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Metal-Free Dehydrogenative Diels−Alder Reactions of Prenyl Derivatives with Dienophiles via a Thermal Reversible Process

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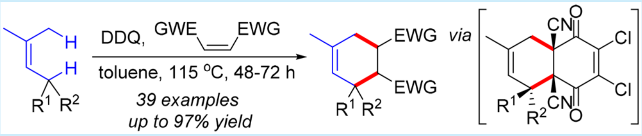
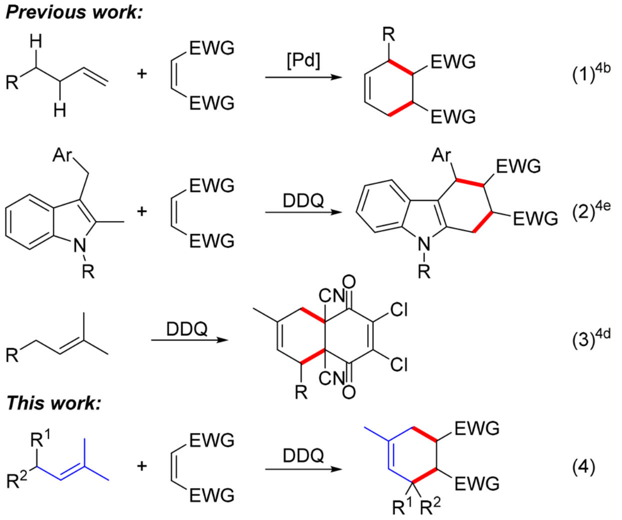
Supporting Information

ABSTRACT: An efficient dehydrogenative Diels−Alder reaction of prenyl derivatives with dienophiles has been developed. The reaction exhibits broad substrate scope and provides efficient access to cyclohexene derivatives with good to excellent yields. A reasonable mechanism involving a metal-free thermal reversible process is proposed.



Cross-dehydrogenative coupling reactions represent a synthetically efficient strategy for functional building blocks in organic chemistry because new C−C bonds are generated via the direct functionalization of inert $C(sp^3)$−H bonds.[1,2] The Diels−Alder reaction, which has irreplaceable advantages in constructing cyclohexene derivatives, has attracted considerable attention, as well.[3] Particularly, synthetic chemists have made great efforts in studying dehydrogenative Diels−Alder (DHDA) reactions in recent years.[4] In 2011, White's group first reported a Pd-catalyzed DHDA reaction of terminal olefins (Scheme 1, eq 1).[4b] Very recently, metal-free DHDA reactions using DDQ as oxidant were developed by Zhang's (Scheme 1, eq 2)[4e] and Antonchick's groups.[4g] Additionally, in 2015, our group also reported a metal-free DHDA reaction of prenyl derivatives, in which DDQ plays a dual role as both an oxidant and a dienophile (Scheme 1, eq 3).[4d] Unfortunately, our attempt to realize the cross-DHDA reaction with diverse dienophiles was met with less success in our previous report.[4d] DDQ is widely used in many reactions as an excellent oxidizing reagent.[5] Due to the electron-withdrawing effect of the cyano groups, it is also a better dienophile.[6] Consequently, metal-free DDQ-mediated DHDA reactions face challenges in terms of chemoselectivity,[4d,f] and DDQ adducts are usually observed. Therefore, converting the DDQ adducts into valuable scaffolds in such DHDA reactions is highly desirable.

Scheme 1. Dehydrogenative Diels−Alder Reactions



The Diels−Alder reaction is reversible at high temperatures,[7] which are usually employed to produce reactive olefins or metastable molecular entities and to protect a double bond against undesired reactions.[8] We envisaged that the DDQ adducts in DHDA reactions could react with other dienophiles to give other cycloadducts via a thermal reversible process, in which DDQ adducts would release DDQ and dienes and DDQ could continue to oxidize substrates to dienes; meanwhile, the resulting dienes can react with other dienophiles to form cyclohexene derivatives. To the best of our knowledge, the DDQ-mediated metal-free cross-DHDA reaction between DDQ adducts and diverse dienophiles has not been reported. Herein, we report an efficient DDQ-mediated DHDA reaction of prenyl derivatives with tetracyanoethylene and other dienophiles via a metal-free thermal reversible process for the first time, leading to a range of cyclohexene derivatives with good to excellent yields (Scheme 1, eq 4).

We began our studies by evaluating the reaction of prenyl benzene (**1a**) with tetracyanoethylene (**2a**) in the presence of DDQ in a ratio of 1:2:1.2 in DCM at ambient temperature for 48 h (Table 1, entry 1). The desired cross-DHDA reaction product **3a** was obtained in 24% yield, together with the DDQ adduct side product **4** in 39% yield. This result indicates that a competition between DDQ and tetracyanoethylene did exist. It seems that DDQ is more reactive than tetracyanoethylene in this Diels−Alder reaction system, which is consistent with our

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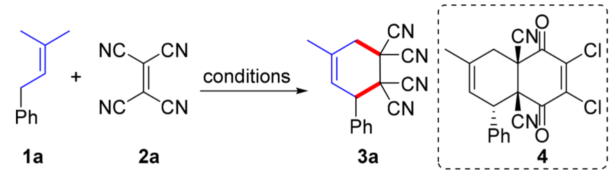
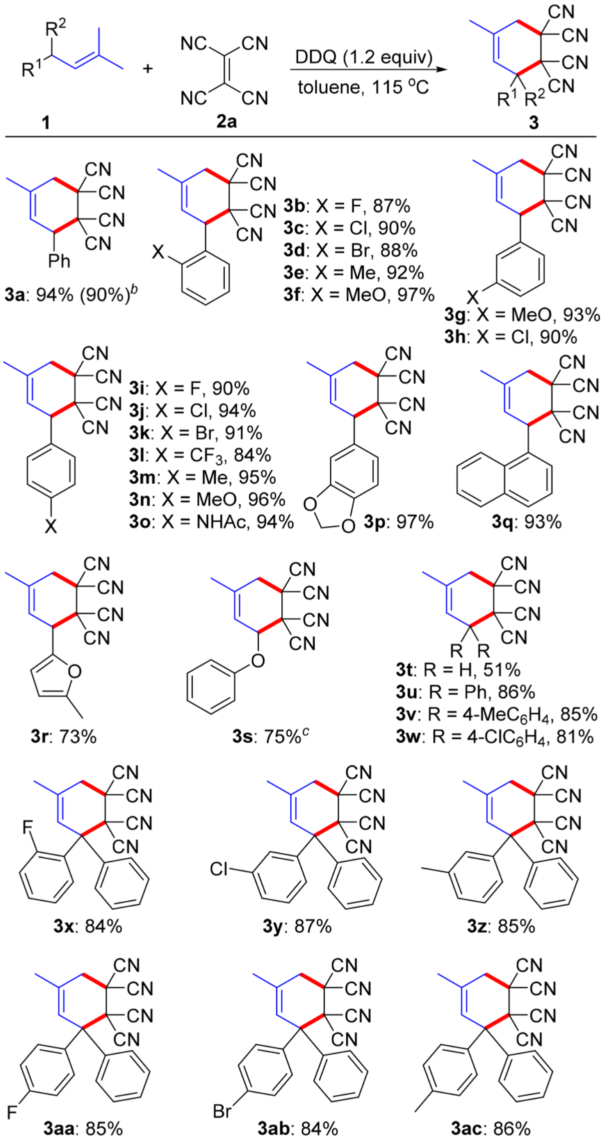
Table 1. Optimization of the Reaction Conditions[a]



entry	oxidant	solvent	temp (°C)	time (h)	yield of **3a** (%)[b]	yield of **4** (%)[b]
1	DDQ	DCM	25	48	24	39
2	DDQ	DCM	0	48	5	43
3	DDQ	DCM	−30	48	0	49
4	DDQ	toluene	80	48	49	23
5	DDQ	toluene	100	48	61	18
6	DDQ	toluene	110	48	88	trace
7	DDQ	toluene	115	48	94	0
8	DDQ	toluene	120	48	94	0
9	DDQ	DCE	90	48	55	15
10	DDQ	PhCl	115	48	89	trace
11	*p*-chloranil[c]	toluene	115	72	47	na
12	BQ[d]	toluene	115	72	nr	na
13	oxone[e]	toluene	115	72	trace	na

[a] Reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), oxidant (0.24 mmol) in solvent (2.0 mL) under N_2. [b] Isolated yield. [c] *p*-Chloranil = 2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione. [d] BQ = *p*-benzoquinone. [e] Oxone = potassium peroxymonosulfate.

Scheme 2. Scope of Prenyl Derivatives[a]



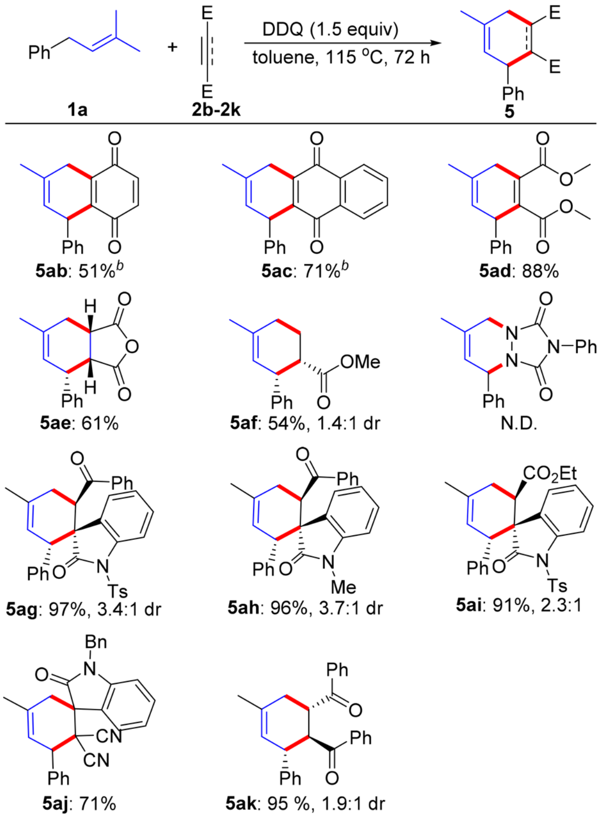
[a] Reactions were carried out with **1** (0.2 mmol), **2a** (0.4 mmol), DDQ (0.24 mmol) in toluene (2.0 mL) at 115 °C under N_2 for 48 h. The yields shown are for isolated products. [b] Gram scale (1.17 g **1a**). [c] Performed at 140 °C.

previously reported results.[4d] As we proposed above, changing the reaction temperature would influence the ratio of the products. Indeed, the reaction temperature is crucial for this reaction; lower temperatures resulted in lower yields of **3a**, and higher temperatures resulted in higher yields (Table 1, entries 1−7). The yield of **3a** was increased to 94% without side product when the reaction was performed at 115 °C (Table 1, entry 7). Various solvents were screened, and toluene gave the best results. Investigation of other oxidants were also attempted, and *p*-chloranil can also give the desired product, albeit with a lower yield (Table 1, entry 11).

With the optimized conditions in hand, we examined this synthetic method in a range of substituted prenyl derivatives. As shown in Scheme 2, this protocol was amenable to a wide range of **1** substrates, and the reactions all proceeded smoothly to yield the corresponding cyclohexene derivatives in excellent yields. Substrates with electron-withdrawing groups (F, Cl, Br, CF_3) or electron-donating groups (Me, OMe, NHAc) at the ortho-, meta-, or para-position of the phenyl ring were well tolerated, and the corresponding products were obtained with excellent yields (**3b**−**p**, 84−97%). These results indicate that the electron effect has little impact on this new DHDA reaction. Notably, the DDQ adduct side product was not detected in these reactions. Naphthalenyl-substituted **1q** returned the desired product in 93% yield. Additionally, furyl-substituted **1r** was also a suitable substrate for this reaction, and the corresponding product **3r** was prepared in 73% yield. Prenyl ether **1s**, which previously failed in such a DHDA reaction, returned the desired product **3s** in 75% yield at a higher temperature. Interestingly, 2-methyl-2-butene **1t** was also tolerated, and the corresponding product **3t** was obtained in 51% yield. Next, the substrate scope with regard to the disubstituted substrate was examined. Substrates with the same or different substituents were all amenable to the reaction (**1u**−**1ac**), and the derived cyclohexene derivatives with an all-carbon quaternary stereocenter were obtained with high yields (**3u**−**3ac**). The structure of **3u** was further confirmed by X-ray crystallography.[9]

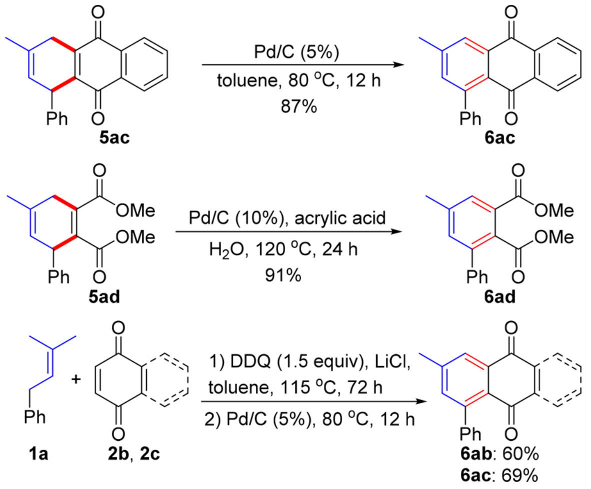
To extend the scope and application of this DHDA reaction, we conducted this reaction with other dienophiles (Scheme 3). Treatment of **1a** with quinones (**2b**, **2c**) in the presence of DDQ and LiCl for 72 h led to the desired products **5ab** and **5ac** in 51 and 71% yields, respectively. It is worth noting that LiCl may play an important role in activating the LUMO of quinones.[10,11] Additionally, DHDA reaction of **1a** with but-2-ynedioic acid dimethyl ester (**2d**) gave 1,2-bis(methoxycarbonyl)-1,4-cyclohexadiene **5ad** in 88% yield. When maleic anhydride **2e** was used as the dienophile, tetrahydroisoindole-1,3-dione **5ae** was generated in 61% yield with *endo*-selectivity, which is widely used as a precursor for the synthesis of (poly)amides, dyes, synthetic resins, etc.[12] Moreover, methyl acrylate **2f**, a weak dienophile, is also tolerated in this DHDA reaction to yield the corresponding product **5af** in 54% yield, albeit with poor

Scheme 3. Scope of Dienophiles[a]

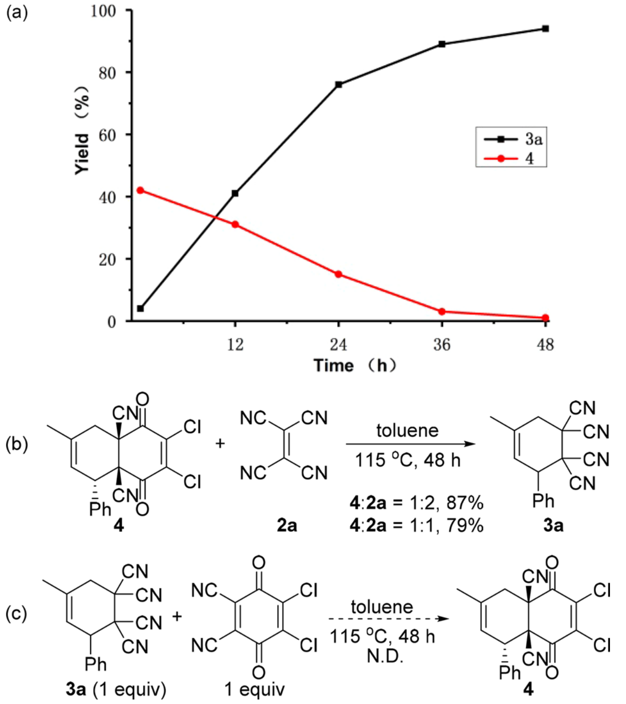


[a]Reactions were conducted with **1a** (0.4 mmol), **2b–2f** (0.2 mmol), DDQ (0.3 mmol) in toluene at 115 °C under N_2 for 72 h. The yields shown are for isolated products. The dr value was determined by ^{1}H NMR; the major isomer is shown. [b]0.2 mmol LiCl was used.

Scheme 4. Demonstration of Synthetic Utility of Products



Scheme 5. Control Experiments[a]



[a]Panel (a) shows the correlation between the yields of **3a**/**4** with the reaction time of the model reaction (Table 1, entry 7).

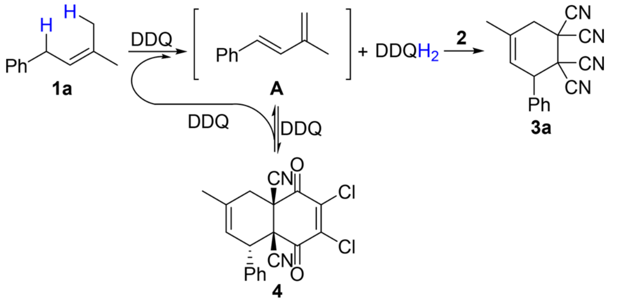
stereoselectivity. Oxindoles that contain a quaternary stereogenic center at the C3 position are fascinating targets in organic synthesis, due to their wide-ranging utility as synthetic intermediates for drugs, clinical pharmaceuticals, and alkaloids.[13] 2,3-Olefinic oxindoles (**2g–j**) with *N*-tosyl, benzyl, or methyl groups could react with **1a**, and spirocyclic oxindoles (**5ag–aj**) were obtained from this new DHDA reaction with good to excellent yields (71–97%). Furthermore, *trans*-dibenzoylethene also returned the desired product **5ak** in 95% yield.

To further validate the synthetic utility of this newly developed protocol, several transformations of these products were carried out. Further dehydrogenation of **5ac** by Pd/C gave the aromatized product 9,10-anthracenedione **6ac** in 87% yield,[14] which is a key intermediate in pharmaceutical and material chemistry.[15] Similarly, **5ad** can be further converted to phthalate **6ad** in excellent yields (91%), which acted as plasticizers or dispersants to improve the elaboration of plasticization efficiency.[16] Notably, this two-step reaction can be performed in one pot, and a measurable increased yield was observed (Scheme 4), and 1,4-benzoquinone **2c** returned the desired product **7** in 60% yield by this strategy. Thus, an effective method for the synthesis of polycyclic aromatic quinones by a one-pot reaction from simple prenyl derivatives and quinones was established based on the newly developed DHDA reaction.

To shed light on the DHDA reaction mechanism, some control experiments were carried out. We conducted five parallel model reactions (**1a** with **2**) under the optimized conditions with different reaction times (0.5, 12, 24, 36, and 48 h). As shown in Scheme 5a, the yields of **3a** and **4** changed with the reaction time. An increase of the yield of **3a** is accompanied by a decrease of the yield of **4**, suggesting that **4** was converted to **3** through a thermal reversible process during the reaction. To further prove this process, DDQ adduct **4** was treated directly with **2a** under the optimal conditions in the absence of DDQ, and as expected, the desired product **3a** was obtained in 87% yield (Scheme 5b). When **2a** was reduced to 1 equiv, **3a** was isolated in 79% yield with 9% of **4** recovered. Moreover, treatment of **3a** with DDQ in a ratio of 1:1 at 115 °C gave no product **4**, suggesting that the thermal stability of **3a** is better than that of **4** (Scheme 5c). These results confirm our proposal that a thermal reversible process occurred in this DHDA reaction.

On the basis of the experimental results mentioned above and previous literature,[4c] a reasonable mechanism was described in Scheme 6. Dehydrogenation of **1a** occurs with DDQ to generate intermediate diene **A** and $DDQH_2$. **A** undergoes a Diels–Alder reaction with **2** or DDQ to give the expected product **3a** or side product **4**. Although DDQ is more reactive than tetracyanoethylene in this Diels–Alder reaction, the DDQ adduct **4** can subsequently break down into the diene intermediate **A** and DDQ via a retro-Diels–Alder reaction at high temperature. Released DDQ continues to circulate as the oxidant; the diene intermediate will be totally consumed to the desired product **3a** after repeating this process many times.

Scheme 6. Proposed Reaction Mechanism



In summary, we have developed an efficient DHDA reaction between prenyl derivatives and active dienophiles via a metal-free thermal reversible process for the first time. This reaction features broad substrate scope and generates synthetically and pharmaceutically valuable products with good to excellent yields. Additionally, the mechanism of this DHDA reaction has also been studied. Further investigations on the application of this strategy to other substrates are 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.8b02469.

Experimental procedures, characterization data for all new compounds, and copies of ^1H, ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1844174 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.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335. (b) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792. (c) Yoo, W.-J.; Li, C.-J. *Top. Curr. Chem.* **2009**, *292*, 281. (d) Ashenhurst, J. A. *Chem. Soc. Rev.* **2010**, *39*, 540. (e) Scheuermann, C. J. *Chem. - Asian J.* **2010**, *5*, 436. (f) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780. (g) Le Bras, J.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170. (h) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (i) Klussmann, M.; Sureshkumar, D. *Synthesis* **2011**, *2011*, 353. (j) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (k) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.* **2012**, *41*, 5588. (l) Zhang, C.; Tang, C. H.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3464. (m) Girard, S. A.; Knauber, T.; Li, C. J. *Angew. Chem., Int. Ed.* **2014**, *53*, 74. (n) Liu, C.; Yuan, J.; Gao, M.; Tang, S.; Li, W.; Shi, R.; Lei, A. *Chem. Rev.* **2015**, *115*, 12138. (o) Krylov, I. B.; Vil', V. A.; Terent'ev, A. O. *Beilstein J. Org. Chem.* **2015**, *11*, 92. (p) Batra, A.; Singh, P.; Singh, K. N. *Eur. J. Org. Chem.* **2016**, *2016*, 4927. (q) Yang, Y.; Lan, J.; You, J. *Chem. Rev.* **2017**, *117*, 8787.

(2) (a) Wendlandt, A. E.; Suess, A. M.; Stahl, S. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 11062. (b) Wu, Y.; Wang, J.; Mao, F.; Kwong, F. Y. *Chem. - Asian J.* **2014**, *9*, 26. (c) Zheng, C.; You, S.-L. *RSC Adv.* **2014**, *4*, 6173. (d) Narayan, R.; Matcha, K.; Antonchick, A. P. *Chem. - Eur. J.* **2015**, *21*, 14678. (e) Hartwig, J. F. *J. Am. Chem. Soc.* **2016**, *138*, 2. (f) Hartwig, J. F.; Larsen, M. A. *ACS Cent. Sci.* **2016**, *2*, 281. (g) Bering, L.; Manna, S.; Antonchick, A. P. *Chem. - Eur. J.* **2017**, *23*, 10936. (h) Hu, X. Q.; Chen, J. R.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2017**, *56*, 1960. (i) Ping, L.; Chung, D. S.; Bouffard, J.; Lee, S.-g. *Chem. Soc. Rev.* **2017**, *46*, 4299. (j) Qin, Y.; Zhu, L.; Luo, S. *Chem. Rev.* **2017**, *117*, 9433. (k) Mihai, M. T.; Genov, G. R.; Phipps, R. J. *Chem. Soc. Rev.* **2018**, *47*, 149.

(3) (a) Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558. (b) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650. (c) Nicolaou, K. C.; Snyder, S. A.; Montagnon, T.; Vassilikogiannakis, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1668. (d) Notz, W.; Tanaka, F.; Barbas, C. F. *Acc. Chem. Res.* **2004**, *37*, 580. (e) Takao, K.; Munakata, R.; Tadano, K. *Chem. Rev.* **2005**, *105*, 4779. (f) Wessig, P.; Müller, G. *Chem. Rev.* **2008**, *108*, 2051. (g) Li, J.-L.; Liu, T.-Y.; Chen, Y.-C. *Acc. Chem. Res.* **2012**, *45*, 1491. (h) Jiang, X.; Wang, R. *Chem. Rev.* **2013**, *113*, 5515.

(4) (a) Li, W.; Zhou, L.; Zhang, J. *Chem. - Eur. J.* **2016**, *22*, 1558. (b) Stang, E. M.; White, M. C. *J. Am. Chem. Soc.* **2011**, *133*, 14892. (c) Qi, C.; Cong, H.; Cahill, K. J.; Müller, P.; Johnson, R. P.; Porco, J. A., Jr. *Angew. Chem., Int. Ed.* **2013**, *52*, 8345. (d) Feng, H. X.; Wang, Y. Y.; Chen, J.; Zhou, L. *Adv. Synth. Catal.* **2015**, *357*, 940. (e) Zhou, L.; Xu, B.; Zhang, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 9092. (f) Kuo, C.-W.; Konala, A.; Lin, L.; Chiang, T.-T.; Huang, C.-Y.; Yang, T.-H.; Kavala, V.; Yao, C.-F. *Chem. Commun.* **2016**, *52*, 7870. (g) Manna, S.; Antonchick, A. P. *Chem. - Eur. J.* **2017**, *23*, 7825. (h) Wu, X.; Zhu, H.-J.; Zhao, S.-B.; Chen, S.-S.; Luo, Y.-F.; Li, Y.-G. *Org. Lett.* **2018**, *20*, 32. (i) Jiang, B.; Liang, Q.-J.; Han, Y.; Zhao, M.; Xu, Y.-H.; Loh, T.-P. *Org. Lett.* **2018**, *20*, 3215.

(5) (a) Walker, D.; Hiebert, J. D. *Chem. Rev.* **1967**, *67*, 153. (b) Zhang, Y. H.; Li, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 4242. (c) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474. (d) Navale, T. S.; Thakur, K.; Rathore, R. *Org. Lett.* **2011**, *13*, 1634. (e) Alagiri, K.; Devadig, P.; Prabhu, K. R. *Chem. - Eur. J.* **2012**, *18*, 5160.

(6) Braude, E. A.; Jackman, L. M.; Linstead, R. P.; Lowe, G. *J. Chem. Soc.* **1960**, *0*, 3123.

(7) (a) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415. (b) Matsukubo, H.; Kato, H. *J. Chem. Soc., Chem. Commun.* **1975**, 840. (c) Bowman, E. S.; Hughes, G. B.; Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 8273.

(d) Froidevaux, V.; Borne, M.; Laborbe, E.; Auvergne, R.; Gandini, A.; Boutevin, B. *RSC Adv.* **2015**, *5*, 37742.

(8) (a) Jenkitkasemwong, Y.; Thebtaranonth, Y.; Wajirum, N. *Tetrahedron Lett.* **1979**, *20*, 1615. (b) Ichihara, A.; Nio, N.; Sakamura, S. *Tetrahedron Lett.* **1980**, *21*, 4467. (c) Siwapinyoyos, T.; Thebtaranonth, Y. *J. Org. Chem.* **1982**, *47*, 598. (d) Asaoka, M.; Naito, S.; Takei, H. *Tetrahedron Lett.* **1985**, *26*, 2103. (e) Ichihara, A. *Synthesis* **1987**, *1987*, 207. (f) Szántay, C.; Moldvai, I.; Tárkányi, G.; Szántay, C. *J. Org. Chem.* **1996**, *61*, 2946. (g) Klunder, A. J. H.; Zhu, J.; Zwanenburg, B. *Chem. Rev.* **1999**, *99*, 1163. (h) Manka, J. T.; Douglass, A. G.; Kaszynski, P.; Friedli, A. C. *J. Org. Chem.* **2000**, *65*, 5202. (i) Sugimoto, H.; Nakamura, S.; Ohwada, T. *J. Org. Chem.* **2007**, *72*, 10088. (j) Adachi, Y.; Nakagawa, H.; Matsuo, K.; Suzuki, T.; Miyata, N. *Chem. Commun.* **2008**, 5149.

(9) For details, see the Supporting Information.

(10) (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1993**, *115*, 11600. (c) Ward, D. E.; Abaee, M. S. *Org. Lett.* **2000**, *2*, 3937. (d) Fukuzumi, S.; Ohkubo, K.; Okamoto, T. *J. Am. Chem. Soc.* **2002**, *124*, 14147. (e) Jones, S.; Valette, D. *Org. Lett.* **2009**, *11*, 5358. (f) Chen, Q.; Chen, H.; Meng, X.; Ma, Y. *Org. Lett.* **2015**, *17*, 5016. (g) Zhao, Y.; Rocha, S. V.; Swager, T. M. *J. Am. Chem. Soc.* **2016**, *138*, 13834. (h) Zhang, Q.; Lv, J.; Li, S.; Luo, S. *Org. Lett.* **2018**, *20*, 2269.

(11) (a) Braun, R.; Sauer, J. *Chem. Ber.* **1986**, *119*, 1269. (b) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595. (c) Forman, M. A.; Dailey, W. P. *J. Am. Chem. Soc.* **1991**, *113*, 2761.

(12) Garg, B.; Bisht, T.; Ling, Y.-C. *RSC Adv.* **2014**, *4*, 57297.

(13) Miyamoto, H.; Okawa, Y.; Nakazaki, A.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2274.

(14) Nguyen Van, T.; D'hooghe, M.; Pattyn, S.; De Kimpe, N. *Synlett* **2004**, *2004*, 1913.

(15) (a) Madje, B. R.; Shelke, K. F.; Sapkal, S. B.; Kakade, G. K.; Shingare, M. S. *Green Chem. Lett. Rev.* **2010**, *3*, 269. (b) Naeimi, H.; Brojerdi, S. S. *Polycyclic Aromat. Compd.* **2014**, *34*, 504. (c) Somai Magar, K. B.; Xia, L.; Lee, Y. R. *Chem. Commun.* **2015**, *51*, 8592. (d) Kim, K.; Min, M.; Hong, S. *Adv. Synth. Catal.* **2017**, *359*, 848. (e) Nicolaou, K. C.; Wang, Y.; Lu, M.; Mandal, D.; Pattanayak, M. R.; Yu, R.; Shah, A. A.; Chen, J. S.; Zhang, H.; Crawford, J. J.; Pasunoori, L.; Poudel, Y. B.; Chowdari, N. S.; Pan, C.; Nazeer, A.; Gangwar, S.; Vite, G.; Pitsinos, E. N. *J. Am. Chem. Soc.* **2016**, *138*, 8235. (f) Basak, S.; Mal, D. *J. Org. Chem.* **2017**, *82*, 11035.

(16) (a) Nakamura, R.; Obora, Y.; Ishii, Y. *Adv. Synth. Catal.* **2009**, *351*, 1677. (b) Sakakura, A.; Ohkubo, T.; Yamashita, R.; Akakura, M.; Ishihara, K. *Org. Lett.* **2011**, *13*, 892. (c) Rashed, M. N.; Siddiki, S. M. A. H.; Ali, M. A.; Moromi, S. K.; Touchy, A. S.; Kon, K.; Toyao, T.; Shimizu, K.-i. *Green Chem.* **2017**, *19*, 3238.