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Au/Ag-Cocatalyzed Aldoximes to Amides Rearrangement under Solvent- and Acid-Free Conditions

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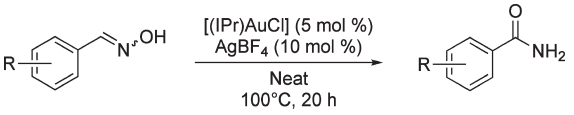
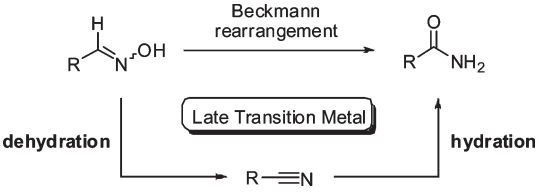


The gold/silver-cocatalyzed conversion of aldoximes into primary amides is reported. The reaction, which proceeds under neat and acid-free conditions, allows for the conversion of a range of aldoximes, and is a rare example of cooperative catalysis involving well-defined gold species.

Introduction

The isomerization of oximes to amides, i.e., the Beckmann rearrangement,[1] is arguably one of the most straightforward synthetic routes to obtain amides. Typically, this isomerization can be effected using strong acids, or other activating agents, usually in stoichiometric amounts and at high temperature.[2] In addition to harsh reaction conditions, one of the main drawbacks of the Beckmann rearrangement is its poor efficiency toward aldoximes, often leading to the formation of nitriles. Recently, the use of late transition metals (LTMs) has allowed for some improvements,[3] and systems based on Ru,[4] Rh,[5] and Ir[6] have shown interesting activities.[7] The current mechanistic hypothesis for the LTM-catalyzed rearrangement of aldoximes involves a dehydration/hydration sequence via the formation of a discrete nitrile intermediate (Scheme 1).[4−6,8]

SCHEME 1. LTM-Catalyzed Rearrangement of Aldoximes



This particular aspect caught our attention, especially in light of our recent discovery that cationic [(NHC)Au^{I}] complexes (NHC = N-heterocyclic carbene) efficiently catalyze the hydration of nitriles,[9] and prompted us to examine the potential of these gold(I) catalysts[10] in the rearrangement of aldoximes.[11] Herein, we report that this transformation is best achieved using a Au/Ag cocatalytic system, which allows, under neat and acid-free conditions, for the formation of a variety of primary amides. In addition to expanding further the scope of

(1) Beckmann, E. *Ber. Dtsch. Chem. Ges.* **1886**, *19*, 988–993.
(2) For reviews, see: (a) Clayden, J.; Greeves, N.; Warren, S.; Wothers, P. *Organic Chemistry*, 1st ed.; Oxford University Press: Oxford, UK, 2001; pp 997−1000. (b) Gawley, R. E. *Org. React.* **1988**, *35*, 1–420.
(3) For very early studies using Ni, see: (a) Field, L.; Hughmark, P. B.; Shumaker, S. H.; Marshall, W. S. *J. Am. Chem. Soc.* **1961**, *83*, 1983−1987. For Ni and Pd, see: (b) Leusink, A. J.; Meerbeek, T. G.; Noltes, J. G. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 123–125.
(4) Owston, N. A.; Parker, A. J.; Williams, J. M. J. *Org. Lett.* **2007**, *9*, 3599–3601.
(5) (a) Park, S.; Choi, Y.-a.; Han, H.; Yang, S. H.; Chang, S. *Chem. Commun.* **2003**, 1936–1937. (b) Fujiwara, H.; Ogasawara, Y.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5202–5205. (c) Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Yamaguchi, K.; Mizuno, N. *Chem. Asian J.* **2008**, *3*, 1715–1721. (d) Kim, M.; Lee, J.; Lee, H.-Y.; Chang, S. *Adv. Synth. Catal.* **2009**, *351*, 1807–1812.
(6) Owston, N. A.; Parker, A. J.; Williams, J. M. J. *Org. Lett.* **2007**, *9*, 73–75.
(7) For a related bimetallic Co−Zn system, see: Mishra, A.; Ali, A.; Upreti, S.; Gupta, R. *Inorg. Chem.* **2008**, *47*, 154–161.
(8) There is a recent report on anhydrous nitrile hydration with use of oximes as the water source: Lee, J.; Kim, M.; Chang, S.; Lee, H.-Y. *Org. Lett.* **2009**, *11*, 5598–5601.
(9) Ramón, R. S.; Marion, N.; Nolan, S. P. *Chem.—Eur. J.* **2009**, *15*, 8695–8697.
(10) (a) For a review on [(NHC)Au] complexes in catalysis, see: Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776–1782. (b) For a more general review on late transition metal-NHC mediated catalysis, see: Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676.
(11) For a review on the reactivity of oximes, see: Garnovskii, D. A.; Kukushkin, V. Y. *Russ. Chem. Rev.* **2006**, *75*, 111–124.

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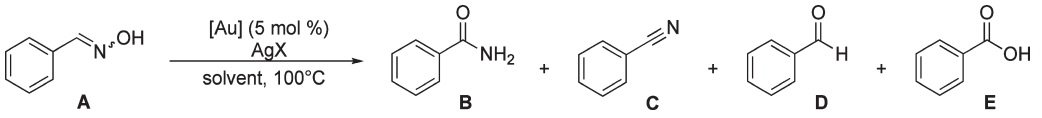
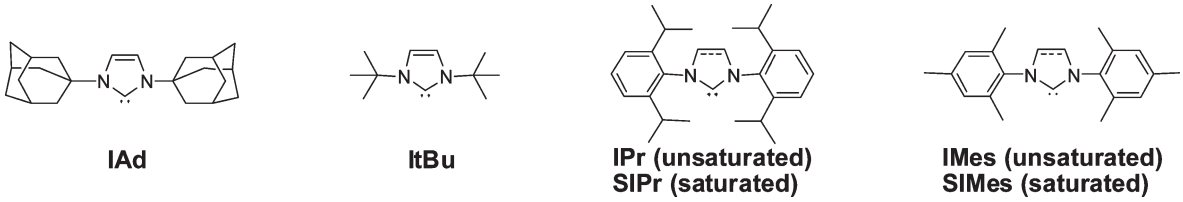
TABLE 1. Optimization of the Reaction Conditions[a]



					yield, %				
entry	catalyst (5 mol %)	solvent	time, h	[AgX] (mol %)	A	B	C	D	E
1	[(IPr)Au(NTf$_2$)]	$CHCl_3$	7		99	< 1	< 1	< 1	< 1
2	[(IPr)AuCl]	$CHCl_3$	7	$AgBF_4$ (5)	80	6	6	7	
3		$CHCl_3$	20	$AgBF_4$ (100)			58	42	
4	[(IPr)AuCl]	$CHCl_3$	7	$AgBF_4$ (10)	29	37	17	17	
5	[(IPr)AuCl]	$CHCl_3$	7	$AgBF_4$ (15)	28	41	15	16	
6[b]	[(IPr)AuCl]	$CHCl_3$	7	$AgBF_4$ (100)	3	46	23	3	2
7	[(IPr)AuCl]	neat	7	$AgBF_4$ (10)	51	47	1	< 1	
8		neat	7	$AgBF_4$ (10)	88	8	3	1	
9	[(IPr)AuCl]	neat	20	$AgBF_4$ (10)	1	95	3	< 1	
10		neat	20	$AgBF_4$ (10)	44	34	16	3	3
11	[(SIPr)AuCl]	neat	20	$AgBF_4$ (10)	3	87	2	< 1	4
12	[(IMes)AuCl]	neat	20	$AgBF_4$ (10)	21	55	8	1	12
13	[(SIMes)AuCl]	neat	20	$AgBF_4$ (10)	12	67	7	1	9
14	[(ItBu)AuCl]	neat	20	$AgBF_4$ (10)	4	80	6	1	6
15	[(IAd)AuCl]	neat	20	$AgBF_4$ (10)	6	78	5	< 1	6
16	[(IPr)AuCl]	neat	20	$AgSbF_6$ (10)	4	92	2	< 1	< 1
17	[(IPr)AuCl]	neat	20	$AgPF_6$ (10)	1	89	5	< 1	2
18	[(IPr)AuCl]	neat	20	AgOTf (10)	12	84	2	< 1	1
19	[(IPr)AuCl]	neat	20	AgOTs (10)	37	60	2	< 1	< 1
20	[(IPr)AuCl]	neat	20		99	< 1	< 1	< 1	< 1
21		neat	20		99	< 1	< 1	< 1	< 1

[a]GC conversions, average of two runs. [b]22% of unidentified products. NHCs used:

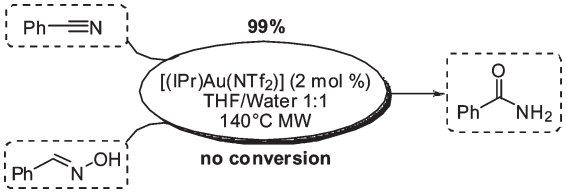


homogeneous gold catalysis, this study represents a rare example of cooperative catalysis involving gold,[12−14] and the first one, to the best of our knowledge, associating gold with silver.[15−18]

Results and Discussion

The optimization studies were initiated with benzaldoxime as a model substrate using the conditions we previously reported for the efficient hydration of nitriles (Scheme 2).[9] Disappointingly, no conversion was observed, as with other related catalytic systems we developed for hydration-type reactivity.[19]

SCHEME 2. Lack of Reactivity for Aldoximes under the Nitrile Hydration Conditions



(12) For a *Highlight* on co-catalysis involving Au, see: Duschek, A.; Kirsch, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 5703–5705.

(13) For reviews on cooperative catalysis, see: (a) Park, Y. J.; Park, J.-W.; Jun, C.-H. *Acc. Chem. Res.* **2008**, *41*, 222–234. (b) Van den Beuken, E. K.; Feringa, B. L. *Tetrahedron* **1998**, *54*, 12985–13011.

(14) For recent examples of Au/Pd-cocatalysis see: (a) Hashmi, A. S. K.; Lothschütz, C.; Döpp, R.; Rudolph, M.; Ramamurthi, T. D.; Rominger, F. *Angew. Chem., Int. Ed.* **2009**, *48*, 8243–8246. (b) Shi, Y.; Ramgren, S. D.; Blum, S. A. *Organometallics* **2009**, *28*, 1275–1277.

(15) For general reviews on cocatalysis, see: (a) Lee, J. M.; Na, Y.; Han, H.; Chang, S. *Chem. Soc. Rev.* **2004**, *33*, 302–312. (b) Wasilke, J.-C.; Obrey, S. J.; Baker, R. T.; Bazan, G. C. *Chem. Rev.* **2005**, *105*, 1001–1020.

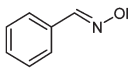
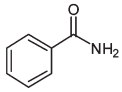
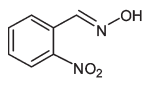
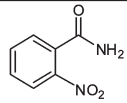
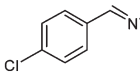
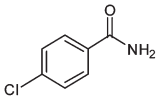
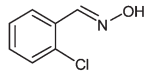
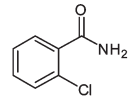
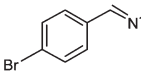
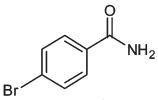
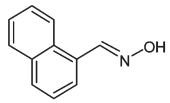
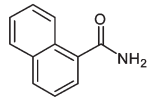
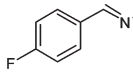
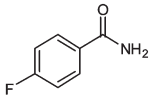
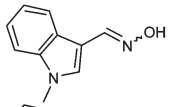
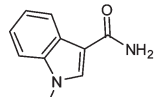
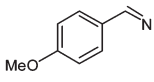
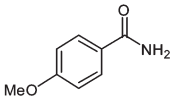
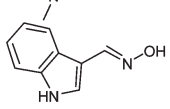
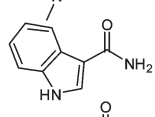
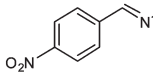
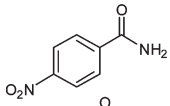
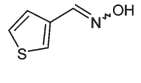
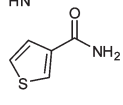
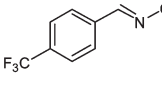
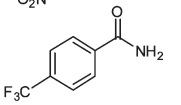
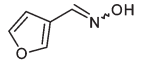
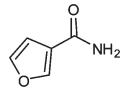
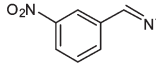
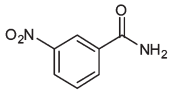
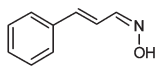
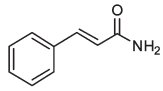
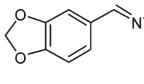
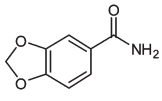
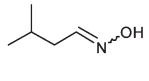
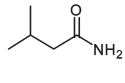
(16) Scarce examples of Au/LTM cocatalysis have been reported. For Re, see: (a) Kuninobu, Y.; Ishii, E.; Takai, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3296−3299. For Pd, see: (b) Jones, L. A.; Sanz, S.; Laguna, M. *Catal. Today* **2007**, *122*, 403–406. (c) Shi, Y.; Peterson, S. M.; Haberaecker, W. W., III; Blum, S. A. *J. Am. Chem. Soc.* **2008**, *130*, 2168–2169.

(17) For rare reports describing cocatalysis between Au and an organocatalyst, see: (a) Binder, J. T.; Crone, B.; Haug, T. T.; Menz, H.; Kirsch, S. F. *Org. Lett.* **2008**, *10*, 1025–1028. (b) Han, Z.-Y.; Xiao, H.; Chen, X.-H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2009**, *131*, 9182–9183. (c) Belot, S.; Vogt, K. A.; Besnard, C.; Krause, N.; Alexakis, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 8923–8926.

(18) Recently, dinuclear Au/Au and Au/Ag intermediates in catalysis have been reported: (a) Weber, D.; Tarselli, M. A.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 5733–5736. (b) Weber, D.; Gagné, M. R. *Org. Lett.* **2009**, *11*, 4962–4965.

(19) (a) Marion, N.; Carlqvist, P.; Gealageas, R.; de Frémont, P.; Maseras, F.; Nolan, S. P. *Chem.—Eur. J.* **2007**, *13*, 6437–6451. (b) Marion, N.; Ramón, R. S.; Nolan, S. P. *J. Am. Chem. Soc.* **2009**, *131*, 448–449. (c) Ramón, R. S.; Marion, N.; Nolan, S. P. *Tetrahedron* **2009**, *65*, 1767–1773.

TABLE 2. Au/Ag-Cocatalyzed Aldoxime to Amide Rearrangement[a]

Entry	Aldoxime	1	Amide	2	Yield[b]	Entry	Aldoxime	1	Amide	2	Yield[b]
1		**1a**		**2a**	92%	10		**1j**		**2j**	27%
2		**1b**		**2b**	87%	11		**1k**		**2k**	37%
3		**1c**		**2c**	90%	12		**1l**		**2l**	25%
4		**1d**		**2d**	85%	13		**1m**		**2m**	46%
5		**1e**		**2e**	95%	14		**1n**		**2n**	53%
6		**1f**		**2f**	84%	15		**1o**		**2o**	99%
7		**1g**		**2g**	77%	16		**1p**		**2p**	68%
8		**1h**		**2h**	94%	17		**1q**		**2q**	25%
9		**1i**		**2i**	98%	18		**1r**		**2r**	24%

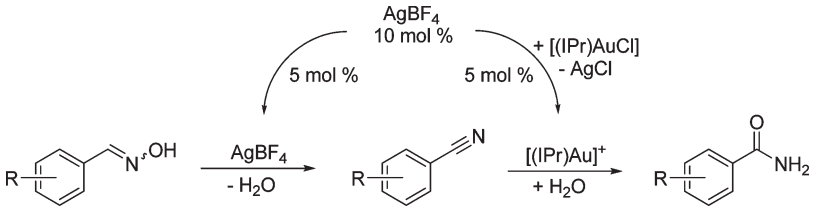
[a]Aldoxime (1 mmol), [(IPr)AuCl] (5 mol %), $AgBF_4$ (10 mol %), 20 h at 100 °C. [b]Isolated yields are average of 2 runs.

We therefore quickly engaged in an extensive screening of catalysts, solvents, and temperatures. Changing the solvent to DCM, THF, toluene, dioxane, DMSO, or isopropanol did not improve conversion (for solvent screenings, see the Supporting Information). The first "encouraging" result, obtained with 5 mol % of [(IPr)AuCl]/$AgBF_4$ in $CHCl_3$, showed conversion of the oxime to the corresponding amide in 6% along with formation of nitrile and aldehyde (Table 1, entry 2). Raising the temperature from 100 to 130°C resulted in higher conversions, but in an increased formation of side products such as benzoic acid and benzaldehyde as well (see the Supporting Information). Interestingly, we soon realized, through a control reaction with only $AgBF_4$ in stoichiometric amount, that silver(I) salts were efficient catalysts for the conversion of benzaldoxime **A** into benzonitrile **C** and benzaldehyde **D** (Table 1, entry 3). As a consequence, we investigated the influence of the amount of silver salt on the aldoxime rearrangement with [(IPr)AuCl] and $AgBF_4$. As shown in Table 1 (entries 4−6) the use of more than 1 equiv of silver tetrafluoroborate with respect to the gold catalyst increased the yield in benzamide **B** from 6% to 37% (Table 1, entry 4). On the other hand, increasing the $AgBF_4$ loading from 10 mol % (37%) to 15 mol % (41%) (Table 1, entries 4 and 5) only has a minor effect on conversion into benzamide. Stoichiometric amounts of silver along with 5 mol % of [(IPr)AuCl] increased the formation of side products (Table 1, entry 6). Remarkably, we next uncovered that neat reactions provided excellent yields of the rearranged amide **B**, suppressing the undesirable formation of benzaldehyde **D** and ensuring complete conversion of nitrile **C** (Table 1, entry 7). A reaction time of 20 h was found optimal (Table 1, entry 9). Noteworthy, we observed amide formation with 10 mol % of $AgBF_4$ as well (Table 1, entries 8 and 10), but conversions were not competitive to the mixed Ag/Au system.

With these conditions in hand, we screened various NHC−gold complexes, as well as several silver salts. As shown in Table 1, IPr was found to be remarkably superior compared to other NHCs tested (Table 1, entry 9). Considering that the reaction very likely involves a nitrile hydration step, the superiority of IPr is in excellent agreement with our previous investigations.[9] Noteworthy, bulky NHCs like ItBu and IAd provided better conversions than the smaller IMes and SIMes (Table 1, entries 11−15). The screening of silver salts (Table 1, entries 8 and 16−19) showcases silver tetrafluoroborate as the cocatalyst of choice. Control experiments with [(IPr)AuCl] only as well as no catalyst at all did not show any conversion (Table 1, entries 20 and 21).

With optimized conditions in hand, we explored the scope of this Au/Ag cocatalytic system. Good to excellent yields were obtained for various aryl aldoximes regardless of the electronic properties of the aromatic substituents (Table 2). Benzamide, as well as *p*-chloro-, *p*-bromo-, and *p*-fluorobenzamide were all

SCHEME 3. Mechanistic Proposal for the Au/Ag-Catalyzed Rearrangement of Aldoximes to Amides



obtained in excellent yields (Table 2, entries 1−4). Electron-donating substituents, such as a methoxy group (Table 2, entry 5), as well as the strongly electron-withdrawing nitro and trifluoromethyl groups (Table 2, entries 6 and 7) afforded good to excellent yields. Moving from *para*-substituted aryl aldoximes to *meta*-subtituted compounds, we obtained 94% yield in *m*-nitrobenzamide **2h** and 98% yield in benzo-1,3-dioxole-5-carboxamide **2i** (Table 2, entries 8 and 9). On the other hand, *ortho*-substituted substrates yielded only moderate amounts of the corresponding amides, regardless of the electronic nature of the substituent (Table 2, entries 10−12). These observations clearly point to deleterious steric hindrance with the present catalytic system since there was hardly formation of any byproduct either. Next, the reaction scope was extended to heteroaromatic and aliphatic aldoximes. 1-Methylindole-3-carboxamide **2m** was formed in 46% yield (Table 2, entry 13), while unprotected indole-3-carboxamide **2n** was obtained in 53% yield (Table 2, entry 14). Interestingly, this shows that the free *N*-indole does not lower the yield by complexation to either of the metal centers. In addition, thiophene-3-carboxamide **2o** and furan-3-carboxamide **2p** were obtained in good to excellent yields (Table 2, entries 15 and 16). Finally, in order to fully assess the limitations of the present catalytic system, more challenging substrates such as cinnamaldoxime **1q** and isobutyroxime **1r** were tested (Table 2, entries 17 and 18). While the low yields of amide obtained in both cases are not synthetically useful, these results are encouraging for future developments.

Mechanistically, the present experimental results point toward a dehydration/hydration sequence (Scheme 3), as proposed in previous related studies.[4−6] The initial dehydration of the oxime into a nitrile is notably supported by two aspects: (1) detection of the nitrile during the optimization studies and (2) the fact that both *E* and *Z* isomers of the oxime[20] can be converted in the primary amide.[21] Furthermore, we have shown that $AgBF_4$ catalyzes the oxime dehydration (Table 1, entry 3) but only poorly the nitrile hydration, and we recently demonstrated that [(IPr)Au(NTf_2)] efficiently performs nitrile hydration[9] but hardly the oxime dehydration (Scheme 2). In summary, these observations strongly support a cocatalyzed dehydration/hydration mechanism (Scheme 1).[4−6]

Interestingly, water scavengers such as molecular sieves or $MgSO_4$ did not inhibit amide formation by stopping the reaction at the nitrile stage,[22] suggesting a concerted mechanism (i.e., by interaction of water with the gold catalyst). The essential role of the silver salt, which serves as both activator of the [(NHC)AuCl] complex and as a catalyst for the oxime dehydration, also raises the interest in the development of well-defined silver catalysts for oxime dehydration and rearrangement.[23]

Conclusion

In summary, we have developed the first gold-based aldoxime to amide rearrangement where a number of aldoximes could be converted into primary amides, regardless of their electronic properties, under neat and acid-free reaction conditions using a Au/Ag cocatalyst. This catalytic system represents a rare example of cocatalysis involving gold in homogeneous catalysis. The fact that it involves silver(I) is of particular interest in this context, since AgX species are traditionally used as gold precatalyst activators. Additionally, the *Entente Cordiale* between gold and silver opens new avenues for cooperative catalysis combining the rich chemistry of both metals.[24,25]

Experimental Section

General Procedure for the Synthesis of Oximes from Aldehydes. To a suspension of 20 mmol of aldehyde in a 1:1:2 mixture of H_2O/EtOH/ice (20 mL) was added 1.39 g (20 mmol) of hydroxylamine hydrochloride, followed by 4 mL of a 50% aqueous solution of NaOH (40 mmol), while keeping the temperature below 30°C. After being stirred at room temperature for the indicated time, the solution was extracted with Et_2O. The aqueous phase was acidified to pH 6 by adding concentrated HCl while keeping the temperature below 30°C and extracted with Et_2O. The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated to give the oxime products.

Benzaldehyde Oxime (1a). Following the general procedure, the title compound (2.27 g, 94%) was obtained after 1 h of stirring as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.64−7.55 (m, 2H), 7.43−7.36 (m, 3H). Data are in good agreement with the literature.[26]

(20) Several aldoximes were used as *E*/*Z* mixtures. See the Supporting Information.

(21) In the case of a typical concerted Beckmann rearrangement (i.e., without intermediacy of a nitrile), only the substituent *anti* to the OH group would migrate, see ref 2.

(22) (a) The reactions were performed in chloroform to ensure scavenging. (b) Similar observations were made by Chang et al. using a rhodium catalyst, see ref 5a.

(23) For reports on oxime dehydration, see: (a) Kukushkin, Y. N.; Bavina, M. V.; Zinchenko, A. V.; Belsky, V. K.; Kukushkin, V. Y. *Polyhedron* **1997**, *16*, 2429–2433. (b) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209–4211. (c) Yamaguchi, K.; Fujiwara, H.; Ogasawara, Y.; Kotani, M.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 3922–3925. (d) Li, Z.; Lu, Z.; Zhu, A.; Feng, X.; Liu, J.; Tian, G. *Catal. Lett.* **2008**, *120*, 100–105.

(24) For recent general reviews on gold catalysis, see: (a) Gorin, D. J.; Sherry, B. D.; Toste, F. D. *Chem. Rev.* **2008**, *108*, 3351–3378. (b) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266–3325. (c) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239–3265. (d) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211.

(25) For recent general reviews on silver catalysis, see: (a) Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3199–3222. (b) Álvarez-Corral, M.; Muñoz-Dorado, M.; Rodríguez-García, I. *Chem. Rev.* **2008**, *108*, 3174–3198. (c) Weibel, J.-M.; Blanc, A.; Pale, P. *Chem. Rev.* **2008**, *108*, 3149–3173. (d) Naodovic, M.; Yamamoto, H. *Chem. Rev.* **2008**, *108*, 3132–3248.

(26) (a) Jain, N.; Kumar, A.; Chauhan, S. M. S. *Tetrahedron Lett.* **2005**, *46*, 2599–2602. (b) Picha, J.; Cibulka, R.; Hampl, F.; Liska, F.; Parik, P.; Pytela, O. *Collect. Czech. Chem. Commun.* **2004**, 397–413. (c) Wang, E.-C.; Huang, K.-S.; Chen, H.-M.; Wu, C.-C.; Lin, G.-J. *J. Chin. Chem. Soc.* **2004**, *51*, 619–627. (d) Berrier, C.; Brahmi, R.; Carreyre, H.; Coustard, J. M.; Jacquesy, J. C.; Violeau, B. *Bull. Soc. Chim. Fr.* **1991**, *128*, 730–737.

***p*-Chlorobenzaldehyde Oxime (1b).** Following the general procedure, the title compound (1.97 g, 64%) was obtained after 6 h of stirring as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.51 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 2H). Data are in good agreement with the literature.[26a]

***p*-Bromobenzaldehyde Oxime (1c).** Following the general procedure, the title compound (3.70 g, 95%) was obtained after 1.5 h of stirring as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.53 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H). Data are in good agreement with the literature.[26b]

***p*-Fluorobenzaldehyde Oxime (1d).** Following the general procedure, the title compound (2.37 g, 85%) was obtained after 6 h of stirring as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.60−7.53 (m, 2H), 7.12−7.04 (m, 2H). ^{19}F NMR (282 MHz, DMSO-d_6): δ −112.4 (s). Data are in good agreement with the literature.[26a,b]

***p*-Methoxybenzaldehyde Oxime (1e).** Following the general procedure from 0.2 mol of 4-methoxybenzaldehyde, the title compound (30.5 g, 100%) was obtained after 1.5 h of stirring as a pale orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.52 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 3.84 (s, 3H). Data are in good agreement with the literature.[26a,b,27]

***p*-Nitrobenzaldehyde Oxime (1f).** Following the general procedure, the title compound (3.00 g, 83%) was obtained after 5 h of stirring as a pale orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.8 Hz, 2H), 8.22 (s, 1H), 7.75 (d, J = 8.8 Hz, 2H). Data are in good agreement with the literature.[28]

***p*-Trifluoromethylbenzaldehyde Oxime (1g).** Following the general procedure, the title compound (1.65 g, 44%) was obtained after 5 h of stirring as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H). ^{19}F NMR (282 MHz, DMSO-d_6): δ −61.5 (s). Data are in good agreement with the literature.[29]

***m*-Nitrobenzaldehyde Oxime (1h).** Following the general procedure, the title compound (2.04 g, 61%) was obtained after 6 h of stirring as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (t, J = 1.9 Hz, 1H), 8.26−8.20 (m, 2H), 7.91 (dt, J = 7.9, 1.2 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H). Data are in good agreement with the literature.[26c,30]

Benzo[1,3]dioxole-5-carboxaldehyde Oxime (1i). Following the general procedure, the title compound (3.32 g, 100%) was obtained after 5 h of stirring as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.18 (s, 1H), 6.97 (d, J = 7.4 Hz, 1H), 6.81 (d, J = 7.4 Hz, 1H), 6.00 (s, 2H). Data are in good agreement with the literature.[26a]

***o*-Nitrobenzaldehyde Oxime (1j).** Following the general procedure, the title compound (2.58 g, 78%) was obtained after 18 h of stirring as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 1H), 8.07 (d, J = 8.2 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 8.2 Hz, 1H). Data are in good agreement with the literature.[26c]

***o*-Chlorobenzaldehyde Oxime (1k).** Following the general procedure, the title compound (2.99 g, 96%) was obtained after 1.5 h of stirring as a pale orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H), 7.86−7.78 (m, 1H), 7.42−7.36 (m, 1H), 7.36−7.23 (m, 2H). Data are in good agreement with the literature.[27]

Naphthalene-1-carboxaldehyde Oxime (1*l*). Following the general procedure, the title compound (3.10 g, 91%) was obtained after 18 h of stirring as a white solid. Mp 96°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.48 (d, J = 8.3 Hz, 1H), 7.93−7.87 (m, 2H), 7.78 (d, J = 7.0 Hz, 1H), 7.62−7.46 (m, 3H). ^{13}C NMR (100 MHz, acetone-d_6): δ 149.7 (CH), 134.9 (C), 131.5 (C), 130.8 (CH), 129.9 (C), 129.6 (CH), 128.1 (CH), 127.8 (CH), 127.0 (CH), 126.3 (CH), 125.8 (CH). HR-MS (ES-): m/z 170.0601, calcd for $C_{11}H_8NO$ 170.0606.

1-Methylindole-3-carboxaldehyde Oxime (1m). Following the general procedure from 10 mmol of 1-methylindole-3-carboxaldehyde, the title compound (1.49 g, 86%, 68:32 mixture of isomers) was obtained as after 18 h of stirring as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H, major), 8.28 (s, 1H, minor), 8.11 (td, J = 7.9; 0.9 Hz, 1H, major), 7.82 (td, J = 7.9; 0.9 Hz, 1H, minor), 7.44−7.22 (m, 4H), 3.89 (s, 3H, minor), 3.83 (s, 3H, major). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2 (CH), 138.0 (CH, minor), 137.3 (C), 134.4 (CH, minor), 132.0 (CH), 124.6 (C), 122.3 (CH), 122.0 (CH, minor), 121.5 (CH), 120.2 (CH), 120.1 (CH, minor), 118.3 (CH, minor), 110.0 (CH), 108.6 (C), 105.3 (C, minor). HR-MS (ES+): m/z 175.0869, calcd for $C_{10}H_{11}N_2O$ 175.0871.

1-*H*-Indole-3-carboxaldehyde Oxime (1n). Following the general procedure, the title compound (1.98 g, 62%) was obtained after 18 h of stirring and recrystallization in chloroform as a white solid. Mp 182°C. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.76 (br s, 1H), 10.45 (br s, 1H), 8.42 (d, J = 2.6 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.28−7.09 (m, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ 139.5 (CH), 136.3 (C), 131.6 (CH), 127.6 (C), 123.0 (CH), 121.1 (CH), 118.9 (CH), 112.5 (CH), 107.8 (C). HR-MS (ES+): m/z 161.0714, calcd for $C_9H_9N_2O$ 161.0715.

3-Thiophenecarboxaldehyde Oxime (1o). Following the general procedure from 10 mmol of 3-thiophenecarboxaldehyde, the title compound (1.27 g, 100%, 64:36 mixture of isomers) was obtained after 18 h of stirring as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (br s, 1H), 8.19 (s, 1H, major), 8.18 (d, J = 1.1 Hz, 1H, minor), 7.51 (dd, J = 5.1; 1.1 Hz, 1H, minor), 7.48 (dd, J = 2.9; 1.1 Hz, 1H, major), 7.40 (d, J = 1.1 Hz, 1H, minor), 7.39 (d, J = 1.1 Hz, 1H, major), 7.35−7.30 (m, 1H, minor), 7.34 (d, J = 2.9 Hz, 1H, major). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6 (CH), 134.2 (C), 131.5 (CH), 129.4 (CH), 126.9 (CH), 126.8 (CH), 125.3 (CH), 124.7 (CH). HR-MS (ES+): m/z 128.0170, calcd for C_5H_6NOS 128.0170.

3-Furancarboxaldehyde Oxime (1p). Following the general procedure from 10 mmol of 3-furancarboxaldehyde, the title compound (1.03 g, 93%, 68:32 mixture of isomers) was obtained after 18 h of stirring as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, major), 8.07 (s, 1H, minor), 7.64 (br s, 1H, minor), 7.45 (t, J = 1.7 Hz, 1H, major), 7.43 (t, J = 1.7 Hz, 1H, minor), 7.36 (br s, 1H, major), 6.68 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2 (CH, major), 144.2 (CH, minor), 143.7 (CH, minor), 142.7 (CH, major), 142.5 (CH, minor), 139.7 (CH, major), 119.6 (C, minor), 116.1 (C, major), 110.8 (CH, major), 107.2 (CH, minor). HR-MS (ES+): m/z 134.0223, calcd for $C_5H_5NO_2Na$ 134.0218.

Cinnamaldehyde Oxime (1q). Following the general procedure, the title compound (2.73 g, 93%, 55:45 mixture of isomers) was obtained after 18 h of stirring as a pale orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (br s, 1H), 7.98−7.94 (m, 1H, *E*), 7.56−7.51 (m, 1H, *Z*), 7.50−7.42 (m, 5H, *Z* + *E*), 7.41−7.27 (m, 7H, *Z* + *E*), 6.90−6.81 (m, 2H, *Z* + *E*). Data are in good agreement with the literature.[28]

3-Methylbutyraldehyde Oxime (1r). Following the general procedure, the title compound (1.76 g, 87%, 47:43 mixture of isomers) was obtained after 18 h of stirring as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (br s, 1H), 7.41 (t, J = 6.7 Hz, 1H, major), 6.45 (br s, 1H, minor), 2.26 (t, J = 5.9 Hz, 1H), 2.07 (t, J = 6.7 Hz, 1H), 1.89−1.74 (m, 1H), 0.93 (t, J = 7.1 Hz, 6H). Data are in good agreement with the literature.[31]

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General Procedure for the Conversion of Oximes into Amides. In a glovebox, the appropriate oxime (1.00 mmol), [(IPr)AuCl] (31 mg, 5 mol %), and $AgBF_4$ (19 mg, 10 mol %) were charged in a 4 mL vial equipped with a stirring bar. The vial was sealed and the reaction mixture was stirred outside the glovebox at 100°C for 20 h and purified by flash chromatography (EtOAc/cyclohexane).

Benzamide (2a). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (111 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (m, 2H), 7.54 (m, 1H), 7.46 (m, 2H), 6.08 (br s, 1H), 5.86 (br s, 1H). Data are in good agreement with the literature.[9]

***p*-Chlorobenzamide (2b).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (135 mg, 87%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (br s, 1H), 7.88 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.46 (br s, 1H). Data are in good agreement with the literature.[9]

***p*-Bromobenzamide (2c).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (180 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.5 Hz, 1H), 6.02 (br s, 1H), 5.81 (br s, 1H). Data are in good agreement with the literature.[9]

***p*-Fluorobenzamide (2d).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (118 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (br s, 1H), 7.93 (dd, J = 8.9; 3.3 Hz, 2H), 7.39 (br s, 1H), 7.28 (t, J = 8.9 Hz, 2H). ^{19}F NMR (282 MHz, DMSO-d_6): δ −110.1 (s). Data are in good agreement with the literature.[6]

***p*-Methoxybenzamide (2e).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (143 mg, 95%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.91 (d, J = 8.8 Hz, 2H), 7.32 (br s, 1H), 6.97 (d, J = 8.8 Hz, 2H), 6.50 (br s, 1 H), 3.85 (s, 3H). Data are in good agreement with the literature.[9]

***p*-Nitrobenzamide (2f).** Following the general procedure, the title compound was isolated after flash chromatography as a pale yellow solid (139 mg, 84%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.32 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H), 7.77 (br s, 1H), 7.01 (br s, 1H). Data are in good agreement with the literature.[9]

***p*-Trifluoromethylbenzamide (2g).** Following the general procedure, the title compound was isolated after flash chromatography as a off-white solid (145 mg, 77%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.14 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.69 (br s, 1H), 6.95 (br s, 1H). ^{19}F NMR (282 MHz, DMSO-d_6): δ −61.8 (s). Data are in good agreement with the literature.[6]

***m*-Nitrobenzamide (2h).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (156 mg, 94%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.69 (dd, J = 2.3; 1.1 Hz, 1H), 8.38 (ddd, J = 8.0; 2.3; 1.1 Hz, 1H), 8.35 (br s, 1H), 8.31 (ddd, J = 8.0; 1.5; 1.1 Hz, 1H), 7.72 (br s, 1H). Data are in good agreement with the literature.[32]

Benzo[1,3]dioxole-5-carboxamide (2i). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (162 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 8.1 Hz, 1H), 7.31 (s, 1H), 6. 48 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 5.82 (br s, 2H). Data are in good agreement with the literature.[33]

***o*-Nitrobenzamide (2j).** Following the general procedure, the title compound was isolated after flash chromatography as a pale yellow solid (44 mg, 27%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.05−7.95 (m, 1H), 7.85−7.75 (m, 1H), 7.72−7.65 (m, 2H), 7.74−7.60 (m, 3H), 7.52 (br s, 1H), 6.99 (br s, 1H). Data are in good agreement with the literature.[6]

***o*-Chlorobenzamide (2k).** Following the general procedure, the title compound was isolated after flash chromatography as a white solid (58 mg, 37%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.53 (dd, J = 7.2, 1.8 Hz, 1H), 7.50−7.32 (m, 3H), 7.21 (br s, 1H), 6.92 (br s, 1H). Data are in good agreement with the literature.[34]

Naphthalene-1-carboxamide (2*l*). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (43 mg, 25%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31−8.28 (m, 1H), 8.01−7.95 (m, 3H), 7.63 (dd, J = 7.0; 1.2 Hz, 1H), 7.59−7.51 (m, 4H). Data are in good agreement with the literature.[35]

1-Methylindole-3-carboxamide (2m). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (80 mg, 46%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.10 (dd, J = 8.0; 1.2 Hz, 1H), 7.85 (s, 1H), 7.43 (dd, J = 8.2; 1.0 Hz, 1H), 7.26 (ddd, J = 8.2; 7.0; 1.2 Hz, 1H), 7.19 (ddd, J = 8.0; 7.0; 1.0 Hz, 1H), 3.85 (s, 3H). Data are in good agreement with the literature.[36]

1-*H*-Indole-3-carboxamide (2n). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (85 mg, 53%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.52 (br s, 1H), 8.13 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 2.9 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 7.40 (br s, 1H), 7.15−7.06 (m, 2H), 6.78 (br s, 1H). Data are in good agreement with the literature.[37]

3-Thiophenecarboxamide (2o). Following the general procedure, the title compound was isolated after flash chromatography as a off-white solid (126 mg, 99%). Mp 67°C. ^{1}H NMR (400 MHz, acetone-d_6): δ 8.10 (dd, J = 2.9; 1.3 Hz, 1H), 7.54 (dd, J = 5.1; 1.3 Hz, 1H), 7.49 (dd, J = 5.1; 2.9 Hz, 1H), 7.27 (br s, 1H), 6.52 (br s, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ 164.9 (C), 138.9 (C), 129.5 (CH), 128.0 (CH), 127.0 (CH). HR-MS (ES+): m/z 149.9986, calcd for C_5H_5NONaS 149.9990.

3-Furancarboxamide (2p). Following the general procedure, the title compound was isolated after flash chromatography as a pale orange solid (75 mg, 68%). ^{1}H NMR (400 MHz, acetone-d_6): δ 8.10 (s, 1H), 7.60 (t, J = 1.6 Hz, 1H), 7.17 (br s, 1H), 6.81 (s, 1H), 6.54 (br s, 1H). Data are in good agreement with the literature.[38]

Cinnamamide (2q). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (37 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 15.6 Hz, 1H), 7.52−7.50 (m, 2H), 7.38−7.36 (m, 3H), 6.48 (d, J = 15.6 Hz, 1H), 5.67 (br s, 2H). Data are in good agreement with the literature.[9]

3-Methylbutyramide (2r). Following the general procedure, the title compound was isolated after flash chromatography as a white solid (24 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (br s, 2H), 2.10−2.08 (m, 3H), 0.98 (d, J = 6.4 Hz, 6H). Data are in good agreement with the literature.[39]

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Supporting Information Available: Optimization tables and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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