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Nickel-Catalyzed Coupling of Fluoroarenes and Amines

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Abstract: The combination of bis(cyclooctadiene)-nickel [$Ni(COD)_2$] and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene hydrochloride (IPr·HCl) effectively catalyzes coupling of fluoroarenes with amines in the presence of sodium *tert*-butoxide (*t*-BuONa). Activated, unactivated and deactivated fluoroarenes as well as fluoropyridines can react with cyclic or acyclic aliphatic amines. The reactions tolerate various functional groups in the fluorides including PhC(O), $C(O)NEt_2$, CF_3, OMe and vinyl groups.

Keywords: catalysis; C−F bond activation; coupling; fluoroarenes; nickel

Introduction

Transition metal-catalyzed reactions of aryl halides with amines such as the Ullmann reaction and the Buchwald–Hartwig reaction are extremely important in organic synthesis.[1–3] Normally the aryl halides used in the catalytic reactions are iodides, bromides and chlorides. It is rare to employ aryl fluorides because of their low reactivity. In contrast, aryl fluorides exhibit higher reactivity than aryl iodides, bromides and chlorides in aromatic nucleophilic substitution (S_NAr) reactions.[3] Hence some catalyst-free S_NAr substitutions of aryl fluorides by nitrogen, oxygen or sulfur nucleophiles have been revealed, but commonly apply to electron-poor aryl fluorides.[3,4] Recently a catalyst-free S_NAr substitution of unactivated fluorobenzenes using azole and indole derivatives was carried out under harsh conditions.[5] An Ru-catalyzed S_NAr reaction of non-activated fluoroarenes with amines was also reported. This reaction was proven to proceed *via* Ru η^6-arene complexes which make fluoroarenes electron-poor. This method led to only low to moderate product yields for the deactivated fluoroarenes.[6] On the other hand, it has been reported that the C−F bonds of fluoroarenes can be transformed to C−C or C−H bonds through transition metal-catalyzed C−F bond activation.[7,8] The purpose of this study is to develop a methodology of the transition metal-catalyzed activation of C−F bonds and carry out couplings of fluoroarenes with amines. Herein we report the results.

Results and Discussion

We chose the coupling of 4-fluorobiphenyl and morpholine as the model reaction to screen the catalysts, bases and solvents (Table 1). It has been reported that nickel-phosphine or nickel-carbene systems could catalyze aryl C−F bond activation and construct new C−C bonds.[3a] We also used nickel catalyst systems for a preliminary test of the amination reaction. A combination of $Ni(COD)_2$ and PCy_3 or dppp led to poor results using *t*-BuONa as a base and toluene as the solvent. Then we tested N-heterocyclic carbene ligands. The combination of $Ni(COD)_2$ and I*t*Bu·HCl (I*t*Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) showed poor catalytic activity under the same conditions as above (Table 1, entry 3). However, the combination of $Ni(COD)_2$ (10 mol%) and IMes·HCl (20 mol%) (IMes = 1,3-dimesitylimidazol-2-ylidene) exhibited a better result, a 69% yield of aminated product being obtained. Further examination showed that $Ni(COD)_2$ (10 mol%) and IPr·HCl (20 mol%) [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] system resulted in higher product yield (Table 1, entry 5). Decreasing the amount of IPr·HCl to 10 mol% led to a little lower yield (87%) (Table 1, entry 6). The combination of $Ni(COD)_2$ (10 mol%), IPr·HCl (10 mol%) and pyridine (10 mol%) also gave a relatively low product yield (78%). It seems that the reactivity is not a result of a monoligated carbene-nickel complex. Fort et al. reported that in a nickel-catalyzed defluorination of fluoroarenes a 1:1 ratio of Ni(0) and IMes system is the most effective catalyst.[8] This may be

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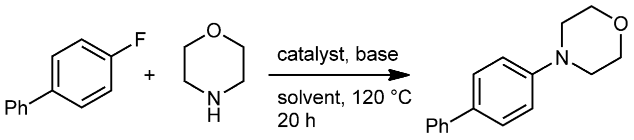
Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	Base	Solvent	Yield [%][b]
1	$Ni(COD)_2$ (10%); PCy_3 (20%)	*t*-BuONa (4.2 equiv.)	toluene	10
2	$Ni(COD)_2$ (10%); dppp (10%)	*t*-BuONa (4.2 equiv.)	toluene	nr
3	$Ni(COD)_2$ (10%); I*t*Bu·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	5
4	$Ni(COD)_2$ (10%); IMes·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	69
5	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	92
6	$Ni(COD)_2$ (10%); IPr·HCl (10%)	*t*-BuONa (4.2 equiv.)	toluene	87
7	$Ni(acac)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	13
8	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuOK (4.2 equiv.)	toluene	40
9	$Ni(COD)_2$ (10%); IPr·HCl (20%)	K_3PO_4 (4.2 equiv.)	toluene	trace
10c)	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	91
11c)	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (3.2 equiv.)	toluene	86
12	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (3.2 equiv.)	toluene	80
13	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (2.2 equiv.)	toluene	46
14[c]	$Ni(COD)_2$ (5%); IPr·HCl (10%)	*t*-BuONa (4.2 equiv.)	toluene	84
15[c]	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	dioxane	90
16[c]	$Ni(COD)_2$ (10%); IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	THF	48
17[c]	IPr·HCl (20%)	*t*-BuONa (4.2 equiv.)	toluene	15

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation, 0.5 mmol of 4-fluorobiphenyl and 2 mmol of morphine were employed.
[b] Yield of isolated products.
[c] Reaction was carried out at 100 °C.

because the two types of reactions proceed *via* different mechanisms. $Ni(acac)_2$ was found to be less effective than $Ni(COD)_2$ in the catalytic process (Table 1, entry 7). The reasons may include: (i) $Ni(acac)_2$ needs to be reduced to a Ni(0) species in the initial stage of the catalytic reaction and an effective reducing agent is absent in the reaction system tested; and (ii) reduction of $Ni(acac)_2$ often generates heterogeneous nanoparticles which may show different catalytic properties from the homogeneous $Ni(COD)_2$ system.[9] Both *t*-BuOK and K_3PO_4 were also proven to be less effective bases in the $Ni(COD)_2$-IPr-catalyzed reaction in comparison with *t*-BuONa. When the reaction temperature was decreased to 100 °C, a similar result to that at 120 °C can be achieved using the same catalyst and base. However, when the amount of *t*-BuONa was decreased to 3.2 or 2.2 equivalents, the reaction afforded lower product yields at either 100 °C or 120 °C (Table 1, entries 11–13). It seems that *t*-BuONa acts not only as a base in the reactions, but also plays a stabilization role for the Ni species in the catalytic cycle.[9c–e,10] Lower catalyst loadings also led to lower yields (Table 1, entry 14). It was also shown that dioxane was as effective as toluene as solvent, but THF was a less effective solvent than toluene (Table 1, entries 15 and 16). In addition, we found that in the absence of $Ni(COD)_2$ the reaction of 4-fluorobiphenyl with morpholine using IPr·HCl (20 mol%) and *t*-BuONa (4.2 equiv.) as additives in toluene at 100 °C gave only a 15% yield of coupling product (Table 1, entry 17). This experimental fact shows that the presence of $Ni(COD)_2$ is essential for the efficient coupling.

Next we examined the scope of fluorides using a combination of $Ni(COD)_2$ (10 mol%) and IPr·HCl (20 mol%) as catalyst, *t*-BuONa (4.2 equiv.) as base and toluene as solvent at 100 °C. Several aryl fluorides were tested using morpholine as the amination reagent. Unactivated and deactivated fluorobenzene derivatives gave excellent reaction results under the optimized conditions (Table 2, entries 1–4). 1-(4-Fluorostyryl)benzene and 1-fluoronaphthalene also showed good reactivity in the amination reaction, both affording excellent yields of cross-coupling products (Table 2, entries 5 and 6). 4-Fluorobenzophenone as an activated substrate led to relatively low product yields for some unclear reason (Table 2, entries 7 and 8). Other activated aryl fluorides such as *N*,*N*-diethyl-4-fluorobenzamide, 1-fluoro-4-(trifluoromethyl)benzene, 2-fluoropyridine and 2-fluoro-4-methylpyridine showed excellent yields in the catalytic reactions (Table 2, entries 9–12). However, reaction of 3-fluoro-

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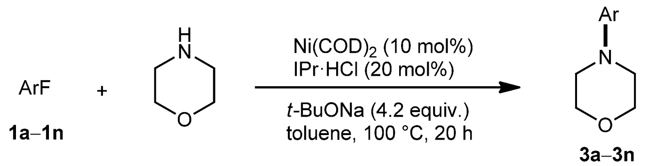
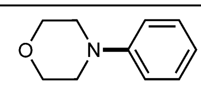
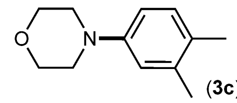
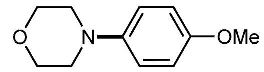
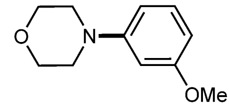
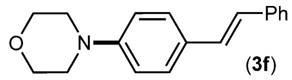
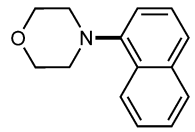
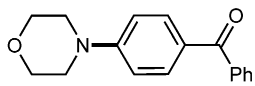
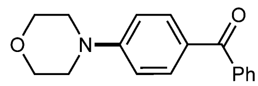
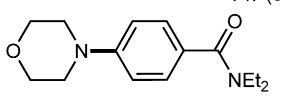
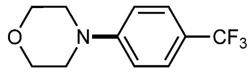
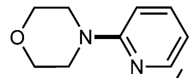
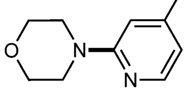
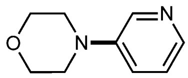
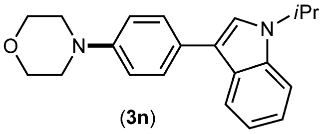
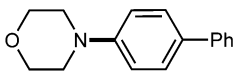
Table 2. Nickel-catalyzed coupling of aryl or heteroaryl fluorides with morphine.[a]



Entry	Product	Yield [%][b]
1	 (**3b**)	93
2	 (**3c**)	87
3	 (**3d**)	85
4	 (**3e**)	87
5	 (**3f**)	86
6	 (**3g**)	98
7	 (**3h**)	72
8[c]	 (**3h**)	75
9	 (**3i**)	86
10	 (**3j**)	94
11	 (**3k**)	82
12	 (**3l**)	84
13	 (**3m**)	66
14[d]	 (**3n**)	89
15[e]	 (**3a**)	88

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation, 0.5 mmol of aryl fluorides, 2 mmol of morphine and 4 mL of toluene were employed.
[b] Yields of isolated products.
[c] 3.2 equivalents of *t*-BuONa were employed.
[d] Reaction was carried out at 120 °C.
[e] 5 mmol of 4-fluorobiphenyl and 20 mmol of morphine were employed.

pyridine under the same conditions led to an only moderate yield (Table 2, entry 13). This is consistent with the reactivity of nucleophilic substitution of 2- and 3-fluoropyridines with oxygen, sulfur and carbon nucleophiles.[11] An indolyl group-substituted fluorobenzene was also coupled with morpholine in excellent yield at 120 °C (Table 2, entry 14). In addition, the coupling reaction can be carried out on a larger scale. Reaction of 5 mmol of 4-fluorobiphenyl and morpholine under the same conditions resulted in the corresponding cross-coupling product in 88% yield (Table 2, entry 15).

The scope of amines in the reaction with aryl fluorides was examined using the same conditions as above (Table 3). Reaction of 4-methylpiperidine with aryl fluorides, including deactivated *p*-$MeOC_6H_4F$, afforded the cross-coupling products in excellent yields (Table 3, entries 1–4). 2-Methylpiperidine gave a lower yield in comparison with 4-methylpiperidine using the same fluoride substrate (Table 3, entry 5). This is probably because of steric hindrance in 2-methylpiperidine. Other cyclic amines including pyrrolidine, 1-methylpiperazine, 1-(pyridin-2-yl)piperazine, and *trans*-decahydroisoquinoline also reacted smoothly with activated and unactivated aryl fluorides. However, the reaction of these amines with deactivated *p*-$MeOC_6H_4F$ resulted in moderate yields (Table 3, entries 6–14). The catalytic system is also effective for the coupling of aryl fluorides with acyclic amines including primary and secondary amines. However, acyclic amines showed relatively low reactivity in the amination reaction (Table 3, entries 15–28). Reaction of acyclic amines with activated aryl fluorides such as *p*-$CF_3C_6H_4F$ and 2-fluoropyridine gave good to excellent yields in most cases, whereas unactivated aryl fluorides afforded only low to moderate yields. The relatively low reactivity of acyclic secondary amines may result from their steric hinderance. The low reactivity of primary aliphatic amines may be due to the formation of catalytically inactive nickel species through chelating of the starting amine towards the nickel catalyst.[9i,12] *N*-Methylaniline displayed lower reactivity than alkyl- or dialkylamines. Reaction of the former with 2-fluoropyridine generated only a 35% yield of *N*-methyl-*N*-phenylpyridin-2-amine.

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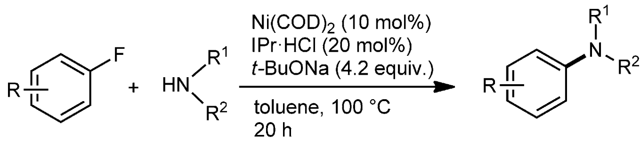
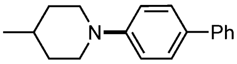
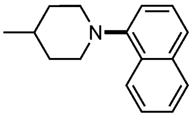
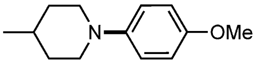
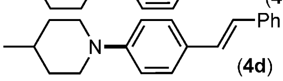
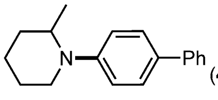
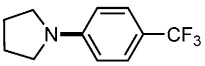
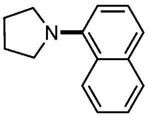
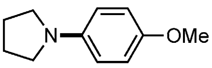
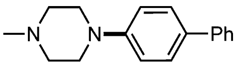
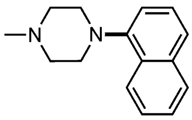
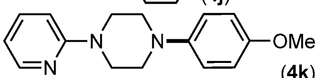
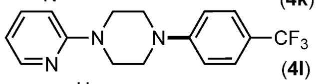
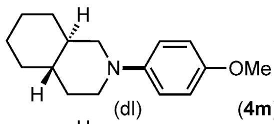
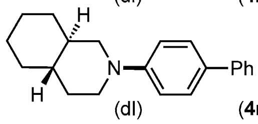
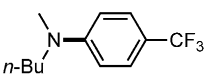
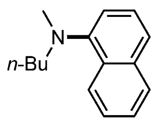
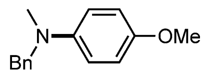
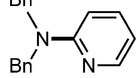
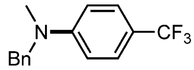
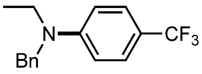
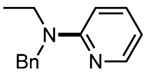
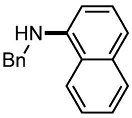
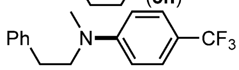
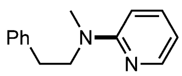
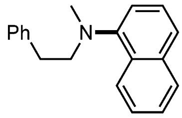
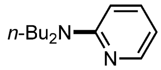
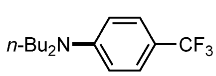
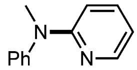
Table 3. Nickel-catalyzed coupling of aryl or heteroaryl fluorides with amines.[a]



Entry	Product	Yield [%][b]
1	 (**4a**)	99
2	 (**4b**)	96
3	 (**4c**)	98
4	 (**4d**)	99
5	 (**4e**)	89
6	 (**4f**)	95
7	 (**4g**)	93
8	 (**4h**)	66
9	 (**4i**)	84
10	 (**4j**)	90
11	 (**4k**)	60
12	 (**4l**)	86
13	 (**4m**)	65
14	 (**4n**)	88
15	 (**5a**)	74
16	 (**5b**)	46
17	 (**5c**)	18
18	 (**5d**)	99
19	 (**5e**)	93
20	 (**5f**)	60
21	 (**5g**)	70
22	 (**5h**)	60
23	 (**5i**)	84
24	 (**5j**)	98
25	 (**5k**)	38
26	 (**5l**)	62
27	 (**5m**)	57
28	 (**5n**)	35

[a] Unless otherwise specified, the reactions were carried out according to the conditions indicated by the above equation, 0.5 mmol of aryl fluorides, 2 mmol of amines and 4 mL of toluene were employed.
[b] Yields of isolated products.

Mechanistically, we observed that either isolated or *in situ* formed IPr_2Ni can catalyze cross-coupling of 1-fluoronaphthalene and 1-methylpiperazine in the presence of *t*-BuONa. This made us to consider an IPr_2NiF intermediate based on the work of Matsubara and co-workers. These authors reported that the reaction of IPr_2Ni with aryl chlorides forms a three-coordinate nickel(I) chloride, IPr_2NiCl, which acts as a catalyst in a cross-coupling reaction of aryl halides with phenylmagnesium chloride.[13] However, further experiments ruled out this possibility in our reaction. Firstly, no biaryl was detected in the reaction of 1-fluoronaphthalene with either isolated or *in situ* formed IPr_2Ni. Biaryl is a concomitant product in the reaction

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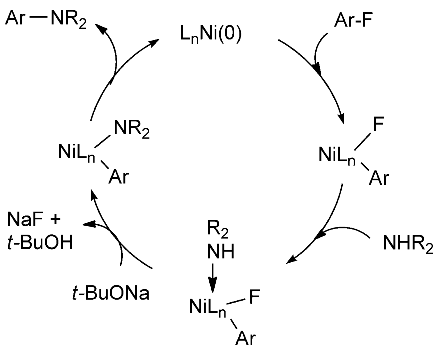

Scheme 1. Proposed mechanism for the coupling of fluoroarenes and amines catalyzed by $Ni(COD)_2$-IPr·HCl-*t*-BuONa system.

of IPr_2Ni with aryl chlorides. Secondly, *in situ* reaction products of 1-fluoronaphthalene (0.25 mmol), $Ni(COD)_2$ (0.25 mmol), IPr·HCl (0.25 mmol) and *t*-BuONa (0.25 mmol) can couple with 1-methylpiperazine (1 mmol) in the presence of *t*-BuONa (1 mmol) to afford 1-methyl-4-(naphthalen-5-yl)piperazine in 63% yield. It seems apparent that an aryl nickel species was formed in this step and then transformed into an arylamido nickel species which underwent reductive elimination to generate the cross-coupling product (Scheme 1). This proposed mechanism is consistent with that of Ni(0)/SIPr complex-catalyzed coupling of aryl chlorides and amines reported by Fort et al.[9i] Studies on the oxidative addition of polyfluorinated pyridines with $Ni(COD)_2$ reported in literature also support Ni(0)/Ni(II) process.[14]

Conclusions

An effective catalyst system consisted of $Ni(COD)_2$ and IPr·HCl has been revealed to promote the coupling of fluoroarenes with amines in the presence of *t*-BuONa. The catalyst is highly efficient for the reaction of cyclic amines with activated, unactivated and deactivated fluoroarenes. Acyclic amines are also effective nucleophiles for the amination of activated aryl fluorides. The reactions can tolerate functional groups in the fluorides including PhC(O), $C(O)NEt_2$, CF_3, OMe and vinyl group as well as nitrogen-containing heterocycles.

Experimental Section

General

The reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. Solvents were distilled under nitrogen over sodium (toluene and 1,4-dioxane) or sodium/benzophenone (THF) and degassed prior to use. All other solvents and reagents were used as received. NMR spectra were determined on a Bruker av300 or a Bruker Avance III 400 NMR spectrometer at room temperature using $CDCl_3$ as solvent. The chemical shifts of the ^{1}H NMR spectra were referenced to TMS and the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonances. HR-MS data were recorded on an Agilent6890/Micromass LCT-MS spectrometer (ESI).

General Procedure for the Cross-Coupling Reactions

A Schlenk tube was charged with $Ni(COD)_2$ (13.8 mg, 0.05 mmol), IPr·HCl (42.6 mg, 0.1 mmol), *t*-BuONa (201.8 mg, 2.1 mmol), aryl fluoride (0.5 mmol) and toluene (3 mL). To the solution was added the amine (2 mmol) at room temperature with stirring. After stirring at 100 °C for 20 h, water (15 mL) was added. The resulting mixture was extracted with Et_2O (3×15 mL). The combined organic phases were dried over Na_2SO_4, concentrated by rotary evaporation and purified by column chromatography on silica gel.

4-(4-Phenylphenyl)morpholine (3a):[15] ^{1}H NMR: $\delta=3.17$ (t, $J=4.8$ Hz, 4H, CH_2), 3.85 (t, $J=4.8$ Hz, 4H, CH_2), 6.95 (d, $J=8.7$ Hz„ 2H, C_6H_4), 7.27 (t, $J=7.5$ Hz, 1H, C_6H_5), 7.39 (t, $J=7.5$ Hz, 2H, C_6H_5), 7.50–7.56 (m, 4H, $C_6H_4+C_6H_5$); ^{13}C NMR: $\delta=49.27$, 66.98, 115.87, 126.62, 127.88, 128.81, 132.76, 140.91, 150.66.

4-Phenylmorpholine (3b):[16] ^{1}H NMR: $\delta=3.13$ (t, $J=4.8$ Hz, 4H, CH_2), 3.83 (t, $J=4.8$ Hz, 4H, CH_2), 6.84–6.91 (m, 3H, C_6H_5), 7.24–7.29 (m, 2H,C_6H_4); ^{13}C NMR: $\delta=$ 49.48, 67.04, 115.82, 120.15, 129.28, 151.41.

4-(3,4-Dimethxyphenyl)morpholine (3c):[17] ^{1}H NMR: $\delta=$ 2.18 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.09 (t, $J=4.5$ Hz, 4H, CH_2), 3.84 (t, $J=4.5$ Hz, 4H, CH_2), 6.64–6.67 (m, 1H, C_6H_3), 6.72 (s, 1H, C_6H_3), 7.02 (d, $J=8.1$ Hz, 1H, C_6H_3); ^{13}C NMR: $\delta=18.88$, 20.31, 50.13, 67.15, 113.59, 117.82, 128.49, 130.36, 137.32, 149.76.

4-(4-Methoxyphenyl)morpholine (3d):[18] ^{1}H NMR: $\delta=$ 3.05 (t, $J=4.8$ Hz, 4H, CH_2), 3.76 (s, 3H, OCH_3), 3.85 (t, $J=$ 4.8 Hz, 4H, CH_2), 6.83–6.90 (m, 4H, C_6H_4); ^{13}C NMR: δ $=51.10$, 55.61, 66.92, 114.63, 118.11, 145.16, 154.38.

4-(3-Methoxyphenyl)morpholine (3e):[19] ^{1}H NMR: $\delta=$ 3.13 (t, $J=4.8$ Hz, 4H, CH_2), 3.78 (s, 3H, OCH_3), 3.83 (t, $J=$ 4.5 Hz, 4H, CH_2), 6.43 (d, $J=6.9$ Hz, 1H, C_6H_4), 6.44 (s, 1H, C_6H_4), 6.52 (d, $J=9$ Hz, 1H, C_6H_4), 7.17 (t, $J=8.4$ Hz, 1H, C_6H_4); ^{13}C NMR: $\delta=49.38$, 55.25, 66.96, 102.32, 104.82, 108.56, 129.94, 152.81, 160.75.

(*E*)-4-(4-Styrylphenyl)morpholine (3f):[20] ^{1}H NMR: $\delta=$ 3.19 (t, $J=4.8$ Hz, 4H, CH_2), 3.87 (t, $J=4.8$ Hz, 4H, CH_2), 6.88–7.08 (m, 4H, Ar+CH), 7.16–7.24 (m, 1H, Ar), 7.34 (t, $J=7.5$ Hz, 2H, Ar), 7.43–7.50 (m, 4H, Ar); ^{13}C NMR: $\delta=$ 49.14, 66.96, 115.62, 126.21, 126.32, 127.20, 127.64, 128.46, 128.75, 129.26, 137.94, 150.85.

4-(Naphthalen-1-yl)morpholine (3g):[21] ^{1}H NMR: $\delta=3.09$ (t, $J=4.5$ Hz, 4H, CH_2), 3.96 (t, $J=4.5$ Hz, 4H, CH_2), 7.07 (d, $J=7.2$ Hz, 1H, $C_{10}H_7$), 7.37–7.50 (m, 3H, $C_{10}H_7$), 7.55 (d, $J=8.1$ Hz, 1H, $C_{10}H_7$), 7.80–7.83 (m, 1H, $C_{10}H_7$), 8.19–8.22 (m, 1H, $C_{10}H_7$); ^{13}C NMR: $\delta=53.59$, 67.56, 114.78, 123.50, 123.89, 125.55, 125.95, 128.57, 128.91, 134.91, 149.54.

4-Morpholinobenzophenone (3h):[22] ^{1}H NMR: $\delta=3.32$ (t, $J=4.6$ Hz, 4H, CH_2), 3.86 (t, $J=4.7$ Hz, 4H, CH_2), 6.89 (d,

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J = 9 Hz, 2H, C_6H_4), 7.43–7.57 (m, 3H, C_6H_5), 7.73 (d, J = 8.1 Hz, 2H, C_6H_5), 7.80 (d, J = 9 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 47.66, 66.67, 113.28, 127.89, 128.20, 129.66, 131.63, 132.53, 138.82, 154.14, 195.30.

***N,N*-diethyl-4-morpholinobenzamide (3i):** Light yellow oil. ^{1}H NMR: δ = 1.18 (t, J = 6.9 Hz, 6H, CH_3), 3.19 (t, J = 4.8 Hz, 4H, CH_2), 3.41 (b, 4H, CH_2), 3.85 (t, J = 4.8 Hz, 4H, CH_2), 6.88 (d, J = 8.7 Hz, 2H, C_6H_4), 7.33 (d, J = 8.7 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 13.73, 48.70, 66.78, 114.63, 128.02, 128.13, 151.84, 171.42; HR-MS (EI) m/z = 262.1674, calcd. for $C_{15}H_{22}N_2O_2$: 262.1681.

4-(4-Trifluoromethylphenyl)morpholine (3j):[23] ^{1}H NMR: δ = 3.22 (t, J = 4.8 Hz, 4H, CH_2), 3.85 (t, J = 4.8 Hz, 4H, CH_2), 6.90 (d, J = 8.7 Hz, 2H, C_6H_4), 7.49 (d, J = 8.7 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 48.26, 66.73, 114.41, 121.07 (q, J = 33.5 Hz), 123.04, 126.54 (q, J = 3.9 Hz), 153.45.

4-(2-Pyridyl)morpholine (3k):[24] ^{1}H NMR: δ = 3.49 (t, J = 4.9 Hz, 4H, CH_2), 3.82 (t, J = 4.8 Hz, 4H, CH_2), 6.62–6.68 (m, 2H, C_5H_4N), 7.47–7.52 (m, 1H, C_5H_4N), 8.20 (d, J = 4.8 Hz, 1H, C_5H_4N); ^{13}C NMR: δ = 45.70, 66.83, 107.00, 113.87, 137.57, 148.04, 159.69.

4-(4-Methyl-2-pyridinyl)morpholine (3l):[23] ^{1}H NMR: δ = 2.27 (s, 3H, CH_3), 3.48 (t, J = 4.8 Hz, 4H, CH_2), 3.81 (t, J = 4.8 Hz, 4H, CH_2), 6.45 (s, 1H, C_5H_4N), 6.50 (d, J = 4.8 Hz, 1H, C_5H_4N), 8.06 (d, J = 4.8 Hz, 1H, C_5H_4N); ^{13}C NMR: δ = 21.42, 45.79, 66.82, 107.45, 115.41, 147.64, 148.46, 159.99.

4-(3-Pyridyl)morpholine (3m):[24] ^{1}H NMR ($CDCl_3$): δ = 3.18 (t, J = 4.8 Hz, 4H, CH_2), 3.87 (t, J = 4.7 Hz, 4H, CH_2), 7.18 (s, 2H, C_5H_4N), 8.14 (s, 1H, C_5H_4N), 8.32 (s, 1H, C_5H_4N); ^{13}C NMR: δ = 48.69, 66.74, 122.21, 123.63, 138.31, 141.10, 147.03.

4-[4-(1-Isopropylindol-3-yl)phenyl]morpholine (3n): White solid; mp 127–129; ^{1}H NMR: δ = 1.50 (d, J = 6.6 Hz, 6H, CH_3), 3.12 (t, J = 4.7 Hz, 4H, CH_2), 3.82 (t, J = 4.7 Hz, 4H, CH_2), 4.56–4.70 (m, 1H, CH), 6.95 (d, J = 8.4 Hz, 2H, C_6H_4), 7.14 (t, J = 6.9 Hz, 1H, Ar), 7.22 (t, J = 7.5 Hz, 1H, Ar), 7.29 (s, 1H, Ar), 7.36 (d, J = 8.1 Hz, 1H, Ar), 7.56 (d, J = 8.7 Hz, 2H, C_6H_4), 7.90 (d, J = 7.8 Hz, 1H, Ar); ^{13}C NMR: δ = 22.82, 47.03, 49.62, 66.98, 109.72, 116.21, 116.69, 119.67, 120.05, 120.76, 121.60, 126.43, 127.86, 128.16, 136.31, 149.41; HR-MS (EI): m/z = 320.1883, calcd. for $C_{21}H_{24}N_2O$: 320.1889.

1-[1,1′-Biphenyl]-4-yl-4-methylpiperidine (4a):[25] ^{1}H NMR: δ = 0.90 (d, J = 6.4 Hz, 3H, CH_3), 1.21–1.35 (m, 2H, CH_2), 1.37–1.49 (m, 1H, CH), 1.66 (d, J = 12.8 Hz, 2H), 2.64 (dt, J = 2.4, 12.4 Hz, 2H), 3.62 (d, J = 12.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H, C_6H_4), 7.15–7.19 (m, 1H, C_6H_5), 7.30 (t, J = 7.6 Hz, 2H, C_6H_5), 7.41 (d, J = 8.8 Hz, 2H, C_6H_4), 7.47 (dd, J = 1.6, 8.8 Hz, 2H, C_6H_5); ^{13}C NMR: δ = 22.02, 30.88, 34.18, 49.86, 116.52, 126.39, 126.57, 127.76, 128.77, 131.69, 141.17, 151.28.

4-Methyl-1-(1-naphthalenyl)piperidine (4b):[26] ^{1}H NMR: δ = 1.03 (d, J = 4.8 Hz, 3H, CH_3), 1.49–1.63(m, 3H, CH + CH_2), 1.77 (d, J = 8.8 Hz, 2H), 2.70 (t, J = 11.2 Hz, 2H, CH_2), 3.36 (d, J = 11.2 Hz, 2H, CH_2), 7.02 (d, J = 7.2 Hz, 1H, Ar), 7.33 (t, J = 7.6 Hz, 1H, Ar), 7.39–7.46 (m, 2H, Ar), 7.48 (d, J = 8 Hz, 1H, Ar), 7.77 (d, J = 8.4 Hz, 1H, Ar), 8.17 (d, J = 8 Hz, 1H, Ar); ^{13}C NMR: δ = 22.21, 31.16, 35.14, 54.06, 114.62, 123.10, 123.96, 125.26, 125.79, 125.97, 128.42, 129.25, 134.89, 150.83.

4-Methyl-1-(4-methoxyphenyl)piperidine (4c): Yellow solid; mp 32 °C; ^{1}H NMR: δ = 0.98 (d, J = 6 Hz, 3H, CH_3), 1.32–1.53 (m, 3H, CH + CH_2), 1.73 (d, J = 12.8, 2H, CH_2), 2.60 (dt, J = 2.4, 11.6 Hz, 2H, CH_2), 3.47 (d, J = 12.4 Hz, 2H, CH_2), 3.76 (s, 3H, CH_3), 6.82 (d, J = 9.2 Hz, 2H, C_6H_4), 6.91 (d, J = 9.2 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 22.01, 30.70, 34.53, 51.80, 55.69, 111.48, 118.86, 146.67, 153.71; HR-MS (EI): m/z = 205.1457, calcd. for $C_{13}H_{19}NO$: 205.1467.

(*E*)-4-(4-Styrylphenyl)piperidine (4d): White solid; mp 140–142 °C; ^{1}H NMR: δ = 0.98 (d, J = 6.3 Hz, 3H, CH_3), 1.26–1.43 (m, 2H, CH_2), 1.45–1.62 (m, 1H, CH), 1.74 (d, J = 11.1 Hz, 2H, CH_2), 2.73 (t, J = 11.3 Hz, 2H, CH_2), 3.71 (d, J = 11.4 Hz, 2H, CH_2), 6.84–7.09 (m, 4H, Ar + CH), 7.14–7.23 (m, 1H, C_6H_5), 7.32(t, J=7.4 Hz, 2H, Ar), 7.40 (d, J = 8.4 Hz, 2H, Ar), 7.47 (d, J = 6.9 Hz, 2H, Ar); ^{13}C NMR: δ = 21.96 30.78, 33.98, 49.66, 116.19, 125.53, 126.22, 126.97, 127.54, 128.67, 138.06, 151.19; HR-MS (EI): m/z = 277.1826, calcd. for $C_{20}H_{23}N$: 277.1830.

2-Methyl-1-(4-phenylphenyl)piperidine (4e): Light yellow solid; mp 56–58 °C; ^{1}H NMR: δ = 0.94 (d, J = 6.6 Hz, 3H, CH_3), 1.44–1.58 (m, 4H, CH_2), 1.63–1.69 (m, 1H, CH), 1.71–1.84 (m, 1H, CH_2), 2.89 (t, J = 9.8 Hz, 1H, CH_2), 3.21 (d, J = 12.2 Hz, 1H, CH_2), 3.90 (s, 1H, CH_2), 6.87 (d, J = 8 Hz, 2H, C_6H_4), 7.15 (t, J = 7.3 Hz, 1H, C_6H_5), 7.28 (t, J = 7.6 Hz, 2H, C_6H_5), 7.39 (d, J = 7.6 Hz, 2H, C_6H_5), 7.46 (d, J = 8 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 13.83, 19.65, 26.19, 31.69, 44.44, 51.07, 117.21, 126.32, 126.52, 127.73, 128.75, 131.48, 141.22, 150.71; HR-MS (EI): m/z = 251.1685, calcd. for $C_{18}H_{21}N$: 251.1674.

1-(4-Trifluoromethylphenyl) pyrrolidine (4f):[27] ^{1}H NMR: δ = 1.96–2.05 (m, 4H, CH_2), 3.29 (t, J = 6.6 Hz, 4H, CH_2), 6.52 (d, J = 8.8 Hz, 2H, C_6H_4), 7.42 (t, J = 8.8 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 25.58, 47.66, 111.00, 116.80 (m), 126.50 (q, J = 3.8 Hz), 127.33, 149.93.

1-(1-Naphthyl)pyrrolidine (4g):[21] ^{1}H NMR: δ = 1.84–1.92 (m, 4H, CH_2), 3.23 (t, J = 5.6 Hz, 4H, CH_2), 6.84 (d, J = 7.6 Hz, 1H, $C_{10}H_7$), 7.23 (t, J = 7.8 Hz, 1H, $C_{10}H_7$), 7.31 (d, J = 7.2 Hz, 3H, $C_{10}H_7$), 7.66–7.69 (m, 1H, $C_{10}H_7$), 8.08–8.11 (m, 1H, $C_{10}H_7$); ^{13}C NMR: δ = 24.91, 52.82, 111.56, 121.41, 124.39, 124.91, 125.63, 126.02, 128.31, 128.37, 135.13, 147.89.

1-(4-Methoxyphenyl)pyrrolidine (4h):[28] ^{1}H NMR: δ = 1.87–1.94 (m, 4H, CH_2), 3.15 (t, J = 6.4 Hz, 4H, CH_2), 3.67 (s, 3H, OCH_3), 6.46 (d, J = 9 Hz, 2H, C_6H_4), 6.77 (d, J = 8.8 Hz, 2H, C_6H_4); ^{13}C NMR: δ = 25.43, 49.04, 56.10, 113.43, 115.18, 142.75, 151.57.

1-[1,1′-Biphenyl]-4-yl-4-methylpiperazine (4i):[25] ^{1}H NMR: δ = 2.32 (s, 3H, CH_3), 2.55 (t, J = 4.8 Hz, 4H, CH_2), 3.23 (t, J = 4.8 Hz, 4H, CH_2), 6.95 (d, J = 8.7 Hz, 2H, C_6H_4), 7.25 (t, J = 7.3 Hz, 1H, C_6H_5), 7.37 (t, J = 7.5 Hz, 2H, C_6H_5), 7.49 (d, J = 8.7 Hz, 2H, C_6H_4), 7.54 (d, J = 7.5 Hz, 2H, C_6H_5); ^{13}C NMR: δ = 46.18, 48.88, 55.10, 116.06, 126.43, 126.51, 127.73, 128.71, 132.21, 140.92, 150.56.

1-Methyl-4-(1-naphthyl)piperazine (4j):[26] ^{1}H NMR: δ = 2.38 (s, 3H, CH_3), 2.68 (s, 4H, CH_2), 3.12 (s, 4H, CH_2), 7.06 (d, J = 7.5 Hz, 1H, $C_{10}H_7$), 7.36 (t, J = 7.8 Hz, 1H, $C_{10}H_7$), 7.40–7.47 (m, 2H, $C_{10}H_7$), 7.51 (d, J = 8.1 Hz, 1H, $C_{10}H_7$), 7.76–7.80 (m, 1H, $C_{10}H_7$), 8.17–8.20 (m, 1H, $C_{10}H_7$); ^{13}C NMR: δ = 46.23, 52.94, 55.69, 114.73, 123.52, 123.61, 125.33, 125.81, 125.91, 128.43, 128.97, 134.81, 149.67.

1-(4-Methoxylphenyl)-4-(pyridin-2-yl)piperazine (4k):[29] ^{1}H NMR: δ = 3.17 (t, J = 5 Hz, 4H, CH_2), 3.68 (t, J = 5 Hz, 4H, CH_2), 3.76 (s, 3H, OCH_3), 6.61–6.70 (m, 2H, C_5H_4N), 6.85 (d, J = 9.3 Hz, 2H, C_6H_4), 6.94 (d, J = 9.1 Hz, 2H, C_6H_4), 7.48 (t, J = 7.8 Hz, 1H, C_5H_4N), 8.21 (d, J = 4.2 Hz,

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1H, C_5H_4N); ^{13}C NMR: δ=45.52, 50.79, 55.62, 107.28, 113.56, 114.58, 118.65, 137.57, 145.77, 148.06, 154.17, 159.56.

1-(4-Trifluoromethylphenyl)-4-(pyridin-2-yl)piperazine (4l): Light yellow solid; mp 126–128 °C; ^{1}H NMR: δ=3.40 (t, J=5.1 Hz, 4H, CH_2), 3.71 (t, J=5.2 Hz, 4H, CH_2), 6.64–6.70 (m, 2H, C_5H_4N), 6.95 (d, J=8.4 Hz, 2H, C_6H_4), 7.48–7.54 (m, 3H, $C_5H_4N+C_6H_4$), 8.22 (d, J=3.9 Hz, 1H, C_5H_4N); ^{13}C NMR: δ=45.06, 47.90, 107.30, 113.86, 114.73, 120.80 (q, J=32.3 Hz), 126.57 (q, J=3.7 Hz), 137.73, 148.16, 153.31, 159.34; HR-MS (EI): m/z=307.1294, calcd. for $C_{16}H_{16}$ F_3N_3: 307.1296.

***trans*-2-(4-Methoxyphenyl)decahydroisoquinoline (4m):** Yellow solid; mp 60–62 °C; ^{1}H NMR: δ=0.90–1.09 (m, 3H, CH_2), 1.26–1.50 (m, 4H, $CH+CH_2$), 1.57–1.76 (m, 5H, $CH+CH_2$), 2.25 (t, J=11.2 Hz, 1H, CH_2), 2.60 (dt, J=2.7, 12.3 Hz, 1H, CH_2), 3.35 (d, J=11.4 Hz, 1H, CH_2), 3.51 (d, J=11.7 Hz, 1H, CH_2), 3.74 (s, 3H, OCH_3), 6.80 (d, J=9 Hz, 2H, Ar), 6.90 (d, J=9 Hz, 2H, Ar); ^{13}C NMR: δ=26.16, 26.55, 30.61, 33.07, 33.23, 41.68, 41.98, 52.12, 55.61, 58.09, 114.42, 118.67, 146.65, 153.53; HR-MS (EI): m/z=245.1777, calcd. for $C_{16}H_{23}NO$: 245.1780.

***trans*-2-(4-Phenylphenyl)decahydroisoquinoline (4n):** White solid; mp 124–126 °C; ^{1}H NMR: δ=0.95–1.12 (m, 3H, CH_2), 1.22–1.49 (m, 4H, $CH+CH_2$), 1.57–1.75 (m, 5H, $CH+CH_2$), 2.38 (t, J=11.5 Hz, 1H, CH_2), 2.74 (dt, J=2.7, 12.3 Hz, 1H, CH_2), 3.58 (d, J=11.7 Hz, 1H, CH_2), 3.76 (d, J=12 Hz, 1H, CH_2), 6.98 (d, J=8.7 Hz, 2H, C_6H_4), 7.25 (t, J=7.5 Hz, 1H, C_6H_5), 7.38 (t, J=7.5 Hz, 2H, C_6H_5), 7.49 (d, J=8.7 Hz, 2H, C_6H_4), 7.55 (d, J=7.8 Hz, 2H, C_6H_5); ^{13}C NMR: δ=26.18, 26.54, 30.53, 32.90, 33.12, 41.68, 41.89, 50.27, 56.19, 116.39, 126.36, 126.57, 127.77, 128.77, 131.53, 141.20, 151.21; HR-MS (EI): m/z=291.1978, calcd. for $C_{21}H_{25}N$: 291.1987.

***N*-Butyl-*N*-methyl-4-(trifluoromethyl)benzenamine (5a):**[30] ^{1}H NMR: δ=0.95 (t, J=7.5 Hz, 3H, CH_3), 1.26–1.43 (m, 2H, CH_2), 1.51–1.61 (m, 2H, CH_2), 2.96 (s, 3H, NCH_3), 3.34 (t, J=7.5 Hz, 2H, CH_2), 6.65 (d, J=8.7 Hz, 2H, C_6H_4), 7.42 (d, J=8.7 Hz, 2H, C_6H_4); ^{13}C NMR: δ=14.06, 20.41, 28.99, 38.41, 52.31, 110.95, 117.07 (q, J=32.6 Hz), 123.63, 126.55 (q, J=3.8 Hz), 127.21, 151.41.

***N*-Butyl-*N*-methylnaphthalen-1-amine (5b):** Yellow oil; ^{1}H NMR: δ=0.91 (t, J=7.3 Hz, 3H, CH_3), 1.30–1.42 (m, 2H, CH_2), 1.58–1.68 (m, 2H, CH_2), 2.84 (s, 3H, NCH_3), 3.07 (t, J=7.5 Hz, 2H, CH_2), 7.09 (d, J=7.5 Hz, 1H, $C_{10}H_7$), 7.38 (t, J=7.8 Hz, 1H, $C_{10}H_7$), 7.41–7.48 (m, 2H, $C_{10}H_7$), 7.51 (d, J=8.4 Hz, 1H, $C_{10}H_7$), 7.77–7.84 (m, 1H, $C_{10}H_7$), 8.21–8.27 (m, 1H, $C_{10}H_7$); ^{13}C NMR: δ=14.17, 20.56, 29.89, 42.59, 57.10, 115.63, 123.09, 124.20, 125.23, 125.79, 125.83, 128.37, 129.81, 134.99; HR-MS (EI): m/z=213.1507, calcd. for $C_{15}H_{19}N$: 213.1517.

***N*-Benzyl-*N*-methyl-4-methoxybenzenamine (5c):**[31] ^{1}H NMR: δ=2.91 (s, 3H, NCH_3), 3.75 (s, 3H, OCH_3), 4.42 (s, 2H, CH_2), 6.74 (d, J=9.3 Hz, 2H, C_6H_4), 6.82 (d, J=9.2 Hz, 2H, C_6H_4), 7.21–7.33 (m, 5H, C_6H_5); ^{13}C NMR: δ=39.20, 55.94, 58.17, 114.71, 114.92, 126.99, 127.27, 128.61, 139.40, 145.01, 151.96.

***N*-Benzyl-*N*-methylpyridin-2-amine (5d):**[31] ^{1}H NMR: δ=3.06 (s, 3H, NCH_3), 4.79 (s, 2H, CH_2), 6.46–6.57 (m, 2H, C_5H_4N), 7.20–7.32 (m, 5H, C_6H_5), 7.39–7.45 (m, 1H, C_5H_4N), 8.18 (d, J=4.8 Hz, 1H, C_5H_4N); ^{13}C NMR: δ=36.26, 53.35, 105.80, 111.94, 127.00, 127.15, 128.64, 137.41, 138.87, 148.12, 159.06.

***N*-Benzyl-*N*-methyl-4-(trifluoromethyl)benzenamine (5e):**[32] ^{1}H NMR: δ=3.08 (s, 3H, NCH_3), 4.58 (s, 2H, CH_2), 6.71 (d, J=8.5 Hz, 2H, C_6H_4), 7.18 (d, J=6.9 Hz, 2H, C_6H_5), 7.22–7.34 (m, 3H, C_6H_5), 7.41 (d, J=8.4 Hz, 2H, C_6H_4); ^{13}C NMR: δ=38.75, 56.21, 111.38, 117.91 (q, J=32.6 Hz), 123.56, 126.60, 126.61 (q, J=3.8 Hz), 127.14, 127.30, 128.89, 138.07, 151.78.

***N*-Benzyl-*N*-ethyl-4-(trifluoromethyl)benzenamine (5f):** Yellow oil; ^{1}H NMR: δ=1.23 (t, J=7.1 Hz, 3H, CH_3), 3.51 (q, J=7.1 Hz, 2H, CH_2), 4.55 (s, 2H, CH_2), 6.68 (d, J=8.4 Hz, 2H, C_6H_4), 7.18–7.34 (m, 5H, C_6H_5), 7.39 (d, J=8.7 Hz, 2H, C_6H_4); ^{13}C NMR: δ=12.14, 45.53, 53.86, 111.26, 117.58 (q, J=32.8 Hz), 123.50, 126.47, 126.68 (q, J=3.8 Hz), 127.22, 128.88, 138.22, 150.70; HR-MS (EI): m/z=279.1237, calcd. for $C_{16}H_{16}F_3N$: 279.1235.

***N*-Benzyl-*N*-ethylpyridin-2-amine (5g):** Yellow oil; ^{1}H NMR: δ=1.08 (t, J=7.1 Hz, 3H, CH_3), 3.49 (q, J=7.1 Hz, 2H, CH_2), 4.65 (s, 2H, CH_2), 6.35 (d, J=8.7 Hz, 1H, C_5H_4N), 6.42 (t, J=6 Hz, 1H, C_5H_4N), 7.10–7.22 (m, 5H, C_6H_5), 7.25–7.31 (m, 1H, C_5H_4N), 8.08 (d, J=4.5 Hz, 1H, C_5H_4N); ^{13}C NMR: δ=12.44, 42.86, 51.04, 105.87, 111.68, 126.90, 127.02, 128.58, 137.28, 139.21, 148.19, 158.24; HR-MS (EI): m/z=212.1308, calcd. for $C_{14}H_{16}N_2$: 212.1313.

***N*-Benzylnaphthalen-1-amine (5h):**[33] ^{1}H NMR: δ=4.39 (s, 2H, CH_2), 4.63 (b, 1H, NH), 6.54 (dd, J=0.8, 7.6 Hz, 1H, Ar), 7.13–7.24 (m, 3H, Ar), 7.25–7.38 (m, 6H, Ar), 7.68–7.74 (m, 2H, Ar); ^{13}C NMR: δ=49.00, 105.56, 118.22, 120.10, 123.65, 125.00, 125.92, 126.68, 127.60, 127.99, 128.84, 134.45, 138.92, 147.92.

4-(Trifluoromethyl)-*N*-methyl-*N*-phenethylbenzenamine (5i): Colorless oil; ^{1}H NMR: δ=2.83 (t, J=7.2 Hz, 2H, CH_2), 2.86 (s, 3H, CH_3), 3.58 (t, J=7.5 Hz, 2H, CH_2), 6.67 (d, J=8.7 Hz, 2H, C_6H_4), 7.15–7.31 (m, 5H, C_6H_5), 7.44 (d, J=8.7 Hz, 2H, C_6H_4); ^{13}C NMR: δ=33.12, 38.66, 54.48, 111.09, 117.46 (q, J=32.7 Hz), 123.61, 126.57, 126.66 (q, J=3.8 Hz), 127.18, 128.77, 128.91, 139.37, 150.96; HR-MS (EI): m/z=279.1202, calcd for $C_{14}H_{16}N_2$: 212.1313.

***N*-Methyl-*N*-phenethylpyridin-2-amine (5j):** Colorless oil; ^{1}H NMR: δ=2.87 (t, J=7.5 Hz, 2H, CH_2), 2.94 (s, 3H, CH_3), 3.74 (t, J=7.5 Hz, 2H, CH_2), 6.44–6.53 (m, 2H, C_5H_4N), 7.07–7.30 (m, 5H, C_6H_5), 7.38–7.44 (m, 1H, C_5H_4N), 8.18 (dd, J=0.9, 3.9 Hz, 1H, C_5H_4N); ^{13}C NMR: δ=33.67, 36.78, 52.38, 105.72, 111.46, 126.22, 128.53, 128.97, 137.15, 139.94, 148.17, 158.42; HR-MS (EI): m/z=212.1309, calcd. for $C_{14}H_{16}N_2$: 212.1313.

***N*-Methyl-*N*-phenethylnaphthalen-1-amine (5k):** Light yellow oil; ^{1}H NMR: δ=2.89–2.95 (m, 5H, CH_2+CH_3), 3.33 (t, J=7.5 Hz, 2H, CH_2), 7.12–7.21 (m, 6H, Ar), 7.35–7.45 (m, 3H, Ar), 7.52 (d, J=8.1 Hz, 1H, Ar), 7.78–7.81 (m, 1H, Ar) 8.12–8.15 (m, 1H, Ar); ^{13}C NMR: δ=34.21, 42.67, 59.00, 115.92, 123.41, 124.17, 125.33, 125.80, 125.86, 126.16, 128.37, 128.46, 128.95, 129.80, 135.01, 140.30, 150.21; HR-MS (EI): m/z=216.1516, calcd. for $C_{19}H_{19}N$: 216.1517.

***N,N*-Dibutylpyridin-2-amine (5l):**[34] ^{1}H NMR: δ=0.95 (t, J=7.3 Hz, 6H, CH_3), 1.29–1.42 (m, 4H, CH_2), 1.52–1.64 (m, 4H, CH_2), 3.42 (t, J=7.5 Hz, 4H, CH_2), 6.40–6.47 (m, 2H, C_5H_4N), 7.34–7.40 (m, 1H, C_5H_4N), 8.12 (d, J=4.8 Hz, 1H, C_5H_4N); ^{13}C NMR: δ=14.18, 20.50, 29.98, 48.54, 105.66, 110.79, 136.98, 148.23, 158.15.

***N,N*-Dibutyl-4-(trifluoromethyl)benzenamine (5m):**[29] ^{1}H NMR: δ=0.96 (t, J=7.3 Hz, 6H, CH_3), 1.29–1.41 (m, 4H, CH_2), 1.51–1.61 (m, 4H, CH_2), 3.28 (t, J=7.5 Hz, 4H,

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CH_2), 6.61 (d, $J=8.7$ Hz, 2H, C_6H_4), 7.39 (d, $J=8.7$ Hz, 2H, C_6H_4); ^{13}C NMR: δ 14.07, 20.43, 29.36, 50.86, 110.71, 116.49 (q, $J=32.7$ Hz), 123.67, 126.62 (q, $J=3.8$ Hz), 127.25, 150.37.

***N*-Methyl-*N*-phenylpyridin-2-amine (5n):**[24] ^1H NMR: $\delta=3.47$ (s, 3H, NCH_3), 6.51–6.62 (m, 2H, C_5H_4N), 7.18–7.31 (m, 4H, $C_5H_4N+C_6H_5$), 7.39 (t, $J=7.7$ Hz, 2H, C_6H_5), 8.23 (d, $J=4.9$ Hz, 1H, C_5H_4N); ^{13}C NMR: $\delta=38.54$, 109.33, 113.26, 125.58, 126.48, 129.84, 136.70, 147.03, 147.93, 159.11.

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