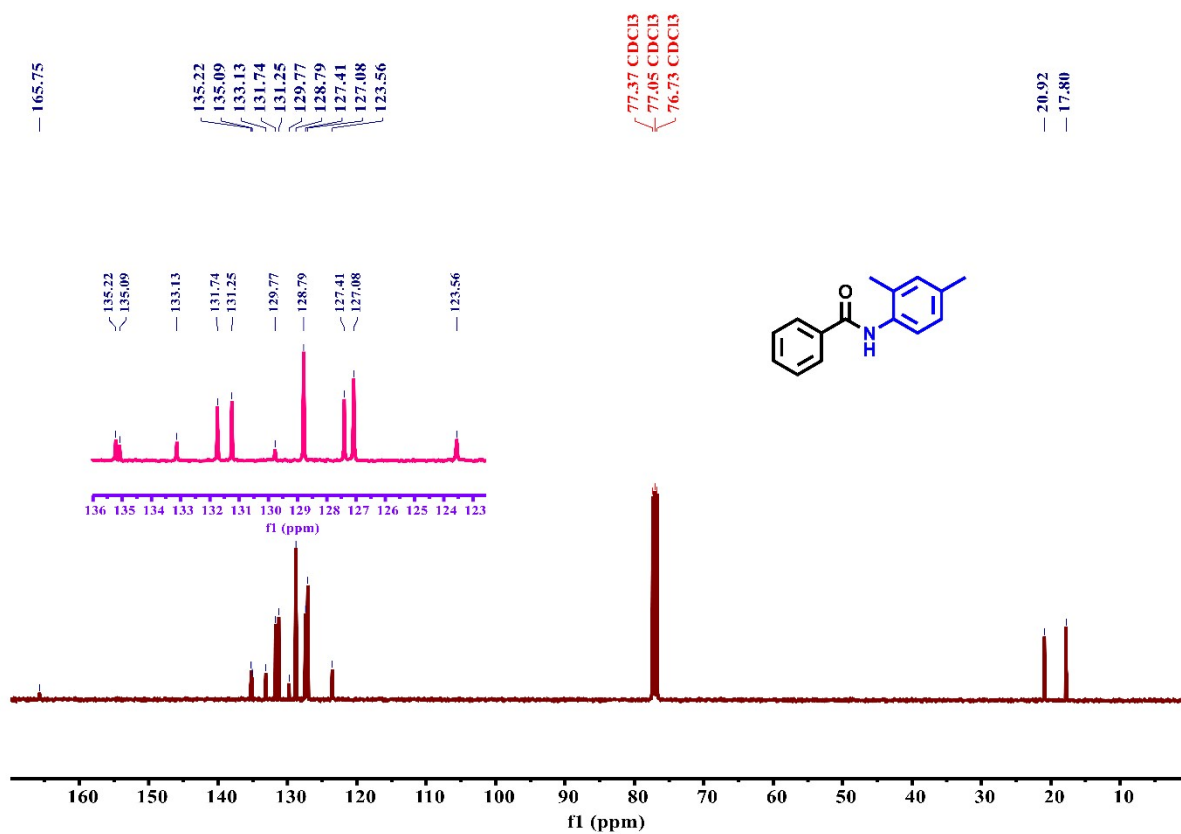
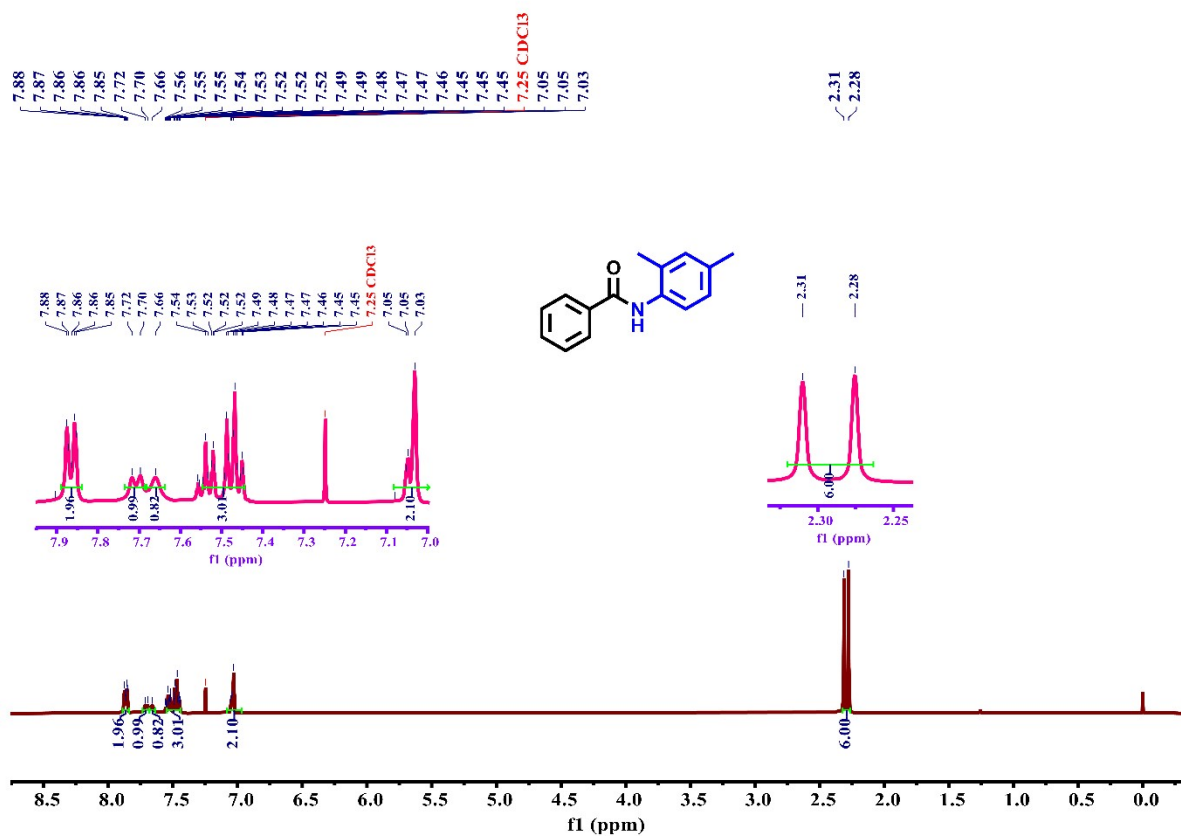
Scheme 1, Entry 9



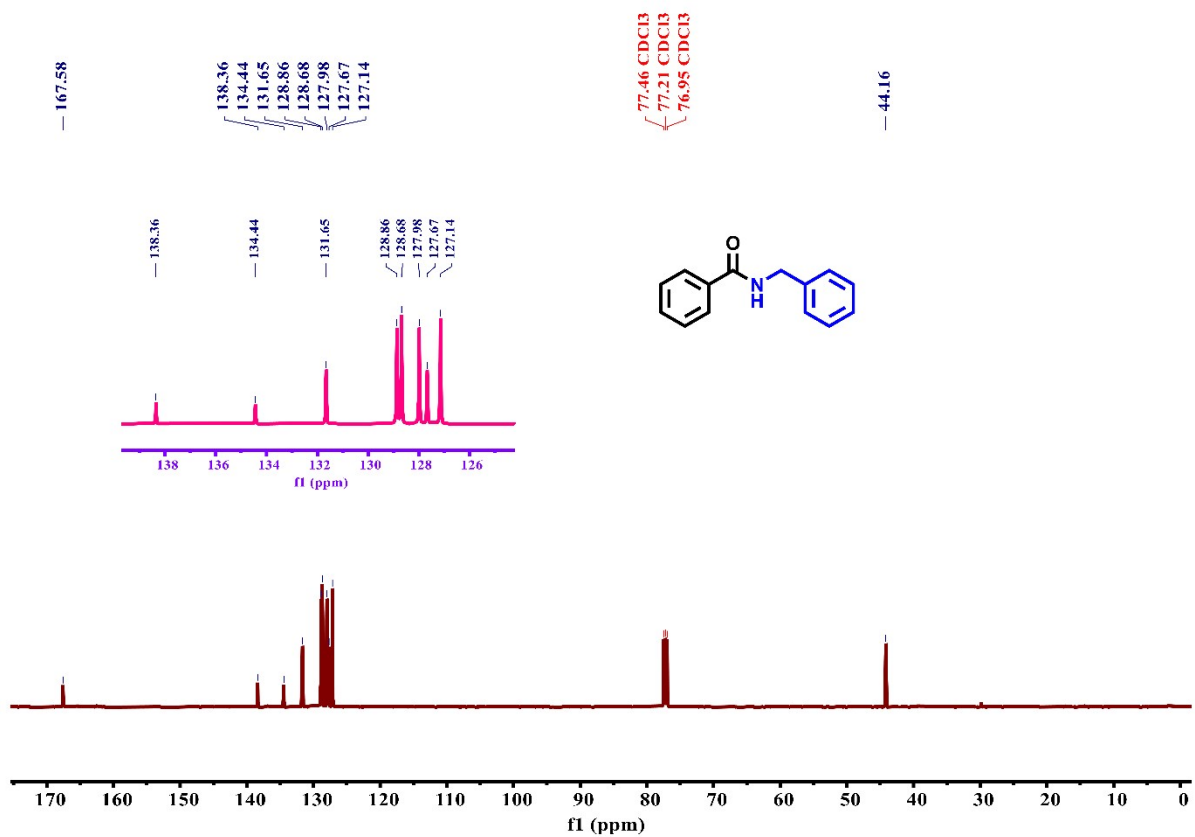
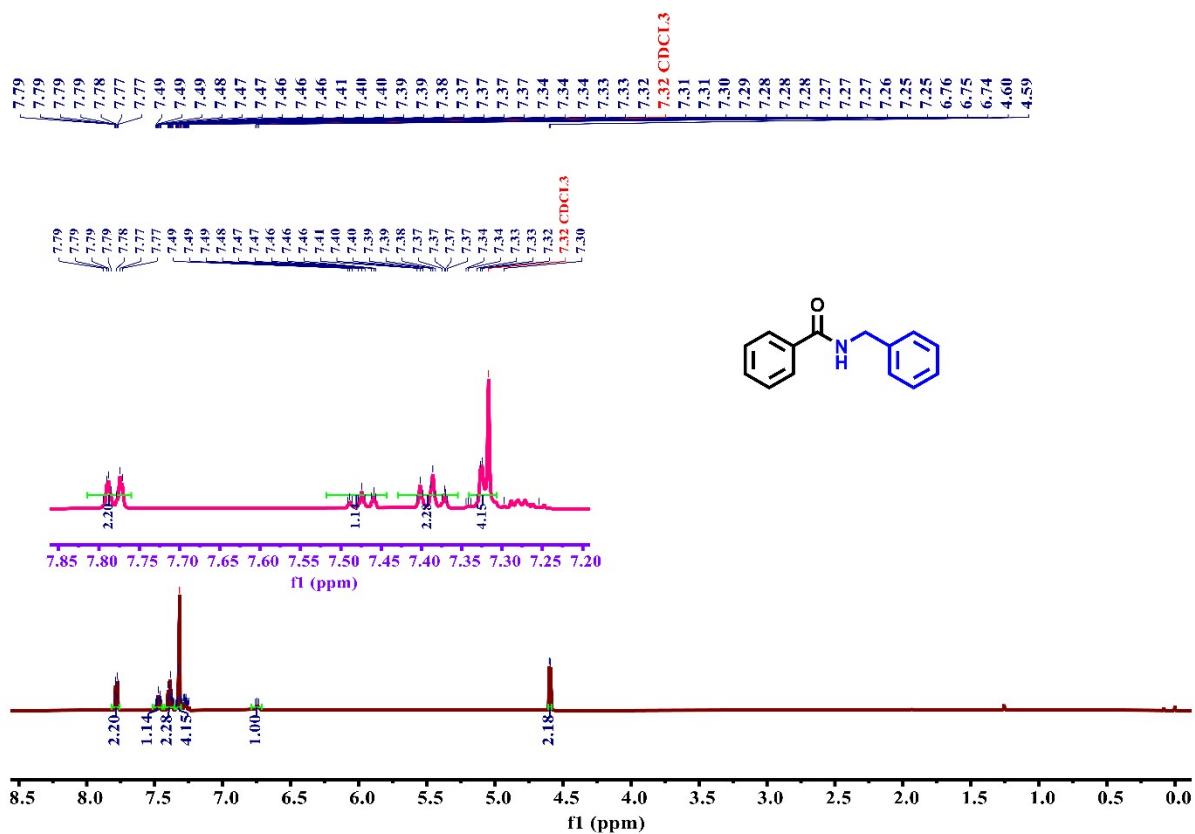
Scheme 1, Entry 10



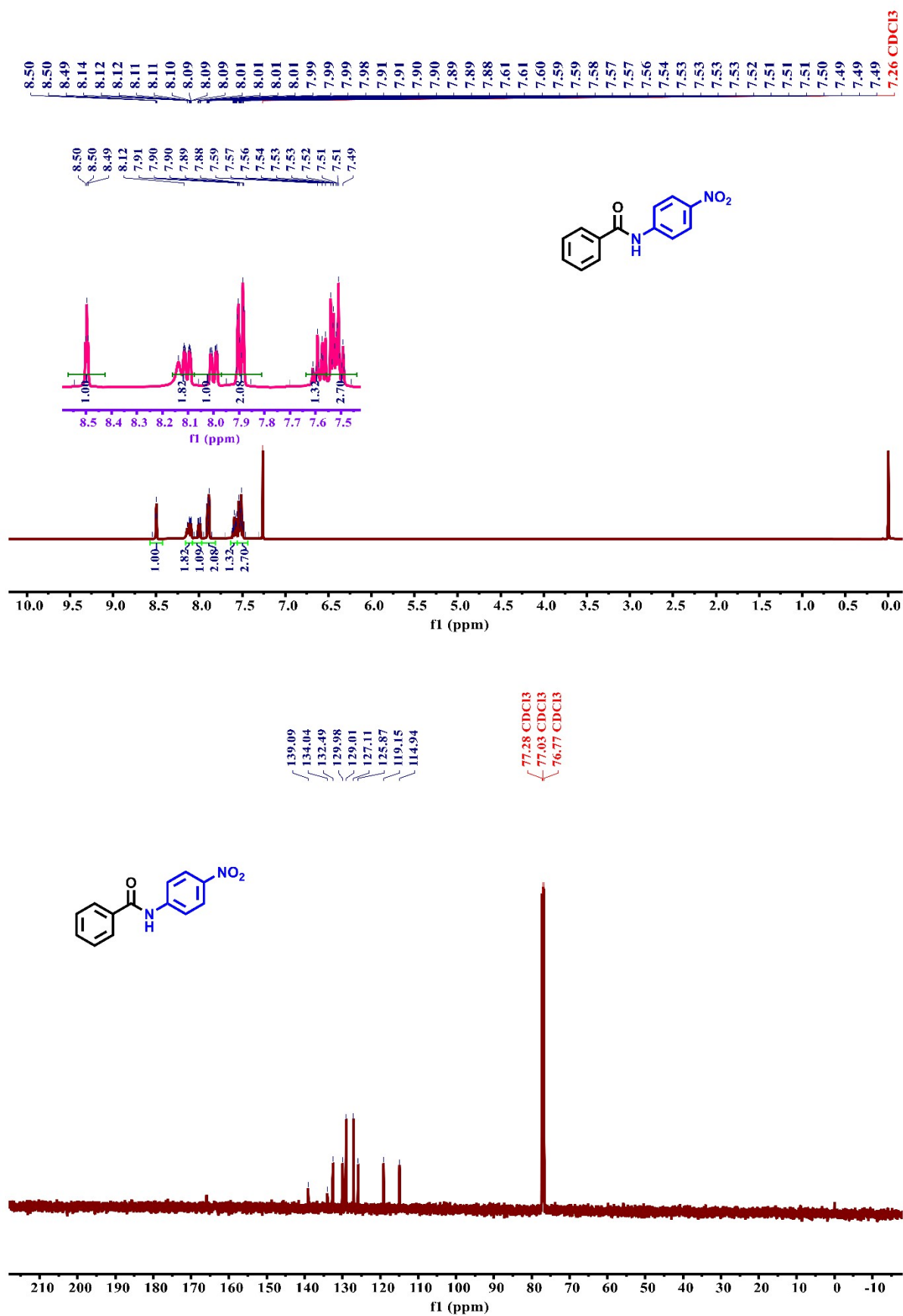
Scheme 1, Entry 11



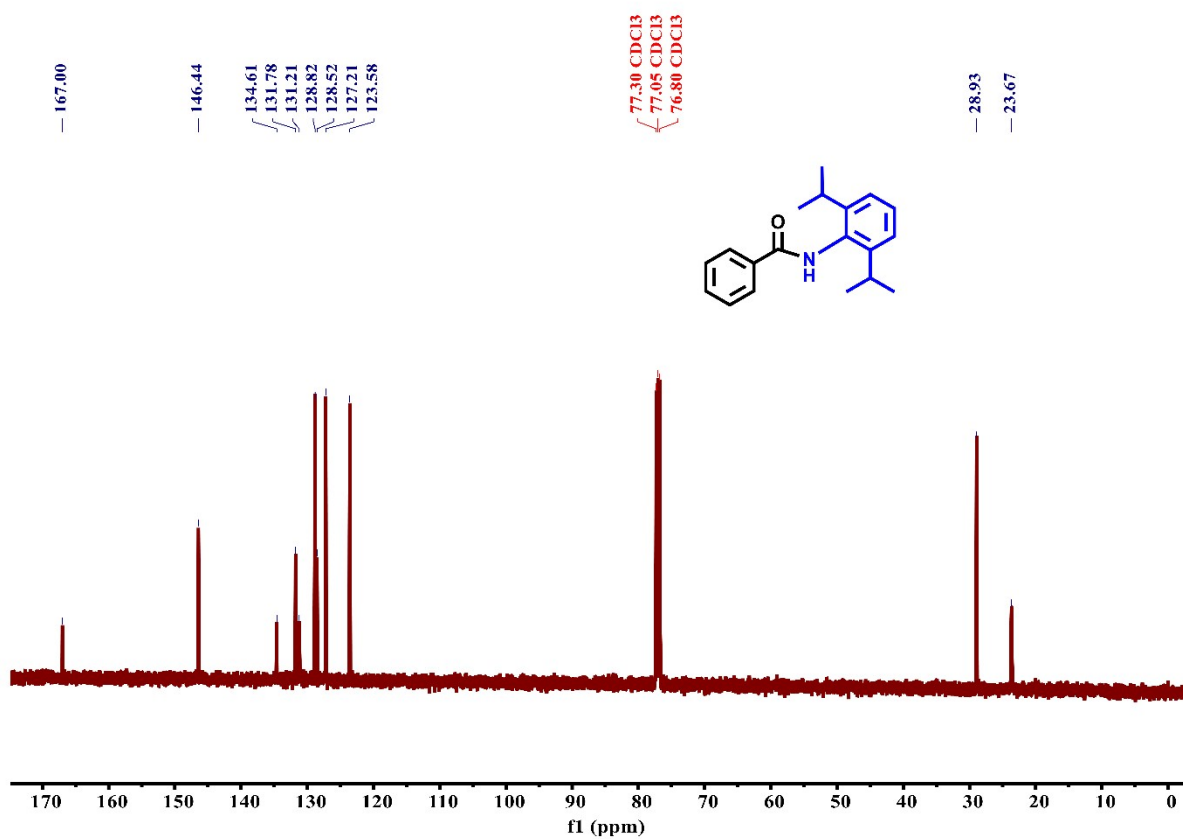
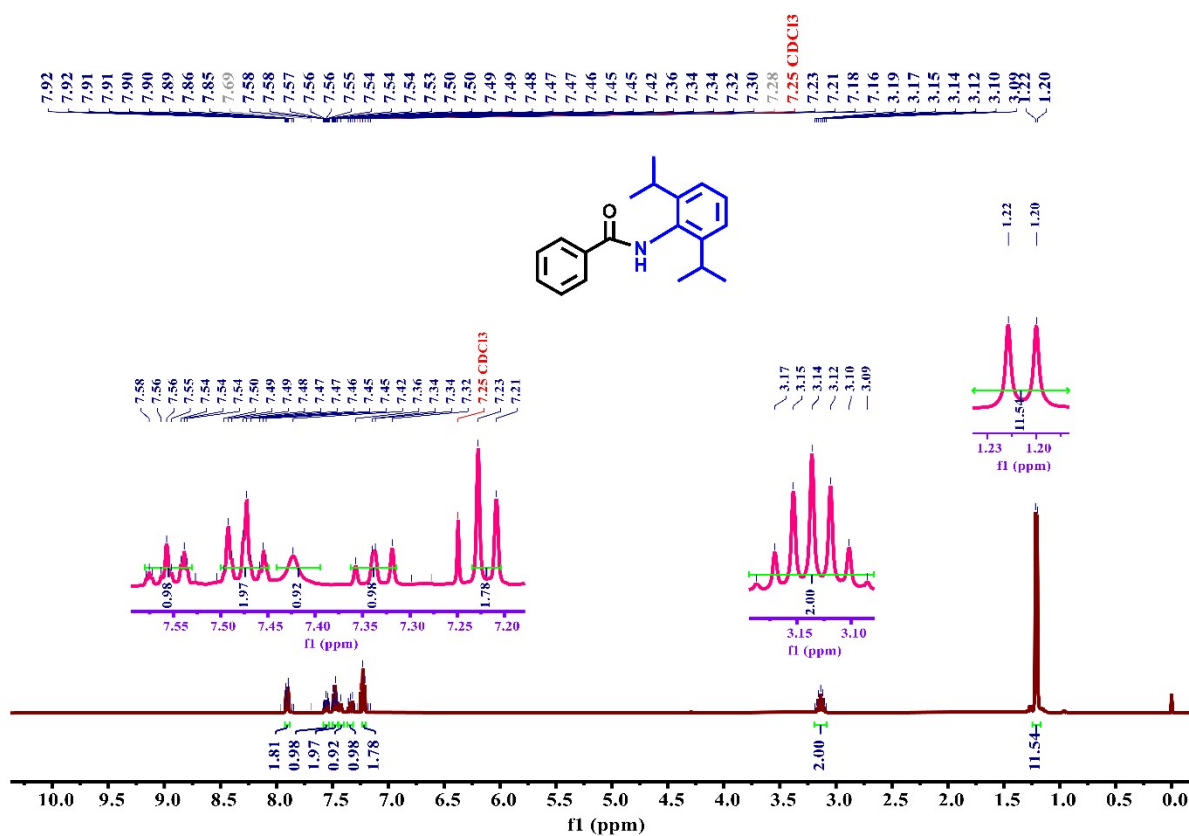
Scheme 1, Entry 12



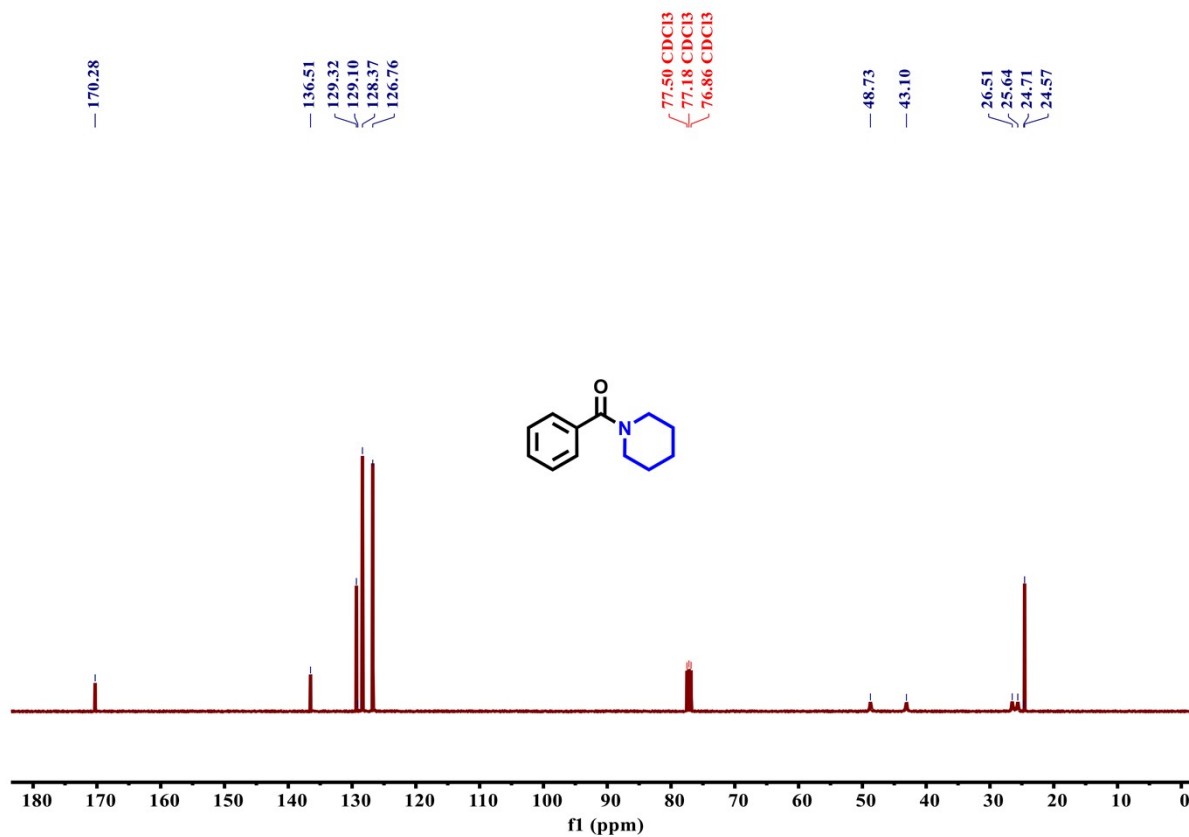
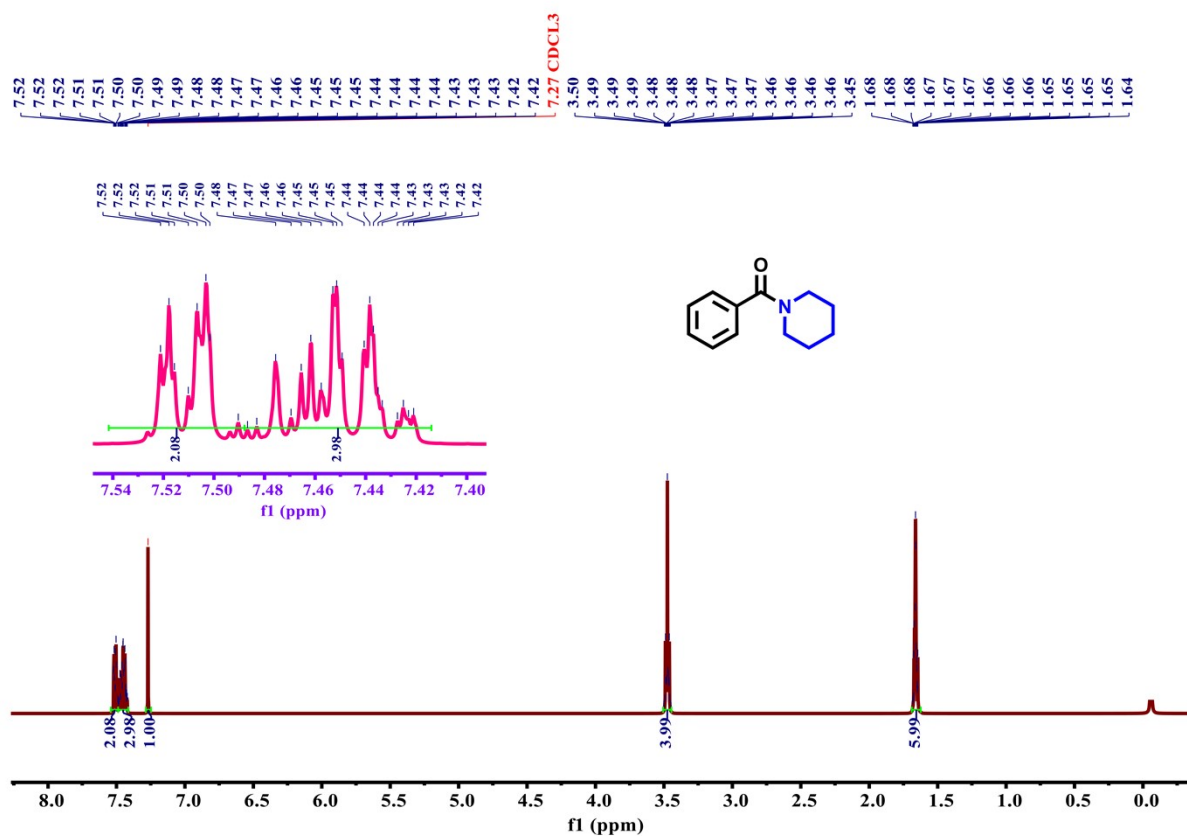
Scheme 1, Entry 13



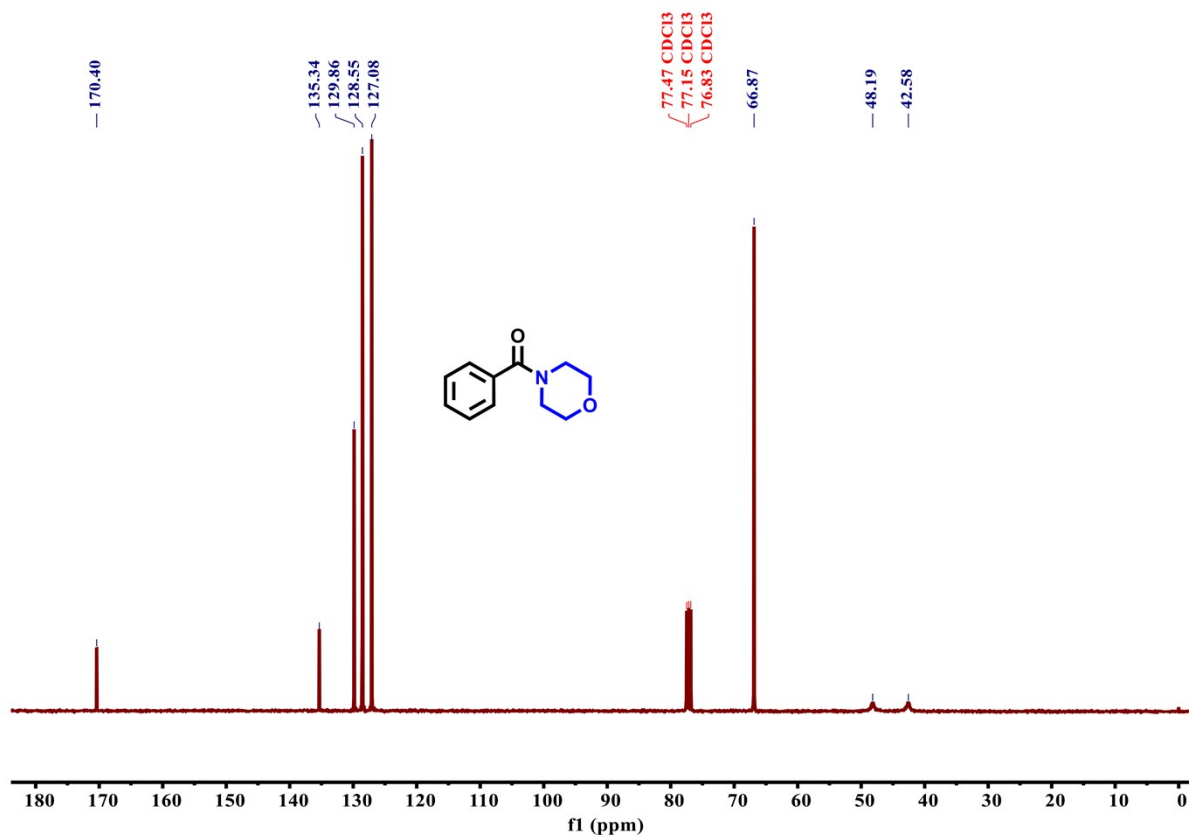
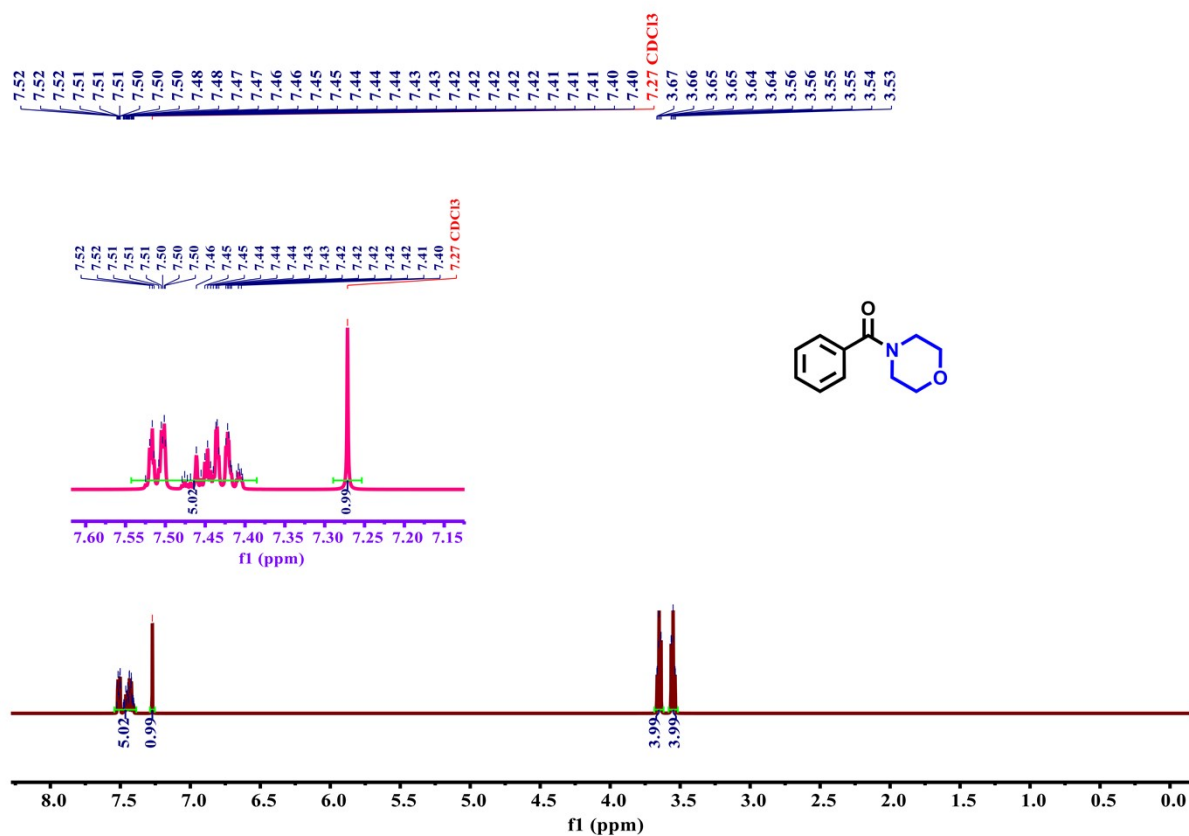
Scheme 1, Entry 14



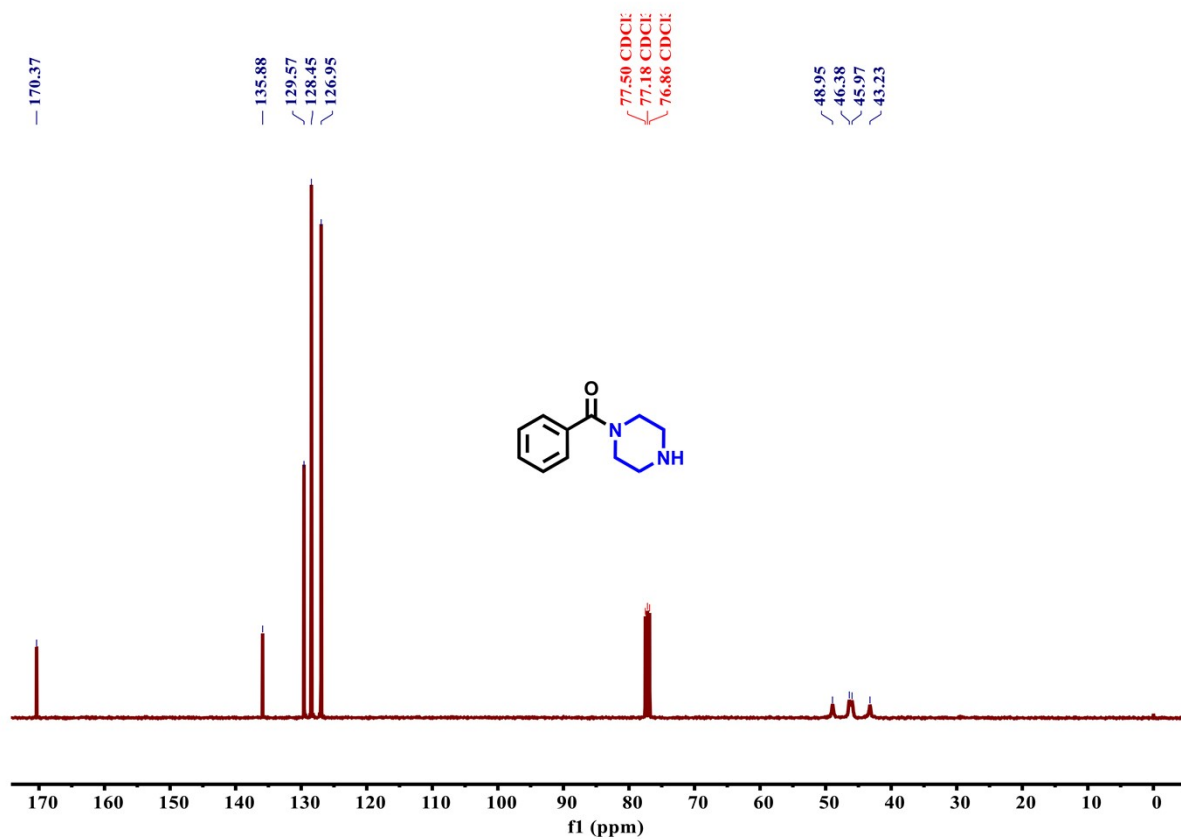
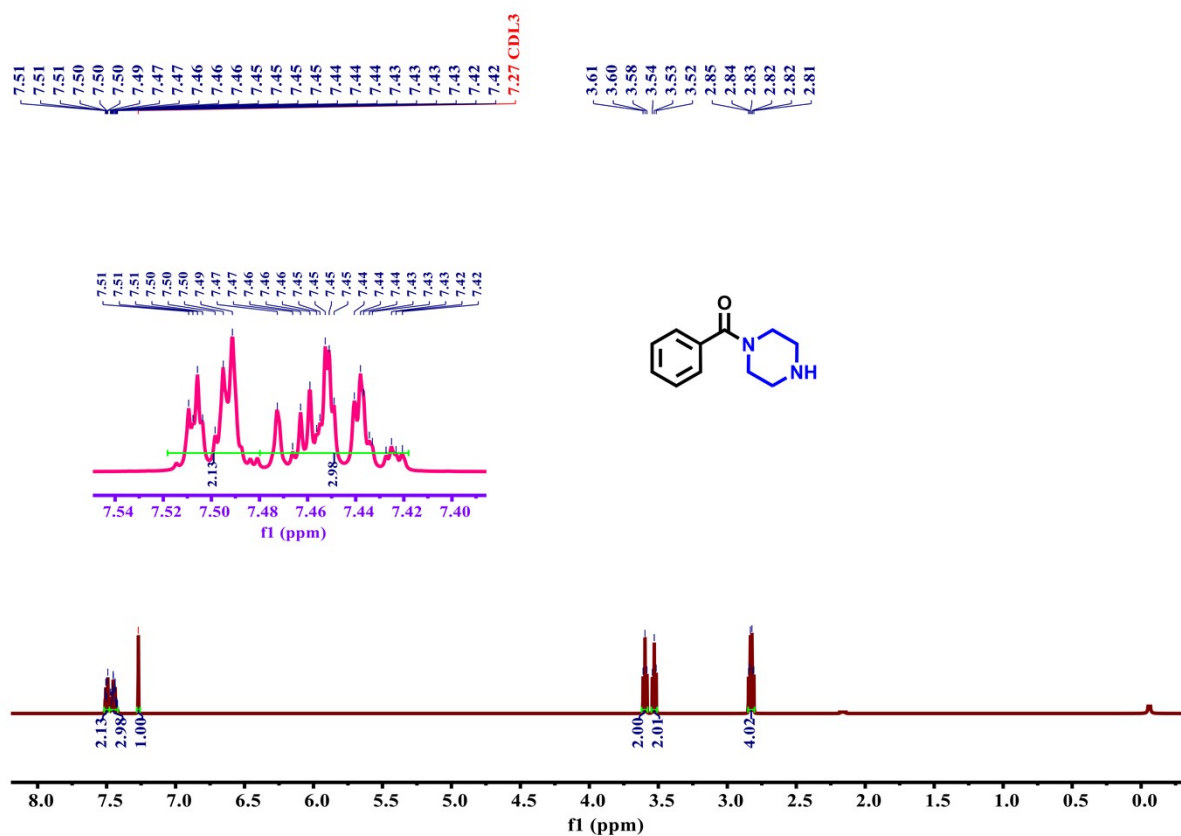
Scheme 2, Entry 15



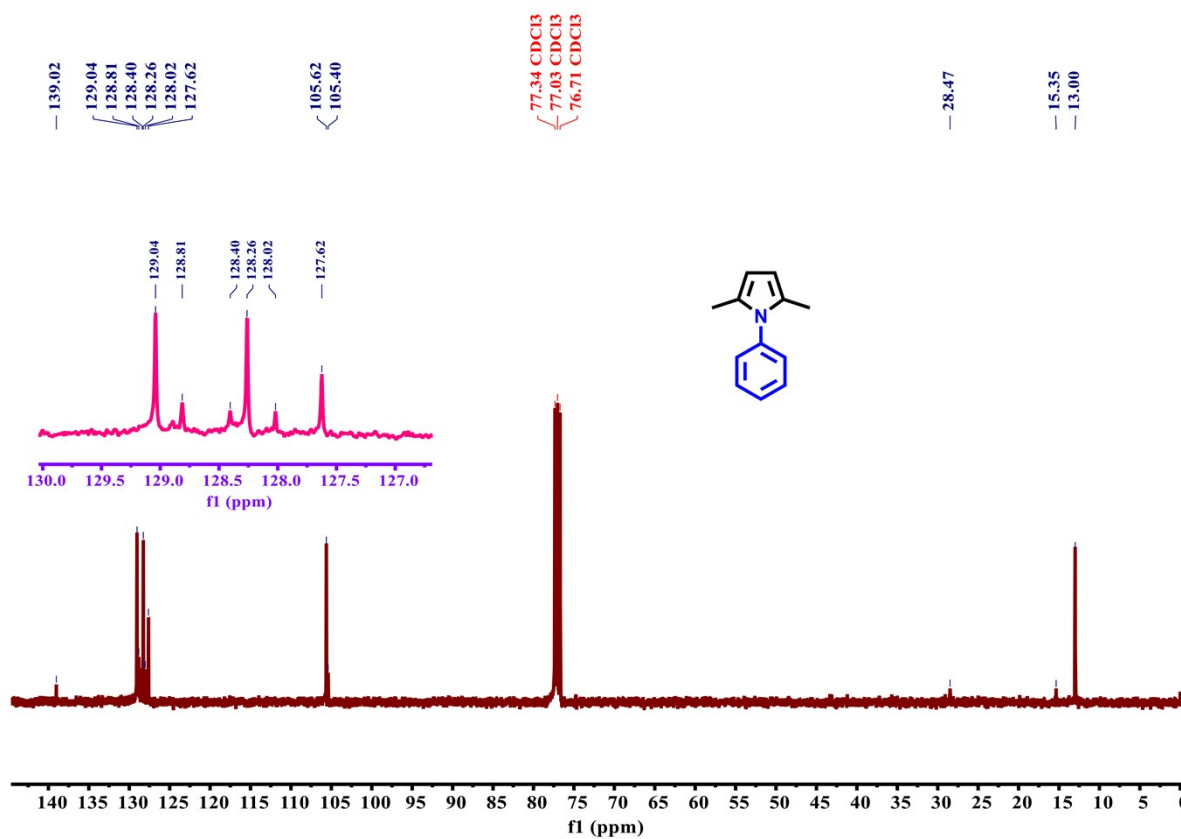
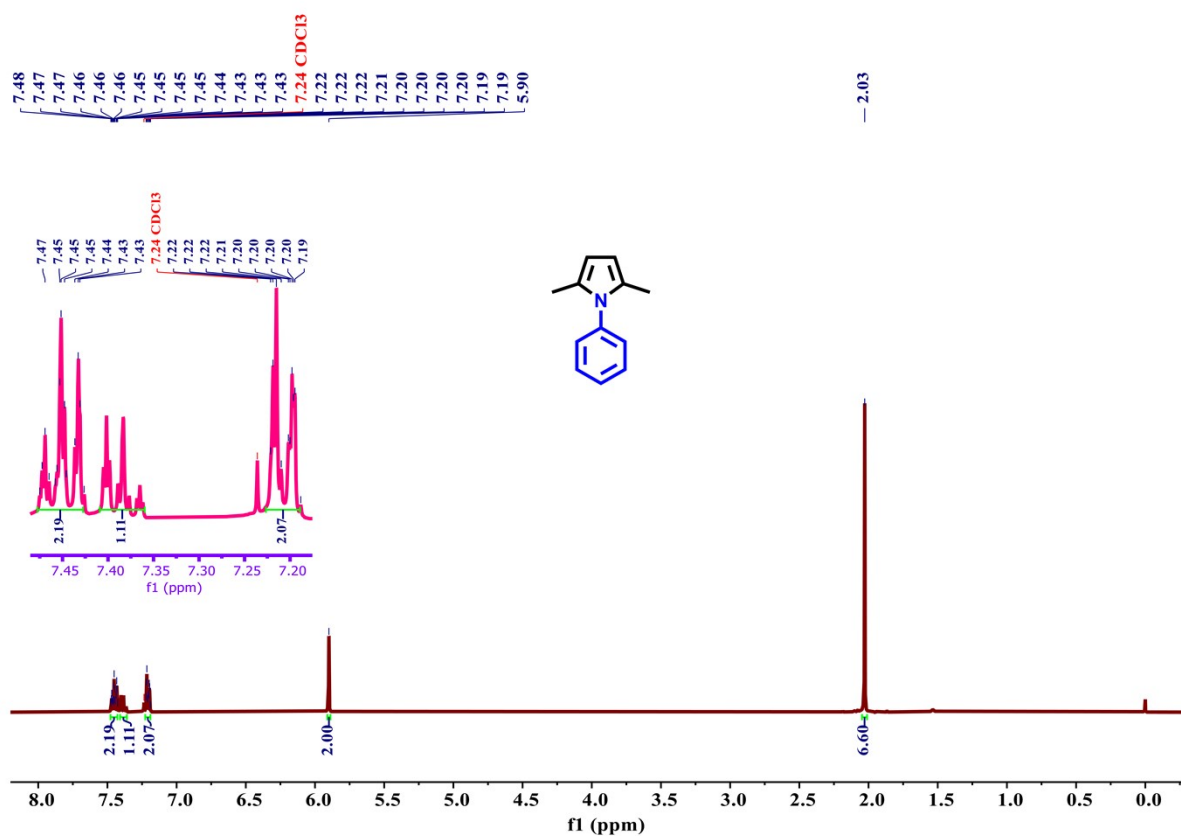
Scheme 2, Entry 16



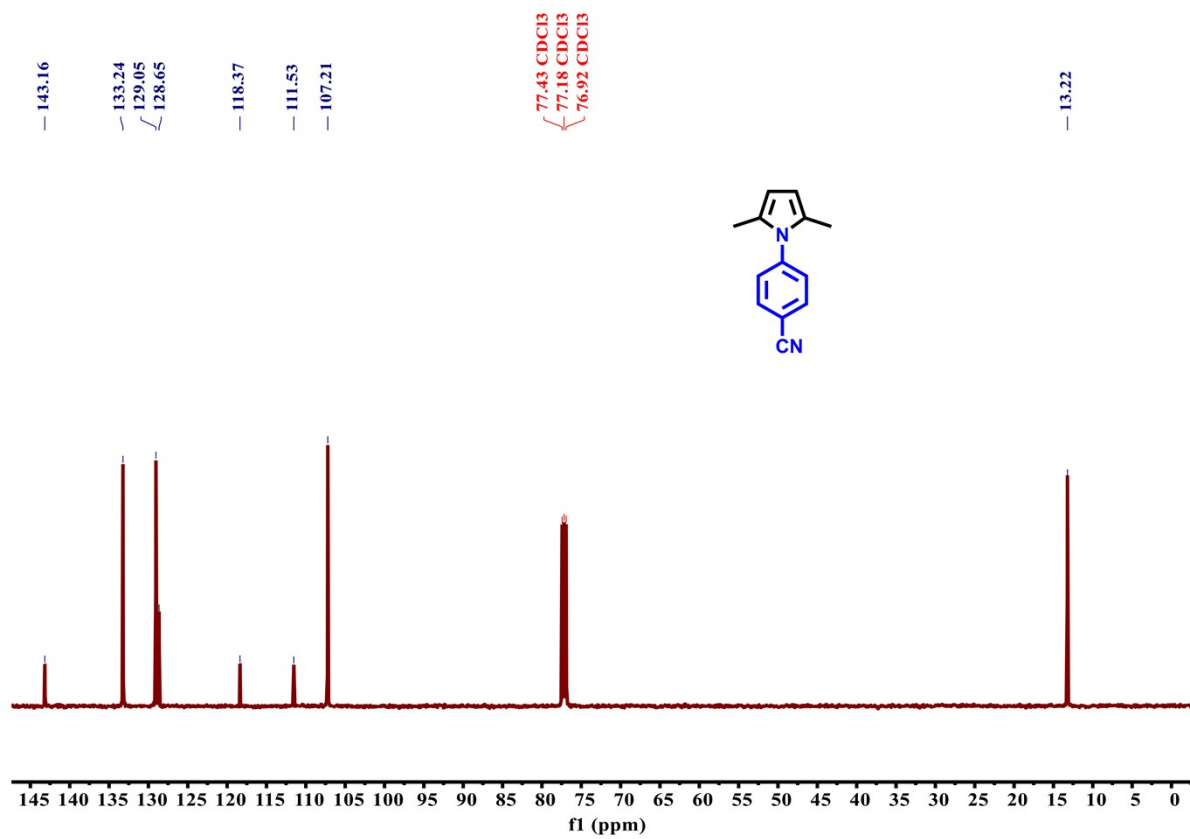
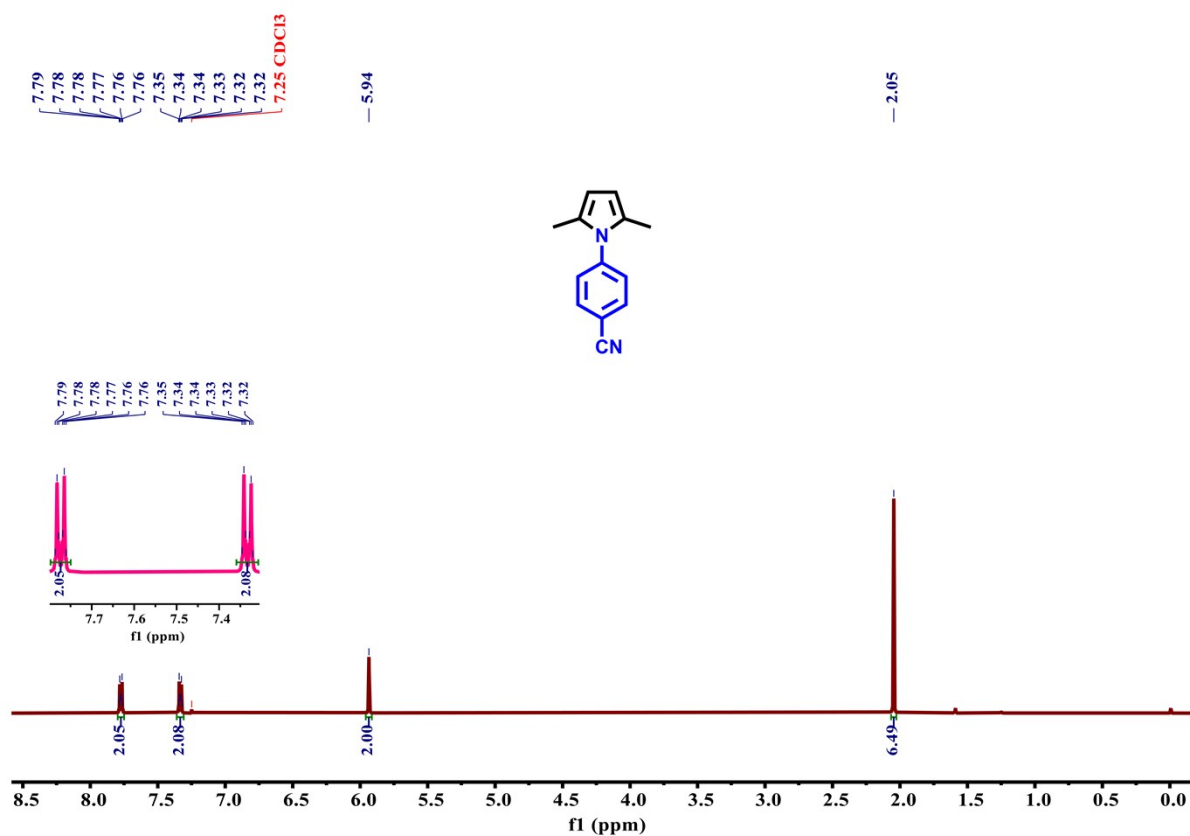
Scheme 2, Entry 17



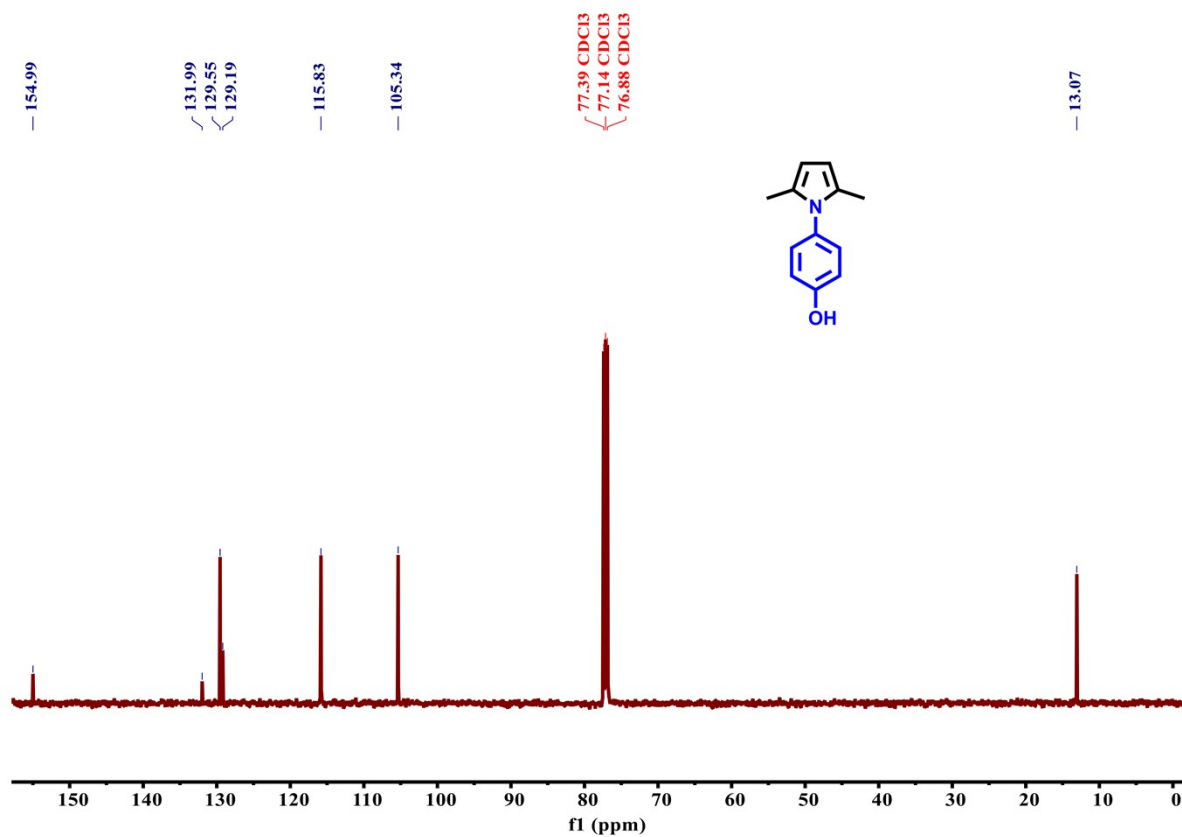
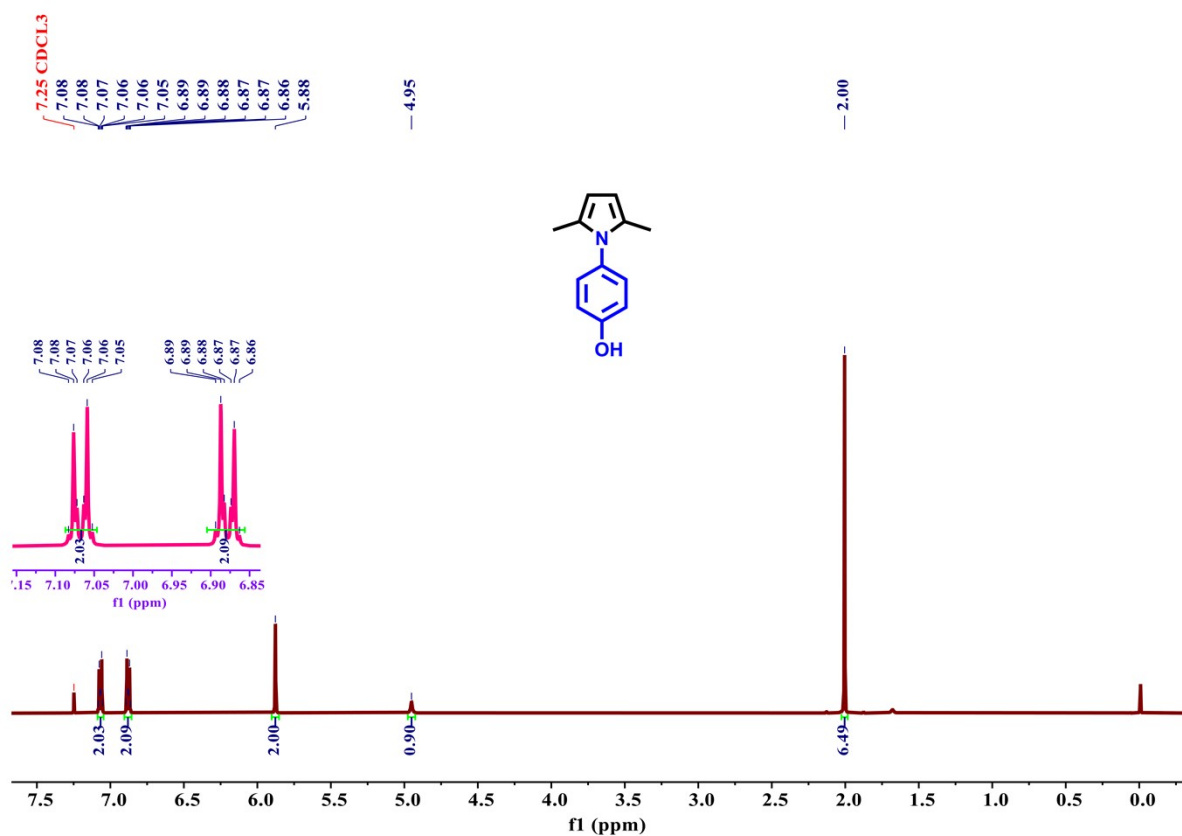
Scheme 3, Entry 19



Scheme 3, Entry 20



Scheme 3, Entry 21



Scheme 3, Entry 22

