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FULL PAPER

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Oxidative acylation of α,α-diarylallylic alcohols: Synthesis of 1,2,4-triarylbutane-1,4-diones

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A metal-free mediated oxidative acylation of α,α-diarylallylic alcohols with simple aromatic aldehydes for the synthesis of 1,2,4-triphenylbutane-1,4-diones is presented. In the presence of TBPB (*tert*-butyl peroxybenzoate), desired products were obtained in good to excellent yields for 28 examples. This protocol features high regioselectivity, wide functional group tolerance and atom economy.

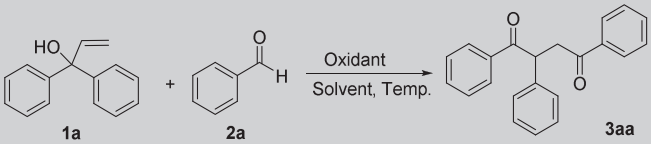
KEYWORDS
α,α-diarylallylic alcohols, 1,4-dione synthesis, oxidative acylation

1 | INTRODUCTION

1,4-Dicarbonyl compounds have attracted considerable attention due to their wide application in organic synthesis especially for natural products and bioactive compounds.[1] They are a type of versatile building blocks for the synthesis of 1,4-diols, as well as five-membered hetereocycles, such as furans, pyrroles, thiophenes and selenophenes.[2] Enormous efforts have been devoted to developing efficient methods for building such a structure of 1,4-dicarbonyl compounds, although each protocol has its limitations.[3]

The traditional synthesis methods were based on a Stetter reaction catalyzed by cyanide or thiazolium salts; however, these can lead to undesired side products.[4] Transition metal-mediated strategies have been developed, including isomerization of alkynediols,[5] difunctionalization of alkenes[6] as well as the reductive coupling of acid chlorides with unsaturated ketones or with cyclopropanols.[7] However, in these cases, the drawbacks include unstable starting materials, reactive intermediates and requirement for special reagents, leading to the weak endurance of substrates. Other approaches include the oxidative homocoupling of ketone enolates and preparation of symmetric 1,4-diketones.[8,9] Sigman and co-workers researched a series of Pd-catalyzed redox-relay reactions between alkenyl alcohols and various aryl coupling partners and prepared ketones and aldehydes with high enantiomeric excess.[10] In this context, many other groups have reported the conversion of substituted allylic alcohols to aldehydes or ketones and multicomponent coupling approaches, including more recent examples from Lei and co-workers,[11] Jiang and co-workers,[12] Kommu and co-workers,[13] Alacid and Nájera,[14] Skrydstrup and co-workers[15] and Pan *et al*.[16] Despite the great successes achieved in this field, some problems exist with these procedures, such as (1) the product will be contaminated with residual metal reagents or organic catalysts used in the reaction, (2) the side reactions of two substrates are difficult to avoid and (3) the use of a toxic reagent, thereby limiting applications, especially in the pharmaceutical industry.

TABLE 1 Optimization of reaction conditions[a]



Entry	Oxidant (equiv.)	Solvent	Temp. (°C)	Yield (%)
1	DTBP (4)[b]	Toluene	110	33
2	TBHP (4)[c]	Toluene	110	83
3	TBHP (4)[d]	Toluene	110	25
4	**TBPB (4)**[e]	Toluene	110	94
5	$K_2S_2O_8$ (4)	Toluene	110	50
6	H_2O_2 (4)	Toluene	110	45
7	O_2	Toluene	110	32
8	TBPB (4)	DCE	110	50
9	TBPB (4)	Xylene	110	59
10	TBPB (4)	*p*-Xylene	110	28
11	TBPB (4)	Chlorobenzene	110	46
12	TBPB (4)	DMF	110	73
13	TBPB (3)	Toluene	110	76
14	TBPB (2)	Toluene	110	59
15	TBPB (4)	Toluene	80	Trace
16	TBPB (4)	Toluene	140	88
17[f]	TBPB (4)	Toluene	110	78

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol) and oxidant in solvent (1 ml), under air, 24 h; isolated yields based on **1a**.

[b]DTBP: di-*tert*-butyl peroxide.

[c]TBHP: *tert*-butyl hydroperoxide (70% in decane).

[d]TBHP: *tert*-butyl hydroperoxide (70% in aqueous solution).

[e]TBPB: *tert*-butyl peroxybenzoate.

[f]Under nitrogen atmosphere.

Therefore, the development of simple, efficient and environmentally benign methods for synthesizing various 1,4-dicarbonyl compounds is appealing.

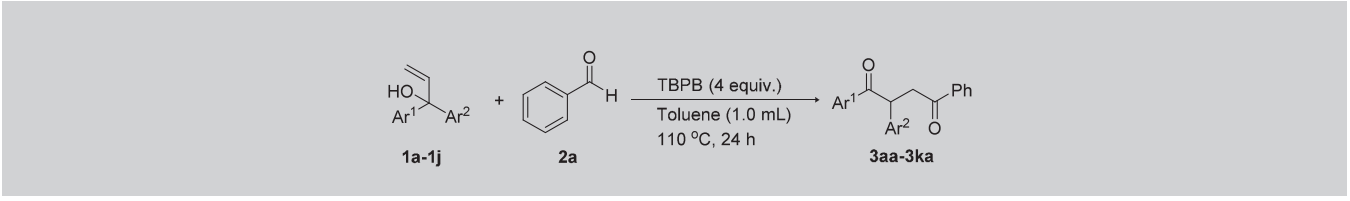
Herein, based on the fact that allyl alcohol is easily isomerized in the reaction, which results in substituent migration rearrangement,[17,18] we report our recent efforts in developing a metal-free mediated oxidative acylation of α,α-diarylallylic alcohols for the synthesis of 1,2,4-triarylbutane-1,4-diones.

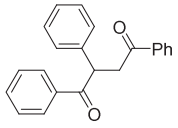
2 | RESULTS AND DISCUSSION

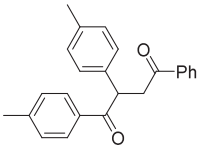
Initially, the reaction of α,α-diphenylallylic alcohol (**1a**) with benzaldehyde (**2a**) was chosen as a model reaction to screen various reaction parameters. The results are summarized in Table 1. Only 33% yield of the desired product **3a** was obtained when di-*tert*-butyl peroxide was used as oxidant and toluene as solvent (Table 1, entry 1). The molecular structure of product **3a** was confirmed from its NMR spectrum. To our delight, an 83% yield of **3a** was obtained in the presence of *tert*-butyl peroxybenzoate (TBPB) in decane (entry 2). However, the reaction using TBHP in water as an oxidant gave a lower yield (25%, entry 3). Surprisingly, an excellent yield of 94% was afforded when TBPB was oxidant and the reaction temperature was 110 °C for 24 h (entry 4). Other oxidants, such as $K_2S_2O_8$, H_2O_2 and O_2, were not found to be very effective in the reaction (entries 5–7). Among the solvents examined (toluene, DCE, xylene, chlorobenzene, DMF), toluene was found to be superior (entries 4, 8–12). Decreasing the loading of TBPB resulted in a significant decrease in the yield (entry 14), while almost no product was obtained at 80 °C (entry 15) when decreasing the reaction temperature. Increasing the reaction temperature, a lower yield of 88% of product **3a** was obtained (entry 16). When the reaction was carried out under nitrogen atmosphere, the desired product **3a** was obtained with a yield of 78% (entry 17), which indicated that a certain amount of oxygen in air could facilitate the reaction. Finally, the optimized reaction conditions were identified as follows: TBPB as the oxidant and toluene as the solvent, at 110 °C in an oil bath under air atmosphere for 24 h.

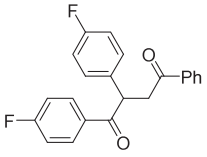
With the optimized reaction conditions in hand (Table 1, entry 4), the scope of α,α-diarylallylic alcohols

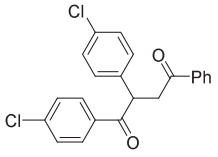
TABLE 2 Substrate scope of α,α-diarylallylic alcohols[a]

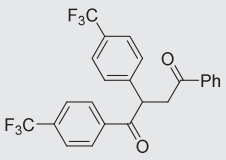


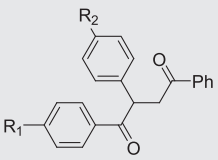

3aa, 94%

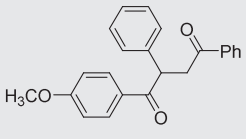

3ba, 70%

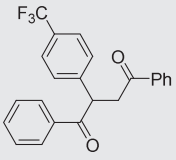

3ca, 35%

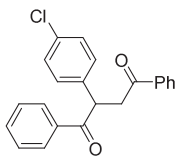

3da, 88%

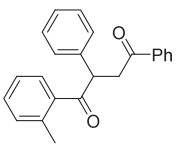

3ea, 75%

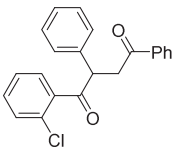

R_1 = Me, R_2 = H, **3fa**
R_1 = H, R_2 = Me, **3fa'**
76% (**3fa:3fa'** = 17:13)[b]


3ga, 97%


3ha, 61%


3ia, 79%

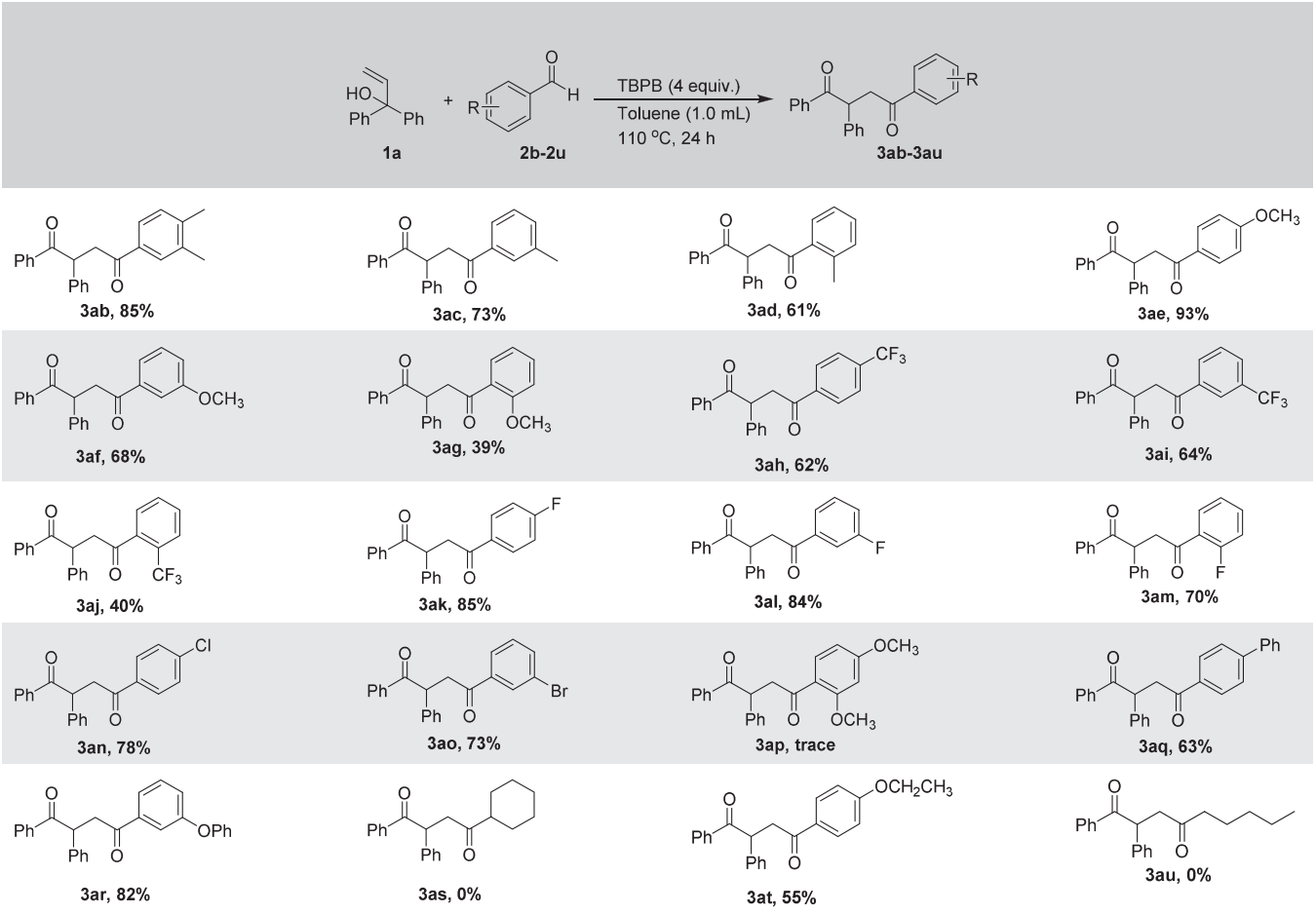

3ja, 76%


3ka, 38%

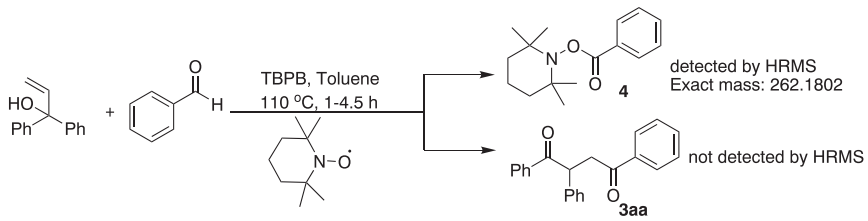
[a]Reaction conditions: **1a–1 k** (0.2 mmol), **2a** (0.3 mmol), TBPB (4 equiv.), in solvent (1 ml), under air, at 120 °C for 24 h; isolated yields based on **1a–1 k**.

[b]Ratio of **3fa** to its isomer was determined by ^{1}H NMR analysis of the isolated product.

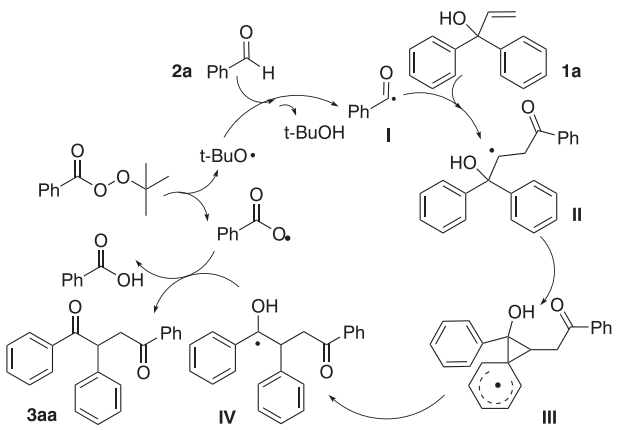
TABLE 3 Substrate scope of aromatic aldehydes[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2b**–**2u** (0.3 mmol), TBPB (4 equiv.), in toluene (1 ml), at 120 °C, under air for 24 h; isolated yields based on **1a**.



SCHEME 1 Experiment for reaction mechanism



SCHEME 2 Plausible reaction mechanism

including symmetric and asymmetric ones was examined in the acylation with benzaldehyde (Table 2). The reaction could proceed well with a series of substituted diarylallylic alcohols, affording the corresponding products **3aa**–**3 ka** in moderate to good yields. For the symmetric α,α-diarylallylic alcohols with electron-donating and electron-withdrawing group in aromatic rings, such as methyl, chloro, fluoro and trifluoromethyl, the reaction proceeded smoothly and provided the desired products in yields of 35–94% (**3aa**–**3ea**). When the aromatic rings in asymmetric α,α-diarylallylic alcohols were substituted by groups such as methyl, methoxy and chloro, the products were isolated in yields of 38–97% (**3fa**–**3 ka**). Moreover, the transformation was obviously

affected by electronic effect and steric hindrance. The major products were obtained by a priority migration of the aromatic ring which had lower electron cloud density (**3ga** and **3 ha**). With asymmetric α,α-diarylallylic alcohols bearing an electron-withdrawing group on the *ortho* position of the aromatic ring, only steric hindrance control product was afforded in a yield of 38% (**3 ka**) by a priority migration of the aromatic ring which had weak space resistance.

Encouraged by the results obtained with α,α-diarylallylic alcohols, this reaction system was applied to expand the substrates to various aromatic aldehydes (Table 3). It was found that various aromatic aldehydes could be employed as suitable substrates under these reaction conditions, giving the corresponding products **3ab**–**3ao**, **3aq**–**3ar** and **3at** in moderate to excellent yields for most cases. The results are summarized in Table 3. The reaction efficiency was not significantly affected by electronic variation of substrates. For instance, aromatic aldehydes with electron-donating and weakly electron-withdrawing substituents, such as Me, MeO, F, Cl, Br, CF_3, Ph and PhO at the *para* position or *meta* position, gave the desired products in good to excellent yields. The steric effect played an important role in the reaction; for example, benzaldehydes bearing an *ortho*-methyl or other groups such as Me, MeO, F and CF_3 led to an evident decrease of reaction yields (**3ad**, **3ag**, **3aj**, **3 am**, **3ap**). While this reaction was not applied to aliphatic aldehydes. When caproaldehyde and cyclohexanecarboxaldehyde were used as the substrates, the corresponding products were not obtained. It is worth noting that all the halogen (F, Cl, Br) atoms substituted on the aromatic ring provided the products in good yields of 70–85% (**3ak**–**3ao**). These results showed that halogen groups especially Cl and Br commonly used in organic synthesis were compatible with the present conditions, which made this reaction particularly attractive for increasing the molecular complexity by various chemical transformations.

To gain further insight into the possible radical mechanism, a control experiment with substrates **1a** and **2a** in the presence of 2 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO) was carried out (Scheme 1). As expected, the formation of the desired product **3aa** was suppressed, and only the TEMPO–benzoyl adduct **4** was observed (determined using high-resolution MS (HRMS) analysis). This result indicated that TBPB-mediated reaction of **1a** with benzaldehyde might be a radical-initiated route to the target product.

A reaction mechanism was proposed, as outlined in Scheme 2, based on the results obtained and previous literature.[18g, 19] First, *tert*-butoxyl radical and benzoate radical were generated by the homolysis of TBPB at high temperature. Benzaldehyde (**2a**) was converted into an acyl radical **I** with the aid of *tert*-butoxyl radical. Then, the radical intermediate **II** was formed by the addition of allylic alcohol **1a** with acyl radical. Subsequently, an intramolecular radical addition of the carbon radical with benzene ring in intermediate **II** occurred to generate the spiro[2,5] octadienyl radical **III**, followed by the migration of the electron-deficient aryl group preferentially releasing **IV**. It is notable that *ortho*-substituted benzene rings are reluctant to migrate owing to a sterically congested radical **III** which is difficult to form, and this is consistent with the experimental results. Finally, the desired product **3aa** was generated by further oxidation or charge migration eliminating the hydrogen radical. The benzoate radical received a hydrogen radical to give a benzoic acid.

3 | CONCLUSIONS

In summary, we have developed a novel acylation of α,α-diarylallylic alcohols via an addition with aryl aldehyde and an aryl rearrangement involving new C (Ar)— C (sp^3) and C (sp^3)— C (CO) bond formation. A variety of 1,2,4-triphenylbutane-1,4-diones were obtained in moderate to excellent yields. In addition, chemoselective migration of the two different aryl groups was observed in the reaction. Currently, experiments towards enlarging the scope of the system to the synthesis of other 1,4-dione compounds and further mechanistic studies are underway in our laboratory.

4 | EXPERIMENTAL

^{1}H NMR spectra were recorded with a Bruker DPX-400 (400 MHz) spectrometer with deuterated chloroform as solutions. The chemical shifts are reported in ppm relative to tetramethylsilane. ^{13}C NMR spectra were recorded at 100 MHz with a Bruker DPX-400. The chemical shifts are reported relative to residual $CHCl_3$ (77.00 ppm). The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants *J* are reported in hertz (Hz). HRMS was conducted using an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionization (ESI). Dichloromethane, ethyl acetate and hexane (analytical grade) were used for column chromatography without purification. The other chemicals were obtained from commercial sources and used as received unless otherwise noted.

4.1 | General Procedure for Preparation of α,α-Diarylallylic Alcohols[20]

A 50 ml dry round-bottom flask was equipped with a magnetic stir bar and charged with diarylmethyl ketone (42 mg, 5 mmol) and tetrahydrofuran (50 ml), which was stirred for 10 min at 0 °C under nitrogen atmosphere. Then, to the reaction system was added ethylmagnesium bromide (6 mmol, 1.2 equiv.). After 20 min, the system was heated to room temperature. Subsequently, the resulting solution was washed with saturated ammonium chloride solution and was extracted with ethyl acetate. Combined organic layers were treated with saturated NaCl aqueous solution, and then the organic layers were dried over Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using hexane–EtOAc as eluent to afford the corresponding desired product.

4.2 | General Procedure for Reaction of α,α-Diarylallylic Alcohols with Arylaldehyde

A 25 ml Schlenk flask was equipped with a magnetic stir bar and charged with α,α-diarylallylic alcohol (0.2 mmol), arylaldehyde **2a** (0.3 mmol, 1.5 equiv.), TBPB (0.8 mmol, 4 equiv.) and toluene (1.0 ml). The resulting mixture was heated at 110 °C for 24 h, and cooled to room temperature. The resulting solution was directly filtered through a pad of silica gel using a sintered glass funnel which then was washed using EtOAc. The resulting solution was concentrated under reduced pressure. The residue was purified by chromatography on silica gel (EtOAc–petroleum ether 1/10–1/15, *v*/v) to give the desired product.

4.2.1 | 1,2,4-Triphenylbutane-1,4-dione (3aa)

Yellow liquid (yield: 94%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.34 (d, J = 7.4 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.49–7.35 (m, 7H), 7.30 (t, J = 7.4, 2H), 7.23–7.20 (m, 1H), 5.33 (dd, J = 10.0, 3.4 Hz, 1H), 4.21 (dd, J = 18.0, 10.1 Hz, 1H), 4.21 (dd, J = 18.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 198.1, 138.7, 136.5, 133.3, 132.9, 129.2, 128.9, 128.6, 128.5, 128.3, 128.2, 127.4, 48.7, 43.9. HRMS (ESI+): calcd for $C_{22}H_{18}O_2$ $[M + H]^+$: 315.1380, found 315.1383.

4.2.2 | 4-Phenyl-1,2-di-p-tolylbutane-1,4-dione (3ba)

Yellow liquid (yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.97 (d, J = 7.4 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 5.27 (dd, J = 9.8, 3.5 Hz, 1H), 4.18 (dd, J = 18.0, 10.0 Hz, 1H), 3.26 (dd, J = 18.0, 3.7 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.6, 198.2, 143.6, 137.0, 136.6, 135.9, 133.9, 128.9, 129.2, 129.1, 128.8, 128.5, 128.2, 128.1, 126.8, 48.2, 43.8, 21.7, 21.1. HRMS (ESI+): calcd for $C_{24}H_{22}O_2$ $[M + H]^+$: 343.1693, found 343.1695.

4.2.3 | 1,2-Bis (4-fluorophenyl)-4-phenylbutane-1,4-dione (3ca)

Yellow liquid (yield: 35%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.04 (dd, J = 8.4, 5.6 Hz, 2H), 7.9 (d, J = 7.4 Hz, 2H), 7.58–7.55 (m, 1H), 7.47–7.43 (m, 2H), 7.33–7.30 (m, 2H), 7.10–7.06 (m, 2H), 7.03–6.98 (m, 2H), 5.26 (dd, J = 9.9, 5.6 Hz, 1H), 4.17 (dd, J = 18.0, 10.1 Hz, 1H), 3.30 (dd, J = 18.0, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 197.9, 197.3, 165.7 (d, J = 254.4 Hz), 162.1 (d, J = 146.7 Hz), 136.3, 134.1 (d, J = 3.4 Hz), 133.5, 132.7 (d, J = 2.7 Hz), 131.6 (d, J = 9.3 Hz), 129.8 (d, J = 8.0 Hz), 128.7, 128.2, 116.2 (d, J = 21.5 Hz),115.7 (d, J = 22.0 Hz), 115.0 (d, J = 21.4 Hz), 47.8, 43.9. ^{19}F NMR (163 MHz, $CDCl_3$, δ, ppm): 15.3. HRMS (ESI+): calcd for $C_{22}H_{16}F_2O_2$ $[M + H]^+$: 351.1191, found 351.1195.

4.2.4 | 1,2-Bis (4-chlorophenyl)-4-phenylbutane-1,4-dione (3da)

Yellow liquid (yield: 88%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.95 (t, J = 7.6 Hz, 4H), 7.63 (t, J = 7.3 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.28 (s, 4H), 5.24 (dd, J = 10.0, 3.7 Hz, 1H), 4.16 (dd, J = 18.1, 10.0 Hz, 1H), 3.30 (dd, J = 18.0, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 197.7, 197.5, 139.6, 136.7, 136.2, 134.6, 133.6, 133.5, 130.3, 129.6, 129.5, 128.9, 128.7, 128.2, 47.9, 43.7. HRMS (ESI+): calcd for $C_{22}H_{16}Cl_2O_2$ $[M + H]^+$: 383.0600, found 383.0605.

4.2.5 | 4-Phenyl-1,2-bis (4-(trifluoromethyl)phenyl)butane-1,4-dione (3ea)

Yellow liquid (yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.30 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.65 (s, 1H), 7.60–7.52 (m, 4H),7.46 (t, J = 7.6 Hz, 3H), 5.39 (dd, J = 10.3, 3.3 Hz, 1H), 4.26 (dd, J = 18.0, 10.3 Hz, 1H), 3.39 (dd, J = 18.0, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 197.5, 197.2, 138.8, 136.7, 135.9, 133.7, 131.9, 131.7, 129.9, 129.7 (dd, J = 7.4, 3.9 Hz), 129.4,

128.7, 128.2, 125.7 (dd, J = 7.5, 3.7 Hz), 124.9 (dd, J = 8.1, 4.3 Hz), 124.7 (dd, J = 7.0, 3.4 Hz), 48.4, 44.0. HRMS (ESI+): calcd for $C_{24}H_{16}F_6O_2$ $[M + H]^+$: 451.1127, found 451.1127.

4.2.6 | 2,4-Diphenyl-1-(p-tolyl)butane-1,4-dione (3fa) and 1,4-diphenyl-2-(p-tolyl) butane-1,4-dione (3fa′)

Yellow liquid (yield: 76%, **3fa**:**3fa′**= 17:13). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.04–7.93 (m, 4H), 7.56–7.52 (m, 1H), 7.50–7.35 (m, 4H), 7.31–7.18 (m, 4H), 7.12–7.10 (m, 1H), 5.33–5.27 (m, 1H), 4.23–4.16 (m, 1H), 3.31–3.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.0, 198.4, 198.2, 198.1, 143.7, 138.9, 137.1, 136.5, 136.4, 135.5, 133.8, 133.2, 132.8, 129.9, 129.2, 129.1, 129.1, 128.9, 128.5, 128.5, 128.2, 128.2, 128.1, 127.3, 48.5, 48.3, 43.9, 43.82, 21.6, 21.0. HRMS (ESI+): calcd for $C_{23}H_{20}O_2$ $[M + H]^+$: 329.1536, found 329.1539.

4.2.7 | 2-(4-Methoxyphenyl)-1,4-diphenylbutane-1,4-dione (3ga)

Yellow liquid (yield: 97%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.25 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.22 (t, J = 7.1 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 5.29 (dd, J = 9.8, 3.6 Hz, 1H), 4.20 (dd, J = 18.0, 10.0 Hz, 1H), 3.82 (s, 3H), 3.27 (dd, J = 18.0, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.2, 197.3, 163.3, 139.2, 136.5, 133.2, 131.3, 129.4, 129.2, 128.6, 128.2, 127.3, 113.7, 55.4, 48.4, 43.8. HRMS (ESI+): calcd for $C_{23}H_{20}O_3$ $[M + H]^+$: 345.1485, found 345.1490.

4.2.8 | 2-(4-(Trifluoromethyl)phenyl)-1,4-diphenylbutane-1,4-dione (3ha)

Yellow liquid (yield: 61%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03–7.96 (m, 4H), 7.57–7.40 (m, 10H), 5.43–5.40 (m, 1H), 4.24–4.17 (m, 1H), 3.36–3.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.4, 197.5, 142.7, 136.3, 136.2, 133.5, 133.3, 129.7 (q, J = 33.0 Hz), 128.9, 128.7, 128.7, 128.2, 126.2 (q, J = 3.6 Hz), 124.0 (q, J = 272.0 Hz), 48.4, 43.7. HRMS (ESI+): calcd for $C_{23}H_{17}F_3O_2$ $[M + H]^+$: 383.1214, found 383.1258.

4.2.9 | 2-(4-Chlorophenyl)-1,4-diphenylbutane-1,4-dione (3ia)

Yellow liquid (yield: 79%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (d, J = 7.4 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.46–7.39 (m, 4H), 7.29 (dd, J = 12.3, 8.5 Hz, 4H), 5.31 (dd, J = 9.8, 3.8 Hz, 1H), 4.17 (dd, J = 18.0, 9.8 Hz, 1H), 3.27 (dd, J = 18.1, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.7, 197.8, 137.1, 136.3, 136.2, 133.4, 133., 129.63, 129.4, 128.9, 128.7(d, J = 1.2 Hz), 128.2, 47.9, 43.7. HRMS (ESI+): calcd for $C_{22}H_{17}ClO_2$ $[M + H]^+$: 349.0990, found 349.0995.

4.2.10 | 2,4-Diphenyl-1-(o-tolyl)butane-1,4-dione (3ja)

Yellow liquid (yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (d, J = 7.5 Hz, 2H), 7.93 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.1 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.30–7.28 (m, 5H), 7.25–7.21 (m, 2H), 7.14 (d, J = 7.4 Hz, 1H), 5.14 (dd, J = 10.5, 3.0 Hz, 1H), 4.27 (dd, J = 18.0, 10.5 Hz, 1H), 3.28 (dd, J = 18.1, 3.1 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 202.7, 198.3, 138.3, 138.3, 137.8, 136.5, 133.3, 131.5, 130.9, 129.1, 128.6, 128.5, 128.4, 128.2, 127.4, 125.5, 51.7, 43.3, 20.7. HRMS (ESI+): calcd for $C_{23}H_{20}O_2$ $[M + H]^+$: 329.1536, found 329.1543.

4.2.11 | 1-(2-Chlorophenyl)-2,4-diphenylbutane-1,4-dione (3ka)

Yellow liquid (yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (d, J = 7.4 Hz, 2H), 7.79 (d, J = 6.2 Hz, 1H), 7.57 (t, J = 7.3 Hz, 1H), 7.48–7.44 (m, 2H), 7.31–7.28 (m, 7H), 7.24–7.22 (m, 1H), 5.16 (dd, J = 9.6, 3.8 Hz, 1H), 4.22 (dd, J = 18.0, 9.7 Hz, 1H), 3.28 (dd, J = 18.1, 3.9 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 200.5, 198.0, 138.5, 136.7, 136.5, 133.4, 131.6, 131.6, 130.6, 129.4, 129.0, 128.8, 128.7, 128.2, 127.7, 126.5, 52.6, 42.6. HRMS (ESI+): calcd for $C_{22}H_{17}ClO_2$ $[M + H]^+$: 349.0990, found 349.0992.

4.2.12 | 4-(3,4-Dimethylphenyl)-1,2-diphenylbutane-1,4-dione (3ab)

Yellow liquid (yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.4 Hz, 2H), 7.75–7.70 (m, 2H), 7.49–7.45 (m, 1H), 7.40–7.35 (m, 4H), 7.32–7.28 (m, 2H), 7.24–7.17 (m, 2H), 5.32 (dd, J = 10.0, 3.5 Hz, 1H), 4.18 (dd, J = 17.9, 10.0 Hz, 1H), 3.29 (dd, J = 17.9, 3.6 Hz, 1H), 2.28 (d, J = 4.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.1, 197.9, 142.8, 138.8, 136.9, 136.6, 134.4, 132.9, 129.8, 129.4, 129.1, 128.9, 128.5, 128.3, 127.3, 125.9, 48.7, 43.9, 20., 19.8. HRMS (ESI+): calcd for $C_{24}H_{22}O_2$ $[M + H]^+$: 343.1693, found 343.1698.

4.2.13 | 1,2-Diphenyl-4-(m-tolyl)butane-1,4-dione (3ac)

Yellow liquid (yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 7.7 Hz, 2H), 7.48–7.45 (m, 1H), 7.40–7.28 (m, 8H), 7.23–7.19 (m, 1H), 5.32 (dd, J = 10.0, 3.5 Hz, 1H), 4.20 (dd, J = 18.0, 10.1 Hz, 1H), 3.29 (dd, J = 18.0, 3.6 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.0, 198.3, 138.8, 138.4, 136.5, 134.0, 132.9, 129.2, 128.9, 128.8, 128.5, 128.5, 128.3, 127.4, 125.4, 48.8, 43.9, 21.4. HRMS (ESI+): calcd for $C_{23}H_{20}O_2$ $[M + H]^+$: 329.1536, found 329.1538.

4.2.14 | 1,2-Diphenyl-4-(o-tolyl)butane-1,4-dione (3ad)

Yellow liquid (yield: 61%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.02 (d, J = 7.4 Hz, 2H), 7.75 (d, J = 7.6 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 7.40–7.36 (m, 2H), 7.34–7.27 (m, 5H), 7.25–7.18 (m, 3H), 5.32 (dd, J = 10.1, 3.7 Hz, 1H), 4.17 (dd, J = 17.9, 10.1 Hz, 1H), 3.25 (dd, J = 17.9, 3.8 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 202.0, 198.9, 138.7, 138.3, 137.4, 136.5, 132.9, 131.9, 131.5, 129.2, 128.9, 128.8, 128.5, 128.3, 127.4, 125.7, 49.2, 46.5, 21.3. HRMS (ESI+): calcd for $C_{23}H_{20}O_2$ $[M + H]^+$: 329.1536, found 329.1539.

4.2.15 | 4-(4-Methoxyphenyl)-1,2-diphenylbutane-1,4-dione (3ae)

Yellow liquid (yield: 93%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.49–7.45 (m, 1H), 7.40–7.35 (m, 4H), 7.32–7.28 (m, 2H), 7.23–7.20 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 5.32 (dd, J = 10.1, 3.6 Hz, 1H), 4.17 (dd, J = 17.9, 10.1 Hz, 1H), 3.84 (s, 3H), 3.26 (dd, J = 17.8, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.1, 196.6, 163.6, 138.8, 136.6, 132.9, 130.5, 129.6, 129.2, 128.9, 128.5, 128.3, 127.3, 113.7, 55.5, 48.7, 43.6. HRMS (ESI+): calcd for $C_{23}H_{20}O_3$ $[M + H]^+$: 345.1485, found 345.1490.

4.2.16 | 4-(3-Methoxyphenyl)-1,2-diphenylbutane-1,4-dione (3af)

Yellow liquid (yield: 68%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.3 Hz, 2H), 7.57 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.7 Hz, 2H), 7.41–7.34 (m, 5H), 7.32–7.28 (m, 2H), 7.24–7.20 (m, 1H), 7.11–7.08 (m, 1H), 5.31 (dd, J = 10.0, 3.4 Hz, 1H), 4.19 (dd, J = 18.0, 10.1 Hz, 1H), 3.81 (s, 3H), 3.25 (dd, J = 18.1, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 197.9, 159.8, 138.6, 137.8, 136.5, 132.9, 129.6, 129.2, 128.9, 128.5, 128.3, 127.4, 120.9, 120.0, 112.1, 55.4, 48.6, 44.1. HRMS (ESI+): calcd for $C_{23}H_{20}O_3$ $[M + H]^+$: 345.1485, found 345.1486.

4.2.17 | 4-(2-Methoxyphenyl)-1,2-diphenylbutane-1,4-dione (3ag)

Yellow liquid (yield: 39%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.3 Hz, 2H), 7.35 (dd, J = 7.7, 1.3 Hz, 1H), 7.50–7.28 (m, 8H), 7.23–7.20 (m, 1H), 7.00–6.94 (m, 2H), 5.31 (dd, J = 10.2, 3.7 Hz, 1H), 4.16 (dd, J = 18.6, 10.2 Hz, 1H), 3.87 (s, 3H), 3.25 (dd, J = 18.7, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.7, 199.3, 159.0, 138.9, 136.7, 133.8, 132.7, 130.6, 129.1, 128.9, 128.5, 128.4, 127.4, 127.1, 120.6, 111.6, 55.5, 49.1, 48.9. HRMS (ESI+): calcd for $C_{23}H_{20}O_2$ $[M + H]^+$: 345.1485, found 345.1489.

4.2.18 | 1,2-Diphenyl-4-(4-(trifluoromethyl)phenyl)butane-1,4-dione (3ah)

Yellow liquid (yield: 62%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.08 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.41–7.30 (m, 6H), 7.25–7.22 (m, 1H), 5.33 (dd, J = 10.0, 3.5 Hz, 1H), 4.21 (dd, J = 18.1, 10.1 Hz, 1H), 3.28 (dd, J = 18.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.7, 197.3, 139.1, 138.4, 136.3, 135.0, 134.5 (dd, J = 65.5, 32.7 Hz), 133.0, 129.3, 128.9, 128.6, 128.5, 128.2, 127.5, 125.7 (dd, J = 7.0, 3.3 Hz), 48.9, 44.0. HRMS (ESI+): calcd for $C_{23}H_{17}F_3O_2$ $[M + H]^+$: 328.1253, found 328.1258.

4.2.19 | 1,2-Diphenyl-4-(3-(trifluoromethyl)phenyl)butane-1,4-dione (3ai)

Yellow liquid (yield: 64%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.23 (s, 1H), 8.16 (d, J = 7.7 Hz, 1H), 8.02 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 7.6 Hz, 1H), 7.60–7.56 (m, 1H), 7.51–7.47 (m, 1H), 7.42–7.30 (m, 6H), 7.25–7.22 (m, 1H), 5.34 (dd, J = 10.1, 3.4 Hz, 1H), 4.22 (dd, J = 18.0, 10.2 Hz, 1H), 3.29 (dd, J = 18.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.7, 196.9, 138.4, 136.9, 136.3, 133.1, 131.3, 131.5 (dd, J = 65.9, 33.0 Hz), 129.7 (dd, J = 7.2, 3.6 Hz), 129.3, 128.9, 128.6, 128.2, 127.6, 125.6 (dd, J = 7.7, 3.7 Hz), 122.3, 48.8, 43.9. HRMS (ESI+): calcd for $C_{23}H_{17}F_3O_2$ $[M + H]^+$: 383.1253, found 383.1257.

4.2.20 | 1,2-Diphenyl-4-(2-(trifluoromethyl)phenyl)butane-1,4-dione (3aj)

Yellow liquid (yield: 40%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (d, J = 7.5 Hz, 2H), 7.72–7.69 (m, 2H), 7.65–

7.62 (m, 1H), 7.57–7.53 (m, 1H), 7.50–7.47 (m, 1H), 7.41–7.37 (m, 2H), 7.31–7.28 (m, 4H), 7.23–7.20 (m, 1H), 5.35 (dd, J = 10.1, 3.6 Hz, 1H), 4.10 (dd, J = 18.4, 10.2 Hz, 1H), 3.12 (dd, J = 18.4, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 202.4, 198.7, 138.2, 136.2, 133.1, 131.9, 130.2, 129.3, 129.0, 128.5, 128.2, 127.6, 127.5, 126.6 (dd, J = 10.0, 5.0 Hz), 49.1, 47.7. HRMS (ESI+): calcd for $C_{23}H_{17}F_3O_2$ $[M + H]^+$: 383.1253, found 383.1256.

4.2.21 | 4-(4-Fluorophenyl)-1,2-diphenylbutane-1,4-dione (3ak)

Yellow liquid (yield: 85%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03–7.98 (m, 4H), 7.47 (t, J = 7.29 Hz, 1H), 7.40–7.36 (m, 3H), 7.34–7.28 (m, 3H), 7.24–7.20 (m, 1H), 7.10 (t, J = 8.5 Hz, 2H), 5.31 (dd, J = 10.1, 3.5 Hz, 1H), 4.18 (dd, J = 17.9, 10.2 Hz, 1H), 3.25 (dd, J = 17.9, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 196.5, 165.9 (d, J = 255 Hz), 138.6, 136.4, 132.9, 130.8 (d, J = 9.4 Hz), 129.3, 128.9, 128.5, 128.2, 128.2, 127.4, 126.9, 115.7 (d, J = 21.9 Hz), 48.8, 43.8. HRMS (ESI+): calcd for $C_{22}H_{17}FO_2$ $[M + H]^+$: 333.1285, found 333.1290.

4.2.22 | 4-(3-Fluorophenyl)-1,2-diphenylbutane-1,4-dione (3al)

Yellow liquid (yield: 84%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.02 (d, J = 7.5 Hz, 2H), 7.76 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 9.1 Hz, 1H), 7.50–7.46 (m, 1H), 7.42–7.29 (m, 7H), 7.24–7.21 (m, 2H), 5.31 (dd, J = 10.1, 3.4 Hz, 1H), 4.18 (dd, J = 18.0, 10.1 Hz, 1H), 3.25 (dd, J = 18.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.75, 196.91, 162.85 (d, J = 247.7 Hz), 138.57 (d, J = 6.2 Hz), 138.5, 136.4, 133.0, 130.3 (d, J = 7.6 Hz), 129.3, 128.9, 128.6, 128.2, 127.5, 123.9 (d, J = 3.0 Hz), 120.29 (d, J = 21.5 Hz), 114.9 (d, J = 22.4 Hz), 48.8, 43.9. HRMS (ESI+): calcd for $C_{22}H_{17}FO_2$ $[M + H]^+$: 333.1285, found 333.1288.

4.2.23 | 4-(2-Fluorophenyl)-1,2-diphenylbutane-1,4-dione (3am)

Yellow liquid (yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.4 Hz, 2H), 7.88–7.84 (m, 1H), 7.54–7.46 (m, 2H), 7.42–7.38 (m, 2H), 7.36–7.28 (m, 4H), 7.24–7.18 (m, 2H), 7.15–7.10 (m, 1H), 5.53–5.29 (m, 1H), 4.23–4.15 (m, 1H), 3.37–3.31 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 196.3 (d, J = 4.1 Hz), 162.3 (d, J = 4.1 Hz), 138.5, 136.5, 134.8 (d, J = 9.0 Hz), 132.9, 130.8 (d, J = 2.3 Hz), 129.2, 128.9, 128.5, 128.3, 127.3, 124.4 (d, J = 3.4 Hz), 116.7 (d, J = 23.7 Hz), 48.8 (d, J = 1.8 Hz), 48.5 (d, J = 8.2 Hz). HRMS (ESI+): calcd for $C_{22}H_{17}FO_2$ $[M + H]^+$: 333.1285, found 333.1291.

4.2.24 | 4-(4-Chlorophenyl)-1,2-diphenylbutane-1,4-dione (3an)

Yellow liquid (yield: 78%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.02 (d, J = 7.4 Hz, 2H), 7.91 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.3 Hz, 1H), 7.42–7.38 (m, 4H), 7.36–7.29 (m, 4H), 7.24–7.21 (m, 1H), 5.31 (dd, J = 10.1, 3.4 Hz, 1H), 4.17 (dd, J = 18.0, 10.1 Hz, 1H), 3.25 (dd, J = 17.8, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.8, 196.9, 139.7, 138.5, 136.3, 134.8, 133.0, 129.6, 129.3, 128.9, 128.9, 128.5, 128.2, 127.5, 48.8, 43.8. HRMS (ESI+): calcd for $C_{22}H_{17}ClO_2$ $[M + H]^+$: 349.0990, found 349.0995.

4.2.25 | 4-(3-Bromophenyl)-1,2-diphenylbutane-1,4-dione (3ao)

Yellow liquid (yield: 73%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.10 (s, 1H), 8.02 (d, J = 7.3 Hz, 2H), 7.90 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.51–7.47 (m, 1H), 7.42–7.40 (m, 2H), 7.35–7.29 (m, 5H), 7.25–7.21 (m, 1H), 5.31 (dd, J = 10.0, 3.6 Hz, 1H), 4.16 (dd, J = 18.0, 10.1 Hz, 1H), 3.25 (dd, J = 18.0, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.7, 196.8, 138.4, 138.2, 136.3, 136.1, 133.0, 131.3, 130.2, 129.3, 128.9, 128.6, 128.2, 127.5, 126.7, 122.9, 48.8, 43.9. HRMS (ESI+): calcd for $C_{22}H_{17}BrO_2$ $[M + H]^+$: 393.0485, found 393.0489.

4.2.26 | 4-([1,1′-Biphenyl]-4-yl)-1,2-diphenylbutane-1,4-dione (3aq)

Yellow liquid (yield: 63%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.05 (d, J = 6.8 Hz, 4H), 7.66 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 7.4 Hz, 2H), 7.51–7.37 (m, 8H), 7.33–7.30 (m, 2H), 7.25–7.21 (m, 1H), 5.55 (dd, J = 10.0, 3.4 Hz, 1H), 4.25 (dd, J = 17.9, 3.5 Hz, 1H), 3.33 (dd, J = 18.0, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 197.7, 145.9, 139.9, 138.7, 136.5, 135.2, 132.9, 129.2, 128.9, 128.8, 128.5, 128.3, 127.4, 127.3, 128.3, 48.8, 43.9. HRMS (ESI+): calcd for $C_{28}H_{22}O_2$ $[M + H]^+$: 391.1693, found 391.1699.

4.2.27 | 4-(3-Phenoxyphenyl)-1,2-diphenylbutane-1,4-dione (3ar)

Yellow liquid (yield: 82%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01 (d, J = 7.4 Hz, 2H), 7.69 (d, J = 7.7 Hz, 1H), 7.59 (s, 1H), 7.46–7.43 (m, 1H), 7.39–7.28 (m, 9H), 7.21–7.17 (m, 2H), 7.11–7.07 (m, 1H), 7.98 (d, J = 7.7 Hz, 2H), 5.29 (dd, J = 10.1, 3.4 Hz, 1H), 4.16 (dd, J = 18.1,

10.2 Hz, 1H), 3.27 (dd, J = 18.1, 3.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 198.9, 197.5, 157.8, 156.6, 138.5, 138.2, 136.5, 132.9, 130.0, 129.3, 128.9, 128.57, 128.3, 127.5, 123.9, 123.6, 123.1, 119.2, 117.9, 48.8, 44.1. HRMS (ESI+): calcd for $C_{28}H_{22}O_3$ $[M + H]^+$: 407.1642, found 407.1645.

4.2.28 | 4-(4-Ethoxyphenyl)-1,2-diphenylbutane-1,4-dione (3ac)

Yellow liquid (yield: 55%). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 8.03 (d, J = 7.3 Hz, 2H), 7.94 (d, J = 8.8 Hz, 2H), 7.49–7.46 (m, 1H), 7.40–7.35 (m, 4H), 7.32–7.28 (m, 2H), 7.23–7.20 (m, 1H), 6.90 (d, J = 8.7 Hz, 2H), 5.31 (dd, J = 10.0, 3.5 Hz, 1H), 4.16 (dd, J = 17.8, 10.1 Hz, 1H), 4.07 (dd, J = 13.9, 7.0 Hz, 2H), 3.26 (dd, J = 17.8, 3.6 Hz, 1H), 1.42 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 199.1, 196.6, 163.1, 138.8, 136.6, 132.9, 130.5, 129.4, 129.2, 128.9, 128.5, 128.3, 127.3, 114.2, 63.8, 48.7, 43.6, 14.7. HRMS (ESI+): calcd for $C_{24}H_{22}O_3$ $[M + H]^+$: 359.1642, found 359.1646.

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