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Asymmetric Organocatalytic Allylic Substitution of Morita–Baylis–Hillman Carbonates with Allylamines for the Synthesis of 2,5-Dihydropyrroles

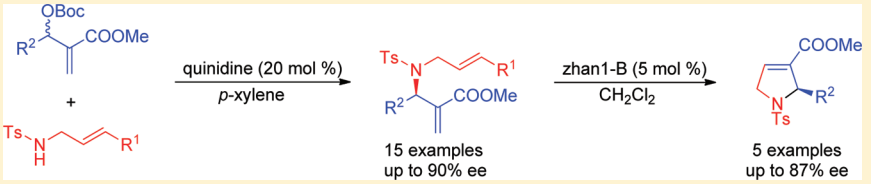
Wangsheng Sun,[†] Xiaozhou Ma,[†] Liang Hong,*[,†] and Rui Wang*[,†,‡]

[†]Key Laboratory of Preclinical Study for New Drugs of Gansu Province, State Key Laboratory of Applied Organic Chemistry and Institute of Biochemistry and Molecular Biology, Lanzhou University, Lanzhou, 730000 China

[‡]State Key Laboratory of Chiroscience, and Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Kowloon, Hong Kong

Supporting Information

ABSTRACT:



The asymmetric allylic substitution reaction of MBH carbonates with allylamines has been developed, which affords *N*-allyl-*β*-amino-α-methylene esters in high yields and enantioselectivities. After a subsequent ring-closure metathesis of the products, a series of optically active 2,5-dihydropyrroles could be obtained smoothly in high yields without any loss of enantioselectivity. Finally, a tentative mechanism for rationalization of the reaction has been proposed.

INTRODUCTION

2,5-Dihydropyrroles are a privileged structural core of bioactive natural and unnatural products, which exhibit important biological and medicinal activity (Figure 1).[1−8] For this reason, the development of methods allowing for efficient and facile construction of 2,5-dihydropyrroles is an important goal in modern organic chemistry that has received considerable attention over the years.[9−17] Over the past decade, *N*-allyl-*β*-amino-α-methylene esters were recognized as the key intermediates for the preparation of 2,5-dihydropyrroles through transition metal-catalyzed ring-closure metathesis (RCM) reactions.[18−21] Construction of the *N*-allyl-*β*-amino-α-methylene ester skeletons by N-allylation of aza-Baylis–Hillman adducts has been documented in the literature (path a, Scheme 1).[22−25] However, to the best of our knowledge, there are no reports on the direct enantioselective route to these complex molecules.

Given the importance of these valuable 2,5-dihydropyrroles and their potential biological properties as well as the lack of efficient asymmetric methods for the preparation of these important agents, the development of new methodologies for their preparation in an enantioselective fashion is of great importance for organic and medicinal chemistry. Recently, the metal-free organic Lewis base-catalyzed substitution of Morita–Baylis–Hillman (MBH) adducts has emerged as a powerful tool for the construction of multifunctional products in one step.[26−35] Our group has also developed some organic Lewis base-catalyzed asymmetric transformations.[36−40] With the aim of expanding our previous studies on the asymmetric allylic substitution,[39,40] we wondered whether this tactic might be extended to other nucleophiles, such as synthetically useful allylamines. Herein, we describe the asymmetric allylic substitution of MBH carbonates with allylamines, which could efficiently afford *N*-allyl-*β*-amino-α-methylene esters with high stereocontrol (path b, Scheme 1).

RESULTS AND DISCUSSION

First, we examined the feasibility of the reaction between the *N*-tosyl allylamine **1a** and MBH carbonate **2a** in the presence of DABCO (20 mol %) in toluene at ambient temperature. To our delight, the reaction proceeded smoothly to furnish the desired product in high conversion (Table 1, entry 1). Encouraged by this result, we examined a range of cinchona alkaloids[41−47] as enantioselective variants for their catalytic ability to promote the substitution reaction. As outlined in Table 1, natural cinchona alkaloid quinidine exhibited the best reactivity and enantioselectivity in the model reaction and proved to be worthy of further investigation (Table 1, entries 2−10). Subsequent screening of the protecting group (Figure 2) on allylamines showed that a variety of substituted arylsulfonyls can be candidates but that *p*-tosyl was optimal (Table 1, entries 2 and 11−18). A survey of solvents revealed that the reaction media had a significant effect on the reaction (Table 1, entries 2 and 19−27). For example, the use of an arene solvent could greatly improve both the reactivity

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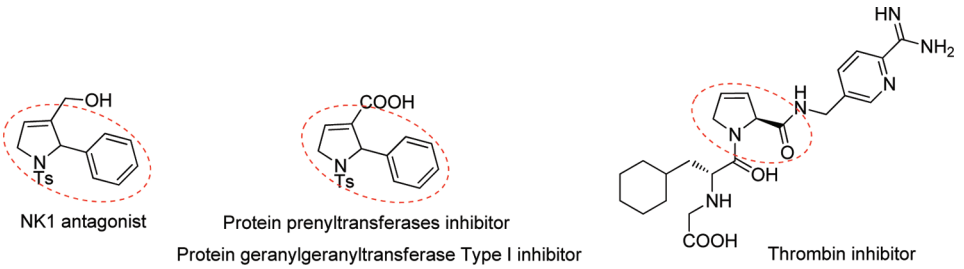
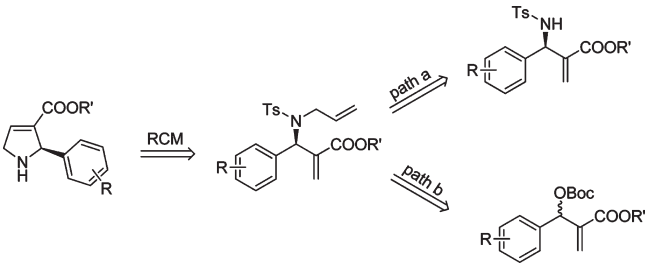


Figure 1. 2,5-Dihydropyrrole structural motifs.

Scheme 1. Synthetic Strategy



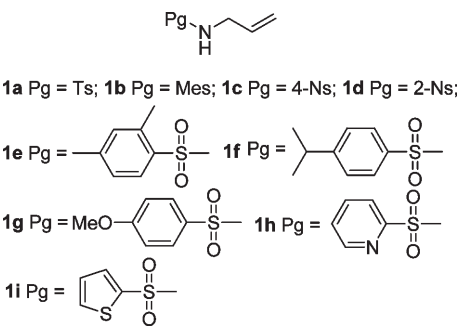


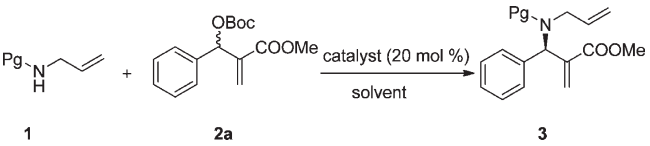
Figure 2. The structures of various allylamines.

and enantioselectivity, and *p*-xylene gave the highest enantioselectivity (Table 1, entry 27). The concentration and ratio of the substrates can also influence the reactivity and enantioselectivity (Table 1, entries 27−29). In addition, lowering the reaction temperature to 0 °C did not have a positive effect on enantioselectivity and greatly decreased the reactivity (Table 1, entry 30).

With the optimized reaction conditions in hand, we next explored the generality of the substitution process (Table 2). Most of the reactions evaluated proceeded smoothly to furnish the desired product **3** in high yields and enantioselectivities. It appears that the position and electronic properties of substituents on aromatic rings have a limited effect on the efficiency of this process (Table 2, entries 1−13). The use of an alkyl-substituted MBH carbonate failed to yield the desired product with high enantioselectivity (Table 2, entry 14). Furthermore, the scope of the reaction can be successfully extended to the allylamine bearing a phenyl group, and good results were also attained (Table 2, entry 15).

To demonstrate the suitability of the current methodology for the synthesis of 2,5-dihydropyrroles, the RCM reaction of compound **3** was examined. To our delight, in all cases, the corresponding 2,5-dihydropyrrole derivatives **4** could be obtained smoothly in excellent yields. As anticipated, the cyclization reaction

Table 1. Catalyst Screening and Reaction Optimization[a]



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

entry	catalyst	1	solvent	conversion (%)[b]	ee (%)[c]
1	DABCO	**1a**	toluene	99	–
2	quinidine	**1a**	toluene	88	80
3	quinine	**1a**	toluene	86	27
4	cinchonine	**1a**	toluene	75	67
5	cinchonidine	**1a**	toluene	73	17
6	β-ICD	**1a**	toluene	<5	n.d.
7	QD-TMS[d]	**1a**	toluene	<5	n.d.
8	$(DHQD)_2PHAL$	**1a**	toluene	79	80
9	$(DHQD)_2AQN$	**1a**	toluene	68	81
10	$(DHQD)_2PYR$	**1a**	toluene	72	70
11	quinidine	**1b**	toluene	85	78
12	quinidine	**1c**	toluene	86	75
13	quinidine	**1d**	toluene	89	76
14	quinidine	**1e**	toluene	78	78
15	quinidine	**1f**	toluene	85	79
16	quinidine	**1g**	toluene	85	79
17	quinidine	**1h**	toluene	86	70
18	quinidine	**1i**	toluene	84	76
19	quinidine	**1a**	CH_2Cl_2	76	48
20	quinidine	**1a**	$CHCl_3$	68	56
21	quinidine	**1a**	ether	46	78
22	quinidine	**1a**	THF	58	69
23	quinidine	**1a**	CF_3Ph	78	69
24	quinidine	**1a**	xylenes	89	78
25	quinidine	**1a**	*o*-xylene	90	78
26	quinidine	**1a**	*m*-xylene	89	80
27	quinidine	**1a**	*p*-xylene	89	83
28	quinidine[e]	**1a**	*p*-xylene	78	85
29	quinidine[e,f]	**1a**	*p*-xylene	88	87
30	quinidine[e,f,g]	**1a**	*p*-xylene	26	88

[a] Unless otherwise specified, the reaction was carried out with 1 (0.20 mmol) and **2a** (0.20 mmol) in the presence of catalyst (0.04 mmol) in solvent (1.0 mL) at ambient temperature for 24 h. [b] Determined by ^1H NMR analysis of the crude mixture. [c] Determined by chiral HPLC on a Chiralcel OD-H column. [d] QD-TMS = The hydroxyl group of quinidine was protected by TMSCl. [e] 2.0 mL solvent was used. [f] The reaction was carried out with **1a** (0.30 mmol) and **2a** (0.20 mmol). [g] The reaction was performed under 0 °C.

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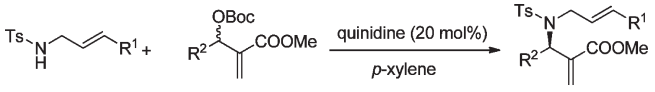
Table 2. Scope of the Reaction[a]

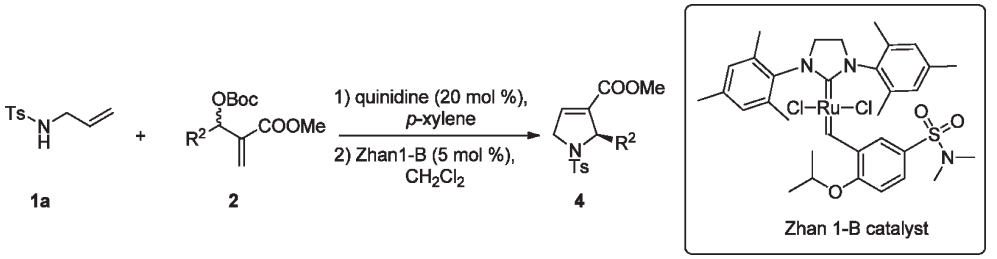


1 2 3

entry	1, R^1	2, R^2	product	yield (%)[b]	*ee* (%)[c]
1	**1a**, H	**2a**, C_6H_5	**3a**	93	87
2	**1a**, H	**2b**, 2-FC_6H_4	**3b**	78	77
3	**1a**, H	**2c**, 2-ClC_6H_4	**3c**	91	83
4	**1a**, H	**2d**, 2-BrC_6H_4	**3d**	87	82
5	**1a**, H	**2e**, 3-ClC_6H_4	**3e**	95	82
6	**1a**, H	**2f**, 3-BrC_6H_4	**3f**	97	83
7	**1a**, H	**2g**, 3-MeC_6H_4	**3g**	88	90
8	**1a**, H	**2h**, 3-$MeOC_6H_4$	**3h**	99	86
9	**1a**, H	**2i**, 4-FC_6H_4	**3i**	87	88
10	**1a**, H	**2j**, 4-ClC_6H_4	**3j**	92	87
11	**1a**, H	**2k**, 4-BrC_6H_4	**3k**	90	86
12	**1a**, H	**2l**, 4-MeC_6H_4	**3l**	96	90
13	**1a**, H	**2m**, 4-$MeOC_6H_4$	**3m**	99	87
14	**1a**, H	**2n**, 	**3n**	60	35
15	**1b**, Ph	**2o**, 4-MeC_6H_4	**3o**	86	85

[a] Unless otherwise specified, the reaction was carried out with 1 (0.30 mmol) and **2** (0.20 mmol) in the presence of 20 mol % quinidine in 2.0 mL of *p*-xylene at ambient temperature for 40 h. [b] Isolated yield. [c] For analysis of the ee values of the products, see the Supporting Information.

Table 3. Synthesis of 2,5-Dihydropyrroles[a]



1a **2** **4**

entry	2, R^2	product	yield (%)[b]	ee (%)[c]
1	**2a**, C_6H_5	**4a**	90	86
2	**2c**, 2-ClC_6H_4	**4b**	87	83
3	**2g**, 3-MeC_6H_4	**4c**	84	87
4	**2k**, 4-BrC_6H_4	**4d**	86	86
5	**2l**, 4-MeC_6H_4	**4e**	92	87

[a] Reaction conditions: see Experimental Section. [b] Isolated yield of the RCM reaction step. [c] For analysis of the ee values of the products, see the Supporting Information.

does not affect the newly formed stereogenic center and provides enantioenriched 2,5-dihydropyrroles (Table 3).

The absolute configuration of the product **3a** was determined to be *R* as shown in Scheme 2. According to the literature,[25,48,49] we prepared (*S*)-**3a** in seven steps from commercially available (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (**6**). Comparison of both the optical rotation values and chiral HPLC retention times allowed us to establish the absolute stereochemistry of the substituted product **3a** to be *R*.

To rationalize our experimental observations, we suggest the mechanism presented in Scheme 3 which parallels that proposed by Lu et al. in 2004.[30,31] First, substrate **2a** undergoes a conjugate addition followed by elimination of carbon dioxide to form adduct A. The in situ-generated *tert*-butoxide anion can deprotonate the pronucleophile allylamine to produce a nucleophilic anion that attacks the olefinic bond of the cation intermediate to afford the observed products.

■ CONCLUSIONS

In summary, we have disclosed an enantioselective allylic substitution reaction of MBH carbonates with allylamines using a commercially available cinchona alkaloid catalyst, yielding highly enantioenriched *N*-allyl-*β*-amino-α-methylene esters, which can be readily transformed to chiral 2,5-dihydropyrroles by easily operative RCM reactions. We have also proposed a tentative mechanism for rationalization of the reaction. Further

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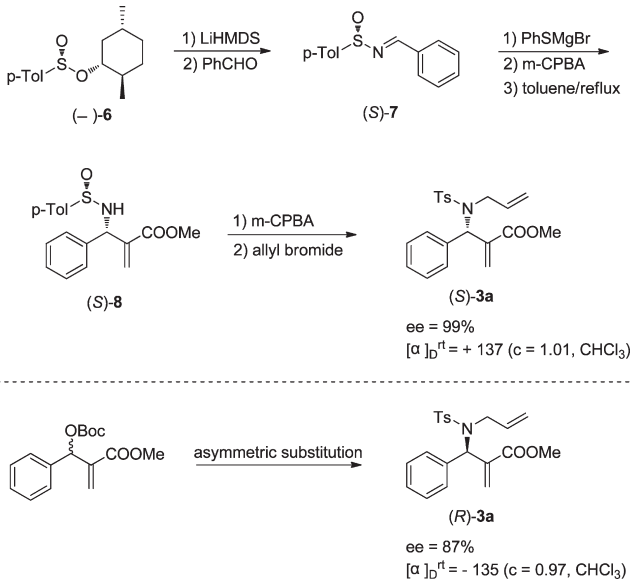
Scheme 2. Absolute Configuration Assignment for 3a



application and exploration of this methodology and biological evaluation are ongoing in our laboratory.

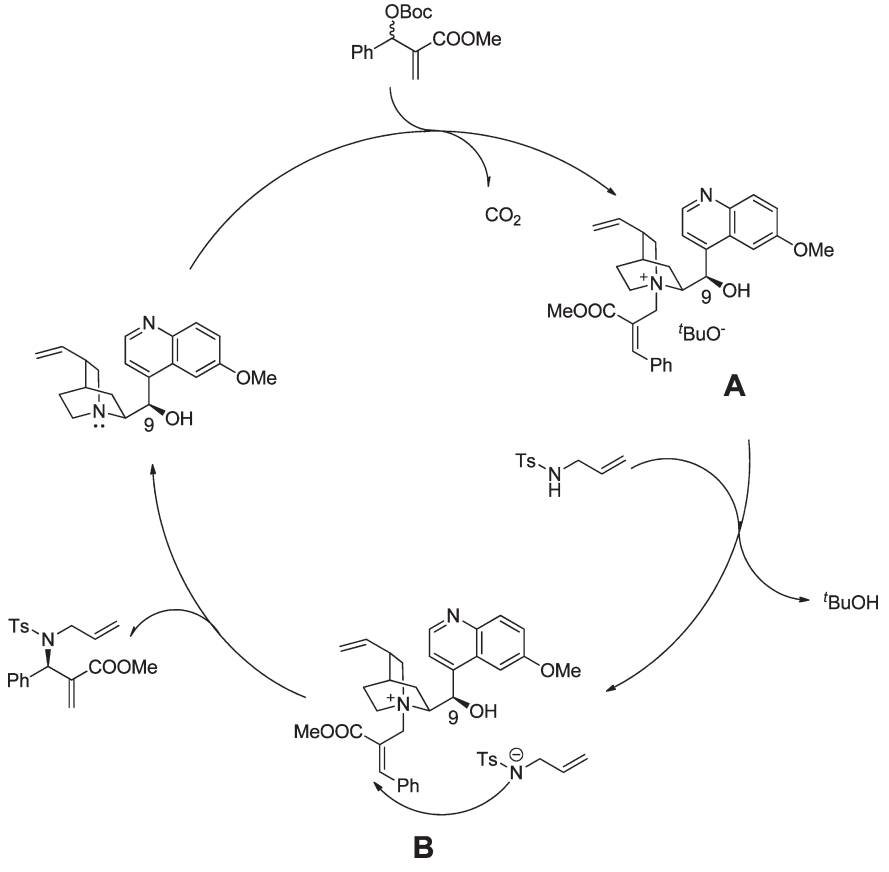
EXPERIMENTAL SECTION

General Procedure for Enantioselective Allylic Substitution Reactions. To a solution of Morita–Baylis–Hillman carbonates **2** (0.20 mmol) in the presence of 20 mol % quinidine in *p*-xylene (2.0 mL) was added allylamines **1** (0.30 mmol), and the resulting solution was stirred for 40 h at ambient temperature. The reaction mixture was directly purified by silica gel chromatography without workup, and fractions were collected and concentrated in vacuo to provide the pure desired products **3**.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(phenyl)methyl)-acrylate (**3a**, Table 2, entry 1).* The title compound (71.3 mg, 93% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 2H), 7.33–7.17 (m, 5H), 7.06–6.95 (m, 2H), 6.45 (d, J = 0.9 Hz, 1H), 6.11 (s, 1H), 5.73 (d, J = 1.5 Hz, 1H), 5.36–5.14 (m, 1H), 4.85 (dd, J = 1.2, 5.7 Hz, 1H), 4.80 (s, 1H), 3.91–3.70 (m, 2H), 3.60 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.2, 139.1, 137.7, 137.0, 134.2, 129.4, 128.5, 128.4, 128.0, 127.9, 127.4, 117.6, 61.7, 51.9, 48.6, 21.5; IR: 3064, 2953, 1724, 1636, 1438, 1342, 1286, 1193, 1116, 1034, 925, 812, 703, 664 cm^{-1}; $[\alpha]^{rt}_D$ = −135 (c = 0.97, $CHCl_3$); HRMS (ESI): $C_{21}H_{23}NO_4S$+H, Calcd: 386.1421, Found: 386.1414; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 13.0, t_{minor} = 17.8, 87% ee.

*(S)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(2-fluorophenyl)-methyl)acrylate (**3b**, Table 2, entry 2).* The title compound (62.7 mg, 78% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.33–7.15 (m, 4H), 7.05 (t, J = 7.5 Hz, 1H), 6.90 (t, J = 8.7 Hz, 1H), 6.54 (s, 1H), 6.28 (s, 1H), 5.88 (d, J = 1.4 Hz, 1H), 5.43–5.29 (m, 1H), 4.82 (dd, J = 13.5, 2.2 Hz, 2H), 3.92 (ddd, J = 37.3, 16.1, 6.5 Hz, 2H), 3.60 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 165.9, 160.6 (J = 247.5 Hz), 143.0, 138.4, 137.8, 133.7, 129.9 (J = 3.0 Hz), 129.8 (J = 3.0 Hz), 129.2, 128.6, 127.4, 124.6 (J = 13.5 Hz), 123.9 (J = 3.75 Hz), 117.7, 115.4 (J = 21.75 Hz), 56.1 (J = 3.75 Hz), 51.9,

Scheme 3. Proposed Mechanism



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49.6, 21.4; IR: 3071, 2953, 1723, 1636, 1490, 1439, 1343, 1286, 1159, 1118, 1093, 1034, 930, 811, 763, 665 cm^{-1}; $[\alpha]^{rt}_D$ = −83 (*c* = 1.11, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}FNO_4S$+H, Calcd: 404.1326, Found: 404.1337; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 8.4, t_{minor} = 10.0, 77% ee.

*(S)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(2-chlorophenyl)-methyl)acrylate (**3c**, Table 2, entry 3).* The title compound (75.9 mg, 91% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.32−7.16 (m, 6H), 6.54 (s, 1H), 6.30 (s, 1H), 5.75 (d, *J* = 1.3 Hz, 1H), 5.52−5.36 (m, 1H), 4.87 (d, d, *J* = 1.2 Hz, 1H), 4.82 (dd, *J* = 1.2, 4.8 Hz, 1H), 3.98 (qd, *J* = 16.0, 6.4 Hz, 2H), 3.59 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 142.9, 138.4, 137.6, 135.2, 134.4, 133.9, 130.1, 129.7, 129.5, 129.2, 129.1, 127.5, 126.6, 117.7, 59.5, 52.0, 50.2, 21.4; IR: 3069, 2922, 1724, 1636, 1440, 1343, 1284, 1159, 1115, 1090, 1037, 911, 812, 731, 663 cm^{-1}; $[\alpha]^{rt}_D$ = −32 (*c* = 1.07, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}ClNO_4S$ +H, Calcd: 420.1031, Found: 420.1024; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 8.9, t_{minor} = 13.1, 83% ee.

*(S)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(2-bromophenyl)-methyl)acrylate (**3d**, Table 2, entry 4).* The title compound (80.5 mg, 87% yield) was prepared as a white solid by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.46 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.7 Hz, 1H),7.24 (td, *J* = 7.2, 1.2 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.15 (td, *J* = 7.8, 1.8 Hz, 1H), 6.54 (s, 1H), 6.26 (s, 1H), 5.68 (d, *J* = 1.3 Hz, 1H), 5.55−5.44 (m, 1H), 4.90 (dd, *J* = 3.9, 1.2 Hz, 1H), 4.86 (dd, *J* = 2.1, 0.9 Hz, 1H), 4.02 (dd, *J* = 3.6, 1.2 Hz, 2H), 3.58 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 142.9, 138.4, 137.7, 136.9, 133.9, 133.1, 130.3, 130.0, 129.3, 129.1, 127.6, 127.2, 124.8, 117.8, 61.9, 52.0, 50.5, 21.4; IR: 3068, 2953, 1724, 1636, 1439, 1343, 1283, 1160, 1114, 1091, 1031, 925, 812, 756, 662 cm^{-1}; $[\alpha]^{rt}_D$ = −8 (*c* = 1.16, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}BrNO_4S$+H, Calcd: 464.0526, Found: 464.0525; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 8.5, t_{minor} = 15.8, 82% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(3-chlorophenyl)-methyl)acrylate (**3e**, Table 2, entry 5).* The title compound (83.8 mg, 95% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 12.6, 4.9 Hz, 2H), 6.95 (dt, *J* = 6.9, 1.5 Hz, 1H), 6.87 (s, 1H), 6.48 (d, *J* = 1.0 Hz, 1H), 6.05 (s, 1H), 5.73 (d, *J* = 1.6 Hz, 1H), 5.44−5.27 (m, 1H), 4.88 (ddd, *J* = 12.0, 6.8, 1.3 Hz, 2H), 3.84 (d, *J* = 6.4 Hz, 2H), 3.62 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 143.5, 139.3, 138.4, 137.5, 134.4, 134.1, 129.7, 129.5, 128.8, 128.6, 128.1, 127.3, 126.6, 117.9, 61.1, 52.1, 49.0, 21.5; IR: 3068, 2954, 1723, 1636, 1597, 1575, 1437, 1342, 1286, 1160, 1117, 1091, 1036, 911, 813, 734, 664 cm^{-1}; $[\alpha]^{rt}_D$ = −93 (*c* = 1.10, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}ClNO_4S$+H, Calcd: 420.1031, Found: 420.1043; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 7.1, t_{minor} = 9.4, 82% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(3-bromophenyl)-methyl)acrylate (**3f**, Table 2, entry 6).* The title compound (89.2 mg, 97% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.48 (s, 1H), 6.03 (s, 1H), 5.74 (d, *J* = 1.1 Hz, 1H), 5.44−5.26 (m, 1H), 4.89 (dd, *J* = 13.4, 8.0 Hz, 2H), 3.83 (d, *J* = 6.3 Hz, 2H), 3.63 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 143.5, 139.5, 138.4, 137.5, 134.1, 131.5, 131.0, 130.0, 129.5, 128.9, 127.4, 127.1, 122.6, 118.0, 61.0, 52.1, 49.0, 21.5; IR: 3066, 2953, 2925, 1724, 1636, 1596, 1570, 1437, 1344, 1287, 1160, 1117, 1091, 1036, 929, 812, 732, 663 cm^{-1}; $[\alpha]^{rt}_D$ = −91 (*c* = 1.14, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}BrNO_4S$+H, Calcd: 464.0526, Found: 464.0532; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 7.4, t_{minor} = 10.0, 83% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(m-tolyl)methyl)-acrylate (**3g**, Table 2, entry 7).* The title compound (69.9 mg, 88% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, CDCl3) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 6.44 (d, *J* = 0.8 Hz, 1H), 6.05 (s, 1H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.38−5.19 (m, 1H), 4.88 (t, *J* = 1.5 Hz, 1H), 4.30 (dt, *J* = 3.0, 1.2 Hz, 1H), 3.79 (d, *J* = 6.4 Hz, 2H), 3.61 (s, 3H), 2.43 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.2, 139.2, 138.1, 137.7, 136.8, 134.4, 129.3, 129.2, 128.7, 128.3, 127.8, 127.5, 125.4, 117.5, 61.7, 52.0, 48.7, 21.4, 21.2; IR: 2952, 1724, 1636, 1601, 1491, 1438, 1343, 1286, 1160, 1117, 1091, 1036, 924, 816, 779, 706, 663 cm^{-1}; $[\alpha]^{rt}_D$ = −101 (*c* = 1.11, $CHCl_3$); HRMS (ESI): $C_{22}H_{25}NO_4S$+Na, Calcd: 422.1397, Found: 422.1394; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 6.6, t_{minor} = 8.9, 90% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(3-methoxyphenyl)-methyl)acrylate (**3h**, Table 2, entry 8).* The title compound (81.8 mg, 99% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.27 (d, *J* = 2.3 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 4.8 Hz, 2H), 6.06 (s, 1H), 5.76 (s, 1H), 5.40−5.17 (m, 1H), 4.88 (d, *J* = 5.2 Hz, 1H), 4.84 (s, 1H), 3.81 (d, *J* = 6.4 Hz, 2H), 3.65 (s, 3H), 3.62 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 159.6, 143.2, 139.1, 138.5, 137.8, 134.4, 129.5, 129.4, 128.0, 127.6, 120.7, 117.7, 113.9, 113.9, 61.7, 55.1, 52.0, 48.7, 21.5; IR: 2953, 1723, 1636, 1601, 1490, 1437, 1342, 1270, 1160, 1117, 1091, 1038, 920, 874, 815, 782, 704, 664 cm^{-1}; $[\alpha]^{rt}_D$ = −127 (*c* = 1.06, $CHCl_3$); HRMS (ESI): $C_{22}H_{25}NO_5S$+H, Calcd: 416.1526, Found: 416.1528; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 9.0, t_{minor} = 12.6, 86% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(4-fluorophenyl)-methyl)acrylate (**3i**, Table 2, entry 9).* The title compound (70.4 mg, 87% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.28 (s, 1H), 7.26 (d, *J* = 2.3 Hz, 1H), 7.05−6.97 (m, 2H), 6.92 (t, *J* = 8.6 Hz, 2H), 6.44 (d, *J* = 0.9 Hz, 1H), 6.07 (s, 1H), 5.72 (d, *J* = 1.6 Hz, 1H), 5.36−5.22 (m, 1H), 4.86 (s, 1H), 4.82 (dd, *J* = 8.2, 1.0 Hz, 1H), 3.81 (qd, *J* = 16.1, 6.4 Hz, 2H), 3.61 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 162.3 (*J* = 246 Hz), 143.3, 138.9, 137.8, 134.2, 133.0 (*J* = 3.0 Hz), 130.3 (*J* = 8.25 Hz), 129.5, 128.1, 127.4, 115.5 (*J* = 21.75 Hz), 61.1, 52.1, 48.8, 21.5; IR: 2953, 2924, 1724, 1636, 1602, 1509, 1438, 1342, 1227, 1159, 1117, 1091, 1035, 930, 815, 662 cm^{-1}; $[\alpha]^{rt}_D$ = −93 (*c* = 0.98, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}FNO_4S$+H, Calcd: 404.1326, Found: 404.1318; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 7.2, t_{minor} = 9.2, 88% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(4-chlorophenyl)-methyl)acrylate (**3j**, Table 2, entry 10).* The title compound (77.3 mg, 92% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 1.1 Hz, 1H), 6.06 (s, 1H), 5.73 (d, *J* = 1.6 Hz, 1H), 5.40−5.21 (m, 1H), 4.89 (s, 1H), 4.84 (dd, *J* = 6.4, 1.2 Hz, 1H), 3.82 (dt, *J* = 5.7, 1.2 Hz, 2H), 3.61 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 143.3, 138.6, 137.6,

135.8, 134.0, 133.8, 129.9, 129.4, 128.6, 128.5, 127.4, 117.9, 61.0, 52.0, 48.9, 21.5; IR: 2952, 1723, 1491, 1342, 1160, 1036, 815 cm^{-1}; $[\alpha]^{rt}_D$ = −114 (*c* = 1.04, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}ClNO_4S$+H, Calcd: 420.1031, Found: 420.1028; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 7.0, t_{minor} = 8.7, 88% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(4-bromophenyl)methyl)acrylate (**3k**, Table 2, entry 11).* The title compound (83.5 mg, 90% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.27 (d, *J* = 2.6 Hz, 1H), 7.25 (s, 1H), 6.93 (s, 1H), 6.90 (s, 1H), 6.46 (d, *J* = 1.1 Hz, 1H), 6.03 (s, 1H), 5.73 (d, *J* = 1.6 Hz, 1H), 5.41−5.22 (m, 1H), 4.89 (s, 1H), 4.85 (dd, *J* = 6.6, 1.2 Hz, 1H), 3.82 (dt, *J* = 4.5, 0.9 Hz, 2H), 3.61 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 143.3, 138.5, 137.6, 136.3, 134.0, 131.6, 130.2, 129.4, 128.6, 127.4, 122.0, 117.9, 61.1, 52.0, 48.9, 21.5; IR: 2952, 2925, 1723, 1636, 1596, 1488, 1438, 1342, 1286, 1160, 1116, 1091, 1036, 930, 815, 730, 691 cm^{-1}; $[\alpha]^{rt}_D$ = −105 (*c* = 0.95, $CHCl_3$); HRMS (ESI): $C_{21}H_{22}BrNO_4S$+H, Calcd: 464.0526, Found: 464.0534; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} =11.2, t_{minor} =16.1, 86% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(p-tolyl)methyl)-acrylate (**3l**, Table 2, entry 12).* The title compound (76.4 mg, 96% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.20 (s, 1H), 7.17 (d, *J* = 1.9 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 6.35 (d, *J* = 0.7 Hz, 1H), 5.98 (s, 1H), 5.68 (d, *J* = 1.5 Hz, 1H), 5.17 (ddt, *J* = 16.8, 10.0, 6.4 Hz, 1H), 4.79 (d, *J* = 8.1 Hz, 1H), 4.74 (s, 1H), 3.71 (d, *J* = 6.3 Hz, 2H), 3.52 (s, 3H), 2.35 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.1, 139.3, 137.8, 137.7, 134.4, 133.8, 129.3, 129.2, 128.4, 127.5, 127.4, 117.5, 61.5, 51.9, 48.5, 21.4, 21.0; IR: 2952, 1723, 1437, 1342, 1159, 1035, 814 cm^{-1}; $[\alpha]^{rt}_D$ = −114 (*c* = 1.11, CHCl3); HRMS (ESI): $C_{22}H_{25}NO_4S$+H, Calcd: 400.1577, Found: 400.1567; HPLC: DAICEL CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 6.9, t_{minor} = 9.3, 90% ee.

*(R)-Methyl 2-((N-Allyl-4-methylphenylsulfonamido)(4-methoxyphenyl)-methyl)acrylate(**3m**, Table 2, entry 13).* The title compound (82.0 mg, 99% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.41 (s, 1H), 6.04 (s, 1H), 5.76 (d, *J* = 1.5 Hz, 1H), 5.24 (m, 1H), 4.87 (d, *J* = 5.3 Hz, 1H), 4.82 (s, 1H), 3.79 (t, *J* = 6.6 Hz, 2H), 3.76 (s, 3H), 3.60 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 159.2, 143.1, 139.3, 137.7, 134.4, 129.8, 129.4, 128.8, 127.4, 127.2, 117.5, 113.8, 61.2, 55.1, 51.9, 48.5, 21.4; IR: 2954, 1724, 1636, 1610, 1512, 1439, 1340, 1254, 1159, 1115, 1091, 1033, 928, 815, 778, 731, 664 cm^{-1}; $[\alpha]^{rt}_D$ = −128 (*c* = 1.00, $CHCl_3$); HRMS (ESI): $C_{22}H_{25}NO_5S$+H, Calcd: 416.1526, Found: 416.1533; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 9.6, t_{minor} = 14.1, 86% ee.

*(R)-Methyl 3-(N-Allyl-4-methylphenylsulfonamido)-2-methylene-5-phenylpentanoate (**3n**, Table 2, entry 14).* The title compound (49.8 mg, 60% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.25 (d, *J* = 1.9 Hz, 2H), 7.23−7.16 (m, 2H), 7.12 (dd, *J* = 8.1, 1.2 Hz, 2H), 6.36 (s, 1H), 5.90−5.78 (m, 1H), 5.77 (d, *J* = 0.7 Hz, 1H), 5.10 (dd, *J* = 26.7, 1.2 Hz, 1H), 5.08 (d, *J* = 1.2 Hz, 1H), 4.87 (t, *J* = 7.5 Hz, 1H), 3.85 (d, *J* = 6.4 Hz, 2H), 3.60 (s, 3H), 2.67−2.51 (m, 2H), 2.40 (s, 3H), 2.21−1.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 142.9, 141.1, 138.1, 138.0, 135.6, 129.3, 128.4, 128.3, 127.9, 127.5, 126.0, 117.7, 57.1, 51.9, 48.3, 33.8, 33.0, 21.5; IR: 2950, 1721, 1438, 1337, 1157, 929, 814 cm^{-1}; $[\alpha]^{rt}_D$ = −28 (*c* = 0.95, $CHCl_3$); HRMS (ESI): $C_{23}H_{27}NO_4S$+H, Calcd: 414.1734, Found: 414.1730; HPLC: CHIRALCEL AD, hexane/iPrOH = 90/10, flow rate = 1.0 mL/min, retention time: t_{major} = 14.2, t_{minor} = 19.4, 35% ee.

*(R,E)-Methyl 2-((N-Cinnamyl-4-methylphenylsulfonamido)(p-tolyl)-methyl)acrylate (**3o**, Table 2, entry 15).* The title compound (81.9 mg, 86% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.33−7.14 (m, 5H), 7.03 (dd, *J* = 6.8, 4.8 Hz, 4H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.44 (s, 1H), 6.14 (s, 1H), 6.00 (d, *J* = 15.9 Hz, 1H), 5.78 (s, 1H), 5.46 (dt, *J* = 15.7, 6.7 Hz, 1H), 4.01 (dd, *J* = 15.9, 7.3 Hz, 1H), 3.86 (dd, *J* = 16.1, 6.2 Hz, 1H), 3.58 (s, 3H), 2.39 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.1, 139.3, 137.9, 137.8, 136.4, 133.9, 132.4, 129.4, 129.2, 128.4, 128.3, 127.5, 127.4, 127.3, 126.1, 125.4, 61.4, 51.9, 47.8, 21.4, 20.9; IR: 2952, 1723, 1438, 1339, 1158, 914, 814 cm^{-1}; $[\alpha]^{rt}_D$ = −88 (*c* = 1.08, $CHCl_3$); HRMS (ESI): $C_{28}H_{29}NO_4S$+H, Calcd: 476.1890, Found: 476.1882; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 80/20, flow rate = 1.0 mL/min, retention time: t_{major} = 10.9, t_{minor} = 12.8, 85% ee.

General Procedure for the Synthesis of 2,5-Dihydropyrroles 4. To a solution of Morita−Baylis−Hillman carbonates **2** (0.20 mmol) in the presence of 20 mol % quinidine in *p*-xylene (2.0 mL) was added allylamine **1a** (0.30 mmol), and the resulting solution was stirred for 40 h at ambient temperature. After purification, to a solution of products **3** in CH_2Cl_2 was added 5 mol % Zhan-1B catalyst, and the mixture was refluxed for 4 h. The resulting mixture was then loaded onto silica gel, and the products **4** were obtained by column chromatography.

*(R)-Methyl 2-Phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4a**, Table 3, entry 1).* The title compound (59.4 mg, 90% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.23 (s, 5H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.78 (dd, *J* = 3.8, 2.0 Hz, 1H), 5.73 (dt, *J* = 3.9, 1.8 Hz, 1H), 4.51 (dt, *J* = 17.1, 2.4 Hz, 1H), 4.38 (ddd, *J* = 17.1, 5.7, 1.8 Hz, 1H), 3.58 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 143.3, 139.3, 135.7, 135.6, 135.4, 129.4, 128.3, 128.0, 127.7, 127.0, 68.9, 54.9, 51.8, 21.4; IR: 1724, 1438, 1348, 1269, 1162, 1091, 817 cm^{-1}; $[\alpha]^{rt}_D$ = −198 (*c* = 1.02, $CHCl_3$); HRMS (ESI): $C_{19}H_{19}NO_4S$+H, Calcd: 358.1108, Found: 358.1107; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 11.3, t_{minor} = 15.6, 86% ee.

*(S)-Methyl 2-(2-Chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4b**, Table 3, entry 2).* The title compound (61.9 mg, 87% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.26−7.20 (m, 1H), 7.17−7.07 (m, 5H), 6.72 (dd, *J* = 4.0, 2.0 Hz, 1H), 6.06 (ddd, *J* = 5.4, 3.5, 1.8 Hz, 1H), 4.43 (ddt, *J* = 17.1, 5.7, 2.1 Hz, 2H), 3.50 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 143.6, 137.2, 136.3, 134.7, 134.6, 133.6, 129.8, 129.7, 129.6, 129.0, 127.3, 126.9, 65.3, 55.4, 51.8, 21.5; IR: 1725, 1440, 1352, 1270, 1191, 1092, 911, 805 cm^{-1}; $[\alpha]^{rt}_D$ = −206 (*c* = 0.98, $CHCl_3$); HRMS (ESI): $C_{19}H_{18}ClNO_4S$+H, Calcd: 392.0718, Found: 392.0714; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 13.9 t_{minor} = 24.2, 83% ee.

*(R)-Methyl 2-m-Tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4c**, Table 3, entry 3).* The title compound (54.8 mg, 90% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.12 (dd, *J* = 7.8, 2.7 Hz, 3H), 7.03 (dd, *J* = 7.2, 0.9 Hz, 2H), 6.91 (s, 1H), 6.77 (dd, *J* = 3.9, 1.8 Hz, 1H), 5.69 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.52 (dt, *J* = 17.1, 2.4 Hz, 1H), 4.38 (ddd, *J* = 17.1, 5.7, 1.8 Hz, 1H), 3.59 (s, 3H), 2.36 (s, 3H), 2.22 (s, 3H); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 162.2, 143.1, 139.0, 137.8, 135.7, 135.5, 129.3, 128.8, 128.2,128.1, 127.0, 125.0, 68.9, 54.9, 51.8, 21.4, 21.3; IR: 2952, 1724, 1457, 1348, 1268, 1162, 1091, 776 cm^{-1}; $[\alpha]^{rt}_D = -157$ (c = 1.02, $CHCl_3$); HRMS (ESI): $C_{20}H_{21}NO_4S$+H, Calcd: 372.1264, Found: 372.1258; HPLC: CHIRALCEL AD, hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 9.9, t_{minor} = 12.6, 87% ee.

*(R)-Methyl 2-(4-Bromophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4d**, Table 3, entry 4).* The title compound (67.3 mg, 86% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 1.8 Hz, 1H), 5.59 (dt, J = 5.4, 1.8 Hz,1H), 4.44 (dt, J = 17.2, 2.5 Hz, 1H), 4.33 (ddd, J = 17.2, 5.7, 2.0 Hz, 1H), 3.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 143.6, 138.5, 136.0, 135.3, 135.2, 131.4, 129.6, 129.4, 127.0, 122.1, 68.3, 55.0, 51.9, 21.5; IR: 2953, 1724, 1595, 1487, 1439, 1350, 1268, 1162, 1091, 813, 732 cm^{-1}; $[\alpha]^{rt}_D = -210$ (c = 0.97, $CHCl_3$); HRMS (ESI): $C_{19}H_{18}BrNO_4S$+H, Calcd: 436.0213, Found: 436.0201; HPLC: CHIRALCEL OD-H, hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 11.1, t_{minor} = 13.0, 86% ee.

*(R)-Methyl 2-p-Tolyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (**4e**, Table 3, entry 5).* The title compound (65.2 mg, 90% yield) was prepared as a pale yellow oil by the general procedure and eluted from silica gel with petroleum ether/AcOEt (2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 8.3 Hz, 2H), 7.13 (dd, J = 10.5, 8.4 Hz, 3H), 7.10 (s, 1H), 7.04 (d, J = 8.0 Hz, 2H), 6.75 (d, J = 1.8 Hz, 1H), 5.68 (dt, J = 5.1, 1.8 Hz, 1H), 4.48 (dt, J = 17.1, 2.5 Hz, 1H), 4.37 (ddd, J = 17.1, 5.5, 2.0 Hz, 1H), 3.58 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 143.2, 137.7, 136.4, 135.6, 135.5, 135.4, 129.4, 128.9, 127.5, 127.1, 68.7, 54.8, 51.8, 21.4, 21.1; IR: 2952, 1724, 1645, 1439, 1349, 1269, 1162, 1090, 813 cm^{-1}; $[\alpha]^{rt}_D = -156$ (c = 1.13, $CHCl_3$); HRMS (ESI): $C_{20}H_{21}NO_4S$+H, Calcd: 372.1264, Found: 372.1271; HPLC: CHIRALCEL AD, hexane/iPrOH = 70/30, flow rate = 1.0 mL/min, retention time: t_{major} = 11.0, t_{minor} = 15.8, 87% ee.

■ ASSOCIATED CONTENT

Supporting Information. General methods, HPLC conditions and chromatograms, and copies of NMR spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hongl@lzu.edu.cn; wangrui@lzu.edu.cn.

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