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Ring opening of DA-cyclopropanes with electron rich arene/heteroarene: synthesis of 2-(2,2-diarylethyl)malonates

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ABSTRACT

An efficient strategy for nucleophilic ring opening of donor-acceptor (DA)-cyclopropanes with electron rich arenes to provide 2-(2,2-diarylethyl)malonates in excellent yields is described. The reaction was found to be successful with heteroarenes as the nucleophile as well. Reaction of enantiopure DA-cyclopropane with arene/heteroarene as the nucleophiles afforded the corresponding 2-(2,2-diarylethyl)malonates with high yield and enantioselectivity (ee 95%). The synthetic utility of the products was demonstrated by converting them easily into other important synthetic scaffolds like functionalized cyclohexene and malonic acid derivatives.

1. Introduction

Donor-acceptor (DA)-cyclopropanes being proclaimed as versatile building blocks have received considerable attention in modern organic synthesis. During the last one decade, there has been prolific expansion of synthetic utilities of these reactive three membered carbacycles.[1] Due to the presence of donor and acceptor functionalities in the ring the intervening C–C bond becomes weaker and furthermore, the interaction of the acceptor terminal with a suitable Lewis acid (LA) catalyst makes this bond even more labile. DA-cyclopropanes mostly tend to undergo two types of synthetic transformations: 1) cycloaddition reactions[2] and 2) ring opening reactions.[3] In the presence of a Lewis acid catalyst, DA-cyclopropanes serve as a 'masked or homo' Michael acceptor which can be intercepted by suitable nucleophiles to generate a number of valuable organic compounds. A large variety of carbon and heteroatomic nucleophiles, both neutral and anionic in nature, have been employed for such synthetic transformations. Though ring opening reactions with anionic nucleophiles are well documented in the literature, employment of neutral nucleophiles like arenes and heteroarenes in the ring opening reactions of DA cyclopropanes is not much explored. There are a few reports on the reaction of DA-cyclopropanes with arenes and heteroarenes.[3f–i,4] But to the best of our knowledge, only few reports are available where only a limited variety of DA-cyclopropanes were utilized along with neutral arene nucleophiles.[4] However, there is no report for the synthesis of nonracemic 2-(2,2-diarylethyl)malonates via ring opening of enantiopure DA-cyclopropane with neutral arenes. It is worth mentioning that ring opening of DA-cyclopropanes e.g., 2-arylcyclopropane-1,1-dicarboxylate with arenes can generate 2-(2,2-diaryl)ethyl malonates which can be converted into several useful synthetic scaffolds upon further synthetic manipulations. Hence further synthetic exploration to this field of DA-cyclopropane chemistry is highly desirable.

In continuation of our research endeavor with DA-cyclopropanes,[5] we have developed an efficient strategy for the synthesis of 2-(2,2-diarylethyl)malonates via LA-catalyzed ring opening of DA-cyclopropanes with arenes and heteroarenes. Herein, we report our results in detail as an article.

2. Results and discussion

As a preliminary study, the reaction of DA-cyclopropane **1a** with 1,3,5-trimethoxybenzene **2a** (1.5 equiv) in the presence of $Yb(OTf)_3$ (20 mol %) as the LA catalyst (Table 1) in dichloromethane was performed to provide the corresponding arylated product **3a** in excellent yield (entry 1, Table 1). $Yb(OTf)_3$ was chosen as the LA catalyst based on our earlier success with this Lewis acid in domino ring opening cyclization (DROC) of DA-cyclopropanes for the synthesis of several valuable synthetic targets.[5] Surprisingly, when 1,2-dichloroethane was used as the reaction medium, almost quantitative yield of **3a** was achieved (entry 2). In the presence of

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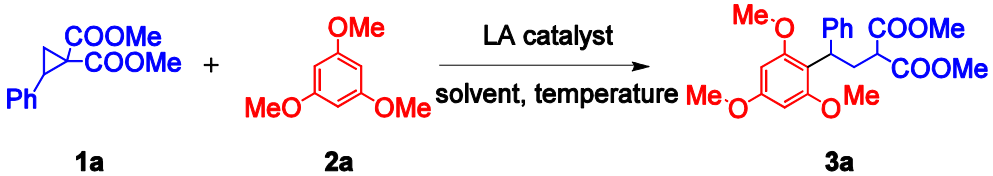
0040-4020/

Table 1
Optimization study



1a **2a** **3a**

Entry	Conditions	Time	Yield (%)
1	$Yb(OTf)_3$ (20 mol %), dichloromethane, rt	5.0 h	86
2	$Yb(OTf)_3$ (20 mol %), 1,2-dichloroethane, rt	7.0 h	99
3	$Yb(OTf)_3$ (1.0 equiv), 1,2-dichloroethane, rt	2.0 h	96
4[a]	**$Yb(OTf)_3$ (20 mol %), 1,2-dichloroethane, rt-65 °C**	**75 min**	**99**
5[a]	$Ti(O^iPr)_4$ (20 mol %), 1,2-dichloroethane, rt-65 °C	25 min	75
6[a]	$Sc(OTf)_3$ (20mol %), 1,2-dichloroethane, rt-65 °C	45 min	92
7[a]	$Zn(OTf)_2$ (20mol %), 1,2-dichloroethane, rt-65 °C	6.0 h	85
8[a]	$Cu(OTf)_2$ (20mol %), 1,2-dichloroethane, rt-65 °C	2.0 h	22
9[a]	$AlCl_3$ (20 mol %), 1,2-dichloroethane, rt-65 °C	30 min	53
10[a]	$FeCl_3$ (20 mol %), 1,2-dichloroethane, rt-65 °C	6.0 h	45

[a] Addition was done at rt and then stirred for 75 min at 65 °C.

stoichiometric amount of the Lewis acid, the reaction took shorter time for complete consumption of **1a** but the product **3a** was obtained with slightly reduced yield (entry 3). When the reaction was performed at 65 °C in the presence of 20 mol % of $Yb(OTf)_3$, it was completed in 75 min providing **3a** in 99% yield (entry 4). Other Lewis acid catalysts e.g., $Ti(O^iPr)_4$, $Sc(OTf)_3$, $Zn(OTf)_2$, $Cu(OTf)_2$, $AlCl_3$ and $FeCl_3$ etc. could not provide better results. In all these cases, either reaction took longer time for completion and/or **3a** was obtained with reduced yield (entry 5–10). So, we decided to proceed further using $Yb(OTf)_3$ as the LA-catalyst and 1,2-dicloroethane as the solvent at 65 °C as the optimum reaction condition.

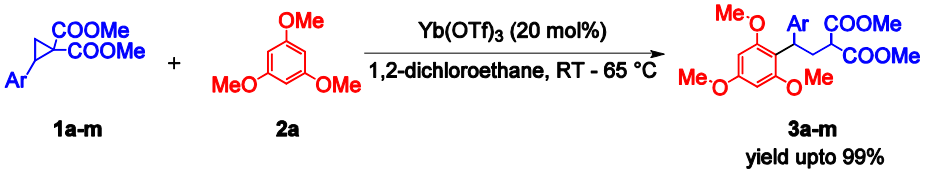
To generalize our approach a number of substituted DA-cyclopropanes (**1b**–**m**) were studied under the optimized reaction condition (Scheme 1) and the results are shown in Table 2. It is important to mention that compounds bearing 1,3,5-trimethoxybenzene or 1,3,5-trihydroxybenzene ring are found to exhibit several interesting biological activities.[6]

Next, to extend the scope of our strategy further, 2-heteroarylcyclopropane-1,1-dicarboxylates **1n**–**o** and 2-styrylcyclopropane-1,1-dicarboxylates **1p**–**q** were reacted with 1,3,5-trimethoxybenzene under our reaction conditions (Schemes 2 and 3). Pleasingly, the corresponding products **3n**–**q** were obtained in excellent yields in all these cases.

It is worth mentioning that in case of styryl substrates **1p**–**q** the nucleophile exclusively attacked the C-2 position of the cyclopropane ring and provided the corresponding products in excellent yields (Scheme 3). No product formation via S_N2' attack of the nucleophile on the double bond was observed.

Diaryl dicarboxylate **3p** was converted into cyclohexene derivative upon allylation of malonate group followed by ring closing metathesis (Scheme 4). This type of cyclohexene ring system is very close to a biologically active natural product (+)-methyllinderatin, a potent antimalarial agent.[7]

We also performed ring opening reactions of several substituted DA-cyclopropanes with indoles as the heteroarenes under our reaction condition (Scheme 5) and the results are described in Table 3. When *N*-methyl indole **2b** was reacted with **1a**, the corresponding dicarboxylate **3r** was obtained in 95% yield. When *p*-methoxy cyclopropane dicarboxylate **1c** was reacted with **2b**, the corresponding product **3s** was obtained in excellent yield. DA-cyclopropane bearing styryl group behaved similarly generating the dicarboxylate derivative **3t** in high yield. DA-cyclopropane **1a** reacts with other substituted *N*-methyl indoles **2c**,**d** to generate the corresponding products **3u**,**v** in excellent yields (Table 3).



1a-m **2a** **3a-m**
yield upto 99%

Scheme 1. Ring opening of DA-cyclopropanes with electron rich arene **2a**.

When *p*-tolyl cyclopropane dicarboxylate **1b** was reacted with **2a**, the corresponding product **3b** was obtained in excellent yield (entry 2, Table 2). DA-cyclopropanes bearing electron-rich aryl groups (**1c**–**f**) behaved similarly generating the dicarboxylates **3c**–**f** in excellent yields (entry 3–6). Halogenated substrates (**1g**–**j**) also smoothly converted into their corresponding products **3g**–**j** upon reaction with **2a** (entry 7–10). When 1-naphthyl substituted DA-cyclopropane **1k** was chosen as the substrate, the corresponding dicarboxylate **3k** was obtained in 80% yield (entry 11). 2-naphthylcyclopropane-1,1-dicarboxylate **1l** reacted in a similar pattern generating **3l** in excellent yield (entry 12). Similarly, when 2-mesitylcyclopropane-1,1-dicarboxylate **1m** was reacted with 1,3,5-trimethoxybenzene **2a**, the corresponding product **3m** was obtained in 82% yield.

Allylation of malonate group of diaryl dicarboxylate **3t** followed by ring closing metathesis gave the cyclohexene derivative **7** in excellent yield (Scheme 6).

Reactions with other arene and heteroarene nucleophiles like 1,2-/1,4-dimethoxybenzene, 1,3-benzodioxole and thiophene etc.

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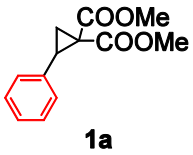
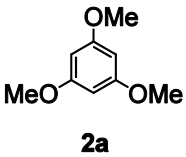
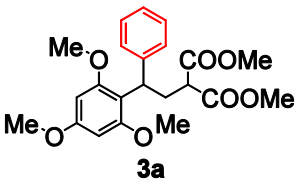
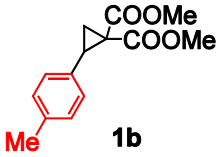
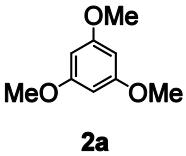
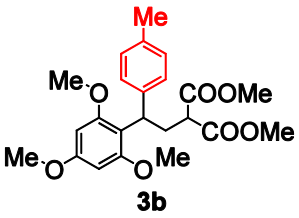
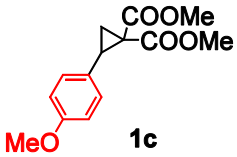
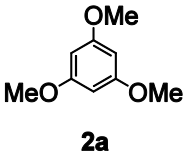
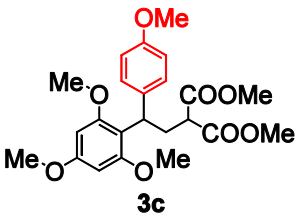
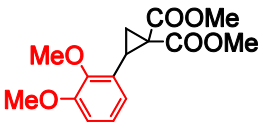
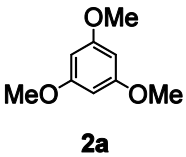
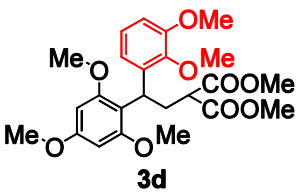
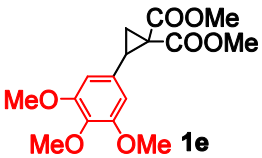
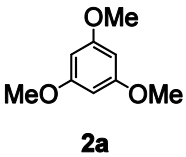
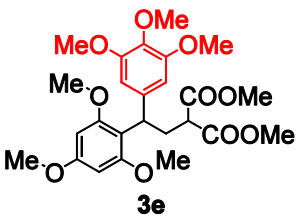
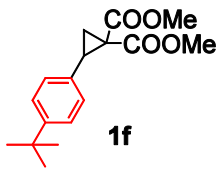
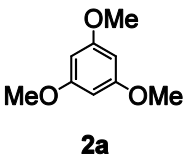
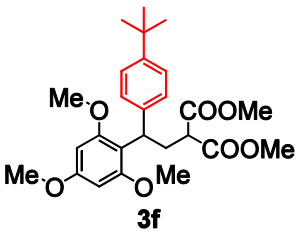
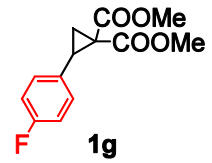
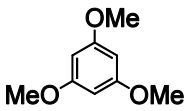
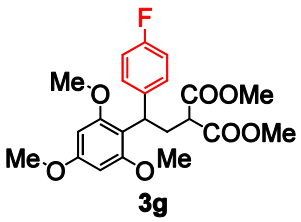
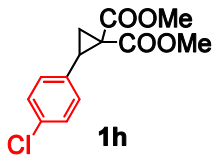
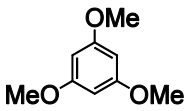
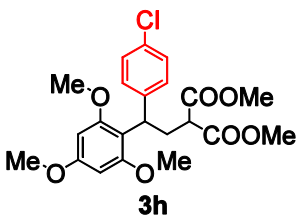
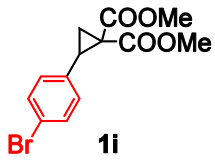
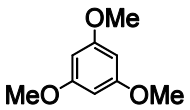
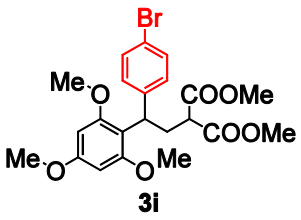
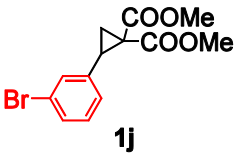
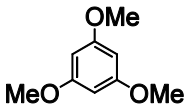
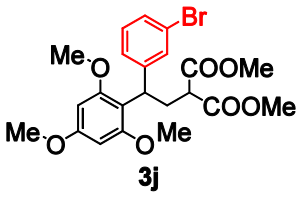
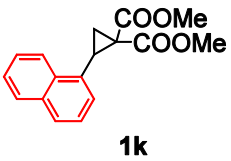
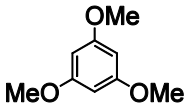
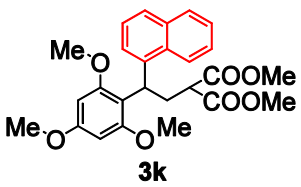
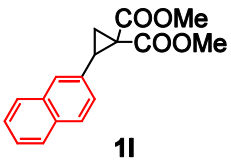
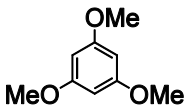
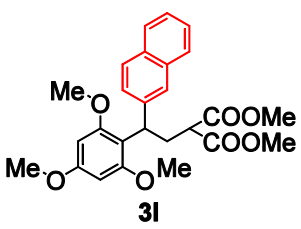
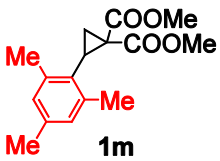
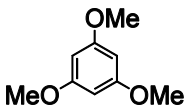
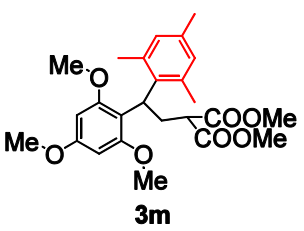
Table 2
Scope of the reaction with DA-cyclopropanes with arene

Entry	DA-cyclopropane	Nucleophile	Product	Yield (%)
1	 **1a**	 **2a**	 **3a**	99
2	 **1b**	 **2a**	 **3b**	95
3	 **1c**	 **2a**	 **3c**	98
4	 **1d**	 **2a**	 **3d**	90
5	 **1e**	 **2a**	 **3e**	93
6	 **1f**	 **2a**	 **3f**	75

(continued on next page)

Table 2 *(continued)*

7	 **1g**	 **2a**	 **3g**	96
8	 **1h**	 **2a**	 **3h**	88
9	 **1i**	 **2a**	 **3i**	90
10	 **1j**	 **2a**	 **3j**	91
11	 **1k**	 **2a**	 **3k**	80
12	 **1l**	 **2a**	 **3l**	89
13	 **1m**	 **2a**	 **3m**	82

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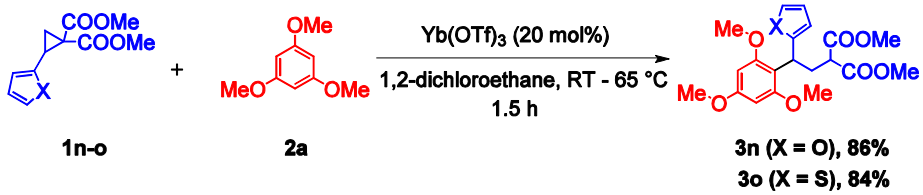
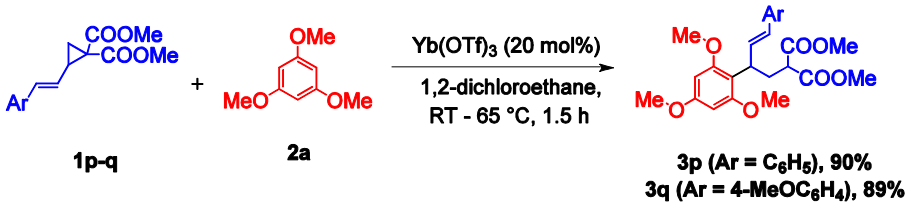
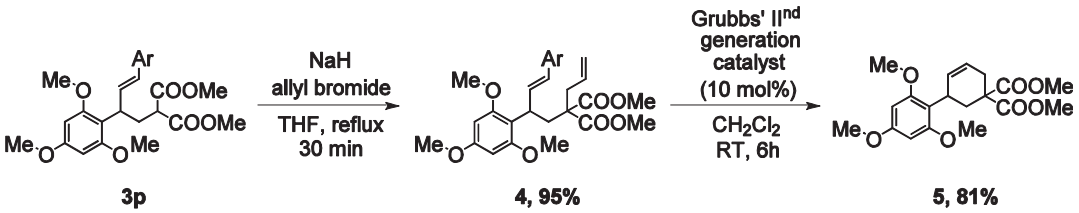


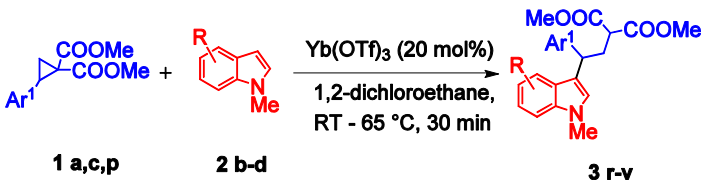
Scheme 2. Synthesis of heteroaryl-substituted dicarboxylates.



Scheme 3. Reactivity of styryl cyclopropane dicarboxylates.



Scheme 4. Synthesis of 1,3,5-trimethoxy phenyl cyclohexene derivative.



Scheme 5. Ring opening of DA-cyclopropanes with indoles.

resulted in complicated reaction mixtures probably due to formation of regioisomers.

In order to extend the synthetic utility of our protocol, the diaryl diarboxylate products (**3a**, **3s**) were hydrolyzed to the corresponding malonic acids under reported conditions (Scheme 7). This type of malonic acid derivatives can be converted to several important compounds of synthetic and biological significance.[8]

To broaden the scope of our strategy, it was extended further for the synthesis of nonracemic 2-(2,2-diarylethyl)malonates. When enantiopure cyclopropane (*S*)-**1a** (ee >99%) was reacted with 1,3,5-trimethoxybenzene **2a** under our optimized condition, to our great pleasure the corresponding nonracemic 2-(2,2-diarylethyl)malonate product (*R*)-**3a** was obtained in high yield and high enantiomeric excess (ee 95%). Similar reaction of (*S*)-**1a** with *N*-methyl indole **2b** afforded the nonracemic 2-(2,2-diarylethyl)malonate product (*R*)-**3r** in high yield and high enantiomeric excess (ee 95%) (Scheme 8).

The proposed mechanism of the reaction with DA-cyclopropane and arene is depicted in Scheme 9. The Lewis acid interacts with two ester moieties of the substrate **1** and the electrophilicity at the C-2 position (often benzylic) of the DA-cyclopropane is enhanced. Next the attack of the arene nucleophile at the C-2 position of the LA-coordinated cyclopropane in an S_N2 fashion followed by aromatization generates the product **3**. Reaction of DA-cyclopropane with heteroarenes follows similar reaction pathways.

3. Conclusion

In conclusion, we have developed a simple and efficient protocol for the synthesis of highly functionalized 2-(2,2-diarylethyl)malonates via LA-catalyzed ring opening of functionalized DA-cyclopropanes with arene and heteroarenes. The synthetic significance of the strategy was demonstrated by easy conversion of the products into other important synthetic scaffolds like functionalized cyclohexene and malonic acid derivatives etc. Nonracemic products with high enantioselectivity could be obtained employing enantiopure cyclopropane as the substrate.

4. Experimental section

4.1. General experimental

Analytical thin layer chromatography (TLC) was carried out using silica gel 60 F_{254} pre-coated plates. Visualization was

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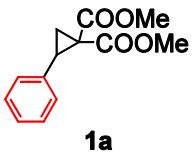
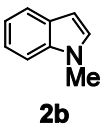
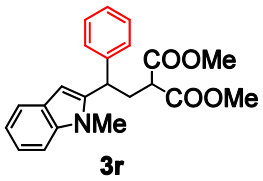
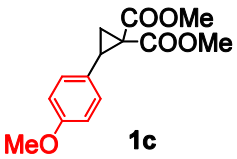
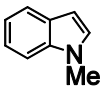
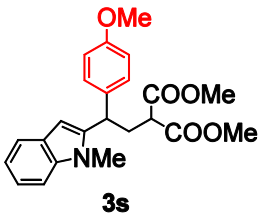
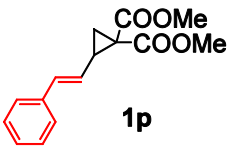
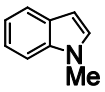
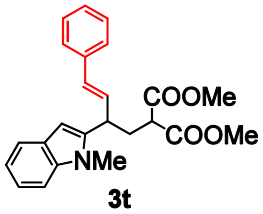
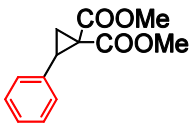
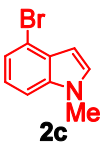
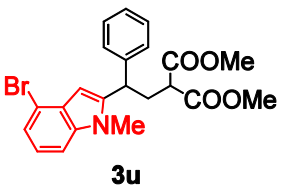
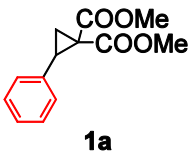
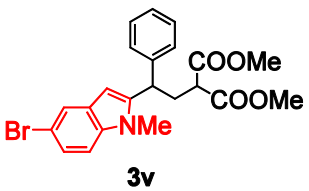
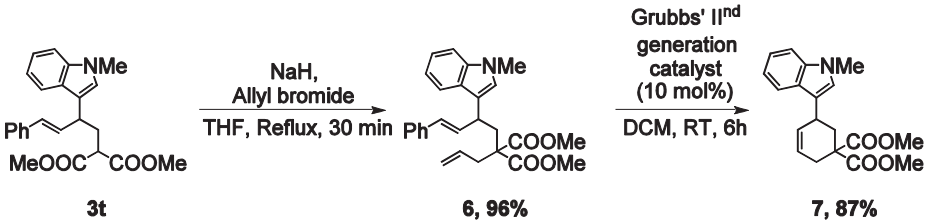
Table 3
Scope of the reaction with DA-cyclopropanes with indoles

Entry	DA-cyclopropane	Nucleophile	Product	Yield (%)
1	 **1a**	 **2b**	 **3r**	95
2	 **1c**	 **2b**	 **3s**	97
3	 **1p**	 **2b**	 **3t**	93
4	 **1a**	 **2c**	 **3u**	94
5	 **1a**	 **2d**	 **3v**	91

accomplished with UV lamp or I_2 stain. Silica gel 230–400 mesh size was used for column chromatography using the combination of ethyl acetate and petroleum ether as an eluent. Unless noted, all reactions were carried out in oven-dried glassware under an atmosphere of nitrogen using anhydrous solvents. Where appropriate, solvents and all reagents were purified prior to use following the guidelines of Perrin and Armarego[9] and Vogel.[10] All racemic 2-arylcyclopropane-1,1-dicarboxylates were prepared using reported



Scheme 6. Synthesis of *N*-methyl indole cyclohexene derivative.

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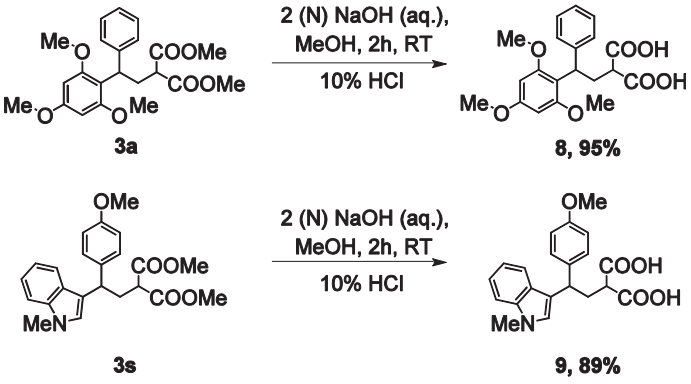


Scheme 7. Hydrolysis of diester **3** to malonic acid derivatives.

method.[11] (*S*)-**1a** was synthesized following literature procedure.[12] All commercial reagents were used as received. IR spectra were recorded either in neat condition or in potassium bromide (KBr) pellet. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 and 500 MHz. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethyl silane (δ 0.00). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 125 MHz. Mass spectra (MS) were obtained using FAB and ESI mass spectrometer (TOF). Melting point was determined using a hot stage apparatus and are reported as uncorrected.

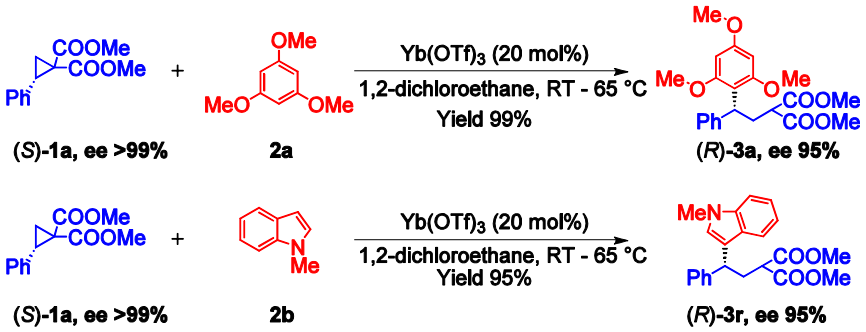
4.2. Dimethyl (*E*)-2-(4-methoxystyryl)cyclopropane-1,1-dicarboxylate (1q)

The compound was synthesized by reacting dimethyl (*E*)-2-(3-(4-methoxyphenyl)allylidene)malonate (250 mg, 0.905 mmol) and trimethylsulphoxonium iodide (239 mg, 1.086 mmol) in presence of NaH (44 mg, 1.086 mmol) in 2.0 mL dry DMF following the literature reported method.[11] Purified with 3% ethyl acetate in hexane solvent. White solid (192 mg, yield 73%). Mp 55–57 °C. R_f 0.35 (20% EtOAc/hexanes). IR (KBr, cm^{-1}) 3003, 2954, 2838, 1727, 1607, 1577, 1513, 1437, 1376, 1327, 1305, 1287, 1255, 1207, 1177, 1130, 1033, 964, 900, 853, 821, 768, 703. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.21 (m, 2H), 6.82 (dd, *J*=6.7, 1.9 Hz, 2H), 6.57 (d, *J*=15.8 Hz, 1H), 5.66 (dd, *J*=15.8, 8.6 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 2.72 (q, *J*=8.6 Hz, 1H), 1.83 (dd, *J*=7.6, 5.0 Hz, 1H), 1.67 (dd, *J*=9.0, 5.0 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 170.1, 168.1, 159.3, 133.4, 129.6, 127.4, 122.2, 114.1, 55.4, 52.9, 52.8, 36.1, 32.0, 21.4; HRMS (ESI-TOF) Calcd for $C_{16}H_{18}NaO_5$ $(M+Na)^+$ 313.1052, found 313.1059.

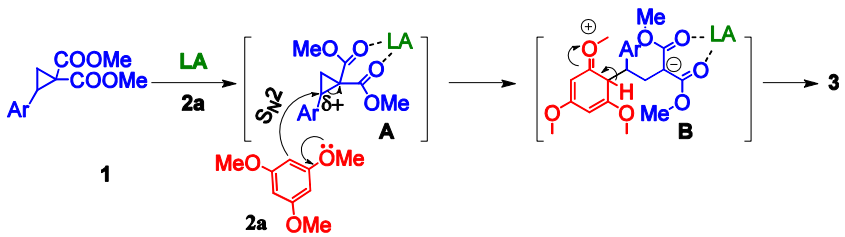
4.3. General procedure for the synthesis of dialkyl (2-(2,2-diaryl)ethyl)malonates 3a–v

To a suspension of $Yb(OTf)_3$ (0.2 mmol) in dry 1,2-dichloroethane (DCE) (1.0 mL), a solution of dialkyl 2-arylcyclopropane-1,1-dicarboxylate **1a–q** (1.0 mmol) and the appropriate arene/heteroarene **2** (2.0 mmol) in dry 1,2-dichloroethane (2.0 mL) was added at room temperature under N_2 atmosphere and the reaction mixture was heated to 65 °C with stirring for appropriate time. After complete consumption of the starting material (monitored by TLC) the reaction was quenched with water (2.0 mL). After separating the organic layer, the aqueous layer was extracted with dichloromethane (4×2.0 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel (230–400 mesh) using ethyl acetate in petroleum ether (20%) as the eluent to afford the pure products **3a–v** as colorless thick liquids or white crystalline or yellowish solid.

*4.3.1. Dimethyl 2-(2-phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (**3a**).* The compound was synthesized by reacting dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (50 mg, 0.213 mmol) and 1,3,5-trimethoxybenzene **2a** (72 mg, 0.426 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (26 mg, 0.043 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition.



Scheme 8. Ring opening of enantiopure DA-cyclopropane with electron rich arene and heteroarene.



Scheme 9. Mechanism of the reaction between DA-cyclopropanes and arene.

Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (85 mg, yield 99%). R_f 0.31 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2952, 2841, 1753, 1734, 1606, 1591, 1494, 1454, 1436, 1418, 1328, 1222, 1205, 1149, 1119, 1061, 1044, 950, 814. ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J=7.8 Hz, 2H), 7.21–7.17 (m, 2H), 7.09 (t, J=7.3 Hz, 1H), 6.08 (s, 2H), 4.60 (dd, J=10.8, 5.7 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.69 (s, 6H), 3.61 (s, 3H), 3.24 (dd, J=9.2, 5.5 Hz, 1H), 2.94–2.86 (m, 1H), 2.75–2.68 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.4, 170.1, 160.1, 159.5, 144.5, 127.8, 127.7, 125.5, 111.4, 91.2, 55.7, 55.3, 52.5, 52.4, 50.8, 37.1, 31.1; HRMS (ESI-TOF) Calcd for $C_{22}H_{26}NaO_7$ $(M+Na)^+$ 425.1576, found 425.1574.

For (*R*)-**3a**: Optical rotation $[\alpha]_D^{25}$=+49.3 (*c* 0.142, $CHCl_3$) for a 95% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (CELLULOSE-2 column), Hexane–Isopropanol 95:5, flow rate=1.0 mL/min, t_R (1)=14.72 min (major), t_R (2)=18.63 min (minor).

*4.3.2. Dimethyl 2-(2-p-tolyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (**3b**).* The compound was synthesized by reacting dimethyl 2-(*p*-tolyl)cyclopropane-1,1-dicarboxylate **1b** (50 mg, 0.201 mmol) and 1,3,5-trimethoxybenzene **2a** (67 mg, 0.402 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (25 mg, 0.040 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (79 mg, yield 95%). R_f 0.32 (35% EtOAc/hexanes). IR (KBr, cm^{-1}) 2924, 2852, 1752, 1734, 1605, 1590, 1513, 1492, 1454, 1435, 1417, 1326, 1221, 1204, 1148, 1118, 1062, 1040, 949, 812. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J=7.8 Hz, 2H), 7.01 (d, J=8.3 Hz, 2H), 6.08 (s, 2H), 4.56 (dd, J=10.8, 5.7 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 9H), 3.61 (s, 3H), 3.23 (dd, J=9.6, 5.5 Hz, 1H), 2.93–2.85 (m, 1H), 2.73–2.65 (m, 1H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 160.0, 159.4, 141.4, 134.8, 128.5, 127.7, 111.5, 91.2, 55.7, 55.3, 52.5, 52.4, 50.8, 36.8, 31.3, 21.0; HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NaO_7$ $(M+Na)^+$ 439.1733, found 439.1736.

*4.3.3. Dimethyl 2-(2-(4-methoxyphenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3c**).* The compound was synthesized by reacting dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate **1c** (50 mg, 0.189 mmol) and 1,3,5-trimethoxybenzene **2a** (64 mg, 0.378 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (23 mg, 0.038 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (80 mg, yield 98%). R_f 0.30 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2924, 1733, 1605, 1511, 1456, 1245, 1204, 1148, 1118, 1035, 813. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J=8.2 Hz, 2H), 6.77–6.74 (m, 2H), 6.09 (s, 2H), 4.55 (dd, J=13.2, 6.0 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.71 (s, 3H), 3.70 (s, 6H), 3.62 (s, 3H), 3.24 (dd, J=9.2, 5.5 Hz, 1H), 2.92–2.85 (m, 1H), 2.73–2.65 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.4, 170.1, 160.0, 159.4, 157.5, 136.7, 128.7, 113.2, 111.7, 91.2, 55.7, 55.3, 55.2, 52.4, 52.3, 50.9, 36.5, 31.5; HRMS (ESI-TOF) Calcd for $C_{23}H_{28}NaO_8$ $(M+Na)^+$ 455.1682, found 455.1669.

*4.3.4. Dimethyl 2-(2-(2,3-dimethoxyphenyl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (**3d**).* The compound was synthesized by reacting dimethyl 2-(2,3-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate **1d** (50 mg, 0.170 mmol) and 1,3,5-trimethoxybenzene **2a** (57 mg, 0.340 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (21 mg, 0.034 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (71 mg, yield 90%). R_f 0.28 (35% EtOAc/hexanes). IR (KBr, cm^{-1}) 3004, 2937, 2840, 1734, 1605, 1590, 1494, 1463, 1420, 1326, 1275, 1218, 1205, 1189, 1151, 1121, 1097, 1065, 1046, 1008, 952, 929, 897, 831, 814, 794, 752, 710. ^1H NMR (500 MHz, $CDCl_3$): δ 7.05 (d, J=8.0 Hz, 1H), 6.95 (t, J=8.0 Hz, 1H), 6.72 (d, J=8.0 Hz, 1H), 6.07 (s, 2H), 4.87 (dd, J=11.0, 5.5 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 3.69 (s, 6H), 3.59 (s, 3H), 3.58 (s, 3H), 3.31 (dd, J=8.6, 5.5 Hz, 1H), 2.86–2.80 (m, 1H), 2.60–2.55 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.5, 170.1, 159.9, 159.7, 152.6, 147.2, 138.4, 122.8, 121.3, 111.4, 109.9, 91.2, 60.1, 55.7, 55.6, 55.3, 52.4, 52.3, 50.7, 31.9, 31.6; HRMS (ESI-TOF) Calcd for $C_{24}H_{30}NaO_9$ $(M+Na)^+$ 485.1788, found 485.1782.

*4.3.5. Dimethyl 2-(2-(2,4,6-trimethoxyphenyl)-2-(3,4,5-trimethoxyphenyl)ethyl)malonate (**3e**).* The compound was synthesized by reacting dimethyl 2-(3,4,5-trimethoxyphenyl)cyclopropane-1,1-dicarboxylate **1e** (50 mg, 0.154 mmol) and 1,3,5-trimethoxybenzene **2a** (52 mg, 0.309 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (19 mg, 0.031 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 25% ethyl acetate in hexane solvent. Thick colorless liquid (71 mg, yield 93%). R_f 0.25 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2938, 2839, 1752, 1735, 1605, 1589, 1508, 1455, 1418, 1327, 1224, 1205, 1150, 1125, 1039, 1011, 950, 816. ^1H NMR (400 MHz, $CDCl_3$): δ 6.55 (s, 2H), 6.10 (s, 2H), 4.53 (dd, J=10.8, 5.7 Hz, 1H), 3.79 (s, 6H), 3.78 (s, 3H), 3.77 (s, 3H), 3.73 (s, 6H), 3.69 (s, 3H), 3.62 (s, 3H), 3.22 (dd, J=9.6, 5.5 Hz, 1H), 2.91–2.84 (m, 1H), 2.70–2.63 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.4, 170.1, 160.1, 159.4, 152.6, 140.3, 136.0, 110.9, 105.1, 91.2, 60.9, 56.1, 55.7, 55.3, 52.5, 52.4, 50.8, 37.6, 31.7; HRMS (ESI-TOF) Calcd for $C_{25}H_{33}O_{10}$ $(M+H)^+$ 493.2074, found 493.2074.

*4.3.6. Dimethyl 2-(2-(4-(tbutyl)phenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3f**).* The compound was synthesized by reacting dimethyl 2-(4-(*tert*-butyl)phenyl)cyclopropane-1,1-dicarboxylate **1f** (50 mg, 0.172 mmol) and 1,3,5-trimethoxybenzene **2a** (58 mg, 0.345 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (21 mg, 0.035 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (59 mg, yield 75%). R_f 0.36 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2954, 2925, 1753, 1736, 1606, 1591, 1492, 1456, 1435, 1417, 1327, 1222, 1204, 1149, 1119, 1063, 1042, 950, 815. ^1H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 4H), 6.09 (s, 2H), 4.58 (dd, J=11.0, 6.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 6H), 3.69 (s, 3H), 3.61 (s, 3H), 3.24 (dd, J=9.6, 5.5 Hz, 1H), 2.96–2.88 (m, 1H), 2.74–2.67 (m, 1H), 1.27 (s, 9H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.5, 170.1, 160.0, 159.5, 148.1, 141.3, 127.5, 124.7, 111.3, 91.1, 55.7, 55.3, 52.5, 52.4, 50.9, 36.8, 34.3, 31.5, 31.4; HRMS (ESI-TOF) Calcd for $C_{26}H_{35}O_7$ $(M+H)^+$ 459.2383, found 459.2383.

*4.3.7. Dimethyl 2-(2-(4-fluorophenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3g**).* The compound was synthesized by reacting dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate **1g** (50 mg, 0.198 mmol) and 1,3,5-trimethoxybenzene **2a** (67 mg, 0.396 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (25 mg, 0.040 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (80 mg, yield 96%). R_f 0.32 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2953, 2842, 1753, 1734, 1606, 1508, 1494, 1455, 1436, 1418, 1326, 1221, 1205, 1150, 1119, 1063, 1041, 1016, 950, 816, 797. ^1H NMR (500 MHz, $CDCl_3$): δ 7.23 (dd, J=8.6, 5.5 Hz, 2H), 6.88 (t, J=8.9 Hz, 2H), 6.09 (s, 2H), 4.57 (dd, J=11.0, 5.5 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.69 (s, 6H), 3.61 (s, 3H), 3.22 (dd, J=9.2, 5.5 Hz, 1H), 2.90–2.84 (m, 1H), 2.71–2.65 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.3, 170.0, 161.0 (d, J_{C-F}=241 Hz), 160.2, 159.3, 140.2, 129.2, 129.1, 114.5, 114.3, 111.2, 91.2, 55.6, 55.3, 52.5, 52.4, 50.7, 36.4, 31.2; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NaFO_7$ $(M+Na)^+$ 443.1482, found 443.1485.

*4.3.8. Dimethyl 2-(2-(4-chlorophenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3h**).* The compound was synthesized by reacting

dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate **1h** (50 mg, 0.186 mmol) and 1,3,5-trimethoxybenzene **2a** (67 mg, 0.372 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (23 mg, 0.037 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (73 mg, yield 88%). R_f 0.31 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2925, 2850, 1752, 1735, 1607, 1591, 1491, 1456, 1435, 1418, 1325, 1222, 1205, 1149, 1119, 1091, 1062, 1041, 1014, 950, 815. ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, J=8.6 Hz, 2H), 7.17–7.14 (m, 2H), 6.08 (s, 2H), 4.56 (dd, J=10.9, 5.7 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.69 (s, 6H), 3.61 (s, 3H), 3.21 (dd, J=9.2, 5.2 Hz, 1H), 2.89–2.83 (m, 1H), 2.70–2.64 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.3, 170.0, 160.3, 159.3, 143.1, 131.0, 129.2, 127.8, 110.9, 91.2, 55.6, 55.3, 52.5, 52.4, 50.7, 36.5, 30.9; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NaClO_7$ $(M+Na)^+$ 459.1187, found 459.1187.

*4.3.9. Dimethyl 2-(2-(4-bromophenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3i**).* The compound was synthesized by reacting dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate **1i** (50 mg, 0.160 mmol) and 1,3,5-trimethoxybenzene **2a** (54 mg, 0.320 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (20 mg, 0.032 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (69 mg, yield 90%). R_f 0.30 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2927, 2841, 1734, 1607, 1591, 1488, 1455, 1435, 1418, 1326, 1222, 1204, 1149, 1119, 1062, 1041, 1010, 950, 814. ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, J=8.0 Hz, 2H), 7.14 (d, J=8.1 Hz, 2H), 6.08 (s, 2H), 4.55 (dd, J=10.9, 5.2 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.69 (s, 6H), 3.61 (s, 3H), 3.21 (dd, J=9.5, 5.5 Hz, 1H), 2.88–2.82 (m, 1H), 2.70–2.64 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.3, 170.0, 160.3, 159.3, 143.6, 130.7, 129.6, 119.2, 110.7, 91.1, 55.6, 55.3, 52.5, 52.4, 50.6, 36.6, 30.8; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NaBrO_7$ $(M+Na)^+$ 503.0681, found 503.0689.

*4.3.10. Dimethyl 2-(2-(3-bromophenyl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3j**).* The compound was synthesized by reacting dimethyl 2-(3-bromophenyl)cyclopropane-1,1-dicarboxylate **1j** (50 mg, 0.160 mmol) and 1,3,5-trimethoxybenzene (54 mg, 0.320 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (20 mg, 0.032 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (70 mg, yield 91%). R_f 0.33 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2925, 2853, 1730, 1594, 1493, 1471, 1442, 1417, 1343, 1311, 1283, 1264, 1223, 1206, 1164, 1152, 1121, 1075, 1062, 1031, 989, 894, 860, 814, 795, 783, 704. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.41 (m, 1H), 7.23–7.18 (m, 2H), 7.06 (t, J=7.8 Hz, 1H), 6.08 (s, 2H), 4.56 (dd, J=11.2, 5.3 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.69 (s, 6H), 3.61 (s, 3H), 3.20 (dd, J=9.6, 5.5 Hz, 1H), 2.89–2.82 (m, 1H), 2.69–2.62 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.2, 169.9, 160.3, 159.3, 147.0, 130.9, 129.3, 128.5, 126.5, 121.9, 110.5, 91.1, 55.6, 55.3, 52.5, 52.4, 50.6, 36.8, 30.8; HRMS (ESI-TOF) Calcd for $C_{22}H_{25}NaBrO_7$ $(M+Na)^+$ 503.0681, found 503.0689.

*4.3.11. Dimethyl 2-(2-(naphthalen-1-yl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3k**).* The compound was synthesized by reacting dimethyl 2-(naphthalen-1-yl)cyclopropane-1,1-dicarboxylate **1k** (50 mg, 0.176 mmol) and 1,3,5-trimethoxybenzene **2a** (59 mg, 0.352 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (22 mg, 0.035 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (64 mg, yield 80%). R_f 0.34 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2952, 2840, 1751, 1733, 1606, 1492, 1454, 1435, 1418, 1331, 1223, 1205, 1148, 1118, 1061, 1035, 950, 781. ^1H NMR (400 MHz, $CDCl_3$): δ 8.22–8.20 (m, 1H), 7.78–7.76 (m, 1H), 7.67–7.63 (m, 2H), 7.43–7.25 (m, 3H), 6.07 (s, 2H), 5.26 (dd, J=11.5, 4.6 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.69 (s, 6H), 3.60 (s, 3H), 3.39 (dd, J=9.2, 5.0 Hz, 1H), 3.07–3.00 (m, 1H), 2.81–2.74 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 160.1, 159.5, 140.0, 133.8, 132.4, 128.6, 126.4, 125.6, 125.0, 124.9, 124.2, 111.1, 91.4, 55.6, 55.3, 52.5, 50.6, 34.0, 32.0; HRMS (ESI-TOF) Calcd for $C_{26}H_{28}NaO_7$ $(M+Na)^+$ 475.1733, found 475.1732.

*4.3.12. Dimethyl 2-(2-(naphthalen-2-yl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3l**).* The compound was synthesized by reacting dimethyl 2-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate **1l** (50 mg, 0.176 mmol) and 1,3,5-trimethoxybenzene **2a** (59 mg, 0.352 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (22 mg, 0.035 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (71 mg, yield 89%). R_f 0.31 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2999, 2952, 2841, 1752, 1734, 1606, 1591, 1493, 1454, 1435, 1418, 1331, 1261, 1224, 1205, 1149, 1118, 1063, 1040, 950, 855, 817, 746. ^1H NMR (400 MHz, $CDCl_3$): δ 7.77–7.72 (m, 3H), 7.65 (d, J=8.2 Hz, 1H), 7.42–7.34 (m, 3H), 6.10 (s, 2H), 4.76 (dd, J=10.8, 5.3 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.69 (s, 6H), 3.63 (s, 3H), 3.30 (dd, J=9.2, 5.5 Hz, 1H), 3.04–2.97 (m, 1H), 2.89–2.81 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.4, 170.1, 160.2, 159.5, 142.0, 133.4, 131.9, 127.8, 127.5, 127.2, 127.1, 125.6, 125.5, 125.0, 111.2, 91.2, 55.7, 55.3, 52.5, 52.4, 50.8, 37.2, 31.0; HRMS (ESI-TOF) Calcd for $C_{26}H_{28}NaO_7$ $(M+Na)^+$ 475.1733, found 475.1736.

*4.3.13. Dimethyl 2-(2-mesityl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (**3m**).* The compound was synthesized by reacting dimethyl 2-mesitylcyclopropane-1,1-dicarboxylate **1m** (50 mg, 0.181 mmol) and 1,3,5-trimethoxybenzene **2a** (61 mg, 0.362 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (23 mg, 0.036 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (66 mg, yield 82%). R_f 0.35 (35% EtOAc/hexanes). IR (KBr, cm^{-1}) 2998, 2953, 2840, 1752, 1735, 1607, 1589, 1454, 1436, 1417, 1327, 1205, 1150, 1122, 1068, 1037, 952, 918, 852, 814, 739. ^1H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 2H), 6.07 (s, 2H), 4.62 (dd, J=12.8, 4.6 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.65 (s, 6H), 3.54 (dd, J=10.8, 2.5 Hz, 1H), 3.06 (td, J=13.5, 2.6 Hz, 1H), 2.24 (s, 6H), 2.18 (s, 3H), 2.21–2.13 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.6, 159.9, 159.7, 139.5, 136.8, 134.6, 129.9, 109.6, 91.0, 55.4, 55.3, 52.4, 52.3, 50.6, 36.9, 32.1, 20.7, 20.2; HRMS (ESI-TOF) Calcd for $C_{25}H_{33}O_7$ $(M+H)^+$ 445.2226, found 445.2228.

*4.3.14. Dimethyl 2-(2-(furan-2-yl)-2-(2,4,6-trimethoxyphenyl)ethyl) malonate (**3n**).* The compound was synthesized by reacting dimethyl 2-(furan-2-yl)cyclopropane-1,1-dicarboxylate **1n** (50 mg, 0.223 mmol) and 1,3,5-trimethoxybenzene **2a** (75 mg, 0.446 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (28 mg, 0.045 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. White crystalline solid (75 mg, yield 86%). Mp 86–88 °C. R_f 0.34 (35% EtOAc/hexanes). IR (KBr, cm^{-1}) 2953, 2840, 1735, 1607, 1592, 1496, 1458, 1437, 1419, 1326, 1222, 1205, 1151, 1119, 1061, 1040, 1011, 950, 917, 817, 733. ^1H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J=1.4 Hz, 1H), 6.23 (dd, J=3.2, 1.8 Hz, 1H), 6.09 (s, 2H), 5.98 (d, J=3.2 Hz, 1H), 4.61 (t, J=8.0 Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.69 (s, 6H), 3.59 (s, 3H), 3.26 (d, J=7.4 Hz, 1H), 2.72 (d, J=7.7 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.2, 169.8, 160.4, 159.6, 157.8, 140.2, 110.0, 108.5, 104.2, 91.2, 55.8, 55.3, 52.5, 52.4, 50.3, 32.0, 30.2; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NaO_8$ $(M+Na)^+$ 415.1369, found 415.1360.

*4.3.15. Dimethyl 2-(2-(thiophen-2-yl)-2-(2,4,6-trimethoxyphenyl) ethyl)malonate (**3o**).* The compound was synthesized by reacting dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate **1o** (50 mg, 0.208 mmol) and 1,3,5-trimethoxybenzene **2a** (70 mg, 0.416 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (26 mg,

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0.042 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (71 mg, yield 84%). R_f 0.33 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2954, 2925, 2854, 1732, 1606, 1590, 1494, 1456, 1418, 1323, 1204, 1149, 1118, 1062, 1037, 950, 815. ^1H NMR (400 MHz, $CDCl_3$): δ 7.03 (dd, J=5.04, 1.4 Hz, 1H), 6.85–6.82 (m, 2H), 6.09 (s, 2H), 4.83 (dd, J=10.3, 6.2 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 6H), 3.69 (s, 3H), 3.62 (s, 3H), 3.23 (dd, J=9.4, 5.7 Hz, 1H), 2.92–2.85 (m, 1H), 2.78–2.71 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.2, 169.8, 160.4, 159.4, 148.7, 126.0, 123.7, 122.8, 110.7, 91.1, 55.7, 55.3, 52.5, 52.4, 50.6, 33.6, 32.9; HRMS (ESI-TOF) Calcd for $C_{20}H_{24}NaO_7S$ $(M+Na)^+$ 431.1140, found 431.1147.

*4.3.16. Dimethyl (E)-2-(4-phenyl-2-(2,4,6-trimethoxyphenyl)but-3-enyl)malonate (**3p**).* The compound was synthesized by reacting dimethyl (*E*)-2-styrylcyclopropane-1,1-dicarboxylate **1p** (50 mg, 0.192 mmol) and 1,3,5-trimethoxybenzene **2a** (65 mg, 0.384 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (24 mg, 0.038 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (74 mg, yield 90%). R_f 0.34 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2951, 2840, 1733, 1590, 1492, 1453, 1435, 1330, 1218, 1203, 1147, 1118, 1060, 1038, 966, 949, 812, 742. ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.31 (m, 2H), 7.26–7.23 (m, 2H), 7.16–7.13 (m, 1H), 6.59 (dd, J=15.8, 8.3 Hz, 1H), 6.38 (d, J=16.0 Hz, 1H), 6.11 (s, 2H), 4.12–4.07 (m, 1H), 3.79 (s, 9H), 3.68 (s, 3H), 3.63 (s, 3H), 3.27 (dd, J=8.1, 6.3 Hz, 1H), 2.51–2.47 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.3, 170.1, 160.0, 159.2, 138.1, 132.5, 129.7, 128.4, 126.8, 126.2, 110.9, 91.2, 55.8, 55.4, 52.5, 52.4, 50.6, 36.8, 32.5; HRMS (ESI-TOF) Calcd for $C_{24}H_{28}NaO_7$ $(M+Na)^+$ 451.1733, found 451.1735.

*4.3.17. Dimethyl (E)-2-(4-(4-methoxyphenyl)-2-(2,4,6-trimethoxyphenyl)but-3-en-1-yl)malonate (**3q**).* The compound was synthesized by reacting dimethyl (*E*)-2-(4-methoxystyryl)cyclopropane-1,1-dicarboxylate **1q** (50 mg, 0.172 mmol) and 1,3,5-trimethoxybenzene **2a** (58 mg, 0.344 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (21 mg, 0.034 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (70 mg, yield 89%). R_f 0.35 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2999, 2952, 2838, 1752, 1734, 1607, 1511, 1493, 1454, 1438, 1419, 1331, 1249, 1220, 1204, 1175, 1149, 1120, 1060, 1036, 969, 951, 815. ^1H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, J=8.0 Hz, 2H), 6.78 (d, J=8.7 Hz, 2H), 6.45 (dd, J=14.4, 8.3 Hz, 1H), 6.32 (d, J=15.8 Hz, 1H), 6.10 (s, 2H), 4.05 (q, J=8.0 Hz, 1H), 3.78 (s, 9H), 3.77 (s, 3H), 3.67 (s, 3H), 3.62 (s, 3H), 3.26 (t, J=7.7 Hz, 1H), 2.46 (t, J=7.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 159.9, 159.1, 158.6, 130.9, 130.3, 129.1, 127.3, 113.8, 111.1, 91.1, 55.8, 55.4, 55.3, 52.5, 52.4, 50.7, 36.8, 32.6; HRMS (ESI-TOF) Calcd for $C_{25}H_{30}NaO_8$ $(M+Na)^+$ 481.1838, found 481.1832.

*4.3.18. Dimethyl 2-(2-(1-methyl-1H-indol-3-yl)-2-phenylethyl)malonate (**3r**).* The compound was synthesized by reacting dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (50 mg, 0.213 mmol) and 1-methylindole **2b** (53 μL, 0.427 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (26 mg, 0.043 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 15% ethyl acetate in hexane solvent. Yellowish solid (74 mg, yield 95%). Mp 90–92 °C. R_f 0.50 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 3026, 2926, 2952, 1751, 1734, 1601, 1547, 1471, 1435, 1374, 1329, 1279, 1259, 1226, 1153, 1042, 1014, 809, 742, 704. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J=8.2 Hz, 1H), 7.32–7.25 (m, 5H), 7.20–7.15 (m, 2H), 7.03–6.99 (m, 1H), 6.87 (s, 1H), 4.22–4.18 (m, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H), 3.41–3.37 (m, 1H), 2.85–2.77 (m, 1H), 2.64–2.57 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.0, 169.9, 143.6, 137.3, 128.6, 128.1, 127.2, 126.6, 126.2, 121.8, 119.6, 119.0, 117.3, 109.2, 52.6, 52.5, 50.2, 40.7, 35.1, 32.8; HRMS (EI-TOF) Calcd for $C_{22}H_{23}NO_4$ $(M)^+$ 365.1627, found 365.1623.

For (*R*)-**3r**: Optical rotation $[\alpha]_D^{25}$=–14.7 (*c* 0.102, $CHCl_3$) for a 95% ee sample. The enantiomeric excess was determined by chiral HPLC analysis (OD-H column), Hexane–Isopropanol 95:5, flow rate=1.0 mL/min, t_R (1)=13.81 min (minor), t_R (2)=20.10 min (major).

*4.3.19. Dimethyl 2-(2-(4-methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl)malonate (**3s**).* The compound was synthesized by reacting dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate **1c** (50 mg, 0.189 mmol) and 1-methylindole **2b** (50 μL, 0.378 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (24 mg, 0.038 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 20% ethyl acetate in hexane solvent. Thick colorless liquid (74 mg, yield 97%). R_f 0.34 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2953, 2926, 2854, 1732, 1610, 1583, 1547, 1511, 1435, 1373, 1327, 1247, 1153, 1034, 807, 742. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44–7.42 (m, 1H), 7.26–7.15 (m, 4H), 7.03–6.99 (m, 1H), 6.85–6.80 (m, 3H), 4.16–4.12 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.72 (s, 3H), 3.66 (s, 3H), 3.39 (dd, J=8.5, 6.6 Hz, 1H), 2.83–2.76 (m, 1H), 2.59–2.52 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.1, 170.0, 158.2, 137.4, 135.6, 129.0, 127.2, 126.1, 121.8, 119.7, 118.9, 117.7, 114.0, 109.2, 55.3, 52.6, 52.5, 50.2, 39.9, 35.2, 32.8; HRMS (ESI-TOF) Calcd for $C_{23}H_{25}NaNO_5$ $(M+Na)^+$ 418.1630, found 418.1631.

*4.3.20. Dimethyl (E)-2-(2-(1-methyl-1H-indol-3-yl)-4-phenylbut-3-en-1-yl)malonate (**3t**).* The compound was synthesized by reacting dimethyl (*E*)-2-styrylcyclopropane-1,1-dicarboxylate **1p** (50 mg, 0.192 mmol) and 1-methylindole **2b** (47 μL, 0.384 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (24 mg, 0.038 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 9% ethyl acetate in hexane solvent. Thick colorless liquid (70 mg, yield 93%). R_f 0.45 (20% EtOAc/hexanes). IR (Neat, cm^{-1}) 3055, 3025, 2952, 2925, 2853, 1751, 1733, 1614, 1599, 1546, 1484, 1469, 1448, 1435, 1374, 1328, 1268, 1254, 1225, 1154, 1104, 1071, 1042, 1014, 968, 909, 841, 810, 743. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J=8.0 Hz, 1H), 7.38–7.19 (m, 5H), 7.13–7.09 (m, 1H), 6.93 (s, 1H), 6.55 (d, J=15.8 Hz, 1H), 6.37 (dd, J=16.0, 8.0 Hz, 1H), 3.82–3.74 (m, 1H), 3.76 (s, 3H), 3.72 (s, 3H), 3.69 (s, 3H), 3.56 (t, J=7.3 Hz, 1H), 2.66–2.59 (m, 1H), 2.54–2.46 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 170.1, 170.0, 137.4, 132.4, 130.4, 128.6, 128.4, 127.3, 127.1, 126.4, 126.0, 121.9, 119.7, 119.1, 115.9, 109.4, 52.6, 50.2, 38.8, 34.3, 32.8; HRMS (ESI-TOF) Calcd for $C_{24}H_{25}NNaO_4$ $(M+Na)^+$ 414.1700, found 414.1682.

*4.3.21. Dimethyl 2-(2-(4-bromo-1-methyl-1H-indol-3-yl)-2-phenylethyl)malonate (**3u**).* The compound was synthesized by reacting dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (50 mg, 0.213 mmol) and 4-bromo-1-methyl-1*H*-indole **2c** (90 mg, 0.427 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (27 mg, 0.043 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 18% ethyl acetate in hexane solvent. Thick colorless liquid (89 mg, yield 94%). R_f 0.42 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 3059, 3027, 2952, 2854, 1751, 1734, 1606, 1550, 1492, 1478, 1451, 1435, 1418, 1330, 1276, 1228, 1189, 1153, 1086, 1022, 908, 839, 770, 738, 703. ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.13 (m, 6H), 7.02–6.97 (m, 2H), 5.10 (t, J=7.9 Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.65 (s, 3H), 3.52–3.48 (m, 1H), 2.70–2.62 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.1, 169.9, 144.5, 138.4, 128.4, 128.3, 128.1, 126.3, 125.2, 124.1, 122.5, 117.9, 114.3, 108.7, 52.6, 52.5, 50.5, 39.0, 36.7, 33.2; HRMS (EI-TOF) Calcd for $C_{22}H_{22}BrNO_4$ $(M)^+$ 443.0732, found 443.0736.

*4.3.22. Dimethyl 2-(2-(5-bromo-1-methyl-1H-indol-3-yl)-2-phenylethyl)malonate (**3v**).* The compound was synthesized by

reacting dimethyl 2-phenylcyclopropane-1,1-dicarboxylate **1a** (50 mg, 0.189 mmol) and 5-bromo-1-methyl-1*H*-indole **2d** (50 μL, 0.378 mmol) in presence of catalytic amount of $Yb(OTf)_3$ (24 mg, 0.038 mmol) in overall 3.0 mL dry DCE following the mentioned optimized reaction condition. Purified with 18% ethyl acetate in hexane solvent. Yellowish solid (86 mg, yield 91%). Mp 124–126 °C. R_f 0.45 (35% EtOAc/hexanes). IR (Neat, cm^{-1}) 2952, 2925, 2854, 1750, 1733, 1601, 1544, 1477, 1435, 1376, 1339, 1274, 1224, 1152, 1072, 1041, 864, 793, 768, 748, 706. ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J*=1.4 Hz, 1H), 7.31–7.17 (m, 5H), 7.11 (d, *J*=8.7 Hz, 1H), 6.88 (s, 1H), 4.14–4.10 (m, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.37–3.33 (m, 1H), 2.77–2.70 (m, 1H), 2.62–2.55 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.9, 168.8, 143.1, 136.0, 128.9, 128.7, 127.9, 127.3, 126.8, 124.7, 122.0, 117.0, 112.5, 110.8, 52.7, 52.6, 50.1, 40.4, 35.1, 33.0; HRMS (EI-TOF) Calcd for $C_{22}H_{22}BrNO_4$ $(M)^+$ 443.0732, found 443.0735.

4.4. General procedure for the synthesis of dimethyl (*E*)-2-allyl-2-(4-phenyl-2-arylbut-3-en-1-yl)malonate 4 and 6

To a suspension of NaH (1.5 mmol) in dry THF (1.0 mL) a solution of dimethyl (*E*)-2-(4-phenyl-2-arylbut-3-en-1-yl)malonate **3p** or **3t** (1.0 mmol) in the same solvent (2.0 mL) was added at room temperature under N_2 atmosphere and stirred for 5 min. Then allyl bromide (1.5 mmol) was added dropwise and the reaction mixture was heated to 65 °C under stirring for 30 min. After complete consumption of the starting material (monitored by TLC) the reaction was quenched with water (2.0 mL). After separating the organic layer, the aqueous layer was extracted with dichloromethane (4×2.0 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel (230–400 mesh) using ethyl acetate in petroleum ether (8%) as the eluent to afford the pure product **4** and **6** as colorless thick liquid.

4.5. General procedure for the synthesis of dimethyl 2′,4′,6′-trimethoxy-1,4-dihydro-[1,1′-biphenyl]-3,3(2*H*)-dicarboxylate 5 or dimethyl 5-(1-methyl-1*H*-indol-3-yl)cyclohex-3-ene-1,1-dicarboxylate 7

To a solution of Grubbs' IInd generation catalyst (0.1 mmol) in dry DCM (0.5 mL), a solution of dimethyl (*E*)-2-allyl-2-(4-phenyl-2-arylbut-3-en-1-yl)malonate **4** or 6 in the same solvent (1.0 mL) was added at room temperature under N_2 atmosphere and the reaction mixture was stirred at room temperature for 6 h. After complete consumption of the starting material (monitored by TLC) the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel (230–400 mesh) using ethyl acetate in petroleum ether (8%) as the eluent to afford the pure product **5** or **7** as colorless thick liquid.

*4.5.1. Dimethyl 5-(2,4,6-trimethoxyphenyl)cyclohex-3-ene-1,1-dicarboxylate (**5**).* The compound was synthesized using the previously mentioned procedure. Thick colorless liquid (33 mg, yield 81%). R_f 0.37 (20% EtOAc/hexanes). IR (Neat, cm^{-1}) 2952, 2839, 1735, 1606, 1591, 1495, 1454, 1435, 1332, 1300, 1249, 1223, 1204, 1174, 1152, 1121, 1079, 1061, 1044, 949, 845, 813. ^1H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 2H), 5.63–5.57 (m, 1H), 5.54–5.50 (m, 1H), 4.02–3.95 (m, 1H), 3.78 (s, 6H), 3.73 (s, 6H), 3.62 (s, 3H), 2.82–2.76 (m, 1H), 2.47–2.40 (m, 1H), 2.30–2.26 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.8, 171.8, 159.8, 159.4, 131.6, 120.7, 112.6, 91.2, 55.9, 55.3, 54.4, 52.7, 52.5, 32.3, 30.2, 29.2; HRMS (ESI-TOF) Calcd for $C_{19}H_{25}O_7$ $(M+H)^+$ 365.1600, found 365.1609.

*4.5.2. Dimethyl 5-(1-methyl-1H-indol-3-yl)cyclohex-3-ene-1,1-dicarboxylate (**7**).* The compound was synthesized using the previously mentioned procedure. Thick colorless liquid (33 mg, yield 87%). R_f 0.38 (20% EtOAc/hexanes). IR (Neat, cm^{-1}) 3027, 2952, 2926, 2854, 1734, 1615, 1550, 1470, 1448, 1433, 1374, 1328, 1296, 1248, 1194, 1175, 1130, 1082, 1057, 1014, 946, 845, 741. ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J*=7.8 Hz, 1H), 7.29–7.19 (m, 2H), 7.11–7.07 (m, 1H), 6.83 (s, 1H), 5.88–5.79 (m, 2H), 3.80 (s, 3H), 3.73 (s, 3H), 3.58 (s, 3H), 2.85–2.81 (m, 1H), 2.75–2.70 (m, 1H), 2.60–2.54 (m, 1H), 2.17 (dd, *J*=13.3, 10.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 172.4, 171.7, 137.3, 130.4, 126.9, 125.8, 124.0, 121.7, 119.3, 118.8, 117.4, 109.4, 53.6, 52.8, 52.6, 35.3, 32.7, 30.9, 30.6; HRMS (EI-TOF) Calcd for $C_{19}H_{22}NO_4$ $(M+H)^+$ 328.1540, found 328.1543.

4.6. General procedure for the synthesis of 2-(2,2-diaryl) ethyl)malonic acids from dialkyl (2-(2,2-diaryl)ethyl)malonates 8 and 9

To a solution of dialkyl (2-(2,2-diaryl)ethyl)malonates **3a** or **3s** (1.0 mmol) in methanol (3.0 mL), a 2(N) aq solution of NaOH (0.2 mL) was added at room temperature and the reaction mixture was kept under vigorous stirring for 2 h. Then the reaction mixture was neutralized with 10% aq HCL solution and the aqueous layer was extracted with ethyl acetate (5×2.0 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel (230–400 mesh) using ethyl acetate in petroleum ether (50%) as the eluent to afford the pure products **8** or **9** as colorless thick liquids.

*4.6.1. 2-(2-Phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonic acid (**8**).* The compound was synthesized by reacting dimethyl 2-(2-phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate **3a** (50 mg, 0.125 mmol) in 500 μL MeOH solvent with 50 μL 2(N) aq NaOH solution following the known reaction condition. Purified with 50% ethyl acetate in hexane solvent. Thick colorless liquid (44 mg, yield 95%). R_f 0.40 (75% EtOAc/hexanes). IR (Neat, cm^{-1}) 2935, 2841, 1713, 1606, 1494, 1454, 1418, 1326, 1224, 1205, 1149, 1119, 1061, 1039, 985, 949, 813, 783, 747. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.25 (m, 2H), 7.22–7.18 (m, 2H), 7.11–7.08 (m, 1H), 6.07 (s, 2H), 4.70 (dd, *J*=11.4, 5.04 Hz, 1H), 3.76–3.74 (m, 3H), 3.70–3.62 (m, 6H), 3.30–3.26 (m, 1H), 3.00–2.93 (m, 1H), 2.76–2.67 (m, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 175.4, 175.1, 160.3, 159.5, 144.2, 127.8, 127.7, 125.5, 110.8, 91.2, 55.6, 55.3, 50.5, 36.9, 31.0; HRMS (ESI-TOF) Calcd for $C_{20}H_{22}NaO_7$ $(M+Na)^+$ 397.1263, found 397.1263.

*4.6.2. 2-(2-(4-Methoxyphenyl)-2-(1-methyl-1H-indol-3-yl)ethyl) malonic acid (**9**).* The compound was synthesized by reacting dimethyl 2-(2-(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)ethyl) malonate **3s** (50 mg, 0.126 mmol) in 500 μL MeOH solvent with 50 μL 2(N) aq NaOH solution following the known reaction condition. Purified with 50% ethyl acetate in hexane solvent. Thick colorless liquid (41 mg, yield 89%). R_f 0.45 (75% EtOAc/hexanes). IR (Neat, cm^{-1}) 2928, 2856, 1722, 1611, 1547, 1511, 1466, 1423, 1375, 1327, 1248, 1178, 1074, 1034, 929, 832, 742. ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J*=8.0 Hz, 1H), 7.22–7.13 (m, 4H), 6.99 (t, *J*=7.3 Hz, 1H), 6.86–6.79 (m, 3H), 4.24–4.18 (m, 1H), 3.75–3.70 (m, 6H), 3.45–3.42 (m, 1H), 2.86–2.80 (m, 1H), 2.61–2.53 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 174.7, 158.3, 137.4, 135.3, 129.0, 127.1, 126.1, 121.8, 119.7, 119.0, 117.3, 114.1, 109.3, 55.3, 50.0, 39.9, 35.0,

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32.8; HRMS (ESI-TOF) Calcd for $C_{21}H_{20}NO_5$ $(M-H)^-$ 366.1341, found 366.1345.

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Supplementary data

Supplementary data (^{1}H NMR and ^{13}C NMR spectra for all the new compounds and HPLC chromatograms of **3a** and **3r**.) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.12.001.

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