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Rhodium(III)-Catalyzed Atroposelective Synthesis of C–N Axially Chiral Naphthylamines and Variants via C–H Activation

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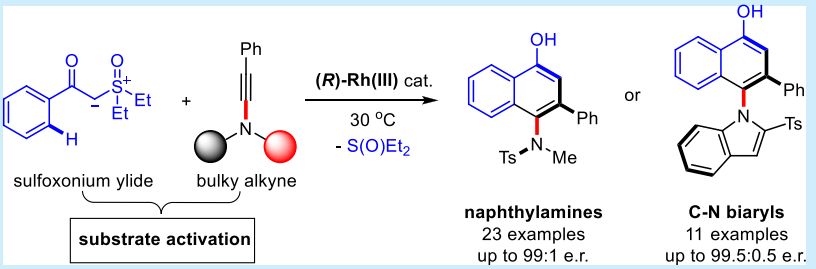

ABSTRACT: Reported herein is the efficient and atroposelective construction of two categories of C–N atropisomers via rhodium(III)-catalyzed C–H activation of sulfoxonium ylides en route to [4+2] annulation with sterically hindered, electron-rich alkynes. This reaction proceeds with high regio- and enantioselectivity under redox-neutral conditions via a double-substrate activation strategy, providing a novel entry to C–N axially chiral 4-functionalized 1-naphthols.

Atropisomerism results from restricted rotation around a single bond that defines a chiral axis.[1] Axially chiral skeletons are ubiquitous in bioactive molecules as well as in natural products.[2] Among them, atropoisomeric biaryls are known to be prominent linkages in abundant natural products and pharmaceutical molecules.[1c,2,3] They also play an important role in a large number of asymmetric catalytic reactions as chiral ligands.[4] Thus, the asymmetric synthesis of atropoisomeric biaryls has been extensively investigated over the past several decades.[3f,5] In sharp contrast to that of the well-developed C–C atropisomers, the construction of C–N atropisomers is comparatively less explored, which is probably due to the synthetic challenges (Scheme 1a).[3d,6]

Axially chiral anilides make up an under-represented class of C–N atropisomers, and the catalytic asymmetric synthesis of axially chiral anilides has attracted only scant attention and it remains a daunting challenge.[6] In 2002, Taguchi and Curran independently reported Pd(II)-catalyzed N-allylation of *o-tert*-butyl anilides, which marks the first example of asymmetric catalytic synthesis of axially chiral acyclic anilides (Scheme 1b, I).[7] Subsequently, several representative strategies have been adopted for the construction of axially chiral anilides. Enantioselective NH functionalization serves as a predominant method by locking the conformation of a preformed C–N axis, such as N-allylation,[8] N-alkylation,[9] or N-arylation.[10] Over the past few years, C–H activation has become an important protocol for the construction of axially chiral compounds.[11] In this context, C–H bond olefination or alkynylation has led to axially chiral anilides (Scheme 1b, II).[12] Alternatively, the enantioselective construction of the Ar–N axis can be realized via organocatalytic Friedel–Crafts amination of 2-naphthols (Scheme 1b, III).[13] Meanwhile, metal-catalyzed asymmetric intermolecular [2+2+2] cycloaddition of 1,6-diynes with ynamides also allowed efficient construction of axially chiral anilides (Scheme 1b, IV).[14]

In analogy to anilides, chiral sulfonamides are also common motifs in drug molecules. To the best of our knowledge, only one report has documented the atroposelective synthesis of sulfonamides by organocatalysis.[8c] Sulfoxonium ylides have been extensively explored for the construction of fused rings via C–H bond activation and annulation reactions.[15] However, no asymmetric system of this coupling has been developed. We now report a novel strategy for the construction of two classes of 1-naphthols bearing a C–N chiral axis by resorting to Rh-catalyzed C–H activation and [4+2] annulation with internal alkynes enabled by substrate activation (Scheme 1c).

We initiated our research by exploring the reaction conditions of the coupling of a sulfoxonium ylide (**1**) and *N*-sulfonylynamides (**2**) in the presence of Cramer's second-generation chiral Rh(III) cyclopentadienyl catalyst[16] (Table 1). As shown in Table 1, a commonly used dimethylsulfoxonium ylide coupled with ynamide **2a** to give naphthylamines (*S*)-**3** in moderate yield and enantioselectivity. Employment of

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Scheme 1. Enantioselective Synthesis of Atropisomeric Anilines

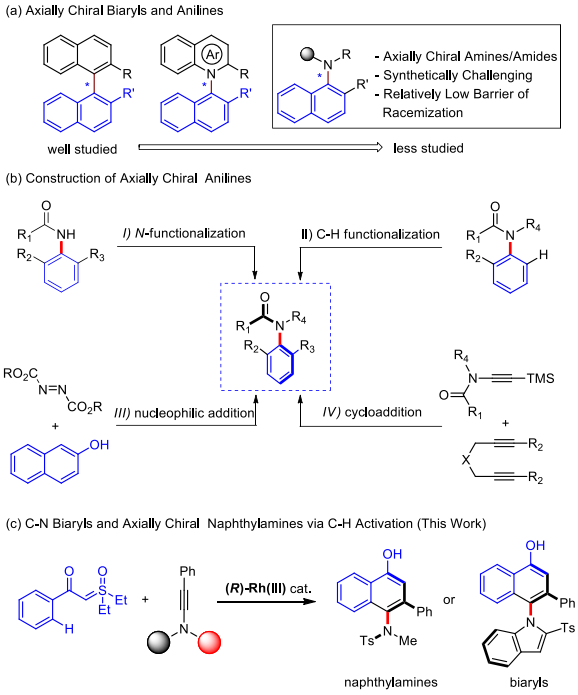
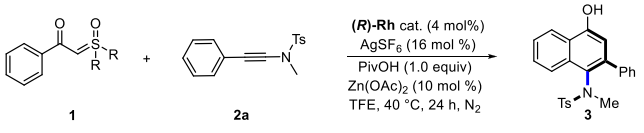
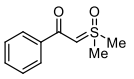
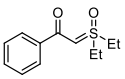
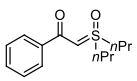
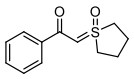


Table 1. Initial Optimization of the Directing Group[a]



Substrate				
Yield(%)	45%	35%	38%	30%
e.r.	74:26	89:11	86:14	70:30

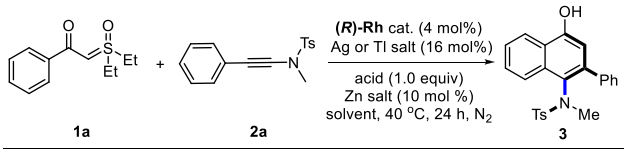
[a]Reaction conditions: sulfoxonium ylide (0.05 mmol), ynamide **2a** (1.5 equiv), (*R*)-**Rh** (4 mol %), $AgSbF_6$ (16 mol %), PivOH (1.0 equiv), $Zn(OAc)_2$ (10 mol %), and TFE (0.5 mL) at 40 °C under N_2 for 24 h.

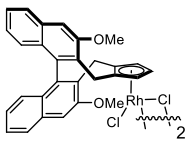
a diethylsulfoxonium ylide resulted in an appreciable increase in enantioselectivity, while inferior selectivity was observed when a dipropyl or cyclic sulfoxonium ylide was employed. Therefore, we chose the diethylsulfoxonium ylide for further optimization.

The coupling of diethylsulfoxonium ylide **1a** and *N*-sulfonyl ynamide **2a** was further screened (Table 2). Solvent screening revealed that DCM was superior to others (entries 1−5). Moreover, the transformation was found to be sensitive to the carboxylic acid additive (entries 6−8). A brief evaluation indictaed that the *tert*-butyl-substituted chiral carboxylic acid (*S*)-**A1**[17] performed best, affording **3** in 73% yield and 93:7 er. After extensive screening, a catalytic amount of $Zn(OTf)_2$ was identified as a superior additive (entries 14 and 15). The annulated product was obtained in an improved yield (78%) and enantioselectivity (95:5 er) when $TlPF_6$ was used as a halide scavenger (entry 15).

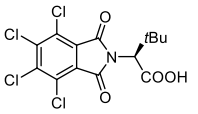
The scope of this coupling system was next explored. A broad range of sulfoxonium ylides have been established using

Table 2. Optimization Studies[a]





(*R*)-Rh cat.



(*S*)-A1

entry	solvent	Ag or Tl salt	acid	yield (%)[e]	er
1	TFE	$AgSbF_6$	PivOH	35	89:11
2	PhCl	$AgSbF_6$	PivOH	52	87.5:12.5
3	1,4-dioxane	$AgSbF_6$	PivOH	38	84:16
4	DCE	$AgSbF_6$	PivOH	60	88.5:11.5
5	DCM	$AgSbF_6$	PivOH	63	89:11
6	DCM	$AgSbF_6$	AcOH	47	90:10
7	DCM	$AgSbF_6$	$AdCO_2H$	70	90.5:9.5
8	DCM	$AgSbF_6$	(*S*)-**A1**	75	92:8
9[b]	DCM	$AgSbF_6$	(*S*)-**A1**	73	93:7
10[b]	DCM	AgOTf	(*S*)-**A1**	71	91.5:8.5
11[b]	DCM	$AgBF_4$	(*S*)-**A1**	68	93:7
12[b]	DCM	$AgPF_6$	(*S*)-**A1**	70	93.5:6.5[f]
13[b,c]	DCM	$AgPF_6$	(*S*)-**A1**	75	89:11
14[b,d]	DCM	$AgPF_6$	(*S*)-**A1**	72	94:6[f]
15[b,d]	DCM	$TlPF_6$	(*S*)-**A1**	78[f]	95:5[f]

[a]Reaction conditions: **1a** (0.05 mmol), **2a** (1.5 equiv), (*R*)-**Rh** (4 mol %), Ag or Tl salt (16 mol %), acid (1.0 equiv), $Zn(OAc)_2$ (10 mol %), and solvent (0.5 mL) at 40 °C under N_2 for 24 h. [b]At 30 °C. [c]No Zn salt. [d]$Zn(OTf)_2$ instead of $Zn(OAc)_2$. [e]Isolated yield. [f]Average of two runs.

enamide **2** as the coupling partner (Scheme 2). Sulfoxonium ylides bearing both electron-donating and -withdrawing groups at the *para* position of the benzene ring were generally tolerated, and the corresponding products (**4**−**7**) were isolated in moderate to good yields and enantioselectivities (92.5:7.5 to 96.5:3.5 er). The reaction enantioselectivity seems sensitive to *meta* substitution. A generally lower enantioselectivity was observed when various *meta* groups were introduced (**8**−**11**), although the regioselectivity was consistently high. The scope of the yanamides was next examined. A range of *N*-sulfonyl ynamides bearing electron-withdrawing and electron-donating substituents, such as alkyl, alkoxyl, phenyl, halide, and ester, at the *para* position of the benzene ring turned out to be applicable with excellent enantioselectivity (**12**−**19**, 65−80% yield, 92.5:7.5−99:1 er). The absolute configuration of product (*S*)-**17** was confirmed by X-ray crystallographic analysis (CCDC 2124766). Furthermore, *N*-sulfonyl ynamide with a 3,5-dimethoxy on the arene ring was also compatible (**22**). Replacing the *N*-Me group in the *N*-sulfonylynamide with the *N*-Ph group afforded product **23** in 84% yield and attenuated enantioselectivity (91:9 er). Extension to several sulfonyl-substituted ynamides was also successful (**24** and **25**). In addition, racemization studies of product **17** gave a barrier $\Delta G^{\ddagger}_{rac}$ of 30.0 kcal/mol in *i*PrOH at 80 °C.

We further investigated the applicability of 1-indoyl-substituted acetylenes as sterically hindered alkynes (Scheme 3). Sulfoxonium ylides bearing phenyl, halogen, and ester groups all underwent smooth reactions under similar reaction

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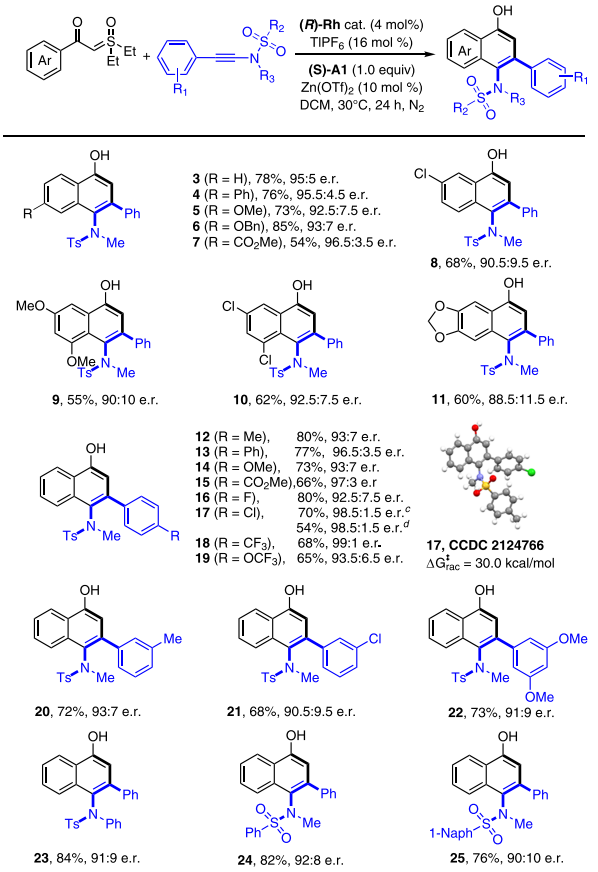
Scheme 2. Scope of [4+2] Annulation of Sulfoxonium Ylides and Ynamides[a,b]



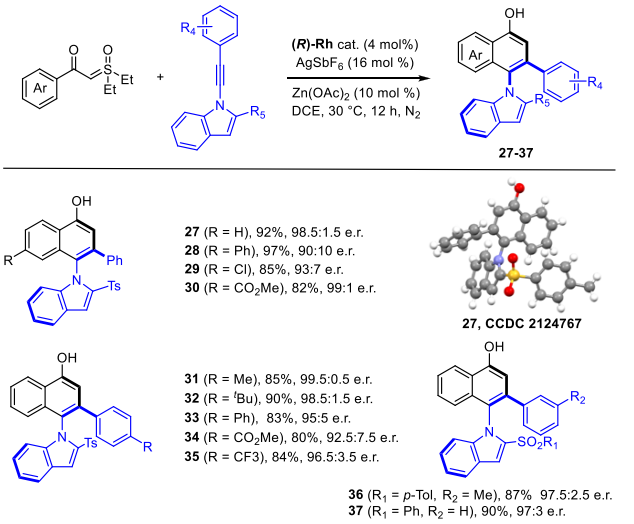
[a]Reactions conditions: sulfoxonium ylide (0.05 mmol), ynamide (1.5 equiv), (*R*)-**Rh** (4 mol %), $TlPF_6$ (16 mol %), chiral acid (*S*)-**A1** (1.0 equiv), and $Zn(OTf)_2$ (10 mol %) at 30 °C in DCM (0.5 mL) under N_2 for 24 h. [b]Isolated yields. [c]On a 0.1 mmol reaction scale. [d]On a 1 mmol reaction scale.

conditions, leading to the C−N axially chiral biaryls in excellent efficiency and high enantioselectivity (**27**−**30**). The *R* configuration of product **27** was confirmed by X-ray crystallography (CCDC 2124767). The alkyne terminus with electron-donating (Me, ^{t}Bu, and Ph) or -withdrawing (CO_2Me and CF_3) groups at position 4 of the phenyl ring coupled to give the desired products in 92.5:7.5−99.5:0.5 er (**31**−**35**). The presence of a *meta* substituent (Me) in the benzene ring was also tolerated (**36**). The 2-substituent in the indole ring of the alkyne was successfully expanded to another sulfonyl group with excellent yield and enantioselectivity (**37**).

To demonstrate the synthetic utility of the chiral products, synthetic applications have been conducted (Scheme 4). O-Protection of **27** with methyl iodide afforded product **38**, which was found to have an estimated $\Delta G^{\ddagger}_{rac}$ of >34.1 kcal/mol in PhMe at 100 °C. Under mild conditions, chiral 1-naphthylamines **17** can be converted to the corresponding triflate **39** in 95% yield, the OTf group of which is considered to be a useful handle in Pd-catalyzed cross-coupling reactions. Therefore, phenylacetylene and phenylpotassium fluoroborate were coupled with triflate **39** in excellent yield. In all cases, only slight erosion of the enantiopurity was detected.

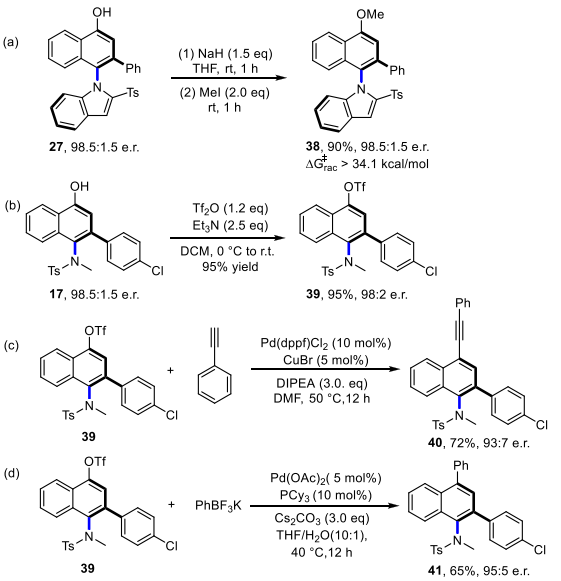
The mechanism of this [4+2] annulation reaction was briefly explored. This C−H activation process was further studied by

Scheme 3. Scope of [4+2] Annulation of Sulfoxonium Ylides and Alkynyl Indoles[a,b]



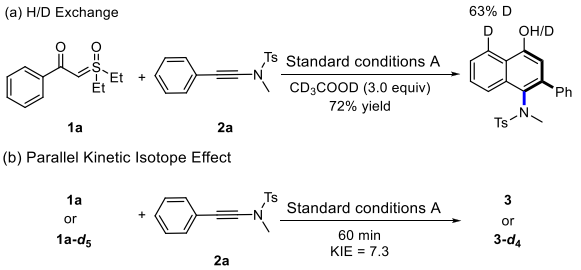
[a]Reactions conditions: sulfoxonium ylide (0.1 mmol), *N*-alkynylindole (1.2 equiv), (*R*)-**Rh** (4 mol %), $AgSbF_6$ (16 mol %), and $Zn(OAc)_2$ (10 mol %) at 30 °C in DCE (1.0 mL) under N_2 for 12 h. [b]Isolated yields.

Scheme 4. Derivatization of Selected Products



KIE measurements of the coupling of sulfoxonium ylide **1a** and ynamide **2a** (Scheme 5), and a k_H/k_D value of 7.3 at a low conversion indicated that C−H cleavage is involved in the

Scheme 5. Mechanistic Studies



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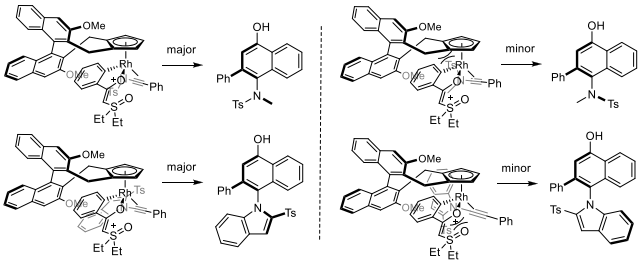
turnover-limiting process. To further explore this C−H activation event, a H/D exchange experiment has been conducted using CD_3COOD as the deuterium source under the standard conditions. NMR analysis revealed that the coupled product was appreciably deuterated (63% D) at the *ortho* position, suggesting the reversibility of the C−H activation event before or after product formation.

The enantioselective control of the chiral axial group for this coupling system is rationalized in Scheme 6. During the C−H activation process, the ylide directing group tends to be pointed outward to reduce the steric repulsion with the chiral ligand. Subsequently, the ynamide substrate approaches with the *N*-sulfonyl group pointed downward. This orientation seems to lead to minimized steric repulsion between the N-substituent and the Cp ring, which eventually leads to the *S*-configured major product. Analogously, in the case of the coupling of the sulfoxonium ylide and *N*-indoyl-substituted acetylenes, the indoyl-substituted acetylene substrate approaches with the indole pointed downward with possible $\pi-\pi$ interactions, providing the *R*-configured product. In both systems, the regioselectivity of the alkyne insertion[18] is likely ensured by the electronic and steric effect of the alkyne, as has been observed in our previous report.[19]

Scheme 6. Enantio-Determining Steps in the Formation of Axial Chirality



In summary, we have developed two classes of asymmetric [4+2] annulative coupling reactions between sulfoxonium ylides and different bulky arylalkynes via Rh(III)-catalyzed C−H activation. The reaction features mild reaction conditions, excellent regioselectivity, and high enantioselectivity. This report serves as a rare example using sulfoxonium ylides as a versatile platform toward asymmetric C−H bond activation. The chiral products may find useful applications as ligands or synthetic building blocks with pharmaceutical interest.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c00686.

Detailed experimental procedures, characterization of new compounds, and copies of NMR spectra (PDF)

Accession Codes

CCDC 2124766−2124767 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Walsh, P. J.; Kozlowski, M. C. *Fundamentals of Asymmetric Catalysis*; University Science Books: Sausalito, CA, 2009. (b) Ma, G.; Sibi, M. P. Catalytic Kinetic Resolution of Biaryl Compounds. *Chem. - Eur. J.* **2015**, *21*, 11644−11657. (c) Wencel-Delord, J.; Panossian, A.; Leroux, F. R.; Colobert, F. Recent advances and new concepts for the synthesis of axially stereoenriched biaryls. *Chem. Soc. Rev.* **2015**, *44*, 3418−3430.

(2) (a) Smyth, J. E.; Butler, N. M.; Keller, P. A. A twist of nature − the significance of atropisomers in biological systems. *Nat. Prod. Rep.* **2015**, *32*, 1562−1583. (b) Clayden, J.; Moran, W. J.; Edwards, P. J.; La Plante, S. R. The Challenge of Atropisomerism in Drug Discovery. *Angew. Chem., Int. Ed.* **2009**, *48*, 6398−6401.

(3) (a) Bringmann, G.; Price Mortimer, A. J.; Keller, P. A.; Gresser, M. J.; Garner, J.; Breuning, M. Atroposelective Synthesis of Axially Chiral Biaryl Compounds. *Angew. Chem., Int. Ed.* **2005**, *44*, 5384−5427. (b) Kozlowski, M. C.; Morgan, B. J.; Linton, E. C. Total synthesis of chiral biaryl natural products by asymmetric biaryl coupling. *Chem. Soc. Rev.* **2009**, *38*, 3193−3207. (c) Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. Atroposelective Total Synthesis of Axially Chiral Biaryl Natural Products. *Chem. Rev.* **2011**, *111*, 563−639. (d) Renzi, P. Organocatalytic synthesis of axially chiral atropisomers. *Org. Biomol. Chem.* **2017**, *15*, 4506−4516. (e) Wang, Y.-B.; Tan, B. Construction of Axially Chiral Compounds via Asymmetric Organocatalysis. *Acc. Chem. Res.* **2018**, *51*, 534−547. (f) Cheng, J. K.; Xiang, S.-H.; Li, S.; Ye, L.; Tan, B. Recent Advances in Catalytic Asymmetric Construction of Atropisomers. *Chem. Rev.* **2021**, *121*, 4805−4902.

(4) (a) Noyori, R.; Takaya, H. BINAP: an efficient chiral element for asymmetric catalysis. *Acc. Chem. Res.* **1990**, *23*, 345−350. (b) Chen, Y.; Yekta, S.; Yudin, A. K. Modified BINOL ligands in asymmetric catalysis. *Chem. Rev.* **2003**, *103*, 3155−3212. (c) Brunel, J. M. Update 1 of: BINOL: a versatile chiral reagent. *Chem. Rev.* **2007**, *107*, PR1−PR45.

(5) Selected reviews: (a) Tanaka, K. Transition-Metal-catalyzed Enantioselective [2 + 2 + 2] Cycloadditions for the Synthesis of

Axially Chiral Biaryls. *Chem. - Asian J.* **2009**, *4*, 508−518. (b) Link, A.; Sparr, C. Stereoselective arene formation. *Chem. Soc. Rev.* **2018**, *47*, 3804−3815. (c) Liao, G.; Zhang, T.; Lin, Z.-K.; Shi, B.-F. Transition Metal-Catalyzed Enantioselective C−H Functionalization via Chiral Transient Directing Group Strategies. *Angew. Chem., Int. Ed.* **2020**, *59*, 19773−19786. (d) Zhang, Y.-C.; Jiang, F.; Shi, F. Organocatalytic Asymmetric Synthesis of Indole-Based Chiral Heterocycles: Strategies, Reactions, and Outreach. *Acc. Chem. Res.* **2020**, *53*, 425−446. (e) Zhang, Q.; Wu, L.-S.; Shi, B.-F. Forging C−heteroatom bonds by transition metal-catalyzed enantioselective C−H functionalization. *Chem.* **2022**, *8*, 384−413.

(6) (a) Takahashi, I.; Suzuki, Y.; Kitagawa, O. Asymmetric synthesis of atropisomeric compounds with an N−C chiral axis. *Org. Prep. Proced. Int.* **2014**, *46*, 1−23. (b) Kitagawa, O. Chiral Pd-Catalyzed Enantioselective Syntheses of Various N−C Axially Chiral Compounds and Their Synthetic Applications. *Acc. Chem. Res.* **2021**, *54*, 719−730. (c) Sweet, J. S.; Knipe, P. C. Catalytic Enantioselective Synthesis of C−N Atropisomeric Heterobiaryls. *Synthesis* **2022**, DOI: 10.1055/s-0040-171989. (d) Rodríguez-Salamanca, P.; Fernández, R.; Hornillos, V.; Lassaletta, J. M. Asymmetric Synthesis of Axially Chiral C−N Atropisomers. *Chem. - Eur. J.* **2022**, DOI: 10.1002/chem.202104442.

(7) (a) Kitagawa, O.; Kohriyama, M.; Taguchi, T. Catalytic Asymmetric Synthesis of Optically Active Atropisomeric Anilides through Enantioselective *N*-allylation with Chiral Pd-tol-BINAP catalyst. *J. Org. Chem.* **2002**, *67*, 8682−8684. (b) Terauchi, J.; Curran, D. P. *N*-Allylation of anilides with chiral palladium catalysts: the first catalytic asymmetric synthesis of axially chiral anilides. *Tetrahedron: Asymmetry* **2003**, *14*, 587−592.

(8) (a) Liu, Y.; Feng, X.; Du, H. Asymmetric synthesis of axially chiral anilides by Pd-catalyzed allylic substitutions with P/olefin ligands. *Org. Biomol. Chem.* **2015**, *13*, 125−132. (b) Li, S.-L.; Yang, C.; Wu, Q.; Zheng, H.-L.; Li, X.; Cheng, J.-P. Atroposelective Catalytic Asymmetric Allylic Alkylation Reaction for Axially Chiral Anilides with Achiral Morita-Baylis-Hillman Carbonates. *J. Am. Chem. Soc.* **2018**, *140*, 12836−12843. (c) Lu, S.; Ng, S. V. H.; Lovato, K.; Ong, J.-Y.; Poh, S. B.; Ng, X. Q.; Kürti, L.; Zhao, Y. Practical access to axially chiral sulfonamides and biaryl amino phenols via organocatalytic atroposelective *N*-alkylation. *Nat. Commun.* **2019**, *10*, 3061.

(9) Shirakawa, S.; Liu, K.; Maruoka, K. Catalytic Asymmetric Synthesis of Axially Chiral *o*-iodoanilides by Phase-transfer catalyzed Alkylations. *J. Am. Chem. Soc.* **2012**, *134*, 916−919.

(10) Kitagawa, O.; Yoshikawa, M.; Tanabe, H.; Morita, T.; Takahashi, M.; Dobashi, Y.; Taguchi, T. Highly Enantioselective Synthesis of Atropisomeric Anilide Derivatives through Catalytic Asymmetric *N*-arylation: Conformational Analysis and Application to Asymmetric Enolate Chemistry. *J. Am. Chem. Soc.* **2006**, *128*, 12923−12931.

(11) Selected reviews: (a) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. Transition metal-catalyzed C−H activation reactions: diastereoselectivity and enantioselectivity. *Chem. Soc. Rev.* **2009**, *38*, 3242−3272. (b) Newton, C. G.; Wang, S.-G.; Oliveira, C. C.; Cramer, N. Catalytic Enantioselective Transformations Involving C−H Bond Cleavage by Transition-Metal Complexes. *Chem. Rev.* **2017**, *117*, 8908−8976. (c) Liao, G.; Zhou, T.; Yao, Q.-J.; Shi, B.-F. Recent advance in the synthesis of axially chiral biaryls via transition metal-catalysed asymmetric C−H functionalization. *Chem. Commun.* **2019**, *55*, 8514−8523. (d) Liu, C.-X.; Zhang, W.-W.; Yin, S.-Y.; Gu, Q.; You, S.-L. Synthesis of Atropisomers by Transition-Metal-Catalyzed Asymmetric C−H Functionalization Reactions. *J. Am. Chem. Soc.* **2021**, *143*, 14025−14040.

(12) (a) Yao, Q.-J.; Xie, P.-P.; Wu, Y.-J.; Feng, Y.-L.; Teng, M.-Y.; Hong, X.; Shi, B.-F. Enantioselective Synthesis of Atropisomeric Anilides via Pd(II)-Catalyzed Asymmetric C−H Olefination. *J. Am. Chem. Soc.* **2020**, *142*, 18266−18276. (b) Wu, Y.-J.; Xie, P.-P.; Zhou, G.; Yao, Q.-J.; Hong, X.; Shi, B.-F. Atroposelective synthesis of *N*-aryl peptoid atropisomers *via* a palladium(II)-catalyzed asymmetric C−H alkynylation strategy. *Chem. Sci.* **2021**, *12*, 9391−9397.

(13) Brandes, S.; Bella, M.; Kjaersgaard, A.; Jørgensen, K. A. Chirally Aminated 2-Naphthols-Organocatalytic Synthesis of Non-Biaryl Atropisomers by Asymmetric Friedel−Crafts Amination. *Angew. Chem., Int. Ed.* **2006**, *45*, 1147−1151.

(14) Tanaka, K.; Takeishi, K.; Noguchi, K. Enantioselective Synthesis of Axially Chiral Anilides through Rhodium-catalyzed [2 + 2 + 2] Cycloaddition of 1,6-Diynes with Trimethylsilylynamides. *J. Am. Chem. Soc.* **2006**, *128*, 4586−4587.

(15) For rhodium catalysis, see: (a) Xu, Y.; Yang, X.; Zhou, X.; Kong, L.; Li, X. Rhodium(III)-Catalyzed Synthesis of Naphthols via C−H Activation of Sulfoxonium Ylides. *Org. Lett.* **2017**, *19*, 4307−4310. (b) Xu, Y.; Zheng, G.; Yang, X.; Li, X. Rhodium(III)-catalyzed chemodivergent annulations between *N*-methoxybenzamides and sulfoxonium ylides via C−H activation. *Chem. Commun.* **2018**, *54*, 670−673. (c) Hu, P.; Zhang, Y.; Xu, Y.; Yang, S.; Liu, B.; Li, X. Construction of (Dihydro)naphtho[1,8-bc]pyrans via Rh(III)-Catalyzed Twofold C−H Activation of Benzoylacetonitriles. *Org. Lett.* **2018**, *20*, 2160−2163. (d) Hanchate, V.; Kumar, A.; Prabhu, K. R. Synthesis of Naphthols by Rh(III)-Catalyzed Domino C−H Activation, Annulation, and Lactonization Using Sulfoxonium Ylide as a Traceless Directing Group. *Org. Lett.* **2019**, *21*, 8424−8428. (e) Wang, P.; Xu, Y.; Sun, J.; Li, X. Rhodium(III)-Catalyzed Chemodivergent Couplings of Sulfoxonium Ylides with Oxa/azabicyclic Olefins. *Org. Lett.* **2019**, *21*, 8459−8463. (f) Wu, X.; Xiao, Y.; Sun, S.; Yu, J.-T.; Cheng, J. Rhodium-Catalyzed Reaction of Sulfoxonium Ylides and Anthranils toward Indoloindolones via a (4 + 1) Annulation. *Org. Lett.* **2019**, *21*, 6653−6657. (g) Zhou, T.; Qian, P.-F.; Li, J.-Y.; Zhou, Y.-B.; Li, H.-C.; Chen, H.-Y.; Shi, B.-F. Efficient Synthesis of Sulfur-Stereogenic Sulfoximines via Ru(II)-Catalyzed Enantioselective C−H Functionalization Enabled by Chiral Carboxylic Acid. *J. Am. Chem. Soc.* **2021**, *143*, 6810−6816. For cobalt catalysis, see: (h) Yu, Y.; Wu, Q.; Liu, D.; Yu, L.; Tan, Z.; Zhu, G. Synthesis of 1-naphthols via Cp*Co(III)-catalyzed C−H Activation and Cyclization of Sulfoxonium Ylides with Alkynes. *Org. Chem. Front.* **2019**, *6*, 3868−3873.

(16) Ye, B.; Cramer, N. A Tunable Class of Chiral Cp Ligands for Enantioselective Rhodium(III)-Catalyzed C−H Allylations of Benzamides. *J. Am. Chem. Soc.* **2013**, *135*, 636−639.

(17) (a) Jang, Y.-S.; Dieckmann, M.; Cramer, N. Cooperative Effects between Chiral Cp^x−Iridium(III) Catalysts and Chiral Carboxylic Acids in Enantioselective C−H Amidations of Phosphine Oxides. *Angew. Chem., Int. Ed.* **2017**, *56*, 15088−15092. (b) Lin, L.; Fukagawa, S.; Sekine, D.; Tomita, E.; Yoshino, T.; Matsunaga, S. Chiral Carboxylic Acid-Enabled Achiral Rhodium(III)-Catalyzed Enantioselective C−H Functionalization. *Angew. Chem., Int. Ed.* **2018**, *57*, 12048−12052. (c) Liu, L.; Song, H.; Liu, Y.-H.; Wu, L.-S.; Shi, B.-F. Achiral Cp^XIr(III)/Chiral Carboxylic Acid-Catalyzed Enantioselective C−H Amidation of Ferrocenes under Mild Conditions. *ACS Catal.* **2020**, *10*, 7117−7122.

(18) Han, X.-L.; Liu, X.-G.; Lin, E.; Chen, Y.; Chen, Z.; Wang, H.; Li, Q. Cp*Co(iii)-Catalyzed oxidative [5 + 2] annulation: regioselective synthesis of 2-aminobenzoxepines via C−H/O−H functionalization of 2-vinylphenols with ynamides. *Chem. Commun.* **2018**, *54*, 11562−11565.

(19) (a) Wang, F.; Qi, Z.; Zhao, Y.; Zhai, S.; Zheng, G.; Mi, R.; Huang, Z.; Zhu, X.; He, X.; Li, X. Rh(III)-Catalyzed Atroposelective Synthesis of Biaryls via C−H Activation and Intermolecular Coupling with Sterically Hindered Alkynes. *Angew. Chem., Int. Ed.* **2020**, *59*, 13288−13294. (b) Wang, F.; Jing, J.; Zhao, Y.; Zhu, X.; Zhang, X.-P.; Zhao, L.; Hu, P.; Deng, W.-Q.; Li, X. Rhodium-Catalyzed C−H Activation-Based Construction of Axially and Centrally Chiral Indenes through Two Discrete Insertions. *Angew. Chem., Int. Ed.* **2021**, *133*, 16764−16769.

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