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DDQ-Mediated Oxidative Radical Cycloisomerization of 1,5-Diynols: Regioselective Synthesis of Benzo[*b*]fluorenones under Metal-Free Conditions

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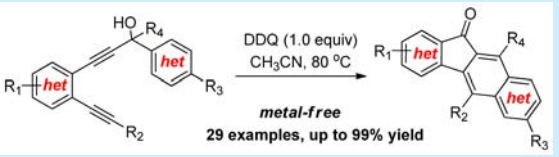
Supporting Information

ABSTRACT: A regio- and chemoselective oxidative cycloisomerization reaction of acyclic 1,5-diynols has been developed. The reaction proceeds under metal-free reaction conditions with high efficiency and broad functional group tolerance, which offers a general and straightforward access to benzo[*b*]fluorenones under metal-free conditions. The preliminary mechanistic studies revealed the possible involvement of a Meyer−Schuster rearrangement combined with an oxidative radical cyclization.



Fluorenone is an important carbocycle that can be frequently found in many biologically active molecules, natural products, and drug candidates.[1] It can also serve as a building block in the synthesis of optoelectronic advanced materials. Because of these features, developing novel and efficient methods for constructing fluorenone derivatives has received considerable attention, including direct oxidation of fluorenes,[2] Friedel−Crafts reactions,[3] metal-catalyzed cyclizations or cycloadditions,[4] and others.[5]

On the other hand, the benzofluorenes—consisting of fused fluorene skeletons with arenes—are very close to optoelectronic materials or related devices due to their highly rigid π-conjugated systems.[6] In addition, families of these linearly polycyclic aromatic hydrocarbons (PAHs) also display very interesting medicinal applications (Figure 1). For example, 5-diazobenzo-

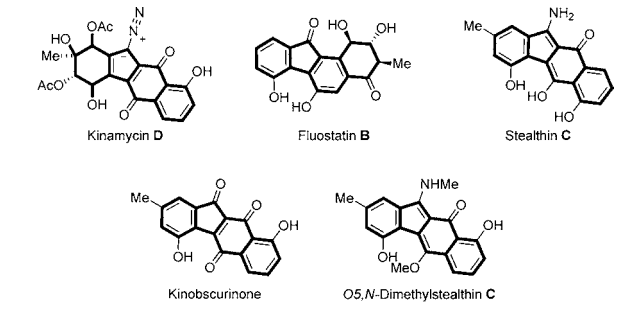
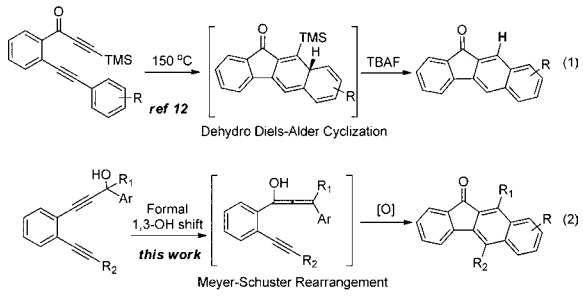


Figure 1. Bioactive substances containing a benzofluorene moiety.

[*b*]fluorene is known as kinamycin D and was isolated from *Streptomyces* proteinase in the 1970s.[7] It is a naturally occurring diazo compound with potent antibiotic activity against Gram-positive organisms.[8] Stealthin C is isolated from an *S. murayamaensis* culture.[9] The Kinobscurinone and *O*5,*N*-dimethylstealthin C are useful advanced intermediates in the biosynthesis of kinamycins.[8a,10]

Despite the critical importance of the benzofluorene derivatives, only a handful of synthetic methods have been reported. In 2000, Domínguez and Saá[11] reported thermal cycloaromatizations of nonconjugated aryldiacetylenes, such as benzotriynes and benzodiynes, to produce benzo[*b*]fluorene and benzo[*c*]fluorene skeletons, respectively. It is known that benzo[*b*]fluorenones and benzo[*c*]fluorenones can be realized in the thermal cyclization of 1-[2-(arylethynyl)phenyl]-3-trimethylsilylpropynones (Scheme 1, eq 1).[12] However, due to

Scheme 1. Benzo[*b*]fluorenone Synthesis via Cycloisomerization Protocols



the inherent radical reorganization processes and the high temperature conditions, the separation of constitutional isomers and the functional tolerance always remain problematic. Recently, we developed a facile approach for the $AgBF_4$-catalyzed tandem electrophilic cycloisomerization of 1,6-diynols with NXS (X = Br or I) to selectively afford halo-substituted benzo[*a*]-fluorenols under very mild conditions.[13]

The Meyer−Schuster rearrangement is an attractive approach for the generation of α,β-unsaturated carbonyl compounds.[14] A

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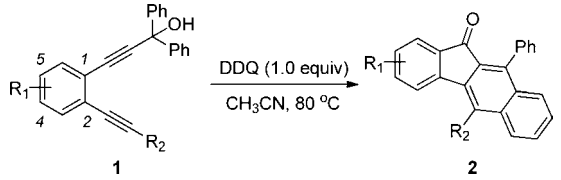
formal 1,3-hydroxyl shift to form the allenol intermediate and tautomerization was proposed as the key step in the rearrangement.[15] Zhang and co-workers reported an interesting Au−Mo cocatalyzed iodo Meyer−Schuster rearrangement for the synthesis of α-iodo-α,β-unsaturated aldehydes or ketones.[16] Reddy and co-workers developed the I_2/NIS-promoted Meyer−Schuster rearrangement of 3-alkoxypropargyl alcohols under metal-free conditions.[17] The avoidance of using transition metals in an organic transformation is significant because the metal species are highly toxic, presenting an intrusive limitation to industrial scale use, especially in the last synthetic stage of the purification of optoelectronic materials or pharmaceutical ingredients. Inspired by the previous achievements of the benzo[*b*]fluorenone synthesis using ynones as the starting materials (Scheme 1, eq 1) and our recent achievements in the metal-catalyzed cycloisomerization of 1,*n*-benzoendiynyls,[13,18] we envisioned that by employing the Meyer−Schuster rearrangement as a key step, a facile metal-free synthesis of benzo[*b*]-fluorenones would be possible when using diynols as starting materials under oxidative conditions (Scheme 1, eq 2).

To verify the hypothesis, we employed benzodiynol **1a** as the substrate in a model reaction. To our delight, treatment of **1a** at 80 °C under open air in anhydrous acetonitrile resulted in a new product that was identified as the expected benzo[*b*]fluorenone **2a**, albeit in very low yield. The yield of **2a** was improved to 59% when the reaction was carried out under an oxygen atmosphere (Table S1, entries 1 and 2). This metal-free and regioselective oxidative cycloisomerization reaction aroused our interest and inspired us to further investigate the reaction conditions. Worse results were observed when a peroxide oxidant such as H_2O_2 or *t*BuOOH was used. A strong oxidant like $K_2S_2O_8$ performed even worse. Pleasingly, a good yield (71%) was obtained when benzoquinone was used (Table S1, entry 6). We next studied the reaction conditions using the benzoquinone analogues as the optimal oxidants. electron-rich benzoquinones such as TMQ (2,3,5,6-tetramethylcyclohexa-2,5-diene-1,4-dione) and **A** (3,3′,5,5′-tetra-*tert*-butyl-[1,1′-bi(cyclohexylidene)]-2,2′,5,5′-tetraene-4,4′-dione) were less effective for the formation of product **2a**. However, electron-deficient benzoquinones such as DCQ (2,5-dichlorocyclohexa-2,5-diene-1,4-dione) and TCQ (2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione) gave improved yields of 83 and 84%, respectively (Table S1, entries 7−10). Good results were obtained when DDQ (4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile) was added as the test oxidant. The yield could be improved to 89% when 1.0 equiv of DDQ was employed. Increasing the oxidant loading to 2.0 equiv only led to a drastic decrease in efficiency (Table S1, entries 11 and 12). The reaction is easily handled because only the catalyst and solvent are required to facilitate the expected oxidative cycloisomerization.

With optimized reaction conditions in hand (Table S1, entry 11), we next investigated the scope of this oxidative cycloisomerization reaction. Since the oxidative cyclization seemed to selectively occur on the aryl group of the starting materials, two phenyl groups on the carbon bearing an OH group in compound **1** were planted. A variety of benzo[*b*]fluorenones **2** could be easily produced in good to excellent yields through this method (Table 1). The influence of the electronic effects attached at the alkyne moiety (R^2) in compound **1** (R^1 = H) was first examined. The reaction displayed excellent functional group compatibility in terms of the substituents attached to the aromatic rings of **1**. Versatile functional arenes with attached substitutions with electron-donating characterisitics (**1a**−**1e**) and those with

Table 1. DDQ-Mediated Oxidative Cycloisomerizations of Benzodiynol 1 To Form Benzo[*b*]fluorenone 2[a]



1 **2**

entry	R^1	R^2 (**1**)	yield of **2**[a] (%)
1	H	Ph (**1a**)	89 (**2a**)
2	H	*p*-MeC_6H_4 (**1b**)	94 (**2b**)
3	H	*p*-$MeOC_6H_4$ (**1c**)	87 (**2c**)
4	H	*p*-*n*-BuC_6H_4 (**1d**)	87 (**2d**)
5	H	*p*-*t*-BuC_6H_4 (**1e**)	94 (**2e**)
6	H	*p*-FC_6H_4 (**1f**)	95 (**2f**)
7	H	*p*-ClC_6H_4 (**1g**)	96 (**2g**)
8	H	*p*-CNC_6H_4 (**1h**)	91 (**2h**)
9	H	*p*-$NO_2C_6H_4$ (**1i**)	69 (**2i**)
10	H	*p*-$COOMeC_6H_4$ (**1j**)	97 (**2j**)
11	H	3-thienyl (**1k**)	99 (**2k**)
12	H	*t*Bu (**1l**)	75 (**2l**)
13	H	cyclopropyl (**1m**)	41 (**2m**)
14	4-MeO	*p*-MeC_6H_4 (**1n**)	65 (**2n**)
15	5-Me	*p*-MeC_6H_4 (**1o**)	88 (**2o**)
16	4-F	*p*-MeC_6H_4 (**1p**)	91 (**2p**)
17	5-CF_3O	*p*-MeC_6H_4 (**1q**)	97 (**2q**)

[a]Benzodiynol **1** (0.20 mmol), DDQ (0.20 mmol), CH_3CN (4.0 mL), 80 °C, 10−12 h. Isolated yield based on **1**.

electron-withdrawing properties (**1f**−**1j**) were well-tolerated and afforded the corresponding products **2b**−**2j** in good to excellent yields (Table 1, entries 1−9). The structure of compound **2b** was identified unambiguously by X-ray diffraction analysis.[19] The strong electron-deficient functional groups such as fluoro (**2f**), cyano (**2h**), nitro (**2i**), and ester groups (**2j**) were tolerated without difficulty. The heterocycle 3-thienyl furnished the desired product **2k** in almost quantitative yield. The efficiency of this reaction was not compromised by the alkyl-substituted substrates—this was demonstrated by the *tert*-butyl and cyclopropyl-substituted products (**2l** and **2m**) that were isolated in serviceable yields (Table 1, entries 11 and 12).

For the various substitutions (R^1) that were attached at the benzonoid core structure of compound **1**, experiments revealed good to excellent yields of the corresponding products **2n**−**2q** whenever the substitutions had electron-donating or fluorine-containing properties. For instance, good yields were observed when methoxyl or methyl groups were attached at the benzonoid position. Corresponding products **2n** or **2o** were isolated in 65 and 88% yields, respectively. The R^1 group with fluorine (**1p**) or trifluoromethoxy (**1q**) substituents underwent the reaction smoothly and afforded the corresponding fluorinated products **2p** and **2q** in excellent yields. The fluoro- and trifluoromethoxyl-substituted benzo[*b*]fluorenones (**2p**, **2q**) were especially noticeable because it is well-known that the fluorinated PAHs can usually exhibit interesting physicochemical and biological properties. These are recently used in the pharmaceutical, agrochemical, and materials-related fields.[20]

The effect of electronic variation of the propargyl alcohol moiety was next examined under optimized conditions (Table 2). For the aromatic functional groups that were located at the alcoholic carbon position of compound **3**, various substitutions including methyl (**3a**), methoxyl (**3b**), fluorine (**3c**), chlorine

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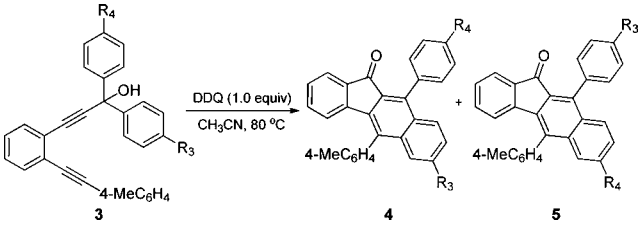
Table 2. Effect of Electronic Variation in the R^3 and R^4 Positions of Benzodiynol 3[a]



entry	R^3, R^4 (3)	yield of 4 + 5[a] (%)	4/5
1	Me, Me (**3a**)	91 (**4a**)	
2	MeO, MeO (**3b**)	87 (**4b**)	
3	F, F (**3c**)	86 (**4c**)	
4	Cl, Cl (**3d**)	88 (**4d**)	
5	Br, Br (**3e**)	73 (**4e**)	
6	MeO, H (**3f**)	95 (**4f** + **5f**)	2.90:1
7	Me, H (**3g**)	96 (**4g** + **5g**)	1.61:1
8	H, F (**3h**)	96 (**4h** + **5h**)	1.76:1
9	H, Cl (**3i**)	99 (**4i** + **5i**)	1.69:1
10	MeO, F (**3j**)	86 (**4j** + **5j**)	1.60:1

[a]Benzodiynol **3** (0.20 mmol), DDQ (0.20 mmol), CH_3CN (4.0 mL), 80 °C, 10−12 h. Isolated yield based on **3**.

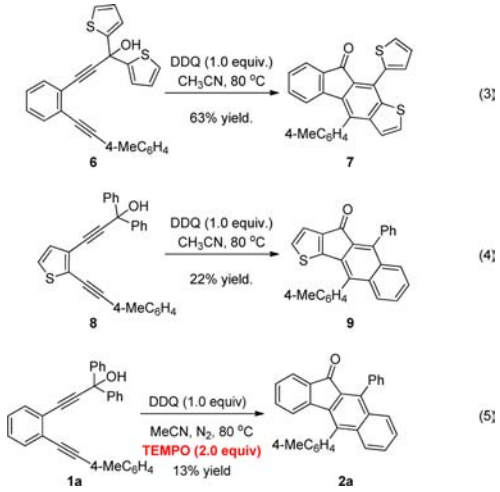
(**3d**), and bromine (**3e**) were introduced into the R^3 and R^4 positions to probe the reactivity and chemoselectivity (Table 2). The reaction showed very good functional group compatibility, and corresponding products **4a**−**4e** were successfully isolated in good to excellent yields (~73−91%).

Chemoselectivity of the reaction was observed when the arene ring in the propargyl position of **3** was attached to substituents with different electronic characterisitics (R^3 and R^4). The dehydrogenative cyclization process was always more likely to occur in the relatively electron-rich phenyl group. For instance, for the reaction of compound **3f**, in which R^3 was an electron-donating methoxyl and R^4 was an electron-neutral H atom, the product **4f** containing the MeO group in the core structure of the tetracyclic ring system was isolated as the major outcome as opposed to its isomer **5f** (Table 2, entry 6). A similar reaction was observed in the reaction of alkyl-substituted compound **3g** (R^3 = Me, R^4 = H). Product **4g** was formed through a cyclization on the 4-methylphenyl group—this was isolated as the major product (Table 2, entry 7). On the other hand, when the R^4 group in compound **3** was an electron-withdrawing halogen group (**3h**, **3i**, and **3j**, in Table 2, entries 8−10) and the phenyl group that linked with the R^3 group (H or MeO) was more electron-rich than that of the R^4-phenyl moiety, the cyclization process was more favored in the electron-rich R^3 arene moiety. The **4h**, **4i**, and **4j** species were isolated as major products. The structure of compound **4j** was firmly established via X-ray diffraction analysis.[19]

To demonstrate the utility of the DDQ-mediated oxidative cycloisomerization method, we finished the synthesis of the heterocyclic-containing fused tetracyclic ketones **7** and **9** (Scheme 2, eqs 3 and 4). The thienyl group was incorporated into a rigid π-conjugated molecule because it can dramatically enhance the photochromic and the fluorescence emission properties of the optoelectronic materials.[21]

The results in Table 2 (entries 6−10) indicate that the reactivities of the aromatic rings which were attached at the hydroxyl carbon were different; the electron-rich arene (substituent with the R^3 group) was higher than the electron-deficient one. Thus, we speculated that a radical pathway should be involved in the key cyclization step. To gain insight into the reaction mechanism, 2.0 equiv of TEMPO was added to the standard reaction condition of compound **1a** (Scheme 2, eq 5). A sluggish conversion was observed—tetracyclic product **2a** was finally isolated in 13% yield.

Scheme 2. Formation of Thienyl-Containing Fused Tetracyclic Ketones



To further confirm that an organic radical species is involved in the overall process, an electron paramagnetic resonance (EPR) experiment was conducted to trap the carbon radical. When compound **1b** was employed as a starting material under the standard conditions for 30 min, we successfully observed a signal from the carbon radical, as shown in Figure 2. This experiment

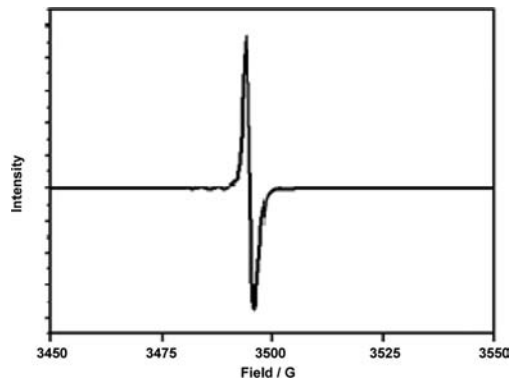


Figure 2. EPR experiment.

suggested that the organic radical is initially generated by DDQ and reacts with the 1,5-diyols in the reaction system to induce subsequent oxidative annulation sequences.

We proposed a plausible mechanism for this cascade cycloisomerization reaction, as depicted in Scheme 3. The Meyer−Schuster rearrangement of compound **1** would be induced to occur first by trace amounts of water or acidic substances under heated conditions that formed an allenol intermediate **I**. This was then oxidized by DDQ to form a DDQH radical and allenol radical **II**.[22] The subsequent intramolecular cascade radical addition with alkene and an alkyne group in species **II** led to the five-membered ring intermediate **III** and the benzo[*b*]fluorenone radical **IV**.[23] Finally, the hydrogen radical from **IV** was trapped by the DDQH radical to produce the final

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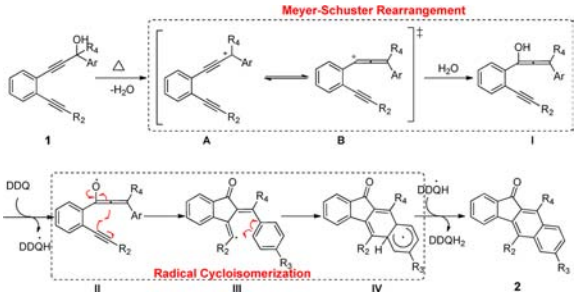
Scheme 3. Proposed Mechanism



product **2** and the concomitant side product $DDQH_2$. Interestingly, to our knowledge, this is the first example of combining the Meyer−Schuster arrangement and oxidative radical cycloisomerization processes in a one-pot reaction model.

In conclusion, we have developed an efficient and selective synthesis of benzo[*b*]fluorenones via DDQ-mediated oxidative cycloisomerizations of easily accessible acyclic 1,5-diynols with excellent functional group tolerance. No metal species were required in the cyclization process, which are significant in the synthesis of optoelectronic materials or pharmaceutical ingredients. Mechanistic studies by TEMPO and EPR experiments revealed that a Meyer−Schuster rearrangement followed by sequential oxidative radical cyclization are involved in the key step of the reaction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03533.

Experimental details, characterizations, and copies of ^{1}H and ^{13}C NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Zeng, M.; Ballard, T. E.; Tkachenko, A.; Burns, V.; Feldheim, D.; Melander, C. *Bioorg. Med. Chem. Lett.* **2006**, *16*, 5148. (b) Perry, P.; Read, M.; Davies, R.; Gowan, S.; Reszka, A.; Wood, A.; Kelland, L.; Neidle, S. *J. Med. Chem.* **1999**, *42*, 2679. (c) Han, Y.; Bisello, A.; Nakamoto, C.; Rosenblatt, M.; Chorev, M. *J. Pept. Res.* **2000**, *55*, 230.

(2) (a) Urgoitia, G.; SanMartin, R.; Herrero, M. T.; Domínguez, E. *Chem. Commun.* **2015**, *51*, 4799. (b) Zhang, J.; Wang, Z.; Wang, Y.; Wan, C.; Zheng, X.; Wang, Z. *Green Chem.* **2009**, *11*, 1973.

(3) (a) Motiwala, H.; Vekariya, R.; Aubé, J. *Org. Lett.* **2015**, *17*, 5484. (b) Reim, S.; Lau, M.; Langer, P. *Tetrahedron Lett.* **2006**, *47*, 6903.

(4) (a) Pünner, F.; Schieven, J.; Hilt, G. *Org. Lett.* **2013**, *15*, 4888. (b) Sun, C.; Liu, N.; Li, B.; Yu, D.; Wang, Y.; Shi, Z. *Org. Lett.* **2010**, *12*, 184. (c) Thirunavukkarasu, V.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 9462. (d) Waldo, J.; Zhang, X.; Shi, F.; Larock, R. *J. Org. Chem.* **2008**, *73*, 6679.

(5) (a) Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 3140. (b) Gonzalez-Cantalapiedra, E.; de Frutos, O.; Atienza, C.; Mateo, M.; Echavarren, A. *Eur. J. Org. Chem.* **2006**, *2006*, 1430. (c) Ferreira, C. S.; Kaiser, C.; Ferreira, V. *Synlett* **2008**, *2008*, 2625.

(6) (a) Kazlauskas, K.; Kreiza, G.; Bobrovas, O.; Adomeniene, O.; Adomenas, P.; Jankauskas, V.; Jursenas, S. *Appl. Phys. Lett.* **2015**, *107*, 043301. (b) Kazlauskas, K.; Kreiza, G.; Radiunas, E.; Adomenas, P.; Adomeniene, O.; Karpavicius, K.; Bucevicius, J.; Jankauskas, V.; Jursenas, S. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12935.

(7) Omura, S.; Nakagawa, A.; Yamada, H.; Hata, T.; Furusaki, A.; Watanabe, T. *Chem. Pharm. Bull.* **1973**, *21*, 931.

(8) (a) Gould, S.; Tamayo, N.; Melville, C.; Cone, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 2207. (b) Mithani, S.; Weeratunga, G.; Taylor, N.; Dmitrienko, G. I. *J. Am. Chem. Soc.* **1994**, *116*, 2209. (c) Gould, S.; Melville, C. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 51.

(9) (a) Gould, S. *Chem. Rev.* **1997**, *97*, 2499. (b) Gould, S.; Melville, C. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 51.

(10) (a) Wang, B.; Guo, F.; Ren, J.; Ai, G.; Fan, K.; Yang, K.; Aigle, B. *Nat. Commun.* **2015**, *6*, 7674. (b) Wang, B.; Ren, J.; Li, L.; Guo, F.; Pan, G.; Ai, G.; Aigle, B.; Fan, K.; Yang, K. *Chem. Commun.* **2015**, *51*, 8845.

(11) (a) Rodríguez, D.; Castedo, L.; Domínguez, D.; Saá, C. *Tetrahedron Lett.* **1999**, *40*, 7701. (b) Rodríguez, D.; Navarro, A.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2000**, *2*, 1497. (c) Rodríguez, D.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *Tetrahedron Lett.* **2002**, *43*, 2717. (d) Rodríguez, D.; Quintás, A.; García, C.; Saá, C.; Domínguez, D. *Tetrahedron Lett.* **2004**, *45*, 4711.

(12) Rodríguez, D.; Martínez-Esperón, M.; Navarro-Vázquez, A.; Castedo, L.; Domínguez, D.; Saá, C. *J. Org. Chem.* **2004**, *69*, 3842.

(13) Chen, Z.; Zeng, M.; Yuan, J.; Yang, Q.; Peng, Y. *Org. Lett.* **2012**, *14*, 3588.

(14) Swaminathan, S.; Narayanan, K. *Chem. Rev.* **1971**, *71*, 429.

(15) For mechanistic studies on the Meyer−Schuster rearrangement, see: (a) Zhu, Y.; Sun, L.; Lu, P.; Wang, Y. *ACS Catal.* **2014**, *4*, 1911. (b) Engel, D.; Dudley, G. *Org. Biomol. Chem.* **2009**, *7*, 4149. (c) Cadierno, V.; Crochet, P.; García-Garrido, S.; Gimeno, J. *Dalton Trans.* **2010**, *39*, 4015. (d) Andres, J.; Cardenas, R.; Silla, E.; Tapia, O. *J. Am. Chem. Soc.* **1988**, *110*, 666.

(16) (a) Ye, L.; Zhang, L. *Org. Lett.* **2009**, *11*, 3646. (b) Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007**, *9*, 2147.

(17) Puri, S.; Thirupathi, N.; Reddy, M. *Org. Lett.* **2014**, *16*, 5246.

(18) Naphthalene: (a) Chen, Z.; Jia, X.; Ye, C.; Qiu, G.; Wu, J. *Chem. - Asian J.* **2014**, *9*, 126. Methyleneindene: (b) Zhu, H.; Huang, J.; Fan, C.; Chen, Z. *Chem. - Asian J.* **2015**, *10*, 1463. (c) Chen, Z.; Jia, X.; Huang, J.; Yuan, J. *J. Org. Chem.* **2014**, *79*, 10674. Trifluoromethanesulfanyl benzofulvene: (d) Xiao, Q.; Zhu, H.; Li, G.; Chen, Z. *Adv. Synth. Catal.* **2014**, *356*, 3809.

(19) CCDC 1414214 (**2b**) and CCDC 1414249 (**4j**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(20) (a) Fuchibe, K.; Mayumi, Y.; Zhao, N.; Watanabe, S.; Yokota, M.; Ichikawa, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 7825. (b) Okazaki, T.; Laali, K. K. *Adv. Org. Synth.* **2006**, *2*, 353.

(21) (a) Takimiya, K.; Osaka, I.; Mori, T.; Nakano, M. *Acc. Chem. Res.* **2014**, *47*, 1493. (b) Tanifuji, N.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2005**, *127*, 13344. (c) Mitsui, C.; Okamoto, T.; Yamagishi, M.; Tsurumi, J.; Yoshimoto, K.; Nakahara, K.; Soeda, J.; Hirose, Y.; Sato, H.; Yamano, A.; Uemura, T.; Takeya, J. *Adv. Mater.* **2014**, *26*, 4546.

(22) For hydroxyl oxidation by DDQ, see: (a) Lemercier, B.; Pierce, J. *Org. Lett.* **2015**, *17*, 4542. (b) Huang, Z.; Jin, L.; Feng, Y.; Yi, H.; Lei, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 7151. (c) Yi, H.; Liu, Q.; Liu, J.; Zeng, Z.; Yang, Y.; Lei, A. *ChemSusChem* **2012**, *5*, 2143.

(23) Jang, Y.; Youn, S. W. *Org. Lett.* **2014**, *16*, 3720.

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