Organic LETTERS

Letter

pubs.acs.org/OrgLett

Enantioselective [4 + 2]-Annulation of Oxadienes and Allenones Catalyzed by an Amino Acid Derived Phosphine: Synthesis of Functionalized Dihydropyrans

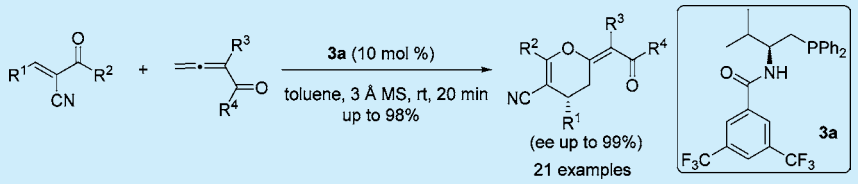
Huanzhen Ni,[†,‡] Weijun Yao,[‡] Abdul Waheed,[§] Nisar Ullah,[*,§] and Yixin Lu[*,†,‡]

[†]Graduate School for Integrative Sciences & Engineering (NGS), Centre for Life Sciences (CeLS), National University of Singapore, #05-01, 28 Medical Drive, Singapore 117456 Singapore

[‡]Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543 Singapore

[§]Chemistry Department, King Fahd University of Petroleum and Materials, Dhahran 31261, Saudi Arabia

Supporting Information

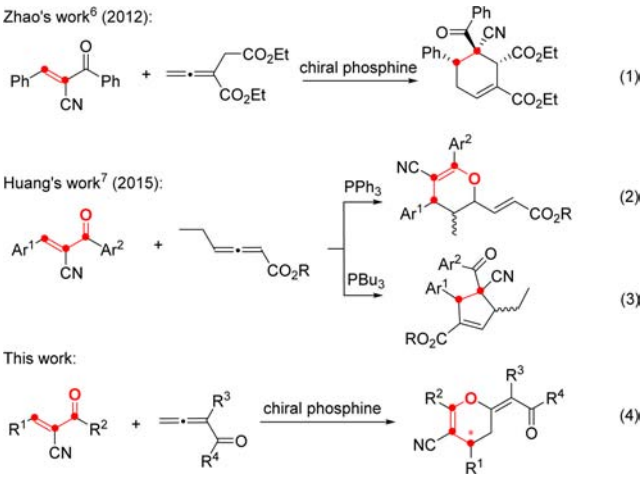


ABSTRACT: An enantioselective [4 + 2]-annulation process between cyano-activated oxadienes and allenones is developed. An L-valine-derived phosphine was efficient in catalyzing the reaction, and a wide range of highly functionalized dihydropyrans were prepared in high yields and with excellent enantioselectivities.

Asymmetric nucleophilic phosphine catalysis has received much attention in the past decade due to its versatility in constructing synthetically useful molecular architectures.[1] In his pioneering study in 1995, Lu first disclosed that electron-deficient allenoates could act as a C3 synthon and react with activated olefins via phosphine catalysis to form cycloaddition products.[2a] Thereafter, phosphine activations of electron-deficient allenes had been intensively investigated, and a wide range of annulation processes, i.e. [3 + 2]-,[2] [4 + 2]-,[3] and [4 + 1]-[4] reactions, were developed. Oxadienes, possessing highly activated C−C double bonds, have been used widely in organic synthesis.[5] However, their application in phosphine catalysis has been very limited. In 2012, Zhao et al. utilized oxadienes as C2 synthons in a [4 + 2]-annulation with α-substituted allenoates.[6] Recently, Huang and co-workers reported divergent phosphine-catalyzed [4 + 2]- and [3 + 2]-annulations, in which the oxadienes acted as either a C4 or C2 synthon.[7] Our group recently[8e] disclosed an enantioselective [4 + 2]-annulation reaction making use of novel reactivity of allenones.[9] As our continuous interest in phoshine catalysis,[8] we wondered whether oxadienes could potentially be used as a C4 synthon,[10] in combination with allene ketones to produce structurally unique ring motifs (Scheme 1). Herein, we document an enantioselective [4 + 2]-annulation process between oxadienes and allenones for the construction of highly functionalized dihydropyrans.[11]

We initiated our studies by investigating the annulation reaction between oxadiene[12] **1a** and allenone[13] **2a** in the presence of a number of amino acid derived phosphine catalysts (Table 1). Simple L-valine-derived amide−phosphine catalysts were very effective, and the products were obtained in excellent

Scheme 1. Phosphine Catalyzed Annulation Reactions Employing Oxadienes

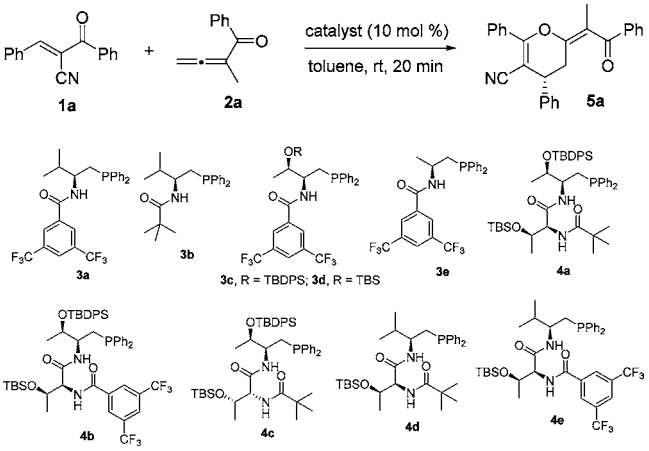


yields and with good enantioselectivities (Table 1, entries 2−3). Changing the catalyst backbone to threonine or alanine did not improve the enantioselectivity of the reaction, and catalysts **3c**, **3d**, and **3e** were found to be less effective (Table 1, entries 4−6). In an effort to further enhance enantioselectivity, we tested a number of dipeptide catalysts. The L-thr-L-thr-derived catalysts **4a** and **4b** provided sufficient activation for the reaction and yielded the products with moderate to good ee values (Table 1,

Received: March 16, 2016
Published: April 19, 2016

DOI: 10.1021/acs.orglett.6b00760
Org. Lett. 2016, 18, 2138−2141

Table 1. Phosphine-Catalyzed [4 + 2]-Annulation between Oxadiene 1a and Allenone 2a: Initial Screening[a]



entry	catalyst	yield (%)[b]	ee (%)[c]
1	$MePPh_2$	80	–
2	**3a**	94	87
3	**3b**	85	84
4	**3c**	87	81
5	**3d**	84	54
6	**3e**	90	75
7	**4a**	86	−80
8	**4b**	89	−73
9	**4c**	70	36
10	**4d**	85	−47
11	**4e**	88	−82

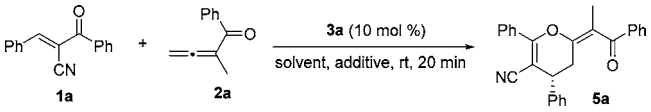
[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), and the catalyst (0.01 mmol) in toluene (0.5 mL) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

entries 7−8). However, the L-thr-D-thr-derived **4c** was found to be a poor catalyst (Table 1, entry 9). It is worth mentioning that employment of (L,L)-dipeptide catalysts led to the formation of products with configurations opposite to those obtained by employing natural amino acid based phosphines. Moreover, L-val-L-thr-derived catalyst **4d** and **4e** were also proven to be inferior (Table 1, entries 10−11). Therefore, catalyst **3a** was chosen as the optimal catalyst for subsequent screenings.

To further enhance the stereoselectivity of the reaction, we continued optimizing a number of reaction parameters (Table 2). Solvent screening revealed that toluene was the best solvent (Table 2, entries 1−5). Lowering the reaction temperature did not offer further improvement (Table 2, entry 6). To our delight, addition of molecular sieves was found to be beneficial (Table 2, entries 7−9). When the reaction was run at room temperature in the presence of 3 Å molecular sieves for 20 min, the desired [4 + 2]-annulation product was isolated in 95% yield and with 90% ee. It is noteworthy that the catalyst loading could be reduced to as low as 1 mol %, with virtually the same ee value and a slightly lower yield attainable (Table 2, entries 10−11).

With the established optimized reaction conditions in hand, we investigated the scope of this [4 + 2]-annulation between oxadienes **1** and allenone **2a**, and the results are summarized in Table 3. Different R^1 and R^2 substituents in oxadienes **1** were well tolerated, and products with good to excellent yields and enantioselectivities were attainable. For oxadienes with aromatic R^1 groups, the presence of halogen atom on the aromatic ring did not affect the enantioselectivity (Table 3, entries 2−3). The

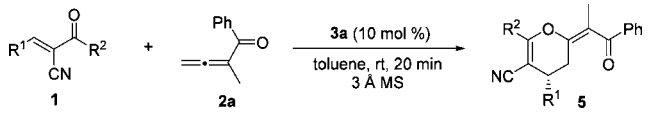
Table 2. Optimization of the Reaction Conditions[a]



entry	solvent	additive	yield (%)[b]	ee (%)[c]
1	toluene	–	94	87
2	ether	–	90	87
3	ethyl acetate	–	78	75
4	chloroform	–	85	83
5	dichloromethane	–	80	86
6[d]	toluene	–	80	87
7	**toluene**	**3 Å MS**	**95**	**90**
8	toluene	4 Å MS	94	89
9	toluene	5 Å MS	94	90
10[e]	toluene	3 Å MS	90	90
11[f]	toluene	3 Å MS	85	89

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), and **3a** (0.01 mmol) under the specified conditions. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at −55 °C. [e]The catalyst loading was 5 mol %, and the reaction time was 1 h. [f]The catalyst loading was 1 mol % and the reaction time was 12 h.

Table 3. Scope of the [4 + 2]-Annulation between Oxadienes 1 with Allenone 2a[a]



entry	**1**, R^1/R^2	**5**	yield (%)[b]	ee (%)[c]
1	**1a**, Ph/Ph	**5a**	95	90
2	**1b**, 4-FC_6H_4/Ph	**5b**	91	92
3	**1c**, 4-ClC_6H_4/Ph	**5c**	94	92
4	**1d**, 4-MeC_6H_4/Ph	**5d**	91	86
5	**1e**, 3-MeC_6H_4/Ph	**5e**	90	85
6	**1f**, 2-MeC_6H_4/Ph	**5f**	94	92
7	**1g**, 4-$MeOC_6H_4$/Ph	**5g**	92	91
8	**1h**, 4-CNC_6H_4/Ph	**5h**	96	91
9	**1i**, 3-$NO_2C_6H_4$/Ph	**5i**	96	94
10	**1j**, 2-naphthyl/Ph	**5j**	94	91
11	**1k**, 2-thienyl/Ph	**5k**	90	90
12	**1l**, (*E*)-PhCH=CH/Ph	**5l**	93	84
13	**1m**, 3-NO_2, 4-ClC_6H_3/Ph	**5m**	94	95
14[d]	**1n**, C_6H_{11}/Ph	**5n**	85	87
15[d]	**1o**, *i*-Pr/Ph	**5o**	79	90
16	**1p**, Ph/*t*-Bu	**5p**	96	90
17	**1q**, Ph/2-thienyl	**5q**	98	93
18	**1r**, Ph/4-ClC_6H_4	**5r**	94	90
19	**1s**, Ph/4-$MeOC_6H_4$	**5s**	95	90

[a]Reactions were performed with **1** (0.1 mmol), **2a** (0.12 mmol), and **3a** (0.01 mmol) in toluene (0.5 mL) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction time was 4 h.

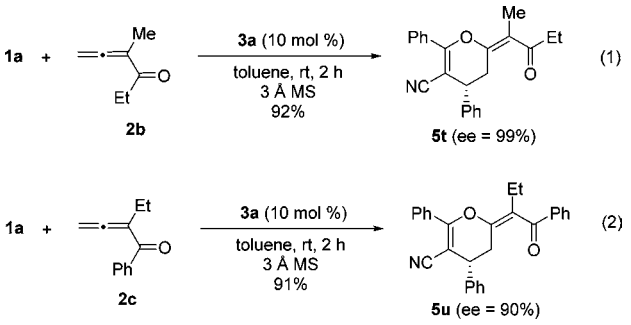
ortho-substituted aromatic moiety in the R^1 structure of oxadienes led to slightly better enantioselectivity compared to *meta*/*para*-substitutions (Table 3, entries 4−6). Both electron-rich and electron-deficient aromatic R^1 groups in oxadiene **1** led to equally good yields and enantioselectivities (Table 3, entries 7−9). Fused aryl, heterocyclic, and doubly substituted aromatic R^1 groups in oxadienes worked well, and the desired products

DOI: 10.1021/acs.orglett.6b00760
Org. Lett. 2016, 18, 2138−2141

were obtained in excellent yields and enantioselectivities in all cases (Table 3, entries 10−11, 13). Vinyl substituted oxadiene also underwent the annulation efficiently to generate products in good yields and slightly lower enantioselectivity (Table 3, entry 12). It is noteworthy that oxadienes with an alkyl R^1 group were also well tolerated, and slightly lower chemical yields and the same level of enantioselectivity were attainable (Table 3, entries 14−15). The ketone moieties of oxadienes could also be varied, with annulation products formed in excellent yields and enantioselectivities (Table 3, entries 16−19).

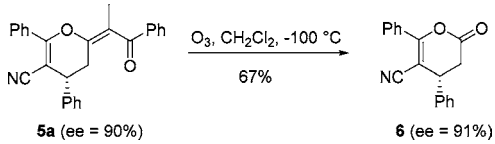
We next tested the suitability of different allenones for the reaction (Scheme 2, eqs 1 and 2). Both allenone **2b** with only

Scheme 2. [4 + 2]-Annulation between Oxadiene 1 and Different Allenones



alkyl substituents and allene ketone **2c** containing mixed alkyl and aryl groups were found to be excellent substrates, affording products in excellent yields and high enantioselectivities. The absolute configurations of the products were assigned based on the X-ray crystallographic analysis of product **5a**. The exocyclic double bond in products **5** has a thermodynamically more favored (*E*)-configuration.[14] The annulation product could be conveniently converted to chiral dihydropyranone **6**, a structural motif often found in bioactive molecules[15] (Scheme 3).

Scheme 3. Synthesis of a Dihydropyranone 6



In conclusion, we have developed the first phosphine-catalyzed enantioselective [4 + 2]-cycloaddition between oxadienes and allenones. In this unique annulation process, oxadienes were employed as C4 synthons and allenones acted as C2 synthons. Highly functionalized dihydropyrans were obtained in high yields and with excellent enantioselectivities. Extension of the reaction partners disclosed in this report to other asymmetric annulation processes is ongoing 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.6b00760.

Crystallographic data for **5a** (CIF)
Experimental details, analytical data and HPLC chromatogram of products, copies of NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: nullah@kfupm.edu.sa.
*E-mail: chmlyx@nus.edu.sg.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Y.L. thanks Singapore A*STAR SERC Public Sector Research Funding (PSF; R-143-000-618-305) and the National University of Singapore (R-143-000-599-112) for generous financial support. N.U. and Y.L. are grateful for the KFUPM−NUS Collaborative Fund support (NUS15103, R-143-004-617-597).

■ REFERENCES

(1) For reviews on nucleophilic phosphine catalysis, see: (a) Lu, X.; Zhang, C.; Xu, Z. *Acc. Chem. Res.* **2001**, *34*, 535. (b) Methot, J. L.; Roush, W. R. *Adv. Synth. Catal.* **2004**, *346*, 1035. (c) Lu, X.; Du, Y.; Lu, C. *Pure Appl. Chem.* **2005**, *77*, 1985. (d) Ye, L.−W.; Zhou, J.; Tang, Y. *Chem. Soc. Rev.* **2008**, *37*, 1140. (e) Cowen, B. J.; Miller, S. J. *Chem. Soc. Rev.* **2009**, *38*, 3102. (f) Wei, Y.; Shi, M. *Acc. Chem. Res.* **2010**, *43*, 1005. (g) Marinetti, A.; Voituriez, A. *Synlett* **2010**, *2010*, 174. (h) Wang, S.−X.; Han, X.; Zhong, F.; Wang, Y.; Lu, Y. *Synlett* **2011**, *2011*, 2766. (i) Zhao, Q.−Y.; Lian, Z.; Wei, Y.; Shi, M. *Chem. Commun.* **2012**, *48*, 1724. (j) Fan, Y. C.; Kwon, O. *Chem. Commun.* **2013**, *49*, 11588. (k) Wang, Z.; Xu, X.; Kwon, O. *Chem. Soc. Rev.* **2014**, *43*, 2927. (l) Xiao, Y.; Sun, Z.; Guo, H.; Kwon, O. *Beilstein J. Org. Chem.* **2014**, *10*, 2089. (m) Wei, Y.; Shi, M. *Chem. - Asian J.* **2014**, *9*, 2720. (n) Li, W.; Zhang, J. *Chem. Soc. Rev.* **2016**, *45*, 1657.

(2) For selected examples on phosphine catalyzed [3 + 2]-annulations of allenoate with activated olefins, see: (a) Zhang, C.; Lu, X. *J. Org. Chem.* **1995**, *60*, 2906. (b) Zhu, G.; Chen, Z.; Jiang, Q.; Xiao, D.; Cao, P.; Zhang, X. *J. Am. Chem. Soc.* **1997**, *119*, 3836. (c) Du, Y.; Lu, X.; Yu, Y. *J. Org. Chem.* **2002**, *67*, 8901. (d) Du, Y.; Lu, X. *J. Org. Chem.* **2003**, *68*, 6463. (e) Pham, T. Q.; Pyne, S. G.; Skelton, B. W.; White, A. H. *J. Org. Chem.* **2005**, *70*, 6369. (f) Lu, X.; Lu, Z.; Zhang, X. *Tetrahedron* **2006**, *62*, 457. (g) Wilson, J. E.; Fu, G. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 1426. (h) Henry, C. E.; Kwon, O. *Org. Lett.* **2007**, *9*, 3069. (i) Cowen, B. J.; Miller, S. J. *J. Am. Chem. Soc.* **2007**, *129*, 10988. (j) Jones, R. A.; Krische, M. J. *Org. Lett.* **2009**, *11*, 1849. (k) Voituriez, A.; Panossian, A.; Fleury-Brégeot, N.; Retailleau, P.; Marinetti, A. *J. Am. Chem. Soc.* **2008**, *130*, 14030. (l) Voituriez, A.; Pinto, N.; Neel, M.; Retailleau, P.; Marinetti, A. *Chem. - Eur. J.* **2010**, *16*, 12541. (m) Xiao, H.; Chai, Z.; Zheng, C.−W.; Yang, Y.−Q.; Liu, W.; Zhang, J.−K.; Zhao, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 4467. (n) Fujiwara, Y.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 12293. (o) Han, X.; Wang, Y.; Zhong, F.; Lu, Y. *J. Am. Chem. Soc.* **2011**, *133*, 1726. (p) Zhang, X.−C.; Cao, S.−H.; Wei, Y.; Shi, M. *Chem. Commun.* **2011**, *47*, 1548. (q) Zhao, Q.; Han, X.; Wei, Y.; Shi, M.; Lu, Y. *Chem. Commun.* **2012**, *48*, 970. (r) Dakas, P.−Y.; Parga, J. A.; Höing, S.; Schöler, H. R.; Sterneckert, J.; Kumar, K.; Waldmann, H. *Angew. Chem., Int. Ed.* **2013**, *52*, 9576. (s) Marco-Martínez, J.; Marcos, V.; Reboredo, S.; Filippone, S.; Martín, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 5115. (t) Wang, D.; Wang, G.−P.; Sun, Y.−L.; Zhu, S.−F.; Wei, Y.; Zhou, Q.−L.; Shi, M. *Chem. Sci.* **2015**, *6*, 7319.

(3) For selected examples on phosphine catalyzed [4 + 2]-annulations, see: (a) Zhu, X.−F.; Lan, J.; Kwon, O. *J. Am. Chem. Soc.* **2003**, *125*, 4716. (b) Wurz, R. P.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 12234. (c) Tran, Y. S.; Kwon, O. *Org. Lett.* **2005**, *7*, 4289. (d) Tran, Y. S.; Kwon, O. *J. Am. Chem. Soc.* **2007**, *129*, 12632. (e) Wang, T.; Ye, S. *Org. Lett.* **2010**, *12*, 4168. (f) Xiao, H.; Chai, Z.; Wang, H.−F.; Wang, X.−W.; Cao, D.−D.; Liu, W.; Lu, Y.−P.; Yang, Y.−Q.; Zhao, G. *Chem. - Eur. J.* **2011**, *17*, 10562. (g) Baskar, B.; Dakas, P.−Y.; Kumar, K. *Org. Lett.* **2011**, *13*, 1988. (h) Tran, Y. S.; Martin, T. J.; Kwon, O. *Chem. - Asian J.* **2011**, *6*, 2101. (i) Chen, X.−Y.; Ye, S. *Eur. J. Org. Chem.* **2012**, *2012*, 5723. (j) Zhong, F.; Han, X.; Wang, Y.; Lu, Y. *Chem. Sci.* **2012**, *3*, 1231. (k) Li, E.; Huang, Y.; Liang, L.; Xie, P. *Org. Lett.* **2013**, *15*, 3138. (l) Gicquel, M.; Gomez,

DOI: 10.1021/acs.orglett.6b00760
Org. Lett. 2016, 18, 2138−2141

C.; Retailleau, P.; Voituriez, A.; Marinetti, A. *Org. Lett.* **2013**, *15*, 4002. (m) Yu, H.; Zhang, L.; Li, Z.; Liu, H.; Wang, B.; Xiao, Y.; Guo, H. *Tetrahedron* **2014**, *70*, 340. (n) Jia, Y.; Tang, X.; Cai, G.; Jia, R.; Wang, B.; Miao, Z. *Eur. J. Org. Chem.* **2015**, *2015*, 4720.

(4) For examples on phosphine catalyzed [4 + 1]-annulations, see: (a) Zhang, Q.; Yang, L.; Tong, X. *J. Am. Chem. Soc.* **2010**, *132*, 2550. (b) Han, X.; Yao, W.; Wang, T.; Tan, Y. R.; Yan, Z.; Kwiatkowski, J.; Lu, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5643. (c) Ziegler, D. T.; Riesgo, L.; Ikeda, T.; Fujiwara, Y.; Fu, G. C. *Angew. Chem., Int. Ed.* **2014**, *53*, 13183. (d) Kramer, S.; Fu, G. C. *J. Am. Chem. Soc.* **2015**, *137*, 3803.

(5) For selected examples on annulation reactions utilizing oxadienes, see: (a) Palasz, A. *Org. Biomol. Chem.* **2005**, *3*, 3207. (b) Zhang, Q.; Fang, T.; Tong, X. *Tetrahedron* **2010**, *66*, 8095. (c) Wang, X.; Fang, T.; Tong, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 5361. (d) Liu, W.; Zhou, J.; Zheng, C.; Chen, X.; Xiao, H.; Yang, Y.; Guo, Y.; Zhao, G. *Tetrahedron* **2011**, *67*, 1768. (e) Das, U.; Huang, C.−H.; Lin, W. *Chem. Commun.* **2012**, *48*, 5590. (f) Chen, X.−Y.; Sun, L.−H.; Ye, S. *Chem. - Eur. J.* **2013**, *19*, 4441. (g) Gu, Y.; Li, F.; Hu, P.; Liao, D.; Tong, X. *Org. Lett.* **2015**, *17*, 1106. (h) Liang, L.; Li, E.; Dong, X.; Huang, Y. *Org. Lett.* **2015**, *17*, 4914. (i) Kendre, D. B.; Toche, R. B.; Jachak, M. N. *J. Heterocycl. Chem.* **2008**, *45*, 667.

(6) Xiao, H.; Chai, Z.; Cao, D.; Wang, H.; Chen, J.; Zhao, G. *Org. Biomol. Chem.* **2012**, *10*, 3195.

(7) Li, E.; Chang, M.; Liang, L.; Huang, Y. *Eur. J. Org. Chem.* **2015**, *2015*, 710.

(8) (a) Wang, T.; Yu, Z.; Hoon, D. L.; Phee, C. Y.; Lan, Y.; Lu, Y. *J. Am. Chem. Soc.* **2016**, *138*, 265. (b) Wang, T.; Hoon, D. L.; Lu, Y. *Chem. Commun.* **2015**, *51*, 10186. (c) Wang, T.; Yu, Z.; Hoon, D. L.; Huang, K.−W.; Lan, Y.; Lu, Y. *Chem. Sci.* **2015**, *6*, 4912. (d) Gandi, V. R.; Lu, Y. *Chem. Commun.* **2015**, *51*, 16188. (e) Yao, W.; Dou, X.; Lu, Y. *J. Am. Chem. Soc.* **2015**, *137*, 54. (f) Wang, T.; Yao, W.; Zhong, F.; Pang, G. H.; Lu, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 2964. (g) Han, X.; Yao, W.; Wang, T.; Tan, Y. R.; Yan, Z.; Kwiatkowski, J.; Lu, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5643. (h) Lee, R.; Zhong, F.; Meng, Y.; Lu, Y.; Huang, K.−W. *Org. Biomol. Chem.* **2013**, *11*, 4818. (i) Zhong, F.; Dou, X.; Han, X.; Yao, W.; Zhu, Q.; Meng, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 943. (j) Zhong, F.; Luo, J.; Chen, G.−Y.; Dou, X.; Lu, Y. *J. Am. Chem. Soc.* **2012**, *134*, 10222. (k) Zhong, F.; Chen, G.−Y.; Han, X.; Yao, W.; Lu, Y. *Org. Lett.* **2012**, *14*, 3764. (l) Han, X.; Zhong, F.; Wang, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 767. (m) Zhong, F.; Wang, Y.; Han, X.; Huang, K.−W.; Lu, Y. *Org. Lett.* **2011**, *13*, 1310. (n) Zhong, F.; Han, X.; Wang, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 7837. (o) Han, X.; Wang, Y.; Zhong, F.; Lu, Y. *Org. Biomol. Chem.* **2011**, *9*, 6734. (p) Han, X.; Wang, S.−X.; Zhong, F.; Lu, Y. *Synthesis* **2011**, *2011*, 1859.

(9) (a) Wallace, D. J.; Sidda, R. L.; Reamer, R. A. *J. Org. Chem.* **2007**, *72*, 1051. (b) Sampath, M.; Loh, T.-P. *Chem. Commun.* **2009**, 1568.

(10) For examples of utilizing activated oxadienes as a C4 synthon in reaction with the MBH carbonates in phosphine catalysis, see: (a) Hu, F.−L.; Wei, Y.; Shi, M. *Chem. Commun.* **2014**, *50*, 8912. (b) Chen, Z.; Zhang, J. *Chem. - Asian J.* **2010**, *5*, 1542.

(11) For selected reviews, see: (a) Nicolaou, K. C.; Synder, S. A. *Classics in Total Synthesis*; Wiley-VCH, Weinhein, 2003. (b) Yeung, K.-S.; Paterson, I. *Chem. Rev.* **2005**, *105*, 4237. (c) Kang, E. J.; Lee, E. *Chem. Rev.* **2005**, *105*, 4348. (d) Inoue, M. *Chem. Rev.* **2005**, *105*, 4379. (e) Aho, J. E.; Pihko, P. M.; Rissa, T. K. *Chem. Rev.* **2005**, *105*, 4406. (f) Nakata, T. *Chem. Rev.* **2005**, *105*, 4314. (g) Smith, A. B.; Fox, R. J.; Razler, T. M. *Acc. Chem. Res.* **2008**, *41*, 675.

(12) When nitro-substituted oxadiene was used, no reaction took place.

(13) When γ-ethyl substituted allenone was examined, no reaction was observed.

(14) Interestingly, the [4 + 2]-annulation product was obtained with a *Z*-configuration in our previous study (ref 8e).

(15) (a) Stokker, G. E. (Merck and Co., Inc., USA) Eur. Patent EP283217A1, 1988. (b) Abood, N. A.; Manning, R. E.; Miyano, M. (G.D. Searle and Co., USA) Int. Patent WO9400424A, 1994.

DOI: 10.1021/acs.orglett.6b00760
Org. Lett. 2016, 18, 2138−2141