Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 4351–4361

TETRAHEDRON

Rhodium-catalyzed addition of arylstannanes to carbon–heteroatom double bond

Shuichi Oi,* Mitsutoshi Moro, Hiroe Fukuhara, Takanori Kawanishi and Yoshio Inoue*

Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, 04 Aramaki-Aoba Aoba-ku, Sendai 980-8579, Japan

Received 1 March 2003; revised 8 April 2003; accepted 10 April 2003

Abstract—The addition of arylstannanes to the carbon–heteroatom double bond in the presence of a catalytic amount of a cationic rhodium complex ($[Rh(cod)(MeCN)_2]BF_4$) was examined. The reactions of aldehydes, α-dicarbonyl compounds, and *N*-substituted aldimines with the arylstannanes gave corresponding alcohols, α-hydroxy carbonyl compounds, and amines, respectively. An arylrhodium complex generated by the transmetalation with the arylstannane was probably the active catalytic species. © 2003 Elsevier Science Ltd. All rights reserved.

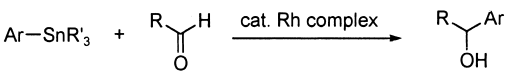
1. Introduction

Transition metal-catalyzed transformations using organometallic reagents are of great importance in modern organic chemistry.[1] One of the recent topics of such transformations is the rhodium-catalyzed addition of the organometallic reagents to the carbon–heteroatom double bonds in such as aldehydes or imines as well as the 1,4-addition to α,β-unsaturated carbonyl compounds.[2] These reactions commonly involve organorhodium complexes as active species generated by the transmetalation with the organometallic reagents such as tin (Sn),[3] boron (B),[4] silicon (Si),[5] lead (Pb),[6] bismuth (Bi),[7] titanium (Ti),[8] and zirconium (Zr).[9] In most cases, they occur chemo- and regioselectively rendering them useful in organic synthesis. They can also be developed for asymmetric reactions induced by chiral catalyst.[10]

The addition of organometallic reagents to aldehydes is the general method to synthesize secondary alcohols. Organolithium and organomagnesium (Grignard reagent) compounds are recognized to be most versatile. However, their extraordinary reactivities as nucleophiles and bases sometimes give rise to the limitations in the synthesis of multifunctional compounds such as natural products. Organotin compounds are the promissing reagents for chemoselective reactions. The allylation of aldehydes with allylstannanes was reported to be promoted by Lewis acids[11] or catalyzed by transition metal complexes such as rhodium,[12] palladium and platinum,[13] and applied successfully in organic synthesis. We reported the arylation of aldehydes with arylstannanes catalyzed by rhodium complexes.[3a] In this paper, we report on the scope and limitation of the rhodium-catalyzed addition reaction of aryltin compounds to the carbon–heteroatom double bonds in such as carbonyl compounds and imines. Aldehydes, α-dicarbonyl compounds, and *N*-substituted aldimines successfully underwent the addition of arylstannanes under mild and neutral conditions, affording corresponding alcohols, α-hydroxy carbonyl compounds, and amines, respectively.

2. Results and discussion

2.1. Addition of arylstannanes to aldehydes



(1)

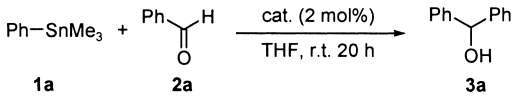
The addition of arylstannanes to aldehydes was studied using a rhodium complex as a catalyst (Eq. (1)). Initially, the addition of trimethylphenylstannane (**1a**) to benzaldehyde (**2a**) was examined in the presence of various transition metal catalysts. The results are summarized in Table 1. All reactions were carried out in THF at room temperature for 20 h with 2 mol% of the catalyst. Among the transition metal complexes of Pd, Rh, Ir, and Ru with chloride and cyclooctadiene ligands (entries 1–4), $[RhCl(cod)]_2$ was found to exhibit catalytic activity, although the yield was low (entry 2). Compared with the neutral chloride complex, cationic Rh complexes, $[Rh(cod)(MeCN)_2]BF_4$ and $[Rh(cod)_2]BF_4$, showed much higher catalytic activity affording the product in 54 and 58% yield, respectively

Keywords: arylation; carbonyl compounds; imines; organotin compounds; rhodium catalyst.

* Corresponding authors. Tel.: +81-22-217-5876; fax: +81-22-217-5873; e-mail: oishu@aporg.che.tohoku.ac.jp

0040–4020/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0040-4020(03)00586-6

Table 1. Transition metal-catalyzed addition of trimethylphenylstannane (**1a**) to benzaldehyde (**2a**)



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

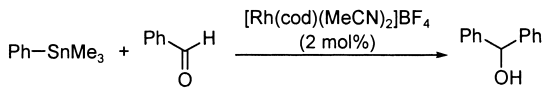
Entry	Catalyst	Yield (%)[a]
1	$PdCl_2(cod)$	0
2	$[RhCl(cod)]_2$	10
3	$[IrCl(cod)]_2$	Trace
4	$[RuCl_2(cod)]_n$	0
5	$[Rh(cod)_2]BF_4$	54
6	$[Rh(cod)(MeCN)_2]BF_4$	58
7	$[Rh(cod)(MeCN)_2]BF_4+2PPh_3$	Trace
8	$[Rh(cod)(MeCN)_2]BF_4$+dppe	26
9	$RhCl(PPh_3)_3$	2
10	$RhCl(CO)(PPh_3)_2$	9
11	$RhH(PPh_3)_4$	0

Common reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), catalyst (0.02 mmol or 0.01 mmol for dimer complex), THF (1.0 mL), rt, 20 h, N_2 atmosphere.
[a] Isolated yield.

(entries 5 and 6). Addition of phosphine ligands such as PPh_3 or dppe to $[Rh(cod)(MeCN)_2]BF_4$ inhibited the reaction (entries 7 and 8). Other Rh complexes, $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $RhH(PPh_3)_4$ did not show good catalytic activity (entries 9–11).

Other conditions in the reaction of **1a** with **2a** were then examined using 2 mol% of $[Rh(cod)(MeCN)_2]BF_4$ as a catalyst (Table 2). THF was the most suitable solvent, while $CHCl_3$ and toluene decreased the yield and acetonitrile completely inhibited the reaction (entries 1–4). The yield increased to 84% when the reaction temperature was raised to 60°C (entry 5), and the reaction appeared to be complete within 5 h at this temperature (entry 6). When the amount of catalyst was decreased to 1 mol%, the yield slightly decreased to 73% (entry 7). Changing the counter anion of the Rh complex from BF_4^- to PF_6^- did not affect the yield (entry 8). The reaction in THF containing 1 mmol of water still gave the product in good yield (entry 9), which is evidence that the reaction was not hindered by water. This point is in strong contrast to the reaction of organolithium or organomagnesium reagent.

Table 2. Rh-catalyzed addition of trimethylphenylstannane (**1a**) to benzaldehyde (**2a**)



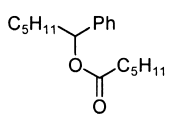
1a **2a** **3a**

Entry	Solvent	Temp. (°C)/time (h)	Yield (%)[a]
1	THF	rt/20	58
2	$CHCl_3$	rt/20	24
3	Toluene	rt/20	20
4	MeCN	rt/20	Trace
5	THF	60/20	84
6	THF	60/5	87
7[b]	THF	60/5	73
8[c]	THF	60/5	83
9[d]	THF	60/5	84

Common reaction conditions: **1a** (1.2 mmol), **2a** (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), solvent (1.0 mL), N_2 atmosphere.
[a] Isolated yield.
[b] 0.01 mmol of catalyst was loaded.
[c] $[Rh(cod)(MeCN)_2]PF_6$ was used as the catalyst.
[d] 1.0 mmol of water was added.

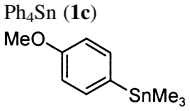
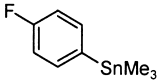
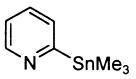
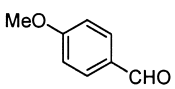
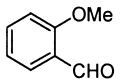
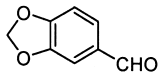
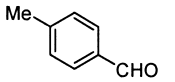
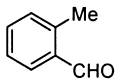
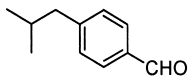
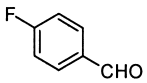
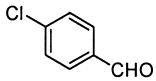
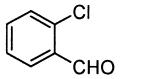
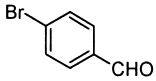
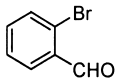
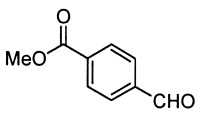
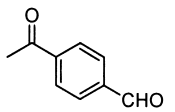
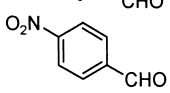
With the optimized reaction conditions (Table 2, entry 6), reactions of various arylstannanes with aldehydes were examined. The results are listed in Table 3. The reaction of tributylphenylstannane (**1b**), instead of trimethylphenylstannane (**1a**), with benzaldehyde (**2a**) gave the product alcohol **3aa** in a lower yield of 65% (entry 2), that would be caused by steric hindrance of the butyl group in the transmetalation step (vide infra). Tetraphenylstannane (**1c**) was much less reactive to give the product in only 17% yield (entry 3). Substituted phenylstannanes, *p*-methoxyphenyltrimethylstannane (**1d**) and *p*-fluorophenyltrimethylstannane (**1e**), also reacted with benzaldehyde affording the corresponding diarylcarbinol (**3da** and **3ea**) in good yield (entries 4 and 5). However, pyridyltrimethylstannane (**1f**) was found not to react with benzaldehyde.

A wide range of aldehydes were employed in the present rhodium-catalyzed addition of arylstannanes. Almost all of the substituted benzaldehydes examined, bearing electron-donating or -withdrawing groups on either ortho or para position, reacted readily with trimethylphenylstannane (**1a**) to give the corresponding alcohols in high yields (entries 7–23). It is noted that the reaction was highly chemoselective, in that other electrophilic functional groups than the aldehyde moiety in **2**, such as methoxycarbonyl (**2m**), acetyl (**2n**), nitro (**2o** and **2p**), and cyano (**2q**) groups remained intact. Halogen substituted benzaldehydes (**2h–l**) were also compatible with the catalytic system. Other aromatic aldehydes, 3-pyridinecarboxaldehyde (**2s**), furfural (**2t**), and 1- and 2-naphthaldehydes (**2u** and **2v**) were also phenylated with **1a**, affording the corresponding diarylcarbinol in good yields (entries 24–27). The yield of the alcohol in the reactions of trimethylphenylstannane (**1a**) with aliphatic aldehydes, hexanal (**2w**), was lower (34%, entry 28) than those with aromatic aldehydes. In the reaction of **2w**, 28% (0.14 mmol) of ester **4aw** was obtained as a by-product, which would be formed by the further reaction of the rhodium or tin alkoxide produced (vide infra) with the starting aldehyde **2w**. To immediately decompose the rhodium or tin alkoxide to alcohol **3aw**, the reaction was performed in the presence of 1 mmol of water. This approach gave the product in an improved yield of 60% (entry 29). Other aliphatic aldehydes with primary, secondary, and tertiary alkyl groups (**2x–2z** and **2α**) were also phenylated by **1a** in the presence of water affording the product alcohol (**3ax–3az** and **3aα**) in relatively good yield (entries 30–33). On the contrary, the rhodium-catalyzed reaction of trimethylphenylstannane (**1a**) with ketones was found to be very sluggish. The reaction with cyclohexanone (**2β**) gave the corresponding alcohol (**3aβ**) in 29% yield (entry 34), however, the reaction with acetophenone did not take place under the same reaction conditions (entry 35). To ensure the chemoselectivity of the reaction toward aldehyde



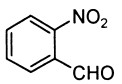
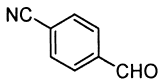
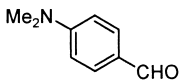
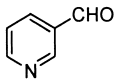
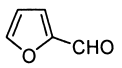
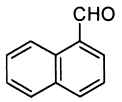
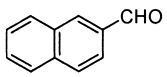
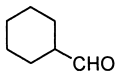
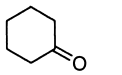
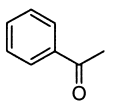
4aw

Table 3. Rhodium-catalyzed addition of arylstannanes **1** to aldehyde **2**

Entry	Arylstannane **1**	Aldehyde **2**	Time (h)	Product	Yield (%)[a]
1	$PhSnMe_3$ (**1a**)	PhCHO (**2a**)	5	**3aa**	87
2	$PhSnBu_3$ (**1b**)	**2a**	5	**3aa**	65
3	Ph_4Sn (**1c**)	**2a**	20	**3aa**	17
4	 (**1d**)	**2a**	2	**3da**	91
5	 (**1e**)	**2a**	2	**3ea**	88
6	 (**1f**)	**2a**	20	–	0
7	$PhSnMe_3$ (**1a**)	 (**2b**)	24	**3ab** (=**3da**)	85
8	**1a**	 (**2c**)	5	**3ac**	94
9	**1a**	 (**2d**)	5	**3ad**	84
10	**1a**	 (**2e**)	24	**3ae**	87
11	**1a**	 (**2f**)	20	**3af**	83
12	**1a**	 (**2g**)	20	**3ag**	78
13	**1a**	 (**2h**)	5	**3ah** (=**3ea**)	90
14	**1a**	 (**2i**)	5	**3ai**	91
15	**1a**	 (**2j**)	5	**3aj**	96
16	**1a**	 (**2k**)	5	**3ak**	91
17	**1a**	 (**2l**)	5	**3al**	72
18	**1a**	 (**2m**)	5	**3am**	96
19	**1a**	 (**2n**)	5	**3an**	96
20	**1a**	 (**2o**)	5	**3ao**	94

(*continued on next page*)

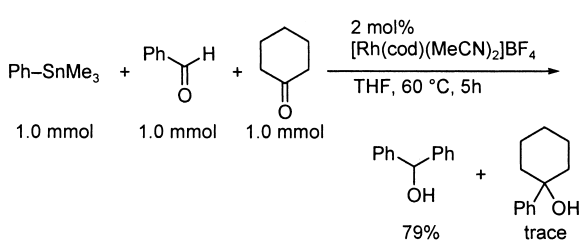
Table 3 (*continued*)

Entry	Arylstannane **1**	Aldehyde **2**	Time (h)	Product	Yield (%)[a]
21	$PhSnMe_3$ (**1a**)	 (**2p**)	5	**3ap**	92
22	**1a**	 (**2q**)	5	**3aq**	90
23	**1a**	 (**2r**)	20	**3ar**	31
24	**1a**	 (**2s**)	20	**3as**	54
25	**1a**	 (**2t**)	5	**3at**	91
26	**1a**	 (**2u**)	5	**3au**	84
27	**1a**	 (**2v**)	5	**3av**	84
28	**1a**	*n*-$C_5H_{11}CHO$ (**2w**)	20	**3aw**	34
29[b]	**1a**	**2w**	24	**3aw**	60
30[b]	**1a**	*n*-$C_9H_{19}CHO$ (**2x**)	24	**3ax**	48
31[b]	**1a**	$PhCH_2CH_2CHO$ (**2y**)	24	**3ay**	57
32[b]	**1a**	 (**2z**)	24	**3az**	45
33[b]	**1a**	*tert*-C_4H_9CHO (**2α**)	20	**3aα**	54
34	**1a**	 (**2β**)	24	**3aβ**	29
35	**1a**	 (**2γ**)	24	–	0

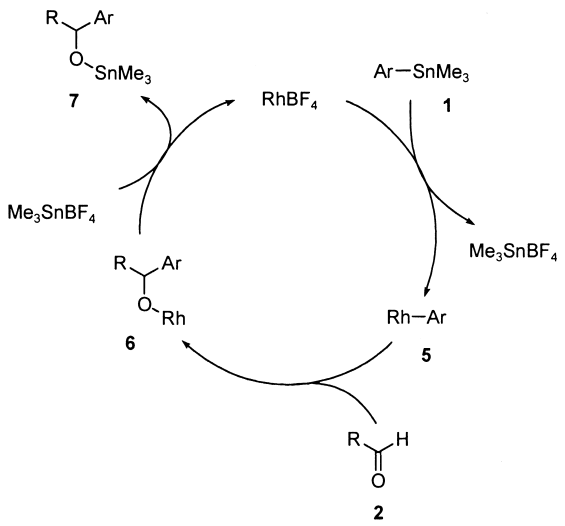
Common reaction conditions: **1** (1.2 mmol), **2** (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), THF (1.0 mL), 60°C, N_2 atmosphere.
[a] Isolated yield.
[b] 1 mmol of water was added.

and ketone, a competitive reaction of benzaldehyde (**2a**, 1 mmol) and cyclohexanone (**2β**, 1 mmol) with **1a** (1 mmol) was carried out at 60°C for 5 h. In result, 79% yield of the product alcohol (**3aa**) from benzaldehyde was obtained preferentially, and only a trace amount of the product alcohol (**3aβ**) from cyclohexanone was formed (Scheme 1).

To gain information on the reaction mechanism, the reactivity of $[Rh(cod)(MeCN)_2]BF_4$ toward trimethylphenylstannane (**1a**) was studied. When 0.1 mmol of $[Rh(cod)(MeCN)_2]BF_4$ was treated with equimolar amount of **1a** and D_2O in THF at 25°C for 20 h, the stannane **1a** was completely consumed and deuterized benzene (44% yield, 78%-*d*) was formed. A control experiment confirmed that the stannane **1a** was inert to water. Considering these results, it is probable that the generation of a water-labile species was formed from $[Rh(cod)(MeCN)_2]BF_4$ and the stannane **1a**, which we attribute to an unstable phenylrhodium species that should decompose rapidly to give benzene. Interestingly, the present addition reaction can be carried out in the presence of water indicating that the unstable phenylrhodium species reacted with aldehydes faster than with water. Unfortunately, peaks corresponding to the phenylrhodium species by ^1H and ^{13}C NMR measurements could not be detected, that would be caused by the instability of the species. However, Hartwig's group reported the generation and characterization of the phosphine-coordinated phenylrhodium complexes, which reacted with aldehydes to give rhodium alkoxides.[14]

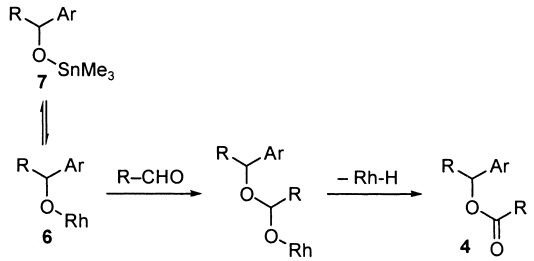


Scheme 1.



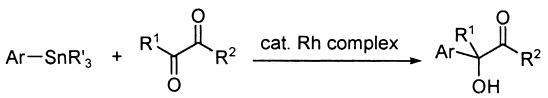
Scheme 2.

Evidence for the formation of phenylrhodium species was also found by the treatment of $[Rh(cod)(MeCN)_2]BF_4$ (0.1 mmol) with 1.0 equiv. of **1a** in the presence of 2.0 equiv. of styrene in THF (1 mL) at room temperature for 20 h that gave *trans*-stilbene in 49% yield. The *trans*-stilbene should be formed by the Heck-type reaction between the phenylrhodium species and the styrene. The presumed reaction pathway for the arylation reaction of aldehydes **2** with arylstannanes **1** is shown in Scheme 2. The transmetalation between the cationic rhodium complex and **1** would produce the arylrhodium intermediate **5**, which adds to an aldehyde to give a rhodium alkoxide **6**. Then, the rhodium alkoxide **6** would afford the stannyl ether **7** and regenerate the cationic rhodium complex. From the result that the addition of phosphine ligands inhibited the reaction, a phosphine-free phenylrhodium species is probably more reactive than that with phosphine ligands. The mechanism for the formation of the ester **4** would involve the insertion of another aldehyde **2** to the Rh–O bond of **6** followed by β-H elimination (Scheme 3). A similar mechanism was proposed by Slough's group in their report on Tishchenko-type disproportionation of aldehydes catalyzed by rhodium complexes[15] and by Hartwig's group in their report on reactivity of aryl- and alkoxy-rhodium complexes.[14]



Scheme 3.

2.2. Addition of arylstannanes to α-dicarbonyl compounds



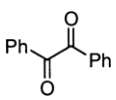
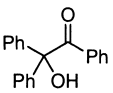
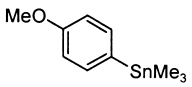
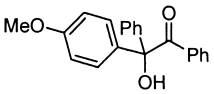
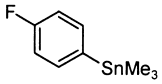
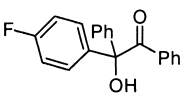
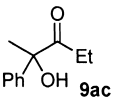
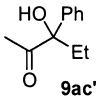
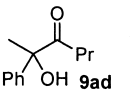
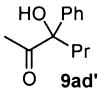
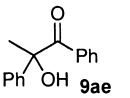
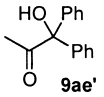
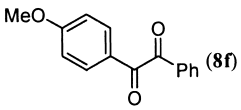
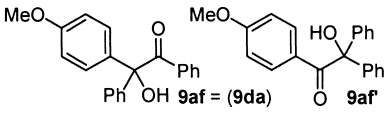
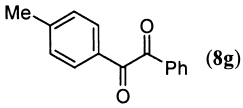
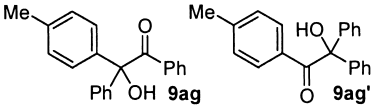
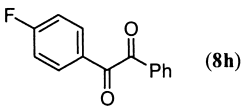
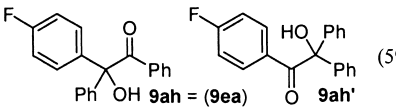
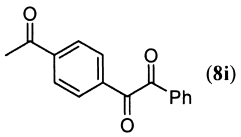
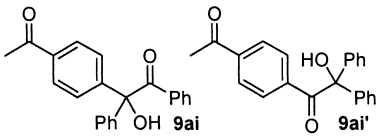
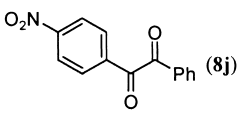
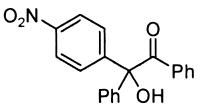
(2)

The rhodium-catalyzed addition of arylstanannes was applied to α-dicarbonyl compounds. As stated above, the reaction was very sluggish with ketones, however, conjugate α-diketones were found to undergo the addition of arylstannanes (Eq. (2)). An advantage of the reaction is that the arylation takes place only at one carbonyl group and the diarylation never occurs even when an excess amount of the arylstannane was used.

The reactions were carried out under the same conditions optimized for the reaction of aldehydes. Results are listed in Table 4. When benzil (**8a**) was treated with 1.2 equiv. of trimethylphenylstannane (**1a**) in the presence of 2 mol% of $[Rh(cod)(MeCN)_2]BF_4$, almost quantitative yield of monophenylated ketoalcohol **9aa** was obtained (entry 1). The reaction using 2.0 equiv. of stannane **1a** gave the same result. Substituted phenylstannanes **1d** and **1e** also added to benzil to give the monoarylated ketoalcohol **9da** and **9ea** (entries 2 and 3). A symmetric aliphatic diketone **8b** reacted with **1a** affording the product **9ab** in a moderate yield of 62% (entry 4). The reaction of an asymmetric diketone **8c** gave 82% yield of a mixture of regioisomers, the adduct on its methyl ketone moiety **9ac** and the adduct on its ethyl ketone moiety **9ac′**, in a ratio of 65:35 (entry 5). The ratio of regioisomers was affected by the difference of bulkiness of two carbonyl groups and the addition took place preferentially on the less hindered carbonyl carbon. A diketone **8d** having a methyl group and a propyl group on each carbonyl carbon gave an improved ratio of regioisomers, **9ad** and **9ad′**, in a ratio of 76:24 (entry 6). A diketone **8e** having a methyl group and a phenyl group on each carbonyl carbon gave a similar ratio of 77:23 (entry 7). To determine the electronic effect on the regioselectivity, the reactions of benzil derivatives having a functional group on one phenyl group **8f**–**8j** were then performed. As a result, the regioselectivity was strongly affected by the electronic nature of the functional groups and the addition took place preferentially on the relatively electron deficient carbonyl carbon. For benzil derivatives having a methoxyl group **8f** and a methyl group **8g**, the addition occurred opposite carbonyl carbons to those with the substituted phenyl groups in ratios of 36:64 and 47:53, respectively (entries 8 and 9). For benzil derivatives having a fluoro group **8h** and an acetyl group **8g**, the regioselectivity reversed to give **9ah** and **9ai** preferentially (entries 10 and 11). The reaction of benzil derivatives having a nitro group **8j** was completely regioselective affording **9aj** as a sole product (entry 12).

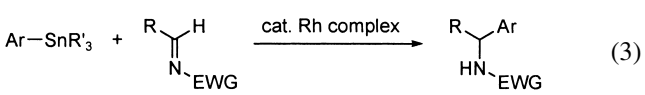
The reactions of glyoxylic acid esters and α-ketoesters were then examined. In these cases, the addition occurred selectively at the formyl group on the glyoxylic acid esters and at the acyl group on the α-ketoesters. As shown in Table 5, the reactions of trimethylphenylstannane (**1a**) with ethyl and isopropyl glyoxylate (**10a** and **10b**) gave corresponding α-phenylated α-hydroxyesters, **11aa** and **11ab**, in 69% and 62% yield, respectively (entries 1 and 2). Ethyl pyruvate (**10c**) and methyl and ethyl benzoylformate (**10d** and **10e**) also underwent the phenylation to give the α-hydroxyesters in good yield. The reaction with dimethyl oxalate (**10f**) did not take place showing that the ester groups did not undergo the addition even though they were conjugated.

Table 4. Rhodium-catalyzed addition of arylstannanes **1** to α-diketones **8**

Entry	Arylstannane **1**	α-Diketone **8**	Product	Yield (%)[a]
1	$PhSnMe_3$ (**1a**)	 (**8a**)	 (**9aa**)	99
2	 (**1d**)	**8a**	 (**9da**)	51
3	 (**1e**)	**8a**	 (**9ea**)	72
4	$PhSnMe_3$ (**1a**)	 (**8b**)	 (**9ab**)	62
5	**1a**	 (**8c**)	 **9ac**  **9ac'** (65:35)	82
6	**1a**	 (**8d**)	 **9ad**  **9ad'** (76:24)	70
7	**1a**	 (**8e**)	 **9ae**  **9ae'** (77:23)	93
8	**1a**	 (**8f**)	 **9af = (9da)** **9af'** (36:64)	89
9	**1a**	 (**8g**)	 **9ag** **9ag'** (47:53)	84
10	**1a**	 (**8h**)	 **9ah = (9ea)** **9ah'** (59:41)	98
11	**1a**	 (**8i**)	 **9ai** **9ai'** (78:22)	84
12	**1a**	 (**8j**)	 (**9aj**)	82

Common reaction conditions: **1** (1.2 mmol), **8** (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), THF (1.0 mL), 60°C, 20 h, N_2 atmosphere.
[a] Isolated yield.

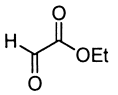
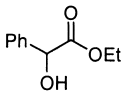
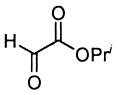
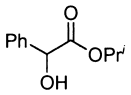
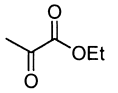
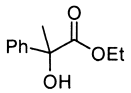
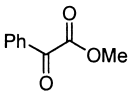
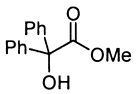
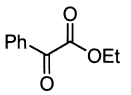
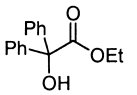
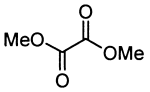
2.3. Addition of arylstannanes to aldimines



(3)

The rhodium-catalyzed addition of organotin compounds was then applied to aldimines (Eq. (3)).[3c–e,g] The results are listed in Table 6. At first, we examined the arylation of *N*-benzylideneaniline (**12a**) with trimethylphenylstannane (**1a**), but no arylation occurred (entry 1). This is probably due to the low electrophilicity of the imine **12a**. Then, *N*-tosylbenzylideneamine (**12b**), which are activated by the electron-withdrawing sulfonyl group on the nitrogen atom, was examined as a substrate. The reaction of **12b** with **1a** proceeded well under the same reaction conditions optimized for the reaction of aldehydes, affording *N*-tosyldiphenylmethylamine (**13ab**) in 98% isolated yield (entry

Table 5. Rhodium-catalyzed addition of arylstannanes **1** to α-ketoesters **10**

Entry	Arylstannane **1**	α-Ketoester **10**	Product	Yield (%)[a]
1	$PhSnMe_3$ (**1a**)	 (**10a**)	 (**11aa**)	69
2	**1a**	 (**10b**)	 (**11ab**)	62
3	**1a**	 (**10c**)	 (**11ac**)	71
4	**1a**	 (**10d**)	 (**11ad**)	60
5	**1a**	 (**10e**)	 (**11ae**)	77
6	**1a**	 (**10f**)	–	0

Common reaction conditions: **1** (1.2 mmol), **10** (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), THF (1.0 mL), 60°C, 20 h, N_2 atmosphere.
[a] Isolated yield.

2). Other electron-withdrawing groups were examined as the activating group of the aldimines. The reaction of *N*-(diethoxyphosphoryl)benzylideneamine (**12c**) with **1a** gave *N*-(diethoxyphosphoryl)diphenylmethylamine (**13ac**) in 84% yield (entry 3). Acyl and alkoxycarbonyl groups can also be employed as the activating group. *N*-Benzoylbenzylideneamine (**12d**) and *N*-(*tert*-butoxycarbonyl)-benzylideneamine (**12e**) reacted with **1a** under the same reaction conditions, affording *N*-benzoyl- and *N*-(*tert*-butoxycarbonyl)diphenylmethylamine (**13ad** and **13ae**) in 48% and 74% yield, respectively (entries 4 and 5).

Ortho- or *para*-substituted *N*-tosylbenzylideneamines with either an electron-withdrawing or -donating group (**12f**–**12k**) also reacted with **1a**, affording the corresponding *N*-tosyldiarylmethylamines (**13af**–**13ak**) in good isolated yields (entries 7–12). The reaction of *N*-tosylfurylideneamine (**12l**) with **1a** gave the product **13al** in 72% yield (entry 13). The reaction of a *N*-tosylaldimine derived from cinnamaldehyde (**12m**) gave not a conjugate adduct but the 1,2-adduct **13am** in 39% yield (entry 14). Ethyl tosyliminoacetate (**12n**), having three electrophilic moieties, ester, imino, and sulfonyl groups, was phenylated selectively at the imino group, affording *N*-tosylphenylglycine ethyl ester (**13an**) in 65% isolated yield (entry 15).

3. Conclusion

Rhodium-catalyzed additions of arylstannanes to carbon–heteroatom double bonds were presented. The reaction of arylstannanes with aldehydes gave arylated secondary alcohols and *N*-tosyl-, -phosphoryl-, -acyl-, and -alkoxycarbonyl-aldimines gave arylated protected secondary amines in good yield. In the reaction of α-diketones, monoarylated products were obtained selectively and the predominant addition was observed for less hindered and more electron deficient carbonyl group. The reaction of α-ketoesters gave α-arylated α-hydroxy esters selectively.

4. Experimental

4.1. General information

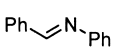
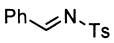
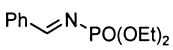
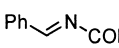
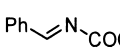
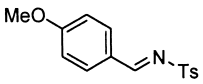
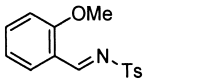
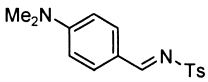
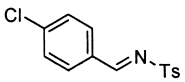
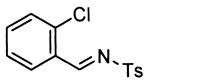
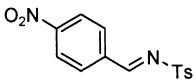
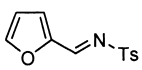
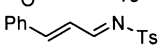
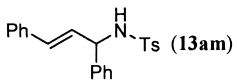
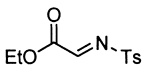
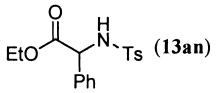
All reactions were carried out in a Schlenk tube under N_2. THF was dried over sodium/benzophenone ketyl, and distilled before use. NMR spectra were recorded using $CDCl_3$ as the solvent. Elemental analyses were performed by the Microanalytical Laboratory of the Institute for Chemical Reaction Science, Tohoku University. Spherical silica gel (40–100 μm, Kanto Chemical) was used for flash chromatography.

4.2. Materials

The organotin compounds **2d**–**2f** were prepared from the corresponding Grignard reagents and trimethylstannyl chloride.[16] Aromatic α-diketones **8f**–**8j** were prepared as described in the literature[17] from corresponding diarylacetylenes.[18] Aldimines **12b** and **12f**–**12m**,[19] **12c**,[20] **12d**,[21] **12e**,[22] and **12n**[23] were prepared as described in the literature.

4.2.1. $Rh(cod)(MeCN)_2]BF_4$.[24] To a solution of $[RhCl(cod)]_2$ (0.8 g, 1.6 mmol) in CH_2Cl_2 (20 mL) and acetonitrile (3.0 mL) was added a solution of $AgBF_4$ (0.7 g, 3.8 mmol) in acetonitrile (3.0 mL) and the mixture was

Table 6. Rhodium-catalyzed addition of phenyltrimethylstannane (**1a**) to imines **12**

Entry	Arylstannane **1**	Imine **12**	Product	Yield (%)[a]
1	$PhSnMe_3$ (**1a**)	 (**12a**)	–	0
2	**1a**	 (**12b**)	**13ab**	98
3	**1a**	 (**12c**)	**13ac**	84
4	**1a**	 (**12d**)	**13ad**	48
5	**1a**	 (**12e**)	**13ae**	74
7	**1a**	 (**12f**)	**13af**	76
8	**1a**	 (**12g**)	**13ag**	75
9	**1a**	 (**12h**)	**13ah**	60
10	**1a**	 (**12i**)	**13ai**	78
11	**1a**	 (**12j**)	**13aj**	79
12	**1a**	 (**12k**)	**13ak**	83
13	**1a**	 (**12l**)	**13al**	72
14	**1a**	 (**12m**)	 (**13am**)	39
15	**1a**	 (**12n**)	 (**13an**)	65

Common reaction conditions: **1** (1.2 mmol), **10** (1.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), THF (1.0 mL), 60°C, 20 h, N_2 atmosphere.
[a] Isolated yield.

stirred at room temperature for 2 h under N_2 with shielding the light. After the precipitated AgCl was filtered off, the solution volume was reduced in vacuo to ca. 5 mL and 20 mL of Et_2O was then added slowly. Precipitated yellow powder was collected by filtration and dried in vacuo to give $[Rh(cod)(MeCN)_2]BF_4$ in 85% yield.

4.3. Rhodium-catalyzed addition of arylstannanes

The general procedure was as follows. To a mixture of the substrate (**2**, **8**, **10**, or **12**, 1.0 mmol) and $[Rh(cod)(MeCN)_2]BF_4$ (7.4 mg, 0.02 mmol) in THF (1 mL) was added the arylstannane (**1**, 1.2 mmol) and stirred at 60°C for the appropriate time. The reaction was quenched by adding a small amount of water and then stirred for 1 h. Et_2O (20 mL) was added to the reaction mixture and the resulting precipitate was removed by filtration. The solvent was removed in vacuo and the residue was purified by flash chromatography (hexane/AcOEt) to give the product. Known compounds were identified by comparing the spectroscopic data with those reported in the literature (Table 7).

4.3.1. (4-Isobutylphenyl)phenylmethanol (3ag). IR (KBr) 3314, 2952, 2868, 1453, 1035, 1017, 774, 749, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 4H), 7.25–7.21 (m, 3H), 7.09 (d, J=7.8 Hz, 2H), 5.76 (s, 1H), 2.44 (d, J=6.8 Hz, 2H), 2.32 (s, 1H), 1.83 (nonet, J=6.8 Hz, 1H), 0.88 (d, J=6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.2, 141.1, 129.2, 128.4, 127.4, 126.5, 126.4, 76.1, 45.1, 30.2, 22.4. Anal. calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.84; H, 8.45.

4.3.2. (2-Bromophenyl)phenylmethanol (3al). IR (neat) 3360, 3062, 1494, 1454, 1183, 1015, 750, 699, 644, 601 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J=16.2, 7.8 Hz, 2H), 7.39–7.23 (m, 6H), 7.12 (t, J=7.6 Hz, 1H), 6.17 (s, 1H), 2.44 (s, 1H). ^{13}C NMR

Table 7. References for known compounds

Compound	Reference	Compound	Reference
3aa	25	**9aa**	43
3da (=**3ab**)	25	**9da** (=**9af**)	44
3ea (=**3ah**)	26	**9ea** (=**9ah**)	44
3ac	27	**9ab**	45
3ad	28	**9ac**	45
3ae	25	**9ac′**	45
3af	25	**9ad**	46
3ai	25	**9ae**	47
3aj	29	**9ae′**	48
3ak	26	**9af′**	49
3ao	30	**9ag**	44
3aq	31	**9ag′**	44
3ar	32	**9ah′**	44
3as	33	**11aa**	50
3at	34	**11ab**	50
3au	35	**11ac**	51
3av	36	**11ad**	52
3aw	37	**11ae**	53
3ax	38	**13ab**	3e
3ay	39	**13ad**	3e
3az	40	**13ae**	54
3aα	41	**13al**	55
3aβ	42	**13am**	56

(100 MHz, $CDCl_3$) δ 142.5, 142.2, 132.8, 129.1, 128.5, 128.4, 127.8, 127.7, 127.0, 122.8, 74.8. Anal. calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21; Br, 30.37. Found: C, 59.798; H, 4.478, Br, 30.60.

4.3.3. (4-Methoxycarbonylphenyl)phenylmethanol (3am). Mp 62–63°C. IR (neat) 3440, 2950, 1720, 1612, 1435, 1280, 1110, 1018, 754, 705 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J=8.3 Hz, 2H), 7.44 (d, J=8.3 Hz, 2H), 7.34–7.25 (m, 5H), 5.84 (s, 1H), 3.87 (s, 3H), 2.64 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 148.7, 143.3, 129.7, 129.2, 128.6, 127.9, 126.6, 126.3, 75.8, 52.1. Anal. calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.02; H, 5.91.

4.3.4. (4-Acetylphenyl)phenylmethanol (3an). IR (neat) 3420, 3030, 1675, 1608, 1498, 1452, 1412, 1360, 1270, 1190, 1042, 1018, 801, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J=8.3 Hz, 2H), 7.46 (d, J=8.3 Hz, 2H), 7.34–7.23 (m, 5H), 5.83 (d, J=2.6 Hz, 1H), 2.86 (d, J=2.6 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 149.0, 143.2, 136.1, 128.6, 128.5, 127.9, 126.5, 126.5, 75.7, 26.5. Anal. calcd for $C_{15}H_{14}O_2$: C, 79.62; H,6.24. Found: C, 79.156; H, 6.085.

4.3.5. (2-Nitrophenyl)phenylmethanol (3ap). IR (neat) 3417, 3032, 1607, 1577, 1538, 1454, 1359, 1178, 1019, 737, 701, 601 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J=7.9, 1.2 Hz, 1H), 7.73 (dd, J=7.9, 1.2 Hz, 1H), 7.62 (dt, J=7.9, 1.2 Hz, 1H), 7.44 (dt, J=7.9, 1.2 Hz, 1H), 7.36–7.30 (m, 4H), 7.29–7.26 (m, 1H), 6.41 (d, J=3.5 Hz, 1H), 2.88 (d, J=3.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 141.6, 138.5, 133.4, 129.5, 128.6, 128.5, 128.1, 127.0, 124.7, 71.5. Anal. calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.277; H, 4.979; N, 6.049.

4.3.6. Hexanoic acid 1-phenylhexyl ester (4aw). IR (neat) 2910, 2845, 1730, 1165 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5H), 5.73 (dd, J=7.7, 6.2 Hz, 1H), 2.31 (dt, J=7.5, 2.3 Hz, 2H), 1.95–1.80 (m, 2H) 1.62 (qui, J=7.5 Hz, 2H), 1.38–1.18 (m, 10H), 0.87 (t, J=7.0 Hz, 3H), 0.86 (t, J=7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 141.1, 128.4, 127.7, 126.5, 75.9, 36.4, 34.6, 31.5, 31.3, 25.2, 24.7, 22.5, 22.3, 14.0, 13.9. Anal. calcd for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.88; H, 9.95.

4.3.7. A mixture of 2-hydroxy-2-phenylhexan-3-one (9ad) and 3-Hydroxy-3-phenylhexan-2-one (9ad′). * Peaks for **9ad′**. IR (neat) 3459, 3060, 2965, 2874, 1709, 1447, 1364, 760, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.30 (m, 5H), 4.61 (s, 1H), 4.51* (s, 1H), 2.41–2.28 (m, 2H), 2.16–2.13* (m, 2H), 2.08* (s, 3H), 1.77 (s, 3H) 1.55–1.45 (m, 2H), 0.99* (t, J=7.3 Hz, 3H) 0.75 (t, J=7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.6, 209.5*, 141.0, 129.3, 128.6, 128.0, 127.9, 126.2, 126.1, 119.6, 82.6*, 79.7, 38.7*, 34.4, 24.0, 23.6*, 17.4*, 16.6, 14.4*, 13.4. Anal. calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.37.

4.3.8. A mixture of 2-(4-acetylphenyl)-2-hydroxy-1,2-diphenylethan-1-one (9ai) and 1-(4-acetylphenyl)-2-hydroxy-2,2-diphenylethan-1-one (9ai′). * Peaks for **9ai′**. IR (neat) 3443, 3059, 3014, 2924, 1681, 1604, 1268, 1058, 818, 764, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.26 (m, 14H), 4.99 (s, 1H), 4.65* (s, 1H), 2.58 (s, 3H), 2.56* (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 200.1, 197.6*, 146.8, 141.56, 141.47, 139.6, 136.6, 134.8, 133.2, 130.8, 128.57, 128.53, 128.50, 128.44, 128.35, 128.25, 128.10, 128.07, 127.8, 85.4*, 85.0, 26.7*, 26.6. Anal. calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.82; H, 5.61.

4.3.9. 2-(4-Nitrophenyl)-2-hydroxy-1,2-diphenylethan-1-one (9aj). Mp 88–89°C. IR (neat) 3457, 3063, 2983, 2855, 1681, 1347, 1236, 1181, 1060, 852, 748, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J=9.0 Hz, 2H), 7.98 (d, J=7.8 Hz, 2H), 7.63 (d, J=9.0 Hz, 2H), 7.49 (t, J=7.5 Hz, 1H), 7.41–7.35 (m, 5H), 7.32 (dd, J=7.8, 7.5 Hz, 2H), 4.93 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 148.8, 147.5, 141.2, 134.5, 133.5, 130.7, 129.3, 128.84, 128.77, 128.4, 127.8, 123.3, 84.8. Anal. calcd for $C_{20}H_{15}NO_4$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.80; H, 4.67; N, 4.27.

4.3.10. *N*-(Diethoxyphosphoryl)diphenylmethylamine (13ac). Mp 111–112°C. IR (KBr) 3221, 2989, 2902, 1496, 1467, 1226, 1121, 1027, 961, 752, 710, 541 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.23 (m, 10H), 5.41 (t, J=9.8 Hz, J_{H-P}=9.8 Hz, 1H), 4.02–3.95 (m, 2H), 3.87–3.81 (m, 2H), 3.46 (dd, J=9.8 Hz, J_{H-P}=10.3 Hz, 1H), 1.17 (t, J=7.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3 (d, J_{C-P}=5.1 Hz), 128.5, 127.3, 127.2, 62.4 (d, J_{C-P}=5.1 Hz), 59.2, 16.0 (d, J_{C-P}=7.5 Hz). Anal. calcd for $C_{17}H_{22}NO_3P$: C, 63.94; H, 6.94; N, 4.39. Found: C, 64.08; H, 6.99; N, 4.43.

4.3.11. *N*-Tosyl-(4-methoxylphenyl)phenylmethylamine (13af). Mp 146.0–147.0°C. IR (KBr) 3239, 2950, 1609, 1509, 1432, 1321, 1251, 1159, 1048, 842, 673, 559 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J=8.30 Hz, 2H), 7.21–7.00 (m, 7H), 6.99 (d, J=8.65 Hz, 2H), 6.73 (d, J=8.65 Hz, 2H), 5.52 (d, J=6.90 Hz, 1H), 5.00 (d,

J=6.90 Hz, 1H), 3.75 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 143.1, 140.7, 137.4, 132.7, 129.3, 128.6, 128.5, 127.4, 127.28, 127.22, 113.9, 60.8, 55.2, 21.4. Anal. calcd for $C_{21}H_{21}NO_3S$: C, 68.64; H,5.76; N,3.81; S,8.73. Found: C, 68.67; H, 5.84; N, 3.80; S, 8.74.

4.3.12. *N*-Tosyl-(2-methoxylphenyl)phenylmethylamine (13ag). Mp 126.6–127.8°C. IR (KBr) 3302, 1599, 1493, 1455, 1333, 1242, 1159, 1094, 1064, 1024, 817, 755, 699, 547 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.51 (d, J=8.22 Hz, 1H), 7.25–6.95 (m, 10H), 6.79 (t, J=7.39 Hz, 1H), 6.67 (d, J=3.20 Hz, 1H), 5.76 (d, J=9.13 Hz, 1H), 5.64 (d, J=9.13 Hz, 1H), 3.59 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 142.6, 140.6, 137.5, 129.4, 128.9, 128.8, 128.0, 127.7, 126.95, 126.93, 126.7, 120.5, 111.0, 58.7, 55.1, 21.3. Anal. calcd for $C_{21}H_{21}NO_3S$: C, 68.64; H, 5.76; N, 3.81; S, 8.73. Found: C, 68.68; H, 5.83; N, 3.81; S, 8.84.

4.3.13. *N*-Tosyl-(4-dimethylaminopheny)phenylmethylamine (13ah). Mp 128.2–128.7°C. IR (KBr) 3311, 1613, 1524, 1324, 1158, 1047, 806, 701, 669, 568, 541 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60–7.56 (m, 2H), 7.33–7.15 (m, 7H), 6.92 (d, J=8.45 Hz, 2H), 6.57 (d, J=8.45 Hz, 2H), 5.51 (d, J=5.95 Hz, 1H), 5.00 (d, J=5.95 Hz, 1H), 2.92 (s, 6H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 142.8, 141.0, 137.5, 129.2, 128.33, 128.30, 128.2, 127.27, 127.23, 127.1, 112.3, 60.9, 40.4, 21.4. Anal. calcd for $C_{22}H_{24}N_2O_2S$: C, 69.44; H, 6.36; N, 7.36; S, 8.43. Found: C, 69.23; H, 6.42; N, 7.28; S, 8.31.

4.3.14. *N*-Tosyl-(4-chlorophenyl)phenylmethylamine (13ai). Mp 119.0–120.0°C. IR (KBr) 3238, 1490, 1432, 1321, 1159, 1091, 1048, 836, 803, 745, 700, 668, 572 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.54 (d, J=8.18 Hz, 2H), 7.25–7.03 (m, 11H), 5.53 (d, J=7.07 Hz, 1H), 5.22 (d, J=7.07 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 143.4, 140.0, 138.9, 137.1, 133.4, 129.4, 128.77, 128.72, 128.6, 127.8, 127.2, 127.1, 60.7, 21.4. Anal. calcd for $C_{20}H_{18}ClNO_2S$: C, 64.59; H, 4.88; Cl, 9.53; N, 3.77; S, 8.62. Found: C, 64.59; H, 4.96; Cl, 9.64; N, 3.71; S, 8.59.

4.3.15. *N*-Tosyl-(2-chlorophenyl)phenylmethylamine (13aj). Mp 172.0–173.2°C. IR (KBr) 3296, 1597, 1494, 1431, 1333, 1155, 1082, 942, 759, 693, 665, 572, 547 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.62 (d, J=8.29 Hz, 2H), 7.33–7.06 (m, 11H), 5.94 (d, J=7.28 Hz, 1H), 5.34 (d, J=7.28 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 143.3, 139.2, 137.5, 132.7, 129.8, 129.3, 128.7, 128.6, 128.5, 127.8, 127.5, 127.2, 127.1, 126.9, 58.6, 21.4. Anal. calcd for $C_{20}H_{18}ClNO_2S$: C, 64.59; H, 4.88; Cl, 9.53; N, 3.77; S, 8.62. Found: C, 64.56; H, 4.88; Cl, 9.69; N, 3.80; S, 8.92.

4.3.16. *N*-Tosyl-(4-nitrophenyl)phenylmethylamine (13ak). Mp 128.5–129.5°C. IR (KBr) 3243, 3065, 1598, 1517, 1447, 1346, 1158, 1094, 1051, 906, 838, 741, 696, 665, 572, 557 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.02 (d, J=8.71 Hz, 2H), 7.52 (d, J=8.27 Hz, 2H), 7.32 (d, J=8.71 Hz, 2H), 7.20–7.10 (m, 5H), 6.96–6.92 (m, 2H), 5.56 (d, J=6.75 Hz, 1H), 5.20 (d, J=6.75 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 147.2, 143.8, 139.2, 136.9, 129.5, 129.1, 128.4, 128.2, 127.3, 127.2, 123.6, 60.9, 21.5. Anal. calcd for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.74; N, 7.33; S, 8.38. Found: C, 62.87; H, 4.85; N, 7.32; S, 8.47.

4.3.17. 2-Phenyl-2-(tosylamino)ethanoic acid ethyl ester (13an). Mp 85–86°C. IR (KBr) 3267, 3031, 2988, 1726, 1388, 1160, 1090, 696 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J=7.9 Hz, 2H), 7.26–7.22 (m, 5H), 7.19 (d, J=7.9 Hz, 2H), 5.77 (d, J=8.1 Hz, 1H), 5.04 (d, J=8.1 Hz, 1H), 4.06–3.94 (m, 2H), 2.38 (s, 3H), 1.09 (t, J=7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.0, 143.4, 136.9, 135.4, 129.4, 128.7, 128.4, 127.2, 127.0, 62.2, 59.3, 21.4, 13.8. Anal. calcd for $C_{17}H_{19}NO_4S$: C, 61.24; H, 5.74; N, 4.20; S, 9.62. Found: C, 61.28; H, 5.68; N, 4.33; S, 9.68.

References

1. Knight, D. W. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 481–520.
2. Review: Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169.
3. (a) Oi, S.; Moro, M.; Inoue, Y. *Chem. Commun.* **1997**, 1621. (b) Oi, S.; Moro, M.; Ono, S.; Inoue, Y. *Chem. Lett.* **1998**, 83. (c) Oi, S.; Moro, M.; Fukuhara, H.; Kawanishi, T.; Inoue, Y. *Tetrahedron Lett.* **1999**, *40*, 9259. (d) Hayashi, T.; Ishigedani, M. *J. Am. Chem. Soc.* **2000**, *122*, 976. (e) Ueda, M.; Miyaura, N. *J. Organomet. Chem.* **2000**, *595*, 31. (f) Li, C. J.; Meng, Y. *J. Am. Chem. Soc.* **2000**, *122*, 9538. (g) Hayashi, T.; Ishigedani, M. *Tetrahedron* **2001**, *57*, 2589. (h) Venkatraman, S.; Meng, Y.; Li, C. J. *Tetrahedron Lett.* **2001**, *42*, 4459. (i) Huang, T. S.; Li, C. J. *Org. Lett.* **2001**, *3*, 2037. (j) Huang, T.; Meng, Y.; Venkatraman, S.; Wang, D.; Li, C. J. *J. Am. Chem. Soc.* **2001**, *123*, 7451. (k) Oi, S.; Moro, M.; Ito, H.; Honma, Y.; Miyano, S.; Inoue, Y. *Tetrahedron* **2002**, *58*, 91.
4. (a) Sakai, M.; Hayashi, H.; Miyaura, N. *Organometallics* **1997**, *16*, 4229. (b) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3279. (c) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579. (d) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1998**, *39*, 8479. (e) Batey, R. A.; Thadani, A. N.; Smil, D. V. *Org. Lett.* **1999**, *1*, 1683. (f) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Tetrahedron Lett.* **1999**, *40*, 6957. (g) Hayashi, T.; Senda, T.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **1999**, *121*, 11591. (h) Takaya, Y.; Senda, T.; Kurushima, H.; Ogasawara, M.; Hayashi, T. *Tetrahedron: Asymmetry* **1999**, *10*, 4047. (i) Sakuma, S.; Sakai, M.; Itooka, R.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 5951. (j) Ueda, M.; Saito, A.; Miyaura, N. *Synlett* **2000**, 1637. (k) Takaya, Y.; Ogasawara, M.; Hayashi, T. *Chirality* **2000**, *12*, 469. (l) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450. (m) Fürstner, A.; Krause, H. *Adv. Synth. Catal.* **2001**, *343*, 343. (n) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957. (o) Itooka, R.; Iguchi, Y.; Miyaura, N. *Chem. Lett.* **2001**, 722. (p) Kuriyama, M.; Tomioka, K. *Tetrahedron Lett.* **2001**, *42*, 921. (q) Reetz, M. T.; Moulin, D.; Gosberg, A. *Org. Lett.* **2001**, *3*, 4083. (r) Sakuma, S.; Miyaura, N. *J. Org. Chem.* **2001**, *66*, 8944. (s) Yamamoto, Y.; Fujita, M.; Miyaura, N. *Synlett* **2002**, 767. (t) Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052. (u) Kuriyama, M.; Nagai, K.; Yamada, K.; Miwa, Y.; Taga, T.; Tomioka, K.

J. Am. Chem. Soc. **2002**, *124*, 8932. (v) Yoshida, K.; Ogasawara, M.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 10984.
5. (a) Oi, S.; Moro, M.; Inoue, Y. *Organometallics* **2001**, *20*, 1036. (b) Huang, T. S.; Li, C. J. *Chem. Commun.* **2001**, 2348. (c) Mori, A.; Danda, Y.; Fujii, T.; Hirabayashi, K.; Osakada, K. *J. Am. Chem. Soc.* **2001**, *123*, 10774. (d) Fujii, T.; Koike, T.; Mori, A.; Osakada, K. *Synlett* **2002**, 298. (e) Koike, T.; Du, X.; Mori, A.; Osakada, K. *Synlett* **2002**, 301. (f) Oi, S.; Honma, Y.; Inoue, Y. *Org. Lett.* **2002**, *4*, 667. (g) Murata, M.; Shimazaki, R.; Ishikura, M.; Watanabe, S.; Masuda, Y. *Synthesis* **2002**, 717. (h) Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97.
6. Ding, R.; Chen, Y. J.; Wang, D.; Li, C. J. *Synlett* **2001**, 1470.
7. (a) Venkatraman, S.; Li, C. J. *Tetrahedron Lett.* **2001**, *42*, 781. (b) Ding, R.; Ge, C. S.; Chen, Y. J.; Wang, D.; Li, C. J. *Tetrahedron Lett.* **2002**, *43*, 7789.
8. Hayashi, T.; Tokunaga, N.; Yoshida, K.; Han, J. W. *J. Am. Chem. Soc.* **2002**, *124*, 12102.
9. Kakuuchi, A.; Taguchi, T.; Hanzawa, Y. *Tetrahedron Lett.* **2003**, *44*, 923.
10. Review: Hayashi, T. *Synlett* **2001**, 879.
11. Review: Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
12. Nuss, J. M.; Rennels, R. A. *Chem. Lett.* **1993**, 197.
13. (a) Nakamura, H.; Asao, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1995**, 1273. (b) Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.
14. Krug, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 1674.
15. Slough, G. A.; Ashbaugh, J. R.; Zannoni, L. A. *Organometallics* **1994**, *13*, 3587.
16. Gilman, H.; Rosenberg, S. D. *J. Am. Chem. Soc.* **1953**, *75*, 2507.
17. Zibuck, R.; Seebach, D. *Helv. Chem. Acta* **1988**, *71*, 237.
18. Alami, M.; Ferri, F.; Linstrumelle, G. *Tetrahedron Lett.* **1993**, *34*, 6403.
19. Love, B. E.; Raje, P. S.; Williams, T. C., II *Synlett* **1994**, 493.
20. Zwierzak, A.; Napieraj, A. *Tetrahedron* **1996**, *52*, 8789.
21. Kupfer, R.; Meier, S.; Würthwein, E.-U. *Synthesis* **1984**, 688.
22. Kanazawa, A. K.; Denis, J.-N.; Greene, A. E. *J. Org. Chem.* **1994**, *59*, 1238.
23. Hamley, P.; Holmes, A. B.; Kee, A.; Ladduwahetty, T.; Smith, D. F. *Synlett* **1991**, 29.
24. Green, M.; Kuc, T. A.; Taylor, S. H. *J. Chem. Soc. (A)* **1971**, 2334.
25. Chen, D.-W.; Ochiai, M. *J. Org. Chem.* **1999**, *64*, 6804.
26. Wang, Z.; Chandler, W. D.; Lee, D. G. *Can. J. Chem.* **1998**, *76*, 919.
27. Wagner, P. J.; Meador, M. A.; Park, B.-S. *J. Am. Chem. Soc.* **1990**, *112*, 5199.
28. Reis, A. L. de A.; Ormelli, C. B.; Miranda, A. L. P.; Fraga, C. A. M.; Barreiro, E. J. *Pharm. Acta Helv.* **1999**, *74*, 19.
29. Gasparrini, F.; Giovannoli, M.; Misiti, D.; Natile, G.; Palmieri, G. *Synth. Commun.* **1988**, *18*, 69.
30. Strazzolini, P.; Giumanini, A. G.; Verardo, G. *Tetrahedron* **1994**, *50*, 217.
31. Lee, J.; Velarde-Ortiz, R.; Guijarro, A.; Wurst, J. R.; Rieke, R. D. *J. Org. Chem.* **2000**, *65*, 5428.
32. Katritzky, A. R.; Toader, D. *J. Org. Chem.* **1997**, *62*, 4137.
33. Gómez, I.; Alonso, E.; Ramón, D. J.; Yus, M. *Tetrahedron* **2000**, *56*, 4043.
34. D'Auria, M. *Heterocycles* **2000**, *52*, 185.
35. Smith, J. G.; Chu, N. G. *J. Org. Chem.* **1981**, *46*, 4083.
36. Krogh, E.; Wan, P. *Can. J. Chem.* **1990**, *68*, 1725.
37. Janssen, A. J. M.; Klunder, A. J. H.; Zwanenburg, B. *Tetrahedron* **1991**, *47*, 7645.
38. Hallouis, S.; Saluzzo, C.; Amouroux, R. *Synth. Commun.* **2000**, *30*, 313.
39. Hattori, K.; Sajiki, H.; Hirota, K. *Tetrahedron* **2001**, *57*, 4817.
40. Kabalka, G. W.; Wu, Z.; Ju, Y. *Tetrahedron* **2001**, *57*, 1663.
41. Guijarro, A.; Ramon, D. J.; Yus, M. *Tetrahedron* **1993**, *49*, 469.
42. Makioka, Y.; Fujiwara, Y.; Kitamura, T. *J. Organomet. Chem.* **2000**, *611*, 509.
43. Maeda, H.; Hino, N.; Yamauchi, Y.; Ohmori, H. *Chem. Pharm. Bull.* **2000**, *48*, 1196.
44. Yoshida, N.; Ohwada, T. *Synthesis* **2001**, 1487.
45. Brunner, H.; Stoehr, F.; Eur, *J. Org. Chem.* **2000**, 2777.
46. Katritzky, A. R.; Zhang, G.; Jiang, J. *J. Org. Chem.* **1995**, *60*, 7605.
47. Wu, T.-C.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 2381.
48. Guijarro, D.; Yus, M. *Tetrahedron* **1994**, *50*, 3447.
49. Zhou, L.; Zhang, Y.; Shi, D. *Synthesis* **2000**, 91.
50. Basavaiah, D.; Krishna, P. R. *Tetrahedron* **1995**, *51*, 2403.
51. Moorlag, H.; Kellogg, R. M. *Tetrahedron: Asymmetry* **1991**, *2*, 705.
52. Dao, L. H.; Maleki, M.; Hopkinson, A. C.; Lee-Ruff, E. *J. Am. Chem. Soc.* **1986**, *108*, 5237.
53. Maeda, H.; Hino, N.; Yamauchi, Y.; Ohmori, H. *Chem. Pharm. Bull.* **2000**, *48*, 1196.
54. Miyawaki, K.; Ueno, F.; Ueda, I. *Heterocycles* **2001**, *54*, 887.
55. Deng, W.-P.; Li, A.-H.; Dai, L.-X.; Hou, X.-L. *Tetrahedron* **2000**, *56*, 2967.
56. Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411.