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An Improved Ruthenium Catalyst for the Environmentally Benign Amination of Primary and Secondary Alcohols

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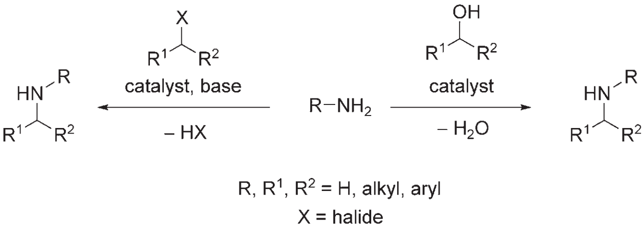
Abstract: The N-alkylation of amines in the presence of different ruthenium catalysts generated in situ was investigated. Among the various catalysts tested, the combination of [$Ru_3(CO)_{12}$] and *N*-phenyl-2-(dicyclohexylphosphanyl)pyrrole showed the best performance. By applying this novel catalyst, a variety of functionalized alcohols and amines were converted into the corresponding secondary amines in high yield.

Keywords: alcohols · amination · amines · ruthenium · transfer hydrogenation

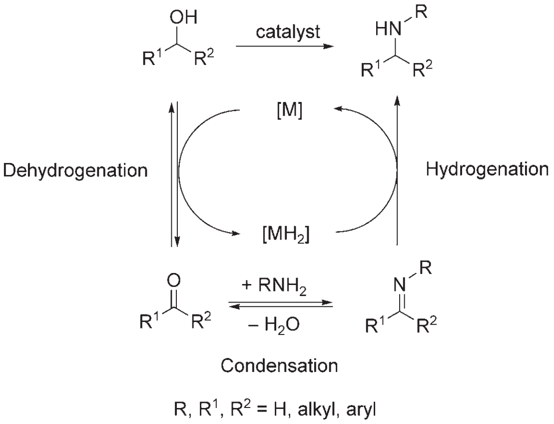
Introduction

A variety of amines is of significant importance for the bulk- and fine-chemical industries not only as building blocks for polymers and dyes, but also for the synthesis of new pharmaceuticals and agrochemicals.[1] Furthermore, a plethora of naturally bioactive compounds such as alkaloids, amino acids, and nucleotides contain amine groups. Despite numerous known procedures, the development of improved methods for the synthesis of amines continues to be a highly challenging and active area of research.[2] In the last decade, various catalytic aminations, such as palladium- and copper-catalyzed amination of aryl halides,[3] hydroamination,[4] and hydroaminomethylation[5] of olefins or alkynes, have received increased attention. However, less interest has been paid to the further development of catalytic alkylations of amines, such as reductive amination.[6]

As opposed to the well-known classic N-alkylations of amines with alkyl halides and reductive alkylations, an atom-economical[7] and environmentally attractive method is the N-alkylation of amines by using primary and secondary alcohols (Scheme 1). This domino reaction sequence is based on the dehydrogenation of the alcohol in situ to give the corresponding aldehyde or ketone. Subsequent imine formation followed by reduction with the hydrogen initially produced leads to the N-alkylated amine (Scheme 2). To obtain the desired amine, it is necessary that the hydrogenation of the imine is irreversible.



Scheme 1. Catalytic N-alkylation of amines with alcohols or alkyl halides.



Scheme 2. Catalytic hydrogen transfer in N-alkylation of amines with alcohols.

Interestingly, the same principle of the dehydrogenation–functionalization–hydrogenation sequence was recently used in alkane metathesis,[8] β alkylation of alcohols,[9] and C–C

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bond formation by the Knoevenagel reaction.[10] The advantages of this type of amination are the ubiquitous availability of alcohols and the high atom efficiency of the reaction sequence, which forms water as the only by-product. Moreover, as opposed to typical reductive aminations, it is possible to run these reactions in the absence of additional hydrogen. Hence, the reaction can be performed at ambient pressure.

Until now, N-alkylation of amines has been predominantly performed with various heterogeneous catalysts at high temperature and pressure. As an example, alkylation of aliphatic amines can be catalyzed by Raney Ni,[11] alumina, silica, or montmorillonite at temperatures greater than 200 °C.[12] Industrial processes that apply such amination reactions in the presence of heterogeneous catalysts involve the methylation of lower aliphatic amines with methanol.[13]

Although the alkylation of amines with alcohols has been frequently applied, there is no catalytic method available for functionalized and sensitive substrates (alcohols and amines) under milder conditions (<100 °C). To stimulate further applications of this chemistry, the development of more-active catalysts, which allow for a broader substrate scope, is highly desirable. A strategy to solve this problem might be the switch from heterogeneous to molecularly defined organometallic catalysts. Here, a variety of transition-metal complexes are known to have high activity for the dehydrogenation of alcohols to ketones and the hydrogenation of the resulting imines to amines via transfer hydrogenation, which are the basic requirements for the catalyst system.

The first homogeneous catalysts for N-alkylation of amines with alcohols were introduced by Grigg et al.[14] and Watanabe et al.[15] in 1981. Thereafter, ruthenium,[16] rhodium,[17] platinum,[18] and iridium complexes[17,19] have been described as homogeneous transition-metal catalysts for such reactions. Unfortunately, for most known homogeneous catalysts, high reaction temperatures (up to 215 °C) and long reaction times are required to obtain sufficient yields of the alkylated amine. With regard to the substrates, mainly primary alcohols have been used in the past because they are more reactive than secondary alcohols. With the exception of $[IrCp^*Cl_2]_2$ (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl), which was introduced by Fujita et al.,[20] and our recently developed ruthenium catalyst system,[21] no efficient catalyst is known for N-alkylation with secondary alcohols.

Abstract in German: Die Synthese von sekundären Aminen aus primären Aminen und Alkoholen ist eine salzfreie und damit umweltfreundliche Alternative zu den bisherigen Alkylierungsverfahren. Durch die in situ Dehydrierung–Kondensation–Hydrierung Reaktionsequenz, welche die Vorteile der Transferhydrierung nutzt, wurden die Produkte atomeffizient hergestellt. Ermöglicht wird dies durch die einen neuartigen Ruthenium Katalysator bestehend aus $[Ru_3(CO)_{12}]$ und *N*-phenyl-2-(dicyclohexylphosphanyl)pyrrol. Der robuste und wasserstabile Katalysator ermöglicht die Synthese von funktionalisierten Aminen in guten bis sehr guten Ausbeuten.

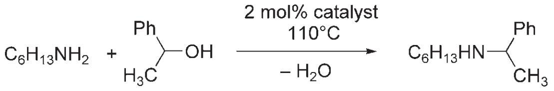
Results and Discussion

On the basis of our interest in intermolecular hydroaminations of olefins and alkynes,[22] we started a program to develop novel catalysts for the amination of alcohols, especially secondary alcohols. In an initial communication, we reported the use of ruthenium/*n*-butyldi-1-adamantylphosphine and ruthenium/tri-*o*-tolylphosphine as catalysts.[21] Herein, we summarize our results from this study and present a significantly improved in situ Ru catalyst that is highly active for the N-alkylation of various amines with different alcohols under comparably mild conditions (100–120 °C).

Initially, the reaction of *n*-hexylamine with 1-phenylethanol was studied as a model reaction. In general, the amination reaction was run without solvent at 110 °C for 24 h in the presence of 2 mol% $[Ru_3(CO)_{12}]$ and 6 mol% of the corresponding phosphine ligand. To obtain complete hydrogenation of the corresponding imine *n*-hexyl-(1-phenylethylidene)amine, an excess of alcohol with respect to amine (typically a 5:1 ratio was employed) was necessary.

At the beginning of our investigation, we focused our attention on the influence of different ruthenium precatalysts (Table 1). Basically, all ruthenium sources tested showed some activity for the conversion of the alcohol. However, only the ruthenium carbonyl cluster $[Ru_3(CO)_{12}]$ catalyzed the N-alkylation of *n*-hexylamine to a significant extent (Table 1, entry 1). Interestingly, the Shvo catalyst,[23] which is known to be highly active in transfer hydrogenations, showed high activity too, but mainly di-*n*-hexylamine was obtained as product (Table 1, entry 7). In the presence of all the other ruthenium complexes tested, the corresponding imine was formed as product. Apparently, the hydrogenation of imines seems to be problematic. These imines were the only observed "by-products" formed with our described catalyst system.

Table 1. Amination of 1-phenylethanol with hexylamine in the presence of different ruthenium precatalysts.[a]

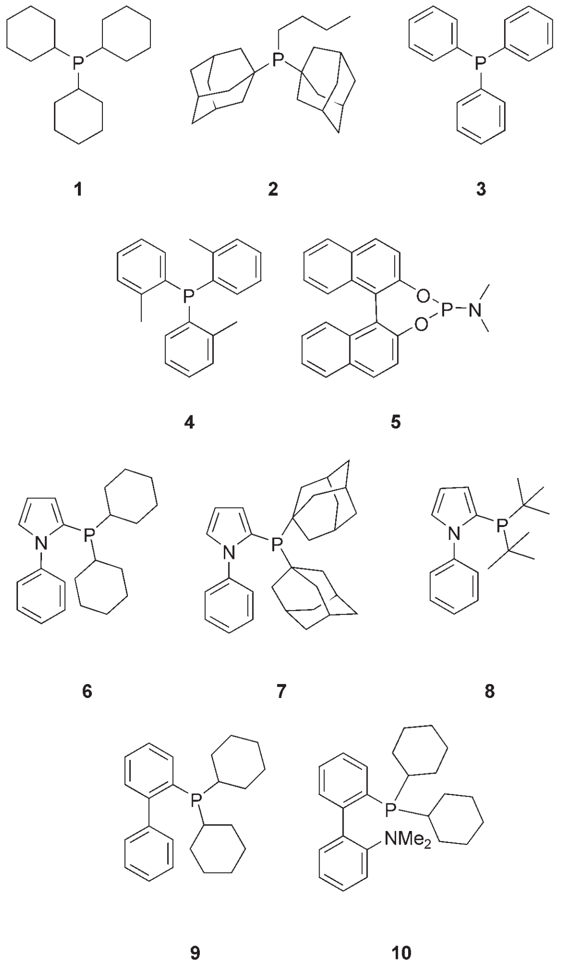


Entry	Catalyst	Conv. [%][b]	Yield [%][b]
1	$[Ru_3(CO)_{12}]$	100	74
2	$[RuCl_2(bpy)_2]\cdot 2H_2O$	22	<1
3	$[Ru(CO)(H)_2(PPh_3)_3]$	65	2
4	$[RuCp_2]$	18	2
5	$[RuCp^*Cl_2]_n$	52	0
6	$[RuCp^*(cod)Cl]$	48	0
7	Shvo catalyst	92	39

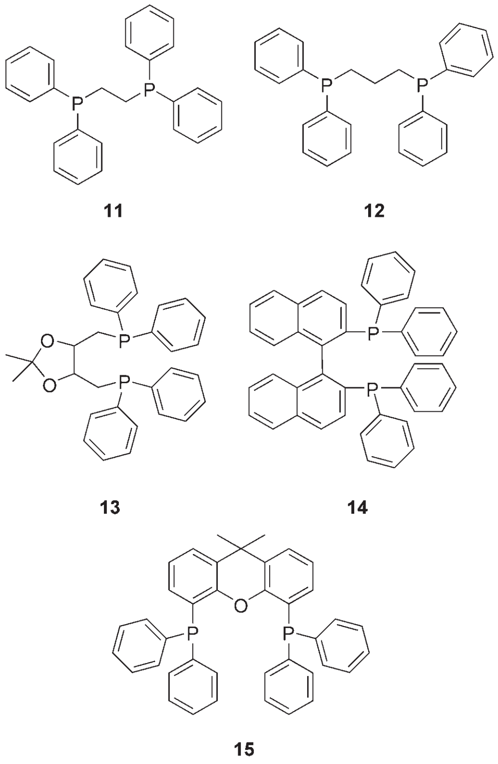
[a] Reaction conditions: 2 mol% catalyst, amine/alcohol = 1:5, 110 °C, 24 h. [b] Conversion and yield determined by GC analysis with hexadecane as internal standard. Conversions and yields are based on the conversion of hexylamine and the corresponding secondary amine. bpy = 2,2′-bipyridine, cod = 1,5-cyclooctadiene, Cp = cyclopentadienyl.

Next, we investigated the influence of monodentate and bidentate phosphine ligands in detail. For the sake of simplicity and practicability, instead of using defined phosphine–ruthenium complexes, we formed the corresponding ruthenium catalysts in situ from commercially available $[Ru_3(CO)_{12}]$ and phosphines **1**–**15** (Schemes 3 and 4) .

We employed the alkyl phosphines **1** and **2** (Table 2, entries 2 and 3), the aryl phosphines **3** and **4** (Table 2, entries 4 and 5), the monophos ligand **5**[24] (Table 2, entry 6), the pyrrole phosphines **6**, **7**, and **8** developed inhouse[25] (Table 2, entries 7–9), as well as the Buchwald ligands **9** and **10**[26] (Table 2, entries 10 and 11) as monodentate ligands. The reactivity of the $[Ru_3(CO)_{12}]$ complex is strongly dependent on the ligand. Notably, the reaction proceeded in 74 % yield without ligand. With respect to the electronic and steric properties of the ligands, no clear trend was observed. For example, electron-rich bulky phosphines such as tricyclohexylphosphine (**1**) and *n*-butyl-di-1-adamantyl-phosphine[27] (**2**) behaved quite differently (Table 2, entries 2 and 3). Similar divergent results were observed for aryl phosphines **3** and **4** (Table 2, entries 4 and 5) and the pyrrole ligands **6**–**8**. In the presence of racemic monophos ligand **5**, only low conversion

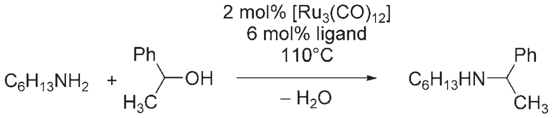


Scheme 3. Monodentate ligands for N-alkylation of *n*-hexylamine with 1-phenylethanol.



Scheme 4. Bidentate ligands for N-alkylation of *n*-hexylamine with 1-phenylethanol.

Table 2. N-alkylation of *n*-hexylamine with 1-phenylethanol in the presence of $[Ru_3(CO)_{12}]$ and different ligands.[a]



Entry	Ligand	Conv. [%][b]	Yield [%][b]
1	none	100	74
2	**1**	100	59
3	**2**	100	90
4	**3**	81	47
5	**4**	100	97
6	**5**	56	33
7	**6**	100	98
8	**7**	100	74
9	**8**	100	84
10	**9**	100	84
11	**10**	88	42
12	**11**	85	30
13	**12**	82	34
14	**13**	80	40
15	**14**	90	50
16	**15**	82	34

[a] Reaction conditions: 2 mmol *n*-hexylamine, 10 mmol 1-phenylethanol, 0.04 mmol $[Ru_3(CO)_{12}]$, 0.12 mmol monodentate ligand (or 0.06 mmol bidentate ligand), 110 °C, 24 h. [b] Conversion and yield determined by GC analysis with hexadecane as internal standard. Conversions and yields are based on the conversion of hexylamine and the corresponding secondary amine.

and yield were obtained. With regard to *N*-phenyl-2-(dicyclohexylphosphanyl)pyrrole, the Buchwald ligands **9** and **10** showed lower activity. Among the different ligands, **2**, **4**, and **6** showed the best performance (100% conversion, ≥90% yield) in the model reaction.

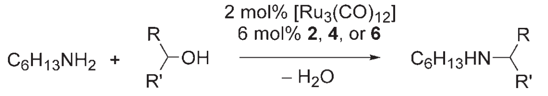
We were also interested in the effect of bidentate ligands. 1,2-Bis(diphenylphosphanyl)ethane (dppe) and 1,3-bis(diphenylphosphanyl)propane (dppp), *rac*-2,2-dimethyl-4,5-bis(diphenylphosphanylmethyl)-1,3-dioxolane (*rac*-diop; **13**), *rac*-2,2′-bis-(diphenylphosphanyl)-1,1′-binaphthyl (*rac*-binap; **14**), and xantphos (**15**) (Table 2, entries 12–16, respectively) showed low reactivity. In general, these ligands inhibit the dehydrogenation of the alcohol and the hydrogenation of the imine. This effect is explained by the fact that the coordination sites on the ruthenium are blocked by the bidentate ligand.

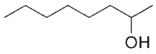
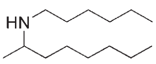
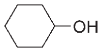
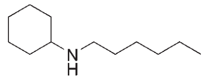
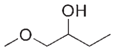
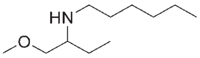
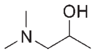
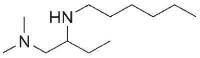
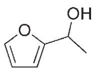
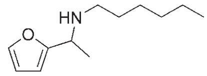
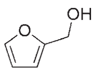
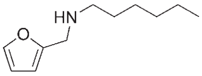
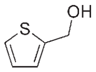
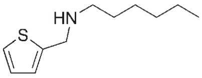
Owing to the superior performance, we compared the in situ system consisting of $[Ru_3(CO)_{12}]$/**2**, $[Ru_3(CO)_{12}]$/**4**, and $[Ru_3(CO)_{12}]$/**6** for the more-difficult reaction of *n*-hexylamine with 2-octanol, cyclohexanol, 1-methoxy-2-butanol, 1-(2-furyl)ethanol, and 2-thiophenylmethanol. In all cases the new catalyst with **6** gave significantly higher product yields compared to **2** and **4** (Table 3, entry 1 vs. 2 and 3, entry 10 vs. 7–9, entry 14 vs. 15, entry 18 vs. 19, entry 22 vs. 23). The reactions of eight different alcohols with *n*-hexylamine in the presence of the best catalyst system are shown in Table 3. At 110 °C, 2-octanol was converted into *N*-hexyl-2-octylamine in the presence of **6** in excellent yield (98%) and selectivity (Table 3, entry 1). In this case, the alcohol/amine ratio could be reduced without much problem to 1:2, whereas the catalyst system containing ligand **4** needed a larger excess of alcohol for the yield to reach 90%.

On the other hand, by decreasing the temperature to 100 °C, a higher alcohol/amine ratio of 1:5 was necessary for excellent yield (Table 3, entries 4 and 5). However, by lowering the temperature to 90 °C, the conversion and yield dropped to 64% and 23%, respectively (Table 3, entry 6). Apparently, the hydrogen-transfer step requires higher reaction temperatures. Below 100 °C, considerable amounts of the corresponding Schiff base were formed. In the presence of $[Ru_3(CO)_{12}]$/**6**, the less-reactive substrate cyclohexanol was converted into *N*-hexylcyclohexylamine in nearly quantitative yield (99%) at 100 °C (Table 3, entry 10). As opposed to ligand **6**, full conversion and yield were achieved with ligand **2** or **4** at 120 °C (Table 3, entries 7 and 8). Notably, functionalized alcohols such as 1-methoxy-2-butanol and 1-(*N*,*N*-dimethylamino)-2-propanol also gave the corresponding secondary amines in 87–93% yield (Table 3, entries 15 and 16). With ligand **4**, only decomposition of 1-methoxy-2-butanol was observed (Table 3, entry 14). Hence, synthetically interesting 1,2-aminoether derivatives as well as 1,2-diamines can be prepared by this route.

Apart from linear and cyclic aliphatic alcohols, we also tested different heterocyclic alcohols. We were pleased to find that 1-(2-furyl)ethanol, 2-furylmethanol, and 2-thio-

Table 3. N-alkylation of *n*-hexylamine with different alcohols in the presence of $[Ru_3(CO)_{12}]$/**2**, $[Ru_3(CO)_{12}]$/**4**, or $[Ru_3(CO)_{12}]$/**6**.[a]



Entry	Alcohol	Product	Ligand	Amine/ alcohol	*T* [°C]	Conv. [%][b]	Yield [%][b]
1			**6**	1:2	110	100	98
2			**2**	1:5	110	100	92
3			**4**	1:5	110	100	90
4			**6**	1:5	100	100	98
5			**6**	1:2	100	90	63
6			**6**	1:5	90	64	23
7			**2**	1:5	120	100	94
8			**4**	1:5	120	100	93
9			**4**	1:5	110	50	38
10			**6**	1:5	100	100	99
11[c]			**6**	1:5	100	84	65
12			**6**	1:2	100	100	78
13			**6**	1:5	90	50	29
14			**4**	1:5	110	80	<6
15			**6**	1:5	110	100	93
16			**6**	1:5	140	100	87 (78)[e]
17			**6**	1:5	120	100	73
18			**4**	1:5	110	100	49
19[d]			**6**	1:5	110	100	74
20			**6**	1:5	110	100	66
21[d]			**6**	1:5	110	100	49
22			**4**	1:5	110	100	70
23			**6**	1:5	110	96	84

[a] Reaction conditions: 2 mol% $[Ru_3(CO)_{12}]$, 6 mol% ligand, 24 h. [b] Conversion and yield determined by GC analysis with hexadecane as internal standard. Conversions and yields are based on the conversion of primary amines and the corresponding secondary amines. [c] 8 h reaction time. [d] 4 mol% $[Ru_3(CO)_{12}]$, 12 mol% ligand. [e] Yield of isolated product.

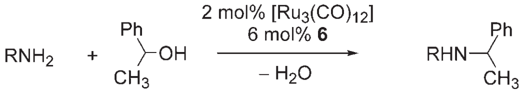
phenylmethanol (Table 3, entries 17, 20, and 23) gave the corresponding secondary *N*-hexylamines in moderate to good yields (66–84 %). Interestingly, at 110 °C the primary furyl alcohol led to more side reactions. Even at a higher catalyst loading of 4 mol %, the yield dropped to 49 % (Table 3, entry 21) owing to the formation of difuryl side products. This demonstrates the importance of the development of new catalysts for this transformation under milder conditions.

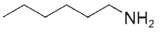
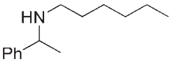
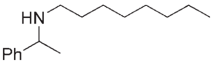
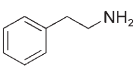
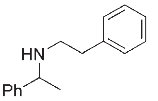
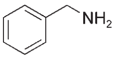
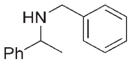
To demonstrate the usefulness of this novel amination catalyst, we explored the alkylation of various amines (Table 4). All catalytic reactions were run at the same reaction temperature to observe the effect of steric and electronic parameters. In some cases no full conversion was observed (Table 4, entries 5, 7, 9, and 13). However, the yield of the corresponding amination product could be optimized by increasing the reaction temperature. As expected, the reactivity and yield of the alkylated amine decreased in the order *n*-hexylamine > *n*-octylamine = 2-phenylethylamine > benzylamine > cyclooctylamine (Table 4, entries 1–3, 5, and 13). These observations can be explained by steric effects of the aliphatic amines, and in the case of aniline by the reduced nucleophilicity. With aniline, no conversion was observed (Table 4, entries 11 and 12). Electron-rich anilines (3,5-dimethoxyaniline and 2,4,6-trimethylaniline) also gave no reaction at all. By comparing the reaction of benzylamine, *p*-methoxybenzylamine, and *p*-chlorobenzylamine, it became clear that there is no strong electronic influence on the reaction (Table 4, entries 5, 7, 9). Notably, at 110 °C the sterically more hindered cyclooctylamine was converted into the desired amine in good yield (80 %) and selectivity (Table 4, entries 13 and 14).

Conclusions

In summary, we have presented a study on the ruthenium-catalyzed N-alkylation of amines with alcohols. We tested 22 different ruthenium complexes as amination catalysts. Among these, the novel in situ catalyst $[Ru_3(CO)_{12}]$/*N*-phenyl-2-(dicyclohexylphosphanyl)pyrrole showed the highest activity and selectivity. The alkylation reactions were performed under significantly milder conditions than those of most known aminations of alcohols and proceeded in good to excellent yield. The catalyst system showed its general applicability in the reaction of 16 different functionalized amines and alcohols.

Table 4. N-alkylation of different amines with 1-phenylethanol in the presence of $[Ru_3(CO)_{12}]$ and ligand **6**.[a]



Entry	Amine	Product	*T* [°C]	Conv. [%][b]	Yield [%][b]
1			110	100	98
2			110	100	92
3			110	98	90
4			120	100	96
5			110	88	68
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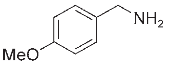
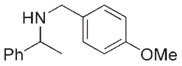
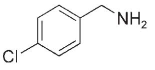
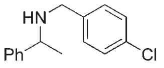
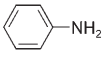
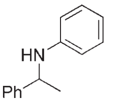
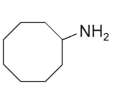
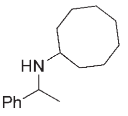
7			110	86	66
8			120	100	84
9			110	89	68
10			120	100	92
11			110	0	0
12			150	5	trace
13			110	80	58
14			120	98	80

[a] Reaction conditions: 1 mmol amine, 5 mmol 1-phenylethanol, 0.02 mmol $[Ru_3(CO)_{12}]$, 0.06 mmol ligand **6**, 110 °C, 24 h. [b] Conversion and yield determined by GC analysis with hexadecane as internal standard. Conversions and yields are based on the conversion of primary amines and the corresponding secondary amines.

Experimental Section

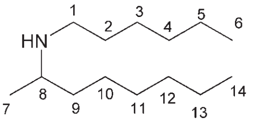
General Remarks

All reactions were carried out under argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros, and Strem and, unless otherwise noted, were used without further purification. Amines and alcohols were distilled under argon. All compounds were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy as well as MS and HRMS. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 300, AV 400, and AV 500 spectrometers. For new substances, complete assignment of the ^{1}H and ^{13}C signals is given. ^{1}H and ^{13}C NMR chemical shifts are reported relative to the center of the solvent resonance ($CDCl_3$: 7.25 (^{1}H), 77.0 ppm (^{13}C)). EI mass spectra were recorded on an AMD 402 spectrometer (70 eV, AMD Intectra GmbH). IR spectra were recorded on a Nicolet Magna 550 spectrometer. Elemental analysis was performed on a C/H/N/S Analysator 932 instrument (Leco). GC was performed on a Hewlett Packard HP 6890 chromatograph with an Optima 5 amine column (Machery-Nagel, 30 m × 0.25 μm, 0.5 μm film thickness, 50–8–200/5–8–260/5–8–280/5–8–300/20). All yields reported in Tables 1–4 were determined by GC with hexadecane as an internal standard. To verify the reproducibility, all reactions were carried out at least twice. In general, large-scale reactions were carried out with tri-*ortho*-tolylphosphine as ligand at 110–140 °C. Here the products were isolated in yields of up to 80 %. The synthesis and experimental data of *N*-(2-thiophenylmethyl)-*n*-hexyl-1-amine hydrochloride has been described previously.[21]

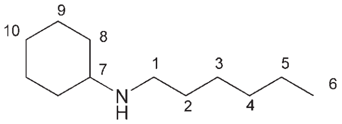
Syntheses

General procedure for the amination reaction: In a pressure tube (ACE) under argon atmosphere, $[Ru_3(CO)_{12}]$ (0.02 mmol) and **6** (0.06 mmol) were dissolved in the alcohol (5 mmol) and amine (1 mmol). The pressure tube was fitted with a teflon cap and heated at 110 °C for 24 h in an oil bath. The yield and conversion was determined by GC. In preparative reactions the excess alcohol was distilled. The residue was purified by column chromatography with hexane/ethyl acetate or chloroform/ethyl acetate to give the corresponding amine as an oil.

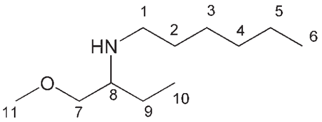
n-Hexyl(1-methylheptyl)amine: FTIR (neat): $\tilde{\nu} = 3290$ (br, NH), 2958 (s), 2926 (vs), 2856 (s), 1684 (m), 1467 (s), 1377 (m), 725 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$–0.87 (m, 6 H, 6-H, 14-H), 0.99 (d, $^{3}J = 6.2$ Hz, 3 H, 7-H), 1.12–1.31 (m, 16 H, 3-H–5-H,9-H–13-H), 1.32–1.48 (m, 3 H, 2-H, NH), 2.45–2.63 ppm (m, 3 H, 1-H, 8-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 14.0, 14.0 ($2\times CH_3$, C6, C14), 20.3 (CH_3, C7), 22.6 ($2\times CH_2$), 26.0 (CH_2), 27.1 (CH_2), 29.5 (CH_2), 30.4 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 37.2 (CH_2), 47.4 (CH_2), 53.2 ppm (CH, C8); MS (EI, 70 eV): m/z (%) = 214 (2) $[M+H]^+$, 213 (2) $[M]^+$, 212 (3) $[M-H]^+$, 198 (41) $[M-CH_3]^+$, 142 (26) $[M-C_5H_{11}]^+$, 129 (40), 128 (100) $[M-C_6H_{13}]^+$, 58 (17), 57 (13), 44 (24), 43 (23), 41 (15), 30 (11); HRMS: m/z calcd for $C_{14}H_{30}N$: 212.2373 $[M-H]^+$; found: 212.2363.



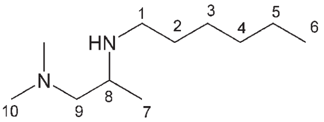
Cyclohexyl-*n*-hexylamine: FTIR (neat): $\tilde{\nu} = 3281$ (br, NH), 2958 (s), 2926 (vs), 2854 (s), 1684 (m), 1450 (s), 1379 (m), 1133 (m), 726 cm^{-1} (m); ^{1}H NMR (500, $CDCl_3$): $\delta = 0.86$ (t, $^{3}J_{5\text{-H},6\text{-H}} = 7.0$ Hz, 3 H, 6-H), 1.03 (m, 2 H, 8-H_{ax}), 1.13 (m, 1 H, 10-H_{ax}), 1.19–1.31 (m, 7 H, 3-H–5-H, 9-H_{ax}), 1.41–1.47 (m, 2 H, 2-H), 1.59 (m, $^{2}J_{10\text{-Heq},10\text{-Hax}} = 12.3$ Hz, 1 H, 10-H_{eq}), 1.70 (m, $^{2}J_{9\text{-Heq},9\text{-Hax}} = 13.2$ Hz, 2 H, 9-H_{eq}), 1.85 (m, $^{2}J_{8\text{-Heq},8\text{-Hax}} = 12.5$ Hz, 2 H, 8-H_{eq}), 2.38 (tt, $^{3}J_{7\text{-H},8\text{-Hax}} = 10.5$ Hz, $^{3}J_{7\text{-H},8\text{-Heq}} = 3.8$ Hz, 1 H, 7-H), 2.58 (t, $^{3}J_{1\text{-H},2\text{-H}} = 7.3$ Hz, 2 H, 1-H), 2.58 ppm (br, 1 H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3, C6), 22.6 (CH_2, C5), 25.1 (CH_2, C9), 26.2 (CH_2, C10), 27.1 (CH_2, C3), 30.5 (CH_2, C2), 31.8 (CH_2, C4), 33.6 (CH_2, C8), 47.1 (CH_2, C1), 56.9 ppm (CH, C7); MS (EI, 70 eV): m/z (%) = 183 (8) $[M^+]$, 140 (94) $[M-C_3H_7]^+$, 112 (100) $[M-C_5H_{11}]^+$, 56 (24), 55 (19), 43 (14), 41 (20), 30 (37), 29 (10); HRMS: m/z calcd for $C_{12}H_{25}N$: 183.1982; found: 183.1979.



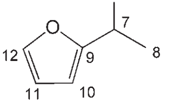
N-(1-methoxy-2-butyl)-*n*-hexylamine: FTIR (neat): $\tilde{\nu} = 3328$ (w, NH), 2958 (s), 2926 (s), 2873 (s), 2840 (s), 1463 (s), 1378 (s), 1198 (s, CO), 1112 cm^{-1} (s, CO); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.87$ (t, $^{3}J = 7.0$ Hz, 3 H, 6-H), 0.89 (t, $^{3}J = 7.6$ Hz, 3 H, 10-H), 1.24–1.33 (m, 6 H, 3-H–5-H), 1.36–1.54 (m, 4 H, 2-H, 9-H), 1.82 (br, 1 H, NH), 2.51–2.65 (m, 3 H, 1-H, 8-H), 3.25 (dd, $^{3}J_{7a\text{-H},8\text{-H}} = 7.1$ Hz, $^{2}J_{7a\text{-H},7b\text{-H}} = 9.5$ Hz, 1 H, 7a-H), 3.33 (s, 3 H, 11-H), 3.37 ppm (dd, $^{3}J_{7b\text{-H},8\text{-H}} = 4.3$ Hz, $^{2}J_{7a\text{-H},7b\text{-H}} = 9.5$ Hz, 1 H, 7b-H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 10.3$ (CH_3, C10), 14.1 (CH_3, C6), 22.7 (CH_2, C5), 24.2 (CH_2, C9), 27.1 (CH_2, C3), 30.4 (CH_2, C2), 31.8 (CH_2, C4), 47.5 (CH_2, C1), 58.9 (CH, C8), 59.0 (CH_3, C11), 74.8 ppm (CH_2, C7); MS (EI, 70 eV) m/z (%): 187 (1) $[M]^+$, 186 (1) $[M-H]^+$, 158 (12) $[M-C_2H_5]^+$, 143 (21), 142 (100) $[M-CH_2OCH_3]^+$, 116 (9) $[M-C_5H_{11}]^+$, 84 (7), 72 (12), 58 (38), 45 (13), 43 (16), 11 (52).



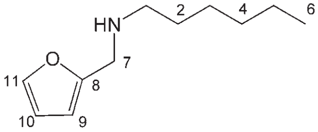
N^2-hexyl-*N*^{1},*N*^{1}-dimethylpropyl-1,2-diamine: FTIR (neat): 3303 (w, NH), 2958 (s), 2927 (s), 2854 (s), 2817 (s), 2792 (s), 2768 (s), 1458 (s), 1376 (m), 1337 (m), 1264 (m), 1143 (m), 1037 (m), 840 cm^{-1} (m); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.82$ (t, $^{3}J = 6.8$ Hz, 3 H, 6-H), 0.91 (d, $^{3}J = 6.2$ Hz, 3 H, 7-H), 1.18–1.30 (m, 6 H, 3-H–5-H), 1.38–1.48 (m, 2 H, 2-H), 1.84 (s, 1 H, NH), 1.94 (dd, $^{3}J_{8a\text{-H},9a\text{-H}} = 4.2$ Hz, $^{3}J_{8b\text{-H},9a\text{-H}} = 12.1$ Hz, 1 H, 9a-H), 2.12 (s, 6 H, 10-H), 2.22 (dd, $^{3}J_{8a\text{-H},9b\text{-H}} = 10.0$ Hz, $^{3}J_{8b\text{-H},9b\text{-H}} = 12.1$ Hz, 1 H, 9b-H), 2.35–2.43 (m, 1 H, 8-H), 2.57–2.67 ppm (m, 2 H, 1-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3, C6), 18.6 (CH_3, C7), 22.7 (CH_2, C5), 27.2 (CH_2, C3), 30.3 (CH_2, C2), 31.8 (CH_2, C4), 45.8 ($2\times CH_3$, C10), 47.8 (CH_2, C1), 50.6 (CH, C8), 66.4 ppm (CH_2, C9); MS (EI, 70 eV): m/z (%) = 128 (100) $[M-C_2H_6NCH_2]^+$, 58 (30) $[C_2H_6NCH_2]^+$.



N-(1-(2-furyl)ethyl-*n*-hexylamine: FTIR (neat): $\tilde{\nu} = 3316$ (br, NH), 3115 (w), 2957 (s), 2927 (s), 2856 (s), 2023 (w), 1938 (w), 1741 (m), 1505 (m), 1466 (m), 1372 (m), 1239 (m), 1150 (m), 1008 (m), 923 (m), 803 (m), 731 cm^{-1} (m); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.86$ (t, $^{3}J = 7.0$ Hz, 3 H, 6-H), 1.23–1.31 (m, 8 H, 2-H–5-H), 1.39 (d, $^{3}J_{7\text{-H},8\text{-H}} = 6.8$ Hz, 3 H, 8-H), 2.50 (t, $^{3}J = 6.8$ Hz, 2 H, 1-H), 3.83 (q, $^{3}J_{7\text{-H},8\text{-H}} = 6.8$ Hz, 1 H, 7-H), 6.11 (dd, $^{3}J_{9\text{-H},10\text{-H}} = 3.2$ Hz, $^{4}J_{9\text{-H},11\text{-H}} = 0.8$ Hz, 1 H, 10-H), 6.29 (dd, $^{3}J_{9\text{-H},10\text{-H}} = 3.2$ Hz, $^{3}J_{10\text{-H},11\text{-H}} = 1.9$ Hz, 1 H, 11-H), 7.33 ppm (dd, $^{3}J_{10\text{-H},11\text{-H}} = 1.9$ Hz, $^{4}J_{9\text{-H},11\text{-H}} =$ 0.8 Hz, 1 H, 12-H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3, C6), 20.4 (CH_3, C8), 22.6 (CH_2, C5), 27.1 (CH_2, C3), 30.2 (CH_2, C2), 31.8 (CH_2, C4), 47.3 (CH_2, C1), 51.3 (CH, C7), 105.1 (CH, C10), 109.8 (CH, C11), 141.3 (CH, C12), 158.1 ppm (C_q, C9); MS (EI, 70 eV): m/z (%) = 195 (1) $[M]^+$, 180 (34) $[M-CH_3]^+$, 124 (6), 110 (6), 96 (18), 95 (100), 41 (15); HRMS: m/z calcd for $C_{12}H_{21}ON$: 195.16177; found: 195.19127.



N-(2-furylmethyl)-*n*-hexylamine: FTIR (neat): $\tilde{\nu} = 3319$ (br, NH), 3119 (w), 2955 (s), 2927 (s), 2856 (s), 1505 (m), 1457 (m), 1148 (m), 1111 (m), 1010 (m), 919 (m), 803 (m), 729 (m), 599 cm^{-1} (m); ^{1}H NMR (500 $CDCl_3$): $\delta = 0.86$ (t, $^{3}J = 7.0$ Hz, 3 H, 6-H), 1.23–1.32 (m, 6 H, 3-H–5-H), 1.47 (m, 2 H, 2-H), 1.83 (br, 1 H, NH), 2.62 (t, $^{3}J_{1,2} = 7.2$ Hz, 2 H, 1-H), 3.76 (s, 2 H, 7-H), 6.15 (dd, $^{3}J_{9\text{-H},10\text{-H}} = 3.2$ Hz, $^{4}J_{9\text{-H},11\text{-H}} = 0.7$ Hz, 1 H, 9-H), 6.29 (dd, $^{3}J_{9\text{-H},10\text{-H}} = 3.2$ Hz, $^{3}J_{10,11} = 1.8$ Hz, 1 H, 10-H), 7.34 ppm (dd, $^{3}J_{10\text{-H},11\text{-H}} = 1.8$ Hz, $^{4}J_{9\text{-H},11\text{-H}} = 0.7$ Hz, 1 H, 11-H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3, C6), 22.6 (CH_2, C5), 27.0 (CH_2, C3), 29.9 (CH_2, C2), 31.7 (CH_2, C4), 46.2 (CH_2, C7), 49.2 (CH, C1), 106.8 (CH, C9), 110.0 (CH, C10), 141.7 (CH, C11), 154.0 ppm (C_q, C8); MS (EI, 70 eV): m/z (%) = 181 (1) $[M]^+$, 110 (26), 96 (8), 81 (100); HRMS: m/z calcd for $C_{11}H_{19}ON$: 181.14612; found: 181.14622.



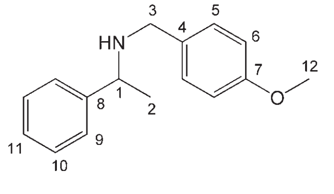
n-Hexyl(1-phenylethyl)amine:[28] FTIR (neat): $\tilde{\nu}=3334$ (br, NH), 3083, 3062, 3026 (w), 2958 (s), 2926 (vs), 2856 (s), 1492 (m), 1452 (vs), 1261 (m), 1130 (m), 1079 (m), 1027 (m), 804 (m), 761 (m), 700 cm^{-1} (s); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.86$ (t, $^{3}J=6.9$ Hz, 3H, CH$_3$), 1.18–1.32 (m, 6H, CH$_2$), 1.34 (d, $^{3}J=6.5$ Hz, 3H, CH$_3$), 1.38–1.51 (m, 2H, CH$_2$), 2.44 (m, 2H, CH$_2$), 3.72 (q, $^{3}J=6.5$ Hz, 1H, CH), 7.20–7.35 ppm (m, 5H, H$_{Ar}$); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$ (CH$_3$), 22.6 (CH$_2$), 24.3 (CH$_3$), 27.0 (CH$_2$), 30.2 (CH$_2$), 31.7 (CH$_2$), 47.9 (CH$_2$), 58.4 (CH), 126.5 (CH, C$_{Ar}$), 126.8 (CH, C$_{Ar}$), 128.3 (CH, C$_{Ar}$), 145.9 ppm (C$_q$, C$_{Ar}$); MS (EI, 70 eV): *m/z* (%)=205 (4) [M]$^+$, 190 (47) [$M-$CH$_3$]$^+$, 134 (25) [$M-$C$_5$H$_{11}$]$^+$, 106 (25), 105 (100) [PhCHCH$_3$]$^+$, 79 (11), 77 (11), 43 (13), 30 (45), 28 (22), 27 (11); HRMS: *m/z* calcd for C$_{14}$H$_{23}$N: 205.18304; found: 205.18278.

n-Octyl(1-phenylethyl)amine:[29] FTIR (neat): 3333 (br, NH), 3083, 3062, 3025 (w), 2958 (s), 2925 (vs), 2854 (s), 1492 (m), 1452 (s), 1132 (m), 761 (m), 700 cm^{-1} (s); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=0.87$ (t, $^{3}J=6.5$ Hz, 3H, CH$_3$), 1.17–1.28 (m, 10H, CH$_2$), 1.34 (d, $^{3}J=6.6$ Hz, 3H, CH$_3$), 1.38–1.51 (m, 2H, CH$_2$), 2.44 (m, 2H, CH$_2$), 3.74 (q, $^{3}J=6.6$ Hz, 1H, CH), 7.19–7.35 ppm (m, 5H, H$_{Ar}$); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=14.0$ (CH$_3$), 22.6 (CH$_2$), 24.4 (CH$_3$), 27.3 (CH$_2$), 29.2 (CH$_2$), 29.5 (CH$_2$), 30.3 (CH$_2$), 31.8 (CH$_2$), 47.9 (CH$_2$), 58.4 (CH), 126.5 (CH, C$_{Ar}$), 126.7 (CH, C$_{Ar}$), 128.3 (CH, C$_{Ar}$), 145.9 ppm (C$_q$, C$_{Ar}$); MS (EI, 70 eV): *m/z* (%)= 233 (3) [M]$^+$, 218 (71) [$M-$CH$_3$]$^+$, 134 (35) [$M-$C$_7$H$_{15}$]$^+$, 106 (24), 105 (100) [PhCHCH$_3$]$^+$, 85 (12), 71 (20), 58 (36), 56 (13), 43 (18), 41 (15), 30 (31), 29 (12); HRMS: *m/z* calcd for C$_{16}$H$_{27}$N: 233.21436; found: 233.21345.

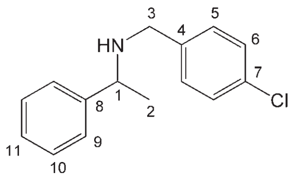
2-Phenylethyl(1-phenylethyl)amine:[30] FTIR (neat): 3318 (br, NH), 3083, 3061, 3026 (w), 2960 (m), 2924 (m), 2835 (m), 1494 (m), 1452 (m), 1130 (m), 1079 (m), 1027 (m), 751 (m), 699 cm^{-1} (s); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=1.24$ (d, $^{3}J=6.6$ Hz, 3H, CH$_3$), 1.40 (s, 1H, NH), 2.59–2.72 (m, 4H, CH$_2$), 3.69 (q, $^{3}J=6.6$ Hz, 1H, CH), 7.06–7.24 ppm (m, 10H, H$_{Ar}$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=24.3$ (CH$_3$), 36.4 (CH$_2$), 49.0 (CH$_2$), 58.2 (CH), 126.0 (CH, C$_{Ar}$), 126.5 (CH, C$_{Ar}$), 126.8 (CH, C$_{Ar}$), 128.4 (2× CH, C$_{Ar}$), 128.6 (CH, C$_{Ar}$), 140.0 (C$_q$), 145.5 (C$_q$); MS (EI, 70 eV): *m/z* (%)=225 (1) [M]$^+$, 224 (1) [$M-$H]$^+$, 210 (8) [$M-$CH$_3$]$^+$, 134 (100) [$M-$C$_7$H$_7$]$^+$, 105 (100) [PhCHCH$_3$]$^+$, 91 (23) [PhCH$_2$]$^+$, 77 (35) [Ph]$^+$; HRMS: *m/z* calcd for C$_{16}$H$_{18}$N$_1$: 224.14338 [$M-$H]$^+$; found: 224.14310.

Benzyl(1-phenylethyl)amine:[31] FTIR (neat): $\tilde{\nu}=3316$ (br, NH), 3084 (w), 3062 (m), 3036 (m), 2969 (m), 2925 (w), 2864 (w), 1686 (m), 1602 (m), 1493 (s), 1493 (s), 1377 (m), 761 (s), 738 (m), 700 cm^{-1} (vs); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.38$ (d, $J=6.5$ Hz, 3H), 1.58 (s, 1H, NH), 3.62 and 3.68 (ABX system, $J=13.1$ Hz, 2H), 3.83 (q, $J=6.5$ Hz, 1H), 7.21–7.40 ppm (m, 10H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=24.5$ (CH$_3$), 51.6 (CH$_2$), 57.7 (CH), 126.7 (CH, C$_{Ar}$), 126.8 (CH, C$_{Ar}$), 126.9 (CH, C$_{Ar}$), 128.1 (CH, C$_{Ar}$), 128.3 (CH, C$_{Ar}$), 128.4 (CH, C$_{Ar}$), 140.6 (C$_q$, C$_{Ar}$), 145.6 ppm (C$_q$, C$_{Ar}$); MS (EI, 70 eV): *m/z* (%)=211 (2), [M]$^+$, 197 (11), 196 (67) [$M-$CH$_3$]$^+$, 105 (15) [PhCHCH$_3$]$^+$, 91 (100) [PhCH$_2$]$^+$, 77 (10); HRMS: *m/z* calcd for C$_{15}$H$_{17}$N: 211.13609; found: 211.136024.

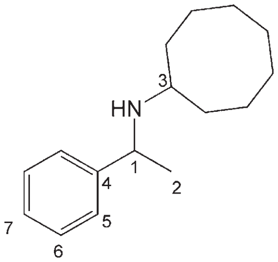
(4-Methoxybenzyl)(1-phenylethyl)amine:[32] FTIR (neat): $\tilde{\nu}=3328$ (br, NH), 3061 (m), 3026 (m), 2995 (m), 2959 (m), 2930 (m), 2833 (m), 1611 (m), 1512 (s), 1451 (m), 1301 (m), 1247 (s), 1036 (m), 822 (m), 761 (m), 702 cm^{-1} (m); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=1.37$ (d, $^{3}J=6.6$ Hz, 3H, 2-H), 1.59 (s, 1H, NH), 3.51 and 3.59 (ABX system, $^{2}J=12.9$ Hz, 2H, 3-H), 3.78 (s, 3H, 12-H), 3.80 (q, $J=6.6$ Hz, 1H, 1-H), 6.81–6.86 (m, 2H, 5-H), 7.17–7.22 (m, 2H, 6-H), 7.23–7.28 (m, 1H, 11-H), 7.32–7.37 (m, 4H, 9-H, 10-H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=24.6$ (CH$_3$, C2), 51.1 (CH$_2$, C3), 55.3 (CH$_3$, C12), 57.5 (CH, C1), 113.8 (CH, C6), 128.5 (CH, C10), 126.8 (CH, C9), 127.0 (CH, C11), 129.4 (CH, C5), 132.9 (C$_q$, C4), 145.7 (C$_q$, C8), 158.6 ppm (C$_q$, C7); MS (EI, 70 eV): *m/z* (%)=241 (11) [M]$^+$, 226 (99) [$M-$CH$_3$]$^+$, 136 (33), 121 (100) [CH$_2$C$_6$H$_4$OMe]$^+$, 105 (35), 91 (16), 77 (31); HRMS: *m/z* calcd for C$_{16}$H$_{19}$N$_1$O$_1$: 241.14612; found: 241.146301.



(4-Chlorobenzyl)(1-phenylethyl)amine: FTIR (neat): $\tilde{\nu}=3331$ (br, NH), 3082 (s), 3061 (s), 3025 (m), 2962 (m), 2924 (m), 2832 (m), 1490 (s), 1451 (m), 1125 (m), 1088 (s), 1015 (m), 761 (m), 701 cm^{-1} (m); ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=1.38$ (d, $^{3}J=6.6$ Hz, 3H, CH$_3$), 3.55 and 3.63 (ABX system, $^{2}J=12.9$ Hz, 2H, CH$_2$), 3.79 (q, $^{3}J=6.6$ Hz, 1H, 1-H), 7.20–7.35 (m, 9H, H$_{Ar}$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=24.5$ (CH$_3$, C2), 50.9 (CH$_2$, C3), 57.5 (CH, C1), 126.7 (CH, C9), 128.5 (CH, C10), 127.1 (CH, C11), 128.5 (CH), 129.5 (CH) (C5, C6), 132.5 (C$_q$, C7), 139.1 (C$_q$, C4), 145.4 ppm (C$_q$, C8); MS (EI, 70 eV): *m/z* (%): 230 (100) [$M-$CH$_3$]$^+$, 125 (100) [ClC$_6$H$_4$CH$_2$]$^+$, 105 (27) [C$_6$H$_5$CH$_2$CH$_3$]$^+$; HRMS: *m/z* calcd for C$_{14}$H$_{13}$N$_1$Cl$_1$: 230.07310 [$M-$CH$_3$]$^+$; found: 230.072815.



Cyclooctyl(1-phenylethyl)amine: FTIR (neat): $\tilde{\nu}=3308$ (br, NH), 3061 (w), 3024 (w), 2920 (vs), 2852 (s), 1668 (m), 1492 (w), 1481 (m), 1471 (m), 1367 (m), 1123 (m), 760 (s), 738 (m), 700 cm^{-1} (s); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=1.31$ (d, $^{3}J=6.6$ Hz, 3H, 2-H), 1.35–1.80 (m, 15H, CH$_2$, NH), 2.49 (m, 1H, 3-H), 3.86 (q, $^{3}J=6.6$ Hz, 1H, 1-H), 7.19–7.33 ppm (m, 5H, H$_{Ar}$); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=23.6$ (CH$_2$), 24.2 (CH$_2$), 24.9 (CH$_3$, C2), 25.6 (CH$_2$), 27.1 (CH$_2$), 27.6 (CH$_2$), 31.0 (CH$_2$), 33.9 (CH$_2$), 54.3 (CH, C3), 54.9 (CH, C1), 126.5 (CH, C5), 126.7 (CH, C7), 128.3 (CH, C6), 146.3 ppm (C$_q$, C4); MS (EI, 70 eV): *m/z* (%)= 231 (17) [M]$^+$, 216 (32) [$M-$CH$_3$]$^+$, 188 (11), 160 (33) [$M-$C$_5$H$_{11}$]$^+$, 147 (19), 126 (15), 106 (32), 105 (100) [PhCHCH$_3$]$^+$, 104 (11), 84 (12), 79 (11), 77 (10), 56 (39), 43 (12), 41 (10); HRMS: *m/z* calcd for C$_{16}$H$_{25}$N: 231.19870; found: 231.19847.



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