Supporting information for

Fabricating CdS/Ag/$BiVO_4$ Z-heterojunction for solvent-free photocatalytic oxidation of amines

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1. Chemicals and reagents

Benzylamine (99.0%), acetonitrile (99.0%, GC), and 1,4-benzoquinone (99%) were purchased from Aladdin Industrial Corporation, China. Bismuth nitrate pentahydrate ($Bi(NO_3)_3$•$5H_2O$, 99.0%), ammonium metavanadate (99%), HNO_3 aqueous solution (65-68%), ammonium hydroxide (25%), ethanethioamide (99.0%), nitric acid, ethanol (99.5%), and ammonium oxalate were obtained from the Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All of the reagents were used as received without further purification.

2. Tables

Table S1 Photocatalytic oxidation of benzylamine to N-benzylidenebenzylamine with different catalysts in different conditions.

Catalysts	Light	Solvents	atmosphere	BA (mmol)	Time (h)	Conv. (%)	Sel. (%)	Fr. ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Ref.
$CdS/Ag/BiVO_4$	10 W LED, 400-405 nm	-	O_2	5	12	73.5	99	6117	This work
$CdS/Ag/BiVO_4$	10 W LED, 400-405 nm	-	O_2	5	24	92.0	99	4185	This work
Au/TiO_2	250 W Halogen	-	air	30	24	12.5	99	5053	[1]
Bi-Ellagate MOF	400 W Halogen	-	air	0.5	24	96	99	4000	[2]
CdS@MIL-101	300W Xe lamp, 420 nm	Toluene	air	0.1	10	93	99	196	[3]
$Q\text{-}BiVO_4$	300W Xe lamp, 420 nm	Acetonitrile	O_2	0.1	4	98.3	98.7	2426	[4]
$PdS/CdS/MoS_2$	300W Xe lamp, 420 nm	N, N-dimethylformamide/H_2O	air	0.5	10	87	99	21533	[5]
BiOCl	300W Xe lamp, 420 nm	N, N-dimethylformamide	O_2	0.09	1	99	99	8648	[6]
CeO_2 /g-C_3N_4	300W Xe lamp, 420 nm	Acetonitrile	O_2	0.9	5	82.2	99	3114	[7]
g-C_3N_4/TiO_2	300W Xe lamp,420 nm	Acetonitrile	O_2	1	3	91	99	7673	[8]
Ni/CdS	300W Xe lamp, 420 nm	Acetonitrile/Water	N_2	0.5	2	99	97	24008	[9]

Table S2 Textural properties of the catalysts.

Catalyst	BET surface area（m^2/g）	BJH pore cumulative volume (cm^3/g)	BJH adsorption average pore diameter (nm)
CdS	39	0.2	26.0
$BiVO_4$	7	0.02	13.2
$Ag/BiVO_4$	12	0.1	36.1
$CdS/Ag/BiVO_4$	25	0.15	23.4

Table S3 Comparation of EATOS parameters in literature for the photocatalytic synthesis of benzylamine to N-benzylidenebenzylamine.

EATOS parameters	This work		Ref.1		Ref.3		Ref.4		Ref.6	
	E_{in}	E_{out}	E_{in}	E_{out}	E_{in}	E_{out}	E_{in}	E_{out}	E_{in}	E_{out}
Solvents	-	-	-	-	0.19	0.19	0.17	0.17	0.55	0.55
Substrates	1.6	-	9.5	-	1.27	-	1.23	-	1.21	0.01
Auxiliary materials (isolation)	-	-	-	-	0.77	0.77	0.75	0.75	1.94	1.94
By-products	-	0.4	-	8.4	-	0.09	-	0.05	-	0.02
Coupled products	-	0.2	-	0.1	-	0.18	-	0.18	-	0.18
Total value of parameters	1.6	0.6	9.5	8.5	2.23	1.23	2.15	1.15	3.70	2.70

Environmental Assessment Tool for Organic Syntheses (EATOS), the software can be obtained free of charge via http://www.metzger.chemie.uni-oldenburg.de/eatos/. The data provided in the literature was not comprehensive, such as auxiliary materials, byproducts, sewage, therefore water and ammonia were uniformly taken as coupled product and their quantity was recorded as 0 kg. Assume that the reaction gases were all oxygen and the by-products were ignored. In addition, compared with the solvent-free system, the solvent system needs to separate the solvent from the product (the environmental impact of the separation of the catalyst from the reaction liquid is not considered). According to the literature, one liter of water was required for every 300 mL of reaction liquid separation. Since the volume of the substrate was small (compared with the solvent), the volume of the substrate itself was ignored when calculating the volume of water required for separation. Therefore, the parameters required for calculation are shown in Table S3. Although Ref.1 was a solvent-free system, the substrate quantity was large (30 mmol) and the yield was low (12.5%) under solvent-free conditions, resulting in the large values of E_{in} and E_{out}.

Table S4 Parameter values in the calculation process for the photocatalytic synthesis of benzylamine to N-benzylidenebenzylamine.

Ref.	Substrates/mol		Catalyst /g	Solvents/mL	Auxiliary materials (isolation)	Coupled products/mol	
	C_7H_9N (benzylamine)	O_2				H_2O	NH_3
This work	5	1.5	0.05	-	-	0	0
1	30	7.5	0.03	-	-	0	0
3	0.1	0.025	0.05	Toluene 2 mL	7 mL	0	0
4	0.1	0.025	0.01	Acetonitrile 2 mL	7 mL	0	0
6	0.09	0.025	0.01	N, N-dimethylformamide 5 mL	16.7 mL	0	0

3. Figures

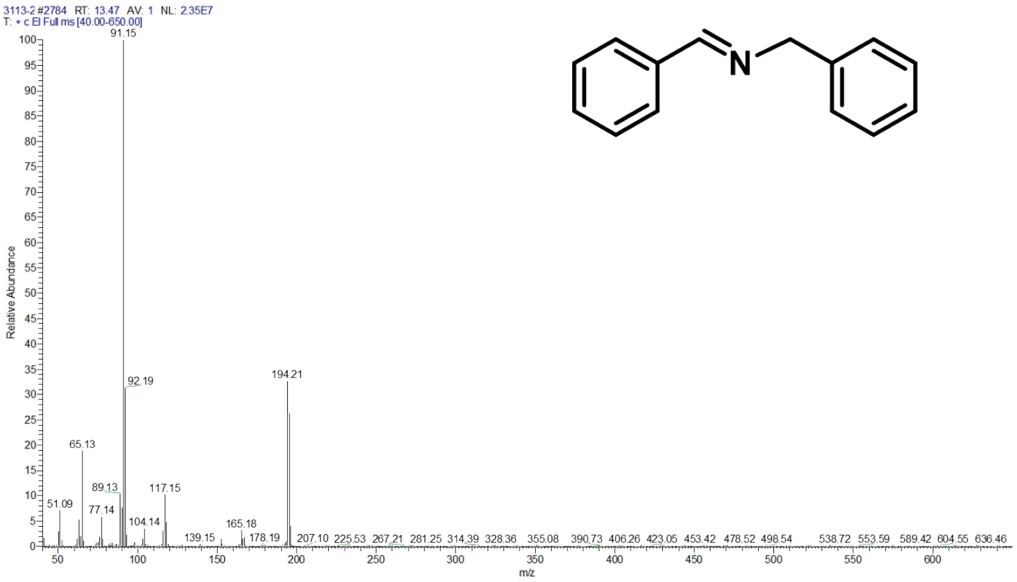

Fig. S1 GC-MS of product.

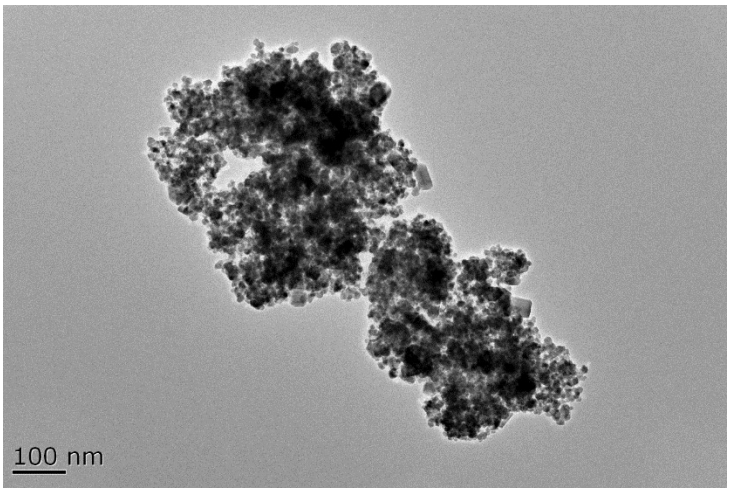

Fig. S2 Low-resolution electron microscopy images.

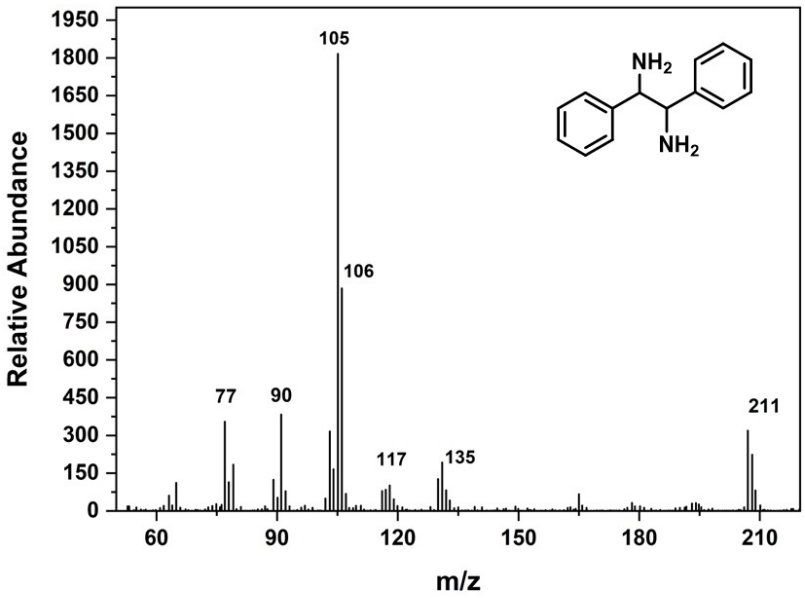

Fig. S3 GC-MS of byproduct.

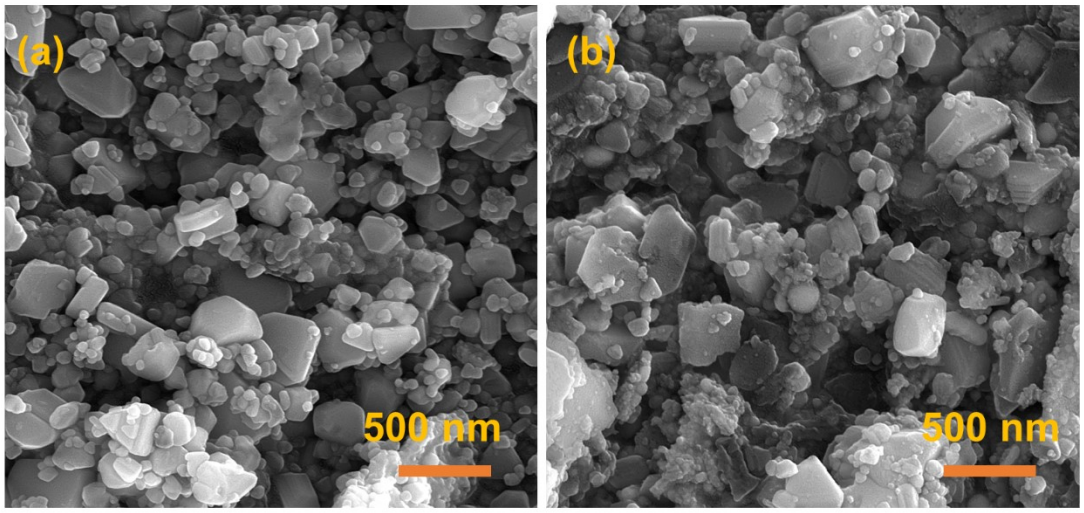

Fig. S4 SEM images of fresh and used catalyst.

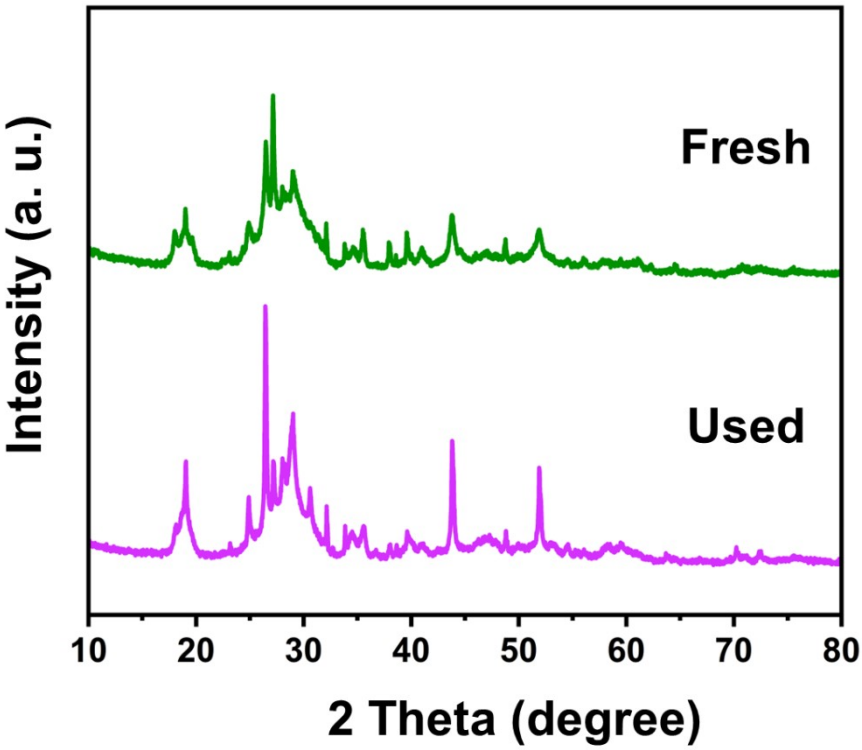

Fig. S5 XRD patterns of fresh and used catalyst.

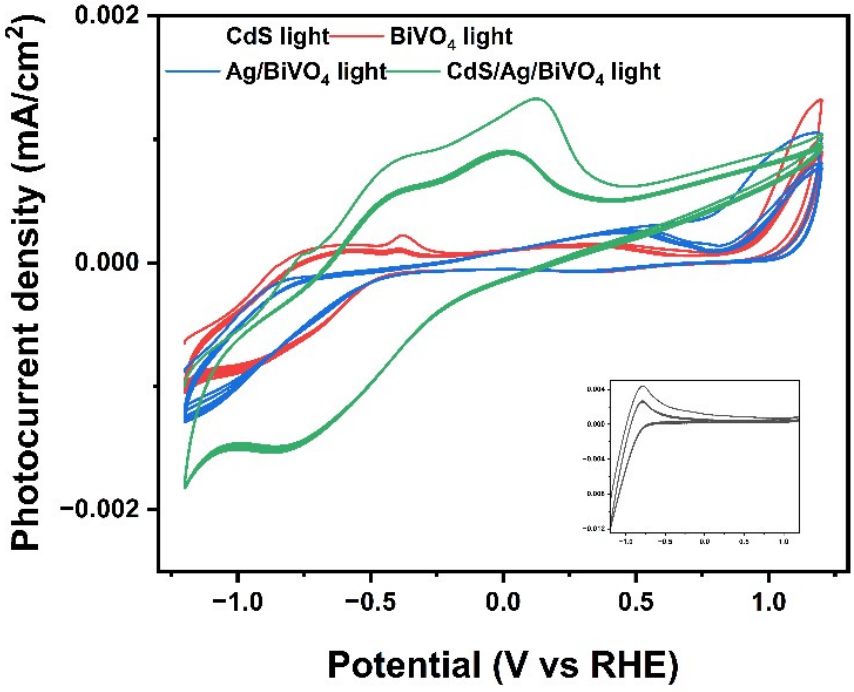

Fig. S6 Cyclic voltammetry curve (CV) of catalysts.

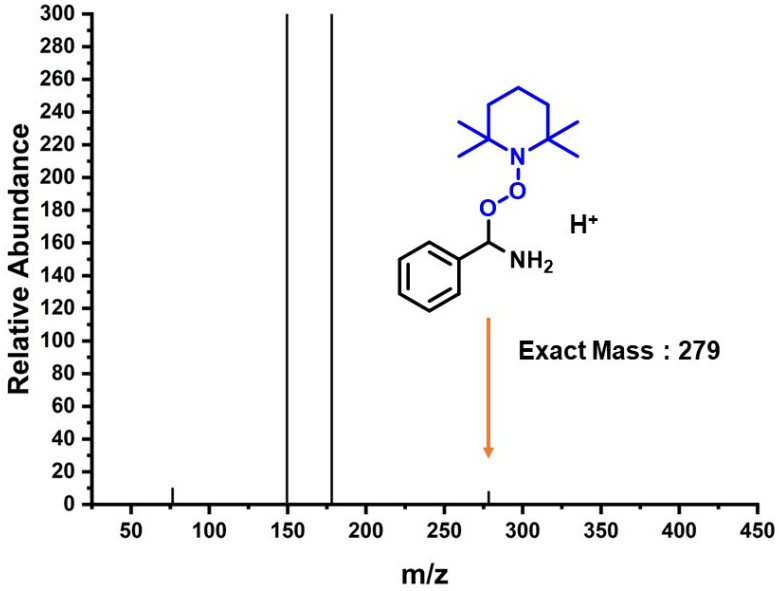

Fig. S7 Mechanistic experiments (Reaction condition: 5 mmol benzylamine, 1 mmol TEMPO, 50 mg catalyst, 1 atm O_2, room temperature, LED 10 W, λ = 400-405 nm, 1 h).

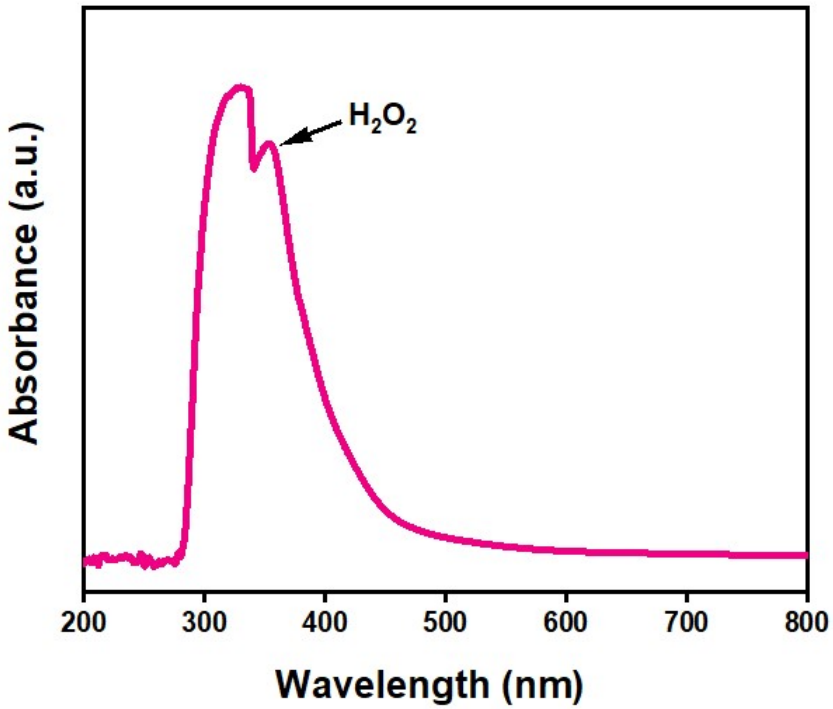

Fig. S8 UV-vis absorption spectrum for detecting the existence of H_2O_2 by using CAB as a catalyst.

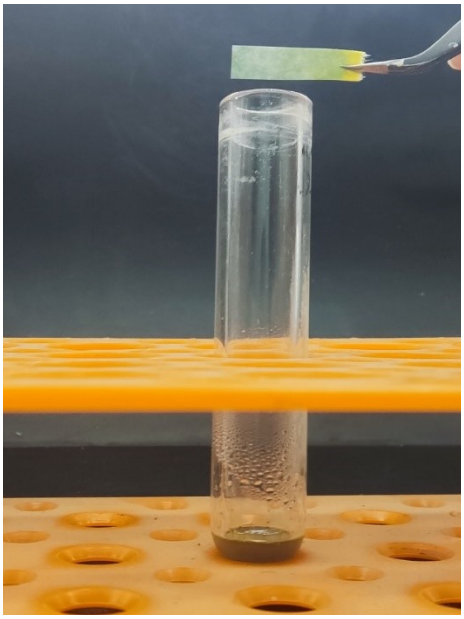

Fig. S9 The pH test paper for testing the production of NH_3.

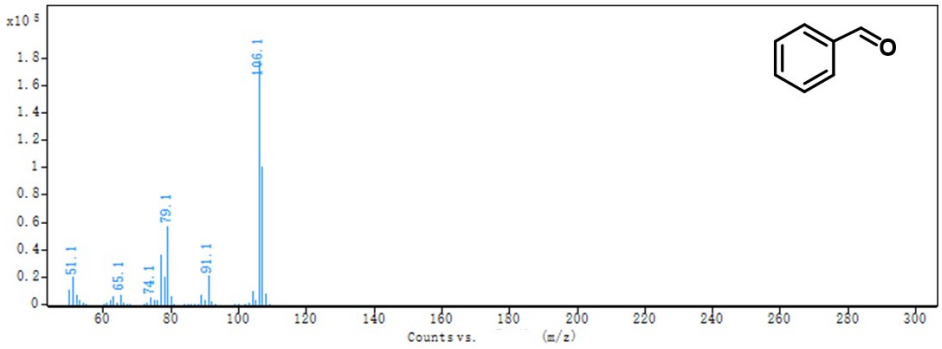

Fig. S10 GC-MS of benzaldehyde.

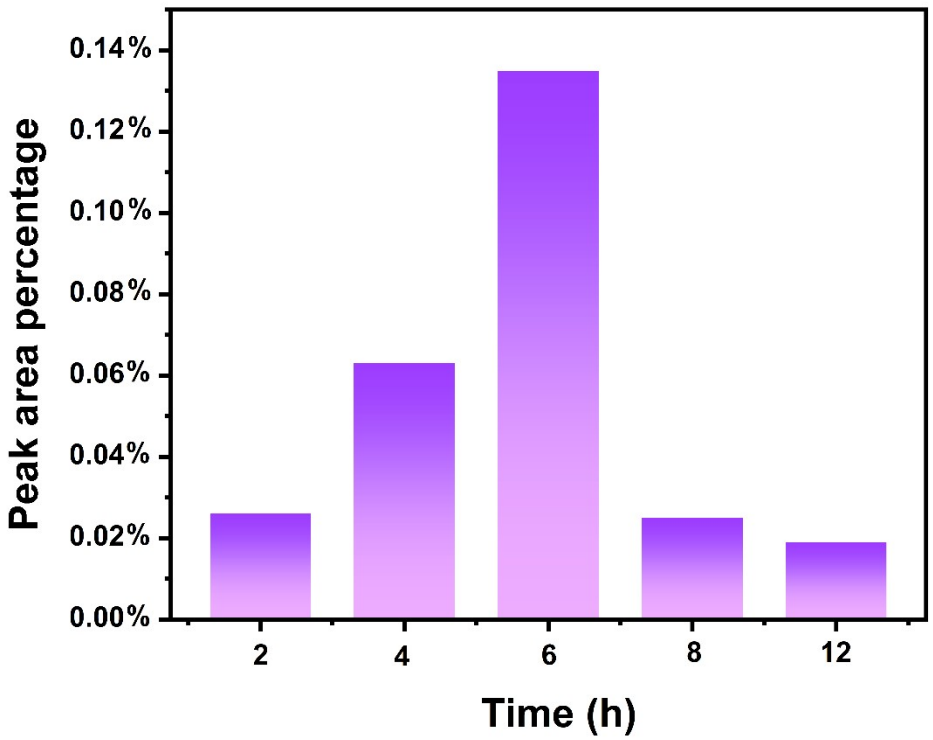

Fig. S11 Peak area percentage of benzaldehyde to internal standard. The Y axis was the peak area ratio of benzaldehyde to the internal standard due to the trace amount of benzaldehyde could not be determined quantitively. It can be found the amount of benzaldehyde was increased and then decreased with the highest content at 6 h, indicating that benzaldehyde was the intermediate compounds during the reaction.

Fig. S12-S22 The MS for the products in Table 2.

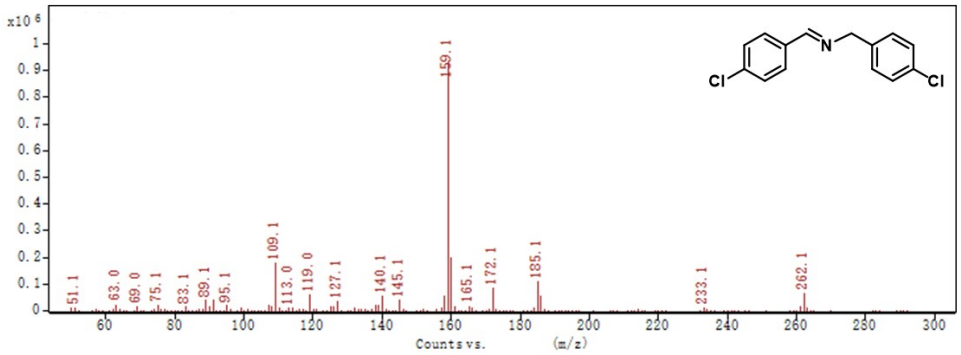

Fig. S12 GC-MS of product in substrate extension entry 1.

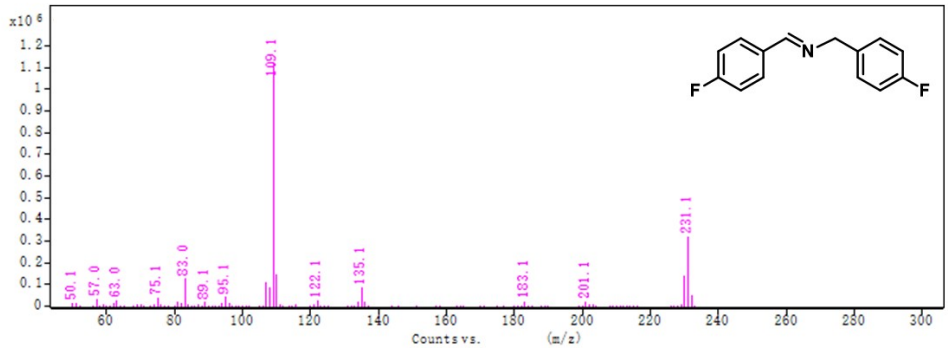

Fig. S13 GC-MS of product in substrate extension entry 2.

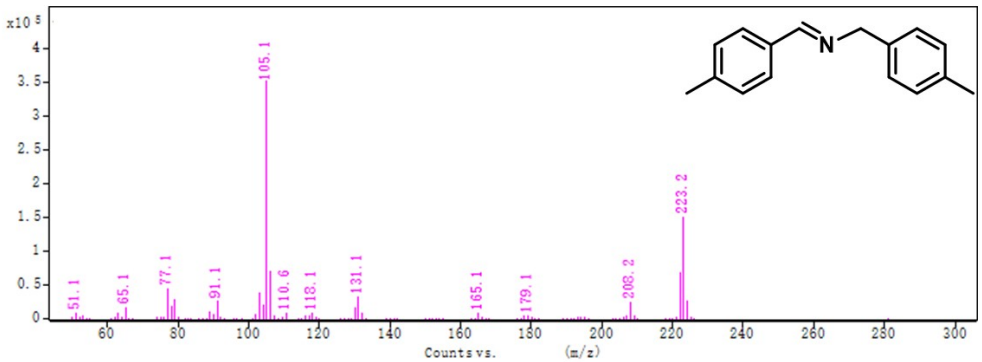

Fig. S14 GC-MS of product in substrate extension entry 3.

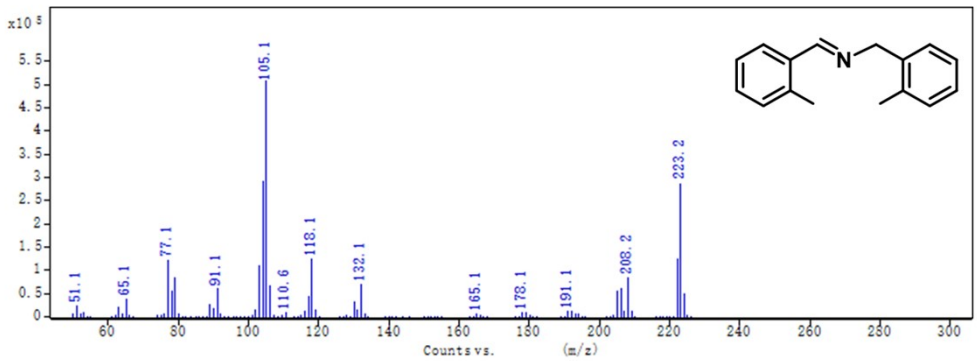

Fig. S15 GC-MS of product in substrate extension entry 4.

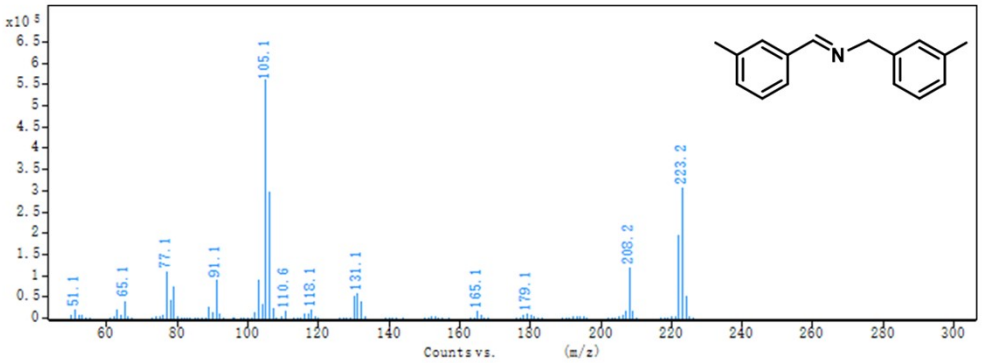

Fig. S16 GC-MS of product in substrate extension entry 5.

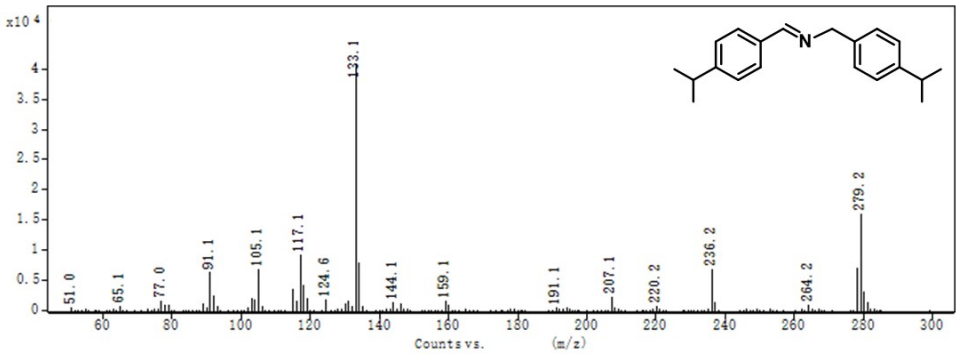

Fig. S17 GC-MS of product in substrate extension entry 6.

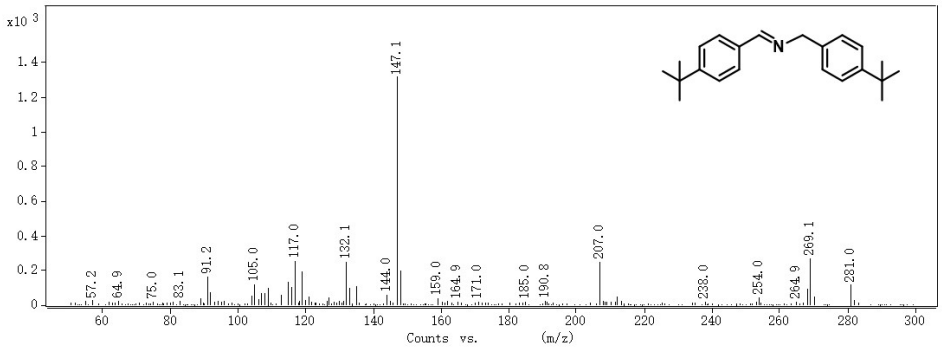

Fig. S18 GC-MS of product in substrate extension entry 7.

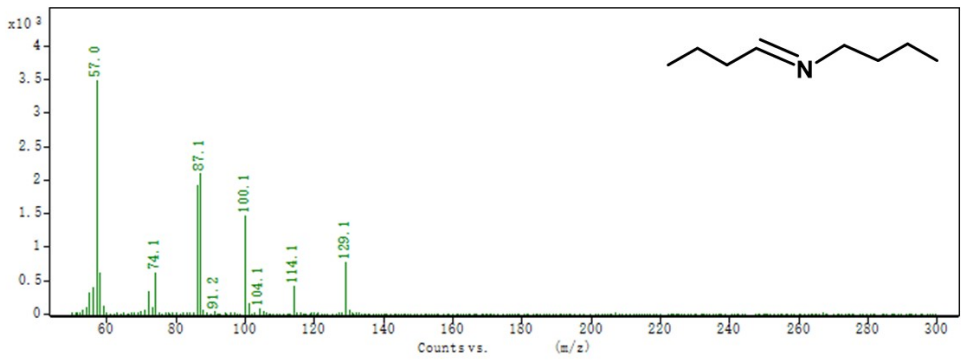

Fig. S19 GC-MS of product in substrate extension entry 8.

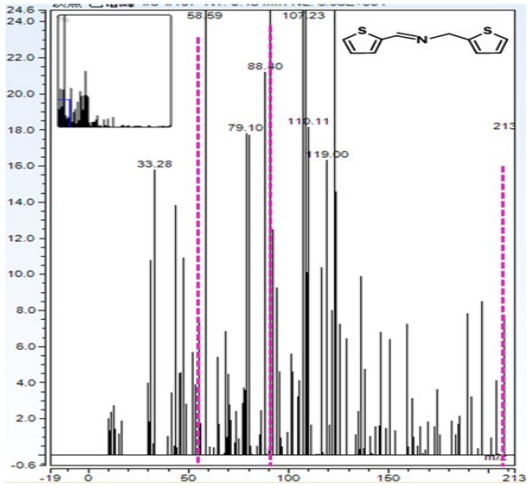

Fig. S20 LC-MS of product in substrate extension entry 9.

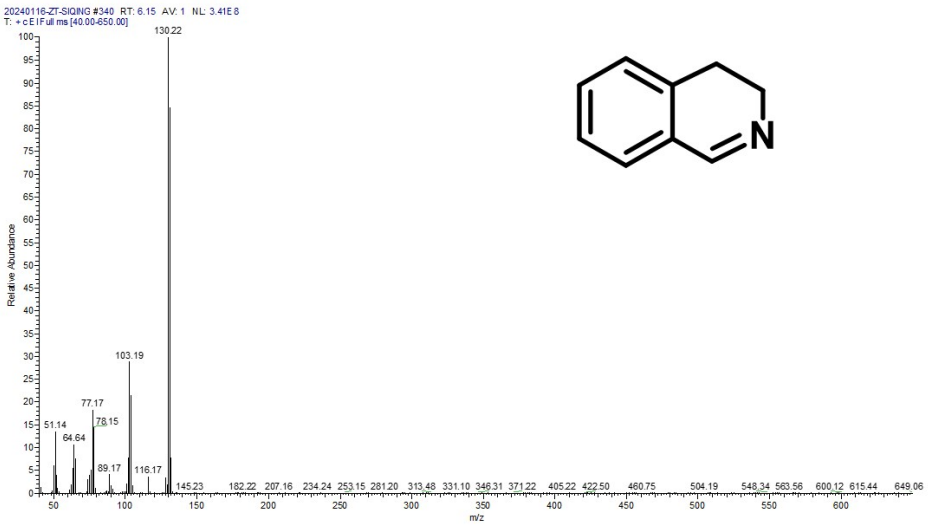

Fig. S21 GC-MS of product in substrate extension entry 10.

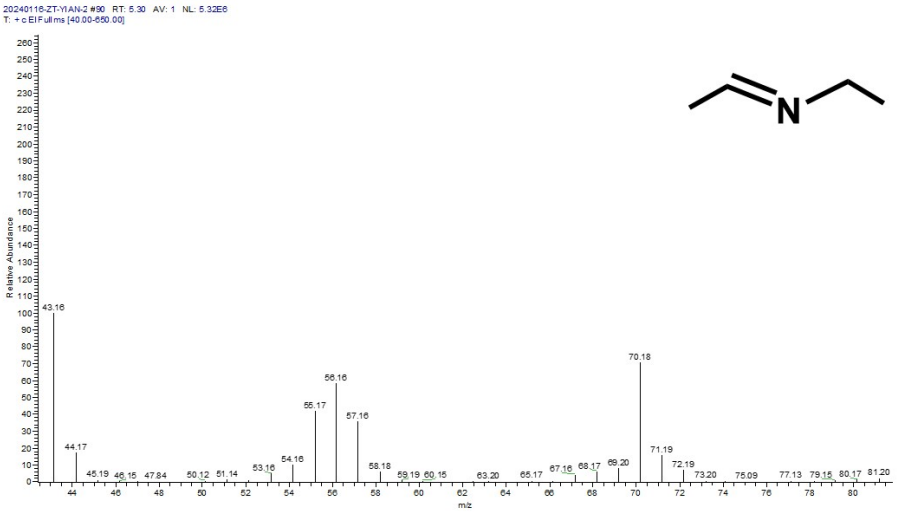

Fig. S22 GC-MS of product in substrate extension entry 11.

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