EXPERIMENTAL

Melting Points: All melting points were recorded on a Superfit (India) capillary melting point apparatus and are uncorrected.

Boiling Points: Boiling points refer to the temperature measured using short path distillation units and are uncorrected.

Elemental Analyses: Elemental analyses were performed on a Perkin–Elmer 240C-CHN analyzer.

Infrared Spectra: Infrared spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. All the spectra were calibrated against polystyrene absorption at 1601 cm$^{-1}$. Solid samples were recorded as KBr wafers and liquid samples as thin film between NaCl plates or solution spectra in CH$_2$Cl$_2$.

Nuclear Magnetic Resonance Spectra: Proton magnetic resonance spectra and carbon-13 magnetic resonance spectra were recorded on a BRUKER-AC-200 spectrometer. $^1$H NMR (200 MHz) spectra for all the samples were measured in chloroform-d, unless otherwise mentioned, with TMS (5 = 0 ppm) as internal standard. $^{13}$C NMR (50 MHz) spectra for all the samples were measured in chloroform-d, unless
otherwise mentioned, with its middle peak of the triplet (8 = \textbf{77.10 ppm}) as internal standard. Spectral assignments are as follows: (1) chemical shifts on the $\delta$ scale, (2) standard abbreviation for multiplicity, that is, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ABq = AB quartet, d of ABq = doublet of AB quartet, b = broad, (3) number of hydrogens integrated for the signal, (4) coupling constant J in Hertz.

Mass \textbf{Spectral Analyses}: Mass spectra were recorded either on VG7070H mass spectrometer using EI technique or on Auto spec mass spectrometer using LSIMS technique (FAB).

\textbf{Optical Rotations}: Optical rotations were measured on JASCO DIP 370 digital polarimeter at the wavelength of the sodium D-line (589 nm) at ambient temperature.

\textbf{Chromatography}: Analytical Thin Layer Chromatography (TLC) was performed on glass plates (7 x 2 cm) coated with Acme's silica gel GF 254 (254 m$\mu$) containing 13% calcium sulfate as a binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using Acme's silica gel (100-200 mesh). High-pressure liquid chromatography (HPLC) analysis was carried out on Shimadzu LC-10AD Chromatopac equipped with SPD-10A UV-VIS detector using HPLC grade solvents.
**General:** All the solvents were dried and distilled using suitable drying agents before use. Moisture sensitive reactions were carried out using standard syringe-septum techniques under nitrogen atmosphere. All reactions were monitored using Thin Layer Chromatography (TLC).
Methyl 2-(hydroxymethyl)prop-2-enoate (100a):

This molecule was prepared according to the procedure developed in our laboratory. A mixture of paraformaldehyde (200 mmol, 6.006 g), aqueous trimethylamine (30%, w/v) (240 mmol, 47.28 mL) and methyl acrylate (400 mmol, 34.4 g) was heated at 60 °C for 6 h. The reaction mixture was then cooled to room temperature. Organic layer was separated and the aqueous layer was extracted with ether (2x25 mL). The combined organic layer was dried over anhydrous sodium sulfate (Na$_2$SO$_4$). Solvent was evaporated and the crude product thus obtained, was distilled under reduced pressure to afford the desired product 100a, as colorless oil, in 50% (11.5 g) yield.

Bp.: 84-85 °C/4 mm (lit. 71-72 °C/2 mm)
IR (Neat): ν 3431, 1720, 1637 cm$^{-1}$
$^1$H NMR: δ 2.28 (b, 1H), 3.79 (s, 3H), 4.33 (s, 2H), 5.84 (s, 1H), 6.26 (s, 1H)
$^{13}$C NMR: 51.65, 51.55, 125.22, 139.46, 166.65

Ethyl 2-(hydroxymethyl)prop-2-enoate (100b):

This was obtained via the treatment of paraformaldehyde with ethyl acrylate in the presence of aqueous trimethylamine (30%, w/v), following a similar procedure described for the molecule 100a, as a colorless liquid.
Yield: 62%

Bp.: 84-87 °C/2.5 mm (lit. \(^{198}\) 65-70 °C/1 mm)

**IR (Neat):** \(\nu\) 3410, 1712, 1639 cm\(^{-1}\)

**\(^1\)H NMR:** 6 \(1.32 (t, 3H, J = 6.8 \text{ Hz}), 2.24 (b, 1H), 4.25 (q, 2H, J = 6.8 \text{ Hz}), 4.33 (s, 2H), 5.82 (s, 1H), 6.25 (s, 1H)\)

**\(^{13}\)C NMR:** \(\delta\) 13.95, 60.69, 61.67, 124.97, 139.75, 166.27

**Butyl 2-(hydroxymethyl)prop-2-enoate (100c):**

This was prepared *via* the reaction of paraformaldehyde with butyl acrylate under the influence of aqueous *trimethylamine* (30%, w/v), following a similar procedure described for the molecule 100a, as a colorless liquid.

Yield: 65%

Bp.: 69-71 °C/0.2 mm (lit. \(^{79}\) 80 °C/0.5 mm)

**IR (Neat):** \(\nu\) 3420, 1712, 1637 cm\(^{-1}\)

**\(^1\)H NMR:** \(\delta\) 0.94 (t, 3H, \(J=7.4\) Hz), 1.30-1.52 (m, 2H), 1.57-1.78 (m, 2H), 2.32 (b, 1H), 4.18 (t, 2H, \(J=6.8\) Hz), 4.32 (s, 2H), 5.81 (s, 1H), 6.24 (s, 1H)

**\(^{13}\)C NMR:** \(\delta\) 13.51, 19.05, 30.49, 61.79, 64.57, 124.92, 139.76, 166.30
Methyl 2-(bromomethyl)prop-2-enoate (101a):

This molecule was prepared according to the literature procedure. To a stirred solution of methyl 2-(hydroxymethyl)prop-2-enoate (100a) (30 mmol, 3.48 g) in benzene (25 mL) was added PBr₃ (75 mmol, 20.3 g) drop wise at room temperature. After stirring 12 h at room temperature, the reaction mixture was carefully poured into ice-cold water and extracted with ether (3x20 mL). The combined organic layer was washed with water, saturated aqueous NaHCO₃ solution and water successively and was dried over anhydrous Na₂SO₄. Solvent was evaporated and the residue thus obtained, was purified by column chromatography (silica gel, 2% EtOAc in hexanes) followed by distillation under reduced pressure to provide the desired product 101a, as a colorless liquid, in 85% (4.55 g) yield.

Bp.: 47-48 °C/3.7 mm (lit. 277 °C, 35-37 °C/1.3 mm)

IR (Neat): v 1728, 1631 cm⁻¹

¹H NMR: 8 3.82 (s, 3H), 4.18 (s, 2H), 5.96 (s, 1H), 6.34 (s, 1H)

¹³C NMR: 8 29.16, 52.16, 129.06, 137.33, 165.20

Ethyl 2-(bromomethyl)prop-2-enoate (101b):

The treatment of ethyl 2-(hydroxymethyl)prop-2-enoate (100b) with PBr₃, following a similar procedure described for the molecule 101a, afforded the desired compound 101b, as a colorless liquid.
Butyl 2-(bromomethyl)prop-2-enoate (101c):

This was prepared via the reaction of butyl 2-(hydroxymethyl)prop-2-enoate (100c) with PBr₃, following a similar procedure described for the molecule 101a, as a colorless liquid.

Yield: 91%

Bp.: 67-68 °C/0.6 mm

IR (Neat): ν 1724, 1631 cm⁻¹

H NMR: δ 0.95 (t, 3H, J = 7.4 Hz), 1.32-1.57 (m, 2H), 1.59-1.81 (m, 2H), 4.18 (s, 2H), 4.22 (t, 2H, J = 6.4 Hz), 5.94 (s, 1H), 6.33 (s, 1H)

¹³C NMR: 6 13.62, 19.12, 29.28, 30.55, 65.07, 128.77, 137.62, 164.81
Methyl 2,4-dimethylidene-5-oxohexanoate (102):

A solution of methyl 2-(bromomethyl)prop-2-enoate (101a) (1 mmol, 0.179 g) and DABCO (2 mmol, 0.224 g) in methyl vinyl ketone (1 mL) was kept at room temperature for 15 minutes. The reaction mixture was diluted with ether (15 mL) and washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide pure methyl 2,4-dimethylidene-5-oxohexanoate (102), as a colorless liquid.

Yield: 82% (0.138 g)

IR(Neat): $\nu$ 1722, 1680, 1631 cm$^{-1}$

$^1$H NMR: 5 2.35 (s, 3H), 3.29 (s, 2H), 3.74 (s, 3H), 5.57 (s, 1H), 5.81 (s, 1H), 6.10 (s, 1H), 6.24 (s, 1H)

$^{13}$C NMR: 5 25.49, 32.35, 51.56, 126.28, 126.62, 137.91, 146.15, 166.84, 198.34

MS (m/z): 168 (M$^+$)

Analysis calcld. for C$_9$H$_{12}$O$_3$: C, 64.27; H, 7.19

Found: C, 64.42; H, 7.21
Ethyl 2,4-dimethylidene-5-oxohexanoate (103):

The treatment of ethyl 2-(bromomethyl)prop-2-enoate (101b) with methyl vinyl ketone, under the influence of DABCO, following a similar procedure described for the molecule 102, provided the desired product 103, as a colorless liquid.

Yield: 78%

IR (Neat): ν 1718, 1680, 1631 cm⁻¹

¹H NMR: δ 1.28 (t, 3H, J = 7.0 Hz), 2.35 (s, 3H), 3.29 (s, 2H), 4.19 (q, 2H, J = 7.0 Hz), 5.55 (d, 1H, J = 1.4 Hz), 5.81 (s, 1H), 6.10 (s, 1H), 6.24 (s, 1H)

¹³C NMR: δ 13.96, 25.55, 32.37, 60.51, 126.25, 126.41, 138.25, 146.30, 166.43, 198.41

Analysis calcd. for C₁₀H₁₄O₃: C, 65.92; H, 7.74

Found: C, 65.69; H, 7.70

Butyl 2,4-dimethylidene-5-oxohexanoate (104):

This product was isolated as a colorless liquid via the reaction of butyl 2-(bromomethyl)prop-2-enoate (101c) with methyl vinyl ketone, in the presence of DABCO, following a similar procedure described for the molecule 102.

Yield: 84%

IR (Neat): ν 1718, 1680, 1631 cm⁻¹
$^1$H NMR: 6 0.93 (t, 3H, $J = 7.1$ Hz), 1.24-1.50 (m, 2H), 1.53-1.73 (m, 2H), 2.34 (s, 3H), 3.29 (s, 2H), 4.13 (t, 2H, $J = 6.8$ Hz), 5.55 (d, 1H, $J = 2.0$ Hz), 5.80 (d, 1H, $J = 1.6$ Hz), 6.10 (s, 1H), 6.24 (s, 1H)

$^{13}$C NMR: 5 13.47, 19.04, 25.55, 30.55, 32.45, 64.45, 126.06, 126.41, 138.34, 146.44, 166.53, 198.35

Analysis calcd. for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63

Found: C, 68.29; H, 8.68

Methyl 2,4-dimethylidene-5-oxoheptanoate (105):

This was prepared via the treatment of methyl 2-(bromomethyl)prop-2-enolate (101a) with ethyl vinyl ketone, under the influence of DABCO, following a similar procedure described for the molecule 102, as a colorless liquid.

Yield: 77%

IR (Neat): $\nu$ 1724, 1680, 1631 cm$^{-1}$

$^1$H NMR: 8 1.10 (t, 3H, $J = 7.2$ Hz), 2.72 (q, 2H, $J = 7.2$ Hz), 3.31 (s, 2H), 3.74 (s, 3H), 5.57 (d, 1H, $J = 12$ Hz), 5.75 (d, 1H, $J = 12$ Hz), 6.09 (s, 1H), 6.23 (s, 1H)

$^{13}$C NMR: $\delta$ 8.14, 30.69, 32.75, 51.64, 125.02, 126.70, 137.98, 145.67, 166.93, 201.17

Analysis calcd. for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74
Found: C, 66.22; H, 7.71

2-[2-(Butoxycarbonyl)prop-2-en-1-yl]cyclohex-2-en-1-one (106):

A solution of butyl 2-(bromomethyl)prop-2-enoate (101c) (1 mmol, 0.221 g) and DBU (2 mmol, 0.304 g) in cyclohex-2-enone (1 mL) was kept at room temperature for 1h. The reaction mixture was diluted with ether (15 mL) and washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide the pure 2-[2-(butoxycarbonyl)prop-2-en-1-yl]cyclohex-2-en-1-one (106), as colorless liquid.

Yield: 80% (0.189 g)

IR (Neat): ν 1718, 1676, 1631 cm⁻¹

¹H NMR: δ 0.93 (t, 3H, J = 7.2 Hz), 1.24-1.52 (m, 2H), 1.54-1.75 (m, 2H), 1.90-2.10 (m, 2H), 2.28-2.51 (m, 4H), 3.22 (s, 2H), 4.13 (t, 2H, J = 6.5 Hz), 5.55 (s, 1H), 6.21 (s, 1H), 6.75 (t, 1H, J = 4.2 Hz)

¹³C NMR: δ 13.48, 19.01, 22.88, 25.93, 30.50, 31.15, 38.25, 64.31, 126.20, 136.95, 138.38, 146.46, 166.68, 198.12

MS (m/z): 236 (M⁺)

Analysis calcd. for C₁₄H₂₀O₃: C, 71.16; H, 8.53

Found: C, 71.30; H, 8.50
Methyl 2-methylidene-4-cyanopent-4-enoate (107):

A solution of methyl 2-(bromomethyl)prop-2-enoate (101a) (1 mmol, 0.179 g) and DABCO (2 mmol, 0.224 g) in acrylonitrile (1 mL) was kept at room temperature for 4 h. The reaction mixture was diluted with ether (15 mL) and washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product thus obtained was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide the pure methyl 2-methylidene-4-cyanopent-4-enoate (107), as colorless liquid.

Yield: 81% (0.122 g)

IR (Neat): ν 2226, 1722, 1635 cm$^{-1}$

$^1$H NMR: δ 3.25 (s, 2H), 3.77 (s, 3H), 5.77 (s, 1H), 5.83 (s, 1H), 5.96 (s, 1H), 6.39 (s, 1H)

$^{13}$C NMR: δ 36.47, 51.85, 117.84, 120.31, 128.21, 132.07, 135.28, 165.97

Analysis calcd. for C$_8$H$_9$NO$_2$: C, 63.57; H, 6.00; N, 9.27

Found: C, 63.78; H, 6.05; N, 9.31

Ethyl 2-methylidene-4-cyanopent-4-enoate (108):

The treatment of ethyl 2-(bromomethyl)prop-2-enoate (101b) with acrylonitrile, under the influence of DABCO, following a similar procedure described for the molecule 107, afforded the desired compound 108, as a colorless liquid.
Yield: 83%

IR (Neat): \( \nu 2226, 1718, 1633 \text{ cm}^{-1} \)

HNMR: \( \delta 1.31 (t, 3H, J = 7.3 \text{ Hz}), 3.25 (s, 2H), 4.22 (q, 2H, J = 7.3 \text{ Hz}), 5.75 (s, 1H), 5.83 (s, 1H), 5.96 (s, 1H), 6.38 (s, 1H) \)

\( ^{13}C \) NMR: \( \delta 13.92, 36.49, 60.92, 117.92, 120.38, 128.02, 132.08, 135.51, 165.51 \)

Analysis calcd. for \( C_9H_{11}NO_2 \): C, 65.44; H, 6.71; N, 8.48

Found: C, 65.17; H, 6.67; N, 8.53

Butyl 2-methylidene-4-cyanopent-4-enoate (109):

This was obtained as a colorless liquid via the reaction of butyl 2-(bromomethyl)prop-2-enoate (101c) with acrylonitrile, in the presence of DABCO, following a similar procedure described for the molecule 107.

Yield: 85%

IR (Neat): \( \nu 2226, 1718, 1633 \text{ cm}^{-1} \)

HNMR: \( \delta 0.94 (t, 3H, 7.3 \text{ Hz}), 1.24-1.52 (m, 2H), 1.54-1.77 (m, 2H), 3.25 (s, 2H), 4.17 (t, 2H, J = 6.9 \text{ Hz}), 5.75 (s, 1H), 5.83 (s, 1H), 5.96 (s, 1H), 6.38(s, 1H) \)
\[ ^{13}\text{C NMR}: \quad 8 \quad 13.47, 19.04, 30.50, 36.57, 64.85, 117.91, 120.54, 127.98, 131.93, 135.62, 165.61 \]

\[ \text{MS (m/z):} \quad 193 \quad (M^+) \]

Analysis calcd. for C\textsubscript{11}H\textsubscript{15}NO\textsubscript{2}: \quad C, 68.37; H, 7.82; N, 7.25

Found: \quad C, 68.13; H, 7.86; N, 7.19

**2,4-Di(methoxycarbonyl)penta-1,4-diene (110):**

A solution of methyl 2-(bromomethyl)prop-2-enoate (101a) (1 mmol, 0.179 g) and DABCO (2 mmol, 0.224 g) in methyl acrylate (1 mL) was kept at room temperature for 7 days. The reaction mixture was diluted with ether (15 mL) and washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide pure 2,4-di(methoxycarbonyl)penta-1,4-diene (110), as colorless liquid.

Yield: \quad 80\% (0.147 g)

\[ \text{IR(Neat):} \quad \nu \quad 1724, 1631 \text{ cm}^{-1} \]

\[ ^{1}\text{H NMR:} \quad 8 \quad 3.33 \text{ (s, 2H)}, 3.74 \text{ (s, 6H)}, 5.60 \text{ (s, 2H)}, 6.25 \text{ (s, 2H)} \]

\[ ^{13}\text{C NMR:} \quad 8 \quad 33.65, 51.69, 126.61, 137.69, 166.85 \]

Analysis calcd. for C\textsubscript{9}H\textsubscript{12}O\textsubscript{4}: \quad C, 58.69; H, 6.57

Found: \quad C, 58.88; H, 6.50
2-Ethoxycarbonyl-4-methoxycarbonylpenta-1,4-diene (111):  
This was prepared via the treatment of ethyl 2-(bromomethyl)prop-2-enoate (101b) with methyl acrylate, under the influence of DABCO, following a similar procedure described for the molecule 110, as a colorless liquid.  
Yield: 84%  
IR(Neat): ν 1722, 1631 cm⁻¹  
¹H NMR: δ 1.28 (t, 3H, J = 7.3 Hz), 3.33 (s, 2H), 3.75 (s, 3H), 4.20 (q, 2H, J = 7.3 Hz), 5.56-5.66 (m, 2H), 6.25 (s, 2H)  
¹³C NMR: 6 14.03, 33.68, 51.73, 60.64, 126.38, 126.62, 137.83, 138.04, 166.42, 166.94  
Analysis calcd. for C₁₀H₁₄O₄: C, 60.59; H, 7.12  
Found: C, 60.42; H, 7.15  

2-(Butoxycarbonyl)-4-methoxycarbonylpenta-1,4-diene (112):  
This compound was isolated as a colorless liquid via the reaction of butyl 2-(bromomethyl)prop-2-enoate (101c) with methyl acrylate, in the presence of DABCO, following a similar procedure described for the molecule 110.  
Yield: 85%  
IR(Neat): ν 1722, 1631 cm⁻¹
\[^{1}\text{H NMR:}\]
\[
\begin{align*}
8 & 0.94 \text{ (t, 3H, } J = 7.0 \text{ Hz), 1.24-1.52 (m, 2H), 1.54-1.75 (m, 2H),} \\
& 3.33 \text{ (s, 2H), 3.75 (s, 3H), 4.15 (t, 2H, } J = 6.4 \text{ Hz), 5.59 (m, 2H),} \\
& 6.26 \text{ (s, 2H)}
\end{align*}
\]

\[^{13}\text{C NMR:}\]
\[
\begin{align*}
8 & 13.51, 19.06, 30.55, 33.66, 51.67, 64.50, 126.32, 126.49, \\
& 137.84, 138.06, 166.45, 166.88
\end{align*}
\]

\[^{13}\text{C NMR:}\]
\[
\begin{align*}
\text{MS (m/z):} & 226 (M^+ )
\end{align*}
\]

Analysis calcd for C\(^{12}\)H\(^{18}\)O\(_4\):  C, 63.70;  H, 8.02

Found:  C, 63.62;  H, 8.04

2-Ethoxycarbonyl-4-methoxycarboonylpenta-1,4-diene (111):

The treatment of methyl 2-(bromomethyl)prop-2-enoate (101a) with ethyl acrylate, under the influence of DABCO, following a similar procedure described for the molecule 110, provided the desired compound 111, as a colorless liquid, in 81% yield.

Spectral data (IR, \(^{1}\text{H and } ^{13}\text{C NMR}) of this molecule are identical with that of the molecule prepared from ethyl 2-(bromomethyl)prop-2-enoate (101b) and methyl acrylate.

2,4-Di(ethoxycarbonyl)penta-1,4-diene (113):

This was obtained as a colorless liquid via the treatment of ethyl 2-(bromomethyl)prop-2-enoate (101b) with ethyl acrylate, under the influence of DABCO, following a similar procedure described for the molecule 110.
Yield: 82%

IR(Neat): v 1720, 1631 cm⁻¹

¹H NMR: 8 1.28 (t, 6H, J = 7.2 Hz), 3.33 (s, 2H), 4.20 (q, 4H, J = 12 Hz), 5.57 (s, 2H), 6.24 (s, 2H)

¹³C NMR: 8 14.02, 33.64, 60.60, 126.29, 138.13, 166.44

Analysis calcd. for C₁₁H₁₆O₄: C, 62.25; H, 7.60

Found: C, 62.48; H, 7.56

2-(Butoxycarbonyl)-4-ethoxycarbonylpenta-1,4-diene (114):

This was prepared via the treatment of butyl 2-(bromomethyl)prop-2-enoate (101c) with ethyl acrylate, in the presence of DABCO, following a similar procedure described for the molecule 110, as a colorless liquid.

Yield: 78%

IR (Neat): v 1720, 1633 cm⁻¹

¹H NMR: 8 0.93 (t, 3H, J = 7.3 Hz), 1.20-1.52 (m, 5H), 1.54-1.76 (m, 2H), 3.33 (s, 2H), 4.09-4.29 (m, 4H), 5.58 (s, 2H), 6.25 (s, 2H)

¹³C NMR: 8 13.56, 14.06, 19.11, 30.60, 33.69, 60.63, 64.54, 126.31, 138.18, 166.47, 166.53

Analysis calcd for C₁₃H₂₀O₄: C, 64.98; H, 8.39

Found: C, 65.14; H, 8.35
Methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a):

A mixture of benzaldehyde (130a) (50 mmol, 5.306 g), methyl acrylate (75 mmol, 6.456 g) and DABCO (15 mol%, 7.5 mmol, 0.841 g) was kept at room temperature for 7 days. The reaction mixture was diluted with ether (50 mL) and washed successively with 2N HCl solution, water and saturated NaHCO₃ solution. The ethereal layer was dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained, was distilled under reduced pressure, to afford the desired product 131a, as a colorless liquid.

Yield: 85% (8.112 g)

Bp.: 121-122 °C/2.4 mm

IR(Neat): v 3470, 1716, 1630 cm⁻¹

¹H NMR: δ 3.02 (d, 1H, J = 5.2 Hz), 3.73 (s, 3H), 5.57 (d, 1H, J = 5.2 Hz), 5.83 (s, 1H), 6.34 (s, 1H), 7.21-7.53 (m, 5H)

¹³C NMR: 51.86, 72.90, 125.78, 126.72, 127.78, 128.39, 141.50, 142.27, 166.74

Methyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (131b):

It was obtained as a colorless liquid via the reaction of 4-methylbenzaldehyde (130b) with methyl acrylate in the presence of a catalytic amount of DABCO, following the similar procedure described for the molecule O1a.
Reaction time: 8 days

Yield: 85%

Bp.: 135-136 °C/2.3 mm

IR (Neat): ν 3439, 1722, 1630 cm⁻¹

**¹H NMR:**

6.2.34 (s, 3H), 2.89 (d, 1H, J = 5.0 Hz), 3.72 (s, 3H), 5.54 (d, 1H, J = 5.0 Hz), 5.85 (s, 1H), 6.32 (s, 1H), 7.15 (d, 2H, J = 8.0 Hz), 7.27 (d, 2H, J = 8.0 Hz)

**¹³C NMR:** 6 21.11, 51.77, 72.68, 125.41, 126.09, 126.72, 137.39, 138.66, 142.44, 166.75

**Methyl 3-(4-ethylphenyl)-3-hydroxy-2-methylene-propanoate (131c):**

This compound was prepared via the coupling of 4-ethylbenzaldehyde (130c) with methyl acrylate in the presence of DABCO (cat.), following a similar procedure described for the molecule 131a, as a colorless viscous liquid.

**Reaction time:** 7 days

**Yield:** 77%

**Bp.:** 152-154 °C/4.8 mm

**IR (Neat):** ν 3462, 1722, 1630 cm⁻¹
Methyl 3-hydroxy-2-methylene-3-(2-methylphenyl)propanoate (131d):

The reaction of 2-methylbenzaldehyde (130d) with methyl acrylate in the presence of DABCO (cat.), following a similar procedure described for the molecule O1a, provided the desired compound 131d, as a colorless liquid.

**Reaction time:** 8 days  
**Yield:** 78%  
**Bp.:** 137-139 °C/4 mm  
**IR (Neat):** ν 3433, 1722, 1630 cm⁻¹  
**¹H NMR:** 8 2.33 (s, 3H), 2.82 (b, 1H), 3.77 (s, 3H), 5.61 (s, 1H), 5.82 (s, 1H), 6.32 (s, 1H), 7.09-7.30 (m, 3H), 7.37-7.49 (m, 1H)  
**¹³C NMR:** δ 19.04, 51.93, 69.08, 125.95, 126.13, 126.38, 127.76, 130.43, 135.72, 138.99, 141.97, 167.05
Methyl 3-hydroxy-3-(4-isopropylphenyl)-2-methylenepropanoate (131e):

This compound was isolated as a colorless viscous liquid via the reaction of 4-isopropylbenzaldehyde (130e) with methyl acrylate in the presence of DABCO (cat.), following a similar procedure described for the molecule 131a.

Reaction time: 7 days
Yield: 75%

Bp.: 160-161 °C/3 mm
IR (Neat): v 3466, 1722, 1630 cm\(^{-1}\)

\(^1\)H NMR: 8 1.24 (d, 6H, J = 7.0 Hz), 2.81-3.02 (m, 1H), 3.10 (b, 1H), 3.73 (s, 3H), 5.55 (d, 1H, J = 5.2 Hz), 5.85 (s, 1H), 6.33 (s, 1H), 7.20 (d, 2H, J = 8.6 Hz), 7.30 (d, 2H, J = 8.6 Hz)

\(^13\)C NMR: 5 23.97, 33.82, 51.81, 72.77, 125.51, 126.43, 126.72, 138.90, 142.39, 148.36, 166.65

Ethyl 3-hydroxy-2-methylene-3-phenylpropanoate (132a):

This product was prepared by the reaction between benzaldehyde (130a) and ethyl acrylate in the presence of catalytic amount of DABCO, following the similar procedure described for the molecule 131a, as colorless liquid.

Reaction time: 7 days
Yield: 80%
Ethyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (132b):

The treatment of 4-methylbenzaldehyde (130b) with ethyl acrylate in the presence of a catalytic amount of DABCO, following the similar procedure described for the molecule O1a, afforded the desired compound 132b, as a colorless liquid.

Reaction time: 8 days

Yield: 75%

Bp.: 130-133 °C/0.9 mm

IR (Neat): v 3466, 1716, 1630 cm⁻¹

¹H NMR: 8 1.25 (t, 3H, J = 7.6 Hz), 2.34 (s, 3H), 2.94 (d, 1H, J = 5.8 Hz), 4.17 (q, 2H, J = 7.6 Hz), 5.55 (d, 1H, J = 5.8 Hz), 5.82 (d, 1H, J = 2.0 Hz), 6.32 (s, 1H), 7.15 (d, 2H, J = 7.8 Hz), 7.27 (d, 2H, J = 7.8 Hz)
Methyl (2E)-2-(hydroxymethyl)-3-phenylprop-2-enoate (135a):

This molecule was prepared according to the procedure developed in our laboratory.\textsuperscript{215}

To a stirred solution of methyl 3-hydroxy-2-methylene-3-phenylpropanoate (O1a) (20 mmol, 3.84 g) and acetic anhydride (24 mmol, 2.45 g) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL), was added TMSOTf (11 mol%, 2.2 mmol, 0.489 g) at room temperature. The reaction mixture was stirred for 2 h, at room temperature. Then CH\textsubscript{2}Cl\textsubscript{2} was removed under reduced pressure and MeOH (40 mL) and K\textsubscript{2}CO\textsubscript{3} (60 mmol, 8.29 g) were added and the reaction mixture was stirred for 1 h at room temperature. Then the solvent MeOH was removed under reduced pressure and the residue was diluted with water (20 mL) and extracted with ether (3x20 mL). The combined organic layer was dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed under reduced pressure. The crude product thus obtained, was purified by column chromatography (silica gel, 8% EtOAc in hexanes) to provide the desired product 135a, as a colorless crystalline solid.

Yield: 60% (2.314 g)

Mp.: 56-58 °C (lit.\textsuperscript{215} 57-58 °C)

IR (KBr): v 3468, 1693, 1630 cm\textsuperscript{-1}

\textsuperscript{1}H NMR: 8 2.55 (t, 1H, J = 6.8 Hz), 3.87 (s, 3H), 4.49 (d, 2H, J = 6.8 Hz),

\textsuperscript{13}C NMR: 6 14.01, 21.07, 60.79, 72.78, 125.15, 126.70, 129.02, 137.31, 138.71, 142.69, 166.33
4-Methoxycarbonyl-1,3-dihydro-2-benzoxepine (133a):
[from methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a)]

To a stirred solution of methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a) (2 mmol, 0.384 g) and paraformaldehyde (2 mmol, 0.06 g) in CH₂Cl₂ (4 mL), was added drop wise conc. H₂SO₄ (2 mmol, 0.196 g) at room temperature. After stirring for 1 h at room temperature, the reaction mixture was diluted with water (4 mL) and extracted with ether (3×10 mL). The combined organic layer was washed with water, dried over anhydrous Na₂SO₄. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to furnish the title molecule 133a, as a colorless solid.

Yield: 60% (0.243 g)

Mp.: 46-48 °C

IR (KBr): ν 1714, 1633 cm⁻¹

¹H NMR: δ 3.81 (s, 3H), 4.69 (s, 2H), 4.80 (d, 2H, J= 1.4 Hz), 7.11-7.48 (m, 4H, aromatic), 7.72 (t, 1H, J= 1.4 Hz)

¹³C NMR: 52.10, 57.64, 128.56, 129.20, 129.63, 131.04, 134.58, 142.68, 168.43

7.31-7.54 (m, 5H), 7.84 (s, 1H)
$^{13}$C NMR: 5 51.82, 72.85, 73.88, 127.17, 127.88, 129.10, 132.45, 133.06, 133.35, 138.68, 141.13, 166.72

MS (m/z): 204 (M$^+$)

Analysis calcd. for C$_{12}$H$_{12}$O$_3$: C, 70.58; H, 5.92

Found: C, 70.45; H, 5.94

4-Methoxycarbonyl-1,3-dihydro-2-benzoxepine (133a):
[from methyl 3-hydroxy-2-methylene-3-phenylpropanoate (O1a) using methanesulfonic acid]

To a stirred solution of methyl 3-hydroxy-2-methylene-3-phenylpropanoate (O1a) (2 mmol, 0.384 g) and paraformaldehyde (2 mmol, 0.06 g) in CH$_2$Cl$_2$ (4 mL) was added methanesulfonic acid (6 mmol, 0.576 g) at room temperature. After stirring 1 h, at room temperature, the reaction mixture was diluted with water (4 mL), and extracted with ether (3×10 mL). The combined organic layer was washed with water and dried over anhydrous Na$_2$SO$_4$. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide the desired compound 133a, as a colorless solid.

Yield: 53% (0.218 g)

Mp.: 46-48 °C

Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are identical with that of the molecule prepared from methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a) and paraformaldehyde, under the influence of conc. H$_2$SO$_4$. 

![Diagram](image_url)
4-Methoxycarbonyl-8-methyl-1,3-dihydro-2-benzoxepine (133b):

This product was obtained by the reaction between methyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (131b) and paraformaldehyde in CH\textsubscript{2}Cl\textsubscript{2} in the presence of conc. H\textsubscript{2}SO\textsubscript{4}, following the similar procedure described for the molecule 133a, as a colorless solid.

Yield: 51%

Mp.: 58-60 °C

IR(KBr): \(\nu 1730, 1635 \text{ cm}^{-1}\)

\(\text{'H NMR: } \delta 2.34 (s, 3H), 3.80 (s, 3H), 4.66 (s, 2H), 4.78 (s, 2H), 6.97 (s, 1H), 7.11 (d, 1H, \text{J} = 7.6 \text{ Hz}), 7.31 (d, 1H, \text{J} = 7.6 \text{ Hz}), 7.69 (s, 1H)\)

\(\text{^13C NMR: } 21.06, 51.72, 72.85, 74.01, 128.01, 128.44, 130.29, 131.24, 133.49, 138.67, 139.49, 141.08, 166.84\)

\(\text{MS (m/z): } 218 (M^+)\)

Analysis calcd. for C\textsubscript{13}H\textsubscript{14}O\textsubscript{3}: C, 71.54; H, 6.47

Found: C, 71.75; H, 6.51

8-Ethyl-4-methoxycarbonyl-1,3-dihydro-2-benzoxepine (133c):

This molecule was prepared via the treatment of methyl 3-(4-ethylphenyl)-3-hydroxy-2-methylenepropanoate (131c) with paraformaldehyde in CH\textsubscript{2}Cl\textsubscript{2}, under the influence
of conc. H₂SO₄, as a colorless viscous liquid, following the similar procedure as
described for the molecule 133a.

Yield: 56%

IR (Neat): ν 1703, 1633 cm⁻¹

¹H NMR: 6 1.22 (t, 3H, J = 7.8 Hz), 2.64 (q, 2H, J = 7.8 Hz), 3.80 (s, 3H),
4.67 (s, 2H), 4.78 (d, 2H, J = 14 Hz)), 6.98 (s, 1H), 7.16 (d, 1H,
J = 7.8 Hz), 7.33 (d, 1H, J = 7.8 Hz), 7.69 (s, 1H, J = 14 Hz)

¹³C NMR: δ 15.04, 28.53, 51.71, 72.85, 74.16, 126.90, 127.27, 130.70,
131.45, 133.62, 138.76, 141.28, 145.87, 166.92

Analysis calcd. for C₁₄H₁₆O₃: C, 72.39; H, 6.94

Found: C, 72.16; H, 6.91

4-Methoxycarbonyl-6-methyl-1,3-dihydro-2-benzoxepine (133d):

This compound was isolated as a colorless solid via the reaction between methyl 3-
hydroxy-2-methylene-3-(2-methylphenyl)propanoate (Old) and paraformaldehyde in
CH₂Cl₂ in the presence of conc. H₂SO₄, following the similar procedure described for
the molecule 133a.

Yield: 48%

Mp.: 59-60 °C

IR (KBr): ν 1707, 1635 cm⁻¹
8-Isopropyl-4-methoxycarbonyl-1,3-dihydro-2-benzoxepine (133e):

The reaction of methyl 3-hydroxy-3-(4-isopropylphenyl)-2-methylenepropanoate (131e) with paraformaldehyde in CH$_2$Cl$_2$ in the presence of conc. H$_2$SO$_4$, following the similar procedure described for the molecule 133a, afforded the desired product 133e, as a colorless solid.

Yield: 44%

Mp.: 57-59 °C

IR (KBr): $\nu$ 1693, 1630 cm$^{-1}$

$^1$H NMR: $\delta$ 1.23 (d, 6H, $J=6.8$ Hz), 2.90 (sept, 1H, $J=6.8$ Hz), 3.80 (s, 3H), 4.68 (s, 2H), 4.79 (s, 2H), 7.01 (d, 1H, $J=2$ Hz), 7.16 (dd, 1H, $J=1.2$ & 7.8 Hz), 7.35 (d, 1H, $J=7.8$ Hz), 7.70 (s, 1H)
$^{13}$C NMR: 6 23.59, 33.83, 51.74, 72.89, 74.20, 125.51, 125.84, 130.71, 131.34, 133.63, 138.69, 141.16, 150.43, 166.89

Analysis calcd. for C$_{15}$H$_{18}$O$_3$: C, 73.15; H, 7.37

Found: C, 72.90; H, 7.42

4-Ethoxycarbonyl-1,3-dihydro-2-benzoxepine (134a):

This compound was obtained as a colorless solid via the reaction between ethyl 3-hydroxy-2-methylene-3-phenylpropanoate (132a) and paraformaldehyde in CH$_2$Cl$_2$ in the presence of conc. H$_2$SO$_4$, following the similar procedure described for the molecule 133a.

Yield: 61%

Mp: 36-39 °C

IR (KBr): v 1707, 1631 cm$^{-1}$

$^1$H NMR: δ 1.34 (t, 3H, $J = 6.8$ Hz), 4.26 (q, 2H, $J = 6.8$ Hz), 4.69 (s, 2H), 4.80 (d, 2H, $J= 1.4$ Hz), 7.09-7.48 (m, 4H), 7.71 (d, 1H, $J= 1.4$ Hz)

$^{13}$C NMR: 8 14.16, 60.77, 72.90, 73.87, 127.16, 127.86, 129.02, 132.74, 133.12, 133.30, 138.38, 141.10, 166.27

Analysis calcd. for C$_{13}$H$_{14}$O$_3$: C, 71.54; H, 6.47

Found: C, 71.40; H, 6.50
4-Ethoxycarbonyl-8-methyl-1,3-dihydro-2-benzoxepine (134b):

This product was prepared by the reaction between ethyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (132b) and paraformaldehyde in CH₂Cl₂ in the presence of conc. H₂SO₄, following the similar procedure described for the molecule 133a, as a colorless viscous liquid.

Yield: 56%

IK (Neat): ν 1699, 1633 cm⁻¹

¹H NMR: δ 1.33 (t, 3H, J = 7.0 Hz), 2.34 (s, 3H), 4.26 (q, 2H, J = 7.0 Hz), 4.66 (s, 2H), 4.78 (s, 2H), 6.97 (s, 1H), 7.15 (d, 1H, J = 7.6 Hz), 7.32 (d, 1H, J = 7.6 Hz), 7.68 (s, 1H)

¹³C NMR: δ 14.18, 21.07, 60.66, 72.89, 74.01, 128.01, 128.44, 130.38, 131.56, 133.46, 138.40, 139.40, 141.06, 166.41

Analysis calcd. for C₁₄H₁₆O₃: C, 72.39; H, 6.94

Found: C, 72.70; H, 6.86

4-Methoxycarbonyl-1,3-dihydro-2-benzoxepine (133a):

[from methyl (2E)-2-(hydroxymethyl)-3-phenylprop-2-enoate (135a)]

This compound was obtained as a colorless solid via the reaction between methyl (2E)-2-(hydroxymethyl)-3-phenylprop-2-enoate (135a) and paraformaldehyde in CH₂Cl₂ in the presence of conc. H₂SO₄, following the similar procedure described for preparation
of the molecule 133a, from methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a) and paraformaldehyde, under the influence of conc. H2SO4.

Reaction time: 1 h

Yield: 59% (0.24 g)

Mp.: 46-48 °C

Spectral data (IR, 1H and 13C NMR) of this molecule are in complete agreement with that of the molecule prepared from methyl 3-hydroxy-2-methylene-3-phenylpropanoate (131a) and paraformaldehyde, under the influence of conc. H2SO4.

(-)-Menthyl acrylate (14):

This molecule was prepared according to the literature procedure. 4

To a stirred solution of (-)-menthol (151) (100 mmol, 15.627 g), acryloyl chloride (150 mmol, 13.576 g) and 4-dimethylaminopyridine (15 mmol, 1.832 g) in anhydrous CH2Cl2 (100 mL), was added triethylamine (150 mmol, 15.167 g) drop wise at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was diluted with ether (100 mL) and washed successively with 2N HCl solution, water, saturated aqueous NaHCO3 solution and water. The ethereal layer was dried over anhydrous Na2SO4, concentrated and the crude product thus obtained, was distilled under reduced pressure to afford 14 as a colorless liquid.

Yield: 78% (16.42 g)
(-)-Menthyl 3-hydroxy-2-methylene-3-phenylpropanoate (152a):

A mixture of benzaldehyde (130a) (150 mmol, 15.9 g), (-)-menthyl acrylate (14) (50 mmol, 10.516 g) and DABCO (50 mmol, 5.609 g) was kept at room temperature for 8 days. The reaction mixture was diluted with ether (100 mL) and washed successively with 2N HCl solution, water and saturated aqueous NaHCO₃ solution. The ethereal layer was dried over anhydrous Na₂SO₄, concentrated and the crude product thus obtained, was purified by column chromatography (silica gel, 10% EtOAc in hexanes) to afford 152a, as a colorless solid.

Yield: 88% (13.924 g)

Mp.: 105-108°C
Optical rotation: $[\alpha]_D^{25} -117.46 (c \ 3.24, \text{CHCl}_3)$

IR (KBr): \( \nu 3312, \ 1712, \ 1639 \ \text{cm}^{-1} \)

$^1$H NMR: \( 5 \ \text{o} -2.01 \ (m, \ 18\text{H}, \ H_2' - H_{10'}) \), \( 3.01 \ (d, \ 1\text{H}, \ J = 6.0 \ \text{Hz}, \ \text{OH}), \ 4.71 \ (dt, \ 1\text{H}, \ J = 10.0 \ \text{Hz}, \ 4.2 \ \text{Hz}, \ H_1'), \ 5.54 \ (d, \ 1\text{H}, \ J = 6.0 \ \text{Hz}, \ H_3), \ 5.81 \ & \ 5.82 \ (2s, \ 1\text{H}, \ \text{diastereomeric Hb}), \ 6.33 \ (s, \ 1\text{H}, \ Ha), \ 7.25-7.46 \ (m, \ 5\text{H}, \ \text{aromatic}) \)

$^3$C NMR: \( 16.07, \ 20.78, \ 21.96, \ 23.31, \ 26.00, \ 31.38, \ 34.20, \ 40.76, \ 47.09, \ 73.32, \ 74.87, \ 125.32, \ 126.69, \ 127.73, \ 128.37, \ 141.56, \ 142.57, \ 165.95 \)

$(-)$-Menthyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (152b):

This product was prepared from 4-methylbenzaldehyde (130b), $(-)$-menthyl acrylate (14) and DABCO following the similar procedure described for the molecule 152a, as a colorless solid.

Reaction time: \( 10 \text{days} \)

Yield: \( 84\% \)

Mp.: \( 120-123^{\circ}\text{C} \)

Optical rotation: $[\alpha]_D^{25} -127.80 (c \ 1.64, \ \text{CHCl}_3)$

IR (KBr): \( \nu 3325, \ 1711, 1637 \ \text{cm}^{-1} \)
\(^1\)H NMR: 6 0.55-2.03 (m, 18H, H2'-H10'), 2.34 (s, 3H, CH₃), 2.89 (d, 1H, J = 5.2 Hz, OH), 4.71 (dt, 1H, J = 10.2 Hz, 4.4 Hz, H1'), 5.51 (d, 1H, /= 5.2 Hz, H3), 5.83 (s, 1H, Hb), 6.33 (s, 1H, Ha), 7.14 (d, 2H, J = 8.0 Hz), 7.24 (d, 2H, J = 8.0 Hz)

\(^3\)C NMR: 8 15.97, 20.75, 21.07, 21.95, 23.14, 25.80, 31.33, 34.13, 40.71, 46.99, 73.00, 74.68, 125.08, 126.64, 129.02, 137.32, 138.58, 142.54, 165.90

\((-\text{-Menthyl 3-(4-chlorophenyl)-3-hydroxy-2-methylene} \text{-propanoate (153):}\)

This compound was isolated as a colorless solid \textit{via} the reaction of 4-chlorobenzaldehyde (130g) with (-)-menthyl acrylate (14) in the presence of DABCO, following the similar procedure described for the molecule 152a.

Reaction time: 7 days

Yield: 87%

Mp.: 52-54 °C

Optical rotation: \([\alpha]_b^{25} = 56.13 (c 2.72, \text{CHCl}_3)\)

IR (KBr): \(\nu 3314, 1712, 1639 \text{ cm}^{-1}\)

\(^1\)H NMR: 5 0.56-2.08 (m, 18H, H2'-H10'), 3.03-3.23 (m, 1H, OH), 4.61-4.86 (m, 1H, H1'), 5.50 (d, 1H, J = 6.0 Hz, H3), 5.77 & 5.81 (2s,
1H, diastereomeric Hb), 6.33 (s, 1H, Ha), 7.21-7.51 (m, 4H, aromatic)

\(^{13}\)C NMR:  5 16.06, 16.22, 20.71, 21.96, 23.23, 23.37, 26.03, 26.21, 31.36,
(mixture of 34.13, 40.65, 40.71, 47.06, 72.70, 72.85, 75.03, 75.15, 125.65,
diastereomers)  127.90, 128.10, 128.49, 133.45, 133.54, 140.09, 142.15, 165.78

\((-\)-Menthyl (2Z)-2-(bromomethyl)-3-phenylprop-2-enoate (154a):

To a stirred solution of \((-\)-menthyl 3-hydroxy-2-methylene-3-phenylpropanoate (152a) (10 mmol, 3.163 g) in \(\text{CH}_2\text{Cl}_2\) (20 mL) was added drop wise HBr (48%, 25 mmol, 4.21 ml) followed by conc. \(\text{H}_2\text{SO}_4\) (10 mmol, 0.98 g) at 0 °C. After stirring for 12 h at room temperature, the reaction mixture was carefully poured into ice-cold water and extracted with ether (3x20 mL). The combined organic layer was washed with water and dried over anhydrous sodium sulfate (\(\text{Na}_2\text{SO}_4\)). Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 2% EtOAc ate in hexanes) to afford the desired compound 154a, as colorless viscous liquid.

Yield: 88% (3.353 g)

Optical rotation:  \([\alpha]_D^{25} = -80.34\ (c\ 3.17,\ \text{CHCl}_3)\)

IR (Neat): \(\nu 1709, 1626\ \text{cm}^{-1}\)
$^1$H NMR:  
8.08 (d, $J = 7.0$ Hz) & 0.89-2.19 (m) (18H, H2′-H10′), 4.40 (s, 2H, CH$_2$Br), 4.89 (dt, 1H, $J = 10.0$ Hz, 4.4 Hz, H1′), 7.29-7.64 (m, 5H, aromatic), 7.80 (s, 1H, H3)

$^{13}$C NMR:  
δ 16.40, 20.85, 22.06, 23.53, 26.37, 26.85, 31.49, 34.33, 40.90, 47.25, 75.49, 128.85, 129.45, 129.58, 134.48, 142.35, 165.63

(−)-Menthyl (2Z)-2-(bromomethyl)-3-(4-methylphenyl)prop-2-enolate (154b):

This compound was prepared by the reaction of (−)-menthyl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (152b) with HBr (48%) in the presence of conc. H$_2$SO$_4$, following the similar procedure described for the molecule 154a, as colorless viscous liquid.

Yield: 89%

Optical rotation:  
$[\alpha]_D^{25}$ −71.96 (c 2.64, CHCl$_3$)

IR (Neat):  
ν 1716, 1624 cm$^{-1}$

$^1$H NMR:  
8.08 (d, $J = 7.0$ Hz) & 0.88-2.21 (m) (18H, H2′-H10′), 2.39 (s, 3H, CH$_3$), 4.40 (s, 2H, CH$_2$Br), 4.87 (dt, 1H, $J = 10.8$ Hz, 4.6 Hz, H1′), 7.26 (d, 2H, $J = 8.0$ Hz, aromatic), 7.48 (d, 2H, J= 8.0 Hz, aromatic), 7.76 (s, 1H, H3)
\(^3\)C NMR: 8 16.38, 20.86, 21.47, 22.07, 23.50, 26.34, 27.24, 31.50, 34.34, 40.92, 47.24, 75.40, 128.51, 129.62, 129.82, 131.65, 139.87, 142.60, 165.82

\((-\)-Menthyl \(2Z\)-2-(bromomethyl)-3-(4-chlorophenyl)prop-2-enoate (155):

The treatment of \((-\)-menthyl 3-(4-chlorophenyl)-3-hydroxy-2-methylene propanoate (153) with HBr (48\%) and conc. H\(2\)SO\(4\), following the similar procedure described for the molecule 154a, afforded the desired compound 155, as a colorless viscous liquid.

Yield: 87\%

Optical rotation: \([\alpha]^{25}_D \sim -81.30 \) (c 2.30, CHCl\(_3\))

IR (Neat): \(v \) 1703, 1626 cm\(^{-1}\)

\(^1\)H NMR: 8 0.81 (d, \(J = 7.0 \) Hz) & 0.87-2.22 (m) (18H, H\(_2\)'-H\(_{10}\)'), 4.35 (s, 2H, CH\(_2\)Br), 4.89 (dt, 1H, \(J = 10.6 \) Hz, 4.4 Hz, H\(_1\)'), 7.37-7.62 (m, 4H, aromatic), 7.73 (s, 1H, H3)

\(^3\)C NMR: 8 16.34, 20.85, 22.05, 23.47, 26.35, 26.43, 31.48, 34.29, 40.87, 47.21, 75.67, 129.16, 130.03, 130.90, 132.88, 135.58, 140.94, 165.40
(-)-Methyl 2-methylene-3-(prop-2-yn-1-yloxy)-3-phenylpropanoate (156a):

To a stirred solution of (-)-menthyl (2Z)-2-(bromomethyl)-3-phenylprop-2-enoate (154a) (1 mmol, 0.379 g) and Et$_3$N (1 mL), was added propargyl alcohol (5 mmol, 0.28 g). After stirring for 12 h at room temperature, the reaction mixture was diluted with ether (15 mL), washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 2% EtOAc in hexanes) to provide pure (-)-menthyl 2-methylene-3-(prop-2-yn-1-yloxy)-3-phenylpropanoate (156a), as colorless viscous liquid.

Yield: 74% (0.261 g)  
de: 18%  
Optical rotation: [α]$^D_{25}$ -60.31 (c 4.15, CHCl$_3$)  
IR (Neat): ν 3308, 2130, 1712, 1631 cm$^{-1}$  
$^1$H NMR: 5 0.55-2.01 (m, 18H, H2’-H10’), 2.40-2.51 (m, 1H, H1’), 3.95-4.25 (m, 2H, CH$_2$C=), 4.58-4.79 (m, 1H, H1’), 5.46 & 5.50 (2s, 1H, diastereomeric H3), 5.91 & 6.00 (2d, 1H, J= 2.0 Hz, Hb), 6.31 & 6.41 (2s, 1H, Ha), 7.21-7.44 (m, 5H, aromatic)  

The underlined peaks are due to the minor diastereomer.
The two singlets at 6 6.31 & 6.41 are due to the p-vinyllic protons (Ha) (cis- to the ester group) of the minor and major diastereomers respectively. The diastereomeric excess was determined by the integration (41:59) of these two singlets and was found to be 18%.

\[ ^{13} \text{C NMR:} \]

\begin{align*}
8 & \quad 15.92, 16.33, 20.66, 20.90, 21.96, 23.09, 23.51, 25.67, 26.26, \\
(\text{mixture of} & \quad 31.34, 34.19, 40.54, 40.78, 47.04, 55.78, 74.55, 74.66, 77.73, \\
\text{diastereomers}) & \quad 77.84, 79.50, 124.33, 124.99, 127.89, 127.98, 128.11, 128.33, \\
& \quad 138.55, 140.83, 141.29, 165.11, 165.26
\end{align*}

The peaks at $\delta$ 165.11 and 165.26 are attributed to the carbonyl carbon of the major and minor diastereomers respectively.

Analysis calcd. for C$_{23}$H$_{30}$O$_3$: C, 77.93; H, 8.53

Found: C, 78.23; H, 8.44

\textit{(-)-Menthyl 2-methylene-3-(4-methylphenyl)-3-(prop-2-yn-1-yloxy)propanoate (156b):}

It was prepared \textit{via} the reaction of (-)-menthyl (2Z)-2-(bromomethyl)-3-(4-methylphenyl)prop-2-enoate (154b) with propargyl alcohol in the presence of triethylamine, following the similar procedure described for the molecule 156a, as a colorless viscous liquid.
Reaction time: 12h

Yield: 67%

de: 23%

Optical rotation: $[\alpha]_D^{25} -60.4 \text{ } (c \text{ } 3.00, \text{ CHCl}_3)$

IR (Neat): $\nu \text{ 3312, 2131, 1714, 1635 cm}^{-1}$

$^1$H NMR: 5 0.55-1.99 (m, 18H, H2'-H10'), 2.33 (s, 3H, CH$_3$), 2.41-2.49 (m, 1H, H1'), 3.94-4.24 (m, 2H, CH$_2$C≡C), 4.59-4.79 (m, 1H, H1'), 5.42 & 546 (2s, 1H, H3), 5.90 & 6.00 (2d, 1H, $J=2.0$ Hz, Hb), 629 & 6.39 (2s, 1H, Ha), 7.13 (d, 2H, $J=7.8$ Hz, aromatic), 7.23 (d, 2H, $J=7.8$ Hz, aromatic)

The underlined peaks arise due to the minor diastereomer.

The two singlets at 5 6.29 & 6.39 are arising from the olefinic (Ha) protons ($cis$- to the ester functionality) of the minor and major diastereomers respectively and are in the ratio of 38.5:61.5, indicating 23% diastereoselectivity in the reaction.

$^{13}$C NMR: 6 15.91, 16.34, 20.68, 20.86, 21.14, 21.98, 23.07, 23.51, 25.62, 26.23, 31.36, 34.21, 40.55, 40.81, 47.04, 55.61, 55.68, 74.48, 74.57, 77.64, 79.62, 124.06, 124.74, 127.85, 127.98, 129.03, 135.50, 137.80, 140.96, 141.49, 165.15, 165.35
The peaks at 6 165.15 and 165.35 are attributed to the carbonyl carbon of ester group of both major and minor diastereomers respectively.

Analysis calcd. for C24H32O3: C, 78.22; H, 8.75
Found: C, 78.00; H, 8.83

(−)-Menthyl 3-(4-chlorophenyl)-2-methylene-3-(prop-2-yn-1-yloxy)propanoate (157):

This product was isolated as a colorless viscous liquid via the reaction of (−)-menthyl (2Z)-2-(bromomethyl)-3-(4-chlorophenyl)prop-2-enoate (155) with propargyl alcohol in the presence of triethylamine, following the similar procedure described for the molecule 156a.

Reaction time: 12 h
Yield: 88%
de: 4%
Optical rotation: [α]D25 −36.45 (c 3.36, CHCl3)
IR (Neat): ν 3308, 2110, 1716, 1635 cm⁻¹

¹H NMR:
8 0.54-2.00 (m, 18H, 芳'HIO), 2.41-2.52 (m, 1H, HC≡C), 3.94-4.27 (m, 2H, CH₂C≡C), 4.56-4.81 (m, 1H, H1'), 5.43 & 5.47 (2s, 1H, diastereomeric H3), 5.94 & 6.02 (2s, 1H, Hb)
diastereomeric Hb), 6.31 & 6.41 (2s, 1H, diastereomeric Ha),
7.30 (s, 4H, aromatic)

The diastereomeric excess was determined by the integration of the two singlets at 8
6.31 & 6.41 (from two diastereomers) arising from the β-vinylic proton (Ha), cis- to the
ester functionality and was found to be 4%.

$^{13}$C NMR: $\delta$ 15.97, 16.37, 20.65, 20.83, 21.98, 23.13, 23.56, 25.81, 26.34,
(mixture of 31.38, 34.20, 40.62, 40.82, 47.12, 55.88, 74.75, 74.87, 74.95,
diastereomers) 77.10, 77.18, 79.27, 79.29, 124.57, 125.27, 128.50, 128.55,
129.25, 129.39, 133.89, 133.98, 137.36, 140.48, 140.96, 164.91,
165.10

The peaks at $\delta$ 164.91 and 165.10 are due to the carbonyl carbon of the major and
minor diastereomers respectively.

Analysis calcd. for C$_{23}$H$_{29}$O$_3$Cl: C, 71.03; H, 7.52
Found: C, 70.75; H, 7.40

(−)-Menthyl 2-methylene-3-phenoxy-3-phenylpropanoate (158a):

A solution of (−)-menthyl (2Z)-2-(bromomethyl)-3-phenylprop-2-enoate (154a) (1
mmol, 0.379 g), phenol (1 mmol, 0.094 g) and Et$_3$N (1 mL) in CH$_2$Cl$_2$ (2 mL), was
stirred at room temperature for 4 hours. Then 2N HCl (5 mL) was added and the
reaction mixture was extracted with ether (2×10 mL). The combined layer was washed
with aqueous NaHCO$_3$ solution, water and dried over anhydrous Na$_2$SO$_4$. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 2% EtOAc in hexanes) to provide pure (-)-menthyl 2-methylene-3-phenoxy-3-phenylpropanoate (158a), as colorless viscous liquid.

Yield: 72% (0.283 g)

de: 35%

Optical rotation: $[\alpha]_D^{25} = -76.16$ (c 5.00, CHCl$_3$)

IR (Neat): $\nu$ 1711, 1635 cm$^{-1}$

$^1$H NMR: $\delta$ 0.56-2.15 (m, 18H, H2'-H10'), 4.64-4.92 (m, 1H, H1'), 5.83 & 5.93 (2s, 1H, H3), 6.13 & 6.15 (2s, 1H, diastereomeric Hb), 6.32 & 6.40 (2s, 1H, Ha), 6.89-7.10 (m, 3H, aromatic), 7.18-7.61 (m, 7H, aromatic)

The underlined peaks are attributed to the minor diastereomer.

The two singlets at $\delta$ 5.83 & 5.93 are attributed to the benzylic (H3) protons of the minor and major diastereomers respectively. The diastereomeric excess was determined by the integration (32.5:67.5) of these two singlets and was found to be 35%.

$^{13}$C NMR: 8  16.09, 16.25, 20.68, 20.88, 22.02, 23.23, 23.45, 25.94, 26.25, (mixture of 31.42, 34.22, 40.71, 40.85, 47.13, 74.92, 77.34, 77.53, 115.86, diastereomers) 115.93, 121.17, 125.45, 126.00, 127.40, 127.52, 128.12, 128.49,
The peaks at 5 165.24 and 165.42 are attributed to carbonyl carbon of ester group of the major and minor diastereomers respectively.

Analysis calcd. for C_{26}H_{32}O_{3}: C, 79.56; H, 8.22

Found: C, 79.76; H, 8.13

(-)-Menthyl 2-methylene-3-(4-methylphenyl)-3-phenoxypropanoate (158b):

This was prepared via the reaction of (-)-menthyl (2Z)-2-(bromomethyl)-3-(4-methylphenyl)prop-2-enoate (154b) with phenol in the presence of triethylamine, following the similar procedure described for the molecule 158a, as a colorless viscous liquid.

Reaction time: 4 h

Yield: 54%

de: 28%

Optical rotation: [α]_{D}^{25} \! \! -71.56 (c 2.11, CHCl_{3})

IR (Neat): v 1711, 1633 cm^{-1}

{^1}H NMR: 8 0.56-2.02 (m, 18H, H2'-H10'), 2.25 (s, 3H), 4.54-4.85 (m, 1H, H1'), 5.73 & 5.84 (2s, 1H, H3), 6.01 & 6.04 (2s, 1H, diastereomeric Hb), 6.22 & 6.31 (2s, 1H, Ha), 6.82-7.03 (m, 3H, aromatic), 7.05-7.48 (m, 6H, aromatic)
The underlined peaks arise due to the minor diastereomer.

The two singlets at $\delta$ 5.73 & 5.84 arise from benzylic methine protons (H3) of the minor and major diastereomers respectively. They are in the ratio of 36:64, indicating that the reaction is 28% diastereoselective.

$^{13}$C NMR: $\delta$ 16.08, 16.26, 20.70, 20.84, 21.18, 22.02, 23.24, 23.45, 25.91, 26.27, 31.43, 34.23, 40.72, 40.89, 47.15, 74.87, 77.23, 77.43, 115.94, 121.09, 125.24, 125.80, 127.36, 127.51, 129.19, 129.35, 135.89, 136.00, 137.76, 137.85, 140.72, 141.32, 157.82, 165.30, 165.52.

The peaks at $\delta$ 165.30 and 165.52 are attributed to carbonyl carbon of ester group of the major and minor diastereomers respectively.

Analysis calcd. for C$_{27}$H$_{34}$O$_3$: C, 79.77; H, 8.43

Found: C, 79.98; H, 8.54

(−)-Menthyl 3-(4-chlorophenyl)-2-methylene-3-phenoxypropanoate (159):

This product was obtained as a colorless viscous liquid via the reaction of (−)-menthyl (2Z)-2-(bromomethyl)-3-(4-chlorophenyl)prop-2-enoate (155) with phenol in the presence of triethylamine, following the similar procedure described for the molecule 158a.
Reaction time: 4h
Yield: 57%
de: 26%

Optical rotation: $[\alpha]_D^{25} -69.81 (c 3.71, \text{CHCl}_3)$

IR(Neat): $\nu$ 1714, 1638 cm$^{-1}$

$^1$H NMR: $\delta$ 0.60-2.10 (m, 18H, H2'-H10'), 4.64-4.88 (m, 1H, H1'), 5.86 & 5.96 (2s, 1H, H3), 6.08 & 6.11 (2s, 1H, Mb), 632 & 6.41 (2s, 1H, Ha), 6.88-7.09 (m, 3H, aromatic), 7.18-7.50 (m, 6H, aromatic)

The underlined chemical shifts values are attributed to the minor diastereomer.

The two singlets at $\delta$ 5.86 & 5.96 are arising from the benzylic methine proton (H3) of the minor and major diastereomers respectively and are in the ratio of 37:63, indicating 26% diastereoselectivity in the reaction.

$^{13}$C NMR: 6 16.16, 16.32, 20.69, 20.86, 22.05, 23.30, 23.52, 26.08, 26.36, 31.46, 34.25, 40.78, 40.91, 47.20, 75.08, 76.80, 76.96, 115.93, 116.01, 121.48, 125.48, 126.12, 128.73, 128.81, 128.96, 129.49, 134.02, 137.64, 137.73, 140.38, 140.92, 157.51, 165.03, 165.24

The peaks at $\delta$ 165.03 and 165.24 are attributed to carbonyl carbon of ester group of the major and minor diastereomers respectively.
Isobornyl sultone (161):

This was prepared according to the literature method.\textsuperscript{278}

A solution of (+)-10-camphorsulfonic acid (160) (120 mmol, 27.876 g) in 60 mL of water was added carefully to solid sodium borohydride (225 mmol, 8.511 g). Water was removed under reduced pressure and the reaction mixture was heated for 4 hours at 120 °C. Absolute ethanol (900 mL) was added and refluxed for 2 hours. Salts were removed by filtration. Ethanol (300 mL) was added to salts, refluxed and again filtered. This process was repeated 3-4 times. Then all the ethanolic solutions were combined and ethanol was removed by distillation. Crude solid thus obtained, was dried at 120 °C for 2 hours. This solid was dissolved in pyridine (48 mL) and freshly crystallized p-toluenesulfonyl chloride (27 g) was added with stirring. After 5 hours at room temperature, the reaction mixture was poured into ice-cold water (120 mL) and refrigerated (-20 °C) overnight. Solid isobornyl sultone (161) was filtered and dried.

Yield: 17.958 g (69%)

Mp.: 114-116 °C (lit.\textsuperscript{279} 116-118 °C)
(1S,2R,4R)-1-(Diisopropylaminosulfonyl)methyl-7,7-dimethylbicyclo(2.2.1)heptan-2-ol (162):

To a stirred solution of ethylmagnesium bromide (480 mmol) in THF, N,N-diisopropylamine (480 mmol, 48.571 g) was added slowly over an hour at room temperature under nitrogen. After the evolution of ethane gas was completely seized, sultone 161 (60 mmol, 12.978 g) in 100 mL of THF was added. After stirring for 24 hours at room temperature, the reaction mixture was poured into 250 mL of cold 2N HCl and extracted with ether (3x80 mL). The combined ethereal solution was washed with aqueous NaHCO₃ solution, brine and dried over anhydrous Na₂SO₄. Solvent was evaporated and crystallization of the resulting crude product from hexane (two times) provided pure 162, as a colorless crystalline solid.

Yield: 72% (13.748 g)
Mp.: 100-103 °C (lit.²⁷⁹ 102-103 °C)
Optical rotation: [α]D²⁵ -34.68 (c 10, EtOH) [lit.²⁸⁰ -34.4 (c 4.74, EtOH)]
IR (KBr): ν 3508 cm⁻¹
¹H NMR: 0.81 (s, 3H, CH₃, H9), 1.06 (s, 3H, CH₃, H8), 1.33 (d, 12H, J = 6.8 Hz, 2×CH(CH₃)₂), 1.56-1.89 (m, 7H, H3, H4, H5, H6), 2.67 & 3.27 (ABq, 2H, J = 13.4 Hz, H10), 3.47 (d, 1H, J = 4.0 Hz, OH) 3.67-3.86 (m, 2H, 2×CH(CH₃)₂), 4.04-4.17 (m, 1H, H2)
I3C NMR: 6 19.90, 20.55, 22.17, 22.50, 27.34, 30.93, 38.83, 44.46, 48.49, 50.74, 54.27, 76.49

(1S,2R,4R)-1-(Diisopropylamino sulfonyl)methyl-7,7-dimethylbicyclo(2.2.1)hept-2-yl acrylate (18):

To a stirred solution of the alcohol 162 (30 mmol, 9.524 g) in 75 mL of dry ether was added slowly ethylmagnesium bromide (30 mmol) in ether (60 mL) at room temperature. After stirring at room temperature for 1 hour, the reaction mixture was cooled to 0 °C. Acryloyl chloride (75 mmol, 6.788 g) in ether (75 mL) was added and stirred at room temperature for 2 h. The reaction mixture was diluted with ether (100 mL) and washed with water (100 mL). The organic layer was dried over anhydrous Na2SO4, concentrated and the solid thus obtained, was crystallized from hexane to give acrylate 18, as a colorless crystalline solid.

Yield: 91% (10.189 g)

Mp.: 116-118 °C (lit.279 117-118 °C)

Optical rotation: [α]D25 -50.44 (c 2.50, acetone)

IR(KBr): ν 1728, 1637 cm⁻¹

1H NMR: 8 0.89 (s, 3H, CH3, H9), 1.01 (s, 3H, CH3, H8), 1.27 & 1.28 (2d, 12H, J = 6.0 Hz, diastereomeric 2×CH(CH3)2), 1.59-2.14 (m, 7H, H3, H4, H5, H6), 2.72 & 3.28 (ABq, 2H, J = 13.0 Hz, H10),
161

3.58-3.82 (m, 2H, 2×CH(CH₃)₂), 5.03-5.16 (m, 1H, H2), 5.78 (dd, 1H, J = 2.0 & 9.6 Hz), 6.07 (dd, 1H, J = 9.6 & 17.4 Hz), 6.33 (dd, 1H, J = 2.0 & 17.4 Hz)

¹³C NMR:

5 19.90, 20.31, 22.21, 22.31, 26.95, 29.82, 39.37, 44.49, 48.11, 49.01, 49.42, 52.92, 78.31, 129.09, 129.61, 164.39

(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-hydroxy-2-methylene-3-phenylpropanoate (163):

A mixture of acrylate (18) (5 mmol, 1.857 g), benzaldehyde (130a) (25 mmol, 2.65 g) and DABCO (5 mmol, 0.56 g) was allowed to react at room temperature for 10 days. The reaction mixture was diluted with ether (10 mL) and washed successively with 2N HCl solution, water and saturated aqueous NaHCO₃ solution. The ethereal layer was dried over anhydrous Na₂SO₄, concentrated and the crude product thus obtained, was purified by column chromatography (silica gel, 10% EtOAc in hexanes) to afford 163, as a colorless solid.

Yield: 92% (2.211 g)

de: 14%

Mp.: 130-132°C
Optical rotation: $\left[\alpha\right]_D^{25} -33.55$ (c 3.07, acetone) [lit. $\left[\alpha\right]_D^{25} -36.6$ (c 0.3, acetone), for $\Delta 5\%de$]

IR (KBr): $v$ 3489, 1718, 1620 cm$^{-1}$

$^1$H NMR: $\delta$ 0.88 (s, 3H, CH$_3$, H9'), 0.96 & 0.97 (2s, 3H, CH$_3$, H8'), 1.21-1.38 (m, 12H, 2xCH(CH$_3$)$_2$), 1.59-2.07 (m, 7H, H3', H4', H5', H6'), 2.65-2.78 (m, 1H, H10'), 3.18-3.47 (m, 2H, H10', OH), 3.57-3.78 (m, 2H, 2xCH(CH$_3$)$_2$), 5.06-5.18 (m, 1H, H2'), 5.56-5.71 (m, 2H, Hb & H3), 6.15 & 6.20 (2s, 1H, Ha), 7.27-7.41 (m, 5H, aromatic)

The underlined peaks are attributed to minor diastereomer.

The two singlets at $\delta$ 6.15 and 6.20 are attributed to the $\beta$-vinyllic protons (Ha) (cis- to ester group) of the minor and major diastereomers respectively and are in the ratio of 57:43, indicating that the reaction is 14% diastereoselective.

$^{13}$C NMR: $\delta$ 19.89, 20.29, 22.09, 22.48, 22.59, 26.95, 30.01, 39.28, 44.39, (mixture of 48.16, 49.03, 49.53, 53.05, 72.54, 73.34, 78.84, 124.83, 125.14, diastereomers) 126.45, 126.61, 127.57, 127.67, 128.30, 141.15, 141.25, 143.20, 143.42, 164.88, 165.05

The peaks at $\delta$ 72.54 & 73.34 and at $\delta$ 164.88 & 165.05 are attributed to benzylic carbon and carbonyl group of major and minor diastereomers respectively.
(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-hydroxy-2-methylene-3-(4-methylphenyl)propanoate (164):

This product was prepared from 4-methylbenzaldehyde (130b), acrylate (18) and DABCO, following the similar procedure described for the molecule 163, as a colorless viscous liquid.

Reaction time: 30 days
Yield: 92%
de: 10%

Optical rotation: $[\alpha]_D^{25} \approx -31.21$ (c 0.66, acetone)

IR (Neat): v 3504, 1714, 1628 cm$^{-1}$

$^1$H NMR: 8 0.88 (s, 3H, CH$_3$, H9'), 0.96 (s, 3H, CH$_3$, H8'), 1.21-1.37 (m, 12H, 2xCH(CH$_3$)$_2$), 1.57-2.07 (m, 7H, H3', H4', H5', H6'), 2.32 (s, 3H), 2.70 & 3.24 and 2.72 & 3.26 (2ABq, 2H, $J = 13.2$ Hz, diastereomeric H10'), 3.04 & 3.31 (2d, 1H, diastereomeric CHOH, $J = 5.0$ Hz, D$_2$O washable), 3.55-3.77 (m, 2H, 2xCH(CH$_3$)$_2$), 5.03-5.17 (m, 1H, H2'), 5.52-5.72 (m, 2H, H3, Hb), 6.12 & 6.18 (2s, 1H, Ha), 7.11-7.28 (m, 4H, aromatic)

The underlined peak is due to minor diastereomer.
The singlets at 5 6.12 and 6.18 are due to β-vinylic (Ha) protons (cis- to ester group) of major and minor diastereomers respectively and are in the ratio of 55:45, indicating that there is 10% diastereoselectivity in the reaction.

\[ ^{13}C\text{ NMR:} \]

5 19.88, 20.28, 20.99, 22.05, 22.49, 22.58, 26.96, 30.02, 39.32, 44.50, 48.18, 48.99, 49.60, 53.13, 72.42, 73.20, 78.84, 124.38, 124.66, 126.40, 126.56, 128.95, 137.08, 137.20, 138.38, 138.46, 143.54, 143.71, 164.86, 165.03

The peaks at 6 72.42 & 73.20 and 8 164.86 & 165.03 are due to benzylic carbon and carbonyl group of major and minor diastereomers respectively.

\((1'S,2'R,4'R)-1'-(\text{Diisopropylaminosulfonyl})\text{methyl}-7',7'-\text{dimethylbicyclo}(2.2.1)\text{hept-2'-yl} 3-(4-\text{ethylphenyl})-3-\text{hydroxy-2-methylenepropanoate} (165):\)

This compound was obtained as a colorless viscous liquid via the reaction of 4-ethyl benzaldehyde (130c) with acrylate (18) in the presence of DABCO, following the similar procedure described for the molecule 163.

Reaction time: 40 days
Yield: 82%
de: 10%
Optical rotation: \[ [\alpha]_D^{25} = -40.63 \ (c \ 1.77, \text{acetone}) \]

IR (Neat): \[ \nu \ 3497, \ 1716, \ 1628 \ \text{cm}^{-1} \]

\[ ^1H \text{NMR:} \]
6 0.79 (s, 3H, CH$_3$, H9'), 0.88 (s, 3H, CH$_3$, H8'), 1.12-1.46 (m, 15H, 2×CH(CH$_3$)$_2$, CH$_3$), 1.62-2.07 (m, 7H, H3', H4', H5', H6'), 2.57-2.76 (m, 3H, CH2CH$_3$, H10'), 3.03 & 3.31 (2d, 1H, diastereomeric CHOH, \( J = 4 \text{Hz, } D_2O \) washable), 3.18-3.32 (m, 1H, H110'), 3.55-3.78 (m, 2H, 2×CH(CH$_3$)$_2$), 5.01-5.17 (m, 1H, H2'), 5.52-5.60 (m, 1H, H3), 5.61 & 5.69 (2s, 1H, Hb), 6.13 & 6.19 (2s, 1H, Ha), 7.10-7.37 (m, 4H, aromatic)

The underlined chemical shift values are due to minor diastereomer.

The peaks at δ 6.13 and 6.19 are attributed to the β-vinylic (Ha) protons (cis- to ester group) of the major and minor diastereomers respectively and are in the ratio of 55:45, indicating that the reaction is 10% diastereoselective.

\[ ^{13}C \text{NMR:} \]
5 15.37, 19.89, 20.29, 22.07, 22.51, 22.61, 26.97, 28.44, 30.04, 39.33, 44.51, 48.20, 49.00, 49.61, 53.14, 72.44, 73.25, 78.86, 124.46, 124.71, 126.47, 126.64, 127.76, 138.61, 138.69, 143.51, 143.61, 164.88, 165.06

The peaks at δ 72.44 & 73.25 and δ 164.88 & 165.06 arise from the benzylic and ester carbonyl carbons respectively of both the diastereomers.
(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl\textsubscript{13}-(4-chlorophenyl)-3-hydroxy-2-methylene propanoate (166):

This product was prepared from 4-chlorobenzaldehyde (130g), acrylate (18) and DABCO in 4 mL of THF, following the similar procedure described for the molecule 163, as a colorless solid.

Reaction time: 10 days
Yield: 91%
dc: 12%
Mp.: 80-82 °C
Optical rotation: $[\alpha]_D^{\text{25}} = -32.45$ (c 2.16, acetone)

**IR(KBr):** $\nu$ 3501, 1714, 1628 cm\textsuperscript{-1}

$^1\text{H} \text{NMR:}$ 6 0.89 (s, 3H, CH\textsubscript{3}, H9\textsuperscript{1}), 0.96 & 1.00 (2s, 3H, CH\textsubscript{3}, H8\textsuperscript{1}), 1.18-1.39 (m, 12H, 2×CH(CH\textsubscript{3})\textsubscript{2}), 1.58-2.10 (m, 7H, H3', H4', H5', H6'), 2.69 & 3.21 and 2.70 & 3.23 (2ABq, 2H, $J = 13.0$ Hz, H10'), 3.25 & 3.54 (2d, 1H, $J = 5.0$ Hz, diastereomeric OH, D\textsubscript{2}O washable), 3.57-3.75 (m, 2H, 2×CH(CH\textsubscript{3})\textsubscript{2}), 5.06-5.17 (m, 1H, H2'), 5.52-5.65 (m, 2H, H3, Hb), 6.15 & 6.18 (2s, 1H, Ha), 7.32 (s, 4H, aromatic)

*The doublet at 8 3.25 merges with ABq.*

The underlined values arise due to minor diastereomer.
The diastereomeric excess was determined by the integration of the peaks at δ 6.15 and 6.18 arising from the β-vinylic (Ha) protons (cis- to ester group) of minor and major diastereomers respectively and was found to be 12%.

$^{13}$C NMR: 5 19.87, 20.23, 22.09, 22.35, 22.49, 26.92, 30.06, 39.26, 44.39, (mixture of 48.16, 49.01, 49.53, 53.08, 71.68, 72.69, 78.88, 78.91, diastereomers) 124.61, 125.12, 127.96, 128.36, 133.22, 140.06, 142.90, 143.33, 164.62, 164.86

The peaks at 5 71.68 & 72.69 and 164.62 & 164.86 are attributed to the benzylic and ester carbonyl carbon of major and minor diastereomers respectively.

$(1'S,2'R,4'R)$-1'-(Diisopropyaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl3-(2-chlorophenyl)-3-hydroxy-2-methylenepropanoate (167):

This compound was obtained as a colorless viscous liquid via the reaction of 2-chlorobenzaldehyde (130h) with acrylate (18) in the presence of DABCO, following the similar procedure described for the molecule 163.

Reaction time: 10 days
Yield: 90%
de: 62%
Optical rotation: \([\alpha]_D^{25} -18.66\) (c 1.50, acetone)

IR (Neat): \(\nu\) 3491, 1716, 1630 cm\(^{-1}\)

\(^1\)H NMR: \(\delta\) 0.81-1.50 (m, 18H, H9', H8', 2\times\text{CH(CH}_3\text{)}_2), 1.58-2.13 (m, 7H, H3', H4', H5', H6'), 2.71 \& 3.25 and 2.73 \& 3.32 (2ABq, 2H, \(J = 13.4\) Hz, Ha'), 3.54-3.86 (m, 3H, 2\times\text{CH(CH}_3\text{)}_2 \& \text{CHOH}, 1H D\text{}_2\text{O washable}), 5.05-5.14 \& 5.14-5.29 (2m, 1H, H2'), 5.38 \& 5.45 (2s, 1H, H3), 5.94-6.05 (m, 1H, Hb), 6.07 \& 6.26 (2s, 1H, Ha), 7.18-7.46 (m, 3H, aromatic), 7.55-7.68 (m, 1H, aromatic).

The underlined peaks are attributed to the minor diastereomer.

The peaks at \(\delta\) 5.38 and 5.45 arise due to the benzylic proton (H3) of minor and major diastereomers respectively and are in the ratio of 19:81, indicating 62% diastereoselectivity in the reaction.

\(^{13}\)C NMR: \(8\) 19.69, 19.95, 20.26, 22.02, 22.59, 26.95, 29.90, 30.30, 39.16, 39.35, 44.38, 48.24, 49.05, 49.55, 52.94, 53.35, 68.88, 69.74, 78.82, 79.04, 125.09, 126.05, 127.01, 128.12, 128.81, 128.97, 129.30, 132.49, 132.83, 138.30, 141.68, 164.92, 165.31

The underlined peaks arise due to the minor diastereomer.
pt-2'-yl 3-(2,4-dichlorophenyl)-3-hydroxy-2-methylenepropanoate (168):

The reaction of 2,4-dichlorobenzaldehyde (130i) with acrylate (18) in the presence of DABCO in 4 mL of THF, following the similar procedure described for the molecule 163, afforded the desired compound 168, as a colorless solid.

**Reaction time:** 10 days

**Yield:** 68%

**Mp.:** 130-132 °C

**Optical rotation:** $[\alpha]_D^{25}$ 4.06 (c 0.64, acetone)

**IR (KBr):** ν 3479, 1714, 1628 cm$^{-1}$

**$^1$H NMR:**

5 0.89 (s, 3H, CH$_3$, H9$'$), 0.97 (s, 3H, CH$_3$, H8$'$), 1.28 (d, 12H, $J = 6.0$ Hz, 2×CH(CH$_3$)$_2$), 1.65-2.11 (m, 7H, H3, H4, H5, H6$'$), 2.73 & 3.31 (ABq, 2H, $J = 13.2$ Hz, H10$'$), 3.55-3.88 (m, 3H, 2×CH(CH$_3$)$_2$ & CHOH, 1H D$_2$O washable), 5.06-5.21 (m, 1H, H2$'$), 5.40 (s, 1H, H3), 5.92 (s, 1H, Hb), 6.23 (s, 1H, Ha), 7.26-7.43 (m, 2H, aromatic), 7.56 (d, 1H, $J = 8.2$ Hz, aromatic)

**$^1$C NMR:**

6 19.73, 20.21, 22.02, 22.52, 26.93, 30.35, 39.37, 44.38, 48.23, 49.04, 49.58, 53.40, 68.47, 79.12, 125.94, 127.23, 129.01, 129.21, 133.42, 133.93, 137.19, 141.55, 164.68
(1'S,2'R,4'R)-1'-((Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl (2Z)-2-(bromomethyl)-3-phenylprop-2-enoate (169):

To a stirred solution of alcohol 163 (5 mmol, 2.387 g) in CH₂Cl₂ (20 mL) was added drop wise HBr (48%, 12.5 mmol, 2.10 mL) followed by conc. H₂SO₄ (5 mmol, 0.49 g) at 0 °C. After 12 h of stirring at room temperature, the reaction mixture was carefully poured into ice-cold water and extracted with ether (2x20 mL). The combined organic layer was washed with water, dried over anhydrous Na₂SO₄ and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to afford 169, as a colorless solid.

Yield: 88% (2.385 g)
Mp.: 106-108 °C
Optical rotation: [α]D +75.03 (c 4.27, CHCl₃)
IR (KBr): ν 1722, 1630 cm⁻¹
H NMR: 6 0.92 (s, 3H, CH₃, H9'), 1.13 (s, 3H, CH₃, H8'), 1.25 (d, 12H, J = 6.6 Hz, 2×CH(CH₃)₂), 1.61-2.18 (m, 7H, H3', H4', H5', H6'), 2.75 & 3.36 (ABq, 2H, J = 13.6 Hz, H10'), 3.57-3.82 (m, 2H, 2×CH(CH₃)₂), 4.32 & 4.42 (ABq, 2H, J = 9.8 Hz, CH₂Br), 5.19-5.28 (m, 1H, H2'), 7.39-7.65 (m, 5H, aromatic), 7.76 (s, 1H, H3)
C NMR: 20.27, 20.42, 22.15, 22.69, 26.67, 27.06, 30.20, 39.51, 44.59, 
48.24, 49.19, 49.78, 53.24, 79.31, 128.91, 129.52, 134.32, 
142.33, 164.69

pt-2'-yl (2Z)-2-(bromomethyl)-3-(4-methylphenyl)prop-2-enoate (170):

This compound was prepared by the reaction of alcohol 164 with HBr (48%) in the 
presence of conc. H2SO4, following the similar procedure described for the molecule 
169, as a colorless solid.

Yield: 95%

Mp.: 134-136 °C

Optical rotation: [α]D25 +87.04 (c 5.00, CHCl3)

IR (KBr): ν 1714, 1624 cm⁻¹

¹H NMR: 0.93 (s, 3H, CH₃, H9'), 1.14 (s, 3H, CH₃, H8'), 1.25 (d, 12H, J = 6.6 Hz, 
= 6.6 Hz, 2×CH(CH₃)₂), 1.60-2.17 (m, 7H, H₃', H4', H5', H6'),
2.40 (s, 3H, CH₃), 2.75 & 3.37 (ABq, 2H, J = 13.4 Hz, H10'),
3.59-3.82 (m, 2H, 2×CH(CH₃)₂), 4.33 & 4.44 (ABq, 2H, J = 10.0 
Hz, CH₂Br), 5.17-5.32 (m, 1H, H2'), 7.27 (d, 2H, J = 8.0 Hz, 
aromatic), 7.47 (d, 2H, J = 8.0 Hz, aromatic), 7.73 (s, 1H, H3)
**13C NMR:**

5 20.27, 20.42, 21.38, 22.13, 22.69, 26.91, 27.07, 30.19, 39.54, 44.66, 48.24, 49.16, 49.82, 53.29, 79.26, 128.66, 129.67, 131.53, 139.99, 142.43, 164.79

(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl (2Z)-2-(bromomethyl)-3-(4-ethylphenyl)prop-2-enoate (171):

This compound was isolated as a colorless solid via the reaction of alcohol 165 with HBr (48%) in the presence of conc. H2SO4, following the similar procedure described for the molecule 169.

**Yield:** 72%

**Mp:** 94-96 °C

**Optical rotation:** $[\alpha]_D^{25} +85.5$ (c 2.60, CHCl$_3$)

**IR (KBr):**

$\nu$ 1712, 1628 cm$^{-1}$

**$^1$H NMR:**

6 0.94 (s, 3H, CH$_3$, H9'), 1.15 (s, 3H, CH$_3$, H8'), 1.17-1.37 (m, 15H, 2×CH(CH$_3$)$_2$ & CH$_2$CH$_3$), 1.50-2.17 (m, 7H, H3', H4', H5', H6'), 2.65-2.81 (m, 3H, CH$_2$CH$_3$ & H10'), 3.37 (d, 1H, $J=13.6$ Hz, H10'), 3.56-3.81 (m, 2H, 2×CH(CH$_3$)$_2$), 4.36 & 4.46 (ABq, 2H, $J=9.8$ Hz, CH$_2$Br), 5.17-5.32 (m, 1H, H2'), 7.30 (d, 2H, $J=$...
$7.8 \text{ Hz, aromatic}$, $7.51 \text{ (d, } 2\text{H, } J = 7.8 \text{ Hz, aromatic})$, $7.75 \text{ (s, } 1\text{H,H3})$

$^{13}$C NMR: $8 15.19, 20.24, 20.40, 22.11, 22.67, 27.03, 28.72, 30.14, 39.50,$
$44.57, 48.20, 49.14, 49.74, 53.20, 79.17, 128.43, 129.81, 131.68,$
$142.48, 146.23, 164.78$

(1'S,2'R,4'R)-1'-(Diiisopropylamino sulfonyl)methyl-7',7'-dimethylbicycle(2.2.1)hept-2'-yI (2Z)-2-(bromomethyl)-3-(4-chlorophenyl)prop-2-enoate (172):

The reaction of alcohol 166 with HBr (48%) in the presence of conc. H$_2$SO$_4$, following the similar procedure described for the molecule 169, provided the desired compound 172, as a colorless solid.

Yield: 93%

Mp.: 152-154°C

Optical rotation: $[\alpha]_D^{25} + 89.44 \text{ (c 5.00, CHCl}_3)$

IR (KBr): v 1720, 1630 cm$^{-1}$

$^1$H NMR: $8 0.93 \text{ (s, } 3\text{H, CH}_3, \text{H9}'), 1.14 \text{ (s, } 3\text{H, CH}_3, \text{H8}'), 1.25 \text{ (d, } 12\text{H, } J = 6.8 \text{ Hz, } 2\text{xCH(CH}_3)_2), 1.62-2.18 \text{ (m, } 7\text{H, H3', H4', H5', H6'}), 2.75 \text{ & 3.35 (ABq, } 2\text{H, } J = 13.2 \text{ Hz, H10'}), 3.57-3.82 \text{ (m, } 2\text{H, } 2\text{xCH(CH}_3)_2), 4.26 \text{ & 4.39 (ABq, } 2\text{H, } J = 10.0 \text{ Hz, CH}_2\text{Br),}$
(1'S,2'R,4'R)-1'-(Diisopropylamino)sulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl (2Z)-2-(bromomethyl)-3-(2-chlorophenyl)prop-2-enoate (173):

This compound was obtained as a colorless solid via the treatment of alcohol 167 with HBr (48%) and conc. H2SO4, following the similar procedure described for the molecule 169.

Yield: 81%

Mp.: 122-124°C

Optical rotation: [α]D^25 +96.96 (c 5.00, CHCl₃)

IR (KBr): ν 1720, 1631 cm⁻¹

¹H NMR:
8 0.93 (s, 3H, CH₃, H9'), 1.14 (s, 3H, CH₃, H8'), 1.24 (d, 12H, J = 6.6 Hz, 2xCH(CH₃)₂), 1.58-2.19 (m, 7H, H3', H4', H5', H6'), 2.74 & 3.34 (ABq, 2H, J = 13.0 Hz, H10'), 3.60-3.82 (m, 2H, 2xCH(CH₃)₂), 4.17 & 4.35 (ABq, 2H, J = 9.8 Hz, CH₂Br), 5.25-
5.40 (m, 1H, H2'), 7.32-7.58 (m, 3H, aromatic), 7.71-7.86 (m, 1H, aromatic), 7.88 (s, 1H, H3)

$^3$C NMR:
6  20.20, 20.41, 22.13, 22.64, 26.02, 27.05, 30.04, 39.40, 44.53, 48.23, 49.18, 49.74, 53.12, 79.30, 127.12, 129.51, 129.92, 130.65, 131.23, 132.77, 134.58, 138.48, 164.04

pt-2'-yl (2Z)-2-(bromomethyl)-3-(2,4-dichlorophenyl)prop-2-enoate (174):
The treatment of alcohol 168 with HBr (48%) and conc. H$_2$SO$_4$, following the similar procedure described for the molecule 169, afforded the desired product 174, as a colorless solid.

Yield: 93%

Mp.: 142-144 °C

Optical rotation: $[\alpha]_D^{25} +111.9$ (c 5.00, CHCl$_3$)

IR(KBr): v 1718, 1635 cm$^{-1}$

$^1$H NMR:
6 0.92 (s, 3H, CH$_3$, H9'), 1.13 (s, 3H, CH$_3$, H8'), 1.24 (d, 12H, J = 6.8 Hz, 2×CH(CH$_3$)$_2$), 1.62-2.16 (m, 7H, H3', H4', H5', H6'), 2.75 & 3.33 (ABq, 2H, J = 13.6 Hz, H10'), 3.56-3.78 (m, 2H, 2×CH(CH$_3$)$_2$), 4.13 & 4.32 (ABq, 2H, J = 9.6 Hz, CH$_2$Br), 5.22-
176

5.33 (m, 1H, H2'), 7.34-7.52 (m, 2H, aromatic), 7.68 (d, 1H, J = 8.2 Hz, aromatic), 7.80 (s, 1H, H3)

$^{13}$C NMR:

20.20, 20.38, 22.17, 22.60, 25.53, 27.04, 30.16, 39.44, 44.63, 48.26, 49.17, 49.83, 53.27, 79.54, 127.51, 129.85, 130.29, 131.41, 131.96, 135.37, 135.95, 137.20, 163.78

(1'S,2'R,4'R)-1'-(Diisopropylaminoisulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 2-methylene-3-(prop-2-yn-1-yloxy)-3-phenylpropanoate (175):

To a stirred solution of allyl bromide 169 (0.5 mmol, 0.27 g) in Et$_3$N (1 mL) was added propargyl alcohol (2.5 mmol, 0.14 g). After stirring for 12 h at room temperature, the reaction mixture was diluted with ether (10 mL) and washed successively with 2N HCl solution and water. The organic layer was dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide pure propargylic ether 175, as a colorless solid.

Yield: 55% (0.142 g)

de: 88%

Mp.: 90-92 °C

Optical rotation: $[\alpha]_D^{25} -104.14$ (c 3.50, CHCl$_3$)
IR (KBr): \[ \nu 3240, 2115, 1716, 1620 \text{ cm}^{-1} \]

\(^1\)H NMR: \[ 5\ 0.85-1.39 \ (m, 18H, H9', H8', 2\times CH(CH_3)_2), 1.56-2.10 \ (m, 7H, H3', H4', H5', H6'), 2.42 \ (t, 1H, J = 2.6 \text{ Hz}, HC≡C), 2.62-2.71 \ (m, 1H, H10'), 3.18-3.36 \ (m, 1H, H10'), 3.54-3.82 \ (m, 2H, 2\times CH(CH_3)_2), 4.02 \text{ & } 4.15 \ (d \text{ of ABq}, 2H, \ = 2.6 \text{ & } 15.6 \text{ Hz}, CH_2C≡C), 5.07-5.17 \ (m, 1H, H2'), 5.52 \text{ & } 5.56 \ (2s, 1H, H3), 5.92 \text{ & } 6.03 (2s, 1H, Hb), 6.18 \text{ & } 6.23 (2s, 1H, Ha), 7.20-7.44 \ (m, 5H, aromatic) \]

The underlined peaks arise due to minor diastereomer.

The two singlets at \( 5.92 \text{ & } 6.03 \) arise from the olefinic (Hb) proton, (trans- to the ester functionality) of major and minor diastereomers respectively. The diastereomeric excess was determined by the integration (94:6) of these two singlets and found to be 88%.

\(^{13}\)C NMR: \[ \delta 19.97, 20.31, 22.01, 22.35, 22.67, 26.96, 29.89, 39.28, 44.43, 48.14, 48.96, 49.57, 52.99, 55.99, 74.62, 77.45, 77.73, 78.48, 78.73, 79.45, 123.72, 127.57, 127.93, 128.26, 138.61, 138.93, 141.64, 142.01, 164.03 \]

The underlined signals are attributed to the minor diastereomer.

MS (\( m/z \)): \[ 516 (M^+) \]

Analysis calcd. for \( C_{29}H_{41}NO_5S \): C, 67.54; H, 8.01; N, 2.72
Found: \[ C, 67.38; H, 8.11; N, 2.73 \]

Selective crystallization:

Crystallization of the molecule 175 (0.2 mmol, 0.103 g) from 10% EtOAc in hexanes provided the single diastereomer (175*) (0.071 g, 69% yield) as evidenced by $^1$H NMR and $^{13}$C NMR spectral data.

de: >99%

Mp.: 90-92 °C

Optical rotation: [α]$_D$$^{25}$ = -109.65 (c 2.31, CHCl$_3$)

IR (KBr): \( \nu \) 3238, 2121, 1716, 1624 cm$^{-1}$

$^1$H NMR: \( \delta \) 0.88 (s, 3H, CH$_3$, H9'), 0.98 (s, 3H, CH$_3$, H8'), 1.29 (d, 12H, J = 6.8 Hz, 2xCH(CH$_3$)$_2$), 1.55-2.12 (m, 7H, H3, H4, H5, H6'), 2.41 (t, 1H, J = 2.2 Hz, HC≡C), 2.70 & 3.26 (ABq, 2H, J = 13.6 Hz, H10'), 3.58-3.80 (m, 2H, 2xCH(CH$_3$)$_2$), 4.02 & 4.15 (d of ABq, 2H, J = 2.0 & 15.6 Hz, CH$_2$C≡C), 5.10 (dd, 1H, J = 3.2 & 7.8 Hz, H2'), 5.51 (s, 1H, H3), 5.91 (s, 1H, Hb), 6.17 (s, 1H, Ha), 7.21-7.46 (m, 5H, aromatic)

$^{13}$C NMR: 20.09, 20.44, 22.13, 22.79, 27.07, 30.00, 39.40, 44.57, 48.27, 49.08, 49.70, 53.13, 56.13, 74.66, 77.87, 78.63, 79.58, 123.76, 127.70, 128.04, 128.38, 139.07, 142.18, 164.15
(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 2-methylene-3-(4-methylphenyl)-3-(prop-2-yn-1-yloxy)propanoate (176):

This compound was isolated as a colorless solid via the reaction of allyl bromide 170 with propargyl alcohol in the presence of triethylamine, following the similar procedure described for the molecule 175.

Reaction time: 12 h
Yield: 68%
de: 84%
Mp.: 104-106 °C
Optical rotation: \([\alpha]_D^{25} -106.65 (c 3.50, \text{CHCl}_3)\)
IR (KBr): \(v 3240, 2117, 1716, 1622 \text{ cm}^{-1}\)

\(^1H\) NMR:

\[
\begin{align*}
0.88-1.45 & \text{ (m, } 18\text{H, } \text{H}9', \text{H}8', 2\times \text{CH(\text{CH}_3)_2} ), \ 1.56-2.11 & \text{ (m, } 7\text{H, } \text{H}3', \text{H}4', \text{H}5', \text{H}6') , \ 2.30 & \text{ & } 2.33 & \text{ (2s, } 3\text{H, } \text{CH}_3 ) , \ 2.42 & \text{ (t, } 1\text{H, } J = 1.8 \text{ Hz, } \text{HC=CH}), \ 2.67 & \text{ & } 2.70 & \text{ (2d, } 1\text{H, } J = 13.4 \text{ Hz, } \text{H}10'), \ 3.21 & \text{ & } 3.26 & \text{ (2d, } 1\text{H, } J = 13.4 \text{ Hz, } \text{H}10'), \ 3.56-3.80 & \text{ (m, } 2\text{H, } 2\times \text{CH(\text{CH}_3)_2} ) , \ 3.96-4.26 & \text{ (m, } 2\text{H, } \text{CH}_2\text{C=CH}), \ 4.95-5.03 & \text{ & } 5.06-5.17 & \text{ (2m, } 1\text{H, } \text{H}2'), \ 5.47 & \text{ & } 5.52 & \text{ (2s, } 1\text{H, } \text{H}3) , \ 5.91 & \text{ (d, } 1\text{H, } J = 1.4 \text{ Hz) & } 6.01 & \text{ (s, } 1\text{H, } \text{Hb) , } 6.16 & \text{ & } 6.21 & \text{ (2s, } 1\text{H, } \text{Ha) , } 7.09-7.38 & \text{ (m, } 4\text{H, aromatic) }
\end{align*}
\]
The underlined peaks are due to the minor diastereomer.

- These doublets are part of the two AB quartets of CH₂ group at C-10' of major and minor diastereomers.

The two singlets at δ 5.91 & 6.01 arise from the β-olefinic (Hb) proton (trans- to the ester functionality) of the major and minor diastereomers respectively and are in the ratio of 92:8, indicating that the reaction is 84% diastereoselective.

\[ ^{13} \text{C NMR:} \quad 5 \ 20.04, 20.38, 21.11, 22.07, 22.42, 22.73, 27.03, \underline{29.64}, 29.95, \]
\[ 39.37, 44.56, 48.21, 49.01, 49.68, 53.10, 55.94, 74.50, 77.34, \]
\[ 77.45, 77.72, 78.54, \underline{78.81}, 79.64, 123.52, 127.59, 129.01, \]
\[ 135.99, \underline{137.62}, \underline{141.91}, 142.30, 164.13 \]

The underlined peaks are attributed to the minor diastereomer.

\[ \text{MS (m/z):} \quad 530 (M^+) \]

Analysis \textit{calcd.} for C\textsubscript{30}H\textsubscript{43}NO\textsubscript{5}S: C, 68.02; H, 8.18; N, 2.64

Found: C, 68.15; H, 8.16; N, 2.68

**Selective crystallization:**

Crystallization of the molecule \textbf{176} (0.21 mmol, 0.111 g) from 10% EtOAc in hexanes provided the single diastereomer (176\*) (0.064 g, 58% yield) \textit{as} evidenced by the \textit{^1H} NMR and \textit{^{13}C}NMR spectral data.
Mp.: 104-106 °C
Optical rotation: $[\alpha]_{D}^{25} -116.26$ (c 2.09, CHCl$_3$
IR (KBr): $\nu$ 3240, 2123, 1716, 1622 cm$^{-1}$
$^1$H NMR: 6 0.88 (s, 3H, CH$_3$, H9'), 0.98 (s, 3H, CH$_3$, H8'), 1.28 (d, 12H, $J$ = 6.8 Hz, 2×CH(CH$_3$)$_2$), 1.56-2.11 (m, 7H, H3', H4', H5', H6'), 2.32 (s, 3H, CH$_3$), 2.40 (t, 1H, $J$ = 2.0 Hz, HC=C), 2.69 & 3.26 (ABq, 2H, $J$ = 13.4 Hz, H10'), 3.63-3.79 (m, 2H, 2×CH(CH$_3$)$_2$), 3.99 & 4.12 (d of ABq, 2H, $J$ = 2.0 & 15.8 Hz, CH$_2$C≡C), 5.09 (dd, 1H, $J$ = 3.2 & 7.8 Hz, H2'), 5.46 (s, 1H, H3), 5.90 (s, 1H, Hb), 6.15 (s, 1H, Ha), 7.12 (d, 2H, $J$ = 7.8 Hz, aromatic), 7.27 (d, 2H, /= 7.8 Hz, aromatic)
$^1$C NMR: 8 20.13, 20.47, 21.22, 22.15, 22.81, 27.10, 29.99, 39.43, 44.61, 48.29, 49.10, 49.73, 53.15, 56.00, 74.57, 77.74, 78.60, 79.71, 123.58, 127.70, 129.12, 136.03, 137.77, 142.30, 164.18

(1$'$S,2$'$R,4$'$R)-1'-(Diisopropylamino)sulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-(4-ethylphenyl)-2-methylene-3-(prop-2-yn-1-yloxy)propanoate (177):

This compound was prepared via the treatment of allyl bromide 171 with propargyl alcohol under the influence of triethylamine, as a colorless solid, following the similar procedure described for the molecule 175.
Reaction time: 12 h

Yield: 72%

de: 87%

Mp.: 74-76 °C

Optical rotation: $[\alpha]_D^{25} -101.88$ (c 2.92, CHCl$_3$)

IR(KBr): $\nu$ 3238, 2120, 1718, 1622 cm$^{-1}$

$^1$H NMR: $\delta$ 0.78-1.41 (m, 21H, H9', H8', 2×CH(CH$_3$)$_2$, -CH$_2$CH$_3$), 1.56-2.15 (m, 7H, H3', H4', H5', H6'), 2.40 (t, 1H, $J = 2.8$ Hz, HC≡C), 2.57-2.78 (m, 3H, -CH2CH3, H10'), 3.16-3.33 (m, 1H, H10'), 3.54-3.81 (m, 2H, 2×CH(CH$_3$)$_2$), 3.95-4.21 (m, 2H, CH$_2$C≡C), 5.04-5.15 (m, 1H, H2'), 5.48 & 5.52 (2s, 1H, H3), 5.91 & 6.02 (2s, 1H, Hb), 6.16 & 622 (2s, 1H, Ha), 7.08-7.35 (m, 4H, aromatic)

The underlined chemical shift values are due to minor diastereomer.

The two singlets at δ 5.91 & 6.02 are attributed the $\beta$-olefinic (Hb) proton ($trans$- to the ester functionality) of the major and minor diastereomers respectively. The diastereomeric excess was determined by the integration (93.5:6.5) of these two singlets and was found to be 87%.
$^{13}$C NMR: 8 14.08, 15.40, 20.05, 20.38, 22.07, 22.43, 22.74, 27.03, 28.54, 29.32, 29.94, 31.90, 39.35, 44.53, 48.20, 49.02, 49.66, 53.06, 55.95, 74.54, 77.41, 77.70, 78.51, 78.76, 79.64, 123.56, 127.63, 127.82, 135.84, 136.18, 141.82, 142.22, 143.97, 164.16

The underlined peaks are attributed to the minor diastereomer.

Analysis calcd. for C$_{31}$H$_{45}$NO$_5$S: C, 68.47; H, 8.34; N, 2.58

Found: C, 68.35; H, 8.30; N, 2.52

(1'S,2'R,4'R)-1'-((Diisopropylaminosulfonyl)methyl)-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-(4-chlorophenyl)-2-methylene-3-(prop-2-yn-1-yloxy)propanoate (178):

The treatment of allyl bromide 172 with propargyl alcohol in the presence of triethylamine, following the similar procedure described for the molecule 175, furnished the desired compound 178, as a colorless solid.

Reaction time: 12 h

Yield: 83%

d.e: 78%

Mp.: 88-91 °

Optical rotation: $[\alpha]_D^{25}$ -107.66 (c 2.68, CHCl$_3$)

IR (KBr): $\nu$ 3231, 2115, 1716, 1626 cm$^{-1}$
$^1$H NMR: 8 0.86-1.45 (m, 18H, H9', H8', 2×CH(CH$_3$)$_2$), 1.56-2.09 (m, 7H, H3', H4', H5', H6'), 2.42 (t, 1H, J = 2.8 Hz, HC≡C), 2.67 & 3.18 and 2.70 & 3.25 (2ABq, 2H, J = 13.4 Hz, H10'), 3.52-3.78 (m, 2H, 2×CH(CH$_3$)$_2$), 3.95-4.22 (m, 2H, CH$_2$C≡C), 5.04-5.16 (m, 1H, H2'), 5.49 & 5.55 (2s, 1H, H3), 5.94 & 6.02 (2s, 1H, Hb), 6.18 & 6.21 (2s, 1H, Ha), 7.26-7.35 (m, 4H, aromatic)

The underlined chemical shift values arise from the minor diastereomer.

The diastereomeric excess was determined by the integration (89:11) of the two singlets at δ 5.94 & 6.02 arising from the olefinic (Hb) protons (trans- to the ester functionality) of major and minor diastereomers respectively and was found to be 78%.

$^{13}$C NMR: δ 19.96, 20.30, 22.04, 22.21, 22.64, 26.96, 29.99, 39.32, 44.50, 48.18, 48.99, 49.66, 53.09, 53.37, 56.09, 74.83, 76.81, 77.10, 78.62, 78.84, 79.23, 123.78, 128.43, 128.77, 128.97, 133.71, 137.64, 137.82, 141.52, 141.77, 163.86

The underlined peaks are attributed to the minor diastereomer.

Analysis calcd. for C$_{29}$H$_{40}$NO$_5$SCl: C, 63.31; H, 7.33; N, 2.55

Found: C, 63.52; H, 7.38; N, 2.58
pt-2'-yl3-(2-chlorophenyl)-2-methylene-3-(prop-2-yn-1-yloxy)propanoate (179):

This compound was isolated as a colorless solid via the reaction of the allyl bromide 173 with propargyl alcohol in the presence of triethylamine, following the similar procedure described for the molecule 175.

Reaction time: 12 h
Yield: 63%
de: 77%
Mp.: 116-118 °C
Optical rotation: $[\alpha]_D^{25} = -54.28$ (c 1.09, CHCl₃)

IR (KBr): ν 3244, 2130, 1711, 1624 cm⁻¹

¹H NMR: 6 0.75 & 0.83 (2s, 3H, CH₃, H9'), 0.78 & 0.95 (2s, 3H, CH₃, H8'), 1.08-1.41 (m, 12H, 2×CH(CH₃)₂), 1.56-2.07 (m, 7H, H3', H4', H5', H6'), 2.27-2.41 (m, 1H, HC≡C), 2.61 & 2.64 (2d, 1H, J = 13.6 Hz, H10'), 3.20 (d, 1H, J = 13.6 Hz, H10'), 3.52-3.76 (m, 2H, 2×CH(CH₃)₂), 4.09-4.23 (m, 2H, CH₂C≡C), 4.91-5.01 & 5.04-5.17 (2m, 1H, H2'), 5.50 & 5.75 (2s, 1H, H3), 5.80 & 5.98 (2s, 1H, Hb), 6.10 & 6.32 (2s, 1H, Ha), 7.12-7.48 (m, 4H, aromatic)
The underlined peaks are due to minor diastereomer.

The two singlets at 8 6.10 & 6.32 are from the olefinic (Ha) protons (cis- to the ester functionality) of major and minor diastereomers respectively. The diastereomeric excess was determined by the integration (88.5:11.5) of these two singlets and was found to be 77%.

\[ ^{13}\text{C NMR:} \]

8 19.69, 20.09, 20.40, 22.07, 22.76, 27.02, 29.86, 30.21, 39.37, 44.54, 48.19, 49.05, 49.63, 53.06, 57.28, 57.42, 74.65, 75.26, 75.55, 78.77, 79.05, 79.49, 125.32, 126.4, 126.79, 128.59, 129.14, 129.39, 129.61, 133.78, 134.26, 136.70, 139.97, 141.11, 163.81, 164.14

The underlined chemical shift values arise due to the minor diastereomer.

Analysis calcd. for C\textsubscript{29}H\textsubscript{40}NO\textsubscript{5}S\textsubscript{Cl}: C, 63.31; H, 7.33; N, 2.55

Found: C, 63.18; H, 7.30; N, 2.60

(1'\text{S},2'R,4'R)-1'-((Diisopropylaminsulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl) 3-(2,4-dichlorophenyl)-2-methylene-3-(prop-2-yn-1-yloxy)propanoate (180): This compound was obtained via the reaction of allyl bromide 174 with propargyl alcohol under the influence of triethylamine, as a colorless viscous liquid, following the similar procedure described for the molecule 175.
Reaction time: 12 h
Yield: 69%
de: 51%
Optical rotation: $[\alpha]_D^{25} = -51.14$ (c 3.15, CHCl$_3$)

IR (Neat): $\nu$ 3304, 2250, 1716, 1589 cm$^{-1}$

$^1$H NMR:

6.08-1.41 (m, 18H, H9', H8', 2xCH(CH$_3$)$_2$), 1.56-2.12 (m, 7H, H3', H4', H5', H6'), 2.36-2.46 (m, 1H, HC≡C), 2.69 & 2.71 (2d, 1H, $J = 13.4$ Hz, H10'), 3.26 (d, 1H, $J = 13.4$ Hz, H10'), 3.58-3.79 (m, 2H, 2xCH(CH$_3$)$_2$), 4.19-4.26 (m, 2H, CH$_2$C≡C), 4.97-5.07 & 5.10-5.19 (2m, 1H, H2'), 5.62 & 578 (2s, 1H, H3), 5.82 & 5.87 (2s, 1H, Hb), 6.18 & 6.37 (2s, 1H, Ha), 7.17-7.48 (m, 3H, aromatic)

The underlined peaks are attributed to the minor diastereomer.

The diastereomeric excess was determined by the integration (75.5:24.5) of the two singlets at 8 6.18 & 6.37 arising from the $\beta$-olefinic (Ha) proton, ($cis$- to the ester functionality) of major and minor diastereomers respectively and was found to be 51%.

$^{13}$C NMR:

$\delta$ 19.73, 20.04, 20.31, 22.06, 22.15, 22.57, 22.67, 26.98, 29.90,
30.24, 39.34, 44.50, 48.16, 49.01, **49.51**, 49.62, 53.06, 57.26, 74.87, **75.03**, 78.77, 79.06, 79.23, 125.34, **126.27**, 127.10, 129.33, 129.66, 134.22, 134.40, **134.82**, 135.39, 135.61, **139.75**, 140.71, 163.58, 163.85

The underlined peaks arise due to minor diastereomer.

Analysis *calcd.* for C_{29}H_{39}NO_{5}S_{2}Cl_{2}: C, 59.58; H, 6.72; N, 2.40

Found: C, 59.38; H, 6.79; N, 2.35

(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 2-methylene-3-phenoxy-3-phenylpropanoate (181):

A solution of the allyl bromide 169 (0.5 mmol, 0.27 g), phenol (0.5 mmol, 0.047 g) and Et_{3}N (1 mL) in CH_{2}Cl_{2} (1 mL), was stirred at room temperature for 4 hours. Then 2N HCl (5 mL) was added slowly and the reaction mixture was extracted with ether (2×10 mL). The combined organic layer was washed with aqueous NaHCO_{3} solution, water and dried over anhydrous Na_{2}SO_{4}. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 4% EtOAc in hexanes) to provide 181, as colorless viscous liquid.

Yield: 48% (0.132 g)

*de*: 82%
Optical rotation: $[\alpha]_D^{25} = -55.56$ (c 1.78, CHCl$_3$)

IR (Neat):
$\nu$ 1716, 1631 cm$^{-1}$

$^1$H NMR:
6 0.76-2.11 (m, 25H, H9', H8', 2×CH(CH$_3$)$_2$, H3', H4'),
H5', H6'), 2.61-2.81 (m, 1H, H10'),* 3.16, 3.22 & 3.28 (3s, 1H, H10'),* 3.54-3.81 (m, 2H, 2×CH(CH$_3$)$_2$), 5.05-5.24 (m, 1H, H2'),
5.78 & 6.02, 6.18, 6.21 & 6.26 (5s, 3H, H3, Hb, Ha), 6.82-7.02
(m, 3H, aromatic), 7.13-7.54 (m, 7H, aromatic)

The underlined peaks are attributed to the minor diastereomer.

*These actually belong to doublet of AB quartet (H10'). Due to merging of peaks of major and minor diastereomers, first part of ABq appears as multiplet at 5 2.61-2.81. Similarly due to merging of one of the peaks of doublet of minor diastereomer with one of the peaks of the major diastereomer, three singlets were observed at $\delta$ 3.16, 3.22 & 3.28 for second part of ABq (of both major and minor diastereomers).

The singlets at $\delta$ 5.78 & 6.02 can be attributed to the benzylic (H3) protons of the major and minor diastereomers respectively and are in the ratio of 91:9, indicating that the reaction is 82% diastereoselective. To further confirm our assignment, we have recorded $^1$H NMR in the presence of chiral shift reagent Eu(hfc)$_3$, which clearly
showed, that the minor peaks originally at $8 \ 6.26$ and $8 \ 6.02$ are in the ratio of 2:1, thus indicating that the peak originally at $5 \ 6.26$ arises due to Hb and Ha protons of minor diastereomer. For further understanding, we have also recorded $^1H$ NMR spectrum in the presence of shift reagent Eu(fod)$_3$, the multiplet originally at $8 \ 5.05$-$5.24$ due to the H2' proton nicely splits into two multiplets at $8 \ 5.44$-$5.52$ and $8 \ 5.53$-$5.65$ in the ratio of 9:91, indicating that the molecule $181$ is 82% diastereomERICALLY pure.

$^{13}$C NMR: \[ \begin{align*}
19.90, & \quad 20.35, \quad 22.12, \quad 22.42, \quad 22.70, \quad 27.03, \quad 29.70, \quad 30.07, \quad 39.40, \\
44.50, & \quad 48.20, \quad 49.06, \quad 49.62, \quad 53.18, \quad 77.09, \quad 78.85, \quad 79.15, \quad 115.40, \\
115.89, & \quad 120.24, \quad 121.07, \quad 125.00, \quad 126.99, \quad 127.16, \quad 128.00, \quad 128.52, \\
129.39, & \quad 139.17, \quad 141.23, \quad 141.90, \quad 157.54, \quad 157.80, \quad 163.55, \quad 164.22.
\end{align*} \]

The underlined peaks are due to the minor diastereomer.

Analysis calcd. for C$_{32}$H$_{43}$NO$_5$S: \[ \begin{align*}
C, & \quad 69.41; \quad H, \quad 7.83; \quad N, \quad 2.53 \\
\end{align*} \]

Found: \[ \begin{align*}
C, & \quad 69.25; \quad H, \quad 7.70; \quad N, \quad 2.55
\end{align*} \]

(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl12-methylene-3-(4-methylphenyl)-3-phenoxypropanoate (182):

It was obtained as a colorless viscous liquid via the reaction of allyl bromide $170$ with phenol in the presence of triethylamine, following the similar procedure described for the molecule $181$. 
Reaction time: 4 h
Yield: 61%
de: 76%
Optical rotation: $[\alpha]_D^{25} = -61.66$ (c 1.26, CHCl$_3$)
IR(Neat): ν 1716, 1631 cm$^{-1}$

$^1$H NMR: 
δ 0.79-2.10 (m, 25H, H9', H8', 2×CH(CH$_3$)$_2$, H3', H4', H5', H6'), 2.30 & 2.33 (2s, 3H, CH$_3$), 2.68 & 3.21 and 2.70 & 3.26 (2ABq, 2H, $J = 13.4$ Hz, H10'), 3.53-3.78 (m, 2H, 2×CH(CH$_3$)$_2$), 5.02-5.22 (m, 1H, H2'), 5.78 & 6.00 (2s, 1H, H3), 6.10-6.28 (m, 2H, Hb, Ha), 6.83-6.98 (m, 3H, aromatic), 7.07-7.41 (m, 6H, aromatic)

The underlined chemical shift values are due to the minor diastereomer.

The singlets at δ 5.78 and 6.00 in the ratio of 88:12 are attributed to the benzylic (H3) protons of major and minor diastereomers respectively, indicating that the reaction is 76% diastereoselective. This is further confirmed by the integration of singlets at δ 2.30 and 2.33 arising from the CH$_3$ protons on the aromatic ring of the minor and major diastereomers respectively. We have also recorded the $^1$H NMR in the presence of shift reagent [sample: Eu(fod)$_3 = 1:1$], the multiplet originally at δ 5.02-5.22 (due to H2')
proton) nicely splits into two **multiplets** at 6 5.34-5.44 and 5.46-5.57 in the ratio of 12:88, also indicating 76% diastereoselectivity in the reaction.

**$^{13}$C NMR:**

8 19.92, 20.35, 21.15, 22.12, **22.42**, 22.71, 27.05, 30.08, 39.44, 44.56, 48.22, 49.05, 49.66, 53.22, **76.65**, 77.07, 78.84, **79.13**, 115.93, 121.00, 124.80, 127.13, 129.22, 129.34, 136.21, 137.69, **141.42**, 142.05, 157.92, 164.27

The underlined peaks are attributed to the minor diastereomer.

Analysis calcd. for C$_{33}$H$_{45}$NO$_5$S: C, 69.81; H, 7.99; N, 2.47

Found: C, 70.00; H, 7.93; N, 2.51

**(1'S,2'R,4'R)-1'-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-(4-ethylphenyl)-2-methylene-3-phenoxypropanoate (183):**

This product was prepared *via* the treatment of allyl bromide 171 with phenol in the presence of triethylamine, following the similar procedure described for the molecule 181, as a colorless viscous liquid.

Reaction time: 4 h

Yield: 66%

de: 78%

Optical rotation: $[\alpha]_D^{25}$ –59.26 (c 1.44, CHCl$_3$)

**IR (Neat):** ν 1718, 1615 cm$^{-1}$
\( ^1\)H NMR: \( \delta \) 0.72-2.11 (m, 28H, H9, H8, 2xCH(CH\(_3\))₂, -CH₂CH₃, H3, H4, H5, H6), 2.52-2.77 (m, 3H, CH₂CH₃ & H10), 3.21 & 3.25 (2d, 1H, \( J = 13.4 \) Hz, H10'), 3.49-3.81 (m, 2H, 2xCH(CH\(_3\))₂), 5.06-5.20 (m, 1H, H2'), 5.78 & 6.01 (2s, 1H, H3), 6.15, 6.19, 6.21 & 6.27 (4s, 2H, Hb, Ha), 6.80-7.01 (m, 3H, aromatic), 7.07-7.42 (m, 6H, aromatic)

The underlined peaks arise due to minor diastereomer.

The two singlets at \( \delta \) 5.78 & 6.01 integrating in the ratio of 89:11 arise from the benzylic (H3) protons of major and minor diastereomers respectively, indicating that there is 78% distereoselectivity in the reaction. This is further confirmed by the integration of two doublets at \( \delta \) 3.21 and 3.25 (second part of d of ABq) arising from the H10' proton of the minor and major diastereomers respectively.

\( ^{13}\)C NMR: 8 15.41, 19.94, 20.38, 22.15, 22.50, 22.74, 27.09, 28.57, 30.14, 39.47, 44.57, 48.25, 49.07, 49.69, 53.24, 77.11, 78.85, 79.18, 115.52, 115.93, 120.00, 121.01, 124.85, 127.18, 128.03, 129.39, 136.42, 141.28, 142.08, 144.00, 157.72, 157.97, 164.32

The underlined chemical shift values are attributed to the minor diastereomer.

Analysis \textbf{calcd.} for C\(_{34}\)H\(_{47}\)NO\(_5\)S: \( \text{C, 70.19; H, 8.14; N, 2.41} \)

Found: \( \text{C, 69.92; H, 8.24; N, 2.38} \)
(1'S,2'R,4'R)-1'-(Diisopropylaminoisulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl 3-(4-chlorophenyl)-2-methylene-3-phenoxypropanoate (184):

The treatment of allyl bromide 172 with phenol under the influence of triethylamine, following the similar procedure described for the molecule 181, afforded the desired compound 184, as a colorless solid.

Reaction time: 4 h
Yield: 63%
de: 81%
Mp.: 46-48 °C
Optical rotation: $[\alpha]_D^{25}$ -75.8 (c 2.50, CHCl$_3$)

IR (KBr): v 1716, 1620 cm$^{-1}$

$^1$H NMR: 5 0.74-1.39 (m, 18H, H9', H8', 2×CH(CH$_3$)$_2$), 1.46-2.08 (m, 7H, H3', H4', H5', H6'), 1.60 & 2.63 (2d, 1H, J = 13.4 Hz, H10'),* 3.06, 3.13 & 3.19 (3s, 1H, H10').** 3.44-3.72 (m, 2H, 2×CH(CH$_3$)$_2$), 4.99-5.12 (m, 1H, H2'), 5.77 & 5.95 (2s, 1H, H3), 6.04-6.21 (m, 2H, Hb, Ha), 6.74-6.92 (m, 3H, aromatic), 7.07-7.42 (m, 6H, aromatic)

The underlined peaks arise due to minor diastereomer.

This is actually first part of doublet of the AB quartet. **This is the second part of doublet of AB quartet in which one of the peaks of doublet of minor diastereomer merges with one of the peaks of the major diastereomer, thus appearing as three singlets.
The two singlets at 5.77 & 5.95 in the ratio of 90.5:9.5 arise from the benzylic (H3) protons of major and minor diastereomers respectively, indicating that the reaction is 81% diastereoselective. This is further confirmed by the integration of the doublets at 5.260 and 2.63 (first part of d of ABq) arising from the H10' proton of the minor and major diastereomers respectively.

\(^{13}\)C NMR: 5 19.86, 20.27, 22.08, 22.60, 26.99, 30.11, 39.37, 44.47, 48.16, 49.01, 49.63, 53.20, 75.84, 76.45, 78.87, 79.11, 115.42, 115.85, 121.29, 124.86, 128.20, 128.55, 128.63, 129.41, 133.73, 137.91, 141.14, 141.52, 157.48, 163.94

The underlined peaks are due to the minor diastereomer.

MS (m/z): 588 (M\(^{+}\))

Analysis calcd. for C\(_{32}\)H\(_{42}\)NO\(_5\)SCI: C, 65.34; H, 7.20; N, 2.38

Found: C, 65.56; H, 7.27; N, 2.35

\((1'S,2'R,4'R)-1'-(\text{Diisopropylaminosulfonyl})\text{methyl}-7',7'-\text{dimethylbicyclo(2.2.1)}\text{hept}-2'-\text{yl} 3-(2\text{-chlorophenyl})-2\text{-methylene-3-phenoxypropanoate (185):}\)

This product was isolated as a colorless viscous liquid via the reaction of allyl bromide with phenol in the presence of triethylamine, following the similar procedure described for the molecule 181.
Reaction time: 4 h

Yield: 64%

de: 67%

Optical rotation: \([\alpha]_D^{25} 2.22 \text{ (c 1.88, CHCl}_3\)\)

IR (Neat): \(\nu 1720, 1635 \text{ cm}^{-1}\)

'H NMR: \(5 0.56, 0.78, 0.75 & 0.80 \text{ (4s, 6H, H9', H8')}, 1.05-2.02 \text{ (m, 19H, 2xCH(CH}_3)_2, H3', H4', H5', H6')}, 2.59 & 3.23 \text{ and 2.62 & 3.19 (2ABq, 2H, / = 13.2 Hz, H10')}, 3.56-3.74 \text{ (m, 2H, 2xCH(CH}_3)_2)}, 4.92-5.02 \text{ & 5.05-5.18 (2m, 1H, H2')}, 5.31 \text{ & 5/77 (2s, 1H, H3)}, 6.15, 6.42, 6.45 \text{ (3s, 2H, Hb, Ha)}, 6.72-6.95 \text{ (m, 3H, aromatic)}, 7.06-7.45 \text{ (m, 6H, aromatic)}

The underlined chemical shifts arise due to the minor diastereomer.

The two singlets at 6 5.31 & 5.77 arise from the benzylic (H3) protons of the major and minor diastereomers respectively. The diastereomeric excess was determined by the integration (83.5:16.5) of these two singlets and was found to be 67%. The diastereoselectivity is further confirmed by the integration of two multiplets at 8 4.92-5.02 & 8 5.05-5.18 which are in the ratio of 16.5:83.5 arising due to H2' proton of minor and major diastereomers respectively.
$^{13}$C NMR: 5 19.38, 19.91, 20.36, 22.16, 22.81, 27.03, 29.99, 30.66, 39.41, 39.58, 44.53, 48.25, 49.04, 49.59, 53.09, 53.44, 74.21, 74.61, 79.00, 79.33, 115.41, 115.78, 120.30, 121.31, 126.13, 127.16, 128.13, 128.70, 129.41, 129.77, 133.35, 134.34, 136.12, 136.45, 138.80, 140.57, 156.06, 157.93, 163.89, 164.28

The underlined peaks are attributed to the minor diastereomer.

Analysis calcd. for C$_{32}$H$_{42}$NO$_5$SCI: C, 65.34; H, 7.20; N, 2.38

Found: C, 65.58; H, 7.14; N, 2.40

(1'S,2'R,4'R)-1-(Diisopropylaminosulfonyl)methyl-7',7'-dimethylbicyclo(2.2.1)hept-2'-yl3-(2,4-dichlorophenyl)-2-methylene-3-phenoxypropanoate (186):

The reaction of allyl bromide 174 with phenol in the presence of triethylamine, following the similar procedure described for the molecule 181, furnished the desired product 186, as a colorless solid.

Reaction time: 4 h

Yield: 59%

de: 54%

Mp.: 50-52 °C

Optical rotation: $\left[\alpha\right]_D^{25}$ -8.96 (c 2.55, CHCl$_3$)

IR (KBr): v 1720, 1635 cm$^{-1}$
$^1$H NMR: 

8 0.69-1.02 (m, 6H, H9', H8'), 1.11-1.47 (m, 12H, 2xCH(CH$_3$)$_2$), 1.54-2.12 (m, 7H, H3', H4', H5', H6'), 2.62-2.83 (m, 1H, H10'), 3.19-3.34 (m, 1H, H10'), 3.59-3.83 (m, 2H, 2xCH(CH$_3$)$_2$), 5.01-5.11 & 5.13-5.23 (2m, 1H, H2'), 5.48 & 5.86 (2s, 1H, H3), 6.25 (s) & 6.42-6.55 (m, 2H, Hb, Ha), 6.81-7.04 (m, 3H, aromatic), 7.14-7.48 (m, 5H, aromatic)

The underlined peaks are due to minor diastereomer.

The two singlets at 8 5.48 & 5.86 in the ratio of 77:23 arise from the benzylic (H3) protons of major and minor diastereomers respectively, indicating 54% diastereoselectivity in this reaction. Diastereoselectivity was further confirmed by the integration of the multiplets at 8 5.01-5.11 & 5.13-5.23 arising from the methine protons at C2' of minor and major diastereomers respectively.

$^{13}$C NMR: 

8 19.44, 19.90, 20.29, 22.13, 22.71, 26.99, 30.04, 30.64, 39.40, 39.56, 44.49, 48.20, 49.01, 49.59, 53.11, 53.42, 73.78, 74.19, 79.00, 79.33, 115.74, 121.51, 126.09, 127.31, 127.46, 127.84, 129.43, 129.63, 134.14, 134.62, 134.80, 134.97, 135.24, 138.67, 140.13, 157.65, 163.60, 163.88

The underlined peaks arise due to the minor diastereomer.

Analysis **calcd.** for C$_{32}$H$_{41}$NO$_5$SCl$_2$:  C, 61.73; H, 6.64; N, 2.25

**Found:**  C, 61.55; H, 6.66; N, 2.19
Reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water:

A mixture of pyridine-4-carboxaldehyde (130j) (2 mmol, 0.214 g), 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) and phenyl vinyl sulfoxide (188) (2 mmol, 0.304 g) in 1 mL of dioxane/water (1:1) was kept at room temperature for 6 h. The reaction mixture was extracted with CHCl₃ (4x40 mL) and washed with brine. The combined organic layer was dried over anhydrous sodium sulfate (Na₂SO₄). Solvent was evaporated and the crude product thus obtained, was subjected to column chromatography (silica gel) which provided phenyl vinyl sulfoxide (188), as colorless liquid, in 47% (0.144 g) (recovered) yield (with 12% EtOAc in hexanes), 4-pyridinemethanol (189) as colorless solid, in 27% (0.060 g) yield (with 100% EtOAc) and 1-phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190), as a colorless liquid, in 10% (0.051 g) yield (with 1% MeOH in EtOAc).

Phenyl vinyl sulfoxide (188):

IR(Neat): \( \nu \) 3479, 1047 cm⁻¹

\(^1\)H NMR: 6.589 (d, 1H, \( J = 9.4 \) Hz), 6.19 (d, 1H, \( J = 16.6 \) Hz), 6.60 (dd, 1H, \( J = 16.6 \) & 9.4 Hz), 7.46-7.69 (m, 5H)

\(^{13}\)C NMR: \( \delta \) 120.26, 124.27, 129.12, 130.90, 142.69, 142.98
4-Pyridinemethanol (189):

Mp.: \( 55-57 ^\circ \text{C} \) (lit.\(^{273} 57-59 ^\circ \text{C} \)

IR (KBr): \( \nu \) 3375 cm\(^{-1} \)

\(^1\text{H} \) NMR: \( 6.26 \) (b, 1H), 4.74 (s, 2H), 7.29 (d, 2H, \( J = 6.0 \) Hz), 8.53 (d, 2H, \( J = 6.0 \) Hz)

\(^{13}\text{C} \) NMR: 6 62.54, 121.34, 148.84, 151.95

1-Phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190):

IR (Neat): \( \nu \) 3435, 1111,1041 cm\(^{-1} \)

\(^1\text{H} \) NMR: 6 2.85-3.23 (m, 2H), 3.62-4.15 (m, 2H), 4.51 & 4.60 (ABq, 2H, \( J = 12.0 \) Hz), 7.23 (d, 2H, \( J = 5.0 \) Hz), 7.36-7.74 (m, 5H), 8.56 (d, 2H, \( J = 5.0 \) Hz)

\(^{13}\text{C} \) NMR: 6 57.85, 63.60, 71.54, 121.72, 123.88, 129.32, 131.09, 143.97, 146.83, 149.72

MS (\( m/z \)): 262 (M\(^{+} \)+1)

However, \(^1\text{H} \) NMR and \(^{13}\text{C} \) NMR spectral data indicate that this molecule is contaminated with ~5-10% impurities. This spectral data (except the impurities) is in complete agreement with that of the pure product 190 obtained via the Michael addition of 189 to 188 in the presence of TMG (187) (page no. 201).
Reaction of 4-pyridinemethanol (189) with phenyl vinyl sulfoxide (188) in the presence of TMG (187):

The treatment of a mixture of 4-pyridinemethanol (189) (1 mmol, 0.109 g) and phenyl vinyl sulfoxide (188) (1 mmol, 0.152 g) with 1,1,3,3-tetramethylguanidine (187) (1 mmol, 0.115 g) for 6 h at room temperature (following the similar work-up procedure described for the reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water) afforded 1-phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190), as a colorless liquid, in 17% (0.045 g) yield along with recovered 4-pyridinemethanol (189) (59%) and phenyl vinyl sulfoxide (188) (20%).

1-Phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190)

IR (Neat): \( \nu \) 3445, 1043, 1113 cm\(^{-1} \)

\(^1\)H NMR: \( \delta \) 2.86-3.20 (m, 2H), 3.67-4.09 (m, 2H), 4.47 & 4.56 (ABq, 2H, \( \gamma = 12.0 \) Hz), 7.19 (d, 2H, \( J = 5.0 \) Hz), 7.38-7.75 (m, 5H), 8.52 (d, 2H, \( J = 5.0 \) Hz)

\(^{13}\)C NMR: 85 57.88, 63.60, 71.56, 121.72, 123.86, 129.34, 131.09, 143.94, 146.81, 149.77

Reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187), in THF-water:

The treatment of a mixture of pyridine-4-carboxaldehyde (130j) (2 mmol, 0.214 g) and phenyl vinyl sulfoxide (188) (2 mmol, 0.304 g) in 1 mL of THF/water (1:1) with
1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g), following the similar procedure described for the reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water, afforded 4-pyridinemethanol (189) as colorless solid, in 23% (0.051 g) yield and 1-phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190), as a colorless liquid, in 11% (0.059 g) yield. Phenyl vinyl sulfoxide (188) was recovered as colorless liquid, in 46% (0.141 g) yield.

4-Pyridinemethanol (189):

Mp.: 55-57 °C (lit.273 57-59 °C)
Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are in agreement with that of the molecule obtained on reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water.

1-Phenylsulfinyl-2-(4-pyridylmethoxy)ethane (190):

Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are identical with that of the molecule obtained by the reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water. $^1$H NMR and $^{13}$C NMR spectral data also indicate the presence of ~5-10% impurities.
Cannizzaro reaction

Reaction between pyridine-4-carboxaldehyde (130j) and 1,1,3,3-tetramethylguanidine (187) in water:

4-Pyridinemethanol (189):

A mixture of pyridine-4-carboxaldehyde (130j) (2 mmol, 0.214 g) and 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) in 0.5 mL of water was kept at room temperature for 5 h. The reaction mixture was extracted with CHCl₃ (4x40 mL) and washed with brine. The combined organic layer was dried over anhydrous sodium sulfate (Na₂SO₄). Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 100% EtOAc) to afford the pure molecule 189, as a colorless solid, in 42% (0.092 g) yield (expected yield, 50% (0.109 g)). Our attempts to isolate the corresponding acid in pure form were not successful.

Mp.: 56-59 °C (lit. 57-59 °C)

Spectral data (IR, ¹H and ¹³C NMR) of this molecule are in complete agreement with that of the molecule obtained on reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water.

Reaction between pyridine-3-carboxaldehyde (130k) and 1,1,3,3-tetramethylguanidine (187) in water:

3-Pyridinemethanol (191):

Treatment of pyridine-3-carboxaldehyde (130k) with 1,1,3,3-tetramethylguanidine (187), following the similar procedure described for the molecule 189 (from pyridine-4-
carboxaldehyde and TMG), provided 3-pyridinemethanol (191), as a colorless liquid, in 43% (0.093 g) yield {expected yield, 50% (0.109 g)}.

Reaction time: 7 h
IR (Neat): \( \nu \ 3308 \text{ cm}^{-1} \)

\[ \begin{align*}
&\text{H NMR:} \quad \delta \ 1.92 (b, 1H), 4.74 (s, 2H), 7.23-7.38 (m, 1H), 7.73 (d, 1H, J = 7.8 \text{ Hz}), 8.52 (d, 1H, J = 4.6 \text{ Hz}), 8.58 (s, 1H) \\
&C NMR: \quad S \ 61.61, 123.57, 135.16, 137.44, 147.68
\end{align*} \]

Reaction between pyridine-2-carboxaldehyde (1301) and 1,1,3,3-tetramethylguanidine (187) in water:

2-Pyridinemethanol (192):
The treatment of pyridine-2-carboxaldehyde (1301) with 1,1,3,3-tetramethylguanidine (187) in water, following the similar procedure described for 189 (from pyridine-4-carboxaldehyde and TMG), afforded the desired molecule 192, as a colorless liquid.

Reaction time: 5 h
Yield: 35% (0.077 g) {expected yield, 50% (0.109 g)}
IR (Neat): \( \nu \ 3356 \text{ cm}^{-1} \)

\[ \begin{align*}
&\text{H NMR:} \quad 5 \ 2.80 (s, 1H), 4.76 (s, 2H), 7.15-7.39 (m, 2H), 7.61-7.78 (m, 1H), 8.57(d, 1H, J = 4.8 \text{ Hz}) \\
&C NMR: \quad S \ 64.43, 120.71, 122.11, 136.81, 148.36, 160.20
\end{align*} \]
Reaction between 4-nitrobenzaldehyde (130m) and 1,1,3,3-tetramethylguanidine (187) in water:

**4-Nitrobenzyl** alcohol (193):

A mixture of 4-nitrobenzaldehyde (130m) (2 mmol, 0.302 g) and 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) in 0.5 mL of water was refluxed for 30 minutes. The reaction mixture was then cooled to room temperature and extracted with CHCl₃ (3x20 mL). The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 20% EtOAc in hexanes) to afford 4-nitrobenzyl alcohol (193), as a yellow colored crystalline solid, in 36% (0.110 g) yield (expected yield, 50% (0.153 g)).

Mp.: 91-93 °C (lit. 92-94 °C)

IR(KBr): ν 3514 cm⁻¹

¹H NMR: δ 1.92 (t, 1H, J = 6.0 Hz), 4.83 (d, 2H, J = 6.0 Hz), 7.53 (d, 2H, J = 8.6 Hz), 8.22 (d, 2H, J = 8.6 Hz)

¹³C NMR: δ 63.93, 123.67, 127.04, 147.29, 148.39

4-Nitrobenzoic acid (194):

The aqueous layer in the above-mentioned experiment was acidified with conc. HCl, extracted with ethyl acetate (2x20 mL). The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. Solvent was evaporated and the crude product thus obtained, was crystallized from EtOAc: hexanes (1:4) to provide 4-nitrobenzoic
acid (194), as colorless crystalline solid, in 42% (0.141 g) yield {expected yield, 50% (0.167 g)}.

\[ \text{M} \ddot{\text{p}}. : \quad 240-243^\circ \text{C} \ (\text{lit.} \ 239-245^\circ \text{C}) \]

IR (KBr): \[ 3150-2300, 1689, 1606 \ \text{cm}^{-1} \]

\(^1\text{H} \text{NMR}:\]
\[ \text{(DMSO-d}_6\text{)} \quad 8.17 \ (d, 2\text{H}, J = 8.6 \text{ Hz}), 8.32 \ (d, 2\text{H}, J = 8.6 \text{ Hz}) \]

\(^{13}\text{C} \text{NMR} :\]
\[ \text{(DMSO-d}_6\text{)} \quad 123.75, 130.81, 136.60, 150.19, 165.92 \]

Reaction between 3-nitrobenzaldehyde (130n) and 1,1,3,3-tetramethylguanidine (187) in water:

3-Nitrobenzyl alcohol (195):

The reaction of 3-nitrobenzaldehyde (130n) with 1,1,3,3-tetramethylguanidine (187) in water (0.5 mL), following the similar procedure as in the case of 4-nitrobenzaldehyde, provided 3-nitrobenzyl alcohol (195), as a yellow colored viscous liquid and 3-nitrobenzoic acid (196), as a light yellow colored crystalline solid.

Reaction time: \[ 10 \text{ h} \]

Yield: \[ 42\% \ (0.128 \text{ g}) \{\text{expected yield, 50\% (0.153 g)}\} \]

IR (Neat): \[ \nu \ 3385 \ \text{cm}^{-1} \]

\(^1\text{H} \text{NMR}:\]
\[ \text{(1H)} \quad 1.91 \ (t, 1\text{H}, J = 5.8 \text{ Hz}), 4.82 \ (d, 2\text{H}, J = 5.8 \text{ Hz}), 7.47-7.62 \ (\text{m}, 1\text{H}), 7.70 \ (d, 1\text{H}, J = 7.6 \text{ Hz}), 8.14 \ (d, 1\text{H}, J = 8.2 \text{ Hz}), 8.25 \ (s, 1\text{H}) \]}
\[ ^{13}\text{C NMR:} \quad 663.50, 121.23, 122.16, 129.28, 132.64, 143.00, 148.14 \]

3-Nitrobenzoic acid (196):

Yield: \( 43\% \) (0.144 g) \{expected yield, 50\% (0.167 g)}

\[ \text{Mp.:} \quad 141-143 \degree \text{C (lit.}^{276} 140-142 \degree \text{C)} \]

IR (KBr): \( \nu \) 3200-2400, 1703, 1618 cm\(^{-1}\)

\[ ^{1}\text{H NMR:} \quad \delta \ 5.70 \text{ (b, 1H), 7.65-7.87 (m, 1H), 8.39-8.65 (m, 2H), 8.91-9.08 (m, 1H)} \]

\[ ^{13}\text{C NMR:} \quad \delta 125.28, 128.37, 129.96, 131.09, 135.80, 148.58, 170.14 \]

4-Pyridinemethanol (189):

\[ \text{[via TMG-mediated cross-Cannizzaro reaction between pyridine-4-carboxaldehyde (130j) and formalin in the ratio of 1:1]} \]

To a mixture of pyridine-4-carboxaldehyde (130j) (2 mmol, 0.214 g) and formalin (37\% w/v) (2 mmol, 0.162 mL) in 0.5 mL of water, was added 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) drop-wise and kept at room temperature for 4 h. The reaction mixture was extracted with CHCl\(_3\) (3x40 mL) and the combined organic layer was washed with brine and dried over anhydrous sodium sulfate (Na\(_2\)SO\(_4\)). Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 100\%EtOAc) to afford the desired product 189, as a colorless solid, in 50\% (0.109 g) yield \{expected yield, 100\% (0.218 g)}.
Mp.: 56-59 °C (lit. 57-59 °C)

Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are identical with that of the molecule obtained on reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water (page no. 200).

The TMG promoted cross-Cannizzaro reaction of pyridine-4-carboxaldehyde (J30j) (2 mmol 0.214 g) with 2, 4, 8 and 16 equivalents of formalin (37% w/v) in the presence of 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) for 1.5, 1.5, 4 and 7 hours respectively, following the similar procedure described for the preparation of 189 [from pyridine-4-carboxaldehyde (130j) and formalin in the ratio of 1:1], provided 4-pyridinemethanol as colorless solid, in 57, 59, 60 and 64% yields respectively.

Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are identical with that of the molecule obtained on reaction of pyridine-4-carboxaldehyde (130j) and phenyl vinyl sulfoxide (188) with TMG (187) in dioxane-water (page no. 200).

3-Pyridinemethanol (191):

[via TMG-mediated cross-Cannizzaro reaction between pyridine-3-carboxaldehyde (130k) and formalin in the ratio of 1:16]

The treatment of a mixture of pyridine-3-carboxaldehyde (130k) (2 mmol, 0.214 g) and formalin (37% w/v) (32 mmol, 2.59 mL) with 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g), following the similar procedure described for the preparation of 189
[from pyridine-4-carboxaldehyde (130j) and formalin in the ratio of 1:1], provided the desired compound 191, as a colorless liquid.  

Reaction time: 1 ½ days  

Yield: 54% (0.118 g) {expected yield, 100% (0.218 g)}

Spectral data (IR, \(^1\)H and \(^{13}\)C NMR) of this molecule are in agreement with that of the molecule prepared from pyridine-3-carboxaldehyde (130k) and 1,1,3,3-tetramethylguanidine (page no. 204).

2-Pyridinemethanol (192):  
\(/via\) TMG-mediated cross-Cannizzaro reaction between pyridine-2-carboxaldehyde (130l) and formalin in the ratio of 1:16]  

This molecule is prepared \(/via\) the reaction of a mixture of pyridine-2-carboxaldehyde (130l) (2 mmol, 0.214 g) and formalin (37% w/v) (32 mmol, 2.59 mL), with 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g), following the similar procedure described for the preparation of 189 [from pyridine-4-carboxaldehyde (130j) and formalin in the ratio of 1:1], as colorless liquid.  

Reaction time: 1 ½ days  

Yield: 51% (0.111 g) {expected yield, 100% (0.218 g)}
Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are in full agreement with that of the molecule prepared from pyridine-2-carboxaldehyde (130l) and 1,1,3,3-tetramethylguanidine (page no. 204).

4-Nitrobenzyl alcohol (193): [via TMG-mediated cross-Cannizzaro reaction between 4-nitrobenzaldehyde (130m) and formalin in the ratio of 1:16]

A mixture of 4-nitrobenzaldehyde (130m) (2 mmol, 0.302 g), formalin (37% w/v) (32 mmol, 2.59 mL) and 1,1,3,3-tetramethylguanidine (187) (2 mmol, 0.23 g) in 0.5 mL of water was refluxed for 6 h. The reaction mixture was then cooled to room temperature, extracted with CHCl$_3$ (20 mL) and washed with water. The organic layer was dried over anhydrous Na$_2$SO$_4$. Solvent was evaporated and the crude product thus obtained, was purified by column chromatography (silica gel, 20% EtOAc in hexanes) to afford 4-nitrobenzyl alcohol (193), as a yellow colored crystalline solid, in 73% (0.224 g) yield {expected yield, 100% (0.306 g)}.

Mp: 92-94 °C (lit.$^{275}$ 92-94 °C)

Spectral data (IR, $^1$H and $^{13}$C NMR) of this molecule are identical with that of the molecule prepared from 4-nitrobenzaldehyde (130m) and 1,1,3,3-tetramethylguanidine (page no. 205).
3-Nitrobenzyl alcohol (195): 

\[via\] TMG-mediated cross-Cannizzaro reaction between 3-nitrobenzaldehyde (130n) and formalin in the ratio of 1:16

This compound was isolated as yellow colored viscous liquid via the treatment of a mixture of 3-nitrobenzaldehyde (130n) and formalin, with 1,1,3,3-tetramethylguanidine (187), following the similar procedure described for the preparation of 193 [from the 4-nitrobenzaldehyde (130m) and formalin in the ratio of 1:16].

Reaction time: 6 h

Yield: 68% (0.209 g) \{expected yield, 100% (0.306 g)\}.

Spectral data (IR, \(^1\)H and \(^{13}\)C NMR) of this molecule are in complete agreement with that of the molecule prepared from 3-nitrobenzaldehyde (130n) and 1,1,3,3-tetramethylguanidine (page no. 206).
$^{13}$C NMR spectrum of 114
$^1$H NMR spectrum of 133a

Spectrum 11
$^1$C NMR spectrum of 133a
$^{13}$C NMR spectrum of 133e
$^1$H NMR spectrum of 156a

(A) Expansion of the diastereomeric β-vinylc (Ha) protons (cis- to ester group), 18% de
$^1$H NMR spectrum of 158a

(A) Expansion of the diastereomeric benzylic (H3) protons, 35% de
$^1$H NMR spectrum of 175

(A) Expansion of the diastereomeric β-vinylic (Hb) protons (trans- to ester group), 88% de
$^1$H NMR spectrum of 175* 

(A) Expansion of the β-vinylic (Hb) proton (trans- to ester group), 100% de
$^{13}$C NMR spectrum of 175
$^{13}$C NMR spectrum of 175*
$^1$H NMR spectrum of 176
(A) Expansion of the diastereomic β-vinylic (Hb) protons (trans- to ester group), 84% de
$^1$H NMR spectrum of 176*

(A) Expansion of the β-vinylic (Hb) proton (trans- to ester group), 100% de
$^1$H NMR spectrum of 181

(A) Expansion of the diastereomeric benzylic (H3) protons, 82% de
Splitting pattern of H3, Hb and Ha protons of the molecule 181 in the presence of Eu(hfc)₃, 82% de

Splitting pattern of H3 and Hb protons of the molecule 181 in the presence of Eu(fod)₃, 82% de
(A) Expansion of the diastereomeric benzyllic (113) protons, 76% de

(B) Expansion of the diastereomeric methyl protons on the aromatic ring, 70% de
Splitting of H2' proton of the molecule 182 in the presence of Eu(fod)3, 76% de

Spectrum 34
$^1$H NMR spectrum of 183

(A) Expansion of the diastereomeric benzylc (H3) protons, 78% ee
$^{13}$C NMR spectrum of 185

*Spectrum 36*
1H NMR spectrum of 190
$^1$H NMR spectrum of 193

Spectrum 41
$^{13}$C NMR spectrum of 194