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Sustainable pathways to bio-based amines via the 'hydrogen borrowing' strategy

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Chapter 2

Efficient nickel-catalysed *N*-alkylation of amines with alcohols

In this chapter a highly active and remarkably easy-to-prepare Ni based catalyst system for the selective N-alkylation of amines with alcohols, that is in situ generated from Ni(COD)₂ and KOH under ligand-free conditions is described. This novel method is very efficient for the functionalization of aniline and derivatives with a wide range of aromatic and aliphatic alcohols as well as diols and exhibits excellent functional group tolerance including halides, benzodioxane and heteroaromatic groups. Several TEM measurements combined with elemental analysis were conducted in order to gain insight into the nature of the active catalyst and factors influencing reactivity.

2.1 Introduction

As was already mentioned in **Chapter 1,** the establishment of novel catalytic systems for the synthesis of higher order amines using sustainable methodologies, in particular, the 'hydrogen borrowing' strategy, is certainly an up-and-coming field of research.[1–4] Thus, in this context and continuing our interest in developing *N*-alkylation reactions using Earth abundant metals[5,6], we sought to develop an efficient catalytic system based on nickel[7].

Inspired by the previously reported homogeneous catalytic systems based on palladium precursors[8] in combination with various ligands and assuming the similar catalytic behavior for the nickel species, which is likely for the metals of the same group in the Periodic Table, we initially screened multiple nickel complexes with different phosphine ligands (Josiphos, Xantphos, DPPF, BINAP and etc.). However, the ligand effect was limited in all cases: the conversion and the selectivity of the model *N*-alkylation reaction are not influenced by the ligand, whereas significantly dependent on the selected base and reaction temperature. These initial findings brought us to the new fascinating area of research - Ni nanoparticle (NiNP) chemistry.

Following the pioneering work of Yus and others, much progress has been made in this area, especially related to transfer hydrogenation chemistry, typically using 2-pronanol.[9] As a specific example, 2-propanol was used as hydrogen source in the reductive amination of aldehydes and ketones catalyzed by NiNP.[10] Furthermore, NiNP catalyst enabled the activation of primary alcohols for reductive aza-Wittig reaction.[11] Interestingly, NiNP chemistry has recently found application in the chemistry of renewable resources. Hartwig and coworkers discovered that *in situ* generated NiNP are highly active for the scission of phenyl ether bonds in simple lignin model compounds[12], while Luque and coworkers have reported on microwave assisted preparation of Ni nanoparticles stabilized by ethylene glycol for the hydrogenolysis of benzyl-phenyl ether.[13] Surprisingly, the efficient *N*-alkylation of amines has not yet been realized with any NiNP system.

Herein, we describe the *N*-alkylation of amines *via* the hydrogen borrowing mechanism, to the best of our knowledge, yet unprecedented by Ni nanoparticles generated *in situ*. This catalyst is conveniently prepared from Ni(COD)$_2$ in the presence of sub-stoichiometric amount of base and shows versatility in the selective monoalkylation of various aniline derivatives with a broad range of alcohols.

2.2 Results and discussion

2.2.1 Establishing an active NiNP catalyst system for *N*-alkylation of amines

In order to establish the desired full hydrogen borrowing cycle that involves alcohol dehydrogenation, as well as imine hydrogenation, we selected benzyl alcohol and aniline as model substrates. Initially, the reaction was conducted with various Ni precursors (**Table 2.1**, entries 1-4) in the range of 120-140 °C under an argon atmosphere. While relatively low

conversion was obtained with precursors Ni(OTf)$_2$ and NiBr$_2$, a high conversion value was detected with Ni(COD)$_2$, which can be attributed to the ease of NiNP generation from this Ni(0) precursor at 140 °C even in the absence of hydrogen gas. Selecting Ni(COD)$_2$ for further study, the effect of various bases was evaluated (**Table 2.1**, entries 1, 5-8) with significant variation in substrate conversion and product selectivity. Interestingly, with KOH a perfect selectivity and conversion was achieved at 140 °C, while the use of K$_2$CO$_3$ gave much poorer results. The optimum reaction temperature was found to be 140 °C as shown by the lower conversion values in experiments conducted at lower temperature range (**Table 2.1**, entries 9 and 10). Without Ni precursor, only traces of product were observed in the presence of base (**Table 2.1**, entry 14). Importantly, the catalyst loading could be lowered to 3 mol% and loading of base to 0.3 equivalents (**Table 2.1**, entry 16). Further, in order to exclude the possibility for small amounts of aldehyde or other impurities in the alcohol starting material to exhibit catalytic activity[14], we have conducted an experiment with freshly distilled benzyl alcohol, with unchanged results (entry 17 *versus* entry 16). Importantly, we also successfully carried out an experiment under non-inert conditions during which all starting materials were handled under air (entry 18).

Table 2.1: Optimization of the reaction conditions for amination of benzyl alcohol (**1a**) with aniline (**2a'**).
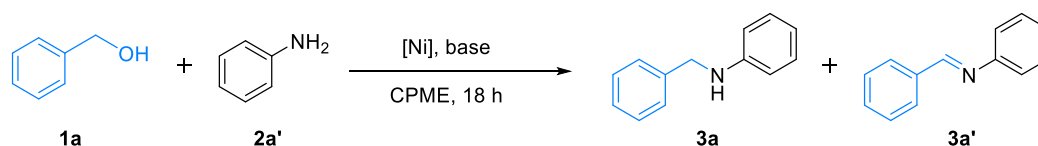
Entry	1a (equiv.)	Base (equiv.)	Precatalyst (mol%)	Temp [°C]	Conv. [%]	Sel. of 3a [%]	Sel. of 3a' [%]
1	2	KOH (0.5)	Ni(COD)$_2$ (5)	140	>99	99	1
2	2	KOH (0.5)	NiCl$_2$(dme) (5)	140	86	79	7
3	2	KOH (0.5)	Ni(OTf)$_2$ (5)	140	73	63	10
4	2	KOH (0.5)	NiBr$_2$ (5)	140	78	70	5
5	2	LiOH (0.5)	Ni(COD)$_2$ (5)	140	>99	7	74
6	2	NaOH (0.5)	Ni(COD)$_2$ (5)	140	>99	10	90
7	2	KO^{t}Bu (0.5)	Ni(COD)$_2$ (5)	140	90	87	3
8	2	K$_2$CO$_3$ (0.5)	Ni(COD)$_2$ (5)	140	10	0	7
9	2	KOH (0.5)	Ni(COD)$_2$ (5)	100	23	16	7
10	2	KOH (0.5)	Ni(COD)$_2$ (5)	120	31	19	9
11	2	KOH (0.1)	Ni(COD)$_2$ (3)	140	67	30	30
12	1.2	KOH (0.3)	Ni(COD)$_2$ (3)	140	94	92	2
13	2	-	Ni(COD)$_2$ (5)	140	73	48	22
14	2	KOH (0.5)	-	140	7	1	6
15[a]	1.5	KOH (0.3)	Ni(COD)$_2$ (3)	140	>99	91	5
16	**1.5**	**KOH (0.3)**	**Ni(COD)$_2$ (3)**	**140**	**>99**	**>99**	**<1**
17[b]	1.5	KOH (0.3)	Ni(COD)$_2$ (3)	140	>99	95	5
18[c]	1.5	KOH (0.3)	Ni(COD)$_2$ (3)	140	>99	93	7
19	1.5	KOH (0.3) +Hg (30)	Ni(COD)$_2$ (3)	140	25	20	5
20[d]	1.5	KOH (0.3)	Ni(COD)$_2$ (3)	140	16	0	16

General reaction conditions: 0.6-1 mmol of **1a**, 0.5 mmol of **2a'**, Ni(COD)$_2$ (0.015-0.025 mmol, 3-5 mol%), KOH (0.05-0.25 mmol, 10-50 mol%), 100-140 °C, 2 mL CPME, 18 h. Conversion and selectivity were determined by GC-FID using decane as an internal standard. [a] At the beginning of the reaction NiNP were generated from Ni(COD)$_2$ (0.015 mmol, 3 mol%) and 2 mL CPME (as a solvent) at 140 °C during 30 min, later KOH (0.15 mmol, 30 mol%), **1a** (0.75 mmol), **2a'** (0.5 mmol) were added and the reaction mixture was stirred and heated at 140 °C for 18 h. [b] Reaction performed with freshly distilled benzyl alcohol. [c] Reaction performed under non-inert conditions. [d] Used pentylamine (0.5 mmol) instead of aniline (**2a'**).

Regarding the mechanism of the target catalytic reaction, under the basic reaction conditions, the S$_N$2 substitution of the OH- group with an amine one could be possible as well. However, taking into account the obtained experimental data, the key intermediates, namely, carbonyl compound and imine were detected that indirectly proved that the developed catalytic reaction proceeds *via* the desired 'hydrogen borrowing' mechanism.

2.2.2 Characterization and nature of the catalyst

To gain additional proof of the heterogeneous nature of the Ni catalyst *in situ* obtained from Ni(COD)$_2$, we conducted several experiments. When we subjected Ni(COD)$_2$ to thermal decomposition in CPME, in the absence of the substrates, followed by the addition of all reactants and base, we obtained 99% of conversion and 91% of product (**Table 2.1**, entry 15), comparable to a regular reaction when typically, solvent and all substrates were added at the same time. Furthermore, when the reaction was conducted in the presence of mercury (**Table 2.1**, entry 19), which is a well-known poison for heterogeneous catalysts, inhibition of the catalysis took place.[15,16] When the poisoning test was repeated in a different fashion, namely initially the reaction was conducted for 1h and analysed, after mercury was added and the reaction was continued for 1 h and analysed again, the two samples taken showed practically identical results, indicating an inhibition of catalytic activity upon addition of mercury. At this point it is worth to mention that although the mercury poisoning test is indicative for a reaction operating with heterogeneous catalyst, it does not exclude processes related to catalyst modification *in situ* such as leaching of soluble monometallic species, or formation of smaller set of clusters of metal particles in solution during catalysis. As described in the excellent review of Ananikov and co-workers[17], several catalytic systems using metal nanoparticles[18] rely on dynamic processes involving a homogeneous or heterogeneous pre-catalyst.

Recycling experiments were successfully conducted, albeit the results showed gradually declining substrate conversion over four consecutive runs (**Figure 2.1**). The drop of the selectivity in each run might be due to dilution of total volume. There may also be a catalyst deactivation effect due to the formation of water in our reaction. To prove the effect of water in our system, the reaction was carried out in the presence of water (0.1 mL) under optimized condition [benzyl alcohol (0.75 mmol), aniline (0.5 mmol), Ni(COD)$_2$ (3 mol%), KOH (30 mol%), 140 °C, 2 mL CPME, 18 h] which gave 20% conversion, 17% corresponding imine **3a'** and 3% product **3a**. In another experiment, Ni(COD)$_2$ (3 mol%), KOH (30 mol%) in CPME were heated to 140 °C, after 1 h the reaction mixture was cooled to RT and water (0.1 mL),

benzyl alcohol (0.75 mmol), aniline (0.5 mmol), were added. Then, the reaction performed at 140 °C for 18 h gave 9% conversion, 0% amine **3a** and 9% imine **3a'**. In these reactions the substantial amount of water which was added in the beginning of the reaction significantly affected the catalysis.

Table 2.2: Recycling test of the *in situ* generated NiNP.

Entry	Time [h]	Conv. [%]	Select. **3a** [%]	Select. **3a'** [%]
	14	>99	90	5
1st reuse	14	70	58	8
2nd reuse	14	50	39	8
3rd reuse	18	36	25	8

General reaction conditions: 1.5 mmol of **1a**, 1 mmol of **2a'**, 0.03 mmol Ni(COD)$_2$, 0.3 mmol KOH, 140 °C, 2 mL CPME. Conversion and selectivity were determined by GC-FID.
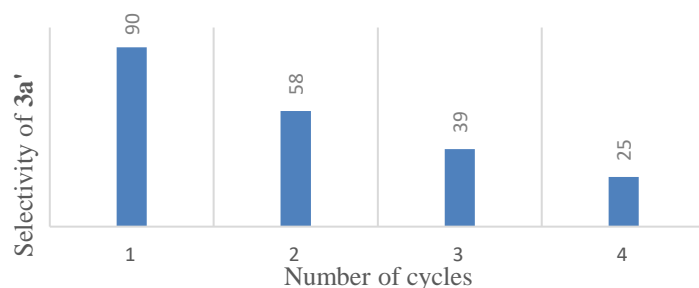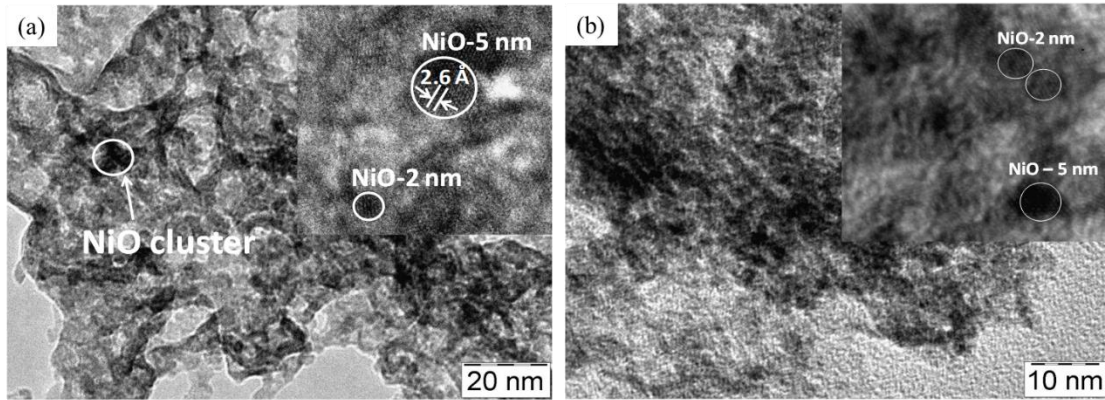

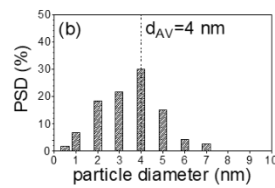**Figure 2.1**: Recycling test of the *in situ* generated NiNP.

Next, a series of TEM measurements were conducted in order to determine the nature and size distribution of the *in situ* generated NiNP[19]. To gain more insight into the possible structural changes imparted by the various components of this peculiar system, a number of experiments were carried out by systematic variation of the base, alcohol and amine and the corresponding TEM images were recorded (**Figure 2.2**).

The first sample (**Figure 2.2a**), prepared by heating Ni(COD)$_2$ in CPME showed Ni oxide clusters of ca. 20 nm in large regions with agglomerated particles sized in the range of 2-5 nm, as expected in the absence of the base and any substrates present. The same sample, however in the presence of KOH (30 mol%) (**Figure 2.2b**), displayed larger Ni oxide clusters (50-100 nm) formed by nanoparticles still of 2-5 nm (**Figure 2.2b**) surrounded by potassium. Caubère,[20] Fort[21] and Hartwig[12] have previously indicated that base can stabilize nickel nanoparticles and this phenomenon is observed in our system as well. In contrast to KOH, the specimen obtained using K$_2$CO$_3$ showed particles with markedly different morphology, with more agglomeration and poor dispersion (≈2%) of Ni nanoparticles (**Figure 2.2c**). This is a likely explanation for the lower catalytic activity of this system (**Table 2.1** entry 1 *versus* entry 8). Next, the influence of the benzyl alcohol was investigated. Isolated Ni oxide clusters of ca. 25 nm (**Figure 2.2d**) with well dispersed nanoparticles (average size 4 nm) were obtained in presence of 1.5 equivalents of benzyl alcohol that confirmed our assumption of a possible stabilization of metal particles by benzyl alcohol, supporting the alcohol–Ni interaction that is necessary for the dehydrogenation reaction. This effect was even more pronounced in the presence of KOH.
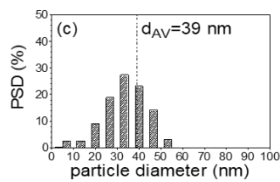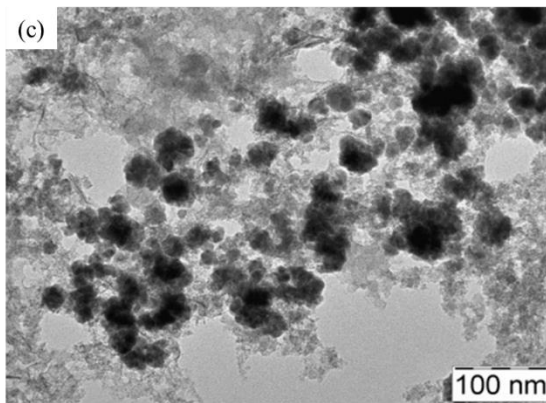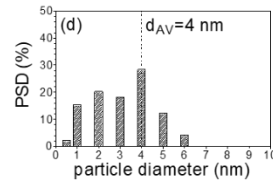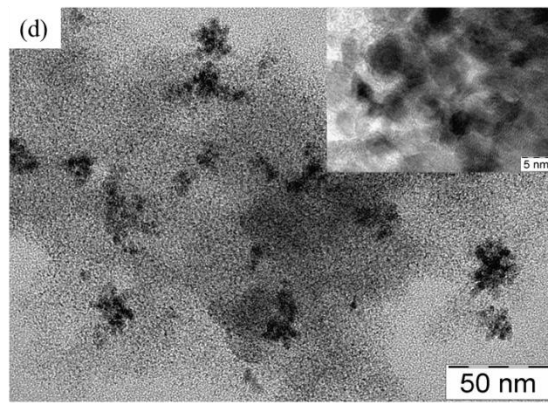
(a) NiO cluster / NiO-5 nm / 2.6 Å / NiO-2 nm — 20 nm

(b) NiO-2 nm / NiO – 5 nm — 10 nm
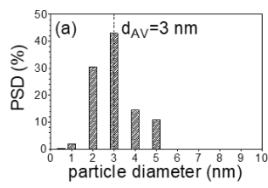
PSD (%) (a) d_AV=3 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), T= 140 °C after 20 min.

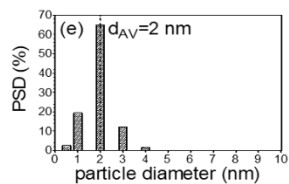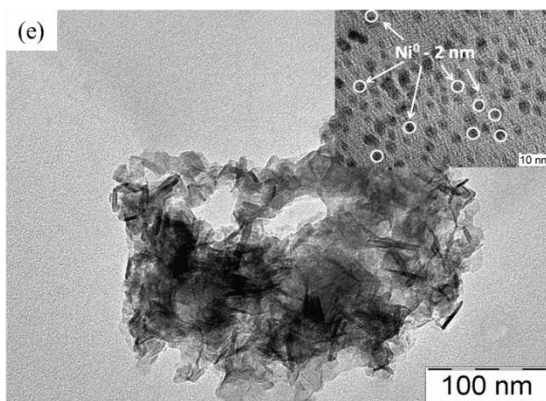PSD (%) (b) d_AV=4 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), KOH (30 mol%), T= 140 °C after 20 min.

(c) — 100 nm

(d) 5 nm — 50 nm

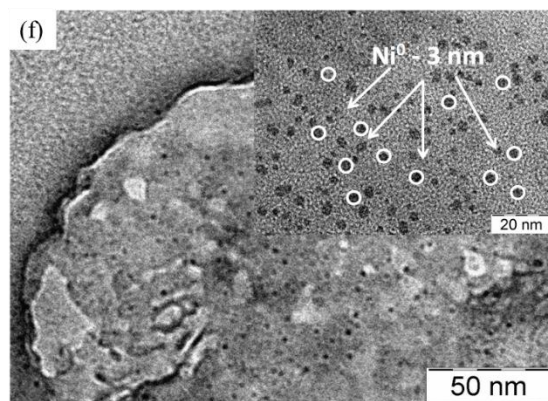PSD (%) (c) d_AV=39 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), K$_2$CO$_3$ (30 mol%), T= 140 °C after 20 min.

PSD (%) (d) d_AV=4 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), benzyl alcohol (0.75 mmol), T= 140 °C after 20 min.

(e) Ni^0 - 2 nm 10 nm — 100 nm

(f) Ni^0 - 3 nm 20 nm — 50 nm

PSD (%) (e) d_AV=2 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol), T= 140 °C after 20 min.
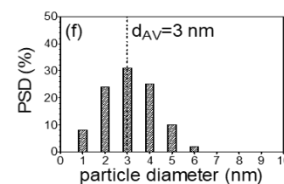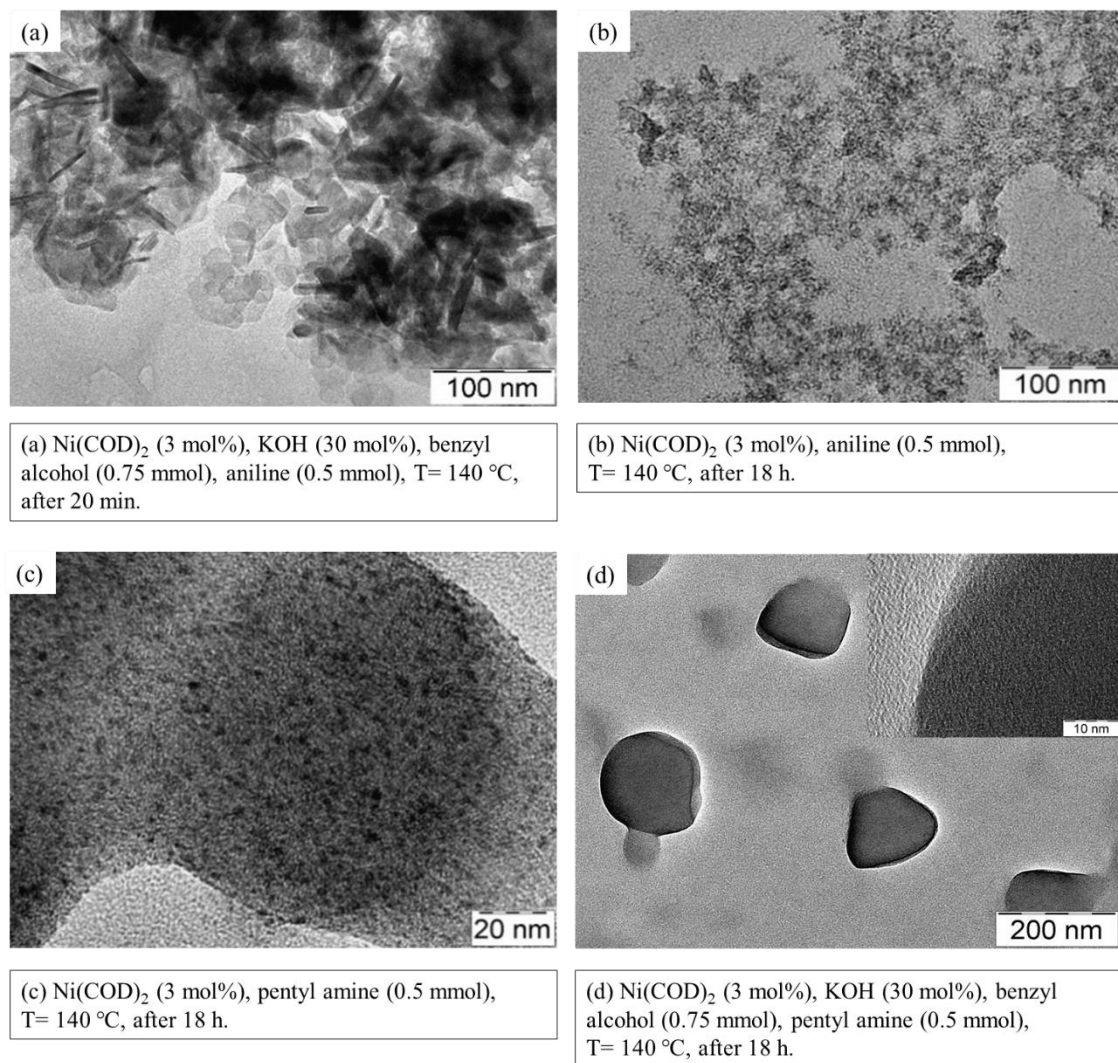
PSD (%) (f) d_AV=3 nm — particle diameter (nm) — Ni(COD)$_2$ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol), aniline (0.5 mmol), T= 140 °C after 18 h.

Figure 2.2: TEM micrographs of *in situ* generated NiNPs under various reaction conditions and particle size distribution of the investigated samples.
*formation of the NiO species as a result of air oxidation during the preparation of the samples for TEM measurements cannot be excluded.

The mixture containing benzyl alcohol and KOH after 20 min (**Figure 2.2e**) showed no visible nickel particles at low magnification. However, at higher magnification, very regularly and finely distributed metal Ni nanoparticles of ca. 2 nm were observed, accounting for a metal dispersion as high as 50% (for EDX analysis of this sample see **Figure 2.4**) – signifying the active system prior to the addition of aniline. The actual reaction mixture, after 20 minutes reaction time showed similar finely dispersed particles (**Figure 2.3a**), while the reaction mixture imaged after 18 hours (**Figure 2.2f**) still showed well dispersed Ni° nanoparticles, although slightly larger than those observed in the initial phase of the reaction. Interestingly, when the Ni particles were generated in presence of pentylamine (**Figure 2.3c**) the TEM images showed that the particles were completely besieged by the amine, whereas in the presence of aniline (**Figure 2.3b**) they were well dispersed. A reaction mixture comprising benzyl alcohol and pentylamine showed similar behaviour (**Figure 2.3d**). This can be explained by a stronger coordination of the more basic (aliphatic) amines to the nickel particles and likely the cause of the poor conversion values obtained in the presence of pentylamine (**Table 2.1**, entry 20) and similar substrates (benzylamine, morpholine).

(a) Ni(COD)$_2$ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol), aniline (0.5 mmol), T= 140 °C, after 20 min.

(b) Ni(COD)$_2$ (3 mol%), aniline (0.5 mmol), T= 140 °C, after 18 h.

(c) Ni(COD)$_2$ (3 mol%), pentyl amine (0.5 mmol), T= 140 °C, after 18 h.

(d) Ni(COD)$_2$ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol), pentyl amine (0.5 mmol), T= 140 °C, after 18 h.

Figure 2.3: Additional TEM micrographs of *in situ* generated NiNPs under various reaction conditions.
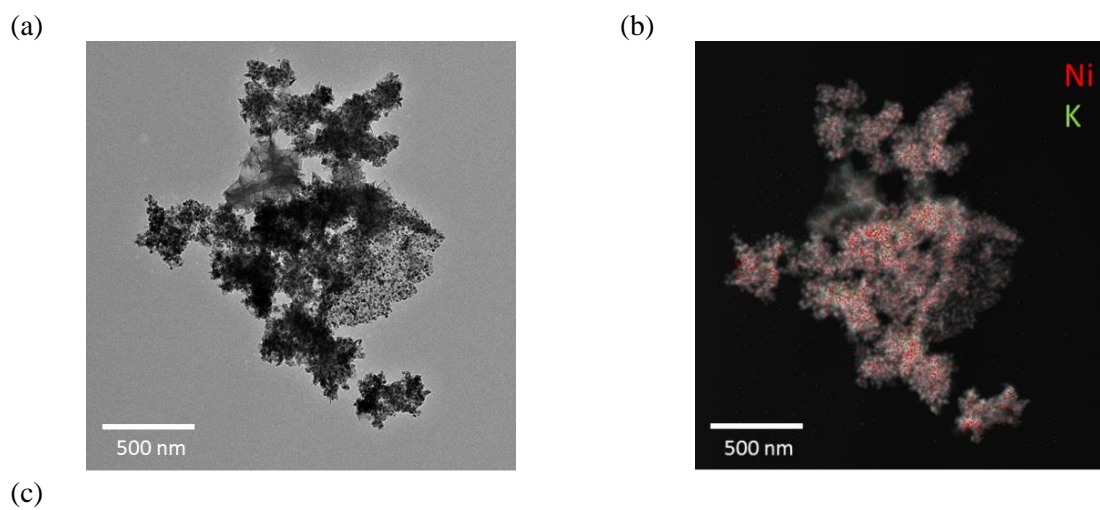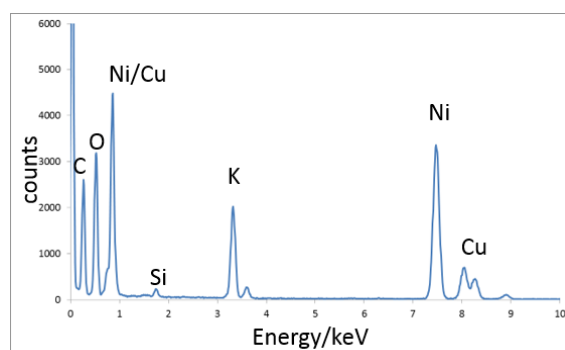
Figure 2.4: Bright-field TEM image of the *in situ* generated NiNPs from Ni(COD)$_2$ (3 mol%), KOH (30 mol%), benzyl alcohol (0.75 mmol) in 1 mL CPME at 140 °C after 20 min (**a**), HAADF-STEM image of the NiNPs with overlay EDX map for Ni and K (**b**), X-ray EDS of the NiNPs from the area in **Figure 2.4b** (**c**).

2.2.3 *N*-alkylation of aniline with a wide range of alcohols

To demonstrate the general applicability of the catalytic system, various (hetero)aromatic and aliphatic alcohols, including diols, were evaluated in the catalytic *N*-alkylation of aniline under optimized conditions (**Table 2.3**). Electron-donating and electron-withdrawing substituted benzyl alcohols were successfully used in the selective mono-alkylation of aniline (**Table 2.3**). Notably, benzyl alcohols (**1a-1e**) with electron-donating substituents, including the sterically more hindered 2-methoxy-benzyl alcohol (**1c**) reacted smoothly with aniline, resulting in very good to excellent (84-98%) isolated yields of **3a-e** (**Table 2.3**). When benzyl alcohols bearing the electron-withdrawing groups –NO$_2$, –CN, –CH$_3$COOCH$_3$, –CF$_3$ were employed, much lower reactivity was observed. Furthermore, the important building block piperonyl alcohol (**1g**) was transformed to the desired product **3g** with 62% isolated yield. Interestingly, heteroaromatic alcohols such as the biomass-derived furfuryl alcohol and 2-(hydroxymethyl)-pyridine were alkylated selectively, albeit with moderate yields (**Table 2.3**, **3h** and **3i**, respectively). Next, aliphatic alcohols as reaction partners in the *N*-alkylation of aniline were investigated. Gratifyingly, short and long chain aliphatic alcohols (**1k-s**) readily afforded the corresponding desired amine products (**3k-s**, 69-90%) under optimized conditions. It was even possible to achieve *N*-alkylation with methanol, but only 38% GC yield of the *N*-methylated product was seen even at high catalyst/base loading. Notably, when 1,5- and 1,6-diols were examined, the mono-alkylated amino alcohols (**3ua**) and (**3va**) were obtained in 63% and 67% isolated yield, respectively, and minor amounts of cyclic products were observed (**Table 2.3**).

Table 2.3: Amination of various alcohols with aniline.
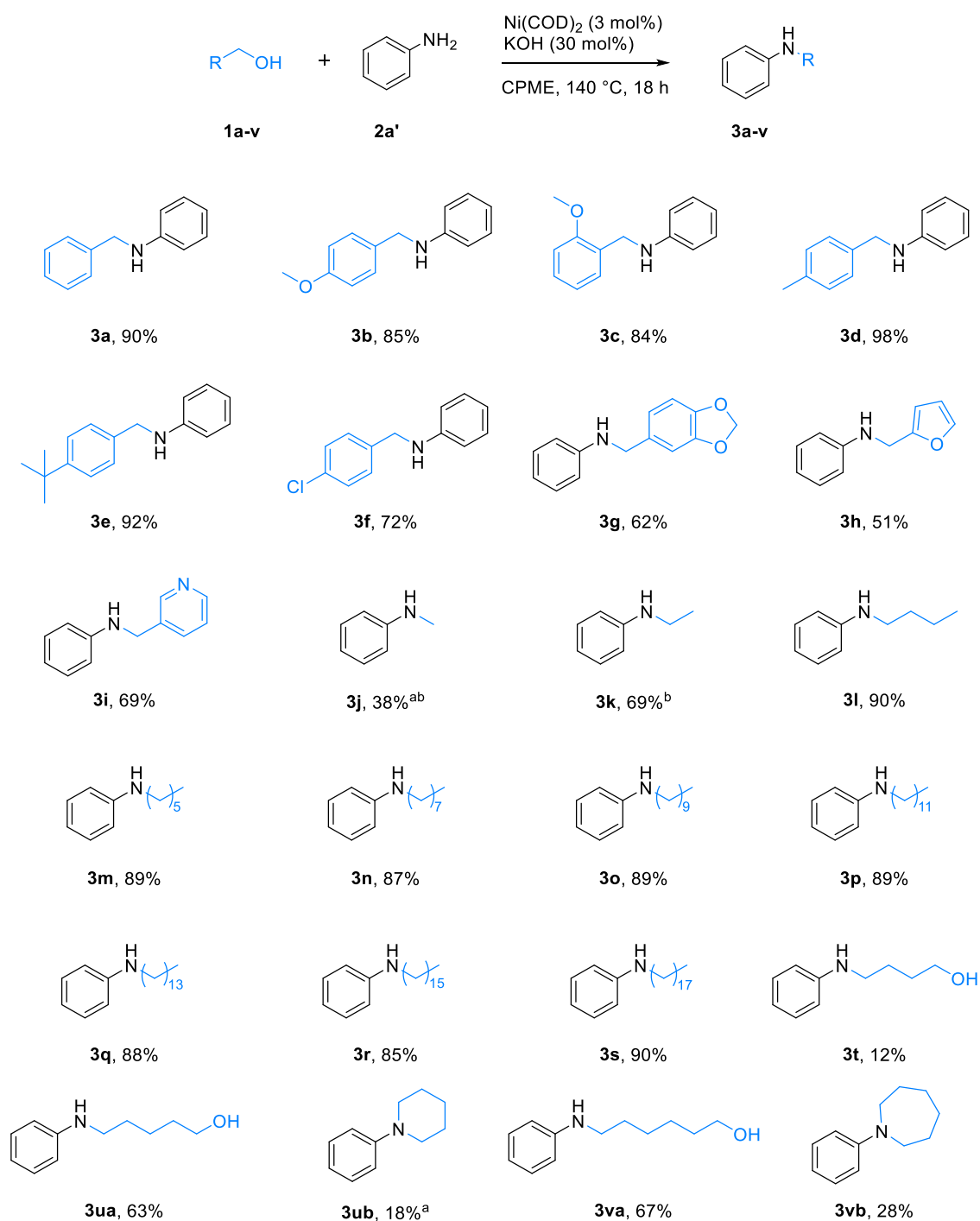
General reaction conditions: 1.5 mmol of **1a-v**, 1 mmol of aniline, Ni(COD)$_2$ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 30 mol%), 140 °C, 2 mL CPME, 18 h. [a] Yield was calculated based on GC-FID. [b] 1 mL of methanol or ethanol, 1 mmol of aniline, Ni(COD)$_2$ (0.1 mmol, 10 mol%), KOH (1 mmol), 150 °C, 2 mL CPME, 48 h.

2.2.4 *N*-alkylation of a variety of amines with 1-butanol

Further expanding the scope of the reaction, *n*-butanol was chosen as coupling partner to a series of diversely substituted aniline derivatives, bearing electron-donating (**2a-e**) and electron-withdrawing (**2i-l**) groups as well as sterically hindered amines (**2f-g**), and diamines (**2m**, **2o-q**), which were selectively alkylated. More specifically, there was no significant difference in the reactivity of *p*-methoxy-aniline (**2a**) compared to *p*-methyl-aniline (**2b**), however a gradual decrease of product yield was observed (77% for **5b**, 53% for **5c**, 32% for **5d**) when the substrate was changed to the *meta-* and *ortho-* substituted analogues. A similar behavior was observed for fluoro-anilines **2i**, **2j** and **2k**. Interestingly, pyrrole substituted aniline furnished 57% isolated yield of **5r**. Aromatic amines bearing the electron-withdrawing groups –CN, –CH$_3$COOCH$_3$ and –CF$_3$ showed low reactivity with 1-butanol, namely only minor amounts of products were observed. Next, when aromatic diamines were used as a substrate, the corresponding mono and di-*N*-alkylated amines were isolated (**Table 2.4**, **5oa-ob** and **5pa-pb**). When cyclohexylamine was used, it gave 32% GC yield of the desired product **5n** and 67% of imine (**5n'**). Other aliphatic amines (benzylamine, pentylamine and morpholine) did not afford any products under the optimized reaction conditions, in accordance with previous TEM investigation that shows stronger coordination of aliphatic amines to the Ni particles likely leading to diminished activity (**Figure 2.3c-d**).

Examples of heterogeneous catalysts comprising nickel on alumina[22,23] or silica[24], γ-Al$_2$O$_3$ supported Ni and Cu bimetallic nanoparticles[25] and Raney-nickel[26] are known for the amination of alcohols. Besides this, a few homogeneous catalytic systems using nickel for alkylation of amines[27,28] and *N*-alkylation of hydrazides and arylamines with racemic alcohols[29] were very recently reported, but to the best of our knowledge, the system described in this chapter is the first example where *in situ* generated Ni nanoparticles act as highly efficient catalysts for the attractive *N*-alkylation of amines. Clear advantages are the Ni loading being as low as 3%, and there is no catalyst preparation or any ligand required. Therefore, we believe our system to be a valuable addition to these examples of Ni catalysts that are either homogeneous or supported heterogeneous in nature. This is an excellent starting point for establishing robust, highly active and recyclable Ni catalyst in the future, for example in combination with systems that have higher ability to stabilize the formed Ni nanopartciles, to increase the stability of the system, such as by using polyethylene glycol (PEG)[30] or ionic liquids[31].

Table 2.4: *N*-alkylation of various aniline with *n*-butanol.
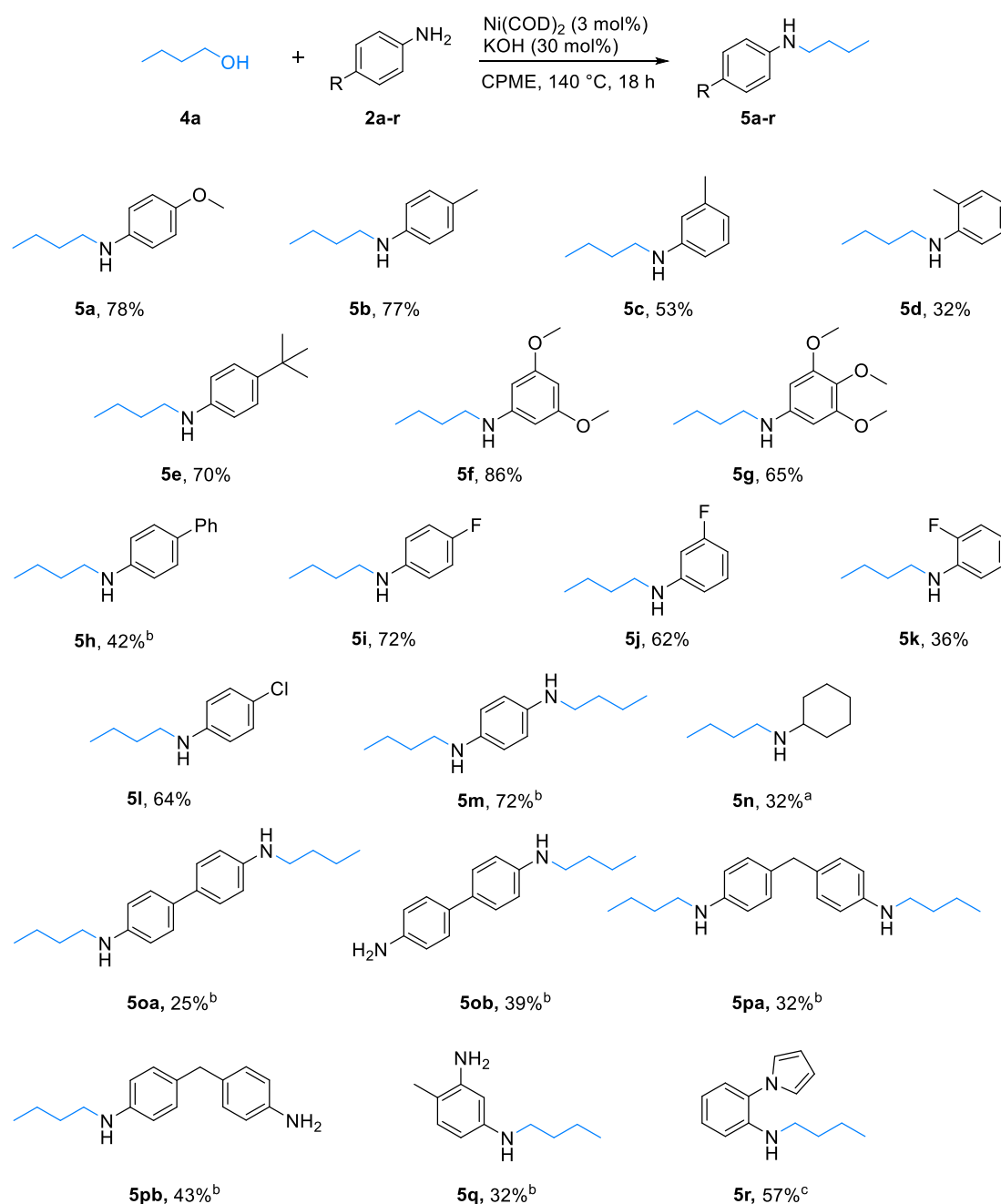
General reaction conditions: 1.5 mmol of *n*-butanol (**4a**), 1 mmol of **2a-r**, Ni(COD)$_2$ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 30 mol%), 140 °C, 2 mL CPME, 18 h. [a] Yield was calculated based on GC-FID. [b] 3 mmol of *n*-butanol, 1.5 mmol of corresponding amine, Ni(COD)$_2$ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 30 mol%), 140 °C, 2 mL CPME, 48 h. [c] 3 mmol of *n*-butanol, 1.5 mmol of corresponding amine, Ni(COD)$_2$ (0.05 mmol, 5 mol%), KOH (0.5 mmol, 50 mol%), 140 °C, 2 mL CPME, 72 h.

2.3 Conclusion

In summary, we have developed a simple and highly active catalytic system for efficient and selective *N*-alkylation of amines with alcohols that can be conveniently prepared using a

catalytic amount (as low as 3 mol%) of Ni(COD)$_2$ and sub-stoichiometric amount of KOH under ligand-free conditions. The described system is tolerant to a variety of functional groups such as halides, benzodioxane and heteroaromatic groups present in either the alcohol or the amine substrate. In order to gain further insight into the nature of the active catalytic system and influence of reaction parameters on catalyst morphology, a series of TEM measurements combined with elemental analysis were performed that found finely dispersed *in situ* generated metal particles in the catalysed reaction. Additional studies revealed that potassium hydroxide is uniquely suited for the stabilization of Ni nanoparticles and that the alcohol substrate also has a stabilizing role. Furthermore, clear differences in the morphology of the particles were seen in the presence of aromatic versus aliphatic amine, the latter leading to poor reactivity due to stronger amine coordination. The substrate scope was well in line with these findings, where the nature of the alcohol reaction partner could be broadly varied (benzyl alcohol, short or long chain aliphatic alcohol, diol) while aniline derivatives were better suited substrates than aliphatic amines. To the best of our knowledge this is the first, very simple yet highly active and selective NiNP catalyst system for the *N*-alkylation of amines with alcohols that operates *via* the 'hydrogen borrowing' strategy.

2.4 Experimental section

2.4.1 General methods

All reactions were carried out under an argon atmosphere using oven (140 °C) dried glassware and using standard Schlenk techniques. Bis(1,5-cyclooctadiene)nickel(0) and nickel(II) trifluoromethanesulfonate were purchased from Strem Chemicals; Nickel(II)chloride ethylene glycol dimethyl ether complex and nickel (II) bromide were purchased from Sigma-Aldrich; Cyclopentyl methyl ether (CPME, 99.9%, anhydrous) was purchased from Sigma-Aldrich and used without further purification. All other reagents were purchased from Sigma-Aldrich, Acros and TCI in reagent or higher grade and were used as received without further purification.

Chromatography and spectroscopy

Column chromatography was performed using Merck silica gel type 9385 230-400 mesh and typically pentane and ethyl acetate as eluent.

Thin layer chromatography (TLC): Merck silica gel 60, 0.25 mm. The components were visualized by UV or KMnO$_4$ staining.

Gas Chromatography with flame ionization detector (GC-FID): Conversions and product selectivities were determined using GC-FID (Agilent Technologies 6890) with an HP-5MS column (30 m x 0.25 mm x 0.25 μm) using nitrogen as carrier gas. The temperature program started at 50 °C and held for 5 min followed by a 10°C/minute temperature ramp to 300 °C and the final temperature was held for 5 min.

Gas Chromatography mass spectrometry (GC-MS): Product identification was performed using a GC-MS (Shimadzu QP2010 Ultra) with an HP-1MS column (30 m x 0.25 mm x 0.25 μm),

and helium as carrier gas. The temperature program started at 40 °C, followed by a 10°C/minute temperature ramp to 250 °C and the final temperature was held for 5 min.

Mass spectrometry: Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI[+]) or a LTQ Orbitrap XL (ESI[+]).

NMR spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 400, Agilent MR 400 (400 and 100.59 MHz, respectively) using $CDCl_3$ as a solvent.^{1}H and[13]C NMR spectra were recorded at room temperature. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 for 1H, 77.00 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br. = broad, m = multiplet), coupling constants (Hz), and integration.

2.4.2 Representative procedures

Representative procedure for catalytic *N*-alkylation of amines with alcohols

An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with the specified amount of alcohol, amine, base, catalyst precursor and solvent. Typically, amine (0.5 mmol, 1 equiv.), alcohol (0.75 mmol, 1.5 equiv.), $Ni(COD)_2$ (0.015 mmol, 3 mol%), KOH (0.15 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL) were used. The solid materials were weighed into the Schlenk tube under air, $Ni(COD)_2$ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at the appropriate temperature (typically 140 ^{o}C) and stirred for a given time (typically 18 h). The reaction mixture was cooled down to room temperature. After taking a sample (app. 0.5 mL) for GC analysis, the crude mixture was filtered through silica gel, eluted with ethyl acetate, and concentrated *in vacuo*. The residue was purified by flash column chromatography to provide the pure amine product.

TEM and STEM/EDX measurements

At the RUG: TEM and STEM/EDX measurements were performed on a FEI Tecnai T20 electron microscope operating at 200 keV. EDX spectra were recorded with an Oxford Instruments X-max 80T SDD detector. Samples were prepared by applying 5 µl of stock solution on a plain carbon coated copper grid. After one minute the excess of the sample was blotted with filter paper.

At CNR-ITAE in Messina, TEM images were acquired and elaborated by a Philips CM12 instrument at 120 kV accelerating voltage, equipped with a high-resolution camera and able to achieve a 0.19 nm point-to-point resolution and a 0.14 nm line resolution. After solvent evaporation, the stock solutions were dispersed in toluene under ultrasound irradiation, put drop-wise on a holey carbon-coated 300 mesh, 3.05 mm Cu grid (TAAB Laboratories

Equipment Ltd, UK) and then dried at room temperature for 1h prior to the measurement. An amount of 200 Ni particles was counted to obtain a particle size distribution histogram for the NiNPs samples.

Recycling test

An oven-dried 20 mL Schlenk tube, equipped with a stirring bar, was charged with aniline (1 mmol, 1 equiv.), benzyl alcohol (1.5 mmol, 1.5 equiv.), Ni(COD)$_2$ (0.03 mmol, 3 mol%), KOH (0.3 mmol, 0.3 equiv., 30 mol%) and cyclopentyl methyl ether (solvent, 2 mL). The solid materials were weighed into the Schlenk tube under air, Ni(COD)$_2$ was weighed in the glovebox; then the Schlenk tube was removed from the glovebox, subsequently connected to an argon line and vacuum-argon exchange was performed three times. Liquid starting materials and solvent were charged under an argon stream. The Schlenk tube was capped and the mixture was rapidly stirred at room temperature for 1 min, then was placed into a pre-heated oil bath at 140 °C and stirred for 14 h. Then the reaction mixture was cooled down to room temperature and connected to an argon line. Under an argon stream, 0.5 mL of the crude mixture was taken and filtered through silica gel, eluted with ethyl acetate and analyzed by GC-FID.

Then for the next cycle to the reaction mixture CPME (0.5 mL), benzyl alcohol (1.5 mmol, 1.5 equiv.) and aniline (1 mmol, 1 equiv.) were added. The Schlenk tube was capped and the mixture was placed into a pre-heated oil bath at 140 °C and stirred for 14 h. The procedure was repeated as before for four consecutive runs.

2.4.3. Spectral data of isolated compounds
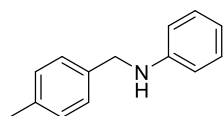
N-benzylaniline (3a)
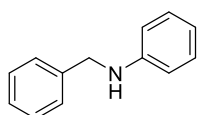
The compound was synthesized using aniline (46.5 mg, 0.5 mmol) and benzyl alcohol (81 mg, 0.75 mmol) to afford **3a** (82 mg, 90% yield). Yellow solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.46-7.33 (m, 5H), 7.28-7.23 (m, 2H), 6.82-6.78 (m, 1H), 6.71 (d, *J* = 7.6 Hz, 2H), 4.39 (s, 2H), 4.05 (*br* s, 1H, NH). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 150.88, 142.18, 132.00, 131.36, 130.23, 129.95, 120.29, 115.58, 51.03. **HRMS** (APCI$^+$, m/z) calculated for C$_{13}$H$_{14}$N [M+H]$^+$: 184.11262; found: 184.11320. The spectral data are identical to the previously reported.[32]
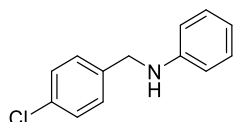
N-(4-methoxybenzyl)aniline (3b)
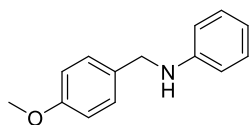
The compound was synthesized using aniline (93 mg, 1 mmol) and 4-methoxybenzyl alcohol (207 mg, 1.5 mmol) to afford **3b** (181 mg, 85% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.81 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 2H), 4.01 (*br* s, 1H, NH), 3.87 (s, 3H, OCH$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 161.59, 150.97, 134.18, 131.99, 131.53, 120.21, 116.77, 115.59, 58.01, 50.49. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{16}$NO [M+H]$^+$: 214.12319; found: 214.12420. The spectral data are identical to the previously reported.[32]

N-(2-methoxybenzyl)aniline (3c)
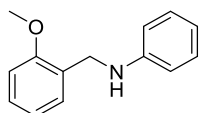
The compound was synthesized using aniline (93 mg, 1 mmol) and 2-methoxybenzyl alcohol (207 mg, 1.5 mmol) to afford **3c** (179 mg, 84% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.35-7.26 (m, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 6.96-6.91 (m, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 4.36 (s, 2H), 4.14 (*br* s, 1H, NH), 3.88 (s, 3H, OCH$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 160.06, 151.10, 131.84, 131.56, 130.96, 130.02, 123.20, 120.00, 115.73, 112.92, 57.98, 46.13. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{16}$NO [M+H]$^+$: 214.12319; found: 214.12437. The spectral data are identical to the previously reported.[33]
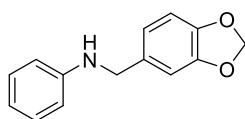
N-(4-methylbenzyl)aniline (3d)

The compound was synthesized using aniline (93 mg, 1 mmol) and 4-methylbenzyl alcohol (183 mg, 1.5 mmol) to afford **3d** (194 mg, 98% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.40-7.35 (m, 4H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 4.44 (s, 2H), 4.10 (*br* s, 1H, NH), 2.57 (s, 3H, CH$_3$). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.11, 139.64, 139.30, 132.18, 132.12, 130.37, 120.32, 115.72, 50.87, 24.00. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{16}$N [M+H]$^+$: 198.12827; found: 198.12912. The spectral data are identical to the previously reported.[34]

### *N*-(4-(*tert*-butyl)benzyl)aniline (3e)
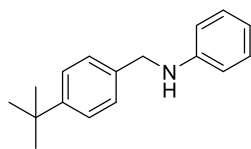
The compound was synthesized using aniline (93 mg, 1 mmol) and 4-*tert*-butylbenzyl alcohol (246 mg, 1.5 mmol) to afford **3e** (220 mg, 92% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.44 (s, 2H), 4.10 (*br* s, 1H, NH), 1.53 (s, 9H, *t*Bu). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 152.98, 151.12, 139.25, 132.09, 130.22, 128.36, 120.28, 115.65, 50.80, 37.34, 34.27. **HRMS** (APCI$^+$, m/z) calculated for C$_{17}$H$_{22}$N [M+H]$^+$: 240.17522; found: 240.17665. The spectral data are identical to the previously reported.[35]

N-(4-chlorobenzyl)aniline (3f)

The compound was synthesized using aniline (93 mg, 1 mmol) and 4-chlorobenzyl alcohol (214 mg, 1.5 mmol) to afford **3f** (157 mg, 72% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.34-7.30 (m, 4H), 7.22-7.18 (m, 2H), 6.78-6.73 (m, 1H), 6.64-6.62 (m, 2H), 4.32 (s, 2H), 4.08 (*br* s, 1H, NH).**^{13}C NMR** (101 MHz, CDCl$_3$): δ 150.47, 140.66, 135.53, 131.97, 131.41, 131.37, 120.50, 115.59, 50.29. **HRMS** (APCI$^+$, m/z) calculated for C$_{13}$H$_{13}$ClN [M+H]$^+$: 218.07365; found: 218.07472. The spectral data are identical to the previously reported.[32]

### *N*-(benzo[d][1,3]dioxol-5-ylmethyl)aniline (3g)

The compound was synthesized using aniline (93 mg, 1 mmol) and piperonyl alcohol (228 mg, 1.5 mmol) to afford **3g** (141 mg, 62% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.22-7.17 (m, 2H), 6.89-6.72 (m, 4H), 6.66-6.64 (m, 2H), 5.95 (s, 2H), 4.25 (s, 2H), 4.01 (*br* s, 1H, NH).**^{13}C NMR** (101 MHz, CDCl$_3$): δ 150.73, 150.57, 149.40, 136.02, 131.93, 123.26, 120.27, 115.55, 110.97, 110.72, 103.66, 50.80. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{14}$NO$_2$ [M+H]$^+$: 228.10245; found: 228.10380. The spectral data are identical to the previously reported.[36]

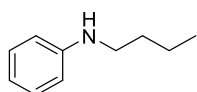### *N*-(furan-2-ylmethyl)aniline (3h)
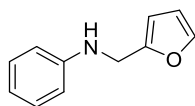
The compound was synthesized using aniline (93 mg, 1 mmol) and furfuryl alcohol (147 mg, 1.5 mmol) to afford **3h** (87 mg, 52% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.39-7.38 (m, 1H), 7.21 (t, *J* = 7.6 Hz, 2H), 6.76 (td, *J* = 7.2 Hz, *J* = 0.8 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 2H), 6.34 (dd, *J* = 2.8 Hz, *J* = 2.0 Hz, 1H), 6.26 (dd, *J* = 2.8 Hz, *J* = 0.8 Hz, 1H), 4.33 (s, 2H), 4.03 (*br* s, 1H, NH). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 155.42, 150.30, 144.57, 131.90, 120.69, 115.82, 113.01, 109.64, 44.11. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{12}$NO [M+H]$^+$: 174.09189; found: 174.09240. The spectral data are identical to the previously reported.[32]

N-(pyridin-3-ylmethyl)aniline (3i)
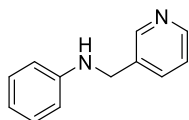
The compound was synthesized using aniline (93 mg, 1 mmol) and 2-pyridinemethanol (164 mg, 1.5 mmol) to afford **3i** (127 mg, 69% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 70:30 to 50:50). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 8.60 (s, 1H), 8.51 (d, *J* = 3.6 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.24-7.16 (m, 3H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 2H), 4.23 (*br* s, 1H, NH). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.77, 151.26, 150.41, 137.77, 137.71, 132.00, 126.22, 120.56, 115.60, 48.35. **HRMS** (APCI$^+$, m/z) calculated for C$_{12}$H$_{13}$N$_2$ [M+H]$^+$: 185.10787; found: 185.10875. The spectral data are identical to the previously reported.[36]
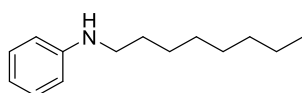
N-ethylaniline (3k)
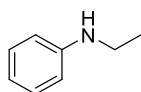
The compound was synthesized using aniline (93 mg, 1 mmol) and ethanol (1 mL, 17 mmol) to afford **3k** (74 mg, 69% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.17 (t, *J* = 7.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 3.54 (*br* s, 1H, NH), 3.16 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.16, 131.92, 119.89, 115.45, 41.15, 17.58. **HRMS** (APCI$^+$, m/z) calculated for C$_8$H$_{12}$N [M+H]$^+$: 122.09697; found: 122.09643. The spectral data are identical to the previously reported.[37]
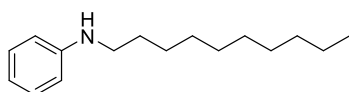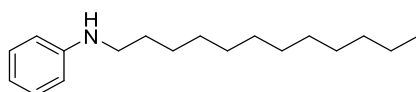
N-butylaniline (3l)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **3l** (134 mg, 90% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.28-7.23 (m, 2H), 6.79-6.75 (m, 1H), 6.69-6.66 (m, 2H), 3.60 (*br* s, 1H, NH), 3.18 (td, *J* = 6.8 Hz, *J* = 2.8 Hz, 2H), 1.71-1.63 (m, 2H), 1.56-1.46 (m, 2H), 1.07-1.02 (m, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.28, 131.92, 119.76, 115.40, 46.39, 34.42, 23.05, 16.66. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{16}$N [M+H]$^+$: 150.12827; found: 150.12869. The spectral data are identical to the previously reported.[38]

N-hexylaniline (3m)
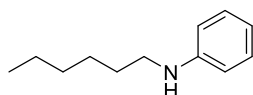
The compound was synthesized using aniline (93 mg, 1 mmol) and 1-hexanol (153 mg, 1.5 mmol) to afford **3m** (157 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.26 (t, *J* = 7.6 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 2H), 3.60 (*br* s, 1H, NH), 3.17 (t, *J* = 7.2 Hz, 2H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.52-1.39 (m, 6H), 1.01 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.29, 131.93, 119.76, 115.41, 46.73, 34.42, 32.30, 29.62, 25.40, 16.80. **HRMS** (APCI$^+$, m/z) calculated for C$_{12}$H$_{20}$N [M+H]$^+$: 178.15957; found: 178.16039. The spectral data are identical to the previously reported.[39]
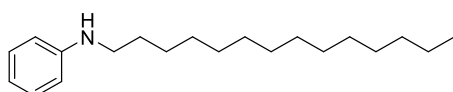
N-octylaniline (3n)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-octanol (195 mg, 1.5 mmol) to afford **3n** (179 mg, 87% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.30 (t, *J* = 7.6 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 2H), 3.64 (*br* s, 1H, NH), 3.21 (t, *J* = 7.2 Hz, 2H), 1.73 (p, *J* = 6.8 Hz, 2H), 1.52-1.45 (m, 10H), 1.06-1.05 (m, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.34, 131.96, 119.79, 115.45, 46.77, 34.68, 32.40, 32.27, 32.12, 30.02, 25.51, 16.92. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{24}$N [M+H]$^+$: 206.19087; found: 206.19195. The spectral data are identical to the previously reported.[33]
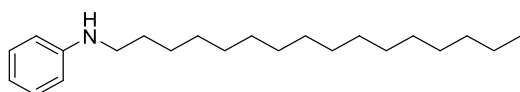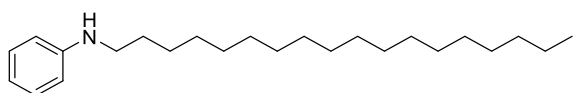
N-decylaniline (3o)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-decanol (237 mg, 1.5 mmol) to afford **3o** (207 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.20 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 2H), 3.56 (*br* s, 1H, NH), 3.12 (t, *J* = 7.2 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.44-1.31 (m, 14H), 0.92 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.21, 131.87, 119.73, 115.35, 46.68, 34.59, 32.30, 32.28, 32.26, 32.15, 32.02, 29.88, 25.37, 16.80. **HRMS** (APCI$^+$, m/z) calculated for C$_{16}$H$_{28}$N [M+H]$^+$: 234.22217; found: 234.22348. The spectral data are identical to the previously reported.[33]

N-dodecylaniline (3p)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-dodecanol (279 mg, 1.5 mmol) to afford **3p** (232 mg, 89% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.26 (t, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.43 (*br*s, 1H, NH), 3.18 (t, *J* = 7.2 Hz, 2H), 1.70 (p, *J* = 7.6 Hz, 2H), 1.51-1.40 (m, 18H), 1.01 (t, *J* = 6.8 Hz, 3H).**^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.28, 131.91, 119.78, 115.41, 46.75, 34.73, 32.49, 32.46, 32.44, 32.43, 32.37, 32.28, 32.17, 29.99, 25.50, 16.90. **HRMS** (APCI$^+$, m/z) calculated for C$_{18}$H$_{32}$N [M+H]$^+$: 262.25348; found: 262.25487. The spectral data are identical to the previously reported.[40]

N-tetradecylaniline (3q)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-tetradecanol (321 mg, 1.5 mmol) to afford **3q** (247 mg, 85% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.20 (t, *J* = 7.6 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.60 (*br* s, 1H, NH), 3.13 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.45-1.31 (m, 22H), 0.93 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.22, 131.87, 119.72, 115.34, 46.68, 34.64, 32.41, 32.39, 32.38, 32.37, 32.33, 32.32, 32.29, 32.17, 32.08, 29.89, 25.40, 16.82. **HRMS** (APCI$^+$, m/z) calculated for C$_{20}$H$_{36}$N [M+H]$^+$: 290.28478; found: 290.28669.

N-hexadecylaniline (3r)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-hexadecanol (364 mg, 1.5 mmol) to afford **3r** (280 mg, 88% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.22 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.6 Hz, 2H), 3.60 (*br* s, 1H, NH), 3.14 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.2 Hz, 2H), 1.46-1.32 (m, 26H), 0.94 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.22, 131.88, 119.73, 115.36, 46.70, 34.65, 32.43, 32.41, 32.39, 32.34, 32.33, 32.30, 32.19, 32.10, 29.91, 25.42, 16.83. **HRMS** (APCI$^+$, m/z) calculated for C$_{22}$H$_{40}$N [M+H]$^+$: 318.31608; found: 318.31829. The spectral data are identical to the previously reported.[41]
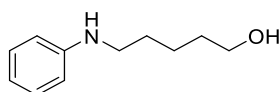
N-octadecylaniline (3s)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1-octadecanol (406 mg, 1.5 mmol) to afford **3s** (311 mg, 90% yield). White solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.23 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.55 (*br* s, 1H, NH), 3.15 (t, *J* = 6.8 Hz, 2H), 1.67 (p, *J* = 7.2 Hz, 2H), 1.47-1.34 (m, 30H), 0.96 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.23, 131.88, 119.75, 115.37, 46.71, 34.69, 32.47, 32.45, 32.43, 32.38, 32.37, 32.33, 32.23, 32.13, 29.94, 25.45, 16.85. **HRMS** (APCI$^+$, m/z) calculated for C$_{24}$H$_{44}$N [M+H]$^+$: 346.34738; found: 346.34949. The spectral data are identical to the previously reported.[42]

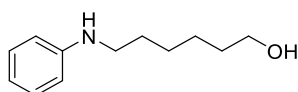### 4-(phenylamino)butan-1-ol (3t)
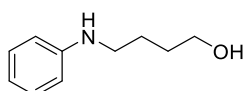
The compound was synthesized using aniline (93 mg, 1 mmol) and 1,4-butanediol (135 mg, 1.5 mmol) to afford **3t** (20 mg, 12% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 40:60). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.18 (t, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.15 (t, *J* = 6.4 Hz, 2H), 2.53 (*br* s, 2H), 1.71-1.69 (m, 4H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 150.95, 131.90, 120.11, 115.61, 65.26, 46.56, 33.02, 28.75. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{16}$NO [M+H]$^+$: 166.12319; found: 166.12374. The spectral data are identical to the previously reported.[43]

### 5-(phenylamino)pentan-1-ol (3ua)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1,5-pentanediol (156 mg, 1.5 mmol) to afford **3ua** (101 mg, 63% yield). Colorless oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 40:60). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.19 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 7.6 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.70 (*br* s, 2H),1.69-1.58 (m, 4H), 1.51-1.44 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.10, 131.90, 119.88, 115.43, 65.33, 46.57, 35.10, 31.97, 26.04. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{18}$NO [M+H]$^+$: 180.13884; found: 180.13961. The spectral data are identical to the previously reported.[44]

5-(phenylamino)hexan-1-ol (3va)

The compound was synthesized using aniline (93 mg, 1 mmol) and 1,6-hexanediol (177 mg, 1.5 mmol) to afford **3va** (130 mg, 67% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 60:40). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.19 (t, *J* = 7.2 Hz, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.73 (*br* s, 2H), 1.67-1.38 (m, 8H).**^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.14, 131.89, 119.85, 115.45, 65.38, 46.60, 35.30, 32.18, 29.64, 28.27.**HRMS** (APCI$^+$, m/z) calculated for C$_{12}$H$_{20}$NO [M+H]$^+$: 194.15449; found: 194.15532.

1-phenylazepane (3vb)
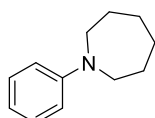
The compound was synthesized using aniline (93 mg, 1 mmol) and 1,6-hexanediol (177 mg, 1.5 mmol) to afford **3vb** (49 mg, 28% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.19 (t, *J* = 7.6 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 1.67-1.28 (m, 10H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.11, 131.89, 119.81, 115.36, 46.54, 32.21, 29.67. **HRMS** (APCI$^+$, m/z) calculated for C$_{12}$H$_{18}$N [M+H]$^+$: 176.14392; found: 176.14445. The spectral data are identical to the previously reported.[45]
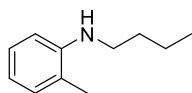
N-butyl-4-methoxyaniline (5a)
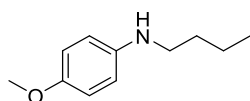
The compound was synthesized using 4-methoxyaniline (123 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5a** (139 mg, 78% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 6.82 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H, OCH$_3$), 3.28 (*br* s, 1H, NH), 3.09 (t, J = 7.2 Hz, 2H), 1.62 (p, J = 7.2 Hz, 2H), 1.46 (sext, J = 7.6 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 154.61, 145.61, 117.57, 116.67, 58.46, 47.37, 34.50, 23.04, 16.64. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{18}$NO [M+H]$^+$: 180.13884; found: 180.13965. The spectral data are identical to the previously reported.[38]

N-butyl-4-methylaniline (5b)
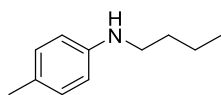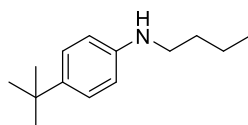

The compound was synthesized using 4-metylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5b** (125 mg, 77% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.08 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.43 (*br* s, 1H, NH), 3.17 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H, CH$_3$), 1.68 (p, J = 7.2 Hz, 2H), 1.51 (sext, J = 7.6 Hz, 2H), 1.05 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 149.07, 132.43, 128.93, 115.63, 46.79, 34.49, 23.11, 23.08, 16.68. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{18}$N [M+H]$^+$: 164.14392; found: 164.14446. The spectral data are identical to the previously reported.[38]
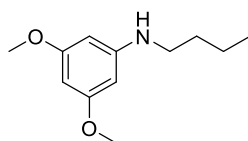
N-butyl-3-methylaniline (5c)
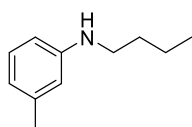
The compound was synthesized using 4-metylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5c** (87 mg, 53% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.14 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.6 Hz, 1H), 6.50-6.48 (m, 2H), 3.54 (*br* s, 1H, NH), 3.16 (t, J = 6.8 Hz, 2H), 2.35 (s, 3H, CH$_3$), 1.66 (p, J = 7.2 Hz, 2H), 1.51 (sext, J = 7.6 Hz, 2H), 1.03 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 151.32, 141.63, 131.79, 120.72, 116.18, 112.58, 46.42, 34.45, 24.35, 23.04, 16.65. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{18}$N [M+H]$^+$: 164.14392; found: 164.14479. The spectral data are identical to the previously reported.[38]
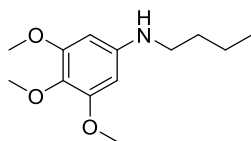
N-butyl-2-methylaniline (5d)

The compound was synthesized using 4-metylaniline (107 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5d** (51 mg, 32% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.18 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 6.70-6.64 (m, 2H), 3.47 (*br* s, 1H, NH), 3.19 (t, J = 6.8 Hz, 2H), 2.17 (s, 3H, CH$_3$), 1.69 (p, J = 7.6 Hz, 2H), 1.49 (sext, J = 8.0 Hz, 2H), 1.01 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 149.09, 132.67, 129.80, 124.33, 119.28, 112.27, 46.32, 34.42, 23.08, 20.12, 16.64. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{18}$N [M+H]$^+$: 164.14392; found: 164.14467. The spectral data are identical to the previously reported.[38]

### 4-(*tert*-butyl)-*N*-butylaniline (5e)

The compound was synthesized using 4-(*tert*-butyl)aniline (149 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5e** (144 mg, 70% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.31 (d, J = 8.8 Hz, 2H), 6.66 (d, J = 8.8 Hz, 2H), 3.52 (*br* s, 1H, NH), 3.19 (t, J = 6.8 Hz, 2H), 1.69 (p, J = 7.6 Hz, 2H), 1.52 (sext, J = 7.6 Hz, 2H), 1.39 (s, 9H, ^{t}Bu), 1.06 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 148.97, 142.50, 128.69, 115.15, 46.64, 36.55, 34.55, 34.32, 23.08, 16.68. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{24}$N [M+H]$^+$: 206.19087; found: 206.19198. The spectral data are identical to the previously reported.[46]

### *N*-butyl-3,5-dimethoxyaniline (5f)

The compound was synthesized using 3,5-dimethoxyaniline (153 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5f** (180 mg, 86% yield). Colorless oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10 to 80:20). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 5.90 (t, J = 2.0 Hz, 1H), 5.82 (d, J = 2.4 Hz, 2H), 3.76 (s, 6H, OCH$_3$), 3.09 (t, J = 6.8 Hz, 2H), 1.60 (p, J = 7.2 Hz, 2H), 1.44 (sext, J = 7.6 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 164.40, 153.19, 94.14, 92.07, 57.72, 46.32, 34.28, 22.99, 16.58. **HRMS** (APCI$^+$, m/z) calculated for C$_{12}$H$_{20}$NO$_2$ [M+H]$^+$: 210.14940; found: 210.15056.

N-butyl-3,4,5-trimethoxyaniline (5g)

The compound was synthesized using 3,4,5-trimethoxyaniline (183 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5g** (156 mg, 65% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10 to 70:30). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 5.82 (s, 2H), 3.80 (s, 6H, OCH$_3$), 3.74 (s, 3H, OCH$_3$), 3.06 (t, *J* = 7.2 Hz, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.41 (sext, *J* = 7.6 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 156.57, 148.05, 132.48, 92.84, 63.69, 58.53, 46.72, 34.34, 22.95, 16.55. **HRMS** (APCI$^+$, m/z) calculated for C$_{13}$H$_{22}$NO$_3$ [M+H]$^+$: 240.15997; found: 240.16133. The spectral data are identical to the previously reported.[47]
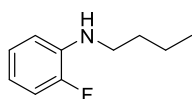
N-butyl-[1,1'-biphenyl]-4-amine (5h)
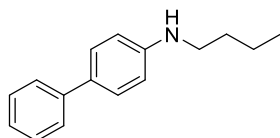
The compound was synthesized using [1,1'-biphenyl]-4-amine (169 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5h** (95 mg, 42% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.55-7.52 (m, 2H), 7.45-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.27-7.25 (m, 1H), 6.71-6.69 (m, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 1.64 (p, *J* = 7.6 Hz, 2H), 1.45 (sext, *J* = 7.6 Hz, 2H), 0.97 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 150.65, 144.03, 132.62, 131.32, 130.59, 128.93, 128.65, 115.61, 46.39, 34.37, 23.02, 16.63. **HRMS** (APCI$^+$, m/z) calculated for C$_{16}$H$_{20}$N [M+H]$^+$: 226.15957; found: 226.16054.
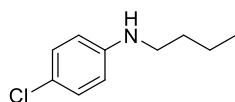
N-butyl-4-fluoroaniline (5i)
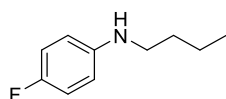
The compound was synthesized using 4-fluoroaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5i** (120 mg, 72% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 6.91 (t, *J* = 8.8 Hz, 2H), 6.55 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 2H), 3.42 (*br* s, 1H, NH), 3.08 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H), 1.46 (sext, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 158.32 (d, *J*$_{C-F}$=235.3 Hz), 147.65, 118.23 (d, *J*$_{C-F}$ = 22.3 Hz), 116.10 (d, *J*$_{C-F}$ = 7.4 Hz), 47.04, 34.33, 22.98, 16.57. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{15}$FN [M+H]$^+$: 168.11885; found: 168.11975.

N-butyl-3-fluoroaniline (5j)
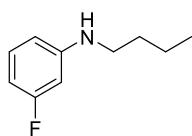
The compound was synthesized using 3-fluoroxyaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5j** (104 mg, 62% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.13-7.08 (m, 1H), 6.41-6.36 (m, 2H), 6.33-6.29 (m, 1H), 3.72 (*br* s, 1H, NH), 3.10 (t, J = 7.2 Hz, 2H), 1.62 (p, J = 7.6 Hz, 2H), 1.45 (sext, J = 7.6 Hz, 2H), 0.99 (t, J = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 166.98 (d, $J_{\text{C-F}}$ = 243.4 Hz), 153.01 (d, $J_{\text{C-F}}$ = 11.1 Hz), 132.84 (d, $J_{\text{C-F}}$ = 10.1 Hz), 111.23 (d, $J_{\text{C-F}}$ = 2.0 Hz), 105.96 (d, $J_{\text{C-F}}$ = 22.2 Hz), 101.78 (d, $J_{\text{C-F}}$ = 25.3 Hz), 46.22, 34.15, 22.93, 16.53. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{15}$FN [M+H]$^+$: 168.11885; found: 168.11952.

### *N*-butyl-4-2-fluoroaniline (5k)

The compound was synthesized using 2-fluoroaniline (111 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5k** (60 mg, 36% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.04-6.96 (m, 2H), 6.72 (t, J = 8.0 Hz, 1H), 6.65-6.60 (m, 1H), 3.88 (*br* s, 1H, NH), 3.17 (t, J = 7.2 Hz, 2H), 1.66 (p, J = 7.6 Hz, 2H), 1.47 (sext, J = 7.6 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 154.19 (d, $J_{\text{C-F}}$ = 238.9 Hz), 139.69 (d, $J_{\text{C-F}}$ = 11.1 Hz), 127.22 (d, $J_{\text{C-F}}$ = 2.0 Hz), 118.81 (d, $J_{\text{C-F}}$ = 7.1 Hz), 116.93 (d, $J_{\text{C-F}}$ = 19.2 Hz), 114.60 (d, $J_{\text{C-F}}$ = 3.0 Hz), 45.94, 34.24, 22.92, 16.55. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{15}$FN [M+H]$^+$: 168.11885; found: 168.11956. The spectral data are identical to the previously reported.[38]

N-butyl-4-chloroaniline (5l)

The compound was synthesized using 4-chloroaniline (128 mg, 1 mmol) and 1-butanol (111 mg, 1.5 mmol) to afford **5l** (117 mg, 64% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 100:0 to 95:5). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.10 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 3.60 (*br* s, 1H, NH), 3.07 (t, J = 6.8 Hz, 2H), 1.59 (p, J = 7.6 Hz, 2H), 1.42 (sext, J = 7.6 Hz, 2H), 0.96 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 149.72, 131.64, 124.19, 116.33, 46.43, 34.18, 22.91, 16.53. **HRMS** (APCI$^+$, m/z) calculated for C$_{10}$H$_{15}$ClN [M+H]$^+$: 184.08930; found: 184.09024. The spectral data are identical to the previously reported.[47]

### N^1,N^4-dibutylbenzene-1,4-diamine (5m)
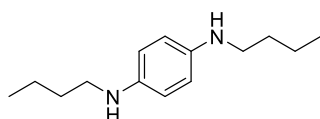
The compound was synthesized using benzene-1,4-diamine (108 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5m** (159 mg, 72% yield). Light orange solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 95:5 to 60:40). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 6.59 (s, 4H), 3.18-3.09 (m, 4H), 1.62 (p, *J* = 7.6 Hz, 4H), 1.46 (sext, *J* = 7.6 Hz, 4H), 1.00 (t, *J* = 7.6 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 143.63, 117.41, 47.79, 34.66, 23.08, 16.68. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{25}$N$_2$ [M+H]$^+$: 221.20177; found: 221.20297. The spectral data are identical to the previously reported.[48]

### N^4,$N^{4'}$-dibutyl-[1,1'-biphenyl]-4,4'-diamine (5oa)
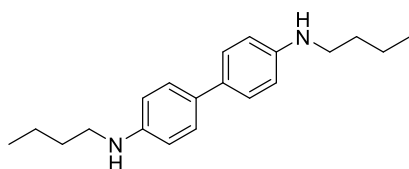
The compoundwas synthesized using benzidine (184 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5oa** (73 mg, 25% yield). Yellow solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.42 (d, *J* = 8.4 Hz, 4H), 6.69 (d, *J* = 8.4 Hz, 4H), 3.61 (*br* s, 2H, NH), 3.18 (t, *J* = 7.2 Hz, 4H), 1.66 (p, *J* = 7.2 Hz, 4H), 1.48 (sext, *J* = 7.2 Hz, 4H), 1.01 (t, *J* = 7.2 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 149.74, 133.20, 129.78, 115.71, 46.55, 34.44, 23.03, 16.65. **HRMS** (APCI$^+$, m/z) calculated for C$_{20}$H$_{29}$N$_2$ [M+H]$^+$: 297.23306; found: 297.23498.

N^4-butyl-[1,1'-biphenyl]-4,4'-diamine (5ob)
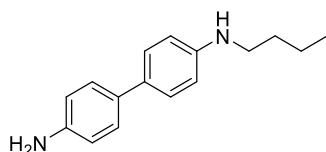
The compound was synthesized using benzidine (184 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5ob** (93 mg, 39% yield). Orange solid was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 70:30). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.42-7.38 (m, 4H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.61 (*br*s, 3H, NH), 3.17 (t, *J* = 7.2 Hz, 2H), 1.65 (p, *J* = 7.6 Hz, 2H), 1.48 (sext, *J* = 7.6 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 149.90, 147.45, 134.70, 132.96, 129.90, 129.83, 118.18, 115.71, 46.53, 34.40, 23.02, 16.65. **HRMS** (APCI$^+$, m/z) calculated for C$_{16}$H$_{21}$N$_2$ [M+H]$^+$: 241.17046; found: 241.17178.

4,4'-methylenebis(*N*-butylaniline) (5pa)
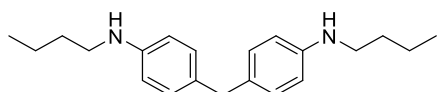
The compound was synthesized using 4,4'-methylenedianiline (198 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5pa** (101 mg, 32% yield). Light yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 90:10). ^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.06 (d, J = 8.0 Hz, 4H), 6.60 (d, J = 8.4 Hz, 4H), 3.84 (s, 2H), 3.44 (*br* s, 2H, NH), 3.15 (t, J = 6.8 Hz, 4H), 1.65 (p, J = 7.2 Hz, 4H), 1.49 (sext, J = 7.6 Hz, 4H), 1.03 (t, J = 7.2 Hz, 6H). ^{13}**C NMR** (101 MHz, CDCl$_3$): δ 149.38, 133.41, 132.28, 115.55, 46.68, 42.85, 34.48, 23.06, 16.68. **HRMS** (APCI$^+$, m/z) calculated for C$_{21}$H$_{31}$N$_2$ [M+H]$^+$: 311.24871; found: 311.25059.

## 4-(4-aminobenzyl)-*N*-butylaniline (5pb)
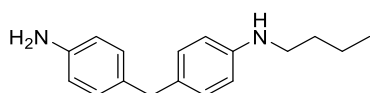
The compound was synthesized using 4,4'-methylenedianiline (198 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5pb** (108 mg, 43% yield). Light yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 70:30). ^{1}**H NMR** (400 MHz, CDCl$_3$): δ 7.07-7.03 (m, 4H), 6.65 (d, J = 8.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 3.85 (s, 2H), 3.53 (*br* s, 3H, NH), 3.15 (t, J = 7.2 Hz, 2H), 1.66 (p, J = 7.6 Hz, 2H), 1.50 (sext, J = 7.6 Hz, 2H), 1.04 (t, J = 7.6 Hz, 3H). ^{13}**C NMR** (101 MHz, CDCl$_3$): δ 149.42, 147.02, 134.89, 133.23, 132.33, 132.30, 117.99, 115.59, 46.69, 42.91, 34.46, 23.07, 16.71. **HRMS** (APCI$^+$, m/z) calculated for C$_{17}$H$_{23}$N$_2$ [M+H]$^+$: 255.18611; found: 255.18753.

N^1-butyl-4-methylbenzene-1,3-diamine (5q)
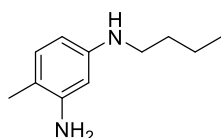
The compound was synthesized using 4-methylbenzene-1,3-diamine (122 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5q** (57 mg, 32% yield). Orange oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 95:5 to 70:30). ^{1}**H NMR** (400 MHz, CDCl$_3$): δ 6.86 (d, J = 8.0 Hz, 1H), 6.05 (d, J = 8.0 Hz, 1H), 6.00 (d, J = 2 Hz, 1H), 3.43 (*br* s, 3H, NH), 3.09 (t, J = 7.2 Hz, 2H), 2.09 (s, 3H, CH$_3$), 1.60 (p, J = 7.2 Hz, 2H), 1.44 (sext, J = 7.6 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}**C NMR** (101 MHz, CDCl$_3$): δ 150.72, 147.95, 133.68, 114.21, 106.66, 102.46, 46.70, 34.46, 23.02, 19.08, 16.63. **HRMS** (APCI$^+$, m/z) calculated for C$_{11}$H$_{19}$N$_2$ [M+H]$^+$: 179.15482; found: 179.15570.

N-butyl-2-(1H-pyrrol-1-yl)aniline (5r)
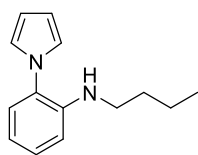
The compound was synthesized using 2-(1H-pyrrol-1-yl)aniline (158 mg, 1 mmol) and 1-butanol (222 mg, 3 mmol) to afford **5r** (121 mg, 57% yield). Yellow oil was obtained after column chromatography (SiO$_2$, Pentane/EtOAc 95:5 to 70:30). **^{1}H NMR** (400 MHz, CDCl$_3$): δ 7.33-7.29 (m, 1H), 7.21-7.19 (m, 1H), 6.87 (t, *J* = 2.0 Hz, 2H), 6.81-6.77 (m, 2H), 6.42 (t, *J* = 2.0 Hz, 2H), 3.83 (*br* s, 1H, NH), 3.16 (t, *J* = 7.2 Hz, 2H), 1.60 (p, *J* = 7.2 Hz, 2H), 1.42 (sext, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$): δ 146.75, 131.61, 129.76, 124.57, 118.78, 113.71, 112.09, 112.08, 45.93, 34.05, 22.93, 16.57. **HRMS** (APCI$^+$, m/z) calculated for C$_{14}$H$_{19}$N$_2$ [M+H]$^+$: 215.15482; found: 215.15568.

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