Supporting Information

Utility of a Rh(III) embedded covalent organic polymer as an efficient photocatalyst for visible-light driven N-formylation of amines and CO_2 reduction under green and sustainable condition

Rhitama Mandal[a], Amitesh Roy[a], Titu Mondal[a], Priyanka Sarkar[a], Subhas Chandra Debnath[a], Swarbhanu Ghosh [b], Aslam Khan,[c] Sk. Manirul Islam[a ,*]

[a]Department of Chemistry, University of Kalyani, Kalyani, Nadia, W.B., India.Pin-741235

[b]Department of Chemistry, McGill University, Montreal, QC, Canada.

[c]King Abdulla Institute of Nanotechnology, King Saud University, Riyadh, 11451, Saudi Arabia

[*]Corresponding Author: Prof. Sk. Manirul Islam *Email: manir65@rediffmail.com

Table of Contents:

1. Instumentation:

Absorption spectroscopy: UV-Vis absorption spectra of the catalyst was recorded on SHIMADZU, UV-2600 UV-Vis spectrometer with a standard 1 cm x 1 cm cuvette.

NMR Spectra: ^{1}H-NMR (Proton nuclear magnetic resonance spectra) were performed on a Bruker 400 MHz spectrometer. Chemical shifts for protons are reported in parts per million (ppm).

PXRD: The PXRD analysis of the photocatalyst (Rh(III)@TPDB) was executed by using an X-ray diffractometer (BRUKER, Powder X-Ray eco D8 ADVANCE) equipped with Ni-filtered Cu Kα (λ= 0.15406 nm) radiation.

IR Spectra: The FTIR spectra of the synthesized and starting materials were conducted by using a Perkin-Elmer spectrophotometer (FT-IR 783) on KBr Pellets.

FE-SEM: FE-SEM images of the catalyst were acquired by using Scanning Electron Microscope (SEM) [JEOL JSM IT 300], which help to know about the morphological information of the sample.

ICP-OES: Inductively coupled plasma spectroscopy (ICP-OES) measurements were conducted using an iCAP 7400 Plus series.

TEM: Transmission Electron Microscope (TEM) [JEOL JEM 2100] was used to get The morphological information of the sample.

BET: The N_2 adsorption-desorption analysis of Rh(III)TPDB sample was conducted by using a BET Surface Analyzer [QUANTACHROME ASIQCOV602-5].

XPS: X-ray photoelectron spectroscopy was executed by using an Omicron Nanotechnology GmbH XPS machine.

Fluorescence Spectroscopy: The Fluorescence Emission spectra was recorded by using Horiba Fluoro Max 4 spectrometer.

EIS analysis: The measurements have been performed in 0.1 M PBS solution and a conventional three-electrode system where COP on the glassy carbon electrode is used as the working electrode and double junction Ag/AgCl saturated with 3.0M KCl is used as a reference electrode. The Platinum wire served as a counter electrode. The electrochemical impedance spectroscopy (EIS) has been carried out in the frequency range of 100 kHz -0.01 Hz with an AC amplitude of 10 mV at a constant the applied potential of 5 mV.

Electrochemical Paramagnetic Resonance (EPR): Electron Paramagnetic Resonance (EPR) spectroscopy was studied by a Bruker spectrometer (Bruker, EMXmicro) operating at X-band frequency (Microwave frequency 9.31 GHz) and magnetic field modulation of 100 kHz, with a microwave power of 48.83 mW and modulation amplitude of 10 G at 85 K.

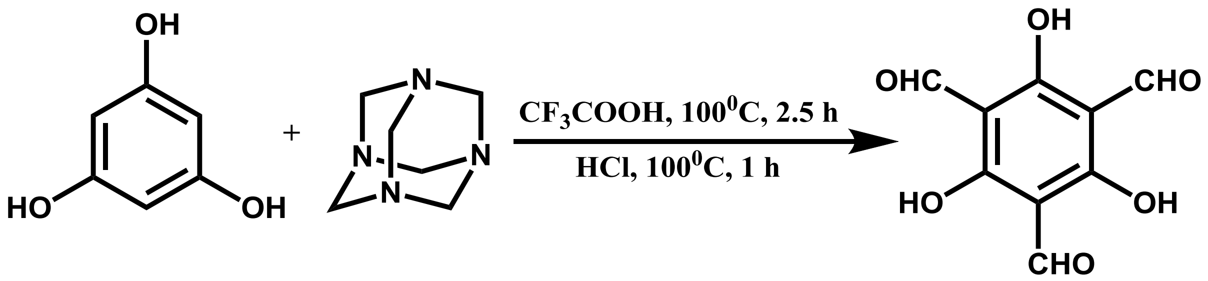
GC: To detect methanol, gas chromatography was done in Varian 430-GC machine.

GC/MS: The detection of methanol in the reaction mixture was conducted by Agilent 7000D Triple Quadrupole GC/MS.

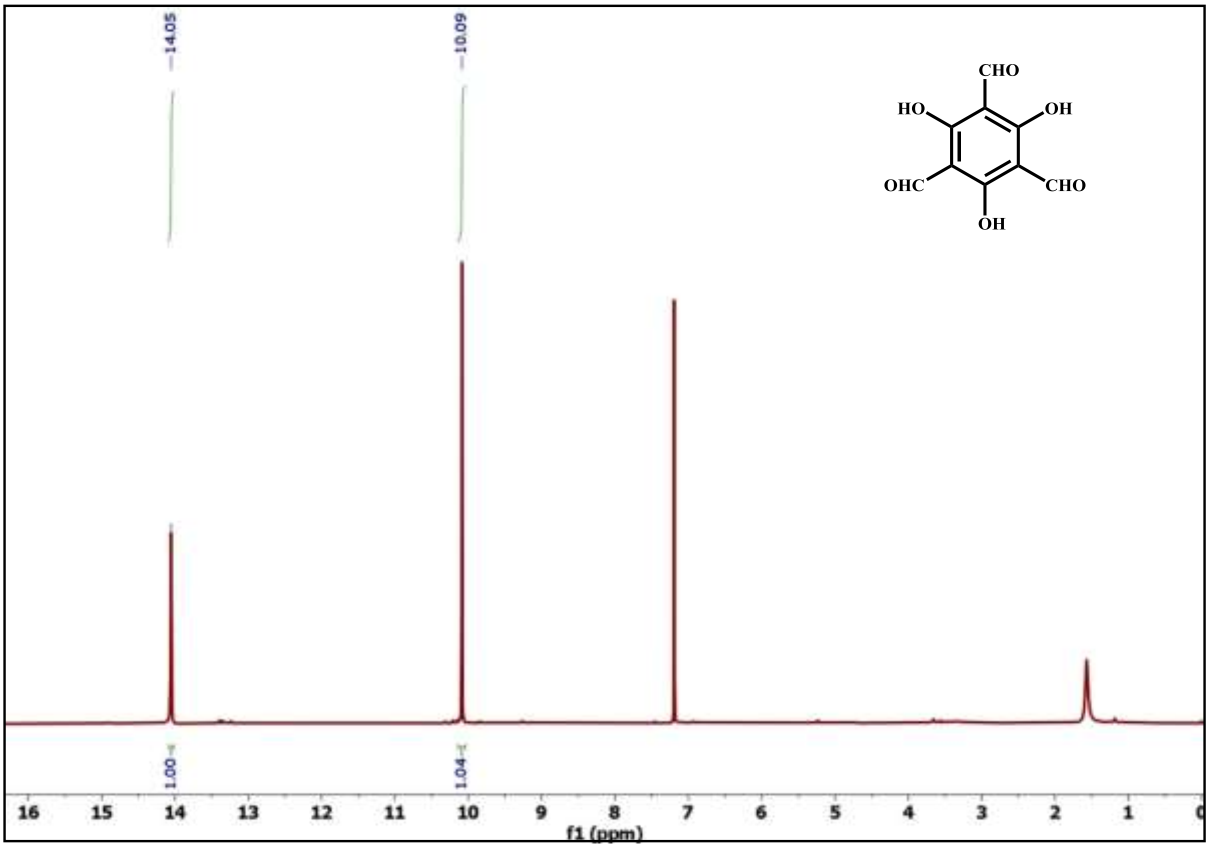
2. Chemicals:

All chemicals were purchased from commercially available sources (e.g. Sigma-Aldrich, TCI, Spectrochem, ThermoFisher, BLD etc) and used as received without further purification. Solvents were distilled and dried through standard methods before use.

3. Synthesis 1,3,5-triformylphloroglucinol [1]:



A mixture of hexamethylenetetramine (15.098 g, 108 mmol) and phloroglucinol (6.014 g, 49 mmol) were added slowly in cold trifluoroacetic acid (90 mL) under an N_2 atmosphere. The reaction mixture was heated at 100 ^{0}C for 2.5 h, then added HCl (3 M, 150 mL) and heated at 100 ^{0}C for another 1 h. After being cooled to room temperature, the solution was extracted with dichloromethane (4 times) and dried over sodium sulfate, and filtered. The obtained extract was concentrated to yield yellow coloured solid (using rotary evaporation) and the obtain crude solid was purified by hot ethanol to yield desired product.



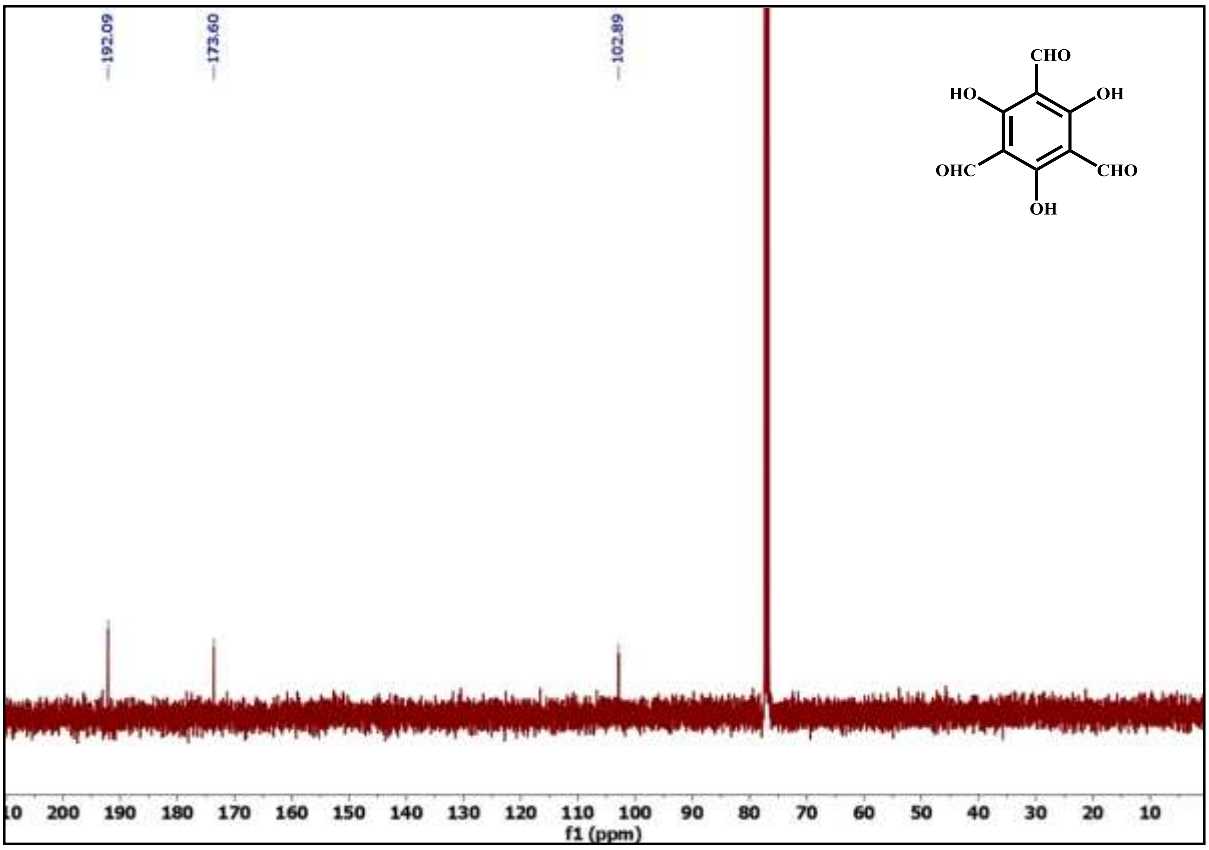


Figure S1: ^{1}H-NMR and ^{13}C-NMR Spectra of 1,3,5-Triformylphuloroglucinol

4. Synthesis of TPDB:

This COP material was prepared using a Schiff-base condensation polymerization method. The reaction involved 1,3,5-triformyl-phloroglucinol (TP: 0.063 g) and 3,3′-diaminobenzidine (DB; 0.048 g) in a mesitylene:dioxane (M:D=1:1) solvent, along with 0.5 mL of 6 M acetic acid as a catalyst. The reactants were initially combined in a Pyrex tube using sonication for 30 minutes to create a completely homogeneous mixture. The tube was then sealed by flame and placed in a 120 °C oven for 72 hours. After this period, the deep red material was filtered and sequentially washed with dioxane, water, and acetone, before being dried under vacuum at 70 °C for 12 hours to yield the benzimidazole-based covalent organic polymer material TPDB.

5. Synthesis of Rh(III)@TPDB:

Rh(III)TPDBCOP was synthesized using a straightforward one-step ultrasonic impregnation reduction technique at ambient temperature (298 K). In a typical procedure, 66 mg of TPDB powder was mixed with a solvent blend of methanol (MeOH, 1.67 mL) and dichloromethane (DCM, 1.33 mL), then carefully added to a two-necked flask and stirred for 20 minutes. Afterward, a 1 mL MeOH solution containing 0.0125 mmol $RhCl_3$ was added and subjected to ultrasonic impregnation for 60 minutes. Inductively coupled plasma spectroscopy (ICP-OES) revealed a Rh loading of 3.87% in the Rh(III)@TPDB COP Catalyst.

6. Photocatalytic N-formylation of amines using Rh(III)@TPDB COP:

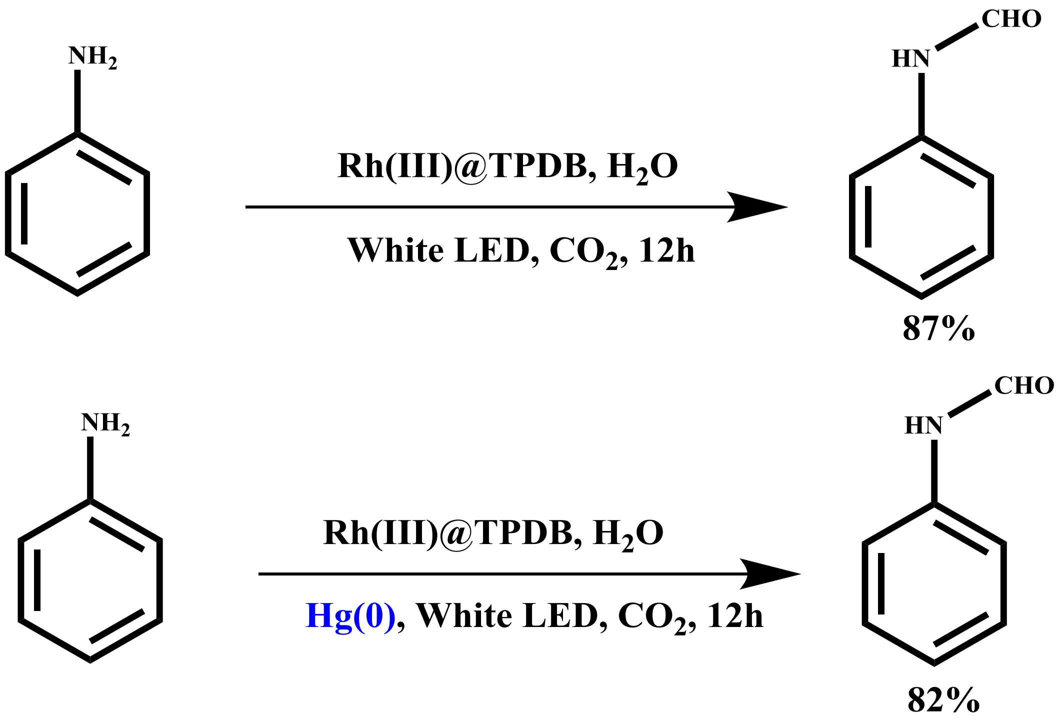
In a typical N-formylation procedure, 1 mmol of the relevant amine was mixed in 3 mL water in a 25 ml dried RB. The reaction mixture was degassed to remove the air, with a simultaneous flow of N_2 gas through the solution for 10-15 minutes to create an inert environment, followed by charging with CO_2 gas (1 atm) for another 30 minutes at room temperature. Following that, a specific amount of catalyst, Rh(III)@TPDB(10 mg), was added to the reaction medium and properly sealed with a septum. The reaction mixture was charged with CO_2 gas (1 atm) for additional 30-40 minutes to create CO_2 ambience throughout the container, and then irradiated with a 20 W white LED light while stirring continuously for 12 hours. The reaction's progression was monitored using the TLC technique at various time intervals. After the experiment, the catalyst was removed from the reaction mixture via filtration, and the filtrate was extracted numerous times with diethyl ether. The organic portion was washed away with distilled water and saturated aqua solution of $NaHCO_3$ one-to-one, dried over Na_2SO_4, followed by evaporating to dryness to get the desired compound. After the whole process, the obtained final compound was examined by using ^{1}H-NMR spectroscopy in $CDCl_3$ solvent.

7. **Photocatalytic reduction of CO_2 using Rh(III)@TPDB COP:**

The photocatalytic reduction of CO_2 (1 atm) was carried out under visible light in 4 h using 10 mg of Rh(III)@TPDB COP catalyst in 5 mL of H_2O, with 1 mmol of triethanolamine (TEOA) as a sacrificial electron donor (SED). Following the reaction, the formation of formic acid was confirmed using UV-visible spectroscopy and methanol formation was confirmed and quantified by gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) analyses.

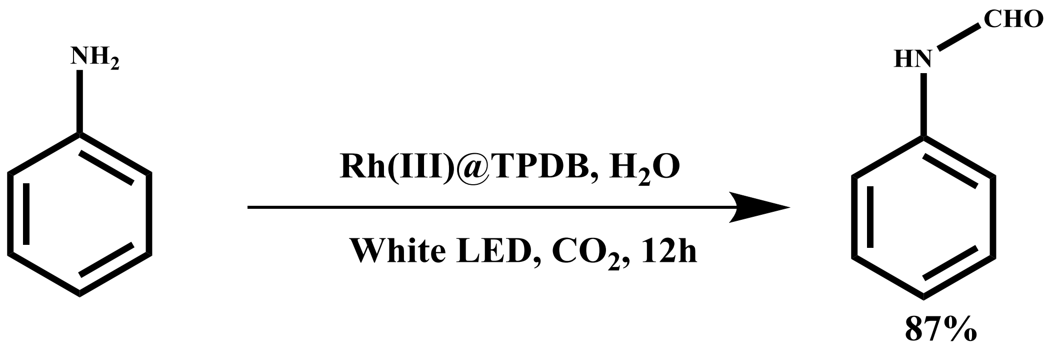
8. Hg poisoning test in the N-formylation of Aniline with Rh(III)@TPDB COP:

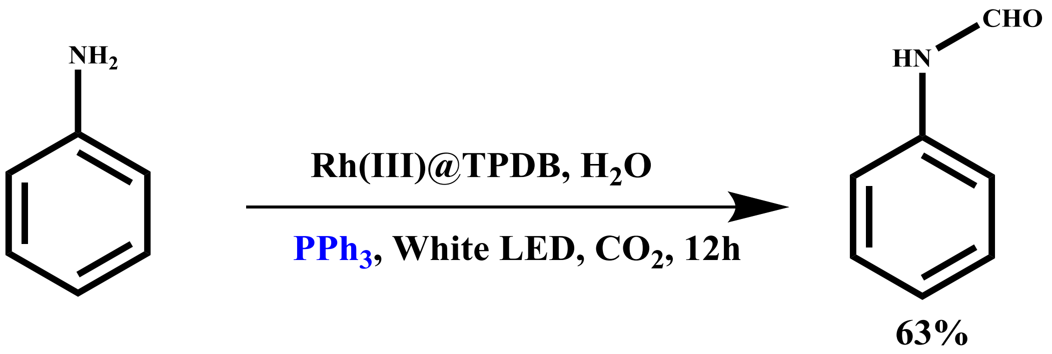
Two different Schlenk tubes containing aniline (1 mmol) and H_2O (3 mL) were charged with 10 mg of Rh(III)@TPDB COP. A drop of mercury was added to one of the reaction mixtures. After charging both reaction mixtures with CO_2 gas (1 atm) for an additional 30 to 40 minutes to establish a CO_2 atmosphere throughout the container, they were exposed to a 20 W white LED light while being constantly stirred for 12 hours. Following the experiment, the catalyst was filtered out of the reaction mixture and the filtrate was extracted using Dichloromethane. There was not much product drop seen above. We thus conclude that any leached Rh nanoparticles were not responsible for the catalytical activity and Rh(III)@TPDB COP was the actual heterogenous catalyst.[3]



9. Surface Blocking Test using triphenylphosphine (PPh_3):

Two separate Schlenk tubes containing aniline (1 mmol) and H_2O (3 mL) were loaded with 10 mg of Rh(III)@TPDB COP catalyst. In one of the reaction systems, triphenylphosphine (PPh_3) was introduced as a surface-blocking ligand. Both reaction mixtures were then purged with CO_2 gas (1 atm) for 30–40 minutes to create a CO_2 -rich atmosphere inside the tubes. Subsequently, the reaction mixtures were irradiated under a 20 W white LED with continuous stirring for 12 hours. After completion of the reaction, the catalyst was separated by filtration and the filtrate was extracted with dichloromethane. A considerable reduction in product formation was observed in the presence of PPh_3 compared to the reaction carried out without PPh_3. This observation suggests that PPh_3 effectively coordinated to the accessible Rh active sites and inhibited their catalytic function. Therefore, the catalytic transformation is mainly attributed to the surface-exposed Rh centers present in the heterogeneous Rh(III)@TPDB COP catalyst.[4]


NH2
Rh(III)@TPDB, H2O
White LED, CO2, 12h
HN
CHO
87%


NH2
Rh(III)@TPDB, H2O
PPh3, White LED, CO2, 12h
HN
CHO
63%

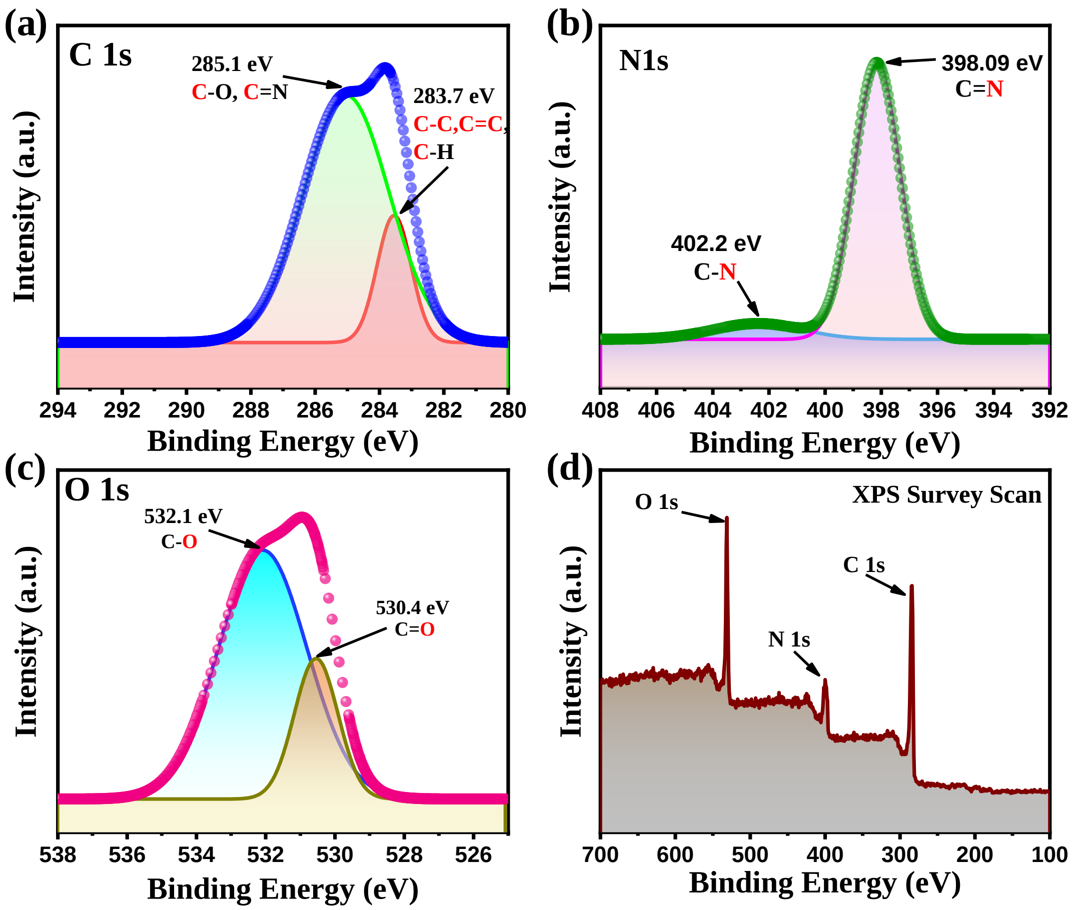


Figure S2. XPS analysis of TPDB COP a) Deconvoluted binding energies of C1s (b), N 1s (c), O1s (d) Full-scale Survey scan

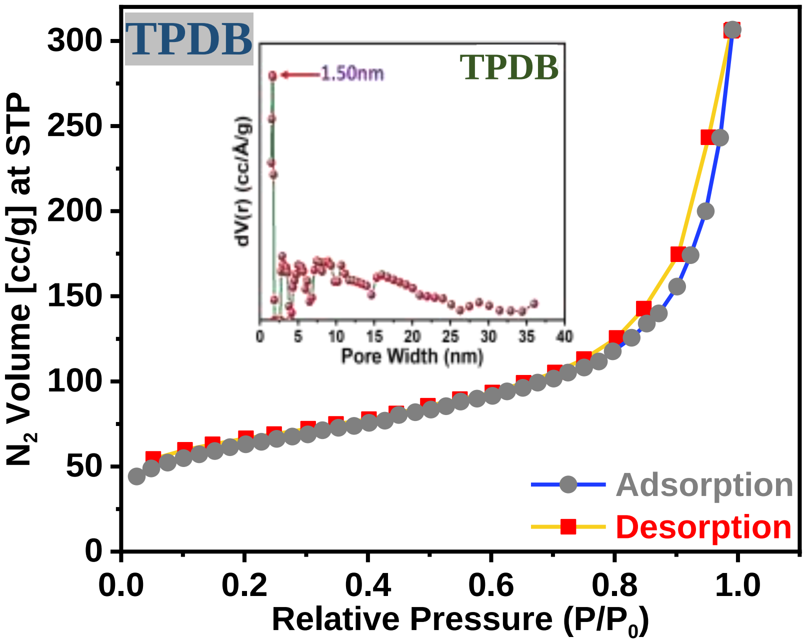


Figure S3. N$_2$ adsorption/desorption isotherm of TPDB COP

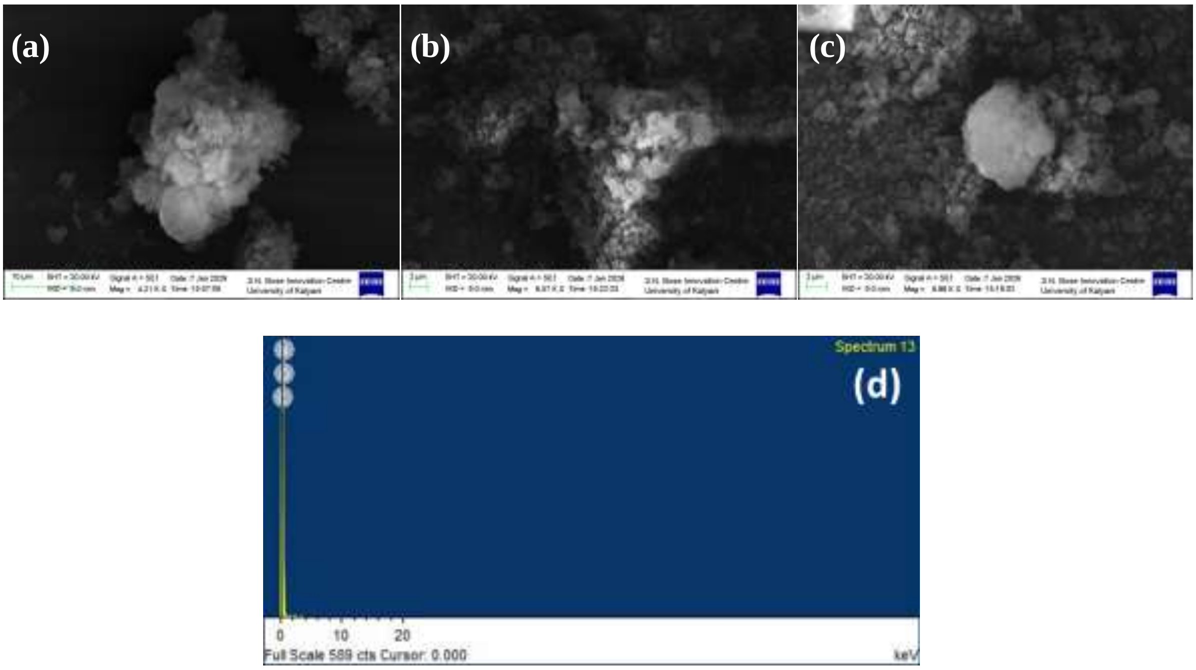


Figure S4. SEM (a, b, c) images, (d) EDAX of TPDB COP

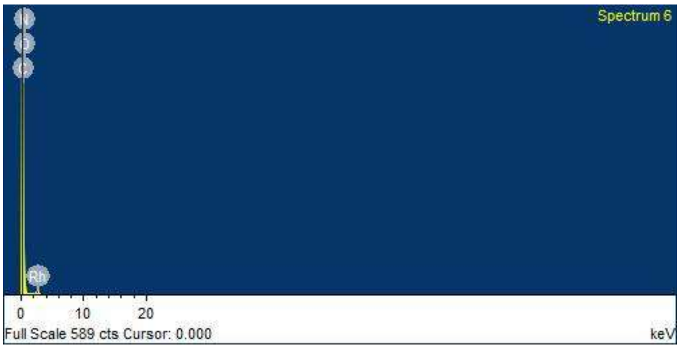


Figure S5. EDAX of Rh(III)@TPDB COP

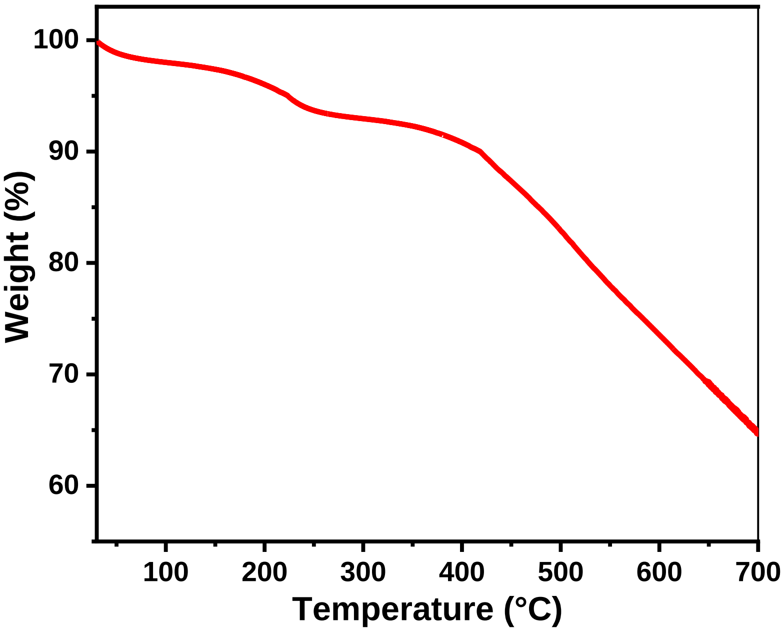


Figure S6. TGA analysis of Rh(III)TPDB COP

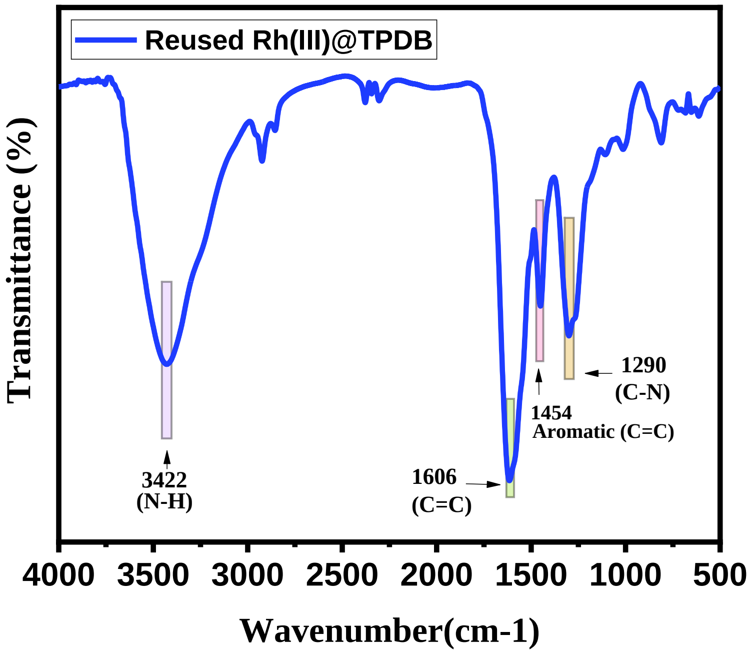


Figure S7. FT-IR Spectra of reused catalyst Rh(III)@TPDB COP

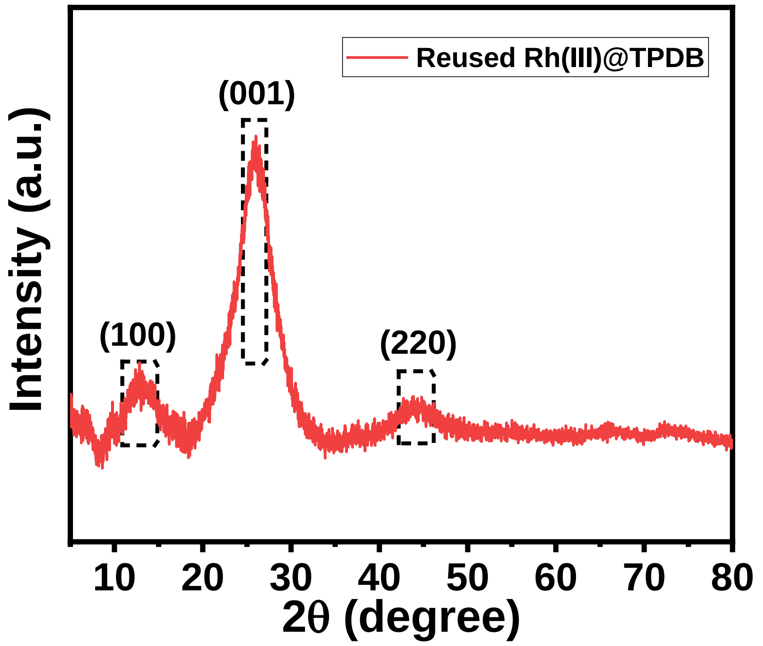


Figure S8. Reused XRD of Rh(III)@TPDB COP

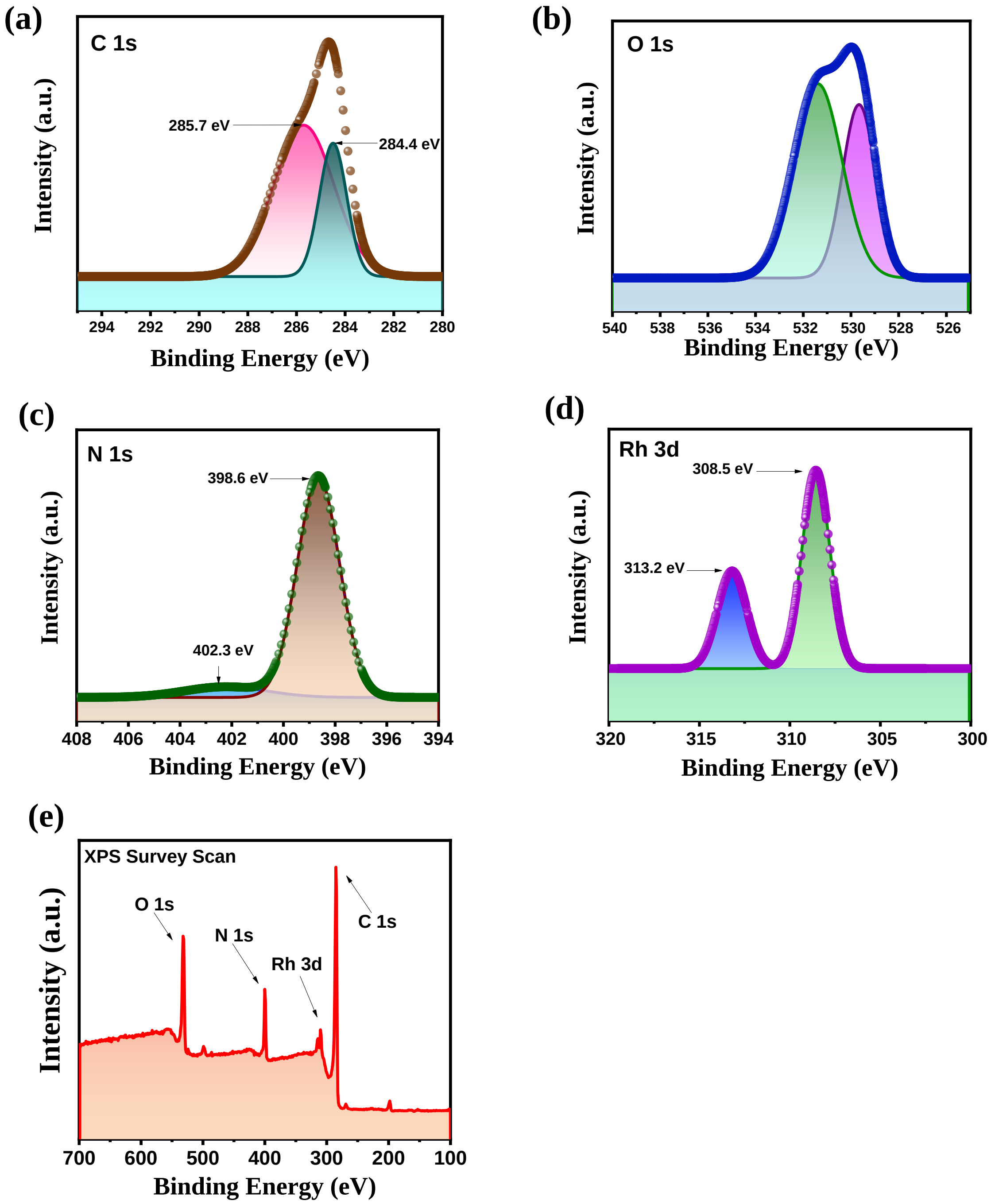


Figure. S9. XPS Analysis of Reused Rh(III)@TPDB COP, a) Deconvoluted binding energies of C1s (b), O1s (c), N1s (d) Rh3d (e) Full-scale Survey scan

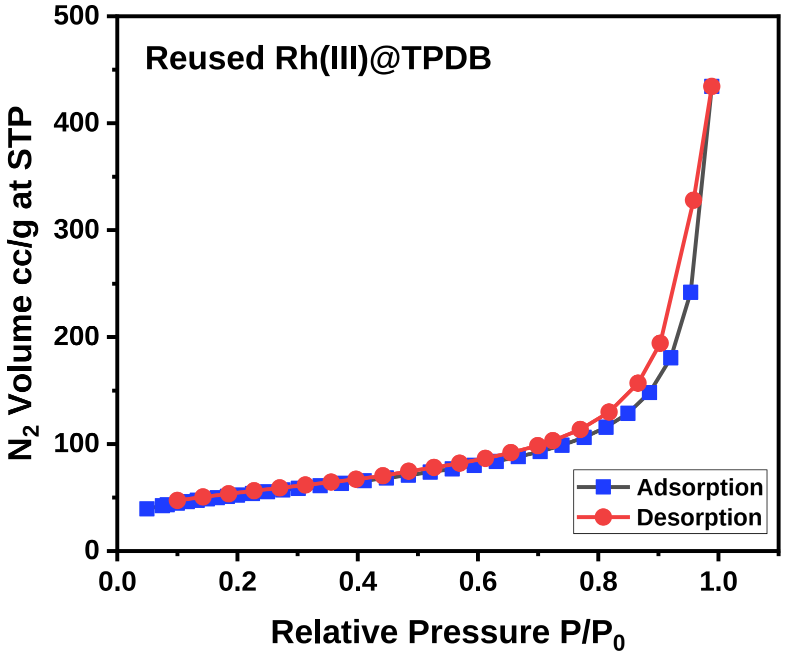


Figure S10. BET isotherm of Reused Rh(III)@TPDB COP

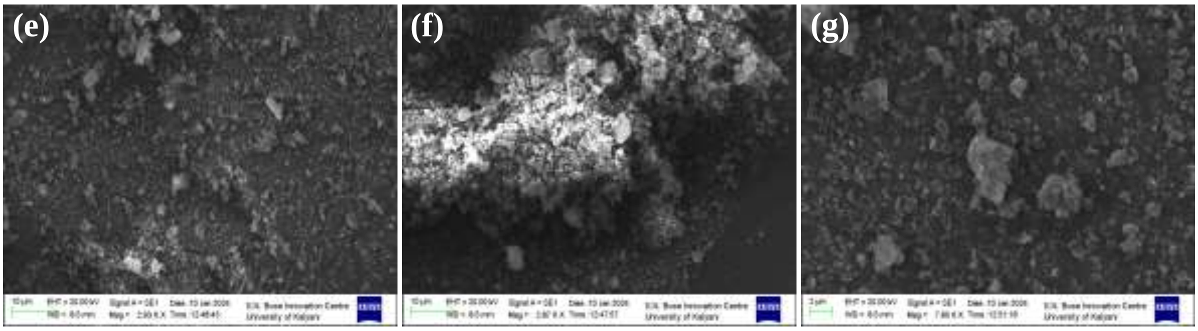


Figure S11. SEM (e, f, g) images of reused catalyst Rh(III)@TPDB COP

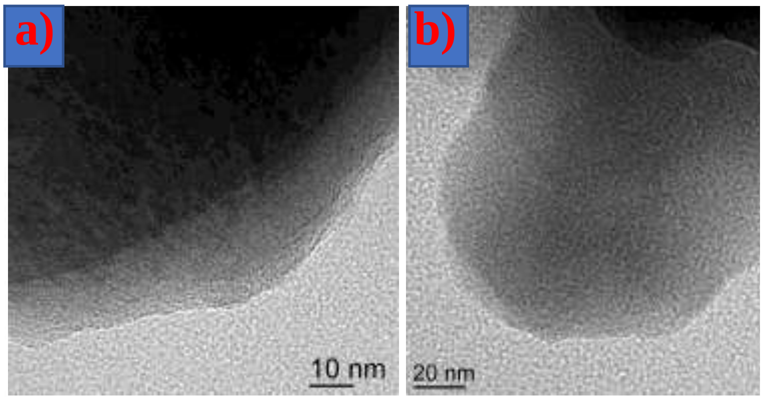


Figure S12. TEM (a, b) images of reused catalyst Rh(III)@TPDB COP

10. Calculation of production rate of products:

Calculation of TON and TOF:

$$\text{Turn Over Number (TON)} = \frac{\text{No. moles of Product formed}}{\text{no. moles of Catalyst used}}$$

$$\text{Turn Over Frequency (TOF)} \frac{\text{No. moles of Product formed}}{\text{no. moles of Catalyst used} * \text{Time (h)}}$$

Calculation of product's yields:

The yields of the reactions were determined using a calibration graph represented in Figure S8. A standard concentration of HCOOH was graphed against the absorbance value from the UV-visible spectra to achieve this.

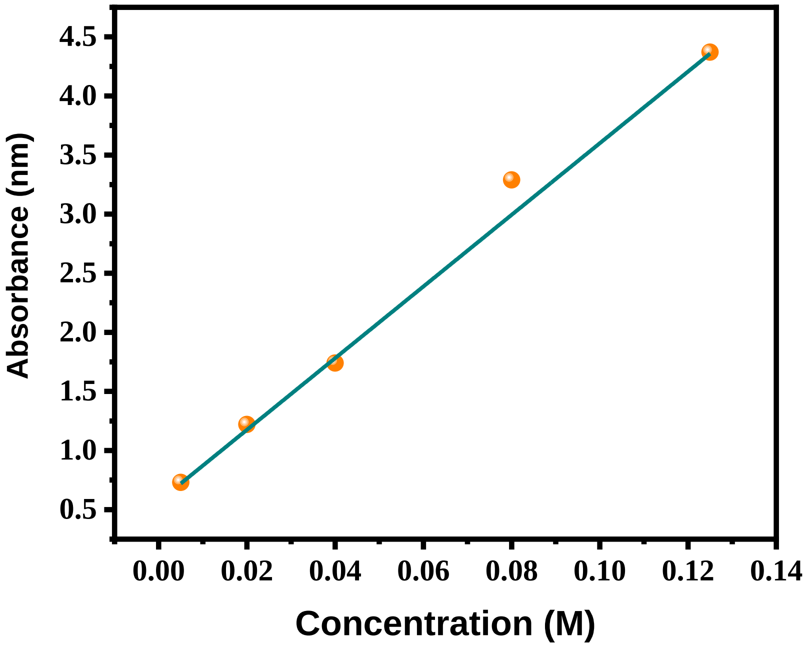


Figure S13. Calibration curve of formic acid (HCOOH) for determination of concentration of HCOOH produced.

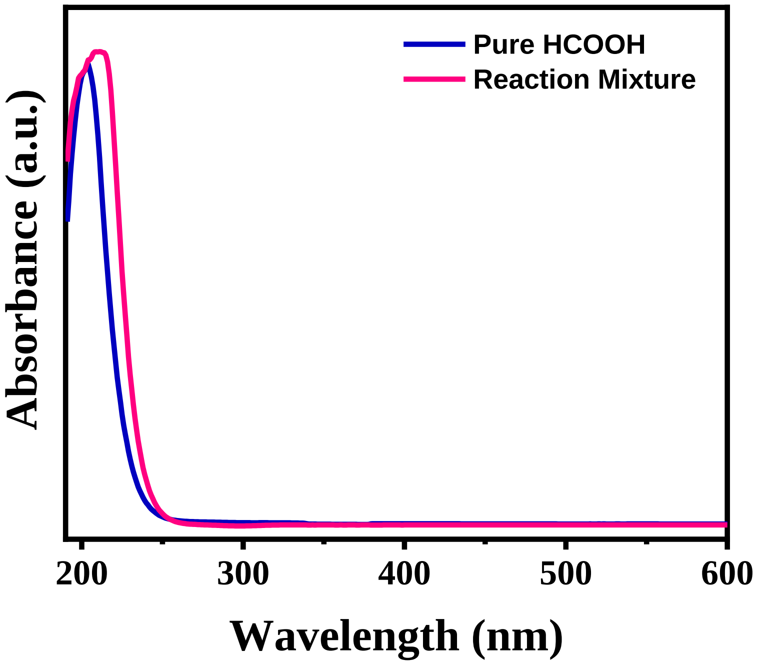


Figure S14. Absorption spectra of Pure HCOOH and reaction mixture containing HCOOH after photocatalytic CO_2 reduction by Rh(III)@TPDB.

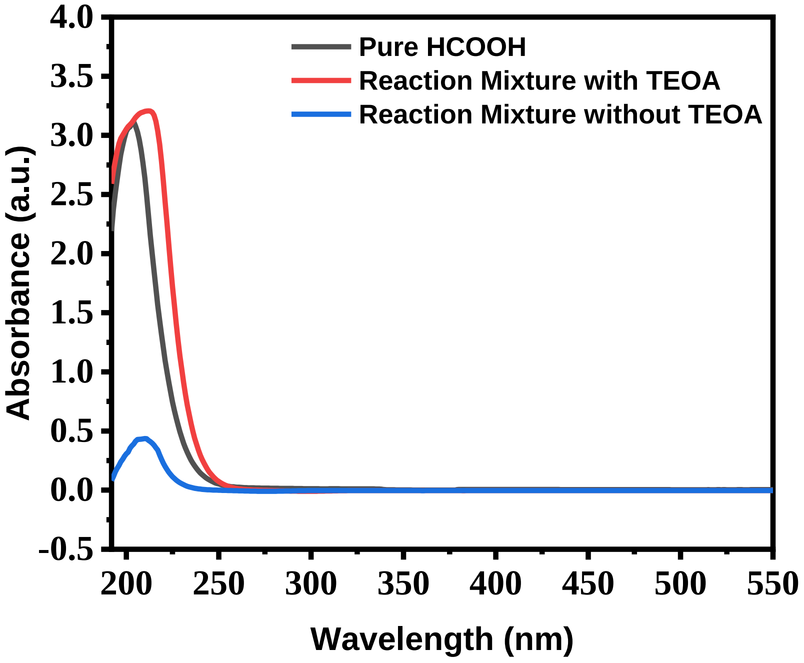


Figure S15. Absorption spectra of Pure HCOOH and reaction mixture after photocatalytic CO_2 reduction by Rh(III)@TPDB in presence of TEOA as Sacrificial Electron Donor (SED) and also in the absence of any SED.

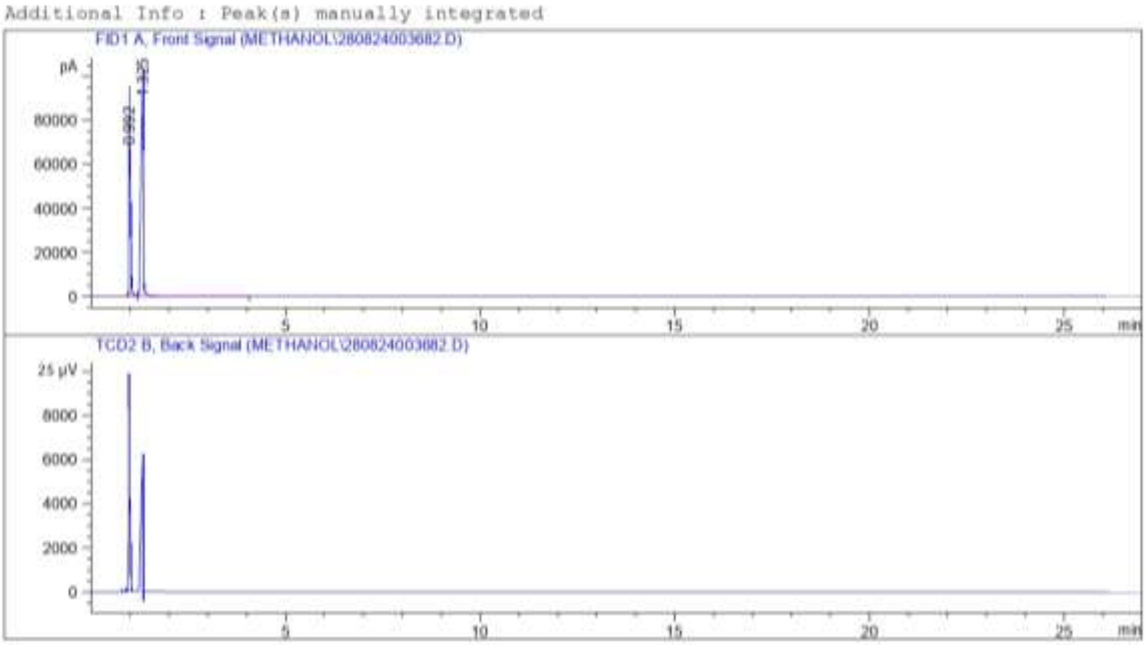


Figure S16. Gas Chromatography (GC) report of pure Methanol

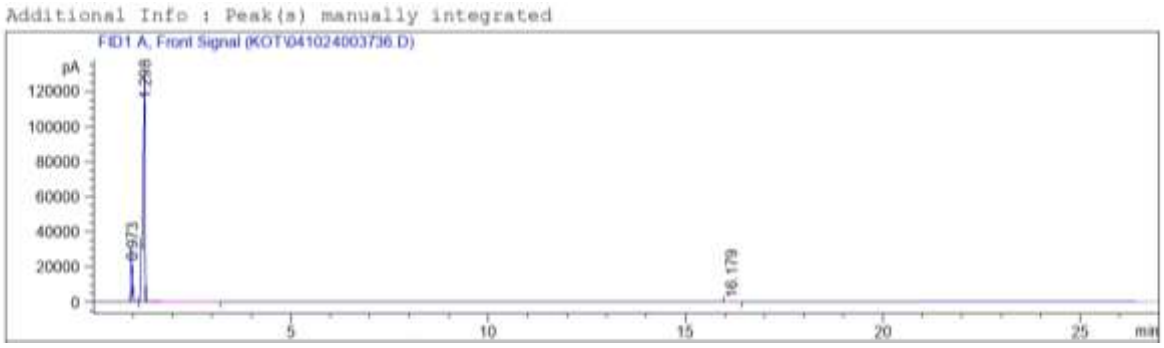


Figure S17. Gas Chromatography (GC) report of the reaction mixture after photocatalytic reaction by Rh(III)@TPDB photocatalyst.

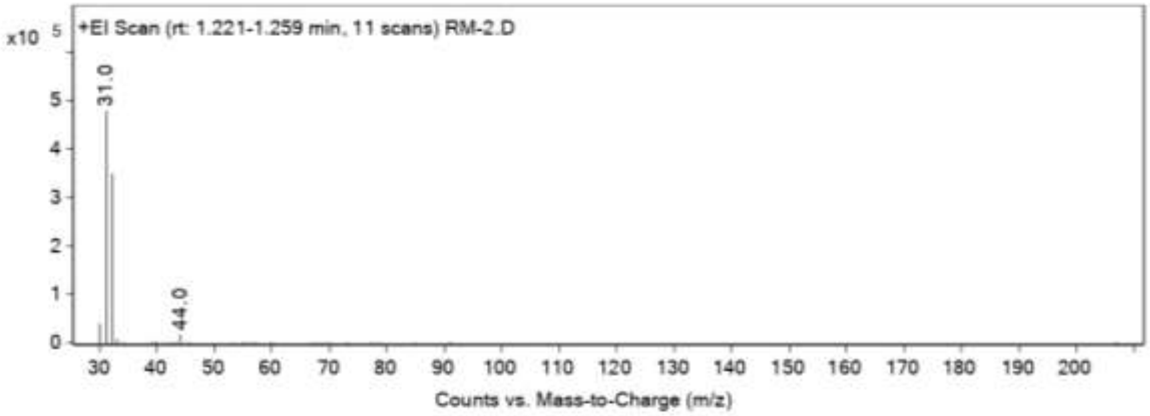
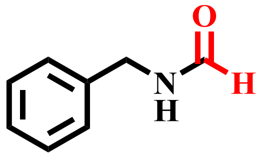
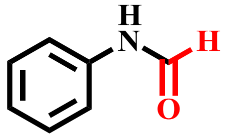
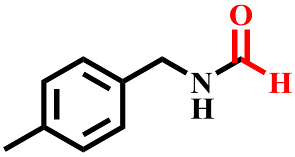
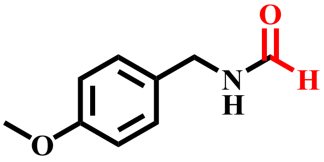
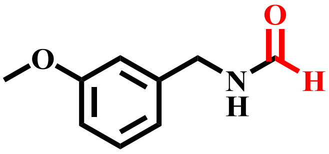
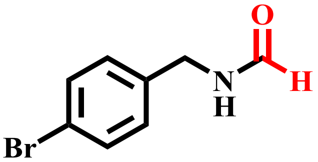
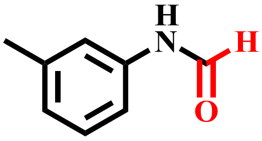
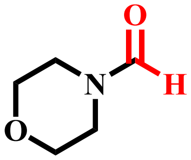


Figure S18. GC-MS data of the reaction mixture after photocatalytic reaction by Rh(III)@TPDB photocatalyst.

11. ^{1}H-NMR & ^{13}C-NMR data of respective N-Formylation [2]:

	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.38 (s, 1H), 7.42 – 7.32 (m, 5H), 4.82 (d, *J* = 1.4 Hz, 2H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (s, 1H), 7.29 – 7.20 (m, 5H).

	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.40 (s, 1H), 7.42 (d, *J* = 2.0 Hz, 2H), 7.41 (d, *J* = 1.9 Hz, 2H), 4.83 (d, *J* = 1.4 Hz, 2H), 2.08 – 1.96 (m, 3H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.36 (s, 1H), 7.40 (d, *J* = 2.2 Hz, 2H), 7.38 (d, *J* = 1.6 Hz, 2H), 4.80 (d, *J* = 1.4 Hz, 2H), 3.79 (s, 1H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 1H), 6.83 – 6.76 (m, 4H), 4.61 (d, *J* = 1.5 Hz, 2H), 3.71 (s, 3H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 4.68 – 4.66 (m, 2H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (s, 1H), 7.31 – 7.23 (m, 4H), 2.35 (s, 3H).
	^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (s, 1H), 3.45 (m, 4H), 2.67 – 2.60 (m, 4H).

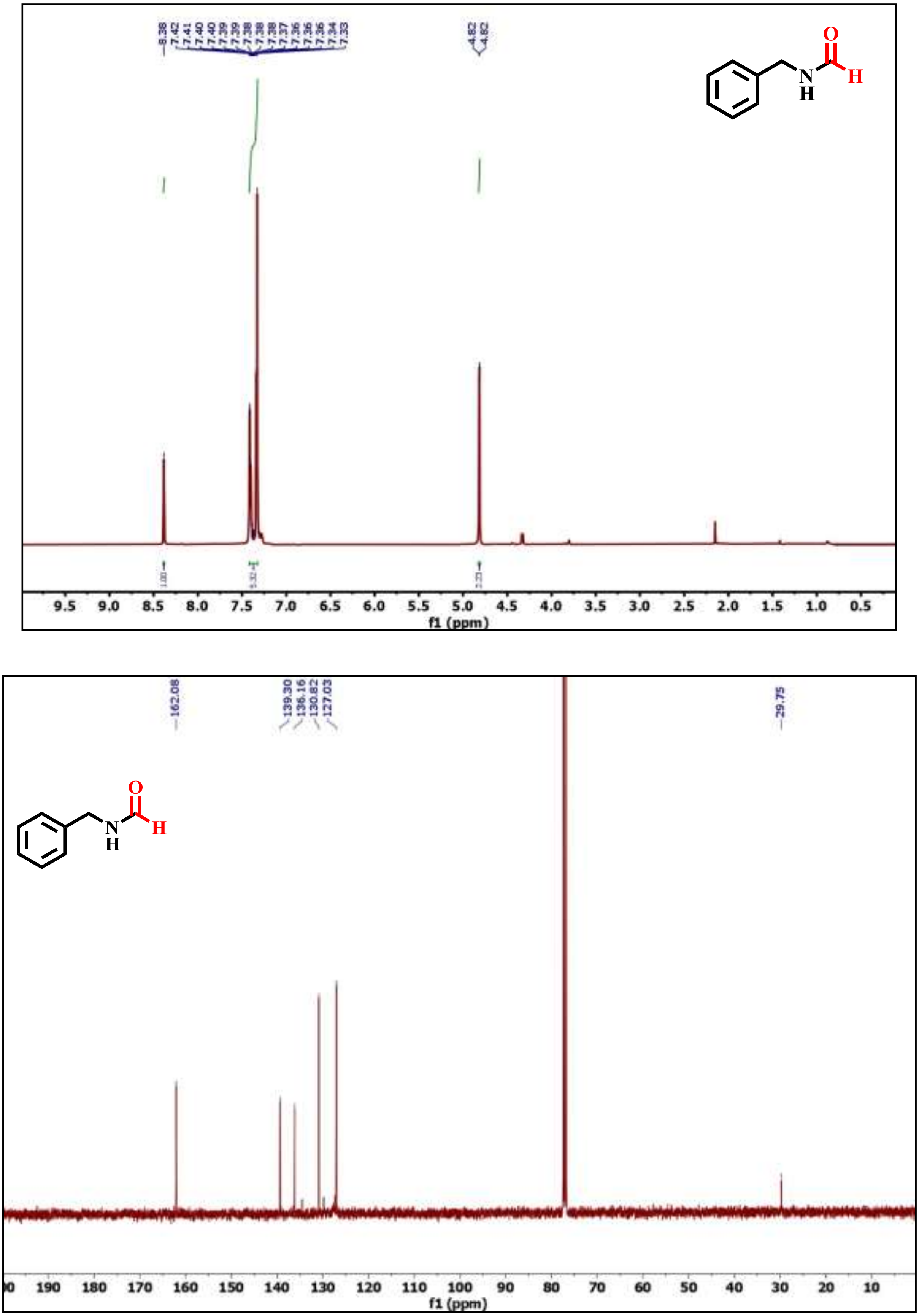


Figure S19: ^{1}H-NMR and ^{13}C-NMR Spectra of N-benzyl formamide

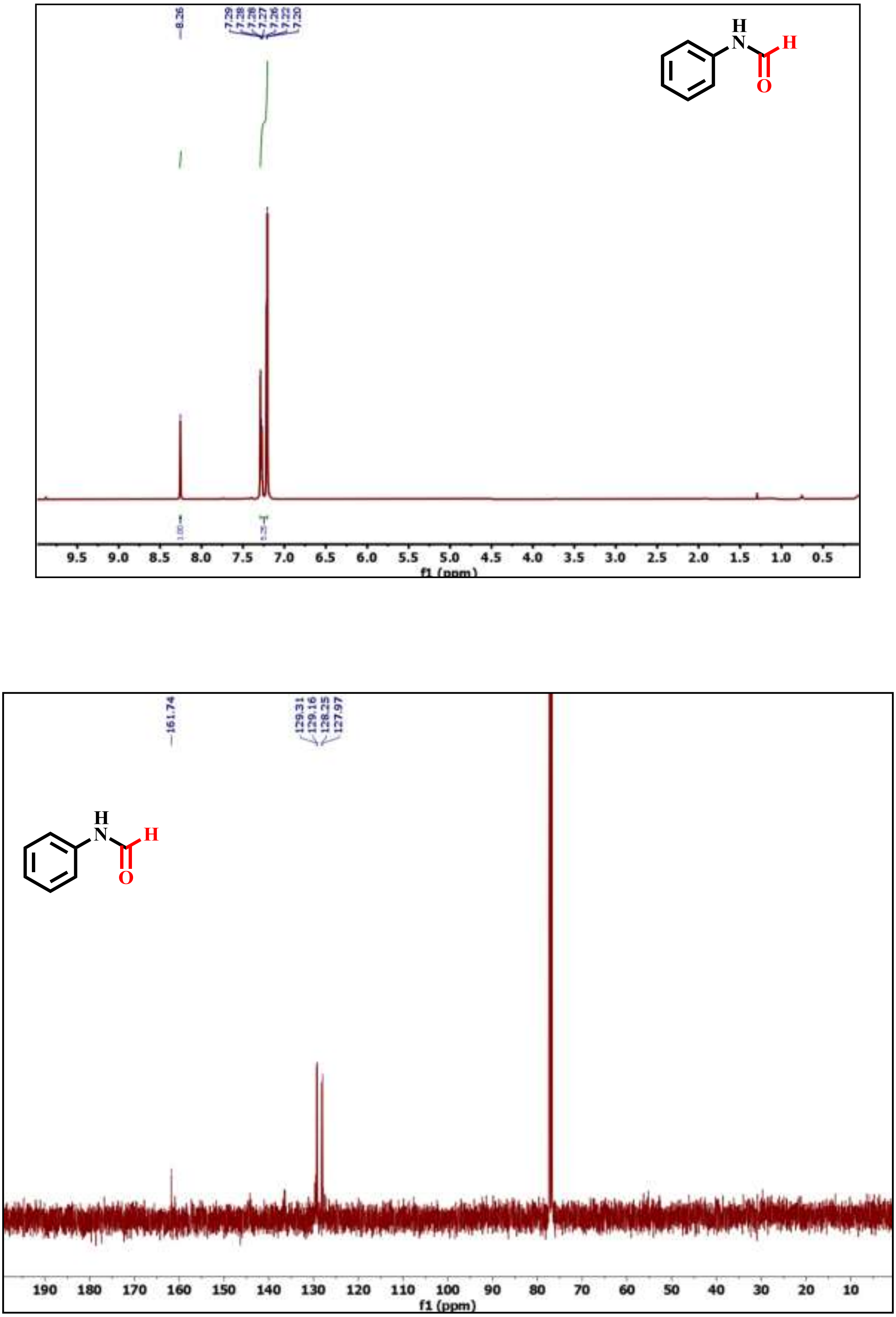
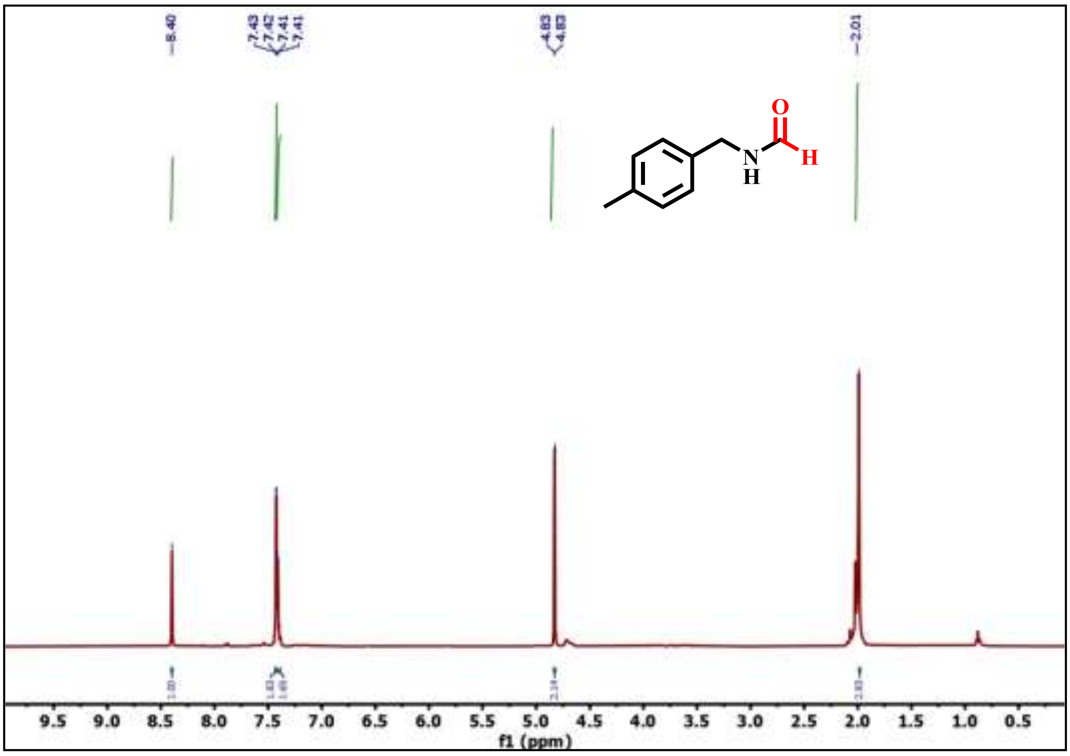


Figure S20: ^{1}H-NMR and ^{13}C-NMR Spectra of N-methyl-N-phenyl formamide



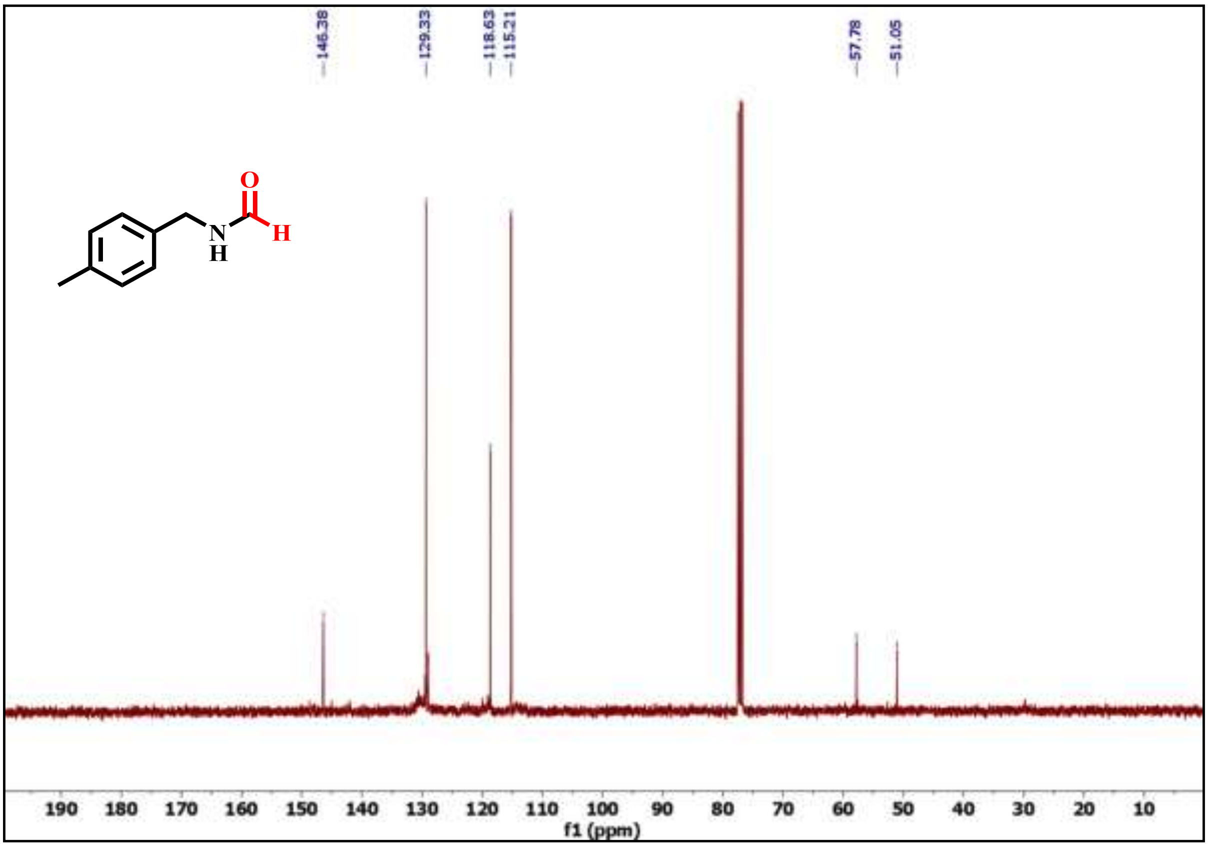


Figure S21: ^{1}H-NMR and ^{13}C-NMR Spectra of N-(4-methylbenzyl) formamide

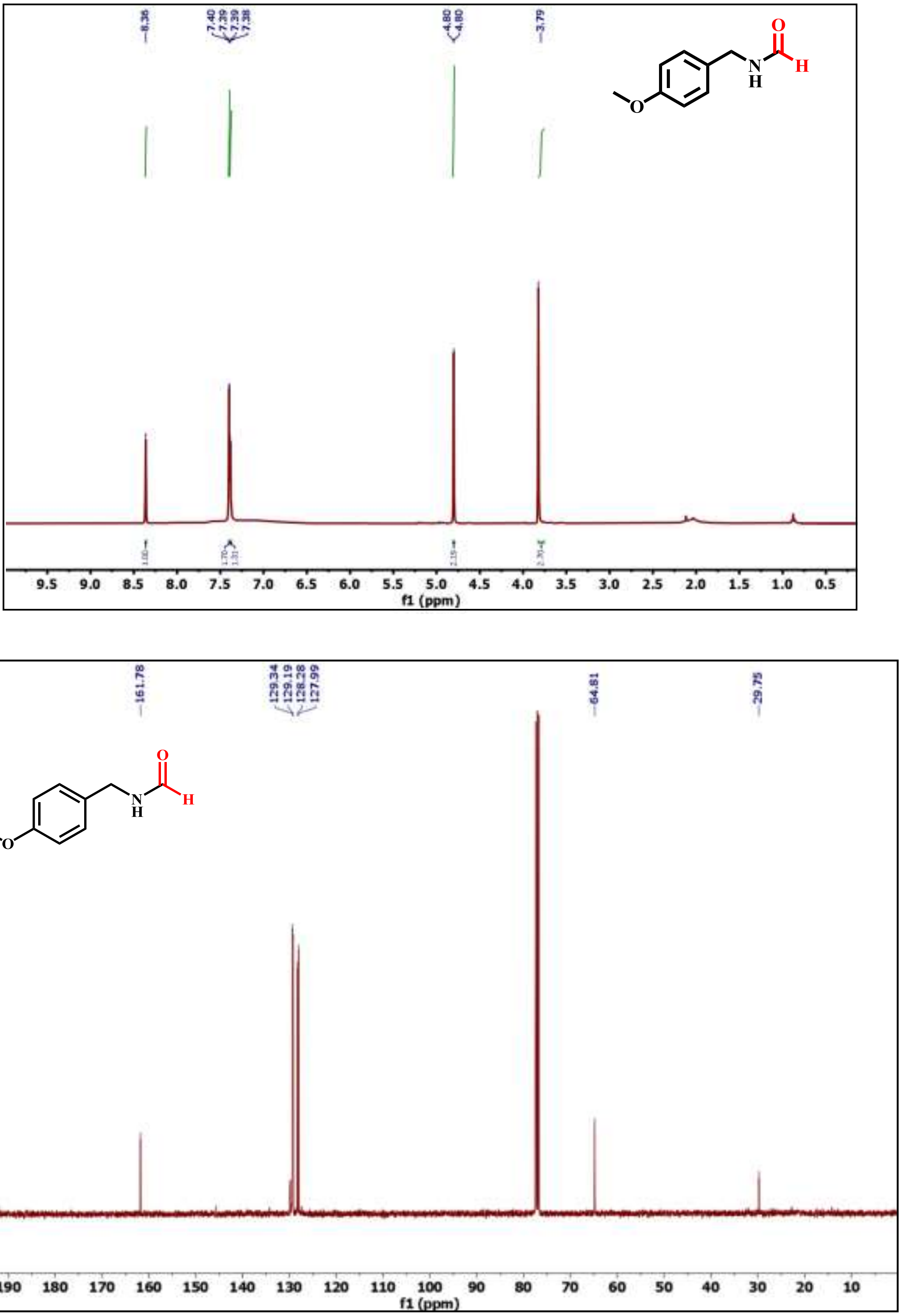


Figure S22: ^{1}H-NMR and ^{13}C-NMR Spectra of N-(4-methoxybenzyl) formamide

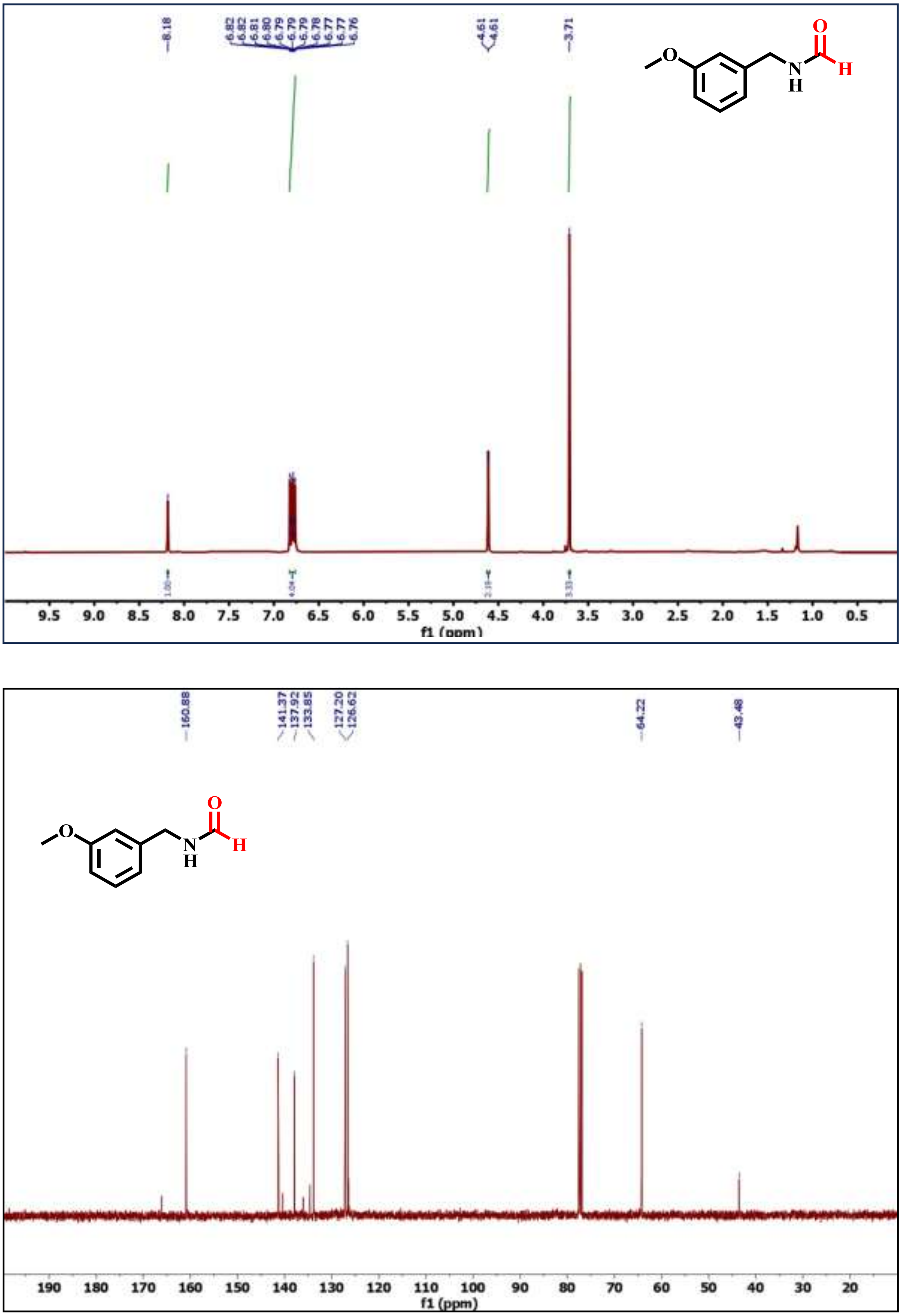


Figure S23: ^{1}H-NMR and ^{13}C-NMR Spectra of N-(3-methoxybenzyl) formamide

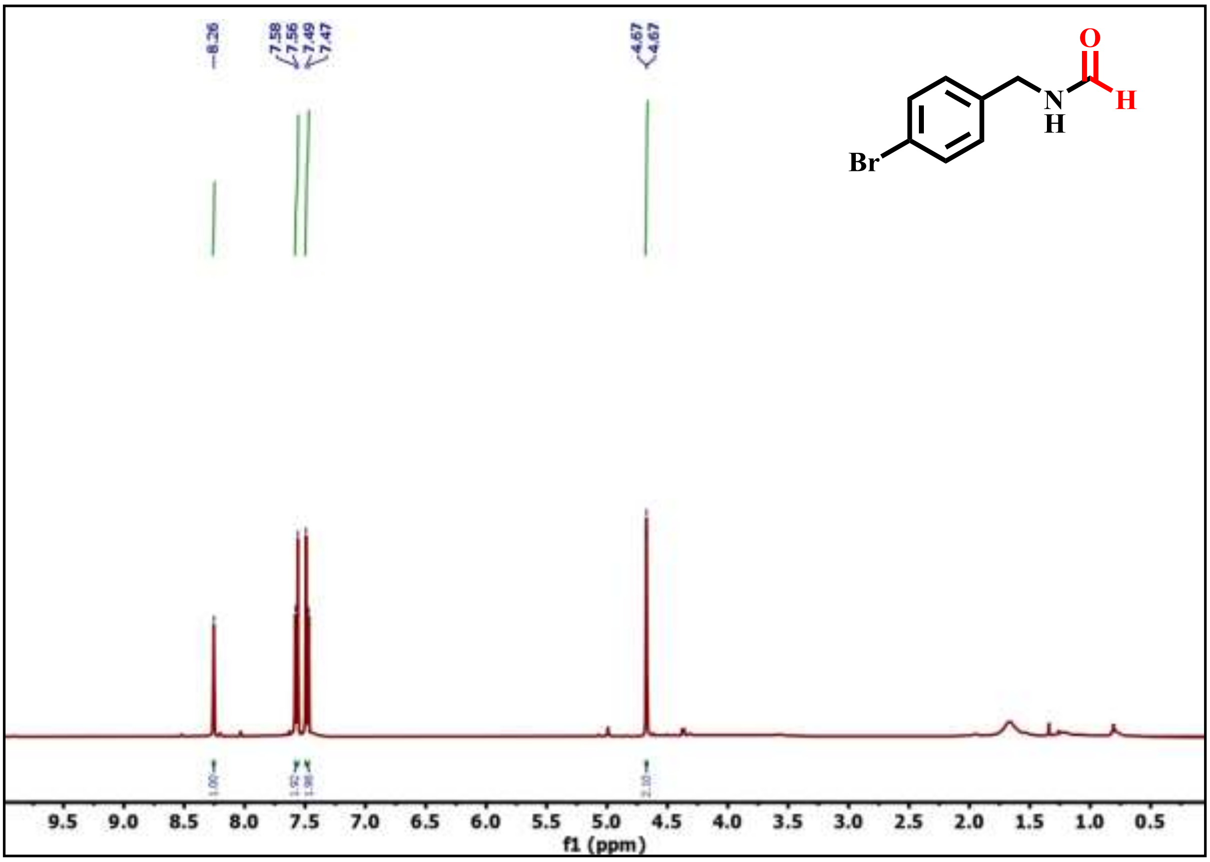


Figure S24: ^{1}H-NMR Spectra of N-(4-bromobenzyl) formamide

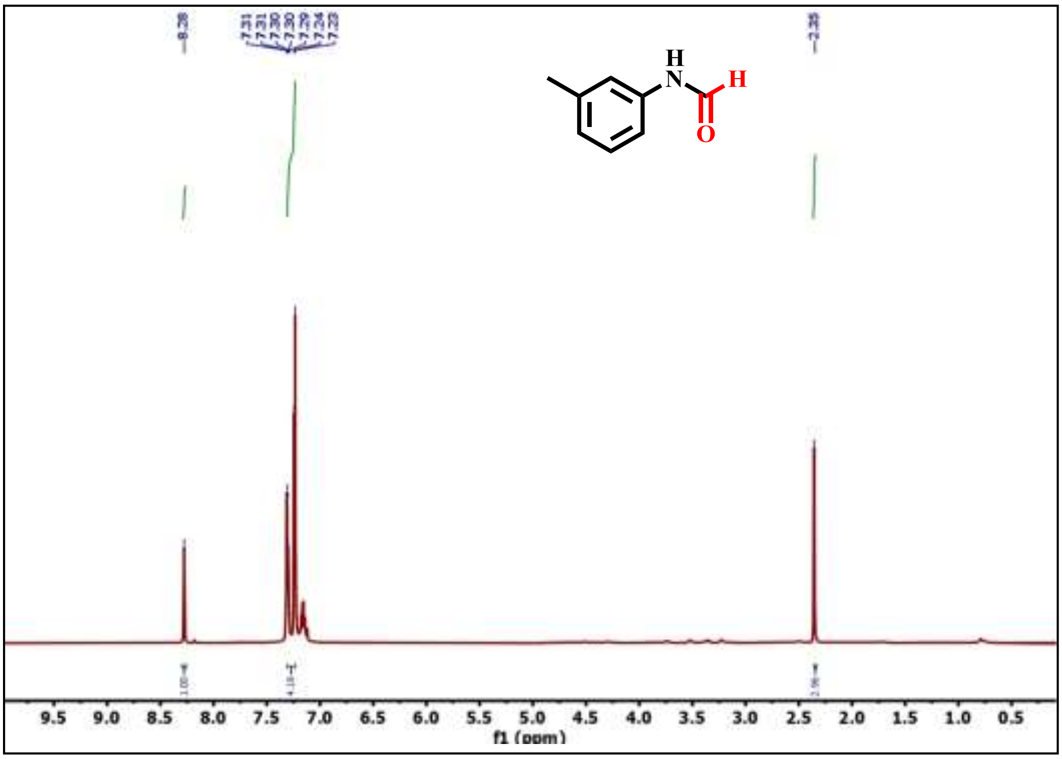


Figure S25: ^{1}H-NMR Spectra of N-methyl-N-(m-tolyl)formamide

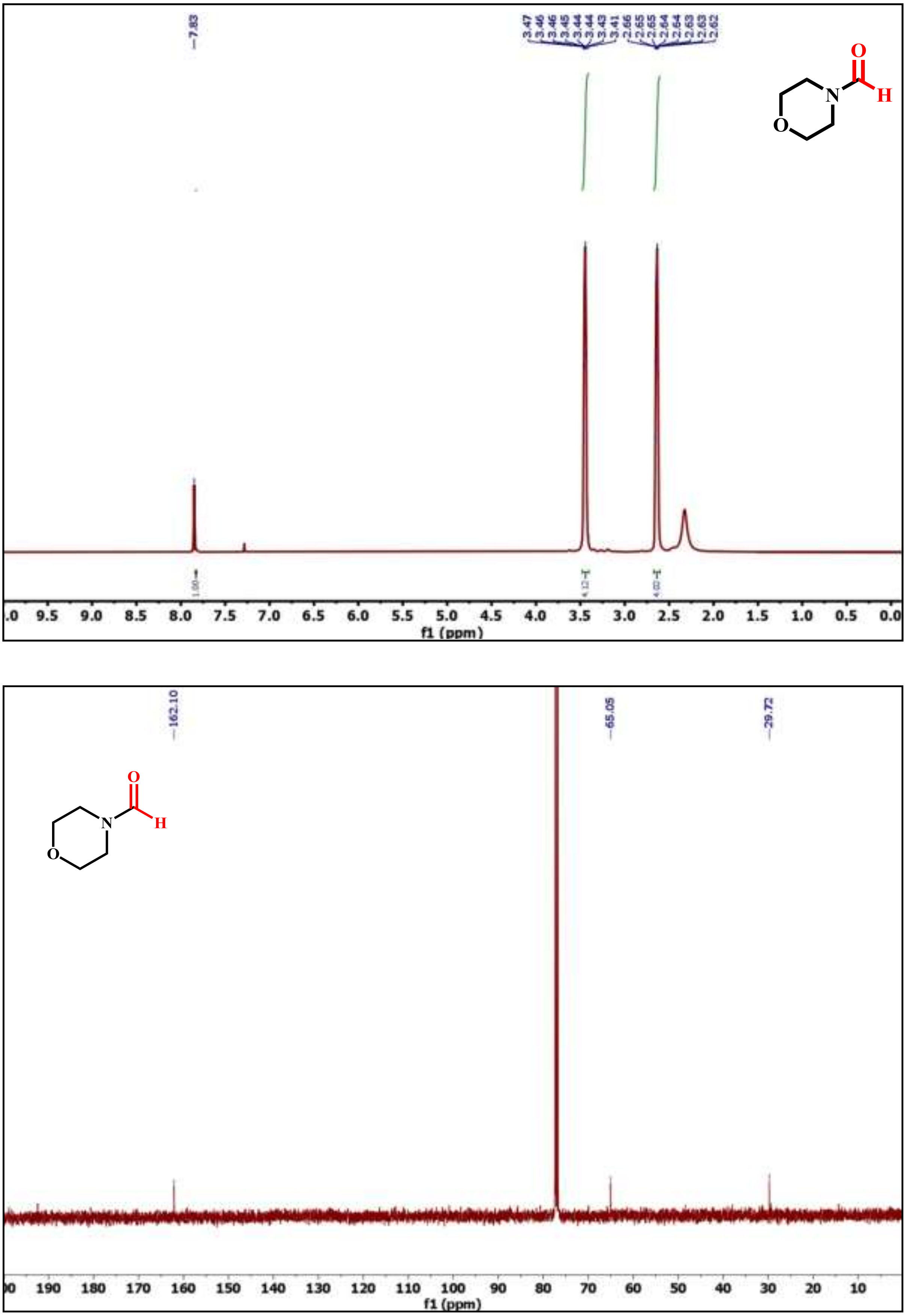


Figure S26: ^{1}H-NMR and ^{13}C-NMR Spectra of morpholine-4-carbaldehyde

12. Reference:

1. T. Mondal, P. Sarkar, M. S. Islam, K. A. Dahlous and S. M. Islam, *ChemSelect,* 2025, **10**, e202403353.
2. S. Das, P. Sarkar, M. Goswami, S. M. Ali, M. R. Mollah and S. M. Islam, *Mater. Chem. Front.*, 2023, **7**, 3349–3364.
3. S. Sarmah, C. Thadhani, A. Kumar and K. Manna, Catal. Sci. Technol., 2026, DOI: 10.1039/D5CY01380A.
4. P. Samanta, A. Sole-Daura, R. Rajapaksha, F. M. Wisser, F. Meunier, Y. Schuurman, C. Sassoye, C. Mellot-Draznieks and J. Canivet, *ACS Catal.*, 2023, **13**, 4193–4204.