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Palladium-catalyzed regio- and stereo-selective phosphination of cyclic biarylsulfonium salts to access atropoisomeric phosphines†

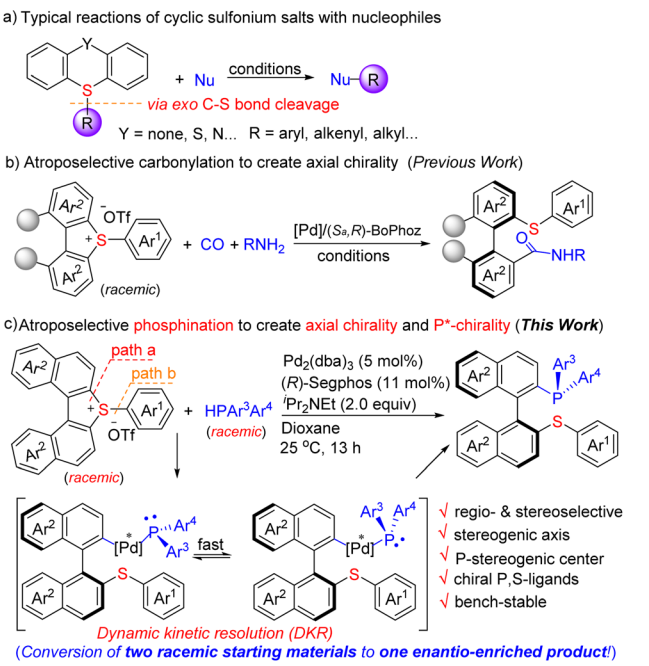
Jinghui Sun,‡ Yifei Yan,‡ Xuanxuan Chen, Zhiwei Huang and Yinhua Huang *

A palladium-catalyzed regio- and stereo-selective phosphination of cyclic biarylsulfonium salts (racemic) with $HPAr^3Ar^4$ for straightforward synthesis of atropoisomeric phosphines (P,S-ligands) bearing a stereogenic axis or both a stereogenic axis and a P-stereogenic center is reported. The high reactivity and regio- and stereo-selectivity originate from the torsional strain release and palladium catalysis, and the construction of a P-stereogenic center is enabled by an efficient dynamic kinetic resolution. The high performance of the nascent P,S-ligands has been demonstrated in palladium-catalyzed asymmetric allylic substitutions, indicating the great potential of the present methodology.

Introduction

Chiral phosphines have demonstrated their high utility in synthetic chemistry and asymmetric catalysis, spurring the development in various areas including biomedicines, drugs and materials science.[1] Among them, atropoisomeric phosphines represented by the iconic BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl)[2] and MOP[3] (monodentate phosphines) have attracted wide interest owing to their excellent axially chiral skeleton and unique properties. The development of efficient synthesis of chiral phosphines has been a long-standing goal. The conventional methods, relying on the use of either a stoichiometric quantity of chiral control elements or phosphine oxides/sulphides/boranes followed by reduction/deprotection, have been the dominant approaches.[2–4] Despite the significant advances made in this area, catalytic, direct and enantioselective synthesis of chiral tertiary phosphines, particularly, chelating phosphines and P-stereogenic phosphines, remains an enduring challenge in organic chemistry. Herein, we report a straightforward synthesis of atropoisomeric phosphines, a type of C_1-symmetric chelating P,S-ligand, potentially offering a high level of structural variations through modular assembly of P- and S-containing building blocks. The key process involves the palladium-catalyzed regio- and stereo-selective phosphination of cyclic biarylsulfonium salts (racemic) with $HPAr^3Ar^4$ to create a stereogenic axis ($Ar^3 = Ar^4$) or both a stereogenic axis and a P-stereogenic center ($Ar^3 \neq Ar^4$) (Scheme 1c).

The key challenges of the present study are (1) the regio- and stereo-selectivity of the C–S bond cleavage[5] of sulfonium salts (racemic), in which two types of $C_{(Ar)}$–S bonds are to be discriminated (path a–b), (2) the nascent P,S-ligands have high affinity to transition metals, which could inhibit the reaction or exclude chiral induction, and (3) the chiral catalyst has to not only reach efficient atroposelectivity[6] to create a stereogenic axis



Scheme 1 Regio- and stereo-selectivity of cyclic sulfonium salts.

College of Materials, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121, P. R. China. E-mail: yhhuang@hznu.edu.cn

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‡ These authors contributed equally.

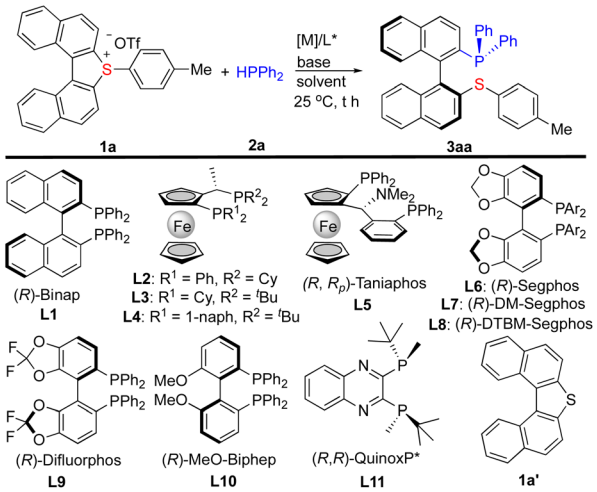
but also construct a P-stereogenic center *via* a dynamic kinetic resolution process (when racemic $HPAr^3Ar^4$ is used) in one step. Nevertheless, by taking the strategy of palladium-catalyzed phosphinative ring-opening of torsional cyclic biarylsulfonium salts, we successfully addressed these challenges. It is highlighted that the nascent chiral P,S-phosphine products are bench-stable and their enantiomeric purity can be further improved to an optically pure level (ee > 99%) just by a single recrystallization. The unique properties of P,S-ligands have been realized recently,[7] indicating that the products have great potential as ligands for asymmetric catalysis.

Sulfonium salts, particularly, cyclic biarylsulfonium salts such as dibenzothiophium and thianthrenium salts, have been demonstrated as versatile electrophilic reagents, and it was generally observed that the cleavage of the *exo* C–S bond proceeded with predominant preference followed by the transfer of the *exo* group during the reaction (Scheme 1a).[8] So far, most of them are limited to non-asymmetric reactions, asymmetric transformation of them being rarely explored. Only one asymmetric example (carbonylation), to the best of our knowledge, has been known (Scheme 1b).[9] We have made continuous efforts in C–X (X = C, P, S, Si, B) bond formation[10] by taking advantage of sulfonium salts and in asymmetric catalysis,[11] which lead us to envision that the merge of the sulfonium salt chemistry and asymmetric catalysis may result in new solutions to construct desired chiral molecules.

Results and discussion

We began our investigation by the reaction of cyclic biarylsulfonium salt **1a** with $HPPh_2$ (**2a**). **1a** is a newly synthesized compound for the present study and its X-ray diffraction analysis (CCDC-2303113)[12] reveals that the two naphthyl rings are twisted by an angle of 27.07°, and that both (*S*)- and (*R*)-conformers exist in the crystal packing (cif). The preliminary investigation identified that $Pd_2(dba)_3$ can efficiently catalyse the reaction to furnish the ring-opening product **3aa**. Subsequently, a variety of chiral ligands were evaluated for the asymmetric transformation. (*R*)-Binap (**L1**) smoothly facilitated the reaction to deliver **3aa** in a 96% yield with 62% ee (entry 1, Table 1). A set of ferrocene bisphosphines (**L2–L5**) were also tested (entries 2–5), and it was found that taniaphos (**L5**) can give comparable results. Several chiral bisphosphines based on biaryl backbone (**L6–L10**) were also tested among which (*R*)-Segphos (**L6**) was found to give the best ee result (entry 6). The increased steric hindrance on the auxiliary (**L7** and **L8**) did not improve the enantioselectivity (entries 8–9). The use of QuinoxP* (**L11**) resulted in a low yield with moderate enantioselectivity (entry 11). Next, bases and solvents were screened in order to improve the enantioselectivity (entries 13–19). It turned out that dioxane is a good solvent and $^iPr_2NEt$ is a good base for this reaction. Finally, fine tuning of the conditions led to **3aa** in a 95% yield with 93% ee (entry 21, standard conditions). Notably, the cleavage of the *exo* C–S bond was not observed under these conditions. The dinaphthothiophene **1a′**, which was reported efficient for Ni-catalyzed asymmetric Grignard cross-coupling,[5a] is not reactive at all under the standard conditions (entry 22), indicating that the reactivity enabled by sulfonium is essential. The X-ray analysis of **3aa** (CCDC-2303114)[12] ambiguously revealed its (*S*)-configuration of the stereogenic axis. Chiral monophosphines which usually do not cause chelation with transition metals *via* catalytic asymmetric C–P bond formation have been documented;[13] however, straightforward synthesis of atropoisomeric P,S-ligands which can readily cause chelation with transition metals, to the best of our knowledge, is not known before.

Table 1 Evaluation of reaction parameters[a]



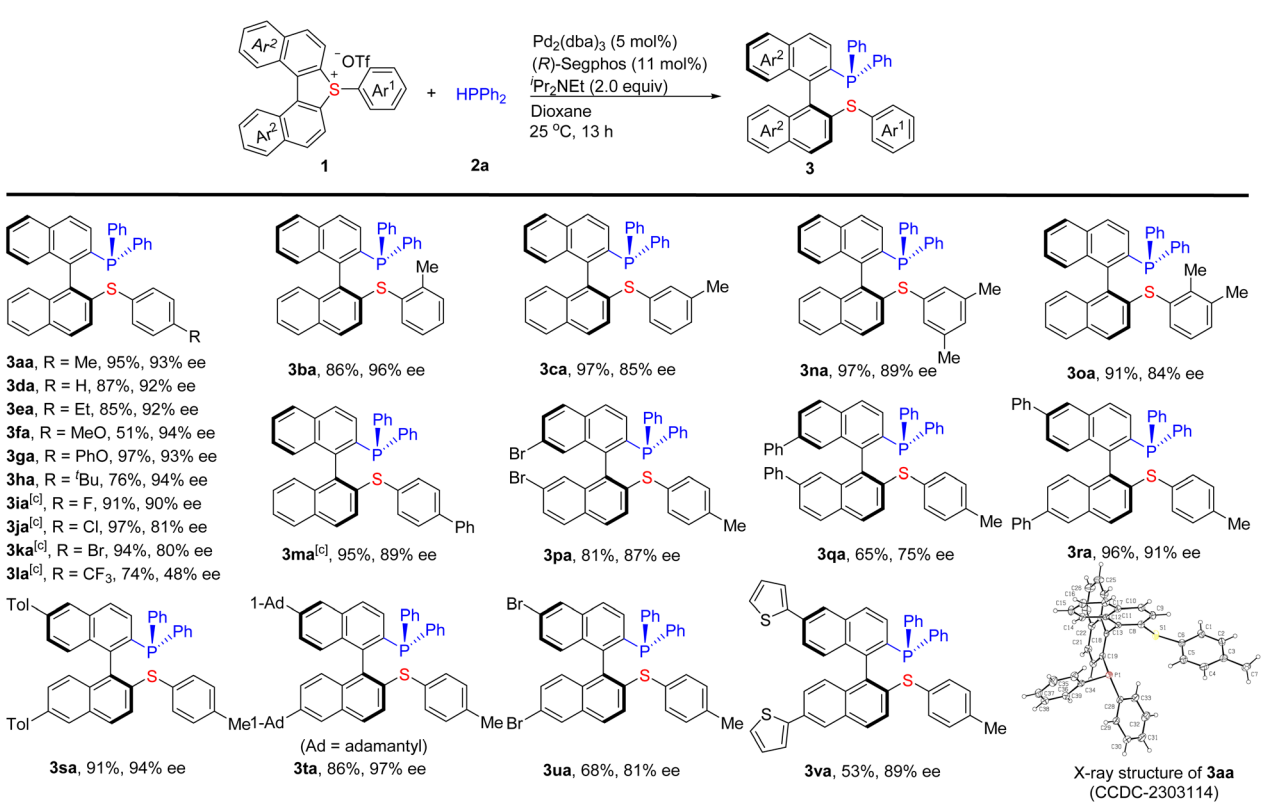
Entry	1	L*	Solvent	Base	Yield[b] (%)	ee[c] (%)
1	**1a**	**L1**	THF	Et_3N	96	62
2	**1a**	**L2**	THF	Et_3N	42	53
3	**1a**	**L3**	THF	Et_3N	58	5
4[d]	**1a**	**L4**	THF	Et_3N	53	0
5	**1a**	**L5**	THF	Et_3N	93	65
6	**1a**	**L6**	THF	Et_3N	58	79
7	**1a**	**L7**	THF	Et_3N	72	52
8	**1a**	**L8**	THF	Et_3N	87	0
9	**1a**	**L9**	THF	Et_3N	39	58
10	**1a**	**L10**	THF	Et_3N	80	63
11	**1a**	**L11**	THF	Et_3N	10	−64
12	**1a**	**L6**	THF	Barton's base	41	<5
13	**1a**	**L6**	THF	Cs_2CO_3	69	40
14	**1a**	**L6**	THF	K_3PO_4	82	77
15	**1a**	**L6**	Dioxane	K_3PO_4	62	87
16	**1a**	**L6**	Toluene	K_3PO_4	85	64
17	**1a**	**L6**	MTBE	K_3PO_4	91	60
18	**1a**	**L6**	DCE	K_3PO_4	81	70
19[e]	**1a**	**L6**	Dioxane	K_2HPO_4	64	90
20[e]	**1a**	**L6**	Dioxane	$^iPr_2NEt$	74	90
21[e,f]	**1a**	**L6**	Dioxane	$^iPr_2NEt$	95	93
22[e]	**1a′**	**L6**	Dioxane	$^iPr_2NEt$	0	n.a.

[a] Reaction conditions: **1** (0.120 mmol), **2a** (0.120 mmol), base (1.5 equiv.), and $Pd_2(dba)_3$ (2.5 mol%) in solvent (4.0 mL) at 25 °C for 13 h, unless otherwise noted. THF = tetrahydrofuran and MTBE = methyl *tert*-butyl ether. [b] The yields were obtained by ^1H NMR analysis of the crude reaction mixture with the aid of $Cl_2CHCHCl_2$ as an internal standard. [c] The ee was determined by HPLC on a chiral stationary phase column. [d] The reaction was performed at 60 °C (no reaction at 25 °C). [e] $Pd_2(dba)_3$ (5 mol%). [f] **1a** (0.132 mmol) and base (2.0 equiv.).

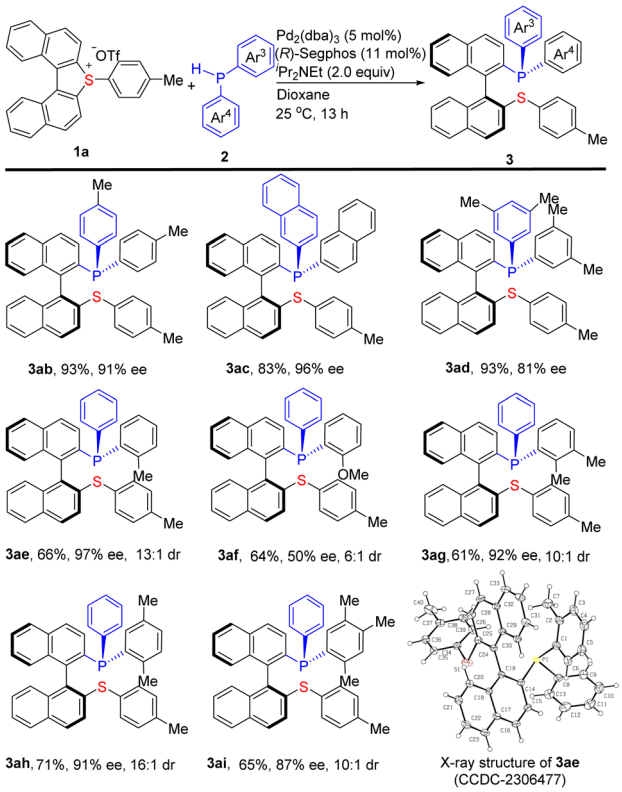
Under the optimized conditions (Table 1, entry 21), a variety of cyclic biarylsulfonium salts reacted smoothly with **2a** to give the desired products **3aa–3va** in good to excellent yields with high enantioselectivities (Scheme 2). Various *para*, *meta*, and *ortho* mono- and disubstituted aromatic rings (Ar^1) at the *exo*-position of **1** are well tolerated. Generally, the steric hindrance on Ar^1 does not influence the reactivity and enantioselectivity. For example, the steric hindrance from the *ortho* methyl substituent of Ar^1 (**1b** and **1o**) and the tertiary butyl at the *para*-position (**1h**) smoothly delivered the corresponding products. A range of functional groups such as ether, halogens (F, Cl, and Br), CF_3 were compatible with the conditions. The electronic properties of the substituents on Ar^1 have an obvious effect on the reaction. The electron neutral (**1d**) and donating groups (**1a–h** and **1m**) substituted on Ar^1 furnished the desired products in good to excellent yields (51–97%) and enantioselectivities (84–94% ee). Comparatively, the electron-deficient ones with halogens (F, Cl, and Br) substituted on Ar^1 (**1i–1k**) gave higher yields (91–97%) with good enantioselectivities (82–90% ee). **1l** bearing a strong electron-deficient CF_3 group resulted in a lower yield (74%) and enantioselectivity (48% ee). The introduction of disubstituents on Ar^1 (**1n** and **1o**) did not affect the reaction. The cyclic biarylsulfonium salts bearing two substituents (including Br, Ph, Tol, and 1-Ad) at the naphthyl rings (Ar^2) (**1p–u**) were also amenable to this protocol and delivered the corresponding products **3p–u** in 65–96% yields with 75–97% ee. It is worth noting that aryl halides including Br (**1k**, **1p**, and **1u**) and Cl (**1j**) can be tolerated under the reaction conditions, which employ palladium (0) as the catalyst. Interestingly, heteroaromatic rings such as 2-thienyl can also be tolerated to give the corresponding product **3va** (53%, 89% ee).

Using the cyclic biarylsulfonium salt **1a**, the scope of the secondary phosphine partners has also been investigated and the results are shown in Scheme 3. Firstly, several symmetrical diarylphosphines $HPAr_2^3$ including **2b–2d** were evaluated for this reaction. The results indicated that all of them are good partners for this transformation delivering the corresponding products **3ab–3ad** in 83–93% yields with 81–96% ee. Motivated by the pivotal role of P-stereogenic phosphines,[14] a series of unsymmetrical diarylphosphines $HPAr^3Ar^4$ ($Ar^3 \neq Ar^4$) were evaluated under the standard conditions. The substrates containing an *ortho*-substituent such as Me (**2e** and **2g–2i**) on one aromatic ring (Ar^4) reacted smoothly with **1a** to give the corresponding products **3ae** and **3ag–ai** bearing both a stereogenic axis and a P-stereogenic center in 61–71% yields with 87–97% ee and ≥10 : 1 dr. Comparatively, the 2-methoxyl substituted **2f** was not so efficient, delivering the corresponding **3af** in 64% yield with 50% ee and 6 : 1 dr. The absolute configuration of **3ae** was unambiguously determined to be (S_{axial},R_P) by single-crystal X-ray diffraction analysis (CCDC-2306477).[12] Other products yielded under the same chiral catalytic conditions are assumed to have identical configuration. Notably, all of the P,S-phosphine products produced by this protocol are bench-stable.

Scale-up (2 mmol) synthesis of **3aa** (92%, 90% ee) and **3ae** (62% ee, 97% ee) has been achieved (Scheme 4a). The yields and enantioselectivities are not obviously influenced, indicating the



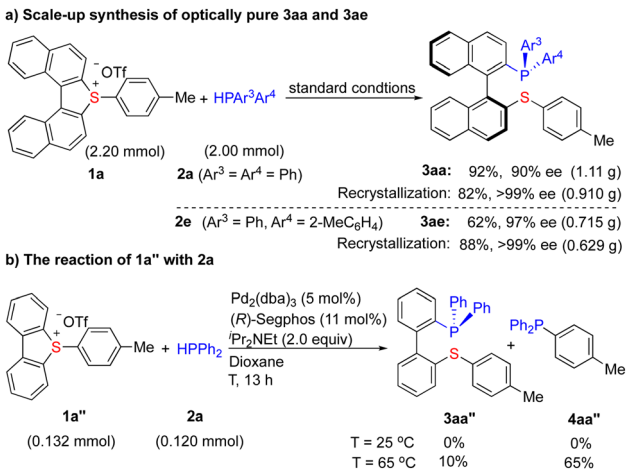
Scheme 2 Substrate scope of cyclic biarylsulfonium salts. [a] Reaction conditions: **1** (0.132 mmol), **2a** (0.120 mmol), $^iPr_2NEt$ (2.0 equiv.), dioxane (4.0 mL), 25 °C, and 13 h. Isolated yield of **3** is given. [b] The ee% was determined by HPLC on a chiral stationary phase column. [c] 0–25 °C.



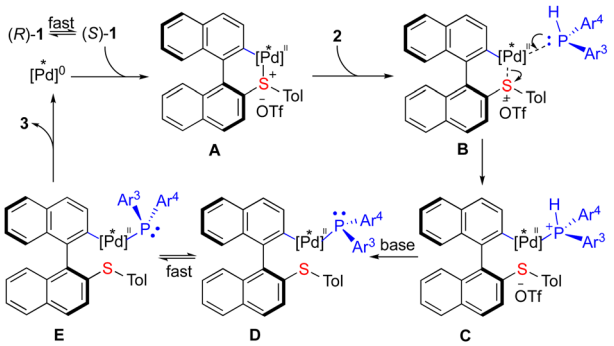
Scheme 3 Substrate scope of secondary phosphines. [a] Reaction conditions: **1a** (0.132 mmol), **2** (0.120 mmol), $^{i}Pr_2NEt$ (2.0 equiv.), dioxane (4.0 mL), 25 °C, and 13 h. Isolated yield of **3** is given. [b] The ee was determined by HPLC on a chiral stationary phase column. The dr ratio was determined by ^{31}P NMR analysis of the crude reaction mixture.

feasibility of scale-up synthesis. Importantly, a simple recrystallization ($CHCl_3$/acetone) further improved the enantiomeric purity of **3aa** (>99% ee) and **3ae** (>99% ee) to an optically pure level, demonstrating the elegance of this protocol.

The use of a non-substituted dibenzothiophium salt **1a″**, which lacks torsional strain, terminates the reaction completely



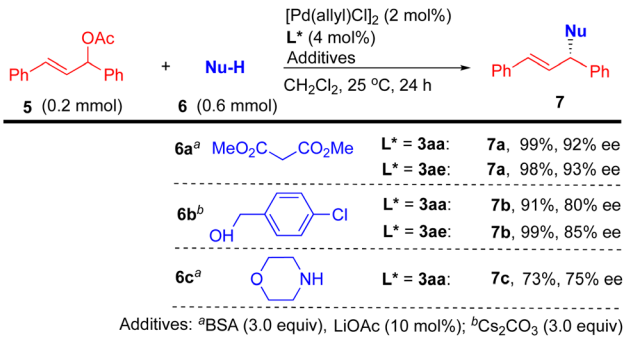
Scheme 4 Scale-up synthesis of optically pure **3aa** and **3ae**.



Scheme 5 Proposed mechanism.

under the standard conditions (Scheme 4b). The raise of temperature (65 °C) delivered **4aa″** (*via exo* C–S cleavage) as a major product (65%) rather than the expected **3aa″** (10%). These results demonstrate that the activation from both sulfonium and torsional strain is essential for this transformation.

To gain a deeper insight into the mechanism, radical trapping experiments have been conducted and the results excluded the radical pathway.[12] A plausible catalytic cycle was proposed as depicted in Scheme 5. (R_a)-**1** and (S_a)-**1** are in rapid equilibrium[5a,9] with each other *via* the rotation of the C_{aryl}–C_{aryl} single bond. The (*R*)-Segphos-ligated $Pd^{(0)}$ complex undergoes oxidative addition preferentially to (*S*)-**1** cleaving an *endo* C–S bond to form biaryl $[Pd]^{II}$ species **A**. The subsequent coordination of **2** (**B**) leads to the formation of complex **C** followed by the abstraction of a proton to give the $[Pd]^{II}$-phosphido species[15] **D** and **E**, which undergo a rapid equilibrium (when $Ar^3 \neq Ar^4$). The subsequent reductive elimination of the more thermodynamic stable **D** furnishes the chiral phosphine product **3** and regenerates the $[Pd]^0$ species, closing a catalytic cycle. The key point is that the equilibrium between **D** and **E** must be much faster than the reductive elimination in this dynamic kinetic resolution process in order to achieve high *enantio*-control of the P-stereogenic center. Notably, the existence of P,S-ligands which have high affinity to metals does not interrupt the catalytic cycle, presumably due to the stronger chelating ability of Segphos coordinated with palladium. It is the combination of the torsional strain release with the dynamic kinetic resolution



Scheme 6 Application of P,S-ligands in Pd-catalyzed allylic substitutions.

process enabled by palladium catalysis that provides a straightforward synthesis of atropoisomeric chelating P-stereogenic phosphines that are otherwise difficult to achieve in a catalytic manner.

Finally, to demonstrate the utility of the nascent P,S-phosphine products, preliminary investigations employing **3aa** or **3ae** as a chiral ligand for the palladium-catalyzed allylic substitution of **5** including alkylation (with **6a**), etherification (with **6b**), and amination (with **6c**) under mild conditions have been carried out (Scheme 6).[16] **3aa** or **3ae** exhibited excellent reactivity (91–99% yields) and enantioselectivity (80–93% ee) in the alkylation and etherification and good reactivity (73%) and enantioselectivity (75% ee) in the amination.

Conclusions

In conclusion, we have disclosed a palladium-catalyzed regio- and stereo-selective phosphination of cyclic biarylsulfonium salts with $HPAr^3Ar^4$. This protocol provides a general method for straightforward synthesis of P,S-ligands bearing a stereogenic axis, or both a stereogenic axis and a P-stereogenic center. The high performance of the nascent P,S-ligands has been demonstrated in palladium-catalyzed asymmetric allylic substitution reactions. Further mechanistic studies and applications of P,S-ligands in asymmetric catalysis are currently underway. We expect the versatile chiral P,S-ligands outlined herein to enable the related symmetric catalysis for the facile synthesis of known and new chiral compounds of interest.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

J. S. and Y. Y. carried out the synthetic and reaction studies, and they contributed equally. Y. H. managed the project and wrote the manuscript. All authors participated in the manuscript preparation.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) Q.-L. Zhou *Privileged Chiral Ligands and Catalysts*, Wiley VCH, 2011, vol. 6; (*b*) V. Iaroshenko *Organophosphorus Chemistry: from Molecules to Applications*, Wiley VCH, Weinheim, 2019; (*c*) W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029–3070; (*d*) T. Baumgartner and R. Réau, *Chem. Rev.*, 2006, **106**, 4681–4727.

2 M. Berthod, G. Mignani, G. Woodward and M. Lemaire, *Chem. Rev.*, 2005, **105**, 1801–1836.

3 T. Hayashi, *Acc. Chem. Res.*, 2000, **33**, 354–362.

4 (*a*) D. S. Glueck, *J. Org. Chem.*, 2020, **85**, 14276–14285; (*b*) M. Dutartre, J. Bayardon and S. Jugé, *Chem. Soc. Rev.*, 2016, **45**, 5771–5794; (*c*) T. Imamoto, *Proc. Jpn. Acad., Ser. B*, 2021, **97**, 520–542.

5 (*a*) T. Shimada, Y.-H. Cho and T. Hayashi, *J. Am. Chem. Soc.*, 2002, **124**, 13396–13397; (*b*) D. Vasu, D. Yorimitsu and A. Osuka, *Angew. Chem., Int. Ed.*, 2015, **54**, 7162–7166.

6 (*a*) J. K. Cheng, S.-H. Xiang, S. Li, L. Ye and B. Tan, *Chem. Rev.*, 2021, **121**, 4805–4902; (*b*) Y.-B. Wang and B. Tan, *Acc. Chem. Res.*, 2018, **51**, 534–547; (*c*) X. Zhang, K. Zhao and Z. Gu, *Acc. Chem. Res.*, 2022, **55**, 1620–1633; (*d*) G. Bringmann, T. Gulder, T. A. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563–639; (*e*) J. WencelDelord, A. Panossian, F. R. Leroux and F. Colobert, *Chem. Soc. Rev.*, 2015, **44**, 3418–3430; (*f*) A. Link and C. Sparr, *Chem. Soc. Rev.*, 2018, **47**, 3804–3815; (*g*) H.-H. Zhang, T.-Z. Li, S.-J. Liu and F. Shi, *Angew. Chem., Int. Ed.*, 2023, **62**, e202311053; (*h*) K. Zhao, L. Duan, S. Xu, J. Jiang, Y. Fu and Z. Gu, *Chem*, 2018, **4**, 599–612.

7 (*a*) F. L. Lam, F. Y. Kwong and A. S. C. Chan, *Chem. Commun.*, 2010, **46**, 4649–4667; (*b*) S. Gladiali, S. Medici, G. Pirri, S. Pulacchini and D. Fabbri, *J. Chem.*, 2001, **79**, 670–678; (*c*) T. Hoshi, K. Sasaki, S. Sato, Y. Ishii, T. Suzuki and H. Hagiwara, *Org. Lett.*, 2011, **13**, 932–935; (*d*) A. Berthelot-Bréhier, A. Panossian, F. Colobert and F. R. Leroux, *Org. Chem. Front.*, 2015, **2**, 634–644.

8 (*a*) L. van Dalsen, R. E. Brown, J. A. Rossi-Ashton and D. J. Procter, *Angew. Chem., Int. Ed.*, 2023, **62**, e202303104; (*b*) H. Meng, M.-S. Liu and W. Shu, *Chem. Sci.*, 2022, **13**, 13690–13707; (*c*) L. Zhang and T. Ritter, *J. Am. Chem. Soc.*, 2022, **144**, 2399–2414; (*d*) H. Yorimitsu, *Chem. Rec.*, 2021, **21**, 3356–3369; (*e*) F. Berger and T. Ritter, *Synlett*, 2022, **33**, 339–345; (*f*) Á. Péter, G. J. P. Perry and D. J. Procter, *Adv. Synth. Catal.*, 2020, **362**, 2135–2142; (*g*) S. I. Kozhushkov and M. Alcarazo, *Eur. J. Inorg. Chem.*, 2020, 2486–2500.

9 Q. Zhang, X. Xue, B. Hong and Z. Gu, *Chem. Sci.*, 2022, **13**, 3761–3765.

10 (*a*) Y. Ye, J. Zhu and Y. Huang, *Org. Lett.*, 2021, **23**, 2386–2391; (*b*) R. Xie, J. Zhu and Y. Huang, *Org. Chem. Front.*, 2021, **8**, 5699–5704; (*c*) Y. Ye, J. Zhu, H. Xie and Y. Huang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212522; (*d*) J. Zhu, Y. Ye and Y. Huang, *Organometallics*, 2022, **41**, 2342–2348; (*e*) J. Zhu, Y. Ye, Y. Yan, J. Sun and Y. Huang, *Org. Lett.*, 2023, **25**, 5324–5328; (*f*) J. Zhu, J. Sun, Y. Yan, Z. Dong and Y. Huang, *J. Org. Chem.*, 2023, **88**, 15767–15771.

11 (*a*) Y. Huang and T. Hayashi, *Chem. Rev.*, 2022, **122**, 14346–14404; (*b*) J. Li, J. Sun, W. Ren, J. Lei, R. Shen and Y. Huang, *Org. Lett.*, 2022, **24**, 2420–2424; (*c*) X. Lu, J. Zhu and Y. Huang, *Org. Lett.*, 2022, **24**, 8816–8820; (*d*) Y. Pan, X. Lu, H. Qiu, H. Tamio and Y. Huang, *Org. Lett.*, 2020, **22**,

8413–8418; (*e*) Y. Huang and T. Hayashi, *J. Am. Chem. Soc.*, 2015, **137**, 7556–7559; (*f*) Y. Huang and T. Hayashi, *J. Am. Chem. Soc.*, 2016, **138**, 12340–12343.

12 For more details, see the ESI†

13 (*a*) D. K. Wicht, I. V. Kourkine, B. M. Lew, J. M. Nthenge and D. S. Glueck, *J. Am. Chem. Soc.*, 1997, **119**, 5039–5040; (*b*) A. D. Sadow, I. Haller, L. Fadini and A. Togni, *J. Am. Chem. Soc.*, 2004, **126**, 14704–14705; (*c*) J.-J. Feng, X.-F. Chen, M. Shi and W.-L. Duan, *J. Am. Chem. Soc.*, 2010, **132**, 5562–5563; (*d*) Y. Huang, S. A. Pullarkat, Y. Li and P.-H. Leung, *Chem. Commun.*, 2010, **46**, 6950–6952; (*e*) Y.-B. Li, H. Tian and L. Yin, *J. Am. Chem. Soc.*, 2020, **142**, 20098–20106; (*f*) W.-J. Yue, J.-Z. Xiao, S. Zhan and L. Yin, *Angew. Chem., Int. Ed.*, 2020, **59**, 7057–7062; (*g*) J. M. Pérez, R. Postolache, M. C. Reis, E. G. Sinnema, D. Vargová, F. Vries, E. Otten, L. Ge and S. R. Harutyunyan, *J. Am. Chem. Soc.*, 2021, **143**, 20071–20076; (*h*) D. Ji, J. Jing, Y. Wang, Z. Qi, F. Wang, X. Zhang, Y. Wang and X. Li, *Chem*, 2022, **8**, 3346–3362; (*i*) Y. Zhang, Y. Jiang, M. Li, Z. Huang and J. Wang, *Chem Catal.*, 2022, **2**, 3163–3173; (*j*) Z. Lu, H. Zhang, Z. Yang, N. Ding, L. Meng and J. Wang, *ACS Catal.*, 2019, **9**, 1457–1463.

14 (*a*) C. Luan, C.-J. Yang, L. Liu, Q.-S. Gu and X.-Y. Liu, *Chem Catal.*, 2022, **2**, 2876–2888; (*b*) J. S. Harvey and V. Gouverneur, *Chem. Commun.*, 2010, **46**, 7477–7485; (*c*) D. S. Glueck, *Chem.–Eur. J.*, 2008, **14**, 7108–7117; (*d*) D. S. Glueck, *Synlett*, 2007, 2627–2634; (*e*) Y. Huang, Y. Li, P.-H. Leung and T. Hayashi, *J. Am. Chem. Soc.*, 2014, **136**, 4865–4868; (*f*) C. Wang, K. Huang and W.-L. Duan, *J. Am. Chem. Soc.*, 2021, **143**, 5685–5690; (*g*) S. Zhang, J.-Z. Xiao, Y.-B. Li, C.-Y. Shi and L. Yin, *J. Am. Chem. Soc.*, 2021, **143**, 9912–9921; (*h*) Y.-B. Li, H. Tian, S. Zhang, J.-Z. Xiao and L. Yin, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117760; (*i*) V. S. Chan, I. C. Stewart, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2006, **128**, 2786–2787; (*j*) V. S. Chan, M. Chiu, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2009, **131**, 6021–6032.

15 (*a*) N. F. Blank, J. R. Moncarz, T. J. Brunker, C. Scriban, B. J. Anderson, O. Amir, D. S. Glueck, L. N. Zakharov, J. A. Golen, C. D. Incarvito and A. L. Rheingold, *J. Am. Chem. Soc.*, 2007, **129**, 6847–6858; (*b*) V. S. Chan, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 15122–15123.

16 (*a*) R. Shintani, W.-L. Duan, K. Okamoto and T. Hayashi, *Tetrahedron: Asymmetry*, 2005, **16**, 3400–3405; (*b*) J. Chen, F. Lang, D. Li, L. Cun, J. Zhu, J. Deng and J. Liao, *Tetrahedron: Asymmetry*, 2009, **20**, 1953–1956; (*c*) F. L. Lam, T. Au-Yeung, F. Y. Kwong, Z. Zhou, K. Y. Wong and A. S. C. Chan, *Angew. Chem., Int. Ed.*, 2008, **47**, 1280–1283; (*d*) J.-H. Wu, S. Fang, X. Zheng, J. He, Y. Ma, Z. Su and T. Wang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309515.