

Electronic Supporting Information materials for

Carbon Nanotubes Heterogenization Improve Cobalt Pyridyldiimine Complexes CO₂ Reduction Activity in Aqueous Carbonate Buffer

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1 Experimental section

1.1 Materials

All reagents were purchased from commercial sources and used without any further purification, unless otherwise stated.

1.2 Instrumentation

Nuclear Magnetic Resonance (NMR) spectroscopy: All spectra were recorded on a Bruker Fourier 300 MHz spectrometer equipped with a dual (^{13}C , ^1H) probe. All measurements were performed at room temperature in a deuterated solvent using residual protons as internal reference.

Mass spectrometry (MS): The electrospray (ESI) time-of-flight (TOF) MS measurements were performed using a Xevo G2-XS QTOF spectrometer (Waters, USA).

1.3 Electrochemical studies

Electrochemical studies under homogeneous conditions

The electrochemical properties of **C2** or **C3** were investigated by cyclic voltammetry (CV) with 0.5 mM of the catalyst in a 0.1 M NBu_4PF_6 acetonitrile solution as the supporting electrolyte. A three-electrode cell set-up was used, consisting of a 3 mm diameter glassy carbon working electrode with a volume of 5 mL, a Pt-mesh counter electrode with a volume of 2 mL, and a saturated calomel reference electrode (SCE electrode) separated by a glass frit. Prior to each CV measurement, the working electrode was polished with 3.0, 1.0, and 0.25 μm diamond paste, followed by sonication in isopropyl alcohol for 1 minute to ensure a clean surface. CV experiments were performed using a Metrohm Autolab PGSTAT12 potentiostat with IR compensation.

Electrochemical studies heterogeneous conditions

To prepare the catalytic ink, 1 mg of the catalyst per 10 mg of multi-walled carbon nanotubes (MWCNT) were mixed in 10 mL of ethanol, followed by a 30 min ultrasonic bath. Then, 100 μL of Nafion solution (10 $\mu\text{L}/\text{mL}$) was added, followed by another 30 minutes of ultrasonication. The ink was applied to a 1 cm^2 carbon paper by drop casting. CPE experiment was performed with 10 $\mu\text{g}/\text{cm}^2$ **C2**/MWCNT or **C3**/MWCNT loaded on carbon paper (as the working electrode) in 0.5 M KHCO_3 in ultrapure water (pH = 8.5) as supporting electrolyte. A three-electrode cell was employed, consisting of a Pt-mesh counter electrode, and a saturated calomel reference electrode (SCE electrode), both separated by a glass frit. Prior to each CPE experiment, the

electrolyte was bubbled with Ar and CO₂, respectively for 30 min. For CPE experiments, a VIONIC potentiostat/galvonostat from Metrohm was employed.

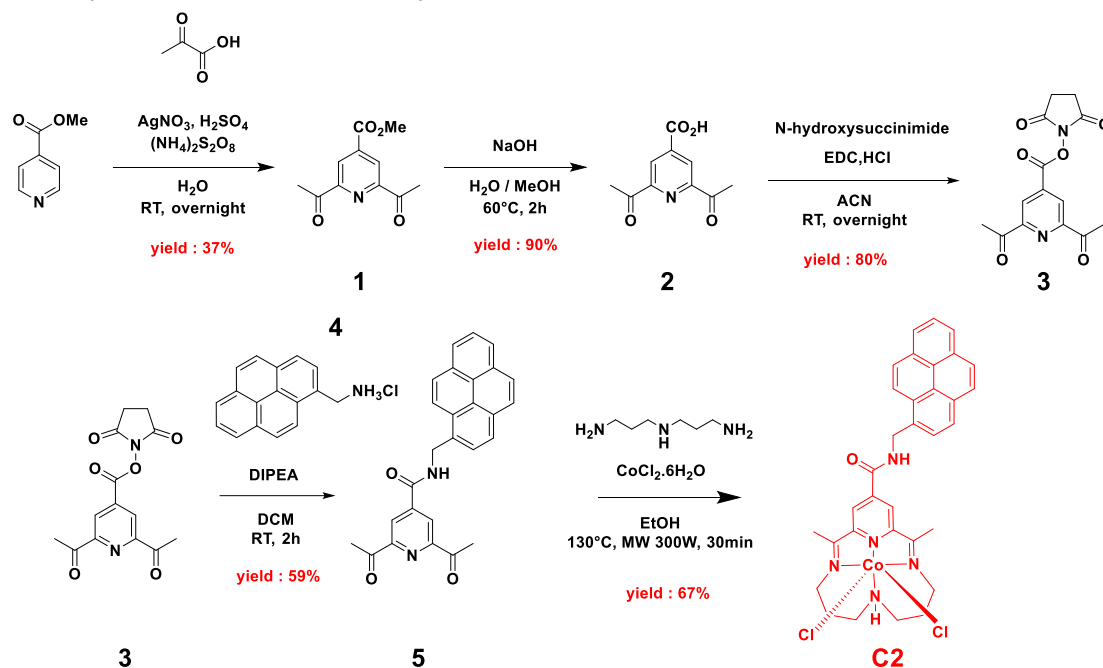
CPE was performed in a three-compartment flow cell electrolyzer. In the cathode compartment, CO₂ was supplied to the gas diffusion electrode (1 cm² C3/MWCNT carbon paper). The electrolyte (0.5 M KHCO₃, pH 8.5) flowed between the GDE and the anion exchange membrane (AEM). The anodic compartment contained a Pt/Ti alloy anode, and the electrolyte flowed between the anode and the membrane. The electrolyte was recycled using peristaltic pumps. An Ag/AgCl electrode was used as the reference electrode.

The potentials were converted to the RHE by the equation: $E_{(vs. RHE)} = E_{(vs. SCE)} + 0.244 V + 0.0591 V \times pH$. IR compensation was used before each experiment (average value is 9.61 Ω).

Gas detection

Gas chromatography analyses of the headspace gas during electrolysis were performed using an Agilent Technologies 7820A GC system with a thermal conductivity detector. A CP-CarboPlot P7 capillary column was used for quantitative detection of CO and H₂ production. Operating conditions were maintained at 150°C for the detector and 34°C for the oven. Argon was used as the carrier gas at a constant pressure of 0.4 bar, flowing at 28.7 mL/min. A 250-μL gas-tight (Hamilton) syringe was used for injection.

2 Synthesis of the compounds



Scheme S1. Synthetic route to catalyst C2.

Compound **1** was prepared according to literature procedure.¹

¹H NMR (300 MHz, Chloroform-*d*) δ 8.72 (s, 2H), 4.00 (s, 3H), 2.81 (s, 6H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 198.60, 164.57, 153.89, 140.18, 124.16, 53.28, 25.86.

Compound 2. A quantity of 200mg (1eq., 0.9mmol) of compound **1** was dissolved in 5 mL of methanol (MeOH) and heated to 60°C. A solution of sodium hydroxide (1.1eq., 0,99mmol, 40mg), dissolved in 1 mL of water, was added dropwise to the reaction mixture, and the resulting solution was stirred for 1 hour. The reaction mixture was then cooled to room temperature (RT), and the pH was adjusted to 2 by the careful addition of a 2 M hydrochloric acid (HCl) solution. Subsequently, 10 mL of water was added, and the reaction mixture was subjected to extraction with ethyl acetate (EtOAc) three times. The combined organic layers were dried over magnesium sulfate (MgSO₄), and the solvent was removed under vacuum, yielding the desired compound as a white solid with a high yield of 90% (170mg).

NMR (¹H, DMSO, 400MHz) δ (ppm): 8.72 (s, 2H), 4.00 (s, 3H), 2.81 (6H).

NMR (¹³C, DMSO, 400MHz) δ (ppm): 198.15, 164.99, 153.37, 141.20, 123.06, 25.52.

HRMS (ASAP+) m/z: [M+H]⁺ calculated for C₁₀H₁₀NO₄:208.0608; found: 208.0610.

Compound 3. A total of 200 mg of compound **2** (1eq, 0.96mmol) was dissolved in 10 mL of acetonitrile. To this solution, EDC-HCl was added (1.2eq., 1.16mmol, 222mg), and the mixture was stirred at room temperature (RT) for 10 minutes. Following this, 1.2 eq. of NHS (1.16mmol, 133mg) were introduced to the reaction, and the stirring continued for an additional 2 hours at RT. The solvent was then removed under reduced pressure, and the resulting residue was re-dissolved in 15 mL of dichloromethane (DCM). This solution was subjected to two washes with 1 M HCl and two washes with a saturated solution of potassium carbonate. The organic layer was subsequently dried with magnesium sulfate (MgSO₄), and the solvent was removed under vacuum, resulting in the isolation of the desired compound as a white solid with a yield of 80% (235mg).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.81 (s, 2H), 2.94 (s, 4H), 2.83 (s, 6H).

¹³C NMR (400 MHz, Chloroform-*d*) δ 197.75, 168.38, 159.92, 154.06, 135.47, 124.33, 25.66.

HRMS (ASAP+) m/z: [M+H]⁺ calculated for C₁₄H₁₃N₂O₆:305.0775; found: 305.0774.

Compound 5. 85 mg of Compound **3** (1eq, 0.28mmol) was dissolved in 10 mL of dichloromethane (DCM) and 0.5 mL of diisopropylethylamine (DIPEA). Subsequently, 1 equivalent of 1-Pyrenemethylamine hydrochloride (1eq., 0.28mmol, 75mg) was added to the solution, and the reaction mixture was stirred for 2 hours. The progress of the reaction was monitored by thin-layer chromatography (TLC) using DCM as the eluent. Upon completion of the reaction, 15 mL of water was added, and the resulting mixture was subjected to extraction with dichloromethane (DCM) twice. The organic layers were combined, and the solvent was evaporated. The crude product obtained was further purified on silica gel, utilizing DCM as the eluent, resulting in the isolation of the desired compound as a yellowish solid with a yield of 59% (69mg).

¹H NMR (300 MHz, Chloroform-*d*) δ 8.24 – 8.17 (m, 3H), 8.14 – 8.01 (m, 4H), 7.99 – 7.88 (m, 4H), 5.25 (d, *J* = 4.9 Hz, 2H), 2.44 (s, 6H).

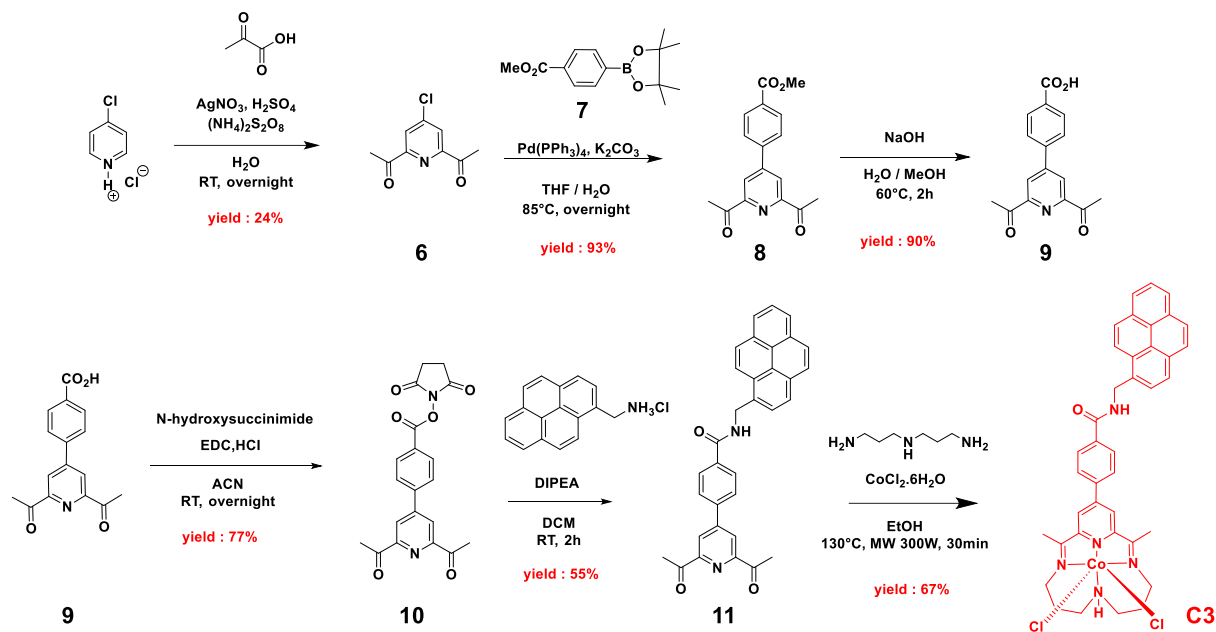
¹³C NMR (101 MHz, Chloroform-*d*) δ 198.76, 164.03, 152.95, 143.55, 133.73 – 123.33 (m), 122.30, 43.06, 25.48.

HRMS (ASAP+) m/z: [M+H]⁺ calculated for C₂₇H₂₁N₂O₃:421.1557; found: 421.1552

Catalyst C2. Compound **5** (50 mg, 0.12mmol) was dispersed in 15 mL of ethanol (EtOH) within a microwave vial and subjected to degassing under argon for 15 minutes. Subsequently, CoCl₂·6H₂O (1eq., 0.12mmol, 29mg) was introduced, and the mixture was further degassed for an additional 5 minutes. Norspermidine (1eq., 0.12mmol, 16mg) was then added to the reaction mixture, which was subjected to microwave irradiation at 130°C, 300 W for 25 minutes. Upon completion of the reaction, the reaction mixture was allowed to cool to room temperature (RT), followed by the addition of 1 mL of 2 M HCl. The resulting solution was left to react for 30 minutes under ambient air conditions. The solution was then concentrated under reduced pressure, dissolved in 20 mL of methanol (MeOH), and filtered through a nylon membrane.

The filtrate obtained was concentrated once again under reduced pressure. The concentrated solution was dispersed in 20 mL of acetonitrile and filtered through a nylon membrane. The resulting solution was dried under reduced pressure, solubilized in 10 mL of MeOH, and precipitated by the addition of a large quantity of diethyl ether (Et₂O). The precipitate was filtered, affording a green solid with a yield of 67% (52mg).

HRMS (ES+) *m/z*: [M+H]⁺ calculated for C₃₃H₃₃N₅OCl₂Co: 644.1393; found: 644.1394.



Scheme S2. Synthetic route to catalyst C3.

Compound 6 was prepared according to literature procedure.²

¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 2H), 2.77 (s, 6H).

¹³C NMR (400 MHz, Chloroform-*d*) δ 198.20, 154.06, 147.07, 125.08, 25.73.

Compound 7. Was prepared following literature³ with small changes: Methyl 4-iodobenzoate (1 g, 3.77mmol) and bis pinacolato diboron (1.1eq., 4.15mmol, 1.05g) are dissolved in 50 mL of dimethylformamide (DMF) and the solution is degassed under argon for 30 minutes. Potassium acetate (3eq., 11.3mmol, 1.11g) and palladium dichloride(diphenylphosphino)ferrocene (PdCl₂(dppf)) (5 mol%, 0.188mmol, 138mg) are then added to the mixture, followed by an additional 5 minutes of degassing. The reaction mixture is heated to 80°C and stirred for 5 hours. The solution is cooled to room temperature and 100 mL of dichloromethane (DCM) is added. The organic layer is washed three times with water and once with a saturated solution of sodium chloride. The solvent is removed under reduced pressure, and the crude product is purified on silica gel using a mixture of DCM and cyclohexane (9:1) as the eluent, yielding the desired compound (0.91g, 92%).

¹H NMR (300 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H), 1.35 (s, 6H).

¹³C NMR (400 MHz, Chloroform-*d*) δ 167.15, 134.65, 132.28, 128.59, 84.18, 52.18, 24.89.

Compound 8. Compound (6) (200 mg, 1.01mmol) and (7) (1.2eq., 1.21mmol, 320mg) were dissolved in 10 mL of a mixture of tetrahydrofuran (THF) and water (3:1) and degassed for 30 minutes under an argon atmosphere. Palladium tetrakis(triphenylphosphine) (Pd(PPh₃)₄) (20 mol%, 0.24mmol, 280mg) and potassium carbonate (K₂CO₃) (3eq., 3.03mmol, 414mg) were then added to the mixture, followed by an additional 5 minutes of degassing under argon. The reaction mixture was heated to 85°C and stirred overnight. The mixture was allowed to cool to room temperature and THF was evaporated under reduced

pressure. The crude product was then extracted three times with dichloromethane (DCM). The combined organic layers were concentrated under reduced pressure. The crude material was purified on silica gel using a mixture of DCM and cyclohexane (9:1) to afford the desired compound as a white solid (93%, 279mg)

¹H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 2H), 8.18 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 3H), 2.83 (s, 6H).

¹³C NMR (400 MHz, Chloroform-*d*) δ 199.29, 166.36, 153.56, 149.49, 140.99, 131.36, 130.53, 127.20, 122.42, 52.35, 25.69.

HRMS (ES+) *m/z*: [M+H]⁺ calculated for C₁₇H₁₆NO₄: 298.1079; found: 298.1077.

Compound 9. Compound (**8**) (70 mg, 0.23mmol) was dispersed in 5 mL of methanol (MeOH), followed by the addition of a solution of NaOH (1.2 eq, 0.28mmol, 11mg) in 0.5 mL of water. The resulting mixture was heated to 60°C and stirred until it became clear. Upon achieving clarity, the mixture was cooled to room temperature, and the pH was adjusted to 4 using a 1 M hydrochloric acid (HCl) solution, resulting in the precipitation of the product. To aid in isolation, 10 mL of water was added, and the mixture was extracted three times with ethyl acetate (EtOAc). The combined organic layers were dried over magnesium sulfate (MgSO₄), and the solvent was removed under vacuum to yield the desired compound as a white solid (60 mg, 90%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 13.14 (s, 1H), 8.44 (s, 2H), 8.13 – 8.00 (m, 4H), 2.78 (s, 6H).

¹³C NMR (404 MHz, DMSO-*d*₆) δ 199.10, 167.24, 153.78, 149.22, 140.41, 132.42, 130.70, 127.97, 122.25, 26.81, 26.09.

HRMS (ASAP-) *m/z*: [M+H]⁺ calculated for C₁₆H₁₂NO₄: 282.0760; found: 282.0766

Compound 10. Compound (**9**) (200 mg, 0.7mmol) was dissolved in 10 mL of acetonitrile (ACN), followed by the addition of EDC·HCl (1.2eq., 0.85mmol, 162mg). The mixture was stirred at room temperature (RT) for 10 minutes. Subsequently, NHS (1.2eq., 0.85mmol, 97mg) was added to the reaction, and stirring was continued for an additional 2 hours at RT. The solvent was then removed under reduced pressure, and the resulting residue was dissolved in 15 mL of dichloromethane (DCM). The solution was washed twice with 1 M hydrochloric acid (HCl) and twice with a saturated solution of potassium carbonate. The organic layer was dried over magnesium sulfate (MgSO₄), and the solvent was removed under vacuum, yielding the desired compound as a white solid with a yield of 77% (205mg).

¹H NMR (300 MHz, Chloroform-*d*) δ 8.48 (s, 2H), 8.29 (d, *J* = 8.7 Hz, 2H), 7.88 (d, *J* = 8.7 Hz, 2H), 2.94 (s, 4H), 2.85 (s, 6H).

¹³C NMR (400 MHz, Chloroform-*d*) δ 199.24, 169.08, 161.28, 153.64, 148.87, 142.98, 131.53, 127.65, 126.26, 122.49, 25.70.

HRMS (ASAP+) *m/z*: [M+H]⁺ calculated for C₂₀H₂₀N₂O₆: 381.1071; found: 381.1087.

Compound 11. Compound (**10**) (250mg, 0.66mmol) was dissolved in 10 mL of dichloromethane (DCM) along with 0.5 mL of DIPEA. Subsequently, 1-pyrenemethylamine (0.95eq., 0.62mmol, 167mg) was added, and the solution was stirred at 35°C overnight. The reaction mixture was then cooled to room temperature, and 15 mL of water was added. The resulting mixture was extracted three times with DCM. The combined organic layers were dried over magnesium sulfate (MgSO₄), and the solvent was removed under reduced pressure. The crude product was purified using recycling size exclusion chromatography using chloroform as eluent. The purified product was then precipitated with methanol to yield the desired compound as a yellowish solid (55%, 180mg).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 2H), 8.21 – 7.97 (m, 9H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 5.37 (s, 2H), 2.79 (s, 6H).

¹³C NMR (300 MHz, Chloroform-*d*) δ 199.29, 166.17, 153.41, 149.25, 139.60, 135.45, 131.35 (d, *J* = 42.0 Hz), 130.75, 129.15, 128.47, 128.02, 127.30, 126.17, 125.52, 124.83, 122.70, 122.18, 42.76, 25.65.

HRMS (ES+) *m/z*: [M+H]⁺ calculated for C₃₃H₂₄N₂O₃Na: 519.1685; found: 519.1666.

Catalyst C3. Compound (**11**) (80 mg, 0.16mmol) was suspended in 10 mL of a 3:1 mixture of ethanol and acetonitrile (EtOH/ACN) and degassed for 15 minutes under an argon atmosphere. Subsequently, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1eq, 0.16mmol, 39mg) and norspermidine (1eq, 0.16mmol, 22mg) were added, and the mixture was subjected to microwave irradiation at 130°C for 25 minutes at 300 W. The resulting solution was cooled to room temperature, and 1 mL of 2 M HCl was added. The mixture was stirred under ambient air for 30 minutes. The solution was then evaporated under reduced pressure, and the residue was dissolved in methanol (MeOH) and filtered. The filtrate was evaporated, and the residue was re-dissolved in acetonitrile (ACN) and filtered again. This procedure was repeated, and the final filtrate was dissolved in 5 mL of MeOH and precipitated in a large volume of diethyl ether (Et_2O). The precipitate was collected by filtration, affording the desired compound as a green solid (67%, 70mg). For further purification, the product can be subjected to Sephadex (LH20) size exclusion chromatography eluted with ACN

HRMS (ES+) m/z: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{37}\text{N}_5\text{OCl}_2\text{Co}$: 720.1719; found: 720.1707.

3 Study under homogeneous conditions (in acetonitrile solvent)

3.1 Electrochemical studies of C2 for CO₂ reduction

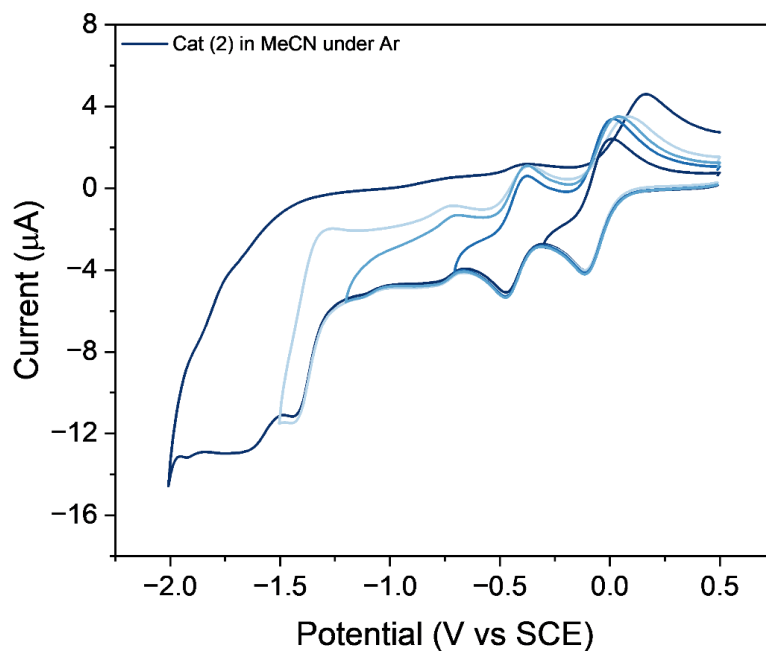


Figure S1. CV of 0.5 mM (C2) under Ar atmosphere in 5 mL MeCN with 0.1 M Bu₄NPF₆ as supporting electrolyte at a scan rate of 0.1 V s⁻¹. A glassy carbon working electrode (3 mm diameter) was used.

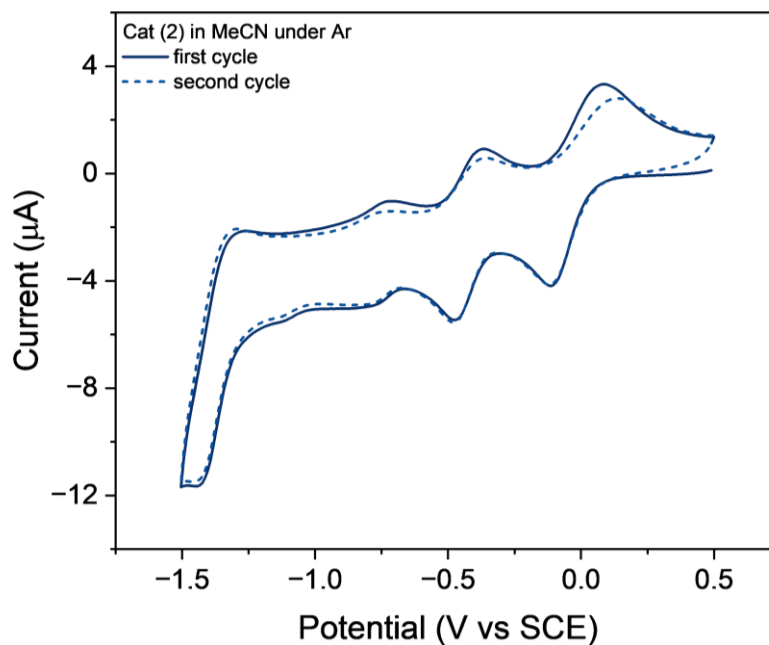


Figure S2. CV of 0.5 mM (C2) under Ar atmosphere in 5 mL MeCN with 0.1 M Bu₄NPF₆ as supporting electrolyte at a scan rate of 0.1 V s⁻¹ for the first and second scan. A glassy carbon working electrode (3 mm diameter) was used.

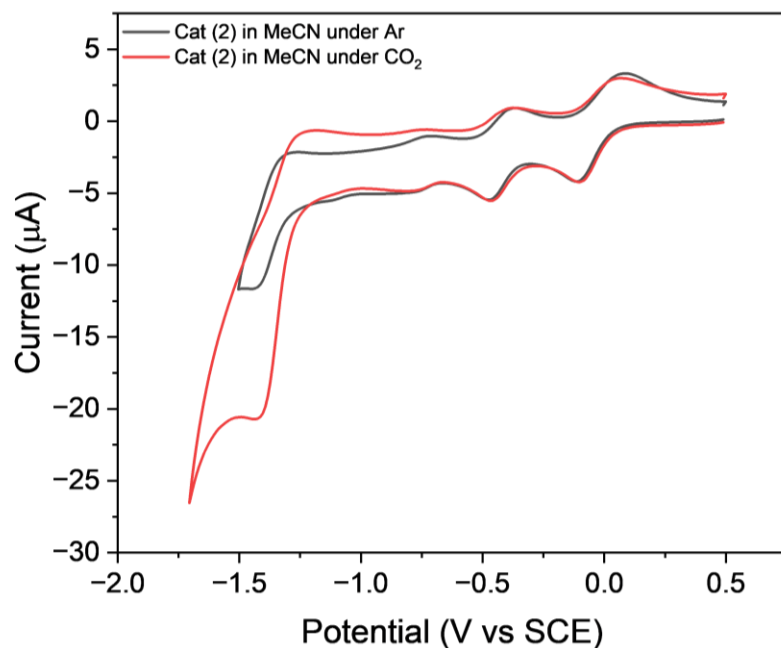


Figure S3. CV of 0.5 mM (**C2**) under CO_2 atmosphere in 5 mL MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V s^{-1} . A glassy carbon working electrode (3 mm diameter) was used.

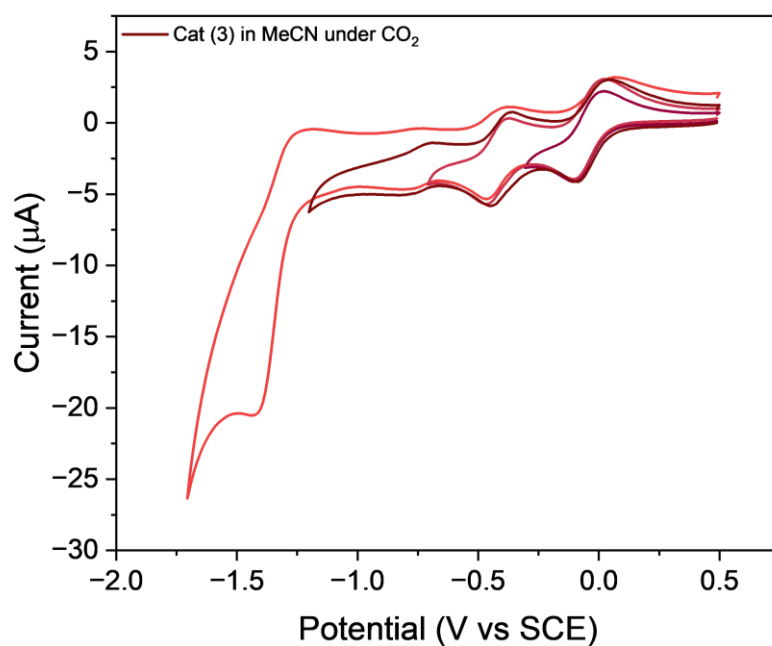


Figure S4. CV of 0.5 mM (**C2**) under CO_2 atmosphere in 5 mL MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V s^{-1} . A glassy carbon working electrode (3 mm diameter) was used.

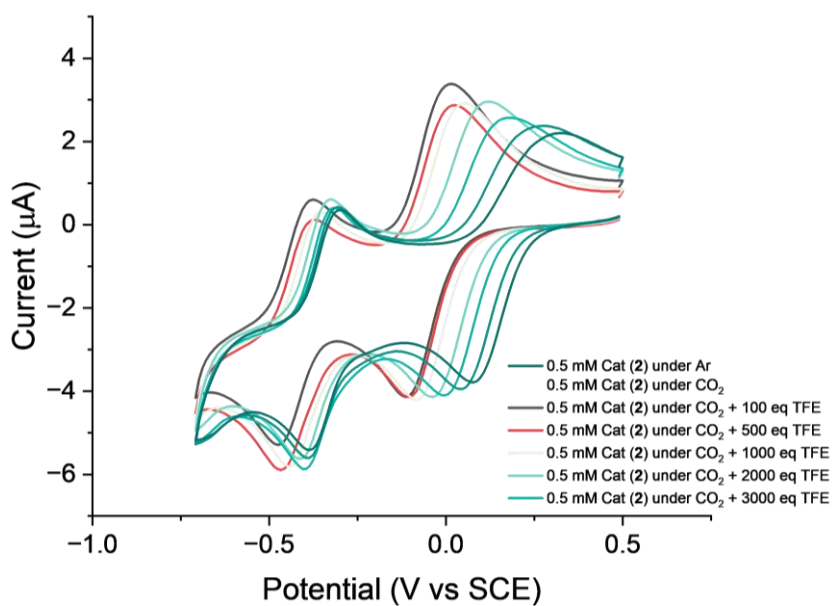
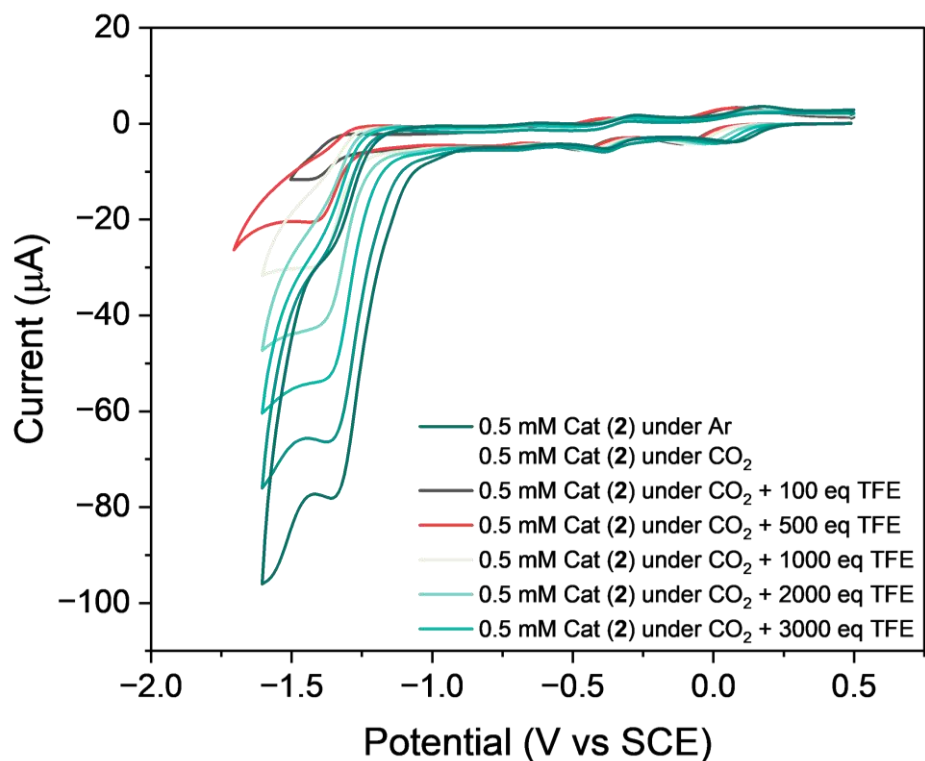


Figure S5. CV of 0.5 mM (C2) under CO_2 atmosphere with increasing the amount of 2,2,2-trifluoroethanol – TFE (from 0 to 4000 eq) in 5 mL MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V s^{-1} . A glassy carbon working electrode (3 mm diameter) was used.

3.2 Electrochemical studies of **C3** for CO₂ reduction

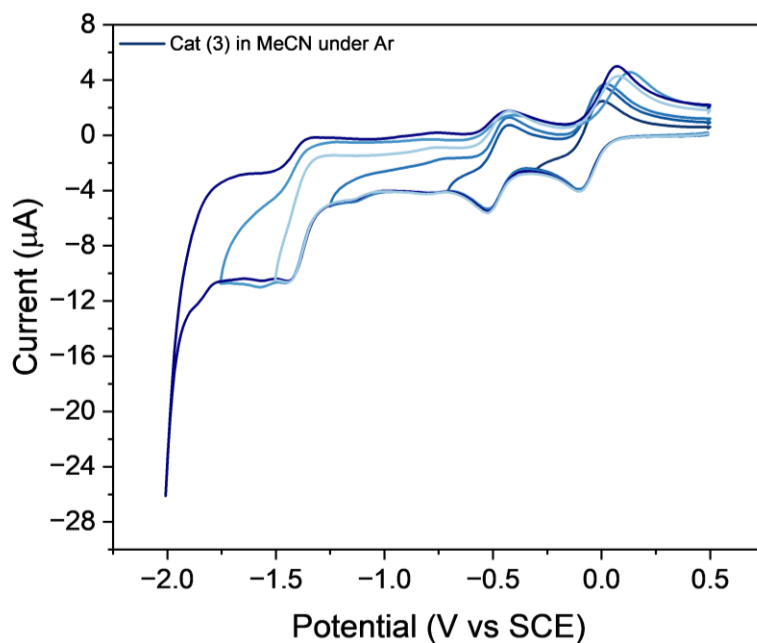


Figure S6. CV of 0.5 mM (**C3**) under Ar atmosphere in 5 mL MeCN with 0.1 M Bu₄NPF₆ as supporting electrolyte at a scan rate of 0.1 V s⁻¹. A glassy carbon working electrode (3 mm diameter) was used.

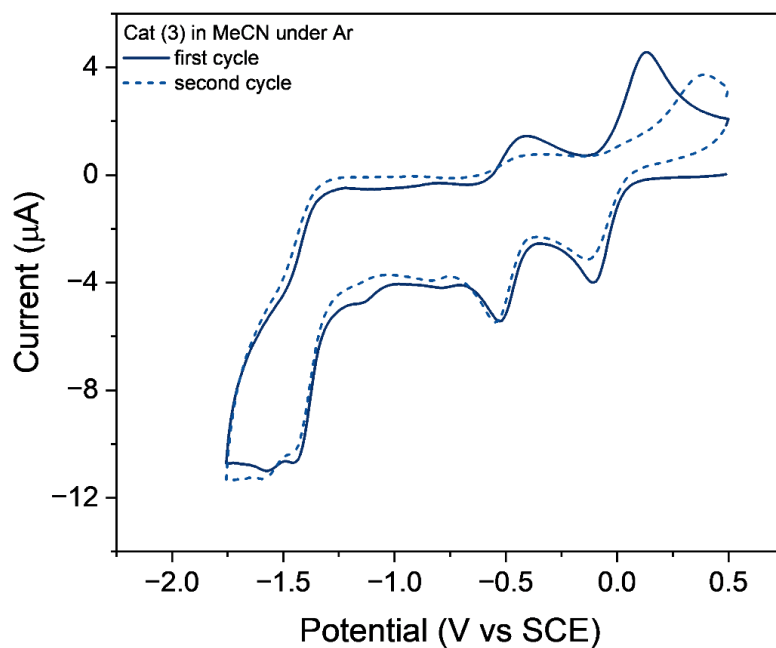


Figure S7. CV of 0.5 mM (**C3**) under Ar atmosphere in 5 mL MeCN with 0.1 M Bu₄NPF₆ as supporting electrolyte at a scan rate of 0.1 V s⁻¹ for the first and second scan. A glassy carbon working electrode (3 mm diameter) was used.

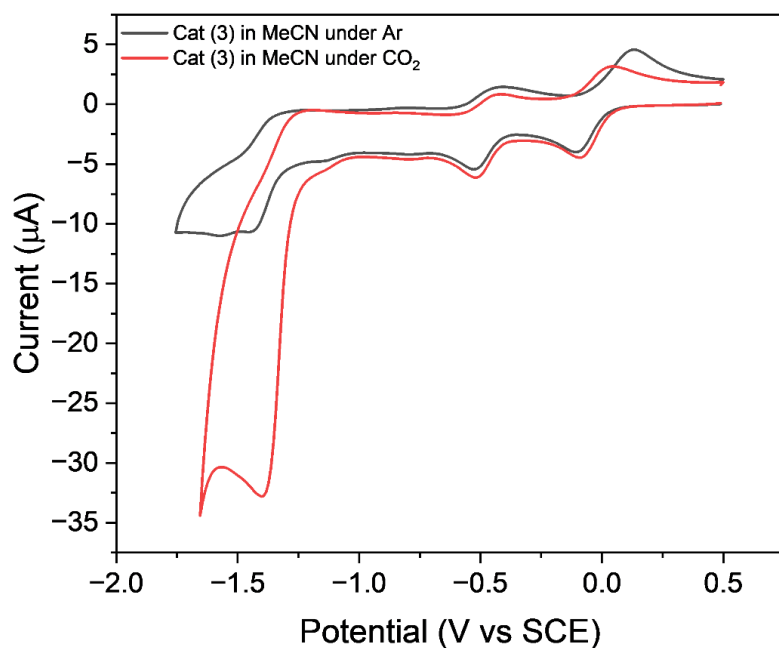


Figure S8. CV of 0.5 mM (**C3**) under CO_2 atmosphere in 5 mL MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V s^{-1} . A glassy carbon working electrode (3 mm diameter) was used.

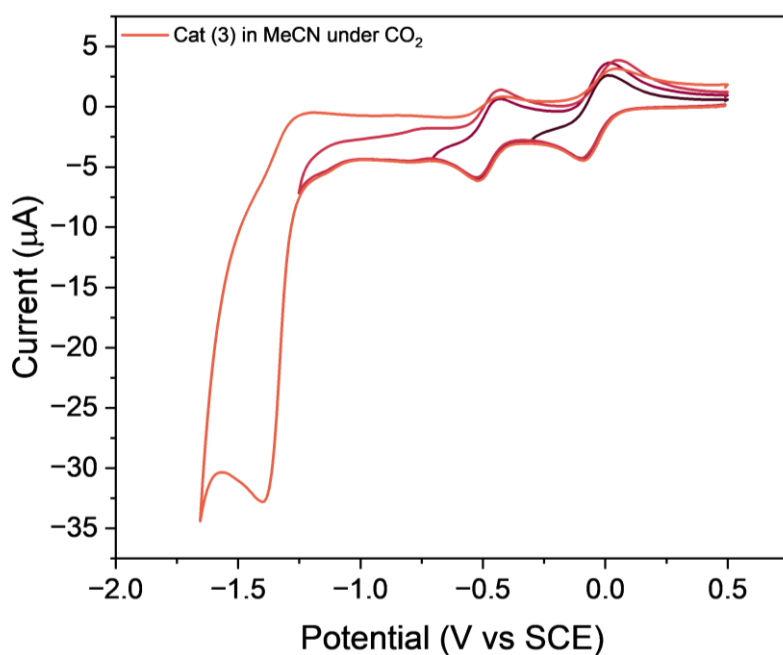


Figure S9. CV of 0.5 mM (**C3**) under CO_2 atmosphere in 5 mL MeCN with 0.1 M Bu_4NPF_6 as supporting electrolyte at a scan rate of 0.1 V s^{-1} (for all cathodic waves). A glassy carbon working electrode (3 mm diameter) was used.

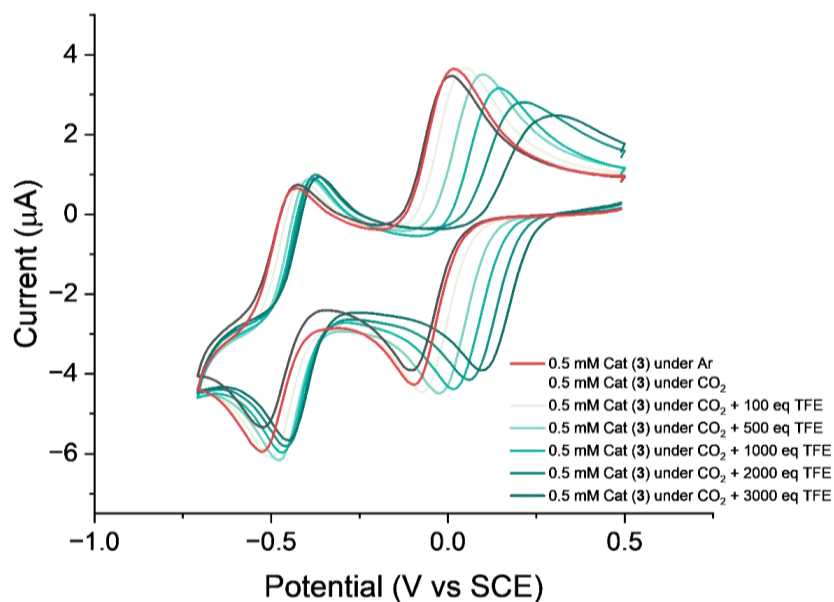
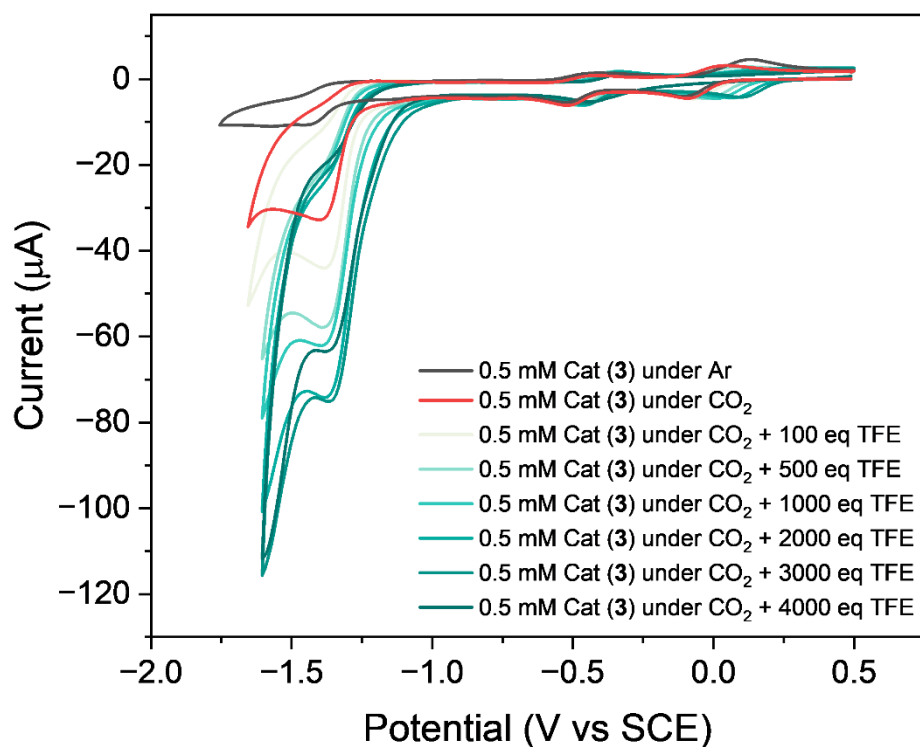


Figure S10. CV of 0.5 mM (C3) under CO₂ atmosphere with increasing the amount of 2,2,2-trifluoroethanol – TFE (from 0 to 4000 eq.) in 5 mL MeCN with 0.1 M Bu₄NPF₆ as supporting electrolyte at a scan rate of 0.1 V s⁻¹. A glassy carbon working electrode (3 mm diameter) was used.

Table S1. Electrocatalytic properties of the complex **C3** during controlled potential electrolysis (CPE) experiments at -1.2 and -1.3 V versus SCE using 0.5 mM of catalyst in 0.1 M Bu₄NPF₆ in acetonitrile as supporting electrolyte under CO₂ in the presence of 3000 equivalent of TFE.

	Cat (3)		Cat (3)	
Applied potential (V vs SCE)	-1.2		-1.3	
Charge passed (C)	0.55		0.61	
Quantity of catalyst (mM)	0.5		0.5	
Time (s)	3600		3600	
	H ₂	CO	H ₂	CO
Selectivity (%)	0	0	11	89
Faradic Efficiency (%)	0	0	1.66	13.37
Total Faradic Efficiency (%)	0		15.0	

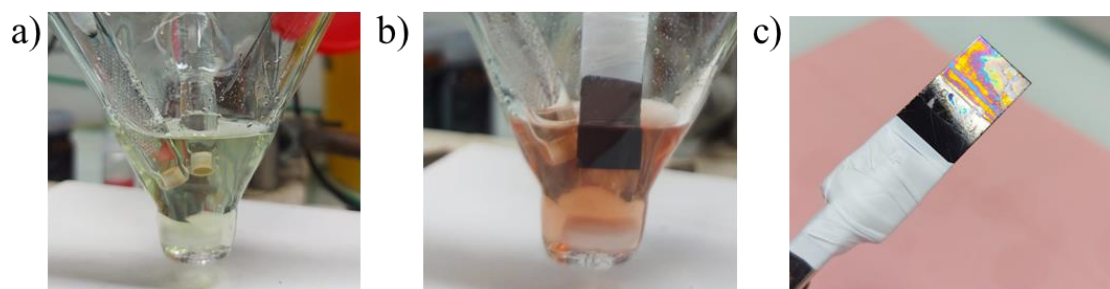


Figure S11. Pictures of the electrolyte during CPE with complex **C3** in acetonitrile + Bu₄NPF₆ (0.1 M) at -1.5 V vs. SCE at the beginning at the electrolysis (a) after 10 minutes (b); picture of the glassy carbon working electrode after 10 minutes electrolysis (c).

4 Study under heterogeneous conditions (in KHCO₃ buffer)

4.1 Cat C2/MWCNT loaded on carbon paper (10 μg/cm²):

Table S2. CPE data for cat C2/MWCNT loaded on carbon paper (10 μg/cm²) at different potentials in 0.5 M KHCO₃ (ultrapure water) as supporting electrolyte under CO₂.

Applied potential (V vs SCE)	-1.2		-1.3		-1.4		-1.4	
Applied potential (V vs RHE)	-0.45		-0.55		-0.65		-0.65	
Charge passed (C)	4.22		11.56		18.26		30.09	
Current density (mA cm ⁻²)	1.17		3.21		5.07		4.18	
Ratio CO/H ₂	28.8		50.3		40.7		20.5	
Time (s)	3600		3600		3600		7200	
Products	H ₂	CO	H ₂	CO	H ₂	CO	H ₂	CO
Selectivity (%)	3	97	2	98	2	98	4	96
Faradaic Efficiency (%)	2.64	76	1.71	86.05	2.58	92.66	5.22	87.40
Total Faradaic Efficiency (%)	78.64		87.76		95.24		92.63	
Partial current density (mA cm ⁻²)	0.04	1.13	0.06	3.15	0.1	4.97	0.17	4.01
TON _{CO}	1078		3343		5715		8839	
TOF _{CO} (s ⁻¹)	0.30		0.93		1.59		1.23	

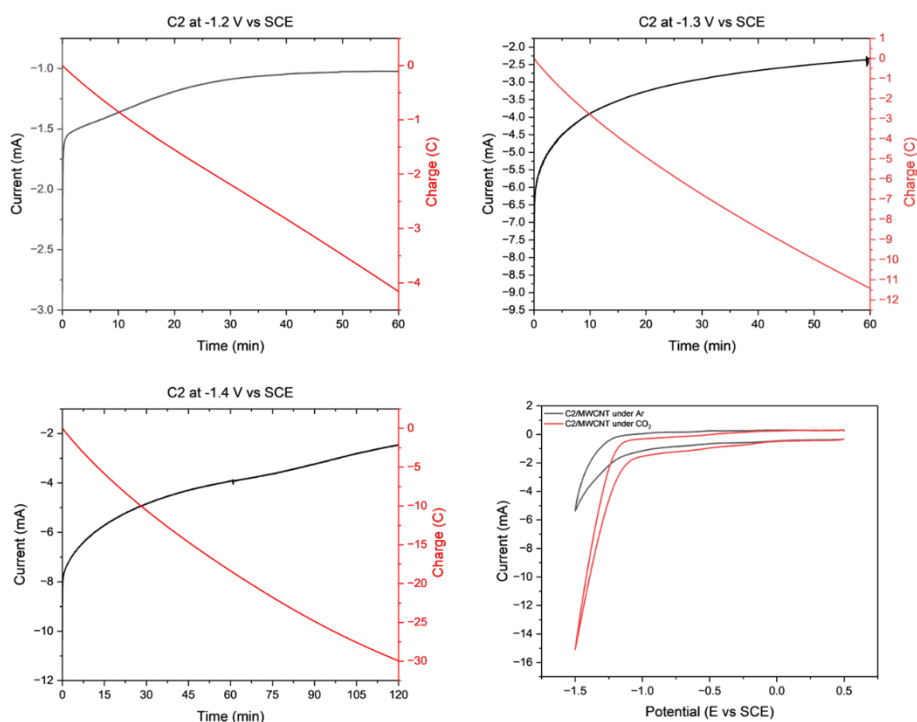


Figure S12. Current (black) and charge (red) overtime during CPE experiment at -1.2 (top-left), -1.3 (top-right) and -1.4 V (bottom-left) vs. SCE using C2/MWCNT loaded on carbon paper in 0.5 M KHCO₃ under CO₂. CV before CPE under Ar (solid black line) and CO₂ (solid red line) – (bottom-right).

4.2 Cat **C3**/MWCNT loaded on carbon paper ($10 \mu\text{g}/\text{cm}^2$):

Table S3. CPE data for cat **C3**/MWCNT loaded on carbon paper ($10 \mu\text{g}/\text{cm}^2$) at different potentials in 0.5 M KHCO_3 (ultrapure water) as supporting electrolyte under CO_2 .

Applied potential (V vs SCE)	-1.2		-1.3		-1.4		-1.4	
Applied potential (V vs RHE)	-0.45		-0.55		-0.65		-0.65	
Charge passed (C)	3.43		9.7		18.33		33.1	
Current density (mA cm^{-2})	0.95		2.69		5.09		4.60	
Ratio CO/H_2	24.3		46.7		33		26.4	
Time (s)	3600		3600		3600		7200	
Products	H_2	CO	H_2	CO	H_2	CO	H_2	CO
Selectivity (%)	4	96	2	98	2	98	2	98
Faradaic Efficiency (%)	2.26	81.31	1.47	101.55	2.03	99.14	2.18	85.13
Total Faradic Efficiency (%)	83.57		103.03		101.17		87.31	
Partial current density (mA cm^{-2})	0.04	0.91	0.05	2.64	0.10	4.99	0.09	4.51
TON_{CO}	1049		3704		6833		10594	
TOF_{CO} (s^{-1})	0.29		1.03		1.90		1.47	

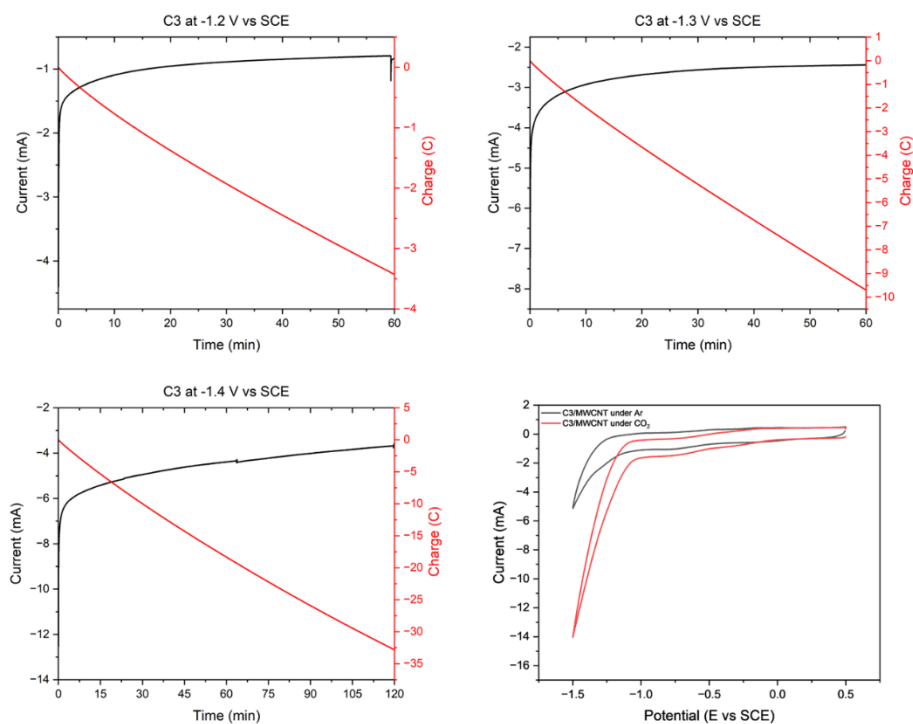


Figure S13. Current (black) and charge (red) overtime during CPE experiment at -1.2 (top-left), -1.3 (top-right) and -1.4 V (bottom-left) vs. SCE using **C3**/MWCNT loaded on carbon paper in 0.5 M KHCO_3 under CO_2 . CV before CPE under Ar (solid black line) and CO_2 (solid red line) – (bottom-right).

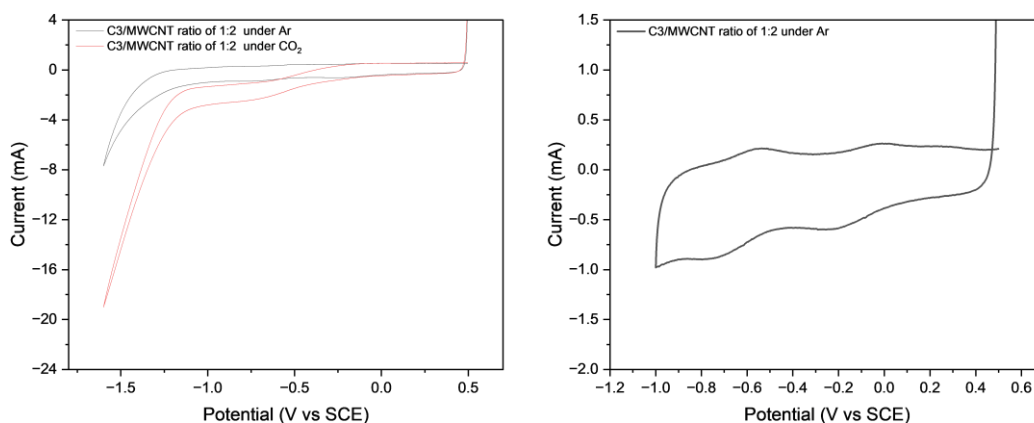


Figure S14. CV for **C3**/MWCNT loaded on carbon paper at the ratio of 1:2 cat:MWCNT in 0.5 M KHCO_3 under Ar (black) and under CO_2 (red). In the right from 0.5 to -1.6 V vs. SCE and in the left from 0.5 to -1.0 V vs. SCE, both at 100 mV s^{-1} .

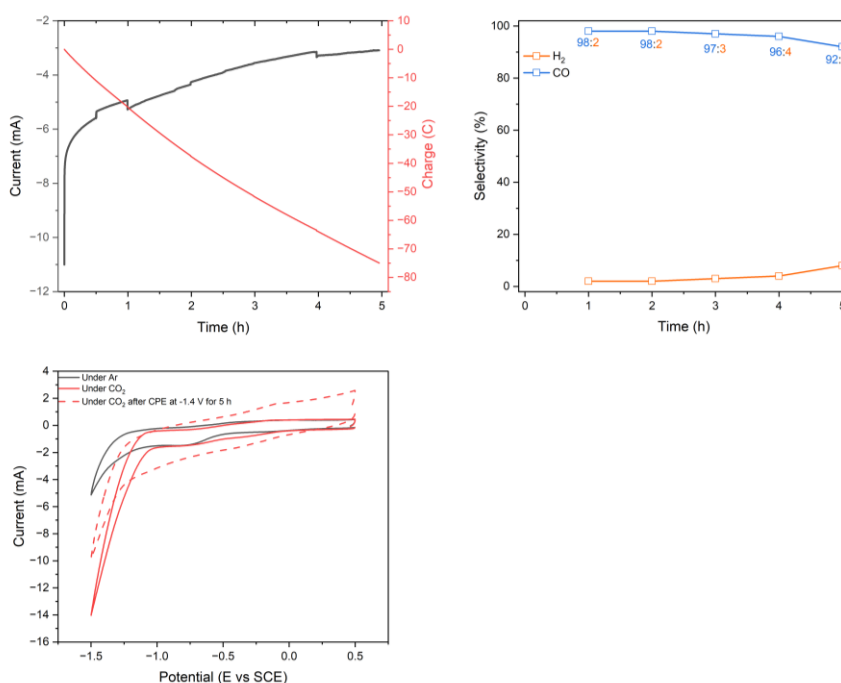


Figure S15. **top-left** - Current (black) and charge (red) overtime during longtime CPE experiment (5 h) at -1.4 V vs. SCE using **C3**/MWCNT loaded on carbon paper in 0.5 M KHCO_3 under CO_2 . **Top-right** – Selectivity for CO:H₂ overtime during CPE. **Bottom-left** – CV before CPE under Ar (solid black line), under CO_2 (solid red line) and after CPE under CO_2 (dash red line).

Table S4. Long-time CPE data for cat **C3**/MWCNT loaded on carbon paper ($10 \mu\text{g}/\text{cm}^2$) at -1.4 V vs SCE in 0.5 M KHCO_3 in ultrapure water as supporting electrolyte under CO_2 .

Time (h)	1		3		5	
Products	H ₂	CO	H ₂	CO	H ₂	CO
Selectivity (%)	2	98	3	97	8	92
TON _{CO}	6704		15309		20757	
TOF _{CO} (s ⁻¹)	1.86		1.42		1.15	

CPE experiments using labelled $^{13}\text{CO}_2$

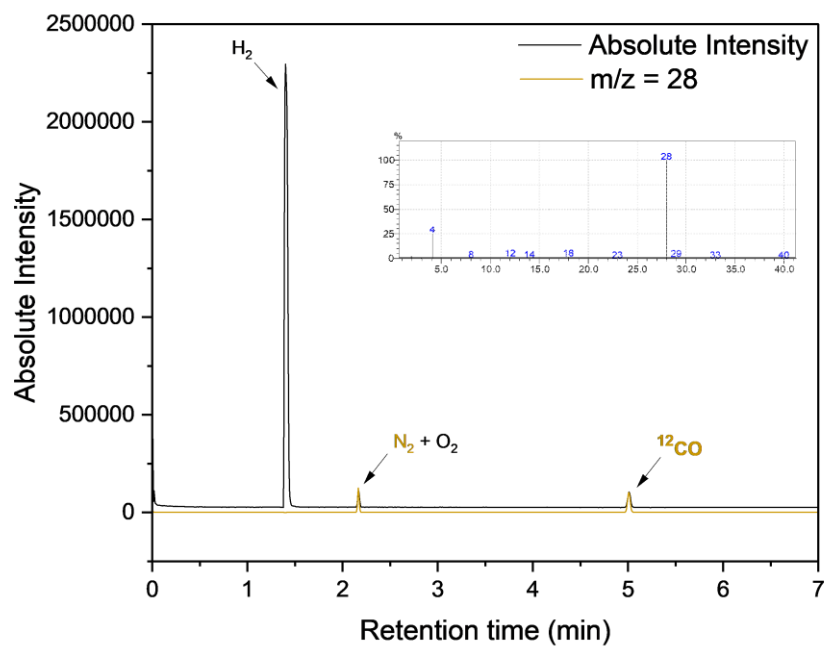


Figure S16. CPE experiment in 0.5 M KHCO_3 under Ar. **insert figure:** MS spectra obtained at a retention time of 5 min.

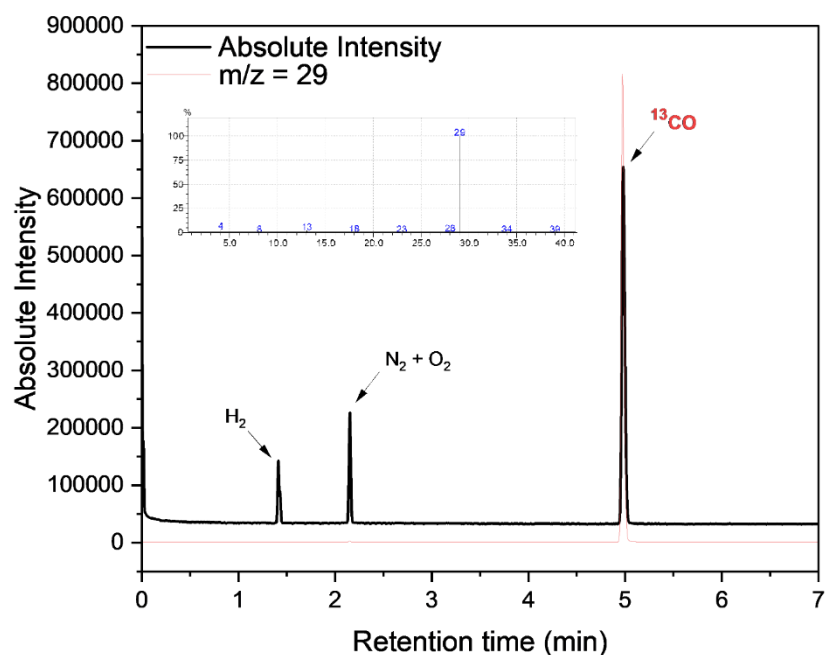


Figure S17. CPE experiment using $^{13}\text{CO}_2$ in 0.5 M PBS (pH 8.5) $^{13}\text{CO}_2$. **insert figure:** MS spectra obtained at a retention time of 5 min.

4.3 Only MWCNT loaded on carbon paper ($10 \mu\text{g}/\text{cm}^2$):

Table S4. CPE data for MWCNT loaded on carbon paper ($10 \mu\text{g}/\text{cm}^2$) at different potentials in 0.5 M KHCO_3 in ultrapure water as supporting electrolyte under CO_2 .

Applied potential (V vs SCE)	-1.4	
Applied potential (V vs RHE)	-0.65	
Charge passed (C)	7.59	
Current density (mA cm^{-2})	2.11	
Time (s)	3600	
Products	H_2	CO
Selectivity (%)	100	0
Faradaic Efficiency (%)	98.3	0
Total Faradic Efficiency (%)	98.3	
Partial current density (mA cm^{-2})	2.11	0

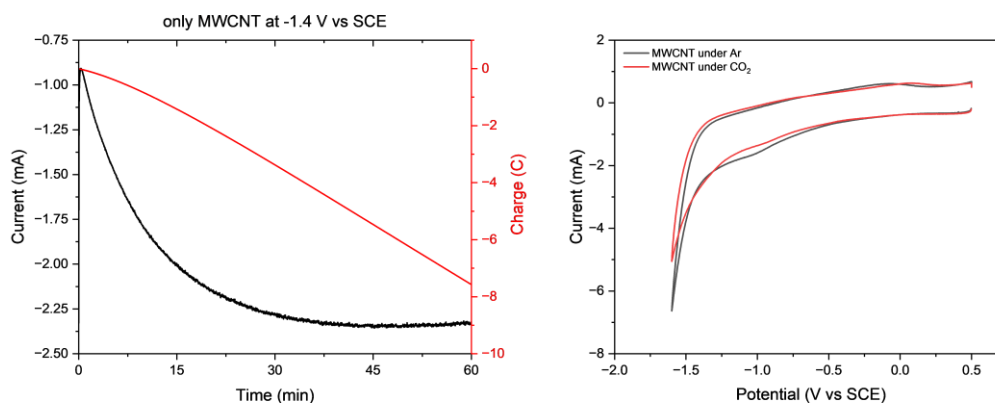


Figure S18. Current (black) and charge (red) overtime during CPE experiment at -1.4 V (left) vs. SCE using only MWCNT loaded on carbon paper in 0.5 M KHCO_3 under CO_2 . CV before CPE under Ar (solid black line) and CO_2 (solid red line) (right).

5 NMR spectra

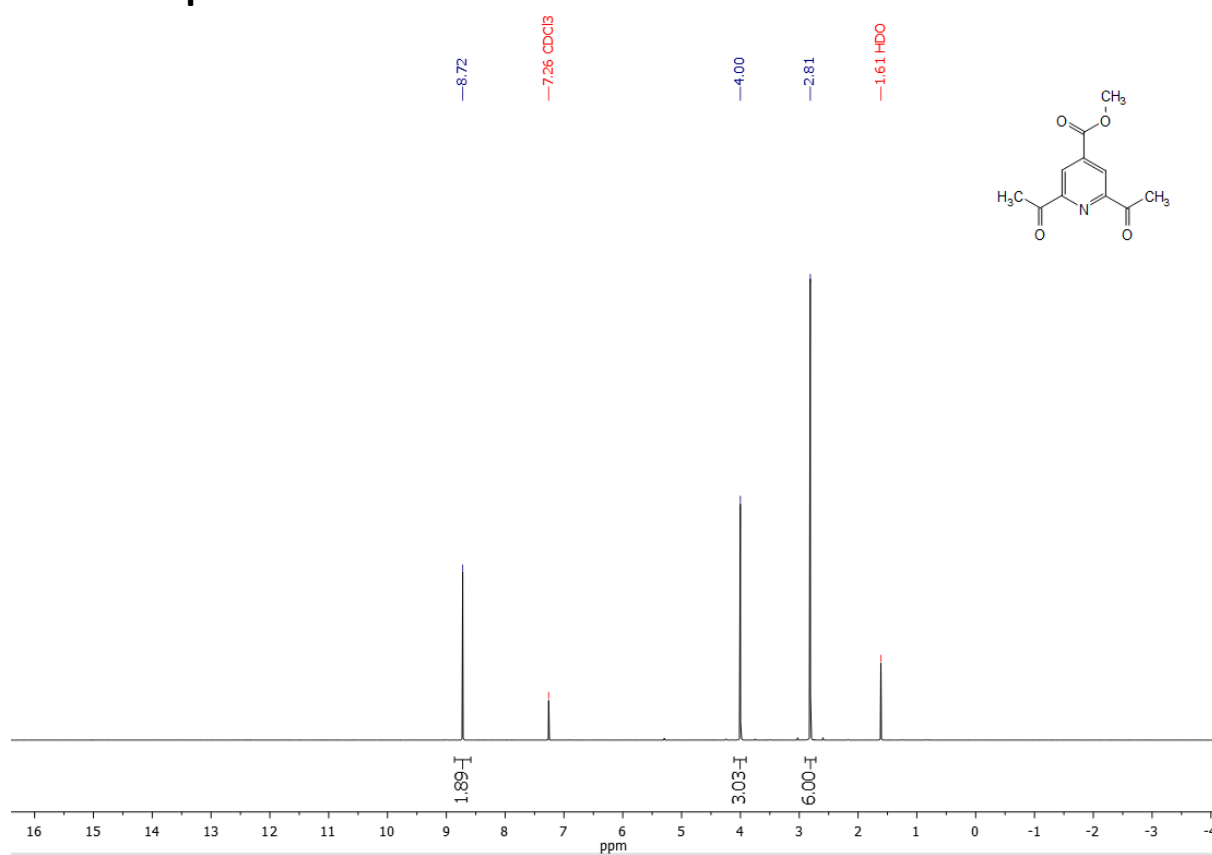


Figure S19. ^1H NMR of compound **1** in CDCl_3

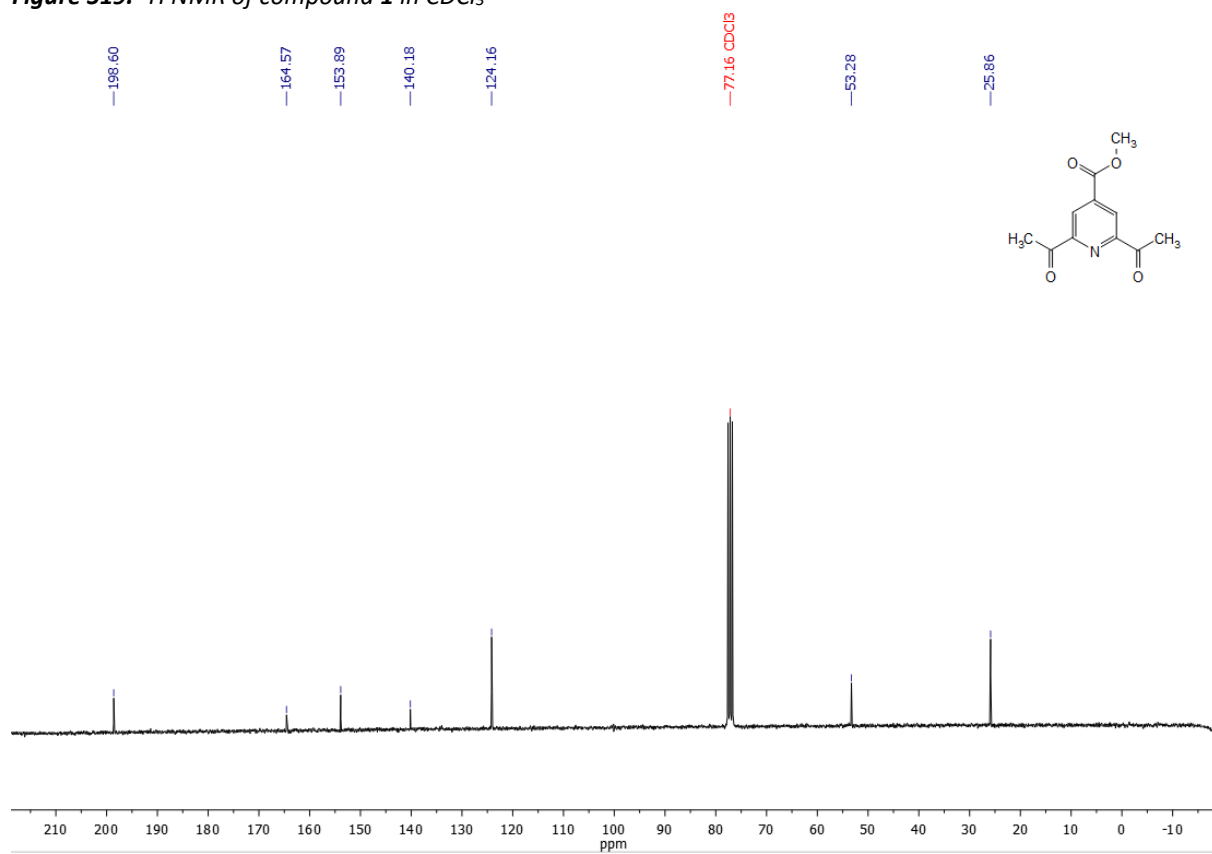


Figure S20. ^{13}C NMR of compound **1** in CDCl_3

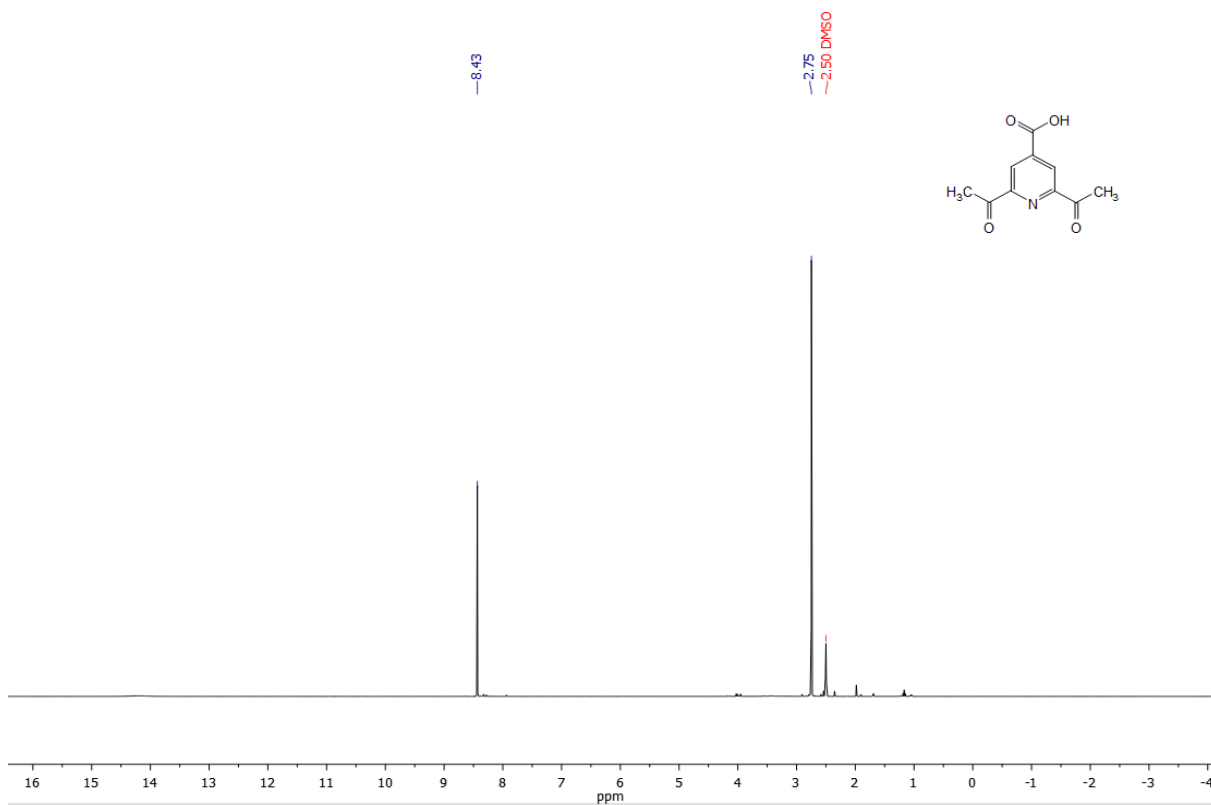


Figure S21. ¹H NMR of compound 2 in DMSO

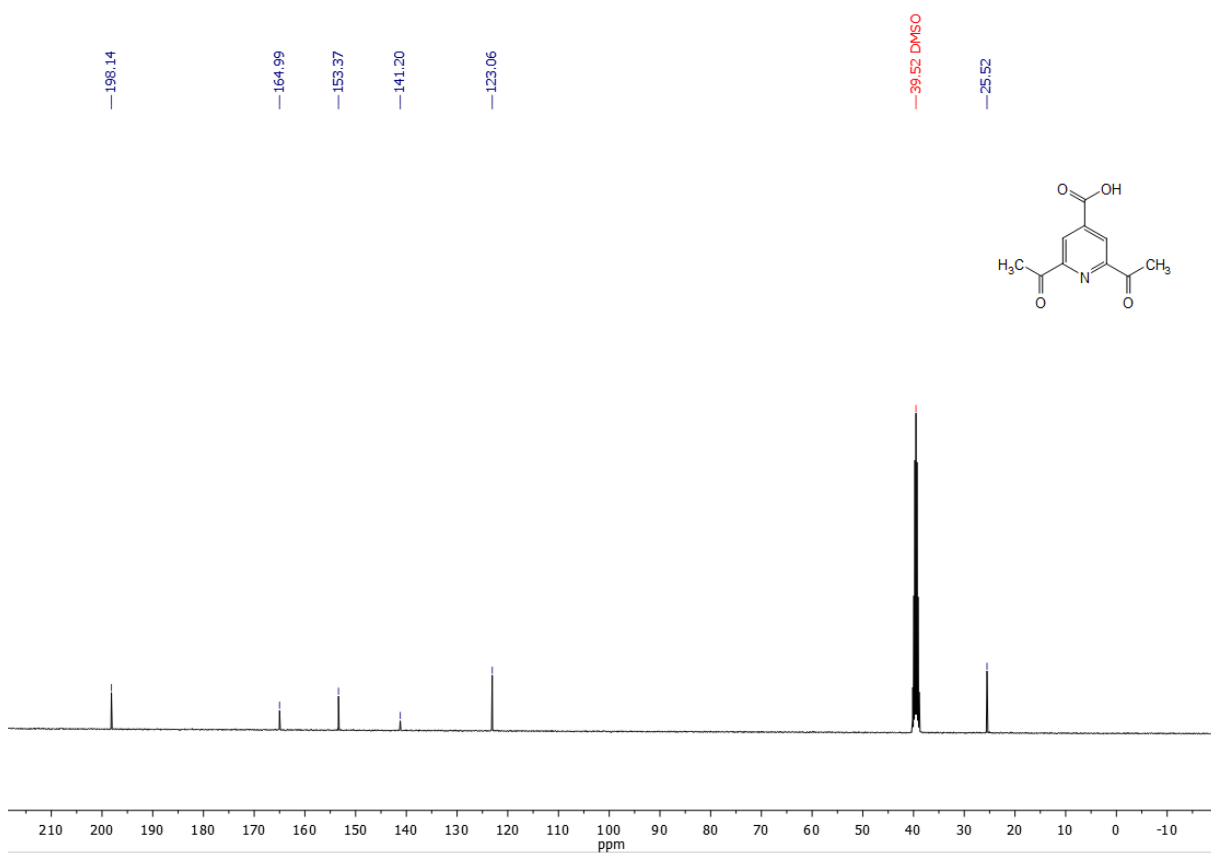


Figure S22. ¹³C NMR of compound 2 in DMSO-d₆.

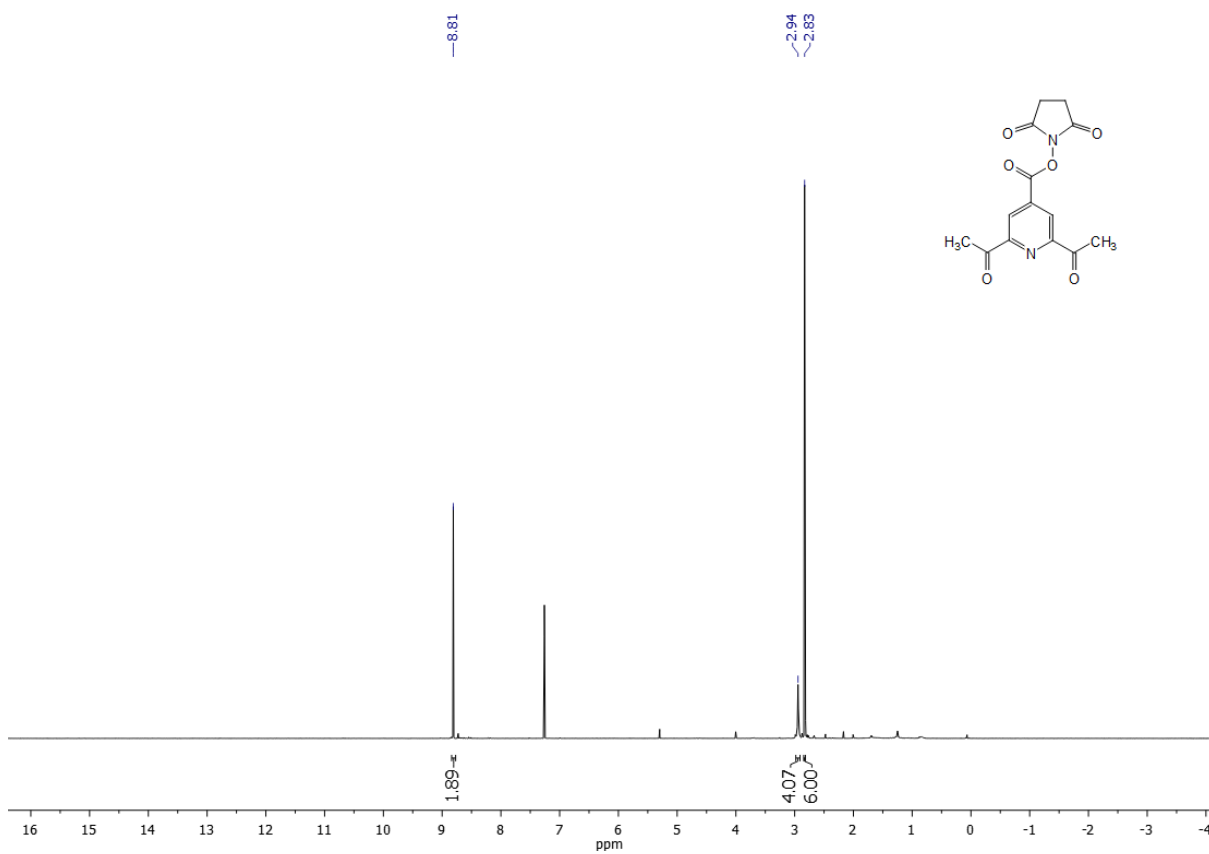


Figure S23. ^1H NMR of compound **3** in CDCl_3 .

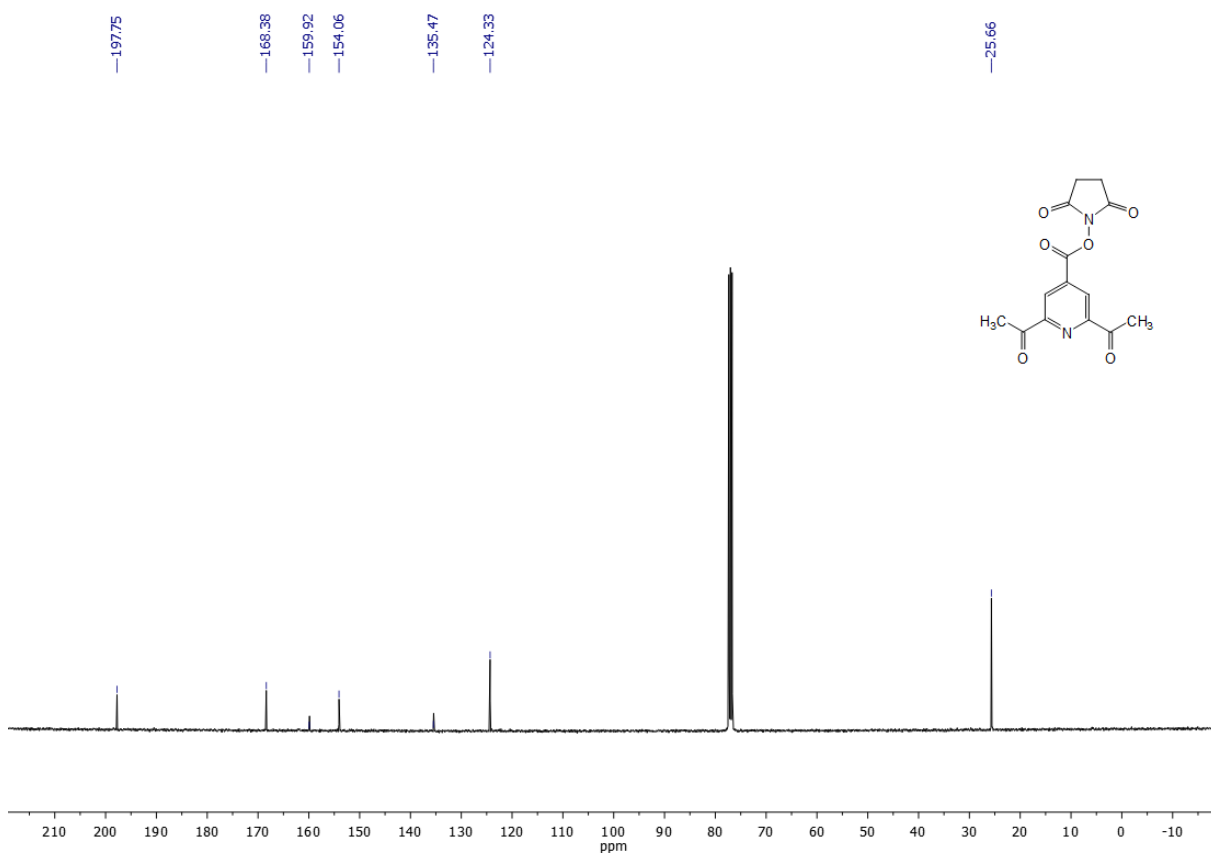


Figure S24. ^{13}C NMR of compound **3** in CDCl_3 .

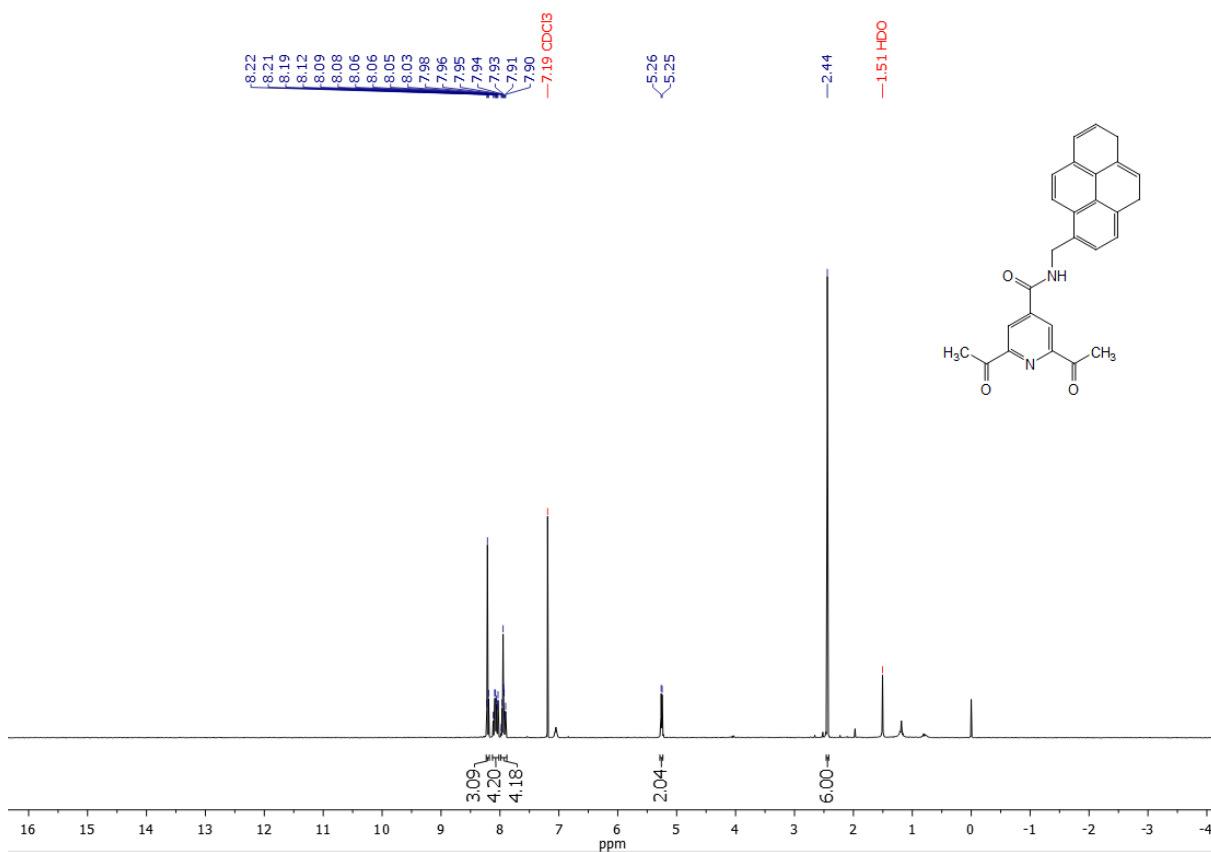


Figure S25. ^1H NMR of compound 5 in CDCl_3 .

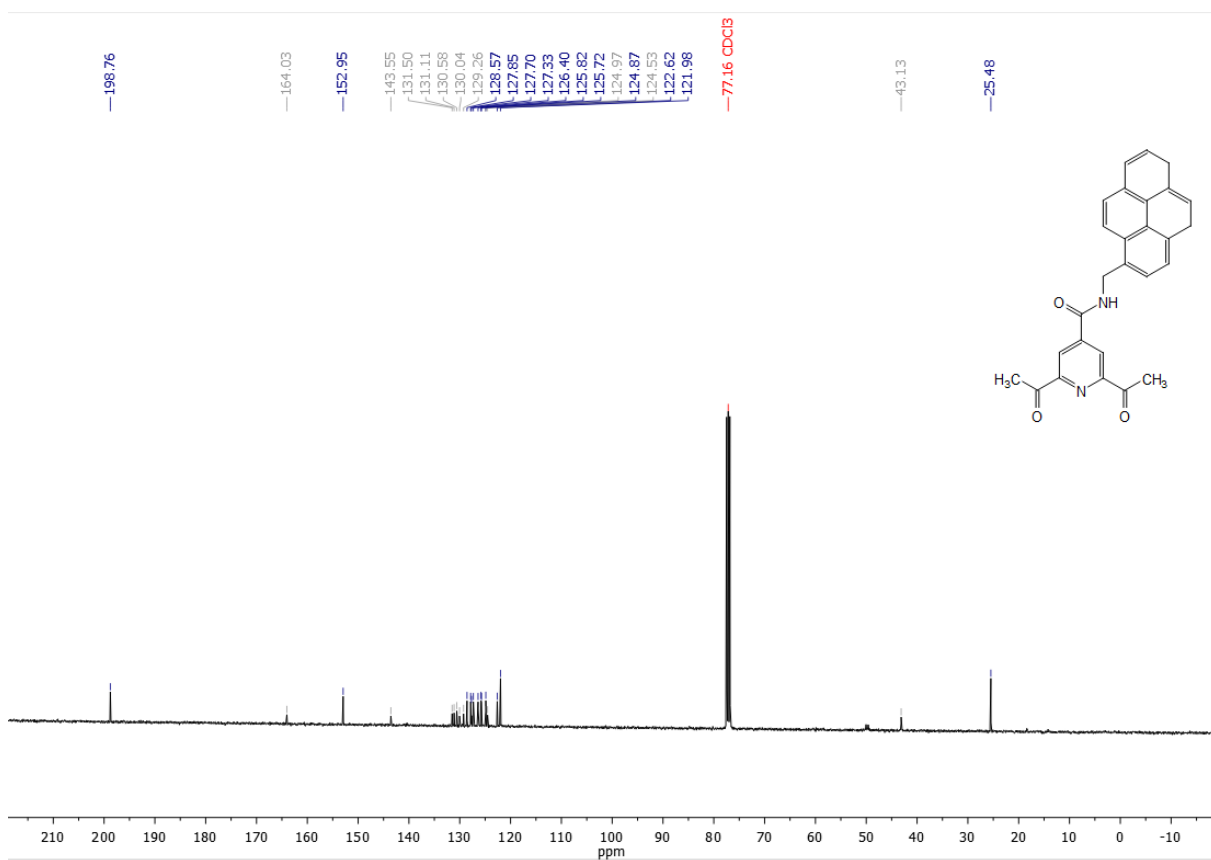


Figure S26. ^{13}C NMR of compound 5 in CDCl_3 .

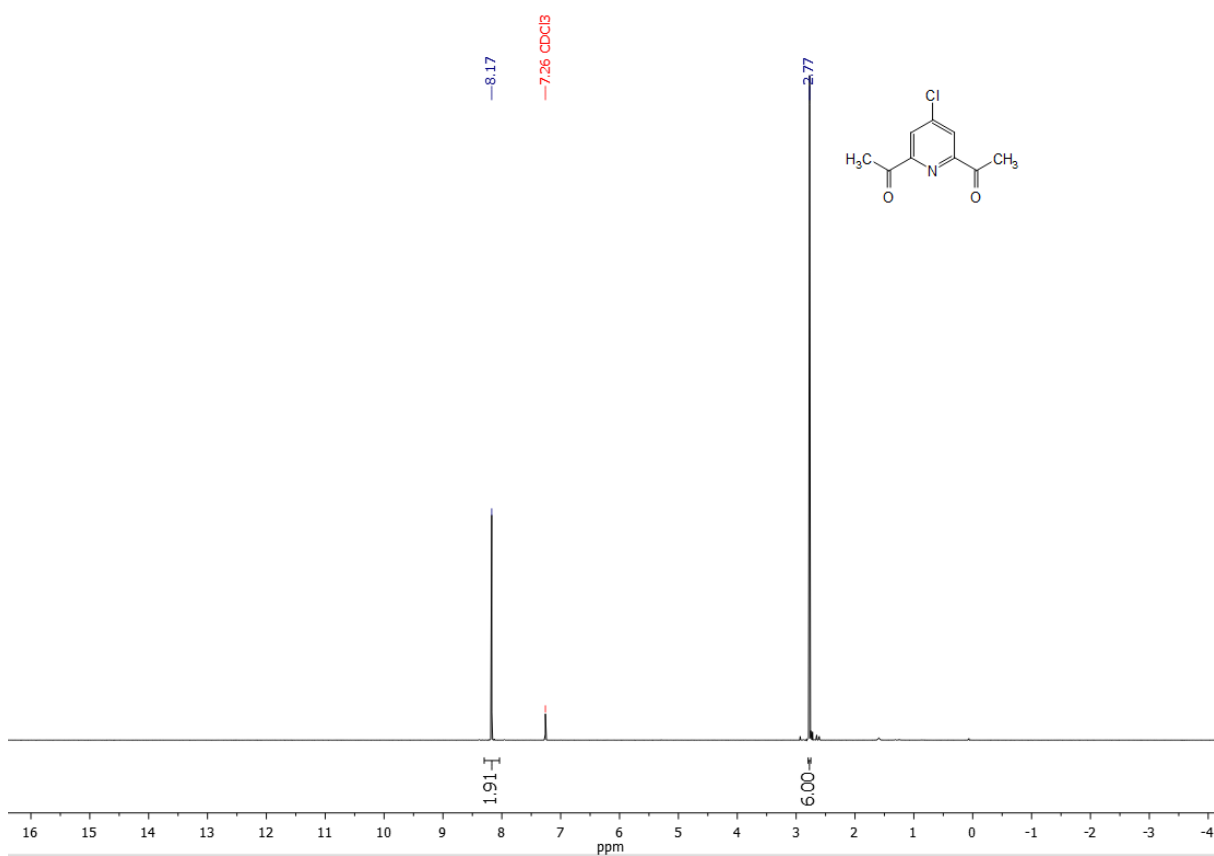


Figure S27. ¹H NMR of compound **6** in CDCl₃.

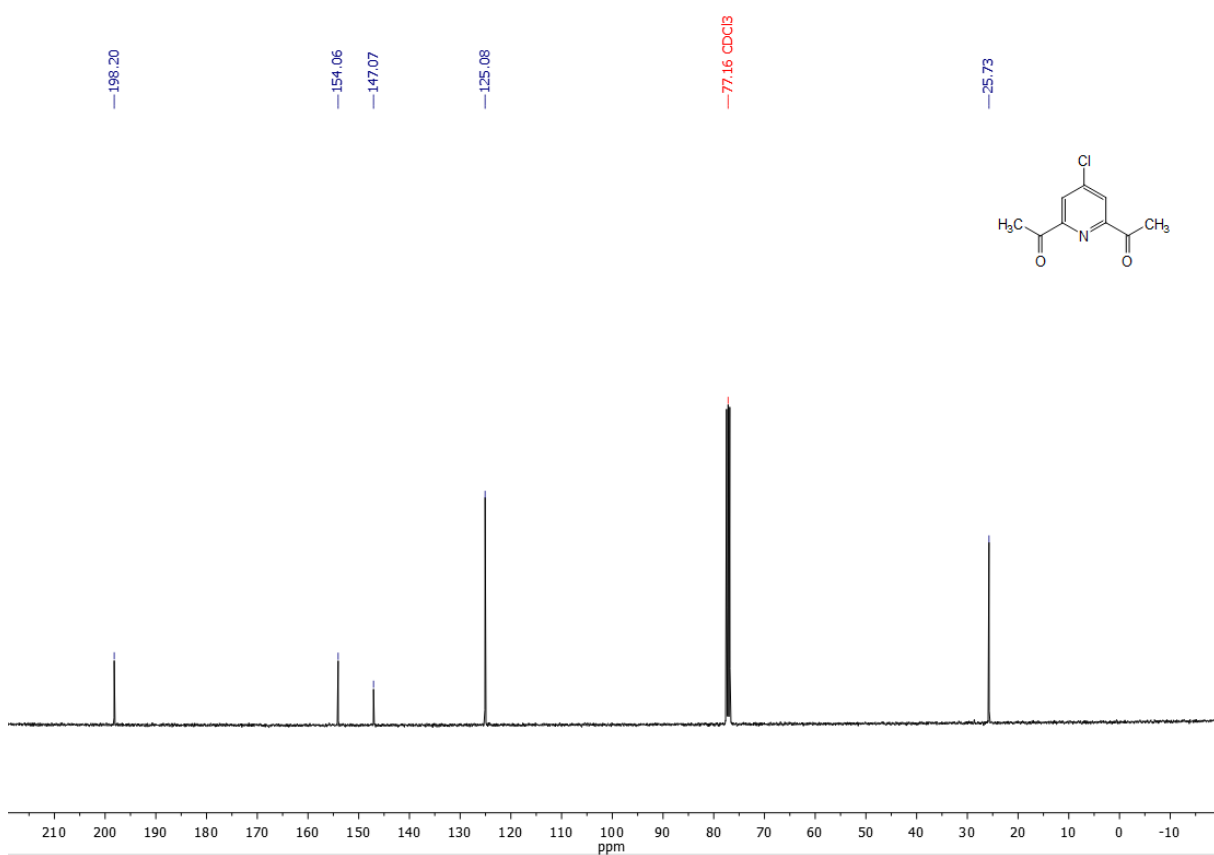


Figure S28. ¹³C NMR of compound **6** in CDCl₃.

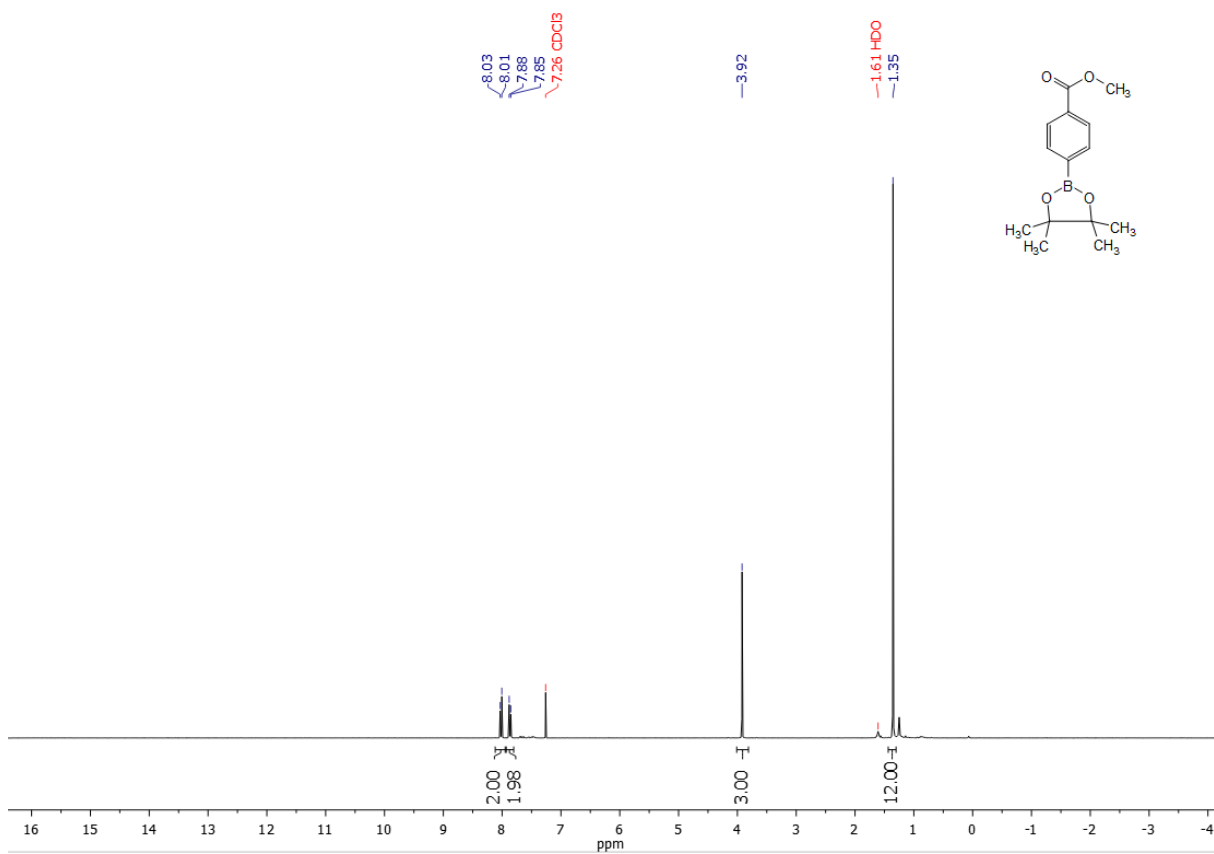


Figure S29. ¹H NMR of compound 7 in CDCl₃.

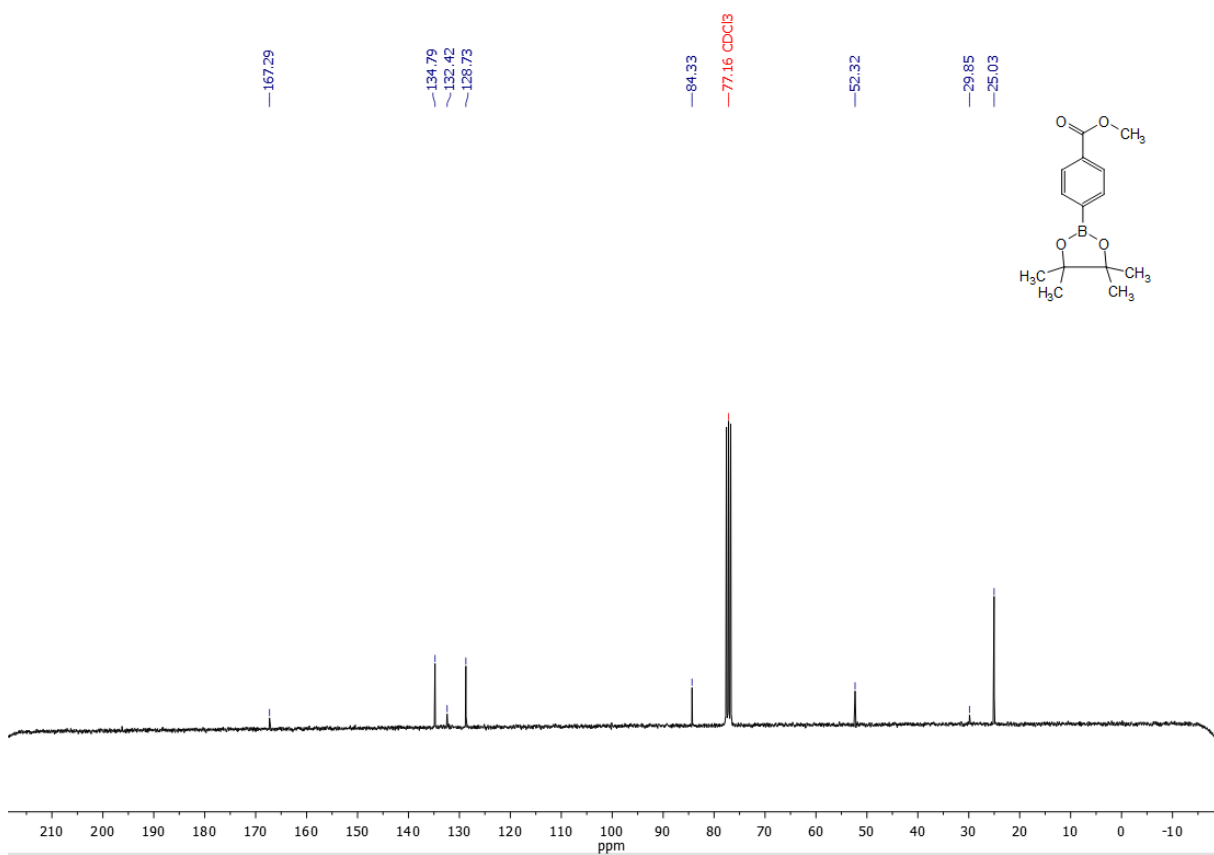


Figure S30. ¹³C NMR of compound 7 in CDCl₃.

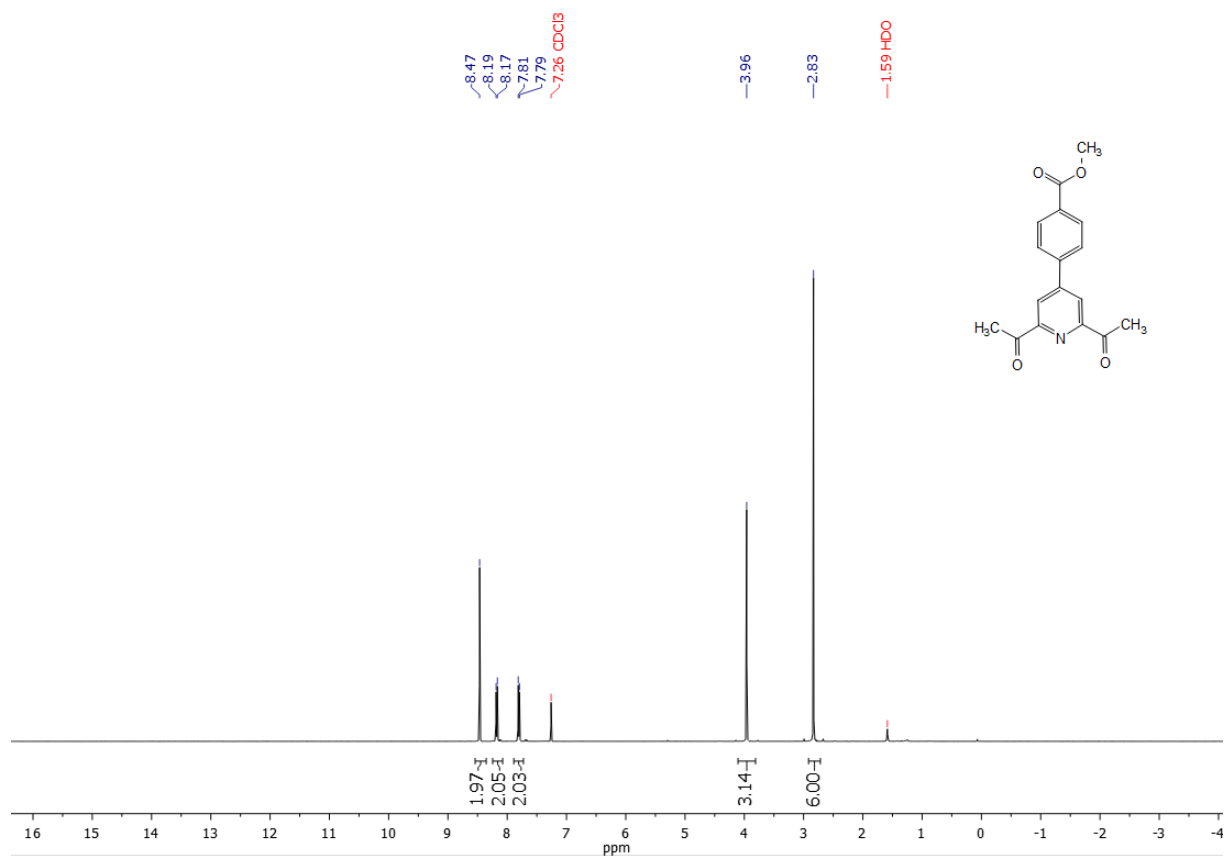


Figure S31. ¹H NMR of compound **8** in CDCl₃.

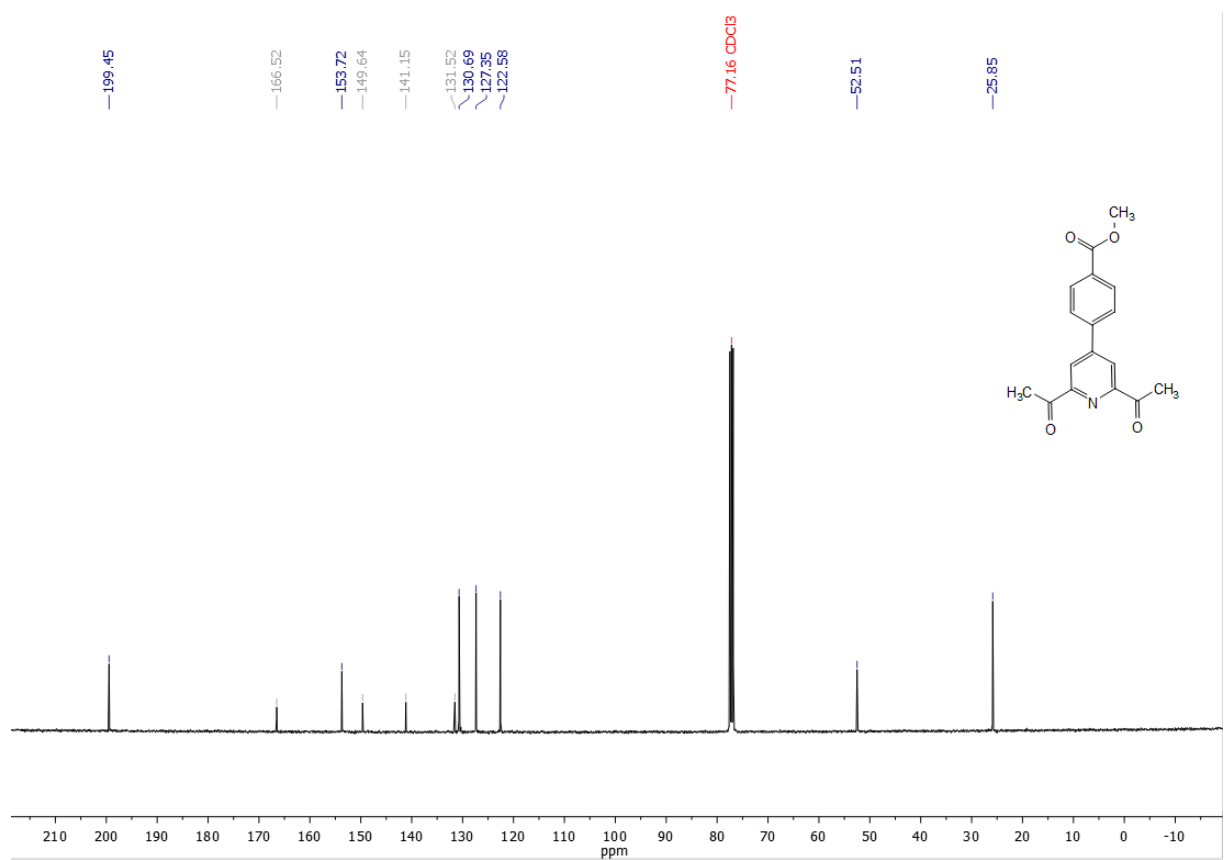


Figure S32. ¹³C NMR of compound **8** in CDCl₃.

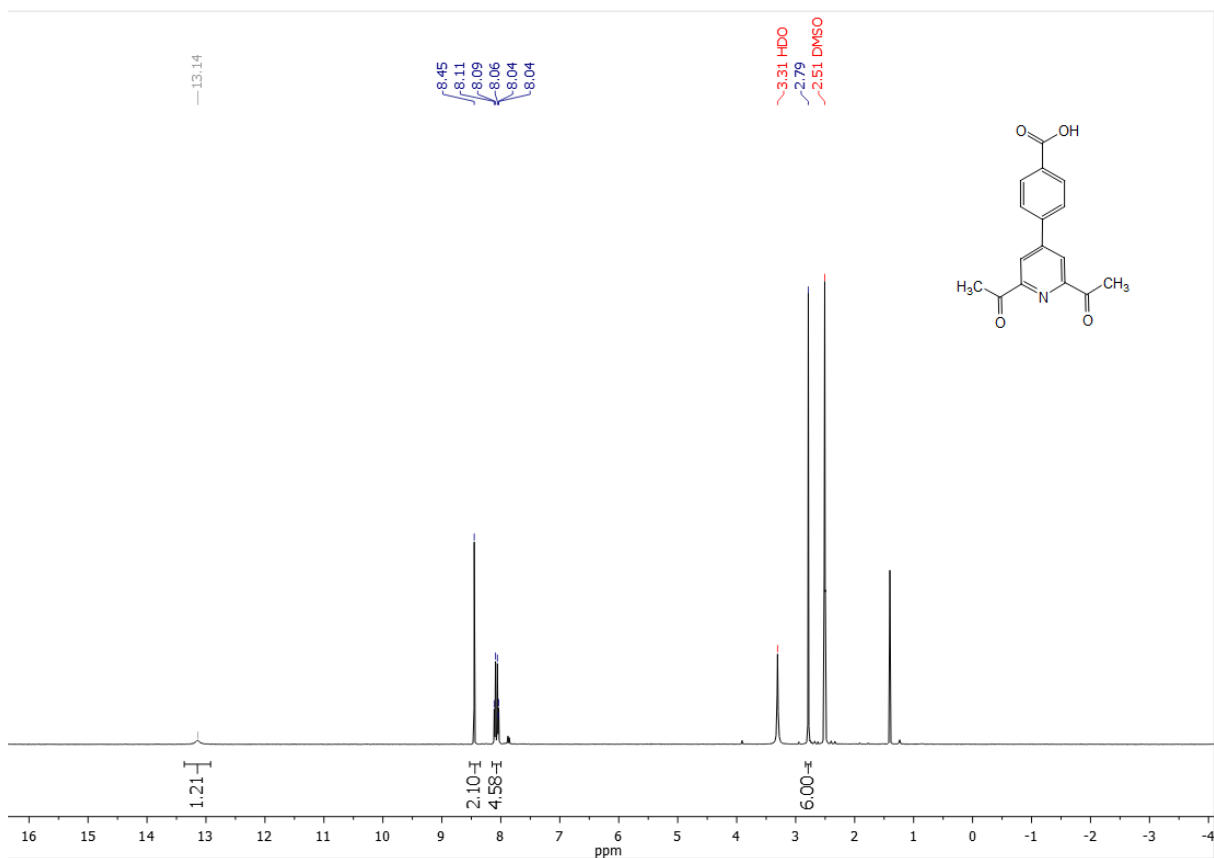


Figure S33. ^1H NMR of compound 9 in DMSO-d_6 .

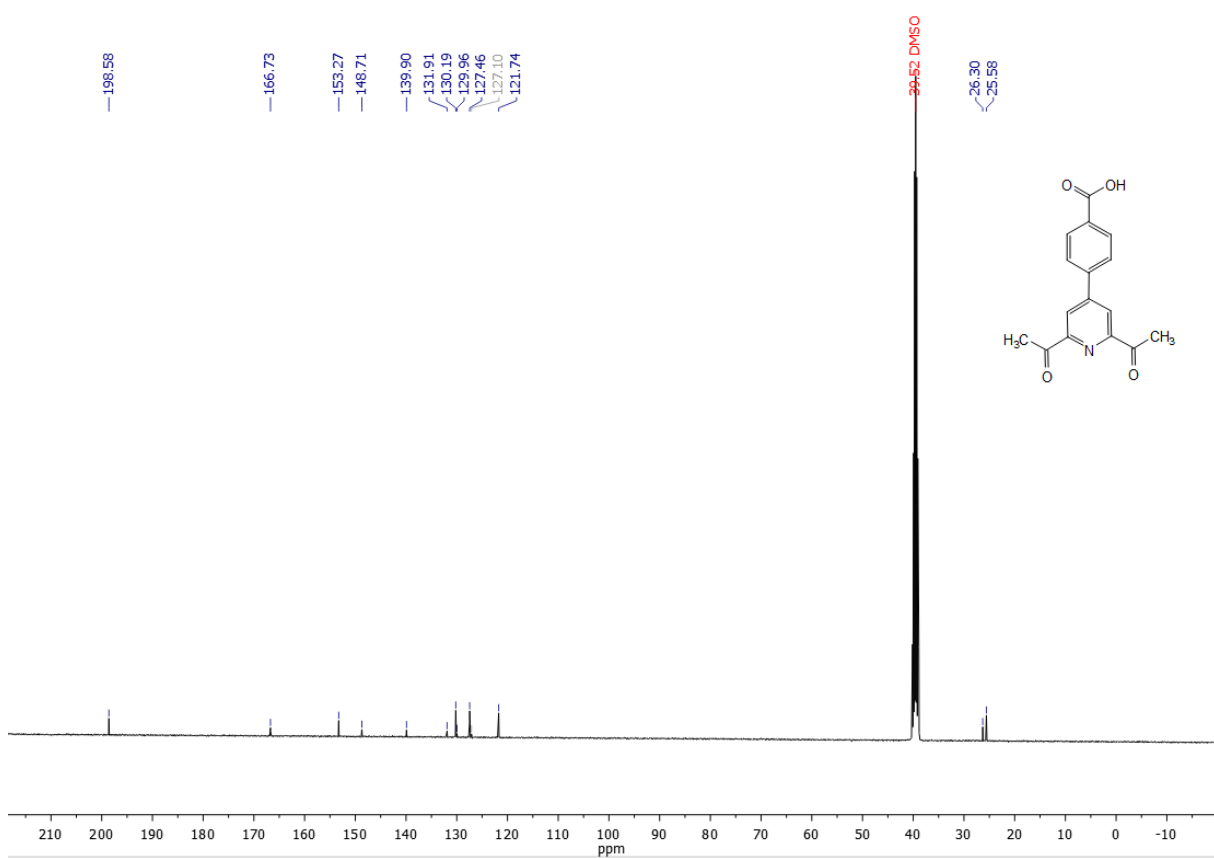


Figure S34. ^{13}C NMR of compound 9 in DMSO-d_6 .

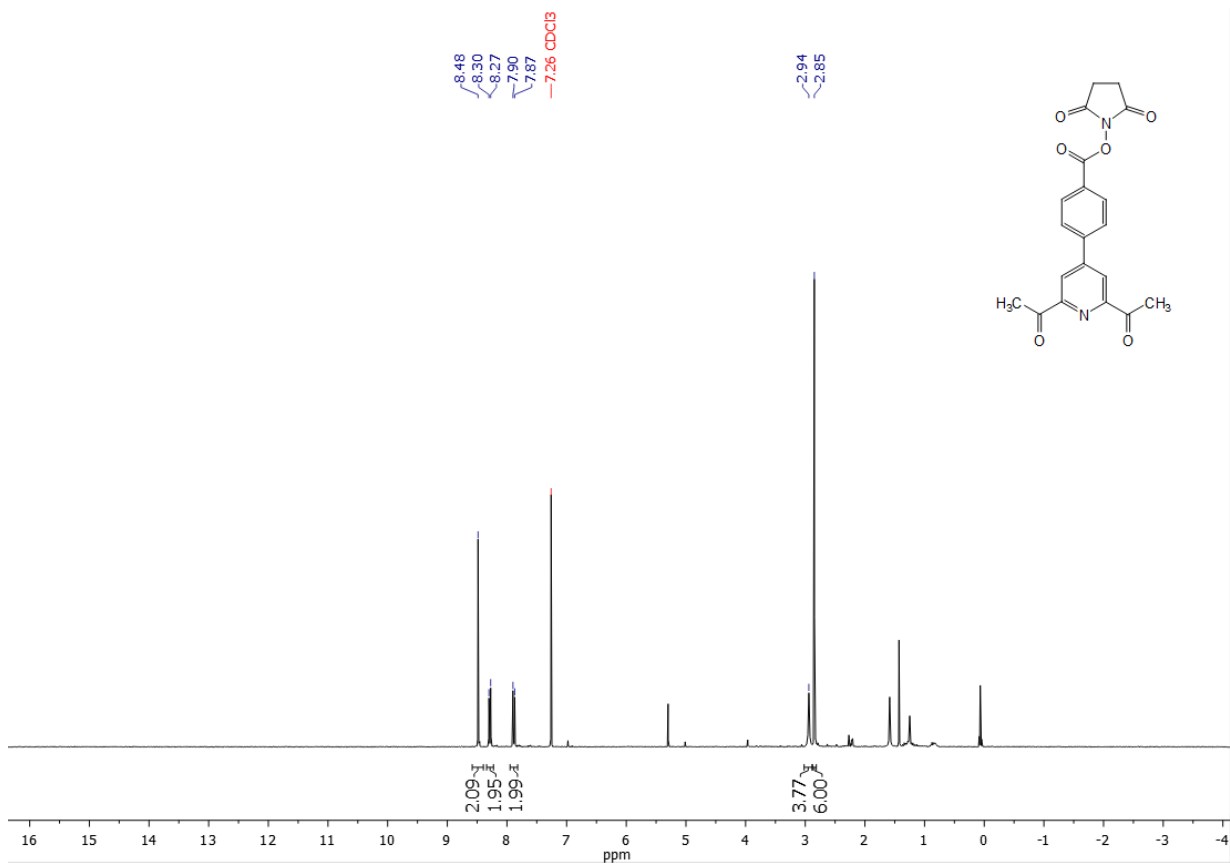


Figure S35. ¹H NMR of compound 10 in CDCl₃.

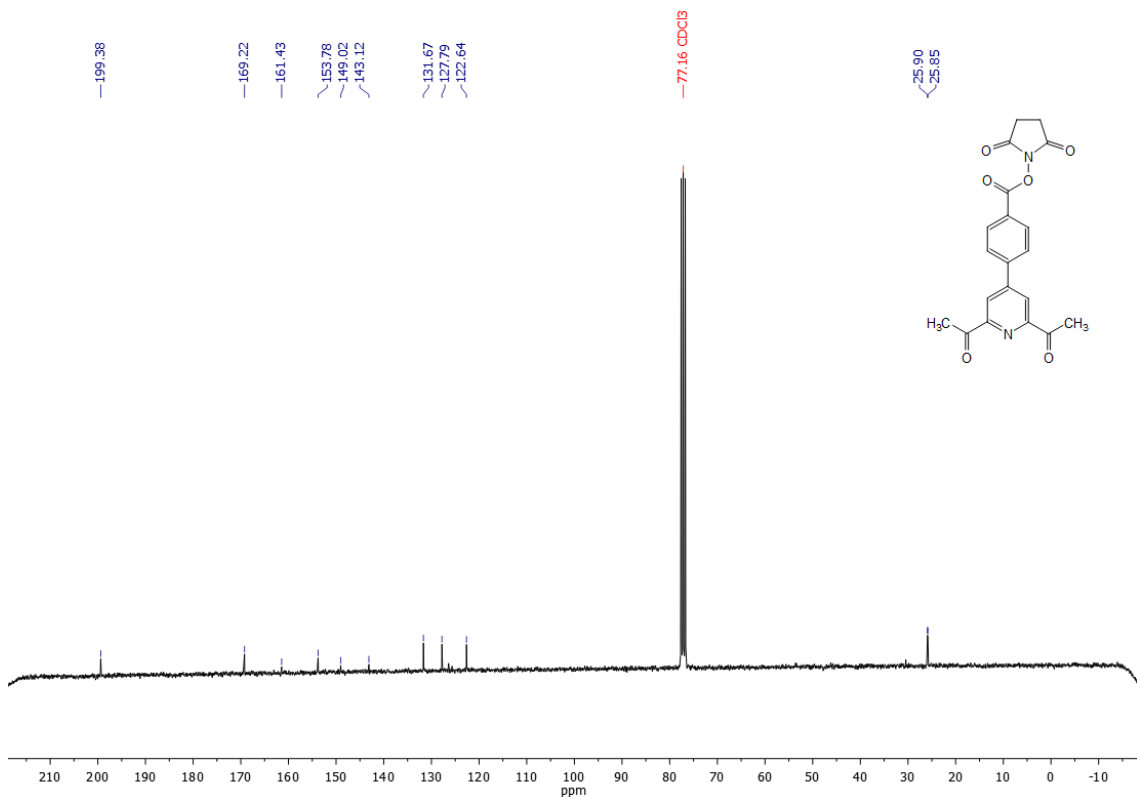


Figure S36. ¹³C NMR of compound 10 in CDCl₃.

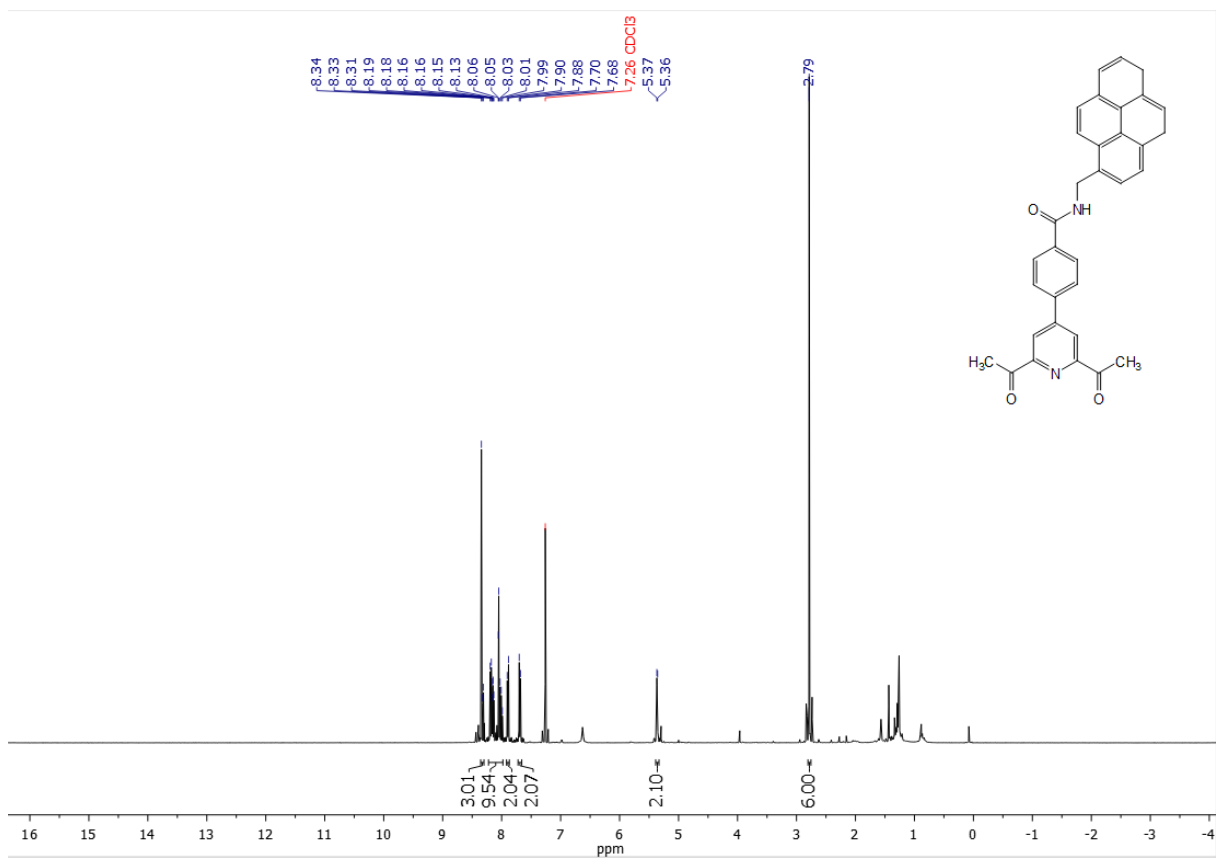


Figure S37. ¹H NMR of compound 11 in CDCl₃.

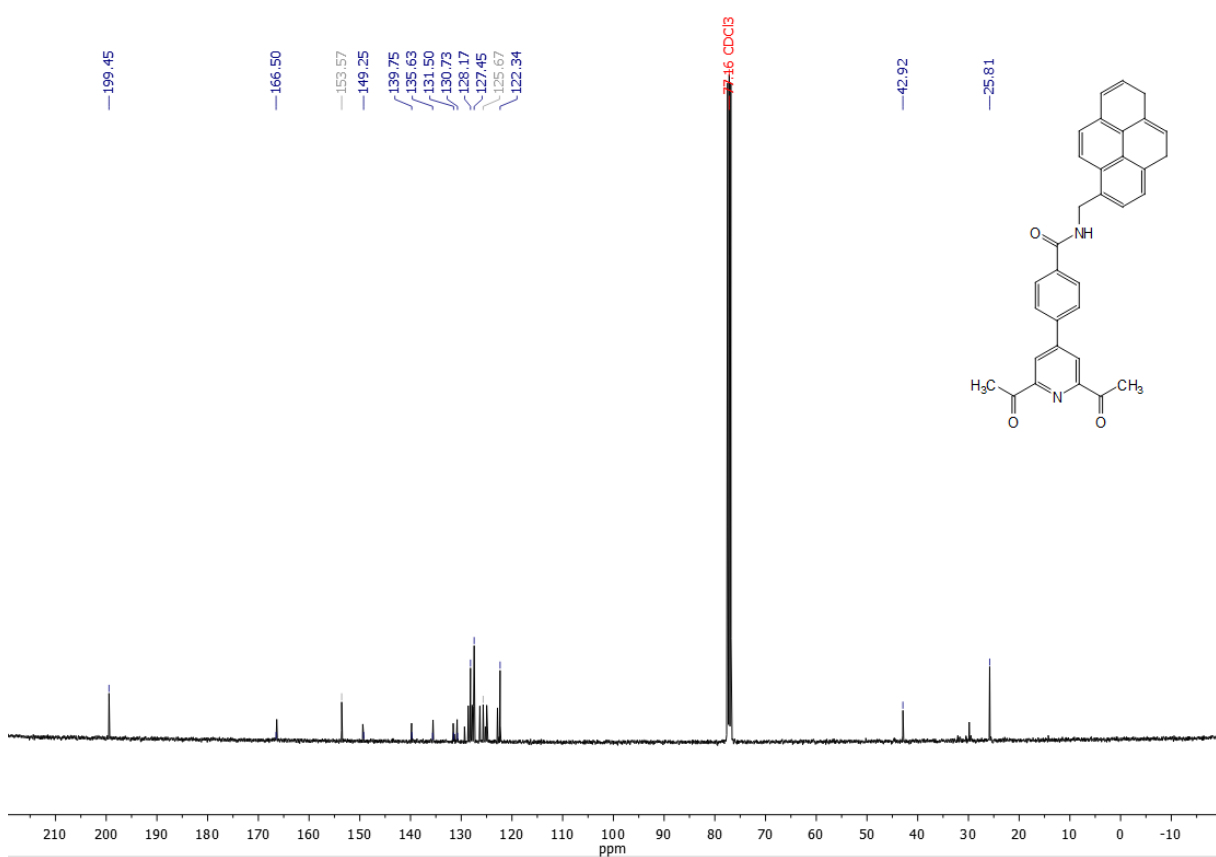


Figure S38. ¹³C NMR of compound 11 in CDCl₃.

6 Mass spectrometric analyses

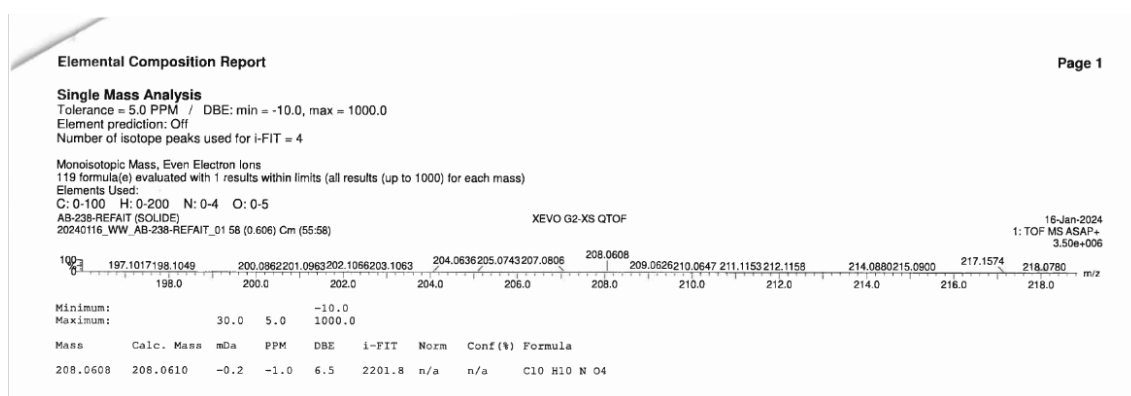


Figure S394. HRMS report of compound 2.

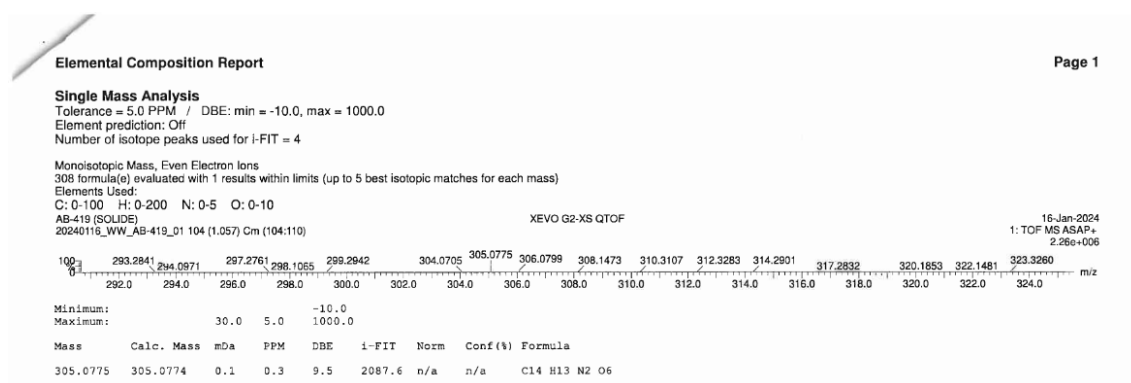


Figure 40. HRMS report of compound 3.

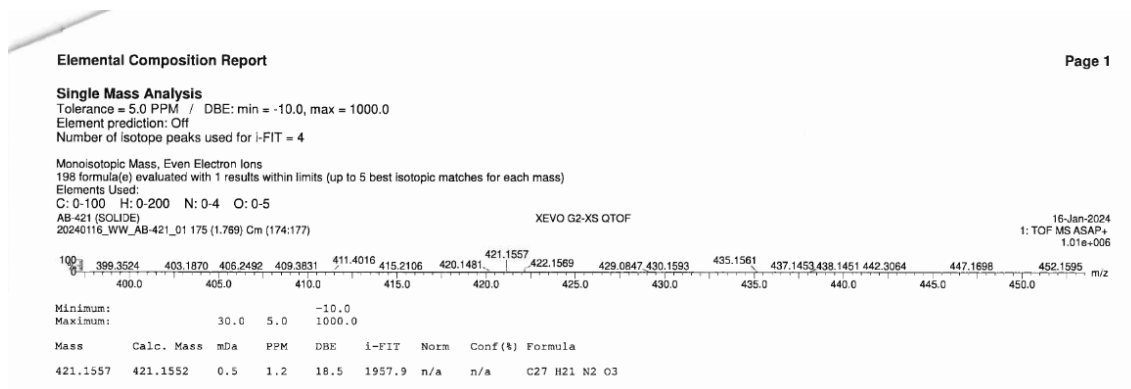


Figure 41. HRMS report of compound 5.

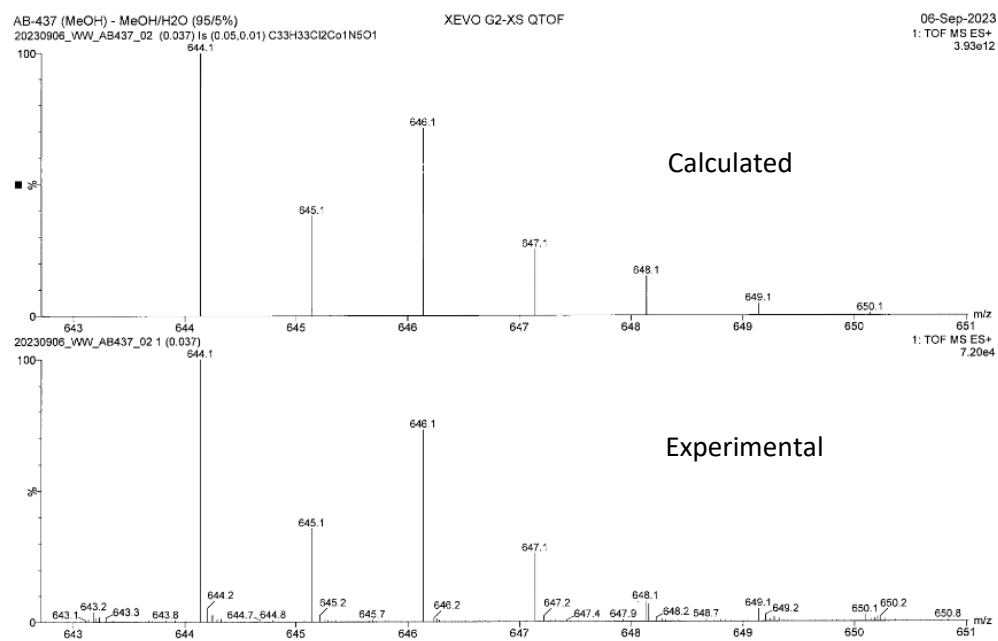
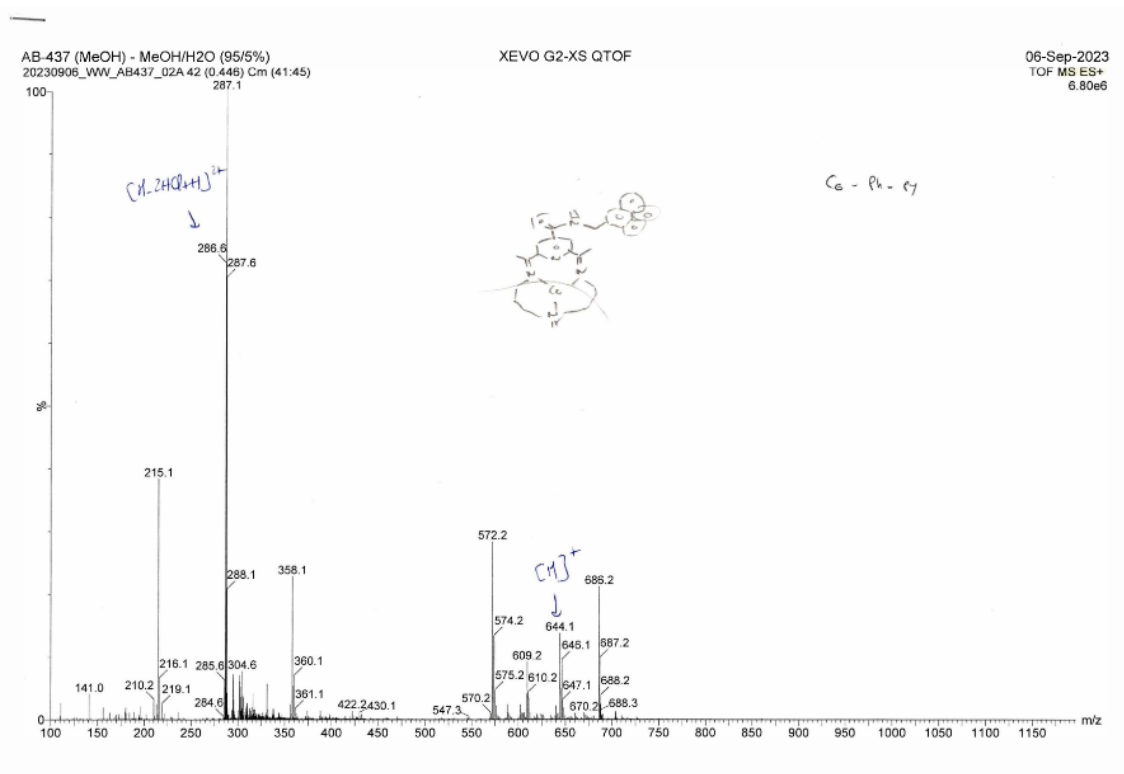


Figure 42. HRMS report of compound **C2**. Upper panel full experimental spectrum, lower panel overlay of the calculated and experimental isotopic pattern on one specific fragment.

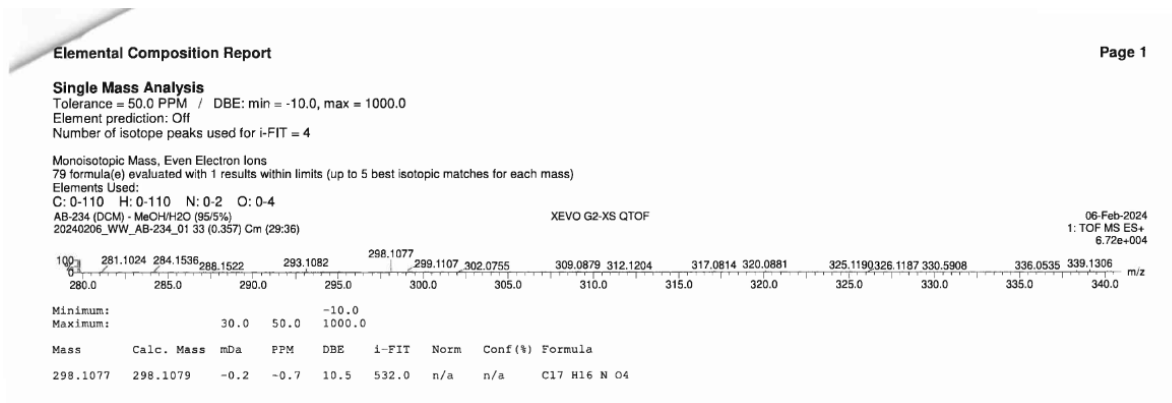


Figure 43. HRMS report of compound 8.

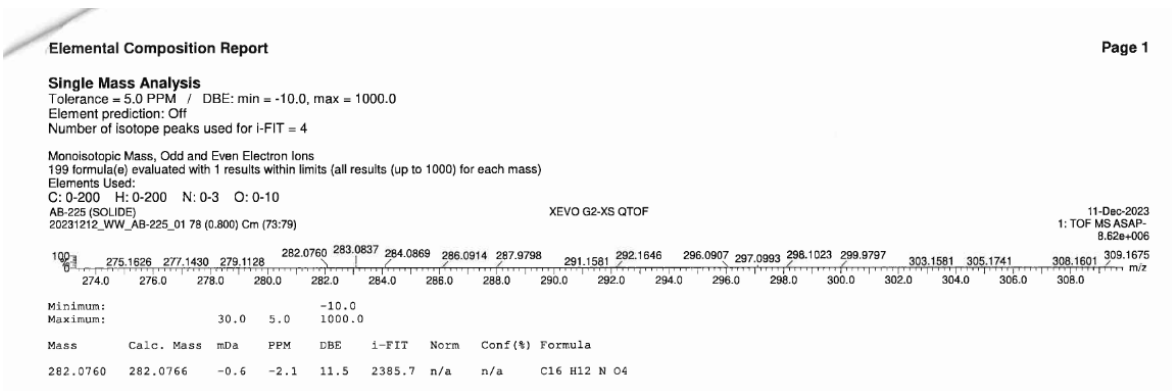


Figure 44. HRMS report of compound 9.

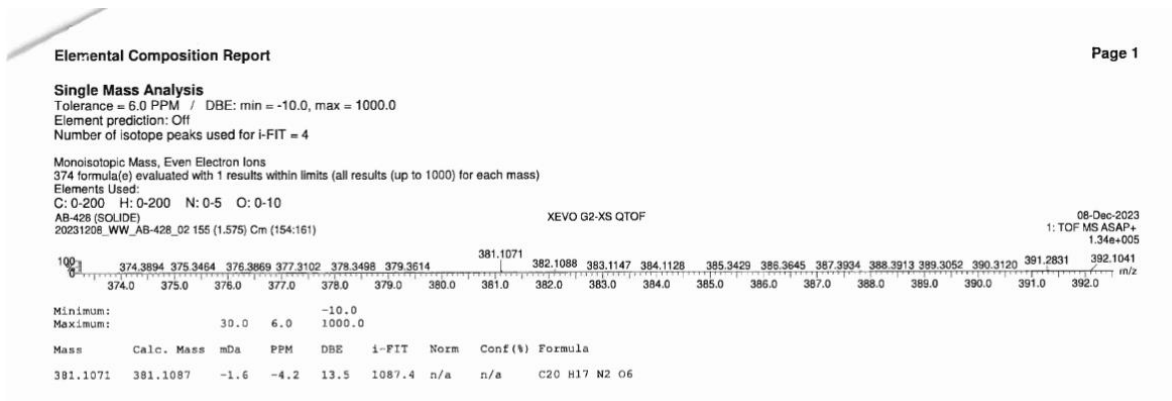


Figure 45. HRMS report of compound 10.

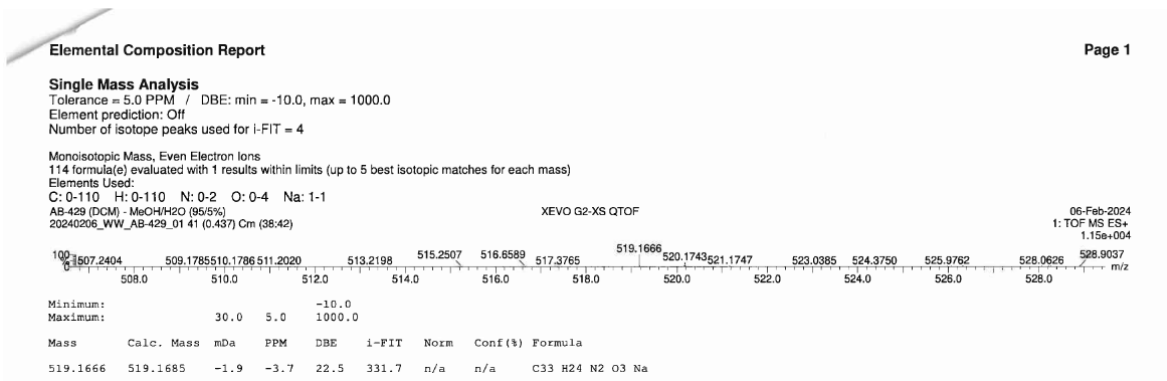


Figure 46. HRMS report of compound **11**.

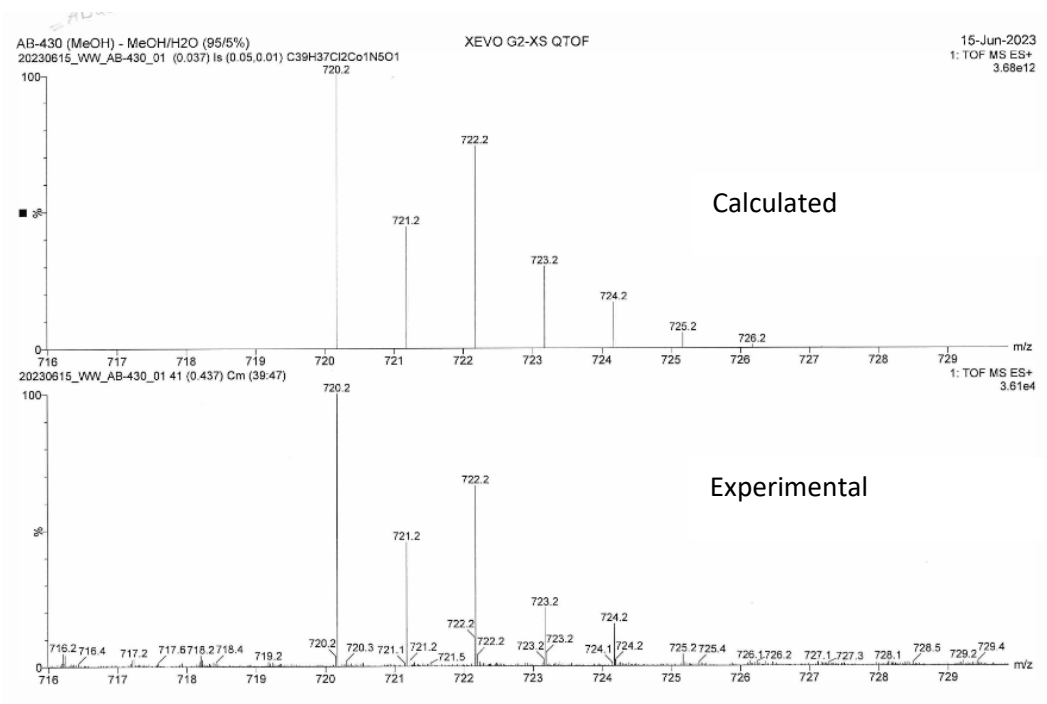
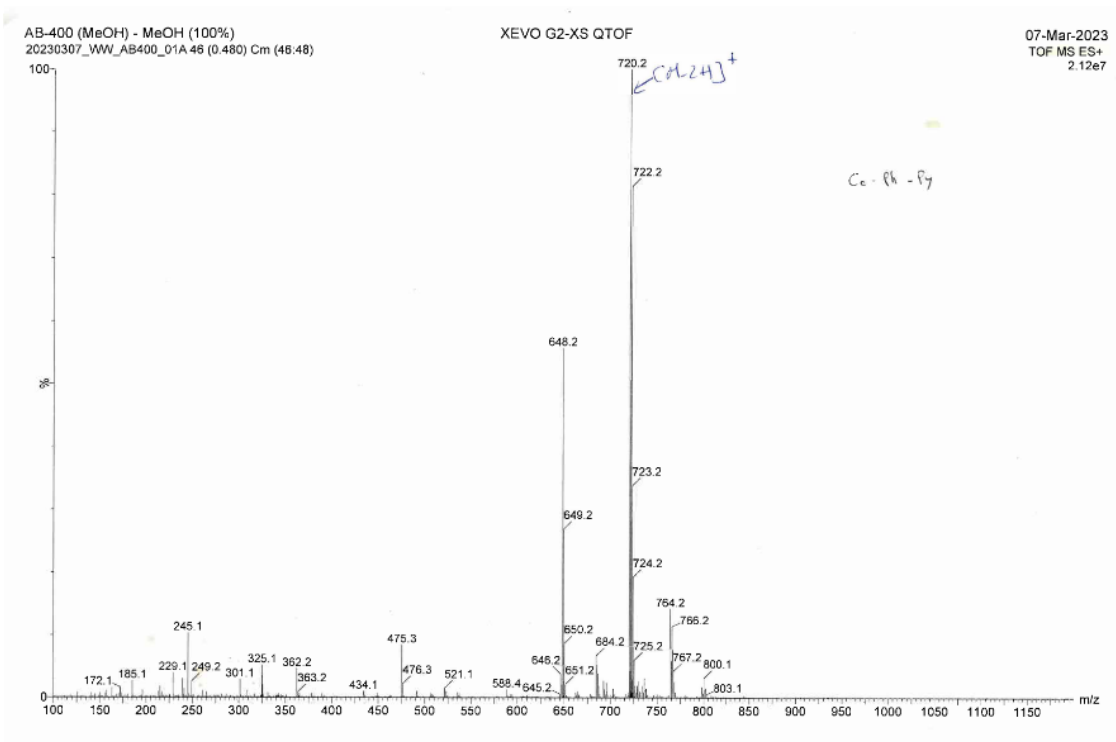


Figure 47. HRMS report of compound **C3**. Upper panel full experimental spectrum, lower panel overlay of the calculated and experimental isotopic pattern on one specific fragment.

7 References

- (1) Li, Z.-W.; Wang, X.; Wei, L.-Q.; Ivanović-Burmazović, I.; Liu, G.-F. Subcomponent Self-Assembly of Covalent Metallacycles Templated by Catalytically Active Seven-Coordinate Transition Metal Centers. *J. Am. Chem. Soc.* **2020**, *142* (16), 7283–7288.
- (2) Gygi, D.; Hwang, S. J.; Nocera, D. G. Scalable Syntheses of 4-Substituted Pyridine–Diimines. *J. Org. Chem.* **2017**, *82* (23), 12933–12938.
- (3) Ye, Q.; Chen, S.; Zhu, D.; Lu, X.; Lu, Q. Preparation of Aggregation-Induced Emission Dots for Long-Term Two-Photon Cell Imaging. *J. Mater. Chem. B* **2015**, *3* (15), 3091–3097.