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Enantioselective Alkynylzinc Addition to Carbonyl Compounds by Tf-based Sulfamide-amine Alcohol Catalysis

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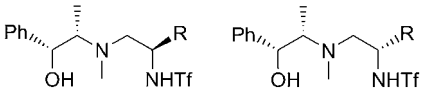
The new Tf-based sulfamide-amine alcohol **3a** was found to be very effective in catalyzing the enantioselective alkynylzinc addition to both aromatic aldehydes and unactivated aromatic ketones without using another metal species under mild condition, providing up to 92% *ee* and 90% *ee* for aldehydes and ketones, respectively.

Keywords sulfamide-amine alcohol, enantioselective addition, propargylic alcohol, alkynylation, carbonyl compound

Introduction

Chiral propargylic alcohols are versatile building blocks for the synthesis of many pharmaceuticals and natural products.[1] A simplest approach to the preparation of those alcohols is enantioselective addition of terminal alkynes to carbonyl compounds.[2] Some excellent work has been reported in this field with high *ee* values.[2-7] Very recently, we reported a series of chiral Ts-based sulfamide-amine alcohol (SAA) ligands for the asymmetric diethylzinc addition to aldehydes without using the titanium complex.[8] Thereafter, we found that the catalysts were also effective for the asymmetric alkynylation of carbonyl compounds.[9] It is well known that enantioselectivities of chiral ligand-catalyzed reactions are always related to the electronic effects of ligands besides their steric effects. Considering the electron-withdrawing nature of *p*-tolylsulfonyl (Ts) in the aforesaid ligands,[10] we turned to the trifluoromethanesulfonyl (Tf), a more strongly electron-withdrawing group and a new class of Tf-based sulfamide-amine alcohols (Tf-based SAA) were prepared through two simple efficient steps (Scheme 1**)**.[11] We found that the Tf-based SAA was more effective for the addition of alkynylzinc to aromatic aldehyes than our Ts-based SAA for this reaction.[9b] As the detail application of our Tf-based SAA ligands to the addition of alkynylzinc to carbonyl compounds, herein, we report that the Tf-based SAA ligands catalyze this reaction under very mild condition in the absence of $Ti(O^iPr)_4$.

Scheme 1 The evaluated Tf-based SAA ligands



(1*R*,1′*R*, 2′*S*)

1a: R = Me
2a: R = ^{i}Pr
3a: R = Ph
4a: R = Bn
5: R = ^{t}Bu

(1*S*,1′*R*, 2′*S*)

1b: R = Me
2b: R = ^{i}Pr
3b: R = Ph
4b: R = Bn

Results and discussion

The Tf-based SAA ligands were applied to the enantioselective addition of alkynylzinc to benzaldehyde and acetophenone in hexane (Table 1). **1a**, **2a**, **3a** and **4a** derived from (*R*)-aziridines gave good enantioselectivities (Table 1, Entries 1, 3, 5, 7, 10, 12, 14 and 16) and were more effective than those (**1b**, **2b**, **3b** and **4b**) derived from (*S*)-aziridines (Table 1, Entries 2, 4, 6, 8, 11, 13, 15 and 17). From the viewpoint of steric effect, the chiral carbon linked to the nitrogen of sulfamide with (*R*) configuration was more favorable than that with (*S*) configuration. The catalytic enantioselectivity increased with the steric hindrance of substituting group at the chiral carbon linked to the nitrogen of sulfamide with (*R*) configuration (Table 1, Entries 1, 3, 5, 7, 10, 12, 14, and 16). However, the *ee* value reduced when the substituting group was *tert*-butyl (Table 1, Entries 9 and 18), which may be explained by that enantioselectivities of chiral ligand-catalyzed reactions are also related to the electronic effects of ligands besides their steric effects. When the substituting group was phenyl, the combined result of steric and electronic effects reached optimization. **3a** was found to be the most effective ligand, affording 88% and 79% *ee* for benzaldehyde and acetophenone, respectively (Table 1, Entries 5 and 14).

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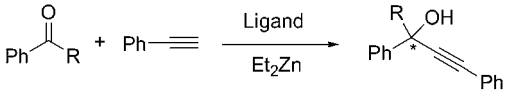
Table 1 Asymmetric alkynylzinc addition to carbonyl compounds catalyzed by Tf-based SAA[a]



Entry	R	Ligand	Yield[b]/%	*ee*[c]/%
1	H	**1a**	58	68
2	H	**1b**	61	2
3	H	**2a**	70	77
4	H	**2b**	63	−6[d]
5	H	**3a**	92	88
6	H	**3b**	74	45
7	H	**4a**	82	76
8	H	**4b**	72	0
9	H	**5**	84	52
10	CH_3	**1a**	86	72
11	CH_3	**1b**	44	14
12	CH_3	**2a**	98	77
13	CH_3	**2b**	42	3
14	CH_3	**3a**	97	79
15	CH_3	**3b**	24	33
16	CH_3	**4a**	70	74
17	CH_3	**4b**	24	16
18	CH_3	**5**	43	70

[a] *n*(Phenylacetylene)/*n*(Et_2Zn)/*n*(carbonyl compound)/*n*(ligand)＝2∶2∶1∶0.1, 1 mL of hexane, r.t., 20 h for aldehyde, 48 h for acetophenone. [b] Isolated yield. [c] The *ee* values were determined by HPLC on a Chiracel OD-H column. [d] The configuration of the product was opposite to others in this table.

To improve the enantioselectivity, the reaction conditions including solvent, temperature and reaction time were optimized using benzaldehyde as the substrate (Table 2, Entries 1—8). We found that the results were strongly influenced by the solvent. When the reaction was carried out in THF or Et_2O, low *ee* values were afforded (Table 2, Entries 1 and 3). However, there was a dramatic enhancement in enantioselectivity when dichloromethane, hexane or toluene was used (Table 2, Entries 2, 4 and 5). Toluene was the best solvent, and the corresponding product was obtained in 99% Yield and 92% *ee* (Table 2, Entry 5). Moreover, decreased *ee* values were provided at lower temperatures (Table 2, Entries 6 and 7). The conditions were also explored with the optimal ligand **3a** using acetophenone as the substrate (Table 2, Entries 9—16). The enantioselectivities were also found to be quite sensitive to the solvents and hexane was found to be the best solvent (Table 2, Entries 9—13). Decreasing the reaction temperature from room temperature led to the best enantioselectivity of up to 88% *ee*, but meanwhile the yield was reduced (Table 2, Entries 14—16).

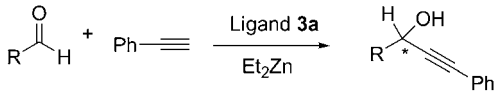
Under the optimized reaction conditions, ligand **3a** was firstly successfully employed to catalyze the asymmetric alkynylzinc addition to aldehydes. As can be seen from the summarized results (Table 3), **3a** was highly efficient for all of aromatic aldehydes studied, and the propargylic alcohols were obtained with 81%—92% *ee* and up to 99% yield (Table 3, Entries 1—13). Moreover, 54% *ee* for cyclohexanecarboxaldehyde was provided (Table 3, Entry 14). While, the alkynylzinc addition to various ketones using the Tf-based SAA **3a** was conducted. As shown in Table 4, **3a** was very efficient for all aromatic ketones with *ortho*-, *meta*-, or

Table 2 Asymmetric alkynylzinc addition to carbonyl compound using **3a** under various conditions[a]

Entry	Carbonyl compound	Solvent	*T*/℃	Time/h	Yield[b]/%	*ee*[c]/%
1	Benzaldehyde	THF	r.t.	20	55	14
2	Benzaldehyde	CH_2Cl_2	r.t.	20	92	85
3	Benzaldehyde	Et_2O	r.t.	20	90	42
4	Benzaldehyde	Hexane	r.t.	20	92	88
5	Benzaldehyde	Toluene	r.t.	20	99	92
6	Benzaldehyde	Toluene	−20	48	50	82
7	Benzaldehyde	Toluene	0	24	50	87
8	Benzaldehyde	Toluene	r.t.	12	90	91
9	Acetophenone	THF	r.t.	48	0	—
10	Acetophenone	CH_2Cl_2	r.t.	48	29	65
11	Acetophenone	Et_2O	r.t.	48	46	76
12	Acetophenone	Toluene	r.t.	48	75	74
13	Acetophenone	Hexane	r.t.	48	97	79
14	Acetophenone	Hexane	0	48	52	88
15	Acetophenone	Hexane	0	72	53	86
16	Acetophenone	Hexane	−20	96	21	87

[a] *n*(Phenylacetylene)/*n*(Et_2Zn)/*n*(carbonyl compound)/*n*(ligand)＝2∶2∶1∶0.1, 1 mL of solvent. [b] Isolated yield. [c] The *ee* values were determined by HPLC on a Chiracel OD-H column.

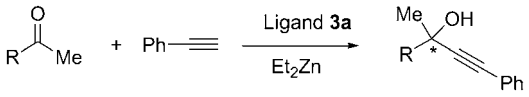
Table 3 Asymmetric alkynylzinc addition to aldehydes by **3a**[a,b]



Entry	R	Yield[c]/%	*ee*[d]/%
1	Ph	99	92
2	*o*-Me-C_6H_4	99	90
3	*m*-Me-C_6H_4	92	90
4	*p*-Cl-C_6H_4	99	89
5	*m*-MeO-C_6H_4	88	83
6	*p*-MeO-C_6H_4	96	89
7	*o*-F-C_6H_4	84	81
8	*m*-F-C_6H_4	99	88
9	*p*-F-C_6H_4	93	85
10	*m*-CF_3-C_6H_4	75	84
11	*p*-CF_3-C_6H_4	99	88
12	3,5-Cl_2-C_6H_3	65	84
13	1-Naphthyl	95	89
14	Cyclohexyl	84	54

[a] *n*(Phenylacetylene)/*n*(Et_2Zn)/*n*(aldehyde)/*n*(ligand) = 2 ∶ 2 ∶ 1 ∶ 0.1, 1 mL of toluene, r.t., 16 h. [b] All reactions were performed under argon at room temperature. [c] Isolated yield. [d] The *ee* values were determined by HPLC on a Chiracel OD-H column.

Table 4 Asymmetric alkynylzinc addition to aromatic ketones by **3a**[a]



Entry	R	Yield[b]/%	*ee*[c]/%
1	C_6H_5	52	88
2	2-Naphthyl	64	87
3	*m*-Me-C_6H_4	90	87
4	*p*-Me-C_6H_4	64	85
5	*p*-Biphenyl	31	90
6	*p*-Cl-C_6H_4	81	82
7	*m*-Cl-C_6H_4	82	81
8	*p*-F-C_6H_4	70	84
9	*m*-F-C_6H_4	77	85
10	*p*-^{t}Bu-C_6H_4	50	90
11	*o*-CF_3-C_6H_4	81	79
12	*m*-CF_3-C_6H_4	72	77
13	*p*-CF_3-C_6H_4	48	75
14	*p*-C_6H_4O-C_6H_4	43	81
15	*p*-(*p*-CH_3O-C_6H_4)-C_6H_4	36	88
16	Cyclopropyl	69	8
17	*tert*-Butyl	23	3

[a] *n*(Phenylacetylene)/*n*(Et_2Zn)/*n*(ketone)/*n*(ligand) = 2 ∶ 2 ∶ 1 ∶ 0.1, 0 ℃, 48 h. [b] Isolated yield. [c] The *ee* values were determined by HPLC on a Chiracel OD-H column.

para-substituted acetophenones containing electron-donating or electron-withdrawing substituents and the propargylic alcohols were obtained with 75%—90% *ee* and up to 90% yield (Table 4, Entries 1—15). The reactions of the alkynylzinc addition to aliphatic ketones such as 1-cyclopropylethanone and 3,3-dimethyl-2-butanone were also carried out, however, only 8% and 3% *ee* values were obtained, respectively (Table 4, Entries 16 and 17).

Conclusion

We have demonstrated that a class of new chiral Tf-based SAA ligands is a highly efficient ligand for the catalytic asymmetric alkynylzinc addition to aromatic aldehydes and unactivated aromatic ketones in the absence of $Ti(O^iPr)_4$, giving up to 92% and 90% *ee* for aldehydes and ketones, respectively. The ligands are stable, easily accessible, and more practical. This work provides a more effective method to this reaction than our Ts-based SAA for this reaction of up to 84% *ee* for aldehydes [9b] and 83% *ee* for ketones.[9d]

Experimental

General methods

All reactions were carried out under an argon atmosphere. All solvents were dried according to standard methods. All aldehydes, ketones and diethylzinc were purchased from Aldrich or Fluka. Reactions were monitored by thin layer chromatography (TLC). Column chromatography purifications were carried out using silica gel. NMR spectra were measured in $CDCl_3$ on a Bruker DRX-400NMR spectrometer (400 MHz) with TMS as an internal reference. Optical rotations were recorded on a JASCO P-1010 polarimeter. The *ee* value determination was carried out using a Chiracel OD-H column on an Agilent HP-1100 HPLC instrument: flow rate, 1 mL•min^{-1}; UV detection at 254 nm.

Spectral data of ligands

Typical procedure for preparation of Tf-based lagands has been shown in our published paper,[11] while the spectral data of Tf-based lagands are listed below.

Trifluoro-*N*-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]propan-2-yl]methanesulfonamide (1a) White solid, yield 34%, m.p. 98—99 ℃; $[\alpha]_D^{26}$ −36.75 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 1.12—1.16 (m, 6H), 2.15 (s, 3H), 2.32 (dd, *J*=10.4, 12.7 Hz, 1H), 2.60 (dd, *J*=4.4, 12.8 Hz, 1H), 2.84—2.87 (m, 1H), 3.55 (dd, *J*=5.2, 10.8 Hz, 1H), 3.80 (s, 2H), 4.66 (d, *J*=7.1 Hz, 1H), 7.26—7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 10.35, 19.35, 35.25, 48.67, 61.94, 66.04, 75.86, 119.81 (q, J_{CF}=320 Hz), 126.17, 128.29, 128.89, 142.83; HRMS calcd for $C_{14}H_{22}F_3N_2O_3S$ $[M+H]^+$ 355.1303, found 355.1316.

Trifluoro-*N*-[(*S*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]propan-2-yl]methanesulfonamide (1b) White solid, yield 44%, m.p. 94—96

℃; $[\alpha]_D^{26}$ −6.75 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 1.02 (d, *J*=9.2 Hz, 3H), 1.15 (d, *J*=6.4 Hz, 3H), 2.29 (s, 3H), 2.47 (dd, *J*=4.4, 13.2 Hz, 1H), 2.56 (dd, *J*=8.4, 13.2 Hz, 1H), 2.89—2.96 (m, 1H), 3.58 (dd, *J*=6.4, 12.4 Hz, 1H), 4.30 (s, 2H), 4.77 (d, *J*=5.6 Hz, 1H), 7.26—7.37 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 8.85, 19.91, 39.87, 49.88, 59.11, 64.96, 76.65, 119.98 (q, J_{CF} = 320 Hz), 126.37, 128.09, 128.74, 142.29; HRMS calcd for $C_{14}H_{22}F_3N_2O_3S$ $[M+H]^+$ 355.1303, found 355.1318.

Trifluoro-*N*-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3-methylbutan-2-yl]methanesulfonamide (2a) White solid, yield 48%, m.p. 116—117 ℃; $[\alpha]_D^{26}$ −22.23 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 0.83 (d, *J*=7.2 Hz, 6H), 1.07 (d, *J*=6.8 Hz, 3H), 1.89—1.95 (m, 1H), 2.17 (s, 3H), 2.46—2.54 (m, 2H), 2.76—2.83 (m, 1H), 3.34—3.39 (m, 1H), 3.40 (s, 2H), 4.68 (d, *J*=6.4 Hz, 1H), 7.26—7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 10.24, 17.31, 18.16, 29.54, 36.63, 55.72, 58.38, 65.64, 75.17, 119.83 (q, J_{CF}=320 Hz), 126.21, 127.93, 128.63, 142.73; HRMS calcd for $C_{16}H_{26}F_3N_2O_3S$ $[M+H]^+$ 383.1616, found 383.1631.

Trifluoro-*N*-[(*S*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3-methylbutan-2-yl]methanesulfonamide (2b) White solid, yield 57%, m.p. 79—80 ℃; $[\alpha]_D^{26}$ −11.95 (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 0.84 (d, *J*=7.0 Hz, 3H), 0.99 (d, *J*=6.8 Hz, 3H), 1.02 (d, *J*=6.8 Hz, 3H), 1.89—1.95 (m, 1H), 2.97 (s, 3H), 2.41 (dd, *J*=4.8, 13.4 Hz, 1H), 2.68 (dd, *J*=8.5, 13.4 Hz, 1H), 2.88—2.91 (m, 1H), 3.33—37 (m, 1H), 3.81 (s, 2H), 4.81 (d, *J*=5.2 Hz, 1H), 7.26—7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 8.72, 17.81, 18.27, 29.99, 40.00, 53.82, 59.50, 76.78, 120.01 (q, J_{CF} = 320 Hz), 126.37, 128.00, 128.68, 142.40; HRMS calcd for $C_{16}H_{26}F_3N_2O_3S$ $[M+H]^+$ 383.1616, found 383.1632.

Trifluoro-*N*-[(*R*)-2-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (3a) White solid, yield 42%, m.p. 141—142 ℃; $[\alpha]_D^{27}$ −42.26 (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 0.61 (d, *J*=6.4 Hz, 3H), 2.21 (s, 3H), 3.06 (dd, *J*=6.4, 12.8 Hz, 1H), 3.34 (dd, *J*=4.8, 9.6 Hz, 1H), 3.42—3.47 (m, 1H), 3.67 (dd, *J*=4.8, 10.0 Hz, 1H), 3.96 (s, 2H), 4.57 (d, *J*=6.0 Hz, 1H), 7.08—7.10 (m, 2H), 7.24—7.40 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 11.48, 36.10, 44.90, 57.48, 66.82, 76.82, 119.91 (q, J_{CF} = 320 Hz), 126.61, 128.02, 128.37, 128.61, 128.82, 137.16, 142.72; HRMS calcd for $C_{19}H_{24}F_3N_2O_3S$ $[M+H]^+$ 417.1460, found 417.1466.

Trifluoro-*N*-[(*S*)-2-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-1-phenylethyl]methanesulfonamide (3b) White solid, yield 35%, m.p. 119—121 ℃; $[\alpha]_D^{26}$ −21.46 (*c* 2.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 0.74 (d, *J*=6.8 Hz, 3H), 1.90 (s, 3H), 3.11 (dd, *J*=6.4, 10.6 Hz, 1H), 3.15 (dd, *J*=4.4, 6.8 Hz, 1H), 3.50—3.56 (m, 1H), 3.70 (dd, *J*=4.4, 11.2 Hz, 1H), 4.03 (s, 2H), 4.51 (d, *J*=7.0 Hz, 1H), 7.05—7.08 (m, 2H), 7.22—7.32 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 12.51, 28.75, 44.41, 64.82, 68.41, 76.82, 120.73 (q, J_{CF} = 320 Hz), 126.32, 128.36, 128.53, 128.64, 128.80, 128.89, 136.16, 142.66; HRMS calcd for $C_{19}H_{24}F_3N_2O_3S$ $[M+H]^+$ 417.1460, found 417.1474.

Trifluoro-*N*-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3-phenylpropan-2-yl]methanesulfonamide (4a) White solid, yield 65%, m.p. 139—141 ℃; $[\alpha]_D^{26}$ −26.27 (*c* 1.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 1.06 (d, *J*=6.7 Hz, 3H), 2.15 (s, 3H), 2.45—2.62 (m, 3H), 2.85—2.88 (m, 1H), 3.06—3.10 (m, 1H), 3.69—3.73 (m, 3H), 4.71 (d, *J*=6.5 Hz, 1H), 7.11 (d, *J*=7.1 Hz, 2H), 7.22—7.38 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 10.28, 36.21, 40.15, 54.44, 59.41, 65.77, 75.08, 120.00 (q, J_{CF}=320 Hz), 126.26, 127.08, 128.13, 128.77, 128.84, 129.55, 136.78, 142.53; HRMS calcd for $C_{20}H_{26}F_3N_2O_3S$ $[M+H]^+$ 431.1616, found 431.1623.

Trifluoro-*N*-[(*S*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3-phenylpropan-2-yl]methanesulfonamide (4b) White solid, yield 60%, m.p. 115—116 ℃; $[\alpha]_D^{26}$ −0.41 (*c* 2.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 1.00 (d, *J*=6.8 Hz, 3H), 2.27 (s, 3H), 2.42 (dd, *J*=4.5, 13.4 Hz, 1H), 2.60 (dd, *J*=8.0, 13.4 Hz, 1H), 2.72 (dd, *J*=8.0, 13.6 Hz, 1H), 2.89—2.96 (m, 2H), 3.70—3.74 (m, 1H), 3.95 (s, 2H), 4.76 (d, *J*=5.6 Hz, 1H), 7.10 (d, *J*=7.0 Hz, 2H), 7.22—7.36 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 8.87, 39.78, 40.19, 55.33, 56.61, 65.16, 76.78, 119.98 (q, J_{CF}=320 Hz), 126.41, 127.00, 128.18, 128.75, 129.68, 136.74, 142.21; HRMS calcd for $C_{20}H_{26}F_3N_2O_3S$ $[M+H]^+$ 431.1616, found 417.1625.

Trifluoro-*N*-[(*R*)-1-[[(1*R*,2*S*)-1-hydroxy-1-phenylpropan-2-yl](methyl)amino]-3,3-dimethylbutan-2-yl]methanesulfonamide (5) White solid, yield 84%, m.p. 106—107 ℃; $[\alpha]_D^{26}$ −18.13 (*c* 1.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 400 MHz) *δ*: 0.96—0.98 (m, 12H), 2.28 (s, 3H), 2.72 (d, *J*=6.4 Hz, 2H), 2.89—2.92 (m, 1H), 3.37—3.41 (m, 1H), 4.95 (d, *J*=3.6 Hz, 1H), 7.23—7.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) *δ*: 9.97, 26.94, 34.42, 38.42, 58.07, 62.69, 66.32, 73.37, 120.00 (q, J_{CF}=320 Hz), 126.23, 127.48, 128.42, 141.766; HRMS calcd for $C_{17}H_{28}F_3N_2O_3S$ $[M+H]^+$ 397.1773, found 397.1759.

Typical procedure for asymmetric additions of phenylacetylene to aldehydes

Under argon, chiral ligand (10 mol%, 0.025 mmol) was dissolved in dry toluene (1.0 mL) at room temperature and stirred for 10 min. Then Et_2Zn (10 wt% in hexane, 0.9 mL) and phenylacetylene (54 μL, 0.5 mmol) were added by syringe. After the mixture was stirred at room temperature for another 1 h, aldehyde (0.25 mmol) was added. The resulting mixture was stirred for 16 h at room temperature. Then the reaction was quenched with aqueous HCl (5%) and the mixture was extracted with ether (6 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The residue was purified by flash col-

umn chromatography to give the product.

1,3-Diphenylprop-2-yn-1-ol[9b] Yield 99%, 92% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=11.6 min and t_{major}=21.1 min.

1-(2-Tolyl)-3-phenylprop-2-yn-1-ol Yield 99%, 90% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=9.3 min and t_{major}=21.1 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.45 (s, 3H), 2.58 (s, 1H), 5.78 (s, 1H), 7.17—7.29 (m, 6H), 7.42—7.45 (m, 2H), 7.69—7.70 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 19.1, 63.0, 86.6, 88.8, 122.7, 126.4, 126.7, 128.4, 128.6, 128.7, 130.9, 131.9, 136.2, 138.5.

1-(3-Tolyl)-3-phenylprop-2-yn-1-ol[9b] Yield 92%, 90% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=10.6 min and t_{major}=25.7 min.

1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-ol Yield 99%, 89% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=9.4 min and t_{major}=29.0 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.78 (s, 1H), 5.63 (s, 1H), 7.27—7.35 (m, 5H), 7.43—7.45 (m, 2H), 7.50—7.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 64.5, 87.1, 88.4, 122.3, 128.3, 128.5, 128.9, 131.1, 131.9, 134.3, 139.2.

1-(3-Anisyl)-3-phenylprop-2-yn-1-ol Yield 88%, 83% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=16.8 min and t_{major}=29.6 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.52 (s, 1H), 3.80 (s, 3H), 5.64 (s, 1H), 6.86—6.88 (m, 1H), 7.16—7.19 (m, 2H), 7.29—7.31 (m, 4H), 7.44—7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 55.5, 65.1, 86.7, 88.9, 112.3, 114.3, 119.2, 122.6, 128.5, 128.8, 129.9, 131.9, 142.4, 160.0.

1-(4-Anisyl)-3-phenylprop-2-yn-1-ol Yield 96%, 89% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=15.1 min and t_{major}=30.4 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.39 (s, 1H), 3.84 (s, 3H), 5.96 (s, 1H), 6.88—7.01 (m, 2H), 7.28—7.32 (m, 4H), 7.46—7.49 (m, 2H), 7.65—7.68 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 55.3, 60.7, 85.6, 88.8, 110.8, 120.6, 127.7, 128.1, 128.2, 129.5, 131.5, 156.5.

1-(2-Fluorophenyl)-3-phenylprop-2-yn-1-ol Yield 84%, 81% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=8.4 min and t_{major}=12.1 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.76 (s, 1H), 5.95 (s, 1H), 7.04—7.09 (m, 1H), 7.14—7.18 (m, 1H), 7.28—7.31 (m, 4H), 7.44—7.46 (m, 2H), 7.69—7.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 59.6, 86.7, 87.8, 115.8, 122.4, 124.5, 128.4, 128.6, 128.8, 130.3, 130.4, 131.9, 161.6.

1-(3-Fluorophenyl)-3-phenylprop-2-yn-1-ol Yield 99%, 88% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=9.2 min and t_{major}=27.3 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.621 (s, 1H), 5.67 (s, 1H), 7.00—7.02 (m, 1H), 7.29—7.36 (m, 6H), 7.45—7.47 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 64.6, 87.1, 88.3, 113.8, 114.0, 116.4, 115.6, 128.6, 129.0, 130.3, 132.0, 143.0, 164.0.

1-(4-Fluorophenyl)-3-phenylprop-2-yn-1-ol[9b] Yield 93%, 85% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=9.0 min and t_{major}=26.2 min.

1-(3-Trifluoromethylphenyl)-3-phenylprop-2-yn-1-ol Yield 75%, 84% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=7.6 min and t_{major}=36.7 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.70 (s, 1H), 5.73 (s, 1H), 7.23—7.35 (m, 3H), 7.45—7.51 (m, 3H), 7.58—7.60 (m, 1H), 7.77—7.79 (m, 1H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 64.6, 87.5, 88.1, 122.2, 123.7, 125.4, 128.6, 129.1, 129.3, 130.3, 131.0, 131.3, 132.0, 141.2.

1-(4-Trifluoromethylphenyl)-3-phenylprop-2-yn-1-ol Yield 99%, 88% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=8.4 min and t_{major}=42.0 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.56 (s, 1H), 5.74 (s, 1H), 7.25—7.37 (m, 3H), 7.45—7.47 (m, 2H), 7.64—7.74 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 64.6, 87.5, 88.1, 122.2, 125.8, 127.2, 128.6, 129.1, 132.0, 144.6.

1-(3,5-Dichlorophenyl)-3-phenylprop-2-yn-1-ol Yield 65%, 84% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=6.6 min and t_{major}=29.6 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.02 (s, 1H), 5.59 (s, 1H), 7.27—7.35 (m, 4H), 7.42—7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 63.9, 87.5, 87.6, 121.9, 125.3, 128.0, 128.6, 129.1, 132.0, 135.3, 143.9.

1-(1-Naphthyl)-3-phenylprop-2-yn-1-ol[9b] Yield 95%, 89% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=17.1 min and t_{major}=36.6 min.

1-Cyclohexyl-3-phenylprop-2-yn-1-ol[9b] Yield 84%, 54% *ee* determined by HPLC analysis (Chiralcel OD-H column, 10% IPA in hexane); retention time, t_{minor}=5.7 min and t_{major}=11.5 min.

Typical procedure for asymmetric additions of phenylacetylene to ketones

Under argon, chiral ligand (10 mol%, 0.025 mmol) was dissolved in dry hexane (1.0 mL) at room temperature and stirred for 10 min. Then, Et_2Zn (10 wt% in hexane, 0.9 mL) and phenylacetylene (54 μL, 0.5 mmol) were added by syringe. After the mixture was stirred at room temperature for another 1 h, the reaction temperature was decreased to 0 ℃. Ketone (0.25 mmol) was added and the resulting mixture was stirred for 48 h at 0 ℃. The reaction was quenched with aqueous HCl (5%) and the mixture was extracted with ether (6 mL×3). The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel [*V*(petroleum ether)/*V*(ethyl acetate)=18∶1] to give the product.

2,4-Diphenyl-but-3-yn-2-ol[7c] Yield 52%, 88% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=9.25 min and t_{major}=11.29 min.

2-(2-Naphthyl)-4-phenyl-but-3-yn-2-ol[9d] Yield 64%, 87% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=13.17 min and t_{major}=18.01 min.

4-Phenyl-2-(*m*-tolyl)-but-3-yn-2-ol Yield 90%, 87% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.18 min and t_{major}=9.58 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.11 (s, 3H), 2.58 (s, 3H), 3.69 (s, 1H), 7.30 (d, J=7.2 Hz, 1H), 7.45—7.51 (m, 4H), 7.69—7.81 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.5, 33.3, 70.3, 84.7, 92.9, 122.2, 122.7, 125.1, 125.7, 128.2, 128.3, 131.7, 137.7, 145.7.

2-(4-Tolyl)-4-phenyl-but-3-yn-2-ol Yield 64%, 85% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.13 min and t_{major}=10.75 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.84 (s, 3H), 2.34 (s, 3H), 2.68 (s, 1H), 7.16 (d, J=8.0 Hz, 2H), 7.28—7.30 (m, 3H), 7.45—7.46 (m, 2H), 7.51—7.61 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.2, 33.4, 70.4, 84.9, 92.8, 122.8, 125.1, 128.4, 128.6, 129.1, 131.9, 137.5, 143.0.

4-Phenyl-2-(4-biphenyl)-but-3-yn-2-ol Yield 31%, 90% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=15.38 min and t_{major}=26.49 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.91 (s, 3H), 2.54 (s, 1H), 7.32—7.35 (m, 4H), 7.42—7.51 (m, 4H), 7.59—7.62 (m, 4H), 7.79 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.5, 70.5, 85.2, 92.6, 120.8, 122.7, 125.7, 126.7, 127.3, 127.6, 128.5, 128.8, 129.0, 132.0, 140.9, 144.9.

2-(4-Chlorophenyl)-4-phenyl-but-3-yn-2-ol Yield 81%, 82% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.52 min and t_{major}=10.26 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.80 (s, 3H), 3.01 (s, 1H), 7.27—7.32 (m, 5H), 7.42—7.45 (m, 2H), 7.59—7.62 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.5, 70.1, 85.3, 92.1, 122.4, 126.4, 126.7, 128.5, 128.8, 131.9, 133.6, 144.4.

2-(3-Chlorophenyl)-4-phenyl-but-3-yn-2-ol[9d] Yield 82%, 81% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=9.15 min and t_{major}=11.21 min.

2-(4-Fluorophenyl)-4-phenyl-but-3-yn-2-ol Yield 70%, 84% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.67 min and t_{major}=10.60 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.81 (s, 3H), 3.20 (s, 1H), 6.97—7.01 (m, 2H), 7.26—7.29 (m, 3H), 7.42—7.44 (m, 2H), 7.63—7.67 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.6, 70.1, 85.3, 92.4, 115.0, 115.2, 122.5, 127.0, 128.5, 128.7, 131.8, 141.6, 161.1, 163.6.

2-(3-Fluorophenyl)-4-phenyl-but-3-yn-2-ol Yield 77%, 85% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.94 min and t_{major}=10.76 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.80 (s, 3H), 3.50 (s, 1H), 6.92—6.94 (m, 1H), 7.21—7.27 (m, 4H), 7.40—7.47 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.6, 70.2, 85.4, 92.3, 112.5, 112.8, 114.6, 114.8, 121.0, 122.6, 128.6, 128.9, 130.1, 130.2, 132.0, 148.7, 148.8, 161.8, 164.2.

2-(4-*tert*-Butylphenyl)-4-phenyl-but-3-yn-2-ol Yield 50%, 90% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=7.31 min and t_{major}=10.46 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.31 (s, 9H), 1.84 (s, 3H), 2.76 (s, 1H), 7.26—7.30 (m, 3H), 7.36—7.40 (m, 2H), 7.44—7.63 (m, 2H), 7.64 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 31.5, 33.5, 34.6, 70.3, 84.9, 92.9, 122.8, 124.9, 125.4, 128.4, 128.5, 131.9, 142.9, 150.7.

2-(2-Trifluoromethylphenyl)-4-phenyl-but-3-yn-2-ol Yield 81%, 79% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.64 min and t_{major}=10.17 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.82 (s, 3H), 3.53 (s, 1H), 7.25—7.30 (m, 3H), 7.41—7.44 (m, 2H), 7.55 (d, J=8.0 Hz, 2H), 7.78 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.6, 70.3, 85.6, 91.9, 122.3, 125.4, 125.5, 125.7, 128.5, 128.9, 130.0 (q, J_{CF}=32 Hz), 131.9, 149.7.

2-(3-Trifluoromethylphenyl)-4-phenyl-but-3-yn-2-ol Yield 72%, 77% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.23 min and t_{major}=10.27 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.84 (s, 3H), 3.28 (s, 1H), 7.26—7.29 (m, 3H), 7.41—7.44 (m, 2H), 7.51 (d, J=8.0 Hz, 1H), 7.87 (d, J=8.0 Hz, 1H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.6, 70.3, 85.7, 91.8, 122.1, 122.1, 122.3, 124.7, 124.7, 128.5, 128.8, 128.9, 129.0, 130.7 (q, J_{CF}=32 Hz), 131.9, 146.9.

2-(4-Trifluoromethylphenyl)-4-phenyl-but-3-yn-2-ol Yield 48%, 75% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=8.11 min and t_{major}=9.48 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.84 (s, 3H), 3.02 (s, 1H), 7.27—7.33 (m, 3H), 7.43—7.46 (m, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.6, 70.3, 85.6, 91.8, 122.3, 123.0, 125.5, 125.7, 128.6, 129.0, 129.8 (q, J_{CF}=32 Hz), 131.9, 149.7.

2-(4-Phenoxyphenyl)-4-phenyl-but-3-yn-2-ol Yield 43%, 81% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=23.42 min and t_{major}=31.27 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.86 (s, 3H), 2.69 (s, 1H), 6.98—7.09 (m, 5H), 7.29—7.34 (m, 5H), 7.45—7.47 (m, 2H), 7.67 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.5, 70.2, 85.1, 92.6, 118.6, 119.2, 122.7, 123.6, 126.8, 127.8, 128.5, 128.7, 130.0, 131.9, 140.6, 157.0.

2-[4-(4-Anisyl)-phenyl]-4-phenyl-but-3-yn-2-ol Yield 36%, 88% *ee* determined by HPLC analysis (Chiralcel OD-H column, 15% IPA in hexane); reten-

tion time, t_{minor}=8.16 min and t_{major}=17.15 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.89 (s, 3H), 2.70 (s, 1H), 3.82 (s, 3H), 6.96 (d, J=8.8 Hz, 2H), 7.30—7.32 (m, 3H), 7.47—7.56 (m, 6H), 7.55 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 33.4, 55.5, 70.4, 85.1, 92.7, 114.4, 120.5, 125.7, 126.7, 126.8, 128.3, 128.5, 128.7, 131.9, 133.4, 140.4, 144.2, 159.4.

2-Cyclopropyl-4-phenyl-but-3-yn-2-ol Yield 69%, 8% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=7.02 min and t_{major}=9.48 min. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.45—0.56 (m, 3H), 0.66—0.68 (m, 1H), 1.20—1.23 (m, 1H), 1.61 (s, 3H), 3.46 (s, 1H), 7.32—7.34 (m, 3H), 7.37—7.39 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 1.7, 1.8, 22.1, 30.0, 68.7, 82.6, 92.0, 123.2, 128.3, 128.6, 131.6.

3,4,4-Trimethyl-1-phenyl-pent-1-yn-3-ol[9d] Yield 23%, 3% *ee* determined by HPLC analysis (Chiralcel OD-H column, 5% IPA in hexane); retention time, t_{minor}=5.32 min and t_{major}=8.47 min.

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