DOI: 10.1002/ejoc.201100501

Novel Quinidine-Derived Organocatalysts for the Asymmetric Substitutions of *O*-Boc-Protected Morita–Baylis–Hillman Adducts

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Keywords: Organocatalysis / Asymmetric catalysis / Nucleophilic substitution / Carbamates

A series of novel quinidine-derived organocatalysts was synthesized and utilized for the asymmetric substitution of *O*-Boc-protected Morita–Baylis–Hillman adducts with various carbamates and tosylcarbamates, affording the corresponding products in good to high yields (up to 91 % yield) with moderate to high *ee* values (up to 96 % *ee*) under mild conditions.

Introduction

Recently, asymmetric substitutions of Morita–Baylis–Hillman (MBH) acetates or carbonates using cinchona alkaloid derived organocatalysts have attracted much attention because this asymmetric synthetic protocol can overcome the shortcomings in direct catalytic asymmetric MBH reactions in terms of substrate scope and catalytic efficiency as well as chiral induction.[1–4] In this aspect, Lu[5a] and Hiemstra[5b] first independently reported 4-(3-ethyl-4-oxa-1-azatricyclo[4,4,0,$0^{3,8}$]dec-5-yl)quinolin-6-ol (also called as β-isocupreidine, β-ICD) catalyzed asymmetric substitution of MBH carbonates with various nucleophiles, affording the corresponding amination products in excellent yields along with modest *ee* values. Moreover, Chen and coworkers recently used hydroquindine(anthraquinone-1,4-diyl) diether [$(DHQD)_2AQN$], hydroquindine-1,4-phthalazinediyl diether [$(DHQD)_2PHAL$], hydroquinidine-2,5-diphenyl-4,6-pyrimidinediyl diether [$(DHQD)_2PYR$], and β-isocupreidine (β-ICD) in asymmetric substitutions of MBH carbonates to achieve C–C bond,[6a–6d] C–N bond,[6e,6f] and C–O bond[6g,6h] formation in good yields along with high enantioselectivities under mild conditions. More recently, Wang's group also reported the use of cinchona alkaloids as catalysts to construct chiral allylic phosphane oxides through substitution of MBH carbonates in excellent yields along with high enantioselectivities.[7] In this paper, we wish to report the synthesis of a series of novel quinidine-derived organocatalysts and their applications in the asymmetric substitution of *O*-Boc-protected MBH adducts with various carbamates and tosylcarbamates, affording the corresponding products in good yields (up to 91% yield) with high *ee* values (up to 96%*ee*) under mild conditions.

Results and Discussion

Initially, we utilized methyl benzoylcarbamate (**1a**, 1.2 equiv.) and *tert*-butyl 2-methylene-1-(4-nitrophenyl)-3-oxobutyl carbonate (**2a**, 1.0 equiv.) as the substrates and the multifunctional cinchona alkaloid β-isocupreidine (β-ICD)[1k,8] (Figure 1) (10 mol-%) as the catalyst in tetrahydrofuran (THF) to examine the reaction outcome, and the results are shown in Table 1. It was found that the corresponding substitution product **3aa** was obtained in 80% yield along with 22%*ee* at room temperature (25 °C; Table 1, Entry 1). We next screened other multifunctional cinchona alkaloid derived organocatalysts cat-**I**–cat-**III**

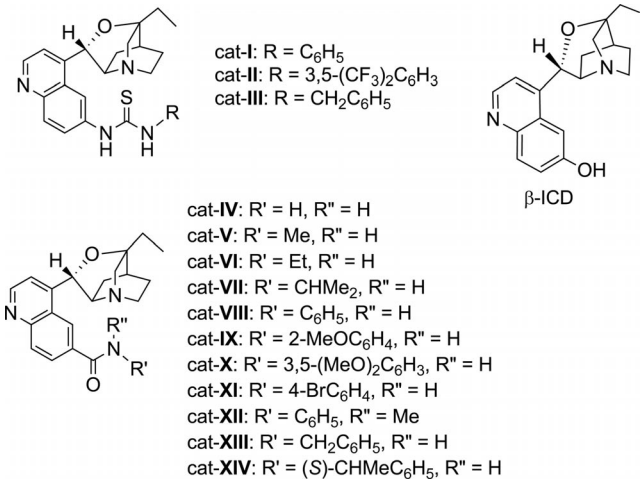

Figure 1. Multifunctional cinchona alkaloid derivatives.

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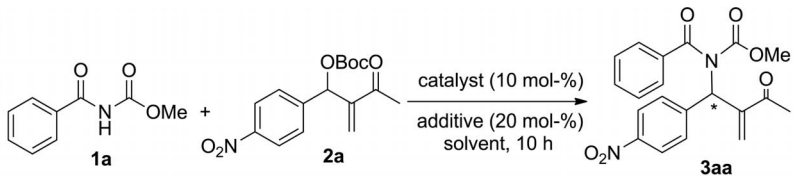
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100501.

Table 1. Optimization of the reaction conditions.[a]

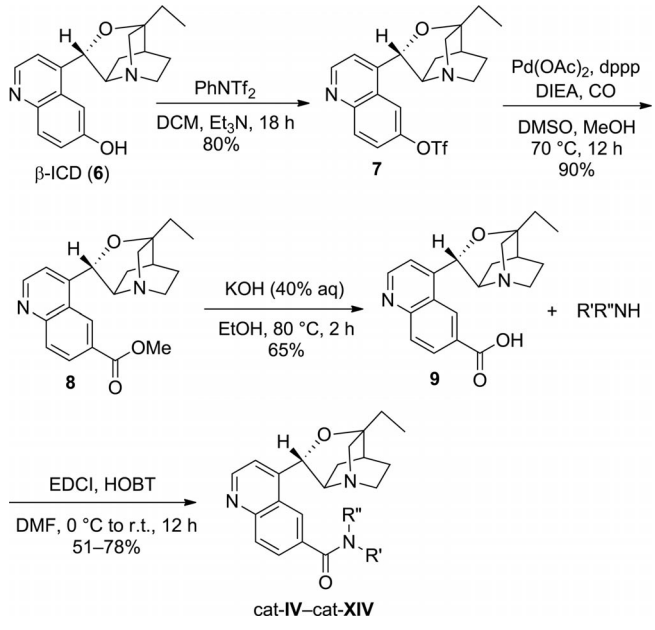


Entry	Catalyst	Additive	*T* [°C]	Solvent	Yield [%][b]	*ee* [%][c]
1	β-ICD	-	25	THF	80	–22
2	cat-**I**	-	25	THF	86	31
3	cat-**II**	-	25	THF	84	17
4	cat-**III**	-	25	THF	89	31
5	cat-**IV**	-	25	THF	74	15
6	cat-**V**	-	25	THF	74	40
7	cat-**VIII**	-	25	THF	86	43
8	cat-**X**	-	25	THF	65	37
9	cat-**XII**	-	25	THF	58	–25
10	cat-**VIII**	-	25	Et_2O	83	41
11	cat-**VIII**	-	25	DCM	80	41
12	cat-**VIII**	-	25	chlorobenzene	80	35
13	cat-**VIII**	-	0	THF	83	60
14	cat-**VIII**	-	–25	THF	90	75
15	cat-**VIII**	-	–30	THF	80	69
16	cat-**VIII**	-	–45	THF	82	65
17	cat-**VIII**	-	–60	THF	64	59
18[d]	cat-**VIII**	-	–78	THF	89	55
19	cat-**VIII**	DIEA	–25	THF	82	70
20	cat-**VIII**	4-nitrophenol	–25	THF	80	64
21	cat-**VIII**	EtOH	–25	THF	85	50
22	cat-**VIII**	*t*-amyl-OH	–25	THF	80	60
23	cat-**VIII**	PhCOOH	–25	THF	80	63
24[e]	cat-**VIII**	-	–25	THF	90	75

[a] All reactions were carried out using **1a** (0.12 mmol) and **2a** (0.10 mmol) in solvent (1.00 mL) for 10 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was carried out at –78 °C for 36 h. [e] The reaction was carried out with cat-**VIII** (20 mol-%).

(Figure 1) in this reaction and found that desired product **3aa** was formed in 84–89% yields along with 17–31%*ee* values (Table 1, Entries 2–4).

Because these cinchona alkaloids derived catalysts are not effective in this particular asymmetric substitution reaction, we attempted to develop other multifunctional cinchona alkaloid derived organocatalysts in this reaction. As shown in Scheme 1, using β-ICD as the starting material, we prepared several novel cinchon alkaloid organocatalysts cat-**IV**–cat-**XIV** through straightforward synthetic methods in moderate to good yields (Scheme 1, see Supporting Information for detailed experimental procedures; Figure 1). Moreover, the structure of β-ICD-derived organocatalyst cat-**VIII** was unambiguously determined by X-ray diffraction.[9] Its ORTEP drawing is shown in Figure 2. Employing these new cinchona alkaloid derived organocatalysts, we then investigated the reaction of **1a** and **2a** in the presence of cat-**IV**, cat-**V**, cat-**VIII**, cat-**X**, and cat-**XII** in THF at 25 °C and found that cat-**VIII** was the best organocatalyst for this reaction (Table 1, Entries 5–9). In the presence of cat-**VIII** (R′ = C_6H_5 and R′ = H), **3aa** was formed in 86% yield and 43%*ee* (Table 1, Entry 7). The examination of solvent effects revealed that THF was the



Scheme 1. The synthetic route for the preparation of novel quinidine-derived organocatalysts.

best solvent for this reaction (Table 1, Entries 10–12). Lowering the reaction temperature to 0 °C or –25 °C afforded **3aa** in 60 and 75%*ee*, respectively, along with good yields in the presence of organocatalyst cat-**VIII** (Table 1, Entries 13 and 14). Further reducing the reaction temperature did not improve the *ee* value of **3aa** (Table 1, Entries 15–18). Moreover, we also attempted to add some additives such as diisopropylethylamine (DIEA), 4-nitrophenol, ethanol, *tert*-amyl alcohol, and benzoic acid to improve the enantiomeric excess of **3aa** in THF at –25 °C. However, no improvement was observed under the standard conditions (Table 1, Entries 19–23). Increasing the employed amount of cat-**VIII** to 20 mol-% did not improve the reaction outcome either (Table 1, Entry 24). Overall, this asymmetric substitution reaction should be carried out at –25 °C in THF using organocatalyst cat-**VIII** as the promoter.

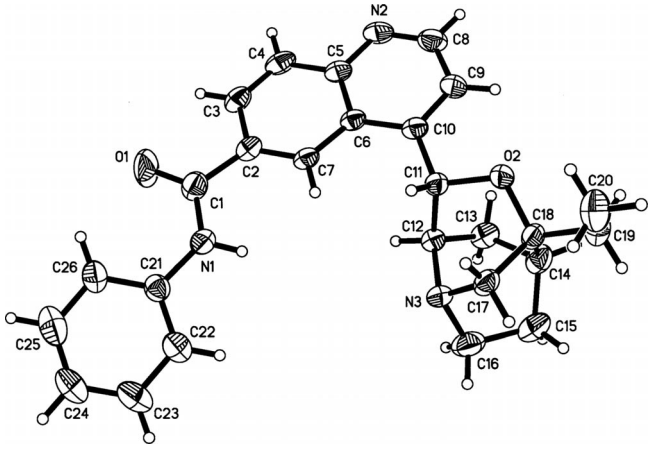
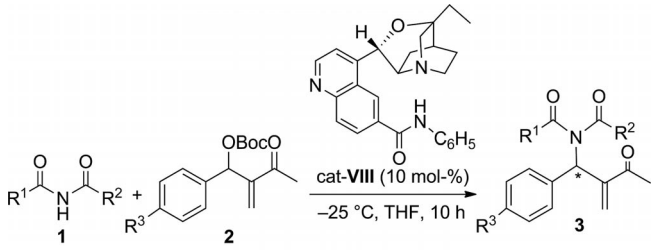


Figure 2. ORTEP drawing of organocatalyst cat-**VIII**.

Under these optimal conditions, we next examined the generality of this reaction with methyl carbamates **1** and *O*-Boc-protected MBH adducts **2**, and the results are summarized in Table 2. As for aromatic carbamates **1b**–**d**, the substitution reaction with **2a** proceeded smoothly to give the corresponding products **3ba**, **3ca**, and **3da** in 80–87% yields and 62–64%*ee* whether they have electron-withdrawing or electron-donating groups on their benzene rings (Table 2, Entries2–4). Changing the ester moiety from OMe to O*i*Bu or C_6H_5 was not detrimental to the outcome of the reaction, as desired product **3ea** or **3fa** was obtained in 82 or 75% yield, respectively, with 65 or 52%*ee*, respectively (Table 2, Entries 5 and 6). Furthermore, in the substitution reaction of **1a** with other *O*-Boc-protected MBH adducts **2b**, **2c**, and **2d**, corresponding products **3ab**, **3ac**, and **3ad** were also obtained in good yields with 55–77%*ee*, suggesting that the electronic properties on the aromatic ring of the MBH adduct did not have an influence on the outcome of the reactions (Table 2, Entries 7–9). Using carbamate **1g** ($R^1 = C_6H_5$ and R^2 = Me) as the substrate afforded desired product **3gd** in 48% yield and 43%*ee*, presumably due to its lability under the standard reaction conditions (Table 2, entry 10).

Table 2. Screening of the asymmetric substitution of MBH adducts **2** with **1** catalyzed by cat-**VIII**.[a]



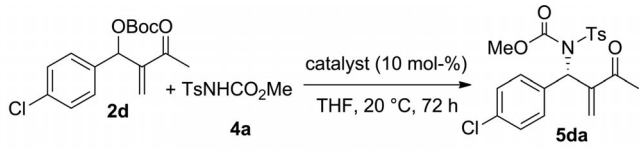
Entry	Substrate	R^1	R^2	R^3	Yield [%][b]	*ee* [%][c]
1	**1a**	C_6H_5	OMe	NO_2 (**2a**)	**3aa**, 90	75
2	**1b**	2,4,6-$Me_3C_6H_2$	OMe	NO_2 (**2a**)	**3ba**, 80	64
3	**1c**	4-ClC_6H_4	OMe	NO_2 (**2a**)	**3ca**, 87	62
4	**1d**	4-$NO_2C_6H_4$	OMe	NO_2 (**2a**)	**3da**, 82	63
5	**1e**	C_6H_5	O*i*Bu	NO_2 (**2a**)	**3ea**, 82	65
6	**1f**	C_6H_5	C_6H_5	NO_2 (**2a**)	**3fa**, 75	52
7	**1a**	C_6H_5	OMe	H (**2b**)	**3ab**, 86	73
8	**1a**	C_6H_5	OMe	Me (**2c**)	**3ac**, 85	55
9	**1a**	C_6H_5	OMe	Cl (**2d**)	**3ad**, 90	77
10	**1g**	C_6H_5	Me	Cl (**2d**)	**3gd**, 48	43

[a] All reactions were carried out using **1** (0.12 mmol) and **2** (0.10 mmol) in THF (1.00 mL) for 10 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

We next attempted to use methyl tosylcarbamate (**4a**) to replace carbamate **1** in this interesting asymmetric substitution reaction. Although organocatalysts β-ICD and hydroquinidine-2,5-diphenyl-4,6-pyrimidinediyl diether [$(DHQD)_2PYR$] and hydroquinine-1,4-phthalazinediyl diether [$(DHQ)_2PHAL$] did not catalyze this reaction under the standard conditions, we were pleased to find that our new organocatalysts cat-**IV**–cat-**VIII** (10 mol-%) could produce corresponding product **5da** in moderate to good yields along with 86–92%*ee* (Table 3, Entries 1–8). The substituent on the aromatic R′ group can significantly affect the reaction outcome. Introducing strongly electron-donating methoxy groups at the 2-position or at the 3- and 5-positions of the benzene ring (organocatalysts cat-**IX** and cat-**X**) afforded the corresponding product **5da** in lower yield and with lower *ee* values (Table 3, Entries 9 and 10). Using organocatalyst cat-**XI** in which the aromatic R′ group has a bromine atom at the 4-position furnished **5da** in 24% yield with 84%*ee* (Table 3, Entry 11). Furthermore, the reaction produced **5da** in 27% yield and 67%*ee* in the presence of organocatalyst cat-**XII** in which R′ is a phenyl group and R′ is a methyl group, suggesting that the NH functional group is required in this reaction to give **5da** in higher yield and with a higher *ee* value (Table 3, Entry 12). Organocatalysts cat-**XIII** and cat-**XIV**, in which R′ is a benzyl group or a substituted benzyl group and R′ is a hydrogen atom, are also effective catalysts in this asymmetric substitution reaction, affording **5da** in 65% yield with 86%*ee* and 68% yield with 89%*ee*, respectively (Table 3, Entries 13 and 14). Using organocatalyst cat-**VIII** (15 mol-%) as the catalyst produced **5da** in 85% yield with 92%*ee* (Table 3, Entry 15). Therefore, the optimal organocatalyst has been identified as cat-**VIII** and a catalyst loading of

15 mol-% is required in this particular asymmetric substitution reaction to give the corresponding product in good yield along with high *ee* values.

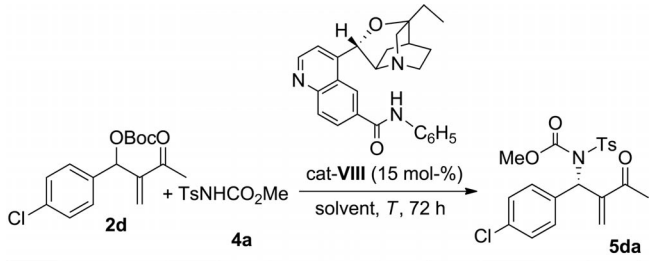
Table 3. Cinchona alkaloid catalyzed asymmetric substitution of MBH adduct **2d** with **4a**.[a]



Entry	Catalyst	Yield [%][b]	*ee* [%][c]
1	β-ICD	trace	-
2	$(DHQD)_2PYR$	trace	-
3	$(DHQ)_2PHAL$	trace	-
4	cat-**IV**	62	89 (*S*)
5	cat-**V**	70	87 (*S*)
6	cat-**VI**	70	86 (*S*)
7	cat-**VII**	35	87 (*S*)
8	cat-**VIII**	75	92 (*S*)
9	cat-**IV**	60	71 (*S*)
10	cat-**X**	23	70 (*S*)
11[d]	cat-**XI**	24	84 (*S*)
12	cat-**XII**	27	67 (*S*)
13	cat-**XIII**	65	86 (*S*)
14	cat-**XIV**	68	89 (*S*)
15[e]	cat-**VIII**	85	92 (*S*)

[a] All reactions were carried out using **2d** (0.10 mmol) and **4a** (0.12 mmol) in THF (1.00 mL) for 72 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was carried out for 80 h. [e] The reaction was carried out with cat-**VIII** (15 mol-%).

Table 4. Optimization of the reaction conditions.[a]



Entry	*T* [°C]	Solvent	Yield [%][b]	*ee* [%][c]
1	20	THF	85	92 (S)
2	20	DCM	35	86 (*S*)
3	20	DCE	50	89 (S)
4	20	$Cl_2CHCHCl_2$	57	89 (S)
5	20	$CHCl_3$	51	89 (S)
6	20	toluene	23	70 (S)
7	20	DMF	N.R.	-
8	20	DMSO	N.R.	-
9	20	1,4-dioxane	45	79 (S)
10	20	Et_2O	N.R.	-
11	20	acetone	33	90 (*S*)
12	20	MeCN	N.R.	-
13[d]	25	THF	57	86 (S)
14[d]	35	THF	71	85 (S)
15[d]	50	THF	85	45 (S)
16	10	THF	trace	-
17	–20	THF	N.R.	-

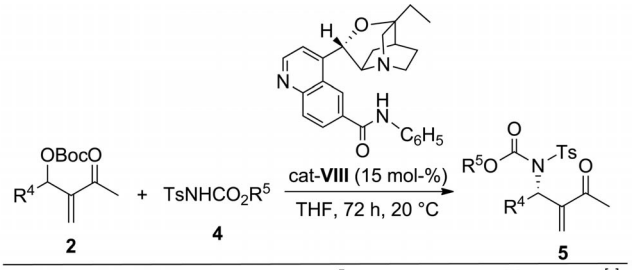
[a] All reactions were carried out using **2d** (0.10 mmol) and **4a** (0.12 mmol) in solvent (1.00 mL) for 72 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was carried out for 24 h.

Further examination of solvent effects disclosed that THF was the solvent of choice in comparison with those reactions carried out in halogenated organic solvents such as dichloromethane (DCM), 1,2-dichloroethane (DCE), or chloroform and in toluene (Table 4, Entries 1–6). In *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), reactant **2d** decomposed during the reaction without the formation of **5da** (Table 4, Entries 7 and 8). In ether or acetonitrile, no reaction occurred because organocatalyst cat-**VIII** was insoluble in these solvents (Table 4, Entries 10 and 12). In 1,4-dioxane and acetone, **5da** was formed in 45% yield along with 79%*ee* and in 33% yield along with 90%*ee*, respectively (Table 4, Entries 9 and 11). Raising the reaction temperature to 25 °C–50 °C did not improve the outcome of the reaction (Table 4, Entries 13–15). When the reaction was carried out at 10 °C or at –20 °C, either a trace amount of **5da** was formed or no reaction occurred (Table 4, entries 16 and 17).

The generality of this asymmetric substitution reaction was examined using a variety of *O*-Boc-protected MBH adducts (MBH carbonate) **2** and tosylcarbamates **4** at 20 °C under the optimal conditions, and the results of these experiments are summarized in Table 5. When *O*-Boc-protected MBH adducts **2** bearing electron-withdrawing groups at the *ortho*-, *meta*-, or *para*-position of the benzene ring were employed as the substrates, the reactions proceeded smoothly to give desired products **5** in 60–91% yield with 76–96%*ee* (Table 5, Entries 1–8). As for *O*-Boc-protected MBH adduct **2i** bearing a nitro group at the *ortho*-position of the benzene ring, electron-neutral *O*-Boc-protected MBH adduct **2b**, and *O*-Boc-protected MBH adduct **2c** having a methyl group at the *para*-position of the benzene ring, the corresponding products **5ia**, **5ba**, and **5ca** were formed in moderate yields of 55–80% with 86–91%*ee*, perhaps due to electronic properties or steric effects (Table 5, Entries 7, 9, and 10). However, their yields could be improved when these reactions were carried out at 30 °C, affording the corresponding products in 80, 85, and 83% yield, respectively, along with similar *ee* values (Table 5, Entries 13–15). As for heterocyclic group containing *O*-Boc-protected MBH adduct **2k**, the reaction also proceeded smoothly to afford corresponding product **5ka** in 69% yield with 83%*ee* under the standard conditions (Table 5, Entry 11), but no reaction occurred with *O*-Boc-protected 2-furan-containing MBH adduct **2l** (Table 5, Entry 12). Other tosylcarbamates such as **4b** and **4c** were also suitable substrates in this reaction, and corresponding products **5db**, **5cb**, **5jb**, and **5dc** were obtained in 76–89% yield with 84–92%*ee* (Table 5, Entries 16–19); other related results as well as more examples are summarized in the Supporting Information (Table S1), suggesting the wide substrate scope in this asymmetric substitution reaction.

The absolute configuration of products **5** was unequivocally assigned the (*S*) configuration by X-ray diffraction of **5fa** bearing a bromine atom on the benzene ring.[10] Its ORTEP drawing is shown in Figure 3.

Table 5. Substrate scope of the cat-**VIII**-catalyzed asymmetric substitution of MBH adducts **2** with **4**.[a]



Entry	Substrate	R^4	R^5	Yield [%][b]	*ee* [%][c]
1	**2a**	4-$NO_2C_6H_4$	Me (**4a**)	**5aa**, 86	96 (*S*)
2	**2d**	4-ClC_6H_4	Me (**4a**)	**5da**, 85	92 (*S*)
3	**2e**	4-$CF_3C_6H_4$	Me (**4a**)	**5ea**, 82	91 (*S*)
4	**2f**	4-BrC_6H_4	Me (**4a**)	**5fa**, 85	86 (*S*)
5	**2g**	3-BrC_6H_4	Me (**4a**)	**5ga**, 89	78 (*S*)
6	**2h**	3-$NO_2C_6H_4$	Me (**4a**)	**5ha**, 88	76 (*S*)
7	**2i**	2-$NO_2C_6H_4$	Me (**4a**)	**5ia**, 60	86 (*S*)
8	**2j**	2-ClC_6H_4	Me (**4a**)	**5ja**, 91	89 (*R*)
9	**2b**	C_6H_4	Me (**4a**)	**5ba**, 80	91 (*S*)
10	**2c**	4-MeC_6H_4	Me (**4a**)	**5ca**, 55	88 (*S*)
11	**2k**		Me (**4a**)	**5ka**, 69	83 (*R*)
12	**2l**	2-furyl	Me (**4a**)	-	-
13[d]	**2b**	C_6H_5	Me (**4a**)	**5ba**, 85	86 (*S*)
14[d]	**2c**	4-MeC_6H_4	Me (**4a**)	**5ca**, 83	84 (*S*)
15[d]	**2i**	2-$NO_2C_6H_4$	Me (**4a**)	**5ia**, 80	90 (*S*)
16	**2d**	4-ClC_6H_4	Et (**4b**)	**5db**, 78	92 (*S*)
17	**2c**	4-MeC_6H_4	Et (**4b**)	**5cb**, 82	90 (*S*)
18	**2j**	2-ClC_6H_4	Et (**4b**)	**5jb**, 89	84 (*R*)
19	**2d**	4-ClC_6H_4	Bn (**4c**)	**5dc**, 76	90 (*S*)

[a] All reactions were carried out using **2** (0.10 mmol) and **4** (0.12 mmol) in THF (1.00 mL) for 72 h. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The reaction was carried out at 30 °C.

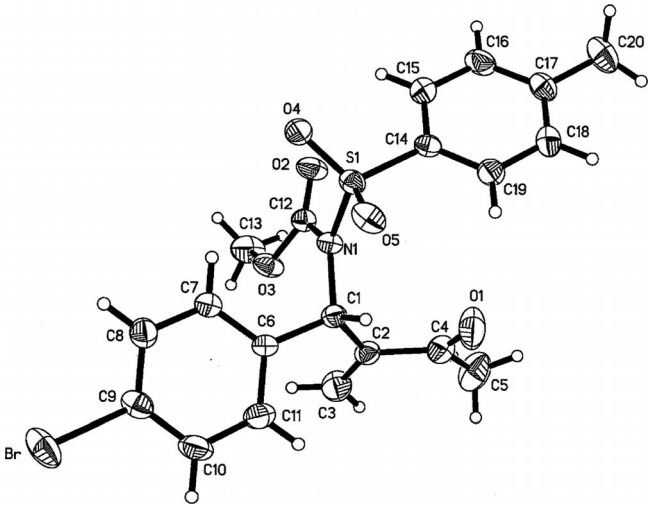


Figure 3. ORTEP drawing of **5fa**.

Conclusions

In summary, we have synthesized a series of novel quinidine-derived organocatalysts for the asymmetric substitutions of *O*-Boc-protected Morita–Baylis–Hillman adducts with various carbamates and tosylcarbamates, affording the corresponding products in good to high yields (up to 91% yield) with moderate to high *ee* value (up to 96%*ee*) under mild conditions, which is applicable to a wide range of substrates from MBH adducts. The obtained multiply functionalized aza-MBH adducts are useful building blocks in a variety of organic syntheses.[3j] Current efforts are in progress to use these novel multifunctional quinidine-derived organocatalysts for other asymmetric catalytic reactions.

Experimental Section

Representative Procedure: A solution of compound **2d** (0.10 mmol, 31.0 mg) and compound **4a** (0.12 mmol, 27.5 mg) in THF (1.00 mL) was stirred at 25 °C for 72 h in the presence of organocatalyst cat-**VIII** (15 mol-%, 6.0 mg) under an argon atmosphere. The solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (petroleum ether/EtOAc, 4:1 to 2:1) to provide product **5da** as a colorless solid (37.5 mg, 85% yield).

(*S*)-Methyl 1-(4-Chlorophenyl)-2-methylene-3-oxobutyl(tosyl)carbamate (5da): Colorless solid (37.5 mg, 85% yield); m.p. 126–129 °C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.41 (s, 3 H), 2.45 (s, 3 H), 3.57 (s, 3 H), 5.96 (d, J = 1.2 Hz, 1 H), 6.42 (d, J = 1.2 Hz, 1 H), 6.67 (s, 1 H), 7.13 (d, J = 8.4 Hz, 2 H), 7.26–7.33 (m, 4 H), 7.80 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6, 26.2, 53.5, 60.0, 128.4, 128.8, 129.0, 129.2, 129.7, 133.5, 136.2, 136.2, 144.8, 146.2, 152.6, 197.8 ppm. IR (neat): $\tilde{\nu}$ = 2957, 2925, 1738, 1681, 1493, 1439, 1361, 1265, 1170, 1090, 1015, 814 cm^{-1}. MS (ESI): *m*/*z* = 444 [M + Na]. HRMS (ESI): calcd. for $C_{20}H_{20}NClNaO_5S$ [M + Na] 444.0643; found 444.0645. $[\alpha]_D^{20}$ = +39.0 (c = 0.3, $CHCl_3$) (92%*ee*). HPLC (Chiralcel AD-H, hexane/*i*PrOH = 80:20, 0.7 mL/min, 254 nm): t_R = 19.02 (major), 24.94 (minor) min.

Supporting Information (see footnote on the first page of this article): Spectroscopic data and chiral HPLC traces of the compounds shown in Tables 1–5, X-ray crystal data of cat-**VIII** and product **5fa**, and detailed experimental procedures.

Acknowledgments

Financial support from the Shanghai Municipal Committee of Science and Technology (08dj1400100-2), the National Basic Research Program of China [(973)-2010CB833302], the Fundamental Research Funds for the Central Universities, and the National Natural Science Foundation of China (21072206, 20472096, 20902019, 20872162, 20672127, 20821002, 20732008, and 20702059) is gratefully acknowledged; Professor Jie Sun is thanked for performing the X-ray diffraction studies.

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[9] Crystal data for organocatalyst cat-**VIII**: Empirical formula: $C_{26}H_{29}N_3O_3$; formula weight: 413.52; crystal color, habit: colorless, prismatic; crystal dimensions: $0.356 \times 0.311 \times 0.270$ mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a = 9.5509(13) Å, b = 12.7565(17) Å, c = 18.691(3) Å, α = 90°, β = 90°, γ = 90°, V = 2277.2(5) Å^3; space group: $P2_12_12_1$; Z = 4; $D_{calcd.}$ = 1.259 g/cm^3; $F(000)$ = 920; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0545, 0.1392. CCDC-770089 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] Crystal data for **5fa**: Empirical formula: $C_{20}H_{20}BrNO_5S$; formula weight: 466.34; crystal color, habit: colorless; crystal dimensions: $0.359 \times 0.321 \times 0.258$ mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: a = 9.5008(10) Å, b = 14.2871(15) Å, c = 15.2971(16) Å, α = 90°, β = 90°, γ = 90°, V = 2075.7(4) Å^3; space group: $P2_12_12_1$; z = 4; $D_{calcd.}$ = 1.492 g/cm^3; $F(000)$ = 952; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0383, 0.0741. CCDC-796340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 8, 2011
Published Online: June 10, 2011

