*Supporting Information*

# Synthesis of adiponitrile from dimethyl adipate and ammonia in vapor-phase over niobium oxide

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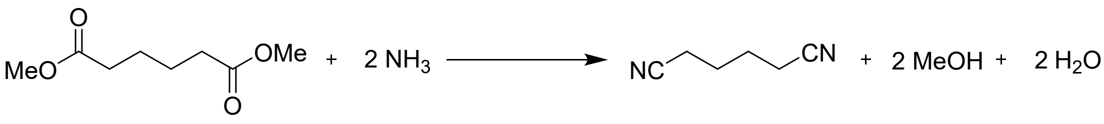
## Table of Content

## 1. The enthalpy change ($\Delta_r$H) for the nitrilation of DMA with $NH_3$

Table S1 Calculated thermochemistry values from Gaussian for the nitrilation reaction.[a]




DMA ADN

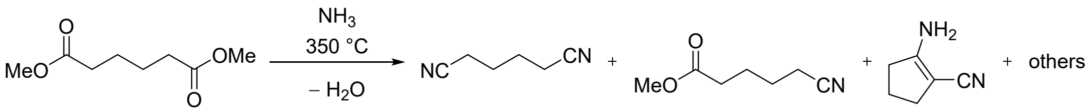
| | R1-DMA | R2-$NH_3$ | P1-AND | P2-MeOH | P3-$H_2O$ |
|---|---|---|---|---|---|
| $\varepsilon_0$ | -614.391 | -56.5827 | -343.0315 | -115.765 | -76.4585 |
| $H_{corr}$ (298K) | 0.23303 | 0.038083 | 0.139967 | 0.055341 | 0.025062 |
| $H_{corr}$ (573K) | 0.262485 | 0.042165 | 0.158251 | 0.061274 | 0.028677 |
| H (298K) | -614.158 | -56.545 | -342.892 | -115.710 | -76.433 |
| H (573K) | -614.128 | -56.541 | -342.873 | -115.704 | -76.430 |

[a] All calculations were conducted using the Gaussian 09 D.01 program.[1] All values are in Hartrees. The geometries were optimized in 298.15 K and 573.15 K under gas phase conditions at the B3LYP/6-311+G(d,p) level. The usual way to calculate Gibbs free energies of reaction is to simply take the appropriate sums and differences for the reactants and products.

$\Delta rH^o(298\ K) = \Sigma(\varepsilon_0 + H_{corr})_{products} - \Sigma(\varepsilon_0 + H_{corr})_{reactions}$

## 2. Catalytic performance of metal oxides

Table S2. Catalytic performance of metal oxides in the nitrilation of dimethyl adipate[a]



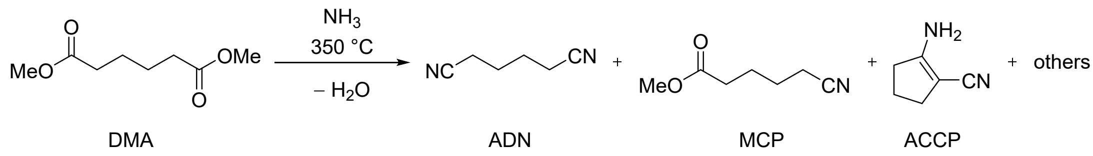

DMA ADN MCP ACCP

| Entry | Cat. | Conv./% | Yield /% | | | | Selectivity /% | | $Y_{MCP}/Y_{ADN}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | ADN | MCP | ACCP | Others | ADN | ADN+MCP | |
| 1 | Glass beads | 7.7 | 0 | 0 | 0 | 3.5 | | 0 | 0 |
| *Acidic metal oxides* | | | | | | | | | |
| 2 | $WO_3$ | 61.0 | 29.7 | 17.8 | 0.4 | 13.1 | 48.7 | 77.9 | 0.030 |
| 3 | $Nb_2O_5$ | 66.5 | 42.2 | 13.6 | 1.4 | 9.3 | 63.5 | 83.9 | 0.041 |
| 4 | $V_2O_5$ | 71.5 | 29.0 | 9.6 | 1.6 | 31.3 | 40.6 | 54.0 | 0.033 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5 | $Ta_2O_5$ | 94.5 | 59.6 | 4.5 | 2.7 | 27.7 | 63.1 | 67.8 | 0.007 |
| *Amphoteric metal oxides* | | | | | | | | | |
| 6 | ZnO | 75.6 | 7.7 | 5.7 | 0.9 | 61.3 | 10.2 | 17.7 | 0.015 |
| 7 | $Al_2O_3$ | 95.5 | 6.2 | 0.9 | 0.6 | 87.8 | 6.5 | 7.4 | 0.009 |
| 8 | $Fe_2O_3$ | 95.6 | 3.9 | 0.5 | 0.5 | 90.7 | 4.1 | 4.6 | 0.003 |
| 9 | $ZrO_2$ | 99.7 | 0.1 | 0.2 | 0.5 | 98.9 | 0.1 | 0.3 | 0.001 |
| 10 | $TiO_2$ | 96.1 | 45.1 | 15.4 | 1.0 | 34.6 | 46.9 | 63.0 | 0.002 |
| 11 | $CeO_2$ | 45.6 | 0.4 | 1.0 | 0.0 | 44.2 | 0.9 | 3.1 | 0.010 |
| *Basic metal oxides* | | | | | | | | | |
| 12 | CaO | 27.5 | 0.3 | 1.9 | 0 | 25.3 | 1.1 | 8.0 | 0.010 |
| 13 | MgO | 19.6 | 0.0 | 0.0 | 0 | 19.6 | 0.0 | 0 | 0 |

[a] Reaction condition: $T$: 350 °C, DMA: 18.3 mmol·h$^{-1}$, $NH_3$: 4.9 L·h$^{-1}$, $NH_3$/DMA = 12:1, LHSV: 0.5 h$^{-1}$, TOS 7 h.

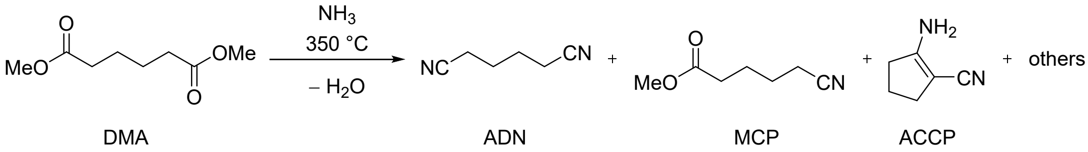
Table S3. Influence of the calcination temperature for preparation of niobium oxide[a]




| Entry | Cat. | Conv ./% | Yield /% | | | | Selectivity /% | | $Y_{MCP}/Y_{ADN}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | ADN | MCP | ACCP | Others | ADN | ADN+MCP | |
| 1 | $Nb_2O_5$-400 | 99.3 | 63.8 | 3.2 | 1.0 | 31.3 | 64.3 | 67.5 | 0.049 |
| 2 | $Nb_2O_5$-600 | 100.0 | 39.5 | 0.3 | 0.2 | 60.0 | 39.5 | 39.8 | 0.008 |
| 3 | $Nb_2O_5$-700 | 99.9 | 58.7 | 0.3 | 3.0 | 37.9 | 58.7 | 59.1 | 0.004 |
| 4 | $Nb_2O_5$-900 | 98.2 | 72.9 | 2.8 | 2.0 | 20.5 | 74.3 | 77.1 | 0.038 |
| 5 | $Nb_2O_5$-1100 | 66.5 | 42.2 | 13.6 | 1.4 | 9.3 | 63.5 | 83.9 | 0.322 |
| 6 | $Nb_2O_5$-C | 67.2 | 43.1 | 12.9 | 1.7 | 9.5 | 64.8 | 83.3 | 0.299 |

[a] Reaction condition: $T$: 350 °C, DMA: 18.3 mmol·h$^{-1}$, $NH_3$: 4.9 L·h$^{-1}$, $NH_3$/DMA = 12:1, LHSV: 0.5 h$^{-1}$, TOS 7 h.

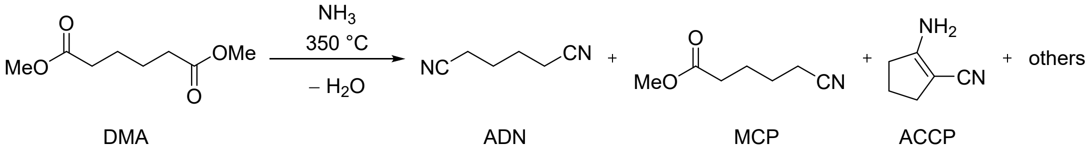
Table S4. Effect of the reaction temperature on the nitrilation of DMA with $NH_3$ using $Nb_2O_5$-1100[a]



| Entry | Temp. | Conv./% | Yield /% | | | | Selectivity /% | | $Y_{MCP}/Y_{ADN}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | ADN | MCP | ACCP | Others | ADN | ADN+MCP | |
| 1 | 310 | 34.2 | 15.1 | 10.6 | 0.4 | 8.1 | 44.2 | 75.1 | 0.701 |
| 2 | 330 | 50.1 | 30.5 | 10.1 | 0.8 | 8.7 | 60.9 | 81.0 | 0.331 |
| 3 | 350 | 66.5 | 42.2 | 13.6 | 1.4 | 9.3 | 63.5 | 83.9 | 0.322 |
| 4 | 370 | 76.4 | 57.4 | 12.6 | 2.0 | 4.4 | 75.1 | 91.6 | 0.220 |
| 5 | 390 | 83.2 | 54.2 | 6.7 | 2.6 | 19.7 | 65.1 | 73.2 | 0.123 |

[a] Reaction condition: DMA: 18.3 mmol·h$^{-1}$, $NH_3$: 4.9 L·h$^{-1}$, $NH_3$/DMA = 12:1, LHSV: 0.5 h$^{-1}$, TOS 7 h.

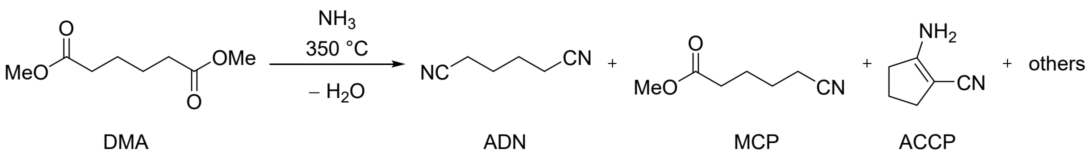
Table S5. Effect of LHSV on the nitrilation of DMA with $NH_3$ using $Nb_2O_5$-1100 [a]



| Entry | LHSV / h$^{-1}$ | Contact time / g-Cat.·h·mol$^{-1}$ | Conv. /% | Yield /% | | | | Selectivity /% | | $Y_{MCP}/Y_{ADN}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | ADN | MCP | ACCP | Others | ADN | ADN+MCP | |
| 1 | 0.15 | 1.49 | 97.3 | 74.6 | 2.8 | 2.4 | 17.5 | 76.7 | 79.5 | 0.037 |
| 2 | 0.20 | 1.12 | 97.7 | 82.4 | 2.6 | 2.7 | 10.0 | 84.3 | 87.0 | 0.032 |
| 3 | 0.25 | 0.90 | 90.7 | 72.4 | 5.8 | 2.4 | 10.1 | 79.8 | 86.2 | 0.080 |
| 4 | 0.30 | 0.75 | 93.0 | 69.0 | 6.3 | 2.3 | 15.4 | 74.2 | 81.0 | 0.091 |
| 5 | 0.35 | 0.64 | 81.5 | 60.3 | 9.3 | 2.1 | 9.8 | 74.0 | 85.4 | 0.154 |
| 6 | 0.50 | 0.45 | 76.4 | 57.4 | 12.6 | 2.0 | 4.4 | 75.1 | 91.6 | 0.207 |

[a] Reaction condition: *T*: 370 °C, $NH_3$/DMA = 12:1, TOS 7 h

Table S6. Effect of $NH_3$/DMA molar ratio on the nitrilation of DMA with $NH_3$ using $Nb_2O_5$-1100 [a]



| Entry | $NH_3$/DMA | Conv./% | Yield /% | Selectivity /% | $Y_{MCP}/Y_{ADN}$ |
|---|---|---|---|---|---|

| | | | ADN | MCP | ACCP | Others | ADN | ADN+MCP | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4 | 96.6 | 20.9 | 2.5 | 0.4 | 72.8 | 21.6 | 24.2 | 0.119 |
| 2 | 8 | 95.0 | 61.2 | 4.0 | 1.6 | 28.2 | 64.4 | 68.6 | 0.062 |
| 3 | 12 | 97.7 | 82.4 | 2.6 | 2.7 | 10.0 | 84.3 | 87.0 | 0.032 |
| 4 | 16 | 94.5 | 75.1 | 4.6 | 2.9 | 11.9 | 79.5 | 84.3 | 0.061 |
| 5 | 20 | 93.6 | 74.9 | 4.4 | 2.5 | 11.8 | 80.0 | 84.7 | 0.059 |
| 6 | 24 | 77.3 | 53.1 | 8.7 | 2.1 | 13.4 | 68.7 | 79.9 | 0.164 |

[a] Reaction condition: *T*: 370 °C, DMA: 7.3 mmol·h$^{-1}$, $NH_3$: 2.0 L·h$^{-1}$, LHSV: 0.2 h$^{-1}$, TOS 7 h

## 3. Acidic parameters of the series catalysts

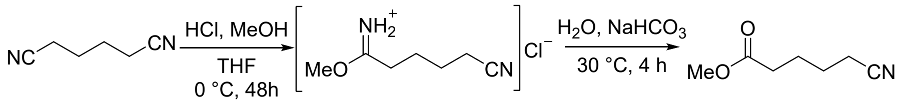
Table S7. Concentrations of Lewis (L) and Brønsted Acid Sites (B) That Bind Pyridine at 150 and 350 °C on $Nb_2O_5$-*T* (*T* = 400, 600, 700, 900, 1100)[a]

| Sample | 150 °C | | | | 350 °C | | | | $(B+L)_{350}/(B+L)_{150}$ |
|---|---|---|---|---|---|---|---|---|---|
| | B | L | B+L | B/L | B | L | B+L | B/L | |
| $Nb_2O_5$-400 | 9.2 | 60.0 | 69.2 | 0.15 | 5.1 | 40.3 | 45.4 | 0.13 | 65.6% |
| $Nb_2O_5$-600 | 3.9 | 49.4 | 53.3 | 0.08 | 2.1 | 19.0 | 21.1 | 0.11 | 39.6% |
| $Nb_2O_5$-700 | 1.9 | 26.9 | 28.8 | 0.07 | 1.0 | 11.9 | 12.9 | 0.08 | 44.8% |
| $Nb_2O_5$-900 | 1.6 | 21.8 | 23.4 | 0.07 | 0.9 | 9.8 | 10.7 | 0.09 | 45.7% |
| $Nb_2O_5$-1100 | 1.0 | 16.9 | 17.9 | 0.06 | 0.7 | 8.7 | 9.5 | 0.09 | 53.1% |

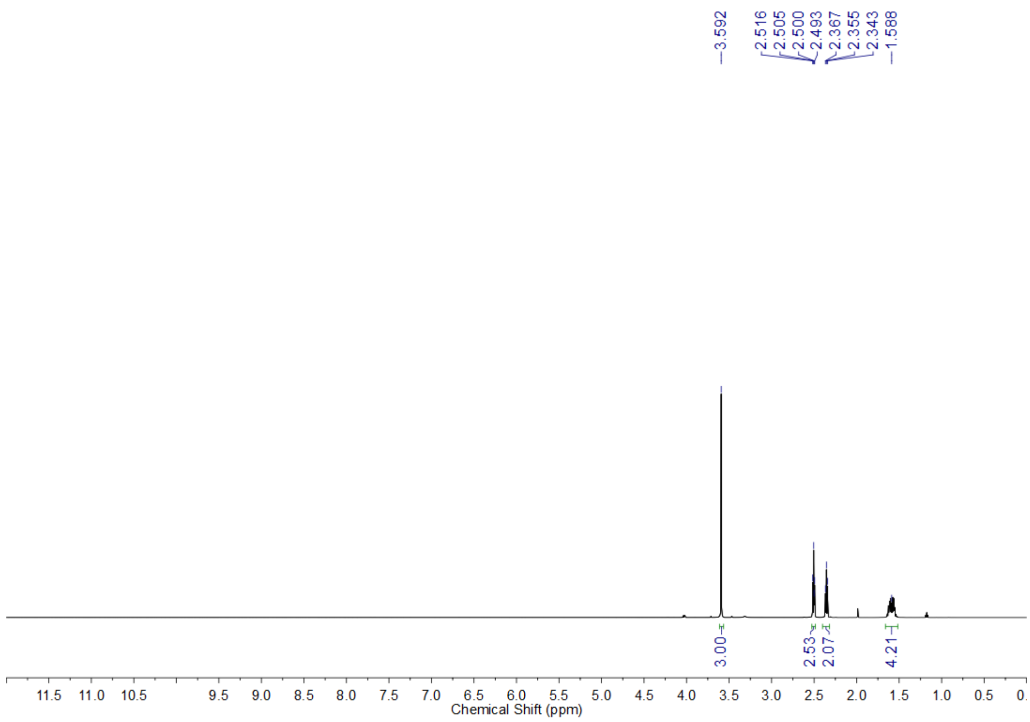
[a] Concentrations in μmol·g$^{-1}$

## 4. Preparation of MCP, ACCP and ADN

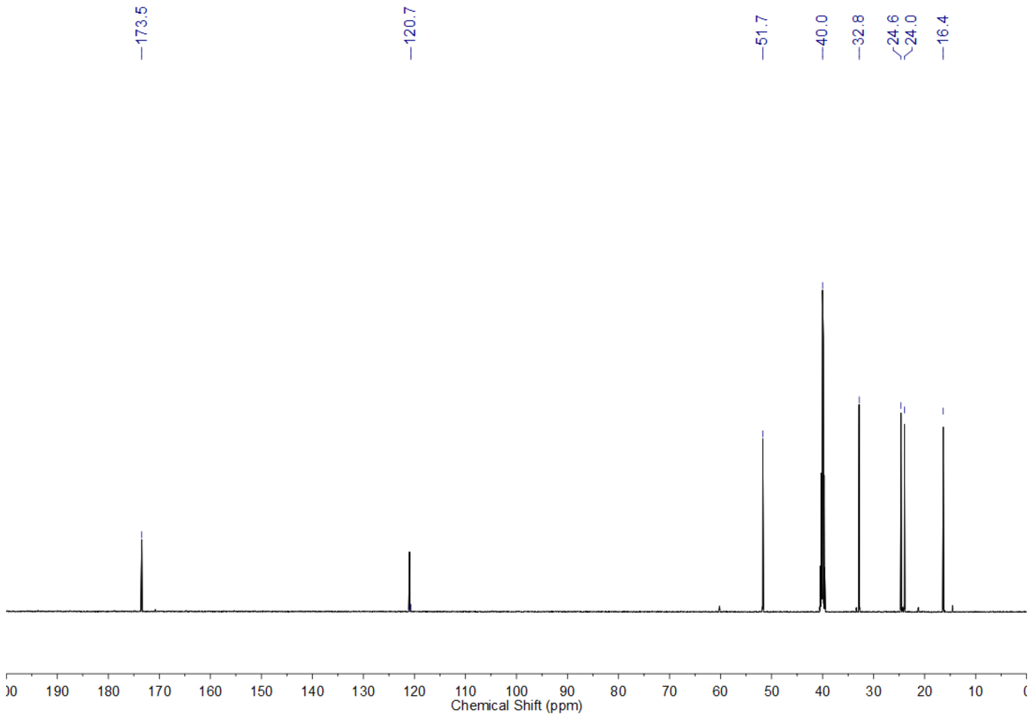
### 4.1. Methyl 5-cyanopentanoate (MCP)




According to the literature,[2] ADN (50 mmol, 5.405 g) and methanol (50 mmol, 1.600 g) were dissolved in THF (50 mL) in a 100 mL three-necked flask. The mixture was stirred at 0 °C for 48 h with a continuous flow of dry HCl. The produced white solid was filtered and washed with petroleum ether and THF. The white solid was slowly added to saturated $NaHCO_3$ solution (200 mL) at 0 °C, and the solution was stirred at 30 °C for 4 h. Then the solution was extracted with ethyl acetate (200 mL*3). The organic phase was dried, filtered and concentrated to give the product MCP. **$^1$H NMR** (600 MHz, 298 K, DMSO): $\delta = 3.59$ (s, 3H), 2.51(t, $^3J_{HH} = 7.2$ Hz, 2H), 2.36 (t, $^3J_{HH} = 7.2$ Hz, 2H), 1.59 (m, 4H). **$^{13}$C {$^1$H} NMR** (151 MHz, 298K, DMSO) $\delta = 173.5$, 120.7, 51.7, 32.8, 24.6, 24.0, 16.4.

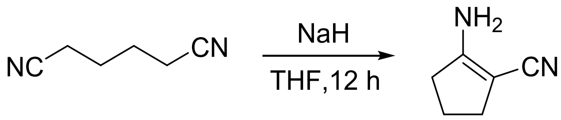



**$^1$H NMR** (151 MHz, 298K, DMSO) of MCP

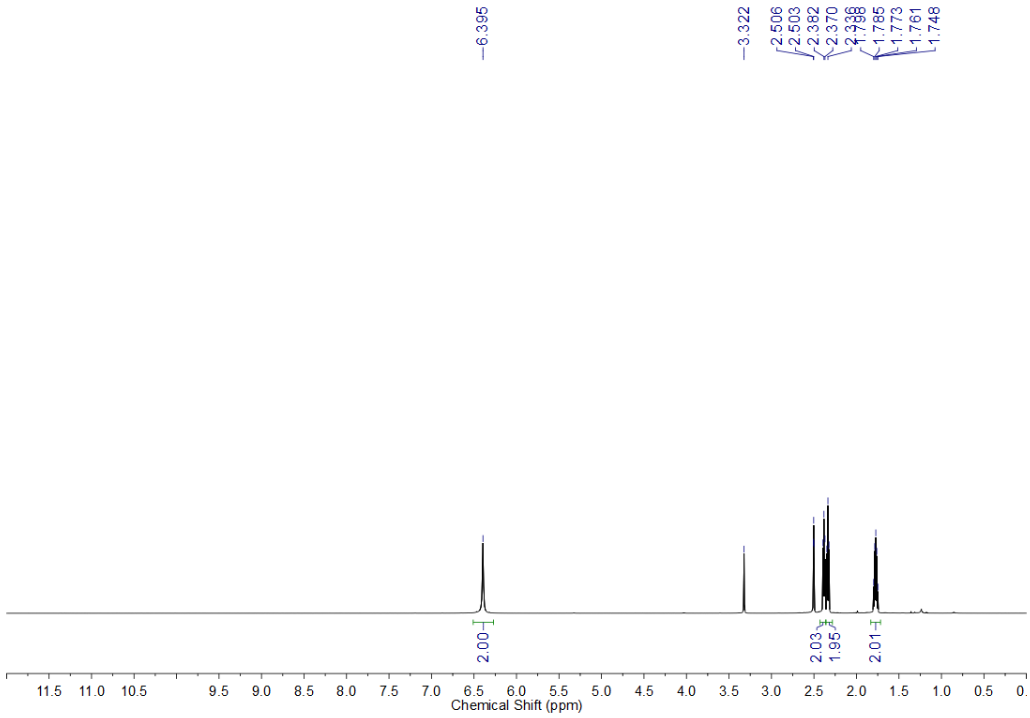



**$^{13}$C {$^{1}$H} NMR** (151 MHz, 298K, DMSO) of MCP

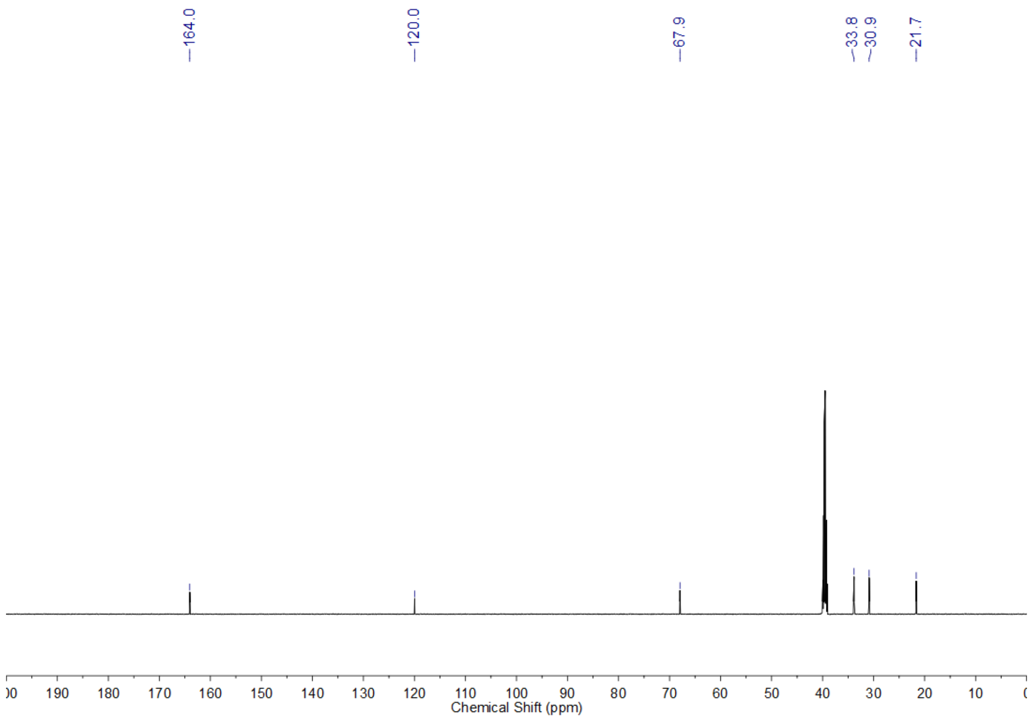
### 4.2. 1-Amino-2-cyano-1-cyclopentene (ACCP)




According to the literature,[3] NaH (60% dispersion in mineral oil, 38.5 mmol, 1.54 g) and dry THF (70 mL) were added to a 250 mL three-necked flask, adiponitrile (35 mmol, 3.79 g) was added, and the mixture was stirred at room temperature for 30 min. Then the mixture was stirred at the reflux temperature room temperature for 12 hours. The cooled reaction solution was quenched by added 30 mL of water and extracted with ethyl acetate (30 mL*3). The organic phase was dried, filtered and concentrated to give crude product. Pure ACCP product was obtained by recrystallization in ethanol. **$^{1}$H NMR** (600 MHz, 298 K, DMSO): $\delta$ = 6.40 (s, 2H), 2.38 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 2.34 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 1.77 (m, 2H). **$^{13}$C {$^{1}$H} NMR** (151 MHz, 298K, DMSO) $\delta$ = 164.1, 120.0, 68.0, 33.8, 30.9, 21.7.

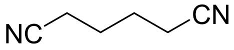



**$^1$H NMR** (600 MHz, 298 K, DMSO) of ACCP

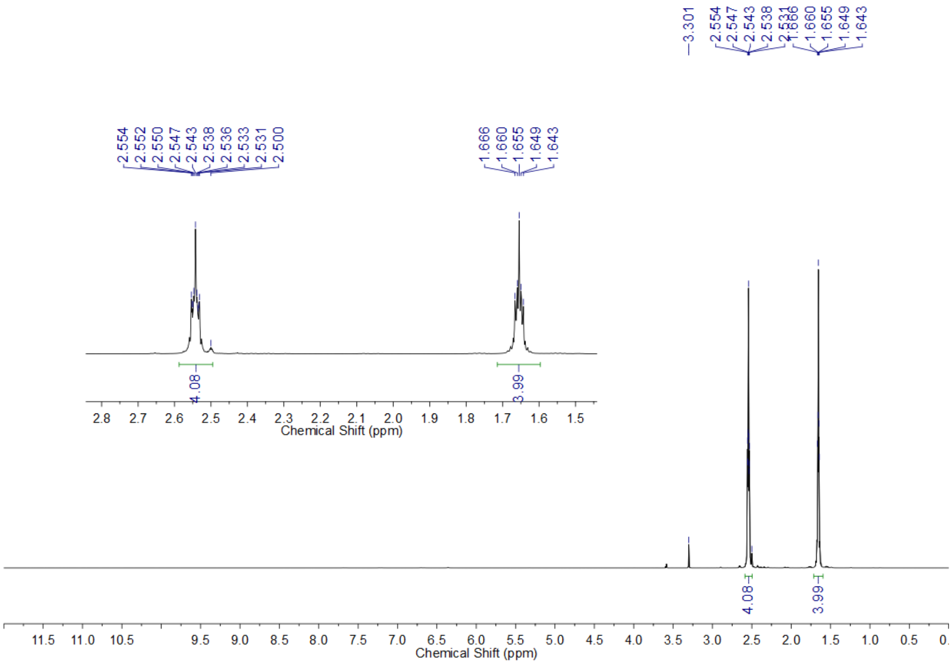



**$^{13}$C {$^1$H} NMR** (151 MHz, 298K, DMSO) of ACCP

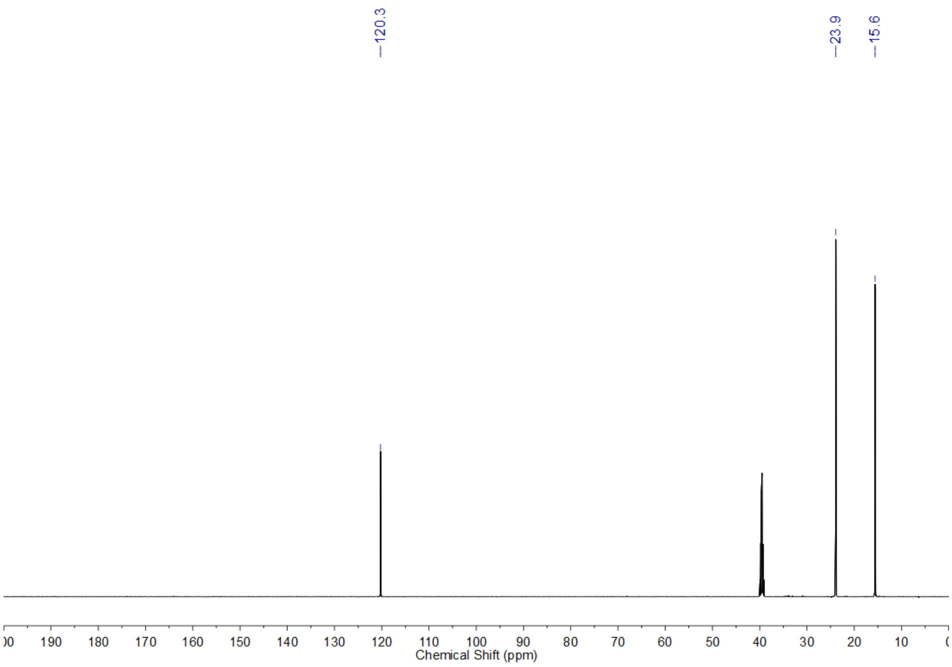
## 4.3. Adiponitrile (ADN)




The adiponitrile product was obtained by reduced-pressure distillation of crude product from the nitrilation of DMA and $NH_3$. **$^{1}$H NMR** (600 MHz, 298 K, DMSO): $\delta$ = 2.54 (m, 4H), 1.66 (m, 4H). **$^{13}$C {$^{1}$H} NMR** (151 MHz, 298K, DMSO) $\delta$ = 120.3, 21.7, 15.6.



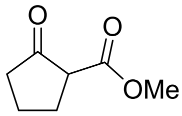

**$^{1}$H NMR** (600 MHz, 298 K, DMSO) of ADN




**$^{13}$C {$^{1}$H} NMR** (151 MHz, 298K, DMSO) of ADN

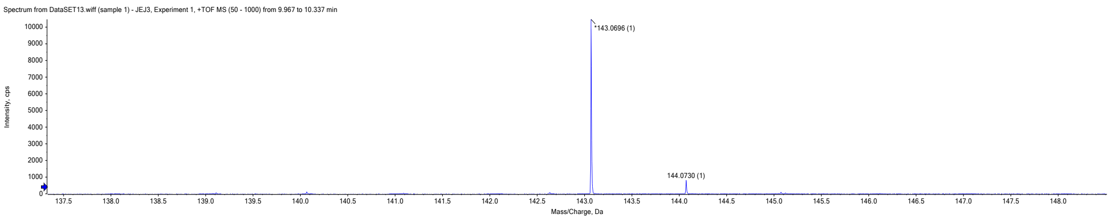
# 5. HRMS Data

## 5.1. 2-Oxocyclo-pentanecarboxylate (MOCPC)

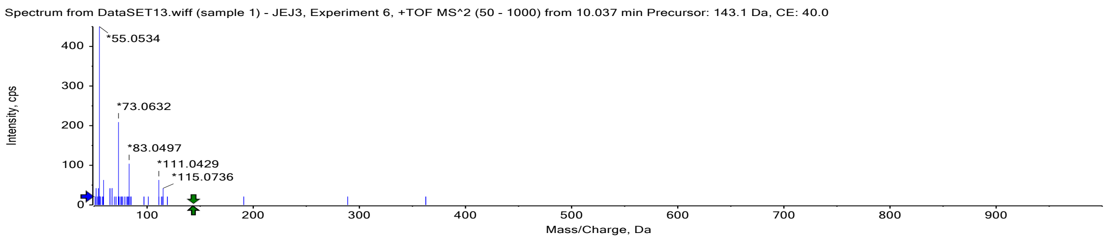



[MOCPC+H]$^+$ ($C_7H_{11}O_3$, Calculated: 143.0708), Found: 143.0696.

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：




➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search



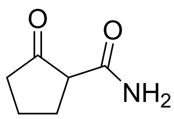

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：

Fragments | Peaks

| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 54.0457 | 9.33 | ☑ | 0.036 | ☑ |
| 55.0175 | 9.56 | ☑ | 0.000 | ☐ |
| 55.0534 | 100.00 | ☑ | 0.036 | ☐ |
| 59.0119 | 14.00 | ☑ | 0.001 | ☐ |
| 67.0549 | 9.33 | ☑ | 0.037 | ☐ |
| 73.0632 | 46.44 | ☑ | 0.035 | ☐ |
| 83.0497 | 23.11 | ☑ | 0.001 | ☐ |
| 111.0429 | 14.00 | ☑ | 0.001 | ☐ |
| 115.0736 | 9.33 | ☑ | 0.002 | ☐ |

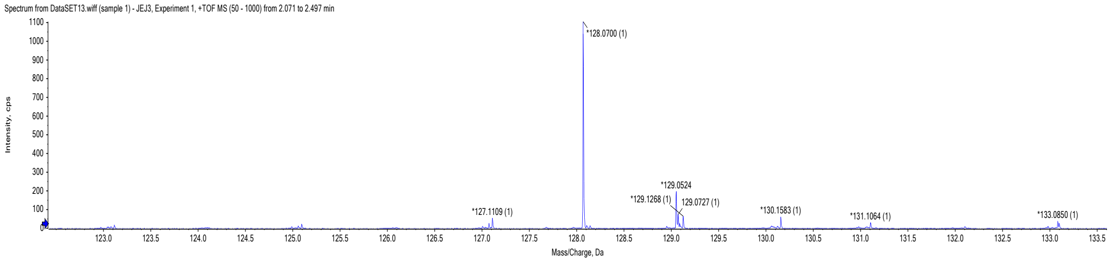
Matches: 9 of 9 peaks, 100.0% of total intensity

## 5.2. 2-Oxocyclopentanecarboxamide (OCPCA)

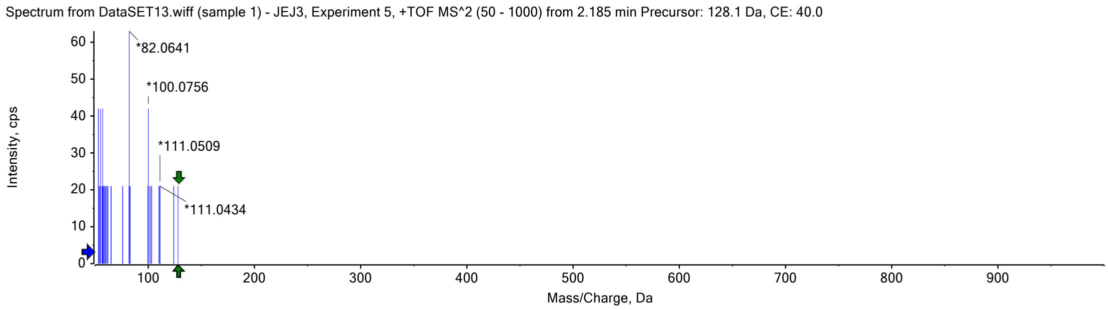



[**OCPCA**+H]$^+$ ($C_6H_{10}NO_2$, Calculated: 128.0712), Found: 128.0700.

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：




➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search



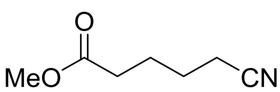

➢ Matching degree between fragments and candidate molecules

Fragments | Peaks

| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 55.0537 | 66.67 | ☑ | 0.036 | ☐ |
| 57.0677 | 66.67 | ☑ | 0.034 | ☐ |
| 57.9389 | 33.33 | ☑ | 0.090 | ☐ |
| 82.0641 | 100.00 | ☑ | 0.035 | ☐ |
| 83.0540 | 33.33 | ☑ | 0.005 | ☐ |
| 100.0756 | 66.67 | ☑ | 0.000 | ☐ |
| 111.0434 | 33.33 | ☑ | 0.001 | ☐ |
| 111.0509 | 33.33 | ☑ | 0.007 | ☐ |
| 128.0669 | 33.33 | ☑ | 0.004 | ☐ |

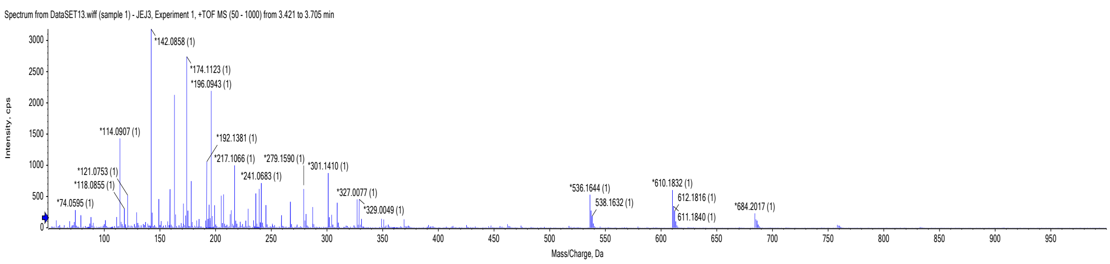
Matches: 9 of 9 peaks, 100.0% of total intensity

## 5.3. Methyl 5-cyanopentanoate (MCP)

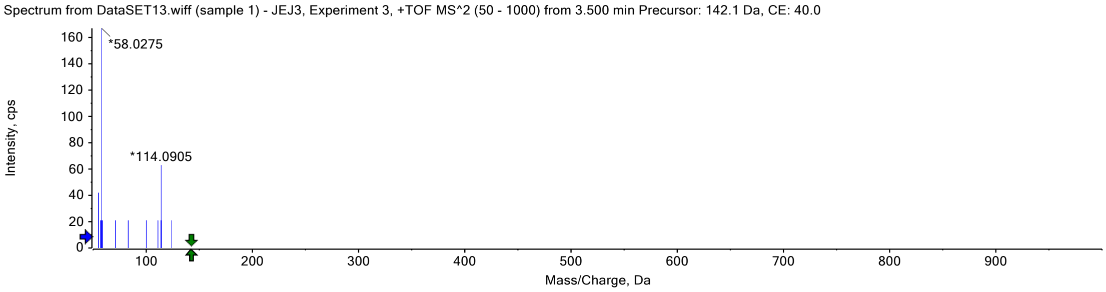



[**MCP**+H]$^+$ ($C_7H_{11}NO_2$, Calculated: 142.0868), Found:142.0858

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：



➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search



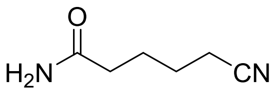

➢ Matching degree between fragments and candidate molecules

Fragments | Peaks

| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 58.0275 | 100.00 | ☑ | 0.023 | ☑ |
| 59.2115 | 12.57 | ☑ | 0.199 | ☐ |
| 114.0905 | 37.72 | ☑ | 0.023 | ☑ |

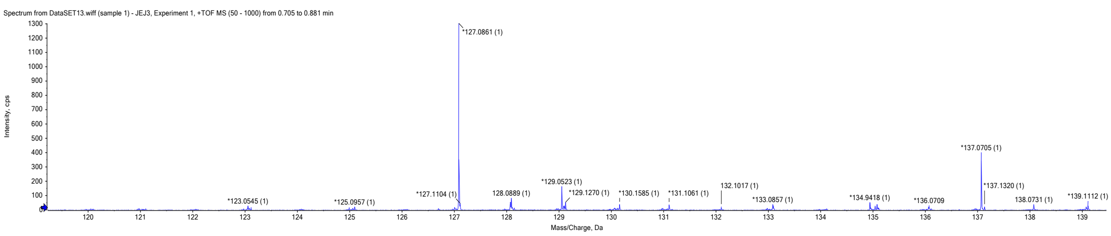
Matches: 3 of 3 peaks, 100.0% of total intensity

## 5.4. 5-Cyanopentanamide (CPA)

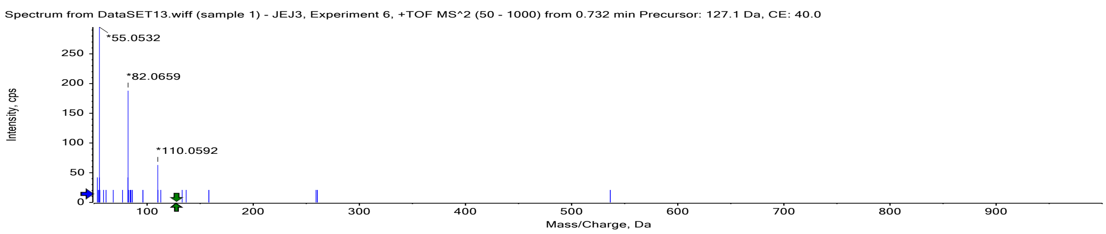



[**CPA**+H]$^+$ ($C_6H_{11}N_2O$, Calculated: 127.0871), Found: 127.0861.

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：




➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search

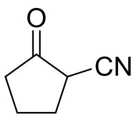


➢ Matching degree between fragments and candidate molecules

| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 53.0391 | 14.24 | ☑ | 0.037 | ☐ |
| 54.0336 | 28.14 | ☑ | 0.000 | ☐ |
| 54.0393 | 14.24 | ☑ | 0.005 | ☐ |
| 54.8948 | 7.12 | ☑ | 0.123 | ☐ |
| 55.0532 | 100.00 | ☑ | 0.035 | ☐ |
| 59.0351 | 7.12 | ☑ | 0.014 | ☐ |
| 82.0659 | 63.73 | ☑ | 0.001 | ☐ |
| 82.0747 | 7.12 | ☑ | 0.010 | ☐ |
| 110.0592 | 21.36 | ☑ | 0.001 | ☐ |

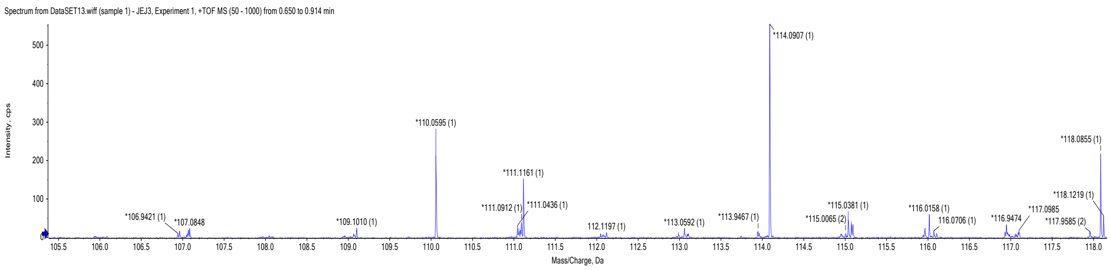
Matches: 9 of 9 peaks, 100.0% of total intensity

## 5.5. 2-Oxocyclopentanecarbonitrile (OCPCN)

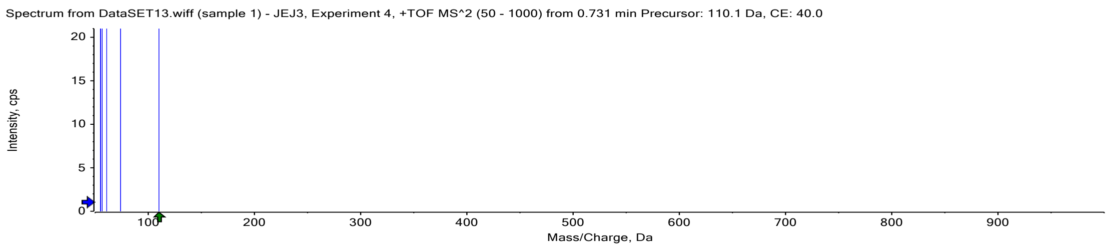



[**OCPCN**+H]$^+$ ($C_6H_8NO$, Calculated: 110.0606), Found: 110.0595.

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：




➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search

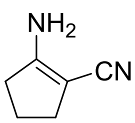



➢ Matching degree between fragments and candidate molecules

| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 55.0561 | 100.00 | ☑ | 0.038 | ☐ |

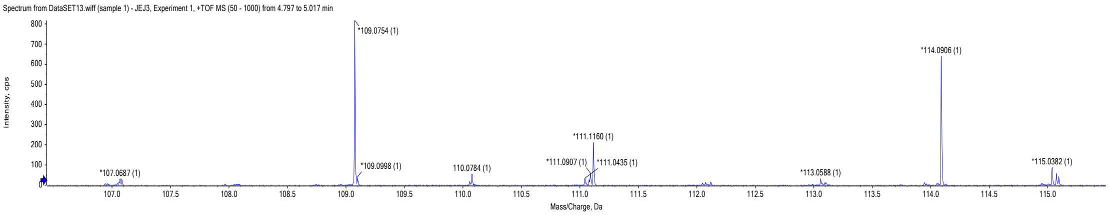
Matches: 1 of 1 peaks, 100.0% of total intensity

## 5.6. 1-Amino-2-cyano-1-cyclopentene (ACCP)

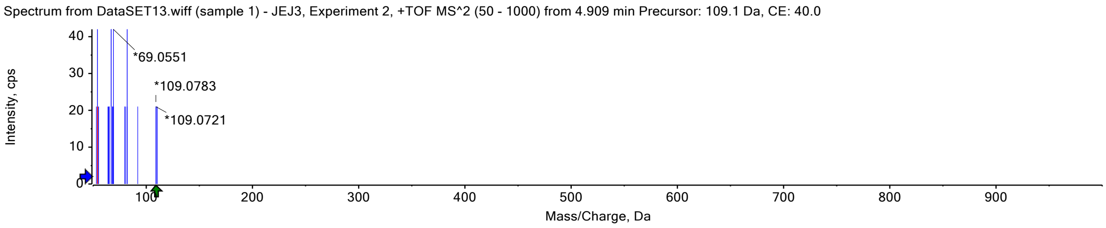



[**ACCP**+H]$^+$ ($C_6H_9N_2$, Calculated: 109.0766), 109.0754.

➢ Evaluation of TOF-MS: Accurate Mass, Isotopes：




➢ Evaluation of TOF-MS/MS (Library Search): MS/MS search



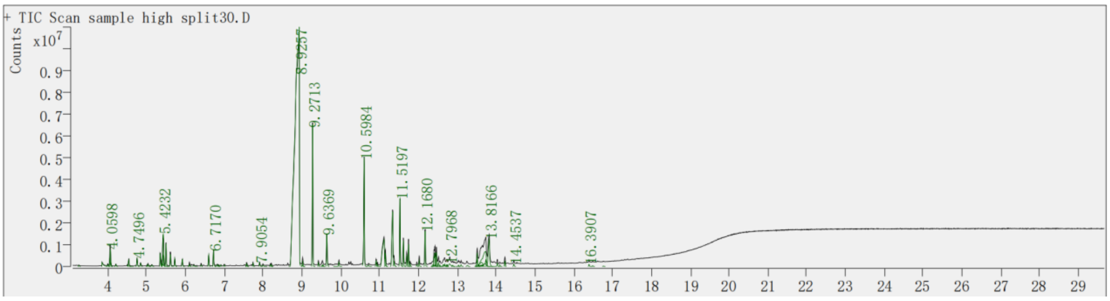

➢ Matching degree between fragments and candidate molecules

Fragments | Peaks

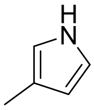
| Mass/Charge | Intensity (%) | Assigned | Error (Da) | Radical |
|---|---|---|---|---|
| 54.0345 | 50.00 | ☐ | | ▣ |
| 65.0360 | 50.00 | ☑ | 0.003 | ☐ |
| 67.0378 | 100.00 | ☑ | 0.016 | ☐ |
| 68.0453 | 50.00 | ☑ | 0.017 | ☑ |
| 69.0551 | 100.00 | ☑ | 0.015 | ☐ |
| 80.0473 | 50.00 | ☑ | 0.002 | ☐ |
| 82.0606 | 50.00 | ☑ | 0.005 | ☐ |
| 109.0721 | 50.00 | ☑ | 0.004 | ☐ |
| 109.0783 | 50.00 | ☑ | 0.002 | ☐ |

Matches: 8 of 9 peaks, 90.9% of total intensity

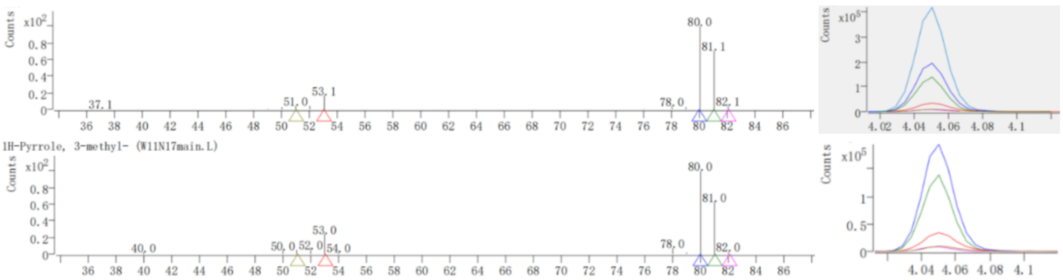
## 6. GC-MS Data



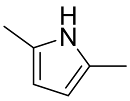

### 6.1. 3-Methyl-1H-pyrrole



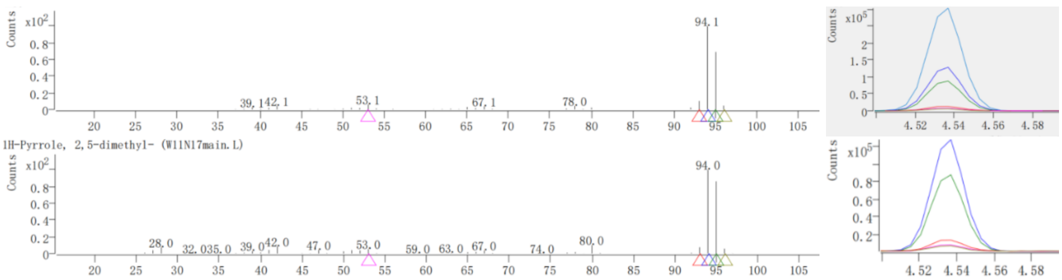
RT: 4.0493 min, Match factor: 97.1



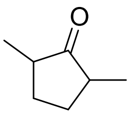

### 6.2. 2,5-Dimethyl-1H-pyrrole



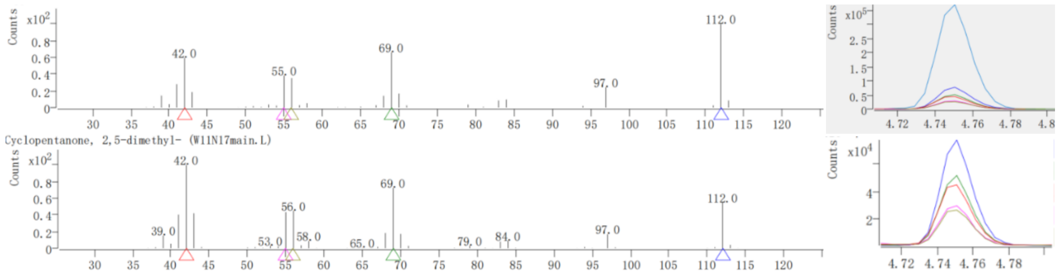
RT：4.5353，Match factor：95.7



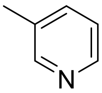

### 6.3. 2,5-Dimethyl-cyclopentanone



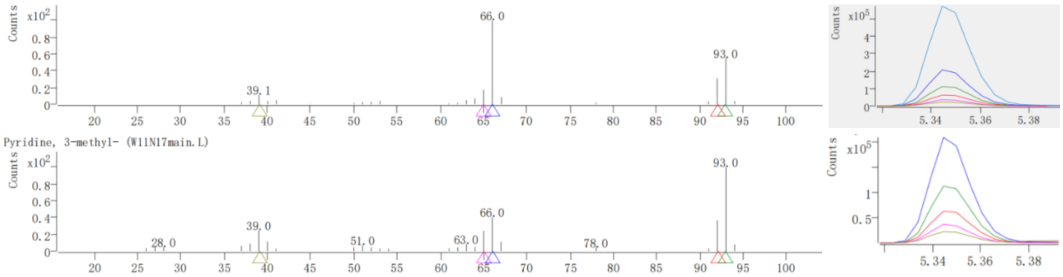
RT: 4.7496 min, Match factor: 96.3



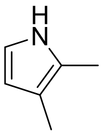

## 6.4. 3-Methyl-pyridine



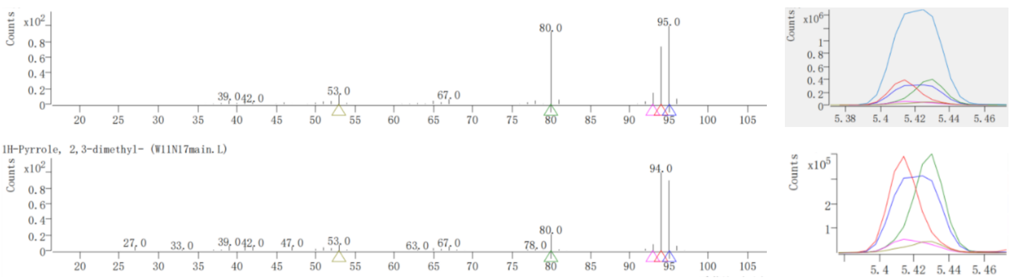

RT:5.029, Match factor: 94.1



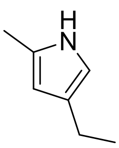

## 6.5. 2,3-Dimethyl-1H-pyrrole



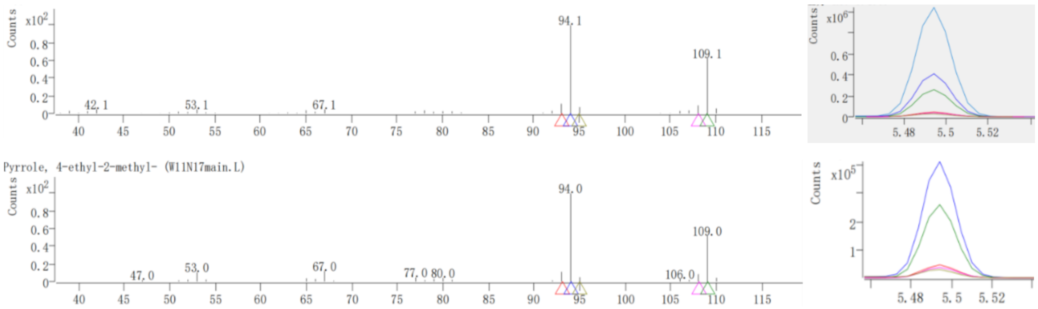

RT: 5423 min, Match factor: 93.2



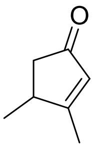

## 6.6. 4-Ethyl-2-methyl-pyrrole



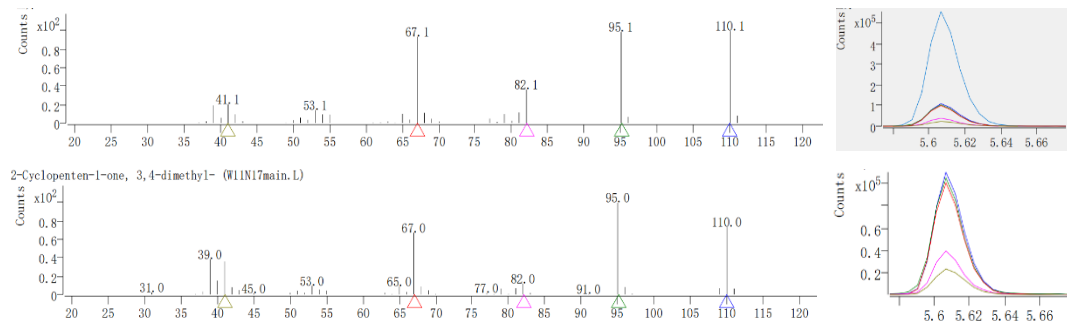

RT:5.4939 min, Match factor: 94.3



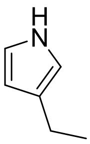

## 6.7. 3,4-Dimethyl-2-cyclopenten-1-one



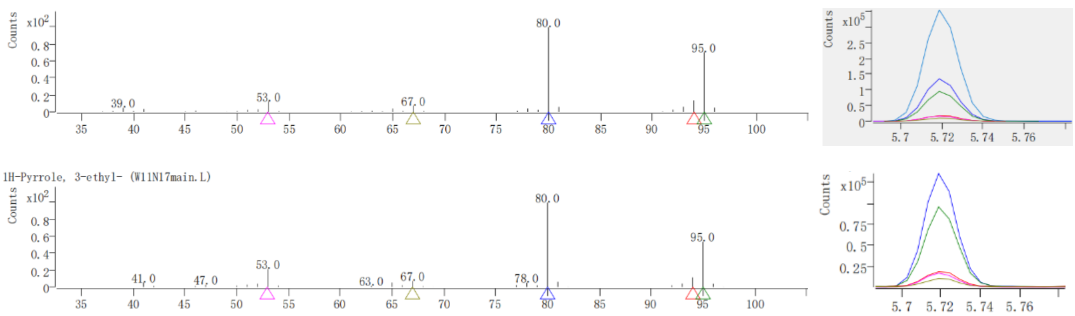
RT: 5.6070 min, Match factor: 93.8



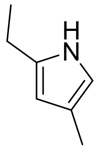

## 6.8. 3-Ethyl-1H-pyrrole



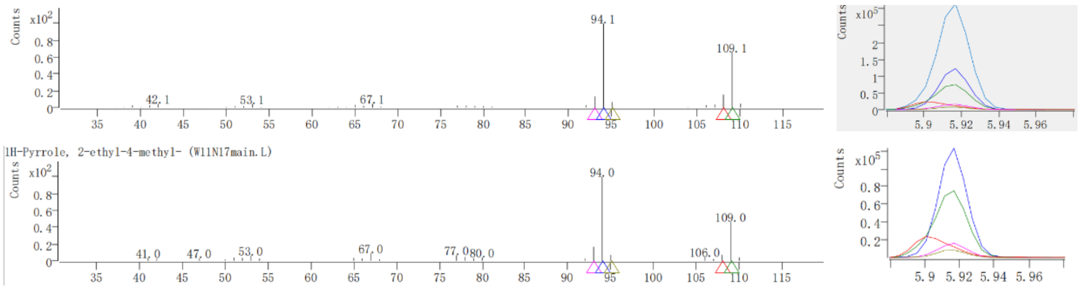
RT: 5.7195 min, Match factor: 96.1



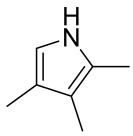
### 6.9. 2-Ethyl-4-methyl-1H-pyrrole



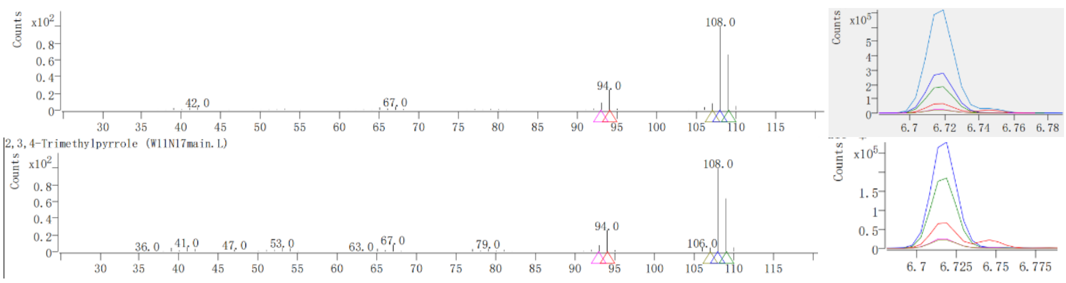
RT: 5.9158 min, Match factor: 95.4



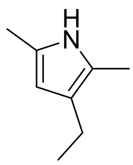

### 6.10. 2,3,4-Trimethylpyrrole



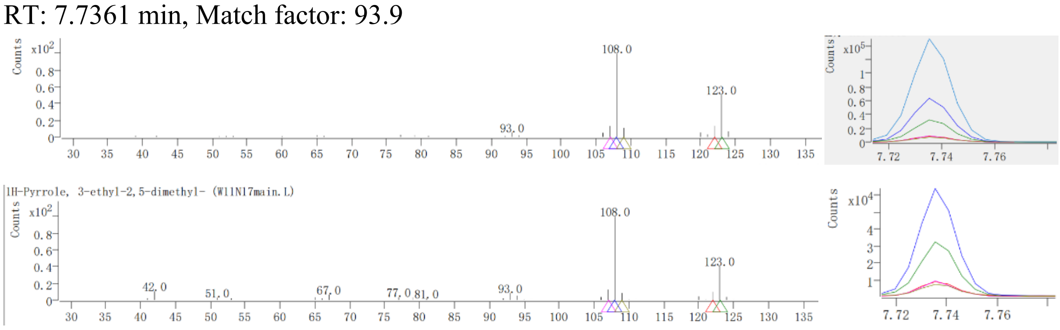
RT: 6.7170 min, Match factor: 96.5



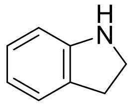

### 6.11. 3-Ethyl-2,5-dimethyl-1H-pyrrole



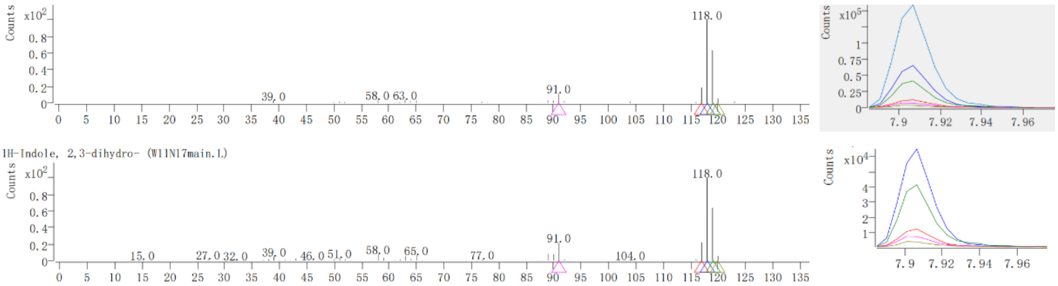
RT: 7.7361 min, Match factor: 93.9



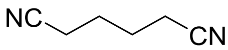
## 6.12. 2,3-Dihydro-1H-indole



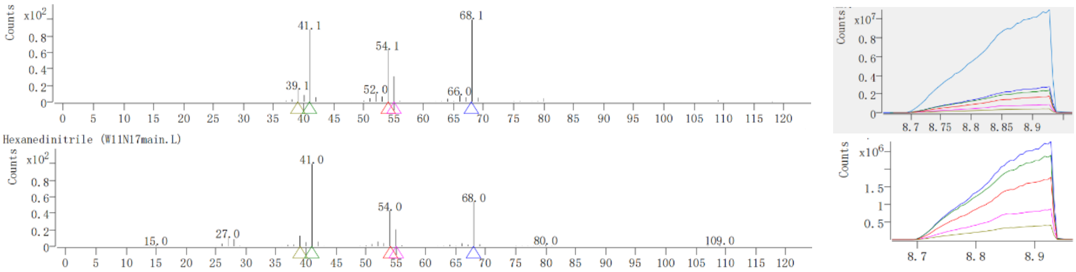
RT: 7.9054 min, Match factor: 93.0



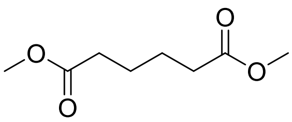

## 6.13. Adiponitrile



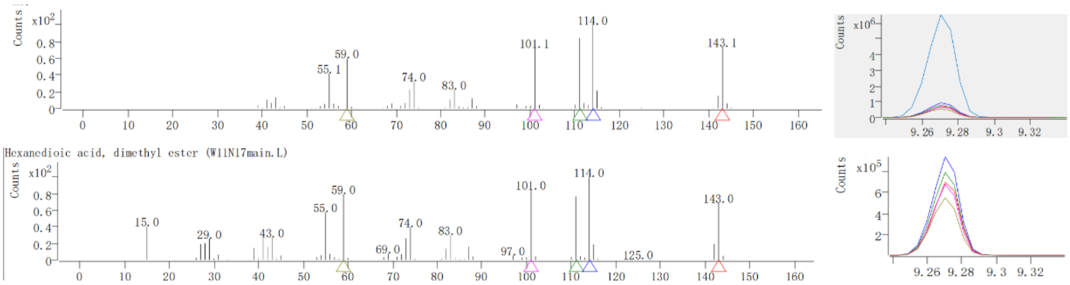

RT: 8.9257 min, Match factor: 97.8



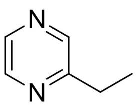

## 6.14. Dimethyl adipate



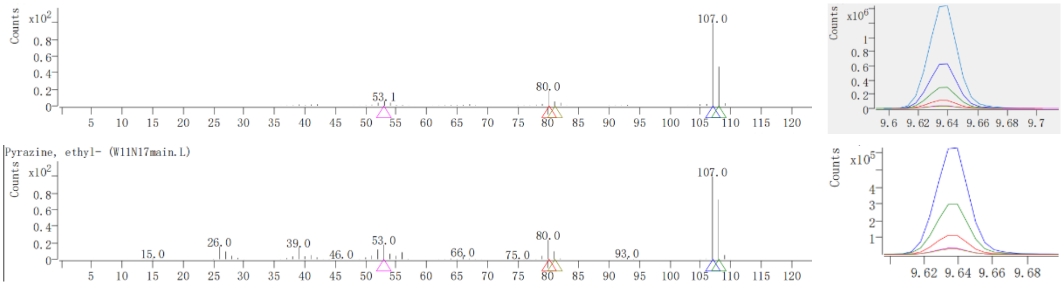
RT: 9.2713 min, Match factor: 98.8



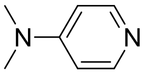

## 6.15. Ethylpyrazine



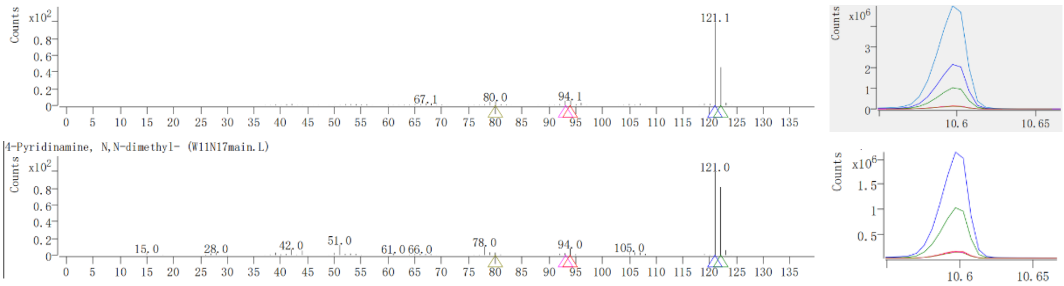
RT: 9.6369 min, Match factor:94.0



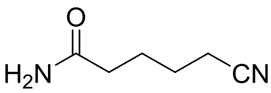

## 6.16. N,N-Dimethyl-4-pyridinamine



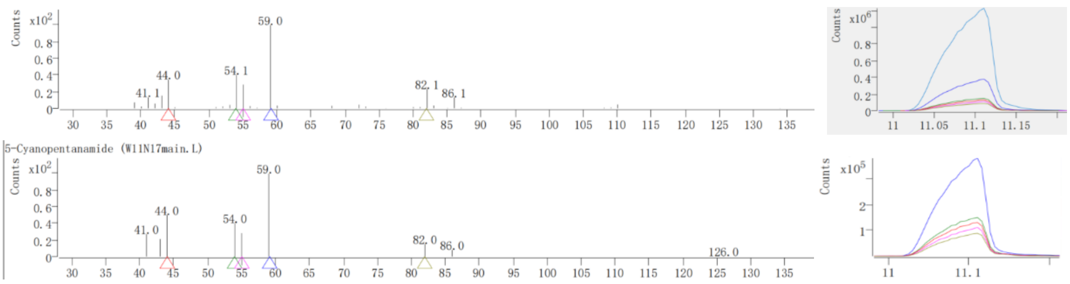
RT: 10.5984 min, Match factor: 90.8



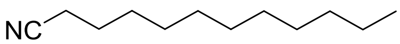

## 6.17. 5-Cyanopentanamide (CPA)



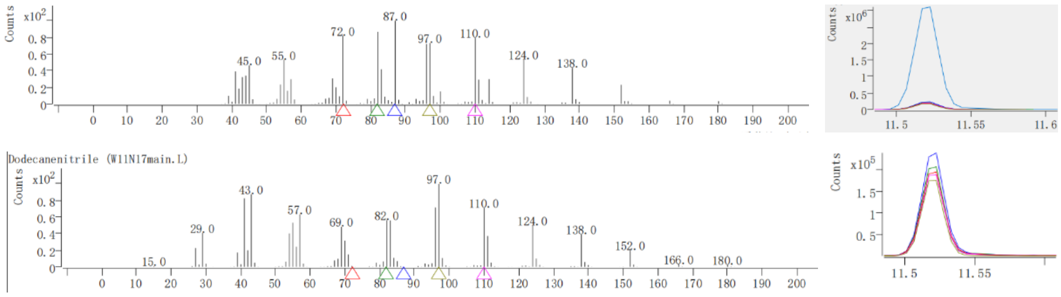
RT:11.1087 min Match factor83.8



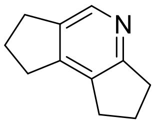

## 6.18. Dodecanenitrile



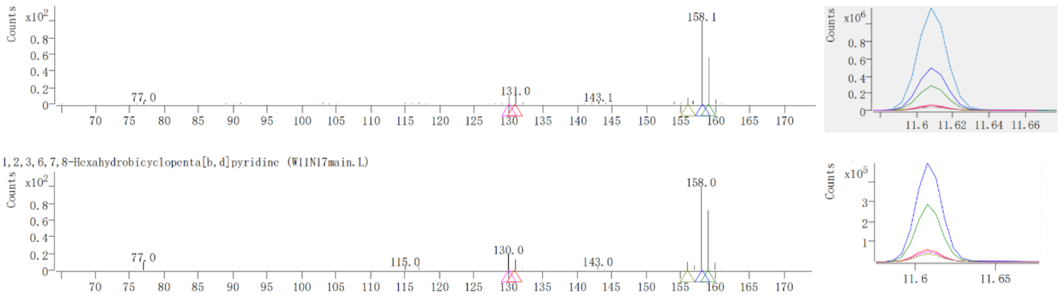
RT: 11.5197, Match factor: 84.0



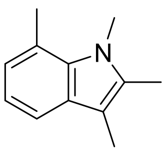

## 6.19. 1,2,3,6,7,8-Hexahydrobicyclopenta[b,d]pyridine



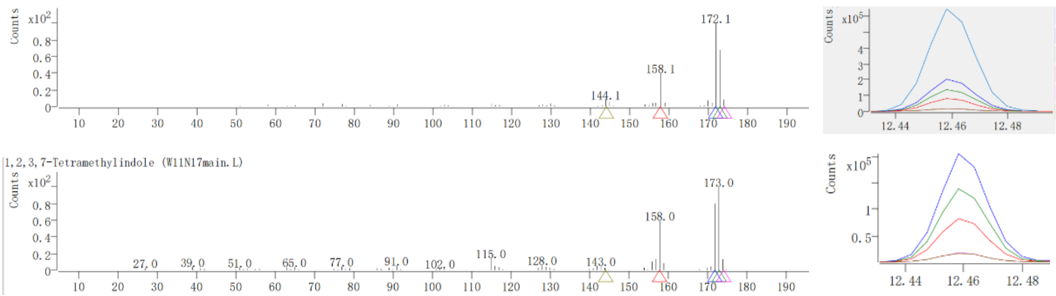

RT: 11.6084 min, Match factor: 92.3



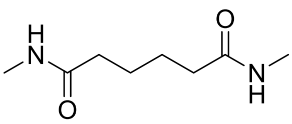

## 6.20. 1,2,3,7-Tetramethylindole



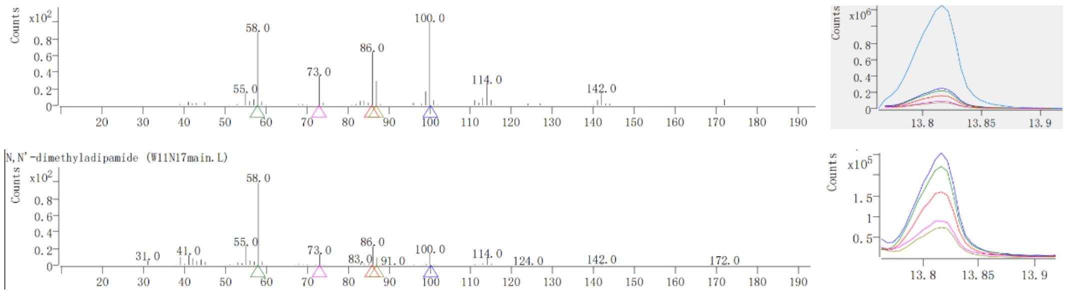

RT: 12.4594 min, Match factor: 90.5



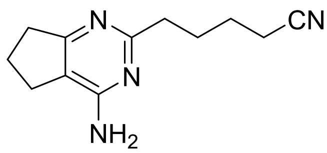

## 6.21. N,N'-dimethyladipamide



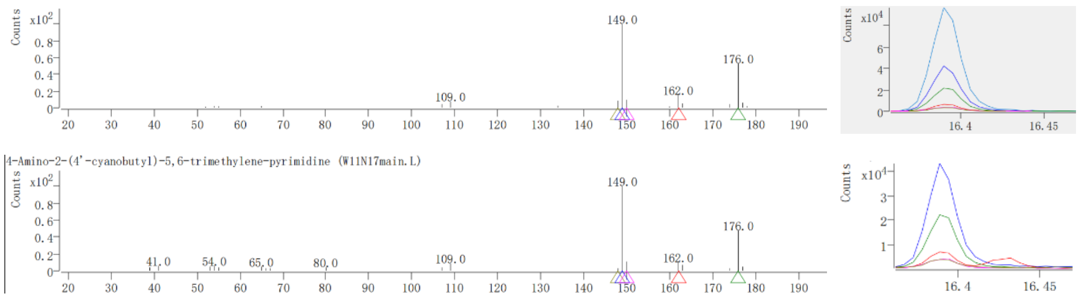

RT: 13.8166 min, Match factor: 83.7




## 6.22. 4-Amino-2-(4'-cyanobutyl)-5,6-trimethylene-pyrimidine




RT: 16.3907 min, Match factor：90.2




# 7. Characterization of spent catalyst

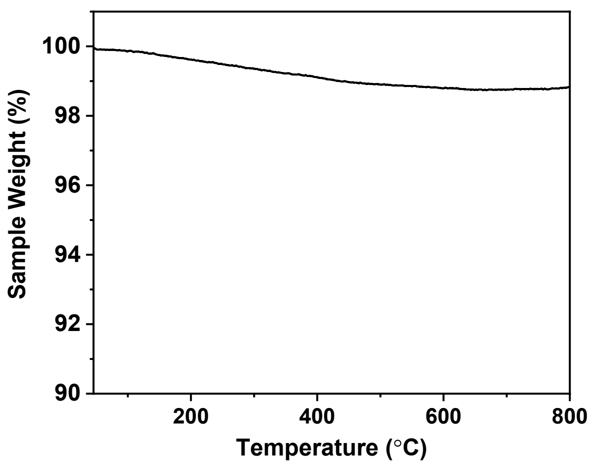



Figure S1. TG spectra of the spent $Nb_2O_5$-1100 catalyst

# 8. Preliminary techno-economic analysis

Table S8. Techno-economic analyses of the industrial process and approach in this work

| | **Hydrocyanation of BD** | **Dimerization of AN [a]** | **Ammonization of AA** | **Nitrilation of DMA** |
|---|---|---|---|---|
| Resource consumption for per t of AND produced [a] | BD: 0.583 t<br>$CH_4$(g): 994 $m^3$<br>$NH_3$(l): 0.537 t | AN: 1.10~1.15 t | AA: 1.5~1.6 t<br>$NH_3$(l): 0.37 t | AA: 1.4 t<br>MeOH: 0.06 t<br>$NH_3$(l): 0.37 t |
| Resource cost for per t of ADN produced [b] (RMB/t ADN) | 11977 | 17380 | 18041 | 16378 |
| General facility energy consumption cost (RMB/t ADN) | 1320 [c] | 2735 [c] | 2218 [c] | 1018 [d] |
| Cost per ton of ADN produced [e] (RMB/t ADN) | 13297 | 20115 | 20258 | 17090 |

[a] Data on resource consumption per ton of ADN in industrial processes were based on the literature.[4] Resource consumption for per ton of ADN produced for nitrilation of DMA was calculated according to **the assumed 95% selectivity of ADN and 90% recovery of methanol**.

[b] Resource cost per t of ADN was calculated according to resource consumption per ton of ADN and the cost of raw materials in Table S9.

[c] Data on general facility energy consumption cost in industrial processes were based on the literature.[4]

[d] General facility energy consumption cost for nitrilation of DMA was estimated by developing an Aspen process model, the detailed data of which are presented in Table S10.

[e] Product cost per ton of ADN consists of resource cost and energy consumption cost. BD = butadiene, AN = acrylonitrile, AA = adipic acid, DMA = dimethyl adipate, and ADN = adiponitrile.

Table S9. Cost of raw materials

| | Cost (2021.09) | Source [a] |
|---|---|---|
| Butadiene (RMB/t) | 9100 | http://www.100ppi.com/ |
| LNG (RMB/t) | 5900 | http://www.100ppi.com/ |
| $NH_3$(l) (RMB/t) | 4650 | http://www.100ppi.com/ |
| Acrylonitrile (RMB/t) | 15800 | http://www.100ppi.com/ |
| Adipic acid (RMB/t) | 10200 | http://www.100ppi.com/ |
| Methanol (RMB/t) | 2750 | http://www.100ppi.com/ |

[a] All commodity prices are obtained from a commodity data group (http://www.100ppi.com/), which offers an integrated price, news and research sharing platform in bulk commodities.

Table S10. General facility energy consumption cost for nitrilation of DMA

| | Energy consumption t/t ADN | Price RMB/t | Energy consumption cost RMB/t ADN |
|---|---|---|---|
| Fuel gas | 0.08 | 3680 | 294.4 |
| Medium-pressure steam | 1.49 | 189 | 281.7 |
| Low-pressure steam | 2.01 | 174 | 350.1 |
| Recycled water | 369.02 | 0.3 | 110.7 |
| Refrigerant | 3.46 | 25.8 | 89.2 |
| Total | | | 1018.5 |

# 9. References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