Carbene adduct of cyclopalladated ferrocenylimine as an efficient catalyst for the amination of aryl chlorides

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Abstract

A novel air- and moisture-stable carbene adduct of cyclopalladated ferrocenylimine has been synthesized and characterized. The structure of this compound was determined by X-ray crystal structure analysis. This adduct has been applied as an efficient catalyst for the amination of aryl chlorides.
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Keywords: Cyclopalladated ferrocenylimine; *N*-Heterocyclic carbene; Amination; Aryl chlorides

1. Introduction

The palladium catalyzed amination of aryl halides (Buchwald–Hartwig amination) is a rapidly developing field due to the importance of the products in many fields, *e.g.* pharmaceuticals, xerography, electronic materials and ligands for transition metals [1]. Employing aryl chlorides for this reaction has been focused recently because aryl chlorides are cheaper and more available than their bromide and iodide counterparts. Not surprisingly, a plethora of palladium catalyst systems, featuring a palladium-bound ligand, are now accessible for accomplishing the transformation involving aryl chlorides. Typically, electron-rich sterically hindered phosphine ligands such as trialkylphosphines [2], aryldialkylphosphines [3–5], ferrocenyldialkylphosphines [6], dialkylphosphinous acids [7], bicyclic triaminophosphines [8] and phosphorinanes [9], have been investigated in these reactions. And a number of reports have shown that Pd complexes derived from sterically hindered and electron-rich phosphines are effective catalysts for this transformation [10].

As an alternative, *N*-heterocyclic carbenes have been proved to be excellent ligands in numerous palladium catalyzed coupling reactions by the virtue of their strong electron-donating properties and their hedge-like steric bulk [11]. In the earlier work, the NHC-palladium moiety has been generated *in situ* by the reaction of a base with a imidazolium salt precursor followed by addition of a palladium source [12]. To circumvent the drawbacks associated with *in situ* generated catalytic systems, some air- and moisture-stable NHC-bearing palladium (NHC = *N*-heterocyclic carbene) complexes has been reported for the cross coupling reactions [13]. Among these NHC-bearing palladium complexes, only several examples about carbene adducts of palladacycle were reported by the groups of Nolan [14], Herrmann [15], Iyer [16] and Bedford [17]. These catalysts combine the stability induced by the presence of a palladacycle framework with the high activity commonly associated with palladium/carbene complexes, and was also demonstrated to be highly active. Especially the carbene–palladacycle complex reported by the group of Nolan has been successfully applied to the Suzuki–Miyaura reaction, α-ketone arylation, dehalogenation reaction and Buchwald–Hartwig amination [14]. However, unlike the Suzuki reaction and Heck arylation, the report

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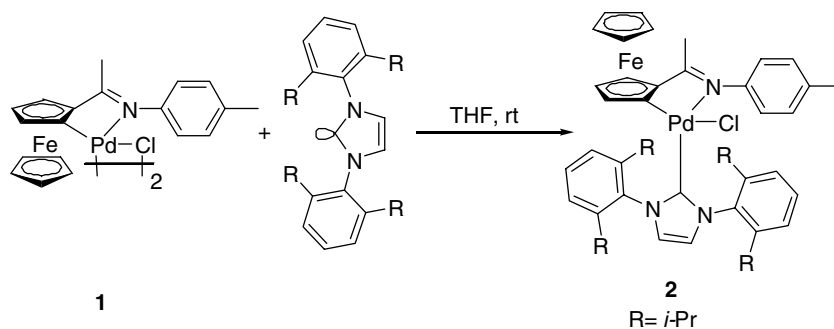
Scheme 1. Synthesis of compound **2**.

of Buchwald–Hartwig amination catalyzed by carbene–palladacycle complex remains elusive. To the best of our knowledge, only one example of carbene adduct of amine-based palladacycle for this reaction has been reported [14b].

Over the past decade, part of our research effort has focused on the synthesis and application of cyclopalladated ferrocenylimines [18], we have found that catalyst **1** is an effective catalyst for various coupling reactions [19]. Taking the advantage of the NHC properties, we synthesized carbene adduct **2**, and studied the catalytic activity of **2** for the amination of aryl chlorides. The results are present below.

2. Results and discussion

2.1. Synthesis and characterization of complex 2

The carbene adduct **2** was prepared in good yield by simple addition of THF solution of the carbene to the

cyclopalladated ferrocenylimine **1** at room temperature under N_2 (Scheme 1). The compound **2** was isolated as a red solid. It is stable to air and moisture. It is very soluble in chloroform, dichloromethane and acetone, but insoluble in petroleum ether and *n*-hexane. Recrystallization from dichloromethane/petroleum ether afforded the corresponding red crystal. This new compound was characterized by IR, ^1H NMR, ^{13}C NMR, DEPT 135, HSQC, MS and high-resolution mass spectra. These spectra were well consistent with the title compound. Moreover, the molecular structure of **2** has also been ascertained by means of X-ray studies. The structure of **2** together with selected bond distances and angles is shown in Fig. 1.

Crystallographic data are presented in Table 1. The Pd atom in **2** is in a slightly distorted square-planar environment bonded to the carbon atom of the carbene, the chlorine atom, the nitrogen atom and the carbon atom of the ferrocenyl moiety. In all cases the plane of Pd is defined by N, C (Cp ring), Cl, C (carbene) atoms with the deviation of Pd1 at 0.0384 Å. The bicyclic system formed by the palladacycle and the C_5H_3 moiety is approximately coplanar (dihedral angle 6.4°), and the dihedral angle between two
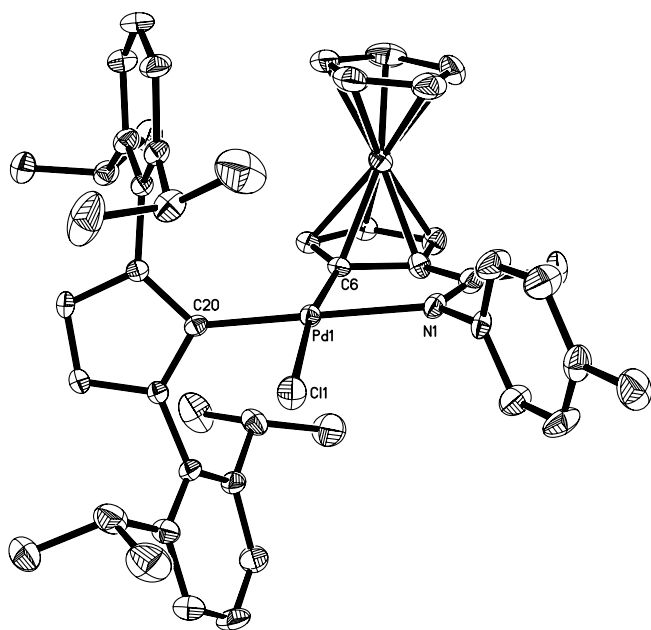

Fig. 1. Molecular structure of compound **2**. Selected bond distances (Å) and angles (°): Pd1–C6 1.983(4), Pd1–C20 1.998(3), Pd1–Cl1 2.379(1), Pd1–N1 2.114(3); C6–Pd1–C20 96.46(15), C6–Pd1–Cl1 170.94(12), C6–Pd1–N1 79.83(14), C20–Pd1–Cl1 90.47(15), C20–Pd1–N1 175.78(13), N1–Pd1–Cl1 93.01(9).

Table 1
Crystallographic and data collection parameters for complex **2**

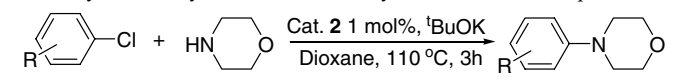| Compound	**2**
Empirical formula	$C_{48}H_{58}Cl_5FeN_3Pd$
Formula weight	1016.47
Temperature (K)	291(2)
Crystal system	Orthorhombic
Space group	$P2(1)2(1)2(1)$
a (Å)	12.371(3)
b (Å)	15.248(3)
c (Å)	26.771(5)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å^3)	5050.1(18)
Calculated density (g cm^{-3})	1.337
Z	4
Absorption coefficient (mm^{-1})	0.942
$F(000)$	2096
Crystal size (mm)	$0.20 \times 0.18 \times 0.17$
Data/restraints/parameters	8586/4/504
Goodness-of-fit on F^2	1.073
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0600$, $wR_2 = 0.1469$
R indices (all data)	$R_1 = 0.0685$, $wR_2 = 0.1530$

Cp rings in **2** is 3.1°. The Pd–C (carbene) bond length (1.998 Å) is similar to the reported data [14b]. The Pd–C (Cp ring) (1.983 Å) and Pd–N (2.114 Å) bond lengths in **2** are longer than those of **1** [20].
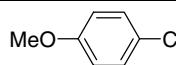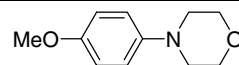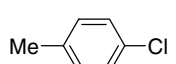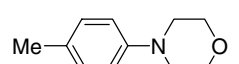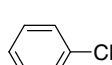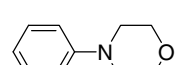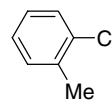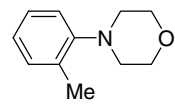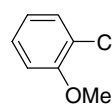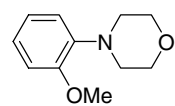
2.2. Catalytic activity

2.2.1. Palladacycle 2 catalyzed aryl chlorides with secondary amines

In order to test the catalytic activity of palladacycle **2**, we initially conducted the reaction of various aryl chlorides with secondary amine morpholine. The results are summarized in Table 2. To our delight, using 1 mol% of **2**, these reactions indeed proceeded smoothly to afford the corresponding products in moderate to good yields. Both electron-poor and electron-rich aryl chlorides reacted to afford the product in high yields (Table 2, entries 1–4,7).
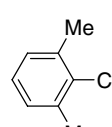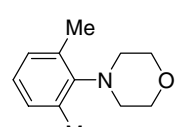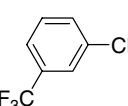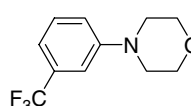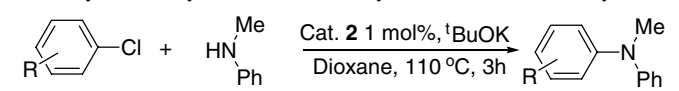
However, the yields were influenced by the steric hindrance of aryl chlorides. 2-Chloroanisole reacted with morpholine giving 87% isolated yield (Table 2, entry 5), while the very sterically hindered 2-chloro-*m*-xylene reacted with morpholine gave 77% isolated yields (Table 2, entry 6).
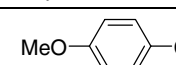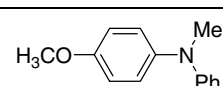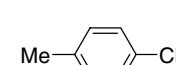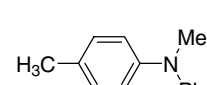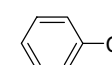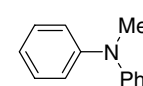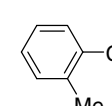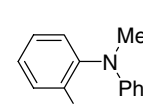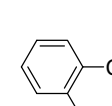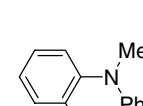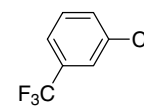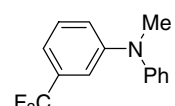
We then studied the reaction of aryl chlorides with *N*-methylaniline. As shown in Table 3, unlike the reaction of aryl chlorides with morpholine, the yields of aryl chlorides reacted with *N*-methylaniline in this system were slightly low.

2.2.2. Palladacycle 2 catalyzed aryl chlorides with various anilines

Having successfully demonstrated the activity of palladacycle **2** catalyzed amination of aryl chlorides with secondary amines, we used this system for the reaction of aryl chlorides with aniline. The results are listed in Table 4. In all the cases aniline could be arylated with elec-

Table 2
Palladacycle **2** catalyzed amination of aryl chlorides with morpholine

Entry[a]	Aryl chloride	Product	Yield (%)[b]
1			99
2			98
3			99
4			99
5			87
6			77
7			98

[a] *Reaction conditions*: cat. **2**, 0.01 mmol, aryl chloride 1.0 mmol, morphline 1.2 mmol, *t*BuOK 1.5 mmol, dioxane 2 ml.
[b] Islolated yields based on aryl chloride.

Table 3
Palladacycle **2** catalyzed amination of aryl chlorides with *N*-methylaniline

Entry[a]	Aryl chloride	Product	Yield (%)[b]
1			85
2			90
3			92
4			88
5			81
6			92

[a] *Reaction conditions*: cat. **2**, 0.01 mmol, aryl chloride 1.0 mmol, *N*-methylaniline 1.2 mmol, *t*BuOK 1.5 mmol, dioxane 2 ml.
[b] Islolated yields based on aryl chloride.
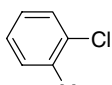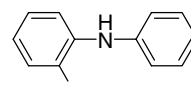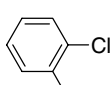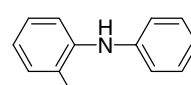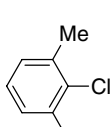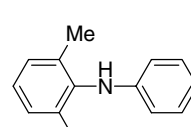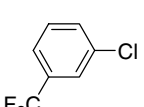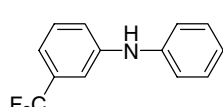
tronically diverse aryl chlorides. Reaction of *ortho*-substituted aryl chlorides with aniline afforded higher yields. This is mainly due to that the *ortho*-substituent of aryl chlorides prevent the formation of triarylamine.

Table 5 summarizes the results of the couplings of various aryl chlorides with 2,5-dimethylaniline. As shown in Table 5, palladacycle **2** was very effective for the arylation of 2,5-dimethylaniline. Nearly all the aryl chlorides reacted with 2,5-dimethylaniline to afford good to excellent yields. *Ortho*-substituted aryl chlorides showed no deleterious effect on this reaction. The *ortho*-substituent of aniline could also promote this reaction.

We also examined the amination of aryl chlorides with sterically hindered 2,6-dimethylaniline. As shown in Table 6, the yields are better than the yields of aniline in most cases. The presence of an *ortho*-substituent on the aryl chloride had no deleterious effect and in fact, coupling occurred in nearly quantitative yield. Especially, the reaction of 2-chloro-*m*-xylene with 2,6-dimethylaniline provided *tetra-ortho*-substituted diarylamine in 99% isolated yield (Table 6, entry 5).
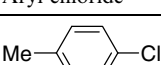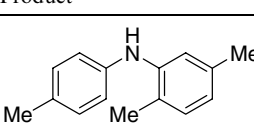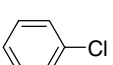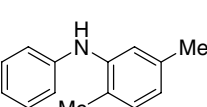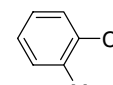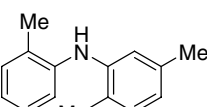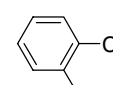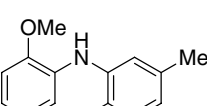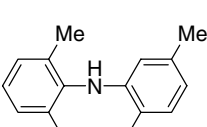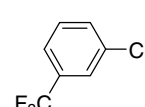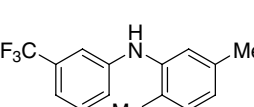
Table 4
Palladacycle **2** catalyzed amination of aryl chlorides with aniline

Entry[a]	Aryl chloride	Product	Yield (%)[b]
1	Me—⟨⟩—Cl	Me—⟨⟩—NH—⟨⟩	65
2	⟨⟩—Cl	⟨⟩—NH—⟨⟩	88
3	⟨⟩—Cl, Me	⟨⟩—NH—⟨⟩, Me	96
4	⟨⟩—Cl, OMe	⟨⟩—NH—⟨⟩, OMe	99
5	Me, ⟨⟩—Cl, Me	Me, ⟨⟩—NH—⟨⟩, Me	89
6	⟨⟩—Cl, F₃C	⟨⟩—NH—⟨⟩, F₃C	76

[a] *Reaction conditions*: cat. **2**, 0.01 mmol, aryl chloride 1.0 mmol, aniline 1.2 mmol, *t*BuOK 1.5 mmol, dioxane 2 ml.
[b] Islolated yields based on aryl chloride.

Table 5
Palladacycle **2** catalyzed amination of aryl chlorides with 2,5-dimethylaniline

Entry[a]	Aryl chloride	Product	Yield (%)[b]
1	Me—⟨⟩—Cl	Me—⟨⟩—NH—⟨⟩—Me, Me	95
2	⟨⟩—Cl	⟨⟩—NH—⟨⟩—Me, Me	96
3	⟨⟩—Cl, Me	Me, ⟨⟩—NH—⟨⟩—Me, Me	99
4	⟨⟩—Cl, OMe	OMe, ⟨⟩—NH—⟨⟩—Me, Me	99
5	Me, ⟨⟩—Cl, Me	Me, Me, ⟨⟩—NH—⟨⟩—Me, Me	98
6	⟨⟩—Cl, F₃C	F₃C, ⟨⟩—NH—⟨⟩—Me, Me	89

[a] *Reaction conditions*: cat. **2**, 0.01 mmol, aryl chloride 1.0 mmol, 2,5-dimethylaniline 1.2 mmol, *t*BuOK 1.5 mmol, dioxane 2 ml.
[b] Islolated yields based on aryl chloride.

2.2.3. Palladacycle **2** catalyzed aryl chlorides with aliphatic amines

It is well known that reactions of primary aliphatic amines with aryl chlorides are not common in amination reaction. We first investigated the efficiency of **2** in the arylation of cyclohexylamine. As shown in Table 7, moderate to good yields were obtained. The steric hindrances of aryl chlorides are favored in this reaction. The reaction of 2-chloro-*m*-xylene with cyclohexylamine provided 99% isolated yield (Table 7, entry 6).
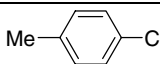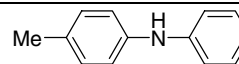
Encouraged by these results, we evaluated the efficiency of palladacycle **2** for the arylation of *n*-dodecylamine under the same condition (Table 7, entries 8–11). In case of *ortho*-substituted phenyl chlorides, high yields of coupled amines

Table 6
Palladacycle **2** catalyzed amination of aryl chlorides with sterically hindered 2,6-dimethylaniline

Entry[a]	Aryl chloride	Product	Yield (%)[b]
1			66
2			94
3			99
4			99
5			99
6			84

[a] *Reaction conditions*: cat, **2**, 0.01 mmol, aryl chloride 1.0 mmol, 2,6-dimethylaniline 1.2 mmol, ^{t}BuOK 1.5 mmol, dioxane 2 ml.
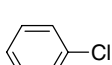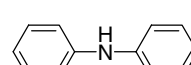[b] Islolated yields based on aryl chloride.

were obtained (Table 7, entries 10,11). In case of aryl chlorides without *ortho*-substituent, both mono and di-substituted amines were obtained (Table 7, entries 8, 9).

Overall, the results above-mentioned that palladacycle **2** is clearly comparable in efficacy to other popular catalysts or ligands currently employed. However, as to the typical amination catalysts or ligands developed by the groups of Buchwald, Hartwig, Nolan and others, due to their wide research and excellent work, the amination can be carried out at room temperature [2b,3a,6a] with a lower catalyst loading [6c,13f,13g] and a weaker base [3e]. So our further research will focus on the development of more efficient catalytic systems for this reaction.

3. Conclusion

A novel air- and moisture-stable carbene–palladacycle complex has been synthesized. The new complex showed good activity as catalyst for the Buchwald–Hartwig amination of a range of aryl chlorides with amines.

4. Experimental

4.1. General comments

Melting points were measured on a WC-1 microscopic apparatus and are uncorrected. IR spectra were recorded on a Bruker VECTOR22 spectrophotometer. ^{1}H NMR, ^{13}C NMR, DEPT and C, H-COSY spectra were recorded on a Bruker DPX-400 spectrometer in CDCl$_3$ with TMS as an internal standard. Mass spectra were measured on a LC-MSD-Trap-XCT instrument. High-resolution mass spectra were measured on a Waters Q-T of Micro spectrometer.

All the solvents were purified by the standard methods. The chloride-bridged palladacyclic dimer [21] and N-heterocyclic carbene [22] were prepared according to the published procedures. The liquid amines were distilled before used, *n*-dodecylamine was used without purification. The aryl chlorides were obtained from commercial sources and used without purification.

4.2. Preparation of adduct 2

The palladacycle dimer **1** (0.1 mmol) was put in a Schlenk tube. Then under the protection of N$_2$, 5 ml THF solution of carbene (0.3 mmol) was added slowly to the dimer via a syringe, stir at room temperature for 2 h. The mixture was filtered, THF was removed in vacuum. The crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:5) to yield the complex (153 mg, 90%). IR (KBr pellet): 2963, 2925, 1569, 1466, 1398, 1325, 1107, 806, 758 cm^{-1}. ^{1}H NMR: δ 7.51 (2H, d, $J = 4.6$ Hz), 7.45–7.36 (2H, m), 7.26 (1H, d, $J = 8.0$ Hz), 7.14–7.12 (3H, m), 7.00 (2H, d, $J = 8.0$ Hz), 6.57 (2H, d, $J = 7.0$ Hz), 4.67–4.63 (1H, m), 4.30–4.27 (2H, m), 3.96 (1H, s), 3.63 (5H, s), 3.41–3.24 (1H, m), 2.93–2.89 (1H, m), 2.80–2.77 (1H, m), 2.24 (3H, s), 1.83 (3H, s), 1.60 (3H, d, $J = 6.5$ Hz), 1.54 (3H, d, $J = 6.5$ Hz), 1.41 (3H, d, $J = 6.5$ Hz), 1.38 (3H, d, $J = 6.5$ Hz), 1.13 (3H, d, $J = 6.8$ Hz), 0.90 (3H, d, $J = 6.8$ Hz), 0.88 (3H, d, $J = 6.9$ Hz), 0.72 (3H, d, $J = 6.5$ Hz). ^{13}C NMR: δ 181.1, 175.4, 148.2, 147.2, 145.2, 144.3, 136.7, 136.5, 133.9, 129.9, 129.4, 128.3, 125.3, 124.6, 124.5, 124.4, 124.2, 123.4, 122.9, 89.9, 77.6, 70.4, 68.9, 66.1, 28.9, 28.7, 28.2, 27.8, 27.0, 25.3, 24.8, 23.7, 23.3, 23.2, 21.7, 21.0, 16.9. Ms: 810.2 [M−Cl]$^+$. HRMS (positive ESI) calc. for [C$_{46}$H$_{54}$ClN$_3$FePd–Cl]$^+$: 810.2702, found: 810.2686.
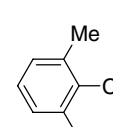
Table 7
Palladacycle **2** catalyzed amination of aryl chlorides with aliphatic amines

Entry[a]	Aryl chloride	Amine	Product	Yield (%)[b]
1	MeO–C₆H₄–Cl	cyclohexyl-NH₂	MeO–C₆H₄–NH–cyclohexyl	91
2	Me–C₆H₄–Cl	cyclohexyl-NH₂	Me–C₆H₄–NH–cyclohexyl	93
3	C₆H₅–Cl	cyclohexyl-NH₂	C₆H₅–NH–cyclohexyl	85
4	2-Me-C₆H₄–Cl	cyclohexyl-NH₂	2-Me-C₆H₄–NH–cyclohexyl	99
5	2-OMe-C₆H₄–Cl	cyclohexyl-NH₂	2-OMe-C₆H₄–NH–cyclohexyl	72
6	2,6-Me₂-C₆H₃–Cl	cyclohexyl-NH₂	2,6-Me₂-C₆H₃–NH–cyclohexyl	99
7	3-F₃C-C₆H₄–Cl	cyclohexyl-NH₂	3-F₃C-C₆H₄–NH–cyclohexyl	90
8	MeO–C₆H₄–Cl	$H_2N(n\text{-}C_{12}H_{25})$	MeO–C₆H₄–NH–n-C₁₂H₂₅	39[c]
9	C₆H₅–Cl	$H_2N(n\text{-}C_{12}H_{25})$	C₆H₅–NH–n-C₁₂H₂₅	59[d]
10	2-Me-C₆H₄–Cl	$H_2N(n\text{-}C_{12}H_{25})$	2-Me-C₆H₄–NH–n-C₁₂H₂₅	99
11	2,6-Me₂-C₆H₃–Cl	$H_2N(n\text{-}C_{12}H_{25})$	2,6-Me₂-C₆H₃–NH–n-C₁₂H₂₅	96

[a] *Reaction conditions*: cat. **2**, 0.01 mmol, aryl chloride 1.0 mmol, aliphatic amine 1.2 mmol, ^{t}BuOK 1.5 mmol, dioxane 2 ml.
[b] Islolated yields based on aryl chloride.
[c] Fifty-five percent of diarylamine (*N*-dodecyl-4,4′-dimethoxydiphenylamine) was also isolated.
[d] Forty percent of diarylamine (*N*-dodecyldiphenylamine) was also isolated.

4.3. General procedure for the coupling reaction

Under the protection of N$_2$, 8.45 mg (1 mol%) of catalyst **2**, 168 mg of KO^{t}Bu, 1 mmol aryl chloride, 1.2 mmol amine and 2 ml dry dioxane were added into oven-dried vials. The reaction was run at indicated temperature with the protection of N$_2$ for 3 h. The reaction mixture was allowed to cool to room temperature and was quenched by filtering through a short silica column (eluent: ethyl acetate) and then concentrated under reduced pressure. After purification by flash chromatography (eluent: ethyl acetate/petroleum ether), the yield was calculated based on the aryl chlorides.

N-(4-Methoxyphenyl)morpholine (Table 2, entry 1) [23]. White solid, m.p.: 72–74 °C (lit. 72–74 °C); ^{1}H NMR: δ 6.89–6.83 (4H, m), 3.85 (4H, t, J = 4.7 Hz), 3.76 (3H, s), 3.05 (4H, t, J = 4.7 Hz).^{13}C NMR: δ 153.9, 145.6, 117.8, 114.4, 67.0, 55.5, 50.8. MS: 193.8 [M+H]$^+$.

N-(4-Methylphenyl)morpholine (Table 2, entry 2) [24]. White solid, m.p.: 47–49 °C; ^{1}H NMR: δ 7.08 (2H, d, J = 8.5 Hz), 6.83 (2H, d, J = 8.5 Hz), 3.85 (4H, t, J = 4.8 Hz), 3.10 (4H, t, J = 4.8 Hz), 2.27 (3H, s). ^{13}C NMR: δ 149.2, 129.7, 129.5, 116.0, 66.9, 49.9, 20.4. MS: 177.9 [M+H]$^+$.

N-Phenylmorpholine (Table 2, entry 3) [23]. White solid, m.p.: 52–54 °C (lit. 51–54 °C); ^{1}H NMR: δ 7.30–7.26 (2H, m), 6.93–6.86 (3H, m), 3.86 (4H, t, J = 4.8 Hz), 3.15 (4H, t, J = 4.8 Hz). ^{13}C NMR: δ 151.1, 129.1, 120.0, 115.6, 66.8, 49.2. MS: 163.9 [M+H]$^+$.

N-(2-Methylphenyl)morpholine (Table 2, entry 4) [13h]. Colorless oil; ^{1}H NMR: δ 7.19–7.15 (2H, m), 7.02–6.97 (2H, m), 3.84 (4H, t, J = 4.5 Hz), 2.89 (4H, t, J = 4.5 Hz), 2.31 (3H, s). ^{13}C NMR: δ 151.2, 132.5, 131.1, 126.6, 123.3, 118.8, 67.4, 52.1, 17.8. MS: 177.9 [M+H]$^+$.

N-(2-Methoxyphenyl)morpholine (Table 2, entry 5) [13h]. Pale yellow oil; ^{1}H NMR: δ 7.03–6.98 (1H, m), 6.93 (2H, d, J = 4.3 Hz), 6.87 (1H, d, J = 7.9 Hz), 3.89 (4H, t, J = 4.6 Hz), 3.86 (3H, s), 3.07 (4H, t, J = 4.5 Hz). ^{13}C NMR: δ 151.6, 140.5, 122.6, 120.5, 117.4, 110.7, 66.6, 54.8, 50.6. MS: 215.8 [M+Na]$^+$, 193.8 [M+H]$^+$.

N-(2,6-Dimethylphenyl)morpholine (Table 2, entry 6) [3b]. White solid, m.p.: 87–89 °C (lit. 86–87 °C); ^{1}H NMR: δ 7.02–6.95 (3H, m), 3.81 (4H, t, J = 4.5 Hz), 3.10 (4H, t, J = 4.5 Hz), 2.35 (6H, s). ^{13}C NMR: δ 147.7, 136.9, 129.0, 125.3, 68.1, 49.9, 19.6. MS: 192.0 [M+H]$^+$.

N-[3-(Trifluoromethyl)phenyl]morpholine (Table 2, entry 7) [25]. Pale yellow oil; ^{1}H NMR: δ 7.37–7.33 (1H, m), 7.10 (2H, d, J = 2.3 Hz), 7.05–7.03 (1H, m), 3.86 (4H, t, J = 4.8 Hz), 3.18 (4H, t, J = 4.8 Hz). ^{13}C NMR: δ 151.4, 131.5 (q, ^{2}J(C,F) = 31.7 Hz), 129.6, 124.3 (q, ^{2}J(C,F) = 270.9 Hz), 118.4, 116.2 (d, ^{3}J(C,F) = 3.7 Hz), 111.8 (d, ^{3}J(C,F) = 3.7 Hz), 66.7, 48.8. MS: 231.8 [M+H]$^+$.

N-Methyl-N-phenyl-4-methoxyaniline (Table 3, entry 1) [5a]. Pale yellow oil; ^{1}H NMR: δ 7.17 (2H, t, J = 7.9 Hz), 7.07 (2H, d, J = 8.9 Hz), 6.87–6.85 (2H, m), 6.77 (3H, d, J = 7.9 Hz), 3.77 (3H, s), 3.22 (3H, s). ^{13}C NMR: δ 156.3, 149.8, 142.3, 129.0, 126.3, 118.4, 115.7, 114.8, 55.5, 40.5. MS: 213.6 [M+H]$^+$.

N-Methyl-N-(4-methylphenyl)aniline (Table 3, entry 2) [5c]. Yellow oil; ^{1}H NMR: δ 7.20 (2H, t, J = 7.9 Hz), 7.08 (2H, d, J = 8.2 Hz), 6.97 (2H, d, J = 8.3 Hz), 6.90 (2H, d, J = 8.0 Hz), 6.84 (1H, t, J = 7.3 Hz), 3.25 (3H, s), 2.29 (3H, s). ^{13}C NMR: δ 149.5, 146.7, 132.1, 130.0, 129.1, 122.7, 119.9, 118.3, 40.4, 20.9. MS: 219.9 [M+Na]$^+$, 197.9 [M+H]$^+$.

N-Methyldiphenylamine (Table 3, entry 3) [4c]. Pale yellow oil; ^{1}H NMR: δ 7.26–7.22 (4H, m), 7.01–6.99 (4H, m), 6.95–6.91 (2H, m), 3.28 (3H, s). ^{13}C NMR: δ 149.1, 129.3, 121.3, 120.5, 40.3. MS: 205.7 [M+Na]$^+$, 183.7 [M+H]$^+$.

N-Methyl-N-(2-methylphenyl)aniline (Table 3, entry 4) [5a]. Pale yellow oil; ^{1}H NMR: δ 7.27–7.11 (6H, m), 6.69 (1H, t, J = 6.8 Hz), 6.52 (2H, d, J = 7.8 Hz), 3.19 (3H, s), 2.12 (3H, s). ^{13}C NMR: δ 149.0, 146.7, 136.7, 131.2, 128.9, 128.2, 127.4, 126.3, 116.7, 112.7, 38.9, 17.8. MS: 236.8 [M+K]$^+$, 197.8 [M+H]$^+$.

N-Methyl-N-phenyl-2-methoxyaniline (Table 3, entry 5) [26]. Pale yellow oil; ^{1}H NMR: δ 7.19–7.12 (4H, m), 6.95–6.94 (2H, m), 6.70 (1H, t, J = 7.3 Hz), 6.64–6.62 (2H, m), 3.72 (3H, s), 3.19 (3H, s). ^{13}C NMR: δ 156.0, 149.4, 136.8, 129.2, 128.8, 127.0, 121.3, 117.2, 113.4, 112.6, 55.6, 39.1. MS: 235.8 [M+Na]$^+$, 213.9 [M+H]$^+$.

N-Methyl-N-[3-(trifluoromethyl)phenyl]aniline (Table 3, entry 6) [5a]. Colorless oil; ^{1}H NMR: δ 7.34–7.31 (2H, m), 7.26 (1H, t, J = 7.9 Hz), 7.12–7.05 (5H, m), 7.03–7.00 (1H, m), 3.31 (3H, s). ^{13}C NMR: δ 149.3, 148.1, 131.5 (q, ^{2}J(C,F) = 31.6 Hz), 129.7, 129.4, 124.3 (q, ^{1}J(C,F) = 270.9 Hz), 123.8, 123.6, 120.4, 115.9 (d, ^{3}J(C,F) = 3.7 Hz), 113.9 (d, ^{3}J(C,F) = 3.7 Hz), 40.3. MS: 252.0 [M+H]$^+$.

N-Phenyl-4-methylaniline (Table 4, entry 1) [27]. White solid, m.p.: 86–87 °C (lit. 86–87 °C); ^{1}H NMR: δ 7.25–7.20 (2H, m), 7.08 (2H, d, J = 8.2 Hz), 7.01–6.98 (4H, m), 6.87 (1H, t, J = 7.3 Hz), 5.68 (1H, s), 2.30 (3H, s). ^{13}C NMR: δ 143.8, 140.2, 130.9, 129.8, 129.3, 120.3, 118.9, 116.8, 20.7. MS: 183.9 [M+H]$^+$.

Diphenylamine (Table 4, entry 2) [23]. White solid, m.p.: 52–53 °C (lit. 52–53 °C); ^{1}H NMR: δ 7.27–7.22 (4H, m), 7.07–7.05 (4H, m), 6.92 (2H, t, J = 7.3 Hz), 5.74 (1H, s). ^{13}C NMR: δ 143.0, 129.3, 121.0, 117.8. MS: 169.9 [M+H]$^+$.

N-Phenyl-2-methylaniline (Table 4, entry 3) [5a]. Yellow oil; ^{1}H NMR: δ 7.25–7.17 (4H, m), 7.14–7.10 (1H, m), 6.95–6.86 (4H, m), 5.35 (1H, s), 2.23 (3H, s). ^{13}C NMR: δ 143.9, 141.2, 130.9, 129.3, 128.2, 126.7, 121.9, 120.4, 118.7, 117.4, 17.9. MS: 206 [M+Na]$^+$, 183.9 [M+H]$^+$.

N-(2-Methoxyphenyl)aniline (Table 4, entry 4) [23]. Pale yellow oil; ^{1}H NMR: δ 7.31–7.24 (3H, m), 7.14–7.12 (2H, m), 6.94–6.91 (1H, m), 6.89–6.83 (3H, m), 6.14 (1H, s), 3.86 (3H, s). ^{13}C NMR: δ 148.2, 142.7, 132.9, 129.2, 121.1, 120.8, 119.8, 118.5, 114.6, 110.5, 55.5. MS: 199.9 [M+H]$^+$.

N-Phenyl-3-(trifluoromethyl)aniline (Table 4, entry 6) [3g]. Yellow oil; ^{1}H NMR: δ 7.32–7.28 (3H, m), 7.24 (1H, s), 7.18–7.15 (1H, m), 7.12–7.07 (3H, m), 7.02–6.99 (1H, m), 5.80 (1H, s). ^{13}C NMR: δ 144.0, 141.7, 131.7 (q, $^2J(C,F) = 31.9$ Hz), 129.8, 129.5, 124.1 (q, $^1J(C,F) = 270.7$ Hz), 122.3, 119.6, 118.9, 116.9 (d, $^3J(C,F) = 3.8$ Hz), 113.2 (d, $^3J(C,F) = 3.8$ Hz). MS: 238.0 [M+H]$^+$.

N-(4-Methylphenyl)-2,5-dimethylaniline (Table 5, entry 1) [28]. Orange solid, m.p.: 46–48 °C; ^{1}H NMR: δ 7.06 (3H, t, $J = 8.5$ Hz), 6.98 (1H, s), 6.89 (2H, d, $J = 8.0$ Hz), 6.69 (1H, d, $J = 7.4$ Hz), 5.25 (1H, s), 2.29 (3H, s), 2.24 (3H, s), 2.18 (3H, s). ^{13}C NMR: δ 141.7, 141.0, 136.4, 130.6, 130.3, 129.7, 123.9, 121.8, 118.6, 117.9, 21.1, 20.6, 17.3. MS: 212.0 [M+H]$^+$.

N-Phenyl-2,5-dimethylaniline (Table 5, entry 2) [5d]. Yellow oil; ^{1}H NMR: δ 7.24–7.20 (2H, m), 7.06 (2H, d, $J = 8.2$ Hz), 6.93–6.91 (2H, m), 6.87 (1H, t, $J = 7.3$ Hz), 6.74 (1H, d, $J = 7.4$ Hz), 5.32 (1H, s), 2.25 (3H, s), 2.18 (3H, s). ^{13}C NMR: δ 144.0, 140.9, 136.4, 130.7, 129.3, 125.3, 122.8, 120.3, 119.5, 117.4, 21.1, 17.4. MS: 198.0 [M+H]$^+$.

N-(2-Methylphenyl)-2,5-dimethylaniline (Table 5, entry 3). White solid, m.p.: 72–73 °C; ^{1}H NMR: δ 7.17 (1H, d, $J = 7.4$ Hz), 7.10–7.05 (2H, m), 6.97 (1H, d, $J = 7.8$ Hz), 6.88 (1H, t, $J = 7.4$ Hz), 6.81 (1H, s), 6.71 (1H, d, $J = 7.6$ Hz), 5.07 (1H, s), 2.24 (6H, s), 2.19 (3H, s). ^{13}C NMR: δ 142.1, 141.7, 136.5, 130.8, 130.7, 127.4, 126.8, 124.6, 122.3, 121.2, 119.1, 118.2, 21.2, 17.9, 17.4. MS: 212.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{15}H_{17}N+H]^+$: 212.1440, found: 212.1439.

N-(2-Methoxyphenyl)-2,5-dimethylaniline (Table 5, entry 4) [3b]. White solid, m.p.: 85–86 °C; ^{1}H NMR: δ 7.19 (1H, s), 7.14 (1H, d, $J = 7.6$ Hz), 7.09–7.06 (1H, m), 6.95–6.84 (3H, m), 6.82 (1H, d, $J = 7.5$ Hz), 5.88 (1H, s), 3.95 (3H, s), 2.33 (3H, s), 2.28 (3H, s). ^{13}C NMR: δ 147.7, 140.0, 135.8, 133.4, 130.1, 125.7, 122.4, 120.3, 119.7, 118.6, 113.9, 109.8, 55.1, 20.6, 16.9. MS: 249.9 [M+Na]$^+$, 227.9 [M+H]$^+$.

N-(2,6-Dimethylphenyl)-2,5-dimethylaniline (Table 5, entry 5). Orange solid, m.p.: 66–68 °C; ^{1}H NMR: δ 7.12–7.04 (3H, m), 7.00 (1H, d, $J = 7.5$ Hz), 6.52 (1H, d, $J = 7.3$ Hz), 5.96 (1H, s), 4.83 (1H, s), 2.27 (3H, s), 2.17 (6H, s), 2.12 (3H, s). ^{13}C NMR: δ 143.3, 138.3, 136.0, 134.9, 129.5, 128.0, 124.9, 119.0, 118.3, 111.9, 20.8, 17.7, 16.7. MS: 226.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{16}H_{19}N+H]^+$: 226.1596, found: 226.1596.

N-[3-(Trifluoromethyl)phenyl]-2,5-dimethylaniline (Table 5, entry 6). White solid, m.p.: 36–37 °C; ^{1}H NMR: δ 7.30–7.26 (1H, m), 7.11 (1H, d, $J = 7.6$ Hz), 7.06–7.03 (3H, m), 6.99 (1H, d, $J = 7.8$ Hz), 6.85–6.83 (1H, m), 5.45 (1H, s), 2.28 (3H, s), 2.18 (3H, s). ^{13}C NMR: δ 144.7, 139.0, 136.2, 131.2 (q, $^2J(C,F) = 31.7$ Hz), 130.5, 129.2, 126.7, 124.0, 123.7 (q, $^1J(C,F) = 270.8$ Hz), 121.2, 118.4, 115.5 (d, $^3J(C,F) = 3.7$ Hz), 112.0 (d, $^3J(C,F) = 3.7$ Hz), 20.5, 16.9. MS: 266.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{15}H_{14}F_3N+H]^+$: 266.1157, found: 266.1151.

2,6-Dimethyl-N-(4-methylphenyl)aniline (Table 6, entry 1) [29]. Yellow oil; ^{1}H NMR: δ 7.11–7.09 (2H, m), 7.07–7.03 (1H, m), 6.96 (2H, d, $J = 8.3$ Hz), 6.44–6.41 (2H, m), 5.12 (1H, s), 2.23 (3H, s), 2.19 (6H, s). ^{13}C NMR: δ 143.8, 138.6, 135.4, 129.7, 128.5, 127.4, 125.3, 113.7, 20.4, 18.3. MS: 211.9 [M+H]$^+$.

N-(2,6-Dimethylphenyl)aniline (Table 4, entry 5; Table 6, entry 2) [23]. White solid, m.p.: 52–53 °C (lit. 53–56 °C) [30]; ^{1}H NMR: δ 7.16–7.06 (5H, m), 6.73 (1H, t, $J = 7.3$ Hz), 6.49 (2H, d, $J = 7.7$ Hz), 5.14 (1H, s), 2.20 (6H, s). ^{13}C NMR: δ 146.3, 138.2, 135.9, 129.3, 128.6, 125.8, 118.2, 113.5, 18.4. MS: 198.0 [M+H]$^+$.

2,6-Dimethyl-N-(2-methylphenyl)aniline (Table 6, entry 3) [29]. White solid, m.p.: 61–63 °C (lit. 64–66 °C) [30]; ^{1}H NMR: δ 7.12–7.04 (4H, m), 6.95 (1H, t, $J = 7.3$ Hz), 6.69 (1H, t, $J = 7.3$ Hz), 6.14 (1H, d, $J = 8.0$ Hz), 4.91 (1H, s), 2.31 (3H, s), 2.17 (6H, s). ^{13}C NMR: δ 144.1, 138.7, 135.5, 130.2, 128.5, 126.9, 125.5, 122.4, 118.0, 111.7, 18.2, 17.6. MS: 212.1 [M+H]$^+$.

N-(2-Methoxyphenyl)-2,6-dimethylaniline (Table 6, entry 4) [2c]. White solid, m.p.: 81–83 °C; ^{1}H NMR: δ 7.12–7.04 (3H, m), 6.86–6.83 (1H, m), 6.74–6.66 (2H, m), 6.13–6.11 (1H, m), 5.52 (1H, s), 3.93 (3H, s), 2.20 (6H, s). ^{13}C NMR: δ 146.2, 137.8, 135.6, 135.4, 127.9, 125.1, 120.5, 116.7, 110.5, 109.3, 55.1, 17.7. MS: 228.1 [M+H]$^+$.

Bis(2,6-dimethylphenyl)amine (Table 6, entry 5) [2c]. White solid, m.p.: 97–99 °C; ^{1}H NMR: δ 6.97 (4H, d, $J = 7.4$ Hz), 6.83 (2H, t, $J = 7.4$ Hz), 4.75 (1H, s), 2.00 (12H, s). ^{13}C NMR: δ 141.6, 129.4, 128.6, 121.6, 19.0. MS: 226.0 [M+H]$^+$.

2,6-Dimethyl-N-[3-(trifluoromethyl)phenyl]aniline (Table 6, entry 6). Yellow oil; ^{1}H NMR: δ 7.21 (1H, t, $J = 7.9$ Hz), 7.15–7.09 (3H, m), 6.96 (1H, d, $J = 7.6$ Hz), 6.71 (1H, s), 6.58 (1H, d, $J = 8.2$ Hz), 5.30 (1H, s), 2.19 (6H, s). ^{13}C NMR: δ 146.6, 137.1, 136.2, 131.7 (q, $^2J(C,F) = 31.6$ Hz), 129.7, 128.8, 126.5, 124.3 (q, $^1J(C,F) = 270.8$ Hz), 116.1, 114.5 (d, $^3J(C,F) = 3.7$ Hz), 109.2 (d, $^3J(C,F) = 3.7$ Hz), 18.3. MS: 266.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{15}H_{14}F_3N+H]^+$: 266.1157, found: 266.1155.

N-Cyclohexyl-4-methoxyaniline (Table 7, entry 1) [31]. White solid, m.p.: 42–43 °C; ^{1}H NMR: δ 6.78–6.74 (2H, m), 6.58–6.55 (2H, m), 3.73 (3H, s), 3.18–3.12 (1H, m), 3.08 (1H, s), 2.05–2.01 (2H, m), 1.77–1.72 (2H, m), 1.65–1.61 (1H, m), 1.39–1.29 (2H, m), 1.25–1.18 (1H, m), 1.15–1.05 (2H, m). ^{13}C NMR: δ 151.8, 141.5, 114.9, 114.8, 55.7, 52.7, 33.6, 25.9, 25.0. MS: 205.9 [M+H]$^+$.

N-Cyclohexyl-4-methylaniline (Table 7, entry 2) [32]. White solid, m.p.: 40–41 °C (lit. 39 °C); ^{1}H NMR: δ 6.96 (2H, d, $J = 8.3$ Hz), 6.52 (2H, d, $J = 8.3$ Hz), 3.34 (1H, s), 3.23–3.18 (1H, m), 2.22 (3H, s), 2.06–2.02 (2H, m), 1.76–1.71 (2H, m), 1.66–1.61 (1H, m), 1.40–1.29 (2H, m), 1.25–1.17 (1H, m), 1.16–1.06 (2H, m). ^{13}C NMR: δ 145.0, 129.7, 126.1, 113.5, 52.0, 33.5, 25.9, 25.0, 20.3. MS: 189.9 [M+H]$^+$.

N-Cyclohexylaniline (Table 7, entry 3) [23]. Pale yellow oil; ^{1}H NMR: δ 7.19–7.13 (2H, m), 6.67–6.66 (1H, m), 6.64–6.58 (2H, m), 3.46 (1H, s), 3.27–3.21 (1H, m),

2.08–2.04 (2H, m), 1.79–1.64 (3H, m), 1.39–1.32 (2H, m), 1.23–1.12 (3H, m). ^{13}C NMR: δ 147.3, 129.2, 116.8, 113.1, 51.6, 33.4, 25.9, 25.0. MS: 175.8 [M+H]$^+$.

N-Cyclohexyl-2-methylaniline (Table 7, entry 4) [8c]. Colorless oil; ^{1}H NMR: δ 7.10–7.01 (2H, m), 6.62–6.58 (2H, m), 3.35–3.26 (2H, m), 2.10–2.05 (5H, m), 1.77–1.73 (2H, m), 1.66–1.62 (1H, m), 1.39–1.33 (2H, m), 1.24–1.16 (3H, m). ^{13}C NMR: δ 145.2, 130.2, 127.0, 121.5, 116.2, 110.1, 51.4, 33.6, 26.0, 25.0, 17.5. MS: 189.9 [M+H]$^+$.

N-Cyclohexyl-2-methoxyaniline (Table 7, entry 5) [6c]. Pale yellow oil; ^{1}H NMR: δ 6.84–6.81 (1H, m), 6.76–6.73 (1H, m), 6.63–6.59 (2H, m), 4.12 (1H, s), 3.82 (3H, s), 3.27–3.21 (1H, m), 2.08–2.04 (2H, m), 1.78–1.62 (3H, m), 1.39–1.17 (5H, m). ^{13}C NMR: δ 146.6, 137.2, 121.2, 115.7, 110.1, 109.5, 55.3, 51.3, 33.4, 26.0, 25.1. MS: 227.9 [M+Na]$^+$, 205.9 [M+H]$^+$.

N-Cyclohexyl-2,6-dimethylaniline (Table 7, entry 6) [33]. Colorless oil; ^{1}H NMR: δ 6.97 (2H, d, J = 7.4 Hz), 6.77 (1H, t, J = 7.4 Hz), 2.97–2.90 (2H, m), 2.25 (6H, s), 1.96–1.93 (2H, m), 1.75–1.71 (2H, m), 1.63–1.60 (1H, m), 1.26–1.08 (5H, m). ^{13}C NMR: δ 145.0, 128.9, 128.6, 121.0, 56.1, 34.9, 25.9, 25.5, 19.0. MS: 203.9 [M+H]$^+$.

N-Cyclohexyl-3-trifluoromethylaniline (Table 7, entry 7). Colorless oil; ^{1}H NMR: δ 7.21 (1H, t, J = 7.9 Hz), 6.87 (1H, d, J = 7.5 Hz), 6.75 (1H, s), 6.70–6.67 (1H, m), 3.73 (1H, s), 3.28–3.22 (1H, m), 2.05–2.01 (2H, m), 1.78–1.73 (2H, m), 1.67–1.62 (1H, m), 1.42–1.31 (2H, m), 1.27–1.09 (3H, m). ^{13}C NMR: δ 147.5, 131.6 (q, ^2J(C,F) = 31.4 Hz), 129.6, 124.5 (q, ^1J(C,F) = 270.7 Hz), 115.9, 113.1 (d, ^3J(C,F) = 3.7 Hz), 109.1 (d, ^3J(C,F) = 3.7 Hz), 51.5, 33.2, 25.8, 24.9. MS: 243.9 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{13}H_{16}F_3N$+H]$^+$: 244.1314, found: 244.1320.

N-Dodecyl-4-methoxyaniline (Table 7, entry 8) [34]. White solid, m.p.: 34–35°C; ^{1}H NMR: δ 6.79–6.75 (2H, m), 6.60–6.56 (2H, m), 3.74 (3H, s), 3.40 (1H, m), 3.05 (2H, t, J = 7.1 Hz), 1.63–1.56 (2H, m), 1.39–1.23 (18H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR: δ 150.4, 141.1, 113.3, 112.5, 54.2, 43.5, 30.3, 28.1, 28.0, 27.9, 27.8, 25.6, 21.1, 12.5. MS: 292.2 [M+H]$^+$.

N-Dodecyl-4,4′-dimethoxydiphenylamine (Table 7, entry 8). White solid, mp: 41–43 °C; ^{1}H NMR: δ 6.86 (4H, d, J = 9.0 Hz), 6.82–6.79 (4H, m), 3.77 (6H, s), 3.54 (2H, t, J = 7.6 Hz), 1.61–1.57 (2H, m), 1.28–1.24 (18H, m), 0.87 (3H, t, J = 6.8 Hz). ^{13}C NMR: δ 154.1, 142.5, 122.0, 114.5, 55.6, 52.9, 31.9, 29.68, 29.66, 29.63, 29.5, 29.3, 27.5, 27.1, 22.7, 14.1. MS: 398.4 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{26}H_{39}NO_2$+H]$^+$: 398.3060, found: 398.3061.

N-Dodecylaniline (Table 7, entry 9) [23]. White solid, m.p.: 25–26 °C; ^{1}H NMR: δ 7.18–7.14 (2H, m), 6.69–6.66 (1H, m), 6.61–6.58 (2H, m), 3.62 (1H, m), 3.09 (2H, t, J = 7.1 Hz), 1.62–1.56 (2H, m), 1.40–1.26 (18H, m), 0.88 (3H, t, J = 6.7 Hz). ^{13}C NMR: δ 146.9, 127.6, 115.5, 111.1, 42.4, 30.3, 28.1, 28.0, 27.9, 27.8, 25.6, 21.1, 12.5. MS: 262.1 [M+H]$^+$.

N-Dodecyldiphenylamine (Table 7, entry 9) [35]. Colorless oil; ^{1}H NMR: δ 7.24 (4H, t, J = 7.9 Hz), 6.98 (4H, d, J = 7.9 Hz), 6.93 (2H, t, J = 7.3 Hz), 3.66 (2H, t, J = 7.8 Hz), 1.66–1.61 (2H, m), 1.28–1.24 (18H, m), 0.87 (3H, t, J = 6.7 Hz). ^{13}C NMR: δ 148.0, 129.2, 121.0, 120.8, 52.4, 31.9, 29.7, 29.6, 29.5, 29.4, 27.4, 27.1, 22.7, 14.2. MS: 338.3 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{24}H_{35}N$+H]$^+$: 338.2849, found: 338.2840.

N-Dodecyl-2-methylaniline (Table 7, entry 10). Pale yellow oil; ^{1}H NMR: δ 7.12 (1H, t, J = 7.6 Hz), 7.03 (1H, d, J = 7.2 Hz), 6.65–6.58 (2H, m), 3.43 (1H, s), 3.14–3.10 (2H, m), 2.12 (3H, s), 1.68–1.61 (2H, m), 1.40–1.26 (18H, m), 0.89–0.86 (3H, m). ^{13}C NMR: δ 146.4, 130.0, 127.1, 121.6, 116.6, 109.6, 44.0, 32.0, 29.7, 29.6, 29.5, 29.4, 27.3, 22.7, 17.5, 14.2. MS: 276.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{19}H_{33}N$+H]$^+$: 276.2692, found: 276.2686.

N-Dodecyl-2,6-dimethylaniline (Table 7, entry 11). Colorless oil; ^{1}H NMR: δ 6.97 (2H, d, J = 7.4 Hz), 6.80 (1H, t, J = 7.4 Hz), 2.96 (3H, t, J = 7.2 Hz), 2.27 (6H, s), 1.58–1.53 (2H, m), 1.38–1.25 (18H, m), 0.88 (3H, t, J = 6.8 Hz). ^{13}C NMR: δ 146.4, 129.1, 128.8, 121.5, 48.7, 32.0, 31.2, 29.7, 29.6, 29.4, 27.2, 22.7, 18.6, 14.2. MS: 290.1 [M+H]$^+$. HRMS (positive ESI) calc. for [$C_{20}H_{35}N$+H]$^+$: 290.2849, found: 290.2849.

4.4. Crystal structure determination

Intensity data of **2** was measured on a Rigaku-Raxis-IV X-ray diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization factors. The structure was solved by direct methods [36] and expanded using Fourier techniques and refined by full-matrix least-squares methods. All calculations were performed using the TEXSAN [37] crystallographic software package of Molecular Structure corporation.

5. Supplementary material

CCDC 634736 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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