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Radical 1,2-Alkylarylation/Acylarylation of Allylic Alcohols with Aldehydes via Neophyl Rearrangement

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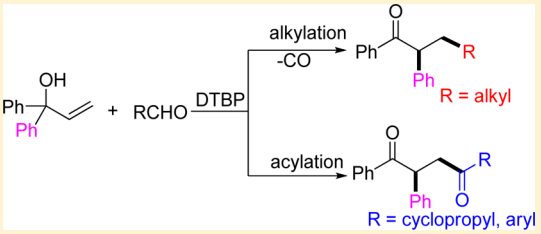
Supporting Information

ABSTRACT: A metal-free 1,2-alkylarylation of allylic alcohols with aliphatic aldehydes through concomitant radical neophyl rearrangement was developed, providing 1,2-diphenyl-3-alkyl propanones in moderate to good yields. Moreover, when cyclopropanecarbaldehyde and aryl carbaldehydes were concerned, acylarylation was involved leading to 1,4-dicarbonyl compounds.



The difunctionalization of simple alkenes, by means of simultaneous installation of two functional groups on the hydrocarbons, has become a powerful approach for the assembly of complex structures in organic synthesis.[1] In this field, the radical-mediated difunctionalization of alkenes has made great progress in the past decade, relying on the great advances in chemo- and regioselective radical reactions.[2,3] However, the vast majority of alkenes utilized are restricted to activated olefins.[3] Therefore, radical difunctionalization of more common, unactivated alkenes still remains a challenging task for chemists. Radical migration, which has been demonstrated as a promising tool in organic synthesis,[4] provided a feasible approach for the difunctionalization of unactivated alkenes.[5−7] For example, Zhu achieved the cyanation, heteroarylation, and alkynylation of unactivated alkenes by means of intramolecular distal functional-group migrations.[6] Radical 1,2-aryl migration classified as radical neophyl rearrangement[7] has been utilized for the difunctionalization of diaryl allylic alcohols using various radical precursors to deliver a variety of α-aryl-β-alkylated ketones.[8] In this area, Ji[9] and Han[10] reported the alkylarylation of allylic alcohols with ethers and alkanes, respectively. However, when alkylating reagents with unsymmetric structures were concerned, regioisomers were obtained.

Aldehydes are readily available and cheap chemicals. They can be easily transformed into relevant acyl radicals in the acylation of organic molecules.[11] On the other hand, aliphatic aldehydes were successfully utilized as ideal linear and branched alkyl radical precursors after decarbonylation under the assistance of proper oxidants.[12] With respect to the universality and importance of aldehydes and alkenes, herein we report a metal-free 1,2-alkylarylation/acylarylation of allylic alcohols with aldehydes through a concomitant neophyl rearrangement.

Initially, the reaction of α,α-diphenyl allylic alcohol (**1a**) with pivalaldehyde (**2a**) was carried out to optimize the reaction conditions. Delightedly, the desired product **3aa** was isolated in 58% yield when DTBP was used as the radical initiator in PhF (Table 1, entry 1). Subsequently, other solvents such as $PhCF_3$, PhCl, PhH, DCE, DCM, and EA were investigated (Table 1, entries 2−7). The results indicated that PhH was the best choice, providing **3aa** in 84% yield (Table 1, entry 4). Other common oxidants such as TBHP and DCP were all inferior to DTBP (Table 1, entries 8−9). The yield of **3aa** dropped obviously at a lower temperature (100 °C), whereas no better result was obtained at elevated temperature (130 °C) (Table 1, entry 4).

Table 1. Screening the Reaction Conditions[a]

entry	oxidant	solvent	yield (%)
1	DTBP	PhF	58
2	DTBP	$PhCF_3$	52
3	DTBP	PhCl	63
4	DTBP	PhH	84 (41)[b] (82)[c] (76)[d]
5	DTBP	DCE	11
6	DTBP	DCM	25
7	DTBP	EA	16
8	TBHP	PhH	12
9	DCP	PhH	28

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), oxidant (0.6 mmol), and solvent (2 mL) at 130 °C under N_2. [b]At 100 °C. [c]At 130 °C. [d]**2a** (0.4 mmol) and DTBP (0.4 mmol). DTBP = Di-*tert*-butyl peroxide, TBHP = *tert*-Butyl hydroperoxide.

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With the optimized reaction conditions established, we set out to explore the scope of this protocol as listed in Figures 1

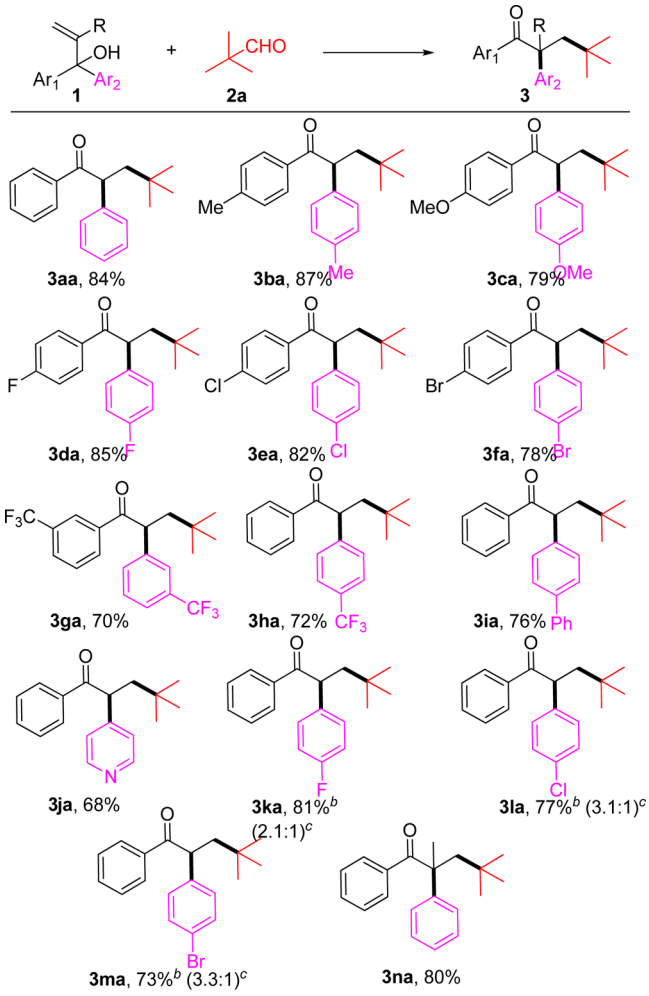


Figure 1. Scope of the α,α-diaryl allylic alcohols.[a] [a] Reaction conditions: **1** (0.2 mmol), **2a** (0.6 mmol), DTBP (0.6 mmol) in PhH (2 mL) at 120 °C under N_2 for 16 h. [b] Total yields of two isomers, and only major products are shown. [c] The ratio of isomers was determined by ^{1}H NMR analysis.

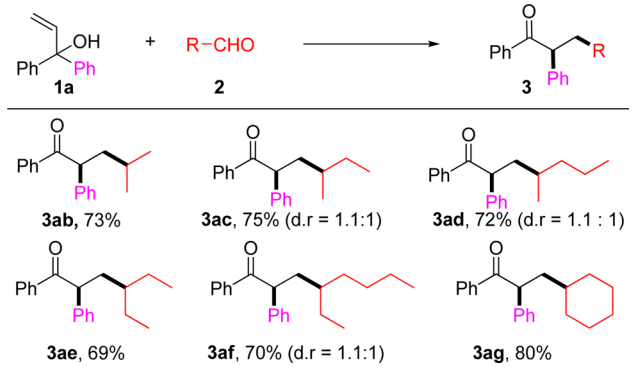


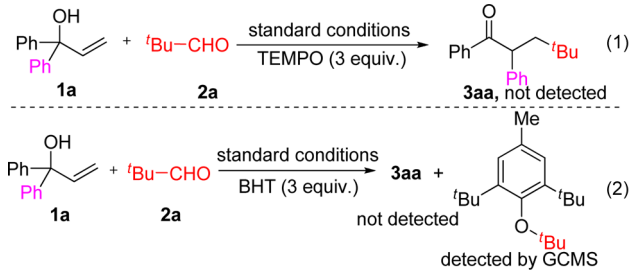
Figure 2. Scope of aliphatic aldehyde. Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DTBP (0.6 mmol) in PhH (2 mL) at 120 °C under N_2 for 16 h. The ratio of isomers was determined by ^{1}H NMR analysis.

and 2. First, we studied the substitution pattern on the aryls of α,α-diaryl allylic alcohols. As expected, substrates with an electron-donating or -withdrawing group all reacted smoothly to generate the desired 1,2-diaryl-3-*tert*-butyl propanones in good to moderate yields. Substrates with methyl, methoxyl, halogen, and trifluoromethyl were all well tolerated. For allylic alcohols with different aryls, two isomers were detected in most cases, and the electron-deficient groups preferentially migrated, although in low selectivity (**3ka**−**3la**, Figure 1). In addition, pyridyl was a good migrating group and provided a sole product, albeit in a relatively lower yield (**3ja**). Moreover, the good tolerance of halogen provides potential handles for more functionalized diaryl ketones (**3da**−**3fa**, **3ka**−**3ma**). Notably, the 2-methyl analogue was also a good reaction partner leading to the corresponding diphenyl ketone in good yield (**3na**, Figure 1).

Next, the scope of aliphatic aldehydes was also tested. Apart from pivalaldehyde, other common alkyl aldehydes, such as isobutyraldehyde (**2b**), 2-methylbutanal (**2c**), 2-methylpentanal (**2d**), 2-ethylbutanal (**2e**), 2-ethylhexanal (**2f**), and cyclohexanecarbaldehyde (**2g**), were all a good choice as a secondary alkyl radical source to produce the corresponding 1,2-diphenyl-3-alkyl propanones in moderate to good yields (**3ab**−**3ag**, Figure 2). Two diastereomers were observed in the ratios of 1.1:1, if unsymmetrical carbon radicals were involved (**3ac**, **3ad**, and **3af**, Figure 2).

To gain insights into the mechanism of this reaction, control experiments were conducted, as shown in Scheme 1. The

Scheme 1. Mechanism Study



transformation was completely inhibited when radical scavenger 2,2,6,6-tetramethylpiperidinooxy (TEMPO) was added to the reaction (eq 1, Scheme 1). The reaction was also effectively suppressed by BHT (2,6-di-*tert*-butyl-4-methylphenol) along with the adduct formed by BHT and *tert*-butyl radical detected by GC-MS (eq 2, Scheme 1). These results indicated radical intermediates were involved in the transformation.

Based on the above experimental results and former reported works,[8] the mechanism of 1,2-alkylarylation of allylic alcohols with aliphatic aldehydes was proposed in Scheme 2. First, acyl radical **A** is produced with the assistance of DTBP and the following decarbonylation leading to *tert*-butyl radical **B**. Then, **B** undergoes intermolecular radical addition to diaryl allylic alcohol **1** to give alkyl radical intermediate **C**. The subsequent intramolecular radical addition provides the spiro[2,5]-octadienyl radical intermediate **D**, which undergoes neophyl rearrangement to produce intermediate **E**. Finally, product **3** is delivered after oxidation by DTBP to a cation and further deprotonation.

Surprisingly, when cyclopropanecarbaldehyde (**2h**) was subjected to the reaction, no decarbonylated diaryl ketone was detected with the isolation of γ-diketones. Obviously,

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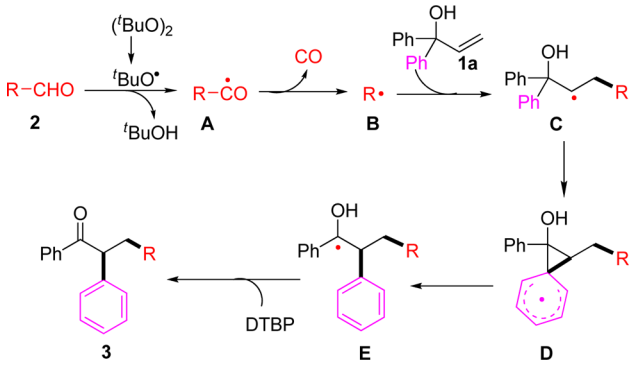
Scheme 2. Proposed Mechanism



acylation was involved instead of decarbonylative alkylation, where cyclopropanecarbaldehyde served as an acylating reagent (**3ah**−**3fh**, Figure 3). Further studies revealed that aryl

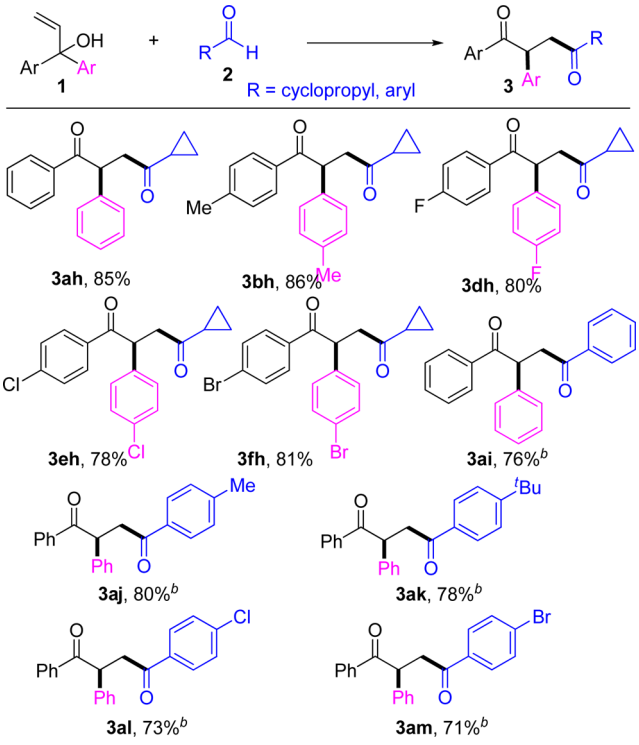


Figure 3. Scope of acylation of α,α-diaryl allylic alcohols.[a] [a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), DTBP (0.6 mmol) in PhH (2 mL) at 120 °C under N_2 for 16 h. [b] 130 °C, 24 h.

carbaldehyde also experienced the same pathway. After neophyl rearrangement and aroylation, the corresponding triaryl γ-diketones were obtained in good yields (**3ai**−**3am**, Figure 3). The occurrence of this phenomenon may be attributed to the relative stabilities of corresponding radical intermediates involved in the above two cases.

In conclusion, we have developed a metal-free decarbonylative alkylarylation of allylic alcohols with aliphatic aldehydes through concomitant radical neophyl rearrangement, providing 1,2-diaryl-3-alkyl propanones in moderate to good yields. In addition, acylarylation occurred when cyclopropanecarbaldehyde and aryl carbaldehydes were used, providing an alternative approach to the synthesis of triaryl γ-diketones.

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 400 or 500 MHz NMR spectrometer. Chemical shifts (δ) are given in ppm relative to TMS, and the coupling constants J are given in Hz. HRMS data were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

Experimental Procedure for the Procedure for Alkylation/Acylation of Allylic Alcohols with Aldehyde. Under N_2, the mixture of aryl allylic alcohols **1** (0.2 mmol), aldehyde **2** (0.6 mmol), DTBP (0.6 mmol, 87.7 mg, 110 μL), and PhH (2 mL) were added into the sealed tube. The reaction mixture was vigorously stirred at 120 °C for 16 h (130 °C and 24 h for aroylation of allylic alcohols). Then, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel to give the products.

*4,4-Dimethyl-1,2-diphenylpentan-1-one (**3aa**).*[13] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (44.7 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 7.7 Hz, 2H), 7.50−7.47 (m, 1H), 7.42−7.38 (m, 2H), 7.33−7.24 (m, 4H), 7.18−7.14 (m, 1H), 4.72 (d, J = 8.6 Hz, 1H), 2.63 (d, J = 13.9, 8.9 Hz, 1H), 1.58 (d, J = 13.8 Hz, 1H), 0.88 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 200.0, 141.1, 137.0, 132.8, 128.9, 128.64, 128.61, 128.2, 126.8, 49.7, 47.6, 31.2, 29.8.

*4,4-Dimethyl-1,2-di-p-tolylpentan-1-one (**3ba**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (51.1 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, J = 7.5 Hz, 2H), 7.21 (d, J = 7.5 Hz, 4H), 7.07 (d, J = 7.5 Hz, 2H), 4.68 (d, J = 8.6 Hz, 1H), 2.62 (dd, J = 13.8, 8.9 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 3H), 1.55 (d, J = 13.9 Hz, 1H), 0.89 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 199.7, 143.5, 138.4, 136.3, 134.5, 129.6, 129.3, 128.8, 127.9, 49.0, 47.5, 31.2, 29.8, 21.6, 21.0. HRMS (ESI) m/z calcd for $C_{21}H_{27}O$ (M + H)$^+$ 295.2056, found 295.2057.

*1,2-Bis(4-methoxyphenyl)-4,4-dimethylpentan-1-one (**3ca**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 20/1) gave a colorless liquid (51.5 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.2 Hz, 2H), 4.63 (dd, J = 8.7, 3.2 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 2.59 (dd, J = 13.9, 8.7 Hz, 1H), 1.55 (dd, J = 13.9, 3.0 Hz, 1H), 0.87 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.8, 163.2, 158.3, 133.6, 130.9, 129.9, 129.1, 114.2, 113.8, 55.4, 55.2, 48.2, 47.5, 31.1, 29.9. HRMS (ESI) m/z calcd for $C_{21}H_{27}O_3$ (M + H)$^+$ 327.1955, found 327.1958.

*1,2-Bis(4-fluorophenyl)-4,4-dimethylpentan-1-one (**3da**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (51.3 mg, 85%). Mp 90−92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03−8.00 (m, 2H), 7.29−7.26 (m, 2H), 7.12−7.08 (m, 2H), 6.99−6.95 (m, 2H), 4.66 (dd, J = 8.3, 2.7 Hz, 1H), 2.57 (dd, J = 13.9, 8.7 Hz, 1H), 1.56 (dd, J = 13.9, 2.1 Hz, 1H), 0.88 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.4, 165.6 (d, J_{C-F} = 253.4 Hz), 161.8 (d, J_{C-F} = 244.2 Hz), 136.6 (d, J_{C-F} = 3.2 Hz), 133.1 (d, J_{C-F} = 2.9 Hz), 131.1 (d, J_{C-F} = 9.3 Hz), 129.6 (d, J_{C-F} = 7.9 Hz), 115.9 (d, J_{C-F} = 3.1 Hz), 115.7 (d, J_{C-F} = 3.4 Hz), 48.7, 47.6, 31.2, 29.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ −105.3, −115.8. HRMS (ESI) m/z calcd for $C_{19}H_{21}F_2O$ (M + H)$^+$ 303.1555, found 303.1556.

*1,2-Bis(4-chlorophenyl)-4,4-dimethylpentan-1-one (**3ea**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (54.8 mg, 82%). Mp 97−99 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.9 Hz, 2H), 7.28−7.24 (m, 4H), 4.65 (dd, J = 8.5, 3.0 Hz, 1H), 2.59 (dd, J = 14.0, 8.6 Hz, 1H), 1.57 (dd, J = 14.0, 2.9 Hz, 1H), 0.89 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.5, 139.5, 139.2, 135.0, 132.9, 129.9, 129.4, 129.2, 129.0, 49.0, 47.4, 31.2, 29.8. HRMS (ESI) m/z calcd for $C_{19}H_{21}Cl_2O$ (M + H)$^+$ 335.0964, found 335.0966.

*1,2-Bis(4-bromophenyl)-4,4-dimethylpentan-1-one (**3fa**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (65.8 mg, 78%). Mp 99−100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.7 Hz,

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2H), 7.39 (d, J = 7.5 Hz, 2H), 7.16 (d, J = 7.6 Hz, 2H), 4.60 (dd, J = 8.4, 2.7 Hz, 1H), 2.56 (dd, J = 13.9, 8.5 Hz, 1H), 1.54 (dd, J = 13.9, 2.5 Hz, 1H), 0.87 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 198.6, 139.7, 135.4, 132.1, 132.0, 130.1, 129.8, 128.3, 120.9, 49.0, 47.4, 31.2, 29.8. HRMS (ESI) m/z calcd for $C_{19}H_{21}Br_2O$ $(M + H)^+$ 422.9954, found 422.9959.

*4,4-Dimethyl-1,2-bis(3-(trifluoromethyl)phenyl)pentan-1-one (**3ga**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (56.3 mg, 70%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, 1H), 8.16 (d, J = 7.8 Hz, 1H), 7.79 (d, J = 7.7 Hz, 1H), 7.61−7.57 (m, 2H), 7.52−7.39 (m, 3H), 4.76 (dd, J = 8.4, 3.3 Hz, 1H), 2.62 (dd, J = 14.0, 8.6 Hz, 1H), 1.61 (dd, J = 14.0, 3.5 Hz, 1H), 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 198.0, 141.3, 137.0, 131.6 (q, J_{C-F} = 26.2 Hz), 131.55, 131.50, 131.3 (q, J_{C-F} = 32.0 Hz), 129.6 (q, J_{C-F} = 3.5 Hz), 129.5, 129.4, 125.3 (q, J_{C-F} = 3.6 Hz), 124.8 (q, J_{C-F} = 3.6 Hz), 124.0 (q, J_{C-F} = 3.5 Hz), 123.9 (q, J_{C-F} = 270.7 Hz), 123.6 (q, J_{C-F} = 271.0 Hz), 49.6, 47.6, 31.3, 29.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.6, −62.9. HRMS (ESI) m/z calcd for $C_{21}H_{21}F_6O$ $(M + H)^+$ 403.1491, found 403.1494.

*4,4-Dimethyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)pentan-1-one (**3ha**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (48.1 mg, 72%). Mp 94−96 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 7.2 Hz, 2H), 7.55−7.51 (m, 3H), 7.46−7.42 (m, 4H), 4.80 (dd, J = 8.7, 3.4 Hz, 1H), 2.63 (dd, J = 14.0, 8.7 Hz, 1H), 1.58 (dd, J = 14.0, 3.4 Hz, 1H), 0.89 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 199.4, 145.1, 136.6, 133.2, 129.1 (q, J_{C-F} = 32.3 Hz), 128.8, 128.6, 128.5, 125.8 (q, J_{C-F} = 3.7 Hz), 124.1 (q, J_{C-F} = 270.3 Hz), 49.4, 47.6, 31.3, 29.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.5. HRMS (ESI) m/z calcd for $C_{20}H_{22}F_3O$ $(M + H)^+$ 335.1617, found 335.1614.

*2-([1,1′-Biphenyl]-4-yl)-4,4-dimethyl-1-phenylpentan-1-one (**3ia**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 30/1) gave a white solid (51.9 mg, 76%). Mp 178−179 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, J = 7.2 Hz, 2H), 7.56−7.51 (m, 5H), 7.46−7.39 (m, 6H), 7.34−7.30 (d, J = 7.6 Hz, 1H), 4.80 (dd, J = 8.8, 3.1 Hz, 1H), 2.72−2.68 (dd, J = 13.9, 8.9 Hz, 1H), 1.54 (dd, J = 13.8, 3.2 Hz, 1H), 0.93 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 200.0, 140.7, 140.2, 139.7, 137.0, 132.9, 128.8, 128.7, 128.6, 127.7, 127.3, 127.0, 49.0, 47.7, 31.3, 29.9. HRMS (ESI) m/z calcd for $C_{25}H_{27}O$ $(M + H)^+$ 343.2056, found 343.2057.

*4,4-Dimethyl-1-phenyl-2-(pyridin-4-yl)pentan-1-one (**3ja**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a white solid (36.3 mg, 68%). Mp 87−89 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.60 (d, J = 1.9 Hz, 1H), 8.43 (d, J = 4.7 Hz, 1H), 7.99 (d, J = 7.2 Hz, 2H), 7.68−7.65 (m, 1H), 7.55−7.51 (m, 1H), 7.45−7.41 (m, 2H), 7.22−7.18 (m, 1H), 4.77 (dd, J = 8.5, 3.8 Hz, 1H), 2.58 (dd, J = 14.0, 8.5 Hz, 1H), 1.58 (dd, J = 14.0, 3.8 Hz, 1H), 0.88 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 199.4, 149.7, 148.2, 136.7, 136.5, 135.4, 133.3, 128.8, 128.5, 123.8, 47.6, 46.7, 31.3, 29.8. HRMS (ESI) m/z calcd for $C_{18}H_{22}NO$ $(M + H)^+$ 268.1696, found 268.1698.

*2-(4-Fluorophenyl)-4,4-dimethyl-1-phenylpentan-1-one (**3ka**) and 1-(4-Fluorophenyl)-4,4-dimethyl-2-phenylpentan-1-one (**3k′a**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (46.0 mg, 81%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.96−7.88 (m, 2H), 7.43−7.39 (m, 0.32H), 7.35−7.31 (m, 0.68H), 7.23−7.16 (m, 3.33H), 7.11−7.06 (m, 0.68H), 6.99−6.95 (m, 1.35H), 6.88−6.84 (m, 0.6H), 4.64 (q, 0.32H), 4.58 (q, 0.69H), 2.56−2.47 (m, 1H), 1.51−1.46 (m, 1H), 0.79 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 199.9, 197.3, 164.2 (d, J_{C-F} = 253.1 Hz), 160.7 (d, J_{C-F} = 244.0 Hz), 139.9, 135.8, 135.7 (d, J_{C-F} = 3.2 Hz), 132.3 (d, J_{C-F} = 3.0 Hz), 131.9, 130.2 (d, J_{C-F} = 9.2 Hz), 128.6 (d, J_{C-F} = 7.8 Hz), 127.9, 127.6 (d, J_{C-F} = 10.7 Hz), 127.0, 125.8, 114.7 (d, J_{C-F} = 21.3 Hz), 114.6 (d, J_{C-F} = 21.7 Hz), 48.6, 47.7, 46.6, 46.5, 30.2, 30.1, 28.8, 28.7. ^{19}F NMR (470 MHz, $CDCl_3$): δ −105.6, −116.0. MS (EI): 284, 269, 227.

*2-(4-Chlorophenyl)-4,4-dimethyl-1-phenylpentan-1-one (**3la**) and 1-(4-Chlorophenyl)-4,4-dimethyl-2-phenylpentan-1-one (**3l′a**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (46.2 mg, 77%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, J = 8.6 Hz, 1.56H), 7.85 (d, J = 8.6 Hz, 0.49H), 7.44−7.39 (m, 1H), 7.34−7.27 (m, 2H), 7.21−7.07 (m, 4H), 4.62 (q, 0.76H), 4.56 (q, 0.24H), 2.56−2.47 (m, 1H), 1.51−1.45 (m, 1H), 0.79 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 198.6, 197.6, 139.7, 138.5, 138.2, 135.7, 134.2, 131.9, 131.6, 128.9, 128.5, 127.9, 127.8, 127.6, 127.5, 127.0, 125.9, 48.7, 47.8, 46.5, 46.4, 30.2, 30.1, 28.8, 28.7. MS (EI): 300, 285, 243.

*2-(4-Bromophenyl)-4,4-dimethyl-1-phenylpentan-1-one (**3ma**) and 1-(4-Bromophenyl)-4,4-dimethyl-2-phenylpentan-1-one (**3m′a**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a white solid (50.2 mg, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 7.5 Hz, 1.52H), 7.77 (d, J = 8.6 Hz, 0.46H), 7.46−7.41 (m, 1.21H), 7.35−7.29 (m, 2.81H), 7.20−7.17 (m, 1H), 7.11 (d, J = 8.4 Hz, 2H), 4.61 (q, 0.76H), 4.55 (q, 0.23H), 2.56−2.47 (m, 1H), 1.51−1.45 (m, 1H), 0.79 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 199.6, 198.9, 140.8, 140.1, 136.7, 135.7, 133.0, 132.0, 131.9, 130.1, 129.9, 129.0, 128.7, 128.6, 128.1, 127.9, 126.9, 120.8, 49.8, 49.0, 47.5, 47.4, 31.3, 31.2, 29.84, 29.81. MS (EI): 344, 329, 287.

*2,4,4-Trimethyl-1,2-diphenylpentan-1-one (**3na**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (44.8 mg, 80%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.33 (m, 7H), 7.31−7.27 (m, 1H), 7.23−7.19 (m, 2H), 2.39 (d, J = 14.6 Hz, 1H), 2.18 (d, J = 14.6 Hz, 1H), 1.75 (s, 3H), 0.85 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 204.8, 144.9, 137.8, 131.1, 129.4, 128.8, 127.8, 126.8, 126.6, 55.1, 51.3, 32.0, 31.8, 25.7. HRMS (ESI) m/z calcd for $C_{20}H_{25}O$ $(M + H)^+$ 281.1900, found 281.1899.

*4-Methyl-1,2-diphenylpentan-1-one (**3ab**).*[14] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (36.8 mg, 73%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 7.4 Hz, 2H), 7.51−7.47 (m, 2H), 7.42−7.38 (m, 2H), 7.34−7.27 (m, 4H), 7.21−7.18 (m, 2H), 4.69 (t, J = 7.2 Hz, 1H), 2.12−2.05 (m, 1H), 1.78−1.71 (m, 1H), 1.55−1.45 (m, 1H), 0.95 (d, J = 6.4 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 200.1, 139.9, 137.0, 132.8, 128.9, 128.7, 128.6, 128.3, 126.9, 51.3, 43.1, 25.8, 22.9, 22.5.

*4-Methyl-1,2-diphenylhexan-1-one (**3ac**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (39.9 mg, 75%). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 7.4 Hz, 2H), 7.51−7.47 (m, 1H), 7.42−7.38 (m, 2H), 7.34−7.27 (m, 4H), 7.22−7.17 (m, 1H), 4.74−4.67 (m, 1H), 2.34−2.27 (m, 0.52H), 1.94 (t, J = 6.9 Hz, 1H), 1.61−1.54 (m, 0.58H), 1.50−1.40 (m, 0.58H), 1.38−1.29 (m, 1H), 1.27−1.12 (m, 1.57H), 0.93 (d, J = 6.4 Hz, 1.47H), 0.88 (d, J = 7.2 Hz, 3H), 0.81 (t, J = 7.3 Hz, 1.61H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 200.2, 200.0, 140.2, 139.7, 137.1, 136.9, 132.8, 132.7, 128.9, 128.8, 128.63, 128.61, 128.54, 128.53, 128.4, 128.2, 126.9, 126.8, 51.2, 51.0, 41.4, 40.6, 32.3, 31.9, 29.7, 29.5, 19.4, 19.1, 11.1. HRMS (ESI) m/z calcd for $C_{19}H_{23}O$ $(M + H)^+$ 267.1743, found 267.1744.

*4-Methyl-1,2-diphenylheptan-1-one (**3ad**).*[15] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (40.3 mg, 72%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.7 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.40 (m, 2H), 7.35−7.28 (m, 4H), 7.23−7.19 (m, 1H), 4.76−4.69 (m, 1H), 2.35−2.28 (m, 0.51H), 1.95 (t, J = 6.8 Hz, 1H), 1.62−1.55 (m, 0.57H), 1.44−1.14 (m, 5H), 0.96−0.94 (m, 1.58H), 0.92−0.88 (m, 3H), 0.83−0.79 (m, 1.48H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 200.3, 200.1, 140.2, 139.7, 137.1, 136.9, 132.83, 132.82, 128.9, 128.8, 128.65, 128.63, 128.56, 128.55, 128.4, 128.2, 126.94, 126.91, 51.2, 51.0, 41.8, 40.9, 39.6, 39.3, 30.5, 30.1, 19.9, 19.8, 19.6, 14.4, 14.3.

*4-Ethyl-1,2-diphenylhexan-1-one (**3ae**).*[15] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (38.6 mg, 69%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.7 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.40 (m, 2H), 7.36−7.28 (m, 4H), 7.23−7.19 (m, 1H), 4.71 (t, J = 7.2 Hz, 1H), 2.21−2.13 (m, 1H), 1.82−1.75 (m, 1H), 1.45−1.28 (m, 4H), 1.21−1.15 (m, 1H), 0.89 (d, J = 7.3 Hz, 3H), 0.81 (d, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 200.2, 140.0, 137.1, 132.8, 128.9, 128.6, 128.5, 128.3, 126.9, 51.1, 37.8, 37.5, 25.3, 25.2, 10.52, 10.50.

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*4-Ethyl-1,2-diphenyloctan-1-one (**3af**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (43.1 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 7.8 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.40 (m, 2H), 7.35−7.28 (m, 4H), 7.23−7.19 (m, 1H), 4.71 (d, J = 7.2 Hz, 1H), 2.21−2.12 (m, 1H), 1.83 (m, 1H), 1.43−1.20 (m, 9H), 0.92−0.90 (m, 1.42H), 0.89−0.87 (m, 1.57H), 0.86−0.85 (m, 1.45H), 0.82−0.79 (m, 1.56H). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 200.2, 200.1, 140.1, 139.9, 137.1, 137.0, 132.8, 128.8, 128.6, 128.5, 128.3, 128.2, 126.9, 51.1, 51.0, 38.0, 37.9, 36.4, 36.3, 32.7, 28.5, 28.4, 25.8, 23.1, 23.0, 14.2, 14.1, 10.5, 10.4. HRMS (ESI) m/z calcd for $C_{22}H_{29}O$ (M + H)$^+$ 309.2213, found 309.2216.

*3-Cyclohexyl-1,2-diphenylpropan-1-one (**3ag**).*[10] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 50/1) gave a colorless liquid (46.7 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, J = 7.2 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.40 (m, 2H), 7.35−7.28 (m, 4H), 7.24−7.19 (m, 1H), 4.74 (t, J = 7.3 Hz, 1H), 2.18−2.10 (m, 1H), 1.87−1.83 (m, 1H), 1.76−1.63 (m, 5H), 1.24−1.08 (m, 4H), 1.01−0.89 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 200.1, 140.0, 136.9, 132.8, 128.9, 128.7, 128.6, 128.3, 126.9, 50.5, 41.7, 35.3, 33.6, 33.3, 26.5, 26.2, 26.1

*4-Cyclopropyl-1,2-diphenylbutane-1,4-dione (**3ah**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (47.3 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 7.8 Hz, 2H), 7.48−7.44 (m, 1H), 7.38−7.35 (m, 2H), 7.29−7.28 (m, 4H), 7.21−7.19 (m, 1H), 5.13 (dd, J = 10.0, 3.6 Hz, 1H), 3.76 (dd, J = 18.0, 10.1 Hz, 1H), 2.92 (dd, J = 18.0, 3.6 Hz, 1H), 1.99−1.93 (m, 1H), 1.06−0.98 (m, 2H), 0.93−0.82 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 208.9, 198.9, 138.6, 136.4, 132.9, 129.1, 128.9, 128.5, 128.2, 127.3, 48.5, 47.8, 20.7, 10.9, 10.8. HRMS (ESI) m/z calcd for $C_{19}H_{19}O_2$ (M + H)$^+$ 279.1380, found 279.1381.

*4-Cyclopropyl-1,2-di-p-tolylbutane-1,4-dione (**3bh**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (52.6 mg, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 8.2 Hz, 2H), 7.18−7.15 (m, 4H), 7.08 (d, J = 7.9 Hz, 2H), 5.08 (dd, J = 10.0, 4.0 Hz, 1H), 3.72 (dd, J = 17.9, 9.9 Hz, 1H), 2.88 (dd, J = 17.9, 4.0 Hz, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 1.98−1.92 (m, 1H), 1.05−0.98 (m, 2H), 0.92−0.81 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 209.0, 198.6, 143.5, 136.9, 135.8, 133.9, 129.8, 129.2, 129.0, 127.9, 47.9, 47.7, 21.6, 21.0, 20.7, 10.8, 10.7. HRMS (ESI) m/z calcd for $C_{21}H_{23}O_2$ (M + H)$^+$ 307.1693, found 307.1696.

*4-Cyclopropyl-1,2-bis(4-fluorophenyl)butane-1,4-dione (**3dh**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (50.2 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99−7.96 (m, 2H), 7.26−7.22 (m, 2H), 7.07−7.02 (m, 2H), 6.99−6.95 (m, 2H), 5.06 (dd, J = 9.9, 4.0 Hz, 1H), 3.72 (dd, J = 18.0, 9.9 Hz, 1H), 2.91 (dd, J = 18.0, 4.0 Hz, 1H), 1.97−1.93 (m, 1H), 1.05−0.97 (m, 2H), 0.94−0.83 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 208.7, 197.3, 165.6 (d, J_{C-F} = 253.3 Hz), 162.0 (d, J_{C-F} = 245.0 Hz), 134.0 (d, J_{C-F} = 3.2 Hz), 132.6 (d, J_{C-F} = 3.0 Hz), 131.4 (d, J_{C-F} = 9.3 Hz), 129.6 (d, J_{C-F} = 8.1 Hz), 134.0 (d, J_{C-F} = 3.2 Hz), 116.1 (d, J_{C-F} = 21.3 Hz), 115.6 (d, J_{C-F} = 21.8 Hz), 47.8, 47.5, 20.6, 10.9, 10.8. ^{19}F NMR (470 MHz, $CDCl_3$): δ −105.2, −114.8. HRMS (ESI) m/z calcd for $C_{19}H_{17}F_2O_2$ (M + H)$^+$ 315.1191, found 315.1194.

*1,2-Bis(4-chlorophenyl)-4-cyclopropylbutane-1,4-dione (**3eh**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (53.9 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.28−7.25 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 5.05 (dd, J = 10.0, 4.0 Hz, 1H), 3.74 (dd, J = 18.1, 10.0 Hz, 1H), 2.93 (dd, J = 18.0, 4.0 Hz, 1H), 2.00−1.94 (m, 1H), 1.08−0.99 (m, 2H), 0.96−0.86 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 208.6, 197.5, 139.5, 136.6, 134.5, 133.4, 130.2, 129.44, 129.41, 128.9, 47.7, 47.6, 20.6, 11.1, 11.0. HRMS (ESI) m/z calcd for $C_{19}H_{17}Cl_2O_2$ (M + H)$^+$ 347.0600, found 347.0602.

*1,2-Bis(4-bromophenyl)-4-cyclopropylbutane-1,4-dione (**3fh**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (70.3 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 5.01 (dd, J = 10.0, 4.0 Hz, 1H), 3.74 (dd, J = 18.0, 10.0 Hz, 1H), 2.93 (dd, J = 18.0, 4.0 Hz, 1H), 1.98−1.92 (m, 1H), 1.03−0.97 (m, 2H), 0.94−0.84 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 208.5, 197.7, 137.4, 134.9, 132.4, 131.9, 130.3, 129.8, 128.3, 121.6, 47.8, 47.6, 20.6, 11.1, 11.0. HRMS (ESI) m/z calcd for $C_{19}H_{17}Br_2O_2$ (M + H)$^+$ 434.9590, found 434.9597.

*1,2,4-Triphenylbutane-1,4-dione (**3ai**).*[16] Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (47.7 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.5 Hz, 2H), 7.59−7.56 (m, 1H), 7.53−7.32 (m, 9H), 7.28−7.24 (m, 1H), 5.36 (dd, J = 10.1, 3.5 Hz, 1H), 4.25 (dd, J = 18.0, 10.1 Hz, 1H), 3.34 (dd, J = 10.1, 3.7, Hz 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.9, 198.1, 138.7, 136.5, 133.3, 132.9, 129.3, 128.9, 128.6, 128.5, 128.3, 128.2, 127.4, 48.7, 43.9.

*1,2-Diphenyl-4-(p-tolyl)butane-1,4-dione (**3aj**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (52.5 mg, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.38 (m, 4H), 7.35−7.31 (m, 2H), 7.28−7.23 (m, 3H), 5.35 (dd, J = 10.1, 3.6 Hz, 1H), 4.22 (dd, J = 17.9, 10.1 Hz, 1H), 3.32 (dd, J = 17.9, 3.6 Hz, 1H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 199.0, 197.7, 144.1, 138.7, 136.5, 134.0, 132.9, 129.3, 129.2, 128.9, 128.5, 128.3, 128.2, 127.4, 48.7, 43.8, 21.7. HRMS (ESI) m/z calcd for $C_{23}H_{21}O_2$ (M + H)$^+$ 329.1536, found 329.1538.

*4-(4-(tert-Butyl)phenyl)-1,2-diphenylbutane-1,4-dione (**3ak**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (57.7 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, J = 8.6 Hz, 2H), 7.97 (d, J = 8.5 Hz, 2H), 7.53−7.49 (m, 3H), 7.45−7.40 (m, 4H), 7.36−7.32 (m, 2H), 7.28−7.24 (m, 1H), 5.39 (dd, J = 10.0, 3.7 Hz, 1H), 4.25 (dd, J = 17.9, 10.0 Hz, 1H), 3.34 (dd, J = 17.9, 3.7 Hz, 1H), 1.37 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 199.0, 197.8, 157.0, 138.8, 136.5, 133.9, 132.9, 129.2, 128.9, 128.5, 128.3, 128.2, 127.4, 125.6, 48.7, 43.8,35.2, 31.1. HRMS (ESI) m/z calcd for $C_{26}H_{27}O_2$ (M + H)$^+$ 371.2006, found 371.2003.

*4-(4-Chlorophenyl)-1,2-diphenylbutane-1,4-dione (**3al**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (50.8 mg, 76%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.6 Hz, 2H), 7.53−7.49 (m, 1H), 7.45−7.31 (m, 8H), 7.28−7.23 (m, 1H), 5.34 (dd, J = 10.1, 3.6 Hz, 1H), 4.20 (dd, J = 18.0, 10.1 Hz, 1H), 3.28 (dd, J = 18.0, 3.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.8, 196.9, 139.7, 138.5, 136.3, 134.8, 133.0, 129.6, 129.3, 128.97, 128.94, 128.6, 128.2, 127.5, 48.8, 43.8. HRMS (ESI) m/z calcd for $C_{22}H_{18}ClO_2$ (M + H)$^+$ 349.0990, found 349.0991.

*4-(4-Bromophenyl)-1,2-diphenylbutane-1,4-dione (**3am**).* Flash column chromatography on silica gel (petroleum ether/ethyl acetate 10/1) gave a colorless liquid (55.7 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 8.6 Hz, 2H), 7.86 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H), 7.53−7.49 (m, 1H), 7.44−7.31 (m, 6H), 7.28−7.23 (m, 1H), 5.35 (dd, J = 10.1, 3.6 Hz, 1H), 4.19 (dd, J = 18.0, 10.1 Hz, 1H), 3.27 (dd, J = 10.1, 3.6 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 198.8, 197.1, 138.5, 136.3, 135.2, 133.0, 131.9, 129.7, 129.3, 128.9, 128.6, 128.5, 128.2, 127.5, 48.8, 43.8. HRMS (ESI) m/z calcd for $C_{22}H_{18}BrO_2$ (M + H)$^+$ 393.0485, found 393.0490.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b01255.

Mechanism study; ^{1}H and ^{13}C NMR spectra of compounds **3aa**−**3na**, **3ab**−**3ag**, **3ah**−**3am**; ^{19}F NMR spectra of compounds **3da**, **3ga**, **3ha**, **3ka**, and **3dh** (PDF)

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Notes

The authors declare no competing financial interest.

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