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Cooperative catalysis of molybdenum with organocatalysts for distribution of products between amines and imines

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ABSTRACT

Multi-amino groups and nitrogen donors compound was discovered as an organocatalyst for *N*-alkylation of alcohols with amines in the presence of $Mo(CO)_6$. The $Mo(CO)_6$/organocatalyst binary system has shown to be a highly active catalyst for the *N*-alkylation reaction between alcohols and amines with excellent tolerance of variable starting materials bearing different functional groups. Of particular note, this method possessing a superiority selectivity in the synthesis of *N*-alkylated amines or imines, which can be controlled by the reaction temperature. The cooperative catalysis mechanism in combination of $Mo(CO)_6$ with organocatalyst was elucidated by control experiments.

1. Introduction

The *N*-alkylation between amines and readily available alcohols is an attractive, elegant, and atom-economic strategy for the synthesis of amines, which play a valuable application in biologically active natural products, pharmaceuticals, and transition metal complexes catalysis as well. [1,2] Since the pioneering works of *N*-alkylation of amines with alcohols over transition metal catalysts were reported independently by Watanabe, [3] Grigg [4] and co-workers in 1981, a wide range of the homogeneous metal catalysts (e.g., Ru [5–11], Ir [12–18], Pd [19], Sm [20], Cu [21–23], Ni [24–27], Mn [28–31], and Fe [32–36]) and heterogeneous metal catalysts (e.g., Ru-Al_2O_3 [37], Ru-Fe_3O_4 [38], Au-TiO_2 [39], and Ni-Al_2O_3 [40]), as well as metal-free catalytic system [41] have also emerged (Scheme 1**a**), with a focus on achieving high catalytic activity and selectivity. Although extensively studied, to the best of our knowledge, the utilization of homogeneous molybdenum catalysts for the synthesis of amines from alcohols has not reported to date.

The overall reaction process for the *N*-alkylation between amines and alcohols involves two key steps: the hydrogen borrowing and the hydrogen autotransfer. In the hydrogen borrowing step, the imine intermediate is formed via the condensation of the obtained aldehyde which generated from the oxidative dehydrogenation of alcohol. The dehydrogenative imines were hydrogenated to deliver amines via the hydrogen auto-transfer reaction. Imines are important building blocks in synthetic chemistry, [42] which makes the controlled-selective synthesis of them is highly desirable. Although a variety of catalytic systems based on metal-free KOH system [43], homogeneous metal catalysts (e.g., Ir [44], Ru [45], Mn [46–49], Os [50], and Mo [51]), and heterogeneous metal catalysts (e.g., Au-Al_2O_3 [52], Co-MnO_2 [53], and MnO_2-GO [54]) have been developed (Scheme 1b), these catalytic reactions are usually performed at high temperature. It is noteworthy that only a heterogeneous gold nanoparticles supported on titanium dioxide catalyst was reported for synthesis of imines by aerobic oxidative coupling of alcohols and amines at room temperature. [55] Thus, the development of homogeneous catalytic systems which can perform with high efficiency at room temperature is still a great challenge.

Recent research found that reaction conditions such as bases, [56–58] molecular sieves (moisture) [59], and atmosphere [60], evidently influence the product distribution between amines and imines (Scheme 2). In previous reports, [26,48,49] amino group or nitrogen donors bearing transition metal complexes have played an important role in the process of acceptorless dehydrogenation and borrowing hydrogen reactions. Therefore, we envisioned to introduce the organocatalysts containing amino group or nitrogen donors to transition metal for *N*-alkylation of amines with alcohols to develop a binary catalytic system with high activity and selectivity.

In this work, we describe a temperature-controlled method for highly selective C—N bond forming reaction of amines with alcohols in the

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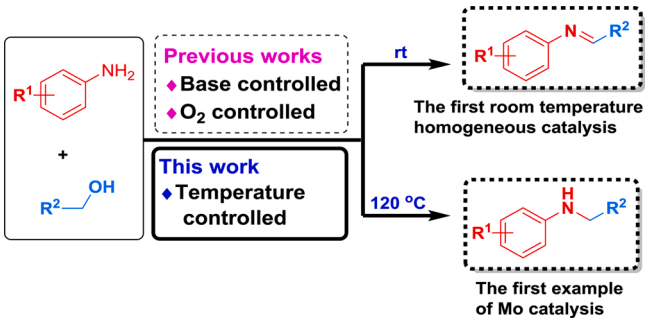
combination of molybdenum with organocatalysts as a binary catalytic system (Scheme 2). This work has four significant advances in this area: (1) the first molybdenum-catalyzed synthesis of amines through the *N*-alkylation of alcohols; (2) the first example of room temperature homogeneous catalytic system for synthesis of imines; (3) the amines and imines selectively obtained under different reaction temperature; (4) the first example of cooperative catalysis between metal and organocatalysts for the *N*-alkylation of alcohols.

2. Results and discussion

The reaction of aniline (**1a**) with benzyl alcohol (**2a**) was used as a benchmark reaction and $Mo(CO)_6$ was employed as metal catalyst to investigate the influence of organocatalysts in the selective *N*-alkylation of amines with alcohols (Table 1). Seven organocatalysts, including diamines (**L1** and **L2**), benzimidazolium salts (**L3-5**), and a pyridine bridged disubstituted nitrogen heterocyclic compound ((**L6**), were evaluated in the selective *N*-alkylation of amines with alcohols. The results indicated that **L1** showed outstanding performance and selectivity not only in synthesis of imines but also in synthesis of amines.

Next, the reaction of aniline (**1a**) with benzyl alcohol (**2a**) was used as a benchmark reaction and $Mo(CO)_6$ combined with organocatalyst **L1** to optimize reaction conditions for synthesis of amine **3a** (Table 2). The influences of loading of $Mo(CO)_6$ and **L1** were evaluated, and it was demonstrated that 4 mol% loading of $Mo(CO)_6$, together with 4 mol% loading of organocatalyst **L1** was appropriate for high transformation (Table 2, entries 2 vs 1, 3 and 4). Besides KO*t*Bu, other bases such as NaO*t*Bu, K_2CO_3, and KOH were examined, and KO*t*Bu exhibited the best performance (Table 2, entries 2 vs 5–7). The solvents had a significant influence on reactivity. Nonpolar or weakly polar organic solvents, such as toluene and 1,4-dioxane, showed better effectiveness, giving a high yield of **3a** (Table 2, entries 2 and 10). Highly polar aprotic solvents, such as DMF and DMSO, were difficult to trigger the reaction (Table 2, entries 8 and 9). Other the common Mo salts, instead of $Mo(CO)_6$, were investigated in this reaction, and it was indicated that they hardly showed any activity (Table 2, entries 11–14) or afforded very low yield (Table 2, entries 15–17). Of particular note, the control experiments in the absence of $Mo(CO)_6$ or organocatalyst **L1** were explored (Table 2, entries 16 and 17), respectively, and it was found that the binary system in combination of $Mo(CO)_6$ with organocatalyst **L1** were necessary for a high yield of **3a** (Table 2, entry 2), because the absence of any one of two resulted in a remarkable decline in the yield of **3a** (Table 2, entries 16 and 17).

To demonstrate the scope and limitation of the developed protocols employing $Mo(CO)_6$ and **L1** as catalysts, a wide range of aryl amines were explored (Table 3). It was found that aryl amines bearing electron-withdrawing group (Table 3, **3b-e**) and electron-donating group (Table 3, **3f** and **3 g**) as well as electron-neutral group (Table 3, **3a**), were suitable for the coupling reaction with benzyl alcohol, affording the desired products in good to excellent yields. When using *meta*-tolylmethanol as a benchmark substrate, the electronic effect of aryl

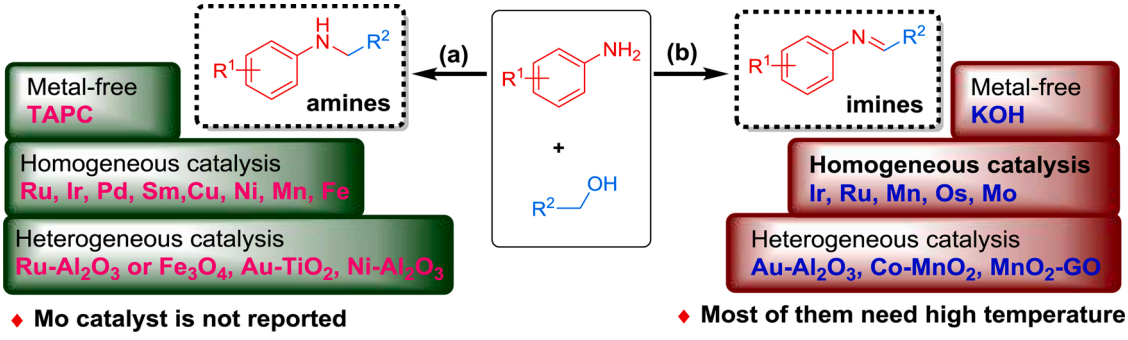


Scheme 2. The selective *N*-alkylation of amines with alcohols.

amines was obvious. The *para*-fluoroaniline containing electron-withdrawing group (Table 3, **3 h**) displayed lower reactivity than *para*-toluidine containing electron-donating group (Table 3, **3i**). The electronic effect of *meta*- or *ortho*-substituted aryl bromides was significant, and aryl bromides with electron-withdrawing group both at *meta*-position and *ortho*-position showed higher reactivity than those with electron-donating group (Table 3, **3 j** and **3k** vs 3 L; **3 m** and **3n** vs **3o**). *Alpha*- or *beta*-naphthyl and benzdioxine amines smoothly reacted with benzyl alcohol to give **3p-r** in moderate to good yields.

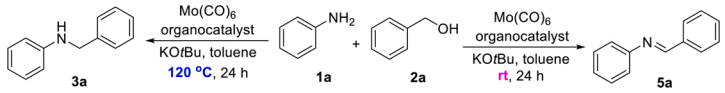
The scope of alcohols was also investigated under the optimized reaction conditions (Table 4). The benzyl alcohols bearing electron-withdrawing group at aryl ring such as chlorine, bromine, fluorine, trifluoromethyl group displayed higher reactivity than those bearing electron-donating group such as methoxy group (Table 4, **a-d** vs **e**; **f** vs **g** and **h**). The electronic effect of *meta*-substituted benzyl alcohols was not obvious, and benzyl alcohols with trifluoromethyl group, chlorine, and methyl group at *meta*-position of benzene ring reacted with aniline to give high yield (Table 4, **i-k**). *Ortho*-methyl group benzyl alcohol also worked well to afford 83 % yield of 4 L. The thiophen-2-ylmethanol also tolerated, giving 83 % yield of **4 m**. The aliphatic alcohols were generally considered as a kind of challenging substrates. Several aliphatic alcohols, such as *n*-propanol, *n*-butanol, and *n*-octanol, were compatible with developed Mo-**L1** catalytic system, affording the products **4n-r** in yields of 28–52 %.

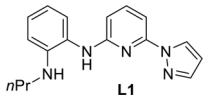
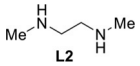
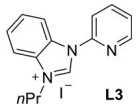
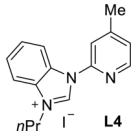
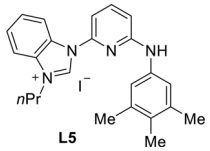
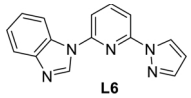
The reaction conditions for synthesis of imines from aniline (**1a**) and benzyl alcohol (**2a**) was optimized by employing the developed binary catalytic system of $Mo(CO)_6$ and organocatalyst **L1** (Table 5). The influences of loading of $Mo(CO)_6$, organocatalyst **L1** and base KO*t*Bu were investigated, and 4 mol% of $Mo(CO)_6$ in combination with 4 mol% of **L1**, together with 1.5 equiv. of KO*t*Bu, was appropriate for the synergistic catalysis in the synthesis of imines (Table 5, entries 2 vs 1 and 3–5). The yield of **5a** was improved when the reaction temperature decreases from 30 °C to room temperature (Table 5, entries 6 vs 2), which owing to lower reaction temperature facilitates the generation of imines in competitive reaction for formation of amines and imines. A slight decrease in activity was observed in the absence of $Mo(CO)_6$, therefore, organocatalyst **L1** was crucial for a high performance of this reaction



Scheme 1. The distribution of the products derived from *N*-alkylation of amines with alcohols.

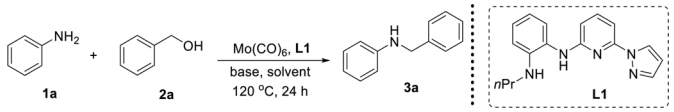
Table 1
Organocatalysts Screening for Mo Catalyzed *N*-Alkylation of **1a** with **2a**.[a]



Entry	Organocatalysts	**3a** yield (%)	**5a** yield (%)
1	 **L1**	96	96
2	 **L2**	20	47
3	 **L3**	58	33
4	 **L4**	34	35
5	 **L5**	40	28
6	 **L6**	45	32

[a] Reaction conditions: the reaction was carried out with **1a** (0.5 mmol), **2a** (0.6 mmol), $Mo(CO)_6$ (0.02 mmol), organocatalysts (0.02 mmol), and base (0.75 mmol) under an air atmosphere at 120 °C in toluene (2.0 mL) for 24 h. [b]Reaction conditions: The recation was carried out with **1a** (0.5 mmol), **2a** (0.6 mmol), $Mo(CO)_6$ (0.02 mmol), organocatalysts (0.02 mmol), and base (0.75 mmol) under an air atmosphere at room temperature in toluene (2.0 mL) for 24 h.

Table 2
Optimization of conditions for synthesis of aimines.[a]



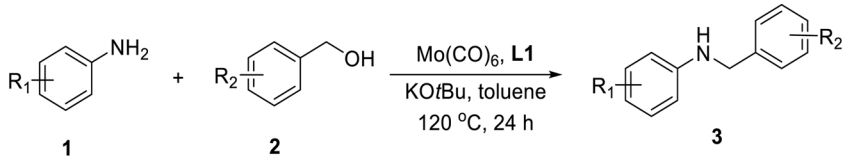
Entry	Mo catalysts (mol%)	L1 (mol%)	Solvent	Base	Yield (%)	Conv. (%)	TON[b]	TOF (h^{-1})[b]
1	$Mo(CO)_6$ (2)	2	toluene	KO*t*Bu	69	79	39.50	1.65
2	$Mo(CO)_6$ (4)	4	toluene	KO*t*Bu	96	>99	24.75	1.03
3	$Mo(CO)_6$ (8)	8	toluene	KO*t*Bu	92	95	12.50	0.52
4	$Mo(CO)_6$ (4)	8	toluene	KO*t*Bu	98	>99	24.75	1.03
5	$Mo(CO)_6$ (4)	4	toluene	NaO*t*Bu	68	73	18.25	0.76
6	$Mo(CO)_6$ (4)	4	toluene	K_2CO_3	trace	12	3.00	0.13
7	$Mo(CO)_6$ (4)	4	toluene	KOH	trace	30	7.50	0.31
8	$Mo(CO)_6$ (4)	4	DMF	KO*t*Bu	trace	18	4.50	0.19
9	$Mo(CO)_6$ (4)	4	DMSO	KO*t*Bu	trace	28	7.00	0.29
10	$Mo(CO)_6$ (4)	4	1,4-dioxane	KO*t*Bu	80	89	22.25	0.93
11	MoO_3 (4)	4	toluene	KO*t*Bu	0	36	9.00	0.38
12	Na_2MoO_4 (4)	4	toluene	KO*t*Bu	0	22	5.50	0.23
13	$H_8MoN_2O_4$ (4)	4	toluene	KO*t*Bu	trace	36	9.00	0.38
14	$C_{10}H_{14}MoO_6$ (4)	4	toluene	KO*t*Bu	0	39	9.75	0.41
15	$MoCl_5$ (4)	4	toluene	KO*t*Bu	18	40	10.00	0.42
16	$Mo(CO)_6$ (4)	0	toluene	KO*t*Bu	29	58	14.50	0.60
17	$Mo(CO)_6$ (0)	4	toluene	KO*t*Bu	16	26	6.50[c]	0.27[c]

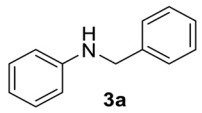
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), Mo catalysts (as indicated in Table 2), **L1** (as indicated in Table 2), base (0.75 mmol) under air at 120 °C solvent (2 mL) for 24 h, isolated yields were determined by column chromatography, conversions were determined by GC. [b]TON and TOF calculation based on amount of Mo $(CO)_6$. [c]TON and TOF calculation based on amount of **L1**.

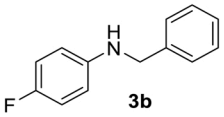
(Table 5, entries 7 vs 6). Control expriments in the absence of organocatalyst **L1** indicated that $Mo(CO)_6$ played a role of promoting agent in synthesis of imines due to the alone use of $Mo(CO)_6$ resulted in a significant loss of activity (Table 5, entries 8 vs 6).

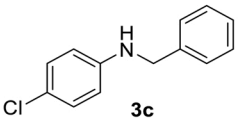
Under the optimzed reaction conditions (room temperature), a range of amines and alcohols were explored for synthesis of imines in the established Mo-**L1** catalytic system (Table 6). The electronic effect of substituents on *para*-position of aryl amines is obvious in this reaction.

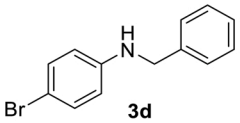
Table 3
Scope of aryl amines: Synthesis of *N*-benzyl aryl amine derivatives.[a]

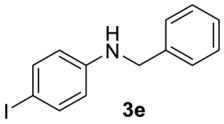


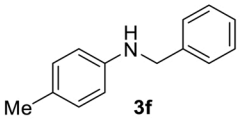

3a
yield 96%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

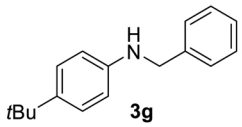

3b
yield 98%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

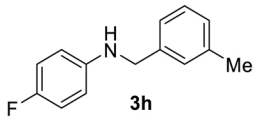

3c
yield 95%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

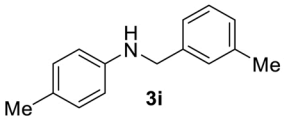

3d
yield 91%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

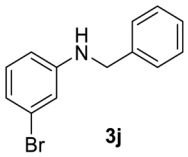

3e
yield 75%; conv. 87%
TON=21.75; TOF=0.91 h^{-1}

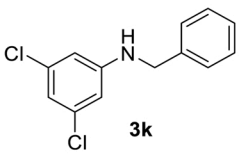

3f
yield 90%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

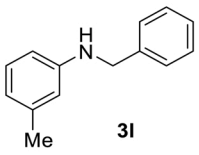

3g
yield 93%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}

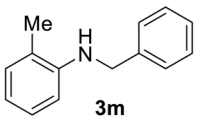

3h
yield 76%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

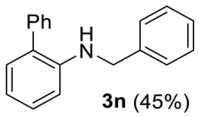

3i
yield 92%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

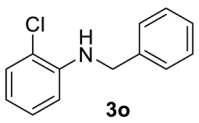

3j
yield 86%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}

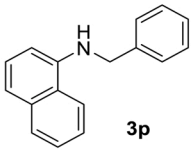

3k
yield 87%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}

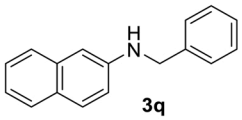

3l
yield 65%; conv. 79%
TON=19.75; TOF=0.82 h^{-1}

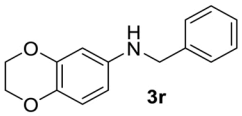

3m
yield 30%[b]; conv. 94%[b]
TON=23.50; TOF=0.98 h^{-1}


3n (45%)
yield 45%; conv. 93%
TON=23.25; TOF=0.97 h^{-1}


3o
yield 77%; conv. 90%
TON=22.50; TOF=0.94 h^{-1}


3p
yield 78%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}

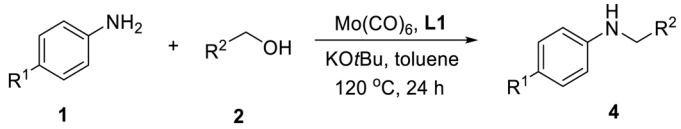

3q
yield 93%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}


3r
yield 65%; conv. 97%
TON=24.25; TOF=1.01 h^{-1}

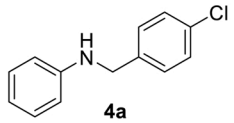
[a] Reaction conditions: the reaction was carried out with **1** (0.5 mmol), **2a** (0.6 mmol), $Mo(CO)_6$ (4 mol%), **L1** (4 mol%), and KO*t*Bu (0.75 mmol) under air at 120 °C in toluene (2.0 mL) for 24 h, isolated yields were determined by column chromatography, conversions were determined by GC, TON and TOF calculation based on amount of $Mo(CO)_6$. [b]125 °C, 36 h.

The aryl amines bearing electron-neutral group (Table 6, **5a**) and electron-donating group such as methyl group (Table 6, **5e**) displayed higher reactivity than those with electron-withdrawing group such as fluorine group, bromine group, and iodine group (Table 6, **5b-d**). The aryl amine with electron-donating methyl group (Table 6, **5 g**) showed higher reactivity than that with electron-withdrawing fluorine group (Table 6, **5f**). *Beta*-naphthyl substituted amine reacted with benzyl alcohol, affording 82 % yield of **5 h**. The aryl amines both bearing electron-withdrawing chlorine group and electron-donating methoxy group delivered moderate yield of the desired produt **5i** and **5 j**, respectively. The aryl amines with chlorine group and methoxy gourp on *meta*-position of benzene ring proceeded well, giving desired products in 81 % and 89 % yields (Table 6, **5k** and 5 L), respectively. *Ortho*-methyl benzyl alcohol showed low reactivity and gave a 45 % yield of **5 m**. The

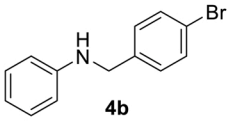
Table 4
Scope of alcohols: Synthesis of *N*-benzyl aniline derivatives.[a]



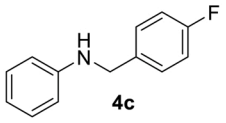
1 2 4



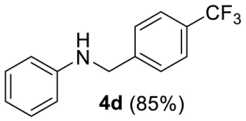
4a
yield 85%; conv. 91%
TON=22.75; TOF=0.95 h^{-1}



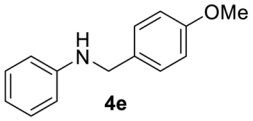
4b
yield 96%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}



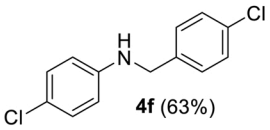
4c
yield 68%; conv. 85%
TON=21.25; TOF=0.89 h^{-1}



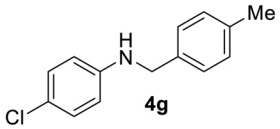
4d (85%)
yield 85%; conv. 88%
TON=22.00; TOF=0.92 h^{-1}



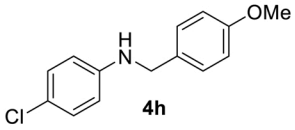
4e
yield 65%; conv. 97%
TON=24.25; TOF=1.01 h^{-1}



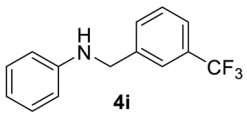
4f (63%)
yield 63%; conv. 81%
TON=20.25; TOF=0.84 h^{-1}



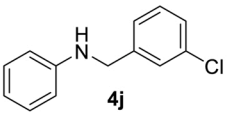
4g
yield 55%; conv. 78%
TON=19.50; TOF=0.81 h^{-1}



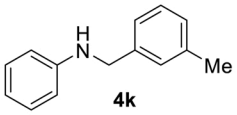
4h
yield 51%; conv. 72%
TON=18.00; TOF=0.75 h^{-1}



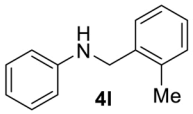
4i
yield 88%; conv. 90%
TON=22.50; TOF=0.94 h^{-1}



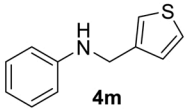
4j
yield 98%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}



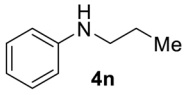
4k
yield 90%; conv. 91%
TON=22.75; TOF=0.95 h^{-1}



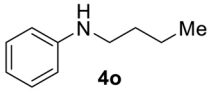
4l
yield 83%; conv. 96%
TON=24.00; TOF=1.00 h^{-1}



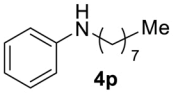
4m
yield 90%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}



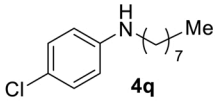
4n
yield 45%; conv. 90%
TON=22.50; TOF=0.94 h^{-1}



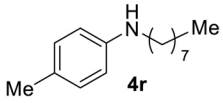
4o
yield 50%; conv. 70%
TON=17.50; TOF=0.73 h^{-1}



4p
yield 52%; conv. 89%
TON=22.25; TOF=0.93 h^{-1}



4q
yield 47%; conv. 69%
TON=17.25; TOF=0.72 h^{-1}



4r
yield 28%; conv. 90%
TON=22.50; TOF=0.94 h^{-1}

[a] Reaction conditions: Reaction was carried out with **1** (0.5 mmol), **2** (0.6 mmol), $Mo(CO)_6$ (4 mol%), **L1** (4 mol%), and KO*t*Bu (0.75 mmol) under air at 120 °C in toluene (2.0 mL) for 24 h, isolated yields were determined by column chromatography, conversions were determined by GC, TON and TOF calculation based on amount of $Mo(CO)_6$.

thiophen-2-ylmethanol was also suitable for this reaction, giving desired product **5n** in 94 % yield.

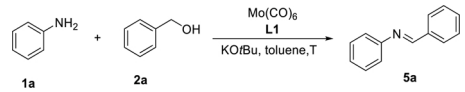
To our delight, this Mo-organocatalyst cooperative catalyzed C—N bond forming approach was also evaluated for the synthesis of resveratrol-derived amines. We note that **6a** and **6b** are important pharmaceutical against Alzheimer's disease, the desired products were obtained with an excellent yield of 85 % and 62 % (Scheme 3), respectively.

To further explore the scope of this method, we next proceeded to evaluate the *ortho*-phenylenediamine. As shown in Scheme 4, *ortho*-phenylenediamine smoothly coupled with benzyl alcohol (**2a**) to give **7a** in a yield of 75 %, which have good agreetment with the results reported by Adhikari and co-workers. [26]

To prove the applications of our developed method, gram-scale experiments were performed for the synthesis of imines with amines, respectively. As shown in Scheme 5, the reactions of aniline (**1a**) with benzyl alcohol (**2a**) were scaled up to the gram scale to give **3a** and **5a** in 76 % of yield and 80 % of yield, respectively.

To explore whether the imines could be converted into amines under standard conditions, a kinetic experiment was performed (Fig. 1). First, the *N*-alkylation of aniline (**1a**) with benzyl alcohol (**2a**) was carried out under room temperature, with imine **3a** obtained in 92 % yield (Fig. 1,

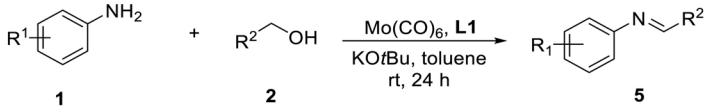
Table 5
Optimization of conditions for synthesis of imines.[a]

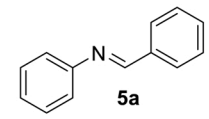


Entry	$Mo(CO)_6$ (mol%)	L1 (mol%)	KO*t*Bu (mol)	T (°C)	Yield (%)	Conv. (%)	TON[b]	TOF (h^{-1})[b]
1	2	2	0.75	30	30	33	16.50	0.69
2	4	4	0.75	30	92	99	24.75	1.03
3	8	8	0.75	30	80	91	11.38	0.47
4	4	4	0.6	30	90	95	23.75	0.99
5	4	4	0.5	30	75	83	20.75	0.86
6	4	4	0.75	rt	96	99	24.75	1.03
7	0	4	0.75	rt	82	90	22.50[c]	0.94[c]
8	4	0	0.75	rt	0	25	6.25	0.26

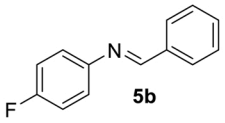
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), **L1** (4 mol%), toluene (2.0 mL) for 24 h, under air, isolated yields were determined by column chromatography, conversions were determined by GC.
[b] TON and TOF calculation based on amount of $Mo(CO)_6$.
[c] TON and TOF calculation based on amount of **L1**.

Table 6
Synthesis of imines from various alcohols and amines.[a]

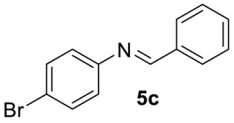




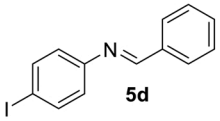
yield 96% (86%[b]); conv. 99%
TON=24.75; TOF=1.03 h^{-1}



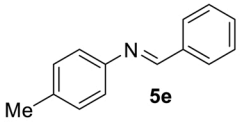
yield 65%; conv. 87%
TON=21.75; TOF=0.91 h^{-1}



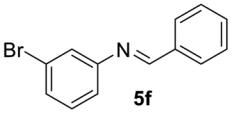
yield 60%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}



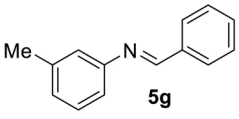
yield 55%; conv. 83%
TON=20.75; TOF=0.86 h^{-1}



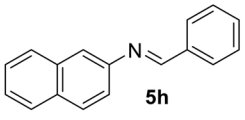
yield 74%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}



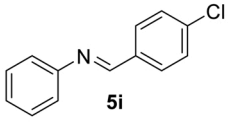
yield 70% (50%[c]); conv. 99%
TON=24.75; TOF=1.03 h^{-1}



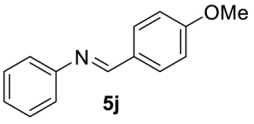
yield 92%; conv. 93%
TON=23.25; TOF=0.97 h^{-1}



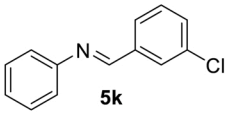
yield 82%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}



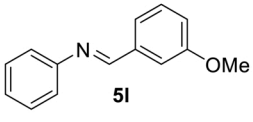
yield 60% (50%[b]); conv. 99%
TON=24.75; TOF=1.03 h^{-1}



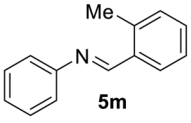
yield 52%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}



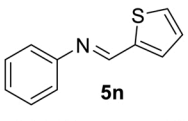
yield 81%; conv. >99%
TON=24.75; TOF=1.03 h^{-1}



yield 80% (60%[b]); conv. 99%
TON=24.75; TOF=1.03 h^{-1}

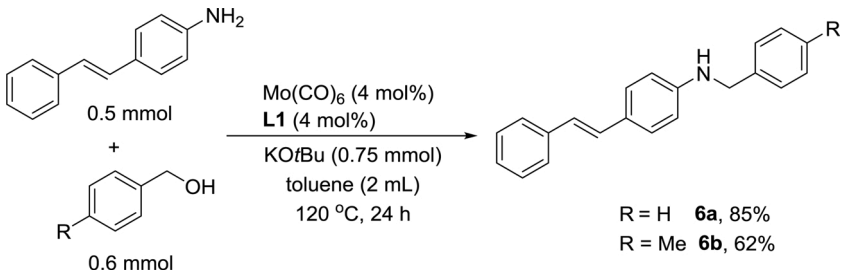


yield 45%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}

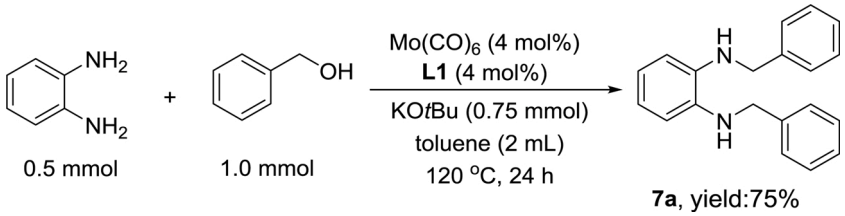


yield 94%; conv. 99%
TON=24.75; TOF=1.03 h^{-1}

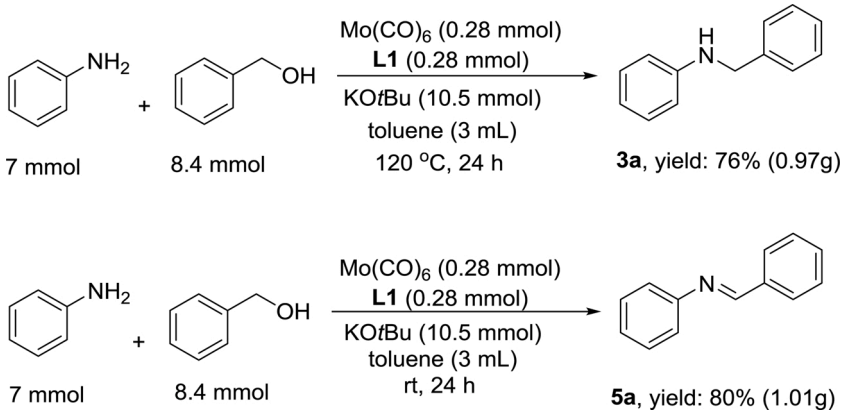
[b]5 h. [c]12 h.
[a] Reaction conditions: Recation was carried out with **1** (0.5 mmol), **2** (0.6 mmol), $Mo(CO)_6$ (4 mol%), **L1** (4 mol%), and KO*t*Bu (0.75 mmol) under air at room temperature in toluene (2.0 mL) for 24 h, isolated yields were determined by column chromatography, conversions were determined by GC, TON and TOF calculation based on amount of $Mo(CO)_6$.



Scheme 3. Application of synthetic method.



Scheme 4. Investigation for *ortho*-phenylenediamine.



Scheme 5. Gram-scale synthesis.

blue area). Then, the reaction mixtures above was heated to 120 °C immediately, and amine **5a** was obtained in 43 % yield (Fig. 1, red area), in which the product yield of **5a** was obviously decreased in comparision with the result in Table 2 (entry 2). Next, we detected the reaction process using GC method. The results indicated that imine **3a** was not stable under high temperature (120 °C) conditions, which led to the poor result. However, as shown in Table 2 (entry 2), imine **3a** generated from **1a** and **2a** under 120 °C will convert immediately into amine **5a** before the decomposition of the intermediate imine **3a**.

The organocatalyst **L1** containing two amino group and multi-nitrogen donors. Therefore, it is crucial for exploring the function of each active site bearing organocatalyst **L1** in the catalytic cycle. To gain mechanistic insight into the active sites, we designed and synthesized a variety of catalysts **A**-**D** to investigate the reaction mechanism.

First, the function of amino groups was explored. When an amino group was protected by an aldehyde group (Fig. 2, **A**), the catalytic activity of catalyst of **A** caused a significant loss, especially in synthesis of amines (Fig. 2, **A** vs **L1**). These results suggest that the amino group bearing *n*-propyl group has played an important role in the catalytic activity and performance.

Then, the amino group between pyridine ring and benzene ring was protected by a methyl group (Fig. 2, **B**). The result showed that methylation of the amino group led to an obvious decrease in product yield (Fig. 2, **B** vs **L1**), however, inhibition of catalytic activity causing by this amino group is lower than the amino group bearing *n*-propyl group (Fig. 2, **B** vs **A**). These results indicated that the amino group bearing *n*-propyl group has played more important role than the amino group bearing aryl ring.

To investigate the effect of pyrazole group bearing organocatalyst **L1**, a catalyst was synthesized by removing pyrazole group from the organocatalyst **L1** (Fig. 2, **C**). In the absence of pyrazole group, amine **3a** was obtained in good yield, however, imine **5a** was difficult to occur (Fig. 2, **C** vs **L1**). These results indicated that pyrazole group is crucial for synthesis of imines, but pyrazole group is negligible in synthesis of amines.

To investigate the effect of pyridine ring bearing organocatalyst **L1**, a catalyst was synthesized by replacing pyridine ring with benzene ring (Fig. 2, **D**). The catalytic activity of **D** showed an obvious decline in synthesis of amines compared with catalyst **C**, suggesting the pyridine ring has an important role in synthesis of amines.

According to the control experiments of designed catalysts in Fig. 2, a possible catalytic cycle for synthesis of imines and amines was proposed (Fig. 3). Under room temperature conditions, the pyrazole group has played an important role in the synthesis of imines, therefore, a possible mechanism was proposed for the synthesis of imines. In this process, carbon monoxide was captured by amino group bearing organocatalyst **L1**, simultaneously generating a key active intermediate **L1A**. The previous report [61] demonstrated that the carbon monoxide was captured

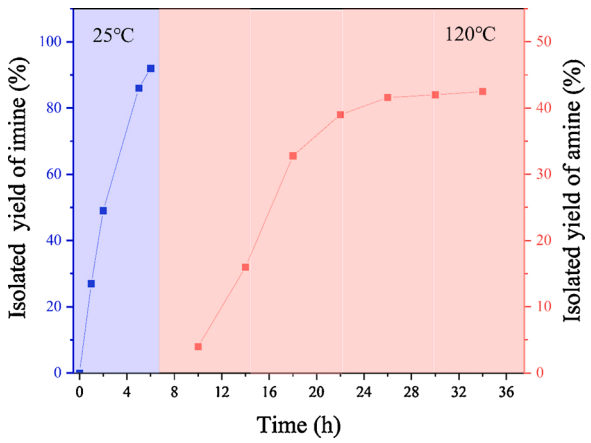


Fig. 1. Investigation for temperature-switchable distribution of products. Reaction conditions for synthesis of imines (blue area): Recation was carried out with **1a** (0.5 mmol), **2a** (0.6 mmol), $Mo(CO)_6$ (4 mol%), **L1** (4 mol%), and KO*t*Bu (0.75 mmol) under air at room temperature in toluene (2.0 mL) for 24 h, isolated yield. Reaction conditions for synthesis of amines (red area): Reaction was carried out with **1a** (0.5 mmol), **2a** (0.6 mmol), $Mo(CO)_6$ (4 mol%), **L1** (4 mol%), and KO*t*Bu (0.75 mmol) under air at 120 °C in toluene (2.0 mL) for 24 h, isolated yield (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

to give a formamide intermediate, which explained the importance of amino group bearing **L1** in the catalytic cycle (Fig. 2, **A** and **B**). Next, the results of another carbonyl group bearing $Mo(CO)_5$ was captured by another amino groups bearing organocatalyst **L1**, which provided two available coordination sites to interact with benzyl alcohol and pyridine nitrogen to generate an intermediate **L1B**. Hydroxyl hydrogen with benzyl alcohol was transferred to pyrazole ring with organocatalyst **L1** to form the intermediate **L1C**, which underwent a C—H bond activation to generate a cyclic intermediate **L1D**. Thereafter, the *beta*-H elimination of **L1D** was occurred to generate **L1E** and aldehyde. Finally, the H_2 was released from **L1E** and regenerated organocatalyst **L1** and $Mo(CO)_6$.

Under high temperature conditions, the imine generated from the reaction of aldehyde with amine was reduced by intermediate **L1E**, simultaneously generating the desired product amines (Fig. 3).

3. Conclusion

In conclusion, a binary system in combination of $Mo(CO)_6$ with organocatalysts are shown to be highly efficient and selective catalysts for the synthesis of amines or imines from aryl amines and alcohols. Both amines and imines selectively achieved from the same set of alcohols and amines using the same catalyst under different reaction temperature. Control experiments implied that the amino groups bearing organocatalysts played a role of carbon monoxide capture agent. While the pyridine ring played an important role in the process of borrowing hydrogen/hydrogen autotransfer for the synthesis of amines. In the synthetic process of imines, pyrazole ring and Mo center played a role in the process of dehydrogenative condensation. The knowledge obtained through cooperative catalysis of molybdenum with organocatalysts in this work provides insight to the rational design of catalysts aiming to improve their catalytic activity.

4. Experimental

4.1. Analytical methods

The NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer using tetramethyl silane (TMS) as an internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). High-resolution mass spectroscopy (HR-MS) data were collected on a Bruker ultrafleXtreme MALDI-TOF/TOF mass spectrometer. GC analyses were carried on a Shimadzu GC-2014 equipped with a packed column (GDX-301, 2 m × 4 mm) using a flame ionization detector. IR spectra were obtained using a Gangdong FTIR-650 spectrometer.

Synthetic Procedures for the Synthesis of Ligand (L1): 1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium iodide was synthesized by previously reported method. A mixture of 1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)-3-propyl-1H-benzo[d]imidazol-3-ium iodide (1 mmol), KOH (1.5 mmol) in H_2O (2 mL) was stirred at 100 °C for 12 h. Extraction by dichloromethane, the residue was further purified by flash column chromatography on silica gel to afford **L1** as a white solid. **L1** was purified by flash chromatography (petroleum ether/EtOAc = 10:1) and gave a white solid (MP: 73.7–74.1 °C, 235 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1 H), 7.72 (m, 1 H), 7.56–7.49 (m, 1 H), 7.32–7.30 (m, 1 H), 7.23–7.17 (m, 2 H), 6.79–6.71 (m, 2 H), 6.45–6.44 (m, 1 H), 6.26–6.24 (m, 1 H), 6.05 (s, 1 H), 3.13–3.09 (m, 2 H), 1.66–1.57 (m, 3 H), 0.95–0.92 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.00, 150.45, 145.04, 141.87, 140.47, 127.96, 127.22, 126.97, 124.82, 116.88, 111.33, 107.43, 104.50, 102.15, 45.61, 22.71, 11.76, ppm. IR (KBr): 2962, 2871, 1609, 1463, 1041, 746 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{17}H_{20}N_5$ $[M+H]^+$ 294.1713, found 294.1727.

3-propyl-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium **iodide (L3)**

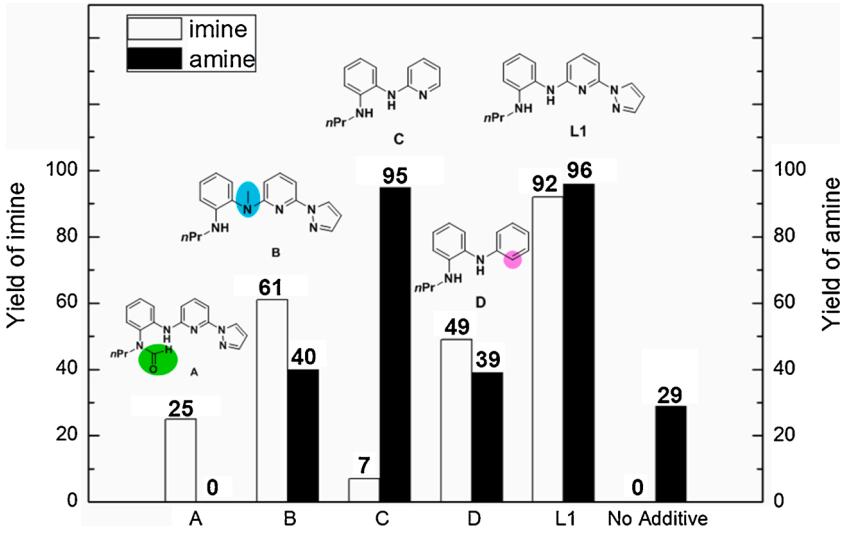


Fig. 2. Control experiments for reaction mechanism.

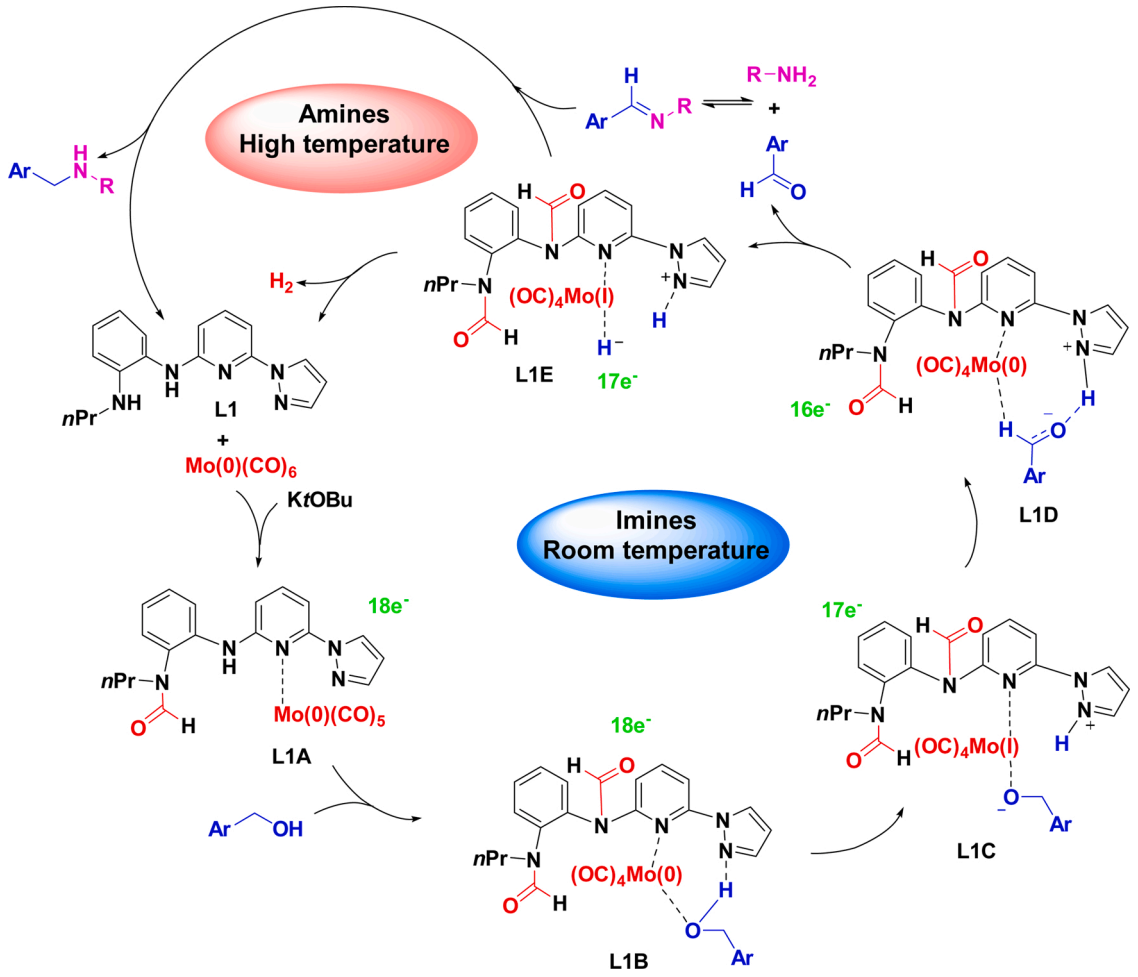


Fig. 3. Suggested mechanism.

was synthesized by previously reported method. **L3** was purified by flash chromatography (Dichloromethane/Methanol = 10:1) and gave a white solid (MP: 157.2–157.7 °C, 318 mg, 87 %). [62] ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.62 (s, 1 H), 8.78–8.77 (m, 1 H), 8.47–8.45 (m, 1 H), 8.33–8.25 (m, 2 H), 8.17–8.15 (m, 1 H), 7.77–7.70 (m, 3 H), 4.64–4.61 (m, 2 H), 2.09–2.03 (m, 2 H), 1.02–0.99 (m, 3 H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.79, 147.86, 142.53, 140.97, 132.09, 129.89, 128.16, 127.58, 125.48, 117.55, 116.48, 114.63, 49.29, 22.51, 11.32, ppm. IR (KBr): 3060, 2877, 1558, 1481, 1234, 759 cm^{-1}.

1-(4-methylpyridin-2-yl)-3-propyl-1H-benzo [d] imidazol-3-ium iodide (L4) was synthesized by previously reported method. [63] **L4** was purified by flash chromatography (Dichloromethane/Methanol = 30:1) and gave a yellow solid (MP: 172.4–174.6 °C, 322 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.63 (s, 1 H), 8.68–8.65 (m, 1 H), 8.54–8.52 (m, 2 H), 7.90–7.88 (m, 1 H), 7.76–7.73 (m, 2 H), 7.36–7.35 (m, 1 H), 4.88–4.84 (m, 2 H), 2.61 (s, 3 H), 2.24–2.19 (m, 2 H), 1.14–1.10 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.07, 148.66, 147.85, 140.17, 131.68, 130.13, 128.29, 127.89, 126.11, 117.93, 117.70, 112.93, 49.49, 23.07, 21.32, 11.09, ppm. IR (KBr): 2964, 1614, 1554, 1257, 759 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{16}H_{18}N_3$ [M-I]$^+$ 252.1495, found 252.1490.

3-propyl-1-(6-((3,4,5-trimethylphenyl)amino)pyridin-2-yl)-1H-benzo[d]imidazol-3-ium **iodide (L5)** was synthesized by previously reported method. **L5** was purified by flash chromatography (Dichloromethane/Methanol = 30:1) and gave a white solid (MP: 140.4–141.3 °C, 324 mg, 65 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.42 (s, 1 H), 9.40 (s, 1 H), 8.50–8.48 (m, 1 H), 8.24–8.22 (m, 1 H), 7.94–7.90 (m, 1 H), 7.79–7.71 (m, 2 H), 7.30–7.26 (m, 3 H), 7.01–6.99 (m, 1 H), 4.58–4.54 (m, 2 H), 2.18 (s, 6 H), 2.08–2.03 (m, 5 H), 1.03–0.99 (m, 3 H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.86, 145.53, 141.94, 140.32, 137.22, 136.30, 131.72, 129.48, 128.44, 127.30, 127.00, 118.80, 116.32, 114.02, 111.06, 104.94, 48.64, 22.01, 20.46, 14.60, 10.85, ppm. IR (KBr): 1455, 1224, 748 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{24}H_{27}N_4$ [M-I]$^+$ 371.2230, found 371.2232.

1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)-1H-benzo[d]imidazole **(L6)** was synthesized by previously reported method. [63] **L6** was purified by flash chromatography (petroleum ether/EtOAc = 2:1) and gave a white solid (MP: 116.2–117.0 °C, 196 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 2 H), 8.09–7.98 (m, 3 H), 7.91–7.89 (m, 1 H), 7.80 (d, J =1.2 Hz, 1 H), 7.46–7.37 (m, 3 H), 6.54–6.53 (m, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.12, 148.41, 144.75, 142.78, 141.73, 141.26, 132.06, 127.32, 124.46, 123.57, 120.91, 112.57, 111.06, 110.02, 108.50, ppm. IR (KBr): 1598, 1471, 1394, 1236, 937, 740 cm^{-1}.

***N*-(2-((6-(1H-pyrazol-1-yl)pyridin-2-yl)amino)phenyl)-*N*-propylformamide (A)**[64]: Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (273 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49–8.48 (m, 2 H), 8.47–8.46 (m, 1 H), 8.38 (s, 1 H), 8.24 (s, 2 H), 8.14–8.12 (m, 2 H), 7.81–7.79 (m, 1 H), 7.75 (m, 2 H), 7.72 (m, 1 H), 7.70–7.66 (m, 2 H), 7.61–7.57 (m, 1 H), 7.49–7.47 (m, 2 H), 7.46–7.40 (m, 2 H), 7.39–7.36 (m, 2 H), 7.28–7.10 (m, 6 H), 6.75–6.72 (m, 5 H), 6.58–6.56 (m, 1 H), 6.48–6.47 (m, 2 H), 6.43–6.42 (m, 1 H), 3.68–3.63 (m, 6 H), 1.63–1.54 (m, 4 H), 1.49–1.41 (m, 2 H), 0.93–0.89 (m, 6 H), 0.83–0.79 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.57, 162.57, 154.92, 153.74, 150.31, 150.23, 141.93, 141.73, 140.39, 140.14, 137.64, 137.15, 131.33, 130.19, 129.78, 129.19, 128.38, 127.22, 127.10, 127.04, 124.69, 124.56, 122.81, 120.98, 107.51, 107.22, 106.94, 105.65, 103.50,

102.34, 52.64, 46.81, 21.90, 20.93, 11.35, 10.78, ppm. IR (KBr): 1670, 1457, 761 cm^{-1}.

N1-(6-(1H-pyrazol-1-yl)pyridin-2-yl)-N1-methyl-N2-propylbenzene-1,2-diamine (B): Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a colorless oil (154 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (m, 1 H), 7.72 (m, 1 H), 7.44−7.40 (m, 1 H), 7.26−7.21 (m, 2 H), 7.09−7.07 (m, 1 H), 6.79−6.73 (m, 2 H), 6.45−6.44 (m, 1 H), 6.09−6.07 (m, 1 H), 2.29 (s, 2 H), 3.13−3.10 (m, 2 H), 1.60−1.55 (m, 3 H), 1.26−1.23 (m, 1 H), 0.92−0.88 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.89, 150.04, 145.20, 141.69, 139.56, 131.14, 128.73, 128.31, 126.95, 117.22, 111.43, 107.14, 105.85, 100.06, 45.36, 37.00, 22.64, 11.66, ppm. IR (KBr): 1614, 1484, 1326, 1041, 748 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{18}H_{22}N_5$ $[M+H]^+$ 308.1870, found 308.1873.

N1-propyl-N2-(pyridin-2-yl)benzene-1,2-diamine (C): Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a colorless oil (195 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (m, 1 H), 7.69 (s, 1 H), 7.23−7.19 (m, 1 H), 7.08−7.00 (m, 2 H), 6.61−6.53 (m, 2 H), 6.47−6.44 (m, 1 H), 6.25−6.23 (m, 1 H), 4.15 (m, 1 H), 2.97−2.93 (m, 2 H), 1.46−1.41 (m, 2 H), 0.79−0.76 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.53, 148.02, 144.93, 137.74, 127.27, 126.85, 125.46, 116.46, 113.79, 110.79, 107.02, 45.39, 22.49, 11.58, ppm. IR (KBr): 3191, 2962, 1596, 1432, 1149, 740 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{14}H_{18}N_3$ $[M+H]^+$ 228.1495, found 228.1497.

N1-phenyl-N2-propylbenzene-1,2-diamine (D): Purification by flash chromatography (petroleum ether/EtOAc = 10:1) gave a yellow oil (102 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10−7.06 (m, 2 H), 7.03−6.99 (m, 2 H), 6.72−6.68 (m, 1 H), 6.64−6.56 (m, 4 H), 4.94 (s, 1 H), 3.94 (s, 1 H), 3.00−2.96 (m, 2 H), 1.52−1.47 (m, 2 H), 0.85−0.81 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 1 45.93, 144.33, 129.35, 128.13, 126.34, 125.08, 119.27, 117.05, 115.30, 111.16, 45.74, 22.73, 11.76, ppm. IR (KBr): 2963, 1596, 1496, 1259, 746 cm^{-1}. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}N_2$ $[M+H]^+$ 227.1543, found 227.1548.

Synthetic Procedures for the Synthesis of Amines: A mixture of aryl amines (0.5 mmol), benzyl alcohol (0.6 mmol), $Mo(CO)_6$ (0.02 mmol, 4 mol%), **L1** (0.02 mmol, 4 mol%), and KOtBu (0.75 mmol) in toluene (2.0 mL) were allowed to react at 120 °C for 24 h under a air atmosphere. The solvent was concentrated under vacuum, and the amines were isolated by flash chromatography.

***N*-benzylaniline (3a)**[31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (88 mg, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 4 H), 7.30−7.26 (m, 1 H), 7.20−7.16 (m, 2 H), 6.75−6.71 (m, 1 H), 6.64−6.62 (m, 2 H), 4.31 (s, 2 H), 3.99 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.23, 139.53, 129.34, 128.70, 127.57, 127.29, 117.61, 112.91, 48.34, ppm.

***N*-benzyl-4-fluoroaniline (3b)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (99 mg, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.33 (m, 4 H), 7.32−7.27 (m, 1 H), 6.92–8.86 (m, 2 H), 6.60−6.54 (m, 2 H), 4.30 (s, 2 H), 3.94 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.19, 154.85, 144.61, 139.37, 128.80, 127.62, 127.44, 115.91, 115.69, 113.80, 113.73, 49.06. ^{19}F NMR (376 MHz, $CDCl_3$): δ -127.90, ppm.

***N*-benzyl-4-chloroaniline (3c)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (103 mg, 95 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.23 (d, J =4.0 Hz, 4 H), 7.22−7.17 (m, 1 H), 7.05−7.01 (m, 2 H), 6.49−6.45 (m, 2 H), 4.22 (s, 2 H), 4.14 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.47, 138.85, 129.22, 128.85, 127.63, 127.56, 122.54, 114.30, 48.65, ppm.

***N*-benzyl-4-bromoaniline (3d)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (119 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.25 (m, 4 H), 7.22−7.19 (m, 1 H), 7.18−7.14 (m, 2 H), 6.43−6.40 (m, 2 H), 4.21 (s, 2 H), 3.99 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.14, 138.96, 132.03, 128.81, 127.50, 127.48, 114.54, 109.22, 48.32, ppm.

***N*-benzyl-4-iodoaniline (3e):** Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (116 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.40 (m, 2 H), 7.36−7.33 (m, 4 H), 7.32−7.28 (m, 1 H), 7.44−7.40 (m, 2 H), 4.31 (s, 2 H), 4.10 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.65, 138.84, 137.82, 128.74, 127.41, 115.10, 78.15, 48.08, ppm.

***N*-benzyl-4-methylaniline (3f)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (89 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.43 (m, 4 H), 7.40−7.36 (m, 1 H), 7.11 (d, J =8.0 Hz, 2 H), 6.67 (d, J =6.8 Hz, 2 H), 4.40 (s, 2 H), 3.97 (s, 1 H), 2.36 (s, 3 H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.00, 139.76, 129.84, 128.68, 127.59, 127.24, 126.82, 113.11, 48.72, 20.50, ppm.

***N*-benzyl-4-(tert-butyl)aniline (3 g)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave acolorless oil (111 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.31 (m, 4 H), 7.28−7.24 (m, 1 H), 7.20 (d, J =8.8 Hz, 2 H), 6.59 (d, J =8.4 Hz, 2 H), 4.30 (s, 2 H), 3.91 (s, 1 H), 1.27 (s, 9 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.99, 140.41, 139.83, 128.71, 127.67, 127.28, 126.13, 112.68, 48.73, 33.97, 31.68, ppm.

4-fluoro-*N*-(3-methylbenzyl)aniline (3 h) [65]: Purification by flash chromatography (petroleum ether/ EtOAc = 50:1) gave a yellow oil (82 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.01 (m, 4H), 6.87−6.77 (m, 2 H), 6.50−6.45(m, 2H), 4.16 (s, 2 H), 3.80 (s, 1 H), 2.27 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.15, 154.82, 144.67, 144.65, 139.26, 138.49, 128.70, 128.42, 128.20, 124.69, 115.90, 115.68, 113.79, 113.71, 49.08, 21.57, ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -127.96, ppm.

4-methyl-*N*-(3-methylbenzyl)aniline (3i)[65]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (97 mg, 92 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.29 (m, 3H), 7.23−7.21 (m, 1 H), 7.14−7.12(m, 2H), 6.69 (d, J =2.0 Hz, 2 H), 4.38 (s, 2 H), 3.97 (s, 1 H), 2.49 (s, 3 H), 2.39(s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.10, 139.68, 138.33, 129.83, 128.59, 128.37, 128.01, 126.75, 124.67, 113.07, 48.75, 21.54, 20.51, ppm.

***N*-benzyl-3-bromoaniline (3 j)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (113 mg, 86 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.36 (m, 4 H), 7.35−7.30 (m, 1 H), 7.04 (t, J =8.0 Hz, 1 H), 6.86 (d, J =8.0 Hz, 1 H), 6.81 (t, J =2.0 Hz, 2 H), 6.56 (dd, J =8.4 Hz, J =2.4 Hz, 1 H), 4.32 (s, 2 H), 4.10 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.46, 138.80, 130.61, 128.83, 127.56, 127.54, 123.36, 120.39, 115.50, 111.60, 48.14, ppm.

***N*-benzyl-3,5-dichloroaniline (3k):** Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (110 mg, 87 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2 H), 7.24−7.21 (m, 3 H), 6.59 (t, J =1.6 Hz, 1 H), 6.38 (d, J =1.6 Hz 1 H), 4.18 (s, 2 H), 4.06 (s, 1 H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.73, 138.18, 135.57, 128.94, 127.75, 127.54, 117.34, 111.07, 48.01, ppm.

***N*-benzyl-3-methylaniline (3 L)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (64 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.36 (m, 4 H), 7.33−7.29 (m, 1 H), 7.10 (t, J =8.0 Hz, 1 H), 6.58 (d, J = 7.6 Hz, 1 H), 6.51−6.47 (m, 2 H), 4.35 (s, 2 H), 3.98 (s, 1 H), 2.31 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.35, 139.68, 139.16, 129.27, 128.74, 127.65, 127.31, 118.65, 113.75, 110.08, 48.47, 21.76, ppm.

***N*-benzyl-2-methylaniline (3 m)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (30 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.35 (m, 4 H), 7.35−7.27 (m, 1 H), 7.13−7.08 (m, 2 H), 6.70 (t, J = 7.6 Hz, 1 H), 6.64 (d, J =8.0 Hz, 1 H), 4.39 (s, 2 H), 3.97 (s, 1 H), 2.18 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.20, 139.63, 130.20, 128.79, 127.67, 127.38, 127.29, 122.04, 117.30, 110.10, 48.44, 17.68, ppm.

***N*-benzyl-[1,1′-biphenyl]-2-amine (3n)**[31]: Purification by flash chromatography (petroleum ether/ EtOAc = 50:1) gave a colorless oil (53 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.47 (m, 4 H), 7.43−7.34 (m, 5 H), 7.32−7.27 (m, 1 H), 7.26−7.22 (m, 1 H), 7.17 (dd, J =7.2 Hz, J =1.6 Hz, 1 H), 6.83 (t, J =7.2 Hz, 1 H), 6.72 (d, J =8.0 Hz, 1 H), 4.45 (s, 1H), 4.38 (s, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

144.99, 139.58, 130.35, 129.50, 129.06, 128.84, 128.71, 127.79, 127.37, 127.16, 117.31, 110.88, 48.25, ppm.

***N*-benzyl-2-chloroaniline (3o)**[66]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a colorless oil (84 mg, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.22 (m, 6 H), 7.07−7.02 (m, 1 H), 6.62−6.57 (m, 2 H), 4.70 (s, 1 H), 4.34 (s, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.94, 138.83, 129.19, 128.80, 127.90, 127.43, 127.34, 119.18, 117.50, 111.61, 47.90, ppm.

***N*-benzylnaphthalen-1-amine (3p)**[31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (91 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.79 (m, 2 H), 7.54−7.41 (m, 4 H), 7.39−7.29 (m, 4 H), 7.26−7.22 (m, 1 H), 6.62 (d, J =8.4 Hz, 1 H), 4.69 (s, 1H), 4.48 (s, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.32, 139.21, 134.42, 128.85, 128.83, 127.87, 127.53, 126.74, 125.88, 124.88, 123.50, 120.02, 117.78, 104.90, 48.74, ppm.

***N*-benzylnaphthalen-2-amine (3q)**[31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (109 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70−7.60 (m, 3 H), 7.45−7.42 (m, 2 H), 7.39−7.34 (m, 3 H), 7.33−7.29 (m, 1 H), 7.23−7.19 (m, 1 H), 6.93 (dd, J =8.8 Hz, J =2.4 Hz, 1 H), 6.86 (d, J =2.0 Hz, 1 H), 4.45 (s, 2 H), 4.25 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.58, 139.08, 135.25, 129.12, 128.83, 127.83, 127.77, 127.52, 126.48, 126.17, 122.31, 118.05, 105.19, 48.67, ppm.

***N*-benzyl-2,3-dihydrobenzo [b] [1,4] dioxin-6-amine (3 r)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (78 mg, 65 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.37 (m, 4H), 7.35−7.29 (m, 1 H), 6.77(d, J =8.4 Hz, 1H), 6.26−6.21 (m, 2 H), 4.29 (s, 2 H), 4.24−4.22 (m, 2 H), 4.20−4.18 (m, 2 H), 3.84 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.05, 143.27, 139.63, 135.69, 128.59, 127.53, 127.15, 117.64, 106.74, 101.57, 64.71, 64.14, 48.96, ppm.

***N*-(4-chlorobenzyl)aniline (4a)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (93 mg, 85 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 4 H), 7.23−7.19 (m, 2 H), 6.79−6.74 (m, 1 H), 6.65−6.63 (m, 2 H), 4.32 (s, 2 H), 4.07 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.93, 138.12, 132.95, 129.40, 128.84, 128.79, 117.90, 112.99, 47.69, ppm.

***N*-(4-bromobenzyl)aniline (4b)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (126 mg, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J =8.4 Hz, 2 H), 7.26−7.24 (m, 2 H), 7.21−7.17(m, 2H), 6.77−6.74 (m, 1 H), 6.62 (d, J = 7.6 Hz, 2 H), 4.29 (s, 2 H), 4.06 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.93, 138.68, 131.84, 129.44, 129.18, 121.06, 117.96, 113.02, 47.79, ppm.

***N*-(4-fluorobenzyl)aniline (4c)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (65 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.31 (m, 2 H), 7.21−7.16 (m, 2 H), 7.06−7.01 (m, 2 H), 6.75−6.71 (m, 1 H), 6.64−6.62 (m, 2 H), 4.31 (s, 2 H), 4.02 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.42, 159.86, 148.09, 135.23, 129.44, 129.19, 129.11, 117.89, 115.70, 115.49, 113.02, 47.77, ppm.

***N*-(4-(trifluoromethyl)benzyl)aniline (4d)** [67]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (107 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J =8.4 Hz, 2 H), 7.49 (d, J =8.0 Hz, 2 H), 7.20−7.16 (m, 2 H), 6.75 (t, J =7.2 Hz, 1 H), 6.62 (d, J = 7.6 Hz, 2 H), 4.42 (s, 2 H), 4.15 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.80, 143.88, 129.48, 127.58, 125.72, 125.69, 118.10, 113.03, 47.93, ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.26, -62.39, -62.40 ppm.

***N*-(4-methoxybenzyl)aniline (4e)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (69 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J =8.4 Hz, 2 H), 7.22−7.18 (m, 2 H), 6.92−6.89(m, 2H), 6.76−6.72 (m, 1 H), 6.67−6.65 (m, 2 H), 4.27 (s, 2 H), 3.96 (s, 1 H), 3.82 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.99, 148.34, 131.54, 129.38, 128.94, 117.63, 114.15, 112.96, 55.43, 47.92, ppm.

4-chloro-N-(4-chlorobenzyl)aniline(4f) [65]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (63 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 4H), 7.13−7.09 (m, 2 H), 6.54−6.50(m, 2H), 4.29 (s, 2 H), 4.05 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.43, 137.58, 133.14, 129.23, 128.95, 128.73, 122.46, 114.07, 47.74, ppm.

4-chloro-N-(4-methylbenzyl)aniline (4 g) [68]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow solid (MP: 64.6–64.8 °C, 95 mg, 82 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.15 (m, 2 H), 7.08−7.07 (m, 2 H), 7.04−7.00 (m, 2 H), 6.48−6.44 (m 2 H), 4.17 (s, 2 H), 3.94 (s, 1 H), 2.27 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.76, 137.17, 135.92, 129.49, 129.16, 127.55, 122.12, 114.03, 48.21, 21.24, ppm.

4-chloro-N-(4-methoxybenzyl)aniline (4 h) [69]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 77.8–78.0 °C, 119 mg, 96 %).1H NMR (400 MHz, CDCl3) δ 7.20−7.17 (m, 2 H), 7.05−7.01 (m, 2 H), 6.82−6.78(m, 2 H), 6.48−6.44 (m,2 H), 4.14 (s, 2 H), 3.93 (s, 1 H), 3.72 (s, 3 H), ppm; 13C NMR (100 MHz, CDCl3) δ 159.02, 146.73, 130.93, 129.16, 128.87, 122.15, 114.17, 114.05, 55.42, 47.95, ppm.

***N*-(3-(trifluoromethyl)benzyl)aniline (4i)** [31]: Purification by flash chromatography (petroleum ether/ EtOAc = 50:1) gave a yellow oil (111 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1 H), 7.59−7.53 (m, 2 H), 7.46 (t, J = 7.6 Hz, 1 H), 7.22−7.17 (m, 2 H), 6.75 (t, J = 7.6 Hz, 1 H), 6.63 (d, J = 7.6 Hz, 2 H), 4.41 (s, 2 H), 4.11 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.87, 140.77, 130.78, 129.48, 129.22, 124.27, 124.23, 124.20, 124.16, 118.14, 113.06, 48.06, ppm. ^{19}F NMR (376 MHz, CDCl3): δ -62.55, ppm.

***N*-(3-chlorobenzyl)aniline (4 j)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (107 mg, 98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1 H), 7.29−7.25 (m, 3 H), 7.23−7.18 (m, 2 H), 6.80−6.74 (m, 1 H), 6.63−6.61 (m, 2 H), 4.31 (s, 2 H), 4.05 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.85, 141.84, 134.56, 129.96, 129.38, 127.46, 127.41, 125.47, 117.90, 112.96, 47.78, ppm.

***N*-(3-methylbenzyl)aniline (4k)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (89 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J =6.8 Hz, 1 H), 7.15−7.07 (m, 5 H), 6.64(t, J =7.2 Hz, 1H), 6.55 (d, J = 7.6 Hz, 2 H), 4.18 (s, 2 H), 3.72 (s, 1 H), 3.28 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.34, 139.48, 138.37, 129.35, 128.63, 128.38, 128.08, 124.68, 117.59, 112.92, 48.43, 21.53, ppm.

***N*-(2-methylbenzyl)aniline(4 L)** [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (82 mg, 83 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J =6.8 Hz, 1 H), 7.26−7.18 (m, 5 H), 6.74 (t, J =7.2 Hz, 1 H), 6.65 (d, J = 7.6 Hz, 2 H), 4.29 (s, 2 H), 3.85 (s, 1 H), 2.39 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.42, 137.13, 136.49, 130.55, 129.42, 128.40, 127.56, 126.30, 117.61, 112.83, 46.53, 19.07, ppm.

***N*-(thiophen-3-ylmethyl)aniline (4 m)** [31]: Purification by flash chromatography (petroleum ether/ EtOAc = 50:1) gave a yellow oil (85 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 3 H), 7.11−7.10 (m, 1 H), 7.06−7.04 (m, 1 H), 6.84 (t, J =7.2 Hz, 1 H), 6.77 (d, J = 7.6 Hz, 2 H), 4.60 (s, 2 H), 4.13 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.75, 143.06, 129.42, 126.99, 125.18, 124.73, 118.24, 113.30, 43.64, ppm.

***N*-propylaniline (4n)**[70]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (30 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 2H), 6.71−6.67 (m, 1 H), 6.61 (d, J = 7.6 Hz, 2H), 3.64 (s, 1 H), 3.11−3.07 (m, 2 H), 1.68−1.62 (m, 2 H), 1.03−0.99 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.65, 129.36, 117.21, 112.83, 45.94, 22.87, 11.78, ppm.

N-butylaniline (4o) [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (37 mg, 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.16 (m, 2H), 6.71−6.67 (m, 1 H), 6.61 (d, J = 7.6 Hz, 2H), 3.60 (s, 1 H), 3.14−3.10 (m, 2 H), 1.63−1.58 (m, 2

H), 1.47-1.41 (m, 2 H), 0.98−0.95 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.67, 129.36, 117.22, 112.83, 43.83, 31.82, 20.45, 14.06, ppm.

***N*-octylaniline (4p)**[31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (53 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.17 (m, 2H), 6.71 (t, *J* =7.2 Hz, 1 H), 6.64−6.61 (m, 2H), 3.60 (s, 1 H), 3.14−3.10 (m, 2 H), 1.67−1.60 (m, 2 H), 1.39−1.31 (m, 10 H), 0.94−0.92 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.68, 129.33, 117.17, 112.79, 44.12, 31.97, 29.72, 29.56, 29.40, 27.32, 22.80, 14.23, ppm.

4-chloro-*N*-octylaniline (4q)[71]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white oil (56 mg, 47 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04−6.99 (m, 2H), 6.44−6.41 (m, 2 H), 3.55 (s, 1H), 3.06−2.96 (m,2 H), 1.57−1.48 (m, 2 H), 1.27−1.20 (m, 10 H), 0.87−0.79 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.13, 129.10, 121.63, 113.82, 113.00, 44.23, 31.94, 29.52, 29.38, 27.25, 22.79, 14.24, ppm.

4-methyl-*N*-octylaniline (4 r)[70]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white oil (31 mg, 28 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92−6.90 (m, 2H), 6.48−6.44 (m, 2 H), 3.38 (s, 1H), 3.01−2.98 (m 2 H), 2.16 (s, 3 H), 1.56−1.49 (m, 2 H), 1.27−1.20 (m, 10 H), 0.83−0.79 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.31, 129.74, 126.34, 112.96, 44.45, 31.89, 29.65, 29.49, 29.34, 27.25, 22.73, 20.43, 14.18, ppm.

Synthetic Procedures for the Synthesis of Imines: A mixture of aryl amines (0.5 mmol), benzyl alcohol (0.6 mmol), $Mo(CO)_6$ (0.02 mmol, 4 mol%), **L1** (0.02 mmol, 4 mol%), and KOtBu (0.75 mmol) in toluene (2.0 mL) were allowed to react at room temperature for 24 h under a air atmosphere. The solvent was concentrated under vacuum, and the imines were isolated by flash chromatography.

(*E*)-N,1-diphenylmethanimine (5a) [49]: Purification by flash chromatography (petroleum ether/ EtOAc = 50:1) gave a yellow solid (MP: 48.0–48.6 °C, 87 mg, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.85−7.82 (m, 2H), 7.42−7.41 (m, 5H), 7.16−7.13 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.55, 152.25, 136.37, 131.52, 129.29, 128.95, 128.92, 126.07, 121.01, ppm.

(*E*)-*N*-(4-fluorophenyl)-1-phenylmethanimine (5b) [72]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 49.8–50.0 °C, 53 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.91−7.89 (m, 2H), 7.52−7.46 (m, 3 H), 7.22−7.18 (m, 2 H), 7.11−7.06 (m, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.59, 160.35, 160.33, 160.16, 148.18, 148.15, 136.18, 131.60, 128.95, 128.91, 122.48, 122.40, 116.12, 115.89, ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -117.29.

(*E*)-*N*-(4-bromophenyl)-1-phenylmethanimine (5c) [73]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 60.0–60.2 °C, 78 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1H), 7.82−7.80 (m, 2H), 7.43−7.39 (m, 5 H), 7.01 (d, *J* =8.4 Hz, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.87, 151.14, 136.06, 132.31, 131.77, 129.02, 128.96, 122.72, 119.43, ppm.

(*E*)-*N*-(4-iodophenyl)-1-phenylmethanimine (5d): Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 81.9–82.0 °C, 84 mg, 55 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.91−7.88 (m, 2H), 7.71−7.69 (m, 2 H), 7.51−7.46 (m, 3 H), 6.99−6.95 (m, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.93, 151.83, 138.30, 136.05, 131.80, 129.04, 128.96, 123.10, 90.43, ppm. HRMS (ESI) *m/z* calcd for C13H10IN $[M+H]^+$ 307.9931, found 307.9946.

(*E*)-1-phenyl-*N*-(p-tolyl)methanimine (5e) [74]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow liquid (72 mg, 74 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (s, 1 H), 7.92−7.90 (m, 2 H), 7.50−7.47 (m, 3 H), 7.22−7.17 (m, 4 H), 2.39 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.73, 149.61, 136.50, 135.93, 131.33, 129.90, 128.88, 128.85, 120.95, 21.15, ppm.

(*E*)-*N*-(3-bromophenyl)-1-phenylmethanimine (5f) [49]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (91 mg, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 1 H), 7.84−7.81 (m, 2 H), 7.44−7.38 (m, 3 H), 7.28−7.27 (m, 2 H), 7.20−7.16 (m, 1 H), 7.08−7.05 (m, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.49, 153.63, 135.95, 131.90, 130.57, 129.11, 128.97, 128.85, 123.84, 122.90, 120.09, ppm.

(*E*)-1-phenyl-*N*-(m-tolyl)methanimine (5 g) [49]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow liquid (90 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1 H), 7.93−7.88 (m, 2 H), 7.51−7.45 (m, 3 H), 7.31−7.26 (m, 1 H), 7.07−7.02 (m, 3 H), 2.40 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.31, 152.24, 139.11, 136.43, 131.44, 129.11, 128.91, 128.89, 126.84, 121.76, 117.97, 21.55, ppm.

(*E*)-*N*-(naphthalen-2-yl)-1-phenylmethanimine (5 h) [49]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 91.8–92.0 °C, 95 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1 H), 7.99−7.95 (m, 2 H), 7.90−7.85 (m, 3 H), 7.62 (d, *J* =1.6 Hz, 1 H), 7.53−7.44 (m, 6 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.66, 149.81, 136.40, 134.24, 132.13, 131.57, 129.08, 129.00, 128.94, 128.05, 127.87, 126.53, 125.47, 121.27, 117.88, ppm.

(*E*)-1-(4-chlorophenyl)-*N*-phenylmethanimine (5i) [38]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow solid (MP: 64.9–65.2 °C, 65 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.87−7.85 (m, 2H), 7.47−7.39 (m, 4H), 7.28−7.21 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.92, 151.82, 137.49, 134.85, 130.08, 129.33, 129.20, 126.33, 120.98, ppm.

(*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine (5 j) [38]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 61.4–62.0 °C, 55 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (s, 1H), 7.53 (s, 1H), 7.43−7.36 (m, 4H), 7.24−7.21 (m, 3 H), 7.06−7.03 (m, 1 H), 3.90 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.40, 159.85, 152.54, 130.66, 129.44, 129.25, 125.69, 121.01, 114.33, 55.59, ppm.

(*E*)-1-(3-chlorophenyl)-*N*-phenylmethanimine (5k): Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white oil (87 mg, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.86 (s, 1H), 7.68−7.65 (m, 1H), 7.38−7.30 (m, 4 H), 7.19−7.12 (m, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.79, 151.58, 138.05, 135.10, 131.39, 130.13, 129.35, 128.45, 127.28, 126.49, 121.00, ppm. HRMS (ESI) *m/z* calcd for $C_{13}H_{11}ClN$ $[M+H]^+$ 216.0575, found 216.0585.

(*E*)-1-(3-methoxyphenyl)-*N*-phenylmethanimine (5 L) [75]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 66.4–66.8 °C, 85 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.46 (s, 1H), 7.35−7.31 (m, 3 H), 7.19−7.13 (m, 4 H), 6.99−6.96 (m, 1 H), 3.82 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.42, 160.15, 152.14, 137.78, 129.86, 129.28, 126.09, 122.48, 121.00, 118.45, 111.95, 55.56, ppm.

(*E*)-*N*-phenyl-1-(o-tolyl)methanimine (5 m) [49]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a orange oil (44 mg, 45 %).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 1H), 8.01−7.99 (m, 1H), 7.34−7.26 (m, 3H), 7.24−7.20 (m, 1 H), 7.17−7.11 (m, 4 H), 2.51 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.23, 152.85, 138.72, 134.25, 131.14, 129.27, 127.97, 126.50, 125.92, 121.03, 19.54, ppm.

(*E*)-*N*-phenyl-1-(thiophen-2-yl)methanimine (5n) [49]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (88 mg, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (s, 1H), 7.57−7.56 (m, 1H), 7.54−7.53 (m, 1 H), 7.46−7.42 (m, 2 H), 7.30−7.18 (m, 4 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.14, 151.56, 142.97, 132.30, 130.42, 129.25, 127.85, 126.14, 121.11, ppm.

(*E*)-N-benzyl-4-styrylaniline (6a) [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 131.9–134.6 °C, 121 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.14 (m, 12 H), 7.02−6.83 (m, 2 H), 6.59−6.56 (m, 2 H), 4.31 (s, 2 H), 4.10 (s, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.88, 139.26, 138.20, 128.91, 128.79, 128.70, 127.89, 127.59, 127.43, 127.14, 126.88, 126.17, 124.72, 113.07, 48.30, ppm.

(*E*)-*N*-(4-methylbenzyl)-4-styrylaniline (6b) [31]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a white solid (MP: 135.9–136.2 °C, 93 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.6 Hz, 2 H), 7.36−7.30 (m, 4 H), 7.27−7.26 (m, 2 H), 7.22−7.15 (m, 3 H), 7.02 (d, J =16.4 Hz, 1 H), 6.90 (d, J =16.4 Hz, 1 H), 6.63 (d, J =8.4 Hz, 2 H), 4.32 (s, 2 H), 3.73−3.72 (m, 1 H), 2.35 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.93, 138.20, 137.11, 136.15, 129.48, 128.92, 128.71, 127.88, 127.61, 127.06, 126.87, 126.16, 124.64, 113.05, 48.08, 21.25, ppm.

N1,N2-dibenzylbenzene-1,2-diamine (7a) [26]: Purification by flash chromatography (petroleum ether/EtOAc = 50:1) gave a yellow oil (216 mg, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.33 (m, 8 H), 6.81−6.78 (m, 2 H), 6.75−6.71 (m, 2 H), 4.32 (s, 4 H), 3.65 (s, 2 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.55, 137.27, 128.73, 127.95, 127.38, 119.57, 112.14, 48.93, ppm.

CRediT authorship contribution statement

Di Wu: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software. **Qingqing Bu:** Data curation, Investigation, Methodology, Software, Writing - review & editing. **Cheng Guo:** Conceptualization, Data curation, Formal analysis, Methodology, Software. **Bin Dai:** Conceptualization, Supervision, Writing - review & editing. **Ning Liu:** Conceptualization, Data curation, Investigation, Methodology, Writing - original draft.

Declaration of Competing Interest

The authors (Di Wu, Qingqing Bu, Cheng Guo, Bin Dai, and Ning Liu) declare no competing financial interest.

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Appendix A. Supplementary data

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