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# Palladium-catalysed *anti*-Markovnikov selective oxidative amination

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**In recent years, the synthesis of amines and other nitrogen-containing motifs has been a major area of research in organic chemistry because they are widely represented in biologically active molecules. Current strategies rely on a multistep approach and require one reactant to be activated prior to the carbon–nitrogen bond formation. This leads to a reaction inefficiency and functional group intolerance. As such, a general approach to the synthesis of nitrogen-containing compounds from readily available and benign starting materials is highly desirable. Here we present a palladium-catalysed oxidative amination reaction in which the addition of the nitrogen occurs at the less-substituted carbon of a double bond, in what is known as *anti*-Markovnikov selectivity. Alkenes are shown to react with imides in the presence of a palladate catalyst to generate the terminal imide through *trans*-aminopalladation. Subsequently, olefin isomerization occurs to afford the thermodynamically favoured products. Both the scope of the transformation and mechanistic investigations are reported.**

Alkene amination reactions, including hydro- and oxidative amination, are atom-economical approaches to the synthesis of ubiquitous C–N bonds[1–7]. Oxidative amination, also known as the aza-Wacker oxidation, differs from hydroamination reactions in that it retains the degree of unsaturation in the product, allowing for further elaboration of this functionality[3–7]. As terminal amines are prevalent in pharmaceuticals, especially distal to polar functionalities[8], the development of an *anti*-Markovnikov-selective aza-Wacker oxidation of unactivated alkenes would represent a significant advance. Such a process would constitute a novel approach to the remote *anti*-Markovnikov amination of organic molecules, and represent a powerful disconnection in organic synthesis. Additionally, when performed aerobically, this transformation would couple two easily accessible starting materials and would generate only an equivalent of $H_2O$ as waste.

The primary challenge in generating the *anti*-Markovnikov product is biasing the aminometallation step to afford the branched [M]–C (where [M] is the metal catalyst) and terminal N–C bonds. Owing to both steric repulsion and the inherent electronic bias of nucleophile addition to alkenes, known as Markovnikov's rule, this selectivity is not generally favoured for an intermolecular aminometallation[6,7]. However, several strategies have been successfully employed to reverse this inherent selectivity. One approach uses activated alkenes that can form $\pi$-benzyl or [M]-enolate intermediates (Fig. 1a)[9–16]. A second approach utilizes an allylic C–H activation followed by nucleophilic attack at the terminal carbon on the resulting π-allyl (Fig. 1b)[17–20]. Alternatively, proximal Lewis basic groups can direct functionalization of the alkene to afford the favoured metallacycle (Fig. 1c)[21–27]. Finally, in stoichiometric investigations, the combination of a palladate complex and sterically hindered amine nucleophiles promoted a *trans*-aminopalladation to functionalize the terminal carbon and produce the *anti*-Markovnikov constitutional isomer (Fig. 1d)[28,29]. However, conditions that afford the *anti*-Markovnikov aza-Wacker product with simple aliphatic alkenes have not been reported in catalytic amination reactions.

We envisioned utilizing a palladate catalyst that could promote a selective *trans*-nucleopalladation by saturating the coordination sites with excess halide, as has been seen in the Wacker oxidation (Fig. 1e)[7,30]. During the *trans*-aminopalladation step, a relatively large nucleophile would be kinetically biased to approach the alkene to form the less hindered C–N bond and would lead to the desired *anti*-Markovnikov product[28,29,31–33]. Although *trans*-aminopalladations with cationic palladium catalysts are known to afford the Markovnikov constitutional isomer[34,35], we hypothesized that the electronic differentiation between the double-bond carbons, which leads to Markovnikov's rule, would be minimized with a less electrophilic anionic palladate catalyst and lead to a more sterically biased transformation[28]. The successful development of an *anti*-Markovnikov selective aminopalladation of simple alkenes would have implications that reach far beyond the aza-Wacker reaction, as aminopalladation is the regioselectivity-determining step in many olefin difunctionalization reactions[34,35]. Thus, the principles we have learned from the studies reported herein could find future applications in other *anti*-Markovnikov aminofunctionalizations of simple alkenes, and thus enable single-step access to a wide class of products[36,37].

## Results and discussion

**Reaction discovery and optimization.** Our initial investigation focused on developing an *anti*-Markovnikov selective oxidative amination of homoallyl benzene (**1a**). As seen in Table 1 and further elaborated in Supplementary Section B, employing known oxidative amination conditions affords the expected Markovnikov isomer exclusively in 88% yield (Table 1, entry 11)[4]. However, in the presence of 10 mol% $Pd(OAc)_2$, the addition of either 40 mol% $Bu_4NCl$ (Table 1, entry 2) or 20 mol% $Bu_4NOAc$ (Table 1, entry 6) reverses the regioselectivity to favour the *anti*-Markovnikov products in 95% (3:1 *anti*-Markovnikov:Markovnikov (a-M:M)) and 59% (1.3:1 a-M:M) total yields, respectively. The *in situ* generation of a palladate complex is supported by the independent synthesis and crystallographic characterization of $[PdCl_4][Bu_4N]_2$ (Supplementary Section I). The significant increase in reactivity of the $Bu_4N^+$ salts relative to $Li^+$ (Table 1, entry 3) or $Cs^+$ (Table 1, entry 4) can be attributed to the increased solubility of the resulting palladate complexes under the reaction conditions. Accordingly, no product was observed when $Na_2PdCl_4$ or $K_2PdCl_4$ was used directly, with or without added acetate sources. Known

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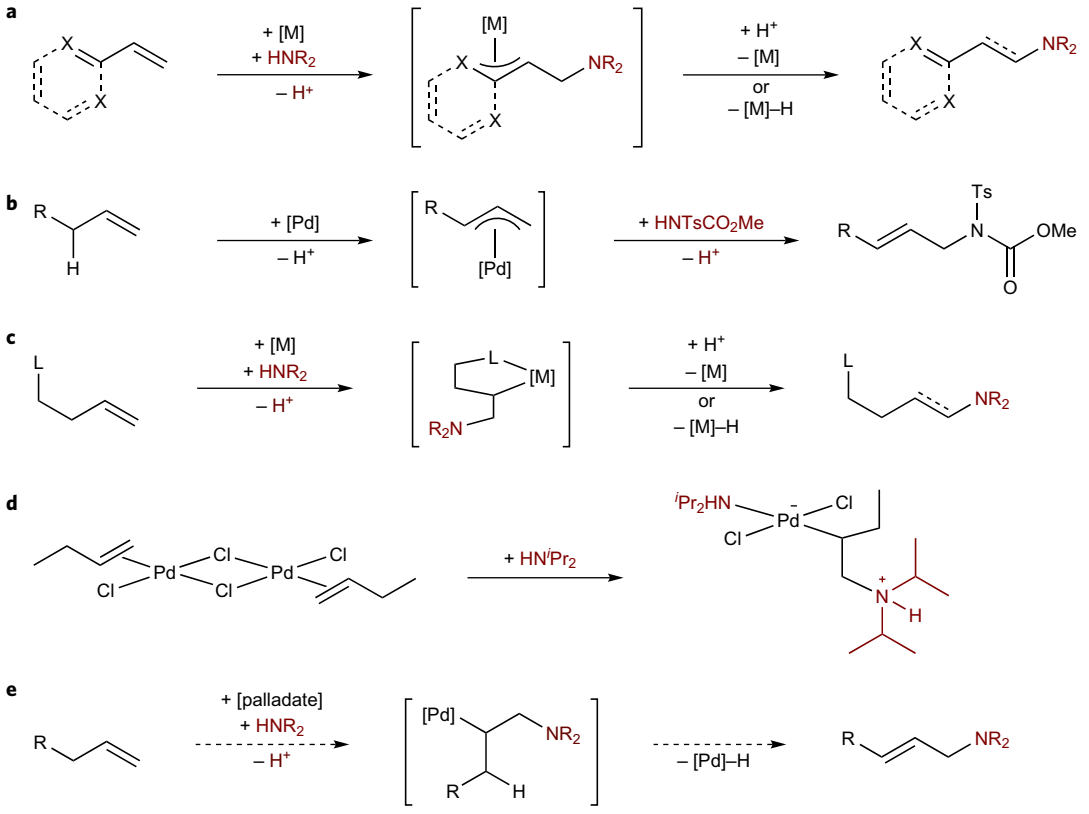



**Figure 1 | Current strategies for the *anti*-Markovnikov oxidative amination of simple alkenes. a**, Use of activated alkenes gives rise to stabilized alkyl–Pd intermediates, which provide a basis for *anti*-Markovnikov selectivity. **b**, Allylic C–H bond activation can afford a $\pi$-allyl intermediate, which can be intercepted by a nucleophile to afford allylic amines. **c**, A tethered directing group can direct functionalization at the terminal position through the formation of a more-stable metallacyclic intermediate. **d**,**e**, Use of a palladate species can kinetically favour *anti*-Markovnikov functionalization of simple aliphatic alkenes, with sterically encumbered nucleophiles in stoichiometric studies (**d**), and catalytically in the present work (**e**). L, nitrogen or oxygen; [M], metal catalyst; R, alkyl chain; Ts, tosyl group ($CH_3C_6H_4SO_2$); X, carbon, nitrogen or oxygen.

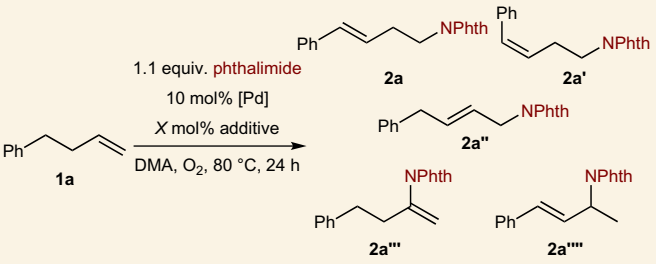
aza-Wacker conditions typically form the enimide, in which the double bond remains unmoved and the nitrogen replaces one of the hydrogen atoms as the exclusive product; however, using the palladate catalyst, mixtures of olefin isomers were observed with the (*E*)-styrenyl isomer (**2a**) as the major product[4,5]. When both additives were present, the regioselectivity improved to afford an 86% combined yield (4:1 a-M:M), with a 62% yield of **2a** (Table 1, entry 8). Further optimization led to the conditions employed in Table 1, entry 9, which afforded **2a** in 60% *in situ* and 57% isolated yield as a single isomer; the combined yield of all the isomers was 75% (8:1 a-M:M) (Table 1, entry 9).

**Reaction generality.** With the optimized conditions identified, we investigated the *anti*-Markovnikov amination of other olefinic substrates. Substitution on the aryl group of homoallylbenzene showed a minimal effect on yield and regioselectivity (**2a**–**2e**). The functionalization of allylbenzene (**1f**) afforded **2f** with a significantly higher selectivity (47:1) and moderate yield (47%). Particularly, electron-poor *p*-$CF_3$-allylbenzene (**1j**) gave **2j** in a much higher selectivity (57:1 a-M:M) than the electron-rich *p*-MeO-allylbenzene (**1g**), which formed **2g** in only a 6:1 a-M:M selectivity. Overall, the selectivity is generally lower for the homologated products (**2a**–**2e**) compared with the allyl benzenes (**2f**–**2j**), with greater quantities of Markovnikov and double-bond isomers observed. Increasingly distal functionality, such as a phenyl ring three methylene units away (**1k**), affords the primary amine derivative **2k** in modest yield and good selectivity (23%, 8:1 a-M:M). However, when substrates lack an inductively withdrawing aryl ring (**1l**), reactivity and regioselectivity are poor.

These studies suggest that proximal electron-withdrawing groups improve the selectivity for the *anti*-Markovnikov isomer. Given this observation, we became interested in investigating homoallylic alcohols as substrates. The alcohol would presumably increase the regioselectivity by acting as an electron-withdrawing group and would, through formation of the ketone, favour a single isomeric product[34,38–42]. Moreover, the reaction would afford the thermodynamic γ-aminoketone product—a common motif and intermediate in biologically active molecules and their synthetic precursors[8]. Excitingly, when homoallylic alcohol **1m** is combined with phthalimide (NPhth) in the presence of 5 mol% $Pd(OAc)_2$ and 20 mol% $Bu_4NCl$, a 77% yield of the γ-aminoketone **2m** is observed. The regioselectivity is also significantly enhanced in favour of the *anti*-Markovnikov product in a 14:1 ratio. This aerobic oxidation reaction can be conducted at ambient pressures, whereas high pressure is a common requirement for other aza-Wacker processes[5]. The reaction is also readily scalable and provides **2m** in 75% yield on a 0.5 mmol scale and 77% yield on a 5.0 mmol scale. Given the presence of the electron-withdrawing oxygen atom, $Bu_4NOAc$ is no longer required to achieve excellent levels of selectivity in most cases. Importantly, the thermodynamically driven isomerization process exclusively generated the ketone product; that is, no enimide or allyl imide products were observed.

Under the modified conditions identified for these alcohol-containing substrates, both electron-withdrawing and -donating groups were tolerated well. It was found that substituting the aryl ring with electron-withdrawing substituents (**1q**–**1u**) generally gave higher yields and regioselectivities of **2q**–**2u** compared with unsubstituted or electron-rich substrates (**2m**–**2p**); for example, **2t**, with a *p*-$CF_3$

**Table 1 | Optimization of oxidative amination reaction on 1a.**




| Entry | Additive (mol%) | Total yield (%)* | Yield 2a (%)* | a-M/M* |
|---|---|---|---|---|
| 1 | None | 20 | <1 | 0.06 |
| 2 | $Bu_4NCl$ (40) | 95 | 68 | 3.0 |
| 3 | LiCl (40) | 32 | 18 | 1.4 |
| 4 | CsCl (40) | 13 | 2 | 0.2 |
| 5 | $Bu_4NI$ (40) | 80 | 24 | 2.3 |
| 6 | $Bu_4NOAc$ (20) | 59 | 26 | 1.3 |
| 7 | NaOAc (20) | 15 | 0 | <0.01 |
| 8† | $Bu_4NCl$ (20), $Bu_4NOAc$ (10) | 86 | 62 | 4.0 |
| 9† | $Bu_4NCl$ (25), $Bu_4NOAc$ (15) | 75 | 60 | 8.0 |
| 10† | $Bu_4NCl$ (30), $Bu_4NOAc$ (20) | 24 | 21 | 130 |
| 11‡ | None | 88 | 0 | NA |

*In situ* yield determined by gas chromatographic analysis and comparison with an internal standard. †5 mol% $Pd(OAc)_2$. ‡Literature conditions for oxidative amination used: $Pd(OAc)_2$ (5 mol%), PhCN (1 M), **1a** (6 equiv.), 60 °C, 1 atm $O_2$. NPhth, phthalimide.

substituent, was formed in 72% yield and 19:1 a-M:M selectivity, whereas **2n**, with a *p*-MeO substituent, was afforded in 56% yield and 14:1 a-M:M selectivity. Steric hindrance on the aryl ring has a deleterious effect on the yield, but results in an increase in the regioselectivity of the reaction. For example, the *o*-tolyl (**2o**) and mesityl (**2p**) products were obtained with improved selectivities (20:1 and 18:1 a-M:M, respectively) as compared with **2m** (14:1 a-M:M), in albeit lower isolated yields (64% for **2o** and 31% for **2p**). Overall, the reaction offers very good functional group tolerance. For example, ethers (**2b**, **2g** and **2n**), chlorides (**2d**, **2i** and **2s**), trifluoromethyl groups (**2e**, **2t** and **2u**) and heterocycles (**2v** and **2w**) were all tolerated well. Additionally, a triflate (**2r**), an α,β-unsaturated ketone (**2x**) and a silyl ether (**2ab**) were unaffected under the reaction conditions. Substrates with free primary alcohols did not afford any of the desired products, as the primary alcohol oxidizes under the reaction conditions.

In the case of alkyl substitution α to the alcohol, we observed a high yield, but significantly diminished *anti*-Markovnikov selectivity under the conditions optimized for the α-aryl alcohols. This is probably because of the diminished inductive effect of alkyl substituents relative to aryl groups. As with the simple alkenes, the addition of $Bu_4NOAc$ (5 mol%) restored the regioselectivity. It was observed that the size of the aliphatic group had an impact on regioselectivity—larger substituents afforded a more-selective transformation (**2y**–**2ab**).

The increase in regioselectivity observed with substrates bearing a homoallylic alcohol suggest that it may be acting as a directing group during the aminopalladation step[21–27]. Although this was not observed in related reactions, it has been proposed in the Wacker oxidation of β-substituted homoallylic alcohols[43], but not unsubstituted homoallylic alcohols or ethers[44]. When **1ac** was subjected to the optimized reaction conditions, **2ac** was afforded in 58% yield as a 3.6:1 mixture of *Z*/*E* isomers and 9:1 mixture of **2ac** to all other constitutional and stereoisomers. These experiments indicate that the coordination of the alcohol to the catalyst is not necessary for an *anti*-Markovnikov selective transformation, although we cannot eliminate the possibility that it is participating in the reaction for these substrates. Similarly, inductively withdrawing imides and amides at the allylic or homoallylic position promoted the *anti*-Markovnikov selective oxidative amination. These substrates, which lack the thermodynamic sink of a styrene or carbonyl, afford the enimide **2ad** and enamide **2ae** with the allylic substrate and the allyl imide **2af** with the homoallylic substrate. Importantly, the resulting terminal phthalimides are easily deprotected. **2a** has been shown to react with $NH_2NH_2$ to afford **2a′** in 85% yield (Table 2)[45]. Additionally, under similar conditions we were able to remove the phthalimide from **2s** to afford cyclic imine **6s** in 78% yield (Table 2).

Next, we sought to explore the scope of the reaction. Other cyclic acidic amine nucleophiles, including succinimide, saccharine and 4-nitrophthalimide were all effective under the reaction conditions, affording **3m**–**5m** in good to very good yields.

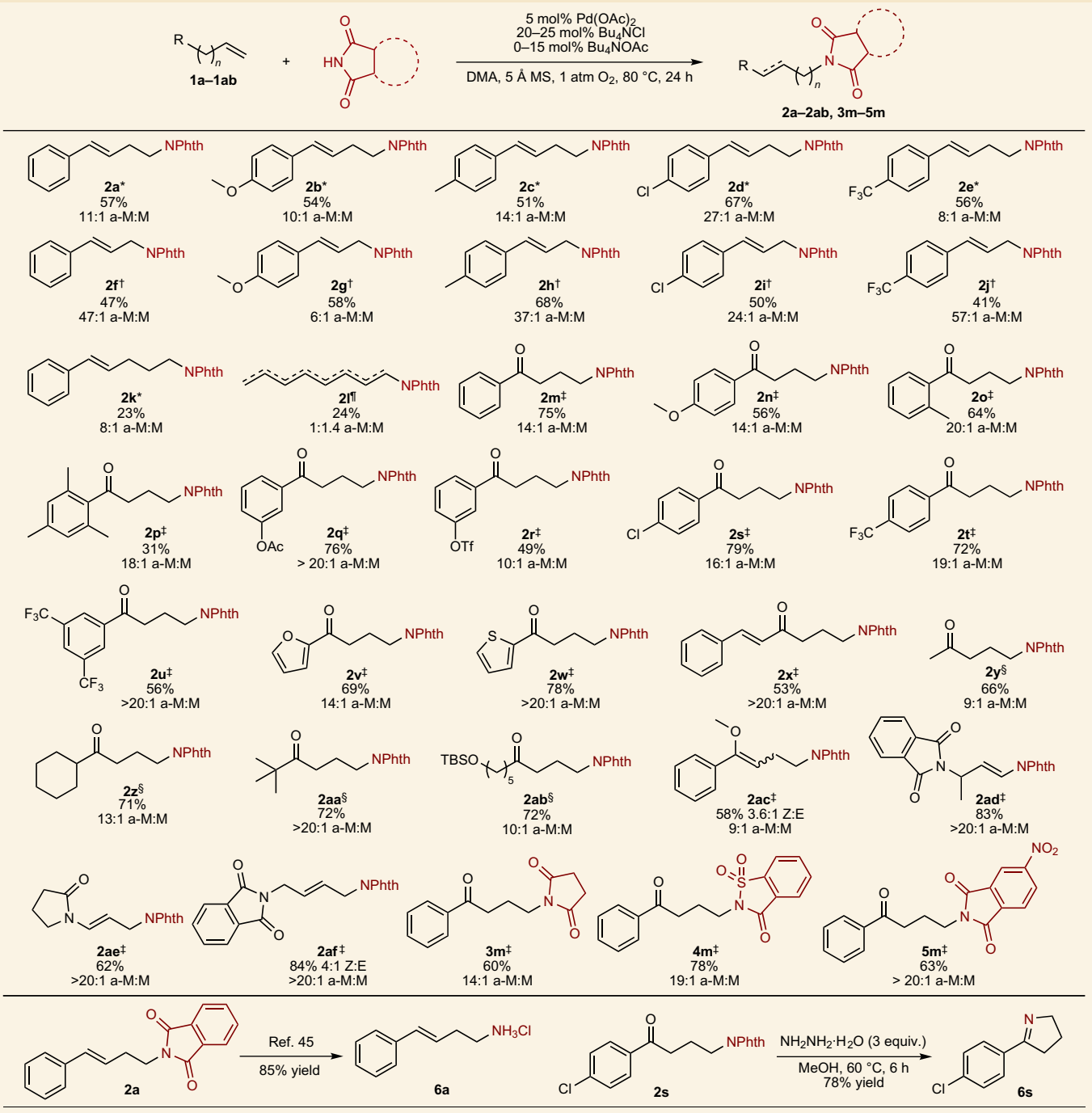
**Mechanistic investigations.** The significant selectivity difference between this transformation and that of other oxidative amination reactions[4,5] led us to probe whether this reaction goes through an aminopalladation mechanism or if it goes through π-allyl Pd intermediates formed via an allylic C–H activation event, as has been demonstrated in related reactions.

To gain mechanistic insight into the nature of the catalytic cycle, we performed kinetic analyses on the optimized reaction conditions for homoallyl benzene. The concentrations of additives were kept constant relative to the palladium(II) acetate for all the investigations, as certain concentrations are required to form the active catalyst (Fig. 2a). Additional $Bu_4NOAc$ was found to have an inhibitory effect on the rate. Interestingly, the results indicate that the reaction is zero order in nucleophile, first order in olefin and 1.4 order in [Pd]. The non-integer order in [Pd] is probably because of an equilibrium between monomeric and dimeric palladate complexes, as both are competent catalysts for the reaction at low concentrations and generate less-active complexes at high concentrations. A similar effect was reported previously by Henry and co-workers[46]. The addition of $Bu_4NOAc$ first shifts the equilibrium towards the dimeric species and thus reduces the concentration of active [Pd] catalysts[47]. To support this conclusion, we determined the order in catalyst in the absence of additional $Bu_4NOAc$ and found an order of 1.1 (Fig. 2b). The oxidative aminations of homoallylic alcohols have similar orders in reagents (Supplementary Section C): zero order in phthalimide, first order in homoallyl alcohol and first order in [Pd]. The order in [Pd] suggests that a monomeric palladate complex is the active catalysts for the homoallylic alcohol system in which $Bu_4NOAc$ is not added to the reaction. These order experiments are consistent with either coordination of the olefin or allylic C–H activation as the turnover-limiting step.

As the optimized conditions are related to Jeffery's conditions for the Heck reaction, which under similar conditions are thought to involve Pd nanoparticles, we sought to determine if the catalyst was homogeneous or heterogeneous[48]. When the reaction is run in the presence of Hg(0), the product is still generated, albeit in lower yield (12–14%). However, an induction period is observed for the Heck reaction, and no induction period was observed in our oxidative amination reaction[48,49]. These studies suggest that the Pd(II) catalytic intermediate is homogeneous, although Pd(0) species may be stabilized as transient nanoparticles prior to oxidation by $O_2$.

The requirement for the olefin to bear an electron-withdrawing group was investigated by performing a Hammett study. A $\rho$ value of 0.878 was observed for a series of homoallylbenzene derivatives, which indicates that electron-withdrawing groups increase the rate of the oxidative amination reaction. This is consistent with either the aminopalladation or C–H activation mechanism. In the first, reducing the electrostatic repulsion between the olefin and electron-rich anionic palladate complex would accelerate the rate of the ligand exchange. A similar effect was reported by Hanley

**Table 2 | *Anti*-Markovnikov oxidative amination of simple alkenes and homoallylic alcohols.**




Bottom line: removal of the terminal phthalimide, in this work affording the cyclic imine (right). *$Bu_4NOAc$ (15 mol%), $Bu_4NCl$ (25 mol%). †$Pd(OAc)_2$ (10 mol%), $Bu_4NOAc$ (10 mol%), $Bu_4NCl$ (40 mol%). ‡$Bu_4NCl$ (20 mol%). §$Bu_4NOAc$ (5 mol%), $Bu_4NCl$ (20 mol%). ||$Bu_4NCl$ (15 mol%). ¶$Bu_4NCl$ (25 mol%).

and Hartwig in computationally comparing the $\Delta\Delta G^{\neq}$ for styrene derivatives that undergo ligand exchange with a neutral Pd(II) complex, for which *m*-MeO-styrene was predicted to have a lower barrier than *p*-Me-styrene[50]. Alternatively, electron-withdrawing groups would stabilize the anionic charge build-up and therefore accelerate the rate of C–H allylic activation through deprotonation.

The order in reagents and Hammett investigations demonstrate that the alkene and the catalyst are both involved during the rate-determining step, but do not allow us to distinguish between aminopalladation or C–H activation, as this would be consistent with the turnover-limiting step being either olefin coordination for the aminopalladation mechanism[6,7] or allylic C–H activation[17–19] in which C–N bond formation occurs after the rate-determining step (Fig. 3a). To eliminate one of the two possible mechanisms, we isotopically labelled the substrate at the allylic position. Substrate **1a-*d*$_2$** subjected to the reaction conditions allowed us to distinguish between the two mechanistic pathways. If the reaction proceeded through the aminopalladation pathway, it is expected that **2a-*d*$_2$** would be the primary product of the reaction, in which one of the deuterium atoms migrates to C3. Additionally, as no C–H bond cleavage would occur until after the turnover-limiting step, no kinetic isotope effect is expected. Alternatively, if the reaction proceeded through an allylic C–H activation pathway, **2a-*d*$_1$** would be formed, with only a single deuterium atom in the product, as the second would have been deprotonated during the C–H activation

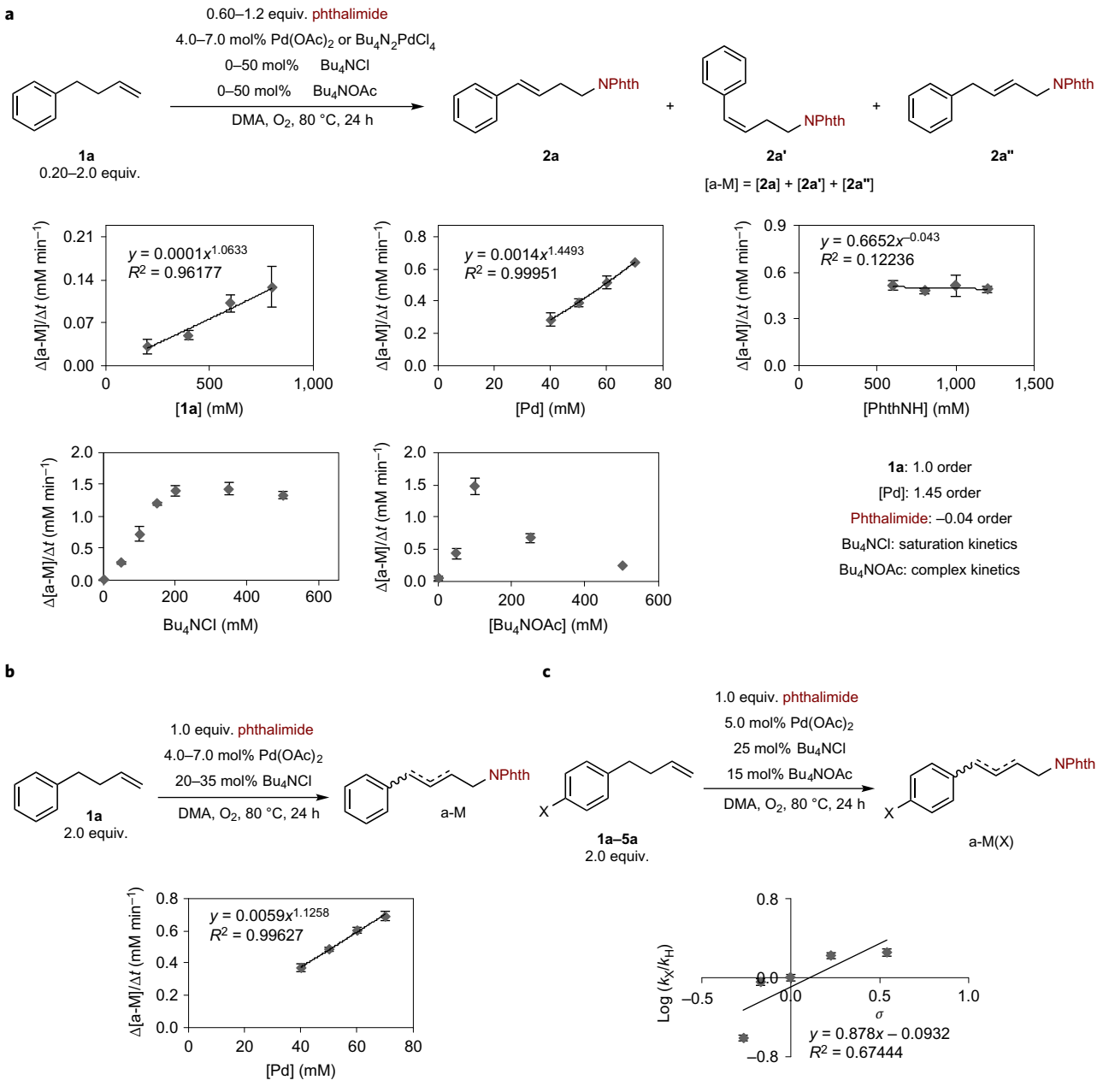



**Figure 2 | Mechanistic investigation of the *anti*-Markovnikov oxidative amination through reagent order determination and Hammett plot analysis.** **a**, Determination of the order in all reagents for the *anti*-Markovnikov selective oxidative amination of **1a** shows first-order kinetics for the alkene, non-integer 1.4 order for the catalyst and zero order for the nucleophile. **b**, Determination in the order of [Pd] when no $Bu_4NOAc$ is added, which indicates first order in the catalyst with a lower acetate equivalence and implicates palladium oligomerization. **c**, A Hammett investigation for the effect of electronics on the aryl ring on the rate of the oxidative amination reaction demonstrates the rate enhancement of electron-withdrawing groups, even several bonds removed from the reactive alkene. Error bars represent the standard deviation of the measured values across three independent runs. DMA, *N*,*N*-dimethyl acetamide.

step. Further, if allylic C–H activation is the turnover-limiting step, a primary kinetic isotope effect would be observed. **1a-$d_2$** subjected to the reaction conditions afforded **2a-$d_2$** selectively and a $k_H/k_D$ of 1.0 was observed, consistent with a reaction that occurs through aminopalladation and not C–H activation (Fig. 3b).

Next, we sought to distinguish between the *cis*- and *trans*-aminopalladation pathways. As the stereochemical outcome of this transformation cannot be determined by examining the stereochemistry of the products after the olefin isomerization has occurred, we chose to investigate styrene as a substrate because it cannot undergo an olefin isomerization and can only afford the enimide product (Fig. 3c). (*Z*)-β-deuterostyrene (**1ag-$d_1$**) subjected to the standard reaction conditions afforded **2ag-$d_1$**, with 79% deuterium α to the phthalimide and 13% α to the phenyl ring (Supplementary Section E). As shown in Fig. 3d, the major isomer is, indeed, consistent with a reaction that occurs through *trans*-aminopalladation followed by β-hydride elimination. The minor isomer, in which the deuterium has migrated, may be the result of an initial *trans*-aminopalladation/β-deuteride elimination to afford the *cis*-diastereomer and subsequent isomerization to the *trans*-product by Pd–D insertion, β-H elimination. A kinetic isotope effect could also account for some of the preference toward hydride elimination if a *cis*-aminopalladation occurred; however, if this was the case, the *cis*-diastereomer (*Z*-**2ag-$d_1$**) would be the expected product.

Combining the mechanistic information garnered from the kinetic data and the isotope labelling studies, the catalytic cycle

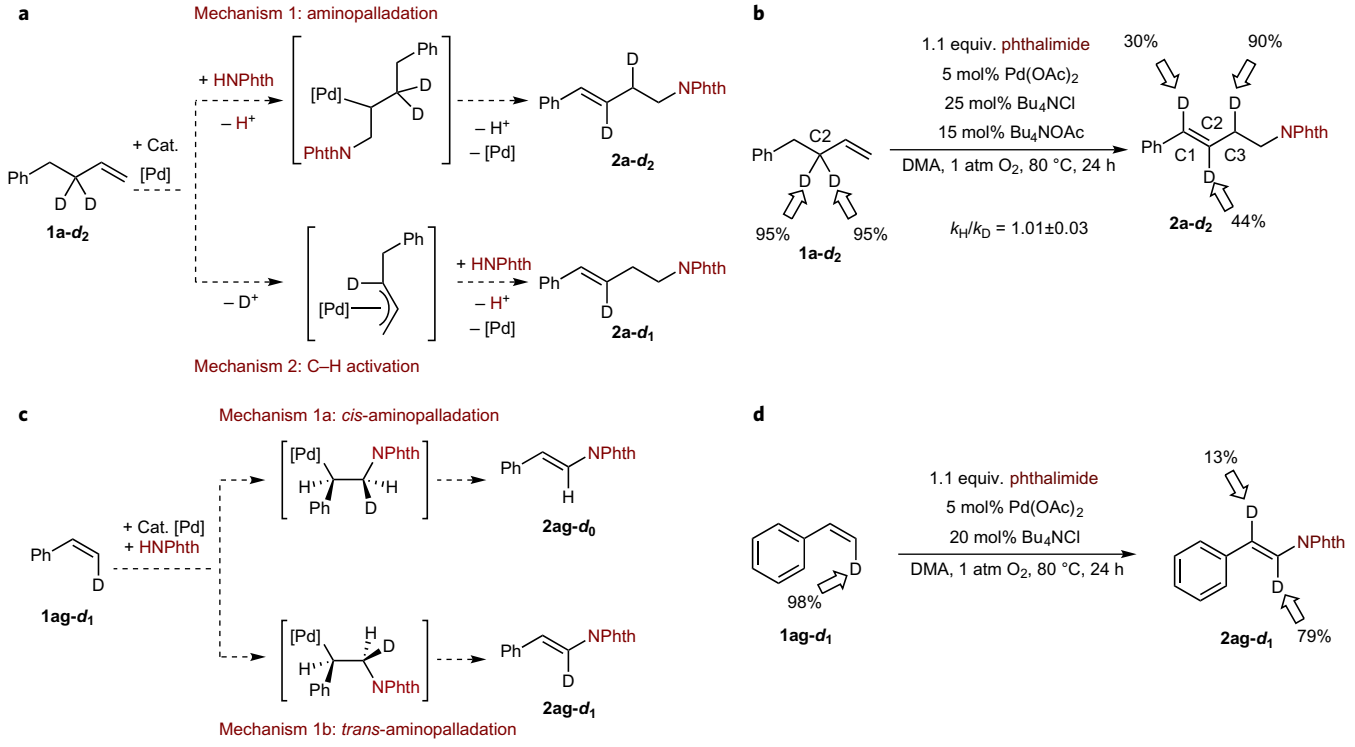



**Figure 3 | Deuterium labelling studies as probes to distinguish between multiple mechanistic pathways. a**, Potential C–H activation and aminopalladation mechanisms. **b**, Isotopic labelling experiments to test the two possible mechanisms show full deuterium retention and no kinetic isotope effect as evidence for aminopalladation and against C–H activation. **c**, Possible outcomes for *cis*- and *trans*-aminopalladation pathways. **d**, Isotopic labelling study to probe the mechanism of aminopalladation shows a predominately deuterium retention at the terminal carbon and thereby indicates an *anti*-aminopalladation pathway (Supplementary Fig. 32). Cat., catalyst.

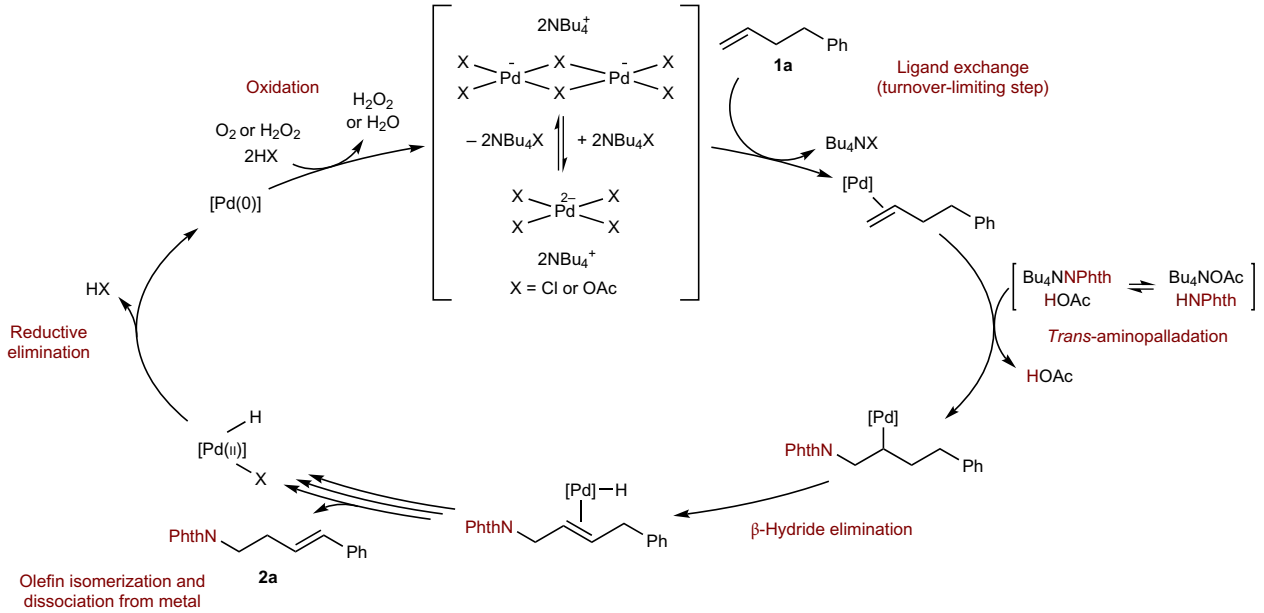



**Figure 4 | A catalytic cycle proposal based on the mechanistic studies undertaken.** The order in reagents implicates the involvement of the alkene and catalyst at or before the rate-determining step and excludes the involvement of the phthalimide. This suggests that alkene binding through associative ligand dissociation is the rate-determining step, and that nucleophilic attack on the bound olefin is fast relative to this. The requirement of some catalytic quantity of acetate suggests its involvement in this process, and its function as a catalytic base is proposed, to generate a nucleophilic anionic phthalimide. Subsequent β-hydride elimination and olefin isomerization generates the most stable olefin isomer, and the resultant Pd–H is then oxidized aerobically to regenerate the palladate.

shown in Figure 4 is proposed. Either the Pd(0) or the Pd(II) palladate complex is the catalyst resting state, with the loss of an anionic ligand required either during or prior to the turnover-limiting olefin coordination. Outer-sphere nucleophilic attack by the phthalimide and olefin isomerization of the Pd(0) all occur between the turnover-limiting step and the catalyst resting state, as supported by

the absence of a kinetic isotope effect. As the reaction does not work in the absence of $Bu_4NOAc$, we propose that it is required to act as a catalytic base under the reaction conditions, and both serves to deprotonate the phthalimide and to undergo reductive elimination from Pd(H)OAc to generate AcOH and Pd(0). The two equivalents of $H^+$ are eventually used in the aerobic oxidation of Pd(0) to Pd(II) to generate $H_2O_2$ or $H_2O$ and regenerate the $AcO^-$.

## Conclusion

In conclusion, we have demonstrated a palladate catalyst that promotes an *anti*-Markovnikov selective aza-Wacker oxidation. Additionally, under the reaction conditions, olefin isomerization occurs to translocate the unit of unsaturation to the most thermodynamically favoured position in the molecule. Further, we have demonstrated that this reaction occurs through a *trans*-aminopalladation mechanism with rate-determining olefin coordination. This report represents a major advance in oxidative amination technology, and constitutes a unique approach to conceptualize the remote amination disconnections in organic synthesis. Our current efforts seek to develop an in-depth mechanistic understanding of the regioselectivity-determining step, as well as to explore the intermediacy and capture of alkylpalladium species for the development of alkene difunctionalization reactions.

**Data availability.** Synthetic procedures, NMR spectra and characterization for all the new compounds, kinetic plots, deuterium labelling data and X-ray diffraction data are available within this article and its Supplementary Information. X-ray structural data for the bis(tetrabutylammonium) tetrachloropalladate [Pd] have also been deposited with the Cambridge Crystallographic Data Centre under CCDC no. 1548343 and are available from CCDC in cif format. Data are also available from the corresponding author on request.

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## Author contributions

D.G.K. and K.L.H. conceived and designed the experiments and wrote the manuscript. D.G.K. and P.J.W. discovered the reaction. D.G.K., J.L.K. and S.N.G. performed the experiments.

## Additional information

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## Competing financial interests

The authors declare no competing financial interests.