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Chemospecific Intramolecular Buchner Reaction Catalyzed by Copper(II) Acetylacetonate

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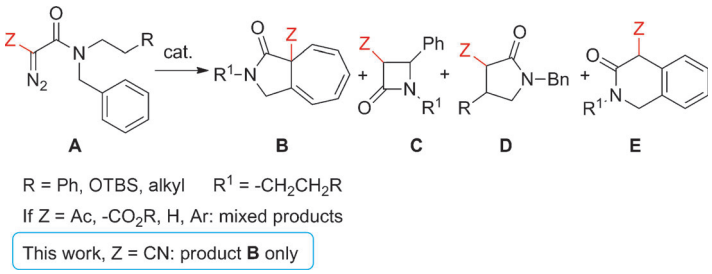
A chemospecific intramolecular Buchner reaction of *N*-benzyl-2-cyano-2-diazoacetamides catalyzed by inexpensive copper(II) acetylacetonate (acac) has been achieved to synthesize a variety of 9-aza-1-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-ones, 5,7-bicyclic products. The methodology involves sole chemoselectivity, an inexpensive metal catalyst, broad substrate scope, and moderate to excellent yields.

Introduction

The Buchner reaction, a two-stage reaction of the addition of a carbene to an aromatic ring and the ring expansion, is an efficient method to synthesize cyclohepta-1,3,5-triene derivatives. Although intramolecular Buchner reactions, especially, the intramolecular Buchner reactions of 2-substituted *N*-benzyl-2-diazoacetamides for the synthesis of 9-azabicyclo-[5.3.0]deca-2,4,6-trien-10-ones (5,7-bicyclic products), have been extensively studied,[1] 2-nonsubstituted,[2] 2-acetyl,[2j,3] 2-methoxycarbonyl,[2j,3c,4] and 2-aryl[5] substituted *N*-benzyl-2-diazoacetamides **A** generally gave rise to the corresponding 5,7-bicyclic products **B**, always accompanied by the aromatic and aliphatic C–H insertion products, such as β-lactams **C**, γ-lactams **D**, and δ-lactams **E**, even as major products, with Rh catalysts (Scheme 1). It has been reported that the α-substituents,[2b,3c,6] the ligands in the catalysts,[2b,7] and even the reaction conditions[2b] (e.g., the reaction temperature and solvents) have great effects on the chemo- and regioselectivities, and efforts have been devoted to achieve high chemoselectivity to obtain the desired products, such as **C**, **D**, and **E**, respectively.[2–7] However, to the best of our knowledge, the specific chemoselectivity towards the Buchner reaction for the preparation of **B** has not been realized in these reactions until now.



Scheme 1. Reactions of substituted *N*-benzyl-2-diazoacetamides.

Recently, Charette et al.[8] and Nani and Reisman[9] achieved chemospecific intermolecular and intramolecular cyclopropanations of 2-diazo-2-cyanoacetyl compounds. In their reactions, the cyano group plays a crucial role in the sole chemoselectivity. The metal carbenoids derived from α-diazo-β-ketonitriles adopt an out-of-plane conformation, so they are more electrophilic than those derived from α-diazo-β-nitro/acyl acetamides and tend to undergo cyclopropanation rather than the C–H insertion.[2b] However, the cyano group is less sterically bulky, which minimizes the destabilizing nonbonding interactions between the metal carbenoid and the arene/alkene moiety in the cyclopropanation transition-sate structure.

In the Buchner reactions studied previously, Rh^{II} catalysts were the most efficient, universal, and widely used metal catalysts.[2–7] However, they are very expensive and not abundant in the Earth.[10] Some relatively cheaper metal catalysts, such as Au,[11] Ru,[12] and Ag,[13] have also been used in the catalysis of the reaction, but with limited application. Cu salts are one class of the most inexpensive metal catalysts and have been applied in carbene-related reactions with excellent catalytic performance.[14] Moreover, Cu^{II} catalysts provide better selectivity for the cyclopropanation than the C–H insertion, even in the systems in which the C–H insertion is geometrically favorable.[9,15] As cyclopropanation is the first stage of the Buchner reaction, the use of Cu^{II} catalysts in the Buchner reaction may probably improve their yields to make the reactions economical and practical.

Herein, we present an inexpensive $Cu(acac)_2$-catalyzed and chemospecific intramolecular Buchner reaction of *N*-benzyl-2-cyano-2-diazoacetamides with a wide substrate scope. The re-

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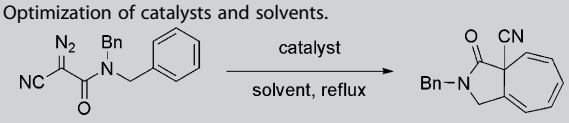
action displays the following advantages: 1) sole chemoselectivity—only Buchner reaction products are obtained; 2) only a nonprecious metal catalyst $Cu(acac)_2$ is used; 3) wide substrate scope—various functional groups are tolerated on the aromatic group in the substrates.

Results and Discussion

N,*N*-Dibenzyl-2-cyano-2-diazoacetamide (**1a**) was prepared from *N*,*N*-dibenzyl-2-cyanoacetamide and triflic azide in the presence of triethylamine[16] and selected as a model to optimize the reaction conditions (Table 1). In all explored solvents, only the desired Buchner reaction product, the 5,7-bicyclic product 9-aza-9-benzyl-1-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one (**2a**), was obtained with slightly different yields under the catalysis of $Rh_2(OAc)_4$ (Table 1, entries 1–5). The catalyst dirhodium(II) caprolactamate [$Rh_2(cap)_4$] with an electron-donating ligand resulted in a decrease in the reaction rate, which required a longer reaction time (Table 1, entry 6). However, different Rh catalysts did not show a clear difference in either chemoselectivity or yield (Table 1, entries 6 and 7). This phenomenon is different from that reported,[2b,7] in which the chemoselectivity depends clearly on the ligands coordinated to Rh. The inexpensive catalyst Co(TDMPP) [TDMPP = tris(2,6-dimethoxyphenly)phosphine] did a poor job in the reaction (Table 1, entry 8). Cupric(II) acetoacetate [$Cu(acac)_2$], a very cheap and easy-to-prepare catalyst,[17] showed a good result and gave rise to the desired product in 60% yield with only 0.5 mol% catalyst loading. Therefore, from an economic viewpoint, we decided to further optimize the reaction conditions with this cheap catalyst.[18] If we increased the catalyst loading, the yield reached 94%, but the reaction time did not decrease (Table 1, entries 9–12). To perform the reaction more efficiently, we changed to a solvent mixture of toluene and 1,2-dichloroethane (DCE) with a higher boiling point, which resulted in the successful reduction of the reaction time to only 0.5 h with a good yield (Table 1, entries 13 and 14). Other cheap Cu^{II} catalysts cupric acetate hydrate and cupric chloride dihydrate also catalyzed the reaction very well (Table 1, entries 15 and 16). Finally, 5 mol% $Cu(acac)_2$ and DCE were selected as the optimized conditions and used in the following studies.

Table 1. Optimization of catalysts and solvents.



1a **2a**

Entry	Solvent	Catalyst	Catalyst loading [%]	*t* [h]	Yield [%][a]
1	toluene	$Rh_2(OAc)_4$	1	0.5	69
2	benzene	$Rh_2(OAc)_4$	1	0.5	69
3	DCM	$Rh_2(OAc)_4$	1	0.5	70
4	$CHCl_3$	$Rh_2(OAc)_4$	1	0.5	61
5	DCE	$Rh_2(OAc)_4$	1	0.5	68
6	DCM	$Rh_2(cap)_4$[b]	0.5	40	59
7	DCM	$Rh_2(oct)_4$	0.5	0.5	63
8	DCM	Co(TDMPP)[c]	1	48	trace[d]
9	DCM	$Cu(acac)_2$	0.5	48	60
10	DCM	$Cu(acac)_2$	1	48	69
11	DCM	$Cu(acac)_2$	2	48	79
12	DCM	$Cu(acac)_2$	5	48	94
13	toluene	$Cu(acac)_2$	5	0.5	90
14	DCE	$Cu(acac)_2$	5	0.5	90
15	DCE	$Cu(OAc)_2 \cdot H_2O$	5	0.5	87
16	DCE	$CuCl_2 \cdot 2H_2O$	5	0.5	86

[a] Isolated yield after column chromatography on silica gel. All reactions were performed on a 1 mmol scale in 10 mL of solvent. Diazo compound **1a** was dissolved in 5 mL of solvent and added dropwise with a syringe over 40 min. [b] Dirhodium(II) caprolactamate. [c] Cobalt(II) *meso*-tetrakis(4-methoxyphenyl)porphyrin. [d] Most of the diazo compound **1a** was recovered.

Various *N*-alkyl-*N*-benzyl-2-cyano-2-diazoacetamides **1** were prepared from the corresponding secondary amines[19] and cyanoacetic acid and investigated under the optimized reaction conditions. All reactions proceeded smoothly under the optimized reaction conditions to afford the Buchner reaction products **2** chemospecifically except for **1r** with an *N*-naphthalen-2-ylmethyl instead of *N*-benzyl groups, which stopped at the first stage of the Buchner reaction to give the cyclopropanation product **3r** (Table 2, entry 18). The results are summarized in Table 2. The diazoamide **1a** produced the desired product **2a** in the highest yield because the same two benzyl groups were on the amide (Table 2, entry 1). Even for *N*-benzyl-diazoamides **1a–f** with benzyl, primary, secondary, and tertiary alkyl groups on the nitrogen atom of the amide (Table 2, entries 1–6), only Buchner reaction products were obtained in all cases. No carbene C–H insertion product on the benzylic, primary, secondary, or tertiary C–H bond was observed, regardless of if the *N*-alkyl group is straight or branched, linear or cyclic, primary, secondary, tertiary, or the even more active benzylic group. However, higher yields were achieved if the *N*-alkyl groups were more sterically bulky. This can be rationalized by the preferred stable conformation of the metal carbene amide intermediates **I** (Figure 1). In the Newman projection of the intermediates, if R^1 is more bulky, conformation **I** is more favorable than **II**, in which two bulky groups exist in the gauche position because of steric hindrance.[2a] Conformation **I** is the reactive conformation that leads to the Buch-

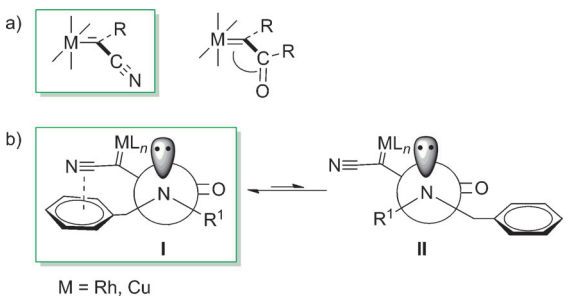
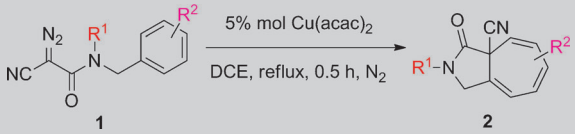
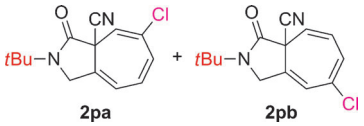
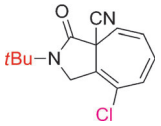
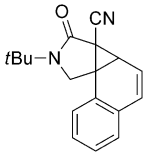


Figure 1. Explanation of the chemospecificity: a) Cyano group and carbenoid are in-plane, carbonyl group and carbenoid are out-of-plane; b) π–π Stacking stabilizes conformation **I**.

Table 2. Intramolecular Buchner reaction of *N*-benzyl-2-cyano-2-diazoacetamides catalyzed by $Cu(acac)_2$.



Entry	R^1, R^2	Product(s)	Yield [%][a]
1	Bn, H	**2a**	90
2	Me, H	**2b**	35
3	Cy, H	**2c**	67
4	*n*Pr, H	**2d**	70
5	*n*Bu, H	**2e**	71
6	*t*Bu, H	**2f**	80
7	*t*Bu, 4-Me	**2g**	58
8	*t*Bu, 4-OMe	**2h**	31
9	*t*Bu, 4-F	**2i**	81
10	*t*Bu, 4-Cl	**2j**	82
11	*t*Bu, 4-Br	**2k**	86
12	*t*Bu, 4-CF_3	**2l**	51
13	*t*Bu, 4-CO_2Me	**2m**	86
14	Cy, 4-CN	**2n**	46
15	*t*Bu, 4-NO_2	**2o**	71
16	*t*Bu, 3-Cl	 **2pa** + **2pb**	64[b]
17	*t*Bu, 2-Cl	 **2q**	86
18	*t*Bu, ($R^2C_6H_4$ = naphth-1-yl)	 **3r**	90

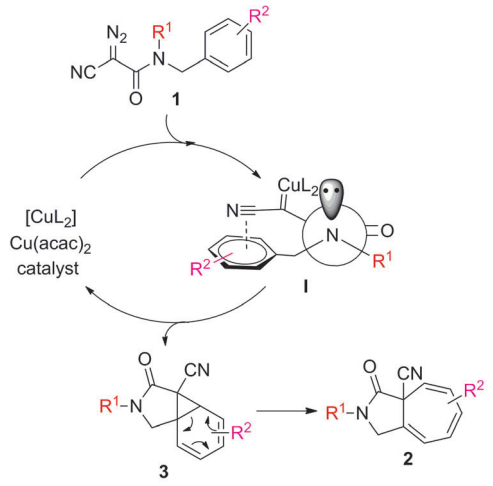
[a] Isolated yield. All reactions were performed under the optimized conditions. [b] Two products **2pa** and **2pb** were obtained in a 1:3 ratio after silica gel column chromatography.

ner reaction. As a result, *N*-benzyl-*N*-*tert*-butyl-2-cyano-2-diazoacetamide (**1f**) defeats other *N*-alkyl-*N*-benzyl-2-cyano-2-diazoacetamides in yield, except for *N*,*N*-dibenzyl-2-cyano-2-diazoacetamide (**1a**), which has two of the same *N*-benzyl groups. Therefore, an *N*-*tert*-butyl group is used as the N-protecting group to obtain higher yields for most of other substrates **1g–m** and **1o–r** (Table 2, entries 7–13 and 15–18). Diazoamides **1g–o** that have various substituents at the *para* position of benzyl group were studied. The substrates with both electron-withdrawing and electron-donating groups work well to afford only Buchner reaction products **2g–o** (Table 2, entries 7–15). For the *ortho*-substituted substrate **1q**, only one product **2q** was generated (Table 2, entry 17). However, the *meta*-substituted substrate **1p** produced two regioisomeric products **2pa** and **2pb** with a low regioselectivity (1:3; Table 2, entry 16). The *N*-naphthalen-2-ylmethyl substrate **1r** only generated the cyclopropanation product **3r** in an excellent yield instead of the 5,7-bicyclic product, which indicates that this substrate does not proceed to the second stage of the standard Buchner reaction (Table 2, entry 18).

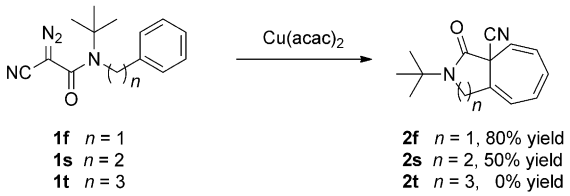
It has been observed that the steric effect of the *N*-alkyl group does not influence the chemoselectivity at all. The chemospecificity was observed in all cases even if R^1 was a less bulky group, such as methyl, *n*-propyl, and *n*-butyl groups. It is proposed that, compared to carbenes with other electron-withdrawing groups (e.g. acetyl and methoxycarbonyl groups), α-cyanocarbenes possess a particular electrophilicity, which is more preferable for the cyclopropanation because the cyano moiety adopts in an in-plane conformation and is less sterically hindered,[11c,d] whereas α-acetyl and methoxycarbonyl carbenes exist in an out-of-plane conformation. In addition, the π–π stacking interaction between the cyano and phenyl groups may play an important role to stabilize conformation **I** to result in the formation of the Buchner products chemospecifically. In our opinion, the π–π stacking interaction should play a more significant effect than steric hindrance in the stabilization of conformation **I** because the steric hindrance of the *N*-alkyl groups only impacts the yield rather than the chemoselectivity (Figure 1).

If we consider the intramolecular Buchner reaction mechanism, we proposed that 2-cyano-2-diazoamides **1** first generate copper carbene intermediates **I** by the release of nitrogen under the catalysis of $Cu(acac)_2$. The intermediate **I** undergoes an intramolecular cyclopropanation through the addition of the copper carbene to the benzene ring in the benzyl group to afford 3-alkyl-2-oxo-benzo[*e*]-3-azabicyclo-[3.1.0]hexane-1-carbonitriles **3**, which further undergo a ring expansion to give rise to the final Buchner reaction products **2** (Scheme 2). The first stage of the Buchner reaction is an electrophilic addition reaction of the metal carbene to the aromatic ring. Padwa and co-workers found that aromatic rings with a higher electron density were more accessible.[2b] However, in our case, we did not observe the same trend for the yield. The electronic effect has an unclear influence on the yield, and the cyclopropanation product **3r** was obtained in our reactions. The results suggest that the cyclopropanation step is the rate-determining step in Padwa's experiments but not in ours. The ring-expansion step could be the rate-determining step in our case.

After success in the synthesis of 5,7-bicyclic products by the Buchner reaction and understanding the reaction mechanism, we attempted to extend the reaction to prepare 6,7- and 7,7-bicyclic products (Scheme 3). *N*-*tert*-Butyl-2-cyano-2-diazo-*N*-(2-phenylethyl/3-phenylpropyl)acetamides (**1s** and **1t**) were prepared and subjected to the reaction. The results indicate that the 6,7-bicyclic product, 10-aza-10-*tert*-butyl-1-cyanobicyclo-[5.4.0]undeca-2,4,6-trien-8-one (**2s**), was successfully constructed in a moderate yield (50%),[20] but the 7,7-bicyclic ring failed possibly because of the long distance between the aromatic ring and the cyano group, which resulted in a weak π–π stack-



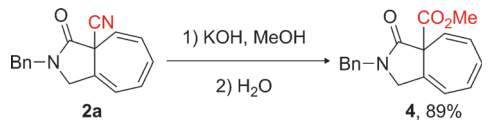
Scheme 2. Proposed mechanism for the $Cu(acac)_2$-catalyzed intramolecular Buchner reaction.



Scheme 3. Extension of the substrate scope.

ing interaction and more difficulty for the Buchner reaction to occur for diazoamide **1t**.

Finally, we tried to convert the cyano group into other functional groups. The cyano group was converted to a carboxylic acid methyl ester in 89% yield after treatment with KOH in methanol (Scheme 4). This strategy provides a chemospecific protocol to access 1-alkoxycarbonyl-substituted 5,7-bicyclic products, whereas the direct metal catalysis of 2-alkoxycarbonyl-*N*-benzyl-2-diazoacetamides results in mixed products (Scheme 1).[2j,3c,4]



Scheme 4. Transformation of the cyano group to a methoxycarbonyl group.

Conclusions

We realized the chemospecific intramolecular Buchner reaction of *N*-benzyl-2-cyano-2-diazoacetamides catalyzed by inexpensive copper(II) acetylacetonate to afford 9-aza-1-cyanobicyclo-[5.3.0]deca-2,4,6-trien-10-ones, the 5,7-bicyclic products, in moderate to excellent yields. The reaction is accessible to a broad substrate scope, regardless of the benzyl groups with various electron-withdrawing and -donating groups. Even the cyanodiazoacetamide that bears an *N*-2-phenylethyl group is also suitable for the synthesis of 10-aza-1-cyanobicyclo-[5.4.0]undeca-2,4,6-trien-11-one, the 6,7-bicyclic product. The current method is an economic, chemospecific, and green version of the intramolecular Buchner reaction that can be used to prepare 9-aza-1-cyanobicyclo[5.3.0]deca-2,4,6-trien-10-one-1-carboxylic acid derivatives chemospecifically through the transformation of the cyano group.

Acknowledgements

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Keywords: copper · fused-ring systems · homogeneous catalysis · nitrogen heterocycles · ring expansion

[1] J. J. Li, *Name reactions, 4th ed.*, Springer, Berlin, **2009**, pp. 78–79; and references cited therein.
[2] a) M. P. Doyle, M. S. Shanklin, H. Q. Pho, *Tetrahedron Lett.* **1988**, *29*, 2639–2642; b) A. Padwa, D. J. Austin, A. T. Price, M. A. Semones, M. P. Doyle, M. N. Protopopova, W. R. Winchester, A. Tran, *J. Am. Chem. Soc.* **1993**, *115*, 8669–8680; c) C. A. Merlic, A. L. Zechman, M. M. Miller, *J. Am. Chem. Soc.* **2001**, *123*, 11101–11102; d) M. P. Doyle, M. Yan, I. M. Phillips, D. J. Timmons, *Adv. Synth. Catal.* **2002**, *344*, 91–95; e) M. P. Doyle, W. H. Hu, A. G. H. Wee, Z. Y. Wang, S. C. Duncan, *Org. Lett.* **2003**, *5*, 407–410; f) Z. H. Qu, W. F. Shi, X. L. Jin, J. B. Wang, *Chin. J. Org. Chem.* **2003**, *23*, 988–995; g) Z. L. Chen, Z. Y. Chen, Y. Z. Jiang, W. H. Hu, *Synlett* **2004**, 1763–1764; h) Z. L. Chen, Z. Y. Chen, Y. Z. Jiang, W. H. Hu, *Tetrahedron* **2005**, *61*, 1579–1586; i) W. J. Liu, Z. L. Chen, Z. Y. Chen, W. H. Hu, *Tetrahedron: Asymmetry* **2005**, *16*, 1693–1698; j) C. P. Park, A. Nagle, C. H. Yoon, C. L. Chen, K. W. Jung, *J. Org. Chem.* **2009**, *74*, 6231–6236; k) J. X. Wang, B. Stefane, D. Jaber, J. A. I. Smith, C. Vickery, M. Diop, H. O. Sintim, *Angew. Chem. Int. Ed.* **2010**, *49*, 3964–3968; *Angew. Chem.* **2010**, *122*, 4056–4060; l) V. K.-Y. Lo, Z. Guo, M. K.-W. Choi, W.-Y. Yu, J.-S. Huang, C.-M. Che, *J. Am. Chem. Soc.* **2012**, *134*, 7588–7591.
[3] a) F. Zaragoza, G. Zahn, *J. Prakt. Chem.* **1995**, *337*, 292–298; b) F. Zaragoza, *Tetrahedron* **1995**, *51*, 8829–8834; c) C. H. Yoon, A. Nagle, C. Chen, D. Gandhi, K. W. Jung, *Org. Lett.* **2003**, *5*, 2259–2262.
[4] a) D. L. Whitehouse, K. H. Nelson, S. N. Savinov, R. S. Lowe, D. J. Austin, *Bioorg. Med. Chem.* **1998**, *6*, 1273–1282; b) C. J. Moody, S. Miah, A. M. Z. Slawin, D. J. Mansfield, I. C. Richards, *J. Chem. Soc. Perkin Trans. 1* **1988**, 4067–4075.
[5] J. Yang, H. Song, X. Xiao, J. Wang, Y. Qin, *Org. Lett.* **2006**, *8*, 2187–2190.
[6] a) H. M. L. Davies, R. E. J. Beckwith, *Chem. Rev.* **2003**, *103*, 2861–2903; b) H. M. L. Davies, E. G. Antoulinakis, *J. Organomet. Chem.* **2001**, *617–618*, 47–55; c) M. P. Doyle, M. S. Shanklin, S. M. Oon, H. Q. Pho, F. R. van de Heide, W. R. Veal, *J. Org. Chem.* **1988**, *53*, 3384–3386; d) A. G. H. Wee, B. Liu, L. Zhang, *J. Org. Chem.* **1992**, *57*, 4404–4414; e) C. H. Yoon, M. J. Zaworotko, B. Moulton, K. W. Jung, *Org. Lett.* **2001**, *3*, 3539–3542; f) P. M. P. Gois, C. A. M. Afonso, *Eur. J. Org. Chem.* **2003**, 3798–3810; g) P. M. P. Gois, C. A. M. Afonso, *Eur. J. Org. Chem.* **2004**, 3773–3788.
[7] a) S. Miah, A. M. Z. Slawin, C. J. Moody, S. M. Sheehan, J. P. M. Marino, A. Semones, A. Padwa, I. C. Richards, *Tetrahedron* **1996**, *52*, 2489–2514; b) C. J. Moody, S. Miah, A. M. Z. Slawin, D. J. Mansfield, I. C. Richards, *Tetrahedron* **1998**, *54*, 9689–9700; c) M. Prein, P. J. Manley, A. Padwa, *Tetrahedron* **1997**, *53*, 7777–7794; d) M. P. Doyle, J. Tauton, H. Q. Pho, *Tetrahedron Lett.* **1989**, *30*, 5397–5400.
[8] V. N. G. Lindsay, D. Fiset, P. J. Gritsch, S. Azzi, A. B. Charette, *J. Am. Chem. Soc.* **2013**, *135*, 1463–1470.
[9] R. R. Nani, S. E. Reisman, *J. Am. Chem. Soc.* **2013**, *135*, 7304–7311.
[10] M. P. Doyle, *J. Org. Chem.* **2006**, *71*, 9253–9260.
[11] I. Rivilla, B. P. Gomez-Emeterio, M. R. Fructos, M. M. Diaz-Requejo, P. J. Perez, *Organometallics* **2011**, *30*, 2855–2860.
[12] B. R. Galan, M. Gembicky, P. M. Dominiak, J. B. Keister, S. T. Diver, *J. Am. Chem. Soc.* **2005**, *127*, 15702–15702.

[13] C. J. Lovely, R. G. Browning, V. Badarinarayana, H. V. R. Dias, *Tetrahedron Lett.* **2005**, *46*, 2453 – 2455.
[14] a) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704 – 724; b) X. Zhao, Y. Zhang, J.-B. Wang, *Chem. Commun.* **2012**, *48*, 10162 – 10173.
[15] a) D. H. Rogers, J. C. Morris, F. S. Roden, B. Frey, G. R. King, F.-W. Russkanmp, R. A. Bell, L. N. Mander, *Pure Appl. Chem.* **1996**, *68*, 515 – 522; b) S. Levin, R. R. Nani, S. E. Reisman, *Org. Lett.* **2010**, *12*, 780 – 783; c) S. Levin, R. R. Nani, S. E. Reisman, *J. Am. Chem. Soc.* **2011**, *133*, 774 – 776.
[16] D. Marcoux, S. Azzi, A. B. Charette, *J. Am. Chem. Soc.* **2009**, *131*, 6970 – 6972.
[17] a) L. David, C. Craciun, O. Cozar, V. Chis, C. Agut, D. Rusu, M. Rusu, *J. Mol. Struct.* **2001**, *563 – 564*, 573 – 578; b) J. P. Muena, M. Villagran, J. Costamagna, M. Aguirre, *J. Coord. Chem.* **2008**, *61*, 479 – 489.
[18] Cu catalysts can improve the selectivity for cyclopropanation (the first stage of the Buchner reaction) compared with Rh catalysts, see Ref. [11]. However, in our case, both Cu and Rh catalysts show the same chemospecificity (the Buchner reaction) and very close yields for the same kind of metal complexes.
[19] J. X. Xu, R. C. Wang, *Arkivoc* **2010**, (*9*), 293 – 299.
[20] In the intramolecular cyclopropanation of α-diazo-β-ketonitriles published by Reisman et al., their reactions did not lead to the ring opening of the cyclopropane derivatives. However, after we analyzed the NMR spectra of **21 h** in their paper and compared it with our spectra, we found that their compound **21 h** corresponds to **2 s** in this text, and **21 d** should also be a ring-opening product. See Ref. [9].

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