ChemPubSoc Europe

DOI: 10.1002/chem.201504784

CHEMISTRY A European Journal Communication

Synthetic Methods

Copper-Mediated [3+2] Annulation of 3-*N*-Hydroxyallylamines with Nitrosoarenes

Satish Ghorpade, Prakash D. Jadhav, and Rai-Shung Liu*[a]

Abstract: Cu-mediated annulations of *N*-hydroxyallylamines with nitrosoarenes proceed through unprecedented formal [3+2] cycloadditions of *N*-hydroxyaminoallyl radicals with nitrosoarenes. Our mechanistic analysis opposes a 5-*endo-trig* cyclization involved in the final ring-closure step. To manifest the reaction utility, chemical elaborations of resulting isoxazolidinyl products into 2- or 3-substituted quinoline *N*-oxides and acyclic 1,3-diamino-2-ols are also described.

[3+2] Cycloaddition reactions are powerful tools to access five-membered carbo- or heterocyclic compounds.[1] Allyl radicals are versatile to react with various π-bond motifs to implement formation of a C–X (X = C, N) bond.[2–4] In the gaseous phase, allylic radicals can undergo [3+2] cycloadditions with butadienes,[3a] acetylenes,[3b] alkenes,[3c] allenes,[3d] and indenes,[3e] albeit with poor chemoselectivity. Such radical [3+2] cycloadditions are unlikely to occur in solution, because a final 5-*endo-trig* cyclization is a difficult process according to Baldwin's rule.[5] We are aware of no example of [3+2] cycloadditions of allyl radicals with any kind of 2π-bond motif, although 5-*endo-trig* cyclizations have been reported for alkenes of special types.[6] The development of such radical [3+2] cycloadditions is highly desirable in allyl radical chemistry.

We reported Cu-catalyzed aerobic oxidations of 3-*N*-hydroxyallylamines to form initially nitroxy radicals **I**,[7,8] which were convertible to 3-*N*-hydroxyaminoallylic radicals **I′**, possibly by an intermolecular hydrogen transfer. The dimerization of **I′** yielded no common 1,5-hexadiene derivatives, but afforded 1,4-dihydroxy-2,3-diaminocyclohexanes **I′**$_2$ efficiently [Eq. (1)].[9] Herein, we report Cu-mediated [3+2] annulation reactions of 3-*N*-hydroxyallylamines with nitrosoarenes to form isoxazolidin-5-yl products **3** [Eq. (2)] with excellent diastereoselectivities (d.r. > 25:1). Notably, the overall transformation represents a 3-amino-1,2-dioxygenation of an allylamine skeleton. Our mechanistic analysis opposes a 5-*endo-trig* radical cyclization; instead, the success of these radical [3+2] annulations is attributed to the relay action of allyl radical **I′** and its *N*-hydroxyamino functionality. Chemical elaborations of resulting product **3** into highly functionalized N- and O-containing compounds will be described.

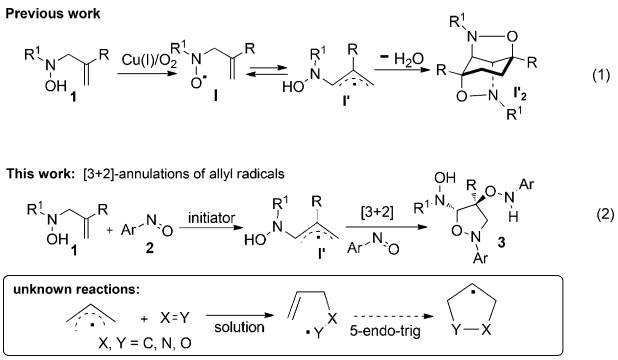
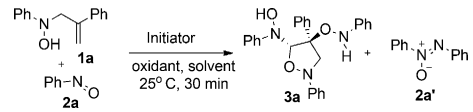


Table 1 shows the optimizations of [3+2] annulation reactions of 3-*N*-hydroxyallylamine **1a** (1.0 equiv) with nitrosobenzene (**2a**; 2 equiv) using various Cu salts, oxidants, and solvents. We initially tested the reaction with $CuBr_2$, $CuCl_2$, CuBr, and CuCl (5 mol%) in toluene/O_2 at 25 °C, affording isoxazolidinyl product **3a** in 24–58% yields (entries 1–4) that indicated the Cu^I is more efficient than the Cu^{II}. The diazene oxide **2a′** was isolated in small proportions (18–20%). Interestingly, the

Table 1. Optimization of reaction conditions.



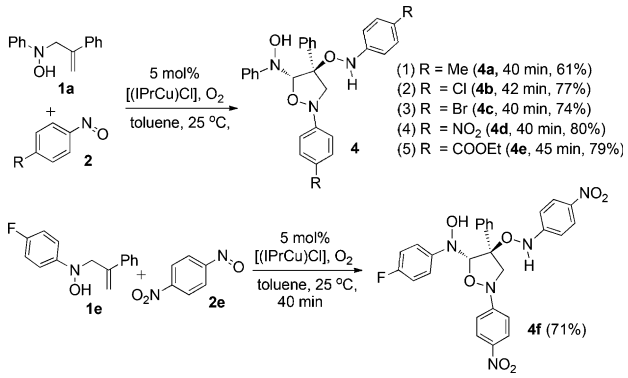
Entry	Initiator [mol%]	Oxidant	Solvent[a]	Products Yield [%][b] 1a	3a	2a′
1	$CuBr_2$ (5)	O_2	toluene	–	24	20
2	$CuCl_2$ (5)	O_2	toluene	–	27	26
3	CuBr (5)	O_2	toluene	–	58	18
4	CuCl (5)	O_2	toluene	–	48	22
5	[(IPr)CuCl] (5)	O_2	toluene	–	73	traces
6	[(IPr)CuCl] (5)	H_2O_2[c]	toluene	–	54	10
7	[(IPr)CuCl] (5)	*t*BuOOH[c]	toluene	–	56	4
8	[(IPr)CuCl] (5)	O_2	DCE	–	62	6
9	[(IPr)CuCl] (5)	O_2	THF	–	67	3
10	[(IPr)CuCl] (5)	N_2	toluene	74	traces	25
11	–	O_2	toluene	–	traces	15
12	TEMPO (10)	N_2	toluene	–	60	5

[a] **1a** (0.15 M, 1 equiv) and **2a** (0.30 M, 2 equiv). [b] Product yields are reported after purification through a neutral alumina column. [c] Molecular sieve 4Å was added.

[a] *Dr. S. Ghorpade, P. D. Jadhav, Prof. Dr. R.-S. Liu*
Department of Chemistry, National Tsing-Hua University
101, Sec. 2, Kuang-Fu Rd., Hsinchu, 30043, Taiwan (P.R. China)
E-mail: rsliu@mx.nthu.edu.tw

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201504784.

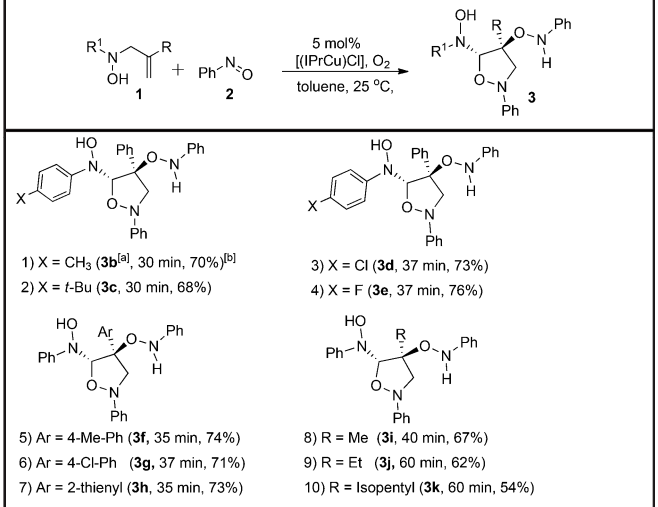
presence of the nitrosobenzene completely suppressed the formation of oxidative dimerization product **I'$_2$**. We envisage that the acidic Cu^{II} complex likely coordinates with *N*-hydroxylamine **1a** to inhibit the formation of nitroxy radicals.[7] Accordingly, we tested electron-rich [(IPr)CuCl] (IPr = 1,3-bis(diisopropylphenyl)imidazol-2-ylidene), which greatly increased the yield of desired **3a** (up to 73%) with diazene oxide **2a'** obtained in a negligible amount. With [(IPr)CuCl] (5 mol%), other oxidants, such as H_2O_2 and *tert*-butyl hydroperoxide (TBHP), afforded desired **3a** in 54% and 56% yields, respectively (entries 6–7). Other solvents, like 1,2-dichloroethane and THF, afforded compound **3a** in 62% and 67% yields, respectively (entries 8 and 9). In the absence of O_2, no reaction occurred, and initial **1a** was recovered in 74% yield (entry 10). Likewise, the reaction led to a mixture of complicated products if no Cu catalysts were employed (entry 11). The use of 2,2,6,6-tetramethylpiperidine *N*-oxide (TEMPO) under N_2 also implemented this annulation, yielding desired **3a** in 60% yield (entry 12). These data suggest that both Cu/O_2 and TEMPO serve as radical initiators. The isoxazolidinyl framework of compound **3a** was inferred from an X-ray diffraction of its relative **4f** (Scheme 1).[10]



Scheme 1. Reaction scope of nitrosoarenes.

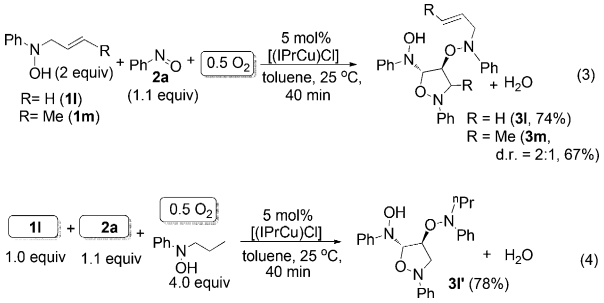
Table 2 shows the generalization of this [3+2] annulation using various 3-*N*-hydroxyallylamines **1b**–**1k** (1.0 equiv) and nitrosobenzene (**2a**; 2.0 equiv). The reactions were mediated with [(IPr)CuCl] (5 mol%) under O_2 (1 atm.) in toluene (25 °C, 0.5–1.0 h), yielding **3b**–**3k** as single diastereomeric products (d.r. > 25:1). We tested the reactions on *N*-hydroxyallylamines **1b**–**1e** bearing electron-rich and -deficient aniline substituents (X = CH_3, *t*Bu, Cl, and F; entries 1–4), the resulting products **3b**–**3e** were obtained in satisfactory yields (68–76%). The reaction is extensible to additional substrates **1f**–**1h** bearing various aryl groups at the alkenyl C2-carbons (Ar = 4-Me-Ph, 4-Cl-Ph, 2-thienyl), yielding desired compounds **3f**–**3h** in 71–74% yields (entries 5–7). To our delight, these annulations were compatible with substrates **1i**–**1k** bearing various alkyl groups at the alkenyl C2-carbons (R = Me, Et, isopentyl); their desired products **3i**–**3k** were obtained in reasonable yields (54–67%; entries 8–10). A complicated mixture of products was obtained when we attempted the reaction on *tert*-butyl-substituted *N*-hydroxyallylamine.

Table 2. Tests on 3-*N*-hydroxyallylamines.



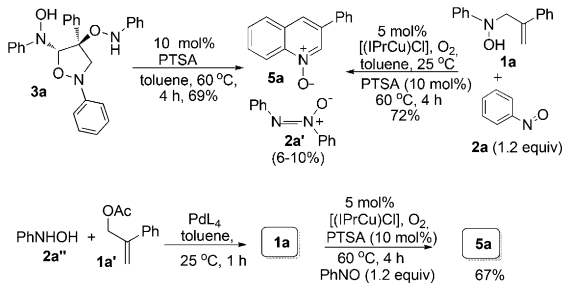
[a] **1b** (0.14 M, 1 equiv) and **2a** (0.30 M, 2 equiv). [b] Product yields are reported after purification through a neutral alumina column.

The Cu-mediated reactions of C2-unsubstituted *N*-hydroxyallylamines **1l** and **1m** with nitrosobenzene (**2a**) proceeded through a distinct aerobic oxidation, such that O_2 was an oxidant rather than a radical activator; the optimized yields of desired **3l** and **3m** were 74% and 67%, respectively, with a molar ratio of amine/**2a** = 2.0:1.1 [Eq. (3)]. Herein, initial *N*-hydroxyallylamine **1l** acted as a nucleophile, which was replaceable by other *N*-hydroxyallylamines. We successfully employed *N*-hydroxyaminopropane (4 equiv) as a nucleophile, affording compound **3l'** in 78% yield [Eq. (4)].



The reaction scope was expanded with various nitrosoarenes (Scheme 1). The reaction of 4-methyl-substituted nitrosobenzene (R = Me) gave isoxazolidin-5-yl species **4a** in 61% yield. The reaction became more efficient with electron-deficient nitrosoarenes (R = Cl, Br, NO_2, and CO_2Et), affording products **4b**–**4e** in 74–80% yields. Electron-deficient nitrosoarenes are more favorable for this reaction presumably because they are efficient electron acceptors.[11] We finally synthesized compound **4f**, which had good crystallinity for X-ray diffraction to confirm the isoxazolidinyl framework.[10]

Scheme 2 shows the elaboration of resulting isoxazolidin-5-yl species **3a** into useful N- and O-containing compounds. Treatment of species **3a** with *p*-TSA (10 mol%) efficiently yielded substituted quinoline *N*-oxide product **5a** and diazene



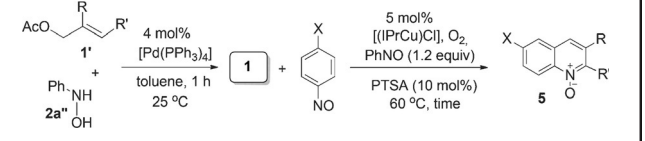
Scheme 2. Chemical elaboration.

oxide in 69% and 6% yields, respectively. Importantly, product **5a** was directly accessible by heating a mixture of nitrosobenzene (**2a**; 2 equiv) and 3-*N*-hydroxyallylamines **1a** (1 equiv) with [(IPr)CuCl]/O_2 (5 mol%) and *p*-TSA (10 mol%) in toluene; the yield of resulting **5a** was 72% along with diazine oxide **2a'** at 10% yield. To highlight the value of intermediate **3a**, we developed a two-step one-pot cascade reaction involving an initial Pd-catalyzed amination of readily available allylic acetate **1a'** in toluene for 1 h, followed by heating the same solution with nitrosobenzene (**2a**; 1.2 equiv), [(IPr)CuCl], and oxygen to yield 3-phenyl quinoline *N*-oxide **5a** efficiently.

Unlike 2-substituted analogues,[12a] the synthesis of 3-substituted quinoline *N*-oxides requires prior synthesis of their quinoline derivatives, which are usefully prepared from the condensation of expensive 2-aminobenzaldehydes with ketones or aldehydes.[12b–d] In this regard, the synthesis of quinoline *N*-oxide **5a** in a Pd/Cu/H^+ relay catalysis (Scheme 2) is appealing, because cheap nitrosoarenes and allylic acetates are employed in this one-pot synthesis. The reaction scope was generalized with various *N*-hydroxyaniline **2a"**, allylic acetates **1'**, and nitrosoarenes **2** in a 1:1:1.2 molar proportions (Table 3).[13] With electron-deficient nitrosobenzenes (X = Cl, Br, and CO_2Et), Cu-mediated annulations with species **1a'** provided 3-substituted quinoline *N*-oxides **5b**–**5d** in satisfactory yields (>71%, entries 1–3). This catalytic synthesis was extendible to additional allylic acetates bearing various aryl and alkyl groups at their C2-carbons (R = 4-tolyl, 4-chlorophenyl, methyl, and isopentyl), yielding 3-substituted quinoline oxides **5e**–**5h** in 61-70% yield (entries 4–7). For unsubstituted and C3-substituted acetates **1l'** and **1m'**–**1o'**, resulting products **5i** and **5j**–**5k** were obtained in 65–70% yields (entries 8–10).

Table 4 shows the applicability of our new method to the efficient synthesis of 1,3-diamino-2-ols through reductive N–O cleavages of compounds **3**; herein, these reactions represents triple N- and O-functionalizations of readily available allylic acetates. The reactions were performed with Pd/C and H_2 (1 atm) in MeOH, yielding desired products **6a**–**6e** exceeding 68% yields (entries 1–5).

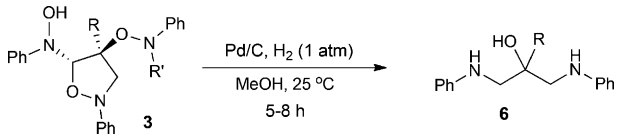
Table 3. Catalytic synthesis of quinoline oxides.



1) X = Cl (**5b**[a], 2.5 h, 68%)
2) X = Br (**5c**, 3 h, 71%)[b]
3) X = COOEt (**5d**, 2 h, 74 %)
4) R = 4-$CH_3C_6H_4$ (**5e**, 3 h, 66%)
5) R = 4-ClC_6H_4 (**5f**, 3 h, 70%)
6) R = Me (**5g**, 3 h, 62%)
7) R = Isopentyl (**5h**, 2.5 h, 61%)
8) R' = H (**5i**, 2 h, 69%)
9) R' = Me, (**5j**, 4 h, 70%)
10) R' = n-Pr, (**5k**, 1 h, 65%)

[a] **1'** (0.3 M) and **2a''** (0.3 M). [b] Product yields are reported after purification through a silica gel column.

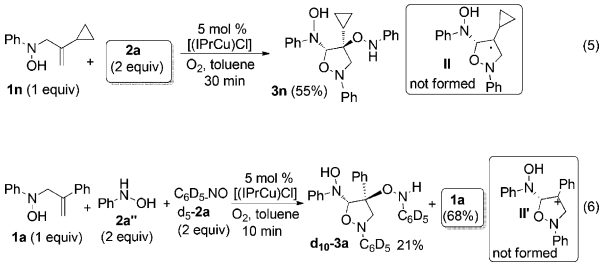
Table 4. Synthesis of 1,3-diamino-2-ols by N–O cleavage.

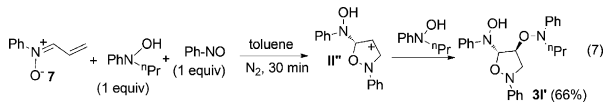


Entry	R	R'	Compounds (*t* [h], yield [%])[b]
1	Ph	H (**3a**)[a]	**6a** (8, 71)
2	4-Me-Ph	H (**3f**)	**6b** (5, 76)
3	CH_3	H (**3i**)	**6c** (6, 74)
4	isopentyl	H (**3j**)	**6d** (5, 68)
5	H	allyl (**3l**)	**6e** (6, 69)

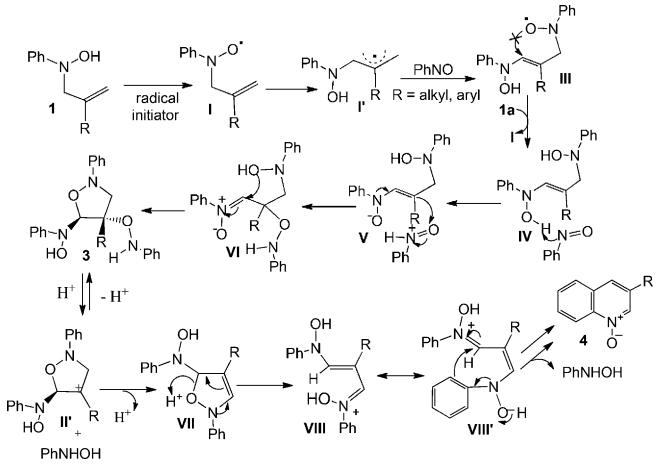
[a] **3a** (0.045 M). [b] Product yields are reported after purification through a silica gel column.

Control experiments [Eqs. (5)–(7)] were carried out to elucidate the mechanism for our major reactions depicted in Tables 1–2 and Scheme 1. We tested a reaction on 2-cyclopropyl-substituted substrate **1n**, giving compound **3n** of the same type [Eq. (5)]; the radical **II** was thus excluded, because the cyclopropane ring of **3n** was not cleaved.[6] To identify the source of the C2-amino group of compound **3a**, compound **1a**, *N*-hydroxyaniline (**2a"**; 2 equiv), and C_6D_5NO (d_5-**2a**) were tested for a brief period (10 min) to attain a 32% conversion of the reaction [Eq. (6)]. The resulting product d_{10}-**3a** contained mainly C_6D_5NH–O– at its C2-carbon (>90%), indicating that the C2-amino group appeared primarily from C_6D_5NO. The formation of carbocation **II'** was unlikely to occur here because potent nucleophile **2a"** did not participate in the reaction. In contrast, the reactions depicted in Equations (3) and (4), likely involve nitrone **7** according to the results in Equation (7), which gave the same product **3l'** as in Equation (4). Such nitrone species are unlikely to form for 2-substituted *N*-hydroxyallylamines according to a separate experiment.[14]





Scheme 3 shows a plausible mechanism to rationalize the major annulations, in which [(IPr)CuCl]/O_2 acts as a radical initiator The key step of this mechanism involves an addition of the nitrosobenzene to *N*-hydroxyaminoallyl radical **I′** to form new nitroxy radical **III**.[11] Notably, such a radical/nitroso addition is operable only for 2-substituted allyl radicals (R = alkyl, aryl), otherwise the nitrone species will form in the case of unsubstituted allylamine **1l** [Eq. (7)]. A 5-*endo-trig* cyclization of radical **III** is excluded because the experiment in Equation (5) opposes radical intermediate **II**. Herein, we postulate that species **III** abstracts a hydrogen from initial **1** to form species **IV** and initial nitroxy radical **I**, thus completing a radical chain reaction. Accordingly, the generation of nitroxy radical **1a** in catalytic amounts is sufficient for the reaction. In species **IV**, we envisage that the *N*-hydroxy group forms a hydrogen bond with the nitroso to increase its electrophilicity, leading to the formation of a C–O bond as depicted by intermediate **V**. This acid-mediated O-nitroso alkylation by enamine nucleophiles has a literature example.[15] The 5-*exo-trig* cyclization of resulting species **VI** is known to be feasible to yield observed product **3a**. Equation (6) excludes the intermediacy of tertiary carbocation **II′**. To examine the reactivity of this carbocation, we treated compound **3** with *p*-TSA to form 2,5-dihydroisoxazole intermediate **VII**, which subsequently underwent an acid-catalyzed ring opening to induce a skeletal rearrangement, yielding observed product **4** through an intramolecular cyclization of resulting intermediates **VIII** or **VIII′**. In the preceding **VI**→**3** transformation, resulting 2,5-dihydroisoxazole species **3** likely exists in two diastereomeric forms; we postulate that the Brønsted acid is likely to exist in this Cu/O_2 system to promote an interconversion between species **3** and carbocation **II′**. The released *N*-hydroxyaniline will be closely associated with carbocation **II**, and its attack on this cation will form single diastereomeric products.



Scheme 3. A postulated mechanism for [3+2] annulations.

Prior to this work, intermolecular [3+2] cycloadditions of allyl radicals with π-bond motifs remained a formidable task in solution chemistry. In summary, we reported the success of such formal cycloadditions in Cu-mediated [3+2] annulations of 3-*N*-hydroxyallylamines with nitrosoarenes. These transformations represent remarkable 3-amino-1,2-dioxygenations of allylamines. Notably, the resulting isoxazolidin-5-yl products can be transformed into 2- or 3-substituted quinoline oxides in the presence of a Brønsted acid. We subsequently employed the Pd/Cu/H^+ relay catalysis to access these quinoline oxides directly from cheap allylic acetates. Our mechanistic analysis indicated that the addition of allyl radicals to nitrosoarenes is feasible only with 2-substituted allyl radicals; nitrone species formed in the case of unsubstituted and 3-substituted allylamines.

Acknowledgements

The authors thank the National Science Council and the Ministry of Education, Taiwan, for supporting this work.

Keywords: annulation · copper · nitrosoarenes · oxidants · radicals

[1] a) F. Cardona, A. Goti, *Angew. Chem. Int. Ed.* **2005**, *44*, 7832 – 7835; *Angew. Chem.* **2005**, *117*, 8042 – 8045; b) L. M. Stanley, M. P. Sibi, *Chem. Rev.* **2008**, *108*, 2887 – 2902; c) T. Hashimoto, K. Maruoka, *Chem. Rev.* **2015**, *115*, 5366 – 5412.

[2] a) D. P. Curran, N. A. Porter, B. Giese, *Stereochemistry of Radical Reactions*, Wiley-VCH, Weinheim, **1996**; b) *Radicals in Organic Synthesis* (Eds.: P. Renaud, M. P. Sibi), Wiley-VCH, Weinheim, **2001**; c) A. J. McCarroll, J. C. Walton, *Angew. Chem. Int. Ed.* **2001**, *40*, 2224 – 2248; *Angew. Chem.* **2001**, *113*, 2282 – 2307; d) G. Stork, M. E. Reynolds, *J. Am. Chem. Soc.* **1988**, *110*, 6911.

[3] a) D. Nohara, T. Sakai, *Ind. Eng. Chem. Res.* **1988**, *27*, 1925 – 1929; b) D. Nohara, T. Sakai, *Ind. Eng. Chem. Fundam.* **1980**, *19*, 340 – 344; c) W. A. Bryce, D. J. Ruzicka, *Can. J. Chem.* **1960**, *38*, 835 – 844; d) D. Nohara, T. Sakai, *Sekiyu Gakkaishi* **1992**, *35*, 163 – 168; e) D. Nohara, T. Sakai, *Sekiyu Gakkaishi* **1988**, *31*, 403 – 409.

[4] Additions to imines, see selected examples: a) M. Aldemir, F. W. Heinemann, H. Kisch, *Photochem. Photobiol. Sci.* **2012**, *11*, 908 – 913; b) H. Keck, W. Schindler, F. Knoch, H. Kisch, *Chem. Eur. J.* **1997**, *3*, 1638 – 1645.

[5] J. E. Baldwin, J. Cutting, W. Dupont, L. Kruse, L. Silberman, R. C. Thomas, *J. Chem. Soc. Chem. Commun.* **1976**, 736 – 738.

[6] a) C. Chatgilialoglu, C. Ferreri, M. Guerra, V. Timokhin, G. Froudakis, T. Gimisis, *J. Am. Chem. Soc.* **2002**, *124*, 10765 – 10772; b) S. Bogen, M. Malacria, *J. Am. Chem. Soc.* **1996**, *118*, 3992 – 3993; c) Y. Yamamoto, M. Ohno, S. Eguchi, *J. Org. Chem.* **1996**, *61*, 9264 – 9271; d) K. Kobayashi, M. Suzuki, H. Suginome, *J. Org. Chem.* **1992**, *57*, 599 – 606.

[7] a) V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 11402 – 11405; b) B. C. Giglio, V. A. Schmidt, E. J. Alexanian, *J. Am. Chem. Soc.* **2011**, *133*, 13320 – 13322; c) V. A. Schmidt, E. J. Alexanian, *Angew. Chem. Int. Ed.* **2010**, *49*, 4491 – 4494; *Angew. Chem.* **2010**, *122*, 4593 – 4596; d) V. A. Schmidt, E. J. Alexanian, *Chem. Sci.* **2012**, *3*, 1672 – 1674; e) R. K. Quinn, V. A. Schmidt, E. J. Alexanian, *Chem. Sci.* **2013**, *4*, 4030 – 4034.

[8] a) Q. Lu, Z. Liu, Y. Luo, G. Zhang, Z. Huang, H. Wang, C. Liu, J. T. Miller, A. Lei, *Org. Lett.* **2015**, *17*, 3402 – 3405; b) A. Studer, *Angew. Chem. Int. Ed.* **2000**, *39*, 1108 – 1111; *Angew. Chem.* **2000**, *112*, 1157 – 1160; c) P. Sharma, R.-S. Liu, *Chem. Eur. J.* **2015**, *21*, 4590 – 4594; d) X.-Y. Jiang, F.-L. Qing, *Angew. Chem. Int. Ed.* **2013**, *52*, 14177 – 14180; *Angew. Chem.* **2013**, *125*,

14427 – 14430; e) A. A. Andia, M. R. Miner, K. A. Woerpel, *Org. Lett.* **2015**, *17*, 2704 – 2707.

[9] S. Ghorpade, R.-S. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 12885 – 12888; *Angew. Chem.* **2014**, *126*, 13099 – 13102.

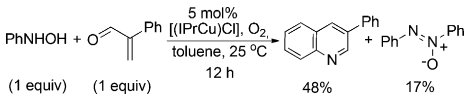
[10] CCDC 1429299 (**4 f**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[11] For the reactions of carbon-based radicals with nitrosoarenes, see selected examples: a) D. J. Fisher, L. G. Burnett, R. Velasco, J. R. d. Alaniz, *J. Am. Chem. Soc.* **2015**, *137*, 11614 – 11617; b) Y. Miura, T. Tomimura, N. Matsuba, R. Tanaka, M. Nakatsuji, *J. Org. Chem.* **2001**, *66*, 7456 – 7463; c) W. Adam, S. E. Bottle, K. Paters, *Tetrahedron Lett.* **1991**, *32*, 4283 – 4286.

[12] a) L.-C. Campeau, D. R. Stuart, J.-P. Leclerc, M. Bertrand-Laperle, E. Villemure, H.-Y. Sun, S. Lasserre, N. Guimond, M. Lecavallier, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 3291 – 3306; b) R. Martínez, D. Ramon, M. Yus, *J. Org. Chem.* **2008**, *73*, 9778 – 9780; c) W. Luo, Q, Mu, W. Qiu, T. Liu, F. Yang, X. Liu, J. Tang, *Tetrahedron* **2011**, *67*, 7090 – 7095; d) M. P. Maguire, K. R. Sheets, K. Mcvety, A. P. Spada, A. Zilberstein, *J. Med. Chem.* **1994**, *37*, 2129 – 2137.

[13] In the mechanism depicted in Scheme 3, *N*-hydroxyaniline will be released and reoxidized by O_2 in the transformation of **3**→**4**, and this equimolar ratio is sufficient for the reaction.

[14] Treatment of *N*-hydoxyaniline, 2-phenyl-2-buten-1-al, and nitrosobenzene produced 3-phenylquinoline in 48% yield; in this case nitrosobenzene did not participate in the reaction. .



[15] Y. Yamamoto, N. Nomiyama, H. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 5962 – 5963.

[16] Generation of oxygen-centered radicals with Cu/O_2, see ref. [8] and a) R. Bag, D. Sar, T. Punniyamurthy, *Org. Lett.* **2015**, *17*, 2010 – 2013; b) Q. Lu, P. Peng, Y. Luo, Y. Zhao, M. Zhou, A. Lei, *Chem. Eur. J.* **2015**, *21*, 18580 – 18583.

Received: November 27, 2015
Published online on January 25, 2016