CHAPTER 4

Intramolecular Homoenolate Reaction of Enals with α,β-Unsaturated Esters: Efficient Synthesis of Coumarin Derivatives

4.1. Introduction

Discovery of novel and efficient synthetic methods is essential for the development of sustainable chemical transformations, especially for carbon-carbon bond formation. Hence, carbon-carbon bond formation has been an area of constant interest and remains a great challenge. During the past two decades, organocatalysis became an important tool in synthetic organic chemistry. Along with this, N-heterocyclic carbenes (NHCs) have assumed a significant role. Following the general trend, most of the NHC catalyzed reactions are also intermolecular, i.e., the reaction sites belong to two or more molecules. This chapter presents a novel NHC catalyzed intramolecular homoenolate reaction for the efficient synthesis of coumarin derivatives. In this context, a brief survey of N-heterocyclic carbene catalyzed intramolecular reactions is essential and is given in the following section. Since coumarin derivatives constitute the target molecules of the work described in this chapter, inclusion of review of the existing methods of coumarin synthesis would be customary. However, a review of coumarin synthesis is already available in the previous chapter (Chapter 3). Therefore to avoid duplication; a review of coumarin synthesis is excluded.

4.2. NHC Catalyzed Intramolecular Reactions

4.2.1. Intramolecular Benzoin Reactions

In 2003, Hachisu et al. reported a catalytic intramolecular crossed aldehyde ketone benzoin reaction for the synthesis of functionalized preanthraquinones (Scheme 4.1).¹ This process offers a simple and remarkably mild entry to useful, orthogonally protected polycyclic quinones with a high degree of regio- and stereoselectivity.
The same group extended the scope of this reaction to aliphatic substrates. After the optimization of reaction conditions, it was found that the five and six-membered cyclic acyloins were formed in good to excellent yields and the competing intramolecular aldol reactions were suppressed (Scheme 4.2). Not surprisingly, the analogous formation of seven-membered rings was found difficult.

First enantioselective intramolecular crossed benzoin reaction catalyzed by \(N\)-heterocyclic carbene was reported by Enders and co-workers. The tetracyclic triazole carbene catalyzed cyclization afforded the \(\alpha\)-ketol with a quaternary stereocenter in high yield and excellent enantioselectivity (Scheme 4.3).

Another triazole carbene catalyzed enantioselective crossed aldehyde ketone benzoin cyclization was reported by Takikawa and co-workers. Both aromatic and aliphatic substrates underwent highly enantioselective cyclization; excellent selectivity was observed for the formation of six-membered rings compared to the five-membered ones.

In 2007, Takikawa and Suzuki utilized this methodology for the synthesis of (\(+\))-Sappanone B (Scheme 4.4). Commercially available 2-hydroxy-4-methoxybenzaldehyde 7 was transformed into aldehyde 8, which upon treatment with triazolium salt in presence of base afforded (\(R\))-9 in 92% yield and 95% ee. Subsequently the latter was transformed to (\(+\))-Sappanone B.
Later, a bio-inspired acyl-anion equivalent macrocyclization and synthesis of a trans-resoricylide precursor was reported (Scheme 4.5). The electron-deficient triazolium salts served as precatalysts for the cyclization, the N-pentafluorophenyl triazole carbene derived from C4 led to cyclization at room temperature within a short time.

In 2008, You and co-workers showed that the efficiency of intramolecular crossed benzoin reaction can be improved by using D-camphor derived triazolium salt (Scheme 4.6). The NHC catalyst derived from C5 and DBU is found to be efficient for intramolecular crossed aldehyde–ketone benzoin reaction, and α-ketol containing a quaternary stereocenter was formed in excellent yield with up to 93% ee.

A stereoselective synthesis of bicyclic tertiary alcohols with quaternary stereocenter was developed via N-heterocyclic carbene catalyzed intramolecular crossed
benzoin reaction (Scheme 4.7). Later the scope of the reaction was explored with chiral catalysts.

A facile one-pot synthetic route to naphthalenone based bicyclic tertiary alcohol from chalcone 17 via intramolecular aldehyde–ketone crossed benzoin condensation reaction catalyzed by NHC was reported (Scheme 4.8). Recently, Greatrex et al. reported NHC-catalyzed carbocyclization of carbohydrate-derived dialdehydes for the synthesis of allo- and epi-inositol. The inososes were stereospecifically reduced using sodium borohydride and then deprotected to give inositol in good yield (Scheme 4.9).

### 4.2.2. Intramolecular Stetter Reaction

Almost 20 years after the initial report of the Stetter reaction, Ciganek reported an intramolecular variant of this reaction in 1995 with thiazolium precatalyst C7 providing chromanone 23 in 86% yield (Scheme 4.10). In 1996, Enders and co-workers illustrated the first asymmetric variant of the intramolecular Stetter reaction utilizing chiral triazolinyldene derived from C8.
In 2002 Rovis and co-workers synthesized a series of triazolium precatalysts, e.g., C9 and these were utilized for the intramolecular Stetter reaction of variety of substrates. The products were obtained in good yields with high enantioselectivities (Scheme 4.11). Among those catalysts, the tetracyclic structure of the catalyst C9 provided sufficient steric bulk on reaction centre.

The reaction works well with a number of acceptors such as α,β-unsaturated esters, amides, alkyl ketones, and phosphine oxides under suitable reaction conditions to afford products in more than 90% ee. Aliphatic substrates also performed well for the construction of five membered rings in good yield and high enantioselectivity. The corresponding six membered cyclization product was formed from substrate endowed with the more electrophilic Michael acceptor, alkylidene malonate (Scheme 4.12).

The scope of this strategy was expanded to enantioselective formation of quaternary stereocenters by inducing the intramolecular addition of aromatic as well as
aliphatic aldehydes to $\beta,\beta$-disubstituted Michael acceptors (Scheme 4.13).\textsuperscript{18} They also demonstrated sensitivity of intramolecular Stetter reaction to the nature and geometry of the Michael acceptor.\textsuperscript{17}

![Scheme 4.13](image)

Utilizing prochiral $\alpha,\alpha$-disubstituted Michael acceptors, the Stetter reaction catalyzed by C10 has proven to be both enantio- and diastereoselective, allowing control of the formation of contiguous stereocenters (Scheme 4.14).\textsuperscript{19}

![Scheme 4.14](image)

Rovis and Liu have accomplished the desymmetrization of cyclohexadienones by using triazolinylidene carbene generated from C9 (Scheme 4.15).\textsuperscript{20} Multiple hydrobenzofuranones were synthesized in good yield with excellent enantio- and diastereoselectivity. Up to three stereocenters as well as a quaternary stereocenter were formed from polysubstituted substrates.

![Scheme 4.15](image)

Markó and co-workers utilized the Stetter reaction in the synthesis of bicycloenediones, proceeding in moderate yields using stoichiometric thiazolium pre-catalyst C7 (Scheme 4.16).\textsuperscript{21} Morita-Baylis-Hillman adduct 38 was formed in three steps from commercially available starting materials, 4-pentenal 36 and the corresponding cyclic enone 37. The carbene induced Stetter reaction followed by acetate elimination and alkene isomerization delivered bicyclic enedione 39.
Trost and co-workers relied on Stetter reaction to set the relative stereochemistry for the core of hirsutic acid C (Scheme 4.17).\textsuperscript{22}

Nicolaou and co-workers reported a formal synthesis of (±)-platensimycin utilizing Stetter methodology (Scheme 4.18).\textsuperscript{23} Aldehyde 44 when treated with achiral \textit{N}-pentafluorophenyl pre-catalyst C4 readily underwent cyclization to yield 45 as a single diastereomer.

Rovis and Orellana have reported the progress toward the synthesis of FD-838.\textsuperscript{24} In four steps, the Stetter substrate 47 was obtained, and it endured cyclization under the influence of aminoindanol derived pre-catalyst C13 to produce spirocycle 48 in good yield and 99% ee (Scheme 4.19).
4.2.3. Intramolecular Hydroacylation Reactions

In 2010, Liu and co-workers reported an NHC catalyzed intramolecular aldehyde-nitrile cross coupling reaction for the synthesis of 3-aminochromenones (Scheme 4.20).\textsuperscript{25}

The authors extended this strategy to an intramolecular Stetter type hydroacylation reaction between an aldehyde and activated alkyne (Scheme 4.21).\textsuperscript{26}

A 1,4-dicarbonyl compound carrying a phosphonate group was synthesised by utilizing a dually NHC-catalyzed domino hydroacylation of salicyl alkynylphosphonates (Scheme 4.22).\textsuperscript{27}
Glorius et al. reported an unprecedented reactivity of acyl anion generated via \(N\)-heterocyclic carbenes, towards hydroacylation of unactivated double bonds (Scheme 4.23).\(^{28}\)

![Scheme 4.23](image)

In 2010 this methodology was extended to the hydroacylation of unactivated alkynes to provide \(\alpha, \beta\)-unsaturated ketone products (Scheme 4.24).\(^{29}\) In addition, these authors and Zeitler et al. reported a rare case of an efficient and selective dually NHC-catalyzed cascade reaction involving the hydroacylation of alkynes and a subsequent intermolecular Stetter reaction.\(^{30}\)

![Scheme 4.24](image)

### 4.2.4. Nucleophilic Substitution Reaction

A novel intramolecular nucleophilic substitution reaction catalyzed by NHC leading to the synthesis of benzopyrones was reported by He et al. (Scheme 4.25). When \(R^1\) was a phenyl group, the cyclization product underwent isomerization, resulting in the benzofuranone. A variety of substrates underwent the reaction in good yields. The formation of benzopyrone was achieved by a direct nucleophilic substitution reaction of NHC-aldehyde umpolung. Mechanism of benzofuranone formation was explained by invoking rearrangement of the intermediate cation followed by intramolecular cyclization.\(^{31}\)

![Scheme 4.25](image)
Recently Zhao et al. reported the first NHC-catalyzed intramolecular $S_{N}2'$ substitution reaction of aldehydes with allylic electrophiles (Scheme 4.26). The reaction exhibited excellent functional group tolerance and afforded good yield of products.$^{32}$

![Scheme 4.26](image)

A variety of benzodioxepinone products were synthesised by an efficient, oxidative carbene-catalyzed lactonization reaction (Scheme 4.27).$^{33}$ The thiazole carbene catalyzed reaction afforded products in good to excellent yield. The selective oxidation was done by azobenzene, which can easily be recovered and reused after applying inexpensive FeCl$_3$ as a formal terminal oxidant.

![Scheme 4.27](image)

4.2.5. Homoenolate Reactions

Glorius and co-workers extended the NHC mediated homoenolate reaction to intramolecular homoenolate addition in modest yield (Scheme 4.28).$^{34}$

![Scheme 4.28](image)

In 2007, Scheidt and co-workers reported the intramolecular desymmetrization of 1,3-diketones utilizing triazolium precatalyst (Scheme 4.29).$^{35}$ The formation of $\alpha,\alpha$-disubstituted cyclopentenones was rationalized by invoking the initial formation of homoenolate followed by $\beta$-protonation and aldol reaction, and subsequent loss of carbon dioxide, along the lines suggested by us previously.$^{36}$
NHC-catalyzed intramolecular cyclization–lactonization of enals to ketones tethered by an amide bond, produced densely functionalized γ-lactam-γ-lactone adducts.\textsuperscript{37} To demonstrate the utility of this method, the authors accomplished a formal synthesis of salinosporamide A, a potent 20S proteasome inhibitor and anti-cancer therapeutic (Scheme 4.30).

4.3. Present Work

The above discussion makes it clear that, in spite of the enormous progress in the area of NHC mediated intermolecular homoenolate chemistry, there are only a few intramolecular homoenolate reactions known in the literature. In view of this, intrigued by the possibility of designing an intramolecular reaction, it was conceptualized that cinnamaldehyde appended with 2-O-alkenoate, on treatment with NHC, was likely to undergo a cascade reaction triggered by the initial formation of homoenolate and its intramolecular Michael addition, and a series of events culminating in the formation of a coumarin derivative (Scheme 4.31).
4.4. Results and Discussion

The present studies were initiated by synthesizing 2-O-alkenoate substituted cinnamaldehydes by the reaction of 2-hydroxycinnamaldehyde and dimethyl acetylenedicarboxylate (DMAD) (Scheme 4.32).

In a preliminary experiment, the 2-substituted cinnamaldehyde 84 was treated with the imidazolium precatalyst C18 and DBU in dry THF under an argon atmosphere (Scheme 4.33). After 24 hours the solvent was removed and the crude product when subjected to column chromatography on silica gel afforded 15% of the product, 4-alkyl substituted coumarin 84a.
The structure of the product was established by common spectroscopic techniques. The proton NMR spectrum showed singlet at $\delta 6.27$ corresponding to the alkenyl proton. The final confirmation was obtained from single crystal X-ray analysis.
Figure 4.3 Single crystal X-ray Structure of 84a, CCDC number: 903579

In view of the success of the reaction, we examined the usefulness of other commonly available NHC catalysts in this reaction. A number of experiments were conducted, and the results are summarised in Table 1. Among the four catalysts investigated, imidazolinium catalyst C21 gave the best result (table 1, entry 7).

Table 4.1. Condition optimization

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Solvent, temp (°C)</th>
<th>Time (h)</th>
<th>Yield(^\circ) (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>C18</td>
<td>DBU</td>
<td>THF, rt</td>
<td>24</td>
<td>15</td>
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<td>C18</td>
<td>DBU</td>
<td>THF, 65 °C</td>
<td>24</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>C18</td>
<td>DBU</td>
<td>PhMe, 110 °C</td>
<td>24</td>
<td>56</td>
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<tr>
<td>4</td>
<td>C21</td>
<td>DBU</td>
<td>THF, rt</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>C21</td>
<td>DBU</td>
<td>THF, 65 °C</td>
<td>24</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>C21</td>
<td>DBU</td>
<td>PhMe, rt</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>7</td>
<td>C21</td>
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<td>2</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>C21</td>
<td>DMAP</td>
<td>PhMe, 110 °C</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>C21</td>
<td>K(_2)CO(_3)</td>
<td>PhMe, rt</td>
<td>24</td>
<td>-</td>
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After having reasonably well established the optimum parameters, the reaction was extended to other substituted cinnamaldehyde derivatives, Table 2.

Table 4.2. Reaction of mixture of E & Z isomers

<table>
<thead>
<tr>
<th>Entry</th>
<th>E: Z isomer ratio(^a)</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>R(^3)</th>
<th>Product</th>
<th>Yield(^b) (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1: 1</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>84a</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>0.65: 1</td>
<td>Me</td>
<td>H</td>
<td>Br</td>
<td>85a</td>
<td>78</td>
</tr>
<tr>
<td>3</td>
<td>0.88: 1</td>
<td>Me</td>
<td>H</td>
<td>t-Bu</td>
<td>86a</td>
<td>70</td>
</tr>
<tr>
<td>4</td>
<td>0.65: 1</td>
<td>Me</td>
<td>H</td>
<td>(\text{i-Pr})</td>
<td>87a</td>
<td>66</td>
</tr>
<tr>
<td>5</td>
<td>1: 1</td>
<td>Me</td>
<td>OMe</td>
<td>H</td>
<td>88a</td>
<td>60</td>
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<tr>
<td>6</td>
<td>0.75: 1</td>
<td>Me</td>
<td>H</td>
<td>OMe</td>
<td>89a</td>
<td>60</td>
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<td>H</td>
<td>Cl</td>
<td>90a</td>
<td>55</td>
</tr>
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<td>Me</td>
<td>H</td>
<td>91a</td>
<td>47</td>
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<tr>
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<td>Me</td>
<td>H</td>
<td>Me</td>
<td>92a</td>
<td>46</td>
</tr>
<tr>
<td>10</td>
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<td>Me</td>
<td>I</td>
<td>H</td>
<td>93a</td>
<td>46</td>
</tr>
<tr>
<td>11</td>
<td>0.6: 1</td>
<td>Me</td>
<td>H</td>
<td>NO(_2)</td>
<td>94a</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>1: 0.61</td>
<td>(\text{t-Bu})</td>
<td>H</td>
<td>Br</td>
<td>95a</td>
<td>21</td>
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<tr>
<td>13</td>
<td>1: 1</td>
<td>Et</td>
<td>H</td>
<td>H</td>
<td>96a</td>
<td>81</td>
</tr>
</tbody>
</table>

\(^a\) E: Z ratio calculated from \(^1\)H NMR, \(^b\) isolated yield

In order to establish advantages, if any, in subjecting the E and Z isomers separately to the cascade process, we prepared them in pure form. When these were
subjected to the reaction conditions identical to those experienced by E-Z mixtures, the same products were obtained in comparable yields. The results are summarised in table 3.

**Table 4.3.** Reaction of E & Z isomers

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Zᵃ</td>
</tr>
<tr>
<td>1</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>84a</td>
<td>83</td>
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<td>Me</td>
<td>OMe</td>
<td>H</td>
<td>88a</td>
<td>63</td>
</tr>
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<td>H</td>
<td>Cl</td>
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<td>69</td>
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</tr>
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<td>H</td>
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<td>85</td>
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<td>Et</td>
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<td>OMe</td>
<td>99a</td>
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<td>Et</td>
<td>OMe</td>
<td>H</td>
<td>100a</td>
<td>67</td>
</tr>
</tbody>
</table>

ᵃisolated yield from (Z) isomer, ᵇisolated yield from (E) isomer.

In order to explore the scope of the coumarin synthesis, we conducted the reaction with substrates derived from other acetylenic esters; the results are presented in Table 4.

**Table 4.4.** Reaction of acetylenic esters

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>R²</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>a</td>
</tr>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>101</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>H</td>
<td>102</td>
<td>21</td>
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<tr>
<td>3</td>
<td>Cl</td>
<td>H</td>
<td>103</td>
<td>60</td>
</tr>
</tbody>
</table>
When the reaction was carried out with 2-O-phenylacrylate substituted cinnamaldehyde 107, methyl 3-(2-oxo-2H-chromen-4-yl)-3-phenylpropanoate 107a was obtained (Scheme 4.34).

The above results suggest that 1,2-substitution of the acetylenic esters is crucial to the selective formation of the homoenolate product over the enolate product.

4.5. Mechanism

The proposed catalytic cycle begins with the initial addition of NHC to the aldehyde leading to the generation of the homoenolate species II. The latter is suitably positioned for a Michael addition to the olefinic ester resulting in a five-membered intermediate III which on fragmentation renders the phenoxy ion IV. The formation of this phenoxy ion may provide the driving force for this reaction. Conceivably V can endure σ-bond rotation and subsequent cyclization concomitant with the ejection of the catalyst to deliver VII; the latter on isomerization affords the final product (Scheme 4.35).
The formation of 3-alkylsubstituted coumarins can be explained as follows; the homoenolate II undergoes a β-protonation leading to the enolate A, which on Michael addition forms a chromane type intermediate B. The phenoxide ion C, formed by the ring fragmentation of B undergoes an intramolecular acylation. Subsequent elimination of carbene followed an isomerization delivers the final product (Scheme 4.36).
4.6. Conclusion

The coumarin synthesis reported herein is noteworthy for its efficiency, novel cascading process involving an intramolecular Michael addition of homoenoate, alkene transfer via Grob type fragmentation, and intramolecular cyclization. It may also be mentioned that the coumarins obtained are endowed with a functionalized carbon chain, thus allowing their further transformation to diverse products of potential value.

4.7. Experimental Section

Melting points were recorded on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded at 500 ($^1$H) and 126 ($^{13}$C) MHz respectively on a Bruker DPX-500 MHz NMR spectrometer. Chemical shifts ($\delta$) are reported relative to TMS ($^1$H) and CDCl$_3$ ($^{13}$C) as the internal standards. Coupling constant ($J$) is reported in Hertz (Hz). Mass spectra were recorded under EI/HRMS or FAB using JEOL JMS 600H mass spectrometer. IR spectra were recorded on a Bruker Alpha-T FT-IR spectrophotometer. Gravity column chromatography was performed using 100-200 mesh silica gel and mixtures of petroleum ether-ethyl acetate were used for elution.

4.7.1. General Experimental Procedures

4.7.1.1. Syntheses of Methyl 3-(2-formylphenoxy) acrylates, dialkyl 2-(2-formyl-phenoxy)maleate

\[
\begin{align*}
\text{Methyl propiolate/dialkyl acetylenedicarboxylate (4.1 mmol, 1 equiv.)} & \text{ was added to a solution of salicylaldehyde (0.5 g, 4.1 mmol, 1 equiv.) in 5mL dichloromethane.} \\
\text{Then a solution of DABCO (0.459 g, 4.1 mmol, 1 equiv.) in 5 mL dichloromethane was} & \text{ added to the above solution drop wise with stirring in an ice bath for 1 h. After the} \\
\text{completion of the reaction, water was added to the mixture and swirled, and the aqueous} & \text{layer was extracted with dichloromethane (3x5 mL). The organic layer was separated and} \\
\text{dried over anhydrous sodium sulfate. After the removal of the solvent, the residue} & \text{obtained was subjected to column chromatography on a silica gel (60-120 mesh) column} \\
\text{using 95:5 hexane: ethyl acetate solvent mixture to afford the product.}
\end{align*}
\]
4.7.1.2. Syntheses of Methyl 3-(2-((E)-3-oxoprop-1-enyl)phenoxy)acrylates, dialkyl 2-(2-((E)-3-oxoprop-1-enyl) phenoxy)maleate

In a 50 mL round bottom flask, methyl 3-(2-formylphenoxy)acrylate (0.983 g, 4.7 mmol) and (Triphenylphosphoranylidene)-acetaldehyde (1.466 g, 4.8 mmol) were taken. Into this was added 10 mL dry THF and refluxed for 3 h. After the completion of the reaction monitored by TLC, solvent was removed and the residue on purification by column chromatography (using 100-200 mesh silica gel and 10: 90 ethyl acetate: hexane mixtures) gave the corresponding phenoxy acrylates/maleates.

4.7.1.3. Synthesis of 3-(2-Hydroxyphenyl) acrylaldehyde (2-hydroxy cinnamaldehyde)

In a round bottom flask, salicylaldehyde (4.7 mmol,) and (Triphenyl–phosphoranylidene)-acetaldehyde (4.8 mmol) were taken. Into this was added 10 mL dry THF and refluxed for 3 h. After the completion of the reaction monitored by TLC, solvent was removed and the residue on purification by column chromatography (using 100-200 mesh silica gel and 90:10 hexane: ethyl acetate mixture) afforded the corresponding 2-hydroxy cinnamaldehydes.

4.7.1.4. Syntheses of Dialkyl 2-(2-((E)-3-oxoprop-1-enyl)phenoxy)fumarates
2-hydroxycinnamaldehyde (2 mmol) was dissolved in aqueous solution of NaOH (2.5 mmol) in a round bottom flask and DMAD (0.284 g, 2 mmol) was added. The reaction mixture was stirred vigorously at room temperature for 1 h. After the completion of the reaction, the solid product formed was separated by vacuum filtration. In the case of liquid products, the reaction mixture was extracted with dichloromethane (3x5 mL) and washed with water. The organic layer was dried over anhydrous sodium sulfate. After the removal of the solvent, the crude product was purified by column chromatography on 60–120 mesh silica gel using 90:10 hexane: ethyl acetate mixture.

4.7.1.5. Syntheses of mixture of E & Z isomers (dialkyl 2-(2-((E)-3-oxoprop-1-enyl)phenoxy) fumarate/maleate)

2-hydroxycinnamaldehyde (2 mmol) was dissolved in 7 mL acetonitrile in a round bottom flask. To this was added DBU (0.20 mmol) followed by DMAD (0.284 g, 2 mmol). The reaction mixture was refluxed for 1 h. After the completion of the reaction, crude mixture was purified by column chromatography on 60-120 mesh silica gel using 90:10 hexane: ethyl acetate mixture.

4.7.1.6. Synthesis of Coumarin Derivatives

Methyl 3-(2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg) and the carbene precursor-1,3-dimesityl imidazolinium chloride (15 mol %) were taken in a round bottom flask; into this was added 7 mL dry toluene followed by DBU (20 mol %) and the reaction mixture refluxed for 2 h under argon atmosphere. The completion of the reaction was monitored by TLC, and the reaction mixture was subjected to column chromatography on silica gel (100-200 mesh) using 90:10 hexane- ethyl acetate mixture.
4.7.2. Characterization Data of Compounds

**Dimethyl 2-((E)-3-oxoprop-1-enyl)phenoxyfumarate (84E)**

**Chemical Formula:** C$_{15}$H$_{14}$O$_6$

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.73 (d, J = 7.8 Hz, 1H), 7.92 (d, J = 16.1 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.8 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 6.79 (dd, J = 16.5 Hz, 7.9 Hz, 2H), 6.69 (s, 1H), 3.77 (s, 3H), 3.72 (s, 3H).

**Dimethyl 2-((E)-3-oxoprop-1-enyl)phenoxymaleate (84Z)**

**Chemical Formula:** C$_{15}$H$_{14}$O$_6$

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.64 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 16.1 Hz, 1H), 7.42 (t, J = 7.7, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.67 (dd, J = 16.1 Hz, 7.6 Hz, 1H), 5.01 (s, 1H), 3.87 (s, 3H), 3.60 (s, 3H).

**Dimethyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxyfumarate (85E)**

**Chemical Formula:** C$_{15}$H$_{13}$BrO$_6$

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, J = 7.6 Hz, 1H), 7.81 (d, J = 16.2 Hz, 1H), 7.75 (d, J = 2.2 Hz, 1H), 7.41 (dd, J = 8.7 Hz, 2.3 Hz, 1H), 6.76 (dd, J = 16.2 Hz, 7.7 Hz, 1H), 6.71 (s, 1H), 6.66 (d, J = 8.7 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H).

**Dimethyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxymaleate (85Z)**

**Chemical Formula:** C$_{15}$H$_{13}$BrO$_6$.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 1.9 Hz, 1H), 7.59 (dd, J = 8.7 Hz, 2.2 Hz, 1H), 7.54 (d, J = 16.2 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 6.73 (dd, J = 11.2 Hz, 4.9 Hz, 1H), 5.15 (s, 1H), 3.94 (s, 3H), 3.70 (s, 3H).

**Dimethyl 2-(4-tert-butyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (86)**

**Chemical Formula:** C$_{19}$H$_{22}$O$_6$.
\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 9.72\) (dd, \(J = 7.7\) Hz, 6.0 Hz, 1.9H), 7.91 (d, \(J = 16.1\) Hz, 0.98H), 7.68 (d, \(J = 2.3\) Hz, 1H), 7.61 (t, \(J = 9.5\) Hz, 2H), 7.50 (dd, \(J = 8.6\) Hz, 2.3 Hz, 1H), 7.34 (dd, \(J = 8.6\) Hz, 2.4 Hz, 1H), 7.10 (d, \(J = 8.6\) Hz, 1H), 6.81 (dd, \(J = 16.1\) Hz, 7.8 Hz, 0.98H), 6.76 (dd, \(J = 16.1\) Hz, 7.7 Hz, 1H), 6.69 (d, \(J = 8.6\) Hz, 0.94H), 6.67 (s, 0.88H), 5.05 (s, 1H), 3.96 (s, 3H), 3.77 (s, 2.67H), 3.72 (s, 3H), 3.68 (s, 2.82H), 1.36 (s, 9H), 1.32 (s, 8H).

**Dimethyl 2-(4-isopropyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (87)**

**Chemical Formula:** C\(_{18}\)H\(_{20}\)O\(_6\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 9.72\) (dd, \(J = 7.7\) Hz, 5.6 Hz, 1.64H), 7.91 (d, \(J = 16.1\) Hz, 0.62H), 7.60 (d, \(J = 16.1\) Hz, 1H), 7.54 (d, \(J = 2.0\) Hz, 0.63H), 7.48 (d, \(J = 2.0\) Hz, 1H), 7.35 (dd, \(J = 8.4\) Hz, 2.0 Hz, 1H), 7.18 (dd, \(J = 8.4\) Hz, 2.1 Hz, 0.64H), 7.10 (d, \(J = 8.4\) Hz, 1H), 6.78 (ddd, \(J = 23.6\) Hz, 16.1 Hz, 7.7 Hz, 1.7H), 6.70 (d, \(J = 8.4\) Hz, 0.64H), 6.67 (s, 0.57H), 5.05 (s, 1H), 3.96 (s, 3H), 3.77 (s, 1.98H), 3.72 (s, 2.09H), 3.68 (s, 3H), 2.96 (dt, \(J = 13.8\) Hz, 6.9 Hz, 0.72H), 2.90 (dt, \(J = 13.8\) Hz, 6.9 Hz, 1H), 1.29 (d, \(J = 6.9\) Hz, 6H), 1.25 (d, \(J = 6.8\) Hz, 3.9H).

**Dimethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (88E)**

**Chemical Formula:** C\(_{16}\)H\(_{16}\)O\(_7\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 9.72\) (d, \(J = 7.8\) Hz, 1H), 7.88 (d, \(J = 16.1\) Hz, 1H), 7.26 (d, \(J = 4.6\) Hz, 1H), 7.08 (t, \(J = 8.0\) Hz, 1H), 6.93 (d, \(J = 8.1\) Hz, 1H), 6.73 (dd, \(J = 16.1\) Hz, 7.8, 1H), 6.23 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.67 (s, 3H).

**Dimethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-enyl)phenoxy)maleate (88Z)**
Chemical Formula: C_{16}H_{16}O_{7}.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.72$ (d, $J = 7.7$ Hz, 1H), 7.61 (d, $J = 16.1$ Hz, 1H), 7.30 – 7.28 (m, 1H), 7.26 (d, $J = 4.3$ Hz, 1H), 7.10 – 7.05 (m, 1H), 6.72 (dd, $J = 16.1$ Hz, 7.6 Hz, 1H), 4.93 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.67 (s, 3H).

Dimethyl 2-(4-methoxy-2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (89E)

Chemical Formula: C_{16}H_{16}O_{7}.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.73$ (d, $J = 7.7$ Hz, 1H), 7.90 (d, $J = 16.1$ Hz, 1H), 7.12 (d, $J = 2.9$ Hz, 1H), 6.87 (dd, $J = 8.9$ Hz, 2.9 Hz, 1H), 6.81 – 6.70 (m, 2H), 6.61 (s, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H).

Dimethyl 2-(4-methoxy-2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (89Z)

Chemical Formula: C_{16}H_{16}O_{7}.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.71$ (d, $J = 7.6$ Hz, 1H), 7.57 (d, $J = 16.1$ Hz, 1H), 7.16 (d, $J = 2.9$ Hz, 1H), 7.11 (d, $J = 8.9$ Hz, 1H), 7.02 (dd, $J = 8.9$ Hz, 2.9 Hz, 1H), 6.71 (dd, $J = 16.1$ Hz, 7.6 Hz, 1H), 5.01 (s, 1H), 3.96 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H).

Dimethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (90E)

Chemical Formula: C_{15}H_{13}ClO_{6}.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.73$ (d, $J = 7.7$ Hz, 1H), 7.83 (d, $J = 16.2$ Hz, 1H), 7.60 (d, $J = 2.5$ Hz, 1H), 7.28 (dd, $J = 8.8$ Hz, 2.5 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.73 (t, $J = 4.3$ Hz, 2H), 3.78 (s, 3H), 3.73 (s, 3H).

Dimethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (90Z)

Chemical Formula: C_{15}H_{13}ClO_{6}.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta = 9.72$ (d, $J = 7.5$ Hz, 1H), 7.68 (d, $J = 2.4$ Hz, 1H), 7.55 (d, $J = 16.2$ Hz, 1H), 7.44 (dd, $J = 8.7$ Hz, 2.3 Hz, 1H), 7.14 (d, $J = 8.7$ Hz, 1H), 6.73 (dd, $J = 16.2$ Hz, 7.6 Hz, 1H), 5.14 (s, 1H), 3.94
(s, 3H), 3.70 (s, 3H).

**Dimethyl 2-(2-methyl-6-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (91)**

Chemical Formula: $C_{16}H_{16}O_6$.

$^1H$ NMR (300 MHz, CDCl$_3$) $\delta = 9.69$ (dd, $J = 11.5$ Hz, 7.8 Hz, 2H), 7.80 (d, $J = 16.1$ Hz, 0.56H), 7.62 – 7.54 (m, 1.2H), 7.45 (d, $J = 7.0$ Hz, 0.57H), 7.36 (d, $J = 7.0$ Hz, 1.53H), 7.31 – 7.20 (m, 1.54H), 7.11 (d, $J = 7.6$ Hz, 0.53H), 7.08 – 6.98 (m, 2.68H), 6.76 – 6.62 (m, 1.16H), 6.22 (s, 1H), 4.80 (s, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.79 (s, 3H), 3.66 (s, 3H), 2.29 (s, 6H).

**Dimethyl 2-(4-methyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (92)**

Chemical Formula: $C_{16}H_{16}O_6$.

$^1H$ NMR (500 MHz, CDCl$_3$) $\delta = 9.71$ (dd, $J = 7.3$ Hz, 6.0, 2H), 7.89 (d, $J = 16.1$ Hz, 1H), 7.58 (d, $J = 16.1$ Hz, 1H), 7.51 (s, 1H), 7.44 (s, 1H), 7.30 – 7.26 (m, 1H), 7.12 (d, $J = 8.3$ Hz, 1H), 7.07 (d, $J = 8.3$ Hz, 1H), 6.80 – 6.69 (m, 2H), 6.67 (d, $J = 8.4$ Hz, 1H), 6.65 (s, 1H), 5.05 (s, 1H), 3.95 (s, 3H), 3.76 (s, 3H), 3.72 (s, 3H), 3.67 (s, 2H), 2.41 (s, 3H), 2.34 (s, 3H).

**Dimethyl 2-(2-iodo-6-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (93)**

Chemical Formula: $C_{15}H_{13}IO_6$.

$^1H$ NMR (500 MHz, CDCl$_3$) $\delta = 9.72$ (d, $J = 7.7$ Hz, 1H), 9.67 (d, $J = 7.7$ Hz, 0.4H), 7.95 (dd, $J = 7.9$ Hz, 1.3 Hz, 1.20H), 7.83 (dd, $J = 7.9$ Hz, 1.4 Hz, 0.42H), 7.75 (d, $J = 16.1$ Hz, 0.45H), 7.71 – 7.66 (m, 3.12H), 7.61 (s, 0.57H), 7.59 (d, $J = 1.4$ Hz, 0.25H), 7.57 (s, 0.86H), 7.21 (dd, $J = 7.6$ Hz, 0.9 Hz, 1.93H), 7.12 (t, $J = 7.9$ Hz, 1.32H), 6.98 (t, $J = 7.8$ Hz, 0.47H), 6.86 (t, $J = 7.8$ Hz, 1.87H), 6.68 (ddd, $J = 21.5$ Hz, 16.1 Hz, 7.6 Hz, 1.88H), 6.34 (s, 0.33H), 4.81 (s, 1H), 4.01 (s, 3H), 3.76 (s, 1.35H), 3.71 (s, 1.34H), 3.68 (s, 3H).
Dimethyl 2-(4-nitro-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (94)

Chemical Formula: C_{13}H_{13}NO_{8}.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta = 9.78$ (d, $J = 7.3$ Hz, 1.58H), 8.57 (d, $J = 2.3$ Hz, 1H), 8.54 (d, $J = 2.4$ Hz, 0.50H), 8.31 (dd, $J = 9.0$ Hz, 2.5 Hz, 1H), 8.21 (dd, $J = 9.0$ Hz, 2.5 Hz, 0.52H), 7.85 (d, $J = 16.2$ Hz, 0.52H), 7.68 (d, $J = 16.2$ Hz, 1H), 7.29 (d, $J = 9.0$ Hz, 1H), 7.26 (s, 0.87H), 6.94 – 6.86 (m, 1.68H), 6.86 (s, 1H), 5.58 (s, 1H), 3.90 (s, 3H), 3.84 (s, 1.4H), 3.76 (s, 3H), 3.74 (s, 1.46H).

Di-tert-butyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (95)

Chemical Formula: C_{21}H_{25}BrO_{6}.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta = 9.65$ (dd, $J = 7.6$ Hz, 4.8 Hz, 1.6H), 7.77 (s, 0.59H), 7.73 (d, $J = 1.8$ Hz, 1H), 7.67 (d, $J = 2.3$ Hz, 1H), 7.53 (d, $J = 16.2$ Hz, 0.69H), 7.48 (dd, $J = 8.6$ Hz, 2.3 Hz, 0.69H), 7.36 (dd, $J = 8.7$ Hz, 2.3 Hz, 1H), 6.98 (d, $J = 8.7$ Hz, 0.68H), 6.70 (d, $J = 7.7$ Hz, 0.62H), 6.68 (dd, $J = 7.6$ Hz, 3.4 Hz, 1H), 6.64 (dd, $J = 8.1$ Hz, 2.8 Hz, 1H), 6.48 (s, 1H), 5.11 (s, 0.58H), 1.43 (s, 5.7H), 1.38 (s, 5.8H), 1.33 (s, 9H), 1.29 (s, 9H).

Diethyl 2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (96E)

Chemical Formula: C_{17}H_{18}O_{6}.

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta = 9.73$ (d, $J = 7.8$ Hz, 1H), 7.93 (d, $J = 16.1$ Hz, 1H), 7.64 (d, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.8$ Hz, 1H), 7.13 (t, $J = 7.6$ Hz, 1H), 6.85 – 6.72 (m, 2H), 6.68 (s, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 4H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H).

Diethyl 2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (96Z)

Chemical Formula: C_{17}H_{18}O_{6}.
Diethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (97E)

Chemical Formula: C$_{17}$H$_{17}$ClO$_6$.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, $J = 7.7$ Hz, 1H), 7.84 (d, $J = 16.2$ Hz, 1H), 7.60 (d, $J = 2.5$ Hz, 1H), 7.28 (dd, $J = 8.7$ Hz, 2.5 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.71 (s, 1H), 4.23-4.16 (m, 4H), 1.24-1.20 (m, 6H).

Diethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (97Z)

Chemical Formula: C$_{17}$H$_{17}$ClO$_6$.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, $J = 7.5$ Hz, 1H), 7.67 (d, $J = 2.4$ Hz, 1H), 7.57 (d, $J = 16.2$ Hz, 1H), 7.44 (dd, $J = 8.6$ Hz, 2.4 Hz, 1H), 7.14 (d, $J = 8.7$ Hz, 1H), 6.73 (dd, $J = 16.4$ Hz, 7.8 Hz, 1H), 5.13 (s, 1H), 4.38 (q, $J = 7.2$ Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.25 (t, $J = 7.2$ Hz, 3H).

Diethyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (98E)

Chemical Formula: C$_{17}$H$_{17}$BrO$_6$.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, $J = 7.7$ Hz, 1H), 7.82 (d, $J = 16.2$ Hz, 1H), 7.74 (d, $J = 2.1$ Hz, 1H), 7.42 (dd, $J = 8.7$ Hz, 2.2, 1H), 6.76 (dd, $J = 16.2$ Hz, 7.7 Hz, 1H), 6.71 (s, 1H), 6.69 (d, $J = 8.7$ Hz, 1H), 4.24-4.16 (m, 4H), 1.23 (m, 6H).

Diethyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (98Z)

Chemical Formula: C$_{17}$H$_{17}$BrO$_6$.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 2.0$ Hz, 1H), 7.58 (dd, $J = 16.5$ Hz, 9.0 Hz, 1H), 6.71 (s, 1H), 6.69 (d, $J = 8.7$ Hz, 1H), 4.71-4.62 (m, 4H), 1.19-1.12 (m, 6H).
Diethyl 2-(4-methoxy-2-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (99E)

Chemical Formula: $C_{18}H_{20}O_7$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.73 (d, $J = 7.7$ Hz, 1H), 7.91 (d, $J = 16.1$ Hz, 1H), 7.11 (d, $J = 3.0$ Hz, 1H), 6.87 (dd, $J = 8.9$ Hz, 3.0 Hz, 1H), 6.78 – 6.72 (m, 2H), 6.60 (s, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.18 (q, $J = 7.0$ Hz, 2H), 3.81 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H).

Diethyl 2-(4-methoxy-2-((E)-3-oxoprop-1-enyl)phenoxy)maleate (99Z)

Chemical Formula: $C_{18}H_{20}O_7$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.71 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 16.1$ Hz, 1H), 7.15 (d, $J = 2.9$ Hz, 1H), 7.12 (d, $J = 8.9$ Hz, 1H), 7.01 (dd, $J = 8.9$ Hz, 2.9 Hz, 1H), 6.71 (dd, $J = 16.1$ Hz, 7.7 Hz, 1H), 5.00 (s, 1H), 4.40 (q, $J = 7.2$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.85 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H), 1.23 (t, $J = 7.2$ Hz, 3H).

Diethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-enyl)phenoxy)fumarate (100E)

Chemical Formula: $C_{18}H_{20}O_7$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 9.72 (d, $J = 7.8$ Hz, 1H), 7.89 (d, $J = 16.1$ Hz, 1H), 7.24 (d, $J = 7.9$ Hz, 1H), 7.08 (t, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.1$ Hz, 1H), 6.74 (dd, $J = 16.1$ Hz, 7.8 Hz, 1H), 6.21 (s, 1H), 4.19-4.12 (m, 4H), 3.76 (s, 3H), 1.25 (t, $J = 7.2$ Hz, 3H), 1.18 (t, $J = 7.1$ Hz, 3H).

Diethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-enyl)phenoxy)maleate (100Z)

Chemical Formula: $C_{18}H_{20}O_7$. 
(E)-Methyl 3-(2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (101)

Chemical Formula: C_{13}H_{12}O_{4}.

$^1$H NMR (500 MHz, CDCl$_3$) δ = 9.72 (d, $J = 7.7$ Hz, 1H), 7.63 (d, $J = 16.1$ Hz, 1H), 7.29 – 7.27 (m, 2H), 7.07 (dd, $J = 6.5$ Hz, 2.9 Hz, 1H), 6.73 (dd, $J = 16.1$ Hz, 7.6 Hz, 1H), 4.92 (s, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.90 (s, 3H), 1.41 (t, $J = 7.3$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H).

Methyl 3-(4-methyl-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (102)

Chemical Formula: C_{14}H_{14}O_{4}

$^1$H NMR (500 MHz, CDCl$_3$): δ = 9.70 (d, 1H, $J = 8$ Hz), 7.75 (d, 1H, $J = 12.5$ Hz), 7.64 (d, 1H, $J = 16$ Hz), 7.44 (s, 1H), 7.27-7.24 (m, 1H), 7.0 (d, 1H $J = 8.3$), 6.72 (dd, 1H, $J = 16.1$, 7.7 Hz), 5.54 (d, 1H, $J = 12$ Hz), 3.73 (s, 3H), 2.39 (s, 3H).

Methyl 3-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (103)

Chemical Formula: C_{13}H_{11}O_{4}Cl

$^1$H NMR (500 MHz, CDCl$_3$): δ = 9.72 (d, 1H, $J = 7.5$ Hz), 7.73 (d, 1H, $J = 12$ Hz), 7.62 (d, 1H, $J = 2$ Hz) 7.42 (dd, 1H, $J = 8.5$ Hz, 9Hz), 7.08 (d, 1H, $J = 8.7$Hz), 6.72 (dd, 1H, $J = 16.2$, 7.5 Hz), 5.61 (d, 1H, $J = 12$Hz), 3.75 (s, 3H)

Methyl 3-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (104)

Chemical Formula: C_{13}H_{11}O_{4}Br

$^1$H NMR (500 MHz, CDCl$_3$): δ = 9.71 (d, 1H, $J = 7.5$ Hz)
Methyl 3-(2-methyl-6-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (105)

Chemical Formula: C_{14}H_{14}O_4

^1H NMR (500 MHz, CDCl₃): δ = 9.61 (d, 1H, J = 8 Hz), 7.69 (d, 1H, J = 12.5 Hz), 7.45 (d, 1H, J = 5 Hz), 7.27 (d, 1H, J = 7.5 Hz), 7.16 (t, 1H, J = 1H), 6.63 (dd, 1H, J₁ = 16.1, J₂ = 7.7 Hz), 4.96 (d, 1H, J = 12.5 Hz), 3.62 (s, 3H), 2.18 (s, 3H).

Methyl 3-(4-tert-butyl-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (106)

Chemical Formula: C_{17}H_{20}O_4

^1H NMR (500 MHz, CDCl₃): δ = 9.7 (d, 1H, J = 7.5 Hz), 7.79 (d, 1H, J = 12 Hz), 7.70 (s, 1H), 7.65 (d, 1H, J = 15.5 Hz), 7.50-7.48 (m, 1H), 7.05 (d, 1H, J = 8.5 Hz), 6.77 (q, 1H, J = 16 Hz), 5.57 (d, 1H, J = 12.5 Hz), 3.74(s, 3H), 1.35 (s, 9H).

Methyl 3-(2-((E)-3-oxoprop-1-enyl)phenoxy)-3-phenylacrylate (107)

Chemical Formula: C_{19}H_{16}O_4.

^1H NMR (500 MHz, CDCl₃) δ = 9.78 (d, J = 7.8 Hz, 1H), 9.69 (d, J = 7.6 Hz, 0.29H), 8.06 (d, J = 16.1 Hz, 1H), 7.71 (dd, J = 7.8 Hz, 1.1 Hz, 0.33H), 7.67 – 7.62 (m, 2H), 7.60 – 7.56 (m, 2H), 7.49 – 7.43 (m, 1.47H), 7.42 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.5 Hz, 0.33H), 7.23 – 7.18 (m, 1H), 7.17 (d, J = 8.0 Hz, 0.33H), 7.03 (t, J = 7.5 Hz, 1H), 6.87 (dd, J = 16.1 Hz, 7.8 Hz, 0.25H), 6.80 – 6.74 (m, 1H), 6.72 (d, J = 8.3 Hz, 1H), 6.24 (s, 1H), 5.12 (s, 0.28H), 3.63 (s, 3H), 3.56 (s, 0.85H).

Dimethyl 2-(2-oxo-2H-chromen-4-yl)succinate (84a)
Following the general procedure, reaction of dimethyl 2-(2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesitylimidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(2-oxo-2H-chromen-4-yl)succinate as white solid.

**Chemical Formula:** C_{15}H_{14}O_{6}

m.p 86–88 °C.

Yield: 93 mg (93%); For Z: 83 mg (83%); For E: 66 mg (66%).

**IR** (film) ν_{max} 2954, 2921, 1723, 1712 cm^{-1}.

**^{1}H NMR (500 MHz, CDCl_{3})** δ = 7.64 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.30 (d, J = 8.3 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 6.27 (s, 1H), 4.44 (dd, J = 9.3 Hz, 5.2 Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 3.18 (dd, J = 17.2 Hz, 9.3, 1H), 2.67 (dd, J = 17.3 Hz, 5.1 Hz, 1H).

**^{13}C NMR (126 MHz, CDCl_{3})** δ = 170.9, 170.8, 159.8, 153.9, 151.2, 132.2, 124.5, 124.1, 117.9, 117.7, 115.2, 53.0, 52.2, 42.3, 35.6. **HRMS** (FAB) calcd for [M+H]^+: 291.0860; found: 291.0873.

**Dimethyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate (85a)**

Following the general procedure, reaction of dimethyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesitylimidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate as white solid.

**Chemical Formula:** C_{15}H_{13}BrO_{6}

m.p 90–92 °C.

Yield: 78 mg (78%); For Z: 75 mg (75%); For E: 69 mg (69%).

**IR** (film) ν_{max} 2954, 1721 cm^{-1}.

**^{1}H NMR (500 MHz, CDCl_{3})** δ = 7.77 (s, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.8 Hz, 1H), 6.29 (s, 1H), 4.37 (dd, J = 9.0 Hz, 5.6, 1H), 3.68 (s, 3H), 3.66 (s, 3H), 3.17 (dd, J = 17.2 Hz, 9.1 Hz, 1H), 2.69 (dd, J = 17.3 Hz, 1H).
5.5 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl₃) $\delta$ = 170.7, 170.4, 159.0, 152.8, 150.2, 135.0, 126.8, 119.6, 119.3, 117.4, 116.0, 53.1, 52.3, 41.9, 35.5. HRMS (FAB) calcd for [M+H]$^+$: 368.9966; found: 369.5410.

Dimethyl 2-(6-tert-butyl-2-oxo-2H-chromen-4-yl)succinate (86a)

Following the general procedure, reaction of dimethyl 2-(4-tert-butyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesitylimidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-tert-butyl-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C₁₉H₂₃O₆.

Yield: 70 mg (70%).

IR (film) $v$ max 2956, 1720 cm⁻¹.

$^1$H NMR (500 MHz, CDCl₃) $\delta$ = 7.67 (s, 1H), 7.60 (d, $J$ = 8.6 Hz, 1H), 7.29 (d, $J$ = 8.6 Hz, 1H), 6.32 (s, 1H), 4.52 (dd, $J$ = 8.3 Hz, 5.7 Hz, 1H), 3.74 (s, 6H), 3.28 (dd, $J$ = 17.1 Hz, 9.1 Hz, 1H), 2.74 (dd, $J$ = 17.1 Hz, 5.1 Hz, 1H), 1.37 (s, 9H). $^{13}$C NMR (126 MHz, CDCl₃) $\delta$ = 171.0, 170.9, 160.0, 151.9, 151.4, 147.5, 129.7, 120.4, 117.2, 115.2, 52.9, 52.2, 42.7, 35.5, 34.7, 31.4. HRMS (FAB) calcd for [M+H]$^+$: 347.1495, found: 347.1519.

Dimethyl 2-(6-isopropyl-2-oxo-2H-chromen-4-yl)succinate (87a)

Following the general procedure, reaction of dimethyl 2-(4-isopropyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesitylimidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-isopropyl-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C₁₈H₂₇O₆.

Yield: 66 mg (66%).

IR (film) $v$ max 2956, 2917, 2850, 1736 cm⁻¹.

$^1$H NMR (500 MHz, CDCl₃) $\delta$ = 7.43 (d, $J$ = 1.5 Hz, 1H), 7.36 (dd, $J$ = 8.4 Hz, 1.9 Hz, 1H), 7.23 (d, $J$ = 8.6 Hz, 1H), 6.25 (s, 1H), 4.44 (dd, $J$ = 9.4 Hz, 5.1 Hz, 1H), 3.67 (s, 6H), 3.18 (dd, $J$ = 17.2 Hz, 9.4 Hz, 1H), 2.97 –
2.89 (m, 1H), 2.66 (dd, \( J = 17.1 \) Hz, 5.2 Hz, 1H), 1.22 (dd, \( J = 6.9 \) Hz, 1.4 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta = 171.03, 171.0, 160.1, 152.3, 151.3, 145.2, 130.6, 130.58, 121.4, 117.6, 115.1, 52.9, 52.2, 42.4, 35.6, 33.8, 24.2, 24.1. HRMS (FAB) calcd for [M+H]+: 333.1330; Found: 333.1351.

**Dimethyl 2-(8-methoxy-2-oxo-2\(H\)-chromen-4-yl)succinate (88a)**

Following the general procedure, reaction of dimethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(8-methoxy-2-oxo-2\(H\)-chromen-4-yl)succinate as white solid.

**Chemical Formula:** \( \text{C}_{16}\text{H}_{16}\text{O}_7 \).

m p 85-87 °C.

Yield: 60 mg (60%); For Z: 63 mg (63%); For \( E \): 81 mg (81%).

IR (film) \( \nu_{\text{max}} \) 2954, 1720 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta = 7.17 \) (d, \( J = 6.5 \) Hz, 2H), 7.03 (dd, \( J = 6.5 \) Hz, 2.9, 1H), 6.26 (s, 1H), 4.41 (dd, \( J = 9.3 \) Hz, 5.1 Hz, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.15 (dd, \( J = 17.2 \) Hz, 9.4 Hz, 1H), 2.67 (dd, \( J = 17.2 \) Hz, 5.2 Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta = 170.9, 159.2, 151.4, 147.9, 143.9, 124.1, 118.6, 115.4, 115.3, 113.9, 56.2, 52.9, 52.2, 42.6, 35.6. HRMS (FAB) calcd for [M+H]+: 321.0966, found:321.0987.

**Dimethyl 2-(6-methoxy-2-oxo-2\(H\)-chromen-4-yl)succinate (89a)**

Following the general procedure, reaction of dimethyl 2-(4-methoxy-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-methoxy-2-oxo-2\(H\)-chromen-4-yl)succinate as white solid.

**Chemical Formula:** \( \text{C}_{16}\text{H}_{16}\text{O}_7 \).

m p 83-85 °C.

Yield: 60 mg (60%); For Z: 65 mg (65%); For \( E \): 78 mg
(78%).

IR (film) \( \nu_{\text{max}} \) 2958, 2917, 2849, 1736, 1721 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) = 7.21 (d, \( J = 12.6 \) Hz, 1H), 7.07 (s, 2H), 6.27 (s, 1H), 4.39 (dd, \( J = 9.1 \) Hz, 5.2 Hz, 1H), 3.80 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 3.19 (dd, \( J = 17.2 \) Hz, 9.2 Hz, 1H), 2.67 (dd, \( J = 17.4 \) Hz, 4.9 Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) = 170.9, 170.8, 160.0, 156.2, 150.9, 148.3, 119.4, 118.6, 118.3, 115.6, 107.0, 55.8, 53.0, 52.3, 42.6, 35.5. HRMS (FAB) calcd for [M+H]\(^+\): 321.0966, found: 321.0977.

**Dimethyl 2-(6-chloro-2-oxo-2\(H\)-chroman-4-yl)succinate (90a)**

Following the general procedure, reaction of dimethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-chloro-2-oxo-2\(H\)-chroman-4-yl)succinate as white solid.

**Chemical Formula:** C\(_{15}\)H\(_{13}\)ClO\(_6\).

mp 89-91 °C.

Yield: 55 mg (55%); For Z: 69 mg (69%); For E: 60 mg (60%).

IR (film) \( \nu_{\text{max}} \) 2955, 2917, 1726 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) = 7.68 (d, \( J = 2.1 \) Hz, 1H), 7.52 (dd, \( J = 8.8 \) Hz, 2.2 Hz, 1H), 7.32 (d, \( J = 8.9 \) Hz, 1H), 6.37 (s, 1H), 4.43 (dd, \( J = 9.0 \) Hz, 5.6 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.24 (dd, \( J = 17.2 \) Hz, 9.1 Hz, 1H), 2.75 (dd, \( J = 16.9 \) Hz, 5.6 Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \( \delta \) = 170.7, 170.4, 159.0, 152.4, 150.3, 132.2, 130.1, 123.8, 119.2, 119.0, 116.1, 53.2, 52.3, 42.0, 35.5. HRMS (FAB) calcd for [M+H]\(^+\): 325.0471, found: 325.0439.

**Dimethyl 2-(8-methyl-2-oxo-2\(H\)-chroman-4-yl)succinate (91a)**

Following the general procedure, reaction of dimethyl 2-(2-methyl-6-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol
% and DBU (20 mol %) afforded dimethyl 2-(8-methyl-2-oxo-2\(H\)-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C\(_{16}H_{16}O_6\).

Yield: 47 mg (47%).

**IR** (film) \(v_{\text{max}}\) 2955, 2918, 1721 cm\(^{-1}\).

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta = 7.53\) (d, \(J = 8.0\) Hz, 1H), 7.41 (d, \(J = 7.4\) Hz, 1H), 7.21 (t, \(J = 7.7\) Hz, 1H), 6.32 (s, 1H), 4.50 (dd, \(J = 9.3\) Hz, 5.2 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.23 (dd, \(J = 17.2\) Hz, 9.4 Hz, 1H), 2.73 (dd, \(J = 17.2\) Hz, 5.2 Hz, 1H), 2.47 (s, 3H). **\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \(\delta = 171.0, 170.9, 159.9, 152.3, 151.6, 133.5, 127.1, 123.9, 121.7, 117.6, 114.9, 52.9, 52.2, 42.5, 35.7, 15.8. **HRMS** (FAB) calcd for [M+H]+: 305.1017, found: 305.1091.

**Dimethyl 2-(6-methyl-2-oxo-2\(H\)-chromen-4-yl)succinate (92a)**

Following the general procedure, reaction of dimethyl 2-(4-methyl-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(6-methyl-2-oxo-2\(H\)-chromen-4-yl)succinate as yellow solid.

**Chemical Formula:** C\(_{16}H_{16}O_6\).

m p 87-89 \(^\circ\)C.

Yield: 46 mg (46%).

**IR** (film) \(v_{\text{max}}\) 2951, 2922, 2854, 1736, 1720 cm\(^{-1}\).

**\(^1\)H NMR** (500 MHz, CDCl\(_3\)) \(\delta = 7.46\) (s, 1H), 7.36 (dd, \(J = 8.4\) Hz, 1.5 Hz, 1H), 7.27 (s, 1H), 6.30 (s, 1H), 4.50 (dd, \(J = 9.5\) Hz, 5.1 Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 3.23 (dd, \(J = 17.2\) Hz, 9.6 Hz, 1H), 2.73 (dd, \(J = 17.2\) Hz, 5.1 Hz, 1H), 2.45 (s, 3H). **\(^{13}\)C NMR** (126 MHz, CDCl\(_3\)) \(\delta = 171.0, 170.9, 159.9, 152.2, 151.1, 134.2, 133.2, 123.8, 117.6, 117.5, 115.0, 52.9, 52.2, 42.1, 35.7, 21.1. **HRMS** (FAB) calcd for [M+H]+: 305.1017, found: 305.1046.

**Dimethyl 2-(8-iodo-2-oxo-2\(H\)-chromen-4-yl)succinate (93a)**
Following the general procedure, reaction of dimethyl 2-(2-iodo-6-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded dimethyl 2-(8-iodo-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C_{15}H_{13}IO_{6}.

**Yield:** 46 mg (46%).

**IR (film)** \(\nu_{\text{max}}\) 2955, 2917, 2850, 1734 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.96\) (d, \(J = 7.9\) Hz, 1H), 7.62 (d, \(J = 8.0\) Hz, 1H), 7.01 (t, \(J = 7.9\) Hz, 1H), 6.28 (s, 1H), 4.42 (dd, \(J = 8.9\) Hz, 5.6 Hz, 1H), 3.66 (s, 3H), 3.66 (s, 3H), 3.18 (dd, \(J = 17.2\) Hz, 9.0 Hz, 1H), 2.67 (dd, \(J = 17.2\) Hz, 5.6 Hz, 1H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 170.8, 170.6, 158.8, 153.1, 150.9, 142.1, 125.7, 124.4, 118.8, 115.9, 85.2, 53.1, 52.3, 42.2, 35.5.

**HRMS** (FAB) calcd for [M+H]\(^{+}\): 416.9827; found: 416.9880.

**Di-tert-butyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate (95a)**

Following the general procedure, reaction of di-tert-butyl 2-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded di-tert-butyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate as white solid.

**Chemical Formula:** C_{21}H_{28}BrO_{6}.

**m p 89-91 °C.**

**Yield:** 21 mg (21%).

**IR (film)** \(\nu_{\text{max}}\) 2957, 2923, 1731 cm\(^{-1}\).

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta = 7.90\) (d, \(J = 2.1\) Hz, 1H), 7.64 (dd, \(J = 8.8\) Hz, 2.2 Hz, 1H), 7.25 (d, \(J = 8.8\) Hz, 1H), 6.36 (s, 1H), 4.28 (dd, \(J = 8.9\) Hz, 5.9, 1H), 3.08 (dd, \(J = 16.8\) Hz, 9.0 Hz, 1H), 2.63 (dd, \(J = 16.8\) Hz, 5.8 Hz, 1H), 1.45 (s, 9H), 1.42 (s, 9H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta = 169.5, 168.9, 159.2, 152.7, 151.0, 134.7, 127.4, 119.9, 119.2, 117.1, 115.6, 82.8, 81.7, 43.6, 36.6,

**Diethyl 2-(2-oxo-2H-chromen-4-yl)succinate (96a)**

Following the general procedure, reaction of diethyl 2-(2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded diethyl 2-(2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C$_{17}$H$_{18}$O$_6$.

Yield: 81 mg (81%); For Z: 68 mg (68%); For E: 72 mg (72%).

IR (film) $\nu_{\text{max}}$ 2917, 2850, 1729 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.65 (d, $J$ = 7.9 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.30 (d, $J$ = 8.3 Hz, 1H), 7.25 (t, $J$ = 7.7 Hz, 1H), 6.28 (s, 1H), 4.41 (dd, $J$ = 9.3 Hz, 5.3 Hz, 1H), 4.17 – 4.06 (m, 4H), 3.15 (dd, $J$ = 17.1 Hz, 9.4 Hz, 1H), 2.65 (dd, $J$ = 17.1 Hz, 5.3 Hz, 1H), 1.20 (t, $J$ = 7.1 Hz, 3H), 1.15 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ = 170.5, 170.4, 159.9, 153.9, 151.5, 132.1, 124.4, 124.2, 117.9, 117.7, 115.1, 62.0, 61.2, 42.6, 35.8, 14.1, 13.9. HRMS (FAB) calcd for [M+H]$^+$: 319.1173; Found: 319.1127.

**Diethyl 2-(6-chloro-2-oxo-2H-chromen-4-yl)succinate (97a)**

Following the general procedure, reaction of diethyl 2-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded diethyl 2-(6-chloro-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

**Chemical Formula:** C$_{17}$H$_{17}$ClO$_6$.

Yield: For Z: 65 mg (65%); For E: 58 mg (58%).

IR (film) $\nu_{\text{max}}$ 2919, 2851, 1731 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 7.72 (s, 1H), 7.53 – 7.49 (m, 1H), 7.31 (dd, $J$ = 8.8 Hz, 1.4 Hz, 1H), 6.38 (s, 1H), 4.41 (dd, $J$ = 8.6 Hz, 5.9 Hz, 1H), 4.19 (ddt, $J$ =
Diethyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate (98a)

Following the general procedure, reaction of diethyl 2-(4-bromo-2-(2H-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded diethyl 2-(6-bromo-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

Chemical Formula: C\textsubscript{17}H\textsubscript{17}BrO\textsubscript{6}

Yield: For Z: 85 mg (85%); For E: 89 mg (89%).

IR (film) \(\nu\)\textsubscript{max} 2981, 2936, 1730 cm\textsuperscript{-1}.

\(^1\)H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta = 7.79\) (d, \(J = 2.0\) Hz, 1H), 7.57 (dd, \(J = 8.8\) Hz, 2.1 Hz, 1H), 7.18 (d, \(J = 8.8\) Hz, 1H), 6.29 (s, 1H), 4.33 (dd, \(J = 9.1\) Hz, 5.6 Hz, 1H), 4.16 – 4.08 (m, 4H), 3.13 (dd, \(J = 17.1\) Hz, 9.1 Hz, 1H), 2.66 (dd, \(J = 17.1\) Hz, 5.6 Hz, 1H), 1.19 (dt, \(J = 14.5\) Hz, 7.1 Hz, 6H). \(^{13}\)C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta = 170.2, 169.9, 158.9, 152.8, 150.3, 134.8, 126.9, 119.7, 119.2, 117.2, 116.0, 62.2, 61.3, 42.3, 35.7, 14.2, 13.9\). HRMS (FAB) calcd for [M+H]\textsuperscript{+}: 397.0279; Found: 397.8125.

Diethyl 2-(6-methoxy-2-oxo-2H-chromen-4-yl)succinate (99a)

Following the general procedure, reaction of diethyl 2-(4-methoxy-2-((E)-2H-oxoprop-1-enyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded diethyl 2-(6-methoxy-2-oxo-2H-chromen-4-yl)succinate as viscous liquid

Chemical Formula: C\textsubscript{18}H\textsubscript{20}O\textsubscript{7}

Yield: For Z: 62 mg (62%); For E: 76 mg (76%).

IR (film) \(\nu\)\textsubscript{max} 2918, 2850, 1735, 1719 cm\textsuperscript{-1}.
Diethyl 2-(8-methoxy-2-oxo-2H-chromen-4-yl)succinate (100a)

Following the general procedure, reaction of diethyl 2-(2-methoxy-6-((E)-3-oxoprop-1-ethyl)phenoxy)but-2-enedioate (100 mg), 1,3-dimesityl imidazolium chloride (15 mol %) and DBU (20 mol %) afforded diethyl 2-(8-methoxy-2-oxo-2H-chromen-4-yl)succinate as viscous liquid.

Chemical Formula: C_{18}H_{26}O_{7}

Yield: For Z: 67 mg (67%); For E: 74 mg (74%).

IR (film) ν_{max} 2916, 2849, 1729 cm\(^{-1}\).

\(^{1}H\) NMR (500 MHz, CDCl\(_3\)) δ = 7.32 – 7.23 (m, 1H), 7.18 – 7.10 (m, 2H), 6.34 (s, 1H), 4.42 (dd, J = 9.2 Hz, 5.3 Hz, 1H), 4.25 – 4.14 (m, 4H), 3.86 (s, 3H), 3.22 (dd, J = 17.1 Hz, 9.2 Hz, 1H), 2.72 (dd, J = 17.1 Hz, 5.2 Hz, 1H), 1.25 (dt, J = 18.8 Hz, 7.1 Hz, 6H). \(^{13}C\) NMR (126 MHz, CDCl\(_3\)) δ = 170.5, 170.3, 160.0, 156.1, 151.1, 148.3, 119.4, 118.5, 118.4, 115.5, 107.1, 62.0, 61.2, 55.8, 42.8, 35.7, 14.1, 14.0. HRMS (FAB) calcd for [M+H]+: 349.1279; Found: 349.1214.

Methyl 3-(2-oxo-2H-chromen-4-yl)propanoate (101a)

Following the general procedure, reaction of (E)-Methyl 3-(2-((E)-3-oxoprop-1-ethyl)phenoxy)acrylate (100 mg), 1,3-dimesityl imidazolium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(2-oxo-2H-chromen-4-yl)propanoate 101a as white solid in 60% (60 mg) and methyl 3-(2-oxo-2H-chromen-3-yl)propanoate 101b as viscous liquid in 30% (30 mg).
Chemical Formula: $\text{C}_{13}\text{H}_{12}\text{O}_4$

m p 64-66 °C.

IR (film) $v_{\text{max}}$ 2917, 1721 cm$^{-1}$.

$^1\text{H NMR}$ ($500$ MHz, CDCl$_3$) $\delta = 7.64$ (d, $J = 7.9$ Hz, 1H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 8.2$ Hz, 1H), 7.29 (t, $J = 7.6$ Hz, 1H), 6.26 (s, 1H), 3.73 (s, 3H), 3.13 (t, $J = 7.6$ Hz, 2H), 2.73 (t, $J = 7.5$ Hz, 2H).

$^{13}\text{C NMR}$ ($126$ MHz, CDCl$_3$) $\delta = 171.7$, 159.9, 153.8, 153.4, 131.7, 124.1, 123.9, 118.9, 117.5, 114.2, 51.9, 3.8, 26.5. HRMS (FAB) calcd for [M+H]$^+$: 233.0806; Found: 233.0845.

Methyl 3-(2-oxo-2$H$-chromen-3-yl)propanoate (101b)

Chemical Formula: $\text{C}_{13}\text{H}_{12}\text{O}_4$

Yield: 30 mg (30%).

IR (film) $v_{\text{max}}$ 2917, 1713 cm$^{-1}$.

$^1\text{H NMR}$ ($500$ MHz, CDCl$_3$) $\delta = 7.60$ (s, 1H), 7.50 – 7.43 (m, 2H), 7.32 (d, $J = 8.3$ Hz, 1H), 7.25 (t, $J = 7.4$ Hz, 1H), 3.67 (s, 3H), 2.89 (t, $J = 7.1$ Hz, 2H), 2.72 (t, $J = 7.1$ Hz, 2H). $^{13}\text{C NMR}$ ($126$ MHz, CDCl$_3$) $\delta = 172.9$, 161.3, 153.4, 139.9, 130.8, 127.8, 127.4, 124.3, 119.4, 116.5, 51.6, 31.9, 26.6. HRMS (FAB) calcd for [M+H]$^+$: 233.0806; Found: 233.0828.

Methyl 3-(6-methyl-2-oxo-2$H$-chromen-4-yl)propanoate (102a)

Following the general procedure, reaction of methyl 3-(4-methyl-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(6-methyl-2-oxo-2$H$-chromen-4-yl)propanoate 102a as white powder in 21% (21 mg) and methyl 3-(6-methyl-2-oxo-2$H$-chromen-3-yl)propanoate 102b as viscous liquid in 14% (14 mg).

Chemical Formula: $\text{C}_{14}\text{H}_{14}\text{O}_4$

IR (film) $v_{\text{max}}$ 2953, 1724 cm$^{-1}$.

$^1\text{H NMR}$ ($500$ MHz, CDCl$_3$): $\delta = 7.40$ (s, 1H), 7.33 (d, $J =$8.4, 1H), 7.23 (d, 1H, $J = 8.4$ Hz), 6.23 (s, 1H), 3.74 (s, 3H), 3.10 (t, 2H, $J = 7.7$ Hz), 2.76 – 2.70 (m, 2H), 2.44 (s,
3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 171.9$, 160.4, 153.5, 151.9, 133.8, 132.7, 123.7, 118.6, 117.2, 114.1, 52.0, 31.8, 26.4, 21.1.

Methyl 3-(6-methyl-2-oxo-2H-chromen-3-yl)propanoate (102b)

Chemical Formula: C$_{14}$H$_{14}$O$_4$

IR (film) $\nu_{\text{max}}$ 2920, 1717 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.53$ (s, 1H), 7.26 (s, 1H), 7.23 – 7.18 (m, 2H), 3.66 (s, 3H), 2.87 (t, 2H, $J = 7.1$ Hz), 2.70 (t, 2H, $J = 7.1$ Hz), 2.40 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 172.8$, 147.2, 140.4, 128.4, 123.6, 116.1, 51.5, 34.5, 32.0, 31.4, 26.7.

Methyl 3-(6-chloro-2-oxo-2H-chromen-4-yl)propanoate (103a)

Following the general procedure, reaction of methyl 3-(4-chloro-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg), 1,3-dimesitylimidazolium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(6-chloro-2-oxo-2H-chromen-4-yl)propanoate 103a as white powder in 60% (60 mg) and methyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)propanoate 103b as white powder in 35% (35 mg).

Chemical Formula: C$_{13}$H$_{11}$O$_4$Cl

IR (film) $\nu_{\text{max}}$ 2921, 1724 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.75$ (d, 1H, $J = 2.2$ Hz), 7.63 (dd, 1H, $J = 8.8, J_2 = 2.2$ Hz), 7.24 (d, 1H, $J = 8.8$ Hz), 6.29 (s, 1H), 3.74 (s, 1H), 3.09 (t, 1H, $J = 7.5$ Hz), 2.74 (t, 1H, $J = 7.5$ Hz). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta = 171.7$, 152.6, 131.8, 130.7, 129.9, 128.8, 123.6, 118.8, 115.1, 52.0, 32.0, 29.4, 22.7.

Methyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)propanoate (103b)

Chemical Formula: C$_{13}$H$_{11}$O$_4$Cl

IR (film) $\nu_{\text{max}}$ 2920, 1739, 1718 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.58$ (d, 1H, $J = 2.2$ Hz), 7.56 (dd, 1H, $J = 8.7, 2.3$ Hz), 7.52 (s, 1H), 7.20 (d, 1H, $J = 8.7$ Hz), 3.67 (s, 3H), 2.88 (t, 2H, $J = 7.0$ Hz),
Methyl 3-(6-bromo-2-oxo-2H-chromen-4-yl)propanoate (104a)

Following the general procedure, reaction of methyl 3-(4-bromo-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(6-bromo-2-oxo-2H-chromen-4-yl)propanoate 104a as white powder in 39% (39 mg) and methyl 3-(6-bromo-2-oxo-2H-chromen-3-yl)propanoate 104b as white powder in 41% (41 mg).

**Chemical Formula:** C₁₃H₁₁O₄Br

**IR (film) v max 2919, 1735 cm⁻¹.**

**¹H NMR (500 MHz, CDCl₃):** δ = 7.75(d, 1H, J = 2.5 Hz), 7.64-7.62(m, 1H), 7.24(d, 1H, J = 9 Hz), 2.29(s, 1H), 3.74(s, 3H), 3.11-3.08(m, 2H), 2.74(t, 2H, J = 7.5 Hz). **¹³C NMR (126 MHz, CDCl₃):** δ = 189.7, 152.6, 134.7, 129.9, 126.7, 123.1, 120.6, 119.1, 117.2, 115.0, 52.1, 31.5, 26.3.

Methyl 3-(6-bromo-2-oxo-2H-chromen-3-yl)propanoate (104b)

**Chemical Formula:** C₁₃H₁₁O₄Br

**IR (film) v max 2916, 1713 cm⁻¹.**

**¹H NMR (500 MHz, CDCl₃):** δ = 7.58 (d, 1H, J = 2 Hz), 7.55(d, 1H, J = 2.5 Hz), 7.52(s, 1H), 7.20(d, 1H, J = 9 Hz), 3.67(s, 3H), 2.89-2.87(m, 2H), 2.71(t, 2H, J = 7 Hz). **¹³C NMR (126 MHz, CDCl₃):** δ = 172.7, 159.7, 138.6, 133.6, 132.1, 129.7, 118.2, 51.7, 31.8, 26.9.

Methyl 3-(8-methyl-2-oxo-2H-chromen-4-yl)propanoate (105a)

Following the general procedure, reaction of methyl 3-(2-methyl-6-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(8-methyl-2-oxo-2H-chromen-4-yl)propanoate 105a as white powder in 19% (19 mg) and methyl 3-(8-methyl-2-oxo-2H-chromen-3-yl)propanoate 105b as viscous liquid in 32% (32 mg).

**Chemical Formula:** C₁₄H₁₄O₄
**Methyl 3-(8-methyl-2-oxo-2H-chromen-3-yl)propanoate (105b)**

Chemical Formula: $C_{14}H_{14}O_4$

IR (film) $\nu_{max}$ 2918, 1720 cm$^{-1}$.

$^1$H NMR (126 MHz, CDCl$_3$): $\delta$ = 7.48 (d, 1H, $J$ = 7.9 Hz), 7.38 (d, 1H, $J$ = 7.3 Hz), 6.26 (s, 1H), 3.73 (s, 3H), 3.15 – 3.09 (m, 2H), 2.75 – 2.70 (m, 2H), 2.47 (s, 3H).

$^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ = 172.0, 160.5, 154.1, 152.1, 136.4, 133.1, 129.7, 129.5, 129.0, 126.9, 123.8, 121.6, 118.6, 113.9, 52.0, 32.0, 31.6, 26.7, 22.7, 15.8.

**Methyl 3-(6-tert-butyl-2-oxo-2H-chromen-4-yl)propanoate (106a)**

Following the general procedure, reaction of methyl 3-(4-tert-butyl-2-((E)-3-oxoprop-1-enyl)phenoxy)acrylate (100 mg), 1,3-dimesityl imidazolinium chloride (15 mol %) and DBU (20 mol %) afforded methyl 3-(6-tert-butyl-2-oxo-2H-chromen-4-yl)propanoate 106a as viscous liquid in 14% (14 mg) and methyl 3-(6-tert-butyl-2-oxo-2H-chromen-3-yl)propanoate 106b as viscous liquid in 4% (4 mg).

Chemical Formula: $C_{17}H_{20}O_4$

IR (film) $\nu_{max}$ 2956, 2869, 1736, 1724 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.58 (s, 1H), 7.56 (d, 1H, $J$ = 2 Hz), 7.29-7.26 (m, 1H), 6.24 (s, 1H), 3.74 (s, 3H), 3.16-3.13 (m, 2H), 2.74 (t, 2H, $J$ = 7.5 Hz), 1.37 (s, 9H). $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ = 171.9, 153.9, 151.8, 147.2, 129.4, 119.9, 118.2, 117.0, 113.9, 52.0, 34.7, 31.8, 31.5, 26.4.
Methyl 3-(6-tert-butyl-2-oxo-2H-chromen-3-yl)propanoate (106b)

Chemical Formula: C_{17}H_{20}O_4

IR (film) \text{v}_{\text{max}} 2957, 1717 \text{cm}^{-1}.

^{1}H \text{ NMR (126 MHz, CDCl}_3): \delta = 7.58 (s, 1H), 7.5 (dd, 1H, J = 8.5 Hz), 7.39 (d, 1H, J = 2.5 Hz), 7.26-7.23 (m, 1H), 3.67 (s, 3H), 2.87 (t, 2H, J = 7 Hz), 2.70 (t, 2H, J = 7 Hz), 1.35 (s, 9H).

Methyl 3-(2-oxo-2H-chromen-4-yl)-3-phenylpropanoate (107a)

Following the general procedure, reaction of methyl 3-(2-((E)-3-oxoprop-1-enyl)phenoxy)-3-phenylacrylate (100 mg), 1,3-dimesitylimidazolinium chloride (15 mol \%) and DBU (20 mol \%) afforded methyl 3-(2-oxo-2H-chromen-4-yl)-3-phenylpropanoate as white solid.

Chemical Formula: C_{19}H_{16}O_4

m p: 112-114 °C.

Yield: 45 mg (45%).

IR (film) \text{v}_{\text{max}} 2954, 2919, 1725 \text{cm}^{-1}.

^{1}H \text{ NMR (500 MHz, CDCl}_3): \delta = 7.65 (d, J = 7.4 Hz, 1H), 7.48 - 7.43 (m, 1H), 7.34 - 7.26 (m, 5H), 7.23 (dd, J = 9.6 Hz, 4.4 Hz, 1H), 7.18 (dd, J = 11.2 Hz, 4.0 Hz, 1H), 6.37 (s, 1H), 4.90 (t, J = 7.6 Hz, 1H), 3.65 (s, 3H), 3.06 (dd, J = 16.2 Hz, 7.5 Hz, 1H), 2.96 (dd, J = 16.2 Hz, 7.7 Hz, 1H).

^{13}C \text{ NMR (126 MHz, CDCl}_3): \delta = 170.9, 160.3, 155.7, 153.9, 139.6, 131.6, 129.3, 129.2, 127.76, 127.6, 124.8, 124.2, 118.6, 117.4, 113.6, 51.9, 42.3, 39.7.


4.8. References