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An Intermolecular Hydroamination of Allenamides with Arylamines Catalyzed by Cationic Au(I) Salts

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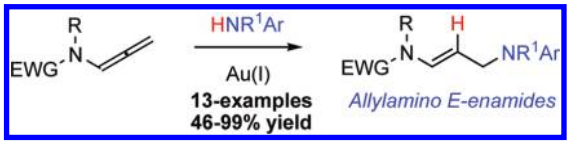
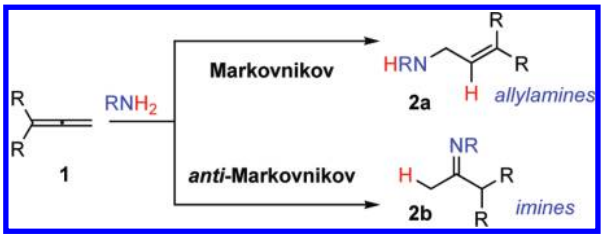


An intermolecular hydroamination of allenamides with arylamines has been achieved under mild Au(I) catalysis conditions delivering allylamino *E*-enamides stereoselectively and in high yield. The reaction is made possible via a convenient method for conjugated *N*-acyliminium formation.

The addition of the N−H bond over alkene and alkyne π-systems, the hydroamination transformation, represents a powerful method for the introduction of the amine functionality.[1] Such transformations give access to a range of valuable nitrogen-containing building blocks such as amines, imines, and enamines. Within this group of reactions the intermolecular hydroamination of allenes has become increasingly important due to the regiochemical factors in such transformations. Allenes (**1**) can undergo either Markovnikov or *anti*-Markovnikov addition, giving rise to allylamines (**2a**) or imines (**2b**) (Scheme 1). This first group of substrates, allylamines, are vital synthetic building blocks since they are contained within a number of important biological systems and are key intermediates in organic synthesis.[2]

A number of transition metal approaches toward the hydroamination of allenes have been reported, including the use of Zr (*anti*-Markovikov), Hg (Markovnikov), Pt (Markovnikov), and Pd (Markovnikov) salts.[3] Additional to these transition metals, Au salts have proved to be particularly attractive in hydroamination reactions due to their low toxicity and increased stability to moisture and air.[4] Consequently, a number of groups have utilized Au salts in these transformations to great effect.[1b,5]

SCHEME 1. The Hydroamination of Allenes



Recently, we reported[6] the first intermolecular hydroarylation of allenamides[7] with electron-rich aromatics using an Au(I) catalyst to give the corresponding enamides. Enamides[8] are a class substrates that have become particularly topical due to their use in the construction of heterocycles and chiral amines and their presence in a number of natural product frameworks.[9] This transformation was high yielding for most substrates and gave exclusively the *E*-enamide.

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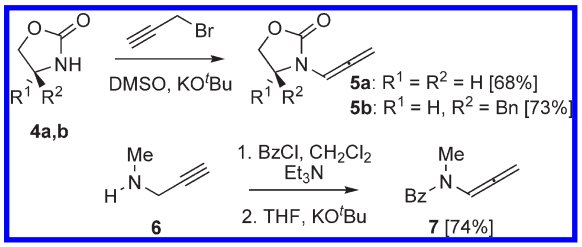
SCHEME 2. The Proposed Hydroamination of Allenamides with Arylamines

SCHEME 3. Preparation of Allenamides 5a,b and 7



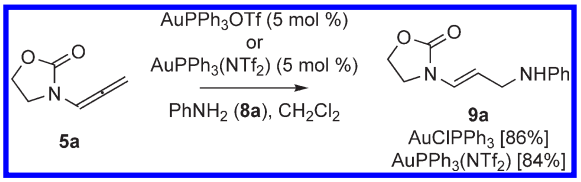
Importantly, unlike many of the methods[10] for enamide preparation, the reaction required no exclusion of air and moisture and the reaction was extremely facile.

While there are reported methods for the Au-catalyzed intermolecular hydroamination of allenes to give allylamines[5] and intermolecular protocols for the hydroaminations of allenamides[7i] within the literature, methods for the intermolecular hydroamination of allenamides remain untouched to our knowledge. Whereas the hydroamination of allenes delivers synthetically useful allylamines, the intermolecular Markovnikov addition of an N−H bond over an allenamide **3** would deliver an allylamino enamide **4**, a substrate that would contain both an allyl amine and an enamide within the one synthetic framework (Scheme 2). Therefore, in this communication we would like to share our results of the first intermolecular hydroamination of allenamides using arylamine derivatives under our Au(I) catalytic conditions.

The allenamides used for this study are shown in Scheme 3. Cyclic allenamides **5a** and **5b** were synthesized by using an adapted method of Heaney,[11] and the acyclic allenamide **7** was synthesized via initial amide formation followed by base-catalyzed rearrangement.[12]

Our starting point would be the conditions used for our hydroarylation protocol.[6] Therefore a solution of allenamide **5a** (1.00 equiv) and aniline **8a** (1.05 equiv) in CH_2Cl_2 was treated with a catalytic amount (5 mol %) of cationic

SCHEME 4. Hydroamination of Allenamide 5a



$Au(I)PPh_3OTf$ generated from $AuClPPh_3$ and AgOTf at room temperature (Scheme 4). To our delight the hydroaminated product **9a** was isolated in 86% yield after chromatography. The enamide was obtained exclusively as the *E*-isomer, and the addition of the N−H bond to the activated allenamide gave the Markovnikov product.

A comparable yield of 84% was also obtained with 5 mol % of the Au(I) complex, $AuPPh_3(NTf_2)$. The stereochemistry of the *E*-enamide double bond was supported by a combination of ^1H and ^{13}C NMR, IR spectroscopy (coupling constant 14.0 Hz and 1673 cm^{-1}), and single crystal X-ray analysis.[13]

The applicability of this protocol was then further explored, the results of which are summarized in Table 1. Haloanilines **8b** and **8f** successfully added to the allenamide giving the enamides **9b** and **9f** in good yield (entries 1 and 5). Introduction of an electron-withdrawing ethyl ester para to the NH_2 gave the enamide **9c** in a moderate 61% yield (entry 2), while a nitro group at the ortho position was tolerated and gave the enamide **9d** quantitatively (entry 3). 2,5-Dimethylaniline **8e** and 3-methoxyaniline **8g** both successfully added to the activated allenamide to give the hydroaminated products **9e** and **9g**, respectively (entries 4 and 6). While 2-fluoroaniline **8h** participated in the reaction to give **9h** (entry 7), unfortunately pentafluoroaniline **8i** failed to add to the activated allenamides, presumeably due to its low nucleophilicity (entry 8). Finally, *N*-methylaniline **8j** readily participated in the hydroamination reaction giving the *N*-methylenamide **9j** in near-quantitative yield (entry 9).

The hydroamination reaction was also performed with chiral and acyclic allenamides and the results are shown in Table 2.

Chiral allenamide **5b** successfully underwent hydroamination with both aniline **8a** and 2-iodoaniline **8f** giving the chiral enamides **10a** and **10b**, respectively (entries 1 and 2). The acyclic allenamide **7** also underwent hydroamination with anilines **8f** and **8g**. While a crude ^1H NMR of enamides **11a** and **11b** indicated full conversion to their enamide products the isolated yields were modest at best. Comparable yields for the formation of **11a** and **11b** were obtained when the Au(I) catalyst $AuPPh_3(NTf_2)$ was used. While enamides **9a**−**j** and **10a**,**b** showed good stability, enamides **11a**,**b** had to be stored under nitrogen to prevent degradation. Additionally, **11a** and **11b** exhibited considerable broadening in their ^1H NMR spectra and the ^{13}C NMR spectra for each showed two distinct conformers suggesting the presence of rotamers; however, these rotamers could be equilibrated at 373 K in d_6-DMSO.

A mechanistic rationale for this transformation is outlined in Scheme 5.

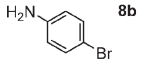
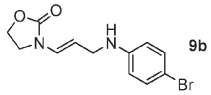
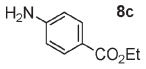
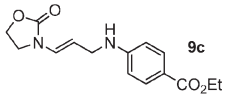
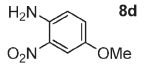
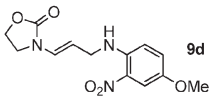
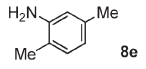
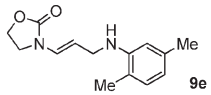
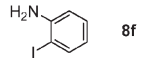
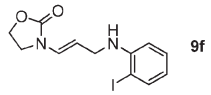
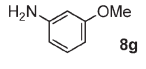
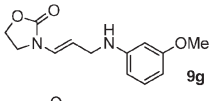
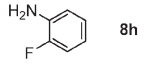
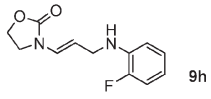
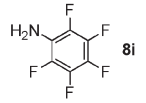
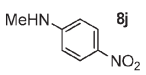
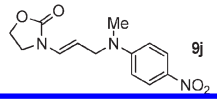
(10) Methods for enamide synthesis: (a) Organocuprate addition to isocyanates: Snider, B. B.; Song, F. *Org. Lett.* **2000**, *2*, 407. (b) Acylation of imines: Boeckman, R. K.; Goldstein, S. W.; Walters, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 8250. (c) *N*-acylation/Peterson elimination: Fürstner, A.; Brehm, C.; Cancho-Grande, Y. *Org. Lett.* **2001**, *3*, 3955. (d) Pd−Cu-catalyzed C−N bond formations: Klapars, A.; Campos, K. R.; Chen, C.; Volante, R. P. *Org. Lett.* **2005**, *7*, 1185. Brice, J. L.; Meerdink, J. E.; Stahl, S. S. *Org. Lett.* **2004**, *6*, 1845. Wallace, D. J.; Klauber, D. J.; Chen, C.; Volante, R. P. *Org. Lett.* **2003**, *5*, 4749. Cesati, R. R., III; Dwyer, G.; Jones, R. C.; Hayes, M. P.; Yalamanchili, P.; Casebier, D. S. *Org. Lett.* **2007**, *9*, 5617. Bolshan, Y.; Batey, R. A. *Angew. Chem.* **2008**, *120*, 2139. *Angew. Chem., Int. Ed.* **2008**, *57*, 2109; Chemler, S. R.; Fuller, P. H. *Chem. Soc. Rev* **2007**, *36*, 1153. (e) Fe, Ru, Ru methods see: Stille, J. K.; Becker, Y. *J. Org. Chem.* **1980**, *45*, 2139. (f) For organometallic additions to ynamides: Gourdet, B.; Rudkin, M. E.; Watts, C. A.; Lam, H. W. *J. Org. Chem.* **2009**, *74*, 7849. (g) For Heck coupling strategies: Vallin, K. S. A.; Zhang, Q.; Larhed, M.; Curran, D. P.; Hallberg, A. *J. Org. Chem.* **2003**, *68*, 6639. Harrison, P.; Meek, G. *Tetrahedron Lett.* **2004**, *45*, 9277. (h) For co-oligomerization of *N*-vinyl amides see: Tsujita, H.; Ura, Y.; Matsuki, S.; Wada, K.; Mitsudo, T.; Kondo, T. *Angew. Chem.* **2007**, *119*, 5252. *Angew. Chem., Int. Ed.* **2007**, *46*, 5160. (i) For oxidative Pd-catalyzed conjugate addition: Lee, J. M.; Ahn, D.-S.; Jung, D. Y.; Lee, J.; Do, Y.; Kim, S. K.; Chang, S. *J. Am. Chem. Soc.* **2006**, *128*, 12954.

(11) Heaney, H.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1973**, 499.

(12) Wei, L.-L.; Mulder, J. A.; Xiong, H.; Zificsak, C. A.; Douglas, C. J.; Hsung, R. P. *Tetrahedron* **2001**, *57*, 459.

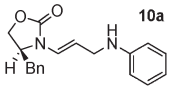
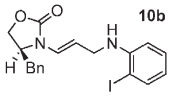
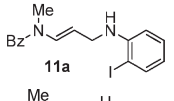
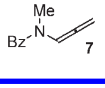
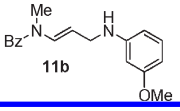
(13) Crystal data for **9a**: $C_{12}H_{14}N_2O_2$, M = 218.25, monoclinic, $I2/a$; a = 16.015(3) Å, b = 5.4583(9) Å, c = 25.143(5) Å, β = 99.848(2)°, V = 2165.5(7) Å^3; D_{calc} = 1.339 g/cm^{-3}; μ(Mo Kα) = 0.093 mm^{-1}; λ = , 0.71073 Å, T = 150(2) K; 12077 total reflections, 3283 unique data (R_{int} = 0.0277); solved by direct methods and refined on F^2 values to give R_1 = 0.0428. See the Supporting Information for further details.

TABLE 1. Substrate Scope for the Au(I)-Catalyzed Hydroamination of Allenamide 5a[a]

entry	substrate	product[b]	yield [%][c]
1	 **8b**	 **9b**	79
2	 **8c**	 **9c**	91
3	 **8d**	 **9d**	99
4	 **8e**	 **9e**	83
5	 **8f**	 **9f**	98
6	 **8g**	 **9g**	61
7	 **8h**	 **9h**	90
8	 **8i**	*No reaction*	0
9	 **8j**	 **9j**	98

[a]Reaction conditions: $AuPPh_3OTf$ (5 mol %), CH_2Cl_2, rt. [b]Data for all new compounds are contained within the Supporting Information. [c]Isolated yields.

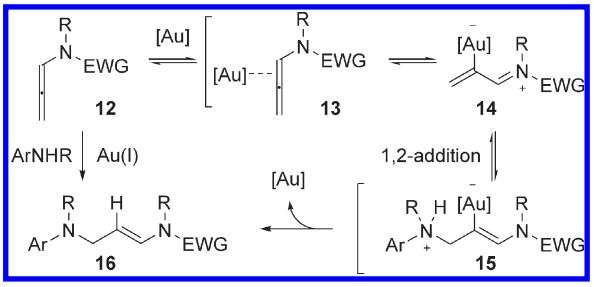
TABLE 2. Variation of the Allenamide in the Au(I)-Catalyzed Hydroamination Reaction[a]

entry	substrate	aniline	product[b]	yield [%][c]
1	 **5b**	**8a**	 **10a**	79
2	 **5b**	**8f**	 **10b**	91
3	 **7**	**8f**	 **11a**	46
4	 **7**	**8g**	 **11b**	47

[a]Reaction conditions: $AuPPh_3OTf$ (5 mol %), CH_2Cl_2, rt. [b]Data for all new compounds are contained within the Supporting Information. [c]Isolated yields.

We believe that the cationic Au(I) salt activates the allenamide **12** to give a conjugated *N*-acyliminium intermediate species **14**. This can undergo either 1,2- or 2,3-addition by a suitable nucleophile. In the case at hand the aniline derivatives undergo 1,2-addition giving **15**, which can then undergo protodemetalation to yield the observed *E*-enamide **16**.

SCHEME 5. Mechanistic Rationale for the Hydroamination Reaction



In summary, we have disclosed an Au(I)-catalyzed protocol for the intermolecular hydroamination of allenamides with arylamines. The reaction is facile, high yielding, and stereoselectively gives the *E*-enamide products. The products of this reaction, allylamino enamides, have the potential to be valuable building blocks in organic synthesis since they contain two vital functionalities, allyl amines and enamides, within one framework. The chemistry of this building block, mechanistic insights, and the addition of alkylamines to the Au-activated conjugated *N*-acyliminium species are currently being studied in our group and will be reported on in due course.

Experimental Section[14]

Representative Hydroamination Method with Allenamide 5a. To a solution of the allenamide **5a** (63 mg, 1.05 equiv, 0.50 mmol) in dichloromethane (3.00 mL) at room temperature was added the aniline derivative (1.05 equiv) followed by $AuPPh_3OTf$ (from $AuClPPh_3$ [12.40 mg, 5.00 mol %, 0.025 mmol] and AgOTf [6.60 mg, 5 mol %, 0.025 mmol]) and the resulting solution was stirred for up to 1 h at room temperature (monitored by tlc). The resulting reaction mixture was then filtered through a plug of Celite and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **9a** was obtained as a pale yellow solid (R_f 0.42) (93 mg, 86%, mp 89−91 °C, CH_2Cl_2/ petroleum ether) [found (ES): MNa^+, $C_{12}H_{14}N_2O_2$, 241.0944, requires MNa^+ 241.0953]; IR (solution, $CHCl_3$) 3441, 3012, 1759, 1673, 1602, 1504, 1482, 1417, 1250 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 7.18 (t, J = 8.4 Hz, 2H), 6.91 (d, J = 14.0 Hz, 1H), 6.72 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 7.6 Hz, 2H), 4.96 (dt, J = 6.4, 14.0 Hz, 1H), 4.42 (dd, J = 8.0, 9.2 Hz, 2H), 3.80 (d, J = 6.4 Hz, 2H), 3.73 (br s, 1H), 3.69 (t, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.3 (C), 147.8 (C), 129.3 (CH), 126.4 (CH), 117.8 (CH), 113.1 (CH), 107.7 (CH), 62.2 (CH_2), 43.8 (CH_2), 42.5 (CH).

Representative Hydroamination Method with Allenamide 5b. To a solution of the allenamide **5b** (50 mg, 1.00 equiv, 0.232 mmol) in dichloromethane (2.00 mL) at room temperature was added the aniline derivative (1.05 equiv) followed by $AuPPh_3OTf$ (from $AuClPPh_3$ [5.80 mg, 5.00 mol %, 0.012 mmol] and AgOTf [3.00 mg, 5 mol %, 0.012 mmol]) and the resulting solution was stirred for up to 1 h at room temperature (monitored by tlc). The resulting reaction mixture was then filtered through a plug of Celite and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **10a** was obtained as a colorless oil (R_f 0.5) (48 mg, 68%); $[\alpha]^{20}_D$ 26.0 (c 1.00, $CHCl_3$) [found (ES): MNa^+, $C_{19}H_{20}N_2O_2$, found 331.1413, requires MNa^+ 331.1422]; IR (solution, $CHCl_3$) 3014, 2926, 1755, 1670, 1503, 1413, 1310, 1238, 1206 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ

(14) Full experimental details and compound data are available in the Supporting Information

7.35−7.26 (m, 3H), 7.20 (t, J = 8.0 Hz, 2H), 7.15−7.13 (m, 2H), 6.84 (d, J = 14.4 Hz, 1H), 6.74 (t, J = 7.6 Hz, 1H), 6.66 (d, J = 8.4 Hz, 2H), 5.22 (dt, J = 6.4, 14.4 Hz, 1H), 4.27−4.17 (m, 3H), 3.87−3.83 (m, 2H), 3.21−3.18 (m, 1H), 2.81−2.76 (m, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 155.8 (C), 147.8 (C), 135.2 (C), 129.3 (CH), 129.3 (CH), 129.0 (CH), 127.4 (CH), 125.3 (CH), 117.9 (CH), 113.2 (CH), 108.3 (CH), 66.7 (CH_2), 55.0 (CH), 44.2 (CH_2), 36.3 (CH_2).

Representative Hydroamination Method with Allenamide 7. To a solution of the allenamide **7** (50 mg, 1.00 equiv, 0.289 mmol) in dichloromethane (3.00 mL) at room temperature was added the aniline derivative (1.05 equiv) followed by AuPPh$_3$OTf (from AuClPPh$_3$ [7.20 mg, 5.00 mol %, 0.014 mmol] and AgOTf [3.70 mg, 5 mol %, 0.014 mmol]) and the resulting solution was stirred for up to 1 h at room temperature (monitored by tlc). The resulting reaction mixture was then filtered through a plug of Celite and the crude mixture purified by column chromatography (ethyl acetate/petroleum ether mixture as indicated). **11a** was obtained as a yellow oil (R_f 0.35) (52 mg, 46%) [found (ES): MNa$^+$, $C_{17}H_{17}IN_2O$, found 331.415.0271, requires MNa$^+$ 415.0283]; IR (solution, $CHCl_3$) 3441, 3011, 1638, 1590, 1506, 1389, 1069 cm^{-1}; ^{1}H NMR (400 MHz; $CDCl_3$) (mixture of rotamers) δ 7.64 (d, J = 7.6 Hz, 1H), 7.49−7.40 (m, 5H), 7.20 (t, J = 7.2 Hz, 1H), 6.78 (br s, 1H), 6.50 (br s, 1H), 6.48−6.44 (m, 1H), 5.16 (br s, 1H), 4.17 (br s, 1H), 3.77−3.75 (m, 2H), 3.27 (br s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) (mixture of rotamers) δ 170.9 (C), 146.4 (C), 139.1 (CH), 135.7 (C), 133.0 (CH), 129.4 (CH), 128.7 (CH), 128.0 (CH), 119.0 (CH), 110.8 (CH), 105.7 (CH), 85.7 (C), 44.1 (CH_2), 30.4 (CH_3).

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Supporting Information Available: Experimental procedures, ^{1}H and ^{13}C NMR spectra, characterization for **9a**−**j**, **10a**,**b**, and **11a**,**b**, and the crystallographic data for **9a**. This material is available free of charge via the Internet at http://pubs.acs.org.