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# Synthesis and Application of Substituted-1,16-dihydroxytetraphenylenes in Catalytic Asymmetric Allylboration of Ketones

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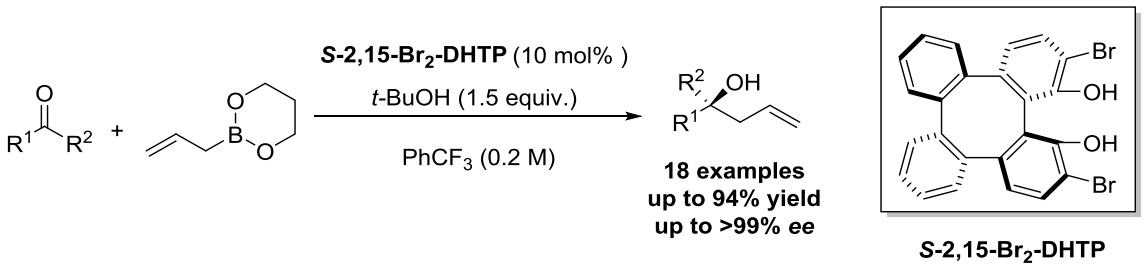



## Abstract

The synthesis and application of a newly designed $C_2$-symmetric chiral substituted-1,16-dihedroxytetraphenylenes (DHTP) is reported. Efficient syntheses of enantiopure substituted-DHTP were accomplished, and these enantiopure

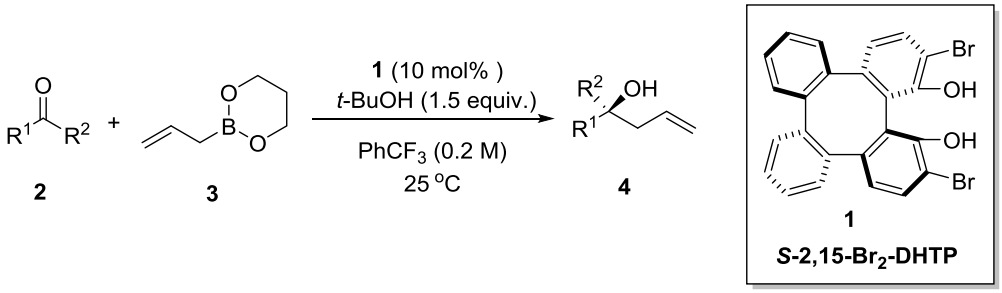
compounds were used as organocatalysts in asymmetric allylboration of ketones under very mild conditions. Accordingly, several tertiary alcohols were generated in moderate to good yields with up to 99% *ee* by using the catalyst (*S*)-2,15-$Br_2$-DHTP. A gram-scale reaction was achieved in 99% yield with 96% *ee*.

## Introduction

The development of novel chiral catalysts has become a very important task in the catalytic asymmetric reactions.[1] Asymmetric organocatalysis has attracted wide interest over the past two decades, especially due to its advantages of environmentally benign, non-toxic nature, and the easy structural modification of organocatalysts' scaffolds.[2] Organocatalysts derived from chiral biphenols are becoming increasingly versatile catalysts, and have been applied to catalyze a lot of asymmetric transformations.[3] Tetraphenylene with a distinct saddle-shaped framework was proved to be a non-planar molecule.[4] The stable and rigid backbone of tetraphenylene has been verified to be a new type of chiral ligands in asymmetric catalysis.[5] However, the limited structure diversity of tetraphenylene, partly due to the lack of effective synthetic method, often hinders their application.

We now report the synthesis of a new $C_2$-symmetry chiral 2,15-substituted and 4,13-substituted 1,16-dihydroxytetraphenylene (DHTP) that shows significantly influence on the catalytic activity by adjusting both the steric and electronic properties with different substituents. We next explored their

application in the asymmetric allylboration of ketones. These reactions proceed smoothly under mild reaction conditions with moderate to excellent enantioselectivities (57-99% *ee*), as can be seen in Scheme 1.

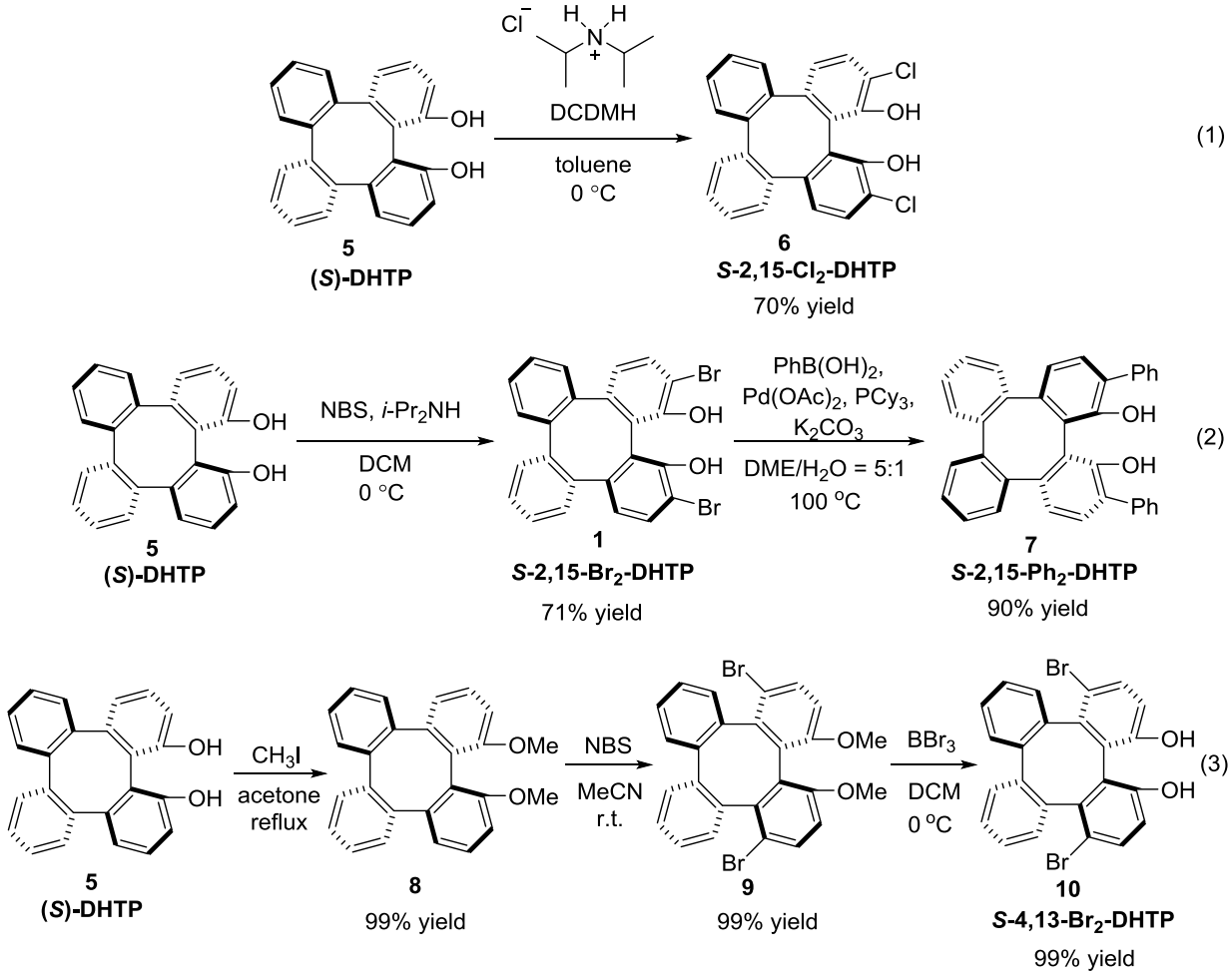



**Scheme 1.** Catalyst **1**-Catalyzed Asymmetric Allylboration of Ketones

## Results and Discussion

Intrigued by the results of 3,3'-substituted BINOLs, we envisioned that by introducing electron-withdrawing groups or bulky groups at the 2,15-positions or 4,13-positions of (*S*)-DHTP (**5**), we might be able to improve the catalyst reactivity for asymmetric reactions. As illustrated in Scheme 2, the synthesis of enantiopure (*S*)-substituted-DHTP (**1**, **6**, **7**, and **10**) started from **5**. (*S*)-2,15-$Cl_2$-DHTP **6** was prepared in 70% yield by chlorination of **5** according to the reported procedures (Scheme 2, eq 1).[6] The bromination of **5** with *N*-bromosuccinimide (NBS) in DCM at 0 °C gave the (*S*)-2,15-$Br_2$-DHTP **1** in 71% yield with high regioselectivity. Then, the Pd-catalyzed cross-coupling reaction of **1** with phenylboronic acid afforded (*S*)-2,15-$Ph_2$-DHTP **7** in 90% yield (Scheme 2, eq 2). In addition, this method could offer an easy access to the disubstituted 2,15-aryl-DHTP. Compound **8** was obtained in nearly quantitative yield by methylation of **5** with iodomethane. Subsequent bomination of **8** with NBS in MeCN at room temperature afforded compound **9** in

quantitative yield with excellent regioselectivity, which was allowed to undergo demethylation with boron tribromide ($BBr_3$) to furnish the desired product (*S*)-4,13-$Br_2$-DHTP **10** in quantitative yield (Scheme 2, eq 3). Starting from compounds **1** and **10**, coupling reactions using different boronic acids could give a series of chiral aryl-substituted DHTP following the aforementioned protocol. At the same time, (±)-2,15-$Br_2$-DHTP and (±)-4,13-$Br_2$-DHTP were readily prepared from (±)-DHTP, making use of the method as described above. The relative configuration of (±)-2,15-$Br_2$-DHTP (CCDC 1880573) and (±)-4,13-$Br_2$-DHTP (CCDC 1880574) were determined by X-ray crystallographic analyses (see the Supporting Information for the relative configuration assignments).

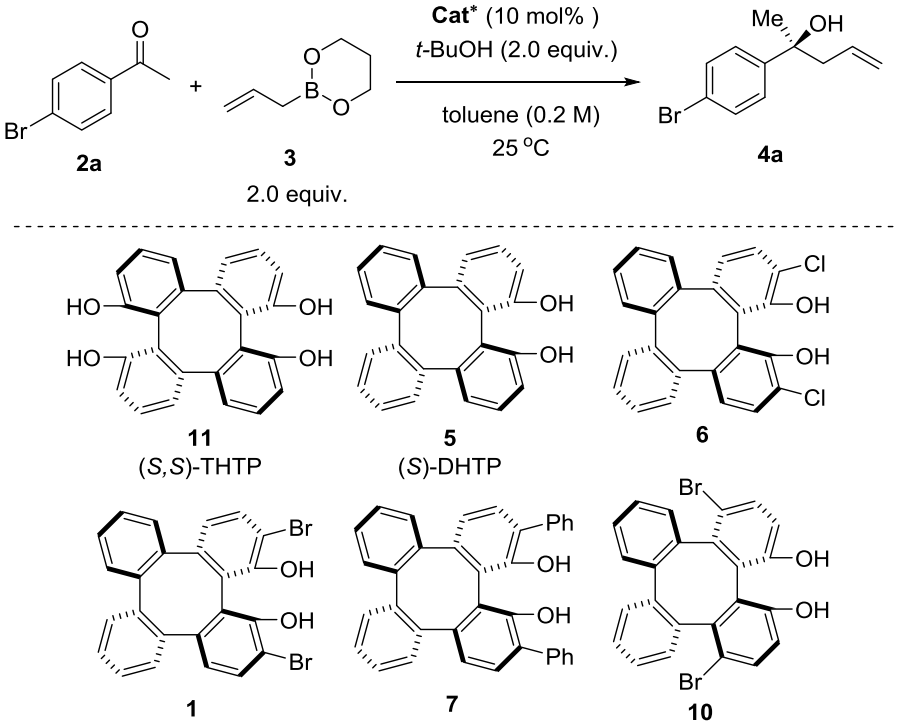



**Scheme 2.** Synthesis of Substituted-DHTP Catalysts

With the new chiral catalysts in hand, we next evaluated the enantioselective allylation of ketones. Asymmetric allylboration of carbonyl compounds using Lewis and Brønsted acid catalysts is an efficient method to synthesize chiral tertiary homoallylic alcohols.[7] Hoveyda reported a class of easily modifiable aminophenol catalysts that could catalyze asymmetric allylation of imines and carbonyls.[8] Research groups of Chong,[9] Schaus,[10] Senanayake,[11] and Szabó[12] employed BINOL derivatives for enantioselective allylboration. In particular, Schaus *et al.* reported the asymmetric allylboration of ketones with acyclic[10a] or cyclic[10b] allylboronates using (*S*)-3,3'-$Br_2$-BINOL as the most effective catalyst through a crucial ligand exchange step[10c], and all electron-rich and electron-deficient aromatic ketones and heteroaromatic ketones proceeded with good results. Inspired by their work, we proceeded to explore the asymmetric allylboration of acetophenone **2a** and *B*-allyl-1,3,2-dioxaboriane **3** as a model reaction in dry toluene at room temperature by using 10 mol% chiral tetraphenylene derivatives **5**, **6**, **1**, **7**, **10**, and (*S,S*)-THTP **11** as catalysts (Table 1). Our results indicated that the use of **11** and **5** gave only low yields (33%-54%) and very poor enantioselectivities (Table 1, entries 1 and 2). To our delight, when the catalyst was replaced by **6**, the model reaction proceeded smoothly to afford the desired product **4a** with 88% *ee* and in 54% yield, indicating that 2,15-substituents have considerable impact on the stereselectivity (Table 1, entry 3). Furthermore, investigation of the substituent effect of the catalysts disclosed that the catalyst bearing two Br group at 2,15-position was the most optimal catalyst in terms of both reactivity and enantioselectivity (Table 1, entries 4-6). With 10 mol% of **1**, the

corresponding product **4a** was generated in 91% yield and 94% *ee* (Table 1, entries 4). When the reaction was carried out in 1 mL toluene, the yield and enantioselectivity dropped slightly (Table 1, entry 7 *vs* entry 4).

**Table 1.** Optimization of the Reaction Conditions[a]




| entry | **Cat*** | solvent | time (h) | yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | **11** | toluene | 48 | 33 | 7 |
| 2 | **5** | toluene | 48 | 54 | 8 |
| 3 | **6** | toluene | 48 | 54 | 88 |
| 4 | **1** | toluene | 48 | 91 | 94 |
| 5 | **7** | toluene | 48 | 62 | 53 |
| 6 | **10** | toluene | 24 | 25 | 50 |
| 7[d] | **1** | toluene | 62 | 67 | 88 |
| 8 | **1** | DCM | 30 | 92 | 88 |
| 9 | **1** | THF | 24 | 16 | 34 |
| 10 | **1** | MeCN | 20 | 33 | 32 |
| 11 | **1** | o-xylene | 48 | 75 | 92 |

| | | | | | |
|---|---|---|---|---|---|
| 12 | **1** | PhCl | 48 | 71 | 89 |
| 13 | **1** | $PhCF_3$ | 48 | 79 | 97 |
| 14[e] | **1** | $PhCF_3$ | 48 | 92 | 98 |
| 15[e,f] | 1 | $PhCF_3$ | 72 | 86 | 97 |
| 16[e,g] | **1** | $PhCF_3$ | 48 | 86 | 93 |
| 17[e,h] | **1** | $PhCF_3$ | 48 | 69 | 93 |
| 18[e,i] | ***R*-2,15-$Br_2$ -DHTP** | $PhCF_3$ | 48 | 97 | -96 |

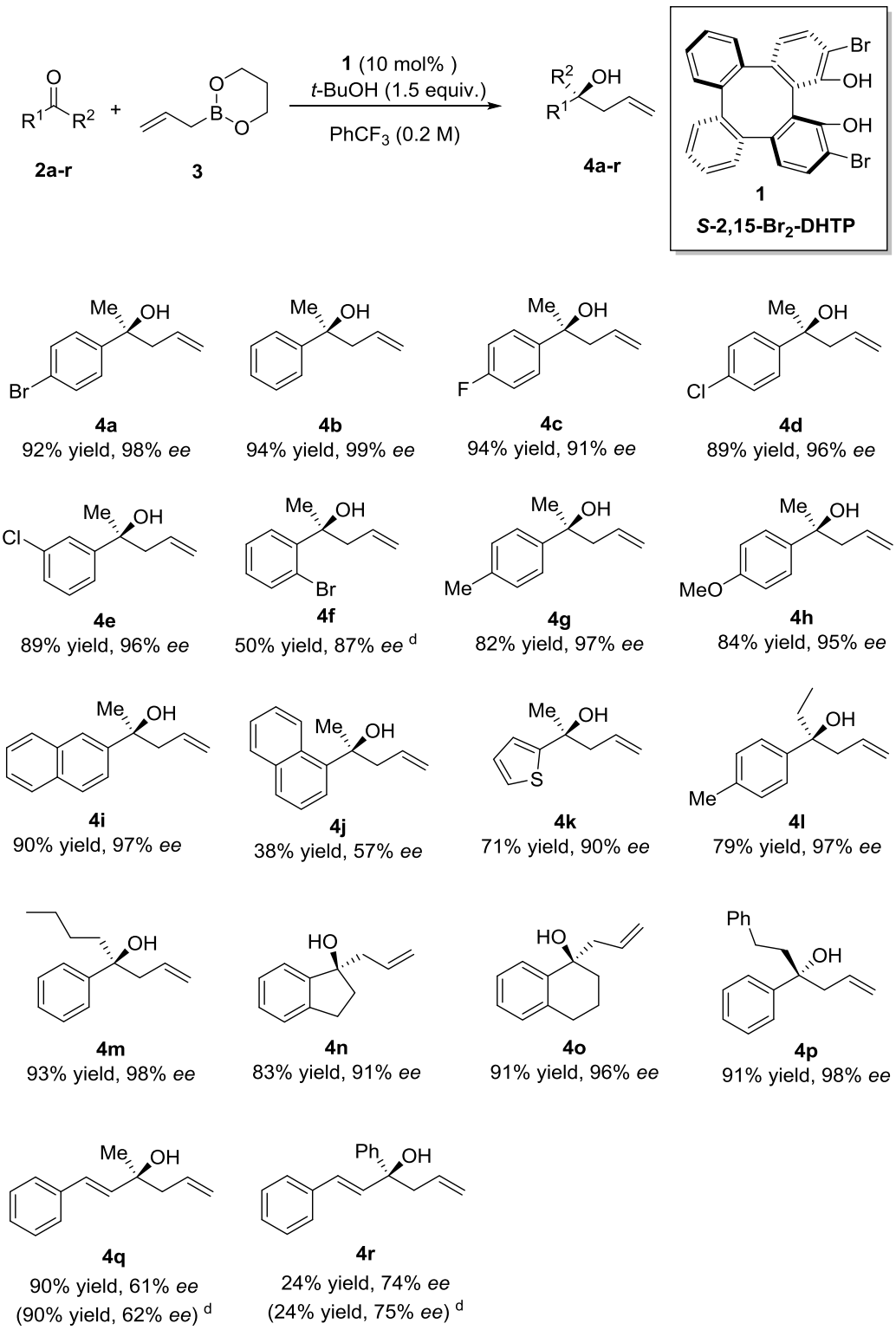
[a]Unless otherwise stated, all reactions were carried out with **2a** (0.1 mmol), *B*-allyl-1,3,2-dioxaboriane **3** (0.2 mmol), catalyst (0.01 mmol), *t*-BuOH (0.2 mmol), and dry solvent (0.5 mL) being stirred at 25 °C under $N_2$ atmosphere. [b]Isolated yield. [c]The *ee* values were determined by chiral HPLC. [d]With toluene (1.0 mL). [e]With *t*-BuOH (0.15 mmol). [f]At 0 °C. [g]At 40 °C. [h]With 5 mol% catalyst **1** as catalyst. [i]With 10 mol% ***R*-2,15-$Br_2$-DHTP** as catalyst.

Further screening of solvents indicated that the reaction media had a remarkable impact on the catalytic effects (Table 1, entries 8-13). Chlorinated solvents such as dichloromethane led to a slightly decreased enantioselectivity (Table 1, entry 8). Both the yield and selectivity were decreased significantly when a polar solvent such as THF or MeCN was used (Table 1, entries 9 and 10). Nonpolar solvents such as $PhCF_3$, PhCl and *o*-xylene appeared to be beneficial (Table 1, entries 11-13), and $PhCF_3$ was the best solvent for the reaction. An improved yield was obtained when 1.5 equiv. of *t*-BuOH was employed, and the reaction was achieved in 92% yield with 98% *ee* (Table 1, entry 14). Meanwhile, varying the reaction temperature with catalyst **1** did not improve the yield and selectivity (Table 1, entries 15 and 16). When the catalyst

loading was decreased to 5 mol%, the desired product was obtained in 69% yield with 93% *ee* (Table 1, entry 17). Fortunately, catalyst **1** could be easily recovered in 90% yield by means of flash chromatography after the reaction，and could be reused without any loss in activity. Meanwhile, the opposite enantiomer of (*S*)-**4a** was formed in 97% yield with -96% *ee* using ***R*-2,15-Br$_2$-DHTP** as the chiral catalyst (Table 1, entry 18). Thus, the optimized experimental conditions were as follows: 10 mol% **1** and 1.5 equiv. *t*-BuOH in toluene (0.2 M) at 25 °C. Fortunately, catalyst **1** could be easily recovered in 90% yield by means of flash chromatography after the reaction，and could be reused without any loss in activity.

With the optimal reaction conditions in hand, the substrate scope of this asymmetric reaction was investigated and the results were summarized in Scheme 3. Reaction of acetophenone **2b** with **3** afforded product **4b** in 94% yield with >99% *ee* (Scheme 3, **4b**). Aryl-substituted ketones, including those with an electron-withdrawing (Scheme 3, **2a, 2c, 2d,** and **2e**) or electron-donating (Scheme 3, **2g** and **2h**) substituent undergo efficient enantioselective addition. The *para*- and *meta*-substituted aryl ketones were suitable for the reaction, affording the corresponding products in good yields (82-94%) with excellent enantioselectivities (91-99% *ee*) (Scheme 3, **4a**, **4c**, **4d**, **4e**, **4g**, and **4h**), but the catalytic system was sensitive to the steric bulk of the substrates, specifically *ortho*-substituted ketone **2f** and 1-naphthyl ketone **2j**, leading to dramatically diminished yields and enantioselectivities (Scheme 3, **4f** and **4j**). In addition, ring-fused naphthyl ketone **2i** and heteroaromatic

thiophene ketone **2k** could also afford their corresponding products with moderate to good yield and moderate to excellent enantioselectivities (Scheme 3, **4i** and **4k**). To our delight, aryl ketones that contain a larger alkyl unit (Scheme 3, **2l** and **2m**), cyclic ketones (Scheme 3, **2n** and **2o**) were also tolerated in the reaction system, giving desired products with 79-93% yield and 91-98% *ee*. The substrate **2p** reacted smoothly with **3** to generate the desired product **4p** in 96% yield and 98% *ee* (Scheme 3, **4p**). In asymmetric allylbortaion of ketones, our designed catalyst **1** ((*S*)-2,15-$Br_2$-DHTP) did not achieve better results than 3,3'-$Br_2$-BINOL which was reported by Schaus' group.[10b] But in some cases, (*S*)-2,15-$Br_2$-DHTP shows similar catalytic activity as 3,3'-$Br_2$-BINOL in asymmetric allylboration reactions (product **4a** and **4b**), and it is a useful alternative to the corresponding BINOL catalysts. Furthermore, products from aryl ketones that contain an alkenyl group were formed with moderate results (Scheme 3, **4q** 90% yield, 61% *ee* and **4r** 24% yield, 74% *ee*), and similar results were achieved when additional catalyst was used (Scheme 3, **4q** 90% yield, 62% *ee* and **4r** 24% yield, 75% *ee*). The absolute configuration of all the products was determined by comparison with literature data.

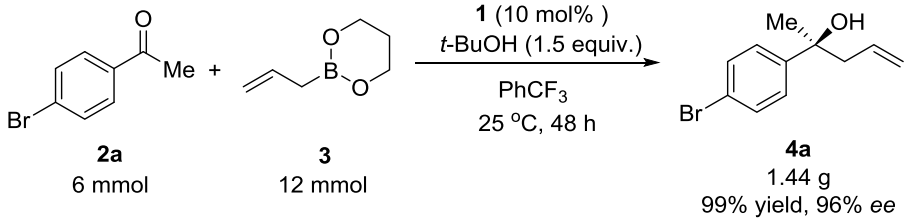



**Scheme 3.** Substrate Scope in the Catalytic Asymmetric Allylboration of Ketones[a,b,c]

[a]Unless otherwise noted, all reactions were carried out with ketone **2a-r** (0.1 mmol), *B*-allyl-1,3,2-dioxaboriane **3** (0.2 mmol), catalyst **1** (0.01 mmol), *t*-BuOH (0.15 mmol), and dry $PhCF_3$ (0.5 mL) being stirred at 25 °C under $N_2$

atmosphere for 48 h-72 h. [b]Isolated yield. [c]The *ee* values were determined by chiral HPLC. [d]With 0.02 mmol catalyst **1**.

To demonstrate the synthetic utility of our reaction, a gram-scale allylboration of acetophenone **2a** was performed under standard conditions. Thus,1.44 g of **4a** was obtained with a similar yield and enantioselectivity (Scheme 4), indicating that the present methodology is amenable to large scale synthesis.




**Scheme 4.** Gram-scale reaction

## Conclusion

In conclusion, a new class of chiral substituted-1,16-dihedroxytetraphenylenes (*S*)-2,15-$Br_2$-DHTP **1**, (*S*)-2,15-$Cl_2$-DHTP **6**, (*S*)-2,15-$Ph_2$-DHTP **7**, (*S*)-4,13-$Br_2$-DHTP **10** has been successfully synthesized. The optimial catalyst (*S*)-2,15-$Br_2$-DHTP **1** provided moderate to high yield and good enantioselectivities for the asymmetric allylboration of ketones under mild reaction conditions with a broad range of aromatic ketones. Further work using (*S*)-2,15-$Br_2$-DHTP **1** as an organocatalyst or a chiral ligand for other catalytic asymmetric C-C bond-forming reactions is in progress in our laboratories.

## EXPERIMENTAL SECTION

**General Information.** Chiral HPLC analysis was recorded on a Shimadzu HPLC

System using a Chiralpak® IC, Chiralpak® AD-H, Chiralcel® OD-H or Chiralcel® OJ-H column. Optical rotations were recorded on an Insmark polarimeter. $^{1}$H NMR spectra were measured on a 400 MHz or 600 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constants in hertz (Hz), integration, assignment. $^{13}$C NMR spectra were measured at 100 MHz or 150 MHz. Chemical shift are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 77.16). High-resolution mass spectra (HRMS) were recorded with a Thermo Fisher Scientific LTQ FT Ultra (ESI) mass spectrometer, Agilent Technologies 6224 TOF LC/MS spectrometer or Bruker Daltonics FTMS-7 mass spectrometer. Low-resolution mass spectrometry (LRMS) were measured on an Agilent Single Quad 1260 LC-MS. Flash chromatography (FC) was performed using silica gel (300-400 mesh). All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques. Commercially available ketones **2a-r** were used as received. The starting material of *B*-allyl-1,3,2-dioxaborinane **3** was prepared according to literature procedure.[10b] (*S,S*)-1,8,9,16-tetrahydroxytetraphenylene **12** ((*S,S*)-THTP) and (*S*)-1,16-dihydroxy tetraphenylene **5** ((*S*)-DHTP) were prepared according to the literature.[5c]

*Synthesis of (S)-2,15-dichlorotetraphenylene-1,16-diol (**6**).*[6] To a solution of (*S*)-DHTP **5** (33.6 mg, 0.1 mmol), catalyst diisopropylamine hydrochloride (1.3 mg, 0.01 mmol, 10 mol%) in toluene (2 mL) was added 1,3-dichloro-5,5-

dimethylhydantoin (DCDMH, 39.4 mg, 0.2 mmol, 2.0 equiv.) at 0 $^{o}$C in the absence of light. The mixture was stirred at 0 $^{o}$C for 12 h and quenched by saturated aqueous $Na_2SO_3$ (5 mL). The solution was diluted with water (5 mL) and extrated with EtOAc (3×10 mL). The combined organic extracts were washed with brine, dried with anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give the compound **6** (28.4 mg, 70% yield) as a colorless solid. mp 212-213 $^{o}$C. HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) $t_R$ (major) = 6.64 min, $t_R$ (minor) = 7.58 min, *ee* = 99%; $[\alpha]_D^{27}$ = 39.2 (*c* 1.0, $CH_2Cl_2$). *Data is consistent with the known racemic compound reported in the literature.*[6] $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 8H), 7.12-7.10 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 5.49 (s, 2H); $^{13}$C {$^1$H} NMR (150 MHz, $CDCl_3$) δ 148.2, 142.9, 141.2, 140.3, 129.3, 128.8, 128.2, 127.9, 127.6, 123.5, 122.2, 119.3; HRMS (ESI) calcd. for $C_{24}H_{13}Cl_2O_2$ ($[M-H]^-$): 403.0283, found: 403.0298.

*Synthesis of (S)-2,15-dibromotetraphenylene-1,16-diol (**1**).* To a solution of (*S*)-DHTP **5** (67.3 mg, 0.2 mmol) and catalyst diisopropylamine (2.0 mg, 0.01 mmol, 10 mol%) in $CH_2Cl_2$ (100 mL) at 0 °C was added dropwise a solution of *N*-bromosuccinimide (NBS, 72.9 mg, 0.41 mmol, 2.05 equiv.) in $CH_2Cl_2$ (100 mL) for 12 h in the absence of light. Immediately after the addition, the reaction mixture was quenched with saturated aqueous $Na_2SO_3$ (10 mL). The solution was diluted with water (15 mL) and the organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined extracts were washed

with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/$CH_2Cl_2$ = 1:1) to afford compound **1** (70.2 mg, 71% yield) as a colorless solid. mp 222-224 °C. HPLC (Chiralpak IC, hexane/*i*-PrOH = 90:10, flow rate 1.0 mL/min, λ = 254 nm) $t_R$ (major) = 5.66 min, $t_R$ (minor) = 7.73 min, *ee* = 99%; $[\alpha]_D^{27}$ = 43.4 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.31-7.29 (m, 4H), 7.25-7.23 (m, 2H), 7.13-7.11 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 2H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) δ 149.1, 143.6, 141.1, 140.3, 131.9, 129.3, 128.2, 127.9, 127.6, 123.5, 122.8, 109.5; HRMS (DART) calcd. for $C_{24}H_{14}Br_2O_2$ ($M^+$): 491.9355, found: 491.9355.

*Synthesis of (S)-2,15-diphenyltetraphenylene-1,16-diol (**7**).* A mixture of compound **1** (74.0 mg, 0.15 mmol), phenylboronic acid (109.7 mg, 0.9 mmol), and $K_2CO_3$ (125 mg, 0.9 mmol) in DME (5 mL) and $H_2O$ (1 mL) were placed in a 25 mL Schlenk tube equipped with a sealed cap. The mixture was degassed through a freeze-pump-thaw cycle (three times). Then $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) and tricyclohexyl phosphine ($PCy_3$, 10.5 mg, 0.0375 mmol) were added under an nitrogen atmosphere. The resulting suspension was heated at 100 °C for 24 h. After evaporation under reduced pressure, the residue was purified by flash chromatography (petroleum ether/EtOAc = 10:1) to give compound **7** (66.0 mg, 90% yield) as a colorless solid. mp 138-140 °C. HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R$ (minor) = 4.93 min, $t_R$ (major) = 6.17 min, *ee* = 99%; $[\alpha]_D^{27}$ = 84.2 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 4H), 7.40 (t, *J* = 7.2 Hz, 4H), 7.32-7.17

(m, 12H), 6.90 (d, *J* = 7.2 Hz, 2H), 5.25 (s, 2H); $^{13}C$ {$^{1}H$} NMR (100 MHz, $CDCl_3$) δ 149.2, 143.8, 141.5, 141.1, 137.4, 130.6, 129.4, 129.3, 128.7, 128.3, 127.7, 127.6, 127.5, 127.4, 122.3, 121.8; HRMS (DART) calcd. for $C_{36}H_{23}O_2$ ($[M-H]^-$): 487.1704, found: 487.1696.

*Synthesis of (S)-1,16-dimethoxytetraphenylene (**8**).* Compound **5** (336.4 mg, 1 mmol) and $K_2CO_3$ (829.3 mg, 6 mmol) were dissolved in acetone (20 mL), and iodomethane (0.4 mL, 6 mmol) was added in one portion. The resulting mixture was heated under reflux for 24 h. The mixture was allowed to cool to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 20:1) to give compound **8** (363.0 mg, 99% yield) as a colorless solid. mp 235-236 °C. $[\alpha]_D^{27}$ = 6.2 (*c* 1.0, $CH_2Cl_2$). *Data is consistent with the known racemic compound reported in the literature.*[5c] $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 8H), 7.13-7.09 (m, 2H), 6.80 (dd, *J* = 14.0, 10.8 Hz, 2H), 3.68 (s, 6H); MS (ESI): *m/z* = 365.2 $[C_{26}H_{20}O_2+H]^+$ ; 387.1 $[C_{26}H_{20}O_2+Na]^+$.

*Synthesis of (S)-1,16-dimethoxy-4,13-dibromotetraphenylene (**9**).* To a solution of compound **5** (36.4 mg, 0.1 mmol) in $CH_3CN$ (10 mL) was added *N*-bromosuccinimide (NBS, 71.2 mg, 0.4 mmol, 4.0 equiv.) in one portion and the mixture was stirred at room temperature for 12 h. The resulting mixture was quenched by saturated aqueous $Na_2SO_3$ (10 mL), and the volatiles were removed under reduced pressure. The aqueous solution was extracted with $CH_2Cl_2$, and the combined extracts were washed with brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated under vacuum. The residue was

purified by flash chromatography (petroleum ether/$CH_2Cl_2$ = 3:1) to give compound **9** (52.0 mg, 99% yield). mp 270-272 °C. $[\alpha]_D^{27}$ = 19.4 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.8 Hz, 2H), 7.30-7.23 (m, 6H), 7.18-7.16 (m, 2H), 6.67 (t, *J* = 8.8 Hz, 2H), 3.69 (s, 6H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) δ 155.8, 142.0, 140.9, 139.8, 132.4, 129.0, 128.4, 128.0, 127.9, 126.8, 114.1, 111.9, 56.4; HRMS (DART) calcd. for $C_{26}H_{19}O_2Br_2$ ($[M+H]^+$): 520.9746, found: 520.9741.

*Synthesis of (S)-4,13-dibromotetraphenylene-1,16-diol (**10**).* To a suspension of compound **9** (52.2 mg, 0.1 mmol) in $CH_2Cl_2$ (10 mL) was added a 1.0 M $CH_2Cl_2$ solution of boron tribromide ($BBr_3$, 2 mL, 2 mmol) dropwise at 0 °C. The reaction mixture was stirred overnight at room temperature and a clear brownish red solution was obtained. The reaction mixture was quenched with water (10 mL) at 0 °C, and then the volatiles were evaporated under reduced pressure. Colorless solid that precipitated was dissolved by addition of ethyl acetate (20 mL). The organic layer was separated and the residual aqueous layer was extracted with ethyl acetate. The combined organic phase was washed with saturated $NaHCO_3$, brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (petroleum ether/EtOAc = 2:1) to give compound **10** (49.0 mg, 99% yield). mp 280-282 °C. HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 80:20, flow rate 1.0 mL/min, λ = 254 nm) $t_R$ (major) = 10.72 min, $t_R$ (minor) = 22.76 min, *ee* = 99%; $[\alpha]_D^{27}$ = 32.5 (*c* 1.0, $CH_2Cl_2$). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.29-7.15 (m, 8H), 6.75 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 2H);

$^{13}C$ {$^{1}H$} NMR (100 MHz, $CDCl_3$) δ 151.4, 143.4, 140.7, 139.1, 134.2, 128.8, 128.4, 128.3, 127.1, 123.0, 116.7, 114.7; HRMS (DART) calcd. for $C_{24}H_{13}O_2Br_2$ ($[M-H]^-$): 490.9288, found: 490.9285.

**General Procedure for the Asymmetric Allylboration of Ketones.** A 10 mL Schlenk tube was charged with a stirring bar and flushed with nitrogen. To the flask was added (*S*)-2,15-dibromotetraphenylene-1,16-diol **1** (0.01 mmol), *t*-BuOH (0.15 mmol), *B*-allyl-1,3,2-dioxaborinane **3** (0.2 mmol), and toluene (0.5 mL). The mixture was stirred at 25 °C for 10 min and ketone **2a-r** (0.1 mmol) was added directly. The reaction mixture was kept stirring at 25 °C for 48 h-72 h. After the removal of solvents via rotary evaporation, the residue was purified through flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 30:1- 15:1) to give pure product **4a-r**.

(*S*)-*(–)-2-(4-bromophenyl)-pent-4-en-2-ol (**4a**).*[10b] Compound **4a** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 92% yield (22.2 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate 1.0 mL/min, λ = 220 nm) $t_R$ (minor) = 16.32 min, $t_R$ (major) = 18.17 min, *ee* = 98%; $[\alpha]_D^{27}$ = –24.4 (*c* 1.0, $CHCl_3$); $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.63-5.56 (m, 1H), 5.13 (d, *J* = 12.8 Hz, 2H), 2.66-2.44 (m, 2H), 2.09 (s, 1H), 1.52 (s, 3H); MS (ESI): *m/z* = 241.0 $[C_{11}H_{13}BrO+H]^+$.

(*S*)-*(–)-2-phenylpent-4-en-2-ol (**4b**).*[10b] Compound **4b** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 94% yield (15.3 mg). HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 11.49 min, $t_R$ (major) = 12.11 min, *ee* =

99%; $[\alpha]_D^{27}$ = –16.8 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.36-7.32 (m, 2H), 7.26-7.22 (m, 1H), 5.64-5.58 (m, 1H), 5.16-5.10 (m, 2H), 2.71-2.47 (m, 2H), 1.97 (s, 1H), 1.55 (s, 3H); MS (ESI): *m/z* = 185.1 $[C_{11}H_{14}O+Na]^+$.

(*S*)-*(–)-2-(4-fluorophenyl)-pent-4-en-2-ol (**4c**)*.[13a] Compound **4c** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 94% yield (17.0 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 98:2, flow rate 0.6 mL/min, λ = 214 nm) $t_R$ (minor) = 14,51 min, $t_R$ (major) = 15.17 min, *ee* = 91%; $[\alpha]_D^{27}$ = –4.7 (c 0.5, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.04-6.99 (m, 2H), 5.63-5.56 (m, 1H), 5.15-5.12 (m, 2H), 2.66-2.46 (m, 2H), 1.54 (s, 3H); MS (ESI): *m/z* = 203.1 $[C_{11}H_{13}FO+Na]^+$.

(*S*)-*(–)-2-(4-chlorophenyl)-pent-4-en-2-ol (**4d**).*[13a] Compound **4d** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 89% yield (17.6 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 17.22 min, $t_R$ (major) = 18.54 min, *ee* = 96%; $[\alpha]_D^{27}$ = –26.4 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2H), 7.31-7.29 (m, 2H), 5.60-5.56 (m, 1H), 5.15-5.10 (m, 2H), 2.67-2.45 (m, 2H), 2.02 (s, 1H), 1.52 (s, 3H); MS (ESI): *m/z* = 219.1 $[C_{11}H_{13}ClO+Na]^+$.

(*S*)-*(–)-2-(3-chlorophenyl)-pent-4-en-2-ol (**4e**).*[13a] Compound **4e** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 89% yield (17.5 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 97:3, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (major) = 8.64 min, $t_R$ (minor) = 9.37

min, *ee* = 96%; $[\alpha]_D^{27}$ = –24.6 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.46-7.45 (m, 1H), 7.31-7.20 (m, 3H), 5.63-5.55 (m, 1H), 5.17-5.12 (m, 2H), 2.68-2.45 (m, 2H), 2.03 (s, 1H), 1.53 (s, 3H); MS (ESI): *m/z* = 219.1 $[C_{11}H_{13}ClO+Na]^+$.

(*S*)-*(–)-2-(2-bromophenyl)-pent-4-en-2-ol (**4f**).*[10b] Compound **4f** was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford a colorless oil in 50% yield (12.0 mg). HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 10.16 min, $t_R$ (major) = 11.72 min, *ee* = 87%; $[\alpha]_D^{27}$ = –7.7 (*c* 0.5, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.31-7.25 (m, 1H), 7.09 (td, *J* = 8.0, 2.0 Hz, 1H), 5.58-5.50 (m, 1H), 5.17-50.7 (m, 2H), 3.28 (dd, *J* = 14, 6.4 Hz, 1H), 2.65 (dd, *J* = 14, 8.4 Hz, 1H), 2.60 (br s, 1H), 1.72 (s, 3H); MS (ESI): *m/z* = 263.0 $[C_{11}H_{13}BrO+Na]^+$.

*(S)-(–)-2-(4-methylphenyl)-pent-4-en-2-ol (**4g**).*[13b] Compound **4g** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 82% yield (14.2 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 13.87 min, $t_R$ (major) = 18.52 min, *ee* = 97%; $[\alpha]_D^{27}$ = –31.3 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.63-5.59 (m, 1H), 5.15-5.08 (m, 2H), 2.69-2.45 (m, 2H), 2.33 (s, 3H), 2.01 (s, 1H), 1.52 (s, 3H); MS (ESI): *m/z* = 199.1 $[C_{12}H_{16}O+Na]^+$.

(*S*)-*(–)-2-(4-methoxyphenyl)-pent-4-en-2-ol (**4h**).*[10b] Compound **4h** was purified by silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford a

colorless oil in 84% yield (16.2 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 19.70 min, $t_R$ (major) = 25.59 min, *ee* = 95%; $[\alpha]_D^{26}$ = –16.7 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 6.90-6.86 (m, 2H), 5.69-5.58 (m, 1H), 5.15-5.10 (m, 2H), 3.80 (s, 3H), 2.68-2.46 (m, 2H), 2.02 (s, 1H), 1.53 (s, 3H); MS (ESI): *m/z* = 215.1 $[C_{12}H_{16}O_2+Na]^+$.

(*S*)-*(–)-2-(naphthalen-2-yl)-pent-4-en-2-ol (**4i**).*[10a] Compound **4i** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 90% yield (19.1 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (major) = 13.59 min, $t_R$ (minor) = 17.66 min, *ee* = 97%; $[\alpha]_D^{27}$ = –24.4 (*c* 1.4, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.93-7.83 (m, 4H), 7.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.51-7.45 (m, 2H), 5.69-5.58 (m, 1H), 5.20-5.11 (m, 2H), 2.84-2.57 (m, 2H), 2.10 (brs, 1H), 1.55 (s, 3H); MS (ESI): *m/z* = 235.1 $[C_{15}H_{16}O+Na]^+$.

(*S*)-*(–)-2-(naphthalen-1-yl)-pent-4-en-2-ol (**4j**).*[8c] Compound **4j** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 38% yield (8.1 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (major) = 11.93 min, $t_R$ (minor) = 13.79 min, *ee* = 57%; $[\alpha]_D^{27}$ = –2.4 (*c* 0.8, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.8 Hz, 1H), 7.89-7.87 (m, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.61-7.40 (m, 4H), 5.71-5.63 (m, 1H), 5.18-5.10 (m, 2H), 3.16-2.81 (m, 2H), 2.24 (brs, 1H), 1.84 (s, 3H); MS (ESI): *m/z* = 235.1 $[C_{15}H_{16}O+Na]^+$.

(*S*)-*(–)-2-thiophen-2-yl-pent-4-en-2-ol (**4k**).*[10b] Compound **4k** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 71% yield (12.0 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 11.97 min, $t_R$ (major) = 12.75 min, *ee* = 90%; $[\alpha]_D^{26}$ = –16.3 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, *J* = 5.2, 1.6 Hz, 1H), 6.96-6.91 (m, 2H), 5.79-5.68 (m, 1H), 5.18-5.13 (m, 2H), 2.73-2.54 (m, 2H), 2.17 (brs, 1H), 1.62 (s, 3H); MS (ESI): *m/z* = 190.9 $[C_9H_{12}SO+Na]^+$.

(*S*)-*(–)-3-(4-methylphenyl)hex-5-en-3-ol (**4l**).* Compound **4l** was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford a colorless oil in 79% yield (15.4 mg). HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 99:1, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 9.00 min, $t_R$ (major) = 9.64 min, *ee* = 97%; $[\alpha]_D^{27}$ = –13.9 (*c* 0.5, $CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 5.62-5.55 (m, 1H), 5.14-5.08 (m, 2H), 2.71-2.45 (m, 2H), 2.33 (s, 3H), 1.92 (s, 1H), 1.86-1.79 (m, 2H), 0.76 (t, *J* = 7.2 Hz, 3H); $^{13}$C {$^1$H} (100 MHz, $CDCl_3$) δ 142.9, 136.0, 133.9, 128.9, 125.5, 119.5, 76.0, 47.0, 35.4, 21.1, 8.0; HRMS (ESI) calcd. for $C_{13}H_{18}ONa$ ($[M+Na]^+$): 213.1250, found: 213.1253.

(*S*)-*(–)-4-penyloct-1-en-4-ol (**4m**).*[10b] Compound **4m** was purified by silica gel chromatography (petroleum ether/EtOAc = 30:1) to afford a colorless oil in 93% yield (19.0 mg). HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 10.54 min, $t_R$ (major) = 11.31 min, *ee* = 98%; $[\alpha]_D^{27}$ = –20.4 (*c* 0.8, $CHCl_3$); $^1$H NMR (600 MHz, $CDCl_3$) δ 7.39-7.25 (m, 4H),

7.16-7.14 (m, 1H), 5.51-5.47 (m, 1H), 5.07-5.02 (m, 2H), 2.73-2.48 (m, 2H), 1.97 (brs, 1H), 1.85-1.75 (m, 2H), 1.26-1.03 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H); MS (ESI): *m/z* = 227.1 $[C_{14}H_{20}O+Na]^+$.

(*S*)-*(–)-1-allyl-2,3-dihydro-1H-inden-1-ol (**4n**).*[10b] Compound **4n** was purified by silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford a colorless oil in 83% yield (14.4 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 12.07 min, $t_R$ (major) = 14.97 min, *ee* = 91%; $[\alpha]_D^{27}$ = –1.4 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 1H), 7.25-7.22 (m, 3H), 5.90-5.79 (m, 1H), 5.18-5.13 (m, 2H), 3.02-2.76 (m, 2H), 2.65-2.47 (m, 2H), 2.35-2.04 (m, 2H),1.99 (brs, 1H); MS (ESI): *m/z* = 197.1 $[C_{12}H_{14}O+Na]^+$.

(*S*)-*(–)-1-allyl-1,2,3-tetrahydronaphthalen-1-ol (**4o**).*[10b] Compound **4o** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 91% yield (17.2 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 98:2, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 12.19 min, $t_R$ (major) = 13.13 min, *ee* = 96%; $[\alpha]_D^{27}$ = –13.4 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.23-7.14 (m, 3H), 5.85-5.77 (m, 1H), 5.17-5.12 (m, 2H), 2.85-2.71 (m, 2H), 2.63-2.60 (m, 2H), 2.08-1.79 (m, 5H); MS (ESI): *m/z* = 211.1 $[C_{13}H_{16}O+Na]^+$.

(*S*)-*(–)-1,3-diphenylhexa-5-en-3-ol (**4p**).* Compound **4p** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 91% yield (23.0 mg). HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 99:1, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (major) = 22.79 min, $t_R$ (minor) = 24.61 min, *ee* =

98%; $[\alpha]_D^{28}$ = –25.9 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 4H), 7.27-7.21 (m, 3H), 7.15-7.08 (m, 3H), 5.60-5.51 (m, 1H), 5.18-5.10 (m, 2H), 2.77-2.62 (m, 2H), 2.56-2.29 (m, 2H), 2.15-2.07 (m, 3H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) δ 145.7, 142.6, 133.4, 128.5, 128.47, 128.46, 126.7, 125.8, 125.4, 120.0, 75.8, 47.8, 44.8, 30.1; HRMS (ESI) calcd. for $C_{18}H_{20}ONa$ ($[M+Na]^+$): 275.1406, found: 275.1405.

(*S*)-*(–)-3-methyl-1-phenylhexa-1,5-dien-3-ol (**4q**).*[8c] Compound **4q** was purified by silica gel chromatography (petroleum ether/EtOAc = 15:1) to afford a colorless oil in 90% yield (17.0 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (minor) = 13.27 min, $t_R$ (major) = 15.25 min, *ee* = 62%; $[\alpha]_D^{26}$ = –20.7 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 5.87-5.78 (m, 1H), 5.18-5.14 (m, 2H), 2.47-2.33 (m, 2H), 1.84 (brs, 1H), 1.38 (s, 3H); MS (ESI): *m/z* = 227.1 $[C_{13}H_{16}O+K]^+$.

(*S*)-*(–)-1,3-diphenylhexa-1,5-dien-3-ol (**4r**).*[13c] Compound **4r** was purified by silica gel chromatography (petroleum ether/EtOAc = 20:1) to afford a colorless oil in 24% yield (6.0 mg). HPLC (Chiralcel OD-H, hexane/*i*-PrOH = 95:5, flow rate 0.8 mL/min, λ = 214 nm) $t_R$ (major) = 13.33 min, $t_R$ (minor) = 15.95 min, *ee* = 75%; $[\alpha]_D^{26}$ = 1.2 (*c* 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52-7.50 (m, 2H), 7.39-7.21 (m, 8H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.75-5.68 (m, 1H), 5.23-5.16 (m, 2H), 2.86-2.74 (m, 2H), 2.28 (brs, 1H); $^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$) δ 145.4, 136.9, 135.3, 133.2, 128.7, 128.5, 128.4,

127.7, 127.1, 126.7, 125.6, 120.3, 75.8, 47.3; HRMS (ESI) calcd. for $C_{18}H_{18}ONa$ ($[M+Na]^+$): 273.1250, found: 273.1243.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: .

Copies of HPLC, $^1H$ NMR and $^{13}C$ NMR traces, X-ray crystal structures of compounds (±)-**1** and (±)-**10** (PDF).

X-ray crystal details for compound (±)-**1** and (±)-**10** (CIF).

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### Notes

The authors declare no competing financial interest.

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