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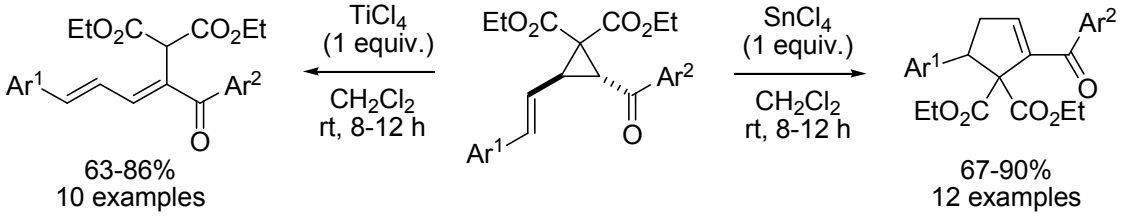
Lewis Acid-Mediated Ring-Opening Reactions of *trans*-2-Aroyl-3-styryl-cyclopropane-1,1-dicarboxylates: Access to Cyclopentenes and *E*,*E*-1,3-Dienes

Murugesan Thangamani and Kannupal Srinivasan*

School of Chemistry, Bharathidasan University, Tiruchirapalli 620 024, Tamil Nadu, India

srinivasank@bdu.ac.in



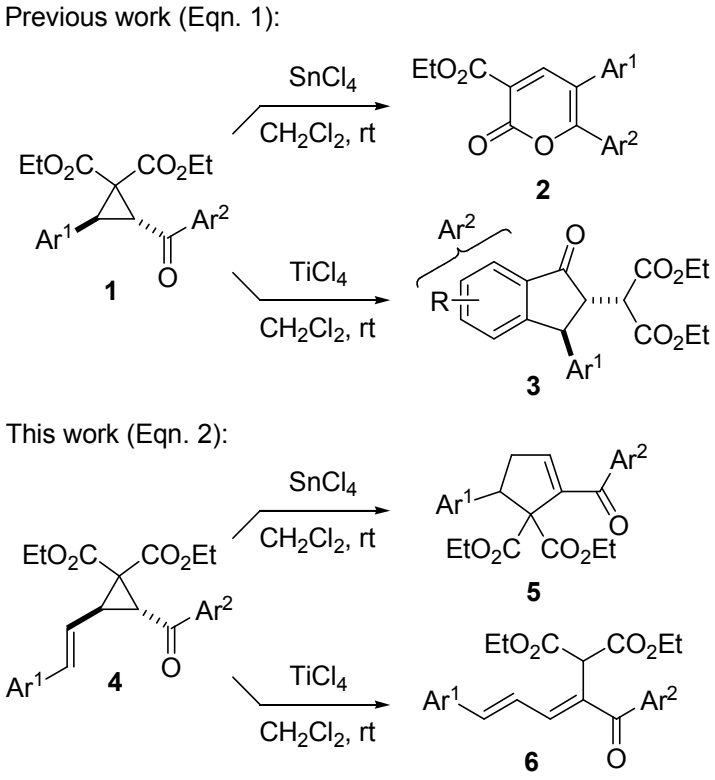
Abstract: The ring-opening reaction of *trans*-2-aroyl-3-styryl-cyclopropane-1,1-dicarboxylates was investigated with different Lewis acids. With $SnCl_4$, the cyclopropane dicarboxylates afforded cyclopentene derivatives through ring opening followed by cyclization (vinylcyclopropane-cyclopentene rearrangement). With $TiCl_4$, they furnished *E*,*E*-1,3-diene derivatives stereoselectively *via* ring opening followed by proton elimination.

INTRODUCTION

The popularity of donor-acceptor (D-A) cyclopropanes as versatile building blocks in organic synthesis is mainly due to their easy accessibility and diverse reactivity.[1] By varying the donor and acceptor groups and placing a suitable group in the other vicinal position, the synthetic potential of D-A cyclopropanes could be expanded vastly. Among different types of reactions of

D-A cyclopropanes, their ring opening triggered by Lewis acids and/or nucleophiles constitutes one of the effective means for synthesizing various cyclic and acylic products.[2]

A previous report from our laboratory has shown that *trans*-2-aroyl-3-aryl-cyclopropane-1,1-dicarboxylates **1** upon treatment with $AlCl_3$ or $SnCl_4$ gave 2-pyrones **2**, whereas with $TiCl_4$, they form 1-indanones **3** (Scheme 1, Eqn. 1).[3] In the present work, we found that similar cyclopropanes **4** having a styryl group instead of aryl as donor behaved very differently with the same Lewis acids and afforded either cyclopentenes **5** or 1,3-dienes **6** as products (Scheme 1, Eqn. 2). The transformation of **4** to **5** is essentially a vinylcyclopropane-cyclopentene rearrangement, which is well-known for its intriguing mechanism and application in the total synthesis of natural products.[4] It is noteworthy that both cyclopentene and 1,3-diene cores are present in numerous natural products[5] and also many cyclopentene and 1,3-diene derivatives serve as valuable synthetic precursors.[6,7] Various methods have been reported for the synthesis of cyclopentenes[8] and also, for 1,3-dienes[9] and the present work represents a novel unified approach for the access of both types of products from D-A cyclopropanes. Moreover, the work demonstrates how a subtle change in the D-A cyclopropane structure influences the reaction outcome drastically.

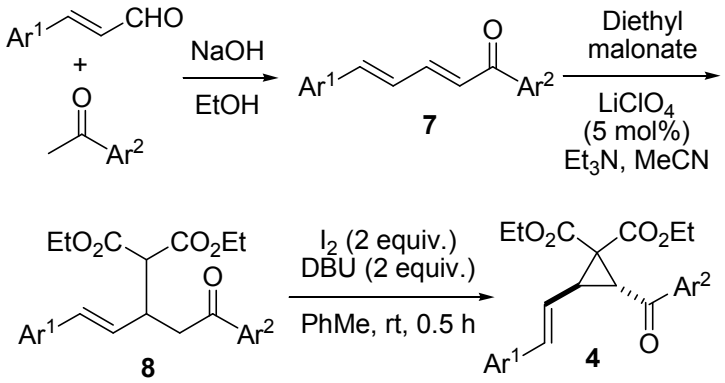


Scheme 1. Comparison of Lewis acid mediated ring opening reactions of **1** and **4**.

RESULTS AND DISCUSSION

The D-A cyclopropanes **4** required for the present study were prepared as single *trans*-diastereomers in 88-94% yields by an iodine/DBU-mediated cyclisation of Michael adducts **8** (Table 1).[10] The Michael adducts were in turn prepared by a base-promoted condensation of cinnamaldehydes with acetophenones to give dienones **7** followed by $LiClO_4$-catalyzed conjugate addition of diethyl malonate to **7**.[11]

Table 1. Preparation of starting D-A cyclopropanes.



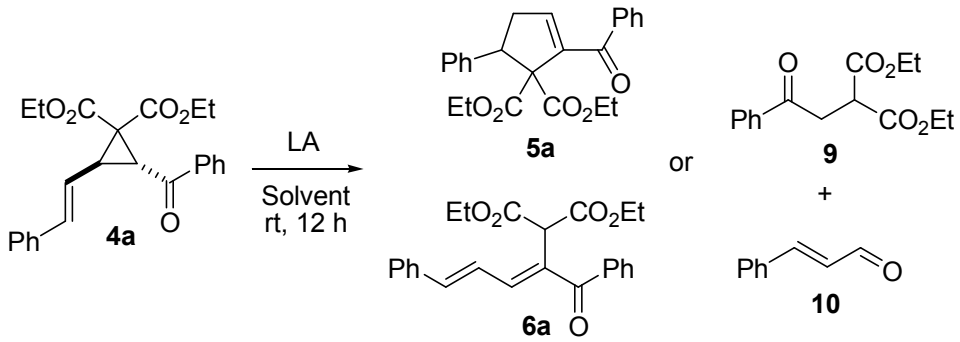
Entry	Ar^1	Ar^2	Yield (%)[a]
1	Ph	Ph	93 (**4a**)
2	4-MeC_6H_4	Ph	90 (**4b**)
3	4-$MeOC_6H_4$	Ph	90 (**4c**)
4	4-ClC_6H_4	Ph	89 (**4d**)
5	4-$NO_2C_6H_4$	Ph	92 (**4e**)
6	2-naphthyl	Ph	88 (**4f**)
7	2-thienyl	Ph	90 (**4g**)
8	Ph	4-MeC_6H_4	90 (**4h**)
9	Ph	4-ClC_6H_4	94 (**4i**)
10	Ph	4-$NO_2C_6H_4$	91 (**4j**)
11	4-MeC_6H_4	4-MeC_6H_4	92 (**4k**)
12	4-MeC_6H_4	4-ClC_6H_4	88 (**4l**)
13	2-thienyl	4-ClC_6H_4	88 (**4m**)

[a]Isolated yield (from **8**)

To begin, we selected D-A cyclopropane **4a** as a model substrate and treated with different Lewis acids (Table 2). When **4a** was treated with one equiv. of $SnCl_4$ in dichloromethane, the reaction gave a cyclopentene derivative **5a** in 92% yield (entry 1). With $AlCl_3$ and $TiCl_4$, the reaction afforded *E,E*-1,3-diene **6a**; however, the yield was better with $TiCl_4$ (entries 2 and 3). It is worth noting that similar olefin products are formed as intermediates in $TiCl_4$-promoted ring opening of **1**, but the intermediates underwent further reaction (Nazarov cyclization[12]) to give indenes **3**.[3] Upon treatment with $BF_3.OEt_2$, **4a** underwent fragmentation to yield phenacyl malonate (**9**, 40%) and cinnamaldehyde (**10**, 36%) (entry 4). When the amount of

Lewis acid was reduced (0.5 equiv.), the pattern of the products was the same, but their yields dropped proportionately (entries 5 and 6). Whilst, an increase in the amount of Lewis acid (1.5 equiv.) did not alter the yields significantly (entries 7 and 8). The same pattern of products, but with inferior yields, were obtained by switching the solvent to 1,2-dichloroethane (entry 9 and 10). The cyclopropane **4a** did not undergo any change upon treatment with other Lewis acids such as $InCl_3$, $ZnCl_2$, $Ni(ClO_4)_2$, $Ag(OTf)_3$, $Cu(OTf)_2$, $In(OTf)_3$, $Sc(OTf)_3$ and $Yb(OTf)_3$ and a Brønsted acid, *p*-TsOH. Thus, we selected $SnCl_4$ or $TiCl_4$ as optimal Lewis acids for the ring-opening of the cyclopropanes to obtain cyclopentenes and 1,3-dienes.

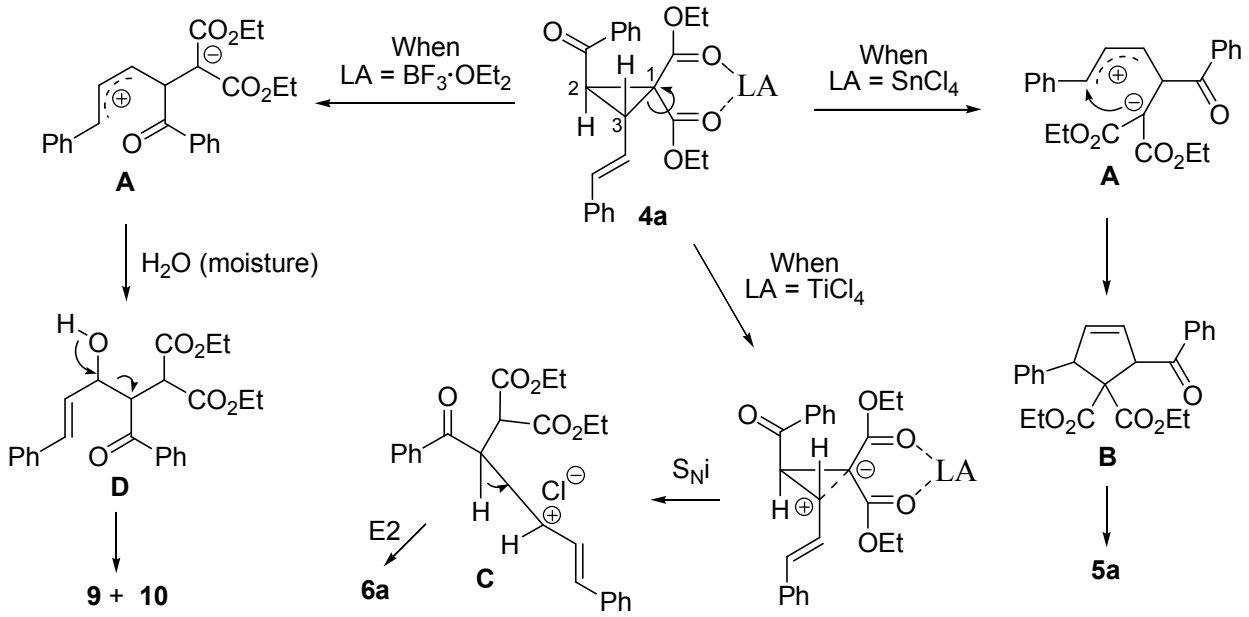
Table 2. Optimization of reaction conditions for ring opening of **4a**



Entry	Lewis acid (equiv)	Solvent	Product and Yield (%)[a]
1	$SnCl_4$ (1.0)	CH_2Cl_2	**5a**, 92
2	$AlCl_3$(1.0)	CH_2Cl_2	**6a**, 66
3	$TiCl_4$(1.0)	CH_2Cl_2	**6a**, 90
4	$BF_3.OEt_2$(1.0)	CH_2Cl_2	**9**,40 + **10**, 36
5	$SnCl_4$ (0.5)	CH_2Cl_2	**5a**, 28
6	$TiCl_4$ (0.5)	CH_2Cl_2	**6a**, 34
7	$SnCl_4$ (1.5)	CH_2Cl_2	**5a**, 90
8	$TiCl_4$ (1.5)	CH_2Cl_2	**6a**, 90
9	$SnCl_4$ (1.0)	1,2-DCE	**5a**, 70
10	$TiCl_4$ (1.0)	1,2-DCE	**6a**, 62

[a]Isolated yield

A plausible mechanism for the formation of the products **5a**, **6a**, **9** and **10** from **4a** is depicted in Scheme 2. When **4a** was treated with $SnCl_4$, the Lewis acid coordinates to the *gem*-diester unit thereby leading to the C1-C3 bond cleavage. The resulting 1,3-zwitterion **A** undergoes intramolecular cyclisation to give cyclopentene **B** (a β,γ-unsaturated ketone), which rearranges to thermodynamically more stable cyclopentene **5a** (an α,β-unsaturated ketone). On the other hand, when treated with $TiCl_4$, **4a** forms the intimate ion pair **C** *via* C1-C3 bond cleavage and S_Ni-like attack by chloride ion (which comes from $TiCl_4$)[3] and the ion pair **C** undergoes an E2-like elimination to give *E,E*-1,3-diene **6a** stereoselectively. In case of $BF_3.OEt_2$, **4a** initially forms the zwitterion **A**, which then combines water (moisture) and undergoes fragmentation to yield **9** and **10**.

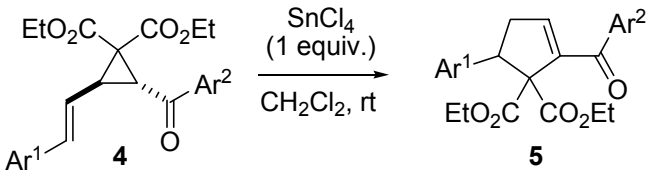


Scheme 2. Mechanism for the formation of different products from **4a** (the Lewis acid coordination is not shown in the intermediate structures for clarity)

Next, we turned our attention on investigating the scope of the $SnCl_4$ and $TiCl_4$-mediated reactions with respect to various D-A cyclopropanes.

As shown in Table 3, D-A cyclopropanes having various aromatic rings as Ar^1 and Ar^2 could be successfully employed for the cyclopentene synthesis. As the Ar^1 ring was involved in the stabilization of positive charge in the zwitterionic intermediate formed during the transformation, the nature of Ar^1 ring was expected to have more influence on the reaction outcome as compared to Ar^2 ring. The presence of electron donating and halogen substituents on the Ar^1 ring was tolerated in the reaction and the expected cyclopentene derivatives **5a–d** were produced in good yields (entries 1–4). However, when an electron withdrawing nitro-substituent was present on the Ar^1 ring, the reaction gave a mixture of fragmentation products, *p*-nitrocinnamaldehyde and phenacyl malonate instead of the expected cyclopentene product (the product pattern was similar to the one obtained with $BF_3.OEt_2$) (entry 5). Apart from substituted phenyl rings, a bulky naphthyl ring (entry 6) or heteroaromatic, 2-thienyl ring (entry 7) could be fruitfully used as Ar^1 to obtain the respective cyclopentene derivatives **5f** and **5g**. As expected, the presence of electron donating/withdrawing and halogen substituents on the Ar^2 ring of the D-A cyclopropanes afforded the corresponding cyclopentenes without any problem (entries 8–10). Finally, cyclopropanes carrying substituents on both aromatic rings (Ar^1 and Ar^2) also gave the respective cyclopentenes in good yields (entries 11–13, the structure of **5l** was confirmed by X-ray crystallographic analysis[13]).

Table 3. The scope of formation of cyclopentenes for various D-A cyclopropanes

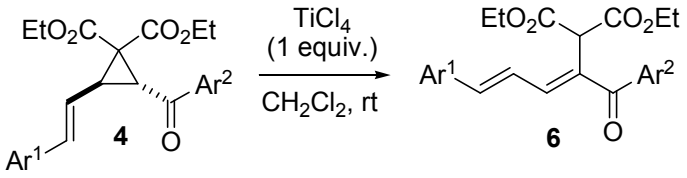


Entry	Ar^1	Ar^2	Yield (%)[a]
1	Ph	Ph	83 (**5a**)
2	4-MeC_6H_4	Ph	86 (**5b**)
3	4-$MeOC_6H_4$	Ph	80 (**5c**)
4	4-ClC_6H_4	Ph	70 (**5d**)[b]
5	4-$NO_2C_6H_4$	Ph	–[c]
6	2-naphthyl	Ph	82 (**5e**)
7	2-thienyl	Ph	75 (**5f**)[b]
8	Ph	4-MeC_6H_4	90 (**5g**)
9	Ph	4-ClC_6H_4	77 (**5h**)
10	Ph	4-$NO_2C_6H_4$	67 (**5i**)
11	4-MeC_6H_4	4-MeC_6H_4	79 (**5j**)
12	4-MeC_6H_4	4-ClC_6H_4	76 (**5k**)
13	2-thienyl	4-ClC_6H_4	71 (**5l**)

[a]Isolated yields. [b]Inseparable impurities (about 5%) were present along with the product. [c]*p*-Nitrocinnamaldehyde (45%) and phenacyl malonate (40%) are produced instead of cyclopentene product

Having studied the scope of cyclopentene synthesis for various D-A cyclopropanes, we next focused attention on synthesis of *E,E*-1,3-dienes from the cyclopropanes (Table 4). Pleasingly, cyclopropanes having electron donating/withdrawing and halogen substituents on both aromatic rings (Ar^1 and Ar^2) as well as those with naphthyl and thienyl rings as Ar^1 were compatible in the transformation and the respective 1,3-dienes were formed in 63-86% yields (entries 1–10, the structure of **6d** was confirmed by X-ray crystallographic analysis[14]). It is interesting to note that the D-A cyclopropane having a *p*-nitrophenyl ring also furnished the expected 1,3-diene without out undergoing any fragmentation reaction as observed with $SnCl_4$.

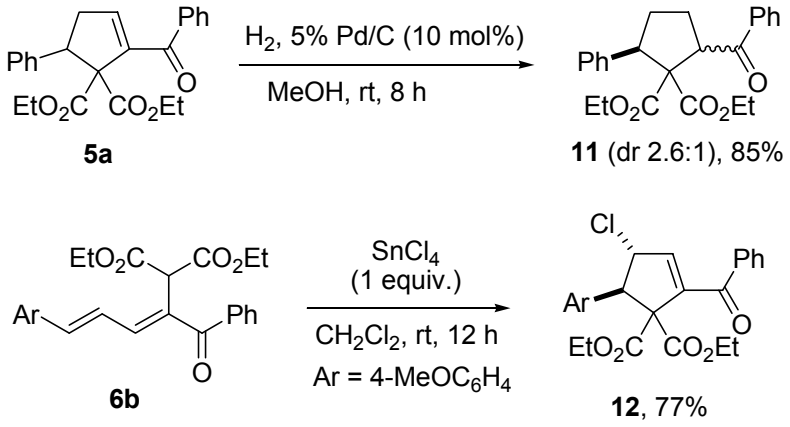
Table 4. The scope of formation of 1,3-dienes for various D-A cyclopropanes



Entry	Ar^1	Ar^2	Yield (%)[a]
1	Ph	Ph	86 (**6a**)
2	4-$MeOC_6H_4$	Ph	80 (**6b**)
3	4-ClC_6H_4	Ph	74 (**6c**)
4	4-$NO_2C_6H_4$	Ph	83 (**6d**)
5	2-naphthyl	Ph	70 (**6e**)
6	2-thienyl	Ph	77 (**6f**)
7	Ph	4-MeC_6H_4	82 (**6g**)
8	Ph	4-ClC_6H_4	75 (**6h**)
9	Ph	4-$NO_2C_6H_4$	63 (**6i**)
10	4-MeC_6H_4	4-MeC_6H_4	78 (**6j**)

[a]Isolated yields.

The products, cyclopentenes and *E,E*-1,3-dienes could serve as versatile synthetic intermediates. To prove the point, we subjected cyclopentene **5a** to catalytic hydrogenation and obtained cyclopentane **11** as a diastereomeric mixture (2.6:1) in 85% total yield (Scheme 3). Similarly, when diene **6b** was treated with $SnCl_4$, it underwent intramolecular cyclization to give chlorocyclopentene derivative **12** in 77% yield.



Scheme 3. Synthetic applications of a cyclopentene and a 1,3-diene

CONCLUSIONS

In conclusion, the treatment of *trans*-2-aroyl-3-styryl-cyclopropane-1,1-dicarboxylates with different Lewis acids gave different types of products. Upon treatment with $SnCl_4$, they underwent vinylcyclopropane-cyclopentene rearrangement *via* tandem ring-opening and ring-closing to yield cyclopentenes. On the other hand, they afforded *E,E*-1,3 dienes by ring-opening and E2-like elimination of proton upon treatment with $TiCl_4$. With $BF_3.OEt_2$, they afforded fragmentation products. The scope of cyclopentene and 1,3-diene synthesis was investigated for various D-A cyclopropanes and established that the protocols are indeed handy for the access of these two classes of compounds.

EXPERIMENTAL SECTION

General remarks: Melting points were determined by the open capillary tube method and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a 400 or 500 MHz NMR spectrometer. HRMS (ESI) were recorded on Exactive Plus EMR Orbitrap or Q-TOF mass

spectrometers. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo-Kα radiation. Thin layer chromatography (TLC) was performed on pre-coated alumina sheets and detected under UV light. *S*ilica gel (100-200 mesh) was used for column chromatography.

General procedure for the synthesis of *trans*-2-aroyl-3-styryl-cyclopropane-1,1-dicarboxylates 4a-m: To a solution of Michael adduct **8**[11] (1 mmol) in toluene (5 mL) were added DBU (0.3mL; 2 mmol) and iodine (508 mg; 2 mmol). The reaction mixture was stirred at ambient temperature for 30 min. After the reaction was complete, the reaction mixture was quenched with aq. $Na_2S_2O_3$ and extracted with ethyl acetate. The organic layer was washed with water and dried (anhydrous Na_2SO_4), and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using ethyl acetate (5-10%)/hexane to give pure product.

Diethyl *trans*-2-benzoyl-3-styrylcyclopropane-1,1-dicarboxylate (4a): Yellow solid; Yield: 366 mg (93%); M. p.: 50–52 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m, 2H), 7.61 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.35–7.23 (m, 5H), 6.80 (d, J = 15.6 Hz, 1H), 6.07 (dd, J = 15.6, 9.2 Hz, 1H), 4.34–4.15 (m, 4H), 3.83 (d, J = 7.2 Hz, 1H), 3.37 (dd, J = 9.2, 6.8 Hz 1H), 1.27 (t, J = 7.2 Hz, 3H),1.16(t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ193.7, 166.7, 165.8, 136.9, 136.5, 135.3, 133.6, 128.74, 128.65, 128.5, 127.9, 126.3, 122.4, 62.4, 61.9, 45.3, 37.0, 36.0, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{24}O_5Na$ 415.1516; found: 415.1511.

Diethyl *trans*-2-benzoyl-3-(4-methylstyryl)-cyclopropane-1,1-dicarboxylate (4b): Yellow liquid; Yield: 365 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* =7.6 Hz, 3H), 7.25 (d, *J* = 8Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.34–4.18 (m, 4H), 3.87 (d, *J* = 7.2 Hz, 1H), 3.41 (dd, *J* = 9.2, 7.2 Hz, 1H), 2.38 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1, 166.8, 165.9, 144.5, 136.5, 135.2, 134.5, 129.4, 128.7, 127.9, 126.3, 122.5, 62.3, 61.8, 45.2, 36.9, 35.9, 21.7, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.1853; found: 407.1852.

Diethyl *trans*-2-benzoyl-3-(4-methoxystyryl)-cyclopropane-1,1-dicarboxylate (4c): Yellow liquid; Yield: 378 mg (90%) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 5.96 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.30–4.15 (m, 4H), 3.84 (d, *J* = 7.2 Hz, 1H), 3.72 (s, 3H), 3.38 (t, *J* = 8.0 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.7, 166.7, 165.9, 159.5, 136.9, 134.7, 133.6, 129.3, 128.7, 128.5, 127.5, 119.9, 114.1, 62.3, 61.8, 55.2, 45.3, 37.0, 36.2, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_6$ 423.1802; found: 423.1796.

Diethyl *trans*-2-benzoyl-3-(4-chlorostyryl)-cyclopropane-1,1-dicarboxylate (4d): Yellow liquid; Yield: 380 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m,2H), 7.60–7.56 (m, 1H), 7.49–7.45 (m, 2H), 7.25 (s, 4H), 6.73(dd, *J* = 16.0, 2.0 Hz, 1H), 6.08 (dd, *J* = 16.0, 6.8 Hz, 1H), 4.23–4.15 (m, 4H), 3.85 (d, *J* = 6.8 Hz, 1H), 3.37 (t, *J* = 8.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 166.6, 165.7, 136.8, 135.0, 133.9, 133.7, 133.4, 128.78, 128.75, 128.5, 127.5, 123.1, 62.4, 61.9, 45.3, 36.9, 35.8, 14.2,

13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427.1303.

Diethyl *trans*-2-benzoyl-3-(4-nitrostyryl)-cyclopropane-1,1-dicarboxylate (4e): Yellow liquid; Yield: 400 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.64–7.60 (m, 1H), 7.53–7.47 (m, 4H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.31 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.35–4.15 (m, 4H), 3.90 (d, *J* = 6.8 Hz 1H), 3.42 (dd, *J* = 9.4, 7.0 Hz, 1H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 166.6, 165.4, 147.0, 142.8, 136.7, 133.8, 133.1, 128.8, 128.5, 127.7, 126.8, 124.1, 62.6, 62.0, 45.4, 36.9, 35.6, 14.1, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_7Na$ 460.1367; found: 460.1356.

Diethyl *trans*-2-benzoyl-3-(2-naphthalen-2-yl-vinyl)-cyclopropane-1,1-dicarboxylate (4f): Yellow liquid; Yield: 388 mg (88%) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01(d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 3H), 7.39–7.27 (m, 7H), 6.84 (d, *J* = 15.6 Hz, 1H), 6.11 (dd, *J* = 15.6, 9.2 Hz, 1H), 4.38–4.20 (m, 4H), 3.82 (d, *J* = 6.8 Hz, 1H), 3.42 (t, *J* = 7.8 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) : δ 192.4, 166.6, 165.7, 140.1, 136.4, 135.4, 135.3, 129.9, 129.1, 128.7, 127.9, 126.3, 122.1, 62.5, 62.0, 45.4, 36.9, 35.89, 14.1, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{28}H_{26}O_5Na$ 465.1672; found: 465.1670.

Diethyl *trans*-2-benzoyl-3-(2-thiophen-2-yl-vinyl)-cyclopropane-1,1-dicarboxylate (4g): Yellow liquid; Yield: 360 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.92 (t, *J* = 5.8 Hz, 3H), 5.91 (dd, *J* = 15.6, 9.2 Hz, 1H), 4.27 (q, *J* = 7.0 Hz, 2H), 4.16 (d, *J* = 7.2 Hz, 2H), 3.81 (d, *J*

= 6.8 Hz, 1H) 3.32 (t, *J* = 8.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.5, 166.6, 165.7, 141.5, 136.8, 133.7, 128.8, 128.5, 128.3, 127.5, 126.0, 124.5, 121.8, 62.4, 61.9, 45.3, 36.8, 35.8, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{22}O_5NaS$ 421.1080; found: 421.1088.

Diethyl *trans*-2-(4-methylbenzoyl)-3-styryl-cyclopropane-1,1-dicarboxylate (4h): Yellow liquid; Yield: 364 (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.35–7.22 (m, 7H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.07 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.30–4.15 (m, 4H), 3.81 (d, *J* = 6.8 Hz, 1H), 3.35 (dd, *J* = 9.0, 7.0 Hz, 1H), 2.40 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ193.1, 166.8, 165.9, 144.6, 136.6, 135.2, 134.5, 129.4, 128.7, 127.9, 126.3, 122.5, 62.3, 61.8, 45.2, 36.9, 35.9, 21.7, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.1853; found: 407.1854.

Diethyl *trans*-2-(4-chlorobenzoyl)-3-styryl-cyclopropane-1,1-dicarboxylate (4i): Yellow liquid; Yield: 401 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.33–7.23 (m, 5H), 6.79 (d, *J* = 16.0 Hz, 1H), 6.09 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.31–4.15 (m, 4H), 3.75 (d, *J* = 6.8 Hz, 1H), 3.36 (t, *J* = 7.8 Hz, 1H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 166.6, 165.6, 140.1, 136.5, 135.4, 135.3, 129.9, 129.1, 128.6, 127.9, 126.3, 122.1, 62.4, 61.9, 45.4, 36.9, 35.8, 14.1, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427.1307.

Diethyl *trans*-2-(4-nitrobenzoyl)-3-styryl-cyclopropane-1,1-dicarboxylate (4j): Yellow liquid; Yield: 398 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34–8.17 (m,4H), 7.35–7.25 (m, 5H), 6.82 (d, *J* = 14.4 Hz, 1H), 6.05 (dd, *J* = 15.8, 9.0 Hz, 1H), 4.31–4.15 (m, 4H), 3.76 (d, *J* = 7.2 Hz, 1H), 3.36 (dd, *J* = 8.8, 7.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.5, 166.3, 165.4, 150.6, 141.2, 136.2, 135.7, 129.5, 128.7, 128.1, 126.3, 124.0, 121.6, 62.7, 62.1, 45.8, 37.1, 36.3, 14.1, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_7Na$ 460.1367; found: 460.1368.

Diethyl *trans*-2-(4-methylbenzoyl)-3-(4-methylstyryl)-cyclopropane-1,1-dicarboxylate (4k): Yellow liquid; Yield: 388 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.28–7.23 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 15.6 Hz 1H), 6.01 (dd, *J* = 16.0, 9.2 Hz, 1H), 4.30–4.15 (m, 4H), 3.80 (d, *J* = 8.2 Hz, 1H), 3.33 (t, *J* = 8.8 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.17 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.2, 166.8, 166.0, 144.5, 137.7, 135.1, 134.5, 133.8, 129.4, 129.3, 128.7, 126.2, 121.4, 62.3, 61.8, 45.2, 36.9, 36.1, 21.7, 21.2, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{29}O_5$ 421.2010; found: 421.2008.

Diethyl *trans*-2-(4-chlorobenzoyl)-3-(4-methylstyryl)-cyclopropane-1,1-dicarboxylate (4l): Yellow liquid; Yield: 386 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz , 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.0 (dd, *J* = 15.6, 9.2 Hz, 1H), 4.33–4.13 (m, 4H), 3.75 (d, *J* = 6.8 Hz, 1H), 3.34 (t, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.69 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.6, 166.6, 165.8, 140.1, 137.8, 135.3, 135.2, 133.6, 129.9, 129.4, 129.1, 126.2, 120.9, 62.5, 62.0, 45.4, 36.9, 36.1, 21.3, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}ClO_5$ 441.1463; found: 441.1461.

Diethyl t*rans*-2-(4-chlorobenzoyl)-3-(2-thiophen-2-yl-vinyl)-cyclopropane-1,1-dicarboxylate (4m): Yellow liquid; Yield: 380 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.15 (t, *J* = 3.2 Hz, 1H), 6.95–6.89 (m, 3H), 5.87 (dd, *J* = 15.6, 9.2

Hz, 1H), 4.34–4.15 (m, 4H), 3.74 (d, J = 6.8 Hz, 1H), 3.30 (dd, J = 15.2, 8.0 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.4, 166.5, 165.6, 141.4, 140.2, 135.2, 129.9, 129.1, 128.4, 127.5, 126.0, 124.6, 121.6, 62.6, 62.0, 45.4, 36.7, 35.8, 14.2, 13.9 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}ClO_5NaS$ 455.0690; found: 455.0690.

General procedure for the synthesis of cyclopentenes 5a–l and 1,3-dienes 6a-j: To a solution of *trans*-2-aroyl-3-styryl-cyclopropane-1,1-dicarboxylates (1 mmol) in dichloromethane (5 mL) was added Lewis acid ($SnCl_4$ for **5** and $TiCl_4$ for **6**; 1 mmol) at room temperature. The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction was complete, the reaction mixture was quenched with ice–water and extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:9) as the eluent to give pure product.

Diethyl 2–benzoyl–5–phenyl–cyclopent–2–ene–1,1–dicarboxylate (5a): Yellow liquid; Yield: 326 mg (83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.89 (m, 2H), 7.55 (t, J = 6.8 Hz, 1H), 7.47–7.44 (m, 2H), 7.39–7.37 (m, 2H), 7.31–7.25 (m, 3H), 6.64 (s, 1H), 4.28–4.21 (m, 3H), 3.81–3.66 (m, 2H), 3.17 (ddd, J = 18.0, 8.4, 1.6 Hz, 1H), 3.05 (ddd, , J = 8.8, 6.8, 2.4 Hz, 1H) , 1.22 (t, J = 8.0 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 170.7, 168.1, 145.3, 142.6, 139.8, 137.7, 132.7, 129.5, 128.8, 128.4, 128.1, 127.4, 72.4, 61.8, 61.2, 51.6, 40.0, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}O_5$ 393.1697; found: 393.1700.

Diethyl 2–benzoyl–5–*p*–tolyl–cyclopent–2–ene–1,1–dicarboxylate (5b): Yellow liquid; Yield: 350 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz , 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz , 2H), 6.64 (t, *J* = 2.2 Hz , 1H), 4.24 (t, J =7.2, 3H), 3.84–3.71 (m, 2H), 3.16 (ddd, *J* = 18.4, 8.4, 2.4, Hz, 1H), 3.02 (ddd, *J* = 18.0, 6.8, 2.0, Hz, 1H) 2.31 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 170.7, 168.1, 145.2, 137.8, 136.9, 136.6, 132.6, 129.4, 128.8, 128.7, 128.3, 72.3, 62.5, 61.7, 61.1, 51.4, 39.9, 21.0, 13.9, 13.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.1853; found: 407.1859.

Diethyl 2–benzoyl–5–(4–methoxyphenyl)–cyclopent–2–ene–1,1–dicarboxylate (5c): Pale yellow liquid; Yield: 336 mg (80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (t, *J* = 4.2 Hz, 2H), 7.59–7.55 (m, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.8Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.65 (t, *J* = 2.4 Hz, 1H), 4.27–4.20 (m, 3H), 3.87–3.73 (m, 5H), 3.16 (ddd, *J* = 18.4, 8.4, 2.4, Hz, 1H), 3.02 (ddd, *J* = 18.4, 7.2, 2.4, Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 170.7, 168.2, 158.9, 145.2, 142.7, 137.7, 132.6, 131.5, 129.9, 129.4, 128.3, 113.4, 72.2, 61.8, 61.2, 55.3, 51.0, 39.9, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_6$ 423.1802; found: 423.1808.

Diethyl 2–benzoyl–5–(4–chlorophenyl)–cyclopent–2–ene–1,1–dicarboxylate (5d): Yellow liquid; Yield: 300 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.87 (m, 2H), 7.57 (d, *J* = 6.4 Hz, 1H), 7.56–7.47 (m, 2H), 7.37–7.22 (m, 3H), 6.82 (dd, *J* = 6.0, 4.8, Hz, 1H), 6.64 (d, *J* = 2.4 Hz, 1H), 4.26–4.21 (m, 3H), 3.86–3.77 (m, 2H), 3.16 (ddd, *J* = 18.0, 8.4, 2.4, Hz, 1H), 3.01(ddd, *J* = 18.4, 7.2, 2.4, Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 170.6, 168.1, 150.0, 144.9, 142.6, 138.0, 137.6, 133.2, 132.7, 130.3,

129.4, 128.4, 128.2, 72.2, 61.7, 61.9, 61.4, 50.8, 39.6, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427.1312.

Diethyl 2–benzoyl–5–naphthalen–2–yl–cyclopent–2–ene–1,1–dicarboxylate (5e): Yellow liquid; Yield: 364 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.92 (m, 2H), 7.82–7.77 (m, 4H), 7.57–7.43 (m, 6H), 6.69 (t, *J* = 2.2, 1H), 4.46 (t, *J* = 7.6 Hz, 1H), 4.29–4.27 (m, 2H), 3.71–3.60 (m, 2H), 3.25 (ddd, *J* = 18.4, 8.4, 2.4, Hz, 1H), 3.16 (ddd, *J* = 18.0, 6.8, 2.4, Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.72 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3, 170.8, 168.1, 145.2, 142.8, 137.8, 137.2, 133.2, 132.72, 132.66, 129.5, 128.4, 127.9, 127.73, 127.70, 127.5, 126.8, 126.1, 125.9, 72.4, 61.9, 61.2, 51.8, 40.0,13.9, 13.4 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{27}O_5$ 443.1853; found: 443.1857.

Diethyl 2–benzoyl–5–thiophen–2–yl–cyclopent–2–ene–1,1–dicarboxylate (5f): Brown liquid; Yield: 300 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.55 (q, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 4.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.94 (t, *J* = 5.2 Hz, 1H), 6.56 (s, 1H), 4.50 (t, *J* = 8.0 Hz, 1H), 4.29–4.21 (s, 2H), 3.91 (q, *J* = 6.8, 2H), 3.92 (q, *J* = 6.8 Hz, 1H), 3.08 (ddd, *J* = 18.4, 6.4, 2.0, Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 170.2, 167.9, 143.9, 142.6, 141.7, 137.3, 132.8, 129.5, 128.4, 126.7, 124.4, 72.0, 62.9, 61.4, 46.8, 40.6, 13.9, 13.7 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}O_5S$ 399.1261; found: 399.1265.

Diethyl 2–(4–methylbenzoyl)–5–phenyl–cyclopent–2–ene–1,1–dicarboxylate (5g): Yellow liquid; Yield: 366 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.31–7.24 (m, 5H), 6.63 (s, 1H), 4.28–4.22 (m, 3H), 3.82–3.62 (m, 2H), 3.19 (ddd, *J* = 18.4, 8.4, 2.4, Hz, 1H), 3.04 (ddd, *J* = 18, 6.8, 2.0, Hz, 1H) 2.42 (s, 3H), 1.21 (t, *J* = 7.2 Hz,

3H), 0.86 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 170.8, 168.2, 144.5, 143.4, 142.6, 139.8, 135.0, 129.6, 129.1, 128.8, 128.1, 127.3, 72.4, 61.8, 61.2, 51.5, 39.9, 21.7, 13.9, 13.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.1853; found: 407.1860.

Diethyl 2–(4–chlorobenzoyl)–5–phenyl–cyclopent–2–ene–1,1–dicarboxylate (5h): Yellow liquid; Yield: 328 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (q, J = 4.8 Hz, 2H), 7.45 (q, J = 5.2 Hz, 2H), 7.38–7.25 (m, 5H), 6.64 (t, J = 2.6 Hz, 1H), 4.28–4.23 (m, 3H), 3.82–3.66 (m, 2H), 3.21 (ddd, J = 18.4, 8.8, 2.8, Hz, 1H), 3.05 (ddd, J = 18.4, 6.8, 2.8, Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.0 170.6, 168.0, 145.1, 142.4, 137.0, 136.0, 128.7, 128.7, 128.1, 127.4, 126.0, 72.5, 61.9, 61.2, 51.6, 40.0, 13.9, 13.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427.1310.

Diethyl 2–(4–nitrobenzoyl)–5–phenyl–cyclopent–2–ene–1,1–dicarboxylate (5i): Brown liquid; Yield: 292 mg (67 %); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.8 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 7.37–7.27 (m, 4H), 6.71 (t, J = 2.4 Hz, 1H), 4.31–4.26 (m, 4H), 3.83–3.66 (m, 2H), 3.25 (ddd, J = 18.8, 8.4, 2.4, Hz, 1H), 3.08 (ddd, J = 18.4, 6.4, 2.0, Hz, 1H), 1.26 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 170.5, 168.0, 150.1, 147.0, 142.7, 142.5, 139.4, 130.3, 128.7, 128.2, 127.6, 123.7, 72.4, 62.1, 61.4, 51.7, 40.3, 14.0, 13.5 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_7Na$ 460.1367; found: 460.1373.

Diethyl 2–(4–methylbenzoyl)–5–*p*–tolyl–cyclopent–2–ene–1,1–dicarboxylate (5j): Pale yellow liquid; Yield: 332 mg (79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 8.4 Hz, 4H), 7.10 (d, J = 7.6 Hz, 2H), 6.60 (s, 1H), 4.22 (d, J = 7.2, 3H), 3.83–3.69

(m, 2H), 3.76 (ddd, J = 34.4, 17.2, 10.0, Hz, 1H), 3.07(ddd, J = 51.6, 18.0, 8.4, Hz, 1H), 2.39 (s, 3H), 2.30 (s, 3H), 1.19 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 170.8, 168.2, 144.6, 143.4 142.6, 136.9, 136.6, 135.0 129.6, 129.1, 128.8, 128.7, 72.3, 61.7, 61.1, 39.9, 21.6, 21.1, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{29}O_5$ 421.2010; found: 421.2015.

Diethyl 2–(4–chlorobenzoyl)–5–*p*–tolyl–cyclopent–2–ene–1,1–dicarboxylate (5k): Yellow liquid; Yield: 336 mg (76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.6 Hz, 2H), 6.63 (s, 1H), 4.27–4.20 (m, 3H), 3.85–3.70 (m, 2H), 3.17 (ddd, J = 18.4, 8.4, 1.2 Hz, 1H), 3.06–3.0 (m, 1H), 2.32 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 0.91(t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.1 170.6, 168.1, 145.3, 142.4, 139.0, 137.0, 136.4, 136.0, 130.9, 128.9, 128.7, 128.6, 72.3, 61.9, 61.3, 51.3, 21.1,40.0, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}ClO_5$ 441.1463; found: 441.1467.

Diethyl 2–(4–chlorobenzoyl)–5–thiophen–2–yl–cyclopent–2–ene–1,1–dicarboxylate (5l): Yellow solid; Yield: 306 mg (71%); 105-107 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 4.8 Hz, 1H), 7.11 (s, 1H), 6.97 (t, J = 4.4 Hz, 1H), 6.59 (s, 1H), 4.51(t, J = 8.0, 1H), 4.27 (q, J = 7.2, 2H), 3.97–3.90 (s, 2H), 3.95–3.89 (m, Hz, 1H), 3.21 (ddd, J = 24.4, 16.4, 8.4, Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H), 1.01 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.9, 170.2, 167.8, 143.9, 142.3, 141.6, 139.2, 135.6, 130.9, 128.8, 126.7, 126.6, 72.1, 62.0, 61.6, 46.8, 40.7, 13.9, 13.6 ppm; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}ClO_5NaS$ 455.0690; found: 455.0696.

(*E,E*)-Diethyl 2–(1–benzoyl–5–phenyl–penta–2,4–dienyl)–dicarboxylate (**6a**): Yellow liquid; Yield: 336 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 4H), 7.37–7.12 (m, 5H), 6.85 (d, *J* = 14.4 Hz, 1H), 5.10 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 168.0, 145.9, 142.8, 138.0, 135.9, 131.8, 131.7, 129.5, 128.9, 128.3, 127.5, 123.3, 61.9, 50.6, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{25}O_5$ 393.1697; found: 393.1702.

(*E,E*)-Diethyl 2–[1–benzoyl–5–(4–methoxy–phenyl)–penta–2,4–dienyl]–dicarboxylate (6b): Yellow liquid; Yield: 338 g (80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70, (d, *J* = 6.8 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47–7.39 (m, 4H), 7.15–7.03 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 14.8 Hz, 1H), 5.10 (s, 1H), 4.26 (q, *J* = 6.8 Hz, 4H), 3.80 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.3, 168.2, 146.8, 142.8, 138.3, 131.6, 130.7, 129.4, 129.2, 128.7, 128.3, 121.2, 114.4, 61.9, 55.4, 50.6, 14.1 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{25}H_{26}O_6Na$ 445.1622; found: 445.1621.

(*E,E*)-Diethyl 2–[1–benzoyl–5–(4–chlorophenyl)–penta–2,4–dienyl]–dicarboxylate (6c): Pale yellow liquid; Yield: 316 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.66 (m, 2H), 7.47–7.44 (m, 4H), 7.39 (m, 3H), 7.17 (d, *J* = 14.8 Hz, 1H), 7.08 (d, *J* = 11.6 Hz, 1H), 6.88 (d, *J* = 14.8, 1H), 5.05 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 167.9, 145.9, 143.2, 138.2, 136.3, 135.8, 131.6, 130.9, 129.7, 129.0, 128.7, 127.6, 123.1, 62.1, 50.7, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427.1315.

(*E,E*)-Diethyl 2–[1–benzoyl–5–(4–nitrophenyl)–penta–2,4–dienyl]–dicarboxylate (6d): Yellow solid; Yield: 348 mg (80%); 128–130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.0, 2H), 7.61–7.57 (m, 3H), 7.51–7.47 (m, 2H), 7.41–7.34 (m, 1H), 7.12 (d, *J* = 11.2 Hz, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 5.13 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 4H), 1.29 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 167.8, 147.8, 144.2, 142.1, 139.1, 137.5, 134.1, 132.2, 129.6, 128.4, 127.9, 127.6, 124.3, 62.2, 50.8, 14.1 ppm; HRMS (ESI-ion trap) *m/z*: $[M]^+$ Calcd for $C_{24}H_{23}NO_7$ 437.1475; found: 437.1473.

(*E,E*)-Diethyl 2–(1–benzoyl–5–naphthalen–2–yl–penta–2,4–dienyl)–dicarboxylate (6e): Dark brown liquid; Yield: 310 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.74 (m, 2H), 7.57–7.54 (m, 1H), 7.48–7.44 (m, 5H), 7.37–7.31 (m, 3H), 7.26–7.12 (m, 3H), 6.85 (d, *J* = 14.4 Hz, 1H), 5.10 (s, 1H), 4.27 (d, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 168.1, 146.0, 142.8, 138.0, 135.9, 131.9, 131.8, 129.6, 129.5, 128.9, 128.3, 127.6, 123.3, 62.0, 50.7, 14.1 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{28}H_{27}O_5$ 443.1853; found: 443.1851.

(*E,E*)-Diethyl 2–(1–benzoyl–5–thiophen–2–yl–penta–2,4–dienyl)–dicarboxylate (6f): Colorless liquid; Yield: 306 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 6.8 Hz, 2H), 7.55–7.52 (m, 1H), 7.47–7.43 (m, 2H), 7.31 (d, *J* = 4.8 Hz, 1H), 7.11–6.94 (m, 5H), 5.05 (s, 1H), 4.29–4.24 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 167.9, 145.6, 141.4, 138.0, 135.2, 131.8, 131.5, 129.57, 129.52, 129.41, 129.37, 129.1, 128.3, 128.2, 127.8, 122.6, 62.0, 50.7, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{23}O_5S$ 399.1261; found: 399.1263.

(*E,E*)-Diethyl 2–[1–(4–methylbenzoyl)–5–phenyl–penta–2,4–dienyl]–dicarboxylate (6g): Yellow liquid; Yield: 332 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 6.8 Hz, 2H), 7.37–7.11 (m, 7H), 6.84 (d, *J* = 14.4 Hz, 1H), 5.08 (s, 1H), 4.26 (q, J = 7.2 Hz, 4H), 2.43 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 168.1, 145.3, 142.5, 142.4, 136.0, 135.2, 131.9, 129.7, 129.5, 129.0, 128.9, 127.5, 123.4, 61.9, 50.8, 21.6, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{27}O_5$ 407.1853; found: 407.1854.

(*E,E*)-Diethyl 2–[1–(4–chlorobenzoyl)–5–phenyl–penta–2,4–dienyl]–dicarboxylate (6h): Colorless liquid; Yield: 320 mg (75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.47–7.44 (m, 4H), 7.39–7.33 (m, 3H), 7.16 (d, *J* = 11.2 Hz, 1H), 7.08 (d, *J* = 11.2 Hz, 1H), 6.87 (d, *J* = 15.2 Hz, 1H), 5.05 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 4H), 1.28 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.1, 167.9, 145.8, 143.1, 138.2, 136.3, 135.8, 131.6, 130.9, 129.7, 129.0, 128.9, 128.8, 128.6, 127.6, 123.1, 62.0, 50.7, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{24}H_{24}ClO_5$ 427.1307; found: 427. 1312.

(*E,E*)-Diethyl 2–[1–(4–nitrobenzoyl)–5–phenyl–penta–2,4–dienyl]–dicarboxylate (6i): Pale Yellow liquid; Yield: 276 mg (63%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.8 Hz, 2H) 7.84 (d, *J* = 8.8 Hz, 2H), 7.47 (q, *J* = 6.0 Hz, 2H), 7.40–7.36 (m, 3H), 7.23–7.16 (m, 1H), 7.06 (d, *J* = 11.2 Hz, 1H), 6.89 (d, *J* = 15.2 Hz, 1H), 5.09 (s, 1H), 4.29 (q, J = 5.6 Hz, 4H), 1.30 (t, *J* = 7.0 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 167.7, 149. 5, 147.3, 144.3 143.7, 135.6, 131.5, 130.1, 130.0, 129.0, 127.7, 123.6, 122.8, 62.1, 50.3, 14.1 ppm; HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_7Na$ 460.1367; found: 460.1369.

(*E*,*E*)-Diethyl 2–[1–(4–methylbenzoyl)–5–*p*–toyl–penta–2,4–dienyl]–dicarboxylate (6j): Yellow liquid; Yield: 296 mg (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.6 Hz, 2H), 7.14 (q, *J* = 6.4 Hz, 4H), 6.82 (q, *J* = 6.4 Hz, 1H), 5.07 (s, 1H), 4.26 (q, *J* = 7.2 Hz, 4H), 2.43 (s, 3H), 2.35 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 168.2, 145.8, 142.6, 142.4, 139.9, 135.3, 133.3, 131.4, 129.7, 129.6, 129.0, 127.5, 122.4, 61.9, 50.8, 21.6, 14.1 ppm; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{26}H_{29}O_5$ 421.2010; found: 421.2014.

Synthesis of diethyl 2–benzoyl–5–phenyl–cyclopentane–1,1–dicarboxylate (11): To a solution of cyclopentene **5a** (98 mg; 0.25 mmol) in MeOH (5 mL) was added 5% Pd/C (53 mg; 10 mol%) and hydrogen gas was bubbled through the reaction mixture for 5 min. The reaction was stirred at room temperature under hydrogen atmosphere (balloon pressure) for 10 h. After the reaction was complete, the reaction mixture was filtered using celite and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography using ethyl acetate/hexane (1:9) to give **11** as a mixture of diastereomers. Pale yellow liquid; Yield: 84 mg (85%). HRMS (ESI-ion trap) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{26}O_5Na$ 417.1672; found: 417.1670. The diastereomers were separated by repeated column chromatography. **Major diastereomer:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 6.4 Hz, 2H), 7.53 (t, *J* = 5.8 Hz, 1H), 7.43 (q, *J* = 7.2 Hz, 4H), 7.26–7.19 (m, 3H), 4.40 (t, *J* = 7.2 Hz, 1H), 4.16–4.08 (m, 2H), 4.00–3.92(m, 2H), 3.83 (q, *J* = 1.6 Hz, 1H), 2.63 (q, *J* = 4.8 Hz, 1H), 2.42 (q, *J* = 7.2 Hz, 1H), 2.28 (q, *J* = 3.6 Hz, 2H), 1.09 (t, *J* = 5.6 Hz, 3H), 1.01 (t, *J* = 5.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 171.4, 169.1, 139.1, 137.1, 132.9, 129.6, 128.5, 128.4, 127.7, 127.0, 67.2, 61.4, 60.9, 55.5, 52.7, 31.4, 28.3. 13.81, 13.7 ppm; **Minor diastereomer:** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 6.4 Hz, 2H), 7.57 (t, *J* = 5.8 Hz, 1H), 7.47 (t, *J* = 6.2 Hz, 2H), 7.19 (t, *J* =

6.0 Hz, 2H), 7.12 (t, *J* = 5.8 Hz, 1H), 7.00 (d, *J* = 6.0 Hz, 1H), 4.26–4.03 (m, 6H), 2.48 (q, *J* = 4.0 Hz, 2H), 1.68–1.40 (m, 6H), 1.26 (t, *J* = 5.6 Hz, 3H), 1.23 (t, *J* = 5.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.8, 168.8, 168.4, 141.4, 137.0, 133.2, 128.7, 128.5, 128.3, 125.8, 61.73, 61.67, 54.0, 44.8, 35.7, 30.2, 27.5, 14.1, 13.9 ppm.

Synthesis of diethyl 5–benzoyl–4–chloro–2–(4–methoxyphenyl)–cyclopent–2–ene–1,1–dicarboxylate (12): To a solution of diene **6b** (106 mg; 0.25 mmol) in dichloromethane (5 mL) was added $SnCl_4$ (30 μL; 0.25 mmol) at room temperature. The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction was complete, the reaction mixture was quenched with ice–water and extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:9) as the eluent to give pure **12**. Pale yellow liquid; Yield: 88 mg (77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.94–7.60 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 2.0 Hz, 1H), 5.43 (q, *J* = 6.0 Hz, 1H), 4.24–4.16 (m, 3H), 4.00 (t, *J* = 7.0, 2H), 3.81 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 168.9, 167.4, 159.4, 142.3, 142.1, 136.5, 133.4, 130.6, 129.6, 128.6, 126.2, 113.7, 71.5, 64.4, 62.1, 60.5, 55.3, 13.74, 13.70 ppm; HRMS (ESI-ion trap) *m/z*: $[M + H]^+$ Calcd for $C_{25}H_{26}ClO_6$ 457.1412; found: 457.1411.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all products and X-ray structural information for **5l** and **6d** (CIF). This material is available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding author

* Fax: +91-431-2407043. Tel: +91-431-2407053. E-mail: *srinivasank@bdu.ac.in*

Notes

The authors declare no competing financial interest.

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(13) CCDC 1573672 for compound **5l**. See the Supporting Information for details.

(14) CCDC 1573675 for compound **6d**. See the Supporting Information for details.