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Chiral phosphine-catalyzed regio- and enantioselective allylic amination of Morita–Baylis–Hillman acetates

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ABSTRACT

Enantioselective allylic substitution of Morita–Baylis–Hillman (MBH) acetates with phthalimide was realized in the presence of a novel L-proline-derived chiral trifunctional phosphine amide ligand to give the corresponding allylic amination adducts in good yields (70–95%) and in modest to good enantioselectivities (34–78% ee's).

1. Introduction

The Morita–Baylis–Hillman (MBH) reaction[1] provides a convenient and atom-economic synthetic method for the preparation of β-hydroxy-α-methylene-carbonyl-containing compounds, which have proven to be valuable synthetic intermediates in further chemical transformations[2] since great progress has been made in the execution of these MBH adducts over the last decade.[3] For example, Pd-catalyzed asymmetric allylic alkylation and amination of MBH adducts, as well as the application in the synthesis of several complex natural products, have been reported by Trost[4a–d] and Hamada,[4e] respectively. On the other hand, the transformation of MBH adducts via direct substitution reactions by using nucleophilic nitrogen-containing organocatalysts has also been developed. For example, the amination of MBH acetates mediated by stoichiometric amounts of 1,4-diazabicyclo[2,2,2]octane (DABCO) was reported by Kim et al.[5] Moreover, Orena et al. recently reported DABCO-catalyzed regioselective allylic amination of MBH products to give the unsaturated β-aminoacid derivatives in good yields.[6] Later on, alkaloid-catalyzed asymmetric versions of the allylic substitution reaction of MBH adducts with a variety of nucleophiles have been extensively disclosed using $(DHQD)_2PHAL$,[5b] quinidine,[7a] brucine,[7b] and other *Cinchona* alkaloid derivatives,[7b,c] to afford the corresponding allylic amination or alkylation products in good yields and in modest to good enantioselectivities.

In 2004, Krische and co-workers reported the first example of phosphine-catalyzed intermolecular allylic substitution reactions of MBH acetates, wherein N- and C-nucleophiles such as 4,5-dichlorophthalimide and 2-trimethylsilyloxyfuran (TMSOF) were utilized to generate allylic amines and γ-butenolides in high regioselectivities and in good yields, respectively.[8a,b] These organocatalysts-promoted allylic substitutions exhibited exceptionally high levels of regiospecificity by virtue of a tandem S_N2'/S_N2' mechanism. To the best of our knowledge, only one asymmetric version of this allylic amination catalyzed by a chiral phosphine has been reported by Hou et al. using planar chiral [2,2]paracyclophane monophosphines to provide the allylic amination products in high regioselectivities and in modest enantioselectivities (9–71% ee's).[9] Their experimental data revealed that the MBH acetates derived from alkyl acrylates gave the allylic amination products in higher enantioselectivities (21–71% ee's), whereas, the MBH acetates derived from methyl vinyl ketone (MVK) afforded the allylic amination products in rather lower enantioselectivities (10–17% ee's). To further extend the substrate scope of this phosphine-catalyzed successive S_N2'/S_N2' reaction, we herein report a variety of chiral phosphine- and chiral phosphine-amide ligand-catalyzed asymmetric allylic aminations by using MVK-derived MBH acetates as substrates to give the corresponding adducts in up to 78% ee and good yields.

2. Results and discussion

The chiral phosphine nucleophilic catalysts for the allylic substitution reaction are shown in Scheme 1. The monophosphine catalysts **MOP1** and **MOP2**,[10] the bifunctional phosphine catalysts **BP1–4** (one phenolic hydroxyl group and one phosphorus atom),[11] and bifunctional phosphine-amide ligands **BPA1–4** (one amide group and one phosphorus atom)[12] were synthesized by the previously reported procedures. The chiral trifunctional phosphine-amide catalyst (a*R*,*S*)-**TPA1** (one amide group, one phosphorus atom, and one amino group) was prepared by reacting (*R*)-(−)-2-(diphenylphoshino)-1,1′-binaphthyl-2′-amine[11] with *N*-Boc-L-proline at room temperature in the presence of 1,3-dicyclohexylcarbodiimide (DCC) and a catalytic amount of *N*,*N*-dimethylamino-

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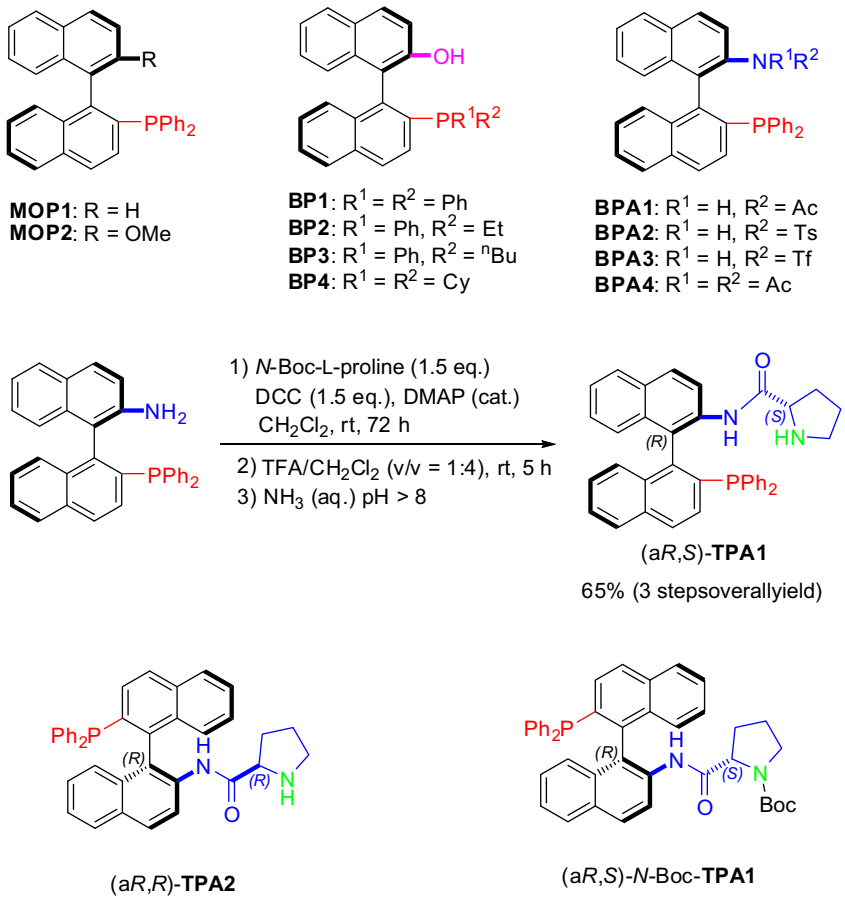


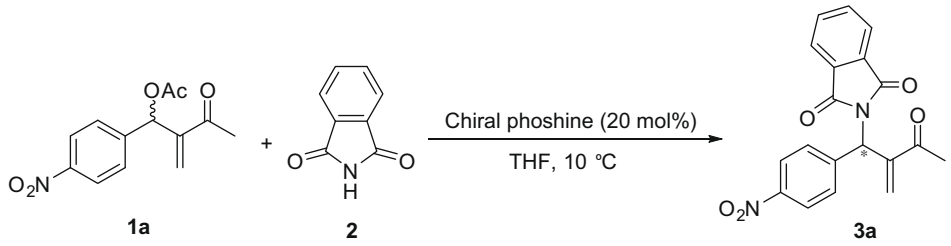
Scheme 1. Chiral monophosphines **MOP1** and **MOP2**, bifunctional phosphines **BP1-4**, bifunctional phosphine-amide catalysts **BPA1-4**, and the synthesis of trifunctional phosphine-amide catalysts (a*R*,*S*)-**TPA1**, (a*R*,*S*)-*N*-Boc-**TPA1**, (a*R*,*R*)-**TPA2**.

pyridine (DMAP) as the condensation agents give the corresponding N-protected organocatalyst (a*R*,*S*)-*N*-Boc-**TPA1**. Then, the *N*-Boc protecting group was removed by typical method, and basified with aqueous ammonia solution to pH > 8, affording (a*R*,*S*)-**TPA1** ligand in 65% overall yield in three steps. Moreover, (a*R*,*R*)-**TPA2** was synthesized from the reaction of (*R*)-(−)-2(diphenylphosphino)-1,1′-binaphthyl-2′-amine with *N*-Boc-D-proline by the same reaction procedure (Scheme 1).

Initial examinations were aimed at determining the most effective chiral phosphine catalyst for the allylic amination reaction by performing the reactions of MVK-derived MBH acetate **1a** with phthalimide **2** in tetrahydrofuran (THF) at 10 °C in the presence of chiral phosphine catalysts (20 mol %). The results of these experiments are summarized in Table 1. Using monophosphine **MOP1** (R = H) and **MOP2** (R = OMe) as catalysts resulted in the corresponding amination product **3a** in good yields and in high regiospecificities as well as in 10% ee and 36% ee (opposite chiral induction), respectively (Table 1, entries 1 and 2). Under identical conditions, chiral phosphine catalyst **BP1**, which is one of the most effective catalysts for aza-MBH reactions,[11a,b] exhibited lower catalytic activity (Table 1, entry 3). Recently, our group designed and synthesized a series of novel chiral bifunctional phosphine catalysts bearing one phenyl group and an electron-donating alkyl group [**BP2** (R^1 = Ph, R^2 = Et) and **BP3** (R^1 = Ph, R^2 = ^{n}Bu)] on the phosphorus atom.[11c,d] These more nucleophilic catalysts showed higher catalytic activities, but the enantioselectivities achieved were rather low, giving the desired products in almost quantitative yields within 12 h along with 12–28% ee's (Table 1, entries 4 and 5). The chiral phosphine catalyst **BP4** with two cyclohexyl groups on the phosphorus atom showed a lower catalytic activity (Table 1, entry 6). Chiral phosphine-amide catalysts were also studied under similar conditions. The bifunctional phosphine-amide catalysts **BPA1** (R^1 = H, R^2 = Ac) and **BPA2** (R^1 = H, R^2 = Ts) afforded product **3a** in good yields and in modest enantioselectivities (Table 1, entries 7 and 8). Interestingly, **BPA3** (R^1 = H, R^2 = Tf) did not promote the reaction, indicating that a moderately acidic amide proton was crucial for the allylic amination reaction (Table 1, entries 7–9). Furthermore, chiral phosphine catalyst **BPA4** bearing more sterically hindered groups (R^1 = R^2 = Ac) did not catalyze the reaction, suggesting that an active amide proton was essential for this reaction (Table 1, entry 10). L-Proline-derived trifunctional phosphine catalyst (a*R*,*S*)-**TPA1** gave the best result, furnishing the amination adduct **3a** in almost quantitative yield (95%) and 52% ee (Table 1, entry 11). Furthermore, D-proline-derived catalyst (a*R*,*R*)-**TPA2** could also facilitate this amination reaction under identical conditions. However, the reaction proceeded rather slowly, affording adduct **3a** in only 40% chemical yield after 72 h at room temperature along with 55% ee (Table 1, entry 12). These results reveal that the chirality of the proline moiety has a certain impact on the reaction outcome, but do not reveal any significant match/mismatch between the chirality of binaphthol and proline. *N*-Boc-protected catalyst (a*R*,*S*)-*N*-Boc-**TPA1** could also catalyze this reaction similarly, affording the desired amination adduct **3a** in 85% yield and 33% ee, suggesting that the active amino proton of the proline moiety might be indispensable in this reaction (Table 1, entry 13).

Based on the above results, (a*R*,*S*)-**TPA1** was determined to be the chiral phosphine catalyst of choice. Therefore, the reaction conditions were further optimized based on the examination of the

Table 1
Optimization of the catalysts in the asymmetric allylic amination of MBH acetates[a]



1a **2** **3a**

Entry	Chiral phosphine	Time (h)	Yield[b] (%)	ee[c] (%)
1	**MOP1**	48	50[d]	10
2	**MOP2**	48	84	−36
3	**BP1**	48	65	14
4	**BP2**	12	86	12
5	**BP3**	10	95	28
6	**BP4**	72	30	13
7	**BPA1**	36	84	37
8	**BPA2**	72	65	13
9	**BPA3**	72	n.r.[e]	n.d.[e]
10	**BPA4**	72	n.r.	n.d.
11	(a***R,S***)-**TPA1**	**36**	**95**	**52**
12	(a*R,R*)-**TPA2**	72	40	55
13	(a*R,S*)-*N*-Boc-**TPA1**	48	85	33

[a] Molecular ratio: **1a**/**2**/chiral phosphine = 100/150/20. Reactions were run in THF (0.2 M) at 10 °C.
[b] Isolated yield.
[c] Determined by chiral HPLC (Daicel AD-H column, hexane/isopropanol = 75/25 (v/v), 254 nm, 0.7 mL/min).
[d] The reaction was run at 50 °C.
[e] n.r. = no reaction, n.d. = not determined.

solvent effects and the reaction temperatures using (a*R,S*)-**TPA1** as the catalyst. The results are outlined in Table 2. It was found that THF is the best solvent in terms of yield and ee of **3a** and in toluene, acetonitrile or ether, compound **3a** was obtained in 62–71% yields and 25–50% ee's under identical conditions (Table 1, entry 11, and Table 2, entries 1, 2, and 4). Examination of the reaction temperature revealed that although no significant decrease in reactivity or enantioselectivity was observed when the reaction was carried out in THF at 50 °C or 5 °C, the ee value decreased remarkably in acetonitrile (Table 2, entries 2 and 3, entries 6 and 7). Increasing the catalyst loading to 30 mol % produced the product in quantitative yield and in higher enantioselectivity (up to 60% ee) (Table 2, entry 5). When the catalyst loading was reduced to 5 mol %, the yield and ee value of **3a** diminished slightly, but the reaction time should be prolonged (Table 2, entry 8). Finally, we found that the optimal reaction condition for this reaction is using 20 mol % of (a*R,S*)-**TPA1** as the catalyst in THF (0.2 M) to perform the reaction at 5 °C.

Table 2
Optimization of the reaction conditions of (a*R,S*)-**TPA1**-catalyzed allylic amination of MBH acetates[a]

Entry	Catalyst loading (X mol %)	Solvent	Time (h)	Temp (°C)	Yield[b] (%)	ee[c] (%)
1	20	Toluene	36	10	68	25
2	20	CH_3CN	48	10	62	50
3	20	CH_3CN	24	50	71	40
4	20	Et_2O	48	10	35	28
5	30	THF	24	10	95	60
6	**20**	**THF**	**48**	**5**	**90**	**53**
7	20	THF	24	50	95	50
8	5	THF	96	50	50	42

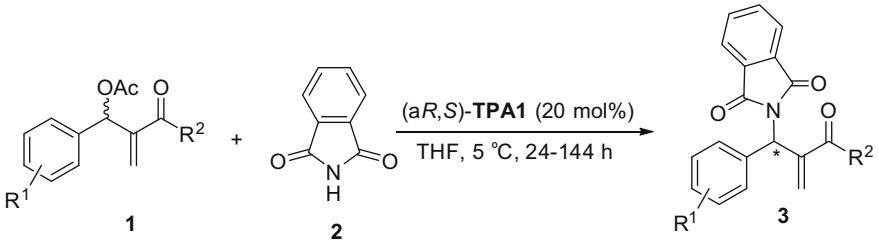
[a] Molecular ratio: **1a**/**2**/(a*R,S*)-**TPA1** = 100/150/X. Reactions were run in solvent (0.2 M).
[b] Isolated yield.
[c] Determined by chiral HPLC (Daicel AD-H column, hexane/isopropanol = 75/25 (v/v), 254 nm, 0.7 mL/min).

To investigate the scope and limitations of this catalytic asymmetric allylic amination reaction of MBH acetates, we subsequently examined a variety of MBH acetates **1** derived from the MVK and ethyl vinyl ketone (EVK) under the optimized conditions. The results are given in Table 3. The corresponding amination adducts **3** were produced smoothly in good yields (70–91%) and in modest to good enantioselectivities (34–78% ee's), whether they had electron-donating or electron-withdrawing substituents on the benzene rings (Table 3, entries 1–12). The substrates with strong electron-withdrawing substituents: **1c** (R^1 = *m*-NO_2), **1i** (R^1 = *p*-CF_3) and **1j** (R^1 = *p*-CN) exhibited better results under identical conditions (Table 3, entries 2, 8, and 9). The *o*-substituent-containing substrate **1f** produced the corresponding product **3f** in the highest enantioselectivity (up to 78% ee) (Table 3, entry 5).

3. Conclusion

In conclusion, we have developed a multi-functional phosphine-catalyzed regio- and enantioselective nucleophilic allylic amination reaction of MBH acetates prepared from MVK and EVK using phthalimide as the pronucleophile. The trifunctional phosphine-amide catalyst (a*R,S*)-**TPA1** derived from L-proline gave the best results in the organophosphine-catalyzed allylic amination reaction of this category of MBH acetates. In general, the substitution reaction proceeded smoothly to afford the tandem S_N2'/S_N2' reaction adducts in good yields (70–95%), high regioselectivities, and medium enantioselectivities (34–78% ee's). As far as we know,

Table 3
Asymmetric allylic amination of various MBH acetates **1** with 2[a]



Entry	R^1	R^2	Time (h)	Yield[b] (%)	ee[c] (%)
1	**1b**, H	Me	72	**3b**, 75	34
2	**1c**, *m*-NO_2	Me	24	**3c**, 79	50
3	**1d**, *p*-Cl	Me	72	**3d**, 80	36
4	**1e**, *m*-Cl	Me	72	**3e**, 75	44
5	**1f**, *o*-Cl	Me	72	**3f**, 85	78
6	**1g**, *p*-Br	Me	72	**3g**, 75	37
7	**1h**, *p*-F	Me	48	**3h**, 78	36
8	**1i**, *p*-CF_3	Me	144[d]	**3i**, 90	50
9	**1j**, *p*-CN	Me	36	**3j**, 91	58
10	**1k**, *p*-Me	Me	72	**3k**, 75	45
11	**1l**, *m*-Me	Me	72	**3l**, 70	43
12	**1m**, *p*-NO_2	Et	24	**3m**, 77	54

[a] Molecular ratio: **1**/**2**/(a*R*,*S*)-**TPA1** = 100/150/20. Reactions were run in THF (0.2 M) at 5 °C.
[b] Isolated yield.
[c] Determined by chiral HPLC.
[d] Reaction was run at −4 °C and 30 mol % (a*R*,*S*)-**TPA1** was used.

this work is one of the best results in the phosphine-catalyzed allylic amination of MVK/EVK-derived MBH acetates. Further application of **TPA** in asymmetric catalysis is currently in progress in our group.

4. Experimental

4.1. General remark

All reactions and manipulations were performed using standard Schlenk techniques. Melting points were measured on a Yanagimoto micro melting apparatus and are uncorrected. NMR spectra were recorded with a Varian Mercury *vx* (300 MHz) or Bruker spectrometer (400 MHz) (^{1}H NMR), at 75 MHz or 100 MHz (^{13}C NMR) in $CDCl_3$, respectively. Chemical shifts were reported in ppm downfield from internal TMS. ^{31}P NMR spectra were recorded at 121 MHz in $CDCl_3$ with 85% H_3PO_4 as the external reference. *J*-values were reported in hertz. Optical rotations were determined at 589 nm (sodium D line) using a Perkin–Elmer 341 MC Polarimeter and $[\alpha]_D$ values are given in units of 10 cm^2 deg^{-1} g^{-1}. Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin–Elmer PE-983 spectrometer with absorption in cm^{-1}. Chiral HPLC was performed by using a SHIMADZU SPD-10A *vp* series instrument with chiral columns (Chiralpak AD-H columns, φ 4.6 × 250 mm, Daicel Chemical Co. Ltd). Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel-coated plates. Flash column chromatography was carried out by using 300–400 mesh silica gel at increased pressure. MBH acetates were prepared using literature method.[9] Racemic amination adducts for chiral HPLC analysis were prepared from the corresponding MBH acetates (0.2 mmol) with phthalimide (0.3 mmol) in the presence of PPh_3 (20–50 mol %) in THF at room temperature (ca. 5 °C).[8a]

4.2. General procedure for the synthesis of chiral trifunctional phosphine amide TPA1

N-Boc-L-proline or *N*-Boc-D-proline (323 mg, 1.5 mmol), DCC (309 mg, 1.5 mmol), and DMAP (12.7 mg, 0.1 mmol) were dissolved in CH_2Cl_2 (10 mL) and the solution was cooled to 0 °C with an ice-water bath and was stirred for 30 min. A solution of (*R*)-(−)-2-(diphenylphoshino)-1,1′-binaphthyl-2′-amine (453 mg, 1.0 mmol) in CH_2Cl_2 (10 mL) was added dropwise over 30 min. When the addition was completed, the reaction mixture was warmed to room temperature and stirred for a further 72 h under an argon atmosphere. Dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. Then, H_2O (5 mL) was added and the product was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed consecutively with 1.0 M $KHSO_4$ (1 × 25 mL), H_2O (1 × 25 mL), 10% $NaHCO_3$ (1 × 25 mL), and H_2O (1 × 25 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was used in the next step without further purification (This residue was purified by flash chromatography on silica gel, to give the catalyst (a*R*,*S*)-*N*-Boc-**TPA1** The above residue was dissolved in a mixed solution of TFA–CH_2Cl_2 (1/4, v/v, 8.0 mL), and the resulting mixture was stirred at room temperature for 5 h. Then, the solution was basified with aqueous ammonia solution (pH > 8) and was extracted with CH_2Cl_2 (3 × 10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: EtOAc/MeOH = 5/1), affording (a*R*,*S*)-**TPA1** or (a*R*,*R*)-**TPA1** as a snow-white solid in 65% or 60% overall yield, respectively.

4.2.1. (2*S*)-*tert*-Butyl 2-((*R*)-2′-(diphenylphosphino)-1,1′-binaphthyl-2-ylcarbamoyl)pyrrolidine-1-carboxylate (a*R*,*S*)-*N*-Boc-TPA1

Yield: 80%; mp 78–80 °C; $[\alpha]_D$ = −22.4 (*c* 0.91, $CHCl_3$); IR (CH_2Cl_2, film) ν 3383, 3053, 2976, 2879, 1698, 1595, 1501, 1390,

1373, 1161, 1118, 819, 743, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.94 (t, J = 7.6 Hz, 2H), 7.82 (d, J = 8.8 Hz, 1H), 7.57–7.52 (m, 2H), 7.35–7.23 (m, 6H), 7.21–6.90 (m, 9H), 6.79 (d, J = 8.0 Hz, 1H), 3.84 (m, 1H), 3.05–2.91 (m, 1H), 2.47–2.35 (m, 1H), 1.83–1.65 (m, 2H), 1.44–1.35 (m, 2H), 1.19 (s, 9H); ^{31}P NMR (121 Hz, $CDCl_3$, 85% H_3PO_4) δ −12.8; ESI-MS m/z 651.3 (M^++1); HRMS (ESI) calcd for $C_{42}H_{40}N_2O_3P$ (M^++1): 651.2777, found: 651.2769.

4.2.2. (2*S*)-*N*-((*R*)-1-(2-(Diphenylphosphino)naphthalen-1-yl)naphthalen-2-yl)pyrrolidine-2-carboxamide (a*R*,*S*)-TPA1

Yield: 65%; mp 109–110 °C; $[\alpha]_D$ = −11.4 (c 2.18, $CHCl_3$); IR (CH_2Cl_2, film) ν 3227, 3053, 2967, 2960, 2868, 2866, 1686, 1620, 1595, 1503, 1455, 1430, 1335, 1265, 1166, 1093, 1026, 820, 749, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.63 (d, J = 8.8 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.93–7.88 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.54 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 7.51–7.44 (m, 1H), 7.30–7.12 (m, 9H), 7.11–7.07 (m, 2H), 7.05–7.00 (m, 2H), 6.86 (t, J = 8.0 Hz, 1H), 6.73 (d, J = 8.8 Hz, 1H), 3.39 (dd, J = 5.6 Hz, 9.2 Hz, 1H), 2.60–2.52 (m, 1H), 2.29–2.21 (m, 1H), 2.03–1.92 (m, 1H), 1.72–1.65 (m, 2H), 1.49–1.35 (m, 2H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 173.2, 140.9, 140.4, 137.8, 137.6, 137.3, 137.1, 136.5, 136.3, 134.1, 133.9, 133.8, 133.6, 133.5, 133.2, 132.6, 132.5, 130.3, 129.9, 129.0, 128.4, 128.3, 128.2, 128.0, 127.93, 127.87, 127.6, 127.0, 126.9, 126.1, 125.8, 125.7, 124.4, 124.3, 124.2, 119.9, 60.8, 46.6, 30.4, 26.0; ^{31}P NMR (121 Hz, $CDCl_3$, 85% H_3PO_4) δ −13.0; ESI-MS m/z 551.2 (M^++1); HRMS (ESI) calcd for $C_{37}H_{32}N_2OP$ (M^++1): 551.2252, found: 551.2248.

4.2.3. (2*R*)-*N*-((*R*)-1-(2-(Diphenylphosphino)naphthalen-1-yl)naphthalen-2-yl)pyrrolidine-2-carboxamide (a*R*,*R*)-TPA2

Yield: 60%; mp 84–85 °C; $[\alpha]_D$ = +20.1 (c 0.53, $CHCl_3$); IR (CH_2Cl_2, film) ν 3390, 3053, 2927, 2868, 1767, 1688, 1503, 1410, 1215, 1166, 910, 744, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.66 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.56 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.34–7.08 (m, 14H), 7.00 (d, J = 8.4 Hz, 1H), 3.32 (dd, J = 3.6 Hz, 9.6 Hz, 1H), 2.28–2.22 (m, 1H), 1.71–1.67 (m, 1H), 1.34–1.26 (m, 2H), 1.17–1.12 (m, 1H), 0.89–0.84 (m, 1H), 0.63–0.52 (m, 1H); ^{31}P NMR (121 Hz, $CDCl_3$, 85% H_3PO_4) δ −14.4; ESI-MS m/z 551.2 (M^++1); HRMS (ESI) calcd for $C_{37}H_{32}N_2OP$ (M^++1): 551.2252, found: 551.2246.

4.3. General procedure for the asymmetric allylic amination of MBH acetates

To a flame-dried Schlenk tube charged with the corresponding MBH acetates **1** (0.2 mmol), phthalimide **2** (0.3 mmol, 44.1 mg), and (a*R*,*S*)-**TPA1** (0.04 mmol, 22.0 mg) was added anhydrous THF (1.0 mL). The reaction mixture was allowed to stir at room temperature (ca. 5 °C) under an argon atmosphere. The reaction was monitored by TLC plate analysis. After the starting substrates were consumed, the solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatography (eluent: EtOAc/petroleum ether = 1/6 to 1/4) to give the corresponding amination adducts **3**.

4.3.1. *N*-[2-Acetyl-1-(4′-nitrophenyl)allyl]-phthalimide 3a[8a]

Yield: 99%; ^1H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J = 9.0 Hz, 2H), 7.83 (dd, J = 3.0 Hz, 5.4 Hz, 2H), 7.74 (dd, J = 3.0 Hz, 5.4 Hz, 2H), 7.56 (d, J = 9.0 Hz, 2H), 6.53 (s, 1H), 6.44 (s, 1H), 5.76 (s, 1H), 2.43 (s, 3H); HPLC condition: Chiralcel AD-H column, λ = 254 nm, eluent: hexane/isopropanol = 75/25, flow rate: 0.7 mL/min, t_{Rmajor} = 29.28 min, t_{Rminor} = 31.12 min; ee% = 52%.

4.3.2. *N*-[2-Acetyl-1-(phenyl)allyl]-phthalimide 3b[8a]

Yield: 75%; $[\alpha]_D$ = +54.3 (c 0.54, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, J = 3.0 Hz, 5.4 Hz, 2H), 7.68 (dd, J = 3.0 Hz, 5.4 Hz, 2H), 7.43–7.25 (m, 5H), 6.37 (d, J = 1.8 Hz, 1H), 6.35 (d, J = 1.8 Hz, 1H), 5.70 (d, J = 2.1 Hz, 1H), 2.41 (s, 3H); HPLC condition: Chiralcel AD-H column, λ = 230 nm, eluent: hexane/isopropanol = 75/25, flow rate: 0.7 mL/min, t_{Rmajor} = 12.63 min, t_{Rminor} = 8.54 min; ee% = 34%.

4.3.3. *N*-[2-Acetyl-1-(3′-nitrophenyl)allyl]-phthalimide 3c

Yield: 79%; $[\alpha]_D$ = −1.7 (c 0.55, $CHCl_3$); IR (CH_2Cl_2, film) ν 3085, 1773, 1718, 1680, 1607, 1522, 1384, 1347, 1108, 1086, 722 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.84 (dd, J = 3.0 Hz, 5.4 Hz, 2H), 7.78–7.70 (m, 3H), 7.54 (t, J = 8.4 Hz, 1H), 6.54 (s, 1H), 6.46 (s, 1H), 5.80 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 167.8, 148.4, 145.1, 139.5, 134.4, 131.5, 129.6, 129.3, 123.6, 123.1, 53. 1, 26.0; EI-MS m/z (relative intensity %): 350 (23), 307 (100), 291 (97), 261 (65), 104 (78); HRMS (EI) Anal. Calcd for $C_{19}H_{14}N_2O_5$: 350.0903. Found: 350.0905; HPLC condition: Chiralcel AD-H column, λ = 254 nm, eluent: hexane/isopropanol = 85/15, flow rate: 1.0 mL/min, t_{Rmajor} = 27.58 min, t_{Rminor} = 33.64 min; ee% = 50%.

4.3.4. *N*-[2-Acetyl-1-(4′-chlorophenyl)allyl]-phthalimide 3d

Yield: 80%; $[\alpha]_D$ = +43.7 (c 0.71, $CHCl_3$); IR (CH_2Cl_2, film) ν 3058, 2924, 2854, 1774, 1719, 1686, 1491, 1384, 1356, 1119, 1015, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, J = 2.8 Hz, 5.6 Hz, 2H), 7.70 (dd, J = 2.8 Hz, 5.6 Hz, 2H), 7.35–7.25 (m, 4H), 6.36 (s, 2H), 5.72 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 167.9, 145.9, 136.0, 134.1, 134.0, 132.6, 131.7, 130.1, 128.9, 123.4, 53.4, 26.1; EI-MS m/z (relative intensity %): 339 (9), 296 (100), 262 (38), 192 (15), 149 (13); HRMS (EI) Anal. Calcd for $C_{19}H_{14}NO_3Cl$: 339.0662. Found: 339.0665; HPLC condition: Chiralcel AD-H column, λ = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.5 mL/min, t_{Rmajor} = 34.02 min, t_{Rminor} = 29.01 min; ee% = 36%.

4.3.5. *N*-[2-Acetyl-1-(3′-chlorophenyl)allyl]-phthalimide 3e

Yield: 75%; $[\alpha]_D$ = +127.4 (c 0.85, $CHCl_3$); IR (CH_2Cl_2, film) ν 3058, 2925, 2854, 1773, 1715, 1681, 1468, 1385, 1364, 1113, 1082, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 2.8 Hz, 5.6 Hz, 2H), 7.71 (dd, J = 2.8 Hz, 5.6 Hz, 2H), 7.39 (s, 1H), 7.37–7.27 (m, 3H), 6.39 (s, 1H), 6.36 (s, 1H), 5.74 (d, J = 0.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 167.9, 145.7, 139.5, 134.5, 134.1, 131.7, 129.9, 129.2, 128.7, 128.3, 126.8, 123.4, 53.4, 26.0; EI-MS m/z (relative intensity %): 339 (10), 296 (100), 262 (28), 192 (8), 149 (14); HRMS (EI) Anal. Calcd for $C_{19}H_{14}NO_3Cl$: 339.0662. Found: 339.0663; HPLC condition: Chiralcel AD-H column, λ = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 19.21 min, t_{Rminor} = 17.02 min; ee% = 44%.

4.3.6. *N*-[2-Acetyl-1-(2′-chlorophenyl)allyl]-phthalimide 3f

Yield: 85%; $[\alpha]_D$ = +49.3 (c 0.5, $CHCl_3$); IR (CH_2Cl_2, film) ν 3065, 2925, 2854, 1774, 1715, 1681, 1468, 1387, 1365, 1109, 1039, 723 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 2.8 Hz, 5.2 Hz, 2H), 7.71 (dd, J = 2.8 Hz, 5.2 Hz, 2H), 7.42–7.35 (m, 2H), 7.27–7.22 (m, 2H), 6.78 (s, 1H), 6.38 (s, 1H), 5.69 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 167.9, 144.5, 134.9, 134.3, 134.1, 133.6, 132.6, 131.7, 129.8, 129.3, 128.7, 126.9, 123.6, 123.4, 51.4, 26.0; EI-MS m/z (relative intensity %): 339 (3), 304 (100), 296 (7), 157 (7), 149 (6); HRMS (EI) Anal. Calcd for $C_{19}H_{14}NO_3Cl$: 339.0662. Found: 339.0665; HPLC condition: Chiralcel AD-H column, λ = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 18.71 min, t_{Rminor} = 14.97 min; ee% = 78%.

4.3.7. *N*-[2-Acetyl-1-(4′-bromophenyl)allyl]-phthalimide 3g

Yield: 75%; $[\alpha]_D$ = +73.0 (*c* 0.1, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 3060, 2925, 2854, 1771, 1714, 1681, 1488, 1384, 1363, 1114, 1012, 721 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.80 (dd, *J* = 3.2 Hz, 4.8 Hz, 2H), 7.70 (dd, *J* = 3.2 Hz, 4.8 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.37 (s, 1H), 6.35 (s, 1H), 5.72 (s, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.0, 167.9, 145.8, 136.5, 134.1, 131.8, 131.6, 130.3, 128.9, 123.3, 122.1, 53.4, 26.0; EI-MS *m/z* (relative intensity %): 383 (9), 340 (70), 262 (100), 193 (16), 130 (49); HRMS (EI) Anal. Calcd for $C_{19}H_{14}NO_3Br$: 383.0157. Found: 383.0158; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 25.13 min, t_{Rminor} = 21.53 min; ee% = 37%.

4.3.8. *N*-[2-Acetyl-1-(4′-fluorophenyl)allyl]-phthalimide 3h

Yield: 78%; $[\alpha]_D$ = +47.4 (*c* 0.31, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 3058, 2925, 2854, 1771, 1714, 1606, 1468, 1385, 1363, 1113, 1088, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (dd, *J* = 2.8 Hz, 5.6 Hz, 2H), 7.70 (dd, *J* = 2.8 Hz, 5.6 Hz, 2H), 7.39 (dd, *J* =1.2 Hz, 8.8 Hz, 2H), 7.03 (t, *J* = 8.8 Hz, 2H), 6.37 (s, 1H), 6.35 (s, 1H), 5.71 (d, *J* = 1.6 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.2, 168.0, 162.4 (d, $^1J_{C-F}$ = 245.6 Hz), 146.3, 134.1, 133.3 (d, $^4J_{C-F}$ = 3.3 Hz), 131.7, 130.5 (d, $^3J_{C-F}$ = 8.2 Hz); 128.7, 123.4, 115.6 (d, $^2J_{C-F}$ = 21.4 Hz), 53.4, 26.1; EI-MS *m/z* (relative intensity %): 323 (8), 281 (16), 280 (100), 176 (26), 133 (19); HRMS (EI) Anal. Calcd for $C_{19}H_{14}NO_3F$: 323.0958. Found: 323.0960; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 23.42 min, t_{Rminor} = 19.01 min; ee% = 36%.

4.3.9. *N*-[2-Acetyl-1-(4′-trifluoromethylphenyl)allyl]-phthalimide 3i

Yield: 90%; $[\alpha]_D$ = +79.0 (*c* 0.5, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 2926, 1774, 1716, 1682, 1468, 1386, 1325, 1167, 1125, 1068, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.83 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.72 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 6.41 (s, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.9, 167.9, 145.5, 141.4, 134.2, 131.6, 130.2 (q, $^2J_{C-F}$ = 32.6 Hz), 129.2, 129.0, 125.6 (q, $^3J_{C-F}$ = 3.6 Hz), 123.9 (q, $^1J_{C-F}$ = 270.6 Hz), 123.4, 53.4, 26.0; EI-MS *m/z* (relative intensity %): 373 (6), 330 (100), 304 (14), 183 (12), 104 (6); HRMS (EI) Anal. Calcd for $C_{20}H_{14}NO_3F_3$: 373.0926. Found: 373.0929; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 90/10, flow rate: 1.0 mL/min, t_{Rmajor} = 20.11 min, t_{Rminor} = 18.68 min; ee% = 50%.

4.3.10. *N*-[2-Acetyl-1-(4′-cyanophenyl)allyl]-phthalimide 3j

Yield: 91%; $[\alpha]_D$ = +49.7 (*c* 0.49, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 3068, 2924, 2854, 2229 (C≡N), 1773, 1719, 1610, 1467, 1384, 1364, 1103, 1068, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.83 (dd, *J* = 3.2 Hz, 5.2 Hz, 2H), 7.73 (dd, *J* = 3.2 Hz, 5.2 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.47 (s, 1H), 6.42 (s, 1H), 5.74 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 197.8, 167.7, 145.1, 142.6, 134.3, 132.4, 131.5, 129.32, 129.28, 123.5, 118.4, 112.0, 52.3, 26.0; EI-MS *m/z* (relative intensity %): 331 (7), 288 (17), 287 (100), 140 (11), 104 (7); HRMS (EI) Anal. Calcd for $C_{20}H_{14}N_2O_3$: 330.1004. Found: 330.0996; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 38.64 min, t_{Rminor} = 54.75 min; ee% = 58%.

4.3.11. *N*-[2-Acetyl-1-(4′-methylphenyl)allyl]-phthalimide 3k

Yield: 75%; $[\alpha]_D$ = +55.0 (*c* 0.30, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 2924, 2853, 1773, 1736, 1712, 1686, 1677, 1467, 1384, 1351, 1105, 1019, 716 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.80 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.68 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.34 (s, 1H), 6.33 (s, 1H), 5.72 (d, *J* = 1.6 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.4, 168.1, 146.5, 137.8, 134.5, 133.9, 131.9, 129.4, 128.7, 128.5, 123.3, 53.8, 26.2, 21.1; EI-MS *m/z* (relative intensity %): 319 (11), 304 (27), 276 (100), 172 (63), 129 (22); HRMS (EI) Anal. Calcd for $C_{20}H_{17}NO_3$: 319.1208. Found: 319.1210; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.7 mL/min, t_{Rmajor} = 22.04 min, t_{Rminor} = 18.54 min; ee% = 45%.

4.3.12. *N*-[2-Acetyl-1-(3′-methylphenyl)allyl]-phthalimide 3l

Yield: 70%; $[\alpha]_D$ = +153.0 (*c* 0.49, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 2926, 2856, 1773, 1736, 1718, 1697, 1677, 1491, 1385, 1351, 1000, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.69 (dd, *J* = 3.2 Hz, 5.6 Hz, 2H), 7.21 (dd, *J* = 7.2 Hz, 13.6 Hz, 2H), 7.19 (s, 1H) 7.12 (d, *J* = 7.2 Hz, 2H), 6.34 (s, 1H), 6.32 (s, 1H), 5.70 (d, *J* = 1.2 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 198.3, 168.1, 146.5, 138.4, 137.4, 133.9, 131.8, 129.2, 128.9, 128.8, 128.5, 125.6, 123.3, 54.0, 26.1, 21.4; EI-MS *m/z* (relative intensity %): 319 (18), 304 (24), 276 (100), 172 (37), 129 (23); HRMS (EI) Anal. Calcd for $C_{20}H_{17}NO_3$: 319.1208. Found: 319.1207; HPLC condition: Chiralcel AD-H column, *λ* = 230 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.5 mL/min, t_{Rmajor} = 27.71 min, t_{Rminor} = 19.54 min; ee% = 43%.

4.3.13. *N*-[2-Propyl-1-(4′-nitrophenyl)allyl]-phthalimide 3m

Yield: 77%; $[\alpha]_D$ = +27.5 (*c* 1.01, $CHCl_3$); IR (CH_2Cl_2, film) *ν* 3082, 1773, 1735, 1718, 1697, 1608, 1521, 1385, 1351, 1107, 1086, 719 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ* 8.21 (d, *J* = 8.8 Hz, 2H) 7.84 (dd, *J* = 2.8 Hz, 5.6 Hz, 2H), 7.74 (dd, *J* = 2.8 Hz, 5.6 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 6.43 (s, 1H), 5.72 (d, *J* = 0.8 Hz, 1H), 2.79–2.85 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 200.4, 167.8, 147.6, 144.7, 144.6, 134.4, 131.6, 129.6, 128.1, 123.9, 123.6, 53.4, 31.0, 8.1; EI-MS *m/z* (relative intensity %): 364 (8), 335 (44), 307 (100), 291 (20), 104 (47); HRMS (EI) Anal. Calcd for $C_{20}H_{16}N_2O_5$: 364.1059. Found: 364.1060; HPLC condition: Chiralcel AD-H column, *λ* = 254 nm, eluent: hexane/isopropanol = 80/20, flow rate: 0.5 mL/min, t_{Rmajor} = 64.35 min, t_{Rminor} = 60.56 min; ee% = 54%.

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