

## [Supplementary Information] for

### The $\pi$ -Conjugated Polymeric Phthalocyanine for Oxidative Coupling of Amines

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Affiliations:XXX

## Contents

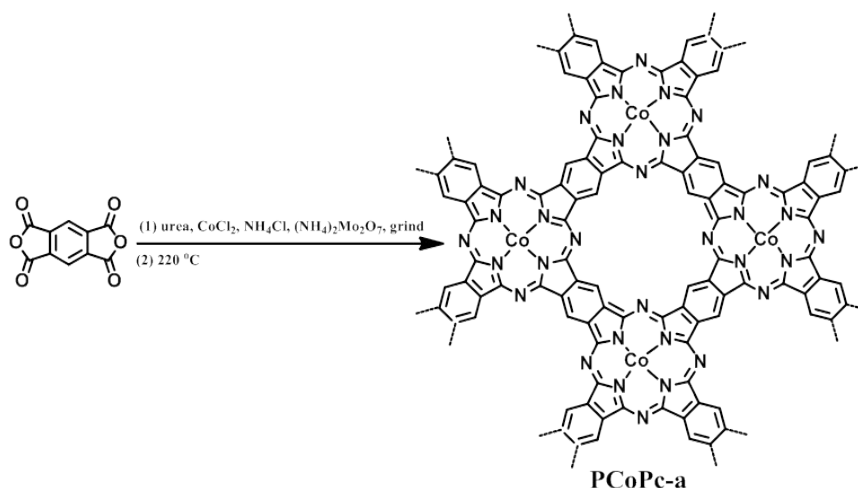
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## Section 1 Details of experiments

### 1.1 Materials

Amines, urea,  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ , phthalic anhydride acid, pyromellitic dianhydride, were obtained from Sigma-Aldrich.  $\text{CoCl}_2$ ,  $\text{FeCl}_2$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ , acetone, methanol, ethanol, tetrahydrofuran (THF), N,N-Dimethylformamide (DMF) were purchased with analytical grade and applied without further purification unless indicated. Deionized water ( $> 18.2 \text{ M}\Omega/\text{cm}$ ) was prepared by water purification system (Millipore, Direct-Q3).

### 1.2 Preparation of polymeric cobalt phthalocyanine (PCoPc-a)



**Scheme S1.** The solid-state assemble method for the preparation of polymeric cobalt phthalocyanine (PCoPc-a).

Typically, polymeric cobalt phthalocyanine were prepared by the method as follows: pyromellitic dianhydride (1.26 g),  $\text{CoCl}_2$  (0.39 g), urea (2.46 g),  $\text{NH}_4\text{Cl}$  (0.6 g) and  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$  (15 mg) were ground together. Thereafter, the mixture was transferred to a muffle furnace and kept heating at 220 °C for 3 h to accomplish the *in situ* solid-state polycondensation. After cooling down to room temperature, purified and dried, the sample is denoted as **PCoPc-a**. The other PFePc-a, PMnPc-a and PCuPc-a were synthesized by the same method except that the salt precursor. The metal-free polymeric phthalocyanine (PPc) was prepared following the same procedure except without the cobalt salt precursor. After washing and drying, the powder samples of PPc can be obtained. The molecular cobalt phthalocyanine (CoPc) was also prepared by the same procedure except that the pyromellitic dianhydride was replaced with phthalic anhydride.

### 1.3 Characterization

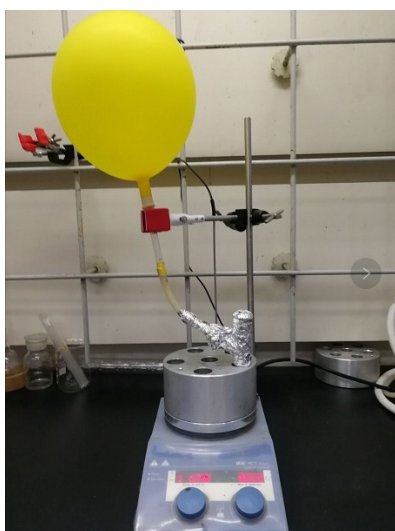
Fourier transform infrared spectroscopy (FT-IR) spectrum was recorded with calcined powders dispersed in KBr using a Perkin-Elmer One FTIR spectrometer. X-ray diffraction data was conducted on PANalytical Empyrean diffractometer, operated at 45 kV and 40 mA (scanning step: 0.02° per step). The diffraction patterns were recorded in the range of 5-80° (2 $\theta$ ). The nitrogen adsorption and desorption isotherms were measured at 77 K under a

micromeritics 3Flex surface area analyzer.  $^{13}\text{C}$  solid-state NMR was performed using a Solid State Varian INOVA 400 MHz. The UV-vis diffuse reflectance spectroscopy of the sample was performed using a UV-2600 spectrophotometer (Shimadzu) in the wavelength range of 200–800 nm. X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 spectrometer with an Al anode source operated at 15 KV and an applied power of 350 W with samples mounted on indium foil. Morphology analysis was performed using Zeiss scanning electron microscope. TEM and EDS characterizations were carried on an FEI Talos transmission electron microscope equipped with a Super-X EDS detector and operated at an accelerating voltage of 200 kV. The electric conductivity of the PCoPc-a was determined in FT-8100B measuring instrument using four-probe method. ICP-atomic emission spectroscopy measurements were conducted on Agilent 725ES. X-ray absorption spectra (XAS) measurements were tested on Beam line BL14W1 at the Shanghai Synchrotron Radiation Facility (SSRF) with the electron storage ring operated at 3.5 GeV, equipped with a double Si(111) crystal monochromator. The XAS data including reference Co foil were collected at the Co K-edge in transmission mode. Data reduction and analysis were performed by Athena software.

#### **1.4. The procedure for oxidative coupling of amines**

The oxidative coupling of amines was carried out in the flask attached

with an O<sub>2</sub> balloon (1 atm) in the absence of light. Briefly, the catalyst (5 mg) was added to 2.5 mL *n*-octane containing amine (0.3 mmol) under magnetic stirring at room temperature. Then it was heated to 120 °C. After proceeding to the desired time, mixtures were cooled down to room temperature. Thereafter, Both 30 mg of internal standard (dodecane) and 2.5 mL of ethyl acetate were added. The crude mixtures were transferred into vials and then analyzed by GC (Agilent 7890A) and GC-MS (Shimadzu GCMS-QP2010 SE).



**Figure S1** Photo of reaction device in this work.

## Section 2 Morphologies and elemental analysis

Scanning electron microscopy (SEM) and transmission electron microscope (TEM) (Figure S2) were employed to observe the morphologies of the polymer and some layer-stacked 2D structures were found. The high-angle annular dark-field (HAADF) imaging with energy dispersive spectroscopy (EDS) elemental mapping via scanning transmission electron microscopy (STEM) confirmed the existence of C, N, and Co species with a good dispersion.

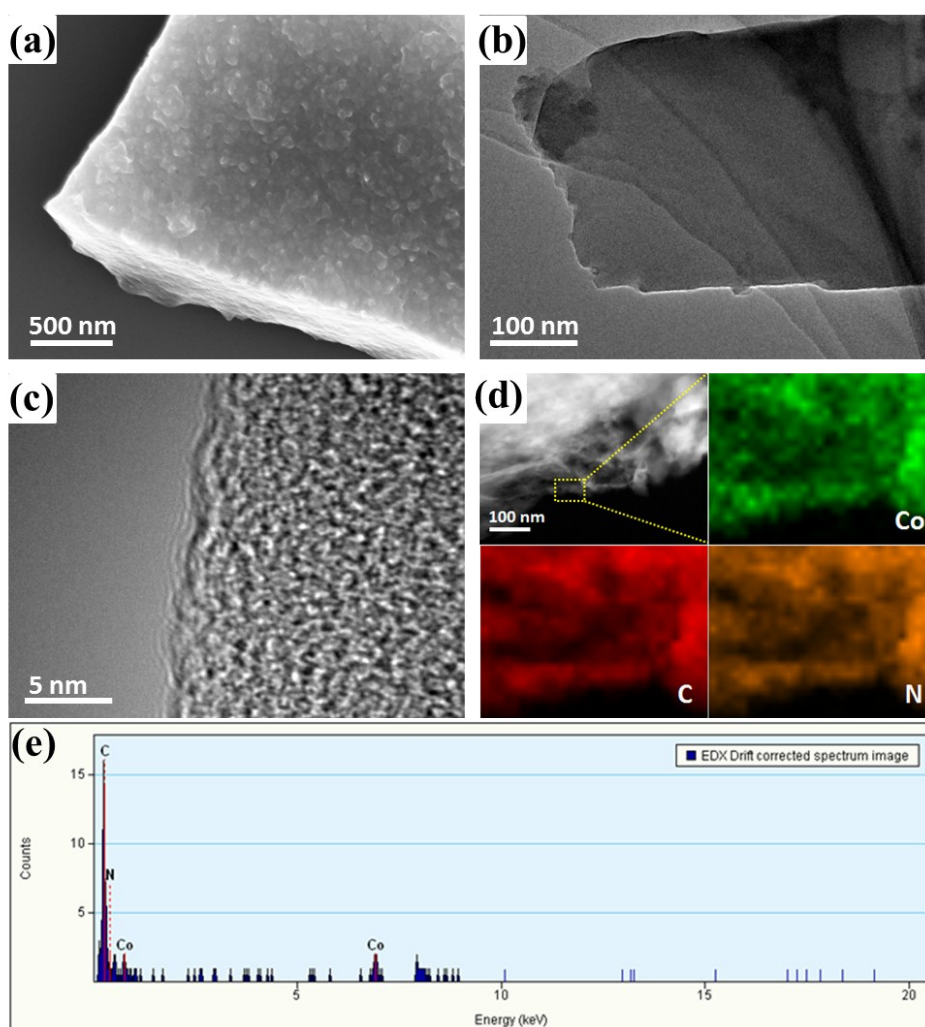
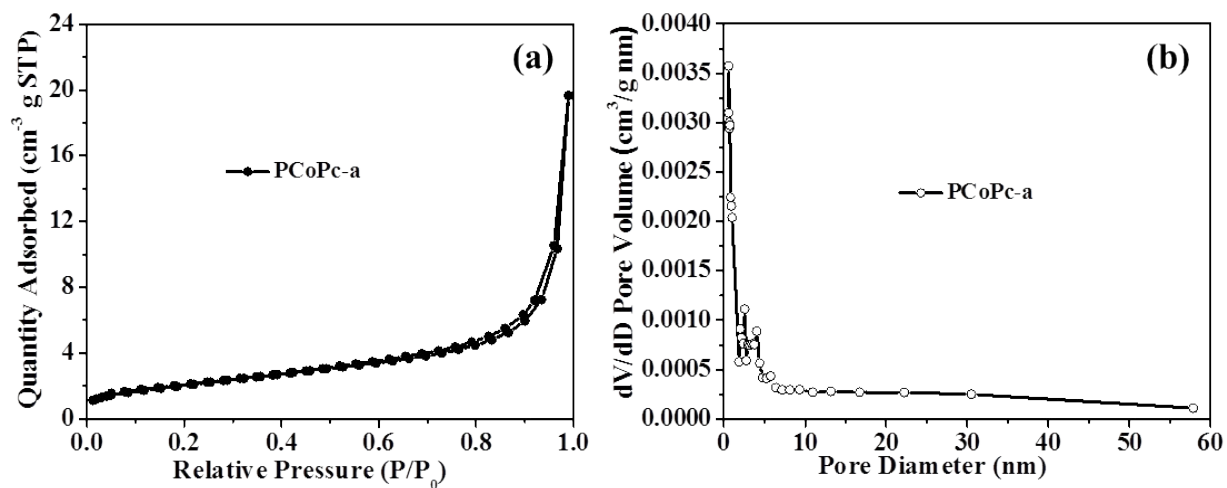


Figure S2. (a) SEM image, (b) low- and (c) high-magnification TEM images of PCoPc-a. (d-e) HAADF image and elemental analysis of P-CoPc-a.

### Section 3 Texture analysis

The specific surface area and the most probable pore radius of the PCoPc-a were calculated by means of the measured isothermal-desorption adsorption curves, which were  $7.4 \text{ m}^2/\text{g}$  and  $0.57 \text{ nm}$ , respectively.



**Figure S3.** (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of PCoPc-a.



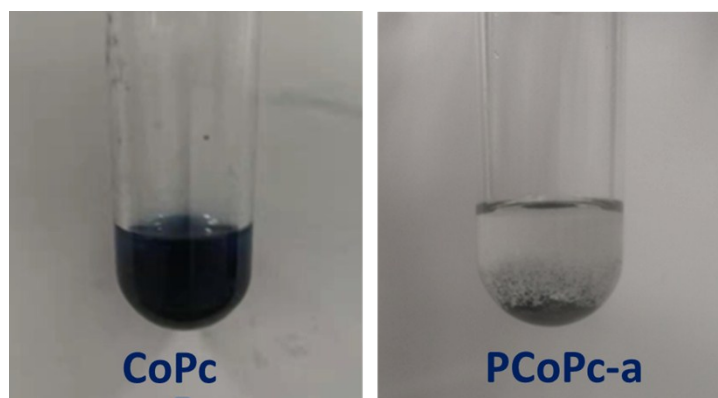
## Section 4 XPS fitting constrains and fitted values

Table S1. XPS peaks constrains and fitted values of PCoPc-a and CoPc.

| Items                       | Mater. | Constrains                         | Fitted  | Constrains                         | Fitted |
|-----------------------------|--------|------------------------------------|---------|------------------------------------|--------|
|                             |        | PCoPc-a                            | PCoPc-a | CoPc                               | CoPc   |
| Co 2p3 location             |        | 780.0 ev (+0.2, -0.1)              | 779.9   | 780.0 ev (+0.2, -0.1)              | 780.2  |
| Co 2p3 FWHM                 |        | 0.5~0.35                           | 2.64    | 0.5~0.35                           | 2.02   |
| Co 2p1 location             |        | = Co 2p3+ 14.99(+0.78, -0.3)       | 795.4   | = Co 2p3+ 14.99(+0.78, -0.3)       | 795.7  |
| Co 2p1 FWHM                 |        | 0.5~0.35                           | 2.64    | 0.5~0.35                           | 2.02   |
| Co 2p spin-sat. location    |        | 782.5 ev (+0.2, -0.1)              | 782.5   | 782.5 ev (+0.2, -0.1)              | 782.5  |
| Co 2p spin-sat. FWHM        |        | 0.5~0.35                           | 3.5     | 0.5~0.35                           | 1.96   |
| Co 2p3 sat. location        |        | 789.0 ev (+0.2, -0.1)              | 789.0   | 789.0 ev (+0.2, -0.1)              | 789.1  |
| Co 2p3 sat. FWHM            |        | 0.5~0.35                           | 2.73    | 789.0                              | 2.80   |
| Co 2p1 sat. location        |        | = Co 2p3 sat.+ 14.99(+0.78, -0.3)  | 803.7   | = Co 2p3 sat.+ 14.99(+0.78, -0.3)  | 804.5  |
| Co 2p1 sat. FWHM            |        | 0.5~0.35                           | 3.28    | 0.5~0.35                           | 2.80   |
| C <sub>α</sub> 1s location  |        | 284 ev (+0.1, -0.1)                | 284.0   | 284 ev (+0.1, -0.1)                | 284.0  |
| C <sub>α</sub> 1s FWHM      |        | 0.5~0.35                           | 1.05    | 0.5~0.35                           | 0.72   |
| C <sub>β</sub> 1s location  |        | =C <sub>α</sub> + 0.51(+0.2, -0.1) | 284.5   | =C <sub>α</sub> + 0.51(+0.2, -0.1) | 284.4  |
| C <sub>β</sub> 1s FWHM      |        | 0.5~0.35                           | 1.54    | 0.5~0.35                           | 0.82   |
| C <sub>γ</sub> 1s location  |        | =C <sub>α</sub> + 1.49(+0.2, -0.1) | 285.3   | =C <sub>α</sub> + 1.50(+0.2, -0.1) | 285.4  |
| C <sub>γ</sub> 1s FWHM      |        | 0.5~0.35                           | 1.21    | 0.5~0.35                           | 0.85   |
| C <sub>π</sub> 1s location  |        | =C <sub>α</sub> + 2.1(+0.2, -0.1)  | 286.0   | =C <sub>α</sub> + 2.1(+0.2, -0.1)  | 286.0  |
| C <sub>π</sub> 1s FWHM      |        | 0.5~0.35                           | 1.68    | 0.5~0.35                           | 1.05   |
| C <sub>π*</sub> 1s location |        | =C <sub>α</sub> +3.5(+0.2, -0.1)   | 287.4   | =C <sub>α</sub> +3.5(+0.2, -0.1)   | 287.5  |
| C <sub>π*</sub> 1s FWHM     |        | 0.5~0.35                           | 1.39    | 0.5~0.35                           | 1.17   |
| N <sub>α</sub> 1s location  |        | 398.3 ev (+0.1, -0.1)              | 398.2   | 398.3 ev (+0.1, -0.1)              | 398.3  |
| N <sub>α</sub> 1s FWHM      |        | 0.5~0.35                           | 1.28    | 0.5~0.35                           | 0.78   |
| N <sub>β</sub> 1s location  |        | =N <sub>α</sub> + 0.5(+0.2, -0.1)  | 398.8   | =N <sub>α</sub> + 0.5(+0.2, -0.1)  | 398.8  |
| N <sub>β</sub> 1s FWHM      |        | 0.5~0.35                           | 2.05    | 0.5~0.35                           | 0.83   |

## Section 5 Comparison of catalyst state

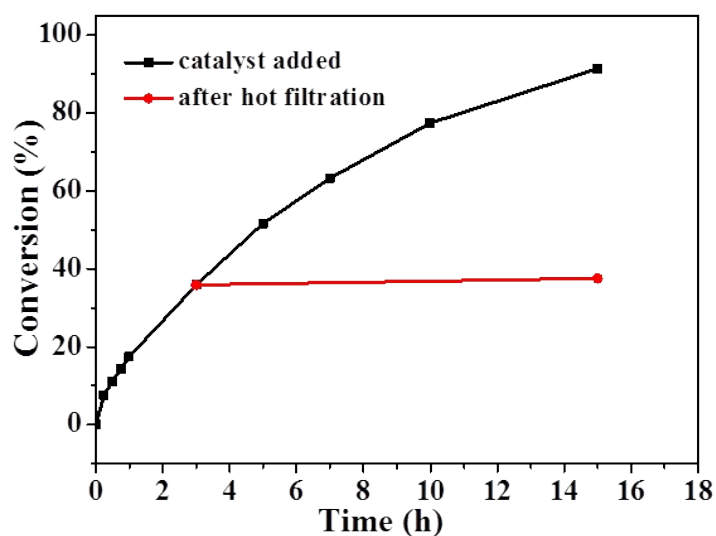
When the molecular CoPc and PCoPc-a polymer were separately mixed with the reaction solution, the former formed a deep blue solution, while the latter could be clearly separated from the solution.



**Figure S4** Photos of reaction mixture by CoPc (the left) and PCoPc-a (the right) using octane as solvent.

## Section 6 Hot filtration test

We detected the conversion of benzylamine at different times and no induction period was found. And a conversion of 91.3% can be achieved after 15 hours. To compare, if PCoPc-a was removed by hot filtration at 3h, the conversion showed no significant change after another 12h, indicating the reaction has stopped after filtration.



**Figure S5.** Filtration test. (Reaction conditions: Benzylamine (0.3 mmol), catalyst (5 mg), n-octane (2.5 mL), O<sub>2</sub> balloon, 120 °C. PCoPc-a was filtrated at 3 h)

## Section 7 Performance for other substrates

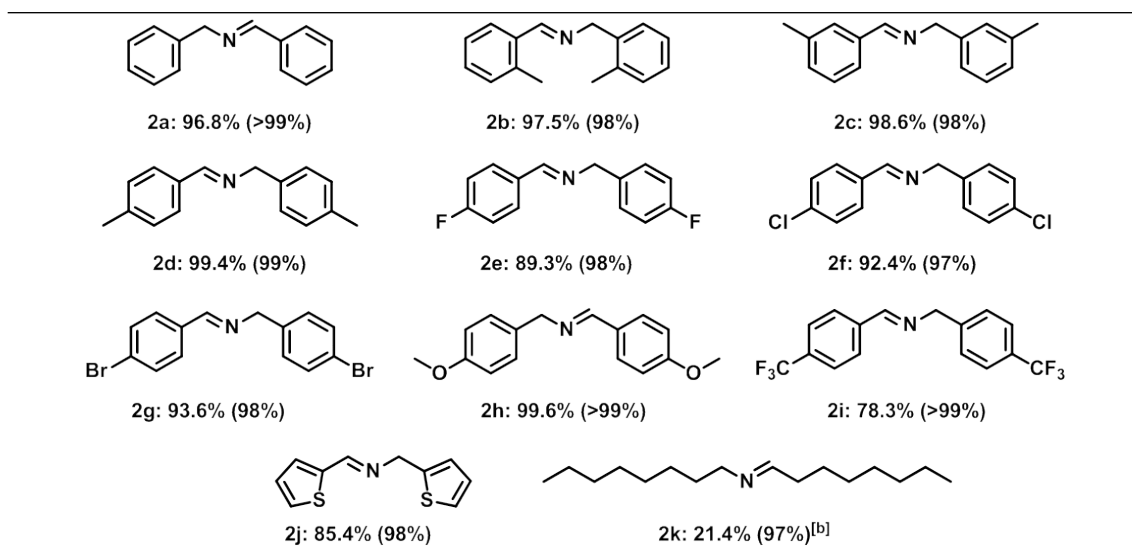
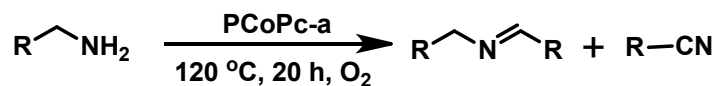
In order to illustrate the applicability of PCoPc-a, a series of substrates were tested under the optimized conditions (Table S1). For instance, the conversion of benzylamine can be further reached 97.2% by simply prolonging the reaction time to 20 h (Table S1, 2a). In general, the substrates bearing electron-withdrawing or electron-donating groups all achieved good conversion and selectivity. The presence of an electron-donating group is more favorable for the reaction (Table S1, 2b-d, 2h). The para-substitute exhibited a higher activity than the corresponding meta- and ortho-substitute ones (Table S1, 2b-d). It is worth noting that heterocyclic amines, such as 2-thiophenemethylamine, which may readily poison the metal catalyst, can also be oxidized to the corresponding high-producing imines (Table S1, 2j). It was also effective for aliphatic amines but with lower yield because of the inactive  $\alpha$ -hydrogen (Table S1, 2k)<sup>1</sup>.

Refer to:

1. B. Chen, L. Y. Wang, W. Dai, S. S. Shang, Y. Lv and S. Gao, *Acs Catal*, 2015, 5, 2788-2794.

**Table S2.** Oxidative coupling of various amines to imines over PCoPc-

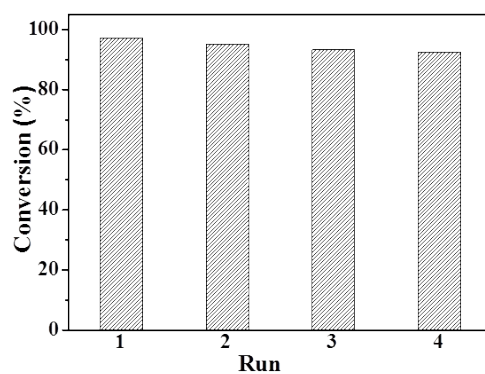
a<sup>[a]</sup>



Reaction conditions: [a] Amine (0.3 mmol), catalyst (5 mg), octane(2.5 mL), O<sub>2</sub> balloon (1 atm), 120 °C, 20 h. The products were determined by GC-MS using dodecane as an internal standard. [b] 10 mg PCoPc-a catalyst.

## Section 8 Recyclability test

Recycling is an important indicator for the stability of the catalyst. After four cycles, the PCoPc-a catalyst still showed a high conversion for the benzylamine oxidative coupling reaction.



**Figure S6.** Recycling experiments for PCoPc-a. (Reaction conditions: Benzylamine (0.6 mmol), catalyst (10 mg), n-octane (2.5 mL), O<sub>2</sub> balloon, 120 °C)

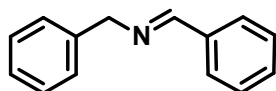
## Section 9 GC-MS spectra of the products

The products were confirmed by GC-MS (Shimadzu GCMS-QP2010 SE).

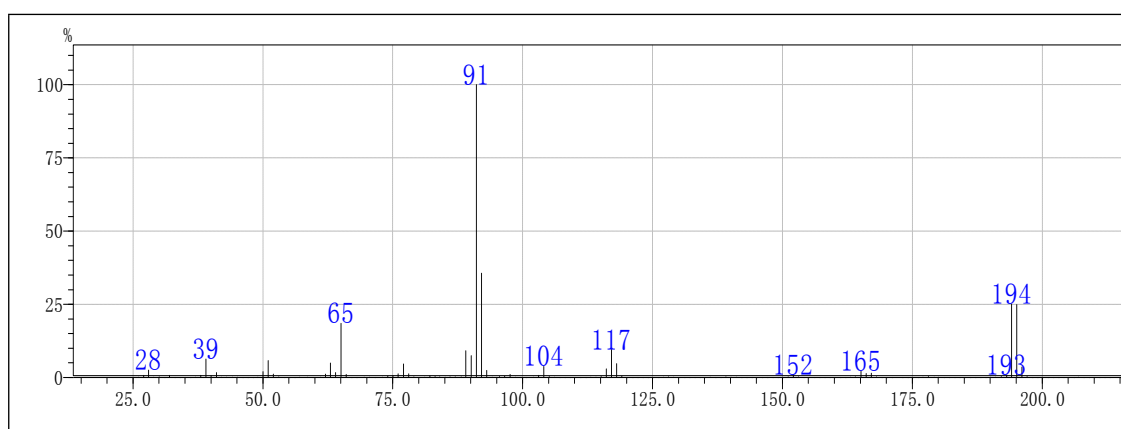
N-Benzylbenzaldimine

CAS No. 780-25-6

Chemical formula: C<sub>14</sub>H<sub>13</sub>N



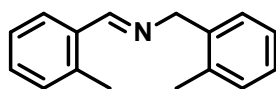
Molecular weight: 195.3



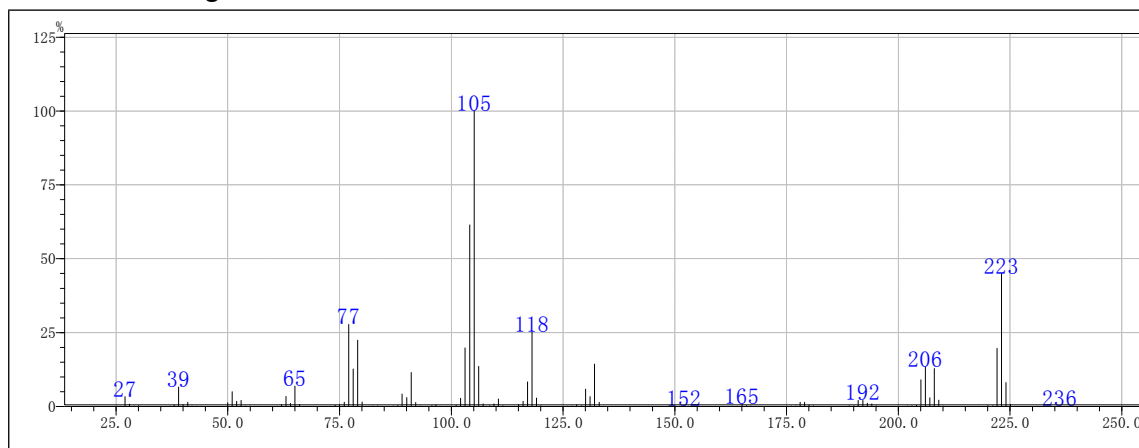
2-Methyl-N-(2-methylbenzyl)benzaldimine

CAS No. 155085-24-8

Chemical formula: C<sub>16</sub>H<sub>17</sub>N



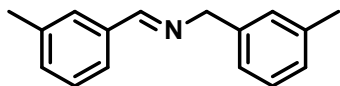
Molecular weight: 223.3



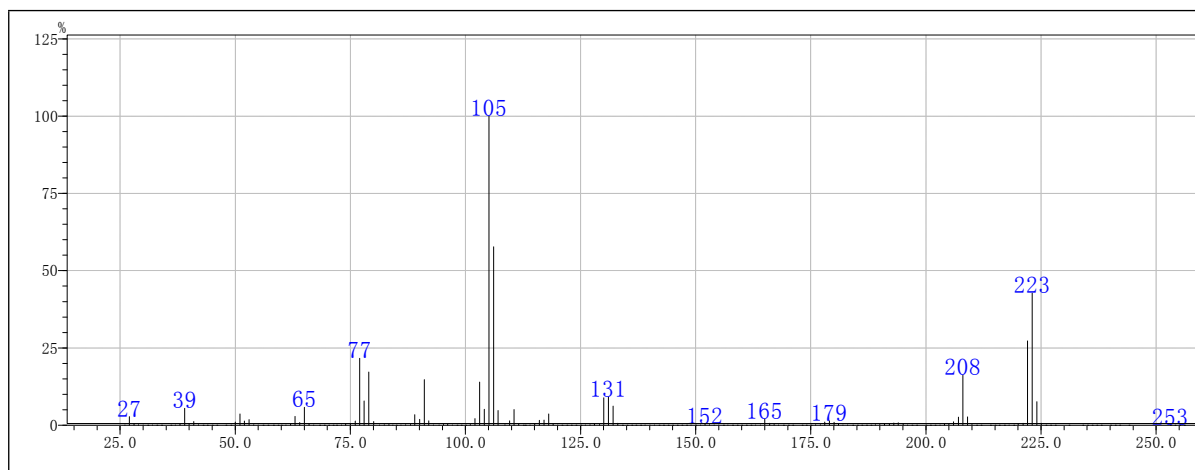
### N-(3-Methylbenzyl)-3-methylbenzalimine

CAS No. 215667-40-6

Chemical formula: C<sub>16</sub>H<sub>17</sub>N



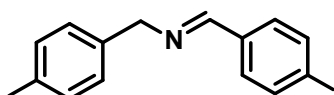
Molecular weight: 223.3



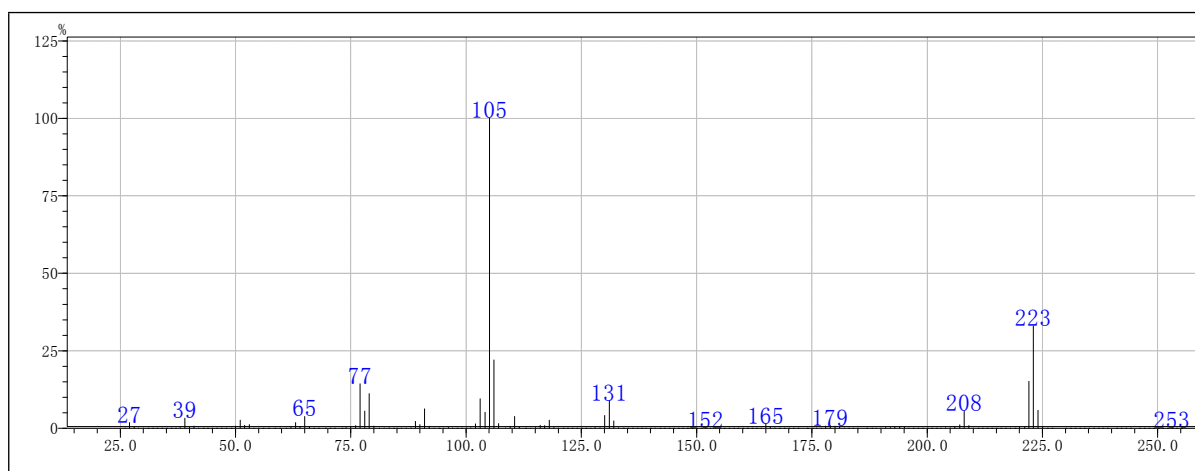
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CAS No. 71022-60-1

Chemical formula: C<sub>16</sub>H<sub>17</sub>N



Molecular weight: 223.3

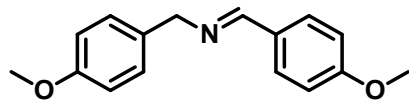




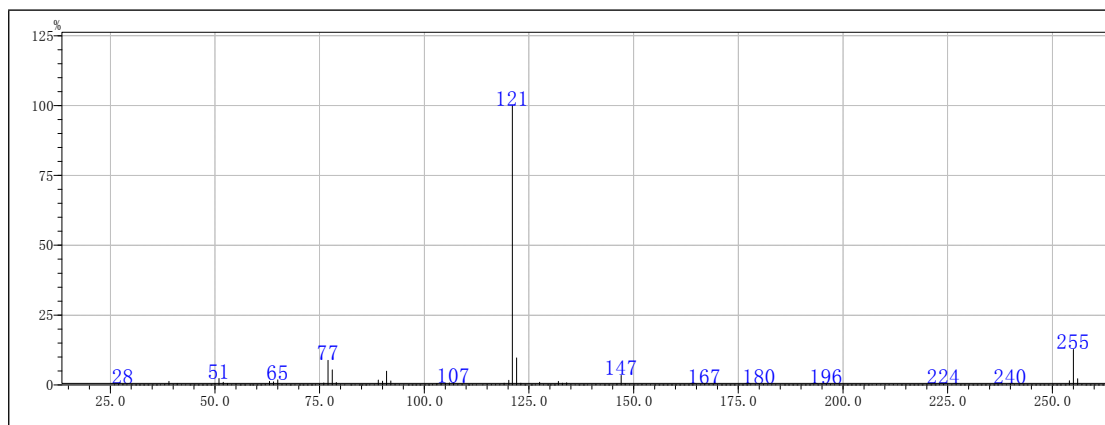
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CAS No. 3261-60-7

Chemical formula: C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>



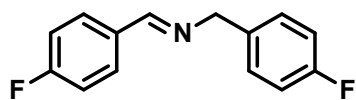
Molecular weight: 255.3



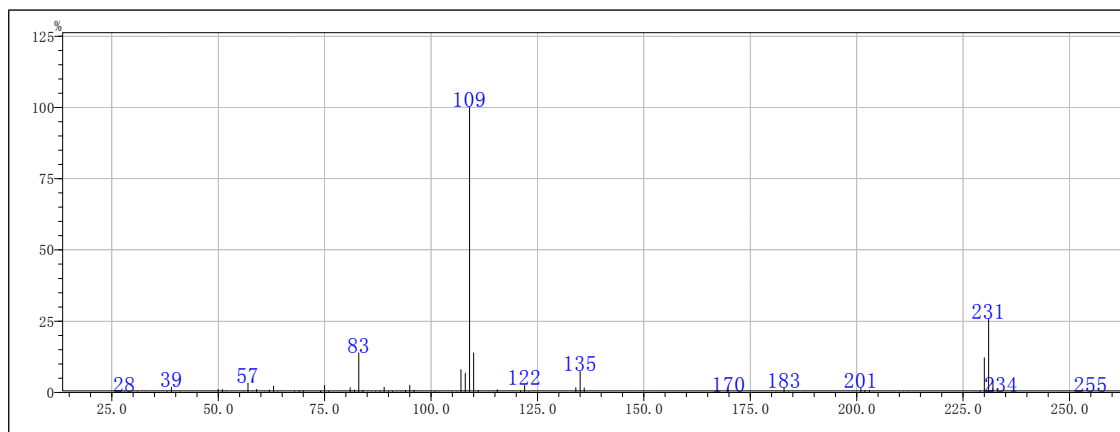
### N-(4-Fluorobenzyl)-4-fluorobenzaldimine

CAS No. 428819-12-9

Chemical formula: C<sub>14</sub>H<sub>11</sub>NF<sub>2</sub>



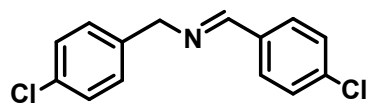
Molecular weight: 231.2



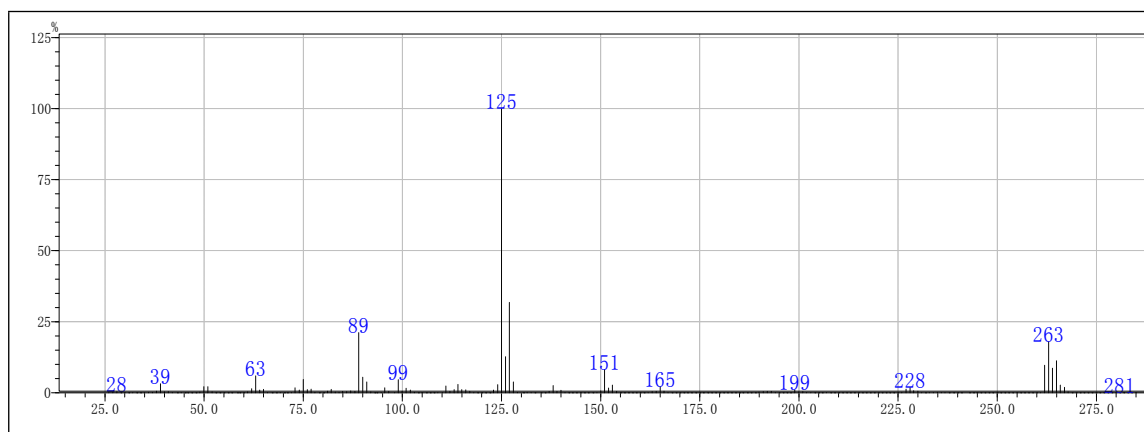
### N-(4-Chlorobenzyl)-4-chlorobenzaldimine

CAS No. 31264-06-9

Chemical formula:  $C_{14}H_{11}NCl_2$



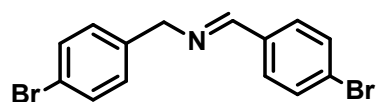
Molecular weight: 264.2



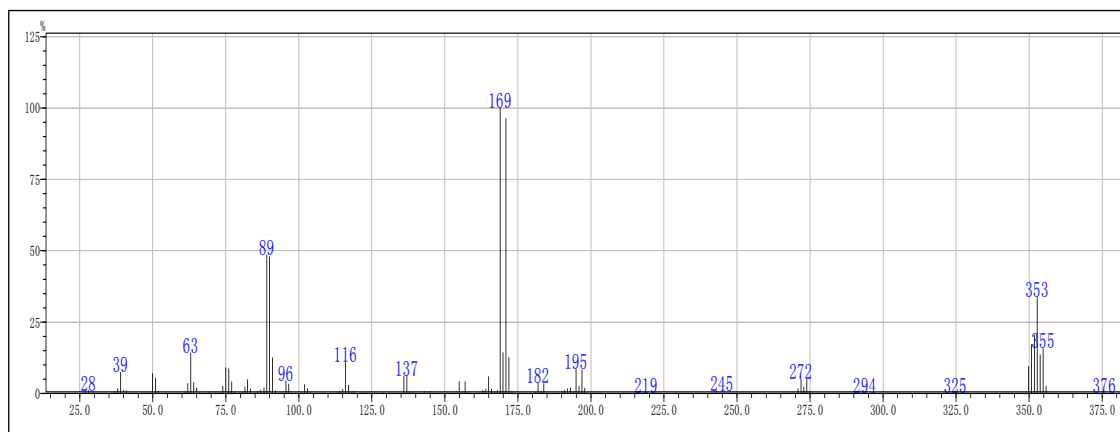
### N-(4-Bromobenzylidene)-4-bromobenzylamine

CAS No. 54560-80-4

Chemical formula:  $C_{14}H_{11}NBr_2$



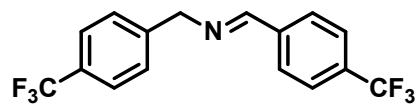
Molecular weight: 353.1



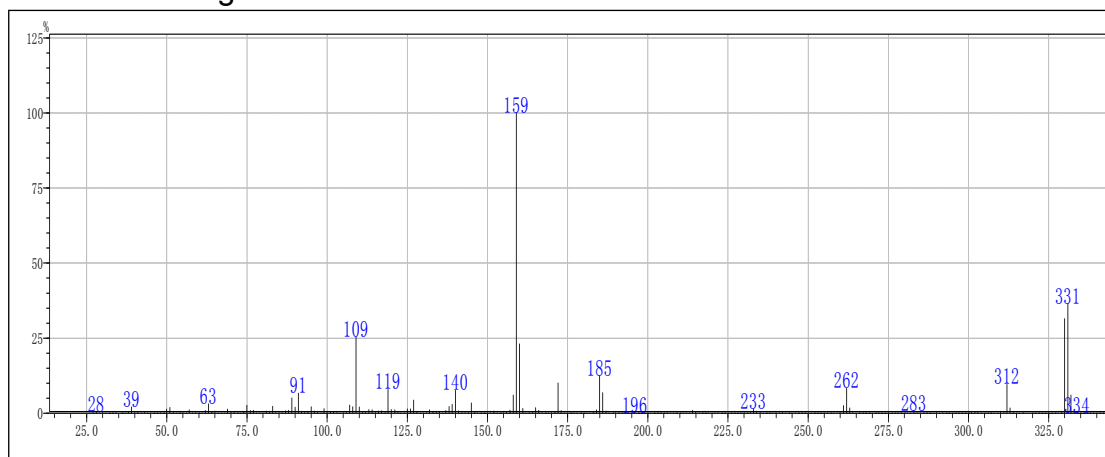
## N-[4-(Trifluoromethyl)benzylidene]-4-(trifluoromethyl)benzylamine

CAS No. 189245-79-2

Chemical formula:  $C_{16}H_{11}NF_6$



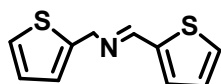
Molecular weight: 331.3



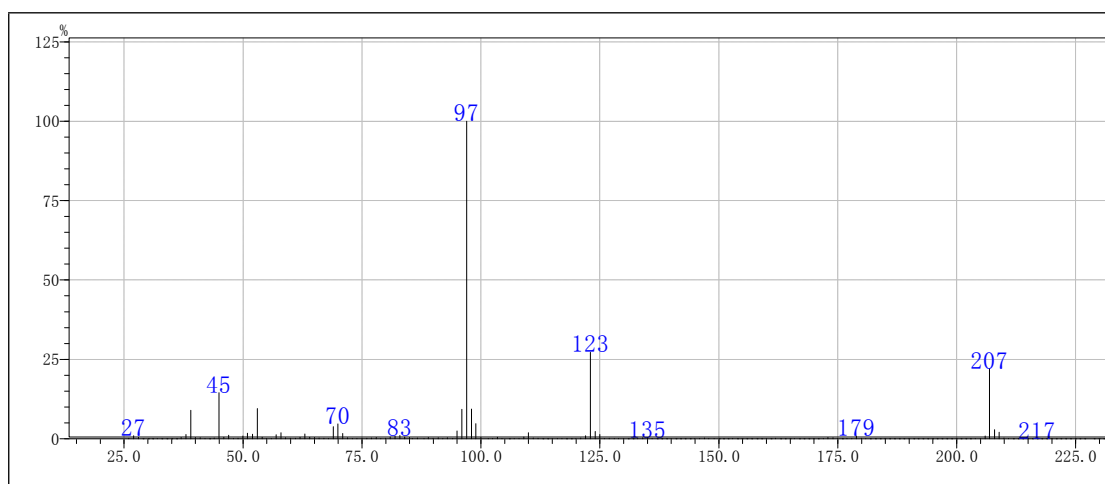
## N-(2-Thienylmethylene)-2-thiophenemethanamine

CAS No. 94488-33-2

Chemical formula:  $C_{10}H_{19}NS_2$



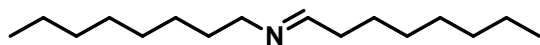
Molecular weight: 207.3



## n-Octylideneoctylamine

CAS No. 10576-04-2

Chemical formula: C<sub>16</sub>H<sub>33</sub>N



Molecular weight: 239.4

