JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

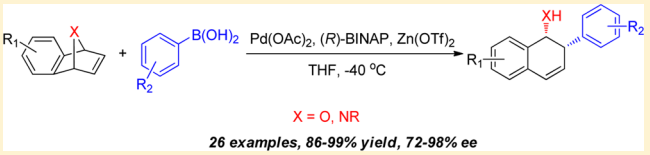
Asymmetric Ring-Opening Reactions of Aza- and Oxa-bicyclic Alkenes with Boronic Acids Using a Palladium/Zinc Co-catalytic System

Wei Zhang,[†] Jingchao Chen,[*,†] Guangzhi Zeng,[†] Fan Yang,[†] Jianbin Xu,[†] Weiqing Sun,[†] Madhuri Vikas Shinde,[†] and Baomin Fan[*,†,‡]

[†]YMU-HKBU Joint Laboratory of Traditional Natural Medicine and [‡]Key Laboratory of Chemistry in Ethnic Medicinal Resources, Yunnan Minzu University, Kunming, Yunnan People's Republic of China

Supporting Information

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



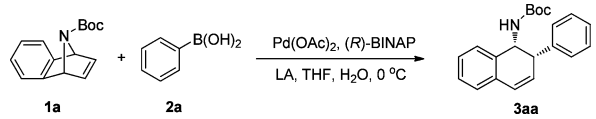
INTRODUCTION

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 reactions (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 long had an interest in this kind of reaction and has studied it with co-catalytic systems comprising chiral transition-metal complexes and Lewis acids as previously employed by pioneers in the field.[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 has attracted our attention as they offered a straightforward method for the preparation of chiral aryltetralins, which are common substructures in bioactive natural products such as chelidonine, corynoline, and wailupemycin D.[15] Although these kind of reactions have been studied with oxabenzonorbornadienes,[3a,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 using a 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

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	NR	
3	$FeCl_2$	48	NR	
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.

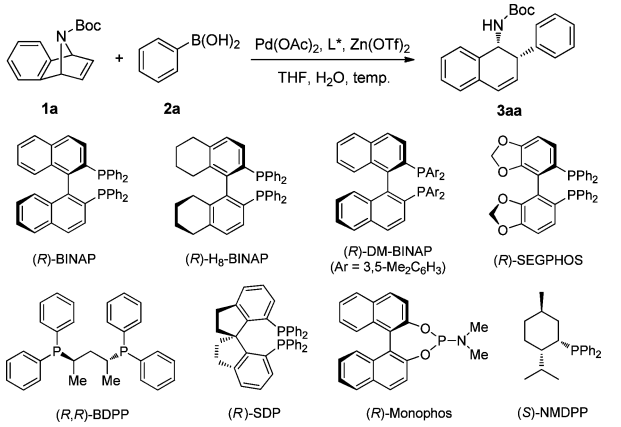
Received: December 21, 2016
Published: January 23, 2017

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647

tested ZnI_2 only gave the desired product **3aa** in trace amounts (Table 1, entry 1), and CuI and $FeCl_2$ also failed to promote the reaction (Table 1, entries 2 and 3). We were delighted to find that when AgOTf was used, **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 and 6). By switching to $Zn(OTf)_2$ and $Fe(OTf)_2$, excellent yields were achieved (Table 1, entries 7 and 8). The next tested Lewis acids such as $Fe(OTf)_3$, $In(OTf)_3$, and $Al(OTf)_3$ were less effective and gave inferior reaction yields (Table 1, entries 9–11). Control experiments further established the requirement of Lewis acids for good enantioselectivity (Table 1, entry 12).

Subsequently, optimization of the reaction conditions for the present reaction was carried out by screening various chiral ligands and reaction temperatures. As the results summarized in Table 2 show, use of BINAP-derived diphosphine ligands such as (*R*)-H_8–BINAP and (*R*)-DM–BINAP gave reduced reaction yields (Table 2, entries 2 and 3), and the evaluation of other bidentate chiral ligands 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 proven 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 proven to be highly active as good reaction results were 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 h (entry 14). The addition of water was proven to be unnecessary because an improved ee was obtained with the reaction yield unchanged from the control experiment. This result can be explained by the undermining of Lewis acid when water was added, thus affecting 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 and 14).

Table 2. Screening of Chiral Ligands and Reaction Temperatures for the ARO Reaction[a]



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

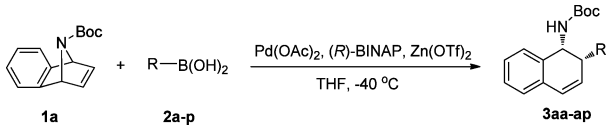
[a]Reaction conditions: The reaction was carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), and 0.1 equiv of $Zn(OTf)_2$ in tetrahydrofuran (2 mL) in the presence of $Pd(OAc)_2$ (5 mol %) and a bidentate ligand (6 mol %) or monodentate ligand (12 mol %) under Ar for the time indicated. [b]Determined 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.

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 halogen groups were unreacted (Table 3, entries 2–4). The electron-withdrawing group substituted phenylboronic acids were also suitable nucleophiles in the present transformation (Table 3, entries 5–8). However, due to steric effects, meta- and ortho-substituted phenylboronic acids exhibited lower reactivities and enantioselectivities toward this asymmetric ring-opening reaction (Table 3, entries 9 and 10). The electron-rich phenylboronic acid **2k** was participated in the reaction, albeit with relatively moderate results (Table 3, entry 11). 2-Naphthylboronic acid was found to be 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-opening products with excellent results (Table 3, entries 13 and 14). However, the present reaction was not suitable for the alkyl and vinyl boronoic acid pinacol esters (Table 3, entries 15 and 16). To illustrate the advantage of the present conditions to the reported method,[15a] the reactions of **2c** and **2m** were also tested by using [Pd $(MeCN)_2Cl_2$], (*S*)-tol-binap, and Cs_2CO_3 in methanol at ambient temperature (Table 3, entries 3 and 13). The results indicated the present conditions showed superior efficiency in terms of the reaction yields and enantioselectivities.

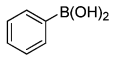
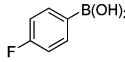
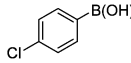
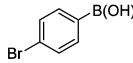
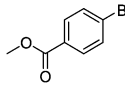
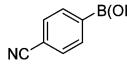
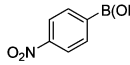
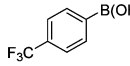
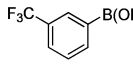
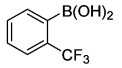
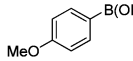
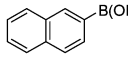
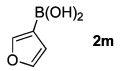
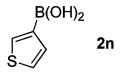
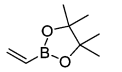
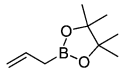
Next, the scope of the reaction was surveyed by a range of bicyclic alkenes, including azabenzonorbornadienes and oxabenzonorbornadienes. As indicated by the experimental results summarized in Table 4, except for dimethoxy-substituted azabenzonorbornadiene (Table 4, entry 3), which gave a decreased yield due to the generation of 2,3-dimethoxy-6-phenylnaphthalene as a side product, all of the azabenzonorbornadienes performed well and gave the corresponding products generally in good results (Table 4, entries 2–6). 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 results superior to those using the literature conditions[15a] (Table 4, entries 2 and 6). To our delight, oxabenzonorbornadienes were also viable substrates to

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641–2647

Table 3. Scope of the Phenylboronic Acids[a]

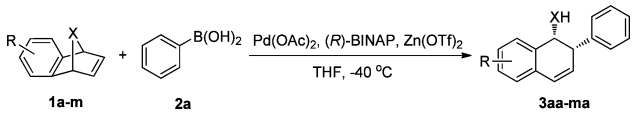


1a 2a-p 3aa-ap

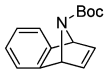
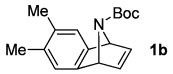
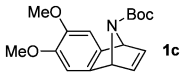
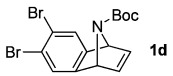
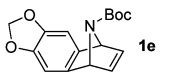
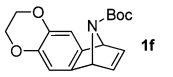
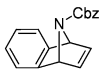
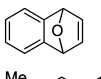
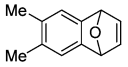
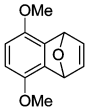
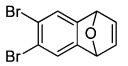
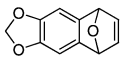
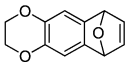
Entry	Boronic acid 2a-p	Time [h]	Yield [%]	ee [%][b]
1	 2a	19	95	94
2[c,d]	 2b	26	97	90
3	 2c	24	90(73)[f]	94(71)[f]
4	 2d	72	99	91
5	 2e	30	98	90
6	 2f	19	97	93
7	 2g	41	99	95
8	 2h	17	98	95
9[c,d]	 2i	70	93	86
10[c,d]	 2j	65	96	72
11[e]	 2k	36	86	90
12[c,d]	 2l	72	93	82
13[c]	 2m	60	91(80)[f]	99(78)[f]
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 parentheses were obtained by using the literature conditions (ref 15a).

Table 4. Scope of the Bicyclic Alkenes[a]



1a-m 2a 3aa-ma

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 parentheses were obtained by using the literature conditions (ref 15a).

give excellent results (Table 4, entries 8−13). Thus, this synthetic protocol was highly effective for both aza- and oxabicyclic alkenes.

Finally, the absolute configurations of the ring-opening products of azabenzonorbornadienes (**3aa**−**an** and **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 the data reported in the literature.[19]

On the basis of our experience of the asymmetric ring-opening reactions[11c,12b] and literature regarding palladium-catalyzed reaction of arylboronic acids,[20] a plausible mechanism for this ring-opening reaction is outlined by the reaction of **1a** and **2a** (Figure 2). The catalytic cycle would be initiated 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 generate intermediate **C**. Then the following *β*-elimination of nitrogen opens the pyrrolidine ring and yields

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647

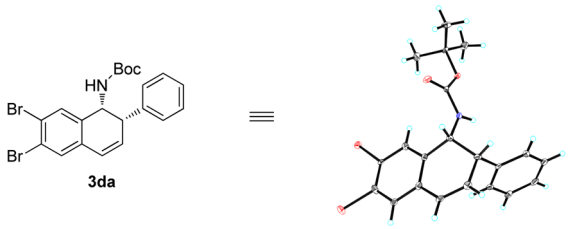


Figure 1. X-ray structure of **3da**.

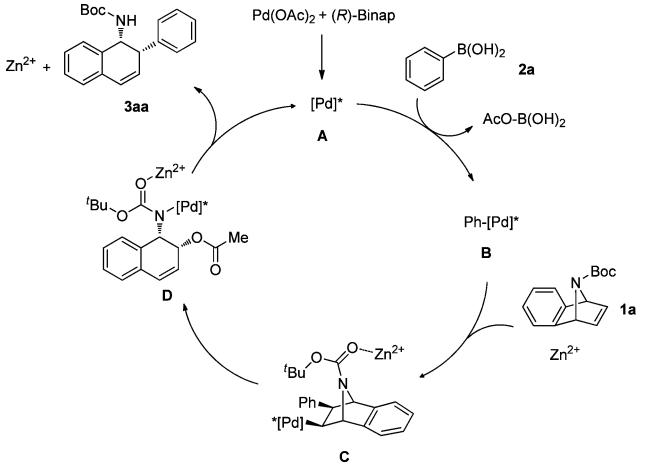


Figure 2. Proposed mechansim for the asymmetric ring-opening reaction.

the ring-opened species **D**. Finally, the ring-opening product **3aa** was 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 alkenes **1a−l** were prepared according to the literature procedures.[21]

General Methods. The reactions and manipulations were performed under an atmosphere of argon using standard Schlenk techniques and a 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 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 are 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 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 of THF were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, $Zn(OTf)_2$ (7.3 mg, 0.02 mmol) was added, the solution was stirred for an additional 10 min, a solution of bicyclic alkene **1a−m** (48.6 mg, 0.2 mmol) in THF (0.7 mL) was added, and the resulting mixture was stirred for an 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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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 a Daicel Chiralcel AS-H column (25 cm × 0.46 cm i.d.), 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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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 a Daicel Chiralcel OD-H column

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647

(25 cm × 0.46 cm i.d.), 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); $^{13}C\{^1H\}$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 i.d.), 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); $^{13}C\{^1H\}$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 i.d.), 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); $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz) 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 i.d.), 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); $^{13}C\{^1H\}$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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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); $^{13}C\{^1H\}$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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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); $^{13}C\{^1H\}$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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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); $^{13}C\{^1H\}$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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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-dihydronaphthalen-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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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-(thiophene-3-yl)-1,2-dihydronaphthalen-1-yl)carbamate (**3an**):*[17] colorless 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 i.d.), 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**):* colorless 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). $^{13}C\{^1H\}$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 i.d.), 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). $^{13}C\{^1H\}$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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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),

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647

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 i.d.), 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 i.d.), 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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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-tetrahydronaphtho[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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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 i.d.), 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 a Daicel Chiralcel AD-H column (25 cm × 0.46 cm i.d.), 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-dihydronaphthalen-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 a Daicel Chiralcel AD-H column (25 cm × 0.46 cm i.d.), 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-dihydronaphthalen-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 i.d.), 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-dihydronaphthalen-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 i.d.), 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 a Daicel Chiralcel OD-H column (25 cm × 0.46 cm i.d.), 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{^{1}H}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 i.d.), 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b03038.

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

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: chenjingchao84@163.com.
*E-mail: adams.bmf@hotmail.com.

ORCID

Baomin Fan: 0000-0003-1789-3741

Notes

The authors declare no competing financial interest.

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647

■ ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (21572198, 21362043, 21302162), the Department of Education of Yunnan Province (ZD2015012), and the Key Laboratory of Chemistry in Ethnic Medicinal Resources, Yunnan Minzu University (MZY1506) for financial support.

■ REFERENCES

(1) For reviews, see: (a) Lautens, M.; Fagnou, K.; Hiebert, S. *Acc. Chem. Res.* **2003**, *36*, 48−58. (b) Rayabarapu, D. K.; Cheng, C.-H. *Acc. Chem. Res.* **2007**, *40*, 971−983.

(2) (a) Petitto, V.; Serafini, M.; Gallo, F. R.; Multari, G.; Nicoletti, M. *Nat. Prod. Res.* **2010**, *24*, 1033−1035. (b) Ndi, C. P.; Semple, S. J.; Griesser, H. J.; Pyke, S. M.; Barton, M. D. *J. Nat. Prod.* **2007**, *70*, 1439−1443. (c) Perrone, R.; Berardi, F.; Colabufo, N. A.; Leopoldo, M.; Tortorella, V.; Fiorentini, F.; Olgiati, V.; Ghiglieri, A.; Govoni, S. *J. Med. Chem.* **1995**, *38*, 942−949.

(3) (a) Lautens, M.; Dockendorff, C.; Fagnou, K.; Malicki, A. *Org. Lett.* **2002**, *4*, 1311−1314. (b) Lautens, M.; Fagnou, K.; Rovis, T. *J. Am. Chem. Soc.* **2000**, *122*, 5650−5651. (c) Lautens, M.; Fagnou, K.; Yang, D.-Q. *J. Am. Chem. Soc.* **2003**, *125*, 14884−14892.

(4) (a) Long, Y.-H.; Yang, D.-Q.; Zhang, Z.-M.; Wu, Y.-J.; Zeng, H.-P.; Chen, Y. *J. Org. Chem.* **2010**, *75*, 7291−7299. (b) Luo, R.-S.; Liao, J.-H.; Xie, L.; Tang, W.-J.; Chan, A. S. C. *Chem. Commun.* **2013**, *49*, 9959−9961. (c) Cheng, H.-C.; Yang, D.-Q. *J. Org. Chem.* **2012**, *77*, 9756−9765.

(5) Feng, C.-C.; Nandi, M.; Sambaiah, T.; Cheng, C.-H. *J. Org. Chem.* **1999**, *64*, 3538−3543.

(6) (a) Chen, C.-L.; Martin, S. F. *J. Org. Chem.* **2006**, *71*, 4810−4817. (b) Duan, J.-P.; Cheng, C.-H. *Tetrahedron Lett.* **1993**, *34*, 4019−4022. (c) Yamamoto, T.; Akai, Y.; Suginome, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 12785−12788; *Angew. Chem.* **2014**, *126*, 12999−13002.

(7) (a) Arrayás, R. G.; Cabrera, S.; Carretero, J. C. *Org. Lett.* **2005**, *7*, 219−221. (b) Gómez Arrayás, R.; Cabrera, S.; Carretero, J. C. *Synthesis* **2006**, *7*, 1205−1219. (c) Millet, R.; Bernardez, T.; Palais, L.; Alexakis, A. *Tetrahedron Lett.* **2009**, *50*, 3474−3477.

(8) Jack, K.; Fatila, E.; Hillis, C.; Tam, W. *Synth. Commun.* **2013**, *43*, 1181−1187.

(9) (a) Lautens, M.; Hiebert, S.; Renaud, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 6834−6839. (b) Bertozzi, F.; Pineschi, M.; Macchia, F.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L. *Org. Lett.* **2002**, *4*, 2703−2705.

(10) (a) Fan, B.-M.; Xu, J.-B.; Yang, Q.-J.; Li, S.-F.; Chen, H.-L.; Liu, S.-S.; Yu, L.; Zhou, Y.-Y.; Wang, L. *Org. Lett.* **2013**, *15*, 5956−5959. (b) Liu, S.-S.; Li, S.-F.; Chen, H.-L.; Yang, Q.-J.; Xu, J.-B.; Zhou, Y.-Y.; Yuan, M.-L.; Zeng, W.-M.; Fan, B.-M. *Adv. Synth. Catal.* **2014**, *356*, 2960−2964. (c) Chen, J.-C.; Liu, S.-S.; Zhou, Y.-Y.; Li, S.-F.; Lin, C.-Y.; Bian, Z.-X.; Fan, B.-M. *Organometallics* **2015**, *34*, 4318−4322.

(11) (a) Yu, L.; Zhou, Y.-Y.; Xu, X.; Li, S.-F.; Xu, J.-B.; Fan, B.-M.; Lin, C.-Y.; Bian, Z.-X. A. S. C.; Chan. *Tetrahedron Lett.* **2014**, *55*, 6315−6318. (b) Lu, Z.-W.; Wang, J.; Han, B.-Q.; Li, S.-F.; Zhou, Y.-Y.; Fan, B.-M. *Adv. Synth. Catal.* **2015**, *357*, 3121−3125. (c) Xu, X.; Chen, J.-C.; He, Z.-X.; Zhou, Y.-Y.; Fan, B.-M. *Org. Biomol. Chem.* **2016**, *14*, 2480−2486.

(12) (a) Li, S.-F.; Chen, H.-L.; Yang, Q.-J.; Yu, L.; Fan, C.-L.; Zhou, Y.-Y.; Wang, J.; Fan, B.-M. *Asian J. Org. Chem.* **2013**, *2*, 494−497. (b) Li, S.-F.; Xu, J.-B.; Fan, B.-M.; Lu, Z.-W.; Zeng, C.-Y.; Bian, Z.-X.; Zhou, Y.-Y.; Wang, J. *Chem. - Eur. J.* **2015**, *21*, 9003−9007.

(13) Yang, F.; Chen, J.-C.; Xu, J.-B.; Ma, F.-J.; Zhou, Y.-Y.; Shinde, M. V.; Fan, B.-M. *Org. Lett.* **2016**, *18*, 4832−4835.

(14) Zhou, Y.-Y.; Gu, C.-P.; Chen, J.-C.; Zhu, M.-N.; Yang, F.; Xu, J.-B.; Fan, B.-M. *Adv. Synth. Catal.* **2016**, *358*, 3167−3172.

(15) Selected examples of chiral aryltetralin containing natural products: (a) Fleming, M. J.; McManus, H. A.; Rudolph, A.; Chan, W. H.; Ruiz, J.; Dockendorff, C.; Lautens, M. *Chem. - Eur. J.* **2008**, *14*, 2112−2124. (b) Ito, M.; Konno, F.; Kumamoto, T.; Suzuki, N.; Kawahata, M.; Yamaguchi, K.; Ishikawa, T. *Tetrahedron* **2011**, *67*, 8041−8049. (c) Piel, J.; Hoang, K.; Moore, B. S. *J. Am. Chem. Soc.* **2000**, *122*, 5415−5416.

(16) (a) Zeng, Z.-Y.; Yang, D.-Q.; Long, Y.-H.; Pan, X.-J.; Huang, G.-B.; Zuo, X.-J.; Zhou, W. *J. Org. Chem.* **2014**, *79*, 5249−5257. (b) Murakami, M.; Igawa, H. *Chem. Commun.* **2002**, 390−391.

(17) Lautens, M.; Dockendorff, C. *Org. Lett.* **2003**, *5*, 3695−3698.

(18) X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk/) under accession code CCDC 1517119.

(19) Pan, X.-J.; Huang, G.-B.; Long, Y.-H.; Zuo, X.-J.; Xu, X.; Gu, F.-L.; Yang, D.-Q. *J. Org. Chem.* **2014**, *79*, 187−196.

(20) (a) Lu, X.-Y.; Lin, S.-H. *J. Org. Chem.* **2005**, *70*, 9651−9653. (b) Mauleón, P.; Alonso, I.; Rivero, M. R.; Carretero, J. C. *J. Org. Chem.* **2007**, *72*, 9924−9935. (c) Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 17276−17277.

(21) (a) Ohwada, T.; Miura, M.; Tanaka, H.; Sakamoto, S.; Yamaguchi, K.; Ikeda, H.; Inagaki, S. *J. Am. Chem. Soc.* **2001**, *123*, 10164−10172. (b) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 2625−2629. (c) Lautens, M.; Fagnou, K.; Zunic, V. *Org. Lett.* **2002**, *4*, 3465−3468.

(22) Zhang, T.-K.; Mo, D.-L.; Dai, L.-X.; Hou, X.-L. *Org. Lett.* **2008**, *10*, 3689−3692.

DOI: 10.1021/acs.joc.6b03038
J. Org. Chem. 2017, 82, 2641−2647