Lewis Acids Promoted Formal Intramolecular [3+2] Parallel and Cross-
Cycloadditions of Cyclopropane 1,1-Diesters with Allenes

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**General Information**

The $^1$H NMR, $^{13}$C NMR and 2D NMR spectra were recorded with Bruker 400 MHz spectrometer instruments in CDCl$_3$. The chemical shifts ($\delta$) were measured in ppm and with the solvents as references (For CDCl$_3$, $^1$H: $\delta$=7.26 ppm, $^{13}$C: $\delta$ 77.16 ppm). The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200–300 mesh) or alumina (100–200 mesh). Thin layer chromatography (TLC) and preparative TLC thin layer chromatography (prep. TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254 nm) or KMnO$_4$. Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource. Most of the allenes and haloallenes in this paper are unstable and must be used immediately after they were synthesized. NOESY (Nuclear overhauser effect spectroscopy); DCM (Dichloromethane); DCE (1,2-dichloroethane); DMF (N,N-dimethyl formamide); DMSO (Dimethylsulfoxide); THF (Tetrahydrofuran); DMAP (4-Dimethylaminopyridine); BHT (2,6-di-tert-butyl-4-methylphenol).

**Synthesis of [4.3.0]nonane and [3.2.1]octane Skeletons.**

**Optimization of LA-regulated [3+2] IMPC and IMCC of cyclopropanes 1a**

Allene 1a was selected as the model substrate to explore the optimized condition for its intramolecular [3+2] cycloaddition, and the results are summarized in Table S-1. When 1a was catalyzed by Sc(OTf)$_3$ (0.2 equiv) in DCE, a mixture of IMPC product (2a) and IMCC product (3a: see the structure in Table 2) was formed. The ratio of 2a to 3a was increased with the increase of temperature, and 2a was obtained with excellent selectivity at reflux (Table S-1, entry 1). Many LAs were screened (Table S-1, entry 2-16) and the results showed that some of them could catalyze the reaction to afford the adduct 2a (and 3a) with
various yields and selectivities. Though catalytic amount of LAs could start the reaction, 1.0 equiv of LAs were used to reduce the reaction time in most cases. The best selectivity for IMCC product 3a was that when Yb(OTf)$_3$ was used as the LA (Table S-1, entry 2). We next turned our attention to screen the solvents. Although the cycloaddition of 1a also gave good yields in toluene, DCE was selected as the solvent for the subsequent experiments. We finally selected the optimized reaction condition as follows: 1) for IMPC: 20 mol% of Sc(OTf)$_3$ was used in DCE at reflux for 12 hours (Table S-1, entry 1); 2) for IMCC: 1.0 equiv of Yb(OTf)$_3$ was used in DCE at further optimized temperature.

**Table S-1. Optimization of LA-regulated [3+2] IMPC and IMCC of cyclopropane 1a**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lewis acid</th>
<th>Solvent</th>
<th>Temperture(°C)</th>
<th>Time</th>
<th>Yield (%) $^b$</th>
<th>2a:3a $^c$</th>
<th>SM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)$_3$ $^d$</td>
<td>DCE</td>
<td>reflux</td>
<td>12 h</td>
<td>81 $^e$</td>
<td>1.0:0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>75-80</td>
<td>12 h</td>
<td>80</td>
<td>22:1.0</td>
<td>0</td>
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<td></td>
<td></td>
<td></td>
<td>50-55</td>
<td>12 h</td>
<td>80 $^e$</td>
<td>1.7:1.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>45-50</td>
<td>27 h</td>
<td>84</td>
<td>1.3:1.0</td>
<td>0</td>
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<td></td>
<td></td>
<td></td>
<td>40-45</td>
<td>48 h</td>
<td>83</td>
<td>1.1:1.0</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35-40</td>
<td>12 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>2</td>
<td>Yb(OTf)$_3$</td>
<td>DCE</td>
<td>70</td>
<td>16 h</td>
<td>23</td>
<td>1.0:4.0</td>
<td>70</td>
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<td></td>
<td></td>
<td></td>
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<td>13 h</td>
<td>80 $^e$</td>
<td>1.0:2.2</td>
<td>/</td>
</tr>
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<td>2 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td>NR</td>
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<td>78</td>
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<td>/</td>
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<td></td>
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<td>NR</td>
<td>/</td>
<td>/</td>
</tr>
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<td>16 h</td>
<td>85</td>
<td>1.0:2.0</td>
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<td>1:1.6</td>
<td>44</td>
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<tr>
<td>8</td>
<td>AgNTf</td>
<td>DCE</td>
<td>55</td>
<td>9 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>reflux</td>
<td>13 h</td>
<td>44</td>
<td>1.0:0</td>
<td>0</td>
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<tr>
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<td>AuPPh$_3$Cl</td>
<td>DCE</td>
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<td>10 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<tr>
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<td>Sn(OTf)$_2$</td>
<td>DCE</td>
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<td>60 h</td>
<td>57</td>
<td>10:1.0</td>
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<td>11</td>
<td>Cu(OTf)$_2$</td>
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<td>2 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td></td>
<td></td>
<td></td>
<td>reflux</td>
<td>12 h</td>
<td>Decomposed</td>
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<tr>
<td>12</td>
<td>Zn(OTf)$_2$</td>
<td>DCE</td>
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<td>12 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td>Entry</td>
<td>Lewis Acid</td>
<td>Solvent</td>
<td>T(°C)</td>
<td>Time</td>
<td>Yield(%)</td>
<td>SM (%)</td>
<td>3g:2g</td>
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<td>13</td>
<td>AgOTf</td>
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<td>70</td>
<td>2 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td>CF₃SO₃H</td>
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<td>0</td>
<td>3 h</td>
<td>30</td>
<td>1.0:0</td>
<td>0</td>
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<td>15</td>
<td>Bi(OTf)₃</td>
<td>DCE</td>
<td>25-30</td>
<td>15 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td>16</td>
<td>NiClO₄·7H₂O</td>
<td>DCE</td>
<td>60</td>
<td>3 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
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<td>17</td>
<td>Yb(OTf)₃</td>
<td>CHCl₃</td>
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<td>5 h</td>
<td>75</td>
<td>1.0:1.0</td>
<td>33</td>
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<tr>
<td>18</td>
<td>Yb(OTf)₃</td>
<td>THF</td>
<td>reflux</td>
<td>5 h</td>
<td>NR</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>19</td>
<td>Yb(OTf)₃</td>
<td>1,4-dioxane</td>
<td>95-100</td>
<td>19 h</td>
<td>40</td>
<td>1.0:1.5</td>
<td>0</td>
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<td>20</td>
<td>Yb(OTf)₃</td>
<td>toluene</td>
<td>95-100</td>
<td>19 h</td>
<td>82</td>
<td>1.0:1.8</td>
<td>19</td>
</tr>
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</table>

a Reaction conditions: 0.04 mmol scale, 1.0 equiv of Lewis acid, 2 mL of solvent, Ar. b The combined yield of 2a and 3a was determined by ¹H NMR spectroscopy using 1-chloro-2,4-dinitrobenzene as internal standard. c The ratios were determined by comparison of the signal at δ₂a 6.32 ppm and δ₃a 4.89 ppm in ¹H NMR. d 20 mol% of Sc(OTf)₃ was used. e Yield of isolated product. NR=no reaction.

Optimization of the reaction temperature of 1g.

Systematic reaction temperature optimization of the 1g was carried out. And the result was listed in Table S-2.

**Table S-2.** Reaction temperature optimization of Yb(OTf)₃-regulated [3+2] IMCC of 1g

<table>
<thead>
<tr>
<th>Entry</th>
<th>T(°C)</th>
<th>Time</th>
<th>Yield(%)</th>
<th>3g:2g</th>
<th>SM(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>reflux</td>
<td>10 h</td>
<td>95 c</td>
<td>0:1.0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>50-55</td>
<td>24 h</td>
<td>95 c</td>
<td>2.0:1.0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>30-35</td>
<td>24 h</td>
<td>71 d</td>
<td>2.3:1.0</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>20-25</td>
<td>24 h</td>
<td>NR</td>
<td>/</td>
<td>98</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1g (1.0 eq.), Yb(OTf)₃ (1.0 eq.), DCE (0.02 M), Ar. b The ratios were determined ¹H NMR. c Isolated yield. d The combined yield was determined by ¹H NMR spectroscopy using 1-chloro-2,4-dinitrobenzene as internal standard. NR=no reaction.
Optimization of LA-regulated [3+2] IMPC of cyclopropanes 1i

Different from the benzofused substrates, substrate 1i with alkyl-chain linker provided a double bond transfer product 2i (from cyclohexane to cyclopentane) at standard reaction condition. To check the possible IMCC of 1i, various LAs, solvents and temperature were screened (Table S-3). Unfortunately, no IMCC product 3i was found in any case.

Table S-3. Optimization of LA-regulated [3+2] IMPC of cyclopropanes 1i

<table>
<thead>
<tr>
<th>Entry</th>
<th>Lewis acid</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Time</th>
<th>Yield (2i) (%)</th>
<th>SM (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)₃</td>
<td>DCE</td>
<td>45 d</td>
<td>6</td>
<td>82 e</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>SnCl₄</td>
<td>DCE</td>
<td>45</td>
<td>6</td>
<td>60 e</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Yb(OTf)₃</td>
<td>DCE</td>
<td>reflux</td>
<td>18</td>
<td>76 e</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Er(OTf)₃</td>
<td>DCE</td>
<td>reflux</td>
<td>11</td>
<td>80</td>
<td>0</td>
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<td>5</td>
<td>BF₃·OEt</td>
<td>DCE</td>
<td>reflux</td>
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<td>38</td>
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<td>6</td>
<td>TiCl₄</td>
<td>DCE</td>
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<td>TMSOTf</td>
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<td>reflux</td>
<td>18</td>
<td>trace</td>
<td>46</td>
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<tr>
<td>8</td>
<td>Sc(OTf)₃</td>
<td>Toluene</td>
<td>55</td>
<td>18</td>
<td>58</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Sc(OTf)₃</td>
<td>THF</td>
<td>reflux</td>
<td>18</td>
<td>12</td>
<td>71</td>
</tr>
</tbody>
</table>

a Reaction conditions: 0.04 mmol scale, 20% equiv of Lewis acid, 2 mL of solvent, Ar. b Optimized temperature. c Determined by ¹H NMR spectroscopy using 1-chloro-2,4-dinitrobenzene as internal standard. d A similar yield was obtained when the reaction was carried out at reflux. e Yield of isolated product.

Intramolecular Parallel-[3+2] and Cross-[3+2] Cycloaddition of cyclopropanes 1

Under an argon atmosphere, to a solution of freshly prepared cyclopropane 1 (1.0 equiv) in dry DCE (0.02 M), Sc(OTf)_3 (0.2 equiv) was added at room temperature. The reaction mixture was drawn to a preheated oil bath (85-90 °C) and stirred at reflux for 12 h or until the reaction was completed by TLC or ^1^H NMR analysis. After filtrated through a pad of silica gel, the organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography to afford adduct 2. If the diastereomers exist in adducts 2, the *syn-2* and *anti-2* are defined as follows:

**Method B:** general procedure for Yb(OTf)_3-promoted [3+2] IMCC of cyclopropanes 1.

Under an argon atmosphere, to a solution of freshly prepared cyclopropane 1 (1.0 equiv) in dry DCE (0.02 M), Yb(OTf)_3 (1.0 equiv) was added at room temperature. The reaction mixture was drawn to a preheated oil bath and stirred at a setted temperature as shown in table 1 until the reaction was completed by TLC or ^1^H NMR analysis. After filtrated through a pad of silica gel, the organic phases were concentrated under reduced pressure and the residue was purified by flash column chromatography to afford adducts 3 (and 2). The analysis samples for single isomers were further purified by preparative thin-layer chromatography. Relative stereochemistry of products was determined by NOESY analysis respectively.

**Method C:** general procedure for Yb(OTf)_3-promoted [3+2] IMCC of cyclopropanes/haloallene 1.

Under an argon atmosphere, to a solution of freshly prepared cyclopropane 1 (1.0 equiv) in dry DCE (0.02 M), Yb(OTf)_3 (1.0 equiv) was added at room temperature. The reaction mixture was drawn to a preheated oil bath (85-90 °C) and stirred at reflux for 12 h or until the reaction was completed by TLC or ^1^H NMR analysis. After filtrated through a pad of silica gel, the organic phases were concentrated under reduced pressure and the residue was purified by flash column chromatography to afford adducts 3 (and 4). The analysis samples for single isomers were further purified by preparative thin-layer chromatography. Relative stereochemistry of products was determined by NOESY analysis respectively.
1,3-Rearrangement of the IMPC product 3 to the IMPC product 2

![Chemical structure of 3 and 2](image)

**Procedure for Sc(OTf)₃-catalyzed rearrangement of 3 to 2.**

Under an argon atmosphere, to a solution of 3 (0.02 mmol) in dry DCE (1 mL), Sc(OTf)₃ (2 mg, 0.004 mmol) was added at room temperature. Then the reaction mixture was reflux for 12 h (24 h for Z-3d). After filtrated through a pad of silica gel, the solvent was evaporated under reduced pressure to afford adduct 2 in pure form.

**Procedure for Yb(OTf)₃-promoted reaction at a similar condition.**

Under an argon atmosphere, to a solution of 3 (0.02 mmol) in dry DCE (1 mL), Yb(OTf)₃ (12 mg, 0.02 mmol) was added at room temperature. Then the reaction mixture was reflux for 12 h. After filtrated through a pad of silica gel, the solvent was evaporated under reduced pressure to afford adduct 2 in pure form (Starting material 3 was recovered if the reaction do not work).

**Functional transformations of 3a and 2a**

To further demonstrate the potential application of the developed method, several one-step functional transformations of the IMCC product 3a and 2a were performed (Scheme 3). The C=C was converted to a conbonyl group (5) in an excellent yield by ozonation cleavage. Epoxide 6 was obtained as a single isomer by oxidation with m-CPBA. Borohydride oxidation provided alcohol 7 as a mixture of two diastereoisomers (dr=2.2:1). A highly stereoselective OsO₄-catalyzed dihydroxylation followed by lactonization provided 8. Catalytic hydrogenation gave 9 as a single isomer and in an excellent yield. The rich functionalizations of C=C will find their potential applications to the synthesis of natural products and analogues with a broad substituent diversity on the C8 of [3.2.1]ocatane skeleton. Another transformation, the Krapcho decarboxylation was also successfully carried out to afford the monoester 10.
Ozonation cleavage of IMPC product 2a followed by in situ Aldol condensation with a preparative silica gel plate separation led to spiro[4.4]nonane skeleton 11.

**Scheme 1 Functional transformations of 3a and 2a**

- O3, CH2Cl2/MeOH, -78 °C; then Me2S, RT, 92%.
- m-CPBA, NaHCO3, CH2Cl2, 77% (single isomer).
- BH3.SMe2, THF; then H2O2, 66% (dr=2.2:1).
- OsO4 (15 mol%), NMO, acetone/H2O, 66%.
- H2 (6 MPa), Pd/C, MeOH, 55 °C, 95% (single isomer).
- Wet DMSO, LiCl, 170 °C, 68% (dr=2.7:1).
- O3, CH2Cl2/MeOH, -78 °C; then Me2S, RT.
- Preparative silica gel plate separation, 69%.

**Dimethyl 10-oxo-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (5)**

A stirred solution of alkene 3a (26 mg, 0.09 mmol) in DCM /MeOH=1:1 (2 mL) at -78 °C was saturated with ozone till a persistent blue color was observed. The resulting mixture was quenched with Me2S (0.5 mL) and warmed to room temperature in a period of 6 hours. The resulting mixture was concentrated in vacuo and the residue was purified by prep. TLC to afford a light yellow oil 5 (24 mg,
92%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 (t, $J$=7.0, 1H), 7.16-7.06 (m, $J$=18.2, 7.6, 2H), 6.90 (d, $J$=7.5, 1H), 3.76 (s, 3H), 3.74 (s, 1H), 3.54 (s, 3H), 3.53-3.47 (m, 1H), 3.31 (dd, $J$=16.6, 2.1, 1H), 2.81 (dd, $J$=14.7, 1.0, 1H), 2.74-2.68 (m, 1H), 2.39 (dd, $J$=14.6, 7.9, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 212.18, 171.44, 168.86, 136.21, 133.18, 129.64, 128.90, 128.70, 126.71, 61.65, 55.54, 53.31, 52.83, 43.73, 43.16, 32.95. HRMS (ESI) Calcd. for C$_{16}$H$_{16}$O$_5$Na$^+$ (M+Na)$^+$: 311.0890 found 311.0888. IR (neat): $\nu$ = 3010, 2957, 2917, 2847, 1737, 1441, 1280, 1223, 1132, 1064, 916, 742 cm$^{-1}$.

Dimethyl 8,9-dihydro-5H-spiro[5,8-methanobenzo[7]annulene-10,2'-oxirane]-6,6(7H)-dicarboxylate (6)

To a stirred solution of alkene 3a (26 mg, 0.09 mmol) in DCM (3 mL) was added NaHCO$_3$ (37 mg, 0.45 mmol) and m-CPBA (85 wt %, 61 mg, 0.3 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. The resulting mixture was concentrated in vacuo and the residue was purified by prep. TLC to afford a light yellow oil 6 (21 mg, 77%) as a single isomer. To confirm the relative stereochemistry of 6, NOESY analysis experiment was carried out. Unfortunately, no useful signal was provided. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19-7.15 (m, 1H), 7.13-7.05 (m, 2H), 6.95 (d, $J$=7.0, 1H), 3.78 (s, 3H), 3.51 (d, $J$=1.8, 1H), 3.39 (s, 3H), 3.27 (dd, $J$=17.0, 5.2, 1H), 3.03 (d, $J$=17.0, 1H), 2.92 (d, $J$=17.2, 1H), 2.91 (d, $J$=17.2, 1H), 2.77-2.66 (m, 2H), 2.14-2.08 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.05, 169.52, 136.40, 134.87, 128.97, 128.87, 127.99, 125.70, 69.61, 67.25, 53.14, 52.64, 51.67, 48.51, 39.33, 38.47, 36.82. HRMS (ESI) Calcd. for C$_{17}$H$_{18}$O$_3$Na$^+$ (M+Na)$^+$: 325.1046 found 325.1045. IR (neat): $\nu$ = 3010, 2953, 2846, 1740, 1440, 1267, 1160, 1066, 908, 746 cm$^{-1}$.
To a solution of BH$_3$SMe$_2$ (0.15 mL, 0.3 mol, 2M in THF) and BHT (1 mg) in dry THF (1 mL) was added a solution of cyclopropane 3a (26 mg, 0.09 mmol) in THF (1 mL) at 0 °C under an argon atmosphere. The mixture was warmed to room temperature and stirred overnight. The reaction was carefully quenched with the addition of 1:1 MeOH/THF (1 mL) dropwise at 0 °C. 5 mL of precooled (0 °C) aqueous phosphate buffer solution (pH 6.87) was then carefully added to the reaction mixture followed by the addition of 30 % H$_2$O$_2$ (aq.) (0.2 mL, 1.8 mmol, 20 equiv). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solution was then extracted with Et$_2$O (3x20 mL). The combined organic fractions were dried over MgSO$_4$. The solvent was evaporated in vacuo. The diastereomer ratio of the crude product was 2.2:1 (determined by $^1$H NMR). The crude product was purified by prep. TLC to afford a main isomer 7 (12 mg) as a light yellow oil. The combined yield was 66%. Main isomer data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.15-7.10 (m, 1H), 7.06-7.01 (m, J=6.6, 2H), 6.92-6.87 (m, 1H), 3.74 (s, 3H), 3.73-3.70 (m, 1H), 3.62 (dd, J=10.9, 6.7, 1H), 3.55 (dd, J=10.8, 7.3, 1H), 3.37 (s, 3H), 3.01 (dd, J=17.9, 2.8, 1H), 2.73 (d, J=17.7, 1H), 2.67 (d, J=14.6, 1H), 2.58-2.52 (m, 3H), 2.28 (dd, J=14.4, 5.3, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.49, 169.99, 135.23, 134.80, 129.50, 128.87, 127.58, 125.67, 67.29, 61.35, 52.87, 52.45, 48.68, 46.69, 39.28, 34.25, 33.70. HRMS (ESI) Calcd. for C$_{17}$H$_{20}$O$_5$Na$^+$ (M+Na)$^+$: 327.1203 found 327.1203. IR (neat): ν = 3289, 3017, 2957, 2927, 1734, 1441, 1369, 1266, 1223, 750 cm$^{-1}$.

Methyl 3a-(hydroxymethyl)-2-oxo-1,2,3a,4,5,9b-hexahydro-1,4-methanonaphtho[2,1-b]furan-1-carboxylate (8)

To a solution of alkene 3a (26 mg, 0.09 mmol) in a mixture of acetone (1 mL) and water (0.1 mL), a solution of OsO$_4$ (0.014 mmol, 4.0 wt % in water, 0.07 mL) and 4-methylmorpholine-4-oxide (NMO)
(0.18 mmol, 0.045 mL of a 50% solution in water) were added successively. The mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated Na₂S₂O₃ solution and extracted with Et₂O (3x10 mL). The combined organic extracts were dried over MgSO₄, filtered, and then evaporated under reduced pressure. The residue was purified by prep. TLC to afford a light yellow oil 8 (17 mg, 66 %). ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.24 (m, 1H), 7.21-7.11 (m, 3H), 3.89 (s, 2H), 3.76 (s, 3H), 3.74 (s, 1H), 3.16 (dd, J=17.4, 2.8, 1H), 2.96 (dd, J=17.4, 2.8, 1H), 2.88-2.82 (m, 1H), 2.29 (dd, J=13.6, 8.0, 1H), 1.97 (dd, J=13.7, 2.4, 1H), 1.88 (br, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 173.19, 167.23, 132.71, 131.38, 130.10, 129.40, 128.93, 126.98, 91.07, 64.73, 59.70, 53.53, 52.82, 36.96, 35.29, 31.49.

HRMS (ESI) Calcd. for C₁₆H₁₇O₅⁺ (M+H)⁺: 289.1071 found 289.1068. IR (neat): ν = 3537, 3068, 2954, 2858, 1786, 1737, 1449, 1331, 1276, 1221, 1129, 1085, 1029, 913, 761, 738 cm⁻¹.

Dimethyl 10-methyl-8,9-dihydro-5H-5,8-methanobenz[7]annulene-6,6(7H)-dicarboxylate (9)

Pd/C (9 mg) was added to a solution of 3a (26 mg, 0.09 mmol) in MeOH (2 mL) under Argon atmosphere. Then the reaction atmosphere was changed to hydrogen (6 MPa) and the reaction mixture was stirred at 55 °C for 24 h. The suspension was filtered over a pad of silica gel and the crude product was confirmed to be a single isomer by ¹H NMR and ¹³C NMR. It was purified by prep. TLC to afford a light yellow oil 9 (25 mg, 95%). To confirm the relative stereochemistry of 9, NOESY analysis experiment was carried out. Unfortunately, no useful signal was provided. ¹H NMR (400 MHz, CDCl₃) δ 7.10 (td, J=7.5, 1.3, 1H), 7.06-6.97 (dd, J=17.5, 7.4, 2H), 6.91 (d, J=7.4, 1H), 3.74 (s, 3H), 3.73 (s, 1H), 3.29 (s, 3H), 3.12 (dd, J=17.1, 5.4, 1H), 2.83 (d, J=17.1, 1H), 2.66 (d, J=14.6, 1H), 2.48 (ddd, J=14.5, 6.9, 1.5, 1H), 2.29-2.21 (m, 2H), 0.98 (d, J=7.2, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.71, 170.49, 140.09, 135.63, 128.97, 128.07, 127.19, 124.89, 67.67, 52.91, 52.82, 52.50, 43.53, 40.77, 38.73, 36.81, 18.41.

HRMS (ESI) Calcd. for C₁₇H₂₀O₄Na⁺ (M+Na)⁺: 311.1254 found 311.1253. IR (neat): ν = 3016, 2957, 2920, 2840, 1737, 1439, 1371, 1256, 1220, 1159, 1067, 751 cm⁻¹.
Methyl 10-methylene-6,7,8,9-tetrahydro-5H-5,8-methanobenzo[7]annulene-6-carboxylate (10)

A mixture of 3a (26 mg, 0.09 mmol), LiCl (64 mg, 1.5 mmol) and DMSO/H2O (20 mL/20µL) was heated at 170 °C for 4 h. The mixture was cooled to room temperature and diluted with water and extracted with DCM (3x75 mL). The combined organic fractions were washed with saturated NaCl solution (20 mL), dried over MgSO4 and evaporated under reduced pressure. The residue was purified by prep. TLC to afford a light yellow oil 10 (14 mg, 68%) as two diastereoisomers (dr=2.7:1). 1H NMR (400 MHz, CDCl3) δ (7.15-6.98)+(6.91-6.86) (2m, 4H), 4.87+4.83 (2d, J=9.7, J=7.1, 2H), 3.70+3.49 (2s, 3H), 3.66 (d, J=5.7, 1H), (3.25-3.17)+(3.14-3.07) (2m, 2H), 3.00-2.93 (m, 1H), 2.91-2.84 (m, 1H), (2.46-2.37)+(2.20-2.02) (m, 2H). 13C NMR (100 MHz, CDCl3), the signal of the main isomer was listed, δ 173.19, 154.05, 139.55, 134.53, 129.23, 127.63, 127.16, 125.71, 101.87, 51.75, 51.59, 50.71, 42.57, 40.06, 30.90. HRMS (ESI) Calcd. for C15H17O2 (M+H)+: 229.1223 found 229.1225. IR (neat): ν = 3068, 2926, 2854, 1735, 1687, 1439, 1346, 1261, 1198, 1167, 1029, 888, 744 cm⁻¹.

Dimethyl 1'-hydroxy-2-oxo-1',3'-dihydrospiro[cyclopentane-1,2'-indene]-4,4-dicarboxylate (11)

A stirred solution of alkene 2a (17 mg, 0.06 mmol) in DCM /MeOH=1:1 (2 mL) at -78 °C was saturated with ozone till a persistent blue color was observed. The resulting mixture was quenched with Me₂S (0.5 mL) and warmed to room temperature and stirred overnight hours. The resulting mixture was concentrated in vacuo and the residue was purified by prep. TLC to afford a light yellow oil 11 (13 mg, 69%). 1H NMR (400 MHz, CDCl3) δ 7.36-7.13 (m, 4H), 5.14+5.08 (2s, 1H), 3.82+3.80 (2s, 6H), 3.22-3.08 (m, 2H), 2.97-2.88 (m, 1H), 2.82-2.68 (m, 1H), 2.44 (d, J=14.4, 1H). 13C NMR (100 MHz, CDCl3), the signal of the main isomer was listed, δ 215.97, 172.54, 171.69, 142.18, 140.20, 129.02, 127.45, 124.69, 124.62, 79.00, 61.96, 54.34, 53.61, 53.47, 45.20,
41.72, 37.18. HRMS (ESI) Calcd. for C_{17}H_{18}O_{6}Na^+ (M+Na)^+: 341.0996 found 341.0996. IR (neat): ν =
3507, 3007, 2955, 2922, 2851, 2255, 1738, 1440, 1398, 1289, 1255, 1210, 1168, 1062, 748 cm⁻¹.

**Preparation of the Starting Materials**

Scheme for the preparation of substrate (1a)

![Scheme for the preparation of substrate (1a)](image)

**Dimethyl 2-(2-iodobenzyl)cyclopropane-1,1-dicarboxylate (S2)¹**

To a solution of S¹ (488 mg, 2.0 mmol) in dried DCM (10 mL) was added Rh₂(esp)₂ (3 mg, 0.004 mmol) under an argon atmosphere at 0 °C. A solution of diazodimethylmalonate (474 mg, 3.0 mmol) in DCM (2 mL) was then added to the reaction mixture. The solution was allowed to warm to room temperature and stirred overnight, at which time TLC analysis indicated the reaction was completed. The mixture was concentrated in vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (10% to 15%) to afford a colorless oil S₂ (531 mg, 71%). ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J=7.9, 1H), 7.37-7.22 (m, 2H), 6.94 (t, J=7.4, 1H), 3.78 (s, 3H), 3.77 (s, 3H),
2.98 (dd, J=15.4, 6.2, 1H), 2.60 (dd, J=15.4, 8.5, 1H), 2.37-2.26 (m, 1H), 1.70-1.65 (m, 1H), 1.53 (dd,
J=9.0, 4.8, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.53, 168.57, 142.31, 139.55, 129.18, 128.56, 128.38,
100.71, 52.85, 52.77, 39.23, 34.15, 27.86, 21.23.

**Dimethyl 2-(2-(propa-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1a)³**

A mixture of cyclopropane S₂ (75 mg, 0.2 mmol), allenylstannane (100 mg, 0.3 mmol)⁴ and LiCl (25 mg,
0.6 mmol) in DMF (3.00 mL) was purged with argon gas for several times. To the mixture were then added Pd(PPh₃)₄ (0.050 mmol). The reaction mixture was stirred at 50 °C for 24 h and treated with 5 mL of saturated KF solution and allowed to stir for 30 min at room temperature, filtered through Celite and silica gel, and eluted with 50 mL of ether. The organic layer was washed with water, dried over MgSO₄ and concentrated in vacuo. The residue was purified on a silica gel column using EtOAc/Hexanes as the
eluent (5%) to afford allene 1a (brown oil, 41 mg, 72%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J=7.6, 1H\)), 7.24-7.13 (m, 3H), 6.34 (t, \(J=6.8, 1H\)), 5.12 (d, \(J=6.8, 2H\)), 3.77 (s, 3H), 3.73 (s, 3H), 3.01 (dd, \(J=15.1, 5.5, 1H\)), 2.47 (dd, \(J=15.1, 8.9, 1H\)), 2.26-2.19 (m, 1H), 1.59 (dd, \(J=7.7, 4.8, 1H\)), 1.48 (dd, \(J=9.0, 4.8, 1H\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 210.66, 170.61, 168.70, 136.43, 131.89, 129.37, 127.83, 127.21, 126.96, 90.88, 78.33, 52.80, 52.73, 34.33, 31.64, 28.46, 21.58. HRMS (ESI) Calcd. for C\(_{17}H_{18}O_4Na^+\) (M+Na\(^+\)): 309.1097 found 309.1102. IR (neat): \(\nu\) = 2954, 1941, 1729, 1437, 1325, 1278, 1213, 1125, 865, 760 cm\(^{-1}\).

Scheme for the preparation of substrate (1b)

![Scheme for the preparation of substrate (1b)](image)

Diethyl 2-(2-iodobenzyl)cyclopropane-1,1-dicarboxylate (S3)

According to the method for preparation of S2, cyclopropane S3 was prepared as a light yellow oil (yield: 79%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.82 (d, \(J=7.8, 1H\)), 7.33-7.27 (m, 2H), 6.95-6.88 (m, 1H), 4.28-4.12 (m, 4H), 2.95 (dd, \(J=15.7, 6.4, 1H\)), 2.59 (dd, \(J=15.7, 8.4, 1H\)), 2.32-2.23 (m, 1H), 1.62 (dd, \(J=7.8, 4.8, 1H\)), 1.47 (dd, \(J=9.0, 4.8, 1H\)), 1.27 (t, \(J=7.2, 3H\)), 1.22 (t, \(J=7.2, 3H\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 170.20, 168.18, 142.44, 139.50, 129.14, 128.53, 128.30, 100.82, 61.69, 61.65, 39.31, 34.46, 27.26, 20.87, 14.27, 14.20.

Diethyl 2-(2-(propa-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1b)

According to the method for preparation of 1a, allene 1b was prepared as a light yellow oil (yield: 68%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45-7.39 (m, 1H), 7.25-7.13 (m, 3H), 6.35 (t, \(J=6.8, 1H\)), 5.12 (d, \(J=6.9, 2H\)), 4.31-4.11 (m, 4H), 3.02 (dd, \(J=15.2, 5.5, 1H\)), 2.48 (dd, \(J=15.1, 8.9, 1H\)), 2.26-2.16 (m, 1H), 1.56 (dd, \(J=7.7, 4.8, 1H\)), 1.44 (dd, \(J=9.0, 4.7, 1H\)), 1.29-1.22 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 210.67, 170.26, 168.32, 136.58, 131.91, 129.36, 127.78, 127.20, 126.91, 90.89, 78.30, 61.62, 34.65, 31.65, 27.89,
21.23, 14.25, 14.19. HRMS (ESI) Calcd. for C_{19}H_{22}O_{4}Na^{+} (M+Na)^{+}: 337.1410 found 337.1405. IR (neat): \nu = 2982, 2936, 2907, 1940, 1721, 1450, 1369, 1318, 1276, 1206, 1133, 854, 751 \text{ cm}^{-1}.

Scheme for the preparation of substrate (1c)

Dimethyl 2-(2-(buta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1c)

According to the method for preparation of 1a, allene 1c was prepared as a mixture of two inseparable diastereomers (brown oil, 68%, the ratio of two diastereomers was about 1:1). \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\): 7.38 (d, \(J = 7.3, 1\)H), 7.20-7.14 (m, 3H), 6.29-6.25 (m, 1H), 5.54-5.46 (m, 1H), 3.77 (2s, 3H), 3.73 (2s, 3H), 3.05 (dd, \(J = 5.4, 2.6, 0.5\)H), 3.02 (dd, \(J = 5.4, 2.6, 0.5\)H), 2.47 (dd, \(J = 9.0, 3.2, 0.5\)H), 2.43 (dd, \(J = 9.0, 3.2, 0.5\)H), 2.27-2.20 (m, 1H), 1.8-1.77 (m, 3H), 1.60-1.57 (m, 1H), 1.51-1.46 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl₃) \(\delta\): 207.09, 207.07, 170.68, 170.66, 168.75, 136.48, 133.03, 133.01, 129.42, 129.40, 127.95, 127.01, 126.91, 91.10, 91.08, 89.01, 88.99, 52.80, 52.74, 34.37, 31.73, 28.59, 28.55, 21.64, 14.21. HRMS (ESI) Calcd. for C_{18}H_{20}O_{4}Na^{+} (M+Na)^{+}: 323.1254 found 323.1253. IR (neat): \nu = 3016, 2956, 1946, 1730, 1583, 1494, 1441, 1326, 1279, 1212, 1129 \text{ cm}^{-1}.

Scheme for the preparation of substrate (1d)

Dimethyl 2-(2-ethynylbenzyl)cyclopropane-1,1-dicarboxylate (S5)

A mixture of aldehyde S4 (1.38 g, 5.0 mmol) and Bestmann reagent (1.44g, 7.5mmol) in MeOH (25 mL) was stirred at room temperature. To this solution was added K₂CO₃ (2.07 g, 15 mmol). The suspension was stirred in dark (the flask was wrapped with aluminum foil) overnight. The reaction was then diluted
with Et₂O (70 mL) and quenched with sat. NaHCO₃ (50 mL). The aqueous layer was extracted with Et₂O (2x50 mL). The combined organic phase was dried over MgSO₄, and concentrated in vacuo. The residue was purified on a silica gel column using EtOAc/Hexanes as the eluent (25%) to afford alkyne S₅ (light yellow oil, 845 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J=7.6, 1H), 7.37-7.26 (m, 2H), 7.22 (t, J=7.3, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.31 (s, 1H), 3.10 (dd, J=14.8, 5.9, 1H), 2.70 (dd, J=14.8, 8.7, 1H), 2.40-2.30 (m, 1H), 1.72-1.65 (m, 1H), 1.51 (dd, J=8.7, 4.6, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.71, 168.67, 142.23, 133.06, 129.20, 128.56, 126.51, 121.75, 82.16, 81.54, 52.81, 52.71, 34.27, 32.87, 28.36, 21.43.

**Dimethyl 2-(2-(4,4-dimethylpenta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1d)**

Under an argon atmosphere, alkyne S₅ (272 mg, 1.0 mmol) was added to a mixture of CuI (38 mg, 0.2 mmol), LitOBu (280 mg, 3.5 mmol) and N-tosylhydrazone (560 mg, 2.2 mmol) in 1,4-dioxane (10 mL). The solution was stirred at 80 °C for 1.5 h, and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature and was filtered through a short silica gel column eluting with Et₂O. The solvent was removed in vacuum to leave a crude mixture, which was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (3 %) to afford allene 1d as a mixture of two inseparable diastereomers (light yellow oil, 130 mg, 38%, the ratio of two diastereomers was about 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J=7.5, 1H), 7.20-7.13 (m, 3H), 6.38 (d, J=6.4, 1H), 5.56 (d, J=6.4, 1H), 3.77 (s, 3H), 3.73 (2s, 3H), 3.08-2.98 (m, 1H), 2.52-2.42 (m, 1H), 2.29-2.18 (m, 1H), 1.60 (dd, J=7.7, 4.8, 1H), 1.48 (dd, J=9.0, 4.8, 1H), 1.13 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 203.44, 170.61, 168.73, 136.22, 136.19, 133.21, 133.18, 129.42, 129.38, 127.29, 127.23, 126.93, 106.42, 106.35, 93.09, 93.04, 52.77, 52.72, 34.37, 34.34, 32.79, 32.77, 31.68, 31.65, 30.33, 28.58, 21.60, 21.56. HRMS (ESI) Calcd. for C₂₁H₂₆O₄Na⁺ (M+Na)⁺: 365.1723 found 365.1721. IR (neat): ν = 3066, 2956, 2870, 1947, 1734, 1602, 1440, 1328, 1278, 1214, 1150, 754 cm⁻¹.

**Scheme for the preparation of substrate (1e)**
Dimethyl 2-(2-(1-acetoxybut-2-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S6)

To a cold (-78 °C), stirred solution of (Z/E)-1-bromopropene (1.0 g, 9.0 mmol) in 20 mL of dry THF was added n-BuLi (1.6 M in hexane, 8.5 mL, 13.6 mmol) dropwise. The reaction mixture was stirred for 2 hours, then the cyclopropane S4 (1.66 g, 6.0 mmol) in 10 mL of dry THF was added. The reaction mixture was stirred for additional 3.5 h at -78 °C to -60 °C, then was quenched with saturated NH₄Cl aqueous solution. The aqueous layer was extracted with Et₂O (3x70 mL) and the combined organic extracts were dried over MgSO₄. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (25 %) to afford propargyl alcohol S15 (see page 9) as a mixture of two inseparable diastereomers (yellow oil, 1.58 g, 90%, the ratio of two diastereomers was about 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.65 (m, 1H), 7.34-7.26 (m, 3H), 5.60 (s, 1H), 3.77-3.71 (3s, 6H), 3.14-3.06 (m, J=15.4, 6.3, 1H), 2.72-2.61 (m, 1H), 2.40-2.25 (m, 2H), 1.90 (s, 3H), 1.68-1.62 (m, 1H), 1.56-1.50 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.66, 170.63, 168.83, 168.75, 138.86, 138.78, 137.38, 137.34, 129.19, 128.64, 127.05, 127.00, 126.94, 83.43, 83.31, 79.11, 62.30, 52.81, 52.71, 34.39, 34.37, 30.45, 30.41, 28.51, 28.42, 21.80, 21.70, 3.83.

To a stirred solution of the propargyl alcohol S15 (632mg, 2.0 mmol from the previous procedure) (see page 9), DMAP (367 mg, 3.0 mmol), and NEt₃ (303 mg, 3.0 mmol) in 20 mL of dry DCM was added Ac₂O (306 mg, 3.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h, then was quenched with saturated NaHCO₃ aqueous solution. The aqueous layer was extracted with DCM and the combined organic extracts were dried over MgSO₄. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (13 %) to afford S6 as a mixture of two inseparable diastereomers (yellow oil, 666 mg, 93%, the ratio of two diastereomers was about 1:1) ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, J=8.0, 0.5H), 7.62 (d, J=8.0, 0.5H), 7.39-7.25 (m, 3H), 6.52 (s, 1H), 3.81-3.71 (4s, 6H), 3.15 (dd, J=15.6, 5.7, 0.5H), 3.03 (dd, J=15.5,
5.8, 0.5H), 2.65 (dd, \( J = 15.5, 8.6, 0.5H \)), 2.57 (dd, \( J = 15.6, 8.8, 0.5H \)), 2.31 (dd, \( J = 14.4, 8.2, 1H \)), 2.12-2.13 (2s, 3H), 1.93-1.87 (m, 3H), 1.69-1.60 (m, 1H), 1.56-1.50 (m, 1H). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 170.61, 169.84, 168.61, 168.57, 137.75, 137.67, 135.61, 135.55, 129.27, 129.15, 128.45, 128.33, 126.97, 84.26, 84.18, 76.00, 75.96, 63.97, 63.93, 52.80, 52.68, 34.39, 30.63, 30.54, 28.18, 28.04, 21.64, 21.55, 21.15, 21.13, 3.91.

**Dimethyl 2-(2-(3-methylbuta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1e)**

To a cold (0 °C), stirred suspension of Cu I (286 mg, 1.5 mmol) and LiBr (133 mg, 1.5 mmol) in 4mL of dry THF was added MeMgBr (3.0 M in Et\(_2\)O, 1.6 mmol) dropwise. The resultant solution was stirred at 0 °C for 30 min, then was cooled down to -78 °C. The solution of the propargyl acetate S6 (179 mg, 0.5 mmol) in 3 mL of THF was added and the reaction mixture was warmed up to -20 °C within 10 h. The reaction was quenched with saturated NH\(_4\)Cl aqueous solution. The resulting solution was extracted with Et\(_2\)O (3x30 mL) and the combined organic extracts were dried over MgSO\(_4\). The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (3 %) to afford allene 1e (68 mg, 43%) as a colorless oil, and recovered stating material S6 (59 mg, 33%). \(^1H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.33 (d, \( J = 7.6, 1H \)), 7.23-7.08 (m, 3H), 6.16 (dt, \( J = 5.8, 2.9, 1H \)), 3.78 (s, 3H), 3.73 (s, 3H), 3.06 (dd, \( J = 14.8, 5.3, 1H \)), 2.43 (dd, \( J = 14.8, 9.0, 1H \)), 2.31-2.18 (m, 1H), 1.82 (d, \( J = 3.0, 3H \)), 1.81 (d, \( J = 2.9, 3H \)), 1.60 (dd, \( J = 7.6, 4.8, 1H \)), 1.48 (dd, \( J = 9.0, 4.7, 1H \)). \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \) 204.31, 170.66, 168.72, 136.48, 133.89, 129.45, 128.14, 126.83, 126.73, 98.26, 89.83, 52.73, 52.68, 34.38, 31.83, 28.63, 21.65, 20.43, 20.41. HRMS (ESI) Calcd. for C\(_{19}\)H\(_{22}\)O\(_4\)Na\(^+\) (M+Na\(^+\)): 337.1410 found 337.1405. IR (neat): v = 2949, 2860, 1951, 1731, 1634, 1441, 1326, 1278, 1212, 1128, 813, 748 cm\(^{-1}\).

**Scheme for the preparation of substrate (1f)**
Dimethyl 2-((1-acetoxy-3-phenylprop-2-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S7)

To a cold (-78 °C), stirred solution of phenylacetylene (490 mg, 4.8 mmol) in 5 mL of dry THF was added n-BuLi (1.6 M in hexane, 2.63 mL, 4.2 mmol) dropwise. The reaction mixture was stirred for 1 h, then the cyclopropane S4 (1.11 g, 4.0 mmol) in 3 mL of dry THF was added. The reaction mixture was stirred for additional 3.5 h at -78 °C to -60 °C. It was quenched with saturated NH₄Cl aqueous solution. The aqueous layer was extracted with Et₂O (3x70 mL) and the combined organic extracts were dried over MgSO₄. The solvent was removed by vacuo and the residue was directly used in the next step without further purification.

To a stirred solution of the propargyl alcohol from the previous procedure, DMAP (586 mg, 4.8 mmol) and NEt₃ (486 mg, 4.8 mmol) in 30 mL of dry DCM was added Ac₂O (490 mg, 4.8 mmol) at 0 °C. The reaction mixture was warm to room temperature and stirred for 1 h, then was quenched with saturated NaHCO₃ aqueous solution. The aqueous layer was extracted with DCM (3x40 mL) and the combined organic extracts were dried over MgSO₄. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (20 %) to afford S7 as a mixture of two inseparable diastereomers (light yellow oil, 666 mg, 93%, the ratio of two diastereomers was about 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.68 (t, J=8.4, 1H), 7.48-7.46 (m, 2H), 7.37-7.28 (m, 6H), 6.79 (s, 1H), 3.75-3.72 (4s, 6H), 3.24 (dd, J=15.6, 5.7, 0.5H), 3.09 (dd, J=15.5, 5.8, 0.5H), 2.74 (dd, J=15.5, 8.7, 0.5H), 2.64 (dd, J=15.6, 8.7, 0.5H), 2.39 -2.28 (m, 1H), 2.15 (s, 3H), 1.70 -1.63 (m, 1H), 1.57 -1.53 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.57, 169.77, 168.62, 168.57, 137.98, 137.93, 135.17, 135.11, 132.02, 131.99, 129.39, 129.37, 129.28, 128.93, 128.74, 128.39, 127.10, 127.08, 122.16, 87.35, 87.29, 85.63, 85.59, 64.16, 64.03, 52.79, 52.72, 34.42, 30.76, 30.68, 28.20, 28.08, 21.69, 21.60, 21.17, 21.15.

Dimethyl 2-((3-phenylbuta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1f)

To a cold (0 °C), stirred suspension of Cul (286 mg, 1.5 mmol) and LiBr (133 mg, 1.5 mmol) in 2 mL of dry THF was added MeMgBr (3.0 M in Et₂O, 0.5 mL, 1.5 mmol) dropwise. The resultant solution was stirred at 0 °C for 30 min, then was cooled down to -78 °C. The solution of the acetate S7 (205 mg, 0.5
mmol) in 2 mL of THF was added. The reaction mixture was warmed to -20 °C and stirred for 7 h. The reaction was quenched with saturated NH₄Cl aqueous solution. The resulting solution was extracted with Et₂O (3x30 mL) and the combined organic extracts were dried over MgSO₄. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (5 %) to afford allene 1f as a mixture of two inseparable diastereomers (light yellow oil, 98 mg, 52%, the ratio of two diastereomers was about 1:1).¹H NMR (400 MHz, CDCl₃) δ 7.47-7.32 (m, 5H), 7.25-7.17 (m, 4H), 6.67 (s, 1H), 3.76 (s, 1.5H), 3.73 (s, 1.5H), 3.70 (s, 1.5H), 3.70 (s, 1.5H), 3.14-3.04 (m, 1H), 2.57-2.46 (m, 1H), 2.29-2.22 (m, 1H+3H), 1.62-1.60 (m, 1H), 1.51-1.45 (m, 1H).¹³C NMR (100 MHz, CDCl₃) δ 207.79, 207.77, 170.64, 170.59, 168.72, 136.87, 136.76, 136.50, 136.44, 132.59, 131.26, 129.61, 129.02, 128.60, 128.34, 128.19, 127.38, 127.12, 127.04, 125.95, 103.88, 103.81, 93.91, 93.74, 52.79, 52.73, 52.68, 34.39, 31.90, 31.85, 28.65, 28.56, 21.68, 16.96. HRMS (ESI) Calcd. for C₂₄H₂₄O₄Na⁺ (M+Na)⁺: 399.1567 found 399.1563. IR (neat): ν = 3018, 2924, 2859, 1934, 1730, 1597, 1489, 1442, 1325, 1277, 1210, 1127, 1067, 1021, 815, 754 cm⁻¹.

Scheme for the preparation of substrate (1g)

Dimethyl 2-(2-(3-hydroxyprop-1-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S8)

Cyclopropane S2 (478 mg, 2 mmol), triethylamine (4 mL), Pd(PPh₃)₂Cl₂ (70 mg, 0.2 mmol) and copper(I) iodide (38 mg, 0.2 mmol) were dissolved in freshly distilled anhydrous THF (4 mL). The reaction mixture was stirred for 10 min under argon. Then propargyl alcohol (1.12 g, 20 mmol) was slowly added. The reaction was stirred at room temperature for 24 h. The solvent was removed in vacuo and the residue was purified by chromatography on silica gel using EtOAc/Hexanes as the eluent (35 %) to afford propargyl alcohol S8 (587 mg, 97%) as a brown oil.¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J=7.5, 1H), 7.34-7.26 (m, 2H), 7.24-7.17 (m, 1H), 4.53 (s, 2H), 3.81 (s, 3H), 3.75 (s, 3H), 3.03 (dd,
$J=14.4, 5.8, 1H), 2.71 (dd, $J=14.4, 9.5, 1H), 2.64 (s, 1H), 2.40-2.31 (m, 1H), 1.80 (dd, $J=7.7, 4.8, 1H), 1.42 (dd, $J=9.1, 4.8, 1H)$. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.67, 169.27, 141.85, 132.22, 128.83, 126.58, 122.37, 91.90, 84.37, 52.98, 52.83, 51.72, 34.56, 32.43, 29.04, 21.11.

**Dimethyl 2-(2-(3-((methylsulfonyl)oxy)prop-1-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S9)**

Alcohol S8 (453 mg, 1.5 mmol) and triethylamine (228 mg, 2.25 mmol) was dissolved in DCM (15 mL), and the solution was cooled to 0 °C under argon. To this solution was added methanesulfonyl chloride (258 mg, 2.25 mmol) slowly and the reaction mixture was stirred for 1 h at 0 °C. The mixture was quenched with sat. NaHCO$_3$ aqueous solution and extracted with DCM (3x30 mL) and the combined organic extracts were dried over MgSO$_4$. After concentration in vacuo, the crude product was purified by flash chromatography on silica gel using EtOAc/Hexanes as the eluent (35 %) to afford tosylate S9 (560 mg, 98%) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J=7.0, 1H), 7.34 (td, $J=7.6, 1.2, 1H), 7.28 (d, $J=7.0, 1H), 7.21 (td, J=7.5, 1.2, 1H), 5.13 (s, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.16 (s, 3H), 3.03 (dd, $J=15.0, 6.0, 1H), 2.64 (dd, $J=15.0, 8.8, 1H), 2.27 (qd, $J=8.8, 6.1, 1H), 1.63 (dd, $J=7.6, 4.8, 1H), 1.46 (dd, $J=9.0, 4.8, 1H)$. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.58, 168.62, 142.33, 132.92, 129.91, 128.74, 126.70, 120.88, 87.94, 85.05, 58.42, 52.87, 52.77, 39.11, 34.27, 32.80, 28.15, 21.33.

**Dimethyl 2-(2-(buta-2,3-dien-2-yl)benzyl)cyclopropane-1,1-dicarboxylate (1g)**

To a cold (0 °C), stirred suspension of CuI (286 mg, 1.5 mmol) and LiBr (133 mg, 1.5 mmol) in 4 mL of dry THF was added MeMgBr (3.0 M in Et$_2$O, 1.5 mmol) dropwise. The resultant solution was stirred at 0 °C for 30 min, then was cooled down to -78 °C. The solution of the tosylate S9 (228 mg, 0.6 mmol) in 2 mL of THF was added and the reaction mixture was stirred at -78 to -60 °C for 6 h. The reaction was quenched with saturated NH$_4$Cl aqueous solution. The resulting solution was extracted with Et$_2$O (3x30 mL) and the combined organic extracts were dried over MgSO$_4$. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes as the eluent (7 %) to afford allene 1g (150 mg, 83%) as a light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31-7.27 (m, 1H), 7.27-7.21 (m, 3H), 4.77 (d, $J=3.2, 1H), 4.75 (d, $J=3.2, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.03 (dd, $J=15.1, 5.5, 1H), 2.56 (dd, $J=15.1, 9.0, 1H), 2.28 (ddd, $J=16.7, 8.9, 5.5, 1H), 2.05 (t, $J=3.2, 3H), 1.63 (dd,
$J=7.7, 4.7, 1\text{H})$, 1.51 (dd, $J=9.0, 4.7, 1\text{H}$). $^{13}\text{C} \text{NMR (100 MHz, CDCl}_3 \delta 207.46, 170.75, 168.75, 137.91, 137.38, 129.23, 128.11, 127.38, 126.73, 98.55, 74.52, 52.76, 52.63, 34.29, 31.90, 28.81, 21.81, 21.11$.

HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_{4}$Na$^+$ (M+Na)$^+$: 323.1254 found 323.1260. IR (neat): $\nu = 2952, 2843, 1951, 1730, 1634, 1438, 1326, 1279, 1211, 1128, 849, 762 \text{ cm}^{-1}$.

Scheme for the preparation of substrate (1h)

2-Allyl-1-iodo-4-methoxybenzene (S11)

To a mixture of S10$^7$ (6.75 g, 20.6 mmol), Cul (572 mg, 3 mmol) and 2,2'-bipyridine (469 mg, 3 mmol) in dry toluene (35 mL), was slowly added vinyl bromide (1.0 M in THF, 45mL, 45mmol) at 0°C under an argon atmosphere. The mixture was allowed to warm to room temperature and stirred for an additional 6 h when TLC indicated the reaction was complete. The reaction was quenched with sat. NH$_4$Cl solution, extracted with Et$_2$O (3x100 mL) and the combined organic layers were dried over MgSO$_4$. The solvent was removed by vacuo and the residue was purified by column chromatography on silica gel using Hexanes as the eluent to afford intermediate S11 (2.32 g, 41%) as a light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J=8.7, 1\text{H})$, 6.80 (d, $J=2.9, 1\text{H})$, 6.52 (dd, $J=8.7, 3.0, 1\text{H})$, 5.94 (ddt, $J=16.8, 10.1, 6.5, 1\text{H})$, 5.19-5.04 (m, 2H), 3.78 (s, 3H), 3.45 (d, $J=6.4, 2\text{H})$. $^{13}\text{C} \text{NMR (100 MHz, CDCl}_3 \delta 160.19, 143.86, 139.92, 135.71, 117.00, 115.83, 114.05, 89.38, 55.46, 45.11$.

Dimethyl 2-(2-iodo-5-methoxybenzyl)cyclopropane-1,1-dicarboxylate (S12)

According to the method for preparation of S2, cyclopropane S12 was prepared as a yellow oil (yield: 91%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J=8.7, 1\text{H})$, 6.86 (d, $J=3.0, 1\text{H})$, 6.53 (dd, $J=8.7, 3.0, 1\text{H})$, 3.77 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 2.92 (dd, $J=15.4, 6.2, 1\text{H})$, 2.54 (dd, $J=15.4, 8.4, 1\text{H})$, 2.31-2.23 (m, 1H), 1.66-1.63 (m, 1H), 1.51 (dd, $J=9.1, 4.8, 1\text{H})$. $^{13}\text{C} \text{NMR (100 MHz, CDCl}_3 \delta 170.51, 168.61, 160.20, 143.40, 139.90, 115.47, 114.25, 89.04, 55.46, 52.86, 52.80, 39.18, 34.15, 27.88, 21.16$. 

S23
Dimethyl 2-(5-methoxy-2-(propa-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1h)

According to the method for preparation of 1a, allene 1h was prepared as a yellow oil (yield: 50%) from S12. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.30 (m, 1H), 6.78-6.74 (m, 2H), 6.27 (t, $J$=6.8, 1H), 5.09 (d, $J$=6.8, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 2.98 (dd, $J$=15.1, 5.6, 1H), 2.44 (dd, $J$=15.1, 8.9, 1H), 2.21 (ddd, $J$=16.6, 8.8, 5.6, 1H), 1.59 (dd, $J$=7.4, 5.1, 1H), 1.49 (dd, $J$=9.0, 4.8, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 210.30, 170.59, 168.73, 158.82, 137.92, 129.12, 124.14, 114.79, 112.63, 90.49, 78.25, 55.41, 52.82, 52.78, 34.31, 31.76, 28.41, 21.53. HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_{5}$Na$^+$ (M+Na)$^+$: 339.1203 found 339.1202. IR (neat): $\nu$ = 2957, 1940, 1728, 1606, 1574, 1501, 1437, 1321, 1288, 1261, 1125, 858 cm$^{-1}$.

Scheme for the preparation of substrate (1i)

Dimethyl 2-(hexa-4,5-dien-1-yl)cyclopropane-1,1-dicarboxylate (1i)

(CH$_2$O)$_n$ (300 mg, 10 mmol), CuI (381 mg, 2.0 mmol), alkyne S13 (897 mg, 4.0 mmol) and dicyclohexylamine (0.36 mmol) were added sequentially to dry dioxane (20 mL) under an argon atmosphere. The resulting mixture was stirred under reflux for 6 h when the reaction was complete as monitored by TLC, and was cooled to room temperature. Water (5 mL) and ether (10 mL) were added and then the aqueous solution was separated and extracted with ether (3×80 mL). The combined organic layers were then washed with brine and dried over MgSO$_4$. Evaporation and column chromatography on silica gel using EtOAc/Hexanes as the eluent (3%) as eluent to afforded allene 1i (563 mg, 59%) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.04 (p, $J$=6.7, 1H), 4.80-4.43 (m, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 2.14-1.95 (m, 2H), 1.94-1.80 (m, 1H), 1.62-1.44 (m, 3H), 1.44-1.31 (m, 2H), 1.25-1.15 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 208.65, 170.99, 168.76, 89.61, 75.03, 52.67, 52.55, 34.00, 28.57, 28.26, 28.11, 27.78, 21.45. HRMS (ESI) Calcd. for C$_{13}$H$_{18}$O$_{4}$Na$^+$ (M+Na)$^+$: 261.1097 found 261.1098. IR (neat): $\nu$ =3005, 2945, 2860, 1953, 1732,1584, 1441, 1329, 1283, 1209, 1128, 849 cm$^{-1}$. 

S24
Scheme for the preparation of substrate (1j)

**Dimethyl 2-(2-(1-hydroxyprop-2-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S14)**

To a solution of alkyne (471 mg, 4.8 mmol) in dry THF (15 mL) at -78 °C was added n-BuLi solution (1.6 M in hexanes, 2.63mL, 4.2 mmol). The solution was stirred at -78 °C for 1h. Then the aldehyde S4 (1.11g, 4.0 mmol) in 3 mL of dry THF was added. The reaction mixture was stirred at -78 °C to -60 °C for 3 h. NH₄Cl solution was added to quench the reaction and the reaction mixture was extracted with Et₂O (3 × 80 mL). The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure to give crude propargylic alcohol.

The crude propargylic alcohol bearing a trimethylsilyl group was dissolved in MeOH/THF (1:1, 10 mL). Then K₂CO₃ (5.53 g, 40 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. The reaction mixture was filtered and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using EtOAc/Hexanes (35%) as the eluent to afford intermediate propargylic alcohol S14 (685 g, 57%) as a light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.73-7.68 (m, 1H), 7.35-7.26 (m, 3H), 5.64-5.60 (m, 1H), 3.74 (2d, 3H), 3.71 (s, 3H), 3.12-3.01 (m, 1H), 2.73-2.63 (m, 2H), 2.37-2.25 (m, 1H), 1.66-1.60 (m, 1H), 1.56-1.49 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 170.63, 170.59, 168.88, 168.79, 137.69, 137.65, 137.57, 137.52, 129.34, 129.28, 129.10, 129.07, 127.23, 127.17, 127.10, 127.08, 83.44, 83.41, 75.32, 75.17, 62.09, 61.94, 52.87, 52.80, 52.78, 34.39, 34.36, 30.42, 28.41, 28.34, 21.84, 21.73.

**Dimethyl 2-(2-(3-bromopropa-1,2-dien-1-y1)benzyl)cyclopropane-1,1-dicarboxylate (1j)**

CBr₄ (531 mg, 1.6 mmol), Ph₃P (420mg, 1.6 mmol), propargylic alcohol S14 (253 mg, 0.8 mmol), iPr₂NEt (207 mg, 1.6 mmol) and P(n-Bu)₃ (18 mg, 0.08 mmol) were successively added to freshly distilled toluene (4 mL). The reaction mixture was stirred at 60 °C for 12 h. To quench the reaction, H₂O (2 mL) was added to the mixture. The mixture was extracted with Et₂O (3×50 mL), and the combined organic
extracts were dried over MgSO₄, filtered, and then evaporated under reduced pressure. The crude product was purified by silica gel using EtOAc/Hexanes (3%) as the eluent to afford bromoallene 1j as a mixture of two inseparable diastereomers (light yellow oil, 228 g, 62%, the ratio of two diastereomers was about 1:1). ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.41 (m, 1H), 7.30-7.25 (m, 3H), 6.55 (d, J=5.8, 1H), 6.36 (dd, J=5.7, 4.3, 1H), 3.80 (s, 1.5H), 3.79 (s, 1.5H), 3.77 (s, 3H), 3.11-3.01 (m, 1H), 2.63-2.52 (m, 1H), 2.29-2.19 (m, 1H), 1.65-1.59 (m, 1H), 1.56-1.50 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 203.95, 203.92, 170.48, 170.46, 168.64, 137.89, 137.87, 129.88, 129.87, 129.63, 129.56, 129.19, 129.17, 128.94, 127.18, 99.78, 74.80, 74.72, 52.84, 52.79, 34.33, 31.55, 31.53, 28.37, 28.35, 21.52, 21.50. HRMS (ESI) Calcd. for C₁₇H₁₇O₄BrNa⁺ (M+Na)⁺: 387.0202 found 387.0197. IR (neat): ν = 3014, 2952, 1948, 1730, 1631, 1439, 1326, 1280, 1212, 1130, 1057, 756, 577 cm⁻¹.

Scheme for the preparation of substrate (1k)

Dimethyl 2-(2-(3-chloropropa-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1k)¹⁰

To a solution of 0.66 g of propargylic alcohol S14 (605 mg, 2.0 mmol) in 10 mL of dry THF were successively added 3.4 mL of n-butyllithium (1.6 M in hexanes, 1.9 mL, 3.0 mmol) in hexane at -78 °C. After 5 min, methanesulfonyl chloride (344 mg, 3.0 mmol) was added and stirred at -78 °C for 20 min. A solution of CuLiCl₂ (a mixture of 3.0 mmol of CuCl and 3.0 mmol LiCl in 10 mL of dry THF) was added at once. The mixture was then allowed to warm to -20 °C in 4 h. The reaction was quenched with water and extracted with Et₂O (3x50 mL). The combined organic extracts were dried over MgSO₄, filtered, and then evaporated under reduced pressure. The crude product was purified by silica gel using EtOAc/Hexanes (7%) as the eluent to afford chloroallene 1k as a mixture of two inseparable diastereomers (light yellow oil, 115 mg, 18%, the ratio of two diastereomers was about 1:1). Starting material S14 was recovered in 42% yield (255 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.49-7.40 (m, 1H),
7.37-7.22 (m, 3H), 6.79 (d, J=5.9, 1H), 6.47-6.39 (m, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.11-3.01 (m, 1H), 2.62-2.50 (m, 1H), 2.28-2.18 (m, 1H), 1.66-1.59 (m, 1H), 1.55-1.49 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 204.57, 204.54, 170.51, 168.69, 137.88, 137.86, 130.28, 129.64, 129.59, 129.19, 129.17, 128.99, 127.20, 101.06, 91.29, 91.24, 52.88, 52.83, 34.35, 31.61, 31.58, 28.37, 21.58, 21.54. HRMS (ESI) Calcd. for C$_{17}$H$_{17}$O$_4$ClNa$^+$ (M+Na)$^+$: 343.0708 found 343.0705. IR (neat): $\nu$ = 3013, 2955, 1941, 1727, 1439, 1326, 1272, 1128, 754 cm$^{-1}$.

Scheme for the preparation of substrate (1l)

Dimethyl 2-(2-(3-bromobuta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1l)

According to the method for preparation of 1j, bromoallene 1l was prepared as a mixture of two inseparable diastereomers (light yellow oil, yield: 75%, the ratio of two diastereomers was about 1:1) from S15 (date see above). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40-7.35 (m, 1H), 7.25-7.20 (m, 3H), 6.38-6.34 (m, 1H), 3.77 (2s, 3H), 3.73 (2s, 3H), 3.05 (dd, J=15.1, 5.6, 1H), 2.55-2.46 (m, 1H), 2.38 (t, J=3.0, 3H), 2.26-2.16 (m, 1H), 1.62-1.56 (m, 1H), 1.52-1.46 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.45, 170.54, 168.68, 137.85, 137.77, 131.02, 130.99, 129.68, 129.63, 129.36, 129.25, 128.58, 127.15, 97.12, 97.03, 90.36, 52.84, 52.79, 34.39, 31.69, 28.52, 28.46, 25.30, 21.60. HRMS (ESI) Calcd. for C$_{18}$H$_{19}$O$_4$BrNa$^+$ (M+Na)$^+$: 401.0359 found 401.0356. IR (neat): $\nu$ = 3014, 2954, 1946, 1729, 1590, 1439, 1326, 1280, 1211, 1128, 1057, 754, 573 cm$^{-1}$.

Scheme for the preparation of substrate (1m)
Dimethyl 2-(2-(3-cyclohexyl-1-hydroxyprop-2-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S16)

To a cold (-78 °C), stirred solution of cyclohexylacetylene (1.0 g, 9.24 mmol) in 15 ml of dry THF was added n-BuLi (1.6 M in hexane, 6.6 mL, 10.5 mmol) dropwise. The reaction mixture was stirred for 1 h, then cyclopropane S4 (1.93 g, 7.0 mmol) in 10 mL of dry THF was added. The reaction mixture was stirred for additional 3.5 h at -78 °C to -60°C, and was quenched with saturated NH₄Cl aqueous solution. The aqueous layer was extracted with Et₂O (3x70 mL) and the combined organic extracts were dried over MgSO₄. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel using EtOAc/Hexanes (15%) as the eluent to afford propargylic alcohol S16 as a mixture of two inseparable diastereomers (colorless oil, 2.21g, yield: 82%, the ratio of two diastereomers was about 1:1).

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.74-7.68 (m, 1H), 7.35-7.24 (m, 3H), 5.63 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.17-3.05 (m, 1H), 2.72-2.60 (m, 1H), 2.45 (s, 1H), 2.40-2.25 (m, 2H), 1.89-1.78 (m, 2H), 1.75-1.63 (m, 3H), 1.58-1.41 (m, 4H), 1.37-1.25 (m, 4H). $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 170.65, 170.62, 168.81, 168.73, 138.91, 138.80, 137.57, 137.50, 129.21, 129.13, 128.61, 128.58, 127.15, 126.86, 92.00, 91.86, 79.78, 62.34, 62.29, 52.78, 52.71, 34.37, 34.33, 32.59, 30.45, 30.39, 29.23, 28.56, 28.52, 25.90, 24.98, 21.82, 21.68.

Dimethyl 2-(2-(3-bromo-3-cyclohexylpropa-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1m)

According to the method for preparation of 1j, bromoallene 1m was prepared as a mixture of two inseparable diastereomers (light yellow oil, yield: 74%, the ratio of two diastereomers was about 1:1) from S16. $^1$H NMR (400 MHz, CDCl₃) $\delta$ 7.44-7.38 (m, 1H), 7.25-7.19 (m, 3H), 6.42 (d, $J$=2.5, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.1-2.96 (m, 1H), 2.60-4.50 (m, 1H), 2.31-2.16 (m, 2H), 2.02 (d, $J$=8.6, 2H), 1.76 (d, $J$=10.5, 2H), 1.69-1.54 (m, 3H), 1.53-1.46 (m, 1H), 1.35-1.13 (m, 4H). $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 200.08, 200.04, 170.44, 168.62, 137.54, 131.14, 131.10, 129.56, 128.68, 128.39, 127.12, 102.00, 101.90, 97.96, 52.76, 52.71, 45.28, 34.36, 34.34, 32.21, 32.16, 31.59, 31.46, 28.51, 28.47, 26.07, 25.96, 21.53, 21.48. HRMS (ESI) Calcd. for C₂₃H₂₇O₄BrNa⁺ (M+Na⁺): 469.0985 found 469.0979. IR (neat): $\nu$ = 3015, 2932, 2855, 1942, 1730, 1491, 1441, 1327, 1281, 1212, 1129, 753 cm⁻¹.
Dimethyl 2-(2-(1-hydroxyhept-2-yn-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (S17)

According to the method for preparation of S16, propargylic alcohol S17 was prepared as a mixture of two inseparable diastereomers (light yellow oil, yield: 83%, the ratio of two diastereomers was about 1:1) from S4. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75-7.67 (m, 1H), 7.39-7.25 (m, 3H), 5.62 (s, 1H), 3.77-3.71 (4s, 6H), 3.15-3.07 (m, 1H), 2.72-2.61 (m, 1H), 2.39-2.23 (m, 4H), 1.65 (dd, $J$=7.7, 4.8, 1H), 1.57-1.49 (m, 3H), 1.49-1.37 (m, 2H), 0.93 (t, $J$=7.2, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.65, 170.62, 168.82, 168.74, 138.89, 138.79, 137.50, 137.42, 129.22, 129.16, 128.64, 128.62, 127.11, 126.90, 88.01, 87.87, 79.86, 79.83, 62.36, 62.30, 52.79, 52.71, 52.69, 34.39, 34.36, 30.70, 30.45, 30.41, 28.53, 28.48, 22.09, 21.80, 21.68, 18.62, 13.69.

Dimethyl 2-(2-(3-bromohepta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1n)

According to the method for preparation of 1j, bromoallene 1n was prepared as a mixture of two inseparable diastereomers (light yellow oil, yield: 76%, the ratio of two diastereomers was about 1:1) from S17. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44-7.38 (m, 1H), 7.28-7.22 (m, 3H), 6.42 (2d, $J$=2.2, 2.1 1H), 3.79 (2s, 3H), 3.75 (2s, 3H), 3.11-3.01 (m, 1H), 2.60-2.48 (m, 3H), 2.27-2.18 (m, 1H), 1.64-1.48 (m, 4H), 1.46-1.35 (m, 2H), 0.93 (t, $J$=7.3, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.87, 200.83, 170.49, 168.65, 137.67, 137.63, 131.07, 131.05, 129.60, 129.58, 128.99, 128.95, 128.48, 127.12, 97.52, 97.48, 96.07, 95.98, 52.80, 52.75, 37.81, 34.37, 34.36, 31.61, 31.54, 30.19, 29.81, 28.48, 21.90, 21.56, 21.52, 13.88. HRMS (ESI) Calcd. for C$_{21}$H$_{25}$O$_4$BrNa$^+$ (M+Na)$^+$: 443.0828 found 443.0825. IR (neat): $\nu$ = 3014, 2953, 1946, 1730, 1582, 1441, 1326, 1280, 1212, 1128, 963, 753 cm$^{-1}$.

Scheme for the preparation of substrate (1o)
Dimethyl 2-(2-(3-chlorohepta-1,2-dien-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1o)$^{11}$

A mixture of propargyl alcohol $S_{17}$ (818 mg, 2.28 mmol), N-halosuccinimide (472 mg, 3.53 mmol) and triphenylphosphine (899 mg, 3.42 mmol) in 20 mL of DCM was stirred magnetically at room temperature for 48 h. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel using EtOAc/Hexanes (3%) as the eluent to afford chloroallene $1o$ as a mixture of two inseparable diastereomers (colorless oil, 339 mg, 40%, the ratio of two diastereomers was about 1:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41-7.36 (m, 1H), 7.25-7.19 (m, 3H), 6.63 (d, $J$=2.1, 0.5H), 6.62 (d, $J$=2.1, 0.5H), 3.77 (2s, 3H), 3.73 (s, 3H), 3.09-2.99 (m, 1H), 2.59-2.49 (m, 1H), 2.48-2.41 (m, 2H), 2.27-2.17 (m, 1H), 1.62-1.54 (m, 3H), 1.52-1.46 (m, 1H), 1.44-1.34 (m, 2H), 0.91 (t, $J$=7.3, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 201.59, 201.54, 170.54, 170.52, 168.68, 137.65, 137.63, 131.39, 131.37, 129.60, 128.99, 128.96, 128.51, 127.12, 108.71, 108.64, 98.91, 98.89, 52.83, 52.81, 52.77, 36.37, 34.40, 34.37, 31.66, 31.58, 29.36, 28.48, 22.03, 21.60, 21.55, 13.92. HRMS (ESI) Calcd. for C$_{21}$H$_{25}$O$_4$ClNa$^+$ (M+Na)$^+$: 399.1334 found 399.1332. IR (neat): $\nu$ = 3016, 2957, 1948, 1731, 1583, 1442, 1327, 1283, 1212, 1129, 964, 756 cm$^{-1}$.

**Characterization Data for Product 2, 3 and 4**

**Dimethyl 3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2a)**

Adduct $2a$ was prepared from cyclopropane $1a$ according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Yield: 81%.

Data for $2a$: white solid, m.p. 89-90 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.17-6.97 (m, 4H), 6.32 (d, $J$=2.0, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.28 (d, $J$=18.3, 1H), 3.08 (d, $J$=18.2, 1H), 2.91 (dd, $J$=14.2, 6.0, 1H), 2.87-2.70 (m, 2H), 2.59 (d, $J$=14.3, 1H), 2.56 (d, $J$=14.6, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$
Diethyl 3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2b)

Adduct 2b was prepared from cyclopropane 1b according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Yield: 78%.

Data for 2b: light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17-6.97 (m, 4H), 6.32 (d, $J$=2.3, 1H), 4.26-4.15 (m, 4H), 3.27 (dd, $J$=18.2, 1.4, 1H), 3.08 (dt, $J$=14.1, 6.2, 1H), 2.91 (dd, $J$=14.1, 6.2, 1H), 2.88-2.77 (m, 1H), 2.73 (dd, $J$=12.1, 7.5, 1H), 2.58 (t, $J$=14.5, 1H), 1.99 (dd, $J$=12.3, 10.9, 1H), 1.30-1.21 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.80, 145.29, 135.25, 134.47, 127.68, 126.77, 126.30, 125.71, 119.75, 61.74, 59.59, 40.72, 38.70, 38.34, 34.72, 14.20, 14.16. HRMS (ESI) Calcd. for C$_{19}$H$_{22}$O$_4$Na$^+$ (M+Na)$^+$: 337.1410 found 337.1414. IR (neat): $\nu$ = 3061, 2981, 2933, 2876, 1730, 1452, 1368, 1275, 1245, 1182, 1065, 753 cm$^{-1}$.

Dimethyl 1-methyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2c).

Adduct 2c were prepared from cyclopropane 1c (diastereomer mixture, 1.0:1.0) according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 94%. A mixture of two inseparable diastereomers ($dr.$ =1.4:1.0). The diastereomers ratio was determined by $^1$H NMR.

Data for 2c: white solid, m.p. 55-58 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18-6.98 (m, 4H), 6.27 (s, 1H), 3.77+3.74 (2s, 3H), 3.73+3.69 (2s, 3H), 3.59-3.42 (m, 1H), 3.26-3.14 +2.78-2.67 (2m, 2H), 2.94-2.81 (m, 1H), 2.55-2.42 (m, 1H), 2.31-2.22+1.77 (m+dd, $J$=12.7, 11.4, 1H), 1.17+1.13 (2d, $J$=7.2, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.35, 172.30, 171.20, 170.86, 151.16, 150.93, 135.32, 135.13, 135.03, 134.69, 127.69, 127.62, 126.78, 126.41, 126.28, 125.92, 125.91, 119.33, 118.70, 64.30, 63.20, 52.89, 52.75, 52.40, 52.21, 44.01, 42.51, 40.32, 38.25, 37.91, 37.45, 35.10, 35.01, 16.93, 15.50. HRMS (ESI) Calcd. for
C_{18}H_{20}O_{4}Na^{+} (M+Na)^{+}: 323.1254 found 323.1251. IR (neat): \nu = 2956, 2877, 1734, 1441, 1253, 1161, 1074, 754 \text{ cm}^{-1}.

**Dimethyl 1-(tert-butyl)-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2d)**

Adduct 2d were prepared from cyclopropane 1d (diastereomers mixture, 1.0:1.0) according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 83%, syn-2d:anti-2d = 2.6:1.0. The diastereomers ratio was determined by \textsuperscript{1}H NMR of the crude product. The main isomer syn-2d could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of syn-2d could be determined by NOESY analysis (see spectrum).

Data for syn-2d: white solid, m.p. 132-134 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.19-7.04 (m, 4H), 6.50 (s, 1H), 3.72 (s, 3H), 3.66 (s, 3H), 3.63 (s, 1H), 2.82 (dd, \textit{J}=14.7, 5.3, 1H), 2.64 (t, \textit{J}=15.1, 1H), 2.43 (dd, \textit{J}=22.5, 10.6, 2H), 2.38-2.25 (m, 1H), 1.04 (s, 9H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 172.63, 171.64, 146.84, 135.48, 127.65, 126.79, 126.74, 126.44, 123.77, 63.83, 58.46, 53.07, 52.39, 38.75, 37.68, 34.75, 33.37, 29.29. HRMS (ESI) Calcd. for C_{21}H_{26}O_{4}Na^{+} (M+Na)^{+}: 365.1723 found 365.1723. IR (neat): \nu = 3055, 2954, 2875, 2833, 1734, 1479, 1440, 1365, 1242, 1153, 1073, 743 \text{ cm}^{-1}.

**Dimethyl 1,1-dimethyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2e)**

Adduct 2e was prepared from cyclopropane 1e according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Yield: 98%.

Data for 2e: light yellow oil. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.18-7.02 (m, 4H), 6.21 (d, \textit{J}=2.8, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 3.15-3.01 (m, 1H), 2.86 (dd, \textit{J}=14.6, 6.4, 1H), 2.71 (t, \textit{J}=15.6, 1H), 2.57 (dd, \textit{J}=13.9, 8.9, 1H), 2.19 (dd, \textit{J}=14.0, 9.2, 1H), 1.38 (s, 3H), 1.26 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \delta 171.64, 171.24, 156.27, 135.39, 135.14, 127.55, 126.71, 126.21, 126.01, 116.84, 67.35, 52.28, 52.23, 47.93, 37.22, 36.33, 35.35, 26.95, 23.97. HRMS (ESI) Calcd. for C_{19}H_{22}O_{4}Na^{+} (M+Na)^{+}: 337.1410 found 337.1410. IR (neat): \nu = 3010, 2960, 2926, 2856, 1734, 1440, 1370, 1264, 1228, 1077, 754 \text{ cm}^{-1}.
Dimethyl 1-methyl-1-phenyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2f)

Adduct 2f and 3f were prepared from cyclopropane 1f (diastereomers mixture, 1.0:1.0) according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 90%, 2f:3f=1.0:2.7, syn-2f:anti-2f =1.4:1.0, Z-3f:E-3f =1.0:1.3. The isomers ratio was determined by ¹H NMR of the crude product. All of the single isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of syn-2d and anti-2d could be determined by NOESY analysis (see spectrum).

Data for syn-2f: white solid, m.p. 115-117 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J=7.6, 2H), 7.34-7.28 (m, 2H), 7.25-7.11 (m, 4H), 7.05 (d, J=6.8, 1H), 6.23 (d, J=2.9, 1H), 3.80 (s, 3H), 3.66-3.54 (m, 1H), 3.22 (s, 3H), 3.02 (dd, J=14.7, 6.3, 1H), 2.76 (dd, J=13.5, 8.0, 1H), 2.67 (t, J=15.4, 1H), 2.21 (dd, J=13.4, 10.9, 1H), 1.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.95, 170.93, 155.90, 143.19, 135.29, 135.09, 129.06, 127.69, 127.58, 126.87, 126.64, 126.27, 121.47, 69.67, 57.19, 52.33, 52.07, 39.08, 38.17, 36.15, 28.75. HRMS (ESI) Calcd. for C₂₄H₂₄O₄Na⁺ (M+Na)⁺: 399.1567 found 399.1562. IR (neat): ν = 3020, 2927, 2857, 1733, 1488, 1441, 1373, 1261, 1234, 1204, 1080, 1036, 759, 701 cm⁻¹.

Data for anti-2f: light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J=7.6, 2H), 7.28-7.09 (m, 6H), 7.01 (d, J=6.7, 1H), 6.14 (d, J=2.9, 1H), 3.72 (s, 3H), 3.40 (s, 3H), 3.36-3.23 (m, 1H), 3.09 (t, J=15.3, 1H), 2.99 (dd, J=14.9, 6.8, 1H), 2.50 (dd, J=13.6, 11.4, 1H), 2.40 (dd, J=13.6, 7.9, 1H), 2.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.23, 170.47, 154.96, 145.21, 135.55, 134.87, 129.10, 127.84, 127.54, 126.88, 126.61, 126.47, 120.95, 69.01, 56.02, 52.43, 52.03, 37.82, 37.21, 33.61, 29.85, 23.56. HRMS (ESI) Calcd. for C₂₄H₂₄O₄Na⁺ (M+Na)⁺: 399.1567 found 399.1564. IR (neat): ν = 3019, 2925, 2854, 1733, 1440, 1372, 1261, 1256, 1153, 1076, 754, 701 cm⁻¹.

Dimethyl 9-methyl-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2g)

Adduct 2g was prepared from cyclopropane 1g according to General Procedure (method A). Purification by column chromatography on silica gel using
EtOAc/Hexanes (5%) as eluent. Yield: 95%.

Data for 2g: light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24-7.16 (m, 2H), 7.13-7.06 (m, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.25 (dd, $J$=18.3, 1.3, 1H), 3.10 (dd, $J$=18.4, 1.3, 1H), 2.88 (dd, $J$=14.2, 5.6, 1H), 2.80-2.67 (m, 1H), 2.51 (t, $J$=14.5, 1H), 2.00 (dd, $J$=3.6, 1.5, 3H), 1.95 (dt, $J$=18.2, 7.5, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.42, 172.34, 139.52, 136.99, 135.24, 127.53, 126.70, 126.14, 124.35, 122.58, 59.48, 52.98, 41.50, 38.74, 37.86, 35.13, 15.00. HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_4$Na$^+$ (M+Na)$^+$: 323.1254 found 323.1258. IR (neat): $\nu$ = 3062, 2951, 2875, 1735, 1440, 1379, 1251, 1202, 1171, 1073, 952, 762, 735 cm$^{-1}$.

Dimethyl 6-methoxy-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (2h)

Adduct 2h was prepared from cyclopropane 1h according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (10%) as eluent. Yield: 78%.

Data for 2h: white solid, m.p. 91-93 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.92 (d, $J$=7.9, 1H), 6.71-6.63 (m, 2H), 6.27 (d, $J$=2.1, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 3.25 (dd, $J$=18.1, 1.5, 1H), 3.05 (dt, $J$=18.2, 2.4, 1H), 2.87 (dd, $J$=14.0, 6.0, 1H), 2.82-2.68 (m, 2H), 2.56 (t, $J$=14.3, 1H), 2.03-1.94 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.31, 172.29, 158.27, 142.27, 136.19, 128.39, 126.56, 119.27, 114.27, 111.24, 59.60, 55.41, 52.97, 40.86, 38.53, 38.39, 35.19. HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_5$Na$^+$ (M+Na)$^+$: 339.1203 found 339.1205. IR (neat): $\nu$ = 3001, 2952, 2875, 1735, 1440, 1379, 1251, 1202, 1171, 1073, 952, 762, 735 cm$^{-1}$.

Dimethyl 5,6,7,7a-tetrahydro-1H-indene-2,2(4H)-dicarboxylate (2i)

Adduct 2i was prepared from cyclopropane 1i according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Yield: 82%.

Data for 2i: light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.44 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.02 (d, $J$=17.0, 1H), 2.83 (d, $J$=17.0, 1H), 2.52 (dd, $J$=12.6, 7.3, 1H), 2.32 (s, 1H), 1.98 (ddd, $J$=12.2, 8.3, 3.6, 3H), 1.81-1.73 (m, 1H), 1.67 (t, $J$=12.2, 1H), 1.48-1.35 (m, 1H), 1.07-0.96 (m, 1H). $^{13}$C NMR (100
MHz, CDCl₃) δ 173.14, 172.84, 140.60, 118.91, 58.19, 52.90, 52.82, 41.16, 39.37, 38.93, 28.65, 25.06, 22.16. HRMS (ESI) Calcd. for C₁₃H₁₉O₄⁺ (M+H)⁺: 239.1278 found 239.1273. IR (neat): ν = 2950, 2863, 1733, 1665, 1439, 1261, 1204, 1170, 1072 cm⁻¹.

**Dimethyl 10-methylene-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3a)**

Adduct 3a was prepared from cyclopropane 1a according to General Procedure (method B). The reaction mixture was heated at 80°C-reflux for 12 h. Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 80%, 3a:2a = 2.2:1.0. The 3a/2a ratio was determined by ¹H NMR of the crude product. 3a could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 1%-2%).

Data for 3a: white solid, m.p. 143-145 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.13 (t, J=7.0, 1H), 7.05 (t, J=7.9, 2H), 6.92 (d, J=7.4, 1H), 4.97 (s, 1H), 4.89 (s, 1H), 4.09 (s, 1H), 3.72 (s, 3H), 3.44 (s, 3H), 3.21 (dd, J=16.6, 4.6, 1H), 2.98 (d, J=16.6, 1H), 2.90 (t, J=6.0, 1H), 2.64 (d, J=14.3, 1H), 2.34 (dd, J=14.1, 7.5, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 171.68, 169.72, 152.03, 138.30, 134.96, 129.11, 128.05, 127.58, 125.74, 103.97, 66.57, 53.24, 52.79, 52.54, 41.69, 40.18, 37.43. HRMS (ESI) Calcd. for C₁₇H₁₈O₄Na⁺ (M+Na)⁺: 309.1097 found 309.1102. IR (neat): ν = 2951, 2843, 1738, 1435, 1269, 1246, 1217, 1157, 1066, 755 cm⁻¹.

**Diethyl 10-methylene-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3b)**

Adduct 3b was prepared from cyclopropane 1b according to General Procedure (method B). The reaction mixture was heated at reflux for 12 h. Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 76%, 3b:2b = 2.1:1.0. The 3b/2b ratio was determined by ¹H NMR of the crude product. 3b could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 1%-2%).

Data for 3b: light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.15-7.09 (m, 1H), 7.08-7.02 (m, 2H), 6.97-6.92 (m, 1H), 4.96 (s, 1H), 4.88 (s, 1H), 4.29-4.10 (m, 1H), 4.18-4.10 (m, 1H), 4.09 (s, 1H), 3.99-3.88 (m, 1H), 3.85-3.75 (m, 1H), 3.21 (dd, J=16.6, 4.6, 1H), 2.99 (d, J=16.6, 1H), 2.90 (t, J=5.8, 1H), 2.64 (d, J=14.3, 1H), 2.32 (dd, J=14.2, 7.6, 1.1, 1H), 1.24 (t, J=7.2, 3H), 1.13 (t, J=7.2, 3H). ¹³C NMR
(100 MHz, CDCl₃) δ 171.28, 169.35, 152.27, 134.99, 129.02, 128.26, 127.50, 125.64, 103.79, 66.49, 61.52, 61.46, 53.09, 41.72, 40.14, 37.47, 14.13, 14.05. HRMS (ESI) Calcd. for C₁₉H₂₂O₄Na⁺ (M+Na)⁺: 337.1410 found 337.1408. IR (neat): ν = 3071, 2981, 2938, 2905, 1735, 1453, 1369, 1242, 1216, 1159, 1064, 744 cm⁻¹.

(Z/E)-dimethyl 10-ethylidene-8,9-dihydro-5H-5,8-methanobenz[7]annulene-6,6(7H)-dicarboxylate (3c)

Adduct 3c were prepared from cyclopropane 1c according to General Procedure (method B). The reaction mixture was heated at 45 °C for 55 h (note: the reaction temperature was crucial). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 91%, 3c:2c = 1.1:1.0, Z-3c:E-2c = 1.0:1.0, 2c: dr. = 2.0:1.0. The isomers ratio was determined by ¹H NMR of the crude product. Z-3c could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3c could be determined by NOESY analysis (see spectrum).

Data for Z-3c: light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.12 (td, J=7.4, 1.4, 1H), 7.08-7.02 (m, 2H), 6.95 (d, J=6.6, 1H), 5.33 (q, J=6.7, 1H), 4.37 (s, 1H), 3.71 (s, 3H), 3.45 (s, 3H), 3.14 (dd, J=16.5, 4.6, 1H), 2.94 (d, J=16.5, 1H), 2.86-2.80 (m, 1H), 2.58 (d, J=14.3, 1H), 2.33-2.25 (m, 1H), 1.73 (d, J=6.7, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.04, 169.92, 143.24, 138.01, 135.68, 129.28, 128.16, 127.48, 125.61, 113.53, 66.98, 52.78, 52.55, 47.97, 41.72, 40.54, 37.24, 13.96. HRMS (ESI) Calcd. for C₁₈H₂₀O₄Na⁺ (M+Na)⁺: 323.1254 found 323.1258. IR (neat): ν = 3016, 2923, 2853, 1737, 1441, 1369, 1220, 1156, 754 cm⁻¹.

(Z)-dimethyl 10-pentylidene-8,9-dihydro-5H-5,8-methanobenz[7]annulene-6,6(7H)-dicarboxylate (Z-3d)

Adduct Z-3d was prepared from cyclopropane 1d according to General Procedure (method B). The reaction mixture was heated at reflux for 20 h. Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 88%, Z-3d:syn-2d = 1.1:1.0. The isomers ratio was determined by ¹H NMR of the crude product. Z-3d
could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of \( Z-3d \) could be determined by NOESY analysis (see spectrum).

Data for \( Z-3d \): light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.11 (t, \( J=7.0, 1H \)), 7.03 (t, \( J=8.5, 2H \)), 6.91 (d, \( J=7.2, 1H \)), 5.27 (s, 1H), 4.63 (s, 1H), 3.71 (s, 3H), 3.42 (s, 3H), 3.13 (dd, \( J=16.4, 4.8, 1H \)), 2.95 (d, \( J=16.5, 1H \)), 2.74 (t, \( J=6.0, 1H \)), 2.52 (d, \( J=14.2, 1H \)), 2.28 (dd, \( J=14.2, 7.2, 1H \)), 1.11 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.98, 170.01, 139.86, 138.71, 135.67, 129.66, 129.18, 127.90, 127.30, 125.51, 67.99, 52.73, 52.49, 48.86, 43.39, 42.69, 36.37, 33.63, 31.08. HRMS (ESI) Calcd. for C\(_{21}\)H\(_{26}\)O\(_4\)Na\(^+\) (M+Na\(^+\)): 365.1723 found 365.1726. IR (neat): \( \nu \) = 3017, 2956, 2859, 1739, 1441, 1368, 1265, 1219, 754 cm\(^{-1}\).

**Dimethyl 10-(propan-2-ylidene)-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3e)**

Adduct 3e was prepared from cyclopropane 1e according to General Procedure (method B). The reaction mixture was heated at 45 °C for 48 h (note: the reaction temperature was crucial). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 93\%, 3e:2e =0.76:1.0. The 3e/2e ratio was determined by \(^1\)H NMR of the crude product. 3e could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%).

Data for 3e: light yellow oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.13-7.08 (m, 1H), 7.06-7.00 (t, \( J=6.6, 2H \)), 6.96-6.91 (m, 1H), 4.35 (s, 1H), 3.71 (s, 3H), 3.45 (s, 3H), 3.20-3.08 (m, 2H), 2.90 (d, \( J=16.0, 1H \)), 2.61 (d, \( J=14.3, 1H \)), 2.34-2.26 (m, 1H), 1.78 (s, 3H), 1.69 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.14, 170.08, 138.82, 135.96, 135.89, 129.29, 128.04, 127.31, 125.44, 120.64, 66.97, 52.71, 52.46, 49.84, 40.47, 37.71, 36.11, 20.42, 20.06. HRMS (ESI) Calcd. for C\(_{19}\)H\(_{22}\)O\(_4\)Na\(^+\) (M+Na\(^+\)): 337.1410 found 337.1412. IR (neat): \( \nu \) = 3003, 2956, 2922, 2858, 1738, 1440, 1369, 1268, 1222, 1062, 754 cm\(^{-1}\).

**(Z/E)-dimethyl 10-(1-phenylethylidene)-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3f)**
Adduct 3f and 2f were prepared from cyclopropane 1f (diastereomers mixture, 1.0:1.0) according to General Procedure (method B). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 87%, 3f:2f = 1.4:1.0, syn-2f:anti-2f = 1.0:2.7, Z-3f:E-3f = 1.0:1.5. The isomers ratio was determined by 1H NMR of the crude product. All of the single isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3f and E-3f could be determined by NOESY analysis (see spectrum) respectively.

Data for Z-3f: light yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.33 (t, J= 7.4, 2H), 7.26 (d, J= 7.3, 1H), 7.21-7.16 (m, 3H), 7.11 (t, J= 7.5, 2H), 7.04 (d, J= 7.5, 1H), 4.53 (s, 1H), 3.76 (s, 3H), 3.48 (s, 3H), 3.24 (dd, J= 16.6, 4.6, 1H), 2.99-2.91 (m, 2H), 2.59 (d, J= 14.3, 1H), 2.23 (dd, J= 14.0, 7.6, 1H), 2.17 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 172.04, 169.94, 143.54, 138.81, 138.12, 135.86, 129.29, 128.30, 128.15, 127.97, 127.56, 126.83, 126.56, 125.66, 66.60, 52.78, 52.54, 50.11, 41.47, 37.78, 36.95, 20.68. HRMS (ESI) Calcd. for C24H24O4Na (M+Na)+: 399.1567 found 399.1566. IR (neat): ν = 3019, 2950, 2924, 2855, 1739, 1440, 1371, 1262, 1223, 1155, 1067, 757, 702 cm⁻¹.

Data for E-3f: light yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.30 (t, J= 7.3, 2H), 7.26-7.20 (m, 1H), 7.17-7.03 (m, 5H), 6.84 (d, J= 7.5, 1H), 4.10 (s, 1H), 3.59 (s, 3H), 3.38 (s, 3H), 3.37-3.32 (m, 1H), 3.28 (dd, J= 16.4, 4.2, 1H), 3.02 (d, J= 16.1, 1H), 2.66 (d, J= 14.3, 1H), 2.40 (dd, J= 14.3, 7.6, 1H), 2.06 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 171.78, 169.92, 143.54, 139.42, 139.27, 135.66, 129.22, 128.03, 127.94, 127.91, 127.34, 126.52, 125.77, 67.00, 52.64, 52.38, 50.66, 40.88, 37.17, 36.79, 29.84, 19.92. HRMS (ESI) Calcd. for C24H24O4Na⁺ (M+Na)+: 399.1567 found 399.1562. IR (neat): ν = 3019, 2952, 2922, 2852, 1739, 1440, 1373, 1263, 1225, 1157, 1070, 756, 702 cm⁻¹.

Dimethyl 5-methyl-10-methylene-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3g)

Adduct 3g was prepared from cyclopropane 1g according to General Procedure (method B). The reaction mixture was heated at 50-55 °C for 48 h (note: the reaction temperature was crucial). Purification by column chromatography on silica gel using
EtOAc/Hexanes (5%) as eluent. Combined yield: 93%, $3g:2g=2.0:1.0$. The $3g/2g$ ratio was determined by $^1H$ NMR of the crude product. $3g$ could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%).

Data for $3g$: light yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.25-7.20 (m, 1H), 7.16-7.08 (m, 2H), 7.06-6.99 (m, 1H), 4.96 (s, 1H), 4.81 (s, 1H), 3.68 (s, 3H), 3.48 (s, 3H), 3.28-3.19 (m, 1H), 3.04 (dd, $J=17.1$, 11.3, 2H), 2.50-2.38 (m, 2H), 1.79 (s, 3H). $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 171.66, 170.46, 157.46, 142.47, 134.79, 129.14, 127.32, 126.38, 125.60, 101.61, 69.18, 52.31, 52.19, 51.77, 44.26, 39.86, 38.03, 16.62. HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_4$Na$^+$ (M+Na)$^+$: 323.1254 found 323.1250. IR (neat): $\nu$ = 3072, 3048, 2948, 2842, 1734, 1437, 1370, 1233, 1160, 754 cm$^{-1}$.

Dimethyl 2-methoxy-10-methylene-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (2h)

Adduct $3h$ was prepared from cyclopropane $1h$ according to General Procedure (method B). Heated at 60-65 °C for 20 d, the reaction has not completed and the ratio of $3h/2h$ was 1.7/1 by $^1H$ NMR analysis of the crude product. A lot of efforts to isolate the adduct $3h$ from the mixture was unsuccessful.

(E/Z)-dimethyl 10-(bromomethylene)-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3j)

Adduct $3j$ were prepared from cyclopropane $1j$ (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 55%, $E$-$3j$: $Z$-$3j$ = 1.0:1.2. The isomers ratio was determined by $^1H$ NMR of the crude product. Both of the isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of $Z$-$3j$ and $E$-$3j$ could be determined by NOESY analysis (see spectrum) respectively.

Data for $E$-$3j$: light yellow oil. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.18-7.12 (m, 1H), 7.10-7.04 (m, 2H), 6.90 (d, $J=7.1$, 1H), 6.15 (s, 1H), 4.19 (s, 1H), 3.73 (s, 3H), 3.45 (s, 3H), 3.40-3.35 (m, 1H), 3.28 (dd, $J=17.1$, 11.3, 2H), 2.50-2.38 (m, 2H), 1.79 (s, 3H). $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 171.66, 170.46, 157.46, 142.47, 134.79, 129.14, 127.32, 126.38, 125.60, 101.61, 69.18, 52.31, 52.19, 51.77, 44.26, 39.86, 38.03, 16.62. HRMS (ESI) Calcd. for C$_{18}$H$_{20}$O$_4$Na$^+$ (M+Na)$^+$: 323.1254 found 323.1250. IR (neat): $\nu$ = 3072, 3048, 2948, 2842, 1734, 1437, 1370, 1233, 1160, 754 cm$^{-1}$. 

S39
J=16.5, 4.7, 1H), 2.97 (d, J=16.4, 1H), 2.70 (d, J=14.4, 1H), 2.37 (dd, J=14.4, 7.6, 1H). 13C NMR (100 MHz, CDCl₃) δ 171.19, 169.18, 148.32, 137.31, 135.02, 129.33, 127.96, 125.93, 96.33, 66.48, 53.44, 53.00, 52.71, 39.62, 38.34, 36.49. HRMS (ESI) Calcd. for C₁₇H₁₇O₄BrNa⁺ (M+Na)⁺: 387.0202 found 387.0206. IR (neat): ν = 3072, 3012, 2955, 2921, 2847, 1739, 1668, 1486, 1440, 1266, 1223, 1163, 1117, 1065, 950, 856, 733, 660 cm⁻¹.

Data for Z-3j: white solid, m.p. 143-145 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.15 (dt, J=7.4, 3.7, 1H), 7.12-7.03 (m, 2H), 7.01 (d, J=7.3, 1H), 6.03 (s, 1H), 4.56 (s, 1H), 3.75 (s, 3H), 3.47 (s, 3H), 3.20 (dd, J=16.3, 4.2, 1H), 3.07-2.96 (m, 2H), 2.67 (d, J=14.3, 1H), 2.38 (dd, J=14.4, 7.8, 1H). 13C NMR (100 MHz, CDCl₃) δ 171.49, 169.24, 148.93, 136.42, 134.75, 129.14, 128.61, 127.95, 126.02, 94.93, 66.23, 53.00, 52.66, 51.45, 41.85, 40.73, 37.68. HRMS (ESI) Calcd. for C₁₇H₁₇O₄BrNa⁺ (M+Na)⁺: 387.0202 found 387.0201. IR (neat): ν = 3072, 3010, 2953, 2920, 2846, 1740, 1670, 1485, 1440, 1277, 1252, 1222, 1164, 1128, 1064, 949, 857, 794, 735, 659 cm⁻¹.

(E/Z)-dimethyl 10-(chloromethylene)-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3k)

Adduct 3k were prepared from cyclopropane 1k (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 40%. E-3k: Z-3k =1.0:1.0. The isomers ratio was determined by ¹H NMR of the crude product. Both of the isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3k and E-3k could be determined by NOESY analysis (see spectrum) respectively.

Data for E-3k: white solid, m.p. 95-97 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.15 (t, J=7.4, 1H), 7.10-7.03 (m, 2H), 6.91 (d, J=7.6, 1H), 6.07 (s, 1H), 4.17 (s, 1H), 3.73 (s, 3H), 3.49-3.40 (m, 4H), 3.27 (dd, J=16.6, 4.4, 1H), 2.97 (d, J=16.7, 1H), 2.69 (d, J=14.5, 1H), 2.35 (dd, J=14.4, 7.6, 1H). 13C NMR (100 MHz, CDCl₃) δ 171.24, 169.21, 145.36, 137.37, 135.02, 129.33, 127.93, 125.90, 107.84, 66.46, 52.99,
52.70, 52.31, 39.64, 36.78, 36.08. HRMS (ESI) Calcd. for C_{17}H_{17}O_{4}ClNa^{+} (M+Na)^{+}: 343.0708 found 343.0710. IR (neat): ν = 3015, 2956, 2922, 2847, 1738, 1439, 1369, 1267, 1223, 1163, 1064, 755 cm⁻¹.

Data for **Z-3k**: white solid, m.p. 137-139 °C. ^1H NMR (400 MHz, CDCl₃) δ 7.18-7.13 (m, 1H), 7.12-7.03 (m, 2H), 7.00 (d, J=7.2, 1H), 5.94 (s, 1H), 4.61 (s, 1H), 3.74 (s, 3H), 3.47 (s, 3H), 3.18 (dd, J=16.9, 4.9, 1H), 3.05-3.96 (m, 2H), 2.67 (d, J=14.4, 1H), 2.36 (dd, J=14.4, 7.5, 1H). ^13C NMR (100 MHz, CDCl₃) δ 171.49, 169.27, 145.82, 134.78, 129.17, 128.58, 127.93, 126.02, 106.73, 66.47, 53.00, 52.67, 49.26, 41.80, 39.41, 37.63. HRMS (ESI) Calcd. for C_{17}H_{17}O_{4}ClNa^{+} (M+Na)^{+}: 343.0708 found 343.0709. IR (neat): ν = 3009, 2955, 2921, 2848, 1738, 1440, 1256, 1220, 1165, 1136, 1065, 802, 740 cm⁻¹.

(E/Z)-dimethyl 10-(1-bromoethylidene)-8,9-dihydro-5H,5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3l)

Adduct 3l were prepared from cyclopropane 1l (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 48%, **E-3l**: Z-3l =1.0:1.0. The isomers ratio was determined by ^1H NMR of the crude product. Both of the isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3l and E-3l could be determined by NOESY analysis (see spectrum) respectively.

Data for **E-3l**: white solid, m.p. 145-147 °C. ^1H NMR (400 MHz, CDCl₃) δ 7.18-7.13 (m, 1H), 7.10-7.03 (m, 2H), 6.92 (d, J=7.7, 1H), 4.37 (s, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 3.37-3.23 (m, 2H), 2.92 (d, J=16.0, 1H), 2.63 (d, J=14.4, 1H), 2.38 (d, 3H), 2.37-2.31 (m, 1H). ^13C NMR (100 MHz, CDCl₃) δ 171.59, 169.30, 141.41, 137.09, 135.66, 129.46, 128.02, 127.89, 125.79, 111.45, 67.10, 52.96, 52.67, 50.67, 41.06, 39.60, 36.45, 25.15. HRMS (ESI) Calcd. for C_{18}H_{19}O_{4}BrNa^{+} (M+Na)^{+}: 401.0359 found 401.0359. IR (neat): ν = 3001, 2958, 2922, 2848, 1738, 1442, 1377, 1266, 1225, 1156, 1077, 802, 761, 745 cm⁻¹.

Data for **Z-3l**: light yellow oil. ^1H NMR (400 MHz, CDCl₃) δ 7.14 (td, J=7.3, 1.1, 1H), 7.06 (dd, J=14.1, 7.4, 2H), 6.99 (d, J=7.1, 1H), 4.54 (s, 1H), 3.75 (s, 3H), 3.46 (s, 3H), 3.27-3.13 (m, 2H), 2.96 (d,
$J$=16.2, 1H), 2.68 (d, $J$=14.4, 1H), 2.41 (dd, $J$=14.1, 7.9, 1H), 2.29 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.66, 169.45, 142.04, 137.25, 134.90, 129.17, 128.56, 127.78, 125.88, 109.88, 66.20, 54.46, 52.98, 52.60, 40.77, 38.14, 37.70, 24.67. HRMS (ESI) Calcd. for C$_{18}$H$_{19}$O$_4$BrNa$^+$ (M+Na)$^+$: 401.0359 found 401.0357. IR (neat): $\nu$ = 3018, 2954, 2923, 2853, 1738, 1437, 1372, 1266, 1224, 1156, 1067, 755 cm$^{-1}$.

($E$/Z)-dimethyl 10-(bromo(cyclohexyl)methylene)-8,9-dihydro-5H-5,8-methanobenz[7]annulene-6,6(7H)-dicarboxylate (3m)

Adduct 3m were prepared from cyclopropane 1m (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 47%, $E$-3m: Z-3m =1.0:1.5. The isomers ratio was determined by $^1$H NMR of the crude product. Both of the isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3m and E-3m could be determined by NOESY analysis (see spectrum) respectively.

Data for $E$-3m: white solid, m.p. 108-110 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17-7.11 (m, 1H), 7.08-7.02 (m, 2H), 6.94-6.90 (m, 1H), 4.48 (s, 1H), 3.72 (s, 3H), 3.46 (s, 3H), 3.37 (dd, $J$=6.3, 4.8, 1H), 3.27 (dd, $J$=16.5, 4.4, 1H), 2.90 (d, $J$=15.6, 1H), 2.72-2.64 (m, 1H), 2.61 (d, $J$=14.4, 1H), 2.36 (dd, $J$=14.1, 7.6, 1H), 1.78 (dd, $J$=24.1, 12.5, 2H), 1.71-1.62 (m, 2H), 1.58-1.30 (m, 4H), 1.23-1.02 (dd, $J$=12.7, 3.4, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.55, 169.37, 140.13, 137.58, 135.57, 129.43, 127.74, 125.73, 125.09, 124.03, 67.17, 54.48, 52.97, 52.59, 43.55, 41.18, 39.73, 35.95, 31.89, 31.31, 26.00, 25.85. HRMS (ESI) Calcd. for C$_{23}$H$_{27}$O$_4$BrNa$^+$ (M+Na)$^+$: 469.0985 found 469.0985. IR (neat): $\nu$ = 2928, 2854, 1740, 1443, 1371, 1265, 1225, 1159, 1099, 1063, 741 cm$^{-1}$.

Data for Z-3m: light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.17-7.12 (m, 1H), 7.10-7.04 (m, 2H), 7.01 (t, $J$=6.3, 1H), 4.57 (s, 1H), 3.73 (s, 3H), 3.47 (s, 3H), 3.35-3.31 (m, 1H), 3.13 (dd, $J$=16.4, 4.3, 1H), 2.96 (d, $J$=15.3, 1H), 2.61 (d, $J$=14.7, 1H), 2.49-2.41 (m, 2H), 1.76 (t, $J$=11.1, 2H), 1.69-1.60 (m, 2H), 1.59-1.42 (m, 4H), 1.36-1.30 (m, 1H), 1.21-1.13 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.54, 169.47, 140.31, 137.30, 134.89, 129.18, 128.72, 127.69, 125.86, 124.03, 66.04, 54.48, 52.91, 52.59, 43.55, 41.56,
37.88, 37.66, 32.50, 31.88, 26.04, 25.99, 25.73. HRMS (ESI) Calcd. for C_{23}H_{27}O_{4}BrNa^+ \text{(M+Na)^+}: 469.0985 found 469.0982. IR (neat): \nu = 3017, 2928, 2853, 1739, 1442, 1370, 1267, 1223, 1158, 1066, 755 \text{ cm}^{-1}.

**(E/Z)-dimethyl 10-(1-bromopentylidene)-8,9-dihydro-5H-5,8-methanobeno[7]annulene-6,6(7H)-dicarboxylate (3n)**

Adduct 3n were prepared from cyclopropane 1n (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 74%, **E-3n**: Z-3n = 1.0:1.0. The isomers ratio was determined by $^1$H NMR of the crude product. Both of the isomers could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of Z-3n and E-3n could be determined by NOESY analysis (see spectrum) respectively.

Data for **E-3n**: white solid, m.p. 87-89 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.14 (t, $J$=6.9, 1H), 7.08-7.01 (m, 2H), 6.90 (d, $J$=7.4, 1H), 4.38 (s, 1H), 3.73 (s, 3H), 3.45 (s, 3H), 3.37-3.23 (m, 2H), 2.91 (d, $J$=16.2, 1H), 2.70-2.48 (m, 3H), 2.36 (dd, $J$=14.2, 7.5, 1H), 1.53-1.41 (m, 2H), 1.24-1.12 (m, 2H), 0.83 (t, $J$=7.3, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.54, 169.35, 141.54, 137.47, 135.56, 129.39, 127.89, 127.77, 125.73, 118.03, 67.20, 52.95, 52.65, 50.90, 41.30, 39.75, 37.64, 36.25, 30.46, 21.99, 14.05. HRMS (ESI) Calcd. for C$_{21}$H$_{25}$O$_4$BrNa$^+$ (M+Na)$^+$: 443.0828 found 443.0826. IR (neat): $\nu$ = 3062, 2957, 2865, 1739, 1440, 1373, 1266, 1225, 1159, 1101, 1067, 801, 755 cm$^{-1}$.

Data for **Z-3n**: light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.14 (td, $J$=7.4, 1.4, 1H), 7.10-6.98 (m, 2H), 7.00 (d, $J$=7.2, 1H), 4.56 (s, 1H), 3.74 (s, 3H), 3.46 (s, 3H), 3.27-3.21 (m, 1H), 3.16 (dd, $J$=16.5, 4.3, 1H), 2.96 (d, $J$=16.2, 1H), 2.66 (d, $J$=14.3, 1H), 2.55-2.36 (m, 3H), 1.54-1.40 (m, 2H), 1.31-1.20 (m, 2H), 0.89 (t, $J$=7.3, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 171.62, 169.44, 141.81, 137.19, 134.86, 129.14, 128.59, 127.74, 125.88, 116.78, 66.17, 54.45, 52.94, 52.60, 41.15, 38.05, 37.75, 36.93, 30.65, 21.72, 14.07, 5.86. HRMS (ESI) Calcd. for C$_{21}$H$_{25}$O$_4$BrNa$^+$ (M+Na)$^+$: 443.0828 found 443.0830. IR (neat): $\nu$ = 3020, 2955, 2860, 1739, 1439, 1370, 1264, 1222, 1156, 1163, 746 cm$^{-1}$. 

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(E/Z)-dimethyl 10-(1-chloropentylidene)-8,9-dihydro-5H-5,8-methanobenzo[7]annulene-6,6(7H)-dicarboxylate (3o)

Adduct 3o were prepared from cyclopropane 1o (diastereomers mixture, 1.0:1.0) according to General Procedure (method C). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 81%, 3o:4n=5.2:1, E-3o/Z-3o=1.2/1, E-4n/Z-4n=1.6/1. The isomers ratio was determined by ¹H NMR of the crude product. The Z-3o and E-3o could be isolated in pure form by preparative TLC (EtOAc/Hexanes, 2%). Relative stereochemistry of E-3o and Z-3o could be determined by NOESY analysis (see spectrum) respectively.

Data for E-3o: light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.11 (m, 1H), 7.08-7.02 (m, 2H), 6.91 (d, J=7.5, 1H), 4.34 (s, 1H), 3.72 (s, 3H), 3.45 (s, 3H), 3.41 (t, J=6.0, 1H), 3.25 (dd, J=16.8, 4.5, 1H), 2.92 (d, J=16.4, 1H), 2.62 (d, J=14.4, 1H), 2.59-2.48 (m, 1H), 2.48-2.39 (m, 1H), 2.34 (dd, J=14.6, 7.4, 1H), 1.54-1.41 (m, 2H), 1.23-1.13 (m, 2H), 0.83 (t, J=7.3, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.58, 169.39, 138.73, 137.56, 129.37, 127.87, 127.74, 125.70, 125.11, 67.22, 52.93, 52.64, 50.76, 39.81, 38.31, 36.66, 35.64, 29.74, 22.10, 14.03. HRMS (ESI) Calcd. for C₂₁H₂₅O₄ClNa⁺ (M+Na)⁺: 399.1334 found 399.1328. IR (neat): ν = 3011, 2956, 2928, 2863, 1738, 1438, 1370, 1265, 1224, 1159, 1064, 740 cm⁻¹.

Data for Z-3o: light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.14 (td, J=7.4, 1.5, 1H), 7.10-7.02 (m, 2H), 7.02-6.97 (m, 1H), 4.60 (s, 1H), 3.73 (s, 3H), 3.46 (s, 3H), 3.22-3.10 (m, 2H), 2.96 (d, J=16.1, 1H), 2.66 (d, J=14.4, 1H), 2.43-2.32 (m, 3H), 1.50 (td, J=14.1, 7.2, 2H), 1.33-1.20 (m, 2H), 0.89 (t, J=7.3, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 171.59, 169.48, 138.83, 137.30, 134.90, 129.16, 128.57, 127.69, 125.86, 124.13, 66.49, 52.91, 52.59, 51.53, 41.09, 38.01, 37.42, 34.93, 29.89, 21.83, 14.04. HRMS (ESI) Calcd. for C₂₁H₂₅O₄ClNa⁺ (M+Na)⁺: 399.1334 found 399.1332. IR (neat): ν = 3011, 2956, 2928, 2863, 1738, 1440, 1267, 1223, 1159, 1065, 755 cm⁻¹.

(E/Z)-dimethyl 1-butylidene-3a,4-dihydro-1H-cyclopenta[b]naphthalene-2,2(3H)-dicarboxylate (4n)
Adduct 4n were prepared from cyclopropane 1n (diastereomers mixture, 1.0:1.0) according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 79%, A mixture of two inseparable diastereomers (E-4n: Z-4n =1.0:1.0). The isomers ratio was determined by $^1$H NMR of the crude product.

Adduct 4n could also be prepared from cyclopropane 1o (diastereomers mixture, 1.0:1.0) according to General Procedure (method A). Purification by column chromatography on silica gel using EtOAc/Hexanes (5%) as eluent. Combined yield: 77%, A mixture of two inseparable diastereomers (E-4n: Z-4n =2.4:1.0). The diastereomers ratio was determined by $^1$H NMR of the crude product. Relative stereochemistry of Z-3o and E-3o could be determined by NOESY analysis (see spectrum).

Data for 4n (E:Z=2.4:1.0): light yellow oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.20-7.04 (m, 4H), 6.72+6.66 (2d, J=2.1, 1H), 6.34+5.97 (2t, J=7.8, J=6.7, 1H), 3.79 (s, 3H), 3.73+3.71 (2s, 3H), 3.05-2.78 (m, 3H), 2.65-2.54 (m, 1H), (2.54-2.46)+(2.28-2.01) (2m, 2H), 2.05+1.89 (2t, J=11.7, J=11.7, 1H), 1.65-1.46 (2m, 2H), 0.99 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.34, 171.58, 170.54, 143.73, 142.62, 135.84, 135.44, 135.20, 135.10, 134.79, 134.69, 134.56, 129.30, 127.68, 127.64, 127.15, 127.05, 126.86, 126.67, 126.44, 123.36, 115.77, 64.93, 63.55, 52.97, 52.91, 42.67, 40.74, 38.77, 38.40, 34.92, 32.31, 32.24, 22.76, 22.38, 14.20, 14.06. HRMS (ESI) Calcd. for C$_{21}$H$_{24}$O$_4$Na$^+$ (M+Na)$^+$: 363.1567 found 363.1565. IR (neat): ν = 2956, 2872, 1734, 1441, 1372, 1262, 1165, 1079, 750 cm$^{-1}$.

**Reference**


NMR Spectra
1b. $^1$H NMR

1b. $^{13}$C NMR
1h. $^1$H NMR

1h. $^{13}$C NMR
11, $^{13}$H NMR

11, $^{13}$C NMR
S69
**syn-2f, $^1$H NMR**

**syn-2f, $^{13}$C NMR**
anti-2f. $^1$H NMR

anti-2f. $^{13}$C NMR
S78
3a. $^{13}$C DEPT135

3b. $^1$H NMR
Z-3I, $^{13}$C DEPT135

Z-3I, NOESY
9. $^{13}$C NMR

10. $^1$H NMR
11 (dr.=3.2/1), $^{13}$C NMR

11 (dr.=3.2/1), $^{13}$C DEPT135

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**Figure 1.** ORTEP drawing for the product 2a (CCDC 947254). The thermal ellipsoids drawn at the 10% probability level.

**Figure 2.** ORTEP drawing for the product 3a (CCDC 947258). The thermal ellipsoids drawn at the 10% probability level.
Figure 3. ORTEP drawing for the product Z-3j (CCDC 947257). The thermal ellipsoids drawn at the 30 % probability level.

Figure 4. ORTEP drawing for the product Z-3k (CCDC 947256). The thermal ellipsoids drawn at the 30 % probability level.
Figure 5. ORTEP drawing for the product \textit{E-3I} (CCDC 947255). The thermal ellipsoids drawn at the 10\% probability level.