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Desilylation-Activated Propargylic Transformation: Enantioselective Copper-Catalyzed [3+2] Cycloaddition of Propargylic Esters with β-Naphthol or Phenol Derivatives

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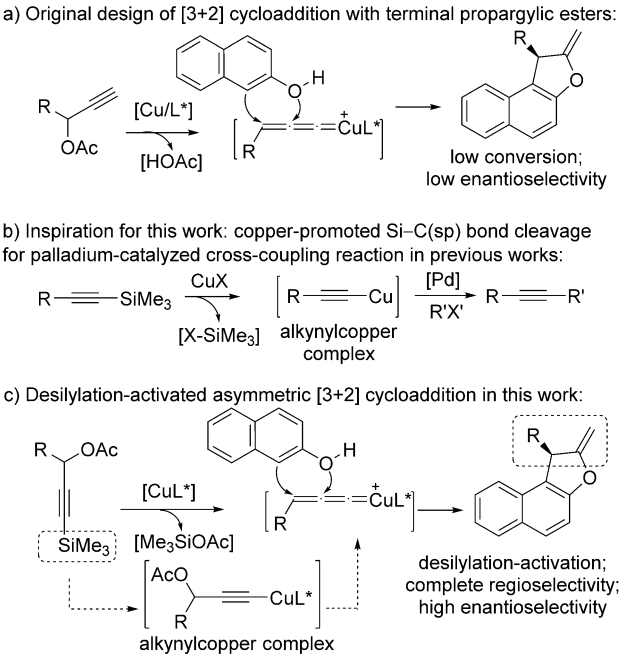
Abstract: *A copper-catalyzed asymmetric [3+2] cycloaddition of 3-trimethylsilylpropargylic esters with either β-naphthols or electron-rich phenols has been realized and proceeds by a desilylation-activated process. Under the catalysis of Cu(OAc)$_2$·H$_2$O in combination with a structurally optimized ketimine P,N,N-ligand, a wide range of optically active 1,2-dihydronaphtho[2,1-b]furans or 2,3-dihydrobenzofurans were obtained in good yields and with high enantioselectivities (up to 96% ee). This represents the first desilylation-activated catalytic asymmetric propargylic transformation.*

Catalytic asymmetric propargylic transformations of terminal propargylic compounds with nucleophiles, transformations featuring metal allenylidene complexes as the key intermediates, have attracted much attention because of its high potential in the enantioselective formation of C–C and C–heteroatom bonds.[1–4] Very recently, we disclosed the first copper-catalyzed asymmetric formal [3+2] cycloaddition of propargylic esters as C$_2$ synthons with C,O-bis(nucleophile)s, β-ketoesters, by a sequential propargylic alkylation/intramolecular hydroalkoxylation process.[5] However, the use of other bis(nucleophile)s for this cycloaddition remains unexplored.[6] Considering the successful application of β-naphthols as C,O-bis(nucleophile)s in the ruthenium-catalyzed [3+3] cycloaddition with propargylic alcohols as C$_3$ synthons,[7] we envisioned that β-naphthols should also be suitable C,O-bis(nucleophile)s for a copper-catalyzed [3+2] cycloaddition, thus generating a chiral dihydronaphthofuran skeleton which possesses important biological activity.[8] The stereoselective construction of such molecules remains a challenge.[9] Our initial studies disclosed that the target [3+2] annulation with terminal propargylic esters really took place, but proceeded in low conversions and enantioselectivities (Scheme 1a). Insufficient ability of terminal propargylic esters towards the active copper allenylidene complexes and the weak nucleophility of β-naphthols may be responsible for this poor result. The development of an alternative strategy for more efficient formation of the copper allenylidene complexes is therefore anticipated. In the past decades, a copper-promoted Si–C(sp) bond cleavage of the alkynylsilane, to form an alkynylcopper species for the palladium-catalyzed Sonogashira cross-coupling reaction, was developed (Scheme 1b).[10] We envisaged that this desilylation-activated strategy should also provide a powerful solution for this copper-catalyzed cycloaddition because a similar alkynylcopper complex needs to be generated for the key copper allenylidene complex (Scheme 1c).[3e] 3-Trimethylsilylpropargylic compounds have been applied in many catalytic reactions recently,[11] however, a catalytic asymmetric transformation via metal allenylidene complexes generated by the desilylation of 3-trimethylsilylpropargylic substrates has never been observed. Herein we report the first desilylation-activated copper-catalyzed asymmetric [3+2] cycloaddition of 3-trimethylsilylpropargylic acetates with either β-naphthols or electron-rich phenols, which provides a new and facile access to either chiral 1,2-dihydronaphtho- or benzofurans, respectively, in a highly enantioenriched form.



Scheme 1. Desilylation-activated strategy for copper-catalyzed asymmetric [3+2] cycloaddition.

To ascertain the viability of the desilylation-activated strategy in the catalytic asymmetric propargylic transforma-

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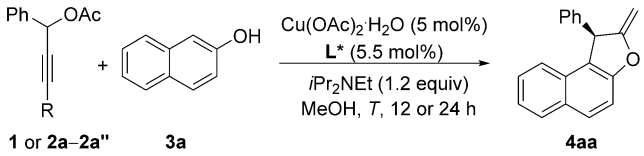
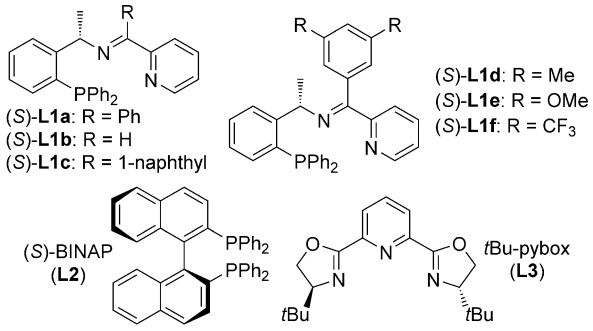
Table 1: Reaction screening.[a]



1 or 2a–2a'' 3a 4aa

Entry	L*	Substrate	T [°C]	Yield [%][b]	ee [%][c]
1	L1a	1: R = H	RT	32	42
2	L2	1: R = H	RT	23	8
3	L3	1: R = H	RT	31	6
4	L1a	2a: R = $SiMe_3$	RT	98	76
5	L1a	2a′: R = $SiEt_3$	RT	74	78
6	L1a	2a″: R = Si*t*BuMe$_2$	RT	–	–
7	L1a	2a: R = $SiMe_3$	−40	86	90
8	L1b	2a: R = $SiMe_3$	−40	77	74
9	L1c	2a: R = $SiMe_3$	−40	71	89
10	L1d	2a: R = $SiMe_3$	−40	87	89
11	L1e	2a: R = $SiMe_3$	−40	83	87
12	L1f	2a: R = $SiMe_3$	−40	92	93

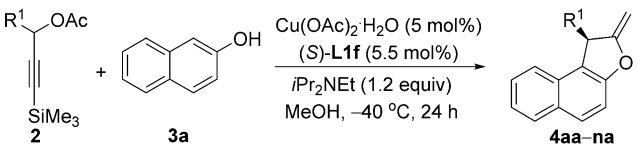
[a] Reaction conditions: **1** or **2a–a″** (0.3 mmol), **3a** (0.36 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.015 mmol, 5 mol%), **L*** (0.0165 mmol, 5.5 mol%), and *i*Pr_2NEt (0.36 mmol, 1.2 equiv) in 3 mL of MeOH for either 12 h at RT or 24 h at −40°C. [b] Yield of isolated product. [c] Determined by chiral-phase HPLC.



tion, 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl acetate (**2a**) was submitted to the reaction with β-naphthol (**3a**). Compared with the terminal alkyne **1**, as shown in Table 1, the target cycloaddition with **2a** in the presence of (*S*)-**L1a** proceeded smoothly, and exclusively gave the cycloadduct **4aa** in nearly quantitative yield and with a significantly improved enantioselectivity of 76% *ee* (entry 4). The sterically hindered (*S*)-**L1a**, recently developed by us,[3l] has been demonstrated to be highly efficient in many copper-catalyzed asymmetric propargylic transformations.[3m–n,r–u,5] 3-Triethylsilyl-propargylic acetate (**2a′**) also performed well (entry 5), however, **2a″**, bearing a *tert*-butyldimethylsilyl group, inhibited the cycloaddition, presumably because of the steric hindrance (entry 6). Lowering the reaction temperature to −40°C greatly improved the enantioselectivity without a significant loss on the yield (entry 7). A further optimization of the P,N,N-ligand structure disclosed that the introduction of a CF_3-group into the 3,5-positions of the phenyl ring in the ketimine moiety [(S)-**L1f**)] led to a substantial increase of not only the yield but also enantioselectivity (entry 12).

With optimized reaction conditions in hand, the substrate scope of the 3-(trimethylsilyl)prop-2-yn-1-yl acetates **2** was

Table 2: Scope with respect to propargylic acetates.[a]



2 3a 4aa–na

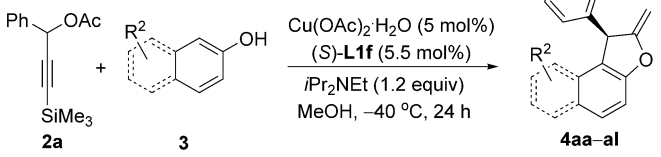
Entry	Substrate (**2**)	Product (**4**)	Yield [%][b]	ee [%][c]
1	**2a**: R^1 = Ph	**4aa**	92 (88)[d]	93 (−93)[d]
2	**2b**: R^1 = 4-$MeOC_6H_4$	**4ba**	88	93
3	**2c**: R^1 = 4-MeC_6H_4	**4ca**	90	93
4	**2d**: R^1 = 4-$CF_3C_6H_4$	**4da**	81	91
5	**2e**: R^1 = 4-FC_6H_4	**4ea**	86	91
6	**2f**: R^1 = 4-ClC_6H_4	**4fa**	86	90
7	**2g**: R^1 = 3-ClC_6H_4	**4ga**	89	94
8	**2h**: R^1 = 2-ClC_6H_4	**4ha**	76	73
9	**2i**: R^1 = 2-naphthyl	**4ia**	88	93
10	**2j**: R^1 = 2-furyl	**4ja**	98	92
11[e]	**2k**: R^1 = $PhCH_2$	**4ka**	49	89
12[e]	**2l**: R^1 = Me	**4la**	54	72
13[e]	**2m**: R^1 = Et	**4ma**	52	91
14[e]	**2n**: R^1 = cyclohexyl	**4na**	48	88

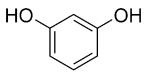
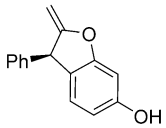
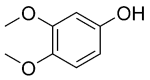
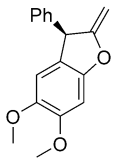
[a] Reaction conditions: **2** (0.3 mmol), **3a** (0.36 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.015 mmol, 5 mol%), (*S*)-**L1f** (0.0165 mmol, 5.5 mol%), and *i*Pr_2NEt (0.36 mmol, 1.2 equiv) in 3 mL of MeOH at −40°C for 24 h, unless otherwise noted. [b] Yield of the isolated product. [c] Determined by chiral-phase HPLC. [d] The data within parentheses were obtained with (*R*)-**L1f**. [e] The reaction was performed at 0°C for 12 h.

first examined, and the results are summarized in Table 2. With (*R*)-**L1f** as the ligand, similar performance was achieved (entry 1). The electronic properties of the substituent at the *para* position of the phenyl ring had little influence on the reactivity and enantioselectivity. Thus, the cyclization of **2b–f** with **3a** proceeded smoothly to give the cycloadducts in good yields (81–90%) and with high enantioselectivities (90–93% *ee*; entries 2–6). However, the reaction was sensitive to the substitution pattern on the phenyl ring. Thus, compared with the 4-chloro substrate **2f**, **2h** with a 2-chloro group led to a significant decrease in the yield and enantioselectivity, while **2g** bearing a 3-chloro group gave a slightly increased yield and enantioselectivity (89% yield and 94% *ee*; entries 6–8). The 2-naphthyl-substituted substrate **2i** was a suitable reaction partner, thus giving the cycloadduct **4ia** in 88% yield and with 93% *ee* (entry 9). The heterocyclic substrate **2j** served well for the cycloaddition, thus producing **4ja** in 98% yield and with 92% *ee* (entry 10). Aliphatic substrates **2k–n** also worked in this cycloaddition, albeit with a lower reaction rate, thus giving rise to the cycloadducts in moderate to high enantioselectivities (72–91% *ee*) with reduced yields (entries 11–14).

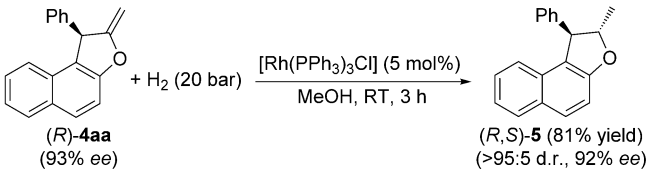
The scope with regard to β-naphthols was also evaluated, and the results are summarized in Table 3. The reaction tolerated both electron-donating and electron-withdrawing groups on the naphthyl skeleton regardless of their substitution patterns (entries 2–10). In all cases, high yields and good to excellent enantioselectivities were achieved. More importantly, the electron-rich phenols **3k** and **3l** were also suitable for this cycloaddition, thus giving the corresponding cycloadducts **4ak** and **4al**, respectively, in good results (entries 11

Table 3: Scope with respect to β-naphthols.[a]

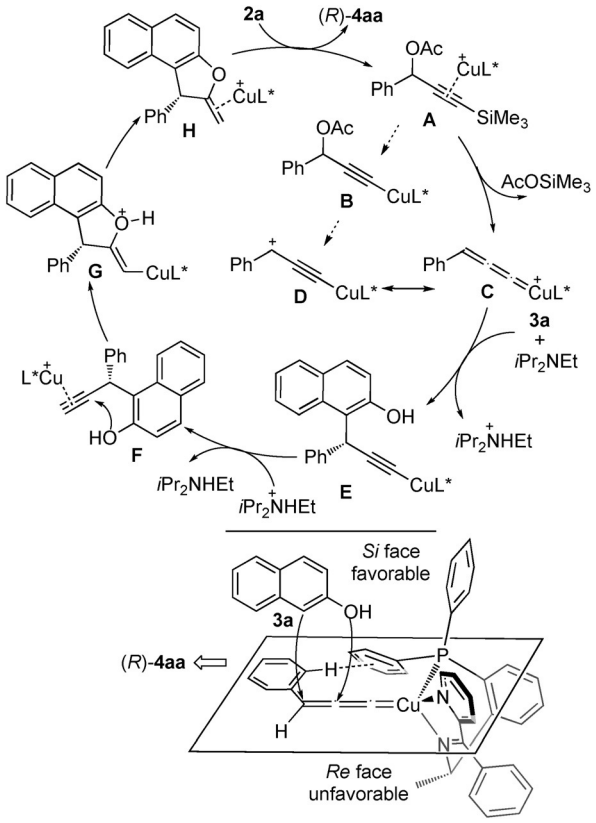


Entry	Substrate (**3**)	Product (**4**)	Yield [%][b]	*ee* [%][c]
1	**3a**: R^2 = H	**4aa**	92	93
2	**3b**: R^2 = 3-OMe	**4ab**	91	92
3	**3c**: R^2 = 6-OMe	**4ac**	82	93
4	**3d**: R^2 = 7-OMe	**4ad**	83	96
5	**3e**: R^2 = 7-Br	**4ae**	82	95
6[d]	**3f**: R^2 = 6-Br	**4af**	83	93
7[d]	**3g**: R^2 = 6-CN	**4ag**	92	91
8[e]	**3h**: R^2 = 3-OH	**4ah**	83	91
9[d]	**3i**: R^2 = 3-CONHPh	**4ai**	87	95
10	**3j**: R^2 = 7-OH	**4aj**	85	88
11[d]			82	80
12[d]			83	90

[a] Reaction conditions: **2a** (0.3 mmol), **3** (0.36 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.015 mmol, 5 mol%), (*S*)-**L1f** (0.0165 mmol, 5.5 mol%), and iPr_2NEt (0.36 mmol, 1.2 equiv) in 3 mL of MeOH at −40 °C for 24 h, unless otherwise noted. [b] Yield of the isolated product. [c] Determined by chiral-phase HPLC. [d] The reaction was performed at −20 °C for 12 h. [e] The reaction was performed at 0 °C for 12 h.



Scheme 2. Hydrogenation of the cycloadduct **4aa**.



Scheme 3. Proposed mechanism.

and 12). The absolute configuration of the cycloadducts was unambiguously established to be *R* by X-ray crystallographic analysis of **4bf** (Figure 1).

The synthetic utility of this method was briefly explored by the hydrogenation of (*R*)-**4aa**, as shown in Scheme 2, which predominantly gave the *trans*-diastereoisomer **5** in high yield and excellent diastereoselectivity without the obvious erosion in enantioselectivity.

Based on the experimental results and previous reports,[3f,l] a reaction pathway is proposed as shown in Scheme 3. In the first step, a copper complex forms the π-complex **A** with **2a**. A copper-promoted Si–C(sp) bond cleavage of **A**, followed by the elimination of an acetoxyl moiety, affords the copper allenylidene complex **C** or its resonance structure **D**. The intramolecular Cu–Si exchange by the elimination of $AcOSiMe_3$ proceeds more readily than the intermolecular base-assisted reaction with terminal propargylic esters for the formation of copper acetylide complex **B**,[10] which should be answered for the observed activation. The nucleophilic attack of the C_α atom of β-naphthol at the C_γ atom of the allenylidene complex **C** gives the copper acetylide complex **E**, which is then converted into the copper π-alkyne complex **F**. Intramolecular nucleophilic attack of the hydroxy group on the C_β atom of **F** generates an alkenyl complex **G**, which is transformed into the copper π-alkene complex **H**. The starting **A** is then regenerated from **H** by liberating **4aa** through ligand exchange with another **2a**. A transition state for the copper allenylidene complex with the chiral P,N,N-ligand is also proposed to explain the observed stereochemistry based on an edge-to-face aromatic interaction[3f] between a phenyl group of the substrate and a phenyl

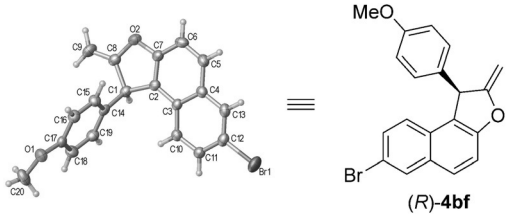


Figure 1. X-ray structure of (*R*)-**4bf**.[12]

group of the ligand (Scheme 3). As a result, the attack at the γ-carbon atom by the C_α atom of β-naphthol happened favorably from the *Si* face to form (*R*)-**4aa** while that from the *Re* face was hampered because of steric hindrance of the ligand.

In conclusion, we have realized a highly enantioselective copper-catalyzed formal [3+2] cycloaddition of 3-trimethylsilylpropargylic acetates with either β-naphthols or electron-rich phenols on the basis of a desilylation-activated strategy. In the presence of a combination of $Cu(OAc)_2{\cdot}H_2O$ and a finely modified ketimine P,N,N-ligand as the catalyst, either chiral 1,2-dihydronaphtho- or benzofurans could be obtained in good yields and with high enantioselectivities. The reaction displayed a wide substrate scope with respect to both 3-trimethylsilylpropargylic acetates and either β-naphthols or phenols. This reaction represents the first desilylation-activated catalytic propargylic transformation, thus suggesting that copper allenylidene complexes can be efficiently generated from 3-trimethylsilylpropargylic esters by a copper-promoted Si–C(sp) bond cleavage. We believe that this strategy will find wide applications in the catalytic asymmetric transformation of propargylic substrates, and further advance the research in this field.

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Keywords: asymmetric catalysis · cycloaddition · copper · heterocycles · reaction mechanisms

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[12] CCDC 1436033 (**4bf**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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