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Novel strategy for the synthesis of chiral *pseudo-ortho*-substituted hydroxy[2.2]paracyclophane-based ligands from the resolved 4-bromo-12-hydroxy[2.2]paracyclophane as a parent compound

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Abstract—A simple and efficient resolution of racemic 4-bromo-12-hydroxy[2.2]paracyclophane into its enantiomers via diastereomeric esters with (1*S*)-(−)-camphanic acid was carried out. New synthetic routes to enantiomerically pure 4,12-dihydroxy- and 4-hydroxy[2.2]paracyclophanes starting from the enantiomers of an intermediate 4-bromo-12-hydroxy[2.2]paracyclophane are proposed.

1. Introduction

Hydroxy-based (e.g., O,O-, N,O-, P,O-, etc.) ligands for asymmetric synthesis and catalysis belong to the most efficient and widely used chiral inductors.[1] In [2.2]paracyclophane chemistry,[2] the key compound for the synthesis of such inductors has been 4-hydroxy[2.2]paracyclophane **1** (Fig. 1). The methods of synthesis[3] and chemical[4] or enzymatic[5] resolution of this compound into enantiomers have attracted considerable attention. Typically, phenol **1** undergoes *ortho*-regioselective substitution reactions; therefore, ligands based on this compound are mainly its *ortho*-derivatives. For instance, phenol **1** was used as the parent compound for the synthesis of **FHPC 2** (R = H),[3c,4a,6] a paracyclophanyl analog of salicylic aldehyde; *ortho*-hydroxyketones **2** (R = Me, Ph)[7] in turn served as the starting compounds in the synthesis of a family of bi-, tri- and tetradentate imine ligands[8] and chiral aminophenols];[9] 1,3-oxazol-2-one **3**;[10] 'bridged' biphenols **4**;[11] diparacyclophanyl biphenol **5**;[12] and arylparacyclophanes **6** (X = OH, OMe).[2a,13] Phenol **1** was also used in the design of a class of bis-bifunctional ligands **7**[2d] by oxidation of **1** to the corresponding quinone[14] followed by the addition of functionally substituted aryllithium derivatives. Compounds **2**–**7** (Fig. 1) and their derivatives proved themselves as efficient chiral ligands and auxiliaries for asymmetric synthesis and catalysis.[15]

In addition to these *ortho*-derivatives, *pseudo-ortho*-disubstituted [2.2]paracyclophanes[15] have successfully been used as ligands. However, there are a few examples of the hydroxy-based *pseudo-ortho*-ligands, for example, 4,12-dihydroxy[2.2]paracyclophane [**PHANOL**, a paracyclophanyl analog of the well-known ligand **BINOL**] **8**,[16] oxazolinylcyclophanyl derivatives **9**,[17] and a planar chiral chelating imidazolium ligands **10**[18] (Fig. 2).

The synthesis of these ligands in enantiomerically pure form was carried out either from optically active starting (R_p)-4,12-dibromo[2.2]paracyclophane **11**[19] (ligands **9** and **10**),[18] or by the resolution of the final product (ligand **8**).[16a,21] The efficient synthesis of the racemic 4-bromo-12-hydroxy[2.2]paracyclophane **12** and its resolution into enantiomers[20] prompted us to elaborate a new approach to enantiomerically pure hydroxy-based *pseudo-ortho*-ligands using the intermediate resolved bromophenol **12** as a source of chirality. It should be noted that (R_p)-**12** could also be obtained from (R_p)-4,12-dibromo[2.2]paracyclophane **11**.[18,19]

In this work, we report on the experimental details of the synthesis of *rac*-**12**, its resolution into enantiomers via diastereomeric esters with (1*S*)-(−)-camphanic acid, and new synthetic routes to enantiomerically pure **PHANOL 8** and 4-hydroxy[2.2]paracyclophane (Fig. 3).

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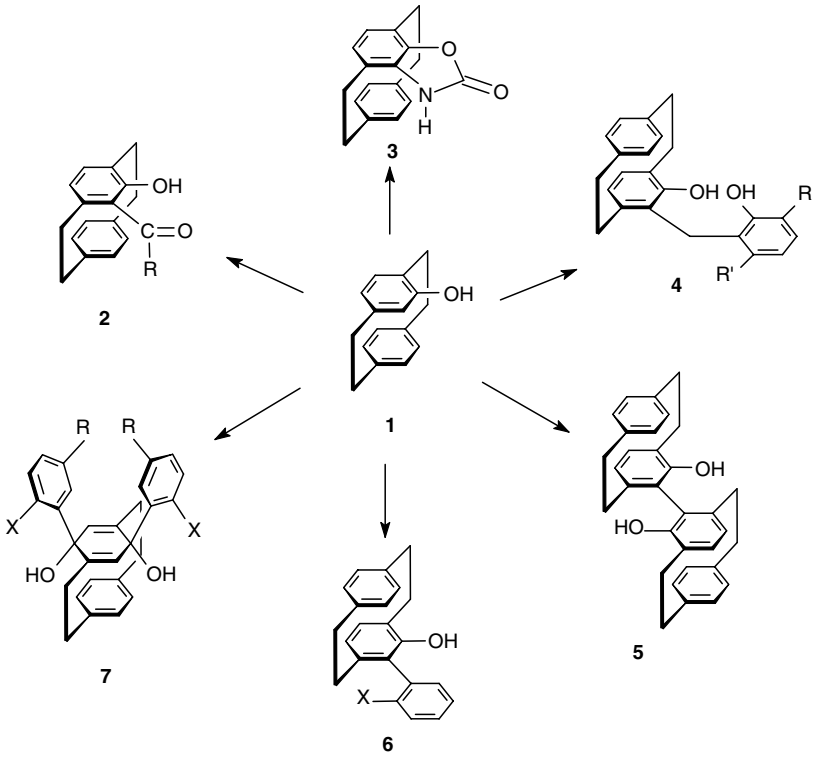


Figure 1. 4-Hydroxy[2.2]paracyclophane **1**, a 'parent' compound for paracyclophanyl hydroxy-based ligands.

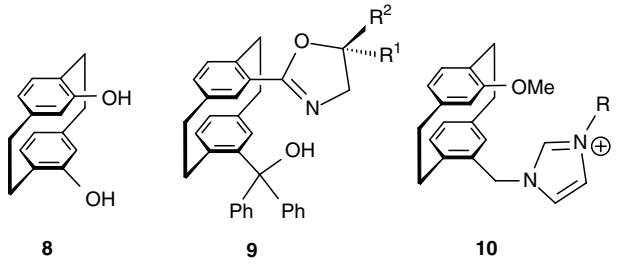


Figure 2. First examples of *pseudo-ortho*-[2.2]paracyclophane ligands having a hydroxy functional moiety.

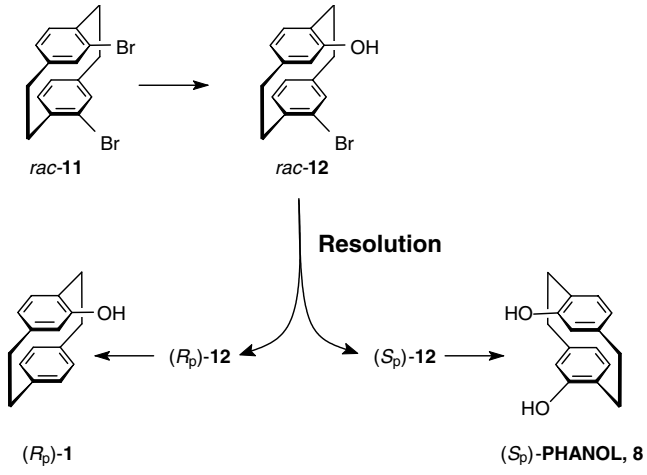


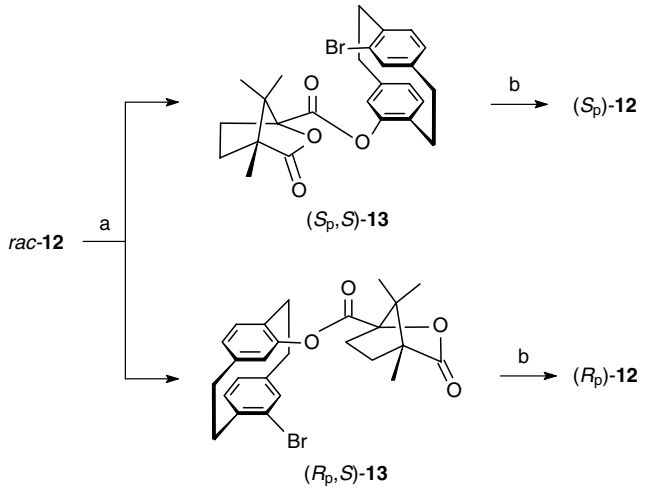
Figure 3. New synthetic routes to compounds **1** and **8** starting from enantiomers of 4-bromo-12-hydroxy[2.2]paracyclophane **12**.

2. Results and discussion

2.1. Synthesis and resolution of 4-bromo-12-hydroxy-[2.2]paracyclophane 12 into enantiomers

Racemic bromophenol **12** was synthesized from the starting racemic dibromide **11** by selective replacement of a bromine atom by the hydroxy group[18,20] and then resolved into enantiomers using (1*S*)-(−)-camphanic acid, a known reagent for the resolution of racemic hydroxy-substituted paracyclophane derivatives.[4a,21] Diastereomeric esters **13** were obtained in high yield (98%) by treating *rac*-**12** with (1*S*)-camphanoyl chloride synthesized from (1*S*)-(−)-camphanic acid and thionyl chloride[22] (Scheme 1). The esterification readily proceeds in pyridine at room temperature in the presence of a small excess of camphanoyl chloride.

The preparative resolution of diastereomeric esters **13** was performed by column chromatography on silica gel (methylene chloride/ethyl acetate = 100:1 mixture as eluent). The combined fraction (R_f 0.50) contained 98% of (S_p,*S*)-**13** and the combined fraction (R_f 0.39) gave 88% of (R_p,*S*)-**13**. To isolate the enantiomers of compound **12**, esters (S_p,*S*)- and (R_p,*S*)-**13** were hydrolyzed with KOH in methanol at room temperature for 2.5 h. The enantiomers, (S_p)- and (R_p)-**12**, were synthesized in almost quantitative yields. Their enantiomeric purity exceeded 99%, which was confirmed by HPLC on a Chiralpak® AD-H column (retention time $t_R = 37.25$ min for (R_p)-**12** and $t_S = 41.00$ min for (S_p)-**12**). The absolute configuration of (S_p)-**12** enantiomer was determined by X-ray analysis of camphanoate (S_p,*S*)-**13** (Fig. 4).



Scheme 1. Resolution of racemic 4-bromo-12-hydroxy[2.2]paracyclophane **12** into enantiomers. Reagents and conditions: (a) (1*S*)-(−)-camphanoyl chloride, Py, room temperature, 6 h, then chromatography on silica gel, 98% for (S_p,*S*)-**13** and 88% for (R_p,*S*)-**13**; (b) KOH, MeOH, room temperature, 2 h, 97% for (S_p)-**12** and 97% for (R_p)-**12**.

2.2. Synthesis of enantiomerically pure PHANOL 8

PHANOL[16] **8** is considered to be a paracyclophanyl analog of the known **BINOL** ligand.[1b] However, biphenol **8** has never been used as an asymmetric ligand in catalysis. This can to some extent be due to the difficulties in the synthesis of its enantiomers.[16,21]

Racemic **PHANOL 8** was first synthesized by Cram and Reich[23] in 1969 from dibromide **11** (Scheme 2) using simultaneous replacement of both the bromines by lithium (*n*-BuLi/Et_2O) followed by oxidation with nitrobenzene. The desired diol was obtained in a low yield (16% only). Recently,[16a] Braddock reported a higher yield of **8** (35–45%) in the reaction carried out in THF instead of Et_2O.

To resolve compound **8** into its enantiomers, two routes were proposed (Scheme 2). Braddock reported a lipase-catalyzed enzymatic kinetic resolution of racemic 4,12-bisacetoxy[2.2]paracyclophane **14** affording enantiomerically pure **PHANOL**.[16a] This procedure takes a long time to complete (more than 14 days) and results in low overall yield [(R_p)-**8**, 30%; (S_p)-**8**, 24%; from dibromide **11**]. A more traditional procedure for the resolution of **8** was developed by Jiang.[21] It involves the synthesis of diastereomeric esters of (1*S*)-camphanic acid **15** followed by their separation by flash chromatography and reduction with $LiAlH_4$. In this case, the yield of each enantiomer of compound **8** was 36% (calculated with respect to the racemic dibromide **11**).

The strategy for the synthesis of enantiomerically pure compound **8** proposed in this work involves the selective replacement of one bromine atom in racemic **11** by the hydroxy group to give bromophenol **12** followed by resolution of *rac*-**12** and the synthesis of the target optically active **8** from the enantiomers of **12** (Scheme 3**A**). Racemic **12** was obtained in 93% yield following the known procedure for the synthesis of (R_p)-**12** from (R_p)-**11**[18] and resolved into enantiomers using (1*S*)-camphanic acid, as described in Section 2.1. Lithiation of (S_p)-**12** with *n*-BuLi (3.2 equiv) in THF at −78 °C followed by treatment with $B(OMe)_3$ and oxidation with H_2O_2 resulted in a mixture of (S_p)-**8** and (S_p)-**1**. The formation of phenol **1** in this reaction can be explained by insufficient reactivity of the intermediate lithium derivative with respect to the $B(OMe)_3$. The compounds synthesized were easily separated by preparative chromatography on SiO_2. The yield of (S_p)-**8** in this reaction was 49% (42% with respect to the starting racemic dibromide **11**), being higher than the yield of (S_p)-**8** synthesized as reported by Braddock and Jiang (24% and 36%, respectively; see Scheme 2). The advantage of our approach consists in the possibility of isolation of not only compound **8**, but also enantiomerically pure 4-hydroxy[2.2]paracyclophane (S_p)-**1** (32%), a valuable parent compound in the chemistry of [2.2]paracyclophane (Fig. 1).

Taking into account the fact that the bromine atom in the bromophenol molecule can not only be replaced by a functional group, but also be eliminated, we carried out the lithiation of enantiomerically pure (R_p)-**12** with an excess of *n*-BuLi. Subsequent hydrolysis gave enantiomerically

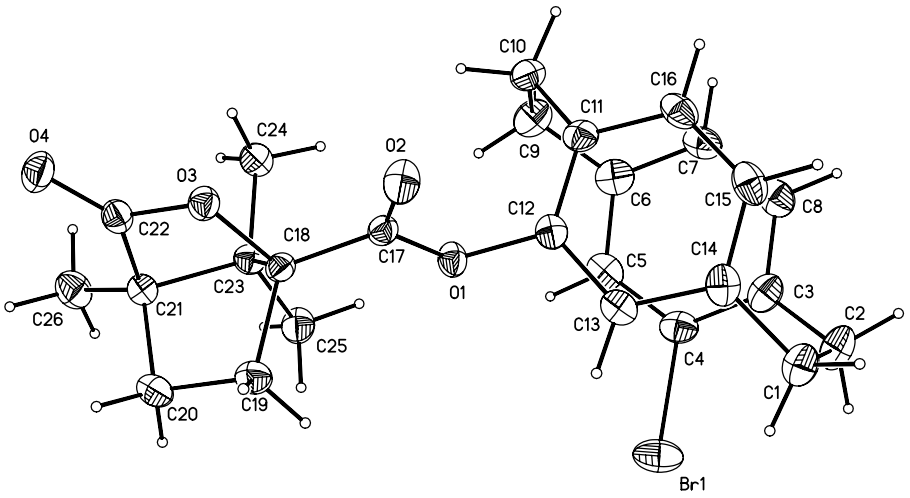
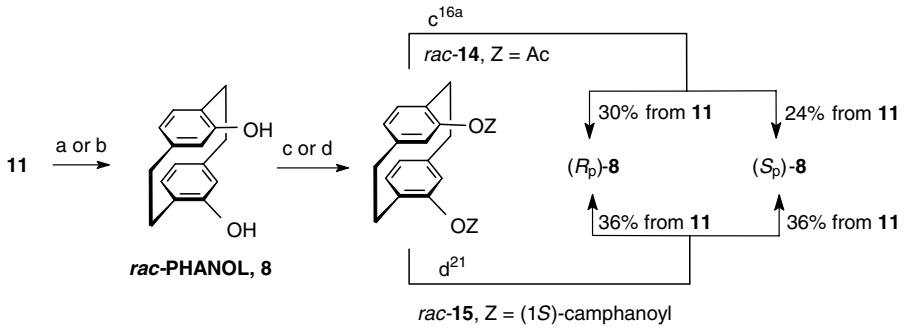
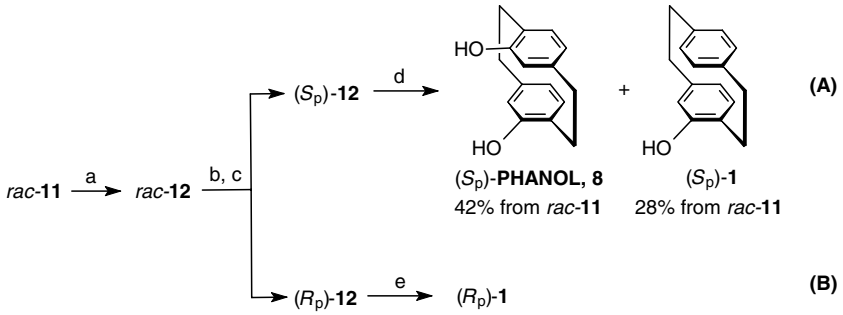


Figure 4. Molecular structure of (+)-(S_p,*S*)-**13**.



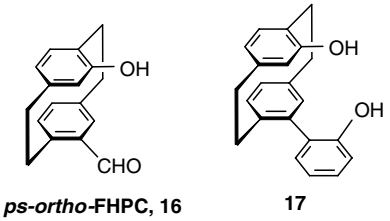
Scheme 2. Synthetic routes to racemic and enantiomerically pure **PHANOL 8**. Reagents and conditions: (a) *n*-BuLi in Et_2O, then $PhNO_2$, 16%; (b) *n*-BuLi in THF, −78 °C, then $PhNO_2$, 35–45%; (c) NaH, AcCl, then enzymatic resolution using the *Candida rugosa* lipase; (d) (1*S*)-(−)-camphanoyl chloride, Py, room temperature, then chromatography on silica gel, then $LiAlH_4$, THF, reflux, 6 h.



Scheme 3. New synthetic routes to enantiomerically pure **PANOL 8** and 4-hydroxy[2.2]paracyclophane **1**. Reagents and conditions: (a) *n*-BuLi, THF, −78 °C, 0.5 h, $B(OMe)_3$, −78 °C to room temperature, then H_2O_2/NaOH, 93%; (b) (1*S*)-(−)-camphanoyl chloride, Py, room temperature, 6 h, then chromatography on silica gel, 98% for (S_p,*S*)-**13** and 88% for (R_p,*S*)-**13**; (c) KOH, MeOH, room temperature, 97% for (S_p)-**12** and 97% for (R_p)-**12**; (d) *n*-BuLi, THF, 0 °C, 2 h, then recooled to −78 °C, $B(OMe)_3$, −78 °C to room temperature, then H_2O_2/NaOH, 49% for (*S*)-**8** and 32% for (*S*)-**1**; (e) *n*-BuLi, THF, 0 °C, 3 h, then H_2O, 98%.

pure phenol **1** (98%) as the only reaction product (Scheme 3**B**). Previously, the enantiomers of **1** was obtained by resolution[4,5] of *rac*-**1** synthesized from 4-bromo[2.2]paracyclophane.[3] The new route to optically active phenol **1** presented in Scheme 3**B** seems to be promising because it allows the resolution of intermediate bromophenol **11** to proceed more readily compared to the resolution of phenol **1**.[4,5]

The presence of the bromine substituent in **12** offers prospects for the synthesis of a variety of *pseudo-ortho*-disubstituted paracyclophanes based on **12**. For instance, lithiation of **12** followed by treatment of the reaction mixture with *N*-formylpiperidine resulted in *pseudo-ortho*-**FHPC 16**.[24] The bi- and tridentate imine ligands based on compound **16** appeared to be efficient in the asymmetric addition of diethylzinc to benzaldehyde.[25] Taking biphenol **17** as an example, we proposed a strategy of the synthesis of bifunctional aryl[2.2]paracyclophanyl ligands using Pd-catalyzed Suzuki coupling of bromophenol **12** with arylboronic acids.[2a]



It is important that 4-bromo-12-hydroxy[2.2]paracyclophane **12** is an analog of phenol **1** and can thus be used for the synthesis of *ortho*-hydroxyparacyclophane-based ligands bearing a bulky bromine substituent in the *pseudo-ortho*-position relative to the hydroxy group. Recently,[26] we have shown that, similarly to phenol **1**, the enantiomerically pure compound **12** can be used as a chiral inductor, namely, recoverable auxiliary reactant in the asymmetric allylboronation of benzaldehyde (ee of the product, 3-buten-1-phenyl-1-ol, up to 59%).

3. Conclusion

Summing up, we have synthesized racemic 4-bromo-12-hydroxy[2.2]paracyclophane **12** and elaborated a simple and efficient procedure for its resolution into enantiomers. New routes to enantiomerically pure **PHANOL 8** and 4-hydroxy[2.2]paracyclophane **1** using enantiomers of **12** were proposed. Further use of bromophenol **12** in the design of enantiomerically pure *pseudo-ortho*-disubstituted paracyclophanes and their application as ligands for asymmetric catalytic reactions is now in progress and will be reported elsewhere.

4. Experimental

4.1. General

Pyridine was distilled twice from KOH. Ethyl acetate was washed with saturated aq K_2CO_3, dried with $CaCl_2$, and

distilled from anhydrous K_2CO_3. THF was distilled from sodium benzophenone ketyl under argon before use. All reactions with *n*-BuLi were performed under an atmosphere of argon. Benzene and toluene were distilled from sodium. (1*S*)-(−)-Camphanic acid was purchased from Fluka. (1*S*)-(−)-Camphanoyl chloride[22] was synthesized following the literature. Optical rotations were recorded on Perkin–Elmer 241 instrument in a thermostatted cell. ^{1}H spectra were recorded on a Bruker AMX-400 spectrometer at 400.13 MHz in $CDCl_3$. The residual signal of the solvent protons with the chemical shifts δ 7.27 ($CDCl_3$) was used as internal standards. Mass spectra were obtained on a KRATOS MS890A mass spectrometer (70 eV). TLC-analyses were performed on silica gel precoated SORBFIL plates PTLC-A-UV (Sorbpolimer). Column chromatography was performed on Kieselgel 60, 230–400 mesh ASTM (Merck). Enantiomeric analyses were carried out by HPLC on Chiralpak® AD-H analytical column using hexane/2-propanol (100/4) as an eluent (1 mL/min) detected at 254 nm.

4.2. *rac*-4-Bromo-12-hydroxy[2.2]paracyclophane 12

Racemic **12** (93%) was synthesized according to a procedure described in the literature for (R_p)-**12**;[18] mp 150.5–153 °C; Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99; Br, 26.35. Found: C, 63.34; H, 4.88; Br, 26.25. The ^{1}H NMR and MS data are in a good agreement with those of (R_p)-**12**.

4.3. (S_p,*S*)-13 and (R_p,*S*)-13

To (1*S*)-(−)-camphanoyl chloride (1.46 g, 6.73 mmol) was added a solution of *rac*-**12** (1.70 g, 5.61 mmol) in pyridine (7 mL). The mixture was stirred at room temperature for 6 h, diluted with H_2O (50 mL), and vigorously stirred until a white precipitate was obtained. The precipitate was removed by filtration, washed with 2 M HCl (100 mL), H_2O (5 × 100 mL), and hexane (30 mL), and dried in vacuo to yield a mixture of diastereomeric esters **13** (2.71 g, 99%), which were purified by chromatography on silica gel using CH_2Cl_2–AcOEt (100:1) as the eluent.

(S_p,*S*)-**13**, TLC $R_f = 0.50$ (CH_2Cl_2–AcOEt, 100:1), eluted first; 1.329 g (98%); mp 144.5–145 °C; $[\alpha]_D^{20} = +19.0$ (*c* 0.97, C_6H_6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.19 (s, 3H, –CH_3); 1.22 (s, 3H, –CH_3); 1.28 (s, 3H, –CH_3); 1.74–1.85 (m, 1H); 1.96–2.08 (m, 1H); 2.13–2.25 (m, 1H); 2.54–2.89 (m, 3H); 2.98–3.27 (m, 5H); 3.38–3.49 (m, 1H); 6.43–6.56 (m, 3H, aromatic H); 6.63 (d, $^3J = 7.8$, 1H, aromatic H); 6.78 (s, 1H, aromatic H); 7.00 (s, 1H, aromatic H); MS (EI), *m*/*z* (rel): 484 (9, M^+), 482 (14, M^+), 403 (15), 357 (11), 317 (12), 304 (14), 302 (17), 300 (42), 224 (15), 223 (100), 222 (11), 221 (19), 185 (11), 184 (16), 182 (13), 178 (12), 167 (15), 149 (38), 135 (11), 125 (23), 121 (16), 120 (74), 109 (33), 103 (20). Anal. Calcd for $C_{26}H_{27}BrO_4$: C, 64.60; H, 5.63; Br, 16.53. Found: C, 64.41; H, 5.51; Br, 16.42.

(R_p,*S*)-**13**, TLC $R_f = 0.39$ (CH_2Cl_2–AcOEt, 100:1), eluted next; 1.199 g (88%); mp 155–156 °C; $[\alpha]_D^{20} = -54.8$ (*c* 0.75, C_6H_6); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (s, 3H, –CH_3); 1.21 (s, 3H, –CH_3); 1.28 (s, 3H, –CH_3); 1.78–1.91 (m, 1H); 2.01–2.13 (m, 1H); 2.27–2.39 (m, 1H); 2.58–2.77 (m, 2H); 2.78–2.89 (m, 1H); 2.91–3.25 (m, 5H); 3.37–3.50 (m, 1H); 6.42–6.57 (m, 3H, aromatic H); 6.63 (d, $^3J = 7.8$, 1H, aromatic H); 6.79 (s, 1H, aromatic H); 7.00 (s, 1H, aromatic H); MS (EI), *m*/*z* (rel): 484 (13, M^+), 482 (14, M^+), 403 (17), 357 (14), 317 (14), 304 (12), 302 (18), 300 (43), 224 (18), 223 (100), 222 (12), 221 (19), 185 (11), 184 (16), 182 (15), 179 (12), 167 (11), 149 (17), 135 (16), 125 (30), 122 (15), 121 (16), 120 (74), 109 (41), 103 (20). Anal. Calcd for $C_{26}H_{27}BrO_4$: C, 64.60; H, 5.63; Br, 16.53. Found: C, 64.57; H, 5.54; Br, 16.28.

4.4. (R_p)-(−)-4-Bromo-12-hydroxy[2.2]paracyclophane (R_p)-12

KOH (0.636 g, 11.4 mmol) was added to a suspension of (R_p,*S*)-**13** (1.300 g, 2.69 mmol) in MeOH (100 mL). The mixture was stirred for 2 h at room temperature, diluted with saturated aqueous NaCl (100 mL) and C_6H_6 (50 mL) vigorously stirred for 0.5 h. The organic layer was separated and the aqueous layer washed with C_6H_6 (2 × 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and chromatographed (C_6H_6) to give bromophenol (R_p)-(−)-**12** (0.791 g, 97%); >99% ee by HPLC analysis ($t_S = 37.25$, $t_R = 41.00$); mp 149–151 °C (Ref. 18 mp 149–153 °C).

4.5. (S_p)-(+)-4-Bromo-12-hydroxy[2.2]paracyclophane (S_p)-12

Compound (S_p)-(+)-**12** was obtained by the same method from (S_p,*S*)-**13** in 97% yield; >99% ee by HPLC analysis; mp 149–152 °C; $[\alpha]_D^{20} = +24.4$ (*c* 0.80, C_6H_6); Anal. Calcd for $C_{16}H_{15}BrO$: C, 63.38; H, 4.99; Br, 26.35. Found: C, 63.11; H, 4.89; Br, 25.81. The ^{1}H NMR and MS data are in a good agreement with those of (R_p)-**12**.[18]

4.6. (S_p)-(−)-PHANOL 8

To a stirred solution of (S_p)-(+)-**12** (0.150 g, 0.495 mmol) in THF (2 mL) at 0 °C under argon, *n*-BuLi (0.49 mL of 3.20 M solution in hexane, 1.583 mmol, 3.2 equiv) was added via syringe. The reaction mixture was stirred for 2 h at 0 °C, recooled to −78 °C and $B(OMe)_3$ (0.257 g, 0.28 mL, 2.47 mmol) was added. The reaction mixture was warmed up to room temperature overnight. Then, NaOH (0.100 g, 2.5 mmol) in H_2O (0.5 mL) and H_2O_2 (0.32 mL of 30% aqueous solution, 2.82 mmol) was added. The mixture was stirred for 3 h at room temperature, diluted with saturated aqueous NaCl (5 mL) and toluene (5 mL). The organic layer was separated and the aqueous layer washed with 1:1 mixture of toluene and THF (3 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by chromatography on SiO_2 (R_f 0.30; hexane/EtOAc, 2:1), to yield compound (S_p)-(−)-**8**[16a] (0.058 g, 49%). From combined fractions with $R_f = 0.53$ the compound (S_p)-(−)-**1**[3c,4] (0.035 g, 32%) was obtained.

4.7. (R_p)-(+)-4-Hydroxy[2.2]paracyclophane (R_p)-1

To a stirred solution of (R_p)-(−)-**12** (0.045 g, 0.148 mmol) in THF (2 mL) at 0 °C under argon, *n*-BuLi (0.14 mL of 3.27 M solution in hexane, 0.445 mmol, 3.0 equiv) was added. The reaction mixture was stirred for 3 h at 0 °C and H_2O (3.0 mL) was added. The organic layer was separated and the aqueous layer washed with benzene (3 × 4 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by chromatography on SiO_2 (benzene), to yield compound (R_p)-(−)-**1**[3c,4] (0.032 g, 98%).

4.8. Crystallographic analysis of (S_p,*S*)-13

Colourless, needle-like crystals were obtained from EtOH, $C_{26}H_{27}BrO_4$, $M_r = 483.39$, dimension: 0.5 × 0.4 × 0.3 mm, crystal system: orthorhombic, space group: $P2_12_12_1$, $a = 11{,}274(3)$ Å, $b = 13.033(4)$ Å, $c = 15.102(4)$ Å, $V = 2219(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.447$ g/cm^3, abs. coeff. μ(Mo-K$_\alpha$) = 1.883 cm^{-1}, T_{min}/T_{max}: 0.587/0.928, θ range: 2.06–29.50°, completeness of dataset: 98.0%, number of reflections collect: 17,385, number of independent reflections: 3396 ($R_{int} = 0.0605$), number of observed reflections [$I > 2\sigma(I)$]: 2930, number of parameters: 280. Final *R* indices: $R_1 = 0.0303$, $wR_2 = 0.0696$. Weighting scheme: $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, $P = 1/3(F_o^2 + 2F_c^2)$, $a = 0.0383$, $b = 0.0000$. $F(000) = 1000$, GOOF 0.988, Largest diff. peak and hole [e Å^{-3}]: 0.982 and −0.603.

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD area detector, using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 59°$) at 120 K. Low temperature of the crystals was maintained with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. Reflection intensities were integrated using SAINT software [SMART V5.051 and SAINT V5.00, Area detector control and integration software, 1998, Bruker AXS Inc., Madison, WI-53719, USA] and semi-empirical method SADABS [G. M. Sheldrick, SADABS, 1997, Bruker AXS Inc., Madison, WI-53719, USA].

The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic (for no-hydrogen atoms) approximation. The H(C) atoms were placed in geometrically calculated positions and were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 U_{eq}(Ci), for methyl groups equal to 1.5 U_{eq}(Cii), where U(Ci) and U(Cii) are, respectively, the equivalent thermal parameters of the atoms to which the corresponding H atoms are bonded.

All calculations were performed on an IBM PC/AT using the SHELXTL software [G. M. Sheldrick, SHELXTL-97, Version 5.10, Bruker AXS Inc., Madison, WI-53719, USA].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition number 654011. These data can be obtained free of charge via http://www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ; fax: +44 1223 335 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers.

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