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

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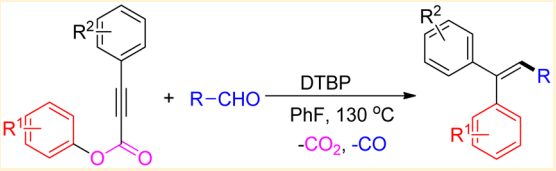
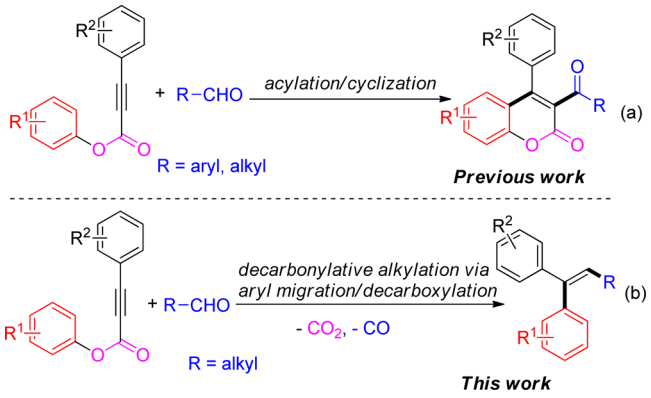
Supporting Information

ABSTRACT: The oxidative difunctionalization of aryl alkynoates with alphatic aldehydes as a 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 to be a promising and convenient procedure to generate various structural complex and synthetically useful compounds due to the ready availability of alkyne derivatives.[1] Among them, 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 co-workers developed the construction of 3-acyl-4-arylcoumarins via metal-free tandem oxidative acylation/cyclization using aldehydes as acyl radical source (Scheme 1(a)).[3] Encouragingly, a great many 3-functionalized coumarins

Scheme 1. Difunctionalization of Alkynoates with Aldehydes



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, and so forth as efficient radical sources through oxidative radical addition and a 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 a 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 an oxidative radical addition/decarboxylation procedure.[7] In the latter case, the direct functionalization of relatively inert C(sp^3)-H bonds were realized to generate alkyl, benzylic, oxyalkyl, and 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 sources would be highly desirable.

Aldehydes are cheap and readily available chemicals that can be easily converted to corresponding acyl radicals for the acylation of various types 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 structurally 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 an alkyl source to generate trisubstituted alkenes (Scheme 1(b)).

Our initial investigations focused on the optimization of the decarbonylative alkylation between diphenyl alkynoate (**1a**) and pivalaldehyde (**2a**) (Table 1). In the presence of di-*tert*-butyl peroxide (DTBP), the desired decarbonylative alkylated product **3aa** could be detected in DCE at 130 °C for 20 h albeit

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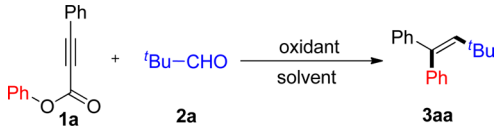
Table 1. Screening the Optimized Reaction Conditions[a]



entry	oxidant[b]	solvent	yield (%)
1	DTBP	DCE	8
2	DTBP	CH_3CN	12
3	DTBP	PhH	50
4	DTBP	PhCl	21
5	DTBP	PhF	85 (62)[c] (66)[d]
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[e] (79)[f] (84)[g]

[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]DTBP = di-*tert*-butyl peroxide, TBHP = *tert*-butyl hydroperoxide, TBPB = *tert*-butyl peroxybenzoate, DCP = dicumyl peroxide, BPO = benzoyl peroxide. [c]Under air. [d]DTBP (1 equiv) was used. [e]At 110 °C. [f]At 120 °C. [g]At 140 °C.

in low yield (Table 1, entry 1). Inspired by this result, other solvents such as acetonitrile, benzene, chlorobenzene, fluorobenzene, trifluoromethylbenzene, and DCM were investigated, and fluorobenzene was proven to be the best choice with an 85% yield of **3aa** (Table 1, entries 2−7). The utilization of a proper oxidant was also crucial to the transformation, as TBHP, TBPB, DCP, and BPO were all inferior to DTBP (Table 1, entries 8−11). Additionally, the yield was sharply reduced under air or with a lower amount of oxidant utilized (Table 1, entry 5). A temperature control experiment suggested that an obviously negative effect was observed at a lower temperature (110 °C), whereas a higher temperature (140 °C) did not result in better yield (Table 1, entry 12).

Then, the generality of this oxidative decarbonylative alkylation of alkynoates with aliphatic aldehydes was investigated. As expected, diaryl alkynoates with either electron-donating or -withdrawing substituents, such as methyl, methoxyl, halogen, and trifluoromethyl on either phenyl of alkynoates, all reacted smoothly with pivalaldehyde and successfully transformed to 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 groups were well tolerated to generate the corresponding products (**3ma** and **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).

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

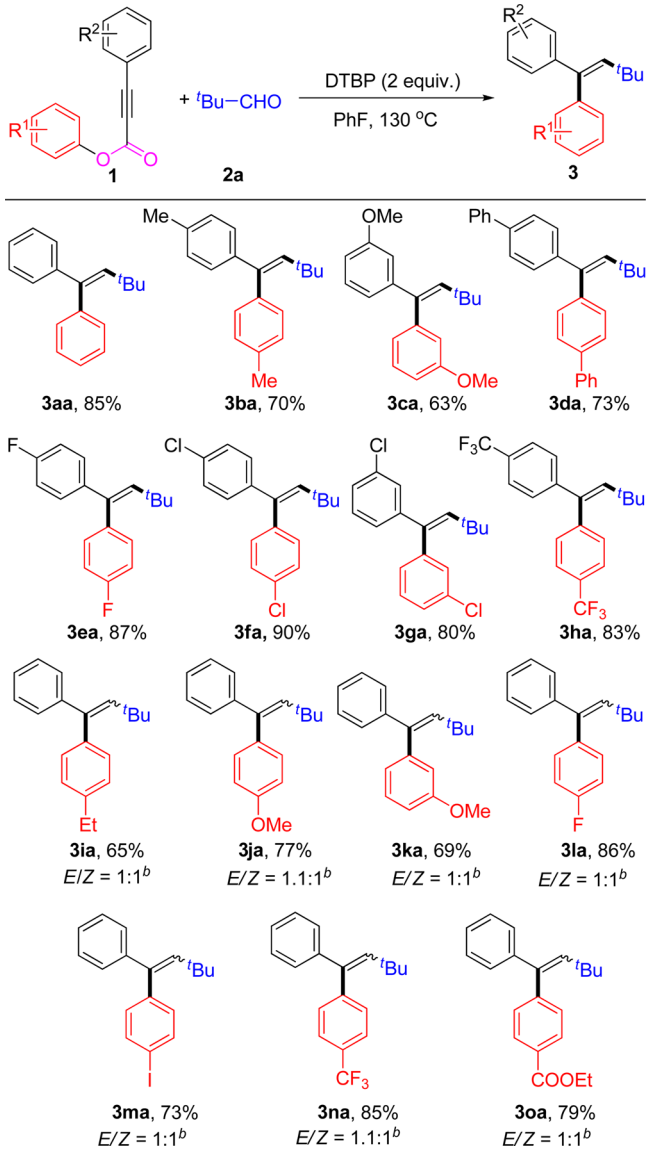


Figure 1. Scope of the Alkynoates. [a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), DTBP (2 equiv) in PhF (2 mL) at 130 °C under N_2 for 20 h. [b]The ratio of the isomers was determined by ^1H NMR.

deliver the desired product. It is worth to note that, although our procedure was similar to that of Wu,[3] no 3-acylated coumarin was detected, which may be due to the relatively higher temperature in our current procedure.

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 (Scheme 2(a)). The addition of 2,6-di-*tert*-butyl-4-methylphenol (BHT) also effectively suppressed the reaction with the adduct formed by BHT and *tert*-butyl radical detected by GC-MS analysis (Scheme 2(b)). These results indicated that radical intermediates were involved.

On the basis of the above experimental results and former reported works, the mechanism was outlined in Scheme 3. First, the thermol homolytic cleavage of DTBP forms a *tert*-butoxy radical, which abstracts the hydrogen atom from

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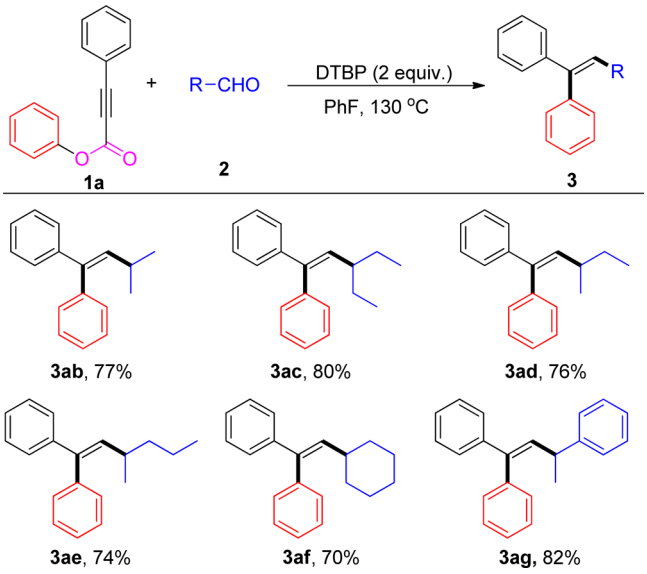
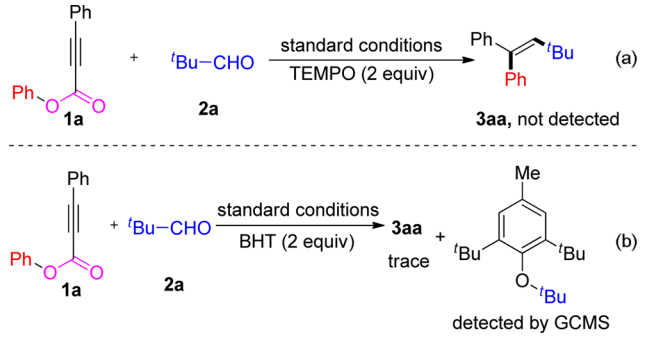
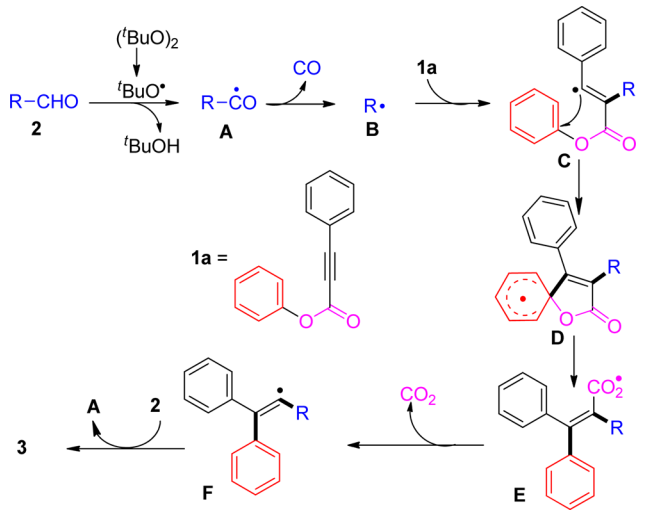


Figure 2. Scope of Alphatic Aldehydes. [a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), DTBP (2 equiv) in PhF (2 mL) at 130 °C under N_2 for 20 h.

Scheme 2. Mechanism Studies



Scheme 3. Proposed Mechanism



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 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**.

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 approach to the convenient generation of 1,1-diaryl-2-alkyl ethylenes using alphatic aldehydes as a 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 to a tube and sealed. The reaction mixture was vigorously stirred at 130 °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). $^{13}C\{^1H\}$ 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). $^{13}C\{^1H\}$ 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 (100:1 petroleum ether/ethyl acetate) 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). $^{13}C\{^1H\}$ 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}): ν 3025, 3027, 2957, 2927, 2863, 1734, 1654, 1609, 1486, 1462, 1447, 1359,

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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}): ν 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}): ν 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}): ν 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%). ^{1}H 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 (100:1 petroleum ether/ethyl acetate) gave a colorless oil (40.9 mg, 77%). ^{1}H 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 (100:1 petroleum ether/ethyl acetate) gave a colorless oil (36.7 mg, 69%). ^{1}H 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%). ^{1}H 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-F} = 6.7 Hz), 160.2 (d, J_{C-F} = 6.9 Hz), 143.8 (d, J_{C-F} = 0.6 Hz), 140.7, 140.6, 140.2 (d, J_{C-F} = 3.1 Hz), 139.9 (d, J_{C-F} = 1.3 Hz), 138.0 (d, J_{C-F} = 11.1 Hz), 136.5 (d, J_{C-F} = 3.5 Hz), 131.8 (d, J_{C-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-F} = 1.7 Hz), 114.6 (d, J_{C-F} = 1.7 Hz), 34.0, 33.9, 31.33, 31.30. IR (cm^{-1}): ν 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}): ν 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-F} = 6.0 Hz), 129.4, 129.2, 128.5 (q, J_{C-F} = 6.0 Hz), 128.2, 128.0, 126.1 (q, J_{C-F} = 2.2 Hz), 125.2 (q, J_{C-F} = 3.7 Hz), 124.9 (q, J_{C-F} = 3.7 Hz), 124.7 (q, J_{C-F} = 3.7 Hz), 122.5, 34.2, 34.0, 31.3, 31.1. IR (cm^{-1}): ν 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 (50:1 petroleum ether/ethyl acetate) 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}) ν 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). $^{13}C\{^1H\}$ 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),

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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). $^{13}C\{^1H\}$ 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%). ^1H 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). $^{13}C\{^1H\}$ 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%). ^1H 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). $^{13}C\{^1H\}$ 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%). ^1H 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). $^{13}C\{^1H\}$ 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02451.

Mechanism study and ^1H and ^{13}C NMR spectra of compounds **3aa**−**3oa** and **3ab**−**3ag** (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(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.* **2015**, *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**, *7*, 7050. (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.

DOI: 10.1021/acs.joc.6b02451
J. Org. Chem. 2016, 81, 12065−12069