Trans-Spanned Palladium Catalyst for Mild and Efficient Amination of Aryl Halides with Benzophenone Imine

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Abstract: A new protocol for palladium-catalyzed Buchwald–Hartwig amination of aryl chlorides and bromides with benzophenone imine as ammonia surrogate is described. The suggested reaction conditions are mild and may therefore be applied to a variety of sensitive starting materials.

Key words: trans-spanning ligands, aminations, palladium-catalyzed, triptycene

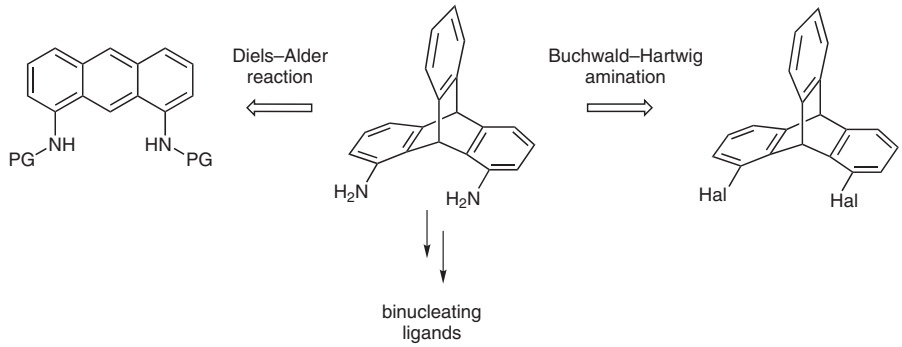
The *N*-aryl moiety represents an important motif in natural products,[1] biologically relevant compounds,[2] polymers,[3] and materials.[4] Classical methods for the synthesis of *N*-aryl compounds proved to be very limited in selectivity and scope.[5] However, during the past decade, great progress has been made in the development of the palladium-catalyzed amination of aryl halides and pseudohalides.[6] A wide range of transition-metal complexes have been shown to successfully catalyze arylation of primary and secondary amines, as well as of ammonia and ammonia equivalents.[7]

During the course of our studies focusing on the development of a new family of bis-imine binucleating ligands,[8] we became interested in the preparation of triptycene-1,8-diamine as a key intermediate. Both catalytic and noncatalytic strategies toward the target were considered (Scheme 1).

The noncatalytic route requires the synthesis of anthracene-1,8-diamine as a precursor – a valuable, known, but somewhat problematic compound. Its synthesis is low yielding and hardly reproducible (15–30% based on the commercial 1,8-dinitroanthraquinone). In addition, it is accompanied by laborious purification workup.[9] Considering this, palladium-catalyzed amination of 1,8-dihalotriptycene – a readily available starting material[10b,11] – appears as the most straightforward route. In addition, the cross-coupling strategy allows more synthetic flexibility for the modification of the frame.

Unfortunately, our first experiments aiming at a double amination of 1,8-dibromotriptycene[10b] by different ammonia surrogates using published protocols encountered unexpected difficulties – unreasonably incomplete conversion, high percentage of hydrogenolyzed by-products, and formation of unidentified substances were observed when we used LiHMDS or NaHMDS as ammonia equivalents and commercially available catalysts.[7e,12]

At this point, we performed a series of experiments in order to discover optimal reaction conditions for the desired transformation. At the first stage, optimization experiments were focused on the following variables: i) ammonia surrogates (freshly prepared vs. commercially available LiHMDS and NaHMDS salts, $NaNH_2$, $LiNH_2$ and benzophenone imine/base), and ii) solvents (toluene, dioxane, and THF) in the presence of three different catalysts – $Pd_2(dba)_3$/Xantphos (**4**),[13a–c] $Pd_2(dba)_3$/X-Phos,[14] and $Pd_2(dba)_3$/2-dicyclohexylphosphinobiphenyl.[7e] On the whole, we found that bidentate Xantphos (**4**) shows superior reactivity over the monodentate ligands and 'optimizable' results were obtained when benzophenone



Scheme 1 Possible syntheses of 1,8-diaminotriptycenes

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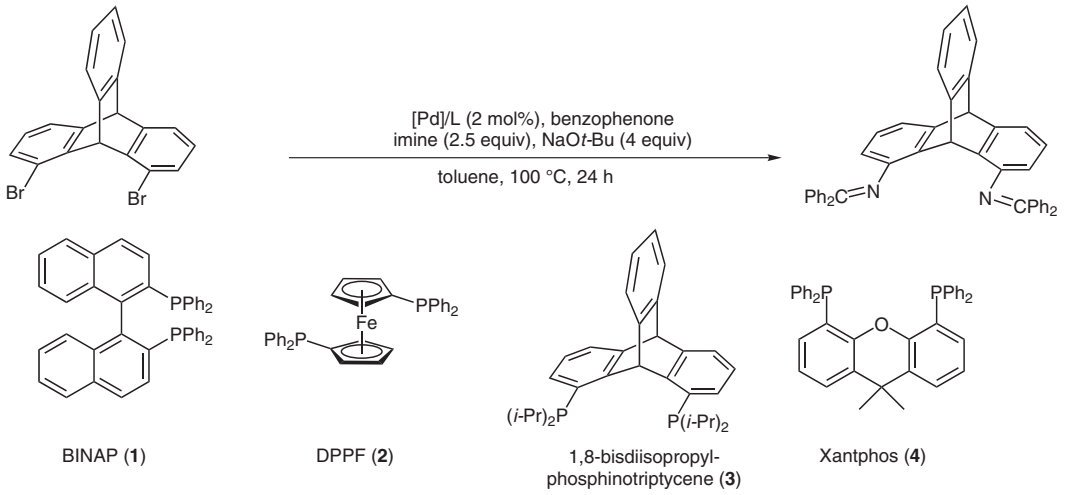
Table 1 Initial Optimization Experiments



Entry	Pd precursor	Ligand	Conversion (%)[a]	Yield (%)[a]
1	$Pd_2(dba)_3$	**1**	10	n/a
2	$Pd_2(dba)_3$	**2**	–	n/a
3	$Pd_2(dba)_3$	**3**	99	70[b]
4	$Pd_2(dba)_3$	**4**	99	93[b]
5	$Pd(OAc)_2$	**3**	90	n/a
6	$Pd(OAc)_2$	**4**	27	n/a

[a] Based on crude NMR analysis; n/a = not applicable.
[b] Missing percentage refers to monosubstituted and dehalogenated species.

imine/*t*-BuONa in toluene was used as an ammonia source.

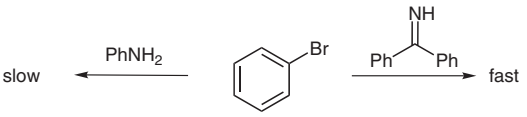
At the second stage, we refined the reaction conditions by choosing the right catalyst precursor/bidentate ligand combination – $PdCl_2$, $Pd(OAc)_2$, and $Pd_2(dba)_3$ in combination with the bidentate BINAP (**1**) (original Buchwald protocol),[7a] DPPF (**2**),[13d] Xantphos (**4**), and 1,8-bisdiisopropylphosphinotriptycene (**3**) were tested (Table 1). The last trans-spanning ligand has been used by us in different transformations previously.[10b,11]

We found that only $Pd_2(dba)_3$/Xantphos (**4**) and the analogous $Pd_2(dba)_3$/1,8-bisdiisopropylphosphinotriptycene (**3**) led to a complete conversion of the starting 1,8-dibromotriptycene. However, the latter, demonstrated somewhat cleaner and faster reaction toward the desired bisaminated product. In addition, unlike Xantphos (**4**), almost complete conversion (up to 90%) was achieved in the presence of catalyst derived from $Pd(OAc)_2$ and 1,8-bisdiisopropylphosphinotriptycene (**3**). Therefore, it was decided to employ this catalyst in the desired transformation.

We were glad to observe that under the chosen conditions (2 mol% of $Pd_2(dba)_3$, 4 mol% of the ligand, 2.3:1 benzophenone imine/1,8-dibromotriptycene ratio, and *t*-BuONa in toluene as a base) the reaction was perfectly scalable (up to 5 g) and yielded 87% of the desired benzophenone imine adduct after 24 hours at 100 °C (Table 2, entry 1). Of course, there was no need for high palladium loading in the small-scale reactions.

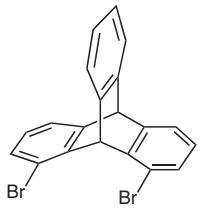
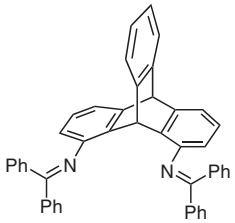
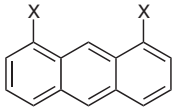
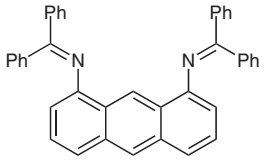
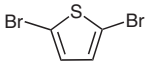
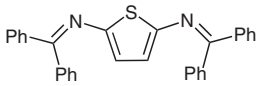
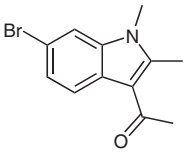
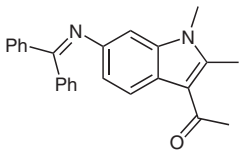
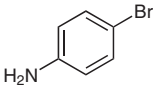
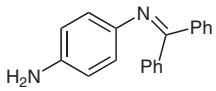
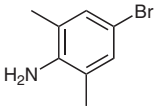
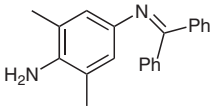
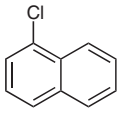
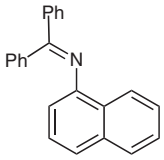
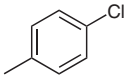
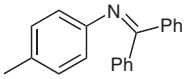
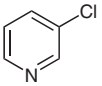
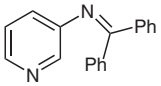
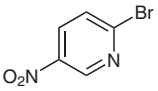
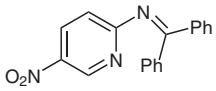
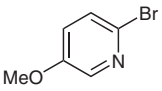
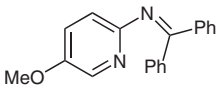
Encouraged by these results, we decided to test the catalyst on other substrates. It was found that, the transformation was successful with aryl chlorides, bromides, and functionalized and functionless aromatic and heteroaromatic compounds (the results are shown in Table 2). In addition to the already described dibromotriptycene, other fascinating compounds can be efficiently aminated by benzophenone imine in the presence of the $Pd_2(dba)_3$/**3** catalyst. Entries 2–5, for example, represent important building blocks for construction of sensors (anthracene-1,8-diamine),[15] biologically active compounds (thiophene-2,5-diamine),[16] and molecular switches (indole derivatives).[17] It is worth noting that their synthesis using other methods is complicated.

Surprisingly, the suggested catalyst can tolerate functional groups containing active hydrogens. So, unlike the original Buchwald protocol[7a] unprotected anilines form



Scheme 2 Selective amination of bromobenzene with benzophenone imine

Table 2 Representative Amination Results

Entry	Substrate	Conditions	Product	Yield (%)[a]	Yield after hydrolysis (%)[b]
1		$Pd_2(dba)_3$/**3** (2 mol%), *t*-BuONa: 5 g scale		87	72
		$Pd_2(dba)_3$/**3** (2 mol%), *t*-BuONa: 3 g scale			
2	X = Br			93	80
3	X = Cl			87	78
4		$Pd(OAc)_2$/**3** (3 mol%), *t*-BuONa		77	n/a[c]
5		$Pd_2(dba)_3$/**3** (0.5 mol%), *t*-BuONa		99	89
6		$Pd(OAc)_2$/**3** (1.5 mol%), *t*-BuONa		87	n/a
7		$Pd(OAc)_2$/**3** (1.5 mol%), *t*-BuONa		84	87
8		$Pd(OAc)_2$/**3** (1.5 mol%), K_3PO_4		99	97
9		$Pd(OAc)_2$/**3** (1.5 mol%), K_3PO_4		99	n/a
10		$Pd(OAc)_2$/**3** (1.5 mol%), K_3PO_4		82	n/a
11		$Pd(OAc)_2$/**3** (1.5 mol%), K_3PO_4		92	n/a
12		$Pd(OAc)_2$/**3** (1.5 mol%), K_3PO_4		81	n/a

[a] Isolated yield (average of two runs).
[b] n/a = not applicable.
[c] The diamine is unstable under the deprotection conditions.

benzophenone imine adducts in very good yields under our reaction conditions (Scheme 2, and Table 2, entries 6,7) and this is in sharp contrast to the vast majority of known catalysts. Although a control experiment between bromobenzene and aniline resulted in the formation of diphenylamine, the reaction was very slow under the present reaction conditions, which explains the selectivity toward benzophenone imine coupling even in the presence of the unprotected aniline group. Unfortunately, when chloro compounds were used instead of their bromo equivalents, the yield dropped owing to more pronounced self-coupling.

In addition, we found that in many cases the use of the costly and air-sensitive Pd(0) precursor is not necessary, and it can be replaced by the more convenient $Pd(OAc)_2$ without affecting the performance of the catalyst (Table 2, entries 4, 6–12). In other simpler cases (Table 2, entries 8–12), *t*-BuONa can also be replaced with the less demanding K_3PO_4. The last result is important because potentially this solves the problem of hydrolyzable and base-sensitive compounds.

Finally, it is interesting to note that, we did not observe significant difference either in the reactivity or selectivity of aryl bromides and aryl chlorides under our reaction conditions (with the exception 4-haloanilines – in these cases, the difference in chemoselectivity is likely due to the difference in pK_a) – decrease in reaction temperature slows down the reactions of both chloro- and bromoarenes. This fact, apparently, supports our previous hypothesis that reductive elimination but not oxidative addition is the rate determining step for our trans-spanned catalyst.[11]

In conclusion, our intention to synthesize a particular substrate disclosed a very useful modification of the Buchwald–Hartwig protocol for the amination of aryl chlorides and bromides with benzophenone imine as ammonia surrogate. Our mild protocol allows very efficient amination of substrates of different steric and electronic demands (including base sensitive) without a need for protection. In many cases simple and cheap catalyst precursors and bases may be used.

$Pd(OAc)_2$ (98%), tris(dibenzylideneacetone)dipalladium(0) [$Pd_2(dba)_3$], K_3PO_4, *t*-BuONa, benzophenone imine (97%), and all starting aryl halides are commercially available or were prepared using published procedures. All reagents were used without further purification. Ligand **3** was synthesized according to the previously published procedure.[10b] All reagents were weighed and handled in air. All reactions were carried out under N_2 (99.999% pure) in oven-dried glassware. Flash column chromatography was performed with ultra pure silica gel (230–400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz or Bruker 400 MHz instrument. The chemical shifts are reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Yields refer to isolated yields of compounds greater than 95% purity as determined ^{1}H NMR analysis. Yields reported in Table 2 are for an average of two runs. Entries 3, 8, 9, and 10 in Table 2 are known compounds. Spectroscopic data of the known compounds match with the data reported in the corresponding references.

Amination of Aryl Halides; Typical Large-Scale Procedure

$Pd_2(dba)_3$ (163.3 mg, 0.17 mmol, 2 mol%), **3** (173.0 mg, 0.34 mmol), 1,8-dibromoanthracene (3 g, 8.91 mmol) and *t*-BuONa (2.5 g, 26.73 mmol, 3 equiv) were placed in a dry 50 mL Schlenk tube equipped with a stir bar under 99.999% N_2. Upon dissolution and after stirring for 30 min in anhyd toluene (20 mL), benzophenone imine (3.45 mL, 20.5 mmol, 2.3 equiv) was injected at once and the sealed tube was thermostated at 100 °C for 24 h. After cooling to r.t., the mixture was washed with H_2O (15 mL), and brine (15 mL), and dried ($MgSO_4$). After evaporation under reduced pressure, MeOH (10 mL) was added and left aside for 2 h to give the precipitated product in at least 95% purity, which was isolated by filtration.

Amination of Aryl Halides; Typical Small-Scale Procedure

$Pd(OAc)_2$ (4.1 mg, 0.02 mmol), **3** (9.0 mg, 0.02 mmol), and *t*-BuONa (235.0 mg, 2.42 mmol) were placed in a dry single-use test tube equipped with a stir bar under 99.999% N_2. Upon dissolution and stirring for 30 min in anhyd toluene (4 mL), 1-chloronaphthalene (170 μL, 1.20 mmol) and benzophenone imine (250 μL, 1.43 mmol) were injected at once and the sealed tube was thermostated at 100 °C for 24 h. After cooling to r.t., the mixture was washed with H_2O (5 mL) and brine (5 mL), and dried ($MgSO_4$). After evaporation under reduced pressure, the product was isolated by flash chromatography.

N^1,N^8-Bis(diphenylmethylene)triptycene-1,8-diamine (Table 2, Entry 1)

Yellow solid; mp 290 °C (dec.).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (4 H, d, *J* = 7.3 Hz), (2 H, t, *J* = 7.3 Hz), 7.36 (2 H, t, *J* = 5.78 Hz), 7.28–7.24 (4 H, m, Ar), 7.15–7.11 (6 H, m, Ar), 7.07–7.05 (4 H, m, Ar), 7.04–6.96 (4 H, m, Ar), 6.69 (2 H, t, *J* = 7.6 Hz), 6.12 (2 H, d, *J* = 7.8 Hz), 6.04 (1 H, s), 5.35 (1 H, s).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 168.8, 146.5, 146.4, 144.5, 139.2, 136.3, 135.9, 130.5, 129.4, 129.0, 128.3, 128.1, 127.8, 124.7, 124.0, 123.3, 118.6, 116.9, 54.5, 43.8.

Anal. Calcd for $C_{46}H_{32}N_2$: C, 90.16; H, 5.26. Found: C, 89.94; H, 4.98.

N^1,N^8-Bis(diphenylmethylene)anthracene-1,8-diamine (Table 2, Entry 2)

Orange solid; mp 197 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (1 H, s), 8.27 (1 H, s), 7.80 (4 H, d, *J* = 7.7 Hz), 7.61 (2 H, d, *J* = 8.5 Hz), 7.42 (2 H, t, *J* = 7.3 Hz), 7.24–7.05 (16 H, m, Ar), 6.59 (2 H, d, *J* = 6.9 Hz).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 168.8, 147.9, 139.2, 136.3, 132.1, 130.5, 129.1, 128.6, 128.5, 128.1, 127.7, 125.7, 125.5, 125.3, 123.1, 119.4, 113.0.

Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.52; H, 5.26. Found: C, 89.84; H, 5.03.

Anthracene-1,8-diamine[18] (Table 2, Entry 3)

Yellow solid; mp 138 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.89 (1 H, s), 8.21 (1 H, s), 7.33–7.20 (4 H, m, Ar), 6.66 (2 H, dd, *J* = 6.2, 1.9 Hz), 5.85 (4 H, s, NH_2).

N^2,N^5-Bis(diphenylmethylene)thiophene-2,5-diamine (Table 2, Entry 4)

Yellow solid; mp 111 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (4 H, d, *J* = 7.0 Hz), 7.58–7.46 (2 H, m, Ar), 7.39–7.33 (10 H, m, Ar), 7.11 (4 H, d, *J* = 7.2 Hz), 6.90 (2 H, s).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 161.6, 149.8, 139.7, 135.9, 130.2, 129.4, 129.2, 128.7, 128.6, 128.1, 125.4.

Anal. Calcd for $C_{30}H_{22}N_2S$: C, 81.41; H, 5.01. Found: C, 81.70; H, 4.91.

1-(6-Amino-1,2-dimethyl-1*H*-indol-3-yl)ethanone (Table 2, Entry 5)
Yellow solid; mp 112 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (1 H, d, *J* = 8.4 Hz), 6.70 (1 H, dd, *J* = 8.5, 2.1 Hz), 6.61 (1 H, d, *J* = 1.7 Hz), 3.60 (3 H, s), 2.71 (3 H, s), 2.62 (3 H, s).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 194.4, 143.3, 142.2, 138.0, 121.4, 119.2, 114.1, 111.9, 95.3, 31.5, 29.3, 12.5.

MS (EI, 70 eV): *m*/*z* = 202 [M^+], 186 [$M^+ - NH_2$].

Anal. Calcd for $C_{12}H_{14}N_2O$: C, 71.26; H, 6.98. Found: C, 71.70; H, 6.91.

***N*^{1}-(Diphenylmethylene)benzene-1,4-diamine (Table 2, Entry 6)**
Yellow solid; mp 171 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (2 H, d, *J* = 7.0 Hz), 7.41–7.16 (8 H, m, Ar), 6.62 (2 H, d, *J* = 8.7 Hz), 6.52 (2 H, d, *J* = 8.6 Hz), 3.50 (2 H, NH_2).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.0, 142.8, 142.4, 140.3, 137.0, 130.3, 129.6, 129.1, 128.4, 128.1, 128.0, 122.9, 115.3.

MS (EI, 70 eV): *m*/*z* = 271 [M^+], 194 [$M^+ - Ph$].

Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92. Found: C, 84.02; H, 5.91.

***N*^{4}-(Diphenylmethylene)-2,6-dimethylbenzene-1,4-diamine (Table 2, Entry 7)**
White solid; mp 163 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (2 H, dd, *J* = 6.9, 1.6 Hz), 7.45 (3 H, m, Ar), 7.31 (3 H, m, Ar), 7.18 (2 H, dd, *J* = 4.3, 2.0 Hz), 6.42 (1 H, s), 3.41 (2 H, s, NH_2), 2.05 (6 H, s).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 166.1, 141.9, 140.6, 138.9, 137.2, 130.1, 129.6, 129.1, 128.2, 128.1, 128.0, 122.2, 121.8, 17.6.

MS (EI, 70 eV): *m*/*z* = 300 [M^+], 223 [$M^+ - NH_2 - C$].

Anal. Calcd for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71. Found: C, 84.08; H, 6.99.

Naphthalen-1-amine[19] (Table 2, Entry 8)
Yellow solid; mp 195 °C (Lit.[19] mp 203 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (2 H, d, *J* = 7.2 Hz), 7.68 (2 H, d, *J* = 2.6 Hz), 7.47–7.28 (2 H, m, Ar), 7.00 (1 H, dd, *J* = 8.7, 2.2 Hz), 3.86 (2 H, NH_2).

***p*-Toluidine[20] (Table 2, Entry 9)**
Yellow solid; mp 39–42 °C (Lit.[20] mp 46–48 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (2 H, d, *J* = 8.1 Hz), 6.66 (2 H, d, *J* = 8.3 Hz), 3.52 (2 H, s, NH_2), 2.28 (3 H, s).

***N*-(Diphenylmethylene)pyridin-3-amine[21] (Table 2, Entry 10)**
Yellow solid; mp 98 °C (Lit.[21] mp 105 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (1 H, d, *J* = 4.4 Hz), 8.06 (1 H, d, *J* = 1.7 Hz), 7.80 (2 H, d, *J* = 7.6 Hz), 7.57 (1 H, t, *J* = 8.7 Hz), 7.47 (2 H, t, *J* = 7.7 Hz), 7.31 (3 H, d, *J* = 6.5 Hz), 7.14 (2 H, d, *J* = 7.5 Hz), 7.10–7.05 (2 H, m, Ar).

***N*^{5}-(Diphenylmethylene)-5-nitropyridin-2-amine (Table 2, Entry 11)**
Yellow solid; mp 78–81 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.17 (1 H, dd, *J* = 2.7, 0.6 Hz), 8.25 (1 H, dd, *J* = 8.8, 2.7 Hz), 7.82 (1 H, d, *J* = 8.2 Hz), 7.51–7.37 (9 H, m, Ar), 6.70 (1 H, dd, *J* = 8.8, 0.6 Hz).

^{13}C NMR (300 MHz, $CDCl_3$): δ = 171.3, 168.1, 146.7, 145.3, 140.0, 133.4, 132.7, 132.4, 130.0, 129.6, 128.3, 128.2, 115.0, 106.9.

MS (EI, 70 eV): *m*/*z* = 303 [M^+], 226 [$M^+ - Ph$].

Anal. Calcd for $C_{18}H_{13}N_3O_2$: C, 71.28, H, 4.32. Found: C, 71.15, H, 4.12.

***N*-(Diphenylmethylene)-5-methoxypyridin-2-amine (Table 2, Entry 12)**
Yellow solid; mp 159 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (2 H, d, *J* = 7.2 Hz), 7.68 (1 H, d, *J* = 2.6 Hz), 7.47–7.28 (6 H, m, Ar), 7.14–7.12 (2 H, m, Ar), 7.00 (1 H, dd, *J* = 8.7, 2.2 Hz), 3.86 (3 H, s).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 169.5, 160.5, 152.5, 141.2, 139.5, 139.2, 136.1, 132.7, 130.9, 129.4, 129.3, 128.9, 128.6, 128.3, 128.2, 127.9, 110.1, 53.4.

MS (EI, 70 eV): *m*/*z* = 288 [M^+], 211 [$M^+ - Ph$].

Anal. Calcd for $C_{19}H_{16}N_2O$: C, 79.14, H, 5.59. Found: C, 78.83, H, 5.13.

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