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Site-Selective C–H Amidation of Azobenzenes with Dioxazolones Under Rhodium Catalysis

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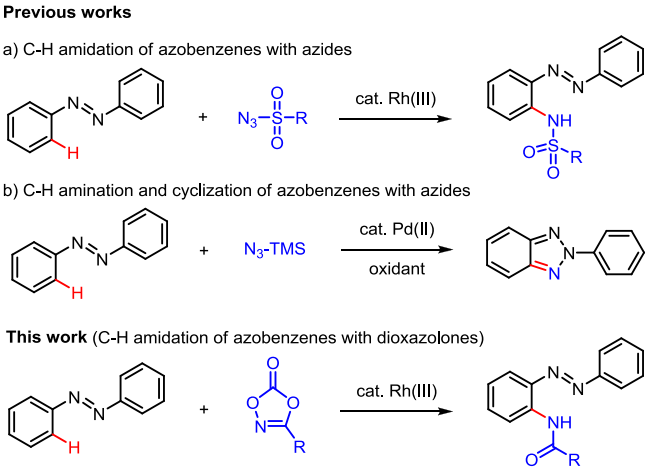
Abstract: The rhodium(III)-catalyzed amidation reaction of azobenzenes with dioxazolones is described. This strategy allows the facile and efficient construction of highly substituted *ortho*-amidated azobenzenes via direct C–H cleavage approach. A range of substrate scope, excellent levels of chemoselectivity as well as high functional group tolerance were observed. In addition, this protocol was used to generate an array of *ortho*-amidated ketazines. Further synthetic transformation of amidated azobenzenes furnished a facile construction of benzimidazole and benzotriazole derivatives.

Transition-metal-catalyzed C−N bond formation reaction through C−H bond activation is among the most important topic in organic synthesis due to the prevalence of nitrogen-containing bioactive molecules.[1] In this area, various coupling partners, such as *N*-carboxylates, *N*-tosylates, *N*-fluorobenzenesulfonimide (NFSI), organic azides and etc, have been used as relevant surrogates for the C−H amination or amidation reactions.[2] Recently, dioxazolones have been also applied to direct C−H amidation reactions of C(sp^2)−H and C(sp^3)−H bonds.[3] For example, Chang described seminal literatures on the C−H amidation reaction of various arenes with dioxazolones as new amidating reagents under Rh(III) and Co(III) catalysis.[3a–c] Li demonstrated the Rh(III)-catalyzed direct amidation of C(sp^3)−H bonds in 8-methylquinolines using dioxazolone derivatives.[3d] In addition, Jiao,[3e] Glorius,[3f] Ackermann,[3g,h] Li,[3i] Zhu[3j] and Sundararaju[3k] respectively disclosed the C−H amidation reactions with dioxazolones using Rh(III) and Co(III) catalysts.

Azobenzenes have emerged crucial organic molecules owing to the prevalence in dye industries and material science.[4] Because of the unique electronic characteristic of conjugated azo motifs, aromatic azo compounds have been recently used in supermolecular recognition, photochemical molecular switches, biosensors, pharmaceuticals, and so forth.[5] With a pioneering work on *ortho*-C–H chlorination of azobenzenes reported by Fahey in 1971,[6] azobenzenes have been intensively studied in the transition-metal-catalyzed C–H functionalization.[7] However, the direct C−N bond formation on azobenzenes has been rarely explored.[8] Lee reported the efficient synthesis of 2-aryl-2*H*-benzotriazoles via the Rh(III)-catalyzed amidation of azobenzenes with sulfonyl azides followed by oxidation reaction.[8a] Jia[8b] and Xu[8c] also described a very similar protocol, which is the Rh(III)-catalyzed coupling reaction between azobenzenes and organic azides. Patel demonstrated a facile approach for the construction of 2-aryl-2*H*-benzotriazoles via the Pd(II)-catalyzed C−N bond formations of azobenzenes with $TMSN_3$.[8d]

In continuation of our efforts towards the C–H functionalization of azobenzenes,[9] we herein reported the rhodium(III)-catalyzed C–H amidation reaction of azobenzenes with dioxazolones to afford various *ortho*-amidated azobenzenes.[10] In addition, this protocol can be successfully applied to the C–H amidation of ketazines. Furthermore, synthetic transformation of amidated azobenzenes showed facile access to benzimidazole and benzotriazole derivatives.



Scheme 1. C–H Amidation Reactions of Azobenzenes.

Our investigation was initiated by examining the coupling of (*E*)-1,2-diphenyldiazene (**1a**) to 3-phenyl-1,4,2-dioxazol-5-one (**2a**) (Table 1). We were delighted to see the coupling between **1a** and **2a** in the presence of $[RhCp^*Cl_2]_2$ and $AgSbF_6$ in DCE solvent at ambient temperature providing the desired product **3a** in 45% yield (entry 1). Control experiments revealed that cationic rhodium catalyst and acetate additive is found to be important for this transformation (entries 2 and 3). Screening of silver additive and solvents showed that $AgNTf_2$ and DCE are optimal additive and solvent for the formation of our desired product **3a** (entries 4–10). Further investigation of acetate additive showed that NaOAc is found to be superior than KOAc, AgOAc and

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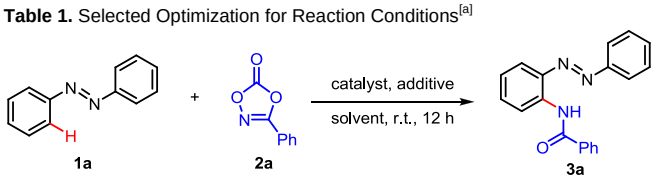
$Cu(OAc)_2$ (entries 11–13). In addition, increasing amount of NaOAc to 20 mol-% provided the decreased formation of **3a** in 44% yield (entry 14). Cationic Ru(II) and Co(III) catalysts were found to be ineffective in this coupling reaction (entries 15 and 16). Finally, it should be mentioned that reaction temperature is quite important to undergo the coupling reaction between **1a** and **2a** in good yield (entries 17 and 18).

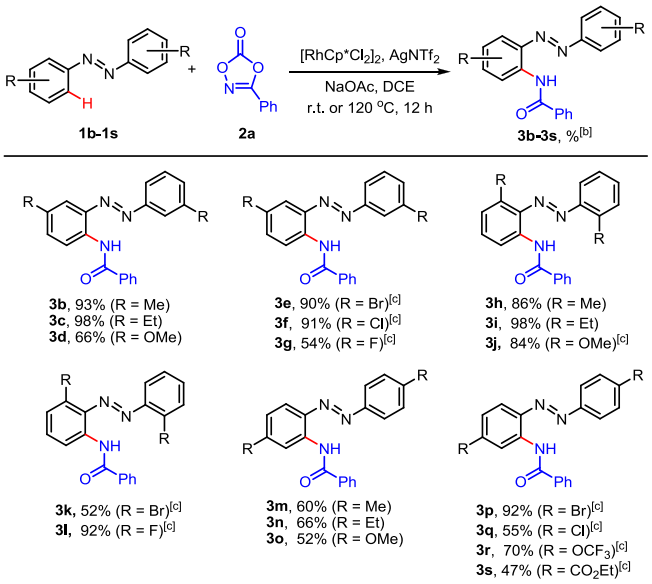
Table 1. Selected Optimization for Reaction Conditions[a]



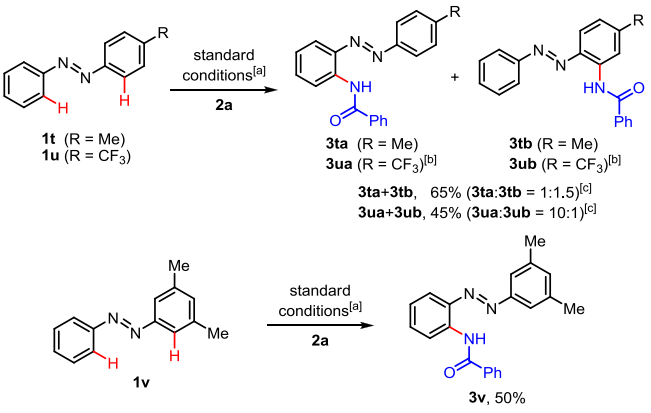
entry	catalyst	additive (mol-%)	solvent	yield[b]
1	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (10)	DCE	45
2	$[RhCp^*Cl_2]_2$	$AgSbF_6$ (10), NaOAc (10)	DCE	61
3	$[RhCp^*Cl_2]_2$	NaOAc (10)	DCE	N.R.
4	$[RhCp^*Cl_2]_2$	$AgPF_6$ (10) , NaOAc (10)	DCE	59
5	$[RhCp^*Cl_2]_2$	$AgBF_4$ (10), NaOAc (10)	DCE	58
6	**$[RhCp^*Cl_2]_2$**	**$AgNTf_2$ (10), NaOAc (10)**	**DCE**	**70**
7	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	THF	20
8	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	MeCN	trace
9	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	EtOAc	34
10	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	MeOH	8
11	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), KOAc (10)	DCE	58
12	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), AgOAc (10)	DCE	64
13	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), $Cu(OAc)_2$ (10)	DCE	60
14	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (20)	DCE	44
15[c]	$[Ru(p\text{-}Cy)Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	DCE	N.R.
16[d]	[CoCp*(CO)I_2]	$AgNTf_2$ (10), NaOAc (10)	DCE	N.R.
17[e]	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	DCE	62
18[f]	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (10), NaOAc (10)	DCE	55

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (2.5 mol-%), additive (quantity noted), solvent (1 mL) under air at room temperature for 12 h in pressure tubes. [b] Isolated yield (%) by flash column chromatography. [c] *p*-Cy = *p*-cymene. [d] 5 mol-% of cobalt catalyst was used. [e] 50 °C. [f] 80 °C.

With the optimized reaction conditions in hand, the substrate scope of symmetrical azobenzenes was examined (Scheme 2). The coupling of 3-phenyl-1,4,2-dioxazol-5-one (**2a**) and *meta*-substituted azobenzenes **1b–1d** with electron-donating groups (Me, Et and OMe) was found to smoothly undergo our desired products **3b–3d** in good to high yields. However, *meta*-substituted azobenzenes **1e–1g** with electron-withdrawing groups was found to be less reactive under the optimal reaction conditions. For an example, **1e** was coupled with **2a** to afford **3e** in 17% yield. After further optimization, we were pleased to find that an increasing amount (3 equiv.) of **2a** at 120 °C under otherwise identical conditions displayed significantly increased formation of **3e** in 90% yield. Above conditions were applied to **1f** and **1g** to afford the corresponding products **3f** and **3g** in 91% and 54% yields, respectively. Moreover, *ortho*-substituted azobenzenes also participated in the C–H amidation reaction to deliver the corresponding products **3h–3l** in moderate go high yields. This reaction was also compatible with *para*-substituted azobenzenes **1m–1s**, and all reactions preferentially furnished mono-amidated products as a single regioisomer.



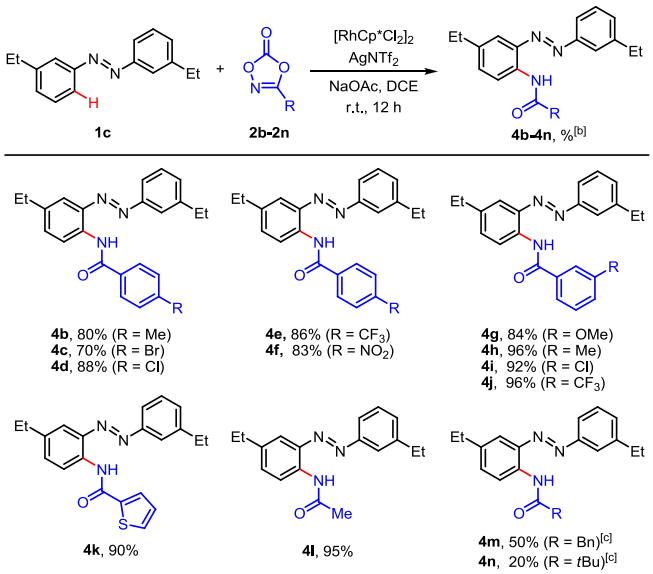
Scheme 2. Scope of Symmetrical Azobenzenes. [a] Reaction conditions: **1b–1s** (0.2 mmol), **2a** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgNTf_2$ (10 mol-%), NaOAc (10 mol-%), DCE (1 mL) under air at room temperature for 12 h in pressure tubes. [b] Isolated yield by flash column chromatography. [c] **2a** (0.6 mmol, 3 equiv.) was used at 120 °C.



Scheme 3. Scope of Unsymmetrical Azobenzenes. [a] Reaction conditions: **1t–1v** (0.2 mmol), **2a** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgNTf_2$ (10 mol-%), NaOAc (10 mol-%), DCE (1 mL) under air at room temperature for 12 h in

pressure tubes. [b] **2a** (0.6 mmol, 3 equiv.) was used at 120 °C. [c] Regioisomeric raio was determined by ^{1}H NMR analysis of crude mixture.

Next, the coupling reaction of unsymmetrical azobenzenes **1t** and **1u** containing electron-donating and electron-withdrawing groups (Me and CF_3) with **2a** was investigated under standard reaction conditions, as shown in Scheme 3. The results revealed that the C–H amidation reaction predominantly occurred on the electron-rich aromatic ring to provide **3tb** and **3ua** as major products, respectively. In addition, when azobenzene **1v** containing sterically different aromatic ring was subjected under standard reaction conditions, a single product **3v** was obtained in 50% yield. This data suggests that the steric environment of azobenzene is also important to tune the regioselectivity of C–H functionalization.

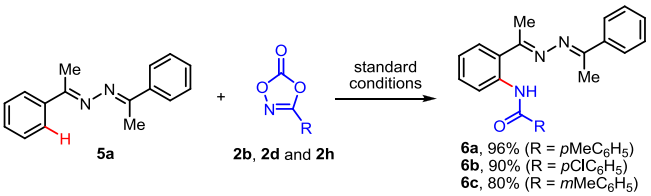


Scheme 4. Scope of Dioxazolones. [a] Reaction conditions: **1c** (0.2 mmol), **2b–2n** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol-%), $AgNTf_2$ (10 mol-%), NaOAc (10 mol-%), DCE (1 mL) under air at room temperature for 12 h in pressure tubes. [b] Isolated yield by flash column chromatography. [c] 100 °C.

To further examine the substrate scope of this process, a range of dioxazolones was screened to couple with azobenzene **1c** (Scheme 4). The reactions between **1c** and dioxazolones **2b–2j** with either electron-rich or electron-deficient groups at *para*- and *meta*-positions of phenyl ring were found to be favored in the amidation reaction to afford the corresponding products **4b–4j** in good to high yields. Particularly noteworthy was the tolerance of nitro or bromo groups as versatile functionalities for further transformation. It should be mentioned that the second C–H amidation on benzamide ring of products **4b–4f** were not detected. This observation is in contrast to a previous literature for the second C–H amidation occurring on *para*-substituted benzamides reported by Li.[3d] In addition, this transformation was compatible with heterocycle-containing dioxazolone **2k** to give our desired product **4k** in 90% yield.

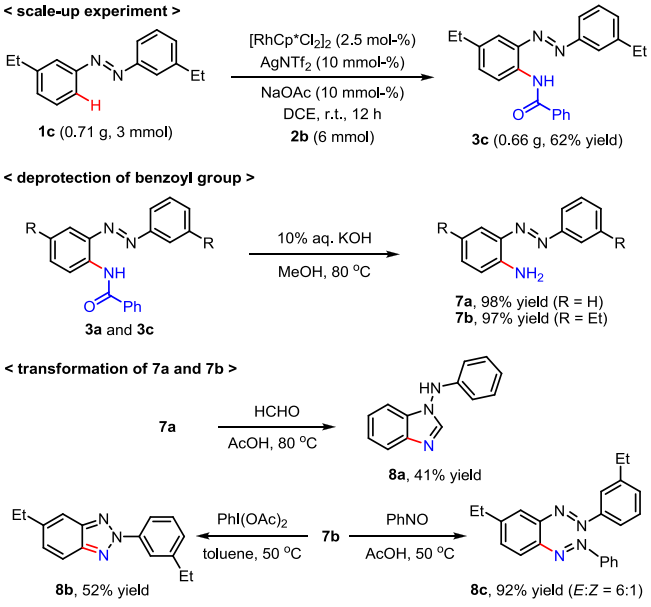
Finally, we were delighted that 3-alkyl-substituted dioxazolones **2l–2n** were also coupled with **1c** to give alkyl amides **4l–4n**.

To extend the scope of our protocol, we envisioned the C–H amidation reaction of other N−N bond containing compounds, i.e. ketazines, which are recently used in the C–H functionalization events.[11] Gratifyingly, ketazine **5a** was smoothly reacted with dioxazolones to furnish *ortho*-amidated ketazines **6a–6c** in high yields (Scheme 5).



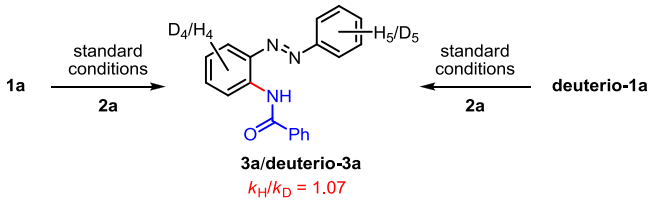
Scheme 5. Amidation of Ketazines with Dioxazolones.

To show the practicality of this transformation, we performed a scale-up experiment using 3 mmol of **1c**, and obtained 0.66 g of **3c** in 62% isolated yield (Scheme 6). To highlight the synthetic utility of amidated azobenzenes, hydrolysis conditions were first subjected to **3a** and **3c** affording 2-amino-azobenzenes **7a** and **7b** in high yields. Further transformation of synthesized amino products **7a** and **7b** was carried out. Benzimidazole derivative **8a** was successfully formed by use of formaldehyde in the presence of AcOH. In addition, treatment of **7b** with $PhI(OAc)_2$ provided 2-aryl-2*H*-benzotriazole **8b** in 52% yield. Moreover, **7b** was readily converted to bis-azobenzene **8c** in 92% yield.[12]



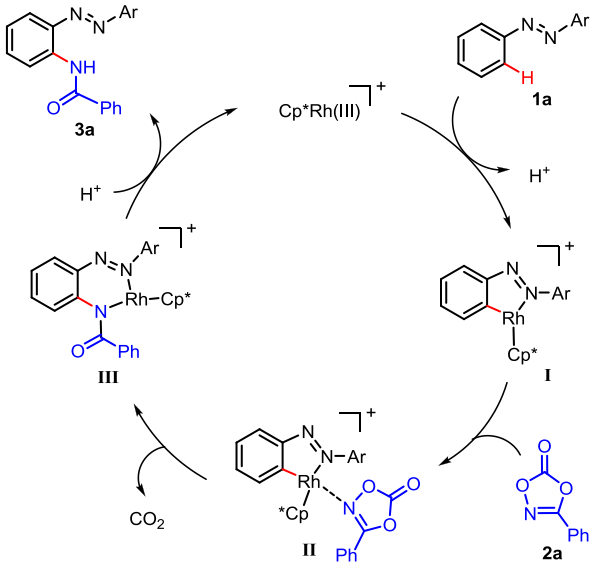
Scheme 6. Scale-up Experiment and Transformation.

To get mechanistic insight, parallel reactions of **1a** and **deuterio-1a** with **2a** under standard reaction conditions were performed, which provided the kinetic isotope effect of 1.07 (Scheme 7), thus suggesting that C−H bond cleavage might be not involved in the rate-determining step.[13]



Scheme 7. Kinetic Isotope Effect Experiment.

Based on KIE experimental data and previous literatures,[3] a proposed reaction pathway is outlined in Scheme 8. In the presence of $AgNTf_2$, a cationic [Cp*Rh(III)] complex is generated in situ as an active catalyst, which coordinates to azobenzene (**1a**) and further undergoes C–H activation to afford rhodacyclic intermediate **I**.[14] Coordination of **2a** and migratory insertion delivers a six-membered Rh(III)-amido species **III** with release of CO_2. Finally, protonation can take place to furnish our desired product **3a**, and the active Rh(III) species can recycle in the catalytic system.



Scheme 8. Proposed Reaction Mechanism.

In conclusion, we have disclosed the rhodium(III)-catalyzed C–H amidation reaction of azobenzenes with dioxazolones. This protocol has been applied to a wide range of substrates, and typically proceeds with excellent levels of chemoselectivity as well as with high functional group tolerance. Additionally, this protocol allows the generation of an array of *ortho*-amidated ketazines. Further transformation of amidated azobenzenes led to facile access to benzimidazole and benzotriazole derivatives.

Acknowledgements

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Keywords: amidation • azobenzenes • C–H functionalization • dioxazolones • rhodium

[1] For recent reviews of C−H functionalization, see: a) N. Kuhl, N. Schröder, F. Glorius, *Adv. Synth. Catal.* **2014**, *356*, 1443–1460; b) Z. Chen, B. Wang, J. Zhang, W. Yu, Z. Liu, Y. Zhang, *Org. Chem. Front.* **2015**, *2*, 1107–1295; c) G. Song, X. Li, *Acc. Chem. Res.* **2015**, *48*, 1007–1020; d) L. Yang, H. Huang, *Chem. Rev.* **2015**, *115*, 3468–3517; e) S. Sharma, N. K. Mishra, Y. Shin, I. S. Kim, *Curr. Org. Chem.* **2016**, *20*, 471–511.

[2] a) K.-H. Ng, A. S. C. Chan, W.-Y. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 12862–12864; b) K. Sun, Y. Li, T. Xiong, J. Zhang, Q. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 1694–1697; c) X. Chen, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 6790–6791; d) T. Kawano, K. Hirano, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2010**, *132*, 6900–6901; e) E. J. Yoo, S. Ma, T.-S. Mei, K. S. L. Chan, J.-Q. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 7652–7655; f) J. Y. Kim, S. H. Park, J. Ryu, S. H. Cho, S. H. Kim, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 9110–9113; g) J. Ryu, K. Shin, S. H. Park, J. Y. Kim, S. Chang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9904–9908; *Angew. Chem.* **2012**, *124*, 10042–10042; h) K. Shin, Y. Baek, S. Chang, *Angew. Chem. Int. Ed.* **2013**, *52*, 8031–8036; *Angew. Chem.* **2013**, *125*, 8189–8194.

[3] a) Y. Park, K. T. Park, J. G. Kim, S. Chang, *J. Am. Chem. Soc.* **2015**, *137*, 4534–4542; b) J. Park, S. Chang, *Angew. Chem. Int. Ed.* **2015**, *54*, 14103–14107; *Angew. Chem.* **2015**, *127*, 14309–14313; c) Y. Park, S. Jee, J. G. Kim, S. Chang, *Org. Process Res. Dev.* **2015**, *19*, 1024–1029; d) H. Wang, G. Tang, X. Li, *Angew. Chem. Int. Ed*. **2015**, *54*, 13049–13052; *Angew. Chem.* **2015**, *127*, 13241–13244; e) Y. Liang, Y.-F. Liang, C. Tang, Y. Yuan, N. Jiao, *Chem. Eur. J.* **2015**, *21*, 16395–16399; f) X. Wang, A. Lerchen, F. Glorius, *Org. Lett.* **2016**, *18*, 2090–2093; g) R. Mei, J. Loup, L. Ackermann, *ACS Catal.* **2016**, *6*, 793–797; h) H. Wang, M. M. Lorion, L. Ackermann, *Angew. Chem. Int. Ed*. **2016**, *55*, 10386–10390; *Angew. Chem.* **2016**, *128*, 10542–10546; i) F. Wang, H. Wang, Q. Wang, S. Yu, X. Li, *Org. Lett.* **2016**, *18*, 1306–1309; j) J. Wang, S. Zha, K. Chen, F. Zhang, C. Song, J. Zhu, *Org. Lett.* **2016**, *18*, 2062–2065; k) N. Barsu, M. A. Rahman, M. Sen, B. Sundararaju, *Chem. Eur. J.* **2016**, *22*, 9135–9138.

[4] a) K. Hunger in *Industrial Dyes: Chemistry, Properties, Applications*, Wiley-VCH, Weinheim, Germany, **2003**; b) A. Bafana, S. S. Devi, T. Chakrabarti, *Environ. Rev.* **2011**, *19*, 350–371.

[5] a) V. Ferri, M. Elbing, G. Pace, M. D. Dickey, M. Zharnikov, P. Samorì, M. Mayor, M. A. Rampi, *Angew. Chem. Int. Ed.* **2008**, *47*, 3407–3409; *Angew. Chem.* **2008**, *120*, 3455–3457; b) T. Muraoka, K. Kinbara, T. Aida, *Nature* **2006**, *440*, 512–515; c) F. Puntoriero, P. Ceroni, V. Balzani, G. Bergamini, F. Vögtle, *J. Am. Chem. Soc.* **2007**, *129*, 10714–10719.

[6] a) D. L. Fahey, *Chem. Commun.* **1970**, 417; b) D. R. Fahey, *J. Organomet. Chem.* **1971**, *27*, 283–292.

[7] For selected examples on C−H functionalization of azobenzenes, see: a) Y. Lian, R. G. Bergman, L. D. Lavis, J. A. Ellman, *J. Am. Chem. Soc.* **2013**, *135*, 7122–7125; b) H. Li, P. Li, L. Wang, *Org. Lett.* **2013**, *15*, 620–623; c) K. Muralirajan, C.-H. Cheng, *Chem. Eur. J.* **2013**, *19*, 6198–6202; d) H. Li, P. Li, H. Tan, L. Wang, *Chem. Eur. J.* **2013**, *19*, 14432–14436; e) Z.-Y. Li, D.-D. Li, W. G. Wang, *J. Org. Chem.* **2013**,

78, 10414–10420; f) H. Li, P. Li, Q. Zhao, L. Wang, *Chem. Commun.* **2013**, *49*, 9170–9172; g) Z. Yin, X. Jiang, P. Sun, *J. Org. Chem.* **2013**, *78*, 10002–10007; h) Y. Lian, J. R. Hummel, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2013**, *135*, 12548–12551; i) H. Song, D. Chen, C. Pi, X. Cui, Y. Wu, *J. Org. Chem.* **2014**, *79*, 2955–2962; j) H. Li, X. Xi, L. Wang, *Chem. Commun.* **2014**, *50*, 4218–4221; k) J. Dong, B. Jin, P. Sun, *Org. Lett.* **2014**, *16*, 4540–4542; l) G. Hong, D. Mao, S. Wu, L. Wang, *J. Org. Chem.* **2014**, *79*, 10629–10635; m) J. R. Hummel, J. A. Ellman, *J. Am. Chem. Soc.* **2015**, *137*, 490–498.

[8] a) T. Ryu, J. Min, W. Choi, W. H. Jeon, P. H. Lee, *Org. Lett.* **2014**, *16*, 2810–2813; b) X. Jia, J. Han, *J. Org. Chem.* **2014**, *79*, 4180–4185; c) H. Wang, Y. Yu, X. Hong, Q. Tan, B. Xu, *J. Org. Chem.* **2014**, *79*, 3279–3288; d) N. Khatun, A. Modi, W. Ali, B. K. Patel, *J. Org. Chem.* **2015**, *80*, 9662–9670.

[9] a) S. Sharma, S. H. Han, S. Han, W. Ji, J. Oh, S.-Y. Lee, J. S. Oh, Y. H. Jung, I. S. Kim, *Org. Lett.* **2015**, *17*, 2852–2855; b) S. Han, N. K. Mishra, S. Sharma, J. Park, M. Choi, S.-Y. Lee, J. S. Oh, Y. H. Jung, I. S. Kim, *J. Org. Chem.* **2015**, *80*, 8026–8035; c) T. Jeong, S. H. Han, S. Han, S. Sharma, J. Park, J. S. Lee, J. H. Kwak, Y. H. Jung, I. S. Kim, *Org. Lett.* **2016**, *18*, 232–235.

[10] After submission of this manuscript, a similar work has been reported, see: B. Jeon, U. Yeon, J.-Y. Son, P. H. Lee, *Org. Lett.* **2016**, DOI: 10.1021/acs.orglett.6b02250.

[11] a) W. Han, G. Zhang, G. Li, H. Huang, *Org. Lett.* **2014**, *16*, 3532–3535; b) J. Wen, A. Wu, M. Wang, J. Zhu, *J. Org. Chem.* **2015**, *80*, 10457–10463; (c) J. Wen, A. Wu, Y. Miao, J. Zhu, *Tetrahedron Lett.* **2015**, *56*, 5512–5516.

[12] For the synthesis and application of bis-azoaromatic compounds, see: S. Roy, S. Pramanik, T. Ghorui, K. Pramanik, *RSC Adv.* **2015**, *5*, 22544–22559.

[13] E. M. Simmons, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2012**, *51*, 3066–3072; *Angew. Chem.* **2012**, *124*, 3120–3126.

[14] For a selected review for the heteroatom-directed rhodacycle intermediates, see: D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624–655.

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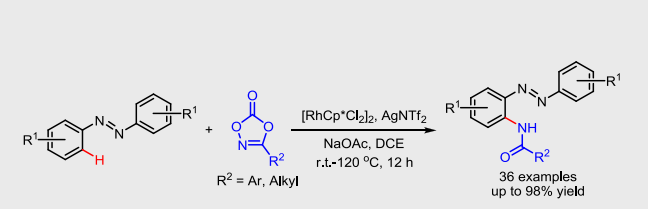
Key Topic: C–H Amidation

COMMUNICATION



The rhodium(III)-catalyzed amidation reaction of azobenzenes with dioxazolones is described. This strategy allows the facile and efficient construction of highly substituted *ortho*-amidated azobenzenes via direct C–H cleavage approach.

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Site-Selective C–H Amidation of Azobenzenes with Dioxazolones Under Rhodium Catalysis