ORGANIC LETTERS

2011
Vol. 13, No. 18
4954–4957

Kinetic Resolution of Hindered Morita–Baylis–Hillman Adducts by Rh(I)-Catalyzed Asymmetric 1,4-Addition/β-Hydroxyelimination

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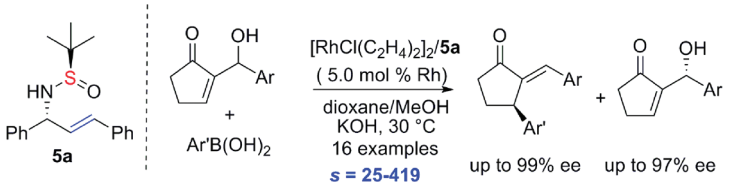
Received July 30, 2011

ABSTRACT



A kinetic resolution of hindered Morita–Baylis–Hillman adducts has been successfully achieved in excellent selectivities via Rh(I)-catalyzed asymmetric 1,4-addition/β-hydroxyelimination with the use of a chiral sulfinamide/olefin hybrid ligand. This study provides a novel and efficient access to both optically active hindered highly functionalized alkenes and Morita–Baylis–Hillman adducts.

Great progress has been made in the field of transition-metal-catalyzed 1,4-additions of organometallic reagents to electron-deficient alkenes. As one excellent subject of such a transformation, Rh(I)-catalyzed asymmetric reactions between organoboron reagents and α,β-unsaturated substrates (Hayashi–Miyaura reaction) have undergone rapid growth and have become an extremely useful synthetic tool to construct carbon–carbon bonds selectively.[1] Particularly, some challenging reactions have been successfully realized with the use of lately emerging chiral alkene ligands,[2–6] such as asymmetric additions to β,β-disubstituted α,β-unsaturated carbonyl compounds to construct all-carbon quaternary stereocenters by Hayashi's group.[7] Although a wide range

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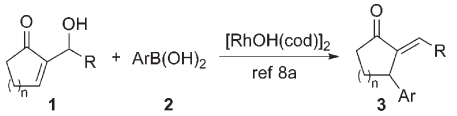
10.1021/ol202069e
Published on Web 08/15/2011

of electron-deficient alkenes have proven to be suitable substrates for the asymmetric Hayashi–Miyaura reactions, nonactivated α,α,β-trisubstituted alkenes are still challenging substrates for this type of reaction. Very recently, Darses and co-workers described a Rh(I)-catalyzed 1,4-addition of arylboronic acids **2** to hindered Morita–Baylis–Hillman (MBH) adducts **1** followed by a β-hydroxyelimination to furnish functionalized alkenes **3** in up to 91% yield (Scheme 1).[8] Two examples for the asymmetric version with C_1-symmetric chiral diene ligands[3f] developed by their own group gave the desired products **3** in 25% yield with 84% ee, which were still not satisfactory, while several well-established chiral phosphane ligands showed little activity for this transformation.[8a] To the best of our knowledge, this is the only report for asymmetric additions to nonactivated α,α,β-trisubstituted alkenes. Further studies on this type of hindered substrates is therefore of great interest.

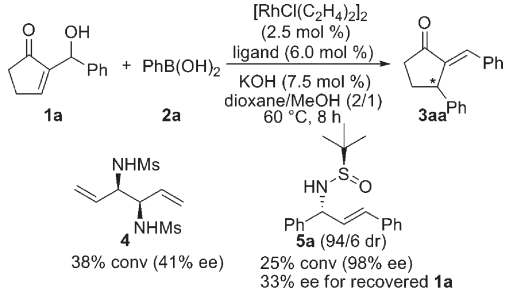
Scheme 1. Rh(I)-Catalyzed Reactions of Hindered MBH Adducts



As part of our interest in exploring novel chiral alkene ligands for transition-metal-catalyzed asymmetric reactions, a variety of acyclic chiral dienes as well as hybrid ligands including P/alkene and sulfinamide/alkene ligands have been developed.[9] Inspired by Darses's work, we envisaged that with the use of our chiral alkene ligands, the difficulties for the asymmetric transformation of nonactivated α,α,β-trisubstituted alkenes can probably be overcome. Herein, we wish to report our preliminary efforts on this subject.

Initially, Rh(I)-catalyzed asymmetric 1,4-addition of phenylboronic acid (**2a**) to hindered MBH adduct **1a** was examined with the use of chiral diene ligand **4**[9d] to afford the desired product **3aa** in 38% conversion and 41% ee. We were pleased to find that the enantioselectivity could be further improved to 98% when a chiral sulfinamide/alkene hybrid ligand **5a**[9i] was employed (Scheme 2). However, the conversion was still very low. This promising enantioselectivity encouraged us to search for the reason for the low reactivity. Considering that MBH adduct **1a** is a chiral compound, we supposed that a kinetic resolution was possible to involve in the recognition process. The ee of recovered **1a** was then determined to be 33% for the *R* configuration. Calculated according to the reported method,[10] the *s*-factor is surprisingly as high as 127, which suggests that there indeed exists an obvious kinetic resolution. Therefore, besides the highly functionalized optically active alkenes, the current study is also likely to provide a novel access to optically active MBH adducts. As we know, Morita–Baylis–Hillman reactions have achieved great success, and the resulting MBH adducts have been widely applied in synthetic chemistry.[11] However, the asymmetric reactions of cyclic enones with aromatic aldehydes are still a challenge.[12] Until very recently, highly enantioselective reactions of cyclopentenone with aromatic aldehydes were realized by Connell and co-workers with the use of Fu's chiral DMAP catalyst.[13,14]

Scheme 2. Initial Studies on Rh(I)-Catalyzed Asymmetric 1,4-Addition to Hindered MBH Adducts



A variety of chiral sulfinamide/alkene ligands were subsequently subjected to Rh(I)-catalyzed asymmetric kinetic resolution of MBH adduct **1a** with phenylboronic acid (**2a**). As shown in Table 1, it was found that the ligands' structures had an obvious impact on both activity and

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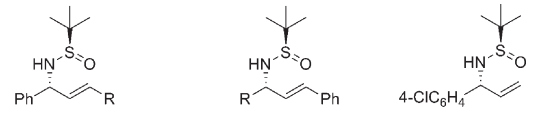
Table 1. Evaluation of Ligands[a]



5a: R = Ph (94/6 dr)
5b: R = 4-MeOC$_6$H$_4$ (88/12 dr)
5c: R = 4-CF$_3$C$_6$H$_4$ (91/9 dr)
5d: R = Me
5e: R = 1-Np (83/17 dr)
5f: R = Me
5g: R = H
5h: (99/1 dr)

entry	ligand	ee (**3aa**) (%)[b]	ee (recovered **1a**) (%)[b]	conversion (%)[c]	*s*-factor[10]
1	**5a**	**98**	**33**	**25**	**137**
2	**5b**	98	21	18	122
3	**5c**	94	10	10	36
4	**5d**	81	30	27	13
5	**5e**	80	10	11	9.9
6	**5f**	69	18	21	6.5
7	**5g**	76	17	18	8.7
8	**5h**	90	33	27	13

[a] All reactions were carried out with **1a** (0.20 mmol), **2a** (0.40 mmol), $[RhCl(C_2H_4)_2]_2$ (0.005 mmol), KOH (0.015 mmol), and ligand (0.012 mmol) in dioxane/MeOH (2/1) (0.60 mL) at 60 °C for 8 h. [b] The ee was determined by chiral HPLC. [c] The conversion was calculated by the following equation: conversion = ee (recovered **1a**)/[ee (recovered **1a**) + ee (**3aa**)].

selectivity. All of the reactions gave the desired product **3aa** with 76−98% ee, but the conversions were very low, which resulted in low ee for recovered MBH adduct **1a** (entries 1−8). Overall, ligand **5a** proved to be the most suitable ligand for this kinetic resolution (Table 1, entry 1).

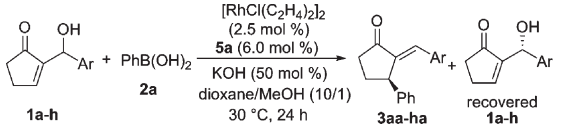
With the use of chiral ligand **5a**, the ee of product **3aa** and the *s*-factor have already reached a high level. The key point is how to improve the reactivity. Therefore, various reaction conditions were further optimized. We were pleased to find that by increasing the amount of KOH from 7.5 mol % to 50 mol % the conversion can be improved from 25% to

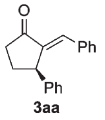
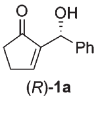
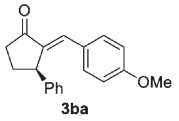
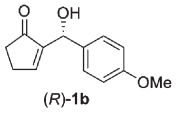
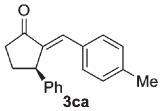
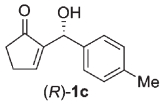
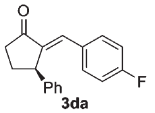
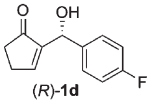
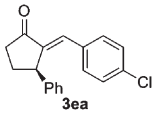
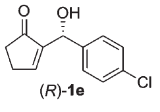
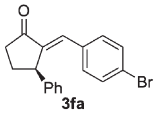
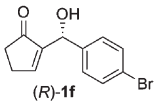
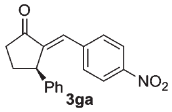
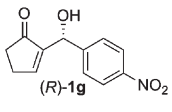
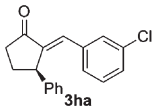
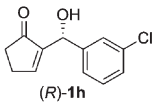
Table 2. Optimization of Reaction Conditions[a]

entry	temp (°C)	KOH (mol %)	ee for **3aa** (%)[e]	ee for **1a** (%)[e]	conv (%)[f]	*s*-factor[10]
1	60	7.5	98	33	25	137
2	60	25	98	40	29	147
3	60	50	97	55	36	114
4	60	100	90	26	22	24
5	60	50	97	65	40	129
6	50	50	98	69	42	207
7[b]	30	50	97	83	46	172
8[b]	16	50	99	48	33	321
9[c]	**30**	**50**	**97**	**87**	**47**	**188**
10[c,d]	30	50	92	64	41	46

[a] All reactions were carried out with **1a** (0.20 mmol), **2a** (0.40 mmol), $[RhCl(C_2H_4)_2]_2$ (0.005 mmol), and **5a** (0.012 mmol) for 8 h unless other stated. For entries 1−4, dioxane/MeOH (2/1) (0.60 mL) was used as solvent; for entries 5−10, dioxane/MeOH (10/1) (0.60 mL) was used as solvent. [b] The reaction time was 16 h. [c] The reaction time was 21 h. [d] Ligand **5a** (55/45 dr) was used. [e] The ee was determined by chiral HPLC. [f] The conversion was calculated by the following equation: conversion = ee (recovered **1a**)/[ee (recovered **1a**) + ee (**3aa**)].

Table 3. Rh(I)-Catalyzed 1,4-Addition/Hydroxyelimination Reactions[a]



entry	product **3**[c,d,e]	recovered **1**[c,d,f]	*s*-factor[10]
	 **3aa**	 (*R*)-**1a**	
1[b]	97% ee (43% yield)	87% ee (51% yield)	188
2	99% ee (36% yield)	70% ee (51% yield)	419
	 **3ba**	 (*R*)-**1b**	
3	98% ee (30% yield)	45% ee (61% yield)	155
	 **3ca**	 (*R*)-**1c**	
4	99% ee (26% yield)	44% ee (59% yield)	308
	 **3da**	 (*R*)-**1d**	
5	98% ee (42% yield)	81% ee (45% yield)	249
	 **3ea**	 (*R*)-**1e**	
6	95% ee (44% yield)	97% ee (44% yield)	165
	 **3fa**	 (*R*)-**1f**	
7	98% ee (41% yield)	78% ee (43% yield)	236
	 **3ga**	 (*R*)-**1g**	
8	97% ee (37% yield)	86% ee (55% yield)	183
	 **3ha**	 (*R*)-**1h**	
9	98% ee (30% yield)	51% ee (51% yield)	165

[a] All reactions were carried out with **1** (0.40 mmol), **2a** (0.80 mmol), $[RhCl(C_2H_4)_2]_2$ (0.010 mmol), KOH (0.20 mmol), and **5a** (0.024 mmol) in dioxane/MeOH (10/1) at 30 °C under argon for 24 h unless other stated. [b] The reaction was carried out in 0.2 mmol scale for 21 h. [c] Yield based on **1**. [d] The ee was determined by chiral HPLC. [e] The absolute configuration was tentatively assigned by analogy with **3ea**. [f] The absolute configuration was determined by comparing the optical rotation with the reported one.

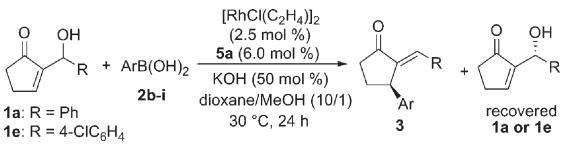
36% (Table 2, entries 1 vs 3). However, when the amount of KOH was further increased to 100 mol %, both the conversion and ee dropped (Table 2, entry 4). Temperature was

another key factor to affect the reactivity. When the temperature was lowered from 60 to 30 °C, the conversion was improved to 47%, and accordingly, excellent ee values for product **3aa** and recovered **1a** were afforded (Table 2, entry 9). Moreover, ligand **5a** with 55/45 dr was also effective for the kinetic resolution to give a slightly lower ee and conversion (Table 2, entry 10), which indicated that it was the sulfur chirality instead of the carbon chirality to determine the process of recognition and asymmetric induction.[9i]

Under the optimized reaction conditions, we next examined the scope of hindered MBH adducts **1** for Rh(I)-catalyzed kinetic resolution reactions with phenylboronic acid (**2a**). As illustrated in Table 3, different substituents on phenyl groups of MBH adducts **1** were well tolerated to furnish the optically active alkenes in 26−44% yield with 95−99% ee, and the recovered MBH adducts **1** in 43−61% yield with 44−97% ee as well (*s*-factor = 155−419, Table 3, entries 1−9). Although MBH adducts derived from cyclohexanone were good substrates in Darses's work,[8a] disappointingly, we found these substrates were less reactive for the current kinetic resolution (< 20% conversion). A variety of arylboronic acids were also tolerated for Rh(I)-catalyzed kinetic resolution reactions of MBH adducts **1a** or **1e** to give the desired products **3** in 22−48% yield with 89−98% ee (Table 4, entries 1−8). However, *ortho*-substituted MBH adducts and arylboronic acids were not suitable substrates for this type of transformation, which was possibly due to the bulky steric hindrance. The absolute configurations of product **3** were tentatively assigned by analogy with compound (*S*)-**3ea**, which was determined by its X-ray structure (see Supporting Information).

On the basis of the previously reported X-ray structure of complex formed between chiral ligand **5a** and $[RhCl(C_2H_4)_2]_2$,[9i] the absolute configurations of products and recovered MBH adducts, and some related literature,[8d,15] a plausible pathway for the asymmetric kinetic resolution is outlined as Figure 1. According to the literature,[8d,15] the hydroxyl group of MBH adduct was supposed to coordinate with rhodium. Because of the steric repulsions in **B**, **C**, and **D**, only (*S*)-**1a** can coordinate with rhodium as **A** to give the corresponding product with *S* configuration.

Table 4. Rh(I)-Catalyzed 1,4-Addition/Hydroxyelimination Reactions with Various Arylboronic Acids[a]



entry	$ArB(OH)_2$	**3** ee (yield) (%)[b,c,d]	recovered **1** ee (yield) (%)[b,c,e]	*s*-factor[10]
1	**2b**: Ar = 4-MeC_6H_4	**3ab**: 96 (33)	**1a**: 67 (53)	99
2	**2c**: Ar = 2-Np	**3ac**: 89 (25)	**1a**: 38 (68)	25
3	**2d**: Ar = 4-^{t}BuC_6H_4	**3ed**: 98 (44)	**1e**: 93 (45)	340
4	**2e**: Ar = 4-PhC_6H_4	**3ee**: 96 (43)	**1e**: 85 (37)	134
5	**2f**: Ar = 4-$HOCH_2C_6H_4$	**3ef**: 93 (32)	**1e**: 50 (55)	45
6	**2g**: Ar = 3-MeC_6H_4	**3eg**: 95 (48)	**1e**: 94 (44)	139
7	**2h**: Ar = 3-ClC_6H_4	**3eh**: 98 (22)	**1e**: 32 (62)	135
8	**2i**: Ar = 3,5-$Me_2C_6H_3$	**3ei**: 92 (39)	**1e**: 66 (50)	48

[a] All reactions were carried out with **1a** (0.40 mmol) (for entries 1 and 2) or **1e** (0.4 mmol) (for entries 3−8), $[RhCl(C_2H_4)_2]_2$ (0.010 mmol), **2** (0.80 mmol), KOH (0.20 mmol), and **5a** (0.024 mmol) in dioxane/MeOH (10/1) at 30 °C under argon for 24 h unless other stated. [b] Yield based on **1**. [c] The ee was determined by chiral HPLC. [d] The absolute configuration was tentatively assigned by analogy with **3ea**. [e] The absolute configuration was determined by comparing the optical rotation with the reported one.

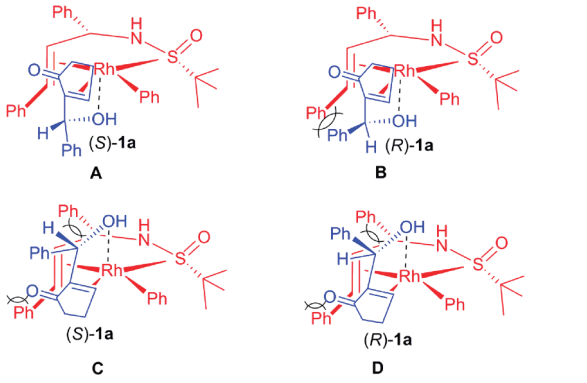


Figure 1. A plausible pathway for the asymmetric kinetic resolution.

In summary, highly enantioselective Rh(I)-catalyzed 1,4-addition/β-hydroxyelimination reactions of nonactivated hindered MBH adducts and arylboronic acids have been successfully achieved with the use of a simple chiral sulfinamide/olefin ligand. Importantly, we found for the first time that there existed a kinetic resolution with an *s*-factor of up to 419 in this transformation. Therefore, besides the highly functionalized chiral alkenes (up to 99% ee), this work also provides a novel access to optically active MBH adducts (up to 97% ee), which are not easily prepared by catalytic asymmetric MBH reactions. Further studies on expanding the substrate scope, exploring more efficient catalysts, and the application of chiral sulfinamide/olefin ligands in asymmetric catalysis are underway in our laboratory.

Acknowledgment. The authors are thankful for the financial support from the National Science Foundation of China (20802079, 21072194) and 973 program (2010CB833300).

Supporting Information Available. The procedure for rhodium-catalyzed additions, characterization of products, X-ray data, and data for the determination of enantiomeric excesses. This material is available free of charge via the Internet at http://pubs.acs.org.