Supporting Information

Phosphine-Catalyzed Regiodivergent Annulations of γ-Substituted Allenoates with Conjugated Dienes

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1. General Experimental Details

All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting Point: heating rate: 4 °C/min, the thermometer was not corrected. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification.

2. General procedure for synthesis of diene

\[
\text{Ar} = \text{CO}_2\text{R}^1 + \text{Ph}_3\text{P} = \text{CO}_2\text{R}^2 \xrightarrow{\text{r.t.}} \text{Ar} = \text{CO}_2\text{R}^1
\]

The general procedure was followed at r.t. with $\beta$, $\gamma$-unsaturated $\alpha$-keto esters $^1$ (5 mmol, 1.0 equiv) and ylide (5 mmol, 1.0 equiv) in 50 mL of DCM. When completed, the resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 °C, 4 × 30 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 20% EtOAc in petroleum ether) to provide the diene 1 as yellow oil.

3. General procedure for synthesis of $\gamma$-substituted allenoates.

\[
\text{R}^3 = \text{CO}_2\text{R}^4 + \text{Ph}_3\text{P} = \text{CO}_2\text{R}^4 \xrightarrow{\text{Et}_3\text{N}} \text{R}^3 = \text{CO}_2\text{R}^4
\]

Allenoate 2 is a known compound and synthesized according to a similar method developed by Hansen. To a solution of yield (0.1 mol) in dichloromethane (400 mL) was added 1.1 equivalent of triethylamine (0.11 mol). After stirred for about 15 minutes, 1.1 equivalent of acyl chloride (0.11 mol) was added dropwise. Then the
reaction mixture was allowed to be warmed up to room temperature and stirred overnight. The resulting mixture was carefully evaporated to remove most of the solvent, and the residue was extracted by petroleum ether (b.p. 30 - 60 ºC, 5 × 100 mL). The combined extracting was concentrated and the residue was subjected to column chromatography (eluant: 5% EtOAc in petroleum ether) to provide the allenoate 2 as yellow oil.


To a dry flask filled with nitrogen were added 1 (0.3 mmol) and 2 (0.45 mmol) in 3 mL CHCl₃. (4-FC₆H₄)₃P (0.06 mmol) was added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: 20% EtOAc in petroleum ether) to afford 3.

**4-Ethyl 3-methyl (E)-6-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-bibiphenyl]-3, 4-dicarboxylate 3a.**

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenoate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3a (107.6 mg, 80% yield) and [3 + 2] adduct (2.7 mg, 2% yield). White solid. **MP:** 123 - 124 ºC. **¹H NMR (300 MHz, CDCl₃)** δ 1.27 (t, J = 7.1 Hz, 3H, CH₃), 1.84 (dd, J = 24.4, 11.7 Hz, 1H, CH), 2.29 – 2.57 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H, CH), 3.60 – 3.66 (m, 1H, CH), 3.74 (s, 3H, COOCH₃), 4.13 – 4.23 (m, 2H, COOCH₂), 5.12 (s, 2H, COOCH₂Ph), 5.68 (d, J = 15.8 Hz, 1H , HC=C), 6.86 (dd,
$J = 15.8, 7.9$ Hz, 1H, C=CH), 7.02 (t, $J = 2.1$ Hz, 1H, HC=C), 7.02 – 7.10 (m, 2H, ArH), 7.26 – 7.36 (m, 8H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, CH$_3$), 31.8 (s, CH$_2$), 42.0 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 51.9 (s, COOC$_2$H$_5$), 61.0 (s, COOCH$_2$H$_2$), 66.2 (s, COOC$_2$H$_2$Ph), 122.0 (s, CH), 127.4 (s, CH), 128.1 (s, 2CH), 128.2 (s, 2CH), 128.5 (s, 2CH), 128.5 (s, 2CH), 135.9 (s, C), 141.2 (s, C), 143.0 (s, CH), 149.5 (s, CH), 165.8 (s, C), 166.7 (s, C), 173.8 (s, C) ppm.

IR (KBr): 2029, 1727, 1370, 1270, 1114, 1032, 733, 700, 524 cm$^{-1}$.


4-Ethyl 3-methyl (E)-6-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-5-methyl-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3b.

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenolate (63.1 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3b (102.1 mg, 85% yield) and [3 + 2] adduct (6.9 mg, 5% yield). Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.04 (d, $J = 6.4$ Hz, 3H, CH$_3$), 1.29 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.01 – 2.20 (m, 2H, 2CH), 3.15 – 3.20 (m, 1H, CH), 3.44 – 3.49 (m, 1H, CH), 3.72 (s, 3H, COOCH$_3$), 4.16 – 4.30 (m, 2H, COOCH$_2$), 5.05 – 5.14 (m, 2H, COOCH$_2$Ph), 5.41 (d, $J = 15.6$ Hz, 1H, HC=C), 6.70 (dd, $J = 15.6$, 9.8 Hz, 1H, HC=C), 7.00 – 7.03 (m, 2H, HC=C; ArH), 7.07 (t, $J = 2.1$ Hz, 1H, ArH), 7.21-7.25 (m, 1H, ArH), 7.27-7.33 (m, 5H, ArH), 7.36 – 7.53 (m, 2H, ArH). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, CH$_3$), 18.4 (s, CH$_3$), 36.5 (s, CH), 48.1 (s, CH), 49.8 (s, CH), 51.5 (s, CH), 51.9 (s, COOCH$_3$), 61.0 (s, COOCH$_2$), 66.1 (s, COOCH$_2$Ph), 123.9 (s, CH), 127.2 (s, CH), 128.0 (s, 2CH), 128.2 (s, CH), 128.3 (s, 2CH), 128.5 (s, 2CH), 128.6 (s, C), 128.7 (s, 2CH), 135.9 (s, C), 141.3 (s, C), 143.1 (s, CH), 148.9 (s, CH), 165.5 (s, C), 166.5 (s, C), 173.9 (s, C). IR (KBr): 2980, 1715, 1388, 1257, 1116, 1033, 751, 705, 523 cm$^{-1}$. HRMS (ESI, m/z): Calcd for C$_{28}$H$_{31}$O$_6$ [M+H]$^+$: 463.2115., found: 463.2116.
4'-Ethyl 5'-methyl \((E\)-2'-\(3\)-(benzyloxy)-3-oxoprop-1-en-1-yl)-1', 2', 3', 4'-tetrahydro-\([1, 1': 3', 1''\)-terphenyl]-4', 5'-dicarboxylate 3c.

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenoate (118.9 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3c (121.2 mg, 77% yield) and [3 + 2] adduct (7.9 mg, 5% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.90 (t, $J = 7.1$ Hz, 3H, CH$_3$), 2.79 (dd, $J = 21.2$, 10.1 Hz, 1H, CH$_3$), 3.18 (t, $J = 11.2$ Hz, 1H, CH), 3.63 – 3.68 (m, 1H, CH), 3.74 – 3.79 (m, 4H, COOCH$_3$; CH), 3.89 – 3.96 (m, 2H, COOCH$_2$), 4.93 – 5.02 (m, 2H, COOCH$_2$Ph), 5.13 (d, $J = 15.6$ Hz, 1H, CH=C), 6.54 (dd, $J = 15.6$, 9.7 Hz, 1H, C=CH), 7.04 – 7.10 (m, 1H, CH=CH$_3$), 7.12 – 7.18 (m, 6H, ArH), 7.21 – 7.23 (m, 1H, ArH), $\delta$ 7.25 – 7.33 (m, 8H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 13.8 (s, CH$_3$), 48.9 (s, CH), 49.8 (s, CH), 50.0 (s, CH), 50.1 (s, CH), 52. (s, COOCH$_3$), 60.6 (s, COOCH$_2$), 65.7 (s, COOCH$_2$Ph), 123.7 (s, CH), 127.3 (s, CH), 127.4 (s, CH), 127.5 (s, 2CH), 128.0 (s, CH), 128.0 (s, 2CH), 128.4 (s, 2CH), 128.4 (s, 2CH), 128.7 (s, 2CH), 128.8 (s, 2CH), 129.0 (s, C), 136.0 (s, C), 139.7 (s, C), 140.9 (s, C), 143.3 (s, CH), 147.9 (s, CH), 165.2 (s, C), 166.3 (s, C), 173.4 (s, C) ppm. IR (KBr): 2982, 1732, 1334, 1080, 1017, 759, 702, 528 cm$^{-1}$. HRMS (ESI, m/z): Calcd for C$_{33}$H$_{33}$O$_6$ [M+H]$^+$: 525.2272, found: 525.2275.

4-Ethyl 3-methyl \((E\)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-\([1, 1\prime\)-biphenyl]-3, 4-dicarboxylate 3d.

The reaction of diene (78.0 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3d (92.7 mg, 80% yield) and [3 + 2] adduct (9.2 mg, 8% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.21 – 1.28 (m, 6H, 2CH$_3$), 1.81 – 1.89
(m, 1H, CH), 2.26 – 2.55 (m, 2H, CH₂), 3.38 – 3.43 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.72 (s, 3H, COOCH₃), 4.07 – 4.13 (m, 2H, COOCH₂), 4.16 – 4.19 (m, 2H, COOCH₂), 5.61 (d, J = 15.2 Hz, 1H, HC=CH), 6.78 (dd, J = 15.7, 7.9 Hz, 1H, C=CH), 6.99 (t, J = 2.1 Hz, 1H, HC=CH), 7.06 – 7.08 (m, 2H, ArH), 7.23 – 7.27 (m, 2H, ArH), 7.29 – 7.32 (m, 1H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, 2CH₃), 31.8 (s, CH₂), 42.0 (s, CH), 43.4 (s, CH), 47.7(s, CH), 51.8 (s, COOCH₂), 60.3 (s, COOCH₂), 61.0 (s, COOCH₂), 122.3 (s, CH), 127.3(s, CH), 128.2 (s, 2CH), 128.8 (s, C), 128.8 (s, 2CH), 141.2 (s, C), 143.0 (s, CH), 148.8 (s, CH), 166.0 (s, C), 166.7 (s, C), 173.8 (s, C) ppm.

IR (KBr): 2982, 1727, 1697, 1280, 1119, 1041, 745, 700, 529 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₂H₂₇O₆ [M+H]^+: 387.1802, found: 387.1804.

4-Benzyl 3-ethyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3e.

The reaction of diene (100.9 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3e (117.9 mg, 85% yield) and [3 + 2] adduct (4.2 mg, 3% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.17 – 1.26 (m, 6H, 2CH₃), 1.85 (dd, J = 24.4, 11.9 Hz, 1H, CH₂), 2.28 – 2.55 (m, 2H, CH₂, CH), 3.39 – 3.44 (m, 1H, CH), 3.67 – 3.74 (m, 1H, CH), 4.09 – 4.16 (m, 4H, 2COOCH₂), 5.17 (dd, J = 34.1, 12.3 Hz, 2H, COOCH₂), 6.00 (d, J = 15.7 Hz, 1H, HC=CH), 6.79 (dd, J = 15.7, 8.0 Hz, 1H, C=CH), 7.02 (t, J = 2.1 Hz, 1H, HC=CH), 7.02 – 7.10 (m, 2H, ArH), 7.25 – 7.27 (m, 1H, ArH), 7.28 – 7.30 (m, 2H, ArH), 7.35 – 7.39 (m, 5H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 60.4 (s, CH₂, COOCH₂), 60.9 (s, CH₂, COOCH₂), 66.8(s, COOCH₂), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.7 (s, C), 141.2 (s, C), 142.9 (s, CH), 148.7 (s, CH), 166.1 (s, C), 166.3 (s, C), 173.7 (s, C) ppm. IR (KBr): 2982, 1728, 1370, 1262,
1113, 1035, 753, 703, 523 cm$^{-1}$. **HRMS** (ESI, m/z): Calcd for C$_{28}$H$_{31}$O$_6$ [M+H]$^+$: 463.2115, found: 463.2117.

**4-Benzyl 3-isopropyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3f.**

The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3f (110.1 mg, 77% yield) and [3 + 2] adduct (4.3 mg, 3% yield).

Colorless oil. **1H NMR (300 MHz, CDCl$_3$)** $\delta$ 1.18 – 1.24 (m, 9H, 3CH$_3$), 1.85 (dd, $J$ = 24.1, 11.9 Hz, 1H, CH), 2.29 – 2.34 (m, 1H, CH), 2.51 (dd, $J$ = 19.0, 9.6 Hz, 1H, CH), 3.41 (d, $J$ = 9.7 Hz, 1H, CH), 3.70 – 3.73 (m, 1H, CH), 4.13 (dd, $J$ = 14.0, 6.9 Hz, 2H, CO$_2$CH$_2$), 5.00 – 5.10 (m, 1H, CH), 5.16 (dd, $J$ = 25.8, 12.3 Hz, 2H, CO$_2$CH$_2$Ph), 5.60 (d, $J$ = 15.7 Hz, 1H, HC=C ), 6.79 (dd, $J$ = 15.7, 7.9 Hz, 1H, C=CH), 7.00 – 7.04 (m, 1H, HC=C), 7.08 – 7.11 (m, 2H, ArH), 7.27 – 7.37 (m, 8H, ArH) ppm.

**13C NMR (75 MHz, CDCl$_3$)** $\delta$ 14.2 (s, CH$_3$), 21.7 (s, CH$_3$), 21.8 (s, CH$_3$), 31.9 (s, CH$_3$), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 60.4 (s, COOCH$_2$), 66.8 (s, COOCH$_2$Ar), 68.5 (s, COOCH), 122.3 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 129.2 (s, C), 135.7 (s, C), 141.3 (s, C), 142.5 (s, CH), 148.8 (s, CH), 165.8 (s, C), 166.1 (s, C), 173.7 (s, C) ppm.

**IR (KBr):** 3029, 1727, 1371, 1261, 1110, 1034, 752, 704, 526 cm$^{-1}$. **HRMS** (ESI, m/z): Calcd for C$_{29}$H$_{33}$O$_6$ [M+H]$^+$: 477.2272, found: 477.2274.

**4-Ethyl 3-isopropyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3g.**
The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3g (104.5 mg, 84% yield) and [3 + 2] adduct (10.0 mg, 8% yield). Colorless oil. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.22 – 1.31 (m, 12H, 4CH\(_3\)), 1.83 (dd, \( J = 24.1, 12.0 \) Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH\(_2\), CH\(_2\)), 3.40 – 3.43 (m, 1H, CH), 3.62 – 3.65 (m, 1H, CH), 4.09 – 4.21 (m, 4H, 2COOCH\(_2\)), 5.03 – 5.11 (m, 1H, COOCH), 5.62 (d, \( J = 15.8 \) Hz, 1H, HC=C), 6.80 (dd, \( J = 15.7, 7.8 \) Hz, 1H, C=CH), 6.93 – 6.98 (m, 1H, HC=C), 7.09 – 7.11 (m, 2H, ArH), 7.28 – 7.35 (m, 3H, ArH) ppm. \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (s, CH\(_3\)), 14.2 (s, CH\(_3\)), 21.7 (s, CH\(_3\)), 21.8 (s, CH\(_3\)), 32.0 (s, CH\(_2\)), 42.1 (s, CH), 43.2 (s, CH), 47.8 (s, CH), 60.3 (s, COOCH\(_2\)), 61.0 (s,COOCH\(_2\)), 68.4 (s, COOCH), 122.2 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, 2CH), 129.4 (s, C), 141.4 (s, C), 142.3 (s, CH), 148.9 (s, CH), 165.8 (s, C), 166.1 (s, C), 173.9 (s, C) ppm. IR (KBr): 3007, 1732, 1371, 1255, 1117, 1033, 750, 705, 526 cm\(^{-1}\). HRMS (ESI, m/z): Calcd for C\(_{24}\)H\(_{31}\)O\(_6\)[M+H]\(^+\): 415.2115, found: 415.2117.

EtO\(_2\)C\[\begin{array}{c}  \text{CO}_2\text{Bn} \\ \text{CO}_2\text{"Bu} \end{array}\]

4-Benzyl 3-butyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3h.

The reaction of diene (109.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3h (116.3 mg, 79% yield) and [3 + 2] (5.8 mg, 2% yield). White solid. MP: 74 – 75 °C. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 0.90 (t, \( J = 7.4 \) Hz, 3H, CH\(_3\)), 1.24 (t, \( J = 7.1 \) Hz, 3H, CH\(_3\)), 1.30 – 1.37 (m, 2H, CH\(_2\)), 1.51 – 1.60 (m, 2H, CH\(_2\)), 1.85 (dd, \( J = 24.3, 11.8 \) Hz, 1H, CH), 2.28 – 2.35 (m, 1H, CH), 2.45 – 2.55 (m, 1H, CH), 3.39 – 3.44 (m, 1H, CH), 3.67 – 3.75 (m, 1H, CH), 4.02 – 4.16 (m, 4H, 2COOCH\(_2\)), 5.16 (dd, \( J = 36.3, 12.3 \) Hz, 2H, COOCH\(_2\)Ph), 5.60 (d, \( J = 15.8 \) Hz, 1H, HC=C), 6.79 (dd, \( J = 15.7, 8.0 \) Hz, 1H, C=CH), 7.01 (t, \( J = 2.1 \) Hz, 1H, HC=C), 7.07 – 7.10 (m, 2H, ArH), 7.26 – 7.30 (m, 2H, ArH), 7.32 – 7.35 (m, 2H, ArH), 7.36 – 7.38
Dibenzyl \((E)-6-(3\text{-ethoxy-3-oxoprop-1-en-1-yl})-1, 4, 5, 6\text{-tetrahydro-} \quad [1, 1'\text{-biphenyl}]-3, 4\text{-dicarboxylate} \ 3i.\

The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product \(3i\) (141.6 mg, 90% yield) and \([3 + 2]\) adduct (3.2 mg, 2% yield). Colorless oil. \(^1\text{H NMR (300 MHz, CDCl}_3\) \(\delta 1.24 \quad (t, J = 7.1 \text{ Hz, CH}_3), 1.80 – 1.92 \quad (m, 1H, CH), 2.30 – 2.36 \quad (m, 1H, CH), 2.51 \quad (dd, J = 18.6, 8.8 \text{ Hz, 1H, CH}), 3.42 \quad (d, J = 9.7 \text{ Hz, 1H}), 3.72 – 3.76 \quad (m, 1H, CH), 4.13 \quad (dd, J = 14.0, 6.9 \text{ Hz, 2H, COOCH}_2), 4.98 – 5.18 \quad (m, 4H, 2\text{COOCH}_2\text{-Ph}), 5.60 \quad (d, J = 15.8 \text{ Hz, 1H, HC=C}), 6.79 \quad (dd, J = 15.7, 8.0 \text{ Hz, 1H, C=CH}), 7.07 – 7.09 \quad (m, 3H, HC=C, ArH), 7.26 – 7.30 \quad (m, 13H, ArH) \text{ ppm.} \(^{13}\text{C NMR (75 MHz, CDCl}_3\) \(\delta 14.2 \quad (s, \text{CH}_3), 31.9 \quad (s, \text{CH}_2), 42.1 \quad (s, \text{CH}), 43.5 \quad (s, \text{CH}), 47.8 \quad (s, \text{CH}), 60.4 \quad (s, \text{COOCH}_2), 66.6 \quad (s, \text{COOCH}_2), 66.8 \quad (s, \text{COOCH}_2), 122.4 \quad (s, \text{CH}), 127.3 \quad (s, \text{CH}), 128.2 \quad (s, \text{2CH}), 128.2 \quad (s, \text{CH}), 128.3 \quad (s, \text{2CH}), 128.3 \quad (s, \text{2CH}), 128.5 \quad (s, \text{2CH}), 128.5 \quad (s, \text{2CH}), 128.7 \quad (s, \text{C}), 128.8 \quad (s, \text{2CH}), 135.7 \quad (s, \text{C}), 135.7 \quad (s, \text{C}), 141.1 \quad (s, \text{C}), 143.5 \quad (s, \text{CH}), 148.6 \quad (s, \text{CH}), 166.1 \quad (s, \text{C}), 166.1 \quad (s, \text{C}), 173.6 \quad (s, \text{C}) \text{ ppm.} \quad \text{IR (KBr):} \quad 3002, 1715, 1362, 1221, 1165, 1005, 751, 700, 529 \text{ cm}^{-1}. \quad \text{HRMS (ESI, m/z): Calcd for C}_{33}\text{H}_{35}\text{O}_6 \quad [\text{M+H}]^+: 525.2272, \quad \text{found: 525.2271.}
Diethyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1,1'-biphenyl]-3,4-dicarboxylate 3j.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3j (99.7 mg, 86% yield) and [3 + 2] aadduct (4.6 mg, 4% yield).

White solid. **MP:** 87 - 88 °C. **1H NMR (300 MHz, CDCl₃)** δ 1.24 – 1.30 (m, 6H, 2CH₃), 1.84 (q, J = 11.8 Hz, 1H, CH), 2.27 – 2.56 (m, 2H, CH₂), 3. 39 – 3.44 (m, 1H, CH₂), 3.60 – 3.64 (m, 1H, COOCH₃), 4.14 – 4.24 (m, 4H, 2COOCH₂), 5.62 (d, J = 15.8 Hz, 1H, HC=C), 6.81 (dd, J = 15.8, 8.0 Hz, 1H, C=CH), 7.00 (t, J = 2.0 Hz, 1H, HC=C), 7.08 – 7.10 (m, 2H, ArH), 7.26 – 7.35 (m, 3H, ArH) ppm. **13C NMR (75 MHz, CDCl₃)** δ 14.1 (s, 2CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₂), 60.9 (s, COOCH₂), 61.0 (s, COOCH₂), 121.7 (s, CH), 127.3 (s, CH), 128.2 (s, CH₂), 128.8 (s, 2CH), 129.1 (s, C), 141.3 (s, C), 142.6 (s, CH), 149.1 (s, CH), 166.3 (s, C), 166.5 (s, C), 173.9 (s, C) ppm. **IR (KBr):** 3001, 1733, 1335, 1217, 1092, 1037, 779, 704, 528 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₂H₂₇O₆ [M+H]⁺: 387.1802, found: 387.1801.

4-Benzyl 3-ethyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1'-biphenyl]-3, 4-dicarboxylate 3k.

The reaction of diene (100.9 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3k (107.6 mg, 80% yield) and [3 + 2] adduct (4.0 mg, 3% yield).

White solid. **MP:** 70 - 71 °C. **1H NMR (300 MHz, CDCl₃)** δ 1.20 (t, J = 7.1 Hz, 3H, CH₃), 1.85 (q, J = 11.9 Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H,
CO₂Me

CO₂Me

MeO₂C

\[
\text{4-Benzyl 3-methyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-}
\text{[1, 1'-biphenyl]-3, 4-dicarboxylate 3l.}
\]

The reaction of diene (97.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3l (93.8 mg, 72% yield) and [3 + 2] adduct (5.2 mg, 4% yield).

Colorless oil. \(^1\)H NMR (300 MHz, CDCl₃) \(\delta\) 1.85 (q, \(J = 11.9\) Hz, 1H, CH), 2.28 – 2.56 (m, 2H, CH₂), 3.39 – 3.44 (m, 1H, CH), 3.63 (s, 3H, COOCH₃), 3.67 (s, 3H, COOCH₂), 3.70 – 3.73 (m, 1H, CH), 5.18 (q, \(J = 12.2\) Hz, 2H, COOCH₂Ph), 5.58 – 5.63 (m, 1H, CH=C), 6.80 (dd, \(J = 15.8, 8.0\) Hz, 1H, C=CH), 7.02 (t, \(J = 2.1\) Hz, 1H, CH=C), 7.06 – 7.09 (m, 2H, ArH), 7.21 – 7.26 (m, 1H, ArH), 7.28 – 7.34 (m, 3H, ArH), 7.36 – 7.39 (m, 4H, ArH) ppm. \(^13\)C NMR (75 MHz, CDCl₃) \(\delta\) 31.9 (s, CH₂), 42.1 (s, CH), 43.5 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₃), 51.9 (s, COOCH₂), 66.8 (s, COOCH₂Ph), 122.0 (s, CH), 127.4 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.4 (s, 2CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 135.8 (s, C), 141.1 (s, C), 143.2 (s, CH), 149.0 (s, CH), 166.5 (s, C), 166.6 (s, C), 173.6 (s, C) ppm. IR (KBr): 2993, 1715, 1699, 1284, 1109, 1035, 760, 702, 533 cm\(^{-1}\). HRMS (ESI, m/z): Calcd for C₂₇H₂₉O₆ [M+H]⁺: 449.1959, found: 449.1960.
C_{28}H_{31}O_{6}[M+H]^+: 435.1802, found: 435.1804.

4-Benzyl 3-isopropyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3m.

The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3m (110.0 mg, 80% yield) and [3+2] adduct (6.9 mg, 5% yield).

White solid. **MP:** 78 - 79 °C.

\[ ^{1}H\text{ NMR (300 MHz, CDCl}_3\] \(\delta\) 1.18 – 1.24 (m, 6H, 2CH_3), 1.77 – 1.91 (m, 1H, CH), 2.28 – 2.35 (m, 1H, CH), 2.47 – 2.56 (m, 1H, CH), 3.39 – 3.43 (m, 1H, CH), 3.66 (s, 3H, COOCH_3), 3.70 – 3.74 (m, 1H, CH), 5.00 – 5.08 (m, 1H, COOCH), 5.11 – 5.23 (m, 2H, COOCH_2Ph), 5.52 – 5.66 (m, 1H, CH=C), 6.80 (dd, \(J = 15.7, 8.0\) Hz, 1H, C=CH), 6.95 – 7.03 (m, 1H, CH=C), 7.08 – 7.10 (m, 2H, ArH), 7.26 – 7.37 (m, 8H, ArH) ppm.

\[ ^{13}C\text{ NMR (75 MHz, CDCl}_3\] \(\delta\) 21.7 (s, CH_3), 21.8 (s, CH_3), 31.9 (s, CH_2), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s CH,), 51.5 (s, COOCH_3), 66.8 (s, COOCH_2Ph), 68.5 (s, COOCH), 121.9 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.2 (s, 2CH), 128.2 (s, CH), 128.3 (s, CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 129.2 (s, C), 135.7 (s, C), 141.3 (s, C), 142.5 (s, CH), 149.1 (s, CH), 165.8 (s, C), 166.5 (s, C), 173.7 (s, C) ppm. **IR (KBr):** 3003, 1715, 1361, 1221, 1165, 1005, 735, 703, 530 cm\(^{-1}\). **HRMS (ESI, m/z):** Calcd for C_{28}H_{31}O_{6}[M+H]^+: 463.2115, found: 463.2116.

4-Ethyl 3-isopropyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3n.

The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1)
afforded the product 3n (102.1 mg, 85% yield) and [3 + 2] adduct (8.4 mg, 7% yield).

White solid. **MP:** 94 - 95 °C. **1H NMR (300 MHz, CDCl₃)** \(\delta\) 1.22 – 1.30 (m, 9H, 3CH₃), 1.77 – 1.89 (m, 1H, CH), 2.26 – 2.55 (m, 2H), 3.40 (d, \(J = 9.6\) Hz, 1H, CH), 3.57 – 3.61 (m, 1H, CH), 3.66 (s, 3H, COOCH₃), 4.17 (q, \(J = 7.1\) Hz, 2H, COOCH₂), 5.02 – 5.10 (m, 1H, COOCH), 5.61 (d, \(J = 15.7\) Hz, 1H, CH=C), 6.80 (dd, \(J = 15.7, 8.1\) Hz, 1H, C=CH), 7.08 – 7.10 (m, 2H, ArH), 7.25 – 7.34 (m, 3H, ArH) ppm. **13C NMR (75 MHz, CDCl₃)** \(\delta\) 14.1 (s, CH₃), 21.7 (s, CH₃), 21.8 (s, CH₃), 32.0 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.5 (s, COOCH₂), 61.0 (s, COOCH₂Ph), 68.4 (s, COOCH), 121.8 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.8 (s, 2CH), 129.4 (s, C), 141.3 (s, C), 142.3 (s, CH), 149.2 (s, CH), 165.8 (s, C), 166.5 (s, C), 173.9 (s, C) ppm. **IR (KBr):** 2981, 1716, 1372, 1267, 1178, 1002, 752, 702, 530 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₃H₂₉O₆ [M+H]⁺: 401.1959, found: 401.1960.

4-Benzyl 3-butyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro -[1, 1'-biphenyl]-3, 4-dicarboxylate 3o.

The reaction of diene (109.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3o (98.6 mg, 69% yield) and [3 + 2] adduct (11.5 mg, 8% yield).

Colorless oil. **1H NMR (300 MHz, CDCl₃)** \(\delta\) 0.91 (t, \(J = 7.3\) Hz, 3H, CH₃), 1.28 – 1.38 (m, 2H, CH₂), 1.51 – 1.60 (m, 2H, CH₂), 1.85 (q, \(J = 12.0\) Hz, 1H, CH), 2.29 – 2.34 (m, 1H, CH), 2.51 (q, \(J = 9.0\) Hz, 1H, CH), 3.40 – 3.43 (m, 1H, CH), 3.67 (s, 3H, COOCH₂), 3.70– 3.73 (m, 1H, CH), 3.99 – 4.16 (m, 2H, COOCH₂), 5.17 (q, \(J = 12.3\) Hz, 2H, COOCH₂Ph), 5.60 (d, \(J = 15.7\) Hz, 1H, CH=C), 6.80 (dd, \(J = 15.7, 8.1\) Hz, 1H, C=CH), 7.02 –7.10 (m, 3H, CH=C, ArH), 7.26 – 7.37 (m, 8H, ArH) ppm. **13C NMR (75 MHz, CDCl₃)** \(\delta\) 13.7 (s, CH₃), 19.1 (s, CH₂), 30.5 (s, CH₂), 31.9 (s, CH), 42.1 (s, CH), 43.7 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₂), 64.8 (s, COOCH₂), 66.8
(s, COOCH₂Ph), 121.9 (s, CH), 127.3 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.6 (s, 2CH), 128.8 (s, 2CH), 128.9 (s, C), 135.7 (s, C), 141.2 (s, C), 142.8 (s, CH), 149.0 (s, CH), 166.3 (s, C), 166.5 (s, C), 173.7 (s, C) ppm. **IR (KBr):** 3029, 1727, 1379, 1270, 1163, 1032, 733, 700, 520 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₂₉H₃₃O₆ [M+H]⁺: 477.2272, found: 477.2273.

**Dibenzyl ε-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro- [1, 1’-biphenyl]-3, 4-dicarboxylate 3p.**

The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv) after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3p (85.7 mg, 56% yield) and [3 + 2] adduct (6.1 mg, 4% yield). Colorless oil. **¹H NMR (300 MHz, CDCl₃)** δ 1.87 (q, J = 12.0 Hz, 1H, CH), 2.29 – 2.56 (m, 2H, CH₂), 3.41 – 3.44 (m, 1H, CH), 3.68 (s, 3H, CH₃), 3.72 – 3.77 (m, 1H, CH), 4.99 – 5.14 (m, 4H, 2COOCH₂), 5.61 (d, J = 15.7 Hz, 1H, HC=C), 6.80 (dd, J = 15.7, 8.0 Hz, 1H, C=CH), 7.08 – 7.09 (m, 3H, HC=C, ArH), 7.30 – 7.35 (m, 13H, ArH) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 31.9 (s, CH₂), 42.1 (s, CH), 43.6 (s, CH), 47.8 (s, CH), 51.6 (s, COOCH₂), 66.7 (s, COOCH₂), 66.8 (s, COOCH₂), 122.0 (s, CH), 127.4 (s, CH), 128.2 (s, 2CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.3 (s, 2CH), 128.5 (s, 2CH), 128.6 (s, 2CH), 128.7 (s, C), 128.9 (s, 2CH), 135.7 (s, C), 135.7 (s, C), 141.1 (s, C), 143.5 (s, CH), 149.0 (s, CH), 166.0 (s, C), 166.5 (s, C), 173.6 (s, C) ppm. **IR (KBr):** 2982, 1733, 1433, 1269, 1170, 1009, 732, 704, 541 cm⁻¹. **HRMS (ESI, m/z):** Calcd for C₃₂H₃₀O₆Na [M+Na]⁺: 533.1935, found: 533.1934.
4-Benzyl 3-ethyl ε-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-4′-fluoro-1, 4, 5, 6-tetrahydro-[1, 1′-biphenyl]-3, 4-dicarboxylate 3q.

The reaction of diene (106.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3q (113.8 mg, 79% yield) and [3 + 2] adduct (11.5 mg, 8% yield).

Colorless oil. \(^1\text{H NMR (300 MHz, CDCl}_3\) δ 1.17 – 1.26 (m, 6H, 2CH\(_3\)), 1.76 – 1.90 (m, 1H, CH), 2.28 – 2.49 (m, 2H, CH\(_2\)), 3.38 – 3.43 (m, 1H, CH), 3.66 – 3.74 (m, 1H, CH), 4.05 – 4.18 (m, 4H, COOCH\(_2\)Ph), 5.16 (q, \(J = 12.3\) Hz, 2H, COOCH\(_2\)Ph), 5.59 (d, \(J = 15.7\) Hz, 1H, HC=C ), 6.76 (dd, \(J = 15.7, 8.1\) Hz, 1H, C=CH), 6.97 – 7.05 (m, 5H, HC=C, ArH), 7.33 – 7.38 (m, 5H, ArH) ppm. \(^{13}\text{C NMR (75 MHz, CDCl}_3\) δ 14.1 (s, CH\(_3\)), 14.2 (s, CH\(_3\)), 31.9 (s, CH\(_2\)), 42.1 (s, CH), 43.8 (s, CH), 47.0 (s, CH), 60.4 (s, COOCH\(_2\)), 61.0 (s, COOCH\(_2\)), 66.8 (s, COOCH\(_2\)Ph), 115.7 (d, \(J = 21.4\) Hz, 2CH), 122.6 (s, CH), 128.3 (s, CH), 128.3 (s, 2CH), 128.6 (s, 2CH), 129.1 (s, C), 129.7 (d, \(J = 8.0\) Hz, 2CH), 135.7 (s, C), 137.0 (d, \(J = 3.2\) Hz, C), 142.5 (s, CH), 148.4 (s, CH), 161.9 (d, \(J = 245.8\) Hz, C), 166.0 (s, C), 166.1 (s, C), 173.6 (s, C) ppm. \(\text{IR (KBr): 2987, 1733, 1433, 1269, 1184, 1003, 735, 708, 541 cm}^{-1}\). \(\text{HRMS (ESI, m/z): Calcd for C}_{28}\text{H}_{30}\text{FO}_{6}\) [M+H]^+: 481.2021, found: 481.2022.

4-Benzyl 3-ethyl ε-4′-fluoro-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1′-biphenyl]-3, 4-dicarboxylate 3r.

The reaction of diene (106.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3r (123.2 mg, 88% yield) and [3 + 2] adduct (4.2 mg, 3% yield).

Colorless oil. \(^1\text{H NMR (300 MHz, CDCl}_3\) δ 1.20 (t, \(J = 7.1\) Hz, 3H, CH\(_3\)), 1.84 (q, \(J = 12.0\) Hz, 1H, CH), 2.27 – 2.50 (m, 2H, CH\(_2\)), 3.38 – 3.43 (m, 1H, CH), 3.67 (s, 3H, COOCH\(_3\)), 3.72 – 3.81 (m, 1H, CH), 4.06 – 4.19 (m, 2H, COOCH\(_2\)), 5.16 (q, \(J = 12.3\) Hz, 2H, COOCH\(_2\)Ph), 5.59 (d, \(J = 15.7\) Hz, 1H, HC=C ), 6.76 (dd, \(J = 15.7, 8.2\) Hz,
1H, C=CH), 6.97 – 7.07 (m, 5H, HC=C, ArH), 7.32 – 7.37 (m, 5H, ArH) ppm. 13C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 31.9 (s, CH₂), 42.1 (s, CH), 43.9 (s, CH), 47.0 (s, CH), 51.6 (s, CH₂), 61.0 (s, COOCH₂), 66.8 (s, COOCH₂Ph), 115.7 (d, J = 21.4 Hz, 2CH), 122.2 (s, CH), 128.3 (s, 2CH), 128.3 (s, CH), 128.6 (s, 2CH), 129.1 (s, C), 129.7 (d, J = 8.0 Hz, 2CH), 135.7 (s, C), 137.0 (d, J = 3.2 Hz, C), 142.4 (s, CH), 148.7 (s, CH), 161.9 (d, J = 246.0 Hz, C), 166.1 (s, C), 166.4 (s, C), 173.5 (s, C) ppm. IR (KBr): 2951, 1731, 1435, 1270, 1184, 1008, 732, 708, 542 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₇H₂₈FO₆ [M+H]^+: 467.1864, found: 467.1866.

4-Benzyl 3-ethyl (E)-4'-bromo-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3,4-dicarboxylate 3s.

The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3s (123.4 mg, 76% yield) and [3 + 2] adduct (9.2 mg, 6% yield). Colorless oil. 1H NMR (300 MHz, CDCl₃) δ 1.20 – 1.25 (m, 6H, 2CH₃), 1.78 – 1.97 (m, 1H, CH), 2.19 – 2.46 (m, 2H, CH₂), 3.30 – 3.40 (m, 1H, CH), 3.57 – 3.76 (m, 1H, CH), 3.99 – 4.28 (m, 4H, 2COOCH₂), 5.16 (dd, J = 33.4, 12.0 Hz, 2H, COOCH₂Ph), 5.52 – 5.71 (m, 1H, HC=C), 6.75 (dd, J = 15.2, 7.8 Hz, 1H, C=CH), 6.95 – 7.05 (m, 3H, HC=C, ArH ), 7.28 – 7.45 (m, 7H, ArH) ppm. 13C NMR (75 MHz, CDCl₃) δ 14.1 (s, CH₃), 14.2 (s, CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.6 (s, CH), 47.2 (s, CH), 60.5 (s, COOCH₂), 61.0 (s, COOCH₂Ph), 66.8 (s, COOCH₂Ph), 121.2 (s, C), 122.7 (s, CH), 128.31 (s, 2CH), 128.32 (s, CH), 128.6 (s, 2CH), 129.3 (s, C), 129.9 (s, 2CH), 131.9 (s, 2CH), 135.7 (s, C), 140.3 (s, C), 142.0 (s, CH), 148.2 (s, CH), 166.0 (s, C), 166.1 (s, C), 173.5 (s, C) ppm. IR (KBr): 2980, 1715, 1368, 1267, 1094, 1033, 751, 698, 519 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₈H₃₆BrO₆ [M+H]^+: 541.1220, found: 541.1218.
4-Benzyl 3-ethyl (E)-4′-bromo-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1,1′-biphenyl]-3, 4-dicarboxylate 3t.

The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3t (120.2 mg, 76% yield) and [3 + 2] adduct (11.0 mg, 7% yield). Colorless oil. \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.20 (t, \(J = 7.1\) Hz, 6H, 2CH\(_3\)), 1.77 – 1.89 (m, 1H, CH), 2.18 – 2.50 (m, 2H, CH\(_2\)), 3.35 – 3.41 (m, 1H, CH), 3.66 – 3.73 (m, 4H, CH, COOCH\(_3\)), 4.05 – 4.18 (m, 2H, COOCH\(_2\)), 5.16 (q, \(J = 12.3\) Hz, 2H, COOCH\(_2\)Ph), 5.57 – 5.63 (m, 1H, CH=C), 6.75 (dd, \(J = 15.7, 8.2\) Hz, 1H, C=CH), 6.94 – 6.97 (m, 3H, CH=C, ArH), 7.33 – 7.39 (m, 5H, ArH), 7.42 – 7.45 (m, 2H, ArH) ppm. \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 14.1 (s, CH\(_3\)), 31.9 (s, CH\(_2\)), 42.0 (s, CH), 43.7 (s, CH), 47.2 (s, CH), 51.6 (s, COOCH\(_3\)), 61.0 (s, COOCH\(_2\)), 66.8 (s, COOCH\(_2\)Ph), 121.3 (s, C), 122.3 (s, CH), 128.30 (s, 2CH), 128.33 (s, CH), 128.6 (s, 2CH), 129.4 (s, C), 129.9 (s, 2CH), 132.0 (s, 2CH), 135.7 (s, C), 140.2 (s, C), 141.9 (s, CH), 148.5 (s, CH), 166.1 (s, C), 166.4 (s, C), 173.5 (s, C) ppm. IR (KBr): 2932, 1727, 1384, 1280, 1119, 1041, 745, 697, 533 cm\(^{-1}\). HRMS (ESI, m/z): Calcd for C\(_{27}\)H\(_{28}\)BrO\(_6\) [M+H]\(^+\): 527.1064, found: 527.1063.

4-Ethyl 3-methyl (E)-6-(3-methoxy-3-oxoprop-1-en-1-yl)-3′-methyl-1, 4, 5, 6-tetrahydro-[1,1′-biphenyl]-3, 4-dicarboxylate 3u.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3u (99.7 mg, 86% yield) and [3 + 2] adduct (2.3 mg, 3% yield). Colorless oil. \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 1.25 – 1.29 (m, 3H, CH\(_3\)), 1.76 – 1.88
(m, 1H, CH), 2.28 – 2.32 (m, 4H, CH, CH₃), 2.47 – 2.56 (m, 1H, CH), 3.37 (d, J = 9.7 Hz, 1H, CH), 3.56 – 3.61 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 3.73 (s, 3H, COOCH₃), 4.14 – 4.23 (m, 2H, COOCH₂), 5.64 (d, J = 15.8 Hz, 1H, CH=CH), 6.81 (dd, J = 15.8, 7.9 Hz, 1H, C=CH), 6.88 – 6.99 (m, 3H, CH=CH, ArH), 7.04 – 7.07 (m, 1H, ArH), 7.16 – 7.21 (m, 1H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (s, CH₃), 21.4 (s, CH₃), 42.0 (s, CH₂), 42.0 (s, CH), 43.3 (s, CH), 47.7 (s, CH), 51.5 (s, COOCH₂), 61.0 (s, COOCH₂), 121.8 (s, CH), 125.3 (s, CH), 128.1 (s, CH), 128.6 (s, C), 128.7 (s, CH), 128.7 (s, CH), 138.5 (s, C), 141.1 (s, C), 143.2 (s, CH), 149.2 (s, CH), 166.5 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. IR (KBr): 2980, 1731, 1435, 1270, 1184, 1036, 732, 708, 542 cm⁻¹. HRMS (ESI, m/z): Calcd for C₂₂H₂₇O₆ [M+H]+: 387.1802, found: 387.1801.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3v (90.4 mg, 78% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.27 (t, J = 7.1 Hz, 3H, CH₃), 1.82 (q, J = 12.0 Hz, 1H, CH), 2.00 – 2.05 (m, 1H, CH), 2.10 – 2.13 (m, 1H, CH), 2.26 – 2.29 (m, 1H, CH), 2.32 (s, 3H, CH₃), 2.45 – 2.54 (m, 1H, CH), 3.36 – 3.39 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.67 (s, 3H, COOCH₃), 3.73 (s, 3H, COOCH₃), 4.14 – 4.23 (m, 2H, COOCH₂), 5.63 (d, J = 15.8 Hz, 1H, HC=CH), 6.20 (dd, J = 15.8, 7.9 Hz, 1H, C=CH), 6.95 – 6.99 (m, 3H, CH=CH, ArH), 7.10 – 7.13 (m, 2H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.2 (s, CH₃), 21.0 (s, CH₃), 31.9 (s, CH₂), 42.0 (s, CH), 43.4 (s, CH), 47.4 (s, CH), 51.5 (s, COOCH₃), 51.9 (s, COOCH₂), 61.0 (s, COOCH₂), 121.8 (s, CH), 128.0 (s, 2CH), 128.6 (s, C), 129.5 (s, 2CH), 136.9 (s, C), 138.1 (s, C), 143.4 (s, CH), 149.3 (s, CH), 166.5(s, C), 166.8 (s, C), 173.9 (s, C) ppm. IR (KBr): 2957, 1723, 1434, 1260, 1161, 1032, 732, 705, 541
cm^{-1}. **HRMS** (ESI, m/z): Calcd for C_{22}H_{27}O_{6} [M+H]^+: 387.1802, found: 387.1803.

![Diagram](image)

**Diethyl (E)-4'-bromo-6-(3-methoxy-3-oxoprop-1-en-1-yl)-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3w.**

The reaction of diene (124.6 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.4 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3w (113.1 mg, 81% yield) and [3 + 2] adduct (12.6 mg, 9% yield).

Colorless oil. **^{1}H NMR (300 MHz, CDCl_{3})**: δ 1.24 – 1.29 (m, 3H, CH_{3}), 1.82 (q, J = 12.0 Hz, 1H, CH), 2.26 – 2.50 (m, 2H, CH_{2}), 3.37 – 3.41 (m, 1H, CH), 3.60 – 3.64 (m, 1H, CH), 3.68 (s, 3H, COOCH_{3}), 4.12 – 4.25 (m, 4H, 2COOCH_{2}), 5.62 (d, J = 15.7 Hz, 1H, HC=C), 6.76 (dd, J = 15.7, 8.2 Hz, 1H, C=CH), 6.93 – 6.98 (m, 3H, HC=C, ArH), 7.39 – 7.45 (m, 2H, ArH) ppm. **^{13}C NMR (75 MHz, CDCl_{3})**: δ 14.1 (s, 2CH_{3}), 31.9 (s, CH_{2}), 42.0 (s, CH), 43.6 (s, CH), 47.2 (s, CH), 51.6 (s, COOCH_{2}), 61.0 (s, COOCH_{2}), 61.1 (s, COOCH_{2}), 121.2 (s, C), 122.2 (s, CH), 129.5 (s, C), 129.9 (s, 2CH), 132.0 (s, 2CH), 140.3 (s, C), 141.8 (s, CH), 148.6 (s, CH), 166.1 (s, C), 166.4 (s C.), 173.7 (s, C) ppm. **IR (KBr)**: ν = 2951, 1731, 1435, 1270, 1184, 1008, 732, 708, 542 cm^{-1}. **HRMS** (ESI, m/z): Calcd for C_{22}H_{26}BrO_{6} [M+H]^+: 465.0907, found: 465.0906.

![Diagram](image)

**4-Ethyl 3-methyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-3'-methyl-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3x.**

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3x (87.7 mg, 73% yield) and [3 + 2] adduct (15.6 mg, 13% yield).
Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.24 – 1.27 (m, 6H, 2CH$_3$), 1.77 – 1.89 (m, 1H, CH), 2.24 – 2.29 (m, 1H, CH), 2.33 (s, 3H, CH$_3$), 2.51 (dd, $J$ = 18.5, 8.9 Hz, 1H, CH), 3.36 – 3.39 (m, 1H, CH), 3.61 – 3.65 (m, 1H, CH), 3.74 (s, 3H, COOCH$_3$), 4.09 – 4.21 (m, 4H, COOCH$_2$), 5.63 (d, $J$ = 15.7 Hz, 1H, HC=C), 6.80 (dd, $J$ = 15.8, 7.7 Hz, 1H, C=CH), 6.88 – 6.94 (m, 2H, HC=C; ArH), 6.96 – 6.99 (m, 1H, ArH), 7.05 – 7.07 (m, 1H, ArH), 7.17 – 7.22 (m, 1H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, 2CH$_3$), 21.1 (s, CH$_3$), 31.8 (s, CH$_2$), 42.0 (s, CH), 43.2 (s, CH), 47.7 (s, CH), 51.9 (s, COOCH$_3$), 60.3 (s, COOCH$_2$), 61.0 (s, COOCH$_2$), 122.2 (s, CH), 125.3 (s, CH), 128.1 (s, CH), 128.6 (s, C), 128.7 (s, CH), 128.8 (s, CH), 138.5 (s, C), 141.1 (s, C), 143.3 (s, CH), 148.9 (s, CH), 166.2 (s, C), 166.8 (s, C), 173.9 (s, C) ppm.


4-Ethyl 3-methyl (E)-6-(3-ethoxy-3-oxoprop-1-en-1-yl)-4'-methyl-1, 4, 5, 6-tetrahydro-[1, 1'-biphenyl]-3, 4-dicarboxylate 3y.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 3y (105.7 mg, 88% yield) and [3 + 2] adduct (6.0 mg, 5% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.26 (dd, $J$ = 15.3, 7.6 Hz, 6H, 2CH$_3$), 1.83 (dd, $J$ = 24.1, 12.0 Hz, 1H, CH), 2.27 – 2.29 (m, 1H, CH), 2.33 (s, 3H, CH$_3$), 2.49 (dd, $J$ = 18.7, 8.9 Hz, 1H, CH), 3.38 (d, $J$ = 9.7 Hz, 1H, CH), 3.61 – 3.64 (m, 1H, CH), 3.74 (s, 3H, COOCH$_3$), 4.10 – 4.21 (m, 4H, COOCH$_2$), 5.64 (d, $J$ = 15.8 Hz, 1H, HC=C), 6.80 (dd, $J$ = 15.7, 7.8 Hz, 1H, C=CH), 6.90 – 6.96 (m, 1H, HC=C), 6.99 – 7.04 (m, 2H, ArH), 7.11 – 7.13 (m, 2H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, CH$_3$), 14.2 (s, CH$_3$), 21.1 (s, CH$_3$), 31.9 (s, CH$_2$), 42.0 (s, CH), 43.4 (s, CH), 47.4 (s, CH), 51.9 (s, COOCH$_3$), 60.3 (s, COOCH$_2$), 61.0 (s, COOCH$_2$), 122.2 (s, CH), 128.0 (s, 2CH), 128.6 (s, C), 129.5 (s, 2CH), 136.9 (s, C), 138.2 (s, C), 138.5 (s, C), 139.1 (s, C), 143.3 (s, CH), 148.9 (s, CH), 166.2 (s, C), 166.8 (s, C), 173.9 (s, C) ppm.
143.4 (s, CH), 149.0 (s, CH), 166.1 (s, C), 166.8 (s, C), 173.9 (s, C) ppm. IR (KBr): 2989, 1716, 1435, 1257, 1092, 1037, 735, 692, 551 cm⁻¹. HRMS (ESI, m/z): Calcd for C_{23}H_{29}O_{6}[M+H]^+: 401.1959, found: 401.1961.

5. General procedure for synthesis of 4.

\[
\begin{align*}
R^2O_2C & \quad \text{Ar} & \quad \text{CO}_2R^1 \\
CO_2R^3 & \quad \text{CO}_2R^2 & \quad \text{PBu}_3 (20 \text{ mol} \%) \\
\text{CHCl}_3, \text{r.t.} & \quad \text{4} \\
\end{align*}
\]

To a dry flask filled with nitrogen were added 1 (0.3 mmol) and 2 (0.45 mmol) in 3 mL CHCl₃. PBu₃ (0.06 mmol) was added. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: 20% EtOAc in petroleum ether) to afford 4.

\[
\begin{align*}
\text{CO}_2\text{Bn} & \quad \text{CO}_2\text{Et} \\
\text{CO}_2\text{Me} & \quad \text{Ph} \\
\end{align*}
\]

3-Benzyl 2-ethyl 1-methyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-tricarboxylate 4a.

The reaction of diene (78.1 mg, 0.3 mmol, 1.0 equiv) and allenoate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4a (117.0 mg, 87% yield).

Colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 0.99 (t, J = 7.1 Hz, 3H, CH₃), 1.13 (d, J = 7.3 Hz, 3H, CH₃), 3.52 – 3.54 (m, 1H, CH), 3.75 (s, 3H, COOCH₃), 3.86 – 3.94 (m, 2H, COOCH₂Ph ), 4.57 (s, 1H, CH), 5.19 (q, J = 12.5 Hz, 2H, COOCH₂Ph ), 6.40 (q, J = 16.4 Hz, 2H, CH=CH), 6.82 (s, 1H, CH=C), 7.19 – 7.25 (m, 2H, ArH), 7.25 – 7.34 (m, 8H, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 13.1 (s, CH₃), 14.0 (s, CH₃), 46.6 (s, CH), 51.3 (s, COOCH₃), 56.8 (s, CH), 59.9 (s, COOCH₂), 60.8 (s, C), 65.4 (s,
COOCH$_2$-Ph), 125.5 (s, 2CH), 126.4 (s, CH), 126.9 (s, CH), 127.1 (s, 2CH), 127.2 (s, CH), 127.5 (s, 2CH), 127.6 (s, 2CH), 129.7 (s, CH), 131.9 (s, C), 134.8 (s, C), 135.6 (s, C), 147.1 (s, CH), 162.8 (s, C), 169.4 (s, C), 171.9 (s, C) ppm. **IR (KBr):** 2981, 1733, 1455, 1258, 1119, 1024, 733, 698, 550 cm$^{-1}$. **HRMS (ESI, m/z):** Calcd for C$_{27}$H$_{29}$O$_6$ [M+H]$^+$: 449.1959, found: 449.1957.

2-Benzyl 3-ethyl 1-isopropyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-tricarboxylate 4b.

The reaction of diene (105.1 mg, 0.3 mmol, 1.0 equiv) and allenolate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4b (117.3 mg, 82% yield).

Colorless oil. **$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.22 – 1.28 (m, 12H, 4CH$_3$), 3.49 – 3.56 (m, 1H, CH), 4.13 – 4.20 (m, 2H, COOCH$_2$), 4.65 (s, 1H, CH), 4.99 – 5.05 (m, 2H, COOCH$_2$-Ph), 5.09 – 5.16 (m, 1H, COOCH), 6.23 – 6.38 (m, 2H, CH=CH), 6.79 (s, 1H, CH=C), 7.17 – 7.23 (m, 5H, ArH), 7.26 – 7.35 (m, 5H, ArH) ppm. **$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.1 (s, CH$_3$), 15.2 (s, CH$_3$), 21.6 (s, 2CH$_3$), 47.9 (s, CH), 57.3 (s, CH), 60.7 (s, COOCH$_2$), 61.6 (s, C), 66.7 (s, COOCH$_2$-Ph), 69.3 (s, COOCH), 125.6 (s, CH), 126.4 (s, 2CH), 127.8 (s, CH), 128.0 (s, CH), 128.3 (s, 2CH), 128.4 (s, 2CH), 128.6 (s, 2CH), 131.8 (s, CH), 132.6 (s, C), 135.7 (s, C), 136.6 (s, C), 148.1 (s, CH), 164.0 (s, C), 171.0 (s, C), 173.0 (s, C) ppm. **IR (KBr):** 2982, 1723, 1453, 1256, 1116, 1030, 734, 682, 551 cm$^{-1}$. **HRMS (ESI, m/z):** Calcd for C$_{29}$H$_{33}$O$_6$ [M+H]$^+$: 477.2272, found: 477.2276.

2, 3-Diethyl 1-isopropyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-
tricarboxylate 4c.
The reaction of diene (86.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4c (90.7 mg, 73% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.14 (t, $J = 7.1$ Hz, 3H, CH$_3$), 1.23 – 1.25 (m, 3H, CH$_3$), 1.29 – 1.34 (m, 9H, 3CH$_3$), 3.48 – 3.56 (m, 1H, CH), 4.04 – 4.11 (m, 2H, COOCH$_2$), 4.18 – 4.23 (m, 2H, COOCH$_2$), 4.58 (s, 1H, CH), 5.12 – 5.21 (m, 1H, COOCH), 6.33 (q, $J = 16.5$ Hz, 2H, CH=CH), 6.78 (s, 1H, CH=C), 7.27 – 7.31 (m, 5H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, 2CH$_3$), 15.2 (s, CH$_3$), 21.7 (s, 2CH$_3$), 47.8 (s, CH), 57.3 (s, CH), 60.6 (s, COOCH$_2$), 60.8 (s, COOCH$_2$), 61.5 (s C$_3$), 69.2 (s, COOCH), 125.8 (s, CH), 126.3 (s, 2CH), 127.8 (s, CH), 128.6 (s, 2CH), 131.6 (s, CH), 132.7 (s, C), 136.8 (s, C), 147.9 (s, CH), 164.07 (s, C), 171.16 (s, C), 173.07 (s, C) ppm. IR (KBr): 2980, 1723, 1454, 1257, 1116, 1029, 735, 692, 550 cm$^{-1}$.

$^1$ HRMS (ESI, m/z): Calcd for C$_{24}$H$_{31}$O$_6$ [M+H]$^+$: 415.2115, found: 415.2117.

1. 2-Dibenzyl 3-methyl (E)-5-methyl-1-styrylcyclopent-3-ene-1, 2, 3-tricarboxylate 4d.
The reaction of diene (119.5 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.5 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4d (137.8 mg, 90% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.22 (d, $J = 7.4$ Hz, 3H, CH$_3$), 3.54 – 3.59 (m, 1H, CH), 3.68 (s, 3H, COOCH$_3$), 4.69 (t, $J = 1.7$ Hz, 1H, CH), 5.04 (s, 2H, COOCH$_2$Ph), 5.26 (s, 2H, COOCH$_2$Ph), 6.19 (q, $J = 16.6$ Hz, 2H, CH=CH), 6.81 (t, $J = 2.1$ Hz, 1H, CH=C), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.24 (m, 7H, ArH), 7.31-7.35 (m, 6H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 15.2 (s, CH$_3$), 47.9 (s, CH), 51.7 (s, CH), 57.2 (s, COOCH$_3$), 61.7 (s, C), 66.8 (s, COOCH$_2$Ph), 67.4 (s, COOCH$_2$Ph), 125.1 (s, CH), 126.4 (s, 2CH), 127.8 (s, CH), 128.0 (s, CH), 128.35 (s, 2CH), 128.35
3-Benzyl 2-ethyl 1-methyl (E)-5-methyl-1-(4-methylstyryl)cyclopent-3-ene-1,2,3-tricarboxylate 4e.

The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenolate (84.7 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4e (116.5 mg, 84% yield).

Colorless oil. \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.07 (t, \( J = 7.1 \) Hz, 3H, CH\(_3\)), 1.23 – 1.25 (m, 3H, CH\(_3\)), 2.33 (s, 3H, CH\(_3\)), 3.54 – 3.61 (m, 1H, CH), 3.83 (s, 3H, COOCH\(_3\)), 4.00 (q, \( J = 7.1 \) Hz, 2H, COOCH\(_3\)), 4.57 – 4.63 (m, 1H, CH), 5.19 (m, 2H, COOCH\(_2\)Ph), 6.18 – 6.32 (m, 2H, CH=CH), 6.86 – 6.87 (m, 1H, CH=C), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.23 (m, 2H, ArH), 7.35 – 7.38 (m, 5H, ArH) ppm. \( ^{13}C \) NMR (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (s, CH\(_3\)), 15.3 (s, CH\(_3\)), 21.2 (s, CH\(_3\)), 48.0 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH\(_3\)), 61.0 (s, COOCH\(_3\)), 61.5 (s, COOCH\(_3\)), 66.4 (s, COOCH\(_2\)Ph), 124.3 (s, CH), 126.3 (s, 2CH), 128.2 (s, 2CH), 128.5 (s, 2CH), 129.3 (s, 2CH), 131.8 (s, CH), 132.3 (s, C), 133.7 (s, C), 135.7 (s, C), 137.8 (s, C), 149.0 (s, CH), 163.8 (s, C), 171.1 (s, C), 174.3 (s, C) ppm. IR (KBr): 2980, 1734, 1435, 1264, 1114, 1035, 734, 692, 550 cm\(^{-1}\). HRMS (ESI, m/z): Calcd for C\(_{28}\)H\(_{31}\)O\(_6\) [M+H]\(^{+}\): 511.2115, found: 511.2116.
2, 3-diethyl 1-methyl (E)-5-methyl-1-(4-methylstyrlyl)cyclopent-3-ene-1, 2, 3-tricarboxylate 4f.
The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4f (87.5 mg, 76% yield). Colorless oil. \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.15 (t, \( J = 7.1 \) Hz, 3H, CH\(_3\)), 1.23 – 1.31 (m, 6H, 2CH\(_3\)), 2.33 (s, 3H, CH\(_3\)), 3.53 – 3.60 (m, 1H, CH), 3.83 (s, 3H, COOCH\(_3\)), 4.08 (q, \( J = 7.1 \) Hz, 2H, COOCH\(_2\)), 4.16 – 4.24 (m, 2H, COOCH\(_2\)), 4.59 (s, 1H, CH), 6.18 – 6.32 (m, 2H, CH=CH), 6.81 (s, 1H, CH=C), 7.09 – 7.12 (m, 2H, ArH), 7.20 – 7.23 (m, 2H, ArH) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (s, CH\(_3\)), 14.2 (s, CH\(_3\)), 15.3 (s, CH\(_3\)), 21.2 (s, CH\(_3\)), 47.9 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH\(_3\)), 60.6 (s, COOCH\(_2\)), 60.9 (s, COOCH\(_2\)), 61.5 (s, C), 124.4 (s, CH), 126.3 (s, 2CH), 129.3 (s, 2CH), 131.7 (s, CH), 132.7 (s, C), 133.7 (s, C), 137.7 (s, C), 148.2 (s, CH), 164.0 (s, C), 171.1 (s, C), 174.4 (s, C) ppm. IR (KBr): 2978, 1714, 1454, 1264, 1114, 735, 693, 550 cm\(^{-1}\). HRMS (ESI, m/z): Calcd for C\(_{23}\)H\(_{29}\)O\(_6\) [M+H]\(^+\): 401.1959, found: 401.1962.

2, 3-Diethyl 1-methyl (E)-5-methyl-1-(3-methylstyrlyl)cyclopent-3-ene-1, 2, 3-tricarboxylate 4g.
The reaction of diene (82.3 mg, 0.3 mmol, 1.0 equiv) and allenoate (56.8 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4g (105.6 mg, 88% yield). Colorless oil. \( ^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 1.16 – 1.31 (m, 9H, 3CH\(_3\)), 2.33 (s, 3H, CH\(_3\)), 3.56 – 3.58 (m, 1H, CH), 3.83 (s, 3H, COOCH\(_3\)), 4.06 – 4.23 (m, 4H, 2COOCH\(_2\)), 4.55-4.59 (m, 1H, CH), 6.27-6.40 (m, 2H, CH=CH), 6.81 (s, 1H, CH=C), 7.05 – 7.07 (m, 1H, ArH), 7.11 – 7.22 (m, 3H, ArH) ppm. \( ^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 14.1 (s, CH\(_3\)), 14.2 (s, CH\(_3\)), 15.3 (s, CH\(_3\)), 21.2 (s, CH\(_3\)), 47.9 (s, CH), 52.8 (s, CH), 57.3 (s, COOCH\(_3\)), 60.7 (s, COOCH\(_2\)), 60.9 (s, COOCH\(_2\)), 61.6 (s, C), 123.5
(s, CH), 125.2 (s, CH), 127.0 (s, CH), 128.5 (s, CH), 128.7 (s, CH), 132.0 (s, CH), 132.7 (s, C), 136.5 (s, C), 138.1 (s, C), 148.2 (s, CH), 164.0 (s, C), 171.1 (s, C), 174.3 (s, C) ppm. IR (KBr): 2981, 1711, 1454, 1263, 1116, 1030, 735, 692, 550 cm$^{-1}$.


CO$_2$Et
\[\text{1, 2-Diethyl 3-methyl (E)-1-(2-methylstyryl)cyclopent-3-ene-1, 2, 3-tricarboxylate 4i.}\]

The reaction of diene (106.0 mg, 0.3 mmol, 1.0 equiv) and allenoate (50.5 mg, 0.45 mmol, 1.5 equiv), after a flash column chromatography (petroleum: AcOEt = 5:1) afforded the product 4i (123.5 mg, 89% yield).

Colorless oil. $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.12 - 1.26 (m, 6H, 2CH$_3$), 2.24 - 2.28 (m, 3H, CH$_3$), 3.56 - 3.63 (m, 1H, CH), 3.81 (s, 3H, COOCH$_2$), 4.13 - 4.20 (m, 2H, COOCH$_2$), 4.67 (s, 1H, CH), 4.96 - 5.12 (m, 2H, COOCH$_2$Ph), 6.09 - 6.14 (m, 1H, CH=C), 6.50 (d, $J = 16.4$ Hz, 1H, C=CH), 6.82 (s, 1H, CH=C), 7.12 - 7.27 (m, 4H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.1 (s, CH$_3$), 15.3 (s, CH$_3$), 19.6 (s, CH$_3$), 47.8 (s, CH), 52.7 (s, CH), 57.3 (s, COOCH$_3$), 60.7 (s, COOCH$_2$), 61.9 (s, C), 66.8 (s, COOCH$_2$Ph), 125.7 (s), 126.2 (s), 126.7 (s), 127.8 (s), 128.1 (s), 128.3 (s), 130.1 (s), 130.2 (s), 132.6 (s), 135.5 (s), 135.6 (s), 135.8 (s), 148.4(s), 148.4(s), 163.9 (s), 171.0 (s), 174.3(s) ppm. IR (KBr): 2979, 1733, 1455, 1257, 1119, 1024, 733, 698, 550 cm$^{-1}$. HRMS (ESI, m/z): Calcd for C$_{28}$H$_{31}$O$_6$ [M+H]$^+$: 463.2115, found: 463.2119.
afforded the product 4i (114.4 mg, 82% yield).

Colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.14 (t, $J = 7.0$ Hz, 3H, CH$_3$), 1.22 – 1.24 (m, 3H, CH$_3$), 1.31 – 1.36 (m, 3H, CH$_3$), 1.53 – 1.59 (m, 1H, CH), 3.75 (s, 3H, COOCH$_3$), 4.08 (q, $J = 7.1$ Hz, 2H, COOCH$_2$), 4.30 (q, $J = 14.3$, 7.2 Hz, 2H, COOCH$_2$), 4.59 (s, 1H, CH), 6.29-6.38 (m, 2H, CH=CH), 6.73-6.86 (m, 1H, CH=C), 7.17 – 7.22 (m, 2H, ArH), 7.41 – 7.44 (m, 2H, ArH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 14.2 (s, CH$_3$), 14.2 (s, CH$_3$), 15.2 (s, CH$_3$), 47.9 (s, CH), 51.8 (s, CH), 57.2 (s, COOCH$_3$), 60.9 (s, COOCH$_2$), 61.5 (s, C), 61.8 (s, COOCH$_2$), 121.7 (s, C), 126.5 (s, CH), 127.8 (s, 2CH), 130.6 (s, CH), 131.7 (s, 2CH), 132.4 (s, C), 135.6 (s, C), 148.2 (s, CH), 164.4 (s, C), 171.0 (s, C), 173.4 (s, C) ppm. IR (KBr): 2981, 1714, 1435, 1258, 1118, 1032, 735, 693, 550 cm$^{-1}$. HRMS (ESI, m/z): Calcd for C$_{22}$H$_{26}$BrO$_6$ [M+H]$^+$: 465.0907, found: 465.0906.

6. Copies of $^1$H NMR, $^{13}$C NMR Spectra

![Compound 3a $^1$H NMR Spectra](image)

![Compound 3a $^{13}$C NMR Spectra](image)
Compound 3b $^1$H NMR

Compound 3b $^{13}$C NMR
Compound 3c $^1$H NMR

Compound 3c $^{13}$C NMR
Compound 3d $^1$H NMR

Compound 3d $^{13}$C NMR
Compound 3e $^1$H NMR

Compound 3e $^{13}$C NMR
Compound 3f \(^1\)H NMR

Compound 3f \(^13\)C NMR
Compound 3g $^1$H NMR

Compound 3g $^{13}$C NMR
Compound 3h $^1$H NMR

Compound 3h $^{13}$C NMR
Compound 3j $^1$H NMR

Compound 3j $^{13}$C NMR
Compound 3k $^1$H NMR

Compound 3k $^{13}$C NMR
Compound 3l $^1$H NMR

Compound 3l $^{13}$C NMR
Compound 3m $^1$H NMR

Compound 3m $^{13}$C NMR
Compound 3o $^1$H NMR

Compound 3o $^{13}$C NMR
Compound 3p $^1$H NMR

Compound 3p $^{13}$C NMR
Compound 3q $^1$H NMR

Compound 3q $^{13}$C NMR
Compound 3r $^1$H NMR

Compound 3r $^{13}$C NMR
Compound 3s $^1$H NMR

Compound 3s $^{13}$C NMR
Compound 3t $^1$H NMR

Compound 3t $^{13}$C NMR
Compound 3u $^1$H NMR

Compound 3u $^{13}$C NMR
Compound 3v $^1$H NMR

Compound 3v $^{13}$C NMR
Compound 3x $^1$H NMR

Compound 3x $^{13}$C NMR
Compound 3y $^1$H NMR

Compound 3y $^{13}$C NMR
Compound 4a $^1$H NMR

Compound 4a $^{13}$C NMR
Compound 4b $^1$H NMR

Compound 4b $^{13}$C NMR
Compound 4d $^1\text{H}$ NMR

Compound 4d $^{13}\text{C}$ NMR
Compound 4e $^1$H NMR

Compound 4e $^{13}$C NMR
Compound 4g $^1$H NMR

Compound 4g $^{13}$C NMR
Compound 4i $^1$H NMR

Compound 4i $^{13}$C NMR
7. X-ray crystal structure

Table 1 Crystal data and structure refinement for 3w

<table>
<thead>
<tr>
<th>Identification code</th>
<th>20190496</th>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C_{22}H_{25}BrO_{6}</td>
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<tr>
<td>Formula weight/K</td>
<td>465.33</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<td>Space group</td>
<td>P2_1/n</td>
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<td>a/Å</td>
<td>6.04519(13)</td>
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<tr>
<td>b/Å</td>
<td>20.9360(4)</td>
</tr>
<tr>
<td>c/Å</td>
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<td>α/°</td>
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</tr>
<tr>
<td>β/°</td>
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<tr>
<td>γ/°</td>
<td>90</td>
</tr>
<tr>
<td>Volume/Å³</td>
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<tr>
<td>Z</td>
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<tr>
<td>( \rho_{\text{calc}} )/g/cm³</td>
<td>1.368</td>
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<tr>
<td>μ/mm⁻¹</td>
<td>2.765</td>
</tr>
<tr>
<td>F(000)</td>
<td>960.0</td>
</tr>
<tr>
<td>Crystal size/mm³</td>
<td>0.19 × 0.14 × 0.13</td>
</tr>
<tr>
<td>Radiation</td>
<td>CuKα (( \lambda = 1.54184 ))</td>
</tr>
<tr>
<td>2θ range for data collection/°</td>
<td>8.446 to 134.14</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-5 ≤ h ≤ 7, -24 ≤ k ≤ 25, -21 ≤ l ≤ 21</td>
</tr>
</tbody>
</table>
Reflections collected: 8982
Independent reflections: 4030 [R_{int} = 0.0284, R_{sigma} = 0.0359]
Data/restraints/parameters: 4030/29/293
Goodness-of-fit on F^2: 1.032
Final R indexes [I>=2σ (I)]: R_1 = 0.0588, wR_2 = 0.1584
Final R indexes [all data]: R_1 = 0.0708, wR_2 = 0.1732
Largest diff. peak/hole / e Å^3: 1.03/-0.68

^1H and ^13C NMR Spectral Data of 4a

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<tr>
<th>Position</th>
<th>^1H NMR (300 MHz)</th>
<th>^13C NMR (75 MHz)</th>
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</thead>
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<tr>
<td>1</td>
<td>1.13 (d, J = 7.3 Hz, 3H, CH₃) ppm</td>
<td>14.0 ppm</td>
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<tr>
<td>2</td>
<td>3.52 – 3.54 (m, 1H, CH) ppm</td>
<td>46.6 ppm</td>
</tr>
<tr>
<td>3</td>
<td>6.82 (s, 1H, CH=C) ppm</td>
<td>147.1 ppm</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>131.9 ppm</td>
</tr>
<tr>
<td>5</td>
<td>5.19 (q, J = 12.5 Hz, 2H, COOCH₂Ph) ppm</td>
<td>65.4 ppm</td>
</tr>
<tr>
<td>6</td>
<td>4.57 (s, 1H, CH)</td>
<td>56.8 ppm</td>
</tr>
<tr>
<td>7</td>
<td>3.86 – 3.94 (m, 2H, COOCH₂) ppm</td>
<td>59.9 ppm</td>
</tr>
<tr>
<td>8</td>
<td>0.99 (t, J = 7.1 Hz, 3H, CH₃) ppm</td>
<td>13.1 ppm</td>
</tr>
<tr>
<td>9</td>
<td>60.8 ppm</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
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</tr>
<tr>
<td>10</td>
<td>3.75 (s, 3H, COOCH$_3$) ppm</td>
<td>51.3 ppm</td>
</tr>
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<td>11</td>
<td>6.35 (d, $J = 16.4$ Hz, 1H, C=CH) ppm</td>
<td>126.9 ppm</td>
</tr>
<tr>
<td>12</td>
<td>6.45 (d, $J = 16.4$ Hz, 1H, CH=C) ppm</td>
<td>135.6 ppm</td>
</tr>
</tbody>
</table>