Boron tribromide as a reagent for anti-Markovnikov addition of HBr to cyclopropanes†

Matthew H. Gieuw, a Shuming Chen, b Zhihai Ke, a K. N. Houk b,* a and Ying-Yeung Yeung b,* a

Although radical formation from a trialkylborane is well documented, the analogous reaction mode is unknown for trihaloboranes. We have discovered the generation of bromine radicals from boron tribromide and simple proton sources, such as water or tert-butanol, under open-flask conditions. Cyclopropanes bearing a variety of substituents were hydro- and deuterio-brominated to furnish anti-Markovnikov products in a highly regioselective fashion. NMR mechanistic studies and DFT calculations point to a radical pathway instead of the conventional ionic mechanism expected for BBr₃.

The Lewis acidic nature of organoboranes is well understood, but the participation of BR₃ in free-radical processes was largely overlooked until 1966.¹ Since the discovery of the potential of organoborane species to undergo radical reactions, many novel and synthetically useful transformations were developed.² Trialkyboranes (BR₃) can easily undergo bimolecular homolytic substitution (S₂(2)) at the boron atom to generate alkyl radicals (Scheme 1A). It was found that alkoxyl, dialkylaminyl, alkylthiyl and carbon-centered radicals, triplet ketones, and triplet oxygen can all initiate the radical reaction by substituting one of the alkyl groups of trialkyboranes to liberate alkyl radicals.³ BET₃/O₂ is arguably the most studied organoborane radical-initiating system, with the peroxy radical being the key to propagate the reaction. Apart from being a radical initiator, BET₃, along with trace amount of O₂, can also undergo conjugate addition to unsaturated ketones and aldehydes; addition to ethenyl- and ethynyloxiranes, azidoalkenes, and imines; and addition-elimination to nitroalkenes and nitroarenes, styryl sulfones, sulfoxides and sulfonimides.³ However, apart from changing BET₃ to other trialkyboranes or catecholborane to carry out similar radical reactions, the radical-reaction potential of other organoboranes remains underexplored, given the ease and mild conditions under which they initiate radical chains, often with trace amount of O₂ in air at low temperature. The application of such a mild radical-initiation system to stereoselective radical reactions would drastically change the reaction outcome especially when intermediates and products are thermally unstable.⁴

Halogenation is an important class of transformations and the resultant halogenated products can easily be manipulated to give a wide range of functional molecules.⁵ While trihaloboranes have been employed as halogenating or haloborating agents, their role in reactions is either ambiguous or thought to be exclusively Lewis acidic.⁶ To date, the use of trihaloboranes as a halogen radical donor has not been reported. With BR₃/O₂ being a versatile radical-initiator and conjugate-addition system, we envisioned that a suitable halogenated-borane might work similar to that of trialkyboranes in the generation of reactive, yet stable enough halogen radicals for selective halogenation reactions (Scheme 1B).

Trialkyboranes readily undergo Sₙ₂ reactions because the formation of stronger B–X (e.g. B–O) bonds via substitution is highly exothermic.³ The BDEs (B–C) of BMe₃, BET₃, BPh₃, and BBr₃ range from 344 to 354 kJ mol⁻¹ at 298 K, while their typical autoxidation products, B(OH)₃, B(OH)₄, and B(OEt)₃, have BDEs (B–O) ranging from 519 to 522 kJ mol⁻¹ at 298 K.⁷ We hypothesized that organohaloboranes (BX₃) similar to trialkyboranes would be a halogen

†Department of Chemistry, State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, NT Hong Kong, China. E-mail: yyyeung@cuhk.edu.hk
²Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA. E-mail: houk@chem.ucla.edu
³ Electronic supplementary information (ESI) available. CCDC 1941104. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc02567d

Scheme 1 Classical radical reactions with trialkyboranes and our work on radical bromination using BBr₃.
radical donor from a thermodynamic viewpoint. As the common trihaloboranes (BX₃) BF₃, BCl₃ and BBr₃ have BDEs (B–X) of 644.3, 442.3 and 367.1 kJ mol⁻¹ at 298 K, respectively, BBr₃ was the logical option for our purpose. Although the BDE (B–I) of BI₃ is the lowest among all trihaloboranes and found to be 278.2 kJ mol⁻¹ at 0 K, it was not considered suitable as I₂ has proven to be a very efficient radical quencher in such reactions, and even rigorously purified BI₃ invariably contains a trace amount of I₂.

Compared to activated cyclopropanes, oxidative functionalization of unactivated cyclopropanes gives a wide range of useful molecules that are otherwise not readily accessible, and protocols for the Markovnikov-selective functionalization of unactivated cyclopropanes have been reported. Halolyses of cyclopropanes to give 1,3-dihaloalkanes by molecular halogens are also documented although the reactions commonly suffer from the formation of side products via electrophilic aromatic halogenation. In contrast, obtaining products with anti-Markovnikov regioselectivity has been considered one of the top challenges in industry. Anti-Markovnikov functionalization of unactivated cyclopropanes mostly relies on photo-initiated radical processes with generally poor regioselectivity and limited scope. To the best of our knowledge, anti-Markovnikov hydrohalogenation of cyclopropanes has not been reported.

Very recently, an anti-Markovnikov hydroboration for unactivated cyclopropanes has been reported using boron tribromide and phenylsilane. The reaction was carried out under inert and anhydrous conditions, and mechanistic studies pointed to an ionic mechanism with Lewis acid–base interactions. We show that with a simple twist in the reaction conditions, which is to introduce oxygen, a drastically different reaction outcome and mechanism could be realized. We now report the study and application of BBr₃ as a radical Br donor for the anti-Markovnikov addition of HBr to cyclopropanes.

With all these considerations in mind, we initially envisioned that BBr₃/O₂ as a suitable system to generate bromine radicals, and cyclopropylbenzene (1a) as the model substrate to capture them. The radical reaction might then be terminated by another halogen radical from reagents such as N-chlorosuccinimide or N-iodosuccinimide. Unfortunately, messy mixtures were obtained for all entries (see the ESI, Scheme S1†). On the other hand, a simple proton source, H₂O, was found to be effective in terminating the radical species. In the control experiment with only BBr₃ and cyclopropylbenzene (1a) (Scheme 2, entry 1), the anti-Markovnikov hydrobrominated product 2a was obtained in 24% yield, together with the formation of Markovnikov product 3a (trace) and dibrominated cyclopropane 4a (11%). We reasoned that the proton source was the trace amount of moisture in commercial BBr₃ solution.

Although it is well known that boron-based Lewis acids are moisture sensitive, counter-intuitively, the addition of 1.5 equivalents of H₂O had a positive impact on the yield of 2a, which was dramatically improved to 80% (Scheme 2, entry 2). Excess water led to a reduction in the yield of 2a and the regioselectivity (Scheme 2, entry 3). Replacing water with ethanol as the proton source resulted in a significant drop in reaction efficiency (Scheme 2, entry 4). In contrast, bulkier alcohols such as t-PrOH or t-BuOH (Scheme 2, entries 5 and 6) and less nucleophilic alcohols such as CF₃CH₂OH (Scheme 2, entry 7) gave comparable performance to that of water.

Further study revealed that achieving anti-Markovnikov addition of HBr to cyclopropanes in conventional systems is not a trivial task (Scheme 3). For instance, no reaction was observed when 1a was treated with HBr in either aqueous or water/AcOH co-solvent systems at room temperature. Heating both reactions only yielded the Markovnikov product 3a in 16–23% yield, and no anti-Markovnikov product 2a was detected.
The classical radical bromination protocol with BBr\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} only furnished dibrominated product 4a in 29% yield. Similar to the uniqueness of BBr\textsubscript{3}/O\textsubscript{2} in several aforementioned radical reactions\textsuperscript{4}, the incapability of these control experiments in producing 2a as a product contrasted starkly with our BBr\textsubscript{3}/O\textsubscript{2} conditions, which generated a reactive yet selective bromine radical.

Next, we expanded the substrate scope to other unactivated cyclopropanes using either water or t-BuOH as the proton source (Scheme 4). Electron-neutral, deficient and sterically bulky substrates 1a–1g gave the desired anti-Markovnikov products 2a–2g in good yields and regioselectivity. Cyclopropanes with electron-deficient substituents including nitriles (1j–n) and ester (1o) also worked well with excellent regioselectivity. This protocol also exhibits high chemoselectivity towards cyclopropanes. Aryl methyl ether (2i), which is known to be easily cleaved by BBr\textsubscript{3} even at low temperature, remained intact under our reaction conditions.\textsuperscript{39} Due to the tendency of aryl vinyl ketones to polymerize, they are known to be unsuitable for 1,4-conjugate additions mediated by trialkylboranes.\textsuperscript{30} Nevertheless, aryl cyclopropyl ketones (1h–i) were converted into the corresponding products in high yields, and polymerization was not observed. 1,1-Disubstituted (1p) and simple alkyl (1q) cyclopropanes were also compatible to give products 2p and 2q. When cyclopropyl carboxylic acid (1r) was used as the substrate, the unstable product 2r was detected using HRMS and crude \textsuperscript{1}H NMR, and γ-butyrolactone was obtained ultimately through cyclization upon a basic work-up procedure. Indene-derived cyclopropyl substrate 1s was also compatible to give 2s. Scaled-up reactions were also performed on selected examples (2a, 2h, 2o, and 2r) and excellent regioselectivities were still obtained.

Cyclopropanes 1t–1y with secondary and tertiary alcohols also gave the corresponding anti-Markovnikov products in excellent yields and with high regioselectivities (Scheme 5). The structure of 2x was confirmed unambiguously by X-ray crystallography.\textsuperscript{41} The hydroxyl groups in the substrates were converted into bromides simultaneously by the action of BBr\textsubscript{3} to give a series of useful dibromides.\textsuperscript{42} We were interested in whether alcohol-containing substrates can be hydrobrominated in the absence of an external proton source. To our delight, 1t was able to undergo anti-Markovnikov hydrobromination to give 2t with only a slight drop in yield (76%), and 2u was produced in quantitative yield. The hydroxyl groups in 1x and 1y appear to be crucial because a sluggish reaction was observed for 1-phenyl-2-methylcyclopropane that bears no hydroxyl substituent.

By substituting H\textsubscript{2}O and t-BuOH with D\textsubscript{2}O and t-BuOD, deuteriobrominations were also carried out and the corresponding mono-deuterium-labeled compounds were obtained smoothly (Scheme 6). Our protocol offered excellent regiocontrol in the mono-deuteriation to give 2-D. Unactivated (1a and 1e) and activated cyclopropanes (1j–k, 1m, and 1o) with various substituents worked well and excellent levels of deuterium incorporation were achieved.

The conversion of products 2 into primary alcohols and amines through nucleophilic substitution proved
straightforward. For instance, alcohol 5a and amine 5b were readily prepared from 2a with high conversion (Scheme 7). As the direct synthesis of primary alcohols and amines through anti-Markovnikov hydration and hydroamination has proven to be challenging,22 our protocol provides useful precursors for the synthesis of these highly desired compounds.

We envision a radical reaction pathway between BBr3 and O2, but given the Lewis acidity of BBr3 and Lewis basicity of H2O and alcohols, an acid-mediated pathway cannot be ruled out.23 However, such a pathway appears highly unlikely, as the treatment of cyclopropanes with aqueous HBr yielded no anti-Markovnikov product 2a (Scheme 3). Several control experiments were performed to further probe the reaction mechanism.

The addition of a radical scavenger, BHT or TEMPO, in slight excess of BBr3 completely shut down the formation of anti-Markovnikov product 2a, and a significant amount of Markovnikov product 3a was detected (Scheme 8A). The addition of the acceptor olefin acrylonitrile completely suppressed the reaction. The absence of light had no impact on the reaction, thereby eliminating the possibility of a photo-triggered pathway. The presence of oxygen was crucial for both the yield and the regioselectivity. The reaction proceeded smoothly to give the desired product 2a (80%) in open air. In contrast, the yield of anti-Markovnikov product 2a dropped to 14% and that of the Markovnikov product 3a increased to 17% when the reaction was conducted with degassed CH2Cl2 and 1a. Deuteriobromination of 1g was also conducted with t-BuOD as the deuterium source (Scheme 8B). Other than the benzylic deuteriation product 2g-D (25%), a substantial amount of 2g-D' (75%) was
When i-PrOH and BBr₃ were mixed in CD₂Cl₂ under air, the ¹¹B signal of BBr₃ (39 ppm) disappeared and a new signal at 25.0 ppm emerged. A new proton signal at ~2.68 ppm also appeared in the ¹H NMR study of the same sample. The two new signals (25.0 ppm in ¹¹B NMR and ~2.68 ppm in ¹H NMR) diminished gradually upon the addition of 1a and the amount of anti-Markovnikov product 2a increased accordingly (see the ESI, Fig. S5†). On the other hand, a new ¹¹B NMR signal at 18.9 ppm (but no signal at 25.0 ppm) was observed when the same mixture was prepared in the absence of O₂ and attributed to the formation of the Lewis adduct between i-PrOH and BBr₃ (see the ESI, Fig. S6†). Thus, it is reasonable to propose that the active species, responsible for initiating the anti-Markovnikov hydrobromination of cyclopropanes, was formed only in the presence of O₂.

A DFT computational study was also performed to shed light on the mechanism (Fig. 1). While there are no reports on radical reactions triggered by BBr₃/O₂, we speculate that the reaction mechanism might be analogous to the classical BR₃/O₂ system in which the putative peroxy-boron species A is generated⁶⁹ at the initiation stage of the radical process (Fig. 1A) and corresponds to the new NMR signals (25.0 ppm in ¹¹B NMR and ~2.68 ppm in ¹H NMR).³,²⁰,²¹ Based on the calculated energy profile, species A is capable of brominating cyclopropane 1a through a radical mechanism to give B (Fig. 1B). It is also calculated that A and A’ could be in equilibrium, but species A (ΔG = −7.6 kcal mol⁻¹) was found to be a more competent Br donor than A’ (ΔG = 0.6 kcal mol⁻¹) in the halogen atom transfer (XAT), potentially due to the intramolecular hydrogen bond that stabilizes the by-product I (Fig. 1C). It was also calculated that BBr₃ can reversibly react with water to give adduct C (¹¹B NMR signal = 18.9 ppm). Species C is unable to serve as a Br radical donor to brominate cyclopropane 1a (ΔG = 69.6 kcal mol⁻¹).

However, species C is capable of acting as a hydrogen radical donor to species B, furnishing the desired product 2a. This result is in alignment with the proposal in the literature in which trialkylborane-ROH complexes (R = H, Me) might act as H-donors as a result of the weakened O–H bond.²² Species D, which is formed from species C after the hydrogen atom transfer (HAT), was calculated to be a competent Br radical donor to brominate cyclopropane 1a to give B, thereby propagating the radical chain. Thus, we propose that oxygen is required only in the initiation stage for the generation of species A, while species C and D are responsible for propagation.

Indeed, the reaction was sluggish under an inert atmosphere, while the re-introduction of oxygen into a system initially free of oxygen triggered the anti-Markovnikov hydrobromination (see the ESI, Scheme S2†). The HAT from species A to 1a was also explored computationally, but species A could not be optimized as a stable energy minimum. Species C may also serve as a hydrogen radical donor and react with cyclopropane 1a to give species D and E, which would go on to produce the Markovnikov product 3a. However, this hydrogen atom transfer reaction is endergonic by 31.2 kcal mol⁻¹ (Fig. 1C), making it a minor pathway compared to the competing hydrogen atom transfer from C to B that gives D and 2a (Fig. 1A). This result is obtained. In contrast, no aromatic deuteration was observed when phenanthrene (6) was used as the substrate under the same conditions. The formation of 2g-D‘ could be attributed to the isomerization of benzylic radical species (also see the ESI, Fig. S1†). This preliminary evidence pointed at a radical mechanism, although a carbocation intermediate cannot be ruled out completely.

Consistent with literature reports on BR₃,⁴³,⁴⁴ the reactivity of BBr₃ towards homolytic debromination decreases sharply along the series BBr₃, BBr₃OR, and BBr(OR)₂ as a consequence of π-bonding between oxygen and boron. With 0.5 equiv BBr₃, only 21% of 2a was obtained even with a prolonged reaction time of 24 h. These data indicated that only the first equivalent of Br from BBr₃ is crucial for the reactivity, and contribution from the possible BBr₃(OR)₁⁻₂ byproducts should be insignificant.

A series of ¹H and ¹¹B NMR experiments were conducted to gain further insight. Upon mixing BBr₃ with 1a in the absence of O₂ and a proton source, both 1a and BBr₃ were mostly consumed, and a new ¹¹B signal at 64 ppm (see the ESI, Fig. S²†) emerged as a singlet, which is characteristic of an alkylidihalo-borane species.⁴⁵,⁴⁶ From ¹H NMR, it is clear that 1a is ring-opened (see the ESI, Fig. S4†), and the species has a similar NMR pattern to a hydroborated cyclopropane, which has been reported as a reaction intermediate in literature examples (see the ESI, Fig. S3†).³⁷ Direct bromoboration of alkenes or allenes with BBr₃ is well documented.⁴⁷,⁴⁸ While this new species cannot be clearly identified, it is speculated that it could be the direct bromoboration product or hydroxyboration product. Nevertheless, it is clear that the interaction between BBr₃ and 1a does not lead to the anti-Markovnikov product 2a in the absence of O₂ and a proton source.

| condition          | reactant 1a | 2a  | 3a  |
|--------------------|-------------|-----|-----|
| BHT (1 equiv)      | 14%         | 0%  | 53% |
| TEMPO (1 equiv)    | 25%         | 0%  | 40% |
| acrylonitrile (1 equiv) | 95%     | 0%  | 0%  |
| absence of light   | 0%          | 76% | 7%  |
| under air          | 0%          | 80% | 5%  |
| solvent degassed   | 58%         | 14% | 17% |
consistent with the experimental observation that the Markovnikov product 3a became dominant when the reaction was conducted under an inert atmosphere (Scheme 8A).

In the $^1$H NMR study of the reaction using 1a, apart from 2a, 3a and 4a (Scheme 2), a trace amount of allylbenzene was detected initially and diminished over time. We speculate that the allylbenzene (Fig. 1A, species G) might be formed through the zwitterionic species F as proposed in the recent studies by Wang and Shi. The eventual disappearance of allylbenzene could be attributed to the radical bromination to give species H and the subsequent formation of 2a.

In a deuterium labeling experiment with 1a as the substrate and D$_2$O as the deuterium source, we observed exclusive deuterium incorporation at the benzylic carbon to give product 2a-D, potentially through the C(1) radical species B1 (Scheme 9, eqn (1)). However, the deuterium incorporation pattern is vastly different when using allylbenzene instead of 1a, for which C(2) deuterated product 2a-D' was obtained predominately (Scheme 9, eqn (2)) (also see the ESI, Fig. S7†). The formation of 2a-D' from allylbenzene may proceed through the C(2) radical species H1. As a small amount of 2a-D (9%) was also detected in the reaction with allylbenzene, attributed to the slow 1,2-hydrogen shift$^{54}$ converting H1 to the more stable benzylic radical B1. These results suggest that the 1,2-hydrogen shift between the radical species H and B (Fig. 1A) should be much slower than the radical protonation.

Fig. 1 Reaction mechanism. (A) Plausible reaction pathways. (B) Calculated free energy profile of the anti-Markovnikov hydrobromination of 1a at the ωB97X-D/6-311++G(d,p), SMD(CH$_2$Cl$_2$)//ωB97X-D/6-31+G(d,p) level of theory. (C) Potential competing pathways.
process, implying that allylbenzene is unlikely to be the key intermediate in the reaction.

Conclusions

In summary, we have discovered and exploited the potential of BBr3 to serve as a bromine radical donor in the presence of O2 and a proton source. Through our protocol, cyclopropanes are opened regioselectively to obtain anti-Markownikov hydro- and deuteriobrominated products in high yields. Mechanistic studies and DFT calculations demonstrate the importance of O2 in the radical initiation process. Further efforts to utilize this reactivity mode of BBr3 on different classes of substrates are currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Hong Kong Special Administrative Region General Research Funding (grant no. CUHK14304918), The Chinese University of Hong Kong Direct Grant (grant no. 4053394), and Innovation and Technology Commission to the State Key Laboratory of Synthetic Chemistry (GHP/004/16GD). K. N. H thanks the National Science Foundation (Grant CHE-1764328) for financial support. Calculations were performed on the Hoffman2 cluster at the University of California, Los Angeles, and the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation (Grant OCI-1053575).

Notes and references

1 (a) A. G. Davies and B. P. Roberts, Chem. Commun., 1966, 298–299; (b) A. G. Davies and B. P. Roberts, J. Chem. Soc. B, 1967, 17–22.
2 Radicals in Organic Synthesis, ed, P. Renaud and M. P. Sibi, Wiley-VCH, Weinheim, 2001.
3 C. Ollivier and P. Renaud, Chem. Rev., 2011, 101, 3415–3434.
4 (a) F. R. Mayo and C. Walling, Chem. Rev., 1940, 27, 351–412; (b) M. D. Bach and E. Bosch, Tetrahedron Lett., 1986, 27, 641–644; (c) K. Nozaki, K. Oshima and K. Utimoto, Tetrahedron Lett., 1988, 29, 6127–6128; (d) K. Nozaki, K. Oshima and K. Utimoto, Bull. Chem. Soc. Jpn., 1990, 63, 2578–2583; (e) P. A. Evans and J. D. Roseman, J. Org. Chem., 1996, 61, 2252–2253.
5 (a) M. Hudlicky and T. Hudlicky, Formation of carbon-halogen bonds in, The Chemistry of Functional Groups, Supplement D, ed. S. Patai and Z. Rappoport, John Wiley and Sons Ltd., New Jersey, 1983; (b) Formation of carbon-halogen bonds (Cl, Br, I), in PATAI’S Chemistry of Functional Groups, ed. Y. Sasson, John Wiley and Sons Ltd, 2009.
6 (a) Boron Tribromide in Encyclopedia of Reagents for Organic Synthesis, ed. A. Suzuki, S. Hara and X. Huang, John Wiley & Sons Ltd., 2006; (b) Boron Trichloride in Encyclopedia of Reagents for Organic Synthesis, ed. N. Miyaura, Y. Yamamoto and N. Miyaura, John Wiley & Sons Ltd., 2006; (c) P. Laszlo and M. Teston, J. Am. Chem. Soc., 1990, 112, 8750–8754.
7 J. B. Holbrook, B. C. Smith, C. E. Housecroft and K. Wade, Polyhedron, 1982, 1, 701–706.
8 N. N. Greenwood, in Comprehensive Inorganic Chemistry, ed. A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973.
9 J. D. Grant and D. A. Dixon, J. Phys. Chem. A, 2009, 113, 777–787.
10 (a) M. M. Midland and H. C. Brown, J. Am. Chem. Soc., 1971, 93, 1506–1508; (b) G. W. Kabalka, J. Organomet. Chem., 1971, 33, C25–C28.
11 L. V. McCurry and D. R. Carpenter, J. Electrochem. Soc., 1960, 107, 38–42.
12 (a) H.-U. Reissig and R. Zimmer, Chem. Rev., 2003, 103, 1151–1196; (b) M. Yu and B. L. Pagenkopf, Tetrahedron, 2005, 61, 321–347; (c) F. De Simone and J. Waser, Synthesis, 2009, 20, 3353–3374; (d) F. de Nanteuil, F. de Simone, R. Frei, F. Benfatti, E. Serrano and J. Waser, Chem. Commun., 2014, 50, 10912–10928; (e) T. F. Schneider, J. Kaschel and D. B. Werz, Angew. Chem., Int. Ed., 2014, 53, 5504–5523; (f) M. A. Cavitt, L. H. Phun and S. France, Chem. Soc. Rev., 2014, 43, 804–818; (g) Y. Xia, X. Liu, H. Zheng, L. Lin and X. Feng, Angew. Chem., Int. Ed., 2015, 54, 227–230; (h) Y. Xia, L. Lin, F. Chang, X. Fu, X. Liu and X. Feng, Angew. Chem., Int. Ed., 2015, 54, 13748–13752; (i) Y. Xia, L. Lin, F. Chang, Y. Liao, X. Liu and X. Feng, Angew. Chem., Int. Ed., 2016, 55, 12228–12232; (j) Y. Xia, F. Chang, L. Lin, Y. Xu, X. Liu and X. Feng, Org. Chem. Front., 2018, 5, 1293–1296.
13 V. Nair, S. B. Panicker and S. Mathai, Res. Chem. Intermed., 2003, 29, 227–231.
14 C. Rössner and U. Hennecke, Org. Lett., 2015, 17, 3226–3229.
15 Y.-C. Wong, Z. Ke and Y.-Y. Yeung, Org. Lett., 2015, 17, 4944–4947.
16 Z. Ke, Y.-C. Wong, J.-Y. See and Y.-Y. Yeung, Adv. Synth. Catal., 2016, 358, 1719–1724.
17 M. H. Gieau, V. M.-Y. Leung, Z. Ke and Y.-Y. Yeung, Adv. Synth. Catal., 2018, 360, 4306–4311.
