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Letter

Asymmetric Synthesis of 2,2-Disubstituted Dihydroquinolines via Rhodium-Catalyzed Dearomative Arylation and Alkenylation of 2-Substituted Quinolinium Salts

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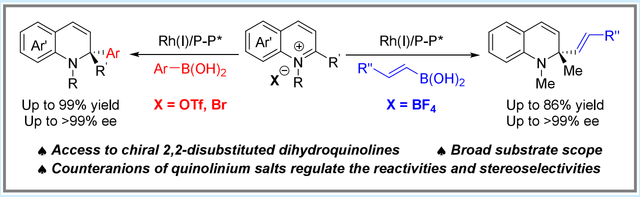
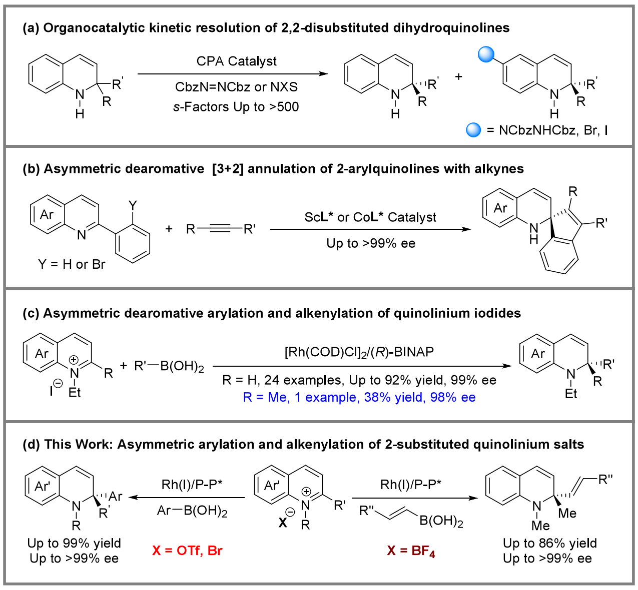
ABSTRACT: A synthetic protocol for the construction of chiral 2,2-disubstituted dihydroquinolines via rhodium-catalyzed asymmetric dearomative arylation and alkenylation of 2-substituted quinolinium salts has been disclosed. 2-Substituted quinolinium triflates and bromide preferred to undergo asymmetric arylation with arylboronic acids, and 2-substituted quinolinium tetrafluoroborate favored to carry out asymmetric alkenylation with alkenylboronic acids, providing a series of chiral 2,2-disubstituted dihydroquinolines with high yields and enantioselectivities. The key for this dearomative reaction stands in the counteranions of 2-substituted quinolinium salts, which guarantee the reactivities and stereoselectivities at the same time.



Enantioenriched tetrahydroquinolines (THQs) and dihydroquinolines (DHQs) belong to the nontrivial and common class of chiral nitrogen-containing heterocycles, which widely exist in natural products, pharmaceuticals, and biologically active molecules.[1] Due to the significant importance, their asymmetric synthesis has elicited considerable interests.[2−7] As DHQs can be conveniently transformed into THQs through reduction and functionalization, the development of efficient synthesis of chiral DHQs has gained substantial attention.[3−7] In contrast to the enantioselective synthesis of 2-substituted DHQs, the construction of chiral 2,2-disubstituted DHQs is more challenging due to intrinsic steric hindrance. There are few reports on the asymmetric synthesis of optically active 2,2-disubstituted DHQs.[5−7] In 2021, Yang and co-workers developed kinetic resolution of 2,2-disubstituted DHQs through chiral phosphoric-acid-catalyzed amination and halogenation, delivering chiral 2,2-disubstituted DHQs with high enantioselectivities (Scheme 1a).[5] Hou's group and Jia's group realized a modular access to chiral spirodihydroquinolines with excellent enantioselectivities, independently. Hou's group reported scandium-catalyzed asymmetric dearomative [3 + 2] annulation of 2-arylquinolines with alkynes,[6] and Jia's group disclosed cobalt-catalyzed asymmetric dearomative [3 + 2] umpolung annulation of 2-*o*-bromoarylquinolines with alkynes (Scheme 1b).[7] Despite these fascinating works for the preparation of chiral 2,2-disubstituted DHQs, developing a straightforward and facile strategy for the synthesis of enantioenriched 2,2-disubstituted DHQs is still in high demand.

Asymmetric dearomative nucleophilic addition of active quinolinium salts is an attractive and practical approach for providing chiral 2-substituted DHQs.[4] Previously, Wei, Wang,

Scheme 1. Asymmetric Synthesis of 2,2-Disubstituted Dihydroquinolines



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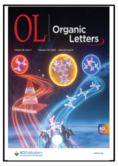
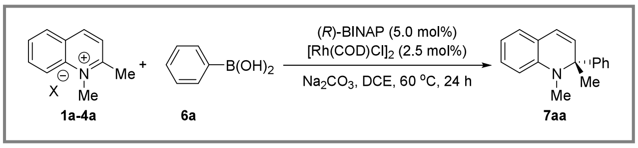


and co-workers disclosed an elegant rhodium-catalyzed asymmetric dearomative arylation and alkenylation of *N*-ethylquinolinium iodides, giving 2-substituted DHQs with high yields and enantioselectivities. Nevertheless, it was not compatible for 2-substituted quinolinium iodide, giving the corresponding product chiral 2,2-disubstituted dihydroquinoline in only 38% yield (Scheme 1c).[4d] Depending on our continuous efforts in asymmetric hydrogenation of *N*-heteroarenes to synthesize *N*-heterocycles[8] and considering that the counteranions of *N*-heteroarenium salts play a crucial role in the improvement for the reactivity of hydrogenation, we envisaged that the appropriate regulation of the counteranions of 2-substituted quinolinium salts would facilitate the asymmetric dearomative nucleophilic addition of 2-substituted quinolinium salts with high yields and enantioselectivities. Herein, we disclosed a direct synthetic approach toward chiral 2,2-disubstituted DHQs via rhodium-catalyzed asymmetric dearomative arylation and alkenylation of 2-substituted quinolinium salts with regulation of the counteranions (Scheme 1d). 2-Substituted quinolinium triflates and bromide were favorable for asymmetric arylation, and 2-substituted quinolinium tetrafluoroborate was suitable for asymmetric alkenylation, giving a wide range of chiral 2,2-disubstituted DHQs with high yields and excellent enantioselectivities.

To test our hypothesis, we initially explored the effect of counteranions on the asymmetric dearomatization of 2-methylquinolinium salts with phenylboronic acid **6a**. The reaction was conducted using $[Rh(COD)Cl]_2$ and (*R*)-BINAP as the catalyst and sodium carbonate as the base in dichloroethane at 60 °C for 24 h (Table 1). In accordance with our prediction, the counteranions of 2-methylquinolinium salts significantly impact the reactivity and enantioselectivity. When 1,2-dimethylquinolinium iodide **1a** was employed, the desired product **7aa** was obtained with 16% yield and 51% ee (entry 1). When the quinolinium salt was changed from iodide to tetrafluoroborate **2a**, the yield of **7aa** increased to 39% (entry 2). Using 1,2-dimethylquinolinium hexafluorophosphate **3a** and 1,2-dimethylquinolinium triflate **4a**, the target product was achieved with 63 and 71% yields, respectively (entries 3 and 4). These results suggested that more hydrophobic quinoliniums, which contain more hydrophobic counteranions, consistently gave higher yields according to previous literature reports.[9]

Table 1. Evaluation of Counteranions[a]

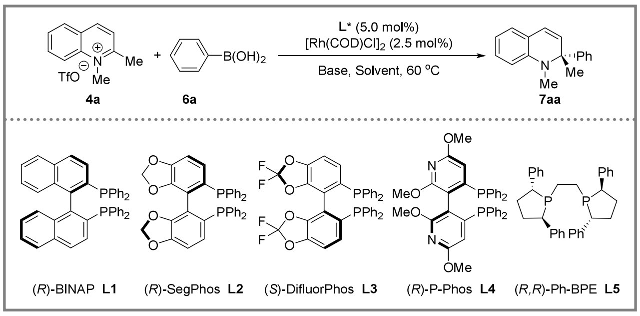


entry	X	yield (%)[b]	ee (%)[c]
1	I (**1a**)	16	51
2	BF_4 (**2a**)	39	69
3	PF_6 (**3a**)	63	97
4	OTf (**4a**)	71	96

[a]Reaction conditions: 2-methylquinolinium salts (0.20 mmol), **6a** (0.50 mmol), $[Rh(COD)Cl]_2$ (2.5 mmol %), (*R*)-BINAP (5.0 mol %), Na_2CO_3 (0.50 mmol), and DCE (3.0 mL) at 60 °C for 24 h. [b]Isolated yield. [c]Determined by chiral HPLC.

Based on the aforementioned evaluation of counteranions of quinolinium salts, 1,2-dimethylquinolinium triflate **4a** and phenylboronic acid **6a** were chosen as model substrates to further optimize the reaction conditions (Table 2). We initially investigated the effect of bases on this dearomative reaction. In the absence of a base, the asymmetric arylation shut down (entry 6). Triethylamine and *N*,*N*-diisopropylethylamine were suitable bases (entries 1−6). In view of all things, triethylamine could give satisfying results (92% yield and 98% ee) and was proven to be the best base. Subsequently, the assessment of solvents revealed that ethanol was the preferable solvent to generate **7aa** in >95% yield and 98% ee (entries 7−10). We then turned attention to chiral ligands. Gratifyingly, the ee value was improved to >99% when (*R*)-SegPhos (**L2**) was used (entry 11). (*S*)-DifluorPhos (**L3**) with an electron-withdrawing functional group was employed, providing the desired product with excellent enantioselectivity and 74% yield (entry 12). When the catalyst loading and amount of boronic acid were reduced, the yield and enantioselectivity were not affected (entries 15 and 16). In order to guarantee a high yield and ee value, 5.0 mol % catalyst and 2.5 equiv of phenylboronic acid were utilized. Finally, the yield and enantioselectivity of **7aa** were maintained when the reaction temperature was reduced from 60 to 40 °C (entry 17).

Table 2. Optimization of Reaction Conditions[a]

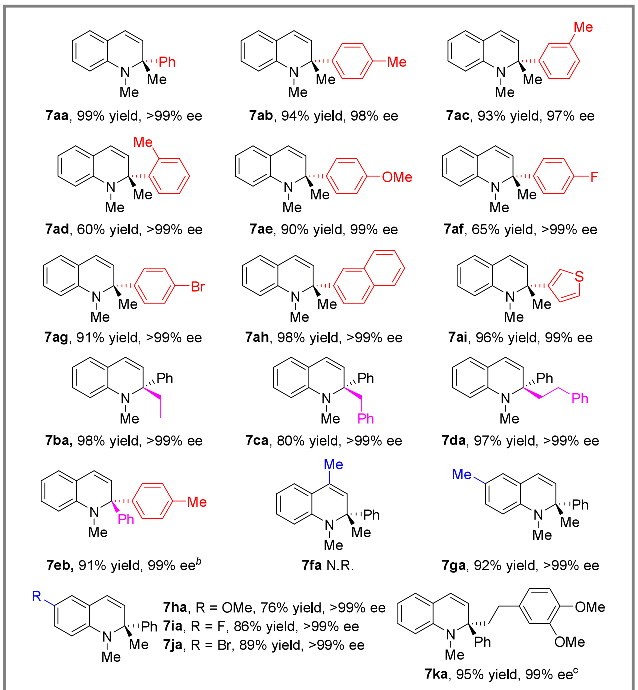


entry[a]	base	solvent	L*	yield (%)[b]	ee (%)[c]
1	Na_2CO_3	DCE	**L1**	71	96
2	K_2CO_3	DCE	**L1**	85	98
3	Cs_2CO_3	DCE	**L1**	80	98
4	Et_3N	DCE	**L1**	92	98
5	DIPEA	DCE	**L1**	92	97
6	--	DCE	**L1**	trace	--
7	Et_3N	THF	**L1**	90	96
8	Et_3N	toluene	**L1**	93	97
9	Et_3N	CH_3CN	**L1**	trace	--
10	Et_3N	EtOH	**L1**	>95	98
11	Et_3N	EtOH	**L2**	>95	>99
12	Et_3N	EtOH	**L3**	74	96
13	Et_3N	EtOH	**L4**	>95	98
14	Et_3N	EtOH	**L5**	84	97
15[d]	Et_3N	EtOH	**L2**	>95	>99
16[e]	Et_3N	EtOH	**L2**	>95	>99
17[f]	Et_3N	EtOH	**L2**	>95 (99)[g]	>99

[a]Reaction conditions: **4a** (0.20 mmol), **6a** (0.50 mmol), $[Rh(COD)Cl]_2$ (2.5 mmol %), L* (5.0 mol %), base (0.50 mmol), and solvent (3.0 mL) at 60 °C for 24 h. [b]The yield was measured by analysis of ^1H NMR spectra, using 1,3,5-trimethoxybezene as the internal standard. [c]Determined by chiral HPLC. [d]$[Rh(COD)Cl]_2$ (1.25 mmol %) and L* (2.5 mol %). [e]**6a** (0.30 mmol) and Et_3N (0.30 mmol). [f]At 40 °C. [g]Isolated yield.

With the optimal conditions in hand, we investigated the generality and practicality of this asymmetric arylation (Scheme 2). Initially, the substrate scope of arylboronic acid 6 was evaluated. Regardless of the electronic properties and positions of the substituents on the aromatic ring, a broad range of arylboronic acids **6b**−**6g** were effective in producing target 2,2-disubstituted DHQs **7ab**−**7ag** with excellent enantioselectivities and moderate to good yields. Furthermore, 2-naphthaleneboronic acid **6h** and 3-thiopheneboronic acid **6i** also participated in this asymmetric dearomative reaction successfully, affording **7ah** and **7ai** in high yields and enantioselectivities. Next, we examined the scope of 2-substituted quinolinium triflates **4**. The tolerance of various alkyl groups at the C2 position of the quinolinium ring was first investigated. The results showed that all kinds of 2-alkyl-substituted quinolinium salts transformed to their corresponding products **7ba**−**7da** with satisfactory yields and up to >99% ee. Moreover, 2-phenylquinolinium triflate **6e** was also the suitable reaction partner, affording **7eb** with 91% yield and 99% ee under standard reaction conditions for 72 h. Nevertheless, introducing a methyl group at the C4 position of the quinolinium ring prevented the formation of the desired product **7fa**. Additionally, we conducted the reaction at the standard conditions using Rh(COD)$_2$BF$_4$ instead of [Rh(COD)Cl]$_2$, and the desired product **7fa** could still not be observed, which might be caused by steric hindrance. Electron-donating and electron-withdrawing substituents at the C6 position of the quinolinium ring were acceptable for this protocol, generating products **7ga**−**7ja** in moderate to good yields with excellent enantioselectivities. The absolute configuration of product **7ja** was determined to be *R* based on its single-crystal X-ray analysis (see the Supporting Information for details), and other products were determined by analogy.

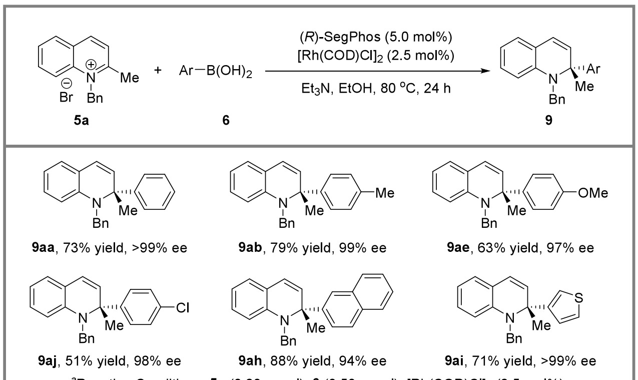
Scheme 2. Substrate Scope: 2-Substituted Quinolinium Triflates 4 and Arylboronic Acids 6



[a]Reaction Conditions: **4** (0.20 mmol), **6** (0.50 mmol), [Rh(COD)Cl]$_2$ (2.5 mol%), (*R*)-SegPhos (**L2**) (5.0 mol%), Et$_3$N (0.50 mmol), EtOH (3.0 mL), 40 °C, 24 h. [b]72 h. [c](*S*)-SegPhos (5.0 mol%), 60 °C.

Considering the easy deprotection of the *N*-benzyl group, asymmetric arylation of *N*-benzyl-2-methylquinolinium bromide **5a** with arylboronic acids **6** was also investigated (Scheme 3). The dearomative arylation of **5a** with phenylboronic acid **6a** proceeded smoothly and gave 2,2-disubstituted DHQ **9aa** with 73% yield and >99% ee by increasing the reaction temperature to 80 °C (see Table S1 in the Supporting Information for details). With the introduction of methyl and methoxy groups at the *para* position of the aromatic ring, the desired products **9ab** and **9ae** were obtained with moderate yields and excellent ee values. In addition, 2-naphthaleneboronic acid and 3-thiopheneboronic acid were also suitable, and the target products **10ah** and **10ai** were obtained with excellent enantioselectivities.

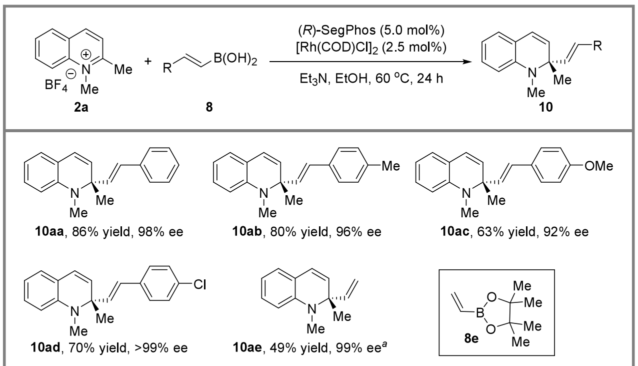
Scheme 3. Asymmetric Arylation of *N*-Benzyl-2-methylquinolinium Bromide 5a



[a]Reaction Conditions: **5a** (0.20 mmol), **6** (0.50 mmol), [Rh(COD)Cl]$_2$ (2.5 mol%), (*R*)-SegPhos (**L2**) (5.0mol%), Et$_3$N (0.50 mmol), EtOH (3.0 mL), 80 °C, 24 h.

To expand the scope of organic boronic acids, we examined the applicability of alkenylboronic acids **8** in these dearomative reactions of 2-substituted *N*-methylquinolinium salts (Scheme 4). When tetrafluoroborate **2a** was utilized, the corresponding alkenylation product **10aa** was obtained with 86% yield and 98% ee at 60 °C (see Table S2 in the Supporting Information for details). Different kinds of aryl-substituted alkenylboronic acids were well-tolerated, affording the desired products **10ab**−**10ad** in moderate yields with excellent enantioselectiv-

Scheme 4. Asymmetric Alkenylation of 2-Substituted Quinolinium Tetrafluoroborate 2a

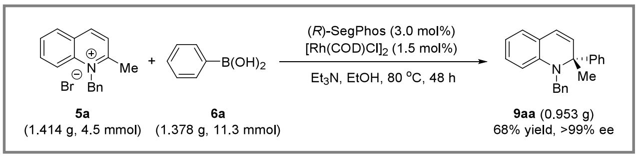


[a]Reaction Conditions: **2a** (0.20 mmol), **8** (0.50 mmol), [Rh(COD)Cl]$_2$ (2.5 mol%), (*R*)-SegPhos (**L2**) (5.0mol%), Et$_3$N (0.50 mmol), EtOH (3.0 mL), 60 °C, 24 h.

ities. Notably, simple vinylboronic acid pinacolester **8e** was a suitable reaction partner, and the dearomative alkenylation product **10ae** was obtained with a moderate 49% yield and 99% ee. For alkyl-substituted alkenylboronic acids, which were successfully utilized in Wei's and Wang's work,[4d] the reaction failed to obtain the target products. Moreover, when the reactions were proceeded under the standard conditions using $Rh(COD)_2BF_4$ instead of $[Rh(COD)Cl]_2$, the desired product could still not be achieved.

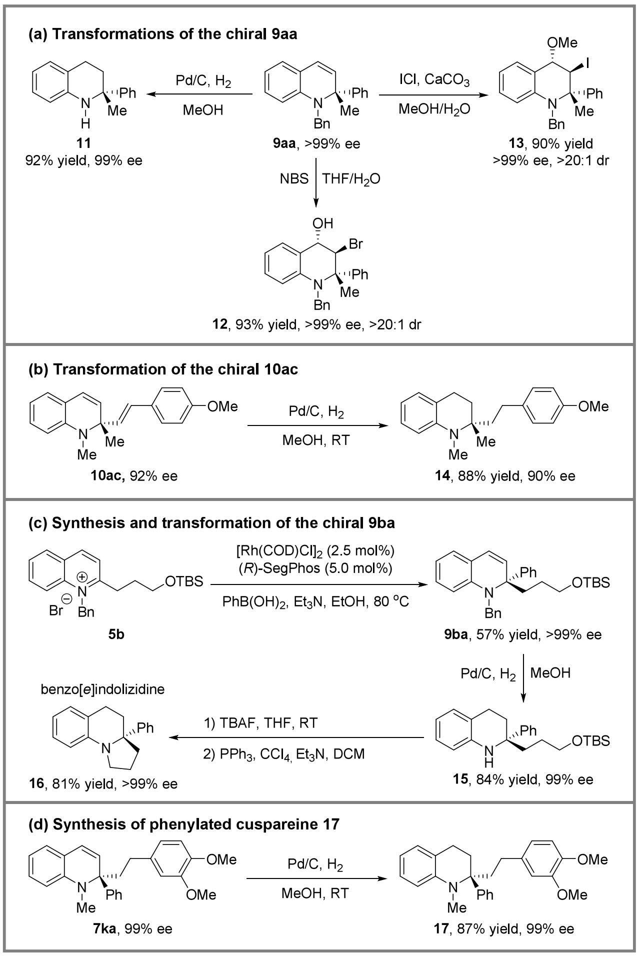
To illustrate the practicality of this rhodium-catalyzed dearomative reaction, a gram-scale synthesis of **10aa** was carried out (Scheme 5). The product was isolated with 68% yield and >99% ee under the standard conditions without obvious loss of reactivity and enantioselectivity.

Scheme 5. Gram-Scale Experiment



The synthetic utility was verified by the transformations of chiral 2,2-disubstituted DHQs (Scheme 6). Chiral *N*-benzyl-2,2-disubstituted DHQ **9aa** underwent hydrogenolysis and hydrogenation to provide 2,2-disubstituted THQ **11** with 92% yield and 99% ee. Treatment of **9aa** with different halogenated reagents produced the corresponding 3,4-difunctionalized THQ derivatives **12** and **13** with high diastereoselectivities and without erosion of optical purities (Scheme 6a). The configuration of the hydroxyl and bromo groups in product **12** was assigned as (*S*,*S*) by the NOE spectrum (see the Supporting Information for details). Subsequently, hydrogenation of 2-alkenyl-2-methyldihydroquinoline **10ac** gave chiral THQ **14** with 88% yield and 90% ee (Scheme 6b). Asymmetric dearomative arylation of quinolinium salt **5b** with phenylboronic acid afforded *N*-benzyl-2,2-disubstituted DHQ **9ba** (57% yield and >99% ee) under standard conditions. Hydrogenolysis and hydrogenation of **9ba** delivered THQ **15** in 84% yield with 99% ee. Obtained THQ **15** went through deprotection of the TBS group, Appel reaction, and intramolecular cyclization to afford benzo[*e*]indolizidine **16** with 81% yield and the retained ee (Scheme 6c), which is a prevalent motif in indolizidine and quinolizidine alkaloids.[10] As cuspareine belongs to Hancock alkaloid,[11] phenylated cuspareine **17** was synthesized in 87% yield via hydrogenation of chiral DHQ **7ka** (Scheme 6d).

Scheme 6. Synthetic Transformations



In summary, we have established rhodium-catalyzed asymmetric dearomative arylation and alkenylation of 2-substituted quinolinium salts, providing various chiral 2,2-disubstituted DHQs with excellent yields and enantioselectivities. The counteranions of 2-substituted quinolinium salts played a predominant role in this asymmetric arylation and alkenylation, facilitating both high reactivities and stereoselectivities. 2-Substituted quinolinium triflates and bromide were preferable for asymmetric arylation, and 2-substituted quinolinium tetrafluoroborate was suitable for asymmetric alkenylation. The gram-scale experiments and synthetic transformations demonstrated the potential utility of this dearomative strategy. We hope that this work will pave the way for the construction of chiral 2,2-disubstituted DHQs and THQs.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c05303.

Experimental procedures, characterization data, single-crystal X-ray data, and copies of NMR and HPLC spectra (PDF)

Accession Codes

Deposition Number 2246605 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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