The Journal of Organic Chemistry

Subscriber access provided by EPFL | Scientific Information and Libraries

Note

Metal-free Cascade Oxidative Decarbonylative Alkylation/ Arylation of Alkynoates with Alphatic Aldehydes

Changduo Pan, Yu Chen, Shuai Song, Lei Li, and Jin-Tao Yu

J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 08 Nov 2016

Downloaded from http://pubs.acs.org on November 8, 2016

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society.
However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Metal-free Cascade Oxidative Decarbonylative Alkylation/Arylation of Alkynoates with Alphatic Aldehydes

Changduo Pan,*,†,‡ Yu Chen,† Shuai Song,† Lei Li,† and Jin-Tao Yu*,‡

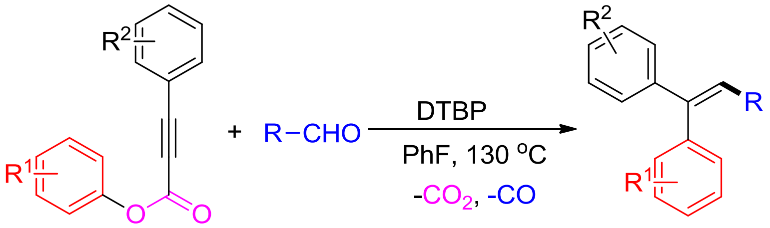
† *School of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, P. R. China*

‡ *School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, Changzhou University, Changzhou 213164, P. R. China*

panchangduo@jsut.edu.cn; yujintao@cczu.edu.cn

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT

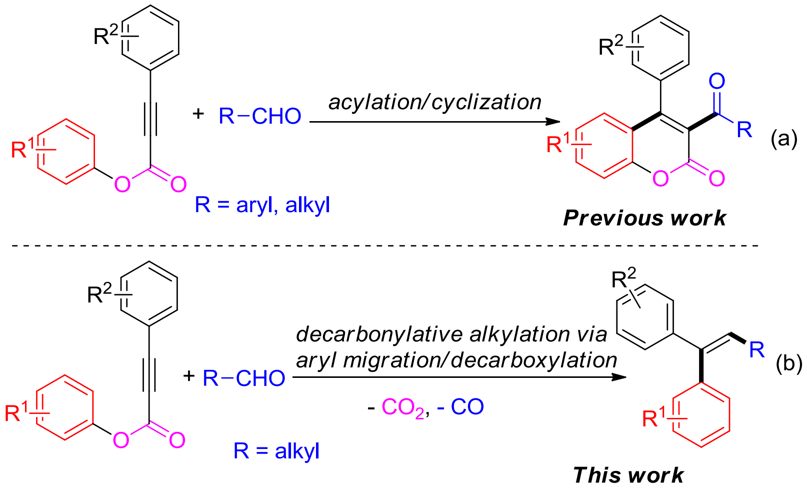


The oxidative difunctionalization of aryl alkynoates with alphatic aldehydes as cheap and abundant alkyl radical source was developed, providing a variety of trisubstituted alkenes in moderate to good yields. In this reaction, radical decarbonylative alkylation of C-C triple bond, 1,4-aryl migration, and decarboxylation were involved under metal-free conditions.

Difunctionalization of the ubiquitous carbon-carbon triple bond is believed as a promising and convenient procedure to generate various structural complex and synthetic useful compounds due to the readily availability of alkyne derivatives.[1] Among them, the radical oxidative coupling reactions have played important roles in synthetic organic chemistry and offered many complementary methods to efficiently increase the molecular complexities.[2] As a specific case, activated alkynes such as alkynoates were widely utilized in organic synthesis. For example, Wu and coworkers developed the construction of 3-acyl-4-arylcoumarins via metal-free tandem oxidative acylation/cyclization using aldehydes as acyl radical source (eq (a), Scheme 1).[3] Encouragingly, a great many of 3-functionalized coumarins were successfully obtained by employing *H*-phosphonates, Togni's reagent, ethyl bromodifluoroacetate, arylsulfinic acids/sulfonyl hydrazides, $AgSCF_3$ and AgSCN, α-keto acids, xanthates, *N*-iodosuccinimide, etc. as efficient radical sources through oxidative radical addition and 6-*endo*/5-*exo* cyclization procedure.[4] On the other hand, the copper-mediated radical addition to the carbon-carbon triple bond of alkynoates followed by dearomative *ipso*-cyclization led to the products with an unexpected oxa-spiro skeleton.[5] Radical aryl migration reactions are common and promising strategy in organic synthesis.[6] The 1,4-aryl migration was also involved in the difunctionalization of alkynoates to furnish various trisubstituted olefins via oxidative radical addition/decarboxylation procedure.[7] In the later case, the direct functionalization of relative inert C(sp^3)-H bonds were realized to generate alkyl, benzylic, oxyalkyl, amidomethyl radicals. However, those alkylating reagents are limited to compounds with symmetric structures or only one existing type of (activated) C(sp^3)–H bond to reduce the possible regioisomers. However, more convenient and efficient methods to provide structural complex alkyl radicals from readily available source would be highly desirable.

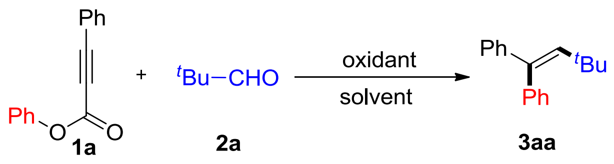
Aldehydes are cheap and readily available chemicals that can be easily converted into corresponding acyl radicals for the acylation of various type of molecules.[8] Moreover, they can also be employed as precursors for decarbonylative reactions catalyzed by transition-metals.[9] Recent studies revealed that the decarbonylation of aldehydes could also occur in the absence of transition-metals to provide structural diversified aryl/alkyl radicals in the construction of C-C bonds under the assistance of proper oxidants.[10] As part of our ongoing interest in the direct difunctionalization of alkynes,[4c,7e,11] herein we report a general procedure involving the metal-free oxidative decarbonylative alkylation/arylation of alkynoates using alphatic aldehydes as alkyl source to generate trisubstituted alkenes (eq (b), Scheme 1).

Scheme 1. Difunctionalization of Alkynoates with Aldehydes



Our initial investigations focused on the optimization of the decarbonylative alkylation between diphenyl alkynoate (**1a**) and pivalaldehyde (**2a**) (Table 1). In the presence of DTBP (di-*tert*-butyl peroxide), the desired decarbonylative alkylated product **3aa** could be detected in DCE at 130 °C for 20 h albeit in low yield (entry 1, Table 1). Inspired by this result, other solvents, such as acetonitrile, benzene, chlorobenzene, fluorobenzene, trifluoromethylbenzene and DCM were investigated, and fluorobenzene was proved to be the best choice with an 85% yield of **3aa** (entries 2-7, Table 1). The utilization of proper oxidant was also crucial to the transformation, as TBHP, TBPB, DCP and BPO were all inferior to DTBP (entries 8-11, Table 1). Additionally, the yield was sharply reduced under air or with less amount of oxidant utilized (entry 5, Table 1). Temperature control experiment suggested that an obviously negative effect was observed at a lower temperature (110 °C), while a higher temperature (140 °C) didn't result in better yield (entry 12, Table 1).

Table 1. Screening the Optimized Reaction Conditions.[a]



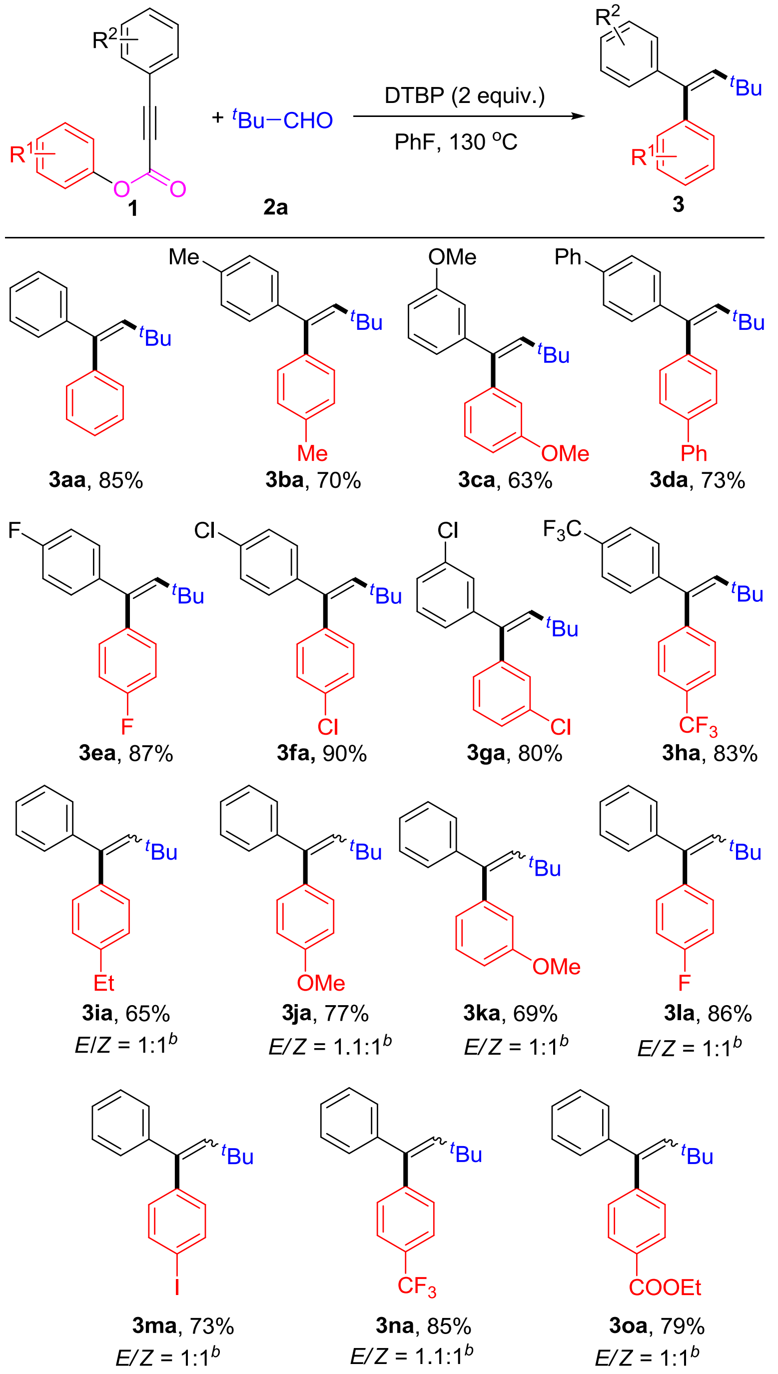
Entry	Oxidant	Solvent	Yield (%)
1	DTBP	DCE	8
2	DTBP	CH_3CN	12
3	DTBP	PhH	50
4	DTBP	PhCl	21
5	DTBP	PhF	85 (62)[b] (66)[c]
6	DTBP	$PhCF_3$	67
7	DTBP	DCM	16
8	TBHP	PhF	18
9	TBPB	PhF	27
10	DCP	PhF	70
11	BPO	PhF	23
12	DTBP	PhF	68[d] (79)[e](84)[f]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), oxidant (2 equiv) in solvent (2 mL) at 130 °C under N_2 for 20 h. [b] under air. [c] DTBP (1 equiv) was used. [d] 110 °C. [e] 120 °C. [f] 140 °C. DTBP = di-*tert*-butyl peroxide, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butyl peroxybenzoate, DCP = dicumyl peroxide, BPO = benzoyl peroxide.

Then, the generality of this oxidative decarbonylative alkylation of alkynoates with aliphatic aldehydes was investigated. As expected, diaryl alkynoates with either electron-donating or electron-withdrawing substituents, such as methyl, methoxyl, halogen and trifluoromethyl on either phenyl of alkynoates all reacted smoothly with pivalaldehyde and successfully transformed into the desired 1,1-diaryl-2-*tert*-butyl ethylenes in moderate to good yields (**3aa-3oa**,

Figure 1). In addition, volatile C-I bond and ester group were well tolerated to generate the corresponding products (**3ma** & **3oa**, Figure 1). Interestingly, alkynoates with *meta*-substitution on phenyls gave slightly lower yields compared with substrates with *para*-substituted groups (**3ga** *vs* **3fa**, **3ja** *vs* **3ka**, Figure 1). Unsymmetrical aryl alkynoates were employed to examine the stereoselectivity of the reaction, giving the mixed *E/Z* isomers (**3ia**–**3oa**, Figure 1),

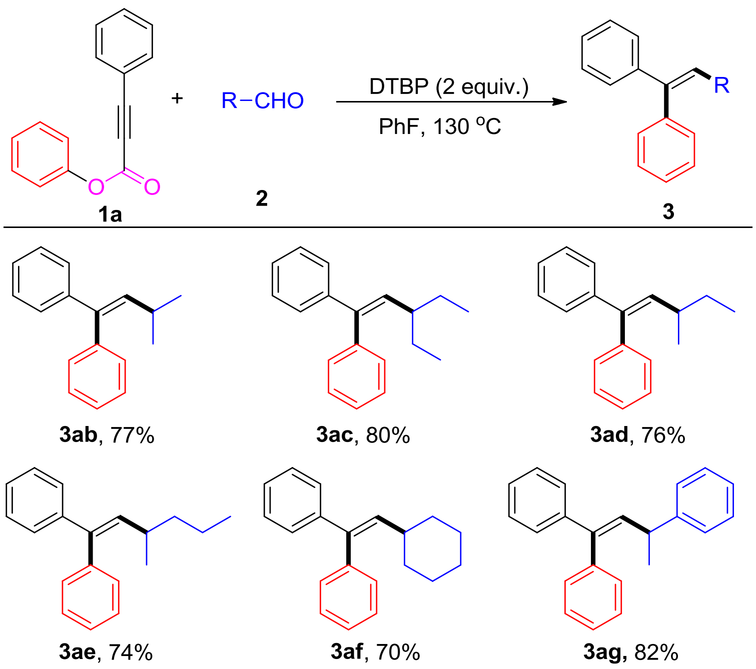
Figure 1. Scope of the Alkynoates.[a]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), DTBP (2 equiv) in PhF (2 mL) at 130 °C under N_2 for 20 h. [b] The ratio of the isomers was determined by ^1H NMR.

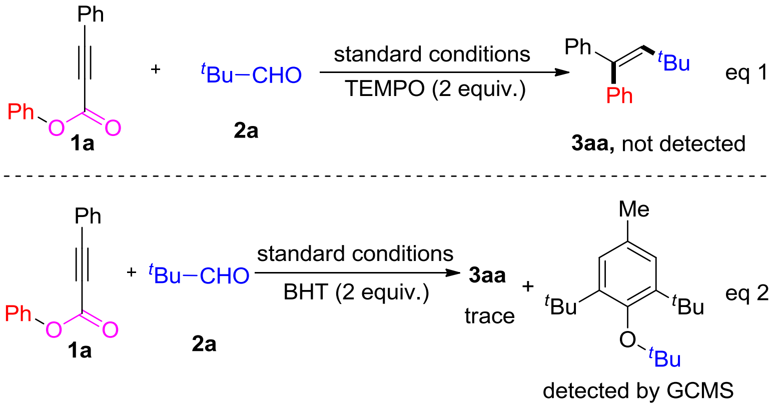
Apart from pivalaldehyde, other secondary alkyl aldehydes, such as isobutyraldehyde (**2b**), 2-ethylbutanal (**2c**), 2-methylbutanal (**2d**), 2-methylpentanal (**2e**), cyclohexanecarbaldehyde (**2f**) and 2-phenylpropanal (**2g**) were also good choices of secondary alkyl radical sources to produce the corresponding 1,1-diphenyl-2-alkyl ethylenes in moderate to good yields (**3ab-3ag**, Figure 2). Unfortunately, attempts to utilize primary alkyl aldehydes, such as hexaldehyde, failed to deliver the desired product. It is worth to note that, although our procedure was similar with Wu's,[3] no 3-acylated coumarin was detected, which may be due to the relatively higher temperature in our current procedure.

Figure 2. Scope of Alphatic Aldehydes.[a]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), DTBP (2 equiv) in PhF (2 mL) at 130 °C under N_2 for 20 h.

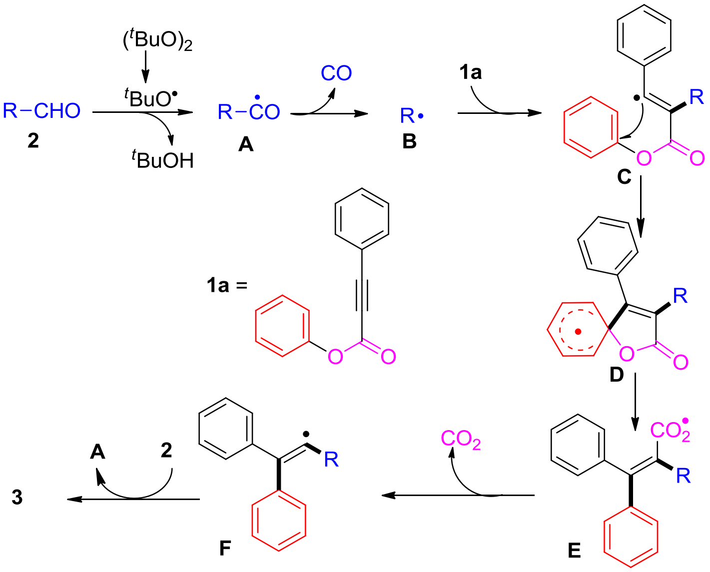
Scheme 2. Mechanism Studies.



Finally, control experiments were conducted to gain insights into the reaction mechanism as shown in Scheme 2. The transformation was completely inhibited when 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was added to the reaction as radical scavenger under standard conditions (eq 1, Scheme 2). The addition of BHT (2,6-di-*tert*-butyl-4-methylphenol) also effectively suppressed the reaction with the adduct formed by BHT and *tert*-butyl radical detected by GC-MS analysis (eq 1, Scheme 2). These results indicated radical intermediates were involved.

Based on the above experimental results and former reported works, the mechanism was outlined in Scheme 3. Firstly, the thermol homolytic cleavage of DTBP forms a *tert*-butoxy radical, which abstracts the hydrogen atom from aldehyde to provide *tert*-butyl alcohol and acyl radical **A**. Then, **A** undergoes decarbonylation to release CO and produce the *tert*-butyl radical **B**, which selectively adds to the α-carbon of the C−C triple bond in alkynoate **1a** and gives an active vinyl radical **C**. Next, the intramolecular radical *ipso*-cyclization of **C** forms a spiro intermediate **D**, which readily undergoes 1,4-aryl migration and subsequent decarboxylation affording another vinyl intermediate **F** and CO_2. Finally, **F** abstracts hydrogen from aldehyde **2** to generate product **3** as well as the acyl radical **A**.

Scheme 3. The Proposed Mechanism.



In summary, we have developed a metal-free cascade oxidative decarbonylative alkylation of diaryl alkynoates with aliphatic aldehydes to provide a series of trisubstituted olefins in moderate to good yields. The subsequent decarbonylation, radical addition, 1,4-aryl migration and decarboxylation processes were involved with the cascade cleavage of C(sp^3)–C(sp^2), C(sp^2)-O, C(sp^2)–C(sp^2) bonds and the construction of C(sp^3)–C(sp^2) and C(sp^2)–C(sp^2)

bonds in one-pot. This procedure offers a new complementary to the convenient generation of 1,1-diaryl-2-alkyl ethylenes using alphatic aldehydes as cheap and abundant alkyl radical source.

EXPERIMENTAL SECTION

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 M NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, the coupling constants *J* are given in Hz. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode. IR spectra were recorded on a spectrometer using KBr disks.

Experimental General Procedure for the Reaction: Under N_2, the mixture of alkynoate **1** (0.2 mmol), aliphatic aldehyde **2** (0.4 mmol), DTBP (0.4 mmol, 58.5 mg) and PhF (2 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 130 ^{o}C for 20 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the products.

(3,3-Dimethylbut-1-ene-1,1-diyl)dibenzene (3aa). [9f] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (40.1 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.32 (m, 3H), 7.27-7.18 (m, 7H), 6.11 (s, 1H), 0.99 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 144.1, 140.8, 140.1, 139.0, 130.4, 128.0, 127.8, 126.9, 126.7, 126.6, 34.0, 31.3.

4,4'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis(methylbenzene) (3ba). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (36.9 mg, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.17-7.04 (m, 8H), 6.05 (s, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 0.98 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 141.6, 139.2, 138.8, 137.9, 136.2, 130.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.1, 126.7, 33.9, 31.4, 21.3, 21.0. IR (cm^{-1}): *ν* 3021, 2956, 2922, 2865, 1654, 1630, 1509, 1473, 1459, 1362, 1249, 1188, 1021. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}$ $(M+H)^+$ 265.1951, found 265.1950.

3,3'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis(methoxybenzene) (**3ca**). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 100/1) gave a colorless oil (37.3 mg, 63%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, *J* = 6.9 Hz, 1H), 7.21-7.17 (m, 1H), 6.89-6.75 (m, 6H), 6.11 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 1.01 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 159.3, 159.1, 145.4, 141.9, 140.1, 138.6, 128.9, 128.7, 122.9, 119.5, 115.9, 113.1, 112.3, 111.5, 55.2, 33.9, 31.2. IR (cm^{-1}): *ν* 3024, 2956, 2865, 2834, 1734, 1653, 1596, 1577, 1485, 1463, 1364, 1284, 1239, 1213, 1165, 1050. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}O_2$ $(M+H)^+$ 297.1849, found 297.1851.

4,4''-(3,3-Dimethylbut-1-ene-1,1-diyl)di-1,1'-biphenyl (3da). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (56.6 mg, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72-7.59 (m, 6H), 7.54-7.41 (m, 7H), 7.38-7.32 (m, 5H), 6.23 (s, 1H), 1.06 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 143.1, 140.9, 140.8, 140.5, 139.8, 139.6, 139.5, 138.3, 130.8, 128.8, 128.78, 128.72, 127.3, 127.2, 127.04, 127.01, 126.8, 126.5, 34.1, 31.4. IR (cm^{-1}): *v* 3025, 3027, 2957, 2927, 2863, 1734, 1654, 1609, 1486, 1462, 1447, 1359, 1247, 1190, 1007. HRMS (ESI): *m/z* calcd for $C_{30}H_{29}$ $(M+H)^+$ 389.2264, found 389.2266.

4,4'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis(fluorobenzene) (3ea). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (47.3 mg, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.17-7.10 (m, 4H), 7.08-7.02 (m, 2H), 6.95-6.89 (m, 2H), 6.04 (s, 1H), 0.97 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 163.5 (d, J_{C-F} = 6.0 Hz), 160.3 (d, J_{C-F} = 5.3 Hz), 140.5, 140.0 (d, J_{C-F} = 3.0 Hz), 137.0, 136.4 (d, J_{C-F} = 3.5 Hz), 131.7 (d, J_{C-F} = 7.5 Hz), 128.4 (d, J_{C-F} = 6.8 Hz), 115.0 (d, J_{C-F} = 4.5 Hz), 114.7 (d, J_{C-F} = 5.3 Hz), 34.0, 31.3. IR (cm^{-1}): *v* 3031, 2959, 2927, 2868, 1656, 1600, 1508, 1480, 1461, 1367, 1223, 1158, 1053. HRMS (ESI): *m/z* calcd for $C_{18}H_{19}F_2$ $(M+H)^+$ 273.1449, found 273.1450.

4,4'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis(chlorobenzene) (3fa).[12] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (54.7 mg, 90%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.32 (m, 2H), 7.23-7.21 (m, 1H), 7.20-7.18 (m, 1H), 7.14-7.05 (m, 4H), 6.08 (s, 1H), 0.97 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 142.1, 141.2, 138.8, 136.8, 133.0, 132.6, 131.6, 130.4, 129.5, 128.5, 128.4, 128.2, 128.17, 128.12, 34.1, 31.3.

3,3'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis(chlorobenzene) (3ga). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (48.6 mg, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.32-7.29 (m, 2H), 7.19-7.17 (m, 4H), 7.10-7.07 (m, 1H), 7.03-6.99 (m, 1H), 6.09 (s, 1H), 0.98 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 145.3, 142.0, 141.9, 136.6, 134.1, 133.9, 130.2, 129.3, 129.2, 128.5, 127.3, 126.9, 126.8, 125.2, 34.2, 31.2. IR (cm^{-1}): *v* 3062, 2959, 2902, 2866, 1654, 1589, 1562, 1473, 1363, 1278, 1244, 1160, 1095, 1078. HRMS (ESI): *m/z* calcd for $C_{18}H_{19}Cl_2$ $(M+H)^+$ 305.0858, found 305.0862.

4,4'-(3,3-Dimethylbut-1-ene-1,1-diyl)bis((trifluoromethyl)benzene) (3ha). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (61.7 mg, 83%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 6.19 (s, 1H), 0.97 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 146.7, 143.9, 143.1, 136.8, 130.6, 129.4, 129.2 (q, J_{C-F} = 32.2 Hz), 128.5, 125.9, 125.4 (q, J_{C-F} = 3.7 Hz), 125.1 (q, J_{C-F}= 3.7 Hz), 125.0 (q, J_{C-F}= 3.7 Hz), 34.3, 31.2. IR (cm^{-1}): *v* 3065, 2962, 2912, 2870, 1662, 1613, 1574, 1465, 1324, 1248, 1166, 1127, 1068, 1017. HRMS (ESI): *m/z* calcd for $C_{20}H_{19}F_6$ $(M+H)^+$ 373.1385, found 373.1382.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-ethylbenzene (3ia). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (34.3 mg, 65%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.16 (m, 6H), 7.14-7.04 (m, 3H), 6.08 (d, 1H), 2.73-2.66 (q, 1H), 2.65-2.57 (q, 1H), 1.28 (t, *J* = 7.6 Hz, 1H), 1.21 (t, *J* = 7.6 Hz, 1H), 0.98 (s, 4.5H), 0.97 (s, 4.5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 144.4, 142.7, 142.6, 141.5, 140.9, 140.1, 139.3, 139.1, 137.9, 130.3, 130.2, 127.9, 127.7, 127.5, 127.2, 126.9, 126.7, 126.6, 126.5, 34.0, 33.9, 31.4, 28.6, 28.4, 15.6, 15.5. IR (cm^{-1}): *ν* 3021, 2960, 2929, 2867, 1654, 1630, 1597, 1508, 1474, 1460, 1443, 1362, 1249, 1189, 1029. HRMS (ESI): *m/z* calcd for $C_{20}H_{25}$ $(M+H)^+$ 265.1951, found 265.1950.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-methoxybenzene (3ja).[13] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 100/1) gave a colorless oil (40.9 mg, 77%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.15 (m, 5H), 7.12-7.07 (m, 2H), 6.87 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 6.06 (s, 0.44H), 5.99 (s, 0.47H), 3.82 (s, 1.4H), 3.76 (s, 1.58H), 0.97 (s, 4.62H), 0.94 (s, 4.39H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 158.5, 158.4, 144.4, 141.0, 140.3, 138.7, 138.5, 138.4, 136.8, 132.9, 131.4, 130.3, 128.0, 127.9, 127.7, 126.9, 126.7, 126.5, 113.4, 113.2, 55.3, 55.2, 33.9, 33.8, 31.4, 31.3.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-3-methoxybenzene (3ka). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 100/1) gave a colorless oil (36.7 mg, 69%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.12 (m, 6H), 6.86-6.70 (m, 3H), 6.09 (s, 0.5H), 6.06 (s, 0.5H), 3.79 (s, 1.5H), 3.74 (s, 1.5H), 0.98 (s, 4.5H), 0.95 (s, 4.5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 159.3, 159.1, 145.7, 143.8, 142.1, 140.6, 140.3, 140.0, 138.84, 138.80, 130.3, 128.9, 128.7, 128.0, 127.8, 126.8, 126.6, 123.0, 119.5, 115.9, 113.1, 112.2, 111.5, 55.2, 55.1, 34.0, 33.9, 31.3, 31.2. IR (cm^{-1}): *ν* 3057, 2952, 2865, 1654, 1633, 1596, 1577, 1486, 1463, 1429, 1363, 1285, 1226, 1139, 1051. HRMS (ESI): *m/z* calcd for $C_{19}H_{23}O$ $(M+H)^+$ 267.1743, found 267.1744.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-fluorobenzene (3la). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (43.7 mg, 86%). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.10 (m, 7H), 7.03 (t, *J* = 8.7 Hz, 1H), 6.90 (t, *J* = 8.7 Hz, 1H), 6.09 (s, 0.5H), 6.01 (s, 0.5H), 0.96-0.95 (d, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 163.5 (d, $J_{C\text{-}F}$ = 6.7 Hz), 160.2 (d, $J_{C\text{-}F}$ = 6.9 Hz), 143.8 (d, $J_{C\text{-}F}$ = 0.6 Hz), 140.7, 140.6, 140.2 (d, $J_{C\text{-}F}$ = 3.1 Hz), 139.9 (d, $J_{C\text{-}F}$ = 1.3 Hz), 138.0 (d, $J_{C\text{-}F}$ = 11.1 Hz), 136.5 (d, $J_{C\text{-}F}$ = 3.5 Hz), 131.8 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.2, 128.4, 128.3, 128.1, 127.9, 126.9, 126.8, 126.7, 114.8 (d, $J_{C\text{-}F}$ = 1.7 Hz), 114.6 (d, $J_{C\text{-}F}$ = 1.7 Hz), 34.0, 33.9, 31.33, 31.30. IR (cm^{-1}):

v 3051, 3020, 2958, 2924, 2865, 1654, 1631, 1507, 1474, 1460, 1443, 1363, 1221, 1157, 1029, 1014. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}F$ $(M+H)^+$ 255.1544, found 255.1546.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-iodobenzene (3ma). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (52.8 mg, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.34-7.29 (m, 1H), 7.25-7.12 (m, 4H), 6.96-6.89 (m, 2H), 6.08 (s, 0.5H), 6.06 (s, 0.5H), 0.96 (s, 4.5H), 0.94 (s, 4.5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 143.7, 143.5, 140.7, 140.6, 140.4, 140.1, 138.2, 137.9, 137.2, 137.0, 136.9, 132.3, 130.3, 128.8, 128.2, 128.1, 127.9, 127.0, 126.9, 126.8, 92.4, 92.1, 34.1, 34.0, 31.4, 31.2. IR (cm^{-1}): *v* 3056, 3021, 2957, 2926, 2864, 1653, 1633, 1597, 1491, 1481, 1460, 1443, 1386, 1359, 1246, 1188, 1059, 1006. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}I$ $(M+H)^+$ 363.0604, found 363.0609.

1-(3,3-Dimethyl-1-phenylbut-1-en-1-yl)-4-(trifluoromethyl)benzene (3na). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (51.7 mg, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.38-7.28 (m, 3H), 7.26-7.11 (m, 4H), 6.14 (s, 0.5H), 6.13 (s, 0.45H), 0.97 (s, 4.59H), 0.95 (s, 4.42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 147.6, 144.8, 143.2, 142.2, 141.0, 139.9, 138.1, 137.7, 130.7, 130.3, 129.6 (q, $J_{C\text{-}F}$ = 6.0 Hz), 129.4, 129.2, 128.5 (q, $J_{C\text{-}F}$ = 6.0 Hz), 128.2, 128.0, 126.1 (q, $J_{C\text{-}F}$ = 2.2 Hz), 125.2 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.9 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.7 (q, $J_{C\text{-}F}$ = 3.7 Hz), 122.5, 34.2, 34.0, 31.3, 31.1. IR (cm^{-1}): *v* 3056, 3022, 2960, 2867, 1615, 1493, 1474, 1407, 1364, 1325, 1165, 1125, 1067, 1016. HRMS (ESI): *m/z* calcd for $C_{19}H_{20}F_3$ $(M+H)^+$ 305.1512, found 305.1515.

Ethyl 4-(3,3-dimethyl-1-phenylbut-1-en-1-yl)benzoate (3oa). Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless oil (48.7 mg, 79%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.38-7.12 (m, 7H), 6.18-6.11 (d, 1H), 4.42-4.30 (m, 2H), 1.41 (t, *J* = 7.1 Hz, 1.5H), 1.36 (t, *J* = 7.1 Hz, 1.5H), 0.97-0.96 (d, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 166.6, 166.5, 148.5, 145.9, 143.3, 142.0, 140.7, 140.0, 138.5, 138.1, 130.4, 130.3, 129.3, 129.1, 129.0, 128.4, 128.3, 128.1, 127.9, 127.0, 126.8, 126.7, 60.9, 60.8, 34.2, 34.0, 31.3, 31.2, 14.4, 14.3. IR (cm^{-1}) *v* 3057, 2958, 2905, 2868, 1717, 1606, 1491, 1474, 1463, 1444, 1403, 1365, 1274, 1175, 1101, 1021. HRMS (ESI): *m/z* calcd for $C_{21}H_{25}O_2$ $(M+H)^+$ 309.1849, found 309.1850.

(3-Methylbut-1-ene-1,1-diyl)dibenzene (3ab).[14] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (34.2 mg, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40-7.26 (m, 3H), 7.25-7.12 (m, 7H), 5.89 (d, *J* = 10.1 Hz, 1H), 2.50-2.38 (m, 1H), 1.01 (t, *J* = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 142.7, 140.5, 139.1, 137.3, 129.8, 128.1, 128.0, 127.1, 126.8, 126.7, 28.8, 23.3.

(3-Ethylpent-1-ene-1,1-diyl)dibenzene (3ac).[9f] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (40 mg, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.28 (m, 3H), 7.26-7.14 (m, 7H), 5.82 (d, J = 10.5 Hz, 1H), 2.08-1.96 (m, 1H), 1.48-1.34 (m, 2H), 1.32-1.25 (m, 2H), 0.84 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 142.8, 141.7, 140.8, 134.9, 130.0, 128.1, 127.0, 126.7, 126.6, 42.2, 28.5, 12.0.

(3-Methylpent-1-ene-1,1-diyl)dibenzene (3ad).[9f] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (35.9 mg, 76%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.28 (m, 3H), 7.27-7.14 (m, 7H), 5.85 (d, J = 10.3 Hz, 1H), 2.27-2.12 (m, 1H), 1.39-1.29 (m, 2H), 0.99 (d, J = 6.7 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 142.4, 140.7, 140.3, 136.2, 129.8, 128.2, 128.1, 127.1, 126.8, 126.7, 35.5, 30.4, 21.1, 12.0.

(3-Methylhex-1-ene-1,1-diyl)dibenzene (3ae). Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (37 mg, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.28 (m, 3H), 7.27-7.14 (m, 7H), 5.85 (d, J = 10.3 Hz, 1H), 2.34-2.24 (m, 1H), 1.35-1.16 (m, 4H), 1.00 (d, J = 6.6 Hz, 3H), 0.-0.79 (t, J = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 142.7, 140.6, 140.0, 136.4, 129.8, 128.1, 128.0, 127.0, 126.7, 40.0, 33.6, 21.5, 20.7, 14.2. IR (cm^{-1}): *ν* 3057, 3023, 2956, 2924, 2869, 1653, 1598, 1562, 1494, 1455, 1444, 1377, 1072, 1031. HRMS (ESI): *m/z* calcd for $C_{19}H_{23}$ (M+H)$^+$ 251.1794, found 251.1795.

(2-Cyclohexylethene-1,1-diyl)dibenzene (3af).[9f] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (36.7 mg, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39-7.26 (m, 3H), 7.25-7.16 (m, 7H), 5.89 (d, J = 10.0 Hz, 1H), 2.14-2.05 (m, 1H), 1.69-1.60 (m, 5H), 1.22-1.11 (m, 5H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 142.9, 140.6, 139.5, 136.0, 129.8, 128.1, 128.0, 127.2, 126.8, 126.7, 38.3, 33.3, 26.0, 25.6.

But-1-ene-1,1,3-triyltribenzene (3ag).[9f] Flash column chromatography on silica gel (petroleum ether) gave a colorless oil (46.6 mg, 82%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.41-7.29 (m, 4H), 7.25-7.13 (m, 11H), 5.89 (d, J = 10.4 Hz, 1H), 3.65-3.54 (m, 1H), 1.38 (d, J = 6.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 146.2, 142.4, 140.2, 140.1, 134.2, 129.8, 128.5, 128.3, 128.1, 127.3, 127.1, 127.0, 126.9, 126.0, 39.3, 22.4.

ACKNOWLEDGMENT

We thank the National Natural Science Foundation of China (21602086 and 21672028), the Natural Science Foundation for Colleges and Universities of Jiangsu Province (16KJB150002) and Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology (BM2012110) for financial supports.

Supporting Information:

Mechanism study, ^{1}H and ^{13}C NMR spectra of compounds **3aa-3oa, 3ab-3ag**. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCE

1 (a) Wille, U. *Chem. Rev.* **2013**, *113*, 813. (b) Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698. (c) Gao, P.; Song, X.-R.; Liu, X.-Y.; Liang, Y.-M. *Chem. Eur. J.* **2015**, *21*, 7648. (d) Koike, T.; Akita, M. *Org. Chem. Front.* **2016**, *3*, 1345.

2 (a) Liu, C.; Liu, D.; Lei, A. *Acc. Chem. Res.* **2014**, *47*, 3459. (b) Liu, Q.; Jackstell, R.; Beller, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 13871. (c) Tang, S.; Liu, K.; Liu, C.; Lei, A. *Chem. Soc. Rev.* **2015**, *44*, 1070. (d) Yu, J.-T.; Pan, C. *Chem. Commun.* **2016**, *52*, 2220.

3 Mi, X.; Wang, C.; Huang, M.; Wu, Y.; Wu, Y. *J. Org. Chem.* **2015**, *80*, 148.

4 (a) Li, Y.; Lu, Y.; Qiu, G.; Ding, Q. *Org. Lett.* **2014**, *16*, 4240. (b) Mi, X.; Wang, C.; Huang, M.; Zhang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 3356. (c) Pan, C.; Chen, R.; Shao, W.; Yu, J.-T. *Org. Biomol. Chem.* **2016**, *14*, 9033 and references cited therein

5 (a) Wei, W.-T.; Song, R.-J.; Ouyang, X.-H.; Li, Y.; Li, H.-B.; Li, J.-H. *Org. Chem. Front.* **2014**, *1*, 484. (b) Hua, H.-L.; He, Y.-T.; Qiu, Y.-F.; Li, Y.-X.; Song, B.; Gao, P.; Song, X.-R.; Guo, D.-H.; Liu, X.-Y.; Liang, Y.-M. *Chem. Eur. J.* **2015**, *21*, 1468.

6 (a) Studer, A.; Bossart, M. *Tetrahedron* **2001**, *57*, 9649. (b) Chen, Z.-M.; Zhang, X.-M.; Tu, Y.-Q. *Chem. Soc. Rev.* **2015**, *44*, 5220.

7 (a) Ni. S.; Zhang, Y.; Xie, C.; Mei, H.; Han, J.; Pan, Y. *Org. Lett.* **201**5, *17*, 5524. (b) Miao, T.; Xia, D.; Li, Y.; Li, P.; Wang, L. *Chem. Commun.* **2016**, *52*, 3175. (c) Kong, D.-L.; Cheng, L.; Wu, H.-R.; Li, Y.-X.; Wang, D.; Liu, L. *Org. Biomol. Chem.* **2016**, *14*, 2210. (d) Wang, J.; Mou, X.-Q.; Zhang, B.-H.; Liu, W.-T.; Yang, C.; Xu, L.; Xu, Z.-L.; Wang, S.-H. *Tetrahedron Lett.* **2016**, *57*, 1239. (e) Pan, C.; Zhang, H.; Zhu, C. *Tetrahedron Lett.* **2016**, *57*, 595. (f) Ni, S.; Sha, W.; Zhang, L.; Xie, C.; Mei, H.; Han, J.; Pan, Y. *Org. Lett.* **2016**, *18*, 712. (g) Ni, S.; Zhang, L.; Zhang, W.; Mei, H.; Han, J.; Pan, Y. *J. Org. Chem.* **2016**, *81*, 9470.

8 (a) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991. (b) Wu, X.-F. *Chem. Eur. J.* **2015**, *21*, 12252.

9 (a) Shuai, Q.; Yang, L.; Guo, X.; Basle, O.; Li, C.-J. *J. Am. Chem. Soc.* **2010**, *132*, 12212. (b) Guo, X.; Wang, J.; Li, C.-J. *J. Am. Chem. Soc.* **2009**, *131*, 15092. (c) Yang, L. Guo, X.; Li, C.-J. *Adv. Synth. Catal.* **2010**, *352*, 2899. (d) Guo, X.; Wang, J.; Li, C.-J. *Org. Lett.* **2010**, *12*, 3176. (e) Yang, L.; Zeng, T.; Shuai, Q.; Guo, X.; Li, C.-J.

Chem. Commun. **2011**, *47*, 2161. (f) Zong, Z.; Wang, W.; Bai, X.; Xi, H.; Li, Z. P. *Asian J. Org. Chem.* **2015**, *4*, 622. (g) Kang, L.; Zhang, F.; Ding, L.-T.; Yang, L. *RSC Adv.* **2015**, *5*, 100452.

10 (a) Li, Y.; Pan, G.-H.; Hu, M.; Liu, B.; Song, R.-J.; Li, J.-H. *Chem. Sci.* **2016**, DOI: 10.1039/c6sc02451c. (b) Tang, R. J.; He, Q.; Yang, L. *Chem. Commun.* **2015**, *51*, 5925. (c) Tang, R. J.; Kang, L.; Yang, L. *Adv. Synth. Catal.* 2015, **357**, 2055. (d) Yang, L.; Lu, W.; Zhou, W.; Zhang, F. *Green Chem.* **2016**, *18*, 2941. (e) Paul, S.; Guin, J. *Chem. Eur. J.* **2015**, *21*, 17618. (f) Ouyang, X.-H.; Song, R.-J.; Liu, B.; Li, J.-H. *Adv. Synth. Catal.* **2016**, *358*, 1903. (g) Lv, L.; Bai, X.; Yan, X. Li, Z. *Org. Chem. Front.* **2016**, *3*, 1509.

11 Pan, C.; Huang, B.; Hu, W.; Feng, X.; Yu, J.-T. *J. Org. Chem.* **2016**, *81*, 2087.

12 Zhang, L.; Yu, X.; Zhang, L.; Zhou, X.; Lin, Y. *Org. Chem. Front.* **2014**, *1*, 929.

13 Ahlquist, M.; Fabrizi, G.; Cacchi, S.; Norrby, P. *J. Am. Chem. Soc.* **2006**, *128*, 12785.

14 He, Z.; Kirchberg, S.; Froehlich, R.; Studer, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 3699.