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Diastereoselective Friedel–Crafts Alkylation of Hydronaphthalenes

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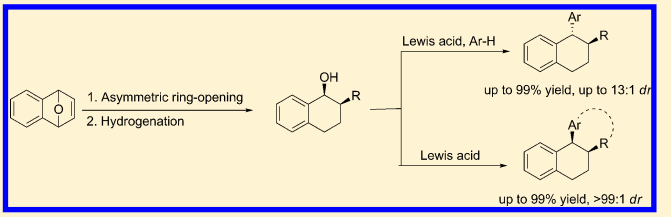
Supporting Information

ABSTRACT: An efficient and versatile synthesis of chiral tetralins has been developed using both inter- and intramolecular Friedel–Crafts alkylation as a key step. The readily available hydronaphthalene substrates were prepared via a highly enantioselective metal-catalyzed ring opening of *meso*-oxabicyclic alkenes followed by hydrogenation. A wide variety of complex tetracyclic compounds have been isolated with high levels of regio-, diastereo-, and enantioselectivity.



INTRODUCTION

Aryltetralin lignans, a subclass of the large lignan family of secondary metabolites, display a substantial range of biological activity.[1] Selected examples include lasofoxifene for the treatment of osteoporosis and podophyllotoxin as an anticancer agent (Figure 1).[2,3] Structurally, they are characterized by a substituted 1,2,3,4-tetrahydronaphthalene core with up to four contiguous chiral centers. Their challenging structures and important biological roles have led to interest in developing an efficient stereocontrolled synthesis of this class of natural products.[4]

Our group has had a long-standing interest in the asymmetric Pd(II)- or Rh(I)-catalyzed ring-opening reactions (ARO) of *meso*-oxabiyclic alkenes to produce both *trans*- and *cis*-1,2-disubstituted dihydronaphthalenols. High yields and excellent enantioselectivities can be achieved using a wide variety of nucleophiles such as dialkylzincs, aryl and vinylboronic acids, thiols, alcohols, amines, and hydrides (Scheme 1).[5−8] This reaction may be performed in a racemic fashion or enantioselectively using a Josiphos-type ligand (PPF-P*t*Bu$_2$) or with Tol-BINAP.

Our group has recently investigated the combination of the ARO methodology with a diastereoselective Friedel–Crafts (FC) alkylation of the resulting benzylic alcohol to readily synthesize chiral aryltetralin products. Within the field of FC alkylation, there is growing interest in the utilization of π-activated alcohols instead of the less available and more toxic organo-halides.[9] Recent advances in this area have shown that these substrates can display facial preferentiality, resulting in a formal diastereoselective Friedel–Crafts alkylation of benzylic alcohols.[10] In particular, Bach and co-workers have reported a highly diastereoselective Friedel–Crafts alkylation of 1-arylalkanoles via the formation of chiral benzylic carbocations.[11] More recently, we have demonstrated that the derivatization of amine ring-opened products **10** with inter-[12] and intramolecular[13] Friedel–Crafts alkylations can proceed with high yield and diastereoselectivity (Scheme 2) and most importantly with retention of the enantioselectivity. Herein, we report the inter- and intramolecular diastereoselective FC alkylations of tetralin **11** to efficiently and selectively access chiral carbocycles.

RESULTS AND DISCUSSION

We first investigated the conversion of the tetrahydronaphthalenol **12** to the arylated product **13**. Substrate **12** is readily prepared by performing an asymmetric Pd(II)-catalyzed ring opening of *meso*-oxabicyclic alkene **4** followed by hydrogenation. A wide variety of Lewis acids (LA) have been tested, and Al(III) chloride proved to be the most effective (Table 1). Treatment of substrate **12** with 10 equiv of anisole in the presence of a stoichiometric amount of $AlCl_3$ in nitromethane ($MeNO_2$)[14] at room temperature delivered the desired *trans*-alkylated product **13** in 98% yield and good diastereoselectivity (Table 1, entries 1 and 2). The high level of *trans*-selectivity obtained is noteworthy, and the change in selectivity as a function of the nucleophile suggests that the reaction suggests that the reaction may proceed through the formation of an intermediate benzylic carbocation species. Performing the reaction with a catalytic amount of Lewis acid did not lead to the formation of the desired product **13**, generating instead unidentified side products (Table 1, entry 4). Additionally, varying the temperature of the reaction was found to have little influence on the selectivity (Table 1, entry 5). Finally, carrying out the reaction according to Bach's protocol also resulted in the formation of *trans*-alkylated product **13** in good yield and selectivity (Table 1, entry 7). However, this procedure was found to be limited to the use of activated nucleophiles, the eliminated product **14** being otherwise predominantly formed.

Having optimized the conditions, we then went on to explore the substrate scope for intermolecular FC alkylation of the chiral benzylic alcohol **12** (Scheme 3).

The use of heteroaromatics such as thiophene, pyrrole, and indole as nucleophiles resulted in the formation of the

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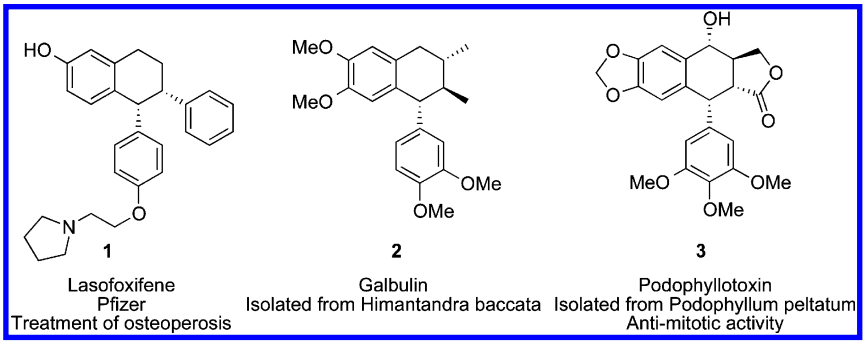
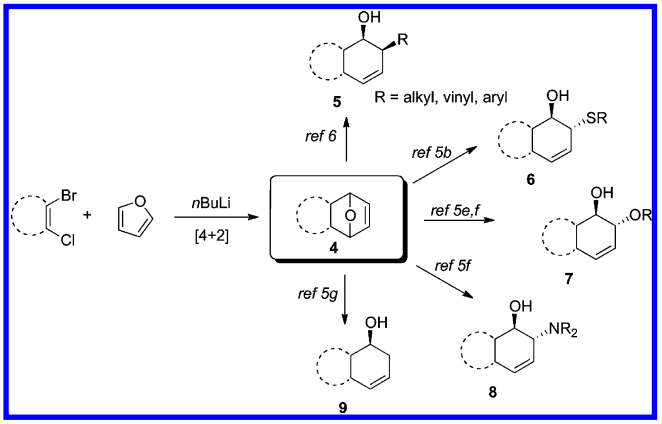


Figure 1. Examples of aryltetralin lignans.

Scheme 1. Asymmetric Ring Opening of *meso*-Oxabicycle 4



corresponding tetralins **15**, **16**, and **17** in excellent yields albeit with lower diastereoselectivities. While electron-rich nucleophiles such as veratrole, anisole, and phenol led to the formation of the tetralins **13**, **18**, and **19** almost quantitatively and with high diastereoselectivity, less nucleophilic aromatics such as toluene and xylenes failed to deliver the desired products, instead forming predominantly the eliminated byproduct **14**. Additionally, no reaction of tetrahydronaphthalenol **12** with furan derivatives, silyl enol ethers, or acetylacetonates occurred under these conditions.[15] It is important to note that the high enantioselectivity established in the Pd(II)-catalyzed ring-opening step is maintained throughout the entire synthetic sequence, suggesting that **14** is not an intermediate in the pathway leading to the FC product.

We next attempted to enhance the diastereoselectivity of the reaction by introducing a more bulky aryl group at the 2-position of the hydronaphthalenes. This can be easily achieved by altering the boronic esters used in the asymmetric Rh(I)-catalyzed ring-opening step (Scheme 4).

As previously reported, ring opening of *meso*-oxabicyclic alkenes using sterically hindered boronic esters proceeds in reasonable yields only at elevated temperatures, causing a reduction in the enantioselectivity of the reaction.[6b] However, to our delight, the use of bulky aryltetralins **22** did lead to an improvement of the diastereoselectivity for the Friedel–Crafts alkylation (Scheme 5).

Treatment of tetrahydronaphthalenol **22a** with anisole in the presence of $AlCl_3$ afforded the desired tetralin **23a** in 90% yield and with a 6.7:1 *trans*:*cis* diastereomeric ratio. Introducing substituents at the 2- and 5-position on the phenyl ring further increased the *trans*:*cis* diastereomeric ratio up to 13.3:1 (Scheme 5, compound **23e**). Single-crystal X-ray analysis of tetralin **23d** confirmed the *trans* arrangement of substituents.

We next investigated the intramolecular variant of the Friedel–Crafts alkylation (Scheme 6). As shown in Scheme 6, readily accessible aryl and alkenylboronic esters can be fixed onto the hydronaphthalene during the asymmetric Pd(II)- or Rh(I)-catalyzed ring-opening step of the synthetic sequence.

We first examined the conversion of the biphenyl tetralin **26** into the hexahyrophenanthrene **30a** (Scheme 7).[16]

Intramolecular Friedel–Crafts arylation of biphenyl tetralin **26a** afforded exclusively the *cis* product in quantitative yield. This observation complements results published previously by our group and others.[11,17] Introduction of substituents on the tetralin and nucleophile continued to give the Friedel–Crafts arylated product **30b**,**c** in good yields and *cis*-diastereoselectivity. Single-crystal X-ray analysis of tetralin **30a** confirmed the *cis* arrangement of substituents.

Scheme 2. Inter- and Intramolecular Friedel–Crafts Alkylation

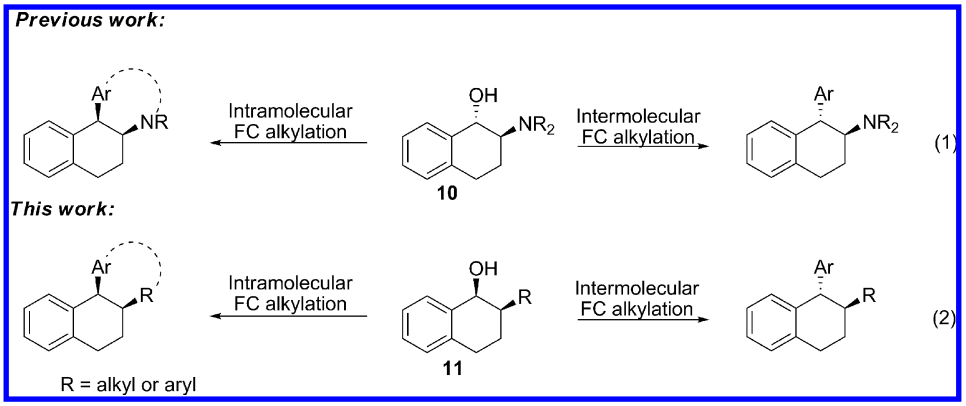


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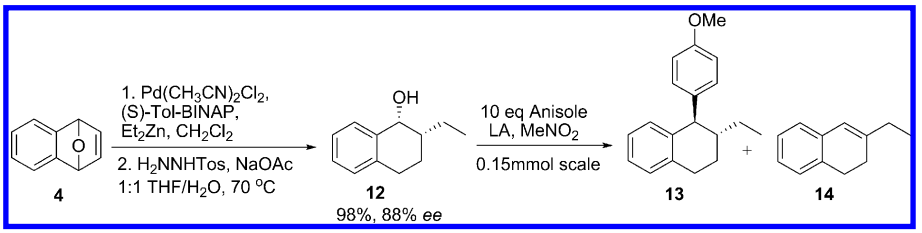
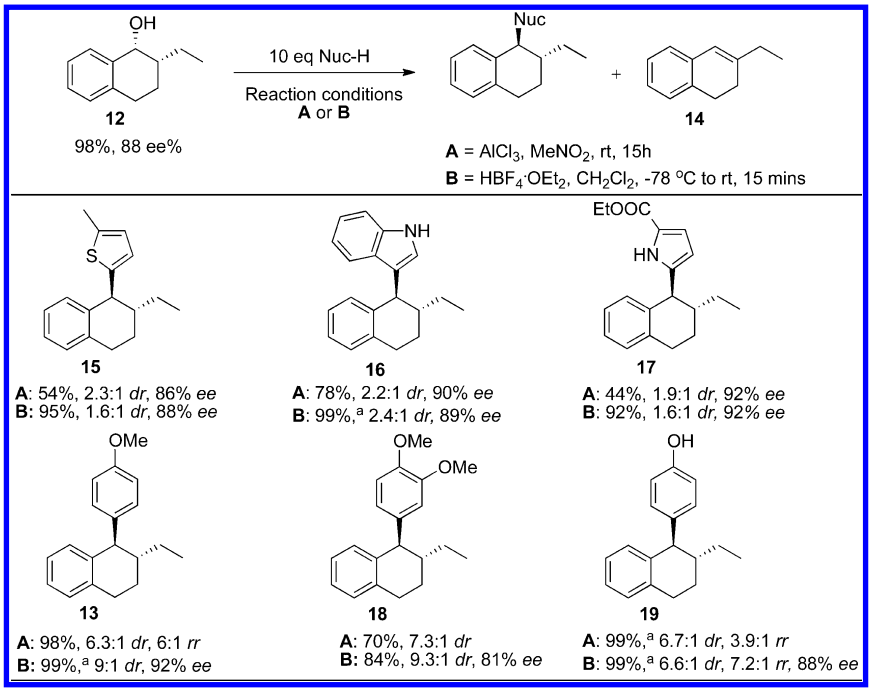
Table 1. Optimization of Friedel–Crafts Alkylation



entry	acid	equiv	temp (°C)	time (h)	yield **13** (%),[a] (dr, rr)[b]	yield **14** (%)
1	$AlCl_3$	1	rt	15	98[c] (dr 6.3:1, rr 6:1)	
2	$AlCl_3$	1	rt	1	94[c] (dr 6.5:1, rr 10:1)	
3	$AlCl_3$	2	rt	0.25	93 (dr 6.7:1, rr 7:1)	
4	$AlCl_3$	0.1	rt	24	no product	
5	$AlCl_3$	1	0	15	68 (dr 4.5:1, rr 10:1)	
6	$FeCl_3$	1	rt	15	88 (dr 4.2:1, rr 8:1)	
7[d]	$HBF_4{\cdot}OEt_2$	1.2	−78	0.25	99[c] (dr 9:1)	
8	$BF_3{\cdot}OEt_2$	1	rt	15	39 (dr 4.6:1)	32
9	pTsOH	1	rt	15	22 (dr 4.2:1)	77
10	TFA	1	60	24	11 (dr 4.6:1, rr 9:1)	61
11	$Zn(OTf)_2$	0.1	60	24	6 (dr 3.1:1)	94
12	$Cu(OTf)_2$	0.1	60	48	no product	
13	$Bi(OTf)_3$	0.1	rt	15		98
14	$AuCl_3$	0.1	60	24	no product	

[a]Yield determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture, in the presence of *p*-nitroacetophenone as an internal standard. [b]The dr for *trans*:*cis* products, rr for *para*:*ortho* products. [c]Isolated yield [d]Reaction was performed in CH_2Cl_2, warmed from −78 °C to rt (ref 3).

Scheme 3. Intermolecular Friedel–Crafts Alkylation Scope



[a]Crude yield, no purification required.

We next investigated the intramolecular Friedel–Crafts alkylation of styryl tetralin **29**. Friedel–Crafts alkylation yields almost exclusively the *cis* tetracyclic product with high yields with a variety of tethered nucleophiles (Scheme 8).[18]

A wide range of substitution patterns are tolerated with this protocol, with *ortho*- and *para*-methoxy-substituted phenyls giving high yields of the corresponding tetralins **31d** and **31e** and *meta*-methoxy-substituted phenyls giving a slightly lower yield of tetralin **31f**. Surprisingly, having a disubstituted phenyl nucleophile as seen in tetracyclic product **31d** also lowered the diastereoselectivity to 1.8:1 of the *cis*:*trans* products. This may be due to the enhanced nucleophilicity of the veratrole or due to the introduction of an *ortho* substituent. The intramolecular variant of this protocol can also allow

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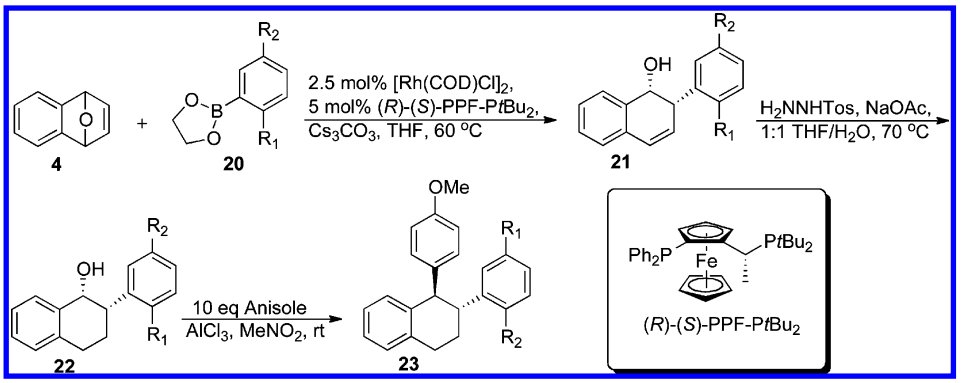
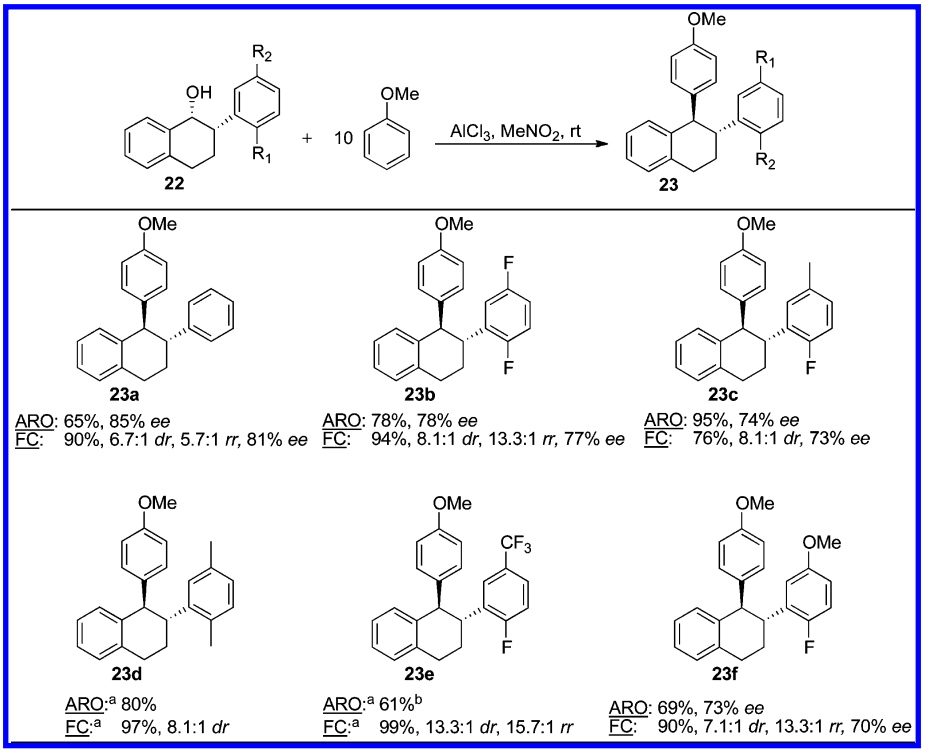
Scheme 4. Synthetic Sequence for Intermolecular Friedel–Crafts Alkylation

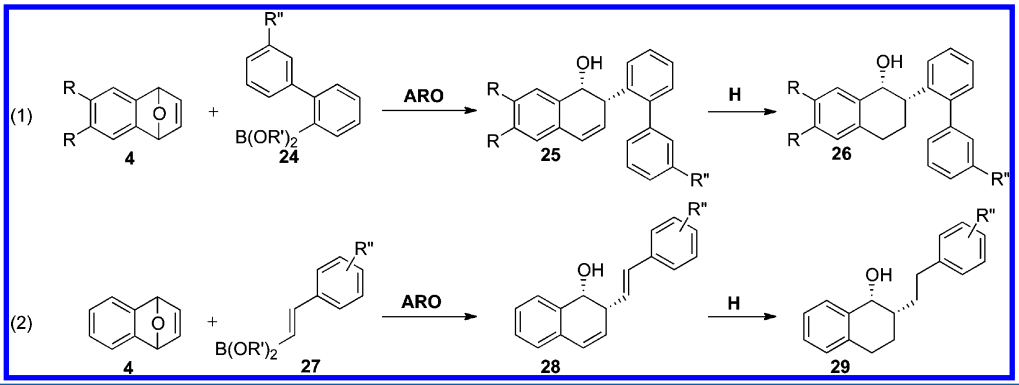


Scheme 5. Improving Diastereoselectivity



[a]No ee determined as no suitable conditions could be found to achieve peak separation. [b]Yield averaged over ARO and hydrogenation step.

Scheme 6. Synthetic Sequence for Intramolecular Friedel–Crafts Alkylation



Friedel–Crafts alkylation to occur with more electron-poor nucleophiles such as the *para*-fluoro-substituted phenyl in **31b**, which is a challenging and rarely used nucleophile in diastereoselective Friedel–Crafts methodologies. Heteroaromatic nucleophiles are also tolerated in this protocol, as seen in product **31c**.

Attempts to increase the ring size of the resulting tetracyclic structure by increasing the length of the tether yielded the

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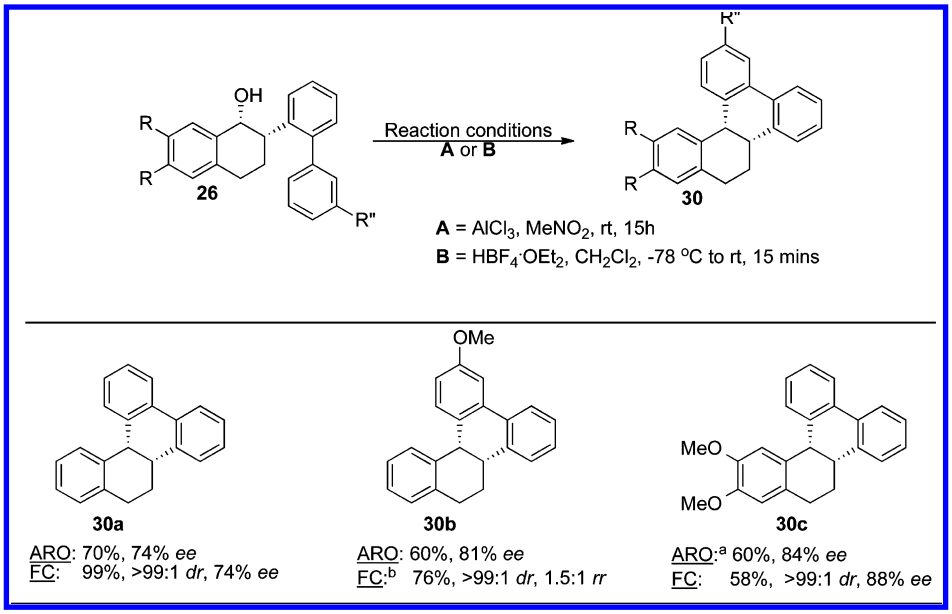
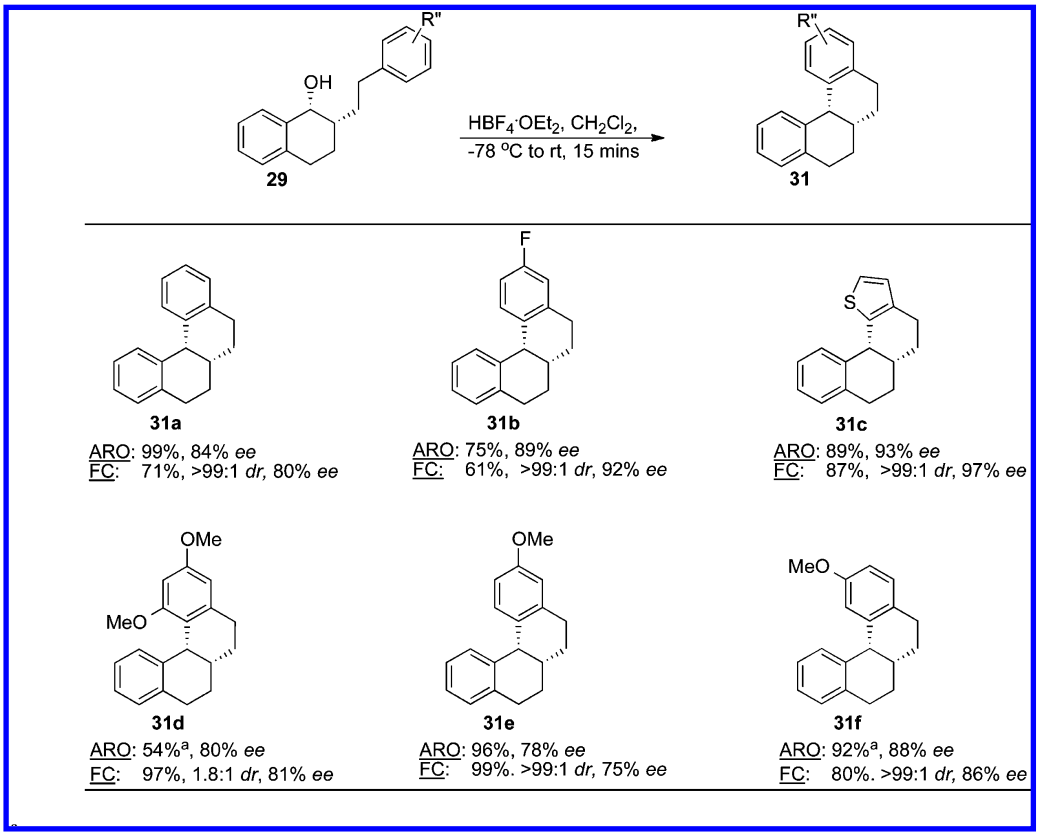
Scheme 7. Intramolecular Friedel–Crafts Arylation with Biphenyl Tetralin 26



[a]Yield averaged over ARO and hydrogenation step; ee determined from hydrogenated product **26c**. [b]No ee determined as no suitable conditions were found to achieve peak separation.

Scheme 8. Intramolecular Friedel–Crafts Alkylation of Styryl Tetralin 29



[a]Yield based on recovered starting material.

unexpected spirocyclic product **36** as a racemic mixture in 75% yield (Scheme 9). A possible pathway might be a Wagner–Meerwein-type hydrogen shift to form the more stabilized carbocation. Further attempts to increase the ring size using 2-phenoxyphenylboronic acid or 2-(3-methoxyphenoxy)-phenylboronic acid resulted predominantly in the elimination product though traces of the desired arylated product could be seen using FC method **B**.

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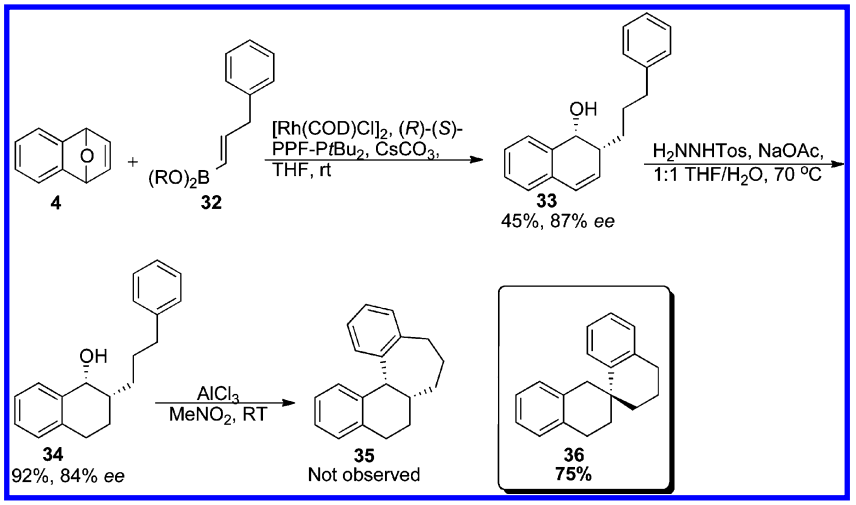
Scheme 9. Increasing Ring Size



CONCLUSION

We have shown that asymmetric transition-metal-catalyzed ring opening and diastereoselective Friedel–Crafts methodologies can be tied in order to rapidly synthesize a wide variety of aryltetralins in high yield and enantioselectivity. The initial metal-catalyzed asymmetric ring-opening step establishes the regiochemistry and the absolute stereochemistry with excellent selectivities. Intermolecular Friedel–Crafts reaction of the resulting products lead to the *trans* product with moderate diastereoselectivity, which can be enhanced by adding steric bulk around the hydronaphthalene core. The intramolecular variant leads to almost exclusively the *cis* product. Numerous aryltetracyclic products with various substitution patterns have been synthesized, showing that this methodology is very useful for the rapid synthesis of analogues. Future work will focus on utilizing this methodology in the synthesis of aryltetralin lignans and other similar natural products.

EXPERIMENTAL SECTION

For general experimental methods see Supporting Information. Characterization data and experimental methods for **4**, **5**–**11**, **12**, **21a**, **22a**, and **24a** were reported previously.[5−7,17−20]

(1*R*,2*R*)-2-Ethyl-1,2-dihydronaphthalen-1-ol. $Pd(MeCN)_2Cl_2$ (46 mg, 0.18 mmol) and (*R*)-Tol-BINAP (119 mg, 0.18 mmol) were dissolved in dry CH_2Cl_2 (20 mL) under argon, and the mixture was stirred for 1 h at rt. The catalyst solution was then transferred via canula to a solution of oxabicyclic alkene **4** (500 mg, 3.50 mmol) in dry CH_2Cl_2 (50 mL). The mixture was cooled to −20 °C, and $ZnEt_2$ (1.0 M in hexane, 5.3 mL, 5.25 mmol) was added dropwise. The resulting red solution was stirred for 6 h over which time it reached room temperature. The mixture was quenched by the addition of saturated NH_4Cl solution, and the aqueous phase was extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/Et_2O 85:15, R_f = 0.43 in hexane/EtOAc 7:3) to afford the title compound (590 mg, 97%) as a colorless oil. The characterization data were fully concordant with that already reported in the literature:[6a] ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.2, 1.0 Hz, 1H), 7.30–7.19 (m, 2H), 7.12 (dd, J = 7.2, 1.3 Hz, 1H), 6.54 (dd, J = 9.6, 2.7 Hz, 1H), 5.83 (ddd, J = 9.6, 2.7, 1.1 Hz, 1H), 4.61 (dd, J = 7.2, 4.7 Hz, 1H), 2.37 (dtt, J = 10.5, 5.1, 2.7 Hz, 1H), 1.90–1.76 (m, 1H), 1.70–1.56 (m, 1H), 1.53 (d, J = 7.7 Hz, 1H), 1.09 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 132.9, 131.2, 128.7, 127.8, 127.7, 126.9, 126.6, 70.1, 42.4, 22.3, 12.0; IR (NaCl) 3395, 3031, 2960, 2931, 2874, 2361, 2341, 1487, 1454, 1379, 1201, 1119, 1069, 1052, 941, 786, 768, 695 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{14}O$ [M^+] 174.1045; found 174.1043; $[\alpha]_D^{28}$ = +97.0 (*c* 1.0, $CHCl_3$) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 12.99 min [minor], t_R = 13.57 min [major].

Representative Procedure 1 for the Hydrogenation of Ring-Opened Substrate (1*R*,2*R*)-2-Ethyl-1,2-dihydronaphthalen-1-ol: *(1S,2S)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-ol* (**12**). A magnetically stirred solution of (1*R*,2*R*)-2-ethyl-1,2-dihydronaphthalen-1-ol (482 mg, 2.77 mmol) in THF (20 mL) and H_2O (20 mL) was treated with tosylhydrazine (2.57 g, 13.9 mmol) and sodium acetate (2.27 g, 27.7 mmol), and the resulting mixture was heated to reflux for 15 h. The mixture was then cooled to rt, treated with saturated K_2CO_3 solution, and the separated aqueous phase extracted with ether (3×). The combined organic layers were then dried ($MgSO_4$) and concentrated under reduced pressure and the ensuing residue subjected to flash chromatography (hexane/EtOAc 9:1, R_f = 0.23 in hexane/EtOAc 85:15) to afford the title compound (577 mg, 99%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.32 (m, 1H), 7.25–7.17 (m, 2H), 7.16–7.10 (m, 1H), 4.67 (s, 1H), 2.88 (dt, J = 17.1, 4.1 Hz, 1H), 2.82–2.71 (m, 1H), 1.80–1.54 (m, 5H), 1.53–1.36 (m, 2H), 1.05 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 137.3, 130.2, 129.2, 128.1, 126.2, 69.9, 41.6, 29.4, 24.6, 22.9, 11.8; IR (NaCl) 3364, 3061, 3020, 2958, 2031, 2874, 1605, 1455, 1432, 1273, 1130, 1072, 1033, 1008, 953, 931, 902, 853, 822, 774, 738 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{16}O$ [M^+] 176.1201; found 176.1204; $[\alpha]_D^{28}$ = −57.7 (*c* 1.0, $CHCl_3$) for 88% ee.

Procedure for Optimization Studies of Friedel–Crafts Alkylation of 12. A magnetically stirred solution of benzylic alcohol **12** (26.4 mg, 0.15 mmol) and anisole (163 μL, 1.50 mmol) was treated with the desired Lewis or Brønsted acid catalyst in either stoichiometric (0.15 mmol) or catalytic amounts (0.015 mmol) and stirred under N_2 for 16 h. The mixture was then treated with *p*-nitroacetophenone (1.14 M in $MeNO_2$, 131.6 μL, 0.15 mmol) as an internal standard in CH_2Cl_2 (1.5 mL), diluted with CH_2Cl_2 (3 mL), quenched with H_2O, the aqueous phase then extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. Product yield was then determined by analysis of the ^1H NMR spectrum of the crude reaction mixture.

Representative Procedure 2 for the $AlCl_3$-Catalyzed Friedel–Crafts Alkylation of 12: *(1S,2S)-2-Ethyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene* (**13**). To a solution of alcohol **12** (53 mg, 0.30 mmol) and anisole (0.33 mL, 3.00 mmol) in CH_2Cl_2 (1 mL) was added $AlCl_3$ (40 mg, 0.30 mmol), and the resulting mixture was stirred for 16 h at rt. The mixture was then diluted with CH_2Cl_2 (10 mL) and poured into saturated $NaHCO_3$ solution (10 mL). The separated aqueous phase was then extracted with CH_2Cl_2 (2 × 15 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The ensuing residue was subjected to flash chromatography (hexanes/EtOAc 98:2

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to 85:15, R_f = 0.49 in hexanes/EtOAc 9:1) to afford a ca. 6.3:1 mixture of diastereomers (rr 6:1) of the title compound (78 mg, 98%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.19−6.87 (m, 5H), 6.82 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 7.7 Hz, 1H), 3.79 (s, 3H), 3.69 (d, J = 8.5 Hz, 1H), 2.98−2.77 (m, 2H), 2.10−1.99 (m, 1H), 1.78−1.67 (m, 1H), 1.54−1.40 (m, 2H), 1.23−1.07 (m, 1H), 0.89 (t, J = 7.4 Hz, 3H); *minor diastereomer* (selected signals) δ 4.11 (d, J = 4.9 Hz, 1H), 0.95 (t, J = 7.1 Hz, 3H); *regioisomer* (selected signals) δ 4.30 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 156.0, 140.3, 139.1, 137.3, 130.7, 130.4, 128.7, 125.8, 125.7, 113.7, 55.3, 51.0, 43.8, 28.9, 26.3, 26.0, 11.4; *minor diastereomer* (selected signals) δ 131.3, 113.1, 12.2; IR (NaCl) 3058, 2997, 2958, 2931, 2874, 2836, 2361, 1611, 1583, 1511, 1491, 1462, 1378, 1301, 1245, 1177, 1108, 1037, 945, 823, 783, 741 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{22}O$ [M$^+$] 266.1671; found 266.1674; $[\alpha]_D^{27}$ = +23.0 (c 1.0, $CHCl_3$) for 92% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexanes, 0.80 mL/min, 254 nm); t_R = 6.43 min [minor], t_R = 9.97 min [major].

Representative Procedure 3 for the HBF_4·OEt_2-Catalyzed Friedel−Crafts Alkylation of 12 (13): To a solution of alcohol **12** (53 mg, 0.30 mmol) and anisole (0.33 mL, 3.00 mmol) in CH_2Cl_2 (1 mL) was added HBF_4·OEt_2 (45 μL, 0.33 mmol) at −78 °C. The mixture was stirred for 5 min at −78 °C and then for 15 min at rt. The mixture was then treated with saturated $NaHCO_3$ solution. The separated aqueous phase was then extracted with Et_2O. The combined organic phases were washed sequentially with saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$), and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (hexanes/EtOAc 9:1) to afford a ca. 9:1 mixture of diastereomers (rr > 95:5) of the title compound (80 mg, quant) as a colorless oil.

2-((1S,2R)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-5-methylthiophene (15): ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.17−7.04 (m, 4H), 6.53 (m, 2H), 3.99 (d, J = 7.8 Hz, 1H), 2.91−2.87 (m, 2H), 2.41 (s, 3H), 2.14−2.07 (m, 1H), 1.90−1.78 (m, 2H), 1.64−1.51 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); *minor diastereomer* (selected signals) δ 6.50 (d, J = 3.5 Hz, 1H), 4.31 (d, J = 3.5 Hz, 1H), 1.48−1.39 (m, 2H), 1.22−1.09 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 148.2, 140.1, 138.9, 138.0, 126.5, 130.3, 128.6, 126.0, 125.6, 124.1, 46.68, 44.0, 28.1, 25.5, 23.8, 15.4, 11.3; *minor diastereomer* (selected signals) δ 144.7, 136.1, 130.5, 129.0, 126.4, 125.6, 124.1, 44.4, 40.5, 29.3, 26.7, 23.8, 15.2, 12.0; IR (NaCl) 3059, 3017, 2959, 2872, 2860, 1491, 1450, 1435, 796, 741, 426, 421, 415, 402 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{20}S$ [M$^+$] 256.1286; found 256.1286.

Procedure 2 with 2-methylthiophene: Column chromatography (hexanes/EtOAc 98:2) yielded a ca. 2.3:1 mixture of diastereomers (rr > 95:5) of the title compound (24.9 mg, 54%) as a colorless oil; HPLC analysis (Chiralcel ODH, 1% iPrOH/hexanes, 1.00 mL/min, 254 nm); 86% ee, t_R = 5.07 min [minor], t_R = 5.64 min [major].

Procedure 3 with 2-methylthiophene: Column chromatography (hexanes/EtOAc 98:2) yielded a ca. 1.6:1 mixture of diastereomers (rr > 95:5) of the title compound (112.7 mg, 95%) as a colorless oil; $[\alpha]_D^{28}$ = +74.6 (c 1.0, $CHCl_3$) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 5.08 min [major], t_R = 5.66 min [minor].

3-((1S,2R)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indole (16): ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.88 (s, br, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 8.2 Hz, 1H), 7.22−7.04 (m, 6H), 6.77 (d, J = 2.4 Hz, 1H), 4.11 (d, J = 7.3 Hz, 1H), 2.97−2.94 (m, 2H), 2.12−2.05 (m, 1H), 1.62−1.51 (m, 2H), 1.37−1.26 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); *minor diastereomer* (selected signals) δ 7.91 (s, br, 1H), 7.61 (d, J = 3.5 Hz, 1H), 6.64 (d, J = 2.5 Hz, 1H), 4.54 (d, J = 4.8 Hz, 1H), 3.10−3.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 139.7, 137.1, 136.9, 130.7, 129.7, 126.7, 125.9, 125.7, 123.5, 122.0, 121.7, 119.9, 119.4, 111.4, 42.4, 41.0, 28.0, 26.2, 25.5, 11.5; *minor diastereomer* (selected signals) δ 141.6, 136.6, 126.1, 130.7, 129.0, 124.2, 121.8, 119.5, 119.5, 41.4, 29.5, 26.5, 23.6, 12.1; IR (NaCl) 3419, 3056, 3015, 2958, 2926, 2872, 2859, 1600, 1488, 1454, 1417, 1377, 1350, 1338, 1265, 1350, 1338, 126, 1245, 1222, 1093, 1011, 807, 756, 739, 580 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{22}N$ [M + H]$^+$ 276.1752; found 276.1752.

Procedure 2 with Indole: Column chromatography (hexanes/EtOAc 9:1, R_f = 0.77 in hexanes/EtOAc 9:1) yielded a ca. 2.2:1 mixture of diastereomers (rr > 95:5) of the title compound (24.1 mg, 78%) as a brown oil; $[\alpha]_D^{29}$ = +17.1 (c 1.0, $CHCl_3$) for 90% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 15.34 min [major], t_R = 20.78 min [minor].

Procedure 3 with Indole: Column chromatography (hexanes/EtOAc 9:1) yielded a ca. 2.4:1 mixture of diastereomers (rr > 95:5) of the title compound (85.9 mg, quant) as a brown oil; HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); 89% ee, t_R = 15.43 min [minor], t_R = 21.28 min [major].

Ethyl 5-((1R,2S)-2-ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-pyrrole-2-carboxylate (17): ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.17−6.98 (m, 4H), 6.86−6.84 (m, 1H), 6.03−6.01 (m, 1H), 4.27 (q, J = 7.0 Hz, 2H), 3.85 (d, J = 8.2 Hz, 1H), 2.86 (t, J = 6.6 Hz, 2H), 2.05−1.98 (m, 1H), 1.86−1.77 (m, 2H), 1.57−1.44 (m, 2H), 1.32 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H); *minor diastereomer* (selected signals) δ 6.81−6.79 (m, 1H), 5.90−5.89 (m, 1H), 4.20 (d, J = 5.5 Hz, 1H), 3.00−2.89 (m, 2H), 1.27 −1.17 (m, 4H), 1.14−1.04 (m, 2H), 0.98 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 161.52, 141.85, 139.63, 137.14, 130.11, 129.23, 126.66, 126.25, 121.93, 115.74, 110.26, 44.98, 42.40, 28.30, 26.34, 25.96; *minor diastereomer* (selected signals) δ 136.93, 130.64, 129.57, 126.93, 121.78. 115.57, 110.65, 42.97, 40.72, 29.36, 26.64, 24.37; IR (NaCl) 3441, 2961, 2932, 2874, 1670, 1484, 1438, 1318, 1205, 1142, 1206, 796, 764, 739 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{24}NO_2$ [M + H]$^+$ 298.1809; found 298.1807.

Procedure 2 with Ethyl Pyrrole-2-carboxylate: Column chromatography (hexanes/EtOAc 9:1) yielded a ca. 1.9:1 mixture of diastereomers (rr > 95:5) of the title compound (21.7 mg, 44%) as a colorless oil; $[\alpha]_D^{29}$ = −18.2 (c 1.0, $CHCl_3$) for 92% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 9.10 min [major], t_R = 12.18 min [minor].

Procedure 3 with Ethyl Pyrrole-2-carboxylate: Column chromatography (hexanes/EtOAc 9:1) yielded a ca. 1.6:1 mixture of diastereomers (rr > 95:5) of the title compound (34.3 mg, 92%) as a colorless oil; HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); 92% ee, t_R = 9.11 min [minor], t_R = 11.86 min [major].

(1S,2S)-1-(3,4-Dimethoxyphenyl)-2-ethyl-1,2,3,4-tetrahydronaphthalene (18): ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.21−6.88 (m, 3H), 6.78 (t, J = 7.6 Hz, 2H), 6.68−6.53 (m, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 3.68 (d, J = 8.8 Hz, 1H), 3.01−2.81 (m, 2H), 2.12−1.99 (m, 1H), 1.81−1.70 (m, 1H), 1.55−1.39 (m, 2H), 1.25−1.09 (m, 1H), 0.90 (t, J = 7.4 Hz, 3H); *minor diastereomer* (selected signals) δ 4.12 (d, J = 5.0 Hz, 1H), 0.97 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 149.0, 147.4, 140.1, 139.4, 137.2, 130.6, 128.7, 125.8, 125.7, 121.8, 112.5, 111.0, 56.0, 56.0, 51.6, 43.6, 29.0, 26.4, 26.2, 11.3; *minor diastereomer* (selected signals) δ 140.4, 136.9, 136.5, 130.8, 128.9, 126.0, 122.7, 114.1, 110.5, 48.9, 40.9, 29.3, 23.2, 12.2; IR (NaCl) 2997, 2957, 2932, 2873, 2836, 2361, 1590, 1515, 1490, 1463, 1417, 1342, 1258, 1231, 1186, 1141, 1030, 806, 768, 740 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{24}O_2$ [M$^+$] 296.1776; found 296.1781.

Procedure 2 with Veratrole: Column chromatography (hexanes/EtOAc 98:2 to 85:15, R_f = 0.30 in hexane/EtOAc 85:15) yielded a ca. 88:12 mixture of diastereomers of the title compound (62 mg, 70%) as a colorless oil.

Procedure 3 with Veratrole: Kugelrohr distillation (118 °C at 55 mmHg) yielded a ca. 9.3:1 mixture of diastereomers of the title compund (41.0 mg, 84%) as a colorless oil; $[\alpha]_D^{27}$ = +25.3 (c 0.5, $CHCl_3$) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexane, 0.80 mL/min, 254 nm); t_R = 6.43 min [major], t_R = 7.13 min [minor].

4-((1S,2S)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)phenol (19): ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.15−6.91 (m, 5H), 6.75−6.73 (m, 1H), 4.77 (s, br, 1H), 3.69 (d, J = 8.6 Hz, 1H), 2.91−2.28 (m 2H), 2.06−2.00 (m, 1H), 1.74−1.71 (m, 2H), 1.51−1.41 (m, 2H), 1.21−1.14 (m, 1H), 0.90 (t, J = 7.4 Hz, 3H); *minor diastereomer* (selected signals) δ 6.85−6.73 (m, 2H), 6.68−6.66

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(m, 1H), 4.11 (d, J = 5.1 Hz, 1H), 1.64−1.62 (m, 1H), 1.07 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 153.56, 140.06, 139.09, 137.16, 130.55, 130.39, 128.52, 125.59, 125.51, 115.02, 50.76, 43.60, 28.73, 26.07, 25.82, 11.18; *minor diastereomer* (selected signals) δ 155.44, 131.34, 130.60, 129.63, 126.79, 125.82, 120.73, 115.29, 114.38, 48.24, 40.84, 29.17, 26.22, 22.74, 12.00; IR (NaCl) 3346, 2959, 2928, 2872, 1612, 1511, 1455, 1241, 1172, 824, 741, 407 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{24}NO$ [M + NH_4]$^+$ 270.1858; found 270.1858.

Procedure 2 with Phenol: Column chromatography (hexanes/EtOAc 9:1) yielded a ca. 6.7:1 mixture of diastereomers (rr 3.9:1) of the title compound (126.0 mg, quant) as a white solid, mp = 48−54 °C.

Procedure 3 with Phenol: Column chromatography (hexanes/EtOAc 9:1) yielded a ca. 6.6:1 mixture of diastereomers (rr 7.2:1) of the title compound (100.9 mg, quant) as a white solid; $[\alpha]_D^{29}$ = +16.8 (c 0.3, $CHCl_3$) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 13.64 min [minor], t_R = 20.13 min [major].

Representative Procedure 4 for the Rh-Catalyzed Asymmetric Ring Opening of Substrate 4: *(1R,2S)-2-phenyl-1,2-dihydronaphthalen-1-ol (**21a**).* A 100 mL flask was charged with $[Rh(COD)Cl]_2$ (43 mg, 0.086 mmol), (*R*)-(*S*)-PPF-P(*t*-Bu)$_2$ (95 mg, 0.175 mmol), and oxabicyclic alkene **4** (506 mg, 3.50 mmol). A stir bar was added and the flask was sealed and flushed with argon before distilled THF (20 mL) was added. Phenylboronic acid ethylene glycol ester (609 mg, 4.20 mmol) was then added by syringe as a THF solution (3 mL), followed by Cs_2CO_3 (5M) in H_2O (0.35 mL). The reaction was stirred for 16 h at rt. The reaction mixture was filtered on a short silica gel pad, washing with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the crude product purified by column chromatography (hexanes/EtOAc 9:1) to afford the title compound (507 mg, 65%) as a colorless oil. The characterization data were fully concordant with that already reported in the literature:[6g] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.21 (m, 8H), 7.17 (dd, J = 7.2, 1.2 Hz, 1H), 6.71 (dd, J = 9.6, 2.0 Hz, 1H), 6.13 (dd, J = 9.6, 4.0 Hz, 1H), 4.94 (dd, J = 7.7, 6.2 Hz, 1H), 3.88 (ddd, J = 6.0, 4.0, 2.1 Hz, 1H), 1.46 (d, J = 8.0 Hz, 1H); $[\alpha]_D^{28}$ = −76.7 (c 1.2, $CHCl_3$) for 85% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm); t_R = 16.41 min [major], t_R = 31.53 min [minor].

*(1R,2S)-2-Phenyl-1,2,3,4-tetrahydronaphthalen-1-ol (**22a**). Procedure 1 from **21a**:* Column chromatography (hexanes/EtOAc 85:15, R_f = 0.18 in 85:15 EtOAc/hexanes) yielded the title compound (462 mg, 99%) as a white solid. The characterization data were fully concordant with that already reported in the literature:[19] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43−7.33 (m, 5H), 7.32−7.17 (m, 4H), 4.80 (t, J = 2.8 Hz, 1H), 3.13 (dt, J = 12.9, 2.8 Hz, 1H), 3.05 (ddd, J = 17.1, 5.5, 2.1 Hz, 1H), 2.95 (dd, J = 12.0, 5.7 Hz, 1H), 2.46 (ddd, J = 25.1, 12.7, 5.6 Hz, 1H), 2.04−1.92 (m, 1H), 1.56 (d, J = 3.6 Hz, 1H); $[\alpha]_D^{28}$ = +126 (c 1.2, $CHCl_3$) for 93% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm); t_R = 20.41 min [major], t_R = 30.96 min [minor].

*(1S,2S)-1-(4-Methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydronaphthalene (**23a**). Procedure 2 from **22a**:* Column chromatography (hexanes/EtOAc 95:5, R_f = 0.63 in hexanes/EtOAc 9:1) to afford a ca. 6.7:1 mixture of diastereomers (rr 5.7:1) of the title compound (84 mg, 90%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) *p-regioisomer, major diastereomer* δ 7.21−7.07 (m, 6H), 7.07−6.98 (m, 3H), 6.87−6.76 (m, 2H), 6.69 (d, J = 8.6 Hz, 2H), 4.14 (d, J = 9.7 Hz, 1H), 3.74 (s, 3H), 3.18−2.98 (m, 2H), 2.93 (dt, J = 16.6, 4.2 Hz, 1H), 2.19−2.08 (m, 2H); *minor diastereomer* (selected signals) δ 6.54 (d, J = 8.6 Hz, 2H), 6.33 (d, J = 8.6 Hz, 2H), 4.30 (d, J = 4.9 Hz, 1H); *o-regioisomer, major diastereomer* δ 7.19−7.07 (m, 1H), 7.07−6.98 (m, 1H), 6.86−6.76 (m, 1H), 6.74 (d, J = 8.2 Hz, 1H), 4.70 (d, J = 8.9 Hz, 1H), 3.49 (s, 1H), 3.17 (td, J = 9.1, 4.5 Hz, 1H), 3.13−3.02 (m, 1H), 2.90 (dt, J = 16.6, 4.6 Hz, 1H), 2.15 (d, J = 4.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) *p-regioisomer, major diastereomer* δ 157.9, 145.4, 140.4, 138.2, 137.2, 130.5, 130.3, 128.8, 128.2, 127.7, 126.1, 126.0, 125.9, 113.5, 55.3, 52.6, 50.4, 30.3, 30.1; *minor diastereomer* (selected signals) δ 131.6, 128.4, 127.9, 126.3, 112.5, 30.0; *o-regioisomer, major diastereomer* (selected signals) δ 157.7, 145.7, 140.4, 137.3, 134.7, 130.5, 129.9, 128.6, 127.9, 127.7, 127.2, 125.9, 125.6, 120.7, 111.1, 55.6, 48.1, 30.1, 29.7; HRMS (EI) calcd for $C_{23}H_{22}O$ [M$^+$] 314.1671; found 314.1668; $[\alpha]_D^{27}$ = −46.8 (c 1.0, $CHCl_3$) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1 mL/min, 254 nm); t_R = 4.96 min [minor], t_R = 8.92 min [major].

Representative Procedure 5 for the Protection of Boronic Acids as Boronic Ethylene Glycol Esters: *2-(2,5-Difluorophenyl)-1,3,2-dioxaborolane (**20b**).* (2,5-Difluorophenyl)boronic acid (800 mg, 5.07 mmol) was dissolved in toluene (80 mL), and ethylene glycol (314 mg, 5.07 mmol) was added. The mixture was heated to 150 °C with magnetic stirring under Dean−Stark and reflux for 24 h. The mixture was allowed to cool to rt, and the solvent was removed under reduced pressure to afford the title compound (933 mg, quant) as a white solid: mp 45−46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 3.7 Hz, 1H), 7.16−7.10 (m, 1H), 7.02 (td, J = 8.8, 4.0 Hz, 1H), 4.42 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 122.4, 122.3, 122.2, 120.3, 120.2, 120.1, 120.0, 116.9, 116.8, 116.6, 116.6, 66.2; IR (NaCl) 3468, 2959, 1640, 1485, 1435, 1420, 1400, 1343, 1254, 1188, 1115, 1084, 1022, 895, 818, 764 cm^{-1}; HRMS (EI) calcd for $C_8H_7BF_2O_2$ [M$^+$] 184.0507; found 184.0507.

*(1R,2S)-2-(2,5-Difluorophenyl)-1,2-dihydronaphthalen-1-ol (**21b**). Procedure 4 from **4**:* Column chromatography (pentane/Et_2O 98:2 to 95:5) yielded the title compound (128.5 mg, 78%) as an off-white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.25 (m, 3H), 7.19 (dd, J = 7.2, 1.4 Hz, 1H), 7.06−6.98 (m, 2H), 6.95−6.89 (m, 1H), 6.75 (dd, J = 9.6, 2.5 Hz, 1H), 6.00 (dd, J = 9.6, 3.4 Hz, 1H), 4.88 (t, J = 6.0, 1H), 4.25 (dt, J = 5.3, 2.8 Hz, 1H), 1.67 (d, J = 7.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 160.1, 158.4, 158.4, 157.7, 157.7, 156.0, 156.0, 135.5, 132.1, 129.2, 129.0, 128.5, 128.0, 127.6, 127.0, 117.7, 117.7, 117.5, 117.4, 116.5, 116.4, 116.3, 116.2, 115.4, 115.3, 115.2, 115.1, 70.4, 40.2, 40.2; IR (NaCl) 3391, 3071, 3040, 2924, 2855, 2361, 1628, 1593, 1493, 1454, 1424, 1277, 1238, 1177, 1142, 1072, 995, 980, 945, 876, 826, 768, 741, 694, 629 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{12}F_2O$ [M$^+$] 258.0856; found 258.0856; $[\alpha]_D^{28}$ = +189.0 (c = 1.0, $CHCl_3$) for 78% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 10.60 min [minor], t_R = 13.88 min [major].

*(1R,2S)-2-(2,5-Difluorophenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**22b**). Procedure 1 from **21b**:* Column chromatography (pentanes/EtOAc 8:2) yielded the title compound (695 mg, 89%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.3, 1.5 Hz, 1H), 7.30−7.23 (m, 2H), 7.21−7.19 (m, 1H), 7.11 (m, 1H), 7.03 (td, J = 9.2, 4.6 Hz, 1H), 6.96−6.90 (m, 1H), 4.86 (t, J = 3.5 Hz, 1H), 3.05 (ddd, J = 17.1, 5.7, 2.0 Hz, 1H), 2.99−2.91 (m, 1H), 2.41 (qd, J = 12.5 Hz, 5.6 Hz, 1H), 1.91−1.85 (m, 1H), 1.54 (d, J = 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 160.0, 157.9, 157.8, 157.6, 157.6, 155.5, 155.4, 137.6, 136.2, 131.7, 131.6, 131.5, 131.4, 130.3, 129.2, 128.4, 126.4, 116.5, 116.4, 116.2, 116.2, 116.1, 116.0, 115.9, 115.8, 114.4, 114.3, 114.2, 114.1, 100.0, 69.5, 69.5, 38.7, 38.7, 29.4, 21.1; IR (NaCl) 3314, 3078, 3063, 3024, 2916, 2839, 2361, 2342, 1628, 1593, 1493, 1454, 1424, 1377, 1316, 1278, 1246, 1173, 1142, 1080, 1053, 1010, 957, 907, 872, 814, 779, 745 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{14}F_2O$ [M$^+$] 260.1013; found 260.1013; $[\alpha]_D^{28}$ = +189.0 (c = 1.0, $CHCl_3$).

*(1R,2R)-2-(2,5-Difluorophenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**23b**). Procedure 2 from **22b**:* Preparative thin layer chromatography (hexanes/EtOAc 9:1) yielded a ca. 8.1:1 mixture of diastereomers (rr 13.3:1) of the title compound (89 mg, 94%) as an off-white oil; ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.18−7.11 (m, 2H), 7.03 (t, J = 8.1 Hz, 1H), 6.88−6.85 (m, 2H), 6.84−6.73 (m, 4H), 6.72−6.68 (m, 2H), 4.17 (d, J = 10.1 Hz, 1H), 3.74 (s, 3H), 3.40 (td, J = 9.8, 3.7 Hz, 1H), 3.15−3.07 (m, 1H), 2.93 (dt, J = 16.8, 4.3 Hz, 1H), 2.19−2.07 (m, 2H) ppm; *minor diastereomer* (selected signals) δ 7.25−7.18 (m, 2H), 7.00−6.94 (m, 3H), 6.58−6.55 (m, 2H), 6.43−6.40 (m, 2H), 6.10−6.05 (m, 1H), 4.51 (d, J = 5.0 Hz, 1H), 3.70 (s, 3H), 1.79−1.75 (m, 1H), 0.89−0.87 (m, 1H); *regioisomer* (selected signals) δ 4.74 (d, J = 5.8 Hz, 1H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 158.0, 139.7, 136.9, 136.5, 131.1, 130.1, 130.1,128.7, 126.0, 125.9, 116.4, 116.3, 116.1, 116.0, 115.2, 115.2, 115.0, 114.9, 113.9, 113.8, 113.7,

113.6, 113.5, 112.6, 77.4, 77.0, 76.7, 55.1, 51.0, 51.0, 43.0, 29.8, 29.0, 29.0; *minor diastereomer* (selected signals) δ 159.9, 159.9, 157.8, 157.7, 157.5, 157.5,155.4, 155.4, 133.9, 133.8, 133.7, 133.7, 131.1, 130.8, 128.9, 126.3, 53.4, 48.0, 37.8, 29.6, 21.5; IR (NaCl) 3731, 3445, 3422, 2932, 2839, 2361, 2334, 2064, 1643, 1616, 1501, 1462, 1427, 1387, 1366, 1339, 1300, 1246, 1207, 1178, 1146, 1107, 1038, 976, 868, 818, 745 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{20}F_2O$ [M^+] 350.1482; found 350.1482; $[\alpha]_D^{28}$ = −78.6 (c = 1.0, $CHCl_3$) for 77% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexanes, 1.00 mL/min, 269 nm); t_R = 4.69 min [minor], t_R = 5.30 min [major].

*2-(2-Fluoro-5-methylphenyl)-1,3,2-dioxaborolane (**20c**). Procedure 5 from 2-Fluoro-5-methylphenyl)boronic acid:* The title compound (435 mg, 93%) was isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.7, 5.4 Hz, 1H), 7.26−7.22 (m, 1H), 6.94 (t, J = 8.9 Hz, 1H), 4.40 (s, 4H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 164.4, 137.2, 137.1, 134.2, 134.2, 133.0, 133.0, 115.2, 115.0, 66.0, 20.5; IR (NaCl) 2982, 2913, 2361, 1616, 1493, 1416, 1335, 1285, 1219, 1126, 1076, 1003, 945, 818, 736, 648 cm^{-1}; HRMS (EI) calcd for $C_9H_{10}BFO_2$ [M^+] 180.0758; found 180.0758.

*(1R,2S)-2-(2-Fluoro-5-methylphenyl)-1,2-dihydronaphthalen-1-ol (**21c**). Procedure 4 from **20c**:* Flash chromatography (pentanes/EtOAc 95:5 to 9:1) to afford the title compound (335 mg, 95%) as an off-white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.33 (m, 1H), 7.36−7.24 (m, 2H), 7.19−7.18 (m, 1H), 7.11 (dd, J = 7.1, 1.9 Hz, 1H), 7.06−7.02 (m, 1H), 6.99−6.95 (m, 1H), 6.74 (dd, J = 9.6, 2.6 Hz, 1H), 6.04 (dd, J = 9.6, 2.6 Hz, 1H), 4.82 (s, 1H), 4.26 (dt, J = 5.1, 2.9 Hz, 1H), 2.29 (s, 3H), 1.62 (d, J = 4.6, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 158.1, 135.5, 133.6, 133.6, 132.2, 131.2, 131.1, 129.3, 129.2, 128.7, 128.6, 128.5, 128.1, 127.8, 126.7, 125.7, 125.5, 115.1, 114.9, 70.2, 40.2, 40.2, 20.8; IR (NaCl) 3553, 3430, 3036, 2924, 2859, 2361, 1497, 1454, 1381, 1281, 1238, 1204, 1072, 991, 880, 818, 764 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}FO$ [M^+] 254.1107; found 254.1107; $[\alpha]_D^{28}$ = −56.5 (c = 1.0, $CHCl_3$) for 74% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 8.88 min [minor], t_R = 14.27 min [major].

*(1R,2S)-2-(2-Fluoro-5-methylphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**22c**). Procedure 1 from **21c**:* Flash chromatography (hexanes/EtOAc 8:2) yielded the title compound (265 mg, 92%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.3, 1.3 Hz, 1H), 7.29−7.22 (m, 2H), 7.20−7.18 (m, 1H), 7.16 (dd, J = 7.1, 1.8 Hz, 1H), 7.06−7.02 (m, 1H), 6.98−6.93 (m, 1H), 4.85 (s, 1H), 3.44 (dt, J = 13.2, 2.5 Hz, 1H), 3.05 (ddd, J = 17.1, 5.5, 1.8 Hz, 1H), 2.99 - 2.90 (m, 1H), 2.45 (qd, J = 12.7, 5.8 Hz, 1H), 2.35 (s, 3H), 1.90−1.84 (m, 1H), 1.53 (d, J = 4.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 157.8, 137.7, 136.5, 133.5, 133.4, 130.5, 129.9, 129.8, 129.1, 129.0, 128.9, 128.5, 128.5, 128.2, 126.2, 114.9, 114.7, 69.6, 69.6, 53.4, 38.7, 38.7, 30.9, 29.7, 21.0, 21.0; IR (NaCl) 3538, 3318, 3024, 2928, 2839, 2338, 1605, 1497, 1454, 1435, 1381, 1242, 1207, 1088, 1053, 961, 941, 810, 775, 741 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{17}FO$ [M^+] 256.1263; found 256.1263; $[\alpha]_D^{28}$ = −20.9 (c = 0.5, $CHCl_3$).

*(1R,2R)-2-(2-Fluoro-5-methylphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**23c**). Procedure 2 from **22c**:* Column chromatography (pentanes/EtOAc 98:2) yielded a ca. 8.1:1 mixture of diastereomers of the title compound (62 mg, 76%) as a pink oil; ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.16−7.10 (m, 2H), 7.02 (t, J = 8.0 Hz,1H), 6.92−6.88 (m, 2H), 6.86−6.83 (m, 2H), 6.79 (d, J = 7.8 Hz, 1H), 6.76−6.72 (m, 1H), 6.70−6.66 (m, 2H), 4.22 (d, J = 10.2 Hz, 1H), 3.73 (s, 3H), 3.36 (td, J = 10.8, 2.9 Hz, 1H), 3.14−3.06 (m, 1H), 2.92 (dt, J = 16.6, 3.1, 1H), 2.23 (s, 3H), 2.21−2.07 (m, 2H); *minor diastereomer* (selected signals) δ 7.19−7.17 (m, 1H), 7.08−7.06 (m, 1H), 6.98−6.95 (m, 2H), 6.57−6.53 (m, 2H), 6.39−6.36 (m, 2H), 6.11 (d, J = 7.5 Hz, 1H), 4.38 (d, J = 5.0 Hz, 1H), 3.69 (s, 3H), 1.78−1.74 (m, 1H), 1.53 (s, 3H), 0.90−0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 160.0, 157.8, 157.6, 140.2, 137.5, 136.8, 133.1, 133.0, 131.5, 131.3, 131.3, 130.2, 130.1, 129.2, 129.2, 128.6, 127.8, 127.7, 125.8, 125.8, 115.0, 114.7, 113.3, 112.3, 55.1, 51.0, 51.0, 43.2, 30.1, 29.3, 29.3, 20.8; *minor diastereomer* (selected signals) δ 139.6, 136.4, 134.8, 130.8, 129.7, 129.6, 128.9, 128.5, 127.6, 127.5, 127.1, 126.2, 125.9, 114.2, 113.9, 112.3, 55.1, 48.3, 37.6, 29.8, 29.7, 21.6, 20.6; IR (NaCl) 3441, 2059, 2017, 2928, 2835, 2361, 2064, 1613, 1586, 1508, 1454, 1300, 1246, 1215, 1177, 1107, 1038, 818, 779, 748 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{23}FO$ [M^+] 346.1733; found 346.1733; $[\alpha]_D^{28}$ = +42.6 (c = 1.0, $CHCl_3$) for 73% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm); t_R = 4.29 min [minor], t_R = 4.49 min [major].

*2-(2,5-Dimethylphenyl)-1,3,2-dioxaborolane (**20d**). Procedure 5 from (2,5-Dimethylphenyl)boronic Acid:* The title compound (586 mg, quant) was isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.15 (dd, J = 1.5, 7.7 Hz, 2H), 7.07 (d, J = 7.7 Hz, 1H), 4.33 (s, 4H), 2.49 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 136.9, 134.0, 132.0, 130.0, 65.8, 21.8, 20.8; IR (NaCl) 3013, 2974, 2909, 2862, 1609, 1574, 1497, 1481, 1385, 1367, 1331, 1277, 1207, 1146, 1076, 1007, 945, 876, 817, 783, 733, 671, 656 cm^{-1}; HRMS (EI) calcd for $C_{10}H_{13}BO_2$ [M^+] 176.1009; found 176.1006.

*(1S,2R)-2-(2,5-Dimethylphenyl)-1,2-dihydronaphthalen-1-ol (**21d**). Procedure 4 from **20d**:* Flash chromatography (pentanes/Et_2O 95:5) yielded the title compound (94 mg, 65%) as a white, viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.29 (m, 2H), 7.27−7.23 (m, 1H), 7.19−7.17 (m, 1H), 7.12−7.08 (m, 2H), 7.01−6.99 (m, 1H), 6.71 (dd, J = 9.6, 2.6 Hz, 1H), 6.06 (dd, J = 9.6, 2.3 Hz, 1H), 4.74 (t, J = 4.6 Hz, 1H), 4.16 (dt, J = 5.1, 9.2 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.54 (d, J = 5.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 135.8, 135.3, 133.4, 132.5, 130.6, 130.5, 130.1, 128.7, 128.0, 127.9, 127.8, 127.8, 126.6, 69.5, 43.4, 21.1, 19.3; IR (NaCl) 3522, 3422, 3032, 2920, 2731, 1613, 1501, 1451, 1377, 1288, 1192, 1157, 1072, 1034, 991, 945, 92, 872, 806, 768, 690, 667, 629 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}O$ [M^+] 250.1358; found 250.1358; $[\alpha]_D^{28}$ = −7.4 (c = 1.0, $CHCl_3$).

*(1S,2R)-2-(2,5-Dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**22d**). Procedure 1 from **21d**:* Column chromatography (pentanes/EtOAc 95:5 to 9:1) to afford the title compound (396 mg, 87%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 1H), 7.29−7.25 (m, 1H), 7.23−7.19 (m, 2H), 7.13−7.10 (m, 2H), 7.01−6.99 (m, 1H), 4.74 (bs, 1H), 3.30 (dt, J = 12.9, 2.6 Hz, 1H), 3.05 (ddd, J = 19.0, 5.4, 1.8 Hz, 1H), 2.98−2.89 (m, 1H), 2.52 (qd, J = 12.7, 5.4, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 4.26 (dt, J = 5.2, 3.0 Hz, 1H), 3.68 (s, 3H), 1.83 (dqt, J = 12.87, 2.2, 1.2 Hz, 1H), 1.60 (d, J = 3.1, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 137.7, 136.9, 135.6, 132.8, 130.7, 130.6, 129.1, 128.5, 128.1, 127.3, 126.1, 68.8, 42.0, 30.2, 22.0, 21.3, 19.1; IR (NaCl) 3530, 3329, 3021, 2920, 2874, 2835, 1609, 1501, 1454 m 1381, 1157, 1084, 967, 941, 903, 810, 771, 737 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{20}O$ [M^+] 252.1514; found 252.1514; $[\alpha]_D^{28}$ = −50.0 (c = 1.0, $CHCl_3$)

*(1S,2S)-2-(2,5-Dimethylphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**23d**). Procedure 2 from **22d**:* Preparatory thin layer chromatography (hexanes/EtOAc 9:1, R_f = 0.73 in hexanes/EtOAc 9:1) yielded a ca. 8.1:1 mixture of diastereomers (rr > 95:5) of the title compound (122 mg, 97%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.19−7.10 (m, 3H), 7.06−7.02 (m, 1H), 6.86−6.82 (m, 3H), 6.79−6.75 (m, 2H), 6.67−6.63 (m, 2H), 4.19 (d, J = 10.0 Hz, 1H), 3.72 (s, 3H), 3.27 (td, J = 10.4, 3.9 Hz, 1H), 3.09 (m, 1H), 2.92 (dt, J = 16.5, 3.9, 1H), 2.30 (s, 3H), 2.05−2.00 (m, 2H), 1.79 (m, 3H); *minor diastereomer* (selected signals) δ 6.98−6.96 (m, 1H), 6.56−6.53 (m, 2H), 6.28−6.25 (m, 2H), 4.27 (d, J = 4.8 Hz, 1H), 3.70 (s, 3H), 3.54 - 3.50 (m, 1H), 2.41 (s, 3H), 2.27 (s, 1H), 2.11 (d, J = 4.6 Hz, 1H), 1.25 (s, 3H), 0.90−0.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 157.7, 143.5, 140.6, 138.1, 137.3, 135.2, 132.8, 130.3, 130.2, 129.8, 128.6, 126.9, 126.4, 125.8, 125.6, 113.2, 55.1, 52.4, 45.0, 30.6, 30.4, 21.3, 19.0; *minor diastereomer* (selected signals) δ 131.5, 130.8, 129.5, 128.9, 128.7, 126.3, 126.2, 125.8, 112.1, 109.5, 55.2, 47.9, 40.9, 30.2, 22.7, 20.9, 19.0; IR (NaCl) 3473, 3013, 2928, 2862, 2839, 2334, 1640, 1613, 1586, 1508, 1458, 1300, 1246, 1177, 1107, 1038, 814, 745 cm^{-1}; HRMS (EI) calcd for $C_{25}H_{26}O$ [M^+] 342.1984; found 342.1984; $[\alpha]_D^{28}$ = 35.5 (c = 1.0, $CHCl_3$).

*2-(2-Fluoro-5-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**20e**). Procedure 5 from (2-Fluoro-5-(trifluoromethyl)phenyl)-boronic Acid:* The title compound (881 mg, 98%) was isolated as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 5.1, 2.2 Hz, 1H), 7.72 (septet of doublets, J = 2.5, 0.5 Hz, 1H), 7.16 (t, J = 8.7 Hz, 1H), 4.43 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.2,

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167.6, 167.6, 134.5, 134.5, 130.9, 130.9, 130.8, 130.8, 122.5, 116.2, 116.0, 66.2; IR (NaCl) 3422, 2990, 2920, 1624, 1597, 1497, 1435, 1400, 1373, 1350, 1311, 1231, 1165, 1123, 1084, 995, 945, 833, 748 cm^{-1}; HRMS (EI) calcd for $C_9H_7BF_4O_2$ [M^+] 235.0475; found 235.0475.

*(1R,2S)-2-(2-Fluoro-5-(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-ol (**21e**). Procedure 4 from **20e**:* Flash chromatography (pentanes/EtOAc 98:2 to 7:3) yielded the title compound as a mixture with some oxabenzonorbornadiene starting material (identified by ^1H NMR). Separation of the starting material from the desired product was not further attempted. Rather, the crude was continued to the hydrogenation step.

*(1R,2S)-2-(2-Fluoro-5-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**22e**). Procedure 1 from **21e**:* Flash chromatography (pentanes/EtOAc 95:5) to afford the title compound (177 mg, 61% (over 2 steps)) as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 6.6, 2.0 Hz, 1H), 7.54 (m, 1H), 7.33 (dd, J = 7.2, 1.2 Hz, 1H), 7.31−7.27 (m, 1H), 7.26−7.15 (m, 3H), 4.86 (t, J = 3.3 Hz, 1H), 3.48 (dt, J = 13.2, 2.5 Hz, 1H), 3.08 (ddd, J = 17.1, 5.6, 1.7 Hz, 1H), 3.01−2.92 (m, 1H), 2.49 (qd, J = 12.7, 5.7 Hz, 1H), 1.95−1.86 (m, 1H), 1.53 (d, J = 4.9, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.2, 131.0, 130.9, 130.3, 129.3, 128.5, 127.4, 127.4, 127.4 127.3, 126.4, 125.6, 125.5, 125.5,, 125.5, 115.8, 115.5, 69.4, 69.4, 38.6, 29.5, 21.2; IR (NaCl) 3376, 2924, 2851, 1640, 1605, 1501, 1424, 1331, 1269, 1169, 1126, 1088, 1053, 961, 907, 829, 779, 741 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{14}F_4O$ [M^+] 310.0981; found 310.0981; $[\alpha]_D^{28}$ = −40.7 (c = 1.0, $CHCl_3$).

*(1R,2R)-2-(2-Fluoro-5-(trifluoromethyl)phenyl)-1-(4-methoxyphenyl)-1,2,3,4- tetrahydronaphthalene (**23e**). Procedure 2 from **22e**:* Preparative thin layer chromatography (hexanes/EtOAc 8:2) yielded a ca. 13.3:1 mixture of diastereomers (rr 7:1) of the title compound (91 mg, quant) as an off-white oil; ^1H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.43 (dd, J = 6.4, 1.9 Hz, 1H), 7.39−7.35 (m, 1H), 7.17−7.11 (m, 2H), 7.03, (t, J = 8.1 Hz, 1H), 6.96 (t, J = 9.2 Hz, 1H), 6.85−6.81 (m, 2H), 6.78 (d, J = 7.8 Hz, 1H), 6.70−6.67 (m, 2H), 4.19 (d, J = 10.6 Hz, 1H), 3.73 (s, 3H), 3.46 (td, J = 11.1, 2.9 Hz, 1H), 3.19−3.10 (m, 1H), 2.97 (dt, J = 16.5, 4.0, 1H), 2.22 (qd, J = 12.1, 4.8 Hz, 1H), 2.15−2.18 (m, 1H); *minor diastereomer* (selected signals) δ 7.56 (dd, J = 6.7, 2.0 Hz, 1H), 7.20 (dd, J = 7.3, 1.1 Hz, 1H), 7.10−7.08 (m, 2H), 6.91−6.90 (m, 1H), 6.57−6.53 (m, 2H), 6.51 (dd, J = 6.6, 1.7 Hz, 1H), 6.37−6.33 (m, 2H), 4.35 (d, J = 5.0, 1H), 3.68 (s, 3H), 1.80−1.75 (m, 1H), 0.94−0.90 (m, 2H); *regioisomer* (selected signals) δ 7.72−7.70 (m, 1H), 7.54−7.52 (m, 1H), 4.85 (d, J = 10.2 Hz, 1H), 3.55 (s, 3H), 1.68 (q, J = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 158.0, 139.7, 136.5, 136.4, 133.1, 132.9, 131.0, 130.0, 130.0, 128.7, 126.4, 126.4, 126.3, 126.3, 126.3, 126.0, 125.9, 125.0, 124.9, 124.9, 124.8, 116.0, 115.7, 113.5, 112.7, 77.3, 77.0, 76.7, 55.1, 51.3, 51.3, 43.2, 30.0, 29.3, 29.3; *minor diastereomer* (selected signals) δ 163.6, 163.6, 161.1, 161.1, 133.1, 132.9, 131.0, 130.8, 130.0, 130.0, 128.9, 128.5, 127.9, 127.4, 126.7, 126.6, 126.4, 126.4, 126.3, 126.3, 125.7, 125.2, 125.0, 125.0, 124.9, 124.9, 124.8, 124.8, 124.8, 122.5, 120.7, 114.9, 112.7, 48.2, 38.7, 37.5, 21.6, 11.0; IR (NaCl) 3433, 3422, 3067, 3021, 2932, 2839, 1728, 1609, 1508, 1458, 1331, 1242, 1169, 1126, 1076, 1038, 903, 826, 745 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{20}F_4O$ [M^+] 400.1450; found 400.1450; $[\alpha]_D^{28}$ = +26.2 (c = 1.0, $CHCl_3$).

*2-(2-Fluoro-5-methoxyphenyl)-1,3,2-dioxaborolane (**20f**). Procedure 5 from (2-Fluoro-5-methoxyphenyl)boronic Acid:* The title compound (937 mg, quant) was isolated as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22−7.21 (m, 1H), 6.99−6.98 (m, 1H), 6.97 (d, J = 1.8 Hz, 1H), 4.41 (s, 4H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 160.6, 119.9, 119.8, 116.4, 116.1, 100.0, 66.1, 55.8; IR (NaCl) 3445, 3422, 2963, 2916, 2839, 1640, 1420, 1335, 1292, 1207, 1126, 1069, 1038, 995, 945, 880, 818, 733 cm^{-1}; HRMS (EI) calcd for $C_9H_{10}BFO_3$ [M^+] 196.0707; found 196.0707.

*(1R,2S)-2-(2-Fluoro-5-methoxyphenyl)-1,2-dihydronaphthalen-1-ol (**21f**). Procedure 4 from **20f**:* Flash chromatography (pentanes/EtOAc 9:1) yielded the title compound (747 mg, 69%) as an off-white oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 1H), 7.32−7.24 (m, 2H), 7.18 (dd, J = 7.2, 1.3 Hz, 1H), 7.00 (t, J = 9.2 Hz, 1H), 6.83−6.80 (m, 1H), 6.77−7.75 (m, 1H), 6.73 (dd, J = 7.4, 2.2 Hz, 1H), 6.04 (dd, J = 9.6, 3.4 Hz, 1H), 4.89 (t, J = 6.0, 1H), 4.26 (dt, J = 5.2, 3.0 Hz, 1H), 3.68 (s, 3H), 1.68 (d, J = 6.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 155.7, 155.7, 154.3, 135.5, 132.2, 128.7, 128.7, 128.5, 128.2, 127.4, 126.7, 126.6, 126.5, 115.9, 115.7, 115.7, 115.6, 113.5, 113.4, 77.4, 77.1, 76.7, 70.3, 55.7, 40.2, 40.2; IR (NaCl) 3422, 2835, 1640, 1505, 1107, 1076, 1042, 1076, 1042, 991, 945, 860, 725 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{15}FO_2$ [M^+] 270.1056; found 270.1056; $[\alpha]_D^{28}$ = +226.5 (c = 0.5, $CHCl_3$) for 73% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm); t_R = 13.84 min [minor], t_R = 20.97 min [major].

*(1R,2S)-2-(2-Fluoro-5-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**22f**). Procedure 1 from **21f**:* Flash chromatography (pentanes/EtOAc 95:5) yielded the title compound (598 mg, 83%) as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.3, 1.5 Hz, 1H), 7.29−7.18 (m, 3H), 7.00 (t, J = 9.3 Hz, 1H), 6.91 (dd, J = 5.9, 3.1 Hz, 1H), 6.76 (dt, J = 8.9, 3.6 Hz, 1H), 4.86 (t, J = 3.2 Hz, 1H), 3.79 (s, 3H), 3.45 (dt, J = 13.2, 2.8 Hz, 1H), 3.04 (ddd, J = 17.0, 5.5, 1.9 Hz, 1H), 2.99−2.90 (m, 1H), 2.43 (qd, J = 12.6, 5.6 Hz, 1H), 1.92−1.85 (m, 1H), 1.55 (d, J = 4.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 155.7, 137.6, 136.4, 130.5, 130.5, 129.1, 128.2, 126.3, 115.6, 115.4, 115.2, 115.2, 112.2, 112.2, 100.0, 69.6, 69.6, 55.7, 38.9, 29.6, 21.1; IR (NaCl) 3445, 3422, 2936, 2835, 2357, 2087, 1640, 1497, 1454, 1427, 1296, 1204, 1150, 1088, 1057, 1038, 945, 806, 775, 741 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{17}FO_2$ [M^+] 272.1213; found 272.1213; $[\alpha]_D^{28}$ = −62.8 (c = 1.0, $CHCl_3$).

*(1R,2R)-2-(2-Fluoro-5-methoxyphenyl)-1-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (**23f**). Procedure 2 from **22f**:* Preparative thin layer chromatography (hexanes/EtOAc 8:2) yielded a ca. 7.1:1 mixture of diastereomers (rr 13.3:1) of the title compound (118 mg, 89%) as an off-white oil; ^1H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.16−7.10 (m, 2H), 7.03 (t, J = 7.3 Hz, 1H), 6.89−6.86 (m, 2H), 6.81−6.76 (m, 2H), 6.70−6.66 (m, 2H), 6.65−6.64 (m, 1H), 6.62−6.58 (m, 1H), 4.21 (d, J = 10.0 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.38 (td, J = 10.3, 3.5 Hz, 1H), 3.14−3.06 (m, 1H), 2.92 (dt, J = 16.7, 4.3, 1H), 2.15−2.06 (m, 2H); *minor diastereomer* (selected signals) δ 7.20−7.14 (m, 1H), 7.08−7.06 (m, 1H), 6.58−6.55 (m, 2H), 6.44−6.40 (m, 2H), 5.85 (dd, J = 5.9, 3.1 Hz, 1H), 4.39 (d, J = 5.0 , 1H), 3.48 (s, 3H), 1.21−1.20 (m, 1H); *regioisomer* (selected signals) δ 4.77 (d, J = 9.4 Hz, 1H), 3.66 (s, 3H), 3.60 (s, 3H), 3.50 (d, J = 2.4 Hz, 1H), 2.85 (t, J = 4.8 Hz, 1H), 1.80−1.75 (m, 2H); *regioisomer; minor diastereomer* (selected signals) δ 3.91 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 158.1, 140.2, 137.5, 137.0, 130.4, 130.3, 128.9, 126.1, 126.1, 115.9, 115.7, 114.4, 114.3, 113.6, 112.7, 112.1, 112.0, 77.6, 77.3, 77.2, 77.0, 76.9 55.8, 55.3, 51.1, 51.1, 43.5, 30.1, 29.3, 29.3; *minor diastereomer (selected signals):* δ 156.5, 155.7, 154.2, 133.0, 132.8, 131.4, 131.0, 114.4, 112.7, 29.9; IR (NaCl) 3449, 3001, 2932, 2835, 2361, 2334, 1609, 1589, 1500, 1458, 1296, 1246, 1296, 1211, 1180, 1107, 1038, 818, 745 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{23}FO_2$ [M^+] 362.1682; found 362.1682; $[\alpha]_D^{28}$ = +70.2 (c = 1.0, $CHCl_3$) for 70% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm); t_R = 4.58 min [minor], t_R = 5.20 min [major].

*2-(2-Biphenyl)-1,3,2-dioxaborolane (**24a**). Procedure 5 from 2-(2-Biphenyl)boronic Acid:* The title compound (2.77 g, 98%) was isolated as a colorless oil. The characterization data were fully concordant with that already reported in the literature:[20] ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 7.4, 0.9 Hz, 1H), 7.53−7.46 (m, 1H), 7.44−7.31 (m, 7H), 4.21 (s, 4H).

*(1R,2S)-2-(2-Biphenyl)-1,2-dihydronaphthalen-1-ol (**25a**). Procedure 4 from **24a**:* Flash chromatography (hexanes/EtOAc 9:1 to 85:15, R_f = 0.28 in hexanes/EtOAc 85:15) yielded the title compound (264 mg, 60%) as a colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.17 (m, 12H), 7.13 (d, J = 7.5 Hz, 1H), 6.64 (dd, J = 9.6, 2.5 Hz, 1H), 6.05 (dd, J = 9.6, 3.3 Hz, 1H), 4.61 (dd, J = 6.8, 6.2 Hz, 1H), 4.20−4.10 (m, 1H), 1.48 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.6, 136.5, 135.7, 132.4, 131.0, 130.5, 129.6, 129.4, 128.6, 128.4, 128.1, 127.9, 127.6, 127.6, 127.3, 127.1, 126.6, 70.5, 43.3; IR (NaCl) 3534, 3424, 3056, 3025, 2361, 2338, 1735, 1452, 1244 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{16}$ [$M-H_2O$]$^+$: 280.1252; found 280.1254; $[\alpha]_D^{28}$ = −163 (c 0.4, $CHCl_3$) for 74% ee, as determined by

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HPLC analysis (Chiralcel ODH, 10% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 5.99 min [minor], t_R = 11.59 min [major].

*(1R,2S)-2-(2-Biphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**26a**). Procedure 1 from **25a**:* Flash chromatography (hexanes/EtOAc 95:5, R_f = 0.20 in hexanes/EtOAc 85:15) yielded the title compound (471 mg, 98%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.8, 1.1 Hz, 1H), 7.44−7.05 (m, 12H), 4.46 (d, J = 2.7 Hz, 1H), 3.30 (dt, J = 12.8, 2.8 Hz, 1H), 2.95 (ddd, J = 16.9, 5.1, 2.0 Hz, 1H), 2.84−2.68 (m, 1H), 2.43 (qd, J = 12.7, 5.2 Hz, 1H), 1.92−1.79 (m, 1H), 1.59 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.8, 140.0, 138.0, 136.7, 130.6, 130.5, 129.3, 129.1, 128.5, 128.3, 128.0, 127.7, 127.1, 126.5, 126.2, 70.0, 41.8, 29.9, 23.0; IR (NaCl) 3317, 3057, 3023, 2931, 2361, 2338, 1598, 1575, 1480, 1450, 1453, 1383, 1272, 1242, 1216, 1088, 1050 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{20}O$ [M$^+$] 300.1514; found 300.1507; $[\alpha]_D^{28}$ = −94.9 (c 1.0, $CHCl_3$) for 74% ee, as determined by HPLC analysis (Chiralcel ODH, 10% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 5.45 min [minor], t_R = 8.26 [major].

*(4bR,10bR)-4b,5,6,10b-Tetrahydrobenzo[g]chrysene (**30a**). Procedure 2 from **26a**:* Flash chromatography (hexanes to hexanes/EtOAC 95:5, R_f = 0.59 in hexanes/EtOAc 95:5) to afford the title compound (56 mg, quant) as a white solid, mp 114−115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.38−7.09 (m, 9H), 6.85 (d, J = 7.6 Hz, 1H), 3.17 (dt, J = 11.5, 4.1 Hz, 1H), 2.96 (ddd, J = 17.7, 10.1, 7.8 Hz, 1H), 2.83 (dd, J = 17.3, 5.3 Hz, 1H), 1.99−1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.7, 136.6, 136.5, 133.6, 133.5, 131.6, 129.8, 128.8, 128.1, 128.1, 127.7, 127.4, 126.9, 125.4, 124.0, 124.0, 42.8, 39.6, 28.5, 24.6; IR (NaCl) 3342, 3062, 3017, 2886, 2927, 1917, 1597, 1493, 1451, 1090, 772, 749, 756, 738, 621 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{18}$ [M$^+$] 282.1409; found 282.1404; $[\alpha]_D^{28}$ = +161 (c 1.0, $CHCl_3$) for 74% ee, as determined by HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 5.42 min [major], t_R = 6.61 min [minor].

6-(2-Bromophenyl)-2-methyl-1,3,5,7,2,6-tetraoxazaborocane-4,8-dione. The title compound was synthesized according to a procedure of Burke and co-workers. A round-bottom flask equipped with a stir bar was charged with 2-bromophenylboronic acid (2 g, 10 mmol), *N*-methyliminodiacetic acid (1.47 g, 10 mmol), and toluene/DMSO (100 mL:40 mL). The flask was fitted with a Dean−Stark trap and a reflux condenser, and the mixture was refluxed with stirring for 20 h. The reaction solution was allowed to cool to rt and the solvent was removed in vacuo. The product was eluted with Et_2O:MeCN 1:1. The title compound was isolated as a white crystalline solid (3.05 g, 96%). The characterization data were fully concordant with that already reported in literature:[21] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.5, 2.0 Hz, 1H), 7.61 (dd, J = 8.0, 1.2 Hz, 1H), 7.36 (td, J = 7.5, 1.2 Hz, 1H), 7.27 (td, J = 7.6, 1.9 Hz, 1H), 4.03 (d, J = 16.6 Hz, 2H), 3.96 (d, J = 16.8 Hz, 2H), 2.81 (s, 3H).

6-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-2-methyl-1,3,5,7,2,6-tetraoxazaborocane-4,8-dione. To a mixture of 6-(2-bromophenyl)-2-methyl-1,3,5,7,2,6-tetraoxazaborocane-4,8-dione (664 mg, 2 mmol)), 3-methoxyboronic acid (365 mg, 2.4 mmol), and K_3PO_4 (1.27 g, 6 mmol) in THF (18 mL) was added a premixed solution of $Pd(OAc)_2$ (67 mg, 0.1 mmol) and cyclohexyl-JohnPHOS (70 mg, 0.2 mmol) under a nitrogen atmosphere. The mixture was stirred at 65 °C for 20 h. After cooling to room temperature, the mixture was filtered through a pad of silica gel and Celite. Evaporation of the volatile material under vacuum followed by purification by flash column chromatography (Et_2O to 3:1 Et_2O/CH_3CN) afforded the title compound as a brown oil (452 mg, 56%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.0, 2.0 Hz, 1H), 7.42 (m, 2H), 7.30 (m, 1H), 7.22 (dd, J = 7.4, 1.6 Hz, 1H), 6.89 (m, 2H), 3.85 (s, 3H), 2.48 (s, 3H), 2.01 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 145.4, 142.8, 132.59, 129.0, 127.6, 127.5, 125.3, 119.9, 116.5, 113.8, 111.6, 53.4, 45.4; IR (NaCl) 3007, 2956, 2917, 2837, 1767, 1489, 1476, 1336, 1297, 1211, 1196, 1113, 1029, 1005, 887, 863, 754, 705, 642 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{22}BN_2O_5$ [M + NH_4]$^+$ 357.1622; found 357.1622.

*2-(3′-Methoxy-[2-biphenyl]-2-yl)-1,3,2-dioxaborolane (**24b**).* To a solution of 6-(3′-methoxy-[1,1′-biphenyl]-2-yl)-2-methyl-1,3,5,7,2,6-tetraoxazaborocane-4,8-dione (342 mg, 1 mmol) in THF (30 mL) was added aq NaOH (1 N, 3 mL, 3 mmol) at rt. The mixture was stirred vigorously for 15 min. Mixture was diluted with pH 7 sodium phosphate buffer, then extracted with Et_2O (3×). The organic phase was dried ($MgSO_4$) and evaporated under vacuum, leaving the boronic acid (898 mg, quant) as a brown oil. Procedure 5 was then followed to produce the title compound (687 mg, 85%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.4, 1.0 Hz, 1H), 7.51−7.46 (m, 1H), 7.42−7.34 (m, 2H), 7.31 (t, J = 7.9 Hz, 1H), 7.01−6.94 (m, 2H), 6.90 (ddd, J = 8.2, 2.6, 1.0 Hz, 1H), 4.22 (s, 4H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 288.4, 277.0, 274.0, 264.3, 259.7, 258.4, 258.1, 255.7, 250.7, 249.9, 243.6, 242.0, 195.2, 184.5; IR (NaCl) 3056, 2963, 2907, 2834, 1596, 1584, 1560, 1478, 1437, 1388, 1366, 1333, 1258, 1212, 1178, 1119, 1082, 1048, 1019, 987, 942, 864, 801, 787, 764 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{15}O_3B$ [M$^+$] 254.1114; found 254.1112.

*(1R,2S)-2-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-1,2-dihydronaphthalen-1-ol (**25b**).* To a mixture of oxabicyclic akene **4** (40 mg, 0.281 mmol) and **24b** (72 mg, 0.283 mmol) in MeOH (3 mL) was added a premixed solution of $Pd(CH_3CN)_2Cl_2$ (3.6 mg, 0.014 mmol) and (*S*)-Tol-BINAP (10.4 mg, 0.015 mmol) under an argon atmosphere. The vial was sealed, and Cs_2CO_3 in H_2O (5 M) was syringed in. The reaction was stirred at 60 °C for 16 h. After cooling to rt, the mixture was filtered through a pad of silica gel. Evaporation of the volatile material under vacuum followed by flash column chromatography (hexanes/EtOAc 4:1) afforded the title compound as a brown oil (42 mg, 60% bsrm): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.36 (m, 1H), 7.31−3.17 (m, 7H), 7.11 (d, J = 7.6 Hz, 1H), 6.93−6.85 (m, 3H), 6.62 (dd, J = 9.6, 2.5 Hz, 1H), 6.03 (dd, J = 9.7, 3.3 Hz, 1H), 4.62 (m, 1H), 4.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.8, 142.6, 136.3, 135.5, 132.3, 130.9, 130.1, 129.4, 129.2, 128.4, 127.9, 127.7, 126.4, 121.7, 112.6, 70.4, 55.2, 43.1 IR (NaCl) 3416, 3058, 3019, 2926, 2858, 2836, 1607, 1579 1498, 1451, 1254, 1212, 1043, 1021, 762, 745, 412, 403 cm^{-1}. LRMS (ESI) calcd for $C_{23}H_{20}O_2$ [M − H_2O]$^+$ 210.14; found 311.1; $[\alpha]_D^{27}$ = −1.3 (c 1.0, $CHCl_3$) for 81% ee, as determined by HPLC analysis (Chiralcel ADH, 8% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 4.04 min [minor], t_R = 15.58 min [major].

*(1R,2S)-2-(3′-Methoxy-[1,1′-biphenyl]-2-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (**26b**). Procedure 1 from **25b**:* Flash chromatography (hexane/EtOAc 95:5, R_f = 0.20 in hexane/EtOAc 85:15) yielded the title compound (21 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.8, 1.4 Hz, 1H), 7.40 (td, J = 7.5, 1.7 Hz, 1H), 7.31 (td, J = 7.4, 1.4 Hz, 2H), 7.28−7.10 (m, 6H), 6.89 (t, J = 1.3 Hz, 1 H), 6.87 (t, J = 1.2 Hz, 1H), 4.50 (m, 1H), 3.32 (dt, J = 12.9, 2.9 Hz, 1H), 2.99−2.92 (m, 1H), 2.77 (ddd, J = 17.2, 12.0, 5.5 Hz, 1H), 2.51−2.38 (m, 1H), 1.81−1.89 (m, 1H), 1.59 (d, J = 3.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 143.0, 142.3, 139.8, 137.9, 126.6, 130.4, 130.3, 129.2, 129.0, 127.9, 128.4, 127.6, 126.3, 126.0, 121.6, 115.0, 112.4, 66.9, 55.2, 41.6, 29.8, 22.9; IR (NaCl) 3379, 2933, 1605, 1575, 1475, 1463, 1424, 1317, 1297, 1214, 1178, 1046, 1020, 959, 760, 739, 704 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{26}NO_2$ [M + NH_4]$^+$: 348.1964; found 348.1964; $[\alpha]_D^{26}$ = −1.2 (c 1.00, $CHCl_3$).

*(4bR,10bR)-13-Methoxy-4b,5,6,10b-tetrahydrobenzo[g]chrysene (**30b**). Procedure 3 from **26b**:* Flash chromatography (hexanes/Et_2O 99:1) yielded the title compound (10 mg, 76%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *major regioisomer* δ 7.78 (d, J = 7.4 Hz, 1H), 7.49−7.16 (m, 8H), 6.94−6.92 (m, 1H), 6.71 (d, J = 2.7 Hz, 1H), 4.21 (d, J = 5.1 Hz, 1H), 3.83 (s, 3H), 3.18−3.13 (m, 1H), 3.01−2.84 (m, 2H), 1.92−1.75 (m, 2H); *minor regioisomer* (selected signals) δ 7.67 (dd, J = 7.4, 1.6 Hz, 1H), 6.85 (td, J = 7.1, 7.1, 2.2 Hz, 1H), 6.68 (d, J = 2.3 Hz, 1H), 4.64 (d, J = 5.5 Hz, 1H), 3.93 (s, 3H), 3.40−3.37 (m, 1H), 2.82−2.73 (m, 2H), 2.44−2.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *major regioisomer* δ 158.6, 136.4, 134.5, 131.4, 131.0, 129.7, 128.5, 128.1, 128.0, 128.0, 127.3, 126.7, 125.6, 125.3, 125.2, 123.1, 110.0, 109.3, 55.4, 35.7, 34.9, 28.5, 24.5; *minor regioisomer* (selected signals) δ 117.3, 112.4, 55.7, 41.9, 39.6, 24.8, 23.7; IR (NaCl) 3418, 2926, 2849, 1642, 1490, 1464, 1253, 1218, 1044, 1023, 751, 741 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{24}NO$ [M + NH_4^+] 330.1858; found 330.1858.

*(1R,2S)-2-([1,1′-Biphenyl]-2-yl)-6,7-dimethoxy-1,2-dihydronaphthalen-1-ol (**25c**). Procedure 4 from **24a**:* Flash chromatography

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(hexanes/EtOAc 7:3) yielded the title compound (141 mg, 20%) as a colorless solid, mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.24 (m, 9H), 6.80 (s, 1H), 6.67 (s, 1H), 6.55 (dd, J = 9.6, 2.4 Hz, 1H), 5.95 (dd, J = 9.6, 3.3 Hz, 1H), 4.52 (t, J = 5.8 Hz, 1H), 4.13−4.06 (m, 1H), 3.88 (s, 1H), 3.86 (s, 1H), 1.44 (d, J = 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 143.0, 141.6, 136.7, 130.5, 129.7, 129.4, 129.1, 128.4, 127.9, 127.3, 127.2, 127.1, 125.5, 111.3, 110.1, 70.4, 56.2, 56.2, 43.3; IR (NaCl) 3515, 2001, 2956, 2935, 2835, 2359, 2340, 1605, 1512, 1478, 1463, 1452, 1288, 1266, 1211, 1168, 115, 1071, 1027, 909, 861, 775 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{20}O_2$ [M−H_2O]$^+$: 340.1463; found 340.1479.

*(1R,2S)-2-([1,1′-Biphenyl]-2-yl)-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalen-1-ol (**26c**). Procedure 1 from **25c**:* Flash chromatography (hexane/EtOAc 7:3, R_f = 0.15 in EtOAc/hexane 7:3) to afford the title compound (119 mg, quant) as a colorless solid, mp 63−65 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, J = 7.8, 1.3 Hz, 1H), 7.45−7.22 (m, 8H), 6.70 (s, 1H), 6.57 (s, 1H), 4.39 (s, 1H), 3.83 (d, J = 1.4 Hz, 6H), 3.28 (dt, J = 12.8, 2.8 Hz, 1H), 2.85 (ddd, J = 16.5, 5.1, 2.2 Hz, 1H), 2.75−2.62 (m, 1H), 2.43−2.32 (m, 1H), 1.88−1.79 (m, 1H), 1.55 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.7, 141.9, 140.0, 130.7, 130.0, 129.7, 129.3, 129.1, 128.5, 128.4, 128.3, 127.8, 127.2, 126.5, 113.0, 111.4, 77.6, 77.2, 76.9, 69.8, 56.2, 56.1, 42.0, 29.7, 23.2; IR (NaCl) 3441, 2921, 2851, 2361, 2341, 1643, 1515, 1463, 1338, 1230, 1164, 1122, 1019 756, 703, 679, 678, 659, 651 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}O_3Na$ [M + Na]$^+$: 383.1617; found 363.1617; $[\alpha]_D^{28}$ = −50.0 (c 1.0, $CHCl_3$) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 15% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 17.39 min [minor], t_R = 31.00 min [major].

*(4bR,10bR)-8,9-Dimethoxy-4b,5,6,10b-tetrahydrobenzo[g]-chrysene (**30c**). Procedure 2 from **26c**:* Flash chromatography (hexanes to hexanes/EtOAC 9:1, R_f = 0.37 in hexanes/EtOAc 95:5) yielded the title compound (40 mg, 58%) as a white solid, mp 68−70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 1H), 7.76 (dd, J = 7.7, 1.2 Hz, 1H), 7.38−7.24 (m, 5H), 7.16 (td, J = 7.5, 1.2 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 6.72 (s, 1H), 6.68 (s, 1H), 4.19 (d, J = 4.9 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.19−3.10 (m, 1H), 2.90 (ddd, J = 17.8, 10.6, 7.4 Hz, 1H), 2.75 (ddd, J = 17.1, 6.6, 2.3 Hz, 1H), 1.92−1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 146.9, 139.0, 133.4, 128.7, 128.4, 128.1, 127.8, 127.4, 126.9, 124.0, 123.9, 114.2, 112.3, 56.2, 56.0, 42.4, 39.9, 28.3, 24.6; IR (NaCl) 2997, 2931, 2855, 2253, 1512, 1452, 1235 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}O_2$ [M + H$^+$] 343.1692; found 343.1702; $[\alpha]_D^{28}$ = +153 (c 1.0, $CHCl_3$) for 88% ee, as determined by HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 23.71 min [major], t_R = 30.42 min [minor].

*(1R,2R)-2-((E)-Styryl)-1,2-dihydronaphthalen-1-ol (**28a**). Procedure 4 from (E)-Styrylboronic Acid:* Flash chromatography (hexanes/EtOAc 95:5 to 9:1) yielded the title compound (730 mg, 84%) as a white solid, mp 93−97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 5.6, 3.0 Hz, 1H), 7.39−7.32 (m, 2H), 7.31−7.24 (m, 4H), 7.24−7.18 (m, 1H), 7.13 (dd, J = 5.7, 3.1 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.58 (d, J = 9.6 Hz, 1H), 6.15 (dd, J = 15.9, 8.9 Hz, 1H), 6.01 (dd, J = 9.5, 4.7 Hz, 1H), 4.92 (dd, J = 8.8, 5.8 Hz, 1H), 3.34 (dt, J = 9.2, 5.7 Hz, 1H), 1.81 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 137.0, 134.4, 132.7, 129.1, 128.7, 128.2, 128.1, 127.9, 127.8, 126.6, 126.5, 126.1, 126.1, 70.9, 45.4; IR (NaCl) 3410, 3027, 2917, 2361, 2338, 1651, 1574, 1543, 1489, 1451, 1379, 1051, 966, 787, 748 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{16}O$ [M$^+$] 248.1201; found 248.1199; $[\alpha]_D^{28}$ = −35.5 (c 1.1, $CHCl_3$) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 32.11 min [minor], t_R = 33.64 min [major].

Representative Procedure 6 for the Reduction of Alkenylboronic Acid Ring-Opened Products. *(1R,2R)-2-Phenethyl-1,2,3,4-tetrahydronaphthalen-1-ol (**29a**).* A magnetically stirred solution of the alkene **28a** (638 mg, 2.57 mmol) in THF (44 mL) and H_2O (44 mL) was treated with tosylhydrazine (4.78 g, 25.7 mmol) and sodium acetate (4.21 g, 51.4 mmol), and the resulting mixture was heated to reflux for 20 h. The mixture was then cooled to rt, treated with saturated K_2CO_3 solution, and the separated aqueous phase extracted with ether (3×). The combined organic layers were then dried ($MgSO_4$) and concentrated under reduced pressure, and the ensuing residue was subjected to flash chromatography (hexane/EtOAc 9:1, R_f = 0.31 in EtOAc/hexane 85:15) to afford the title compound (674 mg, quant) as a colorless solid, mp 48−50 °C: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.08 (m, 9H), 4.68 (s, 1H), 2.94−2.65 (m, 4H), 2.12−1.89 (m, 1H), 1.86−1.64 (m, 4H), 1.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.7, 137.2, 130.2, 129.2, 128.6, 128.5, 128.1, 126.3, 125.9, 70.0, 39.1, 33.5, 33.4, 29.3, 23.1; IR (NaCl) 3364, 3024, 2926, 2859, 2361, 2341, 1603, 1496, 1454, 1431, 1102, 1080, 968, 941, 902, 775, 739, 698, 668 cm-1; HRMS (EI) calcd for $C_{18}H_{20}O$ [M$^+$] 252.1514; found 252.1507; $[\alpha]_D^{28}$ = +57.0 (c 1.0, $CHCl_3$) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm); t_R = 30.14 min [major], t_R = 31.75 min [minor].

*(6aS,12bS)-5,6,6a,7,8,12b-Hexahydrobenzo[c]phenanthrene (**31a**). Procedure 3 from **29a**:* Flash chromatography (pentane/Et_2O 99:1 to 98:2, R_f = 0.69 in hexanes/EtOAc 95:5) to afford the title compound (68 mg, 97%) as a white solid, mp 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.05 (m, 8H), 3.99 (d, J = 5.2 Hz, 1H), 2.90−2.76 (m, 4H), 2.47−2.36 (m, 1H), 1.98 (td, J = 11.2, 5.6 Hz, 2H), 1.55 (dq, J = 13.0, 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.6, 130.0, 128.7, 126.1, 125.4, 43.0, 32.5, 28.2, 27.4; IR (NaCl) 3059, 3016, 1924, 2858, 2361, 1489, 1449, 786, 748 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{18}$ [M$^+$] 234.1409; found 234.1411; $[\alpha]_D^{26}$ = +207.1 (c 0.5, $CHCl_3$) for 80% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 6.47 min [major], t_R = 7.14 min [minor].

*(1S,2S)-2-((E)-3-Fluorostyryl)-1,2-dihydronaphthalen-1-ol (**28b**). Procedure 4 from (E)-3-Fluorostyrylboronic Acid:* Flash chromatography (pentane/EtOAc 9:1) yielded the title compound (88.8 mg, 75%) as white crystalline needles, mp 171−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.44 (m, 1H), 7.31−7.27 (m, 2H), 7.25−7.21 (m, 1H), 7.15−7.10 (m, 2H), 7.06−7.06 (m, 1H), 6.93−6.88 (m, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.58 (dd, J = 9.4, 1.6 Hz, 1H), 6.19 (dd, J = 15.8, 8.6 Hz, 1H), 5.99 (dd, J = 9.4, 4.7 Hz, 1H), 4.92 (dd, J = 8.6, 5.5 Hz, 1H), 3.34 (ddd, J = 8.6, 5.5, 4.7 Hz, 1H), 1.76 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 136.8, 132.9, 132.4, 129.9, 128.6, 128.2, 128.1, 127.9, 237.7, 126.5, 114.5, 114.3, 112.9, 112.7, 70.8, 45.2; IR (NaCl) 3365, 3033, 1607, 1583, 1485, 1446, 1143, 779, 685 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{15}FO$ [M + NH_4^+] 284.1451; found 284.1451; $[\alpha]_D^{26}$ = +117 (c 1.1, $CHCl_3$) for 89% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 4.53 min [major], t_R = 7.61 min [minor].

*(1S,2S)-2-(3-Fluorophenethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**29b**). Procedure 6 from **28b**:* Flash chromatography (pentane/EtOAc 9:1, R_f = 0.55 in pentane/EtOAc 9:1) yielded the title compound (61.8 mg, 82%) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 1H), 7.26−7.21 (m, 3H), 7.15−7.13 (m, 1H), 6.96 (dt, J = 10.1, 2.3 Hz, 1H), 6.88 (td, J = 8.5, 2.6 Hz, 1H), 4.69 (app. s, 1H), 2.92−2.73 (m, 4H), 2.02−1.97 (m, 1H), 1.82−1.72 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.5, 130.0, 129.7, 129.7, 129.1, 128.0, 126.2, 124.1, 115.3, 115.1, 112.5, 69.8, 38.9, 33.1, 33.0, 29.1, 22.9; IR (NaCl) 2927, 1588, 1488, 1452, 1254, 1159, 1139, 781, 75, 691, 590 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}FO$ [M$^+$] 270.1420; found 270.1420; $[\alpha]_D^{26}$ = −66.0 (c 0.3, $CHCl_3$).

*(6aR,12bS)-3-Fluoro-5,6,6a,7,8,12b-hexahydrobenzo[c]-phenanthrene (**31b**). Procedure 3 from **29b**:* Flash chromatography (pentane/toluene 98:2, R_f = 0.63 in pentane/toluene 98:2) yielded the title compound (29.3 mg, 61%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.11 (m, 3H), 7.05−6.99 (m, 2H), 6.88−6.79 (m, 2H), 3.93 (d, J = 5.0 Hz, 1H), 2.84−2.78 (m, 4H), 2.43−2.34 (m, 1H), 2.02−1.90 (m, 2H), 1.58−1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 139.7, 138.9, 127.6, 124.7, 131.3, 129.9, 128.9, 126.4, 125.6, 115.2, 112.3, 42.5, 32.6, 28.4, 28.2, 27.3, 27.1; IR (NaCl) 2923. 2854, 2359, 2330, 2322, 2312, 1491, 867, 773, 742, 676 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}F$ [M$^+$] 252.1314; found 252.1309; $[\alpha]_D^{27}$ = −14.9 (c 1.0, $CHCl_3$) for 92% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 3.41 min [minor], t_R = 7.66 min [major].

*(1R,2S)-2-((E)-2-(Thiophen-3-yl)vinyl)-1,2-dihydronaphthalen-1-ol (**28c**). Procedure 4 from (E)-4,4,5,5-Tetramethyl-2-(2-(thiophen-3-yl)vinyl)-1,3,2-dioxaborolane:* Column chromatography (pentane/EtOAc 9:1, R_f = 0.45 in pentane/EtOAc 9:1) yielded the title compound (375 mg, quant) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.42 (m, 1H), 7.29−7.26 (m, 1H), 7.24−7.22 (m, 1H), 7.17−7.15 (m, 1H), 7.14−7.12 (m, 1H), 6.66 (d, J = 15.8 Hz, 1H), 6.56 (dd, J = 9.5, 1.5 Hz, 1H), 6.03−5.95 (m, 2H), 4.90 (dd, J = 8.7, 5.8 Hz, 1H), 3.33−3.26 (m, 1H), 1.79 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 136.9, 128.9, 128.4, 128.02, 127.94, 127.6, 126.7, 126.4, 126.0, 125.7, 125.0, 122.0, 119.3, 70.8, 45.1; IR (NaCl) 3396, 3095, 3032, 1385, 1246, 1156, 1049, 963, 788, 766 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{13}S$ [M−H_2O]$^+$: 237.0738; found 237.0738; $[\alpha]_D^{28}$ = −165 (c 1.0, $CHCl_3$) for 93% ee, as determined by HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 3.67 min [minor], t_R = 12.51 min [major].

*(1R,2S)-2-(2-(Thiophen-3-yl)ethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**29c**). Procedure 1 from **28c**:* Column chromatography (hexanes/EtOAc 95:5 to 9:1, R_f = 0.62 in hexanes/EtOAc 9:1) yielded the title compound (24.1 mg, 69%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 1H), 7.25−7.19 (m, 3H), 7.17−7.16 (m, 1H), 4.69 (d, J = 5.9 Hz, 1H), 2.91−2.72 (m, 4H), 2.02−1.97 (m, 1H), 1.92−1.73 (m, 4H), 1.41 (d, J = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.3, 126.3, 125.4, 124.5, 124.3, 123.0, 122.5, 121.6, 116.3, 115.6, 66.2, 32.3, 25.4, 24.0, 19.2; IR (NaCl) 3408, 2926, 2857, 1455, 1262, 1155, 1099, 1062, 942, 904, 773, 758, 740 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}NOS$ [M + NH_4]$^+$ 276.1422; found 276.1432; $[\alpha]_D^{27}$ = −8.2 (c 0.5, $CHCl_3$).

*(5aS,11bR)-4,5,5a,6,7,11b-Hexahydrophenanthro[4,3-b]thiophene (**31c**). Procedure 3 from **30a**:* Flash chromatography yielded the title compound (pentane/toluene 95:5) yielded the title compound (12.3 mg, 87%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.0 Hz, 1H), 7.23−7.15 (m, 2H), 7.11−7.09 (m, 1H), 7.05 (dd, J = 5.1, 0.8 Hz, 1H), 6.76 (d, J = 5.1 Hz, 1H), 4.18 (d, J = 4.7 Hz, 1H), 2.86−2.82 (m, 2H), 2.71−2.67 (m, 2H), 2.38 (ddd, J = 10.0, 4.7, 3.3 Hz, 1H), 2.05−1.88 (m, 2H), 1.85−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.5, 133.61, 129.5, 129.1, 127.7, 126.7, 126.6, 125.7, 122.6, 40.7, 33.6, 29.0, 28.0, 23.7, 22.3; IR (NaCl) 2922, 2887, 2854, 2841, 2366, 2321, 1612, 1493, 1451, 1339, 742, 703 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}S$ [M + H]$^+$ 241.1051; found 241.1051; $[\alpha]_D^{28}$ = +46 (c 0.5, $CHCl_3$) for 97% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 6.29 min [major], t_R = 6.99 min [minor].

*(1R,2R)-2-((E)-3,5-Dimethoxystyryl)-1,2-dihydronaphthalen-1-ol (**28d**). Procedure 4 from (E)-2-(3,5-Dimethoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:* Column chromatography (pentane/EtOAc 4:1, R_f = 0.45 in pentane/EtOAc 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46−7.44 (m, 1H), 7.30−7.25 (m, 2H), 7.14−7.12 (m, 1H), 6.60−6.56 (m, 2H), 6.50 (d, J = 2.0 Hz, 2H), 6.35 (t, J = 2.3 Hz, 1H), 6.15 (dd, J = 15.7, 9.0 Hz, 1H), 5.99 (dd, J = 9.4, 4.7 Hz, 1H), 4.90 (dd, J = 8.6, 5.9 Hz, 1H), 3.77 (s, 3H), 3.36−3.31 (m, 1H), 1.81 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 138.8, 136.9, 134.2, 132.5, 128.8, 128.1, 128.0, 127.7, 126.6, 126.4, 126.0, 104.5, 99.9, 70.7, 55.4, 45.2; IR (NaCl) 3447, 2359, 2340, 1591, 1577, 1569, 1559, 1539, 1457, 1424, 1205, 1152, 1065, 800 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}O_3$ [M + H$^+$] 309.1503; found 309.1503; $[\alpha]_D^{28}$ = −109 (c 0.3, $CHCl_3$) for 80% ee, as determined by HPLC analysis (Chiralcel ADH, 8% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 22.59 min [minor], t_R = 32.34 min [major].

*(1R,2R)-2-(3,5-Dimethoxyphenethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**29d**). Procedure 1 from **28d**:* Column chromatography (pentane/EtOAc 9:1) yielded the title compound (45 mg, 49%) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 1H), 7.22−7.19 (m, 2H), 7.13−7.11 (m, 1H), 6.40 (d, J = 2.3 Hz, 2H), 6.30 (t, J = 2.2 Hz, 1H), 4.68 (d, J = 2.0 Hz, 1H), 3.78 (s, 6H), 2.91−2.67 (m, 4H), 2.02−1.91 (m, 1H), 1.76−1.73 (m, 4H), 1.65 (d, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 138.6, 137.0, 130.0, 129.1, 128.0, 126.2, 108.5, 97.7, 69.9, 55.3, 38.9, 33.6, 33.1, 29.1, 22.9; IR (NaCl) 3400, 2931, 1606, 1595, 1459, 1428, 1205, 1151, 1058, 773, 740, 593, 584 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{23}O_2$ [M − OH]$^+$ 295.1698; found 295.1692; $[\alpha]_D^{26}$ = +26.9 (c 0.3, $CHCl_3$).

*(6aS,12bR)-1,3-Dimethoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene (**31d**). Procedure 3 from **29d**:* Column chromatography (pentane/Et_2O 95:5, R_f = 0.25 in pentane/Et_2O 95:5) yielded the title compound (20 mg, 97%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereomer* δ 7.10−6.98 (m, 3H), 6.66 (d, J = 7.4 Hz, 1H), 6.39 (d, J = 2.7 Hz, 1H), 6.29 (d, J = 2.4 Hz, 1H0, 4.16 (d, J = 5.5 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.85−2.76 (m, 3H), 2.73−2.66 (m, 1H), 2.33−2.19 (m, 2H), 1.55−1.37 (m, 3H); *minor diastereomer* (selected signals) δ 7.15−6.98 (m, 3H), 6.67 (d, J = 7.4, 1H), 6.41 (d, J = 2.4 Hz, 1H), 6.35 (d, J = 2.4 Hz, 1H), 3.59 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *major diastereomer* δ 158.9, 139.8, 139.1, 137.4, 128.2, 127.5, 125.5, 125.3, 120.4, 104.5, 95.8, 55.3, 55.2, 36.1, 32.5, 30.0, 28.8, 26.7, 25.7; *minor diastereomer* (selected signals) δ 140.5, 134.2, 130.9, 127.6, 123.4, 103.6, 33.4, 29.1, 28.6, 27.0; IR (NaCl) 3401, 2925, 2850, 2364, 2331, 1656, 1417, 1365, 1044, 850, 832, 668, 592, 577 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{23}O_2$ [M + H]$^+$ 295.1704; found 295.1704; $[\alpha]_D^{26}$ = +2.9 (c 1.0, $CHCl_3$) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 0.80 mL/min, 254 nm); t_R = 7.09 min [major], t_R = 9.48 min [minor].

*(1S,2S)-2-((E)-3-Methoxystyryl)-1,2-dihydronaphthalen-1-ol (**28e**). Procedure 4 from (E)-3-Methoxystyrylboronic Acid:* Flash chromatography (pentane/EtOAc 4:1, R_f = 0.21 in pentane/EtOAc 9:1) yielded the title compound (214 mg, 96%) as yellow powder, mp 75−78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 −7.41 (m, 1H), 7.28−7.22 (m, 2H), 7.17 (t, J = 7.8 Hz, 1H), 7.12−7.09 (m, 1H), 6.92 (d, J = 7.4 Hz, 1H), 6.87−6.86 (m, 1H), 6.77 −6.75 (m, 1H), 6.61−6.54 (m, 2H), 6.14 (dd, J = 16.0, 9.0 Hz, 1H), 5.97 (dd, J = 9.6, 4.5 Hz, 1H), 4.88 (dd, J = 7.8, 5.9 Hz, 1H), 3.76 (s, 3H), 3.33−3.28 (m, 1H), 1.97 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 138.2, 136.8, 133.4, 132.4, 129.4, 128.8, 128.0, 127.9, 126.3, 125.9, 119.0, 113.2, 111.6, 70.6, 55.2, 45.1; IR (NaCl) 3433, 3061, 3029, 2956, 2915, 2834, 2360, 1597, 1579, 1486, 1262, 1155, 1046, 969, 788, 769 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{16}O$ [M − H_2O]$^+$ 260.1201; found 261.1271; $[\alpha]_D^{29}$ = +271 (c 0.3, $CHCl_3$) for 78% ee, as determined by HPLC analysis (Chiralcel ADH, 5% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 23.68 min [major], t_R = 25.33 min [minor].

*(1S,2S)-2-(3-Methoxyphenethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**29e**). Procedure 1 from **28e**:* Column chromatography (hexanes/EtOAc 9:1, R_f = 0.37 in hexanes/EtOAc 9:1) yielded the title compound (89 mg, 66%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 1H), 7.22−7.18 (m, 3H), 7.13−7.11 (m, 1H), 6.85 (d, J = 7.4 Hz, 1H), 6.79−6.78 (m, 1H), 6.73 (dt, J = 8.2, 1.4 Hz, 1H), 4.67 (d, J = 4.7 Hz, 1H), 3.86 (s, 3H), 2.91−2.71 (m, 4H), 2.98 (dt, J = 8.9, 6.7 Hz, 1H), 1.82−1.72 (m, 4H), 1.42 (d, J = 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.26, 138.6, 137.0, 130.0, 129.3, 128.0, 126.2, 120.9, 114.2, 111.0, 69.9, 55.2, 38.9, 33.3, 29.2, 22.9; IR (NaCl) 3387, 2928, 2858, 2358, 1584, 1488, 1452, 1428, 1314, 1259, 1151, 1041, 969, 941, 871, 773, 738, 695 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{29}NO_2$ [M + NH_4]$^+$ 300.1964; found 300.1964; $[\alpha]_D^{26}$ = +57.3 (c 0.5, $CHCl_3$).

*(6aR,12bS)-3-Methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]phenanthrene (**31e**). Procedure 3 from **29e**:* Filtration through a silica plug provided the title compound (41.1 mg, quant) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14−7.09 (m, 3H), 7.06−7.04 (m, 1H), 6.99−6.97 (m, 1H), 6.70−6.68 (m, 2H), 3.90 (d, J = 5.1 Hz, 1H), 3.78 (s, 3H), 2.81−2.76 (m, 4H), 2.36 (tq, J = 8.3, 5.0 Hz, 1H), 1.99−1.87 (m, 2H), 1.57−1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 139.5, 138.8, 137.7, 131.1, 130.0, 128.7, 126.1, 125.5, 113.8, 111.4, 55.4, 42.3, 32.8, 28.6, 27.4; IR (NaCl) 3418, 2925, 2858, 1609, 1496, 1454, 1254, 1153, 1042, 743 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}O$ [M + H]$^+$ 265.1589; found 265.1589; $[\alpha]_D^{28}$ = −3 (c 0.5, $CHCl_3$) for 75% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 6.57 min [minor], t_R = 7.73 min [major].

*(1S,2S)-2-((E)-4-Methoxystyryl)-1,2-dihydronaphthalen-1-ol (**28f**). Procedure 4 from (E)-3-Methoxystyrylboronic Acid:* Flash chromatography (pentane/EtOAc 9:1, R_f = 0.35 in pentane/EtOAc

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9:1) yielded the oxabicyclic alkene **4** starting material (18.2 mg, 0.122 mmol), and the title compound (49.7 mg, 0.179 mmol, 54% (92% based on recovered starting material)) as a brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47−7.45 (m, 1H), 7.29−7.25 (m, 4H), 7.13−7.11 (m, 1H), 6.83−6.81 (m, 2H), 6.62−6.55 (m, 2H), 6.03−5.94 (m, 2H), 4.91 (dd, J = 9.0, 5.9 Hz, 1H), 3.79 (s, 3H), 3.34−3.29 (m, 1H), 1.83 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.0, 133.79, 132.6, 129.6, 129.2, 127.9, 127.9, 127.5, 127.5, 127.4, 126.3, 125.8, 123.3, 114.1, 113.9, 70.6, 55.3, 45.3; IR (NaCl) 3451, 3031, 2955, 2925, 2853, 2836, 2361, 2324, 1615, 1511, 1455, 1377, 1250, 1175, 1035, 968, 823, 787, 675 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}O_2$ [M$^+$] 278.1307; found 278.1313; $[\alpha]_D^{27}$ = +111 (c 0.5, $CHCl_3$) for 88% ee, as determined by HPLC analysis (Chiralcel ADH, 5% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 4.49 min [minor], t_R = 23.76 min [major].

*(1S,2S)-2-(4-Methoxyphenethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**29f**).* *Procedure 1 from **28f**:* Flash chromatography (pentane/EtOAc 9:1) yielded the title compound (67.5 mg, 87%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.35 (m, 1H), 7.72−7.13 (m, 5H), 6.87−6.83 (m, 1H), 4.69 (s, 1H), 3.80 (s, 3H), 2.92−2.73 (m, 4H), 1.99−1.94 (m, 1H), 1.83−1.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 138.6, 137.0, 124.6, 130.0, 129.2, 129.1, 127.9, 126.1, 113.5, 69.8, 55.2, 38.8, 33.4, 32.4, 29.1, 22.9; IR (NaCl) 3428, 2930, 2860, 1611, 1511, 1454, 1300, 1245, 1177, 1036, 941, 825, 739 cm^{-1}; HRMS (ESI) calcd for: $C_{19}H_{21}O$ [M − OH]$^+$ 265.1600; found 265.1600; $[\alpha]_D^{26}$ = +57.3 (c 0.5, $CHCl_3$).

*(6aR,12bS)-2-Methoxy-5,6,6a,7,8,12b-hexahydrobenzo[c]-phenanthrene (**31f**).* *Procedure 3 from **29f**:* Flash chromatography (pentane/Et_2O 99:1) yielded the title compound (10.8 mg, 80%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17−7.05 (m, 5H), 6.74 (dd, J = 8.2, 2.7 Hz, 1H), 6.64 (d, J = 2.7 Hz, 1H), 3.94 (d, J = 5.5 Hz, 1H), 3.74 (s, 3H), 2.83−2.74 (m, 4H), 2.40−2.34 (m, 1H), 1.99−1.91 (m, 2H), 1.56−1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 140.1, 138.7, 137.5, 129.8, 129.5, 129.3, 128.6, 126.0, 125.3, 115.4, 111.5, 55.2, 43.1, 32.3, 29.7, 28.1, 27.6, 27.1; IR (NaCl) 2921, 2850, 2360, 2341, 1700, 1612, 1505, 1489, 1447, 1279, 1245, 1152, 1042, 772, 744, 668 cm^{-1}; HRMS (ESI) calcd for: $C_{19}H_{21}O$ [M + H]$^+$ 265.1592; found 265.1592; $[\alpha]_D^{28}$ = −3 (c 0.5, $CHCl_3$) for 86% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 6.57 min [minor], t_R = 7.73 min [major].

Prop-2-yn-1-ylbenzene. The title compound was synthesized according to a procedure of Newton and co-workers. 1-Phenylpropyne (7.55 g, 65.0 mmol) was added, under nitrogen athmosphere, to a solution of BuLi (1.8 M in hexane, 85 mL, 152 mmol) in dry Et_2O (80 mL) at 0 °C. After stirring at rt for 3 days, the mixture was quenched by slow addition of water (50 mL) and the separated organic layer was dried ($MgSO_4$) and concentrated. The residual oil was purified by distillation in vacuo to afford the title compound (5.04 g, 67%) as a colorless oil. The characterization data were fully concordant with that already reported in the literature:[22] ^{1}H NMR (400 MHz, CDCl3) δ 7.43−7.18 (m, 5H), 3.61 (d, J = 2.7 Hz, 2H), 2.18 (t, J = 2.7 Hz, 1H).

*2,4,6-Tris((E)-3-phenylprop-1-en-1-yl)boroxine (**32**).* $BHBr_2$·SMe2 (1.0 M in CH_2Cl_2, 12 mL, 12.0 mmol) was added to to a solution of prop-2-yn-1-ylbenzene in CH_2Cl_2 (15 mL) at 0 °C. The mixture was stirred for 2 days at rt, then for 4 h at 60 °C. After cooling to rt, the mixture was slowly poured into mixture of Et_2O (20 mL) and water (10 mL) at 0 °C and stirred for 1 h. The phases were separated, and the organic phase was washed with water and brine, dried ($MgSO_4$), and the solvent was evaporated. The residual oil was subjected to flash column chromatography (CH_2Cl_2 to CH_2Cl_2/Et_2O 95:5, R_f = 0.19 in hexane/EtOAc 1:1) to afford the title compound (361 mg, 25%) as a colorless oil. The compound could not be obtained in a pure form and was used without further purification in the next step; HRMS (EI) calcd for $C_{27}H_{27}B_3O_3$ [M$^+$] 432.2239; found 432.2257.

*(1R,2R)-2-((E)-3-Phenylprop-1-en-1-yl)-1,2-dihydronaphthalen-1-ol (**33**).* *Procedure 4 from **41**:* Flash chromatography (hexane/EtOAc 9:1, R_f = 0.23 in hexane/EtOAc 85:15) yielded the title compound (167 mg, 67%) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 5.1, 3.6 Hz, 1H), 7.31−7.23 (m, 4H), 7.22−7.12 (m, 3H), 7.09 (dd, J = 5.3, 3.5 Hz, 1H), 6.52 (dd, J = 9.6, 1.1 Hz, 1H), 5.94 (dd, J = 9.6, 4.6 Hz, 1H), 5.92−5.83 (m, 1H), 5.54 (dd, J = 15.3, 8.6 Hz, 1H), 4.81 (dd, J = 8.2, 5.8 Hz, 1H), 3.38 (d, J = 6.9 Hz, 2H), 3.23−3.11 (m, 1H), 1.77 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 137.1, 134.3, 132.7, 129.6, 128.6, 128.5, 128.2, 128.0, 127.6, 127.5, 126.5, 126.3, 126.3, 70.7, 44.8, 39.3; IR (NaCl) 3548, 3426, 3060, 3028, 2900. 2836, 2360, 1602, 1440, 1281, 1189, 1157, 1115, 1075, 1050, 1011, 972, 945, 883, 786, 765, 747, 698 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{18}O$ [M$^+$] 262.1358; found 262.1354; $[\alpha]_D^{28}$ = −72.6 (c 1.0, $CHCl_3$) for 87% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm); t_R = 25.82 min [major], t_R = 29.03 min [minor].

*(1R,2R)-2-(3-Phenylpropyl)-1,2,3,4-tetrahydronaphthalen-1-ol (**34**).* *Procedure 1 from **33**:* Flash chromatography (hexane/EtOAc 85:15, R_f = 0.25 in EtOAc/hexane 85:15) to afford the title compound (128 mg, 92%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.09 (m, 9H), 4.64 (s, 1H), 2.93−2.59 (m, 4H), 1.91−1.62 (m, 6H), 1.53−1.33 (m, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 142.8, 138.8, 137.2, 130.2, 129.2, 128.6, 128.5, 128.1, 126.3, 125.8, 70.1, 39.7, 36.4, 31.47, 29.4, 29.2, 23.1; IR (NaCl) 3386, 3024, 2929, 2858, 2361, 2341, 1452, 114, 941, 773, 741 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}$ [M − H_2O]$^+$ 248.1565; found 248.1563; $[\alpha]_D^{28}$ = +75.5 (c 1.1, $CHCl_3$).

*3,3′,4,4′-Tetrahydro-1H,2′H-1,2′-spirobi[naphthalene] (**36**).* *Procedure 2 from **34**:* Flash chromatography (hexanes to hexanes/EtOAC 98:2, R_f = 0.74 in hexane/EtOAc 95:5) to afford the title compound (38 mg, 75%) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 7.7 Hz, 1H), 7.22−7.02 (m, 6H), 3.12 - (d, J = 16.7 Hz, 1H), 3.02−2.75 (m, 5H), 2.25 (ddd, J = 12.9, 11.7, 6.2 Hz, 1H), 1.88−1.70 (m, 4H), 1.70−1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 137.2, 136.7, 135.9, 129.6, 129.3, 128.9, 126.8, 126.2, 125.8, 125.7, 125.7, 43.0, 36.0, 35.7, 32.1, 30.9, 26.6, 19.3; IR (NaCl) 3059, 3015, 2926, 2862, 2677, 2360, 2341, 1915, 1581, 1489, 1450, 1346, 1292, 1095, 786, 756, 746, 733 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}$ [M$^+$] 248.1565; found 248.1567. HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); t_R = 4.10 min, t_R = 4.42 min.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, reaction procedures, complete characterization data and copies of ^{1}H NMR and ^{13}C NMR spectra for compounds **12**−**36**. This material is available free of charge via the Internet at http://pubs.acs.org.

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