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Synthesis and separation of two stereoisomers of deuterated tetrasubstituted allylic alcohols *via* consecutive dual 1,2-metallate shifts

Puhui Li,[a] Yajun Yu,[a] Xingxing Ma*[ab] and Qiuling Song *[acd]

Herein, we report an efficient strategy for the synthesis and stereoisomer separation of deuterated tetrasubstituted allylic alcohols from alkynyl tetracoordinate boron species using readily available D_2O as the deuterium source in a single vessel system. This transformation proceeds *via* consecutive dual 1,2-metallate shifts, achieving efficient construction of both isomeric deuterated allylic alcohols without the requirement for condition optimization or the selection of special reagents and substrates upon oxidation. And the method features quantitative deuterium incorporation (>99%), broad substrate scope, and direct access to pharmaceutically relevant scaffolds under mild conditions.

Introduction

Transformations of alkynes into alkenes are a cornerstone reaction in organic synthesis, providing a versatile route to construct carbon–carbon double bonds with defined stereochemistry.[1–3] Achieving precise control over the geometry (*E*/*Z*) of these alkenes is paramount, as it profoundly influences the molecule's physical properties, biological activity, and subsequent reactivity.[4–9] Nevertheless, exercising this control remains a significant and ongoing challenge. Additionally, a mixture of isomers is of limited value, since the distinct properties of each stereoisomer are often essential for downstream applications or biological evaluation. Consequently, the formation of a mixture poses a formidable challenge for separation due to the nearly identical physicochemical properties (*e.g.*, polarity, boiling point) of the (*E*)- and (*Z*)-isomers, making many techniques largely ineffective. This inherent difficulty underscores the critical need for developing novel synthetic strategies that can either achieve high stereoselectivity or provide a means for the straightforward separation of the resulting isomeric products.

Deuterated molecules represent a significant class of high value-added compounds. In pharmaceutical chemistry, the strategic incorporation of deuterium atoms into organic molecules can modulate key pharmacokinetic properties, including absorption, distribution, metabolism, and excretion (ADME).[10–12] Consequently, deuterium-containing drugs are increasingly employed in clinical settings. Within synthetic chemistry, deuterium-labeled molecules serve as indispensable tools for elucidating hydrogen sources in reaction systems, tracing reaction pathways, and measuring kinetic isotope effects (KIE) to probe reaction mechanisms.[13] Deuterated olefins, a prominent subset of deuterium compounds, are prevalent structural motifs in both natural products and synthetic pharmaceuticals (Scheme 1a).[14–17] Current synthetic strategies for accessing deuterated olefins exhibit limitations. Traditional ionic approaches, employing strong acids (*e.g.*, DCl, D_2SO_4) or bases (*e.g.*, NaOD) and organometallic reagents to facilitate H/D exchange, often suffer from poor functional group compatibility and low chemoselectivity.[18] Transition metal catalysis (utilizing Ir, Pd, Pt, Ru, Rh, *etc.*) *via* C–H activation offers an alternative, but typically requires expensive catalysts and ligands under demanding reaction conditions.[18–21] Single-electron transfer processes provide another route, although they encompass diverse reaction types with varying efficiencies. Despite these advances, the development of novel, robust, and practical methodologies for assembling deuterated olefins from readily accessible substrates under mild conditions remains highly desirable.[16,18,22]

Organoboron compounds represent a vital class of synthetic intermediates with broad applications in pharmaceutical chemistry and materials science.[23–26] Among these, allylboronates have garnered increasing attention as versatile precursors for constructing diverse allylic compounds through metal-catalyzed reactions,[27–30] radical transformations,[31] and migration processes.[32–35] Despite their utility, synthetic access to allylboronates remains limited. Representative advances include Morkens' report[36] of a palladium-catalyzed enantioselective conjunctive cross-coupling to access terminal and

[a]Key Laboratory of Molecule Synthesis and Function Discovery, Fujian Province University, College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350108, China. E-mail: maxx@fzu.edu.cn; qsong@fzu.edu.cn

[b]Hubei Key Laboratory of Pollutant Analysis & Reuse Technology, College of Chemistry and Chemical Engineering, Hubei Normal University, Huangshi, 435002, China

[c]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, China

[d]School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan, 453007, China

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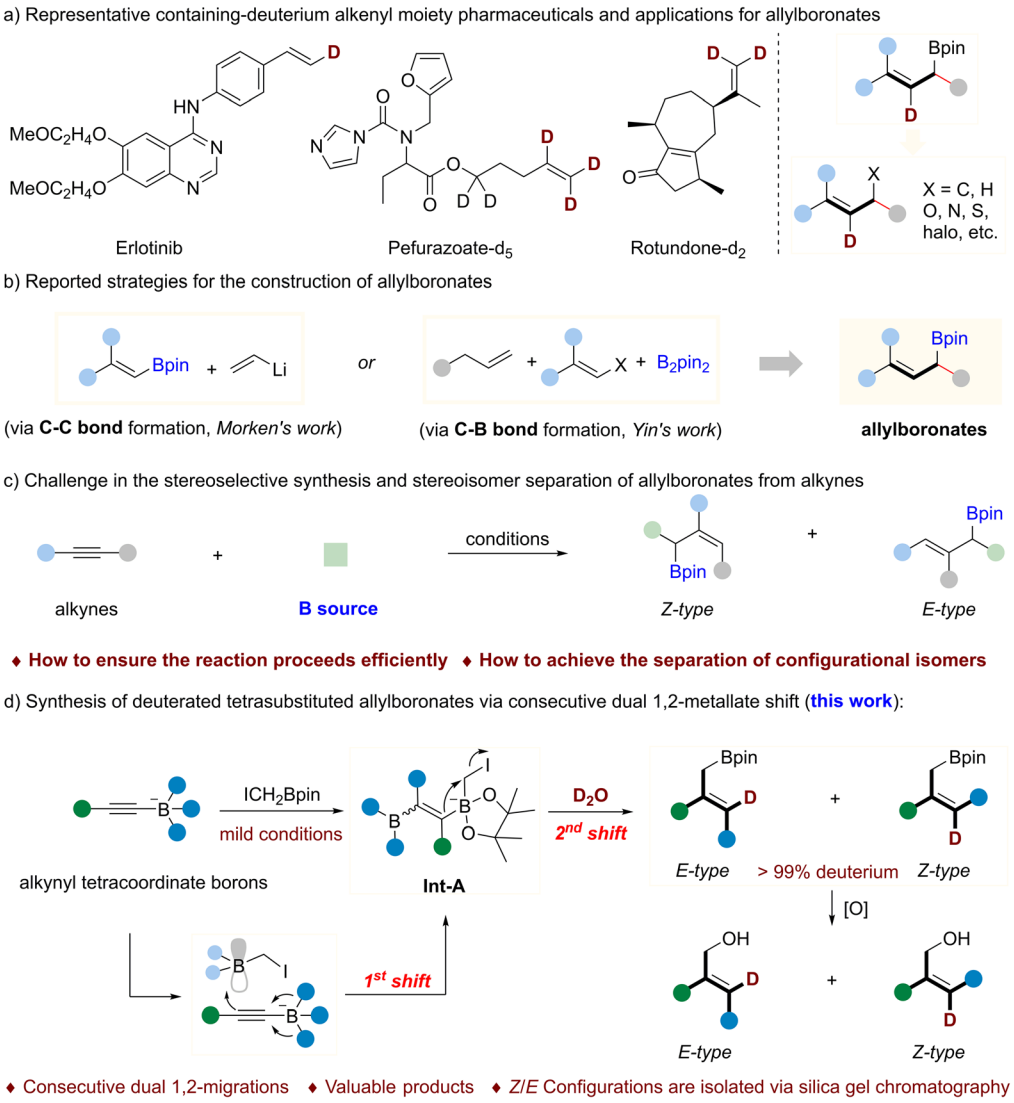

Scheme 1 Significance of deuterated olefins and approaches to allylborons. (a) Representative containing-deuterium alkenyl moiety pharmaceuticals and applications for allylboronates; (b) representative methods for the construction of allylboronates; (c) challenge in the stereoselective synthesis of allylboronates from alkynes; (d) synthesis of deuterated tetrasubstituted allylboronates *via* consecutive dual 1,2-metallate shift (this work).

internal α-chiral allylboronates (Scheme 1b, left). Separately, Yin's group[37–39] achieved allylboronate synthesis *via* nickel- or palladium-catalyzed reactions of undirected alkenes.

B_2pin_2, and alkenyl halides or triflates (Scheme 1b, right). Notably, tetracoordinate boron species—characterized by transmetalation and migration capabilities—have emerged as key motifs within the organoboron family.[26] Building on our sustained interest in this field, our group has developed novel metallate shift transformations.[40–44] Recently, we disclosed four distinct alkynyl tetracoordinate boron migrations involving dual 1,2-aryl or 1,2/1,3-aryl shifts to access tetrasubstituted olefins.[45] Additionally, we achieved photo-induced tri-functionalization of bromostyrenes through remote radical migrations of tetracoordinate boron species.[46,47] However, a key limitation in the synthesis of allylboronates from alkynes is the inherent formation of a mixture of configurational isomers (Scheme 1c). As established, such mixtures are of limited practical value, and their separation remains a major challenge due to the nearly identical physicochemical properties of the isomers. Consequently, this system presents two inherent challenges: (1) How to ensure the reaction proceeds efficiently; (2) How to achieve the separation of configurational isomers (Scheme 1c).

We herein report a strategy for the efficient synthesis and separation of both configurational isomers of deuterated tetrasubstituted allylboron compounds, derived from alkynyl tetracoordinate boron precursors. The transformation proceeds *via* consecutive dual 1,2-metallate shifts, mediated by commercially available ICH_2Bpin and readily accessible D_2O as a convenient deuterium source (Scheme 1d). Notably, both stereoisomeric deuterated allyl alcohols can be selectively obtained through straightforward oxidation of the resulting

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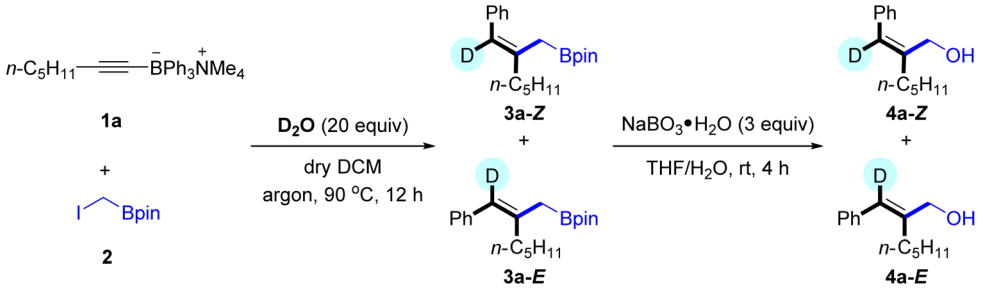
Table 1 Reaction condition optimizations[a]



Entry	Variation from standard conditions	Yield of **3a**[b]	Yield of **4a-*Z***[b]	Yield of **4a-*E***[b]
1	None	82% (73%)[c]	37% (34%)[c]	45% (39%)[c]
2	Dry THF as solvent	11%	3%	8%
3	Dry MeCN as solvent	48%	36%	12%
4	Dry DMF as solvent	4%	2%	2%
5	At 60 °C	50%	25%	25%
6	At 100 °C	54%	25%	29%
7	6 h instead of 12 h	63%	30%	33%
8	18 h instead of 12 h	82%	40%	42%
9	X = Cl	9%	4%	5%
10	X = Br	63%	33%	30%

[a] Reaction conditions: the reaction was carried out with **1a** (0.24 mmol), ICH_2Bpin **2** (0.2 mmol), D_2O (20 equiv.), in 1 mL dry DCM at 90 °C for 12 h. [b] Yields were determined by gas chromatography (GC) using *n*-decane as the internal standard. [c] Isolated yield of corresponding alcohols products **4a-*Z*** and **4a-*E*** by oxidation. Unless otherwise specified, the deuterium incorporation for product exceeds 99%.

allylboronates followed by silica gel chromatography. This method achieves quantitative deuteration (>99% D-incorporation) and exhibits a broad substrate scope, unprecedented consecutive double 1,2-migrations, and direct access to two valuable deuterated stereodefined architectures.

Our investigation into the synthesis of deuterated tetrasubstituted allylboronates commenced with alkynyl tetracoordinate boron **1a**, ICH_2Bpin (**2**) and D_2O in anhydrous DCM at 90 °C. To our delight, the target product **3a** was obtained in 82% yield and corresponding *Z*/*E*-configurations were detected in 37% and 45% yields, respectively. Initial solvent screening identified anhydrous DCM as optimal, outperforming THF, CH_3CN as well as DMF (Table 1, entries 1–4). Subsequent temperature optimization (entries 5 and 6) established 90 °C as ideal, while the lower (60 °C) and higher (100 °C) temperatures afforded product **3a** in diminished yields. Besides, different reaction time for this process was explored, suggesting that the best reasonable reaction time is 12 h. The desired product was obtained in 63% yield (**3a-*Z***: 30%; **3a-*E***: 33%) when reaction time is decreased to 6 h. (see SI for details). Upon replacing ICH_2Bpin by $BrCH_2Bpin$ or $ClCH_2Bpin$, the yield of **3a** significantly dropped (entries 9 and 10). Therefore, the optimal reaction conditions of this reaction were believed as: alkyne tetracoordinate boron tetramethylammonium hept-1-yn-1-yltriphenylborate **1a** (1.5 equivalents), ICH_2Bpin (1 equivalent) and D_2O (20 equivalents) in 1 mL DCM, at 90 °C for 12 hours under argon atmosphere. Then, the corresponding alcohols **4a-*Z*** and **4a-*E*** were afforded by the oxidation of **3a-*Z*** and **3a-*E***, and could be isolated respectively through column chromatography.

After determining the optimal reaction conditions, we turned our attention to investigate the substrate scope. As showed in Scheme 2, the scope of the long chain alkyl substituted tetracoordinate alkynyl borons was first investigated, affording the target product (**4a–4d**) with good yields. And a scale-up reaction of **1a** was performed to give the target products **4a** in 63% yield (Scheme 2). Reaction of tetramethylammonium (3-cyclohexylprop-1-yn-1-yl)triphenylborate (**1e**) with ICH_2Bpin occurred to produce the target products **4e** in 67% yield (**4e-*Z***, 27% yield and **4e-*E***, 40% yield). Besides, tetramethylammonium triphenyl(3-phenylprop-1-yn-1-yl)borate (**1f**) was also suitable for this system, providing the wanted products **4f** in good yields and deuteration. Subsequently, various phenylethyl-containing substrates (**1g–1k**) were tested under the standard reaction conditions, providing the target products **4g–4k** in moderate to good yield. In addition, (*Z*/*E*)-4-(naphthalen-2-yl)-2-(phenylmethylene-d)butan-1-ol (**4l**) was formed by the reaction of tetramethylammonium (4-(naphthalen-2-yl)but-1-yn-1-yl)triphenylborate (**1l**) with **2a** under the same reaction conditions. Subsequently, various ether-containing aliphatic tetracoordinate alkynyl borons were investigated for exploring the reaction scope, in general, the reaction tolerated an array of substituents with different steric and electronic properties. The *para*-substituted group on the aromatic ring were investigated, both electron-withdrawing groups including cyano (**4m**) and halo (**4n**) and electronic-donating groups including phenyl (**4o**), methoxyl (**4p**) and isopropyl (**4q**) were compatible with this reaction conditions with good results. 2-Substituted substrates (**1r** and **1s**) could form the

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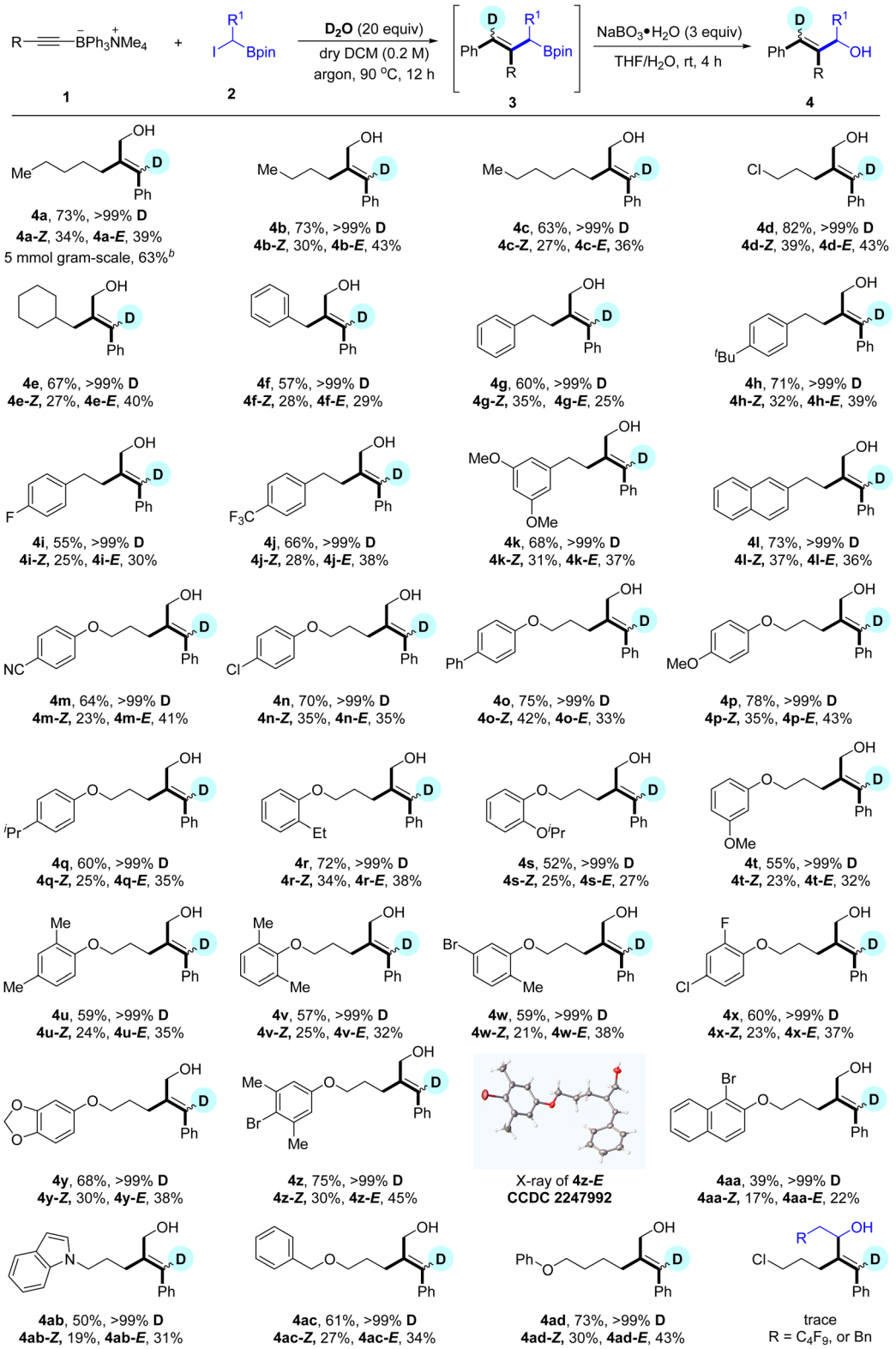

Scheme 2 Substrate scope[a]Reaction conditions: the reaction was carried out with **1** (0.24 mmol), compound **2** (0.2 mmol), D_2O (20 equiv.), in 1 mL dry DCM at 90 °C for 12 h, then **3** and $NaBO_3 \cdot H_2O$ (3 equiv.) in 2 mL THF, 1 mL H_2O at room temperature for 4 h. Isolated yields, *Z*/*E* were determined by ^{1}H NMR. [b]Yield of **4a**-*Z* and **4a**-*E*.

desired products **4r** and **4s** in 72% (*Z*-type: 34% yield, *E*-type, 38% yield) and 52% yields (*Z*-type: 25% yield, *E*-type: 27% yield), respectively with excellent deuteration. The substrate tetramethylammonium (5-(3-methoxyphenoxy)pent-1-yn-1-yl) triphenylborate (**1t**) underwent the standard reaction conditions to obtain the products **4t** in 55% yield with >99%

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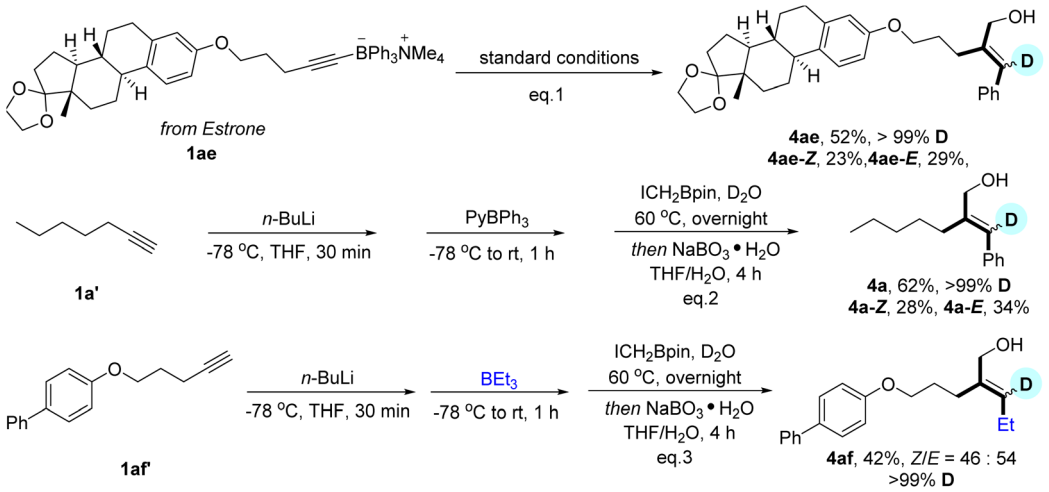
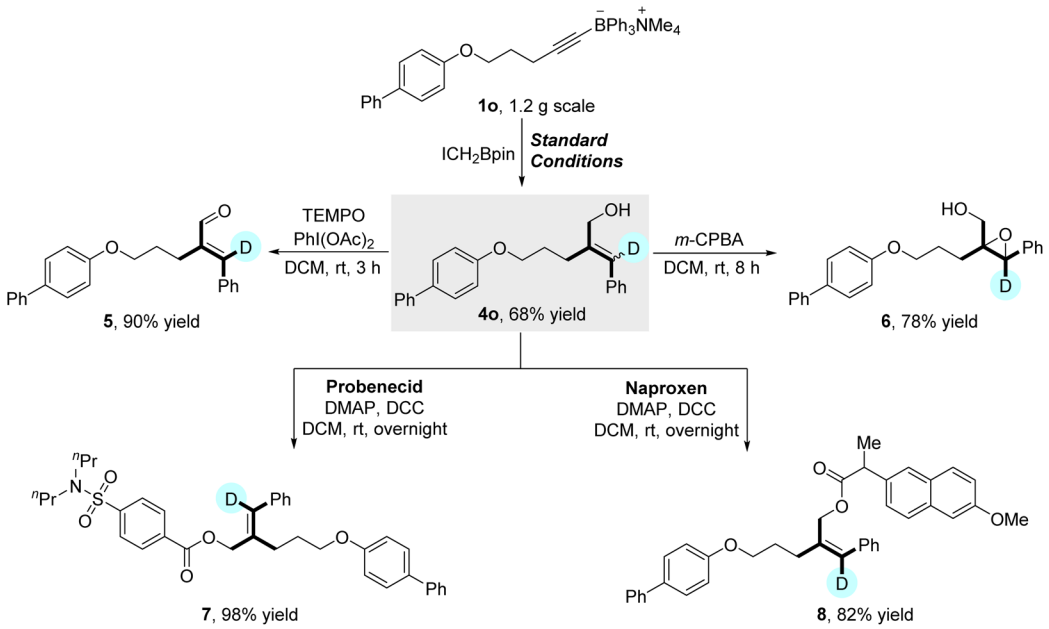


Scheme 3 Exploration of migratory group. [a]Reaction conditions: terminal alkyne (1.5 equiv.), *n*-BuLi (1.5 equiv.) in 8 mL THF at −78 °C for 30 min; $BEt_3 \cdot THF$ (1.5 equiv.), under argon, 1 h; ICH_2Bpin (1 mmol), D_2O (20 equiv.), at 60 °C, overnight; then $NaBO_3 \cdot H_2O$ (3 equiv.), 4 mL H_2O at rt for 4 h. Isolated yields.

deuteration. The reaction conditions were also compatible with disubstituted substrates (**1u–1y**), which afford the target products **4u–4y** with good results. The trisubstituted substrates (**1z**) worked well in this system, providing the 5-(4-bromo-3,5-dimethylphenoxy)-2-(phenylmethylene-d)pentan-1-ol (**4z**) in 75% yield (*Z*-type: 30% yield, *E*-type, 45% yield) with excellent deuteration. And fortunately, the absolute structure of **4z-*E*** was unequivocally confirmed by X-ray crystallographic analysis (see SI for the details). Notably, fused ring, such as naphthalene ring (**1aa**), and aza-containing substrates, such as indole (**1ab**) underwent the above reaction conditions access to the corresponding products (**4aa** and **4ab**) in 39% and 50% yield with beautiful deuteration. In addition, other ether-containing substrates, such as tetramethylammonium (5-(benzyloxy)pent-1-yn-1-yl)triphenylborate (**1ac**) and tetramethylammonium (6-phenoxyhex-1-yn-1-yl)triphenylborate (**1ad**), could also generate the target products **4ac–4ad** in 61% and 73% yield, correspondingly, with >99% deuteration. We next tested whether other boronic ester enable to induce 1,2-migration of the alkynyl tetracoordinated borons. Different α-iodoboronates were tested under the standard reaction conditions, unfortunately, this transformation could not proceed smoothly (Scheme 2).

Moreover, this protocol enables the direct deuteration of complex pharmaceuticals. Employing an estrone derivative (**1ae**) as the substrate afforded deuterated product **4ae** in 52%



Scheme 4 Transformations of the product. Unless otherwise specified, the deuterium incorporation for all products exceeds 99%.

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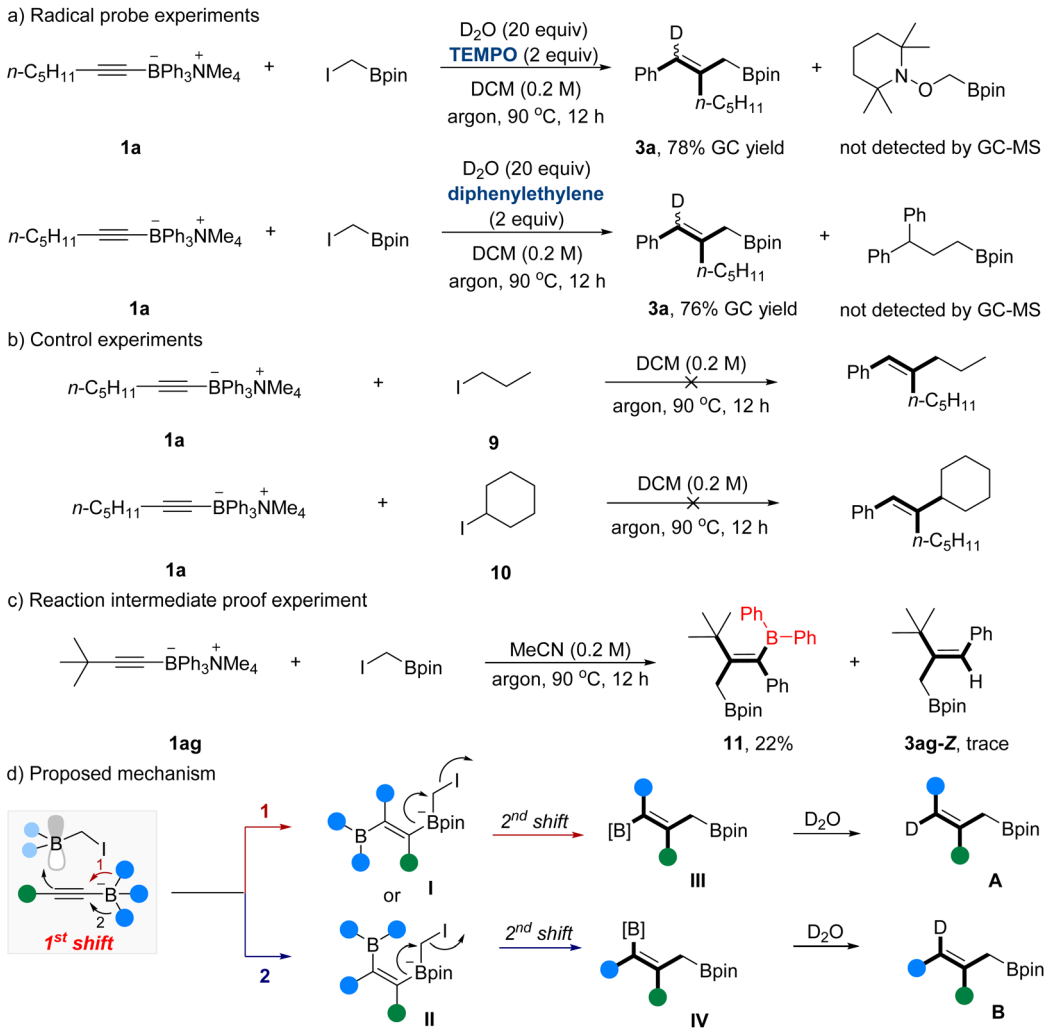

Scheme 5 Mechanistic studies and proposed mechanism.

yield with quantitative deuterium incorporation (>99% D) (Scheme 3, eq. 1). Importantly, this protocol also worked well by a one-pot process from terminal alkynes to access the corresponding products (Scheme 3, eq. 2). We subsequently examined the compatibility of alternative migratory groups beyond phenyl, including alkyl and diverse aryl substituents, *via* a one-pot synthesis protocol (Scheme 3, eq. 3). The ethyl group demonstrated successful migration, affording product **4af** in 42% yield. This result confirms the feasibility of accessing complex deuterated architectures from commercially available alkyne precursors in a single transformation.

To demonstrate the synthetic utility of this methodology, we performed derivatizations of the products (Scheme 4). A gram-scale reaction (1.2 g) of tetramethylammonium (5-([1,1′-biphenyl]-4-yloxy)pent-1-yn-1-yl)triphenylborate afforded deuterated product **4o** in 68% yield. Selective oxidation of deuterated allylic alcohol **4o-*E*** yielded α,β-unsaturated aldehyde **5** in 90% yield with quantitative deuterium retention (>99% D). Similarly, epoxidation of **4o-*Z*** provided epoxide **6** in 78% yield and >99% deuterium incorporation. Furthermore, we applied this approach to late-stage diversification of pharmaceuticals. Esterification of probenecid and naproxen with deuterated intermediates afforded products **7** and **8** in 98% and 82% yields, respectively, with quantitative deuteration.

To elucidate the migration mechanism between alkynyl tetracoordinate boron species and ICH_2Bpin under optimized conditions, we conducted mechanistic investigations (Scheme 5). Radical trapping experiments using 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or 1,1-diphenylethylene revealed no trapped intermediates, excluding a single-electron transfer (SET) pathway. Control experiments substituting ICH_2Bpin with 1-iodopropane (**9**) or iodocyclohexane (**10**) under standard conditions yielded no 1,2-migration product, demonstrating that the initial migration requires Lewis acidic activation by the boronic ester (Scheme 5b). Substrate scope studies revealed significantly diminished yield for **4af**. Further analysis indicated that proximal oxygen atoms (within two carbons of the triple bond) inhibit reactivity, whereas substrates with distal oxygen (**4ad**, **4ae**) or no oxygen (**4f**) perform optimally (Scheme 2). This suggests competitive coordination of ICH_2Bpin to oxygen, impeding boronic ester-directed migration. When sterically hindered substrate **1ag** was employed, the

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diphenylboron-retained product **11** was isolated in 22% yield, implying deuteration occurs *via* protonation by the diphenylboron moiety (Scheme 5c). Based on these findings and precedent literature,[34,48] we propose a mechanistic pathway (Scheme 5d): ICH_2Bpin acts as a Lewis acid to activate the alkyne, triggering stereorandom initial 1,2-migration to form intermediates **I**/**II**. Subsequent Matteson-type 1,2-migrations[49] afford tetrasubstituted allylboronates **III**/**IV**, which undergo deuteration *via* D_2O to yield final products **A**/**B**.

Conclusions

In summary, we have developed a novel strategy for synthesizing two different isomers of deuterated tetrasubstituted allylboronates. Oxidation of these compounds provides access to valuable deuterated allylic alcohols as separable stereoisomers. This approach constructs sterically congested deuterated architectures from commercially accessible terminal alkynes using operationally simple deuteration with benign D_2O under mild conditions. Mechanistic studies establish that dual sequential 1,2-migration reactions, enabled by commodity reagent ICH_2Bpin, govern the transformation.

Author contributions

Q. S. and X. M. conceived and designed the experiments. P. L. and Y. Y. performed experiments and analyzed the data. Q. S. and X. M. wrote the paper. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings of this article are available within the paper and its Supplementary Information.

CCDC 2247992 contains the supplementary crystallographic data for this paper.[50]

Supplementary information: [experimental procedures and characterization data]. See DOI: https://doi.org/10.1039/d5sc06886j.

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