Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2022, **13**, 775

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

Received 12th October 2021
Accepted 20th December 2021

DOI: 10.1039/d1sc05629h

rsc.li/chemical-science

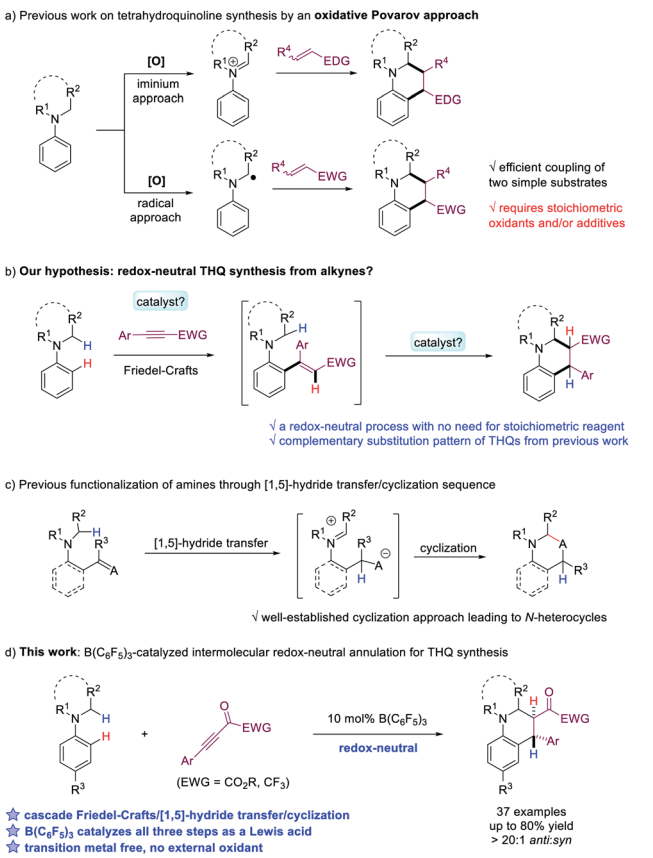
Borane-catalyzed cascade Friedel–Crafts alkylation/[1,5]-hydride transfer/Mannich cyclization to afford tetrahydroquinolines†

Bei-Bei Zhang, Shuo Peng, Feiyi Wang, Cuifen Lu, Junqi Nie, Zuxing Chen, Guichun Yang* and Chao Ma *

An unprecedented redox-neutral annulation reaction of tertiary anilines with electron-deficient alkynes was developed that proceeds through a cascade Friedel–Crafts alkylation/[1,5]-hydride transfer/Mannich cyclization sequence. Under $B(C_6F_5)_3$ catalysis, a range of functionalized 1,2,3,4-tetrahydroquinolines were facilely constructed in moderate to good yields with exclusive 3,4-*anti*-stereochemistry. The commercial availability of the catalyst and the high atom and step economy of the procedure, together with metal-free and external oxidant-free conditions, make this an attractive method in organic synthesis.

Introduction

Tetrahydroquinoline (THQ) is one of the most valuable N-heterocyclic scaffolds that exists in a large number of natural products and bioactive molecules.[1] Due to its importance, development of efficient methods to construct the THQ skeleton has been extensively explored in organic synthesis. Various approaches have been established, including intramolecular cyclization,[2] Povarov reactions,[3] hydrogenation of quinolines[4] and others.[5] Among all the strategies, the oxidative Povarov reaction, a dehydrogenative [4 + 2] annulation reaction between *N*-alkylanilines and alkenes, represents a promising protocol for the construction of THQs from simple starting materials (Scheme 1a).[6] In this reaction, two new C–C bonds were formed *via* a cascade sp^3 and sp^2 C–H functionalization process. However, such a process requires stoichiometric oxidants to convert *N*-alkylanilines to iminium ions or α-aminoalkyl radical intermediates, which then undergo reaction with activated olefins. The development of redox-neutral [4 + 2] annulation reaction for the synthesis of THQs, which avoids the use of external oxidants, will be highly desirable. We hypothesize that the combination of *N*-alkylanilines and electron-deficient alkynes represents a promising approach (Scheme 1b). In addition to the attractive feature of high atom-economy, it is worth noting that THQs produced in this fashion also possess complementary substitution patterns compared to previous work. However, challenges need to be addressed to identify an effective catalytic system that promotes an efficient cascade Friedel–Crafts type addition to the alkyne followed by cyclization.



Scheme 1 Different catalytic strategies for THQ synthesis.

Hubei Collaborative Innovation Centre for Advanced Organic Chemical Materials, College of Chemistry and Chemical Engineering, Ministry of Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, Hubei University, Wuhan, 430062, P. R. China. E-mail: machao@hubu.edu.cn; yangguichun@hubu.edu.cn

† Electronic supplementary information (ESI) available. CCDC 2114097 and 2114110. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc05629h

For the proposed cyclization step, it is noteworthy that a [1,5]-hydride transfer/cyclization process has been developed into a powerful and versatile protocol for the synthesis of structurally diverse O- or N-heterocycles including THQs in recent years (Scheme 1c).[7] In such processes, *ortho*-substituted functionalities such as aldehydes, ketones, imines and electron-deficient alkenes serve as hydride acceptors to construct N-heterocycles with high efficiency and fidelity.[8] However, it is necessary to construct *ortho*-disubstituted substrates for intramolecular cyclization to proceed in literature precedents. If the substrate synthesis from readily available building blocks can be coupled with the cyclization into a cascade process, it should lead to a highly attractive and flexible synthesis of valuable heterocycles.

The last decade has witnessed an explosive development of tris(pentafluorophenyl)borane-catalyzed reactions.[9] In addition, $B(C_6F_5)_3$-promoted hydride transfer of amines and *N*-alkylanilines[10] has also resulted in various step- and atom-economical transformations of these valuable substrates.[11–14] In particular, $B(C_6F_5)_3$-catalyzed intramolecular cyclization of *ortho*-substituted *N*,*N*-dialkyl arylamines *via* hydride transfer to afford tetrahydroquinoline derivatives was realized by the Paradies group and Wang group, respectively.[15,16] Nevertheless, the synthesis of tetrahydroquinolines through $B(C_6F_5)_3$-catalyzed intermolecular redox-neutral annulation still remains elusive in the literature.

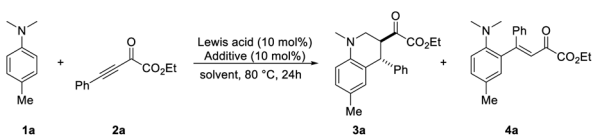
Herein, we report an unprecedented intermolecular redox-neutral annulation reaction of *N*-alkylanilines with electron-deficient alkynes catalyzed by $B(C_6F_5)_3$ to deliver a range of poly-substituted tetrahydroquinolines in good to high yields (Scheme 1d). Our mechanistic studies indicate that this efficient and flexible [4 + 2] annulation reaction involves a cascade Friedel–Crafts alkylation/[1,5]-hydride transfer/Mannich cyclization sequence. In all the steps, $B(C_6F_5)_3$ serves as an effective Lewis acid catalyst with the cooperative effect from TMSOTf.

Results and discussion

At the outset, we intend to study the annulation reaction of *N*-alkylanilines with alkynes by using $B(C_6F_5)_3$ as the catalyst. To our delight, the reaction between *N*,*N*-4-trimethylaniline **1a** and β,γ-alkynyl-α-ketoester **2a** occurred smoothly with 10 mol% $B(C_6F_5)_3$ in toluene at 80 °C. The desired 3,4-*anti*-tetrahydroquinoline **3a** was obtained in 46% yield and > 20 : 1 dr with concomitant formation of the conjugate addition product **4a** (Table 1, entry 1). Several other common Lewis acids such as $Cu(OTf)_2$, $Mg(OTf)_2$, $In(OTf)_3$ and $BF_3\cdot OEt_2$ turned out to be ineffective for the reaction (entries 2–5). Gratifyingly, the use of a catalytic amount of TMSOTf as an additive, which has been proved to improve the reaction efficiency by the Wang group[15b] and the Oestreich group,[12g] was beneficial for the [4 + 2] annulation reaction, affording the desired product **3a** in 69% yield, while no byproduct **4a** was observed (entry 6). Next, the solvent effect was evaluated. While dioxane, *m*-xylene and DCM gave slightly lower or similar yields (entries 7–9), no product or significantly decreased yield was obtained by the use of MeCN or THF as the solvent (entries 10–11). No improvement was obtained by increasing the amount of TMSOTf (entry 12). It is noteworthy that no product could be detected when TMSOTf itself was employed as the catalyst (entry 13).

With the optimal conditions in hand (Table 1, entry 6), the generality of this $B(C_6F_5)_3$-catalyzed redox-neutral annulation reaction between *N*-alkylanilines **1** and electron-deficient alkynes **2** was investigated (Scheme 2). Various *para*-

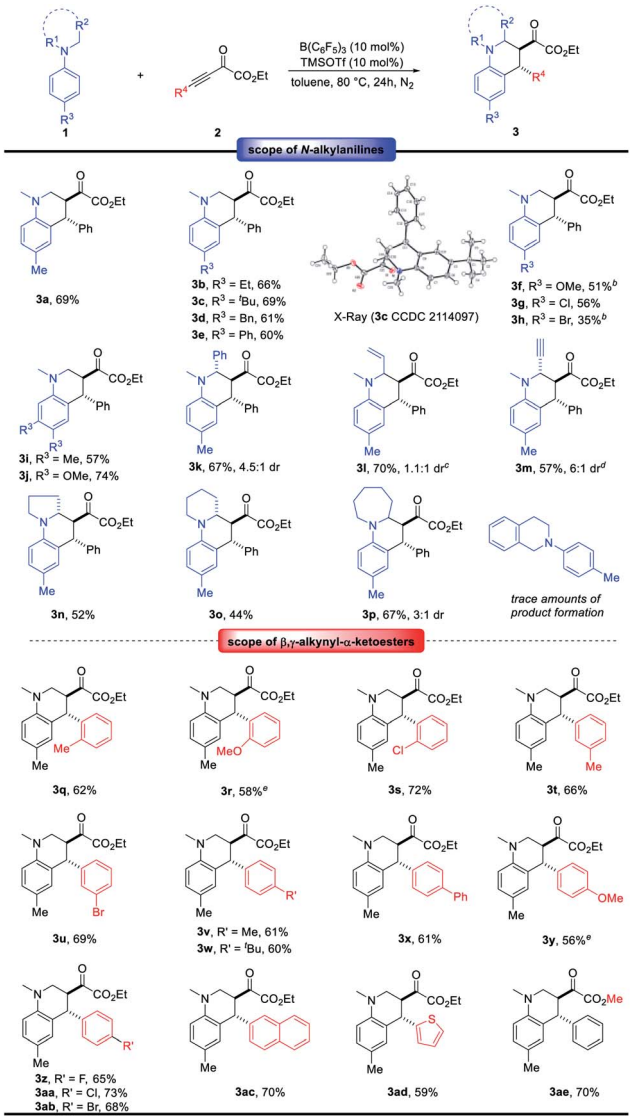
Table 1 Optimization of the reaction conditions[a]



1a 2a 3a 4a

Entry	Lewis acid	Additive	Solvent	Yield[b] of **3a** (%)	Yield[b] of **4a** (%)
1	$B(C_6F_5)_3$	None	Toluene	46	27
2	$Cu(OTf)_2$	None	Toluene	<2	<2
3	$Mg(OTf)_2$	None	Toluene	<2	<2
4	$In(OTf)_3$	None	Toluene	<2	<2
5	$BF_3\cdot OEt_2$	None	Toluene	<2	<2
6	**$B(C_6F_5)_3$**	**TMSOTf**	**Toluene**	**69**	**<2**
7	$B(C_6F_5)_3$	TMSOTf	Dioxane	58	19
8	$B(C_6F_5)_3$	TMSOTf	*m*-Xylene	63	<5
9	$B(C_6F_5)_3$	TMSOTf	DCM	69	<2
10	$B(C_6F_5)_3$	TMSOTf	MeCN	<2	<2
11	$B(C_6F_5)_3$	TMSOTf	THF	<5	10
12[c]	$B(C_6F_5)_3$	TMSOTf	Toluene	68	<2
13	None	TMSOTf	Toluene	<2	<2

[a] Unless otherwise noted, the reactions were carried out by stirring **1a** (0.24 mmol), **2a** (0.2 mmol), $B(C_6F_5)_3$ (0.02 mmol) and additive (0.02 mmol) in 1 mL of solvent at 80 °C for 24 hours under N_2. [b] Isolated yield, >20 : 1 dr of **3a** was determined by ^1H NMR. [c] With 20 mol% TMSOTf.

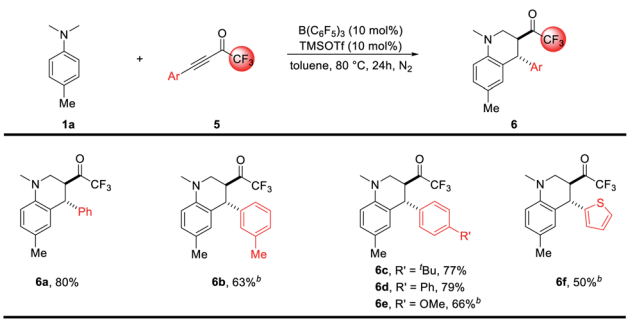


Scheme 2 Scope of redox-neutral annulation between *N*-alkylanilines and β,γ-alkynyl-α-ketoesters. [a] See Table 1 and ESI† for a detailed procedure, unless otherwise noted, the dr of **3** was >20 : 1. [b] The reaction was performed with 10 mol% $B(C_6F_5)_3$ and 20 mol% TMSOTf for 48 hours. [c] The reaction was performed at 25 °C for 48 hours. [d] The reaction was performed with 15 mol% $B(C_6F_5)_3$ and 10 mol% TMSOTf at 25 °C for 72 hours. [e] The reaction was performed for 36 hours.

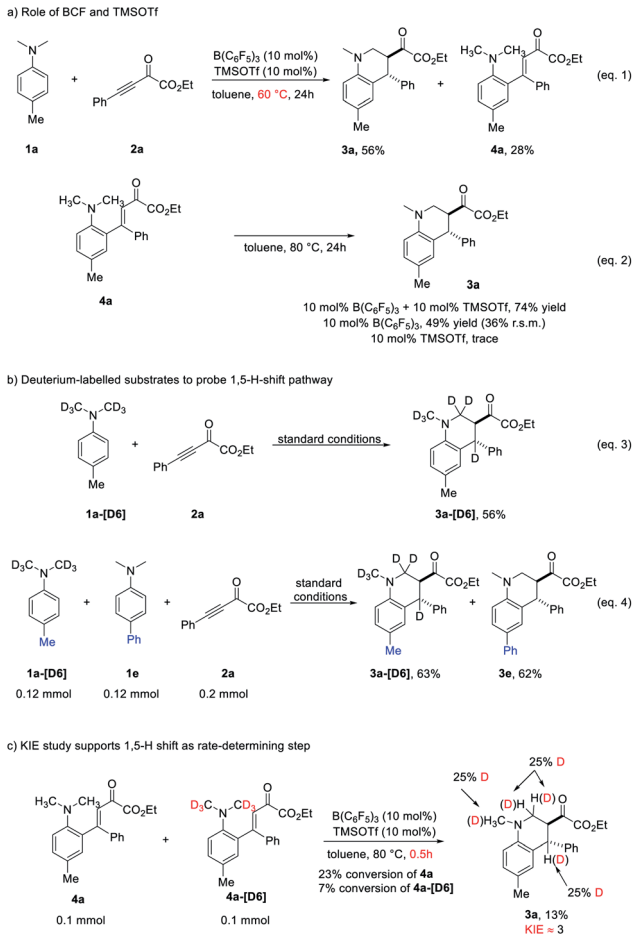
substituted *N*,*N*-dimethylanilines **1** were compatible in this reaction and delivered the corresponding products **3a–3g** in 51–69% yields. The structure of **3c** has been unambiguously confirmed by X-ray crystallographic analysis. A lower yield was obtained for 4-bromo-*N*,*N*-dimethylaniline. Disubstituted *N*,*N*-dimethylanilines underwent conjugate addition favorably at the sterically less demanding position, furnishing products **3i** and **3j** in 57 and 74% yields, respectively. When one of the methyl groups on the amino moiety was replaced by the benzyl group, the reaction proceeded chemoselectively at the benzyl group to form **3k** in 67% yield with 4.5 : 1 dr, which indicates the superior hydride donor capability of benzylic over primary C–H bonds.[8d,i,k,t] The structure of **3k** has been unambiguously confirmed by X-ray crystallographic analysis (see ESI†). Additionally, different functional groups on the amino moiety including alkene and alkyne were well tolerated under this catalytic system at ambient reaction temperature. The desired products **3l** and **3m** were obtained in moderate yields. Cyclic amine derivatives showed good reactivity in this reaction, and products **3n–3p** were obtained in 44–67% yields. When studying further *N*,*N*-dialkyl arylamines, we found that *N*-aryl tetrahydroisoquinoline was not compatible with the reaction conditions, and only trace amounts of product were observed. Next, the variation of β,γ-alkynyl-α-ketoesters **2** was studied. Substrates **2** containing electron-neutral, electron-donating and electron-withdrawing groups on the *ortho*-, *meta*- and *para*-positions on the aryl ring were well tolerated under the standard reaction conditions, giving products **3q–3ab** in 56–73% yields and high *anti* diastereoselectivity. In addition, 2-naphthyl and 2-thienyl substituents have been tested, providing products **3ac** and **3ad** in 70 and 59% yields, respectively. The reaction of methyl ester with **1a** led to the desired product **3ae** in 70% yield.

The redox-neutral annulation between *N*,*N*-4-trimethylaniline **1a** and trifluoromethyl-α,β-ynones **5** was also investigated. As exemplified in Scheme 3, the reactions went smoothly under the current $B(C_6F_5)_3$ catalytic system. An array of trifluoromethylated tetrahydroquinolines **6a–6f** were prepared in moderate to good yields with high diastereoselectivity (>20 : 1, *anti* : *syn*).

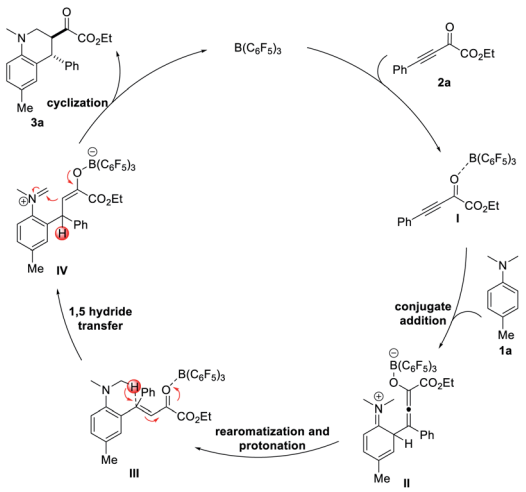
To shed light on the mechanism of the redox-neutral annulation, a series of control experiments were performed (Scheme 4). When the reaction between **1a** and **2a** was performed at a slightly lower temperature (60 °C) for 24 hours, the starting material **2a** was consumed and the desired product **3a** was obtained in diminished yield with concomitant formation of **4a** (Scheme 4a, eqn (1)). Subsequently, annulation of **4a** could occur under the standard conditions to generate **3a** in 74% yield (Scheme 4a, eqn (2)). These results indicated that a cascade Friedel–Crafts alkylation/intramolecular hydride transfer/Mannich cyclization sequence was included in the redox-neutral [4 + 2] annulation reaction. The hydride transfer is probably the rate-determining step. We performed the intra-



Scheme 3 Scope of redox-neutral annulation between *N*-alkylanilines and trifluoromethyl-α,β-ynones. [a] See Table 1 and ESI† for a detailed procedure, the dr of **6** was >20 : 1. [b] The reaction was performed with 10 mol% $B(C_6F_5)_3$ and 20 mol% TMSOTf for 52 hours.



Scheme 4 Control experiments.



Scheme 5 Proposed catalytic cycle.

$B(C_6F_5)_3$ (Scheme 4a, eqn (2)). The reactivity of intramolecular cyclization could be enhanced in the presence of TMSOTf. However, probably due to the relatively weak Lewis acidity, TMSOTf itself was unable to promote the reaction. Next, the reaction of isotope-labelled **1a-[D6]** with **2a** under standard conditions was performed, giving **3a-[D6]** in 56% yield with deuterium exclusively transferred to the benzylic position (Scheme 4b, eqn (3)). Besides, the reaction of **2a** with a mixture of **1a-[D6]** and **1e** under standard conditions provided a mixture of **3a-[D6]** and **3e** without exchange of H/D (Scheme 4b, eqn (4)). These observations suggested that a [1,5]-hydride shift process was involved in the reaction and excluded the hydride abstraction mediated by the borane.[15] A crossover experiment using **4a** and **4a-[D6]** was performed then in a shortened reaction time (Scheme 4c). At low conversions, a significant kinetic isotope effect (KIE) of 3.0 was observed, revealing that the [1,5]-hydride transfer could be involved in the rate-determining step.

Based on the experimental results and previous report,[15c] a plausible mechanism for the $B(C_6F_5)_3$-catalyzed redox-neutral [4 + 2] annulation of *N*-alkylanilines and electron-deficient alkynes is proposed in Scheme 5. The reaction is initiated by the activation of β,γ-alkynyl-α-ketoester **2a** with $B(C_6F_5)_3$, which results in the formation of electrophilic alkyne **I**. *N*,*N*-4-trimethylaniline **1a** reacts with intermediate **I** to form allenolate intermediate **II**. Subsequent rearomatization and protonation of the allenolate generate intermediate **III**. 1,5-Hydride transfer then occurs with the assistance of $B(C_6F_5)_3$ to afford iminium enolate **IV**. Final intramolecular Mannich cyclization produced tetrahydroquinoline product **3a** with the regeneration of $B(C_6F_5)_3$.

Conclusions

In summary, we have developed a $B(C_6F_5)_3$-catalyzed cascade reaction of tertiary anilines with electron-deficient alkynes to construct poly-substituted tetrahydroquinoline derivatives with excellent step and atom economy. This redox neutral reaction involves a sequential Friedel–Crafts alkylation/[1,5]-hydride transfer/Mannich cyclization sequence without using a transition metal or an external oxidant. An array of 1,2,3,4-tetrahydroquinolines were accessed in high efficiency and diastereoselectivity.

Data availability

All experimental and characterization data in this article are available in the ESI.† Crystallographic data for compounds **3c** and **3k** have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under accession numbers CCDC 2114097 and 2114110, respectively.†

Author contributions

B.-B. Z. performed the synthetic experiments and analysed the data, with help from S. P., F. W., C. L., J. N. and Z. C.; C. M. and G. Y. directed the project and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the generous financial support from the National Natural Science Foundation of China (21901066 and 21702053) and the Hubei Provincial Department of Education project (Q20181003). We thank Professor Yu Zhao for helpful discussions.

Notes and references

1 (*a*) V. Sridharan, P. A. Suryavanshi and J. C. Menéndez, *Chem. Rev.*, 2011, **111**, 7157–7259; (*b*) I. Muthukrishnan, V. Sridharan and J. C. Menéndez, *Chem. Rev.*, 2019, **119**, 5057–5191.

2 (*a*) M. Kretzschmar, F. Hofmann, D. Moock and C. Schneider, *Angew. Chem., Int. Ed.*, 2018, **57**, 4774–4778; (*b*) S. C. Cosgrove, J. M. C. Plane and S. P. Marsden, *Chem. Sci.*, 2018, **9**, 6647–6652; (*c*) J.-S. Yu, M. Espinosa, H. Noda and M. Shibasaki, *J. Am. Chem. Soc.*, 2019, **141**, 10530–10537; (*d*) F. Mühlhaus, H. Weißbarth, T. Dahmen, G. Schnakenburg and A. Gansäuer, *Angew. Chem., Int. Ed.*, 2019, **58**, 14208–14212; (*e*) W. Liu, P. Zhou, J. Lang, S. Dong, X. Liu and X. Feng, *Chem. Commun.*, 2019, **55**, 4479–4482; (*f*) Y.-H. Wang, J.-S. Tian, P.-W. Tan, Q. Cao, X.-X. Zhang, Z.-Y. Cao, F. Zhou, X. Wang and J. Zhou, *Angew. Chem., Int. Ed.*, 2020, **59**, 1634–1643; (*g*) R. K. Tak, F. Amemiya, H. Noda and M. Shibasaki, *Chem. Sci.*, 2021, **12**, 7809–7817.

3 (*a*) T. S. Bush, G. P. A. Yap and W. J. Chain, *Org. Lett.*, 2018, **20**, 5406–5409; (*b*) P. Cerfontaine, F. Driessens, M.-F. Deltent and S. Petit, *Org. Process Res. Dev.*, 2020, **24**, 807–816; (*c*) J.-X. Huang, K.-Q. Hou, Q.-L. Hu, X.-P. Chen, J. Li, A. S. C. Chan and X.-F. Xiong, *Org. Lett.*, 2020, **22**, 1858–1862; (*d*) Y.-Q. Zhang, Y.-P. Zhang, Y.-X. Zheng, Z.-Y. Li and L.-W. Ye, *Cell Rep. Phys. Sci.*, 2021, **2**, 100448.

4 (*a*) I. Sorribes, L. Liu, A. Doménech-Carbó and A. Corma, *ACS Catal.*, 2018, **8**, 4545–4557; (*b*) H. Wang, Y. Huang, Q. Jiang, X. Dai and F. Shi, *Chem. Commun.*, 2019, **55**, 3915–3918; (*c*) C. Liu, M. Wang, S. Liu, Y. Wang, Y. Peng, Y. Lan and Q. Liu, *Angew. Chem., Int. Ed.*, 2021, **60**, 5108–5113.

5 (*a*) M.-M. Zhang, Y.-N. Wang, B.-C. Wang, X.-W. Chen, L.-Q. Lu and W.-J. Xiao, *Nat. Commun.*, 2019, **10**, 2716; (*b*) E. M. Larin, J. Loup, I. Polishchuk, R. J. Ross, A. Whyte and M. Lautens, *Chem. Sci.*, 2020, **11**, 5716–5723; (*c*) K. Yuan, F. Dong, X. Yin, S.-S. Li, L. Wang and L. Xu, *Org. Chem. Front.*, 2020, **7**, 3868–3873; (*d*) X. Yan, L. Ge, M. Castiñeira Reis and S. R. Harutyunyan, *J. Am. Chem. Soc.*, 2020, **142**, 20247–20256; (*e*) Q.-F. Xu-Xu, X. Zhang and S.-L. You, *Org. Lett.*, 2020, **22**, 1530–1534; (*f*) S. N. Fairuz Binte Sheikh Ismail, B. Yang and Y. Zhao, *Org. Lett.*, 2021, **23**, 2884–2889.

6 (*a*) S. Murata, M. Miura and M. Nomura, *J. Org. Chem.*, 1989, **54**, 4700–4702; (*b*) L. Huang, X. Zhang and Y. Zhang, *Org. Lett.*, 2009, **11**, 3730–3733; (*c*) M. Nishino, K. Hirano, T. Satoh and M. Miura, *J. Org. Chem.*, 2011, **76**, 6447–6451; (*d*) S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran and M. Rueping, *J. Am. Chem. Soc.*, 2013, **135**, 1823–1829; (*e*) C. Min, A. Sanchawala and D. Seidel, *Org. Lett.*, 2014, **16**, 2756–2759; (*f*) G.-Q. Xu, C.-G. Li, M.-Q. Liu, J. Cao, Y.-C. Luo and P.-F. Xu, *Chem. Commun.*, 2016, **52**, 1190–1193; (*g*) M.-N. Zhao, L. Yu, R.-R. Hui, Z.-H. Ren, Y.-Y. Wang and Z.-H. Guan, *ACS Catal.*, 2016, **6**, 3473–3477; (*h*) P. Huang, P. Wang, S. Wang, S. Tang and A. Lei, *Green Chem.*, 2018, **20**, 4870–4874; (*i*) X.-L. Yang, J.-D. Guo, T. Lei, B. Chen, C.-H. Tung and L.-Z. Wu, *Org. Lett.*, 2018, **20**, 2916–2920; (*j*) J. Li, Z. Gu, X. Zhao, B. Qiao and Z. Jiang, *Chem. Commun.*, 2019, **55**, 12916–12919; (*k*) J. Y. Hwang, A. Y. Ji, S. H. Lee and E. J. Kang, *Org. Lett.*, 2020, **22**, 16–21.

7 For selected recent reviews, see: (*a*) B. Peng and N. Maulide, *Chem.–Eur. J.*, 2013, **19**, 13274–13287; (*b*) M. C. Haibach and D. Seidel, *Angew. Chem., Int. Ed.*, 2014, **53**, 5010–5036; (*c*) S. J. Kwon and D. Y. Kim, *Chem. Rec.*, 2016, **16**, 1191–1203; (*d*) X.-D. An and J. Xiao, *Org. Chem. Front.*, 2021, **8**, 1364–1383, for a recent general review on C–H bond functionalization of amines, see: (*e*) S. Dutta, B. Li, D. R. L. Rickertsen, D. A. Valles and D. Seidel, *SynOpen*, 2021, **05**, 173–228.

8 For pioneer work, see: (*a*) W. D. Verboom, N. Reinhoudt, R. Visser and S. Harkema, *J. Org. Chem.*, 1984, **49**, 269–276; (*b*) W. H. N. Nijhuis, W. Verboom and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1987, **109**, 3136–3138, for selected examples, see: (*c*) S. J. Pastine, K. M. McQuaid and D. Sames, *J. Am. Chem. Soc.*, 2005, **127**, 12180–12181; (*d*) S. Murarka, C. Zhang, M. D. Konieczynska and D. Seidel, *Org. Lett.*, 2009, **11**, 129–132; (*e*) P. A. Vadola and D. Sames, *J. Am. Chem. Soc.*, 2009, **131**, 16525–16528; (*f*) S. Murarka, I. Deb, C. Zhang and D. Seidel, *J. Am. Chem. Soc.*, 2009, **131**, 13226–13227; (*g*) Y. K. Kang, S. M. Kim and D. Y. Kim, *J. Am. Chem. Soc.*, 2010, **132**, 11847–11849; (*h*) G. Zhou and J. Zhang, *Chem. Commun.*, 2010, **46**, 6593–6595; (*i*) W. Cao, X. Liu, W. Wang, L. Lin and X. Feng, *Org. Lett.*, 2011, **13**, 600–603; (*j*) M. C. Haibach, I. Deb, C. K. De and D. Seidel, *J. Am. Chem. Soc.*, 2011, **133**, 2100–2103; (*k*) K. Mori, K. Ehara, K. Kurihara and T. Akiyama, *J. Am. Chem. Soc.*, 2011, **133**, 6166–6169; (*l*) I. D. Jurberg, B. Peng, E. Wostefeld, M. Wasserloos and N. Maulide, *Angew. Chem., Int. Ed.*, 2012, **51**, 1950–1953; (*m*) K. Mori, T. Kawasaki and T. Akiyama, *Org. Lett.*, 2012, **14**, 1436–1439; (*n*) Y.-Y. Han, W.-Y. Han, X. Hou, X.-M. Zhang and W.-C. Yuan, *Org. Lett.*, 2012, **14**, 4054–4057; (*o*) K. Mori, K. Kurihara, S. Yabe, M. Yamanaka and T. Akiyama, *J. Am. Chem. Soc.*, 2014, **136**, 3744–3747; (*p*) K. Mori, N. Umehara and T. Akiyama, *Adv. Synth. Catal.*, 2015, **357**, 901–906; (*q*) C. W. Suh, S. J. Kwon and D. Y. Kim, *Org. Lett.*, 2017, **19**, 1334–1337; (*r*) S.-S. Li, L. Zhou, L. Wang, H. Zhao, L. Yu and J. Xiao, *Org. Lett.*, 2018, **20**, 138–141; (*s*) K. Mori, R. Isogai, Y. Kamei, M. Yamanaka and T. Akiyama, *J. Am. Chem. Soc.*, 2018, **140**, 6203–6207; (*t*) T. Yoshida and K. Mori, *Chem. Commun.*, 2018, **54**, 12686–12689; (*u*) S. Zhao, X. Wang, P. Wang, G. Wang, W. Zhao, X. Tang and M. Guo, *Org. Lett.*, 2019, **21**, 3990–3993; (*v*) M. Kataoka, Y. Otawa, N. Ido and K. Mori, *Org. Lett.*, 2019, **21**, 9334–9338; (*w*) K. Yokoo and K. Mori, *Org. Lett.*, 2020, **22**, 244–248.

9 For selected reviews, see: (*a*) R. L. Melen, *Chem. Commun.*, 2014, **50**, 1161–1174; (*b*) M. Oestreich, J. Hermeke and J. Mohr, *Chem. Soc. Rev.*, 2015, **44**, 2202–2220; (*c*) D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306–316; (*d*) J. R. Lawson and R. L. Melen, *Inorg. Chem.*, 2017, **56**, 8627–8643; (*e*) J. Lam, K. M. Szkop, E. Mosaferi and D. W. Stephan, *Chem. Soc. Rev.*, 2019, **48**, 3592–3612; (*f*) H. Fang and M. Oestreich, *Chem. Sci.*, 2020, **11**, 12604–12615; (*g*) Y. Ma, S.-J. Lou and Z. Hou, *Chem. Soc. Rev.*, 2021, **50**, 1945–1967; (*h*) G. Kumar, S. Roy and I. Chatterjee, *Org. Biomol. Chem.*, 2021, **19**, 1230–1267.

10 For pioneer work, see: (*a*) N. Millot, C. C. Santini, B. Fenet and J. M. Basset, *Eur. J. Inorg. Chem.*, 2002, 3328–3335, for selected reviews, see: (*b*) F. Focante, P. Mercandelli, A. Sironi and L. Resconi, *Coord. Chem. Rev.*, 2006, **250**, 170–188; (*c*) S. Basak, L. Winfrey, B. A. Kustiana, R. L. Melen, L. C. Morrill and A. P. Pulis, *Chem. Soc. Rev.*, 2021, **50**, 3720–3737.

11 (*a*) M. Shang, J. Z. Chan, M. Cao, Y. Chang, Q. Wang, B. Cook, S. Torker and M. Wasa, *J. Am. Chem. Soc.*, 2018, **140**, 10593–10601; (*b*) J. Z. Chan, A. Yesilcimen, M. Cao, Y. Zhang, B. Zhang and M. Wasa, *J. Am. Chem. Soc.*, 2020, **142**, 16493–16505; (*c*) Y. Aramaki, N. Imaizumi, M. Hotta, J. Kumagai and T. Ooi, *Chem. Sci.*, 2020, **11**, 4305–4311; (*d*) G. Wicker, R. Schoch and J. Paradies, *Org. Lett.*, 2021, **23**, 3626–3630.

12 (*a*) J. Zhang, S. Park and S. Chang, *J. Am. Chem. Soc.*, 2018, **140**, 13209–13213; (*b*) R. Li, Y. Chen, K. Jiang, F. Wang, C. Lu, J. Nie, Z. Chen, G. Yang, Y.-C. Chen, Y. Zhao and C. Ma, *Chem. Commun.*, 2019, **55**, 1217–1220; (*c*) Y. Chang, A. Yesilcimen, M. Cao, Y. Zhang, B. Zhang, J. Z. Chan and M. Wasa, *J. Am. Chem. Soc.*, 2019, **141**, 14570–14575; (*d*) M. Zhou, S. Park and L. Dang, *Org. Chem. Front.*, 2020, **7**, 944–952; (*e*) Y. Chen, H.-L. Wan, Y. Huang, S. Liu, F. Wang, C. Lu, J. Nie, Z. Chen, G. Yang and C. Ma, *Org. Lett.*, 2020, **22**, 7797–7803; (*f*) Y. Chang, M. Cao, J. Z. Chan, C. Zhao, Y. Wang, R. Yang and M. Wasa, *J. Am. Chem. Soc.*, 2021, **143**, 2441–2455; (*g*) H. Fang, K. Xie, S. Kemper and M. Oestreich, *Angew. Chem., Int. Ed.*, 2021, **60**, 8542–8546.

13 (*a*) A. F. G. Maier, S. Tussing, T. Schneider, U. Flörke, Z.-W. Qu, S. Grimme and J. Paradies, *Angew. Chem., Int. Ed.*, 2016, **55**, 12219–12223; (*b*) M. Kojima and M. Kanai, *Angew. Chem., Int. Ed.*, 2016, **55**, 12224–12227.

14 (*a*) J. M. Farrell, Z. M. Heiden and D. W. Stephan, *Organometallics*, 2011, **30**, 4497–4500; (*b*) Y. Han, S. Zhang, J. He and Y. Zhang, *J. Am. Chem. Soc.*, 2017, **139**, 7399–7407; (*c*) T. Wang, L. Wang, C. G. Daniliuc, K. Samigullin, M. Wagner, G. Kehr and G. Erker, *Chem. Sci.*, 2017, **8**, 2457–2463; (*d*) S. Zhang, Y. Han, J. He and Y. Zhang, *J. Org. Chem.*, 2018, **83**, 1377–1386; (*e*) J. Zhang and S. Chang, *J. Am. Chem. Soc.*, 2020, **142**, 12585–12590; (*f*) S. Basak, A. Alvarez-Montoya, L. Winfrey, R. L. Melen, L. C. Morrill and A. P. Pulis, *ACS Catal.*, 2020, **10**, 4835–4840.

15 (*a*) A. F. G. Maier, S. Tussing, H. Zhu, G. Wicker, P. Tzvetkova, U. Flörke, C. G. Daniliuc, S. Grimme and J. Paradies, *Chem.–Eur. J.*, 2018, **24**, 16287–16291; (*b*) J.-J. Tian, N.-N. Zeng, N. Liu, X.-S. Tu and X.-C. Wang, *ACS Catal.*, 2019, **9**, 295–300, for $B(C_6F_5)_3$ catalyzed [1,5]-hydride transfer/cyclization of *ortho*-substituted *N*-alkylanilines, see: (*c*) R. Zhou and J. Paradies, *Eur. J. Org. Chem.*, 2021, 6334–6339.

16 For other examples on $B(C_6F_5)_3$-catalyzed synthesis of tetrahydroquinolines *via* hydrosilylation or hydroboration, see: (*a*) N. Gandhamsetty, S. Joung, S.-W. Park, S. Park and S. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 16780–16783; (*b*) N. Gandhamsetty, S. Park and S. Chang, *Synlett*, 2017, **28**, 2396–2400; (*c*) F. Ding, Y. Zhang, R. Zhao, Y. Jiang, R. L.-Y. Bao, K. Lin and L. Shi, *Chem. Commun.*, 2017, **53**, 9262–9264; (*d*) E. Kim, H. J. Jeon, S. Park and S. Chang, *Adv. Synth. Catal.*, 2020, **362**, 308–313.