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Impregnated Ruthenium on Magnetite as a Recyclable Catalyst for the N-Alkylation of Amines, Sulfonamides, Sulfinamides, and Nitroarenes Using Alcohols as Electrophiles by a Hydrogen Autotransfer Process[†]

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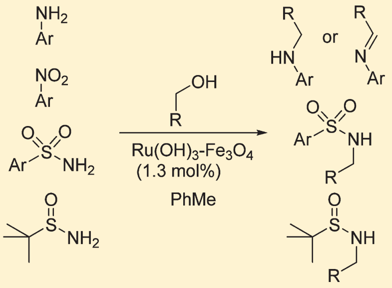
Supporting Information

ABSTRACT: Various impregnated metallic salts on magnetite have been prepared, including cobalt, nickel, copper, ruthenium, and palladium salts, as well as a bimetallic palladium−copper derivative. Impregnated ruthenium catalyst is a versatile, inexpensive, and simple system for the selective N-monoalkylation of amino derivatives with poor nucleophilic character, such as aromatic and heteroaromatic amines, sulfonamides, sulfinamides, and nitroarenes, using in all cases alcohols as the initial source of the electrophile, through a hydrogen autotransfer process. In the case of sulfinamides, this is the first time that these amino compounds have been alkylated following this strategy, allowing the use of chiral sulfinamides and secondary alcohols to give the alkylated compound with a diastereomeric ratio of 92:8. In these cases, after alkylation, a simple acid deprotection gave the expected primary amines in good yields. The ruthenium catalyst is quite sensitive, and small modifications of the reaction medium can change the final product. The alkylation of amines using potassium hydroxide renders the N-monoalkylated amines, and the same protocol using sodium hydroxide yields the related imines. The catalyst can be easily removed by a simple magnet and can be reused up to ten times, showing the same activity.



1. INTRODUCTION

Because of the demands of our society, recycling initiatives are rapidly increasing. This affects many different aspects of our day-to-day lives. In this context, recoverable catalysts are attracting increasing attention and importance under the umbrella of so-called green chemistry. Heterogeneous catalyst and reagents[1] play an important role with respect to the economy and also to the well being of society as a whole. Without effective heterogeneous catalysis, the manufacture of many materials and foodstuffs would not be possible.

There are many ways to immobilize catalysts on a solid support, depending on both the catalyst and support. One of the most used supports are the metal oxides,[2] including magnesia, alumina, silica, zirconia, and ceria.[3] There are several protocols for the preparation of a metallic catalyst supported on metal oxides[4] such as ion exchange, grafting, deposition−precipitation, coprecipitation, and impregnation.[5] The impregnation protocol allows all metallic active species to be at the surface of the catalyst and therefore enhances their activity. There are three standard steps in its preparation: (a) a solution of the metallic salt contacts the metal oxide support, (b) drying of either the solution or the filtered support, and (c) thermal activation.

Magnetite (Fe_3O_4), as any other metal oxide, can be used as support, as demonstrated in medicine, biology, and material science.[6] This support introduces a new advantage due to its easy recovery by a magnet. However, its broad use in organic chemistry has not been attained owing to the axiomatic idea that magnetite is unstable. Very recently the use of Fe_3O_4 as a catalyst[7] in various organic reactions has pointed out the incongruence of this idea. The impregnation of different metallic salts on magnetite has been performed for titanium,[8] manganese,[9] iron,[10] cobalt,[11] copper,[12] ruthenium,[13] rhodium,[14] palladium,[14,15] and platinum[14] derivatives. However, their applications in organic chemistry have been quite limited.

On the other hand, hydrogen autotransfer[16] is a reaction of great interest nowadays in C−C bond formation processes (Scheme 1).[17] This interest is directed toward the use of amines, and other nitrogenated compounds, as nucleophiles to yield the corresponding N-alkylated products.[18] The reason for this change is derived from the great variety of amines present in Nature, as well as their relevant importance in the pharmaceutical and agrochemical industries as usual building blocks. The extremely high advantage of this N-alkylation process, compared with classical protocols,[19] is based on the simplicity of the protocol, avoiding the use of either mutagenic alkyl halides, sulfates, etc., or carbonyl compounds that are difficult to store, as well as the reduction of wastes.

2. RESULTS AND DISCUSSION

Besides the use of impregnated ruthenium on magnetite in the Meerwein−Ponndorf−Verley type process,[13c] there is no report on the use of this type of catalyst in hydrogen autotransfer

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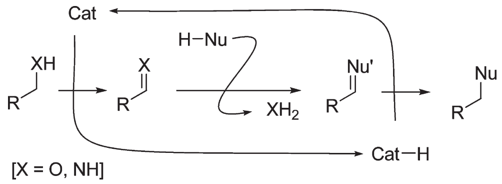
Scheme 1. General Scheme for a Hydrogen Autotransfer Process



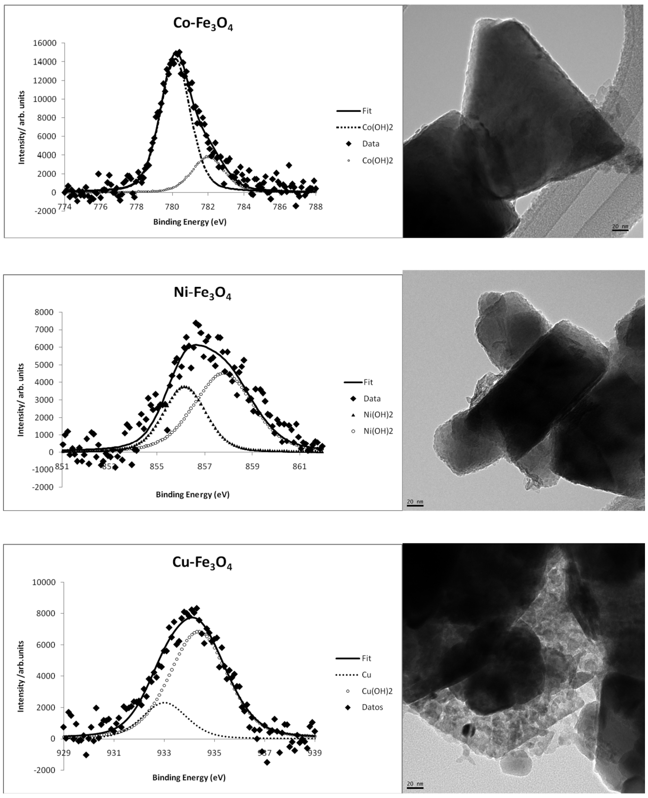


Figure 1. X-ray photoelectron spectra and TEM images for cobalt, nickel, and copper catalysts.

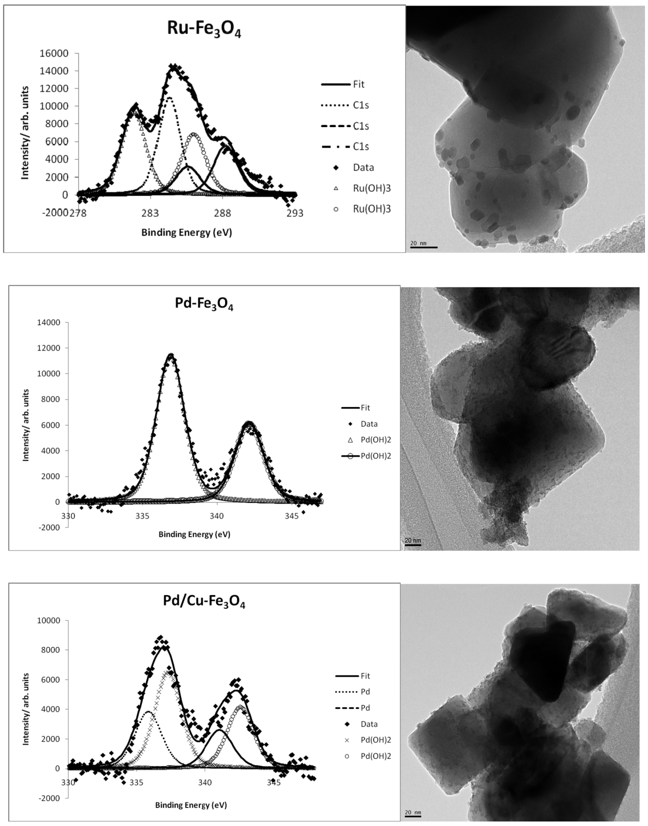


Figure 2. X-ray photoelectron spectroscopy and TEM image for ruthenium, palladium, and palladium/copper catalysts.

processes. There is only one example of N-alkylation of sulfonamides using bulk ruthenium−magnetite catalyst,[20] prepared by coprecipitation/calcination. With this study, we aim to show the great potential of this type of catalyst.

2.1. Synthesis and Characterization of Catalysts. All the catalysts were easily prepared by addition of commercial microparticles of magnetite to an aqueous solution of the corresponding metal chloride. The corresponding impregnated magnetite catalysts were obtained by increasing the pH of the solution up to nearly 13 by addition of 2 M aqueous NaOH, filtering, washing with water, and evaporation of water at 100 °C during 24 h. In the case of palladium derivatives, a great excess of potassium chloride was added to the initial solution in order to increase the solubility of the palladium chloride.

The cobalt catalyst had a total incorporation of cobalt(II) species of 1.7%, and 12.8% incorporation on the surface. The BET area surface was 8.7 m^2/g, almost the same as the starting magnetite (9.8 m^2/g), and the distribution of cobalt seemed to be homogeneous on the surface of the magnetite according to the TEM images (Figure 1, first row).

The nickel catalyst had a total incorporation of nickel(II) species of 1.2%, and 10.2% incorporation on the surface. The BET area surface was 8.2 m^2/g, and the distribution of nickel was homogeneous (Figure 1, second row).

The copper catalyst had a total incorporation of copper(0) and copper(II) species (in a 1:4 ratio, respectively) of 1.6%, and 2.6% on the surface. The BET area surface was 6.2 m^2/g, and the distribution of copper was homogeneous (Figure 1, third row).

The ruthenium catalyst had a total incorporation of ruthenium(III) species from 3.0 to 2.1%, and around 15.1% incorporation on the surface. The BET area surface was 9.2 m^2/g, and the distribution of ruthenium species was not homogeneous on the surface of magnetite according to the TEM images (Figure 2, first row).

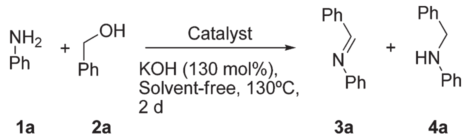
The palladium catalyst had a total incorporation of palladium(II) species of 2.6%, and 24.8% incorporation on the surface. The BET area surface was 13.6 m^2/g and the distribution of palladium was homogeneous (Figure 2, second row).

The bimetallic palladium−copper catalyst had a total incorporation of 3.2% for Pd(0) and Pd(II) species (in a 3:2 ratio, respectively) and 1.1% for Cu, with the incorporationof palladium on the surface determined as 22.2%, and the copper layers being placed between the palladium layer and magnetite. The BET area surface was 19.42 m^2/g, and the distribution of palladium was homogeneous (Figure 2, third row).

Once the catalysts were prepared and characterized, we examined their activity in various hydrogen autotransfer processes.

2.2. N-Arylation of Amines. The first studied process was the alkylation of amines using alcohols. The reaction depicted in

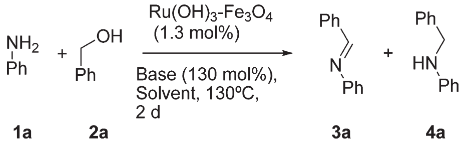
Table 1. Optimization of Impregnated Metal on Magnetite Catalyst



entry	catalyst (mol %)	yield **3a** (%)[a]	yield **4a** (%)[a]
1	$Co(OH)_2-Fe_3O_4$ (1.4)[b]	1	48
2	$Ni(OH)_2-Fe_3O_4$ (1.2)[b]	16	24
3	$Cu(OH)_2-Fe_3O_4$ (1.3)[b]	0	40
4	$Cu(OH)_2-Fe_3O_4$ (1.3)[b,c]	80	0
5	$Ru(OH)_3-Fe_3O_4$ (1.3)	40	45
6	$Pd(OH)_2-Fe_3O_4$ (1.2)[b]	8	34
7	$Pd(OH)_2-Fe_3O_4$ (1.2)[b,c]	30	10
8	$Pd(II/0)/Cu-Fe_3O_4$ (1.5/0.8)[b]	3	22

[a] Isolated yield. [b] Reaction performed during 4 days. [c] Reaction performed using K_2CO_3 (130 mol %) as base.

Table 2. Optimization of Reaction Conditions



entry[a]	solvent	base	yield **3a** (%)[b]	yield **4a** (%)[b]
1[c]	dioxane	KOH	22	22
2[c]	PhMe	KOH	0	56
3[c]	MeCN	KOH	0	0
4	PhMe	*t*BuOK	0	31
5	PhMe	NaOH	89	0
6[d]	PhMe	K_2CO_3	42	0
7[d]	PhMe	—	9	0
8[e]	PhMe	KOH	0	42
9[f]	PhMe	KOH	73	0
10[g]	PhMe	KOH	0	99
11[g,h]	PhMe	KOH	18	35
12[g,i]	PhMe	KOH	0	97

[a] Reaction performed using 150 mol % of **1a**. [b] Isolated yield. [c] Reaction performed during 24 h. [d] Reaction performed during 5 d. [e] Reaction performed at 150 °C. [f] Reaction performed at 90 °C. [g] Reaction performed using 200 mol % of **2a**. [h] Reaction performed using 0.26 mol % of catalyst. [i] Reaction performed using 2.6 mol % of catalyst.

Table 1 using aniline (**1a**), a low nucleophilic amine, and benzyl alcohol (**2a**) was chosen as the standard in order to optimize the different parameters of the reaction.

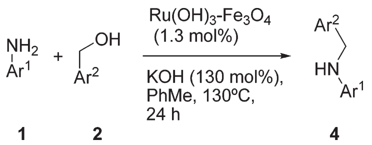
The reaction was initially conducted in the absence of solvent at 130 °C and in the presence of potassium hydroxide under an argon atmosphere, which is one of the most typical reaction conditions for the alkylation of aniline using the hydrogen autotransfer strategy.[7d,21] The reaction using the cobalt catalyst gave a mixture of imine **3a** (6%) and alkylated aniline **4a** (22%) after a 2 day reaction time, with an increased time of up to 4 days not improving the results (1 and 48%, respectively, see Table 1, entry 1). The reaction with the nickel catalyst also gave a modest result (entry 2). The reaction with copper catalysts gave only the expected amine **4a**, although with a modest yield. Meanwhile, the change of base to a weaker one (potassium carbonate) surprisingly permitted the preparation of the corresponding imine as the only isolated product (compare entries 3 and 4 in Table 1). The reaction using the ruthenium derivative gave the best conversion in only 2 days (entry 5 in Table 1). Finally, we studied the reaction with palladium catalysts. In the case of using only impregnated palladium on magnetite as catalyst, we obtained a mixture of both products in a moderate yield, after a 4 day reaction time. Whereas the change of the base to potassium carbonate did not improve the results, only a change of the ratio of the obtained products was observed. Then we tried the system in which Pd(0) and Pd(II) species are on the surface of the catalyst in order to test the activity of initial nanoparticles of palladium(0), but they showed a behavior similar to that obtained that with the +2 oxidation state (compare entries 6−8 in Table 1).

As the ruthenium derivative rendered the best conversion, we conducted the study with this catalyst. Initially we studied the effect of the solvent at 130 °C during 24 h under argon atmosphere, finding that the reaction in dioxane gave a mixture of products **3a** and **4a** in equal amounts, in toluene only amine **4a** was detected, and in acetonitrile the reaction failed (compare entries 1−3 in Table 2 and entry 5 in Table 1). Once toluene was discovered as the best solvent in terms of selectivity, the role of the base was investigated. The reaction with a more basic compound such as potassium *tert*-butoxide gave results (entry 4) similar to those with KOH. Surprisingly, the reaction under similar conditions but using sodium hydroxide gave only imine **3a** in good yield (entry 5). The reaction with potassium carbonate also gave imine **3a** as the only isolated product, albeit in lower yield, with the reaction giving a far inferior yield of imine **3a** in the absence of base after 5 days (entries 6 and 7 in Table 2). Once potassium hydroxide was found as the best base to obtain amine **4a**, the influence of temperature was tested, with higher temperatures (150 °C) not having any accountable effect on the yield, and lower ones (90 °C) rendering imine **3a** in good yield instead of the expected amine (entries 8 and 9 in Table 2). Then we increased the amount of alkylating agent **2a** up to 200 mol %, and under these new reaction conditions the expected amine **4a** was obtained in practically quantitative yield (Table 2, entry 10), with imine **3a** not being detected in the crude reaction medium. Finally, the amount of catalyst was evaluated (entries 11 and 12 in Table 2); the decrease from 1.3 to 0.26 mol % had a great impact not only on the chemical yield but also on the selectivity, whereas the increase up to 2.6 mol % did not have any appreciable effect either on the yield or on the product distribution.

After finding the best conditions (Table 2, entry 10), we examined the problem of catalyst recycling. Once the reaction was finished, the catalyst was trapped with a simple magnet, washed with toluene, and reused for other cycle. The catalyst could be reused 10-fold with no significant detrimental effect on the excellent chemical yield obtained, being always higher than 90% (see Supporting Information for the corresponding graphic).

Then we studied the scope of the reaction using various aromatic amines **1** and benzylic alcohol derivatives **3** (Table 3). The reaction using various substituted anilines with electron-donating or -withdrawing groups gave practically the same chemical yield. Only in the case of 2-methoxyaniline did the reaction time have to be increased in order to reach the previous

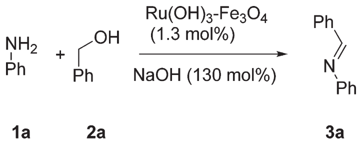
Table 3. Alkylation of Aromatic Amines



entry	Ar^1	Ar^2	compound	yield (%)[a]
1[b]	Ph	Ph	**4a**	99
2[c]	4-MeOC$_6$H$_4$	Ph	**4b**	71
3[b]	2-MeOC$_6$H$_4$	Ph	**4c**	99
4[b]	3-ClC$_6$H$_4$	Ph	**4d**	99
5[d]	Ph	4-MeOC$_6$H$_4$	**4e**	82
6[d]	Ph	4-ClC$_6$H$_4$	**4f**	94
7	2-pyridyl	Ph	**4g**	99
8	2-pyridyl	4-MeC$_6$H$_4$	**4h**	99
9	2-pyridyl	4-MeOC$_6$H$_4$	**4i**	99
10	2-pyridyl	2-MeOC$_6$H$_4$	**4j**	99
11	2-pyridyl	4-ClC$_6$H$_4$	**4k**	99
12	4-pyridyl	Ph	**4l**	99
13	2-pyrimidyl	Ph	**4m**	99
14[b]	5-methylthiazol-2-yl	Ph	**4n**	90

[a] Isolated yield. [b] Reaction performed during 2 d. [c] Reaction performed during 7 d. [d] Reaction performed during 5 d.

Table 4. Optimization of Reaction Conditions for Imine 3a Formation



entry[a]	solvent	T (°C)	t (h)	yield **3a** (%)[b]
1	dioxane	130	48	0
2	PhMe	130	48	80
3	MeCN	130	48	0
4	PhMe	150	48	59
5	PhMe	90	48	52
6[c]	PhMe	130	24	89
7[c,d]	PhMe	130	24	47
8[c,e]	PhMe	130	24	88

[a] Reaction performed using 150 mol % of **1a**. [b] Isolated yield. [c] Reaction performed using 150 mol % of **2a**. [d] Reaction performed using 0.26 mol % of catalyst. [e] Reaction performed using 2.6 mol % of catalyst.

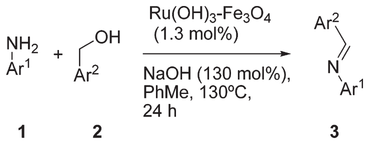
results (compare entries 1−4 in Table 3). The reaction also gave excellent results in the case of 4-substituted benzylic alcohols, independently of the electronic nature of the substitution (compare entries 1, 5, and 6 in Table 3). Heteroaromatic amines could also be used, obtaining in all cases practically quantitative yields, independently of the substitution of the alcohols (Table 3, entries 7−11), the position of the nitrogen atom (compare entries 7 and 12 in Table 3), or the number of the nitrogen atoms in the aromatic ring (Table 3, entry 13). Note that even electron-rich five-membered aromatic amines could be used with similar results (entry 14 in Table 3). However, the reaction failed when the aliphatic *tert*-butylamine was used as the nucleophilic partner in the presence of benzyl alcohol or when 1-hexanol was used as the electrophilic partner in the presence of aniline, showing the high selectivity of the catalyst.

The real role of the base is not clear from a mechanistic point of view, but it seems to be connected initially with the deprotonation of the primary alcohol and to force the dehydrogenation step, forming the aldehyde, because the reaction of pyridin-2-amine with benzyl alcohol failed in the absence of KOH. However, the same reaction using the in situ-prepared potassium alkoxide (by deprotonation of benzyl alcohol with potassium hydride) yields the expected product **4g** in good yield. When the reaction was performed using an equimolecular amount of benzaldehyde and benzyl alcohol and in the absence of base, compound **16a** was not detected after 2 days, indicating that the base also has a role in the final hydrogenation step of imines. The reaction of an equal mixture of 4-methoxybenzyl alcohol and α,α-dideuterobenzyl alcohol with pyridin-2-amine under standard conditions gave a mixture of the related monodeuteated products **4i** and **4g** at the benzylic position, respectively, with the incorporation of deuterium being about 70%, according to the GC-MS spectrum. This indicates that between the ruthenium-catalyzed steps, of the dehydrogenation of the alcohol and of the hydrogenation of the imine, the one step that occurs outside the metal coordination sphere is the condensation reaction.[22]

From the results shown in Table 2, we found that very small changes of the reaction conditions could change the main product of the reaction, the results using sodium and potassium hydroxides being very spectacular (Table 2, entries 5 and 10). In the case of using sodium hydroxide, the corresponding imine **3a** was isolated as the main product (see Table 4). In general, imines have widespread applications in laboratory and industrial synthetic processes,[23] with their traditional synthesis implying the condensation between amines and carbonyl compounds (ketones or aldehydes) in acidic media with azeotropic distillation to expel the liberated water. Another interesting and ecological alternative is the aerobic oxidation of secondary amines,[24] with the preparation of imines using alcohols and amines as starting materials under aerobic oxidation conditions being a more difficult task.[25,26] To the best of our knowledge, there is only one example of formation of imines using alcohols and amines without any type of oxidant,[27] which used a sophisticated pincer-ruthenium complex[28] as catalyst, liberating hydrogen. In our case, the ruthenium-impregnated magnetite is also able to catalyze this transformation in the absence of any type of oxidant. For this reason, further effort was made in order to optimize the imine preparation. Using only toluene as reaction media, the expected imine **3a** was obtained (Table 4, entries 1−3), with the optimum temperature being 130 °C (compare entries 2, 4, and 5 in Table 4). The use of an excess of alcohol has a beneficial impact on the chemical yield; meanwhile, the use of a lower amount of catalyst led to a decrease in the chemical yield, with an increase of catalyst up to 2.6 mol % not improving the initial result (Table 4, entries 6−8).

Under the best reaction conditions (Table 4, entry 6), we studied the recycling of the catalyst. Once the reaction was finished, the catalyst was trapped with a simple magnet, washed with toluene, and reused for other cycles, and the catalyst could be reused 10-fold with a only a marginal detrimental effect on the obtained chemical yield (see Supporting Information for the corresponding graphic). The ICP-OES analyses showed only 0.5 ppm of ruthenium species in the solution, which is the same amount found in the case of N-alkylation.

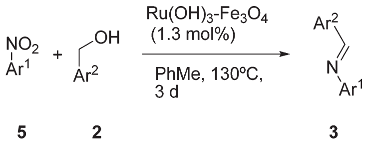
Table 5. Preparation of Aromatic Imines from Amines



entry	Ar^1	Ar^2	compound	yield (%)[a]
1	Ph	Ph	**3a**	89
2	4-MeOC$_6$H$_4$	Ph	**3b**	91
3[b]	3-ClC$_6$H$_4$	Ph	**3c**	77
4	Ph	4-MeOC$_6$H$_4$	**3d**	83
5	Ph	4-ClC$_6$H$_4$	**3e**	79

[a] Isolated yield. [b] Reaction performed during 4 d at 90 °C.

Table 6. Preparation of Aromatic Imines from Nitroarenes



entry[a]	Ar^1	Ar^2	base (mol %)	imine	yield (%)[b]
1	Ph	Ph	KOH (800)	**3a**	5
2	Ph	Ph	KOH (300)	**3a**	99
3	Ph	Ph	KOH (100)	**3a**	0
4	Ph	Ph	—	**3a**	59
5	Ph	Ph	K$_2$CO$_3$ (300)	**3a**	76
6	Ph	Ph[c]	KOH (300)	**3a**	42
7	Ph	Ph[d]	KOH (300)	**3a**	78
8	4-MeOC$_6$H$_4$	Ph	KOH (300)	**3b**	57
9	3-ClC$_6$H$_4$	Ph	KOH (300)	**3c**	12[e]
10	Ph	4-MeOC$_6$H$_4$	KOH (300)	**3d**	50
11	Ph	4-MeOC$_6$H$_4$	K$_2$CO$_3$ (300)	**3d**	44
12	Ph	4-ClC$_6$H$_4$	KOH (300)	**3e**	92

[a] Reaction performed using 800 mol % of **2**. [b] Isolated yield. [c] Reaction performed using only 300 mol % of **2a**. [d] Reaction performed using 1600 mol % of **2a**. [e] 49% of the amine **4d** was isolated.

The scope of the reaction is presented in Table 5. The reaction could be carried out with similar results using substituted anilines, independently of the electronic nature of substitution (Table 5, entries 1−3); for the case of chlorinated aniline, the temperature used was lower in order to avoid the reduction of the imine **3c** to the corresponding amine **4d**. It was also possible to use various substituted benzylic alcohols **2**, obtaining similar yields for the expected imines **3** (entries 4 and 5 in Table 5).

In order to elucidate the behavior of the impregnated ruthenium on magnetite, we could stop the reaction at the formation stage of imine **3** or finish the reaction at the formation of amine **4** only by changing the cation of the hydroxide derivative. We initially studied the BET area of the catalyst after it was used in the presence of either potassium hydroxide or sodium hydroxide. The area for catalyst in the first case (using KOH) was 6.2 m^2/g and in the second case (using NaOH) was 19.2 m^2/g. Although the areas are different, both are in the same range of the starting catalyst (9.2 m^2/g), indicating that there is no significant physical change at the surface of catalyst. Moreover, the TEM images of the three cases are quite similar. Then we saw that the nanosize distribution of ruthenium particles at the surface of the catalyst was similar for the three cases: 60% for particles between 0.5 and 2 nm for the initial catalyst, 79% for the catalyst used with KOH, and 60% for the catalyst used with NaOH (see Supporting Information for the corresponding graphics). The XPS data of the recovered catalyst for both protocols showed the maintenance of ruthenium(III) species and the adsorption of potassium (36%) and sodium (44%) at the surface (1 nm depth). However, this new adsorption seems to have no importance, because after carrying out the reaction with NaOH and preparing compound **3a**, the recycled catalyst was used in the presence of KOH under standard conditions and gave the related amine **4a**.

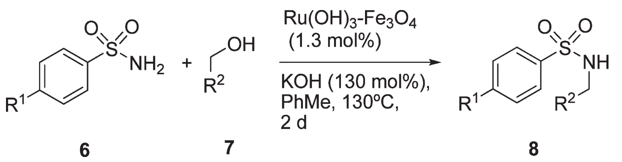
Finally, we considered the possibility of an extra dehydrogenation step in the conversion of amine **4a** to imine **3a**. However, the treatment of amine **4a** with NaOH in the presence of ruthenium catalyst under the conditions described in entry 6 of Table 4 did not produce the expected imine **3a** after a 4 day reaction time. The same result was obtained using NaOH and 3 equiv of water, which is the byproduct of the condensation reaction. In conclusion, we do not have any satisfactory explanation for the effect of the cation present in the base on the course of the reaction in our experiments.

2.2. Reaction with Nitroarenes. Very recently, various nitroarenes have been used as a masked nitrogen source in the formation of aromatic imines through the hydrogen autotransfer process using a large excess of benzyl alcohol derivatives (1700 mol %), anilines, and an iridium carbine complex (2 mol %) in moderate to good yields (17−92%) after 1 day at 110 °C.[29] On the other hand, tertiary amines could be obtained by the same strategy, but using in this case a large excess of alcohol (750 mol %), catalytic amounts of a phosphane−ruthenium complex (7.5 mol %), and a carbene ligand (7.5 mol %) at 150 °C during 1 day,[30] with the corresponding tertiary amines being obtained in yields ranging from 32 to 88%. We assumed that our very selective ruthenium catalyst could perform the same transformation, stopping the reaction before the final polyalkylation process.

As we anticipated, the reaction of nitrobenzene (**5a**) with a large excess of benzyl alcohol (**2a**) and potassium hydroxide gave a complicated mixture after a 3 day reaction time in toluene under argon atmosphere; the corresponding imine **3a** was isolated but the related amine **4a** or *N*,*N*-dibenzylaniline was not detected. Decreasing the amount of base (300 mol %) gave a significant improvement in the obtained yield, being practically quantitative. These results were not improved with a further decrease or elimination of base (compare entries 1−4 in Table 6). The use of a weaker base such as potassium carbonate had only a marginal effect on the chemical yield (Table 6, entry 7). Then the amount of benzyl alcohol (**2a**) was changed but resulted in no improvement in the yield (compare entries 2, 6, and 7 from Table 6).

Once the best conditions were found, other substrates were subjected to the same reaction process. Substitution on the nitroarene derivative had an important effect on the yield, in all cases being lower than that for simple nitrobenzene (entries 8 and 9 in Table 6). Note that in the case of 1-chloro-3-nitrobenzene, a significant amount of monalkylated amine **4d** was isolated along with the expected imine **3c**, indicating a facile reduction of the imine **3c** under these reaction conditions, as previously highlighted in the case of aniline derivatives (Table 5, entry 3). The reaction using 4-methoxybenzyl alcohol also gave a moderate

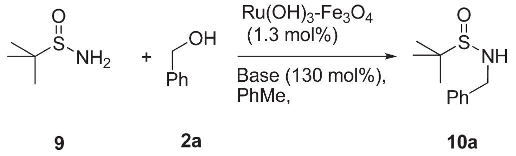
Table 7. Alkylation of Sulfonamides



entry[a]	R^1	R^2	compound	yield (%)[b]
1	Me	Ph	**8a**	86
2	Me	3-ClC_6H_4	**8b**	99
3	Me	2,3-$(OCH_2O)C_6H_3$	**8c**	99[c]
4	Me	1-naphthyl	**8d**	96[c]
5	Me	cC_6H_{11}	**8e**	99[c]
6	H	Ph	**8f**	99

[a] Reaction performed using 200 mol % of **7**. [b] Isolated yield. [c] Reaction performed during 4 d.

Table 8. Optimization of Reaction Conditions



entry[a]	solvent	base	*T* (°C)	*t* (h)	yield **10a** (%)[b]
1	PhMe	KOH	130	96	10
2	PhMe	KOH	100	5	53
3	PhMe	KOH	85	5	76
4	Ddioxane	KOH	85	96	0
5	MeCN	KOH	85	96	0
6	PhMe	NaOH	85	5	70
7	PhMe	*t*BuOK	85	5	69
8	PhMe	K_2CO_3	85	48	0
9[c]	PhMe	KOH	85	5	64
10[c]	PhMe	NaOH	85	5	58

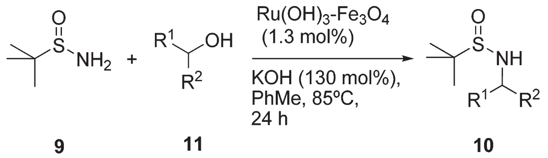
[a] Reaction performed using 200 mol % of **2a**. [b] Isolated yield. [c] Reaction performed using only 100 mol % of **2a**.

yield using potassium hydroxide or potassium carbonate (Table 6, entries 10 and 11). However, when the reaction was performed using 4-chlorobenzyl alcohol, an excellent yield for the corresponding imine was obtained (entry 12 in Table 6).

The above reaction strategy is an alternative to the classical reduction of nitroarenes without hydrogen, because the real source of hydrogen is the alcohol. In addition, this protocol allows the in situ protection of the amine group as an imine by the reaction with the aldehyde formed in the dehydrogenation step.

2.3. N-Alkylation of Sulfonamides. Another type of nitrogen-containing compound that has been very recently alkylated using various transition metal catalysts[20,21h,21m,31] through a hydrogen autotransfer process are the sulfonamides. On the basis of our continued interest in the synthesis and use of various sulfonamides as ligands,[32] we examined the alkylation of this type of compound using impregnated ruthenium on magnetite catalyst (see Table 7).

Table 9. Alkylation of Sulfinamides



entry	R^1	R^2	compound	yield (%)[a]
1	H	Ph	**10a**	76[b]
2	H	4-ClC_6H_4	**10b**	75
3	H	4-$MeOC_6H_4$	**10c**	68
4	H	furan-2-yl	**10d**	78[c]
5	H	$Me(CH_2)_6$	**10e**	67[c]
6	H	*i*Pr	**10f**	72
7	Me	Ph	**10g**	30[d]
8[e]	Me	Ph	**10g’**	28[f]

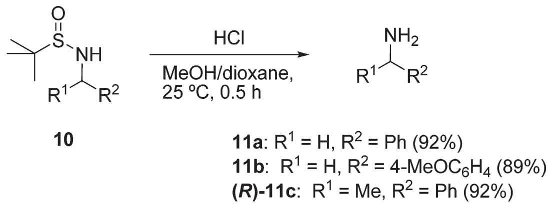
[a] Isolated yield. [b] Reaction performed during 5 h. [c] Reaction performed during 48 h. [d] Mixture of four possible diastereoisomers. [e] The reaction was performed using chiral (*R*)-2-methyl-2-proanesulfinamide **9**. [f] A 92:8 mixture of two diastereoisomers was isolated.

2.4. N-Alkylation of Sulfinamides. Encouraged by the success obtained in the alkylation of various nitrogen-containing compounds using impregnated ruthenium on magnetite, we examined the the alkylation of sulfinamide **9** using this strategy of hydrogen autotransfer, unknown until now (Table 8).

The reaction of 2-methylpropane-2-sulfinamide (**9**) with a double amount of benzyl alcohol (**2a**) was chosen as a standard in order to optimize all parameters (Table 8). The reaction in toluene at 130 °C under argon atmosphere using potassium hydroxide as base gave the expected compound **10a** after 4 days with a modest yield and gave a huge amount of various byproducts. The reaction was then repeated at lower temperatures in order to avoid the decomposition of the starting amide and the final product, finding that the best result was obtained at 85 °C (compare entries 1−3 in Table 8). The change of toluene to dioxane or acetonitrile as solvent had a very negative impact on the yield, the reaction failing in these media (Table 8, entries 4 and 5). Other bases such as sodium hydroxide or potassium *tert*-butoxide could be used to render the final compound **10a** with results similar to that obtained using potassium hydroxide (entries 6 and 7 in Table 8). However, the reaction failed when using a weaker base such as potassium carbonate. Finally, note that the reaction using only a stoichiometric amount of benzyl alcohol and either potassium or sodium hydroxide gave the expected product **10a** with slightly lower yield (entries 9 and 10 in Table 8).

More interesting is the fact that the former reaction could be carried out using primary aliphatic alcohols with or without substitution at the β position, such as for 1-heptanol or isobutyl alcohol (Table 9, entries 5 and 6), in similar yields. The reaction with secondary alcohols gave the corresponding compound **10** in a lower yield. Thus, the reaction of racemic **9** with 1-phenylethanol gave the compound **10g** in a modest yield, and as a mixture of the four possible isomers, according to the chiral-HPLC analyses (33, 33, 17, and 17%, respectively). However, when the same reaction was performed using the related starting chiral material (*R*)-**9**, compound **10g**′ was obtained as a mixture of only two diastereoisomers, with the diastereoisomeric ratio being 92:8. This last result indicated that this new reaction could be used in

Scheme 2. Liberation of Primary Amines



asymmetric synthesis to prepare chiral amino derivatives, and we are now studying the scope of this process.

Finally, the removal of the sulfinyl group was performed using the typical acid protocol to give the expected primary amine **11** with good chemical yields in all three cases tested (Scheme 2).[33] In the case of the sulfinamide **10g′**, the absolute configuration at the stereogenic carbon atom placed at the α-position of the obtained amine **11c** was assigned as (*R*), according to literature values.[34]

The entire process, N-alkylation of the sulfinamide and deprotective acid treatment, is an interesting alternative to the direct monoalkylation of ammonia, which is a difficult task using the hydrogen autotransfer strategy.[35] Moreover, the possibility to perform the entire transformation in an asymmetric way gives extra value to this methodology.

3. CONCLUSIONS

In conclusion, inexpensive and easily prepared impregnated ruthenium on magnetite has been shown to be an active, stable, versatile, and highly selective catalyst for the selective monoalkylation of aromatic amines and sulfonamides through a hydrogen autotransfer process. The protocol has been applied for the first time successfully to sulfinamides and, in the case of chiral starting compounds; the corresponding diastereoselective reaction was performed. The combined alkylation−deprotection process of sulfinamide case is an alternative to the direct monoalkylation of ammonia, which could also be applied to chiral primary amines.

The protocol of impregnation is simple and reproducible, permitting the easy preparation of the corresponding catalysts derived not only from ruthenium but also from cobalt, nickel, copper, palladium, and polymetallic systems such as those derived from palladium and copper.

4. EXPERIMENTAL SECTION

4.1. General Procedure for the Preparation of Catalysts. To a stirred solution of the metal salt MCl_x (1 mmol) in deionized water (120 mL) was added Fe_3O_4 (4 g, 17 mmol, powder <5 μm, BET area: 9.86 m^2/g). After 10 min at room temperature, the mixture was slowly basified with NaOH (1 M) until pH around 13. The mixture was stirred during 1 day. Subsequently, the catalyst was filtered under vacuum and washed several times with deionized water (3 × 10 mL). The solid residue was dried at 100 °C during 24 h.

4.2. Representative Procedure for the Alkylation of Amines and Sulfonamides. To a stirred solution of amine or sulfonamide (**1** or **6**, 1 mmol) in toluene (3 mL) under argon atmosphere were added $Ru(OH)_3{-}Fe_3O_4$ (50 mg), KOH (1.3 mmol, 73 mg), and the corresponding alcohol (**2** or **7**, 2 mmol). The resulting mixture was stirred at 130 °C until the end of reaction. The catalyst was removed by a magnet, and the resulting mixture was quenched with water and extracted with EtOAc. The organic phases were dried over $MgSO_4$, followed by evaporation under reduced pressure to remove the solvent. The product was purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **4** or **8**. Yields are included in Table 3 and 7. Physical and spectroscopic data, as well as literature for known compounds, are as follows:

*N-Benzylaniline (**4a**)*:[7d]. mp 37−40 °C (hexane); R_f 0.5 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3414, 1603 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.98 (s, br, 1H), 4.3 (s, 2H), 6.60−6.63, 6.67−6.73, 7.13−7.19, 7.23−7.37 (4 m, 2, 1, 2, and 5H, respectively); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.2, 112.8 (2C), 117.5, 127.2, 127.5 (2C), 128.6 (2C), 129.2 (2C), 139.4, 148.1; EI-MS *m/z*: 184 (M^+ + 1, 13%), 183 (M^+, 100), 182 (38), 180 (10), 106 (20), 91 (100), 77 (18), 65 (14).

*N-Benzyl-4-methoxyaniline (**4b**)*:[7d]. R_f 0.43 (hexane/ethyl acetate: 4/1); IR (film): ν 3405, 1525, 1281 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.5−3.8 (s, br, with s at 3.68, 1 and 3H, respectively), 4.22 (s, 2H), 6.54−6.57 (m, 2H), 6.73−6.76 (m, 2H), 7.23−7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.1, 55.6, 114 (2C), 114.8 (2C), 127, 127.4 (2C), 128.5 (2C), 139.6, 142.3, 152; EI-MS *m/z*: 214 (M^+ + 1, 16%), 213 (M^+, 100), 212 (11), 198 (11), 122 (78), 91 (65), 65 (11).

*N-Benzyl-2-methoxyaniline (**4c**)*:[7d]. R_f 0.43 (hexane/ethyl acetate: 4/1); IR (film): ν 3423, 1603, 1509, 1292 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 4.3 (s, 2H), 4.61 (s, br, 1H), 6.57−6.86, 7.22−7.39 (2 m, 4 and 5H, respectively); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48, 55.4, 109.3, 110, 116.6, 121.3, 127.1, 127.5, 128.5, 138.1, 139.5, 146.7; EI-MS *m/z*: 214 (M^+ + 1, 16%), 213 (M^+, 100), 212 (21), 198 (34), 120 (12), 92 (13), 91 (70), 65 (15).

*N-Benzyl-3-chloroaniline (**4d**)*:[7d]. R_f 0.5 (hexane/ethyl acetate: 4/1); IR (film): ν 3420, 1585, 1077 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.2 (s, br, 1H), 4.39 (s, 2H), 6.6−6.63, 6.75−6.77, 6.88−6.89, 7.19−7.24 (4 m, 1, 1, 1 and 1H, respectively), 7.44−7.56 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.7, 110.9, 112.3, 117, 127.2 (2C), 127.3 (2C), 128.5, 130.1, 134.8, 138.6, 149; EI-MS *m/z*: 219 (M^+ + 1, 21%), 218 (M^+, 15), 217 (64), 216 (19), 91 (100).

*N-(4-Methoxybenzyl)aniline (**4e**)*:[7d]. R_f 0.53 (hexane/ethyl acetate: 4/1); IR (film): ν 3412, 1603, 1259 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H), 4.1 (s, br, 1H), 4.37 (s, 2H), 6.76−6.78, 6.86−6.91, 7.01−7.05, 7.3−7.36, 7.41−7.44 (5 m, 2, 1, 2, 2 and 2H, respectively); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 55, 112.7 (2C), 113.8 (2C), 117.2, 128.6 (2C), 129.1 (2C), 131.3, 148.1, 158.6; EI-MS *m/z*: 213 (M^+, 29%), 122 (10), 121 (100), 77 (10).

*N-(4-Chlorobenzyl)aniline (**4f**)*:[7d]. R_f 0.43 (hexane/ethyl acetate: 4/1); IR (film): ν 3419, 1596, 1089 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.04 (s, br, 1H), 4.3 (s, 2H), 6.58−6.62, 6.69−6.74, 7.14−7.19, 7.26−7.31 (4 m, 2, 1, 2, and 4H, respectively); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.6, 112.8 (2C), 117.8, 128.7 (2C), 128.7 (2C), 129.3 (2C), 132.8, 138, 147.8; EI-MS *m/z*: 219 (M^+ + 1, 21%), 218 (M^+, 14), 217 (63), 216 (15), 182 (12), 127 (33), 125 (100), 106 (10), 89 (13), 77 (12).

*N-Benzylpyridin-2-amine (**4g**)*:[7d]. mp 94−96 °C (hexane); R_f 0.2 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3217, 1598, 1578, 1529 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.46 (d, *J* = 5.8 Hz, 2H), 5.26 (s, br, 1H), 6.31−6.34 (m, 1H), 6.51−6.56 (m, 1H), 7.29−7.32 (m, 6H), 8.02−8.04 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.1, 106.6, 112.9, 127, 127.2 (2C), 128.5 (2C), 137.3, 139.1, 148, 158.6; EI-MS *m/z*: 185 (M^+ + 1, 14%), 184 (M^+, 100), 183 (52), 107 (18), 106 (75), 91 (36), 79 (26), 78 (20), 65 (12).

*N-(4-Methylbenzyl)pyridin-2-amine (**4h**)*:[7d]. mp 73−77 °C (hexane); R_f 0.17 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3210, 1599, 1570, 1521 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.32 (s, 3H), 4.42 (d, *J* = 5.7 Hz, 2H), 5.02 (s, br, 1H), 6.32−6.34 (m, 1H), 6.53−6.56 (m, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.34−7.36 (m, 1H), 8.05−8.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21, 46, 106.6, 112.9, 127.3 (2C), 129.2 (2C), 136, 136.7, 137.3, 148.1, 158.6; EI-MS *m/z*: 199 (M^+ + 1, 15%), 198 (M^+, 100), 197 (45), 183 (16), 120 (71), 105 (49), 79 (22), 78 (19), 77 (14).

N-(4-Methoxybenzyl)pyridin-2-amine (**4i**):[7d]. mp 128−130 °C (hexane); R_f 0.07 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3231, 1603, 1574, 1531, 1506, 1238 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.77 (s, 3H), 4.40 (d, J = 5.5 Hz, 2H), 5.01 (s, br, 1H), 6.33−6.36 (m, 1H), 6.54−6.58 (m, 1H), 6.86 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.6 Hz, 2H), 7.35−7.4 (m, 1H), 8.06−8.07 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 45.7, 55.2, 106.7, 112.9, 113.9 (2C), 128.6 (2C), 131.1, 137.3, 148.1, 158.6, 158.7; EI-MS m/z: 215 (M$^+$ + 1, 10%), 214 (M$^+$, 68), 213 (14), 136 (22), 121 (100), 78 (18).

N-(2-Methoxybenzyl)pyridin-2-amine (**4j**):[7d]. mp 54−56 °C (hexane); R_f 0.9 (ethyl acetate); IR (KBr): ν 3256, 1607, 1234 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.79 (s, 3H), 4.46 (d, J = 6.1 Hz, 2H), 5.2 (s, br, 1H), 6.33−6.35 (m, 1H), 6.48−6.51 (m, 1H), 6.82−6.91, 7.19−7.3 (2 m, 2 and 2H, respectively), 7.31−7.34 (m, 1H), 8.03−8.05 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 41.4, 55.1, 106.5, 110, 112.6, 120.3, 126.9, 128.1, 128.5, 137.2, 147.9, 157.2, 158.8; EI-MS m/z: 215 (M$^+$ + 1, 12%), 214 (M$^+$, 77), 213 (14), 199 (27), 184 (15), 183 (100), 181 (14), 180 (13), 136 (36), 121 (27), 107 (14), 105 (12), 91 (63), 79 (19), 78 (30), 66 (13).

N-(4-Chlorobenzyl)pyridin-2-amine (**4k**):[7d]. mp 103−105 °C (hexane), R_f 0.9 (ethyl acetate); IR (KBr): ν 3225, 1607, 1570, 1533, 1081 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.4 (d, J = 5.9 Hz, 2H), 5.44 (s, br, 1H), 6.28−6.30 (m, 1H), 6.51−6.55 (m, 1H), 7.22−7.32 (m, 4H), 7.33−7.34 (m, 1H), 7.99−8.01(m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 45.3, 106.6, 113, 128.5 (2C), 128.5 (2C), 132.6, 137.4, 137.7, 147.9, 158.4; EI-MS m/z: 220 (M$^+$ + 1, 33%), 219 (M$^+$, 27), 218 (100), 217 (41), 142 (32), 140 (98), 127 (16), 125 (45), 107 (11), 89 (17), 79 (31), 78 (22).

N-Benzylpyridin-4-amine (**4l**):[7d]. R_f 0.07 (ethyl acetate); IR (film): ν 3246, 1604, 1524 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.35 (d, J = 5.2 Hz, 2H), 5.24 (s, br, 1H), 6.46 (d, J = 6.3 Hz, 2H), 7.26−7.35 (m, 5H), 8.12 (d, J = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 46.7, 107.6, 127.2 (2C), 127.5 (2C), 128.7 (2C), 137.7, 149.1 (2C), 153.6; EI-MS m/z: 185 (M$^+$ + 1, 12%), 184 (M$^+$, 86), 183 (23), 91 (100), 65 (11).

N-Benzylpyrimidin-2-amine (**4m**):[7d]. mp 70−75 °C (hexane); R_f 0.73 (ethyl acetate); IR (KBr): ν 3242, 1597, 1527 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.60 (d, J = 6.1 Hz, 2H), 6.38 (t, J = 4.8 Hz, 1H), 7.04 (s, br, 1H), 7.24−7.36 (m, 5H), 7.99 (s, br, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 45.5, 110.4, 127.2, 127.8 (2C), 128.6 (2C), 139.2, 157.9 (2C), 162.4; EI-MS m/z: 186 (M$^+$ + 1, 13%), 185 (M$^+$, 100), 184 (71), 108 (11), 106 (45), 91 (23), 80 (10), 79 (14).

N-Benzyl-5-methylthiazol-2-amine (**4n**):[7d]. mp 86−91 °C (hexane); R_f 0.3 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3188, 1589, 1560 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.2 (s, 3H), 4.38 (s, 2H), 6.43 (s, br, 1H), 6.58 (s, 1H), 7.24−7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 11.9, 49.7, 120.8, 127.4, 127.6 (2C), 128.5 (2C), 135.4, 137.9, 169; EI-MS m/z: 205 (M$^+$ + 1, 10%), 204 (M$^+$, 63), 203 (23), 106 (11), 91 (100), 65 (13).

N-Benzyl-4-methylbenzenesulfonamide (**8a**):[21h]. mp 118−120 °C (hexane); R_f 0.27 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3278, 1600, 1328, 1169, 715 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.43 (s, 3H), 4.11 (d, J = 6.2 Hz, 2H), 4.73 (t, J = 6 Hz, 1H), 7.17−7.32, 7.74−7.78 (2 m, 7 and 2H, respectively); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.5, 47.2, 127.2 (2C), 127.8 (2C), 127.9, 128.7 (2C), 129.7 (2C), 136.2, 136.8, 143.5; EI-MS m/z: 261 (M$^+$, 0.2%), 106 (100), 92 (13), 91 (38), 79 (10), 65 (11).

N-(3-Chlorobenzyl)-4-methylbenzenesulfonamide (**8b**):[21h]. mp 70−73 °C (hexane); R_f 0.23 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3262, 1597, 1571, 1321, 1158, 1089, 687 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.37 (s, 3H), 4.0 (d, J = 6.5 Hz, 2H), 4.55 (s, 1H), 7.03−7.26 (m with d at 7.21, J = 8.2 Hz, 6H), 7.66 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.3, 46.2, 125.8, 126.8 (2C), 127.5, 127.6, 129.5 (2C), 129.6, 134, 136.5, 138.4, 143.4; EI-MS m/z: 295 (M$^+$, 0.7%), 142 (32), 140 (100), 92 (18), 91 (32), 65 (10).

N-(Benzo[d][1,3]dioxol-5-ylmethyl)-4-methylbenzenesulfonamide (**8c**):[21h]. mp 134−137 °C (hexane); R_f 0.57 (hexane/ethyl acetate: 3/2); IR (KBr): ν 3260, 1592, 1324, 1256, 1154, 1097, 1063, 1024, 922, 669 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.43 (s, 3H), 4.0 (d, J = 6.2 Hz, 2H), 4.9 (t, J = 6.1 Hz, 1H), 5.9 (s, 2H), 6.61−6.68 (m, 3H), 7.29 (d, J = 8 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.5, 47.1, 101.1, 108.4, 121.3, 127.1 (2C), 129.7 (2C), 130.1, 136.9, 143.4, 147.2, 147.8; EI-MS m/z: 305 (M$^+$, 12%), 150 (36), 149 (100), 148 (32), 135 (13), 91 (14), 65 (12).

4-Methyl-N-(naphthalen-2-ylmethyl)benzenesulfonamide (**8d**):[21h]. mp 159−162 °C (hexane); R_f 0.63 (hexane/ethyl acetate: 3/2); IR (KBr): ν 3293, 1596, 1339, 1158, 668 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.43 (s, 3H), 4.51 (d, J = 6 Hz, 2H), 4.74 (t, J = 5.7 Hz, 1H), 7.25−7.34, 7.45−7.49, 7.74−7.76, 7.81−7.83, 7.87−7.89 (5 m, 4, 2, 3, 1 and 1H, respectively); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.5, 45.4, 123.2, 125.1, 126, 126.7, 126.9, 127.2 (2C), 128.7, 129, 129.7 (2C), 131.2, 131.3, 133.8, 136.5, 143.5; EI-MS m/z: 311 (M$^+$, 14%), 156 (52), 155 (57), 154 (100), 141 (15), 129 (18), 128 (18), 127 (17), 91 (15).

N-(Cyclohexylmethyl)-4-methylbenzenesulfonamide (**8e**):[21h]. mp 78−82 °C (hexane); R_f 0.87 (hexane/ethyl acetate: 3/2); IR (KBr): ν 3285, 1596, 1314, 1154, 676 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.83−0.88, 1.07−1.25 (2 m, 2 and 3H, respectively), 1.36−1.41 (m, 1H), 1.61−1.72 (m, 5H), 2.42 (s, 3H), 2.75 (t, J = 6.7 Hz, 2H), 4.78 (s, br, 1H), 7.3 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 8.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 21.5, 25.6 (2C), 26.2, 30.5 (2C), 37.7, 49.3, 127 (2C), 129.6 (2C), 137.1, 143.2; EI-MS m/z: 267 (M$^+$, 7%), 186 (11), 185 (10), 184 (100), 155 (100), 96 (10), 91 (60), 65 (13), 55 (11).

N-Benzylbenzenesulfonamide[31a] (**8f**). mp 85−87 °C (hexane); R_f 0.13 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3325, 1611, 1586, 1318, 1161, 676 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.13 (d, J = 6.2 Hz, 2H), 5.38 (t, J = 6.1 Hz, 1H), 7.18−7.28, 7.45−7.5, 7.54−7.6, 7.85−7.88 (4 m, 5, 2, 1 and 2H, respectively); ^{13}C NMR (75 MHz, CDCl$_3$): δ 47, 126.9 (2C), 127.6, 127.7 (2C), 128.5 (2C), 129 (2C), 132.5, 136.2, 139.7; EI-MS m/z: 247 (M$^+$, 0.2%), 106 (100), 104 (12), 91 (14), 79 (15), 78 (13), 77 (37), 51 (11).

4.3. Representative Procedure for the Preparation of Aromatic Imines from Amines. To a stirred solution of amine (**1**, 1 mmol) in toluene (3 mL) under argon atmosphere were added Ru(OH)$_3$−Fe$_3$O$_4$ (50 mg), NaOH (1.3 mmol, 52 mg), and the corresponding alcohol (**2**, 1.5 mmol). The resulting mixture was stirred at 130 °C until the end of reaction. The catalyst was removed by a magnet, and the resulting mixture was quenched with water and extracted with EtOAc. The organic phases were dried over MgSO$_4$, followed by evaporation under reduced pressure to remove the solvent. The product was purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **3**. Yields are included in Table 4. Physical and spectroscopic data, as well as literature for known compounds, are as follows:

N-Benzylideneaniline (**3a**):[26]. R_f 0.37 (hexane/ethyl acetate: 4/1); IR (film): ν 1621, 1597 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.23−7.49, 7.89−7.92 (2 m, 8 and 2H, respectively), 8.46 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 120.9 (2C), 125.9, 128.8 (2C), 128.8 (2C), 129.1 (2C), 131.4, 136.2, 152, 160.4; EI-MS m/z: 182 (M$^+$ + 1, 11%), 181 (M$^+$, 100), 104 (8), 77 (35), 51 (12).

N-Benzylidene-4-methoxyaniline (**3b**):[24k]. mp 66−68 °C (hexane); R_f 0.53 (hexane/ethyl acetate: 4/1); IR (KBr): ν 1609, 1581, 1247 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.85 (s, 3H), 6.95−6.99, 7.26−7.29, 7.49−7.5, 7.91−7.93 (4 m, 2, 2, 3 and 2H, respectively), 8.51 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.4, 114.3 (2C), 122.1 (2C), 128.5 (2C), 128.7 (2C), 131, 136.4, 144.8, 158.2, 158.3; EI-MS m/z: 212 (M$^+$ + 1, 14%), 211 (M$^+$, 88), 210 (15), 197 (15), 196 (100), 167 (22).

N-Benzylidene-3-chloroaniline (**3c**):[36]. R_f 0.87 (hexane/ethyl acetate: 4/1); IR (film): ν 1622, 1582, 1067 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.06−7.09, 7.18−7.21, 7.29−7.32, 7.43−7.51, 7.87−7.9

(5 m, 1, 2, 1, 3, and 2H, respectively), 8.4 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 119.4, 120.9, 125.8, 128.8 (2C), 128.9 (2C), 130, 131.7, 134.7, 135.8, 153.3, 161.3; EI-MS *m*/*z*: 217 (M$^+$ + 1, 31%), 216 (M$^+$, 45), 214 (100), 111 (26), 89 (10), 75 (15).

*N-(4-Methoxybenzylidene)aniline (**3d**)*:[24k]. mp 45−48 °C (hexane); R_f 0.2 (hexane/ethyl acetate: 4/1); IR (KBr): ν 1679, 1600, 1245 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 3.78 (s, 3H), 6.92−6.94, 7.16−7.18, 7.32−7.36, 7.76−7.82 (4 m, 2, 3, 2 and 2H, respectively), 8.32 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$,): δ 54.8, 113.6 (2C), 120.4 (2C), 125, 128.6 (2C), 128.7, 130 (2C), 151.8, 159.1, 161.7; EI-MS *m*/*z*: 213 (M$^+$, 1), 212 (13), 211 (88), 210 (100), 167 (12), 77 (20).

*N-(4-Chlorobenzylidene)aniline (**3e**)*[25e]. mp 51−54 °C (hexane); R_f 0.7 (hexane/ethyl acetate: 4/1); IR (KBr): ν 1621, 1578, 1092 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.17−7.2, 7.35−7.41, 7.75−7.82 (3 m, 3, 4 and 2H, respectively), 8.37 (s, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 120.8 (2C), 128.9 (2C), 129.1 (2C), 129.3, 129.8 (2C), 134.6, 137.2, 151.5, 158.6; EI-MS *m*/*z*: 217 (M$^+$ + 1, 32%), 216 (M$^+$, 46), 215 (95), 214 (100), 104 (10), 77 (43), 51 (13).

4.4. Representative Procedure for the Preparation of Aromatic Imines from Nitroarenes. To a stirred solution of nitroarene (**5**, 1 mmol) in toluene (3 mL) under argon atmosphere were added Ru(OH)$_3$−Fe$_3$O$_4$ (50 mg), KOH (3 mmol, 168 mg), and the corresponding alcohol (**2**, 8 mmol). The resulting mixture was stirred at 130 °C until the end of reaction (see Table 6). The catalyst was removed by a magnet, and the resulting mixture was quenched with water and extracted with EtOAc. The organic phases were dried over MgSO$_4$, followed by evaporation under reduced pressure to remove the solvent. The product **3** was purified by chromatography on silica gel (hexane/ethyl acetate). Yields are included in Table 6.

4.5. Representative Procedure for the Alkylation of Sulfinamides. To a stirred solution of sulfinamide (**9**, 1 mmol) in toluene (3 mL) under argon atmosphere were added Ru(OH)$_3$−Fe$_3$O$_4$ (50 mg), KOH (1.3 mmol, 73 mg), and the corresponding alcohol (**11**, 2 mmol). The resulting mixture was stirred at 85 °C until the end of reaction. The catalyst was removed by a magnet, and the resulting mixture was quenched with water and extracted with EtOAc. The organic phases were dried over MgSO$_4$, followed by evaporation under reduced pressure to remove the solvent. The product was purified by chromatography on silica gel (hexane/ethyl acetate) to give the corresponding products **10**. Yields are included in Table 9. Analytical, physical and spectroscopic data, as well as literature for known compounds, follow:

*N-Benzyl-2-methylpropane-2-sulfinamide (**10a**)*:[37]. mp 58−63 °C (hexane), R_f 0.13 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3205, 1607, 1392, 1370, 1040 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.24 (s, 9H), 3.61 (t, br, *J* = 6 Hz, 1H), 4.3 (dq, ^1J = 15.6 Hz, ^2J = 6.3 Hz, 2H), 7.27−7.35 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.6 (3C), 49.3, 58.6, 127.5, 128 (2C), 128.5 (2C), 138.4; EI-MS *m*/*z*: 211 (M$^+$, 0.1%), 155 (45), 92 (12), 91 (100), 77 (22), 57 (31).

*N-(4-Chlorobenzyl-2-methylpropane-2-sulfinamide (**10b**)*:[38]. mp 113−115 °C; R_f 0.17 (hexane/ethyl acetate: 4/1); IR (KBr): ν 3187, 1592, 1357, 1089, 1031 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.24 (s, 9H), 3.64 (s, br, 1H), 4.25 (dq, ^1J = 14.7 Hz, ^2J = 6.2 Hz, 2H), 7.26−7.32 (m, 4H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.5 (3C), 48.6, 55.8, 128.6 (2C), 129.3 (2C), 133.3, 136.9; EI-MS *m*/*z*: 245 (M$^+$, 0.1%), 189 (25), 139 (10), 138 (12), 127 (33), 125 (100), 77 (22), 57 (61).

*N-(4-Methoxybenzyl)-2-methylpropane-2-sulfinamide (**10c**)*:[39]. R_f 0.1 (hexane/ethyl acetate: 4/1); IR (film): ν 3209, 1611, 1578, 1389, 1368, 1245, 1049 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.23 (s, 9H), 3.58 (s, br, 1H), 3.78 (s, 3H), 4.22 (dq, ^1J = 15.7 Hz, ^2J = 6.1 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.5 (3C), 48.6, 55, 55.6, 113.7 (2C), 129.2 (2C), 130.4, 158.9; EI-MS *m*/*z*: 241 (M$^+$, 0.1%), 122 (10), 121 (100), 57 (12).

*N-(Furan-2-ylmethyl)-2-methylpropane-2-sulfinamide (**10d**)*:[40]. R_f 0.1 (hexane/ethyl acetate: 3/2); IR (film): ν 3212, 1603, 1506, 1361, 1060 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.22 (s, 9H), 3.52 (t, br, *J* = 5.5 Hz, 1H), 4.29 (dq, ^1J = 15.9 Hz, ^2J = 6.1 Hz, 2H), 6.27−6.28, 6.32−6.33, 7.37−7.38 (3 m, 1, 1 and 1H, respectively); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.5 (3C), 42.2, 56, 107.8, 110.3, 142.4, 151.8; EI-MS *m*/*z*: 201 (M$^+$, 0.1%), 145 (33), 82 (14), 81 (100), 77 (11), 57 (47), 53 (12).

*N-Heptyl-2-methylpropane-2-sulfinamide (**10e**)*. R_f 0.1 (hexane/ethyl acetate: 4/1); IR (film): ν 3213, 1361, 1057 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.21 (s, 9H), 1.28−1.4 (m, 8H), 1.52−1.59 (m, 2H), 3.03−3.09 (m, 1H), 3.19−3.23 (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 13.9, 22.5, 22.5 (3C), 26.6, 28.8, 31, 31.6, 45.6, 55.4; EI-MS *m*/*z*: 219 (M$^+$, 0.2%), 163 (67), 146 (47), 114 (18), 78 (17), 77 (11), 57 (100); HRMS calcd (%) for $C_{11}H_{25}NOS\cdot C_4H_{10}$: 163.1031; found: 163.1050.

*N-Isobutyl-2-methylpropane-2-sulfinamide (**10f**)*. R_f 0.1 (hexane/ethyl acetate: 3/2); IR (film): ν 3234, 1361, 1050 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.92 (d, *J* = 2.7 Hz, 3H), 0.94 (d, *J* = 2.8 Hz, 3H), 1.22 (s, 9H), 1.78 (m, 1H), 2.81−2.9, 3.01−3.09 (2 m, 1 and 1H, respectively), 3.3 (t, br, *J* = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 19.9, 20, 22.6 (3C), 29.5, 53.2, 55.6; EI-MS *m*/*z*: 177 (M$^+$, 0.3%), 121 (90), 78 (36), 65 (22), 57 (100); HRMS calcd (%) for $C_8H_{19}NOS\cdot C_4H_{10}$: 121.0561; found: 121.0558.

*2-Methyl-N-(1-phenylethyl)propane-2-sulfinamide (**10g**)*:[41]. R_f 0.03 (hexane/ethyl acetate: 4/1); IR (film): ν 3213, 1603, 1389, 1357, 1049 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.23 (s, 9H); 1.51 (d, *J* = 6.6 Hz, 3H), 3.46 (s, br, 1H), 4.55 (dq, ^1J = 6.5 Hz, ^2J = 2.8 Hz, 1H), 7.26−7.36 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.5 (3C), 22.7, 53.9, 55.4, 126.5 (2C), 127.7, 128.7 (2C), 144; EI-MS *m*/*z*: 225 (M$^+$, 0.1%), 169 (24), 106 (10), 105 (100), 57 (14).

*(R,R)-2-Methyl-N-(1-phenylethyl)propane-2-sulfinamide (**10g′**)*:[41]. R_f 0.03 (hexane/ethyl acetate: 4/1); $[\alpha]_D^{20}$ = −14 (*c* = 1 in EtOAc); IR (film): ν 3213, 1603, 1389, 1357, 1049 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.23 (s, 9H); 1.51 (d, *J* = 6.6 Hz, 3H), 3.46 (s, br, 1H), 4.55 (dq, ^1J = 6.5 Hz, ^2J = 2.8 Hz, 1H), 7.26−7.36 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 22.5 (3C), 22.7, 53.9, 55.4, 126.5 (2C), 127.7, 128.7 (2C), 144; EI-MS *m*/*z*: 225 (M$^+$, 0.1%), 169 (24), 106 (10), 105 (100), 57 (14).

4.6. Representative Procedure for the Preparation of Amines. To a solution of the corresponding sulfinamide (**10**, 1 mmol) in 0.42 mL of MeOH was added 0.41 mL (1.64 mmol) of 4 M HCl 1, 4-dioxane solution at room temperature. The mixture was stirred for 30 min. The mixture was extracted with diethyl ether. The aqueous phases were basified with NaOH solution and extracted again with diethyl ether. The organic phases were evaporated under reduced pressure, and the corresponding amine **11** was obtained pure. Yields are included in Scheme 2. Physical and spectroscopic data, as well as literature for known compounds, are as follows:

*Phenylmethanamine (**11a**)*:[42]. R_f 0.1 (hexane/ethyl acetate: 3/2); IR (film): ν 3372, 1604 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.39 (s, 2H), 3.79 (s, 2H), 7.17−7.32 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 46.1, 126.3, 126.7 (2C), 128.1 (2C), 143; EI-MS *m*/*z*: 108 (M$^+$ + 1, 0.1%), 107 (M$^+$, 100), 106 (100), 104 (11), 91 (31), 89 (10), 79 (90), 78 (32), 77 (56), 65 (11), 63 (10).

*(4-Methoxyphenyl)methanamine (**11b**)*:[42]. R_f 0.07 (hexane/ethyl acetate: 3/2); IR (film): ν 3372, 1610, 1585, 1245, 1033 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.47 (s, 2H), 3.73 (s, 3H), 3.74 (s, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 45.4, 54.7, 113.4 (2C), 127.8 (2C), 135.1, 158; EI-MS *m*/*z*: 137 (M$^+$, 96%), 136 (100), 122 (18), 121 (76), 120 (22), 119 (13), 109 (42), 108 (10), 106 (73), 104 (10), 94 (36), 93 (25), 92 (10), 91 (18), 79 (13), 78 (22), 77 (37), 66 (16), 65 (18), 63 (14).

*(R)-1-Phenylethanamine (**11c**)*:[34]. R_f 0.3 (hexane/ethyl acetate: 3/2); $[\alpha]_D^{20}$ = +23 (*c* = 1 in CHCl$_3$); IR (film): ν 3365, 1604 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.36 (d, *J* = 6.6 Hz, 3H), 1.53 (s, br, 2H),

4.08 (q, *J* = 6.6 Hz, 1H), 7.20−7.34 (m, 5H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 25.5, 51.1, 125.5 (2C), 126.6, 128.3 (2C), 147.6; EI-MS *m*/*z*: 121 (M$^+$, 1%), 106 (100), 104 (18), 79 (29), 78 (11), 77 (23), 51 (13).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. General information, catalyst characterization data, XPS data, TEM images of catalysts, size particle distribution for Ru(OH)$_3$−Fe$_3$O$_4$ (after and before the reactions), graphics of the obtained yields for the reused catalyst, and copies of ^{1}H and ^{13}C NMR for compounds **3**, **4**, **8**, **10**, and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

[†] In memory of our friend Prof. Dr. José M. Concellón.

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