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Catalytic Acceptorless Dehydrogenative Coupling of Arylhydrazines and Alcohols for the Synthesis of Arylhydrazones

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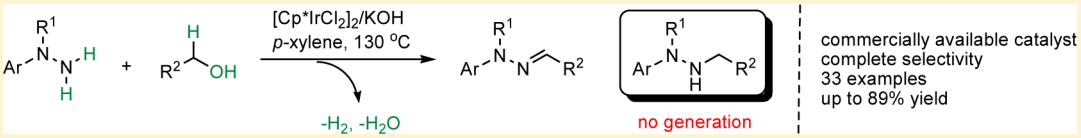
Supporting Information



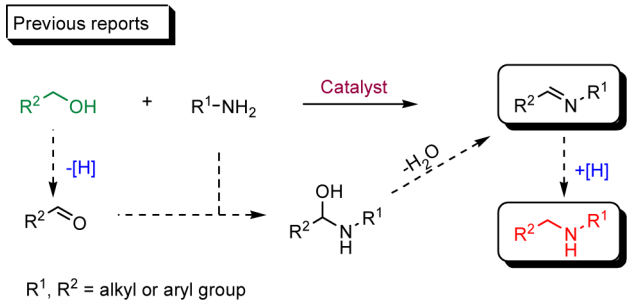
ABSTRACT: The direct synthesis of arylhydrazones via catalytic acceptorless dehydrogenative coupling of arylhydrazines and alcohols has been accomplished. More importantly, complete selectivity for arylhydrazones and none of the *N*-alkylated byproducts were generated in this process, which exhibit new potential and provide a new horizon for the development of catalytic acceptorless dehydrogenative coupling reactions.

INTRODUCTION

Arylhydrazones constitute an important class of nitrogen-containing compounds that have been widely utilized as key synthetic intermediates in the construction of indoles,[1] carbazoles,[2] pyrazoles,[3] indazoles,[4] and other heterocyclic compounds.[5] They also exhibit remarkable biological activities,[6] including applications as inhibitors of macrophage migration inhibitory factor (MIF),[6a] trypanosomatid parasites antagonists,[6b] monoamine oxidase (MAO) inhibitors,[6c] protein tyrosine phosphatase-2 (Shp2) inhibitors,[6d] and potent antimalarial agents.[6e] Traditionally, arylhydrazones are synthesized via the condensation of arylhydrazines or aryldiazonium salts with carbonyl compounds.[1,7] Pd-catalyzed coupling of hydrazones with aryl halides has been developed for the preparation of arylhydrazones.[8] However, the latter procedure suffers from the generation of the stoichiometric amount of halogen acids as harmful byproducts.

In 2010, Milstein and co-workers reported an efficient strategy for the synthesis of imines via direct coupling of amines and alcohols with the liberation of hydrogen gas catalyzed by PNP-type ruthenium princer complexes.[9] This protocol is apparently attractive because alcohols are readily accessible, inexpensive, low toxic, and easy to handle and store. Inspired by Milstein's research, several groups developed further this transformation by using other transition-metal complexes,[10] such as a NHC-type ruthenium complex,[10a] ruthenium complex with a PNP-pincer-type phosphaalkene ligand,[10b] bifunctional ruthenium PCP pincer complex,[10c] POP-type osmium complex,[10d] and cationic cobalt(II) alkyl complex.[10e] Although significant advances have been made,[11] it is still extremely challenging to control selectivity of reactions. In the above process, the resulting imines undergo easily the hydrogenation by the metal hydride species formed in the dehydrogenative step of alcohols, and thus, *N*-alkylated amines would be generated inevitably as byproducts (even with high proportion) based on the "hydrogen autotransfer (or hydrogen-borrowing) process" (Scheme 1).[12] Moreover, the scope of substrates is still limited to amines and these catalysts are generally not commercially available, which limited the application of this strategy. Despite the potential importance, the direct synthesis of arylhydrazones via the acceptorless dehydrogenative coupling of arylhydrazines and alcohols remains unexplored.[13]

Scheme 1. Dehydrogenative Coupling of Amines with Alcohols for the Synthesis of Imines



Recently, we have reported transition-metal-catalyzed regioselective *N*-alkylation with alcohols as alkylating agents for the preparation of 2-(*N*-alkylamino)azoles,[14a−d] 2-(*N*-alkylamino)quinazolines,[14e] *N*,*N*′-alkylarylureas, and *N*,*N*′-dialkylureas.[14f] We have also demonstrated the direct synthesis of *N*-alkylated amides from aldoximes and alcohols via tandem rearrangement/*N*-alkylation reactions catalyzed by a Ru/Ir dual catalyst system,[15] Ir-catalyzed direct coupling of indoles with methanol to 3,3′-bisindoles (3,3′-BIM's),[16] and the *N*-alkylation of sulfonamides with alcohols in water catalyzed by

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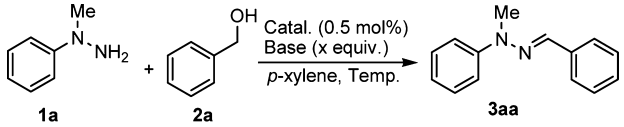
the water-soluble iridium complex [Cp*Ir(6,6′-$(OH)_2$bpy)-(H_2O)][OTf]$_2$.[17] As part of a continuing interest in exploring new potential of alcohols as electrophiles, herein we wish to report the direct synthesis of arylhydrazones via catalytic acceptorless dehydrogenative coupling of arylhydrazines and alcohols.

RESULTS AND DISCUSSION

Our initial efforts focused on the direct coupling of 1-methyl-1-phenylhydrazine **1a** and benzyl alcohol **2a** catalyzed by $[Cp^*IrCl_2]_2$ (Cp* = pentamethylcyclopentadienyl), which is commercially available and has been widely used as the efficient catalyst for the synthesis of *N*-alkylated amines via the *N*-alkylation of amines with alcohols.[18,14b−e] In the presence of $[Cp^*IrCl_2]_2$ (0.5 mol %), the reaction of **1a** and **2a** was carried out in *p*-xylene at 130 °C for 12 h. To our surprise, none of the *N*-alkylated product was detected and only the dehydrogenative coupling product (*E*)-2-benzylidene-1-methyl-1-phenylhydrazine **3aa** was obtained, albeit in 10% yield (Table 1, entry 1). A

Table 1. Coupling of 1-Methyl-1-phenylhydrazine 1a and Benzyl Alcohol 2a under Various Conditions[a]



1a **2a** **3aa**

entry	catal.	base	temp.	*x*	yield (%)[b]
1	$[Cp^*IrCl_2]_2$		130		10
2	$[Cp^*IrCl_2]_2$	Na_2CO_3	130	0.3	12
3	$[Cp^*IrCl_2]_2$	Cs_2CO_3	130	0.3	50
4	$[Cp^*IrCl_2]_2$	NaOH	130	0.3	73
5	**$[Cp^*IrCl_2]_2$**	**KOH**	**130**	**0.3**	**85**
6	$[Cp^*IrCl_2]_2$	KO*t*Bu	130	0.3	78
7	$[Ir(cod)Cl]_2$	KOH	130	0.3	80
8	$[Cp^*RhCl_2]_2$	KOH	130	0.3	63
9	$[Rh(cod)Cl]_2$	KOH	130	0.3	43
10	$[Ru(p\text{-cymene})Cl_2]_2$	KOH	130	0.3	38
11	$[Cp^*IrCl_2]_2$	KOH	130	0.2	77
12	$[Cp^*IrCl_2]_2$	KOH	120	0.3	80
13	$[Cp^*IrCl_2]_2$	KOH	110	0.3	75
14		KOH	130	0.3	n.d.

[a]Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), catal. (0.5 mol %), *p*-xylene (0.5 mL), 12 h. [b]Isolated yield.

series of bases, including Na_2CO_3, Cs_2CO_3, NaOH, KOH, and KO*t*Bu, were used as additives for this reaction. Apart from Na_2CO_3, other bases exhibited an obvious effect on this transformation (Table 1, entries 2−6). Among them, KOH was found to be the most effective and the product **3aa** could be obtained in 85% yield (Table 1, entry 5). Using $[Ir(cod)Cl]_2$ (cod = 1,5-cyclooctadienyl) as an alternative iridium source, the reaction gave the product **3aa** in 80% yield (Table 1, entry 7). When other transition-metal complexes, such as $[Cp^*RhCl_2]_2$, $[Rh(cod)Cl]_2$, and $[Ru(p\text{-cymene})Cl_2]_2$, were tested, the product **3aa** could be obtained in only 38−63% yields (Table 1, entries 8−10). It was also found that decreasing the reaction temperature or reducing the amount of KOH resulted in relatively low yields (Table 1, entries 11−13). In the individual presence of KOH, no reaction took place (Table 1, entry 14).

With the optimal reaction conditions established (Table 1, entry 5), the coupling of **1a** with a variety of benzylic-type alcohols was examined, and these results are summarized in Table 2. Similar to the case of benzyl alcohol **1a**, reactions with benzylic alcohols bearing one or two electron-donating groups, such as methyl **2b**−**2c**, isopropyl **2d**, methoxy **2e**, and dimethoxy **2f**, afforded the corresponding products **3ab**−**3af** in 82−89% yields (Table 2, entries 1−5). Benzylic alcohols bearing one or two halogen atoms, such as fluoro **2g**, chloro **2h**−**2i**, and bromo **2j**, were converted into the desired products **3ag**−**3aj** in 75−87% yields (Table 2, entries 6−9). When benzylic alcohols bearing a strong electron-withdrawing group, such as trifluoromethyl **2k** and trifluoromethoxy **2l**, were used as substrates, products **3ak** and **3al** were obtained in 81% and 88% yields, respectively, although 1 equiv of base was required (Table 2, entries 10−11). This coupling was also applied to naphthalenemethanols **2m**−**2n**, thiophenylmethanol **2o**, and pyridinylmethanol **2p**, affording the desired products **3am**−**3ap** in 78−87% yields (Table 2, entries 12−15). In the case of a challenging secondary alcohol with high steric hindrance **2q**, the corresponding product **3aq** could be successfully obtained in 52% yield (Scheme 2).[19]

Apart from benzylic-type alcohols, a series of aliphatic alcohols were also used as substrates for this coupling reaction (Table 3). When the linear aliphatic alcohols (3 equiv), such as 1-butanol **2r**, 1-hexanol **2s**, and 1-octanol **2t**, were used as reagents and solvents instead of *p*-xylene, the desired products **3ar**−**3at** were obtained in 78−82% yields (Table 3, entries 1−3).[20] Transformations of the branched-chain alcohols, such as 3-methylbutan-1-ol **2u** and cyclohexylmethanol **2v**, afforded also the corresponding products **3au** and **3av** in 75% and 77% yields, respectively (Table 3, entries 4−5).

To expand further the scope of the reaction, the coupling of a range of arylhydrazines with benzyl alcohol **2a** was then investigated (Table 4). Reactions of phenylhydrazines bearing one or two electron-donating substituents, such as methyl **1b**, dimethyl **1c**, and methoxy **1d**, gave the desired products **3ba**−**3da** in 80−82% yields (Table 4, entries 1−3). Phenylhydrazines bearing a halogen atom, such as fluoro **1e** and chloro **1f**, were proven to be suitable substrates, and reactions gave the desired products **3ea** and **3fa** in 75% and 79% yields, respectively (Table 4, entries 4 and 5). Furthermore, phenylhydrazines bearing a stronger electron-withdrawing trifluoromethoxy **1g** and the pyridylhydrazine **1h** were successfully converted into the corresponding products **3ga** and **3ha** in 83% and 72% yields, respectively (Table 4, entries 6 and 7). For phenylhydrazines bearing different alkyl groups on the N1 atom, such as ethyl **1i**, butyl **1j**, and benzyl **1k**, the desired products **3ia**−**3ka** were also obtained in high yields (Table 4, entries 8−10). The unsubstituted phenylhydrazine **1l** could be converted into the desired product **3la**, albeit in 50% yield (Table 4, entry 11).[21]

It should be pointed that none of the *N*-alkylated byproducts were observed in all cases. The experimental results are in sharp contrast with previous reports about transition-metal-catalyzed dehydrogenative coupling of amines and alcohols, in which *N*-alkylated products were inevitably produced.[9,10] In addition, as mentioned in previous reported documents,[13,22] the minor *N*-methylanilines as byproducts (<5% yields) resulting from N−N bond cleavage of arylhydrazines were observed.

On the basis of the previous reports[9,10] and our experimental results, a speculative mechanism is proposed to account for the direct synthesis of arylhydrazones via iridium-catalyzed acceptorless dehydrogenative coupling of arylhydrazines and alcohols (Scheme 3). The initial step involves the formation of alkoxo

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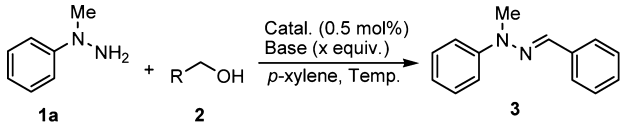
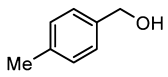
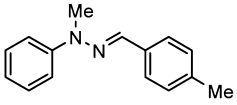
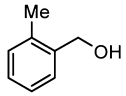
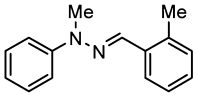
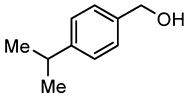
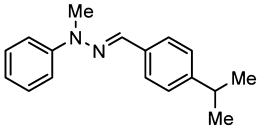
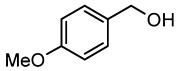
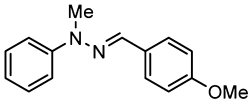
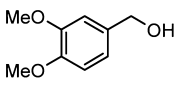
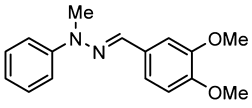
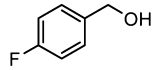
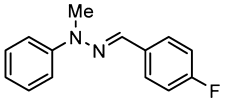
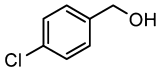
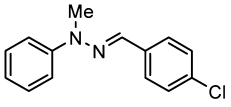
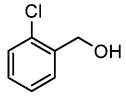
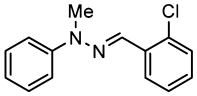
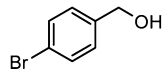
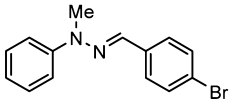
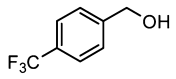
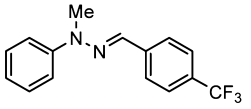
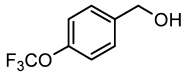
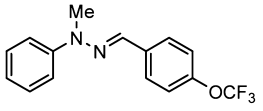
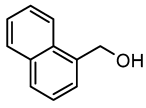
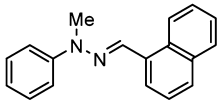
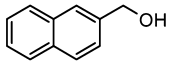
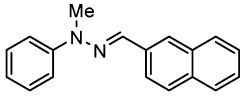
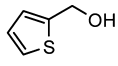
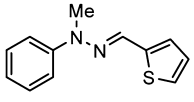
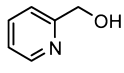
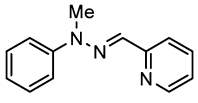
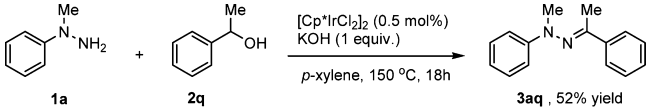
Table 2. Coupling of 1-Methyl-1-phenylhydrazine 1a and a Variety of Benzylic-type Alcohols 2[a,b,c,d,e]



Entry	Alcohol	Product	Yield (%)[b]
1	 **2b**	 **3ab**	89
2	 **2c**	 **3ac**	82[c]
3	 **2d**	 **3ad**	86
4	 **2e**	 **3ae**	87
5	 **2f**	 **3af**	85
6	 **2g**	 **3ag**	75[d]
7	 **2h**	 **3ah**	87
8	 **2i**	 **3ai**	83[c]
9	 **2j**	 **3aj**	87
10	 **2k**	 **3ak**	81[e]
11	 **2l**	 **3al**	88[e]
12	 **2m**	 **3am**	78[c]
13	 **2n**	 **3an**	81
14	 **2o**	 **3ao**	87
15	 **2p**	 **3ap**	80[d]

[a]Reaction conditions: **1a** (1 mmol), **2** (1.2 mmol), $[Cp^*IrCl_2]_2$ (0.5 mol %), KOH (0.3 equiv), *p*-xylene (0.5 mL), 130 °C, 12 h. [b]Isolated yield. [c]150 °C. [d]KOH (0.5 equiv). [e]KOH (1 equiv).

Scheme 2. Coupling of 1a and Secondary Alcohol 2q



iridium species **A** by the reaction of iridium species with alcohols under the acceleration of base. Accompanied by the *β*-hydrogen elimination of alkoxo iridium species **A**, iridium hydride species **B** and aldehydes were generated.[23] Furthermore, the condensation between the resulting aldehydes and arylhydrazines occurred to afford iridium hydride species coordinated with arylhydrazones **C**, which were dissociated subsequently to give iridium hydride species **B** and to release arylhydrazones as products. Finally, catalytic active alkoxo iridium species **A** were regenerated and hydrogen gas was liberated via the reaction of iridium hydride species **B** and alcohols. It is speculated that, under the present reaction conditions, the iridium hydride could not be transferred to the C═N bond of arylhydrazones on the species **C** to form amido-iridium species **D**, which is crucial for the generation of *N*-alkylated products.[24]

To support the proposed mechanism, the liberation of hydrogen gas in the iridium-catalyzed coupling of **1a** and **2a** (Table 1, entry 5) was first confirmed by GC analysis and was measured to be 20.3 mL (22 °C, 101 160 Pa, 84% yield) by a gas buret by water displacement.

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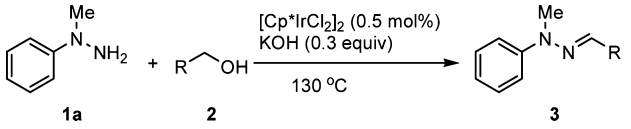
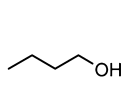
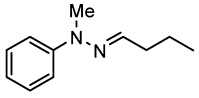
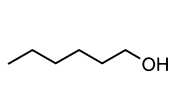
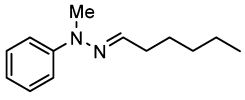
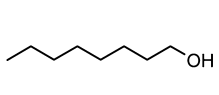
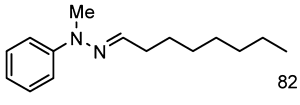
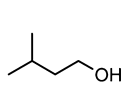
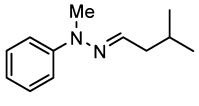
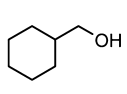
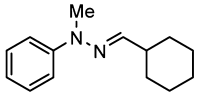
Table 3. Coupling of 1-Methyl-1-phenylhydrazine 1a and a Variety of Aliphatic Alcohols 2[a,b,c]



1a 2 3

Entry	Alcohol	Product	Yield (%)[b]
1			78
	2r	3ar	
2			80[c]
	2s	3as	
3			82
	2t	3at	
4			75
	2u	3au	
5			77[c]
	2v	3av	

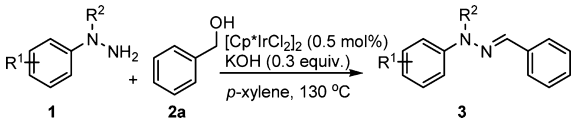
[a]Reaction conditions: **1a** (1 mmol), 2 (3 mmol), $[Cp^*IrCl_2]_2$ (0.5 mol %), KOH (0.3 equiv), 130 °C, 12 h. [b]Isolated yield. [c]18 h.

The catalytic transfer hydrogenation of an arylhydrazone with an alcohol as a hydrogen source was then investigated.[25,26] As shown in Scheme 4, the reaction of **3aa** with **2a** was conducted for 12 h in the presence of the $[Cp^*IrCl_2]_2$/KOH system in *p*-xylene at 130 °C, and none of product **4** was detected from the ^{1}H NMR spectrum of the crude reaction mixture. Similarly, no reaction occurred when isopropanol **5** (3 mL) was used as a hydrogen source. These results confirm that arylhydrazones are stable enough under present reaction conditions, and thus, they could not be hydrogenated by iridium hydride species formed in the dehydrogenative step of alcohols (Scheme 3, from **C** to **D**). Furthermore, the catalytic hydrogenation of **3aa** with H_2 (10 atm) at 130 °C was carried out in the presence of the $[Cp^*IrCl_2]_2$/KOH system for 12 h and no reaction occurred as well (Scheme 5). Apparently, **3aa** could not undergo the hydrogenation with the hydrogen liberated from this step (Scheme 3, from **B** to **A**). These results support the proposed mechanism.

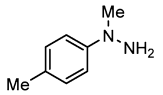
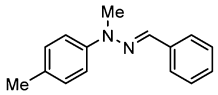
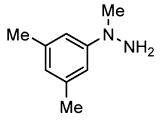
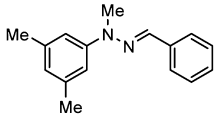
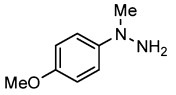
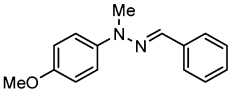
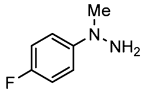
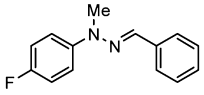
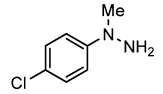
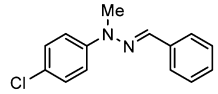
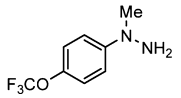
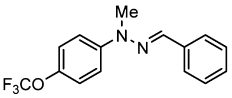
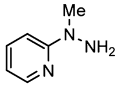
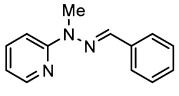
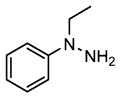
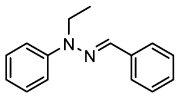
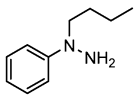
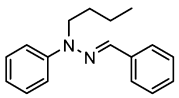
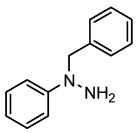
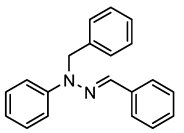
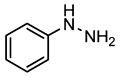
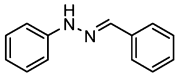
CONCLUSION

In summary, we have demonstrated a novel and efficient strategy for the direct synthesis of arylhydrazones via catalytic coupling of arylhydrazines and alcohols with the liberation of hydrogen gas. More importantly, complete selectivity for arylhydrazones and none of the *N*-alkylated byproducts were generated in this process, which exhibit new potential and provide a new horizon for the development of catalytic acceptorless dehydrogenative coupling reactions.

Table 4. Coupling of a Range of Arylhydrazines 1 and Benzyl Alcohol 2a[a,b,c]



1 2a 3

Entry	Alcohol	Product	Yield (%)[b]
1			80
	1b	3ba	
2			82
	1c	3ca	
3			81
	1d	3da	
4			75
	1e	3ea	
5			79
	1f	3fa	
6			83[c]
	1g	3ga	
7			72
	1h	3ha	
8			80
	1i	3ia	
9			82
	1j	3ja	
10			84
	1k	3ka	
11			50
	1l	3la	

[a]Reaction conditions: **1** (1 mmol), **2a** (1.3 mmol), $[Cp^*IrCl_2]_2$ (0.5 mol %), KOH (0.3 equiv), *p*-xylene (0.5 mL), 130 °C, 12 h. [b]Isolated yield. [c]**2a** (2.0 mmol).

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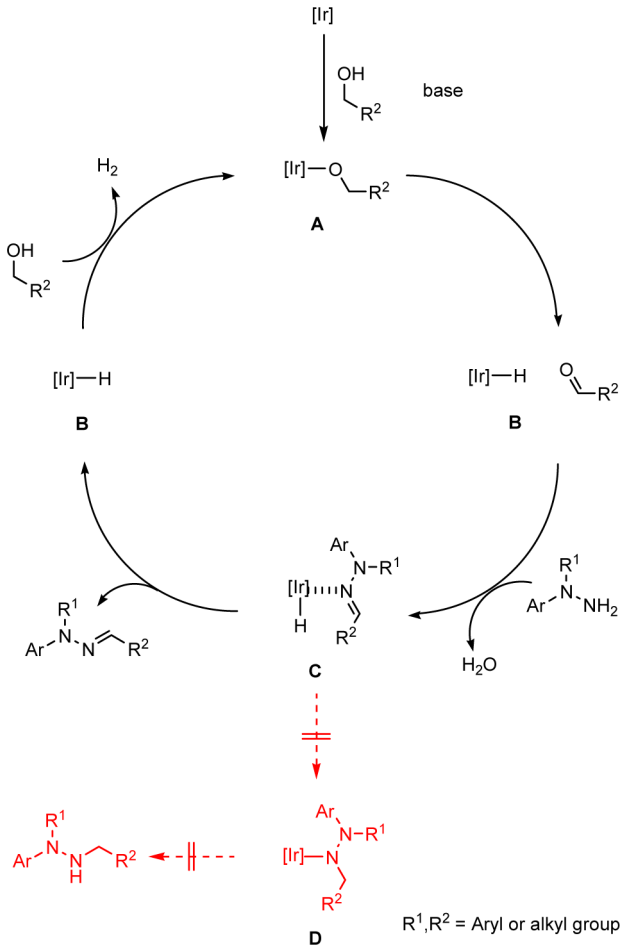
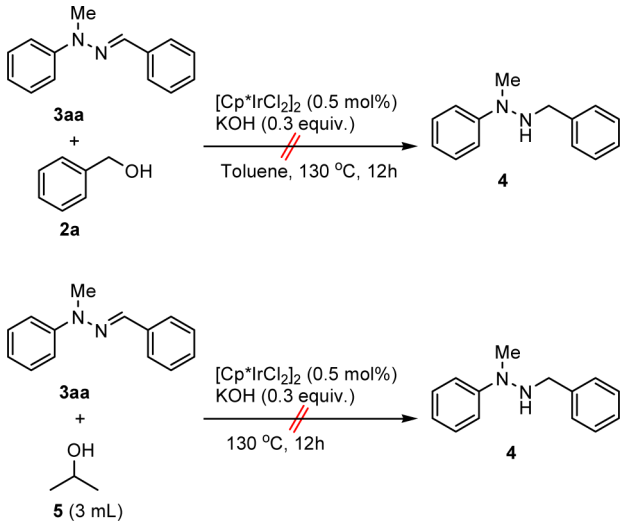
Scheme 3. Possible Reaction Mechanism



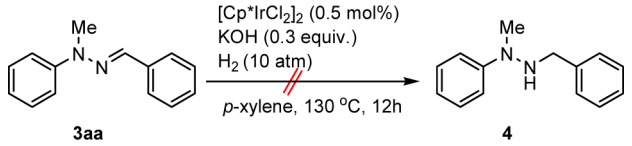
Scheme 4. Ir-Catalyzed Transfer Hydrogenation of an Arylhydrazone with an Alcohol as the Hydrogen Source



EXPERIMENTAL SECTION

General Experimental Details. High-resolution mass spectra (HRMS) were obtained on an HPLC-Q-Tof MS (Micro) spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M + Na]^+$ or $[M + H]^+$. Melting points were measured on a micromelting apparatus. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz using a spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 2.50 ppm for DMSO-d_6. Coupling constants J values are reported in hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$. ^{13}C NMR spectra were routinely run with broadband decoupling. Substrates **1a–g**,[27] **1i–1k**,[27] and **1h**[28] were prepared according to literature methods. Substrate **1l** is commercially available. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates.

Scheme 5. Ir-Catalyzed Hydrogenation of an Arylhydrazone with H_2



Synthesis of $[Cp^*IrCl_2]_2$ (Cp^* = Pentamethylcyclopentadienyl).[29] To an oven-dried, nitrogen-purged 200 mL Schlenk tube were added iridium trichloride hydrate (1 g, 2.83 mmol), pentamethylcyclopentadiene (0.75 mL, 4.72 mmol), and methanol (20 mL). The mixture was heated at reflux for 36 h under an atmosphere of nitrogen. The reaction was allowed to cool to room temperature, and the orange precipitate was collected by filtration. The product was purified by recrystallization from chloroform/hexane. 70% yield (0.79 g); mp 245–246 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 (s, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 86.2, 9.3. $[Cp^*IrCl_2]_2$ is very stabile even under air conditions, and an inert atmosphere is not necessary.

General Procedure for Direct Synthesis of Arylhydrazones via Iridium-Catalyzed Acceptorless Dehydrogenative Coupling of Arylhydrazine and Alcohol. To an oven-dried, nitrogen-purged 25 mL Schlenk tube were added arylhydrazine **1** (1 mmol), alcohol **2** (1.2 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol %), KOH (0.3 mmol, 0.3 equiv), and 0.5 mL of p-xylene. The mixture was heated at 130 °C for 12 h. Then, the reaction mixture was allowed to cool to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

*(E)-2-Benzylidene-1-methyl-1-phenylhydrazine (**3aa**).*[30] 85% yield (178 mg); mp 104–105 °C (lit.[30] mp 104–105 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 2H), 7.50 (s, 1H), 7.40–7.25 (m, 7H), 6.93 (t, J = 7.2 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 136.8, 131.8, 129.0, 128.5, 127.7, 126.0, 120.5, 115.2, 33.0.

*(E)-1-Methyl-2-(4-methylbenzylidene)-1-phenylhydrazine (**3ab**).*[31] 89% yield (199 mg); mp 120–121 °C (lit.[31] mp 110–112 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.49 (s, 1H), 7.38 (d, J = 8.2 Hz, 2H), 7.32 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.92 (t, J = 7.2 Hz, 1H), 3.41 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 137.6, 134.0, 132.1, 129.3, 129.0, 126.0, 120.3, 115.1, 32.9, 21.3; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{17}N_2$ $[M + H]^+$ 225.1392, found 225.1383.

*(E)-1-Methyl-2-(2-methylbenzylidene)-1-phenylhydrazine (**3ac**).* 82% yield (183 mg); mp 65–66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.39–7.37 (m, 2H), 7.34–7.30 (m, 2H), 7.24–7.21 (m, 1H), 7.17–7.16 (m, 2H), 3.42 (d, J = 0.8 Hz, 3H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 135.1, 134.6, 130.7, 130.5, 129.0, 127.5, 126.1, 125.8, 120.5, 115.2, 33.0, 20.0; HRMS(ESI) m/z calcd for $C_{15}H_{17}N_2$ $[M + H]^+$ 225.1392, found 225.1388.

*(E)-2-(4-Isopropylbenzylidene)-1-methyl-1-phenylhydrazine (**3ad**).* 86% yield (216 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.48 (s, 1H), 7.38–7.36 (m, 2H), 7.33–7.29 (m,

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2H), 7.23−7.22 (m, 2H), 6.91 (t, J = 7.1 Hz, 1H), 3.39 (d, J = 0.7 Hz, 3H), 2.91 (heptet, J = 7.0 Hz, 1H), 1.26 (d, J = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 147.9, 134.4, 132.0, 128.9, 126.6, 126.1, 120.3, 115.1, 33.9, 32.9, 23.9. HRMS(ESI) m/z calcd for $C_{17}H_{21}N_2$ $[M + H]^+$ 253.1705, found 253.1700.

(E)-2-(4-Methoxybenzylidene)-1-methyl-1-phenylhydrazine (**3ae**).[31] 87% yield (209 mg); mp 113−114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.48 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 6.92−6.89 (m, 3H), 3.83 (s, 3H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 148.0, 131.9, 129.7, 129.0, 127.3, 120.2, 115.0, 114.0, 55.3, 33.0. HRMS(ESI) m/z calcd for $C_{15}H_{17}N_2O$ $[M + H]^+$ 241.1341, found 241.1332.

(E)-2-(3,4-Dimethoxybenzylidene)-1-methyl-1-phenylhydrazine (**3af**).[32] 85% yield (229 mg); mp 97−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.40 (s, 1H), 7.37−7.30 (m, 4H), 7.12 (d, J = 8.4 Hz, 1H), 6.92 (t, J = 7.0 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 3.96 (s, 3H), 3.91(s, 3H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 149.1, 148.0, 132.0, 130.0, 128.9, 120.2, 119.8, 115.1, 110.9, 107.7, 55.9, 55.8, 33.1.

(E)-2-(4-Fluorobenzylidene)-1-methyl-1-phenylhydrazine (**3ag**). 75% yield (170 mg); mp 96−97 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (t, J = 6.8 Hz, 2H), 7.47 (s, 1H), 7.38−7.31 (m, 4H), 7.06 (t, J = 8.4 Hz, 2H), 6.94 (t, J = 7.0 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 245.7 Hz), 147.8, 133.0, 130.7, 129.0, 127.5 (d, J_{C-F} = 7.6 Hz), 120.6, 115.5 (d, J_{C-F} = 21.6 Hz), 115.3, 33.1; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{14}FN_2$ $[M + H]^+$ 229.1141, found 229.1134.

(E)-2-(4-Chlorobenzylidene)-1-methyl-1-phenylhydrazine (**3ah**).[32] 87% yield (212 mg); mp 108−109 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.43 (s, 1H), 7.37−7.31 (m, 6H), 6.95 (t, J = 7.1 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 135.3, 133.1, 130.3, 129.0, 128.7, 127.1, 120.8, 115.3, 33.1.

(E)-2-(2-Chlorobenzylidene)-1-methyl-1-phenylhydrazine (**3ai**). 83% yield (203 mg); mp 47−48 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 1H), 7.77 (s, 1H), 7.37−7.35 (m, 2H), 7.32−7.28 (m, 3H), 7.23 (t, J = 7.5 Hz, 1H), 7.15−7.11 (m, 1H), 6.94 (t, J = 6.9 Hz, 1H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 133.9, 132.6, 129.6, 129.0, 128.3, 128.1, 126.8, 126.2, 120.9, 115.4, 33.2; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{14}ClN_2$ $[M + H]^+$ 245.0846, found 245.0841.

(E)-2-(4-Bromobenzylidene)-1-methyl-1-phenylhydrazine (**3aj**). 87% yield (250 mg); mp 125−126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.42 (s, 1H), 7.38−7.31 (m, 4H), 6.95 (t, J = 7.1 Hz, 1H), 3.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.7, 135.8, 131.6, 130.4, 129.0, 127.4, 121.3, 120.9, 115.4, 33.2; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{13}BrN_2Na$ $[M + Na]^+$ 311.0160, found 311.0157.

(E)-1-Methyl-1-phenyl-2-(4-(trifluoromethyl)benzylidene)-hydrazine (**3ak**). 81% yield (226 mg); mp 87−88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.0 Hz, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.48 (s, 1H), 7.40−7.33 (m, 4H), 6.98 (t, J = 6.6 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 140.3, 129.8, 129.1, 129.0 (q, J_{C-F} = 32.1 Hz), 126.0, 125.5 (q, J_{C-F} = 3.1 Hz), 124.3 (q, J_{C-F} = 270.4 Hz), 121.3, 115.6, 33.3; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{13}F_3N_2Na$ $[M + Na]^+$ 301.0929, found 301.0927.

(E)-1-Methyl-1-phenyl-2-(4-(trifluoromethoxy)benzylidene)-hydrazine (**3al**). 88% yield (259 mg); mp 59−60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.8 Hz, 2H), 7.46 (s, 1H), 7.38−7.31 (m, 4H), 7.21 (d, J = 8.4 Hz, 2H), 6.95 (tt, J = 7.1 Hz and J = 1.3 Hz, 1H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 147.7, 135.6, 130.0, 129.0, 127.1, 121.1, 120.9, 120.5 (q, J_{C-F} = 255.4 Hz), 115.4, 33.1; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{14}F_3N_2O$ $[M + H]^+$ 295.1058, found 295.1053.

(E)-1-Methyl-2-(naphthalen-1-ylmethylene)-1-phenylhydrazine (**3am**). 78% yield (202 mg); mp 92−93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 8.5 Hz, 1H), 8.17 (s, 1H), 7.99 (d, J = 7.3 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 7.58−7.55 (m, 1H), 7.52−7.49 (m, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 8.0 Hz, 2H), 6.96 (t, J = 7.3 Hz, 1H), 3.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 134.0, 132.1, 130.6, 129.1, 128.7, 128.1, 126.2, 125.6, 125.6, 125.0, 123.9, 120.7, 115.4, 33.1; HRMS(ESI) m/z calcd for $C_{18}H_{17}N_2$ $[M + H]^+$ 261.1392, found 261.1384.

(E)-1-Methyl-2-(naphthalen-2-ylmethylene)-1-phenylhydrazine (**3an**). 81% yield (211 mg); mp 178−179 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.7 Hz and J = 1.6 Hz, 1H), 7.89 (s, 1H), 7.84−7.81 (m, 3H), 7.66 (s, 1H), 7.48−7.42 (m, 4H), 7.37−7.33 (m, 2H), 6.95 (t, J = 7.3 Hz, 1H), 3.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 134.5, 133.6, 133.2, 131.9,129.0, 128.2, 127.9, 127.8, 126.2, 126.1, 125.8, 123.1, 120.6, 115.3, 33.0; HRMS-EI (70 eV) m/z calcd for $C_{18}H_{16}N_2$ $[M + H]^+$ 261.1392, found 261.1379.

(E)-1-Methyl-1-phenyl-2-(thiophen-2-ylmethylene)hydrazine (**3ao**).[30] 87% yield (188 mg); mp 79−80 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.35−7.30 (m, 4H), 7.20 (d, J = 5.1 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 7.01−6.99 (m, 1H), 6.92 (tt, J = 6.7 Hz and J = 1.7 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 142.7, 129.0, 127.1, 126.9, 125.4, 124.8, 120.6, 115.2, 33.2.

(E)-2-((2-Methyl-2-phenylhydrazono)methyl)pyridine (**3ap**).[33] 80% yield (168 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54−8.52 (m, 1H), 8.01 (dt, J = 8.1 Hz and J = 1.0 Hz, 1H), 7.67 (td, J = 7.8 Hz and J = 1.7 Hz, 1H), 7.62 (s, 1H), 7.41−7.38 (m, 2H), 7.36−7.32 (m, 2H), 7.15−7.12 (m, 1H), 6.98 (tt, J = 7.2 Hz and J = 1.2 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 148.9, 147.4, 136.1, 132.5, 129.0, 121.8, 121.2, 119.0, 115.6, 33.3.

(E)-1-Methyl-1-phenyl-2-(1-phenylethylidene)hydrazine (**3aq**).[34] 52% yield (116 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) 7.92−7.91 (m, 2H), 7.44−7.41 (m, 3H), 7.29−7.26 (m, 2H), 6.97 (d, J = 7.7 Hz, 2H), 6.90 (t, J = 7.3 Hz, 1H), 3.17 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 151.3, 138.3, 129.8, 128.8, 128.4, 126.7, 120.0, 115.5, 42.8, 16.5.

(E)-2-Butylidene-1-methyl-1-phenylhydrazine (**3ar**). 78% yield (138 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.21 (m, 4H), 6.87−6.81 (m, 2H), 3.20 (s, 3H), 2.37−2.33 (m, 2H), 1.63−1.56 (m, 2H), 1.01−0.97 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 136.0, 128.9, 119.7, 114.8, 35.0, 33.0, 20.9, 13.8; HRMS-EI (70 eV) m/z calcd for $C_{11}H_{17}N_2$ $[M + H]^+$ 177.1392, found 177.1385.

(E)-2-Hexylidene-1-methyl-1-phenylhydrazine (**3as**). 80% yield (163 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.22 (m, 4H), 6.86−6.81 (m, 2H), 3.20 (s, 3H), 2.38−2.34 (m, 2H), 1.60−1.54 (m, 2H), 1.38−1.34 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 136.2, 128.9, 119.6, 114.8, 33.0, 31.5, 27.3, 22.5, 14.0; HRMS-EI (70 eV) m/z calcd for $C_{13}H_{21}N_2$ $[M + H]^+$ 205.1705, found 205.1700.

(E)-1-Methyl-2-octylidene-1-phenylhydrazine (**3at**). 82% yield (191 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20−7.14 (m, 4H), 6.78−6.73 (m, 2H), 3.12 (s, 3H), 2.30−2.26 (m, 2H), 1.48 (quint, J = 7.4 Hz), 1.32−1.18 (m, 8H), 0.81 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 136.2, 128.9, 119.6, 114.7, 33.0, 32.9, 31.8, 29.2, 29.1, 27.6, 22.6. 14.1; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{25}N_2$ $[M + H]^+$ 233.2018, found 233.2013.

(E)-1-Methyl-2-(3-methylbutylidene)-1-phenylhydrazine (**3au**). 75% yield (142 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28−7.21 (m, 4H), 6.86−6.80 (m, 2H), 3.21 (s, 3H), 2.27−2.24 (m, 2H), 1.88 (heptet, J = 6.8 Hz, 1H), 0.98 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 135.4, 128.9, 119.7, 114.8, 41.9, 33.1, 27.4, 22.4; HRMS-EI (70 eV) m/z calcd for $C_{12}H_{19}N_2$ $[M + H]^+$ 191.1548, found 191.1545.

(E)-2-(Cyclohexylmethylene)-1-methyl-1-phenylhydrazine (**3av**). 77% yield (167 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27−7.22 (m, 4H), 6.83 (t, J = 7.0 Hz, 1H), 6.71(d, J = 5.0 Hz, 1H), 3.18 (s, 3H), 2.36−2.29 (m, 1H), 1.90−1.88 (m, 2H), 1.81−1.77 (m, 2H), 1.70−1.66 (m, 1H), 1.38−1.20 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 140.3, 128.9, 119.5, 114.6, 41.2, 32.7, 31.3, 26.2, 25.8; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{21}N_2$ $[M + H]^+$ 217.1705, found 217.1699.

(E)-2-Benzylidene-1-methyl-1-(p-tolyl)hydrazine (**3ba**). 80% yield (179 mg); mp 81−82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.5 Hz, 2H), 7.45 (s, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 8.0 Hz, 3H), 7.12 (d, J = 8.4 Hz, 2H), 3.40 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.8, 136.9, 131.3, 130.0, 129.5, 128.5, 127.5,

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126.0, 115.5, 33.4, 20.5; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{17}N_2$ $[M + H]^+$ 225.1392, found 225.1389.

*(E)-2-Benzylidene-1-(3,5-dimethylphenyl)-1-methylhydrazine (**3ca**).* 82% yield (196 mg); mp 68−69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.8 Hz, 2H), 7.47 (s, 1H), 7.37 (t, J = 7.4 Hz, 2H), 7.27−7.24 (m, 1H), 7.01 (s, 2H), 6.60 (s, 1H), 3.40 (s, 3H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 138.6, 136.9, 131.5, 128.5, 127.5, 126.0, 122.6, 113.4, 33.3, 21.7; HRMS-EI (70 eV) m/z calcd for $C_{16}H_{18}N_2Na$ $[M + Na]^+$ 261.1368, found 261.1364.

*(E)-2-Benzylidene-1-(4-methoxyphenyl)-1-methylhydrazine (**3da**).* 81% yield (194 mg); mp 128−129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 2H), 7.42 (s, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.29−7.22 (m, 3H), 6.89 (d, J = 9.1 Hz, 2H), 3.79 (s, 3H), 3.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 142.4, 137.0, 131.2, 128.5, 127.4, 125.9, 117.2, 114.4, 55.7, 34.2; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{16}N_2NaO$ $[M + Na]^+$ 263.1160, found 263.1157.

*(E)-2-Benzylidene-1-(4-fluorophenyl)-1-methylhydrazine (**3ea**).* 75% yield (172 mg); mp 82−83 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.4 Hz, 2H), 7.45 (s, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.30−7.23 (m, 3H), 7.03−6.99 (m, 2H), 3.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.7 (d, J_{C-F} = 238.0 Hz), 144.5, 136.6, 132.0, 128.6, 127.7, 126.0, 116.6 (d, J_{C-F} = 7.3 Hz), 115.4 (d, J_{C-F} = 22.0 Hz), 33.6; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{14}FN_2$ $[M + H]^+$ 229.1141, found 229.1138.

*(E)-2-Benzylidene-1-(4-chlorophenyl)-1-methylhydrazine (**3fa**).* 79% yield (193 mg); mp 101−102 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.2 Hz, 2H), 7.50 (s, 1H), 7.37 (t, J = 7.7 Hz, 2H), 7.31−7.25 (m, 5H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 136.4, 132.6, 128.9, 128.6, 128.0, 126.1, 125.4, 116.2, 33.0; HRMS-EI (70 eV) m/z calcd for $C_{14}H_{14}ClN_2$ $[M + H]^+$ 245.0846, found 245.0842.

*(E)-2-Benzylidene-1-methyl-1-(4-(trifluoromethoxy)phenyl)-hydrazine (**3ga**).* 83% yield (244 mg); mp 52−53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.50 (s, 1H), 7.39−7.33 (m, 4H), 7.28 (tt, J = 7.3 Hz and J = 1.2 Hz, 1H), 7.17 (d, J = 9.0 Hz, 2H), 3.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 142.8, 136.4, 132.8, 128.6, 128.0, 126.2, 121.9, 120.7 (q, J_{C-F} = 254.4 Hz), 115.7, 32.9; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{13}F_3N_2ONa$ $[M + Na]^+$ 317.0878, found 317.0875.

*(E)-2-Benzylidene-1-methyl-1-(pyridin-2-yl)hydrazine (**3ha**).*[5d] 72% yield (151 mg); mp 100−101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 4.4 Hz, 1H), 7.75−7.72 (m, 3H), 7.65 (s, 1H), 7.61−7.58 (m, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.78 (t, J = 5.9 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 146.9, 137.4, 136.3, 133.9, 128.6, 128.2, 126.3, 115.4, 109.9, 29.3.

*(E)-2-Benzylidene-1-ethyl-1-phenylhydrazine (**3ia**).* 80% yield (180 mg); oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71−7.69 (m, 2H), 7.55 (s, 1H), 7.38−7.30 (m, 6H), 7.28−7.24 (m, 1H), 6.92 (tt, J = 7.1 Hz and J = 1.2 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 136.9, 130.9, 129.1, 128.5, 127.6, 126.0, 120.3, 114.7, 39.6, 10.1; HRMS-EI (70 eV) m/z calcd for $C_{15}H_{17}N_2$ $[M + H]^+$ 225.1392, found 225.1386.

*(E)-2-Benzylidene-1-butyl-1-phenylhydrazine (**3ja**).* 82% yield (207 mg); mp 64−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 2H), 7.52 (s, 1H), 7.39−7.36 (m, 4H), 7.32 (t, J = 7.8 Hz, 2H), 7.28−7.25 (m, 1H), 6.92 (t, J = 7.2 Hz, 1H), 3.91 (t, J = 7.9 Hz, 2H), 1.68 (quint, J = 7.8 Hz, 2H), 1.47 (sextet, J = 7.4 Hz, 2H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2, 136.9, 130.9, 129.0, 128.5, 127.6, 126.0, 120.2, 114.7, 45.0, 26.9, 20.4, 13.9; HRMS-EI (70 eV) m/z calcd for $C_{17}H_{21}N_2$ $[M + H]^+$ 253.1705, found 253.1698.

*(E)-1-Benzyl-2-benzylidene-1-phenylhydrazine (**3ka**).*[5d] 84% yield (240 mg); mp 109−110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 8.3 Hz, 2H), 7.42−7.39 (m, 3H), 7.36−7.31 (m, 6H), 7.28−7.22 (m, 4H), 6.95 (t, J = 7.3 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 136.5, 135.7, 132.5, 129.1, 129.0, 128.5, 127.8, 127.3, 126.2, 126.0, 120.7, 114.8, 50.4.

*(E)-1-Benzylidene-2-phenylhydrazine (**3la**).*[35] 50% yield (98 mg); mp 157−158 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.66 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 2H), 7.31−7.25 (m, 3H), 7.12 (d, J = 7.8 Hz, 2H), 6.87 (t, J = 7.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 137.3, 135.3, 129.3, 128.6, 128.4, 126.2, 120.1, 112.8.

Catalytic Transfer Hydrogenation of Arylhydrazone 3aa with Benzylic Alcohol 2a as a Hydrogen Source (Scheme 4, Top Equation). To an oven-dried, nitrogen-purged 25 mL Schlenk tube were added arylhydrazone **3aa** (1 mmol), benzyl alcohol **2a** (1.2 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol %), KOH (0.3 mmol, 0.3 equiv), and 0.5 mL of *p*-xylene. The mixture was heated at 130 °C for 12 h. No conversion was observed by the analysis of the spectrum of the crude reaction mixture.

Catalytic Transfer Hydrogenation of Arylhydrazone 3aa with Isopropanol 5 as Hydrogen Source (Scheme 4, Bottom Equation). To an oven-dried, nitrogen-purged 25 mL Schlenk tube were added arylhydrazone **3aa** (1 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol %), KOH (0.3 mmol, 0.3 equiv), and isopropanol **5** (3 mL). The mixture was heated at 130 °C for 12 h. No conversion was observed by the analysis of the spectrum of the crude reaction mixture.

Catalytic Transfer Hydrogenation of Arylhydrazone 3aa with H_2 (Scheme 5). To an oven-dried autoclave containing a stirring bar were added arylhydrazone **3aa** (1 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol %), KOH (0.3 mmol, 0.3 equiv), and *p*-xylene (2 mL). After nitrogen displacement, the autoclave was pressured to 10 atm of hydrogen and stirred at 130 °C for 12 h. The autoclave was cooled down to room temperature, and the remaining hydrogen was carefully vented. No conversion was observed by the analysis of the spectrum of the crude reaction mixture.

Procedure for the Hydrogen Evolution Experiment.[36] Arylhydrazone **3aa** (1 mmol), benzyl alcohol **2a** (1.2 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 0.5 mol %), KOH (0.3 mmol, 0.3 equiv), and 0.5 mL of *p*-xylene were added to a thick walled glass vessel fitted with a side arm and a rubber septum. The vessel was previously degassed three times and placed under a N_2 atmosphere. The vessel was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume), and the entire system was flushed with N_2 for 5 min and allowed to equilibrate for 5 min. The reaction was stirred vigorously at a constant temperature until gas evolution ceased (12 h). The presence of hydrogen in the collected gas was confirmed by GC analysis.

The GC analysis was performed on a gas chromatograph and TCD detector. Injector temprature = 120 °C, column temprature = 120 °C (isothemal), detector temperature (TCD) = 130 °C, carrier gas = He, t = 1.23 min.

The volume of 1 mol of H_2 at 22 °C, 101 160 Pa was calculated according to the van der Waals equation as shown below

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where R = 8.3145 m^3 Pa·mol^{-1}·K^{-1}; T = 295.15 K; p = 101 160 Pa; a = 0.002476 m^6·Pa·mol^{-1}; b = 0.02661 × 10^{-3} m^3·mol^{-1}; thus, V (H_2, 22 °C, 101 160 Pa) = 24.28 L·mol^{-1}.

The collected volume of gas in the experiment above was 20.3 mL, which corresponds to 0.84 mmol of H_2.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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$[Ir(cod)Cl_2]_2$ and $[Rh(cod)Cl_2]_2$ were corrected in Table 1 and the text on August 8, 2014.

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