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Article

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Asymmetric Ring Opening Reactions of Aza- and Oxa-bicyclic Alkenes with Boronic Acids Using a Palladium/Zinc Co-catalytic System

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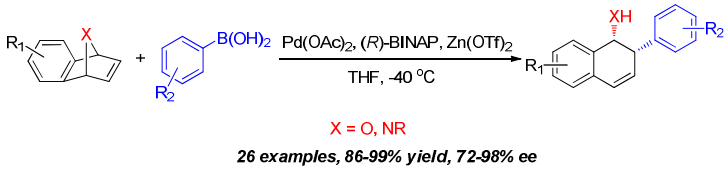
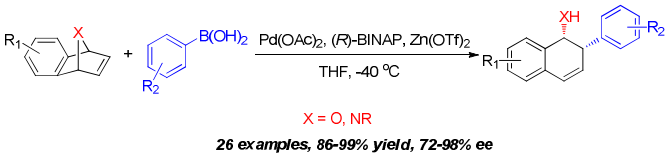


ABSTRACT: The asymmetric ring opening reactions of bicyclic alkenes with boronic acids were accomplished by using a highly active palladium/zinc co-catalytic system. And the co-catalytic system was suitable for both azabenzonorbornadienes and oxabenzonorbornadienes, which were transformed to the corresponding chiral hydronaphthalenes products in high yields (up to 99%) and high optical purities (up to 98% ee). The reaction protocol is general, mild, and with good functional group tolerance.



INTRODUCTION

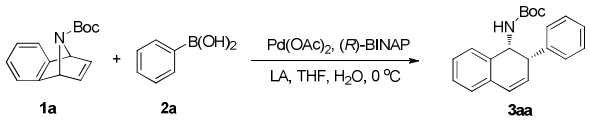
The transition-metal-catalyzed ring opening reactions of heterobicyclic alkenes have received intense attention in the past decade as they represent versatile approaches for chiral hydronaphthalenes,[1] which are frequently found in a plethora of natural products and biologically active molecules.[2] The group of Lautens has taken the lead in exploring rhodium catalyzed asymmetric ring opening reaction (ARO) of heterobicyclic alkenes[3]; and some other groups have also achieved a lot of success by using iridium,[4] nickel,[5] palladium,[6] copper,[7] and ruthenium catalysts[8]. Our group has had long interest in this kind of reactions by studying it by co-catalytic systems comprising chiral transition metal complexes and Lewis acids, which was previously employed by pioneers.[3c,9]. Followed by our previous work that employing alkynes,[10] amines,[11] phenols,[12] alcohols,[13] and organic acids[14] as nucleophiles, the asymmetric ring opening reaction of heterobicyclic alkenes by boronic acids have attracted our attention as they offered straightforward method for the preparation of chiral aryltetralin, which are common substructures in bioactive natural products such as chelidonine, corynoline, and wailupemycin D.[15] Although this kind of reactions have been studied with oxabenzonorbornadienes,[3d,6c,16] only few examples were given with azabenzonorbornadienes[17] in asymmetric fashion. In order to develop a general catalyst system and extend the reaction scope for the asymmetric ring opening reactions of azabenzonorbornadienes with boronic acids, we investigated it by using palladium/zinc co-catalytic system. Moreover, this co-catalytic system also exhibited excellent catalytic ability on the oxabenzonorbornadiene substrates.

RESULTS AND DISCUSSION

According to our previous studies of the asymmetric ring opening reactions, the selection of Lewis acid is crucial to the reaction outcomes. Therefore, our journey commenced by searching for a suitable Lewis acid using the reaction of azabenzonorbornadiene **1a** with phenylboronic acid **2a** in the presence of $Pd(OAc)_2$ and (*R*)-BINAP (Table 1). The initially tested ZnI_2 only give the desired product **3aa** in trace amount (Table 1, entry 1), CuI and $FeCl_2$ also failed to promote the reaction (Table 1, entries 2-3). We were delight to find that by using AgOTf, **3aa** was obtained in 89% yield with 79% enantiomeric excess (Table 1, entry 4). Some other trifluoromethanesulfonic salts were next screened by

assuming that the trifluoromethanesulfonate anion has a unique effect in the present reaction. But the experimental results showed that CuOTf and $Cu(OTf)_2$ led to inferior reaction yields with similar enantioselectivities (Table 1, entries 5-6). By switching to $Zn(OTf)_2$ and $Fe(OTf)_2$, excellent yields were achieved (Table 1, entries 7-8). The next tested Lewis acids such as $Fe(OTf)_3$, $In(OTf)_3$, and $Al(OTf)_3$ were less effective and

Table 1. Screening of Lewis acids for the ARO reaction[a]



1a 2a 3aa

Entry	Lewis acid	Time [h]	Yield [%]	*ee* [%][b]
1	ZnI_2	48	trace	---
2	CuI	48	N.R.	---
3	$FeCl_2$	48	N.R.	---
4	AgOTf	2.5	89	79
5	CuOTf	4.5	76	75
6	$Cu(OTf)_2$	0.5	79	80
7	$Zn(OTf)_2$	0.4	98	77
8	$Fe(OTf)_2$	1	98	77
9	$Fe(OTf)_3$	12	81	79
10	$In(OTf)_3$	14	83	79
11	$Al(OTf)_3$	13	77	79
12	---	60	90	43

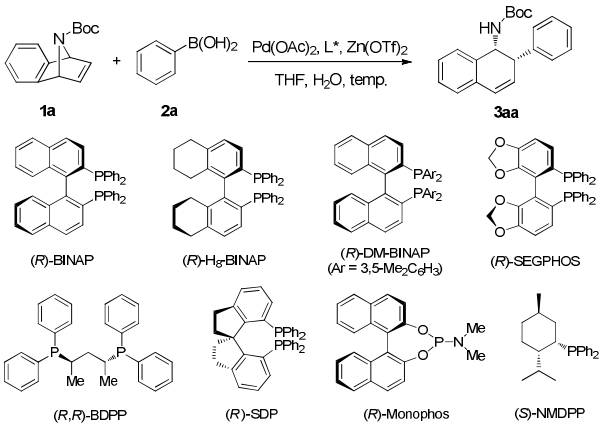
[a]*Reaction conditions:* **1a** (0.2 mmol), **1a**/**2a**/$Pd(OAc)_2$/ (*R*)-BINAP/Lewis acid (1:2:0.05:0.06:0.1), in tetrahydrofuran (2 mL) at 0 °C under Ar for the time indicated. [b]Determined by HPLC with a Chiralcel OD-H column.

gave inferior reaction yields (Table 1, entries 9-11). Control experiment further established the requirement of Lewis acid for good enantioselectivity (Table 1, entry 12).

Subsequently, the reaction conditions optimization of present reaction was carried out by screening various chiral ligands and reaction temperatures. As the results summarized in table 2, the using of BINAP-derived diphosphine ligands such as (*R*)-H_8-BINAP and (*R*)-DM-BINAP both gave reduced reaction yields (Table 2, entries 2 and 3). And the evaluation of other bidentate chiral ligands were failed to give good reaction results (Table 2, entries 4 and 5). The next tested chiral spiro ligand (Table 2, entry 6) and some monophosphine ligands (Table 2, entries 7 and 8) were proved to be ineffective. In order to improve the reaction enantioselectivity, the reaction was carried out by lowering the reaction temperature. The present catalytic system was proved to be highly active as good reaction result was obtained at -20 °C (Table 2, entry 9), and high enantioselectivity was achieved at -40 °C (Table 2, entry 10). However, the reaction performed at -60 °C became sluggish and only a trace amount of the desired product was observed after 72 hours (entry 14). The addition of water was proved to be no need, because an improved *ee* was obtained with the reaction yield unchanged by the control experiment. This result can be explained by the undermining of Lewis acid when water was added, and thus affected the enantioselectivity of the reaction. Although the reaction was performed well in other solvents such toluene and diethyl ether, but the outcomes were inferior compared to tetrahydrofuran (Table 2, entries 13-14).

With the optimized conditions in hand, various boronic acids were reacted with azabenzonorbornadiene **1a**, and the corresponding products **3aa-an** were obtained generally in high yields and excellent enantiomeric excesses (Table 3). Among them, halogen bearing phenylboronic acid showed good tolerance, and the

Table 2. Screening of chiral ligands and reaction temperatures for the ARO reaction[a]



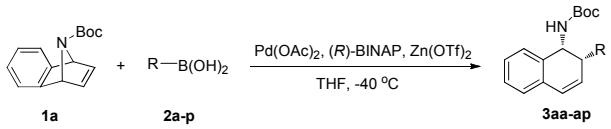
1a 2a 3aa

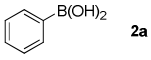
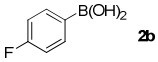
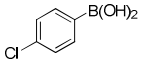
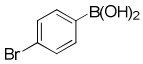
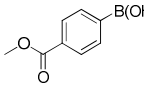
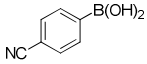
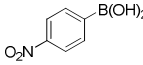
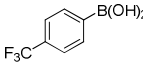
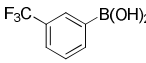
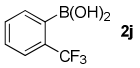
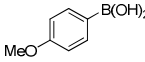
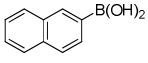
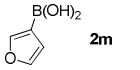
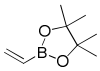
Entry	Ligand	T [°C]	Time [h]	Yield [%]	ee [%][b]
1	(*R*)-BINAP	0	0.5	98	77
2	(*R*)-H_8-BINAP	0	0.5	89	58
3	(*R*)-DM-BINAP	0	0.5	84	77
4	(*R*)-SEGPHOS	0	2	75	31
5	(*R*,*R*)-BDPP	0	2	86	31
6	(*R*)-SDP	r.t.	60	trace	---
7	(*R*)-MONOPHOS	r.t.	60	trace	---
8	(*S*)-NMDPP	r.t.	60	trace	---
9	(*R*)-BINAP	-20	2	95	89
10	(*R*)-BINAP	-40	19	95	93
11	(*R*)-BINAP	-60	72	trace	---
12[c]	(*R*)-BINAP	-40	13	95	94
13[d]	(*R*)-BINAP	-40	40	95	87
14[e]	(*R*)-BINAP	-40	72	84	80

[a]*Reaction conditions:* The reaction was carried out with **1a** (0.2 mmol), **2a** (0.4 mmol) and 0.1 equiv. of $Zn(OTf)_2$ in tetrahydrofuran (2 mL) in the presence of $Pd(OAc)_2$ (5 mol%) and a bidentate ligand (6 mol%) or monodentate ligand (12 mol%) under Ar for the time indicated. [b]Determined by HPLC with a Chiralcel OD-H column. [c]No water was used. [d]Toluene was used as solvent. [e]Diethyl ether was used as solvent.

halogen groups were unreacted (Table 3, entries 2-4). The electron- withdrawing groups substituted phenylboronic acids were also suitable nucleophiles in present transformation (Table 3, entries 5-8). However, caused by the steric effect, meta- and ortho- substituted phenylboronic acids exhibited lower reactivities and

Table 3. Scope of the phenylboronic acids[a]

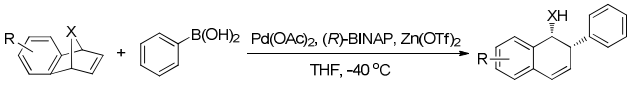


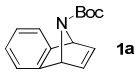
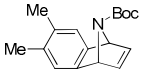
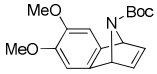
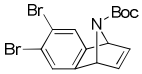
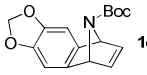
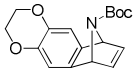
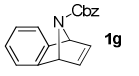
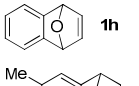
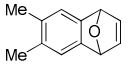
Entry	Boronic acid **2a-n**	Time [h]	Yield [%]	*ee* [%][b]
1	 **2a**	19	95	94
2[c,d]	 **2b**	26	97	90
3	 **2c**	24	90(73)[f]	94(71)[f]
4	 **2d**	72	99	91
5	 **2e**	30	98	90
6	 **2f**	19	97	93
7	 **2g**	41	99	95
8	 **2h**	17	98	95
9[c,d]	 **2i**	70	93	86
10[c,d]	 **2j**	65	96	72
11[e]	 **2k**	36	86	90
12[c,d]	 **2l**	72	93	82
13[c]	 **2m**	60	91(80)[f]	99(78)[f]
14	 **2n**	37	93	98
15	 **2o**	24	26	99
16	 **2p**	24	NR	---

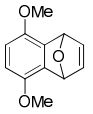
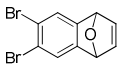
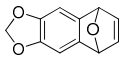
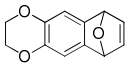
[a]*Reaction conditions:* **1a** (0.2 mmol), **1a**/**2**/$Pd(OAc)_2$/(*R*)-BINAP/$Zn(OTf)_2$ (1:2:0.05:0.06:0.1), in tetrahydrofuran (2 mL) at -40 °C under Ar for the time indicated. [b]Determined by HPLC with a Chiralcel OD-H , AD-H or AS-H column. [c]10% $Pd(OAc)_2$ and 12% (*R*)-BINAP were used. [d]Reacted at 0 °C. [e]Reacted at -20 °C. [f]Results in the parentheses were obtained by using the literature conditions (ref 15a).

enantioselectivities toward this asymmetric ring opening reaction (Table 3, entries 9-10). The electron-rich phenylboronic acid **2k** was participated in the reaction, albeit with relatively moderate result (Table 3, entry 11). 2-Naphthylboronic acid was found less reactive, and a prolonged reaction time was needed to complete full transformation (Table 3, entry 12). In addition to phenylboronic acids, 3-furanylboronic acid **2m** and 3-thienylboronic acid **2n** also gave the corresponding ring

Table 4. Scope of the bicyclic alkenes[a]



Entry	Bicyclic alkene **1a-m**	Time [h]	Yield [%]	ee [%][b]
1	 **1a**	17	95	94
2	 **1b**	39	98(90)[c]	95(60)[c]
3	 **1c**	36	86	93
4	 **1d**	39	96	94
5	 **1e**	33	90	93
6	 **1f**	35	96(88)[c]	91(55)[c]
7	 **1g**	53	94	91
8	 **1h**	19	95	94
9	 **1i**	41	95	94

10		**1j**	28	96	92
11		**1k**	19	96	98
12		**1l**	17	95	95
13		**1m**	16	95	95

[a]*Reaction conditions:* **1** (0.2 mmol), **1**/**2a**/$Pd(OAc)_2$/(*R*)-BINAP/$Zn(OTf)_2$ (1:2:0.05:0.06:0.1), in tetrahydrofuran (2 mL) at -40 °C under Ar for the time indicated. [b]Determined by HPLC with a Chiralcel OD-H or AD-H column. [c]Results in the parentheses were obtained by using the literature conditions (ref 15a).

opening products with excellent results (Table 3, entries 13-14). However, the present reaction was not suitable for the alkyl and vinyl boronoic acid pinacol esters (Table 3, entries 15-16). To illustrate the advantage of present conditions to the reported method[15a], the reactions of **2c** and **2m** were also tested by using [Pd ($MeCN_2$)Cl_2], (*S*)-tol-binap and Cs_2CO_3 in methanol at ambient temperature (Table 3, entries 3 and 13). The results indicated present conditions showed superior efficiency in terms of the reaction yields and enantioselectivities.

Next, the scope of the reaction was surveyed by a range of bicyclic alkenes, including azabenzonorbornadienes and oxabenzonorbornadienes. As the experimental results summarized in table 4, except for dimethoxyl-substituted azabenzonorbornadiene (table 4, entry 3), which gave a decreased yield due to the generation of 2,3-dimethoxy-6-phenylnaphthalene as side-product, all of the azabenzonorbornadienes performed well and gave the corresponding products generally in good results (table 4, entries 2-6). And the bromine groups remained intact that enables further elaboration of the product (table 4, entry 4). As expected, the reactions of **1b** and **1f** also gave superior results than that of the literature conditions[15a] (table 4, entries 2 and 6). To our delight, oxabenzonorbornadienes were also viable substrates to give excellent results (table 4, entries 8-13). Thus, this synthetic protocol was highly effective for both aza- and oxa- bicyclic alkenes.

Finally, the absolute configurations of the ring opening products of azabenzonorbornadienes (**3aa-an** & **3ba-ga**) were identified by X-ray analysis of **3da** (figure 1),[18] and the ring opening products of oxabenzonorbornadienes (**3ha-ma**) were assigned by comparison of the chiral HPLC data of **3ha** with that reported in the literature.[19]

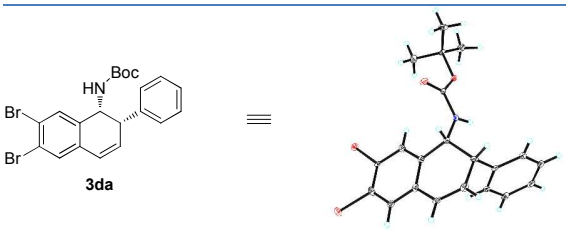


Figure 1. X-ray structure of 3da.

Basis on our experience of the asymmetric ring opening reactions[11c,12b] and literatures of palladium catalyzed reaction of arylboronic acids[20], a plausible mechanism of this ring opening reaction is outlined by the reaction of **1a** and **2a** (Figure 2). The catalytic cycle would be initiated

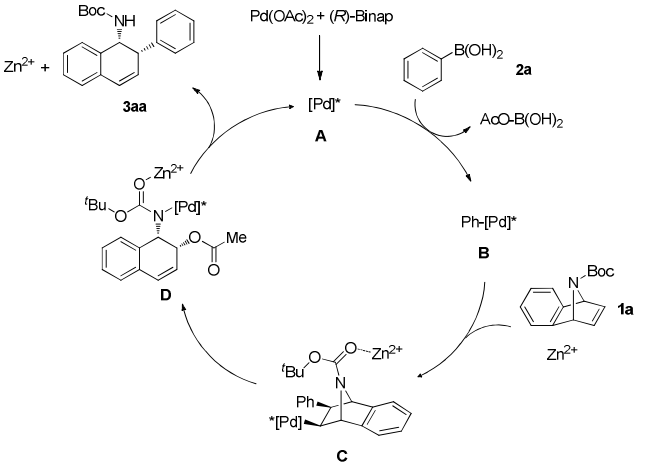


Figure 2. Proposed mechansim for the asymmeric ring opening reaction.

by the coordination of $Pd(OAc)_2$ and (*R*)-Binap to form the chiral palladium catalyst **A**. Subsequently, transmetalation of phenylboronic acid **1a** generates the arylpalladium species **B**, which was followed by insertion of **1a** into the carbon-palladium bond to generated intermediate **C**. Then the following β-elimination of nitrogen opens the pyrrolidine ring and yields the ring-opened species **D**. Finally, the ring opening product **3aa** is given by hydrolysis.

CONCLUSION

In summary, by employing the highly active co-catalytic system comprising $Pd(OAc)_2$, (*R*)-BINAP and $Zn(OTf)_2$, the asymmetric ring opening reactions of both azabenzonorbornadienes and oxabenzonorbornadienes with boronic acids were accomplished with high yields and enantioselectivities. This approach allows for rapid preparation of chiral arytetralin derivatives.

EXPERIMENTAL SECTION

Synthesis of substrates. Bicyclic alkene **1a-l** were prepared according to the literature procedures.[21]

General Method. The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox. Anhydrous THF (Tetrahydrofuran) was distilled from sodium benzophenone ketyl prior to use. ^{1}H and ^{13}C{^{1}H}NMR spectra were recorded at ambient temperature on 400 MHz and 75 MHz spectrometers using tetramethylsilane (TMS) as internal reference. The chemical shifts are quoted in δ units, parts per million (ppm) upfield from the signal of internal TMS. ^{1}H NMR data is represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration and coupling constant(s) *J* in Hertz (Hz). The enantioselective excesses were determined by normal phase HPLC eluted with a mixture of isopropyl alcohol and hexane. High resolution mass spectra (HRMS) were obtained on a double-focusing high resolution magnetic-sector mass-analyzed instrument, operating in an electron impact (EI) mode. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents.

General procedure for the asymmetric ring opening reactions of bicyclic alkene with boronic acids. $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), (*R*)-BINAP (7.5 mg, 0.012 mmol) and 1.0 mL THF were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then $Zn(OTf)_2$ (7.3 mg, 0.02 mmol) was added and stirred for additional 10 min, then a solution of bicyclic alkene **1a-m** (48.6 mg, 0.2 mmol) in THF (0.7 mL) was added, and the mixture was stirred for additional 5 min. The mixture was stirred at -40 °C under argon atmosphere for 15 min, followed by the addition of boronic acid **2a-n** (48.8 mmol, 0.4 mmol) solution in dry THF (0.5 ml). The mixture was then stirred at -40 °C under argon atmosphere with TLC monitoring until the complete consumption of **1a-m**. The reaction mixture was concentrated and the residue was purified by chromatography on a silica gel column to afford the desired product. The enantioselective excess value of the product was determined by HPLC on a chiral stationary phase.

Characterization Data. *tert-butyl ((1R,2S)-2-phenyl-1,2-dihydronaphthalen-1-yl)carbamate (**3aa**):*[17] White solid, 95% yield, 94% *ee*. $[\alpha]_D^{27}$ = -288.8 (c = 5.80×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.09 (m, 9H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.13 (dd, *J* = 9.6, 5.0 Hz, 1H), 5.35 - 5.23 (m, 1H), 4.53 (d, *J* = 9.8 Hz, 1H), 3.86 (s, 1H), 1.40 (s, 9H). The *ee* of **3aa** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 7.7 min, t_{minor} = 9.7 min.

*tert-butyl ((1R,2S)-2-(4-fluorophenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ab**):* White solid, 97% yield, 90% *ee*. Mp 97 - 100 °C. $[\alpha]_D^{27}$ = -169.4 (c = 1.30×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.13 (m , 4H), 7.09 - 7.00 (m, 2H), 6.91 (t, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 9.6 Hz, 1H), 6.09 (dd, *J* = 9.6, 4.9 Hz, 1H), 5.30 - 5.23 (m, 1H), 4.51 (d, *J* = 10.0 Hz, 1H), 3.84 (dd, *J* = 16.2, 10.9 Hz, 1H), 1.40 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 163.4, 160.9, 155.4, 134.5, 133.4, 133.3, 133.2, 130.6, 130.5, 130.2, 128.4, 128.2, 127.8, 126.4, 125.6, 115.3, 115.1, 79.5, 52.3, 44.0, 28.4. HRMS (EI) calcd for $C_{21}H_{22}FNO_2$ $[M]^+$: 339.1635. Found: 339.1621. The *ee* of **3ab** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 9.4 min, t_{minor} = 13.2 min.

*tert-butyl ((1R,2S)-2-(4-chlorophenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ac**):*[17] White solid, 90% yield, 94% *ee*. $[\alpha]_D^{27}$ = -213.5 (c = 1.24×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.10 (m, 6H), 7.02 (d, *J* = 2 Hz, 2H), 6.67 (dd, *J* = 9.7, 1.0 Hz, 1H), 6.08 (dd, *J* = 9.6, 5.0 Hz, 1H), 5.27 (dd, *J* = 9.9, 7.4 Hz, 1H), 4.51 (d, *J* = 10.1 Hz, 1H), 3.84 (t, *J* = 5.7 Hz, 1H), 1.40 (s, 9H). The *ee* of **3ac** was determined by HPLC analysis using Daicel Chiralcel AS-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} =9.2 min, t_{minor} = 10.8 min.

*tert-butyl ((1R,2S)-2-(4-bromophenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ad**):* White solid, 98% yield, 92% *ee*. Mp 113 - 114 °C. $[\alpha]_D^{27}$ = -258.9 (c = 1.66×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.10 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.08 (dd, *J* = 9.6, 4.9 Hz, 1H), 5.31 - 5.20 (m, 1H), 4.50 (d, *J* = 10.0 Hz, 1H), 3.83 (t, *J* = 5.5 Hz, 1H), 1.40 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.3, 136.7, 134.3, 133.2, 131.5, 130.8, 129.8, 128.7, 128.3, 127.9, 126.5, 125.5, 121.2, 79.6, 52.2, 44.2, 28.4. HRMS (EI) calcd for $C_{21}H_{22}BrNO_2$ $[M]^+$: 399.0834. Found: 399.0837. The *ee* of **3ad** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 8.4 min, t_{minor} = 10.8 min.

*methyl 4-((1R,2S)-1-((tert-butoxycarbonyl)amino)-1,2-dihydronaphthalen-2-yl)benzoate (**3ae**):* White solid, 98% yield, 90% *ee*. Mp 144 - 146 °C. $[\alpha]_D^{27}$ = -292.2 (c = 1.44×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.28 - 7.15 (m, 6H), 6.71 (d, *J* = 9.6 Hz, 1H), 6.11 (dd, *J* = 9.6, 4.8 Hz, 1H), 5.31 (dd, *J* = 9.6, 7.5 Hz, 1H), 4.54 (d, *J* = 10.1 Hz, 1H), 3.94 (s, 1H), 3.87 (s, 3H), 1.38 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 166.9, 155.3, 143.3, 134.3, 133.1, 130.2, 129.6, 129.5, 129.1, 128.9, 128.3, 127.9, 127.3, 126.5, 125.6, 79.6, 52.2, 52.1, 44.8, 28.3. HRMS calcd for $C_{23}H_{25}NO_4$ $[M]^+$: 379.1784. Found: 379.1783. The *ee* of **3ae** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 10.3 min, t_{minor} = 13.8 min.

*tert-butyl ((1R,2S)-2-(4-cyanophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)carbamate (**3af**):* White solid, 97% yield, 93% *ee*. Mp 124 - 127 °C. $[\alpha]_D^{27}$ = -233.1 (c = 1.34×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.34 - 7.09 (m, 6H), 6.73 (d, *J* = 9.6 Hz, 1H), 6.07 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.32 – 5.18 (m, 1H), 4.53 (d, *J* = 10.0 Hz, 1H), 3.97 (s, 1H), 1.37 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.0, 144.0, 134.0, 132.8, 132.1, 129.9, 129.3, 128.7, 128.5, 128.2, 126.7, 125.9, 118.8, 111.1, 79.8, 52.2, 45.1, 28.3. HRMS (EI) calcd for $C_{22}H_{22}N_2O_2$ $[M]^+$: 346.1681. Found: 346.1686. The *ee* of **3af** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 7.5 min, t_{minor} = 10.6 min.

*tert-butyl ((1R,2S)-2-(4-nitrophenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ag**):* White solid, 99% yield, 95% *ee*. Mp 115 - 117 °C. $[\alpha]_D^{27}$ = -280.9 (c = 1.26×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 7.32 - 7.18 (m, 6H), 6.75 (d, *J* = 9.6 Hz, 1H), 6.09 (dd, *J* = 9.6, 4.4 Hz, 1H), 5.30 - 5.26 (m, 1H), 4.55 (d, *J* = 9.9 Hz, 1H), 4.01 (d, *J* = 23.6 Hz, 1H), 1.36 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.0, 147.2, 146.2, 133.9, 132.8, 130.0, 129.4, 128.6, 128.6, 128.3, 126.8, 125.9,

123.5, 79.8, 52.2, 44.9, 28.3. HRMS (EI) calcd for $C_{21}H_{22}N_2O_4$ $[M]^+$: 366.1580. Found: 366.1574. The *ee* of **3ag** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 12.4 min, t_{minor} = 17.2 min.

*tert-butyl ((1R,2S)-2-(4-(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ah**):* White solid, 98% yield, 95% *ee*. Mp 82 - 85 °C. $[\alpha]_D^{27}$ = -160.2 (c = 1.72×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 - 7.06 (m, 4H), 7.01 - 6.97 (m, 2H), 6.84 (t, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 9.6 Hz, 1H), 6.02 (dd, *J* = 9.5, 4.9 Hz, 1H), 5.21 - 5.17 (m, 1H), 4.44 (d, *J* = 9.9 Hz, 1H), 3.75 (d, *J* = 24.5 Hz, 1H), 1.32 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100MHz): δ 162.3, 159.9, 154.3, 133.4, 132.3, 132.2, 129.6, 129.5, 129.2, 127.4, 127.2, 126.8, 125.4, 124.5, 114.3, 114.1, 78.5, 51.2, 43.0, 27.3. HRMS (EI) calcd for $C_{22}H_{22}F_3NO_2$ $[M]^+$: 389.1603. Found: 389.1606. The *ee* of **3ah** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 10.4 min, t_{minor} = 16.3 min.

*tert-butyl ((1R,2S)-2-(3-(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ai**):* White solid, 93% yield, 86% *ee*. Mp 80 - 83 °C. $[\alpha]_D^{27}$ = -184.1 (c = 1.32×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 8.1 Hz, 1H), 7.41 - 7.12 (m, 7H), 6.73 (dd, *J* = 9.7, 1.5 Hz, 1H), 6.10 (dd, *J* = 9.6, 4.7 Hz, 1H), 5.27 (dd, *J* = 10.0, 7.1 Hz, 1H), 4.53 (d, *J* = 10.1 Hz, 1H), 3.97 (t, *J* = 5.2 Hz, 1H), 1.37 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.2, 139.1, 134.1, 133.0, 132.4, 129.3, 129.2, 128.8, 128.4, 128.1, 126.6, 126.1, 126.0, 125.8, 124.1, 124.0, 79.7, 52.2, 44.6, 28.2. HRMS (EI) calcd for $C_{22}H_{22}F_3NO_2$ $[M]^+$: 389.1603. Found: 389.1607. The *ee* of **3ai** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: n-hexane/i-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 7.8 min, t_{minor} = 11.3 min.

*tert-butyl ((1R,2S)-2-(2-(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3aj**):* White solid, 96% yield, 72% ee. Mp 118 - 120 °C. $[\alpha]_D^{27}$ = -75.9 (c = 5.8×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.45 - 7.14 (m, 6H), 7.08 (d, *J* = 6.8 Hz, 1H), 6.58 (d, *J* = 8.2 Hz, 1H), 5.93 (dd, *J* = 9.6, 3.3 Hz, 1H), 5.14 (dd, *J* = 10.0, 6.4 Hz, 1H), 4.57 (d, *J* = 10.1 Hz, 1H), 4.28 (d, *J* = 2.8 Hz, 1H), 1.20 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 154.6, 138.8, 134.7, 132.5, 132.0, 131.7, 131.4, 130.5, 130.4, 128.4, 128.3, 128.2, 127.0, 126.6, 126.0, 126.0, 79.3, 51.5, 41.4, 28.3. HRMS (EI) calcd for $C_{22}H_{22}F_3NO_2$ $[M]^+$: 389.1603. Found: 389.1609. The *ee* of **3aj** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 7.4 min, t_{minor} = 8.3 min.

*tert-butyl ((1R,2S)-2-(4-methoxyphenyl)-1,2-dihydronaphthalen-1-yl)carbamate (**3ak**):* White solid, 86% yield, 90% *ee*. Mp 60 - 62 °C. $[\alpha]_D^{26}$ = -210.9 (c = 1.26×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.12 (m, 4H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 9.6 Hz,1H), 6.11 (dd, *J* = 9.6, 5.2 Hz, 1H), 5.30 - 5.26 (m, 1H), 4.52 (d, *J* = 10.0 Hz, 1H), 3.84 - 3.77 (m, 1H), 3.74 (s, 3H), 1.42 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 158.9, 155.6, 134.8, 133.5, 130.8, 130.1, 129.2, 128.0, 128.0, 127.6, 126.3, 125.3, 113.9, 79.4, 55.2, 52.4, 43.9, 28.4. HRMS (EI) calcd for $C_{22}H_{25}NO_3$ $[M]^+$: 351.1834. Found: 351.1816. The *ee* of **3ak** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 8.8 min, t_{minor} = 11.4 min.

*tert-butyl ((1R,2S)-1,2-dihydro-[2,2'-binaphthalen]-1-yl)carbamate (**3al**):* White solid, 93% yield, 82% *ee*. Mp 58 - 60 °C. $[\alpha]_D^{27}$ = -310.1 (c = 7.2×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 - 7.58 (m, 3H), 7.50 (s, 1H), 7.34 - 7.32 (m, 2H), 7.20 - 7.09 (m, 5H), 6.61 (dd, *J* = 24.4, 9.8 Hz, 1H), 6.12 (dd, *J* = 9.6, 5.0 Hz, 1H), 5.33 - 5.29 (m, 1H), 4.47 (d, *J* = 10.0 Hz, 1H), 3.95 (s, 1H), 1.26 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 154.5, 134.2, 133.7, 132.3, 131.7, 129.3, 127.4, 127.1, 127.0, 126.9, 126.7, 126.5, 126.1, 125.4, 124.9, 124.7, 124.4, 78.4, 51.3, 43.8, 27.3. HRMS (EI) calcd for $C_{25}H_{25}NO_2$ $[M]^+$: 371.1885. Found: 371.1893. The *ee* of **3al** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{minor} = 9.0 min, t_{major} = 11.1 min.

*tert-butyl ((1R,2S)-2-(furan-3-yl)-1,2-dihydro-naphthalen-1-yl)carbamate (**3am**):*[17] Colorless oil, 91% yield, 99% *ee*. $[\alpha]_D^{27}$ = -234.7 (c = 1.02×10^{-2}, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.19 (m, 5H), 7.11 (d, *J* = 6.3 Hz, 1H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.05 - 6.09 (m, 1H), 6.01 (s, 1H), 5.22 (dd, *J* = 9.6, 6.9 Hz, 1H), 4.74 (d, *J* = 9.8 Hz, 1H), 3.72 (t, *J* = 5.4 Hz, 1H), 1.45 (s, 9H). The *ee* of **3am** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 7.8 min, t_{minor} = 10.0 min.

*tert-butyl ((1R,2S)-2-(thiophen-3-yl)-1,2-dihydro-naphthalen-1-yl)carbamate (**3an**):*[17] Colourless oil, 93% yield, 98% *ee*. $[\alpha]_D^{27}$ = -310.6 (c = 1.10×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.10 (m, 5H), 6.97 (d, *J* = 1.9 Hz, 1H), 6.73 (d, *J* = 4.6 Hz, 1H), 6.61 (d, *J* = 9.6 Hz, 1H), 6.13 (dd, *J* = 9.6, 5.2 Hz, 1H), 5.28 (dd, *J* = 9.6, 7.2 Hz, 1H), 4.64 (d, *J* = 9.9 Hz, 1H), 3.94 (t, *J* = 5.6 Hz, 1H), 1.43 (s, 9H). The *ee* of **3an** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 8.9 min, t_{minor} = 12.5 min.

*tert-butyl ((1R,2R)-2-vinyl-1,2-dihydronaphthalen-1-yl)carbamate (**3ao**):* Colourless oil, 26% yield, 99% *ee*. $[\alpha]_D^{25}$ = -179.3 (c = 7.3×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 3H), 7.08-7.06 (m, 1H), 6.53-6.50 (m, 1H), 5.96 (dd, *J* = 5.2, 9.6 Hz, 1H), 5.64 (dd, *J* = 8.4, 17.2 Hz, 1H), 5.24-4.86 (m, 4H), 3.16-3.13 (m, 1H), 1.47 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.7, 136.3, 134.8, 133.1, 129.3, 127.9, 127.8, 127.6, 126.4, 125.5, 118.4, 79.5, 51.3, 43.6, 28.4. HRMS (EI) calcd for $C_{17}H_{21}NO_2Na^+$ $[M]^+$: 294.1470. Found: 294.1463. The *ee* of **3ao** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.5 mL/min, 254 nm; t_{major} = 7.5 min.

*tert-butyl ((1R,2S)-6,7-dimethyl-2-phenyl-1,2-dihydronaphthalen-1-yl)carbamate (**3ba**):* White solid, 98% yield, 95% *ee*. Mp 165 - 167 °C. $[\alpha]_D^{27}$ = -260.0 (c = 1.24×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28- 7.17 (m, 3H), 7.16 - 7.05 (m, 2H), 6.93 (d, *J* = 10.8 Hz, 2H), 6.61 (d, *J* = 9.6 Hz, 1H), 6.05 (dd, *J* = 9.6, 4.8 Hz, 1H), 5.26 - 5.17 (m, 1H), 4.53 (d, *J* = 10.0 Hz, 1H), 3.91 - 3.80 (m, 1H), 2.23 (d, *J* = 12.2 Hz, 6H), 1.38 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.4, 138.2, 136.4, 135.7, 132.0, 130.9, 129.3, 129.2, 128.4, 128.2, 127.8, 127.1, 79.3, 52.1, 45.0, 28.4, 19.7, 19.4. HRMS (EI) calcd for $C_{23}H_{27}NO_2$ $[M]^+$: 349.2042. Found: 349.2047. The *ee* of **3ba** was determined by HPLC analysis using Daicel Chiralcel OD-H col-

umn (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 7.8 min, t_{minor} = 10.5 min.

*tert-butyl ((1R,2S)-6,7-dimethoxy-2-phenyl-1,2-dihydronaphthalen-1-yl)carbamate (**3ca**):*[17] White solid, 86% yield, 93% *ee*. $[\alpha]_D^{26}$ = -144.9 (c = 1.09×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.20 (m, 3H), 7.18 - 7.11 (m, 2H), 6.73 (d, *J* = 24.0 Hz, 2H), 6.58 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.03 (dd, *J* = 9.6, 4.7 Hz, 1H), 5.18 (dd, *J* = 10.0, 7.3 Hz, 1H), 4.56 (d, *J* = 10.2 Hz, 1H), 3.88 (d, *J* = 20.9 Hz, 7H), 1.37 (s, 9H). The *ee* of **3ca** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; t_{major} = 5.9 min, t_{minor} = 7.1 min.

*tert-butyl ((1R,2S)-6,7-dibromo-2-phenyl-1,2-dihydronaphthalen-1-yl)carbamate (**3da**):* White solid, 96% yield, 95% *ee*. Mp 124 - 127 °C $[\alpha]_D^{27}$ = -190.2 (c = 1.04×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.0 Hz, 2H), 7.19 - 7.12 (m, 3H), 6.95 (s, 2H), 6.50 (d, *J* = 9.7 Hz, 1H), 6.16 - 6.12 (m, 1H), 5.26 - 5.16 (m, 1H), 4.36 (d, *J* = 10.2 Hz, 1H), 3.75 (dd, *J* = 15.3, 9.1 Hz, 1H), 1.36 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.4, 136.0, 135.6, 134.3, 132.6, 130.9, 130.6, 129.1, 129.0, 128.7, 127.7, 126.3, 123.7, 123.6, 80.0, 51.7, 44.2, 28.4. HRMS (EI) calcd for $C_{21}H_{21}Br_2NO_2Na^+$ $[M]^+$: 499.9837. Found: 499.9827. The *ee* of **3da** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 0.3 mL/min, 254 nm; t_{major} = 15.3 min, t_{minor} = 16.8 min.

*tert-butyl ((5R,6S)-6-phenyl-5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-yl)carbamate (**3ea**):* White solid, 90% yield, 93% *ee*. Mp 185 - 188 °C. $[\alpha]_D^{27}$ = -142.8 (c = 1.04×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 13.0, 6.6 Hz, 3H), 7.13 (d, *J* = 6.7 Hz, 2H), 6.72 (s, 1H), 6.65 (s, 1H), 6.55 (t, *J* = 9.2 Hz, 1H), 6.02 (dd, *J* = 9.6, 4.8 Hz, 1H), 5.92 (d, *J* = 8.5 Hz, 2H), 5.18 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.53 (d, *J* = 10.1 Hz, 1H), 3.84 - 3.74 (m, 1H), 1.38 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.3, 147.3, 146.9, 137.8, 129.1, 128.5, 128.4, 128.1, 127.4, 127.2, 107.1, 101.0, 79.4, 60.4, 52.4, 44.8, 28.4, 21.1, 14.2. HRMS (EI) calcd for $C_{22}H_{23}NO_4$ $[M]^+$: 365.1627. Found: 365.1630. The *ee* of **3ea** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH =95/5, 0.5 mL/min, 254 nm; t_{major} =10.1 min, t_{minor} = 10.9 min.

*tert-butyl ((6R,7S)-7-phenyl-2,3,6,7-tetrahydro-naphtho[2,3-b][1,4]dioxin-6-yl)carbamate (**3fa**):* White solid, 96% yield, 92% *ee*. Mp 202 - 206 °C. $[\alpha]_D^{26}$ = -230.4 (c = 5.4×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.17 (m, 3H), 7.10 (d, *J* = 6.6 Hz, 2H), 6.68 (d, *J* = 10.4 Hz, 2H), 6.54 (d, *J* = 9.6 Hz,1H), 6.02 (dd, *J* = 9.6, 5.1 Hz, 1H), 5.25 - 5.14 (m, 1H), 4.45 (d, *J* = 10.1 Hz, 1H), 4.23 (s, 4H), 3.82 - 3.69 (m, 1H), 1.39 (s, 9H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 155.4, 143.2, 142.6, 137.8, 129.2, 128.8, 128.5, 128.4, 127.5, 127.2, 115.3, 115.0, 79.4, 64.5, 64.4, 51.9, 44.7, 28.4. HRMS (EI) calcd for $C_{23}H_{25}NO_4$ $[M]^+$: 379.1784. Found: 379.1801. The *ee* of **3fa** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH =95/5, 0.5 mL/min, 254 nm; t_{major} = 12.7 min, t_{minor} = 14.1 min.

*benzyl ((1R,2S)-2-phenyl-1,2-dihydronaphthalen-1-yl)carbamate (**3ga**):* Colorless oil, 94% yield, 91% *ee*. $[\alpha]_D^{27}$ = -223.2 (c = 1.32×10^{-2}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 6.85 (m, 14H), 6.58 (d, *J* = 9.6 Hz, 1H), 6.03 (dd, *J* = 9.4, 4.9 Hz, 1H), 5.29 (t, *J* = 8.3 Hz, 1H), 4.97 (dd, *J* = 27.7, 12.2 Hz, 2H), 4.72 (d, *J* = 8.7 Hz, 1H), 3.76 (s, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 156.1, 137.3, 136.5, 134.4, 133.3, 130.3, 129.1, 128.6, 128.4, 128.2, 128.2, 128.2, 127.9, 127.4, 126.5, 125.5, 66.8, 53.0, 44.9. HRMS (EI) calcd for $C_{24}H_{21}NO_2$ $[M]^+$: 355.1572. Found: 355.1573. The *ee* of **3ga** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; t_{major} = 14.9 min, t_{minor} = 20.4 min.

*(1R,2S)-2-phenyl-1,2-dihydronaphthalen-1-ol (**3ha**):*[22] Colorless oil, 96% yield, 94% *ee*. $[\alpha]_D^{27}$ = -172.9 (c = 9.2×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.19 (m, 8H), 7.15 (d, *J* = 7.2 Hz, 1H), 6.68 (dd, *J* = 9.6, 1.6 Hz, 1H), 6.10 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.89 (s, 1H), 3.87 - 3.77 (m, 1H), 1.57 (s, 1H). The *ee* of **3ha** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{major} = 7.6 min, t_{minor} = 10.6 min .

*(1R,2S)-6,7-dimethyl-2-phenyl-1,2-dihydro-naphthalen-1-ol (**3ia**):*[22] White powder, 95% yield, 94% *ee*. $[\alpha]_D^{27}$ = -126.7 (c = 7.6×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.22 (m, 5H), 7.10 (s, 1H), 6.95 (s, 1H), 6.64 (dd, *J* = 9.6, 1.7 Hz, 1H), 6.04 (dd, *J* = 9.6, 3.7 Hz, 1H), 4.83 (t, *J* = 6.3 Hz, 1H), 3.82 (t, *J* = 5.6 Hz, 1H), 2.25 (d, *J* = 6.2 Hz, 6H), 1.46 (d, *J* = 6.6 Hz, 1H). The *ee* of **3ia** was determined by HPLC analysis using Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm; t_{major} = 7.6 min, t_{minor} = 12.4 min.

*(1R,2S)-5,8-dimethoxy-2-phenyl-1,2-dihydro-naphthalen-1-ol (**3ja**):*[22] Colorless oil, 96% yield, 92% *ee*. $[\alpha]_D^{26}$ = +59.3 (c = 6.8×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.37 (m, 4H), 7.31 (t, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.81 (q, *J* = 9.0 Hz, 2H), 6.14 (d, *J* = 9.8 Hz, 1H), 5.09 (s, 1H), 3.81 (dd, *J* = 11.3, 6.0 Hz, 7H), 1.59 (s, 1H). The *ee* of **3ja** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 250 nm; t_{major} = 13.1 min, t_{minor} = 23.9 min.

*(1R,2S)-6,7-dibromo-2-phenyl-1,2-dihydro-naphthalen-1-ol (**3ka**):*[22] White solid, 96% yield, 98% *ee*. $[\alpha]_D^{27}$ = -181.4 (c = 8.8×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.40 (s, 1H), 7.27 (t, *J* = 9.1 Hz, 3H), 7.21 – 7.10 (m, 2H), 6.59 (d, *J* = 9.6 Hz, 1H), 6.19 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 3.81 (t, *J* = 5.5 Hz, 1H), 1.56 (t, *J* = 8.8 Hz, 1H). The *ee* of **3ka** was determined by HPLC analysis using a Daicel Chiralcel AD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 250 nm; t_{major} = 7.1 min, t_{minor} = 8.9 min.

*(5R,6S)-6-phenyl-5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-ol (**3la**):* Colorless oil, 95% yield, 95% *ee*. $[\alpha]_D^{27}$ = -102.8 (c = 9.2×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.21 (m, 5H), 6.85 (s, 1H), 6.67 (s, 1H), 6.57 (dd, *J* = 9.6, 1.7 Hz, 1H), 6.02 (dd, *J* = 9.6, 3.8 Hz, 1H), 5.93 (s, 2H), 4.78 (t, *J* = 6.4 Hz, 1H), 3.81 (s, 1H), 1.50 (s, 1H). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz): δ 147.3, 147.1, 138.0, 130.4, 129.3, 128.7, 128.0, 127.9, 127.4, 126.9, 108.1, 107.1, 101.1, 71.5, 47.4. HRMS (EI) calcd for $C_{17}H_{14}O_3$ $[M]^+$: 266.0943. Found $[M]^+$: 266.0946. The *ee* of **3la** was determined by HPLC analysis using Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 10.7 min, t_{minor} = 14.6 min.

*(6R,7S)-7-phenyl-2,3,6,7-tetrahydronaphtho[2,3-b][1,4]dioxin-6-ol (**3ma**):* Colorless oil, 95% yield, 95% *ee*. $[\alpha]_D^{27}$ = -119.2 (c = 5.2×10^{-3}, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.21 (m, 5H), 6.86 (s, 1H), 6.69 (s, 1H), 6.57 (dd, *J* = 9.6,

1.7 Hz, 1H), 6.00 (dd, *J* = 9.6, 3.9 Hz, 1H), 4.79 (t, *J* = 6.3 Hz, 1H), 4.23 (s, 4H), 3.80 (t, *J* = 5.6 Hz, 1H), 1.47 (s, 1H). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 143.2, 143.1, 138.2, 129.9, 129.3, 128.7, 128.0, 127.6, 127.4, 126.5, 116.3, 115.4, 71.0, 64.5, 64.4, 47.4. HRMS (EI) calcd for $C_{18}H_{16}O_3$ $[M]^+$: 280.1099. Found $[M]^+$: 280.1123. The *ee* of **3ma** was determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 80/20, 1.0 mL/min, 254 nm; t_{major} = 13.7 min, t_{minor} = 18.4 min.

ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of products, HPLC spectra of products, and X-ray crystallographic data (ORTEP) of **3da**.

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Notes

The authors declare no competing financial interest.

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