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ARTICLE

Regioselective differentiation of vicinal methylene C-H bonds enabled by silver-catalysed nitrene transfer

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Silver-catalyzed nitrene insertion enables the formation of benzosultams in good yield and with regioselectivity complementary to other transition metal nitrene-transfer catalysts. Preferential formation of six-membered benzosultam rings predominates for alkyl-substituted benzenesulphonamide precursors. Ligand-controlled tunability is also achieved for benzenesulphonamides with γ-branched alkyl substituents. Mechanistic probes suggest that the reaction pathway differs depending on whether a α (benzylic) or β (homobenzylic) C-H bond undergoes amidation, as well as the catalyst identity.

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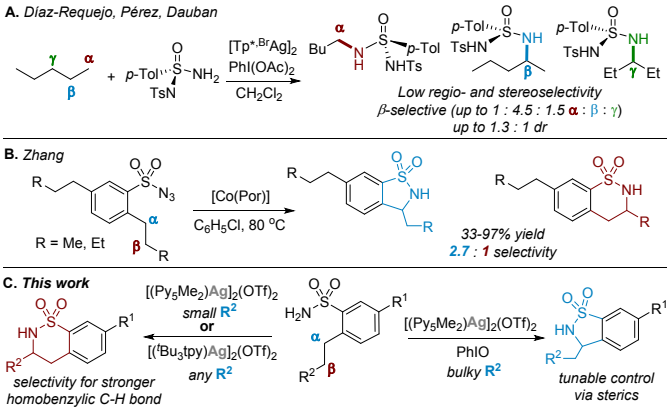
Introduction

Nitrene transfer serves as an effective tool for the rapid and efficient formation of C–N bonds. Contemporary methods involve the use of transition metal complexes to stabilize the formation of transient nitrene intermediates for selective insertion into C–H or C=C bonds. Despite numerous advances in the field, many nitrene insertion reactions remain largely substrate-controlled, due to reactive nitrene species and/or transition metal catalysts possessing specific, rigid ligand architectures that limit the ease of possible steric and electronic modifications.[1-3] These catalysts span many transition metals that include Rh,[4-9] Fe,[10-18] Co,[19,20] Cu,[21-24] and Ag.[25-30] Progress in the field is thus driven by the development of new catalytic systems that complement established trends in terms of chemo-, regio-, and stereoselectivity. Our group has discovered the highly flexible coordination sphere of silver(I) presents new opportunities for catalyst-controlled nitrene transfer.[31-34] In our hands, Ag(I) catalysis displays significant synthetic versatility, enabling tunable, chemoselective aziridination versus allylic C–H insertion in alkenes and allenes,[31,34] effective direct amination of propargylic C–H bonds in the presence of competing insertion sites,[32] and tunable, site-selective C-H amidation of competing C-H bonds.[33]

The selective functionalization of C–H bonds using group transfer reactions remains of intense interest, owing to the ubiquity of these bonds in complex organic frameworks. Regioselectivity amongst vicinal methylene C–H bonds is a particularly daunting challenge, as interrelated steric and electronic environments often preclude effective site-selective functionalization. For example, while silver homoscorpionate complexes, such as $[Tp^{*,Br}Ag]_2$ ($Tp^{*,Br}$: hydrotris(4-bromo-3,5-dimethyl)pyrazolyl borate), are competent in the amination of simple hydrocarbons, these reactions exhibit minimal regioselectivity governed by substrate control (Scheme 1A).[35] Nonetheless, the ability of silver to facilitate these transformations was encouraging, and inspired efforts to utilize our ligand-controlled strategy to improve regioselectivity among vicinal C–H bonds, as well as supplant inherent structural or electronic biases that disfavour functionalization at C-H sites that are typically preferred with other nitrene transfer catalysts.



Scheme 1. Progress in regioselective functionalizations of vicinal C-H bonds.

The prevalence of aliphatic amines in pharmaceutically relevant compounds makes their formation of great interest to the synthetic community.[36] Several examples of C–H amination using benzenesulphonyl azides as nitrene precursors have been reported. Redox-active metals are known to form transient nitrene species from benzenesulphonyl azides, which subsequently insert into C–H bonds with varying regioselectivity. For example, Zhang reported the use of cobalt(II) porphyrin complexes in regioselective benzylic C-H bond amidations (Scheme 1B).[20] Additionally, Katsuki demonstrated enantioinduction in similar reactions employing chiral Ir(I) salen complexes, although the degree of regio- and enantioselectivity was highly variable and substrate-dependent.[37] Unfortunately, the factors that dictate regioselectivity in these systems are poorly understood. Product ratios could be varied by incorporating ancillary substituents on the ligand distal to the metal binding site, suggesting that remote steric interactions between ligand and substrate may have a profound impact on the reaction outcome though conformational control. This concept was further explored by Arnold and co-workers *via* engineering of cP450 enzymes to

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achieve tunable amination at either a benzylic or homobenzylic C-H bond with high levels of regioselectivity.[14] More recently, Hartwig demonstrated the utility of an Ir(Me)-PIX cofactor[13] in addressing issues with competing azide reduction that plague Fe-based metalloenzymes.[38] Despite these advantages, the need for specialized expertise and equipment can be a barrier to widespread use of these strategies; a transition metal catalyst that could be tuned for amidation of benzylic or homobenzylic C-H bonds simply by changing the ligand would be highly desirable.

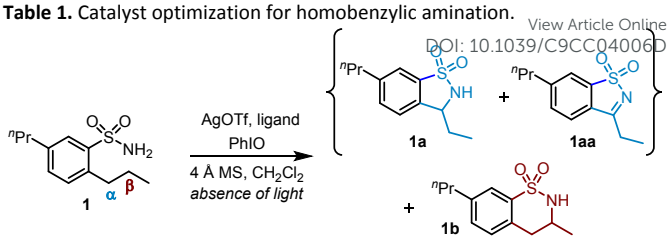
In this paper, we showcase how the unusual features of silver-catalysed benzosultam formation are harnessed for regioselective differentiation of vicinal methylene C-H bonds (Scheme 1C). Convenient features of our system include: 1) the use of sulphonamide precursors that avoids potentially explosive azides, 2) the ability to promote regioselectivity through electronics, 3) preference for amidation of weaker benzylic C–H bonds over their typically more reactive homobenzylic neighbours, and 4) the ability to further tune regioselectivity in bulky substrates *via* orthogonal steric and electronic control.

Results and discussion

Investigations began by employing sulphonamide **1** as a model system to explore the reactivity of various catalysts (Table 1, see Table S1-1 for catalyst structures). Tris(2-pyridylmethyl)amine (tpa) was expected to promote benzylic insertion at the α C-H bond, similar to its previously reported performance with sulfamate esters (entry 1).[32] Remarkably, amination occurred predominantly at the homobenzylic position instead. Total conversion and product yields improved in the absence of light, indicating that catalytic intermediates are vulnerable to photodecomposition on the timescale for C–H amination (entry 2). Further exploration of catalytically competent ligands revealed an optimal balance of yield and regioselectivity in the presence of $[Ag(Py_5Me_2)OTf]_2$ (entry 4). Overoxidation of **1a** to **1aa** is thought to depend on the efficiency of the silver catalyst at breaking down the polymeric PhIO.[39] Bipyridine ligands (entries 6-7) were not as effective in the reaction, although terpyridines, which form dimeric species in solution, performed better (entries 8-9). Comparisons with other established catalyst systems (entries 10-13) highlighted the unique utility of silver in benzenesulphon-amide nitrene insertion; for example, $Rh_2(esp)_2$ (entry 10) demonstrated similar yields to the optimized silver catalysts, but with no regioselectivity. Conversely, modest regioselectivity was achieved with $Rh_2(TPA)_4$, but in poor yield (entry 11). The overall product yield for [Fe(Pc)]Cl was similarly low, but showed moderate selectivity for the benzylic position, consistent with the presence of radical intermediates previously proposed by White for C–H amination.[18] These comparisons underscore the unconventional behaviour of silver catalysts in nitrene insertion.

Having established $[Ag(Py_5Me_2)OTf]_2$ as the optimal catalyst for homobenzylic C–H amination, we next sought to probe the effects of alkyl and aryl substitution on the reaction outcomes (Table 2). While the 2,5-dialkylbenzenesulphonamide **2** behaved similarly to **1**, the introduction of heteroatom substituents *meta* to the sulphonamide groups in **3** and **4** led to exclusive formation of six-membered benzosultams. These results suggest that the electrophilic silver-nitrene intermediate responds to inductive effects through the benzene ring. The effect of the substituent identity on the alkyl side chain was explored with substrates 5-7. Installing a phenyl ring at the β position (5) led to an increase in β C-H insertion, presumably through superior orbital overlap for benzylic activation, as compared to the α position. Truncation of the alkyl chain in **6** demonstrated the limitation of $[Ag(Py_5Me_2)OTf]_2$ for homobenzylic amidation, instead favouring formation of the 5-membered ring. However, the observation of product resulting from amidation at the β C-H in the presence of the more activated benzylic α methylene group was promising for the future design of silver catalysts for selective amidation of primary C-H bonds. Regioselectivity in the presence of $[Ag(Py_5Me_2)OTf]_2$ was completely lost when an ester functionality was installed in **7**, further highlighting the influence of inductive effects on selectivity.

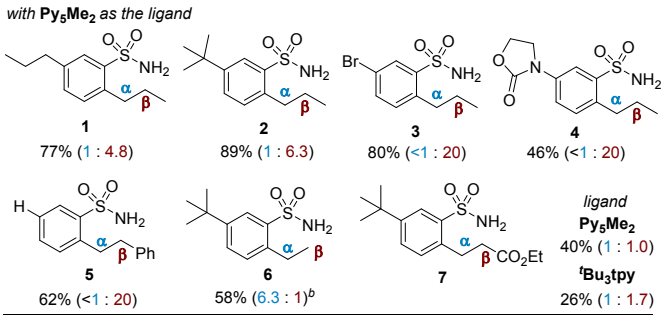
Table 1. Catalyst optimization for homobenzylic amination.



entry[a]	ligand (equiv)	yield (%)[b]	[1a+1aa]:1b	1a:1aa
1[c]	tpa (0.12)	50 [46]	1 : 3.6	>20:1
2	tpa (0.12)	65	1 : 3.3	>20:1
3[d]	tpa (0.12)	53 [41]	1 : 3.6	>20:1
4	**Py_5Me_2 (0.12)**	**86**	**1 : 4.5**	1.6:1
5[e]	Py_5Me_2 (0.12)	58	1 : 4.8	1.6:1
6	$^tBu_2$bipy (0.3)	16 [42]	1 : 1.0	<1:20
7	$(MeO)_2$bipy (0.3)	59	1 : 1.5	1:2.1
8	Me_3tpy (0.12)	91	1 : 3.3	1.9:1
9	$^tBu_3$tpy (0.12)	85	1 : 4.0	2.0:1
10	$Rh_2(esp)_2$[f]	84	1 : 1.0	>20:1
11	$Rh_2(TPA)_4$[f]	40 [45]	1 : 1.6	>20:1
12	[FePc]Cl /$AgSbF_6$[g]	22 [51]	3.0 : 1	>20:1
13[h]	Co(OEP)	92	2.7 : 1	>20:1

[a]**Conditions:** 0.1 equiv AgOTf, x equiv ligand, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH_2Cl_2, protected from light with Al foil. [b]NMR yields. [c]Exposed to ambient light. [d]1.2 equiv $PhI(OAc)_2$. [e]$PhCF_3$ solvent. [f]2%catalyst loading. [g]10% loading. [h]See ref. 20.

Table 2. Substituent effects on regioselectivity.



[a]**Conditions:** 0.1 equiv AgOTf, 0.12 equiv ligand, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH_2Cl_2, protected from light with Al foil. [b]NMR yield; 4:1 amine/imine formation at α position.

To further elucidate the relative roles of steric and electronic effects in benzosultam formation, substrates **8-11** containing alkyl branching were investigated (Table 3). Although previous work with $[Ag(Py_5Me_2)OTf]_2$[33] indicated that sterics would play a predominant role in discriminating between the α and β C–H bonds, results with **8** and **9** proved surprising. Amidation of the tertiary C–H bonds were heavily favoured, leading to single products, irrespective of the location of the methinyl C-H. Discrimination between the methinyl C–H bonds in **10** was especially challenging, giving rise to minimal α selectivity with silver catalysts supported by either Py_5Me_2 or $^tBu_3$tpy. The propensity of the electron-deficient silver

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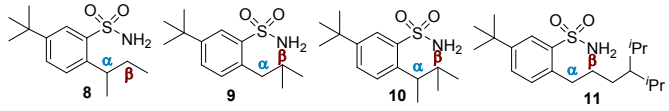
nitrene to favour electron-rich 3° positions appears to supersede steric pressure to deliver the quaternary amide product in high regiomeric excess. Inspired by the excellent regioselectivities observed with **8-9**, **11** was interrogated for the potential to react at a distal C-H bond; however, no macrocyclization was observed and the resulting α/β selectivity was low for Py_5Me_2. Interestingly, the use of [Ag(ᵗButpy)OTf]$_2$ restored the regioselectivity to levels similar to those observed for linear alkyl chains (*vide supra*). These results led to the hypothesis that catalyst control of the reaction might be achievable for systems where the γ position possesses a greater steric profile than that displayed in **11**.

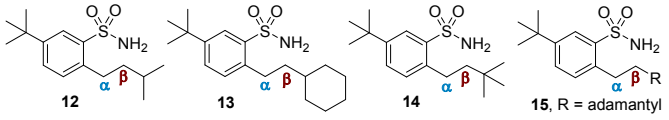
Table 3. Effects of branching on regioselectivity of nitrene transfer.



[a]**Conditions:** 0.1 equiv AgOTf, 0.12 equiv ligand, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH_2Cl_2, protected from light with aluminum foil.

To test this hypothesis, a series of substrates containing varying degrees of substitution at the β carbon were prepared (Table 4). Gratifyingly, [Ag(Py_5Me_2)OTf]$_2$ responded as expected to these modifications, enforcing nitrene insertion activity predominantly at the benzylic methylene, albeit in varying ratios. This effect correlates with the extent of branching at the γ carbon, indicating that altered selectivity can likely be attributed to steric interactions between the substrate and the catalyst (compare substrates **12**-**13** with **14**-**15**). Equally intriguing was the observation that this effect was unique to [Ag(Py_5Me_2)OTf]$_2$. When the catalyst was switched to [Ag(ᵗButpy)OTf]$_2$, the α:β selectivity was largely unaffected by the substitution at β and continued to favor amidation at the β C-H bond. This retention of regioselectivity across **12-15** was observed despite the fact that [Ag(ᵗButpy)OTf]$_2$ displayed activity similar to [Ag(Py_5Me_2)OTf]$_2$ during initial screening studies (see Table 1, entries 4 and 10).

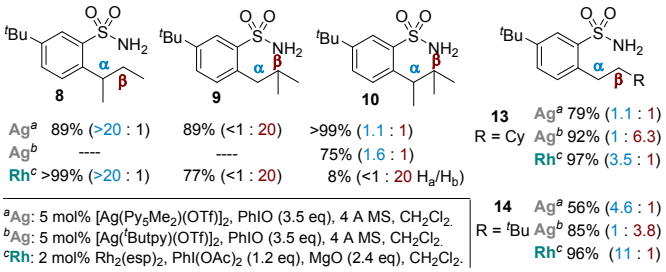
Table 4. Tunable catalyst-controlled regioselectivity through distal sterics.



[a]**Conditions**: 0.1 equiv AgOTf, 0.12 equiv ligand, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH_2Cl_2, covered with foil. [b]2.4:1 amine/imine at α position. [c]6.0:1 amine/imine at α position.

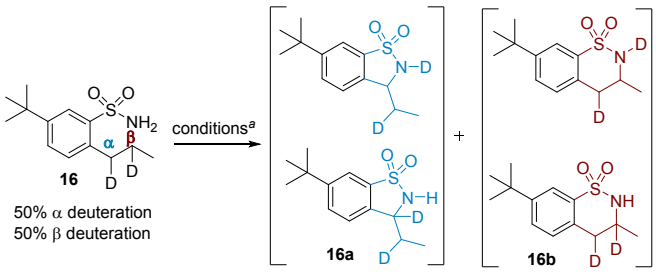
The performance of the silver catalysts [Ag(Py_5Me_2)OTf]$_2$ and [Ag(ᵗButpy)OTf]$_2$ were compared with Rh$_2$(esp)$_2$ to better define how their behaviour diverges from an established system (Table 5). Substrates **8-10** and **13-14** were chosen for their ability to act as effective indicators of steric interactions between substrate and catalyst. Rh$_2$(esp)$_2$ and [Ag(Py_5Me_2)](OTf)$_2$ both preferred methinyl over methylene C–H bonds in **8-9**. However, in contrast to Ag catalysts, Rh$_2$(esp)$_2$ was not effective when a second tertiary position was introduced in **10**, suggesting that the scope of Rh$_2$(esp)$_2$ is limited by if the sterics are too demanding. This conclusion was further supported by the fact that the preference for amidation at the α C-H site improved using Rh$_2$(esp)$_2$ with the sterically biased **13-14** when compared to [Ag(Py_5Me_2)(OTf)]$_2$. The improved regioselectivities for these examples in the presence of Rh$_2$(esp)$_2$ was taken as evidence of the influence of distal sterics, especially given the lack of selectivity for this same catalyst with a sterically-unbiased substrate (see Table 1, entry 12). In contrast, [Ag(ᵗButpy)OTf]$_2$ exhibits complementary site-selectivity that mimics the same results seen for the sterically unhindered **1** (see Table 1, entry 10).

Table 5. Comparisons of catalytic behaviour of Ag complexes with Rh$_2$(esp)$_2$.



[a]Ag: 5 mol% [Ag(Py_5Me_2)(OTf)]$_2$, PhIO (3.5 eq), 4 A MS, CH_2Cl_2. [b]Ag: 5 mol% [Ag(ᵗButpy)(OTf)]$_2$, PhIO (3.5 eq), 4 A MS, CH_2Cl_2. [c]Rh: 2 mol% Rh$_2$(esp)$_2$, PhI(OAc)$_2$ (1.2 eq), MgO (2.4 eq), CH_2Cl_2.

In order to acquire a better understanding of the mechanistic principles guiding reactivity, deuterated **16** was prepared as a probe to elucidate how the pathways of the silver-catalyzed nitrene transfer differ with catalyst identity (Scheme 2). The amidation of **16** with [Ag(ᵗButpy)OTf]$_2$ revealed KIE values of 2.8 and 3.2 at the benzylic and homobenzylic positions, respectively. In contrast, employing [Ag(Py_5Me_2)OTf]$_2$ as the catalyst gave KIE values of 6.7 (benzylic) and 4.2 (homobenzylic). The relatively low KIE values for the former catalyst suggest, but do not prove, that the nitrene insertion behaves as if it is a concerted process, irrespective of whether the C-H bond is benzylic or homobenzylic. Based on our previous investigations into the mechanisms of *intermolecular* nitrene insertion,[34] which show that concerted silver-catalyzed nitrene transfer is forbidden due to its electronic configuration, it is likely the low KIE indicates a barrierless HAT/radical recombination step, rather than a truly concerted C–H amination pathway. However, rapid radical rebound does not allow corroboration of this mechanism through the use of radical inhibitors. The nature of the C–H bond (benzylic *vs.* homobenzylic) had a noticeable effect on the KIE when [Ag(Py_5Me_2)OTf]$_2$ was used in the amidation reaction. The KIE of 6.7 at the benzylic α position suggesting that a stepwise, radical-based pathway may be operative. Similar to C-H amination of the homobenzylic bond, the use of radical inhibitors does not aid in distinguishing between concerted and radical pathways, as the rate of radical rebound in intramolecular reactions is too rapid.



[a]**Conditions:** 0.1 equiv AgOTf, 0.12 equiv ligand, 3.5 equiv PhIO, 4 Å MS, 0.05 M CH_2Cl_2, protected from light with Al foil. [b]Corresponding values from average of 2 runs.

Scheme 2. Kinetic isotope effects for benzylic and homobenzylic sites.

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The KIE of 4.2 at the homobenzylic β C-H bond was also higher than that observed for [Ag(ᵗButpy)OTf]$_2$ at the same site, also suggesting a possible radical intermediate. However, the typical KIEs for such processes are often much higher if the H-atom abstraction process is assumed to occur through a transition state where the Ag, N, and H atom are linear. It may be that the conformational strain required for formation of the 5-membered ring enforces a nonlinear transition state for the HAT/radical rebound process, consistent with the more moderate KIE of 4.2 that was observed experimentally.

Conclusions

Silver(I)-catalyzed nitrene transfer processes continue to show unusual behaviour compared to other transition metals competent for this type of group transfer reaction. Herein, we report the superior ability of silver complexes to consistently enable the amidation of homobenzylic methylene C-H bonds with good selectivity relative to their typically more active benzylic methylene neighbours. Explorations of substituent effects on the aryl ring revealed that the site-selectivity of sulphonamide nitrene insertion strongly depend on electronic factors. Despite this, steric effects between the catalysts and groups on the substrate distal from the reaction center may be exploited to enable tunable control over the regioselectivity. These results showcase silver's unusual versatility; it is not constrained to steric control alone, as comparative studies with $Rh_2(esp)_2$ suggest is the case for dinuclear Rh(II) catalysts, nor is it heavily biased toward sites with low BDE as seen with Zhang's cobalt catalysts. Kinetic isotope effects suggest that homobenzylic C-H amination occurs through a barrierless HAT/radical recombination process, while the mechanism of amidation at the benzylic α site is ligand-dependent, thus demonstrating versatility in terms of the mechanism as well. The adaptable nature of silver described in this manuscript has inspired other work in our group that enables tunable, catalyst control of group transfer reactions, which will be described in forthcoming publications.

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