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Enantioselective allylic substitution of Morita–Baylis–Hillman adducts catalyzed by planar chiral [2.2]paracyclophane monophosphines

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Abstract—Planar chiral [2,2]cyclophane monophosphines are efficient catalyst in the reaction of Morita–Baylis–Hillman adducts with phthalimide. The corresponding allylic substituted products were afforded in high yields and in good to moderate ee.

1. Introduction

The Morita–Baylis–Hillman reaction is one of the most efficient protocols for the synthesis of α-methylene-β-hydroxy-carbonyl compounds, which are versatile intermediates for a variety of synthetically useful compounds.[1,2] Much effort has been devoted to asymmetric Morita–Baylis–Hillman reactions and applications of the reaction products in natural products synthesis. Only a few reports have focused on the enantioselective transformation of Morita–Baylis–Hillman products via direct substitution reactions, chiral tertiary amines and chiral Pd-complexes being the catalyst studied.[3,4] Organophosphine-catalyzed allylic amination and allylic alkylation of MBH adducts have also been reported.[5] When (*R*)-Cl–MeOBIPHEP was used as a catalyst, reaction of the MBH adduct, obtained from *p*-nitrobenzaldehyde and methyl acrylate, with phthalimide gave the allylic substituted product in 80% yield and in 56% ee. However, only one example was given.[5a] To date, no asymmetric version of this transformation has been reported using chiral monophosphines as catalysts. Recently, we synthesized a series of planar chiral [2.2]paracyclophane monophosphines using a chiral palladacycle as a resolving reagent and applied them in asymmetric catalysis.[6] The role of planar chirality in [2.2]paracyclophane has been described.[6,7] To further explore the applications of these planar chiral cyclophane monophosphines in asymmetric catalysis, we studied the use of these organophosphines as catalysts. Herein, we report the application of planar chiral [2.2]paracyclophane monophosphines as organocatalysts in the asymmetric allylic substitution of MBH adducts.

2. Results and discussion

Using MBH adduct **1a** as a substrate and phthalimide **2** as a pronucleophile, the efficiency of cyclophane monophosphines (*R*)-**4** was tested in THF (Eq. 1), and the results are compiled in Table 1.

Table 1. Effect of catalysts on the allylic amination of MBH adduct[a]

Entry	Catalyst	Time (h)	Yield[b] (%)	ee[c] (%)
1	(*R*)-**4a**	62	90	60
2	(*R*)-**4b**	48	95	15
3	(*R*)-**4c**	72	Trace[d]	—
4	(*R*)-**4d**	48	86	8
5	(*R*)-**4e**	24	95	71
6	(*R*)-**4f**	36	75	36
7[e]	(*R*)-**4e**	24	62	69
8[f]	(*R*)-**4e**	24	95	71

[a] Molecular ratio: **1a**/**2**/monophosphine = 100:200:20. Reaction run in THF at rt.
[b] Isolated yield.
[c] Determined by chiral HPLC.
[d] Run at 50 °C.
[e] 5 mol % of (*R*)-**4e** was used.
[f] 50 mol % of (*R*)-**4e** was used.

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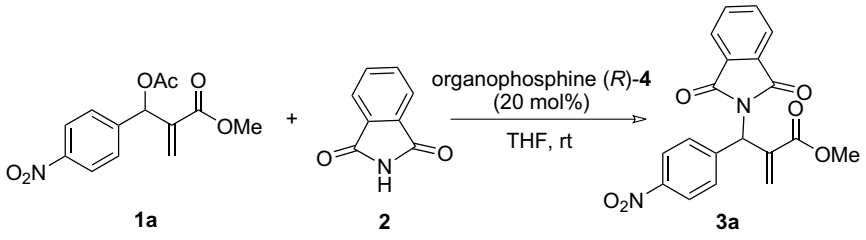
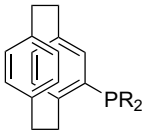
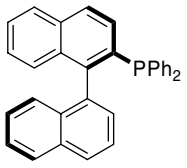




a: R = C_6H_5
b: R = 4-$MeOC_6H_4$
c: R = 4-$CF_3C_6H_4$
d: R = 3,5-$(CH_3)_2C_6H_3$
e: R = c-C_6H_{11}
f: R = i-Pr

It is not surprising that all organophosphines (*R*)-**4** showed catalytic activity; the allylic substituted products being provided in high yields with regiospecificity, except **4c** with trifluoromethyl as a substituent at the *para*-position of the phenyl rings (entry 3) because of electronic reasons. Regarding enantioselectivity, monophosphine **4e** with two cyclohexane rings on the P atom was the best, affording product **3a** in 71% ee and in 95% yield (entry 5) while organophosphine **4a** gave the product in 60% ee though the yield was high (entry 1). However, product **3a** was obtained in only 36% ee using **4f** with two isopropyl groups on the P atom as a catalyst (entry 6). Another monophosphine, (*R*)-MOP **5**,[8] was also tested in the reaction. Product **3a** was provided in 15% yield and in 25% ee. It can also be seen from Table 1 that using 50 mol % of catalyst gave the same results as that using 20 mol % (entry 8) while a decrease in the catalyst loading from 20 mol % to 5 mol % influenced the enantioselectivity little (entry 7).



Using monophosphine **4e**, the effect of different solvents was investigated (Table 2). The results showed that the reactions in DME, THF and dioxane were completed in 24 h, giving product **3a** in higher yields and ee values (entries 5, 6, and 8) while those in other solvents needed more time to complete and provided the product in lower yields and in lower ee (entries 1–4 and 7).

Other pronucleophiles were also used in this phosphine-catalyzed allylic substitution reaction. However, only low yields were given in the reaction of **1a** with *p*-$MeOC_6H_4OH$ or $TsNH_2$ in the presence of 20 mol % of organophosphine (*R*)-**4a**.

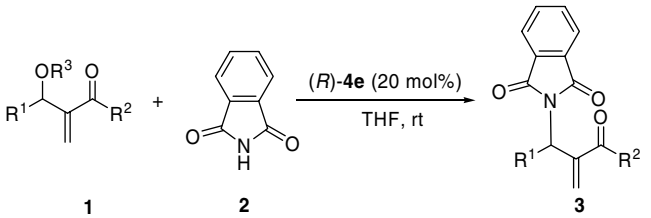
To assess the feasibility of planar chiral [2.2]paracyclophane monophosphine in this reaction, a series of MBH adducts **1** were prepared[5b,9–13] and used in this chiral phosphine-catalyzed allylic substitution reaction (Eq. 2, Table 3).

Table 2. Effect of the solvents on the allylic amination of MBH adduct **1a** with **2**[a]

Entry	Solvent	Time (h)	Yield[b] (%)	ee[c] (%)
1	CH_3CN	48	38	20
2	Toluene	48	49	46
3	CH_2Cl_2	48	54	30
4	*t*-BuOH	48	49	29
5	DME	24	92	72
6	Dioxane	24	98	61
7	Et_2O	48	49	48
8	THF	24	95	71

[a] Molecular ratio: **1a**/**2**/monophosphine = 100:200:20. Reaction run at rt.
[b] Isolated yield.
[c] Determined by chiral HPLC.

The reactions of MBH adducts derived from aromatic aldehydes gave higher yields than those derived from aliphatic ones (entries 1–9 and 12–13 vs entries 10–11). Also the reactions of MBH adducts derived from aromatic aldehydes and acrylates provided the products with better ee than those derived from aliphatic ones (entries 1–9 vs entries 10–11) or derived from methyl vinylketones (entries 1–9 vs entries 12–13). Change of the leaving group R_3 from OAc to OBoc has little influence on the results (entry 4 vs entry 5). The highest ee (71%) and yield (95%) were provided when MBH acetate **1a** was used (entry 1).



Finally, 2-trimethylsilyloxy furan **6** was investigated as a pronucleophile under the above reaction conditions. Corresponding substituted product **7** was afforded in high yield, high diastereoselectivity but moderate enantioselectivity when MBH adduct **1a** was reacted with **6** using 20 mol % of (*R*)-**4e** as catalyst (Eq. 3).

Table 3. Allylic amination of MBH acetates[a]

Entry	Substrate **1**			Yield[b] (%)	ee[c] (%)
	R^1	R^2	R^3		
1	**b**, 4-$NO_2C_6H_4$	OMe	Ac	95	71
2	**ba**, 4-$NO_2C_6H_4$	OEt	Ac	78	29
3	**bb**, 4-$NO_2C_6H_4$	OBu^t	Boc	82	21
4	**a**, C_6H_5	OMe	Ac	80	52
5	**aa**, C_6H_5	OMe	Boc	78	52
6	**ab**, C_6H_5	OEt	Ac	68	66
7	**ac**, C_6H_5	OBu^t	Boc	75	44
8	**c**, 4-ClC_6H_4	OMe	Ac	85	37
9	**d**, 4-$MeOC_6H_4$	OEt	Boc	60	48
10	**e**, Et	OMe	Ac	44	9
11	**f**, Pr^i	OMe	Ac	32	11
12	**g**, C_6H_5	Me	Ac	82	17
13	**h**, 4-$NO_2C_6H_4$	Me	Ac	85	10

[a] Molecular ratio: **1**/**2**/(*R*)-**4e** = 100:200:20. Reaction run in THF at rt.
[b] Isolated yield.
[c] Determined by chiral HPLC.

3. Conclusion

In summary, a planar chiral [2.2]paracyclophane monophosphine has been successfully applied as an organocatalyst in asymmetric allylic amination of MBH adducts. Up to 71% ee was achieved using (*R*)-**4e** as a catalyst, which represents one of the best results in organic molecule-catalyzed allylic amination reactions of MBH adducts.[3a,b,5b] These results also reflect the role of planar chirality in [2,2]cyclophane.[6,14] Further applications of planar chiral [2.2]paracyclophane monophosphine in asymmetric catalysis are in progress.

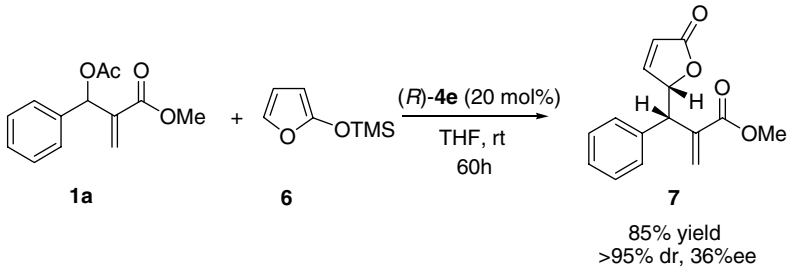
4. Experimental

4.1. General

All reactions were performed under an atmosphere of argon using oven-dried glassware. Solvents were treated prior to use according to the standard method. ^{1}H NMR spectra were recorded in $CDCl_3$ or C_6D_6 at room temperature. Chemical shifts are given in parts per million relative to TMS as an internal standard. Optical rotations were measured with a thermally jacketed 10 cm cell at 25 °C (concentration *c* given as g/100 mL). IR spectra were measured in cm^{-1}. Ee values were determined by chiral HPLC. The commercially available reagents were used as received without further purification. Chiral [2.2]paracyclophane monophosphines (*R*)-**4**[6] and Morita–Baylis–Hillman adducts **1**[5b,9–13] were prepared using literature procedures.

4.2. General procedure for preparation of Morita–Baylis–Hillman adducts

The mixture of aldehyde (50 mmol), activated alkene (75 mmol) and DABCO (10 mmol) was stirred for 3 days. Then pyridine (150 mmol) and dichloromethane (100 mL) were added under stirring. The mixture was cooled to 0 °C and acetyl chloride was added dropwise. Then the reaction mixture was stirred for 4 h at 0 °C. It was quenched with 1 N HCl, and the aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic layer was washed with water (2 × 50 mL) and $NaHCO_3$ (2 × 50 mL), dried over Na_2SO_4. Removal of the solvent in vacuum and purification by column chromatography (ethyl acetate/petroleum ether = 1:5–1:10) gave the product.



(3)

4.2.1. Methyl 2-[(*tert*-butoxycarbonyloxy)(phenyl)methyl]-acrylate 1aa. Yield: 46%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.32 (m, 5H), 6.48 (s, 1H), 6.41 (s, 1H), 5.91 (s, 1H), 3.71 (s, 3H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 165.3, 152.3, 139.6, 137.4, 128.4, 127.6, 125.8, 82.6, 75.7, 52.0, 27.7; ESI-MS *m*/*z*: 315 [M^++Na^+], 347 [M^++MeOH+Na^+]. IR (KBr): 2981, 1747, 1439, 1370, 1278, 1158, 1086, 964, 883, 703 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{16}H_{20}O_5Na^+$: 315.1208. Found: 315.1203.

4.2.2. *t*-Butyl 2-[acetoxy(phenyl)methyl]acrylate 1ac. Yield: 55%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.31 (m, 5H), 6.42 (s, 1H), 6.33 (s, 1H), 5.79 (s, 1H), 1.46 (s, 9H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.1, 152.4, 128.3, 127.8, 124.6, 82.5, 81.4, 76.1, 27.8, 27.7; EI-MS *m*/*z* (relative intensity %): 222 (15), 204 (21), 132 (28), 105 (23), 57 (100). IR (KBr): 2980, 1747, 1369, 1279, 1152, 1086, 968, 883, 756, 700 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{19}H_{26}O_5Na^+$: 357.1677. Found: 357.1672.

4.2.3. *t*-Butyl 2-[acetoxy(4′-nitrophenyl)methyl]acrylate 1bb. Yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H), 6.48 (s, 1H), 6.38 (s, 1H), 5.89 (s, 1H), 1.46 (s, 9H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.6, 152.1, 147.7, 145.2, 139.9, 128.5, 125.7, 123.6, 83.2, 81.9, 74.8, 27.9, 27.4; EI-MS *m*/*z* (relative intensity %): 205 (6), 160 (9), 57 (100), 41 (22). IR (KBr): 2981, 1743, 1369, 1322, 1086, 968, 883, 756, 700 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{19}H_{25}NO_7Na^+$: 402.1523. Found: 402.1525.

4.2.4. Ethyl 2-[(*tert*-butoxycarbonyloxy)(4′-methoxyphenyl)methyl]acrylate 1d. Yield: 18%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.7$ Hz, 2H), 6.42 (s, 1H), 6.38 (s, 1H), 5.90 (s, 1H), 4.16–4.12 (m, 2H), 3.79 (s, 3H), 1.46 (s, 9H), 1.22 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.9, 159.6, 152.4, 139.9, 129.5, 129.2, 124.8, 113.7, 82.4, 75.6, 60.8, 55.2, 27.7, 14.0; ESI-MS *m*/*z*: 359 [M^++Na^+], 391 [M^++MeOH+-Na^+]. IR (KBr): 2981, 1747, 1613, 1515, 1251, 1159, 1034, 966, 885 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{18}H_{24}O_6Na^+$: 359.1468. Found: 359.1465.

4.3. General procedure for asymmetric allylic nucleophilic substitution of Morita–Baylis–Hillman adducts

To a reaction vessel charged with substrate **1** (0.5 mmol), phthalimide **2** or 2-trimethylsilyloxy furan **6** (1 mmol), and (*R*)-[2.2]paracyclophane monophosphine **4e** (0.1 mmol), was added THF (1.6 mL). The reaction was allowed to stir at room temperature until complete consumption of substrate, at that point the reaction mixture was evaporated onto silica gel and the product was purified by silica gel chromatography.

4.3.1. *N*-[(2-Methoxycarbonyl-1-phenyl)allyl]-phthalimide 3a.[5a] Yield: 80%; ee: 52% by HPLC Chiralcel OD-H column with hexane/isopropanol = 70:30, flow rate = 0.6 mL/min, $t_{R1} = 7.29$ min, $t_{R2} = 13.40$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.81 (m, 2H), 7.72–7.69 (m, 2H), 7.45–7.30 (m, 5H), 6.56 (s, 1H), 6.39 (s, 1H), 5.63 (s, 1H), 3.70 (s, 3H); ESI-MS *m*/*z*: 322 [M^++1], 339 [M^++H_2O].

4.3.2. *N*-[(2-Ethoxycarbonyl-1-phenyl)allyl]-phthalimide 3ab. Yield: 68%; ee: 66% by HPLC Chiralpak AD-H column with hexane/isopropanol = 87:13, flow rate = 0.7 mL/min, $t_{R1} = 19.39$ min, $t_{R2} = 22.14$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (m, 2H), 7.70 (m, 2H), 7.45–7.30 (m, 5H), 6.56 (s, 1H), 6.37 (s, 1H), 5.80 (s, 1H), 4.16–4.10 (m, 2H), 1.14 (t, $J = 6.8$ Hz, 3H); EI-MS *m*/*z* (relative intensity %): 335 (M^++5), 289 (100), 261 (90), 233 (55).

4.3.3. *N*-[(2-*tert*-Butoxycarbonyl-1-phenyl)allyl]-phthalimide 3ac. Yield: 75%; ee: 44% by HPLC Chiralpak AD-H column with hexane/isopropanol = 85:15, flow rate = 0.6 mL/min, $t_{R1} = 7.46$ min, $t_{R2} = 11.23$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.70 (m, 4H), 7.46–7.31 (m, 5H), 6.46 (s, 1H), 6.31 (s, 1H), 5.44 (s, 1H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.8, 164.7, 139.2, 137.4, 134.0, 131.8, 128.8, 128.5, 128.0, 123.3, 81.4, 54.9, 27.8; EI-MS *m*/*z* (relative intensity %): 307 (23), 289 (80), 261 (100), 233 (37). IR (KBr): 2978, 1721, 1386, 1251, 1145, 721, 531 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{22}H_{21}NO_4$-Na^+: 386.1362. Found: 386.1363.

4.3.4. *N*-[2-Methoxycarbonyl-1-(4′-nitrophenyl)allyl]-phthalimide 3b.[5a] Yield: 95%; ee: 71% HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.7 mL/min, $t_{R1} = 19.50$ min, $t_{R2} = 23.43$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, $J = 8.9$ Hz, 2H), 7.85 (m, 2H), 7.75 (m, 2H), 7.60 (d, $J = 9.0$ Hz, 2H), 6.63 (s, 1H), 6.52 (s, 1H), 5.66 (s, 1H), 3.72 (s, 3H); EI-MS *m*/*z* (relative intensity %): 367 (M^+ <1), 334 (7), 147 (50), 104 (57), 76 (100), 50 (39).

4.3.5. *N*-[2-(Ethoxycarbonyl)-1-(4′-nitrophenyl)allyl]-phthalimide 3ba. Yield: 78%; ee: 29% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.7 mL/min, $t_{R1} = 17.29$ min, $t_{R2} = 20.88$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (d, $J = 8.9$ Hz, 2H), 7.89–7.75 (m, 4H), 7.63 (d, $J = 8.5$ Hz, 2H), 6.64 (s, 1H), 6.52 (s, 1H), 5.63 (m, 1H), 4.18–4.14 (m, 2H), 1.18 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 165.0, 147.5, 144.2, 136.5, 134.4, 134.3, 131.5, 129.7, 123.8, 123.6, 61.4, 53.7, 13.9; MALDI-MS *m*/*z*: 403 [M^++Na^+]; IR (KBr): 2925, 1717, 1521, 1348, 856, 721, 531 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{20}H_{16}N_2O_6Na^+$: 403.09000. Found: 403.09006.

4.3.6. *N*-[2-*tert*-Butoxycarbonyl-1-(4′-nitrophenyl)allyl]-phthalimide 3bb. Yield: 82%; ee: 21% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.7 mL/min, $t_{R1} = 13.63$ min, $t_{R2} = 21.96$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, $J = 8.9$ Hz, 2H), 7.87 (m, 2H), 7.75 (m, 2H), 7.62 (d, $J = 8.7$ Hz, 2H), 6.52 (s, 1H), 6.44 (s, 1H), 5.50 (s, 1H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.5, 164.0, 147.4, 144.5, 137.9, 134.4, 131.5, 129.7, 128.3, 123.6, 81.9, 53.9, 27.7; EI-MS *m*/*z* (relative intensity %): 334 (15), 306 (12), 188 (7), 57 (100). IR (KBr): 2928, 1727, 1523, 1348, 1148, 722 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{22}H_{20}N_2O_6Na^+$: 431.1216. Found: 431.1214.

4.3.7. *N*-[2-Methoxycarbonyl-1-(4′-chlorophenyl)allyl]-phthalimide 3c. Yield: 85%; ee: 37% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.6 mL/min, $t_{R1} = 8.48$ min, $t_{R2} = 12.10$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.71 (m, 4H), 7.40–7.27 (m, 4H), 6.57 (s, 1H), 7.37 (s, 1H), 5.64 (s, 1H), 3.70 (s, 3H); ESI-MS *m*/*z*: 499 [M^++MeOH+Na^+]. IR (KBr): 2924, 1724, 1492, 1385, 1089, 723 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{19}H_{14}NO_4ClNa^+$: 378.0509. Found: 378.0504.

4.3.8. *N*-[2-Ethoxycarbonyl-1-(4′-methoxyphenyl)allyl]-phthalimide 3d. Yield: 60%; ee: 48% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.6 mL/min, $t_{R1} = 10.98$ min, $t_{R2} = 14.28$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83–7.68 (m, 4H), 7.39 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.53 (s, 1H), 6.32 (s, 1H), 5.59 (s, 1H), 4.14–4.10 (m, 2H), 1.14 (t, $J = 7.0$ Hz, 3H); ESI-MS *m*/*z*: 388 [M^++Na^+], 420 [M^++MeOH+Na^+]. IR (KBr): 2962, 1514, 1259, 1028, 716 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{21}H_{19}NO_5$-Na^+: 388.1144. Found: 388.1155.

4.3.9. *N*-[(2-Methoxycarbonyl-1-ethyl)allyl]-phthalimide 3e. Yield: 44%; ee: 9% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.6 mL/min, $t_{R1} = 6.92$ min, $t_{R2} = 8.33$ min; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.81 (m, 2H), 7.73–7.69 (m, 2H), 6.54 (s, 1H), 6.08 (s, 1H), 5.18–5.12 (m, 1H), 3.73 (s, 3H), 0.97–0.83 (m, 5H); ESI-MS *m*/*z*: 296 [M^++Na^+], 328 [M^++MeOH+Na^+]. IR (KBr): 2965, 1725, 1386, 1260,

722 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{15}H_{15}NO_4Na^+$: 296.0902. Found: 296.0893.

4.3.10. *N*-[(2-Methoxycarbonyl-1-*iso*-propyl)allyl]-phthalimide 3f. Yield: 95%; ee: 60% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.6 mL/min, $t_{R1} = 6.08$ min, $t_{R2} = 7.33$ min; ^1H NMR (300 MHz, $CDCl_3$) δ 7.86–7.69 (m, 4H), 6.65 (s, 1H), 6.31 (s, 1H), 4.98 (m, 1H), 3.76 (s, 3H), 1.00 (d, J = 6.2 Hz, 3H), 0.88 (d, J = 8.0 Hz, 3H); ESI-MS m/z: 310 [M^++Na^+], 342 [M^++MeOH+Na^+]. IR (KBr): 3206, 1726, 1385, 1052, 717, 548 cm^{-1}; HRMS (MALDI): Anal. Calcd for $C_{16}H_{17}NO_4Na^+$: 310.1055. Found: 310.1050.

4.3.11. *N*-[(2-Acetyl-1-phenyl)allyl]-phthalimide 3g.[5a] Yield: 82%; ee: 17% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.7 mL/min, $t_{R1} = 20.21$ min, $t_{R2} = 31.77$ min; ^1H NMR (300 MHz, $CDCl_3$) δ 7.81–7.79 (m, 2H), 7.70–7.67 (m, 2H), 7.38–7.35 (m, 5H), 6.34 (s, 1H), 5.70 (s, 1H), 2.40 (s, 3H).

4.3.12. *N*-[2-Acetyl-1-(4′-nitrophenyl)allyl]-phthalimide 3h.[5a] Yield: 85%; ee: 10% by HPLC Chiralcel OD-H column with hexane/isopropanol = 85:15, flow rate = 0.7 mL/min, $t_{R1} = 29.97$ min, $t_{R2} = 38.25$ min; ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 8.8 Hz, 2H), 7.85–7.71 (m, 4H), 7.56 (d, J = 8.6 Hz, 2H), 6.51 (s, 1H), 6.43 (s, 1H), 5.75 (s, 1H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.9, 144.6, 134.3, 131.4, 129.5, 123.9, 123.6, 64.4, 53.1.

4.3.13. 2-[(5-Oxo-2,5-dihydro-furan-2-yl)-phenyl methyl]-acrylic acid methyl ester 7.[5b] Yield: 59%; dr >95%; ee: 29% by HPLC Chiralcel OD column with hexane/isopropanol = 70:30, flow rate = 0.7 mL/min, $t_{R1} = 14.37$ min, $t_{R2} = 20.21$ min; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.29 (m, 6H), 6.50 (m, 1H), 6.10 (m, 1H), 5.93 (s, 1H), 5.55 (d, J = 8.7 Hz, 1H), 4.12 (d, J = 8.6 Hz, 2H), 3.69 (s, 3H). ^{13}C NMR($CDCl_3$, 75 MHz) δ 172.5, 166.5, 155.5, 138.0, 137.8, 128.8, 128.3, 127.7, 127.5, 121.8, 83.2, 52.1, 49.9.

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