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Observation of the solvent enantio-isotope effect in asymmetric ring-opening of cyclic diaryliodoniums with selenocyanate†

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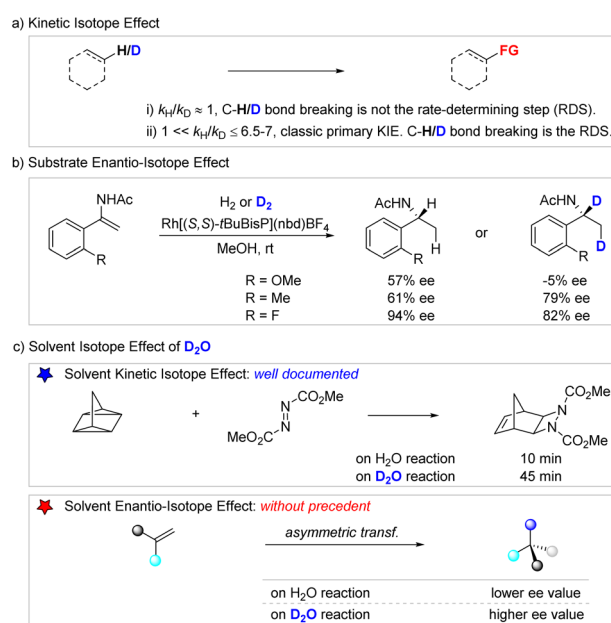
A Cu-catalyzed asymmetric coupling reaction between cyclic diaryliodoniums and the ambident nucleophile KSeCN was reported. Utilizing water as a co-solvent (CH₂Cl₂/H₂O) achieves high chemoselectivity by forming a nitrogen-hydrogen-bond, thereby blocking the N-site of ambident NCSe[−] species, thus realizing efficient C–Se coupling. In contrast to the well-known kinetic isotope effect used to evaluate whether the C–H/D bond cleavage is rate-determining, the influence of deuterium-containing solvents on enantioselectivity remained largely unexplored. In this reaction, we observed a notable enhancement in enantioselectivity upon replacing H₂O with D₂O.

Introduction

Kinetic isotope effect (KIE) experiments have been widely used in modern physical organic chemistry. KIEs, measured by H/D labeling and crossover experiments, are possibly the most widely used methods to establish C–H/D bond breaking as a rate-determining step (Scheme 1a).¹ Imamoto, Gridnev and co-workers observed that replacing H₂ with D₂ also significantly altered the enantioselectivity to various degrees in Rh-catalyzed hydrogenation of enamides (Scheme 1b).² In 2005, Sharpless *et al.* reported a significant solvent isotope effect in an aqueous emulsion [2σ + 2σ + 2π] based-cycloaddition, noting a marked decrease in the reaction rate when H₂O was replaced with D₂O (Scheme 1c).³ McErlean *et al.* similarly observed that the conversion of an aromatic aza-Claisen rearrangement in D₂O was only 40%, compared to full conversion in H₂O over the same period.⁴ While deuterium kinetic isotope effects have been investigated in some aqueous reactions by substituting H₂O with D₂O, the literature remains devoid of any reports of the solvent enantio-isotope effect, such as D₂O displaying an ability to improve enantioselectivity over H₂O.

Selenium is among the fourteen essential trace elements and plays a vital role in human health.⁵ Chiral electrophilic selenium reagents have been used for the enantioselective functionalization of inactivated alkenes.⁶ Significant progress has

recently been achieved in synthesizing optically active chiral selenium compounds through asymmetric difunctionalization of alkenes.⁷ Selenocyanate compounds showed broad utilities in preparing other types of organoselenium compounds.⁸ However, coupling with ambident nucleophiles, such as KSeCN and KSCN, usually encounters chemo-selectivity challenges. A precedent from the Reiser group demonstrated that the C–S *versus* C–N selectivity in Cu-catalyzed coupling involving SCN anions can be manipulated through the electronic properties of free radicals: nucleophilic radicals preferentially attack the

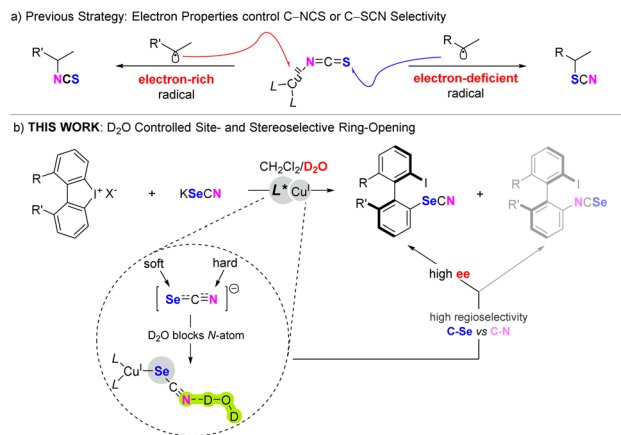


Scheme 1 Deuterium isotope effects.

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Scheme 2 Strategy for site-selective coupling of SeCN or SCN.

electrophilic Cu(II) center, generating a Cu(III) species that affords a C–N coupling product upon reductive elimination (Scheme 2a),⁹ whereas radicals bearing an electron-withdrawing group favor direct attack at the sulfur site, forming a C–S bond directly *via* an outer-sphere mechanism. We reasoned that the softness and relatively larger size of the Se atom facilitate hydrogen bonding with the N atom (Scheme 2b). Considering the significance of selenocyanates and the broad utility of atropisomers,¹⁰ we herein report a Cu-catalyzed asymmetric ring-opening/C–Se coupling reaction of cyclic diaryliodoniums with KSeCN, wherein co-solvent water blocks the N-site of the SeCN anion through hydrogen bonding. Intriguingly, we observed that D₂O (in contrast to H₂O) unexpectedly improved the enantioselectivity of this reaction.

Results and discussion

Optimization

Optimization studies were conducted using dimethyl substituted cyclic diaryliodonium **1a** and KSeCN as the model substrates in dichloromethane at room temperature, with CuI as the catalyst. Chiral bisoxazoline ligands **L1**–**L2** afforded high enantiomeric excesses of *N*-arylated product **4a**, while the stereoselectivity of Se-arylated product **3a** was below 40% ee. Moreover, the reaction exhibited poor chemoselectivity between Se-arylation and *N*-arylation, with **3a/4a** ratios ranging from 1 : 1.5 to 2 : 1 (Table 1, entries 1 and 2). Introduction of benzyl substituted pyridine-2,6-bis(oxazolines) (PyBox) **L3** enhanced the enantioselectivities, shifting the ratio of **3a/4a** to 5/1 (entry 3). However, the PyBox derived from phenylglycinol exhibited no improvement in stereo-inductivity (entries 4 and 5). Chiral indeno-PyBox ligands **L6**–**L8** led to excellent enantioselectivities for both **3a** and **4a**, while modifications of the pyridine ring's electronic properties with chloro or phenoxy groups had minimal impact on the Se-arylation/*N*-arylation ratio (entries 6–8). Guided by our hypothesis that water might influence Se/N selectivity through differential hydrogen bonding affinities, we examined mixed solvent systems. Gratifyingly, employing CH₂Cl₂/H₂O (5 : 1) significantly improved chemoselectivity,

Table 1 Reaction condition optimization^a

Entry	Ligand	Solvent	3a/4a ^b	Yield ^c (%) / ee (%)	
				3a/4a	3a/4a
1	L1	CH ₂ Cl ₂	2/1	54/38	30/94
2	L2	CH ₂ Cl ₂	1/1.5	38/32	55/94
3	L3	CH ₂ Cl ₂	5/1	74/84	20/90
4	L4	CH ₂ Cl ₂	3/1	70/48	22/87
5	L5	CH ₂ Cl ₂	3/1	68/56	18/88
6	L6	CH ₂ Cl ₂	5/1	76/90	16/95
7	L7	CH ₂ Cl ₂	4/1	73/90	20/96
8	L8	CH ₂ Cl ₂	4/1	73/90	19/94
9	L6	CH ₂ Cl ₂ /H ₂ O	16/1	88/86	—/92
10	L6	CH ₂ Cl ₂ /D ₂ O	16/1	90/90	—/94
11 ^d	L9	CH ₂ Cl ₂ /D ₂ O	12/1	83/92	—/92
12 ^d	L10	CH ₂ Cl ₂ /D ₂ O	24/1	92/88	—/86
13 ^d	L11	CH ₂ Cl ₂ /D ₂ O	20/1	90/94	—/90
14 ^d	L11	CH ₂ Cl ₂ /H ₂ O	18/1	90/92	—/—

^a Conditions: 0.10 mmol of cyclic diaryliodoniums (**1a**), 0.20 mmol KSeCN (**2a**), CuI (5 mol%), ligand (10 mol%) in CH₂Cl₂ (0.04 M) [or CH₂Cl₂/H₂O (5 : 1) or CH₂Cl₂/D₂O (5 : 1)] at room temperature. ^b NMR to determine the ratio. ^c Isolated yield. ^d *ent-3a* was obtained.

achieving a 16 : 1 ratio of **3a/4a**, although the enantioselectivity of **3a** decreased slightly to 86% (entry 9). An unexpected discovery was that deuterated water enhanced enantioselectivity, while maintaining a high Se/N ratio (entry 10). Further optimization efforts focused on modifying the indeno structure of PyBox, leading to the identification of the optimal ligand **L11**, which achieved the highest enantioselectivity (94% ee) for **3a** (entries 11–13). Under these optimized conditions with **L11**, using CH₂Cl₂/H₂O as the solvent system *in lieu* of CH₂Cl₂/D₂O resulted in slightly reduced enantiomeric excess (92% ee) (entry 14).

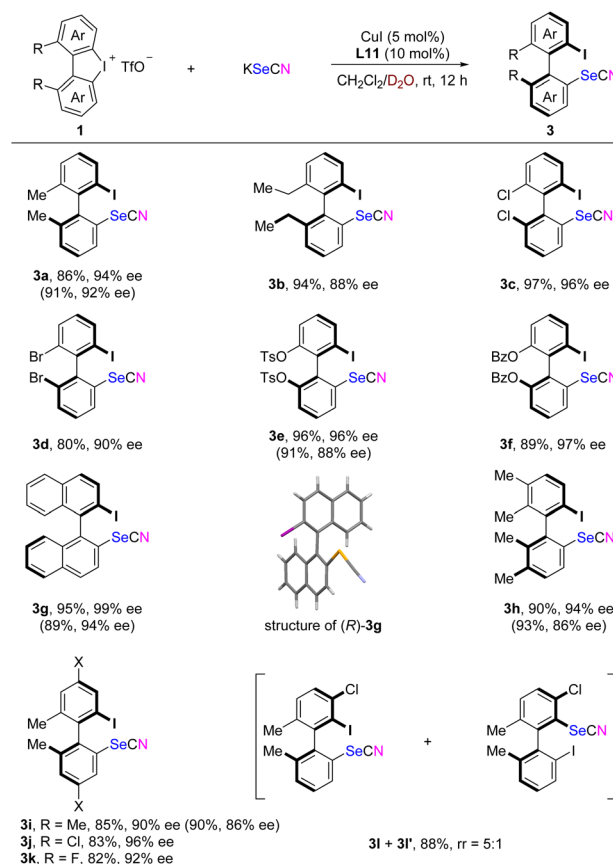
The addition of organic hydrogen bond donor urea did not obviously improve the Se/N selectivity (Scheme 3a). A radical pathway can be ruled out as TEMPO had a minimal effect on product formation. The most intriguing aspect of this reaction is the enhanced enantioselectivity observed with deuterated water (D₂O) compared to regular water (H₂O). While the isotope effect on enantioselectivity has been observed for reactions involving C–H/D bond formation or cleavage,¹¹ our observed



enhancement of enantioselectivity by D₂O is distinct as it occurs without breaking any chemical bonds of D₂O. Therefore, explaining such a deuterium isotope effect on stereoselectivity remains particularly challenging, as both chemical and physical properties, including viscosity, molecular polarizability, or the pK_a value, may contribute to the observed outcomes. Given the pH differences [pH(H₂O) = 6.9976 pD(D₂O) = 7.43 at 25 °C], KHCO₃ and K₂CO₃ were used to adjust the pH of the CH₂Cl₂/H₂O mixture; however, no noticeable improvement in enantioselectivity was observed. We further conducted a series of experiments combining either H₂O or D₂O with CH₂Cl₂, (CH₂Cl)₂, CHCl₃, toluene and THF as a mixed solvent (Scheme 3b). Notably, enantiomeric excess improvements can be observed in CH₂Cl₂, (CH₂Cl)₂, CHCl₃, or toluene when H₂O was replaced by D₂O. Conversely, an opposite trend was observed in THF/H₂O and THF/D₂O solvent systems. A similar enhancement was noted when the reaction was conducted in CH₂Cl₂/CD₃OD instead of CH₂Cl₂/CD₃OH, yielding compound **3a** with an ee value improved from 50% to 64%.

bond strength in D₂O is 0.2–0.3 kcal mol⁻¹ stronger than that in H₂O, suggesting a potential stronger hydrogen bond in the CH₂Cl₂/D₂O system. (b) Studies using X-ray measurements with molecular simulations indicate that the covalent O–D bond in D₂O is 3% shorter than the O–H bond in regular water. (c) The hydrogen-bond network in D₂O is more tetrahedral compared to that in H₂O. These distinctions may create a different three-dimensional environment compared to H₂O, potentially impacting enantioselectivity.

Under optimized conditions, the substrate scope of various diaryliodonium salts was explored (Scheme 4). Pleasingly, high Se/N arylation ratios (typically exceeding 15:1) were consistently observed across all tested substrates. With 2,2'-diethyl-1,1'-biphenyl-derived cyclic diaryliodonium as the substrate, the reaction proceeded smoothly, albeit with slightly reduced stereocontrol (**3b**). Both dichlorinated and dibrominated cyclic diaryliodoniums exhibited good reactivity, resulting in excellent enantioselectivities (**3c** and **3d**). High enantiomeric excess (ee) values were also achieved for the *ortho,ortho'*-dioxxygenated atropisomeric biaryls (**3e** and **3f**). The binaphthyl cyclic

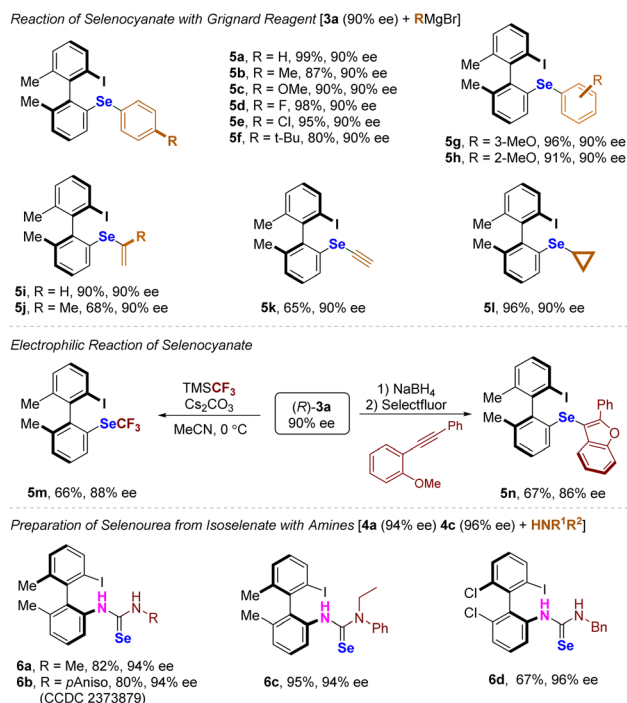


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diaryliodonium underwent a smooth asymmetric ring-opening reaction, yielding excellent yield and near-perfect stereoselectivity (**3g**). This compound also facilitated the determination of the absolute configuration through single crystal X-ray diffraction analysis (CCDC 2373878). Cyclic diaryliodonium bearing additional methyl or chloro groups at the *para*- or *meta*-positions exhibited comparable reactivity and selectivity (**3h–k**). However, unsymmetric cyclic diaryliodonium with a substituent adjacent to the C–I bond displayed poor regioselectivity, consistent with our previous findings in the trifluoromethylthiolation reaction.¹³ For instance, products **3l** and **3l'** were isolated in 18% and 70% yields, respectively, though both the products exhibited excellent ee values.

Isoselenocyanates represent valuable building blocks that were widely used in synthesizing selenium-containing compounds.¹⁴ The classic synthesis involves a two-step modification of corresponding amines *via* Barton's protocol.¹⁵ Although complete control of chemo-selective *N*-arylation remained elusive, we evaluated several substrates in anhydrous CH₂Cl₂ using CuI/L2 as the catalyst, with N/Se ratios ranging from 1:1 to 1.5:1 (see the ESI† for details) (Scheme 5). All substrates tested provided the products in decent isolated yields. Similar to the Se-arylation reaction, the *N*-arylation reaction of 2,2'-diethyl-1,1'-biphenyl-derived cyclic diaryliodonium resulted in a diminished enantioselectivity (**4b**). Notably, cyclic diaryliodoniums bearing dimethyl, dichloro, or dibromo substituents, as well as the binaphthyl substrate, afforded products with excellent stereoselectivities (**4a** and **4c–f**).

The selenium atom in selenocyanate exhibits electrophilic character and readily reacts with Grignard reagents. This reactivity enabled the formation of selenanes **5a–h** in yields ranging from 80–99% without erosion of enantiopurity (Scheme 6). The reaction demonstrated compatibility with vinyl and alkynyl magnesium reagents, although 2-methylalkenyl selene **5j** and alkynyl selene **5k** were obtained in lower yields. Additionally, cyclopropyl magnesium bromide also proved compatible, smoothly yielding **5l** in 96% yield. Selenocyanate **3a** served as



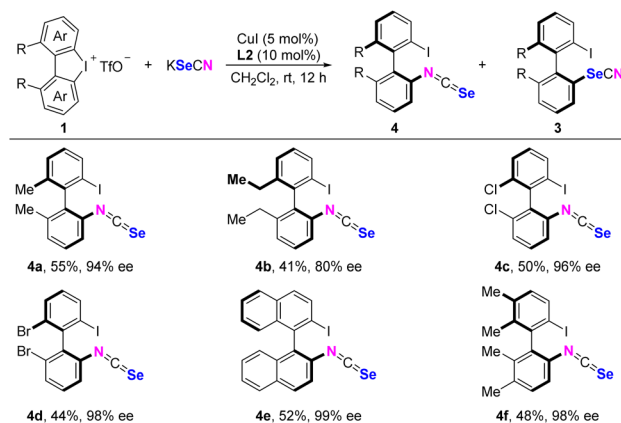
Scheme 6 Synthetic applications.

a versatile synthetic platform for accessing diverse functionalities. Treatment of (*R*)-**3a** with TMSCF₃/Cs₂CO₃ in MeCN yielded the atropisomeric trifluoromethyl selene **5m** in 66% yield. Reduction of **3a** with NaBH₄ produced a diselenide compound upon workup. Subsequent reactions with SelectFluor, followed by an electrophilic cyclization with 1-methoxy-2-(phenylethynyl) benzene, yielded the bicyclic selene **5n** in a moderate yield, albeit with a slight decrease in enantioselectivity.

To further demonstrate synthetic utility, we sought to convert isoselenocyanate (*S*)-**4a** into substituted selenoureas. The transformation was accomplished by simply stirring a mixture of isoselenate (*S*)-**4a** with amines in CH₂Cl₂ at room temperature. Primary amines, *i.e.* methylamine and 4-methoxyaniline readily underwent an addition reaction to produce selenoureas **6a**, **6b** (CCDC 2373879) and **6d** in good yields without compromising stereochemical integrity. Secondary amine, *N*-ethylaniline, also efficiently coupled with isoselenate to provide **6c** in excellent yield.

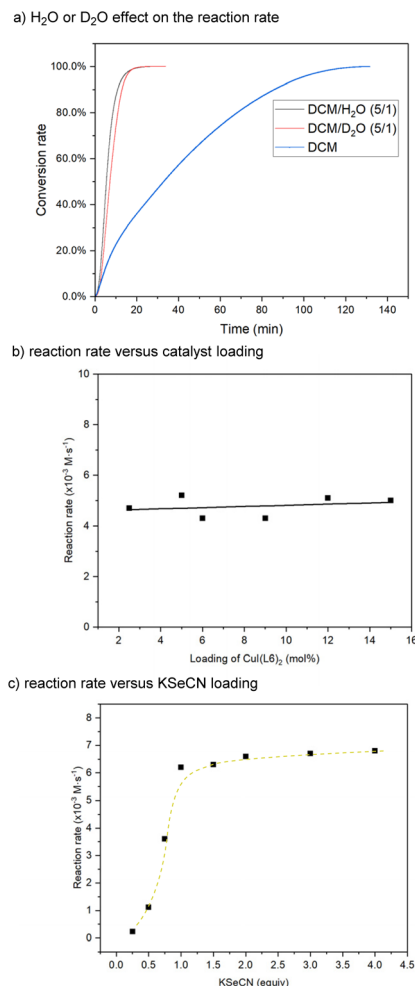
Kinetic studies

The kinetic studies were conducted *via* calorimetry analysis, which enabled us to continuously collect *in situ* data throughout the reaction process.¹⁶ Notably, both water and deuterated water were almost equally effective in accelerating the reaction, showing no obvious isotope effect on the reaction rate. Careful reaction calorimetry measurements showed that the reaction in CH₂Cl₂/D₂O was very slightly slower than that in CH₂Cl₂/H₂O (Scheme 7a). Furthermore, kinetic studies at 30 °C yielded two interesting observations: (i) the reaction exhibited zeroth-order kinetics with respect to the CuI/L6 catalyst (Scheme 7b). (ii) After ensuring complete dissolution of KSeCN in H₂O, kinetics



Scheme 5 Substrate scope of C–N coupling.^a Reaction conditions: cyclic diaryliodonium **1** (0.2 mmol, 1.0 equiv.), KSeCN (0.40 mmol, 2.0 equiv.), CuI (1.9 mg, 0.01 mmol, 5 mol%), L2 (7.0 mg, 0.02 mmol, 10 mol%) in CH₂Cl₂ (5 mL) at 25 °C for 12 h. The ratios of **4** : **3** range from 1:1 to 1.5:1, see the ESI† for details.



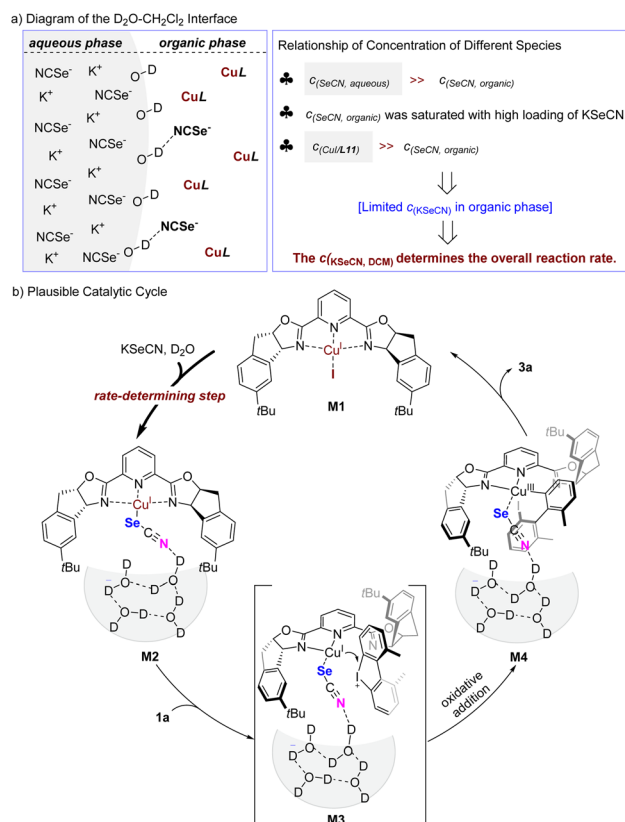


Scheme 7 Kinetic studies.

for varying the loadings of KSeCN were measured (Scheme 7c). The reaction exhibited pseudo-first-order kinetic dependence on KSeCN when the loading ranged from 0.50 to 1.0 equivalent [0.50 to 1.0 mol L⁻¹ in H₂O]. However, at loadings of KSeCN exceeding 1.5 equivalents, the reaction exhibited pseudo-zeroth-order kinetics dependence on the KSeCN concentration.

In an [Ir(COD)py(PCy₃)]PF₆-catalyzed hydrogenation reaction, Rempel and co-workers observed zeroth-order kinetics with respect to catalyst concentration at high catalyst loadings.¹⁷ In our system, the kinetic behavior can be rationalized through phase-transfer considerations. The transfer of KSeCN from the aqueous phase to the organic phase is concentration-dependent only up to 1.0 equivalent of KSeCN (1.0 mol L⁻¹ in H₂O). Beyond this point, the concentration of SeCN anions in the organic phase reaches saturation, remaining relatively unchanged despite a further increase in KSeCN loading. Consequently, the high loading of KSeCN caused zeroth-order dependence on the KSeCN concentration. In contrast, the concentration of the CuI/L₆ catalyst remains in excess compared to KSeCN in the organic phase, causing the reaction to exhibit zeroth-order kinetics with respect to the copper catalyst.

The role of water in accelerating aqueous reactions can be explained using the Marcus–Jung model of hydrogen bonding between the dangling –OH and the lipophilic substrates or Kobayashi's three layers model, which involves partial polarization.¹⁸ We reasoned that the catalytic cycle involves crucial deuterium bond (D–N) formation between D₂O and the SeCN anion (Scheme 8).¹⁹ This biphasic reaction system presents specific concentration dynamics: (i) KSeCN distribution: the concentration of KSeCN in the aqueous phase significantly exceeds its concentration in the organic phase. (ii) SeCN species saturation: at high KSeCN loadings, the concentration of SeCN in the organic phase reaches saturation, resulting in rate independence from further KSeCN addition. (iii) Catalyst excess: the concentration of the copper catalyst remains in excess relative to the organic phase SeCN species, even at high KSeCN loadings. Mechanistically, the catalytic cycle commences with the association of copper/PyBox complex **M1** with selenium cyanate, a step identified as the rate-determining step through the kinetic analysis. Upon loading 2.0 equivalents of KSeCN, the concentration of KSeCN in the organic phase is controlled by its solubility in CH₂Cl₂, other than its mass transfer rate across the phase boundary.²⁰ The N-site blocking effect of the deuterium bond facilitates the formation of Cu–SeCN intermediate **M2**. This intermediate is capable of undergoing oxidative addition with cyclic diaryliodonium **1a** to yield atropisomeric biaryl Cu(III) complex **M4**. Finally, reductive elimination of **M4** produced the target axially chiral product **3a** and a monovalent copper species **M1**.



Scheme 8 Plausible catalytic cycle.



Conclusions

In summary, we have developed a Cu-catalyzed highly chemo- and atroposelective C–Se coupling reaction between cyclic diaryliodoniums and KSeCN in a CH₂Cl₂/D₂O mixed solvent system. The distinctive role of D₂O manifests in two critical ways: (a) as a deuterium bond donor that selectively blocks the N-site of NCSe[−] species, thereby promoting C–Se coupling over C–N coupling; (b) as an enhancer of enantioselectivity compared to regular water, D₂O exhibits noticeable improvement in enantioselectivity. This enhanced stereoselectivity likely stems from either the slightly shorter covalent O–D bond of D₂O than the O–H bond of regular water, or the enhanced tetrahedral ordering of the D₂O hydrogen-bond network. Our findings underscore the importance of the deuterium isotope effect in enantioselectivity control, establishing it as an additional factor worthy of consideration in asymmetric catalysis.

Data availability

The data that support the findings of this study are available in the ESI† or on request from the corresponding authors.

Author contributions

Y. Li: methodology, investigation, data curation, writing – original draft. C. Tao: methodology, investigation. L. Duan: supervision, funding acquisition. Z. Gu: conceptualization, funding acquisition, writing – original draft, writing – review & editing. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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