


Cite this: *RSC Adv.*, 2020, 10, 16942

Received 31st March 2020

Accepted 23rd April 2020

DOI: 10.1039/d0ra02912b

rsc.li/rsc-advances

Dehydration in water: frustrated Lewis pairs directly catalyzed allylization of electron-rich arenes and allyl alcohols†

Hua Zhang,^{ab} Xiao-Yu Zhan,^{ab} Yu Dong,^{ab} Jian Yang,^{ab} Shuai He,^c Zhi-Chuan Shi,^c Xiao-Mei Zhang ^a and Ji-Yu Wang ^{*a}

A frustrated Lewis pair (FLP)-catalyzed allylation of allyl alcohols with electron-rich arenes has been developed. Interestingly, in this reaction, the electron-rich arenes and allyl alcohols are dehydrated in water. What's more, water was the sole byproduct of the reaction. In this protocol, various allyl alcohols can be converted into allyl cations and attacked by the electron-rich arenes to form aryl cation intermediates. Finally, the aryl cation intermediates are deprotonated to give the 1,3-diarylpropenes. In this protocol, indole allyl alcohols can undergo a bimolecular ring closure reaction, and structurally diverse tetrahydroindolo[3,2-*b*]carbazoles could be smoothly obtained. The reaction is not sensitive to oxygen and has been performed on a gram-scale.

Introduction

The Tsuji–Trost allylation reaction¹ is an important way to construct C–C and C–X bonds. In recent years, quite a few breakthroughs have been made in transition metal catalyzed allylation. Muzart,² Ma,³ Tunge,⁴ Bruneau,⁵ and Zhang⁶ *et al.* reviewed the latest developments in transition metal catalyzed allylation. At present, the majority of the existing reports are on the reaction of allyl alcohol derivatives as electrophiles.⁷ The allylation reaction with allyl alcohols as electrophiles has also been reported.⁸ It has attracted the attention of chemists for its good atom economy. At present, the directed distal allylation and alkylation of arenes have been developed.⁹ In addition, selective *para*-functionalization of arenes is also an important research direction.¹⁰ The metal-free catalyzed allylation reaction has attracted much attention due to its environmental friendliness, low toxicity and low catalyst loading. Several metal-free catalysts suitable for allylation reactions have been developed, including calix[*n*]arene sulfonic acids,¹¹ arylboronic acids,¹² water,¹³ 1,3-bis(carboxymethyl)imidazolium,¹⁴ graphene oxide CO₂H,¹⁵ and so on.

In recent years, tris(pentafluorophenyl)borane has received widespread attention as an unconventional, non-toxic, air-stable, water-tolerant, and thermal abiding Lewis acid.¹⁶ Piers reported in 1996 that tris(pentafluorophenyl)borane catalyzed

hydrosilation of aromatic aldehydes, ketones and esters.¹⁷ Oestreich demonstrated the mechanism of Piers and confirmed the stereochemical reversal of silicon using chiral silanes.¹⁸ Stephan demonstrated that the new strategy for chemical storage of hydrogen in macroboranes may involve Lewis acid–Lewis base synergistic reactivity. This strategy was used to reduce the imines, nitriles and aziridines.¹⁹ Fontaine introduced the concept of a frustrated Lewis pairs into hydrocarbon activation, and investigated the carbon dioxide hydroboration of FLP catalysts.²⁰ Repo conducted related research work on the frustrated Lewis pairs in the intramolecular.²¹ In addition, the frustrated Lewis pairs are also used to activate small molecules such as CO₂,²² NO,²³ N₂O,²⁴ SO₂,²⁵ alkenes,²⁶ and alkynes.²⁷ Although many advances have been made in the catalyzed reaction of frustrated Lewis pairs, there are currently no reports about allylation of electron-rich arenes by using the frustrated Lewis pairs as the catalyst.

At present, there are few reports on the reaction of macroboranes in water (Fig. 1). Tang's group reported α -aryl α -diazoesters O–H bond insertion catalyzed by tris(pentafluorophenyl)borane using water as solvent.²⁸ Our group has reported the coupling reaction of naphthoquinones with indoles in water catalyzed by (C₆F₅)₃B.²⁹ The use of macroboranes for dehydration in water may be in line with the concept of green chemistry. Herein, we strived to expand the application range of the frustrated Lewis pairs. What's more, we reported the allylation of a catalyzed electron-rich arenes with allyl alcohols in water by the frustrated Lewis pairs.

Results and discussion

We commenced our investigations by examining the allylation reaction between *N,N*-dimethylaniline (**1a**) and 1,3-diphenylallyl alcohol (**2a**) under various reaction conditions (Table 1). Initially

^aChengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, P. R. China. E-mail: jiyuwang@cioc.ac.cn

^bUniversity of Chinese Academy of Sciences, Beijing 100049, P. R. China

^cSouthwest Minzu University, Chengdu 610041, P. R. China

† Electronic supplementary information (ESI) available: Experimental procedures, spectroscopic data for all compounds. CCDC 1970838 and 1970839. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra02912b



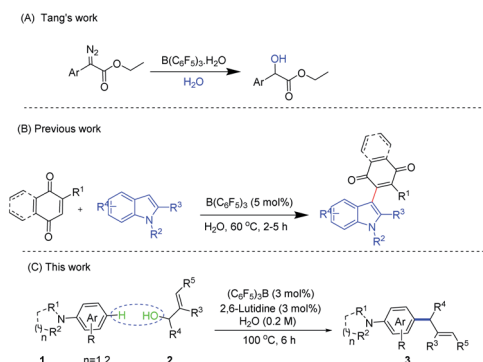
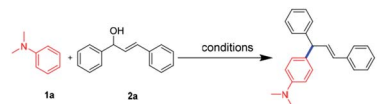


Fig. 1 The reaction of macroboranes in water.

the reaction was carried out under conditions in which $(\text{C}_6\text{F}_5)_3\text{B}$ was used as a catalyst and triphenylphosphine was used as a base. Gratifyingly, a 1,3-diarylpropene product **3a** was observed and isolated in 71% yield (entry 1). Tris(1,3,5-trifluorophenyl)borane and tris(2,4,6-trifluorophenyl)borane had a small amount of product formation as a catalyst (entries 2–3). Unfortunately, when the reaction was carried out in the absence of a base, the yield of the reaction was lowered (entries 4 and 8). It was demonstrated that the base could promote the reaction. Gratifyingly, when the reaction was carried out in water, the product could be obtained in a comparable yield to that in acetonitrile (entry 5). We attempted to

carry out the reaction without the addition of a catalyst and a base, but the yield of the product was greatly reduced (entry 6). In addition, when the catalyst was omitted, only a small amount of product was formed (entry 7). It was demonstrated that the coordination of the catalyst and the base was more favourable for the occurrence of allylation. Subsequently, we examined the effects of a series of bases on the reaction (entries 9–15). When the reaction was carried out under organic bases, the product was able to be obtained in moderate to excellent yields. But when we used inorganic base, the yield would be greatly reduced. This phenomenon indicated that the inorganic base could not form frustrated Lewis pairs with $(\text{C}_6\text{F}_5)_3\text{B}$ to catalyze the reaction. To our surprise, when the reaction was conducted in 2,6-lutidine as a base, we were pleased to find that the yield of **3a** could be dramatically improved to 90% (entry 10). What's more, when the temperature was adjusted to 60 °C, the expected product could not be observed and a lot of the starting materials remained (entry 16). Interestingly, when the temperature was raised to 100 °C, the yield of the product could be increased to 92% (entry 17). Unfortunately, when we performed the reaction using only 2,6-lutidine as a catalyst, we only got trace product (entry 18). In addition, we also tried to decrease the amount of $(\text{C}_6\text{F}_5)_3\text{B}$ and 2,6-lutidine to 1 mol% but the yield was lower (entry 19). At last, the optimal conditions were confirmed: **1a** (0.3 mmol), **2a** (0.3 mmol), $(\text{C}_6\text{F}_5)_3\text{B}$ (3 mol%), 2,6-lutidine (3 mol%), H_2O (1.5 ml), 6 h.

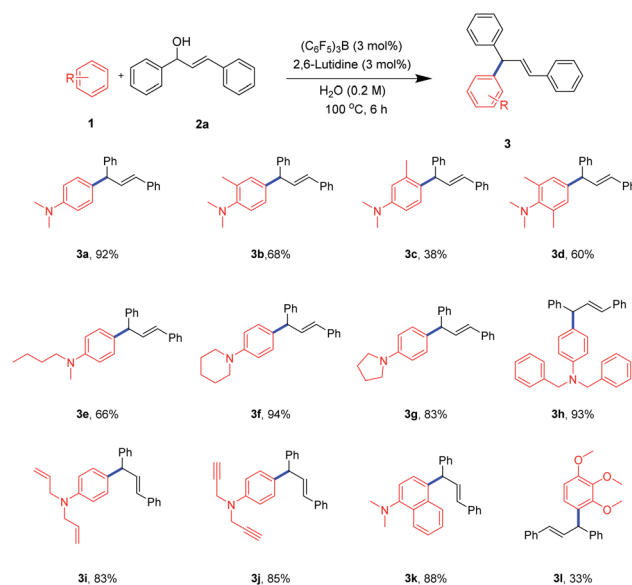
With the optimized reaction conditions in hand, we next set out to explore the universality of this method (Scheme 1). Therefore, a series of electron-rich arenes with significant structural diversity, including anilines and phenyl ether, were subjected to this process. When the reaction was carried out with *N,N*,2-trimethylaniline, we obtained 1,3-diarylpropene in moderate yield (**3b**). When we carried out the reaction with a *meta*-substitution or a 2,6-disubstituted *N,N*-dimethylaniline as a substrate, we were also able

Table 1 Optimization of the reaction conditions^{a,b}


Entry	Catalyst	Base	Solvent	<i>T</i> (°C)	Yield of 3a (%)
1	$(\text{C}_6\text{F}_5)_3\text{B}$	Ph_3P	CH_3CN	80	71
2	$(1,3,5\text{-C}_6\text{H}_2\text{F}_3)_3\text{B}$	Ph_3P	CH_3CN	80	Trace
3	$(2,4,6\text{-C}_6\text{H}_2\text{F}_3)_3\text{B}$	Ph_3P	CH_3CN	80	Trace
4	$(\text{C}_6\text{F}_5)_3\text{B}$	—	CH_3CN	80	58
5	$(\text{C}_6\text{F}_5)_3\text{B}$	Ph_3P	H_2O	80	74
6	—	—	H_2O	80	3
7	—	Ph_3P	H_2O	80	5
8	$(\text{C}_6\text{F}_5)_3\text{B}$	—	H_2O	80	59
9	$(\text{C}_6\text{F}_5)_3\text{B}$	Morpholine	H_2O	80	71
10	$(\text{C}_6\text{F}_5)_3\text{B}$	2,6-Lutidine	H_2O	80	90
11	$(\text{C}_6\text{F}_5)_3\text{B}$	DABCO	H_2O	80	88
12	$(\text{C}_6\text{F}_5)_3\text{B}$	Me_3P	H_2O	80	78
13	$(\text{C}_6\text{F}_5)_3\text{B}$	$\text{P}(\text{OPh})_3$	H_2O	80	86
14	$(\text{C}_6\text{F}_5)_3\text{B}$	$\text{P}(\text{HPh})_2$	H_2O	80	86
15	$(\text{C}_6\text{F}_5)_3\text{B}$	Na_2CO_3	H_2O	100	38
16	$(\text{C}_6\text{F}_5)_3\text{B}$	2,6-Lutidine	H_2O	60	0
17	$(\text{C}_6\text{F}_5)_3\text{B}$	2,6-Lutidine	H_2O	100	92
18	—	2,6-Lutidine	H_2O	100	Trace
19 ^b	$(\text{C}_6\text{F}_5)_3\text{B}$	2,6-Lutidine	H_2O	100	79

^a Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), catalyst (3 mol%), base (3 mol%), solvent (1.5 ml), 6 h; yield refers to isolated product.

^b $(\text{C}_6\text{F}_5)_3\text{B}$ (1 mol%) and 2,6-lutidine (1 mol%) was used.



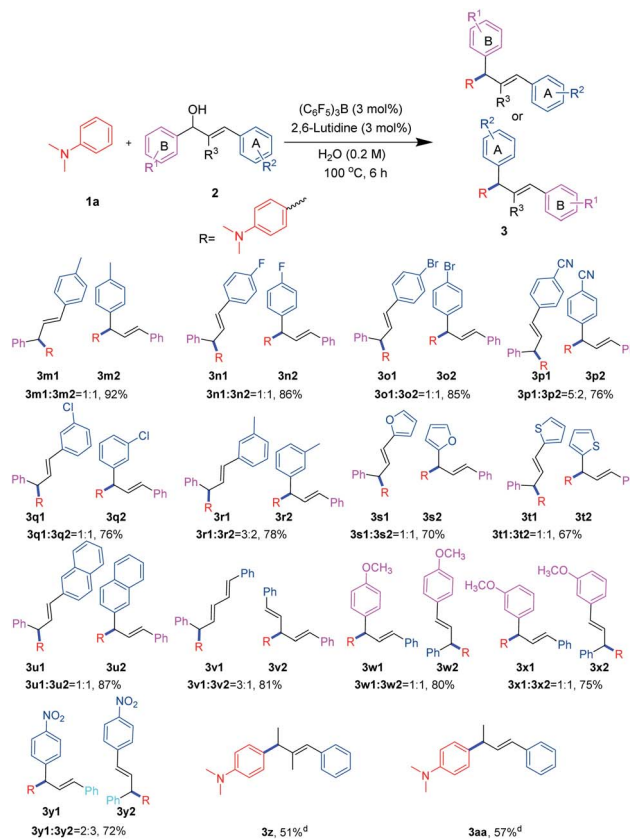
Scheme 1 Substrate scope of electron-rich arenes^{a,b}. ^aReaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), $(\text{C}_6\text{F}_5)_3\text{B}$ (3 mol%), 2,6-lutidine (3 mol%), H_2O (0.2 M), 100 °C, 6 h. ^bIsolated yields.



to obtain an allylated product, albeit at a low yields (**3c–3d**). It was possible that the steric hindrance effect of the *ortho* and *meta* positions prevented the attack of allyl cations and led to a decrease in yield. Further, this protocol could be suitably applied after the methyl group on N was replaced by *n*-butyl group, and the allylation product was obtained in a moderate yield (**3e**). Interestingly, the cyclic aniline compounds were capable of obtaining the allylation products in good to excellent yields (**3f–3g**). What's more, when a largely hindered benzyl group was attached to the N of the aniline, the product was obtained in excellent yield (**3h**). The exciting thing was that this protocol showed good compatibility with carbon–carbon double bonds and carbon–carbon triple bonds (**3i–3j**). Moreover, naphthylamine compound could also be used in this process and gave allylation product in good yield (**3k**). Furthermore, the 1,2,3-trimethoxybenzene was used, and the 1,3-diarylpropene product could also be formed, albeit at a low yield (**3l**, 33%). It might be due to the common steric hindrance effect of *ortho* and *meta* positions, which greatly reduced the yield. This is consistent with the previous results (**3c–3d**).

We next explored the scope of allyl alcohols (Scheme 2). Firstly, we focused our attention on the changes in the allyl alcohol A ring substituent. Unfortunately, the allyl alcohol double bond was shifted and we got a mixture of double bond migrations. TLC showed as only one point that cannot be separated. The ratio of the double bond migration product to non-migrated product was about 1 : 1 by NMR. The possible reason was that the aromatic rings at the ends of allyl cations had almost the same ability to stabilize the positive charge. When the *para* position of the phenyl group was bonded to an electron-donating substituted group, the product was able to be obtained in excellent yield (**3m**). In addition, the *para* position of the phenyl group was attached to an electron withdrawing group such as fluorine, bromine or cyano, and we could also obtain the products in moderate to good yields (**3n–3p**). In particular, the cyano group of the strong electron withdrawing group caused the uneven distribution of the allyl cation charge, resulting in a product ratio of 5 : 2. In addition, the *meta*-substituted benzene ring could also give the products in a moderate yields (**3q–3r**). Excitingly, this reaction also showed good compatibility with heterocycles (**3s–3t**). When the ring A was the naphthalene, we could also carry out the reaction in good yield (**3u**). When the reaction was carried out with (2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-ol, the product was able to be obtained in good yield (**3v**). Next, we would explore the effect of substituent on the B ring on the reaction. When the B ring was attached to an electron donating substituent, we were able to carry out the reaction in moderate to good yields (**3w–3x**). In addition, when the B ring was connected to the electron-withdrawing group, the product was also able to be obtained in moderate yield (**3y**). Unfortunately, alkyl allyl alcohol and polysubstituted allyl alcohol did not perform the reaction smoothly in water, but the product could be obtained in acetonitrile in moderate yields (**3z–3aa**).

The 3 position of indoles is electron-rich, and allylization of indoles have been reported more.³⁰ Herein, we focused our attention to the scope of indoles (Scheme 3). Gratifyingly, various indoles were well applicable in this protocol and were

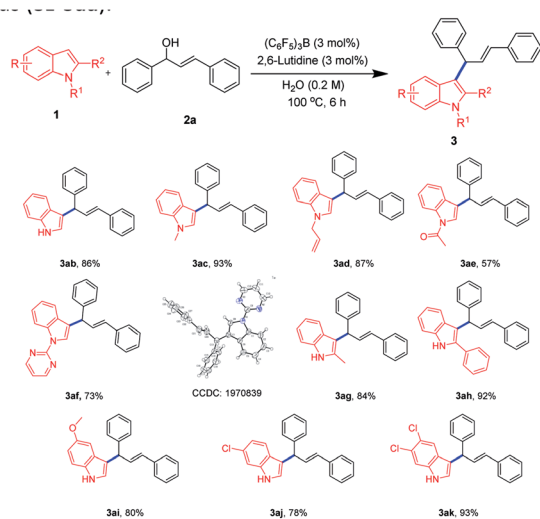


Scheme 2 Substrate scope of allyl alcohols^{a,b,c,d}. ^aReaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), (C₆F₅)₃B (3 mol%), 2,6-Lutidine (3 mol%), H₂O (0.2 M), 100 °C, 6 h. ^bIsolated yields. ^cMixture ratio determined by NMR. ^dAcetonitrile as solvent (seal).

regioselectively allylated to the 3 position of the indoles. In addition, the single-crystal structure of **3af**, **3al** further confirmed the allylation reaction.³¹ As an example, when N1 position of indoles was not attached to a substituent or attached to an electron-donating substituted group such as methyl, allyl, we could proceed smoothly in this process to deliver corresponding allylated products in good to excellent yields (**3ab–3ad**). When N1 position of indoles was substituted by electron-withdrawing groups such as acetyl and pyrimidine we were also able to obtain the products although the yields were slightly reduced (**3ae–3af**). It was possible that the electron-withdrawing group lowered the density of the electrons at the 3-position electrons, thereby reducing the attack activity of the allyl cations. Interestingly, when the C2 position of the indoles was substituted by a methyl group or a phenyl group, we could also obtain the products in a good to excellent yields, demonstrating that the steric hindrance at the C2 position had little effect on the reaction (**3ag–3ah**). In addition, when the C5- or C6-position of the indoles were separately substituted for the substituent, we could obtain the 3-allylated indoles at a good yields (**3ai–3aj**). Excitingly, when the C5 and C6 positions were substituted, we were able to obtain allylated indole in a superior yield (**3ak**).

Surprisingly, (*E*)-3-(1-methyl-1*H*-indol-2-yl)-1-phenylprop-2-en-1-ol (**2q**) and (*E*)-1-(4-bromophenyl)-3-(1-methyl-1*H*-indol-2-

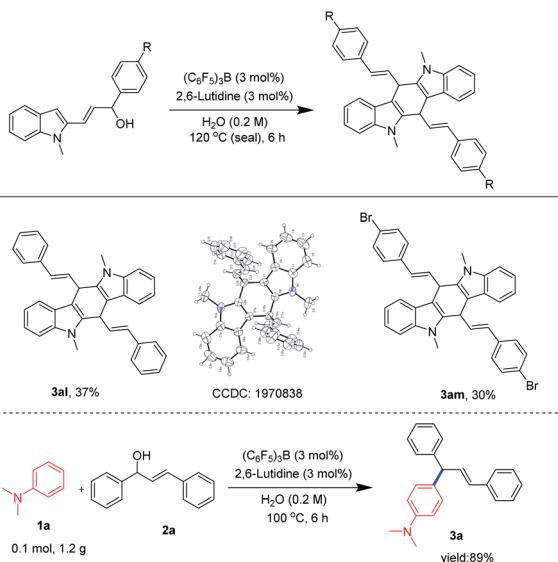




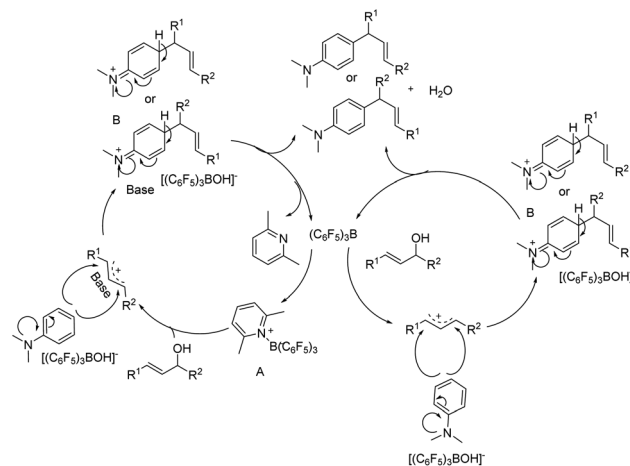
Scheme 3 Substrate scope of indoles^{a,b}. ^aReaction conditions: **1** (0.3 mmol), **2a** (0.3 mmol), (C₆F₅)₃B (3 mol%), 2,6-lutidine (3 mol%), H₂O (0.2 M), 100 °C, 6 h. ^bIsolated yields.

yl)prop-2-en-1-ol (**2r**) were capable of bimolecular ring-closure reaction to obtain tetrahydroindolo[3,2-*b*]carbazoles (**3al**–**3am**). In order to reveal the potential application of this protocol, an amplification scale reaction was implemented. A 1.2 g scale reaction was carried out for *N,N*-dimethylaniline **1a** and (*E*)-3-(1-hydroxy-3-phenylallyl)benzene-1-ylum **2a**, and the product **3a** was isolated in 89% yield (Scheme 4). The result showed that the product yield was not affected after the reaction was scaled up, further indicating that the reaction has great potential for application.

Based on others previously reported in literature,^{19,28,32,33} a plausible mechanism was proposed in Scheme 5. Initially, tris(pentafluorophenyl)borane and 2,6-lutidine formed a frustrated Lewis pairs **A**. **A** interacted with allyl alcohol to form



Scheme 4 Bimolecular ring closure and scale-up reaction.



Scheme 5 Proposed mechanism.

[(C₆F₅)₃B(OH)][−] and an allyl cation stabilized by base. The electron-rich aromatic ring attacked the allyl cation to form aromatic cation intermediate **B**. **B** deprotonated and reacted with [(C₆F₅)₃B(OH)][−] to produce water and target products, while the catalyst and base were circulated. In addition, when there was no base, (C₆F₅)₃B could also convert allyl alcohol to allyl cation, thereby completing the reaction process. However, in the absence of a base, the yield of the reaction product was only moderate (Table 1 entries 5 and 8). It might be that the base helped stabilize the allyl cation and improved the yield.

Conclusions

In summary, a FLP-catalyzed allylization of allyl alcohols with electron-rich arenes in water has been reported for the preparation of 1,3-diarylpropenes. In this protocol, the electron-rich aromatics and allyl alcohols are dehydrated in water. What's more, the reaction has very good atom economy and water is the sole byproduct. This protocol is not only featured with mild conditions and broad scope, but also reveals FLP-catalyzed allylization of electron-rich aromatic rings in water, which would offer a new insight for synthesis of 1,3-diarylpropenes and dihydrocarbazoloindoles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are grateful for the financial support from CAS “Light of West China” Program, Technological Innovation Program of Chengdu, Sichuan Province, China (No. 2018-YF05-00244-SN) and the Applied Basic Research Programs of Sichuan Province, China (No. 20YYJC0492). We would like to thank Dr Daibing Luo from the Analytical & Testing Center of Sichuan University for X-ray diffraction work and single crystal analysis.



References

- (a) J. Tsuji, Carbon-Carbon Bond Formation via Palladium Complexes, *Acc. Chem. Res.*, 1969, **2**, 144–152; (b) B. M. Trost and T. J. Fullerton, New Synthetic Reactions. Allylic Alkylation, *J. Am. Chem. Soc.*, 1973, **95**, 292–294; (c) B. M. Trost, Asymmetric Transition Metal-Catalyzed Allylic Alkylations, *Chem. Rev.*, 1996, **96**, 395–422; (d) B. M. Trost and M. L. Crawley, Asymmetric Transition-Metal-Catalyzed Allylic Alkylations: Applications in Total Synthesis, *Chem. Rev.*, 2003, **103**, 2921–2943.
- J. Muzart, Palladium-catalysed reactions of alcohols. Part B: formation of C-C and C-N bonds from unsaturated alcohols, *Tetrahedron*, 2005, **61**, 4179–4212.
- S.-M. Ma and Z. Lu, Metal-Catalyzed Enantioselective Allylation in Asymmetric Synthesis, *Angew. Chem., Int. Ed.*, 2008, **47**, 258–297.
- J. D. Weaver, A. Recio III, A. J. Grenning and J. A. Tunge, Transition Metal-Catalyzed Decarboxylative Allylation and Benzylolation Reactions, *Chem. Rev.*, 2011, **111**, 1846–1913.
- B. Sundararaju, M. Achard and C. Bruneau, Transition metal catalyzed nucleophilic allylic substitution: activation of allylic alcohols via p-allylic species, *Chem. Soc. Rev.*, 2012, **41**, 4467–4483.
- N. A. Butt and W.-B. Zhang, Transition metal-catalyzed allylic substitution reactions with unactivated allylic substrates, *Chem. Soc. Rev.*, 2015, **44**, 7929–7967.
- (a) M. Choi, J. Park, S. Sharma, H. Jo, S. Han, M. Jeon, N. K. Mishra, S. H. Han, J. S. Lee and I. S. Kim, Trifluoromethylallylation of Heterocyclic C-H Bonds with Allylic Carbonates under Rhodium Catalysis, *J. Org. Chem.*, 2016, **81**, 4771–4778; (b) X. Wei, D.-L. Liu, Q.-J. An and W.-B. Zhang, Hydrogen-Bond Directed Regioselective Pd-Catalyzed Asymmetric Allylic Alkylation: The Construction of Chiral α -Amino Acids with Vicinal Tertiary and Quaternary Stereocenters, *Org. Lett.*, 2015, **17**, 5768–5771; (c) H. Yorimitsu and K. Oshima, Recent Progress in Asymmetric Allylic Substitutions Catalyzed by Chiral Copper Complexes, *Angew. Chem., Int. Ed.*, 2005, **44**, 4435–4439; (d) K. Ohmatsu, M. Ito, T. Kunieda and T. Ooi, Ion-paired chiral ligands for asymmetric palladium catalysis, *Nat. Chem.*, 2012, **4**, 473–477; (e) M. Braun and T. Meier, Tsuji-Trost Allylic Alkylation with Ketone Enolates, *Angew. Chem., Int. Ed.*, 2006, **45**, 6952–6955; (f) L. Du, P. Cao, J.-W. Xing, Y.-Z. Lou, L.-Y. Jiang, L.-C. Li and J. Liao, Hydrogen-Bond-Promoted Palladium Catalysis: Allylic Alkylation of Indoles with Unsymmetrical 1,3-Disubstituted Allyl Acetates Using Chiral Bis(sulfoxide)Phosphine Ligands, *Angew. Chem., Int. Ed.*, 2013, **52**, 4207–4211; (g) A. Misale, S. Niyomchon, M. Luparia and N. Maulide, Asymmetric Palladium-Catalyzed Allylic Alkylation Using Dialkylzinc Reagents: A Remarkable Ligand Effect, *Angew. Chem., Int. Ed.*, 2014, **53**, 7068–7073; (h) X.-Y. Jiang, W.-Y. Chen and J.-F. Hartwig, Iridium-Catalyzed Diastereoselective and Enantioselective Allylic Substitutions with Acyclic α -Alkoxy Ketones, *Angew. Chem., Int. Ed.*, 2016, **55**, 5819–5823; (i) R. Matsubara and T. F. Jamison, Nickel-Catalyzed Allylic Substitution of Simple Alkenes, *J. Am. Chem. Soc.*, 2010, **132**, 6880–6881; (j) K.-Y. Ye, H. He, W.-B. Liu, L.-X. Dai, G. Helmchen and S.-L. You, Iridium-Catalyzed Allylic Vinylation and Asymmetric Allylic Amination Reactions with o-Aminostyrenes, *J. Am. Chem. Soc.*, 2011, **133**, 19006–19014; (k) W.-B. Liu, N. Okamoto, E. J. Alexy, A. Y. Hong, K. Tran and B. M. Toltz, Enantioselective γ -Alkylation of α,β -Unsaturated Malonates and Ketoesters by a Sequential Ir-Catalyzed Asymmetric Allylic Alkylation/Cope Rearrangement, *J. Am. Chem. Soc.*, 2016, **138**, 5234–5237.
- (a) A. J. Grenning and J. A. Tunge, Deacylative Allylation of Nitroalkanes: Unsymmetric Bisallylation by a Three-Component Coupling, *Angew. Chem., Int. Ed.*, 2011, **50**, 1688–1691; (b) Y. Zhang, S.-C. Yin and J.-M. Lu, N-Heterocyclic Carbene-Palladium(II)-1-Methylimidazole Complex Catalyzed Allyl-Aryl Coupling of Allylic Alcohols with Arylboronic Acids in Neat Water, *Tetrahedron*, 2015, **71**, 544–549; (c) Y. Gumrukcu, B. D. Bruin and J. N. H. Reek, Hydrogen-Bond-Assisted Activation of Allylic Alcohols for Palladium-Catalyzed Coupling Reactions, *ChemSusChem*, 2014, **7**, 890–896; (d) S. Krautwald, D. Sarlah, M. A. Schafroth and E. M. Carreira, Enantio- and Diastereodivergent Dual Catalysis: α -Allylation of Branched Aldehydes, *Science*, 2013, **340**, 1065–1068; (e) G. S. Kumar and M. Kapur, Ruthenium-Catalyzed, Site-Selective C-H Allylation of Indoles with Allyl Alcohols as Coupling Partners, *Org. Lett.*, 2016, **18**, 1112–1115; (f) Y. Bunno, N. Murakami, Y. Suzuki, M. Kanai, T. Yoshino and S. Matsunaga, Cp*Co III-Catalyzed Dehydrative C-H Allylation of 6-Arylpyridines and Aromatic Amides Using Allyl Alcohols in Fluorinated Alcohols, *Org. Lett.*, 2016, **18**, 2216–2219; (g) K. Miyata, H. Kutsuna, S. Kawakami and M. Kitamura, A Chiral Bidentate sp^2 -N Ligand, NaphdiPIM: Application to CpRu-Catalyzed Asymmetric Dehydrative C-, N-, and O-Allylation, *Angew. Chem., Int. Ed.*, 2011, **50**, 4649–4653; (h) G. Jiang and B. List, Direct Asymmetric α -Allylation of Aldehydes with Simple Allylic Alcohols Enabled by the Concerted Action of Three Different Catalysts, *Angew. Chem., Int. Ed.*, 2011, **50**, 9471–9474; (i) X.-H. Huo, G.-Q. Yang, D.-L. Liu, Y.-G. Liu, I. D. Gridnev and W.-B. Zhang, Palladium-Catalyzed Allylic Alkylation of Simple Ketones with Allylic Alcohols and Its Mechanistic Study, *Angew. Chem., Int. Ed.*, 2014, **53**, 6776–6780; (j) H. Zhou, L. Zhang, C.-M. Xu and S.-Z. Luo, Chiral Primary Amine/Palladium Dual Catalysis for Asymmetric Allylic Alkylation of β -Ketocarbonyl Compounds with Allylic Alcohols, *Angew. Chem., Int. Ed.*, 2015, **54**, 12645–12648; (k) M.-M. Mastandrea, N. Mellonie, P. Giacinto, A. Collado, S. P. Nolan, G. P. Miscione, A. Bottoni and M. Bandini, Gold(I)-Assisted α -Allylation of Enals and Enones with Alcohols, *Angew. Chem., Int. Ed.*, 2015, **54**, 14885–14889; (l) Y. Kita, R. D. Kavthe, H. Oda and K. Mashima, Asymmetric Allylic Alkylation of β -Ketoesters with Allylic Alcohols by a Nickel/Diphosphine Catalyst, *Angew. Chem., Int. Ed.*, 2016, **55**, 1098–1101; (m) H. Tsukamoto, M. Sato and



- Y. Kondo, Palladium(0)-catalyzed direct cross-coupling reaction of allyl alcohols with aryl- and vinyl-boronic acids, *Chem. Commun.*, 2004, 1200–1201; (n) H. Tsukamoto, T. Uchiyama, T. Suzuki and Y. Kondo, Palladium(0)-catalyzed direct cross-coupling reaction of allyl alcohols with aryl- and vinyl-boronic acids, *Org. Biomol. Chem.*, 2008, **6**, 3005–3013; (o) Y. Gumrukcu, B. D. Bruin and J. N. H. Reek, Dehydrative Cross-Coupling Reactions of Allylic Alcohols with Olefins, *Chem.–Eur. J.*, 2014, **20**, 10905–10909; (p) T. Mita, Y. Higuchi and Y. Sato, Highly Regioselective Palladium-Catalyzed Carboxylation of Allylic Alcohols with CO₂, *Chem.–Eur. J.*, 2015, **21**, 16391–16394; (q) R. Blicke, M. S. Azizi, A. Mifleur, M. Roger, C. Persyn, M. Sauthier and H. Bonin, Nickel-Catalysed Bis-Allylation of Activated Nucleophiles with Allyl Alcohol, *Eur. J. Org. Chem.*, 2016, 1194–1198; (r) J. Y. Hamilton, D. Sarlah and E. M. Carreira, Iridium-Catalyzed Enantioselective Allylic Vinylation, *J. Am. Chem. Soc.*, 2013, **135**, 994–997; (s) P. Trillo, A. Baeza and C. Njira, Direct Nucleophilic Substitution of Free Allylic Alcohols in Water Catalyzed by FeCl₃·6H₂O: Which is the Real Catalyst, *ChemCatChem*, 2013, **5**, 1538–1542.
- 9 (a) T. K. Achar, X.-L. Zhang, R. Mondal, M. S. Shanavas, S. Maiti, S. Maity, N. Pal, R. S. Paton and D. Maiti, Palladium-Catalyzed Directed meta-Selective C-H Allylation of Arenes: Unactivated Internal Olefins as Allyl Surrogates, *Angew. Chem., Int. Ed.*, 2019, **58**, 10353–10360; (b) R. Kankanala, J. P. Biswas, S. Jana, T. K. Achar, S. Porey and D. Maiti, Co-ordination assisted distal C-H alkylation of fused heterocycles, *Angew. Chem., Int. Ed.*, 2019, **58**, 13808–13812; (c) A. Dey, S. K. Sinha, T. K. Achar and D. Maiti, Accessing Remote meta- and para-C(sp²)-H Bonds with Covalently Attached Directing Groups, *Angew. Chem., Int. Ed.*, 2019, **58**, 10820–10843; (d) A. Baccalini, S. Vergura, P. Dolui, S. Maiti, S. Dutta, S. Maity, F. F. Khan, G. K. Lahiri, G. Zanoni and D. Maiti, Cobalt-Catalyzed C(sp²)-H Allylation of Biphenyl Amines with Unbiased Terminal Olefins, *Org. Lett.*, 2019, **21**(21), 8842–8846.
- 10 (a) A. Maji, A. Dahiya, G. Lu, T. Bhattacharya, M. Brochetta, G. Zanoni, P. Liu and D. Maiti, H-bonded reusable template assisted paraselective ketonisation using soft electrophilic vinyl ethers, *Nat. Commun.*, 2018, **9**, 3582–3591; (b) U. Dutta, S. Maiti, S. Pimparkar, S. Maiti, L. R. Gahan, E. H. Krenske, D. W. Lupton and D. Maiti, Rhodium catalyzed template-assisted distal para-C-H olefination, *Chem. Sci.*, 2019, **10**, 7426–7432; (c) A. Maji, S. Guin, S. Feng, A. Dahiya, V. K. Singh, P. Liu and D. Maiti, Experimental and Computational Exploration of Para-Selective Silylation Involving H-Bonded Template, *Angew. Chem., Int. Ed.*, 2017, **56**, 14903–14907; (d) T. Patra, S. Bag, R. Kancherla, A. Mondal, A. Dey, S. Pimparkar, S. Agasti, A. Modak and D. Maiti, Palladium-Catalyzed Directed para C-H Functionalization of Phenols, *Angew. Chem., Int. Ed.*, 2016, **55**, 7751–7755; (e) S. Bag, T. Patra, A. Modak, A. Deb, S. Maity, U. Dutta, A. Dey, R. Kancherla, A. Maji, A. Hazra, M. Bera and D. Maiti, Remote para-C-H Functionalization of Arenes by a D-Shaped Biphenyl Template-Based Assembly, *J. Am. Chem. Soc.*, 2015, **137**, 11888–11891.
- 11 Y.-L. Liu, L. Liu, Y.-L. Wang, Y.-C. Han, D. Wang and Y.-J. Chen, Calix[n]arene sulfonic acids bearing pendant aliphatic chains as recyclable surfactant-type Brønsted acid catalysts for allylic alkylation with allyl alcohols in water, *Green Chem.*, 2008, **10**, 635–640.
- 12 (a) J. A. McCubbin, H. Hosseini and O. V. Krokhn, Boronic Acid Catalyzed Friedel-Crafts Reactions of Allylic Alcohols with Electron-Rich Arenes and Heteroarenes, *J. Org. Chem.*, 2010, **75**, 959–962; (b) C. L. Ricardo, X. Mo, J. A. McCubbin and D. G. Hall, A Surprising Substituent Effect Provides a Superior Boronic Acid Catalyst for Mild and Metal-Free Direct Friedel-Crafts Alkylations and Prenylations of Neutral Arenes, *Chem.–Eur. J.*, 2015, **21**, 4218–4223.
- 13 T. Hirashita, S. Kuwahara, S. Okochi, M. Tsuji and S. Araki, Direct benzylation and allylic alkylation in high-temperature water without added catalysts, *Tetrahedron Lett.*, 2010, **51**, 1847–1851.
- 14 M. A. Soriano, L. H. Martínez and I. M. Pastor, 1,3-Bis(carboxymethyl)imidazolium Chloride as a Metal-Free and Recyclable Catalyst for the Synthesis of N-Allylanilines by Allylic Substitution of Alcohols, *ACS Sustainable Chem. Eng.*, 2018, **6**, 14063–14070.
- 15 M. Gómez-Martínez, A. Baeza and D. A. Alonso, Pinacol Rearrangement and Direct Nucleophilic Substitution of Allylic Alcohols Promoted by Graphene Oxide and Graphene Oxide CO₂H, *ChemCatChem*, 2017, **9**, 1032–1039.
- 16 (a) N. Gandhamsetty, J. Park, J. Jeong, S.-W. Park, S. Park and S. Chang, Chemoselective Silylative Reduction of Conjugated Nitriles under Metal-Free Catalytic Conditions: β -Silyl Amines and Enamines, *Angew. Chem., Int. Ed.*, 2015, **54**, 6832–6836; (b) E. Y.-X. Chen and T. J. Marks, Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure-Activity Relationships, *Chem. Rev.*, 2000, **100**, 1391–1434; (c) K. Ishihara and H. Yamamoto, Arylboron Compounds as Acid Catalysts in Organic Synthetic Transformations, *Eur. J. Org. Chem.*, 1999, 527–538; (d) W. E. Piers and T. Chivers, Pentafluorophenylboranes: from obscurity to applications, *Chem. Soc. Rev.*, 1997, **26**, 345–354; (e) T. Robert and M. Oestreich, Si-H Bond Activation: Bridging Lewis Acid Catalysis with Brookhart's Iridium(III) Pincer Complex and B(C₆F₅)₃, *Angew. Chem., Int. Ed.*, 2013, **52**, 5216–5218; (f) W. Meng, X.-Q. Feng and H.-F. Du, Frustrated Lewis Pairs Catalyzed Asymmetric Metal-Free Hydrogenations and Hydrosilylations, *Acc. Chem. Res.*, 2018, **51**, 191–201; (g) S.-L. Li, G. Li, W. Meng and H.-F. Du, A Frustrated Lewis Pair Catalyzed Asymmetric Transfer Hydrogenation of Imines Using Ammonia Borane, *J. Am. Chem. Soc.*, 2016, **138**, 12956–12962.
- 17 D. J. Parks and W. E. Piers, Tris(pentafluorophenyl)boron-catalyzed Hydrosilylation of Aromatic Aldehydes, Ketones, and Esters, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.
- 18 S. Rendler and M. Oestreich, Conclusive Evidence for an SN₂-Si Mechanism in the B(C₆F₅)₃-catalyzed Hydrosilylation of



- Carbonyl Compounds: Implications for The Related Hydrogenation, *Angew. Chem., Int. Ed.*, 2008, **47**, 5997–6000.
- 19 (a) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, Reversible, Metal-Free Hydrogen Activation, *Science*, 2006, **314**, 1124–1126; (b) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, Rapid Intramolecular Heterolytic Dihydrogen Activation by A Four-Membered Heterocyclic Phosphane-Borane Adduct, *Chem. Commun.*, 2007, 5072–5074; (c) G. C. Welch and D. W. Stephan, Facile Heterolytic Cleavage of Dihydrogen by Phosphines and Boranes, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881; (d) J. S. J. McCahill, G. C. Welch and D. W. Stephan, Reactivity of 'Frustrated Lewis Pairs': Three-Component Reactions of Phosphines, A Borane, and Olefins, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968–4971; (e) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, Metal-Free Catalytic Hydrogenation, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050–8053; (f) D. W. Stephan and G. Erker, Frustrated Lewis Pair Chemistry: Development and Perspectives, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441; (g) D. W. Stephan, Frustrated Lewis Pairs, *J. Am. Chem. Soc.*, 2015, **137**, 10018–10032; (h) D. W. Stephan, Frustrated Lewis Pairs: from Concept to Catalysis, *Acc. Chem. Res.*, 2015, **48**, 306–316; (i) S. A. Weicker and D. W. Stephan, Main Group Lewis Acids in Frustrated Lewis Pair Chemistry: Beyond Electrophilic Boranes, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1003–1016; (j) D. W. Stephan, The Broadening Reach of Frustrated Lewis Pair Chemistry, *Science*, 2016, **354**, aaf7229.
- 20 (a) M. A. Legare, M. A. Courtemanche, E. Rochette and F. G. Fontaine, Metal-Free Catalytic C-H Bond Activation and Borylation of Heteroarenes, *Science*, 2015, **349**, 513–516; (b) M. A. Legare, E. Rochette, L. J. Legare, N. Bouchard and F. G. Fontaine, Bench-Stable Frustrated Lewis Pair Chemistry: Fluoroborate Salts as Precatalysts for The C-H Borylation of Heteroarenes, *Chem. Commun.*, 2016, **52**, 5387–5390; (c) M. A. Courtemanche, M. A. Legare, L. Maron and F. G. Fontaine, A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO₂ to Methanol Using Hydroboranes, *J. Am. Chem. Soc.*, 2013, **135**, 9326–9329; (d) R. Declercq, G. Bouhadir, D. Bourissou, M. A. L  gar  , M. A. Courtemanche, K. S. Nahi, N. Bouchard, F. G. Fontaine and L. Maron, Hydroboration of Carbon Dioxide Using Ambiphilic Phosphine-Borane Catalysts: on the Role of the Formaldehyde Adduct, *ACS Catal.*, 2015, **5**, 2513–2520.
- 21 (a) K. Chernichenko, B. Kotai, I. Papai, V. Zhivonitko, M. Nieger, M. Leskela and T. Repo, Intramolecular Frustrated Lewis Pair with the Smallest Boryl Site: Reversible H₂ Addition and Kinetic Analysis, *Angew. Chem., Int. Ed.*, 2015, **54**, 1749–1753; (b) K. Chernichenko, M. Lindqvist, B. Kotai, M. Nieger, K. Sorochkina, I. Papai and T. Repo, Intramolecular Frustrated Lewis Pair with the Smallest Boryl Site: Reversible H₂ Addition and Kinetic Analysis, *J. Am. Chem. Soc.*, 2016, **138**, 4860–4868.
- 22 C. M. M  ming, E. Otten, G. Kehr, R. Fr  lich, S. Grimme, D. W. Stephan and G. Erker, Reversible Metal-Free Carbon Dioxide Binding by Frustrated Lewis Pairs, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643–6646.
- 23 A. J. P. Cardenas, B. J. Culotta, T. H. Warren, S. Grimme, A. Stute, R. Fr  lich, G. Kehr and G. Erker, Capture of NO by a Frustrated Lewis Pair: A New Type of Persistent N-Oxyl Radical, *Angew. Chem., Int. Ed.*, 2011, **50**, 7567–7571.
- 24 R. C. Neu, E. Otten, A. Lough and D. W. Stephan, The synthesis and exchange chemistry of frustrated Lewis pair-nitrous oxide complexes, *Chem. Sci.*, 2011, **2**, 170–176.
- 25 M. Sajid, A. Klose, B. Birkmann, L. Liang, B. Schirmer, T. Wiegand, H. Eckert, A. J. Lough, R. Fr  lich, C. G. Daniliuc, S. Grimme, D. W. Stephan, G. Kehr and G. Erker, Reactions of phosphorus/boron frustrated Lewis pairs with SO₂, *Chem. Sci.*, 2013, **4**, 213–219.
- 26 C. M. M  ming, S. Fr  el, G. Kehr, R. Fr  lich, S. Grimme and G. Erker, Reactions of an Intramolecular Frustrated Lewis Pair with Unsaturated Substrates: Evidence for a Concerted Olefin Addition Reaction, *J. Am. Chem. Soc.*, 2009, **131**, 12280–12289.
- 27 M. A. Dureen and D. W. Stephan, Terminal Alkyne Activation by Frustrated and Classical Lewis Acid/Phosphine Pairs, *J. Am. Chem. Soc.*, 2009, **131**, 8396–8397.
- 28 H. H. San, S.-J. Wang, M. Jiang and X.-Y. Tang, Boron-Catalyzed O-H Bond Insertion of α -Aryl α -Diazoesters in Water, *Org. Lett.*, 2018, **20**, 4672–4676.
- 29 Y. Dong, H. Zhang, J. Yang, S. He, Z.-C. Shi, X.-M. Zhang and J.-Y. Wang, B(C₆F₅)₃-Catalyzed C-C Coupling of 1,4-Naphthoquinones with the C-3 Position of Indole Derivatives in Water, *ACS Omega*, 2019, **4**, 21567–21577.
- 30 (a) S. Sayin and M. Yilmaz, Synthesis and investigation of catalytic affinities of water-soluble amphiphilic calix[n]arene surfactants in the coupling reaction of some heteroaromatic compounds, *Tetrahedron*, 2016, **72**, 6528–6535; (b) S. Sayin and M. Yilmaz, Br  nsted acidic magnetic nano-Fe₃O₄-adorned calix[n]arene sulfonic acids: synthesis and application in the nucleophilic substitution of alcohols, *Tetrahedron*, 2014, **70**, 6669–6676; (c) G.-P. Fan, Z. Liu and G.-W. Wang, Efficient ZnBr₂-catalyzed reactions of allylic alcohols with indoles, sulfamides and anilines under high-speed vibration milling conditions, *Green Chem.*, 2013, **15**, 1659–1664; (d) D. Das and S. Roy, Palladium(II)-Catalyzed Efficient C-3 Functionalization of Indoles with Benzylic and Allylic Alcohols under Co-Catalyst, Acid, Base, Additive and External Ligand-Free Conditions, *Adv. Synth. Catal.*, 2013, **355**, 1308–1314; (e) M. Bandini, A. Melloni and A. Umani-Ronchi, New Versatile Pd-Catalyzed Alkylation of Indoles via Nucleophilic Allylic Substitution: Controlling the Regioselectivity, *Org. Lett.*, 2004, **6**(18), 3199–3202.
- 31 CCDC 1970839 (**3q**) and CCDC 1970838 (**3al**) contain supplementary crystallographic data for this paper.
- 32 S. J. Geier and D. W. Stephan, Lutidine/B(C₆F₅)₃: At the Boundary of Classical and Frustrated Lewis Pair Reactivity, *J. Am. Chem. Soc.*, 2009, **131**, 3476–3477.
- 33 J.-H. Zheng, X.-T. Fan, B.-Y. Zhou, Z.-H. Li and H.-D. Wang, Tautomerization of 2,6-lutidines in the presence of B(C₆F₅)₃ using catecholborane as a precatalyst, *Chem. Commun.*, 2016, **52**, 4655–4658.

