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Asymmetric synthesis of metallocenes with planar and central chirality by rhodium-catalyzed desymmetrization reactions†

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Metallocenes with planar and central chirality have emerged as a privileged skeleton for chiral ligand design, and such ligands have exhibited tremendous success in various asymmetric catalysis protocols. Herein, we report a rhodium/chiral diene-catalyzed asymmetric desymmetrization of 1,2-diformylmetallocenes with aryl/alkenylboronic acids to give enantio-enriched formylmetallocenes, which are diastereoisomers of Ugi-type products. This catalytic system also enables the kinetic resolution of 2-substituted 1-formylferrocene with a selectivity factor (*s*) of up to 4331. Compared with traditional synthesis methods, our method has the following advantages: (1) opposite diastereoselectivity; (2) catalytic asymmetric synthesis; (3) single-step construction of planar and central chirality. The synthetic utility of the present method is demonstrated by the asymmetric synthesis of a series of chiral phosphine ligands, including Josiphos- and PPFA-type ligands.

Introduction

Metallocenes possessing planar chirality are of great significance in organic synthesis, materials science, and medicinal chemistry.¹ Compounds such as PPFA,² TRAP,³ Josiphos,⁴ BoPhoz,⁵ Walphos,⁶ Taniaphos,⁷ Zhaophos,⁸ and Wudaphos,⁹ which possess both planar and central chirality, are extensively used in asymmetric catalysis. These ligands are typically prepared according to Ugi's procedure, which introduces additional planar chirality besides their inherent central chirality through diastereoselective *ortho*-lithiation (Scheme 1a).¹⁰ One example of this is the synthesis of (*R*,*S*)-ferrocenecarbaldehyde, which has proved successful as a catalyst for the asymmetric alkylation of aldehydes with dialkylzinc reagents, through the *ortho*-lithiation of (*R*)-(2-dimethylaminoethyl)ferrocene (Ugi's amine).^{11b} Chiral Ugi's amine is typically prepared by a conventional method that relies heavily on the optical resolution of its racemate with the aid of resolving agents in specific proportions.^{10a} As a result, the development of highly effective, simple, and reliable techniques for producing metallocenes with both central and planar chirality is seen as

a significant pursuit in the realm of synthetic chemistry. Transition-metal-catalyzed enantioselective C–H functionalization of metallocenes has been the subject of extensive research in relation to catalytic asymmetric synthesis (Scheme 1b).¹² There have been limited studies on the preparation of enantio-enriched planar chiral metallocenes through catalytic desymmetrization of prochiral compounds.¹³ However, the simultaneous introduction of planar and central chirality in metallocenes in a single step with high diastereo- and enantioselectivity has seldom been reported.¹⁴

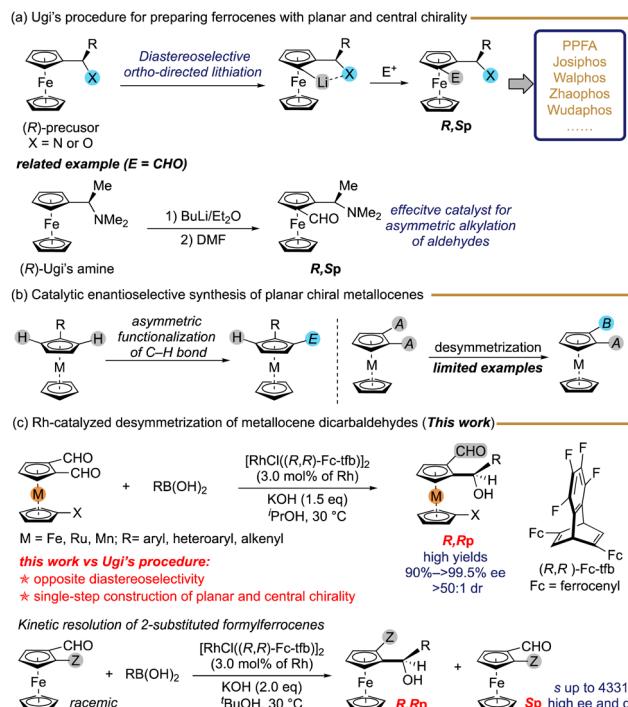
Planar chiral formylferrocenes are an important class of platform molecules, with the potential to be transformed and applied in the synthesis of chiral ligands and catalysts.¹⁵ Herein, we describe a rhodium-catalyzed desymmetrization¹⁶ of organoboronic acids to 1,2-diformylmetallocenes, leading to the formation of chiral metalloceneformaldehydes with both planar and central chirality in high yields with high diastereo- and enantioselectivity (Scheme 1c). Furthermore, we successfully achieved the kinetic resolution of planar chiral 2-substituted formylferrocenes using the same catalytic system. In previous work, the diastereomer of Ugi amine was prepared by multiple-step protection and deprotection, leading to low synthesis efficiency.¹⁷ Our method offers several advantages over Ugi's procedure, including: (1) catalytic asymmetric synthesis; (2) simultaneous generation of planar and central chirality; (3) opposite planar diastereoselectivity; (4) simple and mild reaction conditions. We have demonstrated the practical application of our approach by synthesizing various chiral phosphine ligands, such as Josiphos- and PPFA-type ligands, in an asymmetric manner.

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Scheme 1 Asymmetric synthesis of metallocenes with planar and central chirality.

Results and discussion

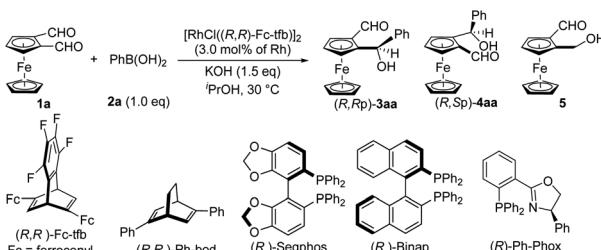
As a model reaction, the addition of $\text{PhB}(\text{OH})_2$ (2a, 1.0 equiv. with respect to 1a) to 1,2-diformylferrocene (1a) was performed in the presence of 3.0 mol% of rhodium catalysts bearing

several types of chiral diene^{16e} and bisphosphine ligands and 1.5 equiv. of KOH in 2-propanol at 30 °C for 10 h (Table 1). The reaction with (R,R)-Fc-tfb¹⁸ as a ligand gave a 93% yield of 3aa with >99.5% ee, and its diastereoisomer 4aa was not detected by ¹H NMR spectroscopy (entry 1). Another commonly used chiral diene ligand, (R,R)-Ph-bod, gave a moderate yield of a mixture of 3aa and 4aa with much lower enantioselectivity (entry 2). Other ligands, namely (R)-Segphos, (R)-Binap, and (R)-Ph-Phox, gave low yields of 3aa with low stereoselectivity, and the formation of side product 5, which was produced by hydrogenation of 1a, was detected in these reactions (entries 3–5). Reactions in other protic solvents, namely dioxane/H₂O and MeOH, gave 3aa with moderate enantioselectivity (entries 6 and 7). The reaction in ¹BuOH also gave 3aa in high yield with high ee and dr (entry 8). The use of PhZnCl in place of $\text{PhB}(\text{OH})_2$ gave a trace amount of 3aa (entry 9).

Having established the optimal reaction conditions (Table 1, entry 1), the substrate scope of this desymmetrization reaction of various 1,2-diformylmetallocenes with $\text{PhB}(\text{OH})_2$ (2a) was examined, and the results are summarized in Scheme 2a. Desymmetrization of 1b, with a Me_3Si -group at the 1'-position of the ferrocene cyclopentadiene moiety, proceeded well to give the corresponding product 3ba with high diastereo- and enantioselectivity (entry 2). Using the present method, chiral ruthenocene derivative 3ca and tricarbonylcyclopentadienyl manganese derivative 3da were successfully obtained in high yields with excellent dr and high ee values under the standard conditions (entries 3 and 4).

Scheme 2b provides an overview of the results obtained for reactions of 1,2-diformylferrocene (1a) with diversely functionalized organoboronic acids 2, including aryl-, heteroaryl-, and

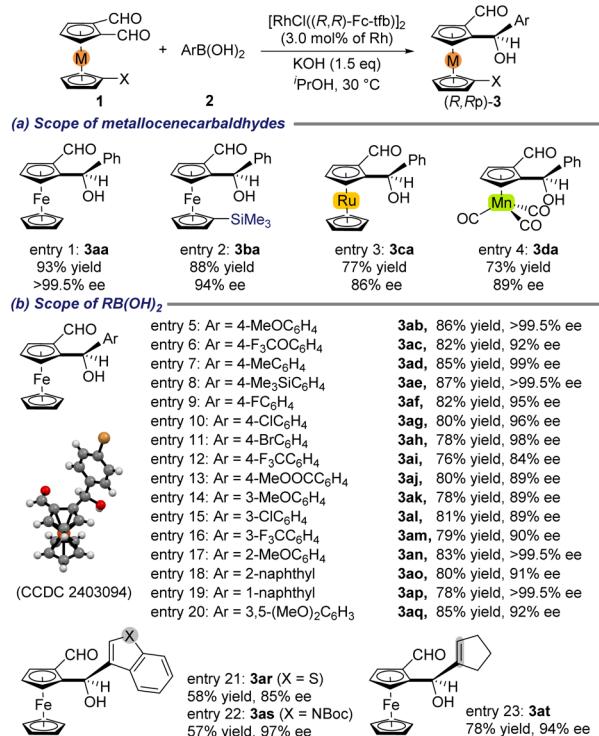
Table 1 Optimization of catalytic conditions^a



Entry	Variations from standard conditions (shown above)	Yield ^b (%) 3aa	dr ^c (3 : 4)	% ee ^d 3aa
1	None	93	>50 : 1	>99.5
2	[RhCl((R,R)-Ph-bod)] ₂	44	67 : 33	51
3	[RhCl(coe)] ₂ + (R)-Segphos	<5	—	—
4	[RhCl(coe)] ₂ + (R)-Binap	11	63 : 37	24
5	[RhCl(coe)] ₂ + (R)-Ph-Phox	10	80 : 20	0
6	Dioxane/H ₂ O (10/1) instead of ⁱ PrOH	90	>50 : 1	79
7	MeOH instead of ⁱ PrOH	20	>50 : 1	79
8	¹ BuOH instead of ⁱ PrOH	94	>50 : 1	96
9 ^e	PhZnCl instead of $\text{PhB}(\text{OH})_2$	<5	—	—

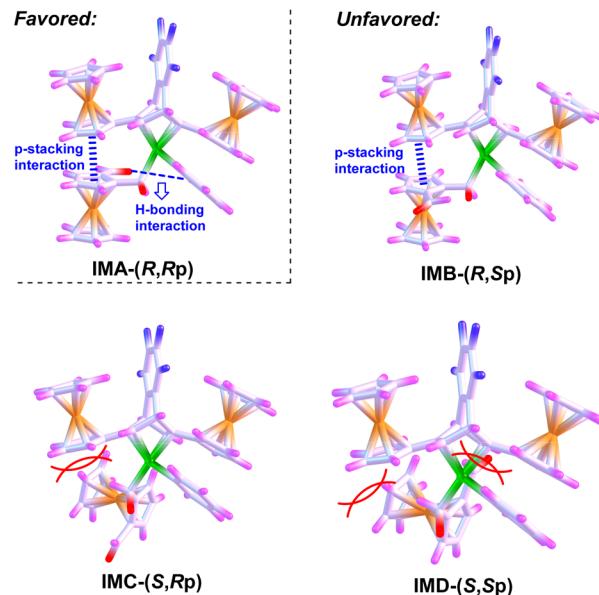
^a Reaction conditions: 1a (0.10 mmol), 2a (0.10 mmol), KOH (0.15 mmol), [RhCl((R,R)-Fc-tfb)]₂ (3.0 mol% Rh), and 2-propanol (1.0 mL) at 30 °C for 10 h. ^b Isolated yield. ^c dr (diastereomeric ratio) was determined by ¹H NMR spectroscopy of the crude reaction mixture. Considering the accuracy of ¹H NMR spectroscopy, the dr is >50 : 1. ^d % ee was determined by HPLC on a chiral stationary phase column. ^e Reaction conditions: 1a (0.10 mmol), PhZnCl (0.20 mmol), [RhCl((R,R)-Fc-tfb)]₂ (3.0 mol% Rh), and THF (1.0 mL) at 30 °C for 10 h.





Scheme 2 Rh-catalyzed desymmetric addition of organoboronic acids to metallocene dicarbaldehydes: substrate scope. Reaction conditions: 1 (0.10 mmol), 2 (0.10 mmol), KOH (0.15 mmol), $[\text{RhCl}((R,R)-\text{Fc-tfb})]_2$ (3.0 mol% Rh), and 2-propanol (1.0 mL) at 30 °C for 10 h. Isolated yield. dr (diastereomeric ratio) was determined by ^1H NMR spectroscopy of the crude reaction mixture. Considering the accuracy of ^1H NMR spectroscopy, the dr is >50 : 1. % ee was determined by HPLC on a chiral stationary phase column. The absolute configuration of 3ah was determined to be *R,R_P* by X-ray crystallographic analysis (CCDC 2403094).

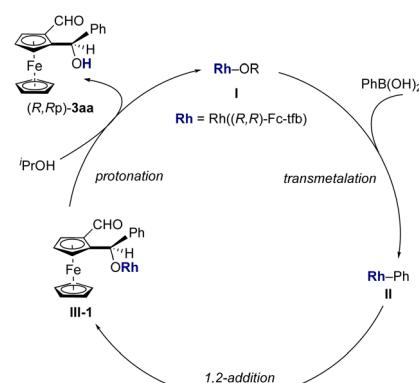
alkenylboronic acids, under the standard conditions. The desymmetric addition proceeded smoothly for $\text{ArB}(\text{OH})_2$ 2b–2j, which are aromatic groups consisting of aryl moieties with methoxy, trifluoromethoxy, methyl, trimethylsilyl, halo, trifluoromethyl, and ester substituents at the *para* position (entries 5–13). The corresponding products 3ab–3aj were obtained in high yields with high diastereo- and enantioselectivity (>50 : 1 dr, 84 ≥ 99.5% ee). However, the presence of electron-withdrawing groups generally decreased the enantioselectivity. Arylboronic acids 2k–2m, with electron-donating and -withdrawing substituents at their *meta* position, gave high yields of the corresponding products 3ak–3am with enantioselectivity of 89–90% ee (entries 14–16). The reaction of *ortho*-substituted arylboronic acid 2n also took place, giving the corresponding product 3an in high yield with excellent diastereo- and enantioselectivity (entry 17). The desymmetric addition of 1a also proceeded smoothly for polysubstituted arylboronic acids 2o–2q to give the corresponding products 3ao–3aq in high yields with both high diastereo- and enantioselectivity (entries 18–20). The desymmetric addition of heteroarylboronic acids 2r and 2s gave moderate yields of the corresponding products 3ar and 3as with both high dr and ee (entries 21 and 22). Desymmetric



Scheme 3 Proposed stereochemical pathway.

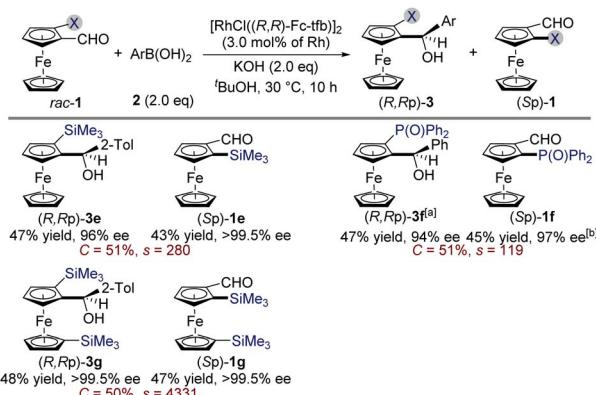
alkenylation of 1a with 1-cyclopentenylboronic acid (2t) also gave a high yield of the corresponding product 3at with high dr and ee (>50 : 1 dr, 94% ee, entry 23).

The *(R,Rp)*-configuration for compound 3ah can be rationalized by the stereochemical pathway shown in Scheme 3. The steric match among the ferrocenyl and aldehyde moieties of 1a, Rh-Ph fragment, and the chiral *(R,R)-Fc-tfb* ligand might be very important for achieving the high level of stereo-control. For chiral recognition of the two enantiotopic aldehyde groups of 1a, the coordination of 1a with Rh/*(R,R)-Fc-tfb* is more favorable in the configuration IMA than in IMB, leading to the formation of planar chirality in the *(Rp)*-configuration. This can originate from the favorable non-covalent interactions, *i.e.* π -stacking interaction between the ferrocenyl moiety of 1a and the ferrocenyl group on the olefin of *(R,R)-Fc-tfb* and hydrogen-bonding interaction between the aldehyde fragment of 1a and the Rh-Ph moiety. To avoid the unfavorable steric hindrance between the carbonyl and ferrocenyl moieties of 1a and the ferrocenyl group



Scheme 4 Proposed catalytic cycle.





Scheme 5 Kinetic resolution of planar chiral 2-substituted formylferrocenes. Reaction conditions: 1 (0.10 mmol), 2 (0.20 mmol), KOH (0.20 mmol), $[\text{RhCl}((R,R)-\text{Fc-tfb})]_2$ (3.0 mol% Rh), and $t\text{BuOH}$ (1.0 mL) at 30 °C for 10 h. Calculated conversion, $C = ee_1/(ee_1 + ee_3)$. The % ee was determined by HPLC on a chiral stationary phase column. Selectivity factor, $s = \ln[(1 - C)(1 - ee_1)]/\ln[(1 - C)(1 + ee_1)]$. Diastereomeric ratio (dr) = >50 : 1 (determined by ^1H NMR spectroscopy). ^aAt 80 °C. ^bCompound 1f was transformed to compound 12a (Scheme 6) for HPLC analysis.

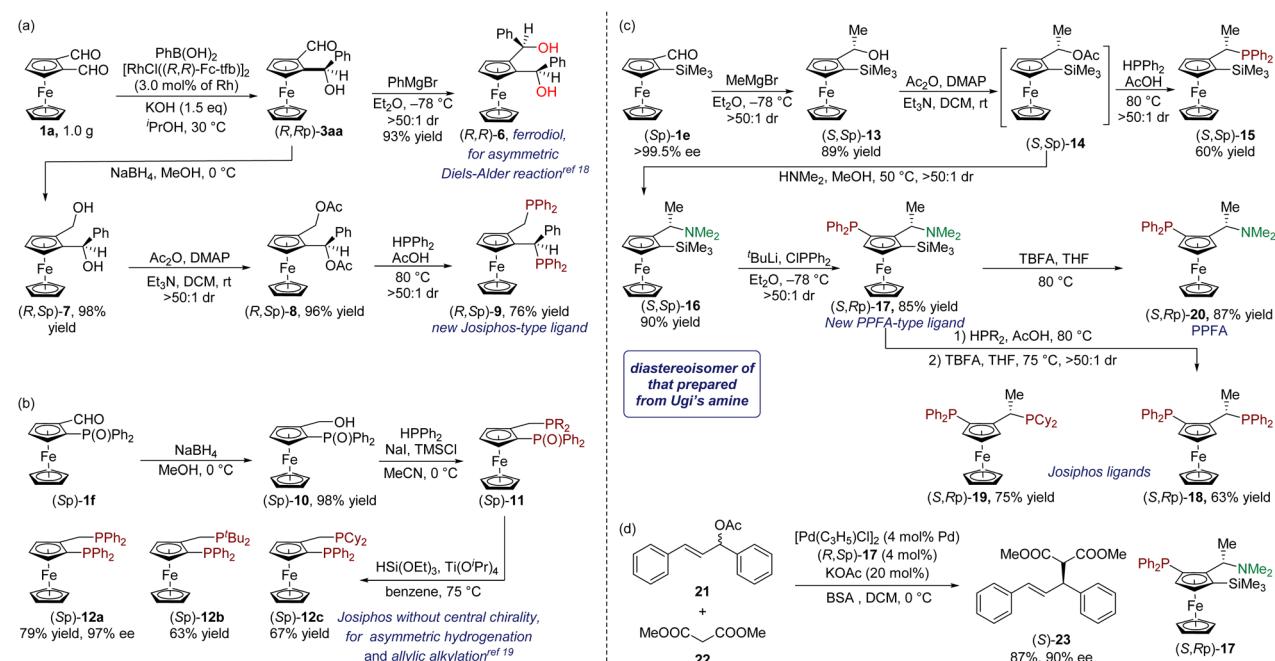
on the olefin of (R,R) -Fc-tfb, **IMA** is preferred to **IMC** or **IMD**, offering the (R) -configuration product. Thus, the Rh/ (R,R) -Fc-tfb catalyst effectively constructs the stereochemical model of (R,Rp) -configuration.

The catalytic cycle for the rhodium/chiral diene-catalyzed asymmetric desymmetrization of 1,2-diformylmetallocenes is proposed in Scheme 4. 1,2-Addition of 1,2-diformylferrocene (**1a**) with phenyl-rhodium species **II**, which is generated by

transmetalation of PhB(OH)_2 with [Rh]-OR species **I**, affords a rhodium alkoxide species **III**. Further protonation of intermediate **III** gives product **3aa** and regenerates [Rh]-OR species **I**.

Next, the Rh/ (R,R) -Fc-tfb catalytic system was successfully applied to the kinetic resolution (KR) of racemic 2-substituted formylferrocenes (Scheme 5). The KR of 2-silyl formylferrocene **1e** with 2-methylphenylboronic acid in the presence of the Rh/ (R,R) -Fc-tfb catalyst in *tert*-butanol proceeded smoothly with 51% conversion, giving the arylation product **3e** (>50 : 1 dr) with 96% ee and recovered **1e** with >99.5% ee, and the corresponding selectivity factor (*s*) for **rac-1e** was 280. This KR methodology also proved to be highly efficient towards **1f** bearing a phosphine oxide group, giving a high *s*-factor value, with a high yield of the corresponding product **3f**, and both **3f** and recovered **1f** having high ee. The KR of **1g**, with a Me_3Si - group at the 1'-position of the ferrocene moiety, proceeded well and gave the corresponding product **3g** with an excellent *s*-factor (*s* = 4331).

To demonstrate the synthetic potential of our method, the products were expeditiously transformed into potentially useful phosphine ligands (Scheme 6). A ferrocenyl-based chiral diol ligand (**FERRODIOL**), prepared from optically pure aminoformylferrocene, has been developed as a chiral ligand for scandium-catalyzed asymmetric Diels–Alder reactions.¹⁹ As shown in Scheme 6a, **FERRODIOL** **6** was easily prepared by the diastereoselective addition of a Grignard reagent to compound **3aa**, which was obtained as indicated in Table 1, entry 1. Moreover, a new Josiphos-type ligand **9** was prepared through a sequence that comprised reduction, acylation, and diastereoselective $\text{S}_{\text{N}}1$ -type reaction with HPPH_2 as a nucleophilic reagent. There are very few examples of bisphosphanes that possess only planar chirality. Here, we successfully prepared



Scheme 6 Synthetic transformations. (a) Scale experiment. (b) Josiphos-type ligands without central chirality. (c) PPFA- and Josiphos-type ligands. (d) Asymmetric allylic alkylation.



several enantiopure Josiphos-type ligands **12a–12c** with planar chirality as the sole source of chirality. Their rhodium complexes proved to be efficient catalysts for the asymmetric hydrogenation of various alkenes (Scheme 6b).²⁰ Thus, starting from **1f**, ligands **12a–12c** were efficiently synthesized through a sequence that involved reduction with NaBH_4 , $\text{S}_{\text{N}}1$ -type reaction, and reduction with HSi(OEt)_3 . Subsequently, addition of Grignard reagent MeMgBr to **1e** yielded alcohol **13**, which was then converted into acetate **14** by treating it with acetic anhydride (Scheme 6c). The crude compound **14** served as the starting material for the synthesis of a ferrocene-derived chiral monophosphine ligand **15** by a simple $\text{S}_{\text{N}}1$ -type reaction with HPPH_2 .²¹ Moreover, compound **14** was also transformed into **16**, the diastereoselectivity of which is opposite to that of the product obtained from Ugi's amine through nucleophilic substitution with HNMe_2 . Furthermore, the chiral PPFA ligand derivative **17** was obtained in 85% isolated yield by diphenylphosphination of the lithiated ferrocene, produced through the reaction of **16** with butyllithium. The efficiency of ligand **17** was demonstrated by a Pd-catalyzed asymmetric allylic alkylation reaction (87% yield, 90% ee) (Scheme 6d).²² Similarly, the new PPFA ligand also underwent $\text{S}_{\text{N}}1$ reactions with HPPH_2 and HPCy_2 , and subsequent desilication afforded Josiphos ligands **18** and **19**, respectively, in high yields. Desilication of compound **17** also gave the normal PPFA ligand **20** in high yield. In summary, various chiral ligands, including FERRODIOL **6**, new Josiphos-type ligand **9**, Josiphos-type ligands **12a–12c** without central chirality, a ferrocene-derived chiral monophosphine ligand **15**, PPFA-type ligand **17**, known Josiphos ligands **18** and **19**, and known PPFA ligand **20**, were successfully produced.

Conclusions

In summary, we have developed a highly efficient synthesis of enantiopure planar and central chiral metallocenes based on rhodium-catalyzed asymmetric addition under mild conditions. These chiral metallocenes, created through the simultaneous construction of planar and central chirality from achiral 1,2-diformylmetallocene, were obtained in high yields with excellent diastereo- and enantioselectivity. Furthermore, the KR reaction proceeded smoothly, achieving a selectivity factor of up to 4331. The synthetic utility of the present method has been demonstrated by the asymmetric synthesis of a series of chiral phosphine ligands, including Josiphos- and PPFA-type ligands.

Data availability

Experimental procedures, compound characterization data and X-ray crystallographic data of compound **3ah**. CCDC 2403094. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5sc00158g>.

Author contributions

N.-N. Hang and E.-G. Tong contributed equally. The manuscript was written through contributions of all authors.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- For selected reviews, see: (a) A. Togni, *Angew. Chem., Int. Ed.*, 1996, **35**, 1475–1477; (b) P. Nguyen, P. Gómez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515–1548; (c) I. Manners, *Science*, 2001, **294**, 1664–1666; (d) L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng and X.-L. Hou, *Acc. Chem. Res.*, 2003, **36**, 659–667; (e) G. C. Fu, *Acc. Chem. Res.*, 2006, **39**, 853–860; (f) R. Gómez Arrayás, J. Adrio and J. C. Carretero, *Angew. Chem., Int. Ed.*, 2006, **45**, 7674–7715; (g) W. Zhang, Y. Chi and X. Zhang, *Acc. Chem. Res.*, 2007, **40**, 1278–1290; (h) L. X. Dai and X. L. Hou, *Chiral Ferrocenes in Asymmetric Catalysis*, Wiley-VCH, GmbH & Co, Weinheim, 2010, pp. 369–396; (i) V. N. Babin, Y. A. Belousov, V. I. Borisov, V. V. Gumennyuk, Y. S. Nekrasov, L. A. Ostrovskaya, I. K. Sviridova, N. S. Sergeeva, A. A. Simenel and L. V. Snegur, *Russ. Chem. Bull.*, 2014, **63**, 2405–2422; (j) M. Patra and G. Gasser, *Nat. Rev. Chem.*, 2017, **1**, 0066; (k) S. Sansook, S. Hassell-Hart, C. Ocasio and J. Spencer, *J. Organomet. Chem.*, 2020, **905**, 121017; (l) L. Cunningham, A. Benson and P. J. Guiry, *Org. Biomol. Chem.*, 2020, **18**, 9329–9370.
- For selected examples, see: (a) T. Hayashi, K. Yamamoto and M. Kumada, *Tetrahedron Lett.*, 1974, **15**, 4405–4408; (b) T. Hayashi, T. Mise, S. Mitachi, K. Yamamoto and M. Kumada, *Tetrahedron Lett.*, 1976, **14**, 1133–1134; (c) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1138–1151; (d) T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika and M. Kumada, *J. Am. Chem. Soc.*, 1982, **104**, 180–186; (e) W. R. Cullen, F. W. B. Einstein, C.-H. Huang, A. C. Willis and E.-S. Yeh, *J. Am. Chem. Soc.*, 1980, **102**, 988–993.
- For selected examples, see: (a) M. Sawamura, H. Hamashima and Y. Ito, *Tetrahedron: Asymmetry*, 1991, **2**, 593–596; (b) M. Sawamura, H. Hamashima, M. Sugawara, R. Kuwano and Y. Ito, *Organometallics*, 1995, **14**, 4549–4558; (c) R. Kuwano, M. Sawamura and Y. Ito, *Tetrahedron: Asymmetry*, 1995, **6**, 2521–2526; (d) M. Sawamura, H. Hamashima and Y. Ito, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 2559–2562; (e) R. Kuwano, M. Kashiwabara, K. Sato, T. Ito, K. Kaneda and Y. Ito, *Tetrahedron: Asymmetry*, 2006, **17**, 521–535; (f) R. Ikeda and R. Kuwano, *Molecules*, 2012, **17**, 6901–6915.
- For selected examples, see: (a) A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert and A. Tijani, *J. Am. Chem. Soc.*, 1994, **116**, 4062–4066; (b) H.-U. Blaser,

W. Brieden, B. Pugin, F. Spindler, M. Studer and A. Togni, *Top. Catal.*, 2002, **19**, 3–16.

5 For selected examples, see: (a) N. W. Boaz, S. D. Debenham, E. B. Mackenzie and S. E. Large, *Org. Lett.*, 2002, **4**, 2421–2424; (b) N. W. Boaz, E. B. Mackenzie, S. D. Debenham, S. E. Large and J. A. Ponasik, *J. Org. Chem.*, 2005, **70**, 1872–1880; (c) J. Deng, X.-P. Hu, J.-D. Huang, S.-B. Yu, D.-Y. Wang, Z.-C. Duan and Z. Zheng, *J. Org. Chem.*, 2008, **73**, 2015–2017; (d) S. W. Krabbe, M. A. Hatcher, R. K. Bowman, M. B. Mitchell, M. S. McClure and J. S. Johnson, *Org. Lett.*, 2013, **15**, 4560–4563.

6 For selected examples, see: (a) T. Sturm, W. Weissensteiner and F. Spindler, *Adv. Synth. Catal.*, 2003, **345**, 160–164; (b) Y. Wang, T. Sturm, M. Steurer, V. B. Arion, K. Mereiter, F. Spindler and W. Weissensteiner, *Organometallics*, 2008, **27**, 1119–1127; (c) M. A. Groß, K. Mereiter, Y. Wang and W. Weissensteiner, *J. Organomet. Chem.*, 2012, **716**, 32–38; (d) A. Zirakzadeh, M. A. Groß, Y. Wang, K. Mereiter, F. Spindler and W. Weissensteiner, *Organometallics*, 2013, **32**, 1075–1084; (e) A. Zirakzadeh, M. A. Groß, Y. Wang, K. Mereiter and W. Weissensteiner, *Organometallics*, 2014, **33**, 1945–1952.

7 For selected examples, see: (a) T. Ireland, G. Grossheimann, C. Wieser-Jeunesse and P. Knochel, *Angew. Chem., Int. Ed.*, 1999, **38**, 3212–3215; (b) M. Lotz, K. Polborn and P. Knochel, *Angew. Chem., Int. Ed.*, 2002, **41**, 4708–4711; (c) K. Tappe and P. Knochel, *Tetrahedron: Asymmetry*, 2004, **15**, 91–102; (d) A. Almássy, E. Rakovský, A. Malastová, Z. Sorádová and R. Šebesta, *J. Organomet. Chem.*, 2016, **805**, 130–138; (e) W. Xiao, S. Chen, X. Liu and Y. Ma, *Chirality*, 2021, **33**, 292–302.

8 For selected examples, see: (a) Q. Zhao, S. Li, K. Huang, R. Wang and X. Zhang, *Org. Lett.*, 2013, **15**, 4014–4017; (b) J. Wen, J. Jiang and X. Zhang, *Org. Lett.*, 2016, **18**, 4451–4453; (c) X. Yin, Y. Huang, Z. Chen, Y. Hu, L. Tao, Q. Zhao, X.-Q. Dong and X. Zhang, *Org. Lett.*, 2018, **20**, 4173–4177; (d) Q. Zhao, C. Chen, J. Wen, X.-Q. Dong and X. Zhang, *Acc. Chem. Res.*, 2020, **53**, 1905–1921; (e) Y. Zhou, S. Guo, Q. Huang, Q. Lang, G.-Q. Chen and X. Zhang, *Chem. Sci.*, 2023, **14**, 4888–4892.

9 For selected examples, see: (a) C. Chen, H. Wang, Z. Zhang, S. Jin, S. Wen, J. Ji, L. W. Chung, X.-Q. Dong and X. Zhang, *Chem. Sci.*, 2016, **7**, 6669–6673; (b) X. Yin, C. Chen, X.-Q. Dong and X. Zhang, *Org. Lett.*, 2017, **19**, 2678–2681; (c) X. Yin, C. Chen, X. Li, X.-Q. Dong and X. Zhang, *Org. Lett.*, 2017, **19**, 4375–4378.

10 For selected examples, see: (a) D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, *J. Am. Chem. Soc.*, 1970, **92**, 5389–5393; (b) C. J. Richards and A. J. Locke, *Tetrahedron: Asymmetry*, 1998, **9**, 2377–2407; (c) H. Nie, L. Yao, B. Li, S. Zhang and W. Chen, *Organometallics*, 2014, **33**, 2109–2114; (d) R. P. Shekurov, A. A. Zagidullin, M. N. Khrizanforov, D. R. Islamov, T. P. Gerasimova, F. F. Akhmatkhanova and V. A. Miluykov, *Dalton Trans.*, 2022, **51**, 18603–18609.

11 (a) O. Riant, O. Samuel, T. Flessner, S. Taudien and H. B. Kagan, *J. Org. Chem.*, 1997, **62**, 6733–6745; (b) S.-i. Fukuzawa and H. Kato, *Synlett*, 1998, **7**, 727–728; (c) A. Urbano, G. Hernández-Torres, A. M. del Hoyo, A. Martínez-Carrión and M. C. Carreño, *Chem. Commun.*, 2016, **52**, 6419–6422.

12 For selected examples, see: (a) C. Pi, Y. Li, X. Cui, H. Zhang, Y. Han and Y. Wu, *Chem. Sci.*, 2013, **4**, 2675–2679; (b) T. Shibata and T. Shizuno, *Angew. Chem., Int. Ed.*, 2014, **53**, 5410–5413; (c) C. Pi, X. Cui, X. Liu, M. Guo, H. Zhang and Y. Wu, *Org. Lett.*, 2014, **16**, 5164–5167; (d) D.-W. Gao, Q. Yin, Q. Gu and S.-L. You, *J. Am. Chem. Soc.*, 2014, **136**, 4841–4844; (e) R. Deng, Y. Huang, X. Ma, G. Li, R. Zhu, B. Wang, Y.-B. Kang and Z. Gu, *J. Am. Chem. Soc.*, 2014, **136**, 4472–4475; (f) D.-W. Gao, C. Zheng, Q. Gu and S.-L. You, *Organometallics*, 2015, **34**, 4618–4625; (g) J. Singh, M. Deb and A. J. Elias, *Organometallics*, 2015, **34**, 4946–4951; (h) Q.-W. Zhang, K. An, L.-C. Liu, Y. Yue and W. He, *Angew. Chem., Int. Ed.*, 2015, **54**, 6918–6921; (i) L. A. López and E. López, *Dalton Trans.*, 2015, **44**, 10128–10135; (j) D.-W. Gao, Q. Gu and S.-L. You, *J. Am. Chem. Soc.*, 2016, **138**, 2544–2547; (k) D.-Y. Zhu, P. Chen and J.-B. Xia, *ChemCatChem*, 2016, **8**, 68–73; (l) C. Nottingham, H. Müller-Bunz and P. J. Guiry, *Angew. Chem., Int. Ed.*, 2016, **55**, 11115–11119; (m) D.-W. Gao, Q. Gu, C. Zheng and S.-L. You, *Acc. Chem. Res.*, 2017, **50**, 351–365; (n) S.-B. Wang, Q. Gu and S.-Li. You, *Organometallics*, 2017, **36**, 4359–4362; (o) D. Schmiel and H. Butenschön, *Organometallics*, 2017, **36**, 4979–4989; (p) J. Xu, Y. Liu, J. Zhang, X. Xu and Z. Jin, *Chem. Commun.*, 2018, **54**, 689–692; (q) W.-J. Kong, Q. Shao, M.-H. Li, Z.-L. Zhou, H. Xu, H.-X. Dai and J.-Q. Yu, *Organometallics*, 2018, **37**, 2832–2836; (r) G. Liao, T. Zhang, Z.-K. Lin and B.-F. Shi, *Angew. Chem., Int. Ed.*, 2020, **59**, 19773–19786; (s) X. Kuang, J.-J. Li, T. Liu, C.-H. Ding, K. Wu, P. Wang and J.-Q. Yu, *Nat. Commun.*, 2023, **14**, 7698; (t) C.-X. Liu, F. Zhao, Q. Gu and S.-L. You, *ACS Cent. Sci.*, 2023, **9**, 2036–2043; (u) C.-X. Liu, S.-Y. Yin, F. Zhao, H. Yang, Z. Feng, Q. Gu and S.-L. You, *Chem. Rev.*, 2023, **123**, 10079–10134; (v) H. Qi, N.-N. Hang and J. Ming, *ChemCatChem*, 2024, **16**, e202400736; (w) Z.-Z. Zhang, G. Zhou, Q. Yue, Q.-J. Yao and B.-F. Shi, *ACS Catal.*, 2024, **14**, 4030–4039; (x) A. Benson, L. Cunningham and P. J. Guiry, *Eur. J. Org. Chem.*, 2024, **27**, e202300951.

13 For selected examples, see: (a) W.-L. Duan, Y. Imazaki, R. Shintani and T. Hayashi, *Tetrahedron*, 2007, **63**, 8529–8536; (b) S. Arae, K. Nakajima, T. Takahashi and M. Ogasawara, *Organometallics*, 2015, **34**, 1197–1202; (c) C. Valderas, L. Casarrubios, M. C. d. l. Torre and M. A. Sierra, *Tetrahedron Lett.*, 2017, **58**, 326–328; (d) M.-L. Delcourt, S. Felder, E. Benedetti and L. Micouin, *ACS Catal.*, 2018, **8**, 6612–6616; (e) A. J. Wright, D. L. Hughes, P. C. B. Page and G. R. Stephenson, *Eur. J. Org. Chem.*, 2019, **2019**, 7218–7222; (f) X. Lv, J. Xu, C. Sun, F. Su, Y. Cai, Z. Jin and Y. R. Chi, *ACS Catal.*, 2022, **12**, 2706–2713; (g) V. Dočekal, F. Koucký, I. Císařová and J. Veselý, *Nat. Commun.*, 2024, **15**, 3090.

14 Y. Yang, N.-N. Hang, H.-Y. Liu, S. Chen and J. Ming, *ACS Catal.*, 2023, **13**, 12464–12471.



15 For selected examples, see: (a) F. Rebière, O. Riant, L. Ricard and H. B. Kagan, *Angew. Chem., Int. Ed.*, 1993, **32**, 568–570; (b) O. Riant, O. Samuel and H. B. Kagan, *J. Am. Chem. Soc.*, 1993, **115**, 5835–5836; (c) D. Schaarschmidt and H. Lang, *Organometallics*, 2013, **32**, 5668–5704.

16 For selected reviews, see: (a) T. Hayashi and K. Yamasaki, *Chem. Rev.*, 2003, **103**, 2829–2844; (b) K. Fagnou and M. Lautens, *Chem. Rev.*, 2003, **103**, 169–196; (c) P. Tian, H.-Q. Dong and G.-Q. Lin, *ACS Catal.*, 2012, **2**, 95–119; (d) M. M. Heravi, M. Dehghani and V. Zadsirjan, *Tetrahedron: Asymmetry*, 2016, **27**, 513–588; (e) Y. Huang and T. Hayashi, *Chem. Rev.*, 2022, **122**, 14346–14404.

17 (a) T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 1138–1151; (b) W. R. Cullen, F. W. B. Einstein, C.-H. Huang, A. C. Willis and E.-S. Yeh, *J. Am. Chem. Soc.*, 1980, **102**, 988–993.

18 T. Nishimura, H. Kumamoto, M. Nagaosa and T. Hayashi, *Chem. Commun.*, 2009, 5713–5715.

19 S.-i. Fukuzawa, K. Fujimoto, Y. Komuro and H. Matsuzawa, *Org. Lett.*, 2002, **4**, 707–709.

20 G. Argouarch, O. Samuel and H. B. Kagan, *Eur. J. Org. Chem.*, 2000, **2000**, 2885–2891.

21 M. Murakami, R. Minamida, K. Itami, M. Sawamura and Y. Ito, *Chem. Commun.*, 2000, 2293–2294.

22 Z. Lu and S. Ma, *Angew. Chem., Int. Ed.*, 2008, **47**, 258–297.

