VIP C–C Activation Very Important Paper

DOI: 10.1002/ange.201310100

Divergent Syntheses of Fused β-Naphthol and Indene Scaffolds by Rhodium-Catalyzed Direct and Decarbonylative Alkyne–Benzocyclobutenone Couplings**

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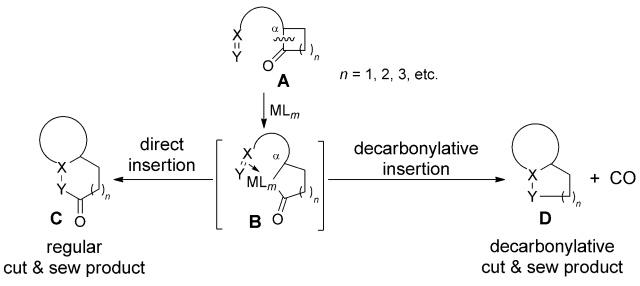
Abstract: *A tunable rhodium-catalyzed intramolecular alkyne insertion reaction proceeding through the C–C cleavage of benzocyclobutenones is described. Selective formation of either the direct or decarbonylative insertion product can be controlled by using different catalytic systems. A variety of fused β-naphthol and indene scaffolds were obtained in good yields with high functional group tolerance. This work illustrates a divergent approach to synthesize fused-ring systems by C–C activation/functionalization.*

Transition-metal-catalyzed C–C activation/functionalization offers unique opportunities to develop novel transformations, because it allows reorganization of bond connections leading to novel molecular structures with high complexity.[1] Lately, cleavage of a C–C bond followed by insertion of an unsaturated unit serves as a rapid and atom-economical[2] approach for constructing homologated or ring-expanded products.[3,11] In particular, the synthesis of fused-ring systems is benefited by this strategy. For instance, we recently developed a rhodium-catalyzed intramolecular carboacylation of olefins with benzocyclobutenones to construct chiral polyfused scaffolds.[4] Good yields and excellent regio- and enantioselectivity were obtained with a broad range of substrates. Such a "cut and sew" transformation[5] involves oxidative addition of a metal into the α C–C bond of a cyclic ketone to generate a key acylmetallacycle intermediate (**B**), which, followed by an intramolecular migratory insertion and reductive elimination, provides the fused-ring system **C** (Scheme 1).

On the other hand, it is well established that the acylmetal complexes (i.e. intermediate **B**) can also undergo reversible CO de-insertion reactions.[6,7] Thus, complementary to the direct insertion reaction (regular "cut and sew"), the corresponding decarbonylative "cut and sew" would provide an [*X* + *Y*-1]-type coupling by extruding CO from the substrate to give the fused ring **D** (Scheme 1), a process which remains largely elusive.[8,9] Herein, we describe our efforts in developing a divergent approach to realize both regular and decarbonylative "cut and sew" transformations through rhodium-catalyzed intramolecular couplings between benzocyclobutenones[10] and alkynes (Scheme 2B). The resulting β-naphthol and indene fused-ring products provided by this approach are useful synthetic building blocks,[11] and have also been found in a number of biologically important molecules (Figure 1).

Catalytic C–C σ-bond cleavage followed by alkyne insertion is of significant synthetic value particularly because it can introduce an olefin moiety which permits further functionalization of the substrate.[12] Alkyne insertion into the saturated cyclobutanones, thus giving cyclohexones, was first reported by Murakami et al. using a nickel catalyst, and a β-carbon elimination mechanism is proposed for the C–C activation step (Scheme 2A).[12e,13] For the unsaturated cyclobutenones, given their unsymmetrical structures, a site-selectivity issue arises concerning which C–C bond to cleave.[10] The intermolecular alkyne insertion into cyclobutenones was previously known to occur either by thermal heating[14] or through catalysis using nickel[15] or rhodium.[16] In all these cases, the C1–C4 bond is cleaved through a vinyl ketene intermediate. For the intramolecular alkyne insertion, we hypothesized that: 1) the alkyne group would serve as a directing group and guide metals to cleave the C1–C2 bond of benzocyclobutenones (Scheme 2B),[4] which, in turn, provides different site selectivity from that of the intermolecular insertion; 2) the resulting "cut and sew" products, conjugated enones, would undergo spontaneous tautomerization to give β-naphthols as the ultimate products.

To test our hypothesis, we started with benzocyclobutenone **1a** as a model substrate (see Table S1 in the Supporting Information; see Table 1 for structures). Wilkinson's catalyst



Scheme 1. A divergent approach for fused-ring synthesis: Regular and decarbonylative cyclization.

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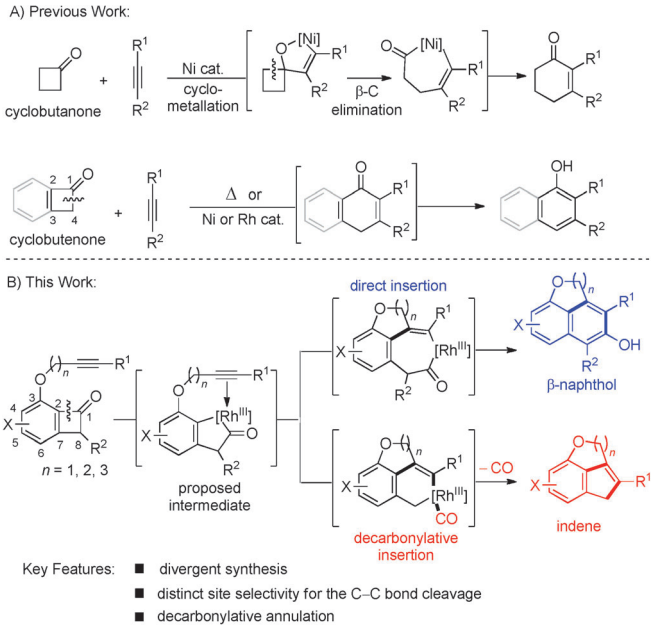
[**] We thank UT Austin and CPRIT for start-up funds, and the Welch Foundation (F 1781) for research grants. G.D. thanks ORAU for a New Faculty Enhancement Award. G.D. is a Searle Scholar. We also thank Prof. Siegel for helpful discussions, and Professors Sessler, Siegel, and Anslyn for the loan of chemicals. Dr. Lynch is acknowledged for X-ray crystallography. We thank Johnson Matthey for a generous donation of Rh salts.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201310100.



Scheme 2. C–C bond cleavage in cyclobutenones and cyclobutanones.

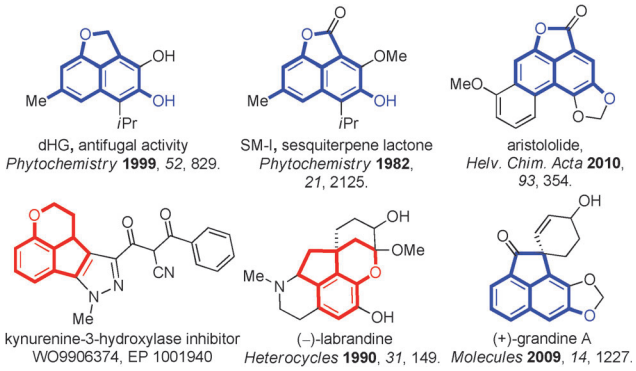
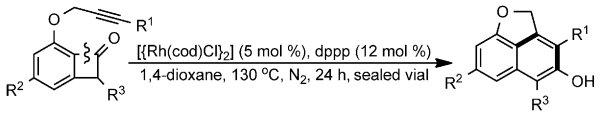
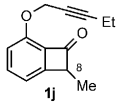
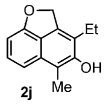
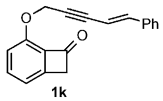
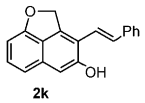


Figure 1. Representative examples of related bioactive molecules.

Table 1: Substrate scope for direct alkyne Insertion.[a]



Entry	Substrate		Product		Yield [%][b]
1	**1a**	R^1 = Et, R^2 = H	**2a**	R^1 = Et, R^2 = H	93
2	**1b**	R^1 = Ph, R^2 = H	**2b**	R^1 = Ph, R^2 = H	86
3	**1c**	R^1 = TMS, R^2 = H	**2c**	R^1 = TMS, R^2 = H	53
4	**1d**	R^1 = Me, R^2 = H	**2d**	R^1 = Me, R^2 = H	67
5	**1e**	R^1 = *p*-C_6H_4OMe, R^2 = H	**2e**	R^1 = *p*-C_6H_4OMe, R^2 = H	93
6	**1f**	R^1 = *p*-$C_6H_4NO_2$, R^2 = H	**2f**	R^1 = *p*-$C_6H_4NO_2$, R^2 = H	40
7	**1g**	R^1 = *p*-C_6H_4F, R^2 = H	**2g**	R^1 = *p*-C_6H_4F, R^2 = H	77
8	**1h**	R^1 = Et, R^2 = Me	**2h**	R^1 = Et, R^2 = Me	83
9	**1i**	R^1 = Et, R^2 = CO_2Me	**2i**	R^1 = Et, R^2 = CO_2Me	78
10	**1j**		**2j**		23[c]
11	**1k**		**2k**		56

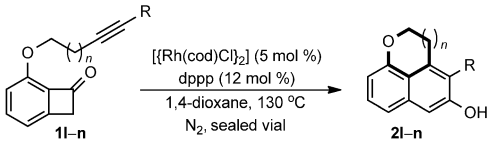
[a] Reaction conditions: [{Rh(cod)Cl}$_2$] (5 mol%), dppp (12 mol%), 1,4-dioxane, 130°C, 24 h, sealed vial. [b] Yields of isolated products. [c] 27% of **1j** was recovered; with 0.1 equiv of $ZnCl_2$ added, only 13% yield of **2j** was isolated. cod = 1,5-cyclooctadiene, TMS = trimethylsilyl.

$[RhCl(PPh_3)_3]$ was initially investigated, and the desired β-naphthol **2a** was isolated, albeit in low yield. Given the importance of bidentate ligands in the related olefin insertion reaction,[4] a series of bidentate phosphine ligands were examined. 1,3-Bis(diphenylphosphanyl)propane (dppp) was found to be most efficient, while the one-carbon unit longer 1,4-bis(diphenylphosphino)butane (dppb) or shorter 1,2-bis-(diphenylphosphino)ethane (dppe) ligand was less effective. A survey of different solvents revealed that 1,4-dioxane provided the highest yield for this transformation, whereas using other solvents resulted in different degrees of decomposition of the starting material or product.

With the optimized reaction conditions in hand, the scope of this reaction was examined (Table 1). Substrates containing alkyl, aryl, or alkenyl alkynes were converted into the corresponding β-naphthols in good to excellent yields.[17] Both electron-donating and electron-withdrawing substituents on the benzocyclobutenone rings were well tolerated (entries 8 and 9, Table 1). Moreover, a number of functional groups were found to be compatible with this transformation, including esters, ethers, trimethylsilyl, nitro groups, aryl fluorides, and conjugated olefins (entries 3, 5–7, 9 and 11, Table 1). Substitution at the C8-position of the benzocyclobutenone slowed the reaction, but the desired polysubstituted naphthol **2j** was nevertheless obtained (entry 10, Table 1). The alkynes **1l**/**1m** are more challenging substrates because the formation of six/seven-membered rings are kinetically less favorable compared to forming five-membered rings [Eq. (1) in Table 2]. Indeed, under the optimized reaction conditions, low conversions were observed for these substrates. However, we recently discovered that using a Lewis acid as a cocatalyst can dramatically enhance the reaction rate of olefin carboacylation, likely because of its coordination with the carbonyl group promoting both oxidative addition and reductive elimination.[4a,18]

Thus, we hypothesized that the related alkyne insertion would benefit from this Lewis-acid effect. To our delight, when 1 equivalent of $ZnCl_2$ was employed as an additive,

Table 2: $ZnCl_2$ as an additive in the formation of six- and seven-membered rings.



(1)

1l	$n=1$, R = Et	
	without $ZnCl_2$	70%, 48 h
	with 10 mol% $ZnCl_2$	81%, 24 h
	with 1 equiv $ZnCl_2$	91%, 24 h
	with 1 equiv $ZnCl_2$, but no [{Rh(cod)Cl}$_2$]/dppp	0%, 24 h
1m	$n=1$, R = Ph	
	without $ZnCl_2$	4%, 24 h
	with 10 mol% $ZnCl_2$	89%, 24 h
	with 1 equiv $ZnCl_2$	91%, 24 h
1n	$n=2$, R = Ph	
	without $ZnCl_2$	0%, 24 h
	with 10 mol% $ZnCl_2$	64%, 24 h
	with 1 equiv $ZnCl_2$, 7.5 mol% [{Rh(cod)Cl}$_2$], 18 mol% dppp	77%, 24 h

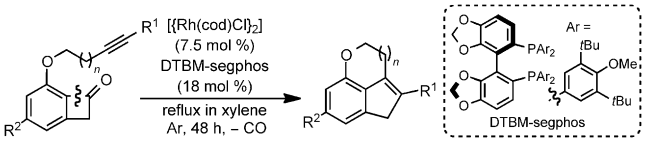
good to excellent yields of the six- and seven-membered fused rings were obtained [Eq. (1)]. A catalytic amount of $ZnCl_2$ (10 mol%) was also found to be effective, albeit with a slightly lower yield. We also found $ZnCl_2$ itself did not catalyze the reaction. The structure of **2l** was unambiguously characterized by X-ray crystallography (see the Supporting Information).

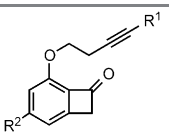
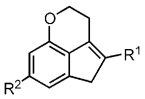
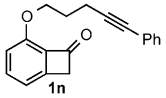
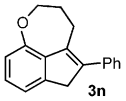
Although the direct decarbonylation of cyclobutanones to give cyclopropanes (ring contraction) has been known for almost two decades since the seminal work by Murakami, Ito, and co-workers,[19] C–C cleavage with subsequent decarbonylation and insertion of an unsaturated moiety has been much underdeveloped. The intermolecular decarbonylative couplings of cyclobutenediones and cyclobutenones with norbornene and ethylene were first reported by Kondo, Mitsudo, and co-workers,[8] and the only example of an intramolecular coupling of squaric acid derivatives and olefins was described by Yamamoto et al.[9] However, to the best of our knowledge, the decarbonylative coupling between any cyclic ketones and alkynes was previously unknown.[20]

The proposed decarbonylative "cut and sew" transformation (Scheme 2B) was explored using **1l** as the model substrate. Given the challenge of removing CO from the metal center, an open system reflux under an argon atmosphere with high-boiling-point solvents was chosen to facilitate CO extrusion from the reaction vessel (see Table S2).[21] Although using PPh_3 as the ligand provided a good conversion, it suffered from poor selectivity of the decarbonylative insertion versus the direct insertion. A number of bidentate phosphine ligands were subsequently investigated. Interestingly, the chiral DTBM-segphos provided the highest conversion and yield for the desired indene product. Although the exact reason why DTBM-segphos facilitates the decarbonylation pathway is unclear, control experiments indicated this four-carbon-linked bidentate ligand was much less effective in promoting the direct alkyne insertion reaction for substrate **1l**,[22] and likely to be a result of a less favorable reductive elimination step from the seven-membered acyl-metallacycle intermediate (Scheme 2B). Having examined a number of different solvents, mixed xylenes proved to be the optimal solvent. Finally, with a slight increase of the catalyst loading, the decarbonylative product, the fused-indene **3l** (see Table 3), was isolated in 64% yield.

The substrate scope for the decarbonylative alkyne insertion was then examined (Table 3).[23] In general, a range of indene-based fused rings were obtained in decent yields. Compared to the ethyl-substituted alkynes, when the aryl-substituted alkynes were employed as the coupling partner, the yields for the decarbonylative insertion were significantly increased (entries 2–7, and 11, Table 3), and is consistent with our earlier observation of the low cyclization rate of phenyl-substituted substrates (e.g. **1m**) in the absence of $ZnCl_2$ [Eq. (1)]. The *ortho*-methyl-substituted phenyl substrate **1t** gave lower yield, and is likely a result of

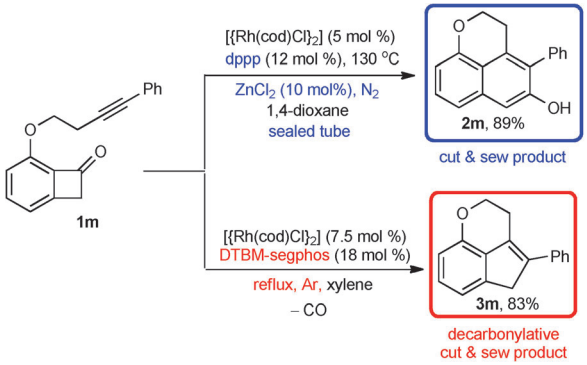
Table 3: Substrate scope for decarbonylative alkyne insertion.[a]



Entry	Substrate		Product		Yield [%][b]
					
1	**1l**	R^1 = Et, R^2 = H	**3l**	R^1 = Et, R^2 = H	64
2	**1m**	R^1 = Ph, R^2 = H	**3m**	R_1 = Ph, R^2 = H	83
3	**1o**	R^1 = *p*-C_6H_4OMe, R^2 = H	**3o**	R^1 = *p*-C_6H_4OMe, R^2 = H	64 (68)
4	**1p**	R^1 = *p*-C_6H_4F, R^2 = H	**3p**	R^1 = *p*-C_6H_4F, R^2 = H	75
5	**1q**	R^1 = *p*-C_6H_4Cl, R^2 = H	**3q**	R^1 = *p*-C_6H_4Cl, R^2 = H	75
6	**1r**	R^1 = 1-naphthyl, R^2 = H	**3r**	R^1 = 1-naphthyl, R^2 = H	76
7	**1s**	R^1 = *p*-$C_6H_4CO_2Me$, R^2 = H	**3s**	R^1 = *p*-$C_6H_4CO_2Me$, R^2 = H	62
8	**1t**	R^1 = *o*-C_6H_4Me, R^2 = H	**3t**	R^1 = *o*-C_6H_4Me, R^2 = H	28 (33)
9	**1u**	R^1 = Et, R^2 = Me	**3u**	R^1 = Et, R^2 = Me	57(62)
10	**1v**	R^1 = Et, R^2 = CO_2Et	**3v**	R^1 = Et, R^2 = CO_2Et	56
11	**1w**	R^1 = Ph, R^2 = Me	**3w**	R^1 = Ph, R^2 = Me	68 (73)
12	**1n**		**3n**		23 (48)

[a] Reaction conditions: [{Rh(cod)Cl}$_2$] (7.5 mol%), DTBM-segphos (18 mol%), xylenes, reflux, 48 h. [b] Yields of isolated products. Values within parentheses are yields based on recovered starting material.

unfavorable steric interactions during the cyclization (entry 8, Table 3). In addition, the seven-membered-ring fused indene product was also obtained (entry 12, Table 3). The structure of indene **3o** was unambiguously characterized by X-ray crystallography (see the Supporting Information).



(2)

In conclusion, we have developed a divergent approach to access fused β-naphthol and indene rings by the rhodium-catalyzed C–C activation of benzocyclobutenones [Eq. (2)]. The unique selectivity of cleaving the usually less-reactive C1–C2 bond distinguishes this direct alkyne insertion from other cyclobutenone–alkyne couplings.[14,15] It is also distinct from the saturated cyclobutanone-[12e] and cyclobutenol-mediated[3k,12f] alkyne insertion reactions because of their different mechanistic feature. Furthermore, it illustrates that the feasibility of a decarbonylative "cut and sew" pathway with C–C activation of benzocyclobutenones, enables an unusual [4+2−1] transformation. Finally, it demonstrates that the selectivity for either the direct or decarbonylative insertion can be controlled by choosing different ligands and other reaction conditions. Efforts towards expansion of the reaction scope (i.e. nitrogen-containing fused rings by both alkene and alkyne insertion), detailed mechanistic studies to enhance the catalyst activity, and application of this method to synthesize bioactive molecules are in progress.[24]

Received: November 20, 2013
Published online: January 21, 2014

Keywords: alkynes · C–C functionalization · cyclization · rhodium · synthetic methods

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[23] The propargyl ether substrates, that is, **1a**, did not provide any indene product, likely because significant ring strain would be generated if the five-membered fused-indene product was formed.

[24] CCDC 967148 (**2l**) and 967149 (**3o**) contain 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.

