Efficient ruthenium catalyzed transfer hydrogenation of functionalized imines by isopropanol under controlled microwave heating[1]

Joseph S.M. Samec, Laetitia Mony, and Jan-E. Bäckvall

Abstract: Transfer hydrogenation of various functionalized imines by isopropanol catalyzed by $[Ru(CO)_2(Ph_4C_4CO)]_2$ (**3**) has been studied. The use of either an oil bath or controlled microwave heating in toluene led to an efficient procedure with high turnover frequencies and the product amines were obtained in high yields. An advantage with catalyst **3** over the conventional $[Ru_2(CO)_4(\mu\text{-}H)(Ph_4C_4COHOCC_4Ph_4)]$ (**1**) is the absence of an initiation period, which results in a faster reaction with **3** as compared to **1**.

Key words: transfer hydrogenation, ruthenium, imines, microwave.

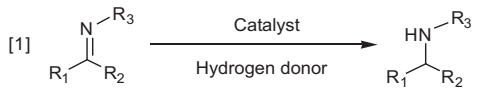
Résumé : On a étudié la réaction de transfert d'hydrogène, catalysée par le $[Ru(CO)_2(Ph_4C_4CO)]_2$ (**3**), de l'isopropanol vers diverses imines fonctionnalisées. L'utilisation d'un bain d'huile ou d'un chauffage par micro-ondes contrôlé dans le toluène conduit à une méthode efficace impliquant des fréquences élevées de renouvellement et à des rendements élevés en amines. Par rapport au catalyseur conventionnel $[Ru_2(CO)_4(\mu\text{-}H)(Ph_4C_4COHOCC_4Ph_4)]$ (**1**), le catalyseur (**3**) ne présente pas de période d'initiation et il en résulte des vitesses de réaction plus rapides avec **3** par comparaison avec **1**.

Mots clés : hydrogénation par transfert, ruthénium, imines, micro-onde.

[Traduit par la Rédaction]

Introduction

The reduction of imines to amines is an important transformation in organic synthesis since amines are useful building blocks for pharmaceuticals and other biologically active compounds. In situ reduction of imines generated by the reaction of ketones with an amine (reductive amination) is a commonly used procedure (1). Although the latter protocol works fine in many systems with various reducing agents (2), it is often associated with low selectivity. Direct reduction of imines can be carried out with hydride reagents (3) or with catalytic hydrogenation (4). More recently, transfer hydrogenation has been reported as a viable alternative for reduction of imines (eq. [1]) (5). The advantage of the latter procedure is that the use of hydrogen gas is avoided and that, e.g., isopropanol can be used as the hydrogen source. The acetone thus produced is readily removed by distillation. The transfer hydrogenation protocol also shows a higher functional group tolerance compared to hydride reagents.



Several transition-metal complexes are known to catalyze the transformation in eq. [1] with isopropanol or formic acid as the hydrogen donor (6–8). Dimeric catalyst **1** (9) (Scheme 1), which has frequently been employed in various hydrogen transfer reactions (10, 11), was recently successfully used in our group for the transfer hydrogenation of imines (8). Catalyst **1** is in equilibrium with monomers **2** and **A** (Scheme 1). The monomer **2** is able to hydrogenate a hydrogen acceptor, e.g., an imine, whereas the monomer **A** can dehydrogenate a hydrogen donor, e.g., isopropanol. These processes interconvert **2** and **A**. We recently showed that the hydrogen transfer from **2** to a ketimine occurs in a stepwise manner (12).

The active monomers **2** and **A** involved in the catalytic hydrogen transfer of imines can also be generated from the dimeric catalyst **3** (13). In the present work we studied the use of catalyst precursor **3** in the hydrogen transfer of functionalized imines.

The use of microwaves to accelerate catalytic reactions has recently attracted attention (14, 15). With the employment of microwaves, the reaction times can be reduced considerably and this is of great use when a larger number of compounds are required (e.g., for screening). In this work we have used microwave heating to lower the catalyst load-

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J.S.M. Samec, L. Mony, and J.-E. Bäckvall.[2] Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91 Stockholm, Sweden.

[1]This article is part of a Special Issue dedicated to Professor Howard Alper.
[2]Corresponding author (e-mail: jeb@organ.su.se).

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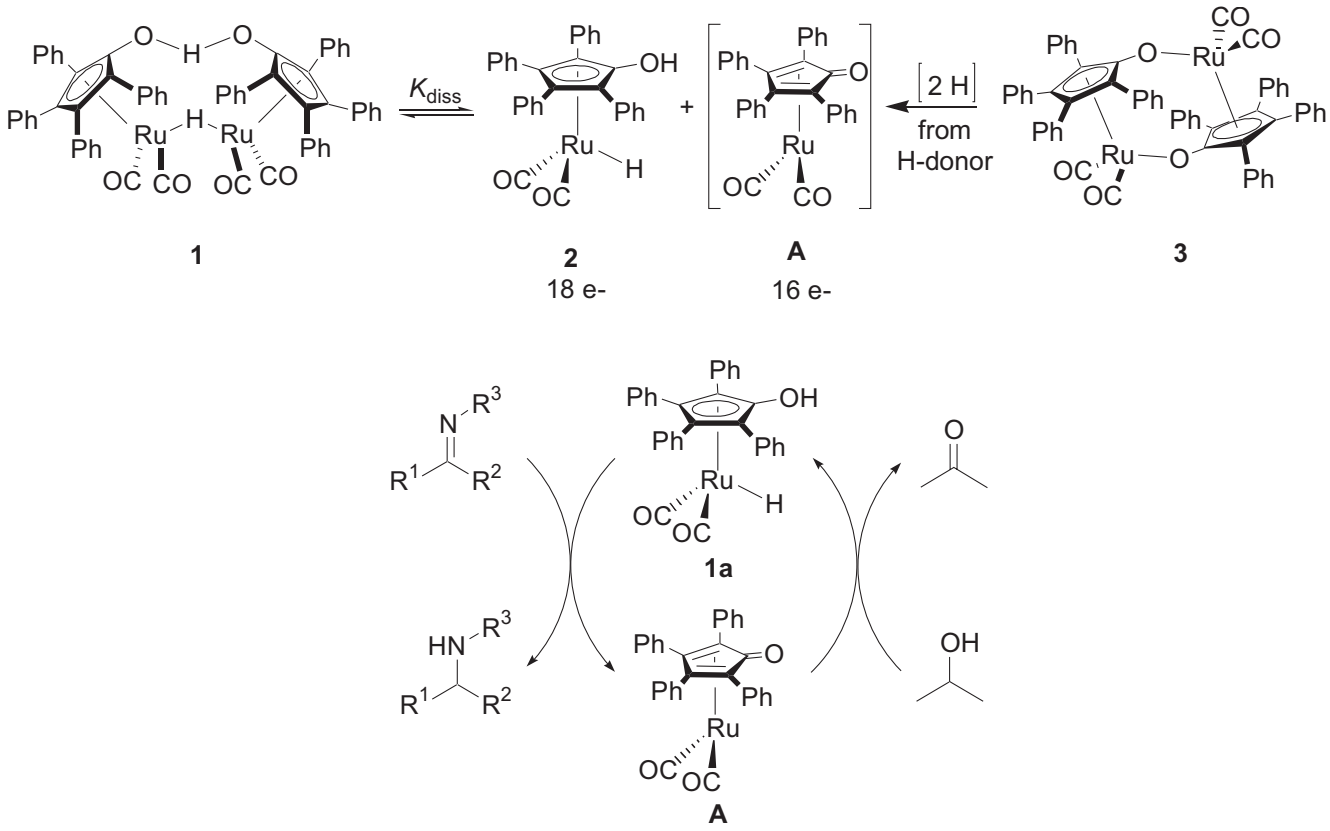
Scheme 1.



ing and reduce reaction times in the transfer hydrogenation of imines to amines with catalyst **3**.

Results and discussion

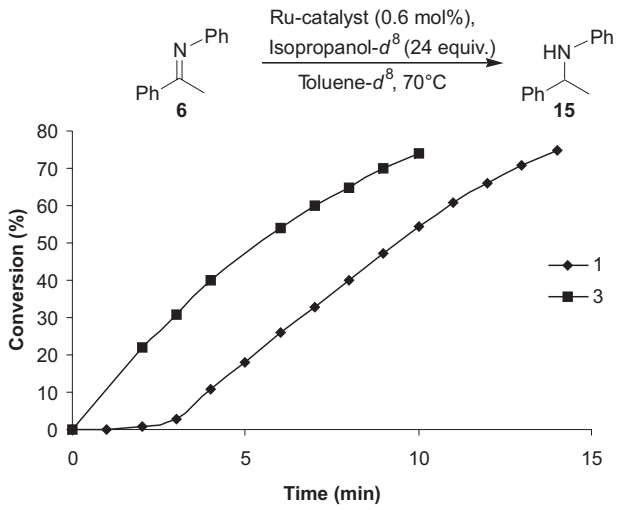
A few procedures for transfer hydrogenation of imines to amines have previously been reported in the literature (6–8). With the objective being to develop a more practical and useful procedure for ruthenium catalyzed transfer hydrogenation of imines by isopropanol, we decided to study the effects of catalyst precursor and temperature.

Choice of the catalyst precursor

Complexes **1** and **3** are catalyst precursors for the hydrogen donor **2** and hydrogen acceptor **A**. To compare **1** and **3** as catalyst precursors they were prepared according to a procedure described by Casey et al. (13). Tetraphenylcyclopentadienone and $Ru_3(CO)_{12}$ were refluxed in MeOH to give the Shvo dimer **1** or in heptane to give **3** (Scheme 2). The products were collected by filtration and recrystallized to give **1** and **3**, respectively, in high yields (~90%).

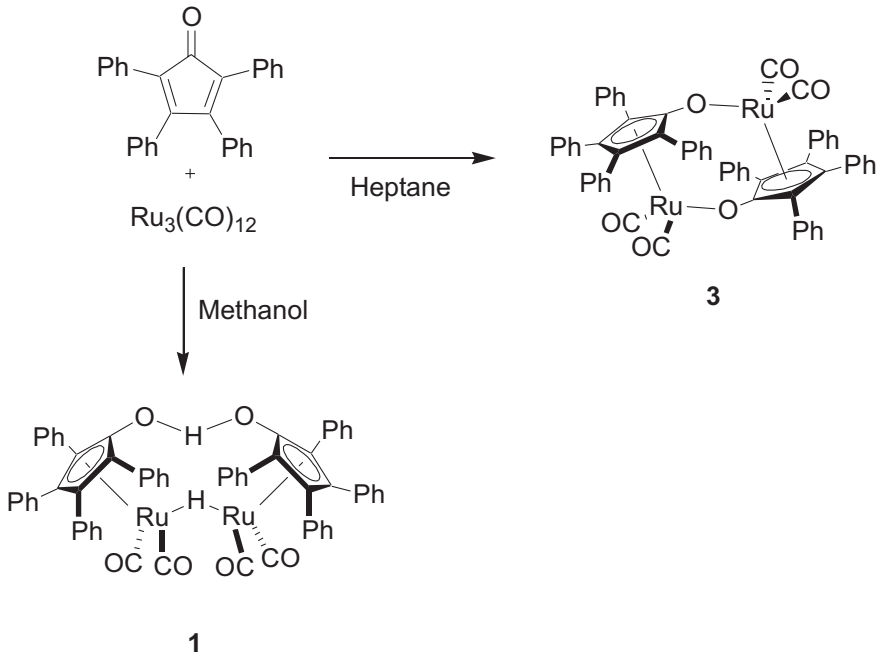
Initial experiments run in an oil bath at 110 °C revealed that catalyst **3** was more efficient than catalyst **1** in the transfer hydrogenation of imines and gave shorter reaction times. To obtain a more detailed comparison between the two catalyst precursors we studied their kinetics in the transfer hydrogenation of imine **6**. Thus, the transfer hydrogenation of imine **6** by isopropanol-d_8 in toluene-d_8 catalyzed by **1** or **3** was monitored by ^{1}H NMR at 70 °C.[3] The results are shown in Fig. 1. From these results, it is evident that catalyst precursor **1** has an initiation period of several minutes, whereas catalyst precursor **3** is active immediately and results in 23% conversion after 2 min. The time to reach 75% conversion was 14 and 10 min for **1** and **3**, respectively. During the first

Fig. 1. Comparison between precatalysts **1** and **3** in the transfer hydrogenation of imine **6** in toluene-d_8 at 70 °C with isopropanol-d_8 using 0.6 mol% catalyst. The conversion was measured by ^{1}H NMR.



[3] Due to the low boiling point of isopropanol, the reactions were run at 70 °C to prevent overpressure in the NMR tube.

Scheme 2.



2 min, the turnover frequency (TOF) was <30 h^{-1} for **1** (<15 h^{-1} per ruthenium atom), whereas it was 1150 h^{-1} for **3** (575 h^{-1} per ruthenium atom). Because of the higher efficiency of **3** over **1**, the former catalyst was chosen for further studies.

Transfer hydrogenation of imines under thermal heating

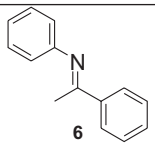
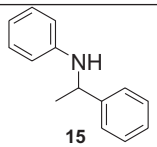
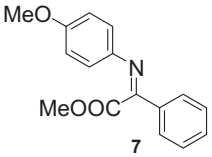
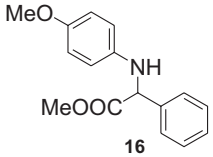
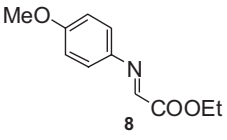
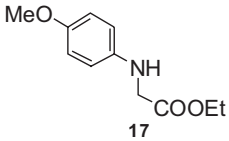
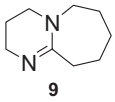
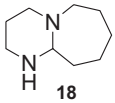
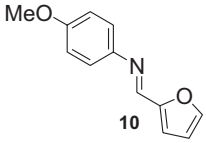
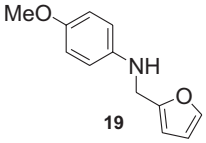
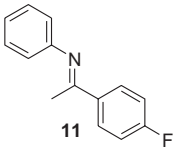
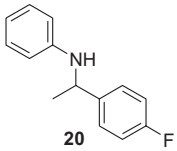
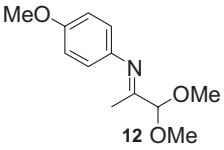
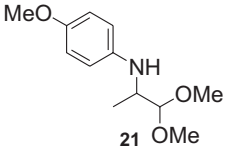
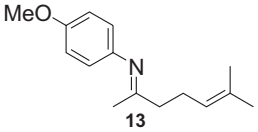
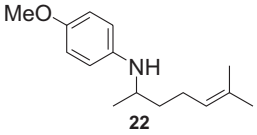
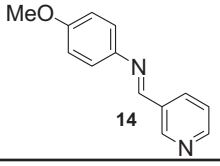
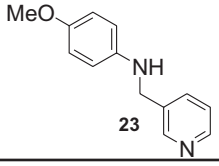
In our previously reported procedure for transfer hydrogenation of various imines by **1** using 24 equiv. of wet isopropanol in benzene at 70 °C, electron-deficient imines had long reaction times (8). For increased efficiency, it was desirable to shorten the reaction times and also to lower the catalyst loading. An increase in temperature would lead to shorter reaction times but it may also decrease the selectivity. With the aim to increase the efficiency of the reaction, the transfer hydrogenation of model substrate **6** by catalyst precursor **3** in isopropanol–toluene at 110 °C was studied. The increase in temperature led to an efficient transfer hydrogenation of **6** where the catalyst loading could be decreased 10 times compared to our previous study (8). This prompted us to study the electron-deficient imine **11**, which required 8 h at 70 °C in benzene. In the present system, imine **11** had reached full conversion within an hour with the same catalyst loading. The present system can also transfer hydrogenate the very electron-deficient imine **14** bearing a pyridyl group. To further extend this protocol and make it an attractive alternative in organic synthesis, we decided to study the transfer hydrogenation of imines having functional groups that make them difficult to reduce to amines. It was found that the present procedure tolerates various functional groups such as esters, amines, ethers, acetals, and olefins (Table 1, entries 2–5, 7, and 8). In conventional reductions using metal hydrides, the workup protocol includes tedious extractions in the presence of strong acids and (or) bases, which not only lowers the yield of the reactions, but also lowers the functional group tolerance. In the present procedure, the only workup is the removal of the solvents. The products are then readily purified by distillation giving the amines in high yield. For example, reduction of imines with either an ester or an acetal functionality, which may cause problems in metal hydride reductions (either during the reaction or in work up) proceeded smoothly with the present method (Table 1, entries 2, 3, and 7).

Transfer hydrogenation under controlled microwave heating

Recently, we showed that the hydrogen transfer from the active catalyst **2** to the imine is not concerted as previously proposed (13), but stepwise (12). In the latter study, we found that microwave irradiation was superior to conventional oil bath heating for the generation of the active species **2** from precursor **3** in a H_2 atmosphere (Scheme 3). Where conventional oil bath heating took several hours and with unsatisfactory results, the microwave-promoted generation of active species **2** was very efficient. Active species **2** can be generated in a minute at 180 °C using microwave irradiation, but with somewhat unreliable results. We found that decreasing the temperature to 120 °C and prolonging the reaction time to 20 min resulted in complete conversion of **3** to **2** with full reproducibility (12).

Initial attempts to perform transfer hydrogenation of imine **6** by precursor **3** in isopropanol and toluene with microwave irradiation gave unreliable results. For example, when imine **6** was run with low catalyst loading (0.03–0.06 mol%) at 110 °C, the results were difficult to reproduce. Increasing the catalyst loading slightly (to 0.1 mol%) gave a smooth transfer hydrogenation of imine **6** to amine **15** within 20 min (Table 2, entry 1). Next, it was of interest to find out if functionalized imines tolerate the transfer hydrogenation with microwave irradiation. We were pleased to find that employing microwave irradiation improved the reduction in most cases even though there were two exceptions: imines **6** and **7** (Table 2, entries 1 and 2) needed

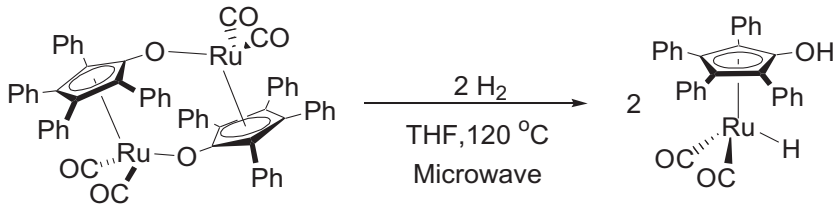
Table 1. Transfer hydrogenation of different amines by wet isopropanol in toluene using **3**.[a]

Entry	Imine	Amine	Catalyst loading (mol%)	Time (min)	Yield (%)[b]
1	 **6**	 **15**	0.03	90	93
2	 **7**	 **16**	0.06	60	93
3	 **8**	 **17**	0.06	60	95
4	 **9**	 **18**	0.3	60	>99[c]
5	 **10**	 **19**	0.3	150	97
6	 **11**	 **20**	1	60	>99[c]
7	 **12**	 **21**	3	60	95
8	 **13**	 **22**	3	60	96
9	 **14**	 **23**	3	240	96

[a]The reactions were carried out using imine (1.0 mmol), catalyst **3** (0.003–0.03 mmol), and isopropanol (24 mmol, 1.85 mL) in toluene (3.15 mL) at 110 °C. Full conversion was measured by ^{1}H NMR.
[b]Isolated yield unless otherwise noted.
[c]Yield determined by ^{1}H NMR.

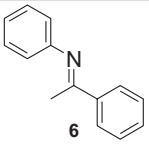
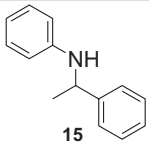
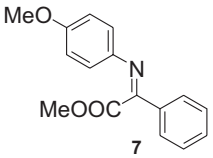
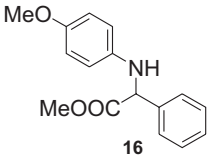
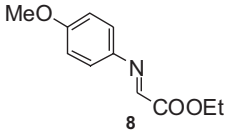
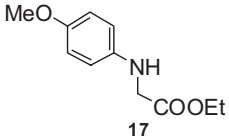
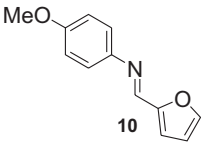
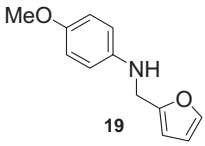
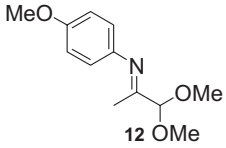
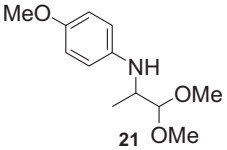
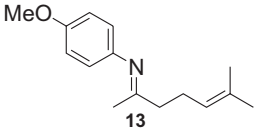
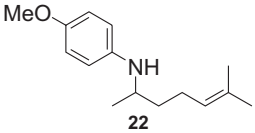
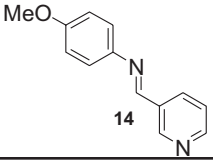
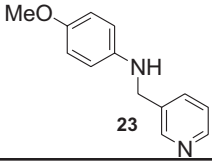
higher catalyst loading in the microwave-assisted transfer hydrogenation than by conventional heating. Except for these examples, the general trend was shorter reaction times (10–20 min) and lower catalyst loading (0.1–0.5 mol%). For example, imine **10**, which needed 0.3 mol% of the catalyst and 150 min using oil bath heating, was finished within 20 min with only 0.1 mol% of the catalyst (Table 2, entry 4). This is an increase of >20 times in efficiency. Imines **12** and **13**, which needed 3 mol% of catalyst loading and 60 min with conventional oil bath heating, only needed 0.5 mol% of the catalyst and were over within 10 min in the microwave-assisted transfer hydrogenation (Table 2, entries 5 and 6). With these two imines, the efficiency is increased by a factor of 36 times. With microwave irradiation, the reaction time was reduced 12 times (from 240 to 20 min) for the electron-deficient imine **14** (Table 2, entry 7).

Scheme 3.



3

Table 2. Transfer hydrogenation of functionalized imines by **3** in wet isopropanol – toluene using microwave irradiation.[a]

Entry	Imine	Amine	Catalyst loading (mol%)	Time (min)	Yield[b]
1	 **6**	 **15**	0.1	20	98
2	 **7**	 **16**	0.5	20	99
3	 **8**	 **17**	0.5	10	99
4	 **10**	 **19**	0.1	20	94
5	 **12**	 **21**	0.5	10	98
6	 **13**	 **22**	0.5	10	95
7	 **14**	 **23**	3	20	98

[a]The reactions were run using imine (0.3 mmol), **3** (0.0003–0.009 mmol), toluene (1.9 mL), isopropanol (1.1 mL) under microwave irradiation for 20 min (110 °C, 2 bar (1 bar = 100 kPa)).
[b]The yield was determined by ^{1}H NMR.

Conclusions

We have developed an efficient transfer hydrogenation protocol for imines. Imines bearing acid-or base-labile functional groups, not compatible with conventional metal hydride reduction, are readily reduced with low catalyst loading and short reaction times to give high yields of the corresponding amines. The use of controlled microwave ir-

radiation led to an efficient procedure where most imines were reduced in greater than 90% yield within 20 min employing 0.1–0.5 mol% of catalyst. This procedure should be a useful complement to existing methods for the reduction of imines to amines.

Experimental section

General methods

^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Varian Mercury spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent as the internal standard, and coupling constants (*J*) are given in Hz. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Toluene was distilled from sodium benzophenone and isopropanol was distilled from CaO before use. All other chemicals were used as received. Short-path distillations were conducted in a Büchi glass oven B-580. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany. Ruthenium complexes **1** and **3** were made according to literature procedures (13).

N-Phenyl-(1-phenylethylidene)amine (6)

This compound was made according to literature procedure (8).

N-(4-Methoxyphenylimino)phenylacetic acid methyl ester (7)

Anisidine (2.46 g, 20 mmol), methylphenyl glyoxylate (13 g, 80 mmol), activated molecular sieves (4 Å, 7 g), and toluene (10 mL) were added to a round-bottomed flask and stirred at room temperature overnight. The reaction mixture was filtered through Celite, the filtrate evaporated, and the crude product was precipitated from CH_2Cl_2–pentane. Yield: 3 g (50%) of yellow-brownish crystals. ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C) δ: 3.69, (s, 3H, $COOCH_3$), 3.81 (s, 3H, OCH_3), 6.87–6.96 (m, 2H, aryl of *p*-methoxyphenyl), 6.97–7.01 (m, 2H, aryl of *p*-methoxyphenyl), 7.45–7.50 (m, 3H, phenyl), 7.84–7.86 (m, 2H, phenyl). ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C) δ: 51.9 (CH_3 of ester), 55.4 (OCH_3), 114.2 (aryl of *p*-methoxyphenyl), 121.1 (aryl of *p*-methoxyphenyl), 127.8 (phenyl), 128.7 (phenyl), 131.5 (phenyl), 134.1 (phenyl), 143.1 (aryl of *p*-methoxyphenyl), 157.3 (aryl of *p*-methoxyphenyl), 159.1 (C=N), 166.1 (C=O).

Ethyl [*N*-(*p*-Methoxyphenyl)imino]acetate (8)

Anisidine (2.46 g, 20 mmol), ethyl glyoxalate (4 mL, 30 mmol), activated molecular sieves (4 Å, 7 g), and benzene (5 mL) were added to a round-bottomed flask and stirred at room temperature overnight. Spectral data were in accordance with those previously reported in the literature (16).

N-[1-(2-Furyl)methylidene]-*N*-(4-methoxyphenyl)amine (10)

Anisidine (2.46 g, 20 mmol), furfural (2.4 g, 25 mmol), activated molecular sieves (4 Å, 7 g), and benzene (5 mL) were added to a round-bottomed flask and stirred at room temperature overnight. The reaction mixture was filtered through Celite, the filtrate evaporated, and the crude product was precipitated from CH_2Cl_2–pentane to yield 2.6 g (55%) of white crystals. Spectral data were in accordance with those previously reported in the literature (17).

N-Phenyl-[1-(4-fluorophenyl)ethylidene]amine (11)

The title compound was made according to the literature procedure (8).

(2,2-Dimethoxy-1-methylethylidene)-(4-methoxyphenyl)-amine (12)

Anisidine (2.47 g, 20 mmol), dimethoxy acetone (3.94 g, 30 mmol), activated molecular sieves (4 Å, 7 g), and benzene (10 mL) were added to a round-bottomed flask and stirred at room temperature overnight. Yield: 4 g (90%) of a colorless oil. ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C) δ: 1.83 (s, 3H, CH_3), 3.49 (s, 6H, OCH_3), 3.80 (s, 3H, OCH_3), 4.65 (s, 1H, CH), 6.72 (m, 2H, aryl of *p*-methoxyphenyl), 6.88 (m, 2H, aryl of *p*-methoxyphenyl). ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C) δ: 13.9 (CH_3), 55.1 (OCH_3), 55.4 (OCH_3), 107.6 (CH), 114.2 (aryl of *p*-methoxyphenyl), 120.7 (aryl of *p*-methoxyphenyl), 142.9 (aryl of *p*-methoxyphenyl), 156.3 (C=N), 168.2 (aryl of *p*-methoxyphenyl). Elemental anal. calcd. for $C_{12}H_{17}NO_3$ (223.27) (%): C 64.55, H 7.68, N 6.28; found: C 64.32, H 7.56, N 6.41.

N-(6-Methyl-2-hept-5-enylidene)-4-anisidine (13)

Anisidine (2.47 g, 20 mmol), 6-methyl-5-hepten-2-one (3 mL, 20 mmol), activated molecular sieves (4 Å, 7 g), and benzene (10 mL) were added to a round-bottomed flask and stirred at room temperature overnight. Yield: 2.74 g (59%) of a yellow oil. Spectral data were in accordance with those previously reported in the literature (18).

N-(4-Methoxyphenyl)-*N*-[(*E*)-1-(3-pyridyl)methylidene]amine (14)

Anisidine (2.46 g, 20 mmol), 3-pyridinecarboxaldehyde (2.67 g, 25 mmol), activated molecular sieves (4 Å, 7 g), and benzene (5 mL) were added to a round-bottomed flask and stirred at room temperature overnight. The reaction mixture was filtered through Celite and the filtrate was evaporated. The starting material was removed by bulb-to-bulb distillation (120 °C, 1 mbar, 1 bar = 100 kPa) and the product was subsequently distilled (160 °C, 1 mbar). Yield: 3.8 g (90%) of yellow crystals. Spectral data were in accordance with those previously reported in the literature (17).

Screening catalysts

Catalyst **1** (1 mg, 1 μmol) or **3** (1 mg, 1 μmol) dissolved in toluene-d_8 (0.48 mL) was added to imine **6** (0.15 mmol) in a vial. The mixture was transferred to a NMR tube and isopropanol-d_8 (0.28 mL, 3.7 mmol) was added. The NMR tube was subsequently shaken and inserted into a prewarmed (70 °C) spectrometer. After initial locking and shimming (~2 min), acquisitions were acquired every minute. The reactions were followed by ^{1}H NMR to ~75% conversion following the appearance of the methyl group of the amine at δ 1.48 and the disappearance of the methyl group of the imine at δ 2.24.

General procedure for the transfer hydrogenation under thermal heating — *N*-Phenyl-1-phenylethylamine (15)

In a typical experiment, imine **6** (0.195 g, 1.0 mmol), catalyst **3** (0.33 mg, 0.3 μmol), toluene (3.15 mL), isopropanol (1.84 mL, 24.0 mmol), and water (42 μL, 1% w/w) were added to a 10 mL Schlenk tube and heated to 110 °C for 90 min. Solvents were evaporated in vacuo and the product was purified by distillation (250 °C, 0.5 mbar) to afford amine **15** (0.182 g, 93%). Spectral data were in accordance with those previously reported in the literature (19).

(4-Methoxyphenylamino)phenylacetic acid methyl ester (16)

The general procedure was followed by using imine **7** (1.9 mmol, 0.5 g), **3** (1.1 μmol, 1 mg), toluene (8 mL), and wet isopropanol (3.5 mL, 48.0 mmol). The product was distilled (250 °C, 0.5 mbar) to afford amine **16** (0.48 g, 93%). Spectral data were in accordance with those previously reported in the literature (20).

***N*-(4-Methoxyphenyl)glycine ethyl ester (17)**

The general procedure was followed by using imine **8** (0.21 g, 1.0 mmol) and **3** (0.65 mg, 0.6 μmol). The product was bulb-to-bulb distilled (200 °C, 0.5 mbar) to afford amine **17** (0.199 g, 95%). ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C) δ: 1.27 (t, 3H, J = 7.1 Hz, CH_3), 3.74 (s, 3H, OCH_3), 3.86 (s, 2H, CH_2), 4.23 (q, 2H, J = 7.1 Hz, CH_2), 6.57–6.60 (m, 2H, aryl of *p*-methoxyphenyl), 6.77–6.81 (m, 2H, aryl of *p*-methoxyphenyl). ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C) δ: 14.4 (CH_3), 47.0 (CH), 55.9 (OCH_3), 61.4 (OCH_3), 114.6 (aryl of *p*-methoxyphenyl), 115.1 (aryl of *p*-methoxyphenyl), 141.5 (aryl of *p*-methoxyphenyl), 152.8 (aryl of *p*-methoxyphenyl), 171.6 (C=O of ester).

Decahydropyrimido[1,2-α]azepine (18)

Imine **9** (0.3 mmol, 45 μL), **3** (0.92 μmol, 1 mg), toluene-d_8 (0.95 mL), and isopropanol-d_8 (0.55 mL, 7.2 mmol) were added to a 10 mL Schlenk tube and heated to 70 °C for 60 min. According to the ^{1}H NMR there was full conversion. The spectral data were in accordance with those previously reported in the literature (21).

Furan-2-ylmethyl(4-methoxyphenyl)amine (19)

The general procedure was followed using imine **10** (0.171 g, 1.0 mmol) and **3** (2.8 μmol, 3 mg). The product was bulb-to-bulb distilled (250 °C, 0.5 mbar) to afford amine **19** (0.167 g, 97%). The spectral data were in accordance with those previously reported in the literature (17).

***N*-Phenyl-1-(4-fluorophenyl)ethylamine (20)**

The general procedure was followed using imine **11** (64 mg, 0.3 mmol) and catalyst **3** (3.2 mg, 3 μmol), isopropanol (0.55 mL, 7.2 mmol), and 0.95 mL of toluene. After 1 h, the sample was cooled down and analyzed by ^{1}H NMR. Conversion was >99%. Spectral data were in accordance to those previously reported in the literature (8).

***N*-(2,2-Dimethoxy-1-methylethyl)-4-methoxyphenyl)amine (21)**

The general procedure was followed by using imine **12** (0.223 g, 1.0 mmol) and **3** (33 mg, 30 μmol). The product was bulb-to-bulb distilled (250 °C, 0.5 mbar) to afford amine **21** (0.202 g, 95%). ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C) δ: 1.15 (d, 2H, J = 6.6 Hz, CH_3), 3.44 (s, 3H, OCH_3), 3.47 (s, OCH_3), 3.53–3.56 (m, 1H, CH), 3.74 (s, 3H, OCH_3 of *p*-methoxyphenyl), 4.27 (d, 1H, J = 3.8 Hz, acetal), 6.60–6.62 (m, 2H, aryl of *p*-methoxyphenyl), 6.76–6.78 (m, 2H, aryl of *p*-methoxyphenyl). ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C) δ: 14.6 (CH_3), 51.6 (CH), 55.5 (OCH_3), 55.7 (OCH_3), 56.5 (OCH_3), 107.1 (CH), 114.9 (aryl of *p*-methoxyphenyl), 115.2 (aryl of *p*-methoxyphenyl), 141.3 (aryl of *p*-methoxyphenyl), 152.2 (aryl of *p*-methoxyphenyl). Elemental anal. calcd. for $C_{12}H_{19}NO_3$ (225.29) (%): C 63.97, H 8.50, N 6.22; found: C 63.74, H 8.39, N 6.35.

***N*-(6-Methyl-2-hept-6-enyl)-4-methoxyaniline (22)**

The general procedure was followed using imine **13** (0.136 g, 1.0 mmol) and **3** (22.5 mg, 20.8 μmol). The product was bulb-to-bulb distilled (250 °C, 0.5 mbar) to afford amine **22** (0.147 g, 96%). Spectral data were in accordance to those previously reported in the literature (18).

4-(Methoxyphenyl)pyridin-3-ylmethylamine (23)

The general procedure was followed using imine **14** (0.212 g, 1.0 mmol) and **3** (33 mg, 30 μmol). The product was bulb-to-bulb distilled (250 °C, 0.5 mbar) to afford amine **23** (205.9 mg, 96%). ^{1}H NMR (400 Hz, $CDCl_3$, 25 °C) δ: 3.74 (s, 3H, OCH_3 *p*-methoxyphenyl), 4.32 (s, 2H, CH_2), 6.58–6.61 (m, 2H, aryl of *p*-methoxyphenyl), 6.76–6.79 (m, 2H, aryl of *p*-methoxyphenyl), 7.26–7.29 (m, 1H, pyridyl), 7.71–7.73 (m, 1H, pyridyl), 8.51–8.52 (m, 1H, pyridyl), 8.62–8.63 (m, 1H, pyridyl). ^{13}C NMR (100 Hz, $CDCl_3$, 25 °C) δ: 46.7 (CH_2), 55.8 (OCH_3), 114.5 (aryl of *p*-methoxyphenyl), 114.9 (aryl of *p*-methoxyphenyl), 122.3 (pyridyl), 134.6 (pyridyl), 141.7 (aryl of *p*-methoxyphenyl), 148.5 (pyridyl), 149.0 (pyridyl), 154.9 (aryl of *p*-methoxyphenyl). Elemental anal. calcd. for $C_{13}H_{14}N_2O$ (214.27) (%): C 72.87, H 6.59, N 13.08; found: C 73.11, H 6.72, N 13.21.

General procedure for the transfer hydrogenation of imines under controlled microwave heating — *N*-Phenyl-1-phenylethylamine (15)

In a typical experiment, imine **6** (58.6 mg, 0.3 mmol), **3** (0.3 mg, 0.3 μmol), toluene (1.9 mL), isopropanol (1.1 mL), and water (25 μL, 1%) were charged into a Pyrex tube (5 mL) fitted with a screw cap with a silicone–teflon septum (Personal Chemistry AB, Uppsala, Sweden). The septum was closed and the vessel inserted into a microwave oven. The microwave was run for 20 min (110 °C, 2 bar). The solvents were evaporated, $CDCl_3$ (0.7 mL) was added, and the solution was transferred to an NMR tube and analyzed by ^{1}H NMR, which showed 98% yield integrating the doublet at δ 1.48 (CH_3) of the amine and the singlet at δ 2.24 (CH_3) of the imine.

Amines **16**–**23** were prepared from the corresponding imines (0.3 mmol) according to the general procedure for

transfer hydrogenation under microwave heating using **3** (0.3–9 μmol). The results are given in Table 2.[4]

Acknowledgments

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[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3697. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml.