



Cite this: *Chem. Sci.*, 2024, 15, 14699

All publication charges for this article have been paid for by the Royal Society of Chemistry

A simple N-heterocyclic carbene for the catalytic up-conversion of aldehydes into stoichiometric super electron donors†

Nadhrata Assani,^a Ludivine Delfau,^b Preslav Smits,^b Sébastien Redon,^a Youssef Kabri,^a Eder Tomás-Mendivil,^b Patrice Vanelle,^a David Martin^{b*} and Julie Broggi^{a*}

Catalytic amounts of 1,3-di(methyl)imidazole-2-ylidene, one of the simplest and most prototypical N-heterocyclic carbenes, can up-convert aldehydes into powerful stoichiometric sources of electrons (Super Electron Donors) for reductive transformations of iodoaryls ($E_{\text{red}} < -2$ V). In particular, the hydroarylation of 1,1'-diarylethylenes, which may require high temperatures and inherently generate stoichiometric amounts of oxidized waste, was performed at room temperature, with the concomitant formation of esters as oxidized co-products.

Received 18th June 2024
Accepted 9th August 2024

DOI: 10.1039/d4sc04011b

rsc.li/chemical-science

Introduction

The development of Organic Electron Donors (OEDs) has allowed for a broad range of selective metal-free reductive transformations.¹ The design of compounds with increasingly reducing power, termed Super Electron Donors (SEDs), has culminated so far in the report of tetra(iminophosphoro)-substituted bispyridinylidene **A**, which can undergo reversible oxidation at $E_{1/2}(\text{A}/\text{A}^{2+}) = -1.7$ V versus SCE and perform the challenging reduction of iodoarenes (Fig. 1a).²

Note that, similarly to other OEDs with dimeric patterns,³ **A** can be generated *in situ* by the deprotonation of precursor **B**, which is air-stable and easier to handle. More generally, a variety of reductant up-conversions^{4,5} of weak reagents into various SEDs have been considered, ranging from *in situ* stoichiometric chemical reactions³ to photoactivation.⁶ Several groups described reactions involving catalytic amounts of chemically upconverted SEDs, such as benzimidazole radical **C**⁷ ($E_{\text{P}}^{\text{ox}} = -2.1$ V),⁸ dioxane-derived radical anion **D**,⁹ diketopiperazine bis-enolate **E**,¹⁰ or phenanthroline-based anion **F**,¹¹ which promote the reductive transformations of halogenoaryls at high temperatures (Fig. 1b–d). In these processes, the stoichiometric sacrificial electron donors are solvents or metallic hydrides. They are required for feeding electrons into the catalytic cycle, but yield wasteful oxidized co-products and can cause side reactions.

On the other hand, aldehydes are ubiquitous synthons in organic synthesis, some of which are available from biomass resources, and they represent a valuable source of electrons. They are up-converted by N-heterocyclic carbenes (NHCs) into Breslow intermediates **G·H** (Fig. 2a).^{12,13} The oxidation of the latter into acyliums **G**⁺ yields numerous valuable products upon reaction with nucleophiles.¹⁴ Yet, very few studies have considered the fate of the oxidative partner. In 1980, Inoue and Higashiuba showed that phenazine ($E_{\text{red}} = -0.6$ V)¹⁵ and azobenzene ($E_{\text{red}} = -1.3$ V)¹⁶ are reduced in the presence of aldehydes under NHC catalysis, yielding dihydrophenazine and benzidine, respectively.¹⁷ The group of Chi also designed a few

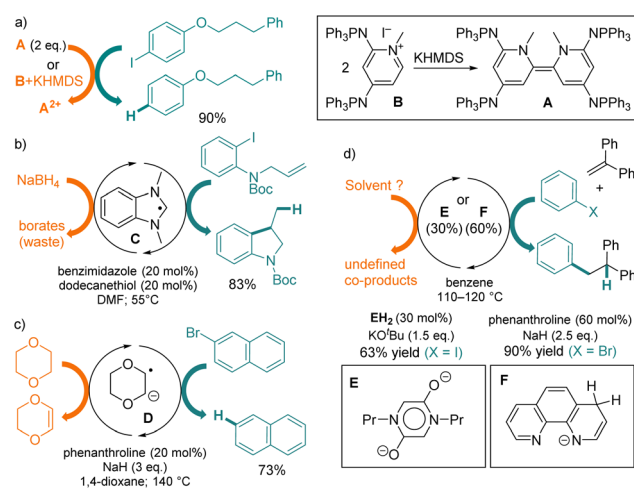


Fig. 1 (a) Reduction of aryl halides with a stoichiometric organic Super Electron Donors (SED, 2 equiv.) **A** or (b–d) with catalytically up-converted SEDs **C–F**.

^aAix Marseille Univ, CNRS, ICR, Institut de Chimie Radicalaire, Faculté de Pharmacie, 13005, Marseille, France. E-mail: julie.broggi@univ-amu.fr

^bUniv. Grenoble-Alpes, UMR CNRS-UGA 5250, CS 40700, 38058 Grenoble, France. E-mail: david.martin@univ-grenoble-alpes.fr

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4sc04011b>



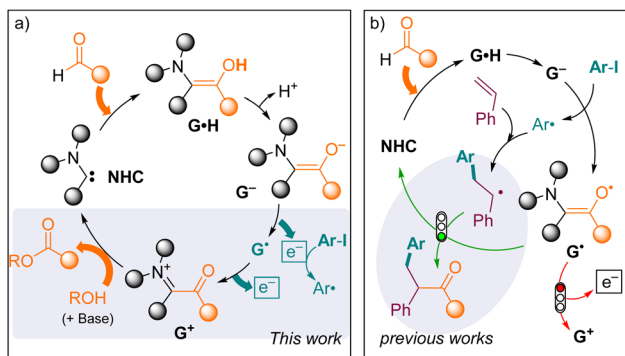


Fig. 2 (a) Reductant up-conversion of aldehydes under NHC catalysis. (b) Interception of G^{\bullet} by transient radicals in the redox-neutral NHC-catalysed acylarylation of styrenes.

NHC-catalyzed reductive functionalization reactions of activated nitrobenzyl bromides ($E_{\text{red}} < -0.8$ V) or nitroalkenes ($E_{\text{red}} < -0.6$ V)¹⁸ in the presence of methanol, with the concomitant formation of a methyl ester.¹⁹ More recently, NHC-catalysed radical transformations of aldehydes²⁰ have advanced to include the activation of more challenging substrates, such as iodoaryls ($E_{\text{red}} < -2$ V),²¹ via single electron transfer (SET) from Breslow-type enolates G^{\bullet} stemming from thiazol-2-ylidenes (Ohmiya group),²³ 1,3,4-triazol-2-ylidenes (Chi group)²⁴ or meso-ionic 1,4,5-triazol-2-ylidenes (Bertrand and Yan groups).²⁵ However, so far, these radical reactions have remained redox-neutral overall, because the transient radicals are intercepted by persistent Breslow-type radicals G^{\bullet} , affording ketone derivatives (Fig. 2b).

Herein, we show that catalytic amounts of 1,3-di(methyl)imidazole-2-ylidene, one of the simplest and most prototypical N-heterocyclic carbenes (NHCs), can up-convert aldehydes into strong SED reagents for the light-free reductive transformations of iodoaryls ($E_{\text{red}} < -2$ V) at room temperature, with the concomitant formation of esters as oxidized co-products.

Results and discussion

We were intrigued by electrochemical²⁶ and computational²⁷ studies, indicating that imidazole-2-ylidene NHCs should provide some of the strongest electron-donor enolates G^{\bullet} with oxidation potentials (*ca.* -2.1 V) lower than those of enolates stemming from thiazolylidenes (-1.4 V) or mesoionic carbenes (-1.8 V), which are known to perform the reductive radical activation of iodoaryls. Thus, although imidazolylidenes have been disregarded as mediocre catalysts for the radical transformations of aldehydes,^{19b,28} we attempted the reductive addition of iodobenzene **2a** to 1,1'-diphenylethylene **3a**, in the presence of benzaldehyde **1a**, potassium *tert*-butoxide and a catalytic amount of the imidazolium precursor of NHC **C2**, featuring bulky 1,3-di(isopropyl)phenyl *N*-substituents (Fig. 3a). After one day at room temperature, NMR monitoring of the crude mixture indicated the presence of 1,1,2-triphenylethane **5aa** with a low, but encouraging, 11% conversion, and the concomitant formation of *tert*-butyl benzoate ester **4a**.

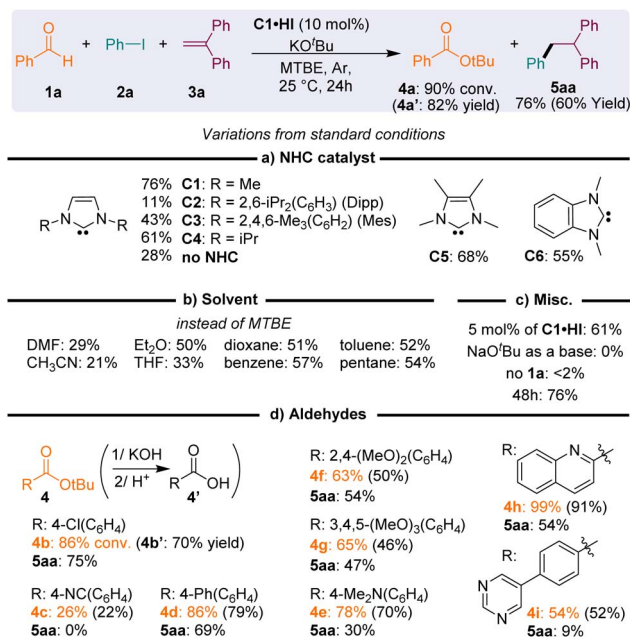


Fig. 3 Optimization of NHC-catalyzed reductive anti-Markovnikov hydroarylation of 1,2-diphenylethylene with phenyl iodide; standard reaction conditions were: **1a** (0.3 mmol), **2a** (0.36 mmol), **3a** (0.20 mmol), **C1•HI** (10 mol%), and KO^tBu (0.3 mmol) in dry MTBE (0.6 mL) under an argon atmosphere for 24 h at 25 °C. Percentages are for the conversion of **3a** into product **5aa**, unless otherwise noted. Values in brackets are yields.

The use of NHCs **C1–6** with decreasing steric bulk increased the conversion of **5aa**, up to 76% with 1,3-di(methyl)imidazolylidene **C1**. The reaction also worked with *N*-methyl substituted NHCs **C5** and **C6** (with 3,4-dimethylimidazole and benzimidazole backbones, respectively), though with slightly lower conversions. The clear reactivity difference of NHCs **C1–6** could not be attributed to the similar reducing power of their Breslow derivative ($E_p \approx -1.1, -1.8$ V vs. SCE, see the ESI†). The deleterious effect of steric hindrance at the *N*-substituents of the NHC catalyst was interpreted as resulting from a significant decrease of the nucleophilicity of the NHC, therefore precluding the fast formation of the Breslow intermediate **G•H**. The steric hindrance of **G•H** itself could also impede the formation of a tight charge transfer complex (CTC) with the substrate, leading to slow electron transfers. Interestingly, 28% conversion was observed in the absence of the NHC, indicating the existence of some background reactions, likely promoted by stoichiometric potassium *tert*-butoxide.²⁹ In the absence of aldehyde **1a**, starting iodoarene **2a** was recovered (<2% **5aa**).

Further optimization established *tert*-butyl methyl ether (MTBE) as the solvent and the reaction performed better at room temperature (25 °C) with a 10 mol% catalyst loading (Fig. 3b and c). The best conversion rates were obtained with non-polar solvents. Note that the conversion rate was not influenced by their C–H bond dissociation energy ($\text{BDE}_{\text{C-H}}$). Solvents with high $\text{BDE}_{\text{C-H}}$ (benzene: 113 kcal mol⁻¹ and pentane: 100 kcal mol⁻¹) exhibited the same reactivity as solvents with lower $\text{BDE}_{\text{C-H}}$ (diethyl ether: 93 kcal mol⁻¹ and



toluene: 89 kcal mol⁻¹). No conversion was observed with sodium *tert*-butoxide as a base, likely due to its poor solubility in MTBE.

Other aryl aldehyde partners were tolerated, provided that they were neither too electron-rich nor too electron-poor (Fig. 3d). This balance is in line with the expected necessity for the aldehyde to be both electrophilic enough for fast addition of the NHC and electron-rich enough to yield a highly reducing Breslow enolate. Satisfyingly, the ester co-product was easily removed from the crude reaction and recovered in good yields by saponification, followed by acidic precipitation of the corresponding carboxylic acid **4'** from the aqueous solution.

Next, we considered various substrates under these optimized conditions (Fig. 4). Aryl iodides bearing electron-donating or electron-withdrawing groups reacted well,

affording the corresponding arylation products **5aa–5ma** in moderate to good yields. Sterically hindered aryl iodides (**2f**, **2h**, and **2j–l**) were also tolerated. Substrate **2m**, featuring both iodoaryl and alkene moieties, underwent intramolecular cyclisation to afford dihydro-benzofuran **5ma**, which was isolated in a modest 30% yield.

A limitation was reached with heterocycles: 2-iodo thiophene **2n** and 4-iodopyridine **2o** were reduced, but less than 10% of the desired addition products **5na** and **5oa** was observed. Indeed, the 1,1'-diphenylethylene **3a** was not sufficiently electron-rich to trap these electrophilic pyridyl and thienyl radicals under our mild room-temperature conditions.³⁰ On the other hand, the reduction of the more challenging iodoester **2p** failed and the starting materials were mainly recovered.

The reductive coupling of iodobenzene also performed well with geminal diaryl- and heteroaryl-ethylenes **3a–g**. Addition to trisubstituted ethylene **3e** was also possible, albeit sluggish (**5ae** conv. 15%). However, neither *trans*-stilbene **3h** nor aliphatic counterparts **3i–k** could trap the phenyl radical, as the formation of the corresponding products **5ah–5ak** was not observed. Note that in the case of the electron poor α -(trifluoromethyl) styrene **3k**, broad band shapes in the ¹H NMR spectra of the crude mixture suggested the formation of oligomers.

Importantly, when styrene was introduced as a radical trap, aryl-acylation products **6** were obtained, indicating the interception of the persistent Breslow-type radical **G'** (Fig. 5a). Although the conditions have not been optimized for this specific reaction, compounds **6** were isolated in 26–45% yields, which compared well with the results of the previously reported

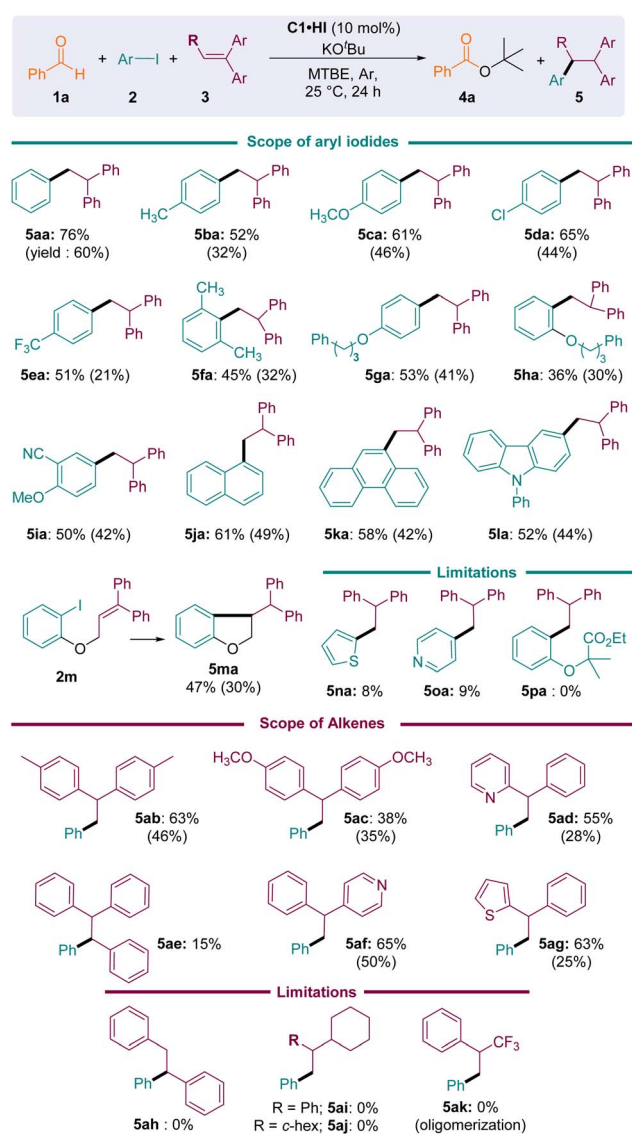


Fig. 4 Substrate scope of the NHC-catalysed hydroarylation of 1,1'-diarylethylenes with aryl iodides under pre-optimized conditions. Conversions were evaluated from the ¹H NMR spectra of the crude reaction. Values in brackets are yields.

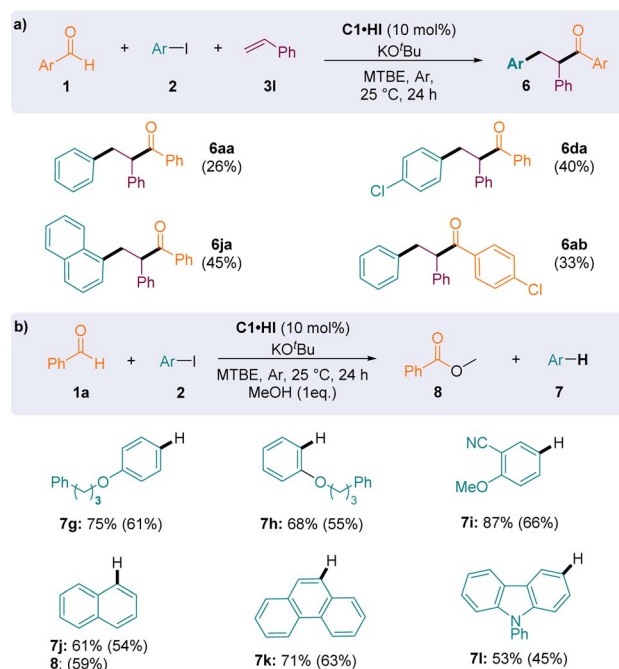


Fig. 5 (a) NHC-catalysed (redox-neutral) aryl-acylation of styrene. (b) NHC-catalysed reduction of iodoaryls to arenes with benzaldehyde as a source of electron. Values in brackets are yields.



methodology of Ohmiya *et al.*, employing thiazolyldene NHC catalysts in DMSO at 80 °C (**6aa**: 34%; **6ja**: 52%; **6ab**: 34%).²³

When the reaction was performed in the absence of alkene and in methanol, two main products could be observed in the ¹H NMR spectra of crude reaction mixtures: the arene **7** resulting from the reduction of iodoaryl **2** and the oxidized ester **8** (Fig. 5b). Using one equivalent of methanol as a nucleophile to release the NHC catalyst **C1** from the oxidized acyliums **G⁺** maintains the catalytic cycle and leads to the formation of the methyl benzoate **8** (59% yield consecutively to the formation of 54% of **7j**). Both oxidative and reductive cycles were concomitant and interdependent, allowing the formation of two distinct redox products in a similar ratio. Arenes **7g–l** were isolated in good yields, after purification by column chromatography.

We performed isotopic labeling experiments in order to get further mechanistic insights. The reduction of iodonaphthalene **2j** with deuterated aldehyde **d-1a** in the presence of one equivalent of deuterated methanol CD₃OD yielded naphthalene with no incorporation of deuterium (Fig. 6a). These protons are likely transferred by the conjugate acid of the base within the catalytic cycle. Therefore, this suggested that aryl radicals **Ar[•]** stemming from the reduction of iodoaryls were not further reduced to aryl anions **Ar⁻**, which would incorporate acidic protons, but most likely abstracted **H[•]** from solvent or other molecules.

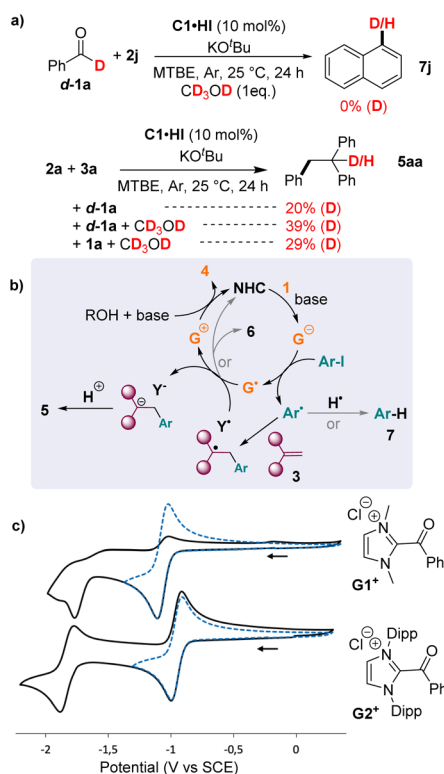


Fig. 6 (a) Experiments with deuterated substrates and additives. (b) Ensnuing mechanistic proposition. (c) Cyclic voltammograms of chloride salts of **G1⁺** and **G2⁺** in 0.1 M ⁿBu₄NPF₆ electrolyte at 100 mV s⁻¹ rates in acetonitrile.

In contrast, the hydroarylation of 1,1'-diphenylethylene **3a** with iodobenzene **2a** and **d-1a** yielded **5aa** with 20% deuterium incorporation^{6d} at the **C1** position. The incorporation increased to 39% when the reaction was performed with an additional equivalent of CD₃OD. This indicated that radical **Y[•]**, stemming from the trapping of **Ar[•]** by **3a**, could be further reduced by Breslow-type enolate **G[•]** to yield anion **Y⁻** and acylium **G⁺** (Fig. 6b). Conversely, in the case of styrene, the reduction of **Y[•]** is slower than its radical coupling with **G[•]**, leading to aryl-acylation products **6**.³¹

To test this mechanistic proposition further, we synthesized chloride salts of Breslow-type acyliums **G1⁺** and **G2⁺**, stemming from benzoyl chloride and NHC catalysts **C1** and **C2**, respectively. Cyclic voltammograms in acetonitrile indicated a first reversible reduction to radical **G[•]** at -1.1 and -0.9 V, respectively. These values indicate that Breslow-type radicals **G[•]** could, indeed, reduce radicals **Y[•]** stemming from 1,1'-diarylethenes (for diphenylmethyl radicals: $E_{1/2}(\text{Y}^-/\text{Y}^\bullet) = -1.3$ – -0.7 V),³² whereas SET to radicals **Y[•]** stemming from styrene would be disfavoured (for benzyl and cumyl radicals: $E_{1/2}(\text{Y}^-/\text{Y}^\bullet) = -1.8$ – -1.4 V).³²

Cyclic voltammograms feature a second reduction wave, which confirmed the strong reducing power of enolates **G⁻** stemming from imidazole-2-ylidenes, although the -1.8 V values for $E_p(\text{G1}^-/\text{G1}^\bullet)$ and $E_{1/2}(\text{G2}^-/\text{G2}^\bullet)$ in acetonitrile are slightly less negative than that reported in the literature (about -2.1 V in dichloromethane).²⁶ Of course, the reducing properties of enolates **G⁻** are expected to depend on the nature of the solvent because polarity stabilizes charged molecules. As a matter of fact, a computational study by Bertrand *et al.* showed that the oxidation potentials of enolates **G⁻** increase with polarity. These compounds are predicted to be especially reducing in low polarity solvents, including MTBE.²⁷ Indeed, compared to MTBE, we observed a drastic drop in the reactivity in polar solvents, which are known to favor electron-transfer reactions (DMF, CH₃CN or THF, Fig. 3b). Note that SET from **G⁻** to aryl iodides is not necessarily favored in non-polar solvents, since the reduction potentials of aryl iodides also increase with polarity. Importantly, despite the necessary caution in interpreting electrochemical data, they once again allowed for rationalizing the main mechanistic outlines of the NHC-catalysed redox processes and must provide useful guidelines for further improvements.

Conclusions

We showed that catalytic amounts of 1,3-di(methyl)imidazole-2-ylidene up-convert aldehydes into powerful stoichiometric sources of electrons, allowing light-free reductive transformations of iodoaryls at room temperature and leading to isolable organic oxidized co-products instead of inorganic wastes. This preliminary study shows the efficiency of this NHC in the reduction of iodoaryls to the corresponding arenes **7**, as well as the hydroarylation of 1,1'-diarylethenes **3**. In the latter case, electrochemical data and isotopic labeling suggest that the outcome of the reaction is determined by the ability of Breslow-type persistent radicals **G[•]** to further reduce radicals **Y[•]**.



In particular, this mechanistic proposition accounts for the formation of aryl-acylation products **6** when styrene is the co-reactant, with **Y'** being then a more difficult-to-reduce benzylic radical.

Prior to our investigations, imidazole-2-ylidenes had been unsuccessfully tested and considered unfit for the promotion of radical transformations of aldehydes. In contrast, this work reveals the unforeseen potential of these NHCs for the generation of strong SED enolates. We are currently reinvestigating the use and scope of this family of organic catalysts for the reductive activation of challenging substrates.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

J. B. and D. M. conceived the project and acquired funding. J. B., D. M., E. T.-M. and P. V. provided resources and supervised the project. N. A., L. D., E. T.-M. and P. S. conducted the investigation and formal analysis of the methodology. All authors contributed to the reviewing and editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was funded by the French National Agency for Research (ANR-20-CE07-0010). P. Smits acknowledges Labex Arcane and CBHEUR-GS (ANR-17-EURE-0003) for funding. We thank the ICMG analytic platform of Grenoble (FR 2607) and the Spectropole of the Fédération des Sciences Chimiques de Marseille for spectroscopic analyses.

Notes and references

- For reviews, see: (a) J. Broggi, T. Terme and P. Vanelle, *Angew. Chem., Int. Ed.*, 2014, **53**, 384–413; (b) J. A. Murphy, *J. Org. Chem.*, 2014, **79**, 3731–3746; (c) E. Doni and J. A. Murphy, *Chem. Commun.*, 2014, **50**, 6073–6087.
- S. S. Hanson, E. Doni, K. T. Traboulsee, G. Coulthard, J. A. Murphy and C. A. Dyker, *Angew. Chem., Int. Ed.*, 2015, **54**, 11236–11239.
- For the *in situ* formation of organic electron donors from air-stable precursors, see: (a) G. Tintori, P. Nabokoff, R. Buhaibeh, D. Bergé-Lefranc, S. Redon, J. Broggi and P. Vanelle, *Angew. Chem., Int. Ed.*, 2018, **57**, 3148–3153; (b) G. Tintori, A. Fall, N. Assani, Y. Zhao, D. Bergé-Lefranc, S. Redon, P. Vanelle and J. Broggi, *Org. Chem. Front.*, 2021, **8**, 1197–1205.
- “Reductant up-conversion” was originally introduced in a broader context by analogy with photon up-conversion: (a) M. A. Syroeshkin, F. Kuriakose, E. A. Saverina, V. A. Timofeeva, M. P. Egorov and I. V. Alabugin, *Angew. Chem., Int. Ed.*, 2019, **58**, 5532–5550; (b) P. Eckhardt, Q. Elliot, I. V. Alabugin and T. Opatz, *Chem.–Eur. J.*, 2022, **28**, e202201637; (c) V. A. Balycheva, B. K. Chabuka, L. R. Kuhn, P. G. Shangin, A. Y. Akyeva, I. V. Krylova, V. A. Korolev, A. V. Lalov, M. P. Egorov, I. V. Alabugin and M. A. Syroeshkin, *J. Phys. Chem. C*, 2024, **128**, 4581–4599.
- See also: (a) A. Studer and D. P. Curran, *Nat. Chem.*, 2014, **6**, 765–773; (b) O. R. Luca, J. L. Gustafson, S. M. Maddox, A. Q. Fenwick and D. C. Smith, *Org. Chem. Front.*, 2015, **2**, 823–848; (c) A. Studer and D. P. Curran, *Angew. Chem., Int. Ed.*, 2016, **55**, 58–102.
- (a) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322–5363; (b) I. Ghosh, T. Ghosh, J. I. Bardagi and B. König, *Science*, 2014, **346**, 725–728; (c) I. A. MacKenzie, L. Wang, N. P. R. Onuska, O. F. Williams, K. Begam, A. M. Moran, B. D. Dunietz and D. A. Nicewicz, *Nature*, 2020, **580**, 76–80; (d) H. Wang, Y. Gao, C. Zhou and G. Li, *J. Am. Chem. Soc.*, 2020, **142**, 8122–8129; (e) X. Mao, M.-M. Li, P. Wang, Q. Cao, W. Zhou and W. Ding, *Org. Lett.*, 2024, **26**, 1265–1270.
- S. Rohrbach, R. S. Shah, T. Tuttle and J. A. Murphy, *Angew. Chem., Int. Ed.*, 2019, **58**, 11454–11458.
- K. A. Ogawa and A. J. Boydston, *Chem. Lett.*, 2014, **43**, 907–909.
- T. Hokamp, A. Dewanji, M. Lübbesmeyer, C. Mück-Lichtenfeld, E.-U. Würthwein and A. Studer, *Angew. Chem., Int. Ed.*, 2017, **56**, 13275–13278.
- (a) E. Doni, S. Zhou and J. A. Murphy, *Molecules*, 2015, **20**, 1755–1774; (b) S. Zhou, E. Doni, G. M. Anderson, R. G. Kane, S. W. MacDougall, V. Ironmonger, T. Tuttle and J. A. Murphy, *J. Am. Chem. Soc.*, 2014, **136**, 17818–17826.
- K. Nozawa-Kumada, S. Onuma, K. Ono, T. Kumagai, Y. Iwakawa, K. Sato, M. Shigeno and Y. Kondo, *Chem.–Eur. J.*, 2023, **29**, e202203143.
- (a) R. Breslow, *J. Am. Chem. Soc.*, 1958, **80**, 3719–3726; (b) R. Breslow and C. Schmuck, *Tetrahedron Lett.*, 1996, **37**, 8241–8242; (c) M. Pareek and Y. Reddi, *Chem. Sci.*, 2021, **12**, 7973–7992.
- (a) A. Berkessel, V. R. Yatham, S. Elfert and J.-M. Neudörfl, *Angew. Chem., Int. Ed.*, 2013, **52**, 11158–11162; (b) M. Paul, P. Sudkaow, A. Wessels, N. E. Schlörer, J.-M. Neudörfl and A. Berkessel, *Angew. Chem., Int. Ed.*, 2018, **57**, 8310–8315; (c) M. Paul, J.-M. Neudörfl and A. Berkessel, *Angew. Chem., Int. Ed.*, 2019, **58**, 10596–10600; (d) M. Paul, K. Peckelsen, T. Thomulka, J. Martens, G. Berden, J. Oomens, J.-M. Neudörfl, M. Breugst, A. J. H. M. Meijer, M. Schäfer and A. Berkessel, *Chem.–Eur. J.*, 2021, **27**, 2662–2669.
- Selected reviews on NHC catalysis: (a) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606–5655; (b) X. Bugaut and F. Glorius, *Chem. Soc. Rev.*, 2012, **41**, 3511–3522; (c) S. De Sarkar, A. Biswas, R. C. Samanta and A. Studer, *Chem.–Eur. J.*, 2013, **19**, 4664–4678; (d) M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496; (e) D. M. Flanagan, F. Romanov-Michailidis, N. A. White and T. Rovis, *Chem.*



- Rev.*, 2015, **115**, 9307–9387; (f) M. H. Wang and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2016, **55**, 14912–14922.
- 15 A. Hollas, X. Wei, V. Murugesan, Z. Nie, B. Li, D. Reed, J. Liu, V. Sprenkle and W. Wang, *Nat. Energy*, 2018, **3**, 508–514.
- 16 J. L. Sadler and A. J. Bard, *J. Am. Chem. Soc.*, 1968, **90**, 1979–1989.
- 17 H. Inoue and K. Higashiuba, *J. Chem. Soc., Chem. Commun.*, 1980, **12**, 549–550.
- 18 J. A. Squella, J. C. Sturm, B. Weiss-lopez, M. Bonta and L. J. Nunez-Vergara, *J. Electroanal. Chem.*, 1999, **466**, 90–98.
- 19 (a) Y. Du, Y. Wang, X. Li, Y. Shao, G. Li, R. D. Webster and Y. R. Chi, *Org. Lett.*, 2014, **16**, 5678–5681; (b) S. Li, Y. Wang, R. S. J. Proctor, Y. Zhang, R. D. Webster, S. Yang, B. Song and Y. R. Chi, *Nat. Commun.*, 2016, **7**, 12933; (c) Y. Wang, Y. Du, X. Huang, X. Wu, Y. Zhang, S. Yang and Y. R. Chi, *Org. Lett.*, 2017, **19**, 632–635; (d) Y. Wang, X. Wu and Y. R. Chi, *Chem. Commun.*, 2017, **53**, 11952–11955.
- 20 For reviews, see: (a) A. V. Bay and K. A. Scheidt, *Trends Chem.*, 2022, **4**, 277–290; (b) K. Liu, M. Schwenzer and A. Studer, *ACS Catal.*, 2022, **12**, 11984–11999.
- 21 L. Pause, M. Robert and J.-M. Savéant, *J. Am. Chem. Soc.*, 1999, **121**, 7158–7159.
- 22 (a) J. K. Mahoney, D. Martin, F. Thomas, C. Moore, A. L. Rheingold and G. Bertrand, *J. Am. Chem. Soc.*, 2015, **137**, 7519–7525; (b) L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil and D. Martin, *Angew. Chem., Int. Ed.*, 2021, **60**, 26783–26789.
- 23 Y. Matsuki, N. Ohnishi, Y. Kakeno, S. Takemoto, T. Ishii, K. Nagao and H. Ohmiya, *Nat. Commun.*, 2021, **12**, 3848.
- 24 F. Su, J. Zou, X. Lv, F. Lu, Y. Long, K. Tang, B. Li, H. Chai, X. Wu and Y. R. Chi, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303388.
- 25 (a) C. Liu, W. Liu, A. Vianna, Z. Zhang, S. Huang, L. Huang, M. Melaimi, G. Bertrand and X. Yan, *Chem Catal.*, 2021, **1**, 196–206; (b) Z. Zhang, L.-L. Zhao, G. Bertrand and X. Yan, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303478; (c) F. Su, F. Lu, K. Tang, X. Lv, Z. Luo, F. Che, H. Long, X. Wu and Y. R. Chi, *Angew. Chem., Int. Ed.*, 2023, **62**, e202310072.
- 26 C. L. Deardorff, E. R. Sikma, C. P. Rhodes and T. W. Hudnall, *Chem. Commun.*, 2016, **52**, 9024–9027.
- 27 F. F. Mulks, M. Melaimi, X. Yan, M.-H. Baik and G. Bertrand, *J. Org. Chem.*, 2023, **88**, 2535–2542.
- 28 For examples, see: (a) W.-D. Liu, W. Lee, H. Shu, C. Xiao, H. Xu, X. Chen, K. N. Houk and J. Zhao, *J. Am. Chem. Soc.*, 2022, **144**, 22767–22777; (b) Y. Q. Liu, Q.-Z. Li, X.-X. Kou, R. Zeng, T. Qi, X. Zhang, C. Peng, B. Han and J.-L. Li, *J. Org. Chem.*, 2022, **87**, 5229–5241; (c) K. She, F. Liang, S. Tian, H. Wang, G. C. Tsui and Q. Wang, *Org. Lett.*, 2022, **24**, 4840–4844; (d) Z. Zhang, X. Zou, Z. Li, Y. Gao, Y. Qu, Y. Quan, Y. Zhou, J. Li, J. Sun and K. Guo, *Org. Chem. Front.*, 2021, **8**, 6074–6079; (e) K. Ota, K. Nagao and H. Ohmiya, *Org. Lett.*, 2020, **22**, 3922–3925; (f) T. Ishii, Y. Kakeno, K. Nagao and H. Ohmiya, *J. Am. Chem. Soc.*, 2019, **141**, 3854–3858.
- 29 Stoichiometric OED species can be *in situ* formed upon the reaction of KO^tBu with electrophiles: (a) S. Zhou, G. M. Anderson, B. Mondal, E. Doni, V. Ironmonger, M. Kranz, T. Tuttle and J. A. Murphy, *Chem. Sci.*, 2014, **5**, 476–482; (b) J. Cuthbertson, V. J. Gray and J. D. Wilden, *Chem. Commun.*, 2014, **50**, 2575–2578; (c) G. Nocera, A. Young, F. Palumbo, K. J. Emery, G. Coulthard, T. McGuire, T. Tuttle and J. A. Murphy, *J. Am. Chem. Soc.*, 2018, **140**, 9751–9757.
- 30 In the literature, the addition of these electrophilic radicals to electron-rich alkenes is at high temperatures or under photoirradiation, see: D. Mirizzi, S. T. Hilton and K. Jones, *Adv. Heterocycl. Chem.*, 2010, **100**, 101–143.
- 31 A more detailed mechanism scheme for the formation of ketone **6** is given in the supporting information.†
- 32 B. A. Sim, P. H. Milne, D. Griller and D. D. M. Wayner, *J. Am. Chem. Soc.*, 1990, **112**, 6635–6638.

