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Optical resolution of 1,16-dihydroxytetraphenylene by chiral gold(III) complexation and its applications as chiral ligands in asymmetric catalysis†

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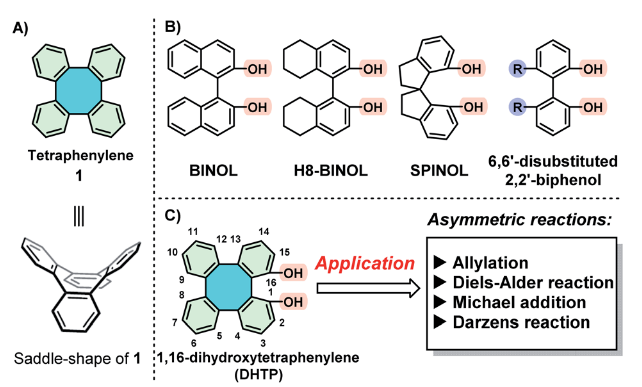
We report herein a novel approach involving optical resolution of (±)-1,16-dihydroxytetraphenylene (**DHTP**) by chiral gold(III) complexation. This method features several key advantages, *i.e.*, recyclability of chiral resolution reagents, feasibility of scaling up to gram quantities, and operational simplicity. On the basis of this method, which led to optically pure **DHTP**, a library of 2,15-diaryl (*S*)-**DHTP**s and several (*S*)-**DHTP**-derived phosphoramidite ligands were synthesized. Finally, the superior performance of a (*S*)-**DHTP** phosphoramidite ligand was demonstrated by efficient iridium-catalyzed asymmetric allylic alkynylation reactions.

Introduction

Tetraphenylene (**1**)[1] is a nonplanar saddle-shaped molecule, featuring four benzene rings that are arranged alternatively above and below its eight-membered ring (Scheme 1A).[2] As a molecule with a D_{2d} molecular symmetry, **1** is achiral in nature. However, chiral tetraphenylenes can be obtained by introducing appropriate substituents into the benzene rings due to the loss of D_{2d} symmetry, and also due to their extraordinarily high molecular inversion barrier.[3] Owing to their unique geometry and rigid molecular frameworks, chiral tetraphenylenes are endowed with great potential to function as excellent chiral ligands/catalysts and building blocks.[3b,4] It is therefore of great interest to design and prepare optically pure tetraphenylenes as novel ligands/catalysts for asymmetric reactions.[1c] In 2005, our group reported for the first time the use of tetraphenylene-derived phosphoramidite as chiral ligands in a Rh-catalyzed asymmetric hydrogenation.[4c] As a result, α-acylaminoacrylates were hydrogenated, leading to quantitative yields with excellent enantioselectivities (94–99% ee). In 2010, we also designed and synthesized tetraphenylene-derived organocatalysts for the Diels–Alder cycloaddition reaction between anthrones and maleimides.[5] However, applications of chiral tetraphenylenes in asymmetric catalysis have still not been attractive, presumably due to the difficulty in obtaining enantiopure tetraphenylenes through asymmetric synthesis[3b,4a,6] or by chiral resolution.[4c,d,7]

Over the past few decades, atropisomeric biphenols, such as **BINOL** (1,1′-bi-2-naphthol), H8-**BINOL**, **SPINOL** (1,1′-spirobiindane-7,7′-diol) and 6,6′-disubstituted-2,2′-biphenol (Scheme 1B), have been well-developed into privileged scaffolds for the design and synthesis of a variety of chiral ligands/catalysts.[8] Inspired by the architectural similarity of these structurally floppy biphenols, we opine that it is thought-provoking to apply structurally rigid 1,16-dihydroxytetraphenylene (**DHTP**)[4b,9] as a platform for comparison, in order to explore their application in asymmetric catalysis (Scheme 1C). Consequently, the development of enantiopure **DHTP**s as chiral ligands/catalysts in various asymmetric reactions, including asymmetric allylation, the Diels–Alder reaction, Michael



Scheme 1 (A) Structure of tetraphenylene; (B) structure of **BINOL**, H8-**BINOL**, **SPINOL** and 6,6′-disubstituted 2,2′-biphenol; (C) structure of 1,16-dihydroxytetraphenylene (**DHTP**).

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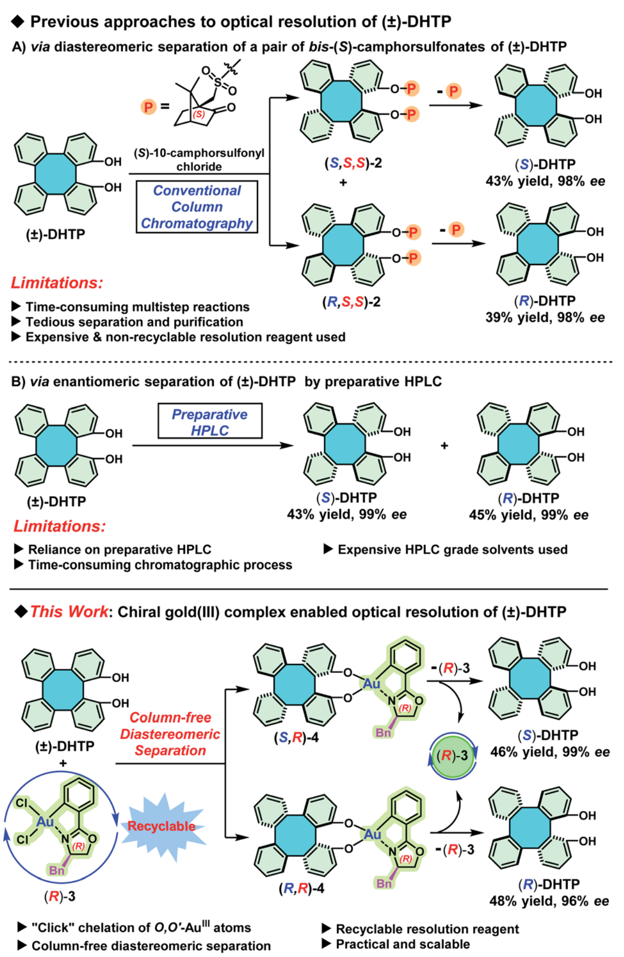
addition and the Darzens reaction, has recently witnessed significant progress.[10] Nonetheless, the utilization of chiral **DHTP**s in asymmetric catalysis is limited and still in its infancy because an efficient approach to enantiomeric (*S*)-**DHTP** and (*R*)-**DHTP** in large quantities is still challenging.[1d,e,g]

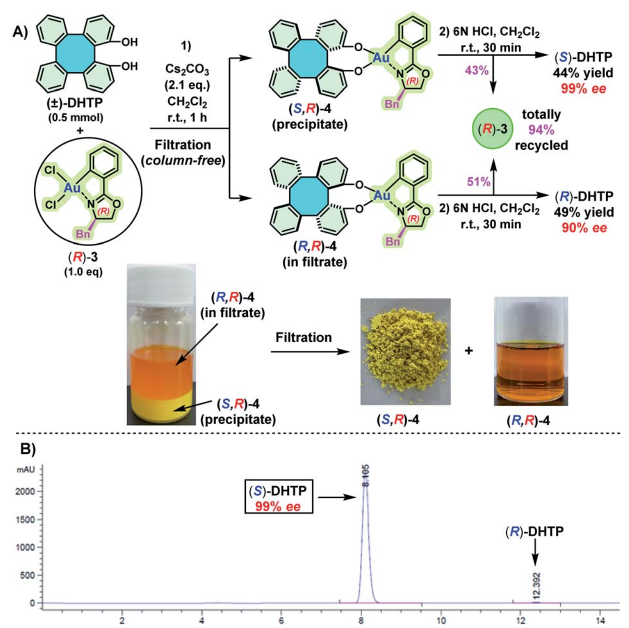
To the best of our knowledge, so far there are only two available pathways to access enantiopure (*S*)-**DHTP** and (*R*)-**DHTP**. The first pathway is the diastereomeric separation of a pair of bis-(*S*)-camphorsulfonates of (±)-**DHTP** by a conventional column chromatographic separation on silica gel (Scheme 2A).[4b] This method suffers from the use of an expensive and non-recyclable chiral resolution reagent, as well as from the tedious and time-consuming chromatographic purification of the resulting diastereomeric camphorsulfonates. The second pathway is the enantiomeric separation of (±)-**DHTP** on a chiral stationary phase by preparative high performance liquid chromatography (Scheme 2B).[10a] Although this method is straightforward, avoiding multistep reactions, its high-cost due to the use of large amounts of expensive HPLC grade solvents is definitely discouraging, not to mention the lengthy chromatographic process. Furthermore, the primary limitation of this approach is that these preparative HPLC instruments and chiral columns, are usually available only in commercial laboratories. Therefore, attempts to look for practical and reliable methods to access enantiopure (*S*)-**DHTP** and (*R*)-**DHTP** in large quantities are urgent and essential. Herein we report a newly developed approach for the optical resolution of (±)-**DHTP** by chiral gold(III) complexes (Scheme 2C). This method not only circumvents expensive and time-consuming chromatographic steps, but most importantly features noteworthy advantages including (a) the recyclability of chiral resolution reagents, (b) the feasibility of gram scale manipulation, and (c) the simplicity of the operation.



Scheme 2 Previous approaches to optical resolution of (±)-DHTP and our newly developed strategy. Bn = benzyl.

Results and discussion

We have previously demonstrated that **BINOL**s and 2,2′-biphenols can be well-chelated with chiral oxazoline-based C^N-cyclometalated gold(III) dichloride [(C^N)AuCl$_2$, C^N = 2-aryl oxazolinyl] to form *C*,*O*- and *O*,*O*′-Au^{III} chelated stable chiral gold(III) complexes, respectively.[11] Hence, we reasoned that (±)-**DHTP** might react with an enantiopure oxazoline-based C^N-cyclometalated gold(III) dichloride, resulting probably in two separable diastereomers as access to optically pure (*S*)-**DHTP** and (*R*)-**DHTP**, respectively. Our investigation commenced with the reaction between (±)-**DHTP** and enantiopure oxazoline-based cyclometalated gold(III) dichloride (*R*)-**3**.[11a] Thus, reaction of (±)-**DHTP** (0.5 mmol) with (*R*)-**3** (0.5 mmol) in the presence of Cs_2CO_3 in CH_2Cl_2 at room temperature (25 °C) gave rapidly a yellow precipitate (Scheme 3A). Interestingly, it was found that the solubility of (*S*,*R*)-**4** and (*R*,*R*)-**4** in CH_2Cl_2 was



Scheme 3 (A) Optical resolution of (±)-DHTP by using enantiopure (*R*)-3. Reaction conditions: step (1): (±)-DHTP (0.5 mmol), (*R*)-3 (0.5 mmol), Cs_2CO_3 (2.1 eq.), CH_2Cl_2 (10 mL), room temperature (25 °C), reaction time: 1 h; step (2): CH_2Cl_2 (10 mL), HCl (6 N, aq.), room temperature, reaction time: 30 min. Yield of the isolated product. (B) HPLC spectrum of the obtained (*S*)-DHTP. Bn = benzyl.

significantly different: (*S*,*R*)-**4** is almost insoluble in CH_2Cl_2, leading to the precipitate, while (*R*,*R*)-**4** showed exceptional solubility in CH_2Cl_2. The precipitate was collected by filtration and washed with H_2O and CH_2Cl_2 to give (*S*,*R*)-**4**. Subsequently, (*S*,*R*)-**4** was treated with 6 N HCl in CH_2Cl_2, followed by column chromatography to give (*S*)-**DHTP** in 44% yield and the recovered (*R*)-**3** in 43% yield.[11a] The optical purity of the obtained (*S*)-**DHTP** was determined to be 99% ee by HPLC analysis (Scheme 3B).[10a] Then, treatment of the filtrate with 6 N HCl afforded (*R*)-**DHTP** in 49% yield with 90% ee, and (*R*)-**3** was recovered in 51% yield. Notably, this optical resolution specifically depended on the use of a benzyl (Bn) substituted chiral oxazoline-based gold(III) complex, because phenyl-, isopropyl- or tertiary butyl-substituted analogs did not lead to the formation of a precipitate, therefore optical resolution could not be realized.

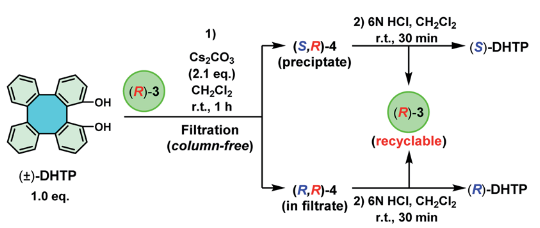
To demonstrate the scalability and practicability of this process, a 30 mmol reaction was first carried out (Table 1, entry 1). Treatment of (±)-**DHTP** (30 mmol, 10.1 g) with (*R*)-**3** (30 mmol, 15.1 g) by the standard procedure provided (*S*)-**DHTP** in 45% yield with 99% ee, (*R*)-**DHTP** in 49% yield with 88% ee, and (*R*)-**3** in 98% yield (14.8 g).

An important advantage of employing (*R*)-**3** instead of (*S*)-10-camphorsulfonyl chloride is its recyclability. Based on recovered (*R*)-**3** (14.8 g) from the 30 mmol reaction, the recyclability of (*R*)-**3** was examined. A series of resolution steps for (±)-**DHTP** in 25, 20, 15, 10 and 5 mmol quantities were carried out by using (*R*)-**3** recovered from the last step, respectively (Table 1, entries 2–6). The results showed that (*R*)-**3** could be repeatedly used for 6 cycles without any adverse effect on resolution performance to give (*S*)-**DHTP** in excellent yield (45–48%) and optical purity (99% ee), as well as in excellent recovery yield (98–99%) of (*R*)-**3** in each cycle. It is noteworthy that the 10 mmol scale resolution process, providing (*S*)-**DHTP** in 46% yield with 99% ee and (*R*)-**DHTP** in 48% yield with 96% ee, was the optimal manipulation result (Table 1, entry 5). To our delight, (*R*)-**3** was still recovered in 98% yield at the end of the 6th cycle. These results indicated that (*R*)-**3** is extremely stable during the optical resolution process and could even be promisingly reused for many more cycles.

The use of (*R*)-**3** only offered (*R*)-**DHTP** with a meager 96% ee. In order to obtain (*R*)-**DHTP** with a higher optical purity, enantiopure (*S*)-**3** was employed to perform the optical resolution of (±)-**DHTP** (Scheme 4). In the reaction of (±)-**DHTP** (10 mmol) with (*S*)-**3** (10 mmol) in the presence of Cs_2CO_3 in CH_2Cl_2 within 1 h, a yellow precipitate was similarly formed. (*R*,*S*)-**4** as the precipitate was collected by filtration, which was subsequently treated with 6 N HCl to give (*R*)-**DHTP** in excellent yield (46%) and in high optical purity (>99% ee). Complex (*S*)-**3** was recovered in 45% yield. Likewise, treatment of the filtrate containing (*S*,*S*)-**4** with 6 N HCl furnished (*S*)-**DHTP** in 52% yield with 90% ee, and (*S*)-**3** in 52% yield.

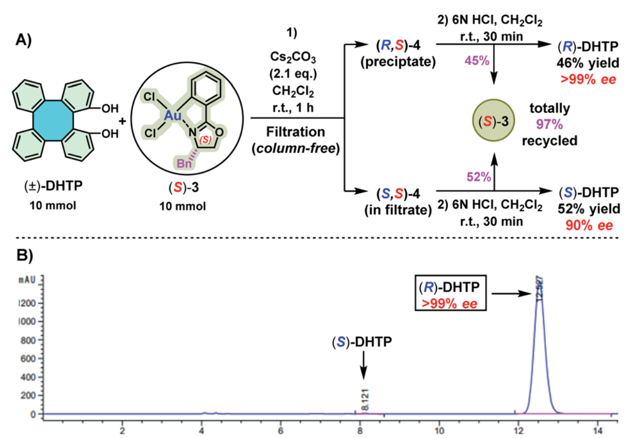
To obtain an insight into the chelated mode of (*S*)-**DHTP** and (*R*)-**DHTP** with (*S*)-**3** and (*R*)-**3**, respectively, the preparation of four **DHTP**/oxazoline Au(III) complexes (*S*,*R*)-**4**, (*R*,*S*)-**4**, (*S*,*S*)-**4** and (*R*,*R*)-**4** by using enantiopure **DHTP** and enantiopure **3** was studied (Scheme 5A). Thus, the treatment of (*S*)-**DHTP** and (*R*)-**DHTP** with (*S*)-**3** and (*R*)-**3** in the presence of Cs_2CO_3 in methanol at room temperature (25 °C) successfully afforded four diastereomers (*S*,*R*)-**4**, (*R*,*S*)-**4**, (*S*,*S*)-**4** and (*R*,*R*)-**4**, respectively, in 86–92% yields. The four resulting chiral Au(III) complexes were light, moisture, and heat insensitive. They remained intact even upon exposure to air for months. These chiral Au(III) complexes were characterized by ^{1}H and ^{13}C NMR spectroscopic studies,

Table 1 Multi-gram scale optical resolution of (±)-DHTP and recyclability experiments of (*R*)-**3** [abc]

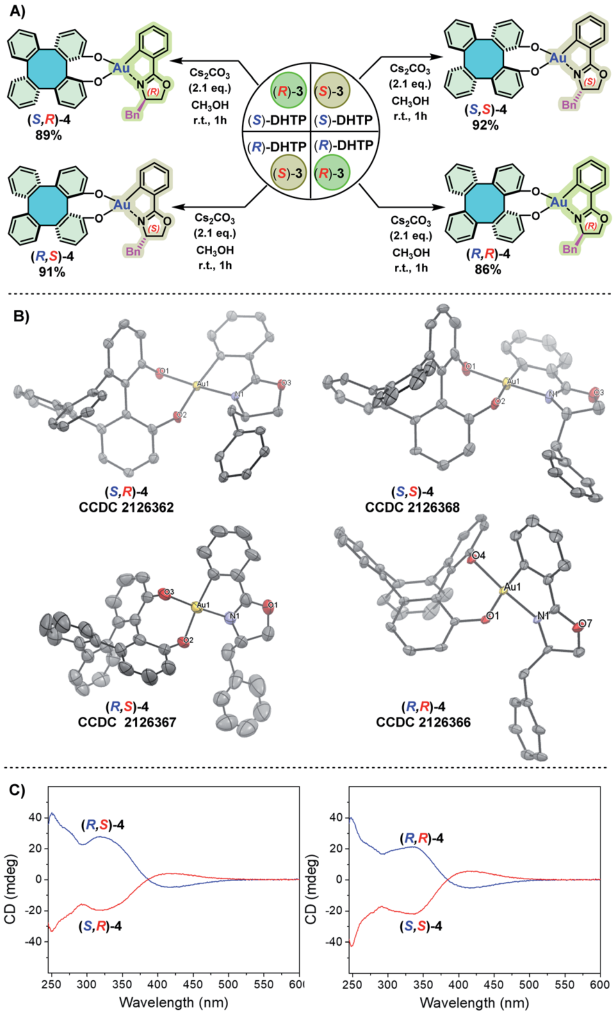


Entry	Scale of (±)-**DHTP** (mmol)	Yield and ee of (*S*)-**DHTP** Yield [ee] (%)	Yield and ee of (*R*)-**DHTP** Yield [ee] (%)	Recovery yield of (*R*)-**3** (%)
1	30	45 [99]	49 [88]	98 (*14.8 g*)
2[d]	25	47 [99]	50 [95]	99
3[d]	20	45 [99]	50 [89]	98
4[d]	15	46 [99]	49 [93]	98
5[d]	**10**	**46 [99]**	**48 [96]**	**99**
6[d]	5	48 [99]	50 [87]	98

[a] Reaction conditions: step (1): (±)-**DHTP** (1.0 eq.), (*R*)-**3** (1.0 eq.), Cs_2CO_3 (2.1 eq.), CH_2Cl_2 ([substrate] = 0.1 M), room temperature (25 °C), reaction time: 1 h; step (2): CH_2Cl_2 ([substrate] = 0.1 M), HCl (6 N, aq.), room temperature, reaction time: 30 min. [b] Yield of the isolated product. [c] ee% was determined by chiral HPLC analysis. [d] (*R*)-**3** was obtained from the last reaction cycle.



Scheme 4 (A) Optical resolution of (±)-DHTP by using enantiopure (*S*)-**3**. Reaction conditions: step (1): (±)-DHTP (10 mmol), (*S*)-**3** (10 mmol), Cs_2CO_3 (2.1 eq.), CH_2Cl_2 (100 mL), room temperature (25 °C), reaction time: 1 h; step (2): CH_2Cl_2 (50 mL), HCl (6 N, aq.), room temperature, reaction time: 30 min. Yield of the isolated product. (B) HPLC spectrum of the obtained (*R*)-DHTP. Bn = benzyl.

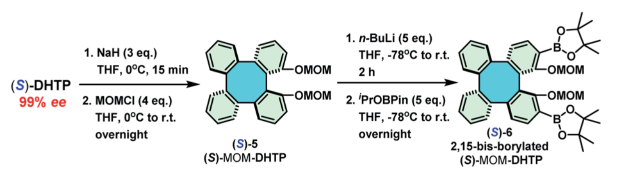


Scheme 5 (A) Synthesis of enantiopure **DHTP**/oxazoline Au(III) complexes. Reaction conditions: **DHTP** (0.1 mmol), **3** (0.11 mmol), Cs_2CO_3 (2.1 eq.), CH_3OH (2 mL), room temperature (25 °C), reaction time: 1 h. Yield of the isolated product. (B) X-ray crystal structures of (*S*,*R*)-**4**, (*R*,*S*)-**4**, (*S*,*S*)-**4** and (*R*,*R*)-**4**. Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules and H atoms are omitted for clarity. (C) Circular dichroism (CD) spectra of (*S*,*R*)-**4** and (*R*,*S*)-**4**, as well as (*S*,*S*)-**4** and (*R*,*R*)-**4** in $CHCl_3$ at a concentration of 2.0×10^{-5} M. Bn = benzyl.

and high-resolution ESI-MS. Furthermore, the configurations of (*S*,*R*)-**4**, (*R*,*S*)-**4**, (*S*,*S*)-**4** and (*R*,*R*)-**4**, all adopting an *O*,*O*′-chelating mode, were confirmed by X-ray crystallographic analyses (Scheme 5B).[12] Circular dichroism (CD) spectroscopy was carried out to give additional chiroptical evidence of these four diastereomers. The symmetry of the CD spectra clearly demonstrated the enantiomeric relationship of (*S*,*R*)-**4** and (*R*,*S*)-**4**, as well as (*S*,*S*)-**4** and (*R*,*R*)-**4** (Scheme 5C).

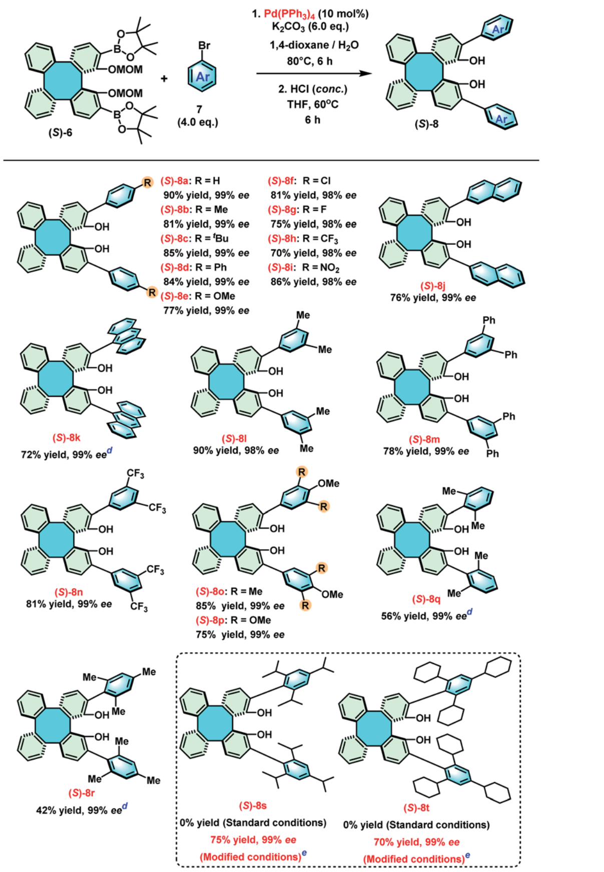
A lot of studies have demonstrated that aryl substituents at C-3 and C-3′ of the **BINOL** skeleton display significant influences towards a variety of asymmetric reactions.[13–18] For this reason, 3,3′-diaryl **BINOL**s are notably privileged skeletons for the construction of valuable chiral ligands/catalysts,[13] such as phosphoramidites,[14] phosphoric acids,[15] phosphoramides,[16] and phase-transfer catalysts.[17] However, due to the synthetic intricacy in realizing enantiopure **DHTP** in significant quantities, an efficient preparative method towards enantiopure 2,15-diaryl **DHTP**s has remained an almost unexplored territory. Consequently, only a very few examples have been reported.[10c] Inspired by the availability of a larger amount of enantiopure **DHTP**, we next turned our attention to constructing a library of 2,15-diaryl **DHTP**s as chiral ligands/catalysts. In accordance with the well-established strategy for preparing 3,3′-diaryl **BINOL**s, a key intermediate, namely, 2,15-bis-borylated (*S*)-MOM-**DHTP** [(*S*)-**6**] was synthesized (Scheme 6).[18] Thus, first the methoxymethylation of (*S*)-**DHTP** (>99% ee) by methoxymethyl chloride in the presence of NaH in THF afforded (*S*)-MOM-**DHTP** [(*S*)-**5**] in 95% yield. Subsequently, a direct *ortho*-lithiation of (*S*)-**5** by *n*-BuLi in dry THF, followed by borylation with ^{i}PrOBPin (2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) provided the key intermediate (*S*)-**6** as a white solid in 90% yield with 99% ee. Notably, the borylation process was carried out on a 20 mmol scale without difficulties.

With an ample quantity of (*S*)-**6** in hand, we started to construct the library of 2,15-diaryl **DHTP**s by Suzuki coupling reactions between (*S*)-**6** and a series of aryl bromides (Table 2).[18] The Suzuki coupling reaction of (*S*)-**6** and phenyl bromide was first performed with $Pd(PPh_3)_4$ in 1,4-dioxane/H_2O at 80 °C using K_2CO_3 as the base, whose coupling product was subsequently treated with concentrated hydrochloric acid to provide 2,15-diphenyl (*S*)-**DHTP** [(*S*)-**8a**] in 90% yield with 99% ee. Then, various 4-substituted phenyl bromides bearing either electron-donating (methyl, *t*-butyl, phenyl and methoxyl) or electron-withdrawing (Cl, F, CF_3, and NO_2) groups were employed to expand the scope of 2,15-diaryl **DHTP**s, providing (*S*)-**8b–i** with good to excellent yields (70–90%). In addition, 2-naphthyl, 9-anthryl, as well as several di- and tri-substituted aryl bromides were also found to be compatible with this coupling process, affording (*S*)-**8j–p** in 75–90% yield. It was uncovered that sterically hindered aryl bromides, such as 2,6-$(Me)_2C_6H_3Br$ and 2,4,6-$(Me)_3C_6H_2Br$, only led to (*S*)-**8q** and (*S*)-**8r** with relatively low yields (56% and 42%, respectively), and extremely sterically hindered aryl bromides, such as 2,4,6-$(^{i}Pr)_3C_6H_2Br$ and 2,4,6-$(Cy)_3C_6H_2Br$ even failed to furnish the corresponding products (*S*)-**8s** and (*S*)-**8t** under standard conditions. Nonetheless, (*S*)-**8s** and (*S*)-**8t** were obtained in good yields (75% and 70%, respectively) under a modified condition in which a catalytic system $Pd(PPh_3)_4/Pd(dba)_2/(\pm)$-**BIDIME** was employed and K_3PO_4 was used as the base in toluene at 100 °C.[18c,19,20] It has been known that the concomitant limitation in the synthesis of



Scheme 6 Synthetic routes for methoxymethylation and borylation of (*S*)-DHTP. MOM = methoxymethyl, Pin = pinacol, and ^{i}PrOBPin = 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

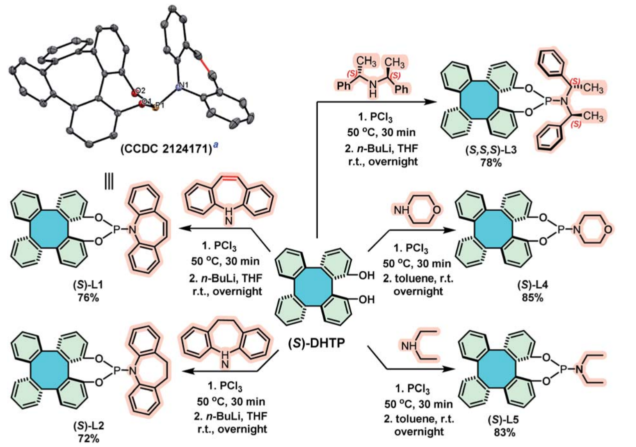
Table 2 Application in the synthesis of 2,15-diaryl DHTPs[abc]



[a] Reaction conditions: step (1): (*S*)-**6** (1 mmol), **7** (4.0 eq.), $Pd(PPh_3)_4$ (10 mol%) K_2CO_3 (6.0 eq.), 1,4-dioxane (16 mL), H_2O (4 mL), 80 °C, reaction time: 6 h; step (2): THF (10 mL), conc. HCl (2 mL), 80 °C, reaction time: 6 h. [b] Yield of the isolated product. [c] ee% was determined by chiral HPLC analysis. [d] Reaction time of step 1 : 24 h. [e] Modified conditions: step (1): (*S*)-**6** (1 mmol), **7** (4.0 eq.), $Pd(PPh_3)_4$ (5 mol%), $Pd(dba)_2$ (10 mol%), (±)-**BIDIME** (20 mol%), K_3PO_4 (6.0 eq.), toluene (20 mL), 100 °C, reaction time: 24 h; step (2): 1,4-dioxane (10 mL), conc. HCl (2 mL), 80 °C, reaction time: 24 h. **BIDIME** = 3-(*tert*-butyl)-4-(2,6-dimethoxy-phenyl)-2,3-dihydrobenzo[*d*][1,3] oxaphosphole.

enantiomerically pure 3,3′-diaryl BINOLs under either basic or acidic conditions is their potential racemization.[13a,21] However, due to the rigidity of the **DHTP**s, their racemization has never been observed. The configurations and optical purities (98–99% ee) of all **DHTP**s remained consistent throughout the synthetic process. For example, (*S*)-**8** showed no racemization even at 60 °C or 80 °C for 6 h or 24 h during the demethoxymethylation step with conc. HCl.

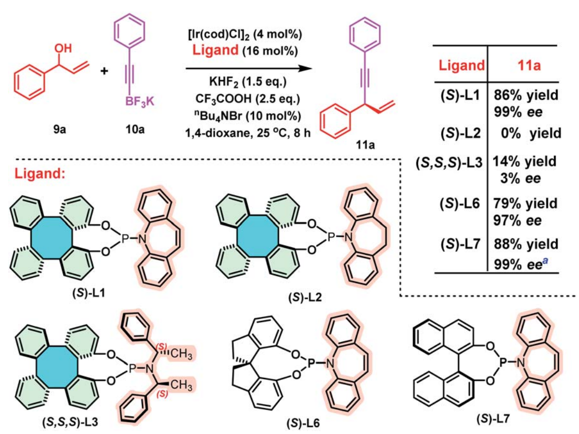
Chiral phosphoramidites have been demonstrated as highly versatile and privileged ligands in metal-catalyzed asymmetric reactions.[14] Thus, the synthesis of (*S*)-**DHTP**-derived phosphoramidite ligands was performed to further demonstrate the potential application of chiral **DHTP** in asymmetric catalysis. Treatment of enantiopure (*S*)-**DHTP** (>99% ee) with PCl_3 in the presence of Et_3N with the subsequent addition of the



Scheme 7 Synthesis of (*S*)-**DHTP** derived phosphoramidite ligands. [a] X-ray crystal structures of (*S*)-**L1**, displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

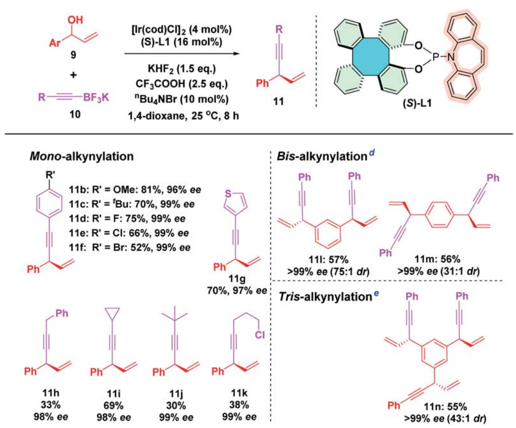
corresponding amine, phosphoramidite ligands (*S*)-**L1**, (*S*)-**L2**, (*S*,*S*,*S*)-**L3**, (*S*)-**L4** and (*S*)-**L5** were obtained in good yields (72–85%), respectively (Scheme 7).[22] In addition, the framework and absolute configuration of (P, olefin)-ligand (*S*)-**L1** were well-defined by X-ray crystallographic analysis (CCDC 2124171†).[12]

Next, we selected an iridium-catalyzed allylic alkynylation between racemic allylic alcohols and potassium alkynyl-trifluoroborates, previously reported by Carreira using **BINOL**-derived (*S*)-**L7** as the chiral ligand, to test the efficiency of (*S*)-**DHTP**-derived phosphoramidite ligands (Scheme 8).[14c,23] Employing (*S*)-**L1** as the chiral ligand, the iridium-catalyzed allylic alkynylation of **9a** and **10a** afforded **11a** in 86% yield with 99% ee. However, **11a** was not obtained when (*S*)-**L2** was used as the ligand under the same conditions. (*S*,*S*,*S*)-**L3** afforded **11a** only in 14% yield with 3% ee. These preliminary results



Scheme 8 Iridium-catalyzed enantioselective allylic alkynylation. Reaction conditions: **9a** (0.2 mmol, 1.0 eq.), **10a** (0.3 mmol, 1.5 eq.), $[Ir(cod)Cl]_2$ (4 mol%), ligand (16 mol%), 1,4-dioxane (0.4 mL), KHF_2 (1.5 eq.), CF_3COOH (2.5 eq.), $^nBu_4NBr$ (10 mol%). Yield of the isolated product. ee% was determined by chiral HPLC analysis. [a] Reaction time: 6 h (see ref. 23).

Table 3 Scope of the enantioselective allylic alkynylation[abc]



[a] Reaction conditions: **9** (0.4 mmol, 1.0 eq.), **10** (0.6 mmol, 1.5 eq.), 1,4-dioxane (0.8 mL). [b] Yield of the isolated product. [c] ee% was determined by chiral HPLC analysis. [d] **9** (0.4 mmol, 1.0 eq.), **10** (1.2 mmol, 3.0 eq.), $[Ir(cod)Cl]_2$ (8 mol%), (*S*)-**L1** (32 mol%), 1,4-dioxane (1.6 mL), KHF_2 (3.0 eq.), CF_3COOH (5.0 eq.), $^nBu_4NBr$ (20 mol%). [e] **9** (0.4 mmol, 1.0 eq.), **10** (1.8 mmol, 4.5 eq.), $[Ir(cod)Cl]_2$ (12 mol%), (*S*)-**L1** (48 mol%), 1,4-dioxane (2.4 mL), KHF_2 (4.5 eq.), CF_3COOH (7.5 eq.), $^nBu_4NBr$ (30 mol%).

indicated that the olefin moiety of the amine might be essential. When a **SPINOL**-based phosphoramidite (*S*)-**L6** was used as the chiral ligand, slightly lower yield (79%) and enantioselectivity (97% ee) of **11a** were achieved, as compared with those resulting from (*S*)-**L1**. For comparison, Carreira reported that the **BINOL**-derived phosphoramidite (*S*)-**L7** gave **11a** in 88% yield with 99% ee.[23]

The results shown by (*S*)-**L1** and **BINOL**-derived (*S*)-**L7** encouraged us to expand the substrate scope to further evaluate the efficiency of (*S*)-**L1** in this iridium-catalyzed enantioselective allylic alkynylation (Table 3). To our delight, a range of phenyl alkynyltrifluoroborates bearing either electron-donating (methoxyl and *t*-butyl) or electron-withdrawing (F, Cl, and Br) groups reacted smoothly under the Ir/(*S*)-**L1** catalytic system, affording the corresponding products **11b–f** in good yields and excellent enantioselectivities. In addition, heteroaromatic (3-thienyl) and aliphatic alkynyltrifluoroborates also gave products **11g–k** in high enantioselectivities although the yields were relatively low. It is noteworthy that substrates containing two allylic alcohol moieties proceeded smoothly, leading to the formation of the corresponding products **11l** and **11m** in good yields (57% and 56%) and in 99% ee. Moreover, a triallylic alcohol substrate also afforded the tris-alkynylation product **11n** containing three chiral centers in good yield (55%) and excellent stereoselectivity (>99% ee with 43 : 1 dr). Even though relatively low yields of some cases were obtained, the high level of enantiocontrol indicates that (*S*)-**L1** indeed exhibits excellent efficiency as **BINOL**-derived phosphoramidite (*S*)-**L7** towards the enantioselective iridium-catalyzed allylic alkynylation reaction. The comparison of X-ray crystallographic structural data of (*S*)-**L1** (CCDC 2124171†) with those of **SPINOL**-derived (*S*)-**L6** (CCDC 1439599) and **BINOL**-derived (*S*)-**L7** (CCDC 694272) indicates that (*S*)-**L1** has a larger dihedral angle (54.6°) between the two phenol rings than the corresponding angles of (*S*)-**L6** (53.2°) and (*S*)-**L7** (53.1°).[24] The larger dihedral angle and the rigid skeleton of tetraphenylene might render (*S*)-**L1** rather sensitive towards steric repulsion from the substrate, thereby leading to excellent enantiocontrol. This outcome points to the prospect that (*S*)-**L1** might be a fine alternative to **BINOL**-derived (*S*)-**L7** in asymmetric catalysis.

Conclusions

In summary, we have established a novel approach to optical resolution of (±)-1,16-dihydroxytetraphenylene (**DHTP**) using chiral gold(III) complexes. This efficient and reliable method can provide (*S*)-**DHTP** and (*R*)-**DHTP** in large quantities. Accordingly, a library of 2,15-diaryl (*S*)-**DHTPs** and several (*S*)-**DHTP**-derived phosphoramidite ligands were synthesized for the first time. The outstanding performance of (*S*)-**DHTP**-derived phosphoramidite ligands was demonstrated by an iridium-catalyzed asymmetric allylic alkynylation reaction. It is envisioned that this practical and scalable approach to optically pure **DHTP** and well-established synthesis of 2,15-diaryl (*S*)-**DHTPs** will open a new synthetic avenue, leading to further development in the application of chiral **DHTP**-derived ligands/catalysts. In this connection, preparations of more (*S*)-**DHTP**-derived mono- and bis-phosphine ligands, as well as chiral phosphoric acid catalysts are currently underway in our laboratory.

Data availability

All experimental and characterization data, as well as NMR spectra are available in the ESI.† Crystallographic data for compounds (*S*)-**L1**, (*S*,*R*)-**4**, (*R*,*R*)-**4**, (*R*,*S*)-**4** and (*S*,*S*)-**4** have been deposited in the Cambridge Crystallographic Data Centre under accession numbers CCDC 2124171, 2126362, 2126366–2126368.†

Author contributions

J.-F. C. and H. N. C. W. conceived the project. J.-F. C. and J. G. performed the experimental work. H.-R. M., W.-B. X. and L. F. synthesized some starting materials, and collected and analysed the spectroscopic data. J.-F. C., H. N. C. W. and Y.-Y. Z. wrote the manuscript. All of the authors discussed the results and contributed to the preparation of the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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