Asian Journal of Chemistry; Vol. 25, No. 13 (2013), 7505-7508

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14943

Enantioselective Alkynylation of Trifluoromethyl Ketones Catalyzed by Chiral Schiff Bases

VASUDEVAN DHAYALAN, RYO MURAKAMI and MASAHIKO HAYASHI*

Department of Chemistry, Graduate School of Science, Kobe University. 1-1 Rokkodai-cho, Nada-ku, Hyogo 657-8501, Japan

*Corresponding author: Fax: +81 78 803-5688; E-mail: mhayashi@kobe-u.ac.jp

(*Received*: 8 December 2012; *Accepted*: 1 July 2013) AJC-13738

Enantioselective alkynylation of trifluoromethyl ketones catalyzed by chiral Schiff bases in the presence of Me_2Zn afforded the corresponding trifluoroalkynyl alcohols in up to 66 % ee.

Key Words: Alkynylation, Asymmetric catalysis, Schiff base, Enantioselectivity.

INTRODUCTION

Optically active propargylic alcohols are important intermediates in organic synthesis[1]. To the best of our knowledge, there have been two reports on the enantioselective alkynylation of trifluoromethyl ketones, so far. In 2007, Shibasaki *et al.*[2] reported alkynylation of trifluoromethyl ketones using CuO-*t*-Bu (prepared from CuOTf and KO-*t*-Bu or $Cu(OTf)_2$ and 2 KO-*t*-Bu)-xantphos or phenanthroline system. Furthermore, they also demonstrated the first example of copper(I) alkoxide-catalyzed asymmetric alkynylation of 2,2,2-trifluoroacetophenone with phenylacetylene using 20 mol % of a CuOTf·1/2toluene-KO-*t*-Bu-chiral pybox complex to afford the alkynylated product in moderate optical yield (52 % ee). They reported only one example of asymmetric version. In 2011, Ma and co-workers[3] used stoichiometric amount of $Ti(O\text{-}i\text{-}Pr)_4$ (2 equiv) and R_2Zn (3.0 equiv) in the presence of cinchona alkaloids and BaF_2 for enantioselective alkynylation of trifluoromethyl ketones, which resulted in the formation of the corresponding alkynylation products in up to 94 % ee[3,4]. Our first report using the chiral Schiff base-$Ti(O\text{-}i\text{-}Pr)_4$ complex in asymmetric silylcyanation of aldehydes[5], we have disclosed the utility of chiral Schiff bases in various types of asymmetric reactions[6,7]. Here, we report a simple system for asymmetric alkynylation of trifluoromethyl ketones, that is, without titanium alkoxide or additives such as BaF_2.

EXPERIMENTAL

All reactions were carried out in well cleaned and oven-dried glassware with magnetic stirring. Operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques. All starting materials were obtained from commercial sources and used without further purification unless otherwise stated. Melting points were measured by Yanaco MP-500D and were not corrected. ^1H and ^{13}C NMR spectra (400 and 100.6 MHz respectively) were recorded on a JEOL JNM-LA 400 instrument using Me_4Si as an internal standard (0 ppm). Mass spectra were measured using Thermo Quest LCQ DECA plus. IR spectra were measured with a Thermo SCIENTIFIC NICOLET iS 5. Elemental analyses were carried out using Yanako CHN recorder MT-5. Preparative column chromatography was carried out using Fuji Silysia BW-820MH silica gel or YMC-GEL Silica (6 nm I-40-63 um). Thin layer chromatography (TLC) was carried out on Merk 25 TLC aluminium sheets silica gel 60 F_{254}. HPLC analyses were carried out in a HITACHI L-2000 series instrument equipped with diode array detector using chiral columns CHIRALCEL OJ-H or CHIRALCEL OD-H (250 mm × 4.6 mm × 5 μm).

General procedure for the synthesis of ketoimine-type chiral Schiff base (4c-4j): A mixture of toluene (10 mL), (S)-(+)-valinol or (S)-(+)-*tert*-leucinol (1.20 mmol), salicylketone (1.0 mmol) and anhydrous Na_2SO_4 (1.0 g) was refluxed at 115 ºC for 48 h. The mixture was filtered through a glass filter and the filtrate was evaporated. The residue was subjected to column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the corresponding ONO-tridentate chiral Schiff base ligand.

(S,E)-2-((3,5-*bis*(trifluoromethyl)phenyl)((1-hydroxy-3-methylbutan-2-ylimino)methyl)-6-*tert*-butylphenol (4f): Yellow liquid; Yield: 57 %; IR (neat, ν_{max}, cm^{-1}): 3419, 2961, 1593, 1275, 1131; ^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.91 (s, 1H), 7.64 (s, 1H), 7.35 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.63 (t, *J* = 7.6 Hz, 1H), 6.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 3.84-

3.76 (m, 2H), 3.10-3.06 (m, 1H), 1.94-1.84 (m, 1H), 1.47 (s, 9H), 0.96 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.9, 162.4, 138.3, 136.7, 131.8 (q, J_{C-F} = 16.6 Hz), 130.0, 129.6, 129.4, 128.1, 127.4, 124.4, 122.6 (m), 121.6, 118.8, 117.0, 68.6, 65.0, 35.6, 30.6, 29.4, 19.7, 18.7; MS (ESI) m/z: 476 ($M+H^+$); Anal. calcd. for $C_{24}H_{27}NO_2F_6$: C, 60.63; H, 5.72; N, 2.95. Found: C, 60.39; H, 5.76; N, 3.03.

(S,E)-2-((3,5-*bis*(trifluoromethyl)phenyl)((1-hydroxy-3-methylbutan-2-ylimino)methyl)-4,6-di-*tert*-butylphenol (4h): Yellow solid; Yield: 48 %; m.p.: 131.8-132.8 ºC; IR (neat, ν_{max}, cm^{-1}): 3585, 2960, 1583, 1277, 1129; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.95 (s, 1H), 7.68 (s, 1H), 7.42 (d, J = 2.4 Hz, 1H), 6.39 (d, J = 2.4 Hz, 1H), 3.84-3.79 (m, 2H), 3.16-3.11 (m, 1H), 1.93-1.85 (m, 1H), 1.48 (s, 9H), 1.09 (s, 9H), 0.95 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 172.1, 160.2, 139.0, 137.7, 136.9, 131.7 (q, J_{C-F} = 18.2 Hz), 129.8, 128.4, 127.7, 125.5, 124.4, 122.4 (m), 121.7, 117.9, 68.7, 65.0, 35.3, 34.0, 31.1, 30.7, 29.5, 19.7, 18.7; MS (ESI) m/z: 532 ($M+H^+$); Anal. calcd. for $C_{28}H_{35}NO_2F_6$: C, 63.26; H, 6.64; N, 2.63. Found: C, 63.43; H, 6.74; N, 2.74.

(S,E)-2,4-di-*tert*-butyl-6-((1-hydroxy-3-methylbutan-2-ylimino)(3,4,5-trifluorophenyl) methyl)phenol (4j): Yellow solid; Yield: 43 %; m.p.: 165.8-166.3 ºC; IR (neat, ν_{max}, cm^{-1}): 3592, 2955, 1585, 1366, 1039; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 2.4 Hz, 1H), 7.10 (s, 1H), 6.84 (s, 1H), 6.57 (d, J = 2.8 Hz, 1H), 3.78 (t, J = 5.2 Hz, 2H), 3.24-3.20 (m, 1H), 1.90-1.84 (m, 1H), 1.47 (s, 9H), 1.14 (s, 9H), 0.93 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 171.9, 160.1, 152.3, 149.8, 141.0 (t, J_{C-F} = 14.9 Hz), 138.8, 138.5 (t, J_{C-F} = 14.9 Hz), 137.5, 130.5 (q, J_{C-F} = 6.6 Hz), 127.6, 125.5, 117.8, 113.8 (d, J_{C-F} = 16.5 Hz), 112.5 (d, J_{C-F} = 19.9 Hz), 68.4, 64.9, 35.2, 34.0, 31.2, 30.6, 29.4, 19.6, 18.8; MS (ESI) m/z: 450 ($M+H^+$); Anal. calcd. for $C_{26}H_{34}NO_2F_3$: C, 69.46; H, 7.62; N, 3.12. Found: C, 69.39; H, 7.72; N, 3.11.

General procedure for chiral Schiff base catalyzed alkynylation of trifluoromethyl ketones: Ethynylbenzene (2 mmol) and dichloromethane (2.5 mL) were added to a Schlenk tube equipped with a stirring bar and the tube was dried under vacuum and filled with argon, followed by Me_2Zn (2.3 mmol) was added slowly under Ar atmosphere and then mixture was stirred at room temperature for 2.5 h. Schiff base ligand (5 mol %) in dichloromethane (2.5 mL) was added. Then the solution was stirred at room temperature for 3 h, trifluoromethyl ketones (1.0 mmol) was added slowly. The resulting mixture was stirred at room temperature for 24 h and quenched with a sat. NH_4Cl solution (10 mL), extracted with dichloromethane (20 mL × 3) the combined organic layer was washed with brine solution (20 mL × 2) and dried (Na_2SO_4). Removal of solvent followed by Kugelrohr distillation afforded the desired trifluoroalkynyl alcohols. The ee values were determined by HPLC analysis (Chiralcel OJ-H and OD-H).

1,1,1-Trifluoro-2,4-diphenylbut-3-yn-2-ol (3a)[3]: 96 % yield, 64 % ee (R), $[\alpha]_D^{29}$ = + 19.2 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 20.6 (c 1.0, CH_2Cl_2, 91 % ee (R)). [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 99/1, 1.0 mL/min, λ = 250 nm, t_R = 19.84 min (R isomer), t_R = 25.78 min (S isomer)].

1,1,1-Trifluoro-2-(4-fluorophenyl)-4-phenylbut-3-yn-2-ol (3b)[3]: 95 % yield, 60 % ee (R), $[\alpha]_D^{31}$ = + 18.4 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = +17.6 (c 1.0, CH_2Cl_2, 90 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, λ = 250 nm, t_R = 17.20 min (R isomer), t_R = 22.95 min (S isomer)].

2-(4-Chlorophenyl)-1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (3c)[3]: 95 % yield, 64 % ee (R), $[\alpha]_D^{29}$ = + 13.5 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 14.9 (c 1.0, CH_2Cl_2, 88% ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 95/5, 0.8 mL/min, λ = 250 nm, t_R = 15.76 min (R isomer), t_R = 18.18 min (S isomer)].

2-(4-Bromophenyl)-1,1,1-trifluoro-4-phenylbut-3-yn-2-ol (3d)[3]: 94 % yield, 66 % ee (R), $[\alpha]_D^{29}$ = + 10.8 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 6.8 (c 1.0, CH_2Cl_2, 86 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 250 nm, t_R = 10.74 min (R isomer), t_R = 12.46 min (S isomer)].

1,1,1-Trifluoro-4-phenyl-2-*p*-tolylbut-3-yn-2-ol (3e)[3]: 90 % yield, 52 % ee (R), $[\alpha]_D^{32}$ = + 12.0 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 11.3 (c 1.0, CH_2Cl_2, 85 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 250 nm, t_R = 13.55 min (R isomer), t_R = 24.56 min (S isomer)].

1,1,1-Trifluoro-2-phenyl-4-*p*-tolylbut-3-yn-2-ol (3f)[3]: 98 % yield, 52 % ee (R), $[\alpha]_D^{27}$ = + 15.5 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 13.8 (c 1.0, CH_2Cl_2, 84 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 250 nm, t_R = 15.58 min (R isomer), t_R = 21.22 min (S isomer)].

2-(4-Chlorophenyl)-1,1,1-trifluoro-4-*p*-tolylbut-3-yn-2-ol (3g)[3]: 98 % yield, 50 % ee (R), $[\alpha]_D^{28}$ = + 11.8 (c 1.0, $CHCl_3$) (lit.[3] $[\alpha]_D^{20}$ = + 10.5 (c 1.0, CH_2Cl_2 CH_2Cl_2 85 % ee (R)). [Daicel Chiralcel OD-H, *n*-hexane/*i*-PrOH = 95/5, 0.6 mL/min, λ = 250 nm, t_R = 10.13 min (R isomer), t_R = 11.16 min (S isomer)].

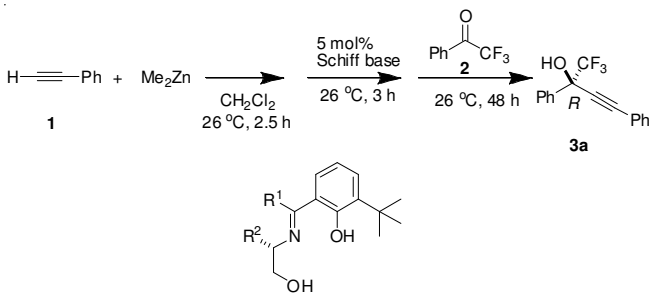
1,1,1-Trifluoro-2-phenyloct-3-yn-2-ol (3h)[3]: 43 % yield, 58 % ee (R), $[\alpha]_D^{29}$ = + 5.7 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 1.6 (c 1.0, CH_2Cl_2, 94 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 92/8, 0.5 mL/min, λ = 250 nm, t_R = 15.95 min (R isomer), t_R = 19.00 min (S isomer)].

1,1,1-Trifluoro-2.6-diphenylhex-3-yn-2-ol (3i)[2]: 59 % yield, 58 % ee, $[\alpha]_D^{30}$ = + 4.9 (c 1.0, CH_2Cl_2). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 250 nm, t_R = 25.02 min (R isomer), t_R = 34.28 min (S isomer)].

4-Cyclopropyl-1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (3j)[3]: 80 % yield, 54 % ee (R), $[\alpha]_D^{31}$ = + 3.9 (c 1.0, CH_2Cl_2) (lit.[3] $[\alpha]_D^{20}$ = + 2.2 (c 1.0, CH_2Cl_2, 65 % ee (R)). [Daicel Chiralcel OJ-H, *n*-hexane/*i*-PrOH = 90/10, 0.8 mL/min, λ = 250 nm, t_R = 17.40 min (R isomer), t_R = 20.24 min (S isomer)].

RESULTS AND DISCUSSION

We first examined the effect of Ti(O-*i*-Pr)$_4$ and found only 5 mol % of a chiral Schiff base and Me_2Zn (2.3 equiv) were necessary for the reaction to proceed, obtaining up to 66 % ee without Ti(O-*i*-Pr)$_4$. In the case of aldimine-type Schiff bases (**4a** and **4b**) the obtained enantioselectivities were significantly low, whereas, in the case of ketoimine-type Schiff bases (**4c** and **4d**) enantioselectivities were increased to 28 and 38 % ee, respectively (**Scheme-I**).

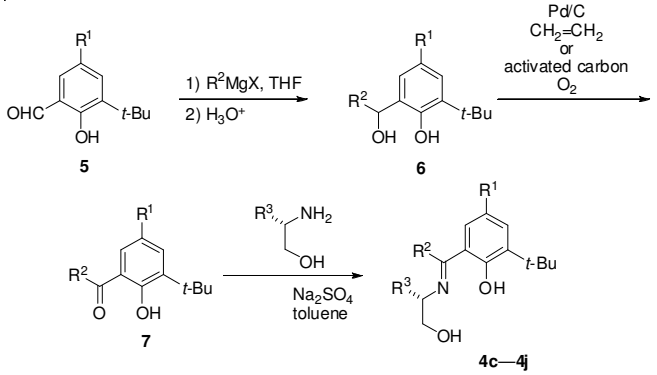


4a; R^1 = H, R^2 = *i*-Pr; 69% yield (0% ee)
4b; R^1 = H, R^2 = *t*-Bu; 94% yield (4% ee)
4c; R^1 = Ph, R^2 = *i*-Pr; 87% yield (28% ee)
4d; R^1 = Ph, R^2 = *t*-Bu; 96% yield (38% ee)

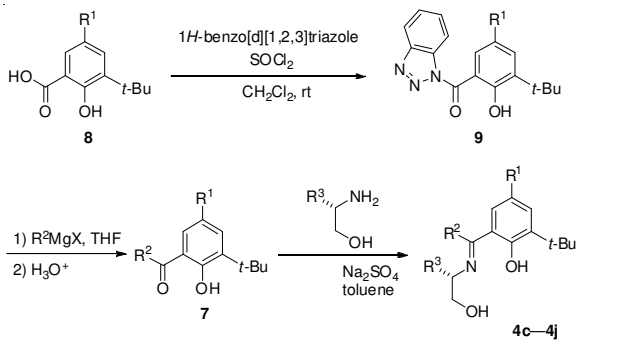
Scheme-I: Enantioselective alkynylation of 2,2,2-trifluoroacetophenone catalyzed by chiral Schiff bases

Accordingly, we prepared a variety of ketoimine-type Schiff bases (**4e-4j**) according to the following two routes (**Scheme-II**). **Route A** is our previous method involving oxidation of benzylic alcohols (**6**) to the corresponding ketones (**7**) followed by condensation with chiral β-amino alcohols. **Route B** involves a novel step starting from salicyl acid derivatives[7]. The reaction of substituted salicylic acids (**8**) with benzotriazole in the presence of 1 equiv of $SOCl_2$ in dichloromethane at room temperature led to the corresponding diaryl ketones (**9**), which further undergo the Grignard reaction with R_2MgX followed by condensation of ketones (**7**) with chiral amino alcohols. Thus, ketoimine-type chiral Schiff bases were prepared easily from commercially available starting materials in short steps with good yields[8].

Route A

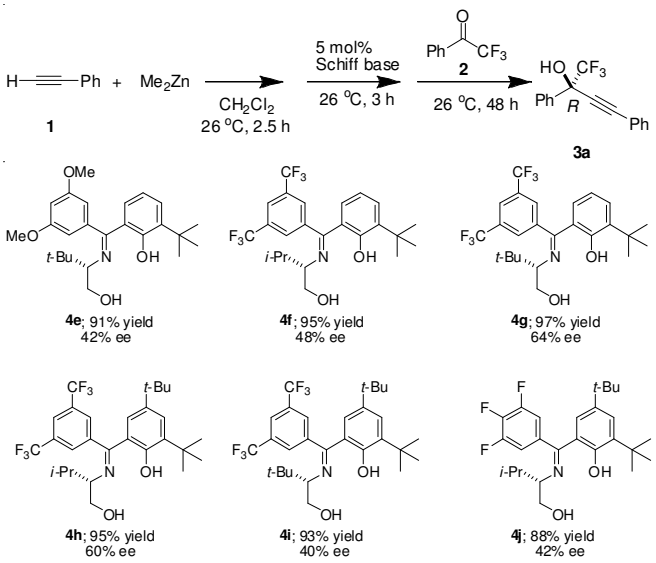


Route B



Scheme-II: Synthesis of ketoimine-type (O,N,O) chiral Schiff bases

Then, we examined the reaction of 2,2,2-trifluoroacetophenone with phenylacetylene. The results are summarized in **Scheme-III**. Among the Schiff bases we examined, Schiff base **4g** prepared from salicyl ketone derivatives having two trifluoromethyl groups on the phenyl group and (S)-(+)-*tert*-leucinol gave the highest ee (64 % ee) in excellent yield (97 % yield). After optimizing the enantioselectivity, we examined the effect of Et_2Zn and Ph_2Zn as additives on asymmetric alkynylation of 2,2,2-trifluoroacetophenone. Chiral Schiff base ligand **4g** (5 mol %) in the presence of additives such as Et_2Zn and Ph_2Zn resulted in corresponding CF_3-substituted tertiary propargyl alcohols in poor enantioselectivities of 8 and 14 % ee (R) with yields of 12 and 96 %, respectively.

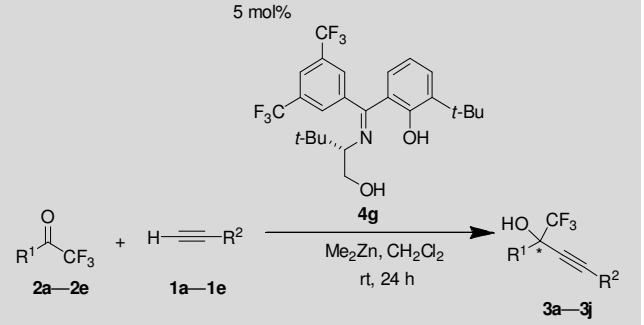


Scheme-III: Enantioselective alkynylation of 2,2,2-trifluoroacetophenone

Next, we established the best reaction system and then examined enantioselective alkynylation of trifluoromethyl ketones. The obtained results are summarized in Table-1. In all cases, the reactions proceeded smoothly in the presence of 5 mol % of chiral Schiff bases affording the product in high chemical yield with moderate to good ee (50-66 % ee (R)). We attempted the enantioselective alkynylation of 2,2,2-trifluoroacetophenone/halogenated trifluoromethyl ketones with 2.3 equiv of Me_2Zn in the presence 5 mol % of chiral ligand **4g** in dichloromethane at room temperature for 24 h, which afforded the corresponding trifluoroalkynyl alcohols in excellent yields (94-96 %) and good enantioselectivities (60-66 % ee (R)) (entries 1-4, Table-1). Under the optimized condition, the reaction of the methyl substituted trifluoromethyl ketone with phenylacetylene furnished the corresponding propargyl alcohol with enantioselectivity of 52 % ee in 90 % yield (entry 5, Table-1), whereas the reaction of trifluoromethyl ketones with methyl substituted phenylacetylene (entries 6 and 7, Table-1) resulted in trifluoromethylated propargylic tertiary alcohols in a comparatively enhanced yield of 98 % with enantioselectivities of 50-52 % ee. The reactions of alkyl substituted acetylenes (entries 8-10, Table-1) with trifluoromethyl ketones afforded the products in moderate to good yields of 43-80 % and reasonable enantioselectivities of 54-58 % ee. Using our developed O,N,O tridentate Schiff base prepared from salicyl ketone derivatives having two trifluoromethyl groups on the phenyl group and (S)-(+)-*tert*-leucinol, enantioselective alkynylation of 2,2,2-trifluoroacetophenone

proceeded smoothly to give the alkynylated product in high yield (up to 98 % yield) and good ee (up to 66 % ee). This is the third report on enantioselective alkynylation of trifluoromethyl ketones. The current method gives higher ee than Shibasaki's method[2] and is much simpler than Ma's method[3].

TABLE-1
ENANTIOSELECTIVE ALKYNYLATION OF TRIFULUOROMETHYL KETONES[a]



Entry	R^1	R^2	Yield (%)[b]	ee (%)[c]
1	Ph	Ph	96	64 (R)
2	4-FC_6H_4	Ph	95	60 (R)
3	4-ClC_6H_4	Ph	95	64 (R)
4	4-BrC_6H_4	Ph	94	66 (R)
5	4-MeC_6H_4	Ph	90	52 (R)
6	Ph	4-MeC_6H_4	98	52 (R)
7	4-ClC_6H_4	4-MeC_6H_4	98	50 (R)
8	Ph	*n*-C_4H_9	43	58 (R)
9	Ph	$Ph(CH_2)_2$	59	58 (+)[d]
10	Ph	Cyclopropyl	80	54 (R)

[a]General reaction condition: **2/1**/Me_2Zn/ligand: 1.0:2.0:2.3:0.05 in CH_2Cl_2 at room temperature (27-29 ºC) for 24 h. [b]Isolated yield after Kugelrohr distillation. [c]ee values were determined by HPLC analysis. Absolute configuration is based on the comparison of the optical rotation with the literature[3]. [d]Absolute configuration was not determined.

Conclusion

In summary, we have successfully developed a simple and practical method for enantioselective alkynylation of trifluoromethyl ketones catalyzed by chiral Schiff base. Trifluoroalkynyl alcohols were obtained using 5 mol % of a chiral Schiff base and Me_2Zn, which significantly simplified the enantioselective synthetic procedure by avoiding the use of titanium alkoxide and other additives. Moderate to good yields of trifluoroalkynyl alcohols with enantioselectivities up to 66 % ee were achieved. The methodology reported in this article can be useful for synthesizing trifluoromethylated propargylic tertiary alcohols enantioselectively. Further studies for improving the enantioselectivity are ongoing.

ACKNOWLEDGEMENTS

This work was supported by a Grant-in-Aid (No. B23350043) for Scientific Research on Innovative Areas 'Molecular Activation Directed toward Straightforward Synthesis', Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and by Special Coordination Funds for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas (Innovative Bioproduction Kobe), MEXT, Japan.

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