Organic LETTERS

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Rh(III)-Catalyzed Direct Coupling of Azobenzenes with α-Diazo Esters: Facile Synthesis of Cinnolin-3(2*H*)-ones

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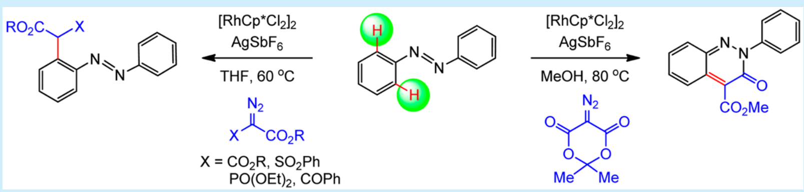
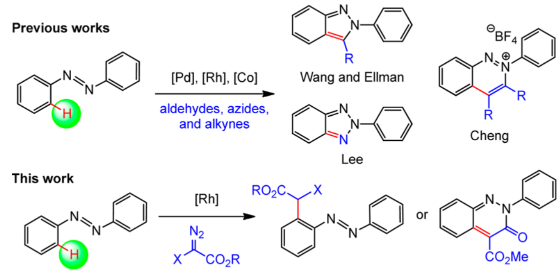
Supporting Information



ABSTRACT: The rhodium(III)-catalyzed direct C−H functionalization of azobenzenes with α-diazo compounds is described. These transformations provide the facile and efficient construction of C2-alkylated azobenzenes or highly substituted cinnolin-3(2*H*)-ones. Furthermore, this protocol leads to the formation of cinnolin-3(2*H*)-ones using a diazo derivative of Meldrum's acid.

Azobenzenes are known as crucial structural units used as light-triggered switches in surface-modified materials,[1] polymers,[2] molecular machines,[3] protein probes,[4] organic dyes,[5] nonlinear optical devices,[6] and chemosensors.[7] The prevalence of azobenzenes in material science and their unique properties have led to the development of many useful methods for their preparation. For example, the reduction of nitro compounds with an excessive amount of reducing agent,[8] the intermolecular coupling reaction of diazo salts with aromatic compounds,[9] and the aerobic oxidative coupling of aryl amines[10] were reported. The transition-metal-catalyzed C−H functionalization has been recognized as a powerful tool for the preparation of complex molecules because of its remarkable potential for step economy and environmental sustainability.[11] In particular, significant effort has been made on catalytic C−H functionalization of azobenzenes using the azo functionality as a directing group. In 1970, Fahey first observed the *ortho*-halogenations of azobenzenes under homogeneous palladium catalysis.[12] Later, Sanford described a single example on the palladium-catalyzed C−H acetoxylation of azobenzenes with $PhI(OAc)_2$.[13] In recent years, the transition-metal-catalyzed C−H functionalizations of azobenzenes have been widely investigated in acylation,[14] amidation,[15] halogenation,[16] alkoxylation,[17] nitration,[18] phosphorylation,[19] addition/cyclization,[20] and alkenylation/cyclization.[21] Notably, the C−H functionalization and intramolecular cyclization using azobenzenes delivers the formation of various bioactive heterocyclic compounds (Scheme 1). For example, Wang demonstrated the Pd(II)-catalyzed oxidative coupling of azobenzenes with aldehydes to give *ortho*-acylated azobenzenes, which were transformed to indazoles via reductive cyclization.[14a] Ellman reported the highly efficient synthesis of indazoles using azobenzenes and aldehydes under Rh(III)[20a] and Co(III)[20b] catalysis. Lee disclosed the C2-selective amidation of azobenzenes followed by oxidative cyclization to afford 2-aryl-2*H*-benzotriazoles.[15a] In addition, Cheng demonstrated the synthesis of cinnolinium salts from azobenzenes and alkynes under rhodium catalysis.[21]

Scheme 1. C−H Functionalization and Intramolecular Cyclization of Azobenzenes



The carbene insertion into the metallacycle species has recently emerged as a new approach toward sp^2 C−H functionalization.[22] In 2012, Yu described an elegant work on the Rh(III)-catalyzed carbene insertion of aromatic C−H bonds using electron-deficient α-diazo compounds to deliver a variety of *ortho*-functionalized arenes.[22b] In the meantime, Rovis, Glorius, and Cui independently reported the facile strategy for the formation of isoindolinones,[22c] isoquinoline/pyridine *N*-oxides,[22d] and azepinones[22e] using diazo compounds under Rh(III) catalysis, respectively. In addition, Wang showed the efficient formation of *ortho*-alkenylated phenols via the Rh(III)-

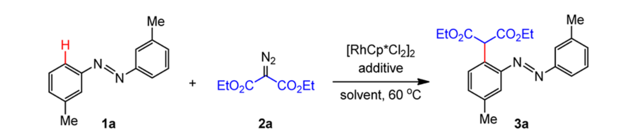
Received: May 3, 2015
Published: May 20, 2015

DOI: 10.1021/acs.orglett.5b01298
Org. Lett. 2015, 17, 2852−2855

catalyzed coupling between *N*-phenoxyacetamides and *N*-tosylhydrazones or α-diazo esters.[22g] In continuation of our recent studies on the rhodium-catalyzed C−H functionalization of aromatic compounds,[23] we herein present the Rh(III)-catalyzed direct C−H alkylations and the formation of cinnolin-3(2*H*)-ones[24,25] using azobenzenes and α-diazo compounds.

Our investigation was initiated by examining the coupling of 1,2-di(*m*-tolyl)diazene (**1a**) and diethyl 2-diazomalonate (**2a**) under rhodium catalysis (Table 1). To our delight, the rhodium

Table 1. Selected Optimization for Reaction Conditions[a]



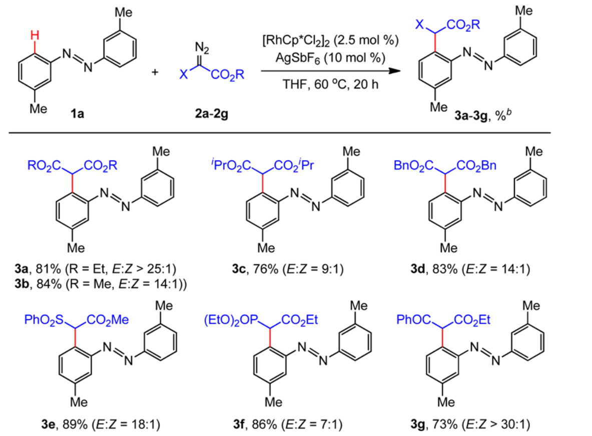
entry	additive (equiv)	solvent	yield[b] (%)
1	AgOAc (15)	DCE	28
2	NaOAc (15)	DCE	N.R.
3	CsOAc (15)	DCE	20
4[c]	$Cu(OAc)_2$ (15)	DCE	trace
5	$AgSbF_6$ (10)	DCE	42
6	$AgSbF_6$ (10) + AgOAc (15)	DCE	31
7	$AgSbF_6$ (10)	MeOH	55
8	$AgSbF_6$ (10)	EtOH	54
9	$AgSbF_6$ (10)	DMF	N.R.
10	$AgSbF_6$ (10)	MeCN	34
11	$AgSbF_6$ (10)	THF	81
12[c]	$AgSbF_6$ (10)	THF	trace

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), additive (quantity noted), solvent (1 mL) at 60 °C for 20 h under air in reaction tubes. [b]Isolated yield by column chromatography. [c]$[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %) was used instead of the rhodium catalyst.

complex, derived from $[Cp^*RhCl_2]_2$ and AgOAc, was found to promote the coupling of **1a** and **2a** in dichloroethane (DCE) at 60 °C for 20 h to afford the monoalkylated compound **3a** in 28% yield (Table 1, entry 1). Screening of additives under otherwise identical conditions showed that cationic rhodium complex, generated from $[Cp^*RhCl_2]_2$ and $AgSbF_6$, was found to be the most effective catalytic system in this reaction to afford our desired product **3a** in 42% yield, whereas other additives such as NaOAc, CsOAc, and $Cu(OAc)_2$ were less effective (Table 1, entries 2−5). In addition, treatment of both AgOAc and $AgSbF_6$ additives was found to be less effective in this coupling reaction (Table 1, entry 6). Further screening of solvents revealed that THF is found to be an optimal solvent to furnish **3a** in 81% yield, but other solvents such as DCE, MeOH, EtOH, DMF, and MeCN showed lower reactivity (Table 1, entries 7−11). Finally, replacement of the Rh catalyst with $[RuCl_2(p\text{-cymene})]_2$ gave no desired product (Table 1, entry 12).

To evaluate the scope and limitation of this process, the optimal reaction conditions were applied to various α-diazo esters **2a−g** (Scheme 2). In the case of symmetrical α-diazo esters **2a−d**, high yields of the desired *ortho*-alkylation adducts were obtained. Additionally, methyl 2-diazo-2-(phenylsulfonyl)-acetate (**2e**) and ethyl 2-diazo-2-(diethoxyphosphoryl)acetate (**2f**) proved to be good coupling partners providing **3e** (89%) and **3f** (86%), respectively. Furthermore, this reaction proceeded with β-keto-α-diazo ester **2g** to afford our desired product **3g** in 73% yield.

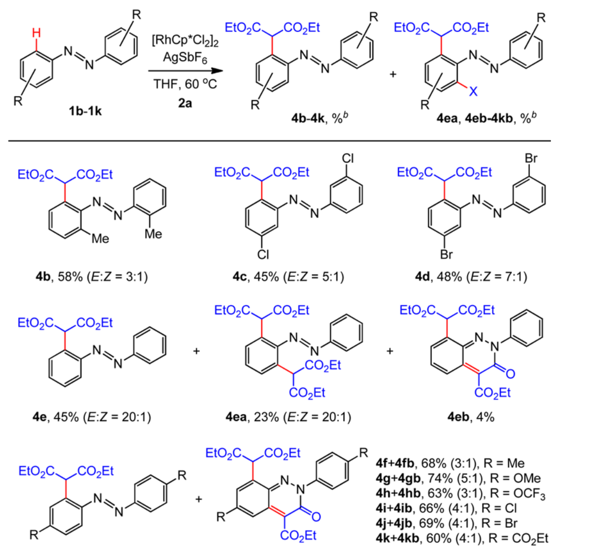
Scheme 2. Scope of α-Diazo Esters[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2a−g** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), THF (1 mL) at 60 °C for 20 h under air in reaction tubes. [b]Isolated yield by flash column chromatography and *E*:*Z* ratio were determined by integral ratio in ^1H NMR.

To further explore the scope and limitation of this transformation, various azobenzenes **1b−k** were screened to couple with **2a**, as shown in Scheme 3. The *ortho*- and *meta*-substituted

Scheme 3. Scope of Azobenzenes[a,c]



[a]Reaction conditions: **1b−k** (0.2 mmol), **2a** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), THF (1 mL) under air at 60 °C for 20 h in reaction tubes. [b]Isolated yield by column chromatography and *E*/*Z* ratio were determined by integral ratio in ^1HNMR. [c]For *E*/*Z* ratio of **4f−k**, see the Supporting Information.

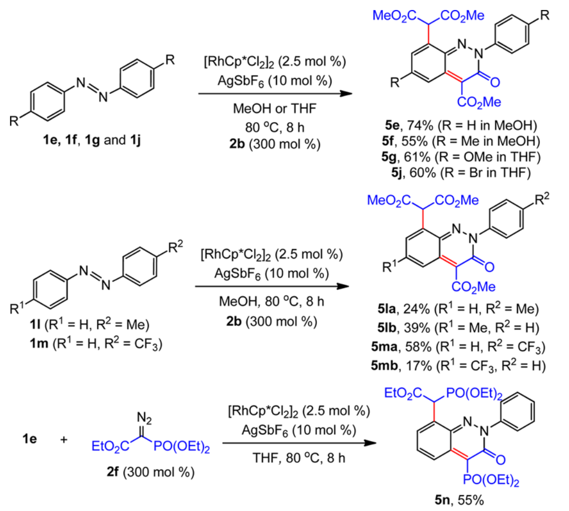
azobenzenes **1b−d** were found to couple with **2a** to give the corresponding products **4b−d** in moderate yields. Unsubstituted azobenzene **1e** provided a separable mixture of monoalkylated compound **4e** (45%) and bisalkylated compound **4ea** (23%) in concomitant with intramolecular cyclization product **4eb** in 4% yield. In addition, symmetrically *para*-substituted azobenzenes **1f−k** with electron-rich and electron-deficient groups (Me, OMe, OCF_3, Cl, Br, and CO_2Et) yielded the monoalkylated products **4f−k** along with cinnolin-3(2*H*)-ones **4fb−kb**.

DOI: 10.1021/acs.orglett.5b01298
Org. Lett. 2015, 17, 2852−2855

Notably, in all cases, a trace amount of bisalkylated products was observed.

Next, we focused on the formation of cinnolin-3(2*H*)-ones by carrying out the reaction of *para*-substituted azobenzenes with **2b** under standard reaction conditions. Treatment of 300 mol % of **2b** in MeOH or THF under otherwise identical conditions provided the desired C8-alkylated cinnolin-3(2*H*)-ones **5e–g** and **5j** in moderate to good yields (Scheme 4). In addition,

Scheme 4. Synthesis of C8-Alkylated Cinnolin-3(2*H*)-ones

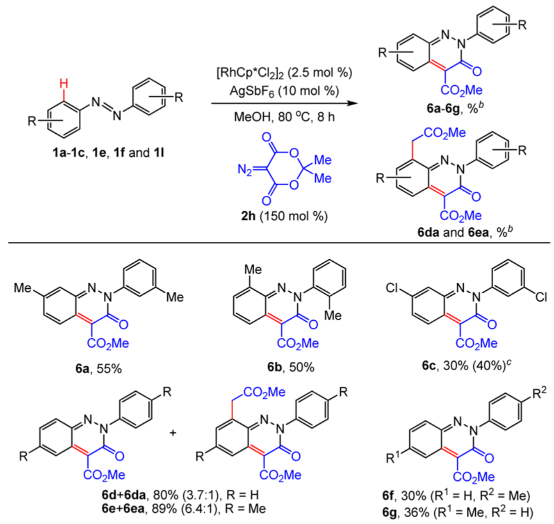


unsymmetrical azobenzenes **1l** and **1m** afforded a mixture of cinnolin-3(2*H*)-ones **5la**/**lb** and **5ma**/**mb** in good combined yields. These results indicate that the regioselectivity for the formation of cinnolin-3(2*H*)-one is higher in electron-rich aromatic rings than electron-deficient aromatic rings. Interestingly, unsymmetrical α-diazo ester **2f** was found to couple with **1e** under the standard reaction conditions to provide C4-diethoxyphosphoryl-substituted product **5n** in 55% yield.

Surprisingly, when azobenzene **1a** was subjected to react with the diazo derivative **2h** of Meldrum's acid in MeOH, cinnolin-3(2*H*)-one **6a** was exclusively obtained in 55% yield. Subsequently, we extended the substrate scope of azobenzenes as shown in Scheme 5. The *ortho*- and *meta*-substituted azobenzenes **1b** and **1c** participated in the formation of cinnolin-3(2*H*)-ones **6b** and **6c**, respectively. In addition, *para*-substituted azobenzenes **1e** and **1f** provided cinnolin-3(2*H*)-ones **6d** and **6e** as major products and C8-alkylated cinnolin-3(2*H*)-ones **6da** and **6ea**. In the case of unsymmetrical azobenzene **1l**, a mixture of cinnolin-3(2*H*)-ones **6f** and **6g** was obtained in 66% combined yield. Finally, we were pleased to find that a C4-carboxylate group on cinnolin-3(2*H*)-one **6a** was efficiently removed under Bu_3SnH-mediated reductive conditions, providing **7a** in 85% yields (Scheme 6).

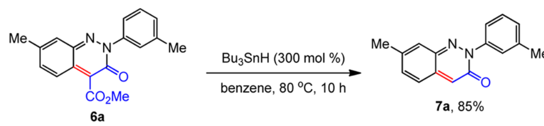
Based on the results of kinetic isotope effect experiments (k_H/k_D = 1.55, see the Supporting Information for details) and precedent literature on C–H functionalization of aromatic compounds using α-diazo esters,[22b,d,i,j] a plausible reaction pathway for the formation of *ortho*-alkylated azobenzenes and cinnolin-3(2*H*)-ones is depicted in Scheme 7. First, coordination of an azo group in azobenzene **1e** to cationic Rh(III) catalyst and subsequent C–H cleavage generates a five-membered rhodacycle **I**.[21] Then coordination of α-diazo compound **2a** to **I** and subsequent release of N_2 affords a metal–carbenoid intermediate **III** through intermediate **II** (pathway A). Migratory insertion

Scheme 5. Reaction of Azobenzenes with a Diazo Derivative of Meldrum's Acid[a]

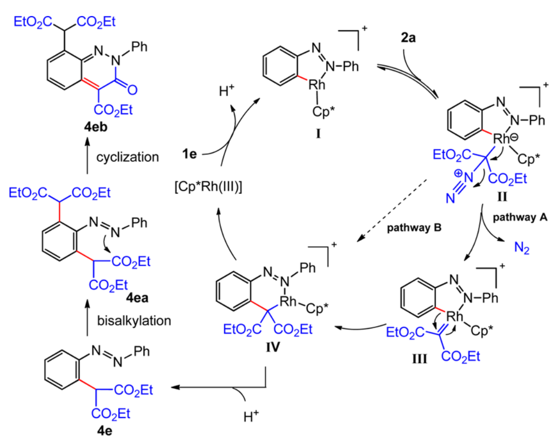


[a]Reaction conditions: **1a–c,e,f ,l** (0.2 mmol), **2h** (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), MeOH (1 mL) under air at 80 °C for 8 h in reaction tubes. [b]Isolated yield by column chromatography. [c]Parentheses shows yield of recovered starting material.

Scheme 6. Transformation of Cinnolin-3(2*H*)-one



Scheme 7. Plausible Reaction Mechanism



would deliver a 6-membered rhodacycle species **IV**, which undergoes protonation to give the alkylated product **4e** and an active Rh(III) catalyst. Alternatively, a direct 1,2-migration route (pathway B) that does not involve a discrete metal–carbenoid intermediate for the formation of **IV** cannot completely be ruled out in the catalytic cycle. Further alkylation of **4e** affords bisalkylated compound **4ea**, which on cyclization and subsequent aromatization delivers cinnolin-3(2*H*)-one **4eb** (see the Supporting Information for the cyclization of **4ea**). In order to investigate whether monoalkylated azobenzenes undergo the cyclization to generate the corresponding cinnolin-3(2*H*)-ones, we performed the reaction of **3a–g** under the optimal conditions. No cyclization was observed in all reactions. Furthermore, the

DOI: 10.1021/acs.orglett.5b01298
Org. Lett. 2015, 17, 2852–2855

formation of cinnolin-3(2*H*)-ones **6a−g**, generated from a diazo derivative of Meldrum's acid **2h**, is not clear at this stage.[26]

In conclusion, we disclosed the rhodium(III)-catalyzed direct C−H alkylation of azobenzenes with α-diazo compounds followed by intramolecular cyclization to afford the cinnolin-3(2*H*)-ones. Furthermore, the coupling reaction of azobenzenes with a diazo derivative of Meldrum's acid in MeOH provided cinnolin-3(2*H*)-ones.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra for all compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01298.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (no. 2013R1A2A2A01005249).

■ REFERENCES

(1) Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samori, P.; Mayor, M.; Rampi, M. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 3407−3409.

(2) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Voegtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714−10719.

(3) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512−515.

(4) (a) Banghart, M. R.; Mourot, A.; Fortin, D. L.; Yao, J. Z.; Kramer, R. H.; Trauner, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9097−9101. (b) Kim, Y.; Phillips, J. A.; Liu, H.; Kang, H.; Tan, W. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 6489−6494.

(5) (a) Hunger, K. *Industrial Dyes: Chemistry, Properties, Applications*; Wiley-VCH: Weinheim, 2003. (b) Bafana, A.; Devi, S. S.; Chakrabarti, T. *Environ. Rev.* **2011**, *19*, 350−370.

(6) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31−75. (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

(7) (a) DiCesare, N.; Lakowicz, J. R. *Org. Lett.* **2001**, *3*, 3891−3893. (b) Chang, K.-C.; Su, I.-H.; Wang, Y.-Y.; Chung, W.-S. *Eur. J. Org. Chem.* **2010**, 4700−4704.

(8) Buckler, S. A.; Doll, L.; Lind, F. K.; Epstein, M. *J. Org. Chem.* **1962**, *27*, 794−798.

(9) Tsai, W. H.; Shiao, Y. J.; Lin, S. J.; Chiou, W. F.; Lin, L. C.; Yang, T. H.; Teng, C. M.; Wu, T. S.; Yang, L. M. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 4440−4443.

(10) (a) Grirrane, A.; Corma, A.; Garca, H. *Science* **2008**, *322*, 1661−1664. (b) Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 6174−6177.

(11) For selected reviews on C−H functionalization, see: (a) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315−1345. (b) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068−5083. (c) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740−4761. (d) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885−1898.

(12) (a) Fahey, D. L. *J. Chem. Soc. D* **1970**, 417a−417a. (b) Fahey, D. L. *J. Organomet. Chem.* **1971**, *27*, 283−292.

(13) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300−2301.

(14) (a) Li, H.; Li, P.; Wang, L. *Org. Lett.* **2013**, *15*, 620−623. (b) Li, H.; Li, P.; Tan, H.; Wang, L. *Chem.−Eur. J.* **2013**, *19*, 14432−14436. (c) Li, Z.-Y.; Li, D.-D.; Wang, W. G. *J. Org. Chem.* **2013**, *78*, 10414−10420. (d) Song, H.; Chen, D.; Pi, C.; Cui, X.; Wu, Y. *J. Org. Chem.* **2014**, *79*, 2955−2962. (e) Li, H.; Li, P.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 9170−9172. (f) Li, H.; Xi, X.; Wang, L. *Chem. Commun.* **2014**, *50*, 4218−4221.

(15) (a) Ryu, T.; Min, J.; Choi, W.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2014**, *16*, 2810−2813. (b) Lian, Y.; Hummel, J. R.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 12548−12551. (c) Jia, X.; Han, J. *J. Org. Chem.* **2014**, *79*, 4180−4185. (d) Wang, H.; Yu, Y.; Hong, X.; Tan, Q.; Xu, B. *J. Org. Chem.* **2014**, *79*, 3279−3238.

(16) Ma, X.-T.; Tian, S.-K. *Adv. Synth. Catal.* **2013**, *355*, 337−340.

(17) (a) Qian, C.; Lin, D.; Deng, Y.; Zhang, X.-Q.; Jiang, H.; Miao, G.; Tang, X.; Zeng, W. *Org. Biomol. Chem.* **2014**, *12*, 5866−5875. (b) Yin, Z.; Jiang, X.; Sun, P. *J. Org. Chem.* **2013**, *78*, 10002−10007.

(18) Dong, J.; Jin, B.; Sun, P. *Org. Lett.* **2014**, *16*, 4540−4542.

(19) Hong, G.; Mao, D.; Wu, S.; Wang, L. *J. Org. Chem.* **2014**, *79*, 10629−10635.

(20) (a) Lian, Y.; Bergman, R. G.; Lavis, L. D.; Ellman, J. A. *J. Am. Chem. Soc.* **2013**, *135*, 7122−7125. (b) Hummel, J. R.; Ellman, J. A. *J. Am. Chem. Soc.* **2015**, *137*, 490−498.

(21) Muralirajan, K.; Cheng, C.-H. *Chem.—Eur. J.* **2013**, *19*, 6198−6202.

(22) For selected examples on C−H functionalization using α-diazo compounds, see: (a) Park, C. P.; Nagle, A.; Yoon, C. H.; Chen, C.; Jung, K. W. *J. Org. Chem.* **2009**, *74*, 6231−6236. (b) Chan, W.; Lo, S.-F.; Zhou, Z.; Yu, W.-Y. *J. Am. Chem. Soc.* **2012**, *134*, 13565−13568. (c) Hyster, T. K.; Ruhl, K. E.; Rovis, T. *J. Am. Chem. Soc.* **2013**, *135*, 5364−5367. (d) Shi, Z.; Koester, D. C.; Boultadakis-Arapinis, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 12204−12207. (e) Cui, S.; Zhang, Y.; Wang, D.; Wu, Q. *Chem. Sci.* **2013**, *4*, 3912−3916. (f) Yu, X.; Yu, S.; Xiao, J.; Wan, B.; Li, X. *J. Org. Chem.* **2013**, *78*, 5444−5452. (g) Hu, F.; Xia, Y.; Ye, F.; Liu, Z.; Ma, C.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 1364−1367. (h) Ai, W.; Yang, X.; Wu, Y.; Wang, X.; Li, Y.; Yang, Y.; Zhou, B. *Chem.—Eur. J.* **2014**, *20*, 17653−17657. (i) Jeong, J.; Patel, P.; Hwang, H.; Chang, S. *Org. Lett.* **2014**, *16*, 4598−4601. (j) Zhang, Y.; Zheng, J.; Cui, S. *J. Org. Chem.* **2014**, *79*, 6490−6500.

(23) (a) Mishra, N. K.; Park, J.; Sharma, S.; Han, S.; Kim, M.; Shin, Y.; Jang, J.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Chem. Commun.* **2014**, *50*, 2350−2352. (b) Sharma, S.; Han, S.; Kim, M.; Mishra, N. K.; Park, J.; Shin, Y.; Ha, J.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Biomol. Chem.* **2014**, *12*, 1703−1706. (c) Han, S.; Shin, Y.; Sharma, S.; Mishra, N. K.; Park, J.; Kim, M.; Kim, M.; Jang, J.; Kim, I. S. *Org. Lett.* **2014**, *16*, 2494−2497.

(24) For selected examples on bioactive molecules containing the cinnolin-3(2*H*)-one moiety, see: (a) Abdelfattah, M. S.; Toume, K.; Ishibashi, M. *J. Antibiot.* **2012**, *65*, 245−248. (b) Stefańska, B.; Arciemiuk, M.; Bontemps-Gracz, M. M.; Dzieduszycka, M.; Kupiec, A.; Martelli, S.; Borowski, E. *Bioorg. Med. Chem.* **2003**, *11*, 561−572.

(25) For selected examples on the synthesis of cinnolin-3(2*H*)-ones, see: (a) Hutchings, M. G.; Devonald, D. P. *Tetrahedron Lett.* **1989**, *30*, 3715−3718. (b) Zey, R. L.; Richter, G.; Randa, H. *J. Heterocycl. Chem.* **1989**, *26*, 1437−1439.

(26) During preparation of our manuscript, Lee et al. reported the synthesis of cinnolin-3(2*H*)-ones, generated from a diazo derivative of Meldrum's acid; see: Son, J.-Y.; Kim, S.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2015**, *17*, 2518−2521.

DOI: 10.1021/acs.orglett.5b01298
Org. Lett. 2015, 17, 2852−2855