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One-pot reductive amination of aldehydes catalyzed by a hydrio-iridium(III) complex in aqueous medium

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Abstract

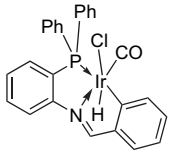
A combination of sodium tetrakis[3,5-di(trifluoromethyl)phenyl]borate [$NaBAr^F_4$] and hydrio-iridium(III) complex efficiently catalyzed the one-pot reductive amination of aldehydes with various amines and ammonia in water under mild conditions in good to excellent yields.

Keywords: Reductive amination; Silane; Carbonyl; Iridium

1. Introduction

For the chemical transformations, one-pot reductive amination of aldehydes and ketones is an important methodology in conversion of carbonyl compounds into the higher alkylated amines.[1] The success of this 'one-pot' fashion relies on the acid-catalyzed formation of intermediate imines and the preferential reduction of C═N. The two commonly used reduction processes are based on either hydride reduction or catalytically hydrogenation. Several reagents, which effect reductive amination have been recently developed.[2] However, most of these reactions require carrying out in organic or aqua mixed solvents, which does not meet the context of green chemistry. Few works concerning this context were reported.[3] Therefore, a more efficient method to carry out this transformation in aqueous medium is still required.

In our previous works, we have found that sodium tetrakis[3,5-di(trifluoromethyl)phenyl]borate is able to show the acidic property on the catalysis of Mannich reaction in aqueous medium.[4] In addition, imine functionality can be successfully reduced by silanes in the presence of the iridium(III) complex **1** as the catalyst.[5] By using the combination of sodium tetrakis[3,5-di(trifluoromethyl)phenyl]borate (denoted as $NaBAr^F_4$) and a hydrio-iridium(III) complex **1** as a catalytic system, we found that experiments on the reductive amination of aldehydes can be carried out in aqueous medium with high yields by using the silane as the reducing agent.



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2. Results and discussion

The reaction of benzaldehyde with aniline served as a model reaction (Eq. 1) for studying the influence of catalysts, additives, and critical reaction parameters such as solvent and temperature. Results are summarized in Table 1.

When a mixture of benzaldehyde (5 mmol), aniline (5 mmol), triethylsilane (10 mmol), $NaBAr^F_4$ (0.01 mmol), and **1** (0.005 mmol) in water (2.0 mL) under air atmosphere was heated at 50 °C for 1 h, the amine **2** was obtained quantitatively (entry 1). Running the reaction at room temperature took 2 h for the completion (entry 2). The catalytic activities of other iridium complexes in this reaction were also examined. $[Ir(COD)Cl]_2$ proved a moderate catalytic activity affording the desired amine

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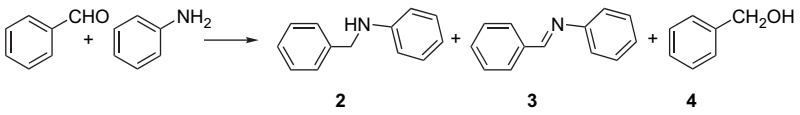
Table 1
Reductive amination of benzaldehyde with aniline[a]

Entry	Complex (mol %)	Additives (mol %)	Reducing agent	Solvent	t (h)	Temp (°C)	Product distribution[b] (%)		
							2	**3**	**4**
1	**1** (0.1)	$NaBAr_4^F$ (0.2)	Et_3SiH	H_2O	1	50	100	—	—
2	**1** (0.1)	$NaBAr_4^F$ (0.2)	Et_3SiH	H_2O	2	rt	100	—	—
3	$[Ir(COD)Cl]_2$ (0.05)	$NaBAr_4^F$ (0.15)	Et_3SiH	H_2O	16	50	50	50	—
4	$[Ir(COD)Cl]_2$ (0.05)[c]	$NaBAr_4^F$ (0.15)	Et_3SiH	H_2O	12	50	—	100	—
5	$[Ir(COD)Cl]_2$ (0.05)	$NaBAr_4^F$ (0.1)	H_2	H_2O	16	50	27	67	6
6	**1** (0.1)	$NaBAr_4^F$ (0.1)	H_2	H_2O	16	50	—	100	—
7	**1** (0.1)	—	Et_3SiH	H_2O	16	50	60	40	—
8	—	$NaBAr_4^F$ (0.2)	Et_3SiH	H_2O	24	50	20	80	
9	**1** (0.1)	$NaBAr_4^F$ (0.2)	$NaBH_4$	H_2O	1	50	5	75	20
10	**1** (0.1)	$NaBAr_4^F$ (0.2)	Silane[d]	H_2O	1	50	39	61	—
11	**1** (0.1)	$NaBPh_4$ (0.2)	Et_3SiH	H_2O	24	50	34	66	—
12	**1** (0.1)	$NaBF_4$ (0.2)	Et_3SiH	H_2O	6	50	75	25	—
13	**1** (0.1)	$NaPF_6$ (0.2)	Et_3SiH	H_2O	6	50	70	30	—
14	**1** (0.1)	$NaBAr_4^F$ (0.2)	Et_3SiH	MeOH	1	50	90	—	10
15	**1** (0.1)	$NaBAr_4^F$ (0.2)	Et_3SiH	THF	1	50	57	38	5

[a] Reaction conditions: benzaldehyde (5 mmol), aniline (5 mmol), Et_3SiH (10 mmol) in solvent (2 mL).
[b] NMR yield.
[c] Addition of 2-(diphenylphosphino)aniline ligand.
[d] Et_3SiH was replaced by polymethylhydrosiloxane.



(1)

product in 50% yield (entry 3). However, a mixture of 2-(diphenylphosphino)aniline and $[Ir(COD)Cl]_2$ did not show any catalytic activity on the reduction of the imine **3**. As for the reducing agent, triethylsilane appears to be the best choice. The use of hydrogen gas or sodium borohydride as the reducing agent provided a less satisfactory result as indicated by the lower yields and the formation of the direct reduction of carbonyl compounds (entry 9). This observation is consistent with the known procedure for the reduction of imines catalyzed by other iridium complexes.[5,6]

It is of interest to note that the tetrakis[3,5-di(trifluoromethyl)phenyl]borate plays an important role in this catalysis. It appears that the sodium salt of tetrakis[3,5-di(trifluoromethyl)-phenyl]borate as the additive gave the best result. On the other hand, other salts such as $NaBF_4$ or $NaPF_6$ only showed moderate activities even for a longer reaction period. In the previous work, we learned that this borate anion can act as a surfactant and stabilize the metal complex.[5,7] In a separate experiment, we also found that the condensation of benzaldehyde and aniline in presence of $NaBAr_4^F$ to yield the corresponding imine was completed within 15 min. This might explain why the reaction is able to carry out in a water solution. Therefore the influence of solvents on this catalysis is also investigated. Running reaction in THF only offers 57% of the desired product or 90% in methanol (entries 14 and 15, Table 1).

In view of the above results, the catalytic system generated from **1** and $NaBAr_4^F$ in water rendered the best yield in reductive amination of benzaldehyde and was followed in the subsequent studies. Various aldehydes and amines were tested under this reaction condition and the results are summarized in

Table 2
Reductive amination of carbonyl compounds in aqueous medium[a]

Entry	R^1CHO	R^2R^3NH	Yield[b] (%)
1	C_6H_5CHO	$C_6H_5NH_2$	92
2	C_6H_5CHO	p-$MeOC_6H_4NH_2$	89
3	C_6H_5CHO	p-$ClC_6H_4NH_2$	90
4	C_6H_5CHO	o-$MeC_6H_4NH_2$	70
5	C_6H_5CHO	3,5-$Me_2C_6H_3NH_2$	86
6	p-$MeOC_6H_4CHO$	$C_6H_5NH_2$	94
7	p-ClC_6H_4CHO	$C_6H_5NH_2$	90
8	o-MeC_6H_4CHO	$C_6H_5NH_2$	92
9	2-Pyridinecarbaldehyde	$C_6H_5NH_2$	41[d]
10	1-Naphthylenecarbaldehyde	$C_6H_5NH_2$	0[c]
11	6-Methoxy-2-naphthylene-carbaldehyde	$C_6H_5NH_2$	90
12	C_6H_5CHO	$C_6H_5CH_2NH_2$	81
13	C_6H_5CHO	n-$C_6H_{13}NH_2$	70
14	C_6H_5CHO	$(C_6H_5)_2NH$	60[d]
15	$C_6H_5CH{=}CHCHO$	$C_6H_5NH_2$	70
16	o-MeC_6H_5CHO	$(C_6H_5)_2NH$	55[d]
17	p-$MeOC_6H_4CHO$	$(C_6H_5)_2NH$	46[d]
18	p-ClC_6H_4CHO	$(C_6H_5)_2NH$	49[d]
19	C_6H_5CHO	Piperidine	25[d]
20	$C_7H_{15}CHO$	$C_6H_5NH_2$	56[d]

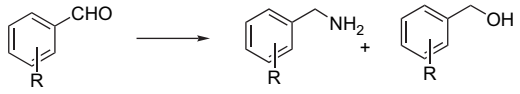
[a] Reaction conditions: carbonyl compound (5 mmol), amine (5 mmol), **1** (0.005 mmol), $NaBAr_4^F$ (0.01 mmol), and Et_3SiH (10 mmol) in H_2O (2 mL) at 50 °C.
[b] Isolated yield.
[c] The corresponding imine was isolated.
[d] All the aldehydes were converted into the corresponding imine as indicated by the ^1H NMR studies.

Table 2. Substituted anilines when reacted with benzaldehyde afforded the corresponding *N*-benzyl derivatives in excellent yields except *o*-toluidine (entries 1–5). Similarly, reactions of a range of substituted benzaldehydes with aniline proceeded smoothly, indicating that the substituents have less effect on this catalysis. Under the reductive conditions, reaction of 1-naphthylenecarbaldehyde with aniline only provided the formation of the corresponding imine, showing that the reduction step did not occur (entry 10). On the other hand, the substituted 2-naphthylenecarbaldehyde gave the desired amine in 90% yield. These results clearly demonstrate that the catalyst is quite sensitive toward the steric environment of the imine substrates.

To screen the overall compatibility of this protocol, the direct reductive amination of benzaldehydes with secondary amines was also studied. However, the desired amine products were obtained in moderate yields (entries 16–19). Furthermore, the ketone substrates were investigated. Under the same conditions, a mixture of cyclohexylbenzylamine (48% yield) and cyclohexanol (32% yield) were obtained by using cyclohexanone and aniline as the substrates. In the case of acetophenone, the formation of 1-phenylethanol by the reduction of the ketone is found to be the major pathway of the catalysis. All of these observations suggest that the catalyst is quite sensitive to the steric bulkiness of the substrates. Thus, a mixture of benzaldehyde (5 mmol) and cyclohexanone (5 mmol) reacted with aniline (5 mmol) in the presence of Et_3SiH (7.5 mmol) to give the *N*-benzylaniline as the only product, and the cyclohexanone remained intact. This outcome clearly shows the selectivity of this method.

Since the reaction can be carried out in water, we envisioned that the use of aqueous ammonia for the reductive amination of the carbonyl compounds, might offer a method to prepare primary amines. Results are summarized in Table 3. In all cases, the major product from each reaction is the direct reduction of the carbonyl function. For example, reaction of benzaldehyde with ammonia followed by the reduction gave 60% yield of the benzyl alcohol, with only 40% of the desired amine product.

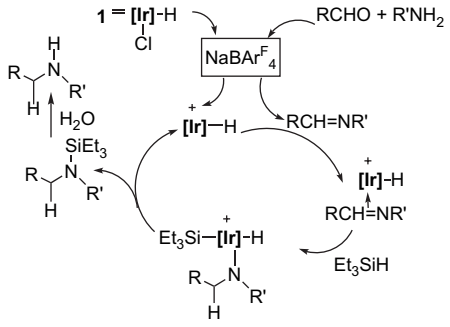
Table 3
Reductive amination of carbonyl compounds in aqueous medium[a]



Entry	R	Product yield[c] (%)	
		Benzylamine	Benzyl alcohol
1	H	40	60
2[b]	H	38	62
3	4-Cl	20	80
4	4-F	18	82
5	2-OMe	16	84
6	2-Me	0	100

[a] Reaction conditions: carbonyl compound (5 mmol), 30% ammonia solution (5 mL), **1** (0.005 mol), $NaBAr^F_4$ (0.01 mmol), and Et_3SiH (10 mmol) in H_2O (2 mL) at rt.
[b] At 50 °C.
[c] NMR yield with the use of anisole as the internal standard.

The mechanistic pathway of the reductive amination catalyzed by **1**/$NaBAr^F_4$ is shown in Scheme 1. Basically, this pathway is quite similar to that reported by Messerle and co-workers in the reduction of imine.[8] Accordingly, the catalytic pathway leading to the amine products via the iridium(III) complex involves the generation of a vacant site for the coordination of an imine substrate followed by the reduction of the imino group to the coordinating amine–silane product, which was subsequently hydrolyzed to yield the final product. In addition, the borate salt also assisted the imine formation and stabilization in aqueous medium.



Scheme 1. Pathway for catalysis.

In summary, a new and chemoselective method for the reductive amination of aldehydes in water under mild reaction conditions has been developed in this work. The advantages of this method are the general applicability with aldehydes in high yields, the observed selectivity, and a very mild reaction conditions such as 0.1 mol % of catalyst in water at 50 °C.

3. Experimental

3.1. General

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted. Chemicals and solvents were of analytical grade and used as received unless otherwise stated. The iridium complex **1** was prepared according to the procedure reported.[5]

3.2. Catalysis: general procedure

A mixture of 0.1 mol % iridium complex and 0.21 mol % $NaBAr^F_4$ was placed in flask under air atmosphere. Then, a mixture of aldehyde (5 mol) and amine (5 mol) in water (2 mL) was added to the above iridium complex. The mixture was stirred at room temperature for 10 min and Et_3SiH (10 mol) was added into the solution. The resulting mixture was heated and kept at 50 °C by an oil bath. The reaction was then monitored by ^1H NMR. After completion of the reaction, brine (3 mL) and CH_2Cl_2 (5 mL) were added. The organic layer

was separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL×2). The combined organic extracts were dried over magnesium sulfate and concentrated. The residue was chromatographed on the silica gel with the elution of a mixture of hexane and ethyl acetate. Products obtained in this work were characterized by spectral methods particularly with ^1H and ^{13}C NMR, and the data were consistent with those reported.

3.2.1. N-Phenylbenzylamine

^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.26 (m, 5H, *phenyl*), 7.19 (t, *J*=8 Hz, 2H, *phenyl*), 6.78 (t, *J*=7 Hz, 1H, *phenyl*), 6.67 (d, *J*=8 Hz, 2H, *phenyl*), 4.35 (s, 2H, −C*H*$_2$NH−), 4.06 (br, 1H, −N*H*−). These data are similar to those reported.[8]

3.2.2. N-(p-Methylphenyl)benzylamine[9]

^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.30 (m, 4H, *phenyl*), 7.27 (m, 1H, *phenyl*), 6.97 (d, *J*=8 Hz, 2H, *phenyl*), 6.56 (d, *J*=8 Hz, 2H, *phenyl*), 4.30 (s, 2H, −C*H*$_2$NH−), 4.11 (br, 1H, −N*H*−), 2.23 (s, 3H, −*Me*).

3.2.3. N-Phenyl-(p-chlorobenzyl)amine[10]

^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 4H, *phenyl*), 7.16 (t, *J*=8 Hz, 2H, *phenyl*), 6.72 (d, *J*=8 Hz, 1H, *phenyl*), 6.60 (d, *J*=8 Hz, 2H, *phenyl*), 4.30 (s, 2H, −C*H*$_2$NH−), 4.15 (br, 1H, −N*H*−). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 137.9, 132.8, 129.3, 128.7, 128.6, 117.8, 112.9, 47.6.

3.2.4. N-(p-Chlorophenyl)benzylamine[11]

^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.25 (m, 5H, *phenyl*), 7.10 (d, *J*=8 Hz, 2H, *phenyl*), 6.54 (d, *J*=8 Hz, 1H, *phenyl*), 4.29 (s, 2H, −C*H*$_2$NH−), 4.19 (br, 1H, −N*H*−).

3.2.5. N-Phenyl-(p-methoxybenzyl)amine[12]

^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J*=8 Hz, 2H, *phenyl*), 7.17 (t, *J*=8 Hz, 2H, *phenyl*), 6.87 (d, *J*=8 Hz, 2H, *phenyl*), 6.63 (d, *J*=8 Hz, 2H, *phenyl*), 6.17 (t, *J*=8 Hz, 1H, *phenyl*), 4.24 (s, 2H, −C*H*$_2$NH−), 4.19 (br, 1H, −N*H*−), 3.79 (s, 3H, −O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 148.0, 131.2, 129.2, 128.8, 117.6, 114.0, 112.9, 55.3, 47.9.

3.2.6. N-Phenyl-(o-methylbenzyl)amine[13]

^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 1H, *phenyl*), 7.22–7.17 (m, 5H, *phenyl*), 6.73 (t, *J*=8 Hz, 2H, *phenyl*), 6.64 (d, *J*=8 Hz, 1H, *phenyl*), 4.27 (s, 2H, −C*H*$_2$NH−), 3.97 (br, 1H, −N*H*−), 2.38 (s, 3H, −*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 136.9, 136.3, 130.4, 129.6, 128.2, 127.4, 126.1, 117.5, 112.7, 46.4, 18.9.

3.2.7. N-Phenyl-(2′-pyridinemethyl)amine[14]

^1H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, *J*=4 Hz, 1H, *phenyl*), 7.63 (t, *J*=8 Hz, 1H, *phenyl*), 7.33 (d, *J*=8 Hz, 1H, *phenyl*), 7.18–7.14 (m, 3H, *phenyl*), 6.70 (t, *J*=8 Hz, 1H, *phenyl*), 6.65 (d, 2H, *phenyl*), 4.46 (s, 2H, −C*H*$_2$NH−), 4.10 (br, 1H, −N*H*−). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 149.0, 147.8, 136.8, 129.2, 122.1, 121.6, 117.6, 113.0, 49.2.

3.2.8. N-(o-Methylphenyl)benzylamine[15]

^1H NMR (400 MHz, $CDCl_3$): δ 7.40–7.28 (m, 5H, *phenyl*), 7.08 (m, 2H, *phenyl*), 6.68 (m, 1H, *phenyl*), 6.63 (m, 1H, *phenyl*), 4.37 (s, 2H, −C*H*$_2$NH−), 3.95 (br, 1H, −N*H*−), 2.17 (s, 3H, −*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 139.3, 130.1, 128.6, 127.6, 127.2, 127.1, 122.0, 117.3, 110.1, 48.3, 17.5.

3.2.9. N-(3,5-Dimethylphenyl)benzylamine[16]

^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 4H, *phenyl*), 7.29–7.26 (m, 1H, *phenyl*), 6.39 (s, 1H, *phenyl*), 6.29 (s, 2H, *phenyl*), 4.30 (s, 2H, −C*H*$_2$NH−), 4.10 (br, 1H, −N*H*−), 2.25 (s, 6H, −*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 139.5, 138.9, 128.6, 127.6, 127.2, 119.7, 110.9, 48.5, 21.5.

3.2.10. (6-Methoxynaphthalen-2-ylmethyl)phenylamine

^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 3H, *phenyl*), 7.44 (dd, *J*=4, 8 Hz, 1H, *phenyl*), 7.19–7.13 (m, 3H, *phenyl*), 7.12 (s, 1H, *phenyl*), 6.72 (t, *J*=8 Hz, 1H, *phenyl*), 6.67 (d, *J*=8 Hz, 2H, *phenyl*), 4.44 (s, 2H, −C*H*$_2$NH−), 4.20 (br, 1H, −N*H*−), 3.91 (s, 3H, −O*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 148.0, 134.4, 133.8, 129.3, 129.2, 128.9, 127.2, 126.4, 126.0, 118.9, 117.7, 113.0, 105.6, 55.3, 48.5. Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.90; H, 6.54; N, 5.05.

3.2.11. Dibenzylamine[14]

^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 8H, *phenyl*), 7.26–7.23 (m, 2H, *phenyl*), 3.80 (s, 4H, −C*H*$_2$NH−). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 128.4, 128.2, 127.0, 53.4.

3.2.12. Hexylbenzylamine[15]

^1H NMR (400 MHz, $CDCl_3$): δ 7.34–7.20 (m, 5H, *phenyl*), 3.77 (s, 2H, −C*H*$_2$NH−), 2.60 (t, *J*=8 Hz, 2H), 1.50–1.45 (m, 2H), 1.32–1.24 (m, 6H), 0.86 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 128.4, 128.1, 126.8, 54.1, 49.5, 31.8, 30.1, 27.0, 22.6, 14.1.

3.2.13. N,N-Diphenylbenzylamine[17]

^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.22 (m, 9H, *phenyl*), 7.10–7.07 (m, 4H, *phenyl*), 6.97–6.93 (m, 2H, *phenyl*), 5.02 (s, 2H, −C*H*$_2$N−). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 139.2, 129.2, 128.5, 126.7, 126.5, 121.3, 120.6, 56.3.

3.2.14. (2-Methylbenzyl)diphenylamine[17]

^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (m, 1H, *phenyl*), 7.24 (t, *J*=7.6 Hz, 4H, *phenyl*), 7.10–7.19 (m, 3H, *phenyl*), 7.06 (m, 4H, *phenyl*), 6.94 (t, *J*=7.6 Hz, 2H, *phenyl*), 4.90 (s, 2H, −C*H*$_2$N−), 2.31 (s, 3H, −*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 136.2, 134.7, 130.0, 129.1, 126.4, 126.1, 126.0, 121.2, 120.4, 54.4, 19.1. Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.77; H, 7.13; N, 4.94.

3.2.15. (4-Chlorobenzyl)diphenylamine

^1H NMR (400 MHz, $CDCl_3$): δ 7.21–7.27 (m, 8H, *phenyl*), 7.03 (m, 4H, *phenyl*), 6.94 (m, 2H, *phenyl*), 4.95 (s, 2H, −C*H*$_2$N−). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 137.5, 132.3, 129.2, 128.6, 127.8, 121.5, 120.5, 55.8. Anal. Calcd

for $C_{19}H_{16}ClN$: C, 77.68; H, 5.49; N, 4.77. Found: C, 77.48; H, 5.81; N, 4.30.

3.2.16. (4-Methoxybenzyl)diphenylamine[18]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (m, 6H, *phenyl*), 7.04 (d, J=7.6 Hz, 4H, *phenyl*), 6.91 (t, J=7.6 Hz, 2H, *phenyl*), 6.82 (d, J=8.4 Hz, 2H, *phenyl*), 4.92 (s, 2H, $-CH_2N-$), 3.76 (s, 3H, $-OMe$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 147.9, 130.9, 129.1, 127.5, 121.2, 120.6, 113.8, 55.7, 55.3.

Acknowledgements

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