Organic LETTERS

Letter

pubs.acs.org/OrgLett

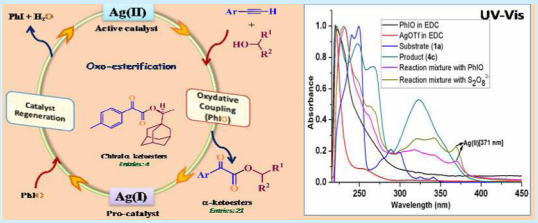
In Situ Generated Ag^{II}-Catalyzed Selective Oxo-Esterification of Alkyne with Alcohol to α-Ketoester: Photophysical Study

Radha M. Laha, Saikat Khamarui, Saikat K. Manna, and Dilip K. Maiti*

Department of Chemistry, University of Calcutta, University College of Science, 92 A. P. C. Road, Kolkata 700009, India

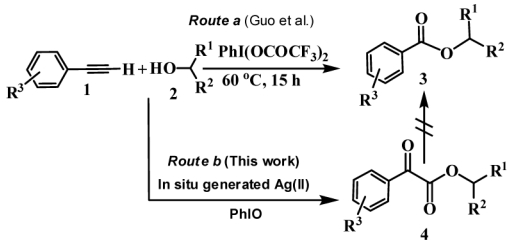
Supporting Information

ABSTRACT: An expert and easy one-step catalytic method for the multi O−C coupling of alkyne is developed for the synthesis of valuable α-ketoesters and their chiral analogues, in contrast to the generation of esters by a noncatalytic method. The in situ generated powerful Ag^{II} catalyst from AgOTf is the workhorse in the oxidative grafting of alkyne with PhIO and alcohol. The radical mechanism is confirmed in our controlled experiments and UV−vis study.



Direct introduction of two vicinal functional groups into a C−C triple bond has found immense application in recent times.[1,2] The intermolecular heterodifunctionalization is an especially attractive process to achieve valuable synthons, intermediates, pharmaceuticals, bioactive natural products, and their synthetic analogues.[1] In a continual effort to study the reaction of alkynes with λ^3-hypervalent iodines[3] under mild reaction conditions,[1b,4] we envisaged that a terminal alkyne can be directly transformed into valuable α-ketoesters (**4**, route b, Scheme 1) through simultaneous installation of two oxo groups

Scheme 1. Selective Synthesis of α-Ketoester over Ester



into both the alkyne carbons and O−C coupling to ≡C−H with alcohols. Interestingly, during preparation of our oxidative difunctionalization strategy, Guo and co-workers published a noncatalytic reaction to esters (**3**, route a, Scheme 1) through cleavage of alkynes with fluorinated λ^3-hypervalent iodine [$PhI(OCOCF_3)_2$] at 60 °C (15 h).[5] Thus, it is a great challenge for direct syntheses of α-ketoesters (**4**, route b) without generation of ester **3**. We were looking for efficient catalyst, neutral hypervalent iodine, and mild reaction conditions to avoid breakage of the labile keto-ester bond (C_2−C_1) of **4**, which may produce the byproduct **3** (route b). Ag^{II} species[6] was the catalyst of choice, and PhIO[7] was chosen as an oxygen source for keeping reaction medium neutral, rather than making harmful acidic conditions for the use of $PhI(OCOR)_2$.

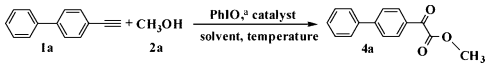
α-Ketoesters and their analogues are widespread in Nature, valuable pharmaceuticals, and bioactive natural products such as cysteine and serine proteinase inhibitors α-ketoester-β-amines, thrombin inhibitor α-ketoester peptides, cancer cell growth inhibitors and insecticidal antibiotic respirantin, and anti-influenza-active angelicin.[8] α-Ketoesters bearing strongly electron-deficient carbonyl and neighboring binding-capable ester functionalities make them useful synthons for asymmetric reduction, fluorination, aminohydroxylation, and aldol reactions, tandem heterocyclization, lactonization, construction of bioactive natural products, and efficient epoxidation catalysis and have strongly chelation-guided optical properties.[9] α-Ketoesters were synthesized using Pd^{II}, Cu^{I}, Cu powder, and I_2-mediated coupling of alcohol to carbon monoxide, 1,3-diketones, 1,3-ketoaldehydes, and acetophenones, respectively.[10] α-Functionalized esters were the preferred precursor for α-ketoesters, which were achieved using Rh^{I}, ^{n}BuLi, Bu_4NF−KF, Ru^{II}, and PDIA−H_2SO_4.[11] There are also a few other reported methods.[12] Syntheses of α-ketoesters were also reported through oxidation of trimethylsilyl-activated acetylenes using OsO_4−$^{t}BuO_2H$,[13a] Co(salen)-catalyzed reaction,[13b] and a similar two-step reaction using the strong oxidant $KMnO_4$ under basic conditions.[13c] Direct synthesis of α-ketoesters and their chiral analogues through coupling of alkyne with alcohol under low catalyst loading will be an exciting addition to the existing approaches.

We have reported several benign strategies using PhIO under neutral conditions.[7a−d] To synthesize α-ketoester **4a**, this work begins with (Table 1) treatment of a mixture of 4-biphenylacetylene (**1a**, 1 mmol), PhIO (3 mmol), and methanol (1 mmol) in 1,2-ethylene dichloride (EDC) with a suitable catalyst (1 mol %). Our early catalyst screening using several potential metal salts and complexes (only two are only shown, entries 1 and 2, Table 1) were unsuccessful. Gratifyingly, upon use of metal catalysts such as Fe^{III}, Pd^{0}, Ir^{III}, and Rh^{III} the reactions were successful (entries 3−6) in producing the desired product **4a**. However, the poor yields were a major concern of these reactions, and the yields were not improved (18−25%)

Received: December 8, 2015

DOI: 10.1021/acs.orglett.5b03484
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Survey and Optimization of the Reaction



entry	catalyst[b]	solvent[c]	temp (°C)	time (h)	yield[d] (%)
1	$Ni(OAc)_2.4H_2O$	EDC	80	8	
2	$RuCl_3.xH_2O$	EDC	80	10	
3	$FeCl_3$	EDC	80	8	20
4	$Pd(PPh_3)_4$	EDC	80	8	25
5	$IrCl_3$	EDC	80	6	18
6	$RhCl_3.3H_2O$	EDC	80	4	22
7	AgOTf	EDC	rt	12	58
8	AgOTf	EDC	80	1.5	68
9	AgOTf	EDC	40	1.5	71
10	**AgOTf[e]**	**EDC**	**40**	**1.5**	**70**
11[f]	AgOTf	EDC	40	1.5	63
12[g]	AgOTf	EDC	40	8.0	
13		EDC	40	9.0	12
14	AgOTf	EDC	80	1	50
15	AgOTf	MeOH	40	1.5	65
16	AgOTf	THF	40	1.5	62
17	AgOTf	$PhCH_3$	40	1.5	45
18	$AgClO_4$	EDC	40	2	60
19	$AgNO_3$	EDC	40	3	40
20	$AgVO_3$	EDC	40	6	25
21	Ag_2O	EDC	40	6	20

[a]PhIO (3 mmol), **1a** (1 mmol), and **2a** (1 mmol). [b]1 mol %. [c]5 mL. [d]Purified by column chromatography. [e]0.1 mol %. [f]PhIO (2.5 mmol). [g]No PhIO.

with higher catalyst loading and reaction temperature. Surprisingly, the yield of **4a** was significantly improved (58%, entry 7) upon use of AgOTf (1 mol %) at ambient temperature. Both the yield (71%) and reaction rate (1.5 h) were further improved under warming (40 °C) conditions (entries 8−11). Optimized conditions were developed using only 0.1 mol % of AgOTf catalyst to complete the reaction within 1.5 h (entry 10) in 70% yield. Our controlled experiments (entries 11−14) confirm the presence of AgOTf catalyst (0.1 mol %) and oxidant PhIO (3 mmol) were essential for the heterodifunctionalization process. EDC was found as the best solvent (entries 10 and 15−17). Other silver salts (entries 18−21) were not found to be better catalysts.

The tolerance of various functionalities was successfully examined for this new method (Scheme 2) through synthesis of a wide range of compounds bearing both unsubstituted and substituted aromatic rings (Table 2), heterocycles (**4t**), biphenyl systems (**4a−e,g,h**), and naphthalene ring (**4i**). The manipulation of substrates has been achieved using primary, secondary (**4d**), and long-chain alcohols (**4e**). Arylalkynes bearing deactivating group halogen, nitrile, nitro, ketone, and ester

Scheme 2. Synthetic Route to α-Ketoesters

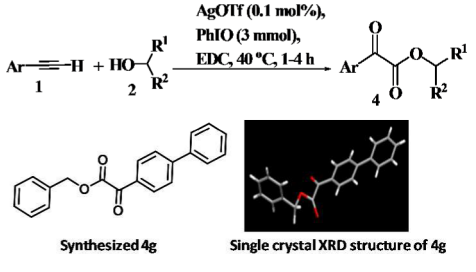
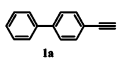
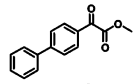
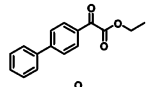
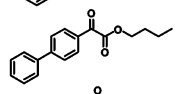
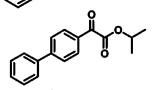
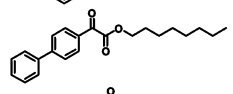
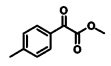
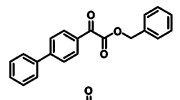
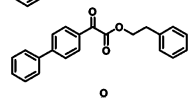
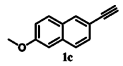
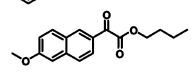
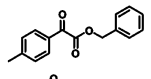
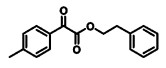
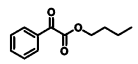
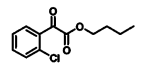
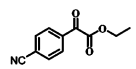
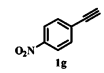
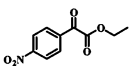
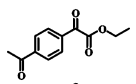
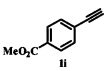
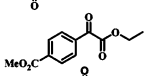
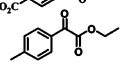
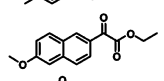
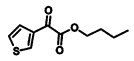
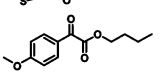


Table 2. Synthesised α-Ketoesters

Entry	Alkyne (1)	Alcohol (2)	Product (4)	Time (h)	Yield (%)
1	 1a	CH_3OH		1.0	4a, 70
2	1a	C_2H_5OH		1.5	4b, 78
3	1a	$^nC_4H_9OH$		1.0	4c, 77
4	1a			1.0	4d, 80
5	1a	$^nC_8H_{17}OH$		1.5	4e, 78
6	 1b	CH_3OH		1.5	4f, 70
7	1a			2.0	4g, 66
8	1a			2.0	4h, 67
9	 1c	$^nC_4H_9OH$		3.0	4i, 55
10	1b			2.0	4j, 70
11	1b			2.0	4k, 74
12	 1d	$^nC_4H_9OH$		2.0	4l, 65
13	 1e	$^nC_4H_9OH$		3.0	4m, 65
14	 1f	C_2H_5OH		3.0	4n, 62
15	 1g	C_2H_5OH		3.0	4o, 65
16	 1h	C_2H_5OH		4.0	4p, 72
17	 1i	C_2H_5OH		3.5	4q, 71
18	1b	C_2H_5OH		2.0	4r, 68
19	1c	C_2H_5OH		3.0	4s, 54
20	 1j	$^nC_4H_9OH$		4.0	4t, 64
21	 1k	$^nC_4H_9OH$		4.0	4u, 52

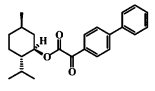
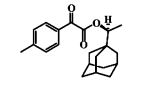
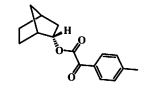
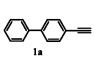
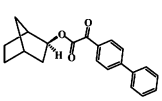
(**4m−q**, entries 13−17) were tolerated, but alkene was not tolerated. The unorthodox carbonylation via an esterification strategy to functionalized α-ketoesters (**4a−u**) was rapid (1.0−4.0 h) and moderate to high yielding (52−80%). The substrate (**1**) bearing a strongly electron-rich aromatic substituent such as alkyne **1c** and **1k** (entries 9, 19, and 21) reduced the yield of **4i**, **4s**, and **4u** substantially (52−55%) because of the formation of

DOI: 10.1021/acs.orglett.5b03484
Org. Lett. XXXX, XXX, XXX−XXX

the corresponding degradation byproduct esters (**3**, Scheme 1). The structure of compound **4g** was confirmed by single-crystal X-ray diffraction data analyses (Scheme 2).[14]

To explore the scope of the benign strategy for synthesis of thermally labile chiral α-ketoesters we have carried out the reaction using secondary chiral alcohols (**5**, Table 3). Gratifyingly, chiral alcohols bearing sterically congested menthyl (**5a**, entry 1, Table 3), adamentyl (**5b**, entry 2), and norbornyl (**5c**,**d**, entries 3 and 4) groups smoothly underwent an oxidative difunctionalization reaction to afford optically pure new α-ketoesters (**6a**–**d**, Table 3). Most of the reported methods have limits for direct access to the chiral α-ketoesters.

Table 3. Scope of the Strategy for Chiral α-Ketoesters

Entry	Alkyne (1)	Chiral Alcohol (5)	Product (6)	Time (h)	6, Yield (%)
1				3.0	6a, 72
2				3.0	6b, 69
3				4.0	6c, 66
4				4.0	6d, 60

The Ag^{II} complex is a metastable species[15] and appeared as a transient intermediate. In our control experiment, we noted that the reaction was almost arrested in the presence of radical scavenger TEMPO. This result suggested the reaction follows a radical pathway. Our UV–vis study of the dynamic reaction along with separate solutions containing EDC and AgOTf, AgOTf with PhIO, and a combination of AgOTf, PhIO, and substrate 4-phenylphenylacetylene (Figure 1) reveals the appearance of a new peak at 371 nm. The peak was intensified upon addition of $K_2S_2O_8$. Kochi and Anderson[15] achieved similar results using a solution of $AgNO_3$ and stronger electron acceptor $S_2O_8^{2-}$, which absorbed at 381 nm[15a] because of forming Ag^{II}. With these experiments we have not only confirmed that this reaction is catalyzed by in situ produced metastable Ag^{II} species from procatalyst[16] AgOTf but also discovered formation of the active oxidative radical Ag^{II} catalyst upon treatment of λ^3-hypervalent iodines. It will definitely find considerable application in frequently used Ag^{I}-hypervalent iodine mediated reactions.

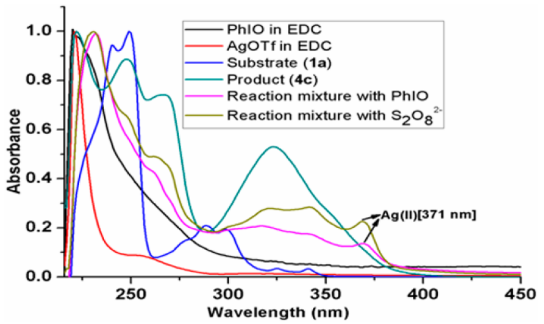
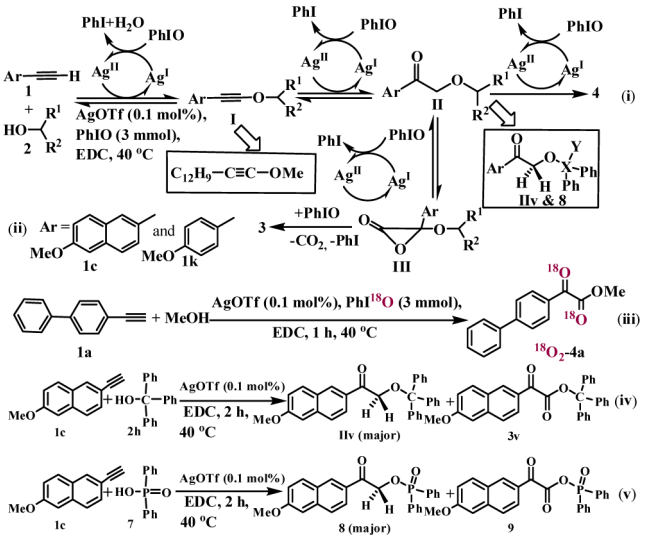


Figure 1. UV–vis study and detection of Ag^{II} species.

Based on our control experiments, UV–vis study, and literature evidence,[6,14,15] we have proposed a radical mechanism for this reaction (Scheme 3). PhIO is a well-known λ^3-hypervalent iodine reagent that follows a radical reaction pathway.[17] PhIO transforms procatalyst Ag^{I} into transient Ag^{II} species through single electron capturing, which converts **1** into the Ar–C≡C$^{\bullet}$ radical followed by O–C coupling with alcohol (**2**) to deliver an intermediate **I** (eq i). The intermediate **I** for **4a** was identified by mass spectrometry (Supporting Information), which appeared at retention time 20.20 min with desired mass 208 ($C_{12}H_9$–C≡C–OCH_3). The reaction is expected to pass through formation of **II** and transfer of "O" from PhIO leading to construction of **4**. Transfer of both "O" from PhIO was established using $PhI^{18}O$, which produced $^{18}O_2$–**4a** (eq iii) of mass 245.0948 (M + H). On the other hand, installation of two "oxo" groups and migration of Ar with release of CO_2 may produce a simple ester (eq ii), which was observed by Guo et al. (**3**, Scheme 1).[5] Upon use of strongly activated alkynes such as **1c** and **1k** (entries 9, 19, and 21, Table 2), we found corresponding esters (**3**) about 5% under the reaction conditions, which were increased by elevated temperature and longer reaction time. Herein, transformation of intermediate **II** to product **4** is expected to be a fast process because our attempts for trapping the intermediate **II** were unsuccessful (eq iv,v). Surprisingly, upon use of electronic and sterically congested triphenyl carbinol (**2h**) and diphenylphosphinic acid (**7**) the corresponding intermediates **IIv** and **8** were trapped, isolated, and characterized. This supports the proposed mechanism.

Scheme 3. Possible Reaction Pathways



In conclusion, we have demonstrated an in situ generation of robust Ag^{II} catalyst from a procatalyst Ag^{I} using PhIO under neutral reaction conditions. Our preliminary mechanistic study reveals that carbonylation via esterification of alkynes follows the radical pathway. It is an expert, selective, and simple method for direct synthesis of α-ketoesters through oxidative grafting of terminal alkynes and alcohols using very low catalyst loading. The simple and benign one-step strategy for the multi O–C coupling reaction brings another frontier into metal catalysis, which is compatible for easy access to valuable chiral α-ketoesters.

DOI: 10.1021/acs.orglett.5b03484
Org. Lett. XXXX, XXX, XXX–XXX

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03484.

X-ray data for **4g** (CIF)
Detailed experimental procedures, XRD, and spectroscopic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dkmchem@caluniv.ac.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support of DST (SR/S1/OC-05/2012 and SR/S5/GC-04/2012) and UGC are gratefully acknowledged.

■ REFERENCES

(1) (a) Chen, Z.; Li, J.; Jiang, H.; Zhu, S.; Li, Y.; Qi, C. *Org. Lett.* **2010**, *12*, 3262. (b) Pandit, P.; Gayen, K. S.; Khamarui, S.; Chatterjee, N.; Maiti, D. K. *Chem. Commun.* **2011**, *47*, 6933. (c) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc.* **2013**, *135*, 11481. (d) Besset, T.; Poisson, T.; Pannecoucke, X. *Eur. J. Org. Chem.* **2015**, *80*, 2765. (e) Lai, J.; Tian, L.; Huo, X.; Zhang, Y.; Xie, X.; Tang, S. *J. Org. Chem.* **2015**, *80*, 5894. (f) Tian, P.-P.; Cai, S.-H.; Liang, Q.-J.; Zhou, X.-Y.; Xu, Y.-H.; Loh, T.-P. *Org. Lett.* **2015**, *17*, 1636.

(2) (a) Chen, Y.; Ho, D. M.; Lee, C. *J. Am. Chem. Soc.* **2005**, *127*, 12184. (b) Zhao, F.; Zhang, D.; Nian, Y.; Zhang, L.; Yang, W.; Liu, H. *Org. Lett.* **2014**, *16*, 5124. (c) Wen, J.; Wei, W.; Xue, S.; Yang, D.; Lou, Y.; Gao, C.; Wang, H. *J. Org. Chem.* **2015**, *80*, 4966.

(3) (a) Wirth, T.; Ochiai, M.; Varvoglis, A.; Zhdankin, V. V.; Koser, G. F.; Tohma, H.; Kita, Y. *Hypervalent Iodine: Modern Developments in Organic Synthesis*; Springer-Verlag: Berlin, 2003. (b) Zhdankin, V. V.; Stang, P. *Chem. Rev.* **2008**, *108*, 5299. (c) Moriarty, R.; Tyagi, M. S. *Org. Lett.* **2010**, *12*, 364−366. (d) Parra, A.; Reboredo, S. *Chem. - Eur. J.* **2013**, *19*, 17244. (e) Sokolovs, I.; Lubriks, D.; Suna, E. *J. Am. Chem. Soc.* **2014**, *136*, 6920. (f) Yang, X.; Wu, T.; Phipps, R. J.; Toste, F. D. *Chem. Rev.* **2015**, *115*, 826.

(4) Khamarui, S.; Maiti, R.; Maiti, D. K. *Chem. Commun.* **2015**, *51*, 384.

(5) Jiang, Q.; Zhao, A.; Xu, B.; Jia, J.; Liu, X.; Guo, C. *J. Org. Chem.* **2014**, *79*, 2709.

(6) (a) Álvarez-Corral, M.; Muñoz-Dorado, M.; Rodrıíguez-García, I. *Chem. Rev.* **2008**, *108*, 3174. (b) Seiple, I. B.; Su, S.; Rodriguez, R. A.; Gianatassio, R.; Fujiwara, Y.; Sobel, A. L.; Baran, P. S. *J. Am. Chem. Soc.* **2010**, *132*, 13194. (c) Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258. (d) Wang, H.; Guo, L.-N.; Duan, X.-H. *Chem. Commun.* **2013**, *49*, 10370. (e) Chen, X.; Li, X.; Chen, X.-L.; Qu, L.-B.; Chen, J.-Y.; Sun, K.; Liu, Z.-D.; Bi, W.-Z.; Xia, Y.-Y.; Wua, H.-T.; Zhao, Y.-F. *Chem. Commun.* **2015**, *51*, 3846.

(7) (a) Chatterjee, N.; Pandit, P.; Halder, S.; Patra, A.; Maiti, D. K. *J. Org. Chem.* **2008**, *73*, 7775. (b) Pandit, P.; Chatterjee, N.; Halder, S.; Hota, S. K.; Patra, A.; Maiti, D. K. *J. Org. Chem.* **2009**, *74*, 2581. (c) Maiti, D. K.; Chatterjee, N.; Pandit, P.; Hota, S. K. *Chem. Commun.* **2010**, *46*, 2022. (d) Pandit, P.; Chatterjee, N.; Maiti, D. K. *Chem. Commun.* **2011**, *47*, 1285. (e) Widger, L. R.; Davies, C. G.; Yang, T.; Siegler, M. A.; Troeppner, O.; Jameson, G. N. L.; Ivanović-Burmazović, I.; Goldberg, D. P. *J. Am. Chem. Soc.* **2014**, *136*, 2699.

(8) (a) Angelastro, M. R.; Mehdi, S.; Burkhart, J. P.; Peet, N. P.; Bey, P. *J. Med. Chem.* **1990**, *33*, 11. (b) Iwanowicz, E. J.; Lin, J.; Roberts, D. G. M.; Michel, I. M.; Seiler, S. M. *Bioorg. Med. Chem. Lett.* **1992**, *2*, 1607. (c) Pettit, G. R.; Smith, T. H.; Feng, S.; Knight, J. C.; Tan, R.; Pettit, R. K.; Hinrichs, P. A. *J. Nat. Prod.* **2007**, *70*, 1073. (d) Yeh, J.-Y.; Coumar, M. S.; Horng, J.-T.; Shiao, H.-Y.; Kuo, F.-M.; Lee, H.-L.; Chen, I.-C.; Chang, C.-W.; Tang, W.-F.; Tseng, S.-N.; Chen, C.-J.; Shih, S.-R.; Hsu, J. T.-A.; Liao, C.-C.; Chao, Y. S.; Hsieh, H.-P. *J. Med. Chem.* **2010**, *53*, 1519. (e) Nie, Y.; Xiao, R.; Xu, Y.; Montelione, G. T. *Org. Biomol. Chem.* **2011**, *9*, 4070. (f) Markovic, D.; Kolympadi, M.; Deguin, B.; Poreé, F.-H.; Turks, M. *Nat. Prod. Rep.* **2015**, *32*, 230.

(9) (a) Juhl, K.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 2420. (b) Chan, W. W.-K.; Yu, W.-Y.; Che, C.-M.; Wong, M.-K. *J. Org. Chem.* **2003**, *68*, 6576. (c) Harb, W.; Ruiz-López, M. F.; Coutrot, F.; Grison, C.; Coutrot, P. *J. Am. Chem. Soc.* **2004**, *126*, 6996. (d) Yang, Y.-H.; Shi, M. *J. Org. Chem.* **2005**, *70*, 10082. (e) Li, H.; Wang, B.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 732. (f) Blay, G.; Fernández, I.; Marco-Aleixandre, A.; Pedro, J. R. *Org. Lett.* **2006**, *8*, 1287. (g) Wu, H.-L.; Wu, P.-Y.; Shen, Y.-Y.; Uang, B.-J. *J. Org. Chem.* **2008**, *73*, 6445. (h) Nakamura, A.; Lectard, S.; Hashizume, D.; Hamashima, Y.; Sodeoka, M. *J. Am. Chem. Soc.* **2010**, *132*, 4036. (i) Štefane, B. *Org. Lett.* **2010**, *12*, 2900. (j) Zhang, J.-C.; Ji, J.-X. *ACS Catal.* **2011**, *1*, 1360. (k) Zhu, X.; Lin, A.; Fang, L.; Li, W.; Zhu, C.; Cheng, Y. *Chem. - Eur. J.* **2011**, *17*, 8281. (l) Xiao, X.; Xie, Y.; Su, C.; Liu, M.; Shi, Y. *J. Am. Chem. Soc.* **2011**, *133*, 12914. (m) Suzuki, S.; Kitamura, Y.; Lectard, S.; Hamashima, Y.; Sodeoka, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 4581. (n) Peng, J.-B.; Qi, Y.; Jing, Z.-R.; Wang, S.-H.; Tu, Y.-Q.; Zhu, D.-Y.; Zhang, F.-M. *Org. Lett.* **2015**, *17*, 1014.

(10) (a) Sakakura, T.; Yamashita, H.; Kobayashi, T.-a.; Hayashi, T.; Tanaka, M. *J. Org. Chem.* **1987**, *52*, 5733. (b) Zhang, C.; Feng, P.; Jiao, N. *J. Am. Chem. Soc.* **2013**, *135*, 15257. (c) Zhang, Z.; Su, J.; Zha, Z.; Wang, Z. *Chem. - Eur. J.* **2013**, *19*, 17711. (d) Sagar, A.; Vidyacharan, S.; Sharada, D. S. *RSC Adv.* **2014**, *4*, 37047. (e) Xu, X.; Ding, W.; Lin, Y.; Song, Q. *Org. Lett.* **2015**, *17*, 516.

(11) (a) Shimizu, H.; Murakami, M. *Chem. Commun.* **2007**, 2855. (b) Su, Y.; Zhang, L.; Jiao, N. *Org. Lett.* **2011**, *13*, 2168. (c) Metz, A. E.; Kozlowski, M. C. *J. Org. Chem.* **2013**, *78*, 717. (d) Nagaki, A.; Ichinari, D.; Yoshida, J.-i. *Chem. Commun.* **2013**, *49*, 3242. (e) Liu, L.; Du, L.; Zhang-Negrerie, D.; Du, d Y.; Zhao, K. *Org. Lett.* **2014**, *16*, 5772.

(12) (a) Zhang, C.; Jiao, N. *Org. Chem. Front.* **2014**, *1*, 109. (b) Gu, P.; Wu, X.-P.; Su, Y.; Xue, X.-Q.; Li, P.; Li, R. *Synlett* **2014**, *25*, 535. (c) Du, J.; Zhang, X.; Sun, X.; Wang, L. *Chem. Commun.* **2015**, *51*, 4372.

(13) (a) Bulman Page, P. C.; Rosenthal, S. *Tetrahedron* **1990**, *46*, 2573. (b) Nishinaga, A.; Maruyama, K.; Yoda, K.; Okamoto, H. *J. Chem. Soc., Chem. Commun.* **1990**, 876. (c) Li, L.-S.; Wu, Y.-L. *Tetrahedron Lett.* **2002**, *43*, 2427.

(14) CCDC no. for **4g**: 1423494.

(15) (a) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 1651. (b) Anderson, J. M.; Kochi, J. K. *J. Org. Chem.* **1970**, *35*, 986.

(16) Ghosh, S.; Khamarui, S.; Gayen, K. S.; Maiti, D. K. *Sci. Rep.* **2013**, *3*, 2987.

(17) (a) Dohi, T.; Takenaga, N.; Goto, A.; Fujioka, H.; Kita, Y. *J. Org. Chem.* **2008**, *73*, 7365. (b) Santana, A. G.; Paz, N. R.; Francisco, C. G.; Suárez, E.; González, C. C. *J. Org. Chem.* **2013**, *78*, 7527. (c) Company, A.; Sabenya, G.; González-Béjar, M.; Gómez, L.; Clémancey, M.; Blondin, G.; Jasniewski, A. J.; Puri, M.; Browne, W. R.; Latour, J.-M.; Que, L., Jr.; Costas, M.; Pérez-Prieto, J.; Lloret-Fillol, J. *J. Am. Chem. Soc.* **2014**, *136*, 4624.

DOI: 10.1021/acs.orglett.5b03484
Org. Lett. XXXX, XXX, XXX−XXX