## REPORT

#### **ORGANIC CHEMISTRY**

# Metal-catalyzed electrochemical diazidation of alkenes

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Vicinal diamines are a common structural motif in bioactive natural products, therapeutic agents, and molecular catalysts, motivating the continuing development of efficient, selective, and sustainable technologies for their preparation. We report an operationally simple and environmentally friendly protocol that converts alkenes and sodium azide— both readily available feedstocks—to 1,2-diazides. Powered by electricity and catalyzed by Earth-abundant manganese, this transformation proceeds under mild conditions and exhibits exceptional substrate generality and functional group compatibility. Using standard protocols, the resultant 1,2-diazides can be smoothly reduced to vicinal diamines in a single step, with high chemoselectivity. Mechanistic studies are consistent with metal-mediated azidyl radical transfer as the predominant pathway, enabling dual carbon-nitrogen bond formation.

icinal diamines are frequently found in pharmaceuticals and medicinally relevant natural products, as well as in privileged molecular catalysts for stereoselective synthesis (1). Despite substantial advances, a broadly applicable methodological approach to their synthesis remains elusive (2). The direct addition of two nitrogen-based functional groups to alkenes-a family of abundant, readily accessible, and structurally diverse feedstocks-is a particularly powerful approach to 1,2-diamine synthesis. Although several methods are available for the oxidative transformation of alkenes into 1,2-diols (3), the analogous extension of this synthetic logic to vicinal diamines remains underdeveloped. Existing methods frequently require stoichiometric heavy metals (e.g., osmium or palladium) or esoteric nitrogenous reagents (e.g., nitrogen oxides, diaziridinones, or N-activated sulfamides) and generally exhibit limited substrate scope (Fig. 1A) (4-10).

In this context, alkene diazidation is an attractive alternative route to vicinal diamine synthesis (11-13), because the resulting 1,2-diazides can readily be reduced to the corresponding diamines (Fig. 1B). Furthermore, organic azides can participate in 1,3dipolar cycloaddition (14), the aza-Wittig reaction (15), Staudinger ligation (16), and C-H bond amination (17), making them highly versatile intermediates for synthetic, materials, and biological applications (18). However, existing protocols uniformly require stoichiometric quantities of reagents including peroxydisulfates (11), highvalent metal salts (11, 12), or hypervalent iodines (13). The use of strong and indiscriminate oxidizing agents precludes the use of substrates with oxidatively labile functionalities, such as alcohol, aldehyde, sulfide, and amine groups. In addition,

Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA. \*Corresponding author. Email: songlin@cornell.edu these oxidants produce environmentally deleterious by-products and present an explosion hazard when used alongside an azide source. An elegant catalytic protocol was recently developed to address these conventional issues with reaction selectivity and substrate generality (*I3*). Nonetheless, both azidotrimethylsilane (TMSN<sub>3</sub>, a toxic and volatile reagent) and hypervalent iodine derivatives compounds that are difficult to handle on a practical scale—remain necessary to drive the diazidation reactivity.

Electrochemistry offers a mild and efficient alternative to conventional chemical approaches for redox transformations (19-21). With sufficient potential bias, common organic starting materials can lose or gain electrons at the electrode surface, readily producing highly reactive intermediates. Electrochemistry allows for precise, external control of chemoselectivity and the flux of reactive intermediates by regulating the applied potential. Such control also maximizes energy efficiency, making electrosynthesis one of the most sustainable approaches for the preparation of complex organic molecules (21). Moreover, because the driving force derives solely from electricity, electrosynthesis can be easily coupled with renewable energy sources such as solar light (22, 23). Recent studies have demonstrated electrochemistry's distinctive capability to engender bond-forming reactions that challenge orthodox methods (24-36). Here we present an electrochemical protocol for the diazidation of alkenes as a general, efficient, and atom-economical approach to vicinal diamine synthesis (Fig. 1C). Anodic generation of azidyl radical  $(N_3)$  from sodium azide (NaN<sub>3</sub>), followed by successive additions of N<sub>3</sub>· to the alkene C=C bond and the incipient carbon radical adduct (I), forms two new C-N bonds, furnishing a vicinal diazide. Hydrogen gas (H<sub>2</sub>) generated from cathodic proton reduction-as evidenced by gas chromatography analysis of the reaction headspace and sodium acetate are the only by-products. Our catalytic system shows an unusual combination of high reactivity and excellent chemoselectivity. As such, it is applicable to the diazidation of a substantially greater variety of alkenes than existing methods, specifically with respect to substitution pattern and functional group compatibility.

Our early efforts demonstrated that electrochemically generated azidyl radical could induce the homolysis of C=C  $\pi$ -bonds. To establish proof of concept, we carried out electrolysis experiments using 4-(tert-butyl)styrene (1a) as the archetypal substrate, oxidatively robust graphite as the anode (working electrode), and platinum (Pt), with its low overpotential for proton reduction, as the cathode (counter electrode). We chose NaN<sub>3</sub> as the azide source, because it is readily available and exhibits markedly lower toxicity and volatility compared with other azide derivatives. With (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical scavenger to trap carbon radical intermediate I, azidooxygenated product 1c formed in high yield and with complete regioselectivity (Fig. 2). However, efforts to trigger diazidation by directly trapping **I** with another equivalent of azidyl radical proved unsuccessful; only traces of 1,2-diazide 1b were detected, despite full consumption of 1a. Owing to their high reactivity, radicals can undergo a variety of transformations, including dimerization, polymerization, oxidation or reduction to ionic species, and reaction with the electrode surface, many of which remain diffusion-controlled and virtually barrierless. Direct sequestration of I by azidyl radical proved too sluggish to outpace competing side reactions, and the majority of the mass balance came from an array of by-products resulting from radical homocoupling (1d) (37) and overoxidation followed by water addition (1e).

To overcome this challenge and accelerate formation of the elusive second C-N bond, we sought to introduce a redox-active catalyst to impart selectivity through kinetic control (38). Such a catalyst could complex with N3- and undergo anodic oxidation to form active metal azidyl (M-N<sub>3</sub>) adducts, which could subsequently react with the in situgenerated carbon radical I via either direct group transfer or oxidative addition followed by reductive elimination to complete diazidation. As such, we envisioned that electrochemistry and redoxactive metal catalysis could act in synergy to harness radical-mediated reactivities. Drawing inspiration from recent work on C-H and alkene azido-functionalization methods catalyzed by transition metals such as copper complexes (8, 39, 40), iron-bisoxazoline (13, 41, 42), manganeseporphyrin (43), and cobalt-Schiff base (44), we surveyed a series of redox-active metal catalysts and ultimately discovered that a catalytic amount of Mn<sup>II</sup> greatly enhanced the propensity of our system to diazidate. After multiple iterations of optimization, we developed a highly efficient diazidation protocol using manganese(II) bromide (MnBr<sub>2</sub>) as the catalyst, acetic acid (HOAc) as the proton source, and reticulated vitreous A Previous work: examples of alkene diamination and diamidation (refs. 4, 6, 9)



B Previous work: examples of alkene diazidation (refs. 11, 13)



C This work: metal-catalyzed electrochemical alkene diazidation



**Fig. 1. Pathways to 1,2-diamine synthesis.** (**A** and **B**) Representative examples of existing 1,2-diamine syntheses compared with (**C**) the proposed electrocatalytic approach. R represents an alkyl, aryl, or similar substituent; Ar, aryl; <sup>t</sup>Bu, *tert*-butyl; Boc, *tert*-butyloxycarbonyl; Ph, phenyl; equiv, equivalent; cat., catalyst; conc., concentrated; e<sup>-</sup>, electron.



Fig. 2. Proof-of-concept experiments. Generation and sequestration of the carbon radical intermediate en route to alkene diazidation are illustrated. h, hour; conv., conversion.

carbon (RVC) as the anode, all in 0.10 M lithium perchlorate (LiClO<sub>4</sub>)/acetonitrile (MeCN; Me, methyl) solution under a nitrogen (N<sub>2</sub>) atmosphere with an applied cell potential ( $E_{\rm cell}$ ) of 2.3 V (corresponding to an initial anodic potential,  $E_{\rm anode}$ , of ~0.62 V versus the ferrocenium ion/ferrocene redox couple). 1,2-Diazide **1b** was isolated in 92% yield in 2.5 hours with an initial current of 10 to 12 mA (33 to 40 mA per cubic centimeter of RVC). Simply passing the reaction mixture through a short silica plug removed polar impurities and furnished spectroscopically pure product.

We also tested the diazidation protocol under conditions of constant current or constant electrode potential. At a controlled current of 8 mA, we observed 90% yield of 1b within 1.5 hours, with  $E_{\text{cell}}$  increasing from 2.1 to 2.4 V. At a controlled  $E_{\text{anode}}$  of 0.72 V, the reaction reached completion within 1.2 hours with an initial current of ~18 mA, furnishing 1b in 86% yield. Thus, Mncatalyzed diazidation proceeded readily at a voltage close to the oxidation potential of azide  $[E(N_3, N_3)] = 0.71 \text{ V}$  and well below the oxidation potential of styrene [E(styrene radical cation/styrene) = 1.55 V]. The Faradaic efficiencies of reaction for these two operations were 87 and 66%, respectively. This finding indicates that most of the electricity passing through the cell was consumed productively, with the remainder likely engaged in nitrogen evolution via azidyl dimerization (45). These key results demonstrate that addition of the Mn catalyst played a pivotal role in inhibiting competing side reactions, thus enhancing chemoselectivity and energy efficiency. As expected, no reaction occurred in the absence of externally applied potential. The reaction system could be further streamlined by replacement of the Pt cathode and DC power supply with graphite and AA batteries, respectively (table S1). Tetraphenylporphinatomanganate(III) chloride also catalyzed alkene diazidation, albeit in lower yield (64%). A number of other transition metal catalysts were surveyed, but none performed as efficiently as Mn (table S1). The identity of the electrolyte did not appreciably affect the diazidation reactivity; using tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in lieu of LiClO<sub>4</sub> resulted in nearly quantitative yield (97%). Our attempts to minimize NaN<sub>3</sub> loading initially proved unsuccessful, primarily as a result of the low solubility and sluggish dissolution of N3<sup>-</sup> in the reaction medium with an excess of alkali metal ions (Na<sup>+</sup> and  $Li^+$ ). Changing the electrolyte to TBAPF<sub>6</sub>, however, allowed the diazidation to proceed efficiently with as few as 3 equivalents of NaN3 (1.5 equivalents per C-N bond). No diazide 1b was produced when RVC recovered from a previous experiment was used as the anode without catalyst addition, suggesting that the diazidation reactivity originated from the dissolved Mn rather than any nanostructured metal oxide deposited on the anode during electrolysis (table S1). In the absence of any catalyst, <10% 1b was observed on full conversion of the styrene. This result again highlights the critical role of the catalyst in modulating radical reactivity.



**Fig. 3. Substrate scope for the electrocatalytic alkene diazidation.** All yields are of isolated products. (**A**) Alkene substitution patterns and electronic properties. (**B**) Functional group compatibility. (**C**) Reduction of diazide to diamine. \*Unless otherwise noted, reaction conditions were as follows: 0.2 mmol alkene, 0.01 mmol MnBr<sub>2</sub>·4H<sub>2</sub>O, 1.0 mmol NaN<sub>3</sub>, 400  $\mu$ l of HOAc, 3.5 ml of LiClO<sub>4</sub> solution in MeCN (0.1 M, 1.75 equiv LiClO<sub>4</sub>), RVC as the anode, Pt as the cathode, under N<sub>2</sub>, at 22 ± 1°C, in a one-compartment cell, at 2.3 V cell potential, for 2 to 6 hours. †Yield of reaction is reported on a 3-mmol scale. ‡With 0.6 mmol NaN<sub>3</sub>. §With TBAPF<sub>6</sub> instead of LiClO<sub>4</sub>. ||With 10 mol% MnBr<sub>2</sub>·4H<sub>2</sub>O. ¶With 300 µl of HOAc. #Reaction at 40°C. \*\*See the supplementary materials for detailed reaction conditions. ††Yield of product is reported with respect to alkene **a**. dr, diastereomeric ratio; OBn, benzyloxy; Ts, *p*-toluenesulfonyl; Et, ethyl.



Fig. 4. Mechanistic investigation of the electrocatalytic alkene diazidation. (A) Radical clock experiments. (B) Proposed catalytic cycle. V, power supply.

We then explored the substrate scope of our optimized electrocatalytic diazidation protocol (Fig. 3A). Aryl-substituted acyclic alkenes underwent smooth conversion to the corresponding 1,2diazides in high yields (1b to 8b). The efficacy of our protocol showed little dependence on the electronic properties of the aryl substituent. The scope of this methodology was then extended to classes of activated and unactivated substrates beyond styrenes. The reaction exhibited extraordinary insensitivity to substitution pattern. Terminal (9b to  ${\bf 12b}),$  1,1- and 1,2-disubstituted  $({\bf 13b}$  to  ${\bf 18b}),$ trisubstituted (19b), and tetrasubstituted (20b and **21b**) alkenes underwent radical diazidation smoothly to produce the corresponding 1.2-diazides in high yields. Because of steric hindrance, tetrasubstituted alkenes remain notoriously challenging to functionalize, and no methods are available for the direct diazidation or diamidation of this class of substrates. In comparison, our electrochemical protocol provides convenient access to 1,1,2,2-tetrasubstituted vicinal diamines in excellent yields (20b and 21b). In particular, product **21b** constitutes a masked  $\alpha$ , $\beta$ -diamino acid with two contiguous, fully substituted carbons. We hypothesize that the unusual substrate generality of this protocol arose from the high reactivity of the electrochemically generated group transfer agent, Mn<sup>III</sup>-N<sub>3</sub>, in addition to its small steric profile. Cyclopropyl-substituted alkene 13a did not yield an appreciable amount of the ring-opened product; this selectivity arises from the substantial difference in stability between the benzylic and primary alkyl radicals en route to 13b and the acyclic product, respectively. Diazidation was nonstereospecific: trans-\beta-Methylstyrene and trans-stilbene afforded diastereomers 16b (3:1 mixture) and 17b (2:1 mixture), respectively. This stereochemical infidelity was consistent with the intermediacy of radical adduct **I**. Cyclic alkenes with all substitution patterns also proved to be suitable substrates, producing predominantly the *trans*-1,2-diazides in robust yields and with good to excellent diastereoselectivity (**22b** to **27b**). Electron-rich heterocycles—including benzofuran and *N*-tosyl indole—dearomatized to form diazides with high diastereomeric ratios (**28b** and **29b**). The stereoselectivity was imparted through a catalyst-controlled process, because in the absence of Mn, reaction with **22a** yielded traces of **22b** in a substantially lower diastereomeric ratio (2:1).

The ability to dial in oxidizing potential at the minimum level required for the desired redox transformation makes electrochemistry an ideal means of functionalizing complex synthetic intermediates (21). For instance, the electrochemical diazidation was conducted at the oxidation potential of the catalyst-azide adduct (~0.62 V; fig. S3), which is below that of many oxidation-sensitive functionalities. As such, substrates containing alcohol, aldehvde, enolizable ketone, carboxylic acid, amine, sulfide, and alkyne groups all proved compatible with the reaction system (30b to 41b; Fig. 3B), showing little evidence of undesired side reactions involving the additional vulnerable functionalities. Ferrocene, a thermodynamically more reducing group (E = 0) than Mn<sup>II</sup>–N<sub>3</sub>, was also tolerated (42b), indicating that the observed high chemoselectivity may also be attributed to catalystinduced kinetic control. In comparison, no previously reported vicinal diamine syntheses using conventional oxidants have proven compatible with a majority of the aforementioned functional groups. Substituents susceptible to nucleophilic displacement by N3-, such as epoxide, ester, alkyl chloride, and alkyl bromide (43b to 46b), were also tolerated, likely as a result of the moderately acidic reaction medium, which attenuates the nucleophilicity of the azide anion. A representative set of 11 alkene substrates was also examined under constant-current conditions and exhibited high Faradaic efficiencies (62 to 99%; fig. S1). Many synthetic methods have been established for the reduction of aliphatic azides to their corresponding amines with high functional group tolerance (table S1). Accordingly, we demonstrated that a number of 1,2-diazides, including those bearing reductively labile groups (31b, 33b, 39b, 40b, and 46b), could be chemoselectively converted to 1,2-diamines (Fig. 3C). The diazidation and reduction procedures could be carried out consecutively without elaborate isolation of the intermediate, thereby constituting a general, safe, and operationally simple method for vicinal diamine synthesis.

The unusually broad substrate scope of the alkene diazidation piqued our interest in elucidating its mechanism, particularly the roles of the anode and Mn catalyst in regulating the generation and reactivity of radical intermediates. Radical clock experiments confirmed the intermediacy of radical adduct I (Fig. 4A): (i) trans-Stilbene and cis-stilbene were converted to a pair of diastereomeric 1,2-diazides with identical diastereomeric ratios, (ii) diene 47a reacted through both diazidation and cyclization to form pyrrolidine 47b, and (iii) cyclopropylsubstituted alkenes 48a and 49a underwent ring opening after the first azidyl addition, furnishing 48b and 49b, respectively, as the major products. The highly electron-deficient, dicarbonylsubstituted radical intermediate originating from substrate **49a** was trapped by Mn<sup>III</sup>-N<sub>3</sub>, the putative active catalyst, to form the diazide in synthetically useful yield, with no evidence of side reactions involving the electrophilic carbon radical (e.g, electroreduction, addition to alkene **49a**, or hydrogen-atom abstraction from a labile C–H bond in the reaction system).

We propose two plausible mechanisms for the diazidation. In the first scenario (Fig. 1C), direct oxidation of N3- to N3. followed by its addition to the alkene and subsequent azidyl transfer from Mn<sup>III</sup>-N<sub>3</sub>, leads to the final product. Alternatively, Mn-assisted delivery of both equivalents of N3. to the olefin (Fig. 4B) completes diazidation. In either case, we propose that the key group transfer agent, Mn<sup>III</sup>-N<sub>3</sub>, forms through ligand exchange from Mn<sup>II</sup>-X (X, Br or OAc) to Mn<sup>II</sup>-N<sub>3</sub> and subsequent anodic oxidation. Voltammetric and spectrophotometric studies substantiated the dual catalytic cycle shown in Fig. 4B. In MeCN, N<sub>3</sub> exhibited an irreversible oxidative wave at ~0.5 V, which shifted positively to 0.84 V on the addition of HOAc, owing to protonation. Mn<sup>II</sup> alone displayed no redox features between 0 and 1.5 V, but on the addition of N<sub>3</sub><sup>-</sup> and HOAc, a series of irreversible anodic events appeared with an onset potential of ~0.5 V. We assigned these waves to the oxidation of azide-bound Mn<sup>II</sup>, because this anionic ligand is known to stabilize the Mn<sup>III</sup> oxidation state (46). Preliminary ultraviolet-visible spectroscopy data (figs. S4 to S5) also suggested that  $Mn^{II}\text{-}N_3$  formed when  $N_3^-$  and  $Mn^{II}$  were mixed and was subsequently oxidized to  $Mn^{III}\text{-}N_3$ at a cell potential of 2.3 V, with a characteristic ligand-to-metal charge-transfer transition at 422 nm (46). Taken together, the data favor predominance of Mn-assisted dual radical group transfer over direct addition of anodically generated N<sub>3</sub>· to the alkene. The unusual combination of exceptional reactivity and excellent chemoselectivity observed in this catalytic system likely originated from the putative azidyl transfer agent, Mn<sup>III</sup>-N<sub>3</sub>. In a manner reminiscent of metal-oxo radical chemistry (47), the redox-active metal catalyst enabled the generation of an azidyl equivalent in a controlled fashion as a Mn-bound complex, preserving the radical character needed to induce C=C  $\pi$ -bond homolysis while diminishing the high propensity of N<sub>3</sub>· to undergo dimerization, C-H or electron abstraction, and other side reactions. This feature, together with the granular control of oxidizing potential granted by electrochemistry, led to the broad substrate generality and high functional group compatibility of our system.

We anticipate that this synthetic protocol will enhance chemists' access to a diverse array of 1,2-diamines. From a broader perspective, we envision that this catalytic electrochemical strategy and the radical transformations that it enables will prove widely applicable in both modern synthetic chemistry and pharmaceutical research.

#### **REFERENCES AND NOTES**

- D. Lucet, T. Le Gall, C. Mioskowski, Angew. Chem. Int. Ed. 37, 2580–2627 (1998).
- 2. F. Cardona, A. Goti, Nat. Chem. 1, 269–275 (2009).
- H. C. Kolb, M. S. VanNieuwenhze, K. B. Sharpless, *Chem. Rev.* 94, 2483–2547 (1994).
   A. O. Chong, K. Oshima, K. B. Sharpless, *J. Am. Chem. Soc.* 99,
- A. O. Onong, R. Oshima, R. D. Sharpiess, J. Am. Onem. Soc. 39, 3420–3426 (1977).
   P. N. Becker, M. A. White, R. G. Bergman, J. Am. Chem. Soc.
- 102, 5676–5677 (1980).
  D. E. Olson, J. Y. Su, D. A. Roberts, J. Du Bois, J. Am. Chem. Soc.
- **136**, 13506–13509 (2014).
- K. Muñiz, L. Barreiro, R. M. Romero, C. Martínez, J. Am. Chem. Soc. 139, 4354–4357 (2017).
- B. Zhang, A. Studer, Org. Lett. 16, 1790–1793 (2014).
  Y. Zhu, R. G. Cornwall, H. Du, B. Zhao, Y. Shi, Acc. Chem.
- Y. Zhu, R. G. Cornwall, H. Du, B. Zhao, Y. Shi, Acc. Chem. Res. 47, 3665–3678 (2014).
- B. Simmons, A. M. Walji, D. W. C. MacMillan, *Angew. Chem. Int. Ed.* 48, 4349–4353 (2009).
- 11. F. Minisci, Acc. Chem. Res. 8, 165–171 (1975).
- W. E. Fristad, T. A. Brandvold, J. R. Peterson, S. R. Thompson, J. Org. Chem. 50, 3647–3649 (1985).
- Y.-A. Yuan, D.-F. Lu, Y.-R. Chen, H. Xu, *Angew. Chem. Int. Ed.* 55, 534–538 (2016).
- H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* 40, 2004–2021 (2001).
- F. Palacios, C. Alonso, D. Aparicio, G. Rubiales, J. M. de los Santos, Tetrahedron 63, 523–575 (2007).
- C. I. Schilling, N. Jung, M. Biskup, U. Schepers, S. Bräse, Chem. Soc. Rev. 40, 4840–4871 (2011).
- E. T. Hennessy, T. A. Betley, *Science* **340**, 591–595 (2013).
  S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed.*
- **44**, 5188–5240 (2005).
- 19. K. D. Moeller, Tetrahedron 56, 9527–9554 (2000).
- J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.* 108, 2265–2299 (2008).
- 21. E. J. Horn, B. R. Rosen, P. S. Baran, ACS Cent. Sci. 2, 302–308 (2016).
- B. H. Nguyen, A. Redden, K. D. Moeller, Green Chem. 16, 69–72 (2014).
- 23. D. M. Schultz, T. P. Yoon, Science **343**, 1239176 (2014).
- T. Shono, N. Kise, T. Suzumoto, T. Morimoto, J. Am. Chem. Soc. 108, 4676–4677 (1986).
- K. D. Moeller, M. R. Marzabadi, D. G. New, M. Y. Chiang, S. Keith, J. Am. Chem. Soc. **112**, 6123–6124 (1990).
- R. D. Little, M. K. Schwaebe, Top. Curr. Chem. 185, 1–48 (1997).
- K. Chiba, T. Miura, S. Kim, Y. Kitano, M. Tada, J. Am. Chem. Soc. 123, 11314–11315 (2001).
- J. B. Sperry, D. L. Wright, J. Am. Chem. Soc. 127, 8034–8035 (2005).

- H.-C. Xu, K. D. Moeller, J. Am. Chem. Soc. 130, 13542–13543 (2008).
- A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel, Angew. Chem. Int. Ed. 49, 971–975 (2010).
- 31. T. Morofuji, A. Shimizu, J. Yoshida, J. Am. Chem. Soc. 135, 5000–5003 (2013).
- 32. B. R. Rosen, E. W. Werner, A. G. O'Brien, P. S. Baran, J. Am. Chem. Soc. **136**, 5571–5574 (2014).
- 33. E. J. Horn et al., Nature 533, 77-81 (2016).
- 34. A. Badalyan, S. S. Stahl, Nature 535, 406-410 (2016).
- P. Xiong, H.-H. Xu, H.-C. Xu, J. Am. Chem. Soc. 139, 2956–2959 (2017).
- 36. L. J. Li et al., J. Org. Chem. 80, 11021-11030 (2015).
- H. Schäfer, Angew. Chem. Int. Ed. Engl. 9, 158–159 (1970).
- R. Francke, R. D. Little, Chem. Soc. Rev. 43, 2492–2521 (2014).
- F. Wang, X. Qi, Z. Liang, P. Chen, G. Liu, Angew. Chem. Int. Ed. 53, 1881–1886 (2014).
- R. Zhu, S. L. Buchwald, J. Am. Chem. Soc. 137, 8069–8077 (2015).
- 41. A. Sharma, J. F. Hartwig, Nature 517, 600-604 (2015).
- 42. E. K. Leggans, T. J. Barker, K. K. Duncan, D. L. Boger, *Org. Lett.* 14, 1428–1431 (2012).
- X. Huang, T. M. Bergsten, J. T. Groves, J. Am. Chem. Soc. 137, 5300–5303 (2015).
- 44. J. Waser, H. Nambu, E. M. Carreira, J. Am. Chem. Soc. 127, 8294–8295 (2005).
- 45. S. J. David, R. D. Coombe, *J. Phys. Chem.* **90**, 3260–3263 (1986).
- C. Baffert, H. Chen, R. H. Crabtree, G. W. Brudvig, M.-N. Collomb, J. Electroanal. Chem. 506, 99–105 (2001).
- 47. J. M. Mayer, Acc. Chem. Res. 31, 441-450 (1998).

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#### SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/357/6351/575/suppl/DC1 Materials and Methods Figs. S1 to S6

Tables S1 and S2 Spectral Data References (48–63)

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A charged approach to forming C–N bonds Adjacent carbon-nitrogen bonds often appear in chemical compounds of pharmaceutical interest. Fu *et al.* developed a versatile method to form these bonds by pairing manganese catalysis with electrochemical azide oxidation in the presence of olefins. A major advantage of the electrochemical approach is the tunable precision of its oxidizing power, which leaves other sensitive substituents such as alcohols and aldehydes intact. The reaction proceeded over several hours at room temperature, forming hydrogen at the counter electrode as a benign by-product. Science, this issue p. 575

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