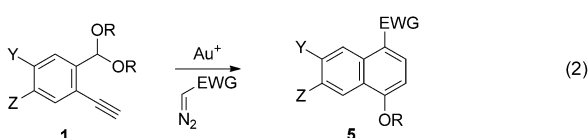
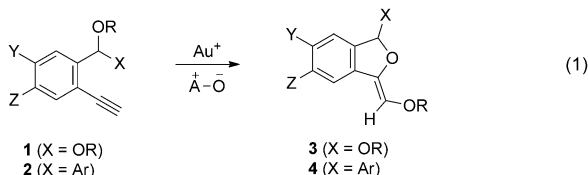


Synthetic Methods

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

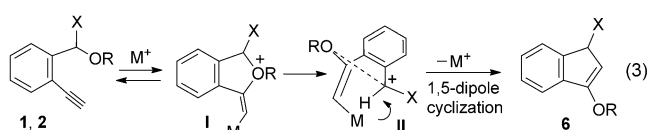
Samir Kundlik Pawar, Chiou-Dong Wang, Sabyasachi Bhunia, Appaso Mahadev Jadhav, and Rai-Shung Liu*

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 $[n\text{C}+1]$ cycloaddition reactions ($n = 4, 5$) impedes their catalytic development. Reported four-carbon-atom motifs include vinyl allenes,^[3] diallenes,^[4] and 3-en-1-yne,^[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 $[n\text{C}+1]$ 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].



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** $\rightarrow$ **I** $\rightarrow$ **II** $\rightarrow$ **6**,

Eq. (3)] is well-accepted for both acetals **1** ($X = \text{OR}$) and benzyl ethers **2** ($X = \text{aryl, alkenyl}$). The new cycloaddition reactions can be viewed as two independent routes that avoid this facile carboalkoxylation.



With AuCl_3 and $[\text{Ph}_3\text{PAu}](\text{OTf})$, 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

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

Entry	Catalyst	<i>t</i> [h]	Yield [%] ^[b]		
			1 a	6 a	3 a
1	$[\text{AuCl}_3]$	6.5	–	75	–
2	$[\text{PPh}_3\text{AuCl}]/\text{AgOTf}$	7.0	–	70	–
3	$[\text{LAuCl}]/\text{AgOTf}$	12.5	–	–	78
4	$[\text{IPrAuCl}]/\text{AgOTf}$	24.0	60	–	–
5	$[\text{LAuCl}]/\text{AgNTf}_2$	13.5	–	–	71
6	$[\text{LAuCl}]/\text{AgSbF}_6$	13.0	–	–	65
7	AgOTf	24.0	81	–	–

[a] $\text{L} = \text{PtBu}_2(o\text{-biphenyl})$, $\text{IPr} = 1,3\text{-bis}(\text{diisopropylphenyl})\text{imidazol-2-ylidene}$, $\text{Tf} = \text{trifluoromethanesulfonyl}$; [**1a**] = 0.20 M. [b] Product yields after purification by silica-gel column chromatography are reported.

$[(\text{PtBu}_2(o\text{-biphenyl}))\text{Au}](\text{OTf})$ 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 $[(\text{PtBu}_2(o\text{-biphenyl}))\text{Au}](\text{OTf})$ tends to stabilize the oxonium intermediate **I** in Equation (3), and impedes the subsequent **I** $\rightarrow$ **II** conversion. $[\text{IPrAu}](\text{OTf})$ (5 mol %), $\text{IPr} = 1,3\text{-bis}(\text{diisopropylphenyl})\text{imidazol-2-ylidene}$ gave unreacted **1a** (recovered in 60 % yield) because of its weak acidity (Table 1, entry 4). We tested the effect of the anion with $[(\text{PtBu}_2(o\text{-biphenyl}))\text{Au}]\text{X}$ ($\text{X} = \text{NTf}_2, \text{SbF}_6$),

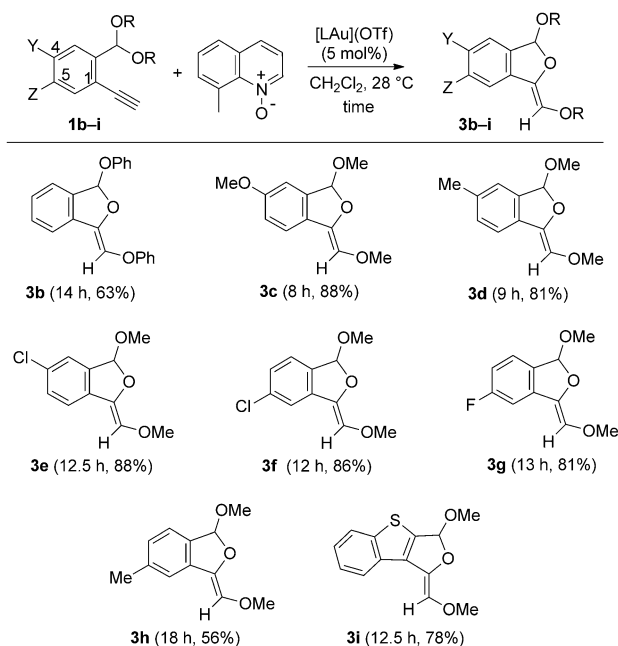
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[**] We thank the National Science Council, Taiwan for financial support of this research.

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 ^1H NMR spectroscopic NOE analysis.^[11]

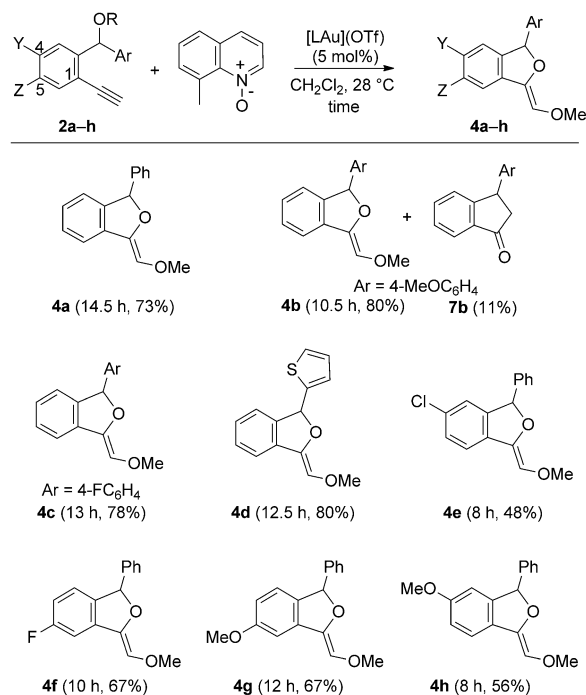
Scheme 1 shows the compatibility of this cycloaddition with the additional acetal substrates **1b–i**; the competitive carboalkoxylation was completely suppressed in all cases. This cycloaddition proceeded well for the 2-ethynylbenzaldehyde acetal **1b**, which bears a diphenoxy group, to give the desired 1,3-dihydroisobenzofuran **3b** in 63 % yield. The



Scheme 1. Reaction scope for the transformation of acetal substrates. $\text{L} = \text{PtBu}_2(o\text{-biphenyl})$, $[\text{I}] = 0.20 \text{ M}$. Product yields after purification by silica-gel column chromatography are reported.

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 ^1H NMR spectra.^[11]

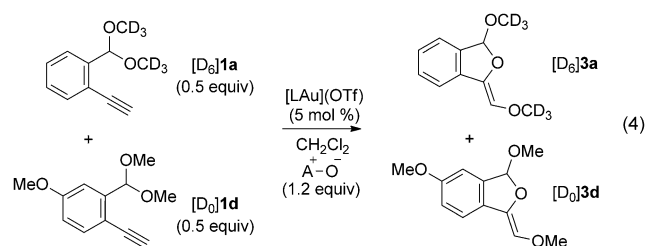
Scheme 2 shows the scope of this reaction for the transformation of benzyl ethers. Compounds **2a–c** (Ar = phenyl, 4-methoxy, and 4-fluorophenyl) were converted into 1,3-dihydroisobenzofurans **4a–c** in 73–80 % yield. In the case of the 4-methoxyphenyl-substituted substrate **2b**, the carboalkoxylation product **7b** was also isolated in 11 % yield. Substrate **2d** containing a 2-thienyl group delivered the



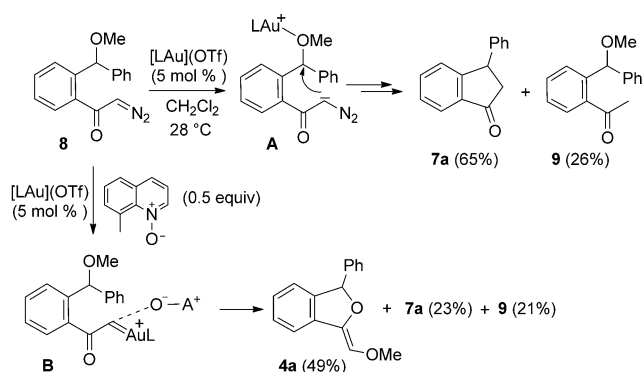
Scheme 2. Reaction scope for the transformation of benzyl ethers. $\text{L} = \text{PtBu}_2(o\text{-biphenyl})$, $[\text{2}] = 0.20 \text{ M}$. Product yields after purification by silica-gel column chromatography are reported.

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 ^1H NMR, HMQC, and HMBC spectra.^[11]

The treatment of a mixture of $[\text{D}_6]\text{1a}$ and nondeuterated **1d** ($[\text{D}_0]\text{1d}$; 0.5 equiv each) with $[(\text{PtBu}_2(o\text{-biphenyl}))\text{Au}](\text{OTf})$ (5 mol %) and 8-methylquinoline oxide (1.2 equiv) in CH_2Cl_2 (28 °C, 12 h) gave only fully deuterated $[\text{D}_6]\text{3a}$ and nondeuterated $[\text{D}_0]\text{3d}$ [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 $[(\text{PtBu}_2(o\text{-biphenyl}))\text{Au}](\text{OTf})$ in CH_2Cl_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



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-

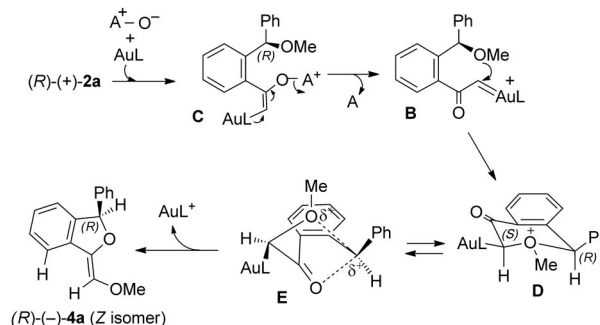
Table 2: Chirality-transfer experiments.

Entry	Ether (<i>ee</i> [%])	<i>t</i> [h]	Product (yield [%], <i>ee</i> [%])
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)

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]

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



Scheme 4. Chirality transfer in the cycloaddition reaction.

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.

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](NTf₂) (L = PtBu₂(*o*-biphenyl); 5 mol %) in CH₂Cl₂ (28 °C, 24 h); instead, the α -diazoester decomposed completely to give alkene **10** (93%; Table 3, entry 1).

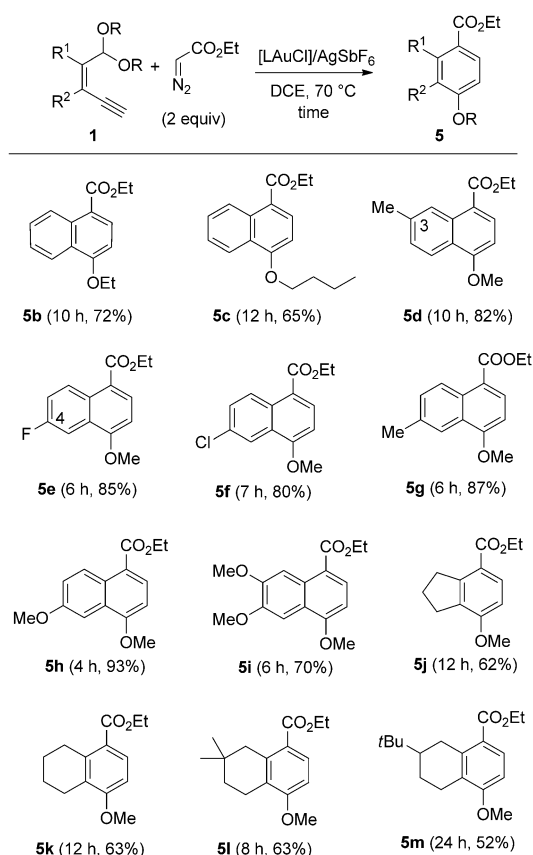
The NTf₂[–] anion enhances the decomposition of the diazo compound to alkene **10**. With relatively acidic [LAu](SbF₆), ethyl 4-methoxy-1-naphthoate (**5a**) was obtained in 63% yield in CH₂Cl₂ (28 °C, 18 h; Table 3, entry 2). The yield of naphthalene derivative **5a** was further improved to 75% in

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

Entry	Catalyst	Solvent	<i>T</i> [°C]	<i>T</i> [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 = PtBu₂(*o*-biphenyl), [**1a**] = 0.10 M. [b] Product yields after purification by silica-gel column chromatography are reported.

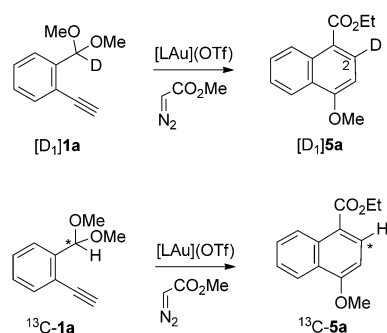
hot 1,2-dichloroethene (DCE; 70 °C, 7 h; Table 3, entry 3). The molecular structure of compound **5a** was determined by X-ray diffraction analysis^[11] and revealed an intriguing skeletal rearrangement.



Scheme 5. Scope of the gold-catalyzed cycloaddition reaction with ethyl diazoacetate. L = *Pr*Bu₂(*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 ¹H NMR NOE spectra.

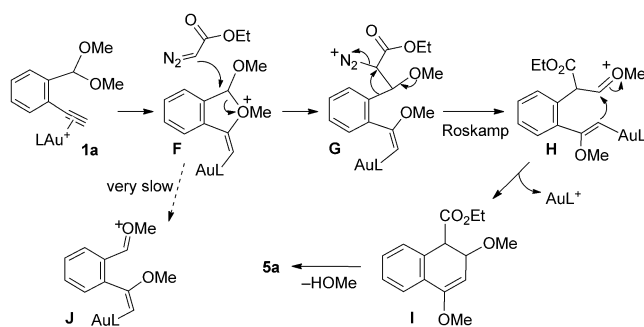
We prepared a sample [D₁]**1a** deuterated at the acetal position and examined its reaction with ethyl diazoacetate and [LAu](OTf) (Scheme 6). The resulting product [D₁]**5a**



Scheme 6. Isotope-labeling experiments.

was fully deuterated at the naphthalene C2 atom. A similar 1,2-carbon-atom shift was observed in the formation of the ¹³C-labeled product ¹³C-**5a** when the substrate was enriched at the same position with ¹³C (Scheme 6).

An alkyne-activation route is postulated for this diazo cycloaddition (Scheme 7). The trapping of intermediate **J**



Scheme 7. Proposed mechanism for the cycloaddition.

with the α -diazoester is an infeasible process, as we assessed previously that [(*Pr*Bu₂(*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-dihydronaphthalene **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).

We have reported herein gold-catalyzed formal cycloaddition reactions of 2-ethynylbenzyl ethers **1** and **2** with 8-methylquinoline oxide and ethyl diazoacetate. With enantio-merically 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.

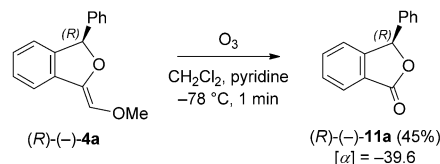
Received: April 11, 2013

Revised: May 15, 2013

Published online: June 13, 2013

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

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