ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/d6cc01204c

Received 26th February 2026,
Accepted 20th April 2026

DOI: 10.1039/d6cc01204c

rsc.li/chemcomm

Cross-coupling of aryl aldehydes and benzyl chlorides enabled by dual N-heterocyclic carbene/cobalt catalysis

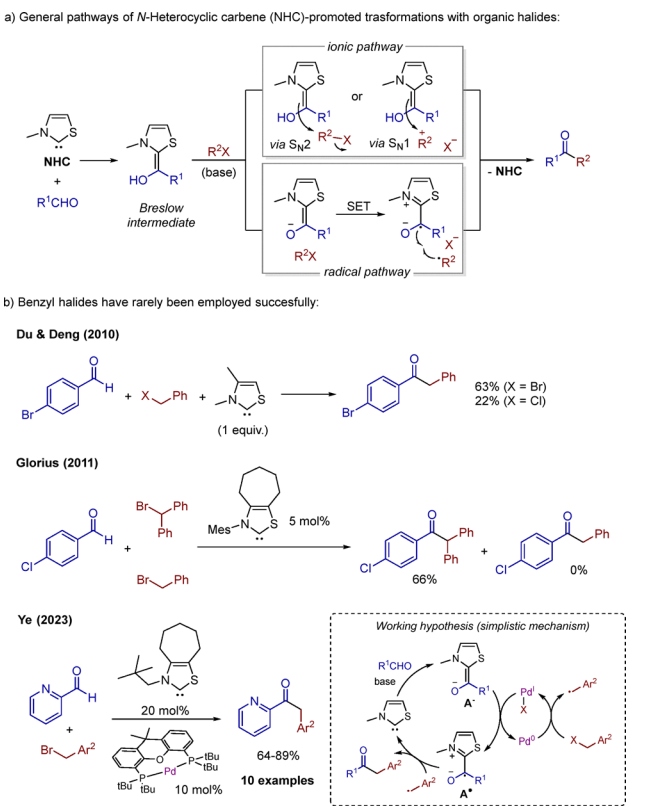
Hassan Jomaa, David Martin and Eder Tomás-Mendivil *

We have developed a dual N-heterocyclic carbene/cobalt-salen catalytic system for the cross-coupling between aryl aldehydes and benzyl chlorides *via* direct C–H activation of aldehydes. The catalysts employed are readily accessible and the transformation affords ketones in moderate to high yields.

N-heterocyclic carbene (NHC) catalysis is an attractive synthetic tool allowing for mild reaction conditions and chemo- and/or enantio-selective transformations.[1] The most common substrates are aldehydes, which react with NHCs to form enaminols (so-called Breslow intermediates)[2] able to react with a wide variety of electrophiles. Traditionally, ionic pathways dominated the field (Scheme 1a); however, in recent years, radical NHC catalysis has been developed for the coupling of unprecedented substrates.[1c–f] Among readily accessible electrophiles, organic halides have been coupled with aldehydes employing NHC catalysis.[3] Aryl iodides[4] and primary and secondary alkyl iodides and bromides[5,6] can be activated employing NHCs as sole catalysts. Cooperative dual NHC/metal radical catalysis[7] employing nickel[8] or palladium[9] has been developed for tertiary alkyl iodides and bromides, respectively.

Strikingly, benzyl halides, classic electrophiles, have been employed only occasionally and with mediocre outcome. Representative examples include the work from Du and Deng *et al.* with a stoichiometric amount of a thiazolium salt for the coupling between aromatic aldehydes and benzyl bromides (and a chloride) in moderate to low yields (Scheme 1b)10 and the competition control experiment from Glorius *et al.* employing diarylbromomethanes and benzyl bromide,11 among others.[6,12] Finally, the most remarkable finding was reported by Zhang and Ye and co-workers in 2023, on a cooperative dual NHC/Pd radical strategy that is applicable to benzyl bromides in good to excellent yields.[9] In this work, it was proposed that enolate $\mathbf{A}^-$ would reduce the metal center and Pd^0 would activate the benzyl bromide. Then, persistent radical $\mathbf{A}^\bullet$ and transient $Bn^\bullet$ would couple releasing the free carbene and product.

Coupling of benzyl chlorides is the next obvious challenge in the field of NHC organocatalysis. We envisioned that applying a dual NHC/metal strategy would promote their use as electrophiles. Square planar $[Co^I(salen)]^-$ complexes are known to activate benzyl chlorides.[13] The reduction potential of $[Co^{II}(salen)]$ complexes stand *ca.* −1.5 V *vs.* SCE,[13b,e–f,14] and



Scheme 1 Representative examples on NHC-catalysed cross-coupling between aldehydes and benzyl halides and cooperative dual NHC/metal catalysis.

Univ. Grenoble Alpes, CNRS, DCM, UMR 5250, 38000 Grenoble, France.
E-mail: eder.tomas-gonzalez-de-mendivil@univ-grenoble-alpes.fr

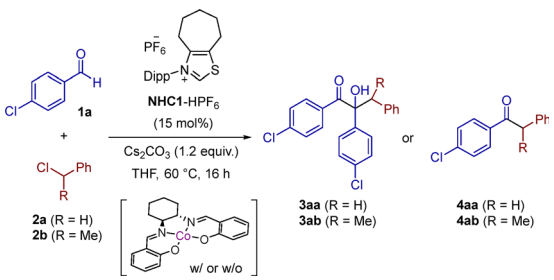
they fall within the range of the reduction power of Breslow-type enolates (−1.9 to −1.4 V *vs.* SCE).[15] Therefore, it is reasonable to propose a dual NHC/Co catalytic cycle where the enolate is able to reduce the cobalt species in order to activate benzyl chlorides.

We began our studies by testing the cross-coupling between 4-chlorobenzaldehyde (**1a**) and benzyl chloride (**2a**) under NHC/metal free conditions, obtaining alkylated benzoin **3aa** in 22% NMR yield (Table 1, entry 1), probably *via* NHC-catalyzed benzoin condensation and alkylation under basic conditions.[16] Then, we tested an **NHC1**/Co-salen combination and **4aa** was formed only in 6% NMR yield (entry 2). Surprisingly most of the aldehyde was still present; *i.e.* the benzoin was not formed, suggesting the deactivation of the NHC. We considered the more bulky (1-chloroethyl)benzene (**2b**) and, to our delight, ketone **4ab** was formed quantitatively (99% NMR yield, entry 4). In the absence of the cobalt catalyst, a moderate yield of 33% was achieved (entry 3).

We chose (1-chloroethyl)benzene **2b** as model substrate to find optimal conditions for the reaction. Initial reaction conditions for the cross-coupling between **1a** (1.2 equiv.) and **2b** (1 equiv.) employing 15 mol% of **NHC1**, 10 mol% of [Co(salen-Cy)] (**Co1**) and Cs_2CO_3 as base in THF gave **4ab** in 99% NMR yield (Table 2, entry 1). We found that in the absence of salen ligand (entry 2) and cobalt complex (entry 3), the yield dropped to *ca.* 30%. This suggests that the carbene is able to promote by itself the cross-coupling albeit with low efficiency. In the absence of **NHC1** the starting materials were recovered (entries 4 and 5). The use of K_2CO_3 instead of Cs_2CO_3 was detrimental (entry 6), probably due to the stabilization of the enolate, lowering its reducing power.[15] Then, we decreased both catalysts' loadings to 10 mol% of **NHC1** and 5 mol% of **Co1** and the yield maintained quantitative (entry 7). The use of the simplest cobalt complex **Co2**, bearing the ethylene-bridged (salen-H) ligand, gave comparable outcome (96%; entry 8). The use of other solvents like acetonitrile, toluene or dimethylsulfoxide instead of tetrahydrofuran gave lower yields (entries 9–11). Finally, we screened different NHCs. Simplification of the backbone of thiazol-2-ylidene from cycloheptyl ring (**NHC1**) to readily accessible dimethyl backbone (**NHC2**) resulted in full conversion and 75% isolated yield (entry 12). Decreasing the steric factors of the carbene by replacing the *N*-(2,6-diisopropylphenyl) (Dipp) group by 2,4,6-trimethylphenyl (Mes), methyl or neopentyl gave lower yields (entries 13–16). This is probably due to the higher pyramidalization around the N-atom which lowers the reducing power of the enolate.[15] The use of Arduengo's imidazolydenes (**NHC7-8**; entries 17 and 18) or Bertrand's mesoionic carbenes (**NHC9**; entry 19) did not lead to product **4ab**.

Then, we studied the scope of the reaction employing the simplest catalytic system: **NHC2** and **Co2** (Scheme 2). Regarding aldehydes, *para*- and *meta*-chloro substitution gave similar yields (61% for **4bb**). Replacing the halogen atom in *para* position with bromine (**4cb**) or fluorine (**4db**) led to lower yields of 27% and 48%, respectively. Electron withdrawing trifluoromethyl (**4eb**) and cyano (**4fb**) groups led to lower yields (25% and 30%, respectively). An electron donating group such as methoxy (**4gb**) gave an isolated yield of 41%. *N*-Dipp substituted

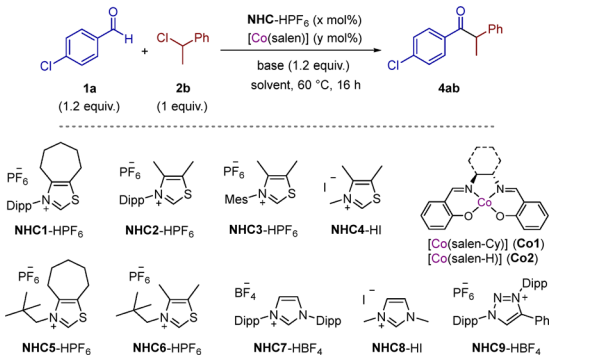
Table 1 Preliminary experiments[a]



Entry	Benzyl chloride	[Co] (*x* mol%)	Yield (%)[b]
1	**2a**	0 mol%	22% (**3aa**)
2	**2a**	10 mol%	6% (**4aa**)
3	**2b**	0 mol%	33% (**4ab**)
4	**2b**	10 mol%	99% (**4ab**)

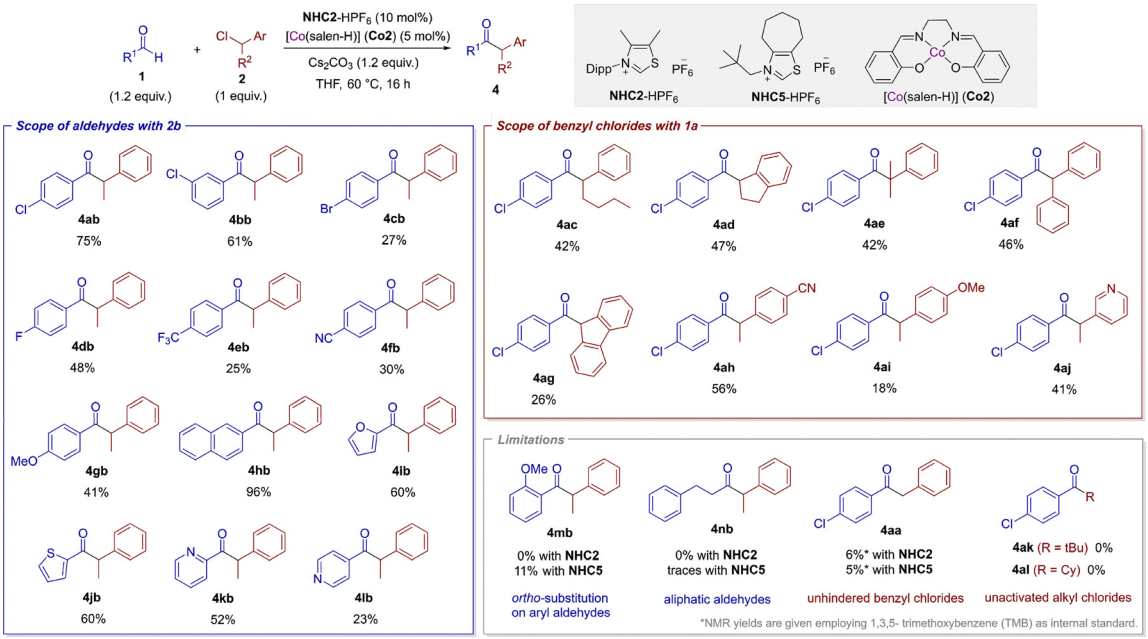
[a] Standard reaction conditions: **1a** (0.3 mmol), **2a-b** (0.25 mmol), **NHC1** (0.038 mmol; 15 mol%), [Co(salen)] (when added), and Cs_2CO_3 (0.3 mmol) in 1 mL of dry THF under argon atmosphere for 16 h at 60 °C. [b] NMR yields for products are given employing 1,3,5- trimethoxybenzene (TMB) as internal standard.

Table 2 Optimization of the reaction conditions[a]



Entry	Reaction conditions	Yield (%)[b]
1	**NHC1** (15 mol%), **Co1** (10 mol%), Cs_2CO_3, THF	99
2	**NHC1** (15 mol%), $CoBr_2$ (10 mol%), Cs_2CO_3, THF	28
3	**NHC1** (15 mol%), Cs_2CO_3, THF	33
4	Cs_2CO_3, THF	0
5	**Co1** (10 mol%), Cs_2CO_3, THF	0
6	**NHC1** (15 mol%), **Co1** (10 mol%), K_2CO_3, THF	54
7	**NHC1** (10 mol%), **Co1** (5 mol%), Cs_2CO_3, THF	99
8	**NHC1** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	96
9	**NHC1** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, Acetonitrile	91
10	**NHC1** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, Toluene	73
11	**NHC1** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, DMSO	70
12	**NHC2** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	99 (75)[c]
13	**NHC3** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	56
14	**NHC4** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	20
15	**NHC5** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	35
16	**NHC6** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	36
17	**NHC7** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	0
18	**NHC8** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	0
19	**NHC9** (10 mol%), **Co2** (5 mol%), Cs_2CO_3, THF	0

[a] Standard reaction conditions: **1a** (0.3 mmol), **2b** (0.25 mmol), **NHC**-HX, [Co(salen)], and base (0.3 mmol) in 1 mL of dry solvent under argon atmosphere for 16 h at 60 °C. [b] NMR yields for **4ab** are given employing 1,3,5- trimethoxybenzene (TMB) as internal standard. [c] Isolated yield.

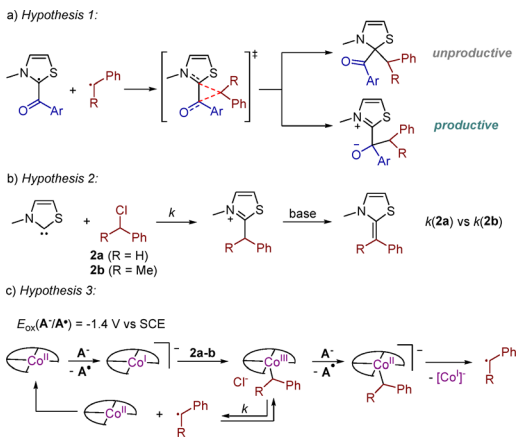


Scheme 2 Scope of the reaction at 1 mmol scale. Isolated yields given are unless otherwise noted.

thiazol-2-ylidenes may find *ortho* substitution problematic.[8] Our system made no exception and *ortho*-methoxy substituted product (**4mb**) was not observed. On the contrary, the use of less hindered *N*-neopentyl **NHC5**[17] led to a poor yield of 11%. 2-naphthyl (**4hb**) gave the highest yield reaching 96%. Heteroaryl functionalities were also compatible: furyl (**4ib**), thiofuryl (**4jb**) and pyridyl (**4kb** and **4lb**) gave moderated isolated yields. Aliphatic aldehydes are not compatible and the use of carbene **NHC5** gave only traces of the desired product **4nb**. Next, benzyl chloride derivatives were screened. Lengthening the aliphatic chain (**4ac**) or incorporating it into a cyclic structure (**4ad**) gave moderate yields. The use of a tertiary chloride gave **4ae** in 42% yield. This is an interesting result from a mechanistic point of view, since the substrate is very unlikely to be activated *via* a S_N2 mechanism; instead XAT is probably preferred (*vide infra*). Diphenylchloromethane and 9-chlorofluorene gave **4af** and **4ag** in modest isolated yields, respectively. *para*-Cyano (**4ah**) and *para*-methoxy (**4ai**) substituted benzyl chlorides are also compatible with higher yield for the electron deficient substrate. The pyridine group in the benzylic fragment gave good yield (**4aj**). As previously stated, unsubstituted benzyl chloride **2a** gives very low yield employing **NHC2**. Employing **NHC5**, **4aa** was obtained in 5% yield. Highly challenging unactivated *tert*-butyl chloride and cyclohexyl chloride did not lead to the desired ketones **4ak** and **4al**, respectively.

Intrigued by the differing reactivity of benzyl chlorides **2a** and **2b**, we postulated three hypotheses (Scheme 3):

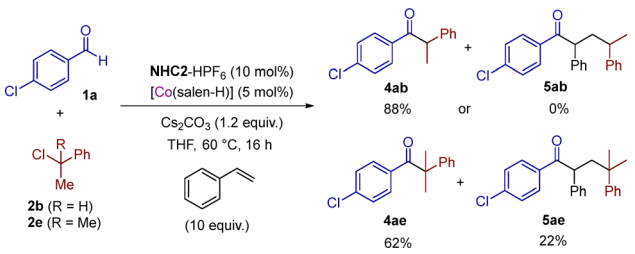
Hypothesis 1: regioselectivity issues in the radical cross-coupling step. Experimental[18] and theoretical[19] studies had proposed that steric factors may rule the cross-coupling between radicals leading to productive or unproductive pathways, which may also be the case herein (Scheme 3a). Note also that, only a few carbenes are known to be compatible in NHC



Scheme 3 Different hypotheses to understand the origin of different reactivity of benzyl chlorides **2a-b**.

radical catalysis with unhindered Bn• radicals: (i) 1,2,4-triazol-5-ylidenes *via* oxidative (photo)redox catalysis,[20,21] (ii) an imidazolydene,[22] and (iii) inefficiently few thiazol-2-ylidenes,[23] except for an efficient *N*-neopentyl thiazol-2-ylidene/Pd cooperative catalytic system.[9] On the contrary, more sterically crowded substituted benzyl radicals (ArCHR)• generated through radical relay strategies employing olefins are widely applied.[4a,b,1c–f,24] Note that (ArCHMe)• has successfully been employed in enantioselective approaches too.[25]

Hypothesis 2: the nucleophilic attack of NHCs to benzyl chlorides to form enamines (Scheme 3b).[26] We reacted **2a-b** with **NHC2** under catalytic conditions for 15 minutes and then aldehyde **1a** was added and reacted for another 4 hours. In both cases, starting materials were recovered, the corresponding



Scheme 4 Radical relay tests. NMR yields are given employing 1,3,5-trimethoxybenzene (TMB) as internal standard.

benzoin was not observed and neither products **3** or **4**. Since this experiment does not discriminate between substrates **2a-b**, such hypothesis was ruled out.

Hypothesis 3: square-planar $[Co^{I}(salen)]^{-}$ complexes are strong nucleophiles and react with ArCHRCl leading to $[Co^{III}(ArCHR)(salen)]$ complexes through a S_N2 mechanism. These species are in equilibrium with $[Co^{II}(salen)]$ and $(ArCHR)^{\bullet}$.[13,27] $[Co^{III}(ArCHR)(salen)]$ can also be reduced to the unstable species $[Co^{II}(ArCHR)(salen)]^{-}$ and its homolytic decomposition leads to $[Co^{I}(salen)]^{-}$ and $(ArCHR)^{\bullet}$. Kinetics control these events and an appropriate match under catalytic conditions may explain the efficient formation of **4ab** in contrast to **4aa**. To probe for the presence of transient benzyl radicals, we tested **2b** under optimized catalytic conditions in the presence of ten equivalents of styrene, but the corresponding radical relay product **5ab** was not formed (Scheme 4). On the contrary, tertiary benzyl chloride **2e** gave ketone **5ae** suggesting the efficient trapping of the transient radical by styrene. This suggests that in the first case a benzyl radical is not released to the medium while in the second case it is, probably *via* a XAT event. In other words, the mechanism, and thus the outcome of the reaction, are substrate dependent (**2a** *vs.* **2b** *vs.* **2e**) and the role of the cobalt catalyst is crucial.

In conclusion, we have developed an efficient NHC promoted cross-coupling reaction between aromatic aldehydes and benzyl chlorides aided by a readily and commercially available cobalt catalyst. In the literature, as far as we are aware, the direct coupling between such substrates yielding ketones has only been reported once employing nickel/photoredox catalysis.[28] Our system is complementary to that one and the results described herein support that merging NHC catalysis with transition metal catalysis has the potential to activate substrates beyond known boundaries.

This work was funded by the French National Agency for Research (ANR-23-CE07–0004–01). H. J. is grateful for the funding of his PhD thesis by this program. We acknowledge the ICMG analytic platform (FR 2607), the CNRS, the University of Grenoble Alpes, the Labex Arcane and CBHEUR-GS (ANR-17-EURE-0003).

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental details. See DOI: https://doi.org/10.1039/d6cc01204c.

References

1 (*a*) D. Enders, O. Niemeier and A. Henseler, *Chem. Rev.*, 2007, **107**, 5606; (*b*) D. M. Flanigan, F. Romanov-Michailidis, N. A. White and T. Rovis, *Chem. Rev.*, 2015, **115**, 9307; (*c*) A. V. Bay and K. A. Scheidt, *Trends Chem.*, 2022, **4**, 277; (*d*) K. Liu, M. Schwenzer and A. Studer, *ACS Catal.*, 2022, **12**, 11984; (*e*) H. Cai, X. Yang, S.-C. Ren and Y. R. Chi, *ACS Catal.*, 2024, **14**, 8270; (*f*) S. Chakraborty, S. Barik and A. T. Biju, *Chem. Soc. Rev.*, 2025, **54**, 1102.
2 (*a*) T. Ukai, S. Tanaka and S. Dokawa, *J. Pharm. Soc. Jpn.*, 1943, **63**, 296; (*b*) S. Mizuhara and P. Handler, *J. Am. Chem. Soc.*, 1954, **76**, 571; (*c*) R. Breslow, *J. Am. Chem. Soc.*, 1958, **80**, 3719.
3 F. Gao, Z. Zhang and X. Yan, *ChemCatChem*, 2024, **16**, e202301331.
4 (*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; (*b*) Y. Matsuki, N. Ohnishi, Y. Kakeno, S. Takemoto, T. Ishii, K. Nagao and H. Ohmiya, *Nat. Commun.*, 2021, **12**, 3848; (*c*) N. Assani, L. Delfau, P. Smits, S. Redon, Y. Kabri, E. Tomás-Mendivil, P. Vanelle, D. Martin and J. Broggi, *Chem. Sci.*, 2024, **15**, 14699; (*d*) B. Huang, Z. Zhang, J. Jiao, W. Liu and X. Yan, *Org. Lett.*, 2024, **26**, 7419; (*e*) S. Liu, S. Zheng, Y. Zhang, K. Lin, W. Li, Z. Li and T. Zhu, *Org. Lett.*, 2026, **28**, 896.
5 (*a*) C. Liu, Z. Zhang, L.-L. Zhao, G. Bertrand and X. Yan, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303478; (*b*) Q.-Z. Li, R. Zeng, P.-S. Xu, X.-H. Jin, C. Xie, Q.-C. Yang, X. Zhang and J.-L. Li, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309572; (*c*) J. Jiao, Z. Zhang, G. Lu, S. Huang, Y. Bian, F. Gao, G. Bertrand and X. Yan, *Chem. Sci.*, 2025, **16**, 9163.
6 Q.-Z. Li, R. Zeng, P.-S. Xu, X.-H. Jin, C. Xie, Q.-C. Yang, X. Zhang and J.-L. Li, *Angew. Chem., Int. Ed.*, 2024, **62**, e202309572.
7 Z.-F. Zhang, C.-L. Zhang and S. Ye, *Chem. – Eur. J.*, 2024, **30**, e202402259.
8 L. Delfau, E. Mauro, J. Pecaut, D. Martin and E. Tomás-Mendivil, *ACS Catal.*, 2024, **14**, 7149.
9 (*a*) Y. Huang, Y.-F. Han, C.-L. Zhang and S. Ye, *ACS Catal.*, 2023, **13**, 11033; (*b*) Y. Huang, X.-H. Wang, C.-L. Zhang and S. Ye, *Org. Lett.*, 2024, **26**, 3441; (*c*) Y. Huang, Y.-F. Han, C.-L. Zhang and S. Ye, *Org. Lett.*, 2025, **27**, 415.
10 L. Lin, Y. Li, W. Du and W.-P. Deng, *Tetrahedron Lett.*, 2010, **51**, 3571.
11 M. Padmanaban, A. T. Biju and F. Glorius, *Org. Lett.*, 2011, **13**, 98.
12 V. Hahnvajanawong, B. Pungpis and P. Theramongkol, *Der Pharma Chem.*, 2016, **8**, 112.
13 (*a*) J.-C. Folest, J.-M. Duprilot, J. Perichon, Y. Robin and J. Devynck, *Tetrahedron Lett.*, 1985, **26**, 2633; (*b*) A. J. Fry and U. N. Sirisoma, *J. Org. Chem.*, 1993, **58**, 4919; (*c*) A. J. Fry and A. H. Singh, *J. Org. Chem.*, 1994, **59**, 8172; (*d*) C. A. Bessel and D. R. Rolison, *J. Am. Chem. Soc.*, 1997, **119**, 12673; (*e*) B.-L. Chen, H.-W. Zhu, Y. Xiao, Q.-L. Sun, H. Wang and J.-X. Lu, *Electrochem. Commun.*, 2014, **42**, 55; (*f*) C. A. Malapit, M. Tanwar, A. D. Pendergast, S. Udyavara, W. D. Beck, R. E. Smith, S. Kadic, T. Primo, D. B. Wu, T. Stone, H. S. White, M. Neurock, M. S. Sigman and S. D. Minteer, *ChemRxiv*, 2021, DOI: 10.26434/chemrxiv-2021-thftp; (*g*) C. Sandford, L. R. Fries, T. E. Ball, S. D. Minteer and M. S. Sigman, *J. Am. Chem. Soc.*, 2019, **141**, 18877.
14 S. Al Zubaydi, I. O. Onuigbo, B. L. Truesdell and C. S. Sevov, *Angew. Chem., Int. Ed.*, 2024, **63**, e202313830.
15 L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil and D. Martin, *Angew. Chem., Int. Ed.*, 2021, **60**, 26783.
16 (*a*) H.-G. Heine, *Liebigs Ann. Chem.*, 1970, **735**, 56; (*b*) Y. Ueno and M. Okawara, *Synthesis*, 1975, 268; (*c*) Z. Wang, L. Gan, Z. Song, Y. Liu and J.-P. Wan, *Chin. J. Chem.*, 2024, **42**, 3041.
17 Y. Kakeno, M. Kusakabe, K. Nagao and H. Ohmiya, *ACS Catal.*, 2020, **10**, 8524.

18 M. N. Alam, S. R. Dash, A. Mukherjee, S. Pandole, U. K. Marelli, K. Vanka and P. Maity, *Org. Lett.*, 2021, **23**, 890.
19 A. V. Bay, K. P. Fitzpatrick, G. A. González-Montiel, A. O. Farah, P. H.-Y. Cheong and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2021, **60**, 17925.
20 A. V. Bay, K. P. Fitzpatrick, G. A. González-Montiel, A. O. Farah, P. H.-Y. Cheong and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2021, **60**, 17925.
21 (*a*) A. V. Davies, K. P. Fitzpatrick, R. C. Betori and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2020, **59**, 9143; (*b*) Q.-Y. Meng, L. Lezius and A. Studer, *Nat. Commun.*, 2021, **12**, 2068; (*c*) H. Huang, Q.-S. Dai, H.-J. Leng, Q.-Z. Li, S.-L. Yang, Y.-M. Tao, X. Zhang, T. Qia and J.-L. Li, *Chem. Sci.*, 2022, **13**, 2584; (*d*) C.-Y. Tan, M. Kim and S. Hong, *Angew. Chem., Int. Ed.*, 2023, **62**, e202306191; (*e*) C. R. Schull, J. Cao, S. R. Mitton-Fry, M. Mrksich and K. A. Scheidt, *ACS Catal.*, 2025, **15**, 1287.
22 M. Jakob, L. Steiner, M. Göbel, J. P. Götze and M. N. Hopkinson, *ACS Catal.*, 2024, **14**, 17642.
23 (*a*) S.-C. Ren, W.-X. Lv, X. Yang, J.-L. Yan, J. Xu, F.-X. Wang, L. Hao, H. Chai, Z. Jin and Y. R. Chi, *ACS Catal.*, 2021, **11**, 2925; (*b*) Y. Man, S. Liu, B. Xu and X. Zeng, *Org. Lett.*, 2022, **24**, 944.
24 For selected examples, see:(*a*) T. Ishii, K. Ota, K. Nagao and H. Ohmiya, *J. Am. Chem. Soc.*, 2019, **141**, 14073; (*b*) J.-L. Li, Y.-Q. Liu, W.-L. Zou, R. Zeng, X. Zhang, Y. Liu, B. Han, Y. He, H.-J. Leng and Q.-Z. Li, *Angew. Chem., Int. Ed.*, 2020, **59**, 1863; (*c*) B. Zhang, Q. Peng, D. Guo and J. Wang, *Org. Lett.*, 2020, **22**, 443; (*d*) I. Kim, H. Im, H. Lee and S. Hong, *Chem. Sci.*, 2020, **11**, 3192; (*e*) S. Jin, X. Sui, G. C. Haug, V. D. Nguyen, H. T. Dang, H. D. Arman and O. V. Larionov, *ACS Catal.*, 2022, **12**, 285; (*f*) F. F. Mulks, M. Melaimi, X. Yan, M.-H. Baik and G. Bertrand, *J. Org. Chem.*, 2023, **88**, 2535.
25 (*a*) S. Byun, M. U. Hwang, H. R. Wise, A. V. Bay, P. H.-Y. Cheong and K. A. Scheidt, *Angew. Chem., Int. Ed.*, 2023, **62**, e202312829; (*b*) X. Liu, S. Xu, H. Chen and Y. Yang, *ACS Catal.*, 2024, **14**, 9144; (*c*) Y. Xu, H. Chen, L. Yu, X. Peng, J. Zhang, Z. Xing, Y. Bao, A. Liu, Y. Zhao, C. Tian, Y. Liang and X. Huang, *Nature*, 2024, **625**, 74; (*d*) C.-B. Li, X.-N. Li, Z.-C. Li, J. Li, Z.-X. Wang, Z.-H. Gao and S. Ye, *Angew. Chem., Int. Ed.*, 2025, e202421151.
26 C. E. I. Knappke, A. J. Arduengo III, H. Jiao, J.-M. Neudörfl and A. J. von Wangelin, *Synthesis*, 2011, 3784.
27 (*a*) D. G. Boucher, A. D. Pendergast, X. Wu, Z. A. Nguyen, R. G. Jadhav, S. Lin, H. S. White and S. D. Minteer, *J. Am. Chem. Soc.*, 2023, **145**, 17665; (*b*) J. Demarteau, A. Debuigne and C. Detrembleur, *Chem. Rev.*, 2019, **119**, 6906; (*c*) F. T. T. Ng, G. L. Rempel, C. Mancuso and J. Halpern, *Organometallics*, 1990, **9**, 2762.
28 X. Li, Y. Mao, P. Fan and C. Wang, *Eur. J. Org. Chem.*, 2022, e202200214.