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Dirhodium(II)-Catalyzed Cyclopropanation of Alkyne-Containing α-Diazoacetates for the Synthesis of Cycloalkynes

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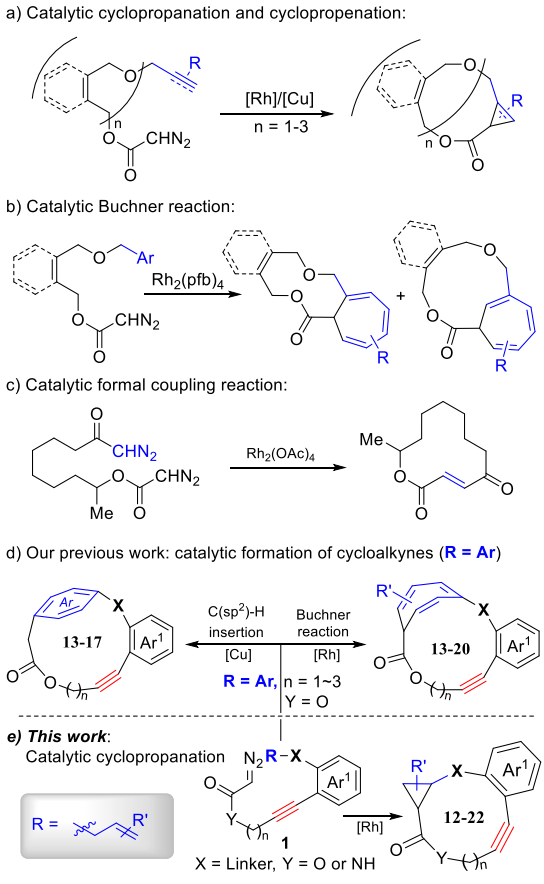
Abstract. An efficient dirhodium(II)-catalyzed macrocyclization reaction of alkyne-containing diazoacetates through intramolecular metal carbene cyclopropanation is described. This method provides a variety of 12- to 22-membered macrocyclic alkynes, which incorporate *ortho*-aryl, cyclopropane, and cyclopropene units, in good to excellent yields under mild reaction conditions.

Keywords: Diazo compounds; Metal carbenes; Macrocyclization; Cyclopropanation; Macrocyclic alkyne

Diazo compounds, pervasively used as carbene precursors, are versatile reagents in modern synthetic organic chemistry.[1] Although transition-metal-catalyzed transformations of diazo compounds allow rapid and efficient assembly of complex molecules and are widely reported,[2] relevant catalytic carbene reactions for the direct construction of macrocyclic rings have received limited attention.[3-7] The seminal work in this content using intramolecular catalytic cyclopropanation reaction for the direct synthesis of macrocyclic molecules has been reported by Doyle,[3a,3b] and later by Charette (Scheme 1a).[3c] Doyle's group generalized this method for the efficient construction of a variety of macrocyclic compounds through intramolecular metal carbene reactions, including cyclopropenation (Scheme 1a),[4] the Buchner reaction (Scheme 1b),[5] formal coupling reactions (Scheme 1c),[6] and others.[7] Despite these achievements, metal carbene reactions have not been documented for the synthesis of macrocyclic alkynes, which may be due to their inherent ring strain as well as the side reaction of metal carbene with alkyne species.[4] Recently, our group have enabled divergent access for the straightforward synthesis of



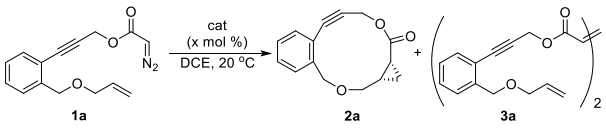
Scheme 1. Macrocycle formation via metal carbene reactions.

cycloalkynes through copper-catalyzed C(sp^2)-H functionalization and rhodium-prompted Buchner reaction (Scheme 1d).[8] Due to longstanding research interest in the construction of privileged cycloalkynes, the development of efficient and practical synthetic routes to access cycloalkynes with broad functional group compatibility and structural diversity is highly desirable.[9]

Over the past few decades, cycloalkynes have attracted considerable attention from chemists because of their unique structures that are prevalent in natural products,[10,11] bioactive molecules,[12] and materials.[13] Thus, a variety of catalytic strategies for the construction of macrocyclic alkynes have been disclosed, such as the palladium-promoted Heck reaction,[14] the copper-catalyzed Castro-Stephenes coupling reaction,[15] ring-closing alkyne metathesis (RCAM),[16] the Nicholas reaction[17,18] and its analogous version.[19] Recently, gold-catalyzed coupling has been reported by the Shi group for the effective construction of cyclic conjugated diynes.[20] In some cases, reductive elimination of cyclic haloalkenes has been applied as an alternative approach for the oriented preparation of alkyne species.[21] Encouraged by these advances and our ongoing interest in the exploration of catalytic carbene chemistry,[8,22] we envisioned that direct intramolecular cyclopropanation of alkyne embedded diazoacetate **1** would occur with the tethered alkene species (R = alkenyl) by avoiding steric strain in the cyclic transition states. Although the carbene/alkyne metathesis (CAM) process of the alkyne motif is kinetically favorable *via* 5- or 6-membered cyclic transition states,[23] the alkene species is more nucleophilic compared to the alkyne species. Moreover, by introducing an *ortho*-disubstituted benzene unit to bend the linear architecture, which will increase the probability of the reaction happening between these two reacting species, other intermolecular side reactions, such as end-to-end cyclization, or dimerization could be avoided. Herein, we report an efficient dirhodium(II)-catalyzed macrocyclization reaction of alkyne-containing diazoacetates **1** through intramolecular metal carbene cyclopropanation. This method provides a variety of 12- to 22-membered macrocyclic alkynes, which incorporate *ortho*-aryl, cyclopropane, and cyclopropene units, in good to excellent yields under mild reaction conditions (Scheme 1e).

The initial exploration was carried out with diazoacetate **1a** as the model substrate in dichloroethane (DCE) at 20 °C in the presence of 4 Å molecular sieve, which has shown a promising effect for the inhibition of the side reaction(s) in our previous study (Table 1).[8] We investigated a range of metal catalysts, including dirhodium, copper, and palladium complexes. Gratifyingly, all of them promote the reaction smoothly when **1a** is added slowly via syringe pump over 4 h under an argon atmosphere (entries 1-5), among which the dirhodium catalysts, both $Rh_2(OAc)_4$ and $Rh_2(esp)_2$, proved to be the better choices for this intramolecular cyclopropanation, providing macrocyclic alkyne **2a** as the only isolated product in 80% and 91% yields, respectively (entries 1 and 2). In the reported literature, both Cu- and Pd-catalysts have shown obvious advantages in metal carbene coupling reactions in comparison with the dirhodium catalysts.[24] In our case, the copper catalysts showed good catalytic activities, and the desired product **2a**

Table 1. Optimization of the reaction conditions.[a)]



Entry	Cat (x mol %)	Yields (%)[b)] **2a/3a**
1	$Rh_2(OAc)_4$ (1.0)	80/<5
2	$Rh_2(esp)_2$ (1.0)	91/<5
3	$Cu(hfacac)_2$ (5.0)	46/37
4	$Cu(OTf)_2$ (5.0)	35/30
5	$[PdCl(\eta^3\text{-}C_3H_5)]_2$ (5.0)	<5/85
6[c)]	$Rh_2(esp)_2$ (1.0)	61/<5
7[d)]	$Rh_2(esp)_2$ (1.0)	89/<5
8[e)]	$Rh_2(esp)_2$ (1.0)	91/<5
9[f)]	$Rh_2(esp)_2$ (1.0)	93/<5
10[g)]	$Rh_2(esp)_2$ (1.0)	88/<5

[a)] The reactions were carried out on a 0.2 mmol scale: to the mixture of corresponding catalyst, and 4 Å MS (100 mg) in DCE (2.0 mL), was added **1a** (54.0 mg, 0.2 mmol) in DCE (2.0 mL) *via* syringe pump over 4 h under argon atmosphere at 20 °C. [b)] Isolated yields. [c)] The reaction was carried out in one-pot. [d)] **1a** was added via syringe pump in 1.0 h. [e)] **1a** was added via syringe pump over 6.0 h. [f)] The reaction was carried out in one-pot in 20 mL DCM. [g)] The reaction was carried out in one-pot in 40 mL DCM.

was obtained only in moderate yields contaminated with dimerization by-product **3a** in almost the same amounts (entries 3 and 4), whereas the use of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ only led to by-product **3a** in 85% yield (entry 5). With $Rh_2(esp)_2$ as the catalyst, either in one-pot or by slow addition of **1a**, the by-product **3a** was not formed (entries 6-10). Comparable excellent yields were obtained by slowly adding the diazo compounds in 1 or 6 hours (entries 7 and 8) or in one-pot under diluted conditions (entries 9 and 10). Considering the cost of the solvent, slowly addition of the diazo compound was used (entry 2). We also investigated asymmetric catalysis for this reaction; although high yields were obtained when the reactions were catalyzed by chiral dirhodium catalysts, their *ee* values were very low (see Table S1 in SI for details, 3%~6% *ee*).

With the optimized reaction conditions in hand, the applicability of the protocol was extended to a variety of alkyne-containing diazoacetates **1** (Scheme 2). Both fluoro- and chloro- substituted phenyl on **1** could tolerate the reaction conditions, and the products **2b** and **2c** were generated as single diastereomers in 76% and 75% yields, respectively. Substrates with cyclohexyl or methyl substitutions on the methylene linkage did not affect the reaction profile, delivering the corresponding products **2d** and **2e** both in high yields, and two isomers were formed in the latter case. The

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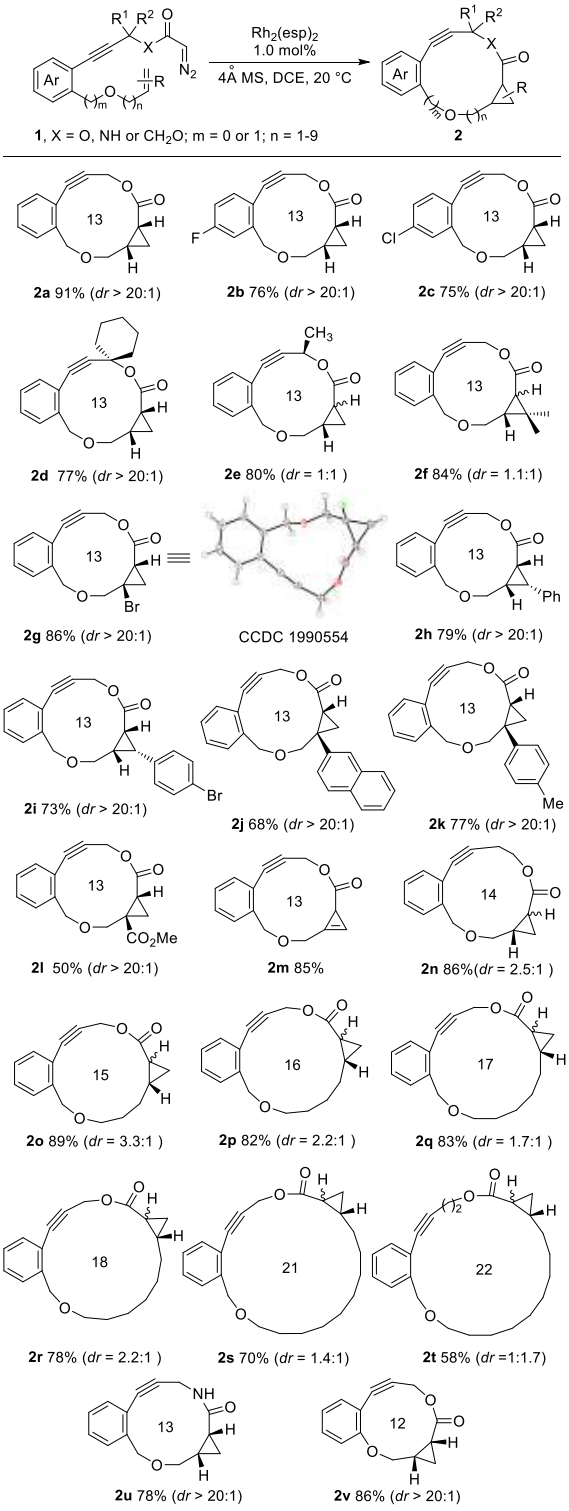
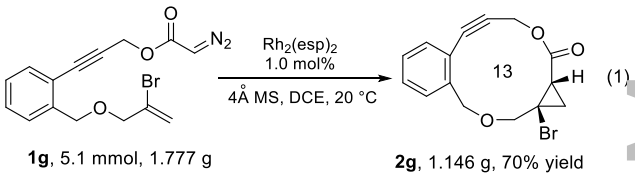


Scheme 2. Substrate scope of cycloalkynes. The reactions were carried out on a 0.2 mmol scale: to the mixture of $Rh_2(esp)_2$ (1.5 mg, 1.0 mol%), and 4 Å MS (100 mg) in DCE (2.0 mL), was added a solution of diazo compound **1** (0.2 mmol) in DCE (2.0 mL) *via* syringe pump over 4 h under argon atmosphere at 20 ℃, and the reaction was stirred for additional 1 h under these conditions. The yields are given in isolated yields.

trisubstituted alkene species worked well and provided **2f** in 84% yield with two diastereomers. Moreover, disubstituted alkenes, including those with bromo-, aryl, naphthyl, and ester substituents, provided the corresponding products in 50%-86% yields with excellent stereoselectivities (**2g-2l**). Notably, cyclopropenation with the diazoacetate that is tethered with a terminal alkyne occurred smoothly under these conditions, forming cycloalkyne **2m** that incorporates a cyclopropene unit in 85% yield. Subsequently, we surveyed these linear materials with different chain lengths, finding that macrocyclic alkynes with ring sizes from 14 to 22 were obtained in 58%-89% yields with moderate diastereoselectivities (**2n-2t**). The stereochemistry of these products was determined by NOE analysis (see Figure S1-4 in SI for details). Moreover, the amide-containing product **2u** and 12-membered cycloalkyne **2v** were isolated as single isomer in 78% and 86% yields, respectively. The structure of **2g** was confirmed by single-crystal X-ray diffraction analysis.[25]

To demonstrate the utility of current method, we performed the reaction on a gram scale (eq 1, 5.1 mmol) to provide 1.146 g pure **2g** in 70% yield. It should be mentioned that the easily transformable bromide survived under the current reaction conditions. Further applications in the construction of macrocyclic alkynes with structural diversity and broad functional group compatibility is envisioned.



In summary, we have developed an efficient dirhodium(II)-catalyzed macrocyclization of alkyne-containing diazoacetates through intramolecular metal carbene cyclopropanation, which provides a straightforward and practical access to a variety of 12- to 22-membered macrocyclic alkynes in good to excellent yields. The salient features of this reaction include mild conditions, amenable to the gram scale, good functional group tolerance, and providing unique cycloalkynes that incorporate *ortho*-aryl, cyclopropane, and cyclopropene units. Further applications of this method for the direct and effective construction of appealing macrocyclic frameworks with structural diversity could be envisioned.

Experimental Section

General Procedure for the Cyclopropanation Reaction (Scheme 2): To a 10-mL oven-dried vial containing a magnetic stirring bar, $Rh_2(esp)_2$ (1.5 mg, 1.0 mol%), and 4Å MS (100 mg) in DCE (2.0 mL), diazo compound **1** (0.2 mmol) in DCE (2.0 mL) was added *via* a syringe pump over 4 h under argon atmosphere at 20 ℃. After addition, the reaction mixture was stirred under these conditions until consumption of the material was complete (monitored by TLC, about 1 hour). Then the reaction mixture was

purified by column chromatography on silica gel without any additional treatment (hexanes : EtOAc = 15:1 to 10:1) to give the pure products **2** in moderate to high yields.

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[25] CCDC 1990554 contains the supplementary crystallographic data for **2g** in 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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Dirhodium(II)-Catalyzed Cyclopropanation of Alkyne-Containing α-Diazoacetates for the Synthesis of Cycloalkynes

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