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Communication

Stereospecific Phosphination and Thioetherification of Organoboronic Esters

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ABSTRACT: Alkyllithium-activated organoboronic esters are found to undergo stereospecific phosphination with copper chloride and chlorophosphines. They also react with thiolsulfonate electrophiles under copper catalysis. These reactions enable stereospecific phosphination and thiolation of organoboronic esters, which are further applied in preparation of chiral ligands and biologically active molecules.

Enantiomerically enriched organophosphorus and organosulfur compounds are frequently employed as pharmaceutical agents, as catalysts, and as ligands for transition metals (Figure 1a).[1] Constructing these motifs is often accomplished by stereoinvertive S_N2 reactions between pnictogen and chalcogen-derived nucleophiles and chiral electrophiles, a task that can be challenging, particularly when using sterically encumbered reactants. Alternative disconnections, such as catalytic enantioselective alkene hydrophosphination/hydrosulfination and related conjugate addition reactions, can be highly effective, but these processes often demand activated substrates, thereby leading to the formation of specialized organophosphorus and organosulfur products.[2] Relative to these important strategies, we considered that an umpolung bond construction employing configurationally stable chiral carbon nucleophiles and electrophilic phosphorus and sulfur reagents could present a useful alternative strategy for stereospecific C−P and C−S bond formation. While a number of chiral organometallic reagents might be envisaged to enable such a bond construction, enantiomerically enriched alkylboronic esters are among the most appealing as they can be easily prepared through a number of straightforward synthesis methods.[3]

While organoboronic esters are readily converted to an array of different functionalized materials through stereospecific 1,2-metalate shift-based mechanisms or through outer-sphere S_E2 addition of boron ate complexes to electrophiles, phosphination and thiolation of alkyl organoboron reagents have only been observed with Lewis acidic trialkylborane reactants (Figure 1b).[5,6] In related studies, Knochel reported transmetalation between trialkylboranes and diisopropylzinc with the resulting organozinc reagent then undergoing coupling with phosphorus and sulfur electrophiles.[7] In this report, we describe a method for the direct stereospecific copper-catalyzed and mediated coupling of alkylboronic esters (**1**) with phosphorus and sulfur electrophiles (Figure 1c).

Recently, we showed that alkyllithium-activated alkylboronic esters can stereospecifically transmetalate to copper or zinc salts, which ultimately enables construction of different types of C−C and C−N bonds while preserving the stereochemical integrity of the reacting carbon center (eqs 1 and 2, Figure 2a).[8] Along these lines, we were especially intrigued by a class of complexes characterized by Beletskaya et al. that comprise copper iodide bound to chlorophosphines.[9] The complex $ICu(ClPPh_2)_3$ was proposed to facilitate soft deprotonation of alkynes prior to an electrophilic trap, which generates alkynylphosphine products. We hypothesized that if similar copper complexes (**3**, Figure 2b) underwent transmetalation with a boron ate complex (**4**), subsequent 1,2-shift from copper to phosphorus might result in stereospecific C−P bond formation.[10] The likelihood for this rearrangement was assessed computationally (Figure 2c) and it was found that migration of an alkyl group from copper to phosphorus in organocopper complex **7** occurs through transition structure **8** with a 21.0 kcal/mol barrier and delivers **9** as the reaction product. Of note, the chloride ion that is initially associated with phosphorus binds to the copper center upon extrusion. Thus, the 1,2-metalate shift involving complex **7** is accomplished as part of a dyotropic rearrangement, which is known for organocopper complexes.[11] Also of note, if the phosphine product is able to dissociate from copper and a new chlorophosphine binds in its place, then a mechanism for catalysis emerges.[12]

As an initial experiment to probe for boronic ester phosphination, a solution of $(Ph_2ClP)_3CuCl$ (**10**) was prepared by mixing copper chloride and three equivalents of chlorodiphenylphosphine. ^{31}P NMR analysis (Figure 3a) shows clean formation of a single phosphorus-containing species (δ 68.4 ppm). Alkyllithium-activated organoboronic ester **11** was then added, and the mixture was allowed to react at 60 °C for 12 h. ^{31}P and ^{11}B NMR spectroscopic analysis showed that both $(Ph_2ClP)_3CuCl$ and the ate complex were

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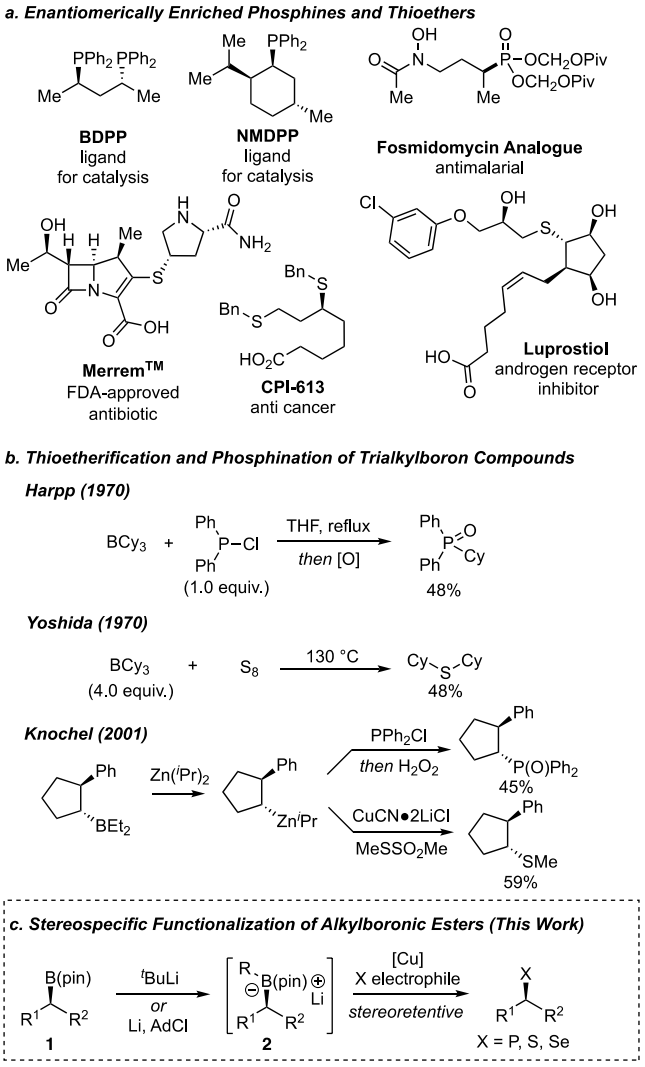

Figure 1. Relevant chiral phosphines and thioethers and approaches to their synthesis from organoboron compounds.

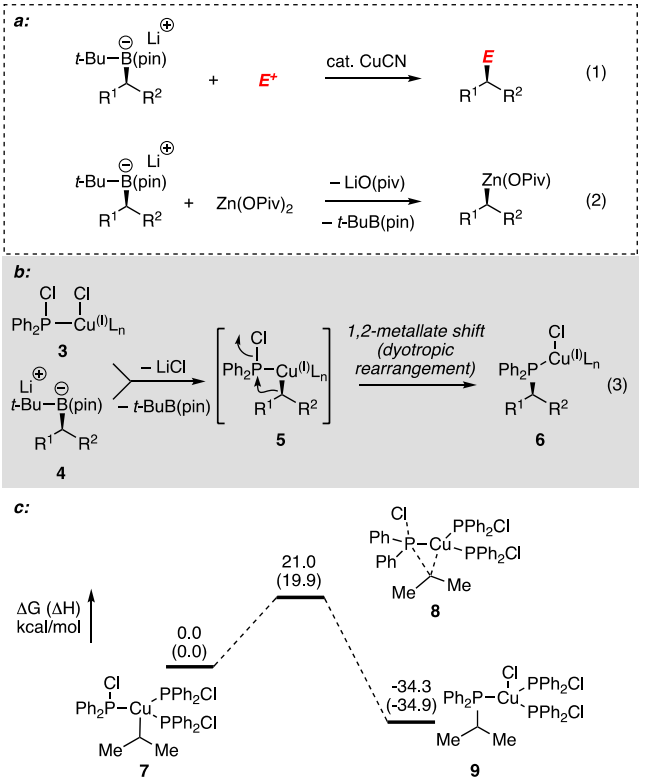

Figure 2. (a) Precedent for stereospecific transmetalation from alkyllithium-activated boronates to other metals. (b) Proposed stereospecific C−P bond formation from organocopper intermediates and (c) calculations that support such a process. Calculations by DFT: M06(D3)/def2tzvpp//b3lyp(D3BJ)/def2svp; see the Supporting Information for details.

completely consumed (Figure 3b). The major product of the reaction exhibits two resonances (^{31}P δ 71.5, 3.5 ppm), which could be assigned to phosphination product **12** by comparison with independently prepared materials (Figure 3c,d). That the independently prepared copper complex of the product exhibits more complex features than that arising from the boronate phosphination reaction can be attributed to the known tendency for CuCl−phosphine complexes to aggregate as chloro-bridged dimers with varying coordination numbers[13] and likely with rapidly exchanging phosphorus ligands.

With NMR analysis suggesting that a successful phosphination occurred, reactions with enantiomerically enriched substrate were examined. As shown in Figure 3e, when boronic ester **13** was activated with *t*-butyllithium and then treated with CuCl and Ph_2PCl for 12 h at 60 °C, the phosphination product **14**, isolated as the borane-protected adduct, was obtained in good yield and excellent stereospecificity.

To learn about the application scope of the phosphination reaction, a series of substrates were examined in the reaction. A few general notes are warranted: (a) to isolate the free phosphine, an aqueous work up with ethylene diamine could be employed to remove the phosphine-bound copper salts;[14] (b) reactions with copper chloride gave higher stereospecificity compared with copper cyanide; (c) for substrates where partial racemization was observed, addition of styrene, a compound proposed to intercept transient carbon-centered radicals, helped retain enantiospecificity.[4a,8c] In addition, it was found that the reaction could be accomplished using a catalytic amount of copper salt when sterically hindered phosphine electrophiles were used (Figure 4, **16** and **17**); however, reaction with unhindered diarylchlorophosphine electrophiles occurred with incomplete conversion when using substoichiometric amounts of copper salt likely because of the strong coordination between copper and the phosphine product. With respect to practical utility, it was found that use of pyrophoric *tert*-butyllithium solutions could be avoided by instead employing adamantyl chloride with *in situ* lithium biphenylide reduction (compound **14**).[8a] Moreover, phosphination of aryl boronic esters can be accomplished with *n*-butyllithium where the phenyl group undergoes preferential transmetalation to copper (compound **24**). Of note, highly encumbered dialkyl or diaryl chlorophosphines can be used in this process (products **15** and **18**) as can diaminochlorophosphines (product **20**). One current limitation is that diaryl chlorophosphines containing electron-withdrawing groups lead to lower reactivity, with pinacol phosphination products observed as the major reaction product (see the Supporting Information). Sterically hindered secondary alkyl boronic esters, as well as some tertiary alkylboronic esters, can be used (products **25** and **27**). Of note, the X-ray structure of **20** was obtained, which

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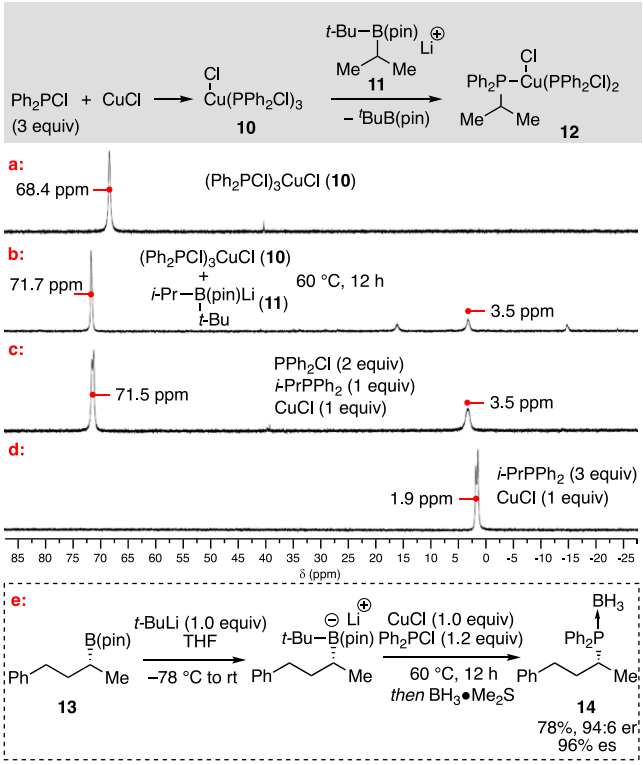

Figure 3. Preliminary analysis of reaction between alkyllithium-activated boronic esters and CuCl(phosphine) complexes by ^{31}P NMR, along with analysis of reaction stereochemistry.

confirmed that the phosphination process occurs with stereoretention.

Alkyllithium-activated boronate complexes were also found to couple with thiolsulfonates in the presence of a catalytic amount of copper cyanide (Figure 5; for mechanistic details, see the Supporting Information). While a small amount of racemization occurs in the absence of styrene, inclusion of this additive allows consistently high levels of stereospecificity for all substrates. It was found that both aryl and alkyl-containing sulfur electrophiles can be used in the coupling process. Alkylboronic esters containing silyl ethers, as well as an alkenyl halide group (**28**–**31**), can be tolerated in this process. Cyclic alkylboronic esters (**34**, **39**, and **40**), as well as some tertiary alkylboronic esters (**35**), can also be used. For arylboronic esters, ^{n}BuLi can once again be used as the activator (**38**). Comparing optical rotation of **32** with literature reported values suggest this process is stereoretentive. Notably, difluoromethylthio- and trifluoromethylthio-ethers (**41** and **42**), important functional groups in biologically active molecules, could be incorporated with good yield and stereospecificity.[15] In these cases, although the corresponding thiolsulfonates reacted with diminished enantiospecificity, reaction with *N*-thiophthalimides[16] gave product in good yield and good stereospecificity. Lastly, considering the biological importance of selenoethers and their applications in catalysis,[17] access to these compounds from boronic esters was examined. Good yield (64%) but racemic coupling was observed with phenylselenium chloride, while use of **43** as electrophile gave product with partial racemization (70%, 65:35 er). Interestingly, selenation occurred without copper and occurs with stereoinversion as the major pathway (59%, 45:55 er). Suspecting that the noncatalyzed reaction results in

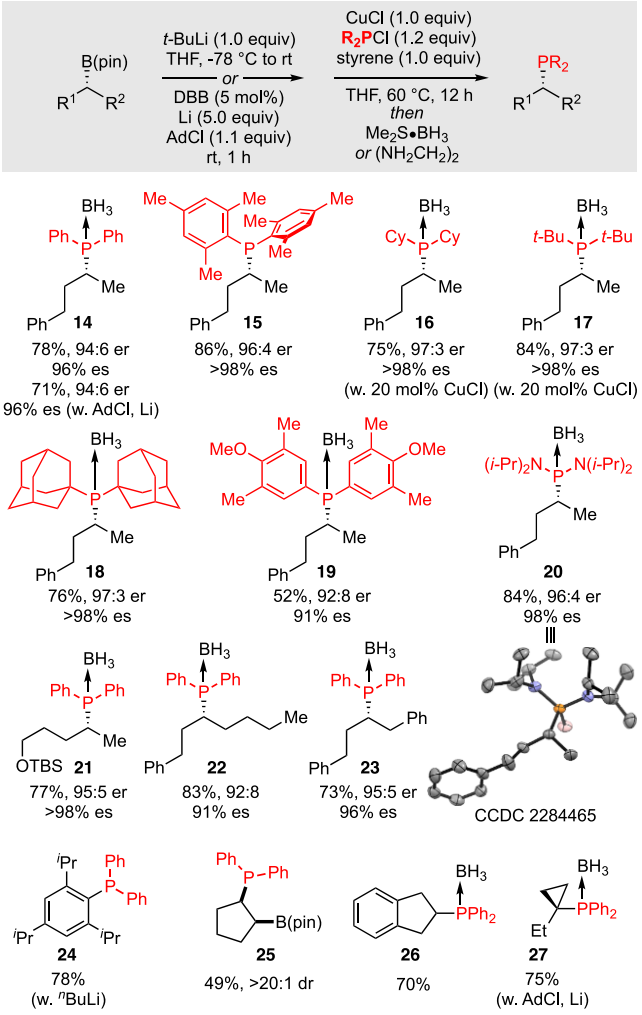

Figure 4. Scope of stereospecific phosphination of alkylboronic esters. Reactions were carried out with 0.20 mmol of alkylboronic esters. Yields are of isolated materials. Enantiomeric ratio was measured by chiral SFC analysis and had an error of ±1%.

racemization during copper catalysis,[4b] an excess amount of copper cyanide was used to outcompete other reaction pathways. This modification delivered product **44** in good yield and good stereospecificity (75%, 92:8 er).

To further demonstrate the synthetic utility of the boronate phosphination, we examined the synthesis of chiral phosphine ligands (Figure 6). BDPP is a widely used bidendate ligand in enantioselective catalysis.[1a] Traditionally, this ligand is prepared by a double substitution reaction with borane-protected dicyclohexylphosphine and enantiomerically enriched sulfonated diols.[18] In this case, catalytic enantioselective double diboration of diene **45**[19] followed by a protodeborylation reaction gives **47**. Double phosphination of **47** gave borane protected **48** in 47% yield and >20:1 dr. Additionally, a 1,3-diphosphine compound with two different phosphines was synthesized using this strategy. Starting from allylbenzene, catalytic enantioselective diboration[20] followed by selective homologation provides enantiomerically enriched 1,3-diboron reagent **50** in good yield. Two consecutive phosphination reactions using different phosphine electrophiles delivers product **52** in good yield and stereospecificity. It should be noted that although selective monophosphination of the 1,2

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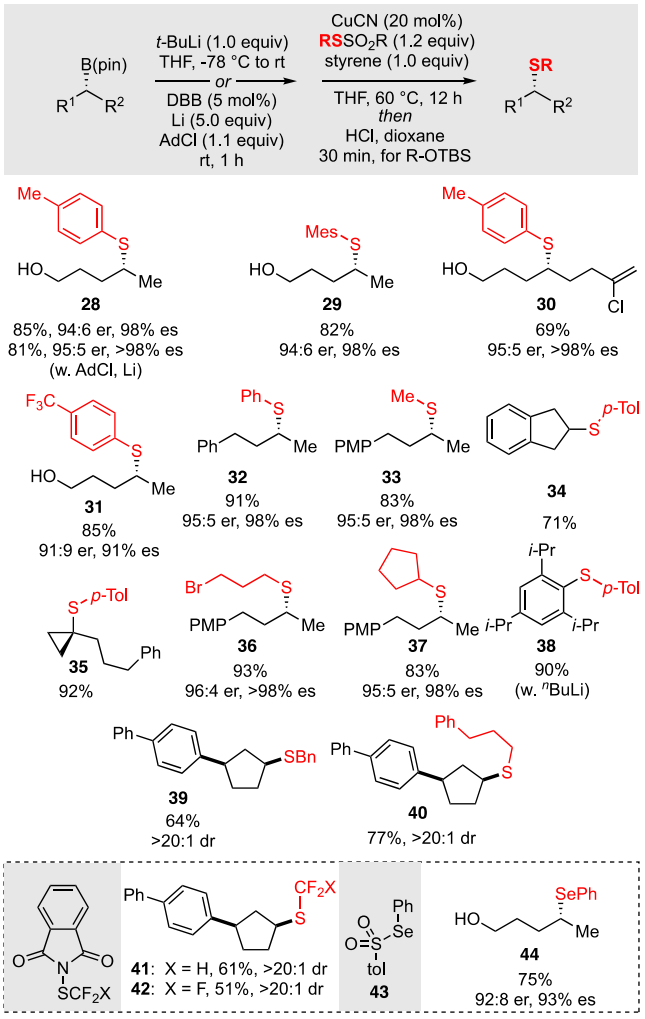

Figure 5. Scope of stereospecific thioetherification of alkylboronic esters. Reactions were carried out with 0.20 mmol of alkylboronic esters. Yields are of isolated materials. Enantiomeric ratio was measured by chiral SFC analysis and had an error of ±1%. Selenylation required 200 mol % CuCN. Difluoromethylthiolation required 100 mol % CuCN.

diboron **49** could also be achieved, attempted phosphination of the internal boron failed to deliver the desired product.

Approaches to the synthesis of biologically active motifs (Figure 7) were also examined. Thus, catalytic enantioselective diboration[20] of aminoalkene **53** followed by copper-catalyzed protodeborylation[21] provided aminoboron intermediate **55** in good yield and good enantiomeric excess. Subsequent stereospecific thioetherification gave **56**, which may be useful for the synthesis of angiogenesis inhibitors (**60**).[22] Alternatively, stereospecific phosphination of aminoboronate **55** using bis(diisopropylamino)chlorophosphine followed by methanolysis and iodine-mediated oxidation yielded amino phosphate ester **59**, which may be of use for preparation of fosmidomycin analogues (**61**).[1b]

In conclusion, we developed efficient methods for stereospecific phosphination and thiolation of alkylboronic esters. This method can be potentially useful for developing new ligands for enantioselective catalysis, as well as synthesizing biologically active compounds.

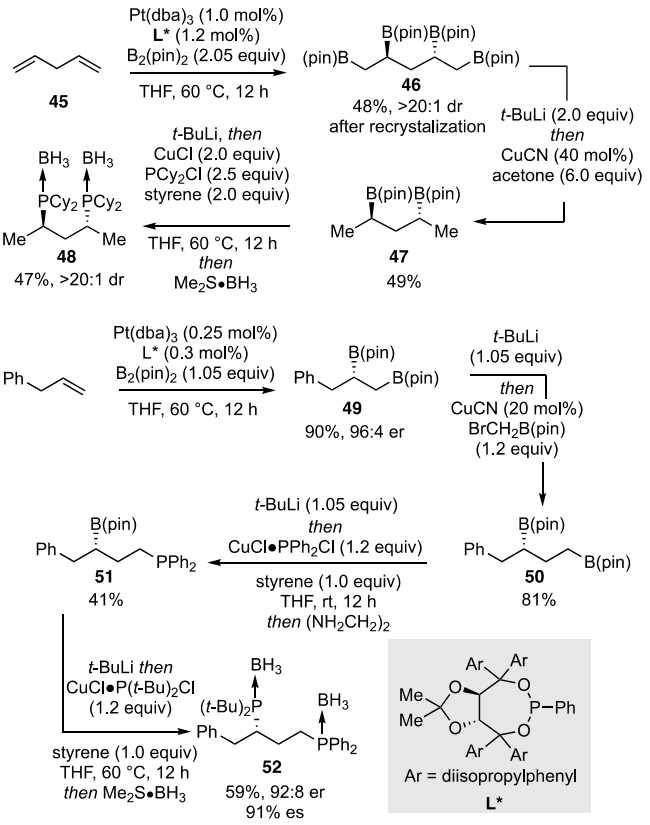

Figure 6. Synthesis of new phosphine ligands with stereospecific phosphination of alkylboronic esters.

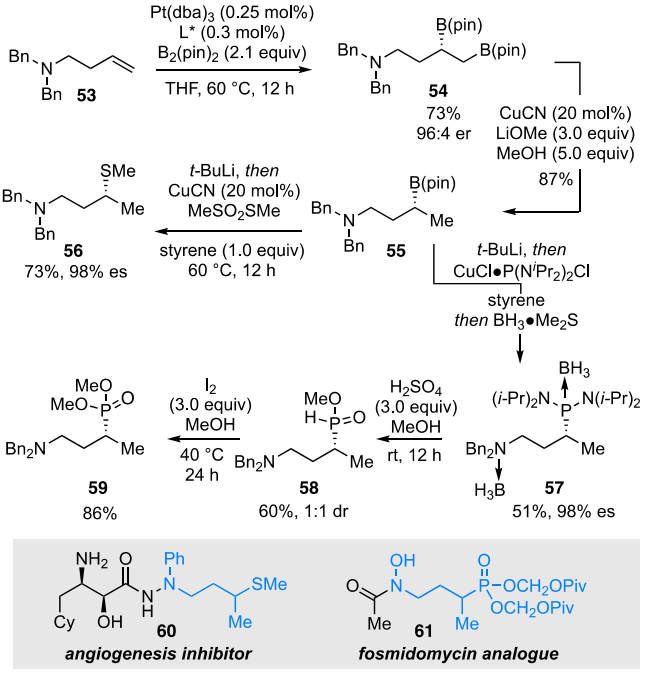

Figure 7. Synthesis of biologically relevant targets with stereospecific phosphination and thiolation of alkylboronic esters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c06526.

Procedures, characterization, and spectral data (PDF)

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Accession Codes

CCDC 2284465 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.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Bakos, J.; Tóth, I.; Heil, B.; Markó, L. A facile method for the preparation of 2,4-bis(diphenylphosphino)pentane (BDPP) enantiomers and their application in asymmetric hydrogenation. *J. Organomet. Chem.* **1985**, *279*, 23−29. (b) Kurz, T.; Schlüter, K.; Kaula, U.; Bergmann, B.; Walter, R. D.; Geffken, D. Synthesis and antimalarial activity of chain substituted pivaloyloxymethyl ester analogues of Fosmidomycin and FR900098. *Biorg. Med. Chem.* **2006**, *14*, 5121−5135. (c) Morrison, J. D.; Masler, W. F. Synthesis of methyl- and neomenthyldiphenylphosphine. Epimeric, chiral, tertiary phosphine ligands for asymmetric synthesis. *J. Org. Chem.* **1974**, *39*, 270−272.

(2) (a) Chen, H.; Jiang, W.; Zeng, Q. Recent Advances in Synthesis of Chiral Thioethers. *Chem. Rec.* **2020**, *20*, 1269−1296. (b) Kolodiazhna, A. O.; Kolodiazhnyi, O. I. Catalytic Asymmetric Synthesis of C-Chiral Phosphonates. *Symmetry* **2022**, *14*, 1758. (c) Lühr, S.; Holz, J.; Börner, A. The Synthesis of Chiral Phosphorus Ligands for use in Homogeneous Metal Catalysis. *ChemCatChem.* **2011**, *3*, 1708−1730. (d) Xie, D.; Chen, Z.; Wang, C.-J.; Dong, X.-Q. Recent Advances in the Asymmetric Catalytic Synthesis of Phosphonates with an α-Chiral Center. *Synthesis* **2023**, *55*, 3057−3072. (e) Yu, J.-S.; Huang, H.-M.; Ding, P.-G.; Hu, X.-S.; Zhou, F.; Zhou, J. Catalytic Enantioselective Construction of Sulfur-Containing Tetrasubstituted Carbon Stereocenters. *ACS Catal.* **2016**, *6*, 5319−5344.

(3) (a) Collins, B. S. L.; Wilson, C. M.; Myers, E. L.; Aggarwal, V. K. Asymmetric Synthesis of Secondary and Tertiary Boronic Esters. *Angew. Chem., Int. Ed.* **2017**, *56*, 11700−11733. (b) Hu, J.; Ferger, M.; Shi, Z.; Marder, T. B. Recent advances in asymmetric borylation by transition metal catalysis. *Chem. Soc. Rev.* **2021**, *50*, 13129−13188.

(4) (a) Larouche-Gauthier, R.; Elford, T. G.; Aggarwal, V. K. Ate Complexes of Secondary Boronic Esters as Chiral Organometallic-Type Nucleophiles for Asymmetric Synthesis. *J. Am. Chem. Soc.* **2011**, *133*, 16794−16797. (b) Sandford, C.; Aggarwal, V. K. Stereospecific functionalizations and transformations of secondary and tertiary boronic esters. *Chem. Commun.* **2017**, *53*, 5481−5494. (c) Sandford, C.; Rasappan, R.; Aggarwal, V. K. Synthesis of Enantioenriched Alkylfluorides by the Fluorination of Boronate Complexes. *J. Am. Chem. Soc.* **2015**, *137*, 10100−10103. (d) Shen, H.-C.; Wang, Z.-S.; Noble, A.; Aggarwal, V. K. Simultaneous Stereoinvertive and Stereoselective C(sp3)−C(sp3) Cross-Coupling of Boronic Esters and Allylic Carbonates. *J. Am. Chem. Soc.* **2024**, *146*, 13719−13726.

(5) Draper, P. M.; Chan, T. H.; Harpp, D. N. The chemistry of phosphorus and sulfur halides. Alkyl transfer from boranes. *Tetrahedron Lett.* **1970**, *11*, 1687−1688.

(6) Yoshida, Z.-i.; Okushi, T.; Manabe, O. In situ preparation of disulfide by the reaction of trialkyl- and triarylborons with sulfur. *Tetrahedron Lett.* **1970**, *11*, 1641−1643.

(7) Hupe, E.; Knochel, P. Stereoselective Synthesis of Secondary Organozinc Reagents and Their Reaction with Heteroatomic Electrophiles. *Org. Lett.* **2001**, *3*, 127−130.

(8) (a) Liang, H.; Morken, J. P. Substrate Plasticity Enables Group-Selective Transmetalation: Catalytic Stereospecific Cross-Couplings of Tertiary Boronic Esters. *J. Am. Chem. Soc.* **2023**, *145*, 20755−20760. (b) Liang, H.; Morken, J. P. Stereospecific Transformations of Alkylboronic Esters Enabled by Direct Boron-to-Zinc Transmetalation. *J. Am. Chem. Soc.* **2023**, *145*, 9976−9981. (c) Xu, N.; Liang, H.; Morken, J. P. Copper-Catalyzed Stereospecific Transformations of Alkylboronic Esters. *J. Am. Chem. Soc.* **2022**, *144*, 11546−11552.

(9) Afanasiev, V. V.; Beletskaya, I. P.; Kazankova, M. A.; Efimova, I. V.; Antipin, M. U. A Convenient and Direct Route to Phosphinoalkynes via Copper-Catalyzed Cross-Coupling of Terminal Alkynes with Chlorophosphanes. *Synthesis* **2003**, *2003*, 2835−2838.

(10) (a) Jarowicki, K.; Kocieński, P.; Komsta, Z.; Wojtasiewicz, A. Copper(I)-Mediated 1,2-Metallate Rearrangements of 1-Metallated Glycals. *Synthesis* **2012**, *44*, 946−952. (b) Jarowicki, K.; Kocienski, P. J. 1,2-Metallate Rearrangements of α-Alkoxyalkyl Cuprates. *Synlett* **2005**, *2005*, 167−169. (c) Kocienski, P.; Barber, C. Synthetic applications of metallate rearrangements. *Pure Appl. Chem.* **1990**, *62*, 1933−1940. (d) Kondo, J.; Inoue, A.; Ito, Y.; Shinokubo, H.; Oshima, K. Preparation of α-silyl- or α,α-bis(silyl)-substituted alkylcopper reagents and their synthetic use. *Tetrahedron* **2005**, *61*, 3361−3369.

(11) (a) Croisant, M. F.; Van Hoveln, R.; Schomaker, J. M. Formal Dyotropic Rearrangements in Organometallic Transformations. *Eur. J. Org. Chem.* **2015**, *2015*, 5897−5907. (b) Fernández, I.; Cossío, F. P.; Sierra, M. A. Dyotropic Reactions: Mechanisms and Synthetic Applications. *Chem. Rev.* **2009**, *109*, 6687−6711.

(12) (a) Glueck, D. S. Catalytic Asymmetric Synthesis of P-Stereogenic Phosphines: Beyond Precious Metals. *Synlett* **2021**, *32*, 875−884. (b) Glueck, D. S. Metal-Catalyzed P−C Bond Formation via P−H Oxidative Addition: Fundamentals and Recent Advances. *J. Org. Chem.* **2020**, *85*, 14276−14285.

(13) (a) Fife, D. J.; Moore, W. M.; Morse, K. W. Solution equilibria of tertiary phosphine complexes of copper(I) halides. *Inorg. Chem.* **1984**, *23*, 1684−1691. (b) Miyaji, T.; Xi, Z.; Nakajima, K.; Takahashi, T. Generation of Copper(I) Complexes with a Tethered Olefin−Phosphine Ligand from CuCl-Mediated Reaction of Alkenylzirconocene with R2PCl. *Organometallics* **2001**, *20*, 2859−2863. (c) Miyaji, T.; Xi, Z.; Ogasawara, M.; Nakajima, K.; Takahashi, T. Alkenylzirconocene-Mediated Preparation of Alkenylphosphines. *J. Org. Chem.* **2007**, *72*, 8737−8740.

(14) Yao, Y.; Deng, Y.; Kong, L.; Au-Yeung, H. Y. Efficient Copper(I) Extraction by Ethylenediamine from Stable Catenane Complexes. *Eur. J. Inorg. Chem.* **2022**, *2022*, No. e202200271.

(15) (a) Toulgoat, F.; Liger, F.; Billard, T., Chemistry of OCF 3, SCF 3, and SeCF 3 Functional Groups. In *Organofluorine Chemistry*;

John Wiley & Sons, Inc.: Hoboken, NJ, 2021; pp 49−97. (b) Wu, J.; Shen, Q. Difluoromethylthiolator: A Toolbox of Reagents for Difluoromethylthiolation. *Acc. Chem. Res.* **2021**, *54*, 2946−2958. (c) Xiong, H.-Y.; Pannecoucke, X.; Besset, T. Recent Advances in the Synthesis of SCF2H- and SCF2FG-Containing Molecules. *Chem.—Eur. J.* **2016**, *22*, 16734−16749. (d) Zheng, H.; Huang, Y.; Weng, Z. Recent advances in trifluoromethylthiolation using nucleophilic trifluoromethylthiolating reagents. *Tetrahedron Lett.* **2016**, *57*, 1397−1409.

(16) (a) Graßl, S.; Hamze, C.; Koller, T. J.; Knochel, P. Copper-Catalyzed Electrophilic Thiolation of Organozinc Halides by Using N-Thiophthalimides Leading to Polyfunctional Thioethers. *Chem.—Eur. J.* **2019**, *25*, 3752−3755. (b) Zhu, D.; Gu, Y.; Lu, L.; Shen, Q. N-Difluoromethylthiophthalimide: A Shelf-Stable, Electrophilic Reagent for Difluoromethylthiolation. *J. Am. Chem. Soc.* **2015**, *137*, 10547−10553. (c) Zhu, D.; Hong, X.; Li, D.; Lu, L.; Shen, Q. A Two-Step, One-Pot, and Multigram-Scale Synthesis of N-Difluoromethylthiophthalimide. *Org. Process Res. Dev.* **2017**, *21*, 1383−1387.

(17) (a) Denmark, S. E.; Hartmann, E.; Kornfilt, D. J. P.; Wang, H. Mechanistic, crystallographic, and computational studies on the catalytic, enantioselective sulfenofunctionalization of alkenes. *Nat. Chem.* **2014**, *6*, 1056−1064. (b) Liao, L.; Zhao, X. Modern Organoselenium Catalysis: Opportunities and Challenges. *Synlett* **2021**, *32*, 1262−1268. (c) Liao, L.; Zhao, X. Indane-Based Chiral Aryl Chalcogenide Catalysts: Development and Applications in Asymmetric Electrophilic Reactions. *Acc. Chem. Res.* **2022**, *55*, 2439−2453. (d) Shao, L.; Li, Y.; Lu, J.; Jiang, X. Recent progress in selenium-catalyzed organic reactions. *Org. Chem. Front.* **2019**, *6*, 2999−3041. (e) Singh, F. V.; Wirth, T. Selenium reagents as catalysts. *Catal. Sci. Technol.* **2019**, *9*, 1073−1091.

(18) Zhou, P.; Shao, X.; Malcolmson, S. J. A Diastereodivergent and Enantioselective Approach to syn- and anti-Diamines: Development of 2-Azatrienes for Cu-Catalyzed Reductive Couplings with Imines That Furnish Allylic Amines. *J. Am. Chem. Soc.* **2021**, *143*, 13999−14008.

(19) Aiken, S. G.; Bateman, J. M.; Liao, H.-H.; Fawcett, A.; Bootwicha, T.; Vincetti, P.; Myers, E. L.; Noble, A.; Aggarwal, V. K. Iterative synthesis of 1,3-polyboronic esters with high stereocontrol and application to the synthesis of bahamaolide A. *Nat. Chem.* **2023**, *15*, 248−256.

(20) (a) Coombs, J. R.; Haeffner, F.; Kliman, L. T.; Morken, J. P. Scope and Mechanism of the Pt-Catalyzed Enantioselective Diboration of Monosubstituted Alkenes. *J. Am. Chem. Soc.* **2013**, *135*, 11222−11231. (b) Kliman, L. T.; Mlynarski, S. N.; Morken, J. P. Pt-Catalyzed Enantioselective Diboration of Terminal Alkenes with B2(pin)2. *J. Am. Chem. Soc.* **2009**, *131*, 13210−13211.

(21) Xu, N.; Kong, Z.; Wang, J. Z.; Lovinger, G. J.; Morken, J. P. Copper-Catalyzed Coupling of Alkyl Vicinal Bis(boronic Esters) to an Array of Electrophiles. *J. Am. Chem. Soc.* **2022**, *144*, 17815−17823.

(22) Craig, R. A.; Megumi, K.; Lynch, L. M.; Patel, J. R.; Sheppard, G. S.; Wang, J.; Yang, F.; Ba-Maung, N. Y. WO2001079157A1, 2002.

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