nature communications

Article

https://doi.org/10.1038/s41467-025-57461-x

Enantioselective construction of inherently chiral pillar[5]arenes via palladium-catalysed Suzuki–Miyaura cross-coupling

Received: 23 October 2024

Accepted: 19 February 2025

Published online: 10 March 2025

Check for updates

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Pillar[n]arenes have broad applications in biological medicine, materials science, and supramolecular gels. Notably, enantiopure pillar[5]arenes are valued for their roles in enantioselective host–guest recognition, chiral sensing, asymmetric catalysis, and related fields. Current methods for obtaining chiral pillar[n]arenes rely heavily on resolution agents or chiral HPLC resolution. However, the synthesis of these compounds via asymmetric catalysis remains challenging. In this study, we develop an asymmetric extended side-arm Suzuki–Miyaura cross-coupling strategy to construct inherently chiral pillar[5]arenes with excellent yields and high enantioselectivities using a palladium catalyst and a Sadphos ligand. The reaction scope extends beyond arylboronic acids to encompass 2-arylvinylboronic acids and other multi-OTf-substituted substrates, all efficiently producing the desired products. Further exploration of the synthetic applications, along with photophysical and chiroptical analyses, confirm the potential of these chiral pillar[5]arenes for diverse applications across multiple disciplines.

Advances in the preparation of cyclic host molecules, including cyclodextrins[1,2], cucurbit[n]urils[3,4], crown ethers[5,6], calix[n]arenes[7], and pillar[n]arenes[8–15], have significantly propelled progress in supramolecular chemistry. A key characteristic of these cyclic host molecules is their ability to recognize guest molecules within their cavities[16]. This distinctive property facilitates their utilization in various applications, such as optically responsive materials, self-assembly systems, host–guest systems, supramolecular polymers, and molecular motors[17–24]. Pillar[n]arene, with its symmetrical pillar architecture, has become notable in the realm of macrocyclic arenes. Since Ogoshi's pioneering report on pillar[n]arenes in 2008[25], these structures have emerged as some of the most valued macrocyclic arenes over the past decade. Compared with other traditional macrocyclic hosts, pillar[n]arenes offer several notable advantages[26]. Firstly, owing to their rigid, electron-rich cavity, they are easy to synthesize and more easily functionalized, making them excellent candidates for constructing molecular aggregates through host–guest complexation. Moreover, chiral pillar[n]arenes are uniquely suited for applications in asymmetric catalysis, circularly polarized luminescence chiroptical materials, chiral host–guest conjugate, chiral supramolecular polymer, and homochiral metal-organic framework (Fig. 1a)[27–32].

In pillar[n]arene structures, the rotation of dialkoxy benzene units around the methylene bridges gives rise to inherent chirality (Fig. 1b)[33], and the dialkoxy benzene units within pillar[n]arene structures can perform a flipping motion along the annulus, termed "oxygen through the annulus rotations" flipping. Although this flipping mechanism has been extensively documented in other macrocyclic arenes, such as calixarenes, its occurrence in pillar[n]arene compounds results in interconversion between the *pS* and *pR* conformers[34]. This interconversion introduces a unique characteristic that can be suppressed by changing the solvent or temperature, or by introducing an achiral

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guest molecule[35]. The diameter of the cavity in pillar[n]arenes is adjustable, with pillar[5]arene having an approximate diameter of 4.7 Å. The incorporation of bulky substituents is beneficial for isolating enantiomers from racemic mixtures because of the ability of the bulky substituents to restrict rotation. Traditionally, chiral pillar[n]arenes have been synthesized by initially incorporating bulky substituents, followed by the separation of enantiomers using chiral high-performance liquid chromatography (HPLC) or resolving agents to isolate racemic mixtures[36,37]. However, the catalytic asymmetric synthesis of inherently chiral pillar[n]arenes remains a significant challenge. Recently, Wang and co-workers reported the enantioselective synthesis of chiral alkyne-substituted pillar[5]arenes via asymmetric Sonogashira cross-coupling[38]. Notably, Wang's method requires high palladium catalyst loadings (30 mol%) and ligands (60%), and it is limited to the synthesis of C_2-symmetric chiral pillar[5]arenes.

The Suzuki–Miyaura coupling, which involves organoboron compounds and (pseudo)halides, is a pivotal carbon–carbon bond forming reaction in drug discovery. This method is particularly renowned for its efficiency in forming $C(sp^2)$–$C(sp^2)$ bonds. While the Suzuki–Miyaura cross-coupling is well established, its asymmetric variant remains underdeveloped[39–45]. Despite notable progress, the asymmetric Suzuki–Miyaura reaction continues to pose significant challenges. Three main strategies have been documented in the literature, including direct cross-couplings of two aryl units[46–57], dynamic kinetic asymmetric transformation[58–66], and desymmetrization (Fig. 1c)[67–71]. However, the synthesis of chiral macrocycles presents additional difficulties due to the diversity of substituents and complex molecular conformations. This highlights the need for innovative strategies to achieve the efficient synthesis of chiral macrocycles[72]. Building on our recent advances in the stereoselective synthesis of inherent chirality[73–75], we developed an asymmetric

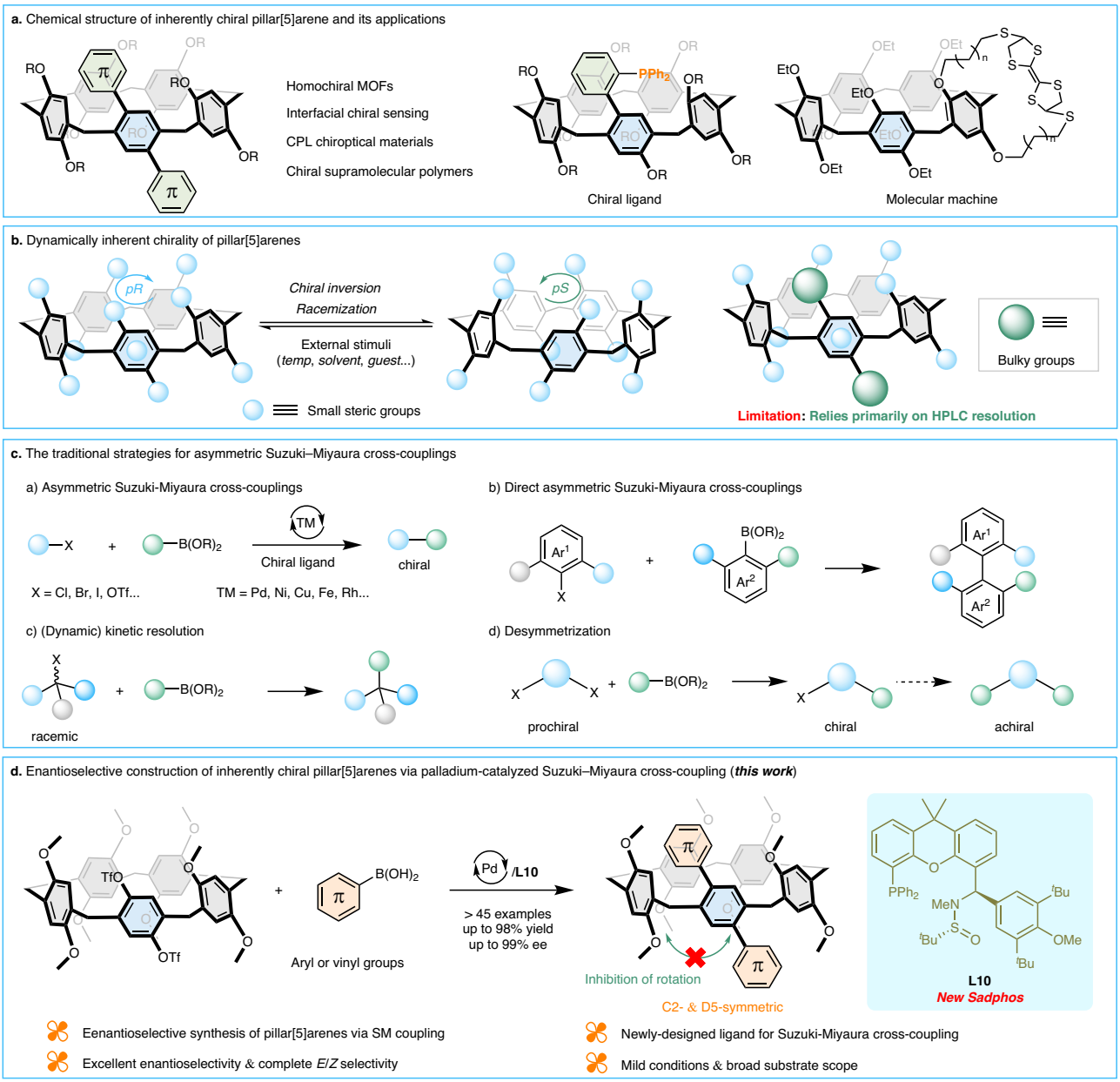

Fig. 1 | Chiral pillar[n]arenes: background and proposal. a Chemical structure of inherently chiral pillar[5]arene. **b** Dynamically inherent chirality of pillar[5]arenes. **c** The traditional strategies for asymmetric Suzuki–Miyaura cross-couplings. **d** This design: palladium-catalyzed Suzuki–Miyaura cross-coupling reactions.

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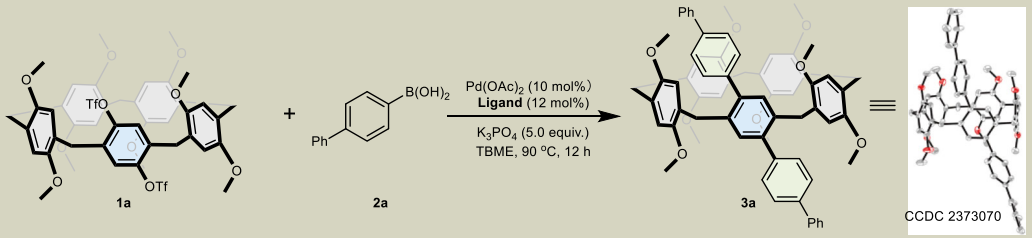
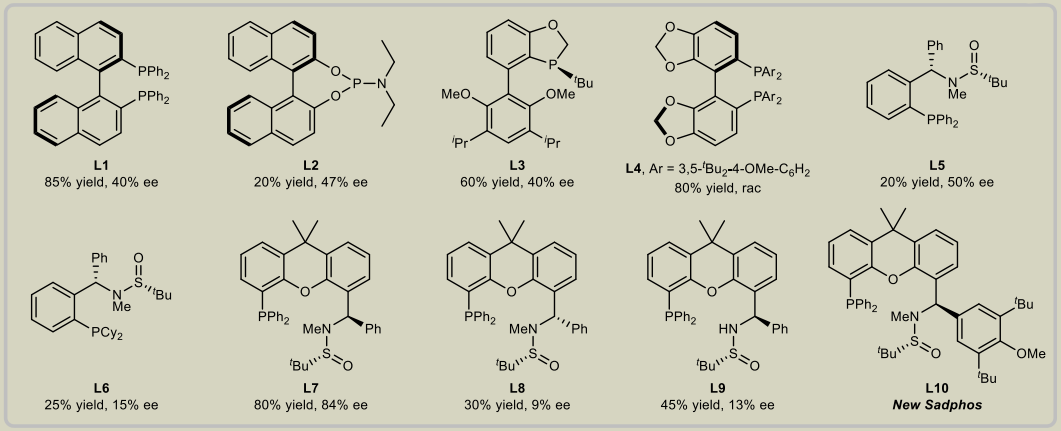
Table 1 | Optimization of the reaction conditions





Entry	[M] (mol%)	Ligand	Base	T (°C)	Solvent	Time (h)	Yield of 3a (%)[a]	Ee of 3a (%)[b]
1	$Pd(OAc)_2$ (10)	**L7**	K_2HPO_4	90	TBME	12	10	86
2	$Pd(OAc)_2$ (10)	**L7**	Na_2CO_3	90	TBME	12	trace	-
3	$Pd(OAc)_2$ (10)	**L7**	K_2CO_3	90	TBME	12	25	62
4	$Pd(OAc)_2$ (10)	**L7**	Cs_2CO_3	90	TBME	12	70	86
5	$Pd(OAc)_2$ (10)	**L7**	Cs_2CO_3	90	Toluene	12	nr	-
6	$Pd(OAc)_2$ (10)	**L7**	Cs_2CO_3	90	THF	12	15	80
7	$Pd(OAc)_2$ (10)	**L7**	Cs_2CO_3	90	1,4-dioxane	12	trace	88
8	$Pd(OAc)_2$ (10)	**L7**	Cs_2CO_3	90	Et_2O	12	10	37
9	$Pd(TFA)_2$ (10)	**L7**	Cs_2CO_3	90	TBME	12	72	88
10	$Pd_2(dba)_3$ (5)	**L7**	Cs_2CO_3	90	TBME	12	65	88
11	$Pd(acac)_2$ (10)	**L7**	Cs_2CO_3	90	TBME	12	35	81
12	$[Pd(allyl)Cl]_2$ (5)	**L7**	Cs_2CO_3	90	TBME	12	82	90
13	$[Pd(allyl)Cl]_2$ (5)	**L7**	Cs_2CO_3	70	TBME	12	73	91
14	$[Pd(allyl)Cl]_2$ (5)	**L10**	Cs_2CO_3	70	TBME	12	75	96
15	$[Pd(allyl)Cl]_2$ (5)	**L10**	Cs_2CO_3	70	TBME	24	88(85)[c]	96

Unless otherwise specified, the reaction conditions were as follows: **1a** (0.10 mmol), **2a** (0.50 mmol), 5–10 mol% [Pd], 12 mol% ligand, and 5.0 equiv. of base in 3.0 mL of solvent at 70–90 °C for 12–24 h under nitrogen. The bold part represents the chiral ligand.

[a]Determined by 1H-NMR analysis.

[b]Determined by chiral HPLC analysis.

[c]Isolated yield.

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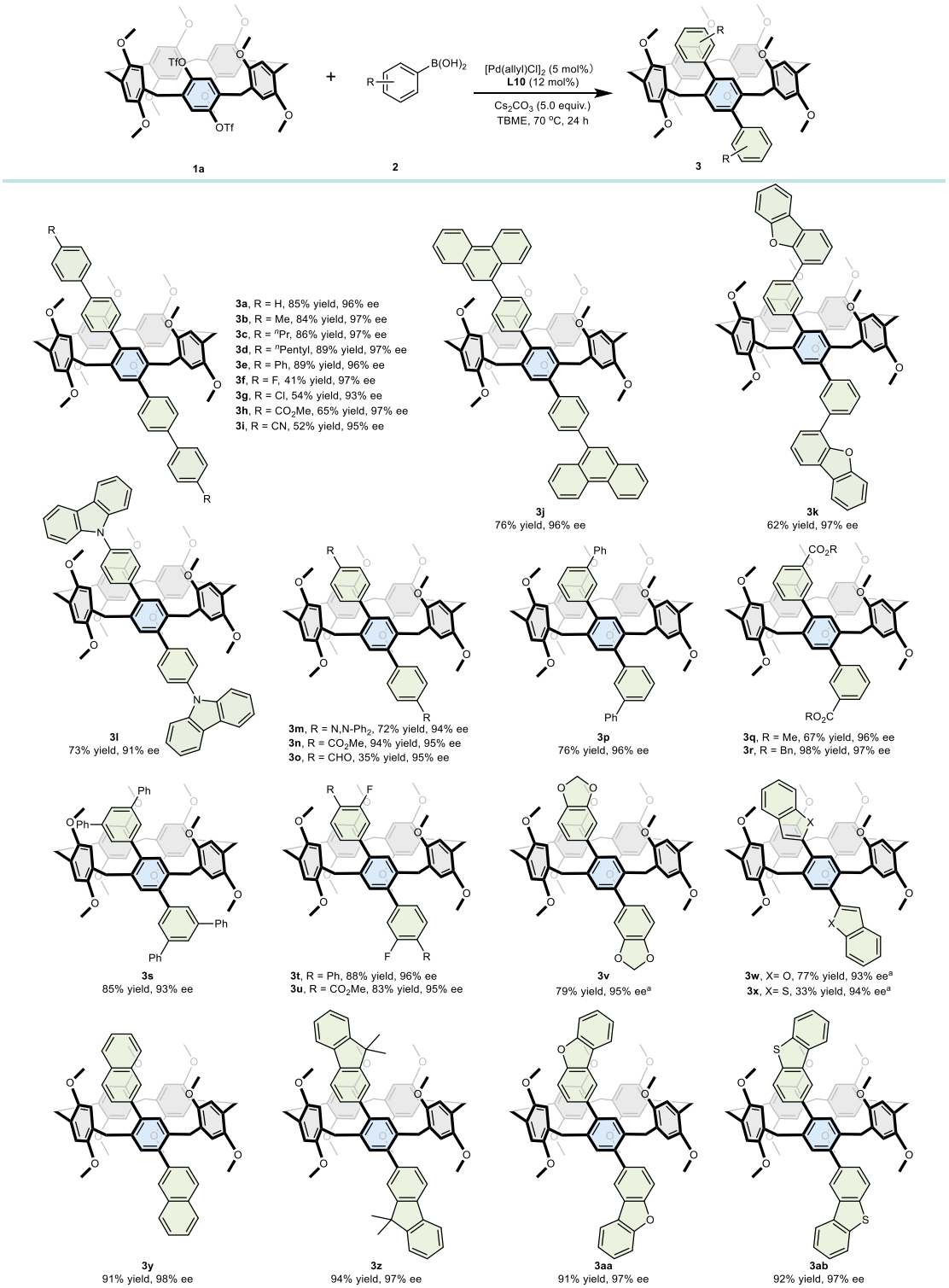
Table 2 | Scope of the reactions of arylboronic acids with OTf-pillar[5]arene 1a



Reaction conditions: **1a** (0.10 mmol), **2** (0.50 mmol), 5 mol% $[Pd(allyl)Cl]_2$, 12 mol% **L10**, 5.0 equiv. of Cs_2CO_3 in 3.0 mL of TBME at 70 °C for 24 h under nitrogen; isolated yield by silica gel chromatography; ee values were determined by chiral HPLC.
[a]72 h.

extended side-arm Suzuki–Miyaura cross-coupling strategy to synthesize chiral pillar[5]arene molecules by iteratively extending the substituents of achiral pillar[5]arenes (Fig. 1d). Unlike the desymmetrization strategy, the product remains achiral after the initial cross-coupling step, as the small substituents can freely rotate around the single bonds. However, further extension of the side arms increases the steric bulk on both sides of the pillar[5]arene, restricting rotation and inducing chirality. A total of 49 structurally diverse C2- and D5-symmetric pillar[5]arenes, including 6-membered aryl, 5-membered heteroaryl, and alkenyl-substituted variants, were

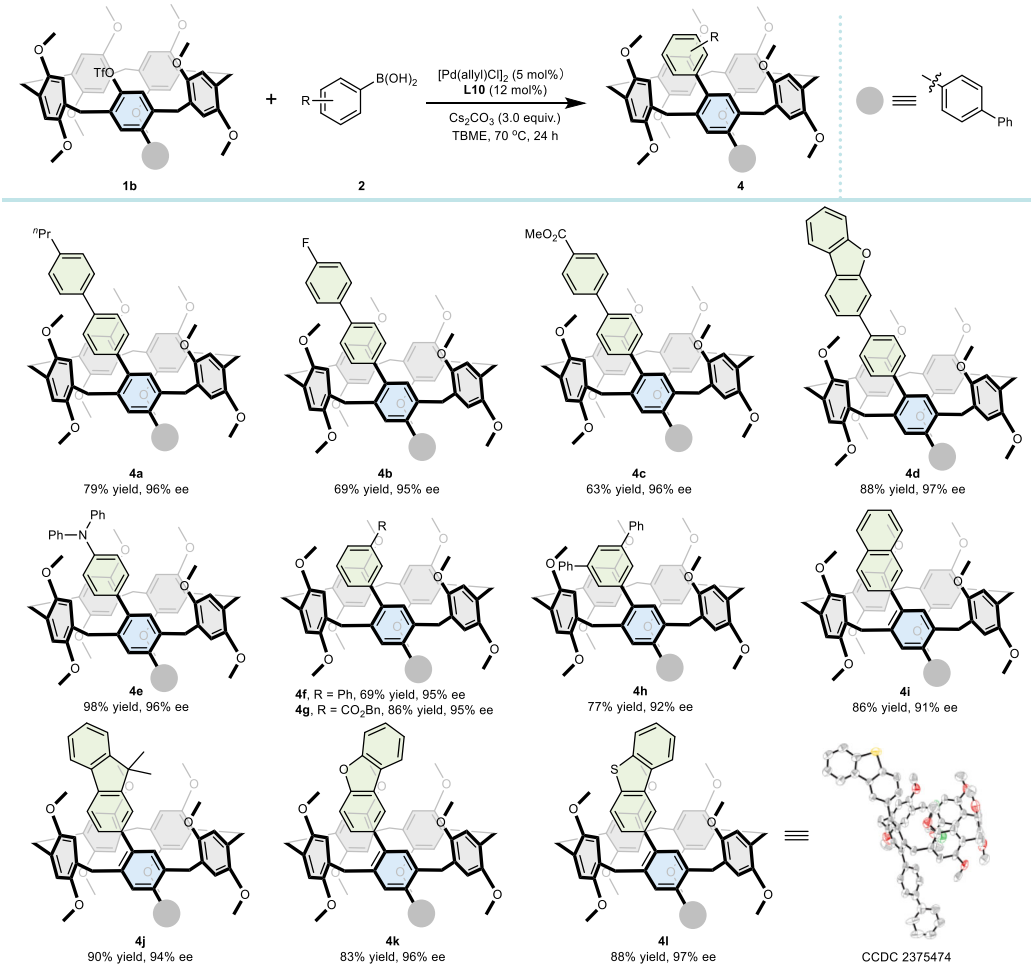
synthesized with excellent yields and outstanding enantioselectivities.

Results

Optimization studies

Our initial research was aimed at enhancing the critical enantioselective control process involved the use of pillar[5]arene-based bifunctional triflate **1a** and 4-phenylbenzene boronic acid **2a** as representative substrates for optimization (Table 1). First, we examined the common chiral ligands (see the Supplementary Information Table S1 for details) under palladium-catalyzed cross-coupling reaction conditions (10 mol% $Pd(OAc)_2$, 12 mol% ligand, 5.0 equiv. K_3PO_4 in TBME at 90 °C for 12 h). The corresponding chiral pillar[5]arene product **3a** was successfully synthesized using chiral ligands, such as (*R*)-BINAP **L1**, phosphinic amide **L2**, and BI-DIME **L3**, achieving satisfactory enantioselectivities (40% to 47% ee). However, product **3a** was afforded in 85% yield but remained racemic with the bulky ligand (*R*)-DTBM-Segphos **L4**. Notably, we attempted to use the sulfonamide phosphine ligand (Sadphos) **L5**, developed by the Zhang group, which has been demonstrated to be highly effective in palladium-catalyzed asymmetric systems[76–78]. Motivated by these encouraging outcomes, we shifted our focus to screening other Sadphos family ligands, **L6** and **L7**, in an effort to further optimize their efficiency and stereoselectivity. To our delight, PC-Phos **L7** exhibited outstanding efficiency (80% yield) and moderate stereocontrol (84% ee)[79–81]. Its diastereomer **L8** demonstrated a low yield and enantioselectivity. Additionally, the use of **L9** resulted in a significant decrease in yield and enantioselectivity. To increase enantioselectivity, various conditions were tested using **L7**. For instance, we evaluated different bases, including K_2HPO_4, Na_2CO_3, K_2CO_3, and Cs_2CO_3 (Table 1, Entries 1–4). While the majority of these bases resulted in the formation of **3a** with reduced reactivity, and Cs_2CO_3 notably improved the enantioselectivity to 86%, although it slightly decreased the yield (Entry 4). Subsequently, the use of toluene as the solvent did not produce the desired product (Entry 5). Further investigation with various ether solvents showed that 1,4-dioxane improved the enantiomeric excess to 88%, but a trace yield was obtained (Entries 6–8). We were pleased to find that screening various palladium catalysts (Entries 9–12) and revealed that $[Pd(allyl)Cl]_2$ provided product **3a** in 82% yield with 90% enantiomeric excess (Entry 12). Significantly, reducing the reaction temperature to 70 °C increased the enantioselectivity to 91% while maintaining excellent yield (Entry 13). Through extensive ligand modifications, we found that increasing the bulkiness of TY-Phos further with the use of **L10** led to improved yield and enantioselectivity (Entry 14). Ultimately, by prolonging the reaction time to 24 h, we obtained product **3a** in 85% isolated yield

Table 3 | Scope of the reactions of arylboronic acids with OTf-pillar[5]arene 1b



Reaction conditions: **1b** (0.10 mmol), **2** (0.30 mmol), 5 mol% $[Pd(allyl)Cl]_2$, 12 mol% **L10**, 3.0 equiv. of Cs_2CO_3 in 3.0 mL of TBME at 70 °C for 24 h under nitrogen; isolated yield by silica gel chromatography; ee values were determined by chiral HPLC.

and 96% enantiomeric excess (Entry 15). The absolute configuration of **3a** was confirmed as a *pR* conformer via X-ray crystallography.

Scope of the reaction

The scope of the enantioselective palladium-catalyzed Suzuki–Miyaura cross-coupling process was investigated, and the results are presented in Table 2. A range of 4-phenylbenzene boronic acid and its *para*-substituted derivatives were investigated, which included various electronic properties and steric influences. The results (**3a**–**3i**) demonstrated excellent yields and remarkable enantioselectivity control. Substrates featuring a strongly coordinating cyano group also yielded favorable results (**3i**), demonstrating both high efficiency (52%) and enantioselectivity (95% ee). Subsequently, substrates incorporating various large ring groups, including phenanthrene (**3j**), dibenzofuran (**3k**), and carbazole (**3l**), afforded moderate to exceptional yields (62–76%) along with high enantioselectivities (91–97% ee). Moreover, substrates substituted with small steric groups, such as *N*,*N*-diphenyl (**3m**), CO_2Me (**3n**), and CHO (**3o**), demonstrated high enantiocontrol. However, due to minimal steric hindrance, phenylboronic acid and *ortho*-substituted phenylboronic acids, such as 2-tolylboronic acid and 2-biphenylboronic acid, were unable to hinder the rotation of pillar[5]arene, failing to induce chiral control. Interestingly, *meta*-substituted phenylboronic acids, specifically those bearing phenyl and ester groups, demonstrated uniform compatibility with the standard conditions, resulting in the desired products **3p**–**3r** with outstanding yields and enantioselectivities between 96% and 97%. The tolerance towards a wide range of disubstituted substrates (**3s**–**3v**) bearing diverse groups remained unaffected by the electronic nature of the substituents. Additionally, 2-benzofuran (**3w**), 2-benzothiophen (**3x**), and 2-naphthyl (**3y**) boronic acids were successfully employed in this methodology. However, pyridin-4-ylboronic acid did not react in the system, likely due to the strong coordinating ability of the pyridine group. Furthermore, 9,9-dimethylfluorene, dibenzofuran, and dibenzothiophene boronic acids were converted into the respective products **3z**–**3ab**, with excellent yields and high enantioselectivities of 97%.

The reaction involved a stepwise asymmetric coupling process, wherein the first-step coupling product **1b** formed in the initial step rapidly underwent racemization. Therefore, we obtained two different aryl-substituted chiral pillar[5]arenes by reacting **1b** with arylboronic acids **2**, as shown in Table 3. Initially,

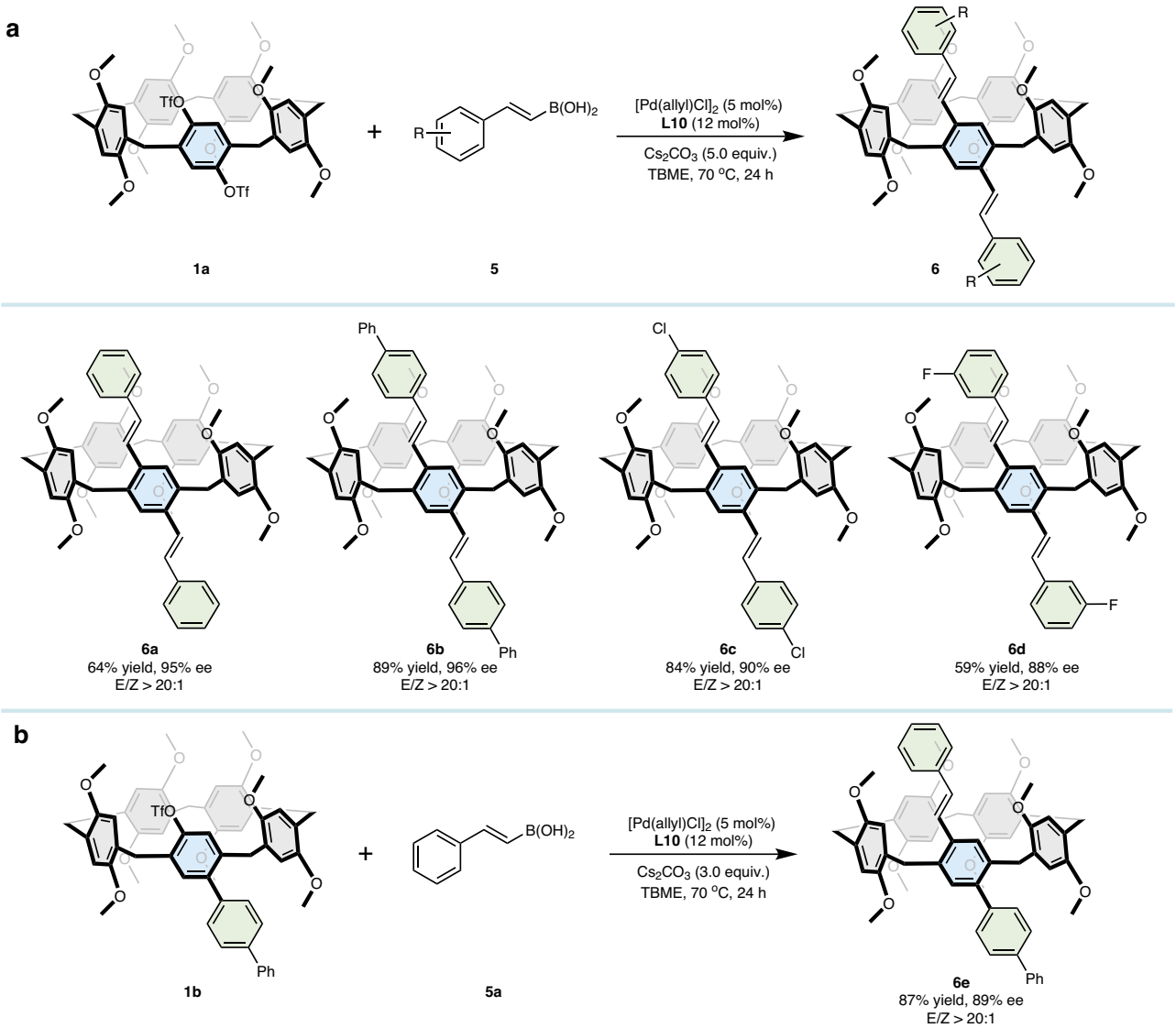


Fig. 2 | Investigation of 1a and 1b with 2-phenylvinylboronic acids 5. a Reaction of **1a** and 2-arylvinylboronic acids **5** results in products **6a**–**6d** under standard conditions. **b** Reaction of **1b** and 2-phenylvinylboronic acid **5a** results in product **6e** under standard conditions.

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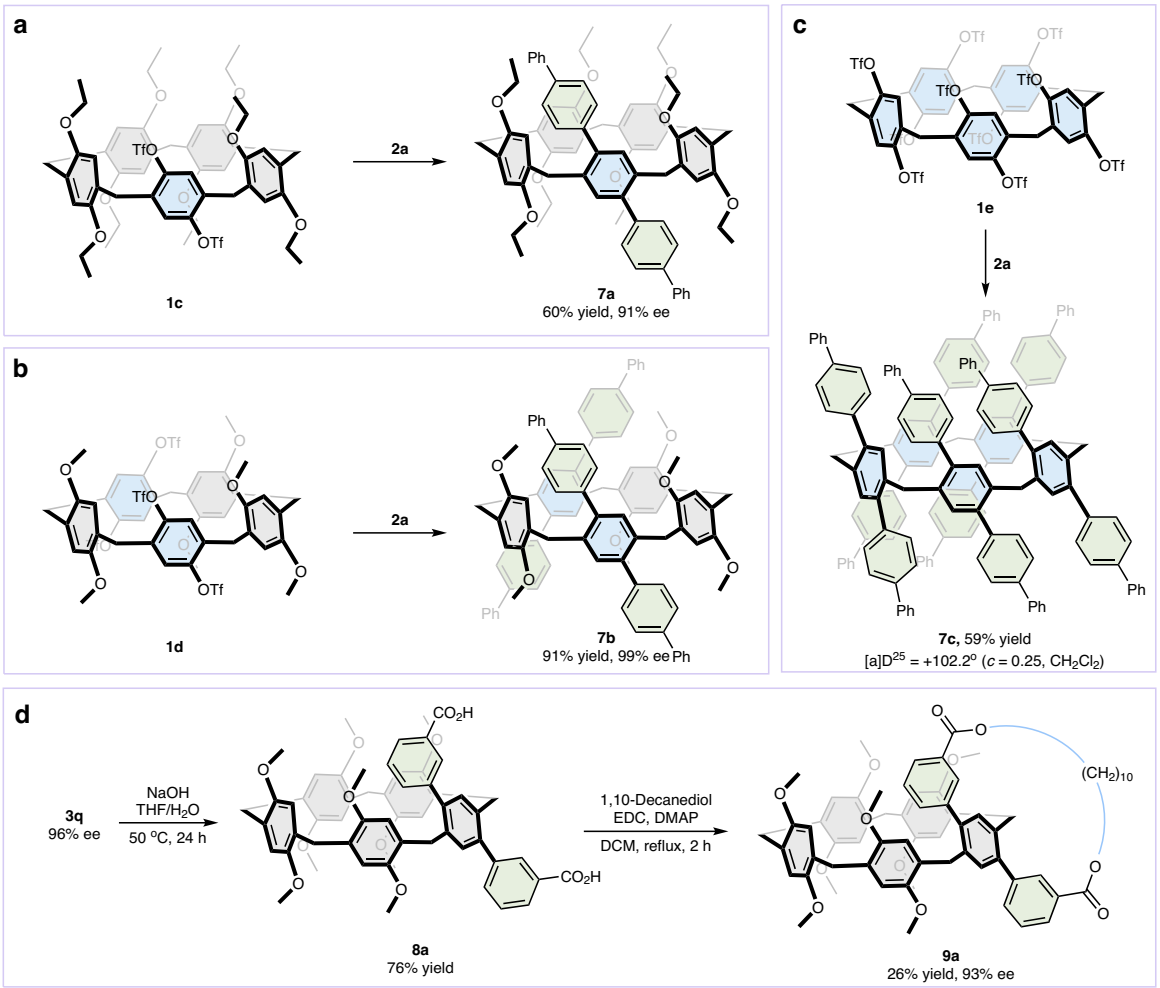


Fig. 3 | Extended applications of the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction. a The reaction of **1c** and **2a** results in product **7a**. **b** The reaction of **1d** and **2a** or $PhB(OH)_2$ results in products **7b** and **7c**. **c** The reaction of **1e** and **2a** results in product **7d**. **d** Application to the synthesis of bicyclic diester compound **9a**.

4-phenylbenzene boronic acid derivatives, including those with *para*-substituents such as *n*-propyl, fluorine, CO_2Me, and dibenzofuran, demonstrated good compatibility with the reaction conditions. The resulting products **4a**–**4d** were obtained with enantiomeric excesses ranging from 95% to 97%. The functional groups, including *N*,*N*-diphenyl (**4o**), phenyl (**4f** and **4h**), and ester (**4g**), all worked well. Finally, substrates with aromatic and heteroaromatic ring substitutions (**4i**–**4l**) yielded functionalized chiral pillar[5]arenes with excellent enantioselectivities.

2-Arylvinylboronic acid is a commonly utilized coupling reagent in palladium-catalyzed Suzuki–Miyaura coupling reactions. We explored the use of 2-phenylvinylboronic acid **5a** in our developed system to evaluate its potential to generate Heck-type chiral pillar[5]arene (Fig. 2a). To our satisfaction, the product **6a** was obtained in a yield of 64% with an enantiomeric excess of 95% and E/Z > 20:1. In addition, the reaction demonstrated broad functional group tolerance, including phenyl (**6b**), chlorine (**6c**), and fluorine (**6d**) substituents. However, alkynyl boronic reagents, such as 2-phenyl-1-ethynylboronic acid pinacol ester and potassium phenylethynyltrifluoroborate, did not lead to the formation of the corresponding products. Furthermore, we efficiently and enantioselectively synthesized product **6e** by employing **1b** in reactions with **5a** in 87% yield with 89% ee (Fig. 2b), which possesses one side that is arylated and the other side that is alkenylated.

Synthetic applications

To showcase the synthetic versatility of our method, we conducted several additional challenging substrates and performed transformations, as illustrated in Fig. 3. The ethyl-substituted compound **1c** derived from 1,4-bis(ethoxy)pillar[5]arene reacted smoothly to produce **7a** in 60% yield with 91% ee (Fig. 3a). Next, we attempted to react the more complex 4OTf-substituted substrate **1d** with **2a**, achieving high efficiency and producing the nearly enantiomerically pure product **7b** (Fig. 3b). Most importantly, the fully aryl-substituted product **7c** with high enantiocontrol could be obtained from 10OTf-pillar[5]arene **1e** by simply prolonging the reaction time (Fig. 3c). Molecular universal joints (MUJs) represent a crucial class of bicyclic pillar[5]arenes that demonstrate chirality inversion in response to variations in temperature and solvent conditions[82–84]. Typically, enantiomers are resolved via chiral-phase HPLC. By employing our method, chiral MUJs **9a** could be synthesized from substrate **3q** through a process involving hydrolysis and subsequent cyclization (Fig. 3d). Additionally, we conducted a gram-scale experiment, where the product **3a** was obtained in excellent yield with no loss of enantioselectivity, further demonstrating the practicality and scalability of our method (see Supplementary Information for more details).

Photophysical and optical property investigations

On the basis of the inherently chiral pillar[5]arenes prepared, we investigated the photophysical characteristics (see the

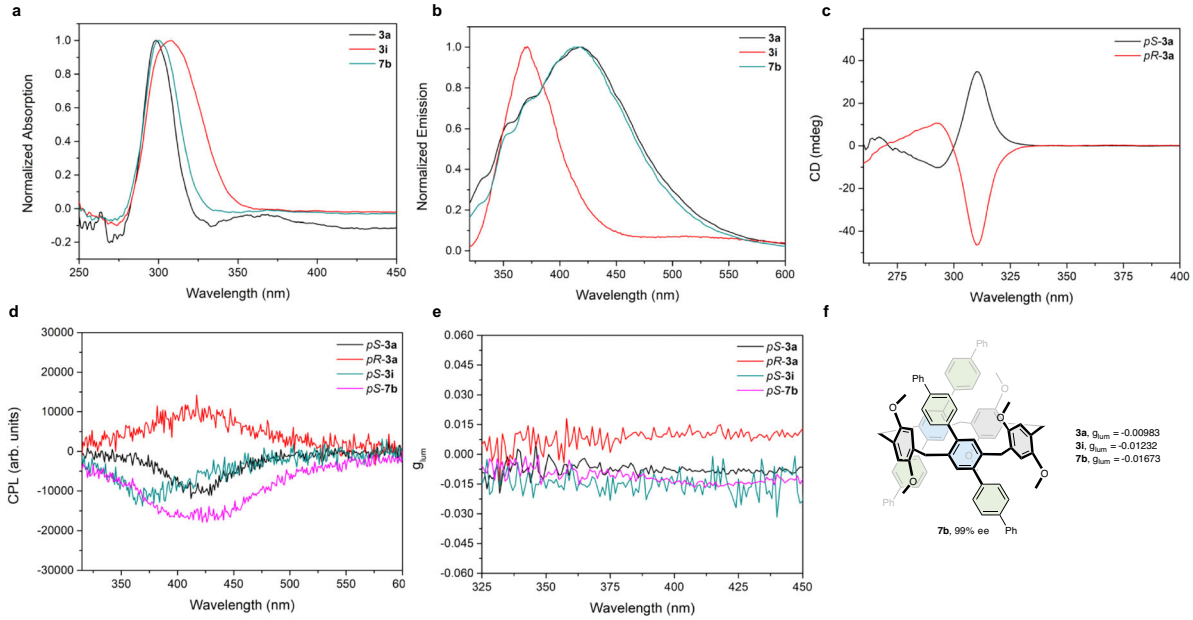


Fig. 4 | Photophysical and optical property investigations. a Absorption spectra of **3a**, **3i**, and **7b** in DCM (1.0×10^{-5} M). **b** Emission spectra of **3a**, **3i**, and **7b** in DCM (1.0×10^{-5} M). **c** CD spectra of ***pR*-3a** and ***pS*-3a** in DCM (1.0×10^{-5} M) at room temperature. **d** CPL spectra of ***pR*-3a**, ***pS*-3a**, ***pR*-3i**, and ***pR*-7b** in DCM (1.0×10^{-5} M) at room temperature and excited at 305 nm. **e** g_{lum} values–wavelength curve for ***pR*-3a**, ***pS*-3a**, ***pR*-3i**, and ***pR*-7b**. **f** Structures of **7b** and g_{lum} values for **3a**, **3i**, and **7b**.

Supplementary Information Figs. S1–S5 for details) of **3a, 3i**, and **7b** (Fig. 4). The ultraviolet-visible (UV-vis) absorption spectra revealed prominent absorption peaks at 305 nm, with additional smaller peaks observed at ~365 nm (Fig. 4a). Upon excitation at the maximum wavelength, fluorescence emission peaks were observed at 420 nm for **3a**, 369 nm for **3i**, and 412 nm for **7b** (Fig. 4b). Notably, as the electronic properties of the substrate increased, there was a distinct red shift in the maximum emission wavelength in the fluorescence spectra. The circular dichroism (CD) spectra of the ***pR*-3a** and ***pS*-3a** enantiomers exhibited pronounced Cotton effects, revealing a distinct mirror image relationship between the *pR* and *pS* forms (Fig. 4c). Additionally, the circularly polarized luminescence (CPL) spectra were recorded for ***pR*-3a, *pS*-3a, *pR*-3i**, and ***pR*-7b**, confirming their CPL activity (Fig. 4d). The luminescence dissymmetry factors $|g_{lum}|$ were quantified (Fig. 4e, f). Notably, compound ***pR*-7b** exhibited a $|g_{lum}|$ value of 0.01673, highlighting its potential for CPL applications. These findings distinctly highlight the considerable promise of chiral pillar[5]arenes in advancing the development of chiral organic luminescent materials and CP-OLEDs[85,86].

Mechanistic investigations

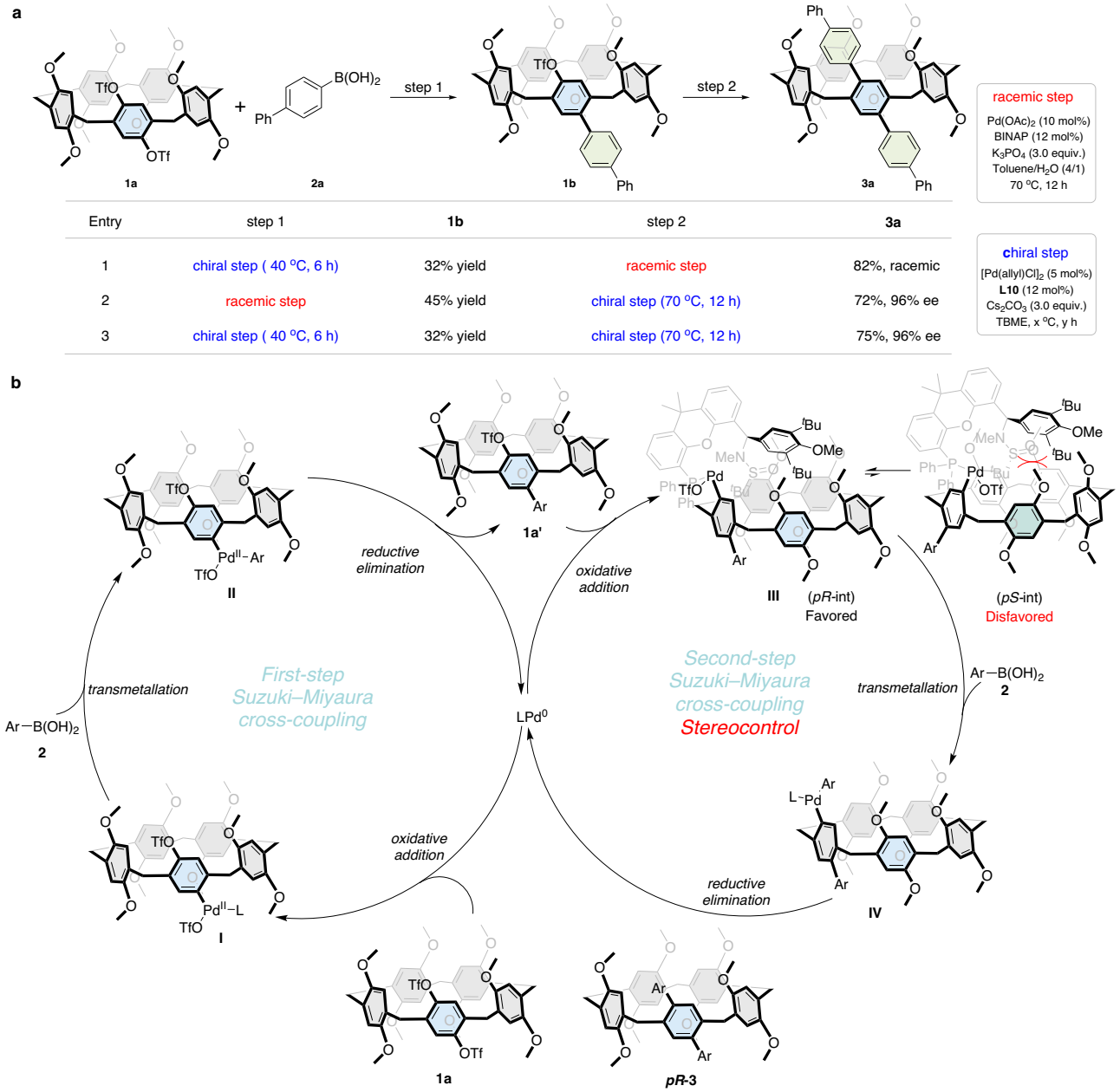
To investigate the stereoselectivity-determining steps of the reaction, we initially performed stepwise control experiments (Fig. 5a). The ligand had no significant impact in the first step, while chiral control was observed in the second step. This result supports the validity of our proposed asymmetric extended side-arm Suzuki–Miyaura cross-coupling strategy. Based on these results and previous studies, we propose the following reaction mechanism (Fig. 5b). The Pd^0 species undergoes oxidative addition to the C–O bond of pillar[5]arene-based bifunctional triflate **1a**, forming Pd^{II} complex **I**. This complex **I** then undergoes transmetallation with arylboronic acid **2** to generate intermediate **III**, which undergoes reductive elimination to deliver product **1a'** and regenerate Pd^0. In the second step of the coupling reaction, a similar catalytic cycle occurs. We proposed an asymmetric induction model for intermediate **III**, where the aryl group of **L10** is positioned near the palladium metal center (Fig. 5b)[81,87]. The electronic properties and the significant steric hindrance of this aryl group play a crucial role in controlling the stereoselectivity of the reaction. In contrast, with ligand **L8**, where the aryl group is positioned farther from the palladium center, the control over stereoselectivity is less effective. Notably, through intermediate **III**, we observed that the steric hindrance of the ligand is critical in determining the stereoselectivity. When considering an alternative *pS*-int transition state, the steric repulsion between the ligand's aryl group and the substrate significantly reduces stereoselectivity, making this transition state less favorable. In this palladium-catalyzed Suzuki–Miyaura cross-coupling reaction, the stereochemical outcome is determined during the oxidative addition of the chiral-ligated palladium complex to the triflate[38]. However, the subsequent transmetallation and reductive elimination steps are also influenced by the steric and electronic properties of the arylboronic acid, which affect the stereoselective control of the reaction[88–90].

In conclusion, we developed an enantioselective palladium-catalyzed Suzuki–Miyaura cross-coupling methodology for the construction of inherently chiral pillar[5]arenes. The pivotal step in continuous enantioselective cross-coupling was effectively accomplished via a chiral Sadphos ligand. This versatile and practical palladium-catalyzed method accommodates a broad spectrum of arylboronic acids and 2-arylvinylboronic acids, facilitating the efficient synthesis of structurally diverse enantioenriched chiral pillar[5]arenes with exceptional enantiocontrol. Additionally, preliminary studies on the photophysical and optical properties of these chiral pillar[5]arenes highlight their potential for use in material science and self-assembly systems.

Methods

General procedure for the synthesis of chiral pillar[5]arenes 3 and 6a–6d

Under nitrogen atmosphere, to a mixture of **1** (0.1 mmol, 1.0 equiv.), **2** or **5** (0.5 mmol, 5.0 equiv.), $[Pd(allyl)Cl]_2$ (5–10 mol%), **L10** (12–24 mol %), and Cs_2CO_3 (0.5 mmol, 5.0 equiv.), followed by the addition of TBME (3.0 mL) in a sealed vial and the reaction was stirred at 70 °C for 24 h. After completion of the reaction, the solvent was removed under



Entry	step 1	1b	step 2	3a
1	chiral step (40 °C, 6 h)	32% yield	racemic step	82%, racemic
2	racemic step	45% yield	chiral step (70 °C, 12 h)	72%, 96% ee
3	chiral step (40 °C, 6 h)	32% yield	chiral step (70 °C, 12 h)	75%, 96% ee

Fig. 5 | Mechanistic investigations. a Investigation of stereoselectivity control by two-step reaction. **b** Proposed reaction mechanism.

vacuum and the crude product was purified directly by column chromatography to afford the desired product **3** or **6a**–**6d**.

General procedure for the synthesis of chiral pillar[5]arenes 4 and 6e

Under nitrogen atmosphere, to a mixture of **1b** (0.1 mmol, 1.0 equiv.), **2** or **5** (0.3 mmol, 3.0 equiv.), $[Pd(allyl)Cl]_2$ (5 mol%), **L10** (12 mol%), and Cs_2CO_3 (0.3 mmol, 3.0 equiv.), followed by the addition of TBME (3.0 mL) in a sealed vial and the reaction was stirred at 70 °C for 24 h. After completion of the reaction, the solvent was removed under vacuum and the crude product was purified directly by column chromatography to afford the desired product **4** or **6e**.

Data availability

The data generated in this study are provided in the Supplementary Information file. The experimental procedures, data of NMR, and HRMS have been deposited in the Supplementary Information file. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2373070 (**3a**) and 2375474 (**4l**) (Supplementary Data 1). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/getstructures. All other data supporting the findings of the study, including experimental procedures and compound characterization, are available within the paper and its Supplementary Information, or from the corresponding author upon request.

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Acknowledgements

This work was supported by the financial support from the Taishan Scholar Youth Expert Program in Shandong Province (tsqn 201909096 R.L.), National Natural Science Foundation of China (22371152 R.L.), National Natural Science Foundation of Shandong (ZR2023JQ006 R.L., ZR2024QB091 L.X.) and Qingdao Natural Science Foundation (23-2-1-244-zyyd-jch R.L.).

Author contributions

T.L., C.S., Y.T., and Y.J. performed the experiments. All authors contributed to the analysis of the experimental results. R.L. and L.X. conceived the study, supervised the project, and wrote the paper.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-025-57461-x.

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Peer review information *Nature Communications* thanks Leyong Wang and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.