Supporting Information

Switchable Aroylation and Diaroylation of Allyl Sulfones with Aldehydes Enabled by Decatungstate Photocatalysis

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Table of Contents

1. General Information ..................................................................................................................................................2
   1.1 Materials and instruments .................................................................................................................................2

2. Experimental procedures ...............................................................................................................................................2
   2.1 Preparation of photocatalyst tetrabutylammonium decatungstate (TBADT) ..............................................2
   2.2 Optimization of reaction conditions ...................................................................................................................2
   2.3 Preparation of starting materials .......................................................................................................................5
   2.4 General experimental procedures for the unsaturated ketones and 1, 5-diketones ..................................7
   2.5 Synthetic applications ........................................................................................................................................7
   2.6 Set of Experiments .............................................................................................................................................8
   2.7 Investigation of the mechanism ........................................................................................................................9
   2.8 Proposed Reaction Mechanisms .....................................................................................................................12

3. Characterization Data for Products ........................................................................................................................13

4. NMR Copies of Products .......................................................................................................................................29

5. Reference ..............................................................................................................................................................82
1. **General Information**

1.1 **Materials and instruments**

All the chemicals were purchased from commercial suppliers, all commercially available reagents were directly used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. All the $^1$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Proton chemical shifts $\delta$ were given in ppm using tetramethylsilane as internal standard. All NMR spectra were recorded in CDCl$_3$ at room temperature (20 ± 3 °C). High-resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system with the ESI technique. The LEDs used are Kessil® PR160L-390 nm lamp.

![Figure S1. Photograph of Photocatalytic reactor used for reactions conducted under irradiation with a Kessil® PR160L-390 nm lamp](image)

2. **Experimental procedures**

2.1 **Preparation of photocatalyst tetrabutylammonium decatungstate (TBADT)**

The photocatalyst was synthesized according to literature report.$^1$ To a 2 L beaker wrapped in aluminum foil for insulation and equipped with a 4” Teflon stir bar were added tetrabutylammonium bromide (4.80 g, 14.9 mmol, 0.49 equiv.) and deionized water (1600 mL). In a separate 4 L beaker wrapped in aluminum foil for insulation and equipped with a 4” Teflon stir bar were added Na$_2$WO$_4$·2H$_2$O (10 g, 30.3 mmol, 1.00 equiv.) and deionized water (1600 mL). Both solutions were rapidly stirred and heated to 90 ºC. When both solutions reached 90 ºC, concentrated HCl was added to each solution until pH stabilized at 2. At this point, the acidified solutions were combined in the 4 L beaker, and the resultant suspension was stirred at 90 ºC for an additional 30 minutes. The reaction mixture was cooled to room temperature, then filtered through a pad of silica gel. The solids were washed with water and left to dry under vacuum. When the silica-supported solids were dry, the receiving flask was exchanged, and the pad was washed with 3 x 200 mL dichloromethane. The filtrate was collected and solvent was removed. The residue was thoroughly dried under vacuum to afford TBADT. Isolated as pale yellow crystals (82% yield). UV-Vis and CV characterization is consistent with literature data.$^1$

2.2 **Optimization of reaction conditions**
Table S1. Optimization of reaction conditions of 3p

![Chemical structure of reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBADT (3 mol %)</td>
<td>Acetone</td>
<td>69</td>
</tr>
<tr>
<td>2[^b]</td>
<td>TBADT (3 mol %)</td>
<td>Acetone</td>
<td>40</td>
</tr>
<tr>
<td>3[^c]</td>
<td>TBADT (3 mol %)</td>
<td>Acetone</td>
<td>55</td>
</tr>
<tr>
<td>4[^d]</td>
<td>TBADT (3 mol %)</td>
<td>Acetone</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>TBADT (3 mol %)</td>
<td>MeCN</td>
<td>34</td>
</tr>
<tr>
<td>6</td>
<td>TBADT (3 mol %)</td>
<td>DCM</td>
<td>13</td>
</tr>
<tr>
<td>7</td>
<td>TBADT (3 mol %)</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>TBADT (2 mol %)</td>
<td>Acetone</td>
<td>44</td>
</tr>
<tr>
<td>9[^e]</td>
<td>TBADT (4 mol %)</td>
<td>Acetone</td>
<td>76</td>
</tr>
<tr>
<td>10</td>
<td>TBADT (5 mol %)</td>
<td>Acetone</td>
<td>48</td>
</tr>
<tr>
<td>11[^f]</td>
<td>TBADT (4 mol %)</td>
<td>Acetone</td>
<td>38</td>
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<tr>
<td>12[^g]</td>
<td>TBADT (4 mol %)</td>
<td>Acetone</td>
<td>47</td>
</tr>
<tr>
<td>13[^g]</td>
<td>TBADT (4 mol %)</td>
<td>Acetone</td>
<td>63</td>
</tr>
</tbody>
</table>

[^a]: Reaction conditions: 1p (0.2 mmol), 2a (0.6 mmol), TBADT (3 mol %) in solvent (3.0 mL) at room temperature for 6 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N<sub>2</sub> atmosphere. Isolated yields are given.  
[^b]: 2a (0.2 mmol),  
[^c]: 2a (0.4 mmol),  
[^d]: 2a (0.8 mmol),  
[^e]: 10 W,  
[^f]: 20 W,  
[^g]: 30 W.

We began to set up our optimal experimental conditions towards ethyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate using the model reaction of 1p and with 2a in the presence of TBADT under N<sub>2</sub> atmosphere with irradiation of a Kessil® PR160L-390 nm lamp (40 W) at room temperature for 6 h, as summarized in Table S2. Initially, by employing 3 mol% of TBADT as the catalyst, the model reaction was performed smoothly at room temperature in acetone (3 mL), affording the desired product 3p in 69% yield (entry 1). With this intriguing result in hand, the influence of the amount of 2a was examined (entries 1-4). The results showed that 2a (0.6 mmol) was proved to be the best choice. Next, we further investigated other different solvents including acetonitrile, dichloromethane and tetrahydrofuran. Acetone was also proved to be the best one among all the solvents tested. The amount of TBADT was then evaluated. To our delight, the yield of 3p was increased from 69% to 76% as the amount of TBADT increased from 3 mol % to 4 mol %. However, when the model reactions were performed in the different light intensities, yield of 3p has not improved further (entries 11-13). After a wide exploration, the optimal conditions were finally established as follows: 1p (0.2 mmol), 2a (0.6 mmol), TBADT (4 mol %), acetone (3 mL) at room temperature for 6 h under N<sub>2</sub> atmosphere with the irradiation of 40 W 390 nm Kessil lamp.
Table S2. Optimization of reaction conditions of 4a

![Chemical structure](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Base</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBADT (3 mol %)</td>
<td>Na₂CO₃</td>
<td>Acetone</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>TBADT (3 mol %)</td>
<td>NaHCO₃</td>
<td>Acetone</td>
<td>43</td>
</tr>
<tr>
<td>3</td>
<td>TBADT (3 mol %)</td>
<td>K₂CO₃</td>
<td>Acetone</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>TBADT (3 mol %)</td>
<td>KHCO₃</td>
<td>Acetone</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>MeCN</td>
<td>42</td>
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<td>7</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>THF</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>DMF</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>DCM</td>
<td>21</td>
</tr>
<tr>
<td>10</td>
<td>TBADT (2 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>TBADT (4 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>54</td>
</tr>
<tr>
<td>12</td>
<td>TBADT (5 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>48</td>
</tr>
<tr>
<td>13ᵇ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>42</td>
</tr>
<tr>
<td>14ᶜ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>67</td>
</tr>
<tr>
<td>15ᵈ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>72</td>
</tr>
<tr>
<td>16ᶜ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>54</td>
</tr>
<tr>
<td>17ᶠ</td>
<td>TBADT (3 mol%)</td>
<td>---</td>
<td>Acetone</td>
<td>17</td>
</tr>
<tr>
<td>18ᵍ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>N.D.</td>
</tr>
<tr>
<td>19ᵇ</td>
<td>TBADT (3 mol %)</td>
<td>---</td>
<td>Acetone</td>
<td>32</td>
</tr>
</tbody>
</table>

ᵃ Reaction conditions: 1a (1.0 mmol), 2a (0.2 mmol), TBADT (3 mol %) and base (2 equiv) in solvent (3.0 mL) at room temperature for 5 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N₂ atmosphere. Isolated yields are given.ᵇ 1a (0.8 mmol),ᶜ 1a (1.2 mmol),ᵈ 1a (1.4 mmol),ᵉ 1a (1.6 mmol),ᶠ No TBADT,ᵍ No light,ʰ Air.

We initially started our study by using benzaldehyde (1a) and ethyl 2-((phenylsulfonyl)methyl)acrylate (2a) as the model substrates in the presence of various bases under irradiation of a Kessil® PR160L-390 nm lamp (40 W) to investigate the reaction conditions. To our delight, the optimal isolated yield was 63% without base (entry 5). Next, the effects of various solvents and the amount of TBADT on the reaction were investigated (entries 5-12). The results indicated that the target product 4a was obtained in the highest yield in acetone and 3 mol % of TBADT. Finally, the amount of 1a was examined, the results indicated that the yield of 4a could
be raised to 72% when the amount of 1a was increased to 1.4 mmol (entry 15). Additionally, poor reactivity was observed when the model reaction was performed without TBADT or 40 W Kessil® PR160L-390 nm lamp respectively (entries 17-18). Therefore, the optimal reaction conditions were thus established as follows: 1a (1.4 mmol), 2a (0.2 mmol), and TBADT (3 mol %) in acetone (3 mL) at room temperature for 5 h under N₂ atmosphere with the irradiation of 40 W 390 nm Kessil Lamp.

**Table S3.** Chemoselectivity of screening of the substrate ratio of aroylation reaction

![Chemoselectivity of screening of the substrate ratio of aroylation reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Substrate ratio (1p:2a)</th>
<th>Product ratios (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBADT (3 mol %)</td>
<td>1:1</td>
<td>40        25</td>
</tr>
<tr>
<td>2</td>
<td>TBADT (3 mol %)</td>
<td>1:2</td>
<td>55        19</td>
</tr>
<tr>
<td>3</td>
<td>TBADT (3 mol %)</td>
<td>1:3</td>
<td>69        13</td>
</tr>
<tr>
<td>4</td>
<td>TBADT (3 mol %)</td>
<td>1:4</td>
<td>55        10</td>
</tr>
<tr>
<td>5ᵇ</td>
<td>TBADT (4 mol %)</td>
<td>1:3</td>
<td>76        11</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: 1p (0.2 mmol), TBADT (3 mol %) in acetone (3.0 mL) at room temperature for 6 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N₂ atmosphere. Isolated yields are given. ᵇ TBADT (4 mol %).

**Table S4.** Chemoselectivity of screening of the substrate ratio of diaroylation reaction

![Chemoselectivity of screening of the substrate ratio of diaroylation reaction](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>PC</th>
<th>Substrate ratio (1a:2a)</th>
<th>Product ratios (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TBADT (3 mol %)</td>
<td>4:1</td>
<td>trace    42</td>
</tr>
<tr>
<td>2</td>
<td>TBADT (3 mol %)</td>
<td>5:1</td>
<td>trace    63</td>
</tr>
<tr>
<td>3</td>
<td>TBADT (3 mol %)</td>
<td>6:1</td>
<td>trace    67</td>
</tr>
<tr>
<td>4</td>
<td>TBADT (3 mol %)</td>
<td>7:1</td>
<td>trace    72</td>
</tr>
<tr>
<td>5</td>
<td>TBADT (3 mol %)</td>
<td>8:1</td>
<td>trace    54</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: 2a (0.2 mmol), TBADT (3 mol %) in acetone (3.0 mL) at room temperature for 5 h under the irradiation of a Kessil® PR160L-390 nm lamp (40 W) in the N₂ atmosphere. Isolated yields are given.
2.3 Preparation of starting materials

Preparation of 2a and 2s

\[
\text{COOR} \quad \text{ArSO}_2\text{Na} \quad \text{MeOH, 65 °C, 2h} \quad \text{COOR} \quad \text{SO}_2\text{Ar}
\]

Scheme S1. General experimental procedures for substrates 2a and 2s

2a and 2s were synthesized according to literature report,\(^2\) to a solution of alkylbromide (1.0 equiv) in dry methanol was added ArSO\(_2\)Na (1.5 equiv). After 2 h of reflux, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in EtOAc and the mixture was washed with water, brine, dried with Na\(_2\)SO\(_4\), filtered and the filtrate was evaporated and purified by column chromatography to afford 2a and 2s.

Preparation of 2t\(^2\)

\[
\text{COOBn} \quad \text{H}_2\text{C}=\text{CHO, DABCO, dioxane/H}_2\text{O} = 1:1 \quad \text{COOBn} \quad \text{PhSO}_2\text{Na} \quad \text{MeOH, 65 °C, 2h} \quad \text{COOBn} \quad \text{SO}_2\text{Ph}
\]

Scheme S2. General experimental procedures for substrate 2t

Step 1. According to a reported literature procedure,\(^2\) to a solution of paraformaldehyde (1.3 equiv) and benzyl acrylate (1.0 equiv) in dioxane-water (1:1, v/v) was added DABCO (1.3 equiv) and the reaction progress was monitored by TLC. Upon completion, the reaction mixture was extracted with EtOAc (× 3) and the combined organic layers were washed with water (x 4) and brine, dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford S-1.

Step 2. To a solution of S-1 was added phosphorus (III) bromide (0.33 equiv) in dry THF (20 mL) at -10 °C under a nitrogen atmosphere. The temperature was allowed to rise to 20 °C and stirring was continued for 3 h. Water (50 mL) was then added and the mixture was extracted with petroleum ether (× 3). The combined organic phase was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give S-2.

Step 3. 2t was finally prepared by experimental procedures for substrate 2a from S-2.

Preparation of 2u-2w\(^2\)

\[
\text{PhSO}_2\text{Na} + (\text{CHO})_n \quad \text{DIPEA, TFA, DMF, 90 °C} \quad \text{R}_0 \quad \text{SO}_2\text{Ph}
\]

Scheme S3. General experimental procedures for substrates 2u-2w
According to a reported literature procedure, a mixture of S-3 (1.0 equiv), DIPEA (1.0 equiv), TFA (2.0 equiv), sodium benzenesulfinate (1.0 equiv) and paraformaldehyde (4.0 equiv) were dissolved in DMF, then, the reaction mixture was heated to 90 °C in a nitrogen atmosphere for 20 h. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, washed with 3 × 20 mL LiCl (5 wt%), and dried over Na₂SO₄. The solid was filtered off and the organic solvent evaporated. The crude product was purified by column chromatography on silica gel to give the 2u-2w as a white solid.

**Preparation of 1q**

1q was synthesized according to literature report, p-hydroxybenzaldehyde (1.0 equiv) and acid (1.0 equiv) and dry CH₂Cl₂ (20 mL) were added sequentially to a dry round-bottom flask at room temperature. The reaction was cooled to 0 °C and a catalytic amount of 4-dimethylaminopyridine (DMAP, 0.1 equiv) and dicyclohexylcarbodiimide (DCC, 2.0 equiv) were added sequentially. The reaction was allowed to slowly warm to room temperature and further stirred for 8 hours. Upon completion, the solution was concentrated in vacuo and purified by column chromatography on silica gel to afford the desired product 1q.

### 2.4 General experimental procedures for the unsaturated ketones and 1, 5-diketones

Aldehyde 1 (0.2 mmol, 1.0 equiv), TBADT (26.6 mg, 4 mol %) and allyl sulfone 2 (0.6 mmol, 3.0 equiv) were added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed using a rubber stopper and the reaction mixture was degassed by bubbling with N₂ for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). The reaction tube was irradiated (at approximately 2-3 cm away from the light source) with a Kessil® PR160L-390 nm lamp (40 W) under vigorous stirring at room temperature. After 6 hours the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate (v/v = 40/1) as eluting solvent to give the desired products 3.
Scheme S6. General experimental procedures for the 1, 5-diketones

TBADT (21 mg, 3 mol %), aldehyde 1 (1.4 mmol, 7.0 equiv) and allyl sulfone 2 (0.2 mmol, 1.0 equiv) were added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed using a rubber stopper and the reaction mixture was degassed by bubbling with N\textsubscript{2} for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N\textsubscript{2} atmosphere). After the reaction, the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate (v/v = 20/1) as eluting solvent to give the desired products 4.

2.5 Synthetic applications

Synthesis of 5\textsuperscript{4}

Scheme S7. Experimental procedures for 5

The reaction was carried out following a modified procedure from Boivin et al.\textsuperscript{4} A solution of compound 4a (65 mg, 0.2 mmol, 1 equiv) in AcOH (5 mL), containing NH\textsubscript{4}OAc (123 mg, 1.6 mmol, 8 equiv) was placed into a 10 mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with N\textsubscript{2}. The solution was then heated at 120 °C for 5 h after which the solvent was evaporated under reduced pressure and the residue was taken up in Et\textsubscript{2}O. The organic layer was washed successively with 2 N aq NaOH and brine, then dried (MgSO\textsubscript{4}). The residue was chromatographed over silica gel (ethyl ether/petroleum ether = 1:50, R\textsubscript{f} = 0.4) to yield the title compound 5 as white solid (45.1 mg, 75%).

Synthesis of 6 \textsuperscript{5}

Scheme S8. Experimental procedures for 6
The reaction was carried out following a modified procedure from Wang et al.\textsuperscript{5} To a solution of hydroxylamine hydrochloride (69.5 mg, 1.0 mmol, 5 equiv) in water was added a solution of sodium acetate (114.8 mg, 1.4 mmol, 7 equiv) in ethanol. The mixture was stirred at room temperature while the unsaturated ketone 3b (43.6 mg, 0.2 mmol, 1 equiv) was added as a solution in ethanol. The mixture was stirred overnight and concentrated in vacuo. Then, the mixture was extracted with ethyl acetate 3 times and the combined extracts were washed with water and brine, dried (MgSO\textsubscript{4}), filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford title compound 6 as colorless oil (26.1 mg, 56%).

2.6 Set of Experiments

A set of experiments that employed 1a and 2a were performed to evaluate the reaction-condition-based sensitivity of this conversion, which will be valuable in increasing the insight of this new synthetic method and reproducibility. Various parameters, including concentration, temperature, oxygen level, water level, light intensity, and scale, were chosen with positive and negative direction relative to the standard reaction conditions. Each experiment only deliberately changed one parameter, while keeping others at standard levels.

Table S5. Set of Experiments

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
<th>Description</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (c)</td>
<td>High c</td>
<td>c + 10% c</td>
<td>69%</td>
</tr>
<tr>
<td></td>
<td>Low c</td>
<td>c - 10% c</td>
<td>70%</td>
</tr>
<tr>
<td>H_2O level</td>
<td>High H_2O</td>
<td>+ H_2O; V_{H_2O} = 1%V_{rxn}</td>
<td>64%</td>
</tr>
<tr>
<td>O_2 level</td>
<td>Air</td>
<td>Air instead of N_2</td>
<td>32%</td>
</tr>
<tr>
<td>Temperature (T)</td>
<td>High T</td>
<td>T + 10 °C</td>
<td>70%</td>
</tr>
<tr>
<td>Light intensity (W)</td>
<td>Low W</td>
<td>W/16</td>
<td>0%</td>
</tr>
<tr>
<td>Scale</td>
<td>Big scale</td>
<td>n·15</td>
<td>59%</td>
</tr>
</tbody>
</table>

2.7 Investigation of the mechanism

TEMPO was used as a radical scavenger

To a 25 mL Schlenk tube was added TBADT (21 mg, 3 mol %), aldehyde 1a (1.4 mmol, 7.0 equiv), allyl sulfone 2a (0.2 mmol, 1.0 equiv) and TEMPO (1.0 mmol, 5.0 equiv). The tube was
sealed with a rubber stopper and the reaction mixture was degassed by bubbling with N₂ for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N₂ atmosphere). As it can be seen, the reaction was completely suppressed, reminding of a radical-involved process. The adduct 7 and 8 were detected by high-resolution mass spectrometry (HRMS) as shown in Figure S2.
To a 25 mL Schlenk tube was added TBADT (21 mg, 3 mol %), aldehyde 1a (1.4 mmol, 7.0 equiv), allyl sulfone 2a (0.2 mmol, 1.0 equiv) and 1,1-diphenylethylene (1.0 mmol, 5.0 equiv). The tube was sealed with a rubber stopper and the reaction mixture was degassed by bubbling with N₂ for 5 min with an outlet needle, followed by the sequential addition via syringe of acetone (3 mL). Then the reaction tube was exposed to a Kessil® PR160L-390 nm lamp (40 W) irradiation (at approximately 2-3 cm away from the light source) at room temperature with vigorous stirring for 5 h (N₂ atmosphere). As it can be seen, the reaction was severely suppressed and the adduct 9 and 10 were detected by high-resolution mass spectrometry (HRMS) as shown in Figure S3.

Figure S2. HR-MS of the reaction when TEMPO was used as a radical scavenger

1,1-diphenylethylene was used as a radical scavenger
**Figure S3.** HR-MS of the reaction when 1,1-diphenylethylene was used as a radical scavenger
2.8 Proposed Reaction Mechanisms

The above mechanistic experiments coupled with precedent related literature collectively point to a plausible mechanism shown in Scheme S9. Initially, the TBADT photocatalyst was excited to generate the triplet excited state *\([W_{10}O_{32}]^{4-}\) under the irradiation of 390 nm Kessil lamp, which abstracted a hydrogen atom from the aldehyde to get a nucleophilic aroyl radical A and \([W_{10}O_{32}]^{5-}\) H⁺. The subsequent interaction of the radical A and allyl sulfone 2 through a sequence of radical addition and β-fragmentation delivered allyl product 3 while producing phenylsulfonyl radical. Finally, the phenylsulfonyl radical was easily reduced by \([W_{10}O_{32}]^{5-}\) H⁺, thereby closing the catalyst cycle after the HAT process.
Scheme S9. Proposed Reaction Mechanism of the aroylation reaction

3. Characterization Data for Products

**ethyl 2-methylene-4-oxo-4-phenylbutanoate (3a)**

![Structural formula of ethyl 2-methylene-4-oxo-4-phenylbutanoate (3a)](image)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3a. Colorless oil (35 mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.04 – 8.00 (m, 2H), 7.62 – 7.58 (m, 1H), 7.51 – 7.47 (m, 2H), 6.43 (d, $J = 0.64$ Hz, 1H), 5.71 (d, $J = 1.0$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 4.02 (d, $J = 0.7$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 196.9, 166.4, 136.6, 134.9, 133.2, 128.6, 128.4, 128.3, 61.0, 41.7, 14.1.

**ethyl 2-methylene-4-oxo-4-(p-tolyl)butanoate (3b)**

![Structural formula of ethyl 2-methylene-4-oxo-4-(p-tolyl)butanoate (3b)](image)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3b. Colorless oil (43 mg, 92% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.90 – 7.90 (m, 2H), 7.30 – 7.28 (m, 2H), 6.41 (d, $J = 0.8$ Hz, 1H), 5.70 (d, $J = 1.1$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.99 (d, $J = 0.6$ Hz, 2H), 2.44 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 196.6, 166.5, 144.1, 135.0, 134.1, 129.3, 128.4, 128.2, 61.0, 41.6, 21.7, 14.1.

**ethyl 4-(4-isopropylphenyl)-2-methylene-4-oxobutanoate (3c)**

![Structural formula of ethyl 4-(4-isopropylphenyl)-2-methylene-4-oxobutanoate (3c)](image)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3c. Colorless oil (34 mg, 65% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.96 – 7.93 (m, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 6.41 (d, $J = 0.7$ Hz, 1H), 5.70 (d, $J = 1.0$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 4.00 (d, $J = 0.5$ Hz, 2H), 3.04 – 2.94 (m, 1H), 1.30 – 1.26 (m, 9H). $^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 196.6, 166.5, 154.8, 135.0, 134.4, 128.5, 128.2, 126.7, 61.0, 41.6, 34.3, 23.7, 14.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{16}$H$_{21}$O$_3$, 261.1485; found: 261.1497.

**ethyl 4-(4-(tert-butyl)phenyl)-2-methylene-4-oxobutanoate (3d)**
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3d. Colorless oil (32 mg, 58% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.97 – 7.93 (m, 2H), 7.53 – 7.48 (m, 2H), 6.42 (s, 1H), 5.70 (d, \(J = 1.0\) Hz, 1H), 4.23 (q, \(J = 7.1\) Hz, 2H), 4.00 (s, 2H), 1.37 (s, 9H), 1.28 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.6, 166.5, 157.0, 135.0, 134.0, 128.3, 128.2, 125.6, 61.0, 41.6, 35.1, 31.1, 14.1. HRMS (ESI-TOF) \(m/z\): [M + H]\(^+\) calcd for C\(_{17}\)H\(_{23}\)O\(_3\), 275.1642; found: 275.1638.

**ethyl 4-([1,1'-biphenyl]-4-yl)-2-methylene-4-oxobutanoate (3e)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3e. White solid (36 mg, 61% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.11 – 8.08 (m, 2H), 7.74 – 7.71 (m, 2H), 7.67 – 7.65 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 6.45 (s, 1H), 5.74 (d, \(J = 1.0\) Hz, 1H), 4.25 (q, \(J = 7.1\) Hz, 2H), 4.05 (s, 2H), 1.30 (t, \(J = 8.0\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.5, 166.4, 145.9, 139.9, 135.3, 134.9, 129.0, 128.9, 128.4, 128.3, 127.3, 61.1, 41.7, 14.1.

**ethyl 4-(4-methoxyphenyl)-2-methylene-4-oxobutanoate (3f)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3f. Colorless oil (23 mg, 47% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.01 – 7.97 (m, 2H), 6.98 – 6.94 (m, 2H), 6.40 (s, 1H), 5.70 (d, \(J = 1.0\) Hz, 1H), 4.22 (q, \(J = 7.1\) Hz, 2H), 3.97 (s, 2H), 3.89 (s, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 195.5, 166.5, 163.6, 135.1, 130.6, 129.6, 128.2, 113.8, 61.0, 55.5, 41.3, 14.1.

**ethyl 4-(4-chlorophenyl)-2-methylene-4-oxobutanoate (3g)**
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3g. Colorless oil (26 mg, 51% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.93 (m, 2H), 7.49 – 7.45 (m, 2H), 6.43 (s, 1H), 5.73 (d, $J = 0.9$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.7, 166.3, 139.7, 134.9, 134.6, 129.7, 129.0, 128.5, 61.1, 41.6, 14.1.

**ethyl 4-(4-bromophenyl)-2-methylene-4-oxobutanoate (3h)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3h. Colorless oil (21 mg, 35% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.61 (d, $J = 8.4$ Hz, 2H), 6.41 (s, 1H), 5.70 (s, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.95 (s, 1H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.9, 166.3, 135.3, 134.5, 131.9, 129.8, 128.6, 128.4, 61.1, 41.6, 14.1.

**ethyl 4-(3-chlorophenyl)-2-methylene-4-oxobutanoate (3i)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3i. Colorless oil (24 mg, 48% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 7.98 (t, $J = 1.8$ Hz, 1H), 7.88 (dt, $J = 7.8$, 1.2 Hz, 1H), 7.58 – 7.55 (m, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 6.44 (s, 1H), 5.73 (d, $J = 0.9$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.7, 166.2, 138.1, 135.0, 134.4, 133.2, 130.0, 128.7, 128.4, 126.4, 61.1, 41.8, 14.1.

**ethyl 4-(3-bromophenyl)-2-methylene-4-oxobutanoate (3j)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3j. Colorless oil (31 mg, 52% yield). $^1$H NMR (400 MHz, Chloroform-d) δ 8.11 (t, $J = 1.8$ Hz, 1H), 7.91 (dt, $J = 7.8$, 1.3 Hz, 1H), 7.71 – 7.69 (m, 1H), 7.36 (t, $J = 7.9$ Hz, 1H), 6.42 (s, 1H), 5.71 (d, $J = 1.0$ Hz, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 3.96 (d, $J = 0.6$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 195.6, 166.2, 138.3, 136.1, 134.4, 131.2, 130.2, 128.7, 126.8, 123.0, 61.1, 41.7, 14.1.

**ethyl 2-methylene-4-oxo-4-(m-tolyl)butanoate (3k)**
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3k. Colorless oil (27 mg, 57% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.80 (d, $J = 8.6$ Hz, 2H), 7.41 – 7.35 (m, 2H), 6.42 (s, 1H), 5.71 (d, $J = 0.8$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 4.01 (s, 2H), 2.44 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.1, 166.4, 138.4, 136.6, 134.9, 134.0, 128.8, 128.5, 128.3, 125.5, 61.0, 41.8, 21.4, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for C$_{14}$H$_{16}$NaO$_3$, 255.0992; found: 255.0997.

**ethyl 4-(2-hydroxypyphenyl)-2-methylene-4-oxobutanoate (3l)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3l. Colorless oil (25 mg, 54% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 12.05 (s, 1H), 7.83 (dd, $J = 8.0$, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.46 (s, 1H), 5.74 (s, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 4.07 (s, 2H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 202.9, 166.2, 162.5, 136.6, 134.3, 130.0, 128.8, 119.0, 118.6, 61.2, 41.4, 14.1. HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{13}$H$_{15}$O$_4$, 235.0965; found: 235.0967.

**ethyl 4-(3,4-dimethylphenyl)-2-methylene-4-oxobutanoate (3m)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3m. Colorless oil (23 mg, 46% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.78 – 7.73 (m, 1H), 7.53 – 7.49 (m, 1H), 7.01 (d, $J = 8.3$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.46 (s, 1H), 5.74 (s, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 3.99 (d, $J = 0.4$ Hz, 2H), 2.34 (s, 6H), 1.28 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.8, 166.5, 142.8, 137.0, 135.1, 134.5, 129.8, 129.4, 128.2, 126.0, 61.0, 41.6, 20.0, 19.8, 14.1.

**ethyl 4-(furan-2-yl)-2-methylene-4-oxobutanoate (3n)**

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3n. Colorless oil (25 mg, 59% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.63 – 7.61 (m, 1H), 7.27 (d, $J = 3.6$ Hz,
ethyl 2-methylene-4-oxo-4-(thiophen-2-yl)butanoate (3o)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3o. Colorless oil (24 mg, 53% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.81 (dd, \(J = 3.8, 1.0\) Hz, 1H), 7.16 (dd, \(J = 4.9, 3.8\) Hz, 1H), 6.43 (s, 1H), 5.77 (d, \(J = 1.0\) Hz, 1H), 4.22 (q, \(J = 7.1\) Hz, 2H), 1.28 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 189.6, 166.3, 143.6, 134.3, 133.9, 132.4, 128.7, 128.1, 61.1, 42.2, 14.1.

ethyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3p)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3p. White solid (41 mg, 76% yield), mp 60 – 61 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.54 (s, 1H), 8.06 (dd, \(J = 8.6, 1.8\) Hz, 1H), 8.00 – 7.98 (m, 1H), 7.91 (t, \(J = 8.5\) Hz, 2H), 7.65 – 7.56 (m, 2H), 6.46 (d, \(J = 0.9\) Hz, 1H), 5.76 (d, \(J = 1.1\) Hz, 1H), 4.24 (q, \(J = 7.1\) Hz, 2H), 4.16 (d, \(J = 0.7\) Hz, 2H), 1.29 (t, \(J = 7.1\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.9, 166.5, 135.7, 135.0, 133.9, 132.5, 130.0, 129.6, 128.50, 128.49, 128.4, 127.8, 126.8, 124.0, 61.1, 41.7, 14.1.

ethyl 4-(4-((2-(4-isobutylphenyl)propanoyl)oxy)phenyl)-2-methylene-4-oxobutanoate (3q)

Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide 3q. Colorless oil (31 mg, 36% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.02 – 7.98 (m, 2H), 7.32 (d, \(J = 8.1\) Hz, 2H), 7.18 (d, \(J = 8.1\) Hz, 2H), 7.15 – 7.11 (m, 2H), 6.42 (d, \(J = 0.5\) Hz, 1H), 5.70 (d, \(J = 0.9\) Hz, 1H), 4.21 (q, \(J = 7.1\) Hz, 2H), 4.00 – 3.95 (m, 3H), 2.50 (d, \(J = 7.2\) Hz, 2H), 1.94 – 1.84 (m, 1H), 1.64 (d, \(J = 7.1\) Hz, 3H), 1.27 (t, \(J = 7.1\) Hz, 3H), 0.93 (d, \(J = 6.6\) Hz, 6H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 195.7, 172.7, 166.3, 154.7, 141.0, 136.8, 134.7, 134.0, 129.8, 129.6, 128.5, 127.2,
methyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3r)

\[
\text{CO}_2\text{Me}
\]

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3r. White solid (36 mg, 71% yield). \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.54 (s, 1H), 8.06 (dd, \(J = 8.6, 1.7\) Hz, 1H), 7.99 (d, \(J = 8.0\) Hz, 1H), 7.91 (t, \(J = 8.4\) Hz, 2H), 7.65 – 7.56 (m, 2H), 6.46 (s, 1H), 5.77 (d, \(J = 0.8\) Hz, 1H), 4.17 (s, 2H), 3.79 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.8, 167.0, 135.7, 134.6, 133.8, 132.5, 130.1, 129.6, 128.7, 128.6, 128.5, 127.8, 126.8, 123.9, 52.2, 41.8. HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calcd for C\(_{26}\)H\(_{30}\)NaO\(_5\), 445.1985; found: 445.1992.

benzyl 2-methylene-4-(naphthalen-2-yl)-4-oxobutanoate (3s)

\[
\text{CO}_2\text{Bn}
\]

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3s. White solid (56 mg, 84% yield), mp 76 – 77 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.52 (s, 1H), 8.06 (dd, \(J = 8.6, 1.7\) Hz, 1H), 7.97 (d, \(J = 8.0\) Hz, 1H), 7.93 – 7.90 (m, 2H), 7.66 – 7.56 (m, 2H), 7.36 – 7.30 (m, 5H), 6.53 (s, 1H), 5.81 (d, \(J = 0.8\) Hz, 1H), 5.24 (s, 2H), 4.19 (s, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 196.8, 166.3, 135.8, 135.7, 134.6, 133.9, 132.5, 130.1, 129.6, 129.1, 128.6, 128.51, 128.50, 128.2, 128.1, 127.8, 126.8, 124.0, 66.8, 41.8. HRMS (ESI-TOF) m/z: [M + Na]\(^+\) calcd for C\(_{16}\)H\(_{14}\)NaO\(_3\), 277.0835; found: 277.0839.

2-methylene-4-(naphthalen-2-yl)-1-phenylbutane-1,4-dione (3t)

\[
\text{O} \quad \text{Ph}
\]

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3t. White solid (39 mg, 65% yield), mp 102 – 103 °C. \(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.58 (s, 1H), 8.07 (dd, \(J = 8.6, 1.7\) Hz, 1H), 8.00 (d, \(J = 8.0\) Hz, 1H), 7.97 – 7.89 (m, 4H), 7.65 – 7.56 (m, 3H), 7.51 – 7.48 (m, 2H), 6.04 (s, 1H), 5.88 (s, 1H), 4.41 (s, 2H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 197.4, 197.2, 142.5, 137.4, 135.7, 133.7, 132.5, 132.3, 130.2, 129.9, 129.7, 128.7, 128.6, 128.5, 128.2, 127.8, 126.8, 123.9, 42.7. HRMS (ESI-TOF) m/z: [M + H]\(^+\) calcd for C\(_{21}\)H\(_{17}\)O\(_2\), 301.1123; found: 301.1129.
2-methylene-4-(naphthalen-2-yl)-1-(p-tolyl)butane-1,4-dione (3u)

Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide 3u. White solid (30 mg, 47% yield), mp 114 – 115 °C. 1H NMR (400 MHz, Chloroform-d) δ 8.58 (s, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.98 – 7.69 (m, 5H), 7.65 – 7.56 (m, 2H), 7.31 (s, 1H), 6.00 (s, 1H), 5.86 (s, 1H), 4.39 (s, 2H), 2.45 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 197.2, 197.1, 143.1, 142.5, 135.7, 134.6, 133.8, 132.5, 130.2, 130.1, 129.7, 128.9, 128.6, 128.5, 128.0, 127.8, 126.8, 123.9, 42.8, 21.7. HRMS (ESI-TOF) m/z: [M + H]+ calcd for C22H19O2, 315.1380; found: 315.1387.

ethyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4a)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4a. Colorless oil (47 mg, 72% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.02 – 7.96 (m, 4H), 7.58 (t, J = 7.4 Hz, 2H), 7.47 (t, J = 7.6 Hz, 4H), 4.18 (q, J = 7.1 Hz, 2H), 3.63 – 3.69 (m, 1H), 3.59 (dd, J = 17.8, 5.7 Hz, 2H), 3.39 (dd, J = 17.7, 6.3 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ 197.9, 174.3, 136.6, 133.3, 128.6, 128.1, 61.0, 39.5, 36.1, 14.1. HRMS (ESI-TOF) m/z: [M + Na]+ calcd for C20H20NaO4, 347.1254; found: 347.1261.

ethyl 4-oxo-2-(2-oxo-2-(p-tolyl)ethyl)-4-(p-tolyl)butanoate (4b)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4b. Colorless oil (47 mg, 66% yield). 1H NMR (400 MHz, Chloroform-d) δ 7.89 (d, J = 8.2 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 4.17 (q, J = 7.1 Hz, 2H), 3.66 – 3.60 (m, 1H), 3.54 (dd, J = 17.7, 5.8 Hz, 2H), 3.35 (dd, J = 17.7, 6.4 Hz, 2H), 2.42 (s, 6H), 1.23 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, Chloroform-d) δ 197.6, 174.5, 144.1, 134.1, 129.3, 128.2, 60.9, 39.4, 36.2, 21.7, 14.1. HRMS (ESI-TOF) m/z: [M + Na]+ calcd for C22H24NaO4, 375.1567; found: 375.1559.

ethyl 4-(4-ethylphenyl)-2-(2-(4-ethylphenyl)-2-oxoethyl)-4-oxobutanoate (4c)
Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4c. Colorless oil (29 mg, 38% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.92 (d, $J = 8.3$ Hz, 4H), 7.29 (d, $J = 8.0$ Hz, 4H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, $J = 17.7$, 5.8 Hz, 2H), 3.35 (dd, $J = 17.6$, 6.4 Hz, 2H), 2.72 (q, $J = 7.6$ Hz, 4H), 1.29 – 1.23 (m, 9H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.6, 174.5, 150.3, 134.3, 128.3, 128.1, 60.9, 39.4, 36.1, 29.0, 15.2, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for C$_{24}$H$_{28}$NaO$_4$, 403.1880; found: 403.1887.

**ethyl 4-(4-isopropylphenyl)-2-(2-(4-isopropylphenyl)-2-oxoethyl)-4-oxobutanoate (4d)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4d. Colorless oil (50 mg, 61% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 (d, $J = 8.3$ Hz, 4H), 7.32 (d, $J = 8.3$ Hz, 4H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, $J = 17.7$, 5.7 Hz, 2H), 3.36 (dd, $J = 17.7$, 6.4 Hz, 2H), 3.01 – 2.94 (m, 2H), 1.28 (d, $J = 6.9$ Hz, 12H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.6, 174.5, 154.8, 134.5, 128.4, 126.7, 60.9, 39.4, 36.2, 34.3, 23.7, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for C$_{26}$H$_{32}$NaO$_4$, 431.2193; found: 431.2188.

**ethyl 4-(4-(tert-butyl)phenyl)-2-(2-(4-(tert-butyl)phenyl)-2-oxoethyl)-4-oxobutanoate (4e)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4e. Colorless oil (53 mg, 61% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 (d, $J = 8.5$ Hz, 4H), 7.49 (d, $J = 8.5$ Hz, 4H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, $J = 17.7$, 5.7 Hz, 2H), 3.36 (dd, $J = 17.6$, 6.4 Hz, 2H), 1.35 (s, 18H), 1.23 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.6, 174.5, 157.0, 134.0, 128.1, 125.6, 60.9, 39.4, 36.2, 35.1, 31.1, 14.1. HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{28}$H$_{37}$O$_4$, 437.2686; found: 437.2686.

**ethyl 4-((1,1'-biphenyl)-4-yl)-2-(2-((1,1'-biphenyl)-4-yl)-2-oxoethyl)-4-oxobutanoate (4f)**
Purification by flash column chromatography (PE: EA, v/v = 15:1) to provide 4f. White solid (60 mg, 63% yield), mp 85 – 86 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.13 – 8.06 (m, 4H), 7.74 – 7.69 (m, 4H), 7.67 – 7.62 (m, 4H), 7.54 – 7.47 (m, 4H), 7.46 – 7.39 (m, 2H), 4.22 (q, $J$ = 7.1 Hz, 2H), 3.75 – 3.69 (m, 1H), 3.65 (dd, $J$ = 17.7, 5.7 Hz, 2H), 3.45 (dd, $J$ = 17.6, 6.3 Hz, 2H), 1.27 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.5, 174.4, 146.0, 140.0, 135.3, 129.0, 128.7, 128.3, 127.3, 61.1, 39.6, 36.2, 14.1. HRMS (ESI-TOF) $m/z$: [M + H]$^+$ calcd for C$_{32}$H$_{29}$O$_4$, 477.2060; found: 477.2067.

**ethyl 4-(4-fluorophenyl)-2-(2-(4-fluorophenyl)-2-oxoethyl)-4-oxobutanoate (4g)**

Purification by flash column chromatography (PE: EA, v/v = 15:1) to provide 4g. Colorless oil (51 mg, 71% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.04 – 7.98 (m, 4H), 7.18 – 7.10 (m, 4H), 4.17 (q, $J$ = 7.1 Hz, 2H), 3.66 – 3.60 (m, 1H), 3.55 (dd, $J$ = 17.8, 5.7 Hz, 2H), 3.34 (dd, $J$ = 17.7, 6.3 Hz, 2H), 1.22 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.3, 174.1, 165.9 (d, $J$ = 255.1 Hz), 133.0 (d, $J$ = 3.0 Hz), 130.7 (d, $J$ = 9.4 Hz), 115.8 (d, $J$ = 21.8 Hz), 61.1, 39.3, 36.1, 14.1. $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -104.72. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for C$_{20}$H$_{18}$F$_2$NaO$_4$, 383.1065; found: 383.1075.

**ethyl 4-(4-chlorophenyl)-2-(2-(4-chlorophenyl)-2-oxoethyl)-4-oxobutanoate (4h)**

Purification by flash column chromatography (PE: EA, v/v = 15:1) to provide 4h. Colorless oil (51 mg, 64% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 – 7.88 (m, 4H), 7.46 – 7.41 (m, 4H), 4.16 (q, $J$ = 7.1 Hz, 2H), 3.65 – 3.59 (m, 1H), 3.53 (dd, $J$ = 17.9, 5.7 Hz, 2H), 3.32 (dd, $J$ = 17.8, 6.3 Hz, 2H), 1.21 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 196.7, 174.0, 139.8, 134.8, 129.5, 129.0, 61.1, 39.4, 36.0, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcd for C$_{20}$H$_{18}$Cl$_2$NaO$_4$, 415.0474; found: 415.0488.

S22
**ethyl 4-(4-bromophenyl)-2-(2-(4-bromophenyl)-2-oxoethyl)-4-oxobutanoate (4i)**

![Structural formula of 4i](#)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4i. Colorless oil (35 mg, 36% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.85 (d, *J* = 8.2 Hz, 4H), 7.65 – 7.59 (m, 4H), 4.17 (q, *J* = 7.0 Hz, 2H), 3.64 – 3.60 (m, 1H), 3.54 (dd, *J* = 17.9, 5.6 Hz, 2H), 3.33 (dd, *J* = 17.8, 6.3 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 196.9, 174.0, 135.2, 132.0, 130.0, 128.6, 61.1, 39.3, 36.0, 14.1. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₂₀H₁₈Br₂NaO₄, 502.9464; found: 502.9470.

**ethyl 4-oxo-2-(2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-(4-(trifluoromethyl)phenyl)butanoate (4j)**

![Structural formula of 4j](#)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4j. White solid (52 mg, 56% yield), mp 88 – 89 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.10 (d, *J* = 8.1 Hz, 4H), 7.76 (dt, *J* = 9.4, 2.2 Hz, 2H), 7.47 (td, *J* = 8.0, 5.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.66 (m, 1H), 3.62 (dd, *J* = 17.9, 5.6 Hz, 2H), 3.41 (dd, *J* = 17.8, 6.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 196.9, 173.7, 139.1, 134.7 (q, *J* = 32.7 Hz), 128.4, 125.8 (q, *J* = 3.7 Hz), 123.5 (q, *J* = 272.7 Hz), 61.3, 39.6, 36.0, 14.1. ¹⁹F NMR (376 MHz, Chloroform-d) δ -63.17. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₂H₁₉F₆O₄, 461.1182; found: 461.1188.

**ethyl 4-(3-fluorophenyl)-2-(2-(3-fluorophenyl)-2-oxoethyl)-4-oxobutanoate (4k)**

![Structural formula of 4k](#)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4k. Colorless oil (32 mg, 44% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.66 (dt, *J* = 9.4, 2.2 Hz, 2H), 7.47 (td, *J* = 8.0, 5.5 Hz, 2H), 7.31 – 7.27 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.68 – 3.62 (m, 1H), 3.56 (dd, *J* = 17.9, 5.7 Hz, 2H), 3.35 (dd, *J* = 17.9, 6.3 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-d) δ 196.6 (d, *J* = 2.1 Hz), 173.9, 162.9 (d, *J* = 248.2 Hz),
ethyl 4-(3-chlorophenyl)-2-(2-(3-chlorophenyl)-2-oxoethyl)-4-oxobutanoate (4l)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4l. Colorless oil (43 mg, 55% yield). ^1H NMR (400 MHz, Chloroform-d) δ 7.95 (s, 2H), 7.86 (d, J = 7.8 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.42 (t, J = 7.9 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.55 (dd, J = 18.0, 5.7 Hz, 2H), 3.34 (dd, J = 17.9, 6.3 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^13C NMR (101 MHz, Chloroform-d) δ 196.6, 173.9, 138.0, 135.0, 133.3, 130.0, 126.2, 61.2, 39.6, 36.1, 14.1. HRMS (ESI-TOF) m/z: [M + Na]^+ calcd for C_{20}H_{18}Cl_{2}NaO_{4}, 415.0474; found: 415.0475.

ethyl 4-oxo-2-(2-oxo-2-(m-tolyl)ethyl)-4-(m-tolyl)butanoate (4m)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4m. Colorless oil (45 mg, 64% yield). ^1H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 8.2 Hz, 4H), 7.43 – 7.33 (m, 4H), 4.18 (q, J = 7.1 Hz, 2H), 3.68 – 3.62 (m, 1H), 3.56 (dd, J = 17.8, 5.7 Hz, 2H), 3.37 (dd, J = 17.7, 6.4 Hz, 2H), 2.42 (s, 6H), 1.24 (t, J = 7.1 Hz, 3H). ^13C NMR (101 MHz, Chloroform-d) δ 198.1, 174.4, 138.4, 136.6, 134.0, 128.6, 128.5, 125.3, 61.0, 39.6, 36.1, 21.3, 14.1. HRMS (ESI-TOF) m/z: [M + Na]^+ calcd for C_{22}H_{24}NaO_{4}, 375.1567; found: 375.1577.

ethyl 4-oxo-2-(2-oxo-2-(o-tolyl)ethyl)-4-(o-tolyl)butanoate (4n)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4n. Colorless oil (27 mg, 38% yield). ^1H NMR (400 MHz, Chloroform-d) δ 7.72 – 7.68 (m, 2H), 7.40 (td, J = 7.5, 1.3 Hz, 2H), 7.31 – 7.24 (m, 4H), 4.19 (q, J = 7.1 Hz, 2H), 3.67 – 3.61 (m, 1H), 3.49 (dd, J = 17.8, 6.2 Hz, 2H), 3.27 (dd, J = 17.8, 6.3 Hz, 2H), 2.52 (s, 6H), 1.26 (t, J = 7.1 Hz, 3H). ^13C NMR (101 MHz,
Chloroform-$d$ $\delta$ 201.7, 174.3, 138.2, 137.4, 132.0, 131.5, 128.6, 125.7, 61.0, 42.3, 36.5, 21.3, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{22}$H$_{24}$NaO$_4$, 375.1567; found: 375.1571.

**ethyl 4-(2-hydroxyphenyl)-2-(2-(2-hydroxyphenyl)-2-oxoethyl)-4-oxobutanoate (4o)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4o. Colorless oil (52 mg, 73% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 12.06 (s, 2H), 7.80 (dd, $J$ = 8.1, 1.4 Hz, 2H), 7.54 – 7.47 (m, 2H), 7.01 (d, $J$ = 8.4 Hz, 2H), 6.96 – 6.90 (m, 2H), 4.20 (q, $J$ = 7.1 Hz, 2H), 3.70 – 3.61 (m, 3H), 3.44 – 3.38 (m, 2H), 1.24 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 203.6, 173.8, 162.4, 136.7, 129.8, 119.2, 119.1, 118.6, 61.3, 39.1, 35.5, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{20}$H$_{20}$NaO$_6$, 379.1152; found: 379.1165.

**ethyl 4-(naphthalen-2-yl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4p)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4p. White solid (43 mg, 51% yield), mp 92 – 93 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.54 (s, 2H), 8.07 (dd, $J$ = 8.6, 1.7 Hz, 2H), 7.98 (d, $J$ = 8.0 Hz, 2H), 7.90 (t, $J$ = 8.0 Hz, 4H), 7.65 – 7.52 (m, 4H), 4.23 (q, $J$ = 7.1 Hz, 2H), 3.83 – 3.75 (m, 3H), 3.62 – 3.56 (m, 2H), 1.26 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.9, 174.4, 135.7, 133.9, 132.5, 129.9, 128.6, 128.5, 127.8, 126.8, 123.7, 61.1, 39.6, 36.3, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{28}$H$_{24}$NaO$_6$, 447.1567; found: 447.1568.

**ethyl 4-(3,4-dimethylphenyl)-2-(2-(3,4-dimethylphenyl)-2-oxoethyl)-4-oxobutanoate (4q)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4q. Colorless oil (61 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.76 (s, 2H), 7.72 (dd, $J$ = 7.8, 1.7 Hz, 2H), 7.22 (d, $J$ = 7.9 Hz, 2H), 4.18 (q, $J$ = 7.1 Hz, 2H), 3.66 – 3.59 (m, 1H), 3.53 (dd, $J$ = 17.7, 5.7 Hz, 2H), 3.34 (dd, $J$ = 17.7, 6.5 Hz, 2H), 2.32 (s, 12H), 1.23 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz,
Chloroform-$d$) $\delta$ 197.8, 174.5, 142.8, 136.9, 134.5, 129.8, 129.2, 125.8, 60.9, 39.4, 36.2, 20.0, 19.8, 14.1. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ calec for $C_{24}H_{28}NaO_4$, 403.1880; found: 403.1883.

**ethyl 4-(2,4-dichlorophenyl)-2-(2-(2,4-dichlorophenyl)-2-oxoethyl)-4-oxobutanoate (4r)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4r. Colorless oil (70 mg, 76% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.54 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 2.0$ Hz, 2H), 7.34 (dd, $J = 8.3$, 2.0 Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.66 – 3.60 (m, 1H), 3.50 (dd, $J = 18.1$, 6.3 Hz, 2H), 3.31 (dd, $J = 18.1$, 6.0 Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 199.3, 173.4, 137.7, 136.8, 132.2, 130.5, 130.4, 127.4, 61.3, 43.4, 36.6, 14.1. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ calec for $C_{20}H_{16}Cl_4NaO_4$, 482.9695; found: 482.9693.

**methyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4s)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4s. White solid (44 mg, 71% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.00 – 7.98 (m, 4H), 7.60 – 7.56 (m, 2H), 7.49 – 7.46 (m, 4H), 3.72 (s, 3H), 3.69 – 3.65 (m, 1H), 3.60 (dd, $J = 17.9$, 5.7 Hz, 2H), 3.40 (dd, $J = 17.8$, 6.4 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.8, 174.9, 137.7, 136.8, 132.2, 130.5, 130.4, 127.4, 61.3, 39.5, 35.9.

**benzyl 4-oxo-2-(2-oxo-2-phenylethyl)-4-phenylbutanoate (4t)**

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4t. White solid (47 mg, 61% yield), mp 65 – 66 °C. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.99 – 7.97 (m, 4H), 7.61 – 7.56 (m, 2H), 7.49 – 7.45 (m, 4H), 7.34 – 7.30 (m, 5H), 5.18 (s, 2H), 3.78 – 3.72 (m, 1H), 3.62 (dd, $J = 18.0$, 5.7 Hz, 2H), 3.42 (dd, $J = 17.9$, 6.5 Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 197.8, 174.2, 136.5, 135.8, 133.3, 128.6, 128.5, 128.11, 128.10, 66.8, 39.5, 36.1. HRMS (ESI-TOF) $m/z$: $[M + Na]^+$ calec for $C_{25}H_{22}NaO_4$, 409.1410; found: 409.1424.
3-benzoyl-1,5-diphenylpentane-1,5-dione (4u)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4u. Yellow solid (39 mg, 54% yield). 1H NMR (400 MHz, Chloroform-d) δ 8.16 – 8.11 (m, 2H), 7.99 – 7.94 (m, 4H), 7.62 – 7.44 (m, 9H), 4.83 – 4.76 (m, 1H), 3.55 (dd, J = 17.9, 6.6 Hz, 2H), 3.36 (dd, J = 17.9, 6.7 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 202.4, 197.6, 136.4, 136.0, 133.4, 133.2, 128.8, 128.7, 128.6, 128.1, 40.4, 37.0.

3-(4-methylbenzoyl)-1,5-diphenylpentane-1,5-dione (4v)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4v. Yellow solid (36 mg, 48% yield), mp 112 – 113 ºC. 1H NMR (400 MHz, Chloroform-d) δ 8.04 (d, J = 8.2 Hz, 2H), 7.97 – 7.95 (m, 4H), 7.60 – 7.56 (m, 2H), 7.48 – 7.45 (m, 4H), 7.32 (d, J = 8.0 Hz, 2H), 4.81 – 4.74 (m, 1H), 3.54 (dd, J = 17.9, 6.6 Hz, 2H), 3.35 (dd, J = 17.9, 6.7 Hz, 2H), 2.44 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 202.0, 197.6, 144.0, 136.5, 133.4, 133.3, 129.5, 128.8, 128.6, 128.1, 40.4, 36.9, 21.7. HRMS (ESI-TOF) m/z: [M + Na]+ calcd for C25H22NaO3, 393.1461; found: 393.1457.

3-(4-bromobenzoyl)-1,5-diphenylpentane-1,5-dione (4w)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4w. Yellow solid (48 mg, 55% yield), mp 123 – 124 ºC. 1H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 7.3 Hz, 4H), 7.63 (d, J = 8.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 2H), 7.45 (t, J = 7.7 Hz, 4H),
4.72 – 4.66 (m, 1H), 3.50 (dd, $J = 17.9, 6.8$ Hz, 2H), 3.34 (dd, $J = 17.9, 6.5$ Hz, 2H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 201.6, 197.5, 136.3, 134.9, 133.5, 132.1, 130.3, 128.7, 128.4, 128.1, 40.6, 36.9. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{24}$H$_{1979}$BrNaO$_3$, 457.0410; found: 457.0414.

ethyl 4-[[1,1'-biphenyl]-4-yl]-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4x)

![ethyl 4-[[1,1'-biphenyl]-4-yl]-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate](image)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4x. White solid (67 mg, 75% yield), mp 77 – 78 °C. $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.54 (s, 1H), 8.14 – 8.04 (m, 3H), 7.98 (d, $J = 8.9$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.67 – 7.53 (m, 4H), 7.53 – 7.46 (m, 2H), 7.45 – 7.39 (m, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.81 – 3.74 (m, 2H), 3.67 (dd, $J = 17.8, 5.4$ Hz, 1H), 3.61 – 3.43 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 197.9, 197.6, 174.8, 146.0, 139.5, 135.2, 133.9, 132.5, 129.9, 129.6, 129.0, 128.7, 128.6, 128.5, 128.3, 127.9, 127.3, 126.8, 123.7, 61.0, 39.74, 39.61, 36.3, 14.2. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{30}$H$_{26}$NaO$_4$, 473.1723; found: 473.1727.

ethyl 4-(4-chlorophenyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate (4y)

![ethyl 4-(4-chlorophenyl)-2-(2-(naphthalen-2-yl)-2-oxoethyl)-4-oxobutanoate](image)

Purification by flash column chromatography (PE:EA, v/v = 15:1) to provide 4y. Yellow oil (63 mg, 77% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.48 (s, 1H), 8.01 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.95 – 7.82 (m, 5H), 7.61 – 7.50 (m, 2H), 7.40 (d, $J = 8.5$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.72 – 3.66 (m, 2H), 3.61 – 3.46 (m, 2H), 3.35 (dd, $J = 17.9, 5.8$ Hz, 1H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 197.7, 196.8, 174.2, 139.1, 135.7, 134.9, 133.8, 132.5, 129.9, 129.6, 129.5, 128.9, 128.6, 128.5, 127.8, 126.9, 123.7, 61.1, 39.52, 39.50, 36.2, 14.1. HRMS (ESI-TOF) $m/z$: [M + Na]$^+$ calcld for C$_{24}$H$_{21}$ClNaO$_4$, 431.1021; found: 431.1024.

ethyl 2,6-diphenylisonicotinate (5)
Purification by flash column chromatography (PE:EA, v/v = 40:1) to provide **5.** White solid (45 mg, 75% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.29 (s, 2H), 8.27 – 8.22 (m, 4H), 7.60 – 7.53 (m, 4H), 7.52 – 7.48 (m, 2H), 4.52 (q, $J$ = 7.1 Hz, 2H), 1.50 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 165.5, 157.8, 139.5, 138.7, 129.5, 128.8, 127.1, 117.8, 61.9, 14.4.

**ethyl (Z)-4-(hydroxyimino)-2-methylene-4-phenylbutanoate (6)**

Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **6.** Colorless oil (30 mg, 65% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 8.56 (d, $J$ = 14.2 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.41 – 7.37 (m, 3H), 6.27 (d, $J$ = 0.8 Hz, 1H), 5.55 (d, $J$ = 0.7 Hz, 1H), 4.26 (q, $J$ = 7.1 Hz, 2H), 3.88 (t, $J$ = 1.6 Hz, 2H), 1.33 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) δ 166.6, 156.6, 135.1, 134.8, 129.4, 128.6, 126.3, 125.8, 61.1, 28.3, 14.2. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for C$_{13}$H$_{16}$O$_3$, 234.1125; found: 234.1136.

4. **NMR Copies of Products**
3a. $^1$H NMR, 400 MHz, CDCl$_3$

3a. $^{13}$C NMR, 101 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 101 MHz, CDCl$_3$
3c, $^1$H NMR, 400 MHz, CDCl$_3$

3c, $^{13}$C NMR, 101 MHz, CDCl$_3$
3d, ^1^H NMR, 400 MHz, CDCl₃

3d, ^13^C NMR, 101 MHz, CDCl₃
$3e$, $^1$H NMR, 400 MHz, CDCl$_3$

$3e$, $^{13}$C NMR, 101 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$.

$^{13}$C NMR, 101 MHz, CDCl$_3$. 

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S35
$^{3g}$, $^1$H NMR, 400 MHz, CDCl$_3$

$^{3g}$, $^{13}$C NMR, 101 MHz, CDCl$_3$
$3h, ^1H$ NMR, 400 MHz, CDCl$_3$

$3h, ^{13}C$ NMR, 101 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
$^3j$ H NMR, 400 MHz, CDCl$_3$

$^13$C NMR, 101 MHz, CDCl$_3$
$^{3}$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$

[Chemical structure image]
$\text{3m, }^1\text{H NMR, 400 MHz, CDCl}_3$

$\text{3m, }^{13}\text{C NMR, 101 MHz, CDCl}_3$
3a, $^1$H NMR, 400 MHz, CDCl$_3$
$^{30}$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
$^3$J, $^1$H NMR, 400 MHz, CDCl$_3$

$^3$J, $^{13}$C NMR, 101 MHz, CDCl$_3$
$\text{3q, } ^1\text{H NMR, } 400\text{ MHz, CDCl}_3$

$\text{3q, } ^{13}\text{C NMR, } 101\text{ MHz, CDCl}_3$
3r, $^1$H NMR, 400 MHz, CDCl$_3$

3r, $^{13}$C NMR, 101 MHz, CDCl$_3$
3s, $^1$H NMR, 400 MHz, CDCl$_3$

3s, $^{13}$C NMR, 101 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 101 MHz, CDCl$_3$
3u, $^1$H NMR, 400 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 101 MHz, CDCl$_3$
$4c$, $^1$H NMR, 400 MHz, CDCl$_3$

$4c$, $^{13}$C NMR, 101 MHz, CDCl$_3$
4d, $^1$H NMR, 400 MHz, CDCl$_3$

4d, $^{13}$C NMR, 101 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_3$

$^{13}C$ NMR, 101 MHz, CDCl$_3$
4g. $^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
$^{19}$F NMR, 376 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

4h, $^{13}$C NMR, 101 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

4f, $^1$H NMR, 400 MHz, CDCl$_3$
4j. $^{13}$C NMR, 101 MHz, CDCl$_3$

4j. $^{19}$F NMR, 376 MHz, CDCl$_3$
4k, $^1$H NMR, 400 MHz, CDCl$_3$

4l, $^{13}$C NMR, 101 MHz, CDCl$_3$
4l, $^1$H NMR, 400 MHz, CDCl$_3$

4k, $^{19}$F NMR, 376 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^1$C NMR, 101 MHz, CDCl$_3$

S64
$^{13}$C NMR, 101 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
4a. $^{13}$C NMR, 101 MHz, CDCl$_3$

4b. $^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

4r

$^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
$^1$H NMR, 400 MHz, CDCl$_3$

$^{13}$C NMR, 101 MHz, CDCl$_3$
S72

4t, $^1$H NMR, 400 MHz, CDCl$_3$

4t, $^{13}$C NMR, 101 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

4v, $^1$H NMR, 400 MHz, CDCl$_3$
$^{13}$C NMR, 101 MHz, CDCl$_3$

$^1$H NMR, 400 MHz, CDCl$_3$
4a. $^{13}$C NMR, 101 MHz, CDCl$_3$
$4\times ^{13}\text{C NMR, 101 MHz, CDCl}_3$

$4\times ^1\text{H NMR, 400 MHz, CDCl}_3$
4. $^{13}$C NMR, 101 MHz, CDCl$_3$

5. $^1$H NMR, 400 MHz, CDCl$_3$
5. $^{13}$C NMR, 101 MHz, CDCl$_3$

6. $^1$H NMR, 400 MHz, CDCl$_3$
5. Reference


