# Supplementary Information

Pairing Shono-type Electro-oxidation with Electro-reduction of Dimethyl Phthalate in a Recycle Flow Reactor

*Zonghan Li[a], Chaoren Shen[a], Kaiwu Dong[a,b,*]*

a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, State Key Laboratory of Petroleum Mo-lecular & Process Engineering, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

b Shanghai Frontiers Science Center of Molecule Intelligent Syntheses, School of Chemistry and Molecular Engi-neering, East China Normal University, Shanghai 200062, China

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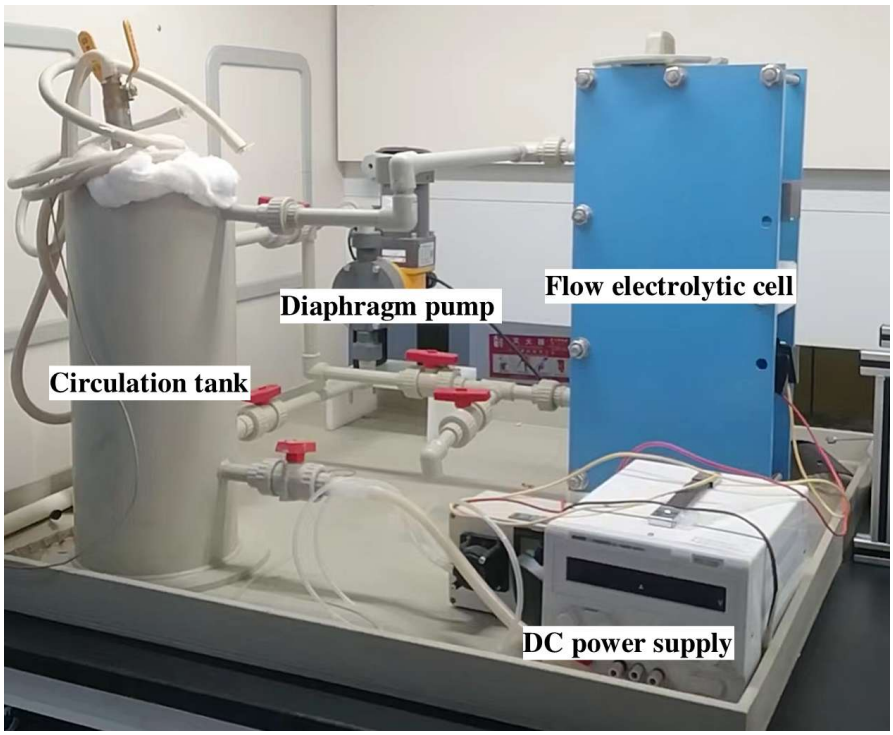



**Figure S1**. The complete device of the mole-scale recycle flow electrolysis.

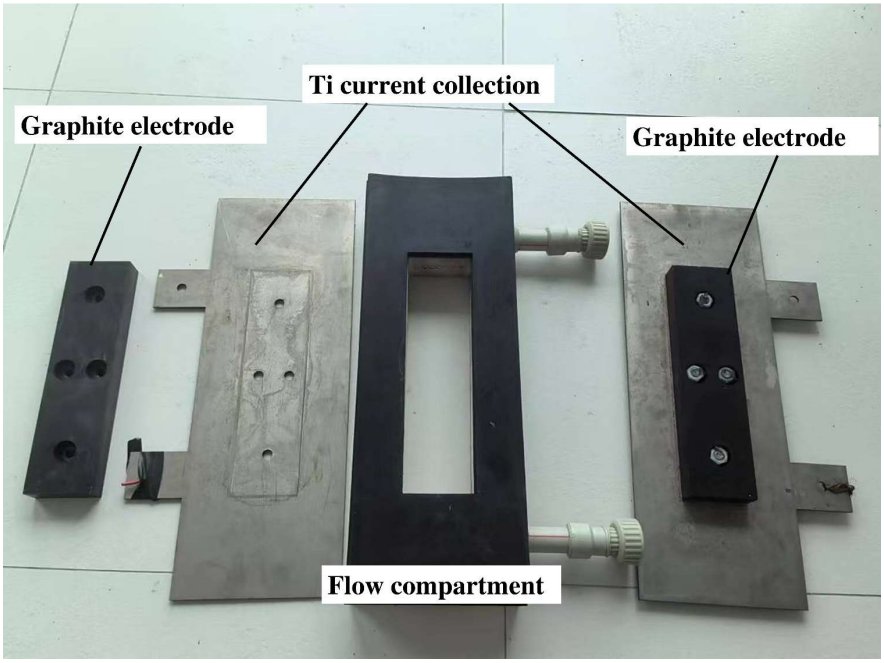



**Figure S2**. Components of the flow electrolytic cell. The graphite electrodes used are 26.6 cm in length and 6.8 cm in width, with a total area of 180 $cm^2$.

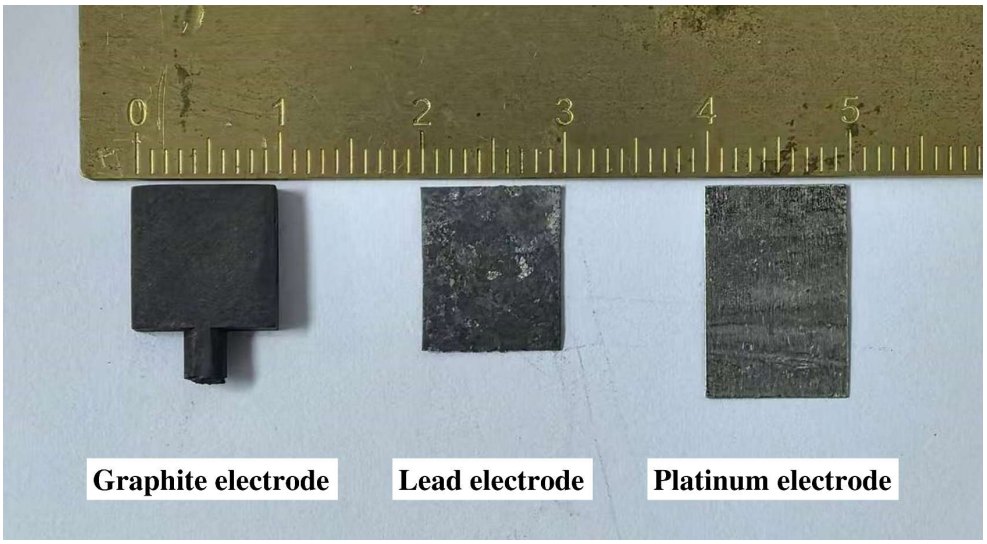



**Figure S3**. Electrode materials for electrolysis cell. By covering a portion of the electrode surface with electrode clips, the effective electrode areas were fixed at 1 cm².

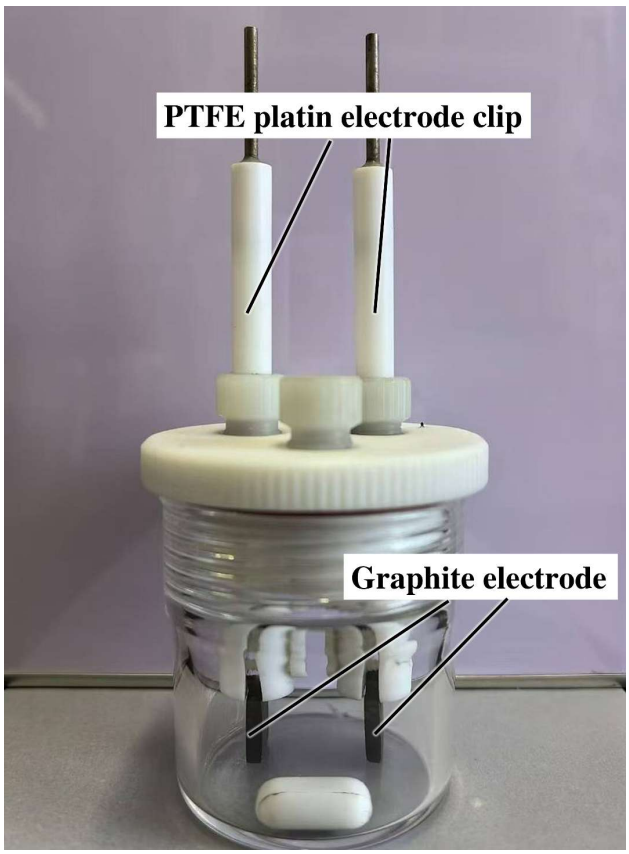



**Figure S4**. The millimole-scale undivided electrolytic cell.

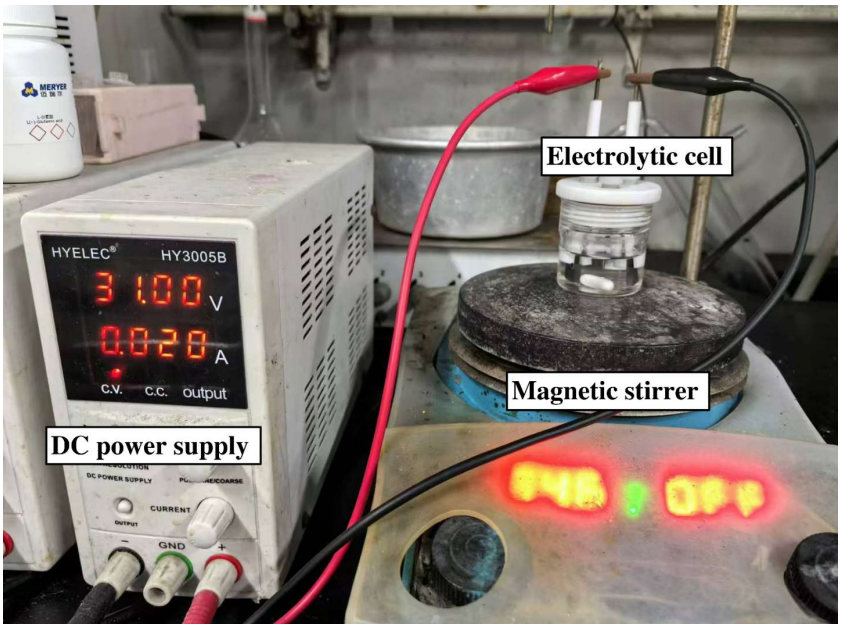



**Figure S5**. The complete device of the millimolar scale undivided electrolysis.

## 2. Preparation and Calibration of Ag/AgI Reference Electrode

A solution of 0.1 M $Bu_4NI$ in MeCN was prepared. It was charged to a fine glass tube with porous ceramics sealed its one end. A silver wire was sticked into the tube to compose a reference electrode. This reference electrode was stored in the solution of 0.1 M $Bu_4NI$ in MeCN. Before use, the reference electrode was calibrated in the solution of 0.1 M $Et_4NBF_4$ in MeOH containing 1 mM Fc. Two Pt wires were used as working and counter electrode. A cyclic voltammetry was conducted.

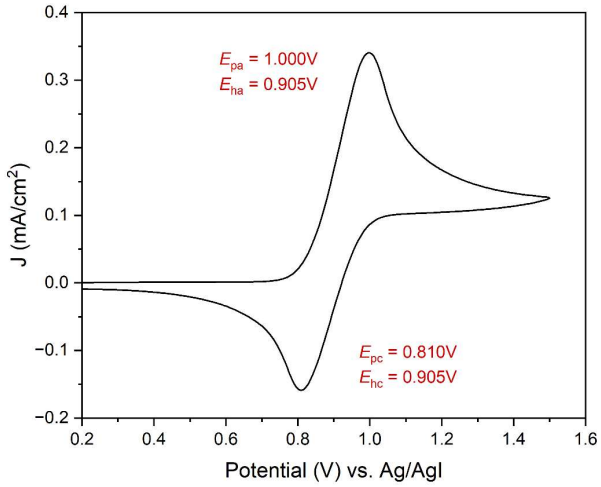



**Figure S6**. CV of 1 mM ferrocene, recorded at scan rate of 50 mV/s at platinum-wire electrodes in 0.1 M $Et_4NBF_4$ in MeOH as supporting electrolyte.

Potential ($Fc^+$/Fc) = ($E_{ha}$ + $E_{hc}$)/2 = +0.905 V vs Ag/AgI

Potential (Ag/AgI) = -0.905 V vs $Fc^+$/Fc

The potential of the reference electrode was -0.905 V referenced to ferrocene. The cyclic voltammetries were conducted with this Ag/AgI reference electrode and referencing the potential to ferrocene.

## 3. Design of Experiment

**Table S1.** Box–Behnken design matrix with three independent variables for response surface design.

| Std. | Run | Variable 1, $X_1$ Conc. of **1a** (M) | Variable 2, $X_2$ Current density (mA/cm$^2$) | Variable 3, $X_3$ Temperature (°C) | Renponse 1, $Y_1$ F.E. of **3a**[a] (%) | Renponse 2, $Y_2$ F.E. of **4a**[a] (%) |
|---|---|---|---|---|---|---|
| 1 | 13 | 0.5 | 50 | 15 | 86.02 | 79.13 |
| 2 | 10 | 1.5 | 50 | 15 | 78.02 | 85.41 |
| 3 | 8 | 0.5 | 150 | 15 | 69.09 | 92.5 |
| 4 | 5 | 1.5 | 150 | 15 | 70.39 | 90.87 |
| 5 | 6 | 0.5 | 100 | 0 | 70.87 | 63.18 |
| 6 | 16 | 1.5 | 100 | 0 | 71.74 | 93.82 |
| 7 | 9 | 0.5 | 100 | 30 | 57.41 | 84.51 |
| 8 | 14 | 1.5 | 100 | 30 | 58.64 | 88.78 |
| 9 | 11 | 1 | 50 | 0 | 93.86 | 76.97 |
| 10 | 15 | 1 | 150 | 0 | 60.44 | 81.22 |
| 11 | 7 | 1 | 50 | 30 | 61.87 | 60.27 |
| 12 | 3 | 1 | 150 | 30 | 61.29 | 90.06 |
| 13 | 2 | 1 | 100 | 15 | 76 | 90.24 |
| 14 | 1 | 1 | 100 | 15 | 77.58 | 92.26 |
| 15 | 12 | 1 | 100 | 15 | 81.35 | 93.92 |
| 16 | 4 | 1 | 100 | 15 | 78.63 | 91.86 |

[a] Determined by GC with methyl benzoate as internal standard. F.E.=($n_e$×$n_{product}$×F)/(I×t).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \sum_{i=1}^{k} \beta_{ii} {X_i}^2 \quad \textbf{(Eq.S1)}$$

$\beta_0$ represents a constant, $\beta_i$, $\beta_{ij}$, $\beta_{ii}$, are coefficients for linear, interaction and quadratic terms, respectively.

$$\begin{aligned} F.E.of\ \mathbf{4a} = {} & 92.07 + 4.95X_1 + 6.61X_2 + 1.05X_3 \\ & -1.98X_1X_2 - 6.59X_1X_3 + 6.38X_2X_3 \\ & +0.1750{X_1}^2 - 5.27{X_2}^2 - 9.67{X_3}^2 \end{aligned} \quad \textbf{(Eq.S2)}$$

Actual factors of the F.E. of **3a** and **4a**:

$$\text{F. E. of } \mathbf{3a} = 107.1325 + 18.21\{\text{Conc. of } \mathbf{1a}[\text{M}]\} - 0.4912\{\text{j}[\text{mA/cm}^2]\} - 0.238167\{\text{t}[^\circ\text{C}]\} + 0.093\{\text{Conc. of } \mathbf{1a}[\text{M}] \cdot \text{j}[\text{mA/cm}^2]\} + 0.012\{\text{Conc. of } \mathbf{1a}[\text{M}] \cdot \text{t}[^\circ\text{C}]\} + 0.010947\{\text{j}[\text{mA/cm}^2] \cdot \text{t}[^\circ\text{C}]\} - 14.42\{\text{Conc. of } \mathbf{1a}[\text{M}]\}^2 + 0.000438\{\text{j}[\text{mA/cm}^2]\}^2 - 0.044978\{\text{t}[^\circ\text{C}]\}^2 \quad \textbf{(Eq.S3)}$$

$$\text{F. E. of } \mathbf{4a} = 29.54125 + 29.585\{\text{Conc. of } \mathbf{1a}[\text{M}]\} + 0.504975\{\text{j}[\text{mA/cm}^2]\} + 1.38758\{\text{t}[^\circ\text{C}]\} - 0.0791\{\text{Conc. of } \mathbf{1a}[\text{M}] \cdot \text{j}[\text{mA/cm}^2]\} - 0.879\{\text{Conc. of } \mathbf{1a}[\text{M}] \cdot \text{t}[^\circ\text{C}]\} + 0.008513\{\text{j}[\text{mA/cm}^2] \cdot \text{t}[^\circ\text{C}]\} + 0.7\{\text{Conc. of } \mathbf{1a}[\text{M}]\}^2 - 0.002107\{\text{j}[\text{mA/cm}^2]\}^2 - 0.042989\{\text{t}[^\circ\text{C}]\}^2 \quad \textbf{(Eq.S4)}$$

**Table S2.** Analysis of variance (ANOVA) of response model of the F.E. of **3a** (**M1**) and response model of the F.E. of 4 (**M2**).

| Factors (coded) | Statistics | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Sum of squares | | df | | Mean square | | *F* | | *p* | |
| | **M1** | **M2** | **M1** | **M2** | **M1** | **M2** | **M1** | **M2** | **M1** | **M2** |
| **Model** | 1605.17 | 1391.81 | 9 | 9 | 178.35 | 154.65 | 27.7 | 4.16 | 0.0003 | 0.0484 |
| $X_1$ - Conc. of **1a** | 2.65 | 195.62 | 1 | 1 | 2.65 | 195.62 | 0.4108 | 5.26 | 0.5452 | 0.0616 |
| $X_2$ - Current density | 428.66 | 349.4 | 1 | 1 | 428.66 | 349.4 | 66.58 | 9.4 | 0.0002 | 0.0221 |
| $X_3$ - Temperature | 416.16 | 8.88 | 1 | 1 | 416.16 | 8.88 | 64.64 | 0.2389 | 0.0002 | 0.6424 |
| $X_1X_2$ | 21.62 | 15.64 | 1 | 1 | 21.62 | 15.64 | 3.36 | 0.4206 | 0.1166 | 0.5406 |
| $X_1X_3$ | 0.0324 | 173.84 | 1 | 1 | 0.0324 | 173.84 | 0.005 | 4.67 | 0.9458 | 0.0739 |
| $X_2X_3$ | 269.62 | 163.07 | 1 | 1 | 269.62 | 163.07 | 41.88 | 4.39 | 0.0006 | 0.0811 |
| $X_1^2$ | 51.98 | 0.1225 | 1 | 1 | 51.98 | 0.1225 | 8.07 | 0.0033 | 0.0295 | 0.9561 |
| $X_2^2$ | 4.8 | 110.99 | 1 | 1 | 4.8 | 110.99 | 0.745 | 2.98 | 0.4212 | 0.1348 |
| $X_3^2$ | 409.66 | 374.23 | 1 | 1 | 409.66 | 374.23 | 63.63 | 10.06 | 0.0002 | 0.0193 |
| **Residual** | 38.63 | 223.13 | 6 | 6 | 6.44 | 37.19 | | | | |
| Lack of fit | 23.44 | 216.28 | 3 | 3 | 7.81 | 72.09 | 1.54 | 31.57 | 0.365 | 0.0091 |
| Pure error | 15.19 | 6.85 | 3 | 3 | 5.06 | 2.28 | | | | |
| **Total** | 1643.8 | 1614.94 | 15 | 15 | | | | | | |

**Table S3.** Coefficients of determination for developed response surface equations.

| Response Variable | $R^2$ | Adj. $R^2$ | Pred. $R^2$ |
|---|---|---|---|
| F.E. of **3a** | 0.9765 | 0.9413 | 0.7554 |
| F.E. of **4a** | 0.8618 | 0.6546 | -1.1503 |

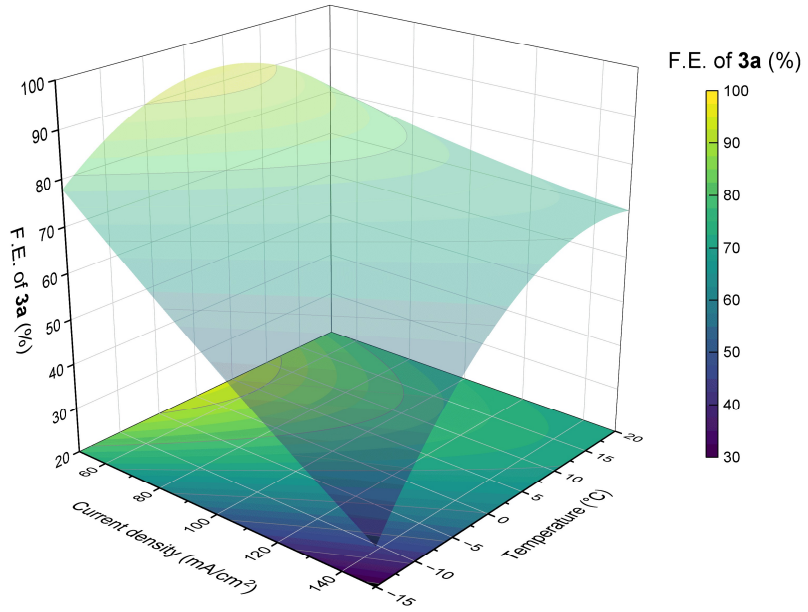



**Figure S7** Response surface of current density and temperature on Faradaic efficiency of producing **3a** at a fixed concentration of reactant **1a** (0.8 M). Reaction conditions: 0.8 M of **1a**, 0.4 M of **2a**, 0.2 M methyltriethylammonium methylsulfate as electrolyte, 2 F/mol with respect to **1a**.

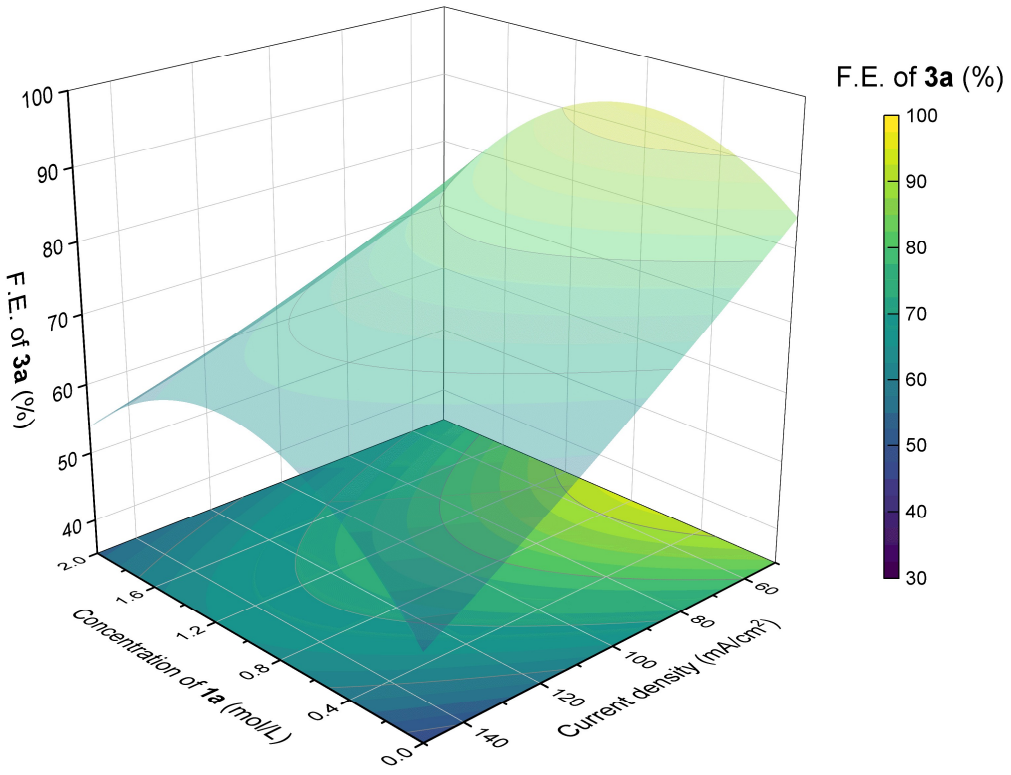



**Figure S8** Response surface of substrate concentration and current density on Faradaic efficiency of producing **3a** at a fixed temperature (3 °C). Reaction conditions: 0.2 M methyltriethylammonium methylsulfate as electrolyte, electrolyze at 3 °C, 2 F/mol with respect to **1a**.

## 4. General remarks

All commercial reagents were used as received without further purification. GC yields were determined on Shimadzu GC-2030. Gas chromatography-mass spectrometry (GC-MS) were detected on Shimadzu GC-2010 gas chromatography coupled to a Shimadzu QP2010 mass selective detector. Cyclic voltammetry investigation was performed on Shanghai Chenhua CHI6081E workstation. 1H NMR spectra were recorded on a Brucker AV-600 (600 MHz). 13C NMR spectra were recorded on a Brucker AV-600 (151 MHz).

## 5. General procedure of electrolysis

**Millimole-scale**: The electrolysis was conducted in an undivided cell. The substrates and supporting electrolyte were dissolved in methanol for electrolysis. The electrodes used are either metal plates or graphite plates with an area of 1 $cm^2$. The electrolysis was conducted under constant current conditions with the electrolysis cell temperature maintained using a thermostatic water bath. The electrolysis duration was controlled using a timed power supply. Conversion, yield and selectivity were determined by GC-FID analysis with methyl benzoate as internal standard. The isolated yields were obtained through column chromatography on silica gel using ethyl acetate and petroleum ether as eluent.

**Mole-scale**: The electrolysis was conducted in an recycle flow reactor. The area of the graphite electrode in the flow cell is 180 $cm^2$. The flow rate of the diaphragm pump utilized in the flow cell can be regulated between 50 and 300 ml/min. The substrates and supporting electrolyte were dissolved in methanol and then added to the circulation tank. The temperature of the reaction system is controlled by circulating coolant through the titanium alloy coil in the circulation tank. The electrolysis duration was controlled using a timed power supply. After the reaction is completed, the methanol is concentrated and removed, then petroleum ether and ethyl acetate are added to facilitate the stratification of the reaction mixture. The lower ionic liquid phase is recovered and used as an electrolyte in subsequent electrolysis. The upper organic phase is concentrated to remove the solvent, followed by vacuum distillation to obtain the product. Compound **3a** begins to distill at 72 °C and compound **4a** begins to distill at 86 °C.

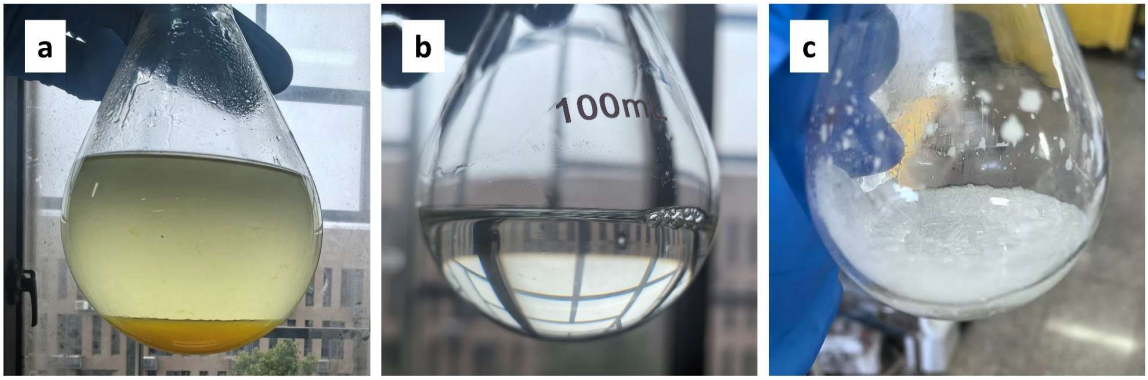



**Figure S9**. The stratified reaction mixture (**a**) and the distilled products **3a** (**b**) and **4a** (**c**).

## 6. Longer-term electrolysis experiment

By increasing the amount of substrate **1a** to 0.20 mol, the electrolysis time was extended to 48 hours for evaluating the stability of the electrodes. After constant current electrolysis for 48 hours, the reaction was stopped. The changes in voltage, yields of products **3a** and **4a**, and current efficiency were almost consistent with those observed in short-duration electrolysis.

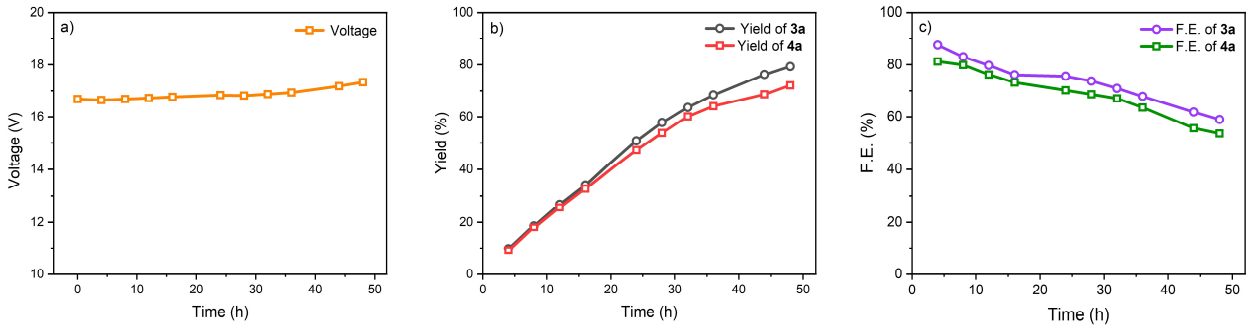



**Figure S10**. The fluctuation of voltage (**a**), the variation of yield (**b**), Faradaic efficiency (**c**) of products **3a** and **4a** during the long-term electrolysis process. Standard conditions: graphite plates with an area of 3 $cm^2$ was used as cathode and anode, **1a** (0.2 mol), **2a** (0.1 mol) and methyltriethylammonium methylsulfate (25 mmol) were dissolved in MeOH (250 mL). Circulating the reaction solution in the flask and electrolytic cell through a peristaltic pump. Electrolysis for 48 h min at 300 mA ($j$ = 100 mA/$cm^2$). Determined by GC-FID with methyl benzoate as internal standard. F.E.= ($n_e \times n_{product} \times F$) / ($I \times t$).

## 7. Electrolyte Recovery Experiment

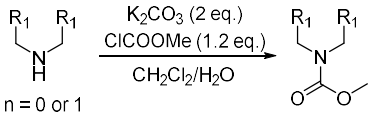
The electrolysis was repeated using the recovered electrolyte to verify its stability. The voltage exhibited a slight increase during the two repeated electrolysis runs, while the current efficiency remained largely consistent.

**Table S4** Voltage and Faradaic efficiency of electrolyte recovery experiment.

| Entry | Variations from standard conditions[a] | Voltage (V) | | F.E.[b] (%) | |
|---|---|---|---|---|---|
| | | 0 h | 5 h 21 min | **3a** | **4a** |
| **S1** | Fresh electrolyte | 21.2 | 22.5 | 89 | 86 |
| **S2** | 1st time of reusing electrolyte | 24.8 | 26.2 | 84 | 83 |
| **S3** | 2nd time of reusing electrolyte | 25.3 | 27.1 | 86 | 82 |

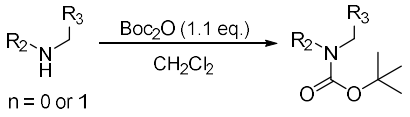
[a] Standard conditions: graphite plates with an area of 1$cm^2$ was used as cathode and anode, **1a** (10 mmol), **2a** (5 mmol) and methyltriethylammonium methylsulfate (1 mmol) were dissolved in MeOH (10 mL), electrolysis for 5 h 21 min at 100 mA ($j$ = 100 mA/$cm^2$). [b] Determined by GC-FID with methyl benzoate as internal standard. F.E.= ($n_e \times n_{product} \times F$) / ($I \times t$).

## 8. General procedure for the synthesis of substrates

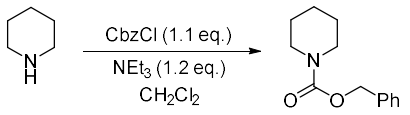



To a 250 mL flask was added $K_2CO_3$ (27 g, 200 mmol, 2 eq.), $H_2O$ (50 mL), $CH_2Cl_2$ (100 mL), piperidine (8.5 g, 100 mmol) and the mixture was cooled to 0 °C. This was followed by dropwise addition of ClCOOMe (11 g, 120 mmol, 1.2 eq.) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. the reaction mixture was poured in a separation funnel, washed

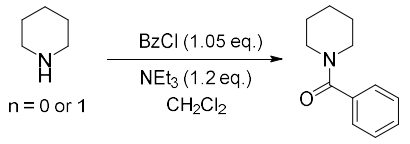
with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and distilled under vacuum to obtain a colorless liquid.



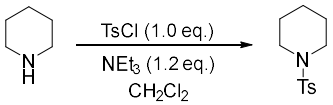

To a 250 mL flask was added $CH_2Cl_2$ (100 mL), $Boc_2O$ (24 g, 110 mmol, 1.1 eq.) and the mixture was cooled to 0 °C. This was followed by dropwise addition of piperidine (8.5 g, 100 mmol) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the reaction mixture was poured in a separation funnel, washed with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and distilled under vacuum to obtain a colorless liquid.



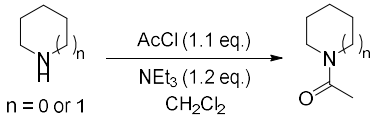

To a 250 mL flask was added $CH_2Cl_2$ (100 mL), $NEt_3$ (12 g, 120 mmol, 1.2 eq.), piperidine (8.5 g, 100 mmol) and the mixture was cooled to 0 °C. This was followed by dropwise addition of CbzCl (18.7 g, 110 mmol, 1.1 eq.) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the reaction mixture was poured in a separation funnel, washed with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and distilled under vacuum to obtain a colorless liquid.



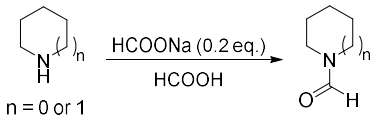

To a 250 mL flask was added $CH_2Cl_2$ (100 mL), $NEt_3$ (12 g, 120 mmol, 1.2 eq.), piperidine (8.5 g, 100 mmol) and the mixture was cooled to 0 °C. This was followed by dropwise addition of BzCl (14.7 g, 105 mmol, 1.05 eq.) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the reaction mixture was poured in a separation funnel and washed with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and distilled under vacuum to obtain a white solid.



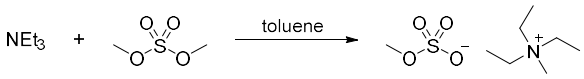
To a 250 mL flask was added $CH_2Cl_2$ (100 mL), $NEt_3$ (12 g, 120 mmol, 1.2 eq.), piperidine (8.5 g, 100 mmol) and the mixture was cooled to 0 °C. This was followed by adding TsCl (19 g, 100 mmol, 1.0 eq.) in batches under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the reaction mixture was poured in a separation funnel, washed with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and diluted with petroleum ether. A white solid precipitate was collected by filtration on a fritted finnel and dried in vacuum to obtain the product.




To a 250 mL flask was added $CH_2Cl_2$ (100 mL), $NEt_3$ (12 g, 120 mmol, 1.2 eq.), piperidine (8.5 g, 100 mmol) and the mixture was cooled to 0 °C. This was followed by dropwise addition of AcCl (8.6 g, 110 mmol, 1.1 eq.) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the reaction mixture was poured in a separation funnel and washed with water and extracted with $CH_2Cl_2$. The combined organic phases were dried over anhydrous $Na_2SO_4$, concentrated under reduced pressure and distilled under vacuum to obtain a colorless liquid.




To a 150 mL flask was added HCOONa (1.36 g, 20 mmol, 0.2 eq.), HCOOH (20 mL) and slowly dropping piperidine (8.5 g, 100 mmol) at room temperature and stirred for 12 h. Then the reaction mixture was concentrated under reduced pressure and distilled under vacuum to obtain a colorless liquid. [1]




To a 1 L flask was added $NEt_3$ (139 mL, 1.0 mol, 1.0 eq.), toluene (500 mL) and the mixture was cooled to 0 °C. This was followed by dropwise addition of dimethyl sulfate (97 mL, 1.0 mol, 1.0 eq.) under stirring. Then the reaction mixture was warmed to room temperature and stirred for 6 h. Next, the organic layer was decanted and washed with ethyl acetate. The solution was concentrated and dried in vacuum to obtain a colorless solid. [2]

## 9. Further transformation of electrolysis products

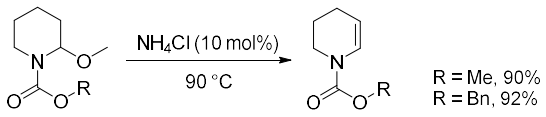
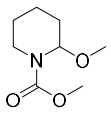


**Figure S11** The further elimination of 2-methoxypiperidine-1-carboxylate to 3,4-dihydropyridine-1(2*H*)-carboxylate promoted by $NH_4Cl$

To a 500 mL flask was added methyl 2-methoxypiperidine-1-carboxylate (130 g, 0.75 mol) and $NH_4Cl$ (13 g, 0.24 mol). The reaction was heated to 90 °C under reduced pressure, and the pressure was adjusted to maintain a gentle boil of the solution, allowing methanol and temperature to distill off. When no more methanol distills off, the vacuum level was increased to allow the product.

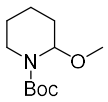
## 10. Characterization data of substrates

**Methyl 2-methoxypiperidine-1-carboxylate (3a)**



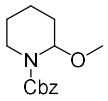
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.41-5.26 (m, 1H), 3.98-3.85 (m, 1H), 3.71 (s, 3H), 3.24 (s, 3H), 2.95 (m, 1H), 1.85 (m, 1H), 1.79-1.71 (m, 1H), 1.43-1.62 (m, 4H) ppm.[3]

**Tert-butyl 2-methoxypiperidine-1-carboxylate (3b)**



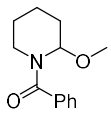
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.38-5.24 (m, 1H), 3.93-3.79 (m, 1H), 3.21 (s, 3H), 2.91-2.84 (m, 1H), 1.82 (m, 1H), 1.74-1.70 (m, 1H), 1.61 (m, 1H), 1.54-1.52 (m, 2H), 1.46 (s, 9H), 1.44 (m, 1H) ppm.[4]

**Benzyl 2-methoxypiperidine-1-carboxylate (3c)**



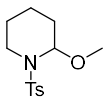
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.36 (m, 4H), 7.34-7.30 (m, 1H), 5.44-5.34 (m, 1H), 5.22-5.10 (m, 2H), 4.03-3.92 (m, 1H), 3.26-3.17 (m, 3H), 3.01-2.95 (m, 1H), 1.89-1.71 (m, 2H), 1.65-1.43 (m, 4H) ppm.[5]

**(2-Methoxypiperidin-1-yl)(phenyl)methanone (3d)**



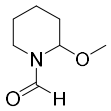
Obtained following **general procedure of electrolysis**. White solid. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.40-7.37 (m, 5H), 5.89 (m, 0.45H), 4.84 (m, 0.55H), 4.43-4.42 (m, 0.55H), 3.45, 3.23 and 2.96 (m, 1.45H), 3.38 and 3.06 (m, 3H), 1.95-1.44 (m, 6H) ppm.[6]

**2-Methoxy-1-tosylpiperidine (3e)**



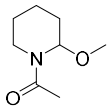
Obtained following **general procedure of electrolysis**. White solid. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.71-7.70 (d, *J* = 8.4, 2H), 7.29-7.28 (d, *J* = 8.4, 2H), 5.14 (m, 1H), 3.55-3.52 (m, 1H), 3.28 (s, 3H), 3.05-3.00 (td, *J* = 13.2, 3.0, 1H), 2.42 (s, 3H), 1.87-1.84 (m, 1H), 1.70-1.63 (m, 1H), 1.51-1.39 (m, 3H), 1.27-1.21 (m, 1H) ppm.[7]

**N-formyl-2-methoxypiperidin (3f)**



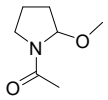
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 8.13-8.10 (m, 1H), 5.49 (m, 0.3H), 4.54 (m, 0.7H), 4.17-4.16 (m, 0.7H), 3.29-3.28 (m, 0.6H), 3.23-3.21 (m, 1H), 3.17-3.15 (m, 2H), 2.73-2.68 (m, 0.7H), 1.97-1.40 (m, 6H) ppm.[8]

**N-acetyl-2-methoxypiperidine (3g)**



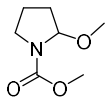
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.76 (m, 0.5H), 4.95 (m, 0.5H), 4.40-4.38 (m, 0.5H), 3.50-3.48 (m, 0.5H), 3.25-3.23 (m, 0.5H), 3.22-3.20 (m, 3H), 2.70 (td, *J* = 13.2, 3.6 Hz, 0.5H), 2.12-2.10 (m, 3H), 1.92-1.74 (m, 2H), 1.67-1.63 (m, 1H), 1.57-1.41 (m, 3H) ppm.[9]

**N-acetyl-2-methoxypyrrolidine (3h)**



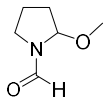
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.39-5.38 (m, 0.4H), 4.91 (m, 0.6H), 3.59-3.52 (m, 1H), 3.36-3.26 (m, 4H), 2.15-2.04 (m, 4H), 1.97-1.66 (m, 3H) ppm.[10]

**Methyl 2-methoxypyrrolidine-1-carboxylate (3i)**



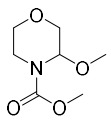
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.18-5.07 (m, 1H), 3.69 (s, 3H), 3.46-3.27 (m, 5H), 2.05-2.00 (m, 1H), 1.91-1.84 (m, 2H), 1.74-1.71 (m, 1H) ppm.[11]

**N-formyl-2-methoxypyrrolidin (3j)**



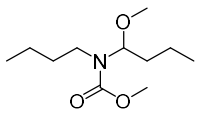
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 8.37 (s, 0.8H), 8.26 (s, 0.2H), 5.34-5.26 (m, 0.2H), 4.90-4.89 (m, 0.8H), 3.54-3.38 (m, 2H), 3.34 (m, 0.5H), 3.23-3.22 (m, 2.5H), 2.06-1.82 (m, 4H) ppm.[12]

**Methyl 3-methoxymorpholine-4-carboxylate (3k)**



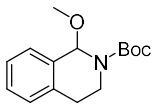
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.16-5.01 (m, 1H), 3.92-3.68 (m, 6H), 3.49 (m, 2H), 3.30-3.28 (m, 4H) ppm. **$^{13}$C NMR** (151 MHz, $CDCl_3$): δ = 156.14, 80.61, 80.11, 69.29, 69.05, 66.49, 66.22, 55.24, 54.86, 52.88, 39.46, 38.83 ppm. HRMS(ESI) calcd for ($C_7H_{13}NO_4$+$Na^+$): 198.0737, found: 198.0734.

**Methyl butyl(1-methoxybutyl)carbamate (3l)**



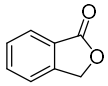
Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 5.29-5.06 (m, 1H), 3.72 (s, 3H), 3.23-3.21 (m, 3H), 3.11-3.04 (m, 2H), 1.66-1.29 (m, 8H), 0.93-0.91 (m, 6H) ppm.[13]

**Tert-butyl 1-methoxy-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3m)**



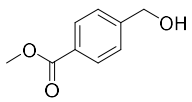

Obtained following **general procedure of electrolysis**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.32-7.31 (m, 1H), 7.24 (m, 2H), 7.14 (m, 1H), 6.11-5.97 (m, 1H), 4.57 (m, 0.2H), 4.19 (m, 0.5H), 3.94 (m, 0.4H), 3.65 (m, 0.3H), 3.44 (s, 3H), 3.34-3.31 (m, 0.6H), 2.93-2.74 (m, 2H), 1.51 (s, 9H) ppm.[14] HRMS(ESI) calcd for ($C_{15}H_{21}NO_3$+$Na^+$): 286.1414, found: 286.1419.

**2-Benzofuran-1(3*H*)-one (4a)**



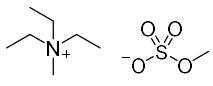

Obtained following **general procedure of electrolysis**. White solid. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.93-7.91 (d, *J* = 7.8Hz, 1H), 7.70-7.67 (t, *J* = 7.8 Hz, 1H), 7.55-7.52 (t, *J* = 7.8 Hz, 1H), 7.50-7.49 (d, *J* = 7.8 Hz, 1H), 5.32 (s, 2H) ppm.[15]

**Methyl 4-(hydroxymethyl)benzoate (4b)**



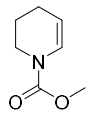

Obtained following **general procedure of electrolysis**. White solid. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 8.02-8.01 (d, *J* = 8.4 Hz, 2H), 7.43-7.42 (d, *J* = 8.4 Hz, 2H), 4.76 (s, 2H), 3.91 (s, 3H), 2.00 (s, 1H) ppm.[15]

**Methyltriethylammonium methylsulfate**



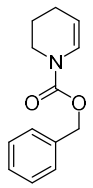

Obtained following **general synthesis of substrates**. Colorless oil. **$^1$H NMR** (600 MHz, $D_2O$): δ = 3.64 (s, 3H), 3.34-3.31 (q, *J* = 7.2 Hz, 6H), 2.94 (s, 3H), 1.31-1.28 (tt, *J* = 7.2, 2.4 Hz, 9H) ppm.[16]

**3,4-Dihydropyridine-1(2*H*)-carboxylate**



Obtained following **further transformation of electrolysis products**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 6.85-6.84 (d, *J* = 8.4 Hz, 0.4H), 6.71-6.70 (d, *J* = 8.4 Hz, 0.6H), 4.92 (m, 0.4H), 4.83 (m, 0.6H), , 3.72 (s, 3H), 3.59-3.55 (m, 2H) 2.01 (m, 2H), 1.80 (m, 2H) ppm.[17]

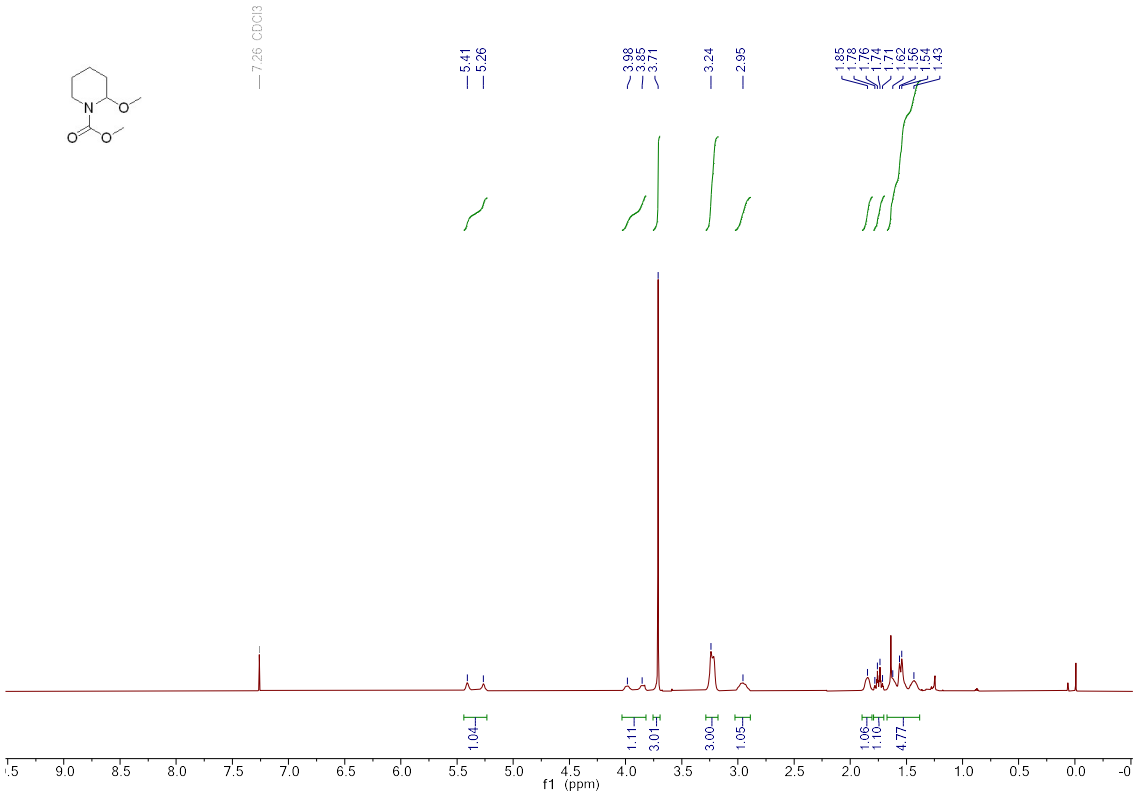
**Benzyl 3,4-Dihydropyridine-1(2*H*)-carboxylate**



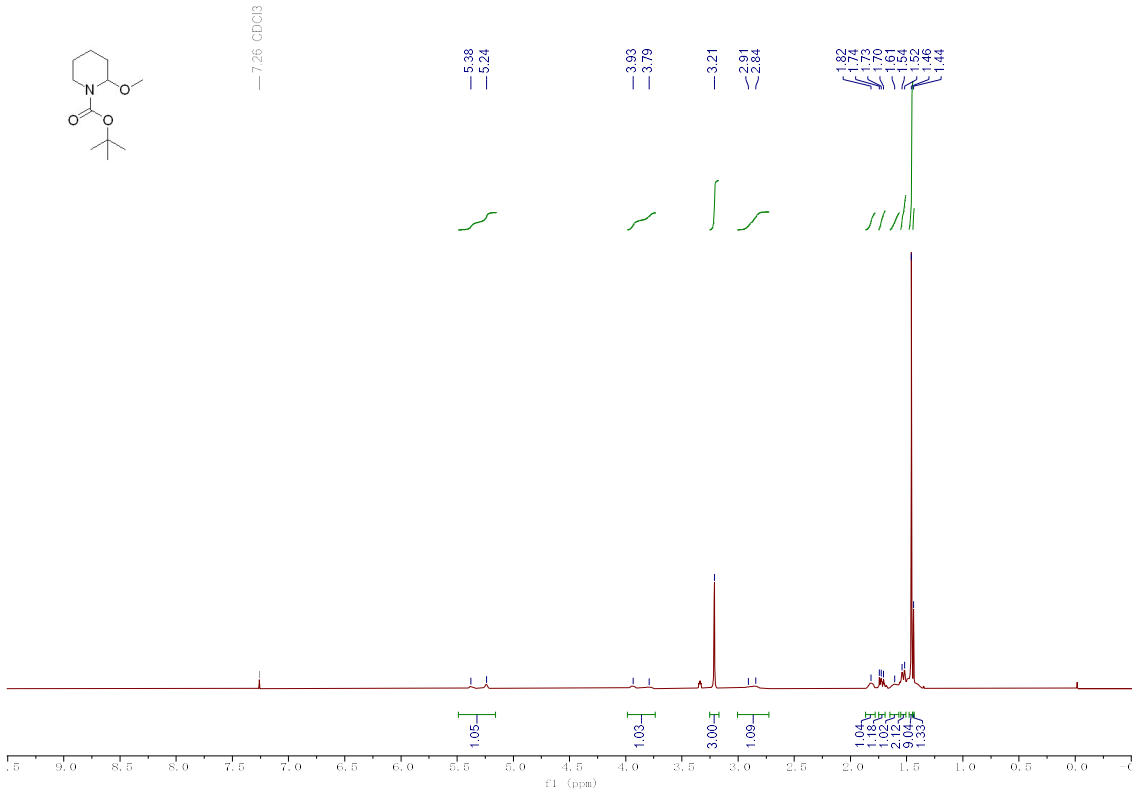
Obtained following **further transformation of electrolysis products**. Colorless oil. **$^1$H NMR** (600 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 5H), 6.90-6.89 (d, *J* = 8.4 Hz, 0.4H), 6.81-6.80 (d, *J* = 8.4 Hz, 0.6H), 5.18 (s, 2H), 4.99-4.96 (dt, *J* = 8.4, 4.2 Hz, 0.4H), 4.87-4.85 (dt, *J* = 8.4, 4,2 Hz, 0.6H), 3.65-3.61 (m, 2H), 2.05-2.04 (m, 2H), 1.85-1.80 (m, 2H) ppm.[18]

## 11. NMR spectrum copies of products

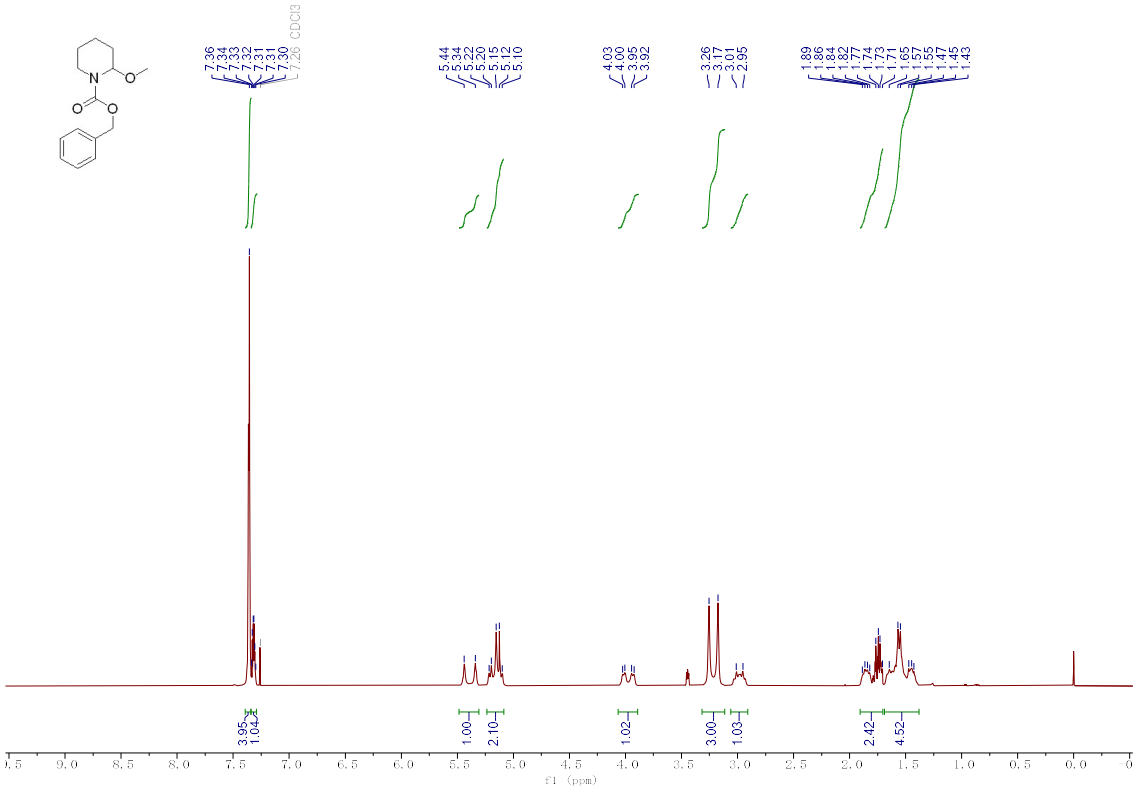
**$^1$H NMR** of **methyl 2-methoxypiperidine-1-carboxylate (3a)**



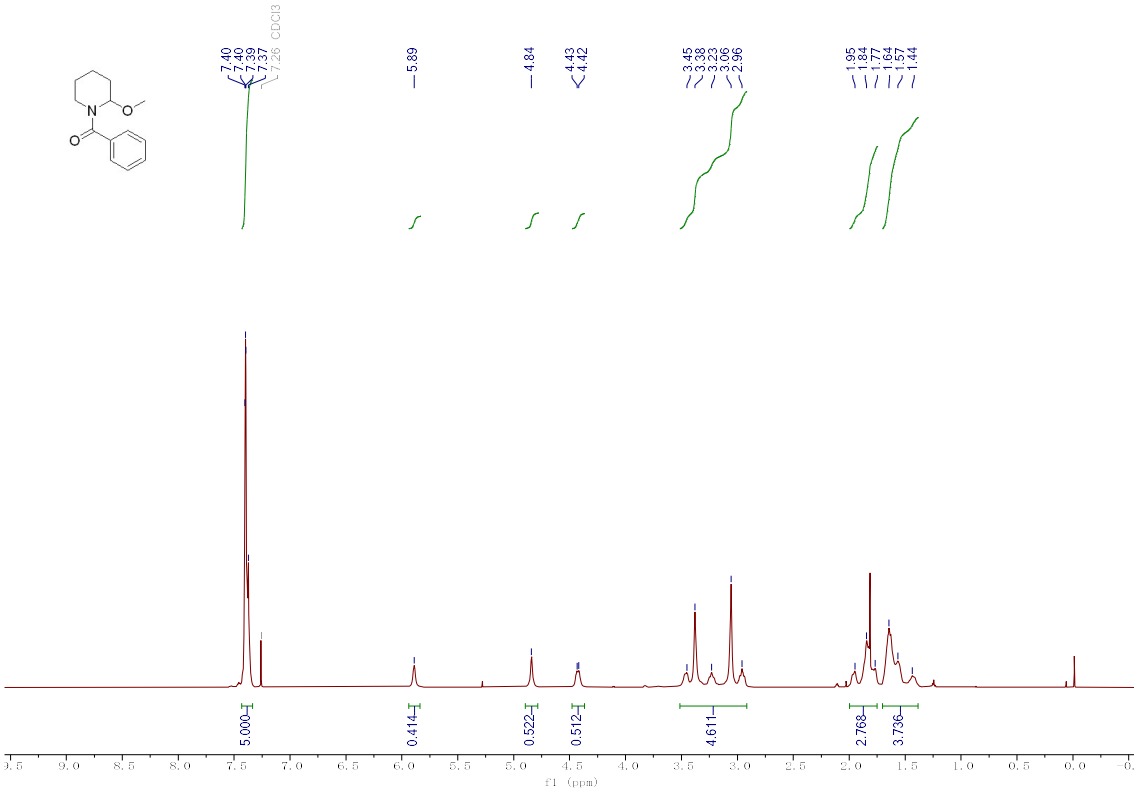

**$^1$H NMR** of **tert-butyl 2-methoxypiperidine-1-carboxylate (3b)**



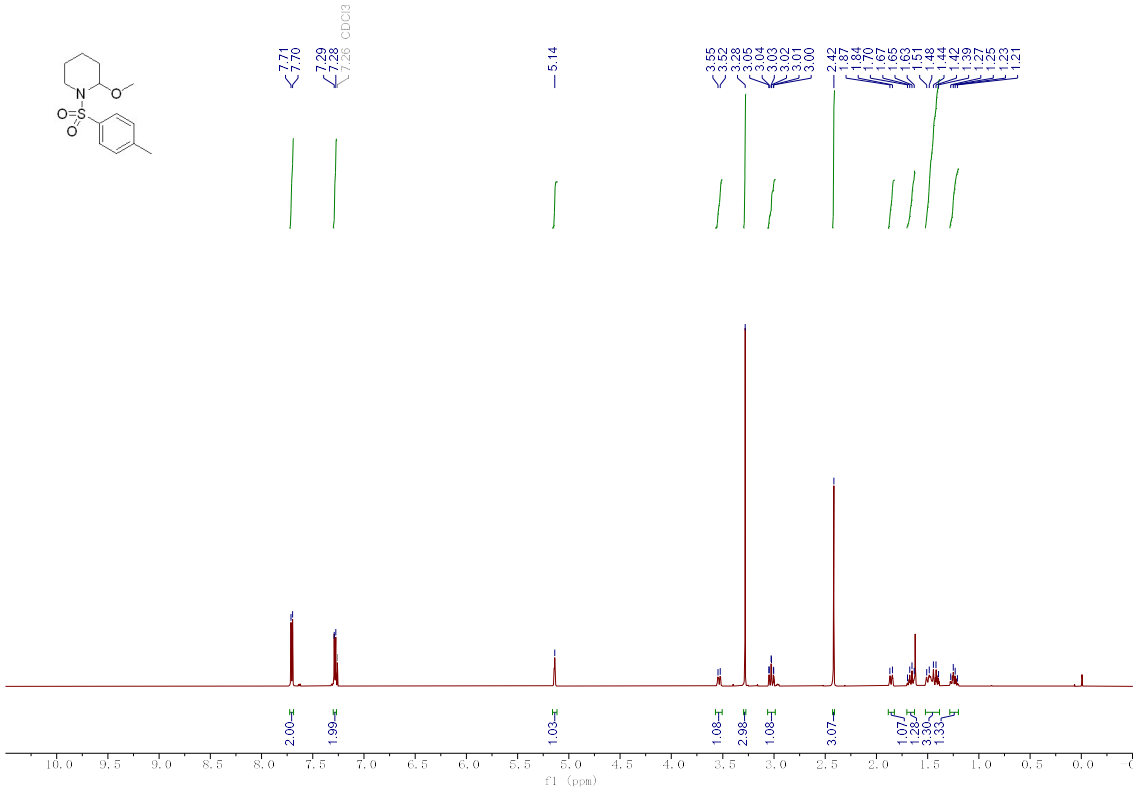
**$^1$H NMR** of **benzyl 2-methoxypiperidine-1-carboxylate (3c)**



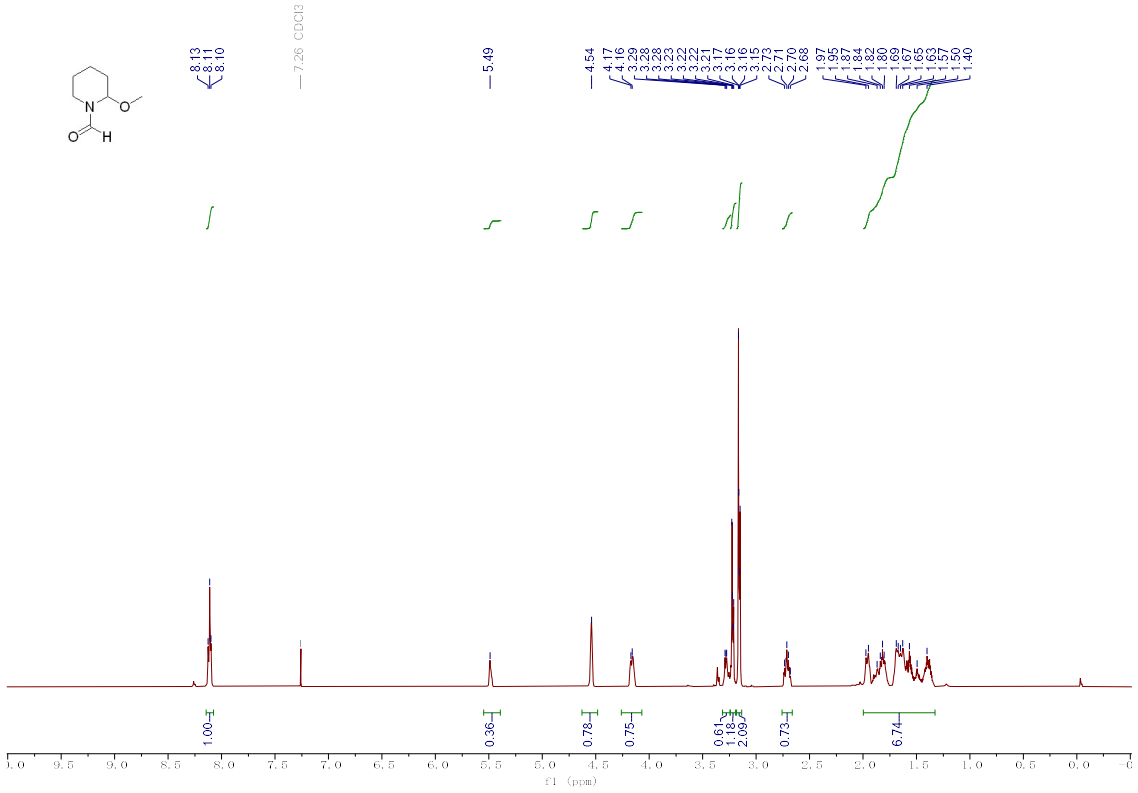

**$^1$H NMR** of **(2-methoxypiperidin-1-yl)(phenyl)methanone (3d)**



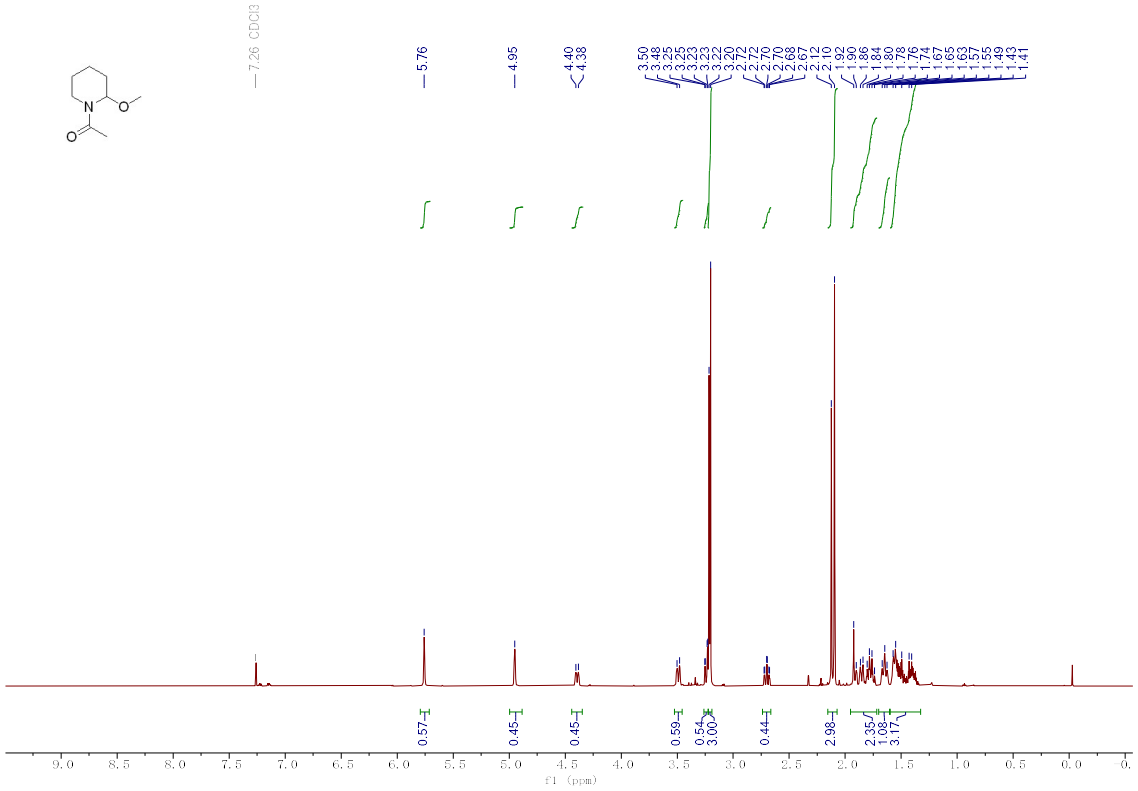
**$^1$H NMR** of **2-methoxy-1-tosylpiperidine (3e)**



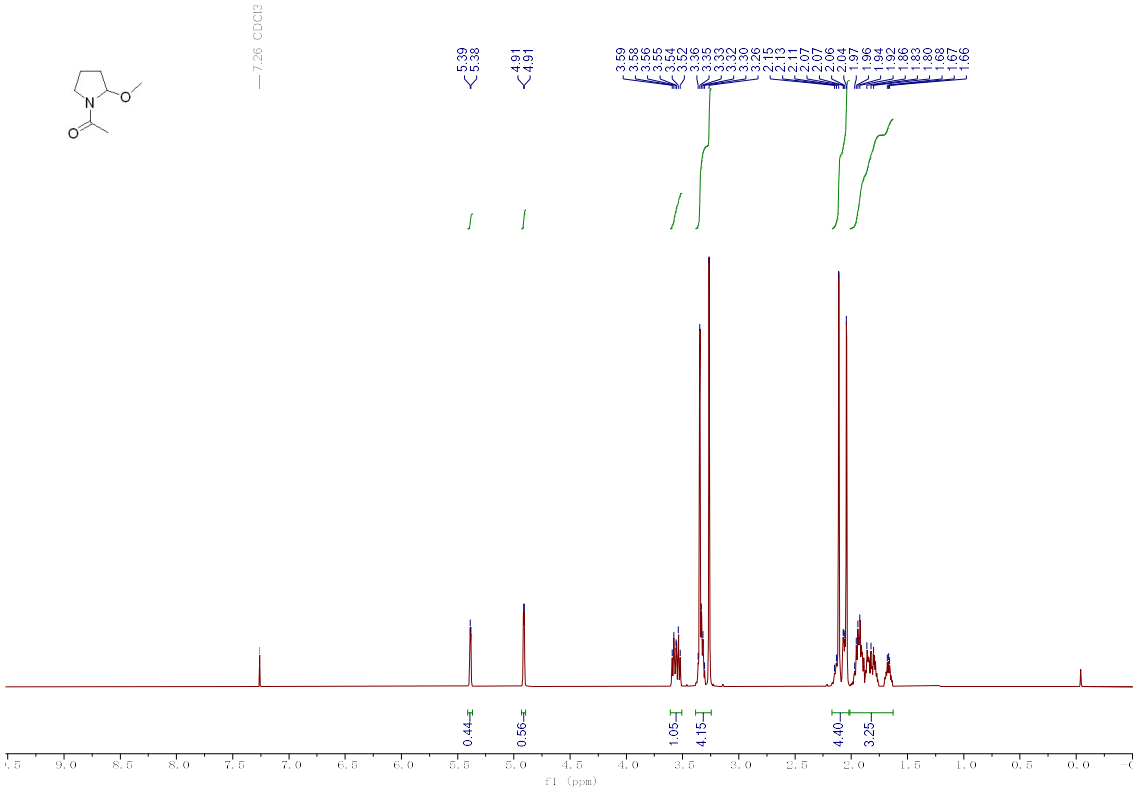

**$^1$H NMR** of **N-formyl-2-methoxypiperidin (3f)**



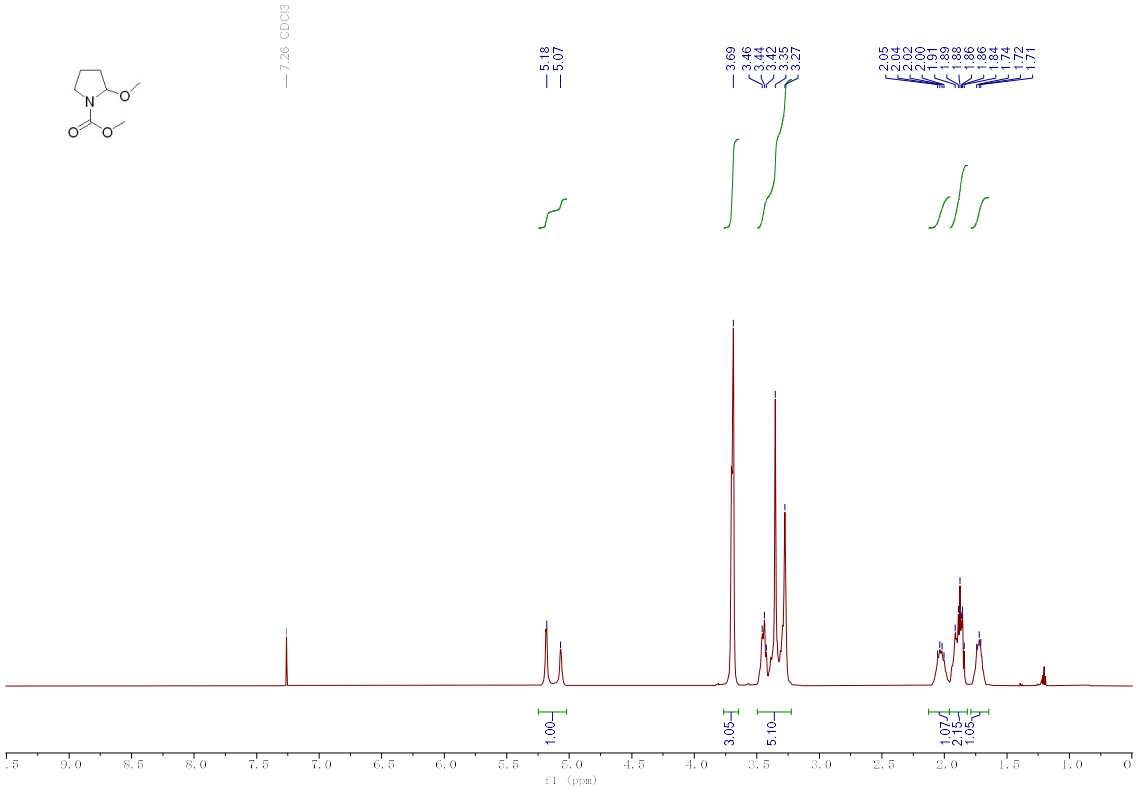
**$^1$H NMR** of **N-acetyl-2-methoxypiperidine (3g)**



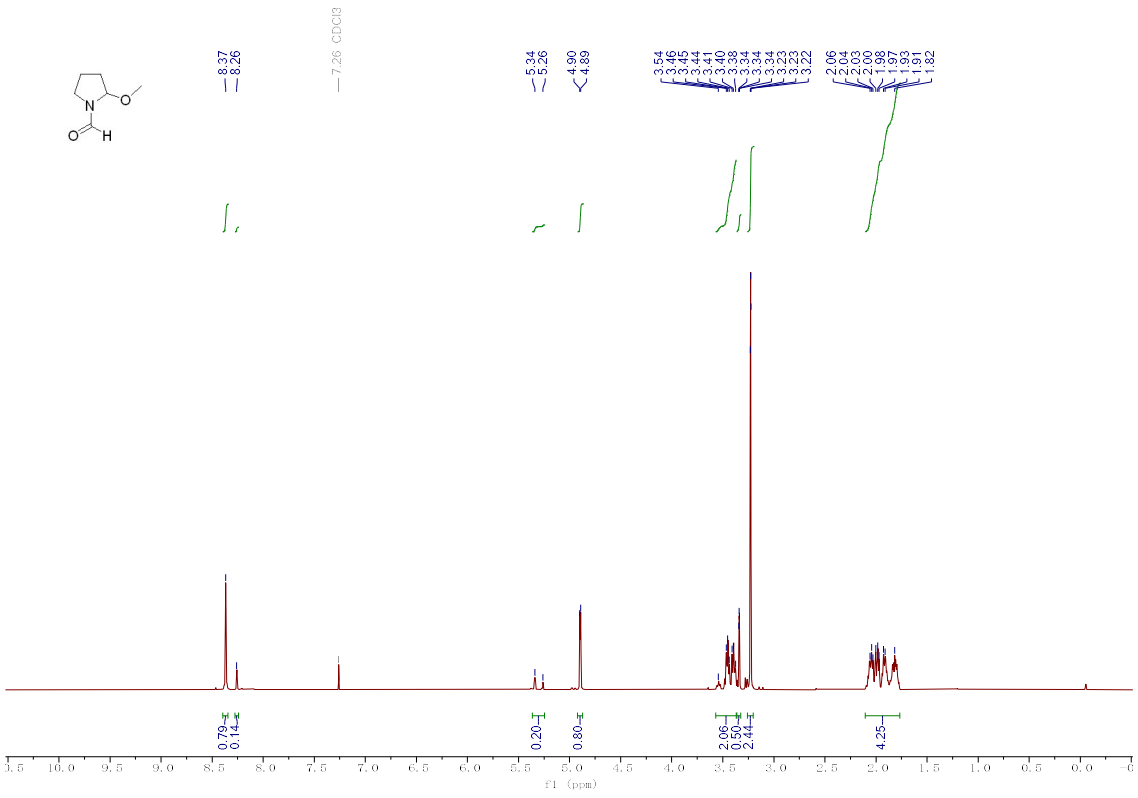

**$^1$H NMR** of **N-acetyl-2-methoxypyrrolidine (3h)**



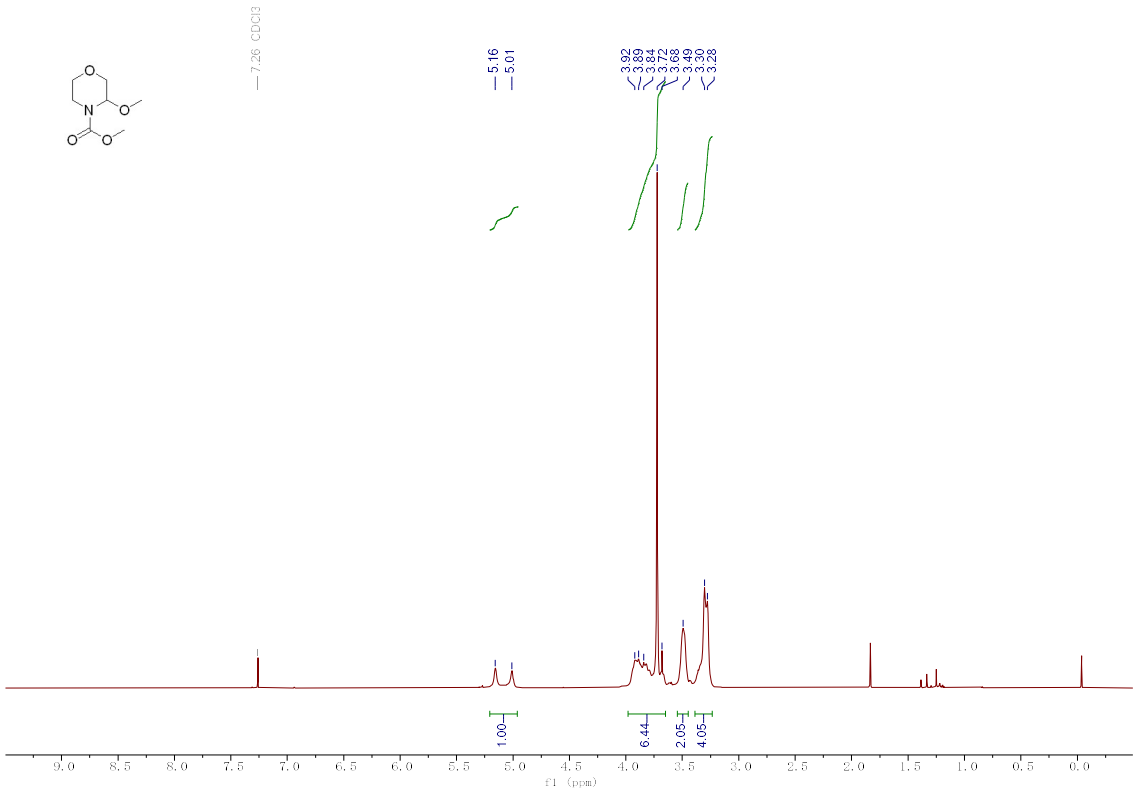
**$^1$H NMR** of **methyl 2-methoxypyrrolidine-1-carboxylate (3i)**



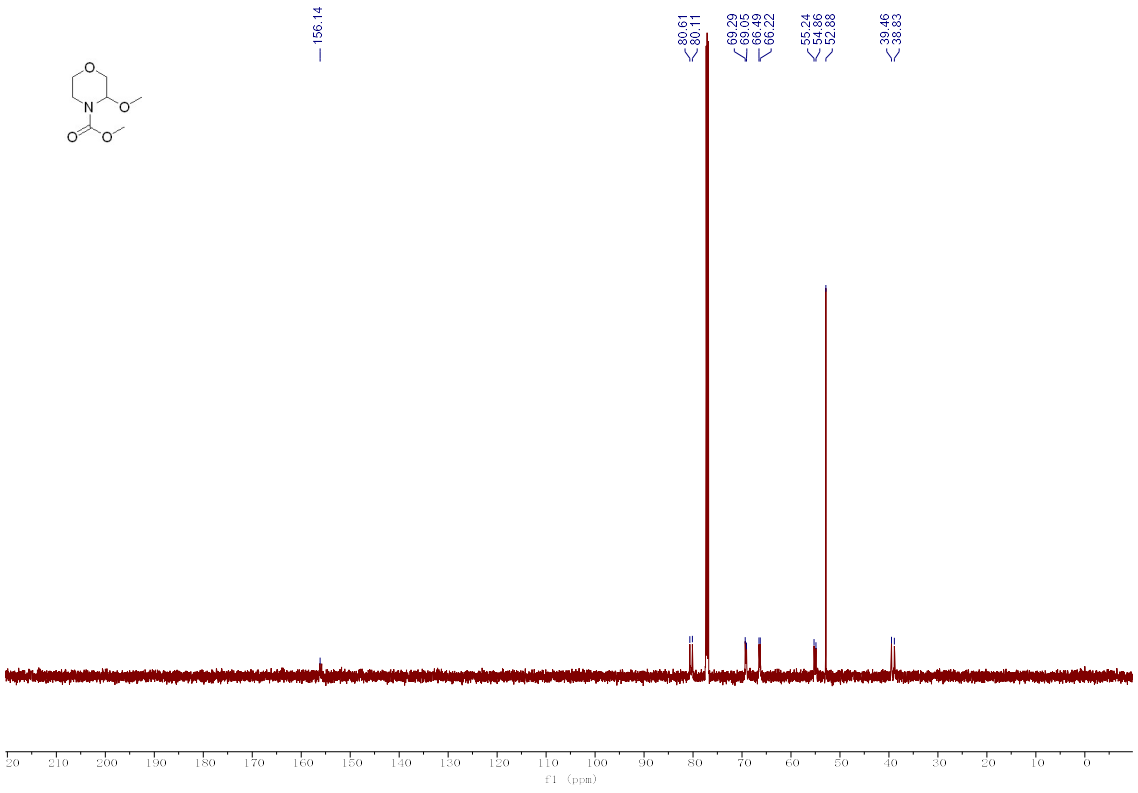

**$^1$H NMR** of **N-formyl-2-methoxypyrrolidin (3j)**



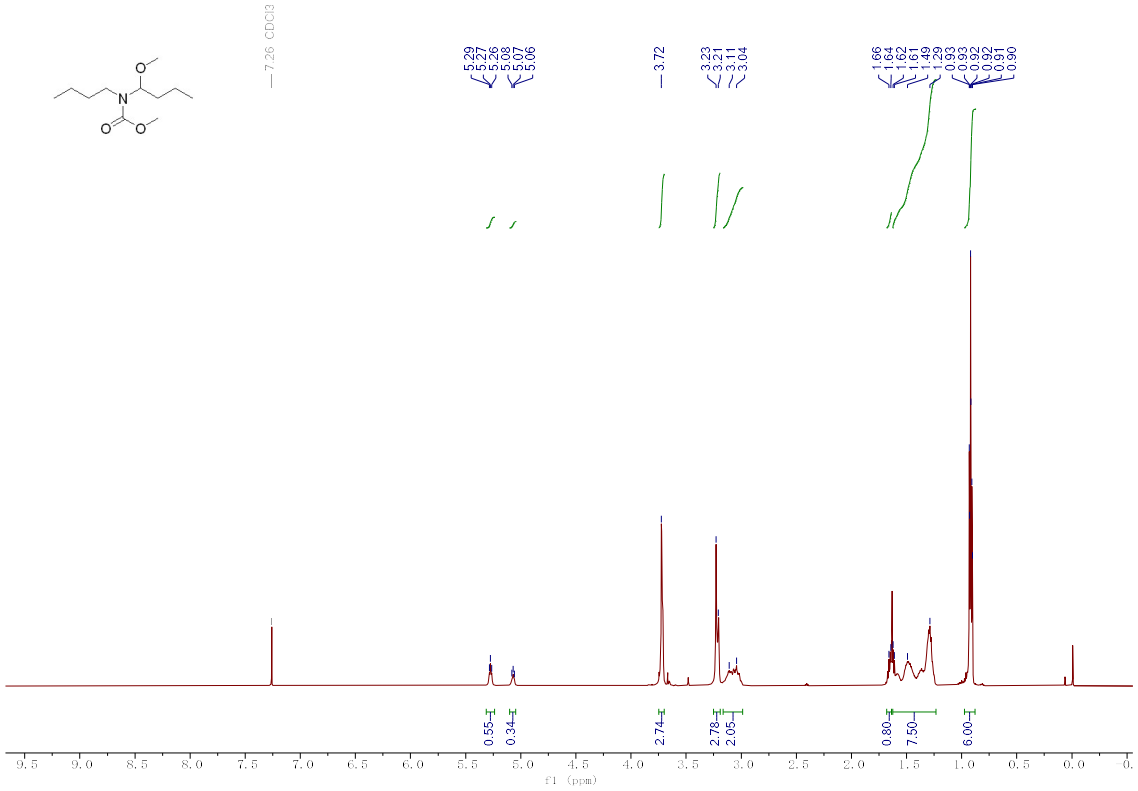
**$^{1}$H NMR** of **methyl 3-methoxymorpholine-4-carboxylate (3k)**



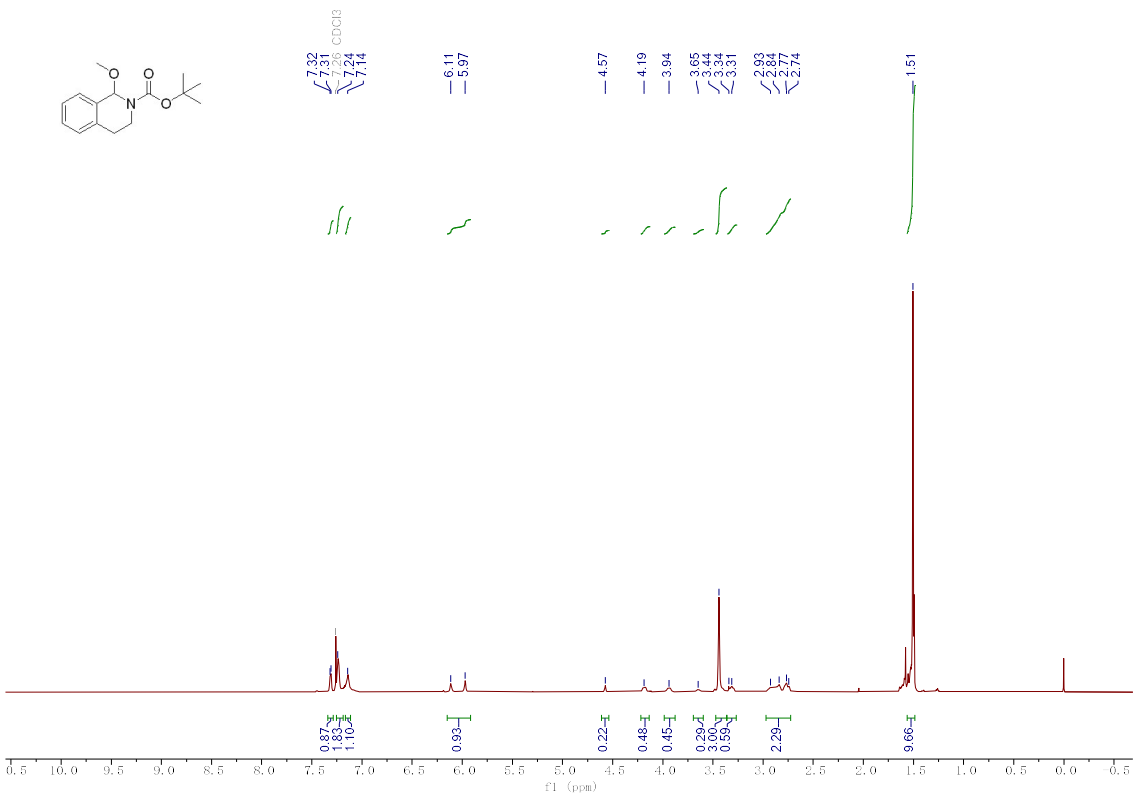

**$^{13}$C NMR** of **methyl 3-methoxymorpholine-4-carboxylate (3k)**



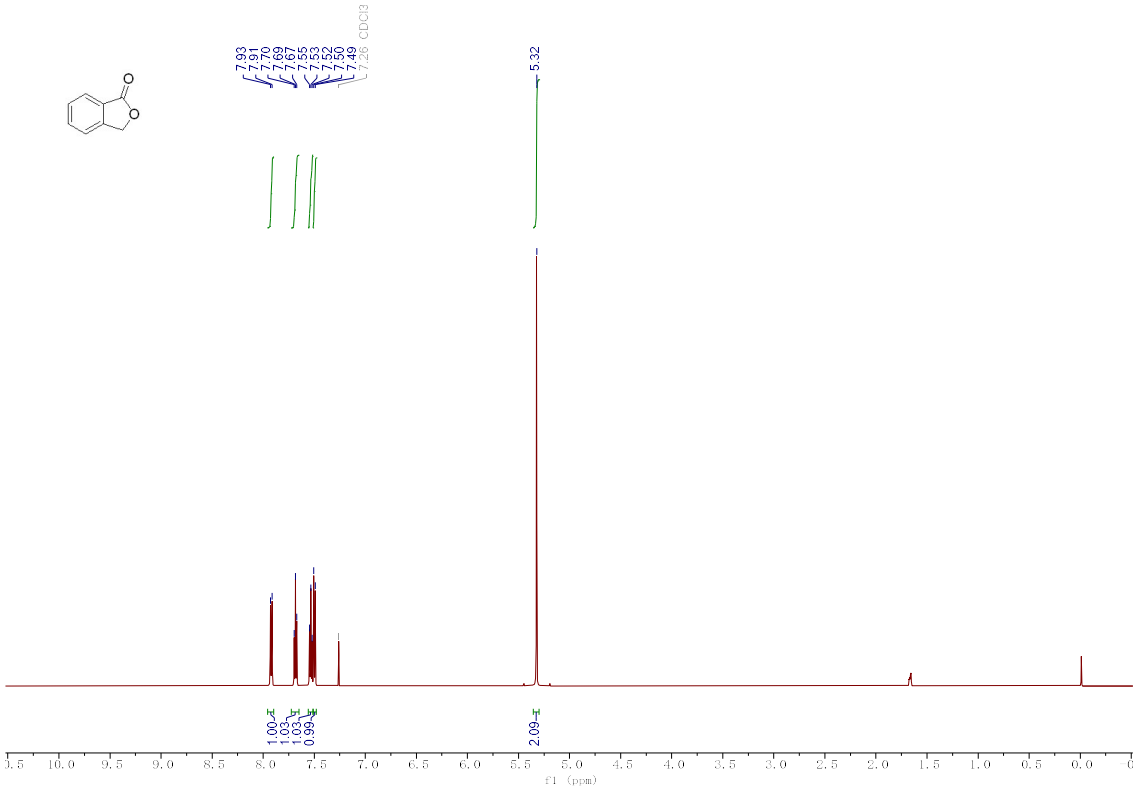
**$^1$H NMR** of **methyl butyl(1-methoxybutyl)carbamate (3l)**



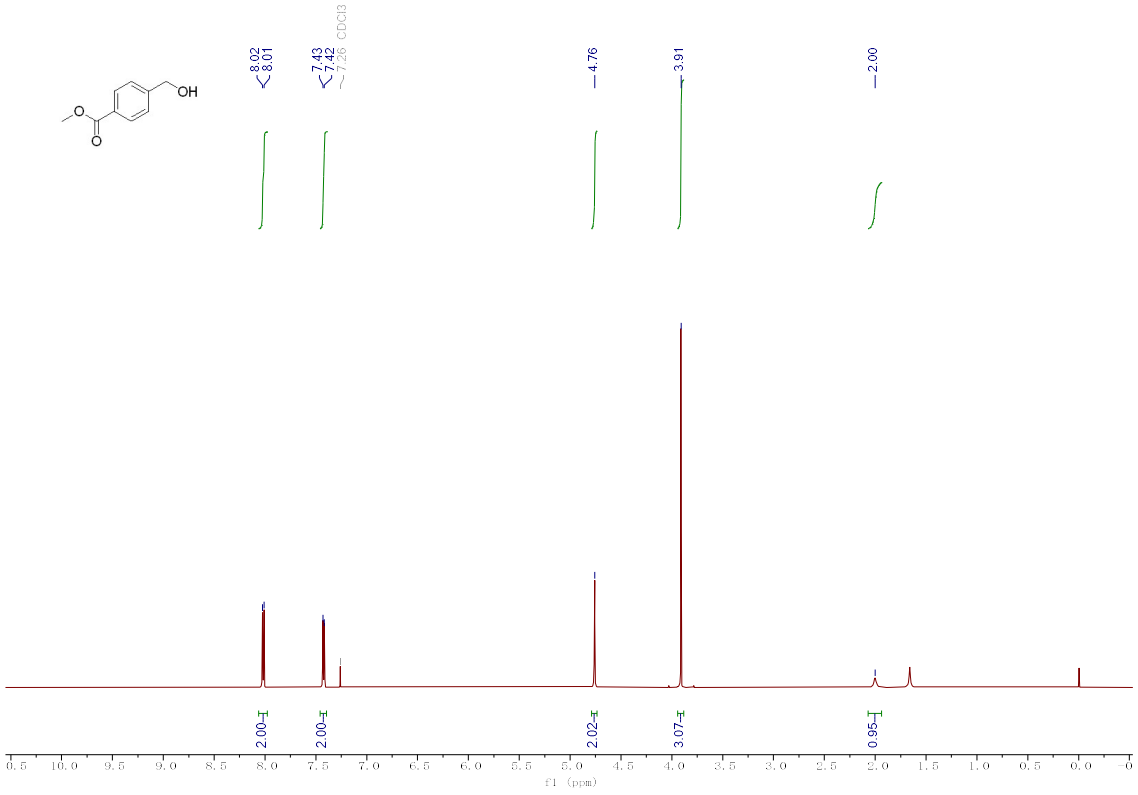

**$^1$H NMR** of **tert-butyl 1-methoxy-3,4-dihydroisoquinoline-2(1H)-carboxylate (3m)**



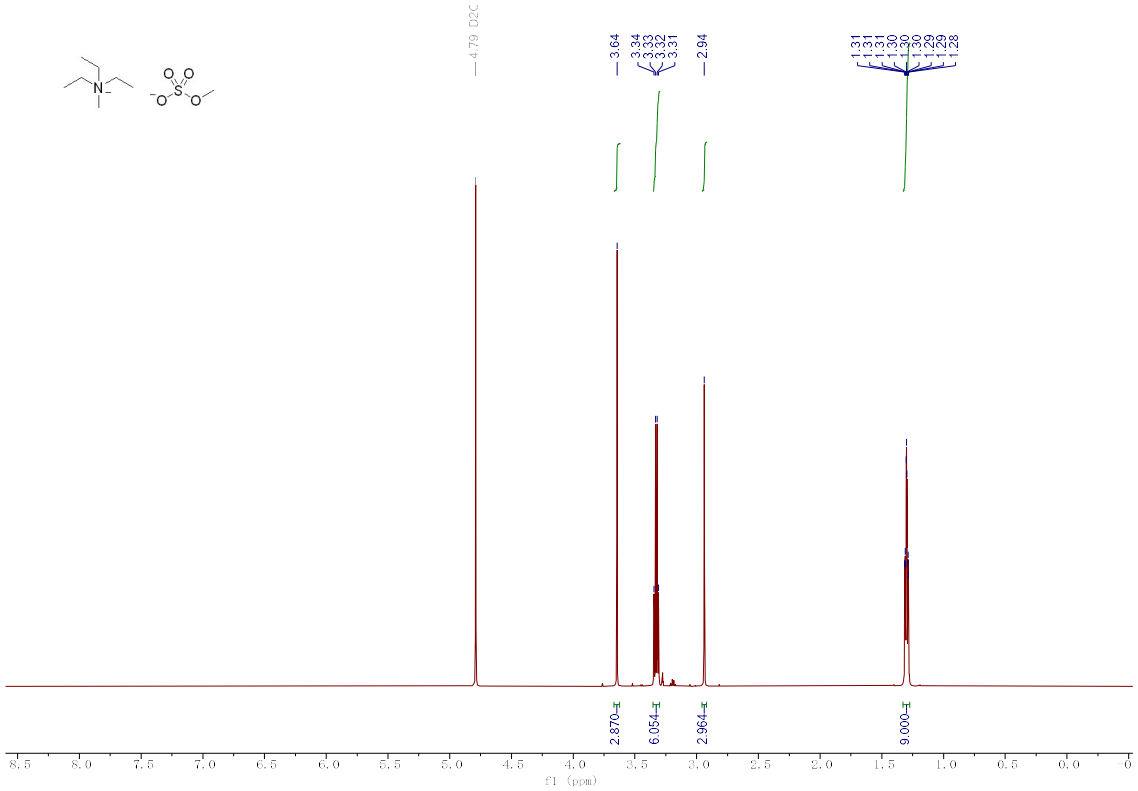
**$^1$H NMR** of **2-benzofuran-1(3H)-one (4a)**



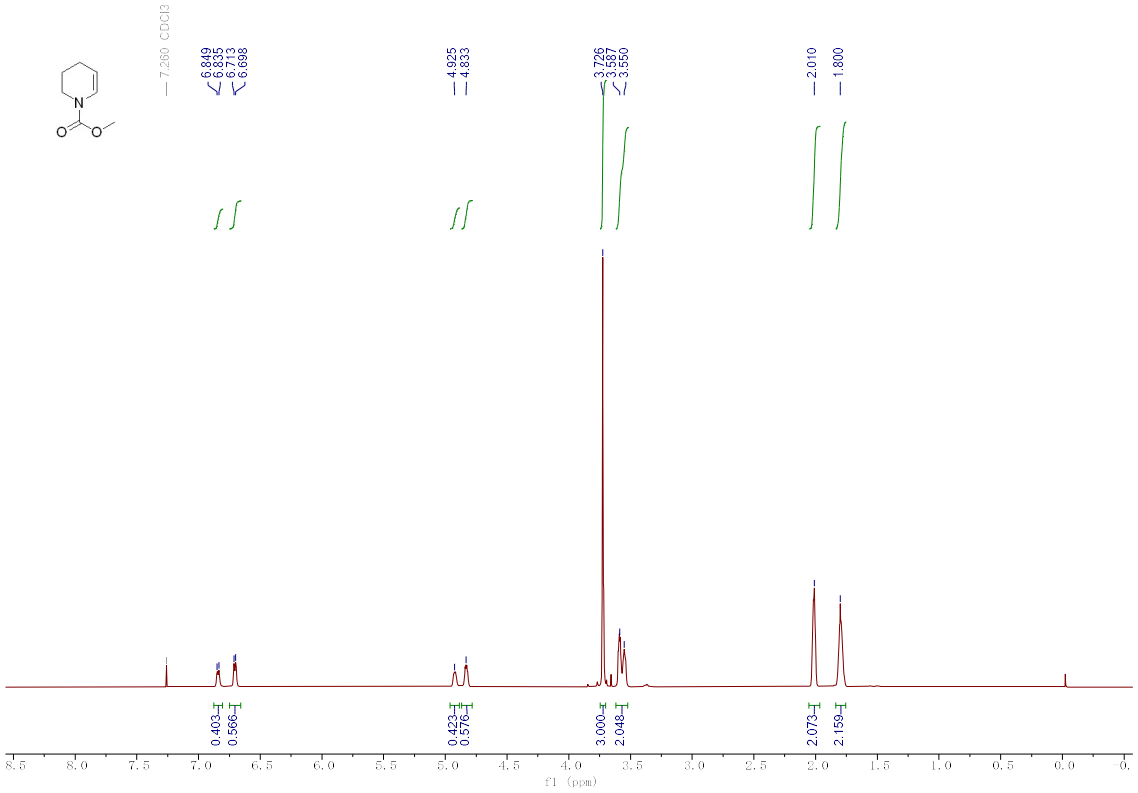

**$^1$H NMR** of **methyl 4-(hydroxymethyl)benzoate (4b)**



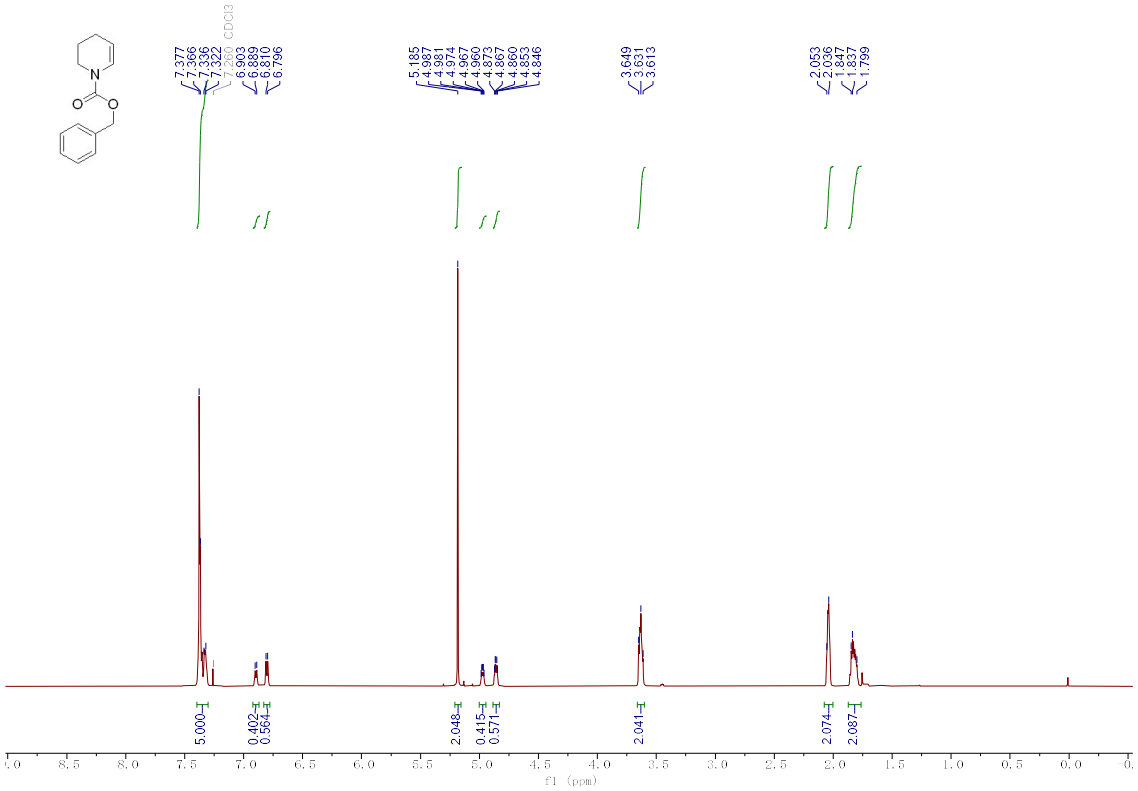
**$^1$H NMR** of **methyltriethylammonium methylsulfate**




**$^1$H NMR** of **3,4-dihydropyridine-1(2*H*)-carboxylate**

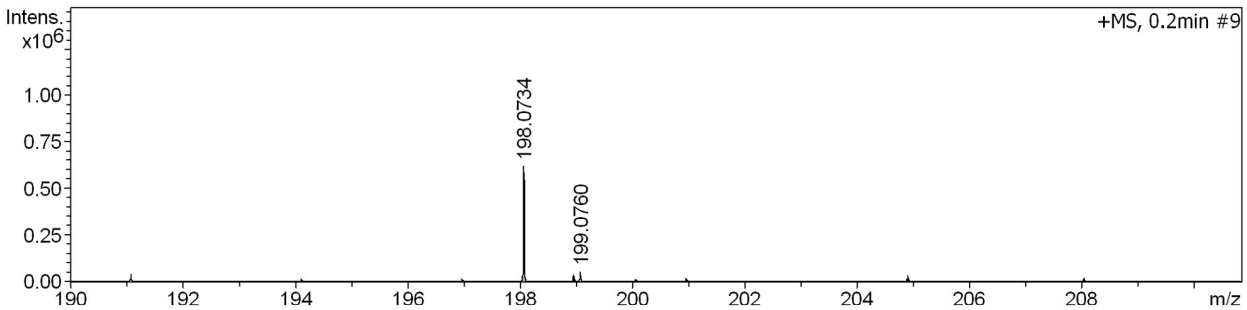


**$^1$H NMR** of **benzyl 3,4-Dihydropyridine-1(2*H*)-carboxylate**




**HRMS(ESI) of Methyl 3-methoxymorpholine-4-carboxylate (3k)**

| **Acquisition Parameter** | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 1.5 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 6.0 l/min |
| Scan End | 1350 m/z | Set Collision Cell RF | 700.0 Vpp | Set Divert Valve | Waste |



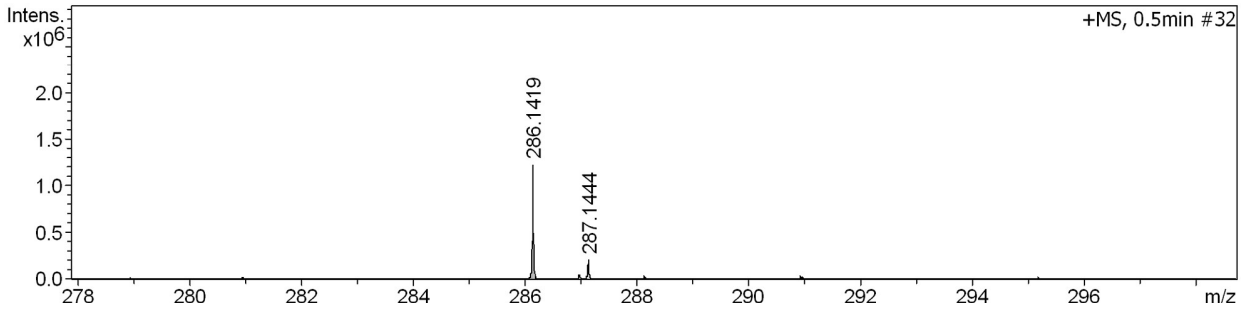

| # | m/z | Res. | S/N | I | I % | FWHM |
|---|---|---|---|---|---|---|
| 1 | 198.0734 | 17593 | 893.2 | 620540 | 100.0 | 0.0113 |
| 2 | 199.0760 | 16242 | 79.1 | 55176 | 8.9 | 0.0123 |
| 3 | 200.0799 | 8508 | 11.9 | 8360 | 1.3 | 0.0235 |

| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | | Score | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 198.0734 | 1 | C7H13NNaO4 | 198.0737 | 1.7 | 4.0 | 1 | 100.00 | 1.5 | even | ok |

**HRMS(ESI)** of **Tert-butyl 1-methoxy-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (3m)**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 1.5 Bar |
| Focus | Active | Set Capillary | 4500 V | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 6.0 l/min |
| Scan End | 1350 m/z | Set Collision Cell RF | 700.0 Vpp | Set Divert Valve | Waste |




| # | m/z | Res. | S/N | I | I % | FWHM |
|---|---|---|---|---|---|---|
| 1 | 286.1419 | 19431 | 1267.8 | 1223380 | 100.0 | 0.0147 |
| 2 | 287.1444 | 15741 | 212.7 | 205728 | 16.8 | 0.0182 |
| 3 | 288.1472 | 13311 | 23.7 | 23000 | 1.9 | 0.0216 |

| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | | Score | rdb | $e^-$ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 286.1419 | 1 | C15H21NNaO3 | 286.1414 | -2.0 | 0.9 | 1 | 100.00 | 5.5 | even | ok |

## 11. GC charts of crude products after paired electrolysis

**GC-FID** of crude products N-formyl-2-methoxypyrrolidin (**3j**) and 2-benzofuran-1(3*H*)-one (**4a**) after electrolysis

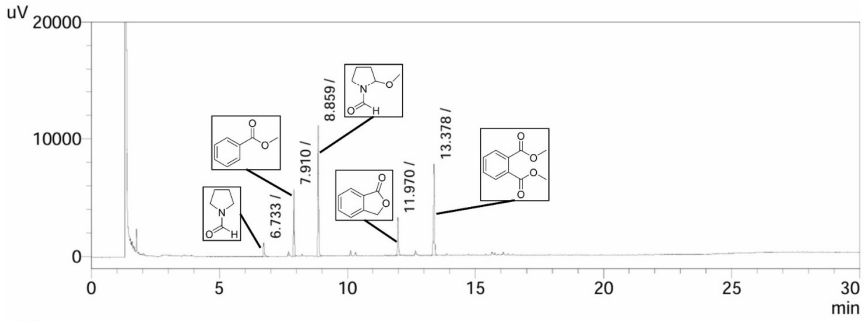
=== Shimadzu LabSolutions Analysis Report ===

Sample Name :
Vial# : 30
Sample Type : 未知
Date Acquired : 2024/1/5 21:13:50
Date Processed : 2025/3/18 13:38:03

Sample ID :
Injection Volume : 1 uL

Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\LZH\lzh-C97.gcd
Method Filename : D:\常用方法290度30分钟.gcm
Batch Filename : E:\LHM\0718\1.qcb




FID1

| Peak# | Ret. Time | Height | Area | Area% | Conc. | Mark |
|---|---|---|---|---|---|---|
| 1 | 6.733 | 1166 | 2851 | 4.013 | 0.000 | M |
| 2 | 7.910 | 5592 | 12502 | 17.602 | 0.000 | |
| 3 | 8.859 | 11026 | 25956 | 36.543 | 0.000 | |
| 4 | 11.970 | 3200 | 7807 | 10.992 | 0.000 | M |
| 5 | 13.378 | 7719 | 21912 | 30.850 | 0.000 | |
| 总计 | | 28702 | 71027 | 100.000 | | |

**GC-FID** of crude products methyl 2-methoxypiperidine-1-carboxylate (**3a**) and phthalic acid after electrolysis

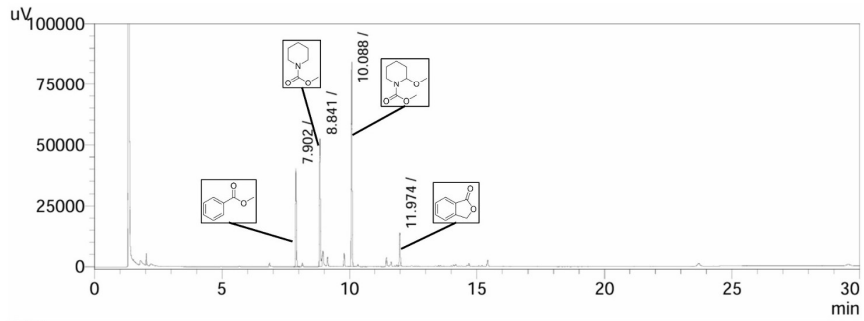
=== Shimadzu LabSolutions Analysis Report ===

Sample Name :
Vial# : 41
Sample Type : 未知
Date Acquired : 2024/3/27 11:31:15
Date Processed : 2025/3/18 13:50:49

Sample ID :
Injection Volume : 1 uL

Acquired by : System Administrator
Modified by : System Administrator

Data Filename : E:\LZH\lzh-C116-ersuan-252.gcd
Method Filename : D:\常用方法290度30分钟.gcm
Batch Filename : E:\LHM\0718\1.qcb




FID1

| Peak# | Ret. Time | Height | Area | Area% | Conc. | Mark |
|---|---|---|---|---|---|---|
| 1 | 7.902 | 39955 | 86325 | 20.264 | 0.000 | M |
| 2 | 8.841 | 52079 | 119783 | 28.118 | 0.000 | M |
| 3 | 10.088 | 84060 | 188150 | 44.167 | 0.000 | M |
| 4 | 11.974 | 13472 | 31737 | 7.450 | 0.000 | M |
| 总计 | | 189566 | 425995 | 100.000 | | |

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