Organic & Biomolecular Chemistry

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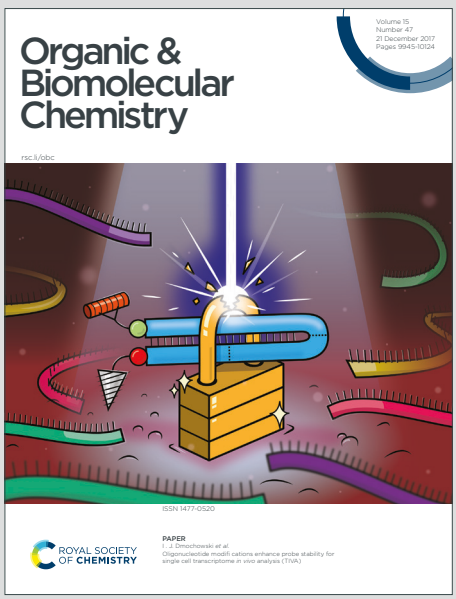

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DOI: 10.1039/C9OB01568J

ARTICLE

Trichloroacetonitrile as an efficient activating agent for *ipso*-hydroxylation of arylboronic acids to phenolic compounds

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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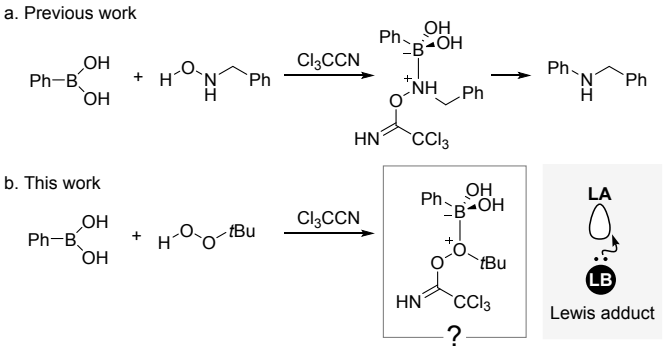
A metal-free and base-free Cl_3CCN mediated method was developed for the *ipso*-hydroxylation of aryl boronic acids to corresponding phenols, which promoted by key unstable Lewis adduct intermediate. This transformation has broad functional group tolerance, and late-stage functionalization were successful as well. After simple investigation, two pathways (radical/ionic mechanism) were suggested, and the beneficial action of blue light needs to be further studied.

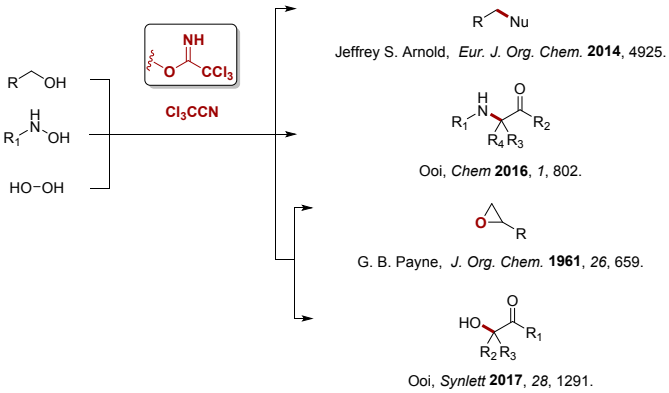
Introduction

Lewis acid and base interactions are widespread phenomena in organic chemistry, which was defined as the Lewis acid-base theory by Gilbert N. Lewis as early as 1923.[1] Lewis acid (LA) species contains an empty orbital, while a Lewis base (LB) contains an unbonded electron pair. A dative bond is formed between the electron acceptor and donator to form a Lewis adduct. A classic and valuable example of Lewis adduct is boron trifluoride diethyl etherate (BF_3•Et_2O),[2] widely used as an easy-to-handle Lewis acid catalyst. Notably, one of the most extensively investigated kind of Lewis adducts is the "frustrated Lewis pairs" (FLP),[3] consist of sterically demanding Lewis donors and acceptors, which remains "unquenched" reactivities and act as both Lewis acids and bases in reactions. Recently, Niu et al. made use of the uncommon *in situ* unfrustrated Lewis adduct of boronic acid and hydroxylamine (B and N atoms) for aminations of boronic acids, with an activating reagent trichloroacetonitrile (CCl_3CN) (Scheme 1).[4] We wondered if there are other practical methods based on *in situ* Lewis adduct intermediates of boronic acids and oxygen-containing compounds.

The CCl_3CN had been proved could transform the hydroxyl group into the trichloroacetimidates,[5,6] which is a good leaving group to achieve multiple types of reactions and construct diverse products (Scheme 2). Payne first developed the epoxidation of alkenes by peroxy trichloroacetimidic acid generated *in situ* from hydrogen peroxide and



Scheme 1 *ipso*-Functionalization of aryl boronic acids promoted by Lewis adduct.



Scheme 2 Research progress of trichloroacetonitrile.

trichloroacetonitrile, besides, discovered that CCl_3CN could increase the rate of the reactions in 1961.[7a,7b] This payne-type oxidation has been classically utilized for glycosylation reactions.[7c,7d] This kind of reactions were developed by researchers in the past decade, the role of trichloroacetonitrile had been deeply studied. Ooi's group developed a strategy for the direct catalytic asymmetric introduction of structurally diverse non-protected amino groups by using trichloroacetonitrile with the hydroxylamines in 2016,[8] they speculated an unstable electrophilic *O*-imino hydroxylamine

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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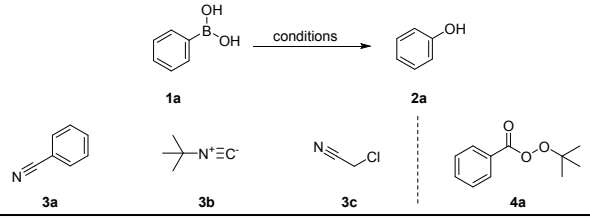
Table 1 Optimization of reaction conditions[a]



Entry	Oxidant	Atmosphere	Solvent	Light	Activator	Yield[b] (%)
1	TBHP[c]	Air	MeCN	blue LED	Cl_3CCN	78%
2	TBHP[c]	Air	MeCN	dark	Cl_3CCN	37%
3	TBHP[c]	Air	THF	blue LED	Cl_3CCN	59%
4	TBHP[c]	Air	DMF	blue LED	Cl_3CCN	N.R.
5	TBHP[c]	Air	DCM	blue LED	Cl_3CCN	trace
6	TBHP[c]	Air	toluene	blue LED	Cl_3CCN	44%
7	TBHP[c]	Air	MeCN	blue LED	**3a**	73%
8	TBHP[c]	Air	MeCN	blue LED	**3b**	75%
9	TBHP[c]	Air	MeCN	blue LED	**3c**	67%
10	TBHP[c]	Air	MeCN	blue LED	--	35%
11	**4a**	Air	MeCN	blue LED	Cl_3CCN	N.R.
12	H_2O_2[d]	Air	MeCN	blue LED	Cl_3CCN	67%
13	TBHP[e]	Air	MeCN	blue LED	Cl_3CCN	70%
14	--	Air	MeCN	blue LED	Cl_3CCN	N.R.
15	TBHP[c]	N_2	MeCN	blue LED	Cl_3CCN	46%
16	TBHP[c]	O_2	MeCN	blue LED	Cl_3CCN	96%
17	--	O_2	MeCN	blue LED	Cl_3CCN	N.R.
18	TBHP[c]	O_2	MeCN	blue LED	--	50%[f]
19	TBHP[c]	O_2	MeCN	--	Cl_3CCN	80%[g]

[a] Reaction conditions: **1a** (0.6 mmol), oxidant (1.0 equiv.), nitriles (1.5 equiv.), solvent (5 mL), blue LED, 12 h, r.t. [b] Isolated yields. [c] TBHP was 5.5 M in decane. [d] H_2O_2 was 30% in H_2O. [e] TBHP was 70% in H_2O, [f] 60h. [g] 40 ℃, 12 h.

was generated. Next year, they reported a method using aqueous hydrogen peroxide and trichloroacetonitrile *in situ* generated peroxy trichloroacetimidic acid, which could act as a competent electrophilic oxygenating agent for the direct *α*-hydroxylation of oxindoles.[9]

Aryl boronic acids have been widely used in synthetic chemistry, materials chemistry and pharmaceutical chemistry on account of its relative stability to water and air, and their wide range of availability.[10] On the other hand, as a kind of cheap, attractive and readily available oxygen-containing compounds, peroxides are widely used for delivering oxygen to various functional groups.[11] Based on the interest of *in situ* unfrustrated Lewis adduct intermediates containing boron and oxygen, we focused on the *ipso*-hydroxylation of arylboronic acids by peroxides as the benchmark reaction to explore the function of Lewis acid and base interactions.

Among the synthetic methods developed to prepare phenols, which are important structural units in pharmaceuticals, agrochemicals, and polymers etc.,[12] oxidation of aryl boronic acid is the most straightforward reaction, and has attracted considerable interest. The first reported oxidation of aryl boronic acids and its derivatives to phenols was realized by Ainley and Challenger in 1930.[13] The initial low yields and undesirable side reactions were improved by various reaction conditions: (1) employing transition-metal catalysts, for instance Cu,[14a-14c] Pd,[14d] Ru,[14e] and Ag;[14f] (2) using stoichiometric amounts of oxidants such as *tert*-butyl hydroperoxide (TBHP),[15a,15b] 3-chloroperoxybenzoic acid (MCPBA),[15c] oxone,[15d,15e] hydroxylamine,[15f] amine oxide,[15g] ozone,[15h] $PhI(OAc)_2$,[15i,15j] benzoquinone,[15k] $NaClO_2$,[15l] sodium sulfite[15m] and sodium ascorbate,[15n] which are also carried out with H_2O_2 in several reports.[15o-15s] (3) electrochemical reactions;[16] (4) aerobic organocatalysis conditions;[17] and (5) photocatalytic reactions.[18] However, most of the existing protocols are not free from limitations such as hazardous metal contamination, long reaction time, high temperature, tedious workup and expensive reagents. Therefore, establishing of mild and base-free oxidation system to overcome these drawbacks for *ipso*-hydroxylation of aryl boronic acids is very much required.

Results and discussion

Initially, phenylboronic acid (**1a**) was employed as a model substrate to optimize reaction conditions (Table 1). When a

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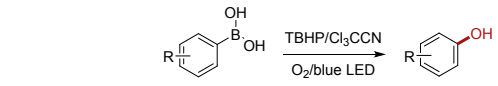
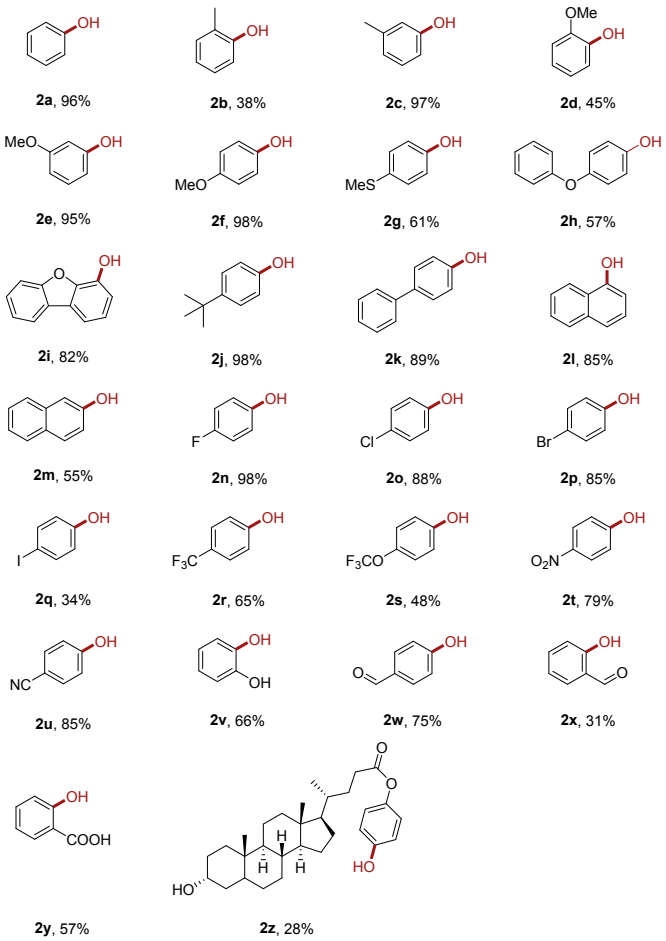
mixture of **1a** (0.6 mmol), TBHP (1.0 equiv) and Cl_3CCN (1.5 equiv) was stirred under blue LED and air conditions at room temperature, to our delight, the desired phenol (**2a**) was obtained in 78% yield after 12 h (Table 1, entry 1). In the absence of blue LED, low yield of **2a** was observed (Table 1, entry 2), which shows that the irradiation with visible light plays an important role for high conversion of the aryl boronic acids. The effect of solvents on the reaction was examined subsequently (Table 1, entries 3-6), and MeCN was found to be the most effective solvent. As the significant activating reagent, a range of nitriles and isocyanides such as benzonitrile (**3a**), 2-isocyano-2-methylpropane (**3b**), and chloroacetonitrile (**3c**) were examined (Table 1, entries 7-9). Although other nitriles or isocyanides could afford moderate yields, it was found that Cl_3CCN still promoted this reaction most efficiently, and was necessary for smooth progress of *ipso*-hydroxylation (Table 1, entry 10). In the course of optimization of oxidant, TBHP was found to be the optimal oxidant (Table 1, entries 11-14). The screening of the amount of Cl_3CCN and TBHP indicated that 1.5 equiv of Cl_3CCN and 1.0 equiv of TBHP were the most suitable for the reaction (Table S1). Interestingly, the reaction gave low yield under an inert N_2 environment (Table 1, entry 15), which indicated that molecular oxygen in air may promote the conversion of **1a**. Therefore, the atmosphere was replaced with O_2 environment, then the reaction occurred to give the desired phenol **2a** in high yield (Table 1, entry 16). But when we replaced the TBHP with oxygen, there was no phenol **2a** been detected (Table 1, entry 17). Subsequently, to figure out if Cl_3CCN was necessary in this reaction, we prolonged reaction time to 60 h and the yield was still undesirable. (Table 1, entry 18). At last, to determine the existence of thermal effects, we heated the reaction to 40 ℃ and the best yield didn't achieve (Table 1, entry 19).

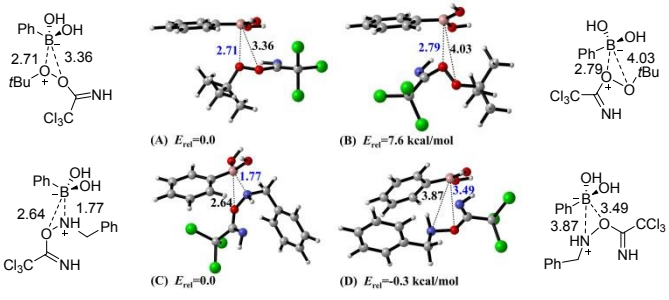
With the optimal reaction condition in hand, we turned our attention to examine the scope of the reaction (Table 2). A wide range of functional groups were tolerant in this transformation, such as sulfide, halide, nitro, nitrile, aldehyde, and carboxyl, etc. The substituted aryl boronic acids bearing electron donating or withdrawing substituents at *para*-position were smoothly oxidized to the corresponding phenols in good to excellent yields (**2f**, **2n**, **2t**, and **2u**). Boronic acids with methoxyl substituent at *meta*- and *para*-position afforded corresponding phenols in high yields (**2e**, **2f**). However, *ortho*-methoxyl (**2d**) and other *ortho*-substituted boronic acids were examined, and low to moderate yields were obtained (**2b**, **2d**, **2v**, **2x**, and **2y**), possibly due to the effect of steric hindrance on interaction of Lewis adduct and substrates. Also, α-naphthylboronic acid **2l** was more efficiently converted into corresponding naphthol than β-naphthylboronic acid **2m**. In addition, bromo and iodo substituted boronic acids were tolerated providing the desired product (**2p**, **2q**), which could be used for subsequent practical functionalization. Noteworthily, oxidation-sensitive substituents (**2g**, **2w**) and substituents bearing active hydrogen (**2v**, **2y**) were also tolerated in the conditions without suffering overoxidation and got good yields. Furthermore, boronic acid derivative of lithocholic acid was successfully converted into corresponding phenol (**2z**).

Table 2 Substrate scope of ipso-hydroxylation of substituted arylboronic acids to corresponding phenols[a,b]





[a]Reaction conditions: arylboronic acids (0.6 mmol), TBHP (5.5M in decane 1.0 equiv.), Cl_3CCN (1.5 equiv.), MeCN (5 mL), blue LED, r.t., O_2, 12 h.
[b]Isolated yields.



Scheme 3 The optimized geometries of aryl boronic acids coordinated by trichloroimidate.

To identify which O atom in TBHP could be coordinated to B atom in aryl boronic acid during *ipso*-hydroxylation, we applied DFT calculations at M062x/6-31G(d) level used Gaussian Program.[19] benzyl group could be more stable than O atom in

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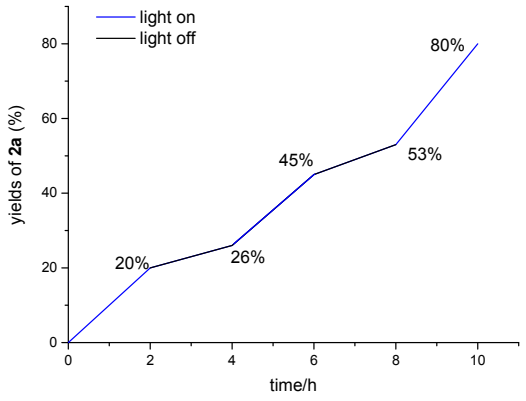
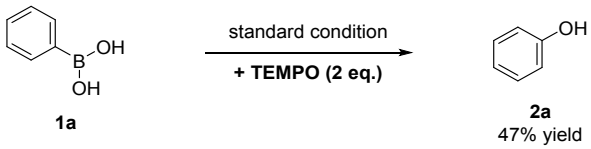


Scheme 4 The light on/off experiments of ipso-hydroxylation aryl boronic acid.

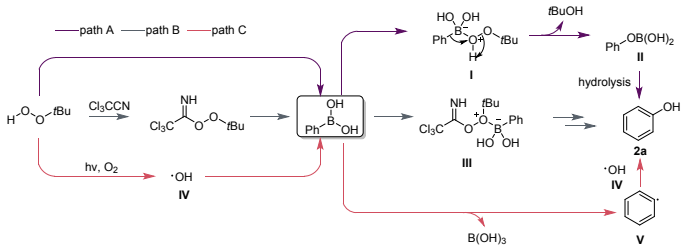
coordinating to B atom (scheme 3 C-D), which was compatible with Niu's suppose. On the other side, in our system, it shows that both of O atoms in TBHP can coordinate to B atom with the distances between O and B atoms of 2.71 and 2.79 Å, respectively (scheme 3 A-B). However, the former is 7.6 kcal/mol lower in energy than the later, indicating that the O atom adjacent to *t*Bu-group is more favourable to be coordinated to B atom during the reaction.

In order to figure out the role of blue LED in this reaction, we conducted the light/dark experiment (Scheme 4). The result shows significant improvement of reaction yield (detected by GC-MS) in blue LED, which means the blue LED does promoted the reaction. Then the consequence of UV-vis absorption spectra (Scheme S2) illustrated the compound (blue line) bathochromic slightly shift up to the visible range in λ = 225 nm and 275 nm.

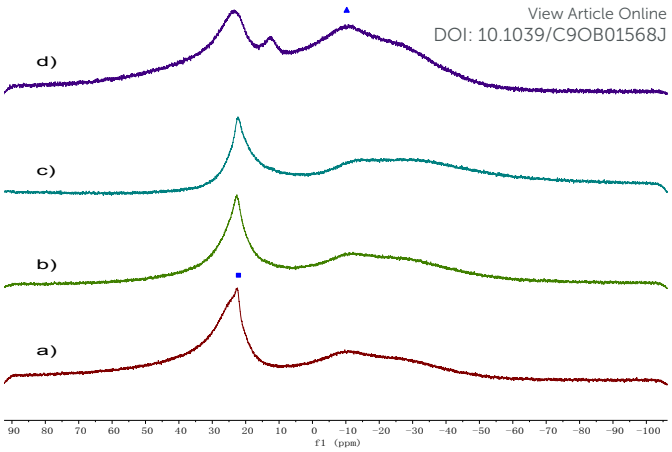
Furthermore, the *ipso*-hydroxylation was partly suppressed and 47% phenol was obtained, when 2,2,6,6-tetramethylpiperidinooxy (TEMPO) as a radical inhibitor was added to model reaction (Scheme 5). Therefore, we speculated



Scheme 5 Simply mechanism investigated.



Scheme 6 Proposed mechanism for the ipso-hydroxylation of aryl boronic acid reaction.



Scheme 7 Intermediate experiment verification of ^{11}B NMR (128 MHz, $CDCl_3$) spectra: a) **1a**; b) reaction in standard conditions after 10 min; c) after 1 h; d) after 8 h. ■1a; ▲III. (see Scheme 8).

the key Lewis adduct intermediate might promote *ipso*-hydroxylation via two pathways, radical and ionic mechanism (Scheme 6). The path A described the directed oxidation of phenylboronic acid to phenol by TBHP. Another possible pathway (path B), which described the combination of TBHP, Cl_3CCN and phenylboronic acid transformed to the highly unstable Lewis adduct intermediate (**III**). Although the detailed process was not fully understood, the trichloroacetimidates intermediate and aryl boronic acid were speculated to form a Lewis adduct, which was similar to Niu's report.[4] Finally, interaction of Hydroxyl radical (**IV**) and arylboronic acid produced a carbon central free radical (**V**), then the reaction of **IV** and **V** formed to the product (**2a**).[20] Noteworthily, the hydroxyl radical might be induced by photolysis of TBHP, and O_2 could boost the production of hydroxyl radical (path C).[21]

Eventually, in order to verify the reaction mechanism, we explored further by ^{11}B NMR spectroscopy in real-time monitoring the progress of the reaction in standard conditions. After 8 h, it showed that **1a** was consumed a lot and a new signal peak at -10.5 ppm appeared. In addition, the amount of the new compound increased over time (scheme 7). Based on the literature,[7a,22] we surmised the new signal may be intermediate **III** (Scheme 6), furthermore, we detected it by GC-MS (see supporting information).

Conclusions

In conclusion, a TBHP and Cl_3CCN mediated, base-free *ipso*-hydroxylation of aryl boronic acid has been developed. The reaction was conducted under blue LED irradiation with oxygen, and had no use for any exogenous base. A broad series of functional groups were tolerated under the standard reaction condition, and resulted corresponding phenols in moderate to excellent yields, even the late-stage functionalization of the derivative of natural product gave the desired product. After the inhibition experiment for radical reaction, a multi of pathway mechanism was suggested. Then, the light/dark experiment demonstrated blue LED promoted the conversion

of the reaction. This methodology is a valuable exploration for application of unstable Lewis adduct intermediates in organic chemistry, and we detected it by ^{11}B NMR spectroscopy and GC-MS. Further investigations on the role of blue LED and practical application of Lewis adduct are currently ongoing in our laboratories.

Experimental section

General procedure for the *ipso*-hydroxylation reaction

Aryl boronic acids (0.6 mmol), 5.5 M TBHP in decane (0.6 mmol, 1.0 equiv.) and Cl_3CCN (0.9 mmol, 1.5 equiv.) were added to a 25 mL pressure tube under oxygen atmosphere. Dry MeCN (5 mL) was added subsequently. The mixture was then stirred under blue LEDs until the starting material had been consumed after 12 h. When the reaction was finished, the crude product was purified by flash chromatography on silica gel (PE/EA).

Placed the reaction device at the center of a stir plate and two parallel 15W blue LED lamps, make sure the fan always working in the process of reacting to eliminated the effect of the heat which generated from blue LED (Scheme S1).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (Grant No. 21871067), the Natural Science Foundation of Guangdong Province (Grant No. 2018A030313038), Shenzhen Fundamental Research Projects (Grant No. JCYJ20180306171838187), the Open Project Program of Hubei Key Laboratory of Drug Synthesis and Optimization, Jingchu University of Technology (No. OPP2015ZD01), the Open Project Program of Beijing National Laboratory for Molecular Sciences (BNLMS201819), and Harbin Institute of Technology (Shenzhen) (Talent Development Starting Fund from Shenzhen Government).

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