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## Silver-catalysed intermolecular benzylic-selective C–H amidation *via* nitrene transfer

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Transition metal-catalysed C–H functionalisation is a powerful strategy to upgrade simple hydrocarbons to versatile synthetic building blocks and is a useful tool for the late-stage functionalisation of complex molecules. In this study, we report an intermolecular, non-directed amidation of benzylic C–H bonds *via* a nitrene transfer pathway. This operationally simple method uses inexpensive silver-based catalysts, only a small excess of substrate and displays broad substrate scope that includes arenes, biaryls, heteroarenes, and complex molecules. Changes to the AgNTf<sub>2</sub>: *tert*-butylterpyridine ligand ratio furnish dimeric or trimeric Ag complexes as the proposed active catalysts; these show differing reactivity and selectivity dependent on the nature of the substrate's benzylic C–H bond.

### Introduction

Transition metal-catalysed C–H functionalisation is a powerful method to efficiently increase the molecular complexity of abundant hydrocarbons.<sup>1</sup> Amines are found in pharmaceuticals, agrochemicals, natural products, and in key ligands for catalysis; thus, there is significant interest in methods for the selective introduction of C–N bonds into readily available precursors.<sup>2</sup> Traditional functional group interconversions,<sup>3</sup> reductive amination,<sup>4</sup> or alkene hydroaminations<sup>5</sup> often involve multiple steps, require precious metal catalysts or are limited in scope. In contrast, nitrene transfer (NT) enables direct conversions of diverse C–H bonds to new C–N bonds<sup>6</sup> using metals that include Rh,<sup>7a–c</sup> Ru,<sup>7d–f</sup> Ir,<sup>7g</sup> Cu,<sup>7h,i</sup> Fe,<sup>7j–m</sup> Co,<sup>7o,p</sup> Mn,<sup>7q</sup> and Ag,<sup>7r–v</sup> among others. While recent reports from the Zhang,<sup>7o,q</sup> White,<sup>7m,q</sup> Chang,<sup>8a</sup> Du Bois,<sup>7b,8b</sup> Pérez,<sup>7r,8c</sup> Dautan,<sup>8e</sup> Arnold<sup>8e,f</sup> and our own group (among others),<sup>7i–v,8g</sup> have driven progress in the field, intermolecular NT into benzylic C–H bonds<sup>9</sup> *via* a nitrene transfer process using Rh,<sup>8b,9a</sup> Ag,<sup>9b,c</sup> Co,<sup>9d</sup> Cu,<sup>9e</sup> Mn,<sup>9f</sup> Fe<sup>9g</sup> catalysts can be challenging. Depending on the metal, disadvantages include high cost,<sup>8b,d,9a</sup> lack of site- and chemoselectivity,<sup>7g,h</sup> the need for pre-oxidized nitrene precursors,<sup>9f</sup> difficult protein purification and aqueous conditions.<sup>9g</sup> Other drawbacks include long reaction times, modest yields and the use of large excesses of the hydrocarbon substrate (>5 equiv.), which limits application to late-stage functionalisation. Thus, simple methods for catalyst-controlled, selective amidations under mild conditions and in high yield are in demand for substrates that contain multiple reactive C–H sites.<sup>10</sup>

Our group has developed a suite of methods for silver-catalysed NT with the capacity for catalyst-controlled, chemo-

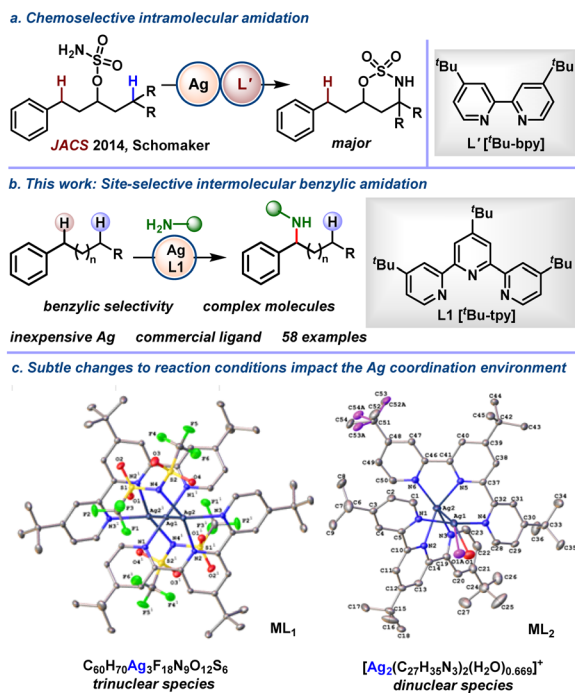
and regiodivergent C–H amidations.<sup>7i–v,11–13</sup> The site-selectivity of intramolecular NT is tunable *via* modifications to the nitrene precursor, ligand, Ag:ligand ratio, or tether length between the nitrogen and the targeted C–H bond. In contrast to NT catalysts with fixed and/or bespoke ligand scaffolds, Ag(I) complexes with simple N-donor ligands can adopt diverse geometries in solution, including linear, tetrahedral, square planar, or seesaw.<sup>14</sup> This unusual feature enables control over the steric environment of the reactive Ag-supported nitrenoid species and precise tuning of chemo-, site-, and stereo-selectivity, typically aided by directing Ag⋯π and arene–arene interactions between the catalyst and the substrate.<sup>11–13</sup>

### Results and discussion

Our previous work on intramolecular NT reactions between two competing C–H bonds showed that the site-selectivity could be tuned through the ligand identity. For example, a silver salt supported by 2 equivalents of a bidentate N-donor ligand, such as *tert*-butylbipyridine (<sup>t</sup>Bu-bpy), preferred reaction at a more electron-rich C–H (Scheme 1a)<sup>12a</sup> over a benzylic C–H bond; however, changing to a fluxional tris(2-pyridylmethyl)amine (tpa) ligand favored benzylic C–H amidation. In another system, altering the ligand on Ag from <sup>t</sup>Bu-bpy to a terpyridine (tpy) favored chemoselective C–H bond amidation over aziridination in homoallylic carbamate precursors (not shown).<sup>13b</sup> Terpyridines have low-lying LUMOs, provide tight chelation with cationic Ag(I) in a stable co-planar conformation and increase the coordination number at the metal, all factors we have observed to impact site-selectivity.<sup>15a,b</sup> We were curious if the selectivity observed with Ag salts supported by multidentate terpyridine-based ligands might be extended to intermolecular amidations of benzylic C–H bonds. In this work, we present

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Scheme 1 Tunable silver-catalysed amidation reactions.

a mild, practical Ag-catalysed method for amidation of benzylic C(sp<sup>3</sup>)-H bonds in arenes, biaryls, heteroarenes, and complex molecules (Scheme 1b). The protocol does not use costly metals or ligands, proceeds quickly at room temperature, and avoids the need for pre-oxidation of the nitrene precursor. An intriguing effect on the geometry of the proposed active Ag catalysts was noted when changing the ratios of AgNTf<sub>2</sub> and L1 (Scheme 1c), with **ML**<sub>1</sub> and **ML**<sub>2</sub> displaying differences in reactivity and selectivity, depending on the substrate (Scheme 2, *vide infra*).

Treatment of ethylbenzene **1a** with 1,1,1,3,3,3-hexafluoropropan-2-yl sulfamate (Hf<sub>3</sub>spNH<sub>2</sub>) as the nitrene precursor using condition **A** afforded an 85% yield of **1b** (Table 1, entry 1), which was lowered to 45% in TFE (entry 2). AgOTf and AgTFA proved less effective (entries 3–4), while lower and higher catalyst loadings also decreased the yields of **1b** (entries 5–6). The identity of the ligand was key in controlling the efficiency and selectivity of the NT event. Screening of a series of bipyridine, phenanthroline, terpyridine, and other bidentate/tridentate ligands (**L2**–**L5**, Table 1; see the SI, Table S16 for additional ligands), showed that <sup>t</sup>Butpy (**L1**) was optimal. The use of 4 Å molecular sieves (MS) as an additive was best (entries 7–8). Changing the solvent to MeCN (entry 9) gave poor yield, while changing the reaction time decreased the yield of **1b** (entries 10–11). Finally, control experiments confirmed that both AgNTf<sub>2</sub> and the ligand are essential for product formation (entries 12–13). For full optimization studies, see Tables S1–S17 in the SI.

The Ag complex formed under reaction condition **A** was subjected to SC-XRD; the resulting **ML**<sub>1</sub> shows an unexpected linear arrangement of three Ag atoms (Scheme 1c). Resubjecting

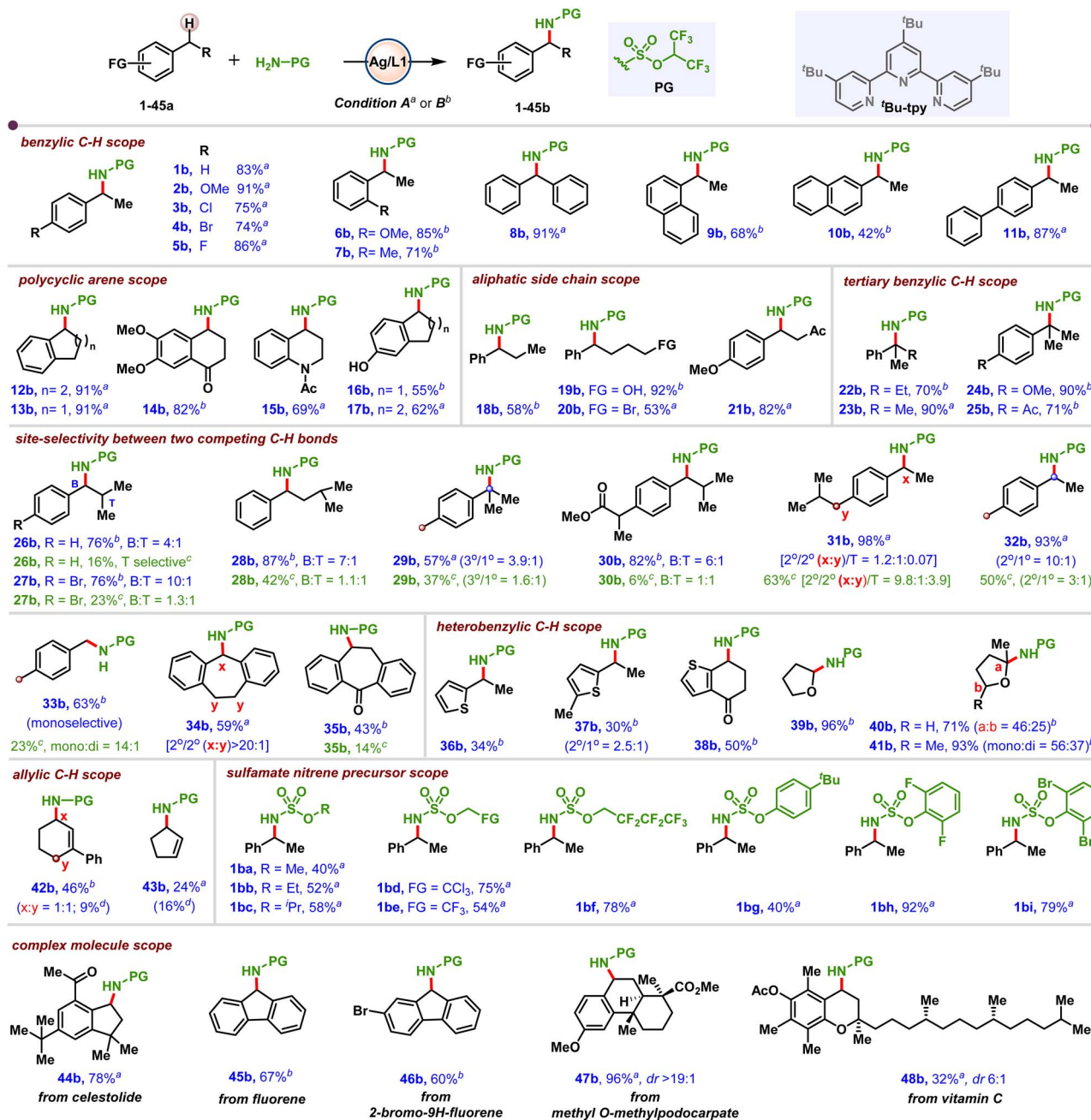
**ML**<sub>1</sub> to condition **A** for the reaction of **1a** to **1b**, minus the addition of AgNTf<sub>2</sub> and **L1** (see details in S4.6.2 of the SI), gave results that were similar to condition **A** only. However, biased substrates with competing benzylic and tertiary C(sp<sup>3</sup>)-H bonds gave poor yield with **ML**<sub>1</sub> (see SI, Tables S18–S33); thus, a second set of conditions was developed (condition **B**, Scheme 2). The solvent was switched to PhH using AgNTf<sub>2</sub> (10 mol%), **L1** (12 mol%), PFI0B (2 equiv.), and 4 Å MS at rt for 4 h to form **ML**<sub>2</sub> (Scheme 1c) as the proposed active catalyst (see Section 4.6.2 in the SI for further details).

With conditions **A** and **B** in hand, the scope of the amidation was explored (Scheme 2). An electron-rich MeO- substituted arene gave excellent yields (**2b**), while halogenated arenes were also well-tolerated (**3a**–**5a**), offering valuable opportunities for subsequent functionalisations. Installing an *ortho*-OMe group in **6a** gave an excellent 85% yield of **6b**, while a Me group resulted in a 71% yield of **7b** due to stereoelectronic factors. Diphenylmethane **8a** afforded a 91% yield of **8b**. The scope was extended to bicyclic arenes and biaryl derivatives, including 1-ethyl naphthalene **9a**, 2-ethyl naphthalene **10a**, and 4-phenyl ethylbenzene **11a**, which delivered good-to-excellent yields of **9b**–**11b**. Polycyclic arenes 1,2,3,4-tetrahydronaphthalene **12a**, 2,3-dihydro-1*H*-indene **13a**, and electron-poor 6,7-dimethoxy-3,4-dihydronaphthalen-1(2*H*)-one derivative **14a** also performed well under this amidation strategy (**12b**–**14b**). An *N*-protected amine derivative reacts smoothly (**15a**), while free amine inhibits the reaction (see the SI for details). Phenolic -OH groups were also tractable under the reaction conditions (**16b**–**17b**). Arenes **18a**–**21a** bearing longer side chains gave good yields of **18b**–**21b**; notably, aliphatic -OH and -Br groups were well-tolerated under the reaction conditions. Tertiary benzylic C-H bonds in **22a**–**25a** were amidated to furnish **22b**–**25b** in excellent yields, suggesting that the **ML**<sub>2</sub> catalytic species proposed to form under condition **B** is better able to tolerate steric congestion as compared to **ML**<sub>1</sub>.

To further challenge our NT protocol, substrates bearing both benzylic and tertiary alkyl C-H bonds (**26a**–**28a**), as well as those containing competing C-H sites (3° vs. 1° in **29a**, 3° vs. 2° in **30a**, 2° vs. 2° in **31a**, 2° vs. 1° in **32a** and 1° vs. 1° in **33a**), were evaluated. For the purposes of comparison, results are also shown for reported Rh-catalysed NT.<sup>16</sup> Precursors **26a**–**30a** afforded good site-selectivity, although as previously mentioned, it was necessary to employ a second set of reaction conditions (condition **B**, see Section 3.2 in the SI for further details) to achieve good results. The less bulky **ML**<sub>2</sub> that is proposed to form under these conditions appears to better tolerate steric congestion than the complex **ML**<sub>1</sub>. Competing 2° vs. 2° benzylic C-H bonds in **31a** gave no selectivity in **31b**, while a 2° benzylic C-H was heavily favored over the primary C-H bond in **32a**.

As expected, the doubly activated C-H bond in **34a** preferentially delivers **34b**, while blocking this site shifts the product to **35b**, albeit in lower yield. Thiophene derivatives **36a**–**38a** were tolerated, giving modest yields of **36b**–**38b**. Amidation at the  $\alpha$ -oxygenated carbon of tetrahydrofuran derivatives **39a**–**41a** furnished excellent yields of **39b**–**41b**, representing a facile way to





Scheme 2 Scope of benzylic-selective intermolecular Ag-catalysed C–H amidation. <sup>a</sup>Condition A: arene (2 equiv.), Hf<sub>2</sub>NH<sub>2</sub> (0.025 mmol), AgNTf<sub>2</sub> (20 mol%), <sup>t</sup>Bu-tpy (12 mol%), PhIO (3 equiv.), 4 Å MS (25 mg), σ-DCB (0.05 M), 4 h, rt, under air. Yields determined from crude NMR of the reaction mixture using 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> as internal standard. <sup>b</sup>Condition B: arene (5 equiv.), Hf<sub>2</sub>NH<sub>2</sub> (0.025 mmol), AgNTf<sub>2</sub> (10 mol%), <sup>t</sup>Bu-tpy (12 mol%), pentafluoriodosobenzene (PFI<sub>2</sub>O, 2 equiv.), 4 Å MS (25 mg), PhH (0.1 M), 4 h, rt, under air. Yields and selectivity are determined from the crude NMR of the reaction mixture using 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> as internal standard. <sup>c</sup>Rh-catalysed conditions from ref. 16. <sup>d</sup>Aziridination product.

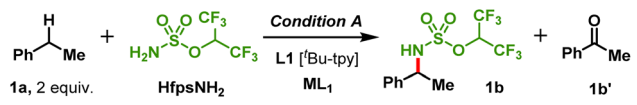
activate this position towards further substitution *via* an oxonium ion.<sup>17</sup>

In addition to benzylic C–H amidation, allylic C–H bonds in **42a–43a** could be functionalised to deliver **42b–43b**, albeit with minor amounts of the aziridination byproduct. The identity of the nitrene precursor was briefly explored, with aliphatic and aromatic side chains on the sulfamate giving the products in

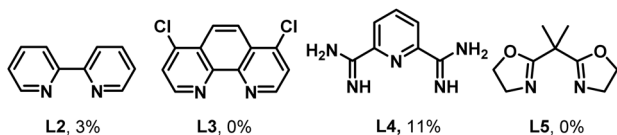
good to excellent yields (**1ba–1bi**). Finally, to demonstrate the potential of this chemistry as a tool for late-stage intermolecular NT in complex molecules, several biorelevant scaffolds including celestolide, fluorene derivatives, methyl *o*-methylpodocarpate and vitamin C were examined (**44a–48a**). The experimental results showed that the trinuclear metal–ligand complex (**ML<sub>1</sub>**) prefers unhindered benzylic C–H bonds, while



Table 1 Selected results from the optimization of inter-molecular Ag-catalysed NT<sup>a,b</sup>



Entry	Change from condition A	1b % yield	1b' % yield
1	None	85	10
2	TFE	45	11
3	AgOTf instead of AgNTf <sub>2</sub>	38	20
4	AgTFA instead of AgNTf <sub>2</sub>	29	3
5	AgNTf <sub>2</sub> (5 mol%)	41	11
6	AgNTf <sub>2</sub> (25 mol%)	76	14
7	3 Å MS	63	4
8	5 Å MS	45	2
9	MeCN	20	5
10	2 h reaction time	29	<1
11	8 h reaction time	60	8
12	No Ag catalyst	0	2
13	No ligand	0	—

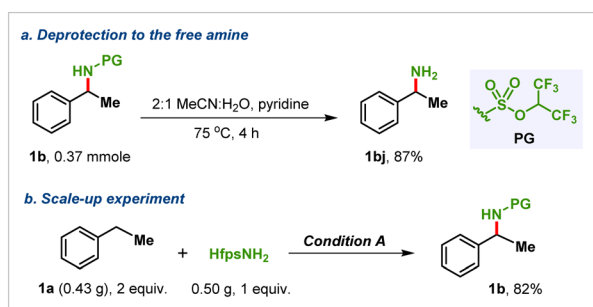


<sup>a</sup> Standard conditions: condition A: arene (2 equiv.), HfpsNH<sub>2</sub> (0.05 mmol), AgNTf<sub>2</sub> (20 mol%), tBu-tpy (12 mol%), PhIO, (3 equiv.), 4 Å molecular sieves (50 mg), σ-DCB (0.05 M), 4 h, rt, under air. <sup>b</sup> Yields determined by crude NMR of the reaction mixture using 1,3,5-(MeO)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> as an internal standard. ML<sub>1</sub> = [Ag<sub>3</sub>(tBu-tpy)<sub>2</sub>(NTf<sub>2</sub>)<sub>3</sub>].

the dinuclear complex ML<sub>2</sub> performs better for NT into more sterically crowded C–H sites (see Section 4.8 in the SI for more details).

The nitrogen protecting group of **1b** was easily removed through a mild hydrolysis to deliver **1bj** (Scheme 3a) in 87% yield. The intermolecular NT chemistry was readily scalable and demonstrated excellent yields using condition A (Scheme 3b and Section 4.2 in the SI).

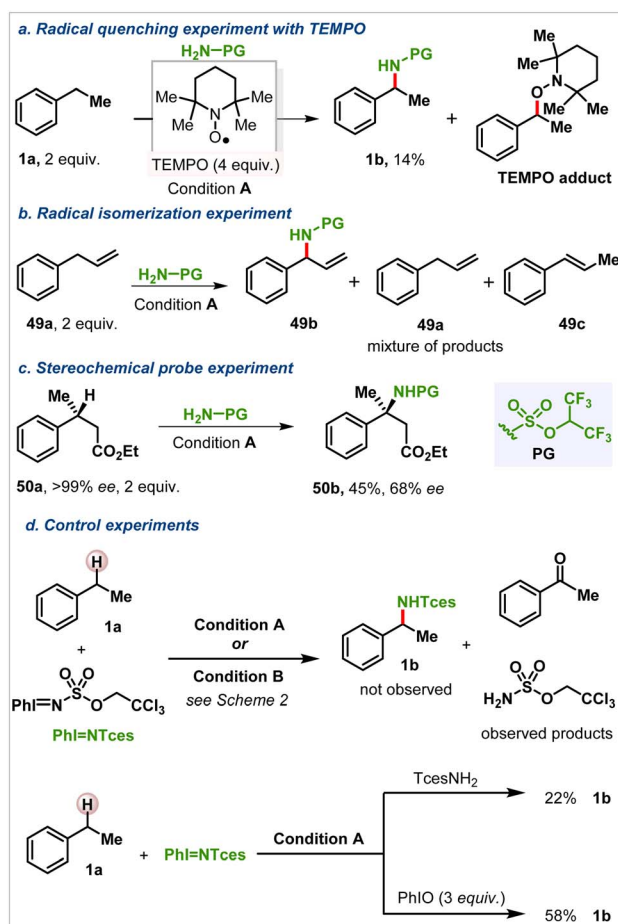
We conducted additional studies to better understand the behavior of this unusual intermolecular Ag-catalysed NT



Scheme 3 Deprotection to the free amine and scale-up of the intermolecular Ag-catalysed NT.

reaction. First, the reaction was performed in the presence of various radical quenchers (Scheme 4a). A TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) adduct was detected in the reaction of **1a** to **1b** (HRMS: *m/z* for [M + H]<sup>+</sup> calc 262.2165; found, 262.1340), formed by the interaction of TEMPO and benzyl radical (Scheme 4a). Coupling this result with the observed isomerization of the double bond of **49a** (Scheme 4b) and a stereochemical probe experiment of **50a** (Scheme 4c) suggested the potential for a relatively long-lived radical species under these reaction conditions.

Interestingly, treatment of **1a** with PhI=NTces (Scheme 4d) did not give the desired **1b**; rather, only a mixture of acetophenone and TcesNH<sub>2</sub> was observed (see Section 4.9 in the SI for further details). We found that the addition of either TcesNH<sub>2</sub> or 3 equiv. PhIO partially restored the desired reactivity; however, efforts to establish a causal relationship between the rates of formation of PhI=NTces and **1b** were unsuccessful due to the heterogeneity of the reaction mixture and our inability to detect an iminoiodinane intermediate by NMR. It is possible that an equilibrium exists between TcesNH<sub>2</sub> and PhI=NTces that heavily favors the former, where excess oxidant helps drive the equilibrium toward the desired reactivity and 'recycle' TcesNH<sub>2</sub>. However, if the reaction proceeds



Scheme 4 Insights into the behavior of benzylic-selective intermolecular Ag-catalysed NT.



through a typical metal-nitrene species derived from an intermediate iminoiodinane, a preformed iminoiodinane should also perform the desired nitrene transfer. These unexpected observations suggest that the reaction mechanism may involve additional processes beyond the simple generation and transfer of an iminoiodinane species, which is the generally accepted mechanistic pathway for these types of nitrene transfer reactions. Further investigation is needed to conclusively establish the mechanism.

## Conclusions

In summary, we have demonstrated a benzylic-selective, non-directed Ag-catalysed intermolecular benzylic amidation of arenes, biaryls, heteroarenes and complex molecules containing these motifs. Three main design principles in this strategy include: (i) targeting the weakest C–H bond *via* a stepwise HAA, (ii) using bulky ligands to favor 2° benzylic sites, and (iii) leveraging the steric differences between di- and trinuclear Ag complexes to further fine-tune the site-selectivity. The method uses inexpensive silver salts, commercially available ligands and proceeds at rt. Ongoing efforts are directed toward exploring the role of non-covalent interactions between the catalyst and substrate, including  $\pi\cdots\pi$  and  $\text{Ag}\cdots\pi$  interactions, that may aid in directing the selectivity of the NT event and stabilize the transition state.<sup>14</sup>

## Author contributions

The manuscript was written by S. P. and J. M. S. All authors have given approval to the final version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

CCDC 2492278 and 2492279 contain the supplementary crystallographic data for this paper.<sup>18a,b</sup>

The data that support the findings in this work are available within the paper and have been included as part of the supporting information (SI). Supplementary information: experimental procedures, full optimization of the methodology, characterization data and spectra for the synthesis of the precursors and products of the silver-catalysed nitrene transfer reactions. Full SC-XRD information is provided for **ML**<sub>1</sub> (CCDC 2492278) and **ML**<sub>2</sub> (CCDC 2492279). Copies of NMR and HPLC spectra are also included. See DOI: <https://doi.org/10.1039/d5sc10184k>.

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## Notes and references

- (a) H. M. L. Davies, J. D. Bois and J.-Q. Yu, *Chem. Soc. Rev.*, 2011, **40**, 1855–1856; (b) J. Yamaguchi, A. D. Yamaguchi and K. Itami, *Angew Chem. Int. Ed. Engl.*, 2012, **51**, 8960–9009; (c) L. Guillemard, N. Kaplaneris, L. Ackermann and M. J. Johansson, *Nat. Rev. Chem.*, 2021, **5**, 522–545.
- (a) S. A. Lawrence, *Amines: synthesis, properties and applications*, Cambridge University Press, New York, NY, 2004; (b) M. B. Smith, *Compendium of organic synthetic methods*, Wiley, New York, NY, 2009, vol. 12; (c) W. S. Emerson, *Organic reactions*, Wiley, New York, NY, 2004; (d) I. Schmeltz and D. Hoffmann, *Chem. Rev.*, 1977, **77**, 295–311.
- (a) F. Khan, M. Dlugosch, X. Liu and M. G. Banwell, *Acc. Chem. Res.*, 2018, **51**, 1784–1795; (b) J.-Q. Chen, J.-H. Li and Z.-B. Dong, *Adv. Synth. Catal.*, 2020, **362**, 3311–3331; (c) P. A. Forero-Cortes and A. M. Haydl, *Org. Process Res. Dev.*, 2019, **23**, 1478–1483; (d) L. Song, L. Cai, L. Gong and E. V. Van der Eycken, *Chem. Soc. Rev.*, 2023, **52**, 2358–2376.
- O. I. Afanasyev, E. Kuchuk, D. L. Usanov and D. Chusov, *Chem. Rev.*, 2019, **119**, 11857–11911.
- (a) J.-H. Xie, S.-F. Zhu and Q.-L. Zhou, *Chem. Rev.*, 2011, **111**, 1713–1760; (b) L. Huang, M. Arndt, K. Gooßen, H. Heydt and L. J. Gooßen, *Chem. Rev.*, 2015, **115**, 2596–2697.
- For selected reviews on transition metal-catalyzed nitrene transfer, see: (a) D. N. Zalatan and J. Du Bois, *Curr. Chem.*, 2009, **292**, 347–378; (b) P. Muller and C. Fruit, *Chem. Rev.*, 2003, **103**, 2905–2920; (c) Z. G. Li and C. He, *Eur. J. Org. Chem.*, 2006, 4313–4322; (d) J. A. Halfen, *Curr. Org. Chem.*, 2005, **9**, 657–669; (e) G. Dequierez, V. Pons and P. Dauban, *Angew. Chem., Int. Ed.*, 2012, **51**, 7384–7395; (f) F. Collet, R. H. Dodd and P. Dauban, *Chem. Commun.*, 2009, **34**, 5061–5074; (g) L. Degennaro, P. Trinchera and R. Luisi, *Chem. Rev.*, 2014, **114**, 7881–7929; (h) M. Ju and J. M. Schomaker, *Nat. Rev. Chem.*, 2021, **5**, 580–594.
- For selected references, see: (a) F. Collet, C. Lescot, C. G. Liang and P. Dauban, *Dalton Trans.*, 2010, **39**, 10401–10413; (b) J. L. Roizen, M. E. Harvey and J. Du Bois, *Acc. Chem. Res.*, 2012, **45**, 911–922; (c) A. Fanourakis, B. D. Williams, K. Paterson and R. J. Phipps, *J. Am. Chem. Soc.*, 2021, **143**, 10070–10076; (d) S.-M. Au, W.-H. Fung, M.-C. Cheng, C.-M. Che and S.-M. Peng, *Chem. Commun.*, 1997, 1655–1656; (e) M. E. Harvey, D. G. Musaev and J. Du Bois, *J. Am. Chem. Soc.*, 2011, **133**, 17207; (f) Y. Nishioka, T. Uchida and T. Katsuki, *Angew. Chem., Int. Ed.*, 2013, **52**, 1739–1742; (g) S. Y. Hong, Y. Park, Y. Hwang, Y. B. Kim, M.-H. Baik and S. Chang, *Science*, 2018, **359**, 1016–1021; (h) D. A. Evans, M. M. Faul and M. T. Bilodeau, *J. Org. Chem.*, 1991, **56**, 6744–6746; (i) F. Dielmann, D. M. Andrada, G. Frenking and G. Bertrand, *J. Am. Chem. Soc.*, 2014, **136**, 3800–3802; (j) S. Kuppaswamy, T. M. Powers,



- B. M. Johnson, M. W. Bezpalko, C. K. Brozek, B. M. Foxman, L. A. Berben and C. M. Thomas, *Inorg. Chem.*, 2013, **52**, 4802–4811; (k) E. R. King, E. T. Hennessy and T. A. Betley, *J. Am. Chem. Soc.*, 2011, **133**, 4917–4923; (l) J. J. Tang, X. Yu, Y. Wang, Y. Yamamoto and M. Bao, *Angew. Chem.*, 2021, **133**, 16562–16571; (m) S. M. Paradine and M. C. White, *J. Am. Chem. Soc.*, 2012, **134**, 2036; (n) W. C. Lee and X. P. Zhang, *Nat. Chem.*, 2023, **15**, 1499–1500; (o) H.-J. Lu, H.-L. Jiang, L. Wojtas and X. P. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 10192–10196; (p) H. J. Lu, V. Subbarayan, J. R. Tao and X. P. Zhang, *Organometallics*, 2010, **29**, 389–393; (q) S. M. Paradine, J. R. Griffin, J. Zhao, A. L. Petronico, S. M. Miller and M. C. White, *Nat. Chem.*, 2015, **7**, 987–994; (r) M. R. Fructos, S. Trofimenko, M. M. Diaz-Requejo and P. J. Perez, *J. Am. Chem. Soc.*, 2006, **128**, 11784; (s) Y. Cui and C. He, *Angew. Chem., Int. Ed.*, 2004, **43**, 4210; (t) J. M. Alderson, J. R. Corbin and J. M. Schomaker, *Acc. Chem. Res.*, 2017, **50**, 2147–2158; (u) W. Liu, I. Choi, E. E. Zerull and J. M. Schomaker, *ACS Catal.*, 2022, **12**, 5527–5539; (v) E. E. Zerull, L. E. Vine and J. M. Schomaker, *Synlett*, 2021, **32**, 30–44.
- 8 For selected references, see: (a) Y. Park, Y. Kim and S. Chang, *Chem. Rev.*, 2017, **117**, 9247–9301; (b) K. W. Fiori and J. Du Bois, *J. Am. Chem. Soc.*, 2007, **129**, 562; (c) B. P. Gomez-Emeterio, J. Urbano, M. M. Diaz-Requejo and P. J. Perez, *Organometallics*, 2008, **27**, 4126–4130; (d) F. Collet, C. Lescot and P. Dauban, *Chem. Soc. Rev.*, 2011, **40**, 1926–1936; (e) T. K. Hyster, C. C. Farwell, A. R. Buller, J. A. McIntosh and F. H. Arnold, *J. Am. Chem. Soc.*, 2014, **136**, 15505–15508; (f) A. Das, S. Gao, S. V. Athavale, E. Alfonzo, Y. Long and F. H. Arnold, *Methods Enzymol.*, 2023, **693**, 1–30; (g) R. M. Ward and J. M. Schomaker, *Handbook of CH-Functionalization (CHF)*, John Wiley & Sons, Chichester, UK, 2022, vol. 13, pp. 1–37.
- 9 (a) A. Nasrallah, V. Boquet, A. Hecker, P. Retailleau, B. Darses and P. Dauban, *Angew. Chem., Int. Ed.*, 2019, **58**, 8192–8196; (b) A. Beltrana, C. Lescot, M. Mar Díaz-Requejo, P. J. Perez and P. Dauban, *Tetrahedron*, 2013, **69**, 4488–4492; (c) N. S. Dolan, R. J. Scamp, T. Yang, J. F. Berry and J. M. Schomaker, *J. Am. Chem. Soc.*, 2016, **138**, 14658–14667; (d) H. Lu, V. Subbarayan, J. Tao and X. P. Zhang, *Organometallics*, 2010, **29**, 389–393; (e) R. T. Gephart and T. H. Warren, *Organometallics*, 2012, **31**, 7728–7752; (f) J. R. Clark, K. Feng, A. Sookezian and M. C. White, *Nat. Chem.*, 2018, **10**, 583–591; (g) C. K. Prier, R. K. Zhang, A. R. Buller, S. B. Chen and F. H. Arnold, *Nat. Chem.*, 2017, **9**, 629–634.
- 10 For selected examples, see: (a) E. Brunard, V. Boquet, E. V. Elslande, T. Saget and P. Dauban, *J. Am. Chem. Soc.*, 2021, **143**, 6407–6412; (b) W. Liu, Z. Ren, A. T. Bosse, K. Liao, E. L. Goldstein, J. Bacsá, D. G. Musaev, B. M. Stoltz and H. M. L. Davies, *J. Am. Chem. Soc.*, 2018, **140**, 12247–12255.
- 11 (a) T. A. Trinh, S. Cherempei, D. S. Rampon and J. M. Schomaker, *Chem. Sci.*, 2025, **16**, 4796–4805; (b) Y. Fu, E. E. Zerull, J. M. Schomaker and P. Liu, *J. Am. Chem. Soc.*, 2022, **144**, 2735–2746.
- 12 (a) M. Huang, T. Yang, J. D. Paretzky, J. F. Berry and J. M. Schomaker, *J. Am. Chem. Soc.*, 2017, **139**, 17376–17386; (b) E. Z. Schroeder, J. H. Kim, Y. Fu, W. Liu, P. Liu and J. M. Schomaker, *Chem. Catal.*, 2025, **5**, 101388.
- 13 (a) J. M. Alderson, A. M. Phelps, R. J. Scamp, N. S. Dolan and J. M. Schomaker, *J. Am. Chem. Soc.*, 2014, **136**(48), 16720–16723; (b) J. W. Rigoli, C. D. Weatherly, J. M. Alderson, B. T. Vo and J. M. Schomaker, *J. Am. Chem. Soc.*, 2013, **135**, 17238–17241.
- 14 For selected references, see: (a) F. Hung-Low, A. Renz and K. K. Klausmeyer, *Polyhedron*, 2009, **28**, 407; (b) F. Hung-Low, A. Renz and K. K. Klausmeyer, *J. Chem. Crystallogr.*, 2011, **41**, 1174; (c) J. Du, T. Hu, S. Zhang, Y. Zeng and X. Bu, *CrystEngComm*, 2008, **10**, 1866; (d) H. Zhang, L. Chen, H. Song and G. Zi, *Inorg. Chim. Acta*, 2011, **366**, 320; (e) K. Xiong, M. Wu, Q. Zhang, W. Wei, M. Yang, F. Jiang and M. Hong, *Chem. Commun.*, 2009, 1840; (f) F. Hung-Low, A. Renz and K. K. Klausmeyer, *J. Chem. Crystallogr.*, 2009, **39**, 438; (g) N. Schultheiss, D. R. Powell and E. Bosch, *Inorg. Chem.*, 2003, **42**, 5304.
- 15 (a) C. Weib, Y. Heb, X. Shia and Z. Song, *Coord. Chem. Rev.*, 2019, **385**, 1–19; (b) R. Abhijnakrishna, K. Magesh, A. Ayushi and S. Velmathi, *Coord. Chem. Rev.*, 2023, **496**, 215380.
- 16 E. N. Bess, R. J. DeLuca, D. J. Tindall, M. S. Oderinde, J. L. Roizen, J. Du Bois and M. S. Sigman, *J. Am. Chem. Soc.*, 2014, **136**, 5783–5789.
- 17 (a) I. Buslov and X. Hu, *Adv. Synth. Catal.*, 2014, **356**, 3325–3330; (b) T. Fuchigami, T. Sato and T. Nonaka, *J. Org. Chem.*, 1986, **51**, 366–369.
- 18 (a) CCDC 2492278: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2pnf2w](https://doi.org/10.5517/ccdc.csd.cc2pnf2w); (b) CCDC 2492279: Experimental Crystal Structure Determination, 2026, DOI: [10.5517/ccdc.csd.cc2pnf3x](https://doi.org/10.5517/ccdc.csd.cc2pnf3x).

