Pd-catalyzed Cyclization of Terminal Alkynes using Diazonaphthoquinones: Synthesis of Naphtho[1,2-b]furans

doi: https://doi.org/10.1246/cl.180803

Pd-catalyzed Cyclization of Terminal Alkynes using Diazonaphthoquinones: Synthesis of Naphtho[1,2-*b*]furans

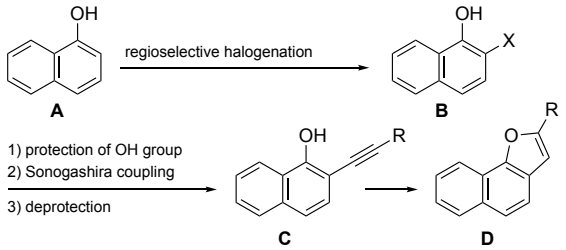
Shuhei Takahashi, [1] Hirokazu Shimooka, [1] Tatsuo Okauchi [1] and Mitsuru Kitamura *[1]
[1] *Department of Applied Chemistry, Graduate School of Engineering, Kyushu Institute of Technology, 1-1 Sensuicho, Tobata, Kitakyushu, 804-8550*

E-mail: kita@che.kyutech.ac.jp

Naphtho[1,2-*b*]furans were synthesized via a Pd-catalyzed reaction of diazonaphthoquinones and terminal alkynes in the presence of CuI and diisopropylamine. This method was then successfully applied to the synthesis of natural product, furomollugin.

Keywords: Diazo compound, Palladium, Naphthofuran

The main text of the article should appear here with headings as appropriate. Naphthofuran and its derivatives, which are often found in nature, have significant biological and pharmacological properties.[1] Naphthofurans can synthesized in a method similar to the preparation of benzofuran, which involves the cyclization of 2-alkynyl-1-phenol derivatives.[2,3] However, several synthetic challenges have remained with respect to the preparation of the precursor for this cyclization. For example, in the preparation of 2-alkynyl naphthol **C**, which is the precursor for naphtho[1,2-*b*]furan **D**, it is required to perform a regioselective halogenation of naphthol **A** and a series of protection and deprotection reactions of the hydroxyl group (Scheme 1).[4]



Scheme 1. Synthesis of naphtho[1,2-*b*]furan.

2-Diazonaphthalen-1-(*2H*)-ones (diazonaphthoquinones, DNQs)[5] are unique α-diazocarbonyl compounds that have an aryl diazonium resonance form (Figure. 1) and are commonly used as photoresists.[6] DNQs are regarded as protected naphthol derivatives and are potentially good aromatic building block, especially for naphthol derivatives. Previously, we have developed an efficient regioselective method for the synthesis of DNQs from the corresponding naphthols via a diazo-transfer with 2-azido-1,3-dimethylimidazolinium chloride (ADMC).[7] This approach allowed the regioselective synthesis of 2-diazonaphthalen-1-(*2H*)-ones from 1-naphthols through a reaction with ADMP. Additionally, we have also investigated the metal-catalyzed synthesis of substituted-naphthol derivatives using DNQs.[8,9]

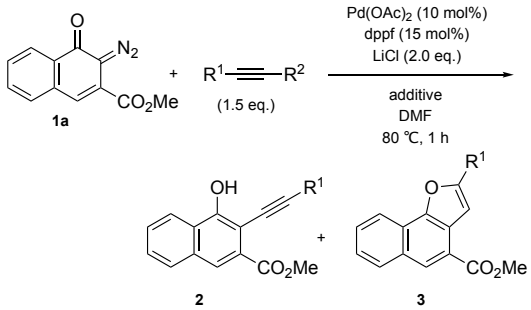
Recent studies have extensively investigated the Pd-catalyzed cross coupling using α-diazocarbonyl compounds via a migratory insertion of a ligand on palladium carbene.[10,11] In fact, we have already successfully synthesized 2-arylnaphthol through a $Pd(OAc)_2$-catalyzed cross coupling between DNQ and aryl boronic acid.[9a] In a continuation study on the Pd-catalyzed cross-coupling reaction of DNQ, we focused on the reaction with alkyne derivatives.

Although the metal-catalyzed reaction between DNQ and alkyne has not yet been reported, reactions between α-diazocarbonyl compounds and alkynes have been previously attempted and several efficient methodologies such as furan synthesis,[12] alkynylation,[13] and allenylation[14] have been developed. In the furan synthesis approach, the Rh-catalyzed reaction via cyclopropenation and the successive ring opening reaction were initially developed,[12a] with several metals being tested for the reactions.[12] Recently, Wang et al. reported the Cu-catalyzed synthesis of furan derivatives through a cascade coupling/cyclization of terminal alkynes using α-diazocarbonyl compounds via Cu-carbene.[12k, l]

In this work, we examined the Pd-catalyzed reaction of DNQ with alkyne, and developed a new method for the synthesis of naphtho[1,2-*b*]furan.

Our study was initiated with the reaction of alkynyl stannane and DNQ in the presence of Pd(0), with the aim to form 2-alkynynaphthalene. The cross-coupling between (tert-butyldimethylsilyl)ethynyl stannane and DNQ 1a proceeded with the addition of catalytic amounts of $Pd(OAc)_2$ and 1,1'-bis(diphenylphosphino)ferrocene (DPPF) in the presence of LiCl in DMF to afford 2-alkynyl naphthalene **2** (Table 1, run 1). In the reaction with alkyl- and phenyl-substituted alkynyl stannanes, the formation of 2-alkynyl naphthalenes **2** was initially observed by thin layer chromatography (TLC), but these were later consumed to afford naphtho[1,2-*b*]furan **3** (runs 2 and 3). By adding CuI to the reaction mixture, the formation of 2-alkynyl naphthalene **2** was not detected, and naphthofuran **3c** was obtained as a sole product (run 4). In addition, when the reaction was carried out using 1-hexyne as a coupling partner via copper acetylide in the presence of K_2CO_3, naphthofuran was formed (run 5). Therefore, naphtho[1,2-*b*]furan derivatives could be successfully synthesized by the Pd-catalyzed reaction of DNQ without using toxic alkynyl stannanes.[15] In order to develop an efficient synthetic method of naphtho[1,2-*b*]furan in particular, we then focused on the Pd-catalyzed reaction of DNQ and terminal alkynes in the presence of Cu salt.

Table 1. Pd-catalyzed coupling of DNQ **1a** and alkynyl stannanes.



Run	R^1	R^2	Additive (equiv.)	Product (Yield/%)
1[a]	TBS	*n*-Bu_3Sn	-	**2a** (46) **3a** (0)
2[a]	Ph	*n*-Bu_3Sn	-	**3b** (40)
3[a]	*n*-Bu	*n*-Bu_3Sn	-	**3c** (24)
4[a]	*n*-Bu	*n*-Bu_3Sn	CuI (2)	**3c** (68)
5[b]	*n*-Bu	H	CuI (2) K_2CO_3 (2)	**3c** (70)

[a]The reaction was performed at 80 °C as a bath temperature. [b] The reaction was performed in the presence of 1-hexyne (3.0 equiv.) and K_2CO_3 (2.0 equiv.) at 40 °C for 30 min and then 60 °C for 40 min.

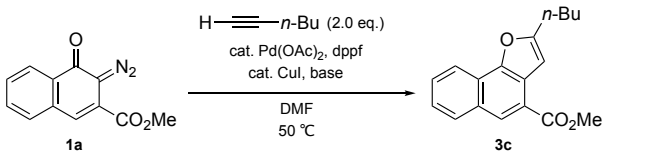
Initially, the reaction conditions were optimized from the reaction between DNQ **1a** and 1-hexyne (Table 2). When the reaction was carried out at 50 °C with 10 mol% $Pd(PPh_3)_4$, 30 mol% CuI, and 2 equiv. K_2CO_3 in DMF for 3 h, the simple coupling product **2** was not obtained and instead, naphthofuran **3c** was obtained in 18% yield (run 1). Then, we examined several combinations of palladium, phosphine, and copper reagents (runs 2-4). As a result, the use of $Pd(OAc)_2$ with DPPF in combination with CuI improved the reaction significantly, giving **3c** in 69% yield (run 4). In addition, *i*-Pr_2NH was found to be the best base among the ones tested (runs 4-7), with naphthofuran **3c** being formed in 87% when 1.2 equiv. of *i*-Pr_2NH was used (run 8).

Further optimization studies on the reaction conditions, including solvents (runs 9-12) and catalyst loading (runs 8 and 13), revealed that 1.5 mol% $Pd(OAc)_2$ with 2.2 mol% DPPF and 4.5 mol% CuI in DMF in the presence of 1.2 equiv. *i*-Pr_2NH at 50 °C efficiently afforded **3a** in 87% yield (Run 13). Although **3a** was still obtained in a reasonable yield (72%) when catalytic amounts (10 mol%) of *i*-Pr_2NH were used instead (run 14), no cyclized product **3a** was formed in the absence of base (run 15). As shown from the results of runs 16-18, the addition of a Pd catalyst, Cu salt, and DPPF is indispensable for this cyclization reaction.

Notably, when Pd(0) complex such as $Pd_2(dba)_3$ [tris(dibenzylideneacetone)dipalladium] was used instead of $Pd(OAc)_2$, **3a** was obtained in 89% (run 19). In the reaction with $Pd_2(dba)_3$, the presence of DPPF was also important for the efficient cyclization (runs 19 and 20).

These results suggested that the $Pd(OAc)_2$-catalyzed reaction proceeded via a Pd(0)-cycle, and that DPPF was used not only as a reductant of the Pd(II) complex but also as a suitable ligand for the Pd(0) complex in the cyclization.

Table 2. Optimization studies on the synthesis of naphthofuran **3c**[a]



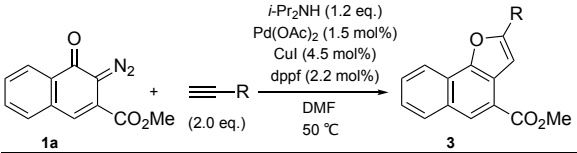
Run	$Pd(OAc)_2$ (mol%)	DPPF (mol%)	CuI (mol%)	Base (equiv.)	T[b] (h)	Yd[b] (%)
1	-[c]	-	30	K_2CO_3[d]	3	18
2	10	-[e]	30	K_2CO_3[d]	2	22
3	10	-[f]	30	K_2CO_3[d]	2	3
4[g]	10	15	30	K_2CO_3[d]	1	69
5	10	15	30	Et_3N[d]	4.5	62
6	10	15	30	Et_2NH[d]	5	60
7	10	15	30	*i*-Pr_2NH[d]	5	77
8	10	15	30	*i*-Pr_2NH[h]	4.5	83
9[i]	10	15	30	*i*-Pr_2NH[h]	7	45
10[j]	10	15	30	*i*-Pr_2NH[h]	8	9
11[k]	10	15	30	*i*-Pr_2NH[h]	6	42
12[l]	10	15	30	*i*-Pr_2NH[h]	4.5	26
13	1.5	2.2	4.5	*i*-Pr_2NH[h]	4.5	87
14	1.5	2.2	4.5	*i*-Pr_2NH[m]	9	72
15	1.5	2.2	4.5	-	5	0
16	-	2.2	4.5	*i*-Pr_2NH[h]	5	0
17	1.5	2.2	-	*i*-Pr_2NH[h]	4	0
18	1.5	-	4.5	*i*-Pr_2NH[h]	5	trace
19	-[n]	2.2	4.5	*i*-Pr_2NH[h]	3	89
20	-[n]	-	4.5	*i*-Pr_2NH[h]	5	2

[a]Reaction conditions: **1a** (0.5 mmol), 1-hexyne (2.0 equiv.), cat. $Pd(OAc)_2$, CuI, DPPF, base in DMF (5 mL) at 50 °C. [b]T: Temperature. Yd: Yield. [c]10 mol% $Pd(PPh_3)_4$. was used instead of $Pd(OAc)_2$. [d]2 equiv. of base were used. [e]30 mol% PPh3 was used instead of DPPF. [f]30 mol% *t*-$Bu_3P{\cdot}HBF_4$ was used instead of DPPF. [g]When $Cu(MeCN)_4PF_6$, $Cu(OTf)_2$ $Cu(OAc)_2$, and Cu powder was used instead of CuI, **3c** was obtained in 59, 60, 49, and 12%, respectively. [h]1.2 equiv. of base was used. [i]In THF. [j]In MeCN. [k]In toluene. [l]In $(ClCH_2)_2$. [m]0.1 equiv. of base was used. [n]0.75 mol% $Pd_2(dba)_4$ was used instead of $Pd(OAc)_2$.

Then, having established the optimized reaction conditions, the scope of the cyclization reaction of terminal alkynes and DNQ was explored.

First, the substituent effect of terminal alkynes was examined (Table 3). Various terminal alkynes with alkyl, aryl, and silyl groups, including bulky *tert*-butyl and *tert*-butyldimethylsilyl (TBS) groups, reacted with DNQ **1a** to afford the corresponding naphthofurans. However, no cyclized product was obtained from the reaction with propargyl alcohol or alkynes substituted with strong electron withdrawing groups (runs 3, 7, 8).

Table 3. Reaction of DNQ with various terminal alkynes[a]



Run	R	Time (h)	**3**	Yield (%)
1	*t*-Bu	8.5	**3d**	62
2	CH_2OTBS	4	**3e**	89
3	CH_2OH	2	**3f**	0
4	Ph	4	**3b**	83
5	*p*-$MeOC_6H_4$	6.5	**3g**	78
6	*p*-$CF_3C_6H_4$	7.5	**3h**	74
7	*p*-$NO_2C_6H_4$	9	**3i**	0
8	CO_2Me	6	**3j**	0
9	TBS	4	**3a**	84

[a]Reaction conditions: **1a** (0.5 mmol), alkyne (2.0 equiv.), $Pd(OAc)_2$ (1.5 mol%), CuI (4.5 mol%), dppf (2.2 mol%), *i*-Pr_2NH (1.2 equiv.) in DMF (5 mL) at 50 °C.

The reaction of **1a** with diyne **4** also proceeded to afford double cyclization product **5** in 66% yield (Eq. 1).

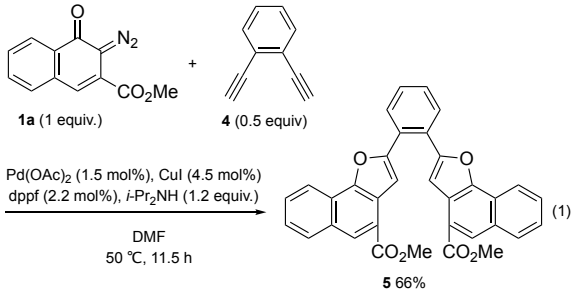
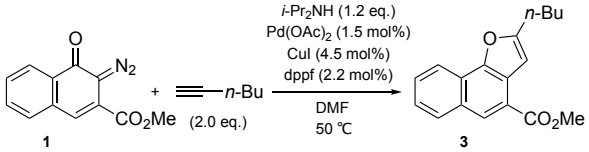


Table 4. Reaction of various DNQs with 1-hexyne[a]



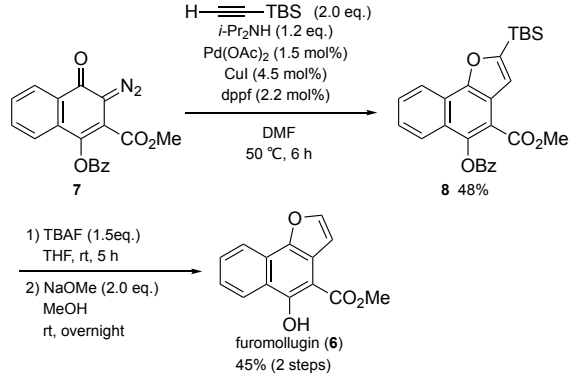
Run	R	**1**	Time (h)	**3**	Yield (%)
1	CO_2Et	**1b**	9	**3k**	78
2	CO_2n-Pr	**1c**	6.5	**3l**	88
3	CO_2Ph	**1d**	4.5	**3m**	62
4	H	**1e**	10	**3n**	9
5	Me	**1f**	10	**3o**	8
6	CH_2OMe	**1g**	10	**3p**	14

[a]Reaction conditions: **1** (0.5 mmol), 1-hexyne (2.0 equiv.), $Pd(OAc)_2$ (1.5 mol%), CuI (4.5 mol%), dppf (2.2 mol%), *i*-Pr_2NH (1.2 equiv.) in DMF (5 mL) at 50 °C.

Next, various 3-substitued DNQs **1** were examined for the naphthofuran formation. As a result, we found that the cyclization was strongly affected by the substituents (Table 4). When substituent R at C-3 position of DNQ was an ester group, the cyclization proceeded efficiently (runs 1-3). However, unsubstituted or alkyl-group substituted DNQ **1e-g** gave naphthofuran **3n-p** in lower yield (runs 4-6).

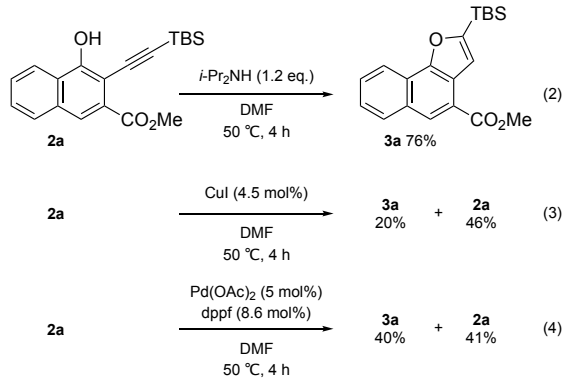
To demonstrate the efficiency of our newly developed method for naphthofuran formation, we addressed the synthesis of the natural product furomollugin (**6**) (Scheme 2).[16]

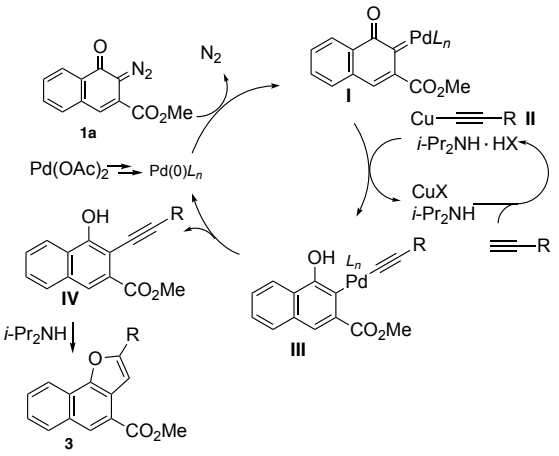
The Pd-catalyzed cyclization of 3-methoxycarbonyl-4-benzoyloxy diazonaphthoquinone **7** with (*tert*-butyldimethylsilyl)acetylene in the presence of CuI proceeded expectedly to afford naphthofuran **8** in 48% yield. After the removal of the TBS group using tetrabutylammonium fluoride (TBAF) and the subsequent removal of the benzoyl group via treatment with sodium methoxide, furomollugin (**6**) was successfully synthesized.



Scheme 2. Synthesis of furomollugin (**6**)

Scheme 2 outlines the possible reaction mechanism for the Pd-catalyzed naphthofuran formation from diazonaphthoquinone **1a** and a terminal alkyne in the presence of a Cu(I) catalyst and base. Since this reaction proceeded similarly to that of a Pd(II) complex ($Pd(OAc)_2$) or Pd(0) complex ($Pd_2(dba)_3$), we assumed that the reaction proceeded via a Pd(0) complex. In particular, we believe that the reaction was initiated by the reaction of Pd(0) with DNQ **1a** to form palladium(0) carbene **I**, which in turn reacted with copper acetylide **II** that was formed by the reaction of terminal alkyne and Cu(I) with amine, thereby giving Pd(II) intermediate **III**. The reductive elimination proceeded to form 2-alkynyl-1-naphthol **IV** and to regenerate the Pd(0) catalyst, after which **IV** was cyclized to naphthofuran **2.** As shown in Eq. 3-5, the cyclization did not occur mainly with the aid of CuI and the Pd complex, but *i*-Pr_2NH.[17] Notably, alkynylnaphthol **2a** was efficiently cyclized to furan **3a** with the help of *i*-Pr_2NH alone, as shown in Eq. 2. In contrast, the cyclization was inefficient only in the presence of a CuI or Pd catalyst, as shown in Eq. 3 and 4.





Scheme 3. Possible reaction mechanisms

In conclusion, we found that the Pd-catalyzed cross-coupling between (*tert*-butyldimethylsilyl)ethynyl stannane and DNQ could successfully proceed to afford alkynyl naphthol. In this work, we developed a method for the synthesis of naphtho[1,2-*b*]furans via a Pd-catalyzed reaction of DNQ and terminal alkynes in the presence of CuI and *i*-Pr_2NH. This approach was then successfully applied to the synthesis of furomollugin. Currently, we are continuously working on the development of a new method to the preparation of aromatic compounds with the use of diazonaphthoquinone.

Supporting Information

Electronic Supplementary Information (ESI) available: experimental procedures and characterization data, including ^1H and ^{13}C NMR spectra for new compounds (file type, i.e., PDF). Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

ACKNOWLEDGMENT

This work was supported by a Grant in Aid for KAKENHI (17K19125).

References and Notes

1 a) H. Itokawa, Z. Z. Ibraheim, Y.-F. Qiao, K. Takeya, *Chem. Pharm. Bull.* **1993**, *41*, 1869. b) V. Srivastava, A. S. Negi, J. K. Kumar, U. Faridi, B. S. Sisodia, M. P. Darokar, S. Luqman, S. P. S. Khanuja, *Bioorg. Med. Chem. Lett*. **2006**, *16*, 911. c) T. A. Dwight, N. R. Rue, D. Charyk, R. Josselyn, B. DeBoef, *Org. Lett.* **2007**, *9*, 3137. d) R. L. Guével, F. Oger, A. Lecorgne, Z. Dudasova, S. Chevance, A. Bondon, P. Barath, G. Simonneaux, G. Salbert, *Bioorg. Med. Chem*. **2009**, *17*, 7021. e) N. Kotoku, K. Higashimoto, M. Kurioka, M. Arai, A. Fukuda, Y. Sumii, Y. Sowa, T. Sakai, M. Kobayashi, *Bioorg. Med. Chem. Lett*. **2014**, *24*, 3389. f) L. Xia, A. Idhayadhulla, Y. R. Lee, S. H. Kim, Y.-J. Wee, *Med. Chem. Res*. **2014**, *23*, 3528.

2 a) Y. Hu, K. J. Nawoschik, Y. Liao, J. Ma, R. Fathi, Z. J. Yang, *Org. Chem.* **2004**, *69*, 2235. b) Y. Hu, Y. Zhang, Z. Yang, R. Fathi, *J. Org. Chem.* **2002**, *67*, 2365. c) Z. Liang, S. Ma, J. Yu, R. Xu, *Tetrahedron* **2007**, *63*, 12877. d) Y. Liang, S. Tang, X.-D. Zhang, L.-Q. Mao, Y.-X. Xie, J.-H. Li, *Org. Lett*. **2006**, *8*, 3017. e) G. W. Kabalka, L. Wang, R. M. Pagni, *Tetrahedron* **2001**, *57*, 8017.

3 R. Irie, A. Tanoue, S. Urakawa, T. Imahori, K. Igawa, T. Matsumoto, K. Tomooka, S. Kikuta, T. Uchida, T. Katsuki, *Chem. Lett*. **2011**, *40*, 1343.

4 a) S. H. Mashraqui, C. D. Mudaliar, H. Hariharasubrahmanian, *Tetrahedron Lett*. **1997**, *38*, 4865. b) M. C. Carreño, J. L. García Ruano, G. Sanz, M. A. Toledo, A. Urbano, *Synlett* **1997**, 1241. c) V. Kavala, S. Naik, B. K. Patel, *J. Org. Chem*. **2005**, 70, 4267. (d) Q. Huang, A. Fazio, G. Dai, M. A. Campo, R. C. Larock, *J. Am. Chem. Soc*. **2004**, *126*, 7460.

5 For a review, see: a) V. V. Ershov, G. A. Nikiforov and C. R. H. I. de Jonge, *Quinone Diazides*, Elsevier: Amsterdam, **1981**. b) H. Zollinger, *Diazo Chemistry*, VCH: Weinheim, **1994**.

6 For reviews, see: a) A. Reiser, H.-Y. Shih, T.-F. Yeh, J.-P. Huang, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2428. b) A. Reiser, J. P. Huang, X. He, T. F. Yeh, S. Jha, H. Y. Shih, M. S. Kim, Y. K. Han, K. Yan, *Eur. Polym. J.* **2002**, *38*, 619. c) S.-Y. Moon, J.-M. Kim, *J. Photochem. Photobiol. C: Photochem. Rev.* **2007**, *8,* 157. d) K.-i. Fukukawa, M. Ueda, *Polym. J.* **2008**, *40*, 281. e) N. Fomina, J. Sankaranarayanan, A. Almutairi, *Adv. Drug Deliv. Rev*. **2012**, *64*, 1005.

7 a) M. Kitamura, N. Tashiro, R. Sakata, T. Okauchi, *Synlett* **2010**, 2503. b) M. Kitamura, N. Tashiro, R. Sakata, T. Okauchi, *Bull. Chem. Soc. Jap.* **2015**, *88*, 824.

8 For a review, see: D. I. A. Othman, M. Kitamura, *Heterocycles* **2016**, *92*, 1761.

9 Our selected study on the metal-catalyzed reaction of diazonaphthoquinones, see: a) M. Kitamura, R. Sakata, T. Okauchi, *Tetrahedron Lett.* **2011**, *52*, 1931. b) M. Kitamura, M. Kisanuki, R. Sakata, T. Okauchi, *Chem. Lett*. **2011**, *40*, 1129. c) M. Kitamura, M. Kisanuki, T. Okauchi, *Eur. J. Org. Chem*. **2012**, 905. d) M. Kitamura, K. Araki, H. Matsuzaki, T. Okauchi, *Eur. J. Org. Chem*. **2013**, 5045. e) M. Kitamura, M. Kisanuki, K. Kanemura, T. Okauchi, *Org. Lett.* **2014**, *16*, 1554. f) M. Kitamura, S. Takahashi, T. Okauchi, *J. Org. Chem*. **2015**, *80*, 8406.

10 For reviews, see: a) Y. Zhang, J. Wang, *Eur. J. Org. Chem*. **2011**, 1015. b) Y. Xia, D. Qiu, J. Wang, *Chem. Rev*. **2017**, *117,* 13810.

11 K. L. Greenman, D. S. Carter and D. L. Van Vranken, *Tetrahedron* **2001**, *57*, 5219.

12 Rh-catalyzed reactions: a) H. M. L. Davies, K. R. Romines, *Tetrahedron* **1988**, *44*, 3343. b) F. R. Kinder, A. Padwa, *Tetrahedron Lett*. **1990**, *31*, 6835. c) A. Padwa, U. Chiacchio, Y. Gareau, J. M. Kassir, K. E. Krumpe, A. M. Schoffstall, *J. Org. Chem*. **1990**, *55*, 414. c) A. Padwa, K. E. Krumpe, Y. Gareau, U. Chiacchio, *J. Org. Chem*. **1991**, *56*, 2523. d) A. Padwa, K. E. Krumpe, J. M. Kassir, *J. Org. Chem*. **1992**, *57*, 4940. e) M. C. Pirrung, J. Zhang, A. T. Morehead, *Tetrahedron Lett.* **1994**, *35*, 6229. f) W. Pang, S. Zhu, Y. Xin, H. Jiang, S. Zhu, *Tetrahedron* **2010**, *66*, 1261. g) J. F. Briones, H. M. L. Davies, *Tetrahedron* **2011**, *67* 4313. Co-catalyzed reaction: h) X. Cui, X. Xu, L. Wojtas, M. M. Kim, X. P. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 19981. Ru-catalyzed reaction: i) L. Xia, Y. R. Lee, *Eur. J. Org. Chem.* **2014***,* 3430. Cu-catalyzed reactions: j) L. Zhou, J. Ma, Y. Zhang, J. Wang, *Tetrahedron Lett*. **2011**, *52*, 5484. k) M. L. Hossain, F. Ye, Y. Zhang, J. Wang, *Tetrahedron* **2014**, *70*, 6957.

13 a) A. Suárez, C. G. Fu, *Angew. Chem. Int. Ed.* **2004**, *43*, 3580. b) L. Zhou, F. Ye, J. Ma, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed*. **2011**, *50*, 3510. c) F. Ye, X. Ma, Q. Xiao, H. Li, Y. Zhang, J. Wang, *J. Am. Chem. Soc*. **2012**, *134*, 5742.

14 C. Wu, F. Hu, Z. Liu, G. Deng, F. Ye, Y. Zhang, J. Wang, *Tetrahedron* **2015**, *71*, 9126.

15 R. D. Kimbrough, *Environ. Health Perspect.* **1976**, *14*, 51.

16 a) H. Itokawa, Y. Qiao, K. Mihara, K. Takeya, *Phytochemistry* **1991**, *30*, 637. b) L. Wu, S. Wang, H. Hua, X. Li, T. Zhu, T. Miyase, A. Ueno, *Phytochemistry* **1991**, *30*, 1710. c) K. Inoue, Y. Shiobara, H. Nayeshiro, H. Inouye, G. Wilson, M. H. Zenk, *Phytochemistry* **1984**, *23*, 307. d) H. Schildknecht, F. Straub, *Justus Liebigs Ann. Chem.* **1976**, 1772.

17 Related base catalyzed cyclization, see: K. Inamoto, N. Asano, Y. Nakamura, M. Yonemoto, Y. Kondo, *Org. Lett.* **2012**, *14*, 2622.