Phosphine Oxide-Catalyzed Asymmetric Aldol Reactions and Double Aldol Reactions

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Chiral phosphine oxides successfully catalyze asymmetric cross-aldol reactions of various carbonyl compounds in a highly enantioselective manner. The phosphine oxide catalysts coordinate to chlorosilanes to form chiral hypervalent silicon complexes in situ, which activate both aldol donors and acceptors, thus realizing cross-aldol reactions between a ketone and an aldehyde, between two aldehydes, between two ketones, and of 2,6-diketones. The use of phosphine oxide catalysis can be further extended to achieve the first catalytic enantioselective double aldol reactions, realizing one-pot stereoselective construction of up to four stereogenic centers.

Key words aldol reaction; phosphine oxide; tandem catalysis; hypervalent silicon complex; stereoselective; sequential activation

1. Introduction

The asymmetric aldol reaction is one of the most powerful and common transformation reactions that contribute greatly to the fields of pharmaceuticals and agricultural chemicals. In particular, ever since the catalysis of the aldol reaction of fructose derivatives in the human body by the glycolytic enzyme aldolase was reported, asymmetric aldol reactions have garnered considerable research attention in the pharmaceutical sciences. Remarkable progress has been achieved in terms of stereocontrol and direction control by developing the Mukaiyama aldol reaction or the Evans aldol reaction. Asymmetric cross-aldol reactions of different carbonyl compounds in the presence of bimetallic catalysts reported by Shibasaki and colleagues as well as the discovery of a proline catalyst by Barbas and List have accelerated the development of catalytic asymmetric direct cross-aldol reactions in the last two decades.

Lewis base-catalyzed aldol reactions of trichlorosilyl enol ethers were pioneered by Denmark et al., who used a chiral phosphoramidite to form a chiral hypervalent silicon complex, which facilitated asymmetric aldol reactions in a highly diastereo- and enantioselective manner. Our group has reported chiral pyridine N-oxides and bisphosphine oxides as catalysts for aldol reactions of trichlorosilyl enol ethers, thus extending the utility of these in organic synthesis. A chiral hypervalent silicon complex, formed from (S)-2,2’-bis(diphenylphosphino)-1,1’-binaphthyl (BINAP) dioxide and trichlorosilyl enol ether, has a strongly electrophilic Si atom and strongly nucleophilic adjacent ligands (Chart 1). Stereoselective coordination of an aldehyde oxygen

Chart 1. Phosphine Oxide-Catalyzed Aldol Reaction

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atom to the chiral hypervalent Si complex facilitates C–C bond formation via a six-membered transition state, providing an aldol adduct with high diastereoselectivity, as reflected by the E/Z ratio of the trichlorosilyl enol ethers, as well as high enantioselectivity. The chiral catalyst then dissociates from the Si atom furnishing a trichlorosilylated product, and then participates in the next catalytic cycle.

Although Lewis base-catalyzed aldol reactions provide $\beta$-hydroxycarbonyl compounds in a highly diastereo- and enantioselective manner, a two-step preparation has been required to obtain the trichlorosilyl enol ethers from the carbonyl compounds. To increase the efficiency and utility of the Lewis base-catalyzed aldol reactions, we envisaged an in-situ preparation of trichlorosilyl enol ethers from carbonyl compounds. In this review, we would like to introduce the sequential formation of hypervalent Si complexes, achieving a variety of catalytic asymmetric cross-aldol reactions. Furthermore, sequential phosphine oxide catalysis has been extended to the first catalytic enantioselective double aldol reactions, thus realizing the rapid synthesis of various natural products and molecular skeletons with multiple stereogenic carbon centers.

2. Asymmetric cross-Aldol Reactions between Carboxyl Compounds with Chiral Hypervalent Silicon Complexes

We initially examined the direct conversion from a mother ketone to a trichlorosilyl enol ether by treatment with silicon tetrachloride and an amine base, based on the reported synthesis of trialkylsilyl enol ethers from ketones and trialkylsilyl bromide or iodide in the presence of amines. However, no conversion to trichlorosilyl enol ethers occurred because of the lower silylating ability of silicon tetrachloride. Since the formation of hypervalent silicon complexes with a Lewis base increased the electrophilicity and Lewis acidity of the Si atom, use of a chiral phosphine oxide, (S)-BINAPO, was investigated next. As expected, the phosphine oxide catalyst successfully promoted the in situ formation of trichlorosilyl enol ether from ketone 1, and the subsequent addition of aldehyde 2 afforded the aldol adduct 3 in moderate yield and stereoselectivity (Chart 2). This result indicates that the phosphine oxide sequentially formed hypervalent Si complexes with silicon tetrachloride and trichlorosilyl enol ether to activate the aldol donor and acceptor, respectively, facilitating the formation of the aldol adduct. Trichlorosilyl triflate mediated the formation of trichlorosilyl enol ethers at $-40^\circ$C, resulting in higher stereoselectivities.

We next conducted enantioselective aldol reactions of various ketones and aldehydes under optimal conditions (Table 1). Trichlorosilyl triflate was able to successfully promote the enolization of an acyclic ketone propiophenone (6) to predominantly form a Z-enol ether, producing the syn-adduct 7 as the major isomer in 71% yield with 83% enantiomeric excess (ee) (entry 2). Cyclohexanone derivatives 8 and 10 also showed high stereoselectivity (entries 3 and 4). Although an $\alpha,\beta$-unsaturated aldehyde 12 showed lower reactivity than aromatic aldehydes, good stereoselectivity was maintained (entry 5). 2-Naphthaldehyde (14) gave the corresponding aldol adduct 15 in 79% yield with high diastereo- and enantioselectivity (entry 6), while para-bromobenzaldehyde (16) bearing an electron-withdrawing substituent resulted in higher enantioselectivity (88% ee) (entry 7).

Although aldol reactions between aldehydes are classically developed C–C bond forming reactions, catalytic asymmetric cross-aldol reactions between two different aldehydes are rare, due to unfavorable side reactions such as self-aldol reactions and dehydration. The hypervalent silicon complex successfully mediated the cross-aldol reaction between aliphatic aldehydes and aromatic aldehydes. Aliphatic aldehydes have low reactivity as aldol acceptors because of the formation of trichlorosilylated chlorohydrins in the reaction media. Therefore, aliphatic isobutyaldehyde (18) was chemoselectively enolized to form the trichlorosilyl enol ether, which would then undergo a cross-aldol reaction with aromatic aldehyde 19. Although stereoselectivity remained unsatisfactory, the reaction proceeded smoothly to yield the cross-aldol adduct 20 without any self-aldol or dehydration products (Chart 3).

In order to construct tetrasubstituted stereogenic carbon centers using an aldol reaction, the ideal aldol acceptors are

![Chart 2. Phosphine-Oxide-Catalyzed cross-Aldol Reaction via the Sequential Formation of Hypervalent Si Complexes](image-url)

**Biography**

Shunsuke Kotani was born in 1980 in Gunma, Japan, and received his B.S. (2003) and M.S. (2005) degrees from Hokkaido University under the guidance of Professor Shunichi Hashimoto. He completed his doctoral studies under the supervision of Professor Makoto Nakajima at Kumamoto University in March 2008. He then moved to the University of California, Irvine, as a JSPS postdoctoral fellow in the group of Professor Scott D. Rychnovsky. In 2009, he began his academic career at Kumamoto University, where he was promoted to associate professor in 2014. He has received the Pharmaceutical Society of Japan Award for Young Scientists (2018). His research interests include the invention of new reactions and stereocontrol in carbon–carbon coupling.

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ketones.\textsuperscript{42} The catalytic asymmetric aldol reaction between two simple ketones is challenging because of the lower electrophilicity and more difficult enantiofacial selection of ketones compared to those of aldehyde acceptors.\textsuperscript{43–47} In direct aldol reactions between two simple ketones, both can function as aldol donors and acceptors; therefore, a precise recognition of the aldol donor and acceptor in the reaction medium is essential. Tanabe and colleagues reported the cross-aldol reaction of two simple ketones via a titanium enolate intermediate produced by a stepwise procedure.\textsuperscript{48–51} We envisaged that the extremely strong silylating ability of trichlorosilyl triflate would enable the complete conversion of ketones to the corresponding trichlorosilyl enol ethers, thus facilitating the cross-aldol reaction between two simple ketones.\textsuperscript{35} First, a trichlorosilyl enol ether was prepared by treating acetone (21) with

Table 1. Phosphine Oxide-Catalyzed Aldol Reaction with Trichlorosilyl Triflate

| Entry | Ketone | Aldehyde | Product | Yield, % | anti / syn\textsuperscript{e} | ee, % (anti)\textsuperscript{f} |
|-------|--------|----------|---------|---------|----------------|------------------|
| 1\textsuperscript{a} | (4) | PhCHO (2) | 5 | 76 | 93 / 7 | 83 |
| 2\textsuperscript{c} | (6) | 2 | 7 | 71 | 27 / 73 | 83\textsuperscript{d} |
| 3\textsuperscript{c} | (8) | 2 | 9 | 81 | 97 / 3 | 82 |
| 4 | (10) | 2 | 11 | 82 | 97 / 3 | 83 |
| 5\textsuperscript{c} | 10 | PhCH=CHO (12) | 13 | 65 | 93 / 7 | 77 |
| 6 | 10 | 2-naphthaldehyde (14) | 15 | 79 | 97 / 3 | 83 |
| 7\textsuperscript{c} | 10 | 4-Br-C\textsubscript{6}H\textsubscript{5}CHO (16) | 17 | 84 | 97 / 3 | 88 |

\textsuperscript{a} Determined by 'H-NMR. \textsuperscript{b} Determined by HPLC analysis. \textsuperscript{c} The reaction mixture was stirred for 3 h before addition of 2. \textsuperscript{d} Ee of syn-isomer. \textsuperscript{e} SiCl\textsubscript{3}OTf was added last. \textsuperscript{f} The reaction was continued for 4 h.

Chart 3. Phosphine Oxide-Catalyzed cross-Aldol Reaction between 18 and 19

Chart 4. Asymmetric cross-Aldol Reactions between 21 and 22

Chart 5. Asymmetric cross-Aldol Reaction Between Two Different Simple Ketones
trichlorosilyl triflate and \( N,N \)-diisopropylethylamine, and then acetophenone \((22)\) was loaded into the reaction mixture (Chart 4). The asymmetric cross-aldol reaction occurred cleanly and smoothly to yield adduct \(23\) in 85% yield with 74% ee. Changing the addition order of these ketones produced the other cross-aldol adduct \(24\) in 75% yield. \(^{52}\)

Cross-aldol reactions between various types of ketones were conducted using the \((S)\)-BINAPO catalyst (Chart 5). The methyl ketone moiety of 2-butanone was predominantly enolized and then reacted with acetophenone to produce the cross-aldol adduct \(25\) in 65% yield with 74% ee. The reaction of cyclohexanone \((4)\) as the aldol donor with various ketones afforded adducts \(24\)–\(30\) with good-to-high diastereoselectivity. Although acetophenone derivatives gave the same level of reactivity and enantioselectivity, propiophenone \((6)\) resulted in decreased reactivity and diastereoselectivity. Benzylacetone, bearing a small steric difference between the two substituents, reacted well to provide good diastereo- and enantioselectivity. \(^{52}\)

As described above, the use of trichlorosilyl triflate realized asymmetric cross-aldol reactions between two ketones in a stepwise manner. However, the stepwise procedure is not applicable to the intramolecular aldol reaction. Furthermore, the \(\beta\)-hydroxycycloalkanones produced are dehydrated to the corresponding 2-cycloalkenones more readily than acyclic \(\beta\)-hydroxycarbonyl compounds. Therefore, there have been few reports of asymmetric preparations of \(\beta\)-hydroxycycloalkanones using intramolecular aldol reactions of diketones. \(^{53,54}\)

Based on our background in Lewis base-catalyzed aldol reactions, we predicted that the trichlorosilyl moiety in the aldol product would suppress dehydration of the aldolate. Furthermore, a sterically congested hypervalent silicon complex formed by chiral phosphine oxide should recognize the smaller alkyl ketone moiety, promoting regioselective enolization (Table 2). When diketone \(31\) was treated with silicon tetrachloride and \(N,N\)-diisopropylethylamine in the presence of a \((S)\)-TMS\(_2\)-BINAPO catalyst, \(^{55,56}\) the \(\beta\)-hydroxycyclohexanone derivative \(32\) was obtained in 82% yield with 91% ee. The hypervalent silicon complex also efficaciously mediated the intramolecular aldol reaction of 2,6-diketones to give \(\beta\)-hydroxycyclohexanones in high yield and with high enantioselectivity. \(^{57}\)

3. Asymmetric Double Aldol Reactions Catalyzed by Chiral Phosphine Oxides

The aldol reaction sequence provides an effective synthetic methodology for polyl and polyketide derivatives, which are found in many medicines as well as in biologically active natural products. Therefore, the one-pot sequential stereoselective aldol reaction allows us to access these derivatives. In 1999, the first example of a stereoselective sequential aldol reaction was shown by Abiko \textit{et al.}, who demonstrated that an acetic acid ester bearing a chiral auxiliary and an aldehyde gave a double aldol adduct with high diastereoselectivity \(^{58-61}\) (Fig. 1-a). Yamamoto and colleagues reported that the tris(trimethylsilyl)silyl (super-silyl) enol ether undergoes a triple aldol reaction \(^{62-65}\) (Fig. 1-b) in a highly \textit{syn}-selective manner, due to the strong steric effect of the super-silyl group.
In 2015, Kanai and Matsunaga's group developed the quadruple aldol reaction of enol boronate catalyzed by a chiral copper complex\(^{66}\) (Fig. 1-c). Recent progress in sequential asymmetric aldol reactions via various approaches has been demonstrated, which enabled us to synthesize a variety of polyols and polyketides. In this chapter, we describe the further extension of phosphine oxide catalysis to develop the first catalytic enantioselective double aldol reactions and other related reactions.

In the above-mentioned Lewis base-catalyzed aldol reactions, chiral hypervalent silicon complexes promoted the formation of trichlorosilyl enol ethers and the subsequent asymmetric cross-aldol reactions with various carbonyl compounds in a highly enantioselective manner. Since the silyl aldolate intermediate produced in the aldol reaction is also a carbonyl compound, it is possible for it to undergo a second aldol reaction, resulting in a catalytic asymmetric double aldol reaction (Fig. 2).

We initially examined the reaction between ketone 22 and aldehyde 2 in the presence of \((S)\)-BINAPO, silicon tetrachloride, and \(N,N\)-disopropylethylamine in dichloromethane at \(-40^\circ\text{C}\) (Chart 6). The reaction furnished the double aldol adduct 43 in 90% yield with good diastereo- and enantioselectivity (dr 81/19, 60% ee (major)). This is the first report of catalytic enantioselective double aldol reactions and other related reactions.

This reaction produced up to three stereogenic centers from simple 2-alkanones and aldehydes in a single operation (Table 4). The reaction of acetone (21) provided a \(C_2\)-symmetrical adduct, 75, as the only diastereomer with 91% ee without undergoing dehydration (entry 9)\(^{66}\).

The above-described methodology was applied to the total synthesis of \((-\)-ericanone (76), which should have antioxidant or antitumor activity due to its similarity to members of the curcuminoind families.\(^{68,70}\) The double aldol reaction of 21 with 4-nosyloxybenzaldehyde (77) furnished the double aldol adduct 78 in 94% yield with 98% ee in the presence of the originally designed (S)-TIP$_2$-BINAPO (Chart 8). Removal of the nosyl groups, followed by reduction of the double bonds, afforded \((-\)-ericanone.\(^{71}\)

The hypervalent silicon complex formed from silicon tetrachloride was able to mediate the double aldol reaction of 2-alkanones in a highly stereoselective fashion. However, other ketones, such as diethyl ketone, did not undergo any double aldol reaction because silyl enol ethers were not generated in the first aldol reaction due to the low silylating ability of the hypervalent silicon complex. Therefore, we used trichlorosilyl triflate, instead of silicon tetrachloride, for the double aldol reaction, and were able to obtain the desired adduct with high diastereo- and enantioselectivity. Fortunately, the double aldol reaction of symmetric ketones gave \(C_2\)-symmetric 2,4-disubstituted 1,5-dihydroxy-3-pentanone derivatives in a single

![Fig. 2. Sequential Mechanism of Phosphine Oxide-Catalyzed Double Aldol Reactions](image)

**Chart 6. Phosphine Oxide-Catalyzed Double Aldol Reactions of Acetophenone and Benzaldehyde**

**Table 3. Phosphine Oxide-Catalyzed Double Aldol Reaction of Aryl Methyl Ketones**

| Entry | Ketone, \(R^1\) | Aldehyde, \(R^2\) | Product | Yield, % | dr$^a$ | ee (major), %$^b$ |
|-------|----------------|----------------|---------|---------|-------|----------------|
| 1     | Ph (22)        | Ph (2)         | 43      | 86      | 78/22 | 70            |
| 2$^a$ | 4-Br-C$_2$H$_5$ (44) | 2         | 47      | 78      | 77/23 | 75            |
| 3$^b$ | PhCH = CH (46) | 2           | 49      | 71      | 77/23 | 71            |
| 4$^c$ | Cyclohexyl (48) | 2           | 51      | 86      | 86/14 | 91            |
| 5     | 2-Furyl (50)   | 2           | 53      | 77      | 98/2  | 93            |
| 6$^c$ | Cyclopentyl (52) | 2         | 55      | 90      | 97/3  | 91            |
| 7$^c$ | 52             | 4-Me-C$_2$H$_5$ (54) | 57      | 93      | 97/3  | 90            |
| 8$^c$ | 52             | 12           | 59      | 80      | 80/20 | 85            |
| 9     | 52             | 2-Furyl (60)  | 61      | 80      | 92/8  | 97            |

$^a$ Determined by $^1$H-NMR. $^b$ Determined by HPLC analysis. $^c$ Reaction continued for 48 h. $^d$ In CH$_2$Cl$_2$ instead of in CH$_2$Cl$_2$/EtCN.
step, while unsymmetrical ketone 94 afforded a more sterically congested molecule 95 bearing four stereogenic centers (Table 5). The enantioselective double aldol reaction could be used to prepare chiral stereopentad precursors in good yield with high enantioselectivity.72)

The double aldol reaction of aryl methyl ketones produced optically active 2-acyl-1,3-diols bearing two stereogenic centers with high enantioselectivity. We envisaged that the double aldol products, generated from β-alkoxyenones, could
be regioselectively cyclized to obtain 2,3-dihydro-4-pyranones with three contiguous stereogenic centers. 4-Methoxy-3-buten-2-one (96) functioned as an aldol donor and reacted with aldehyde 2 under the reaction conditions described in Chart 9. The chiral phosphine oxide effectively facilitated the double aldol reaction of 96 with aldehyde 2, and the subsequent regioselective cyclization afforded the corresponding highly functionalized 2,3-dihydro-4-pyranone 97 in 69% yield with good diastereo- and enantioselectivity. This method offers an alternative to the existing methods for the synthesis of 2,3-dihydro-4-pyranones from the corresponding ketones and aldehydes.73)

To further extend the substrate scope, we studied the reaction of 4-methoxy-3-penten-2-one (98) (Chart 10). Interestingly, 2,6-disubstituted 2,3-dihydro-4-pyranone 99, instead of 2,3-disubstituted 2,3-dihydro-4-pyranone, was obtained in 51% yield with high diastereo- and enantioselectivity (Chart 10). After the first aldol reaction, the amine preferably removed the proton at the α-position to the silyl aldolate to form trichlorosilyl dienolate, and the subsequent vinylogous addition to the aldehyde, followed by cyclization, afforded the 2,6-disubstituted 2,3-dihydro-4-pyranones in a highly stereoselective manner.74)

4. Conclusion
In this study, we obtained phosphine oxide catalysts that sequentially catalyzed asymmetric cross-aldol reactions between different carbonyl compounds via the formation of hypervalent silicon complexes. Moreover, enantioselective double aldol reactions have been developed for the first time, realizing the enantioselective construction of multiple stereogenic carbon centers and asymmetric syntheses of natural product (−)-ericanone and 4-pyranone derivatives. This catalytic system may now be further developed into novel activation systems using hypervalent silicon complexes, realizing chemoselective and stereoselective transformations.

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Conflict of Interest The author declares no conflict of interest.

References
1) Nelson S. G., Tetrahedron Asymmetry, 9, 357–389 (1998).
2) Gröger H., Vogl E. M., Shibasaki M., Chem. Eur. J., 4, 1137–1141 (1998).
3) Mahrwald R., Chem. Rev., 99, 1095–1120 (1999).
4) Palomo C., Oiarbide M., Garcia J. M., Chem. Soc. Rev., 33, 65–75 (2004).
5) Machajewski T. D., Wong C.-H., Angew. Chem. Int. Ed., 39, 1352–1375 (2000).
6) Mukaiyama T., Narasaka K., Banno K., Chem. Lett., 2, 1011–1014 (1973).
7) Mukaiyama T., Banno K., Narasaka K., J. Am. Chem. Soc., 96, 5192–5509 (1974).
8) Evans D. A., Bartroli J., Shih T. L., J. Am. Chem. Soc., 103, 2127–2129 (1981).
9) Yamada Y. M. A., Yoshikawa N., Sasai H., Shibasaki M., Angew. Chem. Int. Ed. Engl., 36, 1871–1873 (1997).
10) Shibasaki M., Yoshikawa N., Chem. Rev., 102, 2187–2210 (2002).
11) List B., Lerner R. A., Barbas C. F., J. Am. Chem. Soc., 122, 2395–2396 (2000).
12) Saito S., Yamamoto H., Acc. Chem. Res., 37, 570–579 (2004).
13) Notz W., Tanaka F., Barbas C. F. III, Acc. Chem. Res., 37, 580–591 (2004).
14) Alcaide B., Almendros P., Eur. J. Org. Chem., 2002, 1595–1601 (2002).
15) Guillena G., Nájera C., Ramón D. J., Tetrahedron: Asymmetry, 18, 2249–2293 (2007).
16) Mukherjee S., Yang J. W., Hoffmann S., List B., Chem. Rev., 107, 5471–5569 (2007).
17) Trost B. M., Brindle C. S., Chem. Soc. Rev., 39, 1600–1632 (2010).
18) Denmark S. E., Beutner G. L., Angew. Chem., 120, 1584–1663 (2008).
19) Denmark S. E., Beutner G. L., Angew. Chem. Int. Ed., 47, 1560–1638 (2008).
20) Benaglia M., Rossi S., Org. Biomol. Chem., 8, 3824–3830 (2010).
21) Denmark S. E., Winter S. B. D., Xu X., Wong K.-T., J. Am. Chem. Soc., 118, 7404–7405 (1996).
22) Denmark S. E., Stavenger R. A., Acc. Chem. Res., 33, 432–440 (2000).
23) Denmark S. E., Wong K.-T., Stavenger R. A., J. Am. Chem. Soc., 119, 2333–2334 (1997).
24) Denmark S. E., Stavenger R. A., Wong K.-T., Tetrahedron, 54, 10389–10402 (1998).
25) Denmark S. E., Stavenger R. A., Wong K.-T., J. Org. Chem., 63, 918–919 (1998).
26) Denmark S. E., Stavenger R. A., J. Am. Chem. Soc., 122, 8837–8847 (2000).
27) Denmark S. E., Eklov B. M., Yao P. J., Eastgate M. D., J. Am. Chem. Soc., 131, 11770–11787 (2009).
28) Nakajima M., Yokota T., Saito M., Hashimoto S., Tetrahedron Lett., 45, 61–64 (2004).
29) Kotani S., Hashimoto S., Nakajima M., Synlett, 2006, 1116–1118 (2006).
30) Kotani S., Hashimoto S., Nakajima M., Tetrahedron, 63, 3122–3132 (2007).
31) Kotani S., Sugiura M., Nakajima M., Chem. Rec., 13, 362–370 (2013).
32) Duhamel P., Hennerequin L., Poirier J. M., Tavel G., Vottero C., Tetrahedron, 42, 4777–4786 (1996).
33) Kotani S., Shimoda Y., Sugiura M., Nakajima M., Tetrahedron Lett., 50, 4602–4605 (2009).
34) Bassindale A. R., Stout T., J. Org. Organomet. Chem., 271, C1–C3 (1984).
35) Kotani S., Aoki S., Sugiura M., Nakajima M., Tetrahedron Lett., 52, 2834–2836 (2011).
36) Northrup A. B., MacMillan D. W. C., J. Am. Chem. Soc., 124, 6709–6790 (2002).
37) Mase N., Tanaka F., Barbas C. F., Angew. Chem. Int. Ed., 43, 2420–2423 (2004).
38) Matsubara R., Kawai N., Kobayashi S., Angew. Chem. Int. Ed., 45, 3814–3816 (2006).
39) Hayashi Y., Aratake S., Okano T., Takahashi J., Sumiya T., Shoji M., Angew. Chem. Int. Ed., 45, 5527–5529 (2006).
40) Kano T., Yamaguchi Y., Tanaka Y., Maruoka K., Angew. Chem. Int. Ed., 46, 1738–1740 (2007).
41) Denmark S. E., Beutner G. L., Wynn T., Eastgate M. D., J. Org. Chem., 70, 5235–5248 (2005).
42) Otsuki K., Suto Y., Kanai M., Shibasaki M., J. Am. Chem. Soc., 125, 5644–5645 (2003).
43) Otsuki K., Zhao D., Suto Y., Kanai M., Shibasaki M., Tetrahedron Lett., 46, 4325–4329 (2005).
44) Otsuki K., Zhao D., Kanai M., Shibasaki M., J. Am. Chem. Soc., 128, 7164–7165 (2006).
45) Yoshida Y., Hayashi R., Sumihara H., Tanabe Y., Tetrahedron Lett., 38, 8727–8730 (1997).
46) Yoshida Y., Matsumoto N., Hamasaki R., Tanabe Y., Tetrahedron Lett., 40, 4227–4230 (1999).
47) Tanabe Y., Matsumoto N., Funakoshi S., Manta N., Synlett, 2001, 1959–1961 (2001).
48) Tanabe Y., Matsumoto N., Higashi T., Misaki T., Itoh T., Yamamoto M., Mitairo K., Nishii Y., Tetrahedron, 58, 8269–8280 (2002).
49) Aoki S., Kotani S., Sugiura M., Nakajima M., Chem. Commun., 48, 5524–5526 (2012).
50) Halland N., Aabørel P. S., Jørgensen K. A., Angew. Chem. Int. Ed., 43, 1272–1277 (2004).
51) Halland N., Aabørel P. S., Jørgensen K. A., Angew. Chem. Int. Ed., 43, 1272–1277 (2004).
52) Alim N. R., Miyazaki S., Shimoda Y., Sugiura M., Nakajima M., Kotani S., Chem. Pharm. Bull., 65, 989–993 (2017).
53) Ogasawara M., Ngo H. L., Sakamoto T., Takahashi T., Lin W., Org. Lett., 7, 2881–2884 (2005).
54) Chen I.-H., Yin L., Itano W., Kanai M., Shibasaki M., J. Am. Chem. Soc., 131, 11664–11665 (2009).
55) Hu A., Ngo H. L., Lin W., Angew. Chem. Int. Ed., 43, 2501–2504 (2004).
56) Boxer M. B., Yamamoto H., J. Am. Chem. Soc., 128, 48–49 (2006).
57) Brady P. B., Yamamoto H., Angew. Chem. Int. Ed., 51, 1942–1946 (2012).
58) Boxer M. B., Yamamoto H., J. Organomet. Chem., 643, 1–5 (2012).
59) Lin L., Yamamoto K., Mitsunuma H., Kanzaki Y., Matsunaga S., Kanai M., J. Am. Chem. Soc., 137, 15418–15421 (2015).
60) Shindo Y., Kotani S., Sugiura M., Nakajima M., Chem. Eur. J., 17, 7992–7995 (2011).
61) Shindo Y., Kudo T., Sugiura M., Kotani S., Nakajima M., Angew. Chem. Int. Ed., 52, 3461–3464 (2013).
62) Bennini B., Chuia A. J., Kauadji M., Fondaneche P., Allais D. P., Tetrahedron Lett., 52, 1597–1600 (2011).
63) Dias L. C., Kuroishi P. K., Polo E. C., de Lucca E. C. Jr., Tetrahedron Lett., 54, 980–982 (2013).
64) Kotani S., Kai K., Sugiura M., Nakajima M., Chem. Asian J., 11, 376–379 (2016).
65) Kotani S., Kai K., Sugiura M., Nakajima M., Org. Lett., 19, 3672–3675 (2017).
66) Kotani S., Miyazaki S., Kawahara K., Shimoda Y., Sugiura M., Nakajima M., Chem. Pharm. Bull., 64, 189–192 (2016).
67) Chen I.-H., Yin L., Itano W., Kanai M., Shibasaki M., J. Am. Chem. Soc., 131, 11664–11665 (2009).
68) Hu A., Ngo H. L., Lin W., Angew. Chem. Int. Ed., 43, 2501–2504 (2004).
69) Ogasawara M., Ngo H. L., Sakamoto T., Takahashi T., Lin W., Org. Lett., 7, 2881–2884 (2005).
70) Kotani S., Aoki S., Sugiura M., Ogawara M., Nakajima M., Org. Lett., 16, 4802–4805 (2014).
71) Kotani S., Aoki S., Sugiura M., Ogawara M., Nakajima M., Org. Lett., 16, 4802–4805 (2014).
72) Abiko A., Liu J.-F., Buske D. C., Moriyama S., Masamune S., J. Am. Chem. Soc., 121, 3774–3789 (2001).
73) Kotani S., Inoue T., Masamune S., J. Am. Chem. Soc., 124, 10759–10764 (2002).
74) Furuno H., Inoue T., Abiko A., Tetrahedron Lett., 43, 8297–8299 (2002).
75) Abiko A., Acc. Chem. Res., 37, 387–395 (2004).
76) Albert B. J., Yamamoto H., Acc. Chem. Res., 49, 2747–2749 (2016).
77) Boxer M. B., Yamamoto H., J. Am. Chem. Soc., 128, 48–49 (2006).
78) Brady P. B., Yamamoto H., Angew. Chem. Int. Ed., 51, 1942–1946 (2012).
79) Brady P. B., Albert B. J., Akakura M., Yamamoto H., Chem. Sci., 4, 1223–1231 (2013).
80) Lin L., Yamamoto K., Mitsunuma H., Kanzaki Y., Matsunaga S., Kanai M., J. Am. Chem. Soc., 137, 15418–15421 (2015).
81) Shimoda Y., Kotani S., Sugiura M., Nakajima M., Chem. Eur. J., 17, 7992–7995 (2011).
82) Shimoda Y., Kudo T., Sugiura M., Kotani S., Nakajima M., Angew. Chem. Int. Ed., 52, 3461–3464 (2013).
83) Bennini B., Chuia A. J., Kauadji M., Fondanecche P., Allais D. P., Tetrahedron Lett., 52, 1597–1600 (2011).
84) Dias L. C., Kuroishi P. K., Polo E. C., de Lucca E. C. Jr., Tetrahedron Lett., 54, 980–982 (2013).
85) Kotani S., Kai K., Shindo Y., Hu H., Gao S., Sugiura M., Ogawara M., Nakajima M., Chem. Asian J., 11, 376–379 (2016).
86) Kotani S., Kai K., Sugiura M., Nakajima M., Org. Lett., 19, 3672–3675 (2017).
87) Kotani S., Miyazaki S., Kawahara K., Shimoda Y., Sugiura M., Nakajima M., Chem. Pharm. Bull., 64, 189–192 (2016).
88) Alim N. R., Miyazaki S., Shimoda Y., Sugiura M., Nakajima M., Kotani S., Chem. Pharm. Bull., 65, 989–993 (2017).