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A New Aspect of Magnesium Bromide-Promoted Enantioselective Aryl Additions of Triaryl(tetrahydrofuran)aluminum to Ketones Catalyzed by a Titanium(IV) Catalyst of *trans*-1,2-Bis(hydroxycamphorsulfonylamino)cyclohexane

Chien-An Chen,[a] Kuo-Hui Wu,[a] and Han-Mou Gau[a,*]

[a] Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, ROC
Fax: +886-4-2286-2547; e-mail: hmgau@dragon.nchu.edu.tw

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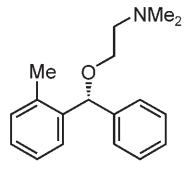
Abstract: A novel aspect of $MgBr_2$-promoted asymmetric triarylaluminum-tetrahydrofuran [$AlAr_3$(THF)] additions to ketones catalyzed by a titanium catalyst of 20 mol% *trans*-1,2-bis(hydroxycamphorsulfonylamino)cyclohexane (**2**) is reported. The catalytic system works excellently for aromatic ketones with either an electron-withdrawing or an electron-donating substituent on the aromatic ring at the 2′-, 3′-, or 4′-positions, affording tertiary alcohols in excellent enantioselectivities of $\geq$90% *ee*, except for the cases of phenyl addition to 2′-methoxyacetophenone and 4-trimethylsilylphenyl (4-$TMSC_6H_4$) addition to acetopheneone.

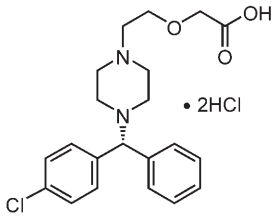
Keywords: asymmetric catalysis; disulfonamides; ketones; magnesium bromide; titanium; triarylaluminums

Introduction

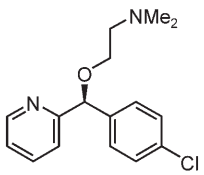
Asymmetric aryl additions to organic carbonyl compounds[1] have attracted considerable attention in recent years due to the great value of chiral diaryl alcohols leading to bioactive compounds such as (*R*)-orphenadrine, (*S*)-carbinoxamine, (*R*)-cetirizine hydrochloride, and (*R*)-clemastine fumarate.[2] Two synthetic protocols have been established for the synthesis of chiral diarylmethanols: (1) asymmetric reduction of ketones[3] and (2) asymmetric aryl additions to aldehydes. After the first phenyl additions reported by Seebach and a co-worker using the titanium-TADDOLate catalyst and the highly reactive PhTi(O-*i*-Pr)$_3$ reagent,[4] various zinc catalytic systems using a variety of arylzinc reagents, such as $ZnPh_2$,[5] mixtures of $ZnEt_2$/$ZnPh_2$,[6] reagents generated from heating $ZnEt_2$ and $ArB(OH)_2$[2b,c,7] or other arylboron compounds,[8] and reagents from reactions of $ZnCl_2$ and aryllithium compounds,[9] have been demonstrated to induce excellent stereocontrol of diarylmethanols. In addition to the above-mentioned phenyltitanium and arylzinc reagents, a few examples of direct arylboron additions catalyzed by rhodium[10] or nickel[11] catalysts have also been demonstrated. In contrast, organoaluminum compounds are more reactive than the zinc or boron reagents and have been applied to a variety of asymmetric addition reactions.[12] Recently, we discovered that $AlAr_3$(THF) compounds are effective reagents in asymmetric aryl additions to aldehydes. The addition reactions catalyzed by the titanium catalyst of 10 mol% commercially available (*R*)-H_8-BINOL are complete in only 10 min at 0 °C, and afford a wide variety of secondary alcohols including diarylmethanols in excellent enantioselectivities of >90% *ee*.[13] Furthermore, the $AlAr_3$(THF) compounds have been proven to be highly efficient cou-



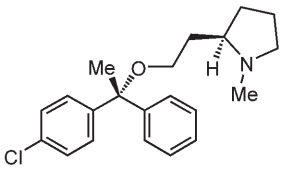
(*R*)-orphenadrine



(*R*)-cetirizine hydrochloride



(*S*)-carbinoxamine



(*R*)-clemastine fumarate

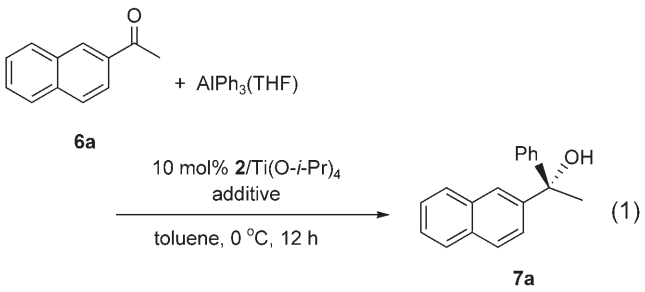
pling reagents with aryl bromides and chlorides catalyzed by the economic $Pd(OAc)_2/PCy_3$ system.[14]

Due to the great success of asymmetric additions to aldehydes,[15] recent studies have shifted addition reactions to the more inert ketone substrates to construct quaternary chiral carbon centers.[16] In contrast to the synthesis of secondary alcohols, the formation of tertiary alcohols cannot be achieved *via* the protocol of reduction of ketones. The first asymmetric phenyl addition to ketones was reported by Fu and a co-worker, who employed a catalytic system of $ZnPh_2$ and 15 mol% (+)-DAIB (**1**) to afford tertiary alcohols with enantioselectivities up to 91% *ee*.[17] Walsh and co-workers synthesized *trans*-1,2-bis(hydroxycamphorsulfonylamino)cyclohexane (**2**),[18] and the titanium complex of 10 mol% **2** has been demonstrated to be an excellent catalyst in asymmetric $ZnPh_2$ additions to ketones with enantioselectivities up to 96% *ee*.[19] Later, the titanium complex of ligand **2** was established to catalyze phenyl additions to α,β-unsaturated ketones to give products in good to excellent enantioselectivities.[20] In contrast, the titanium catalytic system of **3** was reported to give tertiary alcohols in lower yields and lower enantioselectivities.[21] Yus and co-workers demonstrated $ZnPh_2$ addition reactions using a titanium catalyst of 5 mol% **2** to furnish products in good to excellent stereocontrol.[22] They extended the reactions to aryl additions to ketones, employing arylzinc reagents generated by heating $ZnEt_2$ and $ArB(OH)_2$ compounds.[23] The catalytic reactions added aryl groups to aliphatic and aromatic ketones, affording products with enantioselectivities up to 93% *ee*. Hayashi and co-workers reported a rhodium catalyst of (*R*)-MeO-mop (**4**), which catalyzes asymmetric aryl additions to the ketone group of isatin (**5**), and produced products in enantioselectivities up to 91% *ee*.[24] We also reported on a titanium catalytic system of (*S*)-BINOL that catalyzes $AlAr_3(THF)$ additions to a wide variety of ketones, and afforded tertiary alcohols in excellent stereocontrol.[25] Recently, a zinc catalyst of chiral phosphoramides has been established to induce excellent stereocontrol in $ZnPh_2/ZnEt_2$ additions to ketones.[26]

To continue our efforts in asymmetric catalysis[27] and to compare $AlAr_3(THF)$ and arylzinc reagents in asymmetric aryl additions to ketones, we herein report asymmetric $AlAr_3(THF)$ additions to ketones catalyzed by titanium catalysts of chiral ligand **2**, which have been used in titanium-catalyzed arylzinc additions to ketones. We surprisingly found that inorganic salts such as $MgBr_2$ and MgI_2 were essential in promoting the addition reactions affording tertiary alcohols in high yields and excellent enantioselectivities.

Results and Discussion

Asymmetric phenyl additions of $AlPh_3(THF)$ were first optimized on 2′-acetonaphthone [Eq. (1)] and the results are listed in Table 1. When the reaction was



conducted under reaction conditions of 10 mol% **2**, 3.0 equiv. $AlPh_3(THF)$, and 5.0 equiv. $Ti(O\text{-}i\text{-}Pr)_4$, which is the best performing condition for asymmetric $AlEt_3$ additions to aldehydes catalyzed by the titanium catalyst of *N*-sulfonylated amino alcoholate,[28] the $AlPh_3(THF)$ addition reaction proceeded sluggishly affording the tertiary alcohol in only a 21% yield (entry 1) in a reaction time of 12 h. We then searched for reasons for the slow reaction of the titanium catalyst of **2** employing the $AlPh_3(THF)$ reagent, and in one occasion, the reaction using an impure sample of $AlPh_3(THF)$ gave the tertiary alcohol in quantitative yield and a good 88% *ee* (entry 2). Since $AlPh_3(THF)$ was prepared from a reaction of $AlCl_3$ and phenyl-Grignard reagent in THF, the impure sample likely contained a trace amount of magnesium halide, which might play a key role in the promotion of the asymmetric catalytic reaction. Thus, we subsequently examined reactions with additions of various inorganic metal salts. With the addition of 12 mol% $MgBr_2$, the reaction was still slow to afford the product in a slightly higher 38% yield (entry 3). However, when the amount of $MgBr_2$ was increased to 24 mol%, both

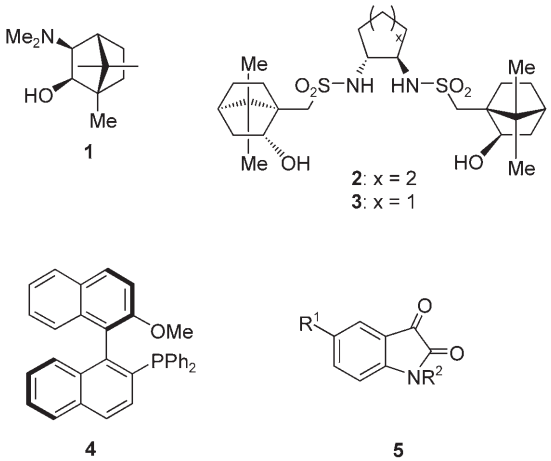


Table 1. Optimization of asymmetric $AlPh_3(THF)$ additions to 2′-acetonaphthone catalyzed by titanium(IV) complexes of *trans*-1,2-bis(hydroxycamphorsulfonylamino)cyclohexane (**2**).[a]

Entry	$AlPh_3(THF)$ [equiv]	$Ti(O\text{-}i\text{-}Pr)_4$ [equiv]	Additive [mol%]	Yield[b] [%]	*ee*[c] [%]
1	3.0	5.0	-	21	n.d.
2	3.0[d]	5.0	-	100	88
3	3.0	5.0	$MgBr_2$ (12)	38	n.d.
4	3.0	5.0	$MgBr_2$ (24)	100	87
5	3.0	5.0	$MgBr_2$ (36)	100	82
6	3.0	5.0	$MgCl_2$ (24)	51	60
7	3.0	5.0	MgI_2 (24)	100	72
8	3.0	5.0	MgO (24)	15	n.d.
9	3.0	5.0	$ZnCl_2$ (24)	53	29
10	3.0	5.0	$Zn(OTf)_2$ (24)	54	5
11	2.5	5.0	$MgBr_2$ (24)	83	84
12	1.5	5.0	$MgBr_2$ (24)	23	n.d.
13	3.0	3.0	$MgBr_2$ (24)	42	n.d.
14[e]	3.0	5.0	$MgBr_2$ (24)	100	82
15[f]	3.0	5.0	$MgBr_2$ (24)	39	n.d.
16[g]	3.0	5.0	$MgBr_2$ (24)	0	-
17[h]	6.0	10.0	$MgBr_2$ (48)	100	92

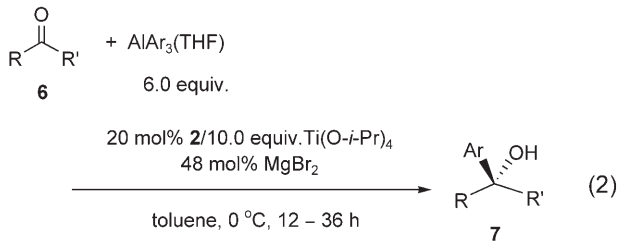
[a] 2′-Acetonaphthone/**2** = 0.50/0.050 mmol; toluene, 7 mL.
[b] Yields are based on ^1H NMR spectra.
[c] The *ee* values were determined by chiral columns from Daicel.
[d] Impure $AlPh_3(THF)$ was used.
[e] 25 °C.
[f] In CH_2Cl_2.
[g] In THF.
[h] 20 mol% ligand **2**.

yield and enantioselectivity increased dramatically to 100% and 87% *ee* (entry 4). This result is comparable to the 88% *ee* obtained from the reaction using the impure $AlPh_3(THF)$ sample. Further increasing $MgBr_2$ to 36 mol% gave the product in 100% yield, but the enantioselectivity dropped to 82% *ee* (entry 5).

We then examined reactions employing other additives such as $MgCl_2$, MgI_2, MgO, $ZnCl_2$, and $Zn(OTf)_2$. Although the above additives, aside from MgO, promoted phenyl additions (entries 6–10), $MgBr_2$ at 24 mol% remained the best choice in terms of both yield and stereoselectivity. While keeping $Ti(O\text{-}i\text{-}Pr)_4$ at 5.0 equiv. and $MgBr_2$ at 24 mol% but tuning $AlPh_3(THF)$ to 2.5 and 1.5 equiv., yields of the product decreased to 83% (84% *ee*, entry 11) and 23% (entry 12), respectively. When 3.0 equiv. $AlPh_3(THF)$ and 3.0 equiv. $Ti(O\text{-}i\text{-}Pr)_4$ were used, the reaction gave the product in a low 42% yield (entry 13). When the reaction was conducted at 25 °C, the product was obtained in 100% yield and a lower 82% *ee* (entry 14). Solvent effects were examined and the product in 38% yield was obtained using the CH_2Cl_2 as solvent (entry 15). In THF, the reaction, however, did not proceed at all (entry 16). When doubling the quantities of **2**, $AlPh_3(THF)$, $Ti(O\text{-}i\text{-}Pr)_4$, and $MgBr_2$, the reaction gave the tertiary alcohol in a quantitative yield and an excellent 92% *ee* (entry 17).

In the case of the titanium-TADDOLate complex-catalyzed $PhTi(O\text{-}i\text{-}Pr)_3$ additions to aldehydes, the lithium salt generated in the preparation of $PhTi(O\text{-}i\text{-}Pr)_3$ needed to be completely removed to ensure high enantioselectivities of the phenylation products.[4] In contrast, this study shows that the titanium catalytic system of **2** using the $AlPh_3(THF)$ reagent is promoted by the $MgBr_2$ additive.

Under the best performing conditions (those of the entry 17 in Table 1), asymmetric $AlAr_3(THF)$ additions to various ketones were examined [Eq. (2)] and



the results are summarized in Table 2. In terms of stereocontrol, the catalytic system worked equally well for aromatic ketones bearing an electron-donating or an electron-withdrawing substituent at 2′-, 3′-, or 4′-position on the aromatic group, affording products with enantioselectivities of $\geq$90% *ee* (entries 1–13), except for the 2′-methoxyacetophenone substrate that gave only 18% *ee* (entry 8). In this study, a significant steric effect was observed in terms of substituted positions of the substituent on the aromatic ring, and longer reaction times were required for hindered aromatic ketones in order to furnish products in good yields. For example, reaction times of 36 h, 18 h, and 24 h were needed for 1′-acetonaphthone (entry 2), 2′-methylacetophenone (entry 3) and 2′-bromoacetophenone (entry 6), giving the corresponding tertiary alcohols in satisfactory 80%, 85%, and 87% yields, respectively. It is worth noting that the phenyl addition

Table 2. Asymmetric aryl additions of $AlAr_3(THF)$ to ketones catalyzed by the titanium(IV) catalytic system of 20 mol% **2** promoted by 48 mol% $MgBr_2$.[a]

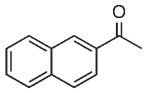
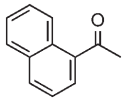
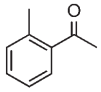
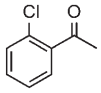
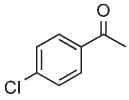
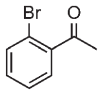
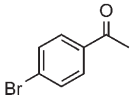
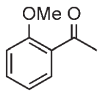
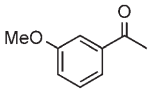
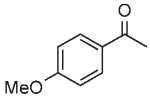
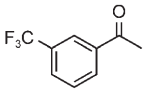
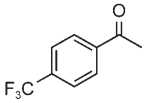
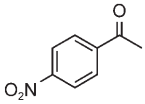
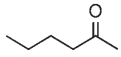
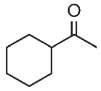
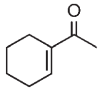
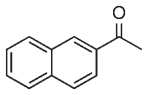
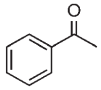
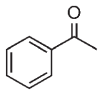
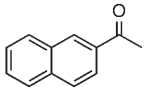
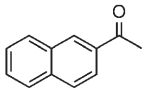
Entry	Ketone **6**		Ar	Time [h]	Product **7**	Yield[b] [%]	*ee*[c] [%]
1	**6a**		Ph	12	**7a**	99	92 (−)
2	**6b**		Ph	36	**7b**	80	93 (−)
3	**6c**		Ph	18	**7c**	85	96 (−)
4	**6d**		Ph	12	**7d**	95	97 (−)
5	**6e**		Ph	12	**7e**	98	92 (+)
6	**6f**		Ph	24	**7f**	87	98 (−)
7	**6g**		Ph	12	**7g**	97	92 (+)
8	**6h**		Ph	12	**7h**	99	18
9	**6i**		Ph	12	**7i**	99	92 (+)
10	**6j**		Ph	12	**7j**	92	90 (−)
11	**6k**		Ph	12	**7k**	98	97 (+)
12	**6l**		Ph	12	**7l**	97	93 (+)
13	**6m**		Ph	12	**7m**	99	92 (+)
14	**6n**		Ph	12	**7n**	97	52
15	**6o**		Ph	12	**7o**	82	83 (+)
16	**6p**		Ph	12	**7p**	87	81 (+)
17	**6q**		Ph	12	**7q**	95	75 (−)

Table 2. (Continued)

Entry	Ketone **6**		Ar	Time [h]	Product **7**	Yield[b] [%]	*ee*[c] [%]
18	**6a**		4-MeC_6H_4	12	**7r**	97	90 (+)
19	**6s**		4-$TMSC_6H_4$	12	**7s**	83	81 (+)
20	**6s**		2-naphthyl	12	**7a′**	95	91 (+)
21[d]	**6a**		Ph	12	**7a**	11	-
22[e]	**6a**		Ph	12	**7a**	52	22

[a] Ketone/$AlAr_3$(THF)/Ti(O-*i*-Pr)$_4$/**2**/$MgBr_2$ = 0.25/1.5/2.5/0.050/0.12 mmol; toluene, 7 mL.
[b] Isolated yields.
[c] The *ee* values were determined by chiral columns from Daicel, and the signs of optical rotations were indicated in parentheses.
[d] 2′-Acetonaphthone/PhTi(O-*i*-Pr)$_3$/Ti(O-*i*-Pr)$_4$/**2**/$MgBr_2$ = 0.25/1.5/2.5/0.050/0 mmol; toluene, 7 mL.
[e] 2′-Acetonaphthone/PhTi(O-*i*-Pr)$_3$/Ti(O-*i*-Pr)$_4$/**2**/$MgBr_2$ = 0.25/1.5/2.5/0.050/0.12 mmol; toluene, 7 mL.

to 2′-methoxyacetophenone afforded the product in a superb 99% yield but only a low 18% *ee* (entry 8). The low enantioselectivity of the $AlPh_3$(THF) addition to 2′-methoxyacetophenone was also observed with the titanium catalyst of (*S*)-BINOL, and this phenomenon is attributed to small differentiations of both orientations of 2′-methoxyacetophenone chelating to the metal center. Phenyl additions to aliphatic ketones and 1-acetyl-1-cyclohexene were also examined. The resulting tertiary alcohols were obtained in good to excellent yields with good enantioselectivities of 75–83% *ee* (entries 15–17), except for the alcohol obtained from the linear 2-hexanone (52% *ee*, entry 14). In addition to the phenyl addition reactions, aryl additions to aromatic ketones were also conducted. The *p*-tolyl addition to 2′-acetonaphthone afforded the product in excellent yield and 90% *ee* (entry 18), and the 4-$TMSC_6H_4$ addition to acetophenone gave the desired product in good yield and good enantioselectivity of 81% *ee* (entry 19). When 2-naphthyl was added to acetophenone, the product **7a′** was obtained in excellent 91% *ee* but in reverse absolute configuration to the product **7a** derived from the addition of phenyl to 2′-acetonaphthone (entry 20).

Phenylzinc or arylzinc additions to ketones catalyzed by the titanium catalyst of **2** have been established. In the study by Walsh and a co-worker using 10 mol% titanium catalyst of **2**, $ZnPh_2$ additions to 5 aromatic, 2 α,β-unsaturated, and 2 aliphatic ketones were conducted at room temperature for reaction times of 6–24 h, affording tertiary alcohols in good to excellent enantioselectivities for aromatic and α,β-unsaturated ketones (88–96% *ee*) and for aliphatic ketones in 75 and 87% *ee*.[19] In the study by Yus et al., a titanium catalyst of 5 mol% **2** was employed at 25 °C for 24 h on 4 examples of $ZnPh_2$ additions to aromatic ketones, furnishing the desired products in enantioselectivities of 80 to 96% *ee*.[22,23] They also demonstrated addition reactions of arylzinc reagents which were generated from heating arylboronic with $ZnEt_2$. The reactions produced tertiary diaryl alcohols in low to moderate yields (31–65%) and in moderate to excellent enantioselectivities from 64 to 93% *ee*. In this study, a wider variety of ketones was examined to produce products in good to excellent yields. With the use of higher catalyst loadings of 20 mol%, phenyl additions to aromatic ketones were demmonstrated giving tertiary diaryl alcohols in excellent enantioselectivities of ≥90% *ee* except the addition to 2′-methoxyacetophenone. The phenyl addition to 1-acetyl-1-cyclohexene afforded the product in lower enantioselectivity, but the additions to aliphatic ketones gave products in comparable enantioselectivities to results from the work by Walsh and a co-worker.[19] For substrates of 4′-bromoacetophenone (**6g**), 3′-(trifluoromethyl)acetophenone (**6k**), 4′-(trifluoromethyl)acetophenone (**6l**), and 3-methyl-2-butanone (**6o**), 1-acetyl-1-cyclohexene (**6q**), $AlPh_3$(THF) additions afforded

(+)-**7g**, (+)-**7k**, (+)-**7l**, (+)-**7o** and (−)-**7q**. These tertiary alcohols have the same signs of optical rotations as products obtained from the phenylzinc addition reactions. This study shows a unique feature of the $MgBr_2$-promoted aryl additions to ketones, and, in general, shorter reaction times of 12 h at 0 °C were enough to produce products in good to excellent yields in comparison to 24 h at 25 °C for arylzinc addition reactions using 5 mol% catalyst. In summary, advantages of $ZnPh_2$ additions to ketones are lower catalyst loadings of 5 to 10 mol% used and no additive required. A major disadvantage of this system is that the arylzinc addition reactions do not give diaryl alcohols in satisfactory yields. In contrast, advantages of the $AlAr_3$(THF) reagents are shorter reaction times, easy preparation of the reagents, and that the reactions can be extended to additions of different aryl groups to ketones giving tertiary diaryl alcohols in good to excellent enantioselectivities.

In studies of titanium-catalyzed asymmetric organozinc or organoaluminum additions to aldehydes, a reaction mechanism *via* addition of organotitanium species to the carbonyl carbon has been established.[4,13,29] To verify if the aryl additions of $AlAr_3$(THF) to ketones proceeded *via* aryltitanium species in this trimetallic reaction system, the catalytic reactions were conducted under the same reaction conditions except replacing $AlPh_3$(THF) with PhTi(O-*i*-Pr)$_3$. In the absence of $MgBr_2$, the reaction gave the product in only 11% yield (Table 2, entry 21) which is even lower than the 21% yield of the $AlPh_3$(THF) addition reaction under conditions without the addition of $MgBr_2$ (Table 1, entry 1). With the addition of 48 mol% $MgBr_2$, the yield of the product improved to 52% but the enantioselectivity was still only 22% *ee* (Table 2, entry 22). The dramatic differences in reactivities and in stereoselectivities observed for additions of $AlPh_3$(THF) and of PhTi(O-*i*-Pr)$_3$ suggest that the $AlAr_3$(THF) addition reactions catalyzed by the titanium catalyst of **2** might not proceed through the same pathway as the titanium-catalyzed organozinc or organoaluminum additions to aldehydes.

Conclusions

Asymmetric $AlAr_3$(THF) additions to ketones catalyzed by the titanium catalyst of 20 mol% *trans*-1,2-bis(hydroxycamphorsulfonylamino)cyclohexane (**2**) are now reported. Several important features were demonstrated in this study. First, a novel aspect of the inorganic salt $MgBr_2$ as a key additive to promote the aryl addition of $AlAr_3$(THF) to ketones was demonstrated. Second, the catalytic system worked excellently for aromatic ketones bearing either an electron-withdrawing or an electron-donating substituent on the aromatic group to afford tertiary alcohols in enantioselectivities of $\geq$90% *ee*, except for 2′-methoxyacetophenone. Third, longer reactions times were required for *ortho*-substituted aromatic ketones to furnish products in good yields. Fourth, the reactions of PhTi(O-*i*-Pr)$_3$ additions to 2′-acetonaphthone catalyzed by the same catalyst gave the product in low yield and low enantioselectivity suggesting that the $AlAr_3$(THF) addition reactions might not proceed *via* aryltitanium species. Further mechanistic studies of aryl additions to aldehydes and to ketones are currently underway.

Experimental Section

General Remarks

$AlAr_3$(THF) was synthesized according to the literature procedure[13] and was stored under a dry nitrogen atmosphere. Ti(O-*i*-Pr)$_4$ was freshly distilled prior to use. Ligand **2** was synthesized according to the literature procedure.[18] $MgBr_2$ was obtained from Strem. Ketones were purchased from Acros and Lancaster. Solvents were dried by heating under refluxing for at least 24 h over P_2O_5 (dichloromethane) or sodium/benzophenone (toluene and THF). All catalytic reactions were carried out under a dry nitrogen atmosphere. ^{1}H NMR (400 MHz) and ^{13}C (100 MHz) spectra were obtained on a Varian Mercury-400 spectrometer, and the ^{1}H and ^{13}C NMR chemical shifts were measured relative to tetramethylsilane at 0.0 ppm as the internal reference. Optical rotations were determined on a Perkin–Elmer 241 polarimeter. High resolution molecular masses of tertiary alcohols were determined by a Finnigan MAT 95XL spectrometer. Enantiomeric excesses of tertiary alcohols were performed on a Rainin Dynamax® or an Agilent 1100 HPLC system using appropriate chiral columns from Daicel.

Syntheses

General Procedure for the Asymmetric Addition of $AlAr_3$(THF) to Ketones: Under a dry nitrogen atmosphere, ligand **2** (0.050 mmol, 0.0273 g), $MgBr_2$ (0.12 mmol, 0.0221 g) and Ti(O-*i*-Pr)$_4$ (2.5 mmol, 0.75 mL) were mixed in dry toluene (1 mL) at room temperature. After stirring the mixture for 1 h at 0 °C, $AlAr_3$(THF) (1.5 mmol, 0.496 g) in toluene (5 mL) was added. The mixture was stirred for 30 min and the resulting solution was treated with a ketone (0.25 mmol). The mixture was allowed to react at 0 °C and quenched with 1 M aqueous HCl (2 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was dried over $MgSO_4$, filtered and concentrated to dryness. The residue was purified by column chromatography to give the tertiary alcohol. The enantiomeric excess of the product was determined by HPLC.

Spectroscopic Data

7a:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 1.2 Hz, 1H), 7.84–7.75 (m, 3H), 7.49–7.25 (m, 8H), 2.27 (br, 1H), 2.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.70, 145.22, 132.96, 132.35, 128.22, 128.18, 127.91, 127.45, 127.00, 126.08, 125.92, 124.91, 123.70, 76.31, 30.66; $[\alpha]_D^{25}$: −16.1 (*c*

1.0, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm; *n*-hexane/2-propanol = 80:20; 1.0 mL min^{-1}; major: 14.5 min, minor: 17.9 min.

7b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.80 (m, 4H), 7.49 (dd, J = 7.2, 8.0 Hz, 1H), 7.38–7.32 (m, 3H), 7.27–7.18 (m, 4H), 2.45 (br, 1H), 2.06 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.53, 142.03, 134.88, 130.66, 129.03, 128.73, 128.27, 127.27, 126.71, 125.36, 125.20,125.13, 124.62, 124.04, 77.09, 32.77; HR-MS: m/z = 248.1193, calcd. for $C_{18}H_{16}O$: 248.1202 [M$^+$]; $[\alpha]_D^{25}$: −95.4 (c 0.94, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, major: 12.9 min, minor: 18.3 min.

7c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.69 (m, 1H), 7.30–7.22 (m, 7H), 7.12–7.10 (m, 1H), 2.12 (br, 1H), 1.98 (s, 3H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.94, 144.57, 137.10, 132.39, 128.06, 127.61, 126.54, 125.93, 125.32, 125.26, 76.73, 32.05, 21.30; HR-MS: m/z = 212.1207, calcd. for $C_{15}H_{16}O$: 212.1201; $[\alpha]_D^{25}$: −60.3 (c 1.8, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 95:5, 1.0 mL min^{-1}, major: 12.2 min, minor: 18.2 min.

7d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, J = 7.6 Hz, 1H), 7.36–7.25 (m, 8H), 3.40 (br, 1H), 1.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.55, 143.63, 132.56, 131.30, 128.86, 128.12, 128.01, 126.88, 126.73, 125.24, 76.69, 29.86; HR-MS: m/z = 232.0651, calcd. for $C_{14}H_{13}ClO$: 232.0655 [M$^+$]; $[\alpha]_D^{25}$: −44.5 (c 1.9, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 8.2 min, minor: 9.7 min.

7e: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 9H), 2.14 (br, 1H), 1.94 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.37, 146.50, 132.64, 128.23, 128.15, 127.28, 127.14, 125.72, 75.80, 30.68; HR-MS: m/z = 232.0656, calcd. for $C_{14}H_{13}ClO$: 232.0655 [M$^+$]; $[\alpha]_D^{25}$: +8.78 (c 3.2, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 15.3 min, minor: 17.6 min.

7f:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (dd, J = 1.6, 7.6 Hz, 1H), 7.54 (dd, J = 1.2, 8.0 Hz, 1H), 7.43–7.39 (m, 1H), 7.30–7.19 (m, 6H), 3.51 (br, 1H), 1.96 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.56, 144.91, 134.88, 129.07, 128.43, 128.13, 127.27, 126.87, 125.56, 122.30, 77.43, 30.27; $[\alpha]_D^{25}$: −43.9 (c 1.4, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 7.9 min, minor: 9.4 min.

7g:[22,23] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.26 (m, 9H), 2.16 (br, 1H), 1.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.30, 147.05, 131.13, 128.26, 127.65, 127.18, 125.72, 120.84, 75.86, 30.66; HR-MS: m/z = 276.0144, calcd. for $C_{14}H_{13}BrO$: 276.0150 [M$^+$]; $[\alpha]_D^{25}$: +7.70 (c 2.3, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 17.3 min, minor: 20.1 min.

7h: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 1H), 7.32–7.17 (m, 6H), 7.04–7.00 (m, 1H), 6.87 (dd, J = 1.2, 8.4 Hz, 1H), 4.67 (s, 1H), 3.56 (s, 3H), 1.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 157.02, 149.59, 135.25, 128.73, 127.66, 126.98, 126.20, 124.80, 120.85, 112.22, 76.20, 55.52, 30.08; HR-MS: m/z = 228.1158, calcd. for $C_{15}H_{16}O_2$: 228.1150 [M$^+$]; HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 80:20, 1.0 mL min^{-1}, major: 6.7 min, minor: 20.7 min.

7i: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2H), 7.34–7.22 (m, 4H), 7.02–6.95 (m, 2H), 6.79 (dd, J = 2.8, 8.4 Hz, 1H), 3.78 (s, 3H), 2.18 (br, 1H), 1.95 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 159.32, 149.69, 147.76, 129.06, 128.07, 126.87, 125.70, 118.30, 111.91, 76.04, 55.08, 30.67; HR-MS: m/z = 228.1154, calcd. for $C_{15}H_{16}O_2$: 228.1150 [M$^+$]; $[\alpha]_D^{25}$: +9.17 (c 3.0, CH_2Cl_2); HPLC analysis: Chiralcel OD, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 98:2, 1.0 mL min^{-1}, major: 24.3 min, minor: 28.5 min.

7j: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.23 (m, 7H), 6.84 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.19 (s, 1H), 1.93 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 158.36, 148.23, 140.27, 128.01, 127.09, 126.73, 125.70, 113.36, 75.82, 55.14, 30.88; HR-MS: m/z = 228.1150, calcd. for $C_{15}H_{16}O_2$: 228.1150 [M$^+$]; $[\alpha]_D^{25}$: −14.6 (c 0.71, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 80:20, 1.0 mL min^{-1}, major: 23.1 min, minor: 19.1 min.

7k:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.53–7.26 (m, 8H), 2.22 (br, 1H), 1.98 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 149.05, 147.04, 129.42, 128.56, 128.40, 127.39, 125.79, 123.74, 123.70, 122.36, 122.33, 75.94, 30.73; $[\alpha]_D^{25}$: +25.6 (c 3.0, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 21.3 min, minor: 30.4 min.

7l:[22,23] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.54 (m, 4H), 7.42–7.26 (m, 5H), 2.21 (br, 1H), 1.97 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 151.92, 147.03, 129.16, 128.84, 128.37, 127.39, 126.12, 125.81, 125.53, 125.11, 125.07, 125.04, 125.00, 122.82, 75.97, 30.56; HR-MS: m/z = 266.0925, calcd. for $C_{15}H_{13}OF_3$: 266.0919 [M$^+$]; $[\alpha]_D^{25}$: +24.8 (c 4.5, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99.5:0.5, 1.0 mL min^{-1}, major: 26.8 min, minor: 32.5 min.

7m: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.8 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.42–7.26 (m, 5H), 2.27 (br, 1H), 1.99 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 155.29, 146.59, 146.41, 128.49, 127.62, 126.61, 125.72, 123.29, 75.88, 30.43; HR-MS: m/z = 243.0886, calcd. for $C_{14}H_{13}NO_3$: 243.0895 [M$^+$]; $[\alpha]_D^{25}$: +38.9 (c 2.6, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 90:10, 1.0 mL min^{-1}, major: 37.3 min, minor: 31.8 min.

7n: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2H), 7.34–7.30 (m, 2H), 7.23–7.20 (m, 1H), 1.95 (br, 1H), 1.81–1.76 (m, 2H), 1.54 (s, 3H), 1.28–1.21 (m, 3H), 1.13–1.09 (m, 1H), 0.85–0.82 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 148.09, 128.02, 126.38, 124.74, 74.63, 43.91, 30.03, 26.10, 22.96, 13.93; HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 9.3 min, minor: 13.5 min.

7o:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.41 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.21 (m, 1H), 2.06–1.99 (m, 1H), 1.53 (s, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 147.72, 127.77, 126.31, 125.20, 76.70, 38.52, 26.53, 17.35, 17.11; $[\alpha]_D^{25}$: +3.33 (c 0.57, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 11.3 min, minor: 17.7 min.

7p:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.39 (m, 2H), 7.35–7.31 (m, 2H), 7.25–7.21 (m, 1H), 1.75–1.56 (m, 6H), 1.53 (s, 3H), 1.20–0.95 (m, 5H); ^{13}C{^{1}H} NMR

(100 MHz, $CDCl_3$): $\delta = 147.85$, 127.79, 126.31, 125.28, 76.61, 48.99, 27.34, 27.17, 26.75, 26.63, 26.37; $[\alpha]_D^{25}$: +18.2 (*c* 0.72, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 10.5 min, minor: 12.8 min.

7q:[19a] ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$–7.41 (m, 2H), 7.34–7.30 (m, 2H), 7.26–7.21 (m, 1H), 5.92–5.90 (m, 1H), 2.13–2.12 (m, 2H), 1.94–1.68 (m, 3H), 1.64 (s, 3H), 1.58–1.52 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 146.80, 142.38, 127.93, 126.51, 125.25, 121.49, 76.97, 28.69, 25.15, 24.48, 22.81, 22.21; $[\alpha]_D^{25}$: −11.3 (*c* 1.1, CH_2Cl_2); HPLC analysis: Chiralcel OD-H, 0.46 cm ø × 15 cm, *n*-hexane/2-propanol = 99:1, 1.0 mL min^{-1}, major: 6.7 min, minor: 8.3 min.

7r: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.96$ (s, 1H), 7.83–7.72 (m, 3H), 7.47–7.38 (m, 3H), 7.33–7.31 (m, 2H), 7.12–7.10 (m, 2H), 2.32 (s, 3H), 2.28 (br, 1H), 2.01 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 145.46$, 144.88, 136.68, 133.01, 132.36, 128.89, 128.24, 127.88, 127.47, 126.06, 125.89, 125.85, 124.93, 123.64, 76.22, 30.73, 20.97; HR-MS: $m/z =$ 262.1364, calcd. for $C_{19}H_{18}O$: 262.1358 [M$^+$]; $[\alpha]_D^{25}$: +0.58 (*c* 0.69, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 70:30, 1.0 mL min^{-1}, major: 12.6 min, minor: 21.9 min.

7s: ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$–7.25 (m, 9H), 2.22 (br, 1H), 1.96 (s, 3H), 0.27 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 148.48$, 147.93, 138.93, 133.26, 128.15, 126.92, 125.81, 125.10, 76.17, 30.75, −1.14; HR-MS: $m/z =$ 270.1433, calcd. for $C_{17}H_{22}SiO$: 270.1440 [M$^+$]; $[\alpha]_D^{25}$: +1.79 (*c* 0.28, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm, *n*-hexane/2-propanol = 95:5, 1.0 mL min^{-1}, major: 12.5 min, minor: 8.1 min.

7a′:[19a] $[\alpha]_D^{25}$: +15.3 (*c* 0.73, CH_2Cl_2); HPLC analysis: Chiralcel OJ, 0.46 cm ø × 25 cm; *n*-hexane/2-propanol = 80:20; 1.0 mL min^{-1}; major: 19.9 min, minor: 16.1 min.

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References

[1] a) C. Bolm, J. P. Hildebrand, K. Muñiz, N. Hermanns, *Angew. Chem.* **2001**, *113*, 3382–3407; *Angew. Chem. Int. Ed.* **2001**, *40*, 3284–3308; b) F. Schmidt, R. T. Stemmler, J. Rudolph, C. Bolm, *Chem. Soc. Rev.* **2006**, *35*, 454–470.

[2] a) S. Stanchev, R. Rakovska, N. Berova, G. Snatzke, *Tetrahedron: Asymmetry* **1995**, *6*, 183–198; b) P.-Y. Wu, H.-L. Wu, B.-J. Uang, *J. Org. Chem.* **2006**, *71*, 833–835; c) G. Lu, F. Y. Kwong, J.-W. Ruan, Y.-M. Li, A. S. C. Chan, *Chem. Eur. J.* **2006**, *12*, 4115–4120.

[3] a) E. J. Corey, C. J. Helal, *Tetrahedron Lett.* **1996**, *37*, 4837–4840; b) T. Ohkuma, M. Koizumi, H. Ikehira, T. Yokozawa, R. Noyori, *Org. Lett.* **2000**, *2*, 659–662.

[4] B. Weber, D. Seebach, *Tetrahedron* **1994**, *50*, 7473–7484.

[5] a) P. I. Dosa, J. C. Ruble, G. C. Fu, *J. Org. Chem.* **1997**, *62*, 444–445; b) C. Bolm, K. Muñiz, *Chem. Commun.* **1999**, 1295–1296; c) W.-S. Huang, Q.-S. Hu, L. Pu, *J. Org. Chem.* **1999**, *64*, 7940–7956; d) G. Zhao, X.-G. Li, X.-R. Wang, *Tetrahedron: Asymmetry* **2001**, *12*, 399–403; e) D.-H. Ko, K. H. Kim, D.-C. Ha, *Org. Lett.* **2002**, *4*, 3759–3762; f) Y.-C. Qin, L. Pu, *Angew. Chem.* **2006**, *118*, 279–283; *Angew. Chem. Int. Ed.* **2006**, *45*, 273–277.

[6] a) W.-S. Huang, L. Pu, *J. Org. Chem.* **1999**, *64*, 4222–4223; b) C. Bolm, N. Hermanns, J. P. Hildebrand, K. Muñiz, *Angew. Chem.* **2000**, *112*, 3607–3609; *Angew. Chem. Int. Ed.* **2000**, *39*, 3465–3467; c) C. Bolm, M. Kesselgruber, N. Hermanns, J. P. Hildebrand, G. Raabe, *Angew. Chem.* **2001**, *113*, 1536–1538; *Angew. Chem. Int. Ed.* **2001**, *40*, 1488–1490; d) M. Fontes, X. Verdaguer, L. Solà , M. A. Pericàs, A. Riera, *J. Org. Chem.* **2004**, *69*, 2532–2543; e) J. K. Park, H. G. Lee, C. Bolm, B. M. Kim, *Chem. Eur. J.* **2005**, *11*, 945–950.

[7] a) C. Bolm, J. Rudolph, *J. Am. Chem. Soc.* **2002**, *124*, 14850–14851; b) J.-X. Ji, J. Wu, T. T.-L. Au-Yeung, C.-W. Yip, R. K. Haynes, A. S. C. Chan, *J. Org. Chem.* **2005**, *70*, 1093–1095; c) A. L. Braga, D. S. Lüdtke, F. Vargas, M. W. Paixão, *Chem. Commun.* **2005**, 2512–2514; d) S. Özçubukçu, F. Schmidt, C. Bolm, *Org. Lett.* **2005**, *7*, 1407–1409.

[8] S. Dahmen, M. Lormann, *Org. Lett.* **2005**, *7*, 4597–4600.

[9] J. G. Kim, P. J. Walsh, *Angew. Chem.* **2006**, *118*, 4281–4284; *Angew. Chem. Int. Ed.* **2006**, *45*, 4175–4178.

[10] a) M. Sakai, M. Ueda, N. Miyaura, *Angew. Chem.* **1998**, *110*, 3475–3477; *Angew. Chem. Int. Ed.* **1998**, *37*, 3279–3281; b) R. B. C. Jagt, P. Y. Toullec, E. P. Schudde, J. G. de Vries, B. L. Feringa, A. J. Minnaard, *J. Comb. Chem.* **2007**, *9*, 407–414.

[11] T. Arao, K. Kondo, T. Aoyama, *Tetrahedron* **2007**, *63*, 5261–5264.

[12] a) A. S. C. Chan, F.-Y. Zhang, C.-W. Yip, *J. Am. Chem. Soc.* **1997**, *119*, 4080–4081; b) B. L. Pagenkopf, E. M. Carreira, *Tetrahedron Lett.* **1998**, *39*, 9593–9596; c) Y.-S. Kwak, E. J. Corey, *Org. Lett.* **2004**, *6*, 3385–3388; d) M. d′Augustin, L. Palais, A. Alexakis, *Angew. Chem.* **2005**, *117*, 1400–1402; *Angew. Chem. Int. Ed.* **2005**, *44*, 1376–1378; e) K. Biswas, O. Prieto, P. J. Goldsmith, S. Woodward, *Angew. Chem.* **2005**, *117*, 2272–2274; *Angew. Chem. Int. Ed.* **2005**, *44*, 2232–2234.

[13] K.-H. Wu, H.-M. Gau, *J. Am. Chem. Soc.* **2006**, *128*, 14808–14809.

[14] S.-L. Ku, X.-P. Hui, C.-A. Chen, Y.-Y. Kuo, H.-M. Gau, *Chem. Commun.* **2007**, 3847–3849.

[15] a) L. Pu, H.-B. Yu. , *Chem. Rev.* **2001**, *101*, 757–824; b) L. Pu, *Tetrahedron* **2003**, *59*, 9873–9886; c) D. J. Ramón, M. Yus, *Chem. Rev.* **2006**, *106*, 2126–2208.

[16] a) D. J. Ramón, M. Yus, *Angew. Chem.* **2004**, *116*, 286–289; *Angew. Chem. Int. Ed.* **2004**, *43*, 284–287; b) C. García, V. S. Martín, *Curr. Org. Chem.* **2006**, *10*, 1849–1889; c) O. Riant, J. Hannedouche, *Org. Biomol. Chem.* **2007**, *5*, 873–888.

[17] P. I. Dosa, G. C. Fu, *J. Am. Chem. Soc.* **1998**, *120*, 445–446.

[18] C. García, L. K. LaRochelle, P. J. Walsh, *J. Am. Chem. Soc.* **2002**, *124*, 10970–10971.

[19] a) C. García, P. J. Walsh, *Org. Lett.* **2003**, *5*, 3641–3644; b) J. M. Betancort, C. García, P. J. Walsh, *Synlett* **2004**, 749–760.
[20] H. Li, C. García, P. J. Walsh, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5425–5427.
[21] C. Anaya de Parrodi, P. J. Walsh, *Synlett* **2004**, 2417–2420.
[22] O. Prieto, D. J. Ramón, M. Yus, *Tetrahedron: Asymmetry* **2003**, *14*, 1955–1957.
[23] V. J. Forrat, O. Prieto, D. J. Ramón, M. Yus, *Chem. Eur. J.* **2006**, *12*, 4431–4445; V. J. Forrat, O. Prieto, D. J. Ramón, M. Yus, *Chem. Eur. J.* **2006**, *12*, 6727.
[24] R. Shintani, M. Inoue, T. Hayashi, *Angew. Chem.* **2006**, *118*, 3431–3434; *Angew. Chem. Int. Ed.* **2006**, *45*, 3353–3356.
[25] C.-A. Chen, K.-H. Wu, H.-M. Gau, *Angew. Chem.* **2007**, *119*, 5469–5472; *Angew. Chem. Int. Ed.* **2007**, *46*, 5373–5376.
[26] M. Hatano, T. Miyamoto, K. Ishihara, *Org. Lett.* **2007**, *9*, 4535–4538.
[27] a) S.-H. Hsieh, H.-M. Gau, *Chirality* **2006**, *18*, 569–574; b) X.-P. Hui, J.-I. Huang, S.-J. Chiou, H.-M. Gau, *J. Chin. Chem. Soc.* **2006**, *53*, 421–427; c) S.-H. Hsieh, H.-M. Gau, *Synlett* **2006**, 1871–1874; d) S.-H. Hsieh, Y.-P. Kuo, H.-M. Gau, *Dalton Trans.* **2007**, 97–106; e) X.-P. Hui, C.-A. Chen, K.-H. Wu, H.-M. Gau, *Chirality* **2007**, *19*, 10–15.
[28] J.-S. You, S.-H. Hsieh, H.-M. Gau, *Chem. Commun.* **2001**, 1546–1547.
[29] a) M. Mori, T. Nakai, *Tetrahedron Lett.* **1997**, *38*, 6233–6236; b) D. J. Ramón, M. Yus, *Tetrahedron* **1998**, *54*, 5651–5666; c) J. Balsells, T. J. Davis, P. Carroll, P. J. Walsh, *J. Am. Chem. Soc.* **2002**, *124*, 10336–10348; d) K.-H. Wu, H.-M. Gau, *Organometallics* **2004**, *23*, 580–588.

