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Visible Light Induced Cyclization to Spirobi[indene] Skeletons from Functionalized Alkylidienecyclopropanes

Jiaxin Liu, Quanzhe Li, Yin Wei, and Min Shi*

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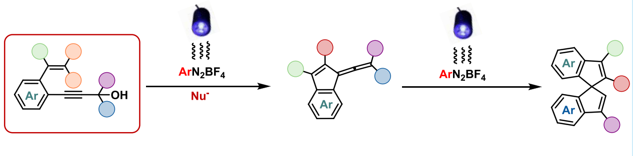
ABSTRACT: In this paper, we revealed a metal-free and visible light photoinduced method for the rapid construction of spirobi[indene] skeletons, providing a simple and efficient way for easy access to spirobi[indene] scaffolds under mild conditions along with a broad substrate scope and good functional group tolerance.



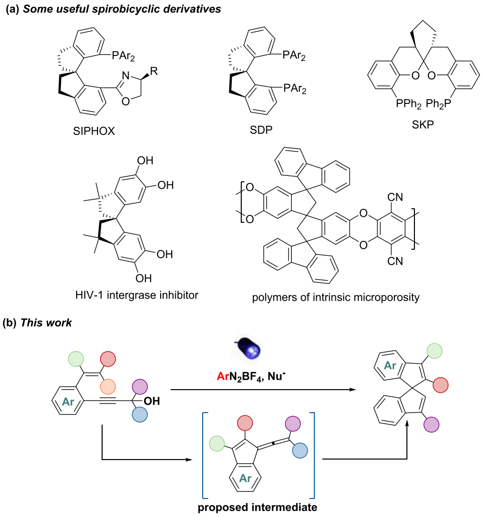
1) Metal free and environmental friendly
2) Broad substrate scope, fuctional group tolerance, and mild conditions
3) Rapid construction of indene fused allene and spirobi[indene] motif

Over the past decade, photoredox catalysis related reaction processes have emerged as powerful synthetic methods for the facile and selective construction of carbon−carbon and carbon−heteroatom bonds through the direct activation of organic compounds via open-shell pathways.[1] In general, the vast majority of photoredox catalysis involved reactions usually proceeded through single-electron-transfer (SET) process[2] or energy transfer process,[3] and the most prominent aspect is the SET process between metal complex/organic dye and organic substrate upon photoexcitation with visible light to generate the highly reactive radical or radical ionic species.[4] Recently, Fu and Shang's groups reported a catalytic intermolecular charge-transfer merged photoredox catalysis process, revealing a new photocatalytic strategy in organic synthesis, in which the use of expensive photocatalyst and the need for absorption of the desired light for each substrate could be avoided.[5] These interesting findings inspired us to explore more easily accessible and simpler photocatalytic protocol in organic synthesis.

Aryldiazonium salt has been recognized and broadly used as a single electron transfer acceptor ($E_{1/2\mathrm{red}} = -0.1$ V vs SCE for phenyldiazonium tetrafluoroborate) to generate aryl radical for further transformation through the release of nitrogen.[6] Combined with photoredox catalysis, we envisioned that aryldiazonium salt could be used as a single electron oxidant to trigger a redox process and subsequently initiate a series of tandem cyclizations.

As far as we know, spirobi[indene] skeletons extensively exist in chiral ligands,[7] polymers of intrinsic microporosity,[8] hydrogen storage materials,[9] drug candidates,[10] and could also be used as polymer membranes for the separation of gases[11] (Scheme 1a). Particularly, the application of axially chiral ligands with spirobicycle skeletons in asymmetric catalysis was developed by Ding,[12] Zhou,[13] and their coworkers. In addition, Tang and his coworkers have recently reported a class of novel deep-blue AIE materials containing spirobi[indene] moieties with high solid-state fluorescent quantum yield.[14] Therefore, the spirobi[indene] skeleton can represent a key intermediate in organic synthesis, material science, and medicinal chemistry. On the basis of our group's previous work, functionalized alkylidienecyclopropanes can smoothly undergo a variety of tandem cyclizations.[15] To this regard, we wish to report a rapid construction of indene fused allenic products and spirobi-

Scheme 1. Several Useful Spirobicyclic Skeletons and This Work



1) Metal free method
2) Broad substrate scope and mild conditions
3) Rapid construction of spirobi[indene] motif

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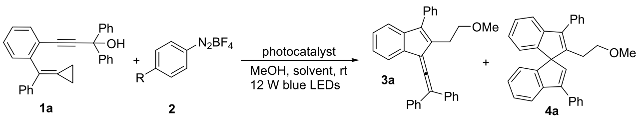
[indene] skeletons from propargyl alcohol-tethered alkenes or alkylidenecyclopropanes with diazonium salt upon visible light irradiation (Scheme 1b, this work).

To verify our working hypothesis, we initially investigated the reaction of propargyl alcohol-tethered alkylidenecyclopropane **1a** using $Ru(bpy)_3(PF_6)_2$ (5 mol %) as the photocatalyst, aryldiazonium salt **2a** (1.0 equiv) as the oxidizing reagent, and methanol (2.0 equiv) as the nucleophile upon visible light irradiation. The reaction proceeded smoothly to give the desired product **4a** in 89% yield under nitrogen atmosphere for 20 h (Table 1, entry 1). More interestingly, the desired product **4a** could also be obtained in 84% yield while in the absence of photocatalyst, suggesting that an autoredox process may occur between **1a** and **2a** upon photoirradiation (Table 1, entry 2). Increasing aryldiazonium salt **2a** to 2.0 equiv did not improve the yield of **4a**, and using 0.1 equiv of **2a** could also give **4a** in 82% yield (Table 1, entries 3 and 4). However, when the reaction time was reduced from 20 to 8 h, **4a** was produced in 44% yield along with an undesired allenic product **3a** in 43% yield (Table 1, entry 5). The yield of **3a** could be enhanced to 97% when the reaction time was further reduced to 2 h, implying that **3a** is the intermediate to give **4a** (Table 1, entry 6). The examination of solvent effects revealed that the use of toluene and MeOH in this reaction did not enhance the yield of **4a** (Table 1, entries 7 and 8). To our delight, we found that the yield of **4a** could be improved to 91% when 4-methylbenzenediazonium tetrafluoroborate salt **2b** was applied in the reaction (Table 1, entry 9). The control experiment demonstrated that the use of aryldiazonium salt is indispensable to produce **4a** (Table 1, entry 10). Meanwhile, the reaction worked efficiently as well under ambient atmosphere and condition (Table 1, entry 11). Subsequently, we investigated this reaction under dark conditions, but none of the desired product was acquired, indicating that the visible light irradiation is essential and the Brønsted acid-promoted process can be partially excluded (Table 1, entry 12) (for more information on the optimization of reaction conditions, see Table S1 in the Supporting Information). The structures of **3a** and **4a** have been unequivocally assigned by X-ray diffraction. The ORTEP drawings and the CIF data are summarized in the Supporting Information.

Table 1. Optimization of the Reaction Conditions for Construction of Spirobi[indene] Skeleton

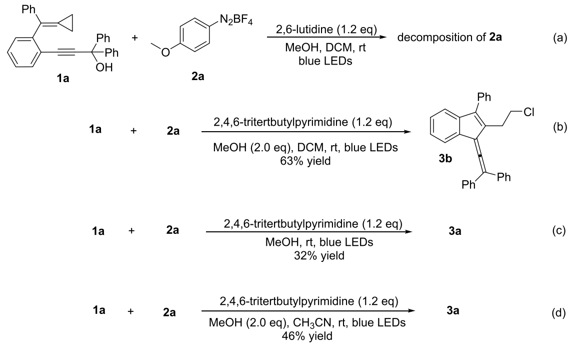


entry[a]	photocatalyst	2, R =	equiv of 2	solvent	yield of 3a	yield of 4a
1	$Ru(bpy)_3(PF_6)_2$	**2a**, -OMe	1.0	DCM		89
2		**2a**, -OMe	1.0	DCM		84
3		**2a**, -OMe	2.0	DCM		88
4		**2a**, -OMe	0.2	DCM		82
5[b]		**2a**, -OMe	1.0	DCM	43	44
6[c]		**2a**, -OMe	1.0	DCM	97	trace
7		**2a**, -OMe	1.0	toluene		
8		**2a**, -OMe	1.0	MeOH		48
9		**2b**, -Me	1.0	DCM		91
10		**2b**, -Me	0	DCM		
11[d]		**2b**, -Me	1.0	DCM		90
12[e]		**2b**, -Me	1.0	DCM		

[a] Reactions were carried out with **1a** (0.2 mmol), **2** (0.2 mmol), catalyst (5 mol %), and MeOH (0.4 mmol) in solvents (2 mL) at ambient temperature using 12W blue light irradiation for 20 h. Yields were determined by isolated product. [b] Reaction time was reduced to 8 h. [c] Reaction time was reduced to 2 h. [d] Using dry solvent without N_2-purged treatment. [e] In dark conditions.

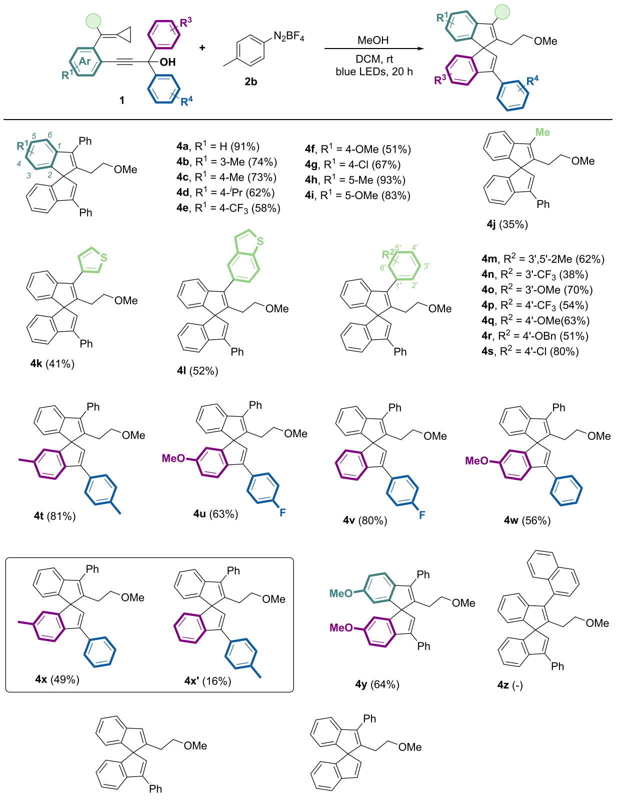
Although aryldiazonium tetrafluoroborate itself is a neutral salt, a Brønsted acid might be potentially generated under the reaction conditions. To exclude the Brønsted acid catalyzed process, control experiments in the presence of a base were performed. Using 2,6-lutidine as a base, the color of the reaction solution immediately became black red under the standard conditions, indicating the decomposition of aryldiazonium tetrafluoroborate salt (Scheme 2a).[16] The use of sterically bulky 2,4,6-tri*tert*-butylpyrimidine as a base to trapping the *in situ* generated proton source, a chlorinated allenic intermediate **3b** was produced in 63% yield (Scheme 2b). Employing MeOH or the mixed MeOH/MeCN as the solvent, the intermediate **3a** was afforded in 32 and 46% yields, respectively (Schemes 2c and 2d). Moreover, upon treating **1a** and **3a** with catalytic amount of $Et_3N{\cdot}3HF$, none of the desired products was obtained. The results of these control experiments excluded a Brønsted acid catalysis process. Furthermore, only the allenic product was obtained in the above control experiments, indicating the requirement of a nonalkaline environment to acquire **4**.

Scheme 2. Control Experiments in the Presence of a Base



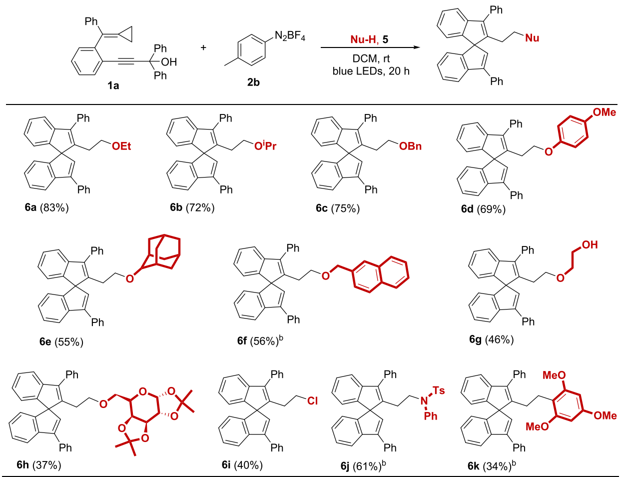
The substrate scope of this novel photoinduced process was then evaluated through variation of the propargyl alcohol-tethered alkylidenecyclopropanes under the optimized conditions, and the results are summarized in Scheme 3. First, alkylidenecyclopropanes **1b**−**1i**, in which R^1 could be diversified substituents whether they were electron-donating or electron-withdrawing ones, delivered the desired products **4b**−**4i** in 51−93% yields. Aliphatic methyl group and heteroaromatic groups were also tolerated, affording the corresponding products **4j**, **4k**, and **4l** in 35, 41, and 52% yields, respectively. For substrates **1m**−**1s**, R^2 could be a variety of substituents, affording the desired products in moderate to good yields ranging from 38 to 80%. It is worth noting that when the substituent was a CF_3 group, the desired

Scheme 3. Substrate Scope of the Propargyl Alcohol-Tethered ACPs 1, 2b, and MeOH



[a]Reactions were carried out with **1** (0.2 mmol), **2b** (0.2 mmol), and MeOH (0.4 mmol) in DCM (2 mL) at ambient temperature using 12 W blue light irradiation for 20 h. Yields were determined by isolated products.

Scheme 4. Substrate Scope of the Propargyl Alcohol-Tethered ACPs 1a, 2b, and Nucleophile 5



[a]Reactions were carried out with **1a** (0.2 mmol), **2b** (0.2 mmol), and Nu-H (0.4 mmol) in DCM (2 mL) at ambient temperature using 12 W blue light irradiation for 20 h. Yields were determined by isolated products. [b]Reactions were carried out with 100 W blue light irradiation for 20 h.

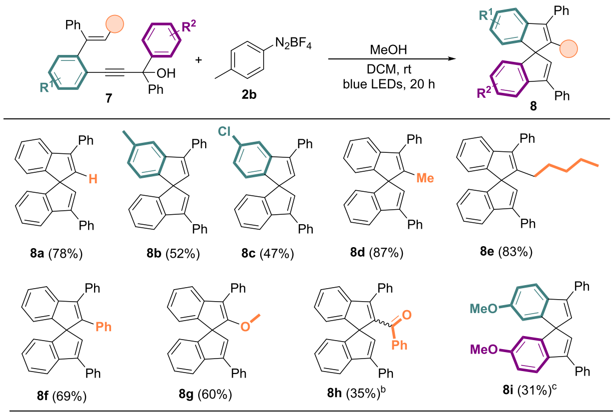
product was given in 38% yield perhaps due to the electronic effect. Then, we examined the substituents at the benzene ring of the propargyl alcohol. The reactions also worked very well, furnishing the desired products **4t**−**4x** in moderate to good yields ranging from 56% to 81%. As being verified in the mechanistic studies, these substrates showed a significant chemoselectivity in the cyclization process with electron-rich aromatic ring to construct the spirobi[indene] skeleton. In the case of substrate **1x**, two regioisomers **4x** and **4x′** were afforded in 43 and 22% yields, respectively. As for substrate **1y** bearing two methoxyl substituents at different benzene rings, the corresponding spirobi[indene] **4y** having two symmetrical methoxy groups was produced in 64% yield, which might be used as a ligand precursor after closing the five-membered ring by a further transformation. Unfortunately, when R^2 was a 1-naphthyl group or a hydrogen atom, we failed to acquire the desired products under the standard reaction conditions. When tetra-substituted propargyl alcohol was replaced with trisubstituted propargyl alcohol, no reaction occurred.

Moreover, the scope of nucleophiles **5** was also examined, and the results are shown in Scheme 4. As for alcoholic nucleophiles, no matter if a primary alcohol, secondary alcohol, benzyl alcohol, phenol, or functionalized alcohol was used as the nucleophile, the desired products **6a**−**6g** were obtained in moderate to good yields ranging from 46 to 83%. Notably, sugar was a suitable nucelophile as well, giving the desired product **6h** in 37% yield with this mild photoinduced protocol. Interestingly, a chlorinated spirobi[indene] **6i** was obtained in 40% yield if using indole as the nucleophile. A photoinduced SET process between indole and DCM caused the C−Cl bond cleavage, and then the chlorine atom was transferred into the spirobi[indene] skeleton to afford **6i**.[17] By changing the alcoholic nucleophile to a nitrogen nucleophile, we found that aniline substituted by an electron-withdrawing Ts group performed well, furnishing the desired product **6j** in 61% yield. Carbon nucleophile could be also utilized in this photoinduced platform, affording the corresponding product **6k** in 34% yield.

To further extend the substrate scope of this photoinduced synthetic method, the corresponding propargyl alcohol-tethered alkenes **7** were used as substrates in this transformation under the standard conditions, and the results are outlined in Scheme 5. Substrates **7a**−**7c** without or with a substituent on the benzene ring gave the desired products **8a**−**8c** in 47−78% yields. A series of substituted alkenes by an alkyl group, a phenyl group, a methoxyl group, or a benzoyl group were all tolerated, affording the desired products **8d**−**8h** in moderate to good yields ranging from 35−87%. It is noticeable that product **8h** was obtained as an atropisomeric mixture. As mentioned above, substrate **7i** bearing two methoxyl groups at different benzene rings could produce a symmetrical spirobi[indene] **8i** in 31% yield, which could be used for the preparation of bidentate ligand by replacing the two methoxy groups with ligated atoms.

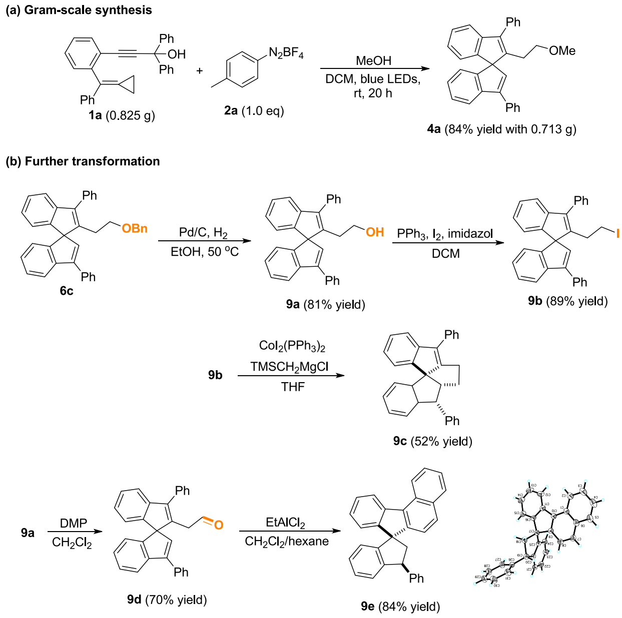
The potential synthetic practicability of this novel protocol on gram-scale was next assessed. As shown in Scheme 6a, the reaction of **1a** (0.825 g, 2.0 mmol) with **2a** (1.0 equiv) produced **4a** in 84% yield (0.713 g) under the optimized reaction conditions. Moreover, to demonstrate the synthetic application of these products derived from this synthetic protocol, the further transformations of **6c** was presented in Scheme 6b. Debenzylation of **6c** was easily achieved in the presence of Pd/C under H_2 atmosphere, giving **9a** in 81% yield. Iodination of **9a** with Appel reaction produced **9b** in 89% yield, which could be transformed to the desired spiropolycyclic product **9c** in 52% yield via a Co-catalyzed

Scheme 5. Substrate Scope of the Propargyl Alcohol-Tethered Alkenes 7, 2b, and MeOH



[a] Reactions were carried out with **7** (0.2 mmol), **2b** (0.2 mmol), and MeOH (0.4 mmol) in DCM (2 mL) at ambient temperature using 12 W blue light irradiation for 20 h. Yields were determined by isolated product. [b] An atropisomeric mixture with major isomer:minor isomer = 3:1. [c] The reaction was carried out in the absence of MeOH.

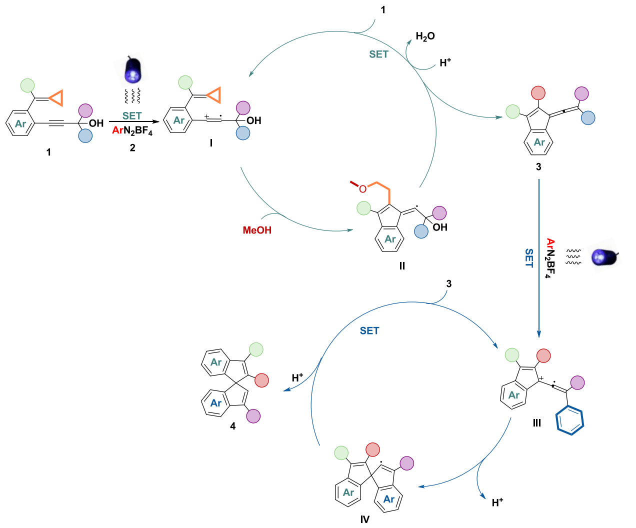
Scheme 6. Gram-Scale Synthesis and Further Transformation of the Obtained Products to Ligand and Spiroaromatic Compound



reductive Heck-type reaction in the presence of $TMSCH_2MgCl$ as a single diastereomer. The relative configuration of **9c** was confirmed by NOESY spectroscopy (see page S106 in the Supporting Information). This synthetic method offered an opportunity to prepare the spirobicyclic ligand skeletons as those of Zhou's and Ding's ligands from the spirobi[indene]s **4y** and **8i**. In addition, the corresponding aldehyde **9d** could be obtained in 70% yield upon oxidation of **9a**, which could be readily transformed to a phenyl group pendant spirocyclic product **9e** in 84% yield upon treatment with $EtAlCl_2$ as a Lewis acid through an intramolecular Friedel−Crafts-type reaction.[14] The structure of **9e** was unequivocally assigned by X-ray diffraction. The ORTEP drawing is shown in Scheme 6, and the CIF data are summarized in the Supporting Information.

The proposed mechanism is outlined in Scheme 7. The reaction would be initiated via a SET between propargyl

Scheme 7. Proposed Mechanism



alcohol-tethered alkylidenecyclopropane **1** and aryldiazonium salt **2** to generate a radical cation **I** upon visible light irradiation. The radical cation **I** would undergo a cyclization followed by a ring-opening process upon nucleophilic attack of methanol to deliver the corresponding radical intermediate **II**. Then, another SET takes place between **II** and **1** to obtain the allenic product **3** accompanied by the regeneration of intermediate **I**. The allenic product **3** could be oxidized by **2** to generate a radical cation **III** upon visible light irradiation. At this stage, the radical cation **III** would give a spirobi[indene] skeletons **IV** under a nucleophilic attack of phenyl group. Hence, another SET takes place between **IV** and **3** to obtain the allenic product **4** accompanied by the regeneration of intermediate **III**.

In summary, we accomplished a direct cascade cyclization of propargyl alcohol-tethered alkenes or alkylidenecyclopropanes for the rapid construction of spirobi[indene] skeletons through a photochemical process. This novel photochemical synthetic protocol exhibits a broad substrate scope, excellent functional group tolerance, and can be successfully adapted to a scale-up application. To the best of our knowledge, this reaction demonstrated an unprecedented photoinduced pathway leading to an overall redox-neutral process in organic synthesis for the rapid construction of molecular complexity. The detailed mechanistic study of this novel synthetic method is currently under investigation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c00787.

> Experimental procedures, characterization data, and NMR spectra (PDF)

Accession Codes

CCDC 1841167, 1846951, and 1905929 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Min Shi − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Sciences, Shanghai 200032, China; Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen, Guangdong 518000, China;* orcid.org/0000-0003-0016-5211; Email: mshi@mail.sioc.ac.cn; Fax: 86-21-64166128

Authors

Jiaxin Liu − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Sciences, Shanghai 200032, China*

Quanzhe Li − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Sciences, Shanghai 200032, China*

Yin Wei − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Science, Chinese Academy of Sciences, Shanghai 200032, China;* orcid.org/0000-0003-0484-9231

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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