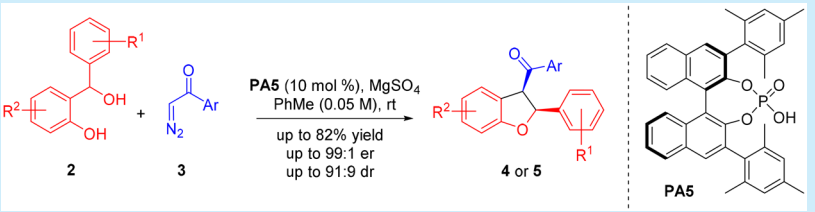
Organic LETTERS
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
Letter
pubs.acs.org/OrgLett

Phosphoric Acid Catalyzed [4 + 1]-Cycloannulation Reaction of *ortho*-Quinone Methides and Diazoketones: Catalytic, Enantioselective Access toward *cis*-2,3-Dihydrobenzofurans

Arun Suneja and Christoph Schneider*

Institut für Organische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

Supporting Information



ABSTRACT: A highly straightforward route to enantiomerically highly enriched *cis*-2,3-dihydrobenzofurans has been achieved via addition of α-diazocarbonyl compounds to *in situ* generated *o*-QMs catalyzed by a chiral Brønsted acid. This catalytic strategy provides a direct access to 2,3-dihydrobenzofurans in high yields and with up to 91:9 dr and 99:1 er at ambient temperature. Moreover, a unique phenonium-type rearrangement accounts for product formation with an inverted 2,3-substitution pattern.

2,3-Dihydrobenzofuran scaffolds are ubiquitously found in numerous complex natural products and pharmaceuticals.[1] Among various bioactive derivatives,[2,3] (+)-conocarpan (**1a**) is reported as an insecticidal,[4] antifungal,[5] and antitrypanosomal agent.[6] The neolignan callislignan A (**1c**) and (2*R*,3*S*)-3,4′-di-*O*-methylcedrusin (**1d**) are natural products containing this subunit and display antibacterial[7] and antitumor[8] activity, respectively (Figure 1).

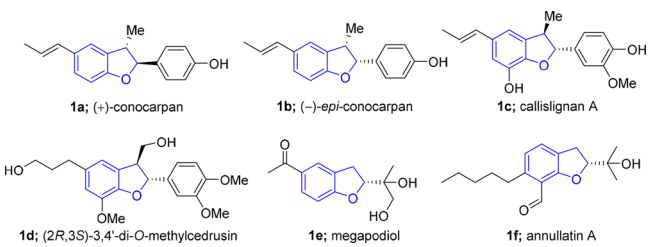
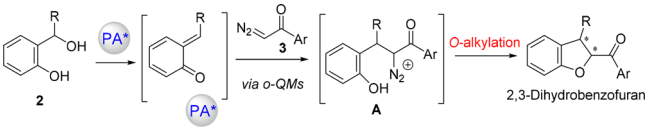


Figure 1. Natural products containing 2,3-dihydrobenzofurans.

Due to their intriguing biological activities, considerable attention has been focused recently toward their stereoselective synthesis.[9] Prominent approaches toward these scaffolds include resolution of racemates,[10a,b] diastereoselective oxidation,[10c] reduction reactions,[10d] intramolecular C−H insertions,[10e] catalytic asymmetric hydrogenations,[10f] and acid promoted cycloaddition reactions.[10g] Another obvious strategy which has been developed only recently is the [4 + 1]-cycloannulation[11] of carbenoid compounds toward *ortho*-quinone methides (*o*-QMs).[12] In this context Zhou and co-workers reported the addition of sulfur ylides to *o*-QMs to afford *trans*-2,3-dihydrobenzofurans with excellent diastereocontrol.[13] The Waser group employed chiral, enantiomerically pure nitrogen ylides in reactions with *o*-QMs to assemble this subunit with both excellent diastereo- and enantiocontrol.[14] Moreover, the Yang group established a bisurea-catalyzed [4 + 1]-annulation of sulfur ylides and *o*-QMs to access monosubstituted 2,3-dihydrobenzofurans with moderate to good enantiocontrol.[15] Finally, Han et al. developed a phase-transfer-catalyzed process for the addition of bromomalonates to stable *o*-QMs that proceeds with excellent enantiocontrol.[16,17]

Despite these advances in the synthesis of mainly *trans*-2,3-dihydrobenzofurans, a catalytic, enantioselective access toward 2,3-*cis*-dihydrobenzofurans is still very limited and has not yet been described using *o*-QM chemistry.[18] We envisioned a direct, Brønsted acid catalyzed [4 + 1]-cycloannulation of *o*-QMs with α-diazocarbonyl compounds to afford the desired heterocycles (Scheme 1). We have recently studied phosphoric acid catalyzed reactions of *o*-QMs with a broad range of π-nucleophiles in great detail and obtained various benzannulated oxygen heterocycles with excellent enantiocontrol.[19,20]

Scheme 1. Design Plan

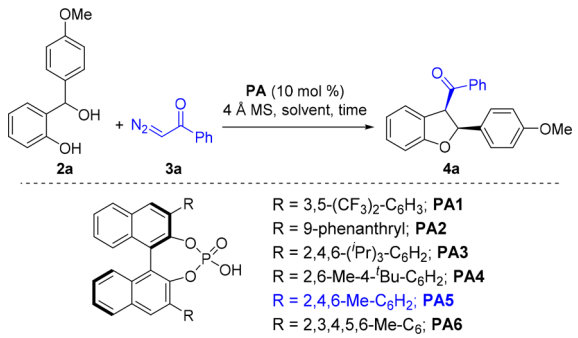


Received: October 16, 2018

DOI: 10.1021/acs.orglett.8b03311
Org. Lett. XXXX, XXX, XXX−XXX

We started our investigations with the reaction of *ortho*-hydroxy benzhydryl alcohol **2a** as a direct *o*-QM precursor and *α*-diazoacetophenone (**3a**) in the presence of chiral Brønsted acid **PA1** (10 mol %) in chloroform ($CHCl_3$) at 23 °C. After a 30 h reaction time, *cis*-2,3-dihydrobenzofuran **4a** was obtained in moderate yield and stereoselectivity (Table 1, entry 1).

Table 1. Optimization Studies[a−k]



entry	PA	solvent	time (h)	**4a** (%)[b,c]	er[d] (major)	dr[e]
1[f]	**1**	$CHCl_3$	30	50	71:29	56:44
2	**1**	$CHCl_3$	24	57	76:24	62:38
3	**2**	$CHCl_3$	24	63	88:12	66:34
4	**3**	$CHCl_3$	24	48	77:23	70:30
5	**4**	$CHCl_3$	24	58	83:17	62:38
6	**5**	$CHCl_3$	18	70	96:4	82:18
7	**6**	$CHCl_3$	20	68	93:7	76:24
8	**5**	CH_2Cl_2	20	64	95:5	77:23
9	**5**	PhMe	16	72	97:3	82:18
10	**5**	*m*-xylene	18	69	95:5	83:17
11	**5**	Et_2O	96	21	86:14	67:33
12[g]	**5**	PhMe	16	70	95:5	81:19
13[h]	**5**	PhMe	16	77	96:4	81:19
14[i]	**5**	PhMe	12	82	97:3	83:17
15[i,j]	**5**	PhMe	24	65	93:7	80:20
16[i,k]	**5**	PhMe	12	82	98:2	86:14

[a]Reactions were carried out with 0.1 mmol of **2a** and 0.11 mmol of **3a** in the presence of catalyst **PA** (10 mol %) in PhMe (0.1 M). [b]Isolated yield of both diastereomers after column purification. [c]Decomposition of the rest of the mass balance. [d]Enantiomeric ratios (er) were determined by chiral HPLC. [e]Diastereomeric ratios (dr) were determined from ^{1}H NMR of crude reaction mixture. [f]No 4 Å MS used. [g]With 3 Å MS (30 mg). [h]With Na_2SO_4 (30 mg). [i]With $MgSO_4$ (30 mg). [j]5 mol % catalyst loading. [k]PhMe (0.05 M) was used as solvent.

Surprisingly, the product displayed an inverted substitution pattern which was unambiguously proven only through a crystallographic analysis of benzofuran **4g** eventually (Figure 4). Thus, the aryl ketone moiety did not appear as the 2-substituent, but rather at the 3-position of the benzofuran. Likewise, the PMP group was located at the 2-position and not the 3-position of the heterocycle as originally expected. Interestingly, the reaction could be expedited in slightly better yield by using 4 Å molecular sieves, affording **4a** in 57% yield with 76:24 er (entry 2).

Encouraged by this initial finding a series of chiral Brønsted acids **PA2**−**PA6** were screened in this model reaction (entries 3−7). Among them, **PA5** was found to be the optimal phosphoric acid[21] catalyst furnishing product **4a** with good chemical yield and enantioselectivity (entry 6). Subsequently various solvents were examined, with toluene turning out to be the optimal choice. Further improvement in terms of both yield and stereoselectivity was achieved with the use of $MgSO_4$ as a dehydrating agent which furnished **4a** with 82% yield and 97:3 er (entry 14). Lowering the catalyst loading to just 5 mol % resulted in a diminished yield and enantioselectivity (entry 15). Optimal results were eventually obtained with a reduced substrate concentration of just 0.05 M in toluene, and 10 mol % of catalyst **PA5** in combination with $MgSO_4$ (30 mg) at room temperature (entry 16).

The substrate scope was investigated next. Initially, a variety of *α*-diazocarbonyl compounds **3** were submitted to reactions with benzhydryl alcohol **2a** under the optimized reaction conditions and each furnished 2,3-dihydrobenzofurans **4a**−**m** in synthetically useful yields (Figure 2). Interestingly, *α*-

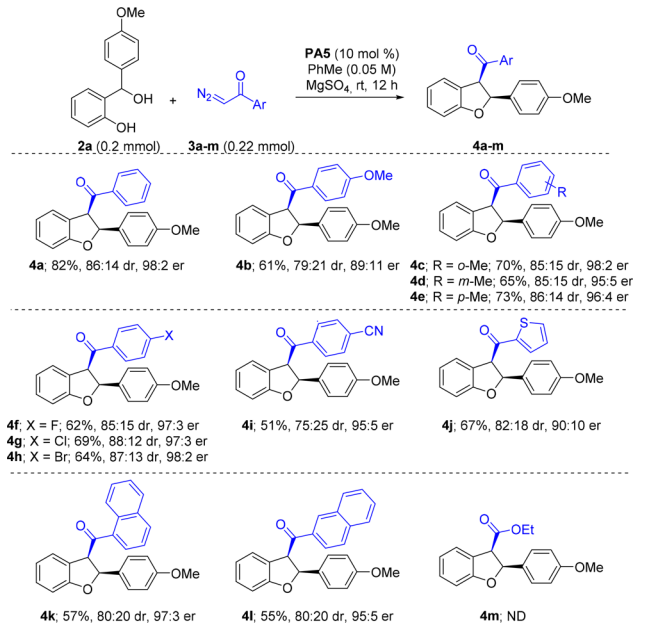


Figure 2. Scope of the reaction with respect to the *α*-diazocarbonyl component.

diazoaryl ketones **3b**−**e** substituted with an electron-donating group reacted smoothly and afforded products **4b**−**e** in good yields, moderate to good diastereocontrol, and excellent enantioselectivities of up to 98:2 er. Notably, steric hindrance had no significant effect on the enantioselectivity of product formation. Moreover, substrates **3f**−**i** bearing electron-withdrawing groups (such as halogen and CN-substituents) afforded **4f**−**i** in synthetically viable yields with enantiomeric ratios of up to 98:2 er.

Heteroaromatic substrates such as **3j**, having a thiophene moiety, afforded product **4j** in 67% yield and 90:10 er. The process also worked fine for substrates **3k** and **3l** carrying a bulky naphthyl group and afforded **4k** and **4l**, respectively, in moderate yields and with excellent enantioselectivities of up to 97:3 er. Ethyl *α*-diazoacetate failed to provide the desired product **4m** even at elevated temperature.

The substrate scope was further examined with diversely substituted *o*-hydroxy benzhydryl alcohols **2** and *α*-diazoaryl ketones **3** as shown in Figure 3. To our delight, a variety of different electron-rich substituents were well tolerated in both the quinone component and methide substituents and afforded dihydrobenzofuran products with good chemical yields and good to very good stereocontrol. Some observations deserve

DOI: 10.1021/acs.orglett.8b03311
Org. Lett. XXXX, XXX, XXX−XXX

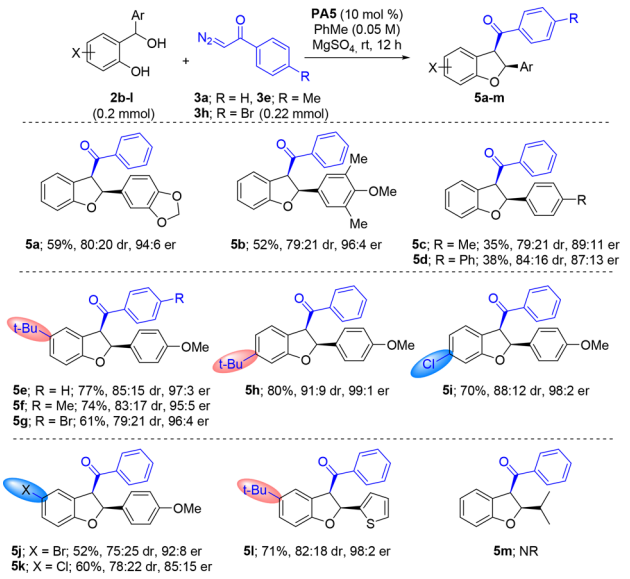


Figure 3. Scope of the reaction with respect to the *o*-hydroxy benzhydryl alcohol component.

mentioning though: only alkoxy-substituted aryl groups and other electron-rich heteroaryl groups were well tolerated as *β*-methide substituents and gave rise to dihydrobenzofurans with good chemical yields (e.g., **5a**–**b**, **5e**–**l**). Less electron-rich *β*-methide substituents provided products with only low to moderate yields (e.g., **5c**–**d**). An alkyl-substituted methide substrate failed altogether to furnish dihydrobenzofuran **5m**.

A range of substrates differing in the quinone moiety were studied as well and furnished products with good chemical yields and good to excellent enantioselectivity. For example, the 5- and 6-substituted benzhydryl alcohols **2f**–**k** with alkyl and halogen substituents afforded benzofurans **5e**–**l** in generally good yields and with excellent enantioselectivity of up to 99:1 er. The diastereoselectivity varied here from 3 to 10:1 *cis*/*trans*.

The crystal structure analysis of the major *cis*-diastereomer of 2,3-dihydrobenzofuran **4g** (CCDC 1871281) confirmed both the relative and absolute configuration of the products and corroborated the structural assignment at the same time (Figure 4). In order to showcase the practical utility of our

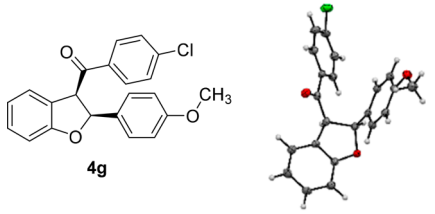
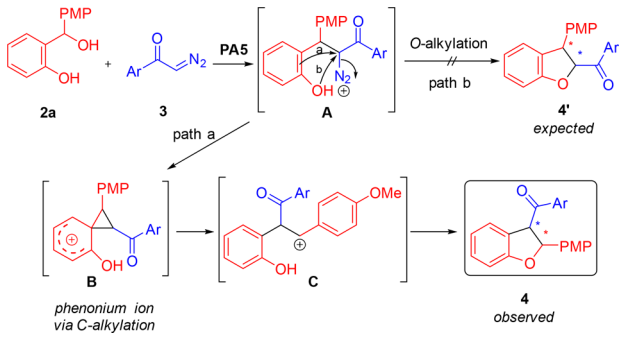


Figure 4. X-ray crystal structure of dihydrobenzofuran **4g**.

process, a scale-up reaction was performed on a 1 mmol scale using catalyst **PA5** (10 mol %) which afforded benzofuran **4a** with high yield and stereoselectivity (79%, 86:14 dr, 98:2 er) which could be enhanced to >99:1 er by a single recrystallization (see the SI for details).

A reasonable mechanism for the unexpected product formation with inverted 2- and 3-substituents is shown in Scheme 2. Initial acid-catalyzed dehydration of **2a** and *o*-QM formation is followed by conjugate addition of *α*-diazoketone **3**

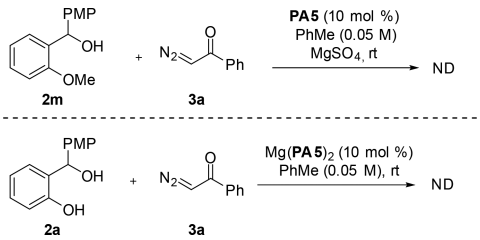
Scheme 2. Plausible Mechanistic Pathway



to afford phenol **A**. Instead of the expected O-alkylation, this electron-rich phenol acts as a C-nucleophile and upon N_2-displacement forms a spirocyclic cyclopropane phenonium ion **B**.[22] The cyclopropane then ring-opens to form a resonance-stabilized carbocation **C** which is trapped by the free phenol to afford the product **4** with inverted 2- and 3-substituents. This mechanistic scenario is further supported through the substituent effects shown in Figure 3 which require a highly electron-rich *β*-methide substituent (e.g., PMP) in the *o*-QM for a successful reaction.

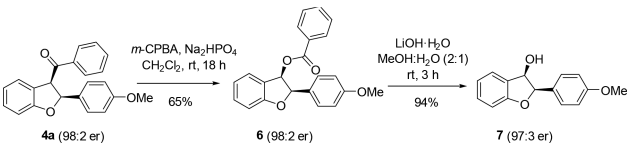
To shed some further light into the process, two control experiments were performed. Phenol-protected benzhydryl alcohol **2m** failed to react with **3a** under otherwise identical conditions further supporting the essential role of the *o*-QM structure for reactivity. Furthermore, a preformed Mg(**PA5**)$_2$ catalyst was not able to catalyze the reaction which rules out the possibility that the added $MgSO_4$ also serves to form an active metal catalyst (Scheme 3).

Scheme 3. Control Experiments



Finally, the products were easily converted into the corresponding 2,3-dihydrobenzofuran-3-ols[23] upon Baeyer–Villiger oxidation[24] and hydrolysis (Scheme 4). There appears

Scheme 4. Synthetic Elaboration



to be a pronounced migratory aptitude of the benzylic carbon over the aryl group which results in the exclusive incorporation of the oxygen atom next to the benzofuran ring. This two-step process proceeds with full retention of configuration and furnishes the product in good overall yield.

In conclusion, we have developed a highly stereoselective, phosphoric acid catalyzed [4 + 1]-cycloannulation of *α*-diazocarbonyl compounds with *in situ* generated *o*-QMs. This

DOI: 10.1021/acs.orglett.8b03311
Org. Lett. XXXX, XXX, XXX–XXX

reaction comprises the first catalytic, enantio- and diastereoselective synthesis of 2,3-dihydrobenzofurans based on *o*-QM chemistry. A unique phenonium rearrangement was responsible for the exchange of the 2- and 3-substituents and delivered highly valuable 2,3-dihydrobenzofurans with an unusual 3-ketoaryl group. The utility of this chemistry has also been demonstrated by a large-scale experiment and further synthetic modifications of the products. Further exploration of this strategy is currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03311.

Experimental procedures and analytical data (^{1}H, ^{13}C NMR spectra and HPLC traces) for all new compounds (PDF)

Accession Codes

CCDC 1871281 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: schneider@chemie.uni-leipzig.de.

ORCID

Christoph Schneider: 0000-0001-7392-9556

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (SCHN 441/11-2) and through gifts of chemicals from BASF and Evonik. We thank Till Friedmann for support in the preparation of starting materials and Dr. Peter Lönnecke (both University of Leipzig) for obtaining the X-ray crystal structure.

■ REFERENCES

(1) (a) Ward, R. S. *Nat. Prod. Rep.* **1999**, *16*, 75. (b) Apers, S.; Paper, D.; Bürgermeister, J.; Baronikova, S.; Van Dyck, S.; Lemière, G.; Vlietinck, A.; Pieters, L. *J. Nat. Prod.* **2002**, *65*, 718. (c) Yamaguchi, S.; Muro, S.; Kobayashi, M.; Miyazawa, M.; Hirai, Y. *J. Org. Chem.* **2003**, *68*, 6274. (d) Apers, S.; Vlietinck, A.; Pieters, L. *Phytochem. Rev.* **2003**, *2*, 201. (e) O'Malley, S. J.; Tan, K. L.; Watzke, A.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 13496. (f) Shen, T.; Wang, X.-N.; Lou, H.-X. *Nat. Prod. Rep.* **2009**, *26*, 916. (g) Manna, S. K.; Bose, J. S.; Gangan, V.; Raviprakash, N.; Navaneetha, T.; Raghavendra, P. B.; Babajan, B.; Kumar, C. S.; Jain, S. K. *J. Biol. Chem.* **2010**, *285*, 22318. (h) Tsui, G. C.; Tsoung, J.; Dougan, P.; Lautens, M. *Org. Lett.* **2012**, *14*, 5542.

(2) Jarvis, B. B.; Pena, N. B.; Comezoglu, S. N.; Rao, M. M. *Phytochemistry* **1986**, *25*, 533.

(3) Asai, T.; Luo, D.; Obara, Y.; Taniguchi, T.; Monde, K.; Yamashita, K.; Oshima, Y. *Tetrahedron Lett.* **2012**, *53*, 2239.

(4) Chauret, D. C.; Bernard, C. B.; Arnason, J. T.; Durst, T. *J. Nat. Prod.* **1996**, *59*, 152.

(5) De Campos, M. P.; Filho, V. C.; Da Silva, R. Z.; Yunes, R. A.; Zacchino, S.; Juarez, S.; Bella Cruz, R. C.; Bella Cruz, A. *Biol. Pharm. Bull.* **2005**, *28*, 1527.

(6) Luize, P. S.; Ueda-Nakamura, T.; Filho, B. P. D.; Cortez, D. A. G.; Nakamura, C. V. *Biol. Pharm. Bull.* **2006**, *29*, 2126.

(7) Rattanaburi, S.; Mahabusarakam, W.; Phongpaichit, S.; Carroll, A. R. *Phytochem. Lett.* **2012**, *5*, 18.

(8) Pieters, L.; Van Dyck, S.; Gao, M.; Bai, R.; Hamel, E.; Vlietinck, A.; Lemière, G. *J. Med. Chem.* **1999**, *42*, 5475.

(9) For reviews, see: (a) Sefkow, M. *Synthesis* **2003**, 2595. (b) Bertolini, F.; Pineschi, M. *Org. Prep. Proced. Int.* **2009**, *41*, 385.

(10) (a) Juhász, L.; Visy, J.; Simonyi, M.; Krohn, K.; Antus, S. *Tetrahedron: Asymmetry* **2002**, *13*, 1219. (b) Mangas-Sánchez, J.; Busto, E.; Gotor-Fernández, V.; Gotor, V. *Org. Lett.* **2010**, *12*, 3498. (c) Juhász, L.; Szilágyi, L.; Antus, S.; Visy, J.; Zsila, F.; Simonyi, M. *Tetrahedron* **2002**, *58*, 4261. (d) Fischer, J.; Savage, G. P.; Coster, M. J. *Org. Lett.* **2011**, *13*, 3376. (e) Ito, M.; Namie, R.; Krishnamurthi, J.; Miyamae, H.; Takeda, K.; Nambu, H.; Hashimoto, S. *Synlett* **2014**, *25*, 288. (f) Ortega, N.; Urban, S.; Beiring, B.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 1710. (g) Gelis, C.; Bekkaye, M.; Lebée, C.; Blanchard, F.; Masson, G. *Org. Lett.* **2016**, *18*, 3422.

(11) For reviews on [4 + 1]-cycloannulation reaction, see: (a) Zhu, C.; Ding, Y.; Ye, L.-W. *Org. Biomol. Chem.* **2015**, *13*, 2530. (b) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Rev.* **2015**, *115*, 5301.

(12) Representative reviews: (a) Bai, W. J.; David, J. G.; Feng, Z. G.; Weaver, M. G.; Wu, K. L.; Pettus, T. R. R. *Acc. Chem. Res.* **2014**, *47*, 3655. (b) Wang, Z.; Sun, J. *Synthesis* **2015**, *47*, 3629. (c) Caruana, L.; Fochi, M.; Bernardi, L. *Molecules* **2015**, *20*, 11733. (d) Jaworski, A. A.; Scheidt, K. A. *J. Org. Chem.* **2016**, *81*, 10145.

(13) Chen, M.-W.; Cao, L.-L.; Ye, Z.-S.; Jiang, G.-F.; Zhou, Y.-G. *Chem. Commun.* **2013**, *49*, 1660.

(14) (a) Meisinger, N.; Roiser, L.; Monkowius, U.; Himmelsbach, M.; Robiette, R.; Waser, M. *Chem. - Eur. J.* **2017**, *23*, 5137. (b) See also: Zielke, K.; Waser, M. *Org. Lett.* **2018**, *20*, 768.

(15) Yang, Q.-Q.; Xiao, W.-J. *Eur. J. Org. Chem.* **2017**, *2017*, 233.

(16) Lian, X.-L.; Adili, A.; Liu, B.; Tao, Z.-L.; Han, Z.-Y. *Org. Biomol. Chem.* **2017**, *15*, 3670.

(17) For further [4 + 1]-cycloannulation reactions with *o*-QMs, see: (a) Osyanin, V. A.; Osipov, D. V.; Klimochkin, Y. N. *J. Org. Chem.* **2013**, *78*, 5505. (b) Wu, B.; Chen, M.-W.; Ye, Z.-S.; Yu, C.-B.; Zhou, Y.-G. *Adv. Synth. Catal.* **2014**, *356*, 383. (c) Lei, X.; Jiang, C.-H.; Wen, X.; Xu, Q.-L.; Sun, H. *RSC Adv.* **2015**, *5*, 14953. (d) Shaikh, A. K.; Varvounis, G. *RSC Adv.* **2015**, *5*, 14892. (e) Rodriguez, K. X.; Vail, J. D.; Ashfeld, B. L. *Org. Lett.* **2016**, *18*, 4514. (f) Jiang, X.-L.; Liu, S.-J.; Gu, Y.-Q.; Mei, G.-J.; Shi, F. *Adv. Synth. Catal.* **2017**, *359*, 3341. (g) Jiang, F.; Luo, G.-Z.; Zhu, Z.-Q.; Wang, C.-S.; Mei, G.-J.; Shi, F. *J. Org. Chem.* **2018**, *83*, 10060.

(18) (a) Natori, Y.; Tsutsui, H.; Sato, N.; Nakamura, S.; Nambu, H.; Shiro, M.; Hashimoto, S. *J. Org. Chem.* **2009**, *74*, 4418. (b) Belmessieri, D.; Morrill, L. C.; Simal, C.; Slawin, A. M. Z.; Smith, A. D. *J. Am. Chem. Soc.* **2011**, *133*, 2714. (c) Wang, H.; Li, G.; Engle, K. M.; Yu, J.-Q.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 6774.

(19) (a) El-Sepelgy, O.; Haseloff, S.; Alamsetti, S. K.; Schneider, C. *Angew. Chem., Int. Ed.* **2014**, *53*, 7923. (b) Saha, S.; Schneider, C. *Chem. - Eur. J.* **2015**, *21*, 2348. (c) Saha, S.; Alamsetti, S. K.; Schneider, C. *Chem. Commun.* **2015**, *51*, 1461. (d) Saha, S.; Schneider, C. *Org. Lett.* **2015**, *17*, 648. (e) Alamsetti, S. K.; Spanka, M.; Schneider, C. *Angew. Chem., Int. Ed.* **2016**, *55*, 2392. (f) Gebauer, K.; Reuß, F.; Spanka, M.; Schneider, C. *Org. Lett.* **2017**, *19*, 4588. (g) Spanka, M.; Schneider, C. *Org. Lett.* **2018**, *20*, 4769.

(20) Selected examples from other groups: (a) Alden-Danforth, E.; Scerba, M. T.; Lectka, T. *Org. Lett.* **2008**, *10*, 4951. (b) Wilcke, D.; Herdtweck, E.; Bach, T. *Synlett* **2011**, *2011*, 1235. (c) Luan, Y.; Schaus, S. E. *J. Am. Chem. Soc.* **2012**, *134*, 19965. (d) Lv, H.; Jia, W. Q.; Sun, L. H.; Ye, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8607. (e) Izquierdo, J.; Orue, A.; Scheidt, K. A. *J. Am. Chem. Soc.* **2013**, *135*, 10634. (f) Hsiao, C. C.; Liao, H. H.; Rueping, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 13258. (g) Zhao, W.; Wang, Z.; Chu, B.; Sun, J. *Angew.*

DOI: 10.1021/acs.orglett.8b03311
Org. Lett. XXXX, XXX, XXX−XXX

Chem., Int. Ed. **2015**, *54*, 1910. (h) Zhao, J. J.; Sun, S. B.; He, S. H.; Wu, Q.; Shi, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 5460. (i) Hsiao, C. C.; Raja, S.; Liao, H. H.; Atodiresei, I.; Rueping, M. *Angew. Chem., Int. Ed.* **2015**, *54*, 5762. (j) Tsui, G. C.; Liu, L.; List, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 7703. (k) Wang, Z.; Ai, F.; Wang, W.; Zhao, G.; Zhu, Z.; Lin, J.; Sun, J. *J. Am. Chem. Soc.* **2015**, *137*, 383. (l) Lai, Z.; Wang, Z.; Sun, J. *Org. Lett.* **2015**, *17*, 6058. (m) Lee, A.; Scheidt, K. A. *Chem. Commun.* **2015**, *51*, 3407. (n) Hu, H.; Liu, Y.; Guo, J.; Lin, L.; Xu, Y.; Liu, X.; Feng, X. *Chem. Commun.* **2015**, *51*, 3835. (o) Caruana, L.; Mondatori, M.; Corti, V.; Morales, S.; Mazzanti, A.; Fochi, M.; Bernardi, L. *Chem. - Eur. J.* **2015**, *21*, 6037. (p) Xie, Y.; List, B. *Angew. Chem., Int. Ed.* **2017**, *56*, 4936. (q) Allen, E. E.; Zhu, C.; Panek, J. S.; Schaus, S. E. *Org. Lett.* **2017**, *19*, 1878. (r) Wang, Z.; Wang, T.; Yao, W.; Lu, Y. *Org. Lett.* **2017**, *19*, 4126. (s) Mei, G. J.; Zhu, Z. Q.; Zhao, J. J.; Bian, C. Y.; Chen, J.; Chen, R. W.; Shi, F. *Chem. Commun.* **2017**, *53*, 2768. (t) Jeong, H. J.; Kim, D. Y. *Org. Lett.* **2018**, *20*, 2944. (u) Zhang, J.; Lin, L.; He, C.; Xiong, Q.; Liu, X.; Feng, X. *Chem. Commun.* **2018**, *54*, 74.

(21) Selected reviews: (a) Akiyama, T. *Chem. Rev.* **2007**, *107*, 5744. (b) Terada, M. *Chem. Commun.* **2008**, 4097. (c) Zamfir, A.; Schenker, S.; Freund, M.; Tsogoeva, S. B. *Org. Biomol. Chem.* **2010**, *8*, 5262. (d) Desai, A. A.; Wulff, W. D. *Synthesis* **2010**, *2010*, 3670. (e) Parmar, D.; Sugiono, E.; Raja, S.; Rueping, M. *Chem. Rev.* **2014**, *114*, 9047.

(22) (a) Guizzardi, B.; Mella, M.; Fagnoni, M.; Albini, A. *J. Org. Chem.* **2003**, *68*, 1067. (b) Tsuji, Y.; Richard, J. P. *J. Phys. Org. Chem.* **2016**, *29*, 557. (c) See also ref 17e.

(23) Fang, L.; Liu, S.; Han, L.; Li, H.; Zhao, F. *Organometallics* **2017**, *36*, 1217.

(24) Suneja, A.; Bisai, V.; Singh, V. K. *J. Org. Chem.* **2016**, *81*, 4779.

DOI: 10.1021/acs.orglett.8b03311
Org. Lett. XXXX, XXX, XXX−XXX