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Construct indeno[1,2-*b*]oxepine or *cis*-cyclopropylacrylate by sulfur ylides†

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For the first time, the [4 + 3] or [2 + 1] annulation of crotonate-derived sulfur ylides with arylidenemalononitrile or arylidene-1*H*-indene-1,3(2*H*)-dione is reported using Na_2CO_3 as the base. This protocol is advantageous as it does not require prior preparation of arylidenemalononitrile or arylidene-1*H*-indene-1,3(2*H*)-dione substrates, due to the independent participation of the base in the two reactions. This mild, operationally multicomponent process can be employed for the transformation of a wide variety of commercially available aldehydes into the corresponding indeno[1,2-*b*]oxepine or cyclopropyl acrylate core in moderate to excellent yields under mild conditions.

1. Introduction

Oxygen-containing heterocyclic compounds, especially unsaturated 7-membered oxacycle (oxepine) frameworks, exhibit a wide range of biological properties, such as ion-channel blocking, antiplasmodial, antiviral, antipsychotic, and antifungal activities.[1] Various natural and marine natural products containing the oxepine motif play a vital role in biological processes.[2] The cyclopropyl group is also a vital structural unit in several synthetic and naturally occurring compounds, exhibiting a wide spectrum of biological properties ranging from enzyme inhibition to herbicidal, antibiotic, antitumor, and antiviral activities.[3] Fig. 1 shows some representative examples of these compounds.

Recently, crotonate-derived sulfur ylides have attracted attention in organic synthesis as sources of one-carbon or three-carbon synthons in the presence of an inorganic base.[4] The ability of crotonate-derived sulfur ylides to undergo [*m* + *n*] cycloaddition reactions with various substrates is exploited to construct several cyclic compounds.[5] Tang and co-workers have synthesized vinylaziridine by the diastereoselective annulation of crotonate-derived sulfur ylides with cyclic ketamine (Scheme 1a).[6] Huang and co-workers have reported access to cyclic 2-alkenyl aziridines by sequential annulation using crotonate-derived sulfur ylides as the C3 synthon with α,β-unsaturated cyclic ketimines (Scheme 1b).[5f,7] Huang has synthesized seven-membered nitrogen-heterocycles with moderate-to-excellent yields by the development of a novel [4 + 3] annulation of aza-dienes with crotonate sulfonium salts (Scheme 1c).[8] On the other hand, multicomponent reactions (MCRs), defined as processes that combine at least three reactants in the same pot to generate a product containing most of the atoms of the starting material, have been extensively exploited to prepare small molecules with step economy, energy conservation, and

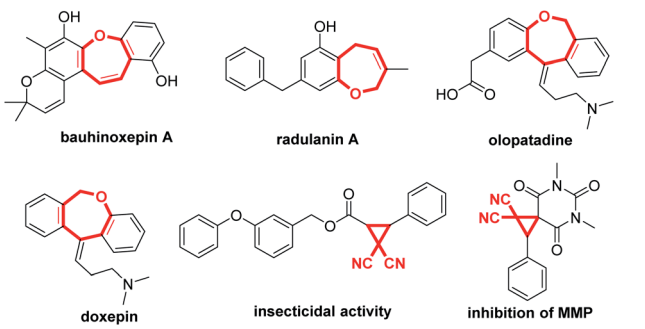
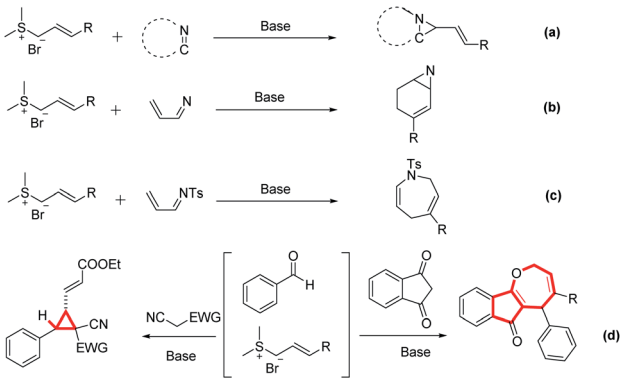


Fig. 1 Biologically active substances containing oxepine motif and cyclopropyl.



Scheme 1 Annulation with crotonate-derived sulfur-ylides.

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emission reduction.[9] As highly reactive reagents, sulfur ylides can react with various electrophiles such as aldehydes, imines, and electron-deficient alkenes.[10] Therefore, the design of MCRs involving sulfur ylides in the presence of aldehydes, 1,3-indanedione, and malononitrile might lead to selectivity problems.

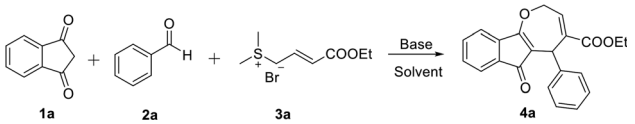
Despite these challenges, it is interesting to develop sulfur ylide-mediated MCRs to construct core structures with medicinal interest. Based on the aforementioned motivation and our continued interest in organocatalysis, herein, the construction of indeno[1,2-*b*]oxepine by the three-component [4 + 3] or [1 + 2] annulation of crotonate-derived sulfur ylides, aldehydes, and 1,3-indanedione or malononitrile (Scheme 1d).

2. Results and discussion

Prior to investigation of the desired MCRs and sulfur ylides, studies were first initiated by investigating reactions between crotonate sulfonium salt **3a** and 2-benzylidene-1*H*-indene-1,3(2*H*)-dione, which was generated by the reaction of 1,3-indanedione (**1a**) and benzaldehyde (**2a**) (Table 1). The reaction was performed in DCM with $NaHCO_3$ as the base at 25 °C (Table 1, entry 1). Gratifyingly, the [4 + 3] annulation product was obtained in 76% yield. The structure of **4a** was confirmed by NMR and HRMS. Reaction conditions were optimized to improve the product yield. Optimization of base was first carried out. When the reaction was conducted in *t*-BuOK, the yield was improved to 85% (Table 1, entry 2). Moderate product yields were observed by using other bases, such as DABCO, TMAF, Cs_2CO_3, NaOH, Et_3N, K_2CO_3 and K_3PO_4 (Table 1, entries 3–9). To our surprise, the product yield was improved to 90% when the base was used instead of Na_2CO_3. Although NaH was also found to afford yields similar to that obtained using Na_2CO_3, the cost-effective base was used for [4 + 3] cyclization (Table 1, entries 10 and 11). After the optimization of the base, the scope of different solvents for the was investigated. Common solvents (CH_3CN, CH_3OH, THF, toluene, DCE) failed to further improve the product yields (Table 1, entries 12–16). In addition, the reaction temperature significantly affected the reaction. By decreasing the temperature from room temperature to 0 °C, the product yield decreased from 90% to 45% even for a longer reaction time of 6 h (Table 1, entry 17). Neither the decrease nor increase the temperature led to the improvement of the yield of **4a** (Table 1, entries 17 and 18).

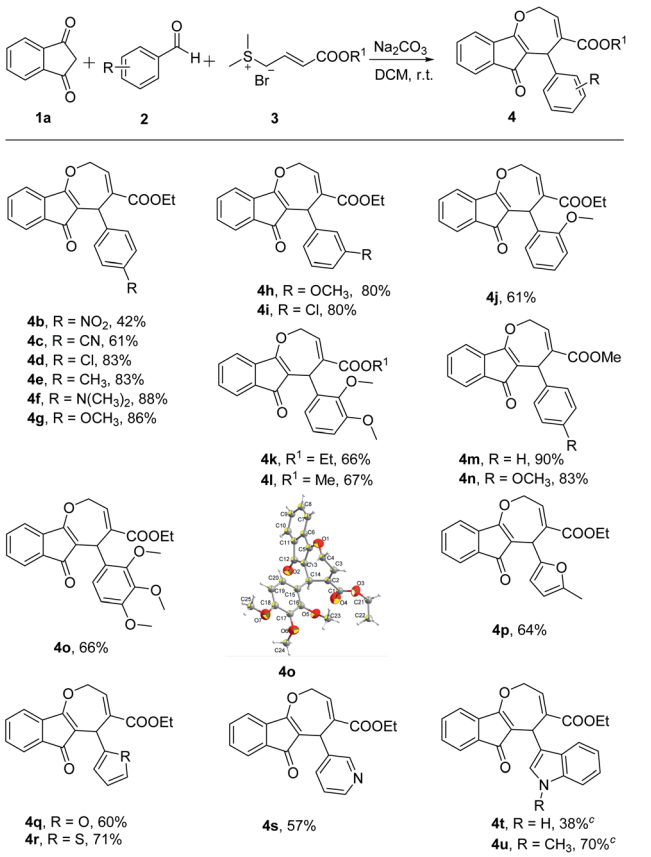
Using optimized reaction conditions (Table 1, entry 11), the substrate scope of the substituted benzaldehydes was first investigated (Scheme 2). Different benzaldehydes with a variety of functional groups such as NO_2, CN, Cl, CH_3, $N(CH_3)_2$, and OCH_3 smoothly reacted with **1a** and **3a** to afford the corresponding indeno[1,2-*b*]oxepine (**4b–4o**) in moderate to excellent yields (42–90%), thus offering a broad range of opportunities for further derivatization. These results revealed that reactions of benzaldehydes bearing electron-donating and electron-

Table 1 Optimization of the MCRs reaction[a]



Entry	Base	Solvent	Temp (°C)	Yield[b] (%)
1	$NaHCO_3$	DCM	25	76
2	*t*-BuOK	DCM	25	85
3	DABCO	DCM	25	75
4	TMAF	DCM	25	76
5	Cs_2CO_3	DCM	25	56
6	NaOH	DCM	25	73
7	Et_3N	DCM	25	70
8	K_2CO_3	DCM	25	79
9	K_3PO_4	DCM	25	50
10	NaH	DCM	25	90
11	**Na_2CO_3**	**DCM**	**25**	**90**
12	Na_2CO_3	CH_3CN	25	79
13	Na_2CO_3	CH_3OH	25	48
14	Na_2CO_3	THF	25	55
15	Na_2CO_3	Toluene	25	67
16	Na_2CO_3	DCE	25	70
17	Na_2CO_3	DCM	0	45
18	Na_2CO_3	DCM	60	88

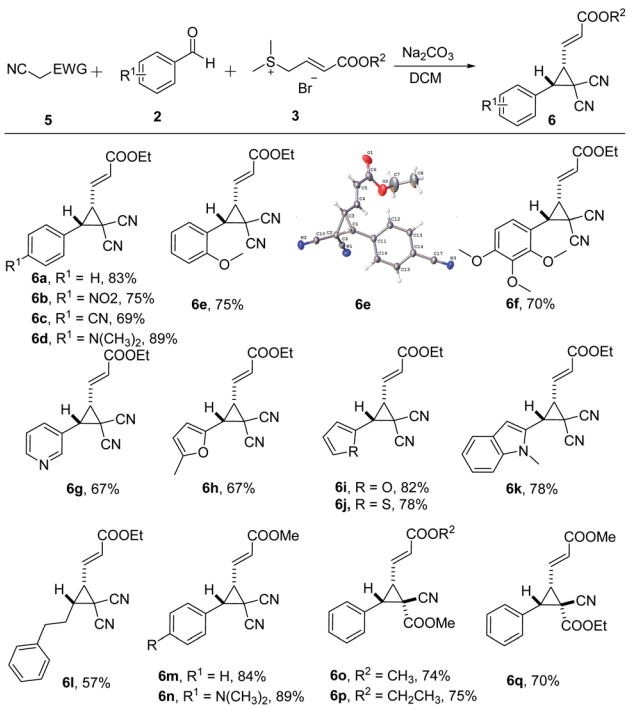
[a] Unless otherwise specified, the reactions were carried out with **1a** (0.2 mmol), **2a** (0.24 mmol) and **3a** (0.3 mmol) in the presence of base (0.4 mmol) in a solvent (2 mL) at 25 °C. [b] Isolated yield.



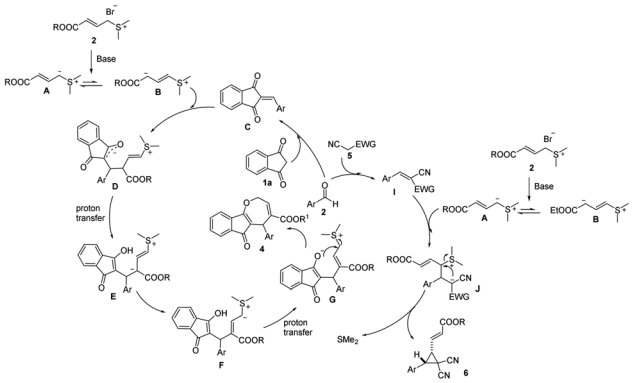
Scheme 2 Scope of the [4 + 3] reactions.[a,b] [a]Unless otherwise specified, the reactions were carried out with **1** (0.2 mmol), **2a** (0.24 mmol) and **3** (0.3 mmol) in the presence of base (0.4 mmol) in a solvent (2 mL) at 25 °C. [b]Isolated yield. [c]The reaction was carried out at 0 °C.

withdrawing groups at the *para* position do not clearly affect this transformation. In particular, aromatic aldehydes bearing a functional group at the *para* position exhibited higher reactivity than their *ortho*- or *meta*-substituted counterpart (**4g** *vs.* **4h** and **4j**). However, for polysubstituted aromatic aldehydes, yields for the desired products were less (**4k**, **4o**) than those for the monosubstituted aromatic aldehydes. In addition, the structure of **4o** was further confirmed by single-crystal X-ray analysis.[11] Moreover, reactions efficiently proceeded when sulfonium salt **3b** was used, affording desired products in moderate to excellent yields (**4l–4n**). As expected, heteroaryl aldehydes, such as 5-methylfurfural, furfural, 2-thenaldehyde, and nicotinaldehyde, performed quite well in the MCRs (**4p–4s**). The use of indole-3-carboxaldehyde afforded low yields of the desired product (**4t**). However, when indole-3-carboxaldehyde was protected using iodomethane, the product yield was increased to 70% (**4u**).

To demonstrate the generality of this transformation, malononitrile was investigated instead of 1,3-indanedione under the optimal conditions. As shown in Scheme 3, electron-withdrawing or electron-donating groups such as nitro, cyano and *N*,*N*-dimethyl, at the *para*-position R^1 in the substrate **2** smoothly reacted with **5a** and **3a** to afford [2 + 1] annulation products **6a–6d** (69–89%) with an excellent *cis*/*trans* ratio. To our delight, the desired *cis*-cyclopropylacrylate **6a** was still exclusively obtained (*cis*/*trans* >99/1) in 80% yield using 1.0 mmol of substrate **5a**. While the methoxy group substituted at the *meta* position in **6e** afforded low product yield (75%), the structure of **6e** was further confirmed by single-crystal X-ray analysis.[12] However, for polysubstituted aromatic aldehydes, the yield of the desired product **6f** was less than that of the monosubstituted aromatic aldehyde. As expected, heteroaryl aldehydes, such as 5-methylfurfural, furfural, 2-thenaldehyde, nicotinaldehyde, and 1-methyl-1*H*-indole-3-carbaldehyde performed quite well in the MCRs (**6g–6k**). In addition, aliphatic aldehydes proved to be suitable substrates to furnish the desired reaction in moderate yields (**6l**, 57%). Moreover, reactions proceeded efficiently proceeded when sulfonium salt **3b** was used, affording desired products in moderate to excellent yields (**6m–6o**, **6q**). Furthermore, cyanoacrylates also afforded the desired products (**6o–6q**). The relative configuration of **6o** was defined on the basis of the phase-sensitive NOESY spectrum. No correlation between hydrogen on cyclopropane and methyl by the NOESY spectrum was observed (see the ESI†).



Scheme 3 Scope of the [2 + 1] reactions.[a,b] [a]Unless otherwise specified, the reactions were carried out with **5** (0.2 mmol), **2** (0.24 mmol) and **3** (0.3 mmol) in the presence of base (0.4 mmol) in a solvent (2 mL) at 25 °C. [b]Isolated yield.



Scheme 4 Plausible reaction mechanism.

Based on the present experimental data and the results described in the literature,[4f–h,5e,7,13] a plausible MCR reaction mechanism can be proposed as shown in Scheme 4. Crotonate-derived ylide **2** was treated with base (Na_2CO_3) to afford allylic ylide **A**, which resonated to **B**. Next, the Michael addition of **B** to **C**, which was formed by **1a** and **2** in the presence of the base catalyst, afforded intermediate **D**. Intermediate **D** subsequently transformed into intermediate **G** *via* two proton-transfer processes, followed by an intramolecular SN_2 nucleophilic substitution to furnish [4 + 3] annulation product **4**. When we **5** was used instead of **1a**, the Michael addition of **A** to **I** in the presence of the base catalyst would lead to intermediate **J**. Then, the subsequent intramolecular nucleophilic addition and elimination of Me_2S further afforded the final product.

3. Conclusions

To the best of our knowledge, for the first time, a novel Na_2CO_3-promoted MCR reaction using crotonate-derived sulfonium salts, aromatic aldehydes, and 1,3-indanedione or malononitrile was developed. Various indeno[1,2-*b*]oxepine and *cis*-cyclopropylacrylate derivatives were obtained in good-to-excellent yields. The advantages of the current protocol included readily available starting materials, mild reaction conditions, good functional group tolerance, and broad substrate scope. Currently, further applications of this MCR

reaction in organic synthesis, as well as investigations on the detailed mechanism, are underway in our laboratory.

4. Experimental section

4.1 General information

Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Agilent DD2400 spectrometer. $CDCl_3$ was used as solvent. Chemical shifts were referenced relative to residual solvent. Melting points were measured with micro melting point apparatus. Infrared spectra were recorded on a FT-IR spectrometer. **1a**, **2** and **5** were prepared from Energy Chemical. **3** were prepared according to the literature procedure.[14]

4.2 Experimental procedures and characterization date

Ethyl-6-oxo-5-phenyl-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4a). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, benzaldehyde **2a** (25.4 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4a** as a Yellow solid (62.3 mg, 90% yield), $R_f = 0.21$ (EtOAc/petroleum ether 1 : 10). Mp 115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.36 (d, J = 6.8 Hz, 1H), 7.28–7.16 (m, 6H), 7.12–7.05 (m, 3H), 5.29 (s, 1H), 4.83 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.6$ Hz, 1H), 4.54 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.6$ Hz, 1H), 4.28–4.16 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.3, 173.6, 166.1, 144.5, 141.9, 139.7, 132.5, 132.1, 131.3, 130.0, 128.6, 127.1, 126.7, 121.3, 118.4, 109.6, 65.1, 61.8, 35.5, 14.3. IR(KBr) ν: 2974, 2918, 1712, 1628, 1579, 1460, 1397, 1243, 1095, 1046. HRMS(EI) (m/z): calcd for $C_{22}H_{18}O_4$ $(M + H)^+$: 347.1278; found: 347.1276.

Ethyl-5-(4-nitrophenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4b). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-nitrobenzaldehyde **2b** (36.2 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4b** as a yellow solid (32.8 mg, 42% yield), $R_f = 0.12$ (EtOAc/petroleum ether 1 : 10). Mp 115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.15 (t, 1H), 8.13 (t, 1H), 7.52–7.47 (m, 3H), 7.39 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.25–7.20 (m, 2H), 5.42 (s, 1H), 4.80 (dd, J_1 = 12.8 Hz, J_2 = 7.2 Hz, 1H), 4.74–4.69 (m, 1H), 4.39–4.26 (m, 2H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.2, 174.1, 165.8, 149.5, 146.8, 143.4, 139.4, 132.8, 132.8, 131.1, 130.5, 128.2, 123.9, 121.6, 118.9, 108.4, 65.2, 62.2, 35.9, 14.3. IR(KBr) ν: 2925, 2855, 1712, 1628, 1523, 1474, 1355, 1116, 990. HRMS(EI) (m/z): calcd for $C_{22}H_{17}NO_6$ $(M + H)^+$: 392.1129; found: 392.1128.

Ethyl-5-(4-cyanophenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4c). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-formylbenzonitrile **2c** (31.4 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4c** as a yellow solid (45.3 mg, 61% yield), $R_f = 0.15$ (EtOAc/petroleum ether 1 : 10). Mp 132 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.57 (d, 2H), 7,46–7.44 (m, 3H), 7.37 (t, J = 7.2 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 2H), 5.38 (s, 1H), 4.81–4.76 (m, 1H), 4.72–4.67 (m, 1H), 4.37–4.24 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.2, 174.1, 165.8, 147.4, 143.4, 139.4, 132.8, 132.7, 132.5, 131.0, 130.4, 128.1, 121.5, 118.9, 118.8, 110.7, 108.3, 65.2, 62.1, 35.9, 14.3. IR(KBr) ν: 2981, 2918, 2231, 1705, 1621, 1515, 1452, 1396, 1242, 1179, 1102, 1046. HRMS(EI) (m/z): calcd for $C_{23}H_{17}NO_4$ $(M + H)^+$: 372.1230; found: 372.1231.

Ethyl-5-(4-chlorophenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4d). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-chlorobenzaldehyde **2d** (33.6 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4d** as a yellow solid (63.1 mg, 83% yield), $R_f = 0.21$ (EtOAc/petroleum ether 1 : 10). Mp 108 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.45 (d, J = 7.2 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.25–7.22 (m, 4H), 7.19–7.15 (m, 2H), 5.31 (s, 1H), 4.89–4.84 (m, 1H), 4.69–4.64 (m, 1H), 4.35–4.25 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.3, 173.8, 166.0, 144.1, 140.5, 139.6, 132.6, 132.6, 132.3, 131.2, 130.2, 128.7, 128.6, 121.4, 118.6, 109.1, 65.1, 62.0, 35.2, 14.3. IR(KBr) ν: 2918, 1705, 1628, 1585, 1410, 1235, 1172, 1109, 1039, 955, 906, 765, 730. HRMS(EI) (m/z): calcd for $C_{22}H_{17}ClO_4$ $(M + H)^+$: 381.0888; found: 381.0890.

Ethyl-6-oxo-5-(*p*-tolyl)-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4e). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5

equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-methylbenzaldehyde **2e** (28.8 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4e** as a Yellow oil (59.8 mg, 83% yield), $R_f = 0.18$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.45 (d, $J = 6.8$ Hz, 1H), 7.37–7.33 (m, 1H), 7.31–7.27 (m, 1H), 7.22–7.13 (m, 4H), 7.08 (d, $J = 8.0$ Hz, 2H), 5.33 (s, 1H), 4.95 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.2$ Hz, 1H), 4.63 (dd, $J_1 = 12.4$ Hz, $J_2 = 8.0$ Hz, 1H), 4.36–4.24 (m, 2H), 2.29 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.4, 173.6, 166.2, 144.6, 139.8, 138.9, 136.3, 132.5, 132.0, 131.3, 130.0, 129.3, 127.1, 121.3, 118.4, 109.8, 65.2, 61.8, 35.3, 21.0, 14.3. IR(KBr) ν: 2911, 2855, 1712, 1628, 1508, 1466, 1403, 1235, 1109, 1039. HRMS(EI) (m/z): calcd for $C_{23}H_{20}O_4$ $(M + H)^+$: 361.1434; found: 361.1436.

Ethyl-5-(4-(dimethylamino)phenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4f). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-(dimethylamino)benzaldehyde **2f** (35.8 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4f** as a yellow oil (68.5 mg, 88% yield), $R_f = 0.15$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.44 (d, $J = 7.2$ Hz, 1H), 7.37–7.33 (m, 1H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.21–7.09 (m, 4H), 6.65 (d, $J = 8.8$ Hz, 2H), 5.27 (s, 1H), 5.01 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.3$ Hz, 1H), 4.63 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.8$ Hz, 1H), 4.35–4.23 (m, 2H), 2.89 (s, 6H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.5, 173.4, 166.4, 149.5, 144.9, 140.0, 132.5, 131.8, 131.4, 129.9, 129.7, 127.9, 121.2, 118.3, 112.8, 110.3, 65.3, 61.8, 40.8, 34.9, 14.4. IR(KBr) ν: 2911, 2841, 1705, 1628, 1515, 1473, 1403, 1340, 1228, 1109, 1046. HRMS(EI) (m/z): calcd for $C_{24}H_{23}NO_4$ $(M + H)^+$: 390.1700; found: 390.1699.

Ethyl-5-(4-methoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4g). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-methoxybenzaldehyde **2g** (32.6 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4g** as a Yellow oil (64.7 mg, 86% yield), $R_f = 0.18$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.44 (d, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.24 (d, $J = 9.2$ Hz, 2H), 7.18–7.12 (m, 2H), 6.81 (d, $J = 8.8$ Hz, 2H), 5.30 (s, 1H), 4.95 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.2$ Hz, 1H), 4.64 (dd, $J_1 = 12.4$ Hz, $J_2 = 8.0$ Hz, 1H), 4.36–4.24 (m, 2H), 3.76 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.4, 173.6, 166.2, 158.4, 144.7, 139.9, 134.0, 132.5, 132.0, 131.3, 130.1, 128.3, 121.3, 118.4, 114.0, 109.9, 65.2, 61.8, 55.4, 35.0, 14.3. IR(KBr) ν: 2925, 1712, 1628, 1515, 1466, 1403, 1249, 1179, 1102, 1039. HRMS(EI) (m/z): calcd for $C_{23}H_{20}NO_5$ $(M + H)^+$: 377.1384; found: 377.1385.

Ethyl-5-(3-methoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4h). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 3-methoxybenzaldehyde **2h** (32.6 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4h** as a yellow oil (60.2 mg, 80% yield), $R_f = 0.18$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.45 (d, $J = 6.8$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 7.22–7.14 (m, 3H), 6.90 (d, $J = 6.8$ Hz, 2H), 6.75–6.72 (m, 1H), 5.34 (s, 1H), 4.97 (dd, $J_1 = 12.4$ Hz, $J_2 = 7.2$ Hz, 1H), 4.63 (dd, $J_1 = 12.4$ Hz, $J_2 = 8.0$ Hz, 1H), 4.37–4.24 (m, 2H), 3.76 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.3, 173.7, 166.1, 159.8, 144.4, 143.6, 139.8, 132.5, 132.2, 131.3, 130.1, 129.6, 121.3, 119.6, 118.5, 113.7, 111.5, 109.5, 65.1, 61.9, 55.3, 35.5, 14.4. IR(KBr) ν: 2932, 2855, 1712, 1628, 1592, 1585, 1452, 1396, 1242, 1109, 1046. HRMS(EI) (m/z): calcd for $C_{23}H_{20}O_5$ $(M + H)^+$: 377.1384; found: 377.1387.

Ethyl-5-(3-chlorophenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4i). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 3-chlorobenzaldehyde **2i** (33.6 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4i** as a yellow oil (60.8 mg, 80% yield), $R_f = 0.22$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.46 (d, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.30 (t, 2H), 7.22–7.16 (m, 5H), 5.33 (s, 1H), 4.87 (dd, $J_1 =$

12.4 Hz, J_2 = 7.2 Hz, 1H), 4.69–4.64 (m, 1H), 4.38–4.24 (m, 2H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.2, 173.9, 165.9, 144.0, 143.9, 139.6, 134.5, 132.6, 132.4, 131.2, 130.2, 129.9, 127.3, 127.0, 125.5, 121.4, 118.6, 108.9, 65.1, 62.0, 35.3, 14.3. IR(KBr) ν: 2925, 2855, 1712, 1628, 1585, 1466, 1403, 1235, 1179, 1102, 1032, 983. HRMS(EI) (m/z): calcd for $C_{22}H_{17}ClO_4$ (M + H)$^+$: 381.0888; found: 381.0886.

Ethyl-5-(2-methoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4j). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 2-methoxybenzaldehyde **2j** (32.6 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4j** as a yellow solid (45.9 mg, 61% yield), R_f = 0.19 (EtOAc/petroleum ether 1 : 10). Mp 195 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.45 (d, J = 6.8 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 7.2 Hz, 1H), 7.19 (t, J = 6.8 Hz, 2H), 6.88–6.81 (m, 2H), 6.70 (t, J = 8.0 Hz, 1H), 5.31 (s, 1H), 5.04 (dd, J_1 = 12.4 Hz, J_2 = 8.0 Hz, 1H), 4.53–4.48 (m, 1H), 4.36–4.27 (m, 2H), 3.73 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.7, 174.5, 166.9, 156.4, 146.5, 139.8, 132.4, 131.4, 130.3, 130.0, 128.7, 128.2, 128.0, 121.2, 120.2, 118.2, 110.8, 107.8, 64.5, 61.2, 55.0, 32.5, 14.4. IR(KBr) ν: 2932, 2848, 1740, 1691, 1642, 1543, 1515, 1459, 1424, 1102, 1046, 997. HRMS(EI) (m/z): calcd for $C_{23}H_{20}O_5$ (M + H)$^+$: 377.1384; found: 377.1386.

Ethyl-5-(2,3-dimethoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno [1,2-*b*]oxepine-4-carboxylate (4k). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 2,3-dimethoxybenzaldehyde **2k** (39.8 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4k** as a yellow solid (53.6 mg, 66% yield), R_f = 0.15 (EtOAc/petroleum ether 1 : 10). Mp 172 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.46 (d, J = 7.2 Hz, 1H), 7.37 (t, 1H), 7.30 (t, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.95 (t, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.82–6.76 (m, 2H), 5.36 (s, 1H), 4.51 (dd, J_1 = 12.4 Hz, J_2 = 8.0 Hz, 1H), 4.51 (dd, J_1 = 12.4 Hz, J_2 = 7.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.7, 174.3, 166.4, 153.2, 146.3, 146.2, 139.8, 136.2, 132.4, 131.5, 130.1, 128.0, 123.5, 121.3, 121.1, 118.3, 111.5, 108.3, 64.8, 61.5, 60.3, 55.9, 32.3, 14.4. IR(KBr) ν: 2918, 2814, 1726, 1466, 1396, 1291, 1228, 1116, 1032, 983. HRMS(EI) (m/z): calcd for $C_{24}H_{22}O_6$ (M + H)$^+$: 407.1489; found: 407.1488.

Methyl-5-(2,3-dimethoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4l). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 2,3-dimethoxybenzaldehyde **2l** (39.8, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4l** as a Yellow solid (52.5 mg, 67% yield), R_f = 0.2 (EtOAc/petroleum ether 1 : 10). Mp 181 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.46 (d, J = 6.8 Hz, 1H), 7.37 (t, 1H), 7.30 (t, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.95 (t, 1H), 6.88 (d, J = 7.2 Hz, 1H), 6.79 (dd, J_1 = 19.2 Hz, J_2 = 8.0 Hz, 2H), 5.34 (s, 1H), 5.00 (dd, J_1 = 12.4 Hz, J_2 = 8.0 Hz, 1H), 4.54–4.49 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.8, 174.4, 166.9, 153.2, 146.2, 145.9, 139.8, 136.1, 132.5, 131.5, 130.1, 128.3, 123.6, 121.3, 121.0, 118.4, 111.6, 108.1, 64.7, 60.3, 55.9, 52.5, 32.3. IR(KBr) ν: 2915, 2808, 1733, 1465, 1387, 1283, 1216, 1109, 1022, 981. HRMS(EI) (m/z): calcd for $C_{23}H_{20}O_6$ (M + H)$^+$: 393.1333; found: 393.1335.

Methyl-6-oxo-5-phenyl-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4m). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, benzaldehyde **2a** (25.4 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4m** as a yellow oil (59.8 mg, 90% yield), R_f = 0.22 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.45 (d, J = 7.2 Hz, 1H), 7.37–7.27 (m, 6H), 7.21–7.15 (m, 3H), 5.37 (s, 1H), 4.91 (dd, J_1 = 12.4 Hz, J_2 = 7.6 Hz, 1H), 4.63 (dd, J_1 = 12.4 Hz, J_2 = 7.6 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.3, 173.6, 166.6, 144.2, 141.7, 139.7, 132.5, 132.4, 131.2, 130.0, 128.6, 127.1, 126.7, 121.2, 118.4, 109.5, 65.1, 52.8, 35.5. IR(KBr) ν: 2925, 2848, 1719, 1628, 1459, 1403, 1242, 1102, 1039, 976. HRMS(EI) (m/z): calcd for $C_{21}H_{16}O_4$ (M + H)$^+$: 333.1121; found: 323.1124.

Methyl-5-(4-methoxyphenyl)-6-oxo-5,6-dihydro-2*H*-indeno [1,2-*b*]oxepine-4-carboxylate (4n). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 4-methoxybenzaldehyde **2g** (32.6 mg, 1.2 equiv.) and DCM (2 mL)

were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4n** as a yellow solid (60.1 mg, 83% yield), $R_f = 0.18$ (EtOAc/petroleum ether 1 : 10). Mp 112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.44 (d, $J = 7.0$ Hz, 1H), 7.35 (t, 1H), 7.29 (t, 1H), 7.23 (d, 2H), 7.20–7.11 (m, 2H), 6.81 (d, $J = 8.8$ Hz, 1H), 5.30 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.4, 173.5, 166.7, 158.4, 144.4, 139.8, 133.9, 132.5, 132.3, 131.3, 130.1, 128.2, 121.3, 118.5, 114.0, 109.9, 65.2, 55.4, 52.8, 35.0. IR(KBr) ν: 2981, 2925, 1712, 1628, 1508, 1459, 1403, 1242, 1186, 1095, 1053. HRMS(EI) (m/z): calcd for $C_{22}H_{18}O_5$ $(M + H)^+$: 363.1227; found: 363.1225.

Ethyl-6-oxo-5-(2,3,4-trimethoxyphenyl)-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4o). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 2,3,4-trimethoxybenzaldehyde **2o** (47 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4o** as a Yellow solid (57.6 mg, 66% yield), $R_f = 0.11$ (EtOAc/petroleum ether 1 : 10). Mp 155 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.44 (d, $J = 7.2$ Hz, 1H), 7.36 (t, 1H), 7.30 (t, 1H), 7.18 (d, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.79 (t, 1H), 6.52 (d, $J = 8.4$ Hz, 1H), 5.25 (s, 1H), 4.56–4.51 (m, 1H), 4.33–4.27 (m, 1H), 4.30 (q, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.8, 174.3, 166.4, 153.1, 151.0, 146.3, 142.5, 139.8, 132.4, 131.4, 130.0, 128.2, 128.1, 123.1, 121.2, 118.3, 108.3, 106.1, 64.7, 61.4, 60.8, 60.4, 56.0, 32.0, 14.4. IR(KBr) ν: 2925, 2855, 1726, 1628, 1466, 1396, 1249, 1109, 1039, 983. HRMS(EI) (m/z): calcd for $C_{25}H_{24}O_7$ $(M + H)^+$: 437.1595; found: 437.1594.

Ethyl-5-(5-methylfuran-2-yl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4p). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 5-methylfuran-2-carbaldehyde **2p** (26.4 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4p** as a yellow oil (44.8 mg, 64% yield), $R_f = 0.23$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.43 (d, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.28 (t, $J = 8.0$ Hz, 1H), 7.19 (t, 2H), 6.05 (d, $J = 2.8$ Hz, 1H), 5.84 (d, $J = 2.0$ Hz, 1H), 5.47 (dd, $J_1 = 12.4$ Hz, $J_2 = 6.8$ Hz, 1H), 5.28 (s, 1H), 4.75 (dd, $J_1 = 12.4$ Hz, $J_2 = 8.0$ Hz, 1H), 4.35–4.21 (m, 2H), 2.22 (s, 3H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.8, 173.5, 165.5, 151.8, 151.4, 141.6, 139.9, 133.1, 132.5, 131.3, 130.0, 121.3, 118.5, 107.6, 107.5, 106.4, 65.4, 61.7, 31.3, 14.3, 13.8. IR(KBr) ν: 2925, 2848, 1719, 1635, 1585, 1459, 1403, 1242, 1109. HRMS(EI) (m/z): calcd for $C_{21}H_{18}O_5$ $(M + H)^+$: 351.1227; found: 351.1225.

Ethyl-5-(furan-2-yl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4q). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, furan-2-carbaldehyde **2q** (23.4 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4q** as a yellow oil (40.3 mg, 60% yield), $R_f = 0.21$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.43 (d, $J = 7.2$ Hz, 1H), 7.35 (t, 1H), 7.29 (d, 2H), 7.19 (dd, $J_1 = 8.0$ Hz, $J_2 = 12.0$ Hz, 2H), 6.27 (dd, $J_1 = 3.2$ Hz, $J_2 = 2.0$ Hz, 1H), 6.18 (d, $J = 3.2$ Hz, 1H), 5.41–5.36 (m, 1H), 5.33 (s, 1H), 4.75 (dd, $J_1 = 12.4$ Hz, $J_2 = 8.0$ Hz, 1H), 4.34–4.23 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.8, 173.7, 165.4, 153.4, 142.1, 141.4, 139.8, 133.3, 132.5, 131.3, 130.1, 121.3, 118.6, 110.5, 107.3, 106.8, 65.3, 61.8, 31.3, 14.3. IR(KBr) ν: 2918, 2848, 1712, 1635, 1543, 1508, 1459, 1403, 1242, 1109, 1046, 1004. HRMS(EI) (m/z): calcd for $C_{25}H_{21}NO_4$ $(M + H)^+$: 337.1071; found: 337.1076.

Ethyl-6-oxo-5-(thiophen-2-yl)-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4r). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, thiophene-2-carbaldehyde **2r** (26.9 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4r** as a yellow oil (50 mg, 71% yield), $R_f = 0.24$ (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.44 (d, $J = 7.2$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.29 (t, 1H), 7.19–7.13 (m, 3H), 6.91–6.88 (m, 2H), 5.46 (s, 1H), 5.19–5.15 (m, 1H) 4.71 (dd, $J_1 = 12.8$ Hz, $J_2 = 8.0$ Hz, 1H), 4.37–4.24 (m, 2H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 193.8, 173.5, 165.5, 145.5, 143.6, 139.6, 132.7, 132.6, 131.1, 130.2, 126.8, 124.7, 124.4, 121.4, 118.7, 109.6, 65.2, 61.9, 32.4, 14.3. IR(KBr) ν: 2925, 2855, 1705, 1628, 1585, 1466, 1396,

1242, 1109, 1046. HRMS(EI) (*m*/*z*): calcd for $C_{20}H_{16}O_4S$ $(M + H)^+$: 353.0842; found: 353.0845.

Ethyl-6-oxo-5-(pyridin-3-yl)-5,6-dihydro-2*H*-indeno[1,2-*b*] oxepine-4-carboxylate (4s). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, nicotinaldehyde **2s** (25.7 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 10) as eluent to give **4s** as a brown oil (39.6 mg, 57% yield), R_f = 0.18 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.56 (s, 1H), 8.44 (d, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 7.2 Hz, 1H), 7.36 (t, 1H), 7.29 (t, J = 7.2 Hz, 1H), 7.22–7.17 (m, 3H), 5.35 (s, 1H), 4.84 (dd, J_1 = 12.4 Hz, J_2 = 7.2 Hz, 1H), 4.73–4.68 (m, 1H), 4.34–4.25 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.2, 174.0, 165.8, 148.4, 148.1, 143.3, 139.5, 137.5, 135.2, 132.7, 132.7, 131.1, 130.3, 129.6, 123.5, 121.4, 118.7, 108.4, 65.2, 62.1, 33.9, 14.3. IR(KBr) ν: 2974, 2925, 1705, 1621, 1585, 1550, 1459, 1410, 1256, 1116, 1046. HRMS(EI) (*m*/*z*): calcd for $C_{21}H_{17}NO_4$ $(M + H)^+$: 348.1230; found: 348.1227.

Ethyl-5-(1*H*-indol-3-yl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*] oxepine-4-carboxylate (4t). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 1H-indole-3-carbaldehyde **2t** (34.8 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4t** as a yellow solid (29.3 mg, 38% yield), R_f = 0.15 (EtOAc/petroleum ether 1 : 10). Mp 183 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.69 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.36 (t, 1H), 7.29 (d, J = 8.0 Hz, 2H), 4.84 (dd, J_1 = 12.4 Hz, J_2 = 7.2 Hz, 1H), 7.12–7.05 (m, 2H), 6.98 (m, 1H), 5.54 (t, J = 1.2 Hz, 1H), 5.40–5.35 (m, 1H), 4.61 (dd, J_1 = 12.4 Hz, J_2 = 8.0 Hz, 1H), 4.39–4.31 (m, 2H), 1.36 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.0, 173.6, 166.1, 144.1, 139.8, 137.0, 132.4, 132.1, 131.3, 129.9, 125.8, 122.9, 122.3, 121.2, 120.1, 119.7, 118.3, 117.4, 111.2, 109.8, 64.5, 61.8, 28.5, 14.3. IR(KBr) ν: 2939, 1719, 1635, 1200, 1144. HRMS(EI) (*m*/*z*): calcd for $C_{25}H_{21}NO_4$ $(M + H)^+$: 86.1543; found: 386.1541.

Ethyl-5-(1-methyl-1*H*-indol-3-yl)-6-oxo-5,6-dihydro-2*H*-indeno[1,2-*b*]oxepine-4-carboxylate (4u). In a 5 mL vial, 1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylium **1a** (29.2 mg, 0.2 mmol, 1.0 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.) and L-proline (2.3 mg, 0.1 equiv.) was added. To this resultant mixture, 1-methyl-1*H*-indole-3-carbaldehyde **2u** (38.1 mg, 1.2 equiv.) and DCM (2 mL) were added and stirred at room temperature overnight. The reaction was confirmed by TLC. Then the solution was diluted with ethyl acetate and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1 : 5) as eluent to give **4u** as a yellow oil (55.9 mg, 70% yield), R_f = 0.12 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.67 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.24–7.18 (m, 3H), 7.12–7.05 (m, 2H), 6.87 (s, 1H), 5.53 (s, 1H), 5.44–5.39 (m, 1H), 4.65–4.60 (m, 1H), 4.39–4.33 (m, 2H), 3.70 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 194.1, 173.6, 166.2, 144.4, 139.9, 137.8, 132.5, 132.1, 131.4, 130.0, 127.7, 126.3, 122.0, 121.3, 120.4, 119.3, 118.3, 115.8, 110.1, 109.3, 64.7, 61.8, 32.9, 29.8, 28.6, 14.4. IR(KBr) ν: 2925, 2855, 1719, 1628, 1585, 1473, 1403, 1235, 1109, 1039, 983. HRMS(EI) (*m*/*z*): calcd for $C_{25}H_{21}NO_4$ $(M + H)^+$: 400.1543; found: 400.1544.

Ethyl-(*E*)-3-(2,2-dicyano-3-phenylcyclopropyl)acrylate (6a). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and benzaldehyde **2a** (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 10) to afford compound **6a** as a brown oil (44.2 mg, 83% yield), R_f = 0.17 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.43 (m, 3H), 7.32 (m, 2H), 6.43–6.34 (m, 2H), 4.23–4.18 (m, 2H), 3.57 (d, J = 9.6 Hz, 1H), 3.15–3.10 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.4, 136.1, 129.9, 129.6, 129.6, 129.1, 128.2, 114.8, 111.1, 61.2, 38.5, 36.4, 14.3, 12.3. IR(KBr) ν: 2927.97, 2253.41, 1721.18, 1646.23, 1271.47, 1162.45, 1039.80, 971.66, 740.00, 692.30. HRMS(EI) (*m*/*z*): calcd for $C_{16}H_{14}N_2O_2$ $(M + H)^+$: 267.1128; found: 267.1123.

Ethyl-(*E*)-3-(2,2-dicyano-3-(4-nitrophenyl)cyclopropyl)acrylate (6b). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 4-nitrobenzaldehyde **2b** (36.2 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6b** as a yellow oil (46.7 mg, 75% yield), R_f = 0.23 (EtOAc/petroleum ether 1 : 5).^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.29 (d, 2H), 7.43 (d, 2H), 7.05 (s, 1H), 4.90 (s, 1H), 4.14 (dd, J_1 = 7.2 Hz, J_2 = 4.0 Hz, 2H), 3.48 (m, 2H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 161.7, 148.6, 141.2, 139.4, 136.6, 129.3, 124.6, 115.9, 113.1, 61.8, 59.6, 44.0, 39.8, 14.1. IR(KBr) ν: 2918, 2245, 1719, 1649, 1494, 1466, 1256, 1165, 1032, 976, 751. HRMS(EI) (*m*/*z*): calcd for $C_{16}H_{13}N_3O_4$ $(M + H)^+$: 312.0979; found: 312.0976.

Ethyl-(*E*)-3-(2,2-dicyano-3-(4-cyanophenyl)cyclopropyl)acrylate (6c). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline

(2.3 mg, 0.1 equiv.) and 4-formylbenzonitrile **2c** (31.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 3) to afford compound **6c** as a white solid (40.2 mg, 69% yield), R_f = 0.22 (EtOAc/petroleum ether 1 : 3). Mp 151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.75 (d, 2H), 7.46 (d, 2H), 6.41 (d, J = 15.2 Hz, 1H), 6.27 (dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 4.21 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 2H), 3.57 (d, J = 10.0 Hz, 1H), 3.20 (t, J = 10.0 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.1, 134.8, 133.3, 133.3, 130.8, 130.1, 117.9, 114.0, 113.9, 110.7, 61.4, 37.5, 35.9, 14.3, 12.4. IR(KBr) ν: 2925, 2231, 1733, 1642, 1438, 1284, 1228, 1046. HRMS(EI) (m/z): calcd for $C_{17}H_{13}N_3O_2$ (M + H)$^+$: 292.1081; found: 292.1080.

Ethyl-(*E*)-3-(2,2-dicyano-3-(4-(dimethylamino)phenyl)cyclopropyl)acrylate (6d). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 4-(dimethylamino)benzaldehyde **2d** (35.8 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6d** as a brown oil (55 mg, 89% yield), R_f = 0.17 (EtOAc/petroleum ether 1 : 5). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.13 (d, 2H), 6.74–6.67 (m, 3H), 6.30 (d, J = 16.0 Hz, 1H), 4.28–4.22 (m, 2H), 3.27 (d, J = 8.4 Hz, 1H), 3.06 (t, J = 8.8 Hz, 1H), 2.98 (s, 6H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.7, 151.2, 138.4, 129.1, 128.2, 115.9, 113.3, 112.7, 112.4, 61.2, 41.1, 40.3, 35.5, 14.9, 14.3. IR(KBr) ν: 2925, 2245, 1712, 1614, 1536, 1354, 1277, 1165, 1095, 1039, 964, 822. HRMS(EI) (m/z): calcd for $C_{18}H_{19}N_3O_2$ (M + H)$^+$: 310.1550; found: 310.1553.

Ethyl-(*E*)-3-(2,2-dicyano-3-(2-methoxyphenyl)cyclopropyl) acrylate (6e). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 2-methoxybenzaldehyde **2e** (32.6 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6e** as a white solid (44.4 mg, 75% yield), R_f = 0.46 (EtOAc/petroleum ether 1 : 3). Mp 118 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.40 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.01–6.94 (m, 2H), 6.45 (dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 6.35 (d, J = 15.6 Hz, 1H), 4.24–4.19 (m, 2H), 3.93 (s, 3H), 3.29 (d, J = 9.6 Hz, 1H), 3.11 (t, J = 9.2 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.6, 158.7, 137.1, 131.2, 130.3, 128.4, 120.8, 116.9, 115.1, 111.7, 111.3, 61.1, 55.8, 36.2, 35.0, 14.3, 13.1. IR(KBr) ν: 2921, 2245, 1714, 1646, 1503, 1462, 1257, 1162, 1026, 978, 753. HRMS(EI) (m/z): calcd for $C_{17}H_{16}N_2O_3$ (M + H)$^+$: 297.1234; found: 297.1229.

Ethyl-(*E*)-3-(2,2-dicyano-3-(2,3,4-trimethoxyphenyl)cyclopropyl)acrylate (6f). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 2,3,4-trimethoxybenzaldehyde **2o** (47 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 3) to afford compound **6f** as a white solid (49.8 mg, 70% yield), R_f = 0.22 (EtOAc/petroleum ether 1 : 3). Mp 115 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 6.81 (d, J = 8.4 Hz, 1H), 6.61 (d, J = 8.4 Hz, 1H), 6.53–6.46 (m, 1H), 6.34 (d, J = 15.6 Hz, 1H), 4.25–4.19 (m, 2H), 4.08 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.29 (d, J = 9.2 Hz, 1H), 3.08 (t, J = 10.0 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl3), δ: 164.6, 155.4, 153.3, 141.9, 137.1, 128.5, 124.7, 115.0, 114.0, 111.8, 106.6, 61.4, 61.1, 61.1, 56.1, 36.2, 35.3, 14.3, 13.0. IR(KBr) ν: 2925, 2848, 2252, 1719, 1656, 1607, 1494, 1466, 1424, 1312, 1263, 1158, 1095, 1039, 976. HRMS(EI) (m/z): calcd for $C_{19}H_{20}N_2O_5$ (M + H)$^+$: 357.1445; found: 357.1447.

Ethyl-(*E*)-3-(2,2-dicyano-3-(pyridin-3-yl)cyclopropyl)acrylate (6g). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and nicotinaldehyde **2s** (25.7 mg, 1.2 equiv.) (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6g** as a yellow oil (35.8 mg, 67% yield), R_f = 0.24 (EtOAc/petroleum ether 1 : 5). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 8.66 (d, J = 3.6 Hz, 1H), 8.52 (s, 1H), 7.56 (dt, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 7.02 (dd, J_1 = 4.0 Hz, J_2 = 2.4 Hz, 1H), 4.81 (s, 1H), 4.19–4.08 (m, 2H), 3.51–3.39 (m, 2H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 161.8, 150.9, 149.2, 139.0, 136.6, 135.8, 130.1, 124.1, 116.1, 113.3, 61.7, 57.8, 43.8, 40.0, 14.1. IR(KBr) ν: 1712, 1642, 1249, 1102, 1025, 709. HRMS(EI) (m/z): calcd for $C_{15}H_{13}N_3O_2$ (M + H)$^+$: 268.1081; found: 268.1085.

Ethyl-(*E*)-3-(2,2-dicyano-3-(5-methylfuran-2-yl)cyclopropyl) acrylate (6h). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 5-methylfuran-2-carbaldehyde **2p** (26.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 10) to afford compound **6h** as a brown oil (36.2 mg, 67% yield), R_f = 0.45 (EtOAc/petroleum ether 1 : 5). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 6.81 (dd, J_1 = 15.6, J_2 = 10.0 Hz, 1H), 6.33 (d, 2H), 5.99 (s, 1H), 4.27–4.21 (m, 2H), 3.43 (d, J = 9.6 Hz, 1H), 3.05 (t, J = 10.0 Hz, 1H), 2.30 (s, 3H), 1.31 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.5, 154.6, 140.5, 135.7, 129.5, 114.2, 113.6, 110.9, 107.2, 61.2, 35.4, 32.9, 14.3, 13.7, 12.7. IR(KBr) ν: 2921, 2362, 1714, 1653, 1278, 1039, 978, 571. HRMS(EI) (m/z): calcd for $C_{15}H_{14}N_2O_3$ (M + H)$^+$: 271.1077; found: 277.1072.

Ethyl-(*E*)-3-(2,2-dicyano-3-(furan-2-yl)cyclopropyl)acrylate (6i). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and furan-2-carbaldehyde **2q** (23.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The

residue was purified by column chromatography (EA : PE, 1 : 10) to afford compound **6i** as a yellow oil (42 mg, 82% yield), R_f = 0.5 (EtOAc/petroleum ether 1 : 5). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.46 (d, 1H), 6.69 (dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 6.48–6.39 (m, 2H), 6.32 (t, J = 17.2 Hz, 1H), 4.26–4.21 (m, 2H), 2.78 (d, J = 10.0 Hz, 1H), 1.81 (s, 1H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.4, 146.5, 144.1, 143.7, 136.5, 128.9, 111.3, 111.2, 110.8, 61.1, 42.5, 37.6, 23.0, 14.2. IR(KBr) ν: 2918, 2245, 1712, 1656, 1452, 1270, 1039, 976, 744, 667. HRMS(EI) (m/z): calcd for $C_{14}H_{12}N_2O_3$ (M + H)$^+$: 257.0921; found: 257.0923.

Ethyl-(*E*)-3-(2,2-dicyano-3-(thiophen-2-yl)cyclopropyl)acrylate (6j). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and thiophene-2-carbaldehyde **2s** (26.9 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 10) to afford compound **6j** as a yellow oil (42.4 mg, 78% yield), R_f = 0.24 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.39 (d, J = 5.2 Hz, 1H), 7.16–7.14 (m, 1H), 7.07–7.04 (m, 1H), 6.67–6.61 (m, 1H), 6.37 (d, J = 15.6 Hz, 1H), 4.23 (q, 2H), 3.59 (d, J = 9.6 Hz, 1H), 3.14 (t, 1H), 1.30 (t, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.4, 135.3, 129.9, 129.8, 129.7, 128.1, 127.8, 114.2, 110.9, 61.3, 36.8, 34.2, 14.3, 13.9. IR(KBr) ν: 2918, 2245, 1719, 1649, 1459, 1375, 1319, 1277, 1172, 1102, 1039, 969, 857, 702. HRMS(EI) (m/z): calcd for $C_{14}H_{12}N_2O_2S$ (M + H)$^+$: 273.0692; found: 273.0694.

Ethyl-(*E*)-3-(2,2-dicyano-3-(1-methyl-1*H*-indol-2-yl)cyclopropyl)acrylate (6k). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 1-methyl-1*H*-indole-3-carbaldehyde **2u** (38.1 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 3) to afford compound **6k** as a brown yellow (49.8 mg, 78% yield), R_f = 0.21 (EtOAc/petroleum ether 1 : 3). Mp 113 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.62 (d, J = 8.0 Hz, 1H), 7.37–7.31 (m, 2H), 7.25–7.22 (m, 1H), 7.06 (s, 1H), 6.79 (dd, J_1 = 15.6 Hz, J_2 = 8.8 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 4.30–4.24 (m, 2H), 3.81 (s, 3H), 3.45 (d, J = 8.4 Hz, 1H), 3.02 (t, J = 8.8 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.7, 138.3, 137.2, 128.4, 127.5, 123.2, 120.7, 118.2, 113.2, 112.9, 110.2, 104.3, 61.3, 36.5, 33.9, 33.3, 14.9, 14.3. IR(KBr) ν: 2918, 1719, 1656, 1466, 1375, 1270, 1214, 1039, 976, 737. HRMS(EI) (m/z): calcd for $C_{19}H_{17}N_3O_2$ (M + H)$^+$: 320.1394; found: 320.1389.

Ethyl-(*E*)-3-(2,2-dicyano-3-phenethylcyclopropyl)acrylate (6l). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 3-phenylpropanal **2v** (32.2 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 10) to afford compound **6l** as a brown oil (33.5 mg, 57% yield), R_f = 0.24 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.32 (t, 2H), 7.24–7.18 (m, 3H), 6.48 (dd, J_1 = 15.6 Hz, J_2 = 10.0 Hz, 1H), 6.18 (d, J = 15.2 Hz, 1H), 4.26–4.20 (m, 2H), 2.91–2.78 (m, 2H), 2.73 (t, J = 10.0 Hz, 1H), 2.24–2.18 (m, 1H), 2.13–1.94 (m, 2H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.5, 139.2, 134.7, 129.5, 129.0, 128.7, 128.7, 128.6, 127.0, 114.6, 111.4, 61.2, 35.6, 35.1, 34.1, 27.4, 14.3, 11.1. IR(KBr) ν: 2924, 1634.18, 1454.10, 1202.00, 1036.32, 748.19, 697. HRMS(EI) (m/z): calcd for $C_{18}H_{18}N_2O_2$ (M + H)$^+$: 295.1441; found: 295.1445.

Methyl-(*E*)-3-(2,2-dicyano-3-phenylcyclopropyl)acrylate (6m). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and benzaldehyde **2a** (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6m** as a white solid (42.3 mg, 84% yield), R_f = 0.16 (EtOAc/petroleum ether 1 : 10). Mp 122 °C; ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.37 (s, 3H), 7.21–7.15 (m, 1H), 6.33–6.32 (m, 2H), 3.69 (d, J = 3.6 Hz, 3H), 3.52 (d, J = 9.6 Hz, 1H), 3.10–3.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 164.4, 135.3, 130.0, 129.7, 129.7, 128.1, 127.8, 114.2, 110.9, 61.3, 36.8, 34.2, 14.3, 13.9. IR(KBr) ν: 2918, 2848, 2252, 1726, 1656, 1438, 1270, 1039, 737, 695. HRMS(EI) (m/z): calcd for $C_{15}H_{12}N_2O_2$ (M + H)$^+$: 253.0972; found: 253.0966.

Methyl-(*E*)-3-(2,2-dicyano-3-(4-(dimethylamino)phenyl)cyclopropyl)acrylate (6n). A mixture of malononitrile **5a** (13.2 mg, 1 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and 4-(dimethylamino)benzaldehyde **2f** (35.8 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6n** as a brown oil (52.5 mg, 89% yield), R_f = 0.34 (EtOAc/petroleum ether 1 : 5). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.13 (d, J = 8.8 Hz, 2H), 6.75–6.68 (m, 3H), 6.31 (d, J = 15.2 Hz, 1H), 3.79 (s, 3H), 3.27 (d, J = 8.4 Hz, 1H), 3.06 (t, J = 8.8 Hz, 1H), 2.98 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.1, 151.2, 138.8, 129.1, 127.7, 115.9, 113.3, 112.6, 112.4, 52.3, 41.2, 40.3, 35.5, 14.9. IR(KBr) ν: 2918, 1726, 1529, 1277, 1116, 1046, 983. HRMS(EI) (m/z): calcd for $C_{17}H_{17}N_3O_2$ (M + H)$^+$: 296.1394; found: 296.1396.

Methyl-1-cyano-2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-3-phenylcyclopropane-1-carboxylate (6o). A mixture of methyl 2-cyanoacetate **5b** (19.8 mg, 1 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and benzaldehyde **2a** (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6o** as a white oil (42.2 mg, 74% yield), R_f = 0.15 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.42–7.36 (m, 3H), 7.29 (d, 2H), 6.95 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.25 (d, J = 15.6 Hz, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.53 (d, J = 8.4 Hz, 1H), 3.08 (t, 1H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.7, 165.1, 139.6, 132.0, 129.1, 129.0, 128.3, 126.6, 115.6, 54.1, 52.0, 39.6, 38.1, 29.8. IR(KBr) ν: 1726, 1649,

1438, 1277, 1249, 983, 702. HRMS(EI) (*m*/*z*): calcd for $C_{16}H_{15}NO_4$ $(M + H)^+$: 286.1074; found: 286.1070.

Methyl-1-cyano-2-((*E*)-3-ethoxy-3-oxoprop-1-en-1-yl)-3-phenylcyclopropane-1-carboxylate (6p). A mixture of 2-cyanoacetate **5b** (19.8 mg, 1 equiv.), (*E*)-(4-ethoxy-4-oxobut-2-en-1-yl) dimethylsulfonium bromide **3a** (76.5 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and benzaldehyde **2a** (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6p** as a white oil (44.9 mg, 75% yield), R_f = 0.16 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.42–7.36 (m, 3H), 7.30 (d, J = 6.8 Hz, 2H), 6.97–6.91 (m, 1H), 6.24 (d, 1H), 4.25–4.19 (m, 2H), 3.88 (s, 3H), 3.54 (d, J = 8.8 Hz, 1H), 3.07 (t, J = 9.2 Hz, 1H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.3, 165.1, 139.3, 132.0, 129.1, 129.0, 128.3, 127.1, 115.6, 60.9, 54.1, 39.6, 38.2, 29.7, 14.3. IR(KBr) ν: 2245, 1712, 1649, 1438, 1277, 1242, 1179, 1123, 1032, 983, 695. HRMS(EI) (*m*/*z*): calcd for $C_{17}H_{17}NO_4$ $(M + H)^+$: 300.1230; found: 300.1232.

Ethyl-1-cyano-2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-3-phenylcyclopropane-1-carboxylate (6q). A mixture of ethyl 2-cyanoacetate **5c** (22.6 mg, 1 equiv.), (*E*)-(4-methoxy-4-oxobut-2-en-1-yl)dimethylsulfonium bromide **3b** (72.3 mg, 1.5 equiv.), Na_2CO_3 (42 mg, 2 equiv.), L-proline (2.3 mg, 0.1 equiv.) and benzaldehyde **2a** (25.4 mg, 1.2 equiv.) in DCM. The reaction mixture was stirred at 0 °C overnight. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography (EA : PE, 1 : 5) to afford compound **6q** as a yellow oil (41.9 mg, 70% yield), R_f = 0.15 (EtOAc/petroleum ether 1 : 10). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.43–7.36 (m, 3H), 7.31–7.29 (m, 2H), 6.96 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.24 (d, J = 15.6 Hz, 1H), 4.36–4.30 (m, 2H), 3.76 (s, 3H), 3.53 (d, J = 8.4 Hz, 1H), 3.06 (t, J = 8.8 Hz, 1H), 1.36 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$), δ: 165.6, 164.5, 139.7, 132.0, 129.0, 128.9, 128.2, 126.4, 115.5, 63.5, 51.9, 39.3, 38.0, 29.9, 14.1. IR(KBr) ν: 2925, 1733, 1649, 1508, 1284, 990, 702. HRMS(EI) (*m*/*z*): calcd for $C_{17}H_{17}NO_4$ $(M + H)^+$: 300.1230; found: 300.1234.

Conflicts of interest

There are no conflicts to declare.

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