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Zinc-Salen-Catalyzed Asymmetric Alkynylation of Alkyl Acylsilanes

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Abstract: Optically active tertiary propargylic alcohols are useful and versatile building blocks in organic synthesis, and their direct access by enantioselective addition of alkyne nucleophiles to ketones has achieved significant progress over the last ten years. In view of the potential applications of acylsilanes as useful synthetic equivalents of aldehydes, we described a general catalytic enantioselective addition of terminal alkynes to alkyl acylsilanes. After reaction optimization involving variation of solvent, temperature, catalyst ratio and various catalysts screen, the *in situ* generated Zn-salen complex was chosen as catalyst. With hexane as solvent, the silylated tertiary propargylic alcohols were obtained in satisfactory yields and *ee*s for both aliphatic and aromatic alkynes.

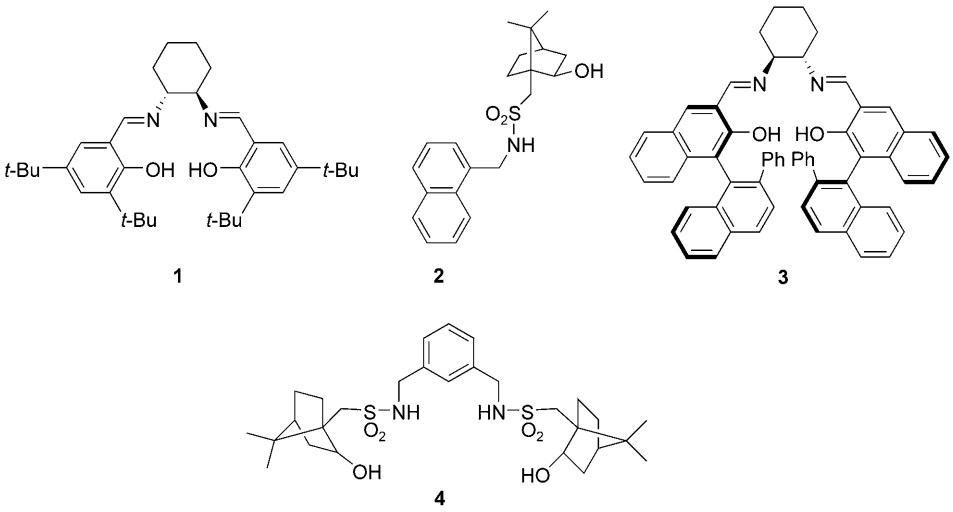
Keywords: acylsilanes; alkynylation; asymmetric catalysis; quaternary stereocenters; salen ligands; silylated propargylic alcohols

Introduction

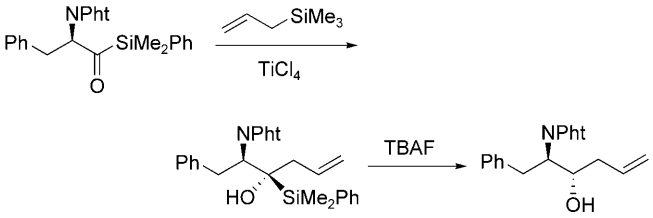
Optically active tertiary propargyl alcohols are versatile building blocks for the syntheses of pharmaceuticals and natural products.[1] A direct access to these chiral compounds is the asymmetric alkynylation of ketones, either using preactivated metal acetylides (such as zinc and silyl acetylides) as nucleophiles,[2] or in the presence of chiral Brønsted base catalysts.[3]

During the past five years, significant improvements have been made in the asymmetric alkynylation of ketones, especially with mild organozinc reagents.[4] Tan and co-workers reported the stoichiometric addition of an *in situ* prepared alkynylzinc to some highly activated ketones with up to 98% *ee* for the synthesis of efavirenz.[5,6] Cozzi realized the first general catalytic enantioselective addition of terminal alkynes to unactivated ketones with the zinc-salen **1** complex as catalyst (Scheme 1). This protocol was proven to be more effective with aliphatic ketones.[7] Nearly at the same time, Chan et al. also reported that a combination of camphorsulfonamide **2** and $Cu(OTf)_2$ promoted the enantioselective addition of an alkynylzinc to aromatic ketones in high yield and up to 97% *ee*.[8] Subsequently Katsuki et al. demonstrated that salen ligand **3** could serve as a quite efficient catalyst for the asymmetric alkynylation of aliphatic ketones (up to 93% *ee*).[9] Wang and co-workers have developed several practical enantioselective additions of phenylacetylene to aromatic ketones with various chiral ligands such as BINOL,[10] *Cinchona* alkaloids,[11] oxazolidines,[12] bis-sulfonamide diols[13] and Schiff bases.[14] In particular, for aliphatic ketones, the bis-sulfonamide diol **4** effectively provided the desired products with high enantioselectivities (91–94% *ee*).

Among the carbonyl derivatives, acylsilanes are very useful substrates,[15,16] which are known to be the synthetic equivalents of aldehydes due to the possibility of a stereospecific desilylation with fluoride ion, especially in the case of chemically and configurationally unstable substrates such as α-amino aldehydes (Scheme 2).[17,18] From a synthetic standpoint, it is highly desirable to develop an efficient approach to enantiomerically pure silylated tertiary propargylic alcohols.[19] Although several catalytic asymmetric reactions using acylsilanes have been developed,[20,21] to the best of our knowledge, the enantioselective alkynylation of acylsilanes has not been reported so far.[22] Herein we describe for the first time the direct catalytic alkynylation of alkyl acylsilane with both aliphatic and aromatic alkynes. Using the *in situ* generated Zn-salen complex as catalyst, optically active silylated propargylic alcohols were obtained in good yields and high enantioselectivities.



Scheme 1. Various efficient ligands for the asymmetric alkynylation of aliphatic ketones.



Scheme 2. Acylsilane as stable synthetic equivalent of α-amino aldehyde.

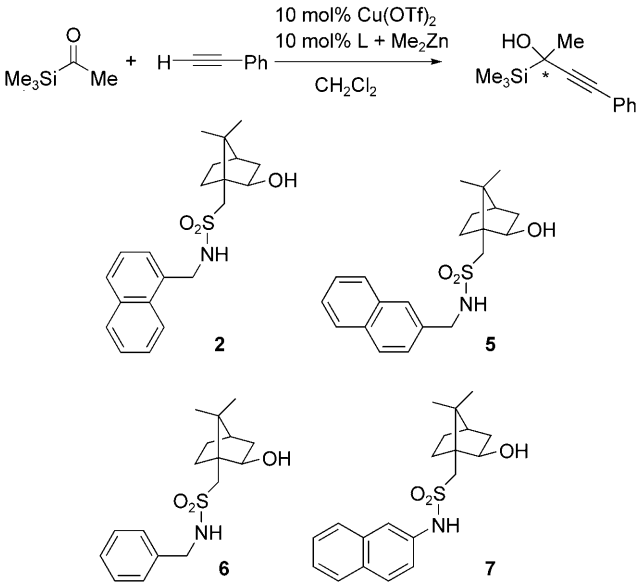
Results and Discussion

Preliminary studies were carried out with the model reaction of acetyltrimethylsilane and phenylacetylene. As camphorsulfonamides have been proved to be an efficient catalyst for the production of chiral tertiary propargylic alcohols,[8] firstly we chose a series of camphorsulfonamides to catalyze the asymmetric alkynylation of alkyl acylsilane (Table 1) under the optimal conditions described in our previous work.[8]

To our surprise, in the presence of Me_2Zn, $Cu(OTf)_2$ and camphorsulfonamide, the reaction gave moderate to good yields but poor enantioselectivity (less than 30%), which was quite different from the excellent behavior of other aliphatic ketones, for example, 88% *ee* for 3-methyl-2-butanone.[8] We attributed this to the influence of the SiR_3 moiety, which compared with the CR_3 moiety, is more electron-releasing, and thereby partially neutralizes and stabilizes more the positive charge at the carbonyl carbon atom, making the reaction less favorable.

Since the bifunctional catalyst Zn(salen) has been proved more effective for the enantioselective alkynylation of aliphatic ketones than for aromatic ketones,[7] using 20 mol% salen (*R,R*)-**1** and 3 equiv. of zinc phenylacetylide, we studied the asymmetric alkynylation of acylsilane at room temperature. Compared with the camphorsulfonamide catalyst, the salen system showed significant improvements

Table 1. Asymmetric addition of phenylacetylene to acetyltrimethylsilane catalyzed by camphorsulfonamides.[a]



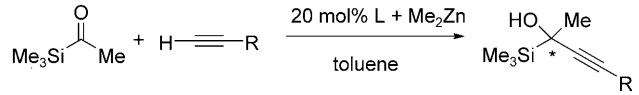
Entry	Ligand	Yield [%][b]	*ee* [%][c]
1	**2**	82	18
2	**5**	45	23
3	**6**	42	2
4	**7**	59	27

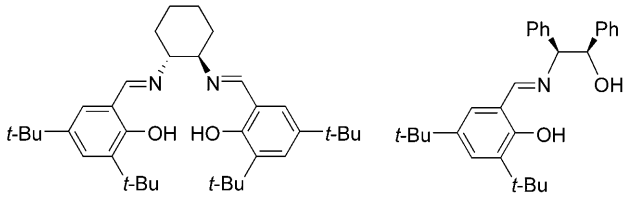
[a] Acylsilane:alkyne:Me_2Zn:$Cu(OTf)_2$:ligand = 0.4:1.2:1.2:0.04:0.04. All reactions were carried out in CH_2Cl_2, 0 °C for 2 days.

[b] Isolated yield.

[c] The enantiomeric excess was determined by HPLC analysis using a Chiralcel OD-H column.

Table 2. Enantioselective alkynylation of acetyltrimethylsilane catalyzed by Me_2Zn and salen ligand.[a]





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Entry	Ligand	Alkyne	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	(*R,R*)-**1**	H—≡—Ph	r.t.	79	58
2	(*R,R*)-**1**	H—≡—Ph	0	66	63
3	(*R,R*)-**1**	H—≡—C$_6$H$_4$—OMe	r.t.	89	59
4	(*R,R*)-**1**	H—≡—C$_6$H$_4$—OMe	0	82	55
5[d]	(1*R*,2*S*)-**8**	H—≡—C$_6$H$_4$—OMe	r.t.	66	1
6	(*R,R*)-**1**	H—≡—cyclohexenyl	r.t.	90	47

[a] Acylsilane:alkyne:Me_2Zn:ligand = 0.4:1.2:1.2:0.08. All reactions were carried out in toluene for 2 days.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] 10 mol% (1*R*,2*S*)-**8** was used.

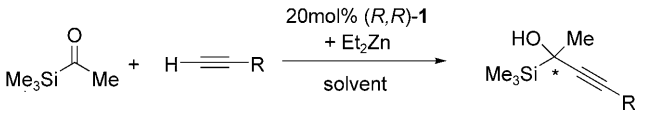
(Table 2), the reaction was completed in two days to afford the silylated tertiary propargylic alcohol in 79% yield, but with moderate enantiomeric excess (58% *ee* for acetyltrimethylsilane, entry 1). The use of low temperature (0 °C) slowed down the reaction considerably, but only a slight increase in *ee* (63% *ee*, entry 2) was observed.

Electron-rich aromatic terminal alkynes such as *p*-methoxyphenylacetylene displayed higher nucleophilic reactivity than unsubstituted phenylacetylene, hence afforded higher conversion but with comparable or a bit lower *ee* (entries 3 and 4). We also tried the asymmetric alkynylation of acylsilane with the chiral Schiff base amino alcohol (1*R*,2*S*)-**8**, but racemic product was obtained (entry 5). Again the commercially available compound (*R,R*)-**1** appeared more suitable for this reaction as in the case of many other metal-salen promoted reactions.[7]

For possible further transformations of the alkene group, such as epoxidation, hydroxylation and ozonolysis, the asymmetric addition of 1-ethynylcyclohexene[14c] to acylsilane should have more potential applications for the synthesis of complex bioactive natural products. We also carried out the catalytic asymmetric addition of 1-ethynylcyclohexene to acylsilane, and observed high yield and moderate enantioselectivity (entry 6).

The replacement of dimethylzinc by diethylzinc afforded a higher reactive alkynylzinc, and hence shorted the reaction time to one day for both aliphatic and aromatic alkynes. Here 1-ethynylhexene and phenylacetylene were chosen as the representatives of aliphatic alkynes and aromatic alkynes, respectively, all the conditions influencing the reaction are summarized in Table 3.

Table 3. Enantioselective alkynylation of acetyltrimethylsilane catalyzed by Et_2Zn and salen ligands.[a]



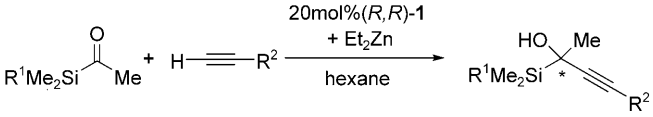
Entry	Alkyne	Solvent	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	H—≡—cyclohexenyl	hexane	r.t.	78	72
2	H—≡—cyclohexenyl	hexane	0	82	76
3	H—≡—cyclohexenyl	hexane	−20	62	69
4	H—≡—cyclohexenyl	CH_2Cl_2	r.t.	89	72
5	H—≡—cyclohexenyl	CH_2Cl_2	0	76	38
6	H—≡—cyclohexenyl	toluene	r.t.	92	65
7[d]	H—≡—cyclohexenyl	toluene	r.t.	90	47
8	H—≡—Ph	toluene	0	82	78
9[d]	H—≡—Ph	toluene	0	66	63
10	H—≡—Ph	hexane	0	81	86
11[e]	H—≡—Ph	hexane	0	79	81

[a] Acylsilane:alkyne:Et_2Zn:ligand = 0.4:1.2:1.2:0.08. All reactions were carried out for 1 day.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] Me_2Zn was used and the reaction time was 2 days.
[e] 10 mol% (*R,R*)-**1** was used.

When varying reaction parameters such as solvent, temperature, and the quantity of salen ligand, we found that the solvent strongly influenced the result of the reaction. Hexane was found to be the best solvent for both aliphatic alkynes and aromatic alkynes. The reaction in CH_2Cl_2 was quite sensitive to temperature, low temperature significantly decreased the *ee* values (entry 4 versus 5). Reducing the amount of ligand from 20 mol% to 10 mol% showed a slight drop in the enantiomeric excess (entry 10 versus 11).

Under the optimal reaction conditions (Table 3 entry 10), ligand (*R,R*)-**1** was employed to catalyze

Table 4. Asymmetric addition of various alkynes to acetyltrimethylsilane and acetyldimethylphenylsilane.[a]

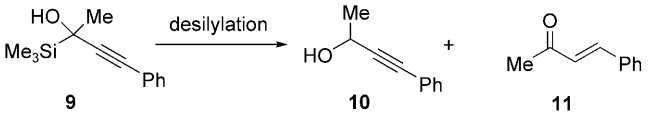


Entry	R^1	Alkynes	Yield [%][b]	*ee* [%][c]
1	Me	H—≡—Ph	81	86
2	Ph	H—≡—Ph	72	88
3	Me	H—≡—C6H4—OMe	88	86
4	Me	H—≡—C6H4—Br	88	83
5	Me	H—≡—cyclohexenyl	82	76
6	Me	H—≡—CH2CH2CH2CH3	74	72
7	Me	H—≡—$SiMe_3$	78	76

[a] Acylsilane:alkyne:Et_2Zn:ligand = 0.4:1.2:1.2:0.08. All reactions were carried out in hexane, 0 °C for 1 day.
[b] Isolated yield.
[c] Determined by HPLC analysis.

the asymmetric addition of various alkynes to acylsilanes. For both aromatic and aliphatic alkynes, chiral silylated tertiary propargylic alcohols were generated in 72–88% *ee* (Table 4 entries 1–7). Aromatic alkynes exhibited better yields and *ee* values than aliphatic alkynes (entries 1–4 versus 5–7). Electron-rich alkynes such as *para*-methoxyphenylacetylene showed comparable *ee* with phenylacetylene (entry 1 versus 3), but higher *ee* than electron-deficient alkynes such as *para*-bromophenylacetylene (entry 1 versus 4). Better enantioselectivity was achieved with acetyldimethylphenylsilane as substrate (entry 2), this could be explained by the large steric hindrance of the Me_2PhSi moiety, which favored the stereoselective addition to afford high selectivity but a slightly lower yield. Good enantioselectivity could also be obtained for silyl-substituted aliphatic alkynes such as trimethylsilylacetylene (entry 7).

The replacement of the silyl group with a proton was also investigated. Treatment of 2-(trimethylsilyl)-4-phenyl-3-butyn-2-ol **9** with TBAF in THF (Scheme 3) led to 4-phenyl-2-buten-2-one **11** in complete conversion rather than the expected desilylated propargylic alcohol **10**, which can be rationalized in terms of a facial Brook rearrangement, occurring in the initial intermediate formed by attack of the fluoride ion on the silicon atom, followed by isomerization. We have also tested other reagents such as CsF, K_2CO_3 and got similar results. To our delight, in the presence of NaOMe, 16% desilylated product was obtained albeit 82% product was rearranged. Further study revealed that KF can catalyze the reaction with



with TBAF, CsF, K_2CO_3, 100% **11** was obtained.
with NaOMe, 16% **10** and 82% **11** were obtained.
with KF, 42% **10** was obtained without other side product.

Scheme 3. Disilylation of 2-(trimethylsilyl)-4-phenyl-3-butyn-2-ol **9**.

solely desilylated product, although product racemization was observed.

Other desilylation approaches such as protecting the hydroxy group prior to desilylation to avoid the possible rearrangement, and changing the $SiMe_3$ group to $SiMe_2Ph$ or $SiMe_2(t\text{-Bu})$, which is more stable towards the desilylation and rearrangement reaction for its large steric hindrance and electronic influences, may help to retain the configuration during the desilylation. Related work is still being carried out in our laboratory.

Conclusions

In summary, a highly efficient catalytic enantioselective addition of terminal alkynes to alkyl acylsilanes is described. In the presence of Zn-salen complex, the expected silylated tertiary propargylic alcohols were obtained in satisfactory yields and *ee*s for both aliphatic and aromatic alkynes, thus proving the generality of the method. Further studies focusing on the uses of homochiral α-alkoxy and α-amino acylsilanes to synthesize polyfunctionalized propargylic alcohols as versatile intermediates for the stereoselective synthesis of biologically active compounds are underway.

Experimental Section

General Information

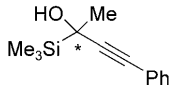
All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ^1H NMR spectra were recorded on a Varian (300 MHz) or a Bruker (400 MHz) spectrometer and the spectra were referenced internally to the residual proton resonance in $CDCl_3$ ($\delta = 7.26$ ppm), or with tetramethylsilane (TMS, $\delta = 0.00$ ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. ^{13}C NMR spectra were recorded on a Varian (300 MHz) or a Bruker (400 MHz) spectrometer with com-

plete proton decoupling, and chemical shifts are reported in ppm from TMS with the solvent as the internal reference ($CDCl_3$, $\delta = 77.0$ ppm). HPLC analyses were conducted on a Shimadzu 10 A or Agilent 1200 instrument using Daicel columns (0.46 cm diameter × 25 cm length). The reactions were carried out in solvents distilled from standard drying agents. All alkynes and ketones were freshly distilled under normal or reduced pressure before use. Ligand (*R,R*)-**1** was synthesized according to the procedure of Jacobsen and co-workers.[23] Acetyldimethylphenylsilane was synthesized according to the procedure of Scheidt and co-workers.[24]

General Procedure for Asymmetric Addition of Alkynes to Ketones

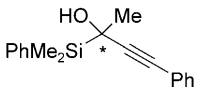
Phenylacetylene (132 μL, 1.2 mmol) and a 1.0 M solution of diethylzinc in hexane (1.2 mL, 1.2 mmol) were added to a dry flask with a hexane solution (1.0 mL) of (*R,R*)-**1** ligand (44 mg, 0.08 mmol). The mixture was stirred at room temperature for 1 hour. Then the flask was put into a 0 °C cold bath with continuous stirring for 1 hour. Acetyltrimethylsilane (58 μL, 0.4 mmol) was sequentially added to the flask *via* syringe. The resulting solution was allowed to stir at 0 °C for 24 h. The mixture was then quenched with 1.0 mL saturated NH_4Cl solution, extracted with ether (3 × 3 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The corresponding propargylic alcohol was purified *via* flash chromatography (silica gel) using 2% ethyl acetate in petroleum ether as eluent. The enantiomeric excess of the product was determined by HPLC analysis on a Daicel Chiralcel OD-H column.

(+)-2-(Trimethylsilyl)-4-phenyl-3-butyn-2-ol



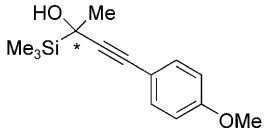
81% yield isolated after 24 h reaction. 86% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 10:90, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 8.0 and t(minor) = 9.7 min; $[\alpha]_D^{25}$: + 48.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.30$–7.27 (m, 2H), 7.18–7.16 (m, 3H), 1.46 (s, 3H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 131.3$, 128.1, 127.8, 123.2, 93.2, 86.3, 61.3, 25.5, −4.3.

(+)-2-(Dimethyl(phenyl)silyl)-4-phenyl-3-butyn-2-ol



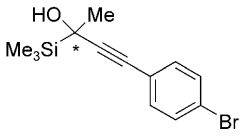
72% yield isolated after 24 h reaction. 88% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 5:95, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 11.0 and t(minor) = 13.9 min; $[\alpha]_D^{25}$: +17.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$,): $\delta =$ 7.61–7.58 (m, 2H), 7.30–7.27 (m, 4H), 7.20–7.18 (m, 4H), 1.44 (s, 3H), 0.42 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 134.6, 131.3, 129.6, 128.1, 127.9, 127.7, 123.2, 93.2, 86.8, 61.3, 25.6, −5.8, −6.0.

(+)-4-(4-Methoxyphenyl)-2-(trimethylsilyl)-3-butyn-2-ol



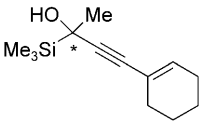
88% yield isolated after 24 h reaction. 86% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 10:90, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 8.8 and t(minor) = 12.2 min; $[\alpha]_D^{25}$: +45.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.21$–7.17 (m, 2H), 6.70–6.65 (m, 3H), 3.63 (s, 3H), 1.42 (s, 3H), 0.08 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.0$, 132.7, 115.3, 113.6, 91.7, 85.9, 61.1, 55.1, 25.4, −4.4.

(+)-4-(4-Bromophenyl)-2-(trimethylsilyl)-3-butyn-2-ol



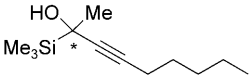
88% yield isolated after 24 h reaction, 83% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 5:95, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 8.4 and t(minor) = 9.1 min; $[\alpha]_D^{25}$: +40.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.32 (m, 2H), 7.16–7.14 (m, 2H), 1.45 (s, 3H), 0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 134.3$, 132.9, 132.0, 122.2, 122.0, 94.4, 85.3, 61.5, 25.3, −4.5.

(+)-4-Cyclohexenyl-2-(trimethylsilyl)-3-butyn-2-ol



82% yield isolated after 24 h reaction. 76% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 2:98, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 8.8 and t(minor) = 9.3 min; $[\alpha]_D^{25}$: +33.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 5.96$–5.93 (m, 1H), 2.02–1.99 (m, 4H), 1.57–1.49 (m, 4H), 1.38 (s, 3H), 0.06 (s, 9H) ; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 133.9$, 120.5, 90.4, 88.0, 61.2, 29.5, 25.6, 22.4, 21.6, −4.4.

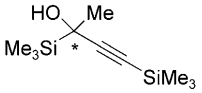
(+)-2-(Trimethylsilyl)-3-nonyn-2-ol



74% yield isolated after 24 h reaction. 72% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 1:99, 208 nm, 0.5 mL min^{-1}). Retention time: t(major) = 9.7 and t(minor) = 10.4 min; $[\alpha]_D^{25}$: +15.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.17$–2.12 (t, $J = 6.88$ Hz, 2H), 1.47–1.40 (m, 2H), 1.35 (s, 3H), 1.32–1.27 (m, 2H), 1.24–1.18 (m, 2H), 0.85–0.80 (t, $J = 6.84$ Hz,

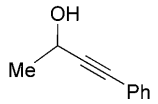
3H), 0.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 86.8$, 84.0, 61.2, 31.1, 28.8, 25.9, 22.3, 19.0, 14.1, −4.4.

(+)-2,4-Bis(trimethylsilyl)-3-butyn-2-ol



78% yield isolated after 24 h reaction, 76% *ee* determined by HPLC analysis (Daicel Chiralcel OD-H column, IPA:hexane = 2: 98, 254 nm, 0.5 mL min^{-1}). Retention time: t(major) = 7.5 and t(minor) = 7.9 min; $[\alpha]_D^{25}$: +18.0 (*c* 1.00 g/100 mL, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.38$ (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 110.3$, 90.4, 61.6, 25.2, 0.0, −4.7.

4-Phenyl-3-butyn-2-ol



Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.44$–7.41 (m, 2H), 7.32–7.30 (m, 3H), 4.76 (q, 1H, $J = 6.5$ Hz), 1.56 (d, 3H, $J = 6.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 131.6$, 128.4, 128.3, 122.6, 90.9, 84.0, 58.9, 24.4

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