



# Ligand-Controlled, Tunable Silver-Catalyzed C–H Amination

Juliet M. Alderson,<sup>†</sup> Alicia M. Phelps,<sup>†</sup> Ryan J. Scamp,<sup>†</sup> Nicholas S. Dolan, and Jennifer M. Schomaker\*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States

**S** Supporting Information

**ABSTRACT:** The development of readily tunable and regioselective C–H functionalization reactions that operate solely through catalyst control remains a challenge in modern organic synthesis. Herein, we report that simple silver catalysts supported by common nitrogenated ligands can be used to tune a nitrene transfer reaction between two different types of C–H bonds. The results reported herein represent the first example of ligand-controlled and site-selective silver-promoted C–H amination.

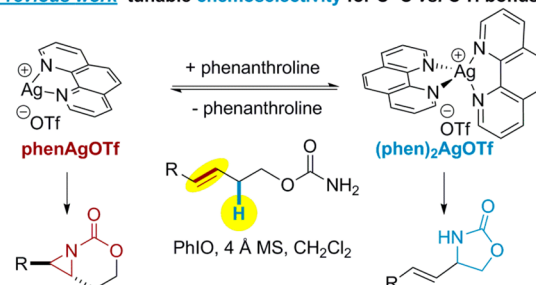
Achieving chemo- and site-selective C–H bond functionalizations in complex molecules remains a challenging problem in synthetic organic chemistry. In many cases, the inherent steric and electronic features of a given substrate dictate the reaction outcome.<sup>1</sup> While directing groups are often employed to override inherent reactivity preferences in a molecule and can be very powerful for the functionalization of a specific C–H bond,<sup>2,3</sup> these approaches are not ideal if the aim is to achieve tunable and site-selective transformations in the presence of multiple possible reactive sites. Our group is interested in developing inexpensive, *catalyst-controlled* methods for late-stage C–H oxidation chemistries, with the ultimate goal of reshaping current synthetic strategies to complex molecules. Here, we describe our progress in promoting tunable silver-catalyzed nitrene transfer reactions where the selectivity of the C–H amination event is controlled solely by the identity of the ligand.

The development of catalysts capable of tunable aminations of C–H bonds in different steric and electronic environments via nitrene transfer has been focused mainly on the use of powerful dinuclear Rh(II) complexes, especially Rh<sub>2</sub>(esp)<sub>2</sub> and related compounds.<sup>4,5</sup> Such catalysts can show excellent selectivity in the presence of multiple reactive sites, but the transformations are primarily substrate-controlled; changing the nature of the ligand does not permit tunable C–H functionalization.<sup>6</sup> Changing from Rh to another metal, such as Fe, can be employed to switch the selectivity of the nitrene transfer, but again, the ability to choose between two electronically or sterically similar C–H bonds by tuning the ligand is not yet possible.<sup>4c,7</sup>

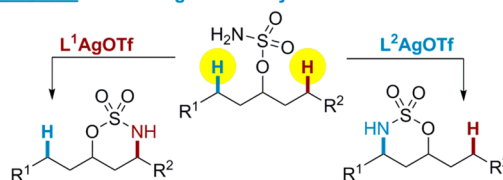
Our group has recently reported that a simple change in the AgOTf/ligand ratio enables highly chemoselective aminations of C=C and C–H bonds (Scheme 1, top).<sup>8</sup> The dynamic behavior of these silver complexes, coupled with steric effects, was primarily responsible for the ability to tune the reactivity between C=C and C–H groups. However, another striking feature of silver-catalyzed nitrene transfer, as compared to Rh- and Fe-based platforms, is the breadth of different ligands that are capable of promoting the amination event.<sup>9</sup> We were curious if

## Scheme 1. Tunable Ag-Catalyzed Nitrene Transfers

**Previous work** tunable chemoselectivity for C=C vs. C–H bonds



**This work** tunable regioselectivity between different C–H bonds



the changes in the coordination geometries of silver complexes enforced by different types of ligands translated into tunable, site-selective amination between C–H bonds in different chemical environments (Scheme 1, bottom).<sup>10</sup>

Sulfamate **1** (Table 1) was used to compare the reactivity between a benzylic C–H bond (**Bn**) and an electron-rich 3° C–H bond (**T**). As expected, the amination of **1** with dinuclear Rh(II) catalysts (Table 1, entries 1–4) favors reaction at **T** to yield **2b**, even when the steric bulk of the catalyst is increased (entry 4).<sup>4c</sup> As previously shown, activation of **Bn** was favored using Ru- and Fe-based catalysts (entries 5–6).<sup>7</sup> In contrast, the modularity and breadth of ligands that could be employed with AgOTf showed that catalyst control of the nitrene transfer could be achieved. The substituted 2,2′-bipyridine (**Bubipy**, **3**, entry 8) preferred activation of **T**, as did ligands **4** and **5** (entries 9–10). Phenanthroline-derived ligands **6–8** (entries 11–13), 2,2′,2′′-terpyridines **10–11** (entries 15–16), and Tp ligand **12** (entry 17)<sup>9f–j</sup> all showed reduced selectivity in favor of **2b**. Interestingly, a silver catalyst supported by tris(2-pyridylmethyl)amine (**tpa**, **9**, entry 14) preferred activation of **Bn**, indicating that Ag-catalyzed C–H amination is tunable through the ligand.

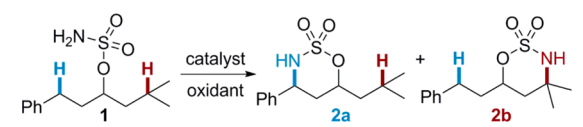
Based on these initial results, **Bubipy** **3** (Condition A) and the **tpa** ligand **9** (Condition B) were chosen to compare the reactivity between a **Bn** and various **T** bonds. Substrates in Table 2 were designed to elucidate the relationship between the steric environment around **T** and the site selectivity. The moderate

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Table 1. Ligand-Controlled, Silver-Catalyzed C–H Amination



entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>	entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>
1 <sup>c</sup>	Rh <sub>2</sub> (OAc) <sub>4</sub>	---	1:1.6	98%	10	5	1:3	1:2.2	77%
2	Rh <sub>2</sub> (OPiv) <sub>4</sub>	---	1:1.5	---	11	6	1:3	1:1.1	84%
3	Rh <sub>2</sub> (esp) <sub>2</sub>	---	1:7	99%	12	7	1:3	1:1.1	82%
4	Rh <sub>2</sub> (O <sub>2</sub> CPh <sub>3</sub> ) <sub>4</sub>	---	1:14	92%	13	8	1:1.2	---	0%
5	Ru <sub>2</sub> (hp) <sub>4</sub> Cl	---	1.4:1	74%	14	9	1:1.2	2.4:1	84%
6	[FePc]Cl	---	1:0	58%	15	10	1:1.2	1:1.4	67%
7	Cu(MeCN) <sub>4</sub> PF <sub>6</sub>	---	---	0%	16	11	1:1.2	1:1.5	93%
8	3	1:3	1:2.8	76%	17	12	1:1.2	1:1.6	84%
9	4	1:3	1:1.6	72%					

<sup>a</sup>C–H insertion: 10 mol % AgOTf, 10–30 mol % ligand, 3.5 equiv of PhIO, 4 Å MS, 0.05 M CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>Rh cat.: 2 mol %, 1.1 equiv of PhI(OAc)<sub>2</sub>, 2.3 equiv of MgO, CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup>See Supporting Information for the conditions for entries 5–7. <sup>d</sup>Total NMR yield. Average of 2 runs, mesitylene internal standard.

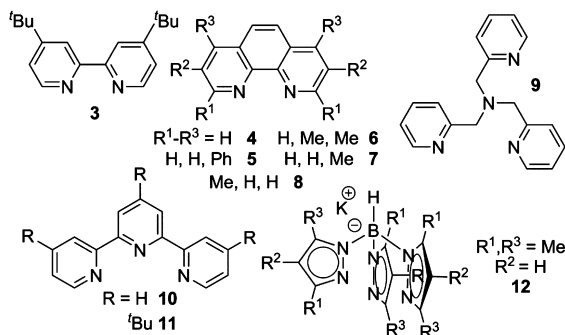
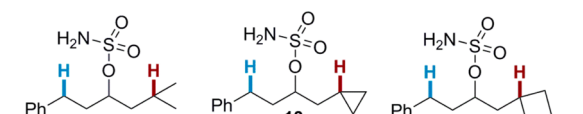


Table 2. Investigation of Steric Effects on Selectivity



entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>	entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>
1 <sup>c</sup>	Rh <sub>2</sub> (OAc) <sub>4</sub>	---	1:1.6	98%	10	5	1:3	1:2.2	77%
2	Rh <sub>2</sub> (OPiv) <sub>4</sub>	---	1:1.5	---	11	6	1:3	1:1.1	84%
3	Rh <sub>2</sub> (esp) <sub>2</sub>	---	1:7	99%	12	7	1:3	1:1.1	82%
4	Rh <sub>2</sub> (O <sub>2</sub> CPh <sub>3</sub> ) <sub>4</sub>	---	1:14	92%	13	8	1:1.2	---	0%
5	Ru <sub>2</sub> (hp) <sub>4</sub> Cl	---	1.4:1	74%	14	9	1:1.2	2.4:1	84%
6	[FePc]Cl	---	1:0	58%	15	10	1:1.2	1:1.4	67%
7	Cu(MeCN) <sub>4</sub> PF <sub>6</sub>	---	---	0%	16	11	1:1.2	1:1.5	93%
8	3	1:3	1:2.8	76%	17	12	1:1.2	1:1.6	84%
9	4	1:3	1:1.6	72%					

Condition A: 10 mol% AgOTf, 30 mol% tBuBipy, 3.5 equiv PhIO, 0.05 M CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt, 30 min.  
Condition B: 10 mol% AgOTf, 12.5 mol% tpa, 3.5 equiv PhIO, 0.05 M CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt, 30 min.


<sup>a</sup>In all cases, the syn diastereomer was produced in >19:1 dr. Yields are isolated yields.

preference for insertion into T over Bn in 1 using (tBuBipy)<sub>2</sub>AgOTf parallels the reactivity of Rh(II) catalysts in intramolecular aminations.<sup>4c</sup> Moving from the isopropyl group of 1 to a cyclopropyl group in 13 gave exclusive Bn activation with both catalysts; however, the yield was superior using (tpa)AgOTf. The high bond dissociation energy (BDE) of the cyclopropyl C–H in 13 (~106 kcal/mol) compared to Bn (~89 kcal/mol) may preclude the formation of 13b.<sup>11</sup> The two catalysts responded

differently to increasing the size of the alkyl group. For (tBuBipy)<sub>2</sub>AgOTf, the selectivity for amination at T vs Bn improved as the size of the alkyl group was increased from the cyclopropyl of 13 to the cyclohexyl of 17 (17b:17a = 8:1). This indicates that moderate steric bulk does not hinder C–H insertion; however, further steric congestion in 18 lowered the T/Bn selectivity to 2.6:1, similar to the ratio observed for 1. In contrast, (tpa)AgOTf reveals selective functionalization of Bn over T for all substrates in Table 2. When T was contained in a cyclic alkane, (tpa)AgOTf appeared to favor Bn to a greater extent as the size of the ring increased, with the exception of 16, where lower selectivity was observed. This could be due to the lower BDE of the cyclopentyl C–H bond of 16 (~96 kcal/mol)<sup>11</sup> compared to the other substrates. Substrates 15 and 18, containing acyclic alkyl groups, showed higher selectivity for the benzylic position as the steric bulk increased. In general, it appears that steric effects influence the selectivity of (tpa)AgOTf to a greater extent than (tBuBipy)<sub>2</sub>AgOTf, which tends to promote reaction at the most electron-rich C–H bond.

The reactivity of the isopropyl 3° C–H bond T was further compared to other types of C–H bonds (Table 3). Reaction of

Table 3. Further Study of Site Selectivity



entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>	entry	cat <sup>a-c</sup>	Ag:L	2a:2b	yield <sup>d</sup>
1 <sup>c</sup>	Rh <sub>2</sub> (OAc) <sub>4</sub>	---	1:1.6	98%	10	5	1:3	1:2.2	77%
2	Rh <sub>2</sub> (OPiv) <sub>4</sub>	---	1:1.5	---	11	6	1:3	1:1.1	84%
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4	Rh <sub>2</sub> (O <sub>2</sub> CPh <sub>3</sub> ) <sub>4</sub>	---	1:14	92%	13	8	1:1.2	---	0%
5	Ru <sub>2</sub> (hp) <sub>4</sub> Cl	---	1.4:1	74%	14	9	1:1.2	2.4:1	84%
6	[FePc]Cl	---	1:0	58%	15	10	1:1.2	1:1.4	67%
7	Cu(MeCN) <sub>4</sub> PF <sub>6</sub>	---	---	0%	16	11	1:1.2	1:1.5	93%
8	3	1:3	1:2.8	76%	17	12	1:1.2	1:1.6	84%
9	4	1:3	1:1.6	72%					

Condition A: 10 mol% AgOTf, 30 mol% tBuBipy, 3.5 equiv PhIO, 0.05 M CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt, 30 min.  
Condition B: 10 mol% AgOTf, 12.5 mol% tpa, 3.5 equiv PhIO, 0.05 M CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt, 30 min.

<sup>a</sup>In all cases, the syn diastereomer was produced in >19:1 dr. Yields are isolated yields.

19 with (tpa)AgOTf preferred the allylic C–H bond, while that of 20 with (tBuBipy)<sub>2</sub>AgOTf favored T over the propargylic C–H bond. The higher BDE of the propargylic C–H of 20, as compared to the allylic C–H of 19, might be responsible for the decreased selectivity with (tpa)AgOTf. As expected, amination of 21 gave 21b as the exclusive product, as 2° C–H bonds are generally less reactive than 3° C–H's. Amination of 21 with (tpa)AgOTf again gave exclusive insertion at the 3° C–H bond, but with an improved yield compared to (tBuBipy)<sub>2</sub>AgOTf. Finally, the amination of 22 shows selectivity between two similar 3° C–H bonds is achievable. This intriguing result demonstrates that even slight differences in sterics and electronics can yield site selectivity with silver catalysis.

Further exploration of the impact of substrate electronics on the selectivity of the nitrene transfer was carried out (Table 4). In 23, the additional Me group increases the electron density of the 3° Bn C–H, resulting in lower selectivity using (tBuBipy)<sub>2</sub>AgOTf. In contrast, the steric congestion at Bn in 23 decreased the preference of (tpa)AgOTf for benzylic amination. Moving the Me group from the benzylic carbon of

Table 4. Exploration of Electronic Effects

<b>A</b>	19% <b>2a</b>	56% <b>2b</b>	<b>A</b> 35% <b>23a</b>
<b>B</b>	60%	24%	58% <b>23b</b>
			(dr 1.5:1) (dr 2.1:1)
			<b>B</b> 48% 51%
			(dr 2.5:1) (dr 1.6:1)
<b>R</b>	<b>a</b>	<b>b</b>	
OMe	<b>A</b> 31% <b>25a</b>	38% <b>25b</b>	
	<b>B</b> 70%	15%	
Me	<b>A</b> 25% <b>26a</b>	52% <b>26b</b>	
	<b>B</b> 66%	15%	
H	<b>A</b> 20% <b>2a</b>	56% <b>2b</b>	
	<b>B</b> 60%	25%	
Br	<b>A</b> 16% <b>27a</b>	44% <b>27b</b>	
	<b>B</b> 55%	33%	
CF <sub>3</sub>	<b>A</b> 11% <b>28a</b>	69% <b>28b</b>	
	<b>B</b> 42%	54%	
<b>R</b>	<b>a</b>	<b>b</b>	
OMe	<b>A</b> 44% <b>29a</b>	23% <b>29b</b>	
	<b>B</b> 51%	23%	
Me	<b>A</b> 39% <b>30a</b>	28% <b>30b</b>	
	<b>B</b> 45%	31%	
Br	<b>A</b> 34% <b>31a</b>	37% <b>31b</b>	
	<b>B</b> 33%	58%	
CF <sub>3</sub>	<b>A</b> 21% <b>32a</b>	53% <b>32b</b>	
	<b>B</b> 19%	61%	

Condition **A**: 10 mol% AgOTf, 30 mol% <sup>t</sup>Bubipy, 3.5 equiv PhIO, CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt. Condition **B**: 10 mol% AgOTf, 12.5 mol% tpa, 3.5 equiv PhIO, CH<sub>2</sub>Cl<sub>2</sub>, 4 Å MS, rt. <sup>a</sup> Isolated yields. <sup>b</sup> Average of two runs; NMR yields using mesitylene as the internal standard.

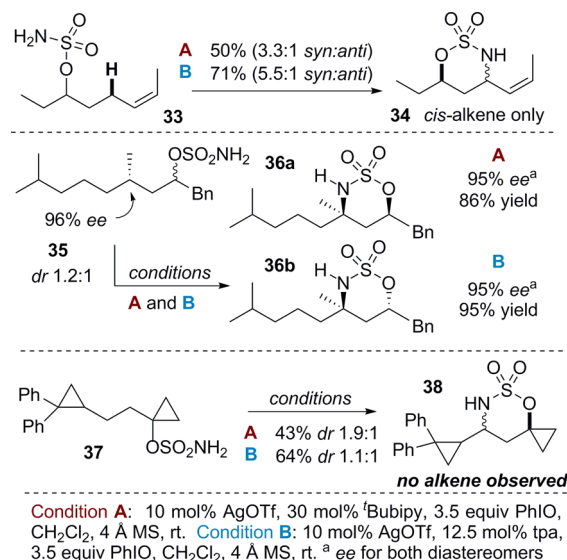
**23** to the *ortho* position in **24** restores selectivity with (tpa)AgOTf, further supporting the observation that steric effects influence the behavior of (tpa)AgOTf to a greater extent than (<sup>t</sup>Bubipy)<sub>2</sub>AgOTf, which tends to be more sensitive to the electron density at the C–H bond.

The sensitivity of (<sup>t</sup>Bubipy)<sub>2</sub>AgOTf for activation of the most electron-rich C–H bond was further supported by substrates **25–28**, where amination of **T** increased as the electron density of **Bn** was decreased. Interestingly, the same trend held true for (tpa)AgOTf, indicating that the two catalysts react similarly to changes in the electronics of the substrate. Insight into the nature of the transition state was obtained through Hammett correlations using the diaryls **29–32**. Because selectivity occurs during the product-determining step, the ratio of the isomeric products offers a direct measure of  $k_{Ar}/k_{Ph}$  and does not require knowledge of the rate-determining step.<sup>4a,c,7b</sup> Hammett plots of both catalysts support the buildup of positive charge at the carbon undergoing reaction (see the Supporting Information for details).<sup>8</sup>

Further exploration of the mechanistic pathway of silver-promoted nitrene transfer was carried out (Scheme 2). No isomerization of the double bond of **33** was noted using either catalyst. A stereochemical probe **35** resulted in no loss in *ee* in the product **36a** or **36b** with either catalyst. Finally, employing the radical clock **37** yielded no alkene products with either (<sup>t</sup>Bubipy)<sub>2</sub>AgOTf or (tpa)AgOTf. All three of these experiments argue against the presence of long-lived radical species in the reaction pathway.

Our initial empirical results for catalyst-controlled tunable amination suggest design principles for developing more selective catalysts. The sensitivity of the bipy-supported catalyst to the electron density of the C–H bond prompted us to briefly explore the impact of the ligand electronics on the site selectivity of nitrene transfer. We were pleased to find that installing an electron-donating *p*-OMe group on the bipy ligand increased the selectivity for **2b:2a** from 1.6:1 in the unsubstituted ligand **39** to

Scheme 2. Mechanistic Studies of Nitrene Transfer



4.0:1 in **41**, providing a clear path for the design of more selective catalysts. In contrast, the tpa-supported catalysts were not as sensitive to ligand electronics (Table 5, compare catalysts **9**, **42**,

Table 5. Insight into Future Catalyst Design

<b>catalyst<sup>a</sup></b>	<b>R</b>	<b>2a:2b</b>	<b>yield<sup>b</sup></b>
<b>3</b>	<sup>t</sup> Bu	1:2.8	76%
<b>39</b>	H	1:1.6	81%
<b>40</b>	Me	1:2.8	73%
<b>41</b>	OMe	1:4.0	76%
<b>catalyst</b>	<b>R<sup>1</sup>, R<sup>2</sup></b>	<b>2a:2b</b>	<b>yield</b>
<b>9</b>	H, H	2.8:1	76%
<b>42</b>	H, NMe <sub>2</sub>	2.2:1	85%
<b>43</b>	H, Cl	2.5:1	91%
<b>44</b>	Me, H	1:2.1	72%
<b>45<sup>c</sup></b>	H, H	1:1.4	57%
<b>9<sup>d</sup></b>	H, H	3.3:1	94%

<sup>a</sup>10 mol % catalyst, 3.5 equiv of PhIO, 4 Å MS, CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup>NMR yields, mesitylene internal standard. <sup>c</sup>One of the pyridines of the ligand was replaced with a benzyl group. <sup>d</sup>The oxidant was PhI(OPiv)<sub>2</sub> instead of PhIO.

and **43**). Interestingly, installing a Me group *ortho* to the pyridines of **44** reversed the selectivity to again favor **T**, while replacing a pyridine arm with a benzyl in **45** also eroded selectivity, suggesting future studies of the tpa-based ligand should focus on the steric features of the catalyst and the oxidant. Indeed, replacing PhIO with PhI(OPiv)<sub>2</sub> increased both the yield and the selectivity. The dynamic behavior of tpa-derived catalysts is influenced by the substitution of the tpa scaffold, and studies to determine how this design feature impacts selectivity are currently underway.

In conclusion, we have developed two silver catalyst systems capable of promoting tunable, regioselective amination of C–H bonds in different chemical environments. Silver catalysts supported by <sup>t</sup>Bubipy appear to prefer amination of the most



electron-rich C–H bond, while silver supported by a tpa ligand is more sensitive to the steric environment around the C–H bond, as well as the bond dissociation energy. Preliminary mechanistic work indicates that if radical intermediates are formed in either pathway, they undergo a rapid rebound, as no loss of stereochemical information is noted.<sup>8</sup> Computational studies are currently underway to obtain a more detailed mechanistic picture of both reaction pathways and gain a better understanding of how the ligand identity affects the electronic and steric nature of the purported silver nitrene intermediate. Another exciting ongoing investigation is utilizing these initial results to parametrize features of both the silver nitrenes and the substrates to develop predictive models for site selectivity in complex substrates.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedure and characterization is provided for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

[schomakerj@chem.wisc.edu](mailto:schomakerj@chem.wisc.edu)

### Author Contributions

<sup>†</sup>J.M.A., A.M.P., and R.J.S. contributed equally.

### Notes

The authors declare no competing financial interest.

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