DOI: 10.1002/adsc.200900548

Synthesis of Selectively Mono-N-Arylated Aliphatic Diamines *via* Iridium-Catalyzed Amine Alkylation

Benoît Blank,[a] Stefan Michlik,[a] and Rhett Kempe[a,*]

[a] Lehrstuhl für Anorganische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany
Fax: (+49)-(0)921-55-2157; phone: (+49)-(0)921-55-2541; e-mail: kempe@uni-bayreuth.de

Received: August 4, 2009; Published online: November 18, 2009

Abstract: A highly selective phosphorus/nitrogen (P,N) ligand-based iridium catalyst system efficiently catalyzes the reaction of arylamines with unprotected amino alcohols, yielding N-arylated aliphatic diamines in yields of up to 93%. The reaction can be performed with a wide variety of branched and linear amino alcohols in combination with various aminopyridines or substituted anilines.

Keywords: amine alkylation; amino alcohols; diamines; iridium

Introduction

Amines are a very important class of compounds. They are the basis of many bulk and fine chemical intermediates, additives, dyes, agrochemicals and pharmaceutical products.[1] Especially di- and polyamines are of great interest since such motifs can be found in many pharmacologically active compounds.[2] In addition, such compounds are used intensively as ligands for catalysts, organometallic reagents and coordination compounds.[3] The development of novel methods for the selective preparation of secondary amines is hence of general interest. The best-known reaction for the alkylation of amines is the nucleophilic substitution reaction of amines with haloalkanes,[4] which is only fairly selective and affords mono, di- and trialkylated amines as well as quaternary ammonium salts. More selective methods are (a) the reductive amination of carbonyl compounds,[5] which is usually performed in two separate steps, (b) the transition metal-catalyzed hydroamination,[6] which is still very challenging for the intermolecular coupling of alkenes with amines, and (c) the hydroaminomethylation[7] of alkenes which requires high-pressure equipment and often lacks a satisfactory regioselectivity in the hydroformylation step. A promising development in this field which has received a lot of attention recently is the direct Ru-[8] or Ir-catalyzed[9,10] alkylation of amines using alcohols.[11]

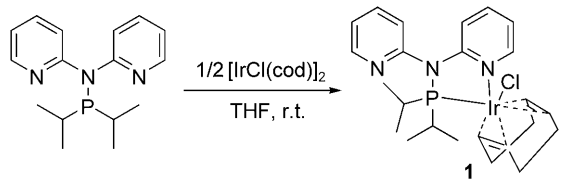
The selective preparation of alkyl diamines bearing one N-aryl moiety and one primary amino function is still very challenging. The Pd-catalyzed aryl amination, which is a very well developed and highly efficient method for the formation of N-aryl bonds,[12] is not really suited for the preparation of selectively mono-N-arylated aliphatic diamines. The main problem is the preferred N,N′-diarylation of the employed aliphatic diamine.[12] In order to establish monoarylation *via* catalytic aryl amination pathways the diamine has to be used in a large excess compared to the aryl halide.[13] The selective catalytic arylations of diamines with chemically inequivalent amine functionalities (branched alkyl backbone) have, to the best of our knowledge, not yet been described. Similar inconveniences as above also apply to the thermic reaction of aryl halides with aliphatic diamines, lacking a selective reaction pathway.[14]

Herein we present a simple and highly selective protocol for the preparation of mono-N-arylated aliphatic diamines *via* Ir-catalyzed alkylation of aromatic amines with unprotected amino alcohols.

Results and Discussion

We recently reported on a novel class of P,N ligand[15] stabilized iridium catalysts[16] that efficiently perform the alkylation of (hetero)aromatic amines with primary alcohols under rather mild reaction conditions. The catalyst is generated *in situ* by simply mixing the corresponding P,N ligand with $[IrCl(cod)]_2$ in THF (Scheme 1).

P,N-iridium complex **1**, bearing isopropyl substituents on the phosphorus center, was in former studies determined to have the best activity for the selective alkylation of aromatic amines with alcohols. The molecular structure of **1** is shown in Figure 1.



Scheme 1. Preparation of the catalyst **1**.

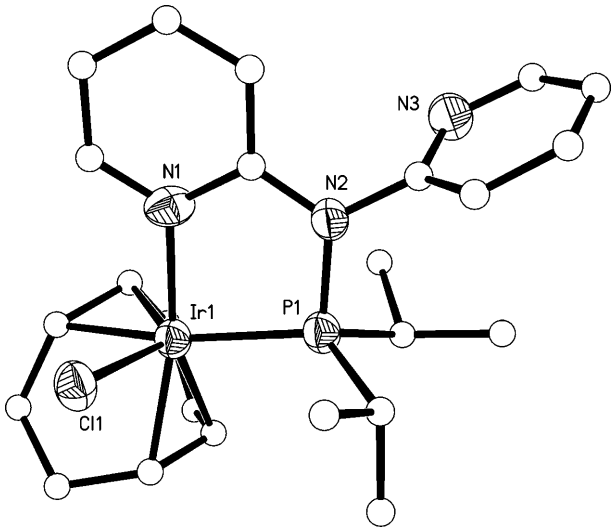
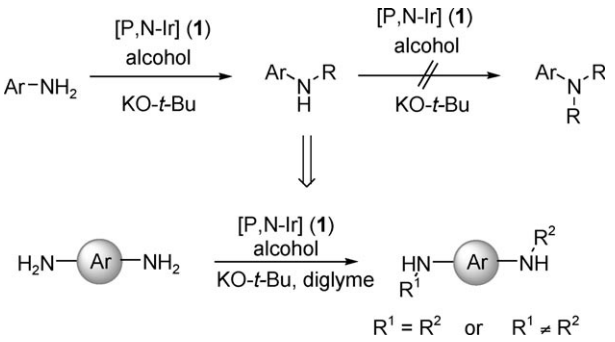


Figure 1. Molecular structure of $[Py_2NP(i\text{-}Pr)_2Ir(cod)Cl]$ (**1**). Selected bond lengths [Å] and angles [°]: Ir1–N1 2.119(3), Ir1–P1 2.2830(10), Ir1–Cl1 2.5459(10), P1–N2 1.730(3), N1–Ir1-P1 80.86(9), N1–Ir1–Cl1 82.93 (9), P1–Ir1–Cl1 103.78(3); N2–P1–Ir1 101.72(11).

This P,N-iridium complex does not only exhibit an excellent catalytic activity and efficiency for the alkylation of amines with simple alcohols (catalyst loadings as low as 0.1 mol% are possible), but also allows the reaction to be performed under mild reaction temperatures of only 70 °C,[17] which is unprecedented since other catalytic systems require temperatures from 110 to 150 °C for the same reaction.

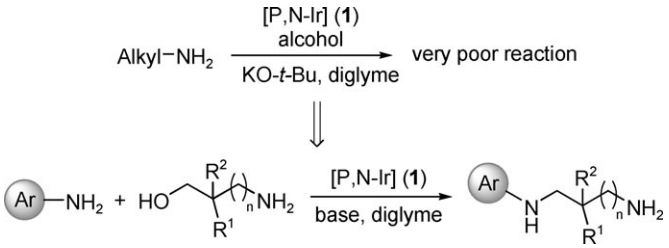
Next to this efficiency, in our former studies we also observed that complex **1** has a very narrow selectivity profile and always leads to a selective monoalkylation of the amine, regardless of the amount of added alcohol, since the secondary amine formed in the reaction does not react further. This selectivity for monoalkylation was hence already exploited in the development of a simple and efficient method for the preparation of symmetric and non-symmetric N,N′-dialkylated aromatic diamines (Scheme 2).[17] Interestingly, catalyst **1** allows only primary alcohols to be used for these transformations whereas secondary alcohols do not react.

We also observed another selectivity of catalyst **1** allowing only the efficient alkylation of aromatic amines, whereas the reaction with aliphatic amines



Scheme 2. Selectivity of **1** for monoalkylation of amines and preparation of N,N′-dialkylated diamines.

proceeded rather poorly.[16] Since such aliphatic amino functions cannot be alkylated with the catalyst system based on **1** we wanted to exploit this selectivity by employing readily available amino alcohols in combination with aromatic amines in order to prepare selectively mono-N-arylated aliphatic diamines that are yet inaccessible (Scheme 3).



Scheme 3. Preparation of mono-N-aryl aliphatic diamines.

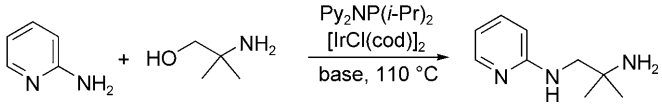
Evaluation of the Reaction Conditions

The first reaction for the alkylation of aromatic amines using amino alcohols was carried out under the previously optimized reaction conditions[16] with catalyst **1**, now employing 2-aminopyridine and 2-amino-2-methyl-1-propanol as test substrates.

Although the high selectivity of **1** for the alkylation of only the aromatic amino function was maintained in the first run, only a poor conversion and yield was obtained (Table 1, entry 1). Therefore a systematic re-evaluation of the reaction conditions was performed (Table 1).

In order to determine whether the low yield resulted from a wrong stoichiometry of starting materials or a higher catalyst deactivation, the reaction was repeated using an excess of base and amino alcohol along with an increased catalyst loading of 5 mol% **1**. The expected diamine was now obtained in 60% yield (Table 1, entry 2), which shows that the reaction is generally possible, but still not very efficient. The base was therefore replaced by NaO-*t*-Bu. Interestingly, this simple exchange now allowed the isolation of

Table 1. Optimization of the reaction conditions for the use of amino alcohols.[a]



Entry	Cat. Loading [mol% **1**]	Equiv. Base	Base	Equiv. Amino Alcohol	Yield [%][b]
1	2.0	1.1	KO-*t*-Bu	1.1	14
2	5.0	3.3	KO-*t*-Bu	1.5	60
3	5.0	3.3	NaO-*t*-Bu	1.5	85
4	5.0	3.3	NaO-*t*-Bu	1.5	49[c]
5	1.0	1.1	NaO-*t*-Bu	1.1	84
6	0.5	1.1	NaO-*t*-Bu	1.1	61

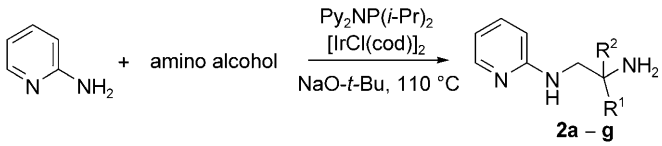
[a] *Reaction conditions:* 1.0 mmol 2-aminopyridine, 1.1–1.5 mmol amino alcohol, 0.25–2.5 mol% $[IrCl(cod)]_2$, 0.5–5.0 mol% $Py_2NP(i\text{-}Pr)_2$, 1.1–3.3 mmol base, 0.3 mL diglyme, 0.2 mL THF, 110 °C, 24 h.
[b] Isolated yield.
[c] Temperature: 70 °C.

the expected diamine in good yield (Table 1, entry 3). Next we tried to perform the reaction under milder reaction conditions at a temperature of 70 °C, which unfortunately led to a decrease of the yield (Table 1, entry 4). It seems that the reaction with amino alcohols requires more drastic conditions than for simple alcohols and therefore a temperature of 110 °C was used for further reactions. Since the low yield of the first run was simply due to the use of KO-*t*-Bu, now using NaO-*t*-Bu the amount of base and amino alcohol could again be reduced to 1.1 equivalents along with a lowered catalyst loading of 1.0 mol% **1**, still affording good yields of the N-arylated diamine (Table 1, entry 5). Further reduction of the catalyst loading to 0.5 mol% **1** was not possible, as a significant decrease of yield was observed (Table 1, entry 6).

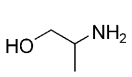
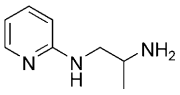
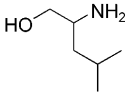
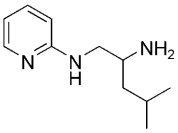
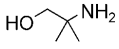
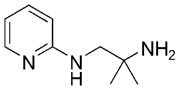
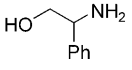
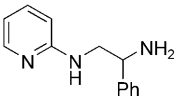
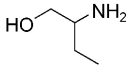
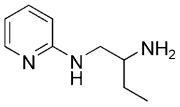
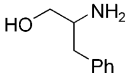
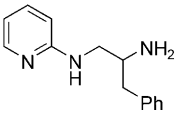
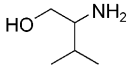
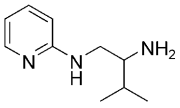
Alkylation of Aromatic Amines with Amino Alcohols

Having successfully optimized the reaction conditions, a variety of different branched amino alcohols was

Table 2. General application of several branched amino alcohols.[a]

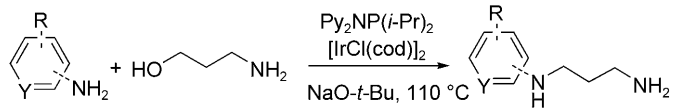


2a – g

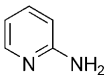
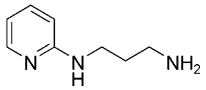
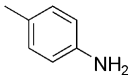
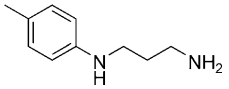
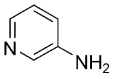
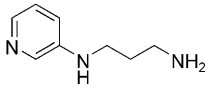
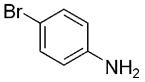
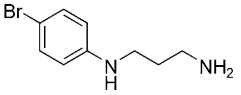
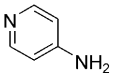
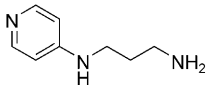
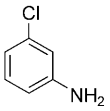
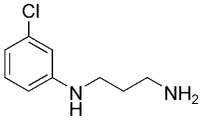
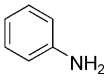
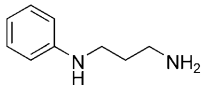
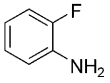
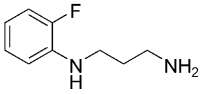
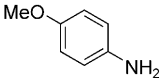
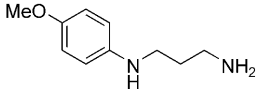
Entry	Amino Alcohol	Product	Yield [%][a]	Entry	Amino Alcohol	Product	Yield [%][b]
1		**2a** 	81	5		**2e** 	89
2		**2b** 	84	6		**2f** 	93
3		**2c** 	70	7		**2g** 	77
4		**2d** 	93				

[a] *Reaction conditions:* 2.0 mmol 2-aminopyridine, 2.2 mmol amino alcohol, 0.5 mol% $[IrCl(cod)]_2$, 1.0 mol% $Py_2NP(i\text{-}Pr)_2$, 2.2 mmol NaO-*t*-Bu, 0.6 mL diglyme, 0.4 mL THF, 110 °C, 24 h.
[b] Isolated yield.

Table 3. Variation of the (hetero)aromatic substrate.[a]



Y = C, N **3a – i**

Entry	Amine	Product	Yield [%][b]	Entry	Amine	Product	Yield [%][b]
1		**3a** 	91	6[e]		**3f** 	71
2[c]		**3b** 	75	7[e]		**3g** 	83
3[d]		**3c** 	68	8[e]		**3h** 	86
4[e]		**3d** 	71	9[e]		**3i** 	63
5[e]		**3e** 	78				

[a] *Reaction conditions:* 2.0 mmol amine, 2.2 mmol 3-amino-1-propanol, 0.5 mol% $[IrCl(cod)]_2$, 1.0 mol% $Py_2NP(i\text{-}Pr)_2$, 2.2 mmol NaO*t*Bu, 0.6 mL diglyme, 0.4 mL THF, 110 °C, 24 h.
[b] Isolated yield.
[c] 2 mol% **1**.
[d] 4 mol% **1**.
[e] 5 mol% **1**.

employed in combination with 2-aminopyridine in order to show the applicability of this method. As depicted in Table 2 the corresponding N-arylated diamines **2a–g** were obtained in yields up to 93%.

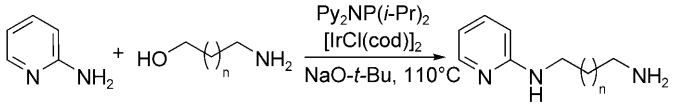
The presented results show that this method is rather efficient for the preparation of diamines with a branched aminoalkyl backbone using a variety of commercially available amino alcohols, which were hitherto unaccessible *via* an arylamination pathway due to a lack of selectivity with alkyl diamines. It is, however, noteworthy to mention that even though chiral β-amino alcohols can be employed, the stereoinformation is lost in the course of the reaction, due to a keto-enol tautomerization of the intermediately formed aldehyde, and therefore only racemic N-arylated diamines are obtained.

In a next step several heteroaromatic amines and functionalized anilines were tested in order to demonstrate the general applicability of this method (Table 3).

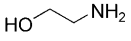
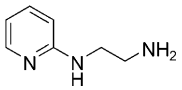
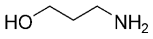
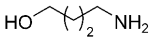
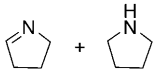
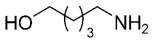
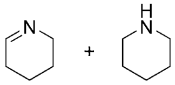
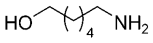
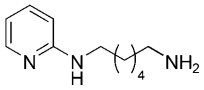
The best catalytic activity of **1** is observed with 2-aminopyridine, whereas the yield decreases with the pyridine nitrogen moving from the 3- to the 4-position, since the catalyst loadings had to be raised to 2 and 4 mol% **1**, respectively (Table 3, entries 2 and 3). Although **1** is especially efficient with heteroaromatic substrates, substituted anilines are also tolerated and afford the corresponding N-arylated diamines **3d–i** in yields from 63% to 86%, however, with a higher catalyst loading of 5 mol% **1**. Substituents in *ortho*, *meta* and *para* positions are tolerated, although substituents in the *ortho* position seem to slightly hinder the reaction as can be determined from entry 9. As observed before,[16,17] catalyst **1** seems to be slightly more efficient when electron-poor (hetero)aromatic amines are employed which is consistent with the results in Table 3, where electron-withdrawing substituents (entries 7–9) seem to have an activating effect on the reaction, in comparison to the reactions with electron-donating substituents (entries 5 and 6).

As shown in Table 2 and Table 3, it is possible to employ linear, as well as branched amino alcohols for this alkylation reaction. Interestingly, the length of the alkyl chain also plays an important role as can be concluded from the results shown in Table 4. With a growing chain length, from 2-amino-1-ethanol to 3-amino-1-propanol, the yield significantly increases due to a greater distance of the electron-rich amino

Table 4. Variation of the chain-length of the amino alcohol.[a]



3j, k

Entry	Alcohol		Product(s)	Yield [%][b]
1		**3j**		71
2		**3a**		91
3				n.d.
4				n.d.
5		**3k**		82

[a] *Reaction conditions:* 2.0 mmol 2-aminopyridine, 2.2 mmol amino alcohol, 0.5 mol% $[IrCl(cod)]_2$, 1.0 mol% $Py_2NP(i\text{-}Pr)_2$, 2.2 mmol NaO-*t*-Bu, 0.6 mL diglyme, 0.4 mL THF, 110 °C, 24 h.
[b] Isolated yield.

function from the alcohol, which facilitates the oxidation of the latter (Table 4, entries 1 and 2). However, when the number of CH_2 groups in the alcohol is four or five, only traces of the expected diamine were observed, because the intramolecular cyclization of the formed amino aldehyde is favoured, mainly affording a mixture of 3,4-dihydro-2*H*-pyrrole and pyrrolidine or 2,3,4,5-tetrahydropyridine and piperidine, respectively (Table 4, entries 3 and 4). The intramolecular formation of a five- or six-membered ring seems to be kinetically favoured compared to the intermolecular reaction with the aromatic amine. Experiments using up to a five-fold excess of 2-aminopyridine and catalyst loadings of 5 mol% **1**, in order to favour the intermolecular reaction, were nevertheless unsuccessful and it was not possible to obtain reasonable amounts of these N-arylated diamines. However, use of 6-amino-1-hexanol again afforded the expected diamine in good yields because the formation of seven-membered rings is more difficult and the intermolecular reaction with the aromatic amine is therefore favoured (Table 4, entry 5).

Conclusions

In conclusion, we have successfully used the chemoselectivity profile, preference for aromatic amines, of our iridium catalyst system based on **1** to develop a novel and general method for the preparation of mono-N-arylated aliphatic diamines. The procedure bases on amine alkylation chemistry using unprotected linear or branched amino alcohols as alkylating agents and also allows the synthesis of selectively mono-N-arylated aliphatic diamines.

Experimental Section

General Considerations

All reactions were carried out under a dry argon or nitrogen atmosphere, using standard Schlenk and glove-box techniques. All chemicals were purchased from commercial sources in purities >97% and used without further purification if not otherwise mentioned in the synthetic procedure. NMR spectra were obtained on a Varian INOVA 400 spectrometer at 300 K. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were performed on a Vario elementar EL *III* and GC-MS analyses on a Thermo Focus GC with a DSQ MS-unit equipped with a HP-5-MS column (30 m × 0.32 μm × 0.25 μm). Flash chromatography was performed over SiO_2 60 (0.040–0.063 mm) from Merck and all used solvents were freshly distilled prior to use.

Typical Procedure

In a Schlenk tube stock solutions of $[IrCl(cod)]_2$ (160 μL, 0.01 mmol, 0.0625 M in THF) and $Py_2NP(i\text{-}Pr)_2$ (160 μL, 0.02 mmol, 0.125 M in THF) were mixed in order to generate the catalyst *in situ*. Then the amine (2.0 mmol, 1.0 equiv.), the amino alcohol (2.2 mmol, 1.1 equiv.) diglyme (300 μL mmol^{-1} amine), THF (200 μL mmol^{-1} amine) were

added. Last, NaO-*t*-Bu (2.2 mmol, 1.1 equiv.) was dissolved in the reaction mixture, the reaction vessel tightly closed and stirred at 110 °C for 24 h. The reaction mixture was cooled to room temperature and quenched with water (2 mL) and CH_2Cl_2 (7–8 mL). Then, 15 mL brine were added and the aqueous layer was extracted with CH_2Cl_2 (6× 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and the solvent removed under vacuum. Finally, the residue was purified by column chromatography (first: diethyl ether/methanol, 1:1, then: diethyl ether/methanol/triethyl amine, 5:5:1) and dried under vacuum.

***N*^{1}-Pyridin-2-yl-propane-1,2-diamine (2a):** Yield: 81%; bp 97 °C at 1.3×10^{-1} mbar. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (ddd, J = 5.1, 1.8, 0.7 Hz, 1H), 7.35 (ddd, J = 8.6, 7.0, 2.0 Hz, 1H), 6.51 (ddd, J = 7.1, 5.0, 0.7 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 4.83 (s br, 1H), 3.29 (ddd, J = 12.6, 6.0, 4.4 Hz, 1H), 3.16–3.07 (m, 1H), 3.06–2.95 (m, 1H), 1.24 (s br, 2H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 148.1, 137.3, 112.7, 107.1, 50.1, 46.4, 22.0; MS (70 eV, EI): m/z (%) = 151 (2, M^+), 119 (2), 108 (100), 95 (18), 79 (38), 51 (6), 44 (4). elemental analysis (%) calcd. for $C_8H_{13}N_3$: C 63.54, H 8.67, N 27.79; found: C 63.29, H 8.770, N 27.75.

2-Methyl-*N*^{1}-pyridin-2-yl-propane-1,2-diamine (2b): Yield: 84%; bp 85 °C at 1.0×10^{-1} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (ddd, J = 5.1, 1.8, 0.7 Hz, 1H), 7.34 (ddd, J = 8.6, 7.0, 2.0 Hz, 1H), 6.50 (ddd, J = 7.1, 5.0, 0.7 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 4.84 (s, 1H), 3.17 (d, J = 6.2 Hz, 2H), 1.14 (s br, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 148.0 137.2, 112.6, 107.3, 53.4, 50.2, 28.9; MS (70 eV, EI): m/z (%) = 165 (4, M^+), 133 (4), 108 (56), 79 (20), 58 (100), 42 (6). elemental analysis (%) calcd. for $C_9H_{15}N_3$: C 65.42, H 9.15, N 25.43; found: C 65.81, H 9.561, N 25.61.

***N*^{1}-Pyridin-2-yl-butane-1,2-diamine (2c):** Yield: 70%; bp 83 °C at 7.2×10^{-2} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (ddd, J = 5.1, 1.8, 0.7 Hz, 1H), 7.35 (ddd, J = 8.8, 7.0, 1.8 Hz, 1H), 6.51 (ddd, J = 7.1, 5.0 1.1 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H), 4.87 (s br 1H), 3.41–3.30 (m, 1H), 3.03–2.95 (m, 1H), 2.89–2.80 (m, 1H) 1.58–1.47(m, 1H), 1.37–1.15 (m, 3H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 148.1, 137.2, 112.7, 107.2, 52.4, 48.1, 29.0, 10.5; MS (70 eV, EI): m/z (%) = 165 (2, M^+), 108 (100), 95 (15), 80 (30), 58 (32); elemental analysis (%) calcd. for $C_9H_{15}N_3$: C 65.42, H 9.15, N 25.43; found: C 65.42, H 9.508, N 24.87.

3-Methyl-*N*^{1}-pyridin-2-yl-butane-1,2-diamine (2d): Yield: 93%; bp 84 °C at 1.1×10^{-1} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (ddd, J = 5.1, 2.0, 0.9 Hz, 1H), 7.35 (ddd, J = 8.6, 7.0, 2.0 Hz, 1H), 6.50 (ddd, J = 7.1, 5.0, 1.1 Hz, 1H), 6.37 (dt, J = 8.4, 0.9 Hz, 1H), 4.94 (s br, 1H), 3.44–3.35 (m, 1H), 3.04–2.94 (m, 1H), 2.72–2.67 (m, 1H), 1.69–1.61 (m, 1H), 1.34 (s br, 2H), 0.94–0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 148.1, 137.2, 112.6, 107.3, 56.3, 46.1, 32.4, 19.4, 17.7; MS (70 eV, EI): m/z (%) = 179 (1, M^+), 136 (5), 119 (8), 108 (100), 95 (11), 80 (25), 72 (29), 55 (14); elemental analysis (%) calcd. for $C_{10}H_{17}N_3$: C 67.00, H 9.56, N 23.44; found: C 66.57, H 9.841, N 23.37.

4-Methyl-*N*^{1}-pyridin-2-yl-pentane-1,2-diamine (2e): Yield: 89%; bp 102 °C at 8.7×10^{-2} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (ddd, J = 5.1, 1.8, 0.7 Hz, 1H), 7.34 (ddd, J = 8.8, 7.0, 1.8 Hz, 1H), 6.50 (ddd, J = 7.1, 5.1, 0.9 Hz, 1H), 6.37 (dt, J = 8.4, 0.9 Hz, 1H), 4.97 (s br, 1H), 3.39–3.31 (m, 1H), 3.04–2.94 (m, 2H), 1.75–1.66 (m, 3H) 1.31–1.18 (m, 2H), 0.91–0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 148.0, 137.2, 112.7, 107.2, 48.7, 48.7, 45.3, 24.7, 23.3, 22.1; MS (70 eV, EI): m/z (%) = 193 (1, M^+), 136 (2), 108 (100), 80 (24), 44 (8); elemental analysis (%) calcd. for $C_{10}H_{16}N_3$: C 68.35, H 9.91, N 21.74; found: C 68.38, H 10.34, N 21.39.

1-Phenyl-*N*^{2}-pyridin-2-yl-ethane-1,2-diamine (2f): Yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (dd, J = 4.9, 0.9 Hz, 1H), 7.40–7.32 (m, 5H), 7.27 (dt, J = 5.3, 2.4 Hz, 1H), 6.55 (dd, J = 6.8, 5.3 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 4.82 (s br, 1H), 4.19 (dd, J = 7.9, 5.3 Hz, 1H) 3.57–3.51 (m, 1H) 3.45–3.38 (m, 1H), 1.64 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 148.1, 143.9, 137.3, 128.6, 127.4, 126.4, 113.0, 107.2, 55.2, 49.8; MS (70 eV, EI): m/z (%) = 213 (3, M^+), 106 (100), 79 (45), 51 (9), 28 (12); elemental analysis (%) calcd. for $C_{13}H_{15}N_3$: C 73.21, H 7.09, N 19.70; found: C 72.71, H 7.147, N 19.63.

3-Phenyl-*N*^{1}-pyridin-2-yl-propane-1,2-diamine (2g): Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (ddd, J = 5.1, 1.8, 0.7 Hz, 1H), 7.36 (ddd, J = 8.5, 7.1, 2.0 Hz, 1H), 7.31–7.25 (m, 2H), 7.22–7.16 (m, 3H), 6.53 (ddd, J = 7.1, 5.1, 0.9 Hz, 1H), 6.36 (d, J = 8.4 Hz, 1H), 4.89 (s br,1H), 3.45–3.40 (m, 1H) 3.28–3.20 (m, 1H) 3.16–3.09 (m, 1H), 2.87 (dd, J = 13.2, 4.8 Hz, 1H), 2.53 (dd, J = 13.4, 8.6 Hz, 1H), 1.22 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 148.1, 138.8, 137.3, 129.2, 128.6, 126.4, 112.8, 107.2, 52.4, 48.1, 42.6; MS (70 eV, EI): m/z (%) = 227 (0.5 M^+), 136 (16), 120 (35), 108 (100), 91 (10), 80 (20); elemental analysis (%) calcd. for $C_{11}H_{19}N_3$: C 73.98, H 7.54, N 18.49; found: C 74.14, H 7.506, N 18.20.

***N*^{1}-Pyridin-2-yl-propane-1,3-diamine (3a):** Yield: 91%; bp 103 °C at 1.3×10^{-1} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, J = 5.1, 0.7 Hz, 1H), 7.39–7.32 (m, 1H), 6.53–6.50 (m, 1H), 6.34 (d, J = 8.4 Hz, 1H), 4.80 (s br, 1H), 3.36–3.30 (m, 2H), 2.81 (t, J = 6.6 Hz, 2H), 1.79–1.69 (m, 2H), 1.27 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 148.2, 137.3, 112.6, 106.7, 40.2, 40.1, 33.0; MS (70 eV, EI): m/z (%) = 151 (38, M^+), 121 (100), 108 (98), 94 (26), 78 (68), 67 (16), 30 (22); elemental analysis (%) calcd. for $C_8H_{13}N_3$: C 63.54, H 8.67, N 27.79; found: C 63.55, H 9.166, N 27.45.

***N*^{1}-Pyridin-3-yl-propane-1,3-diamine (3b):** $[IrCl(cod)]_2$ (320 μL, 0.02 mmol, 0.0625 M in THF), $Py_2NP(i\text{-}Pr)_2$ (320 μL, 0.04 mmol, 0.125 M in THF); yield: 75%; bp 135 °C at 7.4×10^{-2} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (dd, J = 2.9, 0.7 Hz, 1H), 7.90 (dd, J = 4.6, 1.3 Hz, 1H), 7.03 (ddd, J = 8.4, 4.8, 0.7 Hz, 1H), 6.82 (ddd, J = 8.1, 2.9, 1.5 Hz, 1H), 4.23 (s br, 1H), 3.18 (t, J = 6.6 Hz, 2H), 2.84 (t, J = 6.6 Hz, 2H) 1.79–1.69 (m, 2H), 1.26 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 138.5, 136.0, 123.6, 118.2, 42.0, 40.3, 32.4; MS (70 eV, EI): m/z (%) = 151 (48, M^+), 133 (72), 119 (15), 107 (100), 95 (42), 78 (31), 56 (17), 30 (21); elemental analysis (%) calcd. for $C_8H_{13}N_3$: C 63.54, H 8.67, N 27.79; found: C 63.91, H 8.931, N 27.40.

***N*^{1}-Pyridin-4-yl-propane-1,3-diamine (3c):** $[IrCl(cod)]_2$ (27 mg, 0.04 mmol), $Py_2NP(i\text{-}Pr)_2$ (23 mg, 0.08 mmol). Purification by column chromatography (first: diethyl ether/methanol, 1:5, then: diethyl ether/methanol/triethyl amine, 2:10:1); yield: 68%; bp 110 °C at 2.4×10^{-2} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 5.5 Hz, 2H), 6.38 (d, J = 6.2 Hz, 2H), 4.90 (s br, 1H), 3.24–3.17 (m, 2H), 2.84 (t, J = 6.4 Hz, 2H), 1.76–1.69 (m, 2H), 1.18 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 150.0, 107.4, 41.3, 40.4, 31.9; MS (70 eV, EI): m/z = (%): 151 (30, M^+), 133 (100), 107

(99), 95 (54), 78 (27), 56 (25), 51 (19), 30 (33), 28 (48); elemental analysis (%) calcd. for $C_8H_{13}N_3$: C 63.54, H 8.67, N 27.79; found: C 62.89, H 9.078, N 27.45.

***N*^{1}-Phenylpropane-1,3-diamine (3d):**[14b] $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.14$ (t, $J = 7.2$ Hz, 2H), 6.66 (t, $J = 7.3$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 2H), 3.17 (t, $J = 6.7$ Hz, 2H), 2.83 (t, $J = 6.7$ Hz, 2H), 2.15 (s br, 2H), 1.78–1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.5$, 129.2, 117.2, 112.7, 42.1, 40.3, 32.9; MS (70 eV, EI): *m*/*z* (%) = 150 (42, M^+), 132 (40), 106 (100), 93 (25), 77 (30), 57 (27), 51 (10), 30 (17), 28 (17).

***N*^{1}-(4-Methoxyphenyl)propane-1,3-diamine (3e):**[13b] $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.74$ (d, $J = 8.8$ Hz, 2H), 6.55 (d, $J = 8.8$ Hz, 2H), 3.71 (s, 3H), 3.12 (t, $J = 6.8$ Hz, 2H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.59 (s br, 3H), 1.77–1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.0$, 142.7, 114.9, 114.0, 55.8, 43.0, 40.1, 32.6; MS (70 eV, EI): *m*/*z* (%) = 180 (M^+, 47), 162 (10), 148 (15), 136 (100), 123 (30), 108 (28), 77 (12), 57 (13).

***N*^{1}-(4-Methylphenyl)propane-1,3-diamine (3f):**[13b] $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.95$ (d, $J = 8.1$ Hz, 2H), 6.51 (d, $J = 8.4$ Hz, 2H), 3.15 (t, $J = 6.8$ Hz, 2H), 2.82 (t, $J = 6.6$ Hz, 2H), 2.38 (s br, 3H), 2.29 (s, 3H), 1.78–1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 146.2$, 129.7, 126.4, 112.9, 42.4, 40.2, 32.7, 20.4; MS (70 eV, EI): *m*/*z* (%) = 164 (M^+, 36), 146 (15), 132 (26), 120 (100), 107 (32), 91 (33), 77 (21), 65 (17), 57 (19).

***N*^{1}-(4-Bromophenyl)propane-1,3-diamine (3g):**[13b] $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.20$ (d, $J = 8.8$ Hz, 2H), 6.45 (d, $J = 8.8$ Hz, 2H), 3.14 (t, $J = 6.6$ Hz, 2H), 2.84 (t, $J = 6.6$ Hz, 2H), 2.74 (s br, 3H), 1.80–1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.4$, 131.9, 114.2, 108.7, 42.1, 40.0, 31.8; MS (70 eV, EI): *m*/*z* (%) = 230 (24), 228 (M^+, 28), 186 (49), 184 (61), 132 (61), 118 (22), 105 (36), 91 (26), 57 (86), 45 (36), 30 (100).

***N*^{1}-(3-Chlorophenyl)propane-1,3-diamine (3h):** $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.02$ (t, $J = 8.1$ Hz, 1H), 6.60 (dd, $J = 8.0$, 2.0 Hz, 1H), 6.53 (dd, $J = 2.2$, 2.2 Hz, 1H), 6.42 (dd, $J = 8.0$, 2.3 Hz, 1H), 3.13 (t, $J = 6.8$ Hz, 2H), 2.81 (t, $J = 6.8$ Hz, 2H), 1.76–1.67 (m, 2H), NH signals are not given; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.5$, 134.9, 130.1, 116.8, 112.1, 111.0, 42.0, 40.2, 32.2; MS (70 eV, EI): *m*/*z* (%) = 184 (M^+, 37), 166 (32), 140 (100), 132 (37), 111 (23), 75 (25), 57 (79) 45 (28); elemental analysis (%) calcd. for $C_9H_{13}ClN_2$: C 58.54, H 7.10, N 15.17; found: C 58.14, H 7.013, N 14.69.

***N*^{1}-(2-Fluorophenyl)propane-1,3-diamine (3i):** $[IrCl(cod)]_2$ (34 mg, 0.05 mmol), $Py_2NP(i\text{-}Pr)_2$ (29 mg, 0.1 mmol); yield: 63%; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.99$–6.89 (m, 2H), 6.70–6.63 (m, 1H), 6.62–6.54 (m, 1H), 3.21 (t, $J = 6.8$ Hz, 2H), 2.84 (t, $J = 6.8$ Hz, 1.82–1.73 (m, 2H), NH signals are not given; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.9$ (d, $J = 133.6$ Hz), 124.5 (d, $J = 3.5$ Hz), 116.3 (d, $J = 7.1$ Hz), 114.4, 114.2, 111.9 (d, $J = 3.5$ Hz), 41.7, 40.1, 32.7; MS (70 eV, EI): *m*/*z* (%) = 168 (M^+, 37), 151 (35), 150 (36), 124 (100), 111 (34), 83 (28), 77 (50), 57 (78), 56 (52); elemental analysis (%) calcd. for $C_9H_{13}FN_2 \cdot 0.33\,H_2O$: C 62.05, H 7.91, N 16.08; found: C 62.47 , H 7.690, N 15.63.

***N*^{1}-Pyridin-2-yl-ethane-1,2-diamine (3j):** Yield: 71%; bp 90 °C at 1.2×10^{-1} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.05$ (ddd, $J = 5.1$, 1.8, 0.7 Hz, 1H), 7.36 (ddd, $J = 8.6$, 7.0, 2.0 Hz, 1H), 6.52 (ddd, $J = 7.1$, 5.0, 1.0 Hz, 1H), 6.38 (d, $J = 8.4$ Hz, 1H), 4.77 (s br, 1H), 3.35–3.31 (m, 2H), 2.94–2.88 (m, 2H), 1.17 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.9$, 148.1, 137.3, 112.8, 107.1, 44.8, 41.5; MS (70 eV, EI): *m*/*z* (%) = 137 (7, M^+), 109 (4), 107 (100), 95 (36), 78 (46), 51 (8), 30 (9); elemental analysis (%) calcd. for $C_7H_{11}N_3$: C 61.29, H 8.08, N 30.63; found: C 60.90, H 8.332, N 30.22.

***N*^{1}-Pyridin-2-yl-hexane-1,6-diamine (3k):** Yield: 82%; bp 119 °C at 1.1×10^{-1} mbar; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.03$ (ddd, $J = 4.9$, 1.8, 0.9 Hz, 1H), 7.37 (ddd, $J = 8.5$, 6.9, 1.8 Hz, 1H), 6.51 (ddd, $J = 7.1$, 5.1, 0.9 Hz, 1H), 6.33 (dd, $J = 8.4$, 0.9 Hz, 1H), 4.46 (s br, 1H), 3.25–3.18 (m, 2H), 2.65 (t, $J = 7.0$ Hz, 2H), 1.63–1.56 (m, 2H), 1.45–1.30 (m, 6H), 1.21 (s br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 158.9$, 148.2, 137.4, 112.6, 106.3, 42.2, 42.1, 33.8, 29.5, 26.9, 26.7; MS (70 eV, EI): *m*/*z* (%) = 193 (17, M^+), 177 (13), 163 (17), 121 (41), 107 (100), 94 (48), 78 (35), 67 (7), 30 (18), 28 (25); elemental analysis (%) calcd. for $C_{11}H_{19}N_3$: C 68.35, H 9.91, N 21.74; found: C 67.99, H 10.41, N 21.38.

Crystallographic Data

X-ray crystal structure analysis of **1** was performed by using a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[18] SHELXL-97[19] and WinGX.[20] Crystal system: monoclinic, space group: *P*21/*c*, lattice constants[Å,°]: $a = 11.8250(6)$, $b = 23.8930(12)$, $c = 10.0800(5)$, $\alpha = 90.00$, $\beta = 101.079(4)$, $\gamma = 90.00$, V [Å^3]: 2794.9(2), crystal size [mm]: $0.32 \times 0.16 \times 0.13$, $\rho_{calcd.}$ [g cm^{-3}]: 1.652, μ [mm^{-1}] (Mo-K_α): 4.946, T [K]: 133(2), θ range [°]: 52.28–3.41, no. of unique refl.: 5261, no. of obsd. refl. [$I > 2\sigma(I)$]: 4293, no. of parameters: 316, wR^2 (all data): 0.0536, R value [$I > 2\sigma(I)$]: 0.0349. CCDC 742977 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44–1223–336–033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

*This work was supported by NanoCat an International Graduate Program within the Elitenetzwerk Bayern. B. Blank is grateful for a Bavarian Elite Graduation Grant (Graduiertenstipendium nach dem Bayerischen Eliteförderungsgesetz). We thank Dr. G. Glatz for the single crystal X-ray analysis of **1**.*

References

[1] S. A. Lawrence *Amines: Synthesis Properties and Applications*, Cambridge University Press, Cambridge, **2004**.

[2] a) E. B. Villhauer, J. A. Brinkman, G. B. Naderi, B. F. Burkey, B. E. Dunning, K. Prasad, B. L. Mangold, M. E. Russell, T. E. Hughes, *J. Med. Chem.* **2003**, *46*, 2774–2789; b) A. Robinson, G. L. Thomas, R. J. Spandl, M. Welchand, D. R. Spring , *Org. Biomol. Chem.* **2008**, *6*, 2978–2981.

[3] a) J. Aragó, A. Bencini, A. Bianchi, E. Garcia-Espafia, M. Micheloni, P. Paoletti, J. A. Ramirez, P. Paoli, *Inorg. Chem.* **1991**, *30*, 1843–1849; b) C. Bazzicalupi, A. Bencini, H. Cohen, C. Giorgi, G. Golub, D. Meyerstein, N. Navon, P. Paletti, B. Valtancoli, *J. Chem. Soc. Dalton Trans.* **1998**, 1625–1631; c) M. E. G. Skinner, P. Mountford, *J. Chem. Soc. Dalton Trans.* **2002**, 1694–1703.

[4] a) M. B. Smith, J. March, *Advanced Organic Chemistry*, 5th edn., Wiley, New York, **2001**, p 499; b) R. N. Salvatore, C. H. Yoon, K. W. Jung, *Tetrahedron* **2001**, *57*, 7785–7811.

[5] a) E. W. Baxter, A. B. Reitz, *Organic Reactions*, Vol. 59, Wiley, New York, **2002**, p 1; b) R. O. Hutchins, M. K. Hutchins, B. M. Trost, *Comprehensive Organic Synthesis*, Vol. 8, Pergamon Press, Oxford **1991**, pp 25–78; c) C. F. Lane, *Synthesis* **1975**, 135–146; d) G. W. Gribble, *Chem. Soc. Rev.* **1998**, *27*, 395–404; e) A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff, R. D. Shah, *J. Org. Chem.* **1996**, *61*, 3849–3862; f) T. Gross, A. M. Seayad, M. Ahmad, M. Beller, *Org. Lett.* **2002**, *4*, 2055–2058.

[6] a) R. Severin, S. Doye, *Chem. Soc. Rev.* **2007**, *36*, 1407–1420; b) K. C. Hultzsch, D. V. Gribkov, J. F. Hampel, *J. Organomet. Chem.* **2005**, *690*, 4441–4452; c) J. F. Hartwig, *Pure Appl. Chem.* **2004**, *76*, 507–516; d) S. Doye, *Synlett* **2004**, 1654–1672; e) J. Seayad, A. Tillack, C. G. Hartung, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 795–813; f) M. Beller, C. Breindl, M. Eichberger, C. G. Hartung, J. Seayad, O. Thiel, A. Tillack, H. Trauthwein, *Synlett* **2002**, 1579–1594.

[7] a) K.-S. Mueller, F. Koc, S. Ricken, P. Eilbracht, *Org. Biomol. Chem.* **2006**, *4*, 826–835; b) L. Routaboul, C. Buch, H. Klein, R. Jackstell, M. Beller, *Tetrahedron Lett.* **2005**, *46*, 7401–7405; c) A. Moballigh, A. Seayad, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2003**, *125*, 10311–10318; d) P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, B. E. Kitsos-Rzychon, C. L. T. Rische, R. Roggenbuck, A. Schmidt, *Chem. Rev.* **1999**, *99*, 3329–3365.

[8] a) A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Lett.* **2006**, *47*, 8881–8885; b) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, *2*, 403–410; c) M. H. S. A. Hamid, J. M. J. Williams, *Chem. Commun.* **2007**, 725–727; d) M. H. S. A. Hamid, J. M. J. Williams, *Tetrahedron Lett.* **2007**, *48*, 8263–8265; e) A. Tillack, D. Hollman, K. Mevius, D. Michalik, S. Bähn, M. Beller, *Eur. J. Org. Chem.* **2008**, 4745–4750; f) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* **2009**, *131*, 1766–1774; g) J. W. Kima, K. Yamaguchi, N. Mizuno, *J. Catal.* **2009**, *263*, 205–208; h) G. W. Lamb, A. J. A. Watson, K. E. Jolley, A. C. Maxwell, J. M. J. Williams, *Tetrahedron Lett.* **2009**, *50*, 3374–3377; i) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *Org. Lett.* **2009**, 11. 2667–2670.

[9] a) K. Fujita, K. Yamamoto, R. Yamaguchi, *Org. Lett.* **2002**, 4, 2691–2694; b) K. Fujita, Z. Li, N. Ozeki, R. Yamaguchi, *Tetrahedron Lett.* **2003**, *44*, 2687–2690; c) K. Fujita, T. Fujii, R. Yamaguchi, *Org. Lett.* **2004**, *6*, 3525–3528; d) G. Cami-Kobeci, J. M. J. Williams, *Chem. Commun.* **2004**, 1072–1073; e) K. Fujita R. Yamaguchi, *Synlett* **2005**, *4*, 560–571; f) C. T. Eary, D. Clausen, *Tetrahedron Lett.* **2006**, 47, 6899–6902; g) L. U. Nordstrøm, R. Madsen, *Chem. Commun.* **2007**, 5034–5036; h) R. Yamaguchi, S. Kawagoe, C. Asai, K. Fujita, *Org. Lett.* **2008**, *10*, 181–184; i) K. Fujita, Y. Enoki, R. Yamaguchi, *Tetrahedron* **2008**, *64*, 1943–1954; j) G. Cami-Kobeci, P. A. Slatford, M. K. Whittlesey, J. M. J. Williams, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 535–537; k) A. Prades, R. Corber, M. Poyatos, E. Peris, *Chem. Eur. J.* **2008**, *14*, 11474–11479; l) A. Pontes da Costa, M. Viciano, M. Sanaú, S. Merino, J. Tejeda, E. Peris, B. Royo, *Organometallics* **2008**, *27*, 1305–1309; m) H. Aramoto, Y. Obara, Y. Ishii, *J. Org. Chem.* **2009**, *74*, 628–633; n) S. Liu, M. Rebros, G. Stephens, A. Marr, C. *Chem. Commun.* **2009**, 2308–2310; o) K. Fujita, .; A. Komatsubara, R. Yamaguchi, *Tetrahedron Lett.* **2009**, 65, 3624–3628; p) L. Miao, S. C. DiMaggio, H. Shu, M. L. Trudell, *Org. Lett.* **2009**, 11, 1579–1582.

[10] Mechanistic DFT studies of the Ir-catalyzed amination of alcohols: D. Balcells, A. Nova, E. Clot, D. Gnanamgari, R. H. Crabtree, O. Eisenstein, *Organometallics* **2008**, *27*, 2529–2535.

[11] An excellent overview for the "borrowing hydrogen" mechanism can be found here: a) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, 349, 1555–1575; b) T. D. Nixon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 753–762.

[12] For selected reviews please see: a) J. F. Hartwig, *Synlett* **2006**, 1283–1294; b) S. L. Buchwald, C. Mauger, G. Mignani, U. Scholz, *Adv. Synth. Catal.* **2006**, *348*, 23–39; c) O. Navarro, N. Marion, J. Mei, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 5142–5148; d) D. S. Surry, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361.

[13] a) I. P. Beletskaya, A. G. Bessmertnykh, R. Guilard, *Tetrahedron Lett.* **1997**, *38*, 2287–2290; b) I. P. Beletskaya, A. G. Bessmertnykh, A. D. Averin, F. Denat, R. Guilard, *Eur. J. Org. Chem.* **2005**, 261–280; c) A. D. Averin, E. R. Ranyuk, N. V. Lukashev, S. L. Golub, A. K. Buryak, I. P. Beletskaya, *Tetrahedron Lett.* **2008**, *49*, 1188–1191.

[14] a) R. J. Ife, K. W. Catchpole, G. J. Durant, C. R. Ganellin, C. A. Harvey, M. L. Meeson, D. A. A. Owen, M. E. Pearson, B. P. Slingsby, C. J. Theobald, *Eur. J. Med. Chem.* **1989**, *24*, 249–258; b) L. R. Orelli, M. B. Garcia, F. Niemevz, I. A. Perillo, *Synth. Commun.* **1999**, *29*, 1819–1833.

[15] a) T. Schareina, R. Kempe, *Angew. Chem.* **2002**, *114*, 1591–1594; *Angew. Chem. Int. Ed.* **2002**, *41*, 1521–1523; b) S. Proch, R. Kempe, *Angew. Chem.* **2007**, *119*, 3196–3199; *Angew. Chem. Int. Ed.* **2007**, *46*, 3135–3138; c) B. Blank, G. Glatz, R. Kempe, *Chem. Asian J.* **2009**, *4*, 321–327.

[16] B. Blank, M. Madalska, R. Kempe, *Adv. Synth. Catal.* **2008**, *350*, 749–758.

[17] B. Blank, S. Michlik, R. Kempe, *Chem. Eur. J.* **2009**, *15*, 3790–3799.
[18] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, 32, 115–119.
[19] G. M. Sheldrick, *SHELX-97*, *Program for Crystal Structure Analysis*, (Release 97–2), Institut für Anorganische Chemie der Universität, Göttingen, Germany, **1998**.
[20] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

