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Article

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Cu-Catalyzed Asymmetric Hydroboration of Naphthylallylic Compounds for Enantioselective Synthesis of Chiral Boronates

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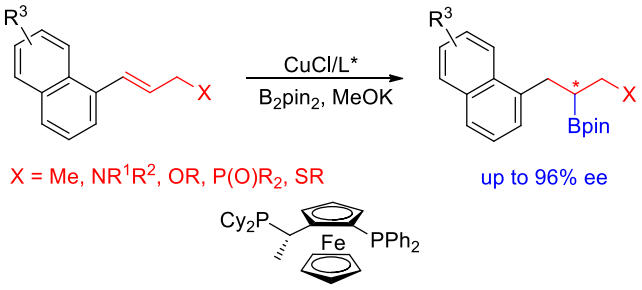


ABSTRACT: A Cu-catalyzed regio- and enantioselective hydroboration of various naphthylallylic compounds affording chiral boronates with high yields and excellent enantioselectivities (up to 96% ee) was presented. The utility of the boronated products is further illustrated by other stereospecific C-B bond transformations to produce amino alcohols and other useful compounds.

INTRODUCTION

Chiral organoboronates play an important role in synthetic chemistry, material science, chemical biology, and are key intermediates in the synthesis of many pharmaceuticals or agrochemicals.[1] Therefore, the synthesis of chiral organoboron compounds has attracted great interest from chemists. Metal-catalyzed enantioselective construction of C−B bond has received

much attention as the resulting boronated products are versatile intermediates, which can be easily transformed into C-O, C-N, C-C, and C-halogen bonds.[2] Over the past few decades, there are many metal precursors employed in asymmetric hydroboration, such as Rh,[3] Ir,[4] Pd,[5] Co [6] and Cu.[7] Amongst the reported methods, copper-catalyzed hydroboration has received considerable attention due to the commercial availability, low cost and stability of copper metal. Yun and co-workers reported copper-catalyzed asymmetric hydroboration of styrenes, borylalkenes and bicyclic alkenes with high enantioselectivities using diphosphine ligands, Tangphos, DTBM-Segphos, and Taniaphos, respectively.[8] Hoveyda group developed highly enantioselective hydroboration of 1, 2-disubstituted and 1, 1-disubstituted aryl alkenes catalyzed by Cu-based bidentate *N*-heterocyclic carbene complexes.[9] Hartwig group successfully applied aliphatic internal alkenes to the copper catalyzed asymmetric hydroboration achieving high regio- and enantioselectivities.[10] Besides, Ito, Lin and Tortosa groups independently developed the methods to stereoselective synthesis of cycloalkanes via Cu-catalyzed asymmetric hydroboration. It was demonstrated that the copper catalyzed asymmetric hydroboration of cycloalkenes,[11] allylic carbonates [12] and phosphates,[13] and homoallylic sulfonates [14] was an efficient approach for synthesis of chiral cycloalkanes. Various α, β-unsaturated compounds including α, β-unsaturated carbonyl compounds,[7a, 7g, 15] α, β-unsaturated nitriles,[7a, 15b] phosphonates [7a, 16] and sulfones,[17] and other α, β unsaturated functional compounds,[8b, 18] were also explored in the copper-catalyzed asymmetric hydroboration by many research groups achieving high yields and enantioselectivities. To the hydroboration of *N*-hetero cyclic substrates, Ito and co-workers made important contribution and reported Cu-catalyzed asymmetric hydroboration of indoles,[19] 1,2-dihydropyridines [20] and 1,2-dihydroquinolines [21] with excellent enantioselectivities. Recently

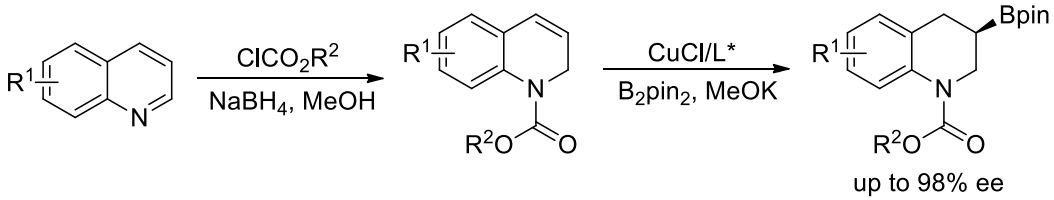
we reported Cu-catalyzed enantioselective hydroboration of *N*-CO_2R-protected 1,2-dihydroquinolines achieving high yields and excellent enantioselectivities.[22] It was also found that Cu-catalyzed asymmetric hydroboration could be successfully applied to the kinetic resolution of racemic *N*-CO_2R-2-substituted 1,2-dihydroquinolines with excellent resolution efficiency under mild conditions (Scheme 1 a-b). [23]

Despite these great progresses, there were few reports on the asymmetric hydroboration of allylic substrates.[12] Naphthylallylic carbamates remain unexplored as the substrates in asymmetric hydroboration so far. Promoted by the great utility of chiral amino organoboron compounds which can be readily converted to the corresponding enantio-rich amino alcohols and other useful molecules, we devote our efforts on the asymmetric hydroboration of the naphthylallylic derivatives including naphthylallylic carbamates as a part of our continuous work. We herein present an efficient approach to the synthesis of chiral noncyclic heteroatom organoboronates via Cu-catalyzed enantioselective hydroboration of naphthylallylic derivatives, which provides chiral organoboronates bearing heteroatom with high regio- and enantioselectivities of up to 96% ee (Scheme 1).

Scheme 1. Cu-catalyzed asymmetric hydroboration of 1,2-dihydroquinolines and naphthylallylic derivatives.

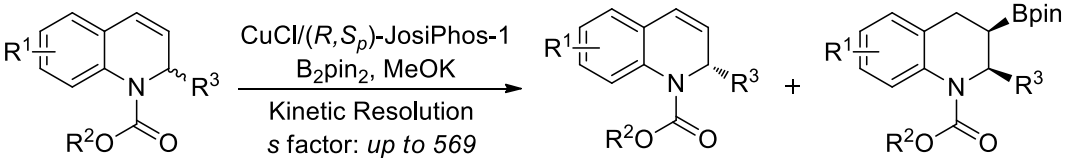
Our previous work:

(a) Cu-catalyzed regio- and enantioselective hydroboration of 1,2-dihydroquinolines



up to 98% ee

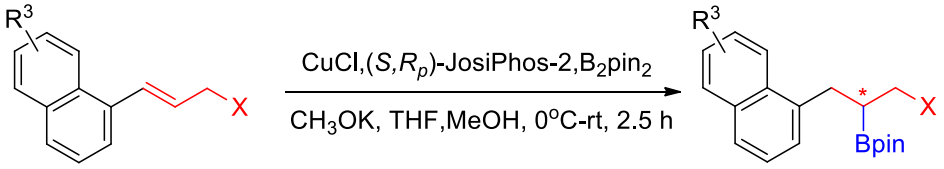
(b) Kinetic resolution of 2-substituted 1,2-dihydroquinolines via asymmetric Cu-catalyzed borylation reaction



rac 98 - 99.9% ee up to 99% ee

this work:

Cu-catalyzed regio- and enantioselective hydroboration of naphthylallylic derivatives



X = Me, NR^1R^2, OR, $P(O)R_2$, SR up to 96% ee

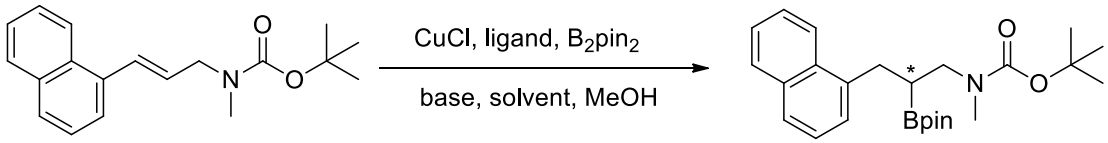
RESULTS AND DISCUSSION

Inspired by our previous work, we prepared (*E*)-*tert*-butyl methyl-(3-(naphthalen-1-yl)-allyl)-carbamate **1a** as the model substrate to optimize the hydroboration conditions. Initially, the reaction was conducted in the presence of CuCl (5 mol%), (R,S_p)-JosiPhos-1 (**L1**) (5 mol%), MeOK (20%) at 0 °C in THF (1.5 mL) and MeOH (2.0 equiv). Although the desired product **2a** was obtained in moderate yield, an excellent enantioselectivity (98% ee) was achieved (Table 1, entry 1). It was found that this transformation could be catalyzed by copper (II) precursors such as $Cu(OAc)_2$ with similar enantioselectivity albeit the lower yield observed (entry 2). The effect of bases on the reaction was then evaluated. When KO^{t}Bu was used

as the base, the hydroboration product could be provided with excellent enantioselectivity (98% ee), but a lower yield was obtained (entry 3). LiO^{t}Bu made the reaction ineffective and no product was observed (entry 4). Encouraged by the excellent enantioselectivity achieved by (*R,S*$_p$)-JosiPhos-1, some other JosiPhos derivatives were further screened in order to get satisfactory yield. To our delight, in a shorter reaction time (*S,R*$_p$)-JosiPhos-2 (**L2**) could make the substrate consume completely giving the hydroboration product **2a** in much better yield (84%) albeit a slightly decrease in enantioselectivity, 93% ee (entry 5). However, (*R*,*S*$_p$)-JosiPhos-3 (**L3**) and (*R*,*S*$_p$)-JosiPhos-4 (**L4**) gave lower or extremely poor results (entries 6 and 7). Besides, several commercial available chiral bisphosphine ligands (**L5** – **L9)** were also evaluated in the hydroboration. It was found that moderate enantioselectivity and yield (53% ee and 48% yield, respectively) were afforded by (*R,R*)-QuinoxP* (**L5**) (entry 8), which exhibited high enantioselectivity and activity in the asymmetric hydroboration of heterocyclic substrates. The ligand (*R*)-DM-Segphos (**L6**), which was widely used and exhibited excellent performance in the hydroboration of various noncyclic alkenes, only provided significantly decreased enantioselectivity and yield (entry 9). Likewise, similar results were obtained when electron-rich (*S,R*)-DuanPhos **(L7)**, (*R,R*)-Me-DuPhos (**L8)** or (*S,S*)-f-spiroPhos (**L9)** were used in the reaction (entry 10-12). The chiral monodentate ligand (*R*)-Monophos **(L10)** was also tested in this reaction, but no product was obtained (entry 13). Despite the relatively lower yield, the highest enantioselectivity achieved by (*R,S*$_p$)-JosiPhos-1 (**L1**) promoted us to improve the yield by further optimization of the reaction time, temperature and solvent effect. However, it was revealed that prolonging the reaction time or adjusting the temperature had no positive influence on the yield. For example, even if the reaction proceeded for 15 hours, the yield still maintained as low as 58%

(entry 14). Increasing the reaction temperature to 40 °C resulted lower yield and enantioselectivity (entry 15). A variety of solvents including CH_2Cl_2, toluene, 1,4-dioxane, and 1,2-dimethoxyethane (DME) were attempted using (R,S_p)-JosiPhos-1 **(L1)** as the ligand. In CH_2Cl_2 or 1,4-dioxane there was almost no product observed (entries 16 and 17). Although the same excellent enantioselectivity could be obtained in toluene or DME, the yields were not satisfactory (entries 18 and 19). Overall considering both yield and enantioselectivity, we consequently chose CuCl/(S,R_p)-JosiPhos-2 **(L2)** (5 mol%) as the catalyst and MeOK as the base in THF for the highest yield and relatively better enantioselectivity.

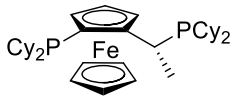
Table 1. Reaction optimization.[a]



1a **2a**

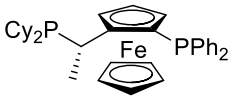
entry	ligand	solvent	base	yield (%)	ee (%)[b]
1	**L1**	THF	CH_3OK	58	98
2[c]	**L1**	THF	CH_3OK	30	94
3	**L1**	THF	KO^tBu	44	98
4	**L1**	THF	LiO^tBu	trace	ND
5[d]	**L2**	THF	CH_3OK	84	93
6	**L3**	THF	CH_3OK	trace	ND
7	**L4**	THF	CH_3OK	21	77
8	**L5**	THF	CH_3OK	53	48
9	**L6**	THF	CH_3OK	32	27

10	**L7**	THF	CH_3OK	67	57
11	**L8**	THF	CH_3OK	82	44
12	**L9**	THF	CH_3OK	11	60
13	**L10**	THF	CH_3OK	trace	ND
14[e]	**L1**	THF	CH_3OK	58	97
15[f]	**L1**	THF	CH_3OK	24	85
16	**L1**	DCM	CH_3OK	trace	ND
17	**L1**	1,4-dioxane	CH_3OK	trace	ND
18	**L1**	toluene	CH_3OK	28	98
19	**L1**	DME	CH_3OK	63	98



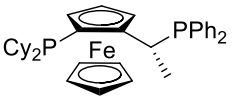
(*R*,S_p)-JosiPhos-1

L1



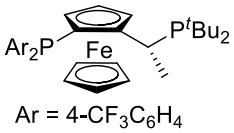
(*S*,R_p)-JosiPhos-2

L2



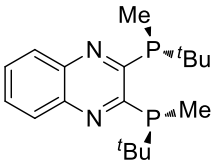
(*R*,S_p)-JosiPhos-3

L3



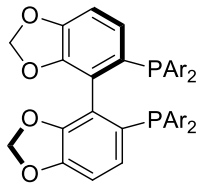
(*R*,S_p)-JosiPhos-4

L4



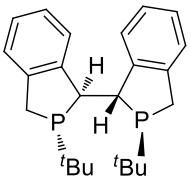
(*R*,*R*)-QuinoxP*

L5



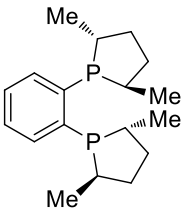
(*R*)-DM-Segphos

L6



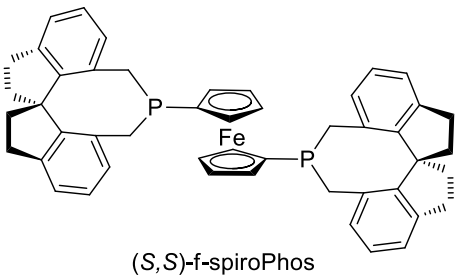
(*S*,*R*)-DuanPhos

L7



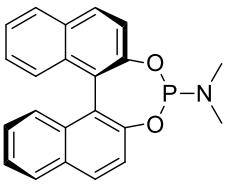
(*R*,*R*)-Me-DuPhos

L8



(*S*,*S*)-f-spiroPhos

L9



(*R*)-Monophos

L10

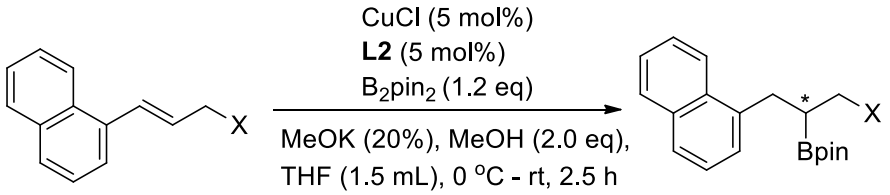
[a] Reaction conditions: CuCl (0.025 mmol), ligand (0.025 mmol), **1a** (0.5 mmol), B_2pin_2 (0.6 mmol), MeOK (0.1 mmol), solvent (1.5 mL), MeOH (1.0 mmol), 0 °C – rt, 5 h. [b] Determined by chiral HPLC analysis. [c] $Cu(OAc)_2$

was used in this reaction. [d] The reaction with a reaction time of 2.5 h. [e] The reaction with a reaction time of 15 h. [f] The reaction was carried out at 40 °C.

With the optimal reaction condition in hand, we then prepared a series of naphthylallylic compounds and applied them to the hydroboration for the investigation of the substrate scope (Scheme 2). At the first, a variety of (*E*)-*tert*-butyl alkyl-(3-(naphthalen-1-yl)-allyl)-carbamates were evaluated in the hydroboration under the optimal condition. This copper catalyst system showed good activity and high enantioselectivity for substrates **1b** – **1d** furnishing boronates **2b** – **2d** in both good yields (76 – 82%) and excellent enantioselectivitives (93 – 94% ee). Changing the alkyl substituent from methyl group to ethyl, propyl, butyl or benzyl on the nitrogen of *N*-Boc substrates had no apparent effect on the enantioselectivities, whereas the yields decreased gradually from 84% to 67%, which was possibly attributed to the bulkier and bulkier steric hindrance of the alkyl substituents. It was notable that the substrate **1f** bearing one more allylic group could also provide the desired product **2f** with high enantioselectivity as well as regioselectivity. However, the dual-Boc-protected substrate **1g** resulted in dramatically decrease in the enantioselectivity and yield. The huge steric hindrance perhaps prevented the efficient coordination of the catalyst to substrate. The substrate **1i** bearing a smaller ethoxycarbonyl group achieved both higher yield and enantioselectivity, 90% and 94% ee, respectively. Additionally, 2-naphtyl substrates **1h**, **1j**, **1k** and **1l** could be hydroborated providing the desired products **2h**, **2j**, **2k** and **2l** with good enantioselectivities from 88 – 90% ee. Remarkably, the NH substrate **1m** without alkyl substituent on the nitrogen could still achieve the comparable yield and enantioselectivity. However, the bis-benzyl substituted **1r** and the *Z*-isomer **1s** only exhibited extremely poor reactivity. It was worth noting that other types of naphthylallylic substrates such as

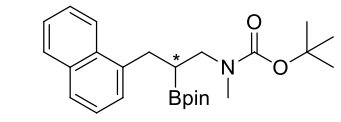
(*E*)-diethyl (3-(naphthalen-1-yl)-allyl)-phosphonate **1n**, (*E*)-3-(naphthalen-1-yl)-allyl acetate **1o**, and (*E*)-(3-(naphthalen-1-yl)-allyl)-(p-tolyl)-sulfane **1p** were suitable for this hydroboration giving the corresponding borylation products **2n** and **2p** with excellent enantioselectivities, 92 – 94% ee. Especially, the substrate **1o** provided the highest enantioselectivity of 96% ee and good yield, 82%. Even if the substrate (*E*)-1-(but-1-en-1-yl)-naphthalene **1q** without any heteroatom could also be hydroborated to produce the **2q** with similar enantioselectivity (92% ee) and yield (72%). The absolute configuration of product **2f** was determined and assigned to be (*S*) configuration by X-ray crystallographic analysis of the corresponding single-crystal structure (See Figure S1 in Supporting Information). Finally, the hydroboration of substrate **1a** was carried out on a gram scale (1.0 g) and the desired product **2a** was obtained with maintained high conversion and enantioselectivity.

Scheme 2. Substrate Scope. [a, b]

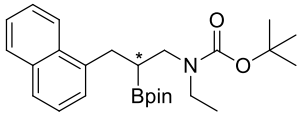


X = Me, NR^1R^2, OR, $P(O)R_2$, SR

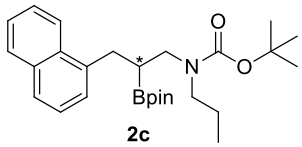
1 **2**



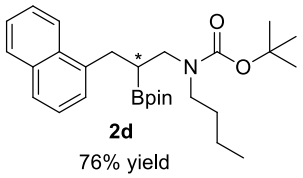
2a
84% yield
93% ee



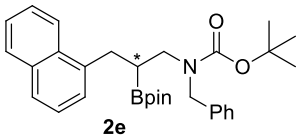
2b
82% yield
93% ee



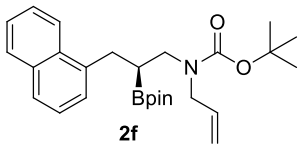
2c
79% yield
94% ee



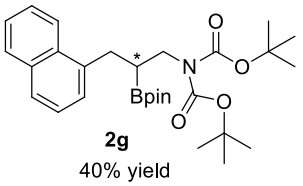
2d
76% yield
93% ee



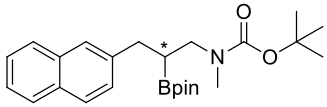
2e
67% yield
90% ee



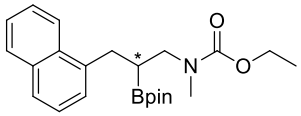
2f
67% yield
90% ee



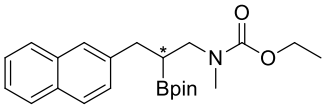
2g
40% yield
58% ee



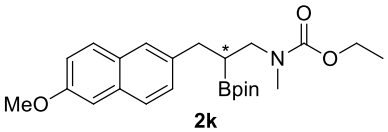
2h
56% yield
88% ee



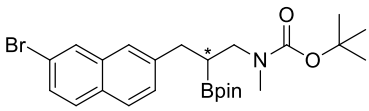
2i
90% yield
94% ee



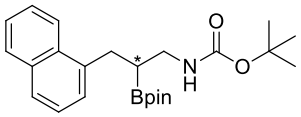
2j
58% yield
90% ee



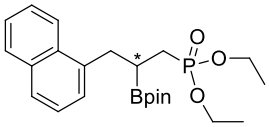
2k
42% yield
90% ee



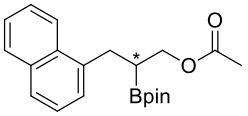
2l
88% yield
90% ee



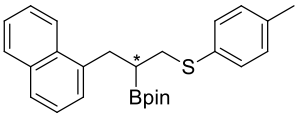
2m
70% yield
92% ee



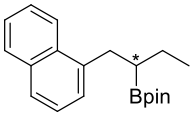
2n
45% yield
94% ee



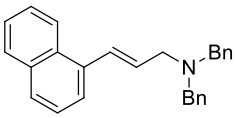
2o [c]
82% yield
96% ee



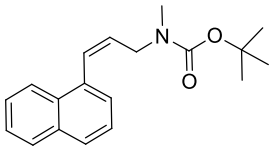
2p
78% yield
92% ee



2q
72% yield
92% ee



1r
n.r



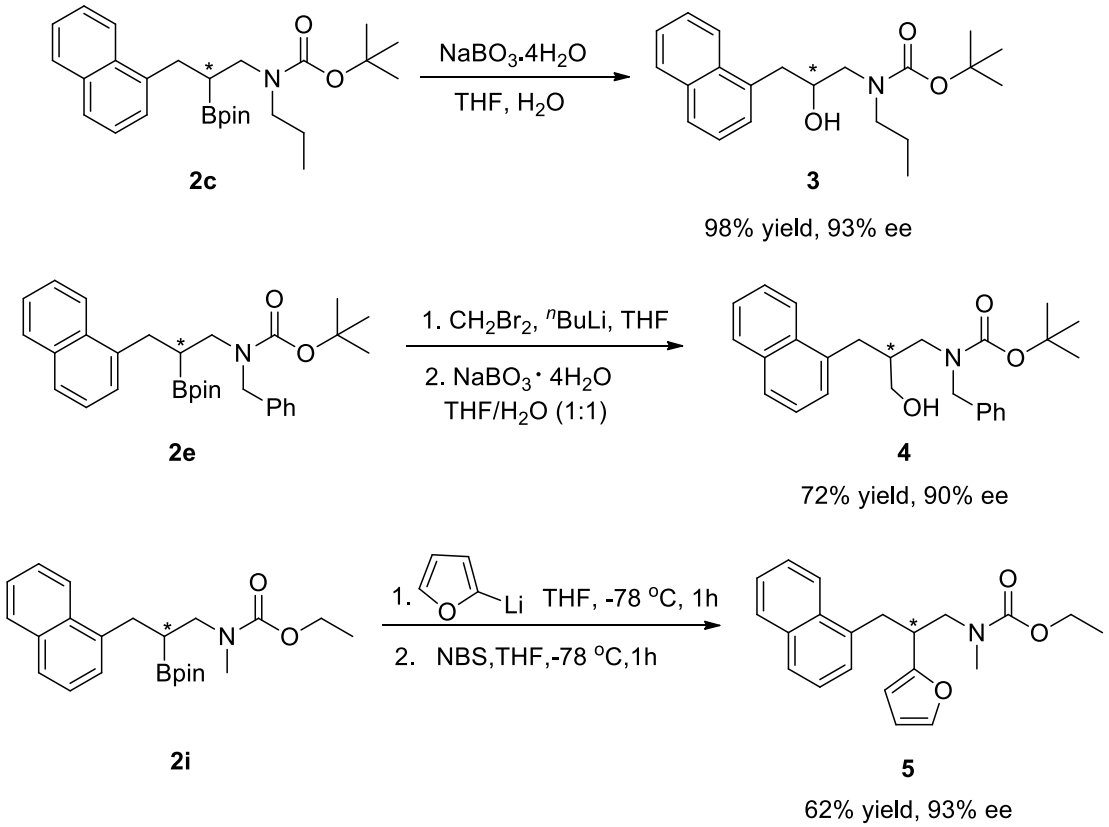
1s
n.r

[a] Unless otherwise mentioned, all reactions were carried out with CuCl (0.025 mmol), (R,S_p)-JosiPhos-2 **(L2)** (0.025 mmol), **1** (0.5 mmol), B_2pin_2 (0.6 mmol), MeOK (0.1 mmol), THF (1.5 mL), MeOH (1.0 mmol), 0 °C – rt, 2.5 h. [b] Enantiomeric excess values were determined by chiral HPLC or SFC analysis. [c] (R,S_p)-JosiPhos-1 **(L1)** was used.

Chiral organoboronates are versatile synthetic intermediates that can be readily converted to

numerous other useful derivatives (Scheme 3).[1a-b] Recently, the synthesis of chiral amino alcohols has always attracted more and more attention from chemists because of their wide application as key intermediates in chiral synthesis and biopharmaceuticals. The product **2c** could be transformed into the chiral β-amino alcohol **3** by oxidation with $NaBO_3$ in high yield with maintained enantioselectivity.[19] The product **2e** could also be successfully converted to the chiral γ-amino alcohol **4** by homologation reaction without any loss of enantioselectivity.[24] Chiral organoboronates as significant coupling reagents played an important role in the construction of C-C bond. The compound **5** could be prepared from the product **2i** obtained by this strategy with high enantioselectivity.[25]

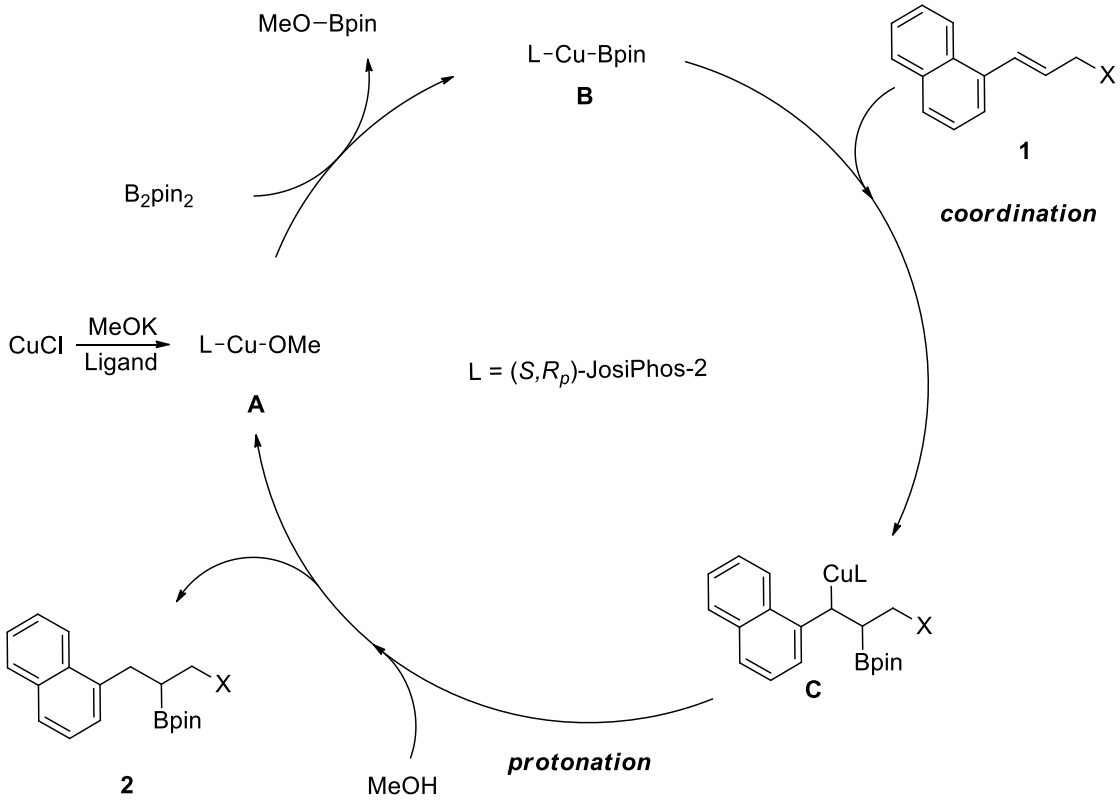
Scheme 3. Representative transformations of products 2.



On the basis of previous reports,[7] a possible catalytic cycle for the hydroboration was proposed as shown in Scheme 4. A diphosphine ligated Cu-OMe complex **A** was initially formed in the

presence of CuCl, the ligand and MeOK, followed by the generation of borylcopper species **B** with B_2pin_2. Subsequently, the coordination and addition of the species **B** to substrate **1** gave the intermediate **C**. The resulting organocopper species reacted with MeOH to yield the protonated product **2** and regenerate the copper methoxide **A**.

Scheme 4. A proposed catalytic cycle for the hydroboration.



CONCLUSIONS

In conclusion, a Cu-catalyzed regio- and enantioselective hydroboration of naphthylallylic carbamates has been first realized affording various chiral amino organoboron compounds with good yields and high enantioselectivities of up to 94% ee. Moreover, other naphthylallylic substrates including naphthylallylic phosphonates, acetates and sulfanes were also suitable for this strategy affording the corresponding products in comparably yields and excellent

enantioselectivities (up to 96% ee).

EXPERIMENTAL SECTION

General Information: All the air or moisture sensitive reactions and manipulations were performed by using standard Schlenk techniques and in a nitrogen-filled glovebox. DME, THF and toluene were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Anhydrous MeOH was distilled from magnesium. ^{1}H NMR and ^{13}C NMR (proton-decoupled) spectra were recorded on (400 MHz) spectrometers or (600 MHz) spectrometers ($CDC1_3$ as the solvent used for the NMR analysis, with TMS as the internal standard. Chemical shifts were reported upfield to TMS (0.00 ppm) for ^{1}H NMR. Data is represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, dd = double of doublets, t = triplet, q = quartet, m = multiplet) and coupling constants (*J*) in Hertz (Hz). Optical rotation was determined using Automatic polarimeter. HRMS were recorded on a mass spectrometer with APCI or ESI.

Preparation and Analytical Data of Substrates 1: To a solution of NaH (60 wt. % in oil) (1.8 g, 45 mmol, 1.5 eq) in (THF, 80 mL) was added a solution of diethyl cyanomethylphosphonate (6.4 g, 36 mmol, 1.2 eq) in dry THF (30 mL) at 0 ºC. After the mixture was stirred for 20 mins at 0 ºC, a solution of naphthaldehyde or substituted naphthaldehyde (30 mmol, 1.0 eq) in dry THF (40 mL) was added dropwise at 0 ºC. The reaction mixture was then allowed to warm to room temperature and stirred overnight. After the conversion was complete, the solution was carefully quenched with ice water and extracted with CH_2Cl_2. The organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 10/1, Rf = 0.3) to give the corresponding

(*E*)-3-(naphthalen-1-yl)-acrylonitrile or substituted compounds as white solid in 92 – 96% yields.[26a]

To an ice-cold solution of $LiAlH_4$ (2.3 g, 60 mmol, 3.0 eq) in dry Et_2O (30 ml) was added a solution of $AlCl_3$ (1.3 g, 10 mmol, 0.5 eq) in dry Et_2O (30 ml) at 0 °C. After the mixture was stirred for 30 mins at 0 °C, a solution of (*E*)-3-(naphthalen-1-yl)-acrylonitrile (3.58 g, 20 mmol, 1.0 eq) in Et_2O (30 ml) was added and stirred for 30 mins. The reaction was carefully quenched with H_2O and filtered. The filtrate was extracted by EtOAc. The organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using CH_2Cl_2/MeOH as an eluent (CH_2Cl_2/MeOH = 10/1, Rf = 0.25) to give the corresponding (*E*)-3-(naphthalen-1-yl)-prop-2-en-1-amine or substituted compounds as colorless oil with 70 –75% yields.[26b]

To a solution of (*E*)-3-(naphthalen-1-yl)-prop-2-en-1-amine (0.79 g, 4.3 mmol, 1.0 eq) in MeCN (20 mL) was added DMAP (4.9 mg, 0.04 mmol, 0.95%). After the mixture was stirred for 20 mins at room temperature, a solution of di-tert-butyl decarbonate (2.8 g, 12.9 mmol, 1.5 eq) or diethyl pyrocarbonate (2.1 g, 12.9 mmol, 1.5 eq) was added. The reaction was quenched with aqueous NH_4Cl solution and extracted with EtOAc after completion monitored by TLC. The organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA, 10/1 – 20/1, Rf = 0.3) to give the corresponding (*E*)-tert-butyl (3-(naphthalen-1-yl)-allyl)-carbamate or (*E*)-ethyl (3-(naphthalen-1-yl)-allyl)-carbamate as a white solid with yields of 82 – 84%.[26c]

The previously obtained product (*E*)-tert-butyl (3-(naphthalen-1-yl)-allyl)-carbamate (1.4 g, 5

mmol, 1.0 eq) and KOH (1.4 g, 25 mmol, 5.0 eq) were dissolved in DMSO (15 mL) under a nitrogen atmosphere. After the mixture was stirred for 20 mins, the halohydrocarbon (7.5 mmol, 1.5 eq) or Boc_2O (3.3 g, 15 mmol, 3 eq) was then added and stirred at room temperature (60 °C for **1g**) overnight. After quenched with aqueous NH_4Cl, the resulting mixture was extracted three times with CH_2Cl_2, dried over anhydrous $MgSO_4$ and filtered. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 10/1 – 30/1, Rf = 0.3) to give the substrates **1a** – **1l** and **1s** as colorless oil in 46 – 56% yields.[26d]

(*E*)-tert-butyl methyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1a): 0.83 g, yield: 56%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.13 – 8.12 (1 H, m), 7.85 – 7.84 (1 H, m), 7.78 – 7.77 (1 H, m), 7.59 – 7.44 (4 H, m), 7.23 (1 H, d, *J* = 15.1 Hz), 6.19 (1 H, s), 4.10 (2 H, d, *J* = 40.7 Hz), 2.98 (3 H, s), 1.55 (9 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 155.7, 134.5, 133.7, 131.2, 128.6, 128.5, 128.0, 126.1, 125.8, 125.7, 124.0, 123.8, 79.4, 51.2, 33.8, 28.6. TOF-HRMS Calcd. for $C_{19}H_{23}NO_2Na$ [M+Na$^+$]: 320.1621, found 320.1618.

(*E*)-tert-butyl ethyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1b): 0.86 g, yield: 55%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (1 H, d, *J* = 7.9 Hz), 7.85 (1 H, d, *J* = 7.0 Hz), 7.78 (1 H, d, *J* = 8.2 Hz), 7.58 (1 H, d, *J* = 6.9 Hz), 7.50 – 7.44 (3 H, m), 7.25 – 7.20 (1 H, m), 6.21 – 6.18 (1 H, m), 4.10 (2 H, s), 3.37 (2 H, s), 1.51 (9 H, s), 1.18 (3 H, t, *J* = 7.2 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 155.5, 134.8, 133.8, 131.3, 129.5, 128.7, 128.0, 126.2, 125.9 125.8, 124.0, 123.9, 79.5, 49.1, 41.7, 29.9, 28.5, 13.9. TOF-HRMS Calcd. for $C_{20}H_{25}NO_2Na$ [M+Na$^+$]: 334.1777, found 334.1776.

(*E*)-tert-butyl (3-(naphthalen-1-yl)-allyl)-(propyl)-carbamate (1c): 0.88 g, yield: 54%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.09 (1 H, d, *J* = 8.1 Hz), 7.85 (1 H, d, *J* = 7.6 Hz), 7.77 (1 H, d, *J* = 8.2 Hz), 7.57 (1 H, d, *J* = 6.8 Hz), 7.54 – 7.46 (2 H, m), 7.44 (1 H, t, *J* = 7.6 Hz), 7.20 (1 H, d, *J* =

14.5 Hz), 6.19 (1 H, s), 4.12 – 4.06 (2 H, m), 3.27 (2 H, d, *J* = 23.9 Hz), 1.62 (2 H, s), 1.50 (9 H, s), 0.92 (3 H, t, *J* = 7.3 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 150 MHz) δ: 155.8, 134.8, 133.7, 131.2, 129.5, 128.6, 127.9, 126.1, 125.9, 125.7, 124.0, 123.8, 79.5, 48.6, 28.6, 21.9, 11.4. TOF-HRMS Calcd. for $C_{21}H_{27}NO_2Na$ [M+Na^+]: 348.1934, found 348.1937.

(*E*)-tert-butyl butyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1d): 0.88 g, yield: 52%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.12 (1 H, d, *J* = 7.9 Hz), 7.91 – 7.83 (1 H, m), 7.79 (1 H, d, *J* = 8.1 Hz), 7.60 (1 H, d, *J* = 7.1 Hz), 7.57 – 7.42 (3 H, m), 7.23 (1 H, d, *J* = 17.4 Hz), 6.22 (1 H, s), 4.11 (2 H, d, *J* = 22.5 Hz), 3.32 (2 H, s), 1.66 – 1.57 (2 H, m), 1.53 (9 H, s), 1.38 (2 H, dt, *J* = 14.6, 7.3 Hz), 0.98 (3 H, t, *J* = 7.3 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 156.2, 135.3, 134.2, 131.7, 129.9, 129.1, 128.4, 126.6, 126.3, 126.2, 124.5, 124.3, 79.9, 49.6, 47.0, 31.2, 29.1, 27.5, 20.7, 14.5. TOF-HRMS Calcd. for $C_{22}H_{29}NO_2Na$ [M+Na^+]: 362.209, found 362.2087.

(*E*)-tert-butyl benzyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1e): 0.88 g, yield: 47%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (1 H, d, *J* = 7.7 Hz), 7.91 – 7.83 (1 H, m), 7.79 (1 H, d, *J* = 8.2 Hz), 7.52 (3 H, t, *J* = 9.2 Hz), 7.44 (1 H, d, *J* = 7.5 Hz), 7.41 – 7.29 (5 H, m), 7.17 (1 H, d, *J* = 15.6 Hz), 6.17 (1 H, s), 4.58 (2 H, s), 4.10 (2 H, d, *J* = 42.3 Hz), 1.54 (9 H, s). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 138.5, 134.7, 133.7, 131.2, 128.7, 128.0, 127.4, 126.1, 125.9, 125.7, 123.9, 80.1, 49.8, 48.7, 28.6, 27.0. TOF-HRMS Calcd. for $C_{25}H_{27}NO_2Na$ [M+Na^+]: 396.1934, found 396.1939.

(*E*)-tert-butyl allyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1f): 0.74 g, yield: 46%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.13 (1 H, d, *J* = 8.3 Hz), 7.90 – 7.82 (1 H, m), 7.78 (1 H, d, *J* = 8.2 Hz), 7.60 (1 H, d, *J* = 7.1 Hz), 7.50 (3 H, ddt, *J* = 17.7, 15.4, 4.4 Hz), 7.24 (1 H, d, *J* = 15.5 Hz), 6.38 – 6.07 (1 H, m), 5.89 (1 H, d, *J* = 5.2 Hz), 5.40 – 5.04 (2 H, m), 4.03 (4 H, d, *J* = 59.4 Hz), 1.56 (9 H, s). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 155.6, 134.8, 134.3, 133.8, 131.3, 129.0, 128.7, 128.1,

126.2, 125.9, 125.8, 124.1, 123.9, 116.5, 79.9, 49.1, 28.6, 27.1. TOF-HRMS Calcd. for $C_{21}H_{25}NO_2Na$ [M+Na$^+$]: 346.1777, found 346,1783.

(*E*)-ditert-butyl (3-(naphthalen-1-yl)-allyl)-carbamate (1g): 1.0 g, yield: 53%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 – 7.97 (1 H, m), 7.78 – 7.73 (1 H, m), 7.68 (1 H, d, *J* = 8.1 Hz), 7.41 (1 H, d, *J* = 7.1 Hz), 7.41 – 7.34 (3 H, m), 7.20 (1 H, d, *J* = 15.6 Hz), 6.15 (1 H, dt, *J* = 15.5, 6.1 Hz), 4.36 (2 H, d, *J* = 6.1 Hz), 1.45 (18 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 152.2, 134.4, 133.3, 130.9, 129.3, 128.2, 128.1, 127.7, 125.7, 125.5, 125.4, 123.7, 82.2, 48.1, 27.9. TOF-HRMS Calcd. for $C_{23}H_{29}NO_4Na$ [M+Na$^+$]: 406.1988, found 406.1983.

(*E*)-tert-butyl methyl-(3-(naphthalen-2-yl)-allyl)-carbamate (1h): 0.73 g, yield: 49%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.78 (3 H, t, *J* = 8.5 Hz), 7.71 (1 H, s), 7.58 (1 H, dd, *J* = 8.5, 1.7 Hz), 7.48 – 7.39 (2 H, m), 6.62 (1 H, d, *J* = 15.6 Hz), 6.28 (1 H, s), 4.03 (2 H, s), 2.90 (3 H, s), 1.50 (9 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 155.9, 134.3, 133.7, 133.1, 128.3, 128.0, 127.8, 126.4, 126.3, 125.9, 123.6, 79.7, 51.3, 33.9, 29.8, 28.6. TOF-HRMS Calcd. for $C_{19}H_{23}NO_2Na$ [M+Na$^+$]: 320.1621, found 320.1618.

(*E*)-ethyl methyl-(3-(naphthalen-1-yl)-allyl)-carbamate (1i): 0.65 g, yield: 48%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (1 H, d, *J* = 7.8 Hz), 7.90 – 7.81 (1 H, m), 7.78 (1 H, d, *J* = 8.2 Hz), 7.58 (1 H, d, *J* = 7.1 Hz), 7.56 – 7.40 (3 H, m), 7.24 (1 H, d, *J* = 15.3 Hz), 6.19 (1 H, s), 4.19 (4 H, dq, *J* = 22.8, 7.1 Hz), 2.99 (3 H, s), 1.31 (3 H, t, *J* =7.1 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 156.7, 134.5, 133.7, 131.2, 129.9, 128.7, 128.3, 128.1, 126.2, 125.9, 125.7, 124.1, 123.8, 100.0, 61.5, 51.1, 33.6, 14.9. TOF-HRMS Calcd. for $C_{17}H_{19}NO_2Na$ [M+Na$^+$]: 292.1308, found 292.1305.

(*E*)-ethyl methyl-(3-(naphthalen-2-yl)-allyl)-carbamate (1j): 0.58 g, yield: 43%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.83 – 7.76 (3 H, m), 7.72 (1 H, d, *J* = 1.6 Hz), 7.59 (1 H, dd, *J* = 8.6, 1.7

Hz), 7.48 – 7.41 (2 H, m), 6.64 (1 H, t, *J* = 12.1 Hz), 6.29 (1 H, s), 4.20 (2 H, q, *J* = 7.1 Hz), 4.10 (2 H, dd, *J* = 16.7, 10.1 Hz), 2.94 (3 H, d, *J* = 12.7 Hz), 1.30 (3 H, t, *J* = 7.1 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 157.1, 134.7, 134.1, 133.6, 133.1, 132.5, 128.8, 128.5, 128.2, 126.9, 126.5, 125.9, 124.1, 70.0, 51.3, 34.0, 15.4. TOF-HRMS Calcd. for $C_{17}H_{19}NO_2Na$ [M+Na^+]: 292.1308, found 292.1305.

(*E*)-ethyl (3-(6-methoxynaphthalen-2-yl)-allyl)-(methyl)-carbamate (1k): 0.69 g, yield: 46%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.66 (3 H, m), 7.54 (1 H, d, *J* = 8.5 Hz), 7.11 (2 H, d, *J* = 13.7 Hz), 6.60 (1 H, d, *J* = 15.8 Hz), 6.21 (1 H, d, *J* = 15.3 Hz), 4.17 (2 H, q, *J* = 7.2 Hz), 4.06 (2 H, s), 3.90 (3 H, s), 2.92 (3 H, s), 1.28 (3 H, t, *J* = 6.9 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 157.9, 134.3, 132.1, 129.6, 129.0, 127.2, 126.2, 124.2 , 119.1, 105.9, 100.0, 61.5, 55.4, 51.1, 14.9. TOF-HRMS Calcd. for $C_{18}H_{21}NO_3Na$ [M+Na^+]: 322.1413, found 322.1419.

(*E*)-tert-butyl (3-(7-bromonaphthalen-2-yl)allyl)(methyl)carbamate (1l): 0.4 g, yield: 46%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.94 (1 H, d, *J* = 1.6 Hz), 7.73 (1 H, d, *J* = 8.4 Hz), 7.65 (1 H, d, *J* = 8.7 Hz), 7.62 – 7.55 (2 H, m), 7.49 (1 H, dd, *J* = 8.7, 2.0 Hz), 6.59 (1 H, d, *J* = 15.7 Hz), 6.27 (1 H, dt, *J* = 13.7, 5.8 Hz), 4.02 (2 H, s), 2.89 (3 H, s), 1.48 (9 H, s). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 155.8, 135.4, 134.8, 131.4, 130.0, 129.4, 129.3, 128.2, 126.8, 125.2, 124.1, 120.4, 79.7, 34.0, 28.6. TOF-HRMS Calcd. for $C_{19}H_{23}NO_2Br$ [M+H^+]: 376.0906, found 376.0912.

(*E*)-tert-butyl (3-(naphthalen-1-yl)allyl)carbamate (1m): 0.6 g, yield: 84%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.93 (1 H, ddt, *J* = 5.3, 3.0, 1.6 Hz), 7.85 (1 H, ddt, *J* = 8.2, 5.6, 2.4 Hz), 7.78 (1 H, d, *J* = 8.2 Hz), 7.51 – 7.47 (2 H, m), 7.43 (1 H, dd, *J* = 8.1, 7.1 Hz), 7.27 (1 H, d, *J* = 7.4 Hz), 7.03 (1 H, d, *J* = 11.3 Hz), 5.97 (1 H, dt, *J* = 11.5, 6.7 Hz), 4.50 (1 H, s), 3.87 (2 H, s), 1.41 (9 H, s). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 150 MHz) δ: 155.8, 133.6, 133.5, 131.8, 130.5, 129.6, 128.5, 127.9, 126.6,

126.2, 125.9, 125.3, 124.8, 79.5, 39.1, 28.5. TOF-HRMS Calcd. for $C_{18}H_{21}NO_2Na$ [M+Na^+]: 306.1464, found 306.1464.

Procedure for the synthesis of (*E*)-diethyl-(3-(naphthalen-1-yl)-allyl)-phosphonate 1n: To a stirred solution of NaH (60 wt. % in oil) (0.44 g, 11 mmol, 1.1 eq) in dry THF (20 mL) was added triethyl phosphonoacetate (2.24 g, 10 mmol, 1.0 eq) in dry THF (20 mL) at 0 ºC. After 20 mins, a solution of 1-naphthaldehyde (1.56 g, 10 mmol, 1.0 eq) was added at 0 ºC. The reaction was quenched after stirred for 10 h with the aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layers were dried over anhydrous $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography on silica gel (PE/EA = 10/1, Rf = 0.5) to give the desired product (*E*)-ethyl 3-(naphthalen-1-yl)-acrylate as a colorless oil in 86% yield.

A solution of (*E*)-ethyl 3-(naphthalen-1-yl)-acrylate (1.58 g, 6.98 mmol, 1.0 eq) in toulene (16.8 mL) was cooled to 0 ºC and treated with diisobutylaluminium hydride (16.75 mmol, 2.4 eq). After stirred at 0 ºC for 30 mins, the reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel (PE/EA = 1/1, Rf = 0.35) to give the product (*E*)-3-(naphthalene-1-yl)- prop-2-en-1-ol as a colorless crystals with the yield of 90%.

A solution of tribromophosphine (3.17 g, 11.7 mmol, 1.85 eq) was slowly added to an ice-cold solution of (*E*)-3-(naphthalen-1-yl)-prop-2-en-1-ol (6.3 mmol, 1.0 eq) in Et_2O (25 mL). The mixture was stirred for 30 mins at 0 °C and 2 h at room temperature. After the conversion was complete, the reaction was quenched with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was purified by column

chromatography on silica gel (PE/EA = 15/1, Rf = 0.5) to give the desired product (*E*)-1-(3-bromoprop-1-en-1-yl)-naphthalene as a colorless oil with a quantitative yield.[26a]

To an ice-cold solution of diethyl phosphite (3.3 mmol 1.1 eq) in THF (15 mL) was added *n*-BuLi (3.3 mmol, 2.5 M in hexanes, 1.1 eq). After the mixture was stirred for 15 mins at -10 °C, a solution of (*E*)-1-(3-bromoprop-1-en-1-yl)-naphthalene (3.0 mmol, 1.0 eq) in THF (5 mL) was added dropwise. After 3 h at -10 °C, a saturated aqueous solution of NH_4Cl was added and the mixture was allowed to warm to room temperature. The reaction mixture was diluted with EtOAc and washed with water. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under vacuum. Purification by column chromatography on silica gel (PE/EA = 1/1, Rf = 0.25) to give the desired product (*E*)-diethyl-(3-(naphthalen-1-yl)-allyl)-phosphonate **1n** as a colorless oil in 53% yield.[27]

(*E*)-diethyl (3-(naphthalen-1-yl)-allyl)-phosphonate (1n): 0.48 g, yield: 53%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.09 (1 H, d, *J* = 8.0 Hz), 7.83 (1 H, d, *J* = 7.6 Hz), 7.76 (1 H, d, *J* = 8.2 Hz), 7.56 (1 H, d, *J* = 7.1 Hz), 7.52 – 7.45 (2 H, m), 7.45 – 7.40 (1 H, m), 7.27 (1 H, dd, *J* = 15.5, 5.2 Hz), 6.19 (1 H, m), 4.15 (4 H, m), 2.89 (2 H, dd, *J* = 22.2, 7.5 Hz), 1.33 (6 H, t, *J* = 7.1 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 134.3, 133.3, 131.8, 131.7, 130.7, 128.2, 127.7, 125.8, 125.5, 125.3, 123.6, 123.4, 121.8, 121.7, 61.7, 31.8, 30.4, 16.2. TOF-HRMS Calcd. for $C_{17}H_{22}O_3P$ [M+H$^+$]: 305.1301, found 305.1307.

Procedure for the synthesis of (*E*)-3-(naphthalen-1-yl)-allyl acetate 1o: To a solution of palladium diacetate (56 mg, 0.25 mmol, 5 mol %) and silver carbonate (0.83 g, 3.0 mmol, 0.6 eq) in toluene (15 mL) was added 1-iodonaphthalene (1.27 g, 5.0 mmol, 1.0 eq) and allyl acetate (1.0

g, 10 mmol, 2.0 eq). The resulting mixture was heated at reflux for 12 h. After the conversion was complete, the reaction mixture was then concentrated by evaporation. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 20/1, Rf = 0.3) to give the corresponding (*E*)-3-(naphthalen-1-yl)-allyl acetate **1o** as a colorless oil in 66% yield.[28]

(*E*)-3-(naphthalen-1-yl)-allyl acetate (1o): 0.75 g, yield: 66%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.12 (1 H, d, *J* = 8.1 Hz), 7.87 (1 H, d, *J* = 8.8 Hz), 7.81 (1 H, d, *J* = 8.2 Hz), 7.62 (1 H, d, *J* = 7.1 Hz), 7.59 – 7.38 (4 H, m), 6.33 (1 H, dt, *J* = 15.6, 6.3 Hz), 4.92 – 4.81 (2 H, m), 2.16 (3 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 170.6, 133.7, 133.4, 131.1, 130.9, 128.4, 128.2, 126.2, 126.0, 125.7, 125.4, 123.9, 123.5, 64.9, 20.8. TOF-HRMS Calcd. for $C_{15}H_{14}O_2Na$ [M+Na$^+$]: 249.0886, found 249.0884.

Procedure for the synthesis of (*E*)-(3-(naphthalen-1-yl) allyl)-(p-tolyl)-sulfane 1p: To an ice-cold solution of (*E*)-1-(3-bromoprop-1-en-1-yl)-naphthalene (1.46 g, 5.9 mmol, 1 eq) in Et_2O (15 mL) was added triethylamine (7.38 mmol, 1.25 eq) and 4-methylbenzenethiol (0.82 g, 7.4 mmol, 1.25 eq) at 0 °C. After the resulting mixture was stirred for 20 mins at 0 °C, the reaction mixture was then allowed to stir at room temperature for 3 d. After the conversion was complete, the organic phase was subsequently washed with water (30 mL), 2 M aqueous HCl-solution (30 mL), and brine (30 mL), and dried over Na_2SO_4, filtered and evaporated. The crude product was recrystallized from the solvent mixture of EA and PE (1:10) to give the corresponding product (*E*)-(3-(naphthalen-1-yl) allyl)-(p-tolyl)-sulfane **1p** as a white solid in 68% yield.[27]

(*E*)-(3-(naphthalen-1-yl)-allyl)-(p-tolyl)-sulfane (1p): light yellow solid, MP: 90– 922 °C, 1.17 g, yield: 68%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.87 – 7.74 (3 H, m), 7.55 – 7.37 (6 H, m), 7.15 (2 H,

d, *J* = 7.9 Hz), 7.04 (1 H, d, *J* = 15.4 Hz), 6.32 – 6.19 (1 H, m), 3.77 (2 H, dd, *J* = 7.3, 1.2 Hz), 2.36 (3 H, s). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 137.0, 134.9, 133.6, 132.1, 131.7, 131.2, 130.1, 129.9, 128.6, 128.5, 128.0, 126.0, 125.9, 125.7, 124.1, 38.5, 21.3. TOF-HRMS Calcd. for $C_{20}H_{18}SNa$ [M+Na^+]: 313.1021, found 313.1028.

Procedure for the synthesis of (*E*)-1-(but-1-en-1-yl)-naphthalene (1q): A solution of ammonium acetate (0.39 g, 5.0 mmol, 0.25 eq) in nitromethane (25 mL) was heated to 90 °C and a solution of 1-naphthaldehyde (3.12 g, 20 mmol, 1.0 eq) was added dropwise. The resulting mixture was heated at reflux for 6 h. Aqueous of water was added and the mixture was extracted three times with CH_2Cl_2, dried over $MgSO_4$, and filtered. The crude material was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 25/1, Rf = 0.3) to give the (*E*)-1-(2-nitrovinyl)-naphthalene as a yellow oil in the yield of 60%.[29]

To a solution of (*E*)-1-(2-nitrovinyl)-naphthalene (0.6 g, 3.0 mmol, 1.0 eq) in Et_2O (30 mL) was added triethylborane (12 mmol, in THF, 4.0 eq) at room temperature. After 30 mins, the starting material was consumed. Aqueous of water was added and the mixture was extracted three times with EtOAc. The organic phase was dried over $MgSO_4$ and filtered. Purification by column chromatography on silica gel using petroleum ether as an eluent (Rf = 0.5) to give the desired product (*E*)-1-(but-1-en-1-yl)-naphthalene **1q** as a colorless oil in 78% yield.

(*E*)-1-(but-1-en-1-yl)-naphthalene (1q): 0.43 g, yield: 78%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.17 (1 H, d, *J* = 8.2 Hz), 7.87 (1 H, d, *J* = 8.2 Hz), 7.77 (1 H, d, *J* = 8.2 Hz), 7.59 (1 H, d, *J* = 7.1 Hz), 7.56 – 7.48 (2 H, m), 7.46 (1 H, t, *J* = 7.7 Hz), 7.15 (1 H, d, *J* = 15.6 Hz), 6.32 (1 H, m), 2.42 – 2.36 (2 H, m), 1.22 (3 H, t, *J* = 7.5 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 136.1, 135.9, 133.8,

131.3, 128.6, 127.3, 126.1, 125.9, 125.8, 125.7, 124.1, 123.6, 26.6, 13.9. TOF-HRMS Calcd. for $C_{14}H_{15}$ [M+H$^+$]: 183.1168, found 183.1165.

(*E*)-N,N-dibenzyl-3-(naphthalen-1-yl)prop-2-en-1-amine (1r): 0.58 g, yield: 90%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.10 (1 H, d, *J* = 7.7 Hz), 7.88 – 7.82 (1 H, m), 7.78 (1 H, d, *J* = 8.2 Hz), 7.57 (1 H, d, *J* = 7.0 Hz), 7.53 – 7.43 (7 H, m), 7.38 – 7.26 (7 H, m), 6.35 (1 H, ddt, *J* = 15.3, 6.4, 2.3 Hz), 3.73 (4 H, s), 3.41 – 3.33 (2 H, m). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 139.8, 135.2, 133.7, 131.2, 131.1, 129.8, 128.9, 128.6, 128.4, 127.8, 127.0, 126.1, 125.8, 125.7, 123.9, 58.2, 56.1. The analytical data are consistent with the literature.[30]

(*Z*)-tert-butyl methyl(3-(naphthalen-1-yl)allyl)carbamate (1s): 0.35 g, yield: 30%; ^{1}H NMR (acetone-D6, 400 MHz) δ: 8.11 (1 H, d, *J* = 8.2 Hz), 7.92 – 7.84 (1 H, m), 7.75 (1 H, dd, *J* = 6.9, 2.6 Hz), 7.54 – 7.44 (2 H, m), 7.43 – 7.37 (2 H, m), 7.06 (1 H, dd, *J* = 43.0, 13.6 Hz), 5.11 (1 H, dt, *J* = 14.0, 6.8 Hz), 3.83 (2 H, d, *J* = 6.6 Hz), 2.95 (3 H, s), 1.41 (9 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 153.0, 137.5, 134.0, 132.0, 130.1, 129.7, 128.8, 127.0, 126.0, 125.7, 125.6, 134.0, 107.0, 106.3, 81.0, 33.7, 31.3, 28.4. TOF-HRMS Calcd. for $C_{19}H_{23}NO_2Na$ [M+Na$^+$]: 320.1621, found 320.1618.

General procedure of Cu-catalyzed enantioselective hydroboration: In a nitrogen-filled glovebox, CuCl (0.025 mmol, 5 mol%), (*S*, R_p)-JosiPhos-2 (**L2**) (0.025 mmol, 5 mol%), B_2pin_2 (0.6 mmol, 1.2 eq), MeOK (0.1 mmol, 0.2 eq) and dry THF (1.0 mL) were placed in an oven-dried Schleck tube which was sealed with a rubber plug. The reaction mixture stirred 10 mins at room temperature. The Schleck tube was then removed from glovebox. After substrates **1** (0.50 mmol, 1.0 eq) was added to the mixture at 0 °C, MeOH (1.0 mmol, 2.0 eq) was added dropwise. After stirred for 30 mins at 0 °C, the reaction mixture was then allowed to warm to ambient temperature

and stirred for 2 h. The reaction mixture was passed through a short silica gel column eluting with Et_2O. The crude mixture was purified by chromatography on silica gel using petroleum ether/EtOAc as an eluent (PE/EA/ = 2/1 to 20/1) to give the n products **2** as light yellow solids or oil. The ee values of **2** were determined by HPLC or SFC analysis on a chiral stationary phase.

The procedure of hydroboration of 1a on a gram scale: In a nitrogen-filled glovebox, CuCl (16.6 mg, 0.17 mmol), (*S*, R_p)-JosiPhos-2 (**L2**) (99.9 mg, 0.17 mmol), B_2pin_2 (1.02 g, 4.0 mmol), MeOK (47.1 mg, 0.67 mmol) and dry THF (10.0 mL) were placed in an oven-dried Schleck tube. The reaction mixture stirred 10 mins at room temperature. The Schleck tube was then removed from glovebox. After substrate **1a** (1.0 g, 3.36 mmol) was added to the mixture at 0 °C, MeOH (6.72 mmol) was added dropwise. After stirred for 30 mins at 0 °C, the reaction mixture was then allowed to warm to ambient temperature and stirred for 2h. The reaction mixture was passed through a short silica gel column eluting with Et_2O. The crude mixture was purified by chromatography on silica gel using petroleum ether/EtOAc as an eluent (PE/EA/ = 10/1) to give the product **2a** as a light yellow oil with the similar yield and enantioselectivity (1.22 g, 85% yield; 94% ee).

tert-butyl methyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2a): light yellow oil, 178.7 mg, yield: 84%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (1 H, d, *J* = 8.2 Hz), 7.81 (1 H, d, *J* = 8.5 Hz), 7.68 (1 H, d, *J* = 8.3 Hz), 7.41 (4 H, dq, *J* = 37.9, 8.4, 7.4 Hz), 3.63 – 2.95 (4 H, m), 2.87 (3 H, d, *J* = 44.5 Hz), 1.95 (1 H, d, *J* = 11.9 Hz), 1.43 (9 H, d, *J* = 32.9 Hz), 1.12 (12 H, d, *J* = 18.7 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 156.1, 134.0, 132.1, 128.8, 126.5, 125.8, 125.3, 124.0, 121.2, 83.4, 79.4, 51.0, 32.0, 28.5, 24.9. TOF-HRMS Calcd. for

$C_{25}H_{36}BNO_4Na$ [M+Na^+]: 448.2634, found 448.2636. 93% ee; $[\alpha]_D^{20}$ = -19.85 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 5 : 95, 1.0 mL/min, 254 nm; t_A = 3.9 min (minor), t_B = 4.3 min (major).

tert-butyl ethyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2b): light yellow solid, MP: 95 – 97 °C, 180.2 mg, yield: 82%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (1 H, d, *J* = 8.0 Hz), 7.85 – 7.76 (1 H, m), 7.67 (1 H, d, *J* = 8.1 Hz), 7.53 – 7.40 (2 H, m), 7.36 (2 H, p, *J* = 6.8 Hz) 3.55 – 3.37 (2 H, m), 3.33 – 3.01 (4 H, m), 1.96 (1 H, s), 1.43 (9 H, s), 1.11 (15 H, d, *J* = 19.1 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 155.8, 133.9, 132.1, 128.7, 126.7, 126.4, 125.7, 125.4, 125.3, 124.0, 83.3, 79,2, 48.1, 42.0, 32.0, 29.8, 28.6, 24.9, 14.2. TOF-HRMS Calcd. for $C_{26}H_{39}BNO_4$ [M+H^+]: 440.2971, found 440.2968. 93% ee; $[\alpha]_D^{17}$ = -17.09 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 4.2 min (minor), t_B = 4.6 min (major).

tert-butyl (3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-(propyl)-carbamate (2c): light yellow solid, MP: 97 – 99 °C, 179.1 mg, yield: 79%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.05 (1 H, s), 7.81 (1 H, d, *J* = 7.9 Hz), 7.67 (1 H, d, *J* = 8.0 Hz), 7.46 (2 H, dt, *J* = 25.6, 7.0 Hz), 7.42 – 7.32 (2 H, m), 3.43 (2 H, d, *J* = 40.5 Hz), 3.13 (4 H, d, *J* = 26.3 Hz), 2.12 – 1.87 (1 H, m), 1.58 – 1.34 (11 H, m), 1.11 (12 H, d, *J* = 29.9 Hz), 0.89 – 0.79 (3 H, m). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 155.9, 134.0, 132.1, 128.7, 126.7, 126.4, 125.7, 125.3, 124.1, 83.3, 79.1, 48.8, 32.0, 29.8, 28.5, 24.9, 21.6, 11.4. TOF-HRMS Calcd. for $C_{27}H_{40}BNO_4Na$ [M+Na^+]: 476.2948, found 476.2942. 94% ee; $[\alpha]_D^{20}$ = -12.50 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 ×

4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 3.7 min (minor), t_B = 4.1 min (major).

tert-butyl butyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2d): light yellow solid, MP: 104 – 106 °C, 177.6 mg, yield: 76%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (1 H, d, *J* = 7.8 Hz), 7.81 (1 H, d, *J* = 8.2 Hz), 7.67 (1 H, d, *J* = 8.0 Hz), 7.46 (2 H, p, *J* = 6.7 Hz), 7.36 (2 H, p, *J* = 7.1 Hz), 3.45 (2 H, d, *J* = 7.3 Hz), 3.33 – 3.02 (4 H, m), 1.98 (1 H, s), 1.62 – 1.26 (13 H, m), 1.11 (12 H, d, *J* = 19.7 Hz), 0.90 (3 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 155.9, 134.0, 132.1, 128.7, 126.7, 126.5, 125.7, 125.4, 125.3, 124.1, 83.3, 79.1, 48.4, 46.7, 32.0, 29.8, 28.6, 24.9, 20.2, 13.9. TOF-HRMS Calcd. for $C_{28}H_{42}BNO_4Na$ [M+Na$^+$]: 490.3104, found 490.3102. 93% ee; $[\alpha]_D^{20}$ = -9.7 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 3.8 min (minor), t_B = 4.2 min (major).

tert-butyl benzyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2e): light yellow oil, 168.0 mg, yield: 67%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (1 H, d, *J* = 7.7 Hz), 7.91 – 7.83 (1 H, m), 7.79 (1 H, d, *J* = 8.2 Hz), 7.52 (3 H, t, *J* = 9.2 Hz), 7.44 (1 H, d, *J* = 7.5 Hz), 7.41 – 7.29 (5 H, m), 7.17 (1 H, d, *J* = 15.6 Hz), 6.17 (1 H, s), 4.58 (2 H, s), 4.10 (2 H, d, *J* = 42.3 Hz), 1.54 (9 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 138.5, 134.7, 133.7, 131.2, 128.7, 128.0, 127.4, 126.1, 125.9, 125.7, 123.9, 80.1, 49.8, 48.7, 28.6, 27.0. TOF-HRMS Calcd. for $C_{31}H_{41}BNO_4$ [M+H$^+$]: 502.3129, found 502.3132. 90% ee; $[\alpha]_D^{20}$ = -3.25 (c = 1.0, $CHCl_3$); HPLC

condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 6.2 min (minor), t_B = 7.0 min (major).

(*S*)-tert-butyl

allyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate

(2f): light yellow solid, MP: 100 – 102 °C, 151.2 mg, yield: 67%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (1 H, d, *J* = 8.1 Hz), 7.82 (1 H, d, *J* = 8.1 Hz), 7.67 (1 H, d, *J* = 7.8 Hz), 7.53 – 7.41 (2 H, m), 7.36 (2 H, p, *J* = 6.7 Hz), 5.78 (1 H, d, *J* = 20.0 Hz), 5.08 (2 H, s), 4.21 – 3.66 (2 H, m), 3.58 – 2.95 (4 H, m), 2.00 (1 H, d, *J* = 22.3 Hz), 1.50 – 1.33 (9 H, m), 1.11 (12 H, d, *J* = 18.4 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 155.8, 134.1, 133.9, 132.1, 128.8, 126.5 125.8, 125.4, 125.3, 124.1 118.1, 116.2 83.3 49.7, 32.0, 29.7 28.5, 24.9, 22.8, 14.2. TOF-HRMS Calcd. for $C_{27}H_{39}BNO_4$ [M+H$^+$]: 452.2972, found 452.2969. 90% ee; $[\alpha]_D^{20}$ = -19.82 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 4.2 min (minor), t_B = 4.6 min (major).

Compound 2g: light yellow solid, MP: 59 – 61 °C, 102.2 mg, yield: 40%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.03 (1 H, d, *J* = 8.0 Hz), 7.83 – 7.77 (1 H, m), 7.66 (1 H, d, *J* = 8.1 Hz), 7.48 – 7.37 (3 H, m), 7.35 – 7.28 (1 H, m), 3.82 (2 H, d, *J* = 7.8 Hz), 3.30 – 3.07 (2 H, m), 2.01 (1 H, q, *J* = 7.8 Hz), 1.46 (18 H, s), 1.09 (12 H, d, *J* = 20.2 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 153.0, 137.8, 134.0, 132.1, 128.7, 126.7, 126.6, 125.7, 125.3, 124.2, 83.3, 82.1, 48.0, 32.1, 28.2, 24.9. TOF-HRMS Calcd. for $C_{29}H_{42}BNO_6Na$ [M+Na$^+$]: 534.3003, found 534.3001. 58% ee; $[\alpha]_D^{20}$ = -14.39 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 3.6 min (minor), t_B = 3.9 min (major).

tert-butyl

methyl-(3-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2h): light yellow solid, MP: 60 – 62 °C, 119.1 mg, yield: 56%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.75 (3 H, dd, *J* = 16.7, 7.9 Hz), 7.64 (1 H, s), 7.45 – 7.30 (3 H, m), 3.46 – 3.20 (2 H, m), 2.86 – 2.79 (5 H, m), 1.86 (1 H, p, *J* = 8.2 Hz), 1.43 (9 H, s), 1.09 (12 H, d, *J* = 14.3 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 156.1, 133.6, 132.1, 127.8, 127.6, 127.5, 126.9, 125.8, 125.1, 83.4, 35.1, 32.0, 29.8, 28.6, 24.9, 22.8, 14.2. TOF-HRMS Calcd. for $C_{25}H_{36}BNO_4Na$ [M+Na$^+$]: 448.2634, found 448.2636. 88% ee; $[\alpha]_D^{20}$ = -9.13 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 5.5 min (minor), t_B = 6.2 min (major).

ethyl

methyl-(3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2i): light yellow oil, 178.8 mg, yield: 90%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.10 (1 H, d, *J* = 7.8 Hz), 7.90 – 7.81 (1 H, m), 7.78 (1 H, d, *J* = 8.2 Hz), 7.58 (1 H, d, *J* = 7.1 Hz), 7.56 – 7.40 (3 H, m), 7.24 (1 H, d, *J* = 15.3 Hz), 6.19 (1 H, s), 4.19 (4 H, dq, *J* = 22.8, 7.1 Hz), 2.99 (3 H, s), 1.31 (3 H, t, *J* =7.1 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 156.7, 134.5, 133.7, 131.2, 129.9, 128.7, 128.3, 128.1, 126.2, 125.9, 125.7, 124.1, 123.8, 100.0, 61.5, 51.1, 33.6, 14.9. TOF-HRMS Calcd. for $C_{23}H_{33}BNO_4$ [M+H$^+$]: 398.2501, found 398.2502. 94% ee; $[\alpha]_D^{18}$ = -5.46 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 7.3 min (minor), t_B = 7.9 min (major).

ethyl

methyl-(3-(naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-carbamate (2j): light yellow oil, 115.2 mg, yield: 58%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02 (1 H, s), 7.81

(1 H, d, *J* = 7.9 Hz), 7.67 (1 H, d, *J* = 7.9 Hz), 7.52 – 7.40 (2 H, m), 7.34 (2 H, q, *J* = 7.4, 5.6 Hz), 4.08 (2 H, dt, *J* = 16.6, 7.9 Hz), 3.61 – 3.26 (2 H, m), 3.15 (2 H, dd, *J* = 20.5, 8.3 Hz), 2.87 (3 H, d, *J* = 39.0 Hz), 1.95 (1 H, t, *J* = 8.3 Hz), 1.25 (3 H, s), 1.11 (12 H, d, *J* = 18.2 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 156.8, 134.0, 132.0, 128.8, 126.8, 126.5, 125.8, 125.4, 125.3, 124.0, 83.4, 61.2, 50.4, 33.8, 31.8, 29.8, 24.8, 22.8, 14.8. TOF-HRMS Calcd. for $C_{23}H_{33}BNO_4$ [M+H$^+$]: 398.2501, found 398.2502. 90% ee; $[\alpha]_D^{20}$ = -13.29 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 8.9 min (minor), t_B = 9.9 min (major).

ethyl (3-(6-methoxynaphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-(methyl)-carbamate (2k): light yellow solid, MP: 88 – 90 °C, 89.7 mg, yield: 42%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62 (2 H, d, *J* = 8.9 Hz), 7.56 (1 H, s), 7.09 (2 H, d, *J* = 8.8 Hz), 4.20 – 3.98 (2 H, m), 3.89 (3 H, s), 3.56 – 3.24 (2 H, m), 3.01 – 2.68 (5 H, m), 1.85 (1 H, p, *J* = 8.1 Hz), 1.23 – 1.19 (3 H, m), 1.09 (12 H, d, *J* = 13.2 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 157.5, 133.1, 129.1, 128.9, 128.2, 126.8, 126.6, 118.6, 105.7, 83.4, 61.2, 55.3, 49.8, 34.8, 24.8, 14.8. TOF-HRMS Calcd. for $C_{24}H_{35}BNO_5$ [M+H$^+$]: 428.2607, found 428.2605. 90% ee; $[\alpha]_D^{20}$ = -49.25 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 12.7 min (minor), t_B = 15.5 min (major).

(3-(7-bromonaphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)(methyl) carbamate (2l): light yellow oil, 221 mg, yield: 88%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.88 (1 H, d, *J* = 1.8 Hz), 7.68 (1 H, d, *J* = 8.4 Hz), 7.63 (1 H, d, *J* = 8.7 Hz), 7.54 (1 H, s), 7.45 (1 H, dd, *J* = 8.7, 1.9 Hz), 7.36 (1 H, d, *J* = 8.3 Hz), 3.57 – 3.09 (2 H, m), 2.83 (5 H, dd, *J* = 15.8, 7.8 Hz), 1.84

(1 H, p, *J* = 8.0 Hz), 1.43 (9 H, s), 1.09 (12 H, d, *J* = 12.6 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 156.0, 140.6, 134.7, 130.5, 129.4, 128.5, 128.2, 127.7, 126.0, 119.8, 83.4, 79.4, 50.3, 35.1, 34.5, 28.6, 24.9. TOF-HRMS Calcd. for $C_{25}H_{36}BBrNO_4$ [M+H$^+$]: 506.1922, found 506.1925. 90% ee; $[\alpha]_D^{22}$ = -13.5 (c = 1.0, CH_2Cl_2); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 5 : 95, 1.0 mL/min, 254 nm; t_A = 5.2 min (major), t_B = 5.9 min (minor).

tert-butyl (3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate (2m): light yellow oil, 145 mg, yield: 70%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.05 (1 H, d, *J* = 8.0 Hz), 7.82 (1 H, d, *J* = 7.8 Hz), 7.73 – 7.65 (1 H, m), 7.53 – 7.41 (2 H, m), 7.36 (2 H, d, *J* = 7.1 Hz), 4.77 (1 H, s), 3.31-3.14 (3 H, m), 3.07 (1 H, dd, *J* = 14.0, 7.5 Hz), 1.75 (1 H, p, *J* = 7.5 Hz), 1.43 (9 H, s), 1.17 (12 H, d, *J* = 13.9 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 156.0, 137.5, 134.0, 132.0, 128.8, 126.8, 126.6, 125.8, 125.5, 125.4, 124.1, 83.6, 78.9, 42.0, 31.7, 28.5, 24.9. TOF-HRMS Calcd. for $C_{24}H_{35}BNO_4$ [M+H$^+$]: 412.2658, found 412.2656. 92% ee; $[\alpha]_D^{22}$ = -5.2 (c = 1.0, CH_2Cl_2); SFC condition: Lux 5μm Amylose-1 (250 × 4.60 mm), ipa : hex = 10 : 90, 3.0 mL/min, 210 nm; t_A = 1.9 min (minor), t_B = 2.1 min (major).

diethyl (3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl)-phosphonate (2n): light yellow oil, 97.3 mg, yield: 45%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.12 (1 H, d, *J* = 8.3 Hz), 7.82 (1 H, d, *J* = 7.9 Hz), 7.69 (1 H, dd, *J* = 5.6, 3.8 Hz), 7.54 – 7.41 (2 H, m), 7.38 – 7.32 (2 H, m), 4.10 – 3.76 (4 H, m), 3.29 (1 H, ddd, *J* = 13.8, 7.5, 2.1 Hz), 3.15 (1 H, dd, *J* = 13.9, 8.1 Hz), 2.05 – 1.94 (1 H, m), 1.91 – 1.81 (1 H, m), 1.80 – 1.71 (1 H, m), 1.25 (3 H, t, *J* = 7.1 Hz), 1.18 (12 H, d, *J* = 22.7 Hz), 1.12 (3 H, t, *J* = 7.1 Hz). $^{13}C\{^{1}H\}$NMR ($CDCl_3$, 100 MHz) δ: 136.5, 133.7,

131.7, 128.4, 126.7, 125.6, 125.2, 124.9, 123.9, 83.2, 61.0, 34.6, 26.7, 25.3, 24.6, 15.9. TOF-HRMS Calcd. for $C_{23}H_{35}BO_5P$ [M+H$^+$]: 433.2314, found 433.2316. 94% ee; $[\alpha]_D^{18}$ = 3.81 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm) (250 × 4.60 mm), ipa : hex = 10 : 90, 1.0 mL/min, 254 nm; t_A = 6.0 min (major), t_B = 7.6 min (minor).

3-(naphthalen-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propyl acetate (2o): light yellow oil, 145.2 mg, yield: 82%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (1 H, d, *J* = 8.3), 7.86 – 7.80 (1 H, m), 7.69 (1 H, p, *J* = 2.9), 7.54 – 7.41 (2 H, m), 7.36 (2 H, d, *J* = 4.9), 4.28 – 4.11 (2 H, m), 3.29 (1 H, dd, *J* = 14.2, 8.0), 3.18 (1 H, dd, *J* = 14.2, 7.6), 2.02 (3 H, s), 1.92 (1 H, p, *J* = 7.3), 1.17 (12 H, d, *J* = 11.2). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 171.1, 137.3, 134.0, 132.0, 128.8, 126.9, 126.7, 125.8, 125.5, 125.4, 124.0, 83.6, 65.9, 30.7, 24.8, 21.0. TOF-HRMS Calcd. for $C_{21}H_{27}BO_4Na$ [M+Na$^+$]: 377.1899, found 377.1903. 96% ee; $[\alpha]_D^{19}$ = 0.70 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Amylose-1 (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 5.2 min (major), t_B = 5.6 min (minor).

4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-3-(p-tolylthio)-propan-2-yl)-1,3,2-dioxaborolane (2p): light yellow oil, 163.2 mg, yield: 78%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.01 – 7.99 (1 H, m), 7.81 (1 H, dd, *J* = 6.6, 2.8 Hz), 7.68 (1 H, dd, *J* = 7.3, 1.7 Hz), 7.46 – 7.39 (2 H, m), 7.36 – 7.30 (2 H, m), 7.18 (2 H, d, *J* = 8.1 Hz), 7.01 (2 H, d, *J* = 8.0 Hz), 3.32 (1 H, dd, *J* = 14.0, 7.2 Hz), 3.23 (1 H, dd, *J* = 14.0, 8.8 Hz), 3.09 (1 H, dd, *J* = 12.5, 7.9 Hz), 3.01 (1 H, dd, *J* = 12.5, 7.1 Hz), 2.29 (3 H, s), 1.89 (1 H, p, *J* = 7.5 Hz), 1.16 (12 H, d, *J* = 30.6 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 137.3, 135.8, 134.0, 133.2, 132.0, 129.9, 129.6, 128.7, 126.8, 126.7, 125.7, 125.4, 125.3, 124.2, 83.6, 36.4, 33.5, 24.8, 21.1. TOF-HRMS Calcd. for $C_{26}H_{32}BO_2S$ [M+H$^+$]: 419.2215, found 419.2220. 92% ee; $[\alpha]_D^{19}$ = 1.91 (c = 1.0, $CHCl_3$); Enantiomeric excess of the corresponding

hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), ipa : hex = 10 : 90, 1.0 mL/min, 254 nm; t_A = 9.6 min (minor), t_B = 10.8 min (major).

4,4,5,5-tetramethyl-2-(1-(naphthalen-1-yl)-butan-2-yl)-1,3,2-dioxaborolane (2q): light yellow oil, 111.7 mg, yield: 72%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 8.09 (1 H, d, *J* = 8.4 Hz), 7.82 (1 H, d, *J* = 8.0 Hz), 7.68 (1 H, d, *J* = 7.6 Hz), 7.46 (2 H, dt, *J* = 24.8, 7.1 Hz), 7.36 (2 H, q, *J* = 7.3 Hz), 3.22 (1 H, dd, *J* = 14.1, 8.3 Hz), 3.09 (1 H, dd, *J* = 14.2, 6.8 Hz), 1.53 (3 H, m), 1.16 (12 H, d, *J* = 26.4 Hz), 0.98 (3 H, t, *J* = 7.2 Hz). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 138.5, 134.0, 132.2, 128.7, 126.5, 125.6, 125.3, 125.2, 124.3, 83.1, 34.2, 24.8, 13.7. TOF-HRMS Calcd. for $C_{20}H_{28}BO_2$ [M+H$^+$]: 311.2181, found 311.2186. 92% ee; $[\alpha]_D^{18}$ = -40.8 (c = 1.0, $CHCl_3$); Enantiomeric excess of the corresponding hydroxyl compound obtained by oxidation with $NaBO_3$ in THF/H_2O (1:1); HPLC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 254 nm; t_A = 9.0 min (minor), t_B = 9.5 min (major).

Procedure for the synthesis of β-amino alcohol 3: In a round bottom flask **2c** (0.2 mmol, 1.0 eq) was dissolved in THF/H_2O (1:1, 4.0 mL). $NaBO_3$•$4H_2O$ (1.0 mmol, 5.0 eq) was added at room temperature. After stirred for 2 h, the reaction mixture was extracted with EtOAc, dried over Na_2SO_4, and filtered. The residue was purified by silica gel chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 1 : 1, Rf = 0.25) to afford **3** as a colorless oil.[19]

tert-butyl (2-hydroxy-3-(naphthalen-1-yl)-propyl)-(propyl)-carbamate (3): 7.3 mg, yield: 98%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.07 (1 H, s), 7.86 (1 H, d, *J* = 8.1 Hz), 7.75 (1 H, d, *J* = 7.8 Hz), 7.56 – 7.44 (2 H, m), 7.40 (2 H, dt, *J* = 13.3, 6.6 Hz), 4.28 – 4.14 (1 H, m), 3.75 – 3.07 (7 H, m), 1.45 (11 H, s), 0.77 (3 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 100 MHz) δ: 157.7, 133.7, 131.9, 128.5, 127.3,

127.0, 125.7, 125.4, 125.2, 123.6, 79.8, 72.1, 53.6, 38.7, 28.1, 21.3, 10.9. TOF-HRMS Calcd. for $C_{21}H_{29}NO_3Na$ [M+Na$^+$]: 366.2039, found 366.2043. 93% ee; $[\alpha]_D^{19}$ = -33.8 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5u Cellulose-4 (250 × 4.60 mm), ipa : hex = 10:90, 1.0 mL/min, 254 nm; t_A = 5.7 min (minor), t_B = 6.4 min (major).

Procedure for the synthesis of γ-amino alcohol 4: To a solution of **2e** (0.113 mmol) and dibromomethane (19.4 μL, 0.28 mmol) in THF (1.2 mL) was added dropwise ^{n}BuLi (0.25 mmol, 2.5 M solution in hexane) at -78 °C under nitrogen atmosphere. The resulting mixture was stirred for 20 mins at -78 °C and then allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc. The resulting organic layer was dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was dissolved in THF/H_2O (1:1, 4.0 mL) and $NaBO_3$•$4H_2O$ (0.57 mmol) was added at room temperature. After stirred for 2 h, the reaction mixture was extracted with EtOAc, dried over Na_2SO_4, and filtered. The residue was purified by silica gel chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 3 : 1, Rf = 0.5) to afford **4**.[24]

tert-butyl benzyl (3-hydroxy-2-(naphthalen-1-ylmethyl)propyl)carbamate (4): light yellow oil, 33.0 mg, yield: 72%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.93 – 7.72 (2 H, m), 7.63 (1 H, d, *J* = 8.2 Hz), 7.43 – 7.35 (2 H, m), 7.32 – 7.24 (1 H, m), 7.20 (1 H, d, *J* = 6.8 Hz), 7.15 – 7.09 (3 H, m), 6.90 (2 H, s), 4.37 (1 H, d, *J* = 15.2 Hz), 3.90 (1 H, d, *J* = 15.3 Hz), 3.78 – 3.61 (1 H, m), 3.48 – 3.31 (2 H, m), 3.08 (1 H, dd, *J* = 13.9, 7.8 Hz), 2.84 (1 H, dd, *J* = 13.9, 6.7 Hz), 2.72 (1 H, d, *J* = 14.3 Hz), 1.88 (1 H, s), 1.38 (9 H, s). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 156.9, 137.4, 136.1, 133.8, 131.7, 128.6, 128.2, 127.3, 127.2, 126.6, 125.6, 125.2, 123.5, 80.5, 60.6, 50.7, 46.5, 39.9, 32.4, 28.1. 90% ee; $[\alpha]_D^{19}$ = -27.8 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5u Cellulose-4 (250 ×

4.60 mm), ipa : hex = 10 : 90, 1.0 mL/min, 254 nm; t_A = 8.0 min (minor), t_B = 12.6 min (major).

Procedure for the synthesis of 5: The stereospecific cross-coupling was performed according to the literature procedure.[25] To a solution of furan (22 μL, 0.3 mmol, 1.5 eq) in THF (1.0 mL) was added ^{n}BuLi (2.5 M in hexane, 0.3 mmol, 1.5 eq) at -78 °C. After the reaction was stirred for 1 hour at -78 °C, the solution of **2i** (41.8 mg, 0.2 mmol) in THF (0.5 mL) was added. The mixture was then stirred for 1 hour at -78 °C. The solution of NBS (53.5 mg, 0.3 mmol, 1.5 eq) in THF (0.5 mL) was subsequently added dropwise. After another 1 h at -78 °C, a saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was then allowed to warm to room temperature. The resulting mixture was extracted with EtOAc and the organic layers were dried over $MgSO_4$, filtered and evaporated. The residue was purified by silica gel column chromatography using petroleum ether/EtOAc as an eluent (PE/EA = 15/1, Rf = 0.35) to give the compound **5** as a light yellow oil.

ethyl (2-(furan-2-yl)-3-(naphthalen-1-yl)-propyl)-(methyl)-carbamate (5): 41.8 mg, yield: 62%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 7.98 (1 H, t, *J* = 8.2 Hz), 7.83 (1 H, t, *J* = 7.5 Hz), 7.68 (1 H, t, *J* = 8.4 Hz), 7.52 – 7.45 (2 H, m), 7.40 – 7.26 (2 H, m), 7.13 (1 H, d, *J* = 7.0 Hz), 6.28 – 6.03 (1 H, m), 5.95 – 5.79 (1 H, m), 4.20 – 3.88 (2 H, m), 3.88 – 3.58 (1 H, m), 3.59 – 3.30 (4 H, m), 2.77 – 2.57 (3 H, m), 1.25 - 1.04 (3 H, m). ^{13}C{^{1}H}NMR ($CDCl_3$, 150 MHz) δ: 155.3, 141.3, 135.5, 133.9, 131.9, 129.0, 127.0, 126.0, 125.4, 123.5, 111.9, 110.4, 107.2, 61.3, 52.9, 39.8, 34.8, 14.5. TOF-HRMS Calcd. for $C_{21}H_{23}NO_3Na$ [M+Na$^+$]: 360.1570, found 360.1575. 93% ee; $[\alpha]_D^{19}$ = -61.7 (c = 1.0, $CHCl_3$); HPLC condition: Lux 5μm Cellulos-1 (250 × 4.60 mm), ipa : hex = 2 : 98, 1.0 mL/min, 210 nm; t_A = 5.6 min (minor), t_B = 6.4 min (major).

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SUPPORTING INFORMATION

NMR and HPLC spectra, the CIF file as well as the crystal parameters for compound **2f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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