Angewandte Chemie

Synthetic Methods

DOI: 10.1002/ange.201303016

Gold-Catalyzed Formal Cycloaddition of 2-Ethynylbenzyl Ethers with Organic Oxides and α-Diazoesters**

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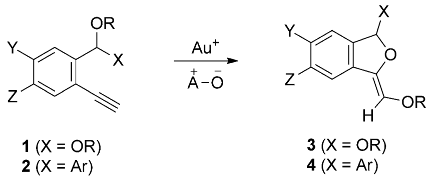
Metal-catalyzed intermolecular cycloaddition reactions are powerful tools for the construction of complex carbo- and heterocyclic frameworks.[1,2] The development of new all-carbon building units is a key focus in this area. Five- and six-membered carbo- and heterocycles are readily accessed by metal-catalyzed [3C+2], [4C+2], and [3C+3] cycloaddition reactions,[1,2] but less commonly through a [4C+1] or [5C+1] cycloaddition route.[3–5] The scarcity of four- and five-carbon-atom building units in [*n*C+1] cycloaddition reactions ($n=4,5$) impedes their catalytic development. Reported four-carbon-atom motifs include vinyl allenes,[3] diallenes,[4] and 3-en-1-ynes,[5] whereas five-carbon-atom units comprise only substituted cyclopropane derivatives[6] and 3-acyloxy-1,4-enynes.[7] We sought a new all-carbon motif for an [*n*C+1] cycloaddition ($n=4,5$). We report herein the gold-catalyzed cycloaddition of 2-ethynylbenzyl ethers **1** and **2** with organic oxides and diazocarbonyl species to give formal cycloadducts **3**, **4**, and **5** [Eqs. (1) and (2); EWG = electron-withdrawing group].



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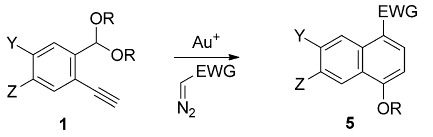
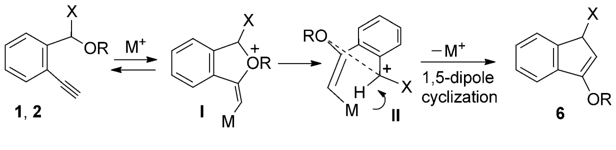


(2)

In the presence of Lewis acids, 2-ethynylbenzyl ethers **1** and **2** form indene derivatives **6** through a facile "1,5-dipole cyclization" of intermediates **II**; the mechanism of this carboalkoxylation[8,9] has been well established by extensive studies.[8,9] This alkyne-activation route [**1**/**2**→**I**→**II**→**6**, Eq. (3)] is well-accepted for both acetals **1** ($X=OR$) and benzyl ethers **2** (X = aryl, alkenyl). The new cycloaddition reactions can be viewed as two independent routes that avoid this facile carboalkoxylation.



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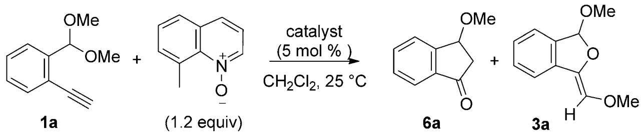
With $AuCl_3$ and $[Ph_3PAu](OTf)$, the reaction between 2-ethynylbenzaldehyde dimethyl acetal (**1a**) and 8-methylquinoline *N*-oxide (1.2 equiv)[10] in dichloromethane gave only the carboalkoxylation product **6a** in 70–75 % yield (Table 1, entries 1 and 2). However, the electron-rich catalyst $[(PtBu_2(o\text{-biphenyl}))Au](OTf)$ gave the formal cycloadduct[10] (*Z*)-1-methoxy-3-(methoxymethylene)-1,3-dihydroisobenzofuran (**3a**) in 78 % yield (Table 1, entry 3). We postulate that electron-rich $[(PtBu_2(o\text{-biphenyl}))Au](OTf)$ tends to stabilize the oxonium intermediate **I** in Equation (3), and impedes the subsequent **I**→**II** conversion. [IPrAu](OTf) (5 mol %, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene) gave unreacted **1a** (recovered in 60 % yield) because of its weak acidity (Table 1, entry 4). We tested the effect of the anion with $[(PtBu_2(o\text{-biphenyl}))Au]X$ ($X=NTf_2$, SbF_6),

Table 1: Gold-catalyzed cycloaddition with various catalysts.[a]



Entry	Catalyst	*t* [h]	Yield [%][b]		
			1a	**6a**	**3a**
1	$[AuCl_3]$	6.5	–	75	–
2	$[PPh_3AuCl]/AgOTf$	7.0	–	70	–
3	[LAuCl]/AgOTf	12.5	–	–	78
4	[IPrAuCl]/AgOTf	24.0	60	–	–
5	$[LAuCl]/AgNTf_2$	13.5	–	–	71
6	$[LAuCl]/AgSbF_6$	13.0	–	–	65
7	AgOTf	24.0	81	–	–

[a] $L=PtBu_2(o\text{-biphenyl})$, IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene, Tf = trifluoromethanesulfonyl; $[\mathbf{1a}]=0.20$ M. [b] Product yields after purification by silica-gel column chromatography are reported.

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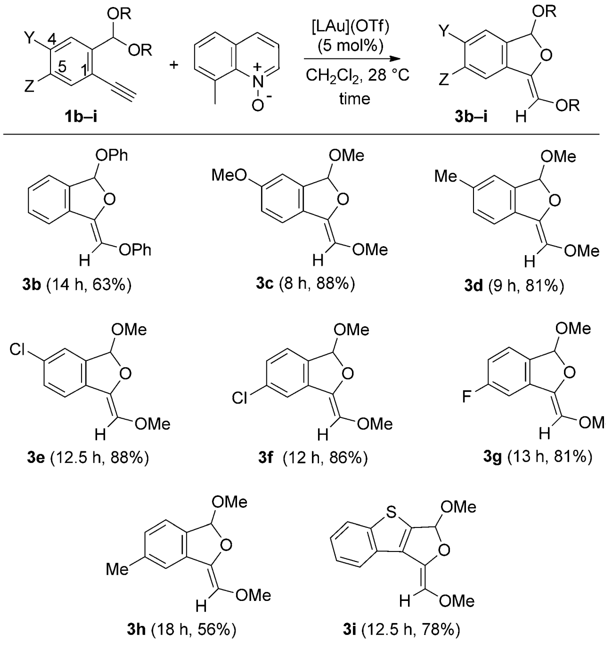
[**] We thank the National Science Council, Taiwan for financial support of this research.

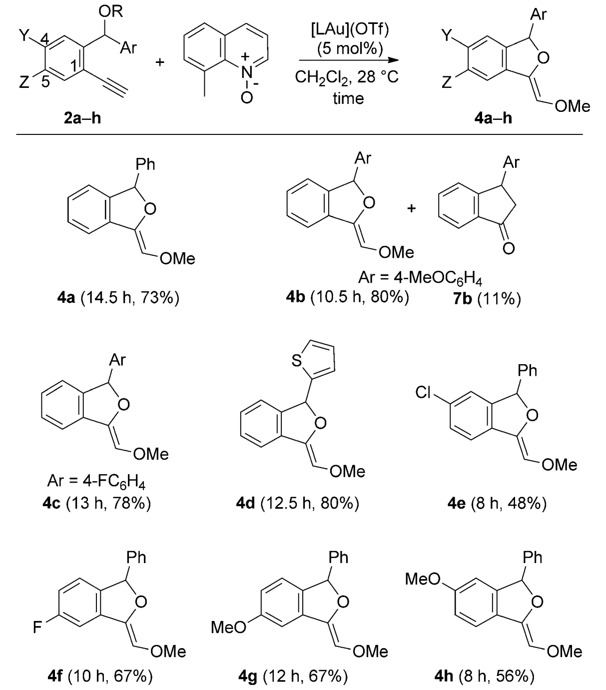
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303016.

which delivered the desired formal cycloadduct **3a** in 71 and 65 % yield, respectively (Table 1, entries 5 and 6). The use of AgOTf alone led to unreacted acetal **1a**, which was recovered in 81 % yield (Table 1, entry 7). The proposed structure of compound **3a** was supported by ^{1}H NMR spectroscopic NOE analysis.[11]

Scheme 1 shows the compatibility of this cycloaddition with the additional acetal substrates **1b–i**; the competitive carboalkoxylation was completely suppressed in all cases. This cycloaddition proceeded well for the 2-ethynylbenzaldehyde acetal **1b**, which bears a diphenoxy group, to give the desired 1,3-dihydroisobenzofuran **3b** in 63 % yield. The reaction could be extended to acetals **1c–e** bearing methoxy, methyl, and chloro substituents at the 4-position of the aromatic ring to give the desired products **3c–e** in 81–88 % yield. The reaction was also extended to acetal substrates **1f–h** with chloro, fluoro, and methyl substituents at the 5-position of the ring; the desired formal cycloadducts **3f–h** were obtained in satisfactory yields (56–86 %). In the case of acetal **1i** containing a benzothiophene bridge, cycloaddition with 8-methylquinoline oxide proceeded smoothly to give the desired product **3i** in 78 % yield. The structures of products **3c**, **3d**, and **3h** were determined from NOE ^{1}H NMR spectra.[11]



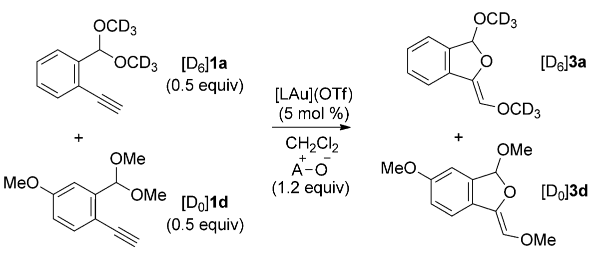
Scheme 1. Reaction scope for the transformation of acetal substrates. L = P*t*Bu$_2$(*o*-biphenyl), [**1**] = 0.20 M. Product yields after purification by silica-gel column chromatography are reported.



Scheme 2. Reaction scope for the transformation of benzyl ethers. L = P*t*Bu$_2$(o-biphenyl), [**2**] = 0.20 M. Product yields after purification by silica-gel column chromatography are reported.

Scheme 2 shows the scope of this reaction for the transformation of benzyl methoxy ethers. Compounds **2a–c** (Ar = phenyl, 4-methoxy, and 4-fluorophenyl) were converted into 1,3-dihydroisobenzofurans **4a–c** in 73–80 % yield. In the case of the 4-methoxyphenyl-substituted substrate **2b**, the carboalkoxylation product **7b** was also isolated in 11 % yield. Substrate **2d** containing a 2-thienyl group delivered the desired product **4d** in 80 % yield. This reaction was compatible with benzyl ethers **2e–h** bearing a chloro, fluoro, or methoxy substituent at the 4- or 5-position of the ethynyl-substituted aromatic ring and provided the desired 1,3-dihydroisobenzofurans **4e–h** in 48–67 % yield. The structure of product **4f** was determined from NOE ^{1}H NMR, HMQC, and HMBC spectra.[11]

The treatment of a mixture of [D$_6$]**1a** and nondeuterated **1d** ([D$_0$]**1d**; 0.5 equiv each) with [(P*t*Bu$_2$(*o*-biphenyl))Au](OTf) (5 mol %) and 8-methylquinoline oxide (1.2 equiv) in CH$_2$Cl$_2$ (28 °C, 12 h) gave only fully deuterated [D$_6$]**3a** and nondeuterated [D$_0$]**3d** [Eq. (4)]. Structural analysis of the cycloadduct **4a** led us to suspect the intermediacy of a gold carbene **B**, as depicted in Scheme 3. When we prepared the α-carbonyl diazo compound **8** and treated it with [(P*t*Bu$_2$(o-biphenyl))Au](OTf) in CH$_2$Cl$_2$, only 3-phenylindanone (**7a**) and its reduced form **9** were obtained, in 65 and 26 % yield, respectively. Product **7a** was produced through intramolecular methoxy displacement of intermediate **A** (see the Supporting Information for the reaction mechanism). In the



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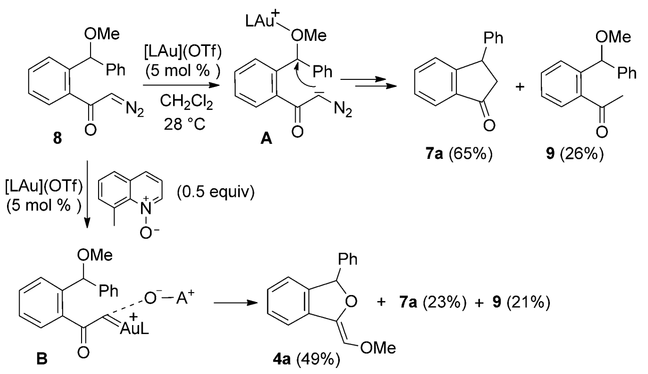
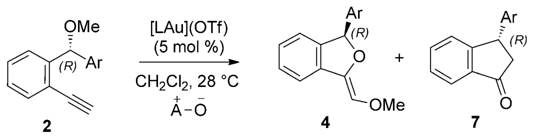


Scheme 3. A viable route involving a gold carbene intermediate.

presence of 8-methylquinoline oxide (0.5 equiv), the desired dihydroisobenzofuran **4a** was obtained as the major product in 49% yield together with side products **7a** (23%) and **9** (21%). These results suggest that the organic oxide facilitates the generation of the gold carbene **B** through a stabilization effect.

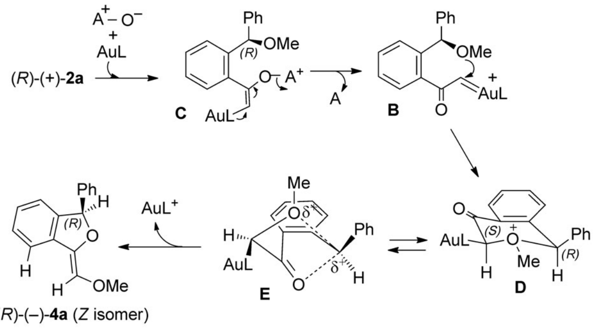
We prepared enantiomerically enriched (*R*)-(+)-**2a** (94.1% *ee*)[12] and examined its gold-catalyzed cycloaddition with 8-methylquinoline oxide. The reaction delivered the 1,3-dihydroisobenzofuran (*R*)-(−)-**4a** (78%, 93.9% *ee*) with complete chirality transfer (Table 2, entry 1). This product was determined to have the *R* absolute configuration,[13] which corresponds to retention of the original configuration. The chirality transfer was also highly effective for the 4-fluorophenyl derivative (*R*)-(+)-**2c** (85.3% *ee*), which was converted into (*R*)-(−)-**4c** with 83% *ee* (Table 2, entry 2). In contrast, a small loss of chirality was notable for the 4-methoxyphenyl derivative (*R*)-(+)-**2b** (87.1% *ee*), which gave (*R*)-(−)-**4b** with 75.2% *ee* (Table 2, entry 3). In this case, we also obtained (*R*)-(+)-**7b** in 9% yield, albeit with low enantioselectivity (33.6% *ee*); this side product is reported to have the *S* configuration as a result of inversion of the configuration, as shown by intermediate **II** in Equation (3).[9a]

Table 2: Chirality-transfer experiments.



Entry	Ether (*ee* [%])	*t* [h]	Product (yield [%], *ee* [%])
1	Ar = Ph, (+)-**2a** (94.1)	18	(−)-**4a** (78, 93.9)
2	Ar = 4-FC$_6$H$_4$, (+)-**2c** (85.3)	20	(−)-**4c** (75, 83.0)
3	Ar = 4-MeOC$_6$H$_4$, (+)-**2b** (87.1)	20	(−)-**4b** (77, 75.2) (+)-**7b** (9, 33.6)

The cross-over experiment in Equation (4) supports an intramolecular alkoxy shift; we postulate a plausible mechanism in Scheme 4. We envisage that 8-methylquinoline oxide (A$^+$-O$^-$) initially attacks the alkyne π system of *R*-(+)-**2a** to give the gold enol ether **C** and subsequently the α-oxo gold carbene **B**.[14] The role of this gold carbene **B** was assessed in a control experiment (Scheme 3). We postulate that a subsequent attack of the methoxy group at the carbene carbon atom generates the oxonium species **D**, which has two axial hydrogen atoms to minimize steric hindrance. Species **D** is expected to form the gold enolate species **E** through a ketone/enol equilibrium. In species **E**, there is a concurrent attack of the ketone moiety at the carbocation center as the methoxy group leaves from the same center; this process is likely to occur because of a stable five-membered-ring transition state. Such a front-on S_N2 attack has been reported once previously for a gold-catalyzed cycloaddition reaction.[15] Finally, the elimination of AuL$^+$ is expected to give (*R*)-(−)-**4a** with a *Z* alkene functionality.

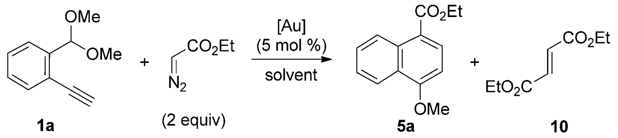


Scheme 4. Chirality transfer in the cycloaddition reaction.

Encouraged by the success of the transformation with 8-methylquinoline *N*-oxide, we sought new cycloaddition reactions with an α-diazoester.[16] No reaction occurred between acetal **1a** and ethyl diazoacetate (2 equiv) with [LAu](NTf$_2$) (L = P*t*Bu$_2$(o-biphenyl); 5 mol%) in CH$_2$Cl$_2$ (28 °C, 24 h); instead, the α-diazoester decomposed completely to give alkene **10** (93%; Table 3, entry 1).

The NTf$_2^-$ anion enhances the decomposition of the diazo compound to alkene **10**. With relatively acidic [LAu](SbF$_6$), ethyl 4-methoxy-1-naphthoate (**5a**) was obtained in 63% yield in CH$_2$Cl$_2$ (28 °C, 18 h; Table 3, entry 2). The yield of naphthalene derivative **5a** was further improved to 75% in

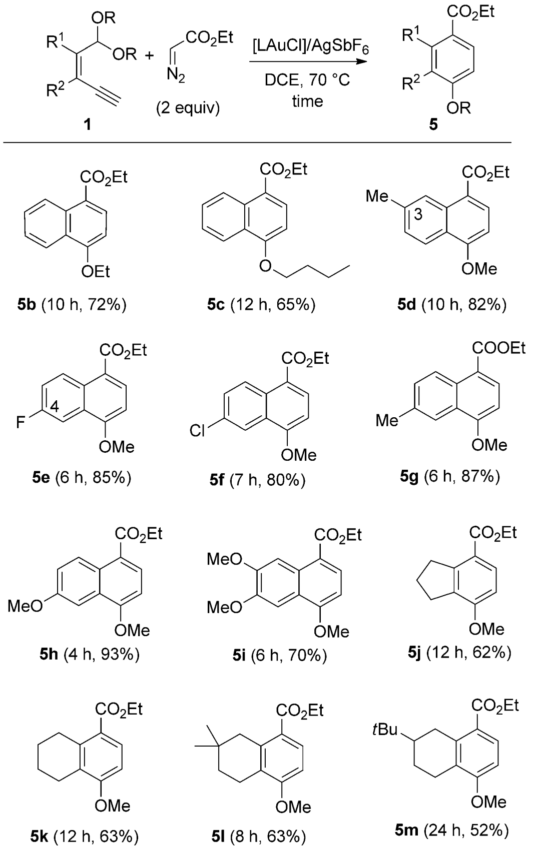
Table 3: Gold-catalyzed cycloaddition with a diazo compound.[a]



Entry	Catalyst	Solvent	*T* [°C]	*T* [h]	Compound (yield [%][b])
1	[LAuCl]/AgNTf$_2$	CH$_2$Cl$_2$	28	18	**1a** (91), **10** (93)
2	[LAuCl]/AgSbF$_6$	CH$_2$Cl$_2$	28	18	**5a** (63), **10** (18)
3	[LAuCl]/AgSbF$_6$	DCE	70	7.0	**5a** (75), **10** (trace)

[a] L = P*t*Bu$_2$(*o*-biphenyl), [**1a**] = 0.10 M. [b] Product yields after purification by silica-gel column chromatography are reported.

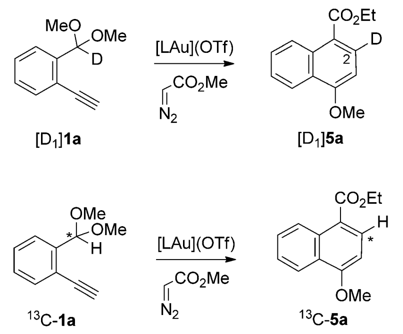
hot 1,2-dichloroethene (DCE; 70 °C, 7 h; Table 3, entry 3). The molecular structure of compound **5a** was determined by X-ray diffraction analysis[11] and revealed an intriguing skeletal rearrangement.



Scheme 5. Scope of the gold-catalyzed cycloaddition reaction with ethyl diazoacetate. L = P*t*Bu$_2$(*o*-biphenyl), [**1**] = 0.10 M. Product yields after purification by silica-gel column chromatography are reported.

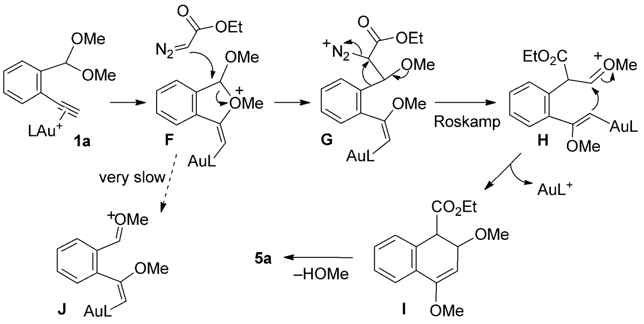
Scheme 5 shows the scope of this reaction with additional 2-ethynylbenzaldehyde acetals and 2-en-4-yne acetals. The cycloaddition was extended to diethyl and di-*n*-butyl acetals to deliver naphthalene derivatives **5b** and **5c** in 72 and 65 % yield, respectively. In the case of the 4-methylbenzaldehyde dimethyl acetal, the corresponding product **5d** was obtained in 82 % yield. This formal cycloaddition also proceeded for 5-substituted benzaldehyde acetals, including substrates with fluoro, chloro, methyl, and methoxy substituents; the corresponding products **5e–h** were obtained in satisfactory yields (80–93 %). The reaction was also applicable to the 4,5-dimethoxybenzaldehyde dimethyl acetal, which was converted into compound **5i** in 70 % yield. This cycloaddition is compatible with 2-en-4-yne acetals: products **5j–m** were obtained in 52–63 % yield. The proposed structure of product **5h** was determined from ^{1}H NMR NOE spectra.

We prepared a sample [D$_1$]**1a** deuterated at the acetal position and examined its reaction with ethyl diazoacetate and [LAu](OTf) (Scheme 6). The resulting product [D$_1$]**5a** was fully deuterated at the naphthalene C2 atom. A similar 1,2-carbon-atom shift was observed in the formation of the ^{13}C-labeled product ^{13}C-**5a** when the substrate was enriched at the same position with ^{13}C (Scheme 6).



Scheme 6. Isotope-labeling experiments.

An alkyne-activation route is postulated for this diazo cycloaddition (Scheme 7). The trapping of intermediate **J** with the α-diazoester is an infeasible process, as we assessed previously that [(P*t*Bu$_2$(o-biphenyl))Au]$^+$ impedes the process **F**→**J**. Accordingly, we postulate that the α-diazoester attacks the oxonium species **F** to generate intermediate **G**, which subsequently undergoes a Roskamp-type rearrangement[17] involving a 1,2-phenyl shift to generate another oxonium intermediate **H**. A subsequent cyclization of species **H** is expected to give the 1,2-dihydronapththalene **I**, which is transformed into the observed naphthalene product **5a** by the loss of methanol. This mechanism rationalizes well the results of the labeling studies (Scheme 6).



Scheme 7. Proposed mechanism for the cycloaddition.

We have reported herein gold-catalyzed formal cycloaddition reactions of 2-ethynylbenzyl ethers **1** and **2** with 8-methylquinoline oxide and ethyl diazoacetate. With enantiomerically enriched benzyl ether substrates, we observed the retention of configuration in the oxide cycloadducts;[18] this process was confirmed to involve a gold carbene intermediate. We also described a distinct cycloaddition of 2-ethynylbenzyl acetals **1** with α-diazoesters; this process leads to a skeletal rearrangement of products. We postulate an attack of the diazo compound on the initial oxonium species in the alkyne-activation route, followed by a Roskamp-type rearrangement and ring closure. The two cycloaddition reactions described highlight the first success in the development of cycloaddition reactions of readily available 2-ethynylbenzyl ethers.

Received: April 11, 2013
Revised: May 15, 2013
Published online: June 13, 2013

Keywords: alkynes · benzyl ethers · diazo compounds · formal cycloaddition · gold catalysis

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[11] ^{1}H NOE and 2D NMR spectra of key compounds are provided in the Supporting Information. CCDC 931674 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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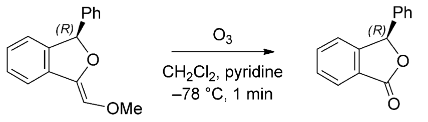

(*R*)-(−)-**4a**

(*R*)-(−)-**11a** (45%)
$[\alpha] = -39.6$

[14] For selected examples, see: a) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258–3259; b) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550–8551; c) B. Lu, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 14070–14072; d) R.-B. Dateer, B. S. Shaibu, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 117–121; *Angew. Chem. Int. Ed.* **2012**, *51*, 113–117; e) Ref. [5c].

[15] S. N. Karad, S. Bhunia, R.-S. Liu, *Angew. Chem.* **2012**, *124*, 8852–8856; *Angew. Chem. Int. Ed.* **2012**, *51*, 8722–8726.

[16] For selected examples of the use of diazocarbonyl species as one-carbon-atom building units in catalytic cycloaddition reactions, see: a) A. DeAngelis, M. T. Taylor, J. M. Fox, *J. Am. Chem. Soc.* **2009**, *131*, 1101–1105; b) Z.-J. Xu, D. Zhu, X. Zeng, F. Wang, B. Tan, Y. Hou, *Chem. Commun.* **2010**, *46*, 2504–2506; c) X. Qi, X. Xu, C.-M. Park, *Chem. Commun.* **2012**, *48*, 3996–3998; d) P. de March, R. Huisgen, *J. Am. Chem. Soc.* **1982**, *104*, 4952–4952.

[17] For selected examples, see: a) T. Hashimoto, H. Miyamoto, Y. Naganawa, K. Maruoka, *J. Am. Chem. Soc.* **2009**, *131*, 11280–11281; b) W. Li, J. Wang, X. Hu, K. Shen, W. Wang, Y. Chu, L. Lin, X. Liu, X. Feng, *J. Am. Chem. Soc.* **2010**, *132*, 8532–8533; c) M. P. Doyle, M. L. Trudell, J. W. Terpstra, *J. Org. Chem.* **1983**, *48*, 5146–5148.

[18] We exclude a double-inversion mechanism for the retention of configuration in Table 2; such a process would presumably involve the attack of OTf^- on intermediate **D** in Scheme 4. However, the formation of the desired product (*R*)-(−)-**4a** with 90.5% *ee* when [LAu](SbF_6) was used with (*R*)-(+)-**2a** (90.5% *ee*) excludes this possibility.