

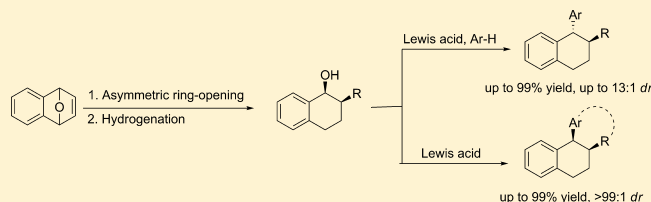
# Diastereoselective Friedel–Crafts Alkylation of Hydronaphthalenes

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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.<sup>1</sup> Selected examples include lasofoxifene for the treatment of osteoporosis and podophyllotoxin as an anticancer agent (Figure 1).<sup>2,3</sup> 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.<sup>4</sup>

Our group has had a long-standing interest in the asymmetric Pd(II)- or Rh(I)-catalyzed ring-opening reactions (ARO) of *meso*-oxabicyclic 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).<sup>5–8</sup> This reaction may be performed in a racemic fashion or enantioselectively using a Josiphos-type ligand (PPF-PtBu<sub>2</sub>) 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  $\pi$ -activated alcohols instead of the less available and more toxic organo-halides.<sup>9</sup> 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.<sup>10</sup> In particular, Bach and co-workers have reported a highly diastereoselective Friedel–Crafts alkylation of 1-aryllkanols via the formation of chiral benzylic carbocations.<sup>11</sup> More recently, we have demonstrated that the derivatization of amine ring-opened products **10** with inter-<sup>12</sup> and intramolecular<sup>13</sup> 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<sub>3</sub> in nitromethane (MeNO<sub>2</sub>)<sup>14</sup> 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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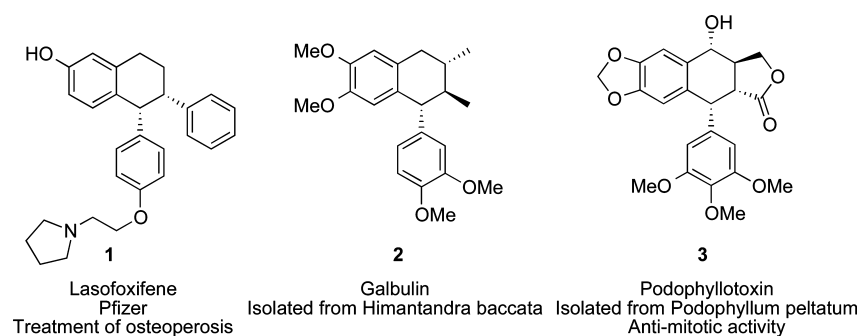
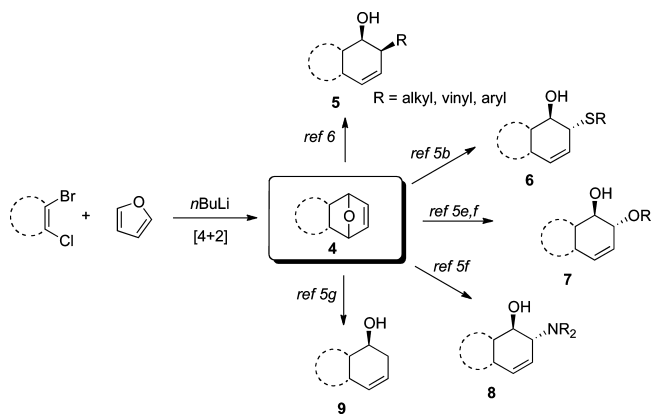


Figure 1. Examples of aryltetralin lignans.

### Scheme 1. Asymmetric Ring Opening of *meso*-Oxabicyclo 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.<sup>15</sup> 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.<sup>6b</sup> 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<sub>3</sub> 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.

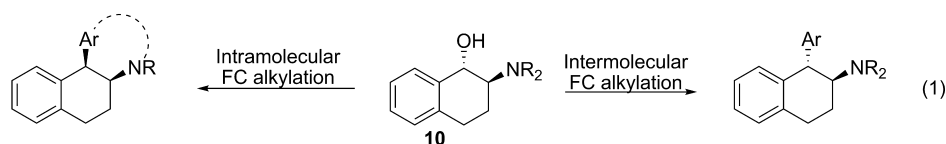
We next investigated the intramolecular variant of the Friedel–Crafts alkylation (Scheme 6). As shown in Scheme 6, readily accessible aryl and alkenylboronic esters can be fixed onto the hydronaphthalene during the asymmetric Pd(II)- or Rh(I)-catalyzed ring-opening step of the synthetic sequence.

We first examined the conversion of the biphenyl tetralin **26** into the hexahydrophenanthrene **30a** (Scheme 7).<sup>16</sup>

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.<sup>11,17</sup> 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

Previous work:



This work:

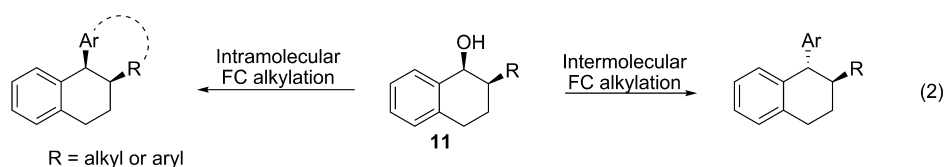
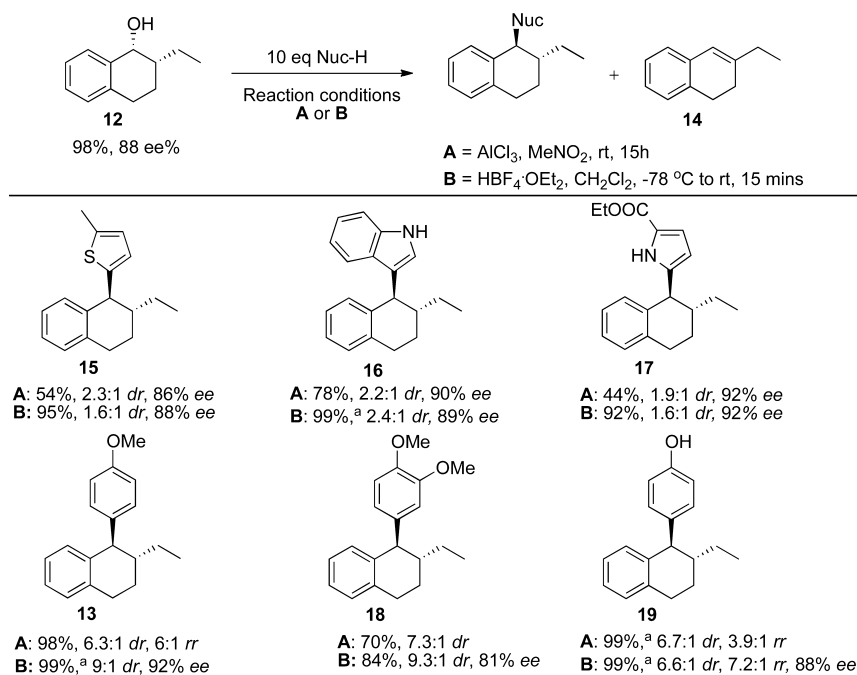


Table 1. Optimization of Friedel–Crafts Alkylation

entry	acid	equiv	temp (°C)	time (h)	yield 13 (%), <sup>a</sup> (dr, rr) <sup>b</sup>	yield 14 (%)
1	AlCl <sub>3</sub>	1	rt	15	98 <sup>c</sup> (dr 6.3:1, rr 6:1)	
2	AlCl <sub>3</sub>	1	rt	1	94 <sup>c</sup> (dr 6.5:1, rr 10:1)	
3	AlCl <sub>3</sub>	2	rt	0.25	93 (dr 6.7:1, rr 7:1)	
4	AlCl <sub>3</sub>	0.1	rt	24	no product	
5	AlCl <sub>3</sub>	1	0	15	68 (dr 4.5:1, rr 10:1)	
6	FeCl <sub>3</sub>	1	rt	15	88 (dr 4.2:1, rr 8:1)	
7 <sup>d</sup>	HBf <sub>4</sub> ·OEt <sub>2</sub>	1.2	-78	0.25	99 <sup>c</sup> (dr 9:1)	
8	BF <sub>3</sub> ·OEt <sub>2</sub>	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) <sub>2</sub>	0.1	60	24	6 (dr 3.1:1)	94
12	Cu(OTf) <sub>2</sub>	0.1	60	48	no product	
13	Bi(OTf) <sub>3</sub>	0.1	rt	15		98
14	AuCl <sub>3</sub>	0.1	60	24	no product	

<sup>a</sup>Yield determined by analysis of the <sup>1</sup>H NMR spectrum of the crude reaction mixture, in the presence of *p*-nitroacetophenone as an internal standard. <sup>b</sup>The dr for *trans:cis* products, rr for *para:ortho* products. <sup>c</sup>Isolated yield <sup>d</sup>Reaction was performed in CH<sub>2</sub>Cl<sub>2</sub>, warmed from -78 °C to rt (ref 3).

## Scheme 3. Intermolecular Friedel–Crafts Alkylation Scope



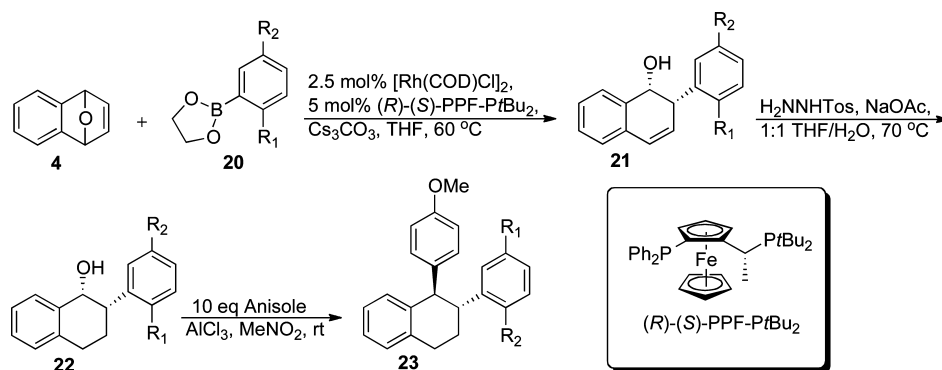
<sup>a</sup>Crude yield, no purification required.

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).<sup>18</sup>

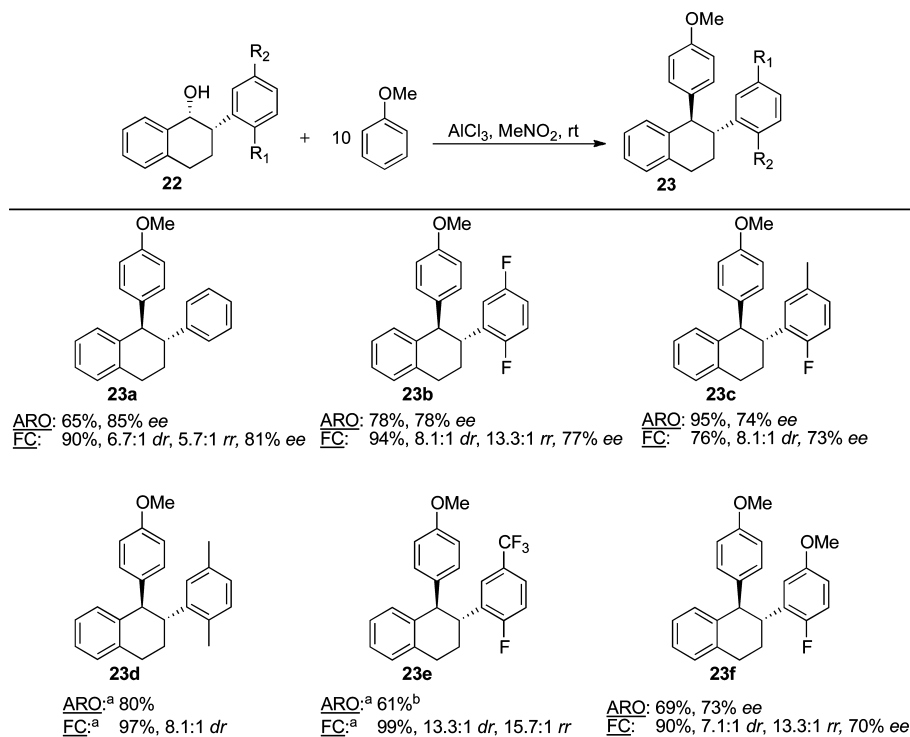
A wide range of substitution patterns are tolerated with this protocol, with *ortho*- and *para*-methoxy-substituted phenyls giving high yields of the corresponding tetralins **31d** and **31e**

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

Scheme 4. Synthetic Sequence for Intermolecular Friedel–Crafts Alkylation

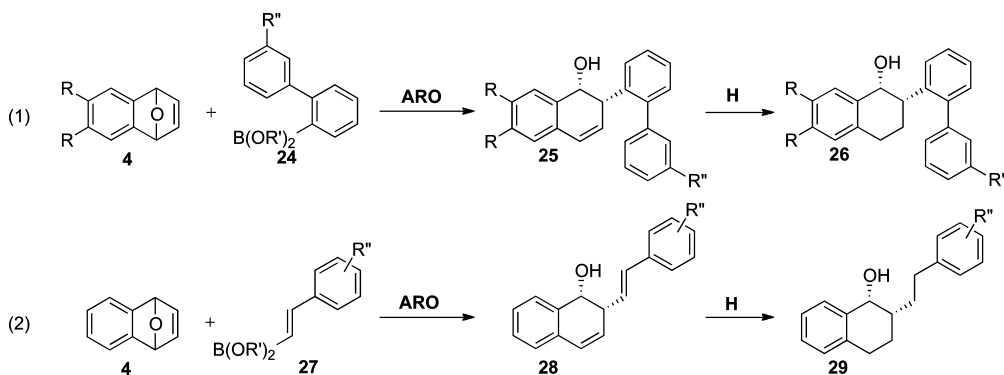


Scheme 5. Improving Diastereoselectivity



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

Scheme 6. Synthetic Sequence for Intramolecular Friedel–Crafts Alkylation

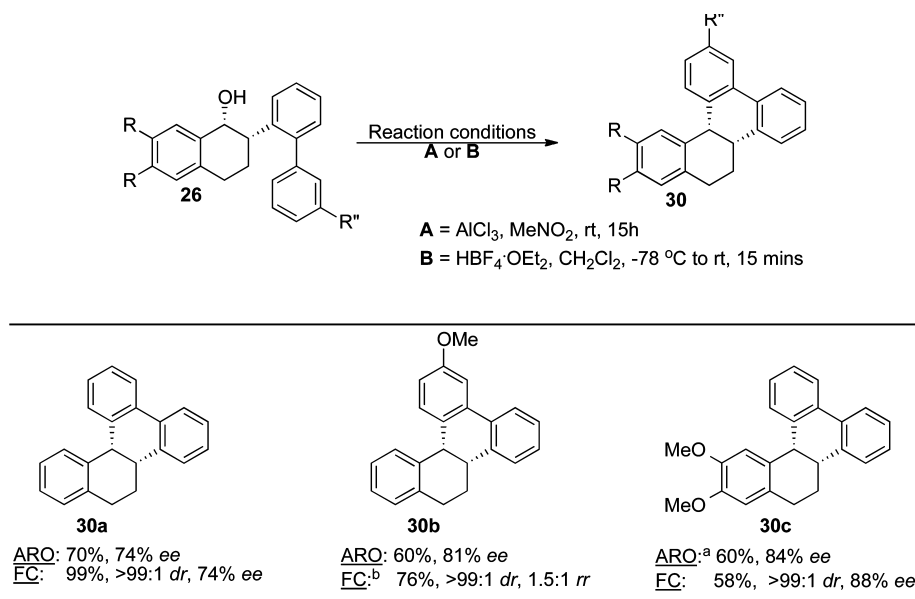


Friedel–Crafts alkylation to occur with more electron-poor nucleophiles such as the *para*-fluoro-substituted phenyl in **31b**, which is a challenging and rarely used nucleophile in diastereoselective Friedel–Crafts methodologies. Heteroaromatic

nucleophiles are also tolerated in this protocol, as seen in product **31c**.

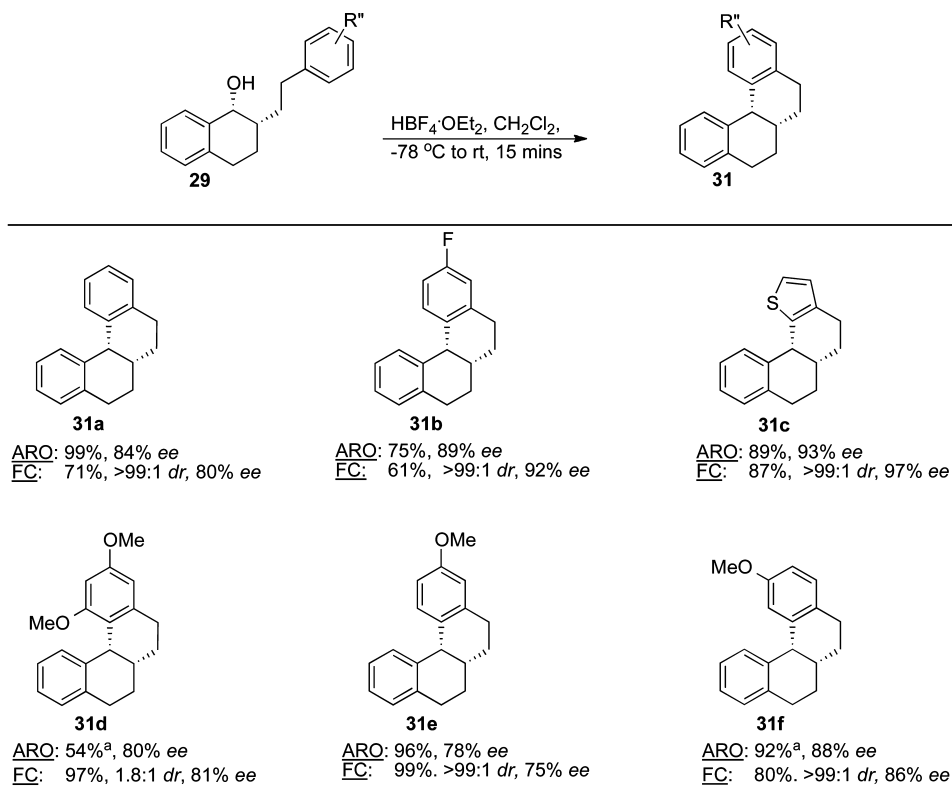
Attempts to increase the ring size of the resulting tetracyclic structure by increasing the length of the tether yielded the

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



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

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

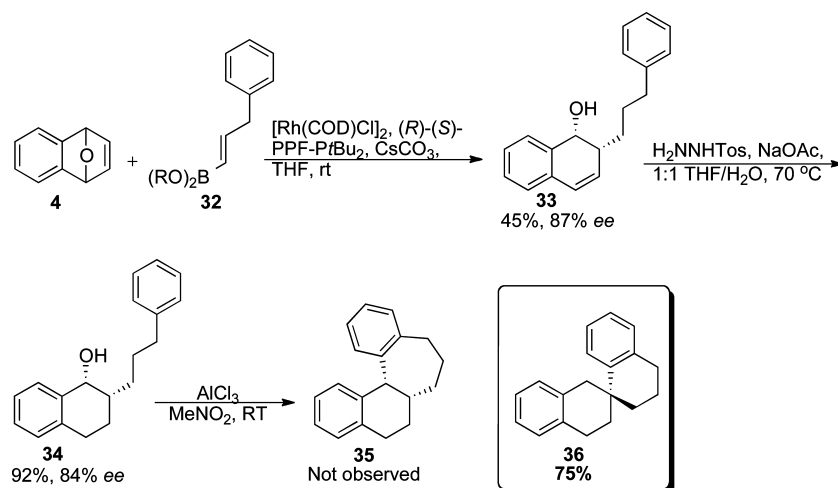


<sup>a</sup>Yield based on recovered starting material.

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**.

## 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.<sup>5–7,17–20</sup>

**(1*R*,2*R*)-2-Ethyl-1,2-dihydronaphthalen-1-ol.** Pd(MeCN)<sub>2</sub>Cl<sub>2</sub> (46 mg, 0.18 mmol) and (*R*)-Tol-BINAP (119 mg, 0.18 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub> (50 mL). The mixture was cooled to –20 °C, and ZnEt<sub>2</sub> (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<sub>4</sub>Cl solution, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. The crude product was purified by flash column chromatography (hexane/Et<sub>2</sub>O 85:15, *R<sub>f</sub>* = 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:<sup>6a</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd

for C<sub>12</sub>H<sub>14</sub>O [M<sup>+</sup>] 174.1045; found 174.1043; [ $\alpha$ ]<sub>D</sub><sup>28</sup> = +97.0 (c 1.0, CHCl<sub>3</sub>) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); *t<sub>R</sub>* = 12.99 min [minor], *t<sub>R</sub>* = 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: (1*S*,2*S*)-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<sub>2</sub>O (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<sub>2</sub>CO<sub>3</sub> solution, and the separated aqueous phase extracted with ether (3×). The combined organic layers were then dried (MgSO<sub>4</sub>) and concentrated under reduced pressure and the ensuing residue subjected to flash chromatography (hexane/EtOAc 9:1, *R<sub>f</sub>* = 0.23 in hexane/EtOAc 85:15) to afford the title compound (577 mg, 99%) as a colorless oil: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>12</sub>H<sub>16</sub>O [M<sup>+</sup>] 176.1201; found 176.1204; [ $\alpha$ ]<sub>D</sub><sup>28</sup> = –57.7 (c 1.0, CHCl<sub>3</sub>) 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<sub>2</sub> for 16 h. The mixture was then treated with *p*-nitroacetophenone (1.14 M in MeNO<sub>2</sub>, 131.6 μL, 0.15 mmol) as an internal standard in CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL), diluted with CH<sub>2</sub>Cl<sub>2</sub> (3 mL), quenched with H<sub>2</sub>O, the aqueous phase then extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was evaporated. Product yield was then determined by analysis of the <sup>1</sup>H NMR spectrum of the crude reaction mixture.

**Representative Procedure 2 for the AlCl<sub>3</sub>-Catalyzed Friedel–Crafts Alkylation of 12: (1*S*,2*S*)-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<sub>2</sub>Cl<sub>2</sub> (1 mL) was added AlCl<sub>3</sub> (40 mg, 0.30 mmol), and the resulting mixture was stirred for 16 h at rt. The mixture was then diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and poured into saturated NaHCO<sub>3</sub> solution (10 mL). The separated aqueous phase was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 15 mL), and the combined organic layers were dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The ensuing residue was subjected to flash chromatography (hexanes/EtOAc 98:2

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:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  4.11 (d,  $J = 4.9$  Hz, 1H), 0.95 (t,  $J = 7.1$  Hz, 3H); regioisomer (selected signals)  $\delta$  4.30 (d,  $J = 7.1$  Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{22}\text{O}$  [ $\text{M}^+$ ] 266.1671; found 266.1674;  $[\alpha]_{\text{D}}^{27} = +23.0$  (c 1.0,  $\text{CHCl}_3$ ) for 92% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexanes, 0.80 mL/min, 254 nm);  $t_{\text{R}} = 6.43$  min [minor],  $t_{\text{R}} = 9.97$  min [major].

**Representative Procedure 3 for the  $\text{HBF}_4\cdot\text{OEt}_2$ -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  $\text{CH}_2\text{Cl}_2$  (1 mL) was added  $\text{HBF}_4\cdot\text{OEt}_2$  (45  $\mu\text{L}$ , 0.33 mmol) at  $-78^\circ\text{C}$ . The mixture was stirred for 5 min at  $-78^\circ\text{C}$  and then for 15 min at rt. The mixture was then treated with saturated  $\text{NaHCO}_3$  solution. The separated aqueous phase was then extracted with  $\text{Et}_2\text{O}$ . The combined organic phases were washed sequentially with saturated  $\text{NaHCO}_3$  solution and brine, dried ( $\text{MgSO}_4$ ), 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):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{20}\text{S}$  [ $\text{M}^+$ ] 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,  $t_{\text{R}} = 5.07$  min [minor],  $t_{\text{R}} = 5.64$  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;  $[\alpha]_{\text{D}}^{28} = +74.6$  (c 1.0,  $\text{CHCl}_3$ ) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 5.08$  min [major],  $t_{\text{R}} = 5.66$  min [minor].

**3-((1S,2R)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indole (16):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{22}\text{N}$  [ $\text{M} + \text{H}$ ] $^+$  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;  $[\alpha]_{\text{D}}^{29} = +17.1$  (c 1.0,  $\text{CHCl}_3$ ) for 90% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 15.34$  min [major],  $t_{\text{R}} = 20.78$  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,  $t_{\text{R}} = 15.43$  min [minor],  $t_{\text{R}} = 21.28$  min [major].

**Ethyl 5-((1R,2S)-2-ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)-1H-pyrrole-2-carboxylate (17):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{24}\text{NO}_2$  [ $\text{M} + \text{H}$ ] $^+$  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;  $[\alpha]_{\text{D}}^{29} = -18.2$  (c 1.0,  $\text{CHCl}_3$ ) for 92% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 9.10$  min [major],  $t_{\text{R}} = 12.18$  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,  $t_{\text{R}} = 9.11$  min [minor],  $t_{\text{R}} = 11.86$  min [major].

**(1S,2S)-1-(3,4-Dimethoxyphenyl)-2-ethyl-1,2,3,4-tetrahydronaphthalen-1-yl (18):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  4.12 (d,  $J = 5.0$  Hz, 1H), 0.97 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{24}\text{O}_2$  [ $\text{M}^+$ ] 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  $^\circ\text{C}$  at 55 mmHg) yielded a ca. 9.3:1 mixture of diastereomers of the title compound (41.0 mg, 84%) as a colorless oil;  $[\alpha]_{\text{D}}^{27} = +25.3$  (c 0.5,  $\text{CHCl}_3$ ) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexane, 0.80 mL/min, 254 nm);  $t_{\text{R}} = 6.43$  min [major],  $t_{\text{R}} = 7.13$  min [minor].

**4-((1S,2S)-2-Ethyl-1,2,3,4-tetrahydronaphthalen-1-yl)phenol (19):**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  6.85–6.73 (m, 2H), 6.68–6.66

(m, 1H), 4.11 (d,  $J = 5.1$  Hz, 1H), 1.64–1.62 (m, 1H), 1.07 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{24}\text{NO}$  [ $\text{M} + \text{NH}_4$ ] $^{+}$  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;  $[\alpha]_{\text{D}}^{29} = +16.8$  (c 0.3,  $\text{CHCl}_3$ ) for 88% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 13.64$  min [minor],  $t_{\text{R}} = 20.13$  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  $[\text{Rh}(\text{COD})\text{Cl}]_2$  (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  $\text{Cs}_2\text{CO}_3$  (SM) in  $\text{H}_2\text{O}$  (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  $\text{CH}_2\text{Cl}_2$ . 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: $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $[\alpha]_{\text{D}}^{28} = -76.7$  (c 1.2,  $\text{CHCl}_3$ ) for 85% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm);  $t_{\text{R}} = 16.41$  min [major],  $t_{\text{R}} = 31.53$  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: $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $[\alpha]_{\text{D}}^{28} = +126$  (c 1.2,  $\text{CHCl}_3$ ) for 93% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm);  $t_{\text{R}} = 20.41$  min [major],  $t_{\text{R}} = 30.96$  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:  $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *p*-regioisomer, major diastereomer  $\delta$  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)  $\delta$  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  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) *p*-regioisomer, major diastereomer  $\delta$  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)  $\delta$  131.6, 128.4, 127.9, 126.3, 112.5, 30.0; *o*-regioisomer, major diastereomer (selected signals)  $\delta$  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  $\text{C}_{23}\text{H}_{22}\text{O}$  [ $\text{M}^{+}$ ] 314.1671; found 314.1668;  $[\alpha]_{\text{D}}^{27} = -46.8$  (c 1.0,  $\text{CHCl}_3$ ) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1 mL/min, 254 nm);  $t_{\text{R}} = 4.96$  min [minor],  $t_{\text{R}} = 8.92$  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;  $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_8\text{H}_7\text{BF}_2\text{O}_2$  [ $\text{M}^{+}$ ] 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 $_2$ O 98:2 to 95:5) yielded the title compound (128.5 mg, 78%) as an off-white oil;  $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{12}\text{F}_2\text{O}$  [ $\text{M}^{+}$ ] 258.0856; found 258.0856;  $[\alpha]_{\text{D}}^{28} = +189.0$  (c 1.0,  $\text{CHCl}_3$ ) for 78% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 10.60$  min [minor],  $t_{\text{R}} = 13.88$  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;  $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}$  [ $\text{M}^{+}$ ] 260.1013; found 260.1013;  $[\alpha]_{\text{D}}^{28} = +189.0$  (c 1.0,  $\text{CHCl}_3$ ).

**(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;  $^{1}\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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)  $\delta$  4.74 (d,  $J = 5.8$  Hz, 1H), 3.61 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{20}\text{F}_2\text{O}$  [ $\text{M}^+$ ] 350.1482; found 350.1482;  $[\alpha]_{\text{D}}^{28} = -78.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for 77% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexanes, 1.00 mL/min, 269 nm);  $t_{\text{R}} = 4.69$  min [minor],  $t_{\text{R}} = 5.30$  min [major].

**2-(2-Fluoro-5-methylphenyl)-1,3,2-dioxaborolane (20c).** Procedure 5 from 2-Fluoro-5-methylphenylboronic acid: The title compound (435 mg, 93%) was isolated as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_9\text{H}_{10}\text{BF}_2$  [ $\text{M}^+$ ] 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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 4.6, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{15}\text{FO}$  [ $\text{M}^+$ ] 254.1107; found 254.1107;  $[\alpha]_{\text{D}}^{28} = -56.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for 74% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 8.88$  min [minor],  $t_{\text{R}} = 14.27$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{17}\text{FO}$  [ $\text{M}^+$ ] 256.1263; found 256.1263;  $[\alpha]_{\text{D}}^{28} = -20.9$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ).

**(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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *major diastereomer*  $\delta$  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,  $J = 16.6, 3.1$  Hz), 2.23 (s, 3H), 2.21–2.07 (m, 2H); *minor diastereomer* (selected signals)  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) *major diastereomer*  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{23}\text{FO}$  [ $\text{M}^+$ ] 346.1733; found 346.1733;  $[\alpha]_{\text{D}}^{28} = +42.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for 73% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm);  $t_{\text{R}} = 4.29$  min [minor],  $t_{\text{R}} = 4.49$  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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{10}\text{H}_{13}\text{BO}_2$  [ $\text{M}^+$ ] 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<sub>2</sub>O 95:5) yielded the title compound (94 mg, 65%) as a white, viscous oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 5.1, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{18}\text{O}$  [ $\text{M}^+$ ] 250.1358; found 250.1358;  $[\alpha]_{\text{D}}^{28} = -7.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

**(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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 12.7, 5.4, 1\text{H}$ ), 2.35 (s, 3H), 2.32 (s, 3H), 4.26 (dt,  $J = 5.2, 3.0$  Hz, 1H), 3.68 (s, 3H), 1.83 (dq,  $J = 12.87, 2.2, 1.2$  Hz, 1H), 1.60 (d,  $J = 3.1, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{20}\text{O}$  [ $\text{M}^+$ ] 252.1514; found 252.1514;  $[\alpha]_{\text{D}}^{28} = -50.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

**(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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) *major diastereomer*  $\delta$  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,  $J = 16.5, 3.9$  Hz), 2.30 (s, 3H), 2.05–2.00 (m, 2H), 1.79 (m, 3H); *minor diastereomer* (selected signals)  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) *major diastereomer*  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{25}\text{H}_{26}\text{O}$  [ $\text{M}^+$ ] 342.1984; found 342.1984;  $[\alpha]_{\text{D}}^{28} = 35.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

**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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 170.2,

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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_9\text{H}_9\text{BF}_4\text{O}_2$  [ $\text{M}^+$ ] 235.0475; found 235.0475.

(1*R*,2*S*)-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  $^1\text{H}$  NMR). Separation of the starting material from the desired product was not further attempted. Rather, the crude was continued to the hydrogenation step.

(1*R*,2*S*)-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 4.9, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_4\text{O}$  [ $\text{M}^+$ ] 310.0981; found 310.0981;  $[\alpha]_{\text{D}}^{28} = -40.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

(1*R*,2*R*)-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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,  $J = 16.5, 4.0, 1\text{H}$ ), 2.22 (qd,  $J = 12.1, 4.8$  Hz, 1H), 2.15–2.18 (m, 1H); minor diastereomer (selected signals)  $\delta$  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,  $J = 5.0, 1\text{H}$ ), 3.68 (s, 3H), 1.80–1.75 (m, 1H), 0.94–0.90 (m, 2H); regioisomer (selected signals)  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{20}\text{F}_4\text{O}$  [ $\text{M}^+$ ] 400.1450; found 400.1450;  $[\alpha]_{\text{D}}^{28} = +26.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_9\text{H}_{10}\text{BFO}_3$  [ $\text{M}^+$ ] 196.0707; found 196.0707.

(1*R*,2*S*)-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 6.0, 1\text{H}$ ), 4.26 (dt,  $J = 5.2, 3.0$  Hz, 1H), 3.68 (s, 3H), 1.68 (d,  $J = 6.8, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{15}\text{FO}_2$  [ $\text{M}^+$ ] 270.1056; found 270.1056;  $[\alpha]_{\text{D}}^{28} = +226.5$  ( $c = 0.5$ ,  $\text{CHCl}_3$ ) for 73% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm);  $t_{\text{R}} = 13.84$  min [minor],  $t_{\text{R}} = 20.97$  min [major].

(1*R*,2*S*)-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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,  $J = 4.2, 1\text{H}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{17}\text{H}_{17}\text{FO}_2$  [ $\text{M}^+$ ] 272.1213; found 272.1213;  $[\alpha]_{\text{D}}^{28} = -62.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).

(1*R*,2*R*)-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;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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,  $J = 16.7, 4.3, 1\text{H}$ ), 2.15–2.06 (m, 2H); minor diastereomer (selected signals)  $\delta$  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,  $J = 5.0, 1\text{H}$ ), 3.48 (s, 3H), 1.21–1.20 (m, 1H); regioisomer (selected signals)  $\delta$  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)  $\delta$  3.91 (s, 3H), 3.86 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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):  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{23}\text{FO}_2$  [ $\text{M}^+$ ] 362.1682; found 362.1682;  $[\alpha]_{\text{D}}^{28} = +70.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ) for 70% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 269 nm);  $t_{\text{R}} = 4.58$  min [minor],  $t_{\text{R}} = 5.20$  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:<sup>20</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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).

(1*R*,2*S*)-2-(2-Biphenyl)-1,2-dihydronaphthalen-1-ol (**25a**). Procedure 4 from **24a**: Flash chromatography (hexanes/EtOAc 9:1 to 85:15,  $R_{\text{f}} = 0.28$  in hexanes/EtOAc 85:15) yielded the title compound (264 mg, 60%) as a colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{16}$  [ $\text{M}-\text{H}_2\text{O}^+$ ]: 280.1252; found 280.1254;  $[\alpha]_{\text{D}}^{28} = -163$  ( $c$  0.4,  $\text{CHCl}_3$ ) for 74% ee, as determined by

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].

(1*R*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{20}\text{O}$  [ $\text{M}^+$ ] 300.1514; found 300.1507;  $[\alpha]_{\text{D}}^{28} = -94.9$  (c 1.0,  $\text{CHCl}_3$ ) 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].

(4*R*,10*R*)-4*b*,5,6,10*b*-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{18}$  [ $\text{M}^+$ ] 282.1409; found 282.1404;  $[\alpha]_{\text{D}}^{28} = +161$  (c 1.0,  $\text{CHCl}_3$ ) 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  $\text{Et}_2\text{O}:\text{MeCN}$  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:<sup>21</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{K}_3\text{PO}_4$  (1.27 g, 6 mmol) in THF (18 mL) was added a premixed solution of Pd(OAc)<sub>2</sub> (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 ( $\text{Et}_2\text{O}$  to 3:1  $\text{Et}_2\text{O}:\text{CH}_3\text{CN}$ ) afforded the title compound as a brown oil (452 mg, 56%):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{18}\text{H}_{22}\text{BN}_2\text{O}_5$  [ $\text{M} + \text{NH}_4$ ]<sup>+</sup> 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  $\text{Et}_2\text{O}$  (3 $\times$ ). The organic phase was dried ( $\text{MgSO}_4$ ) 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:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_3\text{B}$  [ $\text{M}^+$ ] 254.1114; found 254.1112.

(1*R*,2*S*)-2-(3'-Methoxy-[1,1'-biphenyl]-2-yl)-1,2-dihydronaphthalen-1-ol (25b). To a mixture of oxabicyclic alkene 4 (40 mg, 0.281 mmol) and 24b (72 mg, 0.283 mmol) in MeOH (3 mL) was added a premixed solution of Pd( $\text{CH}_3\text{CN}$ )<sub>2</sub>Cl<sub>2</sub> (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  $\text{Cs}_2\text{CO}_3$  in  $\text{H}_2\text{O}$  (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% bsm):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ . LRMS (ESI) calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_2$  [ $\text{M} - \text{H}_2\text{O}$ ]<sup>+</sup> 210.14; found 311.1;  $[\alpha]_{\text{D}}^{27} = -1.3$  (c 1.0,  $\text{CHCl}_3$ ) 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].

(1*R*,2*S*)-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.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{26}\text{NO}_2$  [ $\text{M} + \text{NH}_4$ ]<sup>+</sup>: 348.1964; found 348.1964;  $[\alpha]_{\text{D}}^{26} = -1.2$  (c 1.00,  $\text{CHCl}_3$ ).

(4*R*,10*R*)-13-Methoxy-4*b*,5,6,10*b*-tetrahydrobenzo[*g*]chrysene (30b). Procedure 3 from 26b: Flash chromatography (hexanes/ $\text{Et}_2\text{O}$  99:1) yielded the title compound (10 mg, 76%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major regioisomer  $\delta$  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)  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major regioisomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{24}\text{NO}$  [ $\text{M} + \text{NH}_4$ ]<sup>+</sup> 330.1858; found 330.1858.

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

(hexanes/EtOAc 7:3) yielded the title compound (141 mg, 20%) as a colorless solid, mp 63–65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>24</sub>H<sub>20</sub>O<sub>2</sub> [M–H<sub>2</sub>O]<sup>+</sup>: 340.1463; found 340.1479.

(1*R*,2*S*)-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*<sub>f</sub> = 0.15 in EtOAc/hexane 7:3) to afford the title compound (119 mg, quant) as a colorless solid, mp 63–65 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (ESI) calcd for C<sub>24</sub>H<sub>24</sub>O<sub>3</sub>Na [M + Na]<sup>+</sup>: 383.1617; found 363.1617; [α]<sub>D</sub><sup>28</sup> = –50.0 (c 1.0, CHCl<sub>3</sub>) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 15% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 17.39 min [minor], *t*<sub>R</sub> = 31.00 min [major].

(4*bR*,10*bR*)-8,9-Dimethoxy-4*b*,5,6,10*b*-tetrahydrobenzo[*g*]-chrysenes (30c). Procedure 2 from 26c: Flash chromatography (hexanes to hexanes/EtOAc 9:1, *R*<sub>f</sub> = 0.37 in hexanes/EtOAc 95:5) yielded the title compound (40 mg, 58%) as a white solid, mp 68–70 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (ESI) calcd for C<sub>24</sub>H<sub>23</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 343.1692; found 343.1702; [α]<sub>D</sub><sup>28</sup> = +153 (c 1.0, CHCl<sub>3</sub>) for 88% ee, as determined by HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 23.71 min [major], *t*<sub>R</sub> = 30.42 min [minor].

(1*R*,2*R*)-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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>16</sub>O [M]<sup>+</sup>: 248.1201; found 248.1199; [α]<sub>D</sub><sup>28</sup> = –35.5 (c 1.1, CHCl<sub>3</sub>) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 32.11 min [minor], *t*<sub>R</sub> = 33.64 min [major].

**Representative Procedure 6 for the Reduction of Alkenylboronic Acid Ring-Opened Products.** (1*R*,2*R*)-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<sub>2</sub>O (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<sub>2</sub>CO<sub>3</sub> solution, and the separated aqueous phase extracted with ether (3×). The combined organic layers were

then dried (MgSO<sub>4</sub>) and concentrated under reduced pressure, and the ensuing residue was subjected to flash chromatography (hexane/EtOAc 9:1, *R*<sub>f</sub> = 0.31 in EtOAc/hexane 85:15) to afford the title compound (674 mg, quant) as a colorless solid, mp 48–50 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>20</sub>O [M]<sup>+</sup>: 252.1514; found 252.1507; [α]<sub>D</sub><sup>28</sup> = +57.0 (c 1.0, CHCl<sub>3</sub>) for 84% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm); *t*<sub>R</sub> = 30.14 min [major], *t*<sub>R</sub> = 31.75 min [minor].

(6*aS*,12*bS*)-5,6,6*a*,7,8,12*b*-Hexahydrobenzo[*c*]phenanthrene (31a). Procedure 3 from 29a: Flash chromatography (pentane/Et<sub>2</sub>O 99:1 to 98:2, *R*<sub>f</sub> = 0.69 in hexanes/EtOAc 95:5) to afford the title compound (68 mg, 97%) as a white solid, mp 52–53 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>18</sub> [M]<sup>+</sup>: 234.1409; found 234.1411; [α]<sub>D</sub><sup>26</sup> = +207.1 (c 0.5, CHCl<sub>3</sub>) for 80% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 6.47 min [major], *t*<sub>R</sub> = 7.14 min [minor].

(1*S*,2*S*)-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; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (ESI) calcd for C<sub>18</sub>H<sub>15</sub>FO [M + NH<sub>4</sub><sup>+</sup>]: 284.1451; found 284.1451; [α]<sub>D</sub><sup>26</sup> = +117 (c 1.1, CHCl<sub>3</sub>) for 89% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 4.53 min [major], *t*<sub>R</sub> = 7.61 min [minor].

(1*S*,2*S*)-2-(3-Fluorophenethyl)-1,2,3,4-tetrahydronaphthalen-1-ol (29b). Procedure 6 from 28b: Flash chromatography (pentane/EtOAc 9:1, *R*<sub>f</sub> = 0.55 in pentane/EtOAc 9:1) yielded the title compound (61.8 mg, 82%) as a brown oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>FO [M]<sup>+</sup>: 270.1420; found 270.1420; [α]<sub>D</sub><sup>26</sup> = –66.0 (c 0.3, CHCl<sub>3</sub>).

(6*aR*,12*bS*)-3-Fluoro-5,6,6*a*,7,8,12*b*-hexahydrobenzo[*c*]phenanthrene (31b). Procedure 3 from 29b: Flash chromatography (pentane/toluene 98:2, *R*<sub>f</sub> = 0.63 in pentane/toluene 98:2) yielded the title compound (29.3 mg, 61%) as a colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 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<sup>-1</sup>; HRMS (EI) calcd for C<sub>18</sub>H<sub>17</sub>F [M]<sup>+</sup>: 252.1314; found 252.1309; [α]<sub>D</sub><sup>27</sup> = –14.9 (c 1.0, CHCl<sub>3</sub>) for 92% ee, as determined by HPLC analysis (Chiralcel ODH, 2% iPrOH/hexane, 1.00 mL/min, 254 nm); *t*<sub>R</sub> = 3.41 min [minor], *t*<sub>R</sub> = 7.66 min [major].

(1*R*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{13}\text{S}$  [ $\text{M}-\text{H}_2\text{O}$ ] $^+$ : 237.0738; found 237.0738;  $[\alpha]_{\text{D}}^{28}$  = -165 (c 1.0,  $\text{CHCl}_3$ ) for 93% ee, as determined by HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}}$  = 3.67 min [minor],  $t_{\text{R}}$  = 12.51 min [major].

(1*R*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{22}\text{NOS}$  [ $\text{M} + \text{NH}_4$ ] $^+$ : 276.1422; found 276.1432;  $[\alpha]_{\text{D}}^{27}$  = -8.2 (c 0.5,  $\text{CHCl}_3$ ).

(5*aS*,11*bR*)-4,5,5*a*,6,7,11*b*-Hexahydrophenanthro[4,3-*b*]thiophene (**31c**). Procedure 3 from **30a**: Flash chromatography (pentane/toluene 95:5) yielded the title compound (12.3 mg, 87%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}\text{S}$  [ $\text{M} + \text{H}$ ] $^+$ : 241.1051; found 241.1051;  $[\alpha]_{\text{D}}^{28}$  = +46 (c 0.5,  $\text{CHCl}_3$ ) for 97% ee, as determined by HPLC analysis (Chiralcel ODH, 0.5% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}}$  = 6.29 min [major],  $t_{\text{R}}$  = 6.99 min [minor].

(1*R*,2*R*)-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);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$ : 309.1503; found 309.1503;  $[\alpha]_{\text{D}}^{28}$  = -109 (c 0.3,  $\text{CHCl}_3$ ) for 80% ee, as determined by HPLC analysis (Chiralcel ADH, 8% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}}$  = 22.59 min [minor],  $t_{\text{R}}$  = 32.34 min [major].

(1*R*,2*R*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{23}\text{O}_2$  [ $\text{M} - \text{OH}$ ] $^+$ : 295.1698; found 295.1692;  $[\alpha]_{\text{D}}^{26}$  = +26.9 (c 0.3,  $\text{CHCl}_3$ ).

(6*aS*,12*bR*)-1,3-Dimethoxy-5,6,6*a*,7,8,12*b*-hexahydrobenzo[*c*]phenanthrene (**31d**). Procedure 3 from **29d**: Column chromatography (pentane/Et<sub>2</sub>O 95:5,  $R_f$  = 0.25 in pentane/Et<sub>2</sub>O 95:5) yielded the title compound (20 mg, 97%) as a colorless oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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, 1H), 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)  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) major diastereomer  $\delta$  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)  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{23}\text{O}_2$  [ $\text{M} + \text{H}$ ] $^+$ : 295.1704; found 295.1704;  $[\alpha]_{\text{D}}^{26}$  = +2.9 (c 1.0,  $\text{CHCl}_3$ ) for 81% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 0.80 mL/min, 254 nm);  $t_{\text{R}}$  = 7.09 min [major],  $t_{\text{R}}$  = 9.48 min [minor].

(1*S*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{16}\text{O}$  [ $\text{M} - \text{H}_2\text{O}$ ] $^+$ : 260.1201; found 261.1271;  $[\alpha]_{\text{D}}^{29}$  = +271 (c 0.3,  $\text{CHCl}_3$ ) for 78% ee, as determined by HPLC analysis (Chiralcel ADH, 5% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}}$  = 23.68 min [major],  $t_{\text{R}}$  = 25.33 min [minor].

(1*S*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{29}\text{NO}_2$  [ $\text{M} + \text{NH}_4$ ] $^+$ : 300.1964; found 300.1964;  $[\alpha]_{\text{D}}^{26}$  = +57.3 (c 0.5,  $\text{CHCl}_3$ ).

(6*aR*,12*bS*)-3-Methoxy-5,6,6*a*,7,8,12*b*-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{O}$  [ $\text{M} + \text{H}$ ] $^+$ : 265.1589; found 265.1589;  $[\alpha]_{\text{D}}^{28}$  = -3 (c 0.5,  $\text{CHCl}_3$ ) for 75% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}}$  = 6.57 min [minor],  $t_{\text{R}}$  = 7.73 min [major].

(1*S*,2*S*)-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

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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 137.0, 133.79, 132.6, 129.6, 129.2, 127.9, 127.5, 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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_2$  [ $\text{M}^+$ ] 278.1307; found 278.1313;  $[\alpha]_{\text{D}}^{27} = +111$  (c 0.5,  $\text{CHCl}_3$ ) for 88% ee, as determined by HPLC analysis (Chiralcel ADH, 5% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 4.49$  min [minor],  $t_{\text{R}} = 23.76$  min [major].

(1*S*,2*S*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{O}$  [ $\text{M} - \text{OH}]^+$  265.1600; found 265.1600;  $[\alpha]_{\text{D}}^{26} = +57.3$  (c 0.5,  $\text{CHCl}_3$ ).

(6*aR*,12*bS*)-2-Methoxy-5,6,6*a*,7,8,12*b*-hexahydrobenzo[*c*]phenanthrene (**31f**). Procedure 3 from **29f**: Flash chromatography (pentane/Et<sub>2</sub>O 99:1) yielded the title compound (10.8 mg, 80%) as a yellow oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{O}$  [ $\text{M} + \text{H}]^+$  265.1592; found 265.1592;  $[\alpha]_{\text{D}}^{28} = -3$  (c 0.5,  $\text{CHCl}_3$ ) for 86% ee, as determined by HPLC analysis (Chiralcel ODH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 6.57$  min [minor],  $t_{\text{R}} = 7.73$  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 atmosphere, to a solution of BuLi (1.8 M in hexane, 85 mL, 152 mmol) in dry Et<sub>2</sub>O (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 ( $\text{MgSO}_4$ ) 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.<sup>22</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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**).  $\text{BHB}_2\text{SMe}_2$  (1.0 M in  $\text{CH}_2\text{Cl}_2$ , 12 mL, 12.0 mmol) was added to a solution of prop-2-yn-1-ylbenzene in  $\text{CH}_2\text{Cl}_2$  (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<sub>2</sub>O (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 ( $\text{MgSO}_4$ ), and the solvent was evaporated. The residual oil was subjected to flash column chromatography ( $\text{CH}_2\text{Cl}_2$  to  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  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  $\text{C}_{27}\text{H}_{27}\text{B}_3\text{O}_3$  [ $\text{M}^+$ ] 432.2239; found 432.2257.

(1*R*,2*R*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{18}\text{O}$  [ $\text{M}^+$ ] 262.1358; found 262.1354;  $[\alpha]_{\text{D}}^{28} = -72.6$  (c 1.0,  $\text{CHCl}_3$ ) for 87% ee, as determined by HPLC analysis (Chiralcel ADH, 2% iPrOH/hexane, 1.00 mL/min, 210 nm);  $t_{\text{R}} = 25.82$  min [major],  $t_{\text{R}} = 29.03$  min [minor].

(1*R*,2*R*)-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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{20}$  [ $\text{M} - \text{H}_2\text{O}]^+$  248.1565; found 248.1563;  $[\alpha]_{\text{D}}^{28} = +75.5$  (c 1.1,  $\text{CHCl}_3$ ).

3,3',4,4'-Tetrahydro-1*H*,2'*H*-1,2'-spirobi[naphthalene] (**36**). Procedure 2 from **34**: Flash chromatography (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;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  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);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  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  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{20}$  [ $\text{M}^+$ ] 248.1565; found 248.1567. HPLC analysis (Chiralcel ADH, 1% iPrOH/hexane, 1.00 mL/min, 254 nm);  $t_{\text{R}} = 4.10$  min,  $t_{\text{R}} = 4.42$  min.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

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

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## ■ REFERENCES

- (1) (a) Ward, R. S. *Nat. Prod. Rep.* **1999**, *16*, 75. (b) Ward, R. S. *Nat. Prod. Rep.* **1997**, *14*, 1943. (c) Ward, R. S. *Nat. Prod. Rep.* **1995**, *12*, 1183. (d) Ward, R. S. *Nat. Prod. Rep.* **1993**, *10*, 1. (e) Ward, R. S. *Chem. Soc. Rev.* **1982**, *11*, 75. (f) Brett, W. R. *Practitioner* **1951**, *166*, 77.
- (2) (a) Ke, H. Z.; Qi, H.; Crawford, D. T.; Chidsey-Frink, K. L.; Simmons, H. A.; Thompson, D. D. *Endocrinology* **2000**, *141*, 1338.

(b) Gennari, L.; Merlotti, D.; Valleggi, F.; Martini, G.; Nuti, R. *Drugs Aging* **2007**, *24*, 361.

(3) (a) Jardine, I. *Anticancer Agents Based on Natural Products*; Academic Press: New York, 1980. (b) Weiss, S. G.; Tin-wa, M.; Perdue, R. E.; Farnsworth, N. R. *J. Pharm. Sci.* **1975**, *64*, 95. (c) Keller-Juslen, C.; Kuhn, M.; Stahelin, H.; von Wartburg, A. *J. Med. Chem.* **1971**, *14*, 936.

(4) For a recent review, see: Sellars, J. D.; Steel, P. G. *Eur. J. Org. Chem.* **2007**, 3815.

(5) Rayabarapu, D. K.; Cheng, C.-H. *Acc. Chem. Res.* **2007**, *40*, 971.

(6) Selected examples: (a) Fleming, M. J.; Lautens, M. *Carbon–Heteroatom Bond Formation by Rh(I)-Catalyzed Ring-Opening Reactions in Catalyzed Carbon–Heteroatom Bond Formation*; Yudin, A. K., Ed.; Wiley: New York, 2011; pp 411–436. (b) Leong, P.; Lautens, M. *J. Org. Chem.* **2004**, *69*, 2194. (c) Lautens, M.; Fagnou, K.; Yang, D. *J. Am. Chem. Soc.* **2003**, *125*, 14884. (d) Lautens, M.; Fagnou, K. *J. Am. Chem. Soc.* **2001**, *123*, 7170. (e) Lautens, M.; Fagnou, K.; Taylor, M. *Org. Lett.* **2000**, *2*, 1677. (f) Lautens, M.; Fagnou, K.; Rovis, T. *J. Am. Chem. Soc.* **2000**, *122*, 5650. (g) Lautens, M.; Chiu, P.; Ma, S. H.; Rovis, T. *J. Am. Chem. Soc.* **1995**, *117*, 532.

(7) Selected examples for alkyl zinc compounds: (a) Lautens, M.; Hiebert, S. *J. Am. Chem. Soc.* **2004**, *126*, 1437. (b) Lautens, M.; Hiebert, S.; Renaud, J.-L. *J. Am. Chem. Soc.* **2001**, *123*, 6834. (c) Lautens, M.; Hiebert, S.; Renaud, J.-L. *Org. Lett.* **2000**, *2*, 1971. (d) Lautens, M.; Renaud, J.-L.; Hiebert, S. *J. Am. Chem. Soc.* **2000**, *122*, 1804. Boronic acids: (e) Magnus, H. A.; Fleming, M. J.; Lautens, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 433. (f) Lautens, M.; Dockendorf, C. *Org. Lett.* **2003**, *5*, 3695. (g) Lautens, M.; Dockendorf, C.; Fagnou, K.; Malicki, A. *Org. Lett.* **2002**, *4*, 1311.

(8) For a review, see: Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48.

(9) (a) Emer, E.; Sinisi, R.; Capdevila, M. G.; Petruzzello, D.; De Vincentis, F.; Cozzi, P. *Eur. J. Org. Chem.* **2011**, *4*, 647. (b) Bandini, M.; Tragni, M. *Org. Biomol. Chem.* **2009**, *7*, 1501. (c) Muzart, J. *Tetrahedron* **2008**, *64*, 5815.

(10) (a) Bandini, M.; Umani-Ronchi, A. *Catalytic Asymmetric Friedel–Crafts Alkylations*; Wiley-VCH: Weinheim, Germany, 2009. (b) For review on asymmetric Friedel–Crafts reaction, see: (i) Bandini, M.; Melloni, A.; Umani-Ronchi, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 550. (ii) Bandini, M.; Melloni, A.; Tommasi, S.; Umani-Ronchi, A. *Synlett* **2005**, 1199. (iii) Poulsen, T. B.; Jørgensen, K. A. *Chem. Rev.* **2008**, *108*, 2903. (iv) You, S.-L.; Cai, Q.; Zeng, M. *Chem. Soc. Rev.* **2009**, *38*, 2190.

(11) Selected articles: (a) Stadler, D.; Bach, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 7557. (b) Stadler, D.; Bach, T. *Chem. Asian J.* **2008**, *3*, 272. (c) Rubenbauer, P.; Bach, T. *Adv. Synth. Catal.* **2008**, *350*, 1125. (d) Mühlthau, F.; Stadler, D.; Goeppert, A.; Olah, G. A.; Suryah Prakash, G. K.; Bach, T. *J. Am. Chem. Soc.* **2006**, *128*, 9668. (e) Mühlthau, F.; Schuster, O.; Bach, T. *J. Am. Chem. Soc.* **2005**, *127*, 9348.

(12) Davoust, M.; Kitching, J. A.; Fleming, M. J.; Lautens, M. *Chem.—Eur. J.* **2010**, *17*, 50.

(13) Liébert, C.; Brinks, M. K.; Capacci, A. G.; Fleming, M. J.; Lautens, M. *Org. Lett.* **2011**, *13*, 3000.

(14) Reaction was also tested in a variety of solvents. Performing the reaction with the same conditions in CH<sub>2</sub>Cl<sub>2</sub> and MeNO<sub>2</sub> gave comparable results (97% yield, 8:1 dr, 6.1 rr in CH<sub>2</sub>Cl<sub>2</sub>). However, while doing concurrent studies in the intramolecular cases, we discovered that the substrates did not dissolve well in CH<sub>2</sub>Cl<sub>2</sub>, hence all reactions with AlCl<sub>3</sub> were done in MeNO<sub>2</sub>. Performing the reaction in acetonitrile gave poor selectivities (4.5:1 dr, 4.6:1 rr), and the reaction did not yield any of the desired product when done in 1,4-dioxane.

(15) Reaction with furan, 2-methylfuran, and benzofuran led to unidentified products, whereas reaction with silyl enol ethers, 2,4-pentanedione, and 1,3-cyclohexanedione led predominantly to the elimination product.

(16) Asymmetric ring opening of oxabicyclic alkene **4** with ethylene glycol protected boronic esters **24** required elevated temperatures to

afford the desired product **25**, which again results in a small decrease in enantioselectivity.

(17) (a) Brewster, W. K.; Nichols, D. E.; Riggs, R. M.; Mottola, D. M.; Lovenberg, T. W.; Lewis, M. H.; Mailman, B. R. *J. Med. Chem.* **1990**, *33*, 1756. (b) Hagishita, S.; Shiro, M.; Kuriyama, K. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1655.

(18) Diastereoselectivity is determined by coupling constants in <sup>1</sup>H NMR spectroscopy.

(19) Peach, P.; Cross, D. J.; Kenny, J. A.; Mann, I.; Houson, I.; Campbell, L.; Walsgrove, T.; Wills, M. *Tetrahedron* **2006**, *62*, 1864.

(20) Wong, K.-T.; Chien, Y.-Y.; Liao, Y.-L.; Lin, C.-C.; Chou, M.-Y.; Leung, M. *J. Org. Chem.* **2002**, *67*, 1041.

(21) Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 6716.

(22) Mulvaney, J. E.; Folk, T. L.; Newton, D. J. *J. Org. Chem.* **1967**, *32*, 1674.