EXPERIMENTAL

- **Melting and Boiling Points**
  - All melting points (m.p.) and boiling points (b.p.) are uncorrected and are expressed in degree centigrade (°C), the suffix ‘C’ has been omitted.

- **Infrared Spectrometer**
  - Infrared spectra were recorded using a Perkin-Elmer Model RX 1 FT-IR spectrophotometer. Only principal peaks of interest are reported and expressed in cm⁻¹.

- **Nuclear Magnetic Resonance Spectrometer**
  - The ¹H NMR spectra were recorded on Varian EM-360 (60 MHz) and Brucker AC 300F, 300 MHz spectrometer. Chemical shift values are expressed as δ values (ppm) downfield from tetramethylsilane (TMS) used as internal standard.

- **Column Chromatography**
  - Column chromatography was performed with silica gel (Acme’s Synthetic Chemicals, 100-200 mesh) and eluted with ethylacetate/n-hexane solvent system unless otherwise stated.

- **Thin Layer Chromatography**
  - Thin Layer chromatography was performed using TLC grade silica gel ‘G’ (Acme’s Synthetic Chemicals). The spots were made visible by exposing to iodine vapours.

- **Microwave Oven**
  - The microwave assisted reactions were carried out in BPL BMO 700T (640W) and LG MS-194A (800W) microwave oven.

- **Ultrasonic Source**
  - The ultrasonic reactions were carried out in:
    - Branson B-2200 El, (60 W, 47 kHz) ultrasonic cleaner, using ice-cold water as the medium.
    - Heat system probe sonicator model XL 2015 (20 kHz)
  - Nitrogen gas was purified and dried by passing through columns of copper catalyst (BASF) heated at 200° followed by those of CaCl₂, KOH, dry molecular sieves and P₂O₅.
  - Reagents were transferred using standard syringe spectrum cap techniques.
  - Temp. of -78° was attained by using liquid Nitrogen ethyl acetate slush bath.

*Experimental*
• All solvents and reagents were purified and dried before use according to standard methods.

• All organic extracts with density less than water were dried over anhydrous Na₂SO₄ and all organic extracts with density more than water were dried over CaCl₂ unless otherwise specified.

• THF, diethyl ether and hexane were dried by distilling over sodium benzophenone ketyl prior to use.

• Carbon tetrachloride, chloroform, dichloromethane were dried by distilling over P₂O₅ and stored over calcium chloride.

• DMF was dried by azeotropic distillation with benzene and distilled over CaH₂ and stored over 4Å molecular sieves.

• Pyridine and triethylamine were distilled and stored over KOH pellets.

• DBU was dried by distilling over CaH₂.

• Dilithium Tetrachlorocuprate

Li₂CuCl₄ was prepared by dissolving lithium chloride (0.085 g, 2.0 mmol) in dry THF (5 mL) and cupric chloride (0.135 g, 1.0 mmol) in dry THF (5 mL) separately and then mixing the two to get a blood-red solution.

• Pyridinium Chlorochromate

To 6N HCl (18.4 mL) was added chromium trioxide (10 g, 100 mmol) rapidly with stirring. After 5 min. the homogeneous solution was cooled to 0° and pyridine (7.9 g, 100 mmol) was carefully added over 10 min. duration. The resultant yellow orange solid of pyridinium chlorochromate that precipitated out was filtered and dried for 1h in vacuo, (yield 74%).

• Pyridinium Dichromate

Pyridine (19.71 g, 249 mmol) was added slowly to a cooled solution of chromium trioxide (25 g, 250 mmol) in water (25 mL) at room temperature the solution was diluted with acetone (100 mL) and refrigerated overnight. The resultant orange crystals were collected, washed with acetone and dried under vacuum (yield 68%).

• Quinolinium Chlorochromate

Quinoline (109 mmol, 13 mL) was added dropwise to a cooled and stirred mixture of chromium trioxide (100 mmol, 10 g) and conc. hydrochloric acid (11 mL) in 10 mL of Experimental
water in 250 mL beaker. The yellowish brown solid was obtained which was isolated through suction and dried in vacuo affording 22.4 g (77%) of the reagent (m.p. 65-66°).

- **Quinolinium Fluorochromate**
  Chromium trioxide (15 g, 0.15 mol) was dissolved in water (25 mL) in a beaker and 40% hydrofluoric acid (11.3 mL, 0.23 mol) added to it with stirring at room temperature, a clear solution resulted in within 5 min. To this solution, quinoline (17.7 mL, 0.15 mol) was added slowly with stirring. The mixture was heated on a steam bath for half an hour, then cooled to room temperature and allowed to stand for 1 h. The bright red-orange crystalline quinolinium fluorochromate was isolated by filtration and dried in vacuo for 1 h, m.p. 162-163°, yield 86%.

- **Phosphorus Tribromide**
  To a dry three-necked flask equipped with magnetic stirring bar, dropping funnel and guard tube (CaCl₂) was added red phosphorus (5.6 g, 180 mmol) and CCl₄ (50 mL) (dried over anhydrous CaCl₂) and the flask was ice-cooled. Bromine (40 g, 250 mmol) was introduced via dropping funnel to the stirred reaction mixture. The temperature was then slowly raised and the reaction mixture was heated for half an hour. Filtration was then accomplished over glass wool. The filtrate was distilled to get pure PBr₃ in 94% yield, b.p. 175°.

- **Sodamide**
  Into a three-necked 500 mL round-bottomed flask equipped with a liquid nitrogen reflux condenser, was introduced distilled NH₃ (150 mL). To it was added sodium metal (0.89 g) as small pieces over half an hour with stirring. Excess NH₃ was allowed to evaporate to result in free flowing sodamide (1.5 g).

- **Jones Reagent**
  In a 100 mL conical flask containing chromium trioxide (26.7 g, 2.67 mol) was added conc. H₂SO₄ (23 mL) was added water (77 mL) to result in blood red colour.

**Ethoxy-3,7-dimethyloct-6-ene (2)**

To a 100 mL round-bottomed flask equipped with a magnetic bead and a guard tube containing powdered potassium hydroxide (0.72 g, 12.8 mmol) in dimethylsulphoxide (20 mL) was added citronellol (1, 1 g, 6.4 mmol) and bromoethane (1.04 g, 9.6 mmol) over 5 min. The reaction mixture was allowed to stir overnight, quenched with water (20 mL) and extracted with dichloromethane (2x20 mL). The combined organic extract was washed with

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water (2x5 mL), brine and dried. Solvent was evaporated under vacuum to get the pure product (2, 0.97 g, 82%).

IR (neat)*/ν* max cm⁻¹: 3500, 3010, 2960, 2910, 1640, 500.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, *J*=6Hz, 3H, -CH(CH₃)₂)
1.2 (t, *J*=6Hz, 3H, -OCH₂CH₃)
1.2-1.6 (m, 5H, -CH₂CH₂CH(CH₃)CH₂CH₂-)
1.7 & 1.9 (2s, 6H, (CH₃)₂C=)
2.2-2.6 (m, 2H, -CH₂CH₂CH=)
3.1-3.6 (m, 4H, -CH₂OCH₂CH₂)
5.2 (t, *J*=6Hz, 1H, -CH₂CH=)

3,7-Dimethyloct-6-ene 4'-methylphenylsulphonate (3)

To ice-cold solution of citronellol (1, 1 g, 6.4 mmol) in dry dichloromethane (5 mL) and pyridine (1.03 g, 13.0 mmol) was added a solution of p-toluenesulphonyl chloride (1.32 g, 6.95 mmol) in dry DCM (5 mL). After 5h of stirring, the reaction mixture was diluted with dichloromethane (10 mL). The organic layer was washed with ice-cold 2% HCl (5 mL), ice-cold 2% aq. NaOH (5 mL), cold water (5 mL), brine, dried and concentrated *in vacuo* to afford the pure tosylate (3, 1.79 g, 90%).

IR (neat)*/ν* max cm⁻¹: 3030, 2970, 2900, 1640, 1500, 1450.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, *J*=6Hz, 3H, -CH(CH₃)₂)
1.2-1.6 (m, 5H, -CH₂CH₂CH(CH₃)CH₂CH₂-)
1.6 & 1.8 (2s, 6H, (CH₃)₂C=)
2.1-2.4 (m, 2H, -CH₂CH₂CH=)
2.5 (s, 3H, -C₆H₅CH₃)
4.0 (t, *J*=6Hz, 2H, -CH₂CH₂OSO₂⁻)
5.2 (t, *J*=6Hz, 1H, -CH₂CH=)
7.3 (d, *J*=8Hz, 2H, -ArH)
7.8 (d, *J*=8Hz, 2H, -ArH)

3,7-Dimethyloct-6-ene methylsulphonate (4)

Methanesulphonyl chloride (1.26 g, 11.0 mmol) in dry dichloromethane (5 mL) was added to a mixture of citronellol (1, 1.72 g, 11.0 mmol) and triethylamine (1.11 g, 11.0 mmol) in dry dichloromethane (10 mL) at 0°. The mixture was stirred for 2h, diluted with DCM (2x10 mL), washed with water (5 mL), brine and dried. The solvent was evaporated under

*Experimental*
vacuum to furnish the product which was purified via silica gel column chromatography using 5\% ethyl acetate in \textit{n}-hexane as eluant to afford the mesylate (4, 2.19 g) in 85\% yield.

IR (neat)/\(v_{\text{max}}\) cm\(^{-1}\): 3020, 2990, 2940, 1665, 1460, 1370, 1170.

\(^{1}\text{H NMR (CCl\(_4\), 60 MHz):}\delta\)

1.0 (d, \(J=6\text{Hz}, 3\text{H}, -\text{CHCH}_3\))

1.2-1.5 (m, 5H, -\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CH}_2\text{CH}_2\text{)}

1.7 & 1.8 (2s, 6H, (\text{CH}_3)_2\text{C=})

2.0-2.3 (m, 2H, -\text{CH}_3\text{CH}_2\text{CH=})

3.0 (s, 3H, -\text{OSO}_2\text{CH}_3)

4.2 (t, \(J=6\text{Hz}, 2\text{H}, -\text{CH}_2\text{CH}_2\text{OSO}_2\text{)}\))

5.2 (t, \(J=6\text{Hz}, 1\text{H}, -\text{CH}_2\text{CH=})

\text{Tetrahydropyran-3,7-dimethyloct-6-ene (5)}

To an ice-cold well stirred solution of 3,4-dihydro-2H-pyran (0.27 g, 3.2 mmol) in dry dichloromethane (30 mL) was added a solution of citronellol (1, 0.5 g, 3.2 mmol) in dry dichloromethane (20 mL). Upon complete addition, conc. HCl (2 drops) was added and the contents were stirred overnight at r.t. The reaction mixture was extracted with DCM (3x30 mL), washed with brine, dried and evaporated to get crude product which was passed through a short alumina column eluting with \textit{n}-hexane. Evaporation of solvent \textit{in vacuo} provided pure compound (5, 0.62 g, 80\%).

IR (neat)/\(v_{\text{max}}\) cm\(^{-1}\): 3010, 2990, 2945, 1650, 1500, 1260, 1150.

\(^{1}\text{H NMR (CCl\(_4\), 60 MHz):}\delta\)

1.0 (d, \(J=6\text{Hz}, 3\text{H}, -\text{CHCH}_3\))

1.2-1.6 (m, 11H, ring protons, -\text{CH}_3\text{CH}_2\text{CH(CH}_3\text{)}\text{CH}_2\text{CH=})

1.7 & 1.9 (2s, 6H, (\text{CH}_3)_2\text{C=})

2.0-2.3 (m, 2H, -\text{CH}_3\text{CH}_2\text{CH=})

3.3-3.9 (m, 4H, -\text{CH}_2\text{CH}_2\text{O}, -\text{OCH}_2\text{CH}_2\text{)}

4.8 (t, \(J=4\text{Hz}, 1\text{H}, -\text{OCHO}\text{)}\))

5.2 (t, \(J=6\text{Hz}, 1\text{H}, -\text{CH}_2\text{CH=})

\text{3,7-Dimethyloct-6-enyl ethanoate (6)}

A solution of distilled acetic anhydride (0.86 g, 8.43 mmol) in dry dichloromethane (5 mL) was added to an ice-cold solution of citronellol (1, 1.0 g, 6.41 mmol) and pyridine (0.75 g, 9.5 mmol) in dry dichloromethane (20 mL). The contents were stirred overnight at r.t. The reaction mixture was extracted with diethyl ether (3x20 mL), washed with ice-cold 10\% HCl (5 mL), 5\% NaHCO\(_3\) (5 mL), water, brine and dried. The solvent was evaporated \textit{in vacuo} to afford 3,7-dimethyloct-6-enyl ethanoate (6, 1.14 g, 90\%).

\textbf{Experimental}
IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\) : 3020, 2960, 2910, 1740, 1640, 1500.

\(^1\)H NMR (\(\text{CCl}_4\), 60 MHz): \(\delta\) 1.1 (d, \(J=6\) Hz, 3H, -CHCH\(_3\) )
1.1-1.6 (m, 5H, -CH\(_2\)CH\(_2\)H(CH\(_3\))CH\(_2\)CH\(_3\)-)
1.8 & 1.9 (2s, 6H, (CH\(_3\))\(_2\)C=)
2.1 (s, 3H, -OCOC\(_3\) )
2.0-2.3 (m, 2H, -CH\(_2\)CH\(_3\)=)
4.1 (t, \(J=6\) Hz, 2H, -CH\(_2\)CH\(_2\)OCO-)
5.2 (t, \(J=6\) Hz, 1H, -CH\(_2\)CH=)

8-Bromo-2,6-dimethyloct-2-ene (7)

To a well stirred ice-cold solution of citronellol (1, 1.0 g, 6.41 mmol) and dry pyridine (1.01 g, 12.8 mmol) in dry ether (15 mL) was added dropwise PBr\(_3\) (0.69 g, 2.56 mmol) in dry ether (2 mL). Reaction was monitored via TLC and on completion, the reaction mixture was extracted with diethyl ether (3x10 mL). The combined organic extract was washed with water (2x10 mL), brine and dried. Evaporation of the solvent under reduced pressure afforded, pure 8-bromo-2,6-dimethyloct-2-ene (7, 1.01 g, 72%).

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\) : 3010, 2990, 2950, 1645, 1500, 660.

\(^1\)H NMR (\(\text{CCl}_4\), 60 MHz): \(\delta\) 0.9 (d, \(J=6\) Hz, 3H, -CHCH\(_3\) )
1.2-1.5 (m, 5H, -CH\(_2\)CH\(_2\)H(CH\(_3\))CH\(_2\)CH\(_3\)-)
1.7 & 1.8 (2s, 6H, (CH\(_3\))\(_2\)C=)
2.0-2.3 (m, 2H, -CH\(_2\)CH\(_3\)=)
3.3 (t, \(J=6\) Hz, 2H, -CH\(_2\)CH\(_2\)Br)
5.2 (t, \(J=6\) Hz, 1H, -CH\(_2\)CH=)

2,2-(Ethyleneedioxy)-6-methyIhept-5-ene (8)

In a 100 mL round-bottomed flask was taken 6-methylhept-5-en-2-one (1.0 g, 7.93 mmol) and ethylene glycol (0.25 g, 4.17 mmol) in dry benzene (25 mL). Triethylorthoformate (0.31 g, 2.11 mmol) and \(p\)-TSA (0.02 g, 0.1 mmol) were also added and the reaction mixture was stirred for 3.5h. On quenching with saturated solution of NaHCO\(_3\) (20 mL), the organic layer was separated and concentrated \textit{in vacuo}. The residue was diluted with diethyl ether (2x20 mL) and washed with brine, dried and concentrated under reduced pressure to give product (8) in 85% yield (1.14 g).

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\) : 3020, 2990, 2910, 1650, 1080, 970.

\textit{Experimental}
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 1.3 (s, 3H, CH$_3$C(O)(O)-)
1.6 & 1.8 (2s, 6H, (CH$_2$)$_2$C=)
2.0-2.4 (m, 4H, -CCH$_2$CH$_2$CH=)
4.0 (s, 4H, -OCH$_2$CH$_2$O-)
5.2 (t, $J$=6Hz, 1H, -CH$_2$CH=)

6-Methylhept-5-en-2-ol (9)

6-Methylhept-5-en-2-one (0.38 g, 3.0 mmol) was doped on freshly prepared sodium borohydride-alumina (1.13 g, 3.0 mmol) in a test tube and placed in an alumina bath inside the microwave oven and irradiated at 640 W for 1 min. Upon completion of the reaction, as monitored by TLC, the reaction mixture was extracted with diethyl ether (2x15 mL) and washed with brine and dried. Evaporation of the solvent in vacuo provided 6-methylhept-5-en-2-ol (9, 0.35 g, 92%).

IR (neat)/$\nu$ max cm$^{-1}$: 3500, 3000, 2980, 2945, 1660.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 1.1 (d, $J$=6Hz, 3H, -CHC=)
1.2-1.6 (m, 2H, -CH$_2$C-)
1.7 & 1.8 (2s, 6H, (CH$_2$)$_2$C=)
2.2-2.5 (m, 2H, -CH$_2$C=)
2.6 (bs, 1H, -OH, D$_2$O exchangeable)
3.5-3.9 (m, 1H, -CH$_2$CH(OH)=)
5.2 (t, $J$=6Hz, 1H, -CH$_2$CH=)

General procedure of allylic oxidation using SeO$_2$/TBHP under MWI:

2,6-Dimethyl-8-hydroxyoct-2-enal (18)

A mixture of citronellol (1, 0.5 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butyl hydroperoxide (0.43 g, 4.8 mmol) dissolved in dry DCM (5 mL) was doped on silica gel (1 g). Excess solvent was evaporated to provide free flowing solid, which was exposed to microwave irradiation at 640 W for 10 min. The reaction mixture was extracted with solvent ether (2x20 mL), washed with 10% aq. KOH solution (2x5 mL), water (2x5 mL), brine and dried. Evaporation of the solvent followed by silica gel column chromatography using 2% ethyl acetate in $n$-hexane as the eluent furnished pure 2,6-dimethyl-8-hydroxyoct-2-enal (18, 0.4 g, 74%).

IR (neat)/$\nu$ max cm$^{-1}$: 3400, 3020, 2720, 1700, 1610, 1080, 970.

Experimental
\[ \text{1H NMR (CDCl}_3, 60 \text{ MHz): } \delta \]

1.0 (d, \( J=6 \text{Hz}, 3 \text{H}, -\text{CHCH}_3 \))

1.1-1.6 (m, 5H, -CH\( _2\text{CH}_2\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{-})

1.8 (s, 3H, CH\( _3\text{C}=-\))

2.1-2.6 (m, 2H, -CH\( _2\text{CH}_2\text{CH}=-\))

3.3 (bs, 1H, -OH, D\( _2\text{O} \) exchangeable)

3.7 (t, \( J=6 \text{Hz}, 2 \text{H}, -\text{CH}_2\text{CH}_2\text{OH} \))

6.5 (t, \( J=6 \text{Hz}, 1 \text{H}, -\text{CH}_2\text{CH}=-\))

9.5 (s, 1H, -CHO)

**2,6-Dimethyl-8-ethoxyoct-2-enal (19)**

Ethoxy-3,7-dimethyloct-6-ene (2, 0.59 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) were adsorbed on silica gel (1 g) and subjected to MWI at 640 W for 10 min. The resultant product was worked up as described above to afford compound (19, 0.51 g, 81%).

IR (neat)/\( \nu_{\text{max}} \text{ cm}^{-1} \): 3020, 2720, 1700, 1610, 1080, 950.

\[ \text{1H NMR (CDCl}_3, 60 \text{ MHz): } \delta \]

1.0 (d, \( J=6 \text{Hz}, 3 \text{H}, -\text{CHCH}_3 \))

1.2 (t, \( J=6 \text{Hz}, 3 \text{H}, -\text{OCH}_2\text{CH}_3 \))

1.2-1.6 (m, 5H, -CH\( _2\text{CH}_2\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{-})

1.8 (s, 3H, CH\( _3\text{C}=-\))

2.2-2.6 (m, 2H, -CH\( _2\text{CH}_2\text{CH}=-\))

3.1-3.6 (m, 4H, -CH\( _2\text{CH}_2\text{OCH}_2\text{CH}_3 \))

6.5 (t, \( J=6 \text{Hz}, 1 \text{H}, -\text{CH}_2\text{CH}=-\))

9.5 (s, 1H, -CHO)

**7-Formyl-3-methyloct-6-ene 4’-methylphenylsuphfonate (20)**

Compound (3, 1.0 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) were impregnated on silica gel (1 g) and exposed to MWI at 640 W for 10 min. to provide after the usual work up and purification, pure 20 (0.76 g) in 73% yield.

IR (neat)/\( \nu_{\text{max}} \text{ cm}^{-1} \): 3020, 2990, 2720, 1690, 1625, 1500, 1450, 1070, 960.

\[ \text{1H NMR (CDCl}_3, 60 \text{ MHz): } \delta \]

1.0 (d, \( J=6 \text{Hz}, 3 \text{H}, -\text{CHCH}_3 \))

1.2-1.6 (m, 5H, -CH\( _2\text{CH}_2\text{CH(CH}_3\text{)CH}_2\text{CH}_2\text{-})

1.8 (s, 3H, CH\( _3\text{C}=-\))

2.0-2.3 (m, 2H, -CH\( _2\text{CH}_2\text{CH}=-\))

2.5 (s, 3H, -C\( _6\text{H}_4\text{CH}_3 \))

*Experimental*
4.0 (t, J=6Hz, 2H, -CH₂CH₂SO₂⁻)
6.5 (t, J=6Hz, 1H, -CH₃CH=)
7.3 (d, J=8Hz, 2H, -ArH)
7.8 (d, J=8Hz, 2H, -ArH)
9.5 (s, 1H, -CHO)

7-Formyl-3-methyloct-6-ene methylsulphonate (21)

3,7-Dimethyloct-6-ene methylsulphonate (4, 0.75 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) adsorbed on silica gel (1 g) were exposed to MWI at 640 W for 10 min. The resultant product on usual work up followed by purification via silica gel column chromatography gave compound (21, 0.64 g, 81%).

IR (neat)/νmax cm⁻¹ : 3030, 2990, 2710, 1690, 1620, 1450, 1080, 950.

1H NMR (CCl₄, 60 MHz): δ
1.0 (d, J=6Hz, 3H, -CH(CH₃)₃)
1.2-1.5 (m, 5H, -CH₂CH(CH₃)₂CH₂-)
1.8 (s, 3H, CH₃C=)
2.0-2.5 (m, 2H, -CH₂CH=)
3.0 (s, 3H, -SO₂CH₃)
4.2 (t, J=6Hz, 2H, -CH₂CH₂SO₂⁻)
6.5 (t, J=6Hz, 1H, -CH₂CH=)
9.5 (s, 1H, -CHO)

2,6-Dimethyl-8-tetrahydropyranyloxyoct-2-enal (22)

Compound (5, 0.77 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) adsorbed on silica gel (1 g) were subjected to MWI at 640 W for 10 min. to furnish after the usual work up and purification, pure product 22 (0.64 g) in 78% yield.

IR (neat)/νmax cm⁻¹ : 3010, 2990, 2720, 1700, 1630, 1260, 1070, 950.

1H NMR (CCl₄, 60 MHz): δ
1.0 (d, J=6Hz, 3H, -CH(CH₃)₃)
1.2-1.7 (m, 6H, ring protons, -CH₂CH₂CH(CH₃)₂CH₂CH₂-)
1.8 (s, 3H, CH₃C=)
2.1-2.5 (m, 2H, -CH₂CH₂CH=)
3.3-3.8 (m, 4H, -CH₂CH₂O⁻, -OCH₂CH₂⁻)
4.7 (t, J=4Hz, 1H, -OCHO⁻)
6.5 (t, J=6Hz, 1H, -CH₂CH=)
9.5 (s, 1H, -CHO)

Experimental
7-Formyl-3-methyloct-6-enyl ethanoate (23)

A mixture of 3,7-dimethyloct-6-enyl ethanoate (6, 0.63 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) impregnated on silica gel (1 g) was subjected to MWI at 640 W for 10 min. After the usual work up, the title compound (23, 0.47 g) was obtained in 70% yield.

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\):

\[\begin{array}{c}
3000, 2710, 1705, 1620, 1070, 950.
\end{array}\]

\(^1\)H NMR (CCl\(_4\), 60 MHz): \(\delta\)

\[\begin{array}{c}
1.0 (d, J=6Hz, 3H, -CHCH_3) \\
1.2-1.6 (m, 5H, -CH_2CH_2CH(CH_3)CH_2CH_2-) \\
1.8 (s, 3H, CH_3C=) \\
2.0 (s, 3H, -OCOCH_3) \\
2.2-2.6 (m, 2H, -CH_2CH=) \\
4.1 (t, J=6Hz, 2H, -CH_2CH_2OCO-) \\
6.5 (t, J=6Hz, 1H, -CH=CH-) \\
9.5 (s, 1H, -CHO)
\end{array}\]

8-Bromo-2,6-dimethyloct-2-enal (24)

A mixture of compound (7, 0.7 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) impregnated on silica gel (1 g) on subjection to MWI at 640 W for 10 min. afforded after usual work up crude product. It was purified by silica gel column chromatography using 2% ethyl acetate and n-hexane to yield pure (24, 0.56 g, 75%).

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\):

\[\begin{array}{c}
3030, 2990, 2710, 1700, 1610, 1070, 970, 660.
\end{array}\]

\(^1\)H NMR (CCl\(_4\), 60 MHz): \(\delta\)

\[\begin{array}{c}
1.0 (d, J=6Hz, 3H, -CHCH_3) \\
1.2-1.7 (m, 5H, -CH_2CH_2CH(CH_3)CH_2CH_2-) \\
1.8 (s, 3H, CH_3C=) \\
2.1-2.6 (m, 2H, -CH_2CH=) \\
3.5 (t, J=6Hz, 2H, -CH_2CH_2Br) \\
6.5 (t, J=6Hz, 1H, -CH=CH-) \\
9.5 (s, 1H, -CHO)
\end{array}\]

6,6-(Ethylene dioxy)-2-methylhept-2-enal (25)

Compound (8, 0.54 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) were impregnated on silica gel (1 g) and exposed to MWI at 640 W for 10 min. to provide, after the usual work up and purification, compound (25, 0.45 g) in 77% yield.

Experimental
IR (neat)/v<sub>max</sub> cm<sup>-1</sup>: 3020, 2980, 2710, 1690, 1620, 1080, 950.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz): δ 1.3 (s, 3H, CH<sub>3</sub>(O)(O)-)
1.8 (s, 3H, CH<sub>3</sub>=)
2.2-2.6 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CR=)
4.0 (s, 4H, -OCH<sub>2</sub>CH<sub>2</sub>O-)
6.5 (t, J=6Hz, 1H, -CH<sub>2</sub>CH=)
9.5 (s, 1H, -CHO)

6-Hydroxy-2-methylhept-2-enal (26)
A mixture of 6-methylhept-5-en-2-ol (9, 0.4 g, 3.2 mmol), selenium dioxide (0.17 g, 1.6 mmol) and tert-butylhydroperoxide (0.43 g, 4.8 mmol) impregnated on silica gel (1 g) was exposed to MWI at 640 W for 10 min. The reaction mixture was worked up as usual and purified via silica gel column chromatography using 2% ethyl acetate and n-hexane to afford the title compound (26, 0.3 g) in 69% yield.

IR (neat)/v<sub>max</sub> cm<sup>-1</sup>: 3500, 3010, 2990, 2720, 1700, 1630, 960.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz): δ 1.1 (d, J=6Hz, 3H, -CH<sub>3</sub>)
1.7 (s, 3H, CH<sub>3</sub>=)
2.2-2.5 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH=)
2.5 (bs, 1H, -OH, D<sub>2</sub>O exchangeable)
3.5-3.9 (m, 1H, -CH<sub>2</sub>CH(OH)-)
6.5 (t, J=6Hz, 1H, -CH<sub>2</sub>CH=)
9.5 (s, 1H, -CHO)

General procedure for the preparation of α,β-unsaturated ketones
4-PhenyIbut-3-en-2-one (31)
A mixture of benzaldehyde (10, 0.5 g, 4.7 mmol), acetone (11, 0.27 g, 4.7 mmol) and sodium hydroxide (0.19 g, 4.7 mmol) was ground in a mortar at r.t. for 5 min. The reaction mixture was extracted with diethyl ether (2x20 mL), washed with water (10 mL) and brine. The solvent was evaporated and the resultant product was purified via silica gel column chromatography eluted with 5% ethyl acetate and n-hexane to afford pure product (31, 0.6 g) in 88% yield, m.p. 40-42° (lit. 39-41°).

IR (CHCl<sub>3</sub>)v<sub>max</sub> cm<sup>-1</sup>: 3030, 1685, 1610, 800, 740, 680.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz): δ 2.3 (s, 3H, -COCH<sub>3</sub>)
6.5 (d, J=13.5Hz, 1H, -CH=CHCO-)
7.2-7.6 (m, 6H, C<sub>6</sub>H<sub>5</sub>CH=CHCO-)

Experimental 157
1,3-Diphenylprop-2-enone (32)

A mixture of benzaldehyde (10, 0.5 g, 4.7 mmol), acetophenone (12, 0.56 g, 4.7 mmol) and sodium hydroxide (0.19 g, 4.7 mmol) was ground for 5 min. in a mortar. Water (10 mL) was added to the resultant pale yellow solid and filtered to furnish pure 1,3-diphenylprop-2-enone (32, 0.93 g) in 95% yield, m.p. 58° (lit. 56-57°).

IR (CHCl₃)/ν max cm⁻¹: 3000, 1695, 1615, 810, 740, 660.

¹H NMR (CDCl₃, 60 MHz): δ 7.0-7.6 (s, 9H, \( \text{ArH} \)), 7.8-8.0 (m, 3H, \( =\text{CHCO}^-\)), \( \text{COAr}'\text{H} \)

3-(3',5'-Dimethoxyphenyl)-1-phenylprop-2-enone (33)

A mixture of 3,5-dimethoxybenzaldehyde (13, 0.5 g, 3.0 mmol), acetophenone (12, 0.36 g, 3.0 mmol) and sodium hydroxide (0.12 g, 3.0 mmol) was ground in a mortar at r.t. for 5 min. Usual work up of the reaction mixture provided pure 3-(3',5'-dimethoxyphenyl)-1-phenylprop-2-enone (33, 0.68 g) in 96% yield.

IR (CHCl₃)/ν max cm⁻¹: 3010, 1685, 1610, 1590, 1230, 800, 680.

¹H NMR (CDCl₃, 60 MHz): δ 3.8 (s, 6H, 2x-\( \text{OCH}_3 \)), 6.5 (d, \( J=13.5\text{Hz} \), 1H, \( \text{-CH=CHCO}^-\)), 7.3-7.7 (m, 9H, \( \text{-ArH} \)), \( \text{ArCH=CH}^-\), \( \text{COAr}'\text{H} \)

3-(4'-Methoxyphenyl)-1-phenylprop-2-enone (34)

A mixture of 4-methoxybenzaldehyde (14, 0.5 g, 3.67 mmol), acetophenone (12, 0.44 g, 3.67 mmol) and sodium hydroxide (0.14 g, 3.67 mmol) was ground in a mortar at r.t. for 5 min. The reaction mixture turned pale yellow solid which after usual work up gave 3-(4'-methoxyphenyl)-1-phenylprop-2-enone (34, 0.85 g) in 97% yield, m.p. 77-78°.

IR (CHCl₃)/ν max cm⁻¹: 3000, 1675, 1610, 1580, 610, 580.

¹H NMR (CDCl₃, 60 MHz): δ 3.8 (s, 3H, \( \text{-OCH}_3 \)), 7.0 (d, \( J=8\text{Hz} \), 1H, \( \text{-ArH} \)), 7.2-7.8 (m, 7H, \( \text{-CH=CHCO}^-\)), 8.0-8.2 (m, 3H, \( \text{-OCH}_3 \))
3-(3'-Phenoxyphenyl)-1-phenylprop-2-enone (35)

A mixture of 3-phenoxybenzaldehyde (15, 0.5 g, 2.52 mmol), acetophenone (12, 0.3 g, 2.6 mmol) and sodium hydroxide (0.1 g, 2.6 mmol) was ground in a mortar for 5 min. Usual work up of the reaction mixture afforded pure 35 (0.69 g, 92%).

IR (CHCl$_3$)/$\nu_{\text{max}}$ cm$^{-1}$: 3020, 1690, 1620, 1190, 800, 700.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 6.8-7.5 (m, 13H, H$_A$, CH=C//CO-OPh), 7.8-8.1 (m, 3H, $\text{-Ar'H}$)

bis-1,3-(4'-Chlorophenyl)prop-2-enone (36)

A mixture of 4-chlorobenzaldehyde (16, 0.5 g, 3.56 mmol), 4-chloroacetophenone (17, 0.55 g, 3.56 mmol) and sodium hydroxide (0.14 g, 3.5 mmol) was ground in a mortar for 5 min. which on usual work up furnished the corresponding chalcone (36, 0.92g, 94%).

IR (nujol)/$\nu_{\text{max}}$ cm$^{-1}$: 3010, 1685, 1620, 690.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 7.2-7.8 (m, 7H, CHC//CO-COAr), 7.9-8.2 (m, 3H, $\text{-COAr'H}$)

3-(4'-Chlorophenyl)-1-phenylprop-2-enone (37)

A mixture of 4-chlorobenzaldehyde (16, 0.5 g, 3.56 mmol), acetophenone (12, 0.43 g, 3.56 mmol) and sodium hydroxide (0.14 g, 3.5 mmol) was ground in a mortar for 5 min. The resultant pale yellow solid was worked up in the usual manner to afford pure 37 (0.84 g) in 98% yield m.p. 90° (lit. 90-92°)

IR (nujol)/$\nu_{\text{max}}$ cm$^{-1}$: 3060, 1690, 1610, 970, 670.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 7.3-7.7 (m, 8H, $\text{-COAr'H}$), 7.9-8.2 (m, 3H, $\text{-COAr'H}$)

Experimental
General procedure for chemoselective reduction of α,β-unsaturated aldehydes and ketones using NaBH₄-I₂

2,6-Dimethyloct-2-en-1,8-diol (38)

In a 100 mL two-necked round-bottomed flask equipped with magnetic bead, septum and pressure equilizer was taken a solution of 2,6-dimethyl-8-hydroxyoct-2-enal (18, 1.7 g, 10 mmol) in dry THF (15 mL). To this was slowly added a suspension of sodium borohydride (0.45 g, 12 mmol) in dry THF (15 mL) at r.t. over 10 min. The mixture was stirred till the evolution of gas ceases and to it was slowly added iodine (1.27 g, 5 mmol) in dry THF (15 mL) at 0°. The reaction was monitored by TLC. Dilute HCl (5 mL, 3N) was added carefully and the mixture was extracted with ether. The combined organic extract was washed with 3N NaOH (3x10 mL), brine and dried. Evaporation of the organic layer under vacuum gave crude product which was purified using silica gel column chromatography using 5% ethyl acetate in n-hexane as an eluant to furnish pure unsaturated alcohol (38, 1.63 g, 95%).

IR (neat)/ν_max cm⁻¹ : 3500, 3040, 2990, 2945, 1620, 1450, 870.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, J=6Hz, 3H, -CHCH₃)
1.1-1.6 (m, 5H, -CH₂CH₂CH(CH₃)CH₂CH₂-)
1.7 (s, 3H, CH₃C=)
2.0-2.3 (m, 2H, -CH₂CH₂CH=)
3.6 (t, J=7Hz, 2H, -CH₂CH₂OH)
3.9 (s, 2H, =CH₂OH)
4.2 (bs, 2H, 2x-OH, D₂O exchangeable)
5.2 (t, J=6Hz, 1H, -CH₂CH=)

2,6-Dimethyl-8-ethoxyoct-2-en-1-ol (39)

Reduction of 2,6-dimethyl-8-ethoxyoct-2-enal (19, 1.0 g, 5.0 mmol) in dry THF (15 mL) using NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) provided 2,6-dimethyl-8-ethoxyoct-2-en-1-ol (39, 0.95 g) in 94% yield after the usual work up and purification.

IR (neat)/ν_max cm⁻¹ : 3480, 3010, 2990, 1620, 1460, 1080, 850.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, J=6Hz, 3H, -CHCH₃)
1.2 (t, J=6Hz, 3H, -OCH₂CH₃)
1.2-1.6 (m, 5H, -CH₂CH₂CH(CH₃)CH₂CH₂-)
1.7 (s, 3H, CH₃C=)

Experimental 160
2.0-2.3 (m, 2H, -CH$_2$CH$_2$CH=)
3.1-3.6 (m, 4H, -CH$_2$CH$_2$OCH$_2$CH$_3$)
3.8 (s, 2H, =CHCH$_2$OH)
4.0 (bs, 1H, -OH, D$_2$O exchangeable)
5.2 (t, $J$=6Hz, 1H, -CH$_2$CH=)

3,7-Dimethyl-7-hydroxyoct-6-ene 4'-methylphenylsulphonate (40)

Compound (20, 1.62 g, 5.0 mmol) in dry THF (15 mL) was treated with NaBH$_4$ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) which on usual work up and purification yielded 3,7-dimethyl-7-hydroxyoct-6-ene 4'-methylphenylsulphonate (40, 1.53 g) in 94% yield.

IR (neat)/$\nu$ max cm$^{-1}$ : 3500, 3030, 2990, 2950, 1610, 1450, 830.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$

1.0 (d, $J$=6Hz, 3H, -CHCH$_3$)
1.1-1.6 (m, 5H, -CH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_2$-)
1.7 (s, 3H, CH$_3$C=)
1.9-2.3 (m, 2H, -CH$_2$CH$_2$CH=)
2.5 (s, 3H, -CH$_3$H$_3$)
3.8-4.2 (m, 4H, =CHCH$_2$OH, -CH$_2$CH$_2$OSO$_2$-)
4.1 (bs, 1H, -OH, D$_2$O exchangeable)
5.2 (t, $J$=6Hz, 1H, -CH$_2$CH=)
7.3 (d, $J$=8Hz, 2H, -ArH)
7.8 (d, $J$=8Hz, 2H, -ArH)

3,7-Dimethyl-7-hydroxyoct-6-ene methylsulphonate (41)

7-Formyl-3-methyloct-6-ene methylsulphonate (21, 1.24 g, 5.0 mmol) in dry THF (15 mL) was reduced with NaBH$_4$ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) to yield after usual work up, 3,7-dimethyl-7-hydroxyoct-6-ene methylsulphonate (41, 1.19 g, 95%)

IR (neat)/$\nu$ max cm$^{-1}$ : 3450, 3010, 2980, 1625, 1640, 1450.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$

1.0 (d, $J$=6Hz, 3H, -CHCH$_3$)
1.1-1.5 (m, 5H, -CH$_2$CH$_2$CH(CH$_3$)CH$_2$CH$_2$-)
1.7 (s, 3H, CH$_3$C=)
2.0-2.4 (m, 2H, -CH$_2$CH$_2$CH=)
2.9 (s, 3H, -OSO$_2$CH$_3$)
3.3 (bs, 1H, -OH, D$_2$O exchangeable)
3.9 (s, 2H, =CHCH$_2$OH)

Experimental 161
2.6-Dimethyl-8-tetrahydropyranoxo-2-en-1-ol (42)

Reduction of 2,6-dimethyl-8-tetrahydropyranoxo-2-enal (22, 1.27 g, 5.0 mmol) in dry THF (15 mL) using NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) furnished compound (42, 1.17 g) in 92% yield after the usual work up and purification.

IR (neat) νmax cm⁻¹: 3500, 3020, 2990, 2950, 1610, 1080, 850.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, J=6Hz, 3H, -CH₃)
1.2-1.8 (m, 14H, -CH₂C(H)C(H)CH₂-, ring protons and CH₃C=)
2.0-2.4 (m, 2H, -CH₂CH=)
3.1 (bs, 1H, -OH, D₂O exchangeable)
3.3-3.7 (m, 4H, -CH₂OH, -OCOCH₂-)
3.8 (s, 2H, =CCH₂OH)
4.9 (t, J=4Hz, 1H, =CHO-)
5.2 (t, J=6Hz, 1H, -CH₂CH=)

3.7-Dimethyl-8-hydroxy-6-enyl ethanoate (43)

Treatment of 7-formyl-3-methyl-6-enyl ethanoate (23, 1.06 g, 5.0 mmol) with NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) in dry THF (15 mL) yielded 3.7-dimethyl-8-hydroxy-6-enyl ethanoate (43, 1.0 g, 94%) after the usual work up and purification.

IR (neat) νmax cm⁻¹: 3480, 3010, 2980, 1750, 1620, 1460, 860.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, J=6Hz, 3H, -CH₃)
1.1-1.6 (m, 5H, -CH₂CH₂CH(CH₃)CH₂CH₂-)
1.7 (s, 3H, CH₃C=)
2.0 (s, 3H, =OCOCH₃)
2.0-2.3 (m, 2H, -CH₂CH=)
3.0 (bs, 1H, =OH, D₂O exchangeable)
3.9-4.3 (m, 4H, =CCH₂OH, -CH₂CH₂OCO-)
5.2 (t, J=6Hz, 1H, -CH₂CH=)

8-Bromo-2,6-dimethyl-2-en-1-ol (44)

8-Bromo-2,6-dimethyl-2-enal (24, 1.16 g, 5.0 mmol) in dry THF (15 mL) on reduction with NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) furnished 8-bromo-2,6-dimethyl-2-en-1-ol (44, 1.06 g, 91%) after usual work up followed by purification.

Experimental
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3500, 3010, 2970, 2950, 1630, 660.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$

- 1.2-1.7 (m, 5H, -CH$_2$C(CH$_3$)$_2$CH$_2$-
- 1.7 (s, 3H, CH$_3$C)
- 2.1-2.6 (m, 2H, -CH$_2$C=C-)
- 3.3 (t, J=6Hz, 2H, -CH$_2$CBr)
- 3.8 (s, 2H, =CCH$_2$OH)
- 4.0 (bs, 1H, -OH, D$_2$O exchangeable)
- 5.2 (t, J=6Hz, 1H, -CH$_2$CH=)

6,6-(Ethylenedioxy)-2-methylhept-2-en-1-ol (45)

Compound (25, 0.92 g, 5.0 mmol) in dry THF (15 mL) was reduced with NaBH$_4$ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) which on usual work up and purification through silica gel column chromatography using 10% ethyl acetate in n-hexane furnished pure 6,6-(ethylenedioxy)-2-methylhept-2-en-1-ol (45, 0.85 g) in 92% yield.

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3500, 3020, 2990, 2950, 1620, 1445, 1080, 950.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$

- 1.2 (s, J=6Hz, 3H, CH$_3$C)
- 1.6 (s, 3H, CH$_3$C=C)
- 1.9-2.4 (m, 4H, -CCH$_2$CH$_2$C=C-)
- 3.0 (bs, 1H, -OH, D$_2$O exchangeable)
- 4.0 (s, 6H, -OCH$_2$CH$_2$O-, =CCH$_2$OH)
- 5.2 (t, J=6Hz, 1H, -CH$_2$CH=)

6-Hydroxy-2-methylhept-2-en-1-ol (46)

Reaction of 6-hydroxy-2-methylhept-2-enal (26, 0.71 g, 5.0 mmol) with NaBH$_4$ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) in dry THF (15 mL) yielded after usual work up compound (46, 0.63 g) in 88% yield.

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3450, 3020, 2960, 2940, 1630, 1495, 960.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$

- 1.2 (d, J=6Hz, 3H, -CHCH$_3$)
- 1.6 (s, 3H, CH$_3$C=C)
- 2.1-2.5 (m, 4H, -CH$_2$CH$_2$CH=)
- 2.7 (bs, 2H, 2x-OH, D$_2$O exchangeable)
- 3.5-3.9 (m, 3H, -CH$_2$CH(OH)-, =CCH$_2$OH)
- 5.2 (t, J=6Hz, 1H, -CH$_2$CH=)

**Experimental**
3,7-Dimethyloct-2,6-dien-1-ol (47)

Citral (27, 1.52 g, 10 mmol) in dry THF (15 mL) on reduction with NaBH4 (0.45 g, 12.0 mmol) and iodine (1.27 g, 5.0 mmol) gave 3,7-dimethyloct-2,6-dien-1-ol (47, 1.45 g, 94%) after usual work up and purification.

IR (neat)/vmax cm⁻¹: 3500, 3030, 2990, 2950, 1620, 1080, 680.

¹H NMR (CCl₄, 60 MHz): δ 1.6 and 1.7 (2s, 9H, =CC=C(CH₃)₂)
2.0-2.4 (m, 4H, =CCH₂CH=)
3.5 (bs, 1H, -OH, D₂O exchangeable)
4.1 (d, J=7Hz, 2H, =CHCH₂OH)
5.1-5.5 (m, 2H, -CH₂CH=, =CHCH₂OH)

3-Phenylprop-2-en-1-ol (48)

3-Phenylprop-2-enal (28, 1.32 g, 10 mmol) in dry THF (15 mL) was treated with NaBH₄ (0.45 g, 12.0 mmol) and iodine (1.27 g, 5.0 mmol). Usual work up of the reaction mixture followed by silica gel column chromatography using 10% ethyl acetate in n-hexane furnished pure 3-phenylprop-2-en-1-ol (48, 1.2 g) in 90% yield.

IR (neat)/vmax cm⁻¹: 3440, 3200, 3010, 2965, 1620, 1500, 1460.

¹H NMR (CCl₄, 60 MHz): δ 3.2 (bs, 1H, -OH, D₂O exchangeable)
4.3 (d, J=6Hz, 2H, =CHCH₂OH)
6.3-6.6 (m, 2H, -CH=CH-)
7.3 (d, J=6Hz, 1H, =CHAr)

2-Furanmethanol (49)

Reduction of furfural (29, 0.96 g, 10 mmol) in dry THF (15 mL) with NaBH₄ (0.45 g, 12.0 mmol) and iodine (1.27 g, 5.0 mmol) provided after usual work up and purification 2-furanmethanol (49, 0.89 g, 91%).

IR (neat)/vmax cm⁻¹: 3500, 3025, 2990, 2945, 1620, 1505, 1080, 750.

¹H NMR (CCl₄, 60 MHz): δ 3.2 (bs, 1H, -OH, D₂O exchangeable)
4.5 (s, 2H, -CH₂OH)
6.2-6.4 (m, 2H, -CH=CH-)
7.3 (d, J=6Hz, 1H, =CHAr)

Experimental 164
2-Thiophenemethanol (50)

Treatment of 2-thiophenecarboxaldehyde (30, 0.56 g, 5.0 mmol) in dry THF (15 mL) with NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) after usual work up as described above furnished pure 2-thiophenemethanol (50, 0.52 g) in 92% yield.

IR (neat)/v_max cm⁻¹ : 3460, 3010, 2985, 2950, 1610, 1500, 1080, 750.

¹H NMR (CDCl₃, 60 MHz): δ 3.5 (bs, 1H, -OH, D₂O exchangeable)
4.5 (s, 2H, -CH₂OH)
6.0-6.2 (m, 2H, [TF ])
7.1 (d, J=6Hz, 1H, )

4-Phenylbut-3-en-2-ol (51)

Ketone (31, 0.73 g, 5.0 mmol) in dry THF (15 mL) with NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol) yielded after the usual work up and purification, compound (51, 0.71 g) in 96% yield.

IR (neat)/v_max cm⁻¹ : 3500, 3020, 2970, 1625, 1580, 1120, 960, 710.

¹H NMR (CDCl₃, 60 MHz): δ 1.2 (d, J=6Hz, 3H, -CH₃)
3.5 (bs, 1H, -OH, D₂O exchangeable)
4.1-4.5 (m, 1H, =CHCH₂)
6.2-6.4 (m, 2H, -CH=CH⁻)
7.3 (s, 5H, -ArH)

1,3-Diphenylprop-2-en-1-ol (52)

1,3-Diphenylprop-2-enone (32, 1.04 g, 5.0 mmol) in dry THF (15 mL) was reduced with NaBH₄ (0.23 g, 6.0 mmol) and iodine (0.63 g, 2.5 mmol). The resultant product was worked up as usual followed by purification to furnish pure 1,3-diphenylprop-2-en-1-ol (52, 0.97 g, 93%).

IR (neat)/v_max cm⁻¹ : 3450, 3010, 1630, 1570, 1100, 970, 700.

¹H NMR (CDCl₃, 60 MHz): δ 2.8 (bs, 1H, -OH, D₂O exchangeable)
5.1 (d, J=6Hz, 1H, =CHCH(OH))-)
6.1-6.4 (m, 2H, -CH=CH⁻)
7.1-7.3 (m, 10H, -ArH)

Experimental 165
3-(3',5'-Dimethoxyphenyl)-1-phenylprop-2-en-1-ol (53)

Compound (33, 0.67 g, 2.5 mmol) in dry THF (15 mL) was reacted with NaBH₄ (0.11 g, 3.0 mmol) and iodine (0.32 g, 1.25 mmol) which after usual work up and purification furnished pure (53, 0.62 g) in 92% yield.

IR (CHCl₃)/v max cm⁻¹: 3400, 3020, 1630, 1245, 980, 720.

¹H NMR (CDCl₃, 60 MHz): δ 3.5 (bs, 1H, -OH, D₂O exchangeable)
3.7 (s, 6H, 2x-OCH₃)
5.1 (d, J=6Hz, 1H, =CHCH(OH)-)
6.1-6.4 (m, 2H, -CH=CH-)
7.2-7.5 (m, 8H, -ArH)

3-(4'-Methoxyphenyl)-1-phenylprop-2-en-1-ol (54)

Reduction of ketone (34, 0.6 g, 2.5 mmol) with NaBH₄ (0.11 g, 3.0 mmol) and iodine (0.32 g, 1.25 mmol) in dry THF (15 mL) provided after the usual work up 3-(4'-methoxyphenyl)-1-phenylprop-2-en-1-ol (54, 0.51 g, 85%).

IR (neat)/v max cm⁻¹: 3500, 3020, 1625, 1580, 960, 710.

¹H NMR (CCl₄, 60 MHz): δ 3.7 (s, 3H, -OCH₃)
4.4 (bs, 1H, -OH, D₂O exchangeable)
5.1 (d, J=6Hz, 1H, =CHCH(OH)-)
6.1-6.4 (m, 2H, -CH=CH-)
7.1-7.3 (m, 9H, -ArH)

3-(3'-Phenoxyphenyl)-1-phenylprop-2-en-1-ol (55)

Reduction of 3-(3'-phenoxyphenyl)-1-phenylprop-2-enone (35, 0.75 g, 2.5 mmol) with NaBH₄ (0.11 g, 3.0 mmol) and iodine (0.32 g, 1.25 mmol) in dry THF (15 mL) provided after the usual work up and purification, product 3-(3'-phenoxyphenyl)-1-phenylprop-2-en-1-ol (55, 0.63 g) in 83% yield.

IR (neat)/v max cm⁻¹: 3400, 3010, 1630, 1575, 1180, 950, 730.

¹H NMR (CCl₄, 60 MHz): δ 2.5 (bs, 1H, -OH, D₂O exchangeable)
5.1 (d, J=6Hz, 1H, =CHCH(OH)-)
6.2-6.4 (m, 2H, -CH=CH-)
6.7-7.7 (m, 12H, -ArH)
7.8-8.1 (m, 2H, )

Experimental
**bis-1,3-(4’-Chlorophenyl)prop-2-en-1-ol (56)**

Reduction of bis-1,3-(4’-Chlorophenyl)prop-2-enone (36, 0.7 g, 2.5 mmol) in dry THF (15 mL) with NaBH$_4$ (0.11 g, 3.0 mmol) and iodine (0.32 g, 1.25 mmol) after the usual work up and purification, provided pure unsaturated alcohol (56, 0.57 g, 81%).

IR (nujol)/$\nu_{\text{max}}$ cm$^{-1}$: 3450, 3020, 1625, 1585, 980, 760.

$^1$H NMR (CDCl$_3$, 60 MHz): 6 3.3 (bs, 1H, =OH, D$_2$O exchangeable)
5.1 (d, $J=6$Hz, 1H, =CHC//=OH=)
6.1-6.4 (m, 2H, -CH=CH-)
7.1-7.4 (m, 8H, -ArH)

**3-(4’,-Chlorophenyl)-1-phenylprop-2-en-1-ol (57)**

Treatment of $\alpha$,\$-unsaturated ketone (37, 0.6 g, 2.5 mmol) in dry THF (15 mL) with NaBH$_4$ (0.11 g, 3.0 mmol) and iodine (0.32 g, 1.25 mmol) gave pure 3-(4’-chlorophenyl)-1-phenylprop-2-en-1-ol (57, 0.49 g) in 82% yield after usual work up and purification.

IR (nujol)/$\nu_{\text{max}}$ cm$^{-1}$: 3500, 3000, 1628, 1580, 960, 740.

$^1$H NMR (CDCl$_3$, 60 MHz): 6 3.4 (bs, 1H, =OH, D$_2$O exchangeable)
5.1 (d, $J=6$Hz, 1H, =CHC//=OH=)
6.1-6.3 (m, 2H, -CH=CH-)
7.0-7.3 (m, 9H, -ArH)

**1-Bromopentane (64)**

To a 100 mL round-bottomed flask containing an ice-cold stirring solution of pentan-1-ol (58, 1.21 g, 13.8 mmol) in anhyd. diethyl ether (50 mL), pyridine (0.87 g, 11.1 mmol) was added PBr$_3$ (1.35 g, 4.98 mmol) in dry ether (20 mL) dropwise in about 20 min. The mixture was allowed to stir for 2 h at 0°, lh at room temp and decomposed with saturated aq. NaHCO$_3$ solution (2x5 mL). It was then extracted with ether (2x20 mL) washed with water (2x10 mL), brine and dried. Evaporation of the solvent gave pure 1-bromopentane (64) in 85% yield (1.76 g).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 2960, 1420, 720, 580.

$^1$HNMR (CCl$_4$, 60 MHz) $\delta$: 0.9 (t, $J=7$Hz, 3H, -CH$_2$CH$_3$)
1.1-1.5 (m, 4H, saturated methylene protons)
1.8-2.0 (m, 2H, -CH$_2$CH$_2$Br)
3.5 (t, $J=6$Hz, 2H, -CH$_3$CH$_2$Br)
Cyclohexene (68)

Orthophosphoric acid (80%, 4.0 g, 0.04 mmol) was taken in a 500 mL round-bottomed flask and heated to a temperature of 160°-170° followed by the addition of cyclohexanol (59, 20.0 g, 0.2 mol) over a period of 1.5-2h. On completion of the addition, the temperature of the bath was increased to 200° (the temperature at the top of the column should not rise above 90°). Saturated the distillate with salt and separated the upper layer and dried. Distilled the crude product through an efficient column and collected the pure cyclohexene in 80% yield (68, 13.1 g, b.p. 81-83°).

IR (neat)/ν<sub>max</sub> cm<sup>-1</sup> : 3022, 2930, 1650, 1440, 916, 720.

H NMR (CCl<sub>4</sub>, 60 MHz): δ 1.3-1.8 (m, 4H, )
1.9-2.2 (m, 4H, )
5.8 (s, 2H, )

1-Phenoxyprop-2-ene (69)

A mixture of phenol (63, 0.5 g, 5.32 mmol), anhyd. K<sub>2</sub>CO<sub>3</sub> (1.84 g, 13.3 mmol) and 3-bromopropene (61, 0.72 g, 5.95 mmol) in dry DMF (5 mL) was taken in a pyrex beaker covered with a watch glass and exposed to microwave irradiation at 500 W for 3 min. On cooling, the reaction mixture was extracted with diethyl ether (3x10 mL) and organic extracts were washed with water (2x5 mL), brine and dried. Evaporation of the solvent in vacuo provided the crude product, which was purified via silica gel column chromatography using 2% ethyl acetate in n-hexane as the eluant to furnish pure product (169, 0.64 g) in 90% yield.

IR (neat)/ν<sub>max</sub> cm<sup>-1</sup> : 3070, 3040, 1648, 1580, 1243, 1032, 992, 750.

H NMR (CCl<sub>4</sub>, 60 MHz): δ 4.5 (d, J=5Hz, 2H, -OC(CH<sub>3</sub>)=)
5.0-5.7 (m, 2H, -CH=CH<sub>2</sub>)
5.8-6.4 (m, 1H, -CH<sub>2</sub>CH=CH<sub>2</sub>)
6.9-7.1 (m, 3H, -ArH)
7.2-7.5 (m, 2H, -ArH)

3- Phenylprop-1-ene (70)

A flame dried, nitrogen gas flushed 100 mL, 3-necked round-bottomed flask, fitted with a condensor and an addition funnel was charged with magnesium turnings (0.77 g, 32.0 mmol), dry THF (5 mL) and a small crystal of iodine. To the resulting mixture was added a few drops of bromobenzene (60, 5.0 g, 32.0 mmol) in dry THF (25 mL). The flask

Experimental
was warmed over a hot water bath to initiate the reaction followed by addition of remaining bromobenzene. When all the magnesium turnings had reacted, 3-bromopropene (61, 3.63 g, 30.0 mmol) was added dropwise at -10°, followed by addition of 0.1 M Li₂CuCl₄ in dry THF (2 mL). The temperature (-10°) was maintained for 3h and the reaction was stirred overnight at r.t., quenched with saturated ammonium chloride solution and the organic layer was evaporated in vacuo. The residue was extracted with diethyl ether (3x20 mL), washed with water (2x10 mL), brine and dried. Removal of solvent under vacuum followed by silica gel column chromatography, eluting with n-hexane afforded pure 3-phenylprop-1-ene (70, 2.25 g, 60%).

IR (neat)/νmax cm⁻¹ : 3080, 3020, 1630, 1580, 915.

1H NMR (CCl₄, 60 MHz): δ 3.4 (d, J=6Hz, 2H, ArCH₂CH=)
4.9-5.3 (m, 2H, -CH=CH₂)
5.7-6.3 (m, 1H, -CH₂C//=CH₂)
7.2 (s, 5H, -ArH)

5-Phenylpent-1-ene (71)
Li₂CuCl₄ catalyzed Grignard coupling of 1-bromo-2-phenylethane (62, 2.0 g, 10.8 mmol) and 3-bromopropene (61, 1.24 g, 10.3 mmol) in dry THF (20 mL) afforded 5-phenylpent-1-ene (71, 0.98 g, 62%) after the usual work up and purification as described above.

IR (neat)/νmax cm⁻¹ : 3085, 3010, 1650, 1570, 920.

1H NMR (CCl₄, 60 MHz): δ 1.4-2.2 (m, 4H, -CH₂CH₂CH₂CH=)
2.5 (t, J=7Hz, 2H, ArCH₂CH₂-)
4.8-5.1 (m, 2H, -CH=CH₂)
5.3-6.1 (m, 1H, -CH₂C//=CH₂)
7.1 (s, 5H, -ArH)

Oct-1-ene (73)
1-Pentylmagnesium bromide prepared from 1-bromopentane (64, 1.51 g, 10.0 mmol) and magnesium turnings (0.24 g, 10.0 mmol) in dry THF (20 mL) followed by Li₂CuCl₄ catalyzed coupling with 3-bromopropene (61, 1.16 g, 9.6 mmol) provided after the usual work up and purification, oct-1-ene (73, 0.72 g) in 64% yield.

IR (neat)/νmax cm⁻¹ : 3030, 2980, 2920, 1630, 1460, 985, 720.

Experimental
$^1$H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=6Hz, 3H, -CH₂CH₃)
1.2-1.7 (m, 8H, saturated methylene protons)
1.9-2.4 (m, 2H, -CH₂CH₂CH=)
4.9-5.3 (m, 2H, -CH=CH₂)
5.5-6.2 (m, 1H, -CH₂CH=CH₂)

Non-l-ene (74)

Li₂CuCl₄ catalyzed coupling of 1-hexylmagnesium bromide [prepared from 1-bromohexane (65, 1.65 g, 10.0 mmol) and magnesium turnings (0.24 g, 10.0 mmol) in dry THF (20 mL)] and 3-bromopropene (61, 1.16 g, 9.6 mmol) after the usual work up and purification furnished non-l-ene (74, 0.8 g, 64%).

IR (neat)/νmax cm⁻¹ : 3020, 2985, 2920, 1660, 1470, 970, 715.

$^1$H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=6Hz, 3H, -CH₂CH₃)
1.2-1.8 (m, 10H, saturated methylene protons)
1.9-2.4 (m, 2H, -CH₂CH₂CH=)
4.8-5.2 (m, 2H, -CH=CH₂)
5.4-6.1 (m, 1H, -CH₂CH=CH₂)

Dodec-l-ene (75)

1-Nonylmagnesium bromide prepared from 1-bromononane (66, 2.07 g, 10.0 mmol) and magnesium turnings (0.24 g, 10.0 mmol) in dry THF (20 mL) followed by Li₂CuCl₄ catalyzed coupling with 3-bromopropene (61, 1.16 g, 9.6 mmol) furnished after the usual work up and purification, dodec-l-ene (75, 1.1 g) in 66% yield.

IR (neat)/νmax cm⁻¹ : 3030, 2960, 2910, 1680, 1460, 960, 720.

$^1$H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=6Hz, 3H, -CH₂CH₃)
1.2-1.7 (m, 16H, saturated methylene protons)
1.9-2.4 (m, 2H, -CH₂CH₂CH=)
4.9-5.3 (m, 2H, -CH=CH₂)
5.5-6.2 (m, 1H, -CH₂CH=CH₂)

Methyl undec-10-enoate (77)

A mixture of undec-10-enoic acid (67, 0.74 g, 4.0 mmol), p-toluenesulphonic acid (0.38 g, 2.0 mmol) and methanol (0.13 g, 4.0 mmol) was taken in a 100 mL conical flask. The funnel containing crushed ice was placed on top of flask to minimize evaporation of methanol. The reaction mixture was exposed to microwave irradiation at 320 W for 4 min. On
cooling, the mixture was extracted with ether (2x20 mL) and the solvent was evaporated in vacuo to furnish pure methyl undec-10-enoate (77, 0.7 g) in 88% yield.

\[ \text{IR (neat)/} \nu_{\text{max}} \text{ cm}^{-1} : \]

\[ 3022, 2930, 1650, 1440, 916, 720. \]

\[ ^1\text{H NMR (CDCl}_3, 60 \text{ MHz}): \delta \]

\[ 1.2-1.7 (\text{bs, 12H, saturated methylene protons}) \]

\[ 2.0-2.4 (\text{m, 4H, -CH}_3\text{CH}_2\text{CH}_2\text{=, -CH}_2\text{CH}_2\text{COO-}) \]

\[ 3.7 (\text{s, 3H, -COOCH}_3) \]

\[ 4.8-5.2 (\text{m, 2H, -CH=CH}_2) \]

\[ 5.4-6.2 (\text{m, 1H, -CH}_2\text{CH}=\text{CH}_2) \]

**Procedure for oxidation of olefins using QCC-I; under MWI**

1-Chloro-2-iodocyclohexane (78) and 2-Iodocyclohexanol (88)

A mixture of cyclohexene (68, 0.08 g, 1.0 mmol), quinolinium chlorochromate (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) was irradiated in microwave oven at 210 W for 3 min. On cooling, the resulting mixture was diluted with DCM (3x10 mL) and passed through a short silica column to remove QCC. Evaporation of the solvent in vacuo followed by purification using silica gel column chromatography furnished pure products 1-chloro-2-iodocyclohexane (78, 0.15 g, 64%) and 1-iodocyclohexan-1-ol (88, 0.02 g, 9%).

1-Chloro-2-iodocyclohexane (78)

\[ \text{IR (neat)/} \nu_{\text{max}} \text{ cm}^{-1} : \]

\[ 2900, 1440, 720, 550. \]

\[ ^1\text{H NMR (CDCl}_3, 60 \text{ MHz}): \delta \]

\[ 1.3-1.8 (\text{m, 4H,}\)

\[ H\text{H}\]

\[ 1.9-2.7 (\text{m, 4H,}\)

\[ H\text{H}\]

\[ 4.3-4.7 (\text{m, 2H, -CHI, -CHCl}) \]

2-Iodocyclohexanol (88)

\[ \text{IR (neat)/} \nu_{\text{max}} \text{ cm}^{-1} : \]

\[ 3400, 2900, 1440, 1060, 740. \]

\[ ^1\text{H NMR (CDCl}_3, 60 \text{ MHz}): \delta \]

\[ 1.2-1.7 (\text{m, 4H,}\)

\[ H\text{H}\]

\[ 1.8-2.5 (\text{m, 4H,}\)

\[ H\text{H}\]

\[ 3.1 (\text{bs, 1H, -OH, D}_2\text{O exchangeable}) \]

\[ 3.4-4.2 (\text{m, 2H, -CHI, -CHOH}) \]

**Experimental**
Exposure of a mixture of 3-phenoxyprene (69, 0.13 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) to microwave irradiation at 210 W for 3 min. followed by usual work up of the reaction mixture and purification using silica gel column chromatography furnished pure 2-chloro-1-iodo-3-phenoxyp propane (79, 0.18 g, 64%) and 1-iodo-3-phenoxyp propane-2-ol (89, 0.02 g, 8%).

2-Chloro-1-iodo-3-phenoxyp propane (79)

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3010, 2880, 1540, 1460, 1270, 750, 660, 580, 520.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 4.1 (d, $J=5$ Hz, 2H, -OCH$_2$CH-)
4.3-4.6 (m, 3H, -CH$_2$C=C=C=C=C=C-CI)
7.0-7.2 (s, 3H, -ArH)
7.3-7.6 (s, 2H, -ArH)

1-Iodo-3-phenoxyp propane-2-ol (89)

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3400, 3020, 2910, 2870, 1560, 1275, 1120, 760, 520.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 2.8 (bs, 1H, -OH, D$_2$O exchangeable)
3.4 (d, $J=6$ Hz, 2H, -CHClCH$_2$I)
3.8-4.1 (m, 1H, -CH$_2$CH(OH)CH$_2$I)
4.0 (d, $J=5$ Hz, 2H, -OCH$_2$C=C=C=C=C=C-CI)
6.9-7.1 (s, 3H, -ArH)
7.2-7.6 (s, 2H, -ArH)

2-Chloro-1-iodo-3-phenylpropane (80) and 1-Iodo-3-phenylpropane-2-ol (90)

Subjection of a mixture of 3-phenylprop-1-ene (70, 0.12 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) to MWI at 210 W for 3 min. followed by usual work up and purification using silica gel column chromatography furnished pure 2-chloro-1-iodo-3-phenylpropane (80, 0.2 g, 69%) and 1-iodo-3-phenylpropane-2-ol (90, 0.02 g, 9%).

2-Chloro-1-iodo-3-phenylpropane (80)

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3000, 2980, 2860, 1540, 1440, 580, 520.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 3.0-3.4 (m, 4H, -CH$_2$CHClCH$_2$I)
3.7-4.4 (m, 1H, -CH$_2$CHClCH$_2$I)
7.2 (s, 5H, -ArH)

1-Iodo-3-phenylpropane-2-ol (90)

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3400, 3030, 2880, 1560, 1110, 600, 560.

Experimental
\[^1\text{H NMR (CCl}_4, 60 \text{ MHz)}: \delta \text{ 1.9 (bs, 1H, -OH, D}_2\text{O exchangeable)}
\]
\[ \quad 2.8 \text{ (d, } J=7\text{Hz, 2H, ArCH}_2\text{CH-)}
\]
\[ \quad 3.1-3.2 \text{ (m, 2H, -CH(OH)CH}_2\text{I)}
\]
\[ \quad 3.4-3.7 \text{ (m, 1H, -CH}_2\text{CH(OH)CH}_2\text{I)}
\]
\[ \quad 7.2 \text{ (s, 5H, -ArH)}
\]

**2-Chloro-1-iodo-5-phenylpentane (81) and 1-iodo-5-phenylpentan-2-ol (91)**

A mixture of 5-phenylpent-1-ene (71, 0.15 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) was subjected to MWI at 210 W for 3 min., crude product was obtained after the usual work up of the reaction mixture. The crude product on purification by using silica gel column chromatography furnished pure 2-chloro-1-iodo-5-phenylpentane (81, 0.2 g, 65%) and 1-iodo-5-phenylpentan-2-ol (91, 0.02 g, 7%).

**2-Chloro-1-iodo-5-phenylpentane (81)**

\[^{1}\text{H NMR (CCl}_4, 60 \text{ MHz)}: \delta \text{ 1.4-1.9 (m, 4H, -CH}_2\text{CH}_2\text{CH}_2\text{CH-)}
\]
\[ \quad 2.5 \text{ (t, } J=7\text{Hz, 2H, ArCH}_2\text{CH-)}
\]
\[ \quad 3.1-3.9 \text{ (m, 3H, -CH}_2\text{CHClCH}_2\text{I)}
\]
\[ \quad 7.2 \text{ (s, 5H, -ArH)}
\]

**1-Iodo-5-phenylpentan-2-ol (91)**

\[^{1}\text{H NMR (CCl}_4, 60 \text{ MHz)}: \delta \text{ 1.4-1.8 (m, 4H, -CH}_2\text{CH}_2\text{CH}_2\text{CH-)}
\]
\[ \quad 1.7 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)}
\]
\[ \quad 2.5 \text{ (t, } J=7\text{Hz, 2H, ArCH}_2\text{CH-)}
\]
\[ \quad 3.1-3.8 \text{ (m, 3H, -CH}_2\text{CH(OH)CH}_2\text{I)}
\]
\[ \quad 7.2 \text{ (s, 5H, -ArH)}
\]

**2-Chloro-3-(3',4'-methylenedioxyphenyl)-l-iodopropane (82) and l-iodo-3-(3',4'-methyl enedioxyphenyl)propan-2-ol (92)**

A mixture of 3-(3',4'-methylenedioxyphenyl)prop-1-ene (72, 0.16 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) was exposed to MWI for 3 min. at 210 W. On, cooling, the reaction mixture was worked up as usual followed by purification through silica gel column chromatography provided pure products 2-chloro-3-(3',4'-methyl enedioxyphenyl)-1-iodopropane (82, 0.21 g, 66%) and 1-iodo-3-(3',4'-methylenedioxy phenyl)propan-2-ol (92, 0.02 g, 7%).

**Experimental**
2-Chloro-3-(3',4'-methylenedioxyphenyl)-1-iodopropane (82)
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3000, 2900, 1440, 560, 420.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 3.1-3.8 (m, 4H, -CH$_2$CHClCH$_2$I)
4.0-4.6 (m, 1H, -CH$_2$CHClCH$_2$-)
6.0 (s, 2H, $\text{-CH(O)}$)
6.8 (s, 3H, -ArH)

1-Iodo-3-(3',4'-methylenedioxyphenyl)propan-2-ol (92)
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3400, 3010, 2900, 1600, 1100, 560.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 2.5 (bs, 1H, -OH, D$_2$O exchangeable)
2.9 (d, $J$=6Hz, 2H, -CH$_2$CH(OH)-)
3.3-3.5 (m, 2H, -CH$_2$CH(OH)CH$_2$I)
3.6-3.9 (m, 1H, -CH$_2$CH(OH)CH$_2$I)
6.0 (s, 2H, $\text{-CH(O)}$)
6.9 (s, 3H, -ArH)

2-Chloro-1-iodooctane (83) and 1-iodooctan-2-ol (93)
A mixture of oct-1-ene (73, 0.11 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine
(0.25 g, 1.0 mmol) was subjected to microwave energy at 210 W for 3 min. Usual work up of
the reaction mixture followed by purification through silica gel column chromatography
yielded pure products 2-chloro-1-iodooctane (83, 0.17 g, 63%) and 1-iodooctan-2-ol (93,
0.02 g, 8%).

2-Chloro-1-iodooctane (83)
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 2980, 2910, 2860, 1470, 720, 600, 560.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 0.9 (t, $J$=6Hz, 3H, -CH$_2$CH$_3$)
1.2-1.7 (m, 10H, saturated methylene protons)
3.2-4.1 (m, 3H, -CH$_2$CHClCH$_2$I)

1-Iodoctan-2-ol (93)
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3350, 2980, 2880, 1470, 1120, 730, 510.
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 0.8 (t, $J$=6Hz, 3H, -CH$_2$CH$_3$)
1.2-1.7 (m, 8H, saturated methylene protons)
1.8-2.0 (m, 2H, -CH$_2$CH(OH)-)
3.0 (bs, 1H, -OH, D$_2$O exchangeable)
3.2-3.9 (m, 3H, -CH$_2$CH(OH)CH$_2$I)

Experimental
2-Chloro-1-iodononane (84) and 1-iodononan-2-ol (94)

Subjection of a mixture of non-1-ene (74, 0.13 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) to MWI at 210 W for 3 min., after the usual work up and purification via silica gel column chromatography furnished pure 2-chloro-1-iodononane (84, 0.19 g, 64%) and 1-iodononan-2-ol (94, 0.02 g, 7%).

2-Chloro-1-iodononane (84)

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 2980, 2920, 2880, 1465, 720, 610, 580.

\(^1\)H NMR (CCL\(_4\), 60 MHz): \(\delta\) 0.9 (t, \(J=6\)Hz, 3H, -CH\(_2\)CH\(_3\))
1.2-1.8 (m, 12H, saturated methylene protons)
3.2-4.1 (m, 3H, -CH\(_2\)CH\(_2\)I)

1-Iodononan-2-ol (94)

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 3400, 2960, 2910, 2890, 1460, 1110, 725, 590, 520.

\(^1\)H NMR (CCL\(_4\), 60 MHz): \(\delta\) 0.8 (t, \(J=6\)Hz, 3H, -CH\(_2\)CH\(_3\))
1.2-1.8 (m, 10H, saturated methylene protons)
1.8-2.0 (m, 2H, -CH\(_2\)CH(OH)-)
2.5 (bs, 1H, -OH, D\(_2\)O exchangeable)
3.1-3.8 (m, 3H, -CH\(_2\)CH(OH)CH\(_2\)I)

2-Chloro-1-iodododecane (85) and 1-iodododecan-2-ol (95)

Dodec-1-ene (75, 0.17 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) were irradiated to microwaves at 210 W for 3 min. Usual work up of the reaction mixture yielded crude product which was purified using silica gel column chromatography to furnish pure products 2-chloro-1-iodododecane (85, 0.22 g, 66%) and 1-iodododecan-2-ol (95, 0.03 g, 9%).

2-Chloro-1-iodododecane (85)

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 2990, 2940, 2870, 1475, 700, 600, 560.

\(^1\)H NMR (CCL\(_4\), 60 MHz): \(\delta\) 0.9 (t, \(J=6\)Hz, 3H, -CH\(_2\)CH\(_3\))
1.2-1.8 (bs, 18H, saturated methylene protons)
3.2-4.1 (m, 3H, -CH\(_2\)CH\(_2\)I)

1-Iodododecan-2-ol (95)

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 3450, 2980, 2920, 2880, 1440, 1120, 740, 600.

\(^1\)H NMR (CCL\(_4\), 60 MHz): \(\delta\) 0.9 (t, \(J=6\)Hz, 3H, -CH\(_2\)CH\(_3\))
1.2-1.8 (bs, 16H, saturated methylene protons)

Experimental
2-Chloro-1-iodopentadecane (86) and 1-iodopentadecan-2-ol (96)

A mixture of pentadec-1-ene (76, 0.21 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) on subjection to MWI at 210 W for 3 min. yielded pure 2-chloro-1-iodopentadecane (86, 0.23 g, 62%) and 1-iodopentadecan-2-ol (96, 0.03 g, 9%) after the usual work up and purification.

2-Chloro-1-iodopentadecane (86)

IR (neat)/vmax cm⁻¹ : 2970, 2920, 2840, 1440, 720, 580.

¹H NMR (CCl₄, 60 MHz): δ 0.8 (t, J=6Hz, 3H, -CH₂C₃H₃)
1.1-1.8 (bs, 24H, saturated methylene protons)
3.2-4.2 (m, 3H, -CH₂CH(OH)CH₃)

1-Iodopentadecan-2-ol (96)

IR (neat)/vmax cm⁻¹ : 3500, 2970, 2910, 2880, 1450, 1110, 720, 590.

¹H NMR (CCl₄, 60 MHz): δ 0.8 (t, J=6Hz, 3H, -CH₂C₃H₃)
1.2-1.8 (bs, 22H, saturated methylene protons)
1.8-2.2 (m, 2H, -CH₂CH(OH)⁻)
2.7 (bs, 1H, -OH, D₂O exchangeable)
3.1-3.8 (m, 3H, -CH₂CH(OH)CH₃)

Methyl 10-chloro-11-iodoundecanoate (87) and methyl 10-hydroxy-11-iodoundecanoate (97)

A mixture of 10-methylundecanoate (77, 0.2 g, 1.0 mmol), QCC (0.54 g, 2.0 mmol) and iodine (0.25 g, 1.0 mmol) was irradiated to MWI at 210 W for 3 min. Usual work up of the reaction mixture followed by purification using silica gel column chromatography furnished pure methyl 10-chloro-11-iodoundecanoate (87, 0.24 g, 67%) and methyl 10-hydroxy-11-iodoundecanoate (97, 0.03 g, 10%).

Methyl 10-chloro-11-iodoundecanoate (87)

IR (neat)/vmax cm⁻¹ : 2990, 2920, 1740, 1460, 1180, 720, 660, 540.

¹H NMR (CCl₄, 60 MHz): δ 1.2-1.8 (bs, 14H, saturated methylene protons)
2.2 (t, J=7Hz, 2H, -CH₂COO⁻)
3.3-4.2 (m, 3H, -CH₂CHClCH₃)
3.6 (s, 3H, -COOCH₃)

Experimental
Methyl 10-hydroxy-11-iodoundecanoate (97)

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 3350, 2980, 2910, 1750, 1185, 1120, 725, 650, 580.

\(^1\)H NMR (CCl\(_4\), 60 MHz); \(\delta\)
- 1.2-1.7 (bs, 14H, saturated methylene protons)
- 2.2 (t, \(J=7\)Hz, 2H, \(-\text{CH}_2\text{COO}^-\))
- 3.1-3.3 (m, 2H, \(-\text{CH}_2\text{CH(OH)}\text{CH}_2\text{I}\))
- 3.6 (s, 3H, \(-\text{COOC}^-\))
- 3.4-3.7 (m, 1H, \(-\text{CH}_2\text{CH(OH)}\text{CH}_2\text{I}\))
- 3.9 (bs, 1H, \(-\text{OH}, \text{D}_2\text{O exchangeable}\))

General procedure for monobromination of diols, cyclic ethers and lactones under MWI

3-Bromopropan-1-ol (111)

A mixture of 1,3-propanediol (98, 0.2 g, 2.63 mmol), 48% aq. hydrogen bromide (0.44 g, 5.43 mmol) and tetrabutyl ammonium iodide (0.19 g, 0.52 mmol) was taken in a 100 mL borosil beaker covered with a watch glass and exposed to microwave irradiation at 355 W. After 5 min. of irradiation, the reaction mixture was cooled, extracted with solvent ether (3x10 mL) and washed with saturated sodium bicarbonate solution (2x5 mL), 10% aq. sodium thiosulphate (2x5 mL), water (2x5 mL), brine and dried. Evaporation of solvent in vacuo followed by silica gel chromatography eluting with \(-\)hexane:ethyl acetate (4:1) furnished pure 3-bromopropan-1-ol (111, 0.27 g, 75%).

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 3350, 2930, 2880, 1280, 1040, 720, 560.

\(^1\)H NMR (CCl\(_4\), 300 MHz); \(\delta\)
- 2.0 (m, 2H, \(-\text{CH}_2\text{CH}_2\text{CH}_2\text{I}\))
- 3.4 (t, \(J=6\)Hz, 2H, \(-\text{CH}_2\text{CH}_2\text{Br}\))
- 3.7 (t, \(J=6\)Hz, 2H, \(-\text{CH}_2\text{CH}_2\text{OH}\))
- 6.5 (bs, 1H, \(-\text{OH}, \text{D}_2\text{O exchangeable}\))

4-Bromobutan-1-ol (112)

1,4-Butanediol (99, 0.5 g, 5.56 mmol), 48% aq. hydrogen bromide (0.94 g, 11.57 mmol) and tetrabutylammonium iodide (0.41 g, 1.11 mmol) were taken in a 100 mL beaker and irradiated in the microwave oven at 355 W for 5 min. The resultant product was worked up as usual and purified by silica gel column chromatography eluting with 5% ethyl acetate in \(n\)-hexane as eluant to furnish 4-bromobutan-1-ol (112, 0.65 g, 77%).

IR (neat)/\(\nu_{\text{max}}\) cm\(^{-1}\): 3350, 2940, 1250, 1040, 720, 550.

\(^1\)H NMR (CCl\(_4\), 300 MHz); \(\delta\)
- 1.5-2.2 (m, 4H, saturated methylene protons)
- 3.4 (t, \(J=6\)Hz, 2H, \(-\text{CH}_2\text{CH}_2\text{Br}\))

Experimental 177
3.7 (t, J=6Hz, 2H, -CH$_2$CH$_2$OH)
5.8 (bs, 1H, -OH, D$_2$O exchangeable)

**5-Bromopentan-1-ol (113)**

1,5-Pentanediol (100, 0.2 g, 1.92 mmol), 48% aq. hydrogen bromide (0.32 g, 3.95 mmol) and tetrabutylammonium iodide (0.14 g, 0.38 mmol) on exposure to MWI at 355 W for 5 min. After the usual work up and purification by silica gel column chromatography using 5% ethyl acetate in n-hexane as the eluant, 5-bromopentan-1-ol (113, 0.26 g) was obtained in 81% yield.

**6-Bromohexan-1-ol (114)**

Compound (101, 0.4 g, 3.39 mmol), 48% aq. hydrogen bromide (0.57 g, 7.04 mmol) and tetrabutylammonium iodide (0.25 g, 0.68 mmol) were subjected to MWI at 355 W for 5 min. to furnish after the usual work up and purification by silica gel column chromatography using 5% ethyl acetate in n-hexane as the eluant provided product (114, 0.46 g, 75%).

**7-Bromoheptan-1-ol (115)**

Exposure of 1,7-heptanediol (102, 0.5 g, 3.78 mmol), 48% aq. hydrogen bromide (0.64 g, 7.9 mmol) and tetrabutylammonium iodide (0.28 g, 0.76 mmol) to MWI at 355 W for 5 min. furnished product (115, 0.58 g, 79%) after the usual work up and purification.

**Experimental**
3.1 (bs, 1H, -OH, D$_2$O exchangeable)
3.3 (t, J=6Hz, 2H, -CH$_2$CH$_2$Br)
3.6 (t, J=6Hz, 2H, -CH$_2$CH$_2$OH)

8-Bromo-octan-1-ol (116)

A mixture of 1,8-octanediol (103, 0.2 g, 1.37 mmol), 48% aq. hydrogen bromide (0.23 g, 2.84 mmol) and tetrabutylammonium iodide (0.1 g, 0.27 mmol) was irradiated in the domestic microwave oven at 355 W for 5 min. Usual work up of the reaction mixture followed by column chromatography over silica gel (5% ethyl acetate in n-hexane) yielded 116 in 78% yield (0.22 g).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3350, 2940, 1240, 1090, 725, 580.

$^1$H NMR (CCl$_4$, 300 MHz): $\delta$ 1.3-1.7 (m, 8H, saturated methylene protons)
1.8-2.1 (m, 4H, -CH$_2$CH$_2$Br, -CH$_2$CH$_2$OH)
3.3 (t, J=6Hz, 2H, -CH$_2$CH$_2$Br)
3.6 (t, J=6Hz, 2H, -CH$_2$CH$_2$OH)
4.2 (bs, 1H, -OH, D$_2$O exchangeable)

9-Bromononan-1-ol (117)

1,9-Nonanediol (104, 0.5 g, 3.12 mmol), 48% aq. hydrogen bromide (0.52 g, 6.42 mmol) and tetrabutylammonium iodide (0.23 g, 0.62 mmol) were irradiated in the microwave oven at 355 W for 5 min. to yield compound (117, 0.55 g, 79%) after the usual work up followed by column chromatography over silica gel using 5% ethyl acetate in n-hexane as the eluant.

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3450, 2920, 1275, 1120, 722, 550.

$^1$H NMR (CCl$_4$, 300 MHz): $\delta$ 1.3-1.6 (m, 10H, saturated methylene protons)
1.8-2.1 (m, 4H, -CH$_2$CH$_2$Br, -CH$_2$CH$_2$OH)
3.3 (t, J=6Hz, 2H, -CH$_2$CH$_2$Br)
3.6 (t, J=6Hz, 2H, -CH$_2$CH$_2$OH)
4.0 (bs, 1H, -OH, D$_2$O exchangeable)

10-Bromodecan-1-ol (118)

A mixture of 1,10-decanediol (105, 0.3 g, 1.72 mmol), 48% aq. hydrogen bromide (0.29 g, 3.58 mmol) and tetrabutylammonium iodide (0.12 g, 0.34 mmol) on subjection to MWI at 355 W for 5 min. furnished crude product after the usual work up, which was purified by column chromatography over silica gel using 5% ethyl acetate in n-hexane to afford pure product (118, 0.32 g, 80%).

Experimental 179
IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3420, 2980, 1275, 1050, 720, 560.

$^1$H NMR (CCl₄, 300 MHz): $\delta$ 1.3-1.7 (m, 12H, saturated methylene protons)
  1.8-2.2 (m, 4H, -CH₂CH₂Br, -CH₂CH₂OH)
  2.8 (bs, 1H, -OH, D₂O exchangeable)
  3.4 (t, $J$=6Hz, 2H, -CH₂CH₂Br)
  3.7 (t, $J$=6Hz, 2H, -CH₂CH₂OH)

4-Bromobutan-1-ol (112)

Tetrahydrofuran (106, 0.5 g, 6.94 mmol), 48% aq. hydrogen bromide (1.17 g, 14.44 mmol) and tetrabutylammonium iodide (0.51 g, 1.38 mmol) were taken in a 100 mL conical flask. The flask was placed in a petridish containing ice to decrease evaporation of tetrahydrofuran. The mixture on subjection to MWI for 5 min. at 355 W gave after usual work up and purification by silica gel column chromatography, product (112) in 81% yield (0.86 g).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3350, 3320, 2940, 1230, 1045, 722, 550.

$^1$H NMR (CCl₄, 300 MHz): $\delta$ 1.6-2.2 (m, 4H, saturated methylene protons)
  3.4 (t, $J$=6Hz, 2H, -CH₂CH₂Br)
  3.7 (t, $J$=6Hz, 2H, -CH₂CH₂OH)
  6.2 (bs, 1H, -OH, D₂O exchangeable)

5-Bromopentan-1-ol (113)

A mixture of tetrahydropyran (107, 0.4 g, 4.65 mmol), 48% aq. hydrogen bromide (0.78 g, 9.63 mmol) and tetrabutylammonium iodide (0.34 g, 0.92 mmol) was taken in a 100 mL beaker placed in an ice bath. The reaction mixture was irradiated in microwave oven at 355 W for 5 min. The resultant product was worked up as usual to furnish the pure product (113, 0.6 g, 78%).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3400, 2950, 1280, 1210, 1060, 720, 580.

$^1$H NMR (CCl₄, 300 MHz): $\delta$ 1.4-2.1 (m, 6H, saturated methylene protons)
  2.5 (bs, 1H, -OH, D₂O exchangeable)
  3.4 (t, $J$=6Hz, 2H, -CH₂CH₂Br)
  3.7 (t, $J$=6Hz, 2H, -CH₂CH₂OH)

4-Bromo-1-butanoic acid (119)

A mixture of butyrolactone (108, 0.5 g, 5.81 mmol), 48% aq. hydrogen bromide (0.98 g, 12.09 mmol) and tetrabutylammonium iodide (0.43 g, 1.16 mmol) on subjection to MWI at 355 W for 10 min. furnished crude product. The crude product on purification by
silica gel column chromatography using ethyl acetate:n-hexane::0.5:9.5 gave pure 4-bromo-1-butanoic acid (119) in 87% yield (0.84 g).

IR (neat)/νmax cm⁻¹: 3060, 2950, 1710, 1610, 1430, 960, 722, 580.

¹H NMR (CCl₄, 300 MHz): δ 2.0-2.4 (m, 2H, -CH₂CH₂CO-)
2.6 (t, J=7Hz, 2H, -CH₂COOH)
3.5 (t, J=6Hz, 2H, -CH₂CH₂Br)
11.5 (bs, 1H, -COOH, D₂O exchangeable)

4-Bromo-4-methyl-1-butanoic acid (120)

5-Methylbutyrolactone (109, 0.3 g, 3.0 mmol), 48% aq. hydrogen bromide (0.5 g, 6.17 mmol) and tetrabutylammonium iodide (0.22 g, 0.6 mmol) on exposure to MWI at 355 W for 10 min. yielded after usual work up, crude compound, which was purified through silica gel column chromatography using ethyl acetate:n-hexane::1:9 gave pure 120 (0.48 g, 88%).

IR (neat)/νmax cm⁻¹: 3050, 2920, 2850, 1708, 1600, 940, 725, 528.

¹H NMR (CCl₄, 300 MHz): δ 1.8 (d, J=6Hz, 3H, -CH(CH₃))
1.8-2.3 (m, 2H, -CH₂CH₂CO-)
2.5 (t, J=7Hz, 2H, -CH₂COOH)
3.9-4.4 (m, 1H, -CH₂CH(Br)-)
13.5 (bs, 1H, -COOH, D₂O exchangeable)

5-Bromo-1-pentanoic acid (121)

To a 100 mL Erlenmeyer flask, was added valerolactone (110, 0.5 g, 5.0 mmol), 48% aq. hydrogen bromide (0.84 g, 10.37 mmol) and tetrabutylammonium iodide (0.37 g, 1.0 mmol). The mixture was subjected to MWI at 355 W for 10 min. Usual work up followed by silica gel column chromatography eluting with 5% ethyl acetate in n-hexane furnished pure 5-bromo-1-pentanoic acid (121, 0.75 g, 83%).

IR (neat)/νmax cm⁻¹: 3310, 2980, 1710, 1600, 1440, 975, 720, 560.

¹H NMR (CCl₄, 300 MHz): δ 1.7-2.1 (m, 4H, -CH₂CH₂CH₂CO-)
2.5 (t, J=7Hz, 2H, -CH₂COOH)
3.5 (t, J=6Hz, 2H, -CH₂CH₂Br)
11.0 (bs, 1H, -COOH, D₂O exchangeable)
General procedure for the preparation of mesylates

1,5-Dimethylhex-5-ene methylsulphonate (124)

Methanesulphonyl chloride (0.57 g, 5.0 mmol) in dry dichloromethane (5 mL) was added to the stirred mixture of compound (9, 0.64 g, 5.0 mmol) and triethylamine (0.5 g, 5.0 mmol) in dry dichloromethane (15 mL) at 0°. The mixture was stirred for 1h, followed by dilution with DCM (2x10 mL), separated and subsequently washed with water (5 mL), brine and dried. Solvent was evaporated under vacuum to furnish the crude product which was further purified by silica gel column chromatography using 5% ethyl acetate in n-hexane as eluant to afford the mesylate in 91% yield (124, 0.86 g).

IR (neat)/ν max cm⁻¹ : 3010, 2980, 2910, 1660, 1440, 1385, 1190, 780.

1H NMR (CCl₄, 60 MHz): δ 1.2 (d, J=6Hz, 3H, -CH₂C₃H₃)
1.3-1.5 (m, 2H, -CH₂C₃H₅)
1.7 & 1.8 (2s, 6H, -CH(CH₃)₂)
2.2 (m, 2H, -CH₂CH(CH₃)₂)
3.0 (s, 3H, -OSO₂CH₃)
4.8-5.1 (m, 1H, -CH(OSO₂CH₃)-)
5.2 (t, J=6Hz, 1H, -CH=C-)

1-Tetrahydrofurfuryl methylsulphonate (125)

To a stirred ice-cold solution of tetrahydrofurfuryl alcohol (122, 0.51 g, 5.0 mmol) and triethylamine (0.5 g, 5.0 mmol) in dry DCM (15 mL) was added dropwise methanesulphonyl chloride (0.57 g, 5.0 mmol) at 0°. On completion of the reaction (monitored by TLC), it was worked up as described above to provide mesylate (125, 0.78 g) in 87% yield.

IR (neat)/ν max cm⁻¹ : 2920, 1460, 1380, 1180, 1080.

1H NMR (CCl₄, 60 MHz): δ 1.8-2.1 (m, 4H, ), 3.0 (s, 3H, -OSO₂CH₃)
3.8-4.0 (m, 2H, )
4.1-4.3 (m, 3H, -CHCH₂OSO₂⁻)

1-Cyclohexyl methylsulphonate (126)

Cyclohexanol (59, 0.5 g, 5.0 mmol) and triethyl amine (0.5 g, 5.0 mmol) in dry DCM (15 mL) was ice-cooled and to it was added methanesulphonyl chloride (0.57 g, 5.0 mmol). Progress of the reaction mixture was monitored via TLC followed by usual work up to afford pure (126, 0.82 g) in 92% yield.

Experimental
IR (neat)/vmax cm⁻¹ : 2925, 1345, 1365, 1170, 725.

¹H NMR (CCl₄, 60 MHz): δ 1.2-2.0 (m, 10H, saturated methylene protons)
3.0 (s, 3H, -OSO₂CH₃)
4.4-4.8 (m, 1H, -CH(OSO₂CH₃)⁻)

1-Nonyl methylsulphonate (127)

A mixture of nonan-1-ol (123, 0.72 g, 5.0 mmol), methanesulphonyl chloride (0.57 g, 5.0 mmol) and triethylamine (0.5 g, 5.0 mmol) was stirred at 0° for 30 min. Usual work up of the reaction mixture as described above yielded pure product (127, 1.05 g, 95%).

IR (neat)/vmax cm⁻¹ : 2980, 2920, 1480, 1385, 1180, 720.

¹H NMR (CCl₄, 60 MHz): δ 1.2-1.5 (m, 14H, saturated methylene protons)
3.0 (s, 3H, -OSO₂CH₃)
4.3 (t, J=6Hz, 2H, -CH₂CH₂OSO₂⁻)

6-Bromohexyl methylsulphonate (128)

The stirred reaction mixture comprising of 6-bromohexan-1-ol (114, 0.9 g, 5.0 mmol), methanesulphonyl chloride (0.57 g, 5.0 mmol) and triethylamine (0.5 g, 5.0 mmol) was worked up as usual to furnish pure 6-bromohexyl methylsulphonate (128, 1.19 g) in 93% yield.

IR (neat)/vmax cm⁻¹ : 2930, 1445, 1370, 1165, 725, 520.

¹H NMR (CCl₄, 60 MHz): δ 1.3-1.7 (m, 4H, saturated methylene protons)
1.8-2.2 (m 4H, -CH₂CH₂Br, -CH₂CH₂OSO₂⁻)
3.0 (s, 3H, -OSO₂CH₃)
3.3 (t, J=6Hz, 2H, -CH₂Br)
4.3 (t, J=6Hz, 2H, -CH₂CH₂OSO₂⁻)

Benzyl methylsulphonate (129)

A mixture of phenylmethanol (142, 0.54 g, 5.0 mmol) and triethylamine (0.5 g, 5.0 mmol) in dry DCM (15 mL) was ice-cooled. Methanesulphonyl chloride (0.57 g, 5.0 mmol) was added to it and stirred at 0° for 30 min. The resultant reaction mixture was worked up in the usual manner to afford (129, 0.82 g) in 88% yield.

IR (neat)/vmax cm⁻¹ : 3010, 2920, 1500, 1460, 1375, 1180, 760.

¹H NMR (CCl₄, 60 MHz): δ 3.0 (s, 3H, -OSO₂CH₃)
5.2 (s, 2H, -CH₂OSO₂⁻)
7.5 (s, 5H, -ArH)

Experimental 183
4-Chlorobenzyl methylsulphonate (130)

4-Chlorophenylmethanol (144, 0.71 g, 5.0 mmol) and triethyl amine (0.5 g, 5.0 mmol) in dry DCM (15 mL) was ice-cooled and to it was added methanesulphonyl chloride (0.57 g, 5.0 mmol). The reaction mixture was stirred for 30 min. and worked up as usual to furnish pure mesylate (130, 1.02 g) in 93% yield.

IR (nujol)/vmax cm⁻¹ : 3020, 2920, 1560, 1375, 1160, 860, 740.

¹H NMR (CDCl₃, 60 MHz): δ 3.0 (s, 3H, -OSSOC₃H₃)
5.2 (s, 2H, -CH₂SO₂⁻)
7.1 (s, 4H, -ArH)

4-Nitrobenzyl methylsulphate (131)

To a well stirred, ice-cold solution of 4-nitrophenylmethanol (145, 0.76 g, 5.0 mmol), triethylamine (0.5 g, 5.0 mmol) in dry dichloromethane (15 mL) was added dropwise methanesulphonyl chloride (0.57 g, 5.0 mmol). On completion of the reaction (monitored by TLC), the reaction mixture was worked up in the usual way to furnish pure product (131, 1.03 g, 90%), m.p. 86-88° (lit. 88-90°).

IR (CHCl₃)/vmax cm⁻¹ : 3020, 2900, 1560, 1465, 1370, 1185, 860.

¹H NMR (CDCl₃, 60 MHz): δ 3.0 (s, 3H, -OSSOC₃H₃)
5.2 (s, 2H, -CH₂SO₂⁻)
7.2 (d, J=7Hz, 2H, -ArH)
7.9 (d, J=7Hz, 2H, -ArH)

Phenyl methylsulphonate (132)

To a well stirred ice-cold mixture of phenol (63, 0.47 g, 5.0 mmol), triethylamine (0.5 g, 5.0 mmol) in dry DCM (15 mL) was added dropwise methanesulphonyl chloride (0.57 g, 5.0 mmol) at 0° and stirred for 30min. On completion, the reaction mixture was worked up in the usual way to furnish pure product (132, 0.82 g, 95%), m.p. 58° (lit. 58-60°).

IR (CHCl₃)/vmax cm⁻¹ : 3030, 1580, 1365, 1225, 1190, 730.

¹H NMR (CDCl₃, 60 MHz): δ 3.3 (s, 3H, -OSSOC₃H₃)
7.7 (s, 5H, -ArH)

General procedure for conversion of methylsulphonate esters to iodides

8-Iodo-2,6-dimethyloct-2-ene (133)

A mixture of compound (4, 0.23 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) dissolved in acetone (2.0 mL) was added to neutral alumina (1.0 g). The slurry was...
stirred for 10 min. and excess solvent was evaporated to provide a free flowing mixture which was then exposed to MWI at 640 W for 5 min. On cooling, the reaction mixture was extracted with dichloromethane (2x10 mL), filtered and filtrate was washed with water, brine and dried. Solvent was evaporated in vacuo to furnish pure iodide (133, 0.25 g) in 95% yield.

IR (neat)/v max cm⁻¹ : 2920, 1670, 1470, 825, 600.

¹H NMR (CCl₄, 60 MHz): δ 0.9 (d, J=6Hz, 3H, -CH₃)
1.1-1.4 (m, 5H, -C(CH₃)₂)
1.7 & 1.8 (2s, 6H, =C(CH₃)₂)
2.0-2.3 (m, 2H, -CH₂CH₂C=)
3.3 (t, J=6Hz, 2H, -CH₂I)
5.2 (t, J=6Hz, 1H, -CH₂CH=C-)

6-Iodo-2-methylhept-2-ene (134)
Mesylate (124, 0.2 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) impregnated on neutral alumina (1.0 g) were exposed to MWI at 640 W for 5 min. to furnish after the usual work up the pure product (134, 0.2 g) in 89% yield.

IR (neat)/v max cm⁻¹ : 3020, 2970, 2920, 1665, 1445, 790, 610.

¹H NMR (CCl₄, 60 MHz): δ 1.1 (d, J=6Hz, 3H, -CH₃)
1.2-1.5 (m, 2H, -CH₂CH₂CH-)
1.7 & 1.8 (2s, 6H, =C(CH₃)₂)
2.2 (m, 2H, -CH₂CH₂C=)
4.0-4.3 (m, 1H, -CH(CH₃)I)
5.2 (t, J=6Hz, 1H, -CH₂CH=C-)

Tetrahydrofurfuryl iodide (135)
Compound (125, 0.18 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) were adsorbed on neutral alumina (1.0 g) and subjected to MWI at 640 W for 5 min. The resultant product was worked up as usual to afford pure (135, 0.18 g) in 87% yield.

IR (neat)/v max cm⁻¹ : 2940, 1465, 1345, 1080, 590.

¹H NMR (CCl₄, 60 MHz): δ 1.7-2.1 (m, 4H, )
3.6-3.9 (m, 3H, -CHCH₂I)
4.0-4.2 (s, 2H, )
1-Iodocyclohexane (136)

A solid-supported mixture of 1-cyclohexyl methylsulphonate (126, 0.18 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) on neutral alumina (1.0 g) was subjected to MWI at 640 W for 5 min. The reaction mixture was worked up as usual to provide pure product (136, 0.19 g) in 89% yield.

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2960, 1445, 720, 580.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 1.2-2.0 (m, 10H, saturated methylene protons)
3.9-4.2 (m, 1H, -CH(1)I-)

1-Iodononane (137)

A mixture of 1-nonyl methylsulphonate (127, 0.22 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) doped on neutral alumina (1.0 g) was subjected to MWI at 640 W for 5 min. Usual work up of the reaction mixture yielded pure 1-iodononane (137, 0.23 g, 93%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2960, 1445, 720, 580.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 0.9 (t, J=6Hz, 3H, -CH$_2$CH$_2$)
1.2-1.6 (m, 14H, saturated methylene protons)
3.3 (t, J=6Hz, 2H, -CH$_2$I)

1-Bromo-6-iodohexane (138)

Compound (128, 0.26 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) were impregnated on neutral alumina (1.0 g) and exposed to MWI at 640 W for 3 min. to provide after the usual work up, pure 1-bromo-6-iodohexane (138, 0.26 g) in 90% yield.

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2920, 1485, 725, 575.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 1.2-1.5 (m, 4H, saturated methylene protons)
1.8-2.0 (m, 4H, -CH$_2$Br, -CH$_2$OH)
3.2 (t, J=6Hz, 2H, -CH$_2$I)
3.4 (t, J=6Hz, 2H, -CH$_2$Br)

Benzyl iodide (139)

Neutral alumina (1.0 g) impregnated with compound (129, 0.17 g, 1.0 mmol), anhyd. sodium iodide (0.16 g, 1.1 mmol) was exposed to microwaves at 640 W for 5 min. The reaction mixture was worked up as usual to afford the title compound (139, 0.19 g, 96%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 3030, 2930, 1520, 1460, 740, 580.

Experimental
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 4.5 (s, 2H, -$CH_2$I)  
7.4 (s, 5H, -$ArH$)

**4-Chlorobenzyl iodide (140)**

Impregnation of 4-chlorobenzyl methylsulphonate (130, 0.22 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) on neutral alumina (1.0 g) followed by subjection to MWI at 640 W for 5 min. provided pure 4-chlorobenzyl iodide (140, 0.24 g) after the usual work up in 95% yield.

IR (nujol)/$\nu_{\text{max}}$ cm$^{-1}$: 3000, 2940, 1580, 840, 760, 600.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 4.5 (s, 2H, -$CH_2$I)  
7.4 (s, 4H, -$ArH$)

**4-Nitrobenzyl iodide (141)**

4-Nitrobenzyl methylsulphonate (131, 0.23 g, 1.0 mmol) and anhyd. sodium iodide (0.16 g, 1.1 mmol) doped on neutral alumina (1.0 g) were subjected to MWI at 640 W for 5 min. Usual work up of the reaction mixture afforded pure 4-nitrobenzyl iodide (141, 0.25 g) in 97% yield.

IR (CHCl$_3$)/$\nu_{\text{max}}$ cm$^{-1}$: 3020, 2910, 1540, 1480, 860, 590.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 4.5 (s, 2H, -$CH_2$I)  
7.6 (d, $J=7$Hz, 2H, -$ArH$)  
7.8 (d, $J=7$Hz, 2H, -$ArH$)

**2-Allyloxybenzaldehyde (163)**

A mixture of salicyaldehyde (162, 0.5 g, 4.09 mmol), anhyd. K$_2$CO$_3$ (1.41 g, 10.21 mmol) and 3-bromopropene (61, 0.55 g, 4.55 mmol) in dry DMF (5 mL) was taken in a pyrex beaker covered with a watch glass and exposed to microwave irradiation at 500 W for 3 min. The contents were then cooled and extracted with diethyl ether (3x30 mL) and organic extracts were washed with water (2x5 mL), brine and dried. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography using 2% ethyl acetate in $n$-hexane as the eluant to afford pure product (163, 0.61 g) in 92% yield.

IR (CCl$_4$)/$\nu_{\text{max}}$ cm$^{-1}$: 3080, 2930, 2720, 1710, 1500, 1450, 1250.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 4.6 (d, $J=5$Hz, 2H, -$OCH_2CH=)$  
5.1-5.5 (m, 2H, -$CH=CH_2$)  
5.7-6.3 (m, 1H, -$CH=CH_2$)

*Experimental* 187
6.8-7.2 (m, 2H, 
\[ \text{H} \quad \text{H} \]
\[
\text{1.4-1.9 (m, )}
\]
10.1 (s, 1H, \(-\text{CM})\)

**General procedure for reduction of aldehydes using NaBH\(_4\)-Al\(_2\)O\(_3\) under MWI**

4-Methoxyphenylmethanol (143)

Sodium borohydride-alumina was prepared by thoroughly mixing NaBH\(_4\) (1.0 g) with neutral alumina (9.0 g) and grinding in a mortar. Freshly prepared sodium borohydride-alumina (0.11 g, 3.0 mmol) and 4-methoxybenzaldehyde (14, 0.4 g, 3.0 mmol) were taken in a test tube and placed in an alumina bath inside the microwave oven and irradiated at 640 W for 1 min. Upon completion of the reaction (monitored by TLC), the reaction mixture was extracted with diethyl ether (2x15 mL), filtered and filtrate was washed with brine and dried. Evaporation of the solvent in vacuo provided pure 4-methoxyphenylmethanol (143, 0.38 g, 94%).

\( ^1\text{H NMR (CCl}_4, 60 \text{ MHz}): \delta \)

- 3.2 (bs, 1H, \(-\text{OH}, \text{D}_2\text{O exchangeable})
- 3.7 (s, 3H, \(-\text{OCH}_3)\)
- 4.5 (s, 2H, \(-\text{CH}_2\text{OH})\)
- 6.8 (d, \(J=9\text{Hz}, 2\text{H}, \text{-ArH})\)
- 7.2 (d, \(J=9\text{Hz}, 2\text{H}, \text{-ArH})\)

4-Chlorophenylmethanol (144)

Reduction of 4-chlorobenzaldehyde (16, 0.4 g, 3.0 mmol) by using sodium borohydride-alumina (0.11 g, 3.0 mmol) under MWI at 640 W for 30 sec. followed by the usual work up as described above, gave 4-chlorophenylmethanol (144, 0.38 g) in 93% yield, m.p. 69-71\(^\circ\) (lit. 70-72\(^\circ\)).

\( ^1\text{H NMR (CDCl}_3, 60 \text{ MHz}): \delta \)

- 3.2 (bs, 1H, \(-\text{OH}, \text{D}_2\text{O exchangeable})
- 4.7 (s, 2H, \(-\text{CH}_2\text{OH})\)
- 7.2 (m, 4H, \text{-ArH})

4-Nitrophenylmethanol (145)

A mixture of 4-nitrobenzaldehyde (158, 0.45 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) was subjected to microwaves at 640 W for 30 sec. Usual work up
of the reaction mixture furnished 4-nitrophenylmethanol (145, 0.42 g, 93%), m.p. 91-93° (lit. 92-94°).

IR (CHCl₃)/νₓmax cm⁻¹: 3500, 3060, 2920, 1550, 1440, 1340, 1060, 820.

¹H NMR (CDCl₃, 60 MHz): δ 2.7 (bs, 1H, -OH, D₂O exchangeable)
4.9 (s, 2H, -CH₂OH)
7.7 (d, J=9Hz, 2H, -ArH)
8.4 (d, J=9Hz, 2H, -ArH)

2-Bromophenylmethanol (146)

2-Bromobenzaldehyde (159, 0.55 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) on exposure to microwaves at 640 W for 30 sec. provided after the usual work up, pure compound (146, 0.5 g) in 91% yield, m.p. 80° (lit. 79-82°).

IR (CHCl₃)/νₓmax cm⁻¹: 3400, 3050, 2900, 1510, 1460, 1070, 520.

¹H NMR (CDCl₃, 60 MHz): δ 2.0 (bs, 1H, -OH, D₂O exchangeable)
4.8 (s, 2H, -CH₂OH)
7.1-7.7 (m 4H, -ArH)

4-Hydroxyphenylmethanol (147)

4-Hydroxybenzaldehyde (160, 0.36 g, 3.0 mmol) was reduced with sodium borohydride-alumina (0.11 g, 3.0 mmol) under MWI at 640 W for 30 sec. to yield after the usual work up, pure compound (147, 0.28 g, 77%), m.p. 117° (lit. 118-122°).

IR (CHCl₃)/νₓmax cm⁻¹: 3350, 3060, 2930, 1510, 1460, 1405, 1220, 1100, 825.

¹H NMR (CDCl₃, 60 MHz): δ 2.1 (bs, 1H, -OH, D₂O exchangeable)
4.6 (s, 2H, -CH₂OH)
7.0 (d, J=8Hz, 2H, -ArH)
7.4 (d, J=8Hz, 2H, -ArH)
9.4 (bs, 1H, -OH, D₂O exchangeable)

3-Hydroxyphenylmethanol (148)

A mixture of 3-hydroxybenzaldehyde (161, 0.36 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) was subjected to microwaves at 640 W for 30 sec. to furnish after the usual work up of the reaction mixture, 3-hydroxyphenylmethanol (148, 0.27 g) in 75%, m.p. 70° (lit. 69-72°).

IR (CHCl₃)/νₓmax cm⁻¹: 3500, 3200, 3060, 2960, 1500, 1450, 1060, 900.

Experimental
\[^1\text{H NMR (CDCl}_3, 60\text{ MHz): } \delta 2.5 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)}\]

4.7 (s, 2H, -CH\textsubscript{2}OH)

6.9-7.6 (m, 4H, -ArH)

9.4 (bs, 1H, -OH, D\textsubscript{2}O exchangeable)

2-Hydroxyphenylmethanol (149)

Reduction of 2-hydroxybenzaldehyde (162, 0.36 g, 3.0 mmol) using sodium borohydride-alumina (0.11 g, 3.0 mmol) under MWI at 640 W for 30 sec. provided pure compound (149, 0.28 g) after the usual work up in 78% yield, m.p. 81-83 °C (lit. 83-85°C).

IR (CHCl\textsubscript{3})/\nu\text{max} cm\textsuperscript{-1}: 3500, 3200, 3080, 2920, 1500, 1460, 1120, 730.

\[^1\text{H NMR (CDCl}_3, 60\text{ MHz): } \delta 2.3 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)}\]

4.6 (s, 2H, -CH\textsubscript{2}OH)

6.9-7.5 (m, 4H, -ArH)

9.4 (bs, 1H, -OH, D\textsubscript{2}O exchangeable)

3-Phenoxyphenylmethanol (150)

3-Phenoxybenzaldehyde (15, 0.6 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) were irradiated in the microwave oven at 640 W for 30 sec. The resultant product was worked up as usual to furnish compound (150, 0.55 g, 91%).

IR (CCl\textsubscript{4})/\nu\text{max} cm\textsuperscript{-1}: 3400, 3060, 2930, 1500, 1460, 1180, 1060, 880.

\[^1\text{H NMR (CCl}_4, 60\text{ MHz): } \delta 3.7 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)}\]

4.5 (s, 2H, -CH\textsubscript{2}OH)

6.9-7.5 (m, 9H, -ArH)

2-Allyloxyphenylmethanol (151)

Reduction of 2-allyloxybenzaldehyde (163, 0.49 g, 3.0 mmol) with sodium borohydride-alumina (0.11 g, 3.0 mmol) under MWI at 640 W for 30 sec. furnished after the usual work up, compound (151, 0.46 g) in 93% yield.

IR (CCl\textsubscript{4})/\nu\text{max} cm\textsuperscript{-1}: 3500, 3080, 2930, 1500, 1450, 1230, 1060, 915.

\[^1\text{H NMR (CCl}_4, 60\text{ MHz): } \delta 2.5 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)}\]

4.4-4.6 (m, 4H, -CH\textsubscript{2}OH, -OCH\textsubscript{2}CH=)

5.1-5.5 (m, 2H, -CH=CH\textsubscript{2})

5.7-6.3 (m, 1H, -CH\textsubscript{2}CH=CH\textsubscript{2})

6.6-7.4 (m, 4H, -ArH)

Experimental 190
3,4-Methylenedioxyphenylmethanol (152)

Irradiation of a mixture of 3,4-methylenedioxybenzaldehyde (164, 0.45 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) in a microwave oven at 640 W for 30 sec. furnished after the usual work up of the reaction mixture, pure alcohol (152, 0.43 g) in 95%, m.p. 54° (lit. 53-55°).

IR (CHCl₃)/vmax cm⁻¹: 3400, 3080, 2920, 1500, 1450, 1240, 1100, 820.

¹H NMR (CDCl₃, 60 MHz): δ 3.5 (bs, 1H, -OH, D₂O exchangeable)
4.6 (s, 2H, -CH₂OH)
6.0 (s, 2H, -OCH₂O-)
6.8 (s, 3H, -ArH)

3,5-Dimethoxyphenylmethanol (153)

A mixture of 3,5-dimethoxybenzaldehyde (13, 0.5 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) was subjected to MWI at 640 W for 30 sec. to provide compound (153) after the usual work up in 96% yield (0.48 g), m.p. 48-51° (lit. 47-50°).

IR (CHCl₃)/vmax cm⁻¹: 3350, 3060, 2920, 1510, 1440, 1240, 1070, 890.

¹H NMR (CDCl₃, 60 MHz): δ 1.9 (bs, 1H, -OH, D₂O exchangeable)
3.8 (s, 6H, 2x-CH₃)
4.5 (s, 2H, -CH₂OH)
6.6-6.8 (m, 1H, H₃C-)
7.0 (d, J=3Hz, 2H, OCH₃)

2,5-Dimethoxyphenylmethanol (154)

2,5-Dimethoxybenzaldehyde (165, 0.5 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) were subjected to MWI at 640 W for 30 sec. to furnish after the usual work up of the reaction mixture, compound (154, 0.47 g) in 94% yield.

IR (CCl₄)/vmax cm⁻¹: 3400, 3080, 2920, 1500, 1440, 1240, 1110, 840.

¹H NMR (CCl₄, 60 MHz): δ 1.9 (bs, 1H, -OH, D₂O exchangeable)
3.8 (s, 6H, 2x-CH₃)
4.7 (s, 2H, -CH₂OH)

Experimental
4-Methylphenylmethanol (155)

A mixture of 4-methylbenzaldehyde (166, 0.36 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) was subjected to MWI at 640 W for 30 sec. Usual work up of the reaction mixture yielded pure 4-methylphenylmethanol (155, 0.34 g) in 93% yield, m.p. 57-59° (lit. 59-61°).

IR (CHCl₃)/νmax cm⁻¹: 3450, 2960, 1510, 1440, 1060, 840.

¹H NMR (CDCl₃, 60 MHz): δ 2.5 (s, 3H, -ArCH₃)

3.8 (bs, 1H, -OH, D₂O exchangeable)

4.5 (s, 2H, -CH₂OH)

7.2 (s, 4H, -ArH)

4-Hydroxy-3-methoxyphenylmethanol (156)

Reduction of 4-hydroxy-3-methoxybenzaldehyde (167, 0.45 g, 3.0 mmol) with sodium borohydride-alumina (0.11 g, 3.0 mmol) under MWI at 640 W for 30 sec. furnished 4-hydroxy-3-methoxyphenylmethanol (156, 0.4 g) after the usual work up in 88% yield, m.p. 112-114° (lit. 113-115°).

IR (CHCl₃)/νmax cm⁻¹: 3400, 3060, 2920, 1500, 1400, 1210, 1120, 690.

¹H NMR (CDCl₃, 60 MHz): δ 2.2 (bs, 1H, -OH, D₂O exchangeable)

3.9 (s, 3H, -OCH₃)

4.6 (s, 2H, -CH₂OH)

5.9 (bs, 1H, -OH, D₂O exchangeable)

6.8-7.1 (m, 3H, -ArH)

1-Phenylethanol (157)

Irradiation of a mixture of acetophenone (12, 0.36 g, 3.0 mmol) and sodium borohydride-alumina (0.11 g, 3.0 mmol) in a microwave oven at 640 W for 30 sec. furnished after the usual work up of the reaction mixture, pure compound (157, 0.35 g) in 96%.

IR (CCl₄)/νmax cm⁻¹: 3400, 3060, 2980, 2900, 1500, 1445, 1120, 740.

Experimental
1H NMR (CCl4, 60 MHz): δ 1.3 (d, J=6Hz, 3H, -CHCH3) 3.4 (bs, 1H, -OH, D2O exchangeable) 4.6 (q, J=6Hz, 1H, -CHCH3) 7.3 (s, 5H, -ArH)  

**General procedure of oxidation with QFC**  

**Benzaldehyde (10)**

Phenylmethanol (142, 0.11 g, 1.0 mmol) in dry DCM (1 mL) was added in a test tube containing powdered QFC (0.37 g, 1.5 mmol). Solvent was evaporated over a hot water bath with continuous swirling of the reaction mixture for 2 min. Resultant dry mixture is then placed in an alumina bath and subjected to MWI at 240 W for 3 min. On cooling, the reaction mixture was extracted with DCM (2x10 mL) and passed through a short silica gel column to remove QFC. The filtrate was evaporated in vacuo to afford pure benzaldehyde (10, 0.09 g) in 87% yield.

IR (CCl4)/vmax cm⁻¹: 3010, 2720, 1720, 1500, 1450, 760.

**4-Methoxybenzaldehyde (14)**

A mixture of 4-methoxyphenylmethanol (143, 0.14 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was subjected to MWI at 240 W for 3 min. The reaction mixture on usual work up as described above furnished pure 4-methoxybenzaldehyde (14, 0.13 g) in 95% yield.

IR (CHCl3)/vmax cm⁻¹: 3010, 2850, 2710, 1705, 1500, 1455, 840, 720.

**4-Chlorobenzaldehyde (16)**

4-Chlorophenylmethanol (144, 0.14 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) were exposed to MWI at 240 W for 3 min. Usual work up of the reaction mixture provided pure 4-chlorobenzaldehyde (16, 0.13 g) in 95% yield, m.p. 47° (lit. 47-50°).

IR (CHCl3)/vmax cm⁻¹: 3010, 2710, 1700, 1500, 1455, 840, 720.
4-Nitrobenzaldehyde (158)

Exposure of 4-nitrophenylmethanol (145, 0.15 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) to microwaves at 240 W for 3 min. after the usual work up furnished 4-nitrobenzaldehyde (158, 0.14 g) in 96% yield, m.p. 104-106° (lit. 105-108°).

IR (CHCl₃)/νmax cm⁻¹: 3010, 2720, 1720, 1500, 1485, 1450, 850.

H NMR (CDCl₃, 60 MHz): δ 7.4 (d, J=8Hz, 2H, -ArH)
  7.7 (d, J=8Hz, 2H, -ArH)
  10.0 (s, 1H, -CHO)

2-Bromobenzaldehyde (159)

Subjection of 2-bromophenylmethanol (146, 0.19 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) to microwaves at 240 W for 3 min. after the usual work up provided 2-bromobenzaldehyde (159, 0.18 g) in 96% yield.

IR (CCl₄)/νmax cm⁻¹: 3010, 2710, 1720, 1500, 1455, 745, 610.

H NMR (CDCl₃, 60 MHz): δ 7.3-7.7 (m, 3H, )
  7.8-8.1 (m, 1H, )
  10.3 (s, 1H, -CHO)

4-Hydroxybenzaldehyde (160)

A mixture of 4-hydroxyphenylmethanol (147, 0.12 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was irradiated in a microwave oven at 240 W for 3 min. The resultant mixture was worked up as usual to furnish pure 4-hydroxybenzaldehyde (160, 0.1 g, 85%), m.p. 117° (lit. 117-119°).

IR (CHCl₃)/νmax cm⁻¹: 3500, 3010, 2720, 1720, 1500, 1245, 835.

H NMR (CDCl₃, 60 MHz): δ 7.0 (d, J=8Hz, 2H, -ArH)
  7.9 (d, J=8Hz, 2H, -ArH)
  9.3 (bs, 1H, -OH, D₂O exchangeable)
  10.0 (s, 1H, -CHO)

Experimental

194
3-Hydroxybenzaldehyde (161)

3-Hydroxyphenylmethanol (148, 0.12 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) were irradiated in a microwave oven at 240 W for 3 min. The resultant mixture was worked up as usual to furnish pure 4-hydroxybenzaldehyde (161, 0.09 g, 82%), m.p. 101° (lit. 103-105°).

IR (CHCl₃)/ν max cm⁻¹: 3350, 3000, 2710, 1715, 1510, 1250, 800.

¹H NMR (CDCl₃, 60 MHz): δ 7.0-7.5 (m, 4H, -Ar H)
9.3 (bs, 1H, -OH, D₂O exchangeable)
10.0 (s, 1H, -CHO)

2-Hydroxybenzaldehyde (162)

Exposure of 2-hydroxyphenylmethanol (149, 0.12 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) to MWI at 240 W for 3 min. yielded, after the usual work up, pure 2-hydroxybenzaldehyde (162, 0.1 g, 86%).

IR (CCl₄)/ν max cm⁻¹: 3450, 3020, 2720, 1710, 1500, 1220, 740.

¹H NMR (CCl₄, 60 MHz): δ 6.8-7.2 (m, 2H, H, H')
7.4-7.7 (m, 2H, H)
10.1 (s, 1H, -CHO)
11.1 (bs, 1H, -OH, D₂O exchangeable)

3-Phenoxybenzaldehyde (15)

Oxidation of 3-phenoxyphenylmethanol (150, 0.2 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) under MWI at 240 W for 3 min. furnished, after the usual work up, pure 3-phenoxybenzaldehyde (15, 0.19 g, 96%).

IR (CCl₄)/ν max cm⁻¹: 3010, 2710, 1720, 1520, 1150, 890, 840, 735.

¹H NMR (CCl₄, 60 MHz): δ 7.0-7.7 (m, 9H, -ArH)
10.1 (s, 1H, -CHO)

2-Allyloxybenzaldehyde (163)

A mixture of 2-allyloxyphenylmethanol (151, 0.16 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was subjected to microwaves at 240 W for 3 min. The resultant mixture was worked up as usual to furnish pure 2-allyloxybenzaldehyde (163, 0.15 g) in 94% yield.

IR (CCl₄)/ν max cm⁻¹: 3080, 2930, 2720, 1710, 1500, 1450, 1250.

Experimental 195
$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 4.6 (d, $J=5$Hz, 2H, -OCH$_2$CH=)
5.1-5.5 (m, 2H, -CH=CH$_2$)
5.7-6.3 (m, 1H, -CH=CH$_2$)
6.8-7.2 (m, 2H, )
7.4-7.9 (m, 2H, )
10.1 (s, 1H, -CHO)

3,4-Methylenedioxybenzaldehyde (164)

A mixture of 3,4-methylenedioxyphenylmethanol (152, 0.15 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was irradiated in a microwave oven at 240 W for 3 min. The resultant mixture was worked up in a usual manner to yield pure 3,4-methylenedioxybenzaldehyde (164, 0.14 g) in 94% yield, m.p. 34-36° (lit. 35-37°).

IR (CHCl$_3$)/$\nu_{\text{max}}$ cm$^{-1}$: 3000, 2720, 1710, 1500, 1450.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 6.0 (s, 2H, -OCH$_2$O-)
7.0 (d, $J=7$Hz, 1H, )
7.3-7.6 (m, 2H, )
9.9 (s, 1H, -CHO)

3,5-Dimethoxybenzaldehyde (13)

Exposure of 3,5-dimethoxyphenylmethanol (153, 0.17 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) to MWI at 240 W for 3 min. yielded pure product (13, 0.16 g) after the usual work up in 95% yield, m.p. 47° (lit. 45-48°).

IR (CHCl$_3$)/$\nu_{\text{max}}$ cm$^{-1}$: 3010, 2850, 2710, 1720, 1510, 1240, 890.

$^1$H NMR (CDCl$_3$, 60 MHz): $\delta$ 3.9 (s, 6H, 2x-OCH$_3$)
6.6-6.8 (m, 1H, )
7.0 (d, $J=3$Hz, 2H, )
10.2 (s, 1H, -CHO)

Experimental 196
2,5-Dimethoxybenzaldehyde (165)

A mixture of 2,5-dimethoxyphenylmethanol (154, 0.17 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was irradiated in a microwave oven at 240 W for 3 min. The resultant mixture was worked up in a usual manner to yield pure 2,5-dimethoxybenzaldehyde (165, 0.15 g) in 93% yield, m.p. 47-50° (lit. 49-52°).

IR (CHCl₃)/\(\nu_{\text{max}}\) cm⁻¹: 3020, 2840, 2720, 1715, 1520, 1245, 880.

\(^1\)H NMR (CDCl₃, 60 MHz): 6 3.9 (s, 6H, 2x-OCH₃)
6.7-6.9 (m, 1H, H)
7.0 (d, \(J=3\)Hz, 2H, H)
10.1 (s, 1H, -CHO)

4-Methylbenzaldehyde (166)

Oxidation of 4-methylphenylmethanol (155, 0.12 g, 1.0 mmol) using QFC (0.37 g, 1.5 mmol) under MWI at 240 W for 3 min. furnished pure product (166, 0.11 g) after the usual work up in 94% yield.

IR (CCl₄)/\(\nu_{\text{max}}\) cm⁻¹: 3030, 2920, 2710, 1720, 1540, 1460, 1220, 840.

\(^1\)H NMR (CCl₄, 60 MHz): 6 2.5 (s, 3H, -ArCH₃)
7.4 (d, \(J=8\)Hz, 2H, -ArH)
7.9 (d, \(J=8\)Hz, 2H, -ArH)
10.1 (s, 1H, -CHO)

4-Hydroxy-3-methoxybenzaldehyde (167)

A mixture of 4-hydroxy-3-methoxyphenylmethanol (156, 0.15 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was subjected to MWI at 240 W for 3 min. Usual work up of the reaction mixture furnished pure 4-hydroxy-3-methoxybenzaldehyde (167, 0.13 g) in 90%, m.p. 82° (lit. 81-83°).

IR (CHCl₃)/\(\nu_{\text{max}}\) cm⁻¹: 3500, 3010, 2850, 2720, 1705, 1475, 1315, 1250, 860.

\(^1\)H NMR (CDCl₃, 60 MHz): 6 4.0 (s, 3H, -CH₃)
6.0 (bs, 1H, -OH, D₂O exchangeable)
7.0 (s, 1H, -CHO)

**Experimental**

197
3-Phenylprop-2-enal (28)

Cinnamyl alcohol (48, 0.13 g, 1.0 mmol) was oxidized with QFC (0.37 g, 1.5 mmol) under MWI at 240 W for 3 min. The resultant product was worked up as usual to provide pure 4-phenylprop-2-enal (28, 0.12 g) in 97%.

IR (CCl₄)/ν max cm⁻¹: 3010, 2720, 1710, 1600, 970, 760.

¹H NMR (CCl₄, 60 MHz): δ 6.6 (dd, J=6Hz, 7Hz, 1H, -CHC=CHO)
7.2-7.6 (m, 6H, C₆H₅CH=CH-)
9.8 (s, 1H, -CHO)

2-Furaldehyde (29)

2-Furanmethanol (49, 0.1 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) were subjected to MWI at 240 W for 3 min. Usual work up of the reaction mixture yielded pure 2-furaldehyde (29, 0.09 g) in 91% yield.

IR (CCl₄)/ν max cm⁻¹: 3030, 2710, 1700, 1190, 675.

¹H NMR (CCl₄, 60 MHz): δ 6.7-6.8 (m, 1H, )
7.4 (d, J=4Hz, 1H, )
7.9 (s, 1H, )
9.9 (s, 1H, -CHO)

2-Thiophenealdehyde (30)

A mixture of 2-thiophenemethanol (50, 0.11 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) was exposed to MWI at 240 W for 3 min. followed by usual work up furnished 2-thiophenealdehyde (30, 0.1 g) in 92% yield.

IR (CCl₄)/ν max cm⁻¹: 3020, 2720, 1700, 1180, 680.

¹H NMR (CCl₄, 60 MHz): δ 6.6-6.8 (m, 1H, )
7.3 (d, J=4Hz, 1H, )
7.8 (s, 1H, )
10.0 (s, 1H, -CHO)
Acetophenone (12)

Subjection of 1-phenylmethanol (157, 0.12 g, 1.0 mmol) and QFC (0.37 g, 1.5 mmol) to microwaves at 240 W for 3 min. and after the usual work up provided acetophenone (12, 0.1 g) in 85% yield.

IR (CCl₄)/νmax cm⁻¹: 3000, 1720, 1600, 1500, 1450.

¹H NMR (CCl₄, 60 MHz): δ 2.5 (s, 3H, -COCH₃)
7.4-7.7 (m, 3H, -ArH)
7.9-8.1 (m, 2H, -ArH)

4-Acetoxybenzaldehyde (168)

To a mixture of 4-hydroxybenzaldehyde (160, 1.5 g, 12.2 mmol) and 10% aq. NaOH (20 mL) contained in a 250 mL separatory funnel, was added about 50 g of crushed ice followed by distilled acetic anhydride (1.59 g, 15.5 mmol). The mixture was shaken vigorously for 5 min. and CCl₄ (30 mL) was added and separated. The organic layer was washed with 10% aq. Na₂CO₃ (2x10 mL) until effervescence ceases, washed with water (5 mL), brine and dried. The solvent was evaporated in vacuo to afford pure product (168, 1.81 g, 90%).

IR (neat)/νmax cm⁻¹: 3010, 2970, 1730, 1705, 1520, 1470, 1250, 840.

¹H NMR (CCl₄, 60 MHz): δ 2.2 (s, 3H, -COCH₃)
7.2 (d, J=8Hz, 2H, -ArH)
7.9 (d, J=8Hz, 2H, -ArH)
10.0 (s, 1H, -CHO)

General procedure for the preparation of imines

N-Phenylbenzylidine (169)

Method A

A mixture of benzaldehyde (10, 0.1 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) taken in a 10 mL Erlenmeyer flask was subjected to microwave irradiation at 70 W 30 sec. On cooling, the reaction mixture was extracted with dichloromethane (2x10 mL) and the organic extracts were passed through a short neutral alumina column eluting with n-hexane and dried. Evaporation of the solvent in vacuo furnished pure imine (169, 0.15 g, 90%), m.p. 52° (lit. 52-54°).

Method B

A mixture of benzaldehyde (10, 0.1 g, 1.0 mmol), aniline (0.11g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 30 min at r.t. The reaction mixture was
extracted with DCM (3x10 mL), filtered, dried and solvent evaporated under vacuum. The residue was purified through a neutral alumina column eluting with n-hexane to furnish pure imine (169, 0.14 g, 82%), m.p. 52° (lit. 52-54°).

IR (CHCl₃)/νmax cm⁻¹: 3050, 2920, 1635, 1480, 760.

¹H NMR (CDCl₃, 60 MHz): δ 7.1-7.5 (m, 8H, -ArH)
7.7-7.9 (m, 2H, -ArH)
8.3 (s, 1H, -CH=N-)

*N-Phenyl-4-methoxybenzylidene (170)*

**Method A**
A mixture of 4-methoxybenzaldehyde (14, 0.14 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) on subjection to MWI at 70 W for 30 sec., followed by usual work up afforded pure Schiff base (170, 0.2 g, 95%), m.p. 61-63° (lit. 63°).

**Method B**
A mixture of 4-methoxybenzaldehyde (14, 0.14 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) alongwith molecular sieves (4Å, 2 g) was ground in a mortar for 25 min. Usual work up of the resultant mixture followed by purification as described above afforded pure product (170, 0.19 g, 90%), m.p. 61-63° (lit. 63°).

IR (CHCl₃)/νmax cm⁻¹: 3050, 2920, 1620, 1500, 1240, 860.

¹H NMR (CDCl₃, 60 MHz): δ 3.7 (s, 3H, -OCH₃)
7.1 (d, J=8Hz, 2H, -ArH)
7.3-7.6 (m, 5H, -ArH)
8.0 (d, J=8Hz, 2H, -ArH)
8.5 (s, 1H, -CH=N-)

*N-Phenyl-3-phenoxybenzylidene (171)*

**Method A**
3-Phenoxybenzaldehyde (15, 0.2 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) were taken in a beaker and irradiated in microwave oven at 70 W for 30 sec. The resultant reaction mixture was worked up in a usual way to furnish pure imine (171, 0.25 g) in 90% yield, m.p. 44-46°.

**Method B**
In a mortar, a mixture of 3-phenoxybenzaldehyde (15, 0.2 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar at r.t. for 20 min. to
afford pure N-phenyl-3-phenoxybenzylidine (171, 0.24 g) after usual work up and purification in 87% yield, m.p. 44-46°.

IR (CHCl₃)/v_max cm⁻¹: 3060, 1630, 1490, 1220, 800.

¹H NMR (CDCl₃, 60 MHz): δ 6.9-7.7 (m, 14H, -ArH)
  8.4 (s, 1H, -CH=N-)

N-Phenyl-4-chlorobenzylidine (172)

Method A

4-Chlorobenzaldehyde (16, 0.14 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) were exposed to MWI at 70 W for 30 sec. and furnished N-phenyl-4-chlorobenzylidine (172) after the usual work up in 96% yield (0.21 g), m.p. 65° (lit. 66°).

Method B

A mixture of 4-chlorobenzaldehyde (16, 0.14 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 30 min. Usual work up of the reaction mixture followed by purification afforded pure aldimine (172, 0.2 g) in 94% yield, m.p. 65° (lit. 66°).

IR (nujol)/v_max cm⁻¹: 3030, 2910, 1620, 1580, 840, 700.

¹H NMR (CDCl₃, 60 MHz): δ 7.2 (s, 5H, -ArH)
  7.4 (d, J=8Hz, 2H, -ArH)
  7.8 (d, J=8Hz, 2H, -ArH)
  8.3 (s, 1H, -CH=N-)

N-Phenyl-4-nitrobenzylidine (173)

Method A

A mixture of 4-nitrobenzaldehyde (158, 0.15 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) was subjected to MWI at 70 W for 30 sec. On cooling, the reaction mixture was worked up as described to give N-phenyl-4-nitrobenzylidine (173, 0.21 g) in 95% yield.

Method B

4-Nitrobenzaldehyde (158, 0.15 g, 1.0 mmol), aniline (0.11 g, 1.2mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 25 min. The reaction mixture followed by usual work up and purification furnished pure N-phenyl-4-nitrobenzylidine (173, 0.2 g, 90%).

IR (CHCl₃)/v_max cm⁻¹: 3020, 2920, 1635, 1520, 1480, 1370, 820.

¹H NMR (CDCl₃, 60 MHz): δ 7.1-7.4 (m, 5H, -ArH)
  8.1 (d, J=8Hz, 2H, -ArH)

Experimental
N-Phenyl-2-bromobenzylidine (174)

Method A

On exposure of a mixture of 2-bromobenzaldehyde (159, 0.18 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) to MWI at 70 W for 30 sec. furnished pure N-phenyl-2-bromobenzylidine (174) after usual work up in 97% yield (0.24 g).

Method B

2-Bromobenzaldehyde (159, 0.18 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 25 min. The resultant mixture was worked up in a usual manner to furnish pure aldimine (174, 0.23 g) in 93% yield.

IR (CHCl₃)/νmax cm⁻¹: 3050, 2900, 1635, 1490, 735, 540.

¹H NMR (CDCl₃, 60 MHz): δ 7.2-8.5 (m, 8H, -ArH)

8.5 (d, J=8Hz, 2H, -ArH)
8.6 (s, 1H, -CN=)

N-Phenyl-2-hydroxybenzylidine (175)

Method A

Exposure of a mixture of 2-hydroxybenzaldehyde (162, 0.12 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) to microwaves at 70 W for 30 sec. furnished after the usual work up pure N-phenyl-2-hydroxybenzylidine (175, 0.18 g, 92%), m.p. 50-51° (lit.51°).

Method B

A mixture of 2-hydroxybenzaldehyde (162, 0.12 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 20 min., followed by usual work up afforded pure N-phenyl-2-hydroxybenzylidine (175, 0.19 g) in 97% yield, m.p. 50-51° (lit.51°).

IR (CHCl₃)/νmax cm⁻¹: 3600, 3050, 2910, 1635, 1180, 840.

¹H NMR (CDCl₃, 60 MHz): δ 7.2-7.4 (m, 9H, -ArH)

8.6 (s, 1H, -CN=)
12.3 (bs, 1H, -OH, D₂O exchangeable)

Experimental 202
**N-Phenyl-2-allyloxybenzylidine (176)**

**Method A**

A mixture of 2-allyloxybenzaldehyde (163, 0.16 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) was subjected to MWI at 70 W for 30 sec. On cooling, the reaction mixture was worked up in a usual manner to provide pure imine (176, 0.22 g) in 95% yield.

**Method B**

2-Allyloxybenzaldehyde (163, 0.16 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 25 min. The reaction mixture followed by purification was worked up in a usual manner to provide pure aldimine (176, 0.21 g, 93%).

IR (CHCl₃)/νmax cm⁻¹: 2920, 2880, 1630, 1500, 1260, 1060, 760.

^1H NMR (CDCl₃, 60 MHz): δ 4.4 (d, J=5Hz, 2H, -OCH₂CH=)
5.0-5.1 (m, 2H, -CH₂CH=CH₂)
5.6-6.2 (m, 1H, -CH₂CH=CH₂)
6.9-7.4 (m, 8H, -ArH)
8.1 (d, J=6Hz, 1H, -CH=N-)
8.7 (s, 1H, -CH=N-)

**N-Phenyl-4-acetoxybenzylidine (177)**

**Method A**

A mixture of 4-acetoxybenzaldehyde (168, 0.16 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) on exposure to MWI at 70 W for 30 sec. afforded the pure product (177, 0.22 g) after usual work up in 95% yield, m.p. 54-56°.

**Method B**

When a mixture of 4-acetoxybenzaldehyde (168, 0.16 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 30 min., crude product was obtained after usual work up, which was purified to furnish pure imine (177, 0.21 g) in 93% yield, m.p. 54-56°.

IR (CHCl₃)/νmax cm⁻¹: 3020, 2900, 1730, 1625, 1300, 860.

^1H NMR (CDCl₃, 60 MHz): δ 2.3 (s, 3H, -OCOCH₃)
7.2 (d, J=8Hz, 2H, -ArH)
7.1-7.5 (m, 5H, -ArH)
8.0 (d, J=8Hz, 2H, -CH=N-)
8.5 (s, 1H, -CH=N-)

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**Experimental**
**N-Phenylcinnamylidine (178)**

**Method A**

Cinnamaldehyde (28, 0.13 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) were irradiated in microwave oven at 70 W for 30 sec. Usual work up of the reaction mixture afforded N-phenylcinnamylidine (178, 0.18 g, 88%), m.p. 80-83°.

**Method B**

A mixture of cinnamaldehyde (28, 0.13 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar at r.t. for 30 min. Usual work up and purification furnished pure N-phenylcinnamylidine (178, 0.15 g) in 75% yield, m.p. 80-83°.

IR (CHCl₃)/vmax cm⁻¹: 3050, 2970, 1648, 1610, 960, 740.

¹H NMR (CDCl₃, 60 MHz): δ 7.1-7.7 (m, 12H, C₆H₅CH=CH-, -ArH)
8.2 (dd, J=4Hz, 3Hz, 1H, -C//=N-)

**N-Phenylfurfurylidine (179)**

**Method A**

A mixture of furfural (29, 0.1 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) was exposed to MWI at 70 W for 30 sec. Usual work up of the reaction mixture furnished pure Schiff base (179, 0.17 g) in 95% yield.

**Method B**

Furfural (29, 0.1 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 20 min., followed by usual work up provided pure imine (179, 0.16 g) in 92% yield.

IR (CHCl₃)/vmax cm⁻¹: 3040, 2890, 1620, 1590, 1080, 760.

¹H NMR (CCl₄, 60 MHz): δ 6.5-6.7 (m, 1H, -<svg></svg>)
7.0-7.3 (m, 6H, -ArH, -<svg></svg>)
7.6 (s, 1H, -<svg></svg>)
8.3 (s, 1H, -CH=N-)

**N-Phenylthiophenylidine (180)**

**Method A**

Irradiation of a mixture of 2-thiophenealdehyde (30, 0.11 g, 1.0 mmol) and aniline (0.11 g, 1.2 mmol) in a microwave oven at 70 W for 30 sec. afforded N-phenylthiophenylidine (180) after the usual work up in 99% yield (0.18 g), m.p. 85-87°.
Method B

A mixture of 2-thiophencaldehyde (30, 0.11 g, 1.0 mmol), aniline (0.11 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar at r.t. for 25 min. The reaction mixture was worked up in a usual manner to furnish pure N-phenylthiophenylidine (180, 0.17 g) in 96% yield, m.p. 85-87°.

IR (CHCl3)/\(v_{\text{max}}\) cm\(^{-1}\): 3050, 2870, 1610, 735.

\(^1\)H NMR (CDCl\(_3\), 60 MHz): \(\delta\) 7.1-7.5 (m, 8H, -ArH), 8.5 (s, 1H, -C//=N-)

Mixture of benzaldehyde (10) and acetophenone (12)

Benzaldehyde (10, 0.1 g, 1.0 mmol), acetophenone (12, 0.12 g, 1.0 mmol) and aniline (0.22 g, 2.4 mmol) were subjected to MWI at 70 W for 2 min. Usual work up followed by purification through neutral alumina column chromatography using 2% ethyl acetate in n-hexane as eluant furnished pure N-phenylbenzylidine (169, 0.16 g, m.p. 52°, lit 52-54°) in 95% yield and acetophenone (12) was recovered as such.

IR (CHCl3)/\(v_{\text{max}}\) cm\(^{-1}\): 3050, 2920, 1635, 1480, 760.

\(^1\)H NMR (CDCl\(_3\), 60 MHz): \(\delta\) 7.1-7.5 (m, 8H, -ArH), 7.7-7.9 (m, 2H, //CH\(_2\)//), 8.3 (s, 1H, -CH=N-)

Mixture of 4-methoxybenzaldehyde (14) and acetophenone (12)

A mixture of 4-methoxybenzaldehyde (14, 0.14 g, 1.0 mmol), acetophenone (12, 0.12 g, 1.0 mmol) and aniline (0.22 g, 2.4 mmol) was subjected to MWI at 70 W for 2 min. On cooling, the reaction mixture was worked up as usual followed by purification through neutral alumina column chromatography using 2% ethyl acetate in n-hexane as eluant afforded pure aldimine (170, 0.2 g, m.p. 63°, lit 63°) in 93% yield, whereas acetophenone (12) was obtained unreacted.

IR (CHCl3)/\(v_{\text{max}}\) cm\(^{-1}\): 3050, 2920, 1620, 1500, 1240, 860.

\(^1\)H NMR (CDCl\(_3\), 60 MHz): \(\delta\) 3.7 (s, 3H, -OC\(_3\)//3), 7.1 (d, \(J=8\)Hz, 2H, -ArH), 7.3-7.6 (m, 5H, -ArH), 8.0 (d, \(J=8\)Hz, 2H, -ArH), 8.5 (s, 1H, -CH=N-)

Experimental 205
Mixture of 3-phenylprop-2-enal (28) and 4-phenylbut-3-en-2-one (31)

A mixture of 3-phenylprop-2-enal (28, 0.13 g, 1.0 mmol), 4-phenylbut-3-en-2-one (31, 0.15 g, 1.0 mmol) and aniline (0.2 g, 2.4 mmol) was exposed to MWI at 70 W for 2 min. Usual work up gave crude product which after purification through neutral alumina column chromatography using 2% ethyl acetate in n-hexane as eluant furnished pure aldimine (178, 0.17 g, m.p.80-83°) in 86% yield, whereas unreacted ketone (31) was obtained as such.

IR (CHCl₃)/νₘₐₓ cm⁻¹: 3050, 2970, 1648, 1610, 960, 740.

¹H NMR (CDCl₃, 60 MHz): δ 7.1-7.7 (m, 12H, -ArH), 8.2 (dd, J=4Hz, 3Hz, 1H, -C//=N-)

A-Benzylbenzylidine (181)

Method A

A mixture of benzaldehyde (10, 0.1 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was exposed to MWI at 70 W for 30 sec. to afford pure imine (181, 0.16 g) after the usual work up in 89% yield.

Method B

A mixture of benzaldehyde (10, 0.1 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 20 min at r.t. Usual work up followed by purification yielded pure A-benzylbenzylidine (181, 0.15 g, 83%).

IR (neat)/νₘₐₓ cm⁻¹: 3040, 2920, 1620, 1485, 740.

¹H NMR (CCl₄, 60 MHz): δ 4.7 (s, 2H, -CH₂Ar), 7.2-7.5 (m, 8H, -ArH), 7.7-7.9 (m, 2H, \( \text{CH} = \) ), 8.3 (s, 1H, -CH=N-)

A-Benzyl-4-methoxybenzylidine (182)

Method A

A mixture of 4-methoxybenzaldehyde (14, 0.14 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was subjected to MWI at 70 W for 30 sec.Usual work up of the reaction mixture provided pure N-benzyl-4-methoxybenzylidine (182, 0.22 g, 97%).

Method B

4-Methoxybenzaldehyde (14, 0.14 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) alongwith molecular sieves (4Å, 2 g) were ground in a mortar for 20 min., followed by usual work up furnished aldimine (182, 0.21 g) in 91% yield.
IR (CHCl₃/ν_max cm⁻¹): 3030, 2910, 1635, 1480, 1260, 850.

¹H NMR (CCl₄, 60 MHz): δ 3.6 (s, 3H, -OCH₃)
4.6 (s, 2H, -CH₂Ar)
6.8 (d, J=8Hz, 2H, -ArH)
7.1-7.4 (m, 5H, -ArH)
7.7 (d, J=8Hz, 2H, -ArH)
8.2 (s, 1H, -CH=N-)

N-Benzyl-3-phenoxybenzylidine (183)

Method A

3-Phenoxybenzaldehyde (15, 0.2 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) were irradiated in a microwave oven at 70 W for 30 sec. followed by usual work up furnished pure aldimine (183, 0.26 g) in 91% yield.

Method B

A mixture of 3-phenoxybenzaldehyde (15, 0.2 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 20 min. The reaction mixture was worked up as usual to furnish pure imine (183, 0.26 g) in 90% yield.

IR (CHCl₃/ν_max cm⁻¹): 3050, 2930, 1630, 1485, 1180.
¹H NMR (CCl₄, 60 MHz): δ 4.8 (s, 2H, -CH₂Ar)
7.2-8.1 (m, 14H, -ArH)
8.4 (s, 1H, -CH=N-)

N-Benzyl-4-chlorobenzylidine (184)

Method A

A mixture of 4-chlorobenzaldehyde (16, 0.14 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was exposed to MWI at 70 W for 30 sec. pure N-benzyl-4-chlorobenzylidine (184, 0.21 g) was obtained after the usual work up in 92% yield.

Method B

In a mortar, a mixture of 4-chlorobenzaldehyde (16, 0.14 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4 Å, 2 g) was ground in a mortar for 30 min., followed by usual work up furnished pure N-benzyl-4-chlorobenzylidine (184, 0.2 g) in 90% yield.

IR (nujol/ν_max cm⁻¹): 3050, 2920, 1630, 1570, 830, 680.

Experimental 207
\[ ^1 \text{H NMR} (\text{CDCl}_3, 60 \text{ MHz}): \delta 4.6 \text{ (s, 2H, } -\text{CH}_2\text{Ar)} \]
\[ 7.0-7.3 \text{ (m, 5H, } -\text{ArH)} \]
\[ 7.4 \text{ (d, } J=8\text{Hz, 2H, } -\text{ArH)} \]
\[ 7.8 \text{ (d, } J=8\text{Hz, 2H, } -\text{ArH)} \]
\[ 8.3 \text{ (s, 1H, } -\text{C//=N-)} \]

\textit{N-Benzyl-4-nitrobenzylidine (185)}

\textbf{Method A}

When a mixture of 4-nitrobenzaldehyde (158, 0.15 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was exposed to MWI at 70 W for 30 sec, pure Schiff base (185, 0.22 g) was obtained after the usual work up in 94% yield, m.p. 56° (lit 56°).

\textbf{Method B}

A mixture of 4-nitrobenzaldehyde (158, 0.15 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 25 min. The resultant mixture was worked up as usual to provide pure aldimine (185, 0.22 g, 94%), m.p. 56° (lit 56°).

\[ \text{IR (CHCl}_3)/\nu_{\text{max}} \text{ cm}^{-1}: 3010, 2930, 1630, 1510, 1460, 815. \]

\[ ^1 \text{H NMR} (\text{CDCl}_3, 60 \text{ MHz}): \delta 4.9 \text{ (s, 2H, } -\text{CH}_2\text{Ar)} \]
\[ 7.2-7.8 \text{ (m, 5H, } -\text{ArH)} \]
\[ 8.1 \text{ (d, } J=8\text{Hz, 2H, } -\text{ArH)} \]
\[ 8.4 \text{ (d, } J=8\text{Hz, 2H, } -\text{ArH)} \]
\[ 8.6 \text{ (s, 1H, } -\text{C//=N-)} \]

\textit{N-Benzyl-2-bromobenzylidine (186)}

\textbf{Method A}

A mixture of 2-bromobenzaldehyde (159, 0.18 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was subjected to MWI at 70 W for 30 sec, and afforded pure N-Benzyl-2-bromobenzylidine (186) after usual work up in 95% yield (0.25 g).

\textbf{Method B}

When a mixture of 2-bromobenzaldehyde (159, 0.18 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 25 min., N-benzyl-2-bromobenzylidine (186) was obtained after the usual work up and purification in 93% yield (0.24 g).

\[ \text{IR (CHCl}_3)/\nu_{\text{max}} \text{ cm}^{-1}: 3020, 2920, 1625, 1510, 740, 520. \]

\textit{Experimental}
\(^1\)H NMR (CDCl\(_3\), 60 MHz): \(\delta\) 4.7 (s, 2H, -CH\(_2\)Ar)

7.1-7.3 (m, 8H, -ArH)

8.1 (d, \(J=6\)Hz, 1H, -CH=CH\(_2\))

8.6 (s, 1H, -C//=N-)

\(N\)-Benzyl-2-hydroxybenzylidine (187)

**Method A**

2-Hydroxybenzaldehyde (162, 0.12 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) were exposed to MWI at 70 W for 30 sec. The reaction mixture was cooled and worked up as usual to give \(N\)-benzyl-2-hydroxybenzylidine (187, 0.19 g) in 94% yield.

**Method B**

A mixture of 2-hydroxybenzaldehyde (162, 0.12 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 20 min., which on usual work up furnished \(N\)-benzyl-2-hydroxybenzylidine (187, 0.19 g, 94%).

IR (CHCl\(_3\))/\(\nu_{max}\) cm\(^{-1}\): 3550, 3060, 2920, 1625, 1160, 835.

\(^1\)H NMR (CDCl\(_3\), 60 MHz): \(\delta\) 4.7 (s, 2H, -CH\(_2\)Ar)

7.2-7.4 (m, 9H, -ArH)

8.4 (s, 1H, -CH=N-)

13.4 (bs, 1H, -OH, D\(_2\)O exchangeable)

\(N\)-Benzy 1-2-allyloxybenzylidine (188)

**Method A**

A mixture of 2-allyloxybenzaldehyde (163, 0.16 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) on subjection to MWI at 70 W for 30 sec. followed by usual work up afforded pure imine (188, 0.24 g, 97%).

**Method B**

When a mixture of 2-allyloxybenzaldehyde (163, 0.16 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar for 25 min., pure aldime (188, 0.23 g) was obtained after the usual work up in 93% yield.

IR (neat)/\(\nu_{max}\) cm\(^{-1}\): 2930, 2870, 1630, 1460, 1250, 1060, 750.

\(^1\)H NMR (CCl\(_4\), 60 MHz): \(\delta\) 4.4 (d, \(J=5\)Hz, 2H, -OCH\(_2\)CH=)

4.7 (s, 2H, -CH\(_2\)Ar)

5.1-5.4 (m, 2H, -CH=CH\(_2\))

5.7-6.3 (m, 1H, -CH\(_2\)CH=CH\(_2\))

7.1-7.4 (m, 8H, -ArH)

**Experimental**
**N-Benzyl-4-acetoxybenzylidine (189)**

**Method A**

A mixture of 4-acetoxybenzaldehyde (168, 0.16 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was irradiated in a microwave oven at 70 W for 30 sec. The reaction mixture was worked up in a usual way to furnish pure aldimine (189, 0.24 g, 97%).

**Method B**

4-Acetoxybenzaldehyde (168, 0.16 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar for 30 min. The resultant mixture was worked up as usual to provide pure imine (189, 0.23 g) in 95% yield.

IR (CHCl₃)/νₚ_max cm⁻¹: 3020, 2920, 1735, 1615, 1310, 850.

¹H NMR (CCl₄, 60 MHz): δ 2.3 (s, 3H, -OCOCH₃)

8.0 (d, J=6Hz, 1H, )

8.8 (s, 1H, -CH=N-)

**N-Benzylicinnamylidine (190)**

**Method A**

Cinnamaldehyde (28, 0.13 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) were irradiated in microwave oven at 70 W for 30 sec. Usual work up of the reaction mixture afforded N-benzylicinnamylidine (190, 0.18 g, 84%).

**Method B**

Cinnamaldehyde (28, 0.13 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) were ground in a mortar at r.t. for 25 min., followed by usual work up and purification afforded pure imine (190, 0.16 g) in 76% yield.

IR (CHCl₃)/νₚ_max cm⁻¹: 3010, 2980, 1635, 960, 750.

¹H NMR (CCl₄, 60 MHz): δ

6.6 (t, J=4Hz, 1H, C₆H₅CH=CH-CH=)

6.8 (d, J=4Hz, 1H, C₆H₅CH=CH-)

7.1 (m, 10H, -ArH)

7.8 (dd, J=4Hz, 3Hz, 1H, -CH=N-)

**Experimental**

210
**N-Benzylfurfurylidine (191)**

**Method A**

A mixture of furfural (29, 0.1 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) was subjected to MWI at 70 W for 30 sec. The reaction mixture was worked up as usual to provide pure Schiff base (191, 0.19 g) in 97% yield.

**Method B**

A mixture of furfural (29, 0.1 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar at r.t. for 20 min. The reaction mixture was worked up in a usual manner to furnish pure N-benzylfurfurylidine (191, 0.18 g) in 94% yield.

IR (CHCl₃)/νmax cm⁻¹: 3040, 2890, 1630, 1590, 1080, 760.

¹H NMR (CCl₄, 60 MHz): δ 4.7 (s, 2H, -CH₂Ar)

6.6-6.8 (m, 1H, )

7.2-7.4 (m, 6H, -ArH)

7.7 (s, 1H, )

8.2 (s, 1H, -CH=N-)

**N-Benzylthiophenylidine (192)**

**Method A**

Exposure of a mixture of 2-thiophenealdehyde (30, 0.11 g, 1.0 mmol) and benzylamine (0.13 g, 1.2 mmol) to MWI at 70 W for 30 sec. furnished pure N-Benzylthiophenylidine (192, 0.19 g) after the usual work up in 98% yield.

**Method B**

When a mixture of 2-thiophenealdehyde (30, 0.11 g, 1.0 mmol), benzylamine (0.13 g, 1.2 mmol) and molecular sieves (4Å, 2 g) was ground in a mortar at r.t. for 20 min., N-benzylthiophenylidine (192, 0.19 g), after usual work up was obtained in 99% yield.

IR (CHCl₃)/νmax cm⁻¹: 3050, 2870, 1625, 1610, 735.

¹H NMR (CCl₄, 60 MHz): δ 4.7 (s, 2H, -CH₂Ar)

6.8-7.0 (m, 1H, )
6-Hydroxy-1-tetrahydropyranoxylhexane (193)

A mixture of 1,6-hexanediol (101, 0.5 g, 4.23 mmol), 3,4-dihydro-2H-pyran (0.45 g, 5.29 mmol) and iodine (0.22 g, 0.85 mmol) in dry THF (1 mL) was taken in a 50 mL conical flask, and a small funnel was placed over it to reduce any possible evaporation of solvent. The flask was irradiated in microwave oven at 600 W power for 3 min. After cooling, the reaction mixture was extracted with chloroform (30 mL), washed with 10% aq. sodium thiosulphate solution (2x5 mL), water (2x5 mL), brine and dried. Evaporation of the solvent under vacuum followed by purification by silica gel column chromatography using 5% ethyl acetate in n-hexane as an eluant furnished 6-hydroxy-1-tetrahydropyranoxylhexane (193, 0.66 g, 78%) along with 17% of its diether (0.20 g).

IR (CCl4)/vmax cm⁻¹: 3450, 2960, 1210, 1120, 720.

¹H NMR (CCl4, 60 MHz):  δ  1.3-1.7 (m, 12H, saturated methylene protons)
  1.8-2.1 (m, 2H, -CH2CH2OH)
  3.3-3.9 (m, 6H, -CH2CH2OH, -CH2CH2O-, -OCCH2-)
  4.2 (bs, 1H, -OH, D2O exchangeable)
  4.8 (s, 1H, -CHO)

Tetrahydropyranoxyl-1-hexanal (194)

To a stirred suspension of PDC (3.76 g, 10.0 mmol) in dry DCM (50 mL) taken in 250 mL round-bottomed flask was added 6-hydroxy-1-tetrahydropyranoxylhexane (193, 1.0 g, 5.0 mmol) in dry DCM (20 mL) at 0-10°. Stirring was further continued for 9h. The reaction mixture was passed through a short neutral alumina (active, 30 g) column. Evaporation of solvent in vacuo provided pure (194, 0.69 g, 70%).

IR (CCl4)/vmax cm⁻¹: 3450, 2960, 1730, 1180, 720.

¹H NMR (CCl4, 60 MHz):  δ  1.3-1.7 (m, 12H, saturated methylene protons)
  2.4 (t, J=7Hz, 2H, -CH2CH2CO-)
  3.3-3.9 (m, 4H, -CH2CH2O-, -OCH2CH2-)
  4.8 (t, J=4Hz, 1H, -OCHO-)
  10.1 (s, 1H, -CHO)

Experimental 212
6-Hydroxy-1-tetrahydropyranoloxydodecane (195)

A flame dried nitrogen flushed 250 mL three-necked round-bottomed flask, fitted with a condenser and an addition funnel, was charged with magnesium turnings (0.24 g, 9.87 mmol), anhyd. diethyl ether (10 mL) and a small crystal of iodine. To this stirred mixture was added a few drops of 1-bromohexane (65, 1.61 g, 9.76 mmol) in dry diethyl ether (30 mL). The flask was warmed on a hot water bath and on discharge of violet colour of iodine, the remaining 1-bromohexane (65) was added dropwise over a period of 0.5h. On complete consumption of magnesium metal, the reaction mixture was cooled to 0° and compound (194, 1.76 g, 8.8 mmol) in dry diethyl ether (25 mL) was added dropwise over a period of 1h. Stirring was continued overnight, the reaction mixture was quenched with saturated aq. ammonium chloride solution. The organic layer was separated and washed with water (3x10 mL), brine and dried. Removal of solvent under reduced pressure followed by purification using a silica gel column chromatography eluting with 10% ethyl acetate in n-hexane as an eluant furnished pure 195 (1.98 g, 79%).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3350, 2910, 2910, 1280, 1120.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 0.9 (t, $J$=7Hz, 3H, -CH$_2$CH$_3$).

1.3-1.6 (m, 20H, saturated methylene protons)

1.8-2.1 (m, 4H, -CH$_2$CH(OH)CH$_2$-)

2.3 (bs, 1H, -OH, D$_2$O exchangeable)

3.3-4.0 (m, 5H, -CH$_2$CH$_2$O-, -OCH$_2$CH$_2$-, -CH$_2$CH(OH)-)

4.7 (t, $J$=4Hz, 1H, -OCHO-)

6-Oxo-1-decenoic acid (196)

A round-bottomed flask charged with 6-hydroxy-1-tetrahydropyranoloxydodecane (195, 2.0 g, 7.0 mmol) in acetone (30 mL) was ice-cooled. To the stirred mixture, Jones reagent (7 mL) was added dropwise over a period of 30 min., which resulted in the immediate change of colour of the reaction mixture from orange to olive green. The reaction was allowed to stir for 1h followed by quenching with a few drops of iso-propyl alcohol and mixture was evaporated under reduced pressure. The reaction mixture was extracted with diethyl ether (2x20 mL), washed with water (2x5 mL), brine and dried. The solvent was evaporated in vacuo to furnish pure compound (196, 1.03 g, 69%).

IR (neat)/$\nu_{\text{max}}$ cm$^{-1}$: 3010, 2920, 2850, 1720, 1580, 1220.

Experimental
1H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=7Hz, 3H, -CH₂CH₃)
1.2-1.6 (m, 12H, saturated methylene protons)
2.0-2.5 (m, 6H, -CH₂COCH₂-, -CH₂COOH)
10.3 (bs, 1H, -COOH, D₂O exchangeable)

Pentadecyl 6-oxododecanoate (197)

 Compound (196, 0.86 g, 4.0 mmol), pentadecan-1-ol (0.91 g, 4.0 mmol) and p-toluenesulphonic acid (0.38 g, 2.0 mmol) were introduced in an open Erlenmeyer flask. The mixture was irradiated in microwave oven at 320 W for 4 min. The reaction mixture was then cooled, extracted with diethyl ether (2x10 mL), filtered, washed with water (2x5 mL), brine and dried. Evaporation of solvent under reduced pressure yielded product which was purified by silica gel column chromatography using 5% ethyl acetate in n-hexane as eluant to give compound (197, 1.56 g, 92%).

IR (neat)/νmax cm⁻¹: 2960, 1740, 1720, 1180, 720.

1H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=6Hz, 6H, 2x-CH₂CH₃)
1.2-1.6 (bs, 38H, saturated methylene protons)
2.0-2.4 (m, 6H, -CH₂COCH₂-, -CH₂COO-)
4.1 (t, J=7Hz, 2H, -CH₂OCO-)

Pentadecyl 6-hydroxydodecanoate (198)

 Sodium borohydride-alumina is prepared by throughly mixing NaBH₄ (1.0 g) with neutral alumina (9.0 g) in solid state by grinding in a mortar. Freshly prepared sodium borohydride-alumina (0.11 g, 3.0 mmol) was throughly mixed with neat compound (197, 1.27 g, 3.0 mmol) in a test tube and placed in an alumina bath inside the microwave oven and irradiated at 640 W for 1 min. Upon completion of the reaction, the reaction mixture was washed with diethyl ether (2x15 mL), brine and dried. Evaporation of the solvent in vacuo provided compound (198, 1.11 g, 87%), m.p. 69-71° (lit. 72°).

IR (nujol)/νmax cm⁻¹: 3400, 2980, 1740, 1210, 725.

1H NMR (CDCl₃, 300 MHz): δ 0.9 (t, J=7Hz, 6H, 2x-CH₂CH₃)
1.2-1.6 (bs, 38H, saturated methylene protons)
1.6-1.9 (m, 4H, -CH₂CH(OH)CH₂-)
2.4 (t, J=7Hz, 2H, -CH₂CH₂CO-)
3.0 (bs, 1H, -OH, D₂O exchangeable)
3.6 (t, J=7Hz, 1H, -CH₂CH(OH)-)
4.1 (t, J=7Hz, 2H, -CH₂OCO-)

Experimental
Hexadecanoic acid (200)

A round-bottomed flask charged with hexadecan-1-ol (199, 2.0 g, 8.26 mmol) in acetone (50 mL) was cooled to 0°. To the stirred mixture, Jones reagent (5 mL) was added dropwise over a period of 30 min., which resulted in the immediate change of colour of the reaction mixture from orange to olive green. The reaction was allowed to stir for 1h followed by quenching with a few drops of iso-propyl alcohol and mixture was evaporated under reduced pressure. The reaction mixture was extracted with diethyl ether (2x20 mL), washed with water (2x5 mL), brine and dried. The solvent was evaporated in vacuo to furnish pure compound (200, 1.5 g, 71%, m.p. 60°, lit. 60-62°).

IR (CHCl3)/vmax cm⁻¹: 3400, 2920, 1700, 1590, 1475, 1380, 1160, 940, 720.

¹HNMR (CDCl₃, 300 MHz) δ: 0.8 (t, J=6Hz, 3H, -CH₂C₆H₅)
1.1-1.6 (bs, 26H, saturated methylene protons)
2.3 (t, J=6Hz, 2H, -CH₂COOH)
11.3 (bs, 1H, -COOH, D₂O exchangeable)

Undecyl hexadecanoate (201)

Hexadecanoic acid (200, 1.02 g, 4.0 mmol), undecan-1-ol (0.69 g, 4.0 mmol) and p-toluencesulphonic acid (0.38 g, 2.0 mmol) were introduced in an open Erlenmeyer flask. The reaction mixture was irradiated in a domestic microwave oven at 320 W for 4 min. It was then allowed to cool at room temperature, extracted with diethyl ether (2x10 mL), filtered, washed with water (2x5 mL) and brine. Evaporation of the solvent in vacuo yielded crude product which was purified by silica gel column chromatography using 5% ethyl acetate in n-hexane as an eluant to furnish undecyl hexadecanoate (201, 1.52 g, 93%, m.p. 79-81°, lit. 82°).

IR (CHCl3)/vmax cm⁻¹: 2954, 2850, 1737, 1465, 1370, 1175, 725.

¹HNMR (CDCl₃, 300 MHz) δ: 0.9 (t, J=6Hz, 6H, 2x-CH₂C₆H₅)
1.2-1.7 (bs, 44H, saturated methylene protons)
2.3 (t, J=6Hz, 2H, -CH₂COO⁻)
4.1 (t, J=7Hz, 2H, -CH₂OCO⁻)

1-Bromononane (66)

To a 100 mL round-bottomed flask containing an ice-cold stirring solution of nonan-1-ol (124, 2.0 g, 13.8 mmol) in anhyd. diethyl ether (50 mL), pyridine (0.87 g, 11.1 mmol) was added PBr₃ (1.35 g, 4.98 mmol) in dry ether (20 mL) dropwise in about 20 min. The mixture was allowed to stir for 2h at 0°, 1h at r.t. and decomposed with saturated aq. NaHCO₃ solution (2x5 mL). It was then extracted with ether (2x20 mL) washed with
water (2x10 mL), brine and dried. Evaporation of the solvent followed by distillation gave pure 1-bromononane (66) in 81% yield (2.33 g, b.p. 200°, lit. 201°).

IR (neat)/ν<sub>max</sub> cm<sup>−1</sup>: 2960, 1420, 720, 580.

<sup>1</sup>H NMR (CCl₄, 60 MHz) δ:

0.9 (t, J=7Hz, 3H, -CH₂CH₃)
1.1-1.5 (m, 12H, saturated methylene protons)
1.8-2.0 (m, 2H, -CH₂CH₂Br)
3.5 (t, J=6Hz, 2H, -CH₂CH₂Br)

10-Bromo-1-tetrahydropyranyloxydecane (202)

10-Bromodecan-1-ol (118, 0.24 g, 1.0 mmol) in dry THF (1mL) was mixed with 3,4-dihydro-2H-pyran (0.11 g, 1.25 mmol) and iodine (0.05 g, 0.2 mmol). The mixture was added to a 50 mL conical flask, and a small funnel was placed over it to reduce any possible evaporation of solvent. The flask was irradiated in microwave oven at 600 W of power for 3 min. On cooling, the reaction mixture was diluted with chloroform (30 mL) and washed with 10% aq. sodium thiosulphate solution (2x5 mL), water (2x5 mL), brine and dried. Evaporation of the solvent under vacuum and purification by silica gel column chromatography (1:9 ethyl acetate:n-hexane) furnished 10-bromo-1-tetrahydropyranyloxydecane (202, 0.30 g, 94%).

IR (neat)/ν<sub>max</sub> cm<sup>−1</sup>: 2980, 1210, 1120, 820, 540.

<sup>1</sup>H NMR (CCl₄, 60 MHz) δ:

1.3-1.7 (m, 22H, saturated methylene protons)
3.3-3.8 (m, 6H, -CH₂CH₂Br, -CH₂CH₂O, -OCH₂CH₂-)
4.9 (t, J=4Hz, 1H, -OCHO-)

1-Tetrahydropyranyloxynonadecane (203)

To the stirred solution of Grignard reagent prepared from activated magnesium turnings (0.23 g, 9.65 mmol) and 1-bromononane (66, 2.0 g, 9.65 mmol) in anhyd. diethyl ether (50 mL) at -10° was added dropwise a solution of 10-bromo-1-tetrahydropyranyloxydecane (202, 2.65 g, 8.26 mmol) in dry ether (30 mL). The stirring was continued at same temp. for an additional 30 min. Thereafter the temp. of the reaction mixture was brought to r.t. and copper (I) iodide (0.003 g, 0.018 mmol) was added to it. After stirring the reaction mixture for 15 min at r.t., it was refluxed for 3h (TLC monitoring), decomposed with saturated aq. ammonium chloride solution, extracted with diethyl ether (2x30 mL) and dried. Removal of solvent followed by silica gel column chromatography using 2% ethyl acetate in n-hexane as an eluant afforded 1-tetrahydropyranyloxynonadecane (203, 2.37 g, 78%).
IR (neat)/ν<sub>max</sub> cm<sup>-1</sup>: 2990, 1210, 1120, 725.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ:
- 0.9 (t, J=6Hz, 3H, -CH<sub>2</sub>C<sub>3</sub>)
- 1.1-1.6 (bs, 40H, saturated methylene protons)
- 3.3-3.8 (m, 4H, -CH<sub>2</sub>C<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-)
- 4.9 (t, J=4Hz, 1H, -OCHO-)

1-Bromononadecane (204)
To a 100 mL two-necked round-bottomed flask containing a solution of 1-tetrahydropyranyloxynonadecane (203, 1.0 g, 2.71 mmol) in dry DCM (20 mL) was added dry carbon tetrabromide (1.27 g, 3.82 mmol) under N<sub>2</sub> atmosphere. The reaction mixture was stirred at r.t for 10 min. followed by cooling to 0° and subsequent addition of triphenylphosphine (2.0 g, 7.64 mmol). Stirring was continued overnight at r.t., passed through a short silica gel column and eluted with DCM (20 mL). The solvent was evaporated under reduced pressure to furnish pure 1-bromononadecane (204, 0.73 g, 77%).

IR (neat)/ν<sub>max</sub> cm<sup>-1</sup>: 2960, 1420, 580.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 60 MHz) δ:
- 0.9 (t, J=6Hz, 3H, -CH<sub>2</sub>C<sub>3</sub>)
- 1.2-1.6 (bs, 32H, saturated methylene protons)
- 1.8-2.1 (m, 2H, -CH<sub>2</sub>Br)
- 3.3 (t, J=6Hz, 2H, -CH<sub>2</sub>C<sub>2</sub>Br)

Docos-1-en-3-ol (205)
A flame dried nitrogen flushed 250 mL three-necked round-bottomed flask, fitted with a condenser and an addition funnel was charged with magnesium turnings (0.14 g, 5.76 mmol), anhyd. diethyl ether (10 mL) and a small crystal of iodine. To this stirred mixture was added a few drops of 1-bromononadecane (204, 2.0 g, 5.76 mmol) in dry diethyl ether (50 mL). The flask was warmed on a hot water bath and on discharge of violet colour of iodine, the remaining 1-bromononadecane (204) was added dropwise over a period of 0.5h. On complete consumption of magnesium metal, the reaction mixture was cooled to 0° and acrolein (0.3 g, 5.35 mmol) in dry diethyl ether (25 mL) was added dropwise over a period of 1h. Stirring was continued overnight, the reaction mixture was quenched with saturated aq. ammonium chloride solution. The organic layer was separated and washed with water (2x10 mL), brine and dried. Removal of solvent under reduced pressure followed by purification using a silica gel column chromatography eluting with 10% ethyl acetate in n-hexane furnished pure docos-1-en-3-ol (205, 1.4 g, 75%).

IR (neat)/ν<sub>max</sub> cm<sup>-1</sup>: 3350, 3010, 2920, 1640, 1280, 1160, 725.
$^1$HNMR (CCl₄, 60 MHz) δ: 0.9 (t, J=6Hz, 3H, -CH₂CH₃)
1.1-1.6 (bs, 34H, saturated methylene protons)
1.8-2.0 (m, 2H, -CH₂CH(OH)⁻)
3.2 (bs, 1H, -OH, D₂O exchangeable)
3.9-4.4 (m, 1H, -CH₂CH(=O²⁻))
5.0-5.4 (m, 2H, -CH=CH₂)
5.7-6.3 (m, 1H, -CHCH=CH₂)

**Docos-1-en-3-one (206)**

To a stirred suspension of PDC (2.32 g, 6.17 mmol) in dry DCM (50 mL) taken in 250 mL round-bottomed flask was added compound (205, 1.0 g, 3.09 mmol) in dry DCM (50 mL) at 0-10°. Stirring was continued for 9h and then the reaction mixture was passed through a short alumina (active, 30 g) column. Evaporation of the solvent under reduced pressure provided pure docos-1-en-3-one (206, 0.69 g, 70%).

IR (neat)/ν max cm⁻¹: 3020, 2960, 1700, 1660, 1420, 1210, 720.

$^1$HNMR (CCl₄, 60 MHz) δ: 0.9 (t, J=6Hz, 3H, -CH₂CH₃)
1.1-1.6 (bs, 34H, saturated methylene protons)
2.3 (t, J=6Hz, 2H, -CH₂CH₂CO⁻)
5.7-6.1 (m, 1H, -CHCH=CH₂)
6.3-6.7 (m, 1H, -CH=CH₂)

**Hentriacontan-12-one (207)**

To a 50 mL ultrasound vessel containing 40 mL of aq. ethanol (9:1) at 0°, was added zinc dust (0.22 g, 3.46 mmol), copper (I) iodide (0.2 g, 1.07 mmol) and the mixture was sonicated. To the resultant black suspension formed in 3 min. was added dropwise solution of 1-bromononane (66, 0.5 g, 2.37 mmol) in ethanol (2 mL) over a period of 5 min. followed by addition of compound (206, 0.5 g, 1.55 mmol) in ethanol (2 mL) dropwise. After sonication for 30 min. the reaction was quenched with brine, solvent evaporated in vacuo, taken up in diethyl ether (30 mL), washed with water (2x5 mL), brine and dried. Evaporation of the solvent in vacuo followed by silica gel column purification using n-hexane:ethyl acetate (9:1) gave pure 207 (0.43 g, 62%).

IR (CHCl₃)/ν max cm⁻¹: 2860, 1710, 1440, 720.

$^1$HNMR (CCl₄, 60 MHz) δ: 0.9 (t, J=6Hz, 6H, 2x-CH₂CH₃)
1.2-1.7 (bs, 52H, saturated methylene protons)
2.1-2.5 (m, 4H, -CH₂COCH₂⁻)

**Experimental**
12-Hydroxyhentriacontane (208)

Sodium borohydride-alumina is prepared by thoroughly mixing NaBH₄ (1.0 g) with neutral alumina (9.0 g) in solid state by grinding in a mortar. Freshly prepared sodiumborohydride-alumina (0.02 g, 0.48 mmol) was thoroughly mixed with neat compound (207, 0.21 g, 0.48 mmol) in a test tube and placed in an alumina bath inside the microwave oven and irradiated at 640 W for 1 min. Upon completion of the reaction (monitored by TLC), the reaction mixture was washed with diethyl ether (2x15 mL), brine and dried. Evaporation of the solvent in vacuo provided 12-hydroxyhentriacontane (208, 0.19 g, 92%) as a white solid, m.p. 75° (lit. 77°).

IR (CHCl₃)/ν max cm⁻¹: 3430, 2920, 2852, 1465, 1070, 720.

¹HNMR (CDCl₃, 60 MHz) δ: 0.9 (t, J=6 Hz, 6H, 2x-CH₂CH₃)
1.1-1.6 (bs, 52H, saturated methylene protons)
1.8-2.0 (m, 4H, -CH₂CH(OH)CH₂-)
3.7 (t, J=8 Hz, 1H, -CH₂CH(OH)-)
4.2 (bs, 1H, -OH, D₂O exchangeable)

6-Bromo-1-tetrahydropyranoyloxyhexane (209)

A mixture of 6-bromohexan-1-ol (114, 0.5 g, 2.76 mmol) in dry THF (1 mL), DHP (0.29 g, 3.44 mmol) and iodine (0.14 g, 0.55 mmol) was taken in a 50 mL conical flask, and a small funnel was placed over it to reduce any possible evaporation of solvent. The flask was irradiated in microwave oven at 600 W for 3 min. Immediately on completion, the flask was taken out, diluted with chloroform (30 mL) and washed with 10% aq. sodium thiosulphate solution (2x5 mL), water (2x5 mL), brine, dried and evaporated under vacuum. Purification by silica gel column chromatography eluting with n-hexane gave 6-bromo-1-tetrahydro pyranoyloxyhexane (209, 0.58 g, 85%).

IR (neat)/ν max cm⁻¹: 2927, 1260, 1180, 1120, 722, 560.

¹H NMR (CCl₄, 60 MHz) δ: 1.3-1.7 (m, 14H, saturated methylene protons)
3.3-3.8 (m, 6H, -CH₂CH₂Br, -CH₂CH₂O-, -OCH₂CH₂-)
4.7 (t, J=4 Hz, 1H, -OCHO-)

8-Methyl-1-tetrahydropyranoyloxynonane (210)

To the stirred solution of Grignard reagent prepared from activated magnesium turnings (0.26 g, 10.8 mmol) and 1-iodo-2-methylpropane (2.0 g, 10.8 mmol) in anhyd. diethyl ether (50 mL) was added dropwise a solution of 6-bromo-1-tetrahydro pyranoyloxyhexane (209, 2.47 g, 9.32 mmol) in dry ether (30 mL) at -10°. The stirring was

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continued at same temp. for an additional 30 min. Thereafter the reaction mixture was brought
to r.t. and copper (I) iodide (0.004 g, 0.021 mmol) was added to it. After stirring the reaction
mixture for 15 min at r.t., it was refluxed for 3h (TLC monitoring), decomposed with
saturated ammonium chloride solution in water, extracted with diethyl ether (2x30 mL) and
dried. Removal of solvent followed by silica gel column chromatography using 2% ethyl
acetate in n-hexane afforded 8-methyl-1-tetrahydropyranoxynonane (210, 1.67 g, 74%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}$: 2930, 2850, 1385, 1367, 1210, 1120, 722.
$^1$H NMR (CDCl$_3$, 60 MHz) $\delta$: 0.9 (d, $J=6$Hz, 6H, -CH(CH$_3$)$_2$)
1.2-1.6 (m, 18H, saturated methylene protons)
1.7-1.9 (m, 1H, -CH(CH$_3$)$_2$
3.3-3.9 (m, 4H, -CH$_2$CH$_2$O-, -OCH$_2$CH$_2$-)
4.7 (t, $J=4$Hz, 1H, -OCHO-)

8-Methyl-1-nonanal (211)

A mixture of 8-methyl-1-tetrahydropyranoxynonane (210, 0.76 g, 3.16 mmol), PCC
(1.02 g, 4.72 mmol), silica gel (1 g) in dry DCM (2 mL) was taken in a conical flask. The
solvent was evaporated and the resulting free flowing solid mixture was exposed to MWI at
200 W for 2 min. On cooling, reaction mixture was diluted with DCM (2x20 mL), filtered
through a short pad of silica gel eluting with DCM. The solvent was evaporated under
reduced pressure to yield 8-methyl-1-nonanal (211, 0.45 g, 92%).

IR (neat)/$\nu_{\text{max}} \text{ cm}^{-1}$: 2950, 2860, 2720, 1740, 1383, 1365, 970, 725.
$^1$H NMR (CDCl$_3$, 60 MHz) $\delta$: 1.0 (d, $J=6$Hz, 6H, -CH(CH$_3$)$_2$
1.2-1.7 (m, 10H, saturated methylene protons)
1.8-2.0 (m, 1H, -CH(CH$_3$)$_2$
2.3 (t, $J=7$Hz, 2H, -CH$_2$CH$_2$CHO)
10.1 (s, 1H, -CHO)

8-Hydroxyoctyltriphenylphosphonium bromide (212)

A mixture of 8-bromooctan-1-ol (116, 0.5 g, 2.4 mmol) and triphenylphosphine
(0.63 g, 2.4 mmol) were taken in an Erlenmeyer flask and exposed to microwave radiations at
800 W for 5 min. On cooling, the reaction mixture was washed with warm dry benzene (2x10
mL) and the crude product was recrystallized from ethanol to afford crystals of pure
8-hydroxyoctyltriphenylphosphonium bromide (212, 0.97 g) in 86% yield, m.p. 130°
(lit. m.p. 132-134°).

IR (nujol)/$\nu_{\text{max}} \text{ cm}^{-1}$: 3350, 2910, 1462, 1435, 1210, 1045, 720.

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\[ ^1H \text{NMR (CDCl}_3, 60 \text{ MHz)} \delta: 1.6-2.4 \text{ (m, 12H, saturated methylene protons)} \]
\[ 2.9 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)} \]
\[ 3.4-4.1 \text{ (m, 4H, -CH}_2\text{CH}_3\text{PPPh}_3, -CH}_2\text{CH}_2\text{OH)} \]
\[ 7.5-8.0 \text{ (m, 15H, -ArH)} \]

**16-Methyl-8(Z)-heptadecen-1-ol (214)**

A suspension of 8-hydroxyoctyltriphenylphosphonium bromide (212, 2.0 g, 4.25 mmol) and freshly prepared sodium amide (0.17 g, 4.25 mmol) in dry THF (50 mL) was sonicated at r.t. for 30 min. under nitrogen atmosphere. Once the reaction developed a brick red colour (within 15 min.) indicating formation of ylide (213). The reaction mixture was cooled to -78° and a solution of 8-methyl-1-nonanal (211, 0.64 g, 4.1 mmol) in dry THF (10 mL) was added to it with stirring over a period of 20 min. During the addition slow disappearance of the red colour was noticed. Stirring was continued for 30 min. at the same temp, and then the reaction was brought to r.t. This was diluted to ice-cold water (100 mL) and extracted with diethyl ether (2x30 mL). The combined ethereal extract was washed with brine and dried. Removal of solvent yielded a gummy residue which was dissolved in \( n \)-hexane:ethyl acetate (9:1) and filtered through a bed of silica gel (20 g) to remove the major amount of triphenylphosphine oxide. Evaporation of the solvent gave a pale yellow oil which on chromatography over silica gel eluting with 5% ethyl acetate in \( n \)-hexane furnished 16-methyl-8(Z)-heptadecen-1-ol (214, 0.68 g, 62%).

**IR (neat)/\( \nu_{\text{max}} \) cm\(^{-1}\):**

3370, 3010, 2930, 2860, 1640, 1380, 1365, 1262, 1120, 735, 668.

\[ ^1H \text{NMR (CCl}_4, 60 \text{ MHz)} \delta: 0.9 \text{ (d, J=6Hz, 6H, -CH}(\text{CH}_3)_2) \]
\[ 1.1-1.4 \text{ (bs, 18H, saturated methylene protons)} \]
\[ 1.5-1.7 \text{ (m, 1H, -CH}(\text{CH}_3)_2) \]
\[ 1.8-2.1 \text{ (m, 6H, -CH}_2\text{CH=CHCH}_2, -CH}_2\text{CH}_2\text{OH)} \]
\[ 3.6 \text{ (t, J=6Hz, 2H, -CH}_2\text{CH}_2\text{OH)} \]
\[ 4.0 \text{ (bs, 1H, -OH, D}_2\text{O exchangeable)} \]
\[ 5.1-5.4 \text{ (m, 2H, -CH}_2\text{CH=CHCH}_2) \]

**16-Methyl-8(Z)-heptadecenoic acid (215)**

A round-bottomed flask charged with 16-methyl-8(Z)-heptadecen-1-ol (214, 0.5 g, 1.86 mmol) in acetone (50 mL) was ice-cooled. To the stirred mixture, Jones reagent (5mL) was added dropwise over a period of 30 min., which resulted in the immediate change of colour of the reaction mixture from orange to olive green. The reaction was allowed to stir for

**Experimental**

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1h followed by quenching with a few drops of iso-propyl alcohol and the solvent was evaporated under reduced pressure. The reaction mixture was extracted with diethyl ether (2x25 mL), washed with water (2x5mL), brine and dried. The solvent was evaporated in vacuo to furnish pure 16-methyl-8(Z)-heptadecenoic acid (215, 0.38 g, 72%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 3200, 3010, 2968, 1715, 1580, 1381, 1360, 700.

$^1$H NMR (CCl$_4$, 60 MHz): $\delta$ 0.9 (d, $J=6$Hz, 6H, -CH(CH$_3$)$_2$)

1.1-1.4 (bs, 18H, saturated methylene protons)

1.6-1.8 (m, 1H, -CH(CH$_3$)$_2$)

1.9-2.2 (m, 4H, -CH$_2$CH=CHCH$_2$-)

2.3 (t, $J=7$Hz, 2H, -CH$_2$COOH)

5.1-5.4 (m, 2H, -CH$_2$CH=CHCH$_2$-)

11.5 (bs, 1H, -COOH, D$_2$O exchangeable)

8-Bromo-1-tetrahydropyranloxyoctane (216)

8-Bromoctan-1-ol (116, 0.2 g, 1.0 mmol) in dry THF (1 mL) was mixed DHP (0.1 g, 1.25 mmol) and iodine (0.05 g, 0.2 mmol). The mixture was added to a 50 mL conical flask, and a small funnel was placed over it to reduce any possible evaporation of solvent. The flask was irradiated in microwave oven at 600 W for 3 min. Immediately on completion, the flask was taken out, diluted with chloroform (30 mL) and washed with 10% sodium thiosulphate solution (2x5 mL), water (2x5 mL), brine, dried and evaporated under vacuum. Purification by silica gel column chromatography eluting with n-hexane gave 8-bromo-1-tetrahydro pyranloxyoctane (216, 0.25 g, 88%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2930, 1460, 1280, 1120, 720, 580.

$^1$H NMR (CCl$_4$, 60 MHz) $\delta$: 1.4-1.8 (m, 18H, saturated methylene protons)

3.3-3.8 (m, 6H, -CH$_2$CH$_2$Br, -CH$_2$CH$_2$O-, -OCH$_2$CH$_2$-)

4.7 (t, $J=4$Hz, 1H, -OCHO-)

10-Methyl-1-tetrahydropyranloxyundecane (217)

To the stirred solution of Grignard reagent prepared from activated magnesium turnings (0.26 g, 10.7 mmol) and 1-ido-2-methylpropane (2 g, 10.8 mmol) in anhyd. diethyl ether (50 mL) was added dropwise a solution of 8-bromo-1-tetrahydropyranloxyhexane (216, 2.73 g, 9.32 mmol) in dry ether (30 mL) at -10°. The stirring was continued at same temp. for an additional 30 min. Thereafter the temp. of the reaction mixture was brought to r.t. and copper (I) iodide (0.004 g, 0.021 mmol) was added to it. After stirring the reaction mixture for 15 min at r.t., it was refluxed for 3h (TLC monitoring), decomposed with

Experimental
saturated ammonium chloride solution in water, extracted with diethyl ether (2x30 mL) and dried. Removal of solvent followed by silica gel column chromatography using 10% ethyl acetate in n-hexane afforded 10-methyl-1-tetrahydropyranoylxyundecane (217, 1.79 g, 71%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2928, 2850, 1460, 1385, 1360, 1120, 720.

\(^1\)H NMR (CCl\(_4\), 60 MHz) \(\delta\): 1.0 (d, \(J=6\) Hz, 6H, -CH(C/\(\text{CH}_3\))\(_2\))
1.2-1.6 (m, 22H, saturated methylene protons)
1.7-1.9 (m, 1H, -CH(CH\(_3\))\(_2\))
3.3-3.9 (m, 4H, -CH\(_2\)C/\(\text{CH}_2\)-, -OCH\(_2\)CH\(_2\)-)
4.7 (t, \(J=4\) Hz, 1H, -OCHO-)

10-Methyl-1-undecanal (218)
A mixture of 10-methyl-1-tetrahydropyranoylxyundecane (217, 0.48 g, 1.85 mmol) and PCC (0.88 g, 2.77 mmol) was impregnated on silica gel (1 g) and exposed to MWI at 200 W for 2 min. On cooling, the reaction mixture was extracted with DCM (2x20 mL) and passed through short pad of silica gel eluting with DCM. The solvent was evaporated \textit{in vacuo} to yield 10-methyl-1-undecanal (218, 0.31 g, 90%).

IR (neat)/\nu_{\text{max}} \text{ cm}^{-1}: 2980, 2865, 2710, 1738, 1460, 1387, 1365, 965, 725.

\(^1\)H NMR (CCl\(_4\), 60 MHz) \(\delta\): 1.0 (d, \(J=6\) Hz, 6H, -CH(CH\(_3\))\(_2\))
1.2-1.7 (m, 14H, saturated methylene protons)
1.8-2.0 (m, 1H, -CH(CH\(_3\))\(_2\))
2.3 (t, \(J=7\) Hz, 2H, -CHO)
4.7 (s, 1H, -CHO)

6-Hydroxyhexyltriphenylphosphonium bromide (219)
A mixture of 6-bromohexan-1-ol (2, 0.5 g, 2.76 mmol) and triphenylphosphine (0.72 g, 2.76 mmol) were taken in an Erlenmeyer flask. The reaction mixture was exposed to microwave irradiation at 800 W for 5 min. On cooling, the reaction mixture was washed with warm dry benzene (2x10 mL). The filtrate was recrystallized with ethanol to afford pure crystals of pure 6-hydroxyhexyltriphenylphosphonium bromide (219, 1.0 g) in 82% yield, m.p. 150-153° (lit m.p. 153-154°).

IR (nujol)/\nu_{\text{max}} \text{ cm}^{-1}: 3300, 2920, 1495, 1430, 1208, 1057, 720.

\(^1\)H NMR (CDCl\(_3\), 60 MHz) \(\delta\): 1.6-2.5 (m, 8H, saturated methylene protons)
3.5-4.2 (m, 4H, -CH\(_2\)CH\(_2\)PPh\(_3\)-, -CH\(_2\)CH\(_2\)OH)
4.3 (bs, 1H, -OH, D\(_2\)O exchangeable)
7.5-8.0 (m, 15H, -Ar\(H\))

**Experimental**

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16-Methyl-6(Z)-heptadecen-1-ol (221)

A suspension of 6-hydroxyhexyltriphenylphosphonium bromide (219, 1.58 g, 3.38 mmol) and freshly prepared sodium amide (0.13 g, 3.38 mmol) in dry THF (50 mL) was sonicated at r.t. for 30 min. under nitrogen atmosphere. Once the reaction developed a brick red colour (within 15 min.) indicating formation of ylide (220). The reaction mixture was cooled to -78°C and a solution of 10-methyl-1-undecanal (218, 0.6 g, 3.26 mmol) in dry THF (10 mL) was added to it with stirring over a period of 20 min. During the addition slow disappearance of the red colour was noticed. Stirring was continued for 30 min. at the same temp. and then the reaction was brought to r.t. This was diluted to ice-cold water (100 mL) and extracted with diethyl ether (2x30 mL). The combined ethereal extract was washed with brine and dried. Removal of solvent yielded a gummy residue which was dissolved in n-hexane:ethyl acetate (9:1) and filtered through a bed of silica gel (20 g) to remove the major amount of triphenylphosphine oxide. Evaporation of the solvent gave a pale yellow oil which on chromatography over silica gel eluting with 5% ethyl acetate in n-hexane furnished 16-methyl-6(Z)-heptadecen-1-ol (221, 0.52 g, 59%).

IR (neat)/vmax cm⁻¹: 3350, 3012, 2960, 2857, 1641, 1383, 1367, 1210, 1120, 730, 650.

₁H NMR (CCl₄, 60 MHz) δ:
1.0 (d, J=6Hz, 6H, -CH(CH₃)₂)
1.1-1.4 (bs, 18H, saturated methylene protons)
1.5-1.7 (m, 1H, -CH(CH₂)₂)
1.8-2.1 (m, 6H, -CH₂CH=CHCH₂, -CH₂CH₂OH)
3.0 (bs, 1H, -OH, D₂O exchangeable)
3.6 (t, J=6Hz, 2H, -CH₂CH₂OH)
5.1-5.4 (m, 2H, -CH₂CH=CHCH₂)

16-Methyl-6(Z)-heptadecenoic acid (222)

To a ice-cold mixture of 16-methyl-6(Z)-heptadecen-1-ol (221, 0.5 g, 1.86 mmol) in acetone (50 mL) taken in a round-bottomed flask was added Jones reagent (5 mL) dropwise over a period of 30 min., which resulted in the immediate change of colour of the reaction mixture from orange to olive green. The reaction was allowed to stir for 1h, quenched with a few drops of iso-propyl alcohol followed by evaporation of the solvent under reduced pressure. The reaction mixture was extracted with diethyl ether (50 mL), washed with water (2x5 mL), brine and dried. The solvent was evaporated in vacuo to furnish pure 16-methyl-6(Z)-heptadecenoic acid (222, 0.39 g, 74%).

Experimental
Pent-1-en-3-ol (225)

To a flame dried, nitrogen flushed 250 mL three necked round-bottomed flask, fitted with a condenser and an addition funnel, was added magnesium turnings (2.06 g, 84.68 mmol) and anhyd. diethyl ether (5 mL). To the resulting mixture, bromoethane (224, 9.23 g, 84.68 mmol) in dry diethyl ether (50 mL) was added over a period of 0.5h. On complete consumption of magnesium metal, the reaction mixture was cooled to 0° and prop-2-enal (223, 4.48 g, 80.0 mmol) in dry diethyl ether (50 mL) was added dropwise over a period of 1h and stirring was continued overnight. The reaction mixture was quenched with saturated ammonium chloride solution. The organic layer was separated and washed with brine and dried. Solvent was evaporated under vacuum and the crude product was purified by silica gel column chromatography using 20% ethyl acetate in n-hexane as eluant to furnish pure pent-1-en-3-ol (225, 5.38 g, 82%)

Pent-1-en-3-one (226)

Pyridinium dichromate (34.43 g, 91.56 mmol) and dry DCM (100 mL) was taken in 250 mL round-bottomed flask. To it was added pent-1-en-3-ol (225, 5.25 g, 61.05 mmol) in dry DCM (50 mL) at 0°. The reaction was allowed to stir for 8h at r.t. and passed through a short alumina column. Evaporation of solvent in vacuo furnished pure 226 (3.13 g, 61%).

Experimental

IR (neat)/νmax cm⁻¹: 3250, 3010, 2940, 2852, 1720, 1640, 1590, 1380, 1362, 720, 695.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (d, J=6Hz, 6H, -CH(CH₃)₂)
1.2-1.5 (bs, 18H, saturated methylene protons)
1.6-1.8 (m, 1H, -CH(CH₃)₂)
1.9-2.2 (m, 4H, -CH₂CH=CHCH₂-)
2.3 (t, J=7Hz, 2H, -CH₂COOH)
5.1-5.4 (m, 2H, -CH₂CH=CHCH₂-)
11.5 (bs, 1H, -COOH. D₂O exchangeable)

Pent-1-en-3-ol (225)

IR (neat)/νmax cm⁻¹: 3450, 1660, 1210, 1190.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (t, J=6Hz, 3H, -CH₂CH₃)
1.4-1.7 (m, 2H, -CH₂CH₃)
3.8-4.1 (m, 1H, -CHCH(OH)-)
4.5 (bs, 1H, -OH, D₂O exchangeable)
4.9-5.4 (m, 2H, -CH=CH₃)
5.6-6.2 (m, 1H, -CHCH=CH₂)
1-Phenyl-1-trimethylsilyloxyethene (227)

To a flame dried, nitrogen flushed 100 mL two necked round-bottomed flask equipped with a reflux condenser having bubbler on its top and septum on the second neck, was added a solution of acetophenone (12, 1.0 g, 8.33 mmol) in dry DCM (10 mL) followed by trimethylchlorosilane (0.9 g, 8.33 mmol) and DBU (1.52 g, 10.0 mmol) via a syringe. The mixture was stirred for 2h. Then it was diluted with n-pentane (2x10 mL), washed successively with 1% HCl (2x10 mL), 5% aq. NaHCO₃ (2x10 mL) and dried over anhyd. Na₂SO₄. Evaporation of the solvent in vacuo gave 227 (1.26g, 79%).

1-Phenylheptan-1,5-dione (228)

Alumina (1.0 g, acidic, activated at 200° for 4h) impregnated with anhyd. zinc chloride (0.14 g, 1.0 mmol) was added to a cooled (0°) and well stirred mixture of 1-phenyl-1-trimethylsilyloxyethene (227, 0.19 g, 1.0 mmol) and pent-1-en-3-one (226, 0.1 g, 1.2 mmol). Stirring was continued till completion of reaction (2h) as monitored by TLC. The resulting adduct was isolated by eluting the solid mass with DCM followed by boiling with a few drops of water. The organic layer was separated and evaporated in vacuo followed by silica gel column purification using n-hexane:ethyl acetate::4:1 as eluant to afford 1-phenylheptan-1,5-dione (228, 0.15 g, 75%) as white solid, m.p. 62° (lit m.p. 62-64°).

Experimental

IR (neat)/v_max cm⁻¹: 2920, 1710, 1640, 710.

1H NMR (CCl₄, 60 MHz): δ 1.3 (t, J=6Hz, 3H, -CH₂CH₃)
2.6 (q, J=6Hz, 2H, -CH₂CH₃)
5.7-6.1 (m, 1H, -CH=CH₂)
6.2-6.5 (m, 2H, -CH=CH₂)

IR (neat)/v_max cm⁻¹: 3060, 1640, 1240, 1020, 710.

1H NMR (CCl₄, 60 MHz): δ 0.1 (s, 9H, -OSi(CH₃)₃)
4.3 & 4.8 (2s, 2H, >C=CH₂)
7.1-7.3 (m, 3H, -ArH)
7.4-7.7 (m, 2H, -ArH)

IR (CHCl₃)/v_max cm⁻¹: 3068, 2970, 1710, 1695, 1218, 755, 706.

1H NMR (CDCl₃, 60 MHz): δ 1.0 (t, J=7Hz, 3H, -CH₂CH₃)
1.8-2.1 (m, 2H, -CH₂CH₂CH₂-)
2.3 (q, J=7Hz, 2H, -COCH₂CH₃)
2.6 (t, J=7Hz, 2H, -CH₂CH₂CO-)
7-Phenylheptan-3-one (229)

To a 50 mL ultrasound vessel containing 40 mL of aq. ethanol (9:1) at 0°, was added zinc dust (0.22 g, 3.36 mmol), copper (I) iodide (0.2 g, 1.05 mmol) and the mixture was sonicated. To the resultant black suspension formed in 3 min. was added dropwise solution of 1-bromo-2-phenylethane (62, 0.41 g, 2.21 mmol) in ethanol (2 mL) over a period of 5 min. followed by dropwise addition of pent-1-en-3-one (226, 0.12 g, 1.43 mmol) in ethanol (2 mL). After sonication for 30 min., the reaction was quenched with brine, solvent evaporated in vacuo, extracted with diethyl ether (2x10 mL), washed with water (2x5 mL), brine and dried. Evaporation of the solvent under vacuum followed by silica gel column purification using n-hexane:ethyl acetate::9:1 gave 7-phenylheptan-3-one (229, 0.21 g, 50%).

IR (neat)/νmax cm⁻¹: 3060, 2920, 2858, 1720, 1603, 840, 790.

¹H NMR (CCl₄, 60 MHz): δ 1.0 (t, J=7Hz, 3H, -CH₂CH₃)
1.3-1.7 (m, 4H, -CH₂CH₂CH₂CH₂-)
2.1-2.4 (m, 4H, -CH₂COCH₂)
2.6 (t, J=7Hz, 2H, ArCH₂CH₂-)
7.2 (s, 5H, -ArH)

7-Phenylheptan-3-ol (230)

Sodium borohydride-alumina is prepared by throughly mixing NaBH₄ (1.0 g) with neutral alumina (9.0 g) in solid state by grinding in a mortar. Freshly prepared sodium borohydride-alumina (0.11 g, 3.0 mmol) was thoroughly mixed with 7-phenylheptan-3-one (229, 0.57 g, 3.0 mmol) in a test tube and placed in an alumina bath inside the microwave oven and irradiated at 640 W for 1 min. Upon completion of the reaction, monitored by TLC, the reaction mixture was washed with diethyl ether (2x15 mL), brine and dried. Evaporation of the solvent in vacuo provided 7-phenylheptan-3-ol (230, 0.48 g, 83%).

IR (neat)/νmax cm⁻¹: 3400, 2960, 2856, 1496, 1260, 1095, 793.

¹H NMR (CCl₄, 60 MHz): δ 0.9 (t, J=7Hz, 3H, -CH₂CH₃)
1.2-1.6 (m, 8H, saturated methylene protons)
2.2 ( bs, 1H, -OH, D₂O exchangeable)
2.6 (t, J=7Hz, 2H, ArCH₂CH₂-)
3.2-3.7 (m, 1H, -CH₂CH(OH)CH₂-)
7.2 (s, 5H, -ArH)