OL Organic Letters

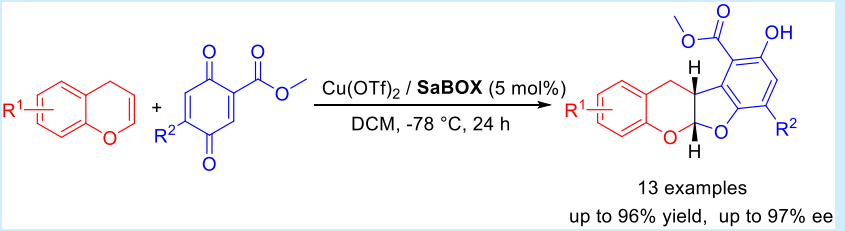
pubs.acs.org/OrgLett Letter

Rapid Construction of Enantioenriched Benzofurochromanes by SaBOX/Copper(II) Catalyzed Enantioselective [3 + 2] Annulation of γ-Chromenes with Quinones

Yang Chen,[‖] Geng-Xie Li,[‖] Ai-Qing Peng, Yong Tang, and Lijia Wang*

Cite This: *Org. Lett.* 2022, 24, 5525−5529 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: A rapid construction of enantioenriched benzofurochromanes was developed by SaBOX/copper(II) catalyzed enantioselective [3 + 2] annulation of γ-chromenes with quinones. This process takes advantage of the simple starting materials and a highly efficient chiral SaBOX/copper(II) catalyst system, leading to a variety of benzofurochromanes in up to 96% yield with up to 97% ee.

Chiral benzofurochromane skeletons, a unique tetracyclic acetal containing isoflavane structure with an oxygen-bridge to connect the pyran ring and the phenyl ring, exist widely in many biologically active natural products (Figure 1).[1]

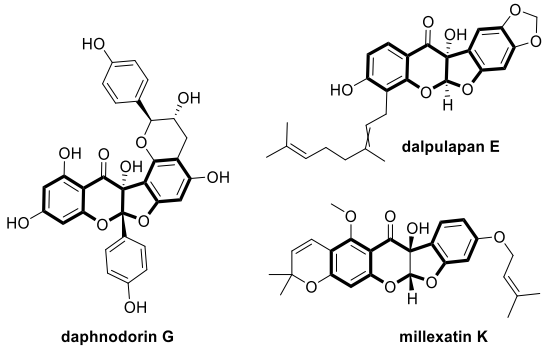


Figure 1. Bioactive natural products containing a benzofurochromane skeleton.

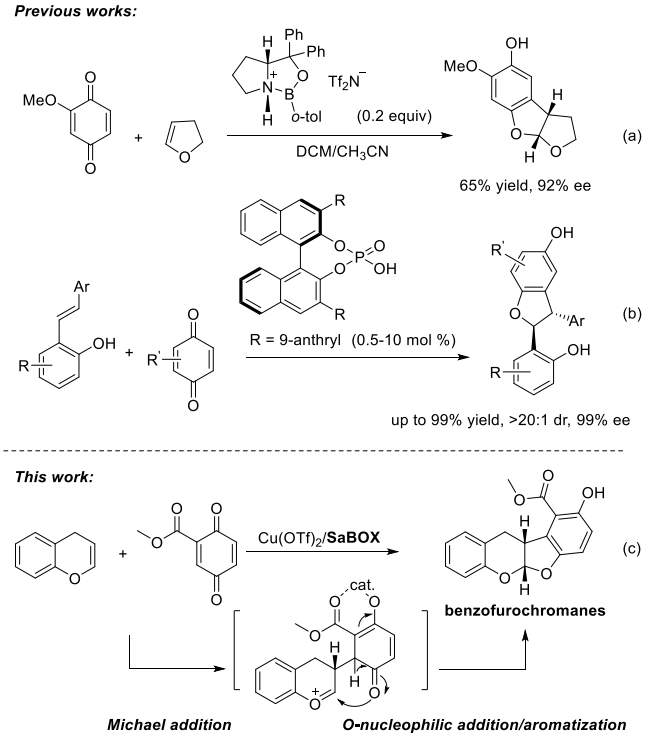
These molecules exhibit high potential in enzymology inhibition, anti-inflammatory action, and antibacterial action.[2] Developing an effective method for the gain of isoflavone derivatives has always been an attractive field for chemists.[3] However, the asymmetric synthesis of such an interesting structure has barely been achieved,[4] probably due to the lack of a concise strategy and efficient catalyst system.

Quinones and their derivatives are cheap and readily available starting materials in organic synthesis, which are favored by chemists as useful arylation reagents in many useful transformations.[5] Owing to their electrophilic reactivity as highly efficient Michael acceptors as well as the robust driving force to aromatization, quinones easily accept a variety of nucleophiles in the conjugated addition reactions and could end up with a phenyl group at appropriate positions. Meanwhile, the carbonyl groups on quinones provide chelating sites to chiral catalysts, which is conducive to the enantioselective control of the reaction. In recent years, a variety of asymmetric catalytic reactions involving quinones as substrates have been developed, including asymmetric α-arylations of carbonyl compounds,[6] asymmetric arylations of 2-naphthols,[7] asymmetric Diels−Alder reactions,[8] asymmetric [2 + 2] cycloaddition reactions,[9] and asymmetric [3 + 2] cycloaddition reactions, and so on.[10] Among those studies, enantioselective reactions of quinones with electron-rich olefins have been met with less success. Only a few examples have been reported. In 2005, Corey and co-workers developed a chiral oxazaborolidinium triflimidate catalyzed enantioselective [3 + 2] cycloaddition reaction of 2,3-dihydrofuran with 1,4-benzoquinones, providing facile access to a variety of chiral phenolic tricycles (Scheme 1a).[11] In 2018, Zhou and co-workers reported an enantioselective [3 + 2] formal cyclo-

Received: June 8, 2022
Published: July 25, 2022

https://doi.org/10.1021/acs.orglett.2c01933
Org. Lett. 2022, 24, 5525−5529

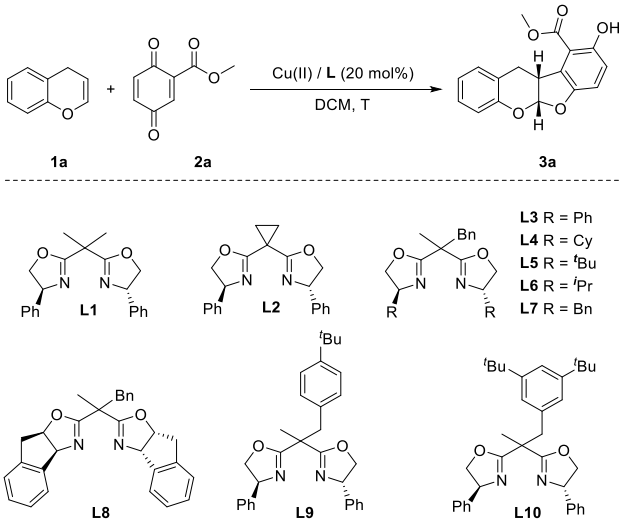
Scheme 1. Asymmetric Tandem [3 + 2] Annulation of Olefins with Quinones



addition of 1-styrylnaphthols with quinones catalyzed by a chiral phosphoric acid, leading to various *trans*-2,3-diarylbenzofurans in up to 99% yield, with up to 99% ee and >20:1 dr (Scheme 1b).[12] Inspired by our recent work on the asymmetric [3 + 2] annulation of indoles with quinones to structurally diverse benzofuroindolines by a SaBOX/copper(II) catalyst,[13] we envisaged that γ-chromenes bearing an electron-rich enol group could enantioselectively attack quinones to generate intermediates via a chiral SaBOX/copper(II) catalyzed Michael addition strategy. Subsequent intramolecular *O*-nucleophilic addition cyclization/aromatization would then generate chiral benzofurochromane (Scheme 1c). Herein, we report the first chiral SaBOX/copper(II) catalyzed [3 + 2] annulation of methyl quinone carboxylates with γ-chromenes, which has resulted in the formation of enantioenriched chiral tetracyclic isoflavane derivatives.

Initially, the reaction was carried out between equivalent amounts of **1a** and **2a** in dichloromethane (DCM) at 0 °C in the presence of a copper complex catalyst, in situ generated from $Cu(OTf)_2$ and a variety of chiral bisoxazoline (BOX) ligands (**L1**−**L10**). To our delight, with **L1**, the desired product **3a** was isolated in 65% yield with 47% ee (entry 1, Table 1). To adjust the bite angle of the copper complex, ligand **L2** was then employed, which led to an obvious influence on both the yield and enantioselectivity (entry 2). The side arm modified BOX (SaBOX) ligands,[14,15] bearing different chiral backbones, including phenyl groups, cyclohexyl groups, *tert*-butyl groups, isopropyl groups, benzyl groups, and indanyl groups were next investigated (entries 3−8). Among these chiral ligands, the ligand **L3** prepared from L-phenylglycine derivatives provided the best ee value (69% ee, entry 3). Further modification of the side arm group was studied by introducing steric hindered groups to the pendant side arm, for example, the *tert*-butyl groups. Compared with **L3**, both **L9**

Table 1. Optimization of Reaction Conditions[a]



entry	Cu(II)	L	T (°C)	t (h)	yield (%)[b]	ee (%)[c]
1	$Cu(OTf)_2$	L1	0	2	65	47
2	$Cu(OTf)_2$	L2	0	2	72	61
3	$Cu(OTf)_2$	L3	0	2	49	69
4	$Cu(OTf)_2$	L4	0	2	50	68
5	$Cu(OTf)_2$	L5	0	2	48	67
6	$Cu(OTf)_2$	L6	0	2	53	43
7	$Cu(OTf)_2$	L7	0	2	47	55
8	$Cu(OTf)_2$	L8	0	2	43	48
9	$Cu(OTf)_2$	L9	0	2	63	75
10	$Cu(OTf)_2$	L10	0	2	80	76
11	$Cu(BF_4)_2$	L10	0	2	54	50
12	$Cu(SbF_6)_2$	L10	0	2	78	61
13[d]	$Cu(OTf)_2$	L10	−60	18	84	89
14[d,e]	$Cu(OTf)_2$	L10	−60	18	81	92
15[e,f]	$Cu(OTf)_2$	L10	−78	24	90	95

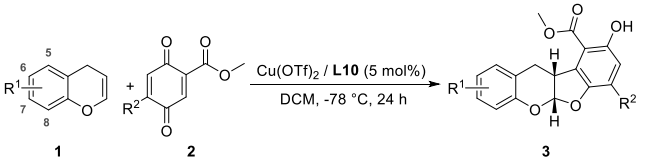
[a]Unless otherwise stated, all reactions were carried out with **1a** (0.20 mmol), **2a** (0.20 mmol), $Cu(OTf)_2$ (0.040 mmol), **L**(0.048 mmol) in DCM (1 mL) at 0 °C. [b]Isolated yield. [c]Determined by chiral HPLC. [d]0.30 mmol of **2a** was used. [e]5 mol % of catalyst was used. [f]0.24 mmol of **1a** and 3 mL of DCM were used.

and **L10** with *tert*-butyl substituted side arm groups could dramatically increase the reactivity and enantioselectivity, of which the bulkier **L10** gave the best yield and ee value (80% yield, 76% ee, entry 10). Other copper(II) salts were also investigated, for example, $Cu(BF_4)_2$ and $Cu(SbF_6)_2$. However, compared with $Cu(OTf)_2$, both the reactivity and the enantioselectivity were decreased, leading to the product in 54% yield with 50% ee and 78% yield with 61% ee, respectively (entries 11−12). Lowing the reaction temperature and altering the substrate ratio of **1a**:**2a** from 1:1 to 1:1.5 caused an obvious improvement, affording the desired product **3a** in 84% yield with 89% ee (entry 13). When the catalyst loading was lowered to 5 mol %, the enantioselectivity was further improved to 92% ee (entry 14). Finally, the optimized reaction condition was obtained by lowering the reaction temperature to −78 °C, furnishing the desired product **3a** in 90% yield with 95% ee after 24 h (entry 15).

With the optimized reaction condition in hand, we next studied the substrate scope of the reaction in Table 2. To our delight, when γ-chromene substrates bearing substituents such as fluoro-, chloro-, and bromo-groups on the 6-position were

https://doi.org/10.1021/acs.orglett.2c01933
Org. Lett. 2022, 24, 5525−5529

Table 2. Substrate Scope[a]



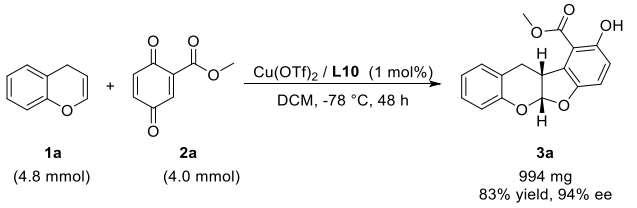
entry[a]	product	R^1	R^2	yield (%)[b]	ee (%)[c]
1	**3a**	H	H	90	95
2	**3b**	6-F	H	90	95
3	**3c**	6-Cl	H	91	97
4	**3d**	6-Br	H	96	97
5	**3e**	6-Me	H	88	95
6	**3f**	6-OMe	H	91	84
7	**3g**	7-Cl	H	82	93
8	**3h**	7-Me	H	87	95
9	**3i**	8-Me	H	83	95
10	**3j**	8-^{t}Bu	H	84	93
11	**3k**	8-Ph	H	90	94
12	**3l**	5,8-Me	H	77	85
13	**3m**	H	OMe	80	97

[a]Unless otherwise stated, all reactions were carried out with **1** (0.24 mmol), **2a** (0.20 mmol), $Cu(OTf)_2$ (0.010 mmol), **L**(0.012 mmol) in DCM (3 mL) at 0 °C. [b]Isolated yield. [c]Determined by chiral HPLC.

employed with the standard reaction condition, both the reactivity and the enantioselectivity were almost unaffected, affording the corresponding products **3b**−**3d** in 90−96% yields with 95−97% ee (entries 2−4, Table 1). Electron-enriched γ-chromenes such as 6-methyl- and 6-methoxy-substituted substrates also worked well under the current reaction condition, delivering the product **3e** in 88% yield with 95% ee, as well as the **3f** in 91% yield with 84% ee (entries 5−6). When a chloro group and methyl group was introduced to the 7-position of γ-chromenes, there was no significant influence on the results, and **3g** and **3h** were obtained in 82% and 87% yields with 93% and 95% ee, respectively, regardless of the electronic nature of the substituents (entries 7−8). The steric effect of bulky substituents at the 8-position was investigated. Compared with the methyl group, the more bulky group such as *tert*-butyl group and phenyl group at the 8-position of γ-chromenes could result in a similar level of yields but a slight decline in enantioselectivity (95% ee versus 93% ee and 94% ee, entry 9 versus entries 10 and 11). Remarkably, disubstituted γ-chromene **1l** could also tolerated in the reaction, providing the corresponding product **3l** in 77% yield with 85% ee (entry 12). It should be noted that 3,4-dihydro-2*H*-pyran also underwent this [3 + 2] annulation, giving the desired benzofuropyran in 83% yield with 57% ee (for details, see Supporting Information). When introducing a methoxy group to the quinone substrate, the reaction worked well and gave the desired product **3m** in 80% yield with 97% ee (entry 13). The absolute configuration of **3d** was determined as 5a*S*,10b*R* by single-crystal X-ray diffraction analysis.[16]

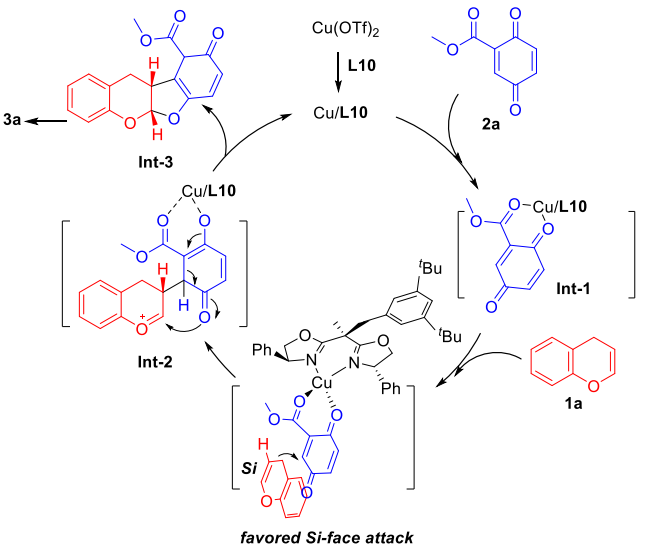
Remarkably, the current reaction is potentially useful. The asymmetric tandem [3 + 2] annulation of γ-chromene with methyl quinone carboxylate could be expanded to gram-scale preparation, providing the rapid construction of chiral benzofurochromanes in a practical way. As shown in Scheme 2, the desired product **3a** was accomplished in 83% yield with 94% ee using only 1 mol % of Cu(II)/**L10** complex as catalyst (Scheme 2).

Scheme 2. Scale-up Experiment



A proposed reaction mechanism was shown in Scheme 3. Initially, the chiral ligand **L10** coordinated with the copper salt

Scheme 3. Proposed Reaction Mechanism



to generate the chiral complex catalyst Cu/**L10**. The substrate **2a** was activated by the catalyst to form **Int-1**. On the basis of a crystal structure of the SaBOX/$CuBr_2$ complex we previously reported,[17] the **L10**/Cu^{2+}/dicarbonyl complex (**Int-1**) might adopt a highly twisted square-planar geometry,[18] which was nucleophile attacked by **1a** on the enantioselective favorable *Si*-face to generate **Int-2**. Then the subsequent intramolecular *O*-nucleophilic addition cyclization occurred to form **Int-3** and release the catalyst. **Int-3** underwent aromatization to give the final product **3a**, of which the absolute configuration is coincident with the experimental results.

In summary, we have developed an efficient method for the copper catalyzed enantioselective tandem [3 + 2] annulation of γ-chromenes with methyl quinone carboxylate, which provides a facile access to the rapid construction of chiral benzofurochromanes in up to 96% yield with up to 97% ee. The remarkable features of this method, such as the mild reaction condition, the wide substrate scope, as well as the low catalyst loading in gram-scale synthesis, allow this asymmetric reaction to be efficient and potentially useful. Efforts to expand this method in the application of the synthesis of natural products are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c01933.

https://doi.org/10.1021/acs.orglett.2c01933
Org. Lett. 2022, 24, 5525−5529

Experimental procedures, compound characterization data, copies of NMR, HRMS and HPLC spectra, and crystallographic data for **3d** (PDF)

Accession Codes

CCDC 2177488 contains 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.

AUTHOR INFORMATION

Corresponding Author

Lijia Wang − *Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, Department of Chemistry, East China Normal University, Shanghai 200062, China*; orcid.org/0000-0002-6657-3392; Email: ljwang@chem.ecnu.edu.cn

Authors

Yang Chen − *Shanghai Engineering Research Center of Molecular Therapeutics and New Drug Development, Department of Chemistry, East China Normal University, Shanghai 200062, China*

Geng-Xie Li − *School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China*

Ai-Qing Peng − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

Yong Tang − *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*; orcid.org/0000-0002-5435-9938

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.2c01933

Author Contributions

‖Y.C. and G.-X.L. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the NSFC (No. 91956103) for the financial support. We thank Mr. Jie Sun (SIOC) for X-ray crystal analysis.

REFERENCES

(1) (a) Wandji, J.; Awanchiri, S. S.; Fomum, Z. T.; Tillequin, F.; Michel-Daniwicz, S. Prenylated isoflavonoids from Erythrina senegalensis. *Phytochemistry* **1995**, *38*, 1309−1313. (b) Awouafack, M. D.; Spiteller, P.; Lamshöft, M.; Kusari, S.; Ivanova, B.; Tane, P.; Spiteller, M. Antimicrobial Isopropenyl-dihydrofuranoisoflavones from Crotalaria lachnophora. *J. Nat. Prod.* **2011**, *74*, 272−278.

(2) (a) Wang, L.; Li, X.; Zhang, S.; Lu, W.; Liao, S.; Liu, X.; Shan, L.; Shen, X.; Jiang, H.; Zhang, W.; Huang, J.; Li, H. Natural products as a gold mine for selective matrix metalloproteinases inhibitors. *Bioorg. Med. Chem.* **2012**, *20*, 4164−4171. (b) Raksat, A.; Maneerat, W.; Rujanapun, N.; Andersen, R. J.; Pyne, S. G.; Laphookhieo, S. Antibacterial and Inhibitory Activities against Nitric Oxide Production of Coumaronochromones and Prenylated Isoflavones from Millettia extensa. *J. Nat. Prod.* **2019**, *82*, 2343−2348. (c) Zhou, D.-C.; Zheng, G.; Jia, L.-Y.; He, X.; Zhang, C.-F.; Wang, C.-Z.; Yuan, C.-S. Comprehensive evaluation on anti-inflammatory and anti-angiogenic activities in vitro of fourteen flavonoids from Daphne Genkwa based on the combination of efficacy coefficient method and principal component analysis. *J. Ethnopharm.* **2021**, *268*, 113683.

(3) (a) *Isoflavones—Chemistry, Analysis, Function and Effects*; Preedy, V. R., Ed.; RSC Publishing: Cambridge, 2013. (b) Donnelly, D. M. X.; Boland, G. M. Isoflavonoids and neoflavonoids: naturally occurring O-heterocycles. *Nat. Prod. Rep.* **1995**, *12*, 321−338. (c) Al-Maharik, N. Isolation of naturally occurring novel isoflavonoids: an update. *Nat. Prod. Rep.* **2019**, *36*, 1156−1195.

(4) Allen, E. E.; Zhu, C.; Panek, J. S.; Schaus, S. E. Multicomponent Condensation Reactions via ortho-Quinone Methides. *Org. Lett.* **2017**, *19*, 1878−1881.

(5) (a) Quideau, S.; Pouysegu, L. Synthetic uses of orthoquinone monoketals and their orthoquinol variants. A review. *Org. Prep. Proced. Int.* **1999**, *31*, 617−680. (b) Abraham, I.; Joshi, R.; Pardasani, P.; Pardasani, R. T. Recent Advances in 1,4-Benzoquinone Chemistry. *J. Brazil. Chem. Soc.* **2011**, *22*, 385−421.

(6) (a) Aleman, J.; Cabrera, S.; Maerten, E.; Overgaard, J.; Jorgensen, K. A. Asymmetric organocatalytic alpha-arylation of aldehydes. *Angew. Chem., Int. Ed.* **2007**, *46*, 5520−5523. (b) Aleman, J.; Richter, B.; Jorgensen, K. A. Organocatalytic highly enantioselective alpha-arylation of beta-ketoesters. *Angew. Chem., Int. Ed.* **2007**, *46*, 5515−5519. (c) Siau, W.-Y.; Li, W.; Xue, F.; Ren, Q.; Wu, M.; Sun, S.; Guo, H.; Jiang, X.; Wang, J. Catalytic and Enantioselective α-Functionalization of Oxindoles Through Oxidative Reactions with Naphthoquinones. *Chem. Eur. J.* **2012**, *18*, 9491−9495. (d) Yu, J. S.; Zhou, F.; Liu, Y. L.; Zhou, J. Organocatalytic asymmetric Michael addition of unprotected 3-substituted oxindoles to 1,4-naphthoquinone. *Beilstein J. Org. Chem.* **2012**, *8*, 1360−1365.

(7) (a) Chen, Y.-H.; Cheng, D.-J.; Zhang, J.; Wang, Y.; Liu, X.-Y.; Tan, B. Atroposelective Synthesis of Axially Chiral Biaryldiols via Organocatalytic Arylation of 2-Naphthols. *J. Am. Chem. Soc.* **2015**, *137*, 15062−15065. (b) Moliterno, M.; Cari, R.; Puglisi, A.; Antenucci, A.; Sperandio, C.; Moretti, E.; Di Sabato, A.; Salvio, R.; Bella, M. Quinine-Catalyzed Asymmetric Synthesis of 2,2′-Binaphthol-Type Biaryls under Mild Reaction Conditions. *Angew. Chem., Int. Ed.* **2016**, *55*, 6525−6529. (c) Xu, C.; Zheng, H.; Hu, B.; Liu, X.; Lin, L.; Feng, X. Chiral cobalt(ii) complex catalyzed Friedel−Crafts aromatization for the synthesis of axially chiral biaryldiols. *Chem. Commun.* **2017**, *53*, 9741−9744. (d) Lu, D.-L.; Chen, Y.-H.; Xiang, S.-H.; Yu, P.; Tan, B.; Li, S. Atroposelective Construction of Arylindoles by Chiral Phosphoric Acid-Catalyzed Cross-Coupling of Indoles and Quinones. *Org. Lett.* **2019**, *21*, 6000−6004. (e) Coombs, G.; Sak, M. H.; Miller, S. J. Peptide-Catalyzed Fragment Couplings that Form Axially Chiral Non-C2-Symmetric Biaryls. *Angew. Chem., Int. Ed.* **2020**, *59*, 2875−2880. (f) Sun, G.; Deng, Z.; Luo, Z.; Wang, Z.; Zhang, J. Organocatalytic Asymmetric Arylation of p-Quinone Phosphonates: A Green Access to Biaryl Monophosphorus Ligands. *Org. Lett.* **2021**, *23*, 7630−7634.

(8) (a) Evans, D. A.; Wu, J. Enantioselective Rare-Earth Catalyzed Quinone Diels−Alder Reactions. *J. Am. Chem. Soc.* **2003**, *125*, 10162−10163. (b) Han, Z.-Y.; Chen, D.-F.; Wang, Y.-Y.; Guo, R.; Wang, P.-S.; Wang, C.; Gong, L.-Z. Hybrid Metal/Organo Relay Catalysis Enables Enynes To Be Latent Dienes for Asymmetric Diels−Alder Reaction. *J. Am. Chem. Soc.* **2012**, *134*, 6532−6535. (c) Albrecht, Ł.; Gómez, C. V.; Jacobsen, C. B.; Jørgensen, K. A. 1,4-Naphthoquinones in H-Bond-Directed Trienamine-Mediated Strategies. *Org. Lett.* **2013**, *15*, 3010−3013. (d) Hashimoto, T.; Nakatsu, H.; Maruoka, K. Catalytic Asymmetric Diels−Alder Reaction of Quinone Imine Ketals: A Site-Divergent Approach. *Angew. Chem., Int. Ed.* **2015**, *54*, 4617−4621. (e) Gu, J.; Xiao, B.-X.; Chen, Y.-R.; Du, W.; Chen, Y.-C. Asymmetric Diels−Alder and Cascade Reaction of Quinone Imine Ketals and 2,4-Dienals: Construction of Chiral Benzo[de]quinolone Derivatives. *Adv. Synth. Catal.* **2016**, *358*, 296−302.

(9) Zheng, H.; Xu, C.; Wang, Y.; Kang, T.; Liu, X.; Lin, L.; Feng, X. Catalytic asymmetric [2 + 2] cycloaddition between quinones and fulvenes and a subsequent stereoselective isomerization to 2,3-dihydrobenzofurans. *Chem. Commun.* **2017**, *53*, 6585−6588.

(10) (a) Liao, L.; Shu, C.; Zhang, M.; Liao, Y.; Hu, X.; Zhang, Y.; Wu, Z.; Yuan, W.; Zhang, X. Highly Enantioselective [3 + 2] Coupling of Indoles with Quinone Monoimines Promoted by a Chiral Phosphoric Acid. *Angew. Chem., Int. Ed.* **2014**, *53*, 10471−10475. (b) Zhao, W.; Wang, Z.; Chu, B.; Sun, J. Enantioselective Formation of All-Carbon Quaternary Stereocenters from Indoles and Tertiary Alcohols Bearing A Directing Group. *Angew. Chem., Int. Ed.* **2015**, *54*, 1910−1913. (c) Sun, X.-X.; Zhang, H.-H.; Li, G.-H.; Meng, L.; Shi, F. Diastereo- and enantioselective construction of an indole-based 2,3-dihydrobenzofuran scaffold via catalytic asymmetric [3 + 2] cyclizations of quinone monoimides with 3-vinylindoles. *Chem. Commun.* **2016**, *52*, 2968−2971. (d) Zhang, X.; Chen, Y.-H.; Tan, B. Organocatalytic enantioselective transformations involving quinone derivatives as reaction partners. *Tetrahedron Lett.* **2018**, *59*, 473−486. (e) Zhang, L.; Hu, J.; Xu, R.; Pan, S.; Zeng, X.; Zhong, G. Catalytic Asymmetric Dearomative [3 + 2] Cyclisation of 1,4-Quinone with 2,3-Disubstituted Indoles. *Adv. Synth. Catal.* **2019**, *361*, 5449−5457. (f) Liu, H.; Yan, Y.; Zhang, J.; Liu, M.; Cheng, S.; Wang, Z.; Zhang, X. Enantioselective dearomative [3 + 2] annulation of 5-amino-isoxazoles with quinone monoimines. *Chem. Commun.* **2020**, *56*, 13591−13594. (g) Luo, W.; Sun, Z.; Fernando, E. H. N.; Nesterov, V. N.; Cundari, T. R.; Wang, H. Formal oxo- and aza-[3 + 2] reactions of α-enaminones and quinones: a double divergent process and the roles of chiral phosphoric acid and molecular sieves. *Chem. Sci.* **2020**, *11*, 9386−9394. (h) Xi, C.-C.; Zhao, X.-J.; Tian, J.- M.; Chen, Z.-M.; Zhang, K.; Zhang, F.-M.; Tu, Y.-Q.; Dong, J.-W. Atroposelective Synthesis of Axially Chiral 3-Arylindoles by Copper-Catalyzed Asymmetric Cross-Coupling of Indoles with Quinones and Naphthoquinones. *Org. Lett.* **2020**, *22*, 4995−5000. (i) Jing, Z.-R.; Liang, D.-D.; Tian, J.-M.; Zhang, F.-M.; Tu, Y.-Q. Enantioselective Construction of 2-Aryl-2,3-dihydrobenzofuran Scaffolds Using Cu/SPDO-Catalyzed [3 + 2] Cycloaddition. *Org. Lett.* **2021**, *23*, 1258−1262.

(11) Zhou, G.; Corey, E. J. Short, Enantioselective Total Synthesis of Aflatoxin B2 Using an Asymmetric [3 + 2]-Cycloaddition Step. *J. Am. Chem. Soc.* **2005**, *127*, 11958−11959.

(12) Feng, W.; Yang, H.; Wang, Z.; Gou, B.-B.; Chen, J.; Zhou, L. Enantioselective [3 + 2] Formal Cycloaddition of 1-Styrylnaphthols with Quinones Catalyzed by a Chiral Phosphoric Acid. *Org. Lett.* **2018**, *20*, 2929−2933.

(13) Liu, Q.-J.; Zhu, J.; Song, X.-Y.; Wang, L.; Wang, S. R.; Tang, Y. Highly Enantioselective [3 + 2] Annulation of Indoles with Quinones to Access Structurally Diverse Benzofuroindolines. *Angew. Chem., Int. Ed.* **2018**, *57*, 3810−3814.

(14) (a) Liao, S.; Sun, X.-L.; Tang, Y. Side Arm Strategy for Catalyst Design: Modifying Bisoxazolines for Remote Control of Enantioselection and Related. *Acc. Chem. Res.* **2014**, *47*, 2260−2272. (b) Wang, L.; Zhou, J.; Tang, Y. Sidearm Modified Bisoxazoline Ligands and Their Applications. *Chin. J. Chem.* **2018**, *36*, 1123−1129.

(15) (a) Hu, J.-L.; Zhou, L.; Wang, L.; Xie, Z.; Tang, Y. Copper Catalyzed Asymmetric [4 + 2] Annulations of D-A Cyclobutanes with Aldehydes. *Chin. J. Chem.* **2018**, *36*, 47−50. (b) Kuang, X.-K.; Zhu, J.; Zhou, L.; Wang, L.; Wang, S. R.; Tang, Y. Synergetic Tandem Enantiomeric Enrichment in Catalytic Asymmetric Multi-Component Reactions (AMCRs): Highly Enantioselective Construction of Tetracyclic Indolines with Four Continuous Stereocenters. *ACS Catal.* **2018**, *8*, 4991−4995. (c) Li, J.; Zheng, L.; Chen, H.; Wang, L.; Sun, X.-L.; Zhu, J.; Tang, Y. Highly enantioselective cyclopropanation of trisubstituted olefins. *Sci. Chin. Chem.* **2018**, *61*, 526−530. (d) Ren, H.; Song, X.-Y.; Wang, S. R.; Wang, L.; Tang, Y. Highly Enantioselective Nickel-Catalyzed Oxa-[3 + 3]-annulation of Phenols with Benzylidene Pyruvates for Chiral Chromans. *Org. Lett.* **2018**, *20*, 3858−3861. (e) Song, X.-Y.; Zhao, L.-P.; Wang, L.; Tang, Y. Highly Stereoselective Direct Construction of Diaryl-Substituted Cyclobutanes. *Chin. J. Chem.* **2020**, *38*, 259−262. (f) Zheng, Z.-B.; Cheng, W.-F.; Wang, L.; Zhu, J.; Sun, X.-L.; Tang, Y. Asymmetric Catalytic [3 + 2] Annulation of Donor-Acceptor Cyclopropane with Cyclic Ketones: Facile Access to Enantioenriched 1-Oxaspiro[4.5]-decanes. *Chin. J. Chem.* **2020**, *38*, 1629−1634. (g) Zhou, L.; Yan, W.-G.; Sun, X.-L.; Wang, L.; Tang, Y. A Versatile Enantioselective Catalytic Cyclopropanation-Rearrangement Approach to the Divergent Construction of Chiral Spiroaminals and Fused Bicyclic Acetals. *Angew. Chem., Int. Ed.* **2020**, *59*, 18964−18969.

(16) CCDC 2177488 (**3d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

(17) Xiong, H.; Xu, H.; Liao, S.; Xie, Z.; Tang, Y. Copper-Catalyzed Highly Enantioselective Cyclopentannulation of Indoles with Donor−Acceptor Cyclopropanes. *J. Am. Chem. Soc.* **2013**, *135*, 7851−7854.

(18) Desimoni, G.; Faita, G.; Jørgensen, K. A. C2-Symmetric Chiral Bis(Oxazoline) Ligands in Asymmetric Catalysis. *Chem. Rev.* **2006**, *106*, 3561−3651.

https://doi.org/10.1021/acs.orglett.2c01933
Org. Lett. 2022, 24, 5525−5529