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Two Distinct Ag(I)- and Au(I)-Catalyzed Olefinations between α-Diazo Esters and *N*-Boc-Derived Imines

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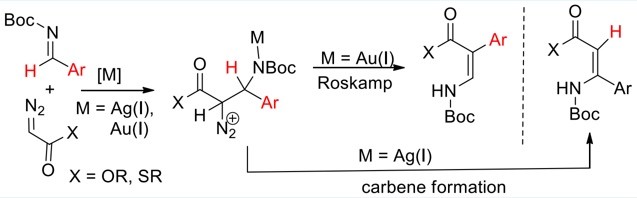
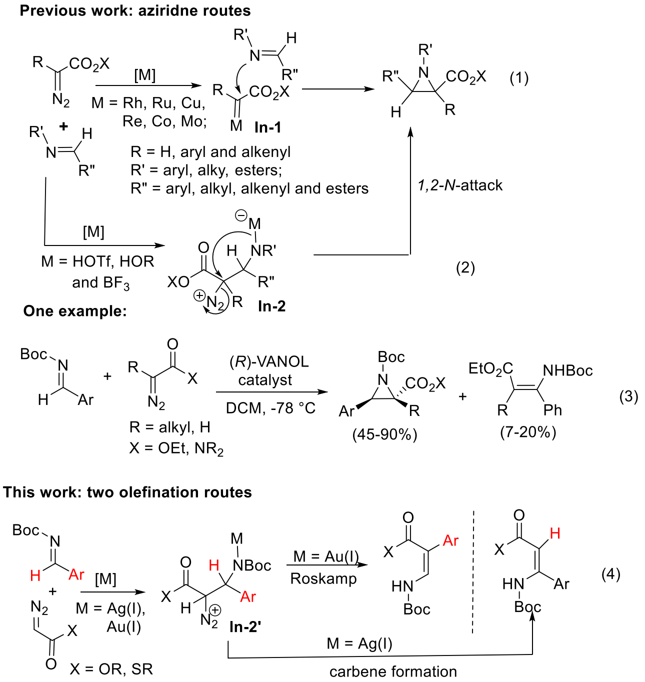
Supporting Information

ABSTRACT: Metal-catalyzed reactions between α-diazo esters and imines were well-known to yield aziridine derivatives exclusively. This work reports two new olefination reactions between *N*-Boc-derived (Boc = *tert*-Butyloxycarbonyl) imines and α-diazo esters with Ag(I) and Au(I) catalysts, respectively. Our mechanistic studies reveal that these new olefinations involve an initial attack of diazo esters on metal/imine complexes to form Mannich-addition intermediates, which subsequently afford α-aryl-β-aminoacrylates via a Roskamp reaction, or to form β-aryl-β-aminoacrylates via the formation of silver carbenes.



α-Diazo carbonyl compounds have found widespread applications in organic synthesis, because they readily form reactive metal carbenes.[1] These metal carbenes undergo various and useful transformations such as X−H insertions (X = C, N, O, S, Si), cyclopropanation, Stevens and Wolff rearrangements, and ylide-based cycloaddition reactions.[2] Equation 1 (Scheme 1) shows one well-known system for catalytic [2 + 1] annulations of numerous imines with diazo esters via α-oxo metal carbenes (**In-1**) that are subsequently captured by nucleophilic imines to yield aziridine products.[3] Such aziridine syntheses have been achieved with less acidic metal catalysts including Rh(II), Ru(II), Cu(I), Re(I), and Co(II). Alternatively, in the case of Brønsted acids and BF_3,[4] diazo esters serve as nucleophiles to attack metal/imine pairs to form intermediates of Mannich type (**In-2**), which also afford aziridines preferably (Scheme 1, eq 2). Equation 3 (Scheme 1) highlights one specific example that employs (*R*)-VANOL to catalyze an asymmetric [2 + 1] annulation of *N*-Boc-derived (Boc = *tert*-Butyloxycarbonyl) imines with α-diazo esters;[4h] herein, α-aryl-β-aminoacrylate was formed also in small proportions, indicative of an unknown path. We are aware of no example to obviate this aziridine chemoselectivity unless α-diazo esters are replaced with α-diazo nitriles.[5] In seeking new chemoselectivity beyond aziridine formation, this work reports two new olefinations between α-diazo esters and *N*-Boc-derived imines using Au(I) or Ag(I) catalysts without additive. With a cationic Au(I) catalyst, these imine/α-diazo ester mixtures yield α-aryl-β-aminoacrylates, involving a Roskamp reaction[6] of intermediates **In-2′**, whereas a Ag(I) catalyst enables the same intermediates to afford β-aryl-β-aminoacrylates via silver carbene intermediates. Our mechanistic analysis supports the roles of intermediates **In-2′** that have been verified with deuterium labeling and other control experiments.

Scheme 1. Aziridine Routes



Importantly, these two new catalytic reactions are accessible to two β-amino acrylates with the same imines and α-diazo esters; these functionalized acrylates are recognized as useful building blocks to construct numerous heterocyclic rings

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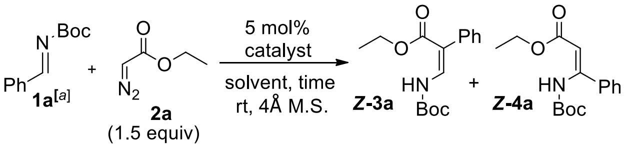
including pyrroles,[7] indoles,[8] oxazoles,[9] pyrazoles,[10] quinolines,[11] pyridines,[12] and dihydropyridines.[13]

Table 1. Optimization and Catalyst Screening

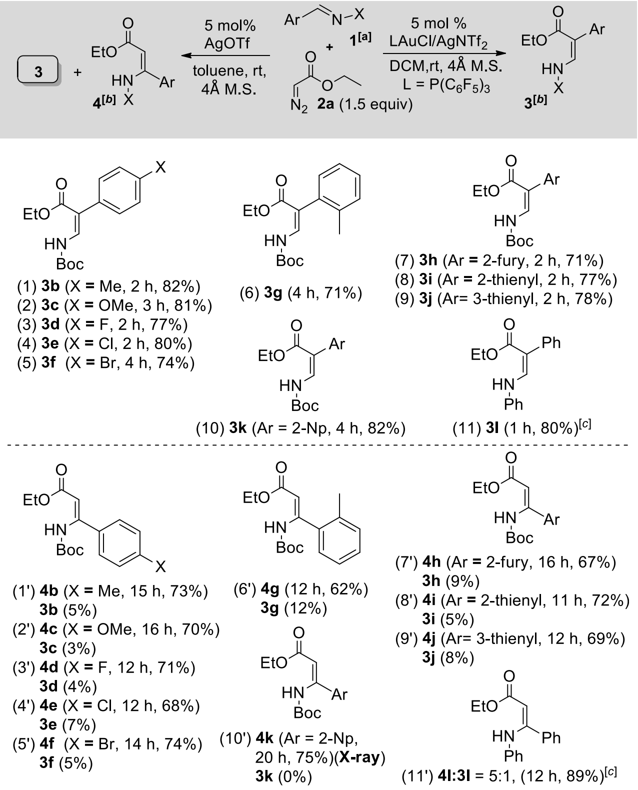


entry	catalyst	solvent	T (h)	yield[b] (%) 3a	4a
1	$(PhO)_3PAuCl/AgNTf_2$	DCM	05	40	10
2	$IPrAuCl/AgNTf_2$[c]	DCM	05	30	08
3	$LAuCl/AgNTf_2$[d]	DCM	04	41	05
4	$(C_6F_5)_3PAuCl/AgNTf_2$	DCM	02	80	
5	$(C_6F_5)_3PAuCl/AgSbF_6$	DCM	03	61	05
6	$(C_6F_5)_3PAuCl/AgOTf$	DCM	06	30	25
7	$(C_6F_5)_3PAuCl/AgNTf_2$	DCE	12	74	05
8	$(C_6F_5)_3PAuCl/AgNTf_2$	toluene	12	25	25
9	$AgNTf_2$	DCM	24	25	40
10	AgOTf	DCM	12	30	53
11	AgOTf	toluene	06	11	71
12	$Rh_2(OAc)_4$	toluene	05		
13	BF_3[e]	DCM	03	65	15
14	HOTf[e]	DCM	15	10	10

[a] [**1a**] = 0.12 M. [b] Product yields are reported after purification from a silica column. [c] IPr = 1,3-bis(diisopropylphenyl) imidazol-2-ylidene. [d] L = P(*t*-Bu)$_2$(*o*-biphenyl). [e] 10 mol % of catalyst was used.

Table 1 shows catalytic optimization between imine **1a** and ethyl *α*-diazoacetate **2a** (1.5 equiv) using various Lewis acid catalysts. Our goal was to switch the chemoselectivity to nonaziridine products. We tested the reaction with $(PhO)_3PAuCl/AgNTf_2$ (5 mol %) in dichloromethane/molecular sieves 4 Å (DCM, 5 h) near 23 °C that afforded *α*-phenyl-*β*-aminoacrylate **3a** and its *β*-phenyl isomer **4a**, respectively, in 40% and 10% yields (entry 1). With other gold catalysts, $L'AuCl/AgNTf_2$ (L′ = IPr and P(*t*-Bu)$_2$(*o*-biphenyl)), these two reactants gave products **3a** and **4a** in 30−41% and 5−8% yields, respectively (entries 2 and 3). To our delight, a switch to $(C_6F_5)_3PAuCl/AgNTf_2$ (5 mol %) afforded *α*-phenyl-*β*-aminoacrylate **3a** in 80% yield (entry 4). Other silver salts $(C_6F_5)_3PAuCl/AgX$ (X = SbF_6 and OTf) became less chemoselective (entries 5 and 6); we noted that compound **4a** was obtained in 25% yield because of the less acidic nature of OTf-. For $(C_6F_5)_3PAuCl/AgNTf_2$, dichloroethane (DCE) provided a satisfactory yield (74%) of compound **3a**, whereas toluene gave a 1:1 mixture of **3a** and **4a** (entries 7 and 8). For $AgNTf_2$ alone in DCM, the reaction chemoselectivity altered to give compounds **3a** and **4a** in 25% and 40% yields, respectively (entry 9). Inspired by this discovery, we tested AgOTf in DCM and toluene, which increased the yields of desired **4a** to 53% and 71%, respectively (entries 10 and 11). The use of $Rh_2(OAc)_4$ led only to diazo decomposition to give a mixture of diethyl fumarate and malonate. For a strong Lewis acid like $BF_3{\cdot}Et_2O$, we obtained 1,2-phenyl migration product **3a** as major species (65%) together with its isomer **4a** in 15% yield (entry 13). In contrast, HOTf (10 mol %) gave the two products **3a** and **3a′** in low yields (entry 14). Compounds **3a** and **4a** presumably bear a *Z*-configuration to form a hydrogen bond between their amino groups and esters. This structural assignment is supported by ^1H nuclear Overhauser effect (NOE) spectra and X-ray diffraction of their related **4k** and **5i** (Supporting Information).

Table 2. Au(I) and Ag(I)-Catalyzed Reactions on Various Imines

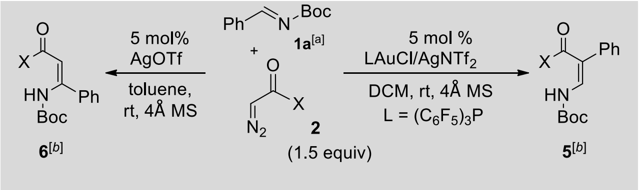


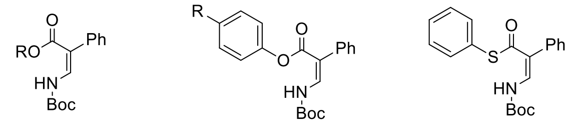
[a] [**1a**] = 0.12 M. [b] Product yields are reported after purification from a silica column. [c] An aziridine was isolated in 5% yield.

We assessed the generality of the two reactions with various *N*-Boc- and *N*-phenyl derived imines **1** and ethyl diazoacetate **2a** using $(C_6F_5)_3PAuCl/AgNTf_2$ and AgOTf; the results are summarized in Table 2. In the case of $(C_6F_5)_3PAuCl/AgNTf_2$, only *α*-aryl-*β*-aminoacrylates **3** were produced exclusively, with satisfactory yields. For AgOTf, *β*-aryl-*β*-aminoacrylates **4** were produced dominantly with 62−74% yields, together with *α*-aryl substituted isomers **3** in small proportions (3−12%). In all cases, we isolated no aziridine derivative in a tractable amount. We prepared *N*-Boc-derived imines **1b**−**1f** bearing various 4-phenyl substituents (X = Me, OMe, F, Cl, Br); their resulting *α*-aryl-*β*-aminoacrylates **3b**−**3f** were isolated in 74−82% yields with $(C_6F_5)_3PAuCl/AgNTf_2$ (entries 1−5). When reactions of these imines were catalyzed with AgOTf, their *β*-aryl-*β*-aminoacrylates **4b**−**4f** were also produced efficiently (68−74%) together with byproducts **3b**−**3f** in 3−7% yields (entries 1′−5′). 2-Methylphenyl imine **1g** was also compatible with Au(I) and Ag(I) catalysts, respectively, rendering *β*-aminoacrylates **3g** and **4g** in 71% and 62% yields (entries 6 and 6′). *N*-Boc-derived imines **1h**−**1j** bearing heteroaromatic moieties (Ar = 2-furyl and 2- and 3-thienyl) were suitable for these two catalytic reactions, affording **3h**−**3j** and **4h**−**4j** in 71−78% and 67−72% yields, respectively (entries 7−9 and 7′−9′). Both Au(I) and Ag(I) catalysts were amenable to imine **1k** bearing a 2-naphthyl group, giving desired products **3k** and **4k** in satisfactory yields (entries 10 and 10′). The molecular structure of compound **4k** was determined with X-ray diffraction (Supporting Information). We performed the reactions also on a distinct *N*-phenyl imine **1l** that delivered the desired olefin **3l** in 80% yield with gold catalyst, and afforded a mixture of two olefins **4l**/**3l** = 5:1 in 89% yield with AgOTf (entries 11 and 11′).

We examined further the two reactions with various *α*-diazo carbonyls **2** and *N*-Boc-derived imine **1a**; the results are summarized in Table 3. We prepared alkyl-derived *α*-diazo esters **2b**−**2e** (R = *t*-butyl, isobutyl, benzyl, and cinnamyl); their reactions with imine **1a** under the gold catalyst afforded the corresponding *α*-phenyl-*β*-aminoacrylates **5b**−**5e** in satisfactory yields (75−82%, entries 1−4); no 1,2-hydrogen migration byproduct **6** was formed in a tractable amount. With AgOTf, a 1,2-hydrogen shift occurred with the same *α*-diazo esters **2b**−**2e**, yielding *β*-phenyl-*β*-aminoacrylates **6b**−**6e** in 61−71% yields, together with **5b**−**5e** in minor proportions (7−10%, entries 1′−4′). These reaction patterns worked also for aryl-derived *α*-diazo esters **2f**−**2h** (X = H, OMe, and Cl); products of two distinct classes **5f**−**5h** (76−83%, entries 5−7) and **6f**−**6h** (64−73%, entries 5′−7′) were obtained, respectively. *α*-Diazo thioester **2i** also followed Au(I) and Ag(I)-directed chemoselectivities, giving the desired *α*- and *β*-phenyl acrylates **5i** and **6i** in 75% and 54% yields (entries 8 and 8′). The molecular structure of species **5i** was confirmed with X-ray diffraction (Supporting Information).

Table 3. Catalytic Reactions with Various *α*-Diazo Carbonyl Species

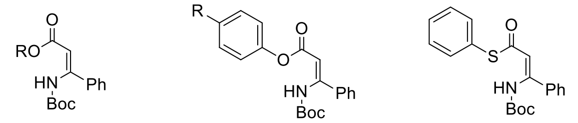




(1) **5b** (R = *t*-butyl, 2 h, 82%)
(2) **5c** (R = isobutyl, 4 h, 80%)
(3) **5d** (R = benzyl, 3 h, 77%
(4) **5e** (R = cinnamyl, 5 h, 75%

(5) **5f** (R = H, 2 h, 83%)
(6) **5g** (R = OMe, 3 h, 76%)
(7) **5h** (R = Cl, 3 h, 81%

(8) **5i** (5 h, 75%)
(X-Ray)



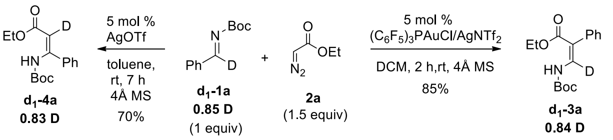
(1′) **6b** (R = *t*-butyl, 15 h, 71%)
5b (8%)
(2′) **6c** (R = isobutyl, 14 h, 69%)
5c (7%)
(3′) **6d** (R = benzyl, 20 h, 62%)
5d (8%)
(4′) **6e** (R = cinnamyl, 16 h, 61%)
5e (10%)

(5′) **6f** (R = H, 16 h, 73%)
5f (4%)
(6′) **6g** (R = OMe, 17 h, 70%)
5g (5%)
(7′) **6h** (R = Cl, 16 h, 64%)
5h (8%)

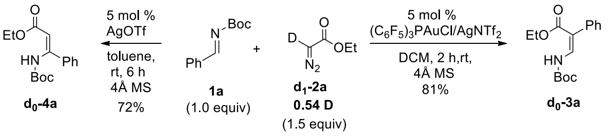
(8′) **6i** (15 h, 54%)
5i (20%)

[a][**1a**] = 0.12 M. [b]Product yields are reported after purification from a silica column.

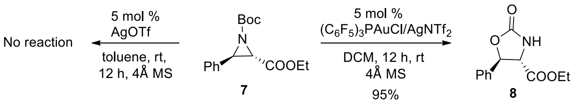
We performed deuterium-labeling experiments to elucidate the mechanisms of formation of *α*- and *β*-aryl-*β*-aminoacrylates **3** and **4**. We prepared imine d$_1$-**1a** containing 0.85 D at the imine proton. With the gold catalyst, its resulting product d$_1$-**3a** was analyzed to contain 0.84 D at the olefinic C(*β*)-carbon, indicative a complete deuterium transfer (eq 5). With a AgOTf catalyst, the resulting product d$_1$-**4a** comprised 0.83 D at the C(*α*)-carbon, showing a minute loss of deuterium (eq 5). We prepared also deuterated *α*-diazo ester d$_1$-**2a** bearing 0.54 D at the C(*α*)-carbon; its catalytic reactions with gold and silver catalysts yielded compounds **3a** and **4a** bearing no deuterium for either sample, indicating a complete loss of deuterium (eq 6). We prepared also an aziridine derivative **7**[14] to examine its role in this catalytic system. As shown in eq 7, this sample remained unreacted in toluene (25 °C, 12 h) with AgOTf, but it was convertible to heterocycle **8** efficiently with the gold catalyst (eq 7). Accordingly, an aziridine species such as **7** is not a precursor for our targets, *β*-aminoacrylates **3a** and **4a**. We prepared also *β*-amino *α*-diazo ester **9**[15] to examine its catalytic role; notably, this species gave our desired compound **4a** with either AgOTf or P(C$_6$F$_5$)$_3$AuCl/AgNTf$_2$ (eq 8). In contrast, the other product **3a** was unattainable from species **9** even with the gold catalyst.



(5)



(6)



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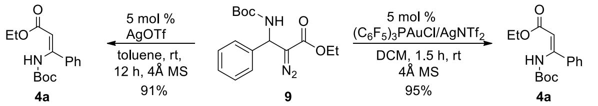
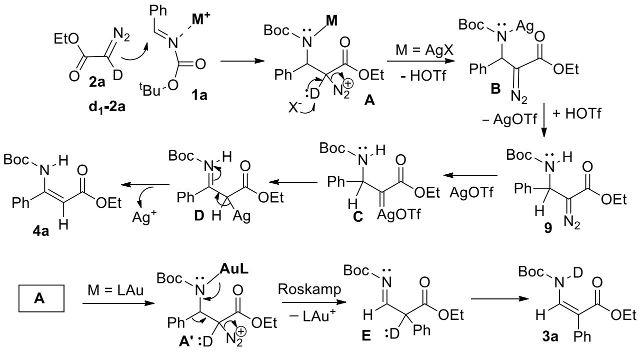


(8)

Scheme 2 depicts a plausible mechanism to rationalize the two olefination products **3a** and **4a**. The control experiment in eq 6 shows a complete loss of deuterium for initial d$_1$-**2a**; to rationalize this observation, we postulate an initial attack of diazo ester d$_1$-**2a** at catalyst-bound imine **1a** that serves an electrophile. For AgOTf catalysis, the diazo deuterium of resulting Mannich-addition intermediate **A** is very acidic and

Scheme 2. A Plausible Reaction Mechanism



easily deprotonated by OTf^- to generate a β-amino-α-diazo ester **B**. This OTf^- effect is also noted in gold catalyst $P(C_6F_5)_3AuOTf$ that leads to formation of undesired **3a** in 25% yield (Table 1, entry 6). A further protodeauration of species **B** affords compound **9** that has been confirmed to be the precursor for β-phenyl-β-amino acrylate **4a**. Accordingly, we postulate a silver carbene **C** to induce a 1,2-hydrogen shift to yield species **D** and ultimately the observed product **4a**. For the gold catalyst, its corresponding intermediate **A′** undergoes a Roskamp reaction[6] to induce a 1,2-phenyl migration, yielding species **B** and ultimately β-amino-α-acrylate **3a**. In gold catalysis, the C−D bond of species d_1-**1a** remains intact, thus retaining the initial deuterium content as shown in eq 5. In silver catalysis, 1,2-hydrogen migration of silver carbenes **C** also occurs with a complete transfer of deuterium[16,17] when d_1-imine **1a** was used. This proposed mechanism is compatible with our two deuterium-labeling experiments.

In summary, catalytic reactions of *N*-Boc-derived imines and α-diazo esters lead to two unprecedented olefinations using Au(I) and AgOTf catalysts. These catalytic systems represent the first examples to obviate the well-known aziridine route. We performed control experiments in a series to reveal that these new olefinations involve initial formation of Mannich addition intermediates that yielded novel β-amino-α-phenyl acrylates via a Roskamp reaction. In contrast, AgOTf enables the same intermediates to generate silver carbenes to induce a 1,2-hydrogen shift. Further elaborations of these nonaziridine routes will be explored in future investigations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02343.

> Experimental procedures, characterization data, crystallography data, and ^1H NMR and ^{13}C NMR for representative compounds (PDF)

Accession Codes

CCDC 1920996 and 1921812 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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