Supporting information

for

Pendant Amine-Promoted Complete Eight-Electron Photoreduction of CO_2 to Methane by a Molecular Nickel Catalyst

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1. Materials and Methods:

1.1 Reagent Information:

$Ni(ClO_4)_2 \cdot H_2O$, 2,6-diaminopyridine, pyridine, NaOH solution and Nitroso benzene, $[Ir\{dF(CF_3)ppy\}_2(bpy)]^+$ and $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+$, CzIPN (1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene), were purchased from Sigma-Aldrich India. Tetrabutyl-ammonium tetrafluoroborate was purchased from TCI India Pvt. Ltd. Acetone (HPLC and Spectroscopy), Dimethylacetamide (HPLC and Spectroscopy grade), triethylamine (AR/ACS) and diethyl ether (AR/ACS), methanol (HPLC and gradient), dichloromethane (AR/ACS), triethanolamine (AR/ACS), Pyridine (AR/ACS), sodium hydroxide (AR), sodium sulphate, anhydrous (AR/ACS), potassium chloride (AR), acetonitrile (HPLC and Gradient) were purchased from Finar Chemicals Pvt. Ltd. India. All the analytical reagents were used in laboratory as received without any further purification. Solvents are distilled using standard protocols. Millipore water (18.2 MΩ.cm resistivities at 298K) was used during experimental analysis. For column chromatography silica gel (100-200 mesh) was supplied from SRL Co. During elution petroleum ether and ethyl acetate mixture was used. Thin layer chromatography was performed on EMD Chemicals Si 60 F254. TLC plates (silica gel 60F254) were supplied from MERCK.

2. Analytical Information:

Characterization of the nickel complex was done by optical spectroscopy, FTIR, EPR, Cyclic Voltammetry, Photocatalytic LED, and Mass spectrometry.

2.1. UV-Visible (UV-Vis) Absorption Spectroscopy:

UV-vis absorption spectra were recorded at room temperature in dimethylacetamide (DMA) solution on Ocean Optics spectrophotometer with 240.00 ms integration time and near 10 average scans. 2 ml of sample was placed in a 3.0 ml quartz cuvette (1 cm path length) placed in an external sample holder connected to light source and detector via optical fibers.

2.2. Fourier Transform Infrared (FT-IR) Spectroscopy:

FT-IR spectra were recorded in % transmittance mode at room temperature using solid KBr pellet on Perkin-Elmer FT-IR spectrometer. Moreover, the FTIR spectra of samples were also recorded in the OTTLE cell by dissolving in DMA.

2.3. Electron Paramagnetic Resonance (EPR) Analyses:

EPR spectra were collected at IIT Bombay on JES - FA200 ESR Spectrometer with X and Q band, a cylindrical mode cavity, at 77K.

2.5. Electrochemical Information:

The cyclic voltammetry (CV) experiment was carried out at room temperature in DMA solution using the Metrohm Auto lab PGSTAT 204 potentiostat.

2.6. Cyclic Voltammetry (CV) Study in Organic Solvent:

The cyclic voltammetry (CV) technique was utilized for studying the electrochemical behavior of molecular complex. These studies were primarily executed in an organic medium (DMA) at room temperature, employing 0.1 M tetrabutylammonium tetrafluoroborate [TBABF] ($^{n}Bu_4N^+$ BF_4^-) as the supporting electrolyte. The analyte concentration was maintained at 1 mM in all the cases unless mentioned otherwise. The cyclic voltammograms were recorded using a three-electrode assembly, employing a 1 mm diameter glassy carbon disc as the working electrode, Pt-wire as a counter electrode, and Ag/AgCl (in 3M KCl) as a reference electrode. All the potential values in organic were reported against ferrocene redox couple ($FeCp_2^{+/0}$). The electrochemistry setup consists of a glass cell (capacity 5mL), covered with PTFE cap containing four inlets. Three of those inlets are utilized for inserting the working, counter, and reference electrodes, while the final inlet was deployed for purging gas.

2.7. Bulk or Control Potential Experiment in DMA Medium:

Bulk Electrolysis (BE) or control potential experiment (CPE) was performed in an air-tight 50 ml four neck glass vessel. Three of these outlets were fitted with various electrodes; 1 cm x 1 cm vitreous carbon as a working electrode; 5 cm coiled platinum wire as a counter electrode, and Ag wire as a reference electrode. The last outlet was closed by a B-14 suba® seal rubber septum, which was used for purging CO_2 (for 30 minutes) before the experiments and for headspace gas collection. During an experiment, 15 mL of 1 mM complexes were added to the vessel, all electrodes (along with a magnetic bead) were inserted along with a B-14 rubber septum cap (in a gas-tight manner). Then, the chrono-coulometric experiment was started at corresponding catalytic potentials in DMA media. The reaction solution was continuously stirred during the experiment. Headspace gas was collected by a GASTIGHT® PTFE leur-lock 1000 series (1001TLL) 1 mL Hamilton® syringe after certain time intervals, and it was analyzed via gas chromatography (GC) instrument on FID mode.

2.8. Photocatalytic Investigation:

Photocatalytic CO_2 reduction experiments were conducted using a 10 mL photocatalytic vial filled with DMA solution. The light source for the photocatalytic experiments was a Kessil KSPR160L-440 nm LED bulb. The complete set of reactions indicated the following optimized conditions for CO_2 reduction for both the catalysts: All the photochemical experiments were carried out under 2 μM catalyst concentration in DMA (2 mL), BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED. Before each experiment, samples were purged for 30 minutes with CO_2 gas to degas the solution and the reaction mixture was continuously stirred during the experiment. The head-space gas was collected by a GASTIGHT® PTFE leur-lock 1000 series (1001TLL) 1 mL Hamilton® syringe after certain time intervals and was analysed via gas chromatography (GC) instrument on FID mode.

2.9. Gas Chromatography Analysis:

The amount of CO_2/CO and CH_4 and CO/CH_4 evolved during catalysis were quantified by using Shimadzu gas chromatography (GC) instrument with TCD/FID detector with a 5 A° molecular sieve/ Porapak-N at room temperature. Instrument calibration build up curve was created manually by injecting variable amount (0.5%-2%) of known CO_2 and CO gas mixtures.

2.10. GC-MS Analysis: To confirm that CO is the exclusive product of CO_2 reduction in the photocatalytic process, the reaction was repeated under identical photochemical conditions using isotopically labeled $^{13}CO_2$ in place of $^{12}CO_2$. The resulting gaseous products were analyzed using a Shimadzu GC-MS-QP2020 equipped with a ShinCarbon ST 100/120 column (2 m, 1 mm, 1/16" OD, Silco). The photocatalytic experiments were conducted with a catalyst concentration of 50 μM in DMA solvent, employing BIH (0.02 M) as the electron donor, under visible-light irradiation provided by a 440 nm LED source.

2.11. CHNS analysis: The CHNS of all the samples were recorded by a Flash smart V CHNS/O instrument made by Thermo Fisher Scientific, which was used to estimate of CHN/CHNS/O in percentage level to high concentration level.

2.12. Dynamic Light Scattering Measurement: Dynamic light scattering (DLS) measurements were performed using a Zetasizer Nano ZS equipped with an avalanche photodiode detector and

correlator system (ZEN 3600, Malvern Instruments). A He–Ne laser operating at 4 mW and emitting vertically polarized light at 638 nm was employed as the excitation source. All measurements were carried out at 25 °C with the scattering angle fixed at 90° under non-invasive back-scattering (NIBS) mode.

2.13. Mass Spectrometry analysis

HRMS of the samples was recorded with a Bruker maXis impact in positive mode.

TON (Turn over number):

To determine the turnover number (TON), we first quantified the total amount of CO produced during the electrochemical reaction. The gaseous products were analyzed using gas chromatography (GC), where the peak area corresponding to CO was compared against a calibrated standard curve to obtain the exact amount of CO generated, expressed in millimoles. In parallel, the millimoles of catalyst introduced into the reaction were calculated based on its known concentration and the solution volume used. The TON was then calculated by dividing the millimoles of CO formed by the millimoles of catalyst present. Thus, the TON directly reflects how many molecules of CO each molecule of catalyst can produce under the given reaction conditions, providing a quantitative measure of catalytic efficiency.

TOF (Turn over frequency):

The turnover frequency (TOF) was determined by dividing the calculated TON by the reaction time corresponding to the formation of the product. In practice, once the TON was obtained from the ratio of CO produced (mmol) to the catalyst used (mmol), the TOF was calculated as TON per unit time (typically expressed in h^{-1}). This value represents how many catalytic cycles each catalyst molecule completes per hour under the applied reaction conditions.

Apparent Quantum Yield measurements (AQY):

The apparent quantum yield was determined following the procedure previously reported by Robert and co-workers in ChemSusChem 2024, 17, e202301892. For the QY calculation, the time interval exhibiting the highest CO production rate (highest TOF) over a minimum continuous

period of 10 h was selected. This approach allows the determination of the maximum observable quantum efficiency of the catalytic system by minimizing the influence of catalyst deactivation, photosensitizer degradation, or product accumulation that may occur during prolonged irradiation. AQY = $(N_e/N_P) \times 100\%$ = (number of reacted electrons/number of incident photons) × 100%; Ne = 2(nCO)(N_A); $N_P = (IAt\lambda)/hc$; The amount of substance of CO (nCO): in mol; Avogadro constant (N_A): 6.023 × 1023 mol^{-1} ; Light power density (I): 50 $mW \cdot cm^{-2}$; Area of irradiation (A): 2.012 cm^2 ; Incident wavelength (λ): 440 nm; Reaction time (t): 10 h; Planck constant (h): 6.626×10^{-34} J·s. The photochemical experiments were carried out under 2 μM catalyst concentration in DMA (2 mL), BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED. Before each experiment, samples were purged for 30 minutes with CO_2 gas to degas the solution and the reaction mixture was continuously stirred during the experiment. The head-space gas was collected by a GASTIGHT® PTFE leur-lock 1000 series (1001TLL) 1 mL Hamilton® syringe after certain time intervals and was analysed via gas chromatography instrument on FID mode.

$$\text{AQY} = (N_e/N_P) \times 100\%$$

$$= 1.912 \times 10^{-3}$$

$$\sim 2 \times 10^{-3}$$

3. Synthesis Procedure:

3.1. 6-amino-2(phenyl-azo)-pyridine:

The ligand 6-amino-2(phenyl-azo)-pyridine (**L1**) was synthesized as per reported by Dutta and co-workers.[1] In Summary, 1.00 g of 2,6-diaminopyridine (9.16 mmol) was dissolved in 10 mL of pyridine and mixed with 5 mL of 50% aqueous NaOH solution. Then 0.96 g of nitroso benzene (9 mmol), dissolved in 5 mL pyridine, was added dropwise to the mixture for 3 hours, followed by reflux for 20 hours. The thin-layer chromatography was utilized for confirmation of completion of reaction. The dark red mixture solution was diluted with water and extracted with dichloromethane (DCM) (4 x 100 mL). A dark red crude was obtained from evaporation of the DCM layer, which

was further purified by column chromatography (100% DCM), using neutral alumina as stationary phase.

3.2. Synthesis of C1 catalyst:

The 6-amino-2(phenyl-azo)-pyridine (99 mg/0.50 mmol) in 10 ml DCM was dropwise added (under N_2) to a methanol/dichloromethane (1:2) mixture containing 92 mg of $Ni(ClO_4)_2 \cdot 6H_2O$ (365.69 g/mol) (0.25 mmol). The mixture solution was stirred for 1 hour at room temperature. Finally, a yellowish-brown solution was obtained that was evaporated under the vacuum. Upon addition of ligand, an immediate color transition to reddish-orange was observed, indicating complexation, followed by the formation of a precipitate. After filtration, sequential washing with water, methanol, and acetonitrile, and drying, **C1** was obtained as a yellowish-brown solid with a yield of ~72%. HRMS (ESI, +ve mode, MeOH) m/z for Z=1) [M + H^+ ($C_{22}H_{20}N_8Ni_1$ + H^+)]: Calculated: 455.12, Experimental: 455.12

3.2. Synthesis of C2 catalyst:

The 6-amino-2(phenyl-azo)-pyridine (99 mg / 0.50 mmol) in 10 ml DCM was dropwise added (under N_2) to a methanol/dichloromethane (1:2) mixture containing 92 mg of $Ni(ClO_4)_2 \cdot 6H_2O$ (365.69 g/mol) (0.25 mmol). The mixture solution was stirred for 1 hour at room temperature. Finally, a yellowish-brown solution was obtained that was evaporated under the vacuum. The precipitate from the mixture was filtered then it was washed with diethyl ether. HRMS (ESI, +ve mode, MeOH) m/z for Z=1) [M + H^+ ($C_{22}H_{20}N_8Ni_1$ + H^+)]: Calculated: 455.12, Experimental: 455.12

3.3. Synthesis of C3 catalyst:

145 mg (0.5 mol) of [2,6-diphenyl(di-azo)] pyridine was dissolved in 10 ml methanol to obtain a reddish colour solution. This methanolic solution was added dropwise to a methanol/dichloromethane (1:2) mixture containing 184 mg of $Ni(ClO_4)_2 \cdot 6H_2O$ (365.69 g/mol) (0.25 mmol). Finally, a yellowish-green solution was obtained that was evaporated under the vacuum. The precipitate from the mixture was filtered then it was washed with diethyl ether.

HRMS (ESI, +ve mode, MeOH) m/z for Z=1) [M + H^+ ($C_{17}H_{13}N_5Ni_1$ + H^+)]: Calculated: 346.05, Experimental: 346.05.

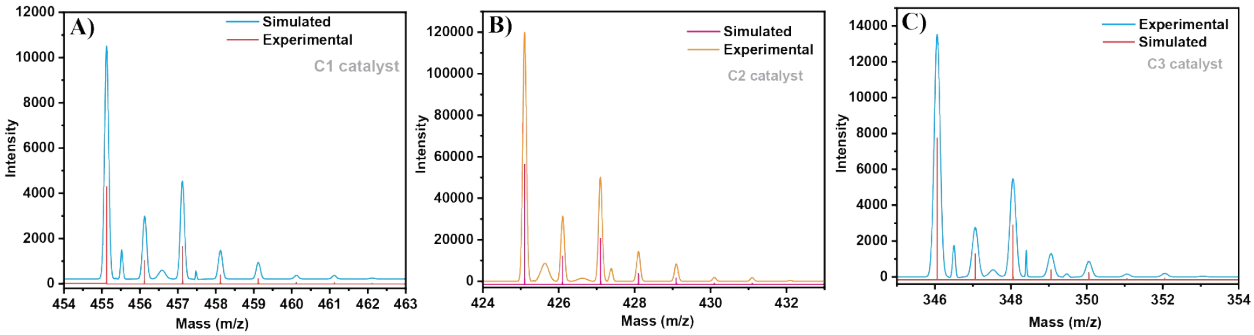
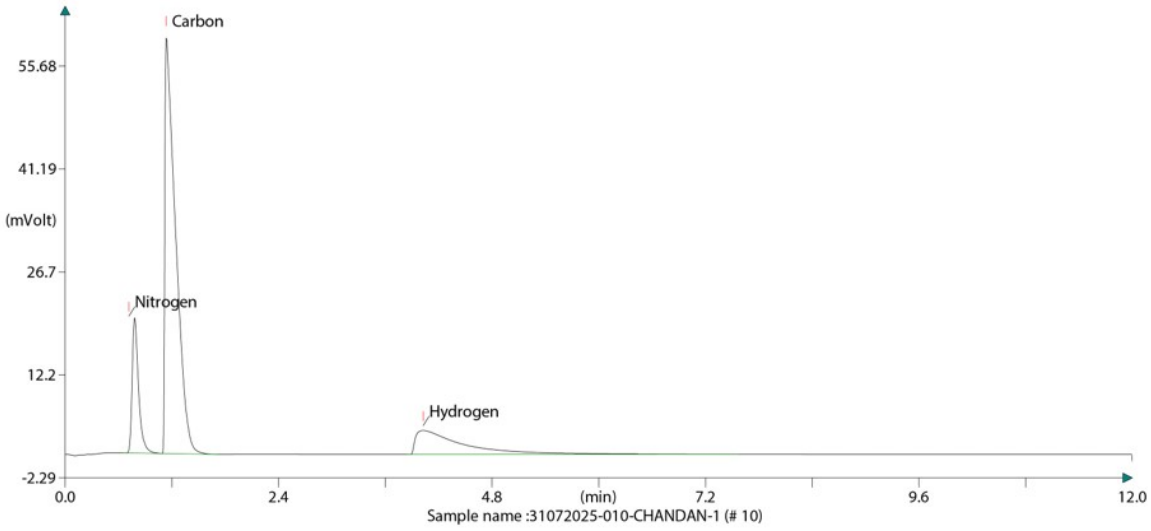
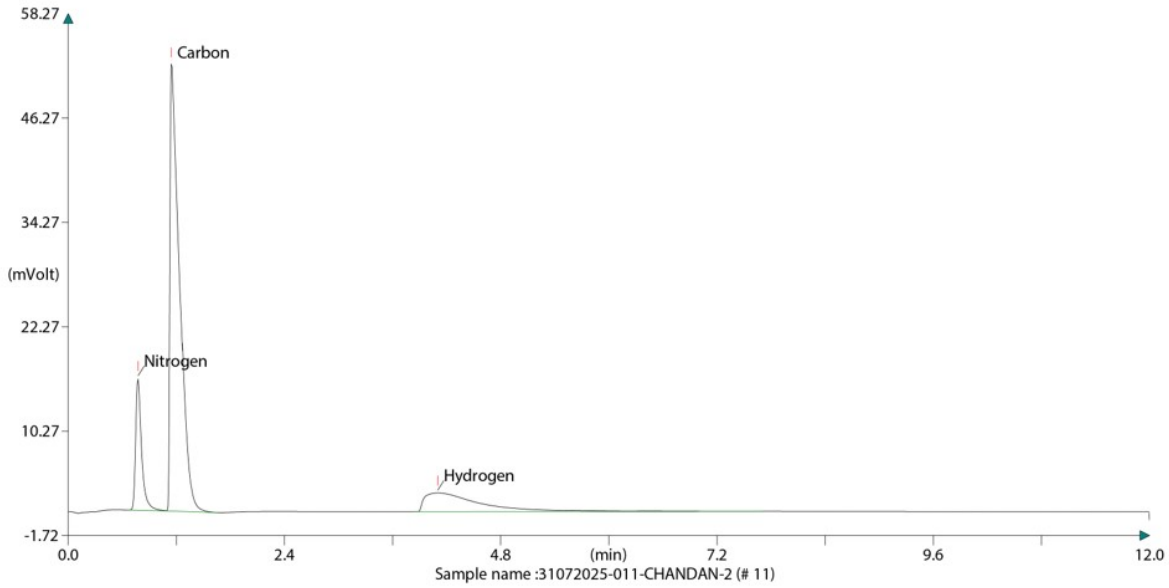


Figure S1. ESI-MS of **C1**, **C2**, and **C3**. Spectra recorded in MeOH at 298 K. (**A**) for **C1**, simulated (red trace), and experimental (black) (**B**) for **C2**, simulated (red trace), and experimental (black trace) (**C**) for **C3**, simulated (red trace), and experimental (black trace): data are stacked for comparison.



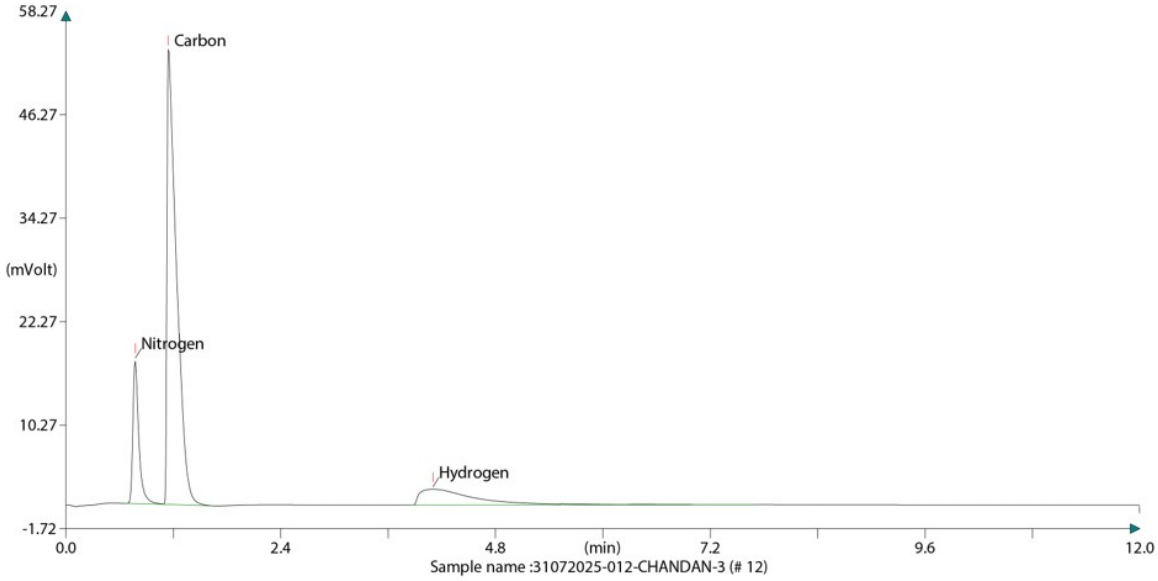
Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.783	904658	17.125	Nitrogen
2	1.133	4770615	40.392	Carbon
3	4.025	1055307	3.011	Hydrogen
		6730580	69.106	

Figure S2: CHN elemental analysis chromatogram and composition data for C1. Experimental value elemental analysis: C, 40.39; H, 3.011; N, 17.12 and Theoretical value: C, 40.40; H, 3.08; N, 17.13.



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.775	724307	13.711	Nitrogen
2	1.142	5005531	42.381	Carbon
3	4.100	1020959	2.913	Hydrogen
		6750797	59.005	

Figure S3: CHN elemental analysis chromatogram and composition data for C2. Experimental value elemental analysis: C, 42.381; H, 2.913; N, 13.71 and Theoretical value: C, 42.35; H, 2.91; N, 13.47.



Peak Number (#)	Retention Time (min)	Area (.1*uV*sec)	Element %	Component Name
1	0.771	766568	14.511	Nitrogen
2	1.148	5017341	42.481	Carbon
3	4.120	950862	2.713	Hydrogen
		6734771	59.705	

Figure S4: CHN elemental analysis chromatogram and composition data for C3. Experimental value elemental analysis: C, 42.481; H, 2.713; N, 14.511 and Theoretical value: C, 42.46; H, 2.72; N, 14.56.

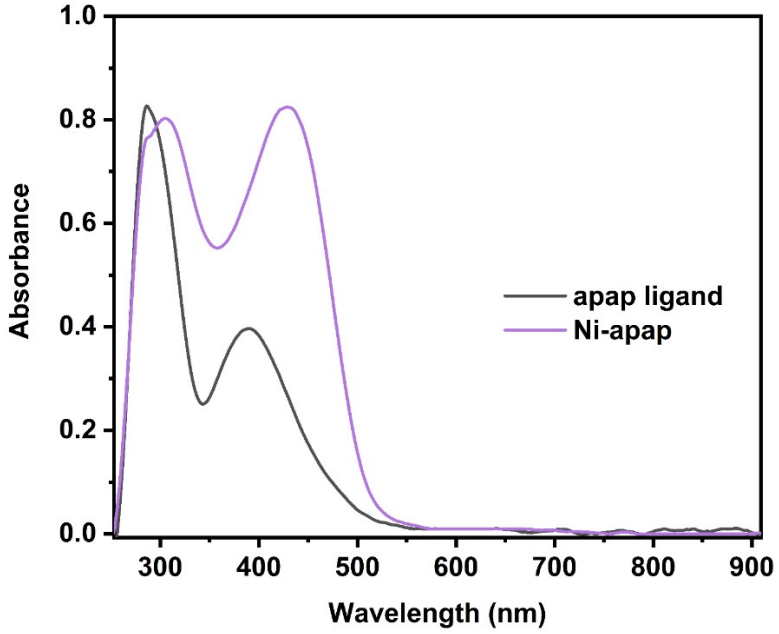


Figure S5. Optical spectral data of the **apap** ligand and the catalyst, Ni-apap **(C1),** with a concentration of 0.1 mM. This spectrum was recorded in the range 200 –1000 nm at 298K in DMA solvent.

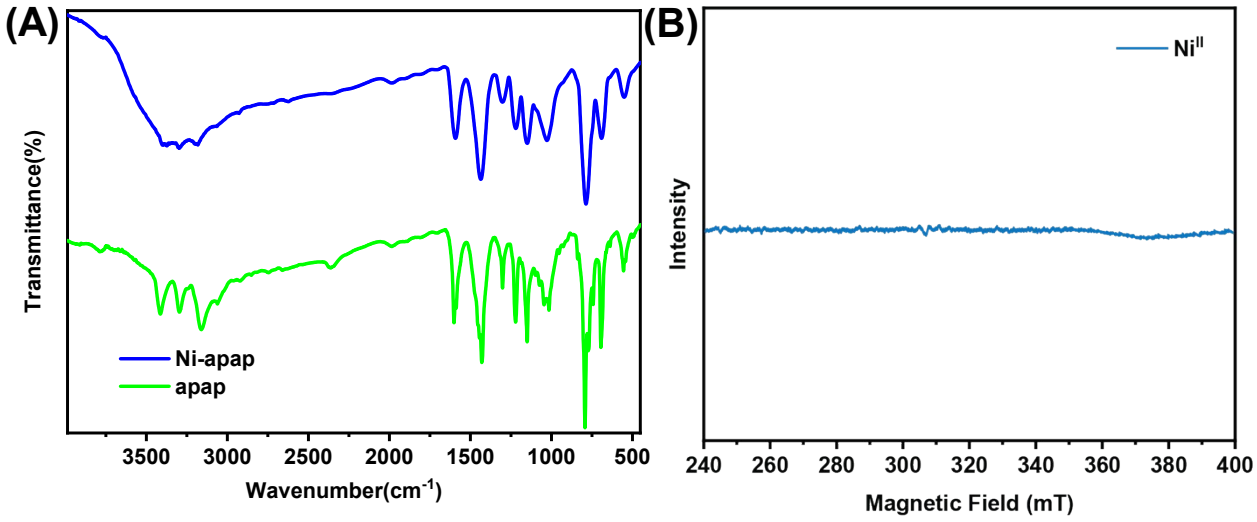


Figure S6. (**A**) FTIR Spectral data of **apap** ligand and Ni_apap **(C1)** complex. This spectrum was recorded in the range 4000 –400 cm^{-1} at 298K. (**B**) The EPR spectrum of Ni^{II} complex, the recorded in DMA solvent at 77 K.

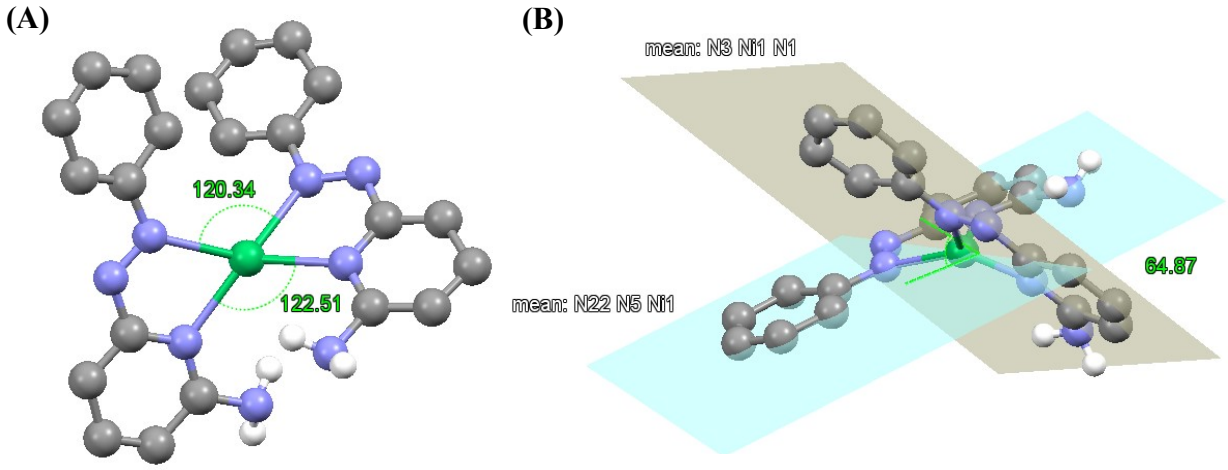


Figure S7. (**A**) DFT-optimized structure of C1. (**B**) Non-planarity of the co-ordinated apap ligand of the catlyst **C1** (DFT optimized).

3.4 General Procedures for synthesis of Cu(I)-based photosensitizers.

For the synthesis of Cu-PS's, all reactions were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk and vacuum line techniques. Solvents were dried by usual methods and distilled before use.

3.5 Synthesis of $[(CuCl)_2\{\{(o\text{-}PPh_2)C_6H_4\}C(O)N(H)CH_2(C_5H_4N)\}_2\text{-}\kappa^2\text{-}P,N]$: Cu-PS-1

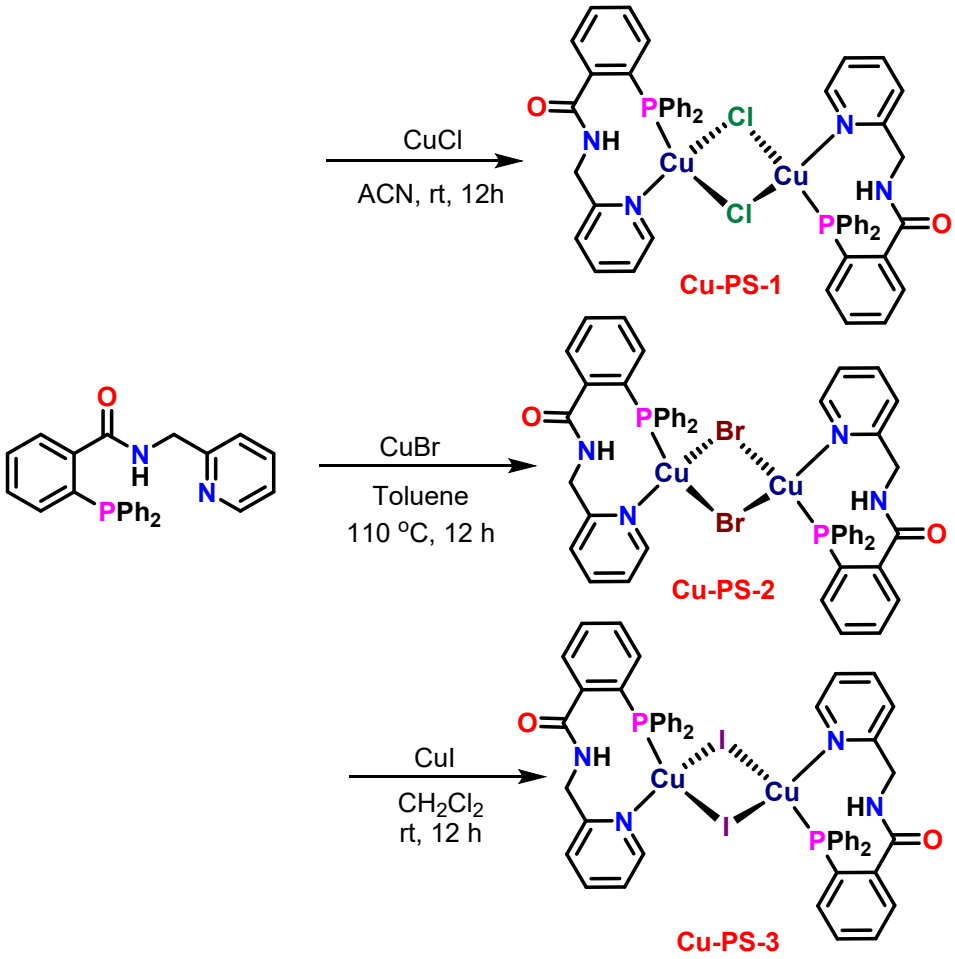
PN(H)N ligand (tridentate pincer ligand 2-(diphenylphosphaneyl)-N-(pyridine-2-ylmethyl)benzamide, $\{(o\text{-}PPh_2)C_6H_4C(O)N(H)CH_2(C_5H_5N)\}$) (0.05 g, 0.1261 mmol) in 10 mL acetonitrile was added to a solution of CuCl (0.024 g, 0.1261 mmol) in 10 ml acetonitrile. The reaction mixture was allowed to stir at room temperature for 12 h. The solvent was completely removed under reduced pressure to afford complex **Cu-PS-1** as white solid. The resulting solid was washed with petroleum ether (2 x 20 mL) to afford analytically pure complex **Cu-PS-1**. Yield: 83% (20 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.91 – 8.86 (m, 2H), 7.85 (t, J = 5.6 Hz, 2H), 7.75 (td, J = 7.7, 1.7 Hz, 2H), 7.56 – 7.51 (m, 4H), 7.48 – 7.43 (m, 8H), 7.41 – 7.30 (m, 8H), 7.26 (ddd, J = 9.3, 5.6, 2.0 Hz, 10H), 6.94 (t, J = 7.8 Hz, 2H), 4.73 (d, J = 5.5 Hz, 4H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 169.5, 156.2, 141.9, 141.7, 137.8, 133.9, 133.8, 133.5, 130.4, 130.2, 130, 128.7, 128.6, 127.8, 123.9, 123.2, 44.8. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$) δ -12.4.

3.6 Synthesis of $[(CuBr)_2\{\{(o\text{-}PPh_2)C_6H_4\}C(O)N(H)CH_2(C_5H_4N)\}_2\text{-}\kappa^2\text{-}P,N]$: Cu-PS-2

PN(H)N ligand (tridentate pincer ligand 2-(diphenylphosphaneyl)-N-(pyridine-2-ylmethyl)benzamide, $\{(o\text{-}PPh_2)C_6H_4C(O)N(H)CH_2(C_5H_5N)\}$) (0.05 g, 0.1261 mmol) in 10 mL toluene was added to a solution of CuBr (0.024 g, 0.1261 mmol) in 10 ml toluene. The reaction mixture was refluxed at 110 ^oC for 12 h. The solvent was completely removed under reduced pressure to afford complex **Cu-PS-2** as white solid. The resulting solid was washed with petroleum ether (2 x 20 mL) to afford analytically pure complex **Cu-PS-2**. Yield: 85% (20 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 – 8.77 (m, 2H), 7.71 (ddd, J = 9.4, 6.5, 2.6 Hz, 4H), 7.59 – 7.28 (m, 21H), 7.25 (dd, J = 5.4, 3.3 Hz, 7H), 7.24 – 7.13 (m, 11H), 6.90 (t, J = 7.8 Hz, 2H), 4.69 (d, J = 5.5 Hz, 4H), 1.59 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.8, 156.8, 156.8, 149.5, 142.6, 142.5, 138, 134.2, 134.1, 134, 132.2, 130.6, 130.4, 130.3, 130.2, 129.4, 129, 128.9, 128.6, 125.6, 124.2, 123.4, 45.4, 21.8. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$) δ -13.

3.7 Synthesis of $[(CuI)_2\{\{(o\text{-}PPh_2)C_6H_4\}C(O)N(H)CH_2(C_5H_4N)\}_2\text{-}\kappa^2\text{-}P,N]$: Cu-PS-3

PN(H)N ligand (tridentate pincer ligand 2-(diphenylphosphaneyl)-N-(pyridine-2-ylmethyl)benzamide, $\{(o\text{-}PPh_2)C_6H_4C(O)N(H)CH_2(C_5H_5N)\}$) (0.05 g, 0.1261 mmol) in 10 mL dichloromethane was added to a solution of CuI (0.024 g, 0.1261 mmol) in 10 ml dichloromethane. The reaction mixture was allowed to stir at room temperature for 12 h. The solvent was completely removed under reduced pressure to afford complex **Cu-PS-3** as white solid. The resulting solid was washed with petroleum ether (2 x 20 mL) to afford analytically pure complex **Cu-PS-3**. Yield: 88% (20 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.68 – 7.66 (m, 1H), 7.51 – 7.48 (m, 5H), 7.47 – 7.42 (m, 9H), 7.40 – 7.34 (m, 9H), 7.33 – 7.28 (m, 8H), 6.93 (t, *J* = 7.9 Hz, 2H), 4.71 (d, *J* = 5.2 Hz, 4H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 170.1, 156.4, 148.8, 138, 133.4, 133.3, 132.1, 131.8, 130.4, 128.7, 128.6, 127.3, 123.7, 123.1, 44.4. **^{31}P{^{1}H} NMR** (162 MHz, DMSO) δ -13.1.



Scheme S1: Synthesis of Cu-PS-1, Cu-PS-2, and Cu-PS-3.

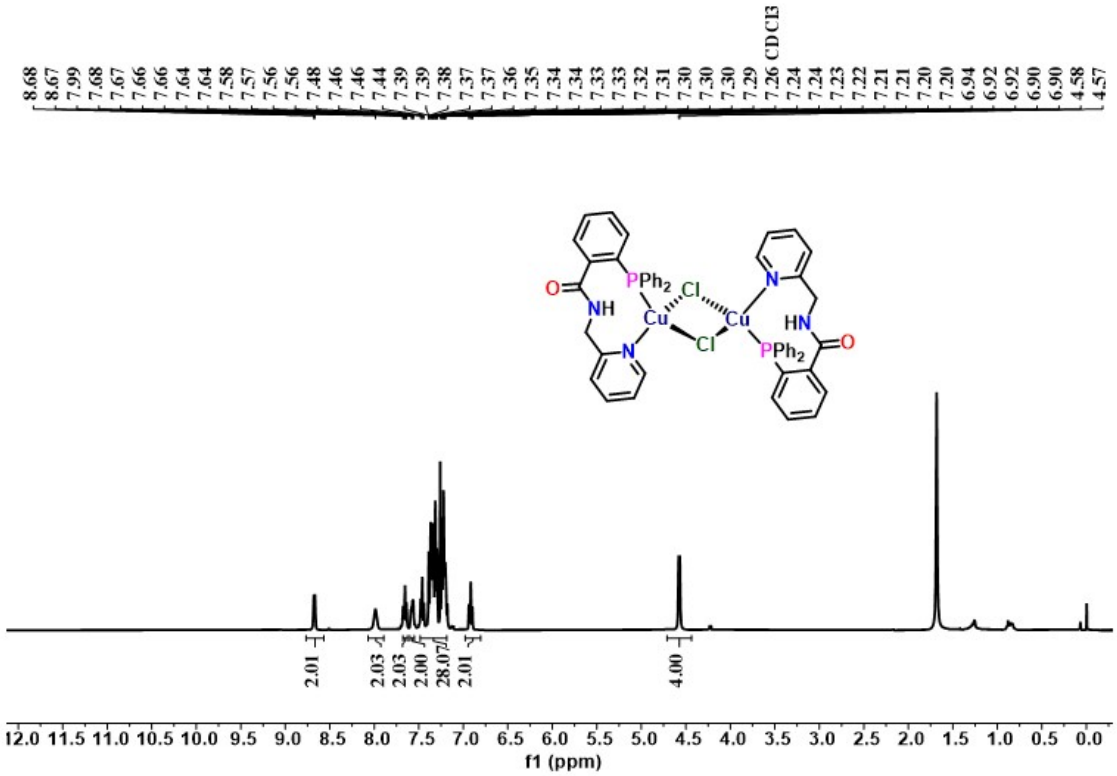


Figure S8. ^{1}H NMR spectrum of **Cu-PS-1** in $CDCl_3$ (400 MHz).

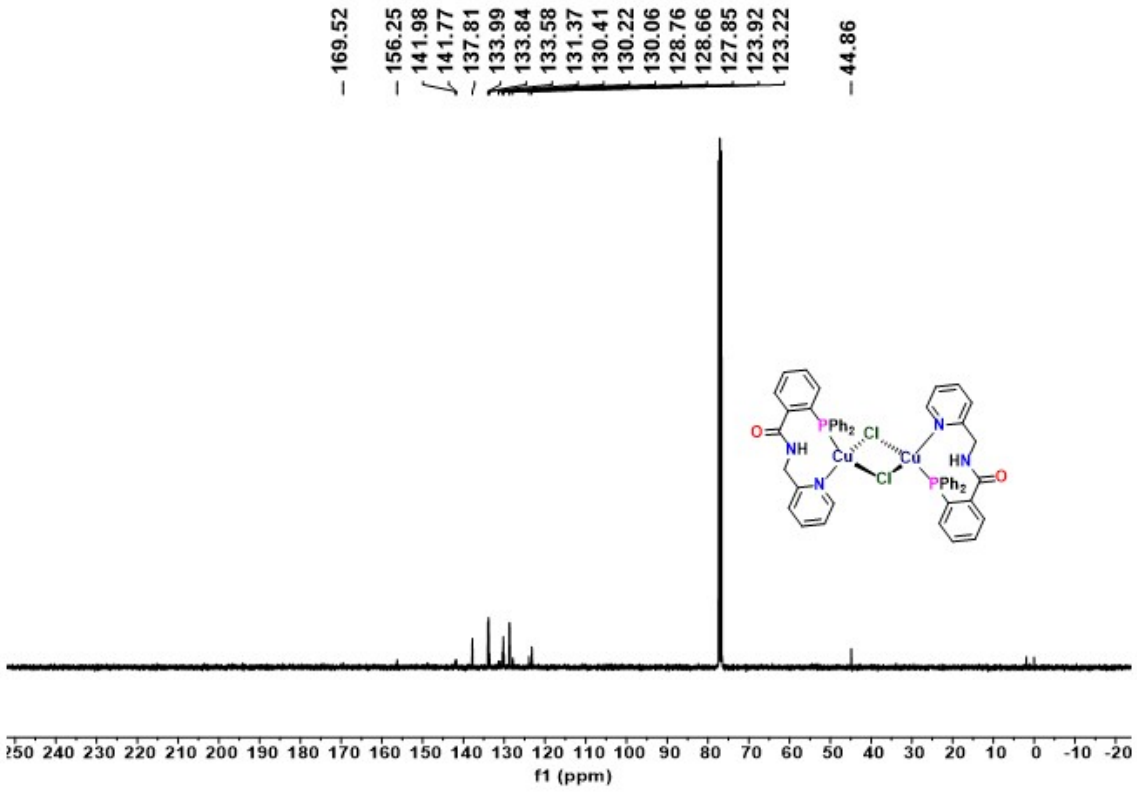


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **Cu-PS-1** in $CDCl_3$ (400 MHz).

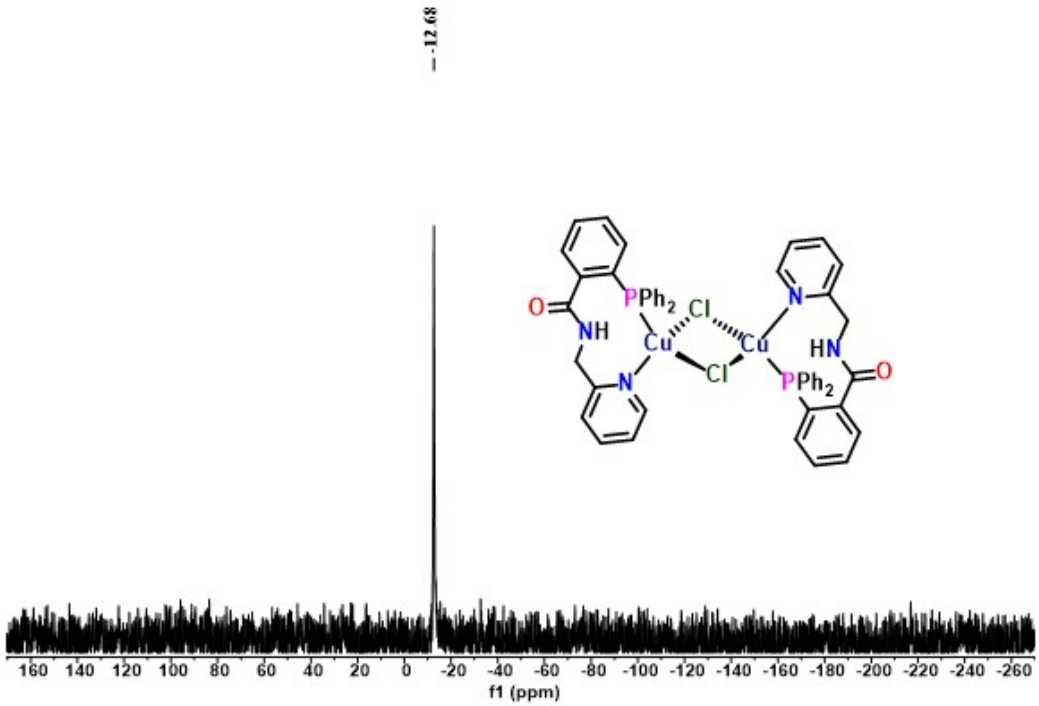


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** in DMSO-d_6 (400 MHz).

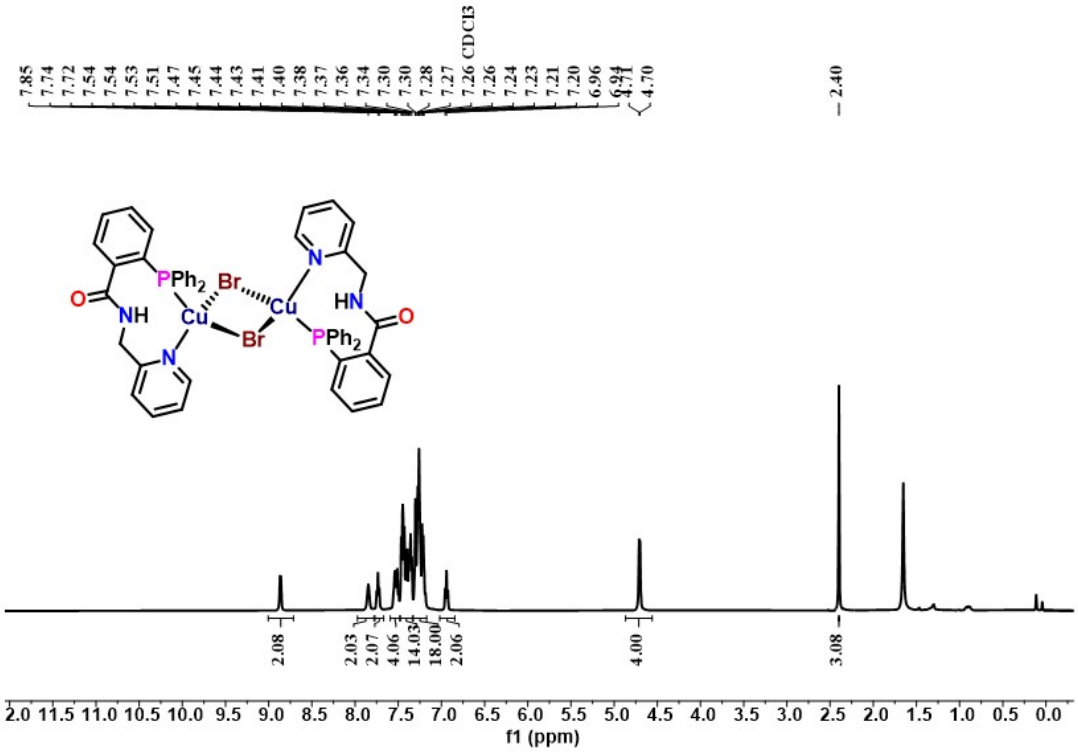


Figure S11. ^{1}H NMR spectrum of **Cu-PS-2** in $CDCl_3$ (400 MHz).

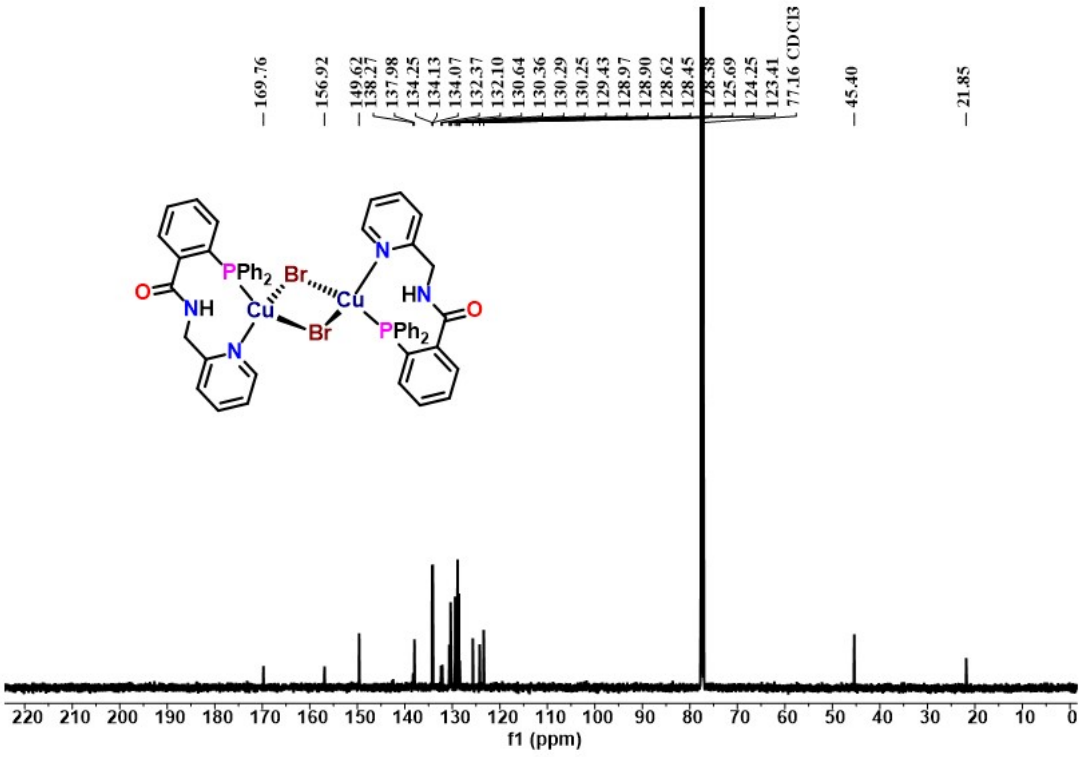


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **Cu-PS-2** in $CDCl_3$ (400 MHz).

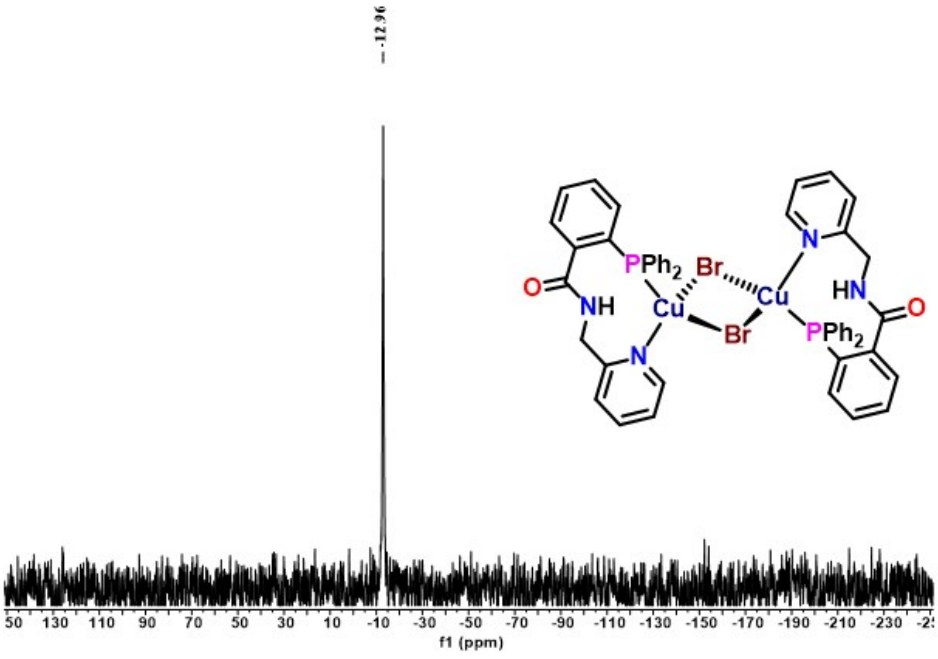


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** in DMSO-d_6 (400 MHz).

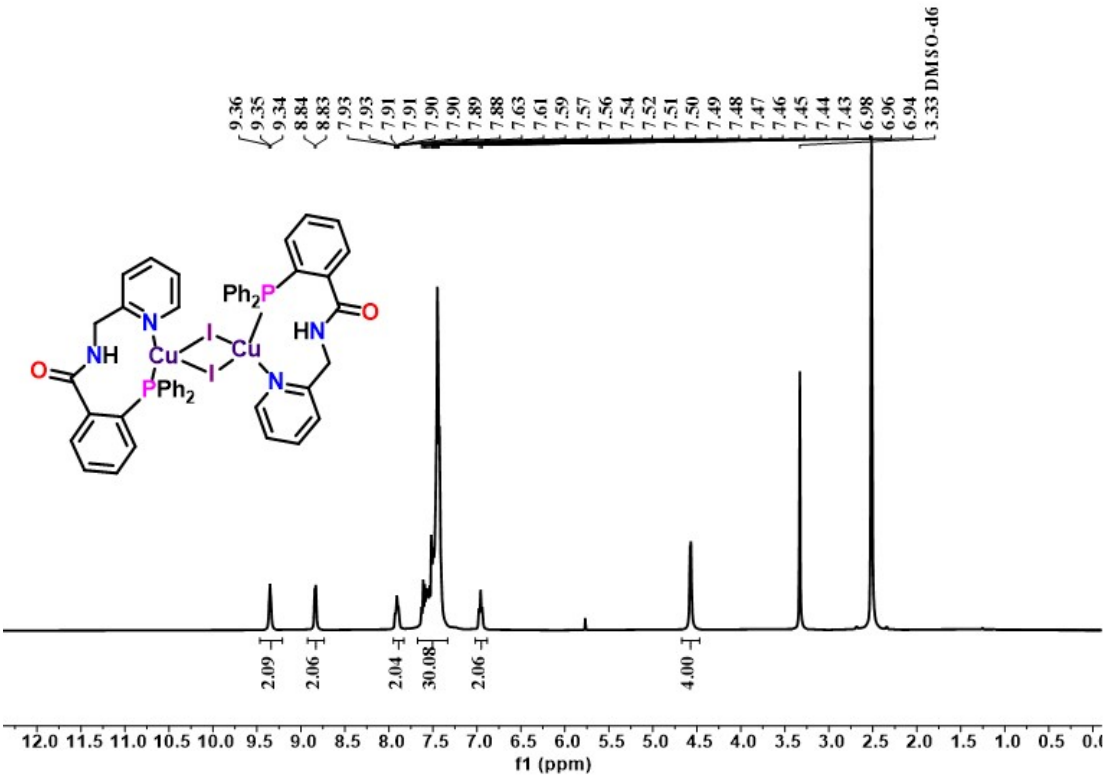


Figure S14. ^{1}H NMR spectrum of **Cu-PS-3** in $CDCl_3$ (400 MHz).

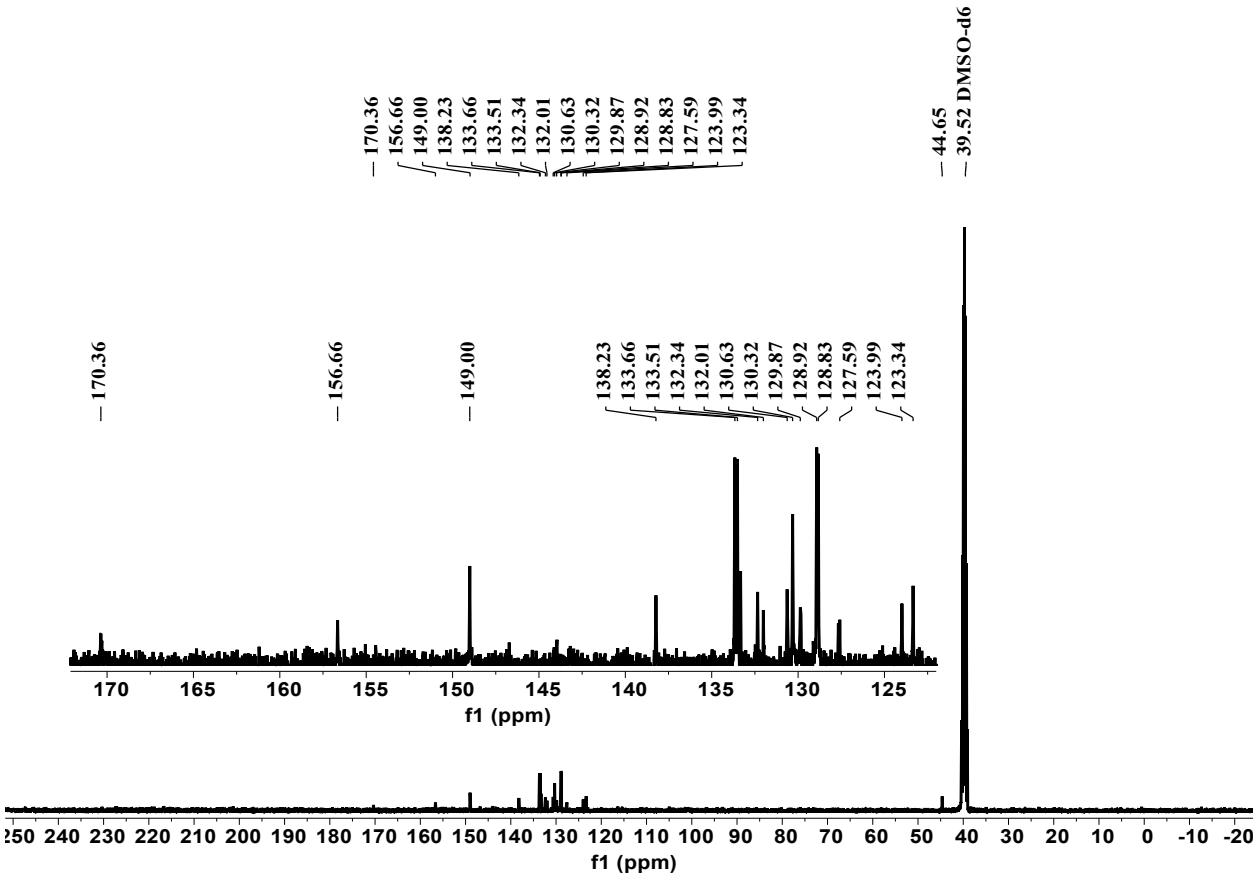


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of **Cu-PS-2** in $CDCl_3$ (101 MHz).

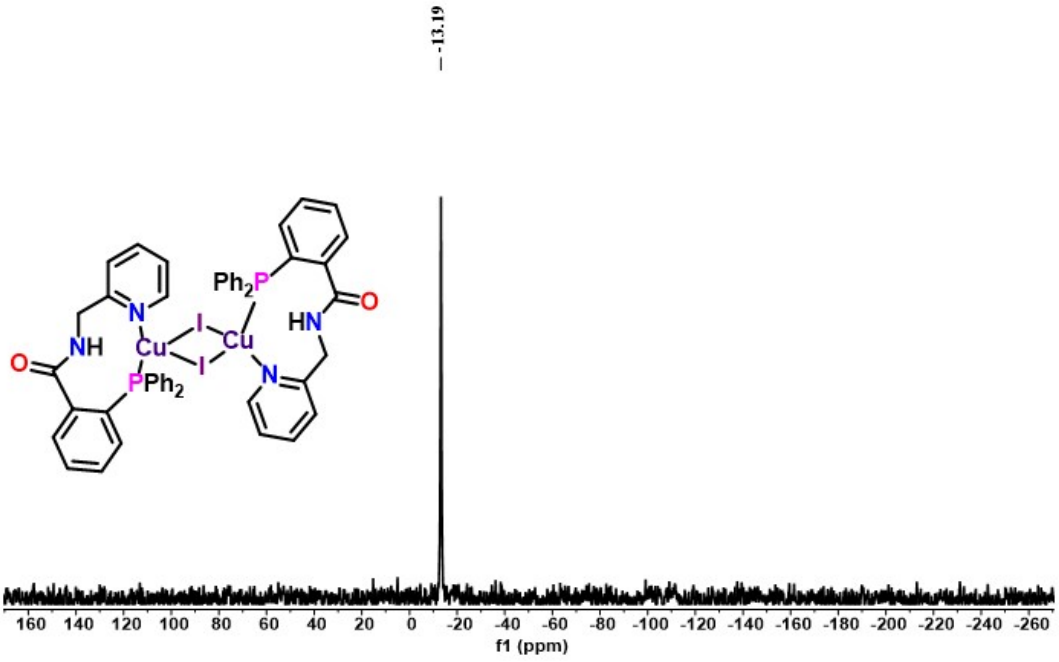


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** in DMSO-d_6 (162 MHz).

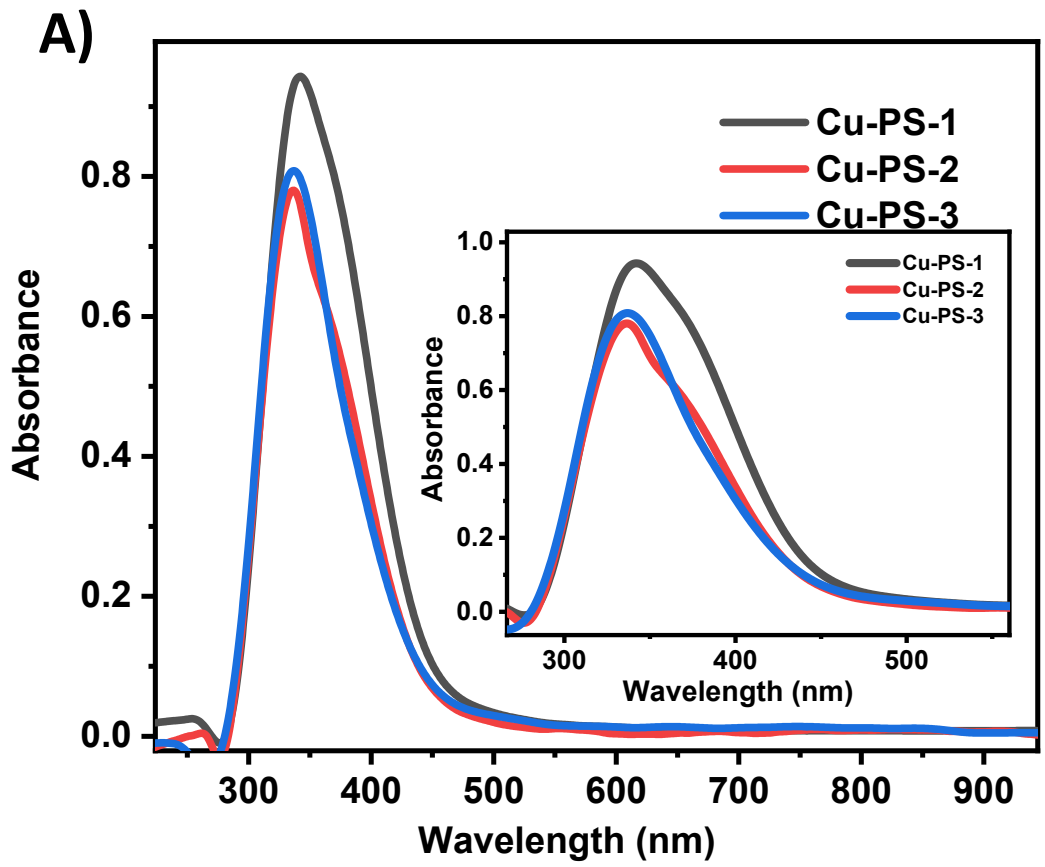


Figure S17: Optical spectral data of the copper photosensitizers (25 μM) **(Cu-PS-1**, **Cu-PS-2**, and **Cu-PS-3)**. This spectrum was recorded in DMA in the range 190 –1000 nm at 298K.

Electrochemistry of all the Cu(I) photosensitizers

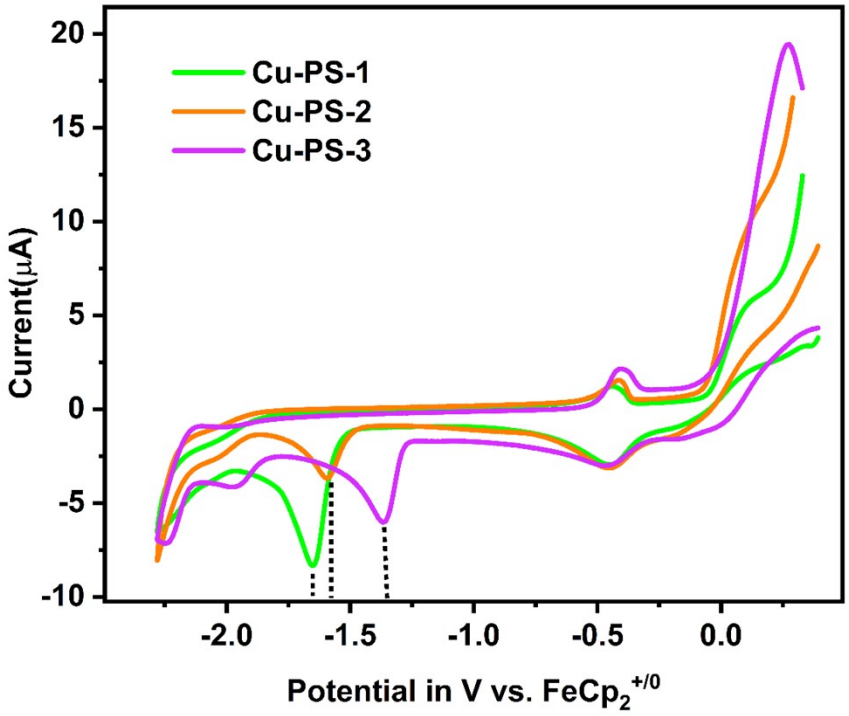


Figure S18. Cyclic Voltammetry study of copper photosensitizers (**Cu-PS-1**, **Cu-PS-2**, **Cu-PS-3**) complex under argon atmosphere in DMA at 298 K temperature.

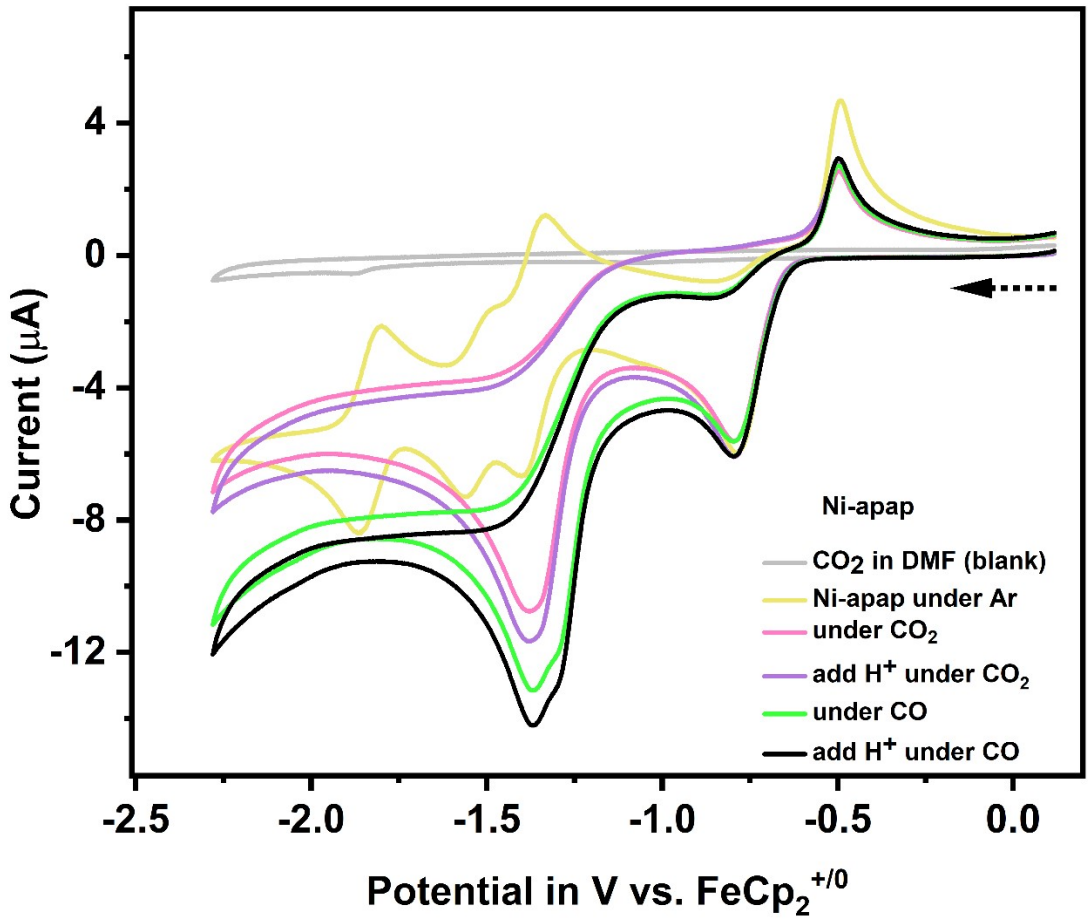


Figure S19. Cyclic Voltammetry study of **C1** complex under argon atmosphere (yellow), CO_2 atmosphere (pink), CO_2 atmosphere in presence of proton source (purple), under CO atmosphere (green), and CO atmosphere in presence of proton source (black) in DMA at 298 K temperature. The arrow indicates the origin and direction of the scan.

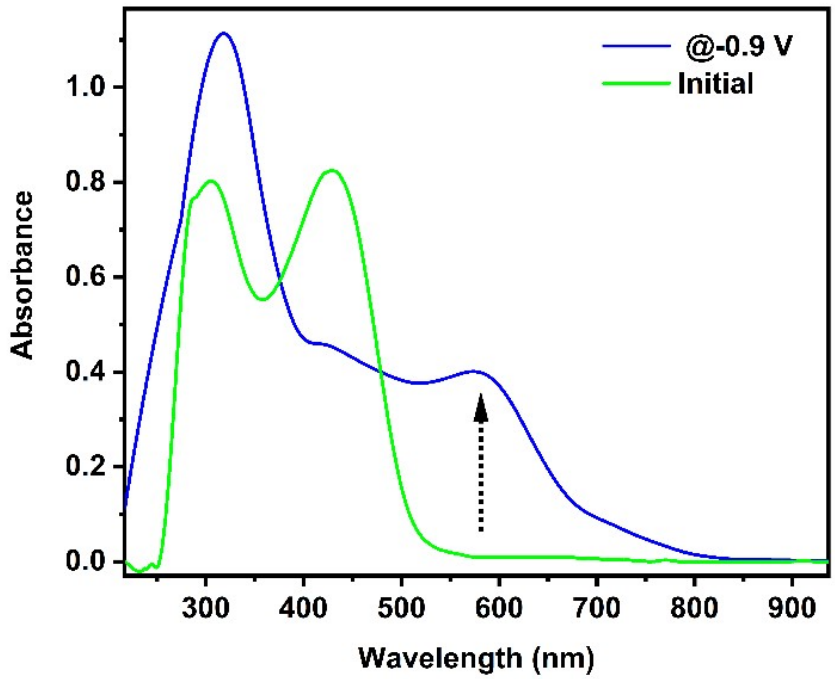


Figure S20. UV- visible spectra of the **C1** under electrochemical condition at no potential (green) and at -0.9 V vs. $FeCp_2^{+/0}$ potential (blue). These spectra was recorded in the range 190 –1000 nm at 298K.

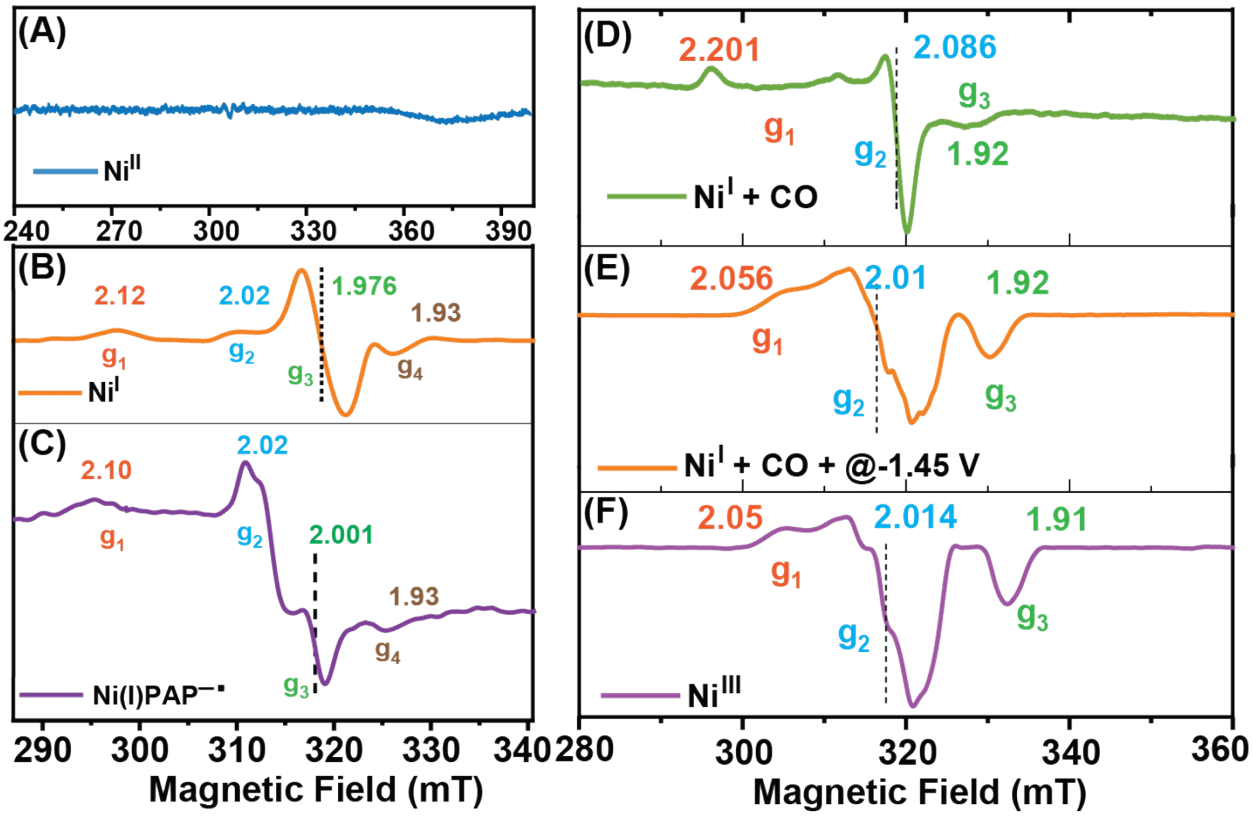


Figure S21. The experimental EPR spectra of with the concentration of 3 mM catalyst (**A**) Ni^{II} (**B**) Ni^{I} (one electron reduction: Ni^{II} + at the applied potential -0.9 V *vs*. $FeCp_2^{+/0}$), (**C**) $Ni^{I}PAP^{-\cdot}$ (two-electron reduction: Ni^{II} + at the applied potential -1.3 V vs. $FeCp_2^{+/0}$). (**D**) The change in EPR spectra under CO-saturated Ni(I)-apap catalyst, after electrochemical one-electron reduction of N(II)-apap without applying any potential (**E**) The change in the EPR spectra under CO at the applied potential -1.5 V vs. $FeCp_2^{+/0}$ starting from one electron reduces the Ni^{I} system. (**F**) The change in EPR spectrum after one-electron oxidation of the C1 complex by CAN. All data recorded in DMA solvent at 77 K.

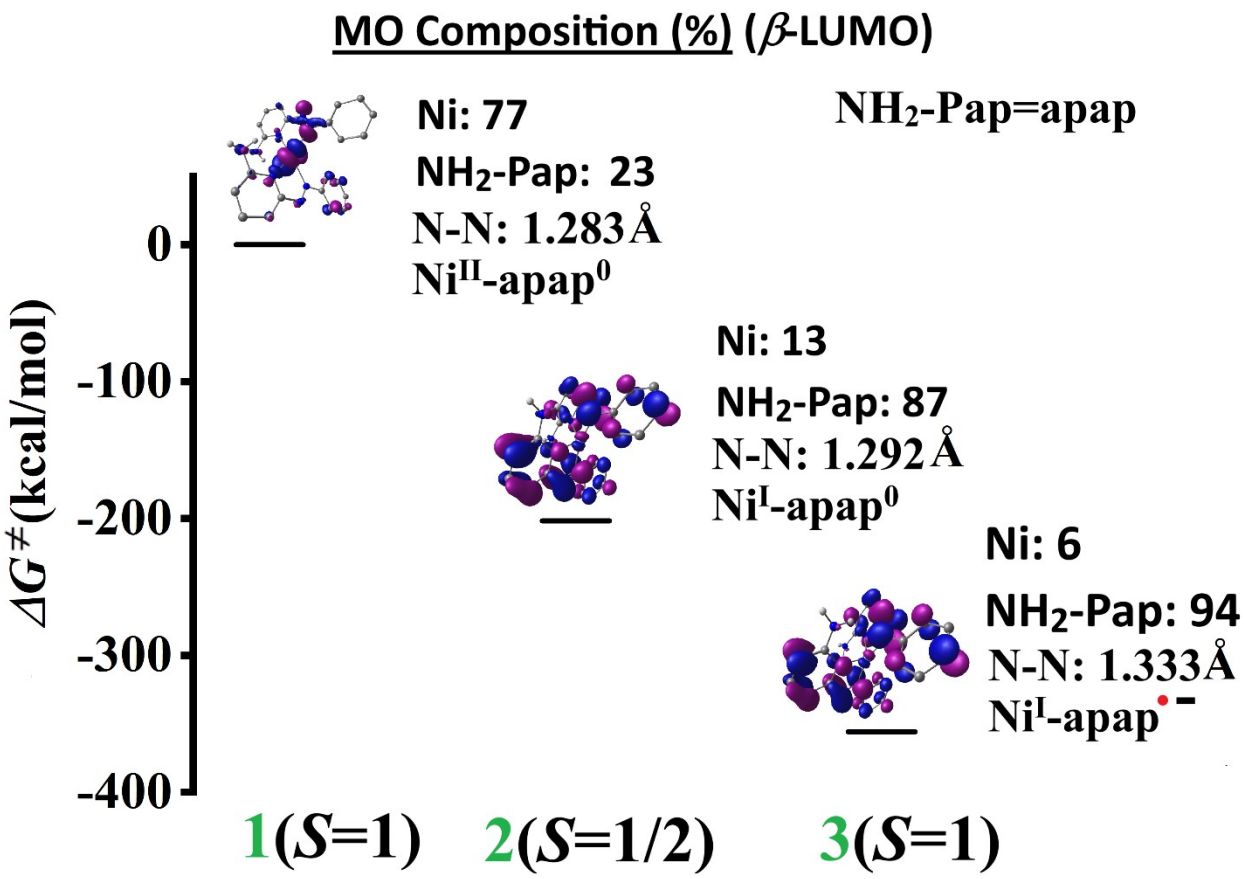


Figure S22. Composition and Energies of Selected Molecular Orbitals of Catalyst **C1**.

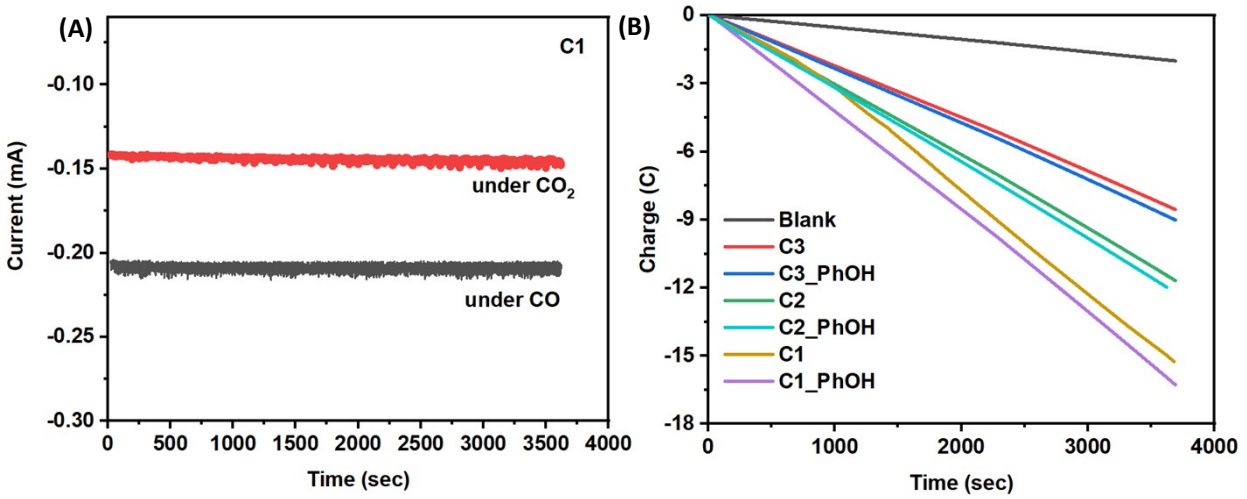


Figure S23. (A) Current vs. Time plot was recorded during the bulk (with phenol) electrolysis of Ni-complex performed at -1.6 V under 1 atm CO_2 and -1.5 V under 1 atm CO vs. $FeCp_2^{+/0}$ in DMA. (**B**) The charge vs. time for all complexes, C1, C2 and C3, with and without phenol.

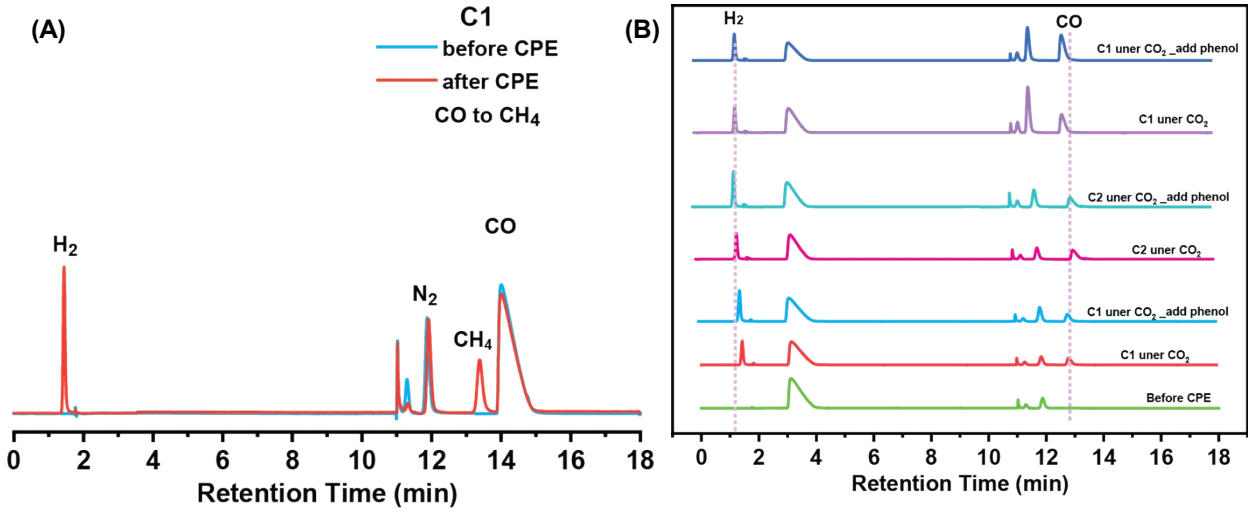


Figure S24. The gas chromatography data recorded for the headspace gas analyte generated during the bulk electrolysis of C1 at (A) -1.5 V vs. $Fc^{+/0}$ in DMA under 1 atm saturated CO and at (B) The gas chromatography data recorded for the headspace gas analyte generated during the bulk electrolysis of all the three catalyst C1, C2 and C3 in DMA under 1 atm saturated CO_2 condition.

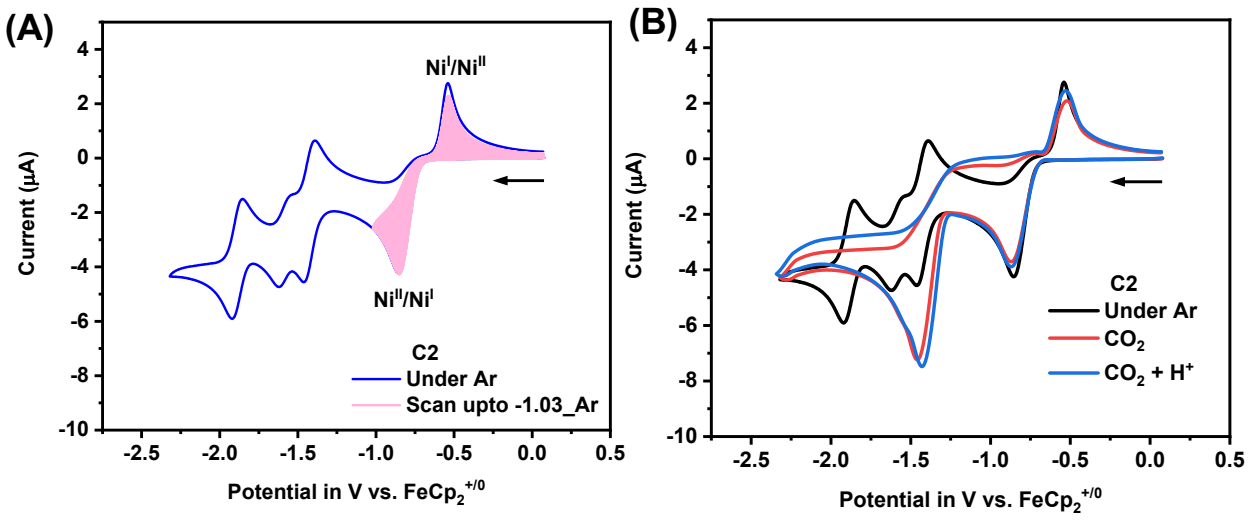


Figure S25. Cyclic Voltammetry (CV) study of **C2** (0.5 mM) complex (**A**) under argon atmosphere full-scan (blue trace): scan till -1.03 V (violet trace) (**B**) under Ar (black trace): under CO_2 atmosphere (red trace), CO_2 atmosphere in presence of proton source (blue trace) in DMA at 298 K temperature. The arrow indicates the origin and direction of the scan.

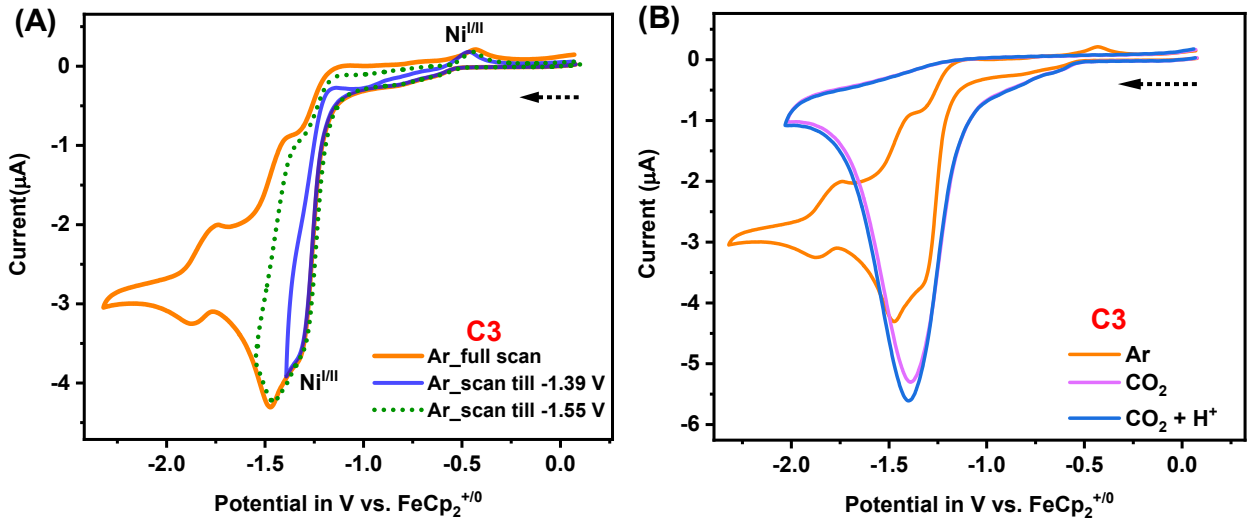


Figure S26. Cyclic Voltammetry (CV) study of **C3** (0.5 mM) complex (**A**) under argon atmosphere full-scan (orange trace): scan till -1.39 V (blue trace): scan up to -1.55 V (green trace) (**B**) under Ar (orange trace): under CO_2 atmosphere (violet trace), CO_2 atmosphere in presence of

proton source (blue trace) in DMA at 298 K temperature. The arrow indicates the origin and direction of the scan.

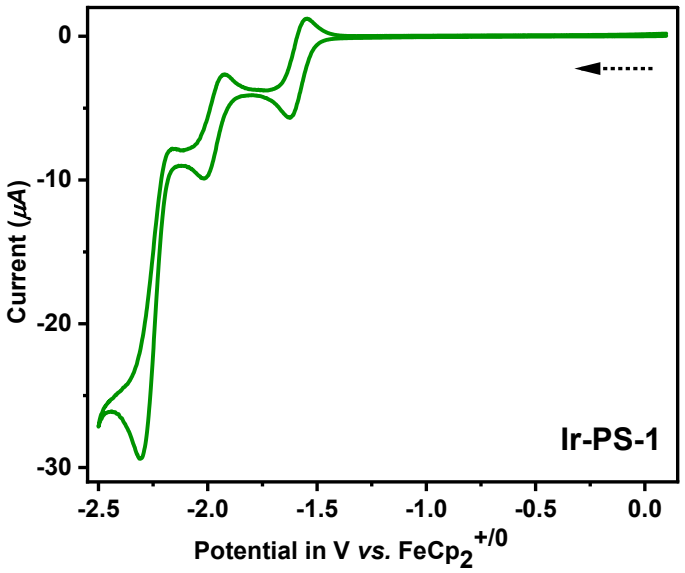


Figure S27. Shows Cyclic Voltammetry (CV) study of **Ir-PS-1** (1.0 mM) complex under Argon atmosphere in DMA at 298 K temperature with scan rate of 100 mV/s.

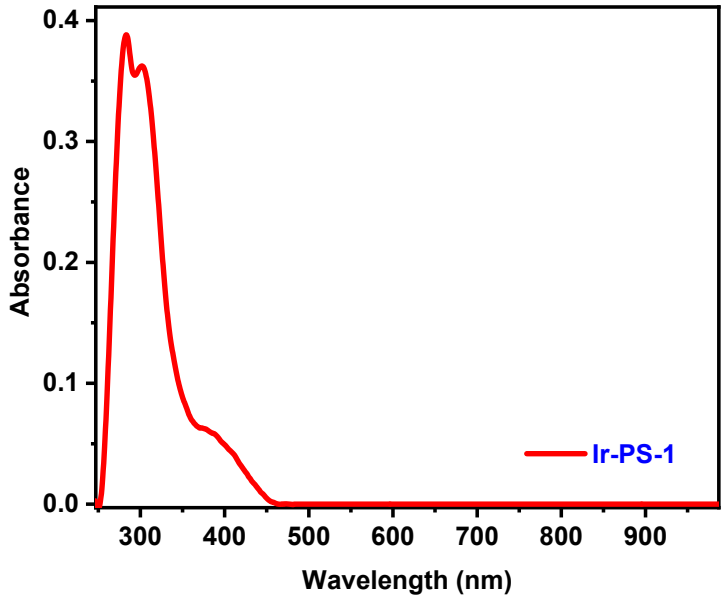


Figure S28. Shows Optical spectral data of the **Ir-PS-1 (**20 μM). This spectrum was recorded in the range 150 –1050 nm at 298 K in DMA solvent.

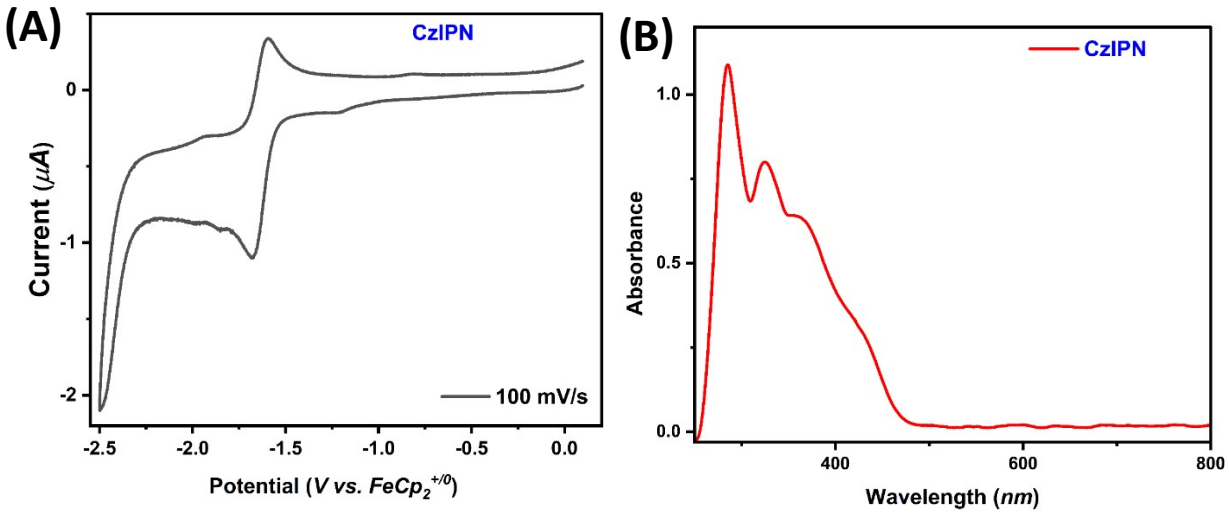


Figure S29. (A) shows Cyclic Voltammetry (CV) study of **CzIPN** (0.5 mM) complex under Argon atmosphere in DMA at 298 K temperature with scan rate of 100 mV/s. **(B)** shows Optical spectral data of the **CzIPN** (25 μM). This spectrum was recorded in the range 15 –1050 nm at 298K in DMA solvent.

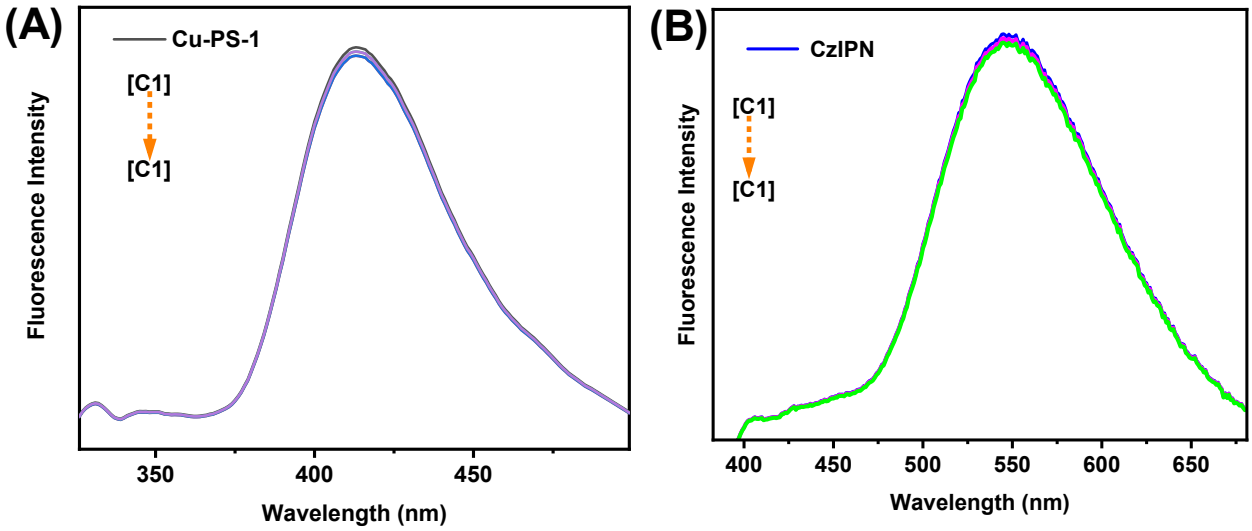


Figure S30. Changes in emission spectra of **(A) Cu-PS-1** and **(B) CzIPN** on gradually increasing **C1** (2-12 mM) concentration in DMA solution at 298 K, respectively.

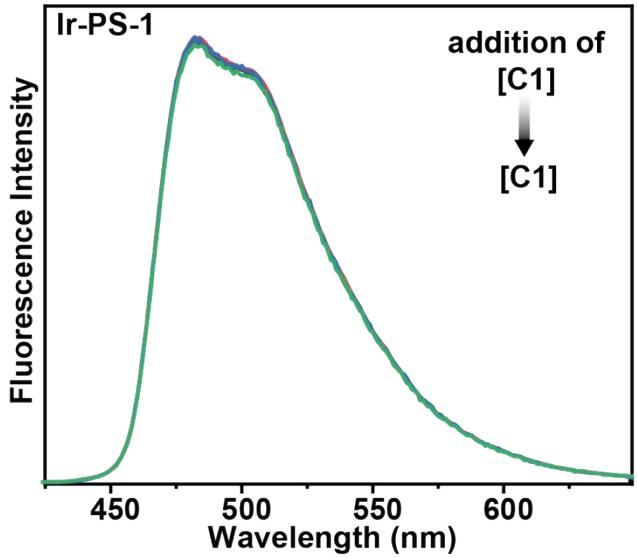


Figure S31. Changes in emission spectra of **Ir-PS-1** on gradually increasing **C1** (2-12 mM) concentration in DMA solution at 298 K.

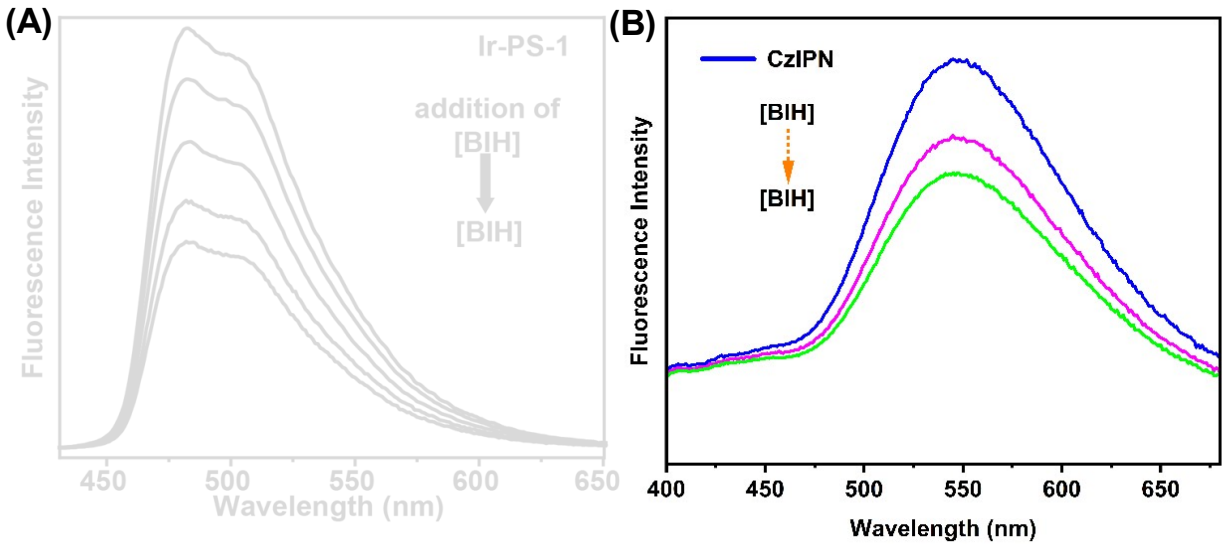


Figure S32. The variation in the emission spectra of **(A) Ir-PS-1** and **(B) CzIPN** upon gradually increasing concentration of BIH (0.2 to 10 mM) in DMA solution at 298 K.

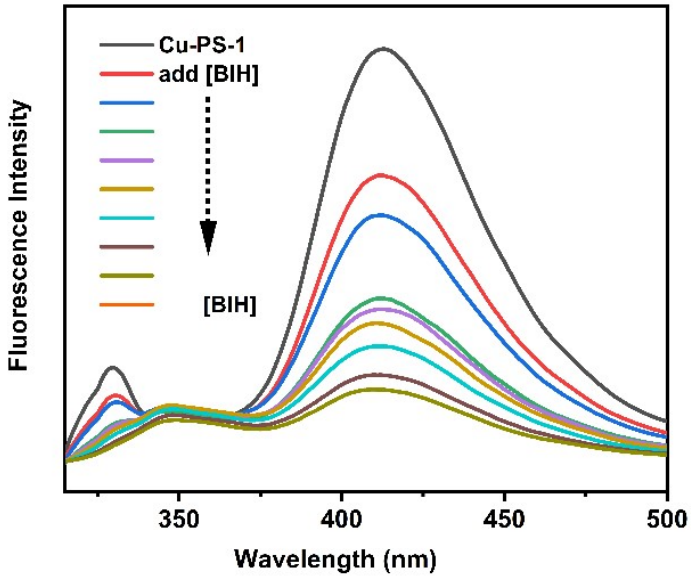


Figure S33. The variation in the emission spectra of **Cu-PS-1** (0.5 mM) upon gradually increasing concentration of BIH (0.2 to 12 mM) in DMA solution at 298 K.

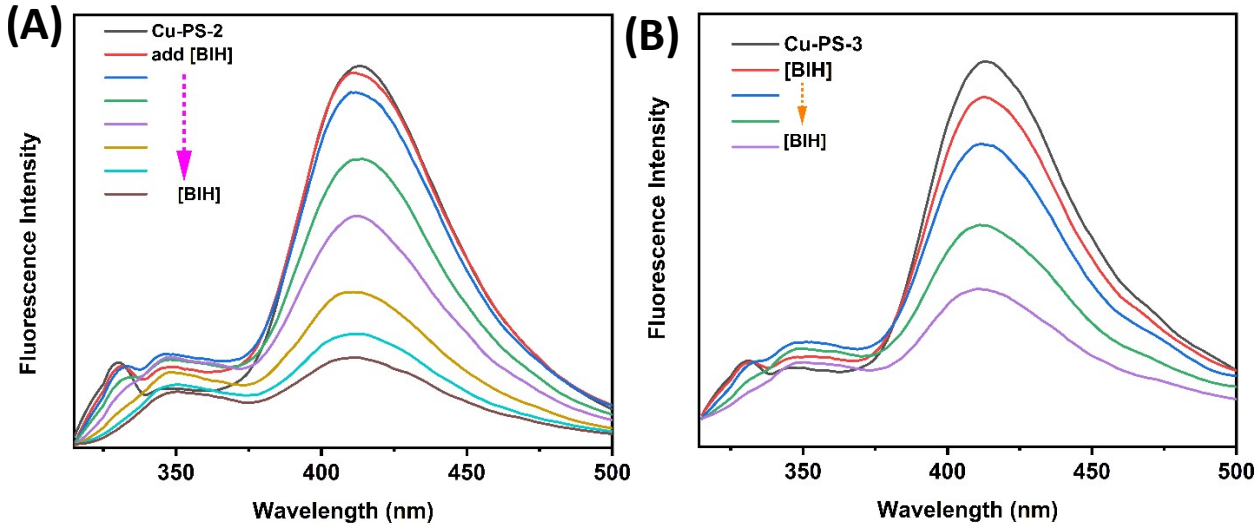


Figure S34. The variation in the emission spectra of (**A**) **Cu-PS-2** (0.5 mM) and (**B**) **Cu-PS-3** (0.5 mM) upon gradually increasing concentration of BIH (0.2 to 12 mM) in DMA solution at 298 K.

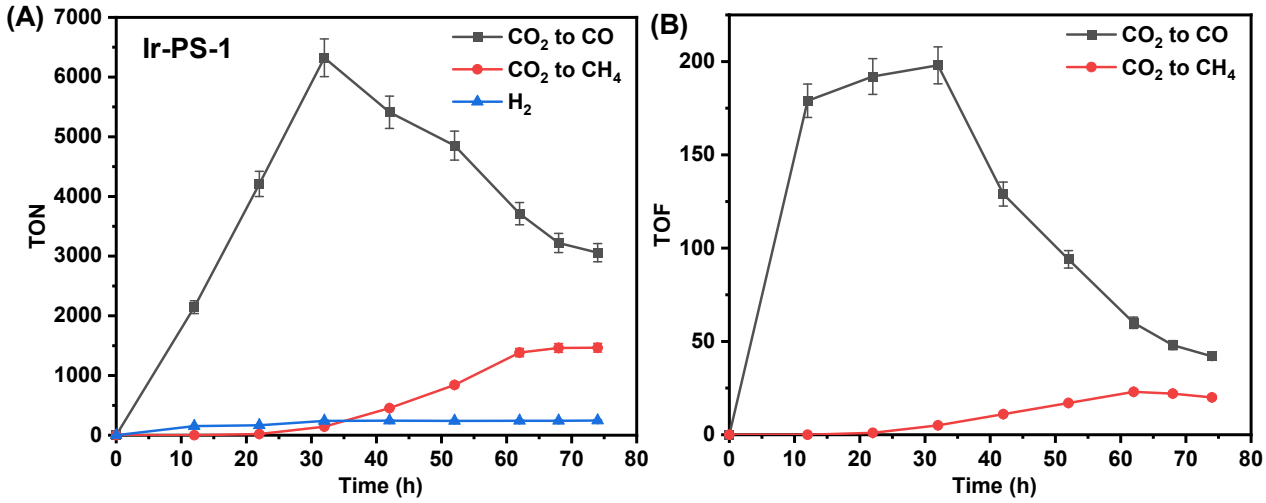


Figure S35. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2(blue) generation from CO_2 over time using of **Ir-PS-1** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

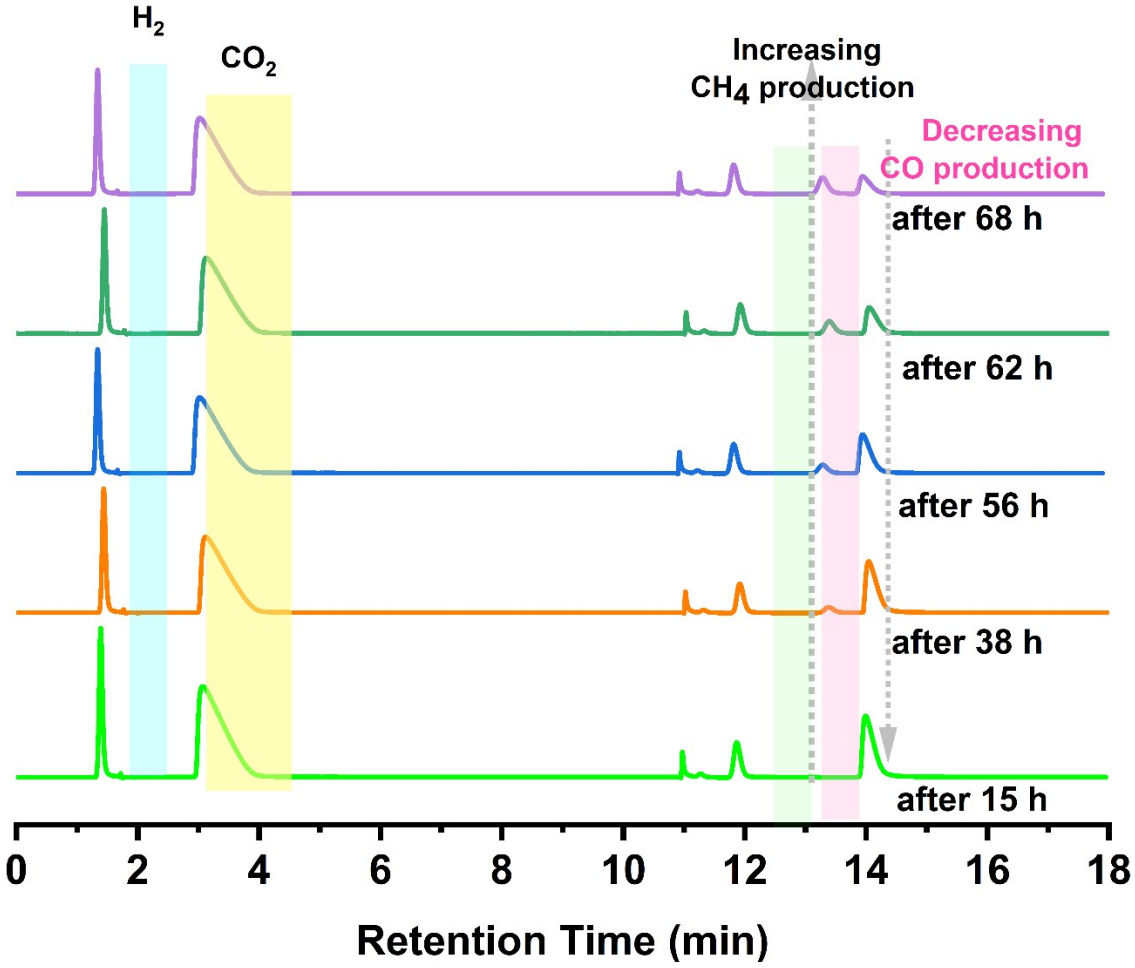


Figure S36. The GC data recorded for the progress of photocatalytic CO and CH_4 generation using **Ir-PS-1** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. Here with increase in the time of irradiation of light, increase in CH_4 production and decrease in CO production was observed. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

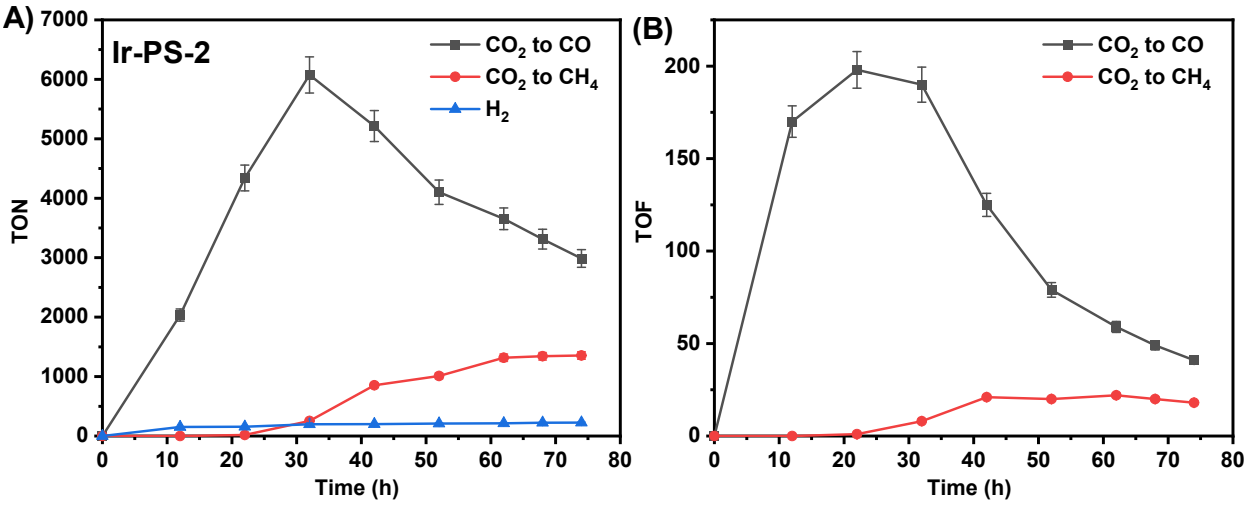


Figure S37. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2(blue) generation from CO_2 over time using of **Ir-PS-2** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

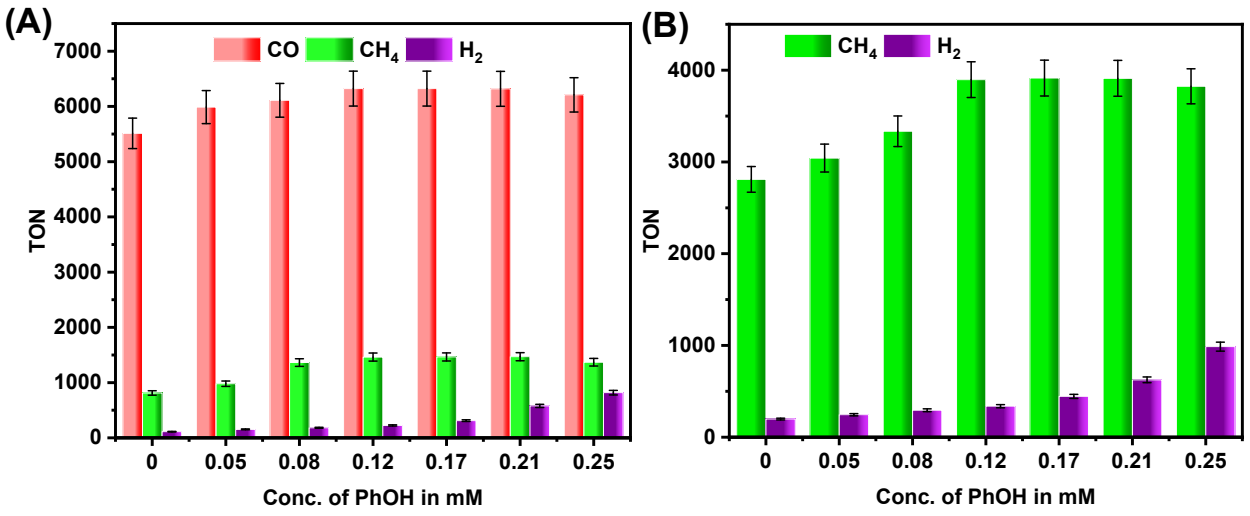


Figure S38. (**A**) Progress of photocatalytic CO_2 to [CO (radish), CH_4 (greenish), and H_2 (deep violet)] and CO to CH_4 generation in terms of TON over time using of **Ir-PS-1** along with **C1** as

photocatalyst (PC) and BIH as sacrificial donor. (**B**) Progress of photocatalytic CO to CH_4 (greenish), and H_2 (deep violet)] generation in terms of TON over time using of **Ir-PS-1** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

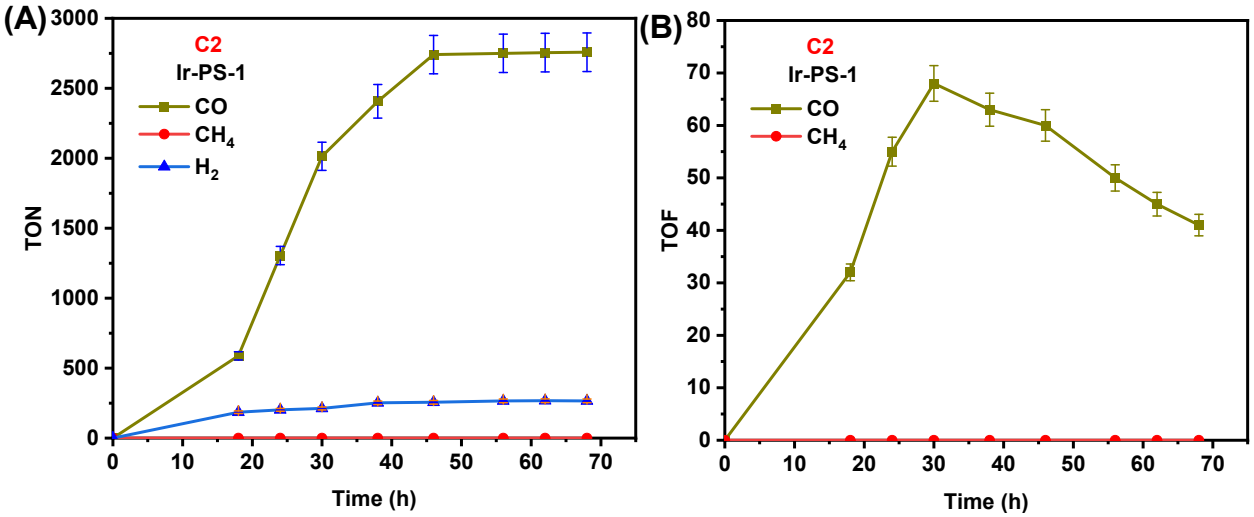


Figure S39. Progress of photocatalytic CO (dark green), CH_4 (red), and H_2(blue) generation from CO_2 over time using of **Ir-PS-1** along with **C2** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

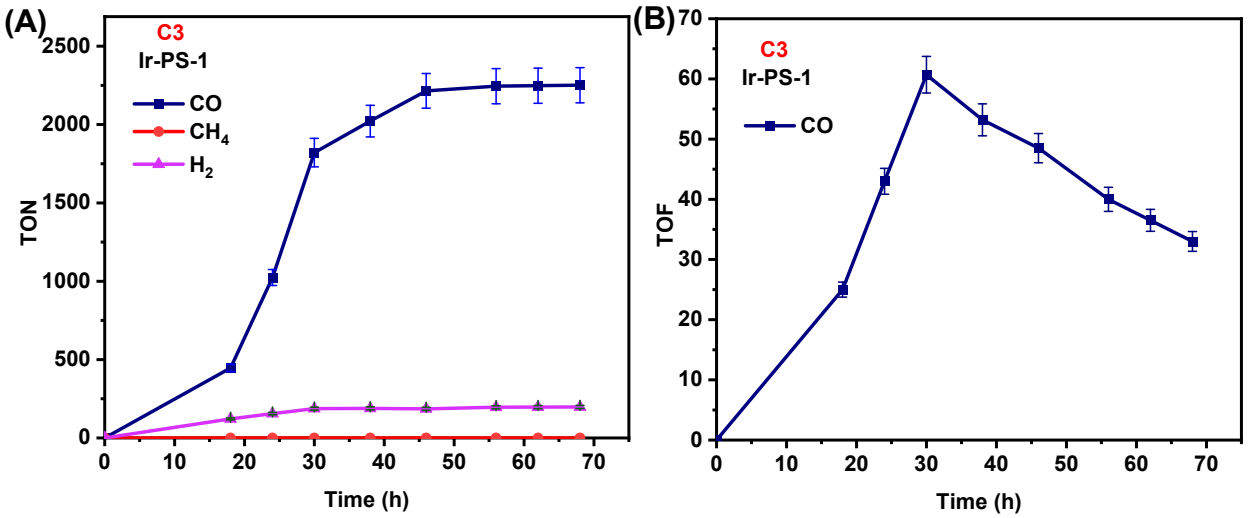


Figure S40. Progress of photocatalytic CO (dark blue), CH_4 (red), and H_2(violet) generation over time using **Ir-PS-1** along with **C3** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

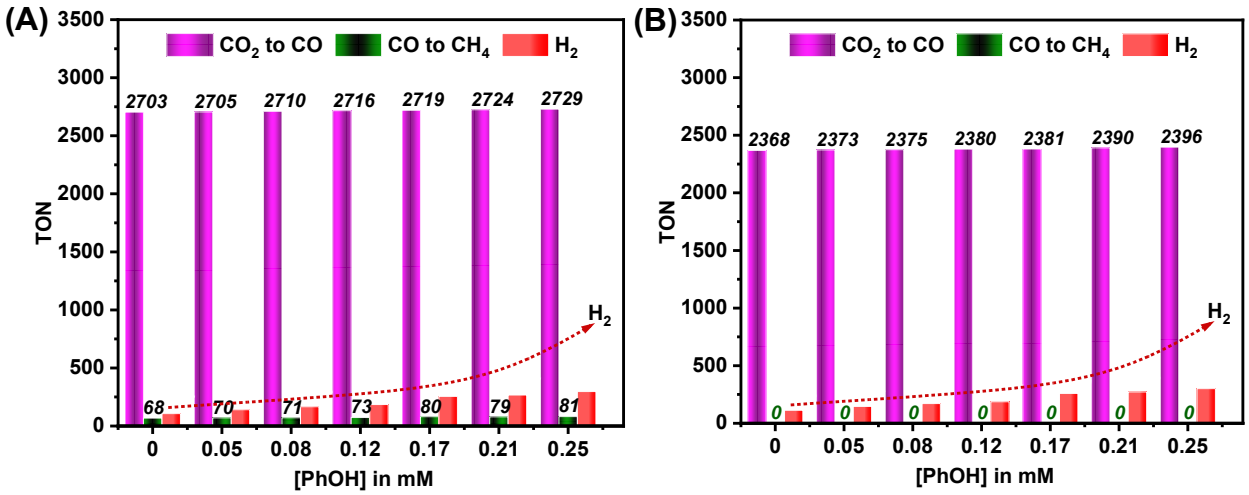


Figure S41. Progress of photocatalytic CO_2 to [CO (deep violet), CH_4 (yellow), and H_2 (red)] and CO to CH_4 generation in terms of TON over time using **Ir-PS-1** and BIH as a sacrificial donor along with catalyst (**A**) **C2** and (**B**) **C3**. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

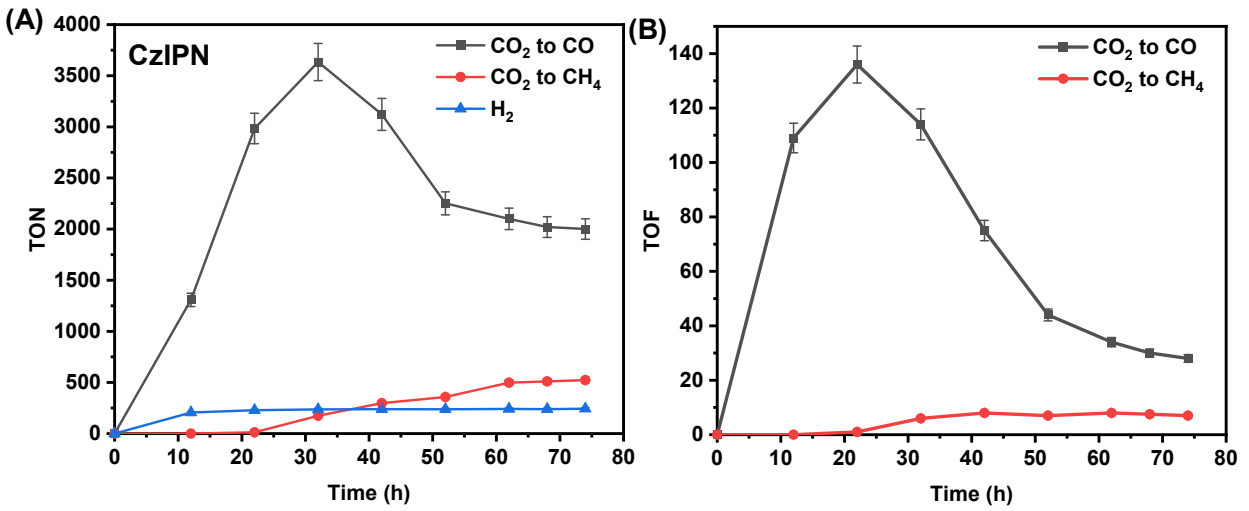


Figure S42. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2(blue) generation from CO_2 over time using of **CzIPN** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a

CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

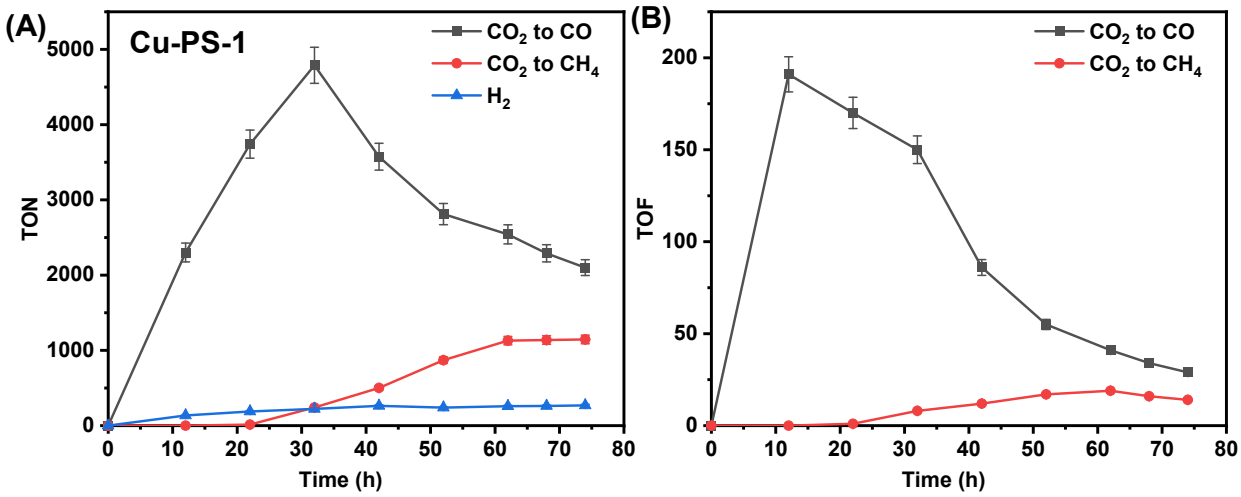


Figure S43. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2(blue) generation from CO_2 over time using of **Cu-PS-1** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

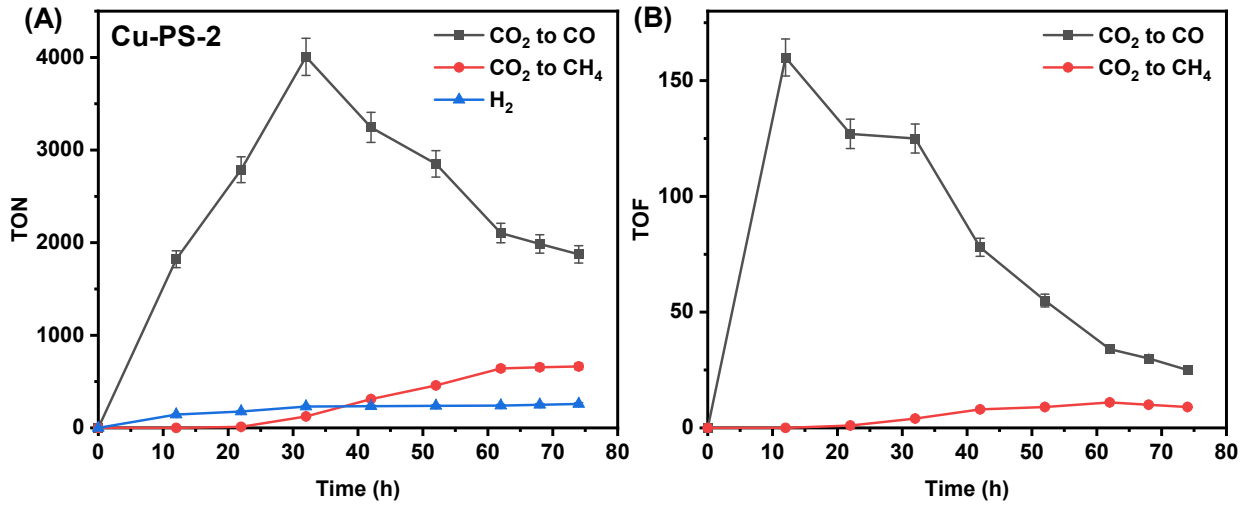


Figure S44. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2(blue) generation from CO_2 over time using of **Cu-PS-2** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

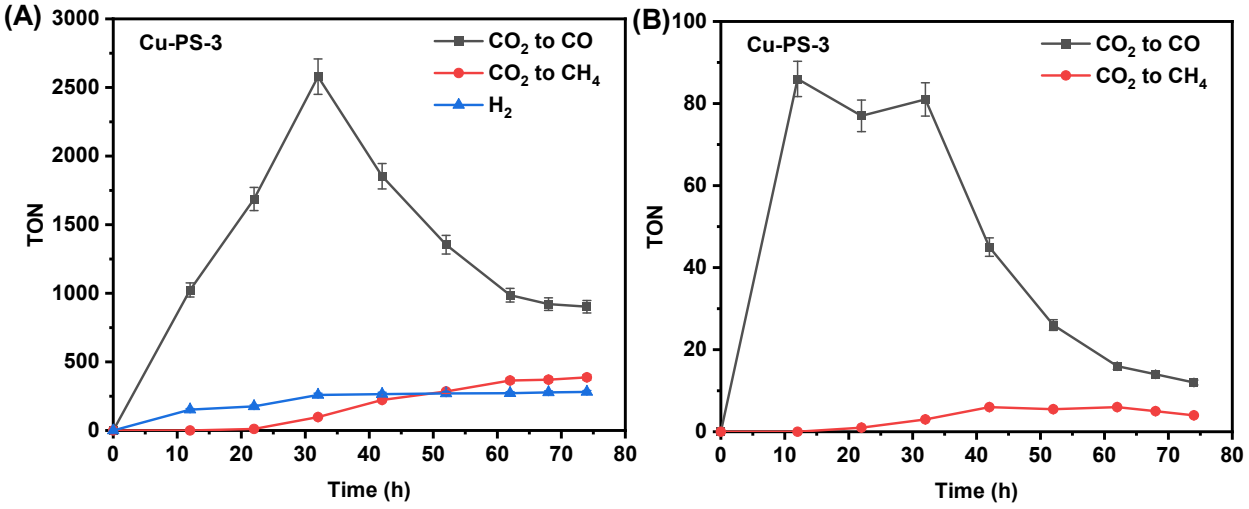


Figure S45. Progress of photocatalytic CO (orange), CH_4 (violet), and H_2 (blue) generation from CO_2 over time using of **Cu-PS-3** along with **C1** as photocatalyst (PC) and BIH as sacrificial donor. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time. The photocatalytic reaction was carried out in a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

Time-dependent NMR studies

To gain insight into the mechanism, the progress of the model reaction was monitored by variable-time ^{1}H and $^{31}P\{^{1}H\}$ NMR in a J. Young NMR tube in DMSO-d_6 under irradiation of visible 440 nm light. Initially, the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra obtained resembled to the exact spectra of $Cu^{I}I$ dimer. The spectra recorded after 32 h showed slight broadening in the $^{31}P\{^{1}H\}$ NMR signal depicting the slight conversion of Cu^{I} to Cu^{II}. However, after 52 h broad and unresolved ^{1}H and

$^{31}P\{^{1}H\}$ spectra were obtained which shows the complete conversion of Cu^{I} to a paramagnetic Cu^{II} species.

Time dependent NMR study of the Cu-PS-3 i.e. $Cu^{I}I$ dimer photosensitizer under the irradition of 440 nm light.

NMR spectra after 1 h

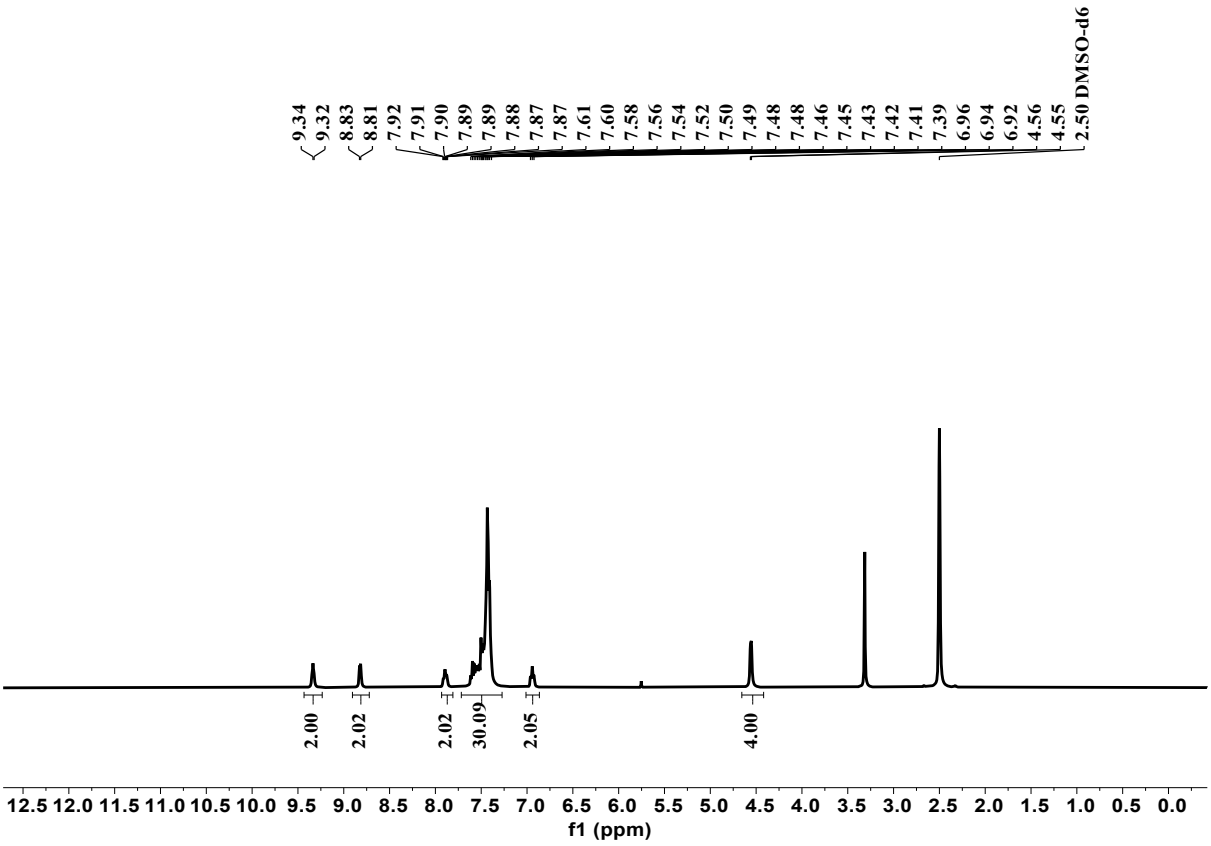


Figure S46: ^{1}H NMR spectrum of **Cu-PS-3** i.e. **$Cu^{I}I$** dimer after 1 h irradiation of light.

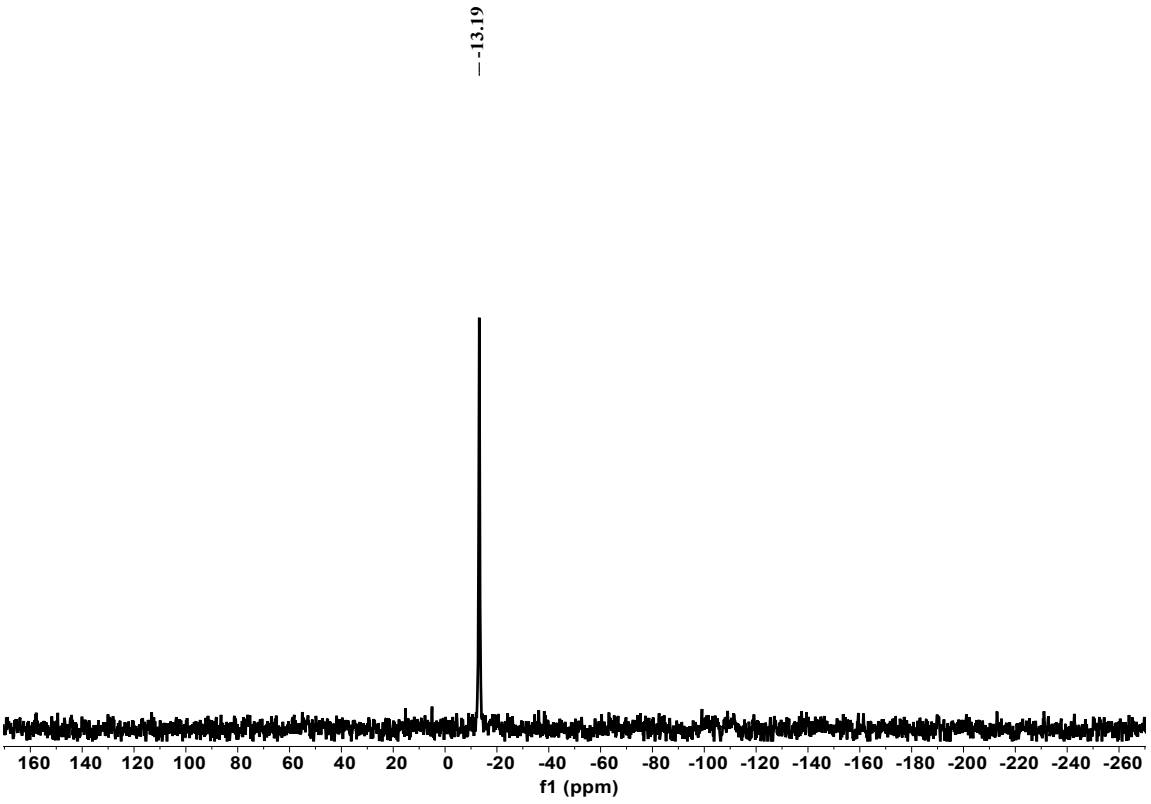


Figure S47: $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 1 h irradiation of light.

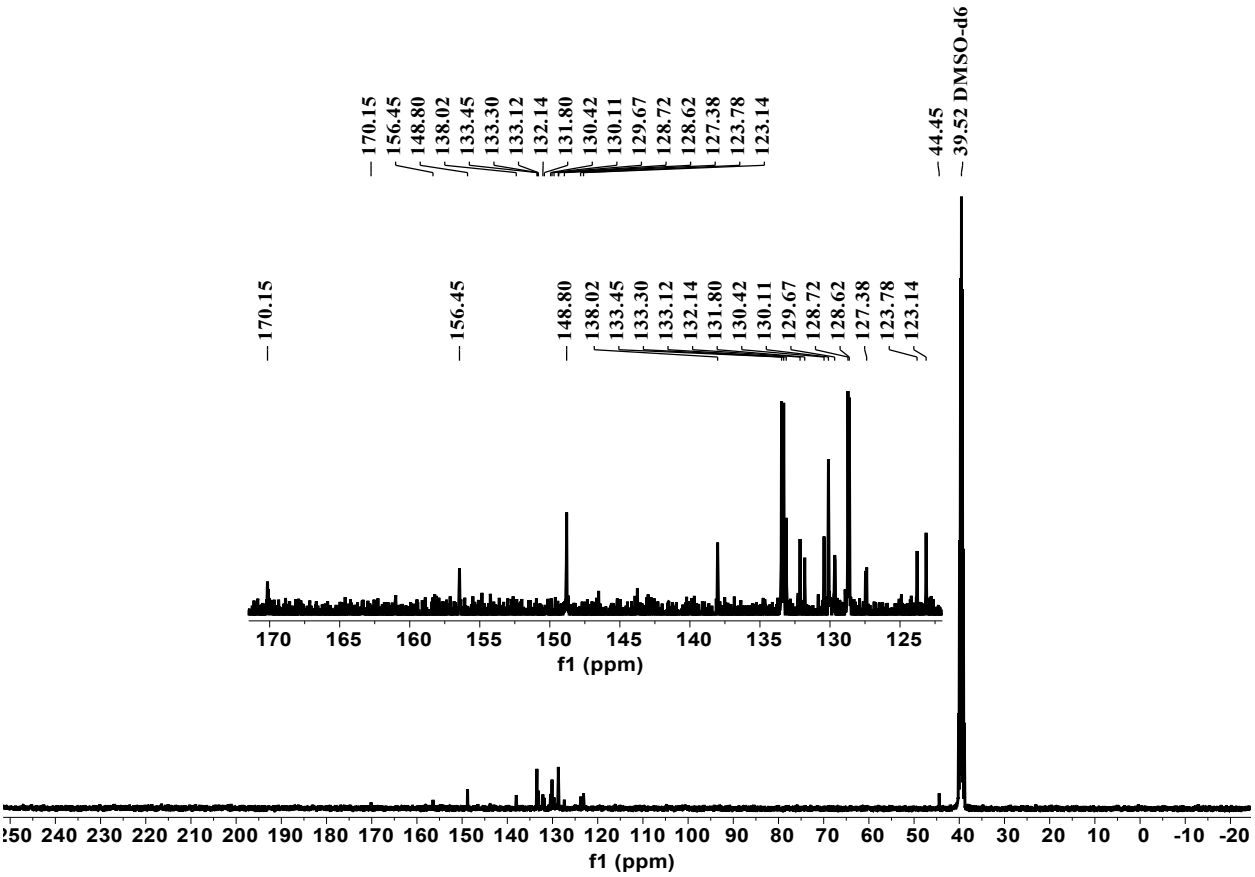


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 1 h irradiation of light.

NMR spectra after 42 h

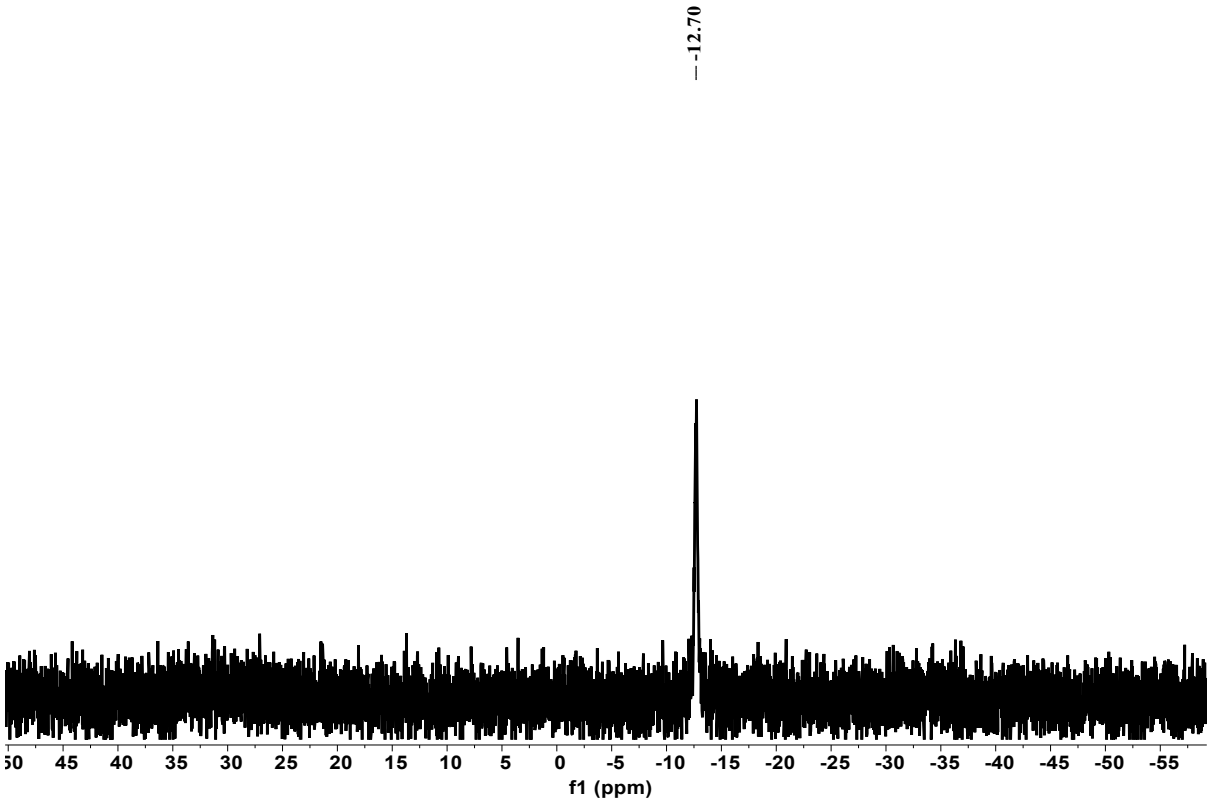


Figure S49: $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 42 h irradiation of light.

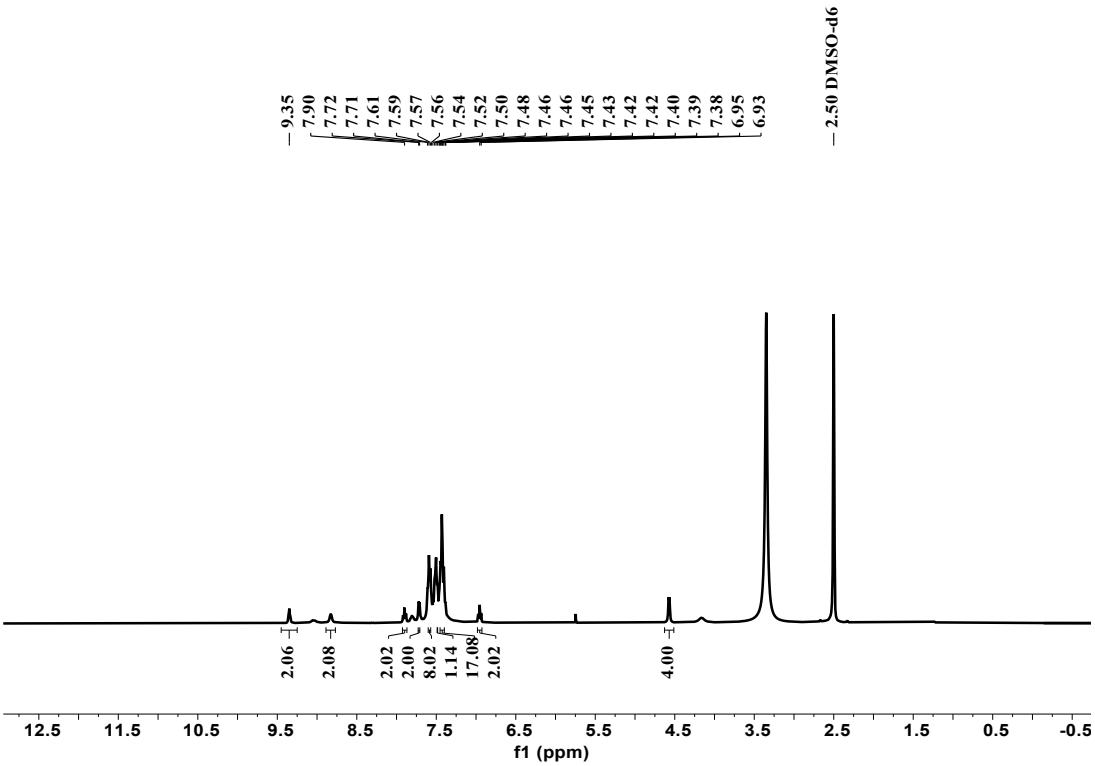


Figure S50: ^{1}H NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 42 h irradiation of light.

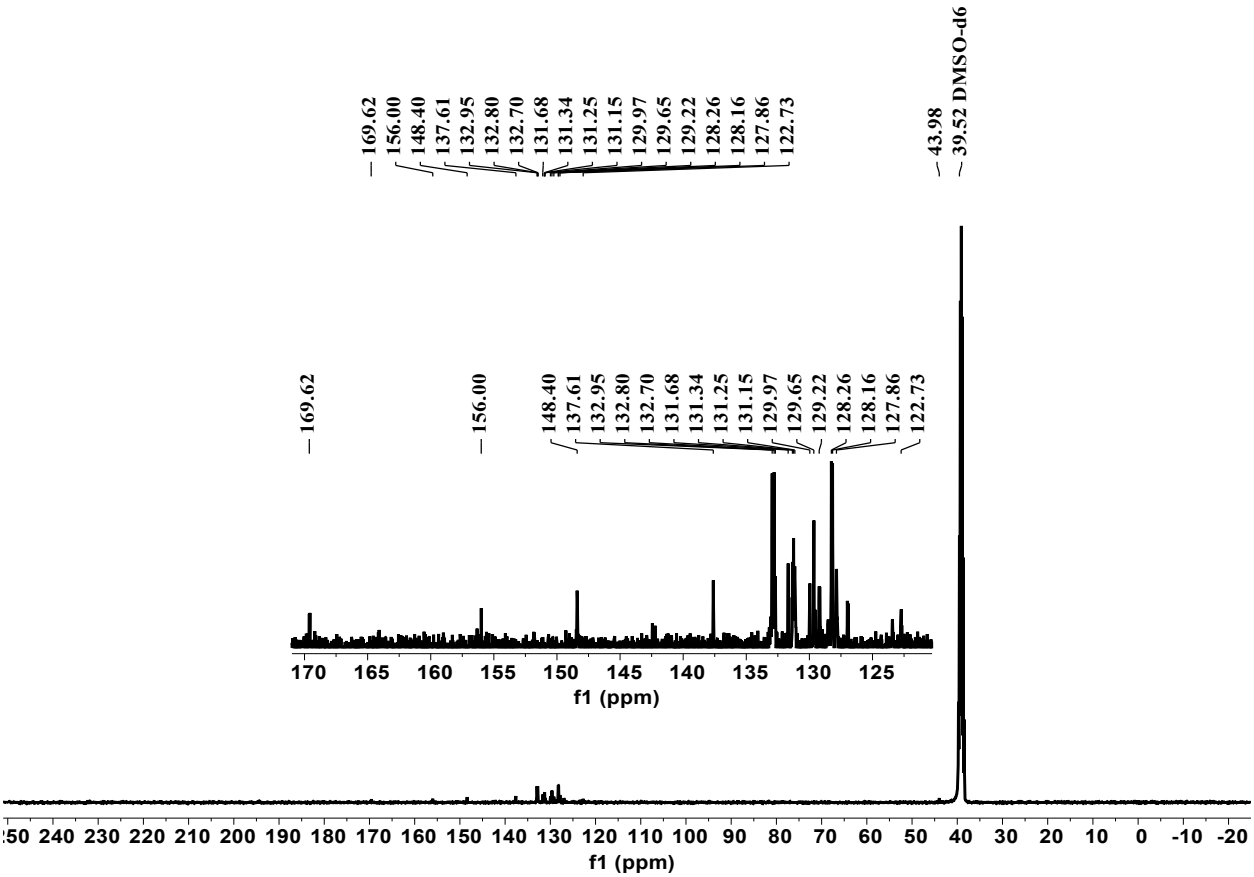


Figure S51: $^{13}C\{^{1}H\}$ NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 42 h irradiation of light.

NMR spectra after 62 h

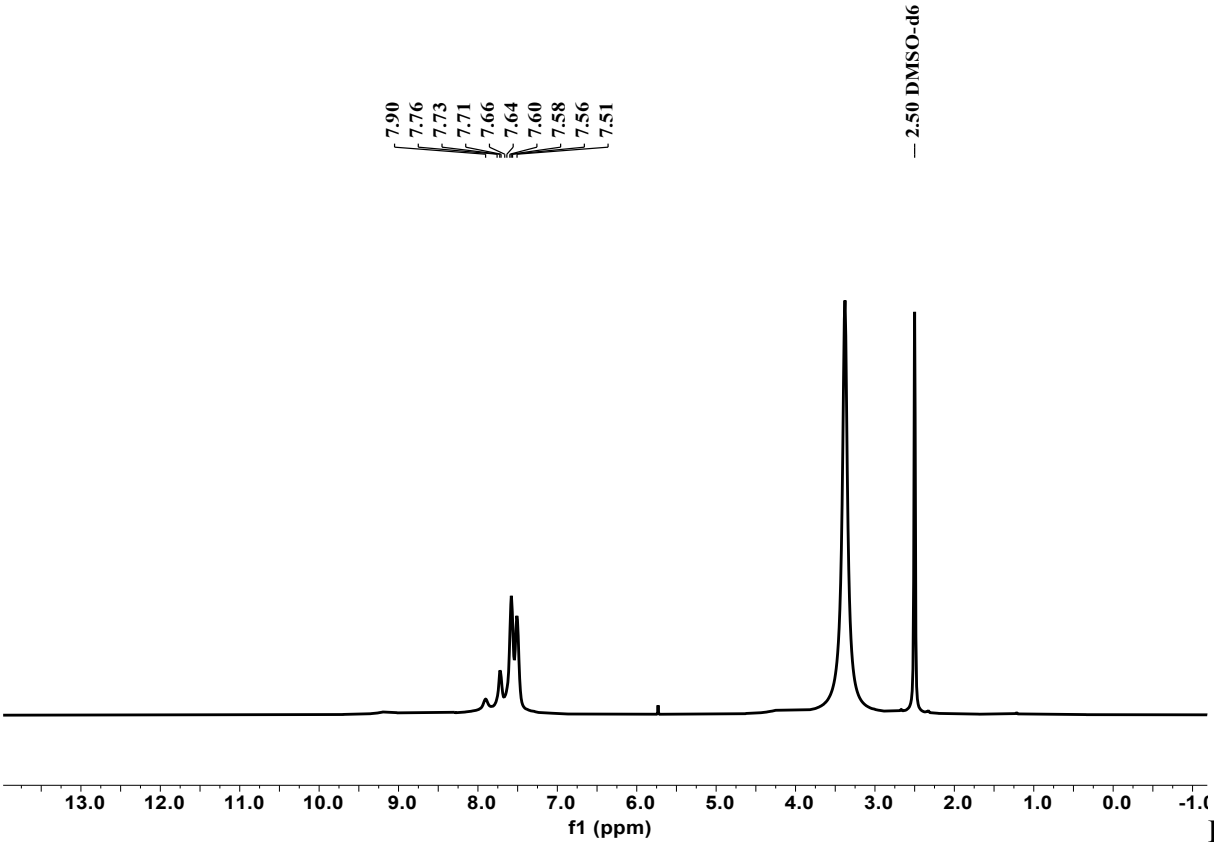


Figure S52: ^{1}H NMR spectrum of **Cu-PS-3** i.e. **Cu^{I}I** dimer after 62 h irradiation of light.

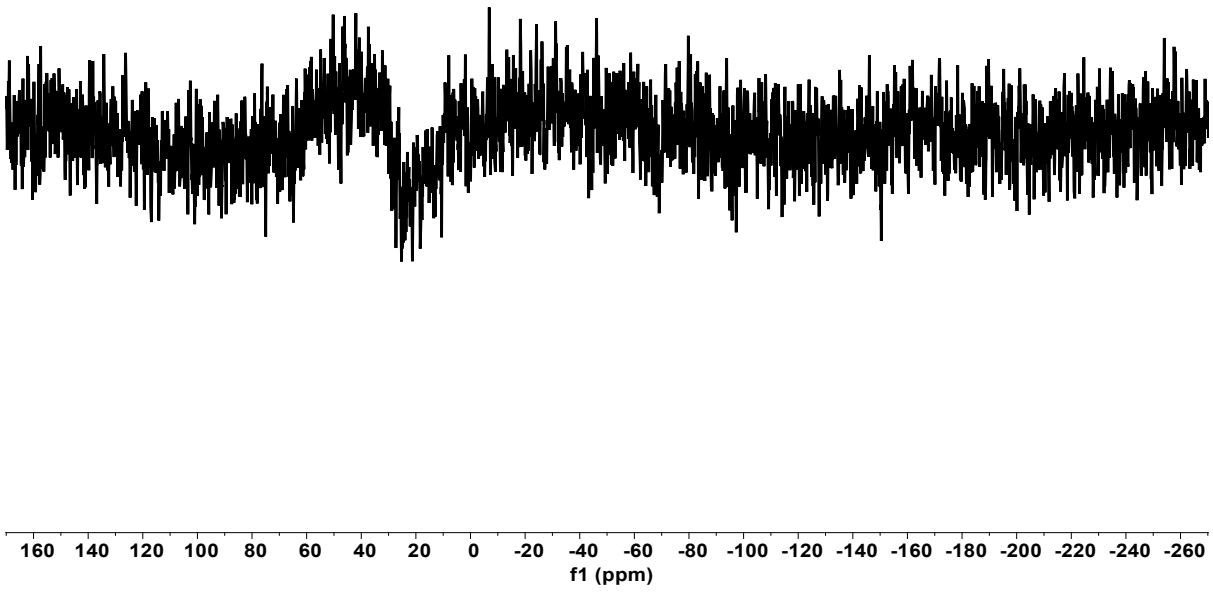


Figure S53: $^{31}P\{^{1}H\}$ NMR spectrum of **Cu-PS-3** i.e. **$Cu^{I}I$** dimer after 62 h irradiation of light.

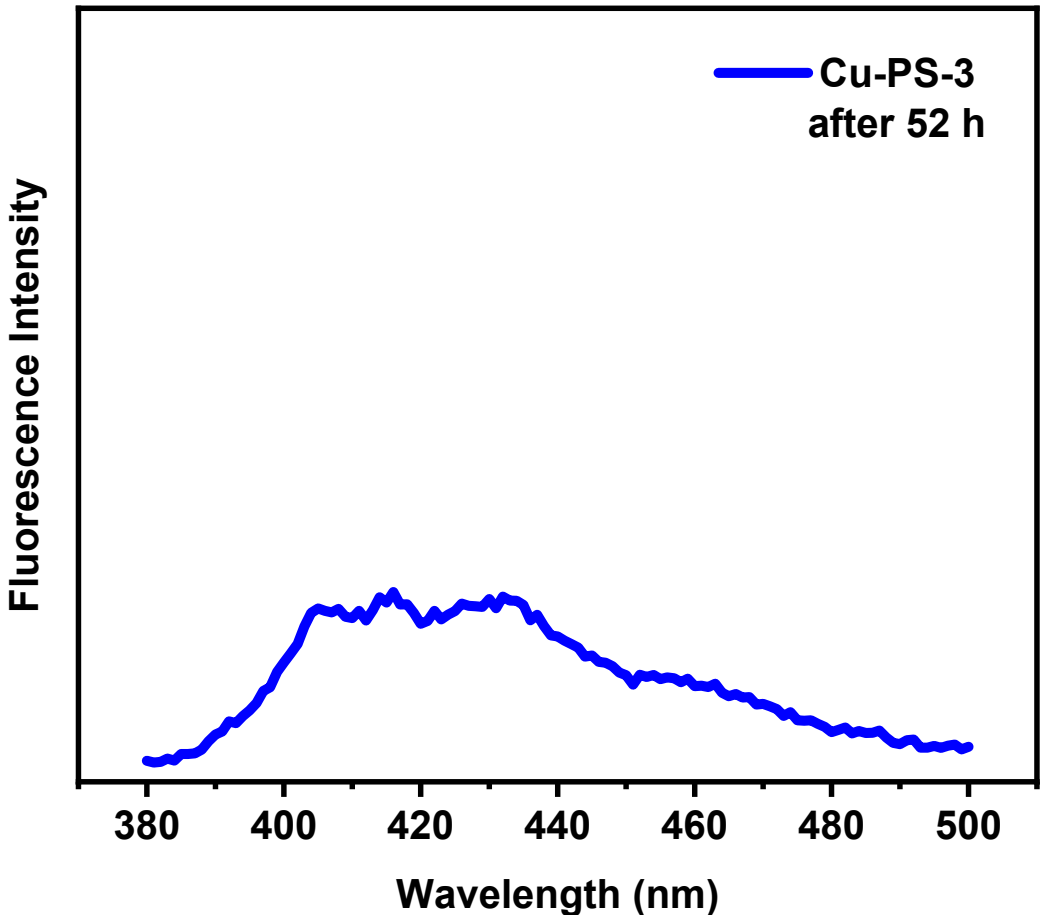


Figure S54: The changes in emission spectra of **Cu-PS-3** after 62 h under the ideal photochemical condition.

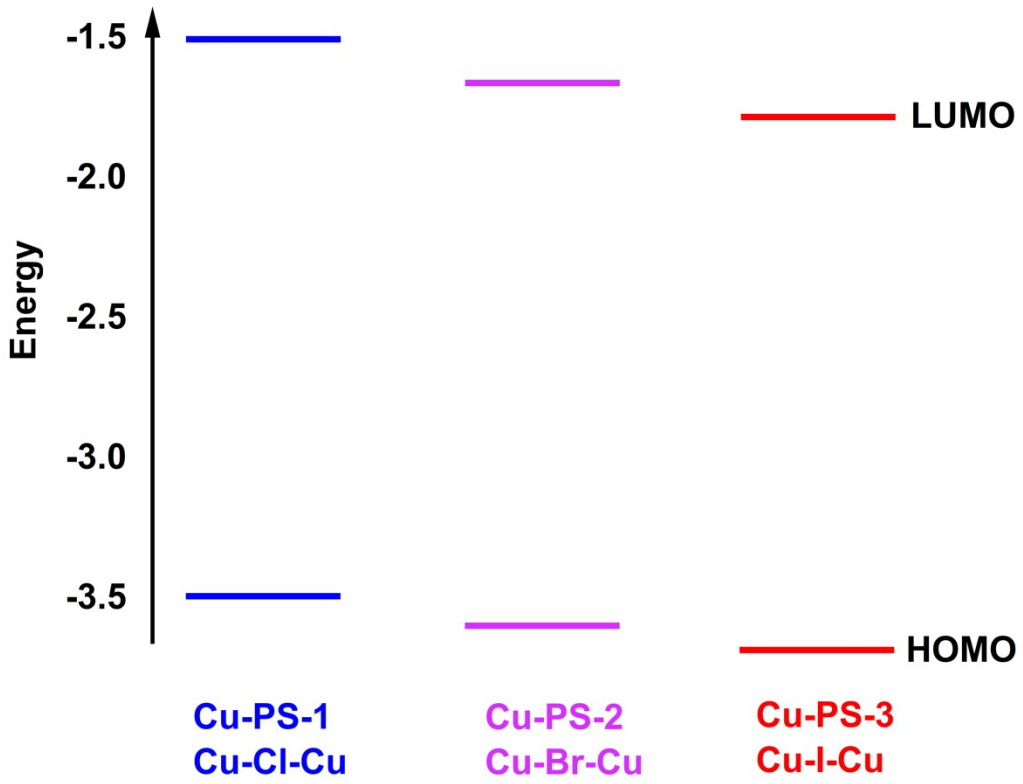


Figure S55. Energy calculation (HOMO-LUMO) for all these Cu-based catalysts (**Cu-PS-1**, **Cu-PS-2**, and **Cu-PS-3** from DFT calculation.

Full geometry optimizations were carried out by using a density functional theory method at the(R)B3LYP level for **Cu-PS-1**, **Cu-PS-2**, and **Cu-PS-3** and at the (U)B3LYP level for **Cu-PS-1**, **Cu-PS-2**, and **Cu-PS-3**. All calculations were performed with the Gaussian 09 program. Full geometry optimization was performed using the DFT method (U)B3LYP functional level. Except for Cu, all other elements were assigned the 6-31G** basis set. The SDD basis set with effective core potential was employed for the Cu atom. Chemissian 1.7[2] was used to calculate the fractional contributions of various groups to each molecular orbital. Calculated structures were visualized with Chemcraft[3]. Vertical electronic excitation based on (U)B3LYP optimized geometries were computed using time-dependent density functional theory (TD-DFT) formalism[4–6] in DMA employing a conductor-like polarisable continuum model (CPCM)[7–9] . Electronic spectra were calculated using the SWizard program.[10]

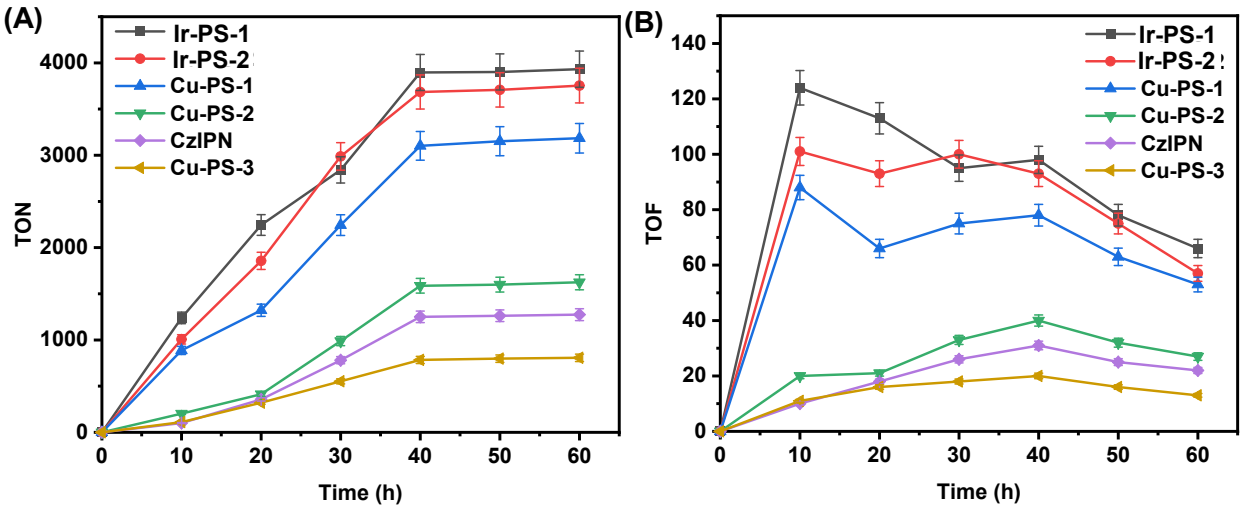


Figure S56. Progress of photocatalytic CH_4 generation from CO over time using different photosensitizers, **Ir-PS-1** (black trace), **Ir-PS-2** (red trace), **CzIPN** (violet trace), **Cu-PS-1** (cyan trace), **Cu-PS-2** (green trace), **Cu-PS-3** (orange yellow trace) along with **C1** as photocatalyst (PC) and BIH as sacrificial donor under saturated CO solution. (**A**) TON values *vs*. time (**B**) TOF values *vs*. time.

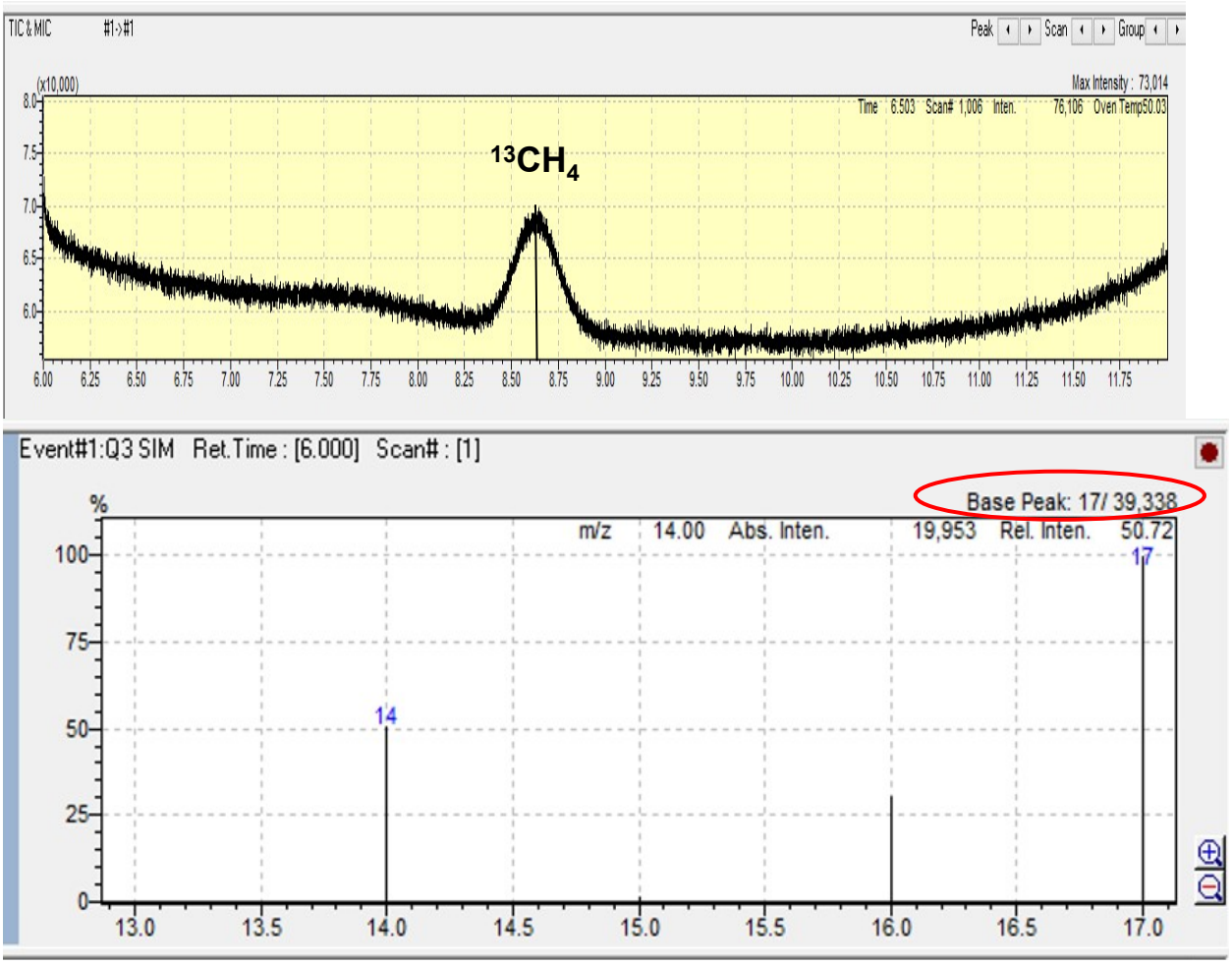


Figure S57. Analytical data of ^{13}C isotopic tracing photocatalytic CO_2 reduction experiment recorded by a Shimadzu GCMS-QP2020 (ShinCarbon ST 100/120, 2m 1mm 1/16" OD Silco). (A) TIC scan (B) $^{13}CH_4$ mass spectrum. Reaction condition: The photocatalytic experiment was performed with a 2 μM concentration of catalyst in DMA as a solvent, and BIH electron donor under irradiation of visible light, 440 LED.

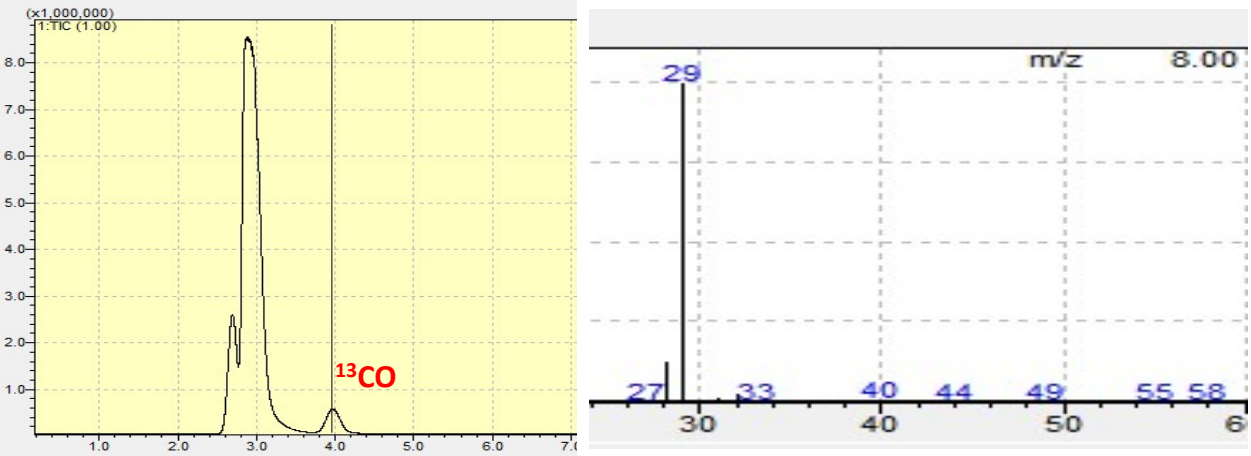


Figure S58. Analytical data of ^{13}C isotopic tracing photocatalytic CO_2 reduction experiment recorded by a Shimadzu GCMS-QP2020 (ShinCarbon ST 100/120, 2m 1mm 1/16" OD Silco). (A) TIC scan (B) ^{13}CO mass spectrum. Reaction condition: The photocatalytic experiment was performed with a 2 μM concentration of catalyst in DMA as a solvent, and BIH electron donor under irradiation of visible light, 440 LED.

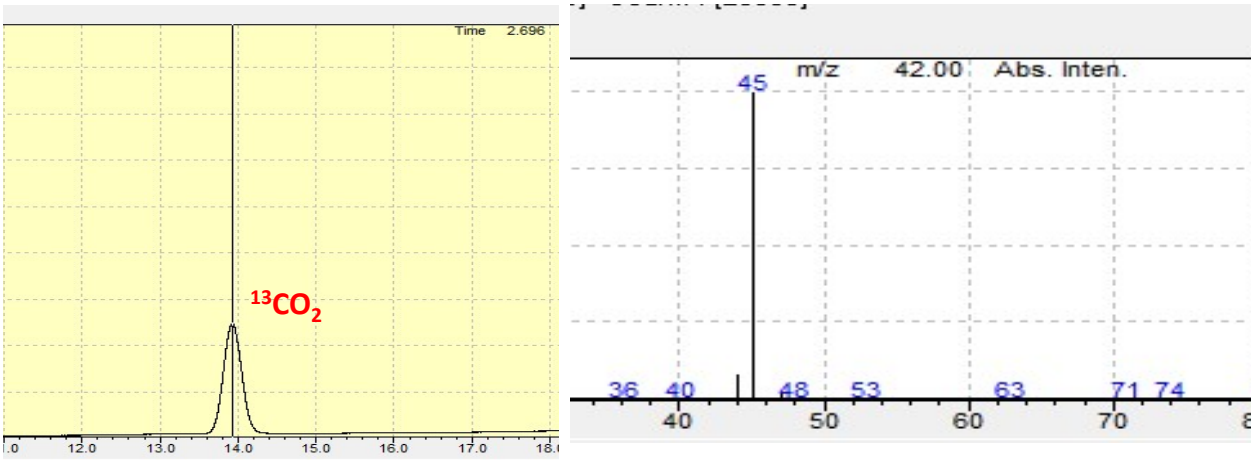


Figure S59. Analytical data of ^{13}C isotopic tracing photocatalytic CO_2 reduction experiment recorded by a Shimadzu GCMS-QP2020 (ShinCarbon ST 100/120, 2m 1mm 1/16" OD Silco). (A) TIC scan (B) $^{13}CO_2$ mass spectrum. Reaction condition: The photocatalytic experiment was performed with a 2 μM concentration of catalyst in DMA as a solvent, and BIH electron donor under irradiation of visible light, 440 LED.

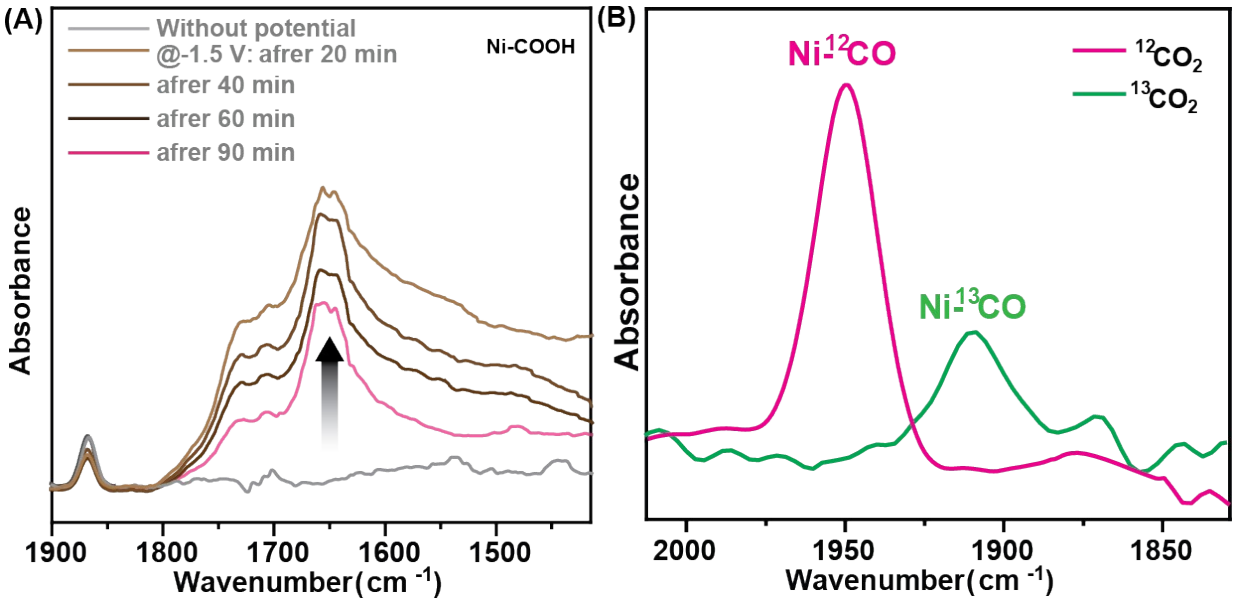


Figure S60. (A) The gradual change in the FTIR spectra of the complex **C1** (30 mM) around the 1760-1500 cm^{-1} region during a spectroelectrochemistry experiment in a 100% CO_2 atmosphere executed at -1.6 V *vs.* $FeCp_2^{+/0}$. The vertical arrows highlight the appearance of $\bar{\nu}_{C\equiv O}$ signal, $\nu_{Ni\text{-}CO}$ signals, $\nu_{Ni\text{-}COOH}$ and simultaneous disappearance of $\bar{\nu}_{CO2.}$ (**B**) FTIR spectra of Ni(II)-^{12}CO (1962 cm^{-1}) vs. Ni(II)-^{13}CO (1911 cm^{-1}) adduct in solvent (catalyst concentration 30 mM). The pink spectra represent the 12CO2 adducts of the catalyst C1, and the green ones represent its $^{13}CO_2$ adducts.

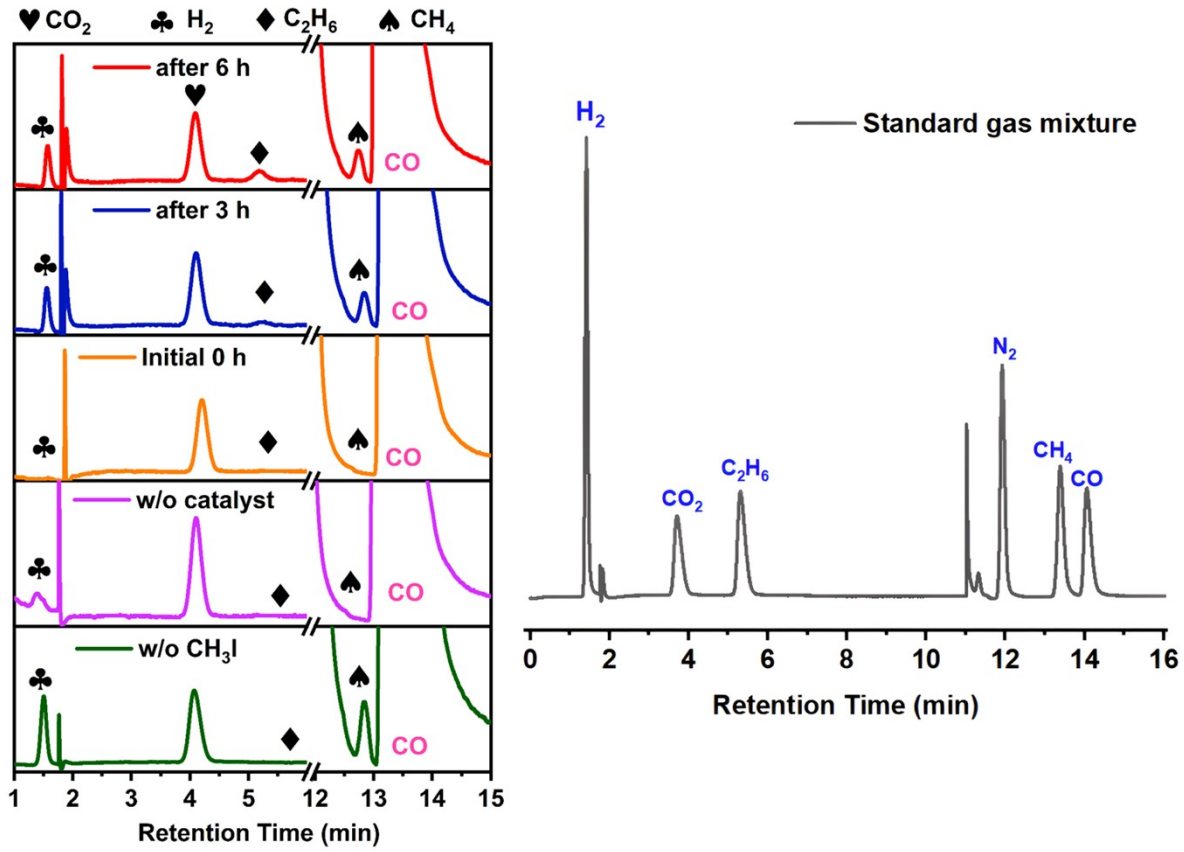


Figure S61. The progress in photochemical CORR reaction monitored via gas chromatography instrument in presence of **Ir-PS-1** as photosensitizer along with **C1** as photocatalyst (PC), CH_3I (5 equivalent with respect to the catalyst) and BIH as sacrificial donor under saturated CO solution. The **orange trace** before the irradiation of light source. The **blue trace** after 1 h irradiation of light source (formation of CH_4 and C_2H_6). The **red trace** after 3 h irradiation of light source (formation of CH_4 and C_2H_6). The **violet trace** under the identical condition without catalyst (no formation of CH_4 and C_2H_6). The **green trace** under the identical condition without CH_3I (only formation of CH_4).

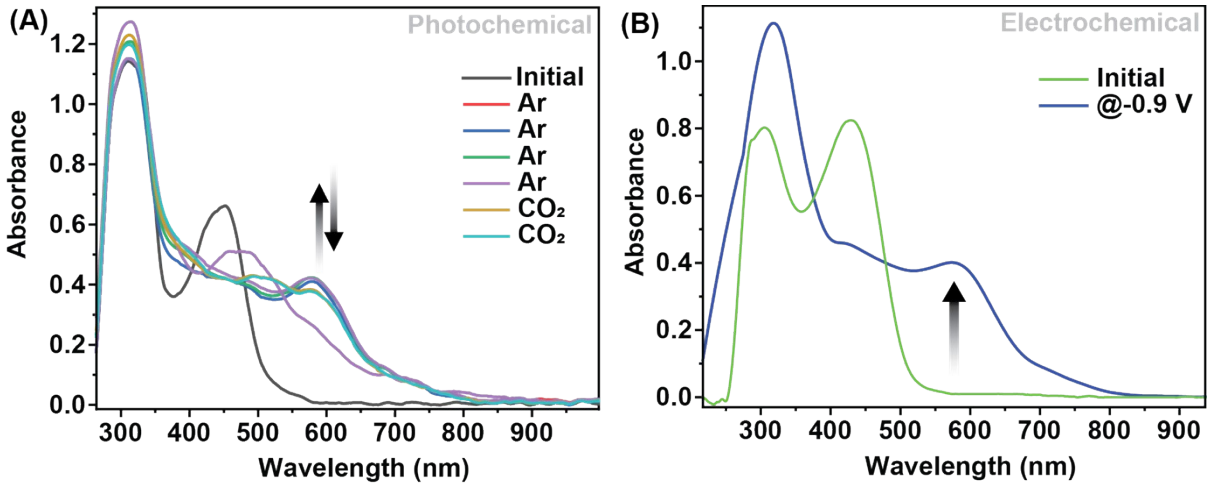


Figure S62. The comparative optical spectra displaying the changes observed for the catalytic solution *photochemical vs. electrochemical*: **A**) C1+PS+BIH (black trace)] sample following irradiation of light under Ar atmosphere: finally, generation of a new peak after 1 h (violet trace) followed by initial red trace and after 1 h CO_2 atmosphere, generation of another new peak (sky-blue trace). **B**) Electrochemically reduction of Ni^{II}/Ni^{I}: without potential (green trace) and after 1 h applied -0.9 V *vs*. $FeCp_2^{+/0}$ potential (blue trace). These spectra were recorded in the range of 190 to 1000 nm at 298K.

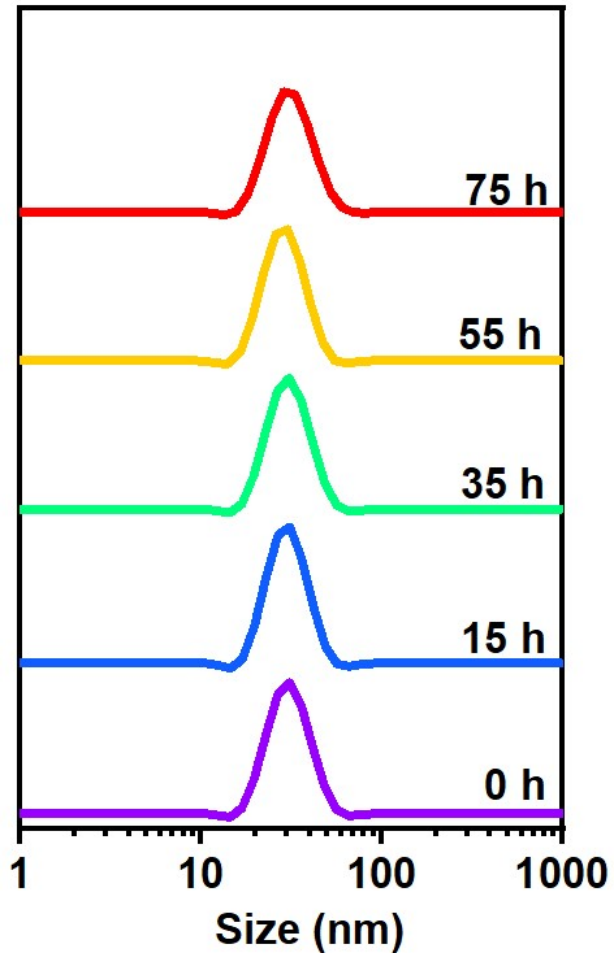


Figure S63. Particle size distribution of a CO_2-saturated DMA solution containing 2 μM of C1, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with different time intervals.

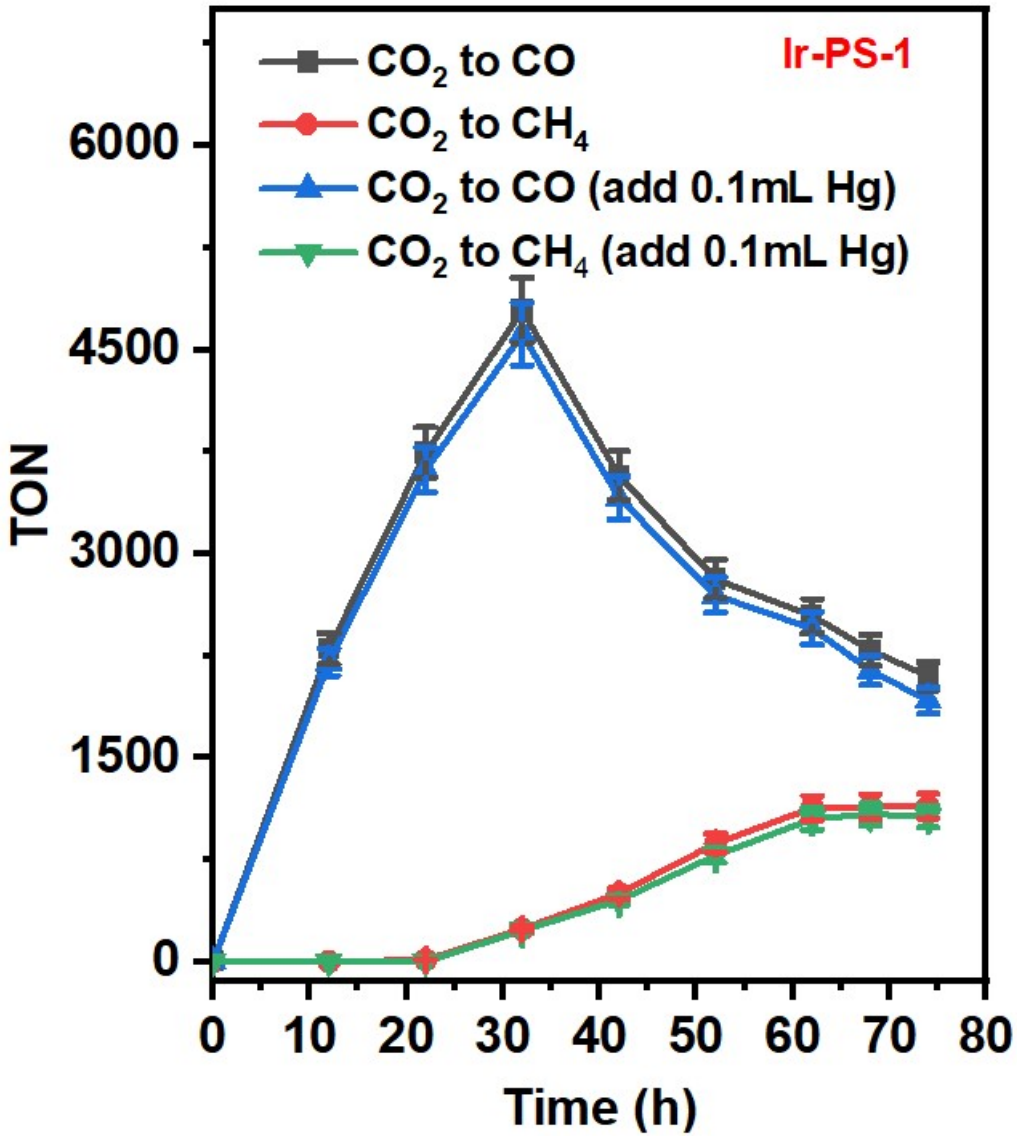


Figure S64. TON versus time during irradiation of 2 μM of **C1**, BIH (0.2 M) as the electron donor, and Photosensitizer (PS) (5 mM), irradiated with a 440 nm LED with Hg (0.1 mL) or without Hg.

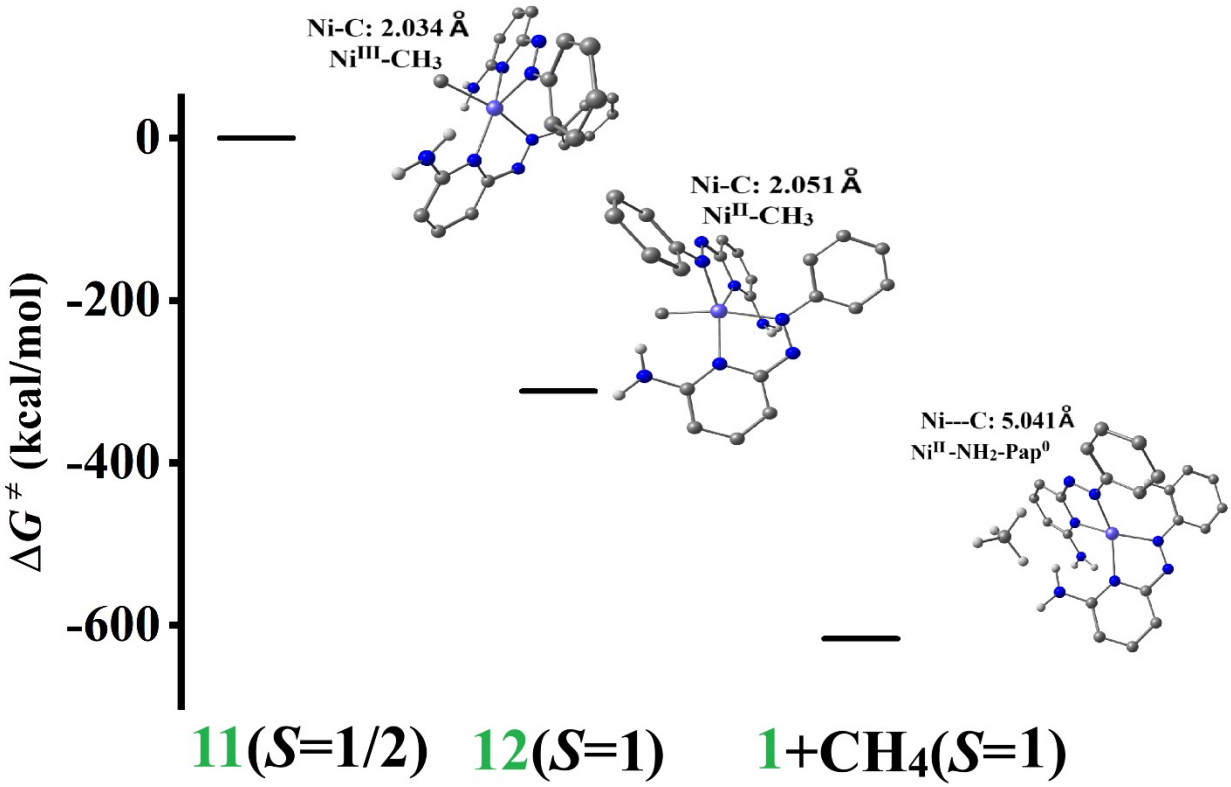


Figure S65. Gibbs free energy diagram (kcal/mol) for DFT-optimized structures of six coordinated CO adducts with the NiL2 complex (**11**) Ni(III)–CH_3, (**12**) Ni(II)–CH_3, and (1) Ni(II) + CH_4. Color codes: carbon → gray, hydrogen→ white, nitrogen → blue, oxygen → red, and nickel → bluish gray.

Table S1. Optimization conditions for photo-catalytic CO_2/CO reduction reaction:

Entry	Catalyst	Solvent	P.S.	S.D.	Proton Source	Atmosphere	TON_{CO}	TON_{CH4}	TON_{H2}
1.	C1	DMA	Ir-PS-1	BIH	-	CO_2	5512	812	127
2.	C1	DMA	Ir-PS-1	BIH	-	**Ar**	-	-	111
3.	C1	DMA	**No PS**	BIH	-	CO_2	-	-	12
4.	C1	DMA	Ir-PS-1	**No BIH**	-	CO_2	-	-	42
5.	**Without C1**	DMA	Ir-PS-1	BIH	-	CO_2	<15	-	67
6.	C1	DMA	Ir-PS-1	BIH	TFE	CO_2	5557	981	207
7.	C1	DMA	Ir-PS-1	BIH	H_2O	CO_2	5784	1290	162
8.	C1	DMA	Ir-PS-1	BIH	PhOH	CO_2	6323	1462	215
9.	C1	ACN	Ir-PS-1	BIH	PhOH	CO_2	5312	1002	214
10.	C1	DMA	Ir-PS-2	BIH	PhOH	CO_2	6074	1317	213
11.	C1	DMA	CzIPN	BIH	PhOH	CO_2	3634	498	235
12.	C1	DMA	Cu-PS-1	BIH	PhOH	CO_2	4789	1130	244
13.	C1	DMA	Cu-PS-2	BIH	PhOH	CO_2	4007	642	240
14.	C1	DMA	Cu-PS-3	BIH	PhOH	CO_2	2579	364	265
15.	C1	DMA	Ir-PS-1	BIH	-	CO	-	2810	198
16.	C1	DMA	Ir-PS-1	BIH	PhOH	CO	-	3897	338
17.	C1	ACN	Ir-PS-1	BIH	PhOH	CO	-	3278	332
18.	C1	DMA	Ir-PS-2	BIH	PhOH	CO	-	3685	346
19.	C1	DMA	CzIPN	BIH	PhOH	CO	-	1250	344

20.	C1	DMA	Cu-PS-1	BIH	PhOH	CO	-	3102	342
21.	C1	DMA	Cu-PS-2	BIH	PhOH	CO	-	1587	348
22.	C1	DMA	Cu-PS-3	BIH	PhOH	CO	-	784	334
23.	C2	DMA	Ir-PS-1	BIH	-	CO_2	2685	-	238
24.	C2	DMA	Ir-PS-1	BIH	PhOH	CO_2	2758	-	257
25.	C2	DMA	Ir-PS-1	BIH	-	CO	-	73	245
26.	C2	DMA	Ir-PS-1	BIH	PhOH	CO	-	88	265
27.	C3	DMA	Ir-PS-1	BIH	-	CO_2	2165	-	243
28.	C3	DMA	Ir-PS-1	BIH	PhOH	CO_2	2251	-	262
29.	C3	DMA	Ir-PS-1	BIH	-	CO	-	-	242
30.	C3	DMA	Ir-PS-1	BIH	PhOH	CO	-	-	267

Table S2. Optimized Cartesian Coordinates Using (U/R)B3LYP/6-31G/SDD Level of Theory for the Optimization Energy Calculations**

1 (*S*=1) E(opt) = -1458.8271362 hartree			
Cartesian Coordinates			
Ni	-2.351405000000	12.825774000000	3.488592000000
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N	-1.234509000000	15.353450000000	2.897282000000
N	-2.330244000000	14.383304000000	4.763974000000
N	-3.351710000000	13.434297000000	6.618552000000
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H	-3.723416000000	13.499708000000	7.551417000000
N	-3.739045000000	11.458860000000	3.946576000000
N	-3.324028000000	10.321878000000	4.373356000000
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H	0.357370000000	13.101121000000	-2.447949000000
C	0.088236000000	14.653839000000	-0.977048000000
H	0.491157000000	15.431026000000	-1.617916000000
C	-0.351160000000	14.973421000000	0.294283000000
H	-0.307201000000	15.989214000000	0.670527000000
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C	-2.730286000000	15.750479000000	6.708411000000
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C	-7.793575000000	12.161232000000	3.299054000000
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C	-6.054701000000	10.616771000000	3.958222000000
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H	0.440145000000	8.075502000000	5.504993000000
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H	1.835527000000	10.051216000000	4.955367000000
C	0.145847000000	11.272562000000	4.363752000000
N	-1.191360000000	11.342847000000	4.196153000000

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2 (*S*=1/2) E(opt) = -1459.1475562 hartree

Cartesian Coordinates

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N	-3.532214000000	13.720341000000	6.728971000000
H	-3.551678000000	12.825688000000	6.261018000000
H	-4.176395000000	13.842482000000	7.491603000000
N	-3.513120000000	11.503402000000	4.041822000000
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C	-1.831654000000	10.051376000000	4.177467000000
N	1.101144000000	12.060789000000	4.020229000000
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H	-3.053321000000	18.198997000000	6.094845000000
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C	-5.278928000000	13.061951000000	3.577763000000
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C	-7.211228000000	11.123766000000	4.106895000000
H	-7.968733000000	10.374637000000	4.315224000000
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C	0.876517000000	9.666456000000	4.254055000000
H	1.954680000000	9.550859000000	4.284255000000
C	0.319664000000	10.955557000000	4.099818000000
N	-1.015102000000	11.135912000000	4.060165000000

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3 (*S*=1) E(opt) = -1459.3336170 hartree

Cartesian Coordinates

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N	-1.188288000000	15.370500000000	2.932987000000

N	-2.279392000000	14.454583000000	4.809151000000
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H	-3.526749000000	12.704846000000	6.005754000000
H	-3.912909000000	13.588710000000	7.408966000000
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H	0.405182000000	13.036576000000	-2.392282000000
C	0.157043000000	14.570986000000	-0.893347000000
H	0.606804000000	15.348651000000	-1.506123000000
C	-0.299045000000	14.888189000000	0.376837000000
H	-0.218268000000	15.892483000000	0.776718000000
C	-0.887718000000	13.891346000000	1.179006000000
C	-0.997514000000	12.583007000000	0.669639000000
H	-1.452034000000	11.815264000000	1.296491000000
C	-0.535484000000	12.281722000000	-0.602510000000
H	-0.630542000000	11.267135000000	-0.980258000000
C	-1.667332000000	15.518441000000	4.189014000000
C	-1.549700000000	16.756729000000	4.845516000000
H	-1.072696000000	17.577421000000	4.323530000000
C	-2.049850000000	16.877487000000	6.129602000000
H	-1.968583000000	17.825265000000	6.654944000000
C	-2.657409000000	15.794325000000	6.762701000000
H	-3.039536000000	15.865798000000	7.775421000000
C	-2.752153000000	14.582062000000	6.062535000000
C	-7.844545000000	12.082184000000	3.320470000000

H	-8.906623000000	12.254815000000	3.172895000000
C	-6.932949000000	13.121330000000	3.135561000000
H	-7.279790000000	14.108831000000	2.844862000000
C	-5.576756000000	12.897703000000	3.322825000000
H	-4.857921000000	13.707375000000	3.185785000000
C	-5.109797000000	11.627431000000	3.696357000000
C	-6.029042000000	10.583938000000	3.885023000000
H	-5.654823000000	9.608278000000	4.173450000000
C	-7.383463000000	10.819628000000	3.694904000000
H	-8.091450000000	10.007491000000	3.838388000000
C	-1.383305000000	9.058251000000	4.933946000000
H	-2.015178000000	8.206015000000	5.152652000000
C	-0.005259000000	9.029062000000	5.076868000000
H	0.487377000000	8.122922000000	5.418303000000
C	0.756068000000	10.155409000000	4.786508000000
H	1.835142000000	10.155948000000	4.900668000000
C	0.103275000000	11.321613000000	4.350636000000
N	-1.234655000000	11.354408000000	4.189426000000

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4 (*S*=1) E(opt) = -1648.3402040 hartree

Cartesian Coordinates

Ni	-2.002341000000	12.867807000000	4.112308000000
N	-1.494922000000	14.159836000000	2.586762000000
N	-1.816922000000	15.378233000000	2.728872000000
N	-2.786924000000	14.670797000000	4.775361000000
N	-3.764339000000	13.968384000000	6.765523000000
H	-3.172853000000	13.148463000000	6.756102000000
H	-4.209085000000	14.200560000000	7.639601000000
N	-3.617396000000	11.574662000000	3.962770000000
N	-3.286030000000	10.299441000000	4.090109000000

C	-1.970109000000	10.044385000000	4.009811000000
N	1.121572000000	11.799411000000	3.185489000000
H	0.830645000000	12.172416000000	2.267592000000
H	2.092930000000	11.487139000000	3.129067000000
C	0.625330000000	13.260326000000	-0.944691000000
H	1.166910000000	13.020774000000	-1.854291000000
C	0.770352000000	14.521767000000	-0.355707000000
H	1.429836000000	15.257739000000	-0.804685000000
C	0.074320000000	14.842144000000	0.806425000000
H	0.176649000000	15.814780000000	1.273272000000
C	-0.771880000000	13.884462000000	1.390797000000
C	-0.919133000000	12.613664000000	0.806913000000
H	-1.605339000000	11.899327000000	1.248922000000
C	-0.221904000000	12.311266000000	-0.365526000000
H	-0.355284000000	11.340759000000	-0.833218000000
C	-2.531967000000	15.669571000000	3.892234000000
C	-2.978215000000	16.974595000000	4.042756000000
H	-2.734808000000	17.712087000000	3.288694000000
C	-3.749285000000	17.268749000000	5.178776000000
H	-4.127819000000	18.272505000000	5.340753000000
C	-4.018752000000	16.271703000000	6.090847000000
H	-4.608249000000	16.469921000000	6.979800000000
C	-3.508926000000	14.957296000000	5.879830000000
C	-7.738185000000	12.422849000000	3.869044000000
H	-8.798751000000	12.652009000000	3.838019000000
C	-6.802517000000	13.361389000000	3.425091000000
H	-7.134905000000	14.319270000000	3.036075000000
C	-5.442878000000	13.068958000000	3.467199000000
H	-4.715641000000	13.784558000000	3.099997000000
C	-4.996421000000	11.823483000000	3.950334000000

C	-5.945580000000	10.874062000000	4.386337000000
H	-5.599285000000	9.915237000000	4.750933000000
C	-7.299901000000	11.182139000000	4.347693000000
H	-8.023586000000	10.449380000000	4.692226000000
C	-1.520170000000	8.702039000000	4.174111000000
H	-2.265704000000	7.952029000000	4.409656000000
C	-0.193399000000	8.391452000000	4.026816000000
H	0.156489000000	7.372456000000	4.149541000000
C	0.728878000000	9.419964000000	3.688553000000
H	1.778647000000	9.206559000000	3.519890000000
C	0.222644000000	10.687506000000	3.574708000000
N	-1.059466000000	11.058106000000	3.738956000000
C	-0.495951000000	13.188194000000	5.458361000000
O	0.608705000000	13.590677000000	5.111790000000
O	-1.131307000000	12.762805000000	6.400510000000
H	1.045736000000	12.591693000000	3.891453000000

TS1 (*S*=1) E(opt) = -1648.3373089 hartree

Cartesian Coordinates

Ni	-2.130498000000	12.855383000000	3.925695000000
N	-1.356508000000	14.193380000000	2.480780000000
N	-1.610542000000	15.427499000000	2.654175000000
N	-2.841145000000	14.717609000000	4.565089000000
N	-4.047822000000	14.068355000000	6.452396000000
H	-3.532374000000	13.196429000000	6.480002000000
H	-4.498470000000	14.338685000000	7.313375000000
N	-3.671780000000	11.489440000000	4.053858000000
N	-3.329252000000	10.231335000000	4.017663000000

C	-1.996380000000	10.007380000000	3.873027000000
N	1.009635000000	11.944726000000	3.347400000000
H	0.813603000000	12.420398000000	2.458999000000
H	1.999882000000	11.705082000000	3.382997000000
C	0.791261000000	13.290936000000	-1.033410000000
H	1.336624000000	13.051451000000	-1.940750000000
C	0.991788000000	14.524484000000	-0.401832000000
H	1.696762000000	15.238075000000	-0.816573000000
C	0.291655000000	14.845849000000	0.756414000000
H	0.432289000000	15.799121000000	1.252341000000
C	-0.614464000000	13.915756000000	1.298080000000
C	-0.811845000000	12.672514000000	0.671358000000
H	-1.535427000000	11.975529000000	1.080511000000
C	-0.111875000000	12.369971000000	-0.497613000000
H	-0.282371000000	11.419967000000	-0.994083000000
C	-2.371972000000	15.727543000000	3.779430000000
C	-2.644655000000	17.072137000000	3.993989000000
H	-2.238349000000	17.808367000000	3.312406000000
C	-3.451630000000	17.410652000000	5.090261000000
H	-3.696721000000	18.447544000000	5.294683000000
C	-3.924888000000	16.409952000000	5.909881000000
H	-4.547178000000	16.635751000000	6.769385000000
C	-3.587068000000	15.050570000000	5.645563000000
C	-7.815749000000	12.212710000000	4.221438000000
H	-8.883158000000	12.406815000000	4.257157000000
C	-6.943224000000	13.181891000000	3.720394000000
H	-7.331540000000	14.127381000000	3.354280000000
C	-5.573796000000	12.936582000000	3.679537000000
H	-4.894544000000	13.678637000000	3.274662000000
C	-5.063754000000	11.706264000000	4.129019000000

C	-5.946056000000	10.726071000000	4.625323000000
H	-5.544450000000	9.781485000000	4.970591000000
C	-7.309633000000	10.988502000000	4.674702000000
H	-7.985205000000	10.235264000000	5.068383000000
C	-1.518660000000	8.679966000000	3.975576000000
H	-2.238659000000	7.896061000000	4.177177000000
C	-0.172695000000	8.427578000000	3.829375000000
H	0.214105000000	7.417291000000	3.905718000000
C	0.707998000000	9.504172000000	3.583118000000
H	1.773321000000	9.343984000000	3.458172000000
C	0.169138000000	10.769421000000	3.503035000000
N	-1.143904000000	11.054733000000	3.620091000000
C	-0.961297000000	12.903121000000	5.579524000000
O	0.237509000000	13.230544000000	5.320697000000
O	-1.567236000000	12.648895000000	6.590940000000
H	0.684424000000	12.691178000000	4.293829000000

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5 (*S*=1) E(opt) = -1648.3565429 hartree

Cartesian Coordinates

Ni	-1.971194000000	12.813478000000	4.223532000000
N	-1.683415000000	14.071764000000	2.583705000000
N	-2.043356000000	15.281124000000	2.713375000000
N	-3.079661000000	14.562933000000	4.723314000000
N	-3.942366000000	13.792094000000	6.731156000000
H	-4.249462000000	12.940465000000	6.273633000000
H	-4.507855000000	14.008791000000	7.542544000000
N	-3.647348000000	11.455029000000	3.894321000000
N	-3.364451000000	10.220484000000	3.908077000000

C	-2.001552000000	9.909208000000	3.847080000000
N	1.168319000000	11.514416000000	3.627071000000
H	0.977288000000	12.464756000000	3.974702000000
H	2.134544000000	11.224287000000	3.633470000000
C	0.395521000000	13.162418000000	-0.951879000000
H	0.924640000000	12.919178000000	-1.868012000000
C	0.457087000000	14.462982000000	-0.435496000000
H	1.039673000000	15.222934000000	-0.946225000000
C	-0.221576000000	14.786602000000	0.732203000000
H	-0.181470000000	15.786222000000	1.147456000000
C	-0.956602000000	13.790008000000	1.399740000000
C	-1.004681000000	12.481707000000	0.895700000000
H	-1.582386000000	11.728692000000	1.417676000000
C	-0.338884000000	12.176631000000	-0.288380000000
H	-0.392052000000	11.171184000000	-0.693392000000
C	-2.739005000000	15.573861000000	3.889700000000
C	-3.025760000000	16.909874000000	4.154140000000
H	-2.721424000000	17.669793000000	3.445463000000
C	-3.683222000000	17.210469000000	5.350637000000
H	-3.923189000000	18.238391000000	5.601304000000
C	-4.032020000000	16.184392000000	6.216996000000
H	-4.549031000000	16.388447000000	7.148614000000
C	-3.709238000000	14.857517000000	5.870146000000
C	-7.753973000000	12.375966000000	4.001204000000
H	-8.811190000000	12.621422000000	4.019343000000
C	-6.851468000000	13.225790000000	3.356229000000
H	-7.207075000000	14.123737000000	2.861110000000
C	-5.492056000000	12.921077000000	3.342081000000
H	-4.783901000000	13.562558000000	2.831252000000
C	-5.039790000000	11.742410000000	3.955270000000

C	-5.946728000000	10.879586000000	4.596853000000
H	-5.579606000000	9.972377000000	5.063024000000
C	-7.298246000000	11.207653000000	4.623298000000
H	-8.000632000000	10.550317000000	5.125977000000
C	-1.704193000000	8.558498000000	3.763937000000
H	-2.509007000000	7.835220000000	3.790922000000
C	-0.351962000000	8.194684000000	3.626460000000
H	-0.067119000000	7.150279000000	3.554039000000
C	0.603169000000	9.180146000000	3.581028000000
H	1.654718000000	8.936523000000	3.470522000000
C	0.227076000000	10.558383000000	3.694210000000
N	-1.076790000000	10.907644000000	3.829752000000
C	-0.526560000000	13.533215000000	5.454653000000
O	0.612338000000	13.777900000000	5.082499000000
O	-0.822399000000	13.806271000000	6.755697000000
H	-1.755145000000	13.592453000000	6.933169000000

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6 (*S*=1) E(opt) = -1572.2216726 hartree

Cartesian Coordinates

Ni	-1.795939000000	12.840648000000	4.094465000000
N	-1.612281000000	14.168318000000	2.532143000000
N	-1.951966000000	15.364201000000	2.792057000000
N	-2.705367000000	14.513730000000	4.882566000000
N	-3.459263000000	13.658418000000	6.910453000000
H	-3.518589000000	12.728913000000	6.522795000000
H	-3.951125000000	13.795986000000	7.781872000000
N	-3.473987000000	11.567152000000	3.833975000000
N	-3.217111000000	10.342795000000	4.059245000000

C	-1.864592000000	10.016662000000	4.159675000000
N	1.282187000000	11.602525000000	3.570628000000
H	1.000741000000	12.276540000000	2.869596000000
H	2.252521000000	11.322918000000	3.506605000000
C	0.072532000000	13.355510000000	-1.225420000000
H	0.500413000000	13.135492000000	-2.198299000000
C	-0.022556000000	14.686126000000	-0.790792000000
H	0.337148000000	15.489573000000	-1.425102000000
C	-0.573561000000	14.984140000000	0.447311000000
H	-0.651801000000	16.007598000000	0.793109000000
C	-1.028878000000	13.930886000000	1.268013000000
C	-0.928237000000	12.593503000000	0.836842000000
H	-1.316009000000	11.794761000000	1.459874000000
C	-0.383141000000	12.312600000000	-0.412868000000
H	-0.323526000000	11.286257000000	-0.759577000000
C	-2.521260000000	15.578741000000	4.045317000000
C	-2.875310000000	16.876626000000	4.375129000000
H	-2.704589000000	17.675273000000	3.663962000000
C	-3.443551000000	17.098460000000	5.643522000000
H	-3.728319000000	18.100565000000	5.946624000000
C	-3.648579000000	16.034357000000	6.494874000000
H	-4.097542000000	16.176891000000	7.472083000000
C	-3.279753000000	14.721941000000	6.083527000000
C	-7.494043000000	12.609205000000	3.232245000000
H	-8.530387000000	12.883137000000	3.061843000000
C	-6.470271000000	13.474045000000	2.832529000000
H	-6.709943000000	14.410122000000	2.339336000000
C	-5.142136000000	13.129002000000	3.058990000000
H	-4.343227000000	13.779508000000	2.725453000000
C	-4.836340000000	11.898543000000	3.670730000000

C	-5.868906000000	11.020073000000	4.064791000000
H	-5.621209000000	10.074937000000	4.532655000000
C	-7.189066000000	11.386630000000	3.849766000000
H	-7.988704000000	10.721351000000	4.158358000000
C	-1.535959000000	8.708598000000	4.473461000000
H	-2.324065000000	7.985407000000	4.643303000000
C	-0.171610000000	8.375833000000	4.559216000000
H	0.128342000000	7.365709000000	4.818152000000
C	0.784286000000	9.330654000000	4.276554000000
H	1.841580000000	9.088291000000	4.292792000000
C	0.374048000000	10.640354000000	3.914434000000
N	-0.931171000000	10.987497000000	3.924066000000
C	-0.013817000000	13.624428000000	5.179968000000
O	0.747579000000	14.146884000000	5.832001000000

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7 (*S*=1) E(opt) = -1572.7169978 hartree

Cartesian Coordinates

Ni	-1.948916000000	12.835934000000	4.033574000000
N	-1.482169000000	14.113844000000	2.511291000000
N	-1.785066000000	15.397903000000	2.706326000000
N	-2.835511000000	14.626373000000	4.679523000000
N	-3.777101000000	13.815041000000	6.643205000000
H	-3.857750000000	12.925484000000	6.166379000000
H	-4.509475000000	13.964885000000	7.322840000000
N	-3.493480000000	11.560871000000	3.986662000000
N	-3.246113000000	10.268668000000	3.956477000000
C	-1.912259000000	9.966511000000	3.919873000000
N	1.175609000000	11.746975000000	3.564288000000

H	0.809208000000	12.507571000000	3.002014000000
H	2.119318000000	11.496410000000	3.302884000000
C	0.610751000000	13.274635000000	-1.059975000000
H	1.148302000000	13.049620000000	-1.976331000000
C	0.550524000000	14.587041000000	-0.576965000000
H	1.048265000000	15.386236000000	-1.120393000000
C	-0.137309000000	14.888454000000	0.593150000000
H	-0.193176000000	15.902884000000	0.967098000000
C	-0.786414000000	13.864750000000	1.321495000000
C	-0.729891000000	12.545507000000	0.823602000000
H	-1.256815000000	11.760230000000	1.354188000000
C	-0.038103000000	12.260009000000	-0.351735000000
H	-0.018128000000	11.238388000000	-0.722043000000
C	-2.477903000000	15.654714000000	3.840134000000
C	-2.833651000000	16.990201000000	4.142460000000
H	-2.537084000000	17.772464000000	3.454821000000
C	-3.541412000000	17.243357000000	5.303133000000
H	-3.826092000000	18.261132000000	5.555139000000
C	-3.899971000000	16.194999000000	6.159670000000
H	-4.455239000000	16.372827000000	7.074165000000
C	-3.519259000000	14.891269000000	5.810671000000
C	-7.606326000000	12.522321000000	3.962562000000
H	-8.661333000000	12.780243000000	3.957830000000
C	-6.672617000000	13.369818000000	3.361702000000
H	-6.999421000000	14.285802000000	2.878091000000
C	-5.317125000000	13.045637000000	3.368437000000
H	-4.590343000000	13.690181000000	2.888462000000
C	-4.882612000000	11.857816000000	3.978085000000
C	-5.824580000000	10.997452000000	4.570826000000
H	-5.477802000000	10.076926000000	5.025466000000

C	-7.174920000000	11.336106000000	4.564441000000
H	-7.895612000000	10.670188000000	5.031167000000
C	-1.516005000000	8.620071000000	4.009126000000
H	-2.277688000000	7.857087000000	4.110674000000
C	-0.160325000000	8.329741000000	3.968652000000
H	0.181070000000	7.301359000000	4.041307000000
C	0.771333000000	9.358145000000	3.811734000000
H	1.834340000000	9.151456000000	3.746800000000
C	0.307799000000	10.679308000000	3.710557000000
N	-1.005627000000	10.978423000000	3.790289000000
C	-0.493386000000	13.434933000000	5.378762000000
O	0.171181000000	13.970112000000	6.132258000000

TS2 (*S*=1/2) E(opt) = -1573.2542502 hartree

Cartesian Coordinates

Ni	-0.816050000000	0.210946000000	-0.070206000000
N	-2.631562000000	0.377404000000	-0.845374000000
N	-2.751785000000	1.047392000000	-1.991685000000
N	-0.505609000000	1.554009000000	-1.536760000000
N	1.726131000000	2.030960000000	-1.008977000000
H	2.600974000000	2.339470000000	-1.430611000000
H	1.614023000000	2.496575000000	-0.100404000000
N	-0.204156000000	0.853590000000	1.728443000000
N	-0.076378000000	-0.108798000000	2.649427000000
C	-0.525944000000	-1.314432000000	2.235503000000
N	-1.618354000000	-2.815130000000	-0.850558000000
H	-1.861869000000	-1.956317000000	-1.325776000000
H	-2.192981000000	-3.605810000000	-1.106327000000

C	-6.092625000000	-1.817647000000	0.198475000000
H	-6.981077000000	-2.374794000000	0.480328000000
C	-5.827725000000	-1.547936000000	-1.148332000000
H	-6.510187000000	-1.899913000000	-1.916983000000
C	-4.690259000000	-0.832454000000	-1.515988000000
H	-4.480188000000	-0.618901000000	-2.557350000000
C	-3.792856000000	-0.376465000000	-0.531766000000
C	-4.064850000000	-0.647423000000	0.820521000000
H	-3.381347000000	-0.280786000000	1.578131000000
C	-5.206553000000	-1.361421000000	1.179399000000
H	-5.408847000000	-1.555718000000	2.228774000000
C	-1.641046000000	1.742369000000	-2.295964000000
C	-1.645868000000	2.640109000000	-3.399344000000
H	-2.565785000000	2.752184000000	-3.961315000000
C	-0.505636000000	3.337085000000	-3.714267000000
H	-0.488154000000	4.021702000000	-4.555657000000
C	0.652995000000	3.166364000000	-2.919460000000
H	1.572876000000	3.697906000000	-3.133395000000
C	0.582917000000	2.289001000000	-1.860164000000
C	1.363435000000	4.627643000000	2.813186000000
H	1.760147000000	5.601364000000	3.083328000000
C	0.456348000000	4.500137000000	1.757033000000
H	0.133812000000	5.378965000000	1.205746000000
C	-0.055125000000	3.249782000000	1.408379000000
H	-0.785706000000	3.159135000000	0.610793000000
C	0.338035000000	2.087729000000	2.109825000000
C	1.253437000000	2.227883000000	3.179049000000
H	1.555968000000	1.342948000000	3.724811000000
C	1.751371000000	3.482232000000	3.518871000000
H	2.457296000000	3.567531000000	4.340900000000

C	-0.533267000000	-2.406508000000	3.132636000000
H	-0.204705000000	-2.245963000000	4.152309000000
C	-0.953139000000	-3.643106000000	2.672116000000
H	-0.968705000000	-4.497677000000	3.342412000000
C	-1.345950000000	-3.803422000000	1.340423000000
H	-1.645592000000	-4.769366000000	0.949464000000
C	-1.325128000000	-2.686043000000	0.487669000000
N	-0.960440000000	-1.462504000000	0.935336000000
C	1.222226000000	-0.515146000000	-0.517079000000
O	1.600445000000	-1.625281000000	-0.471584000000
H	1.694437000000	0.779979000000	-0.784904000000

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8 (*S*=1/2) E(opt) = -1573.2881096 hartree

Cartesian Coordinates

Ni	-1.536189000000	12.110004000000	4.270648000000
N	-1.082966000000	12.810994000000	2.433493000000
N	-1.554622000000	14.007182000000	2.146959000000
N	-2.875461000000	13.655265000000	4.070751000000
N	-4.068393000000	13.299375000000	6.031505000000
H	-3.805206000000	12.326120000000	5.953534000000
H	-4.920586000000	13.475681000000	6.540536000000
N	-2.729338000000	10.504127000000	4.638710000000
N	-2.168502000000	9.486071000000	5.275050000000
C	-0.837692000000	9.651675000000	5.497527000000
N	1.758522000000	11.929320000000	4.501709000000
H	1.374034000000	12.165542000000	3.594447000000
H	2.768405000000	11.892176000000	4.493144000000
C	1.834403000000	11.281470000000	-0.201016000000

H	2.582512000000	10.875493000000	-0.875353000000
C	1.510254000000	12.642381000000	-0.243621000000
H	2.012131000000	13.296333000000	-0.951676000000
C	0.551021000000	13.173026000000	0.612377000000
H	0.288117000000	14.223059000000	0.581571000000
C	-0.105441000000	12.336695000000	1.540451000000
C	0.220753000000	10.966167000000	1.577931000000
H	-0.299827000000	10.319918000000	2.276500000000
C	1.183220000000	10.449317000000	0.712893000000
H	1.417220000000	9.389097000000	0.748160000000
C	-2.512496000000	14.449220000000	3.012479000000
C	-3.110616000000	15.706342000000	2.794408000000
H	-2.786842000000	16.297203000000	1.946777000000
C	-4.089345000000	16.129960000000	3.678285000000
H	-4.578609000000	17.088407000000	3.531348000000
C	-4.454882000000	15.329969000000	4.764388000000
H	-5.225065000000	15.641441000000	5.461660000000
C	-3.809803000000	14.095609000000	4.946932000000
C	-6.813895000000	9.977782000000	3.699075000000
H	-7.864599000000	9.854215000000	3.453458000000
C	-6.017188000000	10.860589000000	2.965739000000
H	-6.444046000000	11.421472000000	2.138926000000
C	-4.668950000000	11.021647000000	3.277675000000
H	-4.043418000000	11.690830000000	2.698220000000
C	-4.094149000000	10.296309000000	4.336963000000
C	-4.897475000000	9.397319000000	5.066999000000
H	-4.444888000000	8.831838000000	5.872514000000
C	-6.243769000000	9.248408000000	4.747599000000
H	-6.854644000000	8.556739000000	5.321733000000
C	-0.150468000000	8.697416000000	6.275025000000

H	-0.710187000000	7.867210000000	6.687491000000
C	1.207032000000	8.865758000000	6.484441000000
H	1.760647000000	8.151905000000	7.087321000000
C	1.877724000000	9.942871000000	5.895950000000
H	2.948639000000	10.071889000000	6.011168000000
C	1.146871000000	10.850716000000	5.118278000000
N	-0.190350000000	10.733481000000	4.953347000000
C	-0.547596000000	13.625980000000	5.126550000000
O	-0.449682000000	13.700887000000	6.312371000000
H	-0.206691000000	14.431123000000	4.426710000000

TS3 (*S*=0) E(opt) = -1573.8627003 hartree

Cartesian Coordinates

Ni	-1.439002000000	12.517461000000	4.262501000000
N	-0.783759000000	12.904674000000	2.458876000000
N	-1.132888000000	14.176179000000	2.020505000000
N	-2.609501000000	13.967633000000	3.833228000000
N	-4.299892000000	13.581418000000	5.429720000000
H	-4.584522000000	12.694734000000	5.005386000000
H	-5.117874000000	14.002739000000	5.866582000000
N	-2.660031000000	10.313272000000	4.174582000000
N	-1.975094000000	9.489588000000	4.857706000000
C	-0.608135000000	9.788820000000	4.915283000000
N	1.578037000000	12.576686000000	4.475456000000
H	0.960908000000	13.116971000000	3.871130000000
H	2.567417000000	12.711927000000	4.320847000000
C	1.535800000000	10.706089000000	-0.333576000000
H	2.132917000000	10.138734000000	-1.041346000000

C	1.503798000000	12.104919000000	-0.380274000000
H	2.084550000000	12.634113000000	-1.132983000000
C	0.740042000000	12.840950000000	0.521144000000
H	0.718153000000	13.922188000000	0.465820000000
C	-0.026094000000	12.196647000000	1.529029000000
C	-0.004425000000	10.780750000000	1.545750000000
H	-0.628628000000	10.255787000000	2.257962000000
C	0.765726000000	10.057470000000	0.637169000000
H	0.748534000000	8.970679000000	0.680158000000
C	-2.067517000000	14.711453000000	2.761131000000
C	-2.570977000000	16.038050000000	2.507039000000
H	-2.076091000000	16.623753000000	1.739875000000
C	-3.647099000000	16.511079000000	3.196782000000
H	-4.039589000000	17.503580000000	2.996902000000
C	-4.285449000000	15.682089000000	4.172563000000
H	-5.195946000000	15.990328000000	4.672940000000
C	-3.721601000000	14.461773000000	4.436289000000
C	-6.819812000000	9.714988000000	3.957379000000
H	-7.894486000000	9.578629000000	3.885543000000
C	-6.175849000000	10.641104000000	3.132051000000
H	-6.745601000000	11.221839000000	2.413543000000
C	-4.796521000000	10.820065000000	3.231694000000
H	-4.274412000000	11.530827000000	2.598452000000
C	-4.053761000000	10.065148000000	4.156690000000
C	-4.703727000000	9.132274000000	4.986188000000
H	-4.121427000000	8.559495000000	5.698291000000
C	-6.080334000000	8.964010000000	4.880947000000
H	-6.584864000000	8.247975000000	5.522726000000
C	0.242785000000	8.754337000000	5.290629000000
H	-0.177470000000	7.779752000000	5.504374000000

C	1.616106000000	9.013086000000	5.355690000000
H	2.309796000000	8.225626000000	5.631324000000
C	2.085142000000	10.279453000000	5.061445000000
H	3.142471000000	10.515739000000	5.105062000000
C	1.164897000000	11.297012000000	4.710617000000
N	-0.163743000000	11.047990000000	4.648084000000
C	-1.492734000000	12.729900000000	6.125108000000
O	-2.388296000000	13.131613000000	6.924632000000
H	-0.551917000000	12.497248000000	6.661162000000
H	-3.386063000000	13.339107000000	6.287110000000

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9 (*S*=0) E(opt) = -1573.8216501 hartree

Cartesian Coordinates

Ni	-1.310985000000	12.618955000000	4.413128000000
N	-0.885394000000	12.919537000000	2.508449000000
N	-1.429449000000	14.029164000000	1.988347000000
N	-2.597946000000	13.984262000000	4.008943000000
N	-3.919904000000	13.757710000000	5.923245000000
H	-3.843018000000	12.759472000000	5.764187000000
H	-4.811286000000	14.015068000000	6.326016000000
N	-2.692038000000	10.596344000000	4.577424000000
N	-1.952074000000	9.607648000000	4.926654000000
C	-0.631454000000	9.916462000000	5.189511000000
N	1.759844000000	12.478856000000	4.441274000000
H	1.181481000000	12.977721000000	3.775679000000
H	2.748208000000	12.487905000000	4.237480000000
C	1.505849000000	10.712566000000	-0.186830000000
H	2.136713000000	10.145893000000	-0.865472000000

C	1.405100000000	12.103754000000	-0.307659000000
H	1.963295000000	12.622485000000	-1.083083000000
C	0.597228000000	12.836319000000	0.554117000000
H	0.509997000000	13.912317000000	0.461690000000
C	-0.126378000000	12.186350000000	1.579822000000
C	-0.044207000000	10.784392000000	1.677122000000
H	-0.650511000000	10.271299000000	2.411372000000
C	0.769036000000	10.062320000000	0.804573000000
H	0.810880000000	8.979784000000	0.892408000000
C	-2.255481000000	14.645050000000	2.832976000000
C	-2.806467000000	15.922207000000	2.534541000000
H	-2.476470000000	16.424910000000	1.633550000000
C	-3.733423000000	16.463911000000	3.391508000000
H	-4.172496000000	17.434856000000	3.180722000000
C	-4.150385000000	15.746585000000	4.536071000000
H	-4.950305000000	16.115469000000	5.169417000000
C	-3.562400000000	14.517764000000	4.809630000000
C	-6.691203000000	9.760674000000	3.571879000000
H	-7.729244000000	9.567157000000	3.317525000000
C	-6.087352000000	10.962295000000	3.194988000000
H	-6.651386000000	11.704415000000	2.637170000000
C	-4.756573000000	11.214221000000	3.522965000000
H	-4.264668000000	12.130340000000	3.214676000000
C	-4.010001000000	10.252907000000	4.230988000000
C	-4.620050000000	9.035570000000	4.601802000000
H	-4.035962000000	8.305261000000	5.149091000000
C	-5.950173000000	8.802488000000	4.276556000000
H	-6.418595000000	7.867758000000	4.572901000000
C	0.141942000000	8.928158000000	5.817545000000
H	-0.347661000000	8.019037000000	6.143747000000

C	1.502649000000	9.149169000000	5.979572000000
H	2.127768000000	8.401279000000	6.458194000000
C	2.069760000000	10.329379000000	5.505422000000
H	3.135639000000	10.516084000000	5.583188000000
C	1.244653000000	11.287514000000	4.891279000000
N	-0.088258000000	11.091995000000	4.746794000000
C	-1.070709000000	13.221678000000	6.098020000000
O	-0.395804000000	12.622893000000	7.072691000000
H	-1.460798000000	14.197351000000	6.415157000000
H	-0.357993000000	13.167606000000	7.875179000000

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10 (*S*=1/2) E(opt) = -1574.4640012 hartree

Cartesian Coordinates

Ni	-1.781572000000	12.599620000000	4.107212000000
N	-1.373537000000	13.547688000000	2.395701000000
N	-1.281701000000	14.840600000000	2.453506000000
N	-1.667412000000	14.552007000000	4.772718000000
N	-1.998466000000	14.225812000000	7.039021000000
H	-1.960540000000	13.230049000000	6.891373000000
H	-2.086779000000	14.571304000000	7.978996000000
N	-3.877801000000	12.637728000000	4.095517000000
N	-4.414493000000	12.081920000000	5.110560000000
C	-3.573584000000	11.253614000000	5.832452000000
N	-0.229244000000	10.009963000000	5.713203000000
H	0.070146000000	10.294778000000	4.785021000000
H	0.292795000000	9.266278000000	6.148411000000
C	-0.524116000000	11.653545000000	-1.272055000000

H	-0.305983000000	11.156809000000	-2.213235000000
C	-0.299232000000	13.028792000000	-1.132899000000
H	0.097404000000	13.595583000000	-1.970755000000
C	-0.572625000000	13.679525000000	0.066666000000
H	-0.399373000000	14.742020000000	0.184871000000
C	-1.085224000000	12.946900000000	1.158731000000
C	-1.311721000000	11.562005000000	1.017560000000
H	-1.729842000000	11.006732000000	1.852455000000
C	-1.032417000000	10.925513000000	-0.191555000000
H	-1.218211000000	9.860409000000	-0.294617000000
C	-1.473986000000	15.388237000000	3.705334000000
C	-1.442265000000	16.780816000000	3.838488000000
H	-1.286444000000	17.393180000000	2.959781000000
C	-1.614489000000	17.322538000000	5.114182000000
H	-1.595322000000	18.399091000000	5.254904000000
C	-1.802735000000	16.485532000000	6.204887000000
H	-1.927582000000	16.877713000000	7.209798000000
C	-1.822152000000	15.083336000000	5.997273000000
C	-6.462543000000	15.102648000000	1.866621000000
H	-7.126410000000	15.732811000000	1.281873000000
C	-5.376659000000	14.472338000000	1.255313000000
H	-5.201880000000	14.599800000000	0.191603000000
C	-4.513578000000	13.674795000000	2.004451000000
H	-3.684640000000	13.162606000000	1.533091000000
C	-4.752540000000	13.488650000000	3.372754000000
C	-5.850653000000	14.115382000000	3.989811000000
H	-6.018451000000	13.963514000000	5.049189000000
C	-6.693512000000	14.923660000000	3.235461000000
H	-7.534558000000	15.418508000000	3.712280000000
C	-4.150241000000	10.549534000000	6.886025000000

H	-5.199634000000	10.700303000000	7.103841000000
C	-3.348821000000	9.653238000000	7.600700000000
H	-3.760918000000	9.086013000000	8.429307000000
C	-2.034184000000	9.473931000000	7.213389000000
H	-1.390430000000	8.757894000000	7.714797000000
C	-1.508598000000	10.212386000000	6.119746000000
N	-2.248096000000	11.149746000000	5.475181000000
C	0.249813000000	12.458784000000	4.240978000000
O	0.673768000000	11.329802000000	3.559909000000
H	0.644459000000	13.398541000000	3.859402000000
H	0.787200000000	11.521952000000	2.619403000000
H	0.397827000000	12.312798000000	5.309219000000

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11 (*S*=1/2) E(opt) = -1498.7688512 hartree

Cartesian Coordinates

Ni	-1.832372000000	12.909655000000	4.306145000000
N	-1.270342000000	13.364516000000	2.396195000000
N	-1.042055000000	14.592939000000	2.184941000000
N	-1.753318000000	14.901231000000	4.430277000000
N	-2.439364000000	15.190028000000	6.641878000000
H	-2.448618000000	14.196979000000	6.808329000000
H	-2.616814000000	15.788132000000	7.434722000000
N	-3.936182000000	12.816134000000	4.326629000000
N	-4.354282000000	11.899552000000	5.100861000000
C	-3.414814000000	10.940366000000	5.457225000000
N	-0.136875000000	9.896742000000	4.470445000000
H	-0.002099000000	10.435363000000	3.627988000000
H	0.442236000000	9.075655000000	4.572904000000

C	-0.450785000000	10.615667000000	-0.664540000000
H	-0.248709000000	9.899242000000	-1.454389000000
C	0.123127000000	11.894101000000	-0.720441000000
H	0.772032000000	12.160774000000	-1.548134000000
C	-0.131107000000	12.823116000000	0.279171000000
H	0.307825000000	13.813144000000	0.248817000000
C	-0.966421000000	12.460662000000	1.355727000000
C	-1.538859000000	11.175261000000	1.419076000000
H	-2.214633000000	10.923929000000	2.230129000000
C	-1.283387000000	10.259981000000	0.401868000000
H	-1.740643000000	9.276455000000	0.430403000000
C	-1.324835000000	15.442949000000	3.251595000000
C	-1.174661000000	16.803702000000	3.051282000000
H	-0.835379000000	17.166481000000	2.088906000000
C	-1.486235000000	17.662572000000	4.122599000000
H	-1.382610000000	18.736665000000	4.010170000000
C	-1.917324000000	17.132311000000	5.317291000000
H	-2.152573000000	17.770639000000	6.162265000000
C	-2.038161000000	15.718713000000	5.464414000000
C	-6.794601000000	15.550571000000	2.928092000000
H	-7.534450000000	16.249185000000	2.550430000000
C	-5.596756000000	15.360340000000	2.231825000000
H	-5.413608000000	15.896641000000	1.306703000000
C	-4.643123000000	14.472832000000	2.719179000000
H	-3.730461000000	14.292053000000	2.165107000000
C	-4.902022000000	13.752995000000	3.900064000000
C	-6.114274000000	13.936449000000	4.598343000000
H	-6.300959000000	13.376368000000	5.506673000000
C	-7.047153000000	14.840142000000	4.110940000000
H	-7.977619000000	14.994141000000	4.647429000000

C	-3.835977000000	9.923911000000	6.293470000000
H	-4.851193000000	9.936332000000	6.669927000000
C	-2.924644000000	8.895353000000	6.602363000000
H	-3.212719000000	8.089869000000	7.269730000000
C	-1.683182000000	8.896001000000	6.011631000000
H	-0.978082000000	8.089926000000	6.184984000000
C	-1.319445000000	9.948331000000	5.121168000000
N	-2.143497000000	11.010404000000	4.920938000000
C	0.122235000000	12.922183000000	4.870863000000
H	0.407206000000	13.952832000000	5.054915000000
H	0.679825000000	12.476219000000	4.052192000000
H	0.106589000000	12.308445000000	5.770046000000

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12 (*S*=1) E(opt) = -1499.2624592 hartree

Cartesian Coordinates

Ni	-1.797201000000	12.818809000000	4.119877000000
N	-1.361498000000	13.491290000000	2.281050000000
N	-0.996652000000	14.732398000000	2.170163000000
N	-1.808901000000	14.873397000000	4.374958000000
N	-2.649351000000	14.895951000000	6.503380000000
H	-3.164984000000	14.054521000000	6.268262000000
H	-3.079103000000	15.451875000000	7.226644000000
N	-3.889372000000	12.735915000000	4.329922000000
N	-4.284051000000	11.986775000000	5.359912000000
C	-3.376234000000	11.063779000000	5.758202000000
N	-0.174383000000	9.778903000000	4.748577000000
H	-0.093047000000	10.274425000000	3.875356000000
H	0.286700000000	8.884700000000	4.796705000000

C	-0.459063000000	10.877255000000	-0.895110000000
H	-0.240148000000	10.193514000000	-1.709903000000
C	0.091897000000	12.163260000000	-0.891003000000
H	0.741738000000	12.476461000000	-1.703234000000
C	-0.181203000000	13.048448000000	0.147392000000
H	0.235909000000	14.047728000000	0.163291000000
C	-1.019583000000	12.644403000000	1.201210000000
C	-1.574361000000	11.352736000000	1.197900000000
H	-2.235466000000	11.057166000000	2.007901000000
C	-1.293469000000	10.476834000000	0.152002000000
H	-1.732355000000	9.483441000000	0.151229000000
C	-1.287283000000	15.491398000000	3.287075000000
C	-1.000945000000	16.861883000000	3.271702000000
H	-0.563535000000	17.304034000000	2.385417000000
C	-1.302653000000	17.592807000000	4.406272000000
H	-1.107388000000	18.660387000000	4.436200000000
C	-1.872336000000	16.965219000000	5.507901000000
H	-2.143237000000	17.525297000000	6.396552000000
C	-2.117836000000	15.584047000000	5.452638000000
C	-6.830459000000	15.333972000000	2.768918000000
H	-7.579593000000	16.004861000000	2.358668000000
C	-5.613074000000	15.142032000000	2.109682000000
H	-5.411740000000	15.660759000000	1.176084000000
C	-4.650257000000	14.284263000000	2.633197000000
H	-3.717260000000	14.125764000000	2.107431000000
C	-4.883294000000	13.590785000000	3.838548000000
C	-6.122002000000	13.779833000000	4.493405000000
H	-6.312754000000	13.233257000000	5.408308000000
C	-7.073231000000	14.643274000000	3.961001000000
H	-8.018738000000	14.777314000000	4.480918000000

C	-3.728499000000	10.202142000000	6.821008000000
H	-4.688718000000	10.345902000000	7.300588000000
C	-2.855790000000	9.190556000000	7.179171000000
H	-3.110543000000	8.508182000000	7.985347000000
C	-1.655141000000	9.024246000000	6.485134000000
H	-0.968821000000	8.217800000000	6.719843000000
C	-1.344967000000	9.924336000000	5.450656000000
N	-2.157807000000	10.955870000000	5.116092000000
C	0.241204000000	12.781334000000	4.340374000000
H	0.619406000000	13.794927000000	4.201016000000
H	0.718438000000	12.115090000000	3.618385000000
H	0.416892000000	12.429632000000	5.359547000000

1+CH_4 (*S*=1) E(opt) = -1499.7475504 hartree

Cartesian Coordinates

Ni	-2.846741000000	13.250927000000	4.075858000000
N	-1.771505000000	13.764275000000	2.442587000000
N	-0.992866000000	14.775607000000	2.546221000000
N	-1.804358000000	14.850676000000	4.767971000000
N	-2.677145000000	14.913758000000	6.913407000000
H	-3.024441000000	13.977292000000	6.766409000000
H	-2.667257000000	15.274375000000	7.853530000000
N	-4.770267000000	12.656624000000	3.984535000000
N	-5.133968000000	11.709267000000	4.767249000000
C	-4.092932000000	11.151216000000	5.500177000000
N	-0.650301000000	11.848871000000	6.127861000000
H	-0.502809000000	12.572134000000	5.439219000000
H	0.168384000000	11.383539000000	6.486380000000

C	-1.546283000000	11.481010000000	-1.082517000000
H	-1.497448000000	10.881864000000	-1.986411000000
C	-0.680504000000	12.571175000000	-0.919636000000
H	0.038148000000	12.812133000000	-1.696608000000
C	-0.732169000000	13.346585000000	0.231345000000
H	-0.066493000000	14.189013000000	0.372038000000
C	-1.666542000000	13.029256000000	1.236189000000
C	-2.537257000000	11.939686000000	1.070716000000
H	-3.261307000000	11.713388000000	1.846759000000
C	-2.471968000000	11.166539000000	-0.085652000000
H	-3.145631000000	10.325084000000	-0.211137000000
C	-1.072858000000	15.427013000000	3.773042000000
C	-0.390503000000	16.628328000000	3.927328000000
H	0.179374000000	17.028092000000	3.098350000000
C	-0.486318000000	17.277419000000	5.165460000000
H	0.028259000000	18.218656000000	5.329293000000
C	-1.237731000000	16.717310000000	6.182255000000
H	-1.322597000000	17.199949000000	7.149899000000
C	-1.904742000000	15.486572000000	5.954718000000
C	-7.775451000000	14.680045000000	1.849493000000
H	-8.541316000000	15.211833000000	1.293548000000
C	-6.427315000000	14.975317000000	1.637552000000
H	-6.140735000000	15.733747000000	0.916263000000
C	-5.445826000000	14.289307000000	2.348081000000
H	-4.394665000000	14.499340000000	2.180567000000
C	-5.813861000000	13.306488000000	3.282089000000
C	-7.173618000000	13.009492000000	3.496896000000
H	-7.443862000000	12.253292000000	4.223254000000
C	-8.142592000000	13.696812000000	2.778536000000
H	-9.191805000000	13.472230000000	2.942483000000

C	-4.348961000000	10.001149000000	6.239393000000
H	-5.342258000000	9.571008000000	6.226935000000
C	-3.288814000000	9.440208000000	6.961603000000
H	-3.443267000000	8.539964000000	7.547493000000
C	-2.039545000000	10.034857000000	6.928269000000
H	-1.206200000000	9.624034000000	7.487924000000
C	-1.852133000000	11.208975000000	6.158452000000
N	-2.873396000000	11.761389000000	5.468242000000
C	1.961268000000	11.966712000000	3.272333000000
H	1.496315000000	12.127512000000	2.297604000000
H	1.313245000000	11.331259000000	3.881776000000
H	2.117538000000	12.928950000000	3.766360000000
H	2.924672000000	11.471482000000	3.138164000000

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